

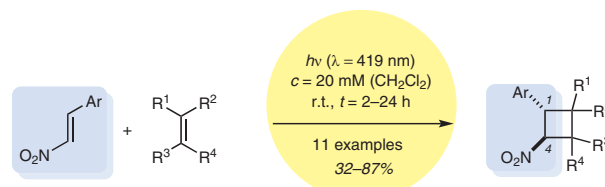
Intermolecular [2+2] Photocycloaddition of β -Nitrostyrenes to Olefins upon Irradiation with Visible Light

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Dedicated to Victor Snieckus, a dear colleague and friend, on
the occasion of his 80th birthday



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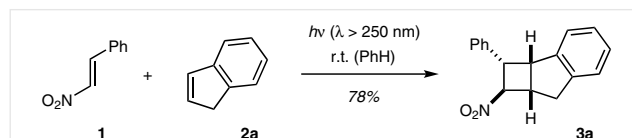
Abstract The title compounds were found to undergo a [2+2] photocycloaddition with olefins at $\lambda = 419$ nm in CH_2Cl_2 as the solvent. The resulting cyclobutanes were isolated in yields of 32–87% (11 examples) and showed a defined relative configuration at C1/C4 in the major diastereoisomer (nitro and aryl *trans*). The analysis of side products and triplet sensitization experiments support a mechanistic scenario in which a 1,4-diradical is formed as a key intermediate.

Key words cycloaddition, cyclobutanes, diastereoselectivity, nitro compounds, photochemistry, stereoselective synthesis, umpolung, visible light

Although [2+2] photocycloaddition chemistry¹ originates historically² from experiments performed with visible light, the advent of artificial UV light sources led – starting in the middle of the 20th century – to the almost exclusive use of short-wavelength ($\lambda = 250$ – 380 nm) irradiation in all areas of photochemistry. Interest in reactions that were promoted by long-wavelength ($\lambda > 380$ nm) irradiation was spurred in the 1970s and in the 1980s by the desire to find suitable energy storage systems mainly based on the [2+2] photocycloaddition of norbornadienes to quadricyclenes.³ Aromatic carbonyl compounds⁴ and transition-metal salts⁵ were found to act as triplet sensitizers in this transformation allowing the reaction to occur with visible light. More recently, triplet energy sensitization has been employed for enantioselective [2+2] photocycloaddition reactions that are promoted by visible light⁷ in the presence of an appropriate sensitizer.⁸ In the context of our work on the activation of chromophors by Lewis or Brønsted acids,⁹ we became interested in the photochemistry of nitrostyrenes.¹⁰ The compound class seemed amenable to un-

dergo direct intermolecular [2+2] photocycloaddition reaction upon excitation with visible light and we report in this communication on our preliminary results on this topic.

Already in the 19th century, the [2+2] photodimerization of *trans*- β -nitrostyrene was observed to occur upon exposure to sunlight.¹¹ However, reactions with olefins in the spirit of an intermolecular [2+2] photocycloaddition have remained rare and were performed exclusