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New Chromophore Types for [2+2] Photocycloaddition Reactions

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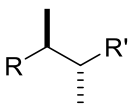
In this thesis, the relative configuration of racemates is represented by straight lines (bold or hashed). The absolute configuration of enantiomerically pure or enriched compounds is represented by wedge-shaped lines (bold or hashed).

racemate 

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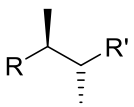
enantiomerically enriched 

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Für meine Familie

Do it with passion, or not at all.

(Rosa Nouchette Carey)

Zusammenfassung

Die [2+2] Photocycloaddition hat sich seit ihrer Entdeckung Ende des 19. Jahrhunderts als eine der am häufigsten verwendeten Cycloadditionsreaktionen in der synthetischen organischen Chemie etabliert. Vor allem in der Synthese von Naturstoffen wird sie mit großem Erfolg als photochemischer Schlüsselschritt eingesetzt. Meist stellen α,β-ungesättigte Ketone (Enone) den Chromophor da, welcher durch Anregung mit Licht einer geeigneten Wellenlänge in einen angeregten Zustand angehoben wird, aus welchem heraus dann in einer inter- oder intramolekularen Reaktion die charakteristischen Cyclobutan Photocycloadditionsprodukte entstehen. Ziel dieser Arbeit war es, neue Chromophore für die [2+2] Photocycloaddition zu erforschen. Es konnte gezeigt werden, dass verschiedene Nitroolefine durch direkte Anregung mit einer Vielzahl von Olefinen in einer intermolekularen [2+2] Photocycloadditionsreaktion mit teilweise hohen Ausbeuten reagieren. Detaillierte Studien zum Mechanismus der Reaktion lieferten Hinweise darauf, dass die Reaktion über die Triplet Hyperpotentialfläche verläuft. Versuche, die Reaktion als intramolekulare Variante oder aber enantioselektiv durchzuführen, scheiterten. Dennoch konnte eine generelle Methode für die intermolekulare [2+2] Photocycloaddition von Nitroolefinen (vornehmlich Nitrostyrolen) etabliert werden. Eine weitere Chromophor-Klasse, die im Zuge dieser Arbeit untersucht wurde, sind Vinylsulfone. Auch diese konnten erfolgreich in intermolekularen [2+2] Photocycloadditionen umgesetzt werden, mit exzellenten Ausbeuten (>99%) und hoher Diastereoselektivität. Studien zur Aktivierung dieses Chromophors durch *Lewis*-Säuren verliefen vielversprechend, es konnte gezeigt werden, dass eine selektive Anregung des komplexierten Substrates durch Triplet-Sensibilisierung möglich ist. Für eine asymmetrische Variante dieser Reaktion konnten die optimalen Bedingungen noch nicht etabliert werden. Zuletzt wurde ein chiraler Thioharnstoff-Thioxanthon Hybrid als potentieller Katalysator für enantioselektive photochemische Reaktionen synthetisiert und evaluiert. Jedoch wurde in keiner der untersuchten Reaktionen ein signifikanter Enantiomerenüberschuss festgestellt.

Abstract

Discovered in the late 19th century, the [2+2] photocycloaddition reaction is nowadays one of the most frequently employed cycloaddition reactions in the field of synthetic organic chemistry. The reaction is used as a key step in many natural product syntheses, with great success. The substrates for such reactions are mostly α,β-unsaturated ketones (i. e. enones), which act as the chromophore that is excited to a high energy excited state by the irradiation with a suitable light source. The photoexcited chromophore subsequently reacts in an inter- or intramolecular reaction, furnishing the characteristic cyclobutane photocycloaddition products. The aim of this work was the evaluation of new chromophore types for [2+2] photocycloaddition reactions. Different nitroolefins were employed successfully as substrates in an intermolecular [2+2] photocycloaddition with various olefins in partially excellent yields. Detailed mechanistic studies revealed, that the reaction course proceeds most likely on the triplet hypersurface. Attempts towards an intramolecular as well as an enantioselective variant of the reaction failed. Nevertheless, a general protocol for the intermolecular [2+2] photocycloaddition of nitroolefins (mostly nitrostyrenes) was established. A second type of chromophores are vinylsulfones, that also readily undergo intermolecular [2+2] photocycloaddition, yielding the respective cyclobutane photoproducts in excellent yields (up to >99%) and high diastereoselectivity. Studies of a potential chromophore activation by *Lewis* acid coordination were promising, it was shown that catalyst-bound substrate can be sensitized selectively. The optimal conditions for an enantioselective variant of the reaction could not yet be established. Lastly, a chiral thiourea-thioxanthone hybrid was synthesized and evaluated as potential catalyst in photochemical reactions. However, no significant enantiomeric excess was observed in any of the test reactions.

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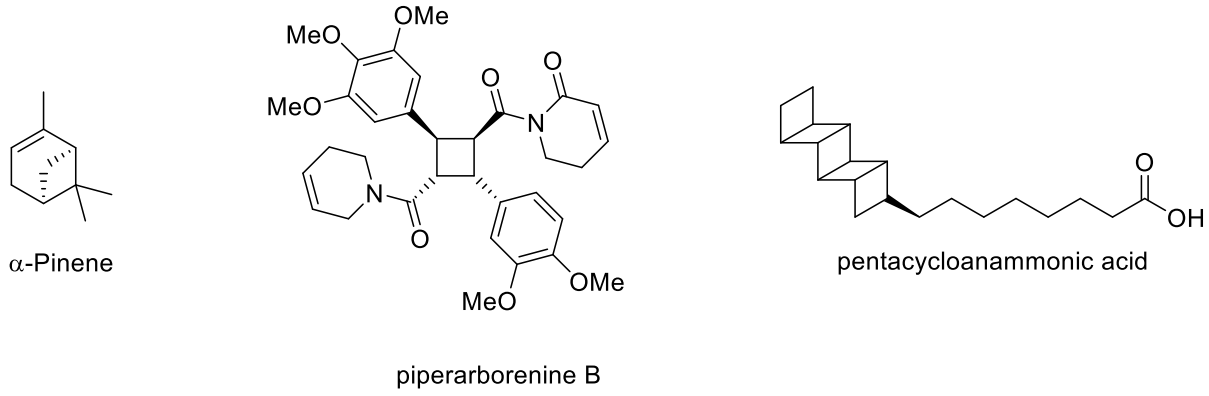
1. Cyclobutanes as Common Structural Motif in Natural Products and their Synthesis by [2+2] Photocycloaddition Reactions

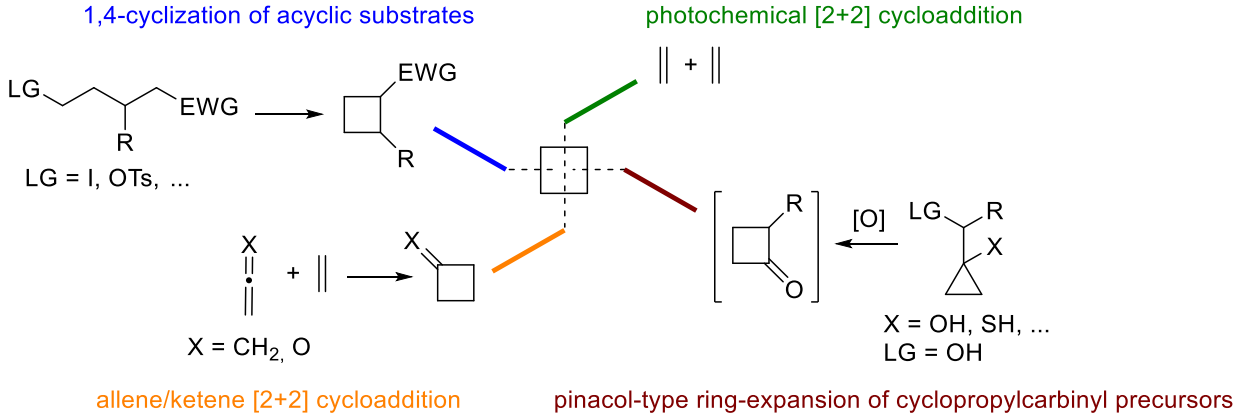
Cyclobutanes can be found as structural motif in a wide variety of natural products,[1–3] despite the high ring strain (111.7 kJ/mol) compared to the more stable and abundant cyclohexane (0 kJ/mol)[4,5] On the one hand, this inherent ring strain, minimized by the adaption of a folded conformation, is responsible for the challenging synthesis and, concurrently, on the other hand it is the reason for the unique reactivity of cyclobutane compounds.[6] The driving force for the latter is clearly the liberation of ring strain, which has been exploited in a manifold of transformations, the most important of which are ring-contraction reactions,[6,7] ring-expansion reactions[6–9] enantioselective *Baeyer-Villiger* oxidations[8,9] and C-C or C-H bond activation.[8–11]

Cyclobutane-containing natural products comprise a variety of classes such as simple terpenes (e. g. α-pinene), pseudodimeric alkaloids (e. g. piperarborenine B) and lipids such as ladderanes, one representative of which is pentacycloanammonic acid (scheme 1).[10,12,13]



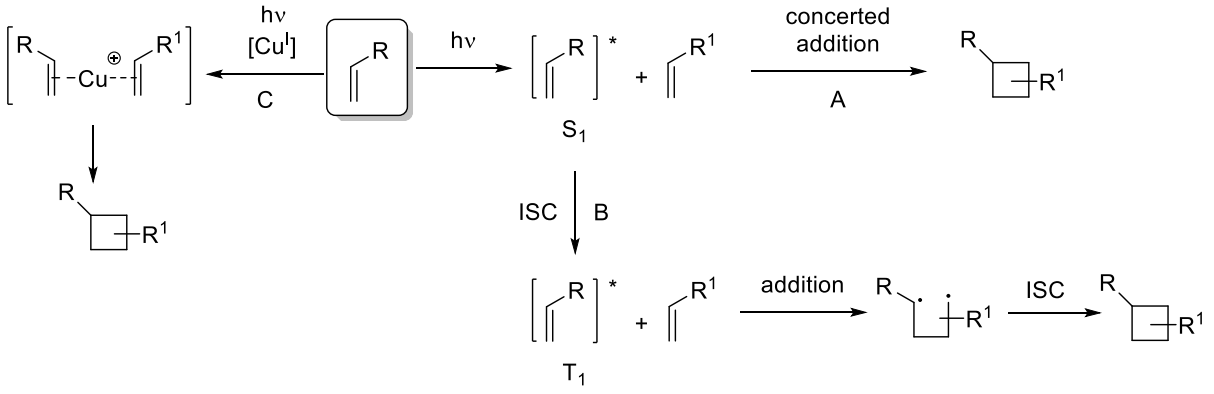
Scheme 1. Examples for cyclobutane-containing natural products.

It has been reported that natural products containing cyclobutanes can have biological activities such as antimicrobial, anticancer and cytotoxic effects.[1,2,12] Furthermore, a selection of cyclobutane-derived amino acids, peptides or nucleosides can potentially act as skin protection against UV irradiation.[1,2] Since cyclobutanes are powerful building blocks especially in natural product synthesis, there is a high interest in the development of stereoselective syntheses and the functionalization of these compounds.[7–10] While several reliable synthetic methods provide access to cyclobutanes,[8,9,14] the most frequently used ones are either ketene [2+2] cycloadditions[15] or [2+2] photocycloadditions (scheme 2).[3,7,14,16]



Scheme 2. Most common synthetic methods for the construction of cyclobutanes (EWG = electron-withdrawing group; LG = leaving group).

With regard to the applicability, the [2+2] photocycloaddition has outperformed other methods both, in the general synthesis of cyclobutane derivatives and in the synthesis of cyclobutane-containing natural products.[3,9,10,14] First reported in 1877,[17] the [2+2] photocycloaddition is nowadays, alongside the *Diels-Alder* reaction,[16] one of the most frequently employed cycloaddition reactions in organic synthesis. Due to several photochemical and photophysical studies, the mechanism of the [2+2] photocycloaddition is well explored.[16,18,19] Upon irradiation of an appropriate unsaturated precursor, the excited substrate can follow three different mechanistic pathways in order to undergo the photocycloaddition (scheme 3).



Scheme 3. Three reaction pathways of the [2+2] photocycloaddition. A: singlet hypersurface. B: triplet hypersurface. C: Cu^{I}-catalysis.

First, the olefin absorbs light of a certain wavelength and is thereby transferred from the electronic ground state S_0 to the first excited singlet state S_1. In this state, it can undergo a concerted addition to another olefin (pathway A). However, the S_1-state of most olefins is short lived. This is due to competitive decay routes such as internal conversion (IC) or fluorescence, which compete with the photocycloaddition reaction. It is possible to enhance the reactivity of

olefins with high lying S_1-states by using copper(I) catalysis (pathway C). The addition of a Cu(I) salt (e. g. CuOTf) leads to the complexation of the olefin, which enables excitation at longer wavelengths and better yields of the target compounds.[16]

Typical substrates for the [2+2] photocycloaddition are α,β-unsaturated ketones (i. e. enones). These compounds undergo rapid intersystem crossing (ISC) after direct excitation to the S_1-state, due to the small energy gap between S_1 and T_1. Addition of a second olefin (intra- or intermolecular) leads to the formation of a 1,4-diradical, which furnishes the photocycloaddition product *via* a second ISC (pathway B). Since the relaxation to the singlet ground state S_0 is a spin-forbidden operation, the T_1-state is relatively long lived. Therefore, most intermolecular [2+2] photocycloaddition reactions are supposed to proceed on the triplet hypersurface, taking into consideration that the reaction depends on the concentration of both reaction partners. In case direct excitation is ineffective or has to be circumvented due to selectivity problems, the population of the triplet state can also be achieved by a triplet energy transfer (sensitization). In this scenario, a sensitizer, i. e. a molecule with a high ISC rate, is excited into the T_1-state and subsequently undergoes energy transfer to a substrate molecule by an electron exchange mechanism (*Dexter* mechanism).[16,20]

At first glance, the retrosynthetic analysis for the construction of cyclobutanes by [2+2] photocycloaddition seems straightforward. It delivers two olefins, which, from a synthetic point of view, simply undergo the photocycloaddition reaction upon irradiation with a light source of a suitable wavelength.[3] More detailed inspection, however, reveals some factors that have to be considered. First, the regio- and stereoselectivity of the reaction are highly dependent on the steric and electronic properties of the starting materials. Second, in intermolecular reactions, homodimerization of the photoprecursors may occur, which impedes a reaction with the other present alkene. Lastly, a photochemically induced *trans-cis*-isomerization of the olefin double bond can lead to a decreased efficiency of the reaction.[11]

Nonetheless, tremendous efforts have been made to overcome these issues, enabling a plethora of different methods applied in total syntheses of natural products with a [2+2] photocycloaddition as the key step.[1,3,10] Considering the importance of this reaction and the high potency of cyclobutane -containing molecules as bioactive compounds (*vide supra*), the pursuit of new substrates for the [2+2] photocycloaddition is of high priority in order to access functionalized cyclobutane structures. The objective of this work was the exploration of new chromophores that seemed amenable to undergo this type of reaction. The products could

potentially serve as starting materials or intermediates in the synthesis of natural products or bioactive molecules.

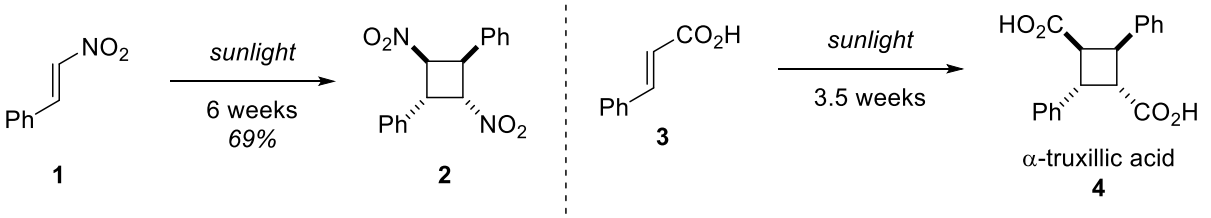
2. [2+2] Photocycloaddition Reactions of Nitroolefins

The nitro group is a versatile functional group in organic synthesis, due to the fact that it is readily transformed in to a variety of different functionalities.[21] The reduction of a nitro group provides convenient access to the respective oximes, hydroxylamines or amines. Further transformations such as elimination or substitution of the nitro group can be performed.[21,22] Therefore, nitro-containing building blocks, especially nitroolefins, represent powerful starting materials as well as intermediates in a plethora of reactions, e. g. as dienophiles in *Diels-Alder*[21–23] or other cycloaddition reactions,[24] as *Michael* acceptors in 1,4-conjugate addition reactions[25–27] and numerous other transformations.[21,22,28,29] Nitroolefins can be easily accessed by the nitroaldol or *Henry* reaction.[30] A condensation of an aldehyde or ketone with nitromethane and subsequent dehydration furnish the corresponding α,β-unsaturated nitro compound.[31,32] Other approaches rely, among others, on the direct nitration of alkenes[21,33] or cross coupling reactions.[34] Nitrostyrenes in particular have shown antimicrobial and antifungal activities,[35] and some of their derivatives are considered as promising anticancer drugs.[36,37] The reactivity of nitroolefins in thermal reactions was reviewed extensively,[21,22,38,39] but also photochemically induced reactions of particularly nitrostyrenes have attracted the interest of organic chemists (*vide infra*).

2.1 Photochemistry of Nitrostyrenes

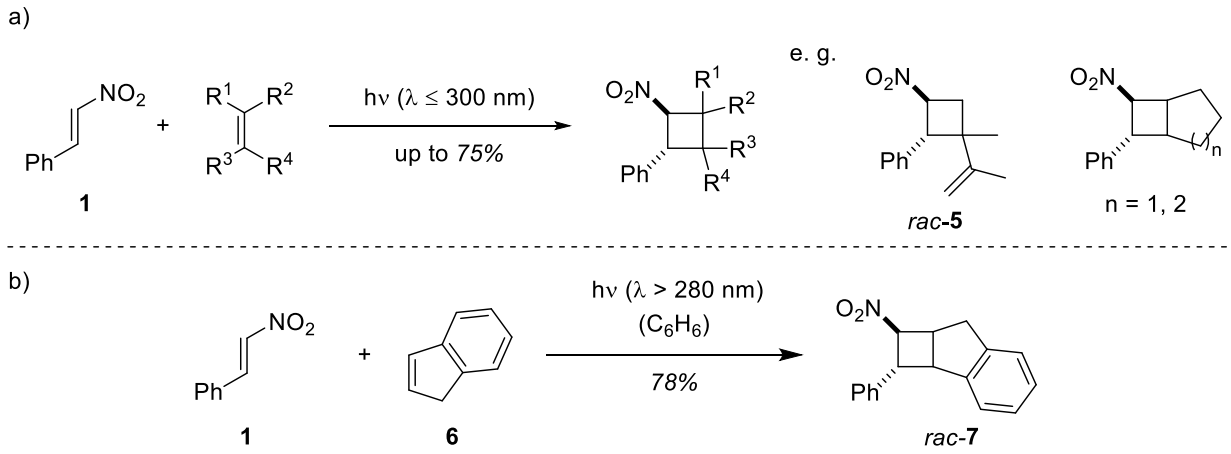
Nitro compounds have been extensively explored in photochemical reactions. Among the most prominent studies are *ortho*-nitro aromatic compounds as photolabile protective groups,[18,40] photoexcited nitrobenzene in cycloaddition reactions[41,42] and the photochemistry of nitronaphthalenes and anthracenes.[43]

As early as in the late 19th century, *Priebs* reported the fading of the characteristic yellow color of *trans*-β-nitrostyrene (**1**) upon light exposure of the sample.[44] Twenty years later, it was proposed by *Meisenheimer*, that photodimerization of nitrostyrene **1** led to the formation of a dimeric structure **2** (scheme 4),[45] analogously to the synthesis of α-truxillic acid (**4**) by irradiation of cinnamic acid (**3**) with sunlight.[46] However, it was not until 1976, when the proposed structure of the head-to-head dimer **2** was established by the group of *Shechter* by extensive derivatization of the photoproduct **2** and careful analysis of the derived products.[47] X-ray crystallographic studies later confirmed the proposed structure of **2**.[48]



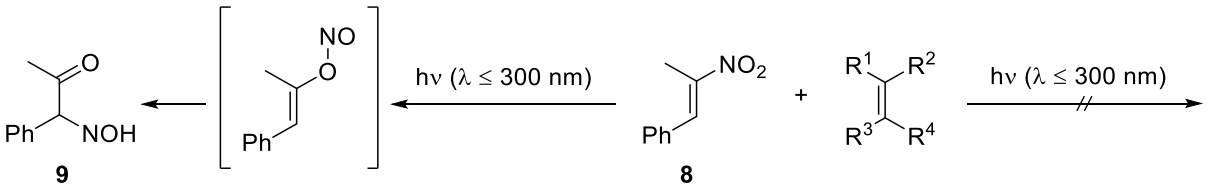
Scheme 4. Photodimerization of *trans*-β-nitrostyrene **1** (left) and cinnamic acid **3** (right) in the solid phase.

Upon irradiation of nitrostyrene **1** in solution, *trans-cis*-isomerization was observed exclusively, impeding a dimerization towards cyclobutane **2**.[49] Only short studies towards intermolecular [2+2] photocycloaddition reactions of nitrostyrenes are reported. *Hoganson* and *Chapman* investigated the intermolecular [2+2] photocycloaddition of nitrostyrene **1** upon irradiation at short wavelength (scheme 5, a).[43,50] While a series of nitrocyclobutane photoproducts was described, only little experimental details and analytical data were provided. The photocycloaddition product *rac*-**5** of nitrostyrene **1** with 2,3-dimethyl-1,3-butadiene was described in a separate publication.[51] Based on circumstantial evidence from the structure of the products obtained, a triplet mechanism was proposed.[43,50] In a report by *Majima* et al. (scheme 5, b), nitrocyclobutane *rac*-**7** was obtained from the [2+2] photocycloaddition of nitrostyrene **1** with indene (**6**) in high yields.[52]



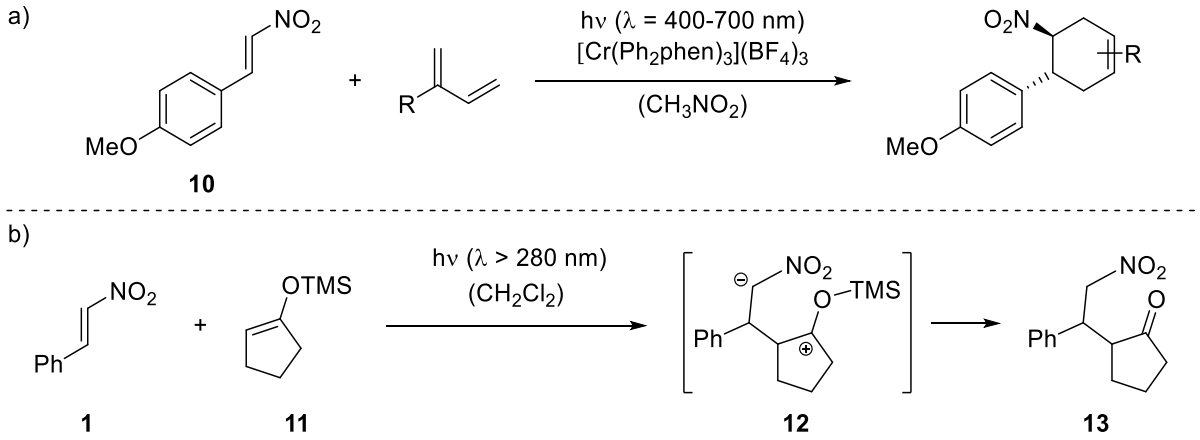
Scheme 5. a) Studies of the intermolecular [2+2] photocycloaddition of nitrostyrene **1** with different olefins by *Hoganson* and *Chapman*. b) [2+2] Photocycloaddition of nitrostyrene **1** with indene (**6**).

Additionally, *Hoganson* and *Chapman* investigated the photochemistry of β-methyl-β-nitrostyrene **8**, which did not add to a second olefin in a photocycloaddition, but underwent a nitro-nitrite rearrangement to the corresponding keto-oxime **9** (scheme 6).[53] This photochemically induced rearrangement was later studied by other groups as well, with regard to the influence of substitution at the aromatic moiety.[54–56]



Scheme 6. Photochemical rearrangement of β-methyl-β-nitrostyrene (**8**).

Further examples for intermolecular photocycloadditions of *trans*-β-nitrostyrene (**1**) were reported by the group of *Ferreira*, who investigated a chromium catalyzed, photochemically induced *Diels-Alder* reaction of nitrostyrene **10** (scheme **7**, a). *Sankararaman* and co-workers presented a photochemical *Michael* addition reaction of nitro- and cyanostyrenes to silyl enol ethers such as **11** and proposed a zwitterionic intermediate **12** involved in the reaction course towards the product **13** (scheme **7**, b).[57]

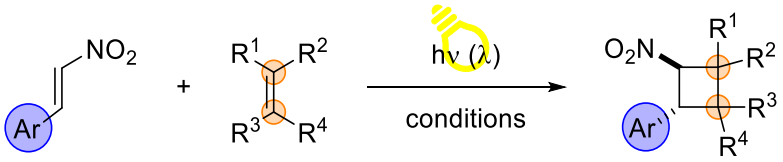


Scheme 7. a) Chromium catalyzed photochemical *Diels-Alder* reaction of nitrostyrene **10**. b) Photochemical *Michael* addition of nitrostyrene **1** to silyl enol ether **11**.

Although short studies of photocycloaddition reactions of nitrostyrenes were reported, a comprehensive study of this chromophore in the [2+2] photocycloaddition reaction has not yet been performed. The products of such a reaction (see scheme 5) are highly interesting with regard to a variety of derivatization reactions possible, thereby furnishing versatile intermediates for further transformations.

2.2 Project Aims

Our initial interest in the [2+2] photocycloaddition on nitrostyrenes as well as nitroolefins in general was attracted by the intriguing reports published on the subject described earlier (*vide supra*). We aspired a comprehensive study of the nitrostyrene chromophore and desired to establish a general protocol for the intermolecular [2+2] photocycloaddition of different nitroolefins to various olefins (scheme 8).



Scheme 8. Intermolecular [2+2] photocycloaddition of nitroolefins.

Additionally, further insights into the photophysical and photochemical behavior of this chromophore should be provided by spectroscopic as well as mechanistical studies. The development of an intramolecular variant should further extend the reaction scope, providing access to more complex structures. Furthermore, methods towards the derivatization of the nitrocyclobutane photoproducts should be evaluated in order to increase the value chain of the method. Finally, the motivation for this project was highly driven by the ambition to develop a protocol for the enantioselective [2+2] photocycloaddition of nitroolefins.

2.3 Photophysical Properties of *trans*-β-Nitrostyrene

A crucial part of photochemistry is the understanding of the behavior of the respective chromophore upon the absorption of light. Photoluminescence spectroscopic studies of the respective compound are crucial in order to obtain the information about the nature of the excited state of the chromophore needed for establishing the optimal reaction conditions. The luminescence characteristics of nitro aromatic compounds are generally well understood and described in the literature.[58–62] Among the nitro aromatic compounds, nitrostyrenes were also investigated regarding their photophysical properties.[63–68] The results of these studies will be elaborated in the following chapter and will be compared with the experimental data obtained during the course of this work.

2.3.1 UV/Vis Spectroscopy

The UV/Vis spectrum of *trans*-β-Nitrostyrene (**1**), a bright yellow colored crystalline solid, showed two characteristic absorption bands (figure 1). The small inset depicts the absorption in the visible light region at higher concentrations, since this absorbance seems to be quite low in intensity given the color of the compound.

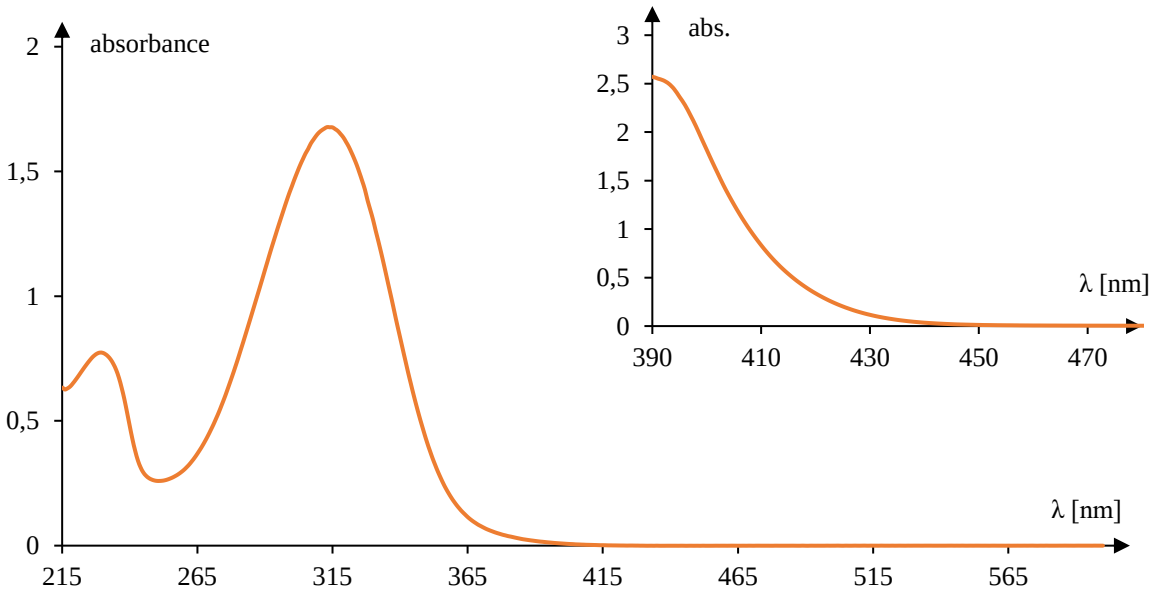


Figure 1. UV/Vis spectrum of *trans*-β-nitrostyrene (**1**) (*c* = 1 mM, CH_2Cl_2; inset: *c* = 20 mM, CH_2Cl_2).

The broad absorption band with the maximum at λ_{max} = 312 nm (ε = 16350 M^{-1} cm^{-1}) is comprised of an intramolecular charge transfer excitation from the highest occupied molecular

orbital (HOMO), that is the π-orbital located at the aromatic ring in conjugation with the double bond, to the lowest unoccupied molecular orbital (LUMO), that is the π*-orbital placed at the nitro group (figure 2).[57,65–67] The nπ*-excitation (exclusively located at the nitro group) is also contributing to this absorption band, while the other characteristic absorption λ_{max} = 229 nm (ε = 7370 M^{-1} cm^{-1}) is described as electronic transitions from the HOMO to higher level MO's.[65,67]

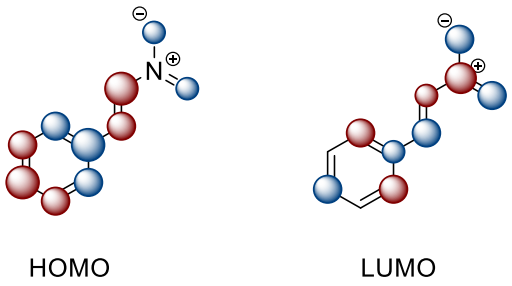


Figure 2. Orbital coefficients of the HOMO and the LUMO of nitrostyrene **1**.[65,67]

In non-polar solvents such as cyclohexane, the absorption maximum was shifted to lower wavelength (λ_{max} = 299 nm), an effect that can attributed to the inferior solvation stabilization of the charge transfer.[57,63,66,68,69] The electronic nature of any substituent exerts significant influence on the absorption. Electron donating groups such as a methoxy or dimethylamino group led to a bathocromic shift as a result of increased charge migration, whereas electron withdrawing groups such as methoxycarbonyl or cyano caused a hypsochromic shift.[65,66]

2.3.2 Luminescence Spectroscopy

In order to elucidate the nature of the excited state of *trans*-β-nitrostyrene (**1**), luminescence spectroscopy was conducted in a solvent mixture of pentane/isopentane (1/1 v/v) at 77 K. Steady state spectra were recorded at room temperature, but no luminescence could be detected. This finding is in accordance with a report by *Cowley*, stating that fluorescence only occurs in nitrostyrenes with increased electron density bearing strongly electron donating substituents at the aromatic core.[66] No fluorescence, but phosphorescence was observed as soon as less or non-electron donating groups such as methoxy or chloro were introduced.[66] In this work, only nitrostyrene **1** was investigated. When the sample was frozen into a glass matrix at 77 K, phosphorescence was observed (figure 3).

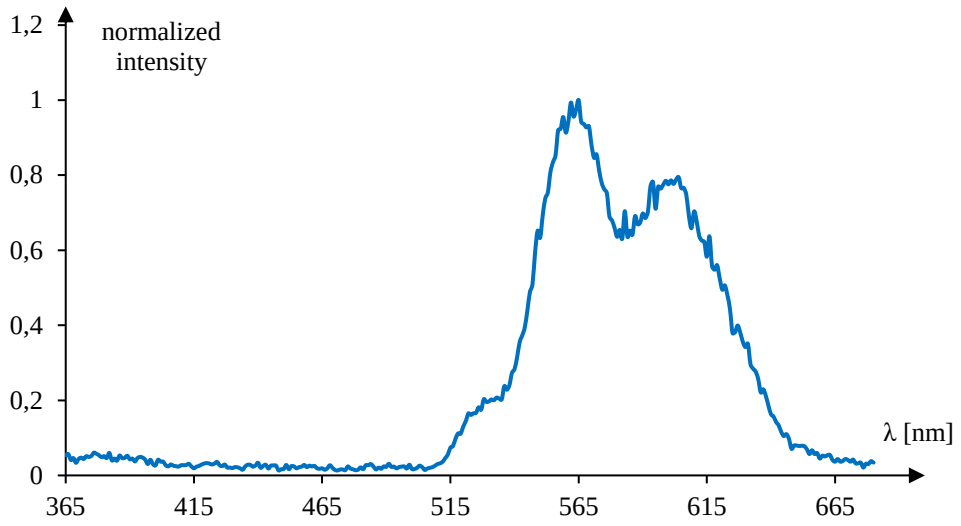


Figure 3. Phosphorescence spectrum of nitrostyrene 1 (*c* = 150 µM, pentane/*iso*-pentane = 1/1 v/v; pulsed measurement at 77 K, flash delay 0.07 µs).

The 0,0-transition located at λ_{max} = 546 nm corresponds to a triplet energy of E_T = 219 kJ/mol. In more polar solvents such as ethanol, a bathochromic shift of the phosphorescence results in a calculated triplet energy of E_T = 229 kJ/mol (λ_{max} = 523 nm). This is again in accordance with findings in the literature, with an emission maximum centered at λ = 524 nm (E_T = 228 kJ/mol) in ethanol as the solvent.[66] In another publication,[67] the triplet energy is calculated to be E_T = 230 kJ/mol.

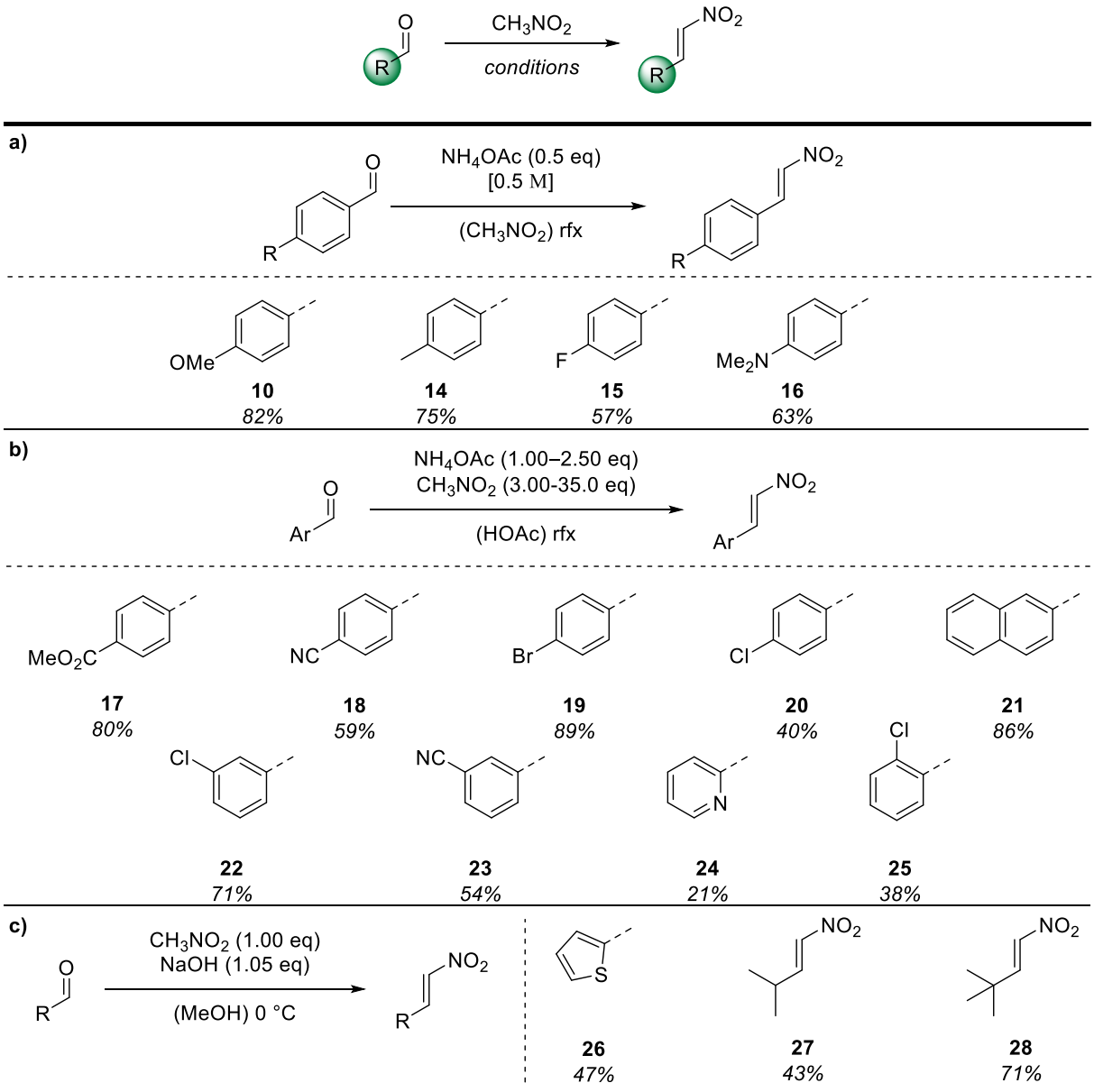
Cowley also determined the lifetime of the excited triplet state as $\tau(T_1)$ = 6 µs. Substituted nitrostyrenes such as *para*-chloro (E_T = 227 kJ/mol) and *para*-methoxy (E_T = 230 kJ/mol) were found to have quite similar photophysical properties. The authors also state that there is a correlation between the absence of fluorescence and the energy of the first excited singlet state S_1, as no fluorescence could be observed when S_1 > 2.95 eV (284 kJ/mol). This is attributed to one or more competitive, rapid and non-radiative relaxation pathway.[66] The most obvious route of decay in this scenario could be the geometrical *trans*-*cis*-isomerization of the nitrostyrene double bond. As stated earlier, nitrostyrenes such as **1** undergo *trans*-*cis*-isomerization upon irradiation in solution,[49,70] to such an extent that the process competes with intermolecular reactions.[43,51,57] Aside from the geometrical isomerization, IC from $S_1(\pi\pi^*)\rightarrow S_1(n\pi^*)$ as well as ISC from $S_1(\pi\pi^*)\rightarrow T_1(n\pi^*)$ (with T_1 as the first excited triplet state) were proposed as the decay routes responsible for the lack of fluorescence.[66] An enhanced intersystem crossing rate from $S_1(\pi\pi^*)\rightarrow T_1(n\pi^*)$ observed in nitronaphthalenes has previously been determined as the reason for the lack of fluorescence in these molecules in particular and possibly in some nitroaromatic compounds in general.[71]

Cowley favored the IC/ISC hypothesis over the isomerization as the explanation for the photoluminescence.[66] A comprehensive study on the photophysical behavior of *para*-dimethylamino nitrostyrene demonstrated, that the ISC in this compound is extremely fast [$\tau(S_1) = 6$ ps],[68] substantiating this argument. A more detailed analysis of the nature of the excited state of nitrostyrene **1** was not performed in this work. *Stern-Volmer* analysis was not possible due to the absence of fluorescence, while short-term spectroscopy could not be performed as an adequate setup was not available.

Summing up, it can be stated that irradiation of nitrostyrene **1** leads to charge-transfer excitation to $S_1(\pi\pi^*)$. From this excited state, three pathways of relaxation are possible: isomerization, IC and ISC. The absence of fluoresce was ascribed to a high ISC rate from $S_1(\pi\pi^*) \rightarrow T_1(n\pi^*)$. The triplet energy, depending on the solvent, can be estimated to be $E_T = 219$ kJ/mol (pentane/isopentane)/ $E_T = 229$ kJ/mol (ethanol). If a photoreaction of nitrostyrene **1** was to be conducted under sensitized conditions, a sensitizer with $E_T \geq 230$ kJ/mol should be chosen.

2.4 *Synthesis of Irradiation Precursors for Intermolecular Photoreactions*

Generally, the nitroolefins that were used as substrates for the [2+2] photocycloaddition reactions were synthesized in one simple step from the corresponding aldehydes and nitromethane in an *Henry* reaction (scheme 9).[30]

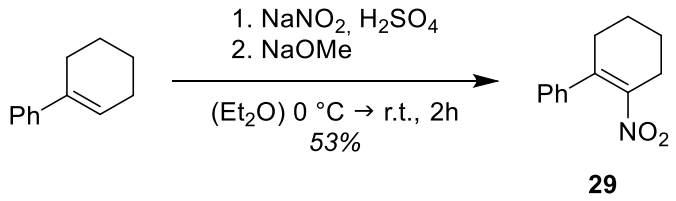


Scheme 9. Synthesis of nitroolefins via *Henry*-reaction.

Three different, slightly modified literature procedures were employed, depending on the respective aldehyde.[72–74] Liquid starting materials were freshly distilled prior to use in order to avoid contamination of oxidation products such as the corresponding carboxylic acid. Under conditions a) or b) (scheme 9), a color change of the refluxing solution indicated a successful elimination of the intermediate alcohol to the nitroolefin. For substrates **26-28**, basic conditions

had to be applied in order to push forward the elimination step of the reaction. The yields obtained ranged from poor to very good (21-89%). No attempts were undertaken to optimize reaction conditions. Only in those cases, when the reaction failed completely under the conditions applied first, an alternative method was chosen.

Another substrate with an endocyclic double bond was synthesized by direct nitration of phenyl-substituted cyclohexene (scheme 10).



29

Scheme 10. Nitration of phenyl-cyclohexene to nitroolefin **29**.

All nitroolefins containing an aromatic moiety in conjugation to the double bond are colored compounds. UV/Vis spectroscopy was conducted with all compounds to analyze the effect of electron donating and withdrawing substituents and the substitution pattern on the absorption of aromatic nitrostyrenes **1**, **10** as well as **14-26** (figure 4).

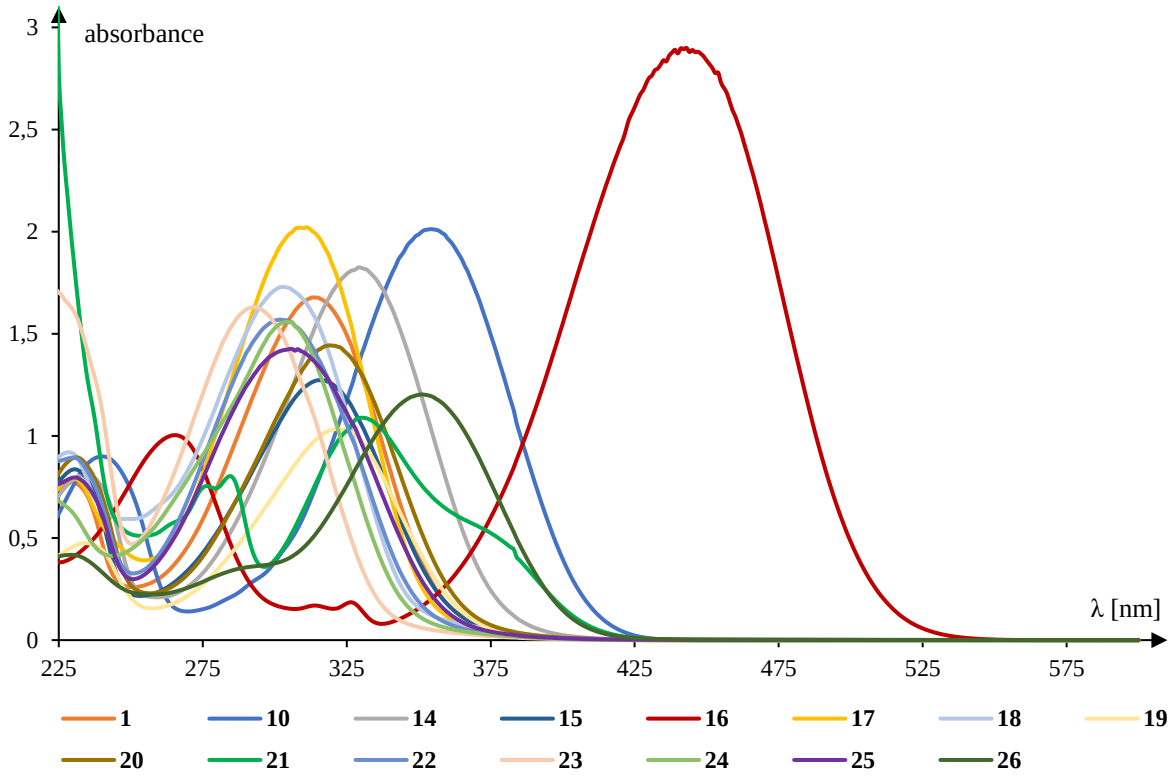


Figure 4. UV/Vis spectra of aromatic nitrostyrenes **1, 10** as well as **14-26** (*c* = 1 mM, CH_2Cl_2).

As it could be expected, the absorption maximum of nitrostyrenes bearing an electron withdrawing group were shifted hypsochromicly, while electron donating substituents led to a bathochromic shift of the absorption. Comparing the influence of the substitution pattern (e.g. *para*-/*meta*-/*ortho*-chloro **20**, **22**, **25**), the absorption of *para*-substituted **20** was slightly shifted to longer wavelengths. Naphthyl (**21**) and thiophenyl (**26**) in conjugation to the nitroolefin expectedly led to a significant shift of the absorption maximum, while the rather electron poor pyridyl moiety (**24**) induced a hypsochromic shift. Generally, the absorption of all aromatic nitrostyrenes tailed into the visible light region, so that irradiation at wavelengths $\lambda > 400$ nm should lead to direct excitation of the substrates and, in the presence of another olefin, to the intermolecular [2+2] photocycloaddition.

The UV/Vis characteristics of nitroolefins **27**-**28** shall be considered separately, due to their significant difference in structure (figure 5).

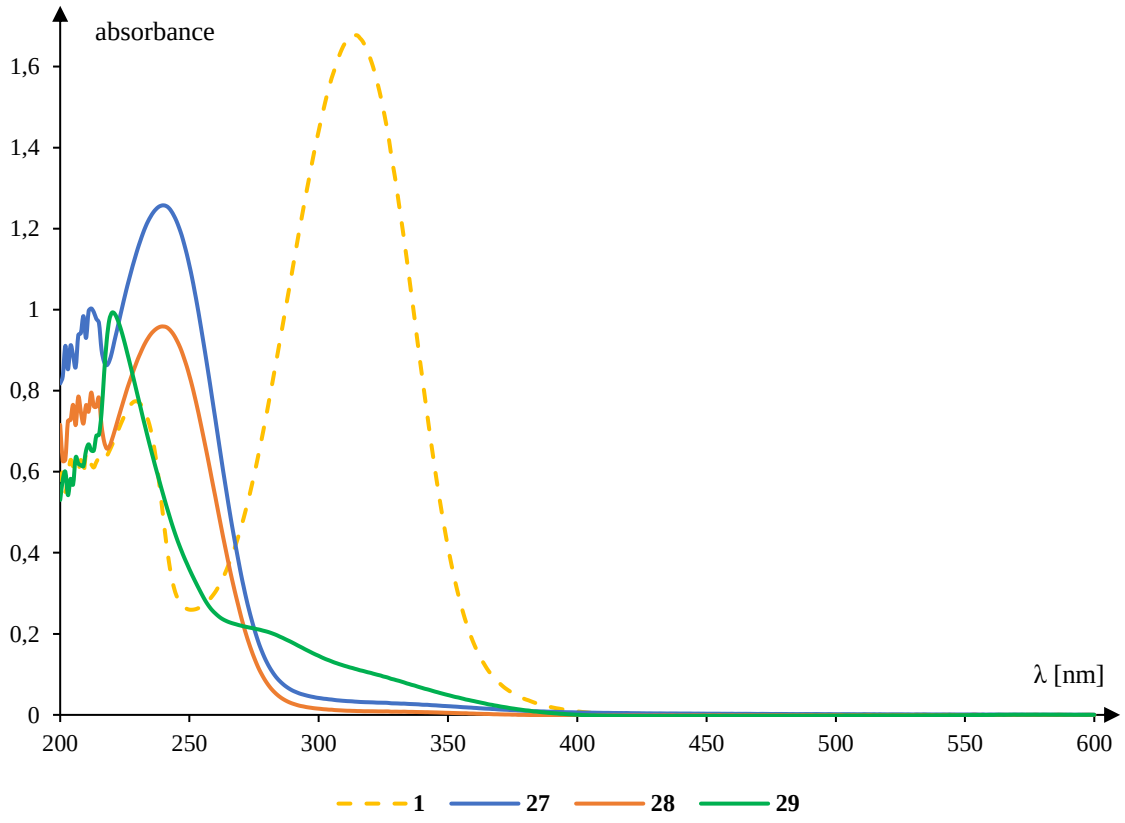


Figure 5. UV/Vis spectra of nitroolefins **27**-**29** (c = 1 mM, CH_2Cl_2).

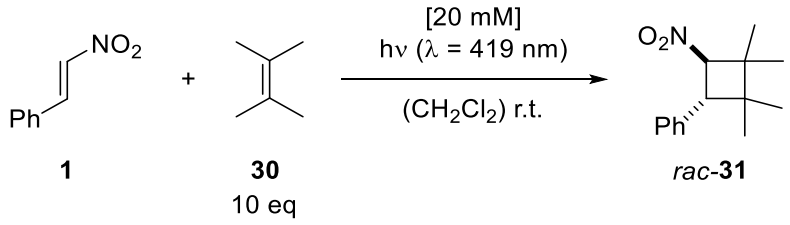
The absence of the aromatic moiety led to a λ_{max} at significant shorter wavelength compared to *trans*-β-nitrostyrene (**1**) (figure 5, dashed orange). This is apparently due to the reduced conjugation of the chromophore. The absorption of nitrostyrene **27** was also significantly shifted hypsochromicly, although conjugation with the phenyl moiety should still be

established. However, it should be noted, that the phenyl and the nitro group are placed in a *cis*-fashion relative towards one another, different to all other substrates.

2.5 Intermolecular [2+2] Photocycloaddition Reactions of Nitrostyrenes

2.5.1 Optimization of Reaction Conditions

Initially, our interest in the [2+2] photocycloaddition of nitroolefins was based on the reaction of *trans*-β-nitrostyrene (**1**) with indene (**6**) reported in 1980.[52] The first experiments on the evaluation of a suitable irradiation wavelength and the solvent were undertaken with this exact same system during the Master's thesis that preceded this work.[75] The longest wavelength at which full conversion was still observed was found to be λ = 419 nm, and the solvent was changed from benzene to less toxic dichloromethane. Later, the reaction partner was switched to 2,3-dimethyl-2-butene (**30**) to avoid the formation of diastereoisomers. Further optimizations of the reaction conditions such as the variation of concentration, temperature and equivalents of the olefin were performed. The final, optimized reaction conditions for the intermolecular [2+2] photocycloaddition of nitrostyrene **1** to cyclobutane *rac*-**31** are depicted in scheme 11.

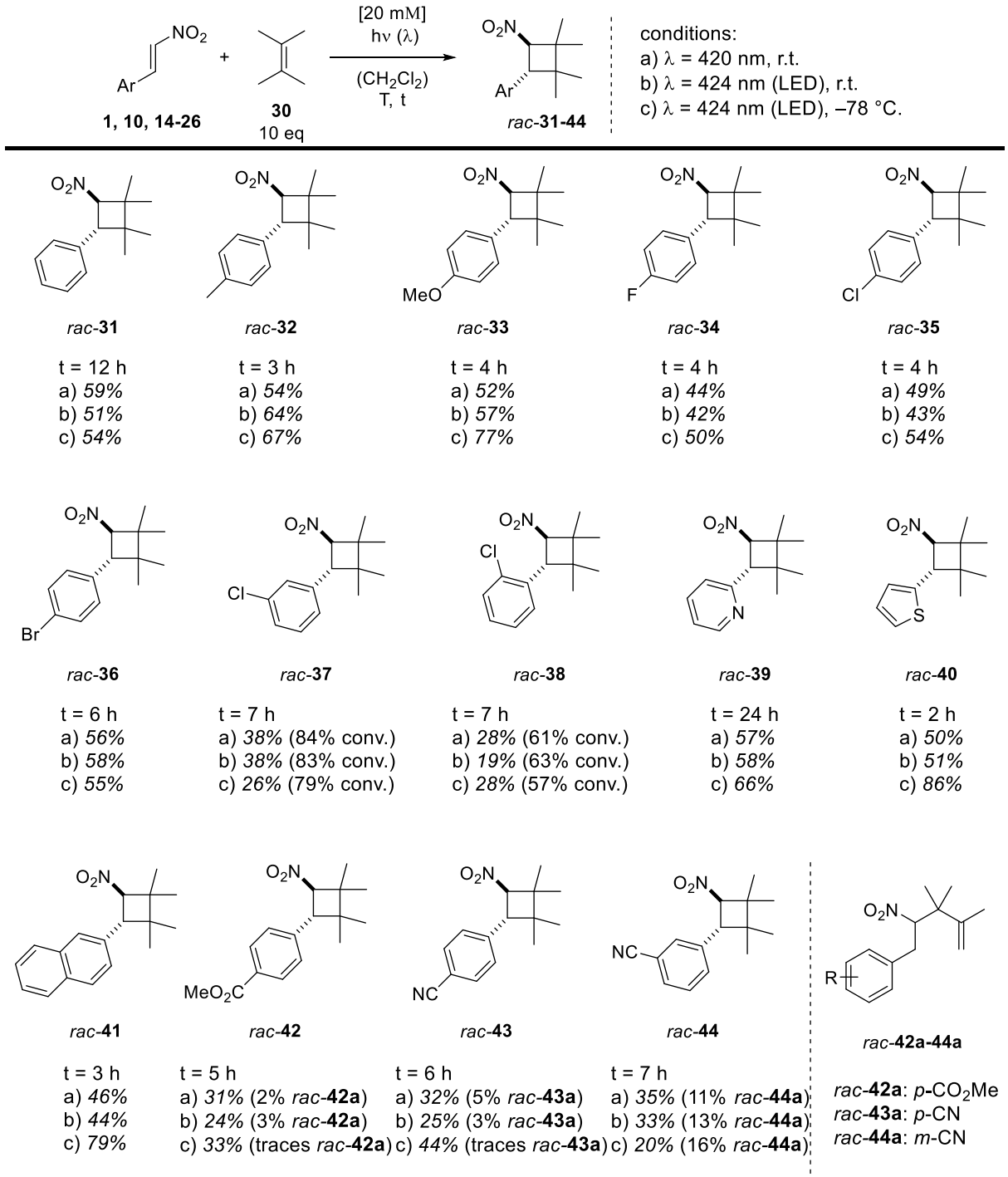


Scheme 11. Optimized reaction conditions for the [2+2] photocycloaddition of nitrostyrene **1**.

In all cases, the nitro and the phenyl group remained in *trans*-configuration relative towards one another in the isolated photoproducts, indicated by the rather large coupling constant ($^3J \approx 10.0$ Hz). The extension of the substrate scope was undertaken on the basis of the described optimized reaction conditions.

2.5.2 Substrate Scope – Nitroolefins

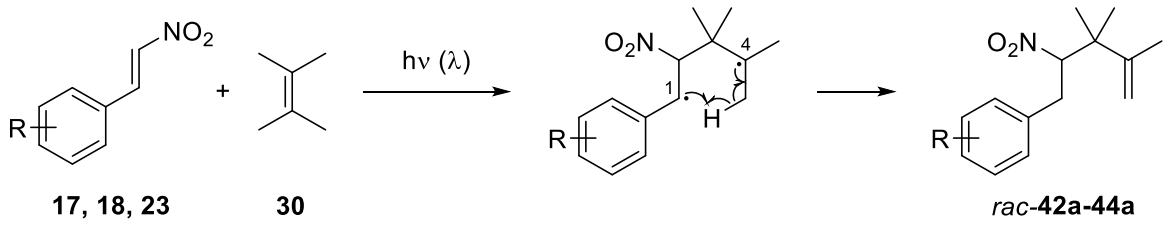
The nitroolefins described in chapter 2.4 were employed as substrates in the intermolecular [2+2] photocycloaddition with 2,3-dimethyl-2-butene (**30**) as the olefin. The light source was varied between λ = 420 nm (16 fluorescent lamps, 128 W, photoreactor) and λ = 424 nm (single LED, 3 W). In addition, the reactions were also performed at low temperature (−78 °C). The results of these experiments are summarized in scheme 12.



Scheme 12. Substrate Scope of nitroolefins **1**, **10** and **14-26** in the intermolecular [2+2] photocycloaddition.

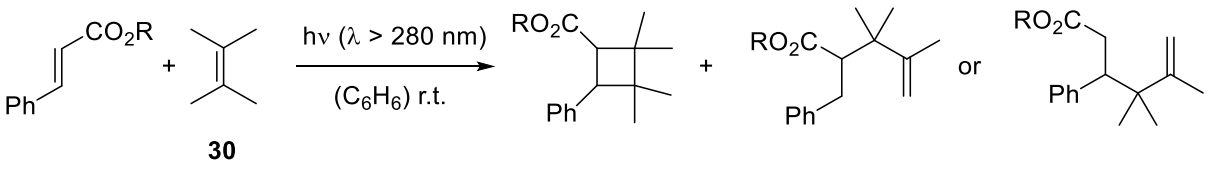
The yields in the intermolecular [2+2] photocycloaddition with olefin **30** ranged from poor to high. Comparing the results with differently substituted nitroolefins at room temperature, some trends become apparent. First, the implementation of electron donating groups (*rac*-**32**, *rac*-**33**) or weak electron withdrawing groups such as halogens (*rac*-**34**, *rac*-**35**, *rac*-**36**) in the *para* position of the aromatic moiety did not change the reaction outcome significantly compared to the unsubstituted nitrostyrene **1** (yields between 42-64%). If a chloro substituent was incorporated in the *meta* (*rac*-**37**) or *ortho* position (*rac*-**38**), the reaction did not reach full

conversion. The yields decreased, and significant amounts of starting material were recovered (up to 43%). The recovered starting material was isomerized in case of *ortho* substituted *rac*-**38** to the corresponding *cis*-isomer. Replacement of the phenyl group with a more electron poor aromatic heterocycle such as pyridine (*rac*-**39**), a more electron rich aromatic heterocycle such as thiophene (*rac*-**40**) or with higher conjugated naphthalene (*rac*-**41**) did not show a noticeable influence on the yield as well (44-58%). With a methoxycarbonyl group in the *para* (*rac*-**42**) or a cyano group in the *para* (*rac*-**43**) or *meta* position (*rac*-**44**), the yields obtained were again slightly lower compared to the reaction with *trans*-β-nitrostyrene (**1**). In these three reactions, by-products, *rac*-**42a**-**44a**, were isolated. The formation of these olefinic by-products could be explained by a photo-ene reaction[76,77] occurring as shown in scheme 13. A hydrogen atom was abstracted from one of the methyl groups in the C4 position of the 1,4-diradical, resulting in the open chain pentenyl structure.



Scheme 13. Proposed formation of side products *rac*-**42a**-**44a**.

A similar finding was reported in the intermolecular [2+2] photocycloaddition of *trans*-cinnamic acid derivatives with e. g. 2,3-dimethyl-2-butene (scheme 14).[76] After irradiation with a medium pressure mercury lamp, a second product was isolated in addition to the desired cyclobutane. Two different structures were proposed for this second photoproduct, and it was hypothesized that these by-products would be formed in a photo-ene reaction occurring on the singlet hypersurface, as no product formation could be observed under sensitized conditions.



Scheme 14. Formation of an olefinic by-product from a photo-ene reaction of *trans*-cinnamic acid derivatives.[76]

The [2+2] photocycloaddition of different nitroolefins was conducted under different conditions with each substrate to evaluate the influence of the type of light source (fluorescent lamps vs. single LED) and temperature (room temperature or −78 °C). In all cases, the results for the irradiation with either fluorescent lamps or the LED were very similar with a difference

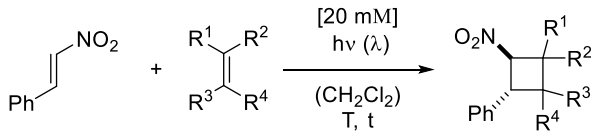
in yield <5%. Apparently, the choice of the light source did not influence the outcome of the reaction substantially. Although the λ_{max} are quite similar (λ_{max} = 419 nm vs. λ_{max} = 424 nm), the power of the fluorescent lamps (128 W) exceeds the LED (3 W) by far. However, there was no noticeable difference in the yield of the reaction, which indicates that the LED already emits a number of photons high enough to transfer every substrate molecule into its excited state.

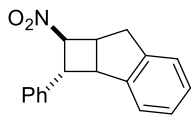
At lower temperatures, in some cases the yield is increased significantly, for example for the methoxy substituted nitrostyrene **9** and the naphthyl- and thiopheyl substituted nitroolefin **21** and **26**. For most of the other substrates, the results for the reaction at −78 °C did not differ discernibly. Apparently, a high electron density enhanced the formation of the [2+2] photocycloaddition product at low temperatures, where other decay pathways such as vibrational relaxation are less dominant. In most other cases, the reaction temperature did not seem to have an impact on the course of the reaction. The reaction times are neither dependent on the source of irradiation, nor on the temperature. With exception of pyridyl derivative **24**, full conversion was reached in two to seven hours.

During the course of the reaction, the starting materials underwent *trans-cis*-isomerization until a photostationary equilibrium with a defined *trans-cis* ratio was reached. Except for *ortho* and *meta* substituted substrates **22** and **25**, the respective starting material was fully consumed. The *trans-cis*-isomerization of nitroolefins as a competing relaxation pathway will be further discussed in the following chapters (*vide infra*).

In total, 14 different nitroolefins were used successfully in the intermolecular [2+2] photocycloaddition with 2,3-dimethyl-2-butene (**30**) under different reaction conditions, yielding the respective cyclobutanes **31**-**44** in mostly good to high yields. Only the dimethylamino-substituted nitrostyrene **16** did not undergo [2+2] photocycloaddition.

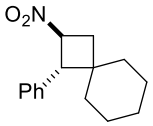
2.5.3 Substrate Scope – Olefins





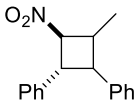
rac-**7**

t = 23 h
a) *87%*, d.r. = 72/28
b) *68%*, d.r. = 72/28
c) *72%*, d.r. = 44/56



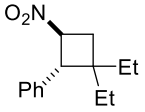
rac-**45**

t = 14 h
a) *51%* (80% conv.)
b) *48%* (89% conv.)
c) *61%* (57% conv.)



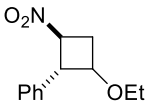
rac-**46**

t = 12 h
a) *52%* (78% conv.), d.r. = 46/54
b) *53%* (80% conv.), d.r. = 49/51
c) *37%* (81% conv.), d.r. = 64/36



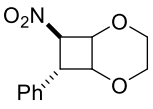
rac-**47**

t = 24 h
a) *43%* (84% conv.)
b) *25%* (37% conv.)
c) *32%* (62% conv.)



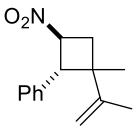
rac-**48**

t = 7 h
a) *43%*, d.r. = 58/42
b) *36%* (80% conv.), d.r. = 62/38
c) *33%* (52% conv.), d.r. = 66/34



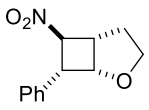
rac-**49**

t = 12 h
a) *72%* (85% conv.), d.r. = 52/19/29
b) *54%* (66% conv.), d.r. = 58/19/23
c) *26%* (71% conv.), d.r. = 58/19/23



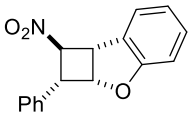
rac-**5**

t = 6 h
a) *75%* (84% conv.), d.r. = 51/49
b) *65%* (72% conv.), d.r. = 55/45
c) *38%* (57% conv.), d.r. = 50/50



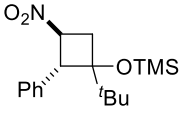
rac-**50**

t = 6 h
a) *36%* (92% conv.)
b) *37%* (87% conv.)
c) *27%* (56% conv.)



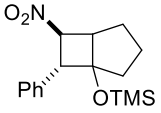
rac-**51**

t = 36 h
a) *47%* (87% conv.)
b) *48%* (64% conv.)
c) *32%* (55% conv.)



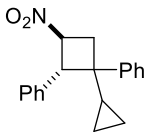
rac-**52**

t = 24 h
a) *34%*, d.r. = 77/23
b) *38%*, d.r. = 77/23
c) *37%* (52% conv.), d.r. = 77/23



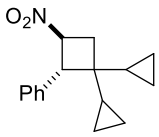
rac-**53**

t = 24 h
a) *35%*, d.r. = 59/41
b) *32%*, d.r. = 59/41
c) *38%*, traces rsm, 61/39



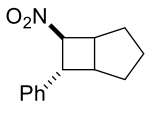
rac-**54**

t = 16 h
a) *88%*, d.r. = 67/33
b) *76%*, d.r. = 56/44
c) *37%* (84% conv.), d.r. = 88/12



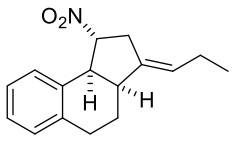
rac-**55**

t = 12 h
a) *70%* + *9%* *rac*-**57**
b) *35%* + *8%* *rac*-**57**
c) *39%* + >4% *rac*-**57**



rac-**56**

57%, d.r. = 87/13
λ = 350 nm,
[100 mM], r.t., 24h



rac-**57**
ring opening product

Scheme 15. Substrate scope of the olefins in the intermolecular [2+2] photocycloaddition with nitrostyrene **1**.

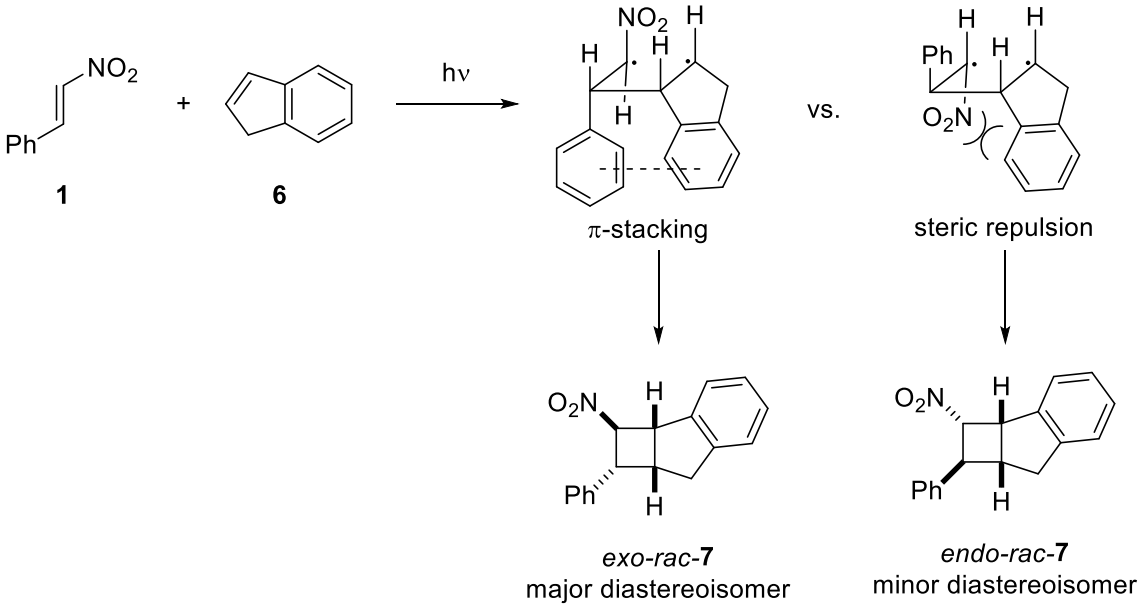
Different olefins were employed in the intermolecular [2+2] photocycloaddition with *trans*-β-nitrostyrene (**1**) to elaborate the substrate scope (scheme 15). The reactions were carried out with each olefin under optimized conditions with the two different light sources (fluorescent lamps vs. LED) and additionally at low temperatures. The yields ranged again from poor to high, with a noticeable number of examples where partially significant amounts of the starting material were recovered. In all cases, the nitro and the phenyl group of the original nitrostyrene remained in *trans* configuration relative towards one another in the isolated photoproducts.

Generally, the olefin scope was limited to simple hydrocarbons or ethers, both cyclic and acyclic. Regarding non-heteroatom containing olefins, the best results were obtained with indene (*rac*-**7**) and 1,1-cyclopropylphenyl ethylene (*rac*-**54**), with a diastereoselectivity of roughly 75:25 and 66:34, respectively. In both cases, the major diastereoisomer was the one with both phenyl entities at the cyclobutane in a formal *cis* configuration relative to each other. The reaction with *trans*-β-methylstyrene (*rac*-**46**) did not show any diastereoselectivity, and starting material was recovered. Irradiation of nitrostyrene **1** in presence of the C_2-symmetric methylene cyclohexane (*rac*-**45**) and 1,1-diethyl ethylene (*rac*-**47**) did also not lead to full conversion after long reaction times of 14 and 24 hours, respectively, with moderate isolated yields. Fortunately, 2,3-dimethyl-1,3-butadiene (*rac*-**5**) did not undergo a *Diels-Alder* reaction but yielded the corresponding cyclobutane as a mixture of diastereoisomers. The photoreactions with ethers were generally performed in moderate yields. While the photocycloaddition with ethyl vinyl ether (*rac*-**48**) resulted in a mixture of diastereoisomers, the formation of three diastereoisomers was observed with 1,4-dioxene (*rac*-**49**), with the *trans*-fused dioxane moiety at the cyclobutane as the major product. Cyclic ethers such as 2,3-dihydrofurane (*rac*-**50**) and benzo[b]furane (*rac*-**51**) added in a highly diastereoselective fashion to the nitrostyrene **1**.

Silyl enol ethers also underwent [2+2] photocycloaddition to nitrostyrene **1**, however the reactions were slow and low yields of the respective cyclobutanes *rac*-**52** and *rac*-**53** were observed. For the acyclic silyl enol ether (*rac*-**52**), one diastereoisomer was formed preferentially with a d.r. of 75:25, while the cyclic silyl enol ether (*rac*-**53**) did not add with noticeable diastereoselectivity. In contrast to a literature known report, no *Michael* addition products were detected in these reactions.[57] A possible deprotection of the silyl enol ether in the cyclobutane photoproduct was also not responsible for the low yields. C_2-symmetric 1,1-dicyclopropyl ethylene was mainly employed in the reaction to investigate the mechanism of the cyclobutane formation (*vide infra*). Indeed, the [2+2] photocycloaddition product (*rac*-**55**) was obtained in 70% yield, along with 9% of a by-product originating from a ring opening of at least one of the cyclopropyl groups. This side product was identified as *rac*-**57**,

the mechanism of its formation will be further disclosed in the respective chapter. For the photocycloaddition of nitrostyrene **1** to cyclopentene, different conditions had to be applied (*rac*-**56**). The reaction was performed at high concentrations of the substrate in a solution of the olefin and the sample was irradiated at shorter wavelength ($\lambda = 350$ nm). The photocycloaddition product *rac*-**56** was obtained in 57% yield, with a high preference for the formation of one diastereoisomer.

Admittedly, the [2+2] photoreaction of nitrostyrene **1** lacks significant simple diastereoselectivity. The formation of a major diastereoisomer, which is in most cases the *exo* product (*exo* referring to a *trans* configuration of the nitro group and the larger moiety of the olefin) can be explained by steric and electronic factors. For example, in the reaction of nitrostyrene with indene (**6**), a favorable π-stacking interaction between both aromatic moieties was proposed, leading to the preferred formation of the *exo* product (scheme 16)

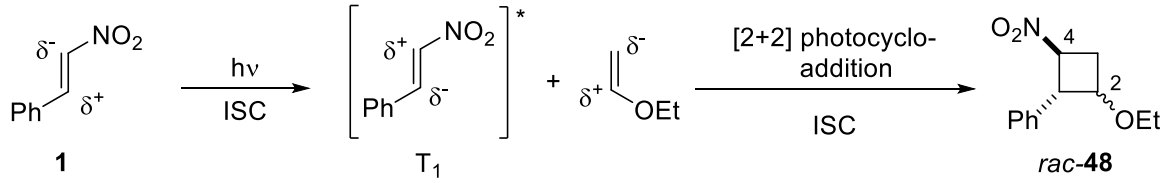


Scheme 16. Diastereoselectivity of the intermolecular [2+2] photocycloaddition of nitrostyrene **1** to indene (**6**).

The steric repulsion between the nitro group and the larger moiety of unsymmetrically substituted olefins might be stronger, forcing this moiety into a formal *cis* configuration relative to the phenyl entity of the former nitrostyrene. Assuming that the reaction proceeds on the triplet hypersurface in a stereoconvergent fashion, the product formation occurs *via* the thermodynamically more stable 1,4-dicradical intermediate which is formed preferentially.[18]

Examining e. g. cyclobutanes *rac*-**45**, *rac*-**47**, *rac*-**50** or *rac*-**53** more carefully, it becomes apparent that the reaction proceeds with an excellent regioselectivity that can be explained with

an inverted polarity (*Umpolung*) of the double bond of nitrostyrene **1** in its excited state (scheme 17).



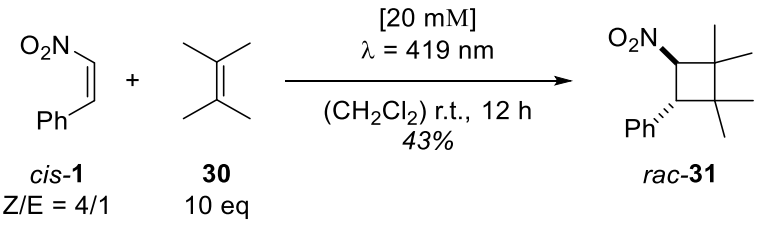
Scheme 17. Regioselectivity in the [2+2] photocycloaddition of nitrostyrene **1**.

With this *Umpolung* of the double bond polarity in the excited triplet state, the α-carbon is nucleophilic, whereas the β-carbon is electrophilic, which accounts for the regioselective addition of the olefins. The photochemical *Umpolung* is also observed in enone chromophors upon excitation and ISC into the triplet state.[78,79] The higher nucleophilicity at the α-carbon in the excited state is also demonstrated by the orbital coefficients of the HOMO of nitrostyrene **1** (Figure 2, chapter 2.3).[65,67] Employing the same nomenclature that has been established for enones, the *head-to-tail* product (HT) was the single regioisomer observed in those reactions with 1-monosubstituted or 1,1-disubstituted ethenes (*head-to-tail* referring to the nitro group and the substituent(s) in the C2- and C4-position of the cyclobutane, e. g. *rac*-**48**). The formation of a *head-to-head* (HH) configured 1,4-diradical during the course of the reaction can not be excluded, as no experiments or calculations were undertaken. However, it can be stated that the cyclization to the cyclobutane can only occur efficiently in the HT diradical, while a hypothetical HH diradical rather undergoes fragmentation towards the respective starting materials.[80]

Comparing the results obtained by irradiation with the two different light sources, no real trend becomes apparent. In some cases, the yields under both conditions were quite similar (e.g. *rac*-**45**, *rac*-**46**, *rac*-**51**), while for other examples a (somewhat significant) decreased yield was registered (*rac*-**47**, *rac*-**49**, *rac*-**55**). At low reaction temperatures, no general trend is visible. Taking a closer look at the olefins individually, it can be noted that the formation of the desired product was decreased substantially for cyclic ethers *rac*-**49**, *rac*-**50** and *rac*-**51**, as well as for the diene *rac*-**5** and the cyclopropyl bearing olefins *rac*-**54** and *rac*-**55**. In these reactions, except for *rac*-**55**, substantial amounts of starting material were recovered (up to 45%). For other olefins, the reaction at −78 °C proceeded with similar results compared to those obtained at room temperature (silyl enol ethers *rac*-**52** and *rac*-**53**, other hydrocarbons *rac*-**7** and *rac*-**48**). However, in all cases except for *rac*-**7**, starting material was recovered. UV/Vis titration of nitrostyrene **1** with different concentrations of some olefins (2,3-dimethyl-2-butene, ethyl vinyl

ether, 1,4-dioxene) did not reveal any changes in the absorption of the nitro compound, thus providing no evidence for the formation of a ground state or excited state complex (exciplex)[18] between both reaction partners. This result is in accordance with prior studies performed by *Hoganson*.[50]

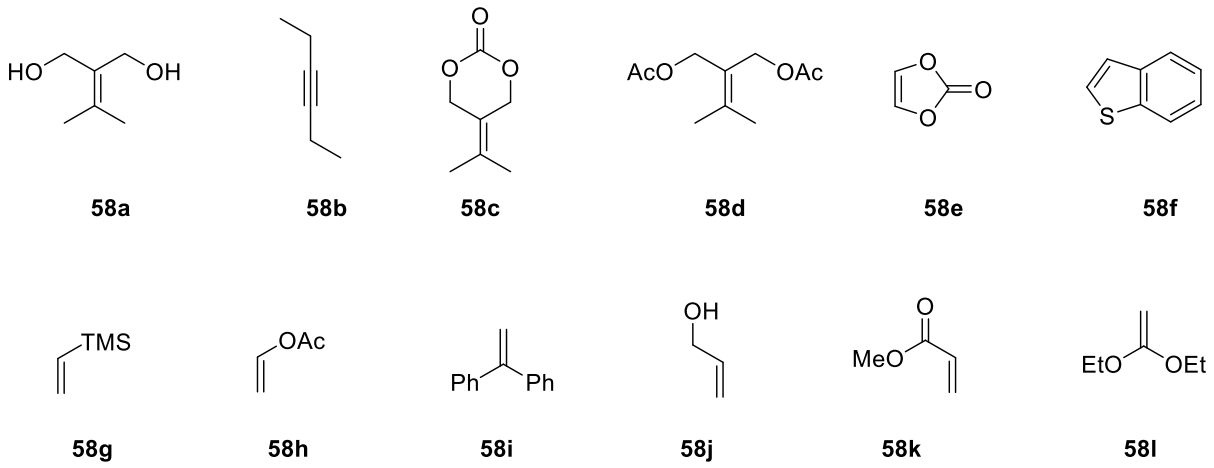
Regarding the reaction times, nitrostyrene **1** reacted rather slowly with most olefins (up to 36 hours reaction time) and often without full conversion. The olefin was employed in ten-fold excess, and although not quantified, large amounts of the olefin were recovered after the reaction was complete (or reached a stationary point at which no further conversion was observed). Although *trans*-*cis*-isomerization of the starting material is an energy-wasting relaxation process formally competing with the photocycloaddition reaction, the process is reversible.[81] It was shown, that when an mixture of β-nitrostyrene enriched with the *cis*-isomer *cis*-**1** (4:1) was used as the starting material in the [2+2] photocycloaddition with 2,3-dimethyl-2-butene (**30**), the reaction still proceeded with full conversion towards the same *trans*-cyclobutane photoproduct *rac*-**31** in comparable yield (scheme 18).



Scheme 18. [2+2] Photocycloaddition of *cis*-enriched nitrostyrene *cis*-**1** to 2,3-dimethyl-2-butene (**30**).

Therefore, the photochemically induced geometrical isomerization itself does not prevent the photocycloaddition reaction, but it is regarded as a major factor responsible for the prolonged reaction times.

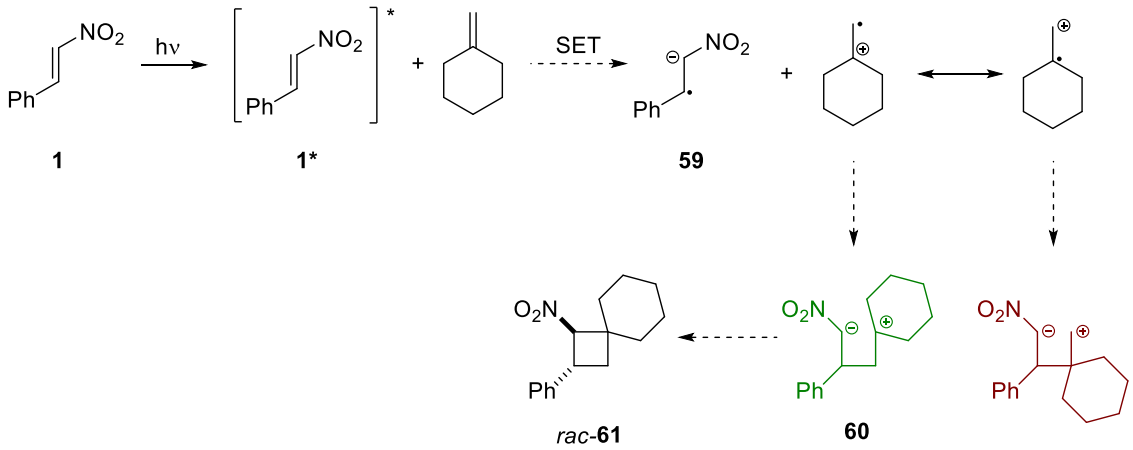
A series of olefins tested was unsuccessful in the [2+2] photocycloaddition reaction with nitrostyrene **1**, either leading to decomposition of the starting material or no conversion was observed (scheme 19).



Scheme 19. Olefins incapable of undergoing [2+2] photocycloaddition with nitrostyrene **1**.

It becomes apparent, that the excited nitrostyrene was unable to undergo photocycloaddition to electron deficient olefins. Alkynes as well as some olefins bearing electron donating groups could also not be converted to the respective cyclobutanes. Surprisingly, di ethoxy substituted olefin **58l** did not react in a [2+2] photocycloaddition reaction but led to the formation of an unidentified by-product in low yields. With diphenyl substituted ethene **58i**, the corresponding cyclobutane was detected by NMR but could never be isolated due to the formation of a major by-product.

Concerning the failure of the photocycloaddition to electron-deficient olefins, similar observations were reported on the intermolecular [2+2] photocycloaddition reaction of cinnamates, and the authors correlated the ability of certain olefins to undergo this reaction with their ionization potentials.[82] No mechanistic studies were undertaken in order to prove this hypothesis, and the question remains whether the authors assume a charge transfer mechanism. Whether single electron transfer (SET) processes[83–86] could be involved in the [2+2] photocycloaddition of nitroolefins could not be answered. There is however circumstantial evidence that contradicts this theory. On the one hand, the regioselectivity observed with non-symmetrical olefins should be inverted if radical ion intermediates were involved (scheme 20).



Scheme 20. Proposed mechanism for a [2+2] photocycloaddition of nitrostyrene **1** involving SET processes.

In principle, the photoexcited nitrostyrene **1*** should be capable of oxidizing the olefin if the redox potential is sufficiently high (*vide infra*). Charge transfer would result in radical anion **59** and the oxidized olefin. Carbon-carbon bond formation between the two radical centers would result in a zwitterionic intermediate **60**. Subsequent cyclobutane formation would lead to a product, *rac*-**61**, with the opposite regioselectivity. The formation of the photoproduct that is actually isolated from the reaction (*rac*-**45**) would in this scenario only be feasible *via* the zwitterionic intermediate formulated on the bottom right. The involvement of a primary carbo cation, however, seems unlikely, due to its instability.

Whether or not the SET between nitrostyrene **1** and any olefin is possible is determined by the difference ΔE of redox potentials of both compounds relative to each other. While the redox potential $E_{1/2}(\mathbf{1}/\mathbf{1}^{\bullet-})$ of nitrostyrene in its ground state is known,[87] the excited state redox potential $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{\bullet-})$ can not be measured and has to be estimated from $E_{1/2}(\mathbf{1}/\mathbf{1}^{\bullet-})$ and the triplet energy $E_{0,0}(\mathbf{1}^*/\mathbf{1})$[88,89] ($E_T$ = 229 kJ/mol, *vide supra*) applying the *Rehm-Weller* equation:[90]

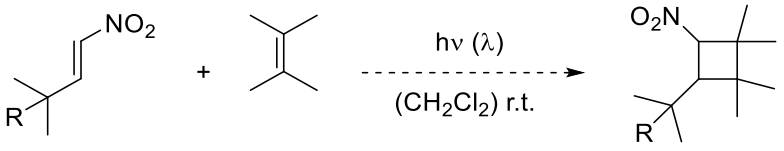
$$E_{1/2}(\mathbf{1}^*/\mathbf{1}^{\bullet-}) = E_{1/2}(\mathbf{1}/\mathbf{1}^{\bullet-}) + E_{0,0}(\mathbf{1}^*/\mathbf{1}) = -0.44\ \text{V} + 2.37\ \text{V} = +1.93\ \text{V}$$

The redox potential of most of the olefins tested are reported in the literature.[91–100] The failure of olefins bearing an electron withdrawing group (**58c**, **58d**, **58e** and **58k**, scheme 19) to undergo [2+2] photocycloaddition to nitrostyrenes could seemingly be explained by the generally high redox potentials ($E_{1/2}$ > 2.0 V). Other reactive olefins, e.g. methylene cyclohexane and 2,3-dimethyl-1,3-butadiene, would, however, not be oxidized by the photoexcited nitrostyrene **1** according to their high redox potentials ($E_{1/2}$ = 2.6 V and $E_{1/2}$ = 1.9 V, respectively). The hypothesis of SETs being involved in the reaction is therefore not sufficiently suited to explain the limited olefin scope.

In total, 14 different olefins were used successfully in the intermolecular [2+2] photocycloaddition with *trans*-β-nitrostyrene (**1**) under different reaction conditions, yielding the respective cyclobutanes in mostly good to high yields.

2.5.4 Other Nitroolefins

The results for the irradiation experiments with aliphatic nitroolefins **27** and **28** are summarized in table 1. With the aromatic moiety missing, these compounds show an absorption at shorter wavelength compared to the nitrostyrenes, due to the reduced conjugation. Therefore, irradiation experiments with direct excitation were carried out at shorter wavelengths.



27, 28 **30** 10-50 eq **62, 63**

Table 1. Irradiation experiments with aliphatic nitroolefins **27** and **28**.

#	substrate	λ [nm]	c [mM]	eq olefin	comment
1	**27**	254	20	10	decomposition[a]
2	**27**	300	20	10	decomposition[a]
3	**28**	254	20	10	decomposition[a]
4[b]	**28**	419	20	10	full conv.; only *Paternó-Büchi*-product with TXT
5[c]	**28**	254	20	50	no conversion
6	**28**	254	100	10	decomposition[a]
7[d]	**28**	254	20	30	decomposition[a]

[a] Full conversion, but no formation a distinguished product. [b] With 9H-thioxanthen-9-one (TXT) (50 mol%) as sensitizer. *Paternó-Büchi* reaction between TXT and olefin **30** observed. [c] With a chiral thiourea (1.00 eq), T = −78 °C. [d] In acetone as the solvent.

Irradiation of the *iso*-propyl derived nitroolefin **27** only led to decomposition of the starting material (entry 1 and 2). This result may not be surprising, as the *iso*-propyl moiety bears an easily abstractable hydrogen atom, and undesired side reactions might lead to the observed decomposition. However, direct irradiation of the *tert*-butyl derived nitroolefin **28** at short wavelength resulted in decomposition as well (entry 3), a higher concentration did not change this outcome (entry 6). Under sensitized conditions, no starting material was detected after three hours, but the desired photoproduct could not be isolated (entry 4). Instead, *Paternó-Büchi* reaction between the carbonyl group of 9H-thioxanthen-9-one (TXT) and the olefin **30** led to the formation of the respective oxetane. The same effect was observed when the reaction was performed in acetone as the solvent, where again *Paternó-Büchi* reaction between the sensitizer and the olefin was observed (entry 7). Addition of a chiral thiourea in stoichiometric amounts

and lower temperatures did not promote the desired [2+2] photocycloaddition (entry 5). With other olefins (e. g. 2,3-dimethyl-1,3-butadiene) at $\lambda = 254$ nm, again decomposition of the starting material was observed.

trans-cis-isomerization of the nitrostyrene starting materials was always observed during the course of the reaction (TLC, GC), and in some cases even outperformed the [2+2] photocycloaddition to such extent, that full conversion was not reached (see schemes 11 and 14). A nitroolefin such as **29** with an endocyclic double bond would not suffer from *trans-cis*-isomerization upon irradiation, as this major decay path would not be accessible. **29** was tested in an intermolecular [2+2] photocycloaddition at different irradiation wavelengths, and the results of these experiments are summarized in table 2.

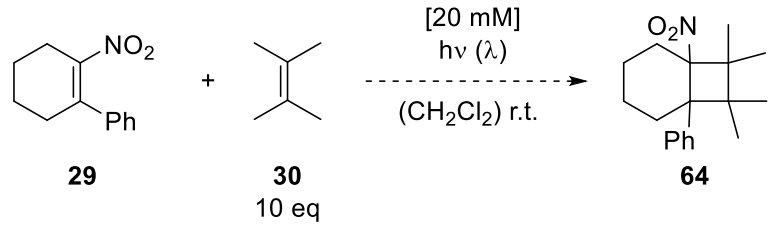


Table 2. Irradiation experiments with nitroolefin **29**.

#	λ [nm]	comment
1	300	no conversion
2	366	no conversion
3	419	no conversion
4[a]	419	decomposition
5[b]	419	no conversion
6	515	decomposition
7	400-700	no conversion

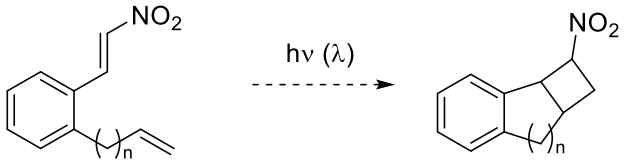
[a] With a chiral thiourea (1.00 eq), 50 eq of the olefin. [b] With TFA (1.00-10.0 eq).

Neither irradiation with light in the UV- (entry 1 and 2), nor in the visible light region (entries 3, 6 and 7) led to the formation of the [2+2] photocycloaddition product. In all cases, only the starting material was recovered. Addition of a chiral thiourea (entry 4) or trifluoroacetic acid (entry 5) was also not successful in inducing the desired photoreaction. Either no conversion or decomposition was observed.

2.5 Attempts Towards Intramolecular [2+2] Photocycloadditions of Nitrostyrenes

2.5.1 Synthesis of Irradiation Precursors for Intramolecular Photocycloaddition

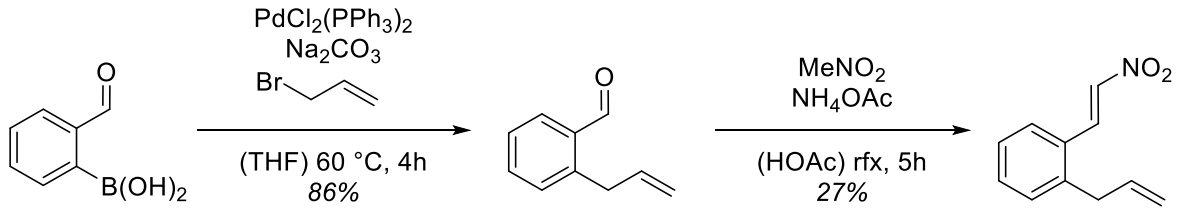
The substrate scope for the intermolecular [2+2] photocycloaddition of nitrostyrenes was successfully explored with a variety of different olefins. Therefore, the possibility of performing this reaction in an intramolecular fashion was evaluated as well. Since the intermolecular reaction failed whenever the aromatic moiety in conjugation to the nitroolefin was missing, it was aimed for substrates containing such a nitrostyrene moiety for the intramolecular variant (scheme 21). A tether should be attached in the C2-position of the aromatic moiety, so that a [2+2] photocycloaddition of the two double bonds would lead to the formation of a tricyclus.



Scheme 21. Potential intramolecular [2+2] photocycloaddition of nitrostyrenes.

The focus was laid on the synthesis of substrates with a chain length of n = 1-3. Unfortunately, despite their similar structure, all three molecules had to be synthesized via different routes.

The synthesis of allyl substituted nitrostyrene **65** (n = 1) started with the *Suzuki* cross-coupling[101,102] of commercially available *ortho*-formylphenylboronic acid and allyl bromide under standard conditions, followed by the *Henry* reaction[30] of the intermediate aldehyde to the desired *ortho* substituted nitrostyrene in an overall yield of 23% (scheme 22).[103]

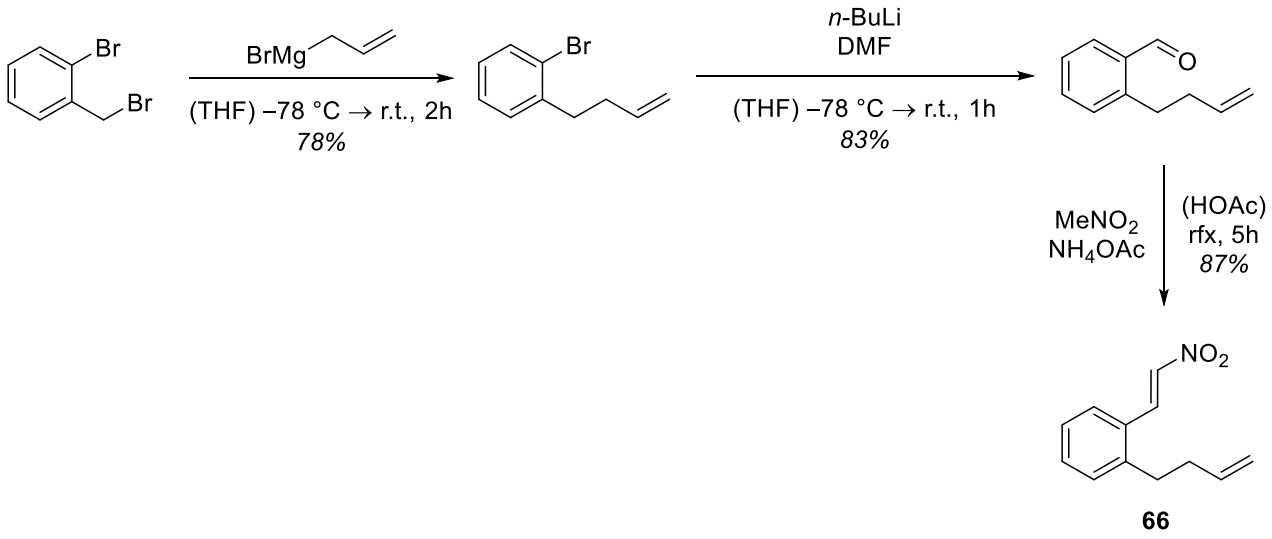


65

Scheme 22. Synthesis of nitrostyrene **65**.

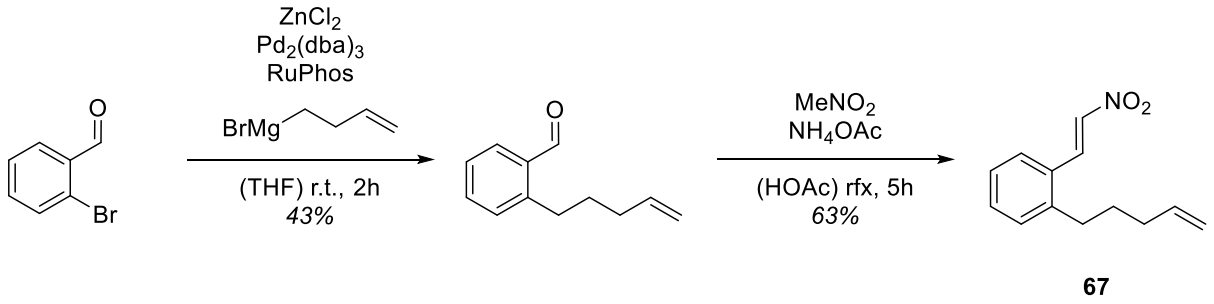
A somewhat unusual substitution reaction[104] of 2-bromobenzyl bromide and allyl magnesium bromide[105] and subsequent *Friedel-Crafts* type acylation[106,107] of the intermediate

bromide[108] led to the aldehyde precursor for the *Henry* reaction that concluded the three step synthesis of 3-butenyl-substituted substrate **66** (n = 2) (Scheme 23).



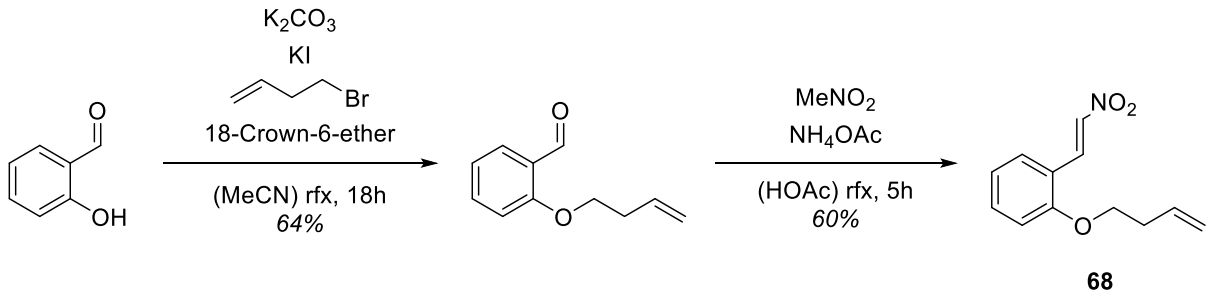
Scheme 23. Synthesis of nitrostyrene **66**.

A slightly different approach was chosen for pentenyl-subsitituted substrate **67** (n = 3). Starting from 2-bromobenzaldehyde, the intermediate aldehyde was generated by the *Negishi* cross-coupling[109] with 3-butenylmagnesium bromide under literature known conditions.[110] The desired nitrostyrene **67** was again obtained by a *Henry* reaction (scheme 24).



Scheme 24. Synthesis of nitrostyrene **67**.

Finally, the set of substrates for the intramolecular reaction was completed by nitrostyrene **68**, containing an oxygen atom in the tether (scheme 25). In the first step, the alkene tether was introduced to salicylic aldehyde in a *Williamson* ether synthesis,[111] and the resulting aldehyde was further converted to the nitrostyrene by *Henry* reaction under the conditions established for **65**-**67** to furnish the final substrate **68**.



Scheme 25. Synthesis of nitrostyrene **68**.

Before testing the newly synthesized substrates in the intramolecular [2+2] photocycloaddition reaction, they were analyzed by UV/Vis spectroscopy in order to estimate the appropriate irradiation wavelength (figure 6).

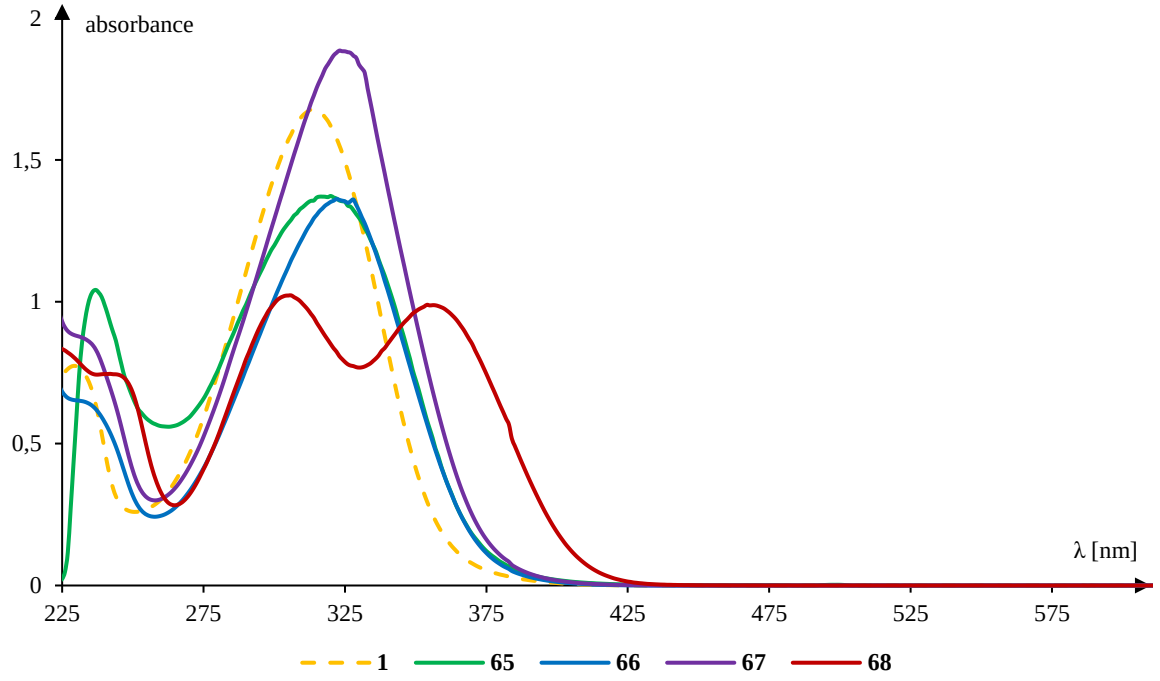


Figure 6. UV/Vis spectra of nitrostyrenes **65-68** (c = 1 mM, CH_2Cl_2).

All four compounds are yellow colored oils or solids. Except for nitrostyrene **68**, the UV/Vis spectra and absorption maxima resembled *trans*-β-nitrostyrene (**1**) ($\varepsilon_{312\ nm}$ = 16350 $M^{-1}\,cm^{-1}$, dashed orange). This is not surprising, since the chromophore is not affected significantly by the *ortho* substitution of the aromatic moiety. For the irradiation of the substrates, wavelengths from λ = 300 nm to λ = 419 nm were considered suitable for the direct excitation of the nitrostyrene moiety.

2.5.2 Irradiation Experiments

Nitrostyrenes **65-68** were irradiated in a dichloromethane solution at room temperature with light of different wavelengths (table 3). The reaction progress was monitored by TLC, and irradiation was stopped when the TLC did not indicate any further conversion over a period of two to three hours.

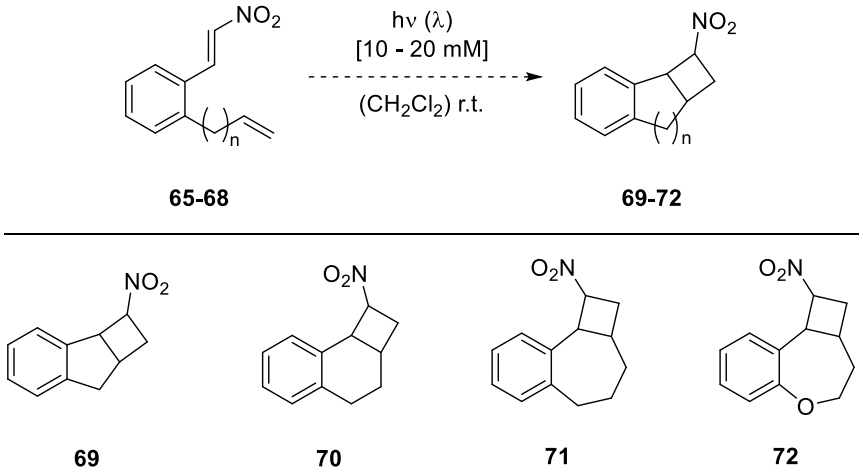


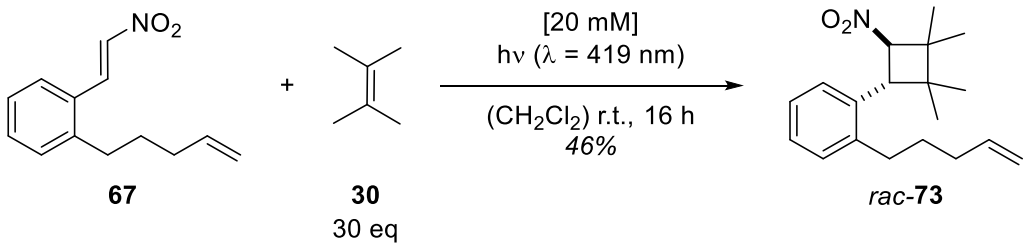
Table 3. Attempts towards the intramolecular [2+2] photocycloaddition of nitrostyrenes **65-68**.

#	substrate	λ [nm]	t [h]	Y [%]	rsm [%]	*trans/cis* (rsm)
1	**65**	300	16	-	quant.	n.d.
2	**65**	366	16	-	quant.	n.d.
3[a]	**66**	419	2	-	77	39/61
4[c]	**66**	419	8	-	61	40/60
5	**67**	419	16	-	quant.	20/80
6[b]	**67**	419	16	-	quant.	18/82
7	**68**	419	16	-	quant.	26/74

[a] Same result after irradiation for eight hours (crude rsm, *trans*/*cis* = 41/59). [b] Reaction was performed with thioxanthone (10 mol-%) as sensitizer. rsm = recovered starting material.

For nitrostyrene **65** (n=1), irradiation at λ = 300 nm after 16 hours only resulted in *trans*-*cis*-isomerization of the starting material (entry 1 and 2). Nitrostyrene **66** also underwent *trans*-*cis*-isomerization upon direct excitation (entry 3) and under sensitized conditions (entry 4). In both cases, isomerized starting material was partially recovered. For these two substrates, it could be argued that the ring closure to the five- and six-membered ring in the photoproducts **69** and **70** might be disfavored due to the ring strain. This issue should be overcome with

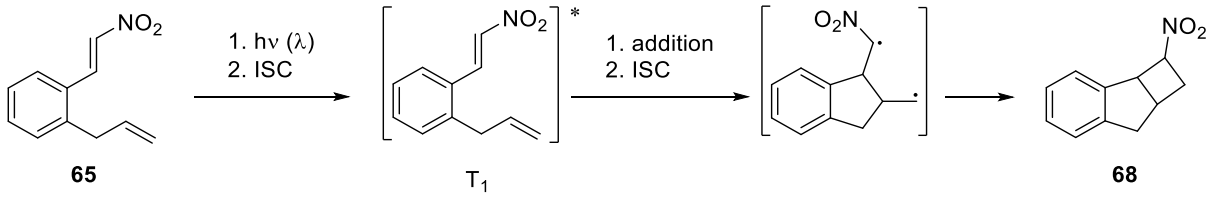
nitrostyrenes **67** and **68**, since the resulting seven-membered ring in both photoproducts **71** and **72** would be more flexible. However, both substrates also did not convert to the desired products upon irradiation with visible light (entry 5 and 7) or under sensitized conditions (entry 6). In order to assure that the reactivity of the nitrostyrene double bond is not impaired, nitrostyrene **67** was irradiated together with 2,3-dimethyl-2-butene (**30**) under the standard conditions for the intermolecular [2+2] photocycloaddition (scheme 26).



Scheme 26. Irradiation of nitrostyrene **67** in presence of 2,3-dimethyl-2-butene **30**.

The corresponding cyclobutane *rac*-**73** was isolated in 46% yield, revealing that the nitrostyrene moiety was excited upon irradiation, but could apparently not react with the tethered alkene. Relaxation to the ground state occurs primarily through *trans-cis*-isomerization.

The failure of the intramolecular [2+2] photocycloaddition reaction was somewhat surprising, given that the nitrostyrene chromophore showed a high similarity to enone systems regarding its reactivity (see photocycloaddition of **147** → **148**, scheme 59). Intramolecular [2+2] photocycloadditions of enones have been reported abundantly in the literature.[16] In these cases, the tether is mostly attached to the β-position of the enone, and the regioselectivity is primarily controlled by the *rule of five* postulated by *Hammond* and *Srinivasan* in 1967.[112,113] For nitrostyrene **65** (n=1), a mechanism similar to that of enones[114] could be proposed: excitation of the nitrostyrene chromophore, addition and subsequent ISC to the alkene tether leads to the kinetically controlled formation of the less stable 1,4-diradical, which then forms the final carbon carbon bond to the cyclobutane (**69**) (scheme 27).



Scheme 27. Proposed mechanism for the intramolecular [2+2] photocycloaddition of nitrostyrene **65**.

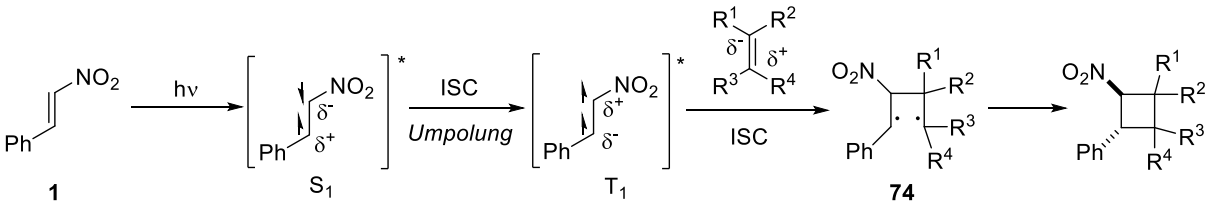
Apparently, the addition step that would lead to the formation of either 1,4-diradical is not feasible for **65**-**68**, as **67** would rather undergo the diffusion controlled intermolecular addition

to olefin **30** than react with the intermolecular double bond. One reason could be, that the alkene moiety is for geometrical reasons not able to reach spatial proximity to the photoexcited nitrostyrene. Although the carbon-carbon single bond(s) in the tether should be able to rotate freely in solution, this must not lead to a transition state that allows the intermolecular addition. The second reason for the failure of the reaction could be the ring strain that has to be overcome during the formation of the 1,4-diradical. Especially in the case of **70**, the energy barrier for the construction of a five-membered ring annelated to a planar aromatic moiety might be too high, since there are other ways for the excited molecule to relax to the ground state that are easily accessible (IC, fluorescence, isomerization). These arguments are however only speculations, since there were no preparative mechanistical or computational studies performed to support these hypotheses. No further attempts towards an intramolecular variant of the [2+2] photocycloaddition of nitrostyrenes were undertaken.

2.6 Mechanistical Aspects

2.6.1 Experimental Studies

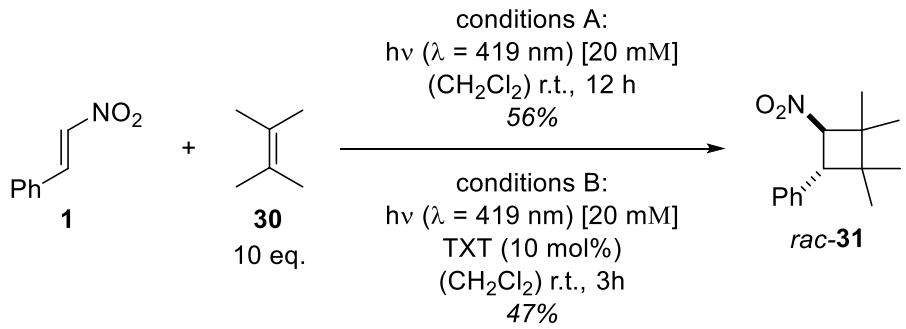
Based on the initial work on the [2+2] photocycloaddition of nitrostyrenes by *Hoganson*[50] and *Chapman*[43] and on the experimental findings presented in chapter 2.5, a mechanism that proceeds on the triplet hypersurface is proposed (scheme 28).



Scheme 28. Overview on the mechanistic proposal for the intermolecular [2+2] photocycloaddition of nitrostyrene **1**.

Upon irradiation, nitrostyrene **1** is excited into the first excited singlet state. ISC to the first excited triplet state induces the *Umpolung* of the double bond. Subsequently, the olefin adds to the photoexcited nitrostyrene, and a second ISC leads to the formation of an intermediate 1,4-diradical (**74**). It is proposed, that the thermodynamically most stable 1,4-diradical is formed, which ultimately collapses to the cyclobutane photocycloaddition product. The evidence for the photochemical *Umpolung* similar to that of enones have already been discussed (*vide supra*).

The hypothesis of a triplet mechanism is further substantiated by the rate acceleration in the presence of substoichiometric amounts of a triplet sensitizer (scheme 29).[115]

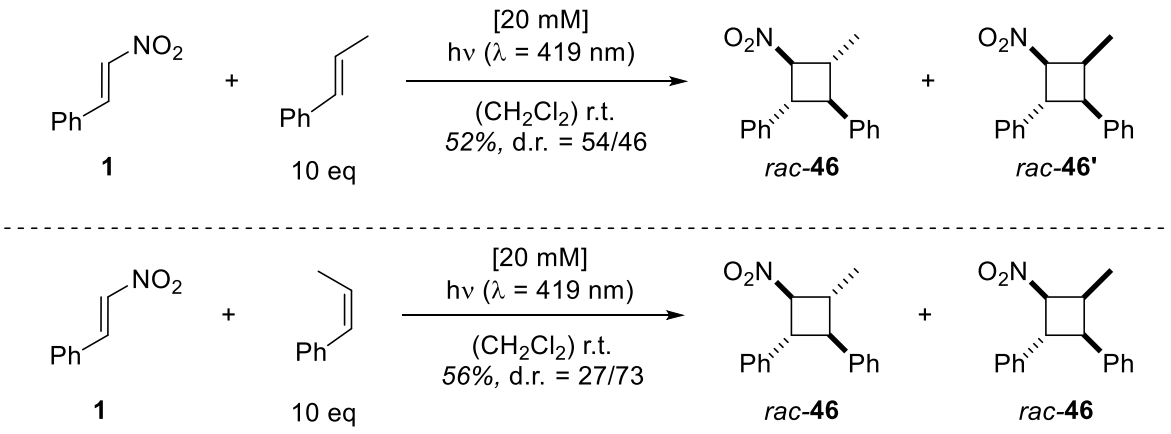


Scheme 29. [2+2] Photocycloaddition of nitrostyrene **1** under sensitized conditions (conditions B).

In absence of the additive, the starting material was completely consumed after twelve hours of irradiation, with a yield of 56% of the photoproduct (conditions A). Under sensitized conditions,

the cyclobutane *rac*-**31** was obtained in 47% yield after full conversion was reached in three hours (conditions B).

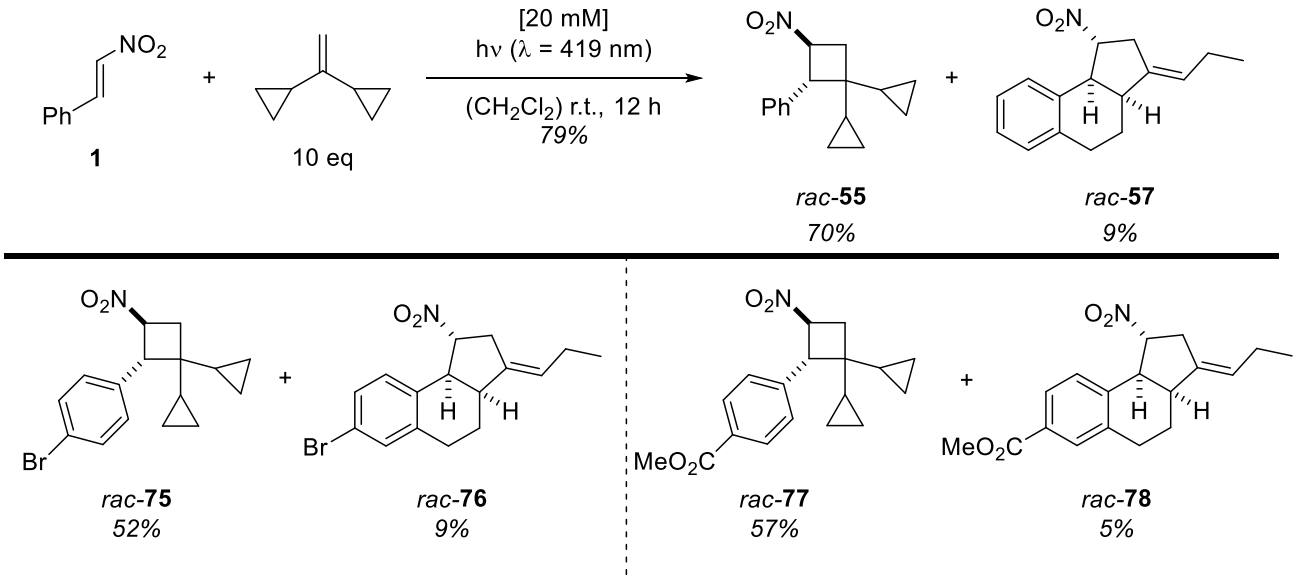
The observed stereoconvergent course of the photocycloaddition of nitrostyrene **1** to β-methylstyrene is an additional indication of a reaction proceeding on the triplet hypersurface (scheme 30).



Scheme 30. [2+2] Photocycloaddition of nitrostyrene **1** with *cis*- and *trans*-β-methylstyrene.

The fact that diastereoisomer *rac*-**46'** with the methyl and the phenyl group in a formal *cis* configuration is obtained in a significant amount from the reaction of nitrostyrene **1** with *trans*-β-methylstyrene indicates the involvement of an intermediate 1,4-diradical (**74**, scheme 28) in the mechanism of product formation. *Vice versa*, the formally *trans* configured diastereoisomer *rac*-**46** is observed in the reaction with *cis*-β-methylstyrene. In both cases, the olefin was recovered exclusively as single diastereoisomer from the reaction mixture after irradiation was stopped. Therefore, isomerization of the olefin upon irradiation can be excluded as explanation for the formation of both diastereoisomers *rac*-**46** and *rac*-**46'** in both reactions (scheme 30). A concerted addition of the olefin to the photoexcited nitrostyrene seems to be unlikely, due to the non-stereospecificy.

So-called radical clock experiments are often conducted to determine the kinetics of free radical reactions.[116] In [2+2] photocycloadditions, an olefin bearing a cyclopropyl group can act as a radical clock, resulting in a fragmentation product[117] that can substantiate the existence of an intermediary 1,4-diradical.[118] This method was applied in the [2+2] photocycloaddition of nitrostyrene **1** with 1,1-dicyclopropyl ethylene, which resulted in the formation of an unusual tricyclic by-product (*rac*-**57**) apart from the cyclobutane photocycloaddition product *rac*-**55** (scheme 31).



Scheme 31. [2+2] Photocycloaddition of nitrostyrene **1** with 1,1-dicyclopropyl ethylene, leading to the formation of by-product *rac*-**57** (top). Products of [2+2] photocycloaddition of bromo-substituted nitrostyrene **19** (bottom left) and methoxycarbonyl-substituted nitrostyrene **17** (bottom right) to 1,1-dicyclopropyl ethylene.

The corresponding bromo (scheme 31, bottom left) and methoxycarbonyl (scheme 31, bottom right) nitrostyrenes **19** and **17** were converted into the corresponding cycloaddition products (*rac*-**75**, *rac*-**76**) and ring opening products (*rac*-**77**, *rac*-**78**) as well.

The structure of *rac*-**57** was elucidated by extensive analysis of the NMR data (figure 7).

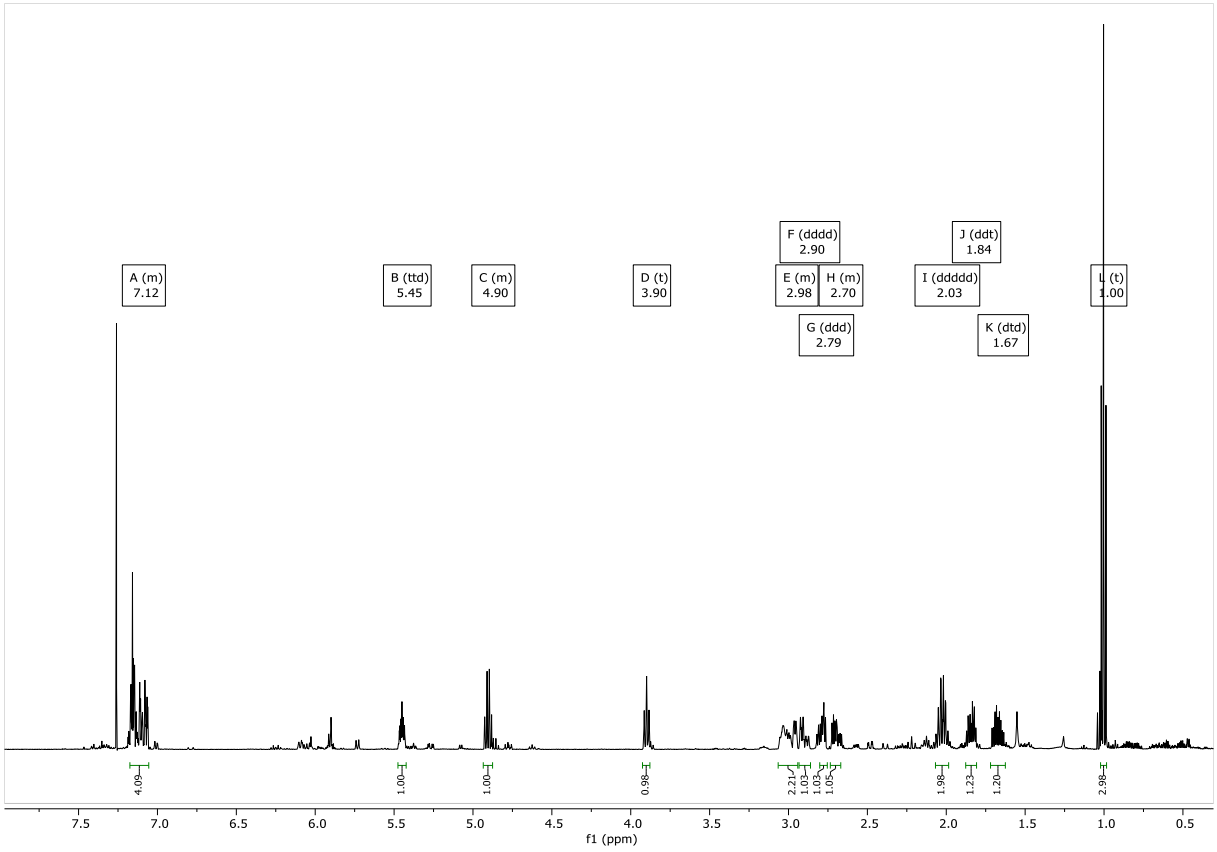
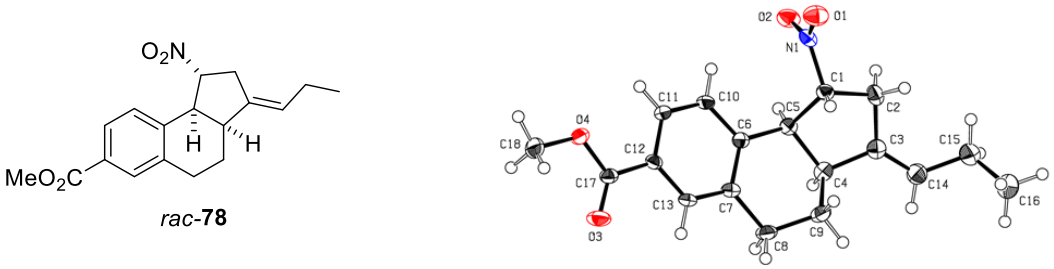


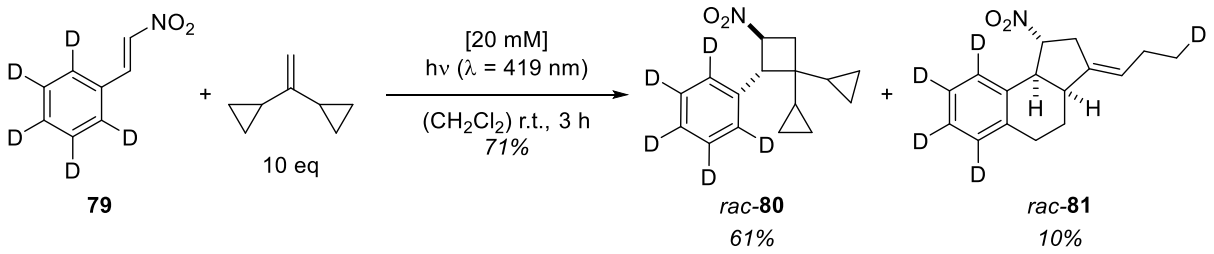
Figure 7. ^{1}H NMR spectrum of compound *rac*-**57**.

From the integral value of 4 for the protons in the aromatic region (δ = 7.12 ppm), it became apparent that one of the phenyl protons had been involved in a (presumably intramolecular) hydrogen abstraction reaction. A second hint towards the structure of **65** is the terminal ethyl group (triplet of three protons at δ = 1.00 ppm and multiplet of two protons at δ = 2.03 ppm). Two-dimensional NMR analysis revealed, that the ethyl group is connected to the tricyclic fragment of the molecule via the significantly low-field shifted olefinic proton (ttd of one proton at δ = 5.45ppm). Confirmation of this structure was achieved by single-crystal X-ray diffraction of methoxycarbonyl substituted *rac*-**78** (scheme 32).



Scheme 32. Confirmation of the structure of ring-opening product *rac*-**78** by single-crystal X-ray diffraction.

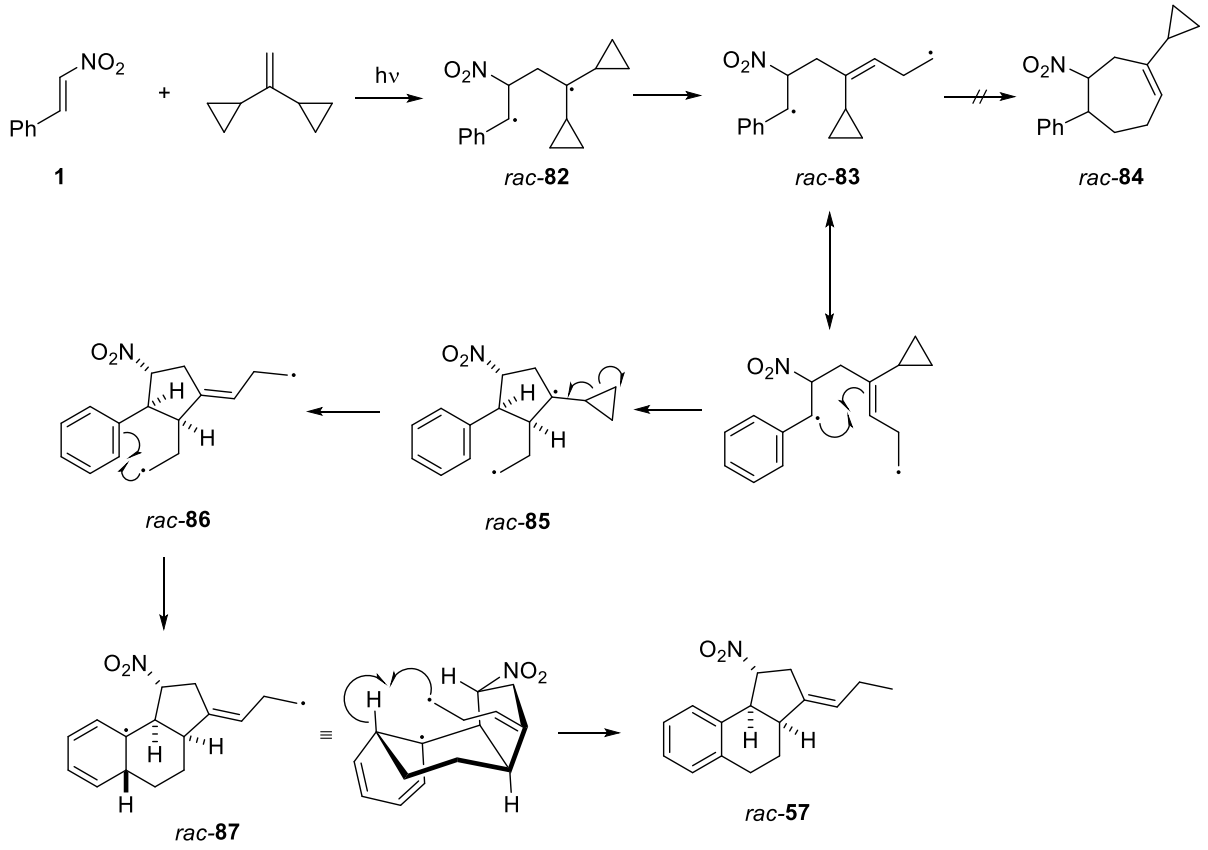
As it could be speculated from the NMR data and as it was confirmed by X-ray analysis, the *ortho*-proton of the phenyl group is abstracted at some point during the reaction sequence. In order to elucidate this mechanistic step, deuterated nitrostyrene **79** was subjected to the intermolecular [2+2] photocycloaddition with 1,1-dicyclopropyl ethylene (scheme 33).



Scheme 33. [2+2] Photocycloaddition of deuterated nitrostyrene **79** to 1,1-dicyclopropyl ethylene.

The corresponding cyclobutane photocycloaddition product *rac*-**80** was isolated in 61%, and 10% of the by-product were obtained. Careful NMR analysis afforded *rac*-**81** as the structure of the by-product and revealed, that the *ortho* deuterium atom was abstracted by one of the opened cyclopropane groups. By conducting the reaction of nitrostyrene **1** with dicyclopropyl ethylene in deuterated dichloromethane, it was ruled out that the hydrogen abstraction could also occur in an intermolecular process. In this case, no deuterium incorporation into the ring opening product was observed.

Based on these findings, the mechanistic proposal for the formation of ring opening products involves formation of a 1,4-diradical *rac*-**82** (scheme 34). Such a 1,4-diradical has already been proposed to be an intermediate in the formation of the by-products observed in some [2+2] photocycloadditions of acceptor substituted nitrostyrenes (*vide supra*).[115] The fragmentation of *rac*-**82** towards the 1,7-diradical *rac*-**83** does not lead to the originally anticipated closure of the seven membered ring in the next step, as products such as *rac*-**84** were not isolated. Instead, closure of the five-membered ring by attack of the benzylic radical at the double bond delivers of a second 1,4-diradical (*rac*-**85**), followed by opening of the second cyclopropyl group (*rac*-**86**). Subsequent six-membered ring formation furnishes the intermediate diradical *rac*-**87**, from which abstraction of the *ortho*-hydrogen atom can easily occur because of the close spatial proximity as illustrated, resulting in the final tricyclic product *rac*-**57**. Other initial mechanistic proposals involving e. g. a carbene intermediate were abandoned, as they could not successfully explain the hydrogen abstraction step.



Scheme 34. Mechanistic proposal for the formation of *rac*-**57**.

Finally, it shall be briefly commented on the nature of the *trans-cis* isomerization of the nitrostyrenes that has been observed in a variety of the photocycloadditions. It was proposed by us and others,[43,50,115] that preferentially the *trans*-isomer of nitrostyrene **1** undergoes the intermolecular [2+2] photocycloaddition. This hypothesis can only be substantiated by the higher extinction coefficient of *trans*-β-nitrostyrene (**1**) ($\varepsilon = 16500\ M^{-1}\ cm^{-1}$) compared to the *cis*-isomer ($\varepsilon = 5200\ M^{-1}\ cm^{-1}$).[48,115] The question, whether the isomerization occurs on the singlet or the triplet hypersurface could not be answered by the mechanistical studies undertaken in this work.

2.6.2 Determination of Quantum Yield

From a photophysical point of view, the intermolecular [2+2] photocycloaddition of nitrostyrene **1** to 2,3-dimethyl-2-butene (**30**) can be described as **1** → *rac*-**31**, as long as these two prerequisites are fulfilled: a) the nitrostyrene chromophore is the only absorbing species in the reaction and b) *rac*-**31** is the only product formed.[18] The probability of a molecule **1** undergoing the defined process (reaction towards *rac*-**31**) upon absorption of a photon is

defined as the quantum yield Φ of the reaction. In the somewhat simplified approach **1** → *rac*-**31**, the quantum yield should lie in the range of $0 \leq \Phi \leq 1$; a maximum theoretical Φ of 1 would indicate, that every photon absorbed leads to the formation of one product molecule. Values of $\Phi \geq 1$ are common for radical chain processes,[119] a scenario that can be excluded for the uncatalyzed [2+2] photocycloaddition of the nitrostyrenes. On the other hand, photochemical processes such as luminescence and internal conversion as well as undesired side reactions would lead to $\Phi \leq 1$.[18,119] In mathematical terms, the quantum yield is determined as follows:

$$\Phi = \frac{n_x}{n_p} = \frac{number\ of\ photochemical\ or\ photophysical\ events\ x}{number\ of\ photons\ absorbed}$$

As both n_X and n_p are measured in moles per Einstein, Φ is unitless.

The quantum yield of the intermolecular [2+2] photocycloaddition of nitrostyrene **1** and olefin **30** was measured in order to find out about the efficiency of the process (for setup and experimental details, see experimental part). Prior to those measurements, the kinetics of the reaction at an irradiation wavelength of λ = 382 nm were monitored by taking small aliquots of the reaction mixture over a period of 60 minutes. These samples were analyzed by calibrated GC. After one hour, a conversion of 30% was reached, with 16% yield of the cyclobutane product *rac*-**31**. Generally, small conversions are beneficial for quantum yield determination to avoid corruption of the experimental results by secondary photoreactions.[18]

For the calculation of the quantum yield of the [2+2] photocycloaddition referred to the product *rac*-**31**, the following equation was applied:

$$\Phi_{rac-\mathbf{31}} = \frac{\dot{n}_{rac-\mathbf{31}}}{I_0 \cdot \bar{\beta}}$$

where $\dot{n}_{rac-\mathbf{31}}$ is the amount of product (mol), I_0 is the molar photon flux and $\bar{\beta}$ is the measured absorbance of the sample at the respective irradiation wavelength. The molar photon flux itself is defined as the amount of photons incident on the sample cell per unit of time. I_0 is dependent on the radiant power of the light source, which was in this case determined by measuring the conversion of a phenylglyoxylic acid actinometer[120] per unit of time. The quantum yield for the photochemically induced Norrish-type I decarboxylation of phenylglyoxylic adic in a solvent mixture of acetonitrile-water (3/1 v/v) is tabulated as Φ = 0.735.[121] Based on the results of the actinometry, a photon flux of $I_0 = 7.24 \cdot 10^{-8}\ Einstein\ s^{-1}$ ($4.36 \cdot 10^{16}\ s^{-1}$) was

calculated. $\bar{\beta}$ was monitored over the reaction time in increments of 30 seconds at λ = 382 nm, and was determined as 0.996. The quantum yield of the reaction **1** → *rac*-**31** was calculated as:

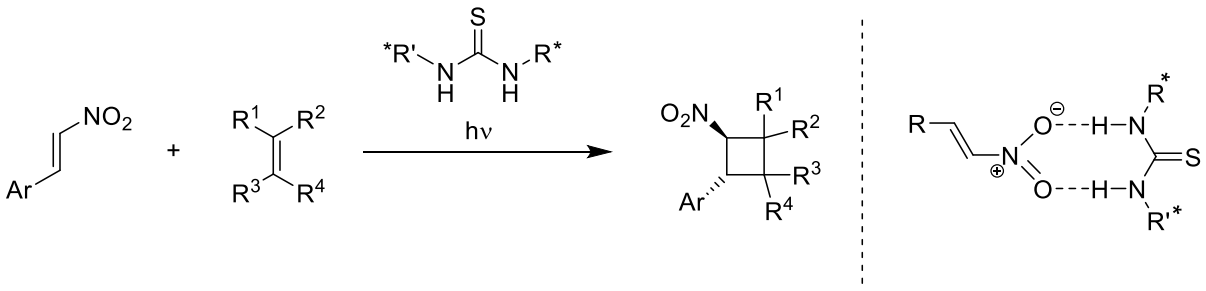
$$\Phi_{rac-\mathbf{31}} = \frac{\dot{n}_{rac-\mathbf{31}}}{I_0 \cdot \bar{\beta}} = \frac{2.678 \cdot 10^{-9}\ mol\ s^{-1}}{7.24 \cdot 10^{-8}\ mol\ s^{-1}\ \cdot 0.996} = 0.0371$$

It was shown by monitoring of the reaction course via GC, that the isomerization process is extremely rapid, and at some point, a photostationary equilibrium is reached. The low quantum yield can partially be attributed to the competing isomerization. Additionally, although full conversion is reached, the yield of the reaction is only moderate. As there were never any by-products (other than *rac*-**42a**-**44a** and *rac*-**57**) isolated, decomposition of the starting material is a major, non-productive decay pathway. The stability of the photoproduct was tested by irradiation of a sample, which yielded the starting material in quantitative yield after 12 hours of irradiation.

2.7 Attempts Towards an Enantioselective [2+2] Photocycloaddition of Nitroolefins

2.7.1 Concept

Although the initial reports on the [2+2] photocycloaddition of the nitrostyrene chromophore obviously justified our pursuit of a more comprehensive study of this reaction, our initial interest on the photochemistry of this compound class was based on the desire to develop a protocol for an enantioselective photochemically induced reaction catalyzed by chiral thioureas (scheme 35). The thiourea should coordinate the nitro group of the substrate by bidentate hydrogen binding (scheme 35, right). Additionally, a bathochromic shift of the absorption maximum would enable a selective excitation of such a catalyst-substrate complex.

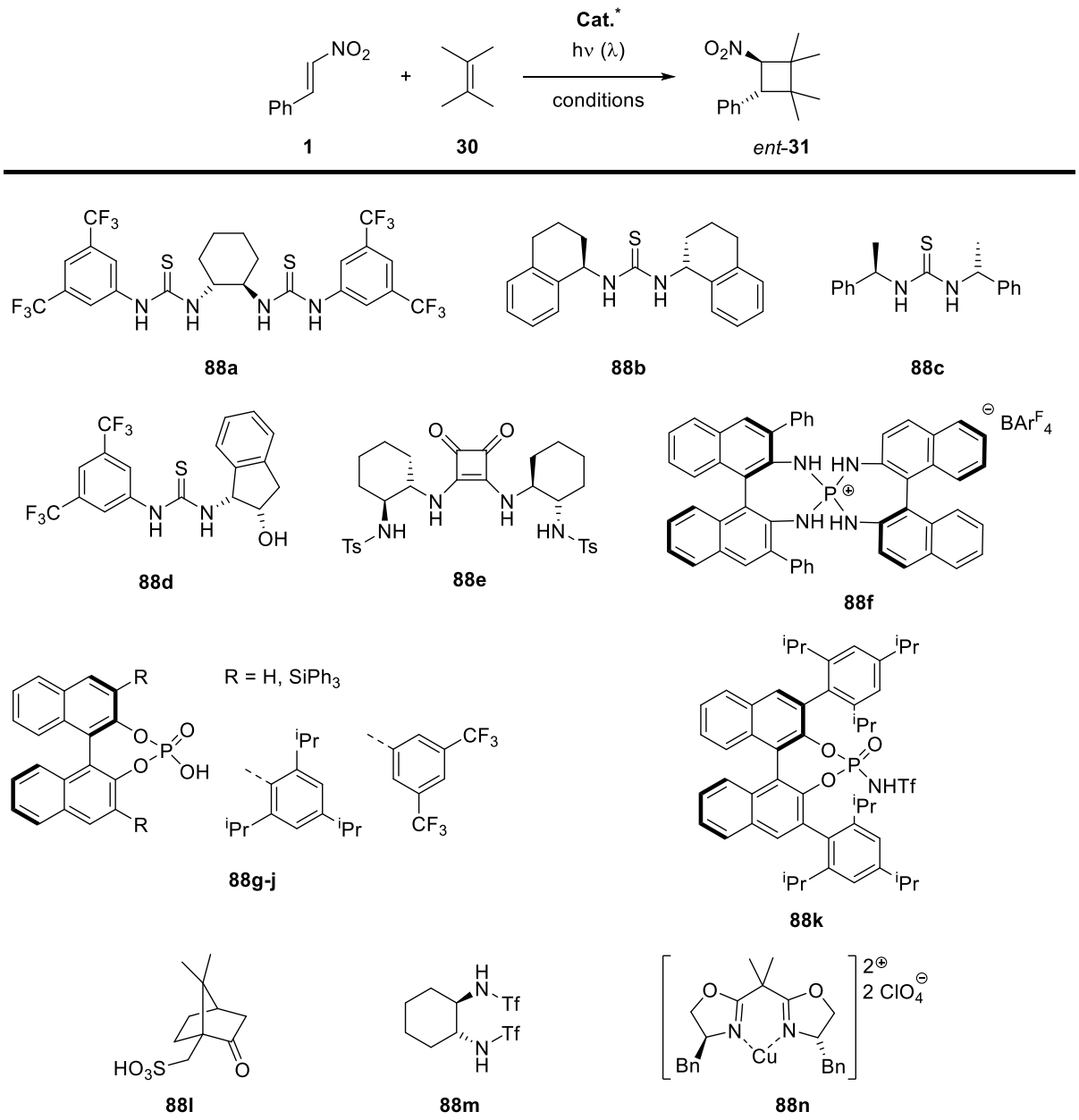


Scheme 35. Concept for an enantioselective [2+2] photocycloaddition of nitrostyrenes catalyzed by chiral thioureas.

A plethora of asymmetric, thiourea-catalyzed thermal reactions of nitro compounds reported in the literature[29,122,123] inspired us to apply the concept of catalysis by coordination of the nitro group by hydrogen bonding from a suitable catalyst with a thiourea binding motif to the [2+2] photocycloaddition of nitrostyrenes. In the Master's thesis preceding this work, the concept of thiourea catalysis of the reaction was investigated by kinetic studies and UV-Vis spectroscopic experiments.[75] It was shown, that the rate of the [2+2] photocycloaddition of nitrostyrene **1** to indene (**6**) can be accelerated by addition of substoichiometric amounts of achiral *Schreiners* thiourea, which led to full conversion of the starting material in a shorter time period.[124,125] A selective excitation of exclusively catalyst-bound substrate was not possible, as the anticipated bathochromic shift of the absorption was not observed in presence of the thiourea. Additionally, even at long irradiation wavelength, the uncatalyzed reaction could not be suppressed. These findings complicated the development of a suitable protocol for the catalysis that requires careful tuning of the reaction parameters.

2.7.2 Photoreactions with Chiral Catalysts

A vast number of chiral small molecule catalysts has been evaluated in the intermolecular [2+2] photocycloaddition of nitrostyrene **1** with 2,3-dimethyl-2-butene (**30**) under different conditions (scheme 36).



Scheme 36. Series of chiral catalysts evaluated in the [2+2] photocycloaddition of nitrostyrene **1**.

Chiral bis-thiourea **88a** had previously been employed successfully in the enantioselective intramolecular [2+2] photocycloaddition of dihydropyridones.[126] When employed in stoichiometric amounts together with 50 mol% of thioxanthone as triplet sensitizer, only racemic photoproduct *ent*-**31** with up to 79% yield was isolated. With other C_2-symmetrical

thioureas such as **88b** and **88c**, cyclobutane *ent*-**31** was obtained in 37% yield (6% *ee*) and 50% yield (7% *ee*), respectively. Bifuncional thiourea **88d**[127] was tested, because it could potentially activate heteroatom-containing olefinic reaction partners by coordination from the hydroxy group. Although the yields in the reactions with **88d** were high (up to 76%), an enantiomeric excess of 10% was not exceeded. Neither changing the solvent nor lowering the reaction temperature could improve these results. Chiral squareamide **88e** and arylaminophosphonium barfate **88f**[128] (kindly supplied by the group of Prof. *Ooi*) furnished racemic product as well. The enantiomeric excess observed with chiral phosphoric acids **88g-j** and phosphonamide **88k** ranged between 6-9% *ee*. Camphorsulfonic acid (**88l**) and triflic amine **88m** afforded photoproduct *ent*-**31** with 4% *ee* and 8% *ee*, respectively. A chiral *Lewis* acid complex (**88n**) was also not able to induce significant enantioselectivity. Some of the catalysts depicted in scheme **36** were evaluated under different conditions (solvent, temperature, amount of catalyst, direct excitation vs. sensitized), but none of these variations resulted in a significant increase of the enantiomeric excess.

The fact, that little to no enantioselectivity was observed in most cases of the [2+2] photocycloaddition of nitrostyrene **1** in presence of any of the catalysts (scheme **36**), can mainly be attributed to the impossible suppression of the racemic background reaction. Due to the absence of a bathochromic shift of the absorption of **1** by any of these catalysts, a selective excitation of a catalyst-substrate complex was not possible. Therefore, a significant amount of uncoordinated substrate can react in those cases where the catalyst was used in substoichiometric amounts. Often racemic product was obtained even though stoichiometric amounts of the respective catalyst were employed. Either a weak interaction of the catalyst and the substrate **1** allow for the uncatalyzed background reaction to occur, or the side differentiation by the catalyst is insufficient, resulting in low *ee*. A second mode of action could be a decrease of the excited state energy of catalyst-bound substrate,[129] which would enable selective sensitization of the catalyst-substrate complex by a suitable sensitizer. In our hands however, conditions to exploit this mode of action could not be established, as all sensitizers tested were either also able to sensitize the background reaction or were not capable in inducing the desired reaction by energy transfer.

A possible activation of the nitroolefin chromophore by achiral *Lewis* acids was tested by addition of a high excess of the respective *Lewis* acid to a sample of nitrostyrene **1** and recording the UV-Vis spectra of the mixture. With weakly coordinating *Lewis* acids [$Cu(OTf)_2$, $BF_3 \cdot OEt_2$], no changes were observed in the absorption. In the presence of strongly coordinating activators such as $EtAlCl_2$, the nitrostyrene absorption vanished completely,

which indicated polymerization of the sample. The same experiments were conducted with achiral halogen bond donors[130,131] that were kindly supplied by the group of Prof. *Huber*, but no effects on the absorption properties were detected.

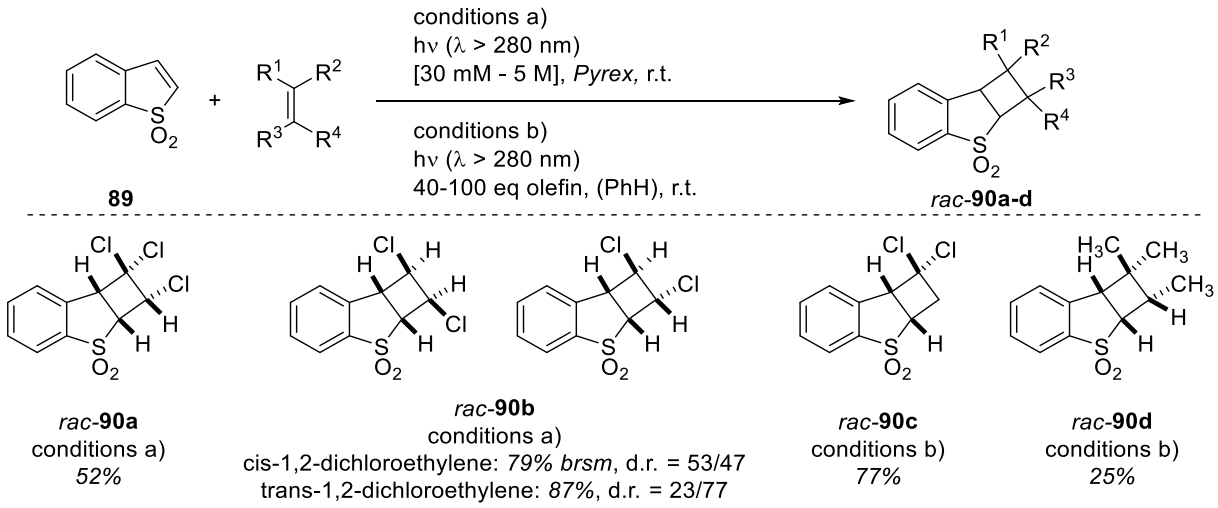
No further studies were conducted on an enantioselective variant of the [2+2] photocycloaddition of nitrostyrenes.

3. Intermolecular [2+2] Photocycloaddition Reactions of Sulfones

3.1 Photochemistry of Sulfones

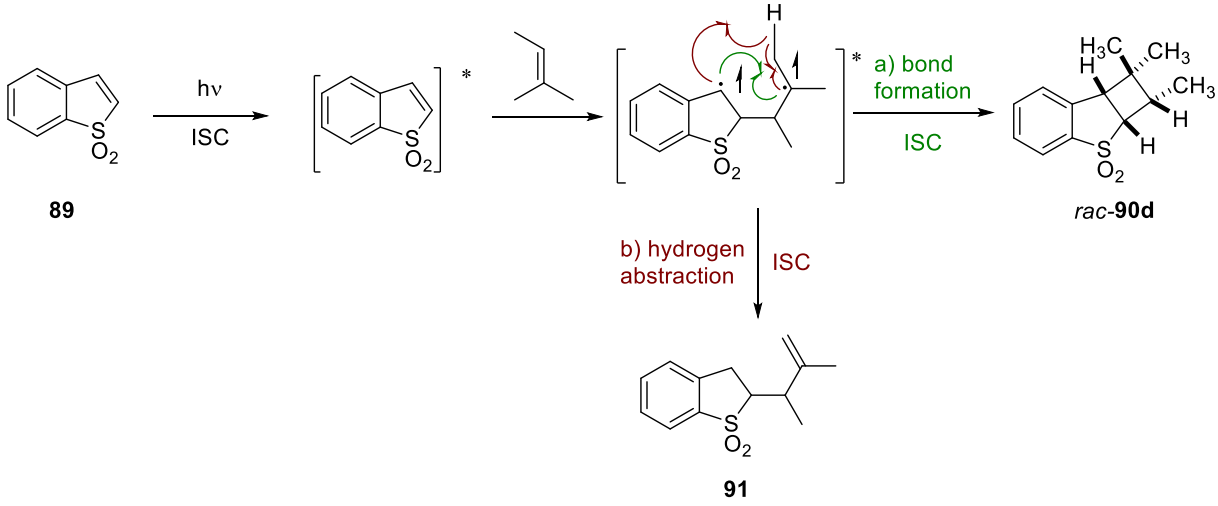
Sulfones are an important class of organic compounds, some of which show biological activity and are used as therapeutic agents,[132–134] although admittedly less important as structural motif in modern drugs than their close relatives, the sulfonamides. The most prominent representative of these compounds is probably 4,4'-sulfonylbisaniline, better known under the tradename *Dapsone*, a drug that is used for treatment of infectious diseases such as malaria and leprocy.[135] Moreover, sulfones are powerful and versatile building blocks in organic synthesis, [136] for example as masked dienes for intramolecular *Diels-Alder* reactions,[137,138] as α-halogensulfones in the *Ramberg-Bäcklund* reaction[139] or in the *Julia* olefination.[140]

In photochemical reactions, sulfones are mostly known to undergo photolysis upon irradiation,[141,142] they are employed as vinylsulfones in photochemically induced dimerization reactions[143–145] or as olefins in intermolecular [2+2] photocycloaddition reactions.[118,146–149] Considering that chromophores bearing an electron withdrawing group in conjugation with a double bond as structural motif (enones, nitroolefins) readily undergo [2+2] photocycloaddition reactions upon direct excitation or under sensitized conditions,[16,115] it seemed reasonable that α,β-unsaturated sulfones would react in the same fashion. Surprisingly, only two publications on the subject can be found in the literature.[150,151] In 1973, *Harpp* and *Heitner* reported the intermolecular [2+2] photocycloaddition of benzo[b]thiophene-1,1-dioxide **89** to different olefins by direct excitation (scheme 37).[150]



Scheme 37. Intermolecular [2+2] photocycloaddition of benzo[b]thiophene-1,1-dioxide (**89**) to different olefins.

Sulfone **89** was either irradiated as a solution in the olefin (conditions a), or with a high excess of the olefin as a solution in benzene as the solvent (conditions b). The respective cyclobutane products *rac*-**90a-d** were isolated in moderate yields, except for *rac*-**90d** which was only obtained in 25%. The reactions were generally performed under a N_2-atmosphere, a reaction with O_2-purged trichloroethylene completely inhibited the photocycloaddition reaction. In the reaction with 2-methyl-2-butene, a by-product, which was identified as **91** (scheme 38), was observed. The formation of **91** most likely occurs upon hydrogen abstraction from an intermediary 1,4-diradical.[150]

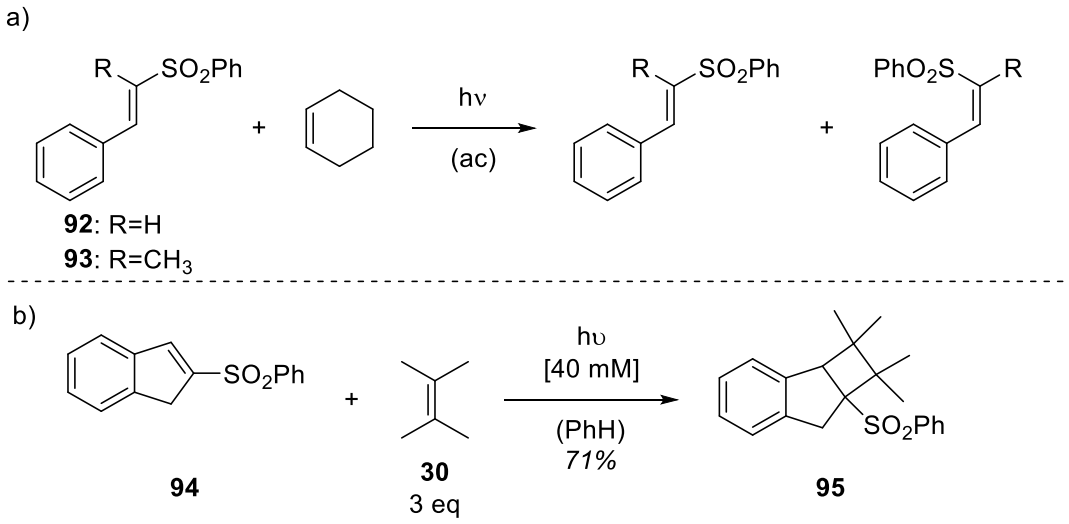


Scheme 38. Mechanistic proposal for the intermolecular [2+2] photocycloaddition of cyclic sulfone **89**.

Based on the experimental data, it was proposed that the mechanism of the [2+2] photocycloaddition of sulfone **89** to different olefins proceeds as depicted in scheme 37.[150] First, the photoexcited triplet sulfone adds to the olefin with high regioselectivity, furnishing an intermediate 1,4-diradical. This initial bond formation occurs between the 2-position of the

sulfone and the less substituted carbon of the olefin, yielding the most stabilized diradical. Depending on the olefin involved, the next step is comprised of the final bond formation and consecutive ISC to the cyclobutane photocycloaddition product in its ground state. The authors also suggested, that the reaction most likely occurs on the triplet hypersurface.[150] This is subsidized by the observation, that the reaction is completely shut down in an oxygen saturated atmosphere and by the fact that the reaction with both *cis*- and *trans*-1,2-dichloroethylene proceeds with stereoconvergence.

The second study on the photocycloaddition of sulfones to olefins was published by *Reid et al*. in 1980.[151] The authors report, that acyclic α,β-unsaturated sulfones did not undergo intermolecular [2+2] photocycloaddition in the presence of olefins. Irradiation of these compounds led to a *trans*-*cis*-isomerization of the double bond, which after four hours resulted in a steady-state of a 1:1 mixture of both isomers (scheme 39, a).

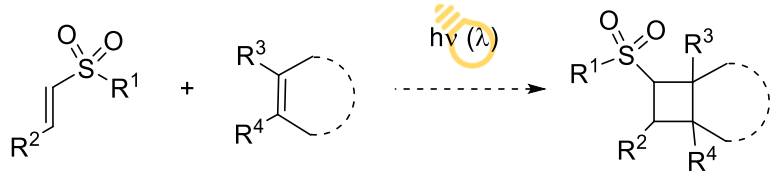


Scheme 39. Study on the solution photochemistry of unsaturated sulfones by the group of *Reid*. a) Irradiation of acyclic sulfones. b) [2+2] Photocycloaddition of 2-benzenesulfonylindene **94**.

With an endocyclic double bond as in compound **94**, the [2+2] photocycloaddition to 2,3-dimethyl-2-butene (**30**) was performed successfully in 71% yield of the respective cyclobutane **95**. The reaction was also performed in presence of cyclohexene and cyclopentene as well as with differently substituted sulfones, but no analytical data for the products was provided.[151] The inability of acyclic α,β-unsaturated sulfones to undergo [2+2] photocycloaddition to olefins was reported earlier, and was attributed to the highly effective *trans*-*cis*-isomerization which was also observed by *Reid*.[143,144]

3.2 Project Aims

On the ground of the successful intermolecular [2+2] photocycloaddition of nitroolefins, it seemed amenable that similarly designed α,β-unsaturated sulfones would be able to undergo the same type of reaction upon irradiation (scheme 40).



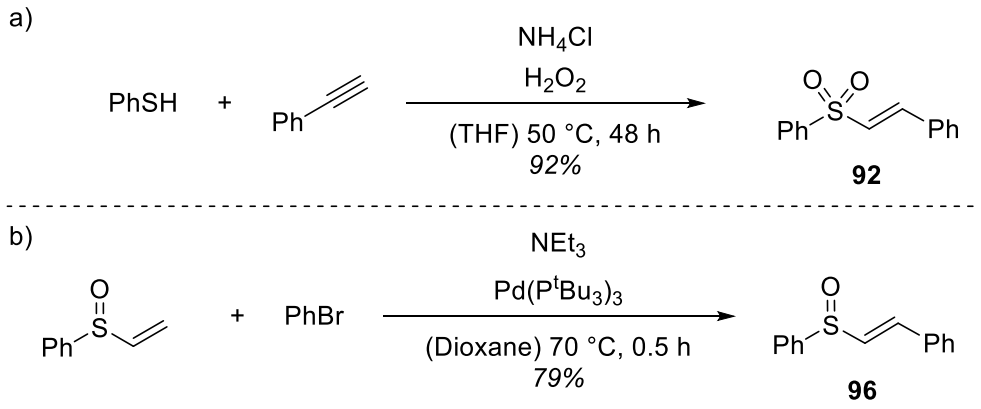
Scheme 40. Envisioned [2+2] photocycloaddition reaction of sulfones.

If these initial experiments proved to be successful, extension of the substrate scope regarding the sulfone and the olefin would show the robustness and generality of the reaction. Furthermore, the photophysical properties of this class of sulfones are widely underexplored in the literature, underlining the need for a comprehensive study by UV/Vis and luminescence spectroscopy. Performing the reaction under sensitized conditions at longer irradiation wavelength would also be desirable, as this promotes the possibility of a dual catalysis approach.

A second point of interest is the possible activation of the vinylsulfone chromophore by noncovalent interactions to a *Lewis*or *Brønsted* acid-based catalyst. There are a few reported examples on *Lewis* acid catalyzed reactions[152–156] of sulfones, although in all cases a second coordination site was present in the sulfone compound, leading to a stronger, bidentate binding of the substrate. Nevertheless, it seemed reasonable that the sulfone could be activated towards a photochemical reaction by coordination of a suitable catalyst, which would in the optimal case lead to a bathochromic shift of the absorption. This would allow for the selective excitation of such a substrate-catalyst complex, probably even under sensitized conditions, and pave the way for performing the reaction in an enantioselective fashion.

3.3 Synthesis of the Test Substrates and Initial Photoreactions

Although it is reported in the literature, that acyclic vinylsulfones were not able to react with olefins due to the competing *trans-cis* isomerization of the starting material,[143,144,151] initial irradiation experiments were planned with (*E*)-[2-(phenylsulfonyl)vinyl]benzene (**92**). The respective sulfoxide **96** was also prepared in order to test its potential as a substrate in an intermolecular [2+2] photocycloaddition (scheme 41).



Scheme 41. Synthesis of test substates. a) Sulfone **92**. b) Sulfoxide **96**.

The sulfone **92** was synthesized in an addition-oxidation sequence from thiophenol and phenylacetylene under metal-free conditions and was isolated exclusively as the *trans*-isomer.[157] While it was reported in the respective publication that sulfoxides can also be obtained selectively by adjusting the reaction conditions (room temperature instead of 50 °C),[157] sulfoxide **96** could in our hands never be isolated employing this procedure as the reaction would always proceed to oxidize the sulfide to the sulfone. Therefore, the desired sulfoxide **96** was synthesized from the corresponding vinyl sulfoxide and bromobenzene in a *Heck* reaction.[158] Sulfone **92**, a colorless crystalline solid, showed a strong absorption in the UV region with λ_{max} = 277 nm (ε = 24560 M^{-1} cm^{-1}), while sulfoxide **96** appeared to be an orange colored oil with λ_{max} = 267 nm (ε = 30000 M^{-1} cm^{-1}) (figure 8). The data obtained for sulfone **97** match the ones reported in the literature.[159,160]

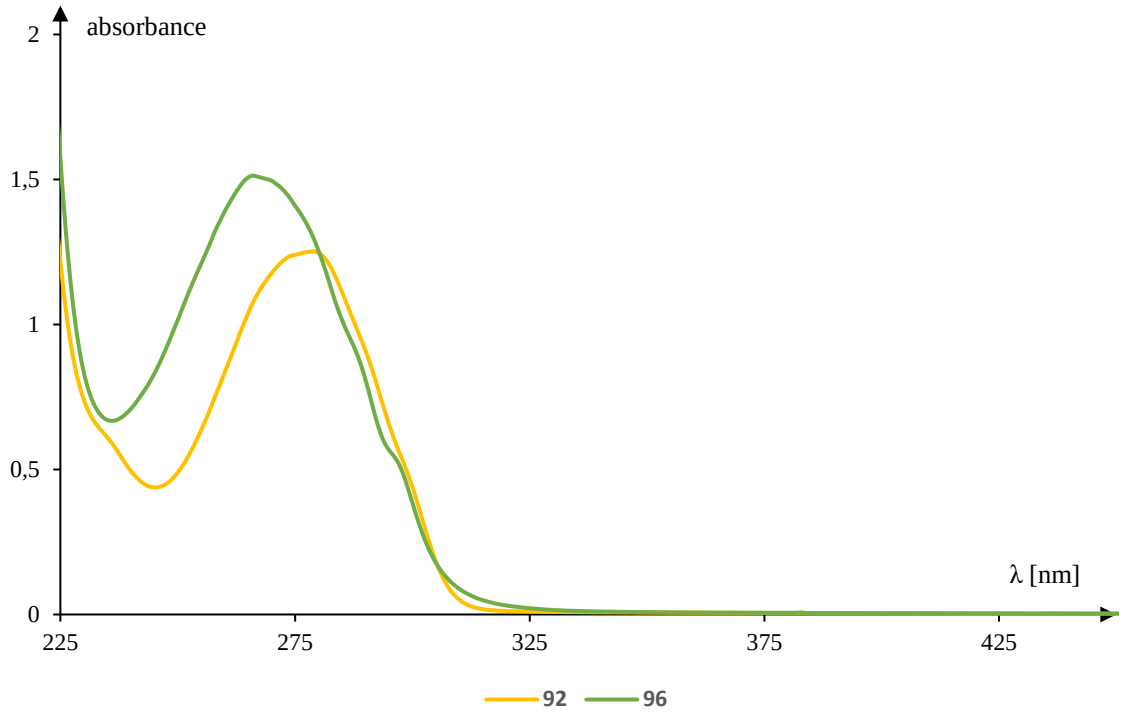
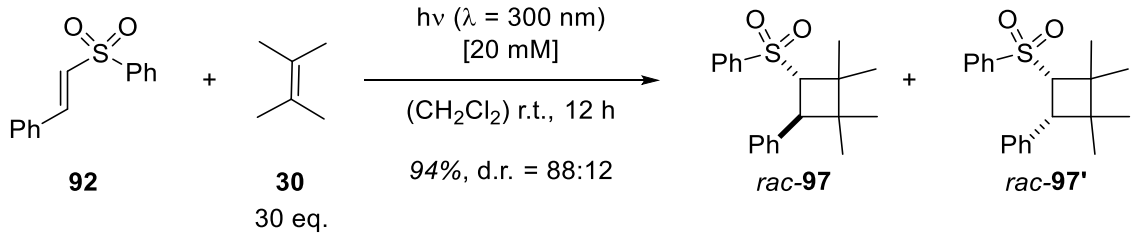


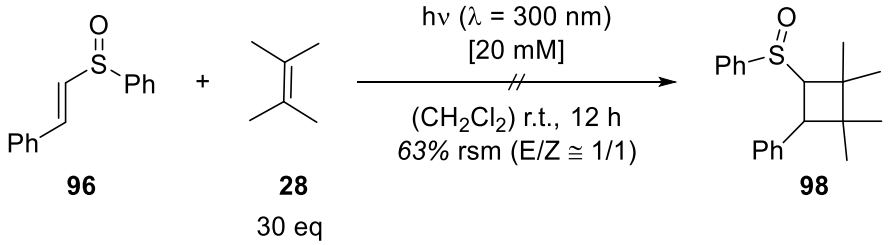
Figure 8. UV/Vis spectra of sulfone **92** and sulfoxide **96** (*c* = 0.5 mM, CH_2Cl_2).

Based on the UV/Vis spectra, an irradiation wavelength of λ = 300 nm was chosen for initial photochemical experiments by direct excitation. Otherwise, the same conditions (except for the excess of the olefin) as for the intermolecular [2+2] photocycloaddition of nitroolefins were applied (scheme 42).



Scheme 42. Test reaction of sulfone **92** with 2,3-dimethyl-2-butene (**30**).

To our delight, the first reaction under non-optimized conditions already yielded 94% of the cyclobutane product as a mixture of two diastereoisomers. After separation by column chromatography, both diastereoisomers could be identified as *rac*-**97** and *rac*-**97'**. Although *trans-cis*-isomerization of the sulfone **92** was observed during the monitoring of the reaction by TLC, the starting material was eventually fully consumed.



Scheme 43. Conditions for the test reaction of sulfoxide **96** with 2,3-dimethyl-2-butene (**30**).

The sulfoxide **96**, however, did not react under the same reaction conditions with the olefin (scheme 43). Therefore, further experiments of this new class of chromophores for [2+2] photocycloaddition reactions were focused on the vinylsulfones.

3.4 Optimization of Reaction Conditions

Despite the fact, that the intermolecular [2+2] photocycloaddition of sulfone **97** with 2,3-dimethyl-2-butene upon direct irradiation was already performed with excellent results, it was tested whether the reaction conditions could further be optimized in regard of the reaction time or the diastereoselectivity (table 4).

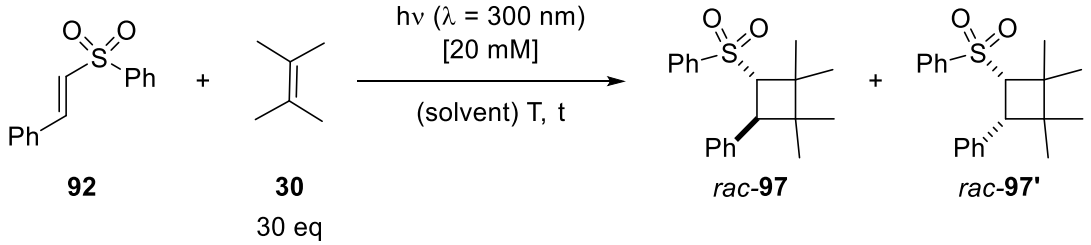


Table 4. Conditions for the optimization of solvent and reaction temperature.

#	solvent	T [°C]	t [h]	Y [%]	d.r.[a]	rsm [%]	*trans*/*cis*[b]
1	CH_2Cl_2	r.t.	12	94	88/12	full conv.	-
2	MeCN	r.t.	15	22	76/24	53	25/75
3	PhH	r.t.	15	49	80/20	24	53/47
4	$PhCF_3$	r.t.	15	64	90/10	29	30/70
5	MeOH	r.t.	15	12	75/25	59	30/70
6	CH_2Cl_2	0 °C	13	96	88/12	full conv.	-
7	CH_2Cl_2	−20 °C	13	92	87/13	full conv.	-
8	CH_2Cl_2	−40 °C	13	97	87/13	full conv.	-
9	CH_2Cl_2	−78 °C	13	99	88/12	full conv.	-
10[c]	CH_2Cl_2	r.t.	15	-	-	quant.	100/0

[a] Major/minor. [b] trans/cis Ratio of reisolated starting material. [c] The reaction was performed without a lightsource.

Changing the solvent led to an incomplete conversion in all cases, with only low to moderate yields of the photocycloaddition product (entries 2-5). The starting material was isolated as a mixture of isomers. Apparently, solvents other than dichloromethane (entry 1) rather promoted the geometrical isomerization than the addition to the olefin. When the reaction temperature was gradually decreased (entries 6-9), the yield could be slightly increased to 99% at −78 °C. The diastereomeric ratio however was unaffected by the change in temperature. Finally, the reaction was performed under the same conditions as the test reaction (entry 1) without a light source in order to ensure that the cyclobutane formation is a photochemically induced reaction (entry 10). After 15 hours, the starting material was reisolated quantitatively and exclusively as the *trans*-isomer.

With dichloromethane identified as the optimal solvent for the reaction, the influence of the irradiation wavelength and the concentration of the sulfone **92** was examined (table 5).

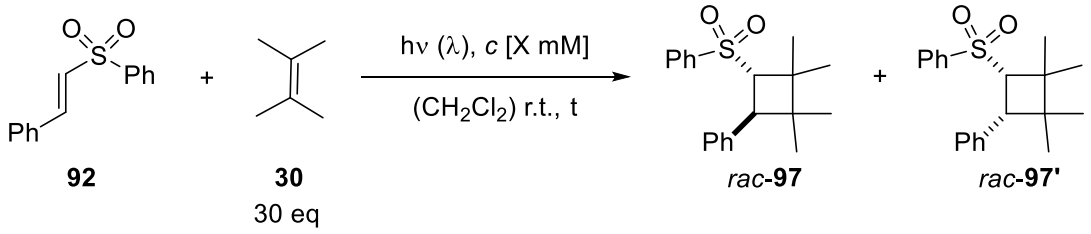


Table 5. Conditions for the optimization of the irradiation wavelength and the concentration.

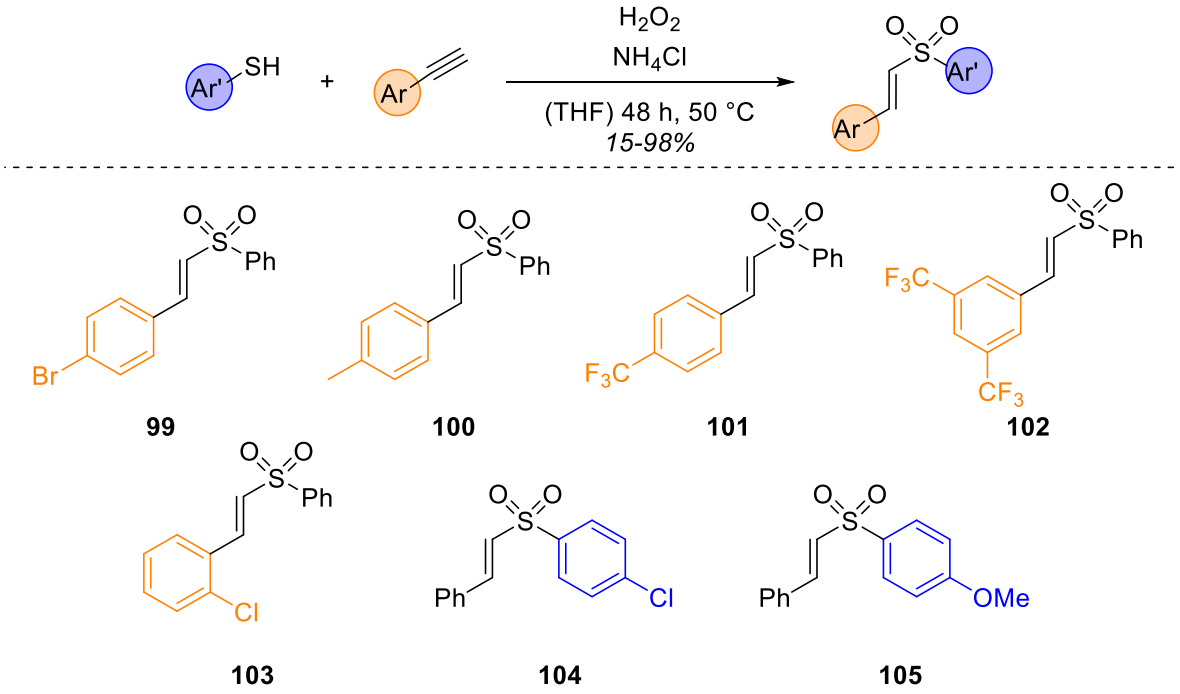
#	λ [nm]	c [mM]	t [h]	Y [%]	d.r.[a]	rsm [%]	*trans*/*cis*
1	300	20	12	94	88/12	full conv.	-
2	350	20	15	75	93/7	24	33/67
3	366	20	15	traces	n.d.	99	80/20
4	419	20	15	-	-	quant.	94/6
5	300	5	12	90	88/12	full conv.	-
6	300	10	12	96	88/12	full conv.	-
7	300	40	12	quant.	90/10	full conv.	-
8	300	100	12	quant.	92/8	full conv.	-

[a] Major/minor. [b] *trans*/*cis* Ratio of reisolated starting material.

At longer irradiation wavelength (λ > 350 nm, entries 3 and 4), no conversion of the starting material was observed. When irradiated at λ = 350 nm, the photoproduct was isolated in 75% yield (entry 2), which can be attributed to the short wavelength tailing of the light source (λ = 310 nm-410 nm). Lower (entry 5 and 6) or higher concentration (entry 7 and 8) did not have a significant impact on neither the yield nor the diastereoselectivity of the reaction. Consequently, the reaction conditions chosen initially (table 4, entry 1 and table 5, entry 1) were employed in further intermolecular [2+2] photocycloadditions of sulfone **97**.

3.5 Substrate Scope

The substrate scope of the intermolecular [2+2] photocycloaddition regarding the sulfone was extended by different substituents on both aromatic moieties (scheme 44). The synthesis was conducted under the conditions already applied for the test substrate.[157] For *ortho* chloro substituted sulfone **103** and *meta* CF_3 substituted sulfone **101**, the respective alkynes were not commercially available and therefore had to be synthesized applying the *Corey-Fuchs* protocol[161] (see experimental part).



Scheme 44. Different sulfone substrates for the [2+2] photocycloaddition.

To evaluate the effect of the substitution on the absorption properties, UV/Vis spectra of all new substrates were recorded (figure 9).

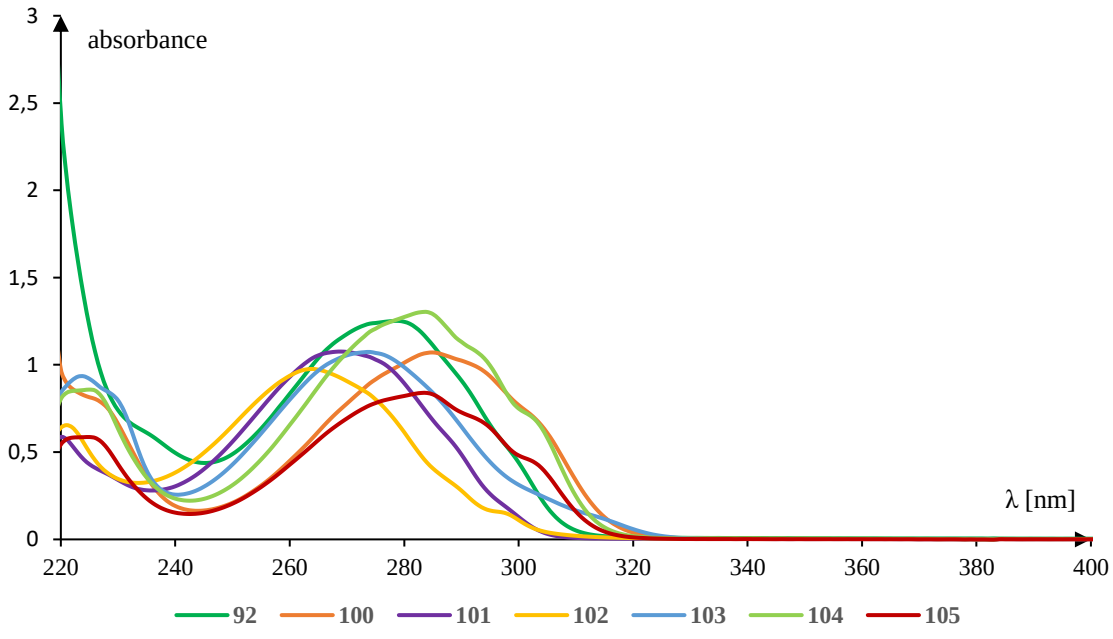
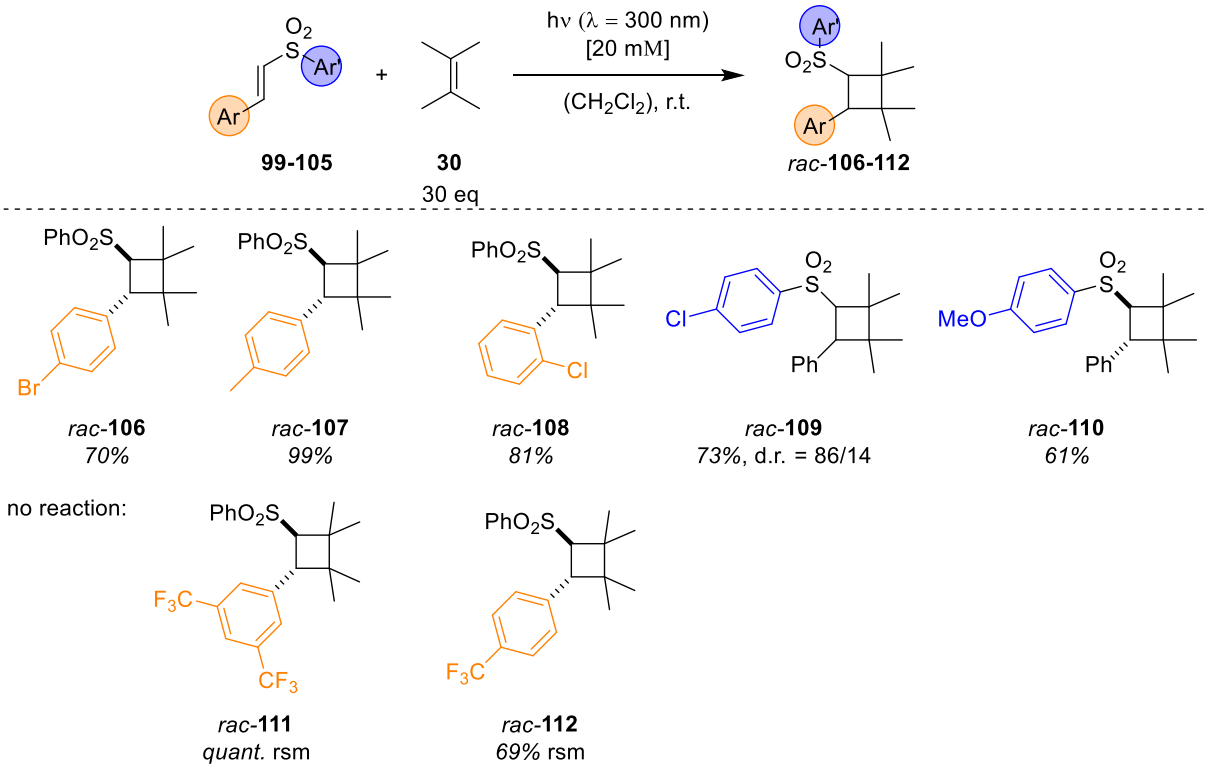


Figure 9. UV/Vis spectra of sulfone substrates **97**, **103-109** (c = 0.5 mM, CH_2Cl_2).

While the absorption bands of all sulfone compounds were located approximately in the same region (λ = 240 nm-330 nm), the λ_{max} was shifted depending on the electronic nature of the substituents and on whether they are located at the styrene or sulfone aromatic moiety. An electron donating substituent at the styrene moiety (**100**) led to a bathocromic shift of the

absorption. The same effect was observed with substitution at the sulfone aromatic moiety, irrespective of their electronic nature (**104** and **105**). As expected, removing electron density at the styrene aromatic moiety by substitution with an electron withdrawing group shifted the λ_{max} to shorter wavelength.

Sulfones **99-105** were evaluated as substrates in the intermolecular [2+2] photocycloaddition to 2,3-dimethyl-2-butene (**30**) by direct excitation at λ = 300 nm (scheme 45).



Scheme 45. Intermolecular [2+2] photocycloaddition of different sulfone substrates.

Weakly electron donating (*rac*-**107**) or electron withdrawing (*rac*-**106**, *rac*-**108**) substituents in the *para* or *ortho* position were tolerated and led to high yields of the cyclobutane as a single diastereoisomer. A stronger electron withdrawing CF_3-group attached to the styrene aromatic moiety impeded the reaction completely. In these reactions, only starting material was isolated, the photoproducts *rac*-**111** and *rac*-**112** were not observed. Substitution at the aromatic moiety of the sulfone was also tolerated (*rac*-**109**, *rac*-**110**). Interestingly, *para* chloro substituted sulfone *rac*-**109** was isolated as a mixture of diastereoisomers as only example in the series of differently substituted sulfones. A certain functional group tolerance can be attributed to the reaction, with the exception of strongly electron withdrawing substituents at the styrene aromatic moiety.

The substrate scope regarding the olefinic reaction partners was not further examined during the course of this work.

3.6 UV-Vis Titration Experiments to Evaluate Chromophore Activation

Asymmetric photocatalysis is in many cases achieved by employing chiral small molecule catalysts that interact with the substrate in its ground state and thereby alter the photophysical properties in a way that the catalyst-substrate complex is excited selectively by the light absorbed.[129,162] An elegant method to achieve this selective excitation is the activation of the respective chromophore by covalent binding (e. g. iminium ion catalysis)[163] or non-covalent coordination (*Lewis* or *Brønsted* acid catalysis).[129,162] This interaction often leads to a bathochromic shift of the absorption maximum.[129,164–166] By irradiation with a suitable light source it can be ensured that the reaction only occurs from catalyst-bound substrate, suppressing any non-catalyzed background reaction with non-coordinated substrate absorbing at shorter wavelength.[129]

Based on these considerations and on their structural similarity to enone systems, it was probed whether the presence of a chemical activator would also lead to a bathochromic shift of the absorption of sulfone **92**. A series of *Lewis* acids was added in high excess to a solution of the sulfone, and the UV/Vis spectra of these mixtures were recorded (figure 10).

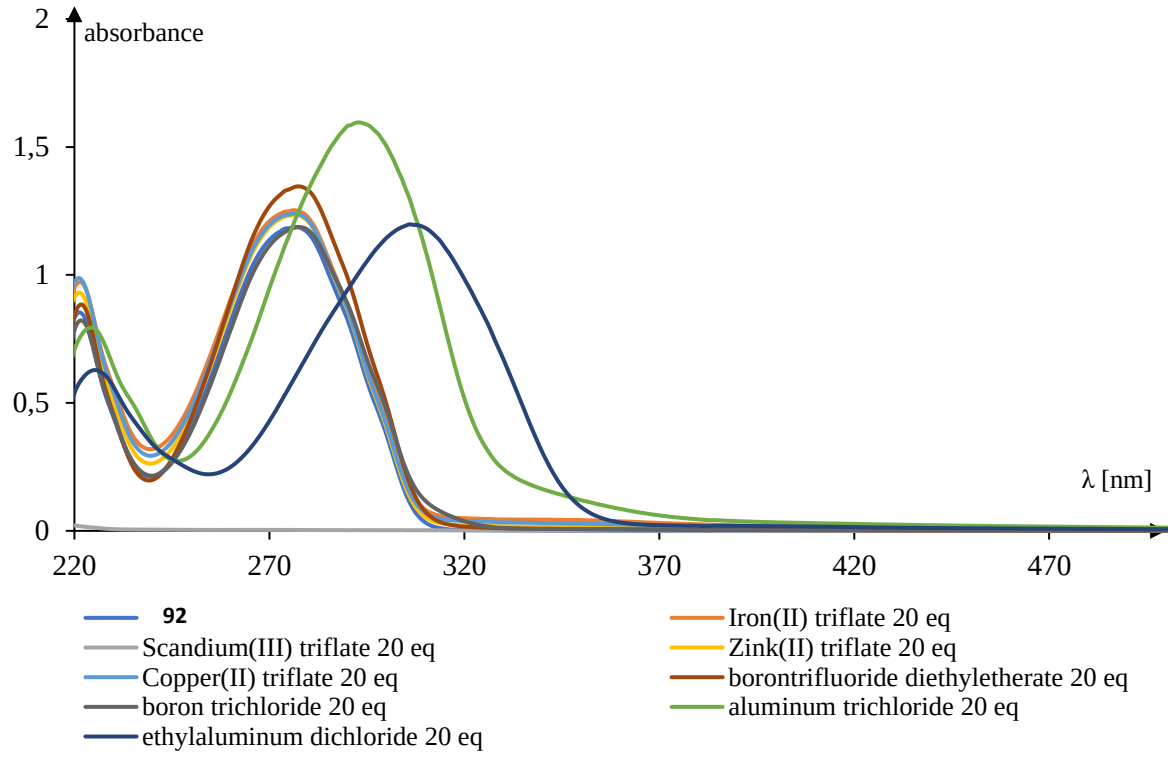


Figure 10. UV/Vis spectra of sulfone **92** in presence of high excess of different *Lewis* acids (c = 0.5 mM, CH_2Cl_2).

With metal salts such as $Zn(OTf)_2$ or $Cu(OTf)_2$ as well as the *Lewis* acidic complex $BF_3{\cdot}OEt_2$ the interaction was apparently not sufficiently strong to induce a change in the absorption. Addition of excess $AlCl_3$, which qualifies as a medium strong *Lewis* acid in the series, led to a shift of the absorption maximum from λ_{max} = 277 nm to λ_{max} = 294 nm ($\Delta\lambda$ = 17 nm) and a slightly intensified absorption (ε = 28820 M^{-1} cm^{-1}). The most significant effect in the UV/Vis spectrum was observed with $EtAlCl_2$, shifting the absorption maximum to λ_{max} = 306 nm ($\Delta\lambda$ = 29 nm). In the presence of BCl_3 on the other hand the regular absorption band vanished completely, indicating the decomposition of sulfone **92** under these conditions. The dependence of the bathochromic shift on different concentration of the *Lewis* acid was further examined by adding increasing amounts of $EtAlCl_2$ to the substrate solution (figure 11).

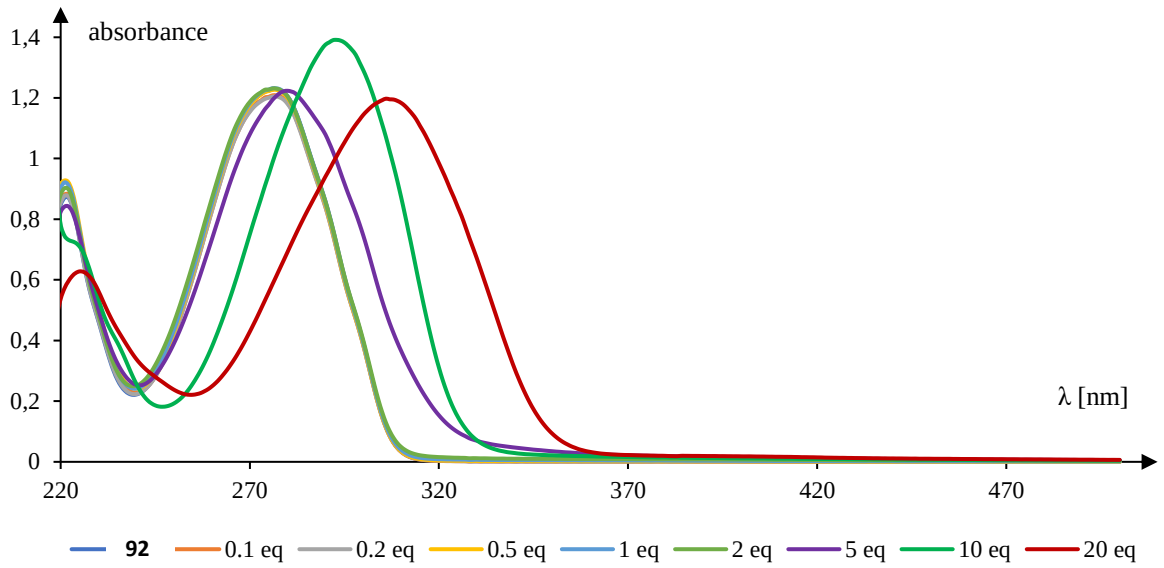
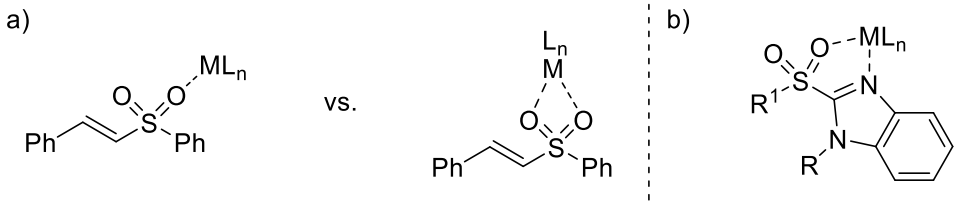


Figure 11. UV/Vis titration of sulfone **92** with different concentrations of $EtAlCl_2$.

A high excess of the *Lewis* acid was required in order to effectively shift the absorption of the sulfone to longer wavelength. It was reported in the literature that $EtAlCl_2$ is capable of establishing non-covalent interactions to sulfones, and it was proposed that the coordination occurs only to one of the oxygen atoms (scheme 46).[155,156] A bidentate coordination of both oxygen atoms can, however, not be excluded, as the mode of interaction between *Lewis* acids and sulfones is not well explored.



Scheme 46. a) Possible coordination modes of sulfone **92** by a *Lewis* Acid. b) Bidentate coordination of a sulfonyl compound.

However, there are only few examples where the activation of sulfones has been put to use in a catalytic reaction, and the mode of interaction between the catalyst and substrate was not studied in detail. This is of high interest regarding the targeted development of a strategy towards the asymmetric catalysis of the [2+2] photocycloaddition of sulfones. In most cases, the sulfone compound contained a second functional group capable of being coordinated by a *Lewis* acid, and asymmetric catalysis is achieved by chelation of both binding sites simultaneously.[154,156,167,168] Additionally, most examples are reported on sulfonamides, with a second coordination site at the nitrogen (scheme 46, right).

Other activating compounds such as *Schreiners* thiourea,[124] trifluoroacetic acid or the *Meggers* catalyst[169] did not induce a bathochromic shift of the absorption of sulfone **92**.

3.7 Luminescence Spectroscopy

As already mentioned, studies of the photophysical behavior of vinylsulfones are virtually non-existent in the literature. Therefore, it was considered as crucial to examine the luminescence spectroscopic properties of this compound class based on the model substrate **92** (figure 12), especially in terms of mechanistic considerations. The luminescence spectra were measured using standard techniques.[18]

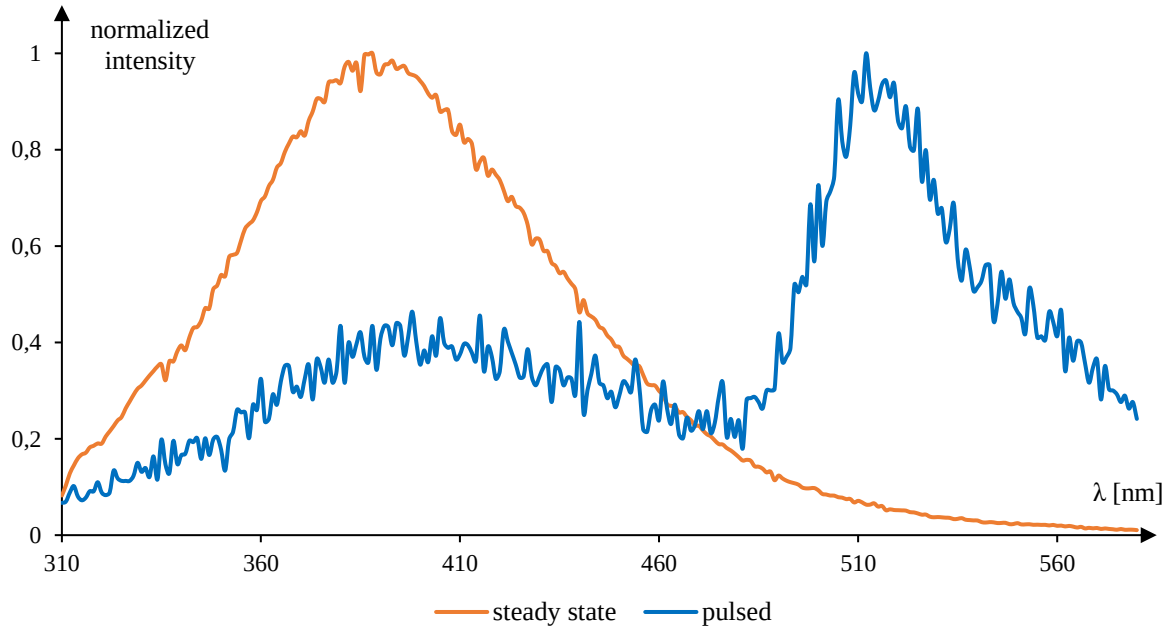


Figure 12. Luminescence spectra of sulfone **92** under steady state (orange) and pulsed (blue) conditions (77 K, *c* = 150 µM, CH_2Cl_2).

No luminescence was detected in solution under steady state conditions at room temperature. At 77 K, strong emission in the range of λ = 310 nm-510 nm from the frozen sample is observed upon excitation at λ = 300 nm (figure 12, orange line). This emission band with a maximum centered at λ_{max} = 376 nm, was assigned as fluorescence. Under pulsed conditions, this fluorescence was still visible, even with a flash delay of 800 µs (figure 12, blue line). The signal intensity of the long wavelength emission in the range of λ = 480 nm-580 nm was too low to be identified as phosphorescence. In order to obtain more reliable data on the phosphorescence, the heavy atom effect[170,171] was exploited by subjecting bromo-substituted sulfone to luminescence spectroscopic analysis (figure 13).

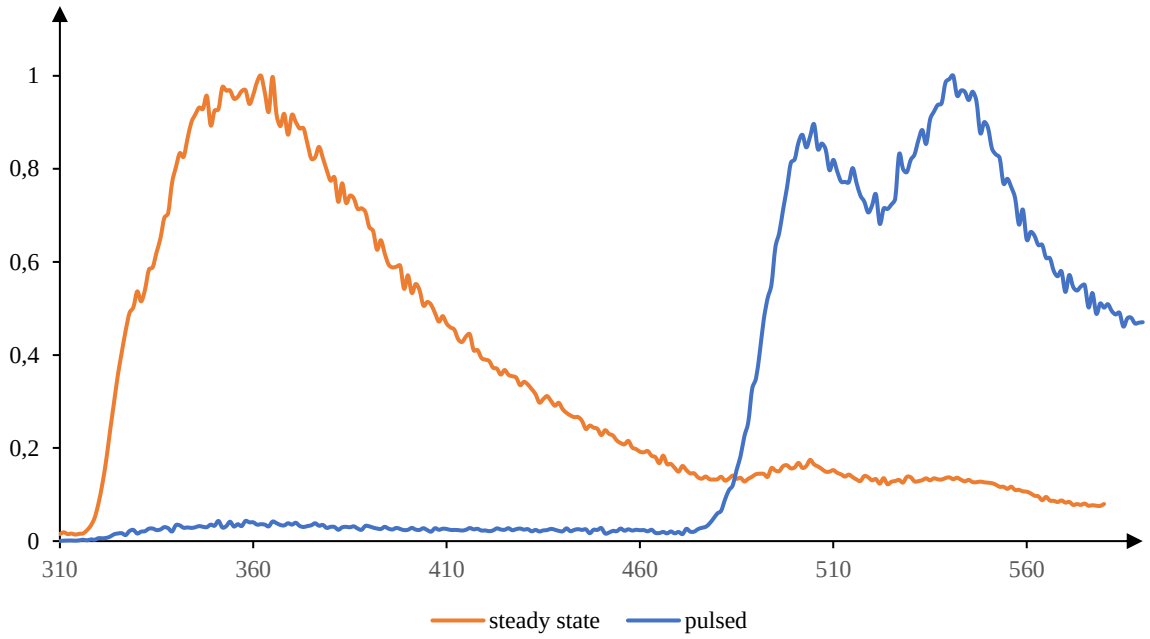
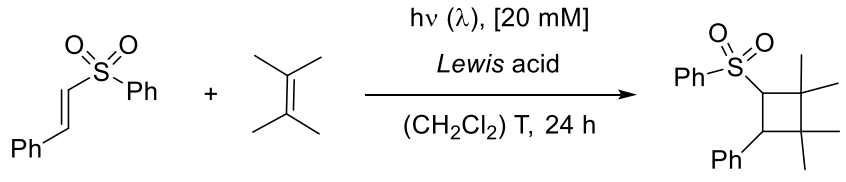


Figure 13. Luminescence spectra of sulfone **99** under steady state (orange) and pulsed (blue) conditions (77 K, *c* = 150 µM, CH_2Cl_2).

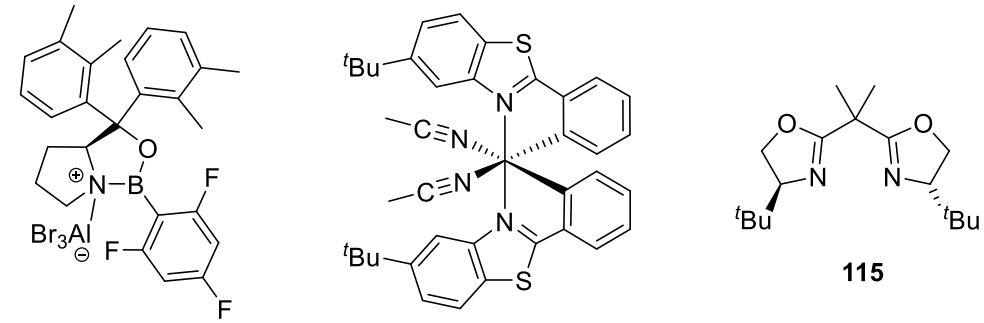
Bromo-substituted sulfone **99** also exhibited strong fluorescence under steady state conditions at 77 K in a range of λ = 315 nm-460 nm, with a slightly hypsochromicly shifted maximum at λ_{max} = 360 nm. However, the pulsed experiment (flash delay 200 µs) revealed an emission with reasonably strong intensity from λ = 480 nm-580 nm. Based on the lifetime of this emission, it was identified as phosphorescence. The energy of the excited triplet state was determined as E_T = 243 kJ/mol at the steepest point of the slope (λ = 490 nm). Cognizance of the triplet energy of the photoexcited sulfone allows for the identification of suitable triplet sensitizers, that could initiate the [2+2] photocycloaddition by energy transfer even at excitation wavelengths λ > 480 nm.

3.8 Lewis Acid Catalysis – Experiments with Direct Excitation

UV-Vis experiments with $EtAlCl_2$ revealed an interaction between the sulfone **92** and the coordinating *Lewis* acid, leading to a bathochromic shift of the absorption maximum. Based on these results, it was aimed for a *Lewis* acid catalyzed version of the intermolecular [2+2] photocycloaddition of the sulfone by irradiation with light in the near UV or visible region (table 6).



92 **30** 30 eq *rac*-**97**



113 **114** **115**

Table 6. Conditions for the *Lewis* acid catalyzed [2+2] photocycloaddition of sulfone **92** with direct excitation.

#	λ [nm]	L. A. (eq)	T [°C]	Y [%]	d.r.[a]	*ee* [%]	rsm [%]	*trans*/*cis*[b]
1	-	$EtAlCl_2$ (20)	r.t.	-	-	-	quant.	100/0
2	366	$EtAlCl_2$ (1.0)	r.t.	traces	n.d.	-	97	77/23
3	366	$AlBr_3$ (1.0)	−78 °C	-	-	-	quant.	53/47
4	366	$AlCl_3$ (1.0)	r.t.	-	-	-	quant.	80/20
5	366	$EtAlCl_2$ (0.5)	r.t.	-	-	-	quant.	70/30
6	300	**113** (0.5)	−78 °C	15	90/10	rac	84	29/71
7	366	**113** (0.5)	−78 °C	traces	>99/1	n.d.[c]	98	77/23
8	419	**114** (0.5)	r.t.	-	-	-	quant.	100/0
9[d]	300	$Zn(OTf)_2$ (0.5) + **115** (.075)	r.t.	quant.	87/13	11	-	-
10[d]	300	$Sc(OTf)_3$ (0.5) + **115** (.075)	r.t.	quant.	86/14	13	-	-
11[d]	300	$Cu(OTf)_2$ (0.5) + **115** (.075)	r.t.	quant.	87/13	2	-	-

[a] ;ajor/minor. [b] *trans*/*cis* Ratio of reisolated starting material. [c] The *ee* could not be determined due to the low quantity. [d] Full conversion was reached after 16 hours.

First, it was ensured that there is no thermal reaction between the sulfone and the olefin initiated by the presence of a *Lewis* acid (entry 1). After 24 hours reaction time with high excess of $EtAlCl_2$, the starting material **92** was recovered quantitatively and exclusively as the

trans-isomer. Irradiation experiments with achiral *Lewis* acids were carried out at λ = 366 nm. At this wavelength, no background reaction was expected (*vide supra*). With stoichiometric amounts of $EtAlCl_2$, only traces of the product were obtained, while the starting material was isomerized (entry 2). The reaction with $AlBr_3$ was performed at −78 °C due to the instability of the *Lewis* acid at room temperature. In this case however, only starting material as a 1:1 mixture of geometrical isomers was isolated (entry 3). The results obtained with $AlCl_3$ were similar to those obtained with $EtAlCl_2$ (entry 4). When the catalyst loading was decreased to 50 mol% (entry 5), no conversion was observed. Although catalysis of the [2+2] photocycloaddition of sulfone **92** by direct excitation was not successful in presence of achiral *Lewis* acids, two attempts towards asymmetric catalysis were undertaken. A chiral oxazaborolidine was employed as the catalyst. This type of Lewis acids has been used in enantioselective photoreactions with remarkable success.[165,166,172] However, in the [2+2] photocycloaddition of sulfone **92**, the oxazaborolidine did not promote the preferred formation of one of the product enantiomers. At λ = 300 nm, the formation of racemic product can be explained by the non-catalyzed background reaction occurring at this irradiation wavelength (entry 6). The low yield of the reaction indicates, that catalyst-bound substrate is unable to undergo the desired [2+2] photocycloaddition, and the energy of the light absorbed is released by geometrical isomerization. Only non-coordinated substrate reacted with the olefin, leading to racemic product. This hypothesis is substantiated by the results of the reaction conducted at λ = 366 nm with almost quantitative recovery of starting material and traces of the cyclobutane **92** (entry 7). The amount of material was too little to allow determination of enantiomeric excess.

A general observation from the results discussed so far is, that the presence of high concentrations of a strongly coordinating *Lewis* acid decreases the rate of the reaction. This finding is in accordance with studies on *Lewis* acid catalysis of photoreactions with different chromophores previously performed in our group.[166,173,174] Under the assumption, that the [2+2] photocycloaddition of sulfone **92** occurs on the triplet hypersurface, a possible explanation for the virtual inhibition of the reaction could be a decreased ISC rate as it has been proposed for dihydropyridones.[173]

Other possible catalysts which did not display any bathochromic shift in the UV/Vis spectrum of sulfone **92** were nonetheless tested in the [2+2] photocycloaddition. No reaction was observed in presence of the *Meggers* catalyst at visible light irradiation (entry 8). *Lewis* acidic catalytic systems such as metal salts in the combination with chiral bisoxazoline (BOX) ligands have been used in the asymmetric catalysis of thermal reactions of sulfones.[152,156,168] With Zn-^{t}BuBOX, Sc-^{t}BuBOX and Cu-^{t}BuBOX, the reaction proceeded with full conversion,

furnishing the respective photocycloaddition products in quantitative yields (entry 9-11). As no bathochromic shift was observed in the UV/Vis titration experiments of sulfone **92** with these metal salts, λ = 300 nm was chosen as the irradiation wavelength. Under these conditions, the reaction might as well proceed uncatalyzed, leading to the formation of racemic product. It was found by *Edtmüller*, that irradiation of 2-aryloxy-cyclohex-2-enones in presence of such chiral catalysts leads to the enantioselective cyclization of these compounds.[174] In this study, the catalyzed reaction was performed under the same conditions as in the racemic case and it was observed that catalyst-bound substrate reacted preferred over uncoordinated substrate. In case of the intermolecular [2+2] photocycloaddition of sulfone **92**, an enantiomeric excess of 11% (entry 9) and 13% (entry 10) was achieved with Zn-^{t}BuBOX and Sc-^{t}BuBOX as the catalysts, respectively. Based on these results, BOX-ligand based *Lewis* acidic systems seem to be capable of promoting this reaction asymmetrically.

3.9 Lewis Acid Catalysis – Experiments Under Sensitized Conditions

The triplet energy of bromo-substituted sulfone **99** was determined as E_T = 243 kJ/mol. Since attempts towards the *Lewis* acid catalyzed [2+2] photocycloaddition of sulfones by direct excitation were unsuccessful, it was examined whether the catalysis could be performed under sensitized conditions (table 7). Four different sensitizers with different triplet energies (**116**-**119**)[175,176] were chosen for these experiments, with either $EtAlCl_2$ or chiral oxazaborolidine **113** as the catalyst. Visible light was chosen as the irradiation wavelength, as all of the sensitizers are intensively colored compounds and absorb light in the range λ > 400 nm.

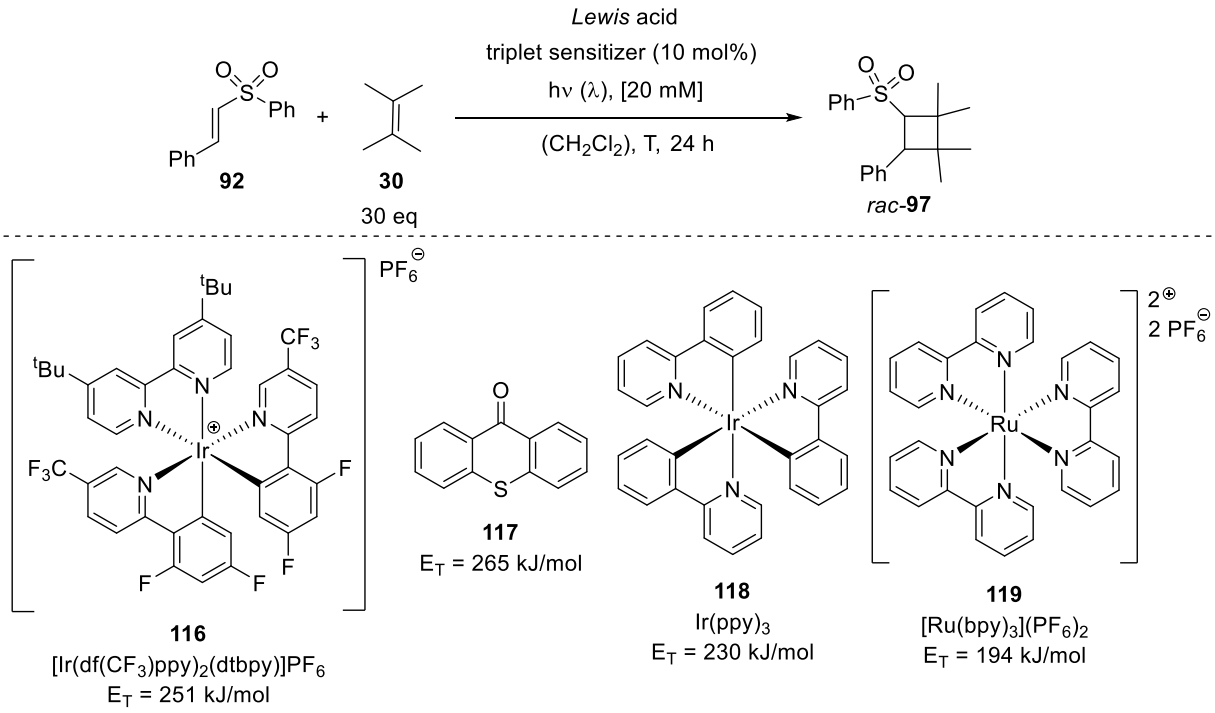


Table 7. Conditions for the *Lewis* acid catalyzed [2+2] photocycloaddition of sulfone **92** under sensitized conditions.

#	λ [nm]	L. A. (eq)	sens.	T [°C]	Y [%]	d.r.[a]	*ee* [%]	rsm [%]	*trans*/*cis*[b]
1	419	-	**116**	r.t.	16	>99/1	-	78	44/56
2	419	-	**117**	r.t.	-	n.d.	-	quant.	47/53
3	398	-	**116**	r.t.	36	>99/1	-	49	44/56
4	419	-	**118**	r.t.	-	-	-	quant.[c]	77/23
5	419	-	**119**	r.t.	-	-	-	quant.[c]	100/0
6	419	$EtAlCl_2$ (1.0)	**116**	r.t.	70	>99/1	-	9	47/53
7	398	$EtAlCl_2$ (1.0)	**116**	r.t.	52[d]	>99/1	-	-	-
8	419	$EtAlCl_2$ (1.0)	**118**	r.t.	-	-	-	quant.[c]	85/15
9	419	$EtAlCl_2$ (1.0)	**119**	r.t.	-	-	-	quant.[c]	100/0
10[e]	419	**113** (0.5)	**116**	−78 °C	6	>20/1	20	91	46/54
11[e]	419	**113** (0.5)	**116**	−60 °C	10	>20/1	15	86	43/57
12[e]	419	**113** (0.5)	**116**	−40 °C	8	>20/1	12	90	40/60

[a] Major/minor. [b] *trans*/*cis* Ratio of reisolated starting material. [c] Crude. [d] Full conversion, but formation of unidentified side product. [e] The reaction was stopped after 48h irradiation.

In the absence of an activating *Lewis* acid, Ir-complex **116** induced the [2+2] photocycloaddition by sensitization (entry 1). The conversion was low, and only 16% of the photoproduct *rac*-**97** were isolated. Thioxanthone (**117**) did not successfully sensitize the reaction (entry 2). Instead, *Paternó-Büchi* reaction[177,178] of the sensitizer with the olefin was observed. With a LED as the light source (λ = 398 nm), the yield of the reaction sensitized by **116** was increased to 36% (entry 3), as this irradiation wavelength has a larger overlap with the absorption of the sensitizer.[176] Other compounds commonly employed as sensitizers such as neutral Ir-complex **118** and Ru-containing **119** did sensitize the reaction (entry 4 and 5), which is not surprising considering the triplet energy of these compounds is lower than that of the sulfone. Addition of stoichiometric amounts of $EtAlCl_2$ to the reaction mixture and irradiation at λ = 419 nm resulted in the formation of cyclobutane *rac*-**97** in high yield and diastereoselectivity (entry 6). This result led to the hypothesis, that activation of sulfone **92** by $EtAlCl_2$ lowers the triplet energy of the excited state, thereby facilitating the triplet energy transfer from **116** by increasing the energy gap ($\Delta E_1 < \Delta E_2$) (figure 14).[129]

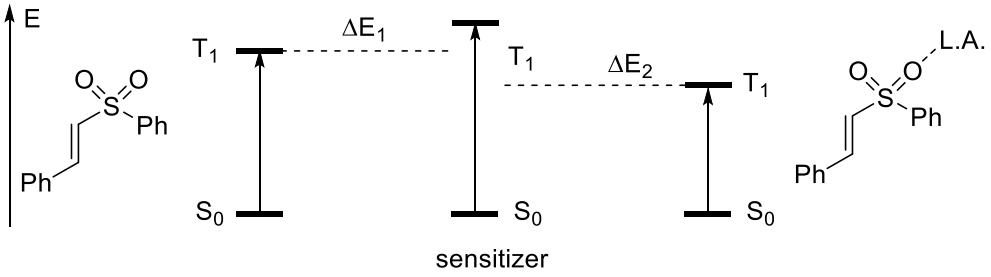


Figure 14. Proposed activation of sulfone **92** by coordination of a *Lewis* acid resulting in a lower triplet energy.

Considering the triplet energy of sulfone **99** (E_T = 243 kJ/mol) and the tabulated E_T of Ir-complex **116** as well as the results from entry 1, the substrate can be sensitized by **116**, but coordination by a *Lewis* acid enables a more effective energy transfer. At shorter irradiation wavelength, the starting material was completely consumed and the yield was increased to 52% (entry 7). However, an unidentified side product was formed. Ir- and Ru-complexes **118** and **119** were also tested under *Lewis* acid catalyzed conditions, but no conversion was observed in these reactions (entry 8 and 9). The conclusion that can be drawn from these results is, that if the coordination of sulfone **92** by the *Lewis* acid leads to a decrease of the triplet energy. This energy lies in the range E_T = 243 kJ/mol < E_T(**92**·L.A.) < E_T = 230 kJ/mol.

As it was shown that the [2+2] photocycloaddition of sulfone **97** can be performed under sensitized conditions in presence of a *Lewis* acid, an enantioselective variant of this reaction was evaluated using oxazaborolidine **113** as chiral catalyst. Initially, the reaction was performed at −78 °C, because it has been shown that **113** is decomposing over time at ambient temperature.

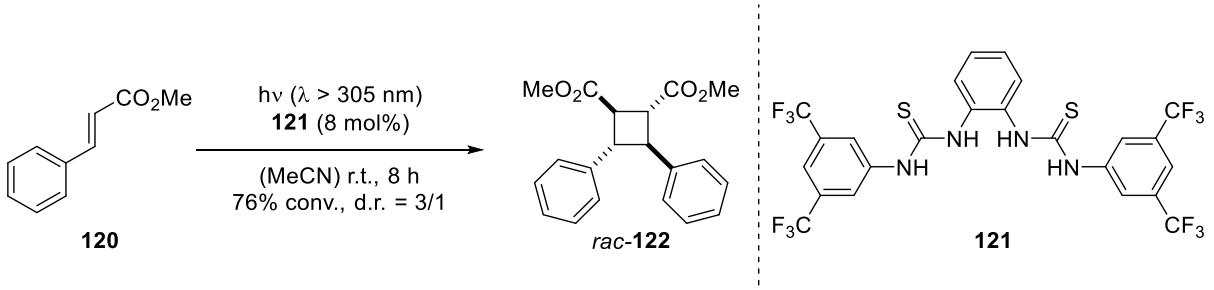
Under these conditions, the reaction rate was low, with only 6% of isolated photoproduct after two days of irradiation (entry 9). The *ee* was determined as 20%, while most of the starting material was recovered as a 1:1 mixture of isomers. Increasing the reaction temperature led to a slight improvement of the yield on the one hand, but a decreased *ee* on the other hand (entry 10 and 11). In principle, oxazaborolidines seem to be suitable for asymmetric catalysis of the [2+2] photocycloaddition. The interaction of sulfone **92** with the catalyst **113** apparently does not induce the same significant activation as $EtAlCl_2$, rendering an effective energy transfer impossible under these conditions. Although the respective cyclobutane was formed with 20% *ee*, the reaction did not proceed with an acceptable rate and the yields of the photoproduct were low. Chiral *Lewis* acid complexes of chiral BOX-ligand **115** were not yet tested under sensitized conditions.

Summing up, sulfones such as **92** can be successfully activated by coordination of at least one of the sulfur oxygens by strongly coordinating *Lewis* acids. This interaction supposedly leads to a decrease of the triplet energy in the excited state, enabling sensitization of sulfone **92** in presence of a *Lewis* acid with a suitable sensitizer.

4. A Chiral Thiourea-Thioxanthone Hybrid as Catalyst in Visible-Light Mediated Photochemical Reactions

4.1 Thiourea Derivatives as Catalysts in Photochemical Reactions

Achieving enantioselectivity in photochemical reactions is a challenging task. The absorption of light from the UV or visible region of the electromagnetic spectrum elevates a molecule to a high energy excited state. Several pathways for releasing this absorbed energy are possible. A catalyst has to interact with this molecule in its excited state in a way, that the reaction leads to the preferred formation of one enantiomer of the desired product over the other.[162] Still, a plethora of concepts has been developed for mastering this task successfully, for example solid state reactions with a chiral host,[179] the use of chiral small molecule catalysts such as chiral amines or *Lewis* acids,[162,163,166,180] or by employing dual catalysis strategies involving electron or energy transfer.[181,182] Thioureas are well established organocatalysts in thermal reactions,[122,183–186] and are obviously suited for binding typical substrates of photochemical reactions such as enones. It seems surprising that to this date, only few examples of photochemical reactions catalyzed by thiourea-based catalysts have been reported. The group of *Beeler* performed a [2+2] photocycloaddition of methyl cinnamate **120** in flow, catalyzed by achiral bis-thiourea **121** derived from *Schreiners* thiourea[124,125] (scheme 47).[187]

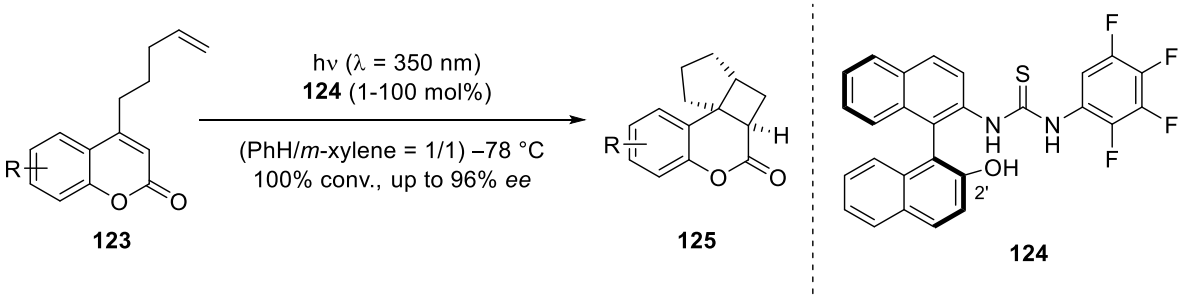


Scheme 47. [2+2] photocycloaddition of cinnamate **120** in flow.

It was proposed, that the cinnamate substrate **120** is activated by lowering the HOMO/LUMO gap when coordinated by the catalyst.[187] The same group was able to show in a related publication, that the rate of this reaction can be improved significantly by liquid-liquid slug flow conditions.[188]

The first example of an enantioselective photoreaction catalyzed by a chiral thiourea was reported by *Sivaguru* and co-workers in 2014.[189] The combitaion of an axially chiral BINOL backbone with a thiourea moiety as the coordination site resulted in a catalyst (**124**) that was

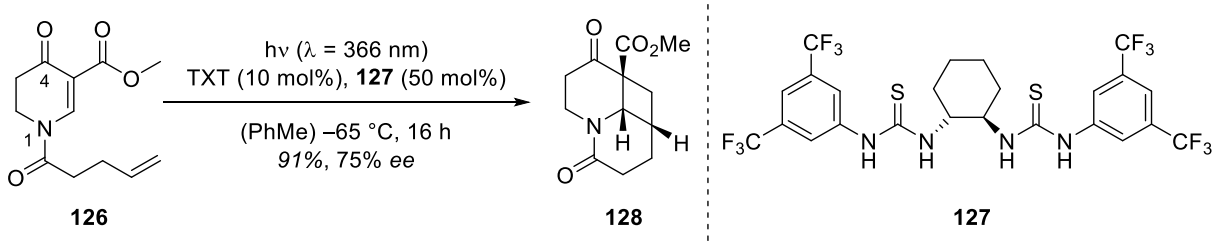
able to induce high enantioselectivities (up to 96% *ee*) in the intramolecular [2+2] photocycloaddition of 4-alkenyl-substituted coumarins **123** (scheme 48).



Scheme 48. Enantioselective intramolecular [2+2] photocycloaddition of coumarins.

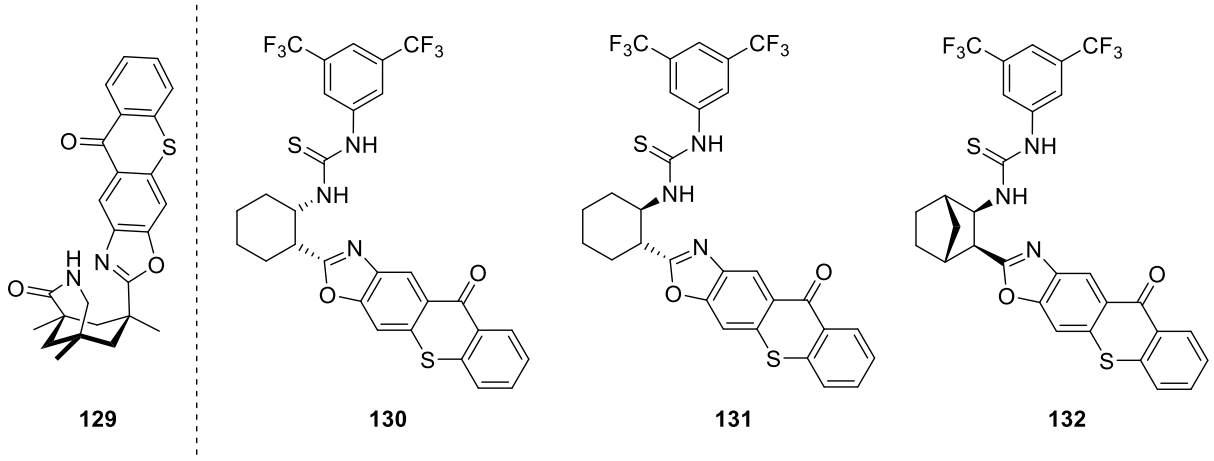
Evaluation of different substituents in the C2'-position of the BINOL moiety revealed, that the presence of a hydroxy group is crucial for achieving high enantiomeric excess. This observation was attributed to a coordination of the endocyclic oxygen atom by hydrogen bonding from the hydroxy group, thus acting as a second binding site. In a parallel study, the group investigated other thioureas as catalysts in the same reaction, but all other tested catalysts failed in inducing high enantioselectivity.[190] Photophysical studies showed, that the coordination of the coumarin substrate by catalyst **124** leads to a bathochromic shift of the absorption maximum, and that both singlet and triplet excited states of the catalyst are quenched in presence of the coumarin. Based on these findings, a mechanistic model was proposed, where the course of the catalytic cycle depends on the catalyst loading. At high catalyst loading, the excited catalyst is quenched by the substrate, whereas at low catalyst loading, the catalyst-substrate complex is excited upon irradiation.[189] A comprehensive study on the thiourea-mediated intermolecular [2+2] photocycloaddition of coumarins was presented two years later, and detailed mechanistic studies showed that coordination of the substrate by the catalyst enhanced intersystem crossing and prolonged excited state lifetimes.[191]

The second example for an enantioselective photoreaction under thiourea catalysis was reported by our group by means of the intramolecular [2+2] photocycloaddition of dihydropyridones **126** in presence of substoichiometric amounts of chiral thiourea **127** and thioxanthone as triplet sensitizer (scheme 49).[126]



Scheme 49. Enantioselective intramolecular [2+2] photocycloaddition of dihydropyridone **128**.

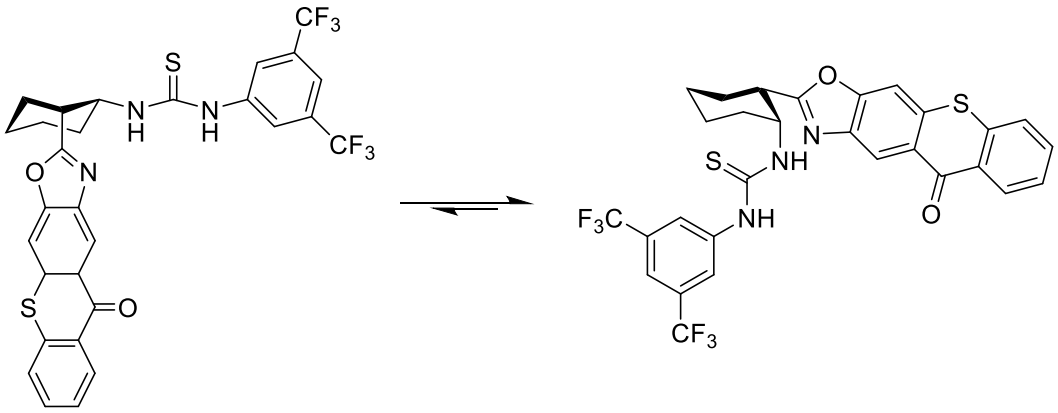
A series of thioureas with differently substituted aromatic moieties were tested, identifying the catalyst depicted in scheme 49 as superior regarding yield and *ee*. A nonsymmetrical binding mode was proposed, where one thiourea unit coordinates the substrate, while the other one acts as a steric shield. This hypothesis was supported by NMR titration studies, revealing that only the signal of carbonyl carbon in the C4-position is shifted significantly. It was also found, that the *ee* of the reaction increased when it was performed under sensitized conditions, which led to the assumption that thioxanthone does not only act as sensitizer but also as steric shield.[126] This discovery led to the pursue of a new project related to the highly successful work on lactame based templates,[38,192–194] where a thiourea binding site and a thioxanthone shield should be merged into one catalyst by connection *via* a chiral backbone. From this project, a series of chiral thiourea-thioxanthone hybrids **130**-**132** was developed (scheme 50) and tested as potential catalysts in photochemical reactions.[195,196]



Scheme 50. Chiral thiourea-thioxanthone hybrids **130**-**132** developed by *Mayr*, based on chiral lactame template **129**.

These thiourea-thioxanthone hybrids should coordinate a suitable substrate by hydrogen bonding from the thiourea, while the thioxanthone moiety acts as a triplet sensitizer and at the same time as a steric shield. After being tested in several photoreactions with different substrates, the catalyst **130** only showed low capacity in inducing high enantioselectivity. NMR studies revealed, that the cyclohexane core structure undergoes a conformational flip in

solution, placing the more sterically demanding oxazoline-fused thioxanthone into the equatorial position (scheme 51).[195] This ring flip resulted in insufficient steric shielding and thereby in low enantiomeric excess.



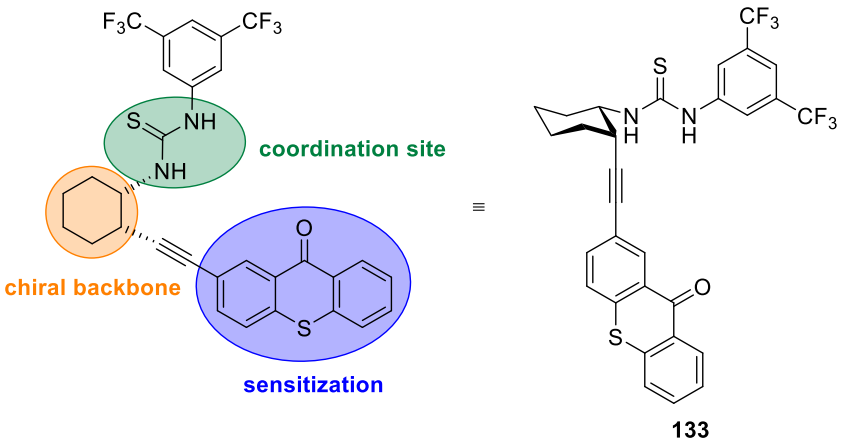
130

Scheme 51. Conformational flip observed for chiral thiourea-thioxanthone hybrid **130** in solution.

In order to circumvent this problem, the cyclohexane moiety was replaced with a more rigid norbornane core (see scheme 50).[195] Catalyst **132** however also failed in inducing high enantioselectivities in all tested reactions.

4.2 Project Aims

The aim of this project was the pursuit of a different strategy towards the asymmetric catalysis of photoreactions by chiral thioureas involving the introduction of an alkyne as linker between the cyclohexane core and the thioxanthone moiety (scheme 52). The reason behind this approach was the assumption, that the alkyne would prevent the conformational flip in solution, because it would be considered as the smaller substituent compared to the thiourea moiety and therefore be fixed in the axial position.



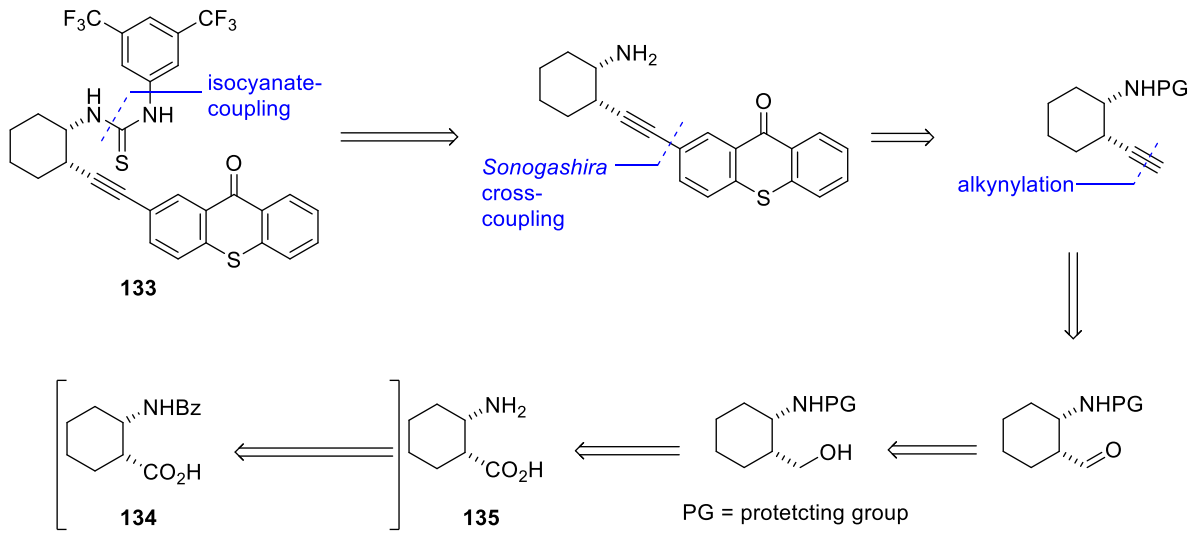
Scheme 52. Chiral thiourea-thioxanthone hybrid **133** with an alkyne linker.

A suitable substrate (e. g. an enone) should be "locked" in one conformation *via* bidentate coordination by the thiourea, while the thioxanthone blocks one side and thus favors the intra- or intermolecular attack from the opposite side. Regarding the substrate scope, the prerequisite is a hydrogen bond acceptor site on the one hand and a chromophore that can react in a photoreaction upon excitation on the other hand.

4.3 Retrosynthetic Analysis and Synthesis of the Thiourea-Thioxanthone Hybrid

4.3.1 Retrosynthetic Analysis

It was envisioned that the synthesis of both the racemic and the enantiomerically pure final catalyst should commence with the commercially available amino acids **134** (Bz = benzoyl) and **135**, respectively (scheme 53). In the final step of the synthesis, an isocyanate coupling of the previously deprotected amine derivative and the commercial isocyanate would furnish the desired target molecules. The key step involved a *Sonogashira* cross coupling[197] of the alkyne and 2-bromothioxanthone.[198] The alkyne should be obtained by an alkynylation from the respective aldehyde, which was generated by a sequence of reduction, protection and consecutive oxidation of the starting amino acid **135**.



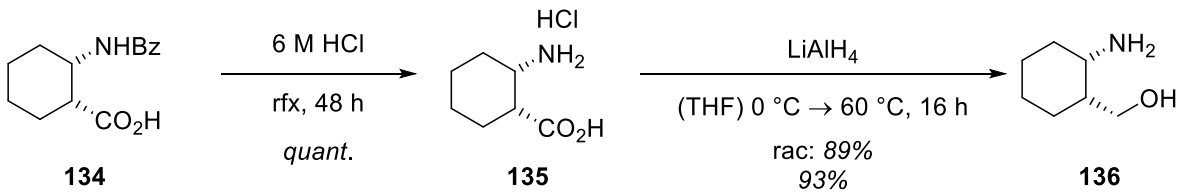
Scheme 53. Retrosynthetic analysis of thiourea-thioxanthone hybrid **133**.

Starting from the commercially available amino acids, the final catalysts would be synthesized over a linear seven step (racemic) or eight step (enantiomerically pure) route.

4.3.2 Synthesis

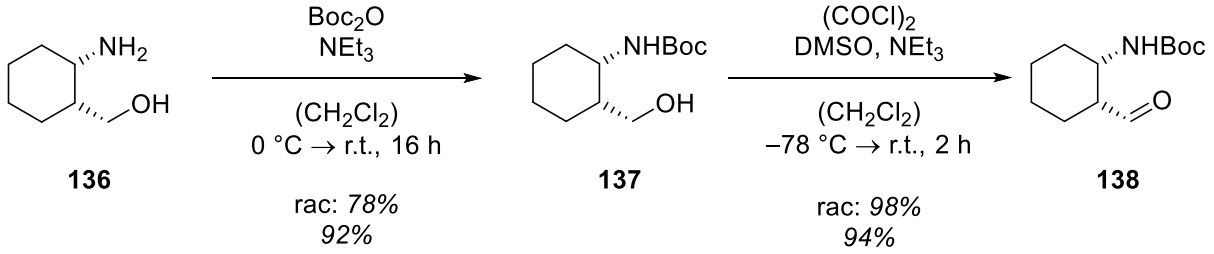
The synthetic route towards the enantiomerically pure version of the catalyst (**133**) will be elaborated at this point, based on the retrosynthetic analysis (scheme 53). The synthesis of the racemic version *rac*-**133**, which was carried out first in order to establish the reaction conditions

most suitable for each step was performed analogously. The yields for the racemic and the enantiomerically enriched route are indicated at each step individually.



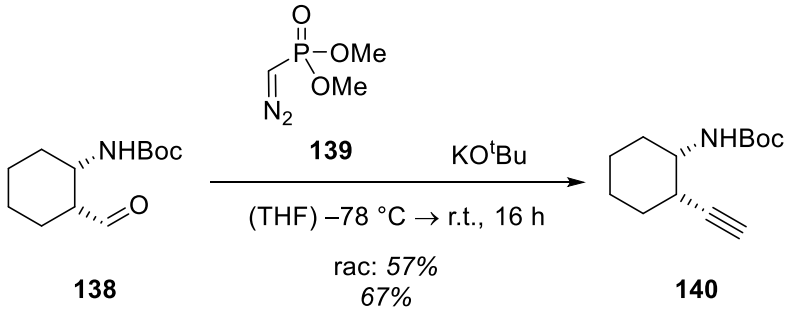
Scheme 54. Deprotection of the commercially available amino acid **134** and subsequent reduction to the alcohol **136**.

The synthesis commenced with the deprotection of the commercially available *N*-protected amino acid **134** (99% *ee*) in refluxing hydrochloric acid,[199] yielding the free amino acid hydrochloride quantitatively (scheme 54). The subsequent reduction[200] was achieved in excellent yields of 89% and 93%, respectively, resulting in the free amino alcohol **138**. The synthesis of the racemic compound started from the commercially available free amino acid.



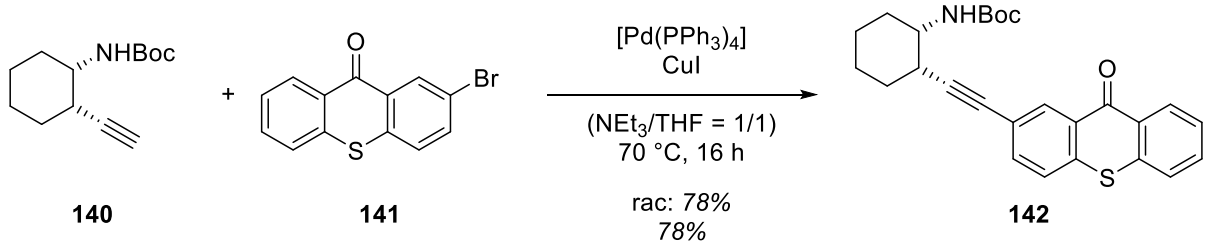
Scheme 55. *N*-protection and subsequent oxidation towards aldehyde **138**.

Subsequently, a *tert*-butyloxycarbonyl (Boc) protecting group was installed at the amine moiety in high to excellent yields,[200,201] followed by the oxidation of the alcohol **136** to the aldehyde **138** under *Swern* conditions (scheme 55).[202,203] The deprotection-protection sequence was regarded necessary, as previously performed experiments showed that the Bz protecting group was reduced to the corresponding benzyl group in the reduction step. The oxidation was also performed with *Dess-Martin* periodinane or 2-iodoxybenzoic acid (IBX) analogously to a literature known procedure for alcohol **136**,[200] but both methods required a purification of the crude product by column chromatography. Decomposition of the aldehyde on silica was observed, resulting in poor yields. The oxidation under *Swern* conditions provided a convenient solution to that problem, since the crude product of this reaction could be employed in the next step without purification.



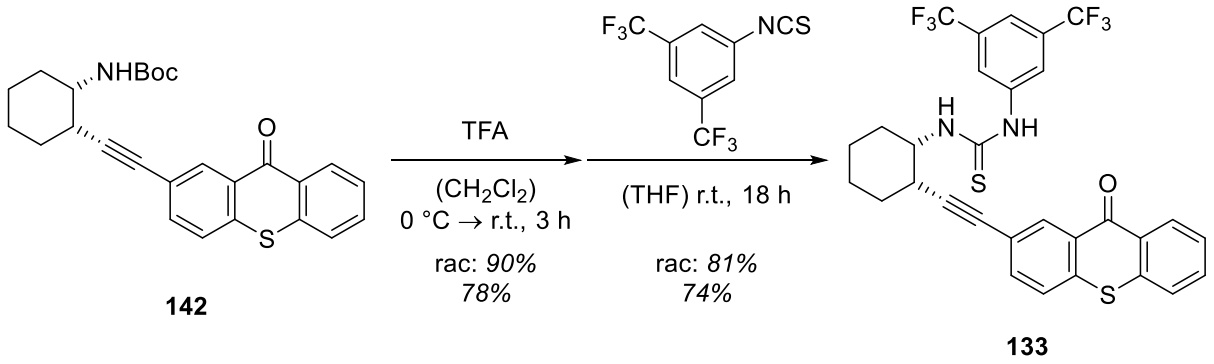
Scheme 56. *Seyferth-Gilbert* homologation of aldehyde **138** to alkyne **140**.

The alkynylation of aldehyde **140** was carried out by employing the *Seyferth-Gilbert* homologation protocol[204,205] with diazophosphonate **139** under basic conditions in moderate yields (scheme 56). The *Seyferth-Gilbert* reagent **139** was synthesized from the corresponding dimethyl (2-oxopropyl) phosphonate in one step (see experimental part). Other alkynylation protocols such as the *Bestmann-Ohira*[206,207] did not improve the yield.



Scheme 57. *Sonogashira* cross coupling of alkyne **140** and bromothioxanthone **141**.

The key step of the synthesis route, the *Sonogashira* cross-coupling[197] of alkyne **140** and bromothioxanthone **141**, was performed in high yields under conditions previously developed in our group for the synthesis of similar template structures (scheme **57**).[208] Other catalysts, bases or solvent mixtures resulted in some cases in significant amounts of the homocoupling product of alkyne **140** . The bromothioxanthone **141** was synthesized from thiosalicylic acid and bromobenzene by sequential *Friedel-Crafts* acylation and aromatic substitution (see experimental part).[198]



Scheme 58. *N*-deprotection of amine **142** and isocyanate coupling towards the final template **133**.

Finally, *N*-Boc deprotection of amine **142** followed by isocyanate coupling concluded the synthesis of catalyst **133** and good to high yields were achieved in both steps (scheme 58). Overall, the target compound was isolated as a single diastereoisomer with high enantiopurity (>99% *ee*) in an eight step synthesis with an overall yield of 24%.[196] The preferred conformation of **133** in solution was found to be as expected, proven by the ^{1}H NMR spectrum (figure 15). No changes in the ^{1}H NMR spectrum were observed, when **133** was left in $CDCl_3$ solution over a period of three days, verifying its conformational stability.[196]

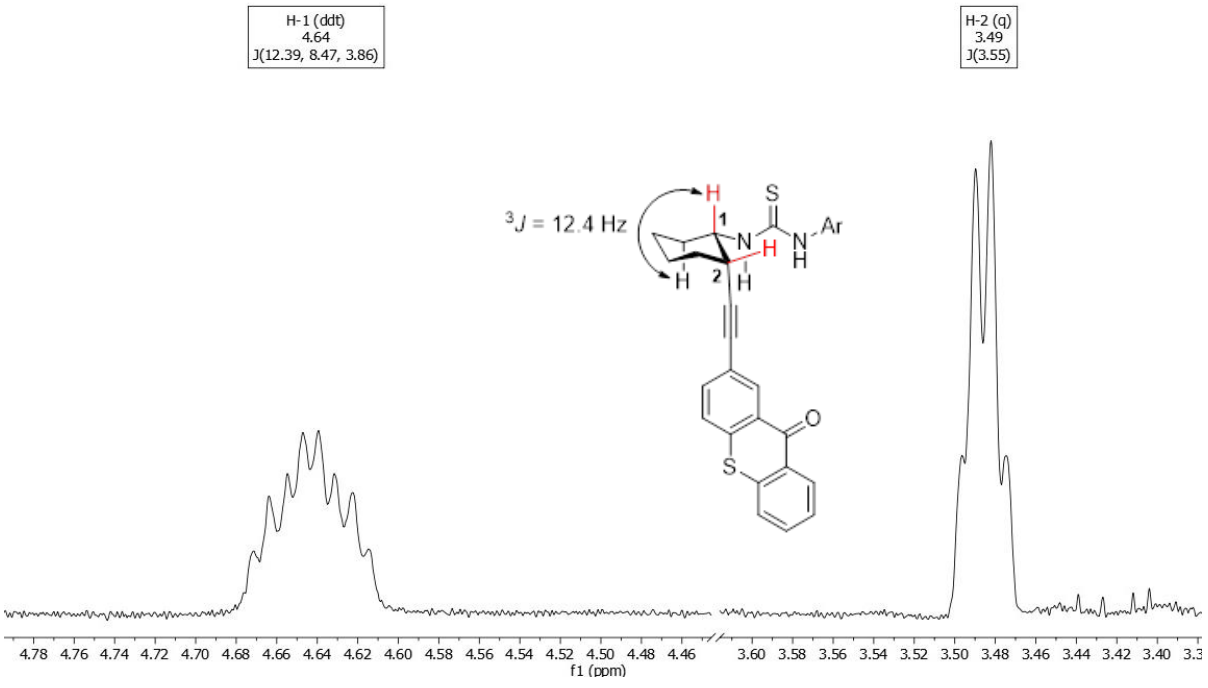


Figure 15. Proof for conformational stability of **133** by ^{1}H NMR coupling constants.

Proton H-1 appears as a virtual ddt, with ^{3}J = 8.4 Hz clearly assigned as the CH-NH-coupling. Therefore, the large coupling constant of ^{3}J = 12.4 Hz is a result of the CH-CH-coupling of H-1 to the axial proton of C-6, while the CH-CH-coupling to both equatorial protons at C-2 and C-6

appears as a virtual triplet with $^{3}J \cong 3.9$ Hz. Proton H-2 shows a virtual quartet with $^{3}J \cong 3.6$ Hz.

Since the final catalyst should also act as sensitizer in photochemical reactions, the absorption characteristics were analyzed by UV-Vis spectroscopy (figure 16).[196]

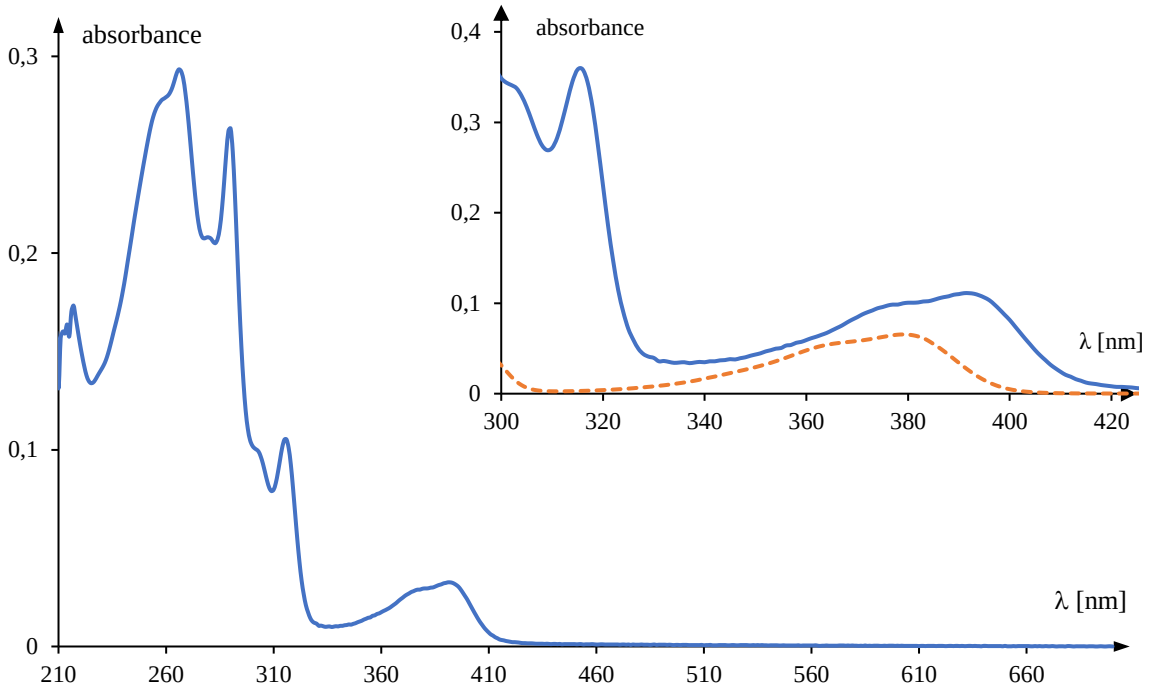
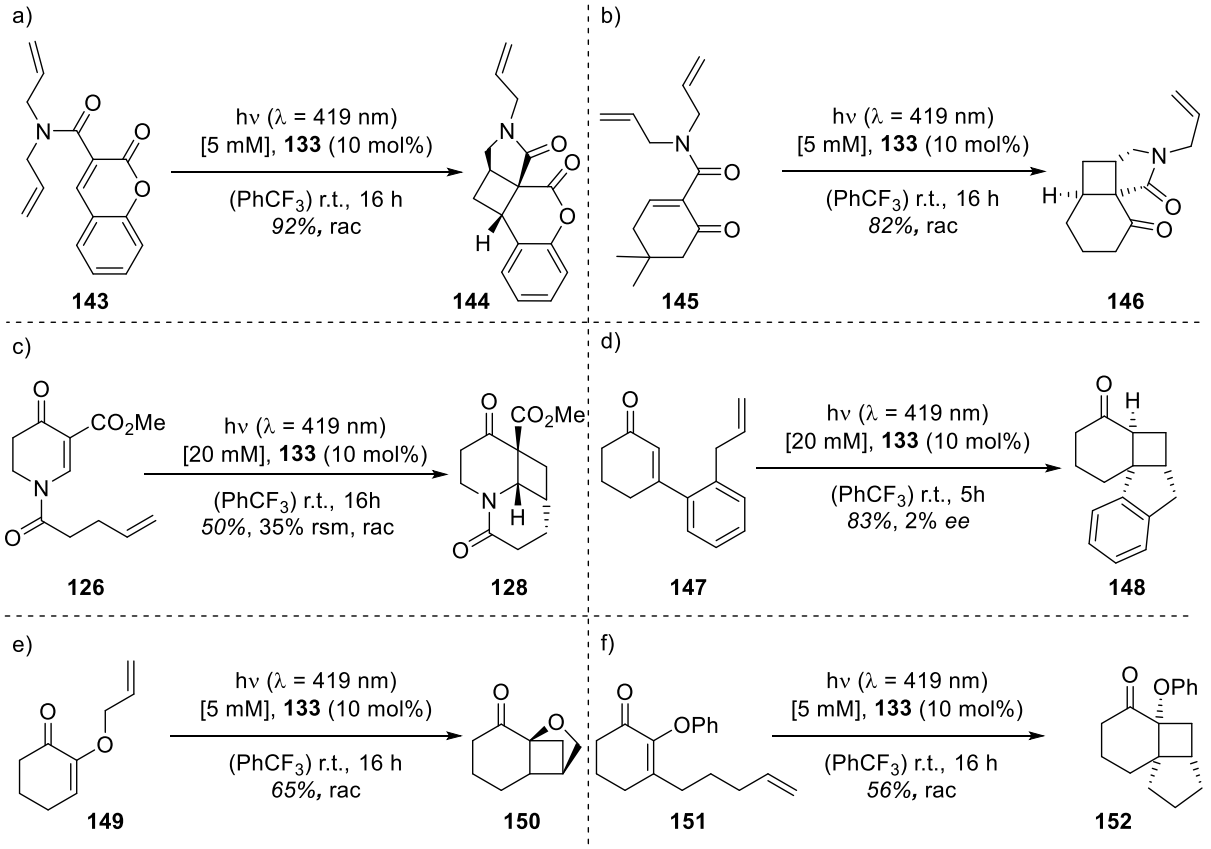


Figure 16. UV-Vis spectrum of thiourea-thioxanthone hybrid **133** (c = 0.1 mM in CH_2Cl_2); inset: Comparison of long wavelength absorption with thioxanthone (orange dotted).

A long wavelength absorption in the visible light region (λ = 360-420 nm) is responsible for the yellow color of catalyst **135**. Comparing the UV-Vis spectra, it becomes apparent that this absorption originates from the thioxanthone chromophore (figure 16, inset). Based on the absorption characteristics, it seemed reasonable that photoreactions with catalyst **133** could be performed by irradiation with light in the visible region. Although no emission spectra of compound **133** were measured, the triplet energy of the final catalyst should be in the same region as the parent chromophore, thioxanthone, with a tabulated E_T = 265 kJ/mol.[175] The same assumption has been made before in case of the chiral thioxanthone-substituted lactam based template,[194,209] and is supported by the fact that the triplet energy of a *tert*-butyl substituted analogue of said catalyst had been determined as E_T = 263 kJ/mol.[210] In principle, compounds that exhibit a triplet energy $E_T \leq 265$ kJ/mol are suitable substrates for reactions with the final catalyst **133**.

4.4 Photochemical Reactions

With the conformationally stable thiourea-thioxanthone hybrid **133** in hand, its potential as a catalyst in photochemical reactions was tested with a variety of substrates, some of which had been successfully employed with other catalysts.[126,166,174,211,212] The conditions chosen for the irradiation experiments were adapted from previous studies of photochemical reactions catalyzed by chiral thioureas (scheme 59).[195] All reactions were performed in advance under sensitized conditions with achiral thioxanthone in order to ensure that the substrate was suitable to test the potential of catalyst **133** by undergoing the respective desired photoreaction. Irradiation at visible light wavelength (λ = 419 nm) does not lead to for direct excitation, as none of the substrates show long wavelength absorption. Therefore, only substrates that are coordinated by the catalyst are able to react, a potential uncatalyzed background reaction can be neglected. A catalyst loading of 10 mol% was chosen, as it has been shown in previous studies that thiourea-templated photochemical reactions require relatively high catalyst loading.[126,189–191] Trifluorotoluene has been shown to be a superior solvent for hydrogen bond mediated enantioselective photoreactions,[209,213] and in the few literature-known examples for enantioselective photocatalysis by thioureas, preferentially aromatic solvents were used.[126,189,190] All photoreactions depicted in scheme 59 are intramolecular [2+2] photocycloaddition reactions of enone chromophores such as cyclohexenones, coumarins or dihydropyridones.

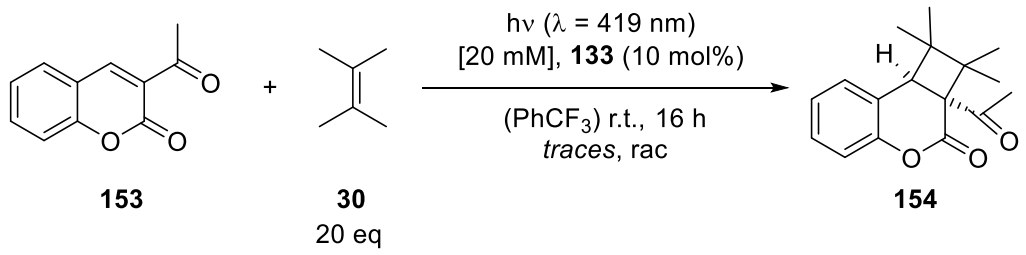


Scheme 59. [2+2] Photocycloaddition reactions catalyzed by chiral catalyst **133.**

The substrates depicted in scheme **59** were regarded as suitable for photoreactions to test catalyst **133** for different reasons: coumarin **143**, cyclic enone **145** and dihydropyridone **126** (scheme 59, a, b and c) with the amide bearing the tether could potentially favor the directed coordination and therefore the asymmetric induction by a two-point coordination of both the ketone and the amide group by the thiourea. With enone **147** (scheme 59, d), potential π-stacking interactions between the thioxanthone moiety and the aryl group of the substrate were evaluated to fix the coordinated substrate in a certain conformation. Enones **149** and **151** (scheme 59, e and f) were tested in order to evaluate the potential of the catalyst in absence of any favorable secondary interactions between the catalyst and the substrate.

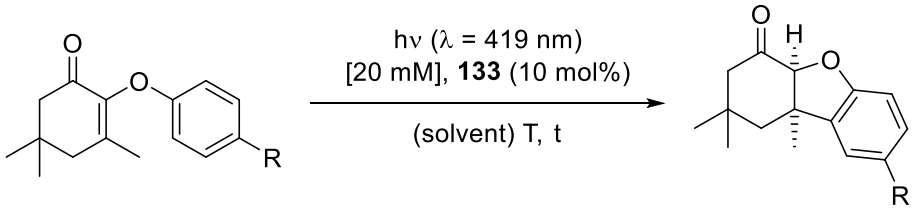
Although the reactions with chiral catalyst **133** proceeded in all cases except for dihydropyridone **126** with complete consumption of the starting material and the respective photocycloaddition product was isolated in moderate to high yields, no asymmetric induction was observed. Some substrates were also tested under different conditions (dichloromethane as solvent, decreased reaction temperature, increased catalyst loading), but none of these alterations lead to a noticeable increase of enantiomeric excess. An attempt towards the intermolecular [2+2] photocycloaddition reaction between coumarin **153** and

2,3-dimethyl-2-butene (**30**) was unsuccessful in presence of catalyst **133** (scheme 60), with only traces of racemic cyclobutane **154** isolated.



Scheme 60. Attempted intermolecular [2+2] photocycloaddition of coumarin **153**.

Inspired by *Edtmüllers* results on the enantioselective [6π]-cyclization of 2-aryloxycyclohex-2-enones[174] and the extensive study on a similar reaction under sensitized conditions by the group of *Smith*,[214] it was envisioned that this substrate class would also be suitable for hydrogen bond mediated catalysis by thiourea catalyst **133**. Therefore, differently substituted 2-aryloxycyclohex-2-enones were screened under different reaction conditions in a photochemical 6π-cyclization reaction mediated by catalyst **133** (table 8).[196]



155a: R=H
155b: R=Me
155c: R=OMe
155d: R=Br

156a: R=H
156b: R=Me
156c: R=OMe
156d: R=Br

Table 8. Conditions for the [6π]-cyclization of 2-aryloxycyclohex-2-enones.

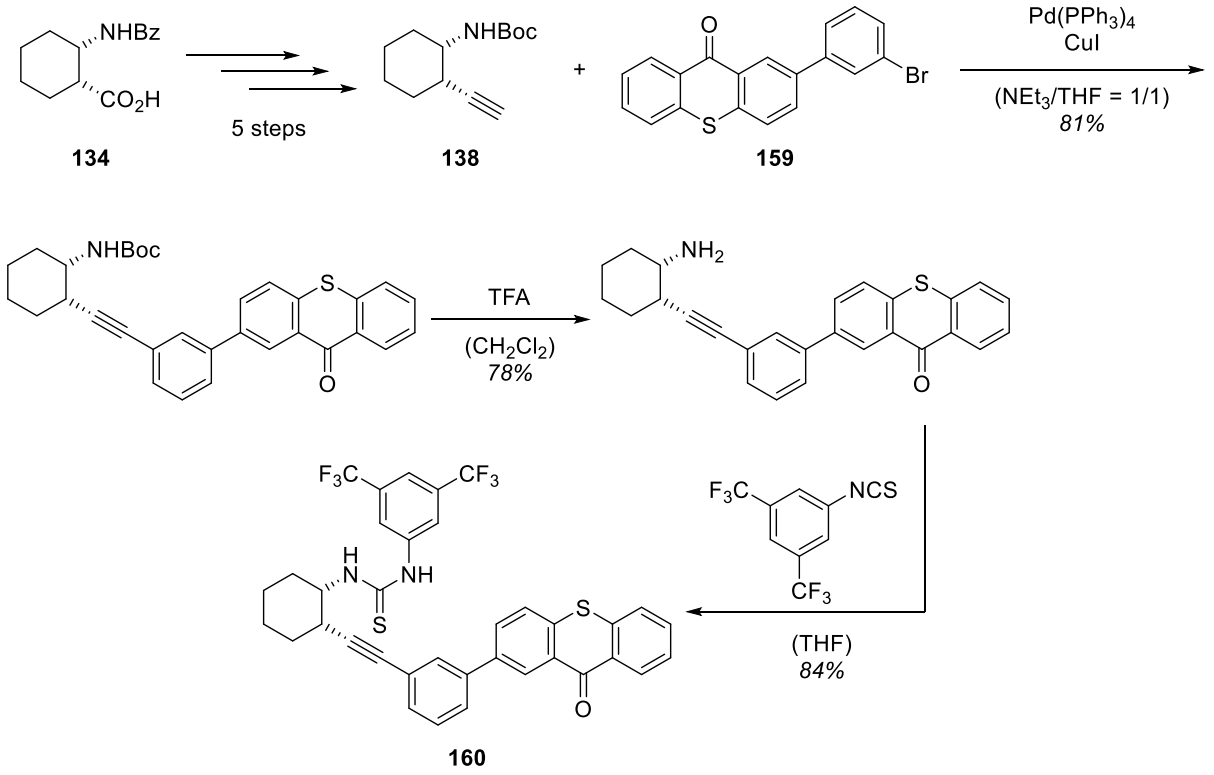
#	substrate	solvent	T [°C]	t [h]	Y [%]	rsm [%]	*ee* [%]
1	**155a**	CH_2Cl_2	r.t.	23	30	61	7
2	**155a**	CH_2Cl_2	−25 °C	39	4	74	n.d.[a]
3	**155a**	TFT	r.t.	23	31	26	8
4[b]	**155a**	TFT	r.t.	23	37	40	3
5[c]	**155a**	TFT	r.t.	23	50	-	0
6	**155b**	CH_2Cl_2	r.t.	23	33	19	9
7	**155b**	TFT	r.t.	23	25	71	7
8	**155c**	TFT	r.t.	23	37	7	9
9	**155d**	TFT	r.t.	23	22	24	12
10	**155d**	CH_2Cl_2	r.t.	23	26	51	12

[a] not measurable due to low quantity. [b] with 5 mol% catalyst. [c] λ = 405 nm (LED).

When the reaction with **155a** was performed with 50 mol% of achiral thioxanthone, 52% of the corresponding photoproduct were isolated after nine hours of irradiation. In presence of chiral catalyst **133** however, the reaction time increased significantly, with only 39% conversion after 23 hours (entry 1) and 26% conversion after 39 hours at lower temperature (entry 2). Whether a decrease in temperature improves the enantioselectivity could not be determined, since the quantity of isolated product **155a** was too low to allow for proper *ee* determination. Changing the solvent (entry 3) or decreasing the catalyst loading (entry 4) did not improve the reaction outcome, while a different light source (entry 5) lead to full consumption of the starting material, but only formation of racemic product. Methyl and methoxy substitution at the aryl moiety (**155b** and **155c**, entries 6-8) furnished racemic products in low yield. Although a bromo substituent (**155d**, entry 9 and 10) lead to a slight increase of enantiomeric excess, the reaction still proceeded very slowly and with low yields. The reaction conditions could not be improved further to reach satisfactory yields and enantiomeric excess.

4.5 Modification of the Thioxanthone Shield

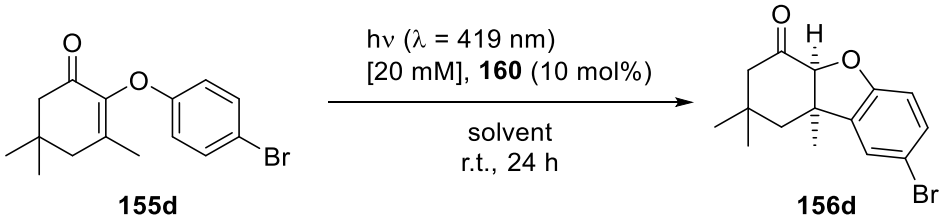
A second generation of thiourea-thioxanthone hybrid **133** with a phenyl group linking the alkyne and the thioxanthone was synthesized (scheme 61), in an attempt to improve site differentiation.



Scheme 61. Synthesis of chiral thiourea-thioxanthone hybrid **160**.

The synthesis of the second-generation catalyst was performed analogously to the route established for **133**, with similar high yields, furnishing **160** as a yellow coloured crystalline solid. Bromothioxanthone **159** was synthesized employing the same conditions as for **139** from thiosalicylic acid and 3-bromobiphenyl (see experimental part).

To evaluate the potential of catalyst **160**, the [6π]-cyclization of bromo-substituted 2-aryloxycyclohex-2-enone **155d** was chosen as test reaction (table 10).



155d **156d**

Table 9. Conditions for the [6π]-cyclization with catalyst *ent*-**160**.

#	solvent	Y [%]	rsm [%]	ee [%]
1	CH_2Cl_2	24	37	13
2	TFT	42	19	9

Catalyst **160** did not improve the enantioselectivity in the test reaction compared to the first-generation catalyst **133** under the conditions tested. Additionally, a noticeable amount of the light absorbed seems to lead to undesired side reactions, as the mass balance of the photoreaction was only around 60%. Catalyst **160** was not tested under further conditions or in other photoreactions.

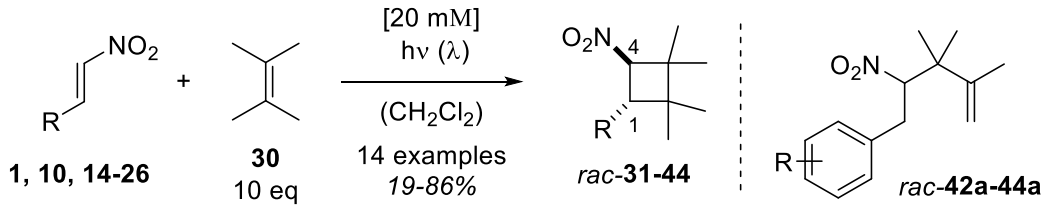
With the results from the test reactions with catalyst **133** and **160** as well as the equally disappointing results from the study performed in parallel by *Mayr*,[195] it was decided to not further pursue the catalysis of photochemical reactions by chiral thiourea-thioxanthone hybrids. Apparently, neither of the potential catalysts developed is capable of inducing high enantioselectivity in photoreactions, because effective site differentiation can not be ensured during the reaction course. Only few examples of (chiral or achiral) thiourea-catalyzed photochemical reactions are reported in the literature.[126,187,190,191] Given their outstanding success as catalysts in organocatalytic reactions with similar substrates[122,183–186] this catalytic concept can apparently not be applied directly from thermal to photochemically induced reactions. It remains open to analyze and explain the failure of thiourea catalyst *ent*-**133** and others by mechanistic studies or calculations to better understand the mode of action between these catalysts and the substrates. *Elsa Rodriguez* also evaluated the potential of squareamides as coordination sites in similar catalyst structures, but these compounds, too, proved to be ineffective catalysts in photoreactions, mostly due to solubility issues.

5. Conclusion and Future Work

[2+2] Photocycloaddition Reactions of Nitroolefins

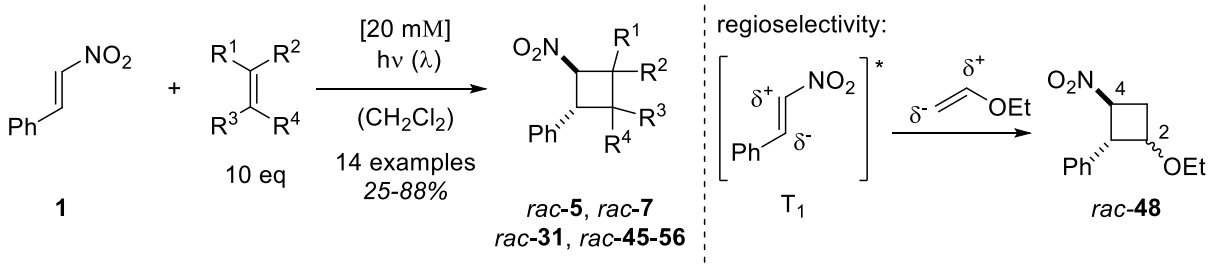
A comprehensive study of the nitrostyrene chromophore was performed and a general protocol for the intermolecular [2+2] photocycloaddition reactions of nitroolefins was established. Analysis of the compound class by spectroscopic tools revealed, that the photophysical properties are highly dependent on the level of conjugation of the π-system and the presence of substituents that affect the electron density.

Furthermore, the substrate scope in the intermolecular [2+2] photocycloaddition of nitroolefins to 2,3-dimethyl-2-butene (**30**) was expanded, yielding the photoproducts selectively in a formal *trans*-configuration at the C-1- and C-4-position (scheme 62). The by-products *rac*-**42a**-**44a** observed in some cases were attributed to an intramolecular hydrogen abstraction occurring in a stabilized 1,4-diradical intermediate.



Scheme 62. Substrate scope of nitroolefins in the intermolecular [2+2] photocycloaddition to 2,3-diemethyl-2-butene (**30**).

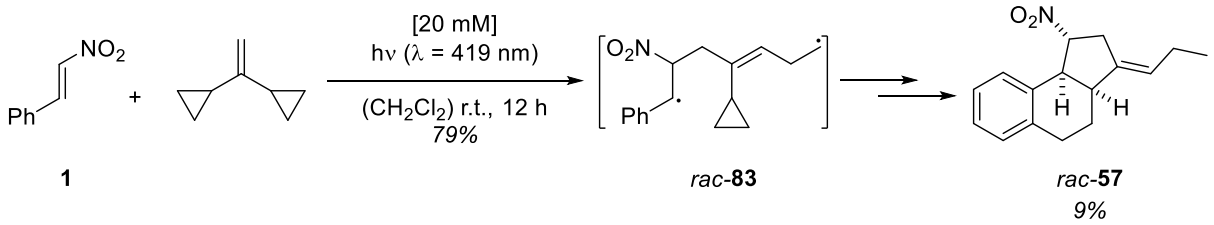
A series of different olefins was successfully employed in the intermolecular [2+2] photocycloaddition with nitrostyrene **1**, furnishing 14 examples of cyclobutane photoproducts formed with excellent regioselectivity which is governed by a photochemical *Umpolung* of the nitrostyrene double bond in the excited state (scheme 63).



Scheme 63. Substrate scope of olefins in the [2+2] photocycloaddition to nitrostyrene **1**.

The olefin scope was limited to hydrocarbons and ethers. Attempts towards an intramolecular variant of the reaction were unsuccessful and it was proposed that the intramolecular ring closure is energetically unfavored.

Experimental results obtained from mechanistical studies hint towards a reaction pathway that proceeds on the triplet hypersurface. A ring opening product with a tricyclic core structure (*rac*-**57**) was obtained in a radical clock experiment and provided experimental proof of a 1,4-diradical (*rac*-**83**) being involved in the course of the reaction (scheme 64). The proposed structure of the ring opening product was confirmed by single crystal X-ray diffraction of the corresponding methoxycarbonyl analogue. The quantum yield of the reaction **1** → *rac*-**31** was determined as $\Phi = 0.04$.

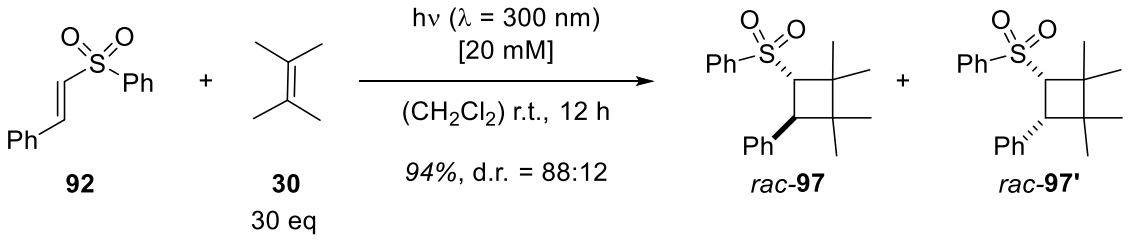


Scheme 64. Ring opening product *rac*-**57** observed in the [2+2] photocycloaddition of nitrostyrene to 1,1-dicyclopropyl ethylene.

The envisioned enantioselective variant of a [2+2] photocycloaddition of nitrostyrenes could not be realized successfully. In all cases with various chiral catalysts, only low enantioselectivites were observed.

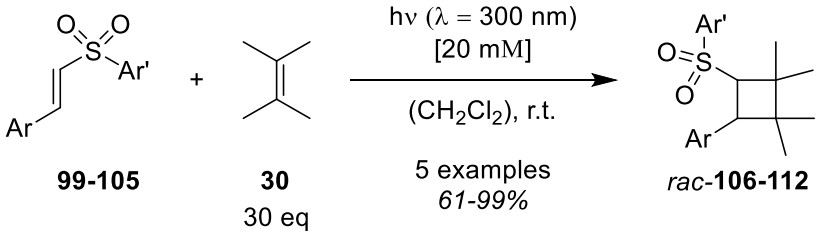
[2+2] Photocycloaddition Reactions of Sulfones

Based on the successful development of a protocol for the intermolecular [2+2] photocycloaddition of nitroolefins, α,β-unsaturated sulfones were evaluated as substrates for the same type of reaction. It was found, that vinylsulfone **92** readily undergoes addition to 2,3-dimethyl-2-butene (**30**), furnishing cyclobutane *rac*-**97** in excellent yields and a diastereoselectivity of d.r. ≥ 9:1 (scheme 65)



Scheme 65. Intermolecular [2+2] photocycloaddition of vinylsulfone **92** to 2,3-dimethyl-2-butene (**30**)

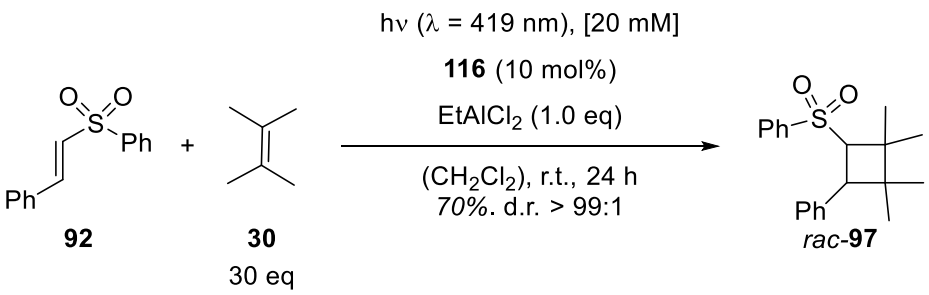
The functional group tolerance of the reaction was tested by applying the optimized reaction conditions, providing access to five photoproducts in moderate to high yields (scheme 66).



Scheme 66. Preliminary substrate scope of vinylsulfones in the intermolecular [2+2] photocycloaddition to olefin **30**.

Photoluminescence spectroscopic studies of **92** showed a strong fluorescence of the sample, and by exploiting the heavy-atom effect, the triplet energy of bromo-substituted vinylsulfone **99** could be determined as E_T = 243 kJ/mol. UV-Vis titration experiments with different *Lewis* acids revealed a strong activation of the sulfone chromophore by $EtAlCl_2$, resulting in a bathochromic shift of the absorption maximum.

A *Lewis* acid catalyzed variant of the [2+2] photocycloaddition of sulfone **92** was explored, direct excitation in presence of a catalyst at longer irradiation wavelength did, however, not lead to high yields of the photoproduct *rac*-**97**. Addition of sensitizer **116** resulted in the successful catalysis of the reaction with high yields and excellent diastereoselectivity (scheme **67**).

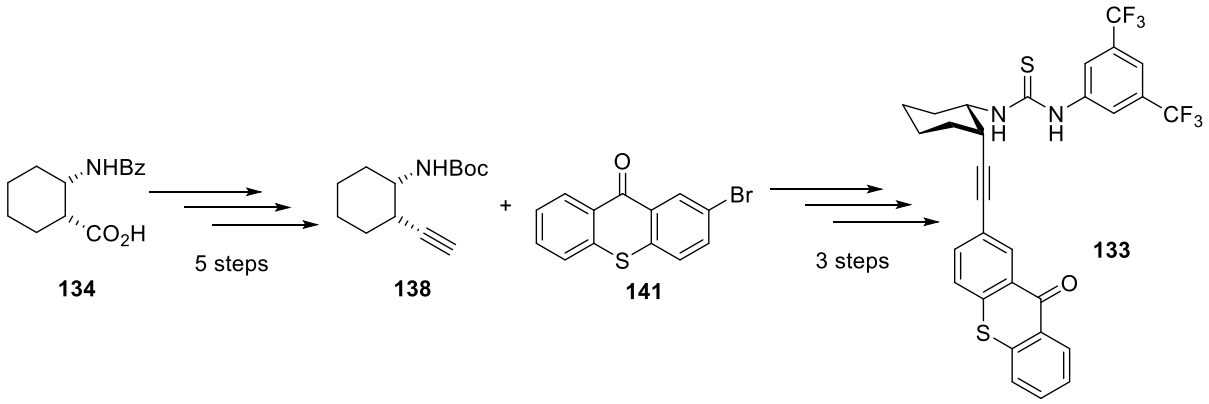


Scheme 67. *Lewis* acid catalyzed intermolecular [2+2] photocycloaddition of sulfone **92** under sensitized conditions.

An asymmetric [2+2] photocycloaddition with a chiral *Lewis* acid could not be performed successfully.

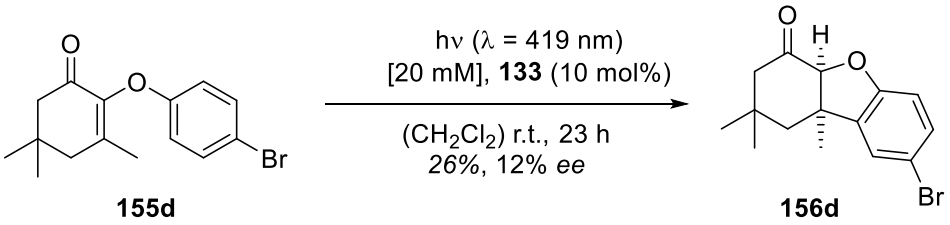
A Chiral Thiourea-Thioxanthone Hybrid as Catalyst in Visible-Light Mediated Photochemical Reactions

A chiral thiourea-thioxanthone hybrid, **133**, was synthesized in eight steps starting from commercially available amino acid **134** (scheme 68). The catalyst was proven to be conformationally stable in solution, with the depicted conformation prevailing.



Scheme 68. Synthesis of chiral thiourea-thioxanthone hybrid **133**.

The catalyst **133** was tested in different photoreactions but was not capable of inducing high enantioselectivity. The best results were obtained in the [6π]-cyclization of 2-arylcyclohex-2-enones (scheme 69). Modification of the thioxanthone shield did not improve the performance of the catalyst.



Scheme 69. Photochemical [6π]-cyclization catalyzed by chiral thiourea-thioxanthone hybrid **133**.

6. Experimental Part

6.1 General Information

All preparations and manipulations of air and moisture sensitive compounds were carried out in flame dried glassware under an argon atmosphere using standard *Schlenk* techniques. Reactions at 0 °C were performed using an ice water cooling bath, reactions at −78 °C were performed using a dry ice/*iso*-propanol cooling bath.

6.2 Solvents and Reagents

Dry solvents. Tetrahydrofuran, dichloromethane and diethyl ether were obtained water and oxygen free by a *Braun* MB SPS purification system using argon as inert gas and MB-Kol-M (3 Å molecular sieves) and MB-Kol-A (activated Al_2O_3) columns to remove residual water. Other dry solvents [acetonitrile (MeCN), benzene (PhH), *N*,*N*-dimethyl formamide (DMF), ethanol (EtOH), methanol (MeOH), toluene (Tol), acetone (Ac), dimethylsulfoxide (DMSO); ≥ 99.8 % puritiy] were purchased from *Acros Organics*, *Sigma Aldrich* or *Fluka* and were used without further purification.

Solvents for photochemical reactions. Solvents for racemic uncatalyzed photochemical reactions were degassed in a continuous argon flow for 15 minutes, during which the previously flame-dried flask was placed inside an ultrasonic bath. Molecular sieves (3 or 4 Å) was added and the solvent was stored in a *Schlenk* flask under an argon atmosphere. Solvents for photochemical reactions in presence of *Lewis* acids were degassed employing the *freeze-pump-thaw* technique[215] and were also stored over molecular sieves under an argon atmosphere.

Technical solvents. Ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), pentane (P), cyclohexane (cHex), methanol (MeOH), toluene (Tol) and diethyl ether (Et_2O) for column chromatography, thin layer chromatography or aqueous work-ups were distilled prior to use.

Chemicals. Unless stated otherwise, all chemicals were purchased from commercial sources and used without further purification.

Commercially available solutions of *n*-butyllithium were titrated with menthol (1,10-phenanthroline as the indicator) prior to use.

Gas. Argon (4.8) and hydrogen (5.0) were obtained from *Westfalen* AG and were used without further purification.

6.3 Analytical Methods and Equipment

Irradiation experiments were performed in a *Rayonet* RPR-100 photochemical reactor (Southern New England Ultra Violet Company, Branford, CT, USA) or similarly designed replicas equipped with fluorescence lamps using either λ_{max} = 300 nm (16 lamps, RPR-3000 Å, 6 W, *Rayonet*),[216] λ_{max} = 366 nm (16 lamps, black light blue, 8 W, *Philips Lightning*),[216] λ_{max} = 350 nm (16 lamps, RPR-3500 Å, 6 W, *Rayonet*),[217] λ_{max} = 419 nm (16 lamps, cool white, 8 W, *Osram*)[194] or λ_{max} = 420 nm (16 lamps, 8 W, *Luzchem* LZC-420).[210] Duran glass phototubes were used for irradiation experiments. Irradiation at lower temperatures were performed with a *Huber* high-performance cryostate.

Irradiation experiments with light emitting diodes (LEDs) were performed in *Schlenk* tubes (Ø = 1.0 cm). High power LEDs with λ_{max} = 424 nm (*Roithner* Lasertechnik, 350 mA, U ~ 3.4 V), λ_{max} = 382 nm (*Avonec*, 700 mA, U ~ 3.8 V) or λ_{max} = 398 nm (*Mouser*, 700 mA, UF ~ 3.4 V),[218] which were mounted on a passive heat sink, were used as the light source. The light was transmitted into the reaction via a Quarz glass rod (Ø = 0.8 cm).

Flash Column Chromatography was performed with silica 60 (*Merck*, 230-400 mesh) as the stationary phase. The eluent mixtures and the diameter of the column are indicated at each experiment individually.

Thin Layer Chromatography (TLC) was performed on silica coated glass plates (*Merck*, silica 60, F_{254}) with detection by UV light (λ = 254 nm) and/or by staining with a potassium permanganate solution [$KMnO_4$] or with a cerium ammonium molybdate solution [CAM] followed by heat treatment.

$KMnO_4$ staining solution. potassium permanganate (3.00 g), potassium carbonate (20.0 g) and aqueous sodium hydroxide solution (5 wt-%, 5.00 mL) in water (300 mL).

CAM staining solution. cerium sulfate tetrahydrate (1.00 g), ammonium molybdate (25.0 g) and concentrated sulfuric acid (25.0 mL) in water (250 mL).

Infrared (IR) Spectra were recorded on a *Perkin Elmer* Frontier IR FTR spectrometer by ATR technique. The signals are given in $\tilde{\nu}$ [cm^{-1}] and the signal intensity is assigned using the following abbreviations: br (broad), vs (very strong), s (strong), m (medium), w (weak).

Nuclear Magnetic Resonance (NMR) Spectra were recorded at room temperature either on a *Bruker* AVHD 300, AVHD 400, AVHD 500 or an AV 500 cryo. ^{1}H NMR spectra were

referenced to the residual proton signal of $CDCl_3$ (δ = 7.26 ppm), CD_3OD (δ = 3.31 ppm), C_6D_6 (δ = 7.16 ppm). ^{13}C NMR spectra were referenced to the ^{13}C-D triplet of $CDCl_3$ (δ = 77.16 ppm), to the ^{13}C-D septet of CD_3OD (δ = 49.00 ppm) or to the ^{13}C-D triplet of C_6D_6 (δ = 128.06 ppm). Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt.*). The following abbreviations for single multiplicities were used: br broad, s singlet, d doublet, t triplet, q quartet, quint quintet, sext sextet, sept septet. Assignment and multiplicity of the ^{13}C NMR signals were determined by two-dimensional NMR experiments (COSY, HSQC, HMBC).

Melting Points were determined using a *Kofler* melting point apparatus ("Thermopan", *Reichert*), with a range quoted to the nearest whole number.

Mass Spectrometry (MS) was performed on an *Agilent* system [mass detection: *Agilent* 5973 Network Mass Selective Detector (EI, 70 eV)], which was coupled to a GC [*Agilent* 6890, column: HP-5MS (Dimethylpolysiloxane, 30 m), carrier gas: Helium].

High Resolution Mass Spectrometry (HRMS) was performed on a *Thermo Scientific* LTQ FT Ultra (ESI) or a *Thermo Scientific* DFS HRMS spectrometer (EI).

UV/Vis Spectroscopy was performed on a *Perkin Elmer* Lambda 35 UV/Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a pathway of d = 1 mm. Solvents and concentrations are given for each spectrum.

Analytical **Gas Chromatography** (GC) was performed on an *Agilent* HP 7890 Series GC-System using an HP-5 column (Poly-dimethyl/diphenyl-siloxane, 95/5) with a flame ionization detector and nitrogen as the carrier gas.

Chiral **Gas Chromatography** (GC) was performed on an *Agilent* 7890 B gas chromatograph using an *Agilent* Cyclosil B column (30 m x 0.25 mm x 0.25 µm, SN: USF620714H) or a *Macherey* Nagel Lipodex E column (25 m x 0.25 mm, SN: 23393 92) with a flame ionization detector. The temperature method is given for the corresponding compounds.

Analytical **HPLC** was performed using a chiral stationary phase (flow rate: 1.0 mL/min, *Daicel* column, time and eluent are given for the corresponding compounds) and UV detection.

Chiral **HPLC** was performed on a *Thermo-Fisher* HPLC system comprising a SR3000 solvent rack, a LPG3400 SD pump, a WPS-3000 SL autosampler, a TCC-3000 SD column compartment and a DAD-300 UV/Vis detector fitted with the appropriate *Diacel* column as the

stationary phase phase (flow rate: 1.0 mL/min, time and eluent are given for the corresponding compounds).

Specific Rotation was determined using a *Bellingham+Stanley* ADP440+ polarimeter and is reported as follows: $[\alpha]_D^T$ (*c* in g per 100 mL solvent).

Single crystal X-ray diffraction data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), a TXS rotating anode with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package. Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen.

6.4 Synthesis of Nitroolefins

General Procedure 1 (GP 1) for the Synthesis of Nitroolefins:

Based on a literature-known procedure,[72] a solution of the aromatic aldehyde (1.00 equiv), nitromethane (3.00 – 35.0 equiv) and NH_4OAc (1.00 – 2.50 equiv) in glacial acetic acid (the concentration is indicated in every experiment individually) was heated at reflux. The progress of the reaction was monitored via TLC. When full conversion was reached, the reaction solution was cooled to room temperature and poured onto ice water. The mixture was partitioned between water and either dichloromethane or ethyl acetate (the solvent used is indicated at each experiment individually). The aqueous layer was extracted twice with the respective solvent (the volumen are indicated at each experiment individually). The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated *in vacou*. If not noted otherwise, the crude product was purified by column chromatography.

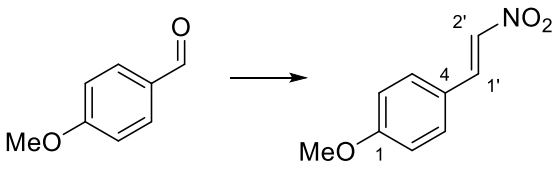
General Procedure 2 (GP 2) for the Synthesis of Nitroolefins:

Based on a literature-known procedure,[73] a solution of the aromatic aldehyde (1.00 equiv) and NH_4OAc (0.50 equiv) in nitromethane (c = 0.5 M) was heated at reflux. The reaction progress was monitored via TLC. When full conversion was reached, water was added, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by recrystallization from ethanol.

General Procedure 3 (GP 3) for the Synthesis of Nitroolefins:

Based on a literature-known procedure,[74] nitromethane (1.00 equiv) was added to a solution of the aldehyde (1.00 equiv) in methanol (c = 2 M). NaOH (1.05 equiv; c = 3.5 M solution in water) was added slowly over 30 minutes at 0 °C. The solution was stirred for 30 minutes at 0 °C, warmed to room temperature and was held at that temperature for 30 minutes. The reaction solution was added to a vigorously stirred aqueous hydrochloric acid solution (3 mL, c = 5 M), which resulted in the formation of a precipitate. The solution was stored at 4 °C overnight, filtered and the precipitate was washed with cold water. The crude product was purified by column chromatography.

(*E*)-1-Methoxy-4-(2‘-nitrovinyl)-benzene (10)



10
$C_9H_9NO_3$
MW = 179.17 g/mol

Following **GP 1**, a solution of freshly distilled anisic aldehyde (1.00 g, 7.34 mmol, 1.00 equiv) and NH_4OAc (283 mg, 3.67 mmol, 0.50 equiv) in nitromethane (13.4 mL) was heated at reflux for one hour. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by recrystallization from ethanol to yield **10** (755 mg, 3.93 mmol, 58%) as yellow colored needles.

TLC: R_f = 0.25 [P/Et_2O = 9/1] [UV].

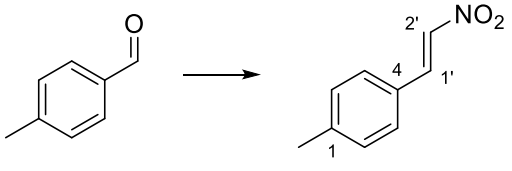
mp: 83 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.97 (d, ^3J = 13.6 Hz, 1H, H-1‘), 7.55−7.49 (m, 3H, H-3, H-5, H-2‘), 6.98−6.93 (m, 2H, H-2, H-6), 3.87 (s, 3H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 163.1 (s, C-1), 139.1 (d, C-1’), 135.2 (d, C-2’), 131.8 (d, 2C, C-3, C-5), 122.7 (s, C-4), 115.1 (d, 2C, C-2, C-6), 55.7 (q, OCH_3).

The analytical data match those reported in the literature.[219]

(*E*)-1-Methyl-4-(2‘-nitrovinyl)-benzene (14)



14
$C_9H_9NO_2$
MW = 163.17 g/mol

Following **GP 1**, a solution of freshly distilled *p*-tolylaldehyde (1.00 g, 8.32 mmol, 1.00 equiv) and NH_4OAc (320 mg, 4.16 mmol, 0.50 equiv) in nitromethane (16.6 mL) was heated at reflux

for one hour. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by recrystallization from ethanol to yield **14** (895 mg, 5.48 mmol, 66%) as pale yellow colored needles.

TLC: R_f = 0.58 [P/Et_2O = 9/1] [UV].

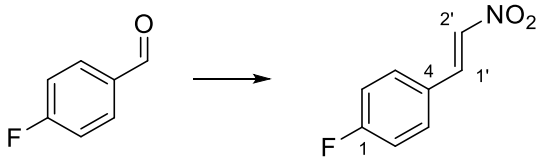
mp: 101 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.99 (d, ^3J = 13.7 Hz, 1H, C-1‘), 7.57 (d, ^3J = 13.7 Hz, 1H, C-2‘), 7.47−7.43 (m, 2H, H-3, H-5), 7.24−7.28 (m, 2H, H-2, H-6), 2.41 (s, 3H, ArCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 143.2 (s, C-1), 139.3 (d, C-1’), 136.5 (d, C-2’), 130.3 (d, 2C, C-3, C-5), 129.3 (d, 2C, C-2, C-6), 127.5 (s, C-4), 21.8 (q, ArCH_3).

The analytical data match those reported in the literature.[219]

(*E*)-1-Fluoro-4-(2‘-nitrovinyl)benzene (15)



15
$C_8H_6FNO_4$
MW = 167.14 g/mol

Following **GP 1**, a solution of 4-fluorobenzaldehyde (500 mg, 4.03 mmol, 1.00 equiv) and NH_4OAc (341 mg, 4.43 mmol, 1.10 equiv) in nitromethane (29 mL) was heated at reflux for 16 hours. The work-up was performed with dichloromethane (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 25 cm, P/Et_2O = 19/1) to yield **15** (375 mg, 2.24 mmol, 57%) as a pale-yellow colored powder.

TLC: R_f = 0.35 (P/Et_2O = 9/1) [UV, $KMnO_4$].

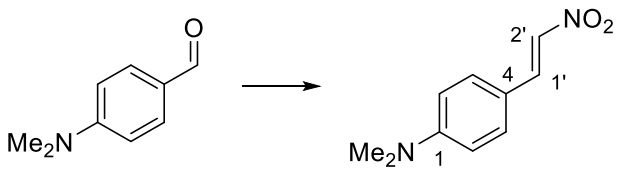
mp: 98 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.98 (d, ^3J = 13.8 Hz, 1H, H-1), 7.58–7.55 (m, 2H, H-2, H-6), 7.53 (d, ^3J = 13.8 Hz, 1H, H-2‘), 7.19–7.10 (m, 2H, H-3, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 165.1 (d, $^1J_{CF}$ = 254.8 Hz, C-1), 137.9 (d, C-1‘), 137.0 (d, C-2‘), 131.4 (d, $^3J_{CF}$ = 8.9 Hz, 2C, C-3, C-5), 126.5 (d, $^4J_{CF}$ = 3.5 Hz, C-4), 116.9 (d, $^2J_{CF}$ = 22.2 Hz, 2C, C-2, C-6).

The analytical data match those reported in the literature.[220]

(*E*)-*N*,*N*-Dimethyl-4-(2’-nitrovinyl)aniline (16)



16
$C_{10}H_{12}N_2O_2$
MW = 192.22 g/mol

Following **GP 1**, a solution of freshly distilled 4-(dimethylamino)benzaldehyde (100 mg, 670 µmol, 1.00 equiv) and NH_4OAc (25.8 mg, 335 µmol, 0.50 equiv) in nitromethane (1.5 mL) was heated at reflux for 16 hours. After cooling to room temperature, the precipitate was filtered, washed with cold methanol and recrystallized from ethanol to yield **16** (81.4 mg, 423 µmol, 63%) as red colored plate crystals.

TLC: R_f = 0.78 [P/Et_2O = 1/1] [UV].

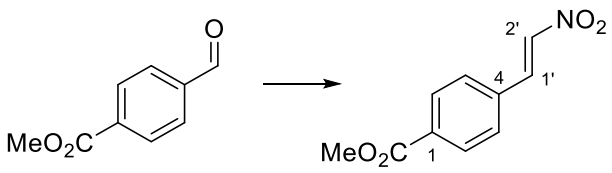
mp: 179 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.97 (d, ^3J = 13.4 Hz, 1H, C-1‘), 7.51 (d, ^3J = 13.4 Hz, 1H, C-2‘), 7.48−7.42 (m, 2H, H-3, H-5), 6.83–6.74 (m, 2H, H-2, H-6), 3.09 (s, 6H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 153.1 (s, C-1), 140.2 (d, C-1’), 132.0 (d, C-2’), 131.2 (d, 2C, C-3, C-5), 117.2 (s, C-4), 112.0 (d, 2C, C-2, C-6), 40.0 (q, *C*H_3).

The analytical data match those reported in the literature.[219]

Methyl (*E*)-4-(2'-nitrovinyl)benzoate (17)



17
$C_{10}H_9NO_4$
MW = 207.19 g/mol

Following **GP 2**, a solution of methyl 4-formylbenzoate (500 mg, 3.05 mmol, 1.00 equiv), NH_4OAc (141 mg, 1.83 mmol, 0.60 equiv) and nitromethane (197 µL, 223 mg, 3.65 mmol, 1.20 equiv) in glacial acetic acid (2.5 mL) was heated at reflux for six hours. The work-up was performed with ethyl acetate (2 × 10 mL) as the solvent. The crude product was purified by column chromatography (3 × 20 cm, CH_2Cl_2) to yield **17** (508 mg, 2.45 mmol, 80%) as a pale yellow colored crystalline solid.

TLC: R_f = 0.40 (CH_2Cl_2) [UV].

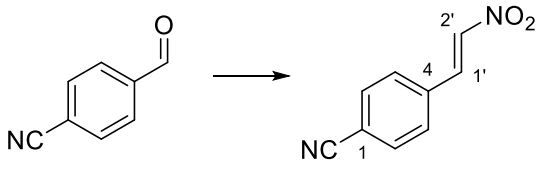
mp: 145 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.13–8.10 (m, 2H, H-2, H-6), 8.02 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.64–7.60 (m, 3H, H-2', H-3, H-5), 3.95 (s, 3H, CO_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 168.6 (s, *C*O_2Me), 138.8 (d, C-2'), 137.7 (d, C-1'), 134.3 (s, C-1), 133.2 (s, C-4), 130.6 (d, 2C, C-2, C-6), 129.1 (d, 2C, C-3, C-5), 52.7 (q, ArCO_2*C*H_3).

The analytical data match those reported in the literature.[219]

(*E*)-4-(2'-Nitrovinyl)-benzonitrile (18)



18
$C_9H_9N_2O_2$
MW = 174.16 g/mol

Following **GP 2**, a solution of freshly distilled *p*-cyanobenzaldehyde (1.00 g, 3.81 mmol, 1.00 equiv), NH_4OAc (734 mg, 9.53 mmol, 2.50 equiv) and nitromethane (623 µL, 710 mg, 11.6 mmol, 3.05 equiv) in glacial acetic acid (7.6 mL) was heated at reflux for four hours. The work-up was performed with dichloromethane (2 × 20 mL) as the solvent. The crude product was purified by column chromatography (3 × 20 cm, CH_2Cl_2) to yield **18** (391 mg, 2.66 mmol, 59%) as a yellow colored crystalline solid.

TLC: R_f = 0.54 (CH_2Cl_2) [UV].

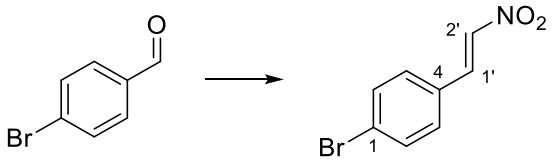
mp: 164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.99 (d, ^3J = 13.8 Hz, 1H, C-1'), 7.77−7.75 (m, 2H, H-3, H-5), 7.67−7.65 (m, 2H, H-2, H-6), 7.61 (d, ^3J = 13.8 Hz, 1H, C-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.6 (d, C-2'), 136.6 (d, C-1'), 134.5 (s, C-1), 133.1 (d, 2C, C-2, C-6), 129.5 (d, 2C, C-3, C-5), 117.9 (s, $C_{ar}CN$), 115.4 (s, C-4).

The analytical data match those reported in the literature.[219]

(*E*)-1-Bromo-4-(2'-nitrovinyl)benzene (19)



19
$C_8H_6BrNO_2$
MW = 228.05 g/mol

Following **GP 2**, a solution of 4-bromobenzaldehyde (1.00 g, 5.40 mmol, 1.00 equiv), nitromethane (10.1 mL, 11.5 g, 189 mmol, 35.0 equiv) and NH_4OAc (500 mg, 6.49 mmol, 1.20 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (4 × 5 cm, cHex/EtOAc = 5/1) to yield **19** (1.11 g, 4.85 mmol, 90%) as a yellow colored crystalline solid.

TLC: R_f = 0.81 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

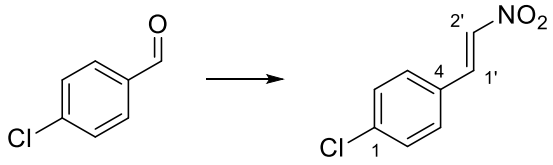
mp: 141 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.95 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.61–7.59 (m, 2H, H-2, H-6), 7.57 (d, ^3J = 13.7 Hz, 1H, H-2'), 7.43–7.40 (m, 2H, H-3, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 137.9 (d, C-1'), 137.6 (d, C-2'), 132.9 (d, 2C, C-2, C-6), 130.5 (d, 2C, C-3, C-5), 129.1 (s, C-1), 126.9 (s, C-4).

The analytical data match those reported in the literature.[219]

(*E*)-1-Chloro-4-(2'-nitrovinyl)benzene (20)



20
$C_8H_6ClNO_4$
MW = 183.59 g/mol

Following **GP 2**, nitromethane (190 µL, 217 mg, 3.56 mmol, 1.00 equiv) and NaOH (1.1 mL, *c* = 3.4 M) were added in sequence to a solution of freshly distilled 4-chlorobenzaldehyde (500 mg, 3.56 mmol, 1.00 equiv) in methanol (1.8 mL). The crude product was purified by column chromatography (3 × 20 cm, P/Et_2O = 19/1) to yield **20** (260 mg, 1.42 mmol, 40%) as yellow colored needles.

TLC: R_f = 0.42 (P/Et_2O = 9/1) [UV].

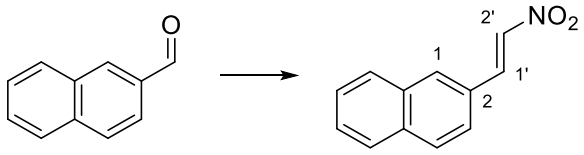
mp: 109 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.96 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.56 (d, ^3J =13.7 Hz, 1H, H-2'), 7.51–7.47 (m, 2H, H-2, H-6), 7.46–7.42 (m, 2H, H-3, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): 138.5 (s, C-1), 137.8 (d, C-1'), 137.6 (s, C-4), 130.4 (d, 2C, C-2, C-6), 129.9 (d, 2C, C-3, C-5), 128.7 (d, C-2').

The analytical data match those reported in the literature.[219]

(*E*)-2-(2'-Nitrovinyl)naphthalene (21)



21
$C_{12}H_9NO_2$
MW = 199.21 g/mol

Following **GP 2**, a solution of 2-naphthaldehyde (1.00 g, 6.40 mmol, 1.00 equiv), NH_4OAc (592 mg, 7.68 mmol, 1.20 equiv) and nitromethane (12.0 mL, 13.7 mg, 224 mmol, 35.0 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 12 cm, CH_2Cl_2) to yield **21** (1.10 g, 5.52 mmol, 86%) as a dark yellow colored crystalline solid.

TLC: R_f = 0.81 (CH_2Cl_2) [UV].

mp: 117 °C.

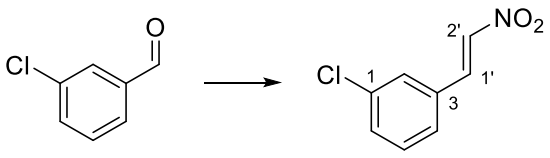
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.17 (d, ^3J = 13.7 Hz, 1H, C-1'), 8.03 (br. s, 1H, H-1), 7.92–7.84 (m, 3H, H_{ar})*, 7.71 (d, ^3J = 13.7 Hz, 1H, C-2'), 7.62–7.54 (m, 3H, H_{ar})*.

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.4 (d, C-1'), 137.3 (d, C-2'), 135.1 (s, C-8a), 133.3 (s, C-4a), 132.4 (d, C-1), 129.5 (d, $C_{ar}H$)*, 128.9 (d, $C_{ar}H$)*, 128.5 (d, $C_{ar}H$)*, 128.1 (d, $C_{ar}H$)*, 127.7 (s, C-2), 127.4 (d, $C_{ar}H$)*, 123.5 (d, $C_{ar}H$)*.

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[219]

(*E*)-1-Chloro-3-(2'-nitrovinyl)benzene (22)



22
$C_8H_6ClNO_2$
MW = 183.59 g/mol

Following **GP 2**, a solution of freshly distilled 3-chlorobenzaldehyde (1.00 g, 21.3 mmol, 1.00 equiv), nitromethane (3.43 mL, 3.91 g, 64.0 mmol, 3.00 equiv) and NH_4OAc (4.11 g, 53.4 mmol, 2.50 equiv) in glacial acetic acid (10 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by column chromatography (6 × 12 cm, cHex/EtOAc = 20/1) to yield **22** (2.80 g, 15.3 mmol, 71%) as a yellow colored solid.

TLC: R_f = 0.22 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

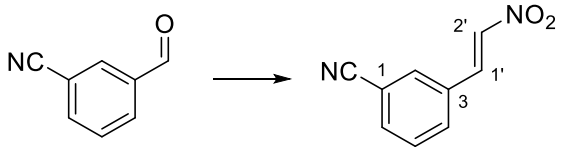
mp: 62 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.94 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.56 (d, ^3J = 13.7 Hz, 1H, H-2'), 7.56−7.54 (m, 1H, H-2), 7.49−7.40 (m, 3H, H-3, H-4, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.3 (d, C-2'), 137.6 (d, C-1'), 135.6 (s, C-3),132.1 (d, C-4) 131.9 (s, C-1), 130.8 (d, C-5), 128.9 (d, C-2), 127.4 (d, C-6).

The analytical data match those reported in the literature.[221]

(*E*)-3-(2'-Nitrovinyl)benzonitrile (23)



23
$C_9H_6N_2O_2$
MW = 174.16 g/mol

Following **GP 2**, a solution of freshly distilled 3-formylbenzonitrile (1.00 g, 7.63 mmol, 1.00 equiv), nitromethane (1.22 mL, 1.40 g, 22.9 mmol, 3.00 equiv) and NH_4OAc (1.47 g, 19.1 mmol, 2.50 equiv) in glacial acetic acid (4 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 10 mL) as the solvent. The crude product was purified by column chromatography (5 × 15 cm, cHex/EtOAc = 20/1) to yield **23** (720 mg, 4.13 mmol, 54%) as a beige colored crystalline solid.

TLC: R_f = 0.59 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

mp: 123 °C.

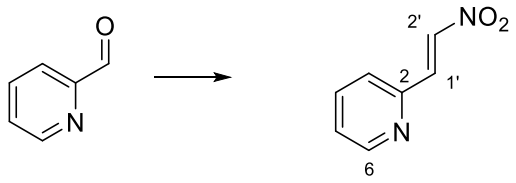
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.00 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.86 (t, ^4J = 1.7 Hz, 1H, H-2), 7.81 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H, H-4, H-6), 7.63 (t, ^3J = 7.7 Hz, 1H, H-5), 7.62 (d, ^3J = 13.7 Hz, 1H, H-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.1 (d, C-1'), 136.4 (d, C-2'), 134.9 (d, C-4)*, 132.8 (d, C-6)*, 132.4 (d, C-2), 131.6 (s, C-3), 130.5 (d, C-5), 117.6 (s, C_{ar}*C*N), 114.2 (s, C-1).

*The assignments are interconvertible.

The analytical data match those reported in the literature.[222]

(*E*)-2-(2'-Nitrovinyl)pyridine (24)



24
$C_7H_6N_2O_2$
MW = 150.14 g/mol

Following **GP 2**, a solution of picolinaldehyde (877 µL, 1.00 g, 9.34 mmol, 1.00 equiv), NH_4OAc (863 mg, 11.2 mmol, 1.20 equiv) and nitromethane (10.0 mL, 11.4 g, 187 mmol, 20.0 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (4 × 15 cm, CH_2Cl_2/MeOH = 99/1 → 95/5) to yield **24** (300 mg, 1.99 mmol, 21%) as a brown colored crystalline solid.

TLC: R_f = 0.21 (CH_2Cl_2/MeOH = 99/1) [UV, $KMnO_4$].

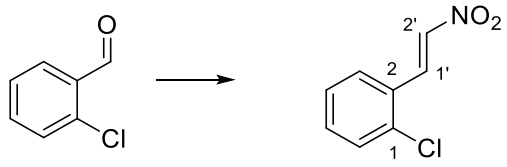
mp: 118 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.80 (d, ^3J = 2.3 Hz, 1H, H-3), 8.72 (dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, 1H, H-6), 8.01 (d, ^3J = 13.8 Hz, 1H, H-1'), 7.87 (*virt*. dt, ^3J = 8.0 Hz, $^3J \cong {}^4J$ = 1.9 Hz, 1H, H-4), 7.63 (d, ^3J = 13.8 Hz, 1H, H-2'), 7.42 (dd, ^3J = 8.0, 4.9 Hz, 1H, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 152.7 (d, C-6), 150.4 (d, C-3), 138.4 (d, C-2'), 135.4 (d, C-1'), 135.2 (d, C-4), 126.3 (s, C-2) 124.1 (d, C-5).

The analytical data match those reported in the literature.[220]

(*E*)-1-Chloro-2-(2'-nitrovinyl)benzene (25)



25
$C_8H_6ClNO_2$
MW = 183.59 g/mol

Following **GP 2**, a solution of freshly distilled 2-chlorobenzaldehyde (2.42 mL, 1.00 g, 21.3 mmol, 1.00 equiv), nitromethane (3.43 mL, 3.91 g, 64.0 mmol, 3.00 equiv) and NH_4OAc (4.11 g, 53.4 mmol, 2.50 equiv) in glacial acetic acid (10 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by column chromatography (6 × 12 cm, cHex/EtOAc = 20/1) to yield **25** (1.51 g, 822 mmol, 38%) as an orange colored crystalline solid.

TLC: R_f = 0.21 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

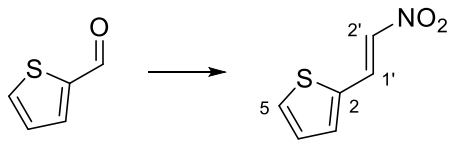
mp: 48 °C.

^{1}H NMR (300 MHz, $CDCl_3$): 8.41 (d, ^3J = 13.8 Hz, 1H, H-1'), 7.59 (d, ^3J = 13.8 Hz, 1H, H-2), 7.61–7.57 (m, 1H, H-3), 7.53–7.48 (m, 1H, H-6), 7.46–7.39 (m, 1H, H-4), 7.37–7.31 (m, 1H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): 139.0 (d, C-1'), 136.2 (s, C-2), 135.2 (d, C-2'), 133.0 (d, C-4), 130.9 (d, C-6), 128.8 (d, C-3), 128.7 (s, C-1), 127.6 (d, C-5).

The analytical data match those reported in the literature.[221]

(*E*)-2-(2'-Nitrovinyl)-thiophene (26)



26
$C_6H_5NO_2S$
MW = 155.12 g/mol

Following **GP 3**, nitromethane (238 µL, 272 mg, 4.46 mmol, 1.00 equiv) and aqueous NaOH solution (1.3 mL, c = 3.6 M) were added in sequence to a solution of freshly distilled 2-thiophenecarbaldehyde (500 mg, 4.46 mmol, 1.00 equiv) in methanol (2.3 mL). The crude product was purified by column chromatography (3 × 20 cm, CH_2Cl_2) to yield **26** (327 mg, 2.11 mmol, 47%) as a brownish colored solid.

TLC: R_f = 0.86 (CH_2Cl_2) [UV].

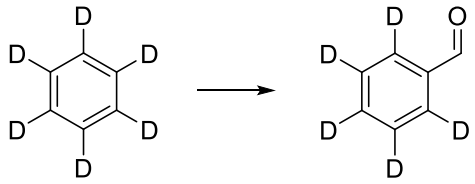
mp: 76 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.16 (d, ^3J = 13.4 Hz, 1H, H-1'), 7.56 (dt, ^3J = 5.1 Hz, ^4J = 0.9 Hz 1H, H-5), 7.48 (d, ^3J = 13.4 Hz, 1H, H-2'), 7.46 (dd, ^3J = 3.7 Hz, ^4J = 0.9 Hz 1H, H-3), 7.15 (dd, ^3J = 5.1 Hz, 3.7 Hz, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.5 (d, C-2'), 134.7 (d, C-3), 133.9 (s, C-2), 132.2 (d, C-1'), 131.7 (d, C-5), 129.0 (d, C-4).

The analytical data match those reported in the literature.[223]

Benzaldehyde-2,3,4,5,6-d_5



C_7HD_5O
MW = 111.15 g/mol

According to a literature known procedure:[224] A solution of benzene-d_6 (1.05 mL, 1.00 g, 11.9 mmol, 1.00 equiv) in dichloromethane (20 mL) was cooled to 0 °C. $TiCl_4$ (2.65 mL,

4.51 g, 23.8 mmol, 2.00 equiv; 1 M solution in CH_2Cl_2) was added slowly. The yellow colored solution was stirred for five minutes, and freshly distilled dichloromethylmethylether (1.08 mL, 1.37 g, 11.9 mmol, 1.00 equiv) was added dropwise. The reaction solution was stirred for 20 minutes at 0 °C, warmed to room temperature was kept at this temperature for further 60 minutes. The reaction mixture was poured onto ice water (50 mL) and was subsequently partitioned between water and dichloromethane (50 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed consecutively with saturated aqueous $NaHCO_3$ solution (150 mL) and saturated aqueous NaCl solution (150 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 200 mbar!). The crude product was purified by column chromatography (4 × 15 cm, P/Et_2O = 5/1) to yield the title compound (660 mg, 5.94 mmol, 50%) as a colorless liquid.

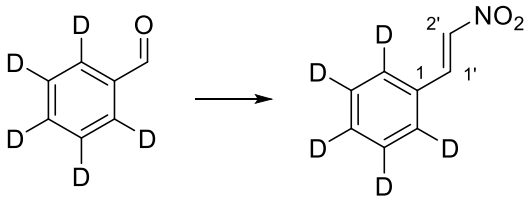
TLC: R_f = 0.54 (P/Et_2O = 2/1) [UV, $KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.0 (s, 1H, ArC*H*O).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 171.9 (d, CHO).

The analytical data match those reported in the literature.[224]

(*E*)-1-(2'-Nitrovinyl)benzene-2,3,4,5,6-d_5 (79)



79
$C_8H_{10}D_5NO_2$
MW = 154.18 g/mol

Following **GP 1**, a solution of benzaldehyde-2,3,4,5,6-d_5 (200 mg, 1.80 mmol, 1.00 equiv), NH_4OAc (166 mg, 2.16 mmol, 1.20 equiv) and nitromethane (3.37 mL, 3.84 g, 63.0 mmol, 35.0 equiv) in glacial acetic acid (5 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 15 cm, P/Et_2O = 5/1) to yield **79** (115 mg, 74.6 mmol, 42%) as yellow colored needles.

TLC: R_f = 0.56 (P/Et_2O = 20/1) [UV, $KMnO_4$].

mp: 56 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3109 (w), 1629 (m, $R_2C{=}CR_2$), 1506 (s, C-NO_2), 1490 (s), 1331 (s, C-NO_2), 1241 (m), 1160 (m), 973 (s), 960 (s), 845 (s).

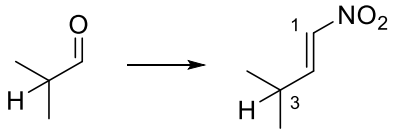
MS (EI, 70 eV): *m/z (%)* = 154 (86) $[M]^+$, 108 (96) $[C_8H_2D_5]^+$, 96 (100) $[C_7H_2D_5]^+$, 81 (67) $[C_6D_5]^+$.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 8.04 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.61 (d, ^3J =13.7 Hz, 1H, H-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.1 (d, C-1'), 137.3 (d, C-2'), 131.8 (t, $^1J_{CD}$ = 24.4 Hz, C_{ar}D-4), 130.1 (s, C-1), 129.0 (t, $^1J_{CD}$ = 24.7 Hz, 2C, C_{ar}D-3, C_{ar}D-5)*, 128.9 (t, $^1J_{CD}$ = 24.3 Hz, 2C, C_{ar}D-2, C_{ar}D-6)*.

* The assignments are interconvertible.

(*E*)-3-Methyl-1-nitrobut-1-ene (27)



27
$C_5H_9NO_2$
MW = 115.13 g/mol

Following **GP 3**, nitromethane (532 µL, 602 mg, 9.86 mmol, 1.00 equiv) and NaOH (3.8 mL, *c* = 6 M) were added successively to a solution of freshly distilled isobutyraldehyde (900 µL, 711 mg, 9.86 mmol, 1.00 equiv) in methanol (10 mL). The crude product was purified by column chromatography (2 × 10 cm, P/E = 19/1) to yield **27** (497 mg, 4.32 mmol, 43%) as a yellow colored liquid.

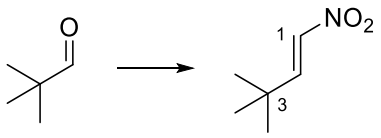
TLC: R_f = 0.50 (P/E = 9/1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.24 (d, ^3J = 13.4 Hz, 1H, H-2,9 6.94 (d, ^3J = 13.4 Hz, 1H, H-1), 2.59 (sept, ^3J = 7.3 Hz, 1H, H-3), 1.14 [d, ^3J = 7.3 Hz, 6H, (CH_3)$_2$CH].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 148.6 (d, C-2), 138.3 (d, C-1), 28.5 (d, C-3), 21.2 [q, $(CH_3)_3CH$].

The analytical data match those reported in the literature.[225]

(*E*)-3,3-Dimethyl-1-nitrobut-1-ene (28)



28
$C_6H_{11}NO_2$
MW = 129.16 g/mol

Following **GP 3**, nitromethane (310 µL, 351 mg, 5.75 mmol, 1.00 equiv) and aqueous NaOH (2.2 mL, *c* = 6.0 M) were added successively to a solution of freshly distilled pivalaldehyde (634 µL, 495 mg, 5.75 mmol, 1.00 equiv) in methanol (5 mL). The crude product was purified by column chromatography (2 × 10 cm, P/E = 19/1) to yield **28** (530 mg, 4.10 mmol, 71%) as a yellow colored liquid.

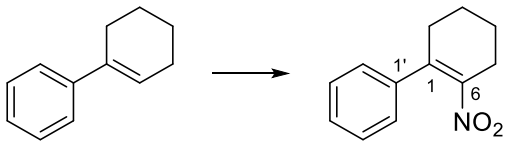
TLC: R_f = 0.58 (P/E = 9/1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.26 (d, ^{3}J = 13.6 Hz, 1H, H-2), 6.89 (d, ^{3}J = 13.6 Hz, 1H, H-1), 1.16 [s, 9H, $C(CH_3)_3$)].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 152.2 (d, C-2), 137.3 (d, C-1), 32.9 (s, C-3), 28.6 [q, $(CH_3)_3C$].

The analytical data match those reported in the literature.[225]

6-Nitro-2,3,4,5-tetrahydro-1,1'-biphenyl (29)



29
$C_{12}H_{13}NO_2$
MW = 203.24 g/mol

According to a literature known procedure:[226] A saturated aqueous solution of $NaNO_2$ (20.5 g, 297 mmol, 47.0 equiv) in water (25 mL) was added to a solution of 2,3,4,5-tetrahydro-1,1'-biphenyl (1.01 mL, 1.00 g, 6.32 mmol, 1.00 equiv) in diethyl ether (25 mL). The reaction solution was cooled to 0 °C and aqueous sulfuric acid solution (25 mL, *c* = 2 M) was added slowly. A color change from blue to green and finally yellow was observed. The reaction mixture was partitioned between the sulfuric acid solution and diethyl ether (*caution*: evolution of nitrous gas!). The organic layer was dried over Na_2SO_4, filtered and the filtrate was stirred at room temperature. A freshly prepared solution of NaOMe [Na (250 mg, 10.8 mmol, 1.70 equiv) in methanol (10 mL); note: the solid Na must be completely dissolved!] was added slowly at room temperature, and the red colored suspension was stirred at room temperature for ten minutes. The reaction solution was poured onto water (50 mL) and the layers were separated. The organic layer was washed with water (4 × 50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (3 × 20 cm, P/Et_2O = 19/1) to yield **29** (682 mg, 3.36 mmol, 53%) as a yellow colored oil.

TLC: R_f = 0.36 (P/Et_2O = 9/1) [UV, $KMnO_4$].

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39–7.28 (m, 3H, *meta*-H_{Ph}, *para*-H_{Ph}), 7.18–7.11 (m, 2H, *ortho*-H_{Ph}), 2.71 (tt, ^3J = 6.3 Hz, ^4J = 2.5 Hz, 2H, CH_2), 2.48 (tt, ^3J = 5.9 Hz, ^4J = 2.5 Hz, 2H, CH_2), 1.92–1.84 (m, 2H, CH_2), 1.82–1.76 (m, 2H, CH_2).

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 146.9 (s, C=C), 139.3 (s, C=C)*, 139.1 (s, C-1')*, 128.8 (d, 2C, *meta*-$C_{Ph}H$), 128.2 (d, *para*-$C_{Ph}H$), 126.4 (d, 2C, *ortho*-$C_{Ph}H$), 32.5 (t, CH_2), 26.9 (t, CH_2), 22.2 (t, CH_2), 22.0 (t, CH_2).

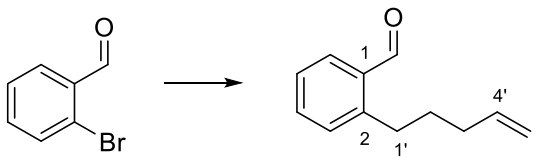
* The assignments are interconvertible.

The analytical data match those reported in the literature.[226]

General Procedure for the Preparation of *Grignard* Reagents

Activated magnesia (0.95 equiv) and one pellet of I_2 were stirred for five minutes, then a litte amount of tetrahydrofuran was added to create a suspension (at least 1.00 mL). A solution of the bromoalkene (1.00 equiv) in tetrahydrofuran (c = 1 M) was added dropwise. The starting point of the reaction was indicated by the decolorization of the solution and heat development. After complete addition of the bromoalkene, the reaction was stirred at room temperature until the magnesia was dissolved completely. The *Grignard* reagent was further used as solution in tetrahydrofuran (c = 1 M).

2-(Pent-4‘-en-1‘-yl)benzaldehyde



$C_{12}H_{14}O$
MW = 174.24 g/mol

According to a modified literature known procedure:[110] The *Grignard* reagent was prepared freshly according to the general procedure from activated magnesia (310 mg, 12.8 mmol, 0.95 equiv) and 5-bromopent-1-ene (1.50 mL, 2.00 g, 13.4 mmol, 1.00 equiv) in tetrahydrofuran (13.5 mL). A solution of $ZnCl_2$ (1.77 g, 13.0 mmol, 2.00 equiv) in tetrahydrofuran (12 mL) was added slowly to the stirred solution of the *Grignard* reagent and the reaction solution was stirred at room temperature for 30 minutes. In parallel, 2-bromobenzaldehyde (1.20 g, 6.49 mmol, 1.00 equiv) was added to a stirred solution of $Pd_2(dba)_3$ (297 mg, 324 µmol, 0.05 equiv) and RuPhos (453 mg, 971 µmol, 0.10 equiv) in tetrahydrofuran (10 mL). The purple colored solution of the aldehyde was added dropwise to the solution of the *Grignard* reagent, resulting in an exothermic reaction. The orange colored reaction solution was stirred at room temperature overnight. Saturated aqueous NH_4Cl solution (30 mL) was added to quench the reaction and the reaction mixture was partitioned between the aqueous and the organic layer. The aqueous layer was extracted with diethyl ether (3 × 30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (5 × 10 cm, P/Et_2O = 19/1) to yield the title compound (482 mg, 2.77 mmol, 43%) as a pale-yellow colored oil.

TLC: R_f = 0.44 (P/Et_2O = 9/1) [UV, $KMnO_4$].

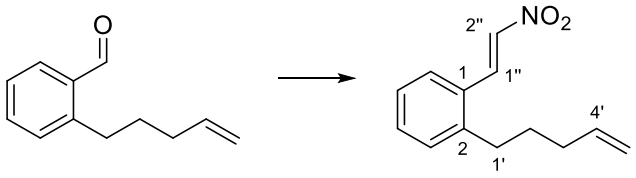
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 10.3 (s, 1H, ArC*H*O), 7.83 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H_{ar})*, 7.50 (td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H_{ar})*, 7.37 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, H_{ar})*, 7.28 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, H_{ar})*, 5.84 (ddt, ^3J = 17.0 Hz, 10.2 Hz, 6.7 Hz, 1H, H-4'), 5.04 (*virt*. dq, ^3J = 17.0 Hz, $^2J \cong {}^4J$ = 1.7 Hz, 1H, C*H*H-5'), 5.00 (ddt, ^2J = 2.3 Hz, ^3J = 10.2 Hz, ^4J = 1.3 Hz, 1H, CH*H*-5'), 3.10–3.00 (m, 2H, CH_2-1'), 2.21-2.09 (m, 2H, CH_2-3'), 1.78–1.67 (m, 2H, CH_2-2').

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 192.5 (d, CHO), 145.7 (s, C-1), 138.8 (d, C-4'), 133.0 (d, C_{ar}H)*, 131.4 (d, C_{ar}H)*, 128.2 (s, C-2), 126.6 (d, C_{ar}H)*, 126.1 (d, C_{ar}H), 114.8 (t, C-5'), 32.0 (t, C-3'), 31.0 (t, C-1'), 26.0 (t, C-2').

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[227]

(*E*)-1-(2''-Nitrovinyl)-2-(pent-4'-en-1'-yl)benzene (67)



67
$C_{13}H_{15}NO_2$
MW = 217.17 g/mol

Following **GP 1**, a solution of 2-(pent-4-en-1-yl)-benzaldehyde (200 mg, 1.15 mmol, 1.00 equiv), NH_4OAc (84.1 mg, 1.09 mmol, 0.95 equiv) and nitromethane (2.34 mL, 2.66 g, 43.6 mmol, 38.0 equiv) in glacial acetic acid (5 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 15 cm, P/E = 19/1) to yield **67** (157 mg, 7.23 mmol, 63%) as a yellow colored oil.

TLC: R_f = 0.64 (P/E = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3072 (w, C_{ar}-H), 2935 (w, C-H), 2869 (w, C-H), 1629 (m, -CH=CH-Ar), 1510 (s, C-NO_2), 1482 (m), 1336 (vs, C-NO_2), 991 (w), 962 [s, (*E*)-CH=CH-R], 912 (m, R-CH-CH_2), 839 (m, C_{ar}-H), 760 (m, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 171 (43) $[C_{13}H_{15}]^+$, 129 (100) $[C_{10}H_9]^+$, 115 (84) $[C_9H_7]^+$, 91 (13) $[C_7H_7]^+$.

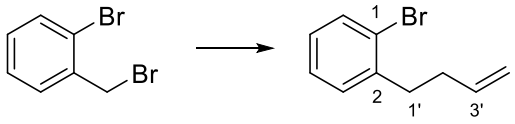
HRMS (ESI): calcd for $C_{13}H_{16}NO_2^+$ $[M+H]^+$: 218.1176; found: 218.1176.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.33 (d, ^3J = 13.5 Hz, 1H, H-1''), 7.55–7.48 (m, 2H, H-2'', H_{ar}*), 7.43−7.40 (m, 1H, H_{ar})*, 7.29−7.25 (m, 2H, H_{ar})*, 5.83 (ddt, ^3J = 16.9 Hz, 10.2 Hz, 6.6 Hz, 1H, H-4'), 5.09–5.00 (m, 2H, CH_2-5'), 2.83–2.76 (m, 2H, CH_2-1'), 2.14 (*virt*. q, $^3J \cong$ 7.0 Hz, 2H, CH_2-3'), 1.75–1.65 (m, 2H, CH_2-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.9 (s, C-1), 138.0 (d, C-2''), 137.9 (d, C-4'), 136.7 (d, ArCH), 132.1 (d, C_{ar}H)*, 130.8 (d, C_{ar}H)*, 128.5 (s, C-2), 127.4 (d, C_{ar}H)*, 127.0 (d, C_{ar}H)*, 115.6 (t, C-5'), 32.8 (t, C-3'), 31.0 (t, C-1'), 25.7 (t, C-2').

* The exact assignment of these signals was not possible.

1-Bromo-2-(but-3'-en-1'-yl)benzene



$C_{10}H_{11}Br$
MW = 211.10 g/mol

According to a literature known procedure:[105] Allylmagnesium bromide (2.20 mL, 319 mg, 2.20 mmol, 1.10 equiv) in diethyl ether (*c* = 1 M) was added dropwise to a solution of 1-bromo-2-(bromomethyl) benzene (500 mg, 2.00 mmol, 1.00 equiv) in tetrahydrofuran (5 mL) at −78 °C. After stirring for one hour at −78 °C, the reaction solution was warmed to room temperature and stirred at this temperature for one hour. The reaction was quenched by the addition of water (20 mL) and partitioned between water and diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (70 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was filtered over silica, and the silica plug was washed with hexanes (20 mL). Removal of all volatiles under reduced pressure yielded the title

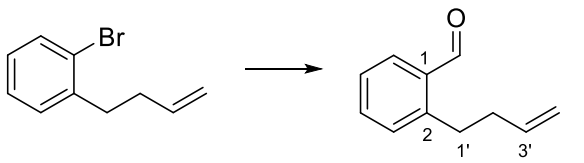
compound (350 mg, 1.66 mmol, 83%) as a colorless liquid. The product was employed in the subsequent step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.53 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, H_{ar})*, 7.25–7.18 (m, 2H, H_{ar})*, 7.05 (ddd, ^3J = 7.9 Hz, 6.4 Hz, ^4J = 2.6 Hz, 1H, H_{ar})*, 5.88 (ddt, ^3J = 17.1 Hz, 10.2 Hz, 6.6 Hz, 1H, H-3'), 5.06 (*virt*. dq, ^3J = 17.1 Hz, $^2J \cong {}^4J$ = 1.7 Hz, 1H, C*H*H-4'), 5.00 (ddt, ^2J = 2.1 Hz, ^3J = 10.2 Hz, ^4J = 1.2 Hz, 1H, CH*H*-4'), 2.87–2.74 (m, 2H, CH_2-1'), 2.38 (dtt, ^3J = 9.3 Hz, 6.6 Hz, ^4J = 1.4 Hz, 2H, CH_2-2').

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[105]

2-(But-3'-en-1'-yl)benzaldehyde



$C_{11}H_{12}O$
MW = 160.22 g/mol

According to a literature known procedure:[108] *n*-BuLi (793 µL, 117 mg, 1.82 mmol, 1.10 equiv; 2.30 M in hexanes) was added dropwise to a solution of 1-bromo-2-(but-3-en-1-yl) benzene (350 mg, 1.66 mmol, 1.00 equiv) in tetrahydrofuran (7 mL) at −78 °C. After one hour, dimethyl formamide (192 µL, 182 mg, 2.49 mmol, 1.50 equiv) was added slowly. The solution was stirred for one hour and the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (20 mL) at −78 °C. After room temperature was reached, the reaction mixture was partitioned between the aqueous NH_4Cl solution and diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the title compound (225 mg, 1.40 mmol, 85%) as a colorless liquid. The product was employed in the subsequent step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 10.3 (s, 1H, ArC*H*O), 7.83 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, H-3)*, 7.51 (td, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H, H-4)**, 7.38 (td, ^3J = 7.5 Hz,

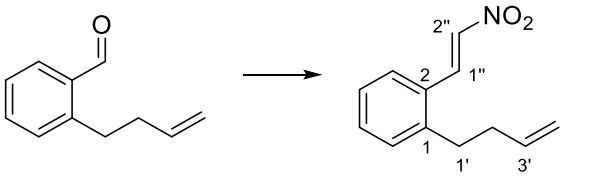
^4J = 1.2 Hz, 1H, H-5)**, 7.28 (dd, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, H-6)*, 5.86 (ddt, ^3J = 17.0 Hz, 10.2 Hz, 6.7 Hz, 1H, H-3'), 5.04 (*virt*. dq, $^3J \cong 17.0$ Hz, $^2J \approx {}^4J$ = 1.6 Hz, 1H, C*H*H-4'), 4.99 (ddt, ^2J = 2.0 Hz, ^3J = 10.2 Hz, ^4J = 1.2 Hz, 1H, CH*H*-4'), 3.18–3.08 (m, 2H, CH_2-1'), 2.42-2.31 (m, 2H, CH_2-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 192.5 (s. CHO), 144.7 (s, C-2), 137.6 (d, C-3'), 133.9 (s, C-1), 133.8 (d, $C_{ar}H$)*, 132.2 (d, $C_{ar}H$)*, 131.2 (d, $C_{ar}H$)*, 126.8 (d, $C_{ar}H$)*, 115.6 (t, C-4'), 36.1 (t, C-2'), 32.2 (t, C-1').

*,** The assignments are interconvertible.

The analytical data match those reported in the literature.[108]

(*E*)-1-(But-3'-en-1'-yl)-2-(2''-nitrovinyl)benzene (66)



66
$C_{12}H_{13}NO_2$
MW = 203.09 g/mol

Following **GP 1**, a solution of 2-(but-3-en-1-yl)benzaldehyde (100 mg, 624 µmol, 1.00 equiv), NH_4OAc (45.7 mg, 593 µmol, 0.95 equiv) and nitromethane (1.24 mL, 1.44 g, 23.7 mmol, 38.0 equiv) in glacial acetic acid (3 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 10 cm, P/Et_2O = 19/1) to yield **66** (108 mg, 531 µmol, 86%) as a yellow colored oil.

TLC: R_f = 0.80 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3074 (w, C_{ar}-H), 2926 (w, C-H), 2873 (w, C-H), 1630 (m, -CH=CH-Ar), 1510 (s, C-NO_2), 1482 (m), 1336 (vs, C-NO_2), 995 (w), 961 (s, (*E*)-CH=CH-R), 913 (m, R-CH-CH_2), 839 (m, $C_{ar}H$), 760 (s, $C_{ar}H$).

MS (EI, 70 eV): *m/z (%)* = 141 (8), 129 (38) $[C_{10}H_9]^+$, 116 (100) $[C_9H_8]^+$, 89 (9).

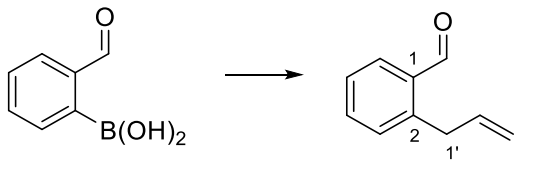
HRMS (ESI): calcd for $C_{12}H_{14}NO_2^+$ $[M+H]^+$: 204.1019; found: 204.1020.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 8.33 (d, ^{3}J = 13.5 Hz, 1H, H-1''), 7. 54–7.52 (m, 1H, H-3), 7.51 (d, ^{3}J = 13.5 Hz, 1H, H-2''), 7.45–7.39 (m, 1H, H-5), 7.31–7.24 (m, 2H, H-4, H-6), 5.84 (ddt, ^{3}J = 16.9 , 10.2 Hz, 6.6 Hz, 1H, H-3'), 5.10–5.04 (m, 1H, C*H*H-4'), 5.03–4.99 (m, 1H, CH*H*-4'), 2.91–2.85 (m, 2H, CH_2-1'), 2.35 (tdt, ^{3}J = 7.9 Hz, 6.6 Hz, ^{4}J = 1.4 Hz, 2H, CH_2-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.2 (s, C-1), 138.0 (d, C-2''), 137.0 (d, C-3'), 136.7 (d, C-1''), 132.1 (d, C-5), 130.8 (d, C-6)*, 128.6 (s, C-2), 127.4 (d, C-3), 127.1 (d, C-4)*, 116.1 (t, C-4'), 35.7 (t, C-2'), 33.0 (t, C-1').

* The assignments are interconvertible.

2-Allylbenzaldehyde



$C_{10}H_{10}O$
MW = 146.07 g/mol

According to a literature known procedure:[103] Na_2CO_3 (267 µL, 283 mg, 2.67 mmol, 2.00 equiv) as a solution in water (*c* = 1 M) and allyl bromide (138 µL, 194 mg, 1.60 mmol, 1.20 equiv) were added successively to a solution of 2-formylphenylboronic acid (200 mg, 1.33 mmol, 1.00 equiv) and $PdCl_2(PPh_3)_2$ (23.3 mg, 33.3 µmol, 2.5 mol%) in tetrahydrofuran (5 mL). The solution was heated at reflux for four hours. Water (10 mL) was added and the reaction mixture was partitioned between water and dichloromethane (20 mL). The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl solution (40 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (3 × 20 cm, cHex/EtOAc = 19/1) to yield the title compound (168 mg, 1.15 mmol, 86%) as a colorless oil.

TLC: R_f = 0.25 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.3 (s, 1H, ArC*H*O), 7.85 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 1H, H_{ar})*, 7.53 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 1H, H_{ar})*, 7.40 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.3 Hz, 1H, H_{ar})*, 7.30 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.3 Hz, 1H, H_{ar})*, 6.04 (ddt, ^{3}J = 17.2 Hz,

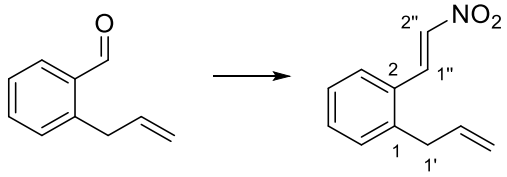
10.2 Hz, 6.2 Hz, 1H, H-2'), 5.09 (*virt*. dq, ^{3}J = 10.2 Hz, $^{2}J \cong {}^{4}J$ = 1.5 Hz, 1H, C*H*H-3'), 4.99 (*virt*. dq, ^{3}J = 17.2 Hz, $^{2}J \cong {}^{4}J$ = 1.7 Hz, 1H, CH*H*-3'), 3.82 (dt, ^{3}J = 6.2 Hz, ^{4}J = 1.7 Hz, 2H, CH_2-1').

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 192.5 (d, Ar*C*HO), 142.4 (s, C-2), 1371 (d, C-2'), 134.1 (d, $C_{ar}H$)*, 134.0 (s, C-1), 131.8 (d, $C_{ar}H$)*, 131.2 (d, $C_{ar}H$)*, 127.1 (d, $C_{ar}H$)*, 116.6 (t, C-3'), 36.7 (t, C-1').

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[103]

(*E*)-1-Allyl-2-(2'-nitrovinyl)benzene (65)



65
$C_{11}H_{11}NO_2$
MW = 189.08 g/mol

Following **GP 1**, a solution of 2-allylbenzaldehyde (100 mg, 680 µmol, 1.00 equiv) and NH_4OAc (27.7 mg, 440 µmol, 0.65 equiv) in nitromethane (1.4 mL) was heated at reflux for four hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was filtered through silica, the silica plug was washed with dichloromethane (10 mL) and all volatiles were removed under reduced pressure. **65** (115 mg, 601 µmol, 89%) was obtained as a yellow colored oil.

TLC: R_f = 0.58 (P/Et_2O = 19/1) [UV, $KMnO_4$].

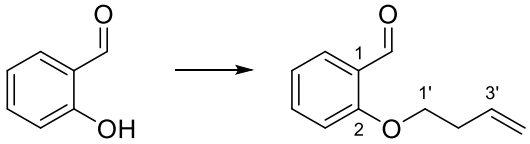
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.31 (d, ^{3}J = 13.5 Hz, 1H, H-1''), 7.54 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.3 Hz, 1H, H_{ar})*, 7.50 (d, ^{3}J = 13.5 Hz, 1H, H-2''), 7.44 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H, H_{ar})*, 7.33–7.28 (m, 2H, H_{ar})*, 5.96 (ddt, ^{3}J = 17.1 Hz, 10.2 Hz, 6.1 Hz, 1H, H-2'), 5.13 (*virt*. dq, ^{3}J = 10.2 Hz, $^{2}J \cong {}^{4}J$ = 1.5 Hz, 1H, C*H*H-3'), 4.98 (*virt*. dq, $^{3}J = {}^{3}J \cong$ 17.1 Hz, $^{2}J \cong {}^{4}J$ = 1.7 Hz, 1H, CH*H*-3'), 3.55 (dt, ^{3}J = 6.1 Hz, ^{4}J = 1.7 Hz, 2H, CH_2-1').

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 140.9 (s, C-1), 138.0 (d, C-2''), 136.8 (d, C-1''), 136.2 (d, C-2'), 132.2 (d, C-5), 131.1 (d, C-6)*, 129.2 (s, C-2), 127.5 (d, C-3), 127.4 (d, C-4)*, 117.1 (t, C-3'), 37.8 (t, C-1').

* The assignments are interconvertible

The analytical data match those reported in the literature.[228]

2-(But-3'-en-1'-yloxy)benzaldehyde



$C_{11}H_{12}O_2$
MW = 176.22 g/mol

According to a literature known procedure:[111] 4-bromobut-1-ene (831 µL, 1.11 g, 8.19 mmol, 2.00 equiv), KI (68.0 mg, 409 µmol, 0.10 equiv), 18-crown-6-ether (54.1 mg, 204 µmol, 0.05 equiv) and K_2CO_3 (1.64 g, 11.9 mmol, 2.60 equiv) were added in sequence to a stirred solution of 2-hydroxybenzaldehyde (431 µL, 500 mg, 4.09 mmol, 1.00 equiv) in acetonitrile (5 mL). The bright yellow colord suspension was stirred over night at 75 °C. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was taken up in water (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with saturated aqueous NaCl solution (75 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the title compound (458 mg, 2.59 mmol, 64%) as a brown colored oil.

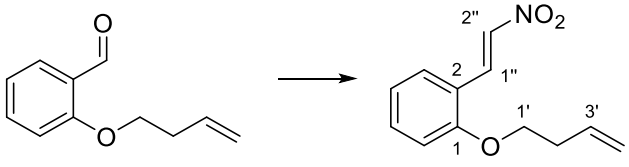
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 10.5 (s, 1H, CHO), 7.83 (dd, ^3J = 7.7 Hz, ^2J = 1.9 Hz, 1H, H_{ar})*, 7.53 (ddd, ^3J = 8.8 Hz, 7.3 Hz, ^2J = 1.8 Hz, 1H, H_{ar})*, 7.02 (t, ^3J = 7.6 Hz, 1H, H_{ar})*, 6.98 (d, ^3J = 8.5 Hz, 1H, H_{ar})*, 5.91 (ddt, ^3J = 17.1 Hz, 10.2 Hz, 6.8 Hz, 1H, H-3'), 5.20 (dd, ^2J = 1.6 Hz, ^3J =17.1 Hz, 1H, C*H*H-4'), 5.14 (dd, ^3J = 10.3 Hz, ^2J = 1.6 Hz, 1H, CH*H*-4'), 4.14 (t, ^3J = 6.5 Hz, 2H, CH_2-1'), 2.61 (*virt*. qt, $^3J = {}^3J \cong 6.6$ Hz, ^4J = 1.4 Hz, 2H, CH_2-2').

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 190.0 (d, CHO), 161.5 (s, C-1), 136.0 (d, C-3)*, 134.1 (d, C-3'), 128.4 (d, C-4)*, 125.2 (s, C-2), 120.9 (d, C-5), 117.7 (t, C-4'), 112.7 (d, C-6), 67.8 (t, C-2'), 33.7 (t, C-3').

* The assignments are interconvertible.

The analytical data match those reported in the literature.[111]

(*E*)-1-(But-3'-en-1'-yloxy)-2-(2''-nitrovinyl)benzene (68)



68
$C_{12}H_{13}NO_3$
MW = 219.24 g/mol

Following **GP 1**, a solution of 2-(but-3'-en-1'-yloxy)benzaldehyde (300 mg, 1.70 mmol, 1.00 equiv), nitromethane (1.82 mL, 2.08 g, 34.1 mmol, 20.0 equiv) and NH_4OAc (157 mg, 2.04 mmol, 1.20 equiv) in glacial acetic acid (5 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 10 mL) as the solvent. The crude product was purified by column chromatograpy (3 × 10 cm, CH_2Cl_2) to yield **68** (225 mg, 1.03 mmol, 60%) as a yellow colored oil.

TLC: R_f = 0.84 (CH_2Cl_2) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3082 (w, C_{ar}-H), 2949 (w, C-H), 2883 (w, C-H), 1622 (s), 1572 (m, C-NO_2), 1499 (s), 1422 (s), 1323 (vs, C-NO_2), 1284 (s), 1162 (s), 1016 (s), 961 [s, (*E*)-CH=CH-R], 920 (s, R-CH-CH_2), 832 (m, C_{ar}-H), 762(s, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 173 (21) $[C_{12}H_{13}O]^+$, 118 (100) $[C_8H_6O]^+$, 89 (16), 55 (41).

HRMS (ESI): calcd for $C_{12}H_{14}NO_3^+$ $[M+H]^+$: 220.0968; found: 220.0970.

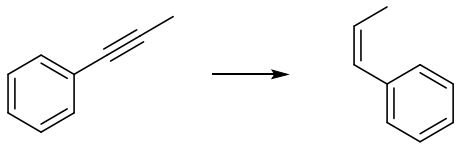
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.10 (d, ^3J = 13.6 Hz, 1H, H-1''), 7.96 (d, ^3J = 13.6 Hz, 1H, H-2''), 7.44 (t, ^3J = 7.6 Hz, 2H, H-3, H-4), 7.02 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, H-5), 6.97 (d, ^3J = 8.3 Hz, 1H, H-6), 5.91 (ddt, ^3J = 17.1 Hz, 10.2 Hz, 6.7 Hz, 1H, H-3'), 5.28 (*virt*. dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1H, C*H*H-4'), 5.20 (*virt*. dq, ^3J = 10.2 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1H, CH*H*-4'), 4.17 (t, ^3J = 6.4 Hz, 2H, CH_2-1'), 2.66 (virt. qt, $^3J = {}^3J \cong$ 6.5 Hz, ^4J = 1.4 Hz, 2H, CH_2-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 159.0 (s, C-1), 138.8 (d, C-2’’), 135.7 (d, C-1’’), 134.1 (d, C-3’), 133.4 (d, C-3)*, 133.2 (d, C-4)*, 121.3 (d, C-5), 119.5 (s, C-2), 118.2 (t, C-4’), 112.2 (d, C-6), 68.0 (t, C-2’), 33.8 (t, C-1‘).

* The assignments are interconvertible.

6.5 Olefin Syntheses

cis-β-Methylstyrene



C_9H_{10}
MW = 118.18 g/mol

According to a literature known procedure:[229] Prop-1-yn-1-ylbenzene (900 µL, 835 mg, 7.19 mmol, 1.00 equiv) and *Lindlar's* catalyst (500 mg) were suspended in 250 mL of freshly distilled cyclohexane. The flask was alternately evacuated and flushed with H_2-gas for four cycles to establish a saturated H_2-atmosphere inside the flask. The flask was charged with H_2 (p = 1 atm) and the suspension was stirred at room temperature. The reaction progress was monitored via TLC. After ten minutes, the suspension was filtered over a plug of CELITE® and the filtrate was concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 150 mbar!). The crude product was purified by column chromatography (5 × 15 cm, P) to yield the title compound (380 mg, 3.22 mmol, 45%) as a colorless liquid.

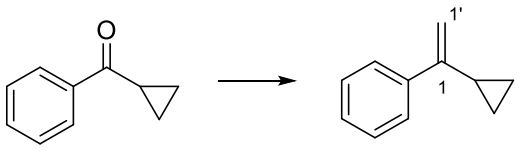
TLC: R_f = 0.62 (P) [UV, $KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.39–7.28 (m, 4H, H_{Ph}), 7.26−7.20 (m, 1H, H_{Ph}), 6.45 (d, ^3J = 11.6 Hz, 1H, PhC*H*=CHCH$_3$), 5.80 (dq, ^3J = 11.6, 7.2 Hz, 1H, PhCH=C*H*CH$_3$), 1.91 (d, ^3J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 137.8 (s, C_{Ph}), 130.0 (d, C_{Ph}H), 128.9 (d, 2C, C_{Ph}H), 128.3 (d, 2C, C_{Ph}H), 126.9 (d, Ph*C*H=CHCH$_3$), 126.5 (d, PhCH=*C*HCH$_3$), 14.8 (q, CH_3).

The analytical data match those reported in the literature.[229]

1,1-Cyclopropylphenyl ethylene



$C_{11}H_{12}$
MW = 144.22 g/mol

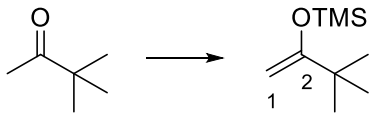
According to a literature known procedure:[230] NaH (547 mg, 27.4 mmol, 2.00 equiv; 60 wt-% in mineral oil) was washed with pentane (4 × 10 mL). The flask was deoxygenated by alternately evacuating and flushing with argon for three cycles. The white powder was dissolved in dimethylsulfoxide (12 mL) and heated to 85 °C, until the evolution of gas ceased. Methyltriphenylphosphonium bromide (9.77 g, 27.4 mmol, 2.00 equiv) was dissolved in warm dimethylsulfoxide (13 mL). The NaH-Suspension was cooled to 0 °C, and the solution of the *Wittig* salt was added quickly to avoid freezing of the solvent. The yellow colored reaction suspension was stirred at room temperature for ten minutes. Subsequently, a solution of cyclopropyl(phenyl)methanone (1.89 mL, 2.00 g, 13.7 mmol, 1.00 equiv) in dimethylsulfoxide (10 mL) was added, and the resulting orange colored suspension was stirred for one hour at room temperature. Water (50 mL) was added, and the reaction mixture was partitioned between water and pentane (200 ml). The aqueous layer was extracted with large excess of pentane (2 × 200 mL). The combined organic layers were washed with saturated aqueous NaCl solution (700 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 500 mbar!). The crude product, a yellow colored oil, was taken up in pentane (50 mL) and filtered through silica. The silica plug was washed carefully with pentane (50 mL) and the filtrate was again concentrated *in vacuo* (> 500 mbar) to yield the title compound (880 mg, 770 mmol, 47%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.64–7.56 (m, 2H, H_{Ph}), 7.39–7.27 (m, 3H, H_{Ph}), 5.28 (d, ^2J = 1.1 Hz, 1H, C*H*H-1') 4.94 (*virt*. t, $^4J \cong {}^2J$ = 1.2 Hz, 1H, CH*H*-1'), 1.66 [ttd, ^3J = 8.3 Hz, 5.4 Hz, ^4J = 1.3 Hz, 1H, C*H*$(CH_2)_2$], 0.97–0.79 [m, 2H, CH(C$H_2)_2$], 0.66–0.52 [m, 2H, CH(C$H_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 149.5 (s, C-1), 141.8 (s, C_{Ph}), 128.3 (d, 2C, C_{Ph}H), 127.6 (d, C_{Ph}H), 126.3 (d, 2C, C_{Ph}H), 109.2 (t, C-1'), 15.8 [d, *C*H$(CH_2)_2$], 6.82 [t, 2C, CH(*C*$H_2)_2$].

The analytical data match those reported in the literature.[231]

[(3,3-Dimethylbut-1-en-2-yl)oxy]trimethylsilane



$C_9H_{20}OSi$
MW = 172.34 g/mol

According to a literature known procedure:[232] TMSCl (1.51 mL, 1.30 g, 12.0 mmol, 1.20 equiv) was added dropwise over a period of ten minutes to a solution of pinacolone (1.25 mL, 1.00 g, 9.98 mmol, 1.00 equiv) and dry triethylamine (1.66 mL, 1.21 g, 12.0 mmol, 1.20 equiv) in acetonitrile (20 mL). Subsequently, a solution of NaI (1.95 g, 13.0 mmol, 1.30 equiv) in acetonitrile (20 mL) was added. The grey colored suspension was stirred for four hours at room temperature and the reaction was quenched by the addition of cold water (50 mL) and cold pentane (40 mL). The resulting three layers were separated, and the aqueous layer was extracted with pentane (3 × 50 mL). The combined organic layers (acetonitrile and pentane) were washed with water, until a neutral pH was reached. The organic layer was washed with saturated aqueous NaCl solution (250 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by distillation over a *Vigreux* column (Ø = 1.5 cm, h = 10 cm) to yield the title compound (800 mg, 4.64 mmol, 47%) as a colorless liquid.

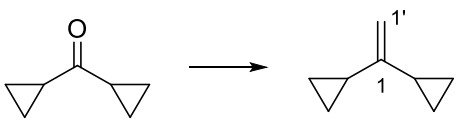
bp: 138–145 °C [p = 1013 mbar].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.08 (d, ^2J = 1.3 Hz, 1H, C*H*H-1), 3.93 (d, ^2J = 1.3 Hz, 1H, CH*H*-1), 1.05 [s, 9H, $Si(CH_3)_3$], 0.21 [s, 9H, $C(CH_3)_3$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 167.4 (s, C-2), 85.9 (t, C-1), 36.6 [s, *C*$(CH_3)_3$], 28.2 [q, C(*C*$H_3)_3$], 0.32 [q, OSi$(CH_3)_3$].

The analytical data match those reported in the literature.[232]

1,1-Diyldicyclopropyl ethylene



C_8H_{12}
MW = 108.18 g/mol

According to a literature known procedure:[230] NaH (1.65 g, 41.3 mmol, 0.91 equiv; 60 wt-% in mineral oil) was washed with pentane (4 × 10 mL). The flask was deoxygenated by alternately evacuating and flushing with argon for three cycles. The white powder was dissolved in dimethylsulfoxide (25 mL) and heated to 85 °C, until the evolution of gas ceased. Methyltriphenylphosphonium bromide (14.2 g, 41.3 mmol, 0.91 equiv) was dissolved in warm dimethylsulfoxide (25 mL). The NaH-suspension was cooled to 0 °C, and the solution of the *Wittig* salt was added quickly to avoid freezing of the solvent. The yellow reaction suspension was stirred at room temperature for ten minutes. Subsequently, a solution of dicyclopropylmethanone (5.15 mL, 5.00 g, 45.4 mmol, 1.00 equiv) in dimethylsulfoxide (50 mL) was added, and the resulting orange colored suspension was stirred for one hour at room temperature. The product was distilled directly from the reaction mixture (T = 120 °C, p = 120 – 60 mbar) and subsequently filtered over silica to remove the residual dimethylsulfoxide, yielding the title compound (3.81 g, 776 mmol, 78%) as a colorless liquid.

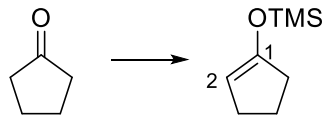
bp: ~ 125 °C [p = 120 – 60 mbar].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.58 (t, ^{4}J = 0.6 Hz, 2H, H-1'), 1.30 [tt, ^{3}J = 8.2, 5.2 Hz, 2H, C*H*$(CH_2)_2$], 0.66–0.57 [m, 4H, CH(C*H*$_2)_2$], 0.56–0.49 [m, 4H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 152.1 (s, C-1), 104.5 (t, C-1'), 15.3 [d, 2C, *C*H$(CH_2)_2$], 5.81 [t, 4C, CH(*C*$H_2)_2$].

The analytical data match those reported in the literature.[233]

(Cyclopent-1-en-1-yloxy)trimethylsilane



$C_8H_{16}OSi$
MW = 156.30 g/mol

According to a literature known procedure:[234] Cyclopentanone (1.05 mL, 1.00 g, 11.9 mmol, 1.00 equiv) and triethylamine (2.07 mL, 1.50 g, 14.9 mmol, 1.15 equiv) was added to a solution of NaI (2.23 g, 14.9 mmol, 1.25 equiv) in acetonitrile (18 mL). TMSCl (1.74 mL, 1.49 g, 13.7 mmol, 1.15 equiv) was added dropwise over a period of 30 minutes. The grey colored suspension was stirred for two hours at room temperature. The reaction mixture was partitioned

between acetonitrile and pentane (20 mL). The acetonitrile layer was extracted with pentane (3 × 20 mL). The combined pentane layers were washed with water, until a neutral pH was reached. Subsequently, the pentane layer was washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by *Kugelrohr* distillation to yield the title compound (1.53 g, 9.79 mmol, 82%) as a colorless liquid.

bp: 50 °C [p = 10 mbar].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.66–4.58 (m, 1H, $CH_2C\mathit{H}$=C), 2.28–2.24 (m, 4H, CH_2), 1.91–1.76 (m, 2H, CH_2), 0.20 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 155.2 (s, C-1), 102.3 (d, C-2), 33.7 (t, CH_2), 28.9 (t, CH_2), 21.5 (t, CH_2), 0.19 [q, $OSi(CH_3)_3$].

The analytical data match those reported in the literature.[234]

6.6 Intermolecular [2+2] Photocycloaddition of Nitroolefins

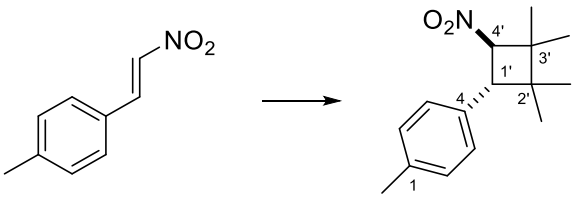
General Procedure 4 (GP 4) for the [2+2] Photocycloaddition of Nitroolefins with 2,3-Dimethyl-2-butene (30)

A solution of the nitroolefin (1.00 equiv) and 2,3-dimethyl-2-butene (**30**) (10.0 equiv) in dichloromethane (c = 20 mM) was irradiated with visible light (the wavelength λ [nm] of the light source is indicated for each reaction individually) at room temperature or at −78 °C. The progress of the reaction was monitored by TLC. After full conversion was reached, irradiation was stopped, and the solvent was removed *in vacuo*. In some cases, the reaction was stopped when the TLC did not indicate any further consumption of the starting material over a period of two to three hours. The crude product was dry loaded onto CELITE® and purified by column chromatography.

General Procedure 5 (GP 5) for the [2+2] Photocycloaddition of *trans*-β-Nitrostyrene (1) with Different Olefins

A solution of *trans*-β-nitrostyrene (**1**) (1.00 equiv) and the olefin (10.0 equiv) in dichloromethane (c = 20 mM) was irradiated with visible light (the wavelength λ [nm] of the light source is indicated for each reaction individually) at room temperature or at −78 °C. The progress of the reaction was monitored by TLC. After full conversion was reached, irradiation was stopped, and the solvent was removed *in vacuo*. In some cases, the reaction was stopped when the TLC did not indicate any further consumption of the starting material over a period of two to three hours. The crude product was dry loaded onto CELITE® and purified by column chromatography.

1-Methyl-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)-benzene (*rac*-32)



14 *rac*-**32**

$C_{15}H_{21}NO_2$

MW = 247.33 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **14** (32.6 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 20/1) to yield *rac*-**32** (26.9 mg, 1.09 mmol, 54%) as a pale-yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **14** (16.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield *rac*-**32** (16.7 mg, 67.5 µmol, 68%) as a pale-yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **14** (16.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield *rac*-**32** (16.5 mg, 66.7 µmol, 67%) as a pale-yellow colored oil.

TLC: R_f = 0.68 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2966 (w, C-H), 2926 (w, C-H), 1540 (s, C-NO_2), 1518 (w), 1459 (w, C_{sp3}-H), 1369 (m, C-NO_2), 1152 (w), 830 (w, C_{ar}-H), 757 (w).

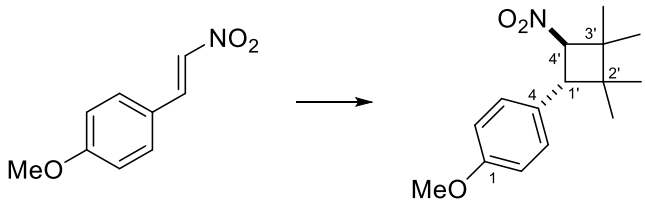
MS (EI): *m/z (%)* = 201 (57) $[C_{15}H_{21}]^+$, 159 (100) $[C_{12}H_{15}]^+$, 105 (45) $[C_8H_9]^+$.

HRMS (EI, 70 eV): calcd for $C_{15}H_{21}NO_2^+$ $[M]^+$: 247.1567; found: 247.1567.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.16−7.12 (m, 2H, H-3, H-5), 7.01–6.98 (m, 2H, H-2, H-6), 4.88 (d, ^{3}J = 10.1 Hz, 1H, H-4'), 3.92 (d, ^{3}J = 10.1 Hz, 1H, H-1'), 2.33 (s, 3H, CH_3Ar), 1.23 (s, 3H, CH_3-3'), 1.16 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.70 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.7 (s, C-1), 133.3 (s, C-4), 129.3 (d, 2C, C-2, C-6), 127.0 (d, 2C, C-3, C-5), 85.1 (d, C-4'), 49.2 (d, C-1'), 45.0 (s, C-2'), 39.2 (s, C-3'), 24.3 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.5 [q, (C-3')*C*H_3], 21.2 (q, *C*H_3Ar), 19.5 [q, (C-2')*C*H_3].

1-Methoxy-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)-benzene (*rac*-33)



10

rac-**33**
$C_{15}H_{21}NO_3$
MW = 263.34 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **10** (35.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for four hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1) to yield *rac*-**33** (27.3 mg, 1.04 mmol, 52%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **10** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield *rac*-**33** (14.3 mg, 54.3 µmol, 58%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **10** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield *rac*-**33** (20.3 mg, 77.1 µmol, 77%) as a yellow colored oil.

TLC: R_f = 0.54 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2963 (w, C-H), 2930 (w, C-H), 2837 (w. O-CH_3), 1613 (w), 1538 (s, C-NO_2), 1459 (m, O-CH_3), 1367 (m, C-NO_2), 1179 (m), 1033 (m), 834 (m, C_{ar}-H), 760 (m).

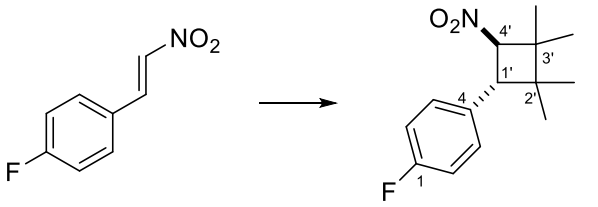
MS (EI): *m/z (%)* = 217 (28) $[C_{15}H_{21}O]^+$, 161 (69) $[C_{11}H_{13}O]^+$, 84 (100) $[C_5H_8O]^+$.

HRMS (EI, 70 eV): calcd for $C_{15}H_{21}NO_3$ $[M]^+$: 263.1516; found: 263.1512.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.04−7.02 (m, 2H, H-2, H-6), 6.89−6.85 (m, 2H, H-3, H-5), 4.86 (d, ^3J = 10.1 Hz, 1H, H-4'), 3.89 (d, ^3J = 10.1 Hz, 1H, H-1'), 3.80 (s, 3H, CH_3O), 1.23 (s, 3H, CH_3-3'), 1.15 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.70 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 158.8 (s, C-1), 128.5 (s, C-4), 128.1 (d, 2C, C-3, C-5), 114.1 (d, 2C, C-2, C-6), 85.4 (d, C-4'), 55.4 (q, CH_3O), 48.4 (d, C-1'), 44.9 (s, C-2'), 39.3 (s, C-3'), 24.6 [q, (C-2')*C*H_3], 22.8 [q, (C-3')*C*H_3], 21.5 [q, (C-2')*C*H_3], 19.5 [q, (C-3')*C*H_3].

1-Fluoro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (*rac*-34)



15 | ***rac*-34** $C_{14}H_{18}FNO_2$ MW = 251.30 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **15** (33.4 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for four hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**34** (22.2 mg, 88.3 µmol, 44%) as a colorless solid.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **15** (16.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**34** (10.5 mg, 41.8 µmol, 42%) as a colorless solid.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **15** (16.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at −78 °C. The crude product was purified by column chromatography (2 × 20 cm, P/Et_2O = 15/1) to yield *rac*-**34** (12.6 mg, 50.1 µmol, 50%) as a colorless solid

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, C_{ar}-H), 2967 (m, C_{ar}-H), 2871 (w), 1538 (vs, C-NO_2), 1510 (s), 1460 (m, C_{sp3}-H), 1371 (s, C-NO_2), 1226 (s, C_{ar}-F), 1151 (m), 1135 (m), 844 (s, C_{ar}-H), 761 (s, C_{ar}-H).

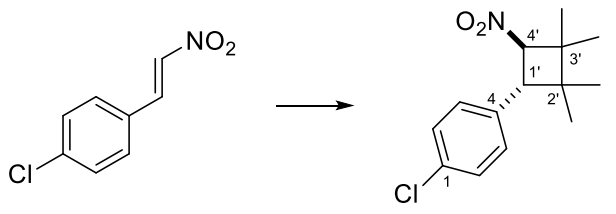
MS (EI): *m/z (%)* = 205 (45) $[C_{14}H_{18}F]^+$, 163 (100) $[C_{11}H_{12}F]^+$, 106 (54) $[C_7H_6F]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{18}FNO_2^+$ $[M]^+$: 251.1316; found: 251.1316.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.09–7.00 (m, 4H, H_{ar}), 4.85 (d, ^3J = 10.1 Hz, 1H, H-4'), 3.92 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 1.14 (s, 3H, CH_3-2'), 0.70 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 162.1 (d, $^1J_{CF}$ = 254.4 Hz, C-1), 132.2 (s, C-4), 128.5 (d, $^3J_{CF}$ = 7.9 Hz, 2C, C-3, C-5), 115.6 (d, $^2J_{CF}$ = 21.4 Hz, 2C, C-2, C-6), 85.2 (d, C-4'), 48.9 (d, C-1'), 45.0 (s, C-3'), 39.3 (s, C-2'), 24.2 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.4 [q, (C-3')*C*H_3], 19.4 [q, (C-2')*C*H_3].

1-Chloro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (*rac*-35)



20 | *rac*-**35**
$C_{14}H_{18}ClNO_2$
MW = 267.70 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **20** (36.7 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for four hours at room temperature. The

crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**35** (26.5 mg, 99.0 µmol, 49%) as a pale yellow colored solid.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **20** (18.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**35** (11.5 mg, 43.0 µmol, 43%) as a pale yellow colored solid.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **20** (18.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**35** (14.4 mg, 53.8 µmol, 54%) as a pale yellow colored solid.

TLC: R_f = 0.54 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3073 (w, C_{ar}-H), 2972 (m, C_{ar}-H), 2958 (w), 1539 (vs, C-NO_2), 1494 (m, C_{sp3}-H), 1370 (s, C-NO_2), 1153 (m), 1135 (m), 1089 (m. C_{ar}-Cl), 877 (m, C_{ar}-H), 839 (s, C_{ar}-H), 767 (s, C_{ar}-H).

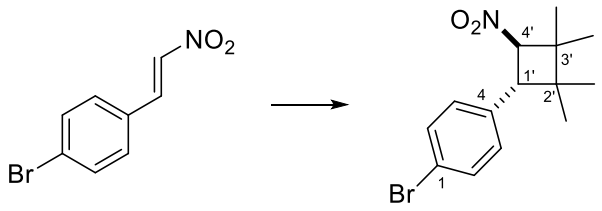
MS (EI): *m/z (%)* = 221 (29) $[C_{14}H_{18}Cl]^+$, 179 (100) $[C_{11}H_{12}Cl]^+$, 125 (64) $[C_7H_6Cl]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{18}ClNO_2^+$ $[M]^+$: 267.1021; found: 267.1021.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.33–7.29 (m, 2H, H-2, H-6), 7.06–7.02 (m, 2H, H-3, H-5), 4.85 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.92 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-2'), 1.17 (s, 3H, CH_3-3'), 1.15 (s, 3H, CH_3-2'), 0.70 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.9 (s, C-4), 133.0 (s, C-1), 128.9 (d, 2C, C-2, C-6), 128.4 (d, 2C, C-3, C-5), 84.9 (d, C-4'), 49.0 (d, C-1'), 45.1 (s, C-3'), 39.4 (s, C-2'), 24.3 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.5 [q, (C-3')*C*H_3], 19.5 [q, (C-2')*C*H_3].

1-Bromo-4-(2‘,2‘,3‘,3‘-tetramethyl-4’-nitrocyclobutyl)benzene (*rac*-36)



19 | ***rac*-36** $C_{14}H_{18}BrNO_2$ MW = 312.31 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **19** (22.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**36** (17.6 mg, 56.4 µmol, 56%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **19** (22.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**36** (18.0 mg, 56.0 µmol, 58%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **19** (22.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**36** (17.0 mg, 54.5 µmol, 55%) as a yellow colored oil.

TLC: R_f = 0.43 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962 (w, C_{ar}-H), 29225 (w, C-H), 1552 (w, C-NO_2), 1464 (w, C_{sp3}-H), 1376 (w, C-NO_2), 1259 (m), 1072 (m, C_{ar}-Br), 1010 (s), 861 (s, C_{ar}-H), 797 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 265 (20) $[C_{14}H_{18}Br]^+$, 168 (100) $[C_{14}H_{18}]^+$, 143 (56) $[C_{11}H_{11}]^+$.

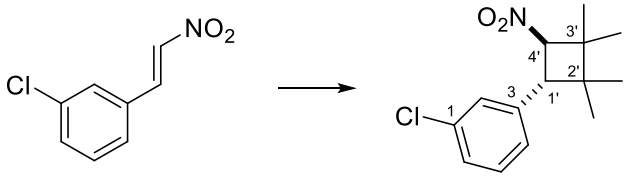
HRMS (ESI): calcd for $C_{14}H_{19}{}^{79}BrNO_2{}^+$ $[M+H]^+$: 312.0594; found: 312.0593.

calcd for $C_{14}H_{19}{}^{81}BrNO_2{}^+$ $[M+H]^+$: 314.0573; found: 314.0573.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.48–7.44 (m, 2H, H-2, H-6), 7.00–6.96 (m, 2H, H-3, H-5), 4.85 (d, ^{3}J = 10.1 Hz, 1H, H-4'), 3.90 (d, ^{3}J = 10.1 Hz, 1H, H-1'), 1.23 (s, 3H, CH_3-3'), 1.17 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.70 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.5 (s, C-1), 131.8 (d, 2C, C-2, C-6), 128.7 (d, 2C, C-3, C-5), 121.1 (s, C-4), 84.8 (d, C-4'), 49.1 (d, C-1'), 45.1 (s, C-3'), 39.4 (s, C-2'), 24.3 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.5 [q, (C-3')*C*H_3], 19.5 [q, (C-2')*C*H_3].

1-Chloro-3-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (*rac*-37)



22

rac-**37**
$C_{14}H_{18}ClNO_2$
MW = 267.75 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **22** (36.7 mg, 200 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**37** (20.4 mg, 76.2 μmol, 38%) as a colorless oil. Starting material in form of *trans*-**22** (9.60 mg, 52.3 μmol, 26%) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **22** (18.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**37** (10.3 mg, 38.5 μmol, 38%) as a colorless oil. Starting material in form of *trans*-**22** (5.00 mg, 27.2 μmol, 27%) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **22** (18.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**37** (6.90 mg, 25.8 μmol, 26%) as a colorless oil. Starting material in form of *trans*-**22** (3.90 mg, 21.2 μmol, 21%) was recovered.

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066 (w, C_{ar}-H), 2967 (m, C_{ar}-H), 1598 (m), 1538 (vs, C-NO_2), 1371 (s, C-NO_2), 1151 (m), 1138 (m), 1081 (m. C_{ar}-Cl), 877 (m, C_{ar}-H), 814 (m, C_{ar}-H), 772 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (32) $[C_{14}H_{18}Cl]^+$, 179 (100) $[C_{11}H_{12}Cl]^+$, 125 (32) $[C_7H_6Cl]^+$.

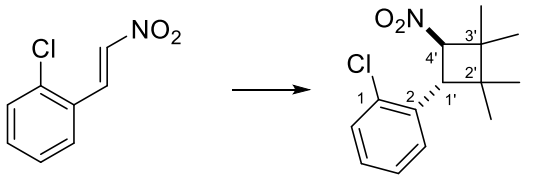
HRMS (ESI): calcd for $C_{14}H_{19}ClNO_2^+$ $[M+H]^+$: 268.1099; found: 268.1098.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29–7.22 (m, 2H, H_{ar})*, 7.09−7.08 (m, 1H, H_{ar})*, 6.99 (dtd, ^3J = 7.1 Hz, ^4J = 1.8 Hz, 0.8 Hz, 1H, H_{ar})*, 4.86 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.93 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-3'), 1.18 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.72 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.6 (s, C-3), 134.7 (s, C-1), 129.9 (d, C_{ar}H)*, 127.3 (d, C_{ar}H)*, 127.2 (d, C_{ar}H)*, 125.2 (d, C_{ar}H)*, 84.7 (d, C-4'), 49.2 (d, C-1'), 45.0 (s, C-3'), 39.5 (s, C-2'), 24.3 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.5 [q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The exact assignment of these signals was not possible.

1-Chloro-2-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (*rac*-38)



25 | ***rac*-38**
$C_{14}H_{18}ClNO_2$
MW = 267.75 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **25** (36.7 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**38** (15.2 mg, 56.8 µmol, 28%) as a colorless oil. Starting material as mixture of isomers (13.5 mg, 73.5 µmol, 39%, *cis*/*trans* = 70/30) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **25** (18.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in

dichloromethane (5 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**38** (4.96 mg, 18.5 μmol, 19%) as a colorless oil. Starting material as mixture of isomers (6.74 mg, 36.7 μmol, 37%, *cis*/*trans* = 92/8) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **25** (18.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**38** (7.46 mg, 27.9 μmol, 28%) as a colorless oil. Starting material in form of *cis*-**25** (7.94 mg, 43.2 μmol, 43%) was recovered.

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3061 (w, C_{ar}-H), 2973 (m, C_{ar}-H), 2960 (w), 1541 (vs, C-NO_2), 1372 (s, C-NO_2), 1153 (m), 1135 (m), 1033 (m. C_{ar}-Cl), 876 (m, C_{ar}-H), 807 (m, C_{ar}-H), 754 (vs, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (32) $[C_{14}H_{18}Cl]^+$, 179 (100) $[C_{11}H_{12}Cl]^+$, 125 (28) $[C_7H_6Cl]^+$.

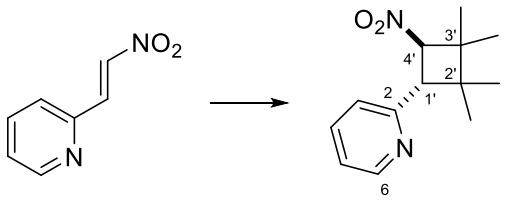
HRMS (ESI): calcd for $C_{14}H_{19}ClNO_2^+$ $[M+H]^+$: 268.1099; found: 268.1094.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.41 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, H-6), 7.28–7.18 (m, 2H, H-5, H-4), 7.16 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H, H-3), 4.99 (d, ^3J = 10.2 Hz, 1H, H-4'), 4.43 (d, ^3J = 10.2 Hz, 1H, H-1'), 1.26 (s, 3H, CH_3-2'), 1.24 (s, 3H, CH_3-3'), 1.19 (s, 3H, CH_3-3'), 0.73 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.7 (s, C-2), 134.1 (s, C-1), 130.3 (d, C-6), 128.4 (d, C-4)*, 128.1 (d, C-3), 126.8 (d, C-5)*, 84.4 (d, C-4'), 46.8 (d, C-1'), 44.5 (s, C-2'), 40.5 (s, C-3'), 24.9 [q, (C-3')*C*H_3], 22.7 [q, (C-2')*C*H_3], 21.8 [q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)pyridine (*rac*-39)



24 *rac*-**39**
$C_{13}H_{18}N_2O_2$
MW = 234.29 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **24** (15.0 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield *rac*-**39** (13.7 mg, 58.5 µmol, 58%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **24** (15.0 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield *rac*-**39** (13.4 mg, 57.2 µmol, 57%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **24** (15.0 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield *rac*-**39** (15.5 mg, 66.2 µmol, 66%) as a yellow colored oil.

TLC: R_f = 0.25 (CH_2Cl_2/MeOH = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3445 (br), 3008 (w, C_{ar}-H), 2930 (w, C-H), 1597 (w, C-NO_2), 1448 (m, C_{sp3}-H), 1386 (m, C-NO_2), 1225 (m), 1052 (s), 1025 (s), 992 (s, C_{ar}-H), 760 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 188 (100) $[C_{13}H_{18}N]^+$, 146 (72) $[C_{10}H_{12}N]^+$, 132 (40) $[C_9H_{10}N]^+$.

HRMS (ESI): calcd for $C_{13}H_{19}N_2O_2^+$ $[M+H]^+$: 235.1441; found: 235.1441.

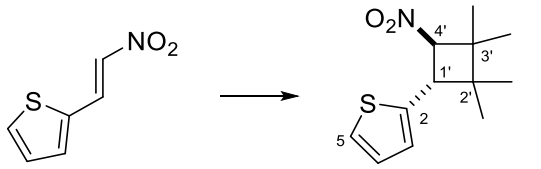
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] 8.59–8.37 (m, 2H, H-5, H-6), 7.43 (dt, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 1H, H-3), 7.31–7.27 (m, 1H, H-4), 4.90 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.96 (d,

^3J = 10.0 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-2'), 1.19 (s, 3H, CH_3-3'), 1.16 (s, 3H, CH_3-2'), 0.73 (s, 3H, CH_3-3').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 148.7 (d, C-5)*, 148.6 (d, C-6)*, 134.5 (d, C-3), 131.9 (s, C-2), 123.4 (d, C-4), 84.2 (d, C-4'), 47.4 (d, C-1'), 45.3 (s, C-3'), 39.4 (s, C-2'), 24.2 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.6 [q, (C-2')*C*H_3], 19.3 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)-thiophene (*rac*-40)



26 *rac*-**40**

$C_{12}H_{17}NO_2S$

MW = 239.33 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **26** (31.0 mg, 200 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for two hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**40** (23.8 mg, 99.4 mmol, 50%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **26** (15.5 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for two hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**40** (12.1 mg, 50.6 μmol, 51%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **26** (15.5 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for two hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**40** (20.5 mg, 85.7 μmol, 86%) as a yellow colored oil.

TLC: R_f = 0.56 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2966 (w, C-H), 2928 (w, C-H), 1539 (s, C-NO_2), 1459 (m, C_{sp3}-H), 1372 (m, C-NO_2), 1033 (w), 848 (w, C_{ar}-H), 693 (s, C-H).

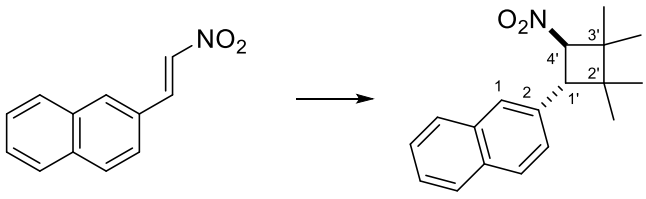
MS (EI): *m/z (%)* = 193 (62) $[C_{12}H_{17}S]^+$, 151 (42) $[C_9H_{11}S]^+$, 84 (100) $[C_4H_4S]^+$.

HRMS (EI, 70 eV): calcd for $C_{12}H_{17}NO_2S^+$ $[M]^+$: 239.0975; found: 239.0975.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.20 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1H, H-5), 6.99 (dd, ^3J = 5.1 Hz, 3.5 Hz, 1H, H-3), 6.80 (*virt*. dt, ^3J = 3.5 Hz, $^4J = {}^4J \cong$ 1.1 Hz, 1H, H-4), 4.78 (d, ^3J = 10.1 Hz, 1H, H-4'),), 4.08 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-2'), 1.13 (s, 3H, CH_3-3'), 1.12 (s, 3H, CH_3-2'), 0.83 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.5 (s, C-2), 127.2 (d, C-4), 124.5 (d, C-5), 124.3 (d, C-2), 87.1 (d, C-4'), 45.6 (d, C-1'), 45.2 (s, C-3'), 39.7 (s, C-2'), 23.6 [q, (C-2')*C*H_3], 22.8 [q, (C-3')*C*H_3], 21.4 [q, (C-2')*C*H_3], 19.3 [q, (C-3')*C*H_3].

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)napthalene (*rac*-41)



21 | ***rac*-41**
$C_{18}H_{21}NO_2$
MW = 283.37 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **21** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**41** (12.9 mg, 45.5 µmol, 46%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **21** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**41** (12.6 mg, 44.7 µmol, 44%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **21** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for three hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**41** (22.4 mg, 79.1 µmol, 79%) as a yellow colored oil.

TLC: R_f = 0.56 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954 (m, C_{ar}-H), 1537 (s, C-NO_2), 1459 (m, C_{sp3}-H), 1367 (m, C-NO_2), 1139 (w), 858 (m, C_{ar}-H), 810 (m, C_{ar}-H), 755 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 237 (28) $[C_{18}H_{21}]^+$, 181 (100) $[C_{14}H_{13}]^+$, 127 (10) $[C_{10}H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$: 284.1645; found: 284.1646.

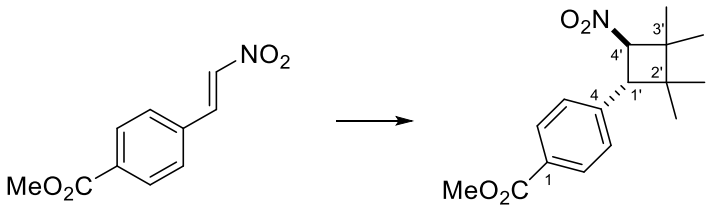
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.85–7.79 (m, 3H, H_{ar})*, 7.54–7.52 (br. s., 1H, H_{ar})*, 7.51–7.43 (m, 2H, H_{ar})*, 7.26–7.23 (m, 1H, H_{ar})*, 5.06 (d, ^3J = 10.1 Hz, 1H, H-4'), 4.14 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.28 (s, 3H, CH_3-2'), 1.26 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 0.73 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.2 (s, C-2), 133.5 (s, C-10)*, 132.6 (s, C-5)*, 128.4 (d, C_{ar})**, 127.8 (d, C_{ar})**, 126.5 (d, C_{ar})**, 125.9 (d, C_{ar})**, 125.7 (d, C_{ar})**, 125.1 (d, C_{ar})**, 85.0 (d, C-4'), 49.6 (d, C-1'), 45.1 (s, C-3'), 39.5 (s, C-2'), 24.4 [q, (C-2')*C*H_3], 22.8 [q, (C-3')*C*H_3], 21.6 [q, (C-2')*C*H_3], 19.5 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

** The exact assignment of these signals was not possible.

Methyl 4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzoate (*rac*-42)



17 *rac*-**42**
$C_{16}H_{21}NO_4$
MW = 291.34 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **17** (41.4 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for five hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield *rac*-**42** (16.8 mg, 57.7 mmol, 32%) and the side product **42a** (1.18 mg, 4.05 µmol, 2%) as a mixture (colorless solid).

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **17** (20.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for five hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield *rac*-**42** (6.45 mg, 22.1 µmol, 22%) and the side product **42a** (0.65 mg, 2.23 µmol, 2%) as a mixture (colorless solid).

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **17** (20.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield *rac*-**42** (9.47 mg, 32.5 µmol, 33%) and the side product **42a** (1.23 mg, 4.22 µmol, 4%) as a mixture (colorless solid).

TLC: R_f = 0.64 (P/Et_2O = 1/1) [UV, $KMnO_4$].

mp: 112 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954 (m, C_{ar}-H), 1717 (vs, C=O), 1541 (s, C-NO_2), 1433 (m, C_{sp3}-H), 1371 (s, C-NO_2), 1277 (s, O=C-OCH_3), 1181 (m), 1151 (m), 1138 (m), 1110 (s, O=C-OCH_3), 1017 (s), 860 (m, C_{ar}-H), 756 (s, C_{ar}-H).

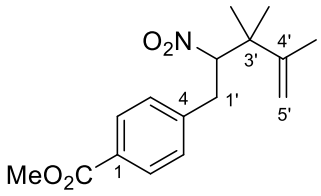
MS (EI): *m/z (%)* = 245 (92) $[C_{16}H_{21}O_2]^+$, 203 (39) $[C_{13}H_{15}O_2]^+$, 171 (51), 159 (34), 84 (100) $[C_6H_{12}]^+$, 69 (35).

HRMS (ESI): calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$ 292.1543; found: 292.1544.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.00 (d, ^3J = 7.3 Hz, 2H, H-2, H-6), 7.18 (d, ^3J = 7.3 Hz, 2H, H-3, H-5), 4.92 (d, ^3J = 9.9 Hz, 1H, H-4'), 4.01 (d, ^3J = 9.9 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 0.69 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 167.0 (s, CH_3CO_2Ar), 141.8 (s, C-1), 130.0 (d, 2C, C-2, C-6), 129.1 (s, C-4), 127.0 (d, 2C, C-3, C-5), 84.6 (d, C-4'), 53.2 (q, CH_3CO_2Ar) 49.5 (d, C-1'), 45.1 (s, C-2'), 39.7 (s, C-3'), 24.3 [q, (C-3')CH_3], 22.7 [q, (C-2')CH_3], 21.5 [q, (C-2')CH_3], 19.5 [q, (C-3')CH_3].

Methyl 4-(4'-methyl-2'-nitropent-4'-en-1'-yl)benzoate (*rac*-42a)



rac-**42a**
$C_{16}H_{21}NO_4$
MW = 291.34 g/mol

TLC: R_f = 0.70 (P/Et_2O = 1/1) [UV, $KMnO_4$].

MS (EI): *m/z (%)* = 245 (21) $[C_{16}H_{21}O_2]^+$, 229 (41) $[C_{15}H_{17}O_2]^+$, 149 (100) $[C_9H_9O_2]^+$, 121 (33) $[C_7H_5O_2]^+$, 83 (54), 55 (24).

HRMS (ESI): calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$ 292.1543; found: 292.1543.

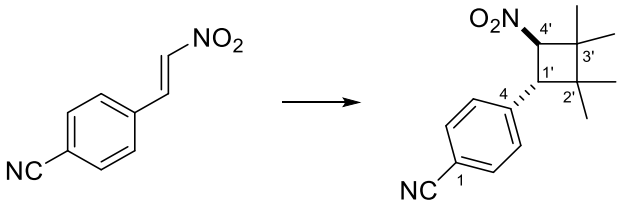
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3096 (w, C_{ar}-H), 2922 (m, C=CH_2), 2854 (m, C-H), 1721 (s, C=O), 1549 (s, C-NO_2), 1436 (m, C_{sp3}-H), 1367 (m, C-NO_2), 1278 (s, O=C-OCH_3), 1182 (m), 1109 (m, O=C-OCH_3), 759 (m, C_{ar}-H).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.95 (d, ^3J = 7.1 Hz, 2H, H-2, H-6), 7.18 (d, ^3J = 7.1 Hz, 2H, H-3, H-5), 5.01 (d, ^4J = 1.1 Hz, 2H, CH_2-5'), 4.80 (*virt*. d, $^3J = {}^3J \cong 11.9$ Hz,

1H, H-2'), 3.33 (*virt*. t, $^2J \cong {}^3J$ = 13.2 Hz, 1H, C*H*H-1'), 2.96 (d, ^2J = 14.8 Hz, 1H, CH*H*-1'), 1.87 [s, 3H, (C-4')CH_3], 1.29 [s, 3H, (C-3')CH_3], 1.23 [s, 3H, (C-3')CH_3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.9 (s, CH_3CO_2Ar), 147.6 (s, C-4'), 142.1 (s, C-4), 130.3 (d, 2C, C-3, C-5), 129.4 (s, C-1), 128.8 (d, 2C, C-2, C-6), 114.2 (t, C-5'), 96.1 (d, C-2'), 52.3 (s, CH_3CO_2Ar), 43.1 (s, C-3'), 34.9 (t, C-1'), 24.7 [q, (C-3')CH_3], 21.7 [q, (C-3')CH_3], 19.7 [q, (C-4')CH_3].

4-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)-benzonitrile (*rac*-43)



18 *rac*-**43**

$C_{15}H_{18}N_2O_2$

MW = 258.32 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **18** (34.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for five hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield *rac*-**43** (15.7 mg, 60.8 mmol, 31%) and the side product **43a** (2.64 mg, 10.2 µmol, 5%) each as a colorless solid.

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **18** (17.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield *rac*-**43** (6.70 mg, 25.9 µmol, 26%) and the side product **43a** (0.9 mg, 3.48 µmol, 3%) each as a colorless solid.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **18** (17.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for four hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield *rac*-**43** (11.4 mg, 43.9 µmol, 44%) as colorless solid. The side product **43a** was only observed in traces.

TLC: R_f = 0.62 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2967 (w, C-H), 2928 (w, C-H), 2228 (m, C-N), 1609 (m), 1539 (vs, C-NO_2), 1459 (m, C_{sp3}-H), 1369 (s, C-NO_2), 1152 (w), 849 (m, C_{ar}-H), 776 (m), 684 (w).

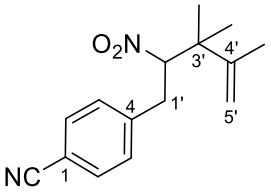
MS (EI): *m/z (%)* = 212 (24) $[C_{15}H_{18}N]^+$, 170 (100) $[C_{12}H_{12}N]^+$, 116 (19) $[C_8H_6N]^+$.

HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2^+$ $[M+H]^+$ 259.1441; found: 259.1440.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.66−7.63 (m, 2H, H-2, H-6), 7.24−7.20 (m, 2H, H-3, H-5), 4.88 (d, ^3J = 10.0 Hz, 1H, H-4'), 4.00 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-3'), 1.21 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 0.71 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 142.2 (s, C-4), 132.5 (d, 2C, C-2, C-6), 127.8 (d, 2C, C-3, C-5), 118.7 (s, N*C*), 111.2 (s, C-1), 84.4 (d, C-4'), 49.6 (d, C-1'), 45.2 (s, C-2'), 33.9 (s, C-3'), 24.3 [q, (C-3')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.5 [q, (C-2')*C*H_3], 19.4 [q, (C-2')*C*H_3].

4-(3',3',4'-Trimethyl-1'-nitropent-4'-en-2'-yl)-benzonitrile (*rac*-43a)



rac-**43a**
$C_{15}H_{18}N_2O_2$
MW = 258.32 g/mol

TLC: R_f = 0.65 (P/Et_2O = 4/1) [UV, $KMnO_4$].

MS (EI): *m/z (%)* = 196 (19) $[C_{14}H_{14}N]^+$, 170 (57) $[C_{12}H_{12}N]^+$, 116 (100) $[C_8H_6N]^+$.

HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2^+$ $[M+H]^+$ 259.1441; found: 259.1438.

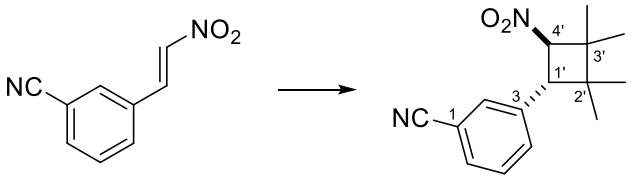
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3071 (w, C_{ar}-H), 2924 (s, C=CH_2), 2855 (s, C-H), 2229 (w, C-N), 1727 (m), 1551 (m, C-NO_2), 1376 (m, C-NO_2), 1119 (s), 862 (m).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.60−7.57 (m, 2H, H-2, H-6), 7.24−7.21 (m, 2H, H-3, H-5), 5.05−5.03 (m, 1H, CH*H*-5'), 5.00 (*virt*. t, ^4J = ^4J ≅ 0.7 Hz, 1H, CH*H*-5'), 4.77 (dd, ^3J = 11.9 Hz, 2.1 Hz, 1H, H-2'), 3.35 (dd, ^2J = 14.8 Hz, ^3J = 11.9 Hz, 1H, C*H*H-1'), 2.96 (dd,

^{2}J = 14.8 Hz, ^{3}J = 2.1 Hz, 1H, ArCH*H*-1'), 1.86 [dd, ^{4}J = 1.4 Hz, 0.7 Hz, 3H, (C-4')CH_3], 1.29 [s, 3H, (C-3')CH_3], 1.23 [s, 3H, (C-3')CH_3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 147.3 (s, C-4'), 142.3 (s, C-4), 132.8 (d, 2C, C-2, C-6), 129.6 (d, 2C, C-3, C-5), 118.7 (s, C_{ar}*C*N), 114.5 (t, C-5'), 111.5 (s, C-1), 95.8 (d, C-2'), 43.1 (s, C-3'), 34.9 (t, C-1'), 24.7 [q, (C-3')*C*H_3], 21.6 [q, (C-3')*C*H_3], 19.5 [q, (C-4')*C*H_3].

3-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)benzonitrile (*rac*-44)



23 | ***rac*-44** $C_{15}H_{18}N_2O_2$ MW = 258.32 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 4**, a solution of nitroolefin **23** (34.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) were irradiated for six hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**44** (18.2 mg, 70.5 µmol, 35%) and the side product **44a** (2.32 mg, 8.99 µmol, 11%) as an inseparable mixture (colorless liquid).

Irradiation at λ = 424 nm (LED): Following **GP 4**, a solution of nitroolefin **23** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) dichloromethane (5 mL) was irradiated for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**44** (8.84 mg, 34.2 µmol, 33%) and the side product **44a** (>1.00 mg, 3.81 µmol, 13%) as an inseparable mixture (colorless liquid).

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 4**, a solution of nitroolefin **23** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**44** (5.12 mg, 19.8 µmol, 20%) and the side product **44a** (1.00 mg, 3.87 µmol, 16%) as an inseparable mixture (colorless liquid).

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, C_{ar}-H), 2960 (m, C_{ar}-H), 2231 (m, -C≡N), 1533 (vs, C-NO_2), 1372 (s, C-NO_2), 1151 (w), 1136 (w), 793 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 212 (32) $[C_{15}H_{18}N]^+$, 170 (100) $[C_{12}H_{12}N]^+$, 116 (20) $[C_8H_6N]^+$.

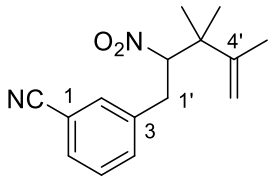
HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2^+$ $[M+H]^+$: 259.1440; found: 259.1442.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.59–7.55 (m, 1H, H_{ar})*, 7.46 (td, ^3J = 7.7 Hz, ^4J = 0.6 Hz, 1H, H_{ar})*, 7.41−7.39 (m, 1H, H_{ar})*, 7.36−7.33 (m, 1H, H_{ar})*, 4.87 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.97 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 0.71 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.2 (s, C-3), 131.5 (d, C_{ar}H)*, 130.9 (d, C_{ar}H)*, 130.6 (d, C_{ar}H)*, 129.6 (d, C_{ar}H)*, 118.7 (s, C_{ar}*C*N), 113.0 (s, C-1), 84.4 (d, C-4'), 49.1 (d, C-1'), 45.2 (s, C-3'), 39.6 (s, C-2'), 24.3 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.5[q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The exact assignment of these signals was not possible.

3-(3',3',4'-Trimethyl-2'-nitropent-4'-en-1'-yl)-benzonitrile (*rac*-44a)



rac-**44a**
$C_{15}H_{18}N_2O_2$
MW = 258.32 g/mol

TLC: R_f = 0.23 (P/Et_2O = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923 (m, C_{ar}-H), 2231 (w), 1549 (vs, C-NO_2), 1365 (m, C-NO_2), 1148 (m), 905 (m), 798 (m, C_{ar}-H), 691 (m, C_{ar}-H).

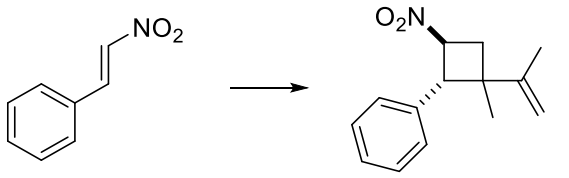
MS (EI): *m/z (%)* = 196 (15) $[C_{14}H_{14}N]^+$, 170 (58) $[C_{12}H_{12}N]^+$, 116 (100) $[C_8H_6N]^+$.

HRMS (ESI): calcd for $C_{14}H_{19}N_2O_2^+$ $[M+H]^+$: 259.1441; found: 259.1439.

^{1}H NMR (500 MHz, Chloroform-d): δ [ppm] = 7.54 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 1H, H-4)*, 7.41–7.38 (m, 2H, H-2, H-5), 7.35 (d, ^{3}J = 8.0 Hz, 1H, H-6)*, 5.04 (s, 1H, C*H*H-5'), 5.00 (s, 1H, CH*H*-5'), 4.76 (dd, ^{3}J = 12.0 Hz, 2.2 Hz, 1H, H-2'), 3.32 (dd, ^{2}J = 15.0, ^{3}J = 11.9 Hz, 1H, C*H*H-1'), 2.94 (dd, ^{2}J = 15.0, ^{3}J = 2.2 Hz, 1H, CH*H*-1'), 1.87 (d, ^{4}J = 1.4 Hz, 3H, CH_3-4'), 1.29 (s, 3H, CH_3-3'), 1.23 (s, 3H, CH_3-3').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 147.3 (s, C-4'), 138.3 (s, C-3), 133.3 (d, C-6)*, 132.4 (d, C-2), 131.2 (d, C-4)*, 129.9 (d, C-5), 118.6 (s, CN), 114.5 (t, C-5'), 113.2 (s, C-1), 96.0 (d, C-2'), 43.0 (s, C-3'), 34.4 (t, C-1'), 24.7 [q, (C-3')*C*H_3], 21.6 [q, (C-3')*C*H_3], 19.6 [q, (C-4')*C*H_3].

[2'-Methyl-4'-nitro-2'-(prop-1''-en-2''-yl)-cyclobutyl]-benzene (*rac*-5)



1 *rac*-**5**
$C_{14}H_{17}NO_2$
MW = 231.30 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 μmol, 1.00 equiv) and 2,3-dimethylbuta-1,3-diene (224 μL, 164 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 40/1) to yield *rac*-**5** (33.5 mg, 2.25 mmol, 75%, *d.r.* = 51:49) as a colorless oil. Starting material as a mixture of isomers (4.7 mg, 31.5 μmol, 16%, *cis*/*trans* = 22:78) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitrostyrene **1** (14.9 mg, 100 μmol, 1.00 equiv) and 2,3-dimethylbuta-1,3-diene (112 μL, 82.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 40/1) to yield *rac*-**5** (15.0 mg, 64.9 μmol, 65%, *d.r.* = 55:45) as a colorless oil. Starting material as a mixture of isomers (4.20 mg, 28.2 μmol, 28%, *cis*/*trans* = 27:73) was recovered.

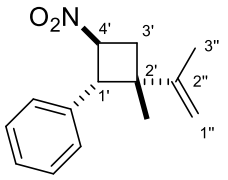
Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitrostyrene **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethylbuta-1,3-diene (112 µL, 82.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 40/1) to yield *rac*-**5** (8.80 mg, 38.1 µmol, 38%, *d.r.* = 50:50) as a colorless oil. Starting material as a mixture of isomers (6.50 mg, 28.1 µmol, 43%, *cis*/*trans* = 24:76) was recovered.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3031 (w, C_{ar}-H), 2965 (w, C-H), 2926 (w, C-H), 1638 (w), 1542 (vs, C-NO_2), 1449 (m, C_{sp3}-H), 1371 (m, C-NO_2), 1119 (w), 895 (m, $R_2C{=}CH_2$), 777 (m), 696 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 185 (19) $[C_{14}H_{17}]^+$, 117 (62) $[C_9H_9]^+$, 91 (100) $[C_7H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{17}NO_2^+$ $[M]^+$: 231.1254; found: 231.1254.

Diastereoisomer *rac*-**5**



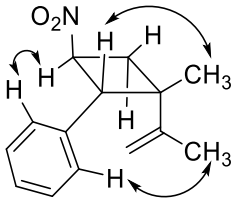
rac-**5**

TLC: R_f = 0.68 (P/Et_2O = 9/1) [UV, $KMnO_4$].

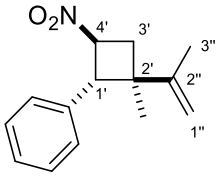
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.33–7.24 (m, 3H, *meta*-H_{ar}, *para*-H_{ar}), 7.22–7.19 (m, 2H, *ortho*-H_{ar}), 5.21 (*virt*. td, $^3J = {}^3J \cong 9.1$ Hz, $^3J = 8.3$ Hz, 1H, H-4‘), 4.93 [q, $^4J = 1.1$ Hz, 2H, (C-1‘‘)CH_2], 3.89 (br. d, $^3J = 9.3$ Hz, 1H, H-1‘), 2.92 (ddd, $^2J = 12.2$ Hz, $^3J = 8.3$ Hz, $^4J = 0.6$ Hz, 1H, CH*H*-3‘), 2.52 [s, 3H, (C-2‘)CH_3], 1.52 (dd, $^2J = 12.2$ Hz, $^3J = 9.1$ Hz, 1H, C*H*H-3‘), 1.08 [t, $^4J = 1.1$ Hz, 3H, (C-2‘‘)CH_3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 146.3 (s, C-2‘‘), 136.5 (s, C_{ar}), 128.6 (d, 2C, *meta*-C_{ar}H), 127.7 (d, *para*-C_{ar}H), 127.4 (d, 2C, *ortho*-C_{ar}H), 112.0 t, C-1‘‘), 76.6 (d, C-4’), 56.8 (d, C-1’), 44.6 (s, C-2’), 36.4 (t, C-3’), 28.7 [q, (C-2’)*C*H_3], 20.6 [q, (C-2‘‘)*C*H_3].

significant NOE contacts



Diastereoisomer *rac*-**5'**



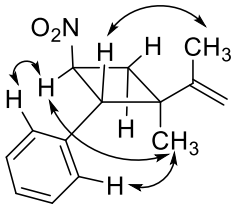
rac-**5'**

TLC: R_f = 0.60 (P/Et_2O = 9/1) [$KMnO_4$].

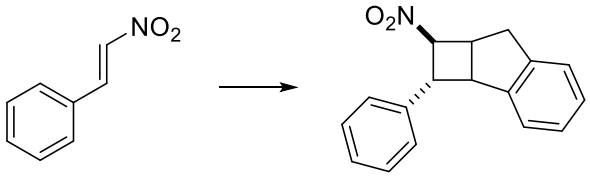
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.33–7.38 (m, 3H, *meta*-H_{ar}, *para*-H_{ar}), 7.24–7.32 (m, 2H, *ortho*-H_{ar}), 5.26 (*virt*. q, $^3J = {}^3J \cong 8.7$ Hz, 1H, H-4‘), 4.91–4.93 [m, 2H, (C-1‘‘)CH_2], 4.26 (d, ^3J = 9.1 Hz, 1H, H-1‘), 2.75 (dd, ^2J = 11.4 Hz, ^3J = 8.7 Hz, 1H, CH*H*-3‘), 2.39 (ddd, ^2J = 11.4 Hz, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 1H, C*H*H-3‘), 1.80 [dd, ^4J = 1.4, 0.8 Hz, 3H, (C-2‘‘)CH_3], 1.04 [br. d, ^4J = 0.7 Hz, 3H, (C-2‘)CH_3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 150.9 (s, C-2‘‘), 136.8 (s, C_{ar}), 128.7 (d, 2C, *meta*-C_{ar}H), 127.7 (d, 2C, *ortho*-C_{ar}H), 127.4 (d, *para*-C_{ar}H), 110.1 t, C-1‘‘), 76.9 (d, C-4’), 53.0 (d, C-1’), 42.5 (s, C-2’), 37.1 (t, C-3’), 21.6 [q, (C-2’)*C*H_3], 18.9 [q, (C-2‘‘)*C*H_3].

significant NOE contacts:



1-Nitro-2-phenyl-1,2,2a,7a-tetrahydro-1*H*-cyclobuta[a]indene (rac-7)



1 *rac*-**7**
$C_{17}H_{15}NO_2$
MW = 265.31 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and indene (234 µL, 232 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for 23 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 100/1) to yield *rac*-**7** (46.2 mg, 174 µmol, 87%, *d.r.* = 72:28) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and indene (117 µL, 116 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 23 hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 100/1) to yield *rac*-**7** (18.0 mg, 67.8 µmol, 68%, *d.r.* = 72:28) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and indene (117 µL, 116 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 23 hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 100/1) to yield *rac*-**7** (19.1 mg, 71.2 µmol, 72%, *d.r.* = 44:56) as a yellow colored oil.

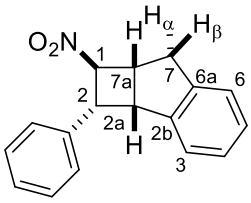
TLC: R_f = 0.19 (P/Et_2O = 100/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3064 (w, C_{ar}-H), 3028 (w, C_{ar}-H), 2921 (w, C-H), 2847 (w, C-H), 1537 (vs, C-NO_2), 1372 (s, C-NO_2), 759 (m, CH_2), 725 (w, C_{ar}-H), 697 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 219 (20) $[C_{17}H_{15}]^+$, 141 (12) $[C_{11}H_9]^+$, 116 (100) $[C_9H_8]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{15}NO_2^+$ $[M]^+$: 265.1097; found: 265.1097.

Diastereoisomer *rac*-**7**



rac-**7**

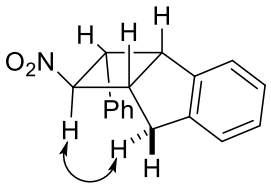
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.34−7.14 (m, 5H, H_{ar})*, 6.99–6.89 (m, 3H, H_{ar})*, 6.46 (d, ^3J = 7.6 Hz, 1H, H_{ar})*, 4.91 (ddd, ^3J = 9.2 Hz, 6.5 Hz, ^4J = 1.0 Hz, 1H, H-1), 4.54 (*virt.* t, $^3J = {}^3J \cong$ 9.4 Hz, 1H, H-2), 4.18 (*virt.* t, $^3J = {}^3J \cong$ 8.4 Hz, 1H, H-2a), 3.75 (*virt.* q, $^3J = {}^3J \cong$ 6.9 Hz, 1H, H-7a), 3.30 (dd, ^2J = 16.8 Hz, ^3J = 6.8 Hz, 1H, H*H*-7$_\beta$), 3.19 (d, ^2J = 16.8 Hz, 1H, *H*H-7$_\alpha$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.1 (s, C-2b)**, 139.6 (s, C-6a)**, 136.1 (s, C_{ar}), 128.3 (d, 2C, *meta*-C_{ar}H)†, 127.9 (d, C_{ar}H)*, 127.7 (d, 2C, *ortho*-C_{ar}H)†, 127.6 (d, C_{ar}H)*, 127.4 (d, C_{ar}H)*, 126.5 (d, C_{ar}H)*, 125.7 (d, C_{ar}H)*, 84.8 (d, C-1), 48.8 (d, C-2), 45.9 (d, C-2a), 42.3 (d, C-7a), 37.5 (t, C-7).

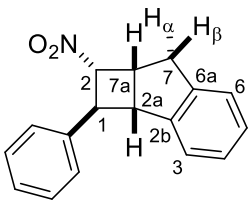
* The exact assignment of these signals was not possible.

**,† The assignments are interconvertible.

significant NOE contacts:



Diastereoisomer *rac*-**7'**



rac-**7'**

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.41–7.38 (m, 2H, H_{ar})*, 7.34–7.30 (m, 4H, H_{ar})*, 7.25–7.19 (m, 3H, H_{ar})*, 5.24 (*virt.* t, $^3J = {}^3J \cong$ 8.9 Hz, 1H, H-1), 4.13 (*virt.* t, $^3J = {}^3J \cong$ 7.7 Hz,

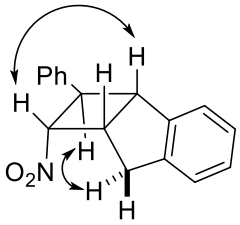
1H, H-2), 3.84–3.77 (m, 1H, H-7a), 3.74 (*virt.* t, $^3J = {}^3J \cong 7.1$ Hz, 1H, H-2a), 3.37 (dd, ^2J = 17.8 Hz, ^3J = 10.2 Hz, 1H, *H*H-7$_\alpha$), 3.08 (dd, ^2J = 17.8 Hz, ^3J = 5.0 Hz, 1H, H*H*-7$_\beta$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 144.8 (s, C-2b)†, 144.2 (s, C-6a)†, 139.8 (s, C_{ar}), 129.1 (d, 2C, *meta*-C_{ar}H)**, 127.6 (d, C_{ar}H)*, 127.5 (d, C_{ar}H)*, 127.3 (d, 2C, *ortho*-C_{ar}H)**, 126.6 (d, C_{ar}H)*, 125.5 (d, C_{ar}H)*, 123.7 (d, C_{ar}H)*, 82.0 (d, C-1), 52.0 (d, C-2), 46.5 (d, C-2a), 40.8 (d, C-7a), 33.8 (t, C-7).

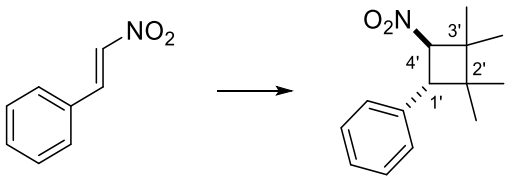
* The exact assignment of these signals is not possible.

**,† The assignments are interconvertible.

significant NOE contacts:



(2‘,2‘,3‘,3‘-Tetramethyl-4‘-nitrocyclobutyl)-benzene (*rac*-31)



1 *rac*-**31**

$C_{14}H_{19}NO_2$

MW = 233.31 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (234 µL, 166 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 20/1) to yield *rac*-**31** (26.9 mg, 1.16 mmol, 59%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitrolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) were irradiated for twelve hours at room temperature. The crude

product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield *rac*-**31** (12.2 mg, 52.3 µmol, 53%) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield *rac*-**31** (13.0 mg, 55.7 µmol, 56%) as a yellow colored oil.

TLC: R_f = 0.41 (P/Et_2O = 20/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3061 (w, C_{ar}-H), 3029 (w, C_{ar}-H), 2965 (m, C-H), 2928 (w, C-H), 1593 (vs, C-NO_2), 1463 (m, C_{sp3}-H), 1369 (s, C-NO_2), 742 (m), 698 (s, C_{ar}-H).

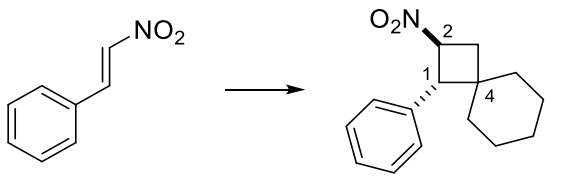
MS (EI): *m/z (%)* = 187 (35) $[C_{14}H_{19}]^+$, 145 (100) $[C_{11}H_{13}]^+$, 91 (39) $[C_7H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{19}NO_2^+$ $[M]^+$: 233.1410; found: 233.1415.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.37–7.30 (m, 2H, *meta*-H_{ar}), 7.28–7.23 (m, 1H, *para*-H_{ar}), 7.13–7.08 (m, 2H, *ortho*-H_{ar}), 4.91 (d, ^3J = 10.1 Hz, 1H, H-4'), 3.97 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-3'), 1.19 (s, 3H, CH_3-2'), 1.15 (s, 3H, CH_3-3'), 0.71 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C_{ar}), 128.6 (d, 2C, *meta*-C_{ar}H), 127.1 (d, *para*-C_{ar}H), 127.0 (d, 2C, *ortho*-C_{ar}H), 84.9 (d, C-4'), 49.4 (d, C-1'), 44.9 (s, C-3'), 39.3 (s, C-2'), 24.3 (q, CH_3-2'), 22.8 (q, CH_3-3'), 21.5 (q, CH_3-2'), 19.5 (q, CH_3-3').

2-Nitro-1-phenylspiro[3.5]nonane (*rac*-45)



1 *rac*-**45**
$C_{15}H_{19}NO_2$
MW = 245.32 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and methylenecyclohexane (240 µL, 192 mg, 2.00 mmol,

10.0 equiv) in dichloromethane (10 mL) was irradiated for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**45** (24.7 mg, 1.01 mmol, 51%) as a colorless oil. Starting material in form of *trans*-β-nitrostyrene (6.00 mg, 40.2 μmol, 20%) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and methylenecyclohexane (136 μL, 96.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**45** (11.8 mg, 48.1 μmol, 48%) as a colorless oil. Starting material as mixture of isomers (1.65 mg, 11.1 μmol, 11%, *cis*/*trans* = 12/88) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and methylenecyclohexane (136 μL, 96.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 14 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**45** (15.0 mg, 61.9 μmol, 61%) as a colorless oil. Starting material as a mixture of isomers (6.64 mg, 42.9 μmol, 43%, *cis*/*trans* = 12:88) was recovered.

TLC: R_f = 0.57 (P/Et_2O = 19/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3062 (w, C_{ar}-H), 2925 (m, C_{sp2}-H), 2852 (w, C_{sp2}-H), 1542 (s, C-NO_2), 1449 (m, C_{sp3}-H), 1370 (m, C-NO_2), 1032 (w), 847 (w, C_{ar}-H), 698 (s, C_{ar}-H).

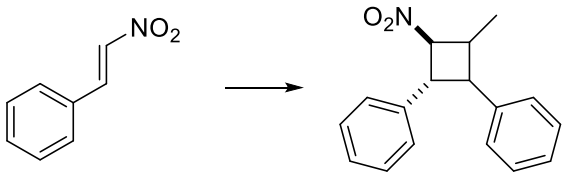
MS (EI): *m/z (%)* = 199 (6) $[C_{15}H_{19}]^+$, 117 (100) $[C_9H_9]^+$, 91 (19) $[C_7H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{15}H_{19}NO_2^+$ $[M]^+$: 245.1410; found: 245.1406.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.36−7.33 (m, 2H, *meta*-H_{ar}), 7.29−7.26 (m, 1H, *para*-H_{ar}), 7.20−7.10 (m, 2H, *ortho*-H_{ar}), 5.27 (virt. q, $^3J = {}^3J \cong 8.6$ Hz, 1H, H-2), 3.81 (d, ^3J = 9.2 Hz, 1H, H-1), 2.49 (dd, ^2J = 11.6 Hz, ^3J = 8.5 Hz, 1H, CH*H*-3),), 2.37 (dd, ^2J = 11.6 Hz, ^3J = 8.6 Hz, 1H, C*H*H-3), 1.82−1.78 (m, 1H, $H_{cyclohexyl}$), 1.72−1.66 (m, 1H, $H_{cyclohexyl}$), 1.67−1.52 (m, 2H, $H_{cyclohexyl}$), 1.48−1.43 (m, 1H, $H_{cyclohexyl}$), 1.36−1.20 (m, 3H, $H_{cyclohexyl}$), 1.13–0.98 (m, 1H, $H_{cyclohexyl}$), 0.94−0.87 (m, 1H, $H_{cyclohexyl}$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.0 (s, C_{ar}), 128.6 (d, 2C, *meta*-$C_{ar}H$), 127.3 (d, 2C, *ortho*-$C_{ar}H$), 127.2 (d, *para*-$C_{ar}H$), 76.4 (d, C-2), 56.1 (d, C-1), 40.6 (t, CH_2), 39.4 (s, C-4), 35.6 (t, C-3), 32.3 (t, CH_2), 25.7 (t, CH_2), 23.0 (t, CH_2), 22.3 (t, CH_2).

(3'-Methyl-4'-nitrocyclobutane)-1,2-diyl-dibenzene (*rac*-46)



1 *rac*-**46**
$C_{17}H_{17}NO_2$
MW = 267.33 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and *trans*-β-methylstyrene (259 µL, 236 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield *rac*-**46** (28.1 mg, 1.05 mmol, 53%, *d.r.* = 46:54) as a colorless oil. Starting material in form of *cis*-β-nitrostyrene (6.60 mg, 42.3 µmol, 22%) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5** a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and *trans*-β-methylstyrene (130 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 50/1) to yield *rac*-**46** (14.6 mg, 54.6 µmol, 53%, *d.r.* = 49:51) as a colorless oil. Starting material in form of *cis*-β-nitrostyrene (3.03 mg, 20.3 µmol, 20%) was recovered.

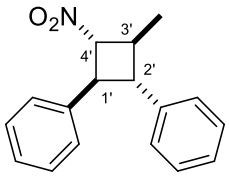
Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and *trans*-β-methylstyrene (130 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 50/1) to yield *rac*-**46** (10.7 mg, 40.0 µmol, 40%, *d.r.* = 64:36) as a colorless oil. Starting material in form of *cis*-β-nitrostyrene (2.80 mg, 18.8 µmol, 19%) was recovered.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3062 (w, C_{ar}-H), 3030 (w, C_{ar}-H), 2962 (w, C-H), 2926 (w, C-H), 1539 (s, C-NO_2), 1452 (m, C_{sp3}-H), 1366 (m, C-NO_2), 1148 (w), 845 (w), 750 (s, C_{ar}-H), 695 (vs, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (59) $[C_{17}H_{17}]^+$, 131(75) $[C_{10}H_{11}]^+$, 118 (100) $[C_9H_{10}]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{17}NO_2^+$ $[M]^+$: 267.1254; found: 267.1255.

Diastereoisomer *rac*-**46**



rac-**46**

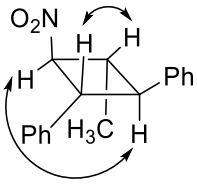
TLC: R_f = 0.47 (P/Et_2O = 19/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.10–6.99 (m, 8H, H_{ar}), 6.94−6.92 (m, 2H, H_{ar}), 4.11 (*virt*. t, $^3J = {}^3J \cong$ 8.5 Hz, 1H, H-4‘), 3.93 (dd, ^3J = 9.8 Hz, 8.5 Hz, 1H, H-1‘), 2.59 (ddq, ^3J = 9.6 Hz, 8.2 Hz, 6.6 Hz, 1H, H-3‘), 2.46 (virt. t, $^3J = {}^3J \cong$ 9.8 Hz, 1H, H-2‘), 0.88 (d, ^3J = 6.6 Hz, 3H, CH_3).

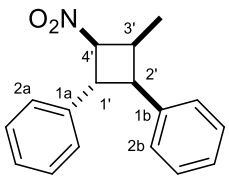
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 140.8 (s, C_{ar}), 139.6 (s, C_{ar}), 129.0 (d, 2C, C_{ar}H)*, 128.9 (d, 2C, C_{ar}H)*, 127.5 (d, C_{ar}H)*, 127.4 (d, C_{ar}H)*, 127.2 (d, 2C, C_{ar}H)*,126.9 (d, 2C, C_{ar}H)*, 85.2 (d, C-4’), 50.2 (d, C-1’), 47.2 (d, C-2’), 43.1 (d, C-3’), 17.4 (q, CH_3).

* The exact assignment of these signals was not possible.

significant NOE contacts:



Diastereoisomer *rac*-**46’**



rac-**46'**

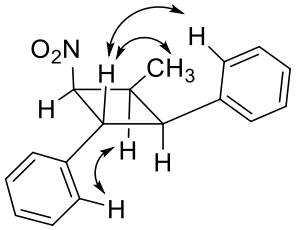
TLC: R_f = 0.43 (P/Et_2O = 19/1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.60−7.16 (m, 6H, H_{ar})*, 6.94−6.91 (m, 2H, H-2b), 6.88−6.86 (m, 2H, H-2a), 5.53 (dd, ^3J = 9.4 Hz, 7.7 Hz, 1H, H-4‘), 4.80 (dd, ^3J = 10.7 Hz, 7.7 Hz, 1H, H-1‘), 3.72 (dd, ^3J = 10.7 Hz, 5.4 Hz, 1H, H-2‘), 3.38 (dqd, ^3J = 9.4 Hz, 7.1 Hz, 5.4 Hz, 1H, H-3‘), 1.37 (d, ^3J = 7.1 Hz, 3H, CH_3).

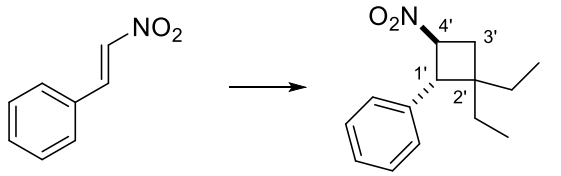
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 138.7 (s, C-1b), 136.5 (s, C-1a), 128.4 (d, 2C, $C_{ar}H$)*, 128.3 (d, 2C, $C_{ar}H$)*, 128.1 (d, 2C, $C_{ar}H$)*, 127.6 (d, 2C, $C_{ar}H$)*, 126.9 (d, $C_{ar}H$)*, 126.7 (d, $C_{ar}H$)*, 82.9 (d, C-4’), 47.4 (d, C-1’), 45.6 (d, C-2’), 38.1 (d, C-3’), 15.3 (q, CH_3).

* The exact assignment of these signals is not possible.

significant NOE contacts:



(2’,2’-Diethyl-4’-nitrocyclobutyl)benzene (*rac*-47)



1 *rac*-**47**
$C_{14}H_{19}NO_2$
MW = 233.31 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and 1,1-diethylethylene (244 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 30/1) to yield *rac*-**47** (20.7 mg, 88.7 mmol, 44%) as a yellow colored oil. Starting material as a mixture of isomers (4.70 mg, 31.5 µmol, 16%, *cis*/*trans* = 44:56) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 1,1-diethylethylene (122 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in

dichloromethane (5 mL) was irradiated for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 30/1) to yield *rac*-**47** (5.80 mg, 24.9 μmol, 25%) as as a yellow colored oil. Starting material as a mixture of isomers (9.50 mg, 63.7 μmol, 63%, *cis*/*trans* = 44:56) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and 1,1-diethylethylene (122 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 14 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 30/1) to yield *rac*-**47** (7.50 mg, 32.2 μmol, 32%) as as a yellow colored oil. Starting material as a mixture of isomers (5.70 mg, 38.2 μmol, 38%, *cis*/*trans* = 36:64) was recovered.

TLC: R_f = 0.45 (P/Et_2O = 19/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3030 (w, C_{ar}-H), 2965 (w, C-H), 1542 (vs, C-NO_2), 1455 (m, C_{sp3}-H), 1366 (m, C-NO_2), 784 (m, C_{ar}-H).

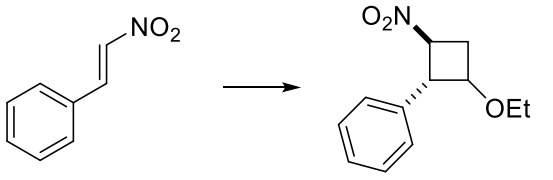
MS (EI): *m/z (%)* = 187 (4) $[C_{14}H_{19}]^+$, 157 (12) $[C_{12}H_{13}]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{14}H_{20}NO_2^+$ $[M+H]^+$: 234.1488; found: 234.1489.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.34 (t, ^3J = 7.5 Hz, 2H, *meta*-H_{ar}), 7.29–7.24 (m, 1H, *para*-H_{ar}), 7.23–7.20 (m, 2H, *ortho*-H_{ar}), 5.27 (*virt*. q, ^3J = ^3J ≅ 8.7 Hz, 1H, H-4'), 3.98 (d, ^3J = 9.1 Hz, 1H, H-1'), 2.40 (dd, ^2J = 11.9 Hz, ^3J = 8.5 Hz, 1H, C*H*H-3), 2.30 (dd, ^2J = 11.9 Hz, ^3J = 8.6 Hz, 1H, CH*H*-3), 1.76 (dq, ^2J = 14.8 Hz, ^3J = 7.5 Hz, 1H, C*H*HCH_3), 1.64 (dq, ^2J = 14.8 Hz, ^3J = 7.5 Hz, 1H, CH*H*CH_3), 1.30–1.19 (m, 2H, C$H_2$$CH_3$), 0.96 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 0.60 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.6 (s, C_{ar}), 128.6 (d, 2C, *meta*-C_{ar}H), 127.5 (d, 2C, *ortho*-C_{ar}H), 127.2 (d, *para*-C_{ar}H), 76.6 (d, C-4'), 53.8 (d, C-1'), 41.8 (s, C-2'), 33.7 (t, C-3'), 31.7 (t, *C*$H_2$$CH_3$), 26.4 (t, *C*$H_2$$CH_3$), 8.62 (q, CH_2*C*H_3), 7.98 (q, CH_2*C*H_3).

2-Ethoxy-4-nitrocyclobutylbenzene (*rac*-48)



1 *rac*-**48**
$C_{12}H_{15}NO_3$
MW = 221.25 g/mol

Irradiation at λ = 419 nm (Fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and ethylvinylether (191 µL, 144 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for seven hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield *rac*-**48** (18.8 mg, 85.0 µmol, 43%, *d.r.* = 58:42) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and ethylvinylether (95.7 µL, 72.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for seven hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield *rac*-**48** (8.03 mg, 36.3 µmol, 36%, *d.r.* = 62:38) as a yellow colored oil. Starting material as a mixture of isomers (3.00 mg, 20.1 µmol, 20%, *cis*/*trans* = 88:12) was recovered.

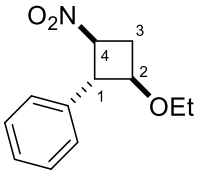
Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and ethylvinylether (95.7 µL, 72.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for seven hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield *rac*-**48** (7.52 mg, 33.4 µmol, 33%, *d.r.* = 66:34) as a yellow colored oil. Starting material as a mixture of isomers (7.20 mg, 32.6 µmol, 48%, *cis*/*trans* = 69:31) was recovered.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3031 (w, C_{ar}-H), 2967 (w, C-H), 2925(w, C-H), 1542 (s, C-NO_2), 1454 (w), 1370 (m, C-NO_2), 1112 (m, C-O-C), 804 (w), 698 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 175 (3) $[C_{12}H_{15}O]^+$, 129 (86), 117 (100) $[C_9H_9]^+$, 91 (56) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{12}H_{16}NO_3^+$ $[M+H]^+$ 222.1125; found: 222.1122.

Diastereoisomer *rac*-**48**



rac-**48**

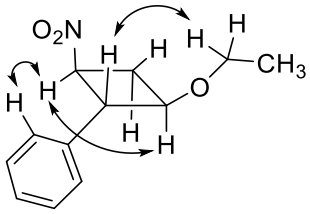
TLC: R_f = 0.47 (P/Et_2O = 4/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.37−7.27 (m, 5H, H_{ar}), 5.38 (*virt*. q, $^3J = {}^3J \cong$ 8.1 Hz, 1H, H-4), 4.36 (*virt*. td, $^3J = {}^3J \cong$ 6.9 Hz, ^3J = 2.2 Hz, 1H, H-2), 4.17 (*virt*. br.t, $^3J = {}^3J \cong$ 7.4 Hz, 1H, H-1), 3.24 (dq, ^2J = 9.2 Hz, ^3J = 7.0 Hz, 1H, OCH*H*CH_3), 2.98 (dq, ^2J = 9.2 Hz, ^3J = 7.0 Hz, 1H, OC*H*HCH_3), 2.95−2.89 (m, 1H, CH*H*-3), 2.58 (ddd, ^2J = 13.3 Hz, ^3J = 8.6 Hz, 2.2 Hz, 1H, C*H*H-3), 0.98 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3).

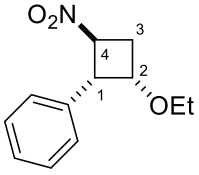
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.2 (s, C_{ar}). 128.6 (d, 2C, *meta*-C_{ar}H)*, 128.5 (d, 2C, *ortho*-C_{ar}H)*, 127.7 (d, *para*-C_{ar}H), 80.4 (d, C-4), 72.7 (d, C-2), 65.2 (t, OCH_2CH_3), 52.2 (d, C-1), 33.7 (t, C-3), 14.9 (q, OCH_2CH_3).

* The assignments are interconvertible.

significant NOE contacts:



Diastereoisomer *rac*-**48'**



rac-**48'**

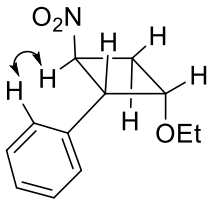
TLC: R_f = 0.57 (P/Et_2O = 4/1) [$KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.38−7.34 (m, 2H, *meta*-H_{ar}). 7.31−7.28 (m, 3H, *ortho*-H_{ar}, *para*-H_{ar}), 4.64 (*virt*. q, $^3J \approx$ 8.5 Hz, 1H, H-4), 4.02 (*virt*. t, $^3J = {}^3J \cong$ 7.9 Hz, 1H, H-1), 3.92 (*virt*. q, $^3J = {}^3J \cong$ 7.5 Hz, 1H, H-2), 3.74 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 2.92 (*virt*.

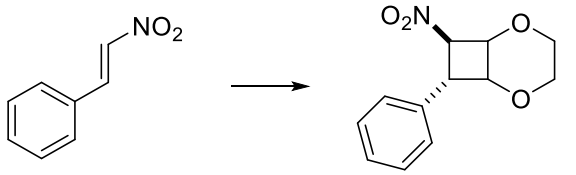
dt, ^2J = 11.7 Hz, $^3J = {}^3J \cong$ 7.2 Hz, 1H, CH*H*-3), 2.64 (*virt*. dt, ^2J = 11.7 Hz, $^3J = {}^3J \cong$ 8.4 Hz, 1H, C*H*H-3), 1.19 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.5 (s, C_{ar}), 129.0 (d, 2C, *meta*-$C_{ar}H$), 127.8 (d, *para*-$C_{ar}H$), 126.7 (d, 2C, *ortho*-$C_{ar}H$), 75.7 (d, C-4), 71.5 (d, C-2), 66.6 (t, OCH_2CH_3), 55.7 (d, C-1), 34.2 (t, C-3), 15.4 (q, OCH_2CH_3).

significant NOE contacts:



7-Nitro-8-phenyl-2,5-dioxabicyclo[4.2.0]octane (*rac*-49)



1 *rac*-**49**
$C_{12}H_{13}NO_4$
MW = 235.24 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (159 µL, 172 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield *rac*-**49** (34.0 mg, 145 µmol, 72%, *d.r.* = 52:19:29) as an orange colored oil. Starting material as a mixture of isomers (4.50 mg, 30.2 µmol, 15%, *cis*/*trans* = 53/47) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (80.0 µL, 86 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield *rac*-**49** (12.7 mg, 54.0 µmol, 54%, *d.r.* = 58:19:23) as an orange colored oil. Starting material as a mixture of isomers (5.00 mg, 33.5 µmol, 34%, *cis*/*trans* = 55/45) was recovered.

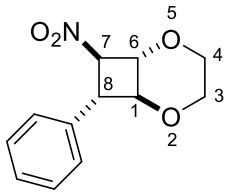
Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (80.0 µL, 86 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield *rac*-**49** (6.1 mg, 25.9 µmol, 26%, *d.r.* = 58:19:23) as an orange colored oil. Starting material as a mixture of isomers (5.90 mg, 39.6 µmol, 39%, *cis*/*trans* = 54/46) was recovered.

TLC: R_f = 0.06 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3031 (w, C_{ar}-H), 2923 (w, C_{ar}-H), 1545 (s, C-NO_2), 1375 (m, C-NO_2), 1132 (m, C-O-C), 1043 (m), 874 (m, C_{ar}-H), 751 (m, C_{ar}-H).

HRMS (ESI): calc. for $C_{12}H_{14}NO_2^+$ $[M+H]^+$: 236.0917; found.: 236.0918.

Diastereoisomer *rac*-**49**



rac-**49**

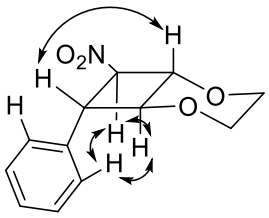
MS (EI): *m/z (%)* = 235 (16) $[C_{12}H_{13}NO_4]^+$, 189 (52) $[C_{12}H_{13}O_2]^+$, 117 (72) $[C_9H_9]^+$, 91 (100) $[C_7H_7]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.02–6.93 (m, 5H, H_{ar}), 4.26 (*virt*. t, $^3J = {}^3J \cong$ 7.8 Hz, 1H, H-7), 3.81 (*virt*. t, $^3J = {}^3J \cong$ 8.6 Hz, 1H, H-6), 3.56 (dd, ^3J = 9.8 Hz, 7.3 Hz, 1H, H-8), 3.40–3.28 (m, 2H, C*H*H-3, C*H*H-4), 3.19–3.15 (m, 2H, CH*H*-3, CH*H*-4), 2.99 (d, ^3J = 9.8 Hz, 1H, H-1).

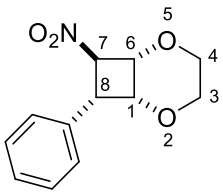
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 136.5 (s, C_{ar}), 129.0 (d, 2C, *ortho*-C_{ar}H)*, 127.9 (d, 2C, *meta*-C_{ar}H)*, 126.9 (d, *para*-C_{ar}H), 82.3 (d, C-7), 77.9 (d, C-6), 75.2 (d, C-1), 68.3 (t, C-3), 68.1 (t, C-4), 51.2 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



Diastereoisomer *rac*-**49'**



rac-**49'**

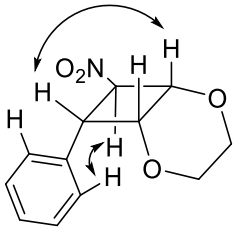
MS (EI): *m/z (%)* = 189 (20) $[C_{12}H_{13}O_2]^+$, 117 (40) $[C_9H_9]^+$, 86 (100) $[C_4H_6O_2]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.13–7.04 (m, 5H, H_{ar}), 5.53 (dd, ^3J = 9.4 Hz, 7.1 Hz, 1H, H-7), 4.11 (dd, ^3J = 7.1 Hz, 4.8 Hz, 1H, H-6), 3.71 (*virt*. t, $^3J = {}^3J \cong$ 5.0 Hz, 1H, H-1), 3.25–3.20 (m, 2H, H-8, C*H*H-4), 2.97–2.93 (m, 1H, CH*H*-4), 2.92−2.88 (m, 1H, C*H*H-3), 2.83 (dd, ^2J = 12.0 Hz, ^4J = 2.8 Hz, 1H, CH*H*-3).

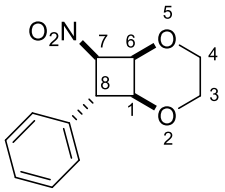
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 134.2 (s, C_{ar}), 128.6 (d, 2C, *ortho*-C_{ar}H)*, 128.0 (d, 2C, *meta*-C_{ar}H)*, 127.5 (d, *para*-C_{ar}H), 82.5 (d, C-7), 69.9 (d, C-6), 69.3 (d, C-1), 63.3 (t, C-3), 61.4 (t, C-4), 43.3 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



Diastereoisomer *rac*-**49''**



rac-**49"**

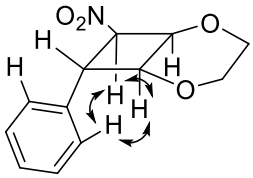
MS (EI): *m/z (%)* = 189 (40) $[C_{12}H_{13}O_2]^+$, 145 (12) $[C_{10}H_9O]^+$, 117 (88) $[C_9H_9]^+$, 86 (100) $[C_4H_6O_2]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.12–6.98 (m, 5H, H_{ar}), 4.95 (*virt*. t, $^3J = {}^3J \cong 9.0$ Hz, 1H, H-8), 4.09–4.05 (m, 1H, H-6), 3.73 (dd, $^3J = 9.0$ Hz, 5.0 Hz, 1H, H-7), 3.46 (dd, $^3J = 9.0$ Hz, 4.2 Hz, 1H, H-1), 3.44–3.36 (m, 1H, C*H*H-3), 3.05–2.97 (m, 2H, CH_2-4), 2.93 (dt, ^2J =11.8 Hz, $^4J = 1.6$ Hz, 1H, CH*H*-3).

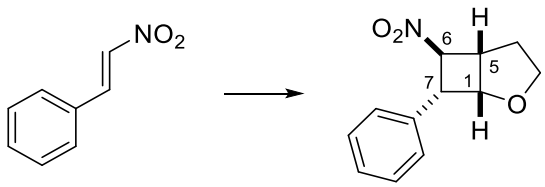
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 138.8 (s, C_{ar}), 128.9 (d, 2C, *ortho*-C_{ar}H)*, 127.4 (d, *para*-C_{ar}H), 126.7 (d, 2C, *meta*-C_{ar}H)*, 77.0 (d, C-7), 71.4 (d, C-6), 66.9 (d, C-1), 63.6 (t, C-4), 60.2 (t, C-3), 45.2 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



6-Nitro-7-phenyl-2-oxabicyclo[3.2.0]heptane (*rac*-50)



1

rac-**50**

$C_{12}H_{13}NO_3$

MW = 219.24 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 μmol, 1.00 equiv) and 2,3-dihydrofurane (152 μL, 140 mg, 2.00 mmol,

10.0 equiv) in dichloromethane (10 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1 → 4/1) to yield *rac*-**50** (15.7 mg, 71.6 µmol, 36%) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (2.30 mg, 15.2 µmol, 8%) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydrofurane (75.5 µL, 70.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1 → 4/1) to yield *rac*-**50** (8.10 mg, 36.9 µmol, 37%) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (2.00 mg, 13.4 µmol, 13%) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydrofurane (75.5 µL, 70.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1 → 4/1) to yield the product *rac*-**50** (6.00 mg, 27.4 µmol, 27%) as yellow colored oil. Starting material as a mixture of isomers (6.60 mg, 44.3 µmol, 44%, *cis*/*trans* = 64:36) was recovered.

TLC: R_f = 0.27 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060 (w, C_{ar}-H), 3036 (w, C_{ar}-H), 2955 (w, C-H), 2866 (w, C-H), 1540 (s, C-NO_2), 1497 (m, C_{sp3}-H), 1372 (m, C-NO_2), 1087 (s, C-O-C), 947 (w), 747 (m, C_{ar}-H), 696 (s, C_{ar}-H).

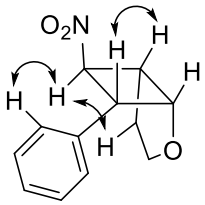
MS (EI): *m/z (%)* = 173 (5) $[C_{12}H_{13}O]^+$, 155 (100) $[C_{12}H_{11}]^+$, 143 (70) $[C_{11}H_{11}]^+$, 91 (38) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{12}H_{14}NO_3^+$ $[M+H]^+$: 220.0968; found: 220.0968.

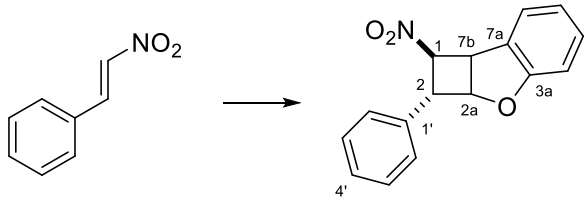
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.29−7.23 (m, 2H, *meta*-H_{ar}), 7.20−7.15 (m, 3H, *ortho*-H_{ar}, *para*-H_{ar}), 4.89 (*virt*. t, $^3J = {}^3J \cong$ 6.3 Hz, 1H, H-1), 4.82 (dd, ^3J = 8.2 Hz, 5.3 Hz, 1H, H-6), 4.21 (*virt*. t, $^3J = {}^3J \cong$ 7.4 Hz, 1H, H-7), 4.00 (ddd, ^2J = 9.8 Hz, ^3J = 7.7 Hz, 2.2 Hz, 1H, CH*H*-3), 3.61−3.55 (m, 1H, H-5), 3.50 (*virt*. dt, ^2J = 9.8 Hz, $^3J = {}^3J \cong$ 5.8 Hz, 1H, C*H*H-3), 1.95−1.92 (m, 1H, C*H*H-4), 1.91−1.82 (m, 1H, CH*H*-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.4 (s, C_{ar}), 128.7 (d, 2C, *meta*-C_{ar}H), 127.3 (d, *para*-C_{ar}H), 127.1 (d, 2C, *ortho*-C_{ar}H), 85.0 (d, C-6), 76.7 (d, C-1), 69.3 (t, C-3), 48.8 (d, C-7), 45.0 (d, C-5), 30.4 (t, C-4).

significant NOE contacts:



1-Nitro-2-phenyl-1,2,2a,7b-tetrahydrocyclobuta[b]benzofuran (*rac*-51)



1

***rac*-51**
$C_{16}H_{13}NO_2$
MW = 267.28 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and benzofurane (108 μL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 36 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**51** (12.5 mg, 46.7 mmol, 47%) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (2.0 mg, 13.4 μmol, 13%) was recovered.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and benzofurane (108 μL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) were irradiated for 36 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**51** (12.8 mg, 47.9 μmol, 48%) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (5.40 mg, 36.2 μmol, 36%) was recovered.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and benzofurane (108 μL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) were irradiated for 36 hours at −78 °C (at that point, no

further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**51** (8.60 mg, 32.2 μmol, 32%) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (6.70 mg, 44.9 μmol, 45%) was recovered.

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3062 (w, C_{ar}-H), 3032 (w, C_{ar}-H), 2923 (w, C-H), 1543 (vs, C-NO_2), 1474 (m), 1368 (m, C-NO_2), 1218 (m), 1095 (s, C-O-C), 1051 (m), 1019 (s), 814 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (12) $[C_{16}H_{13}]^+$, 118 (100) $[C_8H_6]^+$, 90 (8).

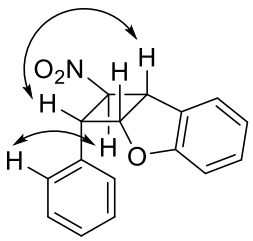
HRMS (ESI): calcd for $C_{16}H_{14}NO_3^+$ $[M+H]^+$: 268.0968; found: 268.0970.

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.98−6.96 (m 3H, *meta*-H_{ar}, *para*-H_{ar}), 6.84 (t, ^3J = 7.5 Hz, 1H, H-5), 6.79 (d, ^3J = 7.5 Hz, 1H, H-4), 6.61–6.56 (m, 2H, *ortho*-H_{ar}), 6.45 (t, ^3J = 7.5 Hz, 1H, H-6), 6.29 (d, ^3J = 7.5 Hz, 1H, H-7), 5.13 (dd, ^3J = 7.4 Hz, 4.2 Hz, 1H, H-2a), 4.97 (ddd, ^3J = 9.4 Hz, 4.2 Hz, ^4J = 1.5 Hz, 1H, H-1), 3.72 (*virt*. t, $^3J = {}^3J \cong$ 9.3 Hz, 1H, H-2), 3.50 (*virt*. t, $^3J = {}^3J \cong$ 8.4 Hz, 1H, H-7b).

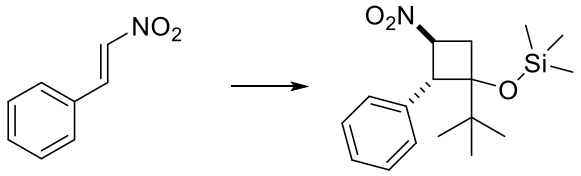
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 160.9 (s, C-3a), 135.4 (s, C-1'), 129.6 (d, C-5), 128.6 (d, *meta*-C_{ar}H/*para*-C_{ar}H)*, 128.3 (d, C-7), 127.9 (d, *meta*-C_{ar}H/*para*-C_{ar}H)*, 127.6 (d, 2C, *ortho*-C_{ar}H)*, 124.9 (s, C-7a), 121.6 (d, C-6), 111.5 (d, C-4), 85.6 (d, C-1), 80.6 (d, C-2a), 45.6 (d, C-2), 44.6 (d, C-7b).

* The exact assignment of these signals was not possible due to the large overlap with the signal of the solvent C_6D_6.

significant NOE contacts:



[1-(*tert*-Butyl)-3-nitro-2-phenylcyclobutoxy]trimethylsilane (*rac*-52)



1 *rac*-**52**
$C_{17}H_{27}NO_3Si$
MW = 321.49 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 μmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (431 μL, 344 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield *rac*-**52** (22.2 mg, 69.0 μmol, 34%, *d.r.* = 77:23) as a yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (216 μL, 172 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield *rac*-**52** (12.3 mg, 38.3 μmol, 38%, *d.r.* = 77:23) as a yellow colored oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (216 μL, 172 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 16 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield *rac*-**52** (11.8 mg, 36.7 μmol, 37%, *d.r.* = 77:23) as a yellow colored oil. Starting material in form of *cis*-β-nitrostyrene (7.20 mg, 48.3 μmol, 48%) was recovered.

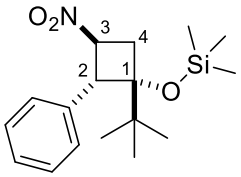
TLC: R_f = 0.70 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3031 (w, C_{ar}-H), 2958 (w, C-H), 1546 (s, C-NO_2), 1480 (m, C_{sp3}-H), 1395 (w), 1368 (m, C-NO_2), 1252 [s, O-Si-C(CH_3)], 1146 (s), 1029 (m), 870 (m, C_{ar}-H), 833 [vs, O-Si-C(CH_3)].

MS (EI): *m/z (%)* = 203 (8) $[C_{14}H_{19}O]^+$, 178 (4) $[C_{12}H_{18}O]^+$, 117 (100) $[C_9H_9]^+$, 73 (36) $[Si(CH_3)_3]^+$.

HRMS (ESI): calcd for $C_{17}H_{28}NO_3Si^+$ $[M+H]^+$: 322.1833; found: 322.1833.

Diastereoisomer *rac*-**52**

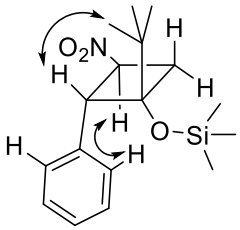


rac-**52**

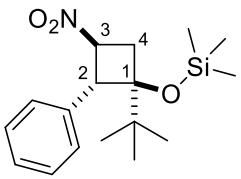
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.33−7.31 (m, 5H, H_{ar}), 5.13 (*virt*. q, $^3J = {}^3J \cong 8.5$ Hz, 1H, H-3), 4.24 (d, $^3J = 8.6$ Hz, 1H, H-2), 2.93 (dd, $^2J = 13.2$ Hz, $^3J = 8.2$ Hz, 1H, C*H*H-4), 2.50 (dd, $^2J = 13.2$ Hz, $^3J = 8.6$ Hz, 1H, CH*H*-4), 0.97 [s, 9H, $C(CH_3)_3$], 0.12 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C_{ar}), 129.0 (d, 2C, *ortho*-$C_{ar}H$), 128.1 (d, 2C, *meta*-$C_{ar}H$), 127.3 (d, *para*-$C_{ar}H$), 83.3 (s, C-1), 78.2 (d, C-3), 52.2 (d, C-2), 37.9 [s, $C(CH_3)_3$], 34.3 (t, C-4), 25.8 [q, 3C, $C(CH_3)_3$], 2.6 [q, 3C, $OSi(CH_3)_3$].

significant NOE contacts:



Diastereoisomer *rac*-**52'**

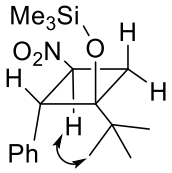


rac-**52'**

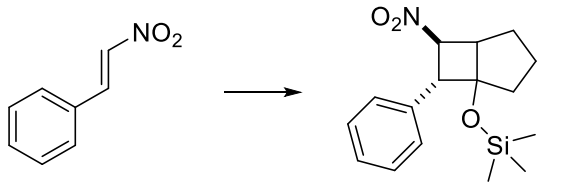
^{1}H NMR (126 MHz, $CDCl_3$): δ [ppm] = 7.35–7.29 (m, 5H, H_{ar}), 5.23 (*virt*. q, $^3J = {}^3J \cong 8.6$ Hz, 1H, H-3), 4.24 (d, $^3J = 8.6$ Hz, 1H, H-2), 2.93 (ddd, $^2J = 13.3$ Hz, $^3J = 8.3$ Hz, $^4J = 0.9$ Hz, 1H, C*H*H-4), 2.50 (dd, $^2J = 13.3$ Hz, $^3J = 8.6$ Hz, 1H, CH*H*-4), 0.97 [s, 9H, $C(CH_3)_3$], 0.12 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 135.9 (s, C_{ar}), 128.4 (d, 2C, *meta*-$C_{ar}H$), 127.8 (d, 2C, *ortho*-$C_{ar}H$), 127.3 (d, *para*-$C_{ar}H$), 80.1 (s, C-1), 73.3 (d, C-3), 61.2 (d, C-2), 38.4 [s, $C(CH_3)_3$], 36.8 (t, C-4), 25.2 [q, 3C, $C(CH_3)_3$], 2.18 [q, 3C, $OSi(CH_3)_3$].

significant NOE contacts:



Trimethyl[(6-nitro-7-phenylbicyclo[3.2.0]heptan-1-yl)oxy]silane (*rac*-53)



1 *rac*-**53**
$C_{16}H_{23}NO_3Si$
MW = 305.45 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 μmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (312 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for 18 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**53** (20.7 mg, 67.8 μmol, 35%, *d.r.* = 59:41) as a colorless oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (156 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**53** (9.8 mg, 32.1 μmol, 32%, *d.r.* = 59:41) as a colorless oil.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (156 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 24 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**53** (11.7 mg, 38.3 μmol, *38*%, *d.r.* = 61:39) as a colorless oil.

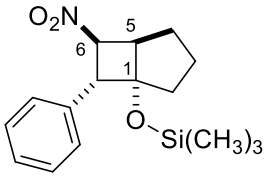
TLC: R_f = 0.70 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3004 (w, C_{ar}-H), 2926 (w, C-H), 1542 (s, C-NO_2), 1497 (m), 1364 (m, C-NO_2), 1264 [w, O-Si-C(CH_3)], 1045 (m), 1018 (m), 891 (m, C_{ar}-H), 822 [m, O-Si-C(CH_3)], 758 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 259 (88) $[C_{16}H_{23}OSi]^+$, 169 (60) $[C_{13}H_{13}]^+$, 91 (28) $[C_9H_9]^+$, 73 (100) $[C_3H_9Si]^+$.

HRMS (ESI): calcd for $C_{16}H_{24}NO_3Si^+$ $[M+H]^+$: 306.1522; found: 306.1522.

Diastereoisomer *rac*-**53**



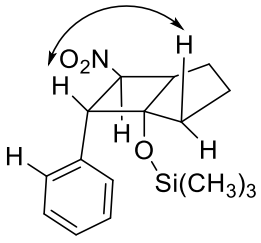
rac-**53**

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.38−7.32 (m, 2H, *meta*-H_{ar}), 7.29−7.25 (m, 3H, *ortho*-H_{ar}, *para*-H_{ar}), 5.35 (dd, ^3J = 10.1 Hz, 8.8 Hz, 1H, H-6), 4.06 (d, ^3J = 8.8 Hz, 1H, H-7), 3.09 (*virt*. t, $^3J = {}^3J \cong$ 9.2 Hz, 1H, H-5), 2.00−1.91 (m, 4H, CH_2-3, C*H*H-2, C*H*H-4), 1.89−1.77 (m, 1H, CH*H*-2), 1.62−1.44 (m, 1H, CHH-4), −0.14 [s, 9H, OSi(CH_3)$_3$].

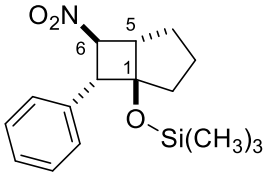
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.5 (s, C_{ar}), 129.5 (d, 2C, *ortho*-C_{ar}H), 128.8/128.5 (d, 2C *meta*-C_{ar}H)*, 127.5/127.3 (d, *para*-C_{ar}H)*, 83.5 (s, C-1), 81.0 (d, C-6), 51.9 (d, C-7), 49.9 (d, C-5), 40.1 (t, CH_2-2), 26.1 (t, CH_2-4), 25.9 (t, CH_2-3), 1.64 [q, 3C, OSi(*C*H_3)$_3$].

* The exact assignment of these ^{13}C-signals was not possible.

significant NOE contacts:



Diastereoisomer *rac*-**53'**



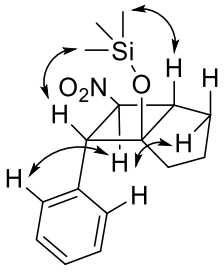
rac-**53'**

^{1}H NMR (126 MHz, $CDCl_3$): δ [ppm] = 7.38–7.32 (m, 2H, *meta*-H_{ar}), 7.29−7.25 (m, 1H, *para*-H_{ar}), 7.24−7.21 (m, 2H, *ortho*-H_{ar}), 4.59 (dd, ^{3}J = 8.3 Hz, 5.4 Hz, 1H, H-6), 4.40 (d, ^{3}J = 8.3 Hz, 1H, H-7), 3.30 (*virt*. t, $^{3}J = {}^{3}J \cong 6.2$ Hz, 1H, H-5), 2.00−1.91 (m, 1H, C*H*H-4), 1.89−1.77 (m, 2H, CH*H*-4, C*H*H-2), 1.71−1.66 (m, 1H, C*H*H-3), 1.62−1.44 (m, 2H, CH*H*-2, CH*H*-3), 0.22 [s, 9H, $OSi(CH_3)_3$].

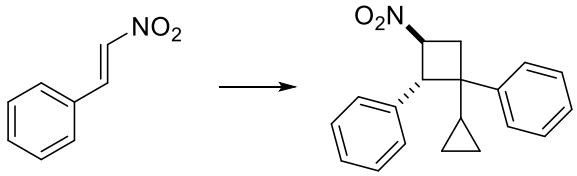
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.3 (s, C_{ar}), 128.8/128.5 (d, *meta*-C_{ar}H)*, 127.5/127.3 (d, *para*-C_{ar}H)*, 126.7 (d, 2C, *ortho*-C_{ar}H), 84.3 (s, C-1), 79.2 (d, C-6), 56.3 (d, C-7), 52.7 (d, C-5), 35.8 (d, CH_2-3), 30.0 (d, CH_2-4), 24.9 (d, CH_2-2), 2.03 [q, 3C, $OSi(CH_3)_3$].

* The exact assignment of these ^{13}C-signals was not possible.

significant NOE contacts:



(1'-Cyclopropyl-3'-nitrocyclobutane-1',2'-diyl)dibenzene (*rac*-54)



1 *rac*-**54**
$C_{19}H_{19}NO_2$
MW = 293.37 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and (1-cyclopropylvinyl)benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 16 hours at room temperature. The

crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**54** (25.6 mg, 86.6 µmol, 88%, *d.r.* = 67:33) as a pale yellow colored oil.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and (1-cyclopropylvinyl)benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 16 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**54** (22.4 mg, 76.4 µmol, 76%, *d.r.* = 56:44) as a pale yellow colored oil.

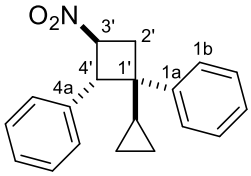
Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 µmol, 1.00 equiv) and (1-cyclopropylvinyl)benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for 16 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**54** (11.1 mg, 37.8 µmol, 37%, *d.r.* = 88:12) as a pale yellow colored oil. Starting material in form of *trans*-β-nitrostyrene (2.41 mg, 16.2 µmol, 16%) was recovered.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3028 (w, C_{ar}-H), 1542 (s, C-NO_2), 1496 (m), 1368 (m, C-NO_2), 1028 (m), 824 (w, C_{ar}-H), 770 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 247 (4) $[C_{19}H_{19}]^+$, 205 (32) $[C_{16}H_{13}]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$: 294.1488; found: 294.1488.

Diastereoisomer *rac*-**54**



rac-**54**

TLC: R_f = 0.69 (P/Et_2O = 9/1) [UV, $KMnO_4$].

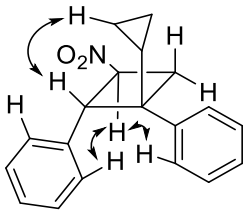
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.17−7.13 (m, 6H, H_{ar})*, 7.00−6.98 (m, 2H, H_{ar})*, 6.83–6.77 (m, 2H, H_{ar})*, 5.13 (*virt.* q, $^3J = {}^3J \cong 9.0$ Hz, 1H, H-3‘), 4.07 (d, ^3J = 9.5 Hz, 1H, H-4‘), 3.01 (dd, ^2J = 12.3 Hz, ^3J = 8.1 Hz, 1H, C*H*H-2‘), 2.60 (dd, ^2J = 12.4 Hz, ^3J = 9.2 Hz, 1H, CH*H*-2‘), 1.43 [tt, ^3J = 8.3 Hz, 5.6 Hz, 1H, C*H*$(CH_2)_2$], 0.77–0.66 [m, 2H, CH(C*H*$_2)_2$], 0.57

[*virt*. tt, $^2J \cong {}^3J$ = 8.6 Hz, ^3J = 5.5 Hz, 1H, CH(CH_2)$_2$], 0.44 [*virt*. dq, ^2J = 9.0 Hz, $^3J = {}^3J \cong$ 5.5 Hz, 1H, CH(CH_2)$_2$].

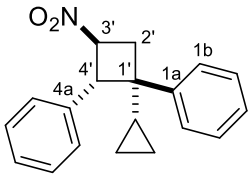
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.1 (s, C-1a), 136.2 (s, C-4a), 128.4 (d, 2C, C_{ar}H)*, 128.3 (d, 2C, C_{ar}H)*, 128.0 (d, 2C, C_{ar}H)*, 127.8 (d, C_{ar}H)*, 127.5 (d, C_{ar}H)*, 126.8 (d, 2C, C_{ar}H)*, 76.9 (d, C-3'), 55.1 (d, C-4'), 47.3 (s, C-1'), 32.1 (t, C-2'), 22.6 [d, *C*H(CH_2)$_2$], 3.21 [t, CH(*C*H$_2$)$_2$], 2.11 [t, CH(*C*H$_2$)$_2$].

* The exact assignment of these signals was not possible.

significant NOE contacts:



Diastereoisomer *rac*-**54'**



rac-**54'**

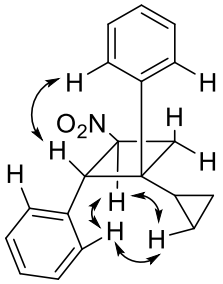
TLC: R_f = 0.58 (P/Et_2O = 9/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.51–7.45 (m, 2H, H_{ar})*, 7.43−7.40 (m, 2H, H_{ar})*, 7.38−7.34 (m, 3H, H_{ar})*, 7.28−7.24 (m, 3H, H_{ar})*, 5.38 (*virt*. q, $^3J = {}^3J \cong$ 8.9 Hz, 1H, H-3'), 4.43 (d, ^3J = 9.3 Hz, 1H, H-4'), 2.91 (dd, ^2J = 12.1 Hz, ^3J = 8.9 Hz, 1H, C*H*H-2'), 2.41 (dd, ^2J = 12.1 Hz, ^3J = 8.1 Hz, 1H, CH*H*-2'), 0.87 [tt, ^3J = 8.3 Hz, 5.7 Hz, 1H, C*H*(CH_2)$_2$], 0.67–0.61 [m, 1H, CH(CH_2)$_2$], 0.48 [*virt*. dq, ^2J = 10.3 Hz, $^3J = {}^3J \cong$ 5.3 Hz, 1H, CH(CH_2)$_2$], 0.42 [*virt*. tt, $^2J \cong {}^3J$ = 8.9 Hz, ^3J = 5.1 Hz, 1H, C*H*(CH_2)$_2$], 0.09 [virt. dq, ^2J = 9.3 Hz, $^3J = {}^3J \cong$ 5.7 Hz, 1H, C*H*(CH_2)$_2$].

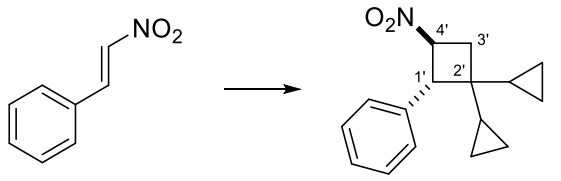
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 148.3 (s, C_{ar}-1a), 136.2 (s, C_{ar}-4a), 128.7 (d, 2C, C_{ar}H)*, 128.7 (d, 2C, C_{ar}H)*, 128.5 (d, 2C, C_{ar}H)*, 127.8 (d, C_{ar}H)*, 126.6 (d, C_{ar}H)*, 125.6 (d, 2C, C_{ar}H)*, 77.8 (d. C-3'), 57.6 (d, C-4'), 45.4 (s, C-1'), 31.9 (t, C-2'), 16.5 [d, *C*H(CH_2)$_2$], 4.36 [t, CH(*C*H$_2$)$_2$], 1.82 [t, CH(*C*H$_2$)$_2$].

* The exact assignment of these signals was not possible.

significant NOE contacts:



(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene (*rac*-55)



1 *rac*-**55**
$C_{16}H_{19}NO_2$
MW = 257.33 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (109 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**55** (18.0 mg, 69.9 μmol, 70%) and the side product *rac*-**57** (2.20 mg, 8.55 μmol, 9%) both as a yellow colored liquid.

Irradiation at λ = 424 nm (LED): Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (109 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**55** (9.00 mg, 34.9 μmol, 35%) and the side product *rac*-**57** (2.00 mg, 7.77 μmol, 8%) both as a yellow colored liquid.

Irradiation at λ = 424 nm (LED) at low temperature: Following **GP 5**, a solution of nitroolefin **1** (14.9 mg, 100 μmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (109 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated for twelve hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield

rac-**55** (10.0 mg, 38.9 µmol, 39%) and the side product *rac*-**57** (>1.00 mg, 3.89 µmol, >4%) both as a yellow colored liquid.

TLC: R_f = 0.58 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, $C_{cyclopropane}$-H), 3004 (w, C_{ar}-H), 1542 (s, C-NO_2), 1449 (w), 1369 (m, C-NO_2), 1017 (s), 822 (w, C_{ar}-H), 758 (s, C_{ar}-H).

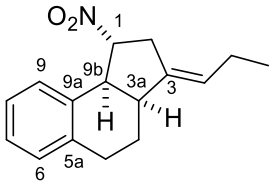
MS (EI): *m/z (%)* = 211 (4) $[C_{16}H_{19}]^+$, 169 (16) $[C_{13}H_{13}]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{16}H_{20}NO_2^+$ $[M+H]^+$: 258.1448; found: 258.1449.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.44–7.20 (m, 5H, H_{ar}), 5.20 (*virt*. q, $^3J = {}^3J \cong 8.7$ Hz, 1H, H-4'), 3.97 (d, ^3J = 9.2 Hz, 1H, H-1'), 2.06 (dd, ^2J = 12.2 Hz, ^3J = 8.7 Hz, 1H, C*H*H-3'), 1.71 (dd, ^3J = 12.2 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.09 [tt, ^3J = 8.4 Hz, 5.5 Hz, 1H, C*H*$(CH_2)_2$], 0.60-0.25 [m, 6H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.20–0.13 [m, 1H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C_{ar}), 128.5 (d, 2C, *meta*-C_{ar}H), 127.7 (d, 2C, *ortho*-C_{ar}H), 127.2 (d, *para*-C_{ar}H), 76.6 (d, C-4'), 55.5 (d, C-1'), 41.7 (s, C-2'), 27.8 (t, C-3'), 20.2 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.93 [t, CH(*C*$H_2)_2$], 1.74 [t, CH(*C*$H_2)_2$], 0.90 [t, CH(*C*$H_2)_2$], 0.72 [t, CH(*C*$H_2)_2$].

1-Nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalene (*rac*-57)



rac-**57**
$C_{16}H_{19}NO_2$
MW = 257.33 g/mol

TLC: R_f = 0.69 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}]: 3419 (br), 2928 (w, CR_3-H), 1722 (w), 1547 (s, C-NO_2), 1367 (m, C-NO_2), 1023 (m), 856 (m, C_{ar}-H), 791 (m, R_2C=CHR).

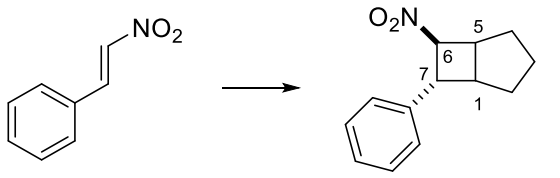
MS (EI): *m/z (%)* = 181 (100) $[C_{14}H_{13}]^+$, 167 (40) $[C_{13}H_{11}]^+$, 128 (16) $[C_{10}H_8]^+$.

HRMS (ESI): calc. for $C_{16}H_{20}NO_2^+$ $[M+H]^+$: 258.1448; found: 258.1449.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.17–7.05 (m, 4H, H_{ar}), 5.45 (ttd, ^3J = 7.1 Hz, ^4J = 2.5 Hz, 1.6 Hz, 1H, C=C*H*CH_2CH_3), 4.90 (*virt*. q, $^3J = {}^3J \cong$ 7.3 Hz, 1H, H-1), 3.90 (*virt*. t, $^3J = {}^3J \cong$ 7.5 Hz, 1H, H-9b), 3.07–2.94 (m, 2H, H-3a, C*H*H-2), 2.90 (dddd, ^2J = 17.3 Hz, ^3J = 7.9 Hz, ^4J = 2.7 Hz, 1.4 Hz, 1H, CH*H*-2), 2.80–2.75 (m, 1H, C*H*H-5), 2.73–2.68 (m, 1H, CH*H*-5), 2.07-1.98 (m, 2H, C=CHC*H*$_2$CH$_3$), 1.84 (ddt, ^2J = 13.8 Hz, ^3J = 6.2 Hz, 4.7 Hz, 1H, C*H*H-4), 1.67 (dtd, ^2J = 13.8 Hz, ^3J = 9.5 Hz, 4.8 Hz, 1H, CH*H*-4), 1.00 (t, ^3J = 7.5 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 138.7 (s, C-3), 137.1 (s, C-5a), 134.4 (s, C-9a), 129.3 (d, C-6), 128.6 (d, C-9), 127.2 (d, C-8), 126.6 (d, C-7), 125.9 (d, *C*=CHCH$_2$CH$_3$), 92.2 (d, C-1), 47.7 (d, C-9b), 42.0 (d, C-3a), 34.6 (t, C-2), 27.8 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H$_2$CH$_3$), 14.1 (q, CH_3).

6-Nitro-7-phenylbicyclo[3.2.0]heptan (*rac*-56)



1 *rac*-**56**
$C_{13}H_{15}NO_2$
MW = 217.27 g/mol

A solution of nitroolefin **1** (37.2 mg, 249 μmol, 1.00 equiv) in cyclopentene (*c* = 100 mM) was degassed under a continuous argon flow in an ultrasonic bath for 15 minutes and was afterwards irradiated at λ = 350 nm (fluorescent lamps) at room temperature. The reaction progress was monitored by TLC. After 24 hours, the irradiation was stopped, and the reaction solution was concentrated *in vacuo*. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield *rac*-**56** (30.8 mg, 141 μmol, 57%, *d.r.* = 83:17) as a colorless oil.

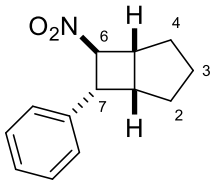
TLC: R_f = 0.43 (P/Et_2O = 20/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3028 (w, C_{ar}-H), 2931 (s, C-H), 2857 (m, C_{sp2}-H), 1537 (vs, C-NO_2), 1447 (w), 1370 (m, C-NO_2), 734 (w, C_{sp2}-H), 697 (m).

MS (EI): *m/z (%)* = 170 (30) $[C_{13}H_{14}]^+$, 117 (100) $[C_9H_9]^+$, 91 (95) $[C_7H_7]^+$.

HRMS (EI, 70 eV): calcd for $C_{13}H_{15}NO_2^+$ $[M]^+$: 217.1097; found: 217.1097.

Diastereoisomer *rac*-**56**:

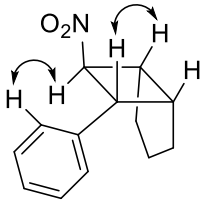


rac-**56**

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37−7.33 (m, 2H, *meta*-H_{ar}), 7.25–7.23 (m, 1H, *para*-H_{ar}), 7.14−7.12 (m, 2H, *ortho*-H_{ar}), 4.86 (dd, ^{3}J = 8.5 Hz, 5.5 Hz, 1H, H-6), 4.39 (*virt.* t, $^{3}J = {}^{3}J \cong$ 9.5 Hz, 1H, H-7), 3.39 (*virt.* q, $^{3}J = {}^{3}J \cong$ 6.5 Hz, 1H, H-5), 3.19–3.14 (m, 1H, H-1), 1.95−1.34 (m, 6H, H-2, H-3, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 137.1 (s, C_{ar}), 128.7 (d, 2C, *meta*-$C_{ar}H$), 126.8 (d, 2C, *ortho*-$C_{ar}H$), 126.7 (d, *para*-$C_{ar}H$), 83.6 (d, C-6), 44.3 (d, C-5), 44.2 (d, C-7), 38.2 (d, C-1), 31.4 (t, CH_2), 26.1 (t, CH_2), 26.0 (t, CH_2),

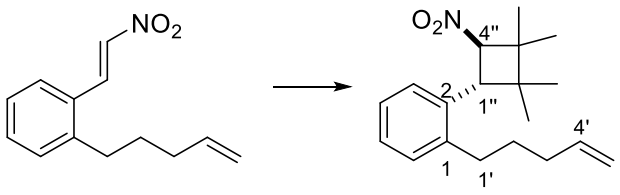
significant NOE contacts:



The NMR data for the minor diastereoisomer could not be fully extracted, due to significant overlap of the signals. Characteristic signals of the cyclobutene protons in the ^{1}H NMR spectra are:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.02 (dd, ^{3}J = 9.6 Hz, 8.3 Hz, 1H), 3.80 (t, ^{3}J = 7.6 Hz, 1H), 3.33 (ddt, ^{3}J = 10.3 Hz, 8.6 Hz, 6.9 Hz, 1H), 2.81 (q, ^{3}J = 6.7 Hz, 1H).

1-(Pent-4'-en-1'-yl)-2-(2'',2'',3'',3''-tetramethyl-4''-nitrocyclobutyl)-benzene (*rac*-73)



67 *rac*-**73**
$C_{19}H_{27}NO_2$
MW = 301.43 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): A solution of nitroolefin **67** (21.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv.) in dichloromethane (5 mL, c = 20 mM) was irradiated at λ_{max} = 419 nm for 18 hours at room temperature. Purification by column chromatography (2 × 15 cm, P/Et_2O = 4/1) yielded *rac*-**73** (13.8 mg, 45.8 µmol, 46%) as a yellow colored oil.

TLC: R_f = 0.68 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066 (w, C_{ar}-H), 2931 (w, C-H), 2870 (w, C-H), 1542 (vs, C-NO_2), 1460 (m), 1371 (s, C-NO_2), 993 (w), 912 (m, R-CH-CH_2), 751 (m, C_{ar}-H).

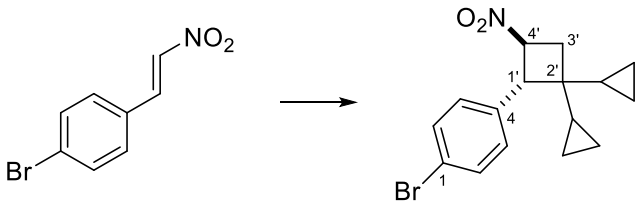
MS (EI): *m/z (%)* = 301 (2) $[C_{19}H_{27}NO_2]^+$, 255 (20) $[C_{19}H_{27}]^+$, 199 (49) $[C_{15}H_{19}]^+$, 143 (100) $[C_{11}H_{11}]^+$

HRMS (ESI): calcd for $C_{19}H_{28}NO_2^+$ $[M+H]^+$: 302.2115; found: 302.2115.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.15−7.09 (m, 3H, H-3, H-4, H-5), 7.07–7.03 (m, 1H, H-6), 5.83 (ddt, ^3J = 17.0 Hz, 10.2 Hz, 6.7 Hz, 1H, H-4'), 5.02 (*virt*. dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.7 Hz, 1H, C*H*H-5'), 4.98–4.92 (m, 2H, CH*H*-5', H-4''), 4.15 (d, ^3J = 10.2 Hz, 1H, H-1''), 2.76 (ddd, ^2J = 14.0 Hz, ^3J = 10.5 Hz, 5.3 Hz, 1H, C*H*H-1'), 2.46 (ddd, ^2J = 14.0 Hz, ^3J = 10.6 Hz, 6.0 Hz, 1H, CH*H*-1'), 2.19–2.03 (m, 2H, H-3'), 1.82–1.72 (m, 1H, C*H*H-2'), 1.70–1.58 (m, 1H, CH*H*-2'), 1.18 (s, 3H, CH_3-3''), 1.10 (s, 3H, CH_3-3''), 1.09 (s, 3H, CH_3-2''), 0.67 (s, 3H, CH_3-2'').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 141.7 (s, C-1), 138.6 (d, C-4'), 133.2 (s, C-2), 129.8 (d, C-6), 127.1 (d, C-5)*, 127.0 (d, C-3), 125.9 (d, C-4)*, 115.3 (t, C-5'), 85.3 (d, C-4''), 45.6 (d, C-1''), 44.4 (s, C-2''), 40.1 (s, C-3''), 33.8 (t, C-3'), 32.4 (t, C-1'), 30.6 (t, C-2'), 24.6 [q, (C-2'')CH_3], 22.8 [q, (C-3'')CH_3], 21.8 [q, (C-2'')CH_3], 19.4 [q, (C-3'')CH_3].

1-Bromo-4-(2',2'-dicyclopropyl-4'-nitrocyclobutyl)benzene (*rac*-75)



19

rac-**75**
$C_{16}H_{18}BrNO_2$
MW = 336.23 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **19** (59.6 mg, 261 µmol, 1.00 equiv) and 1,1-diyclocpropyl ethylene (283 mg, 2.61 mmol, 10.0 equiv) in dichloromethane (20 mL) was irradiated for 16 hours at room temperature. The crude product was purified by column chromatography (3 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**75** (45.8 mg, 1.36 mmol, 52%) and the by-product *rac*-**76** (7.60 mg, 22.6 µmol, 9%) both as a yellow colored oil.

TLC: R_f = 0.20 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3078 (w, $C_{cyclopropane}$-H), 3002 (w, C_{ar}-H), 1542 (vs, C-NO_2), 1489 (m), 1367 (m, C-NO_2), 1072 (m, C_{ar}-Br), 1010 (s), 824 (w, C_{ar}-H), 765 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 289 (4) $[C_{16}H_{18}Br]^+$, 195 (40) $[C_9H_9Br]^+$, 116 (100) $[C_9H_9]^+$, 79 (20) $[Br]^+$.

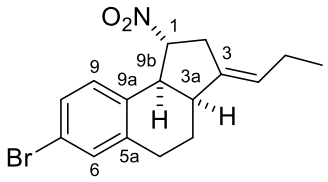
HRMS (ESI): calcd for $C_{16}H_{19}{}^{79}BrNO_2{}^+$ $[M+H]^+$: 336.0594; found: 336.0595.

$C_{16}H_{19}{}^{81}BrNO_2{}^+$ $[M+H]^+$: 338.0573; found: 338.0574.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.50–7.43 (m, 2H, H-2, H-6), 7.18 (d, ^3J = 8.2 Hz, 2H, H-3, H-5), 5.13 (*virt*. q, ^3J = ^3J ≅ 8.7 Hz, 1H, H-4'), 3.90 (d, ^3J = 9.3 Hz, 1H, H-1'), 2.06 (dd, ^2J = 12.2 Hz, ^3J = 8.6 Hz, 1H, C*H*H-3'), 1.71 (ddd, ^2J = 12.3 Hz, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 1H, CH*H*-3'), 1.06 [tt, ^3J = 8.4 Hz, 6.1 Hz, 1H, C*H*$(CH_2)_2$], 0.59–0.46 [m, 3H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.43–0.24 [m, 5H, CH(C*H*$_2)_2$], 0.21–0.12 [m, 1H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.5 (s, C-4), 131.7 (d, 2C, C-2, C-6), 129.4 (d, 2C, C-3, C-5), 121.2 (s. C-1), 76.4 (d, C-4'), 55.1 (d, C-1'), 41.7 (s, C-2'), 27.8 (t, C-3'), 20.1 [d, *C*H$(CH_2)_2$], 14.5 [d, *C*H$(CH_2)_2$], 1.88 [t, CH(*C*H$_2)_2$], 1.77 [t, CH(*C*H$_2)_2$], 0.98 [t, CH(*C*H$_2)_2$], 0.74 [t, CH(*C*H$_2)_2$].

(*E*)-7-Bromo-1-nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene (*rac*-76)



rac-**76**
$C_{16}H_{18}BrNO_2$
MW = 336.23 g/mol

TLC: R_f = 0.64 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3416 (br), 2927 (w), 1549 (s, C-NO_2), 1431 (m, R_2C-H_2), 1368 (m, C-NO_2), 1260 (m), 1068 (m, C_{ar}-Br), 814 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 288 (84) $[C_{16}H_{18}Br]^+$, 261 (56) $[C_{14}H_{14}Br]^+$, 180 (100) $[C_8H_7Br]^+$.

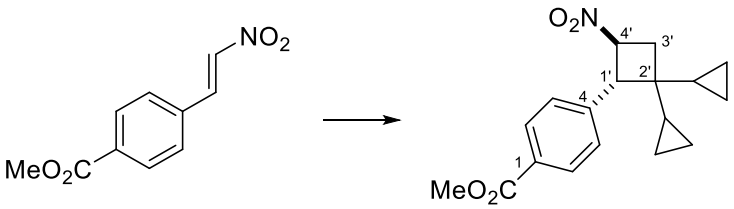
HRMS (ESI): calcd for $C_{16}H_{19}{}^{79}BrNO_2{}^+$ $[M+H]^+$: 336.0594; found: 336.0594.

$C_{16}H_{19}{}^{81}BrNO_2{}^+$ $[M+H]^+$: 338.0573; found: 336.0571.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.27−7.26 (m, 2H, H-6, H-8), 6.93 (d, ^3J = 8.8 Hz, 1H, H-9), 5.45 (*virt*. tq, ^3J = 7.0 Hz, ^4J = ^4J ≅ 2.4 Hz, 1H, C=C*H*CH_2CH_3), 4.84 (*virt*. q, ^3J = ^3J ≅ 7.3 Hz, 1H, H-1), 3.83 (*virt*. t, ^3J = ^3J ≅ 7.6 Hz, 1H, H-9b), 3.05–2.94 (m, 2H, H-3a, C*H*H-2), 2.90 (dddd, ^2J = 17.3 Hz, ^3J = 7.9 Hz, ^4J = 2.7 Hz, 1.4 Hz, 1H, CH*H*-2), 2.76 (dt, ^2J = 16.5 Hz, ^3J = 5.5 Hz, 1H, C*H*H-5), 2.67 (ddd, ^2J = 16.7 Hz, ^3J = 9.4 Hz, 4.8 Hz, 1H, CH*H*-5), 2.02 (dqd, ^2J = 14.5 Hz, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 2H, C=CHC*H*$_2$$CH_3$), 1.82 (ddt, ^2J = 13.8 Hz, ^3J = 6.2 Hz, 4.7 Hz, 1H, C*H*H-4), 1.64 (dtd, ^2J = 13.8 Hz, ^3J = 9.5 Hz, 4.8 Hz, 1H, CH*H*-4), 1.00 (t, ^3J = 7.5 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 139.4 (s, C-9a), 138.3 (s, *C*=CHCH_2CH_3), 133.5 (s, C-5a), 132.1 (d, C-6), 130.2 (d, C-9), 129.8 (d, C-8), 126.3 (d, C=*C*HCH_2CH_3), 121.1 (s, C-7), 92.2 (d, C-1), 47.2 (d, C-9b), 41.8 (d, C-3a), 34.5 (t, C-2), 27.6 (t. C-5), 27.0 (t, C-4), 22.8 (t, C=CH*C*H_2CH_3), 14.0 (q, CH_3).

(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene (*rac*-77)



17 | ***rac*-77** $C_{18}H_{21}NO_4$ MW = 315.37 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following general procedure **5**, a solution of nitroolefin **17** (248 mg, 1.20 mmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (1.29 g, 12.0 mmol, 10.0 equiv) in dichloromethane (60 mL) were irradiated for 16 hours at room temperature. The crude product was purified by column chromatography (4 × 20 cm, P/Et_2O = 40/1) to yield *rac*-**77** (213 mg, 6.75 mmol, 57%) and the by-product *rac*-**78** (16.0 mg, 50.7 μmol, 5%) both as a colorless solid.

TLC: R_f = 0.48 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, $C_{cyclopropane}$-H), 3003 (w, C_{ar}-H), 2845 (w, O-CH_3), 1717 (vs, C=O), 1543 (s, C-NO_2), 1369 (m, C-NO_2), 1277 (vs, O=C-OCH_3), 1107 (s, O=C-OCH_3), 1018 (m), 803 (w, C_{ar}-H).

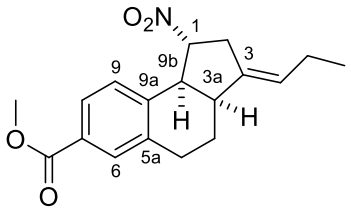
MS (EI): *m/z (%)* = 269 (12) $[C_{18}H_{21}O_2]^+$, 227 (16) $[C_{15}H_{15}O_2]^+$, 175 (100) $[C_{11}H_{11}O_2]^+$, 149 (55) $[C_9H_9O_2]^+$, 115 (66), 91 (46) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_4^+$ $[M+H]^+$: 316.1543; found: 316.1544.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.02 (d, ^3J = 8.3 Hz, 2H, H-2, H-6), 7.38 (d, ^3J = 8.3 Hz, 2H, H-3, H-5), 5.21 (*virt*. q, ^3J = ^3J ≅ 8.7 Hz, 1H, H-4'), 4.02 (d, ^3J = 9.2 Hz, 1H, H-1'), 3.91 (s, 3H, CO_2CH_3), 2.08 (dd, ^2J = 12.3 Hz, ^3J = 8.6 Hz, 1H, C*H*H-3'), 1.73 (dd, ^2J = 12.3 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.15–1.02 [m, 1H, C*H*$(CH_2)_2$], 0.62–0.25 [m, 8H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.19−0.13 (m, 1H, CH(C*H*$_2)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.9 (*C*O_2CH_3), 141.7 (s, C-1), 129.8 (d, 2C, C-2, C-6), 129.2 (s, C-4), 127.6 (d, 2C, C-3, C-5), 76.1 (d, C-4'), 55.6 (d, C-1'), 52.3 (q, CO_2*C*H_3), 42.1 (s, C-2'), 27.8 (t, C-3'), 20.0 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.87 [t, CH(*C*$H_2)_2$], 1.75 [t, CH(*C*$H_2)_2$], 0.98 [t, CH(*C*$H_2)_2$], 0.75 [t, CH(*C*$H_2)_2$].

Methyl-(*E*)-1-nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalene -7-carboxylate (*rac*-78)



rac-**78**
$C_{18}H_{21}NO_4$
MW = 315.37 g/mol

TLC: R_f = 0.53 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3423 (br), 2955 (w, CR_3-H), 1720 (s, C=O), 1550 (s, C-NO_2), 1437 (m, R_2C-H_2), 1368 (m, C-NO_2), 1284 (s, O=C-OCH_3), 1105 (m, O=C-OCH_3), 762 (s, C_{ar}-H).

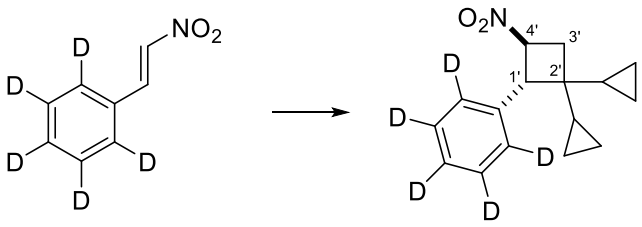
MS (EI): *m/z (%)* = 284 (19) $[C_{17}H_{18}NO_3]^+$, 253 (54), 149 (100) $[C_9H_9O_2]^+$, 115 (49), 91 (63) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$: 316.1543; found: 316.1545.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.80–7.77 (m, 2H, H-6, H-8), 7.14 (d, ^3J = 8.6 Hz, 1H, H-9), 5.46 (*virt*. tq, ^3J = 6.9 Hz, ^4J = ^4J ≅ 2.4 Hz, 1H, C=C*H*CH_2CH_3), 4.88 (*virt*. q, ^3J = ^3J ≅ 7.3 Hz, 1H, H-1), 3.96–3.91 (m, 1H, H-9b), 3.90 (s, 3H, CO_2CH_3), 3.11–2.95 (m, 2H, H-3a, C*H*H-2), 2.95–2.80 (m, 2H, CH*H*-2, C*H*H-5), 2.78–2.66 (m, 1H, CH*H*-5), 2.08–1.96 (m, 2H, C=CHC*H*$_2$$CH_3$), 1.91–1.81 (m, 1H, C*H*H-4), 1.68 (dtd, ^2J = 13.9 Hz, ^3J = 9.3 Hz, 4.8 Hz, 1H, CH*H*-4), 1.00 (t, ^3J = 7.5 Hz, 3H, C=CHCH$_2$C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 138.7 (s, C-3), 137.1 (s, C-5a), 134.4 (s, C-9a), 129.3 (d, C-6), 128.6 (d, C-9), 127.2 (d, C-8), 126.6 (s, C-7), 125.9 (d, *C*=CHCH$_2$$CH_3$), 92.2 (d, C-1), 52.3 (q, CO_2*C*H_3) 47.7 (d, C-9b), 42.0 (d, C-3a), 34.6 (t, C-2), 27.8 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H$_2$$CH_3$), 14.1 (q, C=CHCH$_2$*C*$H_3$).

1-(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene-2,3,4,5,6-d_5 (*rac*-80)



79 *rac*-**80**

$C_{16}H_{14}D_5NO_2$

MW = 262.36 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **79** (62.0 mg, 402 μmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (435 mg, 4.02 mmol, 10.0 equiv) in dichloromethane (20 mL) was irradiated for 14 hours at room temperature. The crude product was purified by column chromatography (3 × 20 cm, P/Et_2O = 40/1) to yield *rac*-**80** (64.0 mg, 244 μmol, 61%) and the side product *rac*-**81** (11.5 mg, 43.8 μmol, 11%) both as a yellow colored oil.

TLC: R_f = 0.6 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, $C_{cyclopropyl}$-H), 3003 (w, C_{ar}-H), 2275 (w), 1542 (s, C NO_2), 1369 (m, C-NO_2), 1018 (m), 824 (w, C_{ar}-H), 696 (w, CH).

MS (EI): *m/z (%)* = 216 (8) $[C_{16}H_{14}D_5]^+$, 173 (10), 133 (15) $[C_{10}H_5D_5]^+$, 122 (100) $[C_9H_4D_5]^+$, 96 (15) $[C_7H_2D_5]^+$, 79 (20).

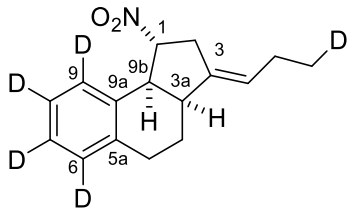
HRMS (ESI): calcd for $C_{16}H_{15}D_5NO_2^+$ $[M+H]^+$: 263.1802; found: 263.1803.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.20 (*virt.* q, ^3J = ^3J ≅ 8.7 Hz, 1H, H-4'), 3.97 (d, ^3J = 9.2 Hz, 1H, H-1'), 2.06 (dd, ^2J = 12.2 Hz, ^3J = 8.7 Hz, 1H, C*H*H-3'), 1.71 (dd, ^3J = 12.2 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.09 [tt, ^3J = 8.3 Hz, 5.5 Hz, 1H, C*H*$(CH_2)_2$], 0.56–0.26 [m, 8H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.20–0.12 [m, 1H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.2 (s, C_{ar}), 76.6 (d, C-4'), 55.4 (d, C-1'), 41.7 (s, C-2'), 27.8 (t, C-3'), 20.2 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.93 [t, CH(*C*H$_2)_2$], 1.73 [t, CH(*C*H$_2)_2$], 0.90 [t, CH(*C*H$_2)_2$], 0.73 [t, CH(*C*H$_2)_2$].

The aromatic ^{13}C-signals of carbons connected to deuterium-atoms were not visible in the ^{13}C-spectrum.

(*E*)-1-Nitro-3-(propylidene-3-*d*)-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene-6,7,8,9-*d*$_4$ (*rac*-81)



rac-**81**
$C_{16}H_{14}D_5NO_2$
MW = 262.36 g/mol

TLC: R_f = 0.70 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3418 (br), 2928 (w, CR_3-H), 1711 (w), 1547 (s, C-NO_2), 1368 (m, C-NO_2), 1261 (w), 1024 (m), 858 (m, C_{ar}-H), 803 (w), 752 (m, R_2C=CHR).

MS (EI): *m/z (%)* = 215 (65) $[C_{16}H_{16}D_5]^+$, 185 (100) $[C_{14}H_9D_4]^+$, 171 (36), 132 (20) $[C_{10}H_4D_4]^+$, 95 (6) $[C_7H_3D_4]^+$.

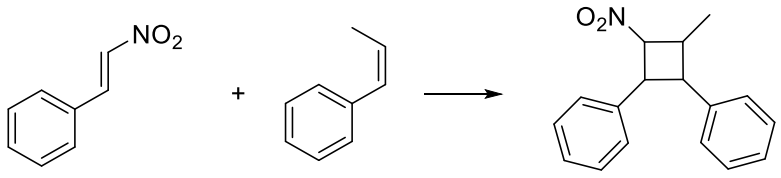
HRMS (ESI): calcd for $C_{16}H_{15}D_5NO_2^+$ $[M+H]^+$: 263.1802; found: 263.1804.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.45 (tq, ^3J = 7.1 Hz, ^4J = 2.4 Hz, 1H, C=C*H*CH_2CH_3), 4.90 (*virt*. q, ^3J = ^3J ≅ 7.4 Hz, 1H, H-1), 3.90 (*virt*. t, ^3J = ^3J ≅ 7.6 Hz, 1H, H-9b), 3.08–2.94 (m, 2H, H-3a, C*H*H-2), 2.90 (dd, ^2J = 17.3 Hz, ^3J = 7.8 Hz, 1H, CH*H*-2), 2.81–2.75 (m, 1H, C*H*H-5), 2.69 (ddd, ^2J = 16.4 Hz, ^3J = 9.1 Hz, 4.8 Hz, 1H, CH*H*-5), 2.05−1.98 (m, 2H, C=CHC*H*$_2$$CH_3$), 1.89–1.79 (m, 1H, C*H*H-4), 1.67 (dtd, ^2J = 14.0 Hz, ^3J = 9.4 Hz, 4.8 Hz, 1H, CH*H*-4), 0.98 (tt, ^3J = 7.6 Hz, ^2J = 2.1 Hz, 2H, CH_2D).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.8 (s, C-3), 137.0 (s, C-5a), 134.4 (s, C-9a), 126.0 (d, *C*=CHCH_2CH_2D), 92.2 (d, C-1), 47.6 (d, C-9b), 42.1 (d, C-3a), 34.6 (t, C-2), 27.7 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H_2CH_2D), 14.1 (t, $^1J_{CD}$ = 19.4 Hz, C=CHCH_2*C*H_2D).

The aromatic ^{13}C-signals of carbons connected to deuterium-atoms were not visible in the ^{13}C-spectrum.

Procedure for the [2+2] photocycloaddition reaction of *trans*-β-nitrostyrene with *cis*-β-methylstyrene

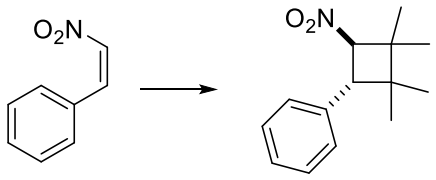


1

rac-**46**
$C_{17}H_{17}NO_2$
MW = 267.33 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of nitroolefin **1** (29.8 mg, 200 µmol, 1.00 equiv) and *cis*-β-methylstyrene (260 µL, 236 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for 15 hours at room temperature (at this point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield *rac*-**46** (45.8 mg, 1.12 mmol, 56%, 73% *brsm*, *d.r.* = 77:23) as a colorless oil. Starting material in form of *cis*-β-nitrostyrene (6.80 mg, 45.6 µmol, 23%) was recovered. The olefin was recovered exclusively as the *cis*-isomer.

Procedure for the [2+2] photocycloaddition reaction of *cis*-β-nitrostyrene with 2,3-dimethyl-2-butene

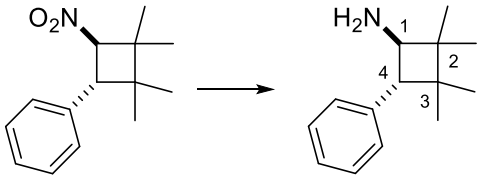


cis-**1**

rac-**31**
$C_{14}H_{19}NO_2$
MW = 233.31 g/mol

Irradiation at λ = 419 nm (fluorescent lamps): Following **GP 5**, a solution of *cis*-β-nitrostyrene (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for nine hours at room temperature. The crude product was purified by column chromatography (3 × 10 cm, P/Et_2O = 99/1 → 9/1) to yield *rac*-**31** (20.2 mg, 86.6 mmol, 43%) as a yellow colored oil. The nitro- and the phenylgroup in the product were found to be exclusively in a *trans*-configuration relative to each other.

2,2,3,3-Tetramethyl-4-phenylcyclobutan-1-amine



rac-**31** $C_{14}H_{21}N$
MW = 203.33 g/mol

According to a literature known procedure:[235] Zn powder (350 mg, 5.36 mmol, 25.0 equiv) was added in small portions to a stirred solution of nitrocyclobutane *rac*-**31** (50.0 mg, 214 µmol, 1.00 equiv) in a mixture of water/acetic acid (2 mL; 1/1 v/v). The suspension was stirred for four hours at room temperature. Aqueous NaOH solution (c = 5 M) was added until pH = 7 was reached. The cloudy solution was extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield 2,2,3,3-Tetramethyl-4-phenylcyclobutan-1-amine (33.6 mg, 165 µmol, 77%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29–7.21 (m, 2H, *meta*-H_{Ph}), 7.19–7.08 (m, 3H, *ortho*-H_{Ph}, *para*-H_{Ph}), 3.37 (d, ^3J = 9.9 Hz, 1H, H-1), 2.86 (d, ^3J = 9.9 Hz, 1H, H-4), 1.51 (br. s, 2H, NH_2), 1.03 [s, 3H, CH_3-2], 1.01 [s, 3H, CH_3-3], 0.93 [s, 3H, CH_3-2], 0.59 [s, 3H, CH_3-3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.6 (s, C_{Ph}), 128.3 (d, 2C, *meta*-$C_{Ph}H$), 127.7 (d, 2C, *ortho*-$C_{Ph}H$), 126.1 (d, *para*-$C_{Ph}H$), 56.8 (d, C-4), 55.5 (d, C-1), 41.7 (s, C-2), 39.6 (s, C-3), 24.2 [q, (C-3)CH_3], 22.6 [q, (C-2)CH_3], 21.1 [q, (C-3)CH_3], 18.7 [q, (C-2)CH_3].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060 (w, C_{Ph}-H), 2959 (m, C_{Ph}-H), 2866 (w), 2604 (w), 1566 (br s, C-NH_2), 1458 (s), 1449 (s), 1358 (m),1337 (s), 1270 (m), 1132 (m), 885 (m), 810 (m, C_{Ph}-H).

MS (EI, 70 eV): *m/z (%)* = 132 (5) $[C_{10}H_{12}]^+$, 119 (100) $[C_9H_{11}]^+$, 91 (13) $[C_7H_7]^+$, 71 (31) $[C_4H_9]^+$, 56 (11).

HRMS (ESI): calcd for $C_{14}H_{22}N^+$ $[M+H]^+$: 204.1741; found: 204.1748.

Procedure for the [2+2] photocycloaddition of *trans*-β-nitrostyrene (1) with 2,3-dimethyl-2-butene (30) and thioxanthone (TXT) as triplet sensitizer

A solution of nitrostyrene **1** (29.8 mg, 199 μmol, 1.00 equiv), thioxanthone (4.24 mg, 20.0 μmol, 0.10 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm at room temperature for three hours. When full conversion was reached, the reaction was stopped, and all volatiles were removed *in vacuo*. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 30/1) to yield *rac*-**31** (22.0 mg, 94.3 μmol, 47%) as a yellow colored oil.

Procedure for the [2+2] photocycloaddition of *trans*-β-nitrostyrene 1 with 1,1-dicyclopropylethene and thioxanthone (TXT) as triplet sensitizer

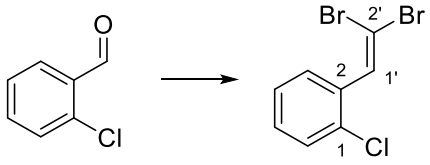
Following general procedure **5**, a solution of *trans*-β-nitrostyrene (**1**) (29.8 mg, 200 μmol, 1.00 equiv) and 1,1-dicyclopropyl ethylene (216 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated for three hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield *rac*-**55** (32.7 mg, 127 μmol, 64%) and the by-product *rac*-**57** (5.30 mg, 20.6 μmol, 10%) both as a yellow colored liquid.

6.7 Synthesis of Irradiation Precursors for the Intermolecular [2+2] Photocycloaddition of Sulfones

General Procedure 6 (GP 6) for the Synthesis of *trans*-Configurated Styryl-Sulfones

According to a literature known procedure:[157] The respective thiol (1.20 equiv), NH_4Cl (1.00 equiv) and H_2O_2 (30 wt-% in H_2O, 80 µL per 100 µmol alkyne) were added successively to a solution of the terminal alkyne (1.00 equiv) in tetrahydrofuran (*c* = 25 M) and the mixture was stirred under air for 48 hours at 50 °C (note: the tetrahydrofuran must contain stabilizer! technical grade solvent was used for this reaction). Water (4 mL per 100 µmol alkyne) was added to quench the reaction. The reaction mixture was partitioned between water and tetrahydrofuran, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (cHex/EtOAc, the ratio is indicated at each experiment individually).

1-Chloro-2-(2',2'-dibromovinyl)benzene



$C_8H_5Br_2Cl$
MW = 296.39 g/mol

According to a literature known procedure:[236] A solution of PPh_3 (11.4 g, 44.0 mmol, 4.00 equiv) in dichloromethane (28 mL) was added slowly over a period of 20 minutes to a solution of CBr_4 (7.22 g, 22.0 mmol, 2.00 equiv) in dichloromethane (20 mL) at 0 °C and the reaction mixture was stirred for ten minutes. Subsequently, freshly distilled 2-chlorobenzaldehyde (1.24 mL, 1.55 g, 11.0 mmol, 1.00 equiv) was added slowly over five minutes and stirring was continued for 40 minutes. The solution was warmed to room temperature and stirred at that temperature for further 40 minutes. All volatiles were removed under reduced pressure. The residue was suspended in a mixture of hexanes/diethylether (100 mL, 1:1/v:v), the precipitate was filtered off and washed with hexanes/diethylether (3 × 40 mL, 1:1/v:v). The filtrate was concentrated under reduced pressure. The resulting yellow colored solid was suspended in a mixture of hexanes/diethylether (40 mL, 5:1/v:v),

filtered off and washed with hexanes/diethylether (3 × 10 mL, 5:1/v:v). The filtrate was again concentrated *in vacuo*. This procedure was repeated once again and the title compound (2.26 g, 7.63 mmol, 69%) was obtained as a yellow colored oil. The title compound was employed in the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.64 (dd, ^{3}J = 5.9 Hz, 3.7 Hz, 1H, H-3), 7.57 (s, 1H, H-1'), 7.43–7.37 (m, 1H, H-6), 7.31–7.27 (m, 2H, H-4, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 134.6 (d, C-1'), 134.3 (s, C-1), 133.2 (s, C-2), 130.3 (d, C_{ar}-H)*, 129.9 (d, C_{ar}-H)*, 129.7 (d, C_{ar}-H)*, 126.7 (d, C_{ar}-H)*, 92.9 (s, C-2').

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[237]

1-Chloro-2-ethynylbenzene

C_8H_5Cl
MW = 136.58 g/mol

According to a literature known procedure.[238] A solution of 1-Chloro-2-(2',2'-dibromovinyl)benzene (2.26 g, 7.63 mmol, 1.00 equiv) in tetrahydrofuran (20 mL) was added dropwise over a period of 30 minutes to a solution of *n*-BuLi (12.4 mL, 2.38 g, 30.5 mmol, 4.00 equiv; 2.5 M in hexanes) in tetrahydrofuran (80 mL) at −78 °C. The reaction solution was stirred at −78 °C, and the reaction progress was monitored by TLC. After two hours, saturated aqueous NH_4Cl solution (100 mL) was added, the reaction was warmed up to room temperature and stirred at that temperature for 45 minutes. The mixture was partitioned between aqueous NH_4Cl solution and tetrahydrofuran, and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with saturated aqueous NaCl solution (300 mL), dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (4 × 12 cm, P/Et_2O = 20/1) to yield the title compound (194 mg, 1.42 mmol, 5%) as a colorless liquid.

TLC: R_f = 0.80 (P/Et_2O = 10/1) [UV, $KMnO_4$].

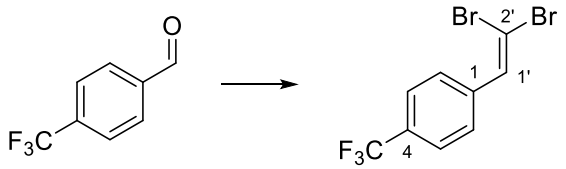
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.53 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, H-3), 7.41 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1H, H-6), 7.29 (td, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, H-4), 7.26–7.19 (m, 1H, H-5), 3.37 (s, 1H, ArC≡C*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C-1), 134.2 (d, $C_{ar}H$)*, 130.0 (d, $C_{ar}H$)*, 129.5 (d, $C_{ar}H$)*, 126.6 (d, $C_{ar}H$)*, 122.2 (s, C-2), 82.5 (d, ArC≡*C*H), 80.4 (s, Ar*C*≡CH).

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[238]

1-(2',2'-Dibromovinyl)-4-(trifluoromethyl)benzene



$C_9H_5Br_2F$
MW = 329.94 g/mol

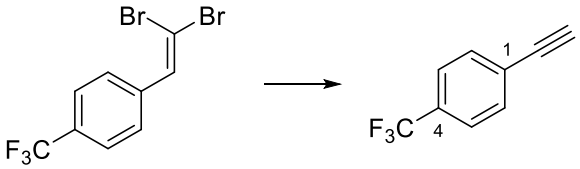
According to a literature known procedure.[236] A solution of PPh_3 (11.4 g, 44.0 mmol, 3.00 equiv) in dichloromethane (28 mL) was added slowly over a period of 20 minutes to a solution of CBr_4 (7.21 g, 21.8 mmol, 1.50 equiv) in dichloromethane (20 mL) at 0 °C and the solution was stirred for ten minutes. Subsequently, freshly distilled 4-(trifluoromethyl)benzaldehyde (1.98 mL, 2.53 g, 14.5 mmol, 1.00 equiv) was added slowly over five minutes and stirring was continued for 40 minutes at 0 °C. The solution was warmed to room temperature and stirred at that temperature for 60 minutes. All volatiles were removed under reduced pressure. The residue was suspended in a mixture of hexanes/diethylether (100 mL, 1:1/v:v), the precipitate was filtered off and washed with hexanes/diethylether (3 × 40 mL, 1:1/v:v). The filtrate was concentrated under reduced pressure. The resulting yellow colored solid was suspended in a mixture of hexanes/diethylether (40 mL, 5:1/v:v), filtered off and washed with hexanes/diethylether (3 × 10 mL, 5:1/v:v). The filtrate was again concentrated *in vacuo*. This procedure was repeated once again and the title compound (4.36 g, 13.2 mmol, 92%) was obtained as a yellow colored oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.59 (br. s, 4H, H-2, H-3, H-5, H-6), 3.19 (s, 1H, H-1').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 138.9 (s, C-1'), 135.7 (s, C-1), 130.4 (q, $^{1}J_{CF}$ = 32.7 Hz, Ar*C*F_3), 128.8 (d, 4C, C-2, C-3, C-5, C-6), 125.6 (q, $^{3}J_{CF}$ = 3.8 Hz, C-4), 92.5 (d, C-2').

The analytical data match those reported in the literature.[239]

4-Ethynyl-α,α,α-trifluortoluene



XY
$C_9H_5F_3$
MW = 170.13 g/mol

n-BuLi (21.2 mL, 4.08 g, 52.2 mmol, 4.00 equiv; 2.5 M in hexanes) was added dropwise over a period of 30 minutes to a solution of 1-(2',2'-Dibromovinyl)-4-(trifluoromethyl)benzene (4.36 g, 13.2 mmol, 1.00 equiv) in tetrahydrofuran (60 mL) at −78 °C. Stirring was continued and the reaction progress was monitored by TLC. After two hours, saturated aqueous NH_4Cl solution (100 mL) was added, the reaction was warmed to room temperature and stirred at that temperature for 45 minutes. The mixture was partitioned between aqueous NH_4Cl solution and dichloromethane, and the aqueous layer was extracted with diethyl ether (2 × 70 mL). The combined organic layers were washed with saturated aqueous NaCl solution (200 mL), dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (5 × 20 cm, P/Et_2O = 20/1) to yield the title compound (680 mg, 3.99 mmol, 30%) as a colorless liquid.

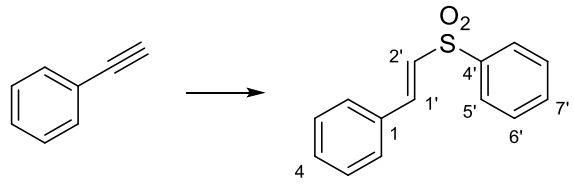
TLC: R_f = 0.88 (P/Et_2O = 10/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.59 (s, 4H, H-2, H-3, H-5, H-6), 3.20 (s, 1H, ArC≡C*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 132.6 (d, 4C, C-2, C-3, C-5, C-6), 130.7 (q, $^{1}J_{CF}$ = 32.8 Hz, Ar*C*F_3), 126.1 (s, C-1), 125.4 (q, $^{2}J_{CF}$ = 3.9 Hz, C-4), 82.3 (s, Ar*C*≡CH), 79.8 (d, ArC≡*C*H).

The analytical data match those reported in the literature.[240]

(*E*)-[2'-(Phenylsulfonyl)vinyl]benzene (92)



92
$C_{14}H_{12}O_2S$
MW = 244.31 g/mol

According to the **GP 6**, a solution of phenylacetylene (540 µL, 500 mg, 4.90 mmol, 1.00 equiv), thiophenol (600 µL, 647 mg, 5.87 mmol, 1.20 equiv), NH_4Cl (262 mg, 4.90 mmol, 1.00 equiv) and H_2O_2 (4.00 mL, 4.44 g, 39.2 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (20 mL) was stirred under air at 50 °C for 72 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 4/1) to yield **92** (1.10 g, 4.50 mmol, 92%) as a colorless solid.

TLC: R_f = 0.57 (cHex/EtOAc = 4/1) [UV, $KMnO_4$].

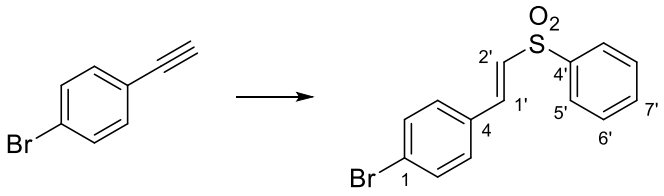
mp: 75 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.98–7.92 (m, 2H, H-5'), 7.69 (d, ^3J = 15.4 Hz, 1H, H-1'), 7.65–7.59 (m, 1H, H-7'), 7.55 (dd, ^3J = 8.5 Hz, 7.0 Hz, 2H, H-6'), 7.49 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 2H, H-2, H-6), 7.44–7.36 (m, 3H, H-3, H-4, H-5), 6.86 (d, ^3J = 15.4 Hz, 1H, H-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 142.6 (d, C-1'), 140.9 (s, C-4'), 133.5 (d, C-7'), 132.5 (s, C-1), 131.4 (d, C-4), 129.5 (d, 2C, C-6'), 129.2 (d, 2C, C-2, C-6), 128.7 (d, 2C, C-3, C-5), 127.8 (d, 2C, C-C-5'), 127.5 (d, C-2').

The analytical data match those reported in the literature.[240]

(*E*)-1-Bromo-4-[2‘-(phenylsulfonyl)vinyl]benzene (99)



99
$C_{14}H_{11}BrO_2S$
MW = 321.20 g/mol

According to the **GP 6**, a solution of 1-bromo-4-ethynylbenzene (500 mg, 2.76 mmol, 1.00 equiv), thiophenol (340 µL, 365 mg, 3.31 mmol, 1.20 equiv), NH_4Cl (148 mg, 2.76 mmol, 1.00 equiv) and H_2O_2 (2.30 mL, 2.51 g, 22.1 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (11 mL) was stirred under air at 50 °C for 72 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 4/1) to yield **99** (628 mg, 1.94 mmol, 70%) as a colorless solid.

TLC: R_f = 0.59 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

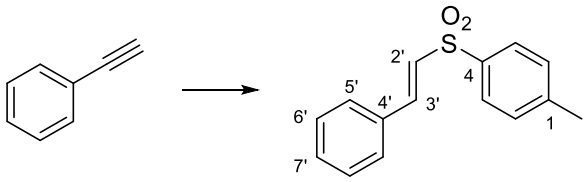
mp: 148 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.97–7.91 (m, 2H, H-6’), 7.66–7.60 (m, 2H, H-1’, H-7’), 7.59–7.50 (m, 4H, H-2, H-6, H-5’), 7.37–7.32 (m, 2H, H-3, H-5), 6.86 (d, ^3J = 15.4 Hz, 1H, H-2’).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.1 (d, C-1’), 140.5 (s, C-4’), 133.5 (d, C-7’), 132.4 (d, 2C, C-2, C-6), 131.3 (s, C-4), 129.9 (d, 2C, C-3, C-5), 129.4 (d, 2C, C-6’), 128.1 (d, C-2’), 127.7 (d, 2C, C-5’), 125.7 (s, C-1).

The analytical data match those reported in the literature.[241]

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (100)



100
$C_{15}H_{14}O_2S$
MW = 258.34 g/mol

According to the **GP 6**, a solution of phenylacetylene (1.08 mL, 1.00 g, 9.79 mmol, 1.00 equiv), *para*-toluenethiol (1.46 g, 11.8 mmol, 1.20 equiv), NH_4Cl (524 mg, 9.79 mmol, 1.00 equiv) and H_2O_2 (8.00 mL, 8.88 g, 78.3 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (40 mL) was stirred under air at 50 °C for 72 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 4/1) to yield **100** (1.70 g, 6.58 mmol, 67%) as a colorless solid.

TLC: R_f = 0.44 (cHex/EtOAc = 4/1) [UV, $KMnO_4$].

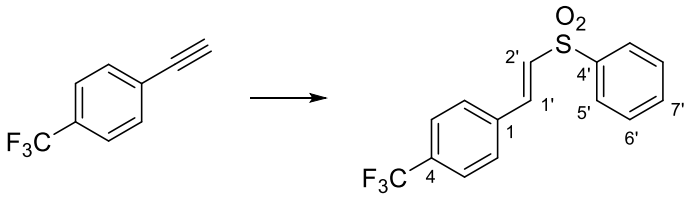
mp: 126 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.83 (d, ^3J = 8.4 Hz, 2H, H-3, H-5), 7.66 (d, ^3J = 15.4 Hz, 1H, H-3'), 7.48 (dd, ^3J = 7.7 Hz, ^4J = 2.0 Hz, 2H, H-5'), 7.43–7.37 (m, 3H, H-6', H-7'), 7.34 (d, ^3J = 8.0 Hz, 2H, H-2, H-6), 6.85 (d, ^3J = 15.4 Hz, 1H, H-2'), 2.44 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 144.5 (s, C-1), 142.1 (d, C-3'), 137.9 (s, C-4), 132.6 (s, C-4'), 131.2 (d, C-7'), 130.1 (d, 2C, C-2, C-6), 129.2 (d, 2C, C-6'), 128.7 (d, 2C, C-5'), 127.9 (d, 2C, C-3, C-5), 127.8 (d, C-2'), 21.8 (q, CH_3).

The analytical data match those reported in the literature.[157]

(*E*)-1-[2'-(Phenylsulfonyl)vinyl]-4-(trifluoromethyl)benzene (101)



101
$C_{15}H_{11}F_3O_2S$
MW = 312.31 g/mol

According to the **GP 6**, a solution of 1-ethynyl-4-(trifluoromethyl)benzene (600 mg, 3.53 mmol, 1.00 equiv), thiophenol (432 µL, 466 mg, 4.24 mmol, 1.20 equiv), NH_4Cl (188 mg, 3.53 mmol, 1.00 equiv) and H_2O_2 (2.88 mL, 3.20 g, 28.2 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (14 mL) was stirred at 50 °C for 48 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 5/1) to yield **101** (138 mg, 441 µmol, 13%) as a colorless solid.

TLC: R_f = 0.54 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

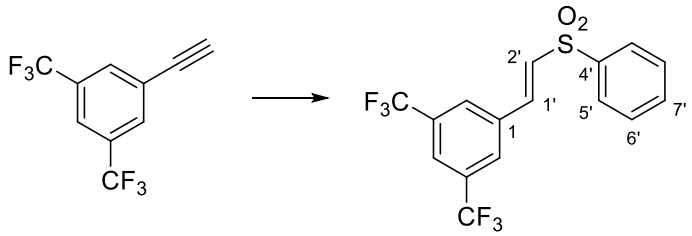
mp: 122 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.98–7.94 (m, 2H, H-5'), 7.71 (d, ^3J = 15.5 Hz, 1H, H-1'), 7.68–7.63 (m, 3H, H-3, H-5, H-7'), 7.60−7.56 (m, 4H, H-6', H-2, H-6), 6.95 (d, ^3J =15.5 Hz, 1H, H-2').

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 140.6 (d, C-1'), 140.3 (s, C-4'), 135.9 (s, C-1), 133.9 (d, C-7'), 132.8 (d, $^2J_{CF}$ = 32.8 Hz, C-4), 130.2 (d, C-2'), 129.6 (d, 2C, C-6'), 128.9 (d, 2C, C-2, C-6), 128.0 (d, 2C, C-5'), 126.2 (q, $^3J_{CF}$ = 3.8 Hz, 2C, C-3, C-5), 123.7 (d, $^1J_{CF}$ = 272.5 Hz, CF_3).

The analytical data match those reported in the literature.[242]

(*E*)-1-[2‘-(Phenylsulfonyl)vinyl]-3,5-bis(trifluoromethyl)benzene (102)



102
$C_{16}H_{10}F_6O_2S$
MW = 308.30 g/mol

According to the **GP 6**, a solution of 1-ethynyl-3,5-bis(trifluoromethyl)benzene (330 µL, 450 mg, 1.89 mmol, 1.00 equiv), thiophenol (160 µL, 170 mg, 1.57 mmol, 1.20 equiv), NH_4Cl (145 mg, 1.89 mmol, 1.00 equiv) and H_2O_2 (1.55 mL, 1.73 g, 15.2 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (8 mL) was stirred at 50 °C for 48 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 5/1) to yield **102** (290 mg, 770 µmol, 49%) as a colorless solid.

TLC: R_f = 0.70 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

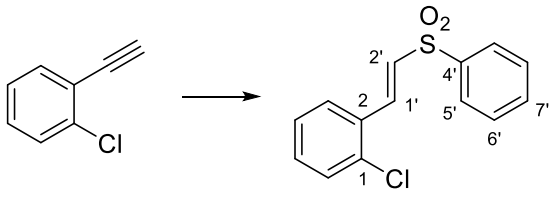
mp: 114 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.97 (d, ^3J = 7.5 Hz, 2H, H-5’), 7.91 (s, 3H, H-2, H-4, H-6), 7.74 (d, ^3J = 15.5 Hz, 1H, H-1’), 7.70−7.65 (m, 1H, H-7’), 7.59 (dd, ^3J = 8.6 7.5 Hz, 2H, H-6’), 7.04 (d, ^3J =15.5 Hz, 1H, H-2’).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 139.8 (s, C-4’), 138.7 (d, C-1’), 134.7 (s, C-1), 134.1 (d, C-7’), 132.9 (d, $^2J_{CF}$ = 33. Hz, 2C, C-3, C-5), 131.9 (d, C-2’), 129.7 (d, 2C, C-6’), 128.3 (d, 2C, C-2, C-6), 128.1 (d, 2C, C-5’), 124.0 (d, C-4), 123.0 (d, $^1J_{CF}$ = 274 Hz, 2C, CF_3).

The analytical data match those reported in the literature.[242]

(*E*)-1-Chloro-2-[2‘-(phenylsulfonyl)vinyl]benzene (103)



103
$C_{14}H_{11}ClO_2S$
MW = 278.75 g/mol

According to the **GP 6**, a solution of 1-chloro-2-ethynylbenzene (100 mg, 732 µmol, 1.00 equiv), thiophenol (90.0 µL, 96.8 mg, 879 µmol, 1.20 equiv), NH_4Cl (39.2 mg, 732 µmol, 1.00 equiv) and H_2O_2 (600 µL, 664 mg, 5.86 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (3 mL) was stirred under air at 50 °C for 48 hours. The crude product was purified by column chromatography (2 × 15 cm, cHex/EtOAc = 5/1) to yield **103** (110 mg, 410 µmol, 57%) as a colorless solid.

TLC: R_f = 0.54 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

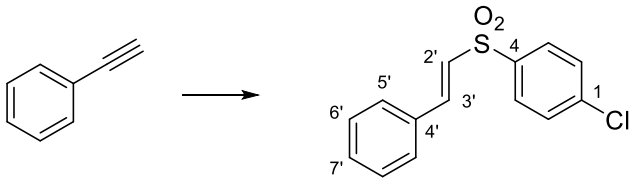
mp: 117 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.09 (d, ^3J = 15.4 Hz, 1H, H-1’), 7.98−7.96 (m, 2H, H-5’), 7.67–7.62 (m, 1H, H-7’), 7.57 (dd, ^3J = 8.4 Hz, 6.9 Hz, 2H, H-6’), 7.51 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, H-3), 7.44 (dd, ^3J = 8.1 Hz, ^2J = 1.3 Hz, 1H, H-6), 7.34 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H-4), 7.28−7.25 (m, 1H, H-5), 6.90 (d, ^3J = 15.4 Hz, 1H, H-2’).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 140.5 (s, C-4’), 138.6 (d, C-1’), 136.9 (s, C-1), 133.7 (d, C-7’), 132.0 (d, C-4), 130.9 (s, C-2), 130.6 (d, C-6), 130.2 (d, C-2’), 129.6 (d, 2C, C-5’), 128.4 (d, C-3), 127.9 (d, 2C, C-6’), 127.4 (d, C-5).

The analytical data match those reported in the literature.[242]

(*E*)-1-Chloro-4-(styrylsulfonyl)benzene (104)



104
$C_{14}H_{11}ClO_2S$
MW = 278.75 g/mol

According to the **GP 6**, a solution of *para*-chloro-phenylacetylene (500 mg, 3.66 mmol, 1.00 equiv), thiophenol (450 µL, 480 mg, 4.39 mmol, 1.20 equiv), NH_4Cl (196 mg, 3.66 mmol, 1.00 equiv) and H_2O_2 (3.00 mL, 3.32 g, 29.3 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (15 mL) was stirred under air at 50 °C for 48 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 5/1) to yield **104** (930 mg, 3.34 mmol, 92%) as a colorless solid.

TLC: R_f = 0.54 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

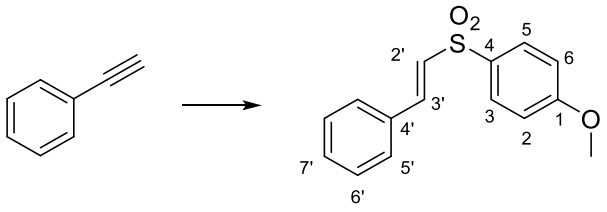
mp: 124 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.98–7.92 (m, 2H, H-3, H-5), 7.67–7.60 (m, 2H, H-3', H-7'), 7.56 (dd, ^3J = 8.5Hz, 7.0 Hz, 2H, H-6'), 7.42 (d, ^3J = 8.6 Hz, 2H, H-5'), 7.37 (d, ^3J = 8.6 Hz, 2H, H-2, H-6), 6.84 (d, ^3J = 15.4 Hz, 1H, H-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.1 (d, C-3'), 140.6 (s, C-4'), 137.4 (s, C-4), 133.7 (d, C-7'), 131.0 (s, C-1), 129.9 (d, 2C, C3, C-5), 129.6 (d, 2C, C-6'), 129.6 (d, 2C, C-2, C-6), 128.0 (d, C-2'), 127.9 (d, 2C, C-5').

The analytical data match those reported in the literature.[241]

(*E*)-1-Methoxy-4-[2'-(phenylsulfonyl)vinyl]benzene (105)



105
$C_{15}H_{14}O_3S$
MW = 274.33 g/mol

According to the **GP 6**, a solution of phenylacetylene (360 µL, 410 mg, 2.45 mmol, 1.00 equiv), 4-methoxythiophenol (381 µL, 411 mg, 2.94 mmol, 1.20 equiv), NH_4Cl (130 mg, 2.45 mmol, 1.00 equiv) and H_2O_2 (2.00 mL, 2.22 g, 19.6 mmol, 8.00 equiv; 30 wt-% in H_2O) in tetrahydrofuran (12 mL) was stirred under air at 50 °C for 48 hours. The crude product was purified by column chromatography (4 × 15 cm, cHex/EtOAc = 5/1) to yield **105** (660 mg, 2.41 mmol, 98%) as a colorless solid.

TLC: R_f = 0.49 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

mp: 136 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.90–7.84 (m, 2H, H-3, H-5), 7.63 (d, ^3J = 15.4 Hz, 1H, H-3'), 7.48−7.46 (m, 2H, H-5', H-6', H-7')*, 7.43–7.35 (m, 3H, H-5', H-6', H-7')*, 7.04-6.98 (m, 2H, H-2, H-6), 6.84 (d, ^3J = 15.4 Hz, 1H, H-2'), 3.87 (s, 3H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 163.7 (s, C-1), 141.4 (s, C-4), 132.6 (d, C-3'), 132.3 (s, C-4')*, 131.1 (s, C-7')*, 130.0 (d, 2C, $C_{ar}H$), 129.2 (d, 2C, $C_{ar}H$), 128.6 (d, 2C, $C_{ar}H$), 128.1 (d, C-2'), 114.7 (d, 2C, C-2, C-6), 55.8 (s, OCH_3).

* The assignments are interconvertible.

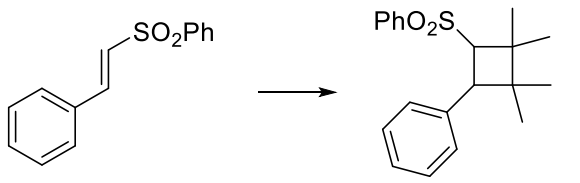
The analytical data match those reported in the literature.[242]

6.8 Intermolecular [2+2] Photocycloaddition of Sulfones

General Procedure 7 (GP 7) for the [2+2] Photocycloaddition of Sulfones with 2,3-dimethyl-2-butene (30)

A solution of the sulfone (1.00 equiv) and 2,3-dimethyl-2-butene (**30**) (30.0 equiv) in dichloromethane (*c* = 20 mM) was irradiated (the wavelength λ [nm] of the light source is indicated at each reaction individually) at room temperature. The progress of the reaction was monitored by TLC. After full conversion was reached, irradiation was stopped, and the solvent was removed *in vacuo*. In some cases, the reaction was stopped when the TLC did not indicate any further consumption of the starting material over a period of two to three hours. The crude product was dry loaded onto CELITE® and purified by column chromatography.

[2,2,3,3-Tetramethyl-4-(phenylsulfonyl)cyclobutyl]benzene (*rac*-97)



92 *rac*-**97**
$C_{20}H_{24}O_2S$
MW = 328.15 g/mol

Following **GP 7**, a solution of sulfone **92** (24.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 300 nm (fluorescent lamps) for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, cHex/EtOAc = 5/1) to yield *rac*-**97** (31.0 mg, 94.4 mmol, 94%, *d.r.* = 88:12) as a colorless solid.

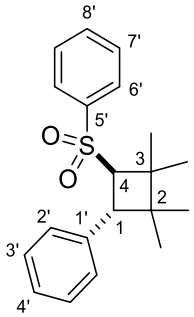
mp: 116 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2965 (w, C-H), 1447 (m, C_{sp3}-H), 1302 (s, SO_2), 1144 (vs, SO_2), 1084 (s), 736 (m), 687 (vs, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 187 (90) $[C_{14}H_{19}]^+$, 145 (100) $[C_{11}H_{13}]^+$, 84 (57) $[C_6H_{12}]^+$.

HRMS (ESI): calcd for $C_{20}H_{25}O_2S^+$ $[M+H]^+$: 329.1570; found: 329.1572.

Diastereomer *rac*-**97**



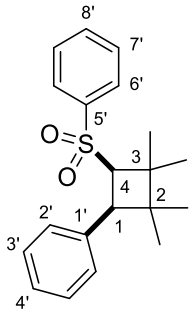
rac-**97**

TLC: R_f = 0.65 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.68–7.65 (m, 2H, H-7'), 6.95–6.87 (m, 3H, H-3', H-4'), 6.86–6.82 (m, 1H, H-8'), 6.75–6.70 (m, 2H, H-6'), 6.56–6.53 (m, 2H, H-2'), 3.87 (d, ^3J = 11.0 Hz, 1H, H-1), 3.70 (d, ^3J = 11.0 Hz, 1H, H-4), 1.70 (s, 3H, CH_3-3), 1.08 (s, 3H, CH_3-2), 0.84 (s, 3H, CH_3-2), 0.38 (s, 3H, CH_3-3).

^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 142.3 (s, C-5'), 136.5 (s, C-1'), 132.7 (d, C-8'), 128.7 (d, 2C, C-6'), 128.6 (d, 2C, C-7'), 128.1 (d, 2C, C-3'), 127.6 (d, 2C, C-2'), 126.6 (d, C-4'), 65.5 (d, C-4), 50.1 (d, C-1), 44.1 (s, C-2), 43.3 (s, C-3), 24.7 [q, (C-3)*C*H_3], 23.5 [q, (C-2)*C*H_3], 20.8 [q, (C-2)*C*H_3], 20.7 [q, (C-3)*C*H_3].

Diastereomer *rac*-**97'**



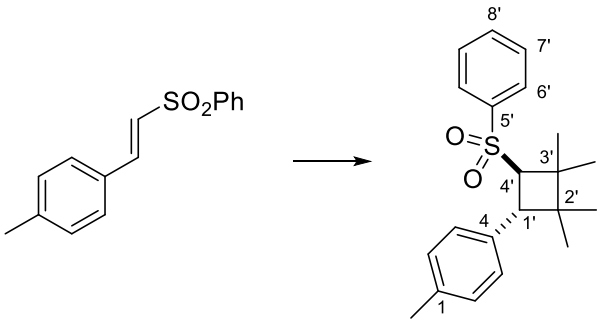
rac-**97'**

TLC: R_f = 0. 69 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.53–7.43 (m, 5H, H-2', H-7', H-8'), 7.32−7.29 (m, 2H, H-6'), 7.25–7.21 (m, 3H, H-3', H-4'), 4.04 (d, ^3J = 10.6 Hz, 1H, H-4), 3.59 (d, ^3J = 10.6 Hz, 1H, H-1), 1.52 (s, 3H, CH_3-3), 1.24 (s, 3H, CH_3-3), 1.15 (s, 3H, CH_3-2), 1.08 (s, 3H, CH_3-2).

^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 141.3 (s, C-5'), 135.0 (s, C-1'), 132.8 (d C-8'), 131.3 (d, 2C, C-2'), 128.7 (d, 2C, C-6'), 127.9 (d, 2C, C-7'), 127.8 (d, 2C, C-3'), 127.0 (d, C-4'), 70.2 (d, C-4), 53.2 (d, C-1), 44.0 (s, C-2), 43.7 (s, C-3), 27.6 [q, (C-3)*C*H$_3$], 26.6 [q, (C-3)*C*H$_3$], 20.9 [q, (C-2)*C*H$_3$], 20.6 [q, (C-2)*C*H$_3$].

1-Methyl-4-[2',2',3',3'-tetramethyl-4'-(phenylsulfonyl)cyclobutyl]benzene (*rac*-107)



100 | ***rac*-107** $C_{21}H_{26}O_2S$ MW = 342.50 g/mol

Following **GP 7**, a solution of sulfone **100** (25.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 300 nm (fluorescent lamps) for 15 hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, cHex/EtOAc = 5/1) to yield *rac*-**107** (31.0 mg, 94.4 mmol, 94%, *d.r.* > 20:1) as a colorless solid.

TLC: R_f = 0.57 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

mp: 94 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2961 (m, C_{sp3}-H), 2925 (m, C-H), 2867 (q, C_{sp3}-H), 1447 (m, C_{sp3}-H), 1304 (s, SO_2), 1148 (vs, SO_2), 1086 (m), 736 (m), 688 (m, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 201 (100) $[C_{15}H_{21}]^+$, 159 (89) $[C_{12}H_{15}]^+$, 145 (73) $[C_{11}H_{13}]^+$, 131 (14) $[C_{10}H_{11}]^+$, 105 (19) $[C_8H_9]^+$, 84 (57) $[C_6H_{12}]^+$.

HRMS (ESI): calcd for $C_{21}H_{27}O_2S^+$ $[M+H]^+$: 343.1726; found: 343.1728.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.72–7.66 (m, 2H, H-6'), 7.50–7.45 (m, 1H, H-8'), 7.31 (t, ^3J = 7.8 Hz, 2H, H-7'), 6.86 (d, ^3J = 7.8 Hz, 2H, H-2, H-6), 6.60 (d, ^3J = 7.8 Hz, 2H,

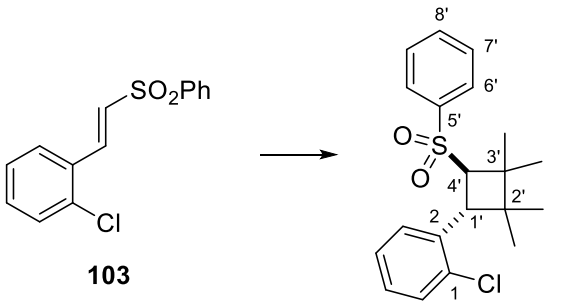
H-3, H-5), 3.77 (s, 2H, H-1', H-4'), 2.23 (s, 3H, $ArCH_3$), 1.55 (s, 3H, CH_3-3'), 1.14 (s, 3H, CH_3-3'), 1.07 (s, 3H, CH_3-2'), 0.57 (s, 3H, CH_3-2').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 141.2 (s, C-5'), 136.0 (s, C-1), 133.2 (d, C-8'), 132.8 (s, C-4), 128.9 (d, 2C, C-7'), 128.7 (d, 2C, C-2, C-6), 128.3 (d, 2C, C-6'), 127.2 (d, 2C, C-3, C-5), 65.5 (d, C-4'), 49.3 (d, C-1'), 44.0 (s, C-3')*, 43.2 (s, C-2')*, 24.7 [q, (C-3')*C*H_3], 23.6 [q, (C-2')*C*H_3], 21.1 (q, $ArCH_3$), 20.7 [q, (C-2')*C*H_3], 20.5 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

The minor diastereoisomer could not be isolated due to the low quantity of the material.

1-Chloro-2-[2',2',3',3'-tetramethyl-4'-(phenylsulfonyl)cyclobutyl]benzene (*rac*-108)



rac-**108**
$C_{20}H_{23}ClO_2S$
MW = 362.91 g/mol

Following **GP 7**, a solution of sulfone **103** (27.9 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 μL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 300 nm (fluorescent lamps) for 20 hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, cHex/EtOAc = 5/1) to yield *rac*-**108** (29.2 mg, 80.5 mmol, 80%) as a colorless solid.

TLC: R_f = 0.64 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

mp: 163 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3065 (w, C_{ar}-H), 2963 (m, C_{sp3}-H), 2926 (m, C-H), 1476 (m, C_{sp3}-H), 1449 (m, C=C), 1306 (s, SO_2), 1148 (vs, SO_2), 1086 (m), 720 (m, C_{ar}-H), 688 (m, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 221 (100) $[C_{14}H_{18}Cl]^+$, 179 (91) $[C_{11}H_{12}Cl]^+$, 165 (55), 125 (31) $[C_7H_6Cl]^+$.

HRMS (ESI): calcd for $C_{20}H_{24}{}^{35}ClO_2S^+$ $[M+H]^+$: 363.1180; found: 363.1182.

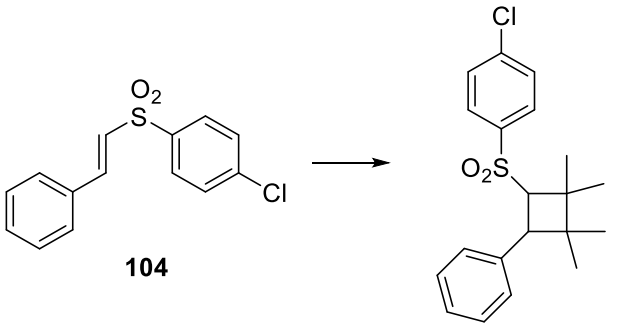
calcd for $C_{20}H_{24}{}^{37}ClO_2S^+$ $[M+H]^+$: 365.1151; found: 365.1153.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.64 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 2H, H-7'), 7.45−7.38 (m, 1H, H-8'), 7.31–7.20 (m, 3H, H-6', H-6), 6.99 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, H-5), 6.77 (td, ^3J = 7.6 Hz, ^3J = 1.3 Hz, 1H, H-4), 6.47 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, H-3), 4.35 (d, ^3J = 11.2 Hz, 1H, H-1'), 3.77 (d, ^3J = 11.2 Hz, 1H, H-4'), 1.60 (s, 3H, CH_3-3'), 1.19 (s, 3H, CH_3-2'), 1.18 (s, 3H, CH_3-3'), 0.64 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 140.9 (s, C-5'), 134.5 (s, C-1), 133.8 (s, C-2), 133.3 (d, C-8'), 129.7 (d, C-6), 128.9 (d, 2C, C-6'), 128.3 (d, C-3), 128.2 (d, 2C, C-7'), 127.7 (d, C-5), 125.9 (d, C-4), 65.3 (d, C-4'), 46.1 (d, C-1'), 44.4 (s, C-2')*, 43.9 (s, C-3')*, 24.8 [q, (C-3')*C*H_3], 24.6 [q, (C-2')*C*H_3], 21.2 [q, (C-2')*C*H_3], 20.5 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

1-Chloro-4-((2,2,3,3-tetramethyl-4-phenylcyclobutyl)sulfonyl)benzene (*rac*-109)



Following **GP 7**, a solution of sulfone **104** (27.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 300 nm (fluorescent lamps) for 20 hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, cHex/EtOAc = 9/1) to yield *rac*-**109** (26.6 mg, 73.3 mmol, 73%, *d.r.* = 86:14) as a colorless solid.

mp: 151 °C.

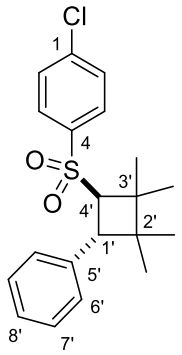
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3065 (w, C_{ar}-H), 2963 (m, C_{sp3}-H), 2927 (m, C-H), 2869 (w, C_{sp3}-H), 1900 (w), 1494 (s, C_{sp3}-H), 1302 (s, SO_2), 1145 (vs, SO_2), 1085 (vs, C-Cl), 1014 (m), 737 (s, C_{ar}-H), 717 (vs, C_{ar}-H), 688 (vs, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 222 (100) $[C_{14}H_{18}Cl]^+$, 179 (93) $[C_{11}H_{12}Cl]^+$, 165 (40), 125 (26) $[C_7H_6Cl]^+$.

HRMS (ESI): calcd for $C_{21}H_{17}{}^{35}ClO_2S^+$ $[M+H]^+$: 363.1180; found: 363.1181.

calcd for $C_{21}H_{17}{}^{37}ClO_2S^+$ $[M+H]^+$: 365.1151; found: 365.1152.

Diastereoisomer *rac*-**109**



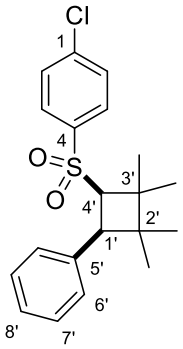
rac-**109**

TLC: R_f = 0.69 (cHex/EtOAc = 5/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.69 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2H, H-6'), 7.51 (t, ^3J = 7.4 Hz, 1H, H-8'), 7.36–7.33 (m, 2H, H-7'), 7.07–6.99 (m, 2H, H-3, H-5), 6.69–6.59 (m, 2H, H-2, H-6), 3.77 (d, ^3J = 11.1 Hz, 1H, H-1'), 3.72 (d, ^3J = 11.1 Hz, 1H, H-4'), 1.55 (s, 3H, CH_3-3'), 1.13 (s, 3H, CH_3-3'), 1.08 (s, 3H, CH_3-2'), 0.57 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.0 (s, C-4'), 134.6 (s, C-5), 133.5 (d, C-8'), 132.4 (s, C-1), 129.1 (d, 2C, C-6'), 128.6 (d, 2C, C-3, C-5), 128.3 (d, 2C, C-7'), 128.2 (d, 2C, C-2, C-6), 65.5 (d, C-4'), 49.1 (d, C-1'), 44.1 (s, C-2'), 43.4 (s, C-3'), 24.7 [q, (C-3')*C*H_3], 23.6 [q, (C-2')*C*H_3], 20.8 [q, (C-2')*C*H_3], 20.5 [q, (C-3')*C*H_3].

Diastereoisomer *rac*-**109'**



rac-**109'**

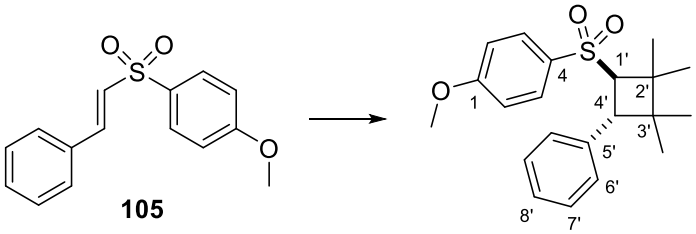
TLC: R_f = 0.64 (cHex/EtOAc = 5/1) [UV, $KMnO_4$].

^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.58–7.53 (m, 2H, H-7'), 7.51−7.48 (m, 1H, H-8'), 7.43 (d, ^3J = 8.6 Hz, 2H, H-3, H-5), 7.38–7.34 (m, 2H, H-6'), 7.21 (d, ^3J = 8.6 Hz, 2H, H-2, H-6), 4.04 (d, ^3J = 10.6 Hz, 1H, H-4'), 3.58 (d, ^3J = 10.6 Hz, 1H, H-1'), 1.47 (s, 3H, CH_3-3'), 1.21 (s, 3H, CH_3-3'), 1.12 (s, 3H, CH_3-2'), 1.06 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.4 (s, C-4), 133.8 (s, C-5'), 133.2 (d, C-8'), 133.1 (s, C-1), 132.6 (d, 2C, C-3, C-5), 128.9 (d, 2C, C-6'), 128.0 (d, 2C, C-2, C-6), 127.9 (d, 2C, C-7'), 70.2 (d, C-4'), 52.7 (d, C-1'), 44.0 (s, C-3')*, 43.9 (s, C-2')*, 27.7 [q, (C-3')*C*H_3], 26.6 [q, (C-2')*C*H_3], 20.9 [q, (C-2')*C*H_3], 20.6 [q, (C-3')*C*H_3].

* The assignments are interconvertible.

1-Methoxy-4-[(-2',2',3',3'-tetramethyl-4'-phenylcyclobutyl)sulfonyl]benzene (*rac*-110)



rac-**110**
$C_{21}H_{26}O_3S$
MW = 358.50 g/mol

Following **GP 7**, a solution of sulfone **105** (27.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 300 nm (fluorescent lamps) for 20 hours at room temperature. The crude product was

purified by column chromatography (2 × 12 cm, cHex/EtOAc = 9/1) to yield *rac*-**110** (21.7 mg, 60.5 mmol, 61%) as a yellow colored solid.

TLC: R_f = 0.54 (cHex/EtOAc = 5/1) [UV, $KMnO_4$].

mp: >230 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2925 (m, C-H), 2854 (m, C-O-CH_3), 1596 (m, C=C), 1498 (m, C=C), 1315 (m, SO_2), 1144 (vs, SO_2), 1086 (m), 720 (m, C_{ar}-H), 688 (m, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 275 (25), 187 (94) $[C_{14}H_{19}]^+$, 145 (100) $[C_{11}H_{13}]^+$, 131 (60) $[C_{10}H_{11}]^+$, 117 (17) $[C_9H_9]^+$, 91 (24) $[C_7H_7]^+$.

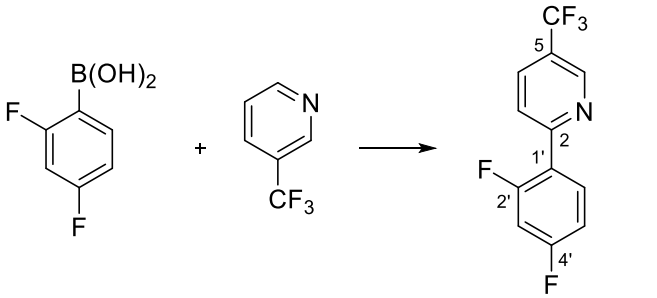
HRMS (ESI): calcd for $C_{21}H_{27}O_3S^+$ $[M+H]^+$: 359.1675; found: 359.1676.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.61–7.55 (m, 2H, H-2, H-6), 7.12–7.04 (m, 3H, H-7', H-8'), 6.78–6.70 (m, 4H, H-3, H-5, H-6'), 3.79 (s, 3H, ArOCH_3), 3.77 (s, 1H, H-1'), 3.76 (s, 1H, H-4'), 1.54 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-2'), 1.09 (s, 3H, CH_3-3'), 0.58 (s, 3H, CH_3-3').

^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 163.5 (s, C-1), 136.1 (s, C-4), 132.9 (d, 2C, C-6'), 130.5 (d, 2C, C-2, C-6), 128.0 (d, C-7'), 127.4 (d, 2C, C-7'), 126.5 (d, C-8'), 114.1 (d, 2C, C-3, C-5), 65.7 (d, C-1'), 55.7 (q, ArOCH_3), 49.8 (d, C-4'), 44.0 (s, C-3')*, 43.2 (s, C-2')*, 24.7 [q, (C-2')*C*H_3], 23.7 [q, (C-3')*C*H_3], 20.8 [q, (C-3')*C*H_3], 20.6 [q, (C-2')*C*H_3].

* The assignments are interconvertible.

2-(2',4'-Difluorophenyl)-5-(trifluoromethyl)pyridine



$C_{12}H_6F_5N$
MW = 259.20 g/mol

According to a literature known procedure:[243] $Pd(PPh_3)_4$ (718 mg, 621 µmol, 20 mol%) and aqueous Na_2CO_3 solution (78 mL, c = 1 M) was added to a solution of (2,4-difluorophenyl)boronic acid (4.91 g, 31.1 mmol, 1.00 equiv) and 3-(trifluoromethyl)pyridine (7.93 g, 34.2 mmol, 1.10 equiv) in tetrahydrofuran (120 mL) and the reaction was stirred at 60 °C for 24 hours. After cooling to room temperatue, water (150 mL) and dichloromethane (150 mL) was added and the solution was stirred vigorously for five minutes. The mixture was partitioned between water and dichloromethane, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with saturated aqueous NaCl solution (400 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (5 × 20 cm, P/Et_2O = 20/1) to yield the title compound (4.87 g, 18.9 mmol, 60%) as a colorless solid.

TLC: R_f = 0.7 (P/Et_2O = 9/1) [UV].

mp: 56 °C.

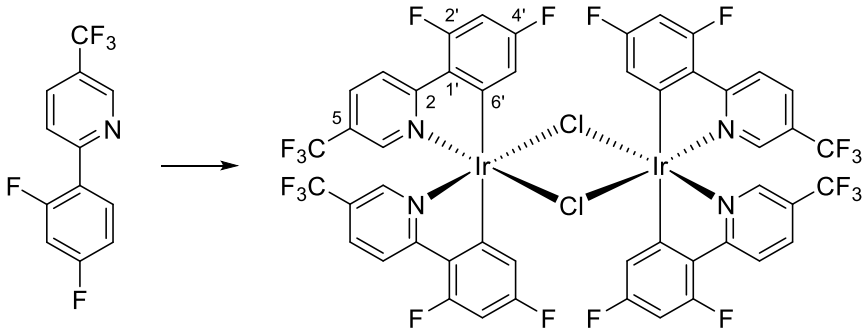
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.96 (d, ^4J = 2.4 Hz, 1H, H-6), 8.09 (*virt*. td, $^4J_{HF} \approx$ 8.9 Hz, ^3J = 7.2 Hz, 1H, H-6‘), 7.99 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H, H-4), 7.90 (d, ^3J = 8.4 Hz, 1H, H-3), 7.04 (dddd, $^3J_{HF}$ = 8.7 Hz, ^3J = 7.2 Hz, ^4J = 2.6 Hz, $^5J_{HF}$ = 1.0 Hz, 1H; H-5‘), 6.95 (ddd, $^3J_{HF}$ = 11.3 Hz, $^3J_{HF}$ = 8.7 Hz, ^4J = 2.6 Hz, 1H, H-3‘).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 164.0 (dd, $^1J_{CF}$ = 252.9 Hz, $^3J_{CF}$ = 12.1 Hz, C-2‘)*, 161.1 (dd, $^1J_{CF}$ = 253.8 Hz, $^3J_{CF}$ = 12.0 Hz, C-4‘)*, 155.9 (s, C-2), 146.7 (q, $^3J_{CF}$ = 4.1 Hz, C-6), 133.9 (q, $^3J_{CF}$ = 3.9 Hz, C-4), 132.6 (dd, $^3J_{CF}$ = 9.9 Hz, 4.1 Hz, C-6‘), 125.3 (q, $^2J_{CF}$ = 33.2 Hz, C-5), 123.8 (d, $^4J_{CF}$ = 10.9 Hz, C-3), 123.7 (q, $^1J_{CF}$ = 272.1 Hz, CF_3), 122.6 (dd, $^2J_{CF}$ = 11.3 Hz, $^4J_{CF}$ = 3.9 Hz, C-1‘), 112.4 (dd, $^2J_{CF}$ = 21.3 Hz, $^4J_{CF}$ = 3.7 Hz, C-5‘), 104.8 (dd, $^2J_{CF}$ = 26.9 Hz, 25.5 Hz, C-3‘).

* The assignments are interconvertible.

The analytical data match those reported in the literature.[243]

Bis-(_μ_)-Chlortetrakis[2-(2',4'-difluorphenyl)-5-(trifluormethyl)pyridinato]-(C^2,_N_)di-iridium(III)



$C_{48}H_{20}Cl_2F_{20}Ir_2N_4$
MW = 1488.02 g/mol

Acoording to a literature known procedure:[243] A suspension of $IrCl_3 \bullet 3H_2O$ (1.00 g, 2.84 mmol, 1.00 equiv) and 2-(2',4'-difluorophenyl)-5-(trifluoromethyl)pyridine (1.69 g, 6.52 mmol, 1.20 equiv) in 2-ethoxyethanol/water (60 mL, 2:1/v:v) was heated to 120 °C for 22 hours. After cooling to room temperature, water (120 mL) was added to the yellow colored suspension. The precipitate was filtered and washed with water (3 × 50 mL) and was subsequently dissolved in dichloromethane. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Residual water was removed under high vacuum to yield the title compound (3.34 g, 2.24 mmol, 79%) as a bright yellow solid.

mp: >230 °C.

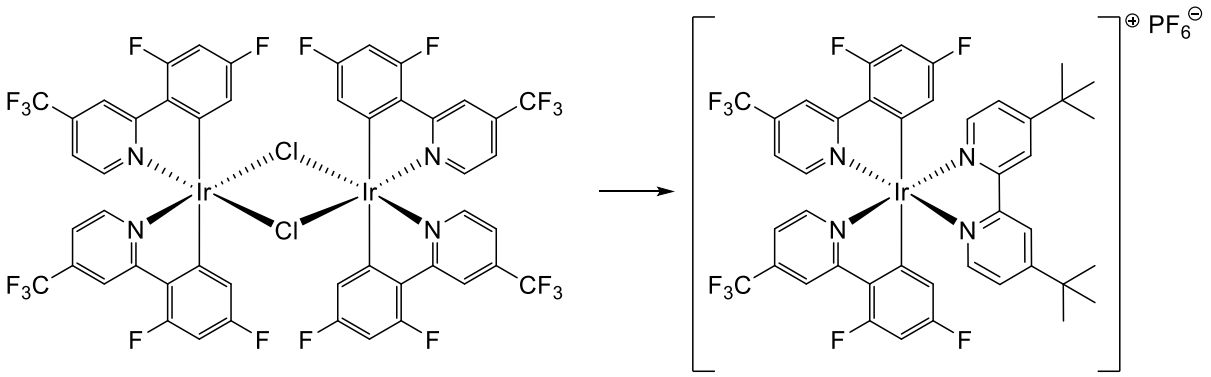
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.51 (d, ^4J = 2.2 Hz, 4H, H-6), 8.46 (dd, ^3J = 8.7 Hz, $^5J_{HF}$ = 2.9 Hz, 4H, H-3), 8.04 (dd, ^3J = 8.7 Hz, ^4J = 2.2 Hz, 4H, H-4), 6.43 (ddd, $^3J_{HF}$ =11.4 Hz, 8.7 Hz, ^4J = 2.2 Hz, 4H, H-3'), 5.12–4.99 (m, 4H, H-5').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 169.04 (d, $^4J_{CF}$ = 6.8 Hz, C-6'), 164.7 (dd, $^1J_{CF}$ = 199.5 Hz, $^3J_{CF}$ = 13.2 Hz, C-2'), 161.6 (dd, $^1J_{CF}$ = 262.0 Hz, $^3J_{CF}$ = 13.4 Hz, C-4'), 148.2 (d, $^4J_{CF}$ = 7.6 Hz, C-6), 147.5 (s, C-2), 136.1 (s, C-4), 126.7 (s, C-5), 124.6 (d, $^2J_{CF}$ = 35.1 Hz, C-1'), 122.8 (d, $^2J_{CF}$ = 20.8 Hz, C-3), 122.3 (q, CF_3), 112.6 (d, $^2J_{CF}$ = 18.3 Hz, C-5'), 99.2 (t, $^2J_{CF}$ = 26.6 Hz, C-3').

* The assignments are interconvertible. The C-F-couplings could not be detected.

The analytical data match those reported in the literature.[243]

{Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (116)



116
$C_{42}H_{34}F_{16}IrN_4P$
MW = 1121.93 g/mol

According to a literature known procedure:[243] A suspension of the Ir-dimer (298 mg, 200 µmol, 1.00 equiv) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (116 mg, 440 µmol, 2.20 equiv) in ethyleneglycol (14 mL) was heated to 150 °C for 24 hours in a sealed tube. After it had cooled to room temperature, the reaction mixture was partitioned between water (140 mL) and cyclohexane (60 mL) and the aqueous layer was washed with cyclohexane (2 × 60 mL). Subsequently, the aqueous layer was heated to 85 °C and a solution of NH_4PF_6 (2.20 g, 13.5 mmol, 68.0 equiv) in water (20 mL) was added. The resulting suspension was cooled to room temperature, the precipitate was filtered off and dried under high vacuum. The crude product was purified by column chromatography (4 × 20 cm, CH_2Cl_2/MeOH = 99/1). The resulting yellow colored solid was recrystallized from acetone (vapor diffusion) to yield **116** (138 mg, 123 µmol, 62%) as a bright yellow colored solid.

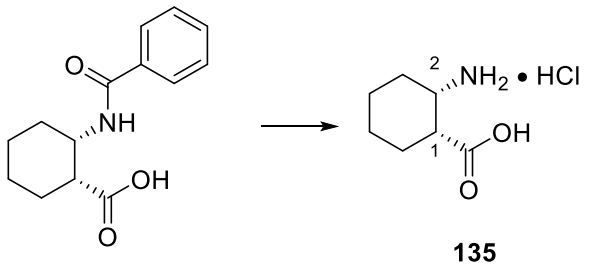
TLC: R_f = 0.33 (CH_2Cl_2/MeOH = 99/1) [UV].

^{1}H NMR (500 MHz, Acetone-d_6): δ [ppm] = 8.94 (d, ^4J =1.9 Hz, 2H, H-6'), 8.61 (dd, ^3J = 8.8 Hz, ^4J = 2.6 Hz, 2H, H-6), 8.40 (dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz, 2H, H-5), 8.18 (d, ^3J = 5.9 Hz, 1H, H-4'), 7.86–7.71 (m, 4H, H-3, H-3'), 6.87 (dd, ^3J = 9.4 Hz, ^4J = 2.3 Hz, 2H, H-4''), 5.97 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 2H, H-6''), 1.42 (s, 18H, CH_3).

The analytical data match those reported in the literature.[243]

6.9 Synthesis of the Chiral Thiourea-Thioxanthone Hybrid

(1*R*,2*S*)-2-Aminocyclohexane-1-carboxylic acid hydrochloride (135)



134 **135**
$C_7H_{14}ClNO_2$
MW = 179.64 g/mol

This reaction was performed according to a literature known procedure.[199] A solution of (1*R*,2*S*)-2-benzamidocyclohexane-1-carboxylic acid (**134**) (3.00 g, 12.1 mmol, 1.00 equiv) in aqueous hydrochloric acid solution (6 N, 150 mL) was stirred at 120 °C for 48 h. Evaporation of all volatiles under reduced pressure yielded **135** as a colorless solid (2.15 g, 12.0 mmol, 99%).

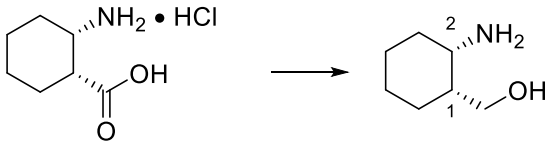
mp: 198-220 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 12.9 (s, 1H, COOH), 8.06 (s, 3H, NH_3), 3.08−3.41 (m, 1H, H-2), 2.89 (*virt*. q, $^3J = {}^3J \cong 4.4$ Hz, 1H, H-1), 1.11−2.06 (m, 8H, H-3. H-4, H-5, H-6).

^{13}C NMR (101 MHz, DMSO-d_6): δ [ppm] = 174.0 (s, COOH), 48.8 (d, C-2), 41.8 (d, C-1), 27.0 (t, C-3), 25.5 (t, C-6), 22.2 (t, C-5), 22.0 (t, C-4),

The analytical data match those reported in the literature.[199]

[(1*R*,2*S*)-2-Aminocyclohexyl]methanol (136)



135 **136**
$C_7H_{15}NO$
MW = 129.20 g/mol

This reaction was performed analogous to a modified literature procedure.[200] Lithiumaluminumhydride (0.68 g, 18.0 mmol, 1.61 equiv) was added in small portions to a solution of (1*R*,2*S*)-2-aminocyclohexane-1-carboxylic acid hydrochloride (**135**) (2.02 g, 11.2 mmol, 1.00 equiv) in tetrahydrofuran (65 mL) at 0 °C. The suspension was warmed to room temperature and then heated at reflux for 16 hours. Afterwards, the suspension was cooled to 0 °C, and saturated aqueous *Rochelle*-salt solution (3 mL), aqueous NaOH solution (9 mL, 15 wt-%) and again saturated aqueous *Rochelle*-salt solution (9 mL) were added successively. The formed colorless, crystalline precipitate was filtered off and washed with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl solution (150 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield **136** (1.37 g, 10.6 mmol, 95%) as a colorless, crystalline solid.

racemic version: the racemic version of this reaction was performed analogously employing commercially available *cis*-2-aminocyclohexane-1-carboxylic acid (500 mg, 3.40 mmol, 1.00 equiv) and lithiumaluminumhydride (200 mg, 5.20 mmol, 1.50 equiv). *rac*-**136** (400 mg, 3.10 mmol, 89%) was isolated as a colorless, slowly crystallizing oil.

mp: 78 °C.

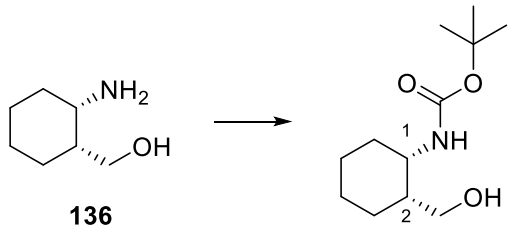
$[\alpha]_D^{20}$: −12 (*c* = 1.00 M, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.79 (dd, ^2J = 11.0 Hz, ^3J = 6.3 Hz, 1H, C*H*HOH), 3.74 (dd, ^2J = 11.0 Hz, ^3J = 3.3 Hz, 1H, CH*H*OH), 3.22 (*virt*. q, $^3J = {}^3J \cong 4.2$ Hz, 1H, H-2), 2.77-2.14 (m, 2H, NH_2), 1.94–1.27 (m, 10H, H-1, H-3, H-4, H-5, H-6, OH).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 66.1 (t, C-1), 51.4 (d, C-7), 40.8 (d, C-2), 32.3 (t, C-6), 24.8 (t, C-3), 24.2 (t, C-4), 21.4 (t, C-5).

The analytical data match those reported in the literature.[200]

***tert*-Butyl-[(1*S*,2*R*)-2-(hydroxymethyl)-cyclohexyl]-carbamate (137)**



137
$C_{12}H_{23}NO_3$
MW = 229.32 g/mol

This reaction was performed analogous to a modified literature procedure.[244] Triethylamine (280 µL, 203 mg, 2.01 mmol, 2.00 equiv) was added to a solution of [(1*S*,2*R*)-2-aminocyclohexyl]-methanol (**136**) (130 mg, 1.01 mmol, 1.00 equiv) in dichloromethane (2 mL). The solution was cooled to 0 °C and Boc_2O (230 mg, 1.06 mmol, 1.05 equiv) was added. The solution was stirred and allowed to warm to room temperature overnight. The reaction was quenched by the addition of aqueous hydrochloric acid solution (5 mL, c = 1 M). The reaction mixture was partitioned between aqueous hydrochloric acid and dichloromethane, and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and successively washed with saturated aqueous $NaHCO_3$ solution (2 × 15 mL) and saturated aqueous NaCl solution (2 × 15 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (3 × 10 cm, cHex:EtOAc = 9:1 → 4:1) to yield **137** (213 mg, 928 µmol, 92%) as a yellow colored oil.

racemic version: the racemic version of this reaction was performed analogously employing alcohol *rac*-**136** (377 mg, 2.92 mmol, 1.00 equiv), triethylamine (813 µL, 590 mg, 5.84 mmol, 2.00 equiv) and Boc_2O (668 mg, 3.06 mmol, 1.05 equiv). *rac*-**137** (525 mg, 2.30 mmol, 78%) was isolated as a yellow colored oil.

TLC: R_f = 0.17 (cHex/EtOAc = 4/1) [UV, KMnO4].

$[\alpha]_D^{20}$: −30 (c = 1.00 M, CH_2Cl_2).

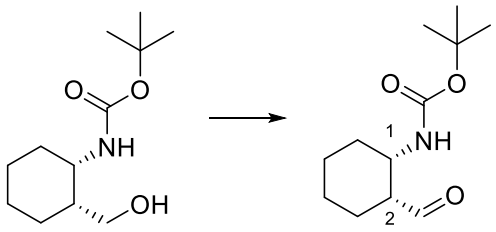
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.77 (d, ^3J = 9.0 Hz, 1H, NH), 4.15 (*virt*. dd, ^3J = ^3J ≅ 11.4 Hz, 4.2 Hz, 1H, H-2), 4.07−4.04 (m, 1H, H-1), 3.34 (dd, ^2J = 11.9 Hz, ^3J = 4.7 Hz,

1H, CH*H*OH), 3.21 (*virt*. dt, ^{2}J = 11.9 Hz, $^{3}J = {}^{3}J \cong 11.4$ Hz, 1H, C*H*HOH), 1.83−1.52 (m, 5H, H-2, H-3, H-5, H-6, OH), 1.36−1.14 (m, 3H, H-3, H-4, H-6), 0.98−0.86 (m, 1H, H-5),

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 157.2 (s, NH*C*O), 80.0 [s, *C*$(CH_3)_3$], 63.9 (t, *C*H_2OH), 45.1 (d, C-1), 43.1 (d, C-2), 30.3 (t, C-6), 28.2 (q, 3C, CH_3), 24.9 (t, C-3), 23.1 (t, C-4), 21.0 (t, C-5).

The analytical data match those reported in the literature.[200]

tert-Butyl-[(1*S*,2*R*)-2-formylcyclohexyl]-carbamate (138)



138 **138**
$C_{12}H_{21}NO_3$
MW = 227.30 g/mol

This reaction was performed analogous to a modified literature procedure.[203] A solution of dimethylsulfoxide (1.38 mL, 1.52 g, 19.5 mmol, 3.00 equiv) in dichloromethane (2 mL) was added dropwise to a solution of oxalyl chloride (0.55 mL, 824 mg, 6.50 mmol, 1.00 equiv) in dichloromethane (16 mL) at −78 °C. The reaction solution was stirred for one hour at −78 °C. Subsequently, a solution of *tert*-butyl-[(1*S*,2*R*)-2-(hydroxymethyl)-cyclohexyl]-carbamate (**137**) (1.49 g, 6.50 mmol, 1.00 equiv) in dichloromethane (7 mL) was added slowly over ten minutes and stirring was continued for ten minutes. Triethylamine (4.50 mL, 3.30 g, 32.5 mmol, 5.00 equiv) was added, the reaction mixture was stirred for 15 minutes at −78 °C and was then allowed to warm to room temperature. The reaction was quenched by addition of water (20 mL) and was partitioned between water and dichloromethane. The aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed successively with saturated aqueous NH_4Cl solution (60 mL) and saturated aqueous NaCl solution (60 mL). The organic layer was dried over Na_2SO_4, filtered and all volatiles were removed in vacuo to yield **138** (1.39 g, 6.12 mmol, 94%) as a brownish colored solid. *ent*-**138** was used in the next step without further purification.

racemic version: the racemic version of this reaction was performed analogously employing oxalyl chloride (122 µL, 181 mg, 1.43 mmol, 1.00 equiv), dimethylsulfoxide (304 µL, 334 mg,

4.28 mmol, 3.00 equiv), alcohol *rac*-**137** (327 mg, 1.43 mmol, 1.00 equiv) and triethylamine (988 µL, 721 mg, 7.13 mmol, 5.00 equiv). *rac*-**138** (319 mg, 14.0 mmol, 98%) was isolated as a brownish colored solid.

mp: 23-25 °C.

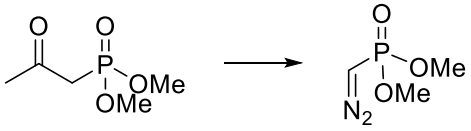
[α]D^{20}: +82.4 (*c* = 0.17 M, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 9.70 (d, ^3J = 4.2 Hz, 1H, CHO), 5.31−5.15 (m, 1H, NH), 3.97 (*virt*. tt, $^3J = {}^3J \cong$ 9.1 Hz, 4.1 Hz, 1H, H-1), 2.71 (*virt*. q, $^3J = {}^3J \cong$ 4.6 Hz, 1H, H-2), 2.01−1.91 (m, 1H, H-3), 1.77−1.53 (m, 6H, H-3, H-4, H-5, H-6), 1.43 (s, 9H, CH_3), 1.38−1.19 (m, 1H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 204.8 (s, CHO), 155.5 (s, NH*C*O), 79.6 [s, *C*$(CH_3)_3$], 52.1 (d, C-2), 48.2 (d, C-1), 29.8 (t, C-6), 28.5 (q, 3C, CH_3), 23.9 (t, C-4), 23.7 (t, C-5), 22.9 (t, C-3).

The analytical data match those reported in the literature.[200]

Dimethyl-(diazomethyl)-phosphonate (139)



139
$C_3H_7N_2O_3P$
MW = 150.07 g/mol

Methanesulfonylchloride (1.40 mL, 2.07 g, 18.1 mmol, 1.50 equiv) was added dropwise over a period of five minutes to a suspension of NaN_3 (1.17 g, 18.1 mmol, 1.50 equiv) in acetonitrile (23 mL) and the suspension was stirred for one hour at room temperature. Dimethyl-(2-oxopropyl)-phosphonate (1.66 mL, 2.00 g, 12.0 mmol, 1.00 equiv) was added dropwise and stirring was continued for five hours at room temperature. Cs_2CO_3 (5.88 g, 18.1 mmol, 1.50 equiv) was added and the yellow suspension was stirred for 14 hours at room temperature. After addition of methanol (23 mL), the reaction was stirred for one hour, before it was quenched by the addition of saturated aqueous NH_4Cl solution (20 mL). The reaction mixture was partitioned between methanol and NH_4Cl solution, and the aqueous layer was

extracted with ethyl acetate (4 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (4 × 25 cm, Et_2O) to yield **139** (1.10 g, 7.32 mmol, 59%) as a yellow colored oil.

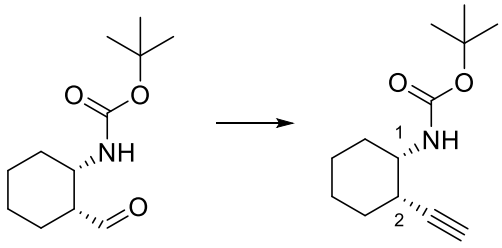
TLC: R_f = 0.34 (Et_2O) [UV, KMnO4].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.77 (d, $^3J_{HP}$ = 11.9 Hz, 6H, OCH_3), 3.76 (d, $^2J_{HP}$ = 11.0 Hz, 1H, CHN_2).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 53.1 (dq, $^2J_{CP}$ = 5.5 Hz, CH_3), 28.8 (dd, $^2J_{CP}$ = 233.6 Hz, CHN_2).

The analytical data match those reported in the literature.[204]

***tert*-Butyl-[(1*S*,2*S*)-2-ethynylcyclohexyl]-carbamate (140)**



138 **140**
$C_{13}H_{21}NO_2$
MW = 223.32 g/mol

KO^{t}Bu (1.45 g, 12.9 mmol, 2.10 equiv) was added to a solution of dimethyl(diazomethyl)phosphonate (**139**) (1.90 g, 12.6 mmol, 2.05 equiv) in tetrahydrofuran (15 mL) were cooled to −78 °C and the reaction solution was stirred for one hour at −78 °C. A solution of aldehyde **139** (1.39 g, 6.16 mmol, 1.00 equiv) in tetrahydrofuran (190 mL) was added slowly. The reaction mixture was stirred for 15 hours and was allowed to warm to room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (80 mL). The mixture was partitioned between aqueous NH_4Cl solution and tetrahydrofuran, and the aqueous layer was extracted with ethyl acetate (3 × 80 mL). The combined organic layers were successively washed with saturated aqueous NH_4Cl solution (2 × 250 mL) and saturated aqueous NaCl solution (2 × 250 mL). The organic layer was dried over Na_2SO_4,

filtered and concentrated in vacuo. The crude product was purified by column chromatography (4 × 20 cm, cHex/EtOAc = 10/1) to yield **140** (0.91 g, 4.07 mmol, 67%) as a colorless solid.

racemic version: the racemic version of this reaction was performed analogously employing dimethyl(diazomethyl)phosphonate (**139**) (677 mg, 451 mmol, 2.05 equiv), aldehyde *rac*-**138** (500 mg, 2.20 mmol, 1.00 equiv) and KO^{t}Bu (518 mg, 4.62 mmol, 2.10 equiv). *rac*-**139** (280 mg, 1.25 mmol, 57%) was obtained as a colorless solid.

TLC: R_f = 0.64 (cHex/EtOAc = 4/1) [UV, KMnO4].

mp: 50 °C.

$[\alpha]_D^{20}$: −24 (*c* = 1.00 M, CH_2Cl_2).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3437 (w, N-H), 3309 (w, C-H), 2977 (w, C_{sp3}-H), 2934 (m, C_{sp2}-H), 2860 (w, C-H), 2111 (w, C≡C), 1702 (s, C=O), 1497 (s, N-H), 1365 (m), 1245 (m), 1165 (s), 944 (w), 864 (w), 779 (w), 626 (m).

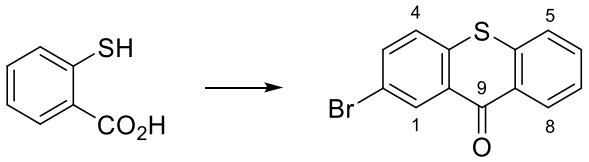
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.80 (d, ^3J = 9.4 Hz, 1H, NH), 3.56 (*virt*. ddt, ^3J = 13.1 Hz, 8.6 Hz, $^3J = {}^3J \cong$ 4.0 Hz, 1H, H-1), 2.96 (br. s, 1H, H-2), 2.11 (d, ^4J = 2.5 Hz, 1H, C≡CH), 1.89−1.80 (m, 1H, H-3), 1.76−1.67 (m, 2H, H-5, H-6), 1.66−1.48 (m, 4H, H-3, H-4, H-6), 1.44 (s, 9H, CH_3), 1.34−1.22 (m, 1H, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 155.2 (s, NH*C*O), 84.1 (s, *C*≡CH), 79.4 [s, *C*$(CH_3)_3$], 71.9 (d, C≡*C*H), 50.5 (d, C-1), 33.4 (d, C-2), 30.2 (t, C-3), 29.0 (t, C-6), 28.6 (q, 3C, CH_3), 25.1 (t, C-5), 20.8 (t, C-4).

MS (EI, 70 eV): *m/z (%)* = 167 (30) $[C_9H_{13}NO_2]^+$, 123 (27) $[C_9H_{13}N]^+$, 106 (27) $[C_8H_{10}]^+$, 57 (100) $[C_4H_8]^+$.

HRMS (ESI): calcd for $C_{13}H_{22}NO_2^+$ $[M+H]^+$: 224.1645; found: 224.1645.

2-Bromo-9*H*-thioxanthen-9-one (141)



141
$C_{13}H_7BrOS$
MW = 291.16 g/mol

According to a literature known procedure:[198] Bromobenzene (1.41 mL, 2.10 g, 13.4 mmol, 2.06 equiv) was added to a solution of thiosalicylic acid (1.00 g, 6.49 mmol, 1.00 equiv) in concentrated sulfuric acid (10 mL). The yellow colored suspension was stirred at room temperature for 16 hours and was subsequently rested without stirring for ten hours. Afterwards, the reaction mixture was heated at reflux for one hour. The resulting dark purple colored solution was poured onto ice water, which resulted in the formation of a brownish colored precipitate. The precipitate was filtered and washed with water until a neutral pH was reached. The brownish colored solid was stirred in aqueous NaOH solution (10 wt-%) for ten minutes, filtered and washed with water. The yellowish crude product (mixture of regioisomers) was purified by column chromatography (5 × 15 cm, Toluene/P = 4/1) to yield **141** (600 mg, 2.06 mmol, 32%) as a pale yellow colored solid.

TLC: R_f = 0.47 (Toluene) [UV].

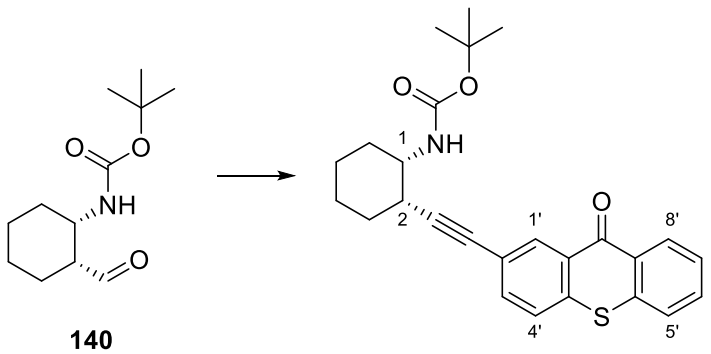
mp: 164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.75 (d, ^4J = 2.2 Hz, 1H, H-1), 8.62 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1H, H-8), 7.72 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, H-3), 7.65 (ddd, ^3J = 8.2 Hz, 6.9 Hz, ^4J = 1.3 Hz, 1H, H-6), 7.59 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, H-5), 7.51 (ddd, ^3J = 8.2 Hz, 6.9 Hz, ^4J = 1.1 Hz, 1H, H-7), 7.47 (d, ^3J = 8.5 Hz, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 178.8 (s, *C*=O), 136.9 (s, C-5a), 136.0 (s, C-4a), 135.2 (d, C-3), 132.6 (d, C-6), 132.5 (d, C-1), 130.5 (s, C-1a), 130.0 (d, C-8), 128.9 (s, C-8a), 127.6 (d, C-4), 126.6 (d, C-7), 126.1 (d, C-5), 120.3 (s, C-2).

The analytical data match those reported in the literature.[198]

***tert*-Butyl-{(1*S*,2*S*)-2-[(9'-oxo-9'*H*-thioxanthen-2'-yl)-ethinyl]-cyclohexyl}-carbamate (142)**



140

142
$C_{26}H_{27}NO_3S$
MW = 433.57 g/mol

A solution of alkyne **140** (80 mg, 360 µmol, 1.00 equiv) and bromothioxanthone **141** (114 mg, 394 µmol, 1.10 equiv) in tetrahydrofuran (18 mL) and freshly distilled triethylamine (18 mL) was degassed by three consecutive *freeze-pump-thaw*[37] cycles. $Pd(PPh_3)_4$ (41.4 mg, 35.8 µmol, 0.10 equiv) and CuI (13.6 mg, 71.6 µmol, 0.20 equiv) were added and the mixture was again degassed by four consecutive *freeze-pump-thaw* cyles. The reaction was heated to 60 °C for 16 hours in a sealed tube. After cooling to room temperature, the volatiles were removed under reduced pressure. The black residue was dissolved in dichloromethane (20 mL) and the organic layer was washed successively with saturated aqueous NH_4Cl solution (2 × 20 mL) and saturated aqueous NaCl solution (2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (2 × 20 cm, cHex/EtOAc = 50/1 → 20/1 → 5/1) to yield the product **142** (121 mg, 280 µmol, 78%) as a yellow colored solid.

racemic version: the racemic version of this reaction was performed analogously employing alkyne *rac*-**140** (100 mg, 448 µmol, 1.00 equiv), bromothioxanthone **141** (143 mg, 493 µmol, 1.10 equiv), $Pd(PPh_3)_4$ (51.8 mg, 44.8 µmol, 0.10 equiv) and CuI (17.1 mg, 89.6 µmol, 0.20 equiv). *rac*-**142** (152 mg, 351 µmol, 78%) was isolated as a yellow colored solid.

TLC: R_f = 0.16 (cHex/EtOAc = 20/1) [UV, $KMnO_4$].

mp: 185−187 °C.

$[\alpha]_D^{20}$: –154 (*c* = 1.00 M, CH_2Cl_2).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3364 (w, N-H), 3058 (w, C_{ar}-H), 2973 (w, C_{sp3}-H), 2934 (w, C_{sp2}-H), 2859 (w, C-H), 2221 (w, C≡C), 1681 (m, C=O), 1642 (m, C=O), 1438 (m, N-H), 1248 (m), 1162 (m), 894 (w), 825 (w), 743 (m), 620 (w).

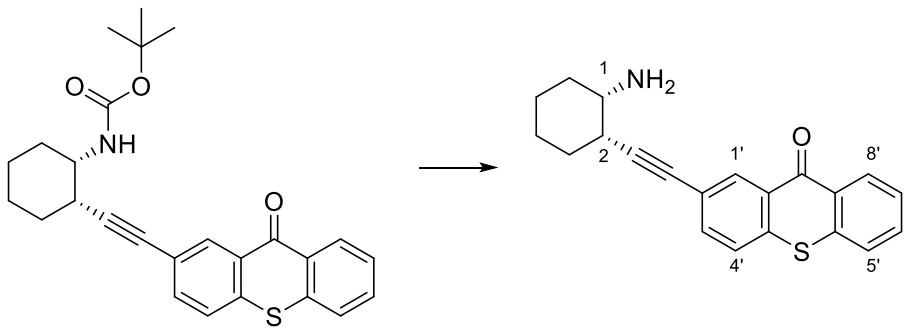
MS (EI, 70 eV): *m/z (%)* = 333 (100) $[C_{21}H_{19}NOS]^+$, 290 (89) $[C_{19}H_{14}OS]^+$, 237 (92) $[C_{15}H_9OS]^+$, 139 (11) $[C_7H_7OS]^+$.

HRMS (ESI): calcd for $C_{26}H_{28}NO_3S^+$ $[M+H]^+$: 434.1784; found: 434.1784.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.66 (d, ^4J = 1.8 Hz, 1H, H-1'), 8.63 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-8'), 7.66−7.64 (m, 2H, H-3', H-6'), 7.61 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1H, H-5'), 7.55 (d, ^3J = 8.4 Hz, 1H, H-7'), 7.53 (dd, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1H, H-4'), 4.85 (d, ^3J = 9.5 Hz, 1H, NH), 3.72−3.62 (m, 1H, H-1), 3.26−3.18 (m, 1H, H-2), 2.02−1.93 (m, 1H, H-3), 1.81−1.75 (m, 2H, H-5, H-6), 1.71−1.57 (m, 4H, H-3, H-4, H-6), 1.47 (s, 9H, CH_3), 1.32−1.40 (m, 1H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 179.5 (s, *C*=O), 155.3 (s, NH*C*O), 137.1 (s, C-5a'), 136.8 (s, C-4a'), 135.1 (d, C-3'), 133.1 (d, C-1'), 132.6 (d, C-6'), 130.1 (d, C-8'), 129.2 (s, C-1a'), 128.8 (s, C-8a'), 126.7 (d, C-7'), 126.2 (d, C-4'), 126.1 (d, C-5'), 122.0 (s, C-2'), 91.3 (s, CH*C*≡CAr), 83.2 (s, CHC≡*C*Ar), 79.6 [s, O*C*$(CH_3)_3$], 51.0 (d, C-1), 34.4 (d, C-2), 30.6 (t, C-3), 29.5 (t, C-6), 28.6 (q, 3C, CH_3), 25.2 (t, C-5), 21.2 (t, C-4).

2'-{[(1*S*,2*S*)-2-Aminocyclohexyl]ethynyl}-9'*H*-thioxanthen-9'-one



142 $C_{21}H_{19}NOS$
MW = 333.45 g/mol

Trifluoroacetic acid (132 µL, 197 mg, 1.73 mmol, 10.0 equiv) was slowly added to a solution of Boc-protected amine **142** (75 mg, 173 µmol, 1.00 equiv) in dichloromethane (2 mL) at 0 °C. After the addition was complete, the reaction solution was stirred at room temperature for two hours. The reaction was quenched by the addition of water (5 mL) and the mixture was

partitioned between water and dichloromethane. The aqueous layer was extracted with dichloromethane (2 × 5 mL). The combined organic layers were successively washed with saturated aqueous $NaHCO_3$ solution (2 × 15 mL) and saturated aqueous NaCl solution (1 × 15 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (2 × 20 cm, CH_2Cl_2/MeOH = 19/1 + 1 vol% NH_3) to yield the title compound (43.3 mg, 130 μmol, 78%) as a slowly crystallizing yellow colored oil.

racemic version: the racemic version of this reaction was performed analogously employing amine *rac*-**142** (115 mg, 265 μmol, 1.00 equiv) and trifluoroacetic acid (203 μL, 302 mg, 2.65 mmol, 10.0 equiv). The racemic title compound (80.0 mg, 265 μmol, 90%) was isolated as a yellow colored solid.

TLC: R_f = 0.54 (CH_2Cl_2/MeOH = 9/1 + 1vol% NH_3) [UV, $KMnO_4$].

[α]$_D^{20}$: –66 (*c* = 1.00 M, CH_2Cl_2).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3360 (w, N-H), 3058 (w, C_{ar}-H), 2929 (m, C_{sp2}-H), 2855 (w, C-H), 2222 (w, C≡C), 1639 (m, C=O), 1591 (m, N-H), 1461 (m), 1438 (m), 1397 (m), 1326 (m), 1079 (w), 917 (w), 742 (m), 635 (w).

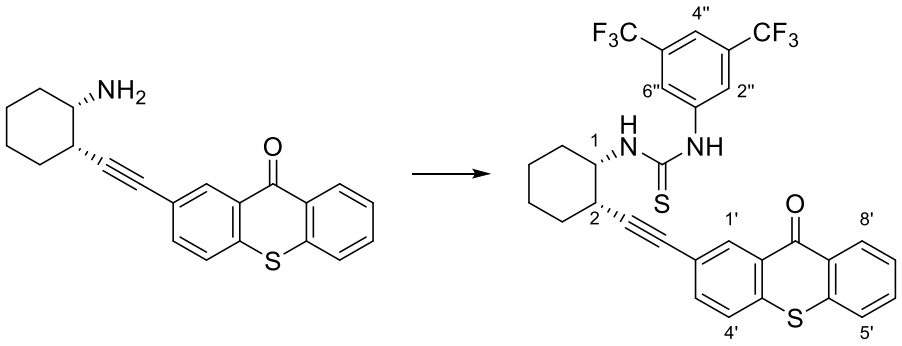
MS (EI, 70 eV): *m/z (%)* = 333 (100) $[C_{21}H_{19}NOS]^+$, 290 (89) $[C_{19}H_{14}OS]^+$, 237 (89) $[C_{15}H_9OS]^+$, 139 (11) $[C_7H_7OS]^+$.

HRMS (ESI): calcd for $C_{21}H_{20}NOS^+$ $[M+H]^+$: 334.1260; found: 334.1259.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.64 (d, ^4J = 1.7 Hz, 1H, H-1'), 8.60 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-8'), 7.64−7.59 (m, 2H, H-6', H-3'), 7.55 (d, ^3J = 7.7 Hz, 1H, H-5'), 7.51−7.45 (m, 2H, H-7, H-4'), 3.04 (*virt*. q, $^3J = {}^3J \cong$ 4.1 Hz, 1H, H-1), 2.83 (*virt*. dt, ^3J = 10.2 Hz, $^3J = {}^3J \cong$ 3.9 Hz, 1H, H-2), 2.00−1.92 (m, 1H, H-6), 1.78−1.46 (m, 8H, H-3, H-4, H-5, H-6, NH_2), 1.36−1.27 (m, 1H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 179.5 (s, C=O), 137.0 (s, C-5a'), 136.6 (s, C-4a'), 135.0 (d, C-3'), 133.0 (d, C-1'), 132.5 (d, C-6'), 130.1 (d, C-8'), 129.2 (s, C-1a'), 129.1 (s, C-8a'), 126.6 (d, C-7'), 126.2 (d, C-4'), 126.1 (d, C-5'), 122.2 (s, C-2'), 92.0 (s, CH*C*≡C), 83.2 (s, CHC≡*C*), 51.9 (d, C-2), 37.5 (d, C-1), 32.7 (t, C-3), 30.2 (t, C-6), 24.6 (t, C-4), 21.8 (t, C-5).

1-[3'',5''-bis(trifluoromethyl)-phenyl]-3-{(1*S*,2*S*)-2-[(9'-oxo-9'*H*-thio-xanthen-2'-yl)-ethinyl]-cyclohexyl}-thiourea (133)



133
$C_{30}H_{22}F_6N_2OS_2$
MW = 604.63 g/mol

1-Isothiocyanato-3,5-bis(trifluoromethyl)benzene (145 µL, 214 mg, 791 µmol, 1.10 equiv) was added to a solution of the amine (240 mg, 730 µmol, 1.00 equiv) in tetrahydrofuran (11 mL) and the reaction mixture was stirred for 16 hours at room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (3 × 15 cm, cHex/EtOAc = 9/1 → 4/1) to yield **133** (330 mg, 550 µmol, 74%) as a bright yellow colored solid.

racemic version: the racemic version of this reaction was performed analogously employing racemic amine (80.0 mg, 240 µmol, 1.00 equiv) and 1-isothiocyanato-3,5-bis(trifluoromethyl) benzene (48.4 µL, 71.6 mg, 264 µmmol, 1.10 equiv). *rac*-**133** (118 mg, 196 µmol, 81%) was isolated as a yellow colored solid.

TLC: R_f = 0. 43 (cHex/EtOAc = 4/1) [UV, $KMnO_4$].

mp: 201-202 °C.

[α]$_D^{20}$: –104 (*c* = 1.00 M, CH_2Cl_2).

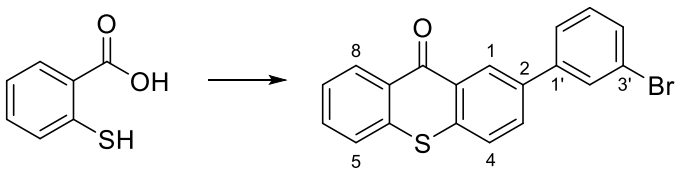
IR (ATR): ṽ [cm^{-1}] = 3327 (br. w, N-H), 3061 (w, C_{ar}-H), 2934 (w, C_{sp2}-H), 2858 (w, C-H), 2223 (w, C≡C), 1618 (m, C=O), 1585 (m, N-H), 1523 (m, N-H), 1276 (m, C-F), 1172 (s, C=S), 1128 (s), 986 (m), 884 (m), 744 (m), 681 (m).

HRMS (ESI): calcd for $C_{30}H_{23}F_6N_2OS_2^+$ $[M+H]^+$: 605.1151; found: 605.1149.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.11 (s, 1H, Ar-N*H*CS), 8.50 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1H, H-8'), 8.32 (d, ^4J = 1.6 Hz, 1H, H-1'), 7.99 (br. s, 2H, H-2'', H-6''), 7.66 (ddd, ^3J = 8.3 Hz, 7.0 Hz, ^4J = 1.3 Hz, 1H, H-6'), 7.58 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1H, H-7'), 7.54−7.49 (m, 2H, H-5', H-4''), 7.38 (d, ^3J = 8.7 Hz, 1H, cyclohexyl-N*H*CS), 7.12 (d, ^3J = 8.3 Hz, 1H, H-4'), 7.04 (d, ^3J = 7.7 Hz, 1H, H-3'), 4.65 (*virt.* ddt, ^3J = 11.8 Hz, 7.7 Hz, $^3J = {}^3J \cong$ 3.5 Hz, 1H, H-1), 3.48 (*virt*. q, $^3J = {}^3J \cong$ 4.0 Hz, 1H, H-2), 2.12−2.06 (m, 1H, H-6), 2.01−1.95 (m, 1H, H-3), 1.88−1.82 (m, 1H, H-5), 1.77 (td, ^3J = 12.4 Hz, 3.8 Hz, 1H, H-6), 1.73−1.67 (m, 1H, H-3), 1.67−1.59 (m, 2H, H-4), 1.50−1.40 (m, 1H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 180.3 (s, C=O), 180.0 (s, C=S), 140.4 (s, C-1''), 137.6 (s, C-5a'), 137.0 (s, C-4a'), 134.8 (d, C-3'), 133.1 (d, C-6'), 132.5 (d, C-1'), 132.3 (s, C-5''), 132.0 (q, CF_3), 131.6 (s, C-3''), 129.8 (d, C-8'), 128.6 (s, C-8a'), 128.3 (s, C-1a'), 127.0 (d, C--5'), 126.3 (d, C-7'), 125.7 (d, C-4'), 124.5 (q, CF_3), 123.8 (d, C-6''), 123.7 (d, C-2''), 121.7 (s, C-2'), 118.4 (d, C-4''), 91.4 (s, CH*C*≡C), 83.2 (s, CHC≡*C*), 54.9 (d, C-1), 33.5 (d, C-2), 30.3 (t, C-3), 28.6 (t, C-6), 25.1 (t, C-5), 21.1 (t, C-4).

2-(3'-Bromophenyl)-9*H*-thioxanthen-9-one (159)



159
$C_{19}H_{11}BrOS$
MW = 367.23 g/mol

This reaction was performed analogous to a modified literature procedure.[198] A solution of thiosalicylic acid (320 mg, 2.08 mmol, 1.00 equiv) and 3-bromo-1,1'-biphenyl (997 mg, 4.28 mmol, 2.06 equiv) in concentrated sulfuric acid (3 mL) was stirred at room temperature for 16 hours and was subsequently rested without stirring for six hours. Afterwards, the reaction was heated at reflux for one hour, and the dark red colored solution was poured onto ice water, which resulted in the formation of a brown colored precipitate. A neutral pH was adjusted by the addition of saturated aqueous $NaHCO_3$ solution. Solid NaCl was added until the solution was saturated, followed by the extraction of the aqueous layer with chloroform (4 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (40 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The remaining yellow colored precipitate in the aqueous layer was filtered and washed with water. The crude product from the extraction

was purified by column chromatography (4 × 10 cm, Toluene/P = 4/1) to yield **159** (192 mg, 510 μmol, 25%) as a yellow colored solid. The precipitate from the aqueous solution was found to be recovered thiosalicylic acid.

TLC: R_f = 0.08 (Toluene) [UV].

mp: 144 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1637 (vs, C=O), 1593 (vs, C=C), 1459 (m), 1438 (m), 1331 (w), 1036 (w), 743 (s, C-H).

HRMS (ESI): calcd for $C_{19}H_{12}{}^{79}BrOS^+$ $[M+H]^+$: 366.9787; found: 366.9784.

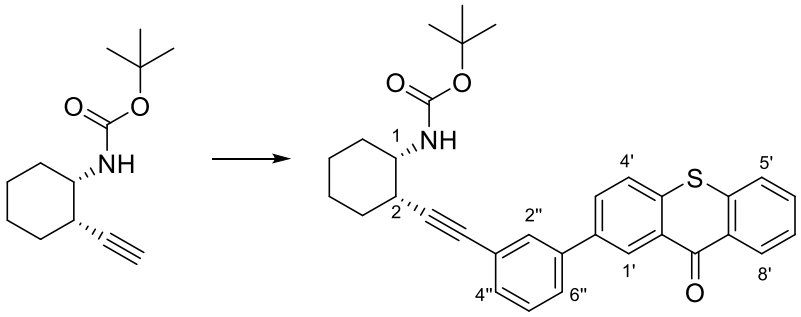
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.83 (d, ^4J = 2.2 Hz, 1H, H-1), 8.65 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, H-8), 7.87–7.82 (m, 2H, H-2', H-3), 7.68 (d, ^3J = 8.4 Hz, 1H, H-4), 7.66–7.63 (m, 2H, H-6, H-6'), 7.61 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, H-5), 7.54–7.49 (m, 2H, H-4', H-7), 7.36 (*virt*. t, $^3J = {}^3J \cong$ 7.9 Hz, 1H, H-5').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 179.8 (s, C=O), 141.6 (s, C-1'), 137.7 (s, C-4a), 137.1 (s, C-5a)*, 136.9 (s, C-2)*, 132.5 (d, C-6), 130.9 (d, C-4')**, 130.8 (d, C-3)**, 130.6 (d, C-5'), 130.2 (d, C-2'), 130.1 (d, C-8), 129.6 (s, C-8a)*, 129.2 (s, C-1a)*, 128.0 (d, C-1), 126.8 (d, C-4), 126.6 (d, C-7), 126.2 (d, C-5), 125.7 (d, C-6'), 123.3 (s, C-3').

* The assignments are interconvertible.

** The exact assignment of these signals is not possible.

***tert*-Butyl-{(1*S*,2*S*)-2-[(3''-(9'-oxo-9'*H*-thioxanthen-2'-yl)phenyl)ethynyl]cyclohexyl} carbamate**



$C_{32}H_{31}NO_3S$
MW = 509.6 g/mol

A solution of alkyne **140** (90 mg, 403 µmol, 1.00 equiv) and 2-(3'-bromophenyl)-9*H*-thioxanthen-9-one **159** (155 mg, 423 µmol, 1.05 equiv) in tetrahydrofuran (18 mL) and freshly distilled triethylamine (18 mL) was degassed by three consecutive *freeze-pump-thaw*[37] cycles. $Pd(PPh_3)_4$ (46.6 mg, 40.3 µmol, 0.10 equiv) and CuI (15.5 mg, 80.6 µmol, 0.20 equiv) was added and the mixture was again degassed by four consecutive *freeze-pump-thaw* cycles. The reaction was heated to 60 °C for 16 hours in a sealed tube. After cooling to room temperature, the volatiles were removed under reduced pressure. The black residue was dissolved in dichloromethane (20 mL) and the organic layer was washed successively with saturated aqueous NH_4Cl solution (2 × 20 mL) and saturated aqueous NaCl solution (2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (2 × 20 cm, cHex/EtOAc = 20/1 → 9/1) to yield the title compound (183 mg, 359 µmol, 81%) as a yellow colored solid.

TLC: R_f = 0.38 (Chx/EtOAc = 4/1) [UV, $KMnO_4$].

mp: 88 °C.

$[\alpha]_D^{20}$: −174 (*c* = 1.00 M, CH_2Cl_2).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3358 (w, N-H), 3058 (w, C_{ar}-H), 2927 (w, C_{sp2}-H), 2855 (w, C-H), 2225 (w, C≡C), 1704 (m, $C{=}O_{Boc}$), 1642 (m, $C{=}O_{Thioxanthone}$), 1591 (m, $C{=}O_{Boc}$), 1438 (m, N-H), 1364 m, C-^{t}Bu), 1245 (m), 1163 (s), 1119 (m), 894 (m, C_{ar}-H), 822 (w, C_{ar}-H), 790 (m, C_{ar}-H).

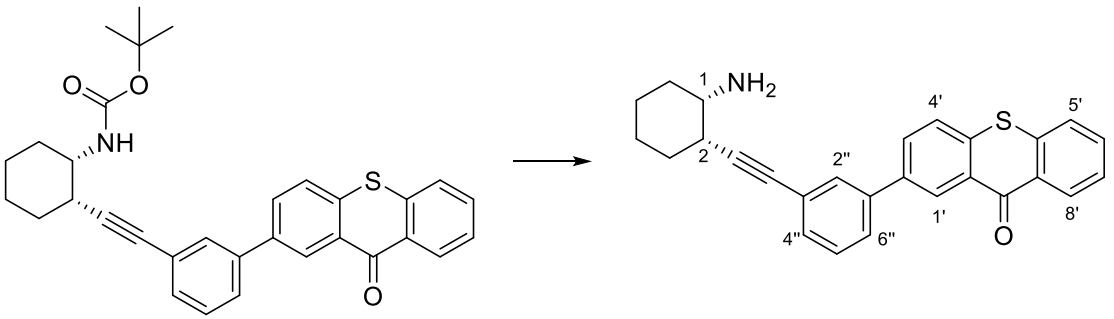
HRMS (ESI): calcd for $C_{32}H_{32}NO_3S^+$ $[M+H]^+$: 510.2097; found: 510.2097.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.86 (d, ^{4}J = 2.2 Hz, 1H, H-1'), 8.65 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.4 Hz, 1H, H-8'), 7.87 (dd, ^{3}J = 8.3 Hz, ^{4}J = 2.2 Hz, 1H, H-3'), 7.78 (br. s, 1H, H-2''), 7.72–7.58 (m, 4H, H-6'', H-4', H-5', H-6'), 7.56–7.39 (m, 3H, H-4'', H-5'', H-7'), 4.90 (d, ^{3}J = 9.3 Hz, 1H, NH), 3.73–3.57 (m, 1H, H-1), 3.21 (*virt*. d, $^{3}J \approx$ 4.1 Hz, 1H, H-2), 2.03–1.95 (m, 1H, C*H*H-6), 1.83–1.74 (m, 2H, C*H*H-3, C*H*H-4), 1.69−1.54 (m, 3H, CH*H*-3, C*H*H-5, CH*H*-6), 1.57–1.52 (m, 1H, CH*H*-5), 1.46 [s, 9H, $OC(CH_3)_3$], 1.42–1.30 (m, 1H, CH*H*-4).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 180.1 (s, C=O), 155.3 (s, NH*C*O), 139.8 (s, C-1''), 138.6 (s, C-5a')*, 137.2 (s, C-4a')*, 136.6 (s, C-2'), 132.3 (d, C-6'), 131.3 (d, C-4''), 131.1 (d, C-3'), 130.4 (d, C-2''), 130.1 (d, C-8'), 129.6 (s, C-1a')$^{\#}$, 129.3 (s, C-8a')$^{\#}$, 129.1 (d, C-5''), 128.0 (d, C-1'), 126.8 (d, C-5'), 126.7 (d, C-6''), 126.6 (d, C-7'), 126.2 (d, C-4'), 124.4 (s, C-3''), 90.1 (s, Ar*C*≡C-Cyclohexane), 84.0 (s, ArC≡*C*-Cyclohexane), 79.5 [O*C*$(CH_3)_3$], 51.0 (d, C-1), 34.3 (d, C-2), 30.7 (t, C-6), 29.5 (t, C-3), 28.6 [q, OC(*C*$H_3)_3$], 25.2 (t, C-4), 21.2 (t, C-5).

*,$^{\#}$ The assignments are interconvertible.

2'-(3''-{[(1S,2S)-2-aminocyclohexyl]ethynyl}phenyl)-9'H-thioxanthen-9'-one



$C_{27}H_{23}NOS$
MW = 409.55 g/mol

Trifluoroacetic acid (225 µL, 336 mg, 2.94 mmol, 10.0 equiv) was slowly added to a solution of Boc-protected amine (150 mg, 294 µmol, 1.00 equiv) in dichloromethane (6 mL) at 0 °C. After the addition was complete, the reaction solution was stirred at room temperature for two hours. The reaction was quenched by addition of water (15 mL) and was partitioned between water and dichloromethane. The aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were successively washed with saturated aqueous $NaHCO_3$ solution (2 × 30 mL) and saturated aqueous NaCl solution (1 × 30 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified

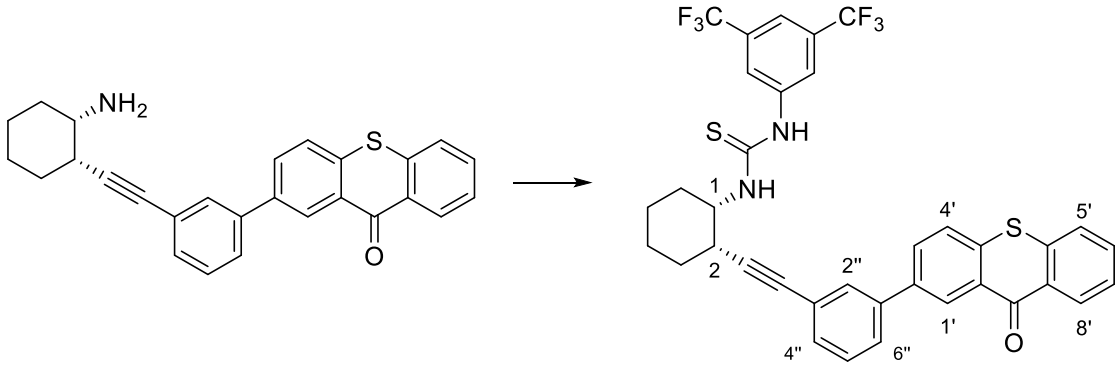
by column chromatography (3 × 15 cm, CH_2Cl_2/MeOH = 19/1 + 1 vol% NH_3) to yield the title compound (86.2 mg, 210 µmol, 78%) as a slowly crystallizing yellow colored oil.

TLC: R_f = 0.53 (CH_2Cl_2/MeOH = 9/1 + 1vol% NH_3) [UV, $KMnO_4$].

HRMS (ESI): calcd for $C_{27}H_{24}NOS^+$ $[M+H]^+$: 410.1573; found: 410.1571.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.86 (dd, ^4J = 2.2 Hz, ^5J = 0.5 Hz, 1H, H-1'), 8.66 (ddd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, ^5J = 0.7 Hz, 1H, H-8'), 7.88 (dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1H, H-3'), 7.80–7.75 (m, 1H, H-2''), 7.69–7.59 (m, 4H, H-6'', H-4', H-5', H-6'), 7.54–7.41 (m, 3H, H-4'', 5'', H-7'), 3.04 (*virt*. q, $^3J \approx$ 4.1 Hz, 1H, H-2), 2.83 (dt, $^3J \approx$ 9.8 Hz, 4.0 Hz, 1H, H-1), 2.04–1.93 (m, 1H, C*H*H-6), 1.82–1.45 (m, 6H, CH_2-3, CH*H*-4, CH_2-5, CH*H*-6), 1.40-1.21 (m, 1H, C*H*H-4).

1†-[3†,5†-bis(Trifluoromethyl)phenyl]-3†-((1S,2S)-2-((3''-(9'-oxo-9'H-thioxanthen-2'-yl)phenyl)-ethynyl)cyclohexyl)thiourea (160)



160
$C_{36}H_{26}F_6N_2OS_2$
MW = 680.73 g/mol

1-Isothiocyanato-3,5-bis(trifluoromethyl)benzene (39.0 µL, 57.5 mg, 213 µmol, 1.10 equiv) was added to a solution of the amine (79 mg, 193 µmol, 1.00 equiv) in tetrahydrofuran (3 mL) and the reaction mixture was stirred for 16 hours at room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (3 × 10 cm, cHex/EtOAc = 9/1 → 4/1) to yield *ent*-**160** (109 mg, 160 µmol, 84%) as a bright yellow colored solid.

TLC: R_f = 0. 35 (cHex/EtOAc = 4/1) [UV, $KMnO_4$].

mp: 168 °C.

[α]$_D^{20}$: –70 (*c* = 1.00 M, CH_2Cl_2).

IR (ATR): ṽ [cm^{-1}] = 3317 (br. w, N-H), 3056 (w, C_{ar}-H), 2933 (w, C_{sp2}-H), 2856 (w, C-H), 2228 (w, C≡C), 1624 (m, C=O), 1587 (m, N-H), 1525 (m, N-H), 1275 (s, C-F), 1169 (s, C=S), 1118 (s), 977 (m, C_{ar}-H), 881 (m, C_{ar}-H), 789 (m, C_{ar}-H).

MS (ESI): 271 (100) $[C_9H_4F_6NS]^+$, 213 (25) $[C_8H_3F_6]^+$, 163 (14) $[C_7H_3F_3]^+$, 69 (6) $[CF_3]^+$.

HRMS (ESI): calcd for $C_{36}H_{27}F_6N_2OS_2^+$ $[M+H]^+$: 681.1464; found: 681.1461.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.77 (d, ^3J = 9.8 Hz, 1H, ArN*H*CS), 8.64 (d, ^4J = 1.9 Hz, 1H, H-1'), 8.56 (d, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, H-8'), 7.85 (d, ^4J = 1.5 Hz, 2H, H-2†, H-6†), 7.64–7.60 (m, 2H, H-3', H-6'), 7.56 (d, ^3J = 8.1 Hz, 1H, H-4'), 7.52 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 1H, H-5'), 7.50–7.49 (m, 2H, H-4†, H-2''), 7.46 (ddd, ^3J = 8.2 Hz, 6.8 Hz, ^4J = 1.3 Hz, 1H, H-7'), 7.42 (dt, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H-6''), 7.21 (t, ^3J = 7.7 Hz, 1H, H-5''), 7.13 (d, ^3J = 7.7 Hz, 1H, H-4''), 7.06 (d, ^3J = 8.5 Hz, 1H, SCN*H*Cyclohexane), 4.61–4.52 (m, 1H, H-1), 3.44–3.41 (m, 1H, H-2), 2.03–1.99 (m, 2H, C*H*H-3, C*H*H-6), 1.85-1.78 (m, 1H, C*H*H-4), 1.78–1.55 (m, 4H, CH*H*-2, CH_2-5, CH*H*-6), 1.47–1.38 (m, 1H, CH*H*-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 180.6 (s, C=O), 179.9 (s, C=S), 139.7 (s, C_{ar}NHCS), 139.3 (s, C_{ar}-1''), 138.4 (s, C-5a')*, 137.5 (s, C-4a')*, 136.8 (s, C-2'), 132.8 (d, C-6'), 132.6 (s, C-3†)$^{\#}$, 132.3 (s, C-5†)$^{\#}$, 131.1 (d, C-4''), 130.9 (d, C-3'), 130.1 (d, C-2''), 123.0 (d, C-8'), 129.2 (s, C-1a')$^{\$}$, 129.0 (s, C-8a')$^{\$}$, 128.9 (d, C-5''), 127.6 (d, C-1'), 126.8 (d, C-5'), 126.7 (d, C-7'), 126.6 (d, C-6''), 126.2 (d, C-4'), 124.3 (q, CF_3), 123.8 (d, 2C, C-3†, C5†), 123.0 (s, C-3''), 121.6 (q, CF_3), 118.8 (d, C-4†), 89.5 (s, Cyclohexyl-*C*≡CAr), 84.7 (s, Cyclohexyl-C≡*C*Ar), 55.2 (d, C-1), 33.4 (d, C-2), 30.4 (t, C-6), 28.6 (t, C-2), 24.9 (t, C-4), 21.1 (t, C-5).

*,$^{\#}$,$^{\$}$ The assignments are interconvertible.

6.10 Crystal Data

CCDC 1915359

$C_{18}H_{21}NO_4$	
M_r = 315.36	D_x = 1.287 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: ? K
Hall symbol: -P 2yn	Mo Kα radiation, λ = 0.71073 Å
a = 17.209 (3) Å	Cell parameters from 6968 reflections
b = 5.0340 (8) Å	θ = 2.5–25.6°
c = 19.434 (3) Å	μ = 0.09 mm^{-1}
β = 104.812 (5)°	*T* = 100 K
V = 1627.6 (5) Å^3	Needle, colourless
Z = 4	0.81 × 0.10 × 0.08 mm
F(000) = 672	
Data collection	
Bruker Photon CMOS diffractometer	2946 independent reflections
Radiation source: TXS rotating anode	2185 reflections with I > 2σ(I)
Helios optic monochromator	R_{int} = 0.097
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 25.3°, θ_{min} = 2.5°
phi– and ω–rotation scans	*h* = −20 20
Absorption correction: multi-scan SADABS 2016/2, Bruker	*k* = −6 5
T_{min} = 0.593, T_{max} = 0.745	*l* = −23 23
32123 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.126$	$W = 1/[\Sigma^2(FO^2) + (0.0548P)^2 + 1.1721P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2946 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
210 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
0 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	

7. Abbreviations

(dF)(CF_3)ppy	3,5-difluoro-2-[5-(trifluoromethyl)pyridin-2-yl]phenyl
Å	Ångström
ac	acetone
Ac	acetyl
Ar	aromatic group
ATR	attenuated total reflection
BINOL	1,1'-bi-2-naphthol
Bn	benzyl
Boc	*tert*-butoxycarbonyl
BOX	bisoxazoline
bp	boiling point
bpy	2,2'-bipyridine
br	broad
brsm	based on recovered starting material
Bz	benzoyl
calcd	calculated
cat	catalyst
cHex	cyclohexane
COSY	correlation spectroscopy
d.r.	diastereomeric ratio
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dtbbpy	4,4'-di-*tert*-butyl-2,2'-bipyridine
ee	enantiomeric excess
EI	electron ionization
equiv	equivalents
ESI	electronspray ionization
E_T	triplet energy
Et	ethyl

EtOH	ethanol
Et_2O	diethyl ether
EWG	electron-withdrawing group
GC	gas chromatography
GP	general procedure
h	hour
HH	head-to-head
HMBC	heteronuclear multiple-bond correlation spectroscopy
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
HSQC	heteronuclear single-quantum correlation spectroscopy
HAT	head-to-tail
hv	denotes irradiation with photons of a specific wavelength
i	*iso*
IC	internal conversion
^{i}Pr	*iso*-propyl
IR	infrared
ISC	intersystem crossing
J	coupling constant
LED	light emitting diode
L.A.	*Lewis* acid
LG	leaving group
L_n	ligand
LUMO	lowest unoccupied molecular orbital
m	*meta*-
MeOH	methanol
Me	methyl
min	minutes
mp	melting point
MS	molecular sieves/mass spectrometry

nHex	*n*-hexane
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
o	*ortho*-
OAc	acetate
Otf	trifluoromethanesulfonate
p	*para*-
P	pentane
PG	protecting group
Ph	phenyl
ppm	parts per million
ppy	2-(- 233 -yridine-2-yl)phenyl
quant	quantitative
rfx	reflux
r.t.	room temperature
rac	racemic
rsm	recovered starting material
S_0	singlet ground-state
S_1	singlet excited state
SET	single electron transfer
t	*tert*
T	temperature
T_1	triplet excited state
^{t}Bu	*tert*-butyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl
Tol	toluene
Ts	toluenesufonyl
Tf	trifluoromethanesulfonate

TXT	thioxanthone
UV	ultraviolet
Vis	visible
Y	yield
v/v	volume per volume
ΔE	electronic energy
Φ	quantum yield
ε	molar extinction coefficient
λ	wavelength
τ_R	retention time

8. References

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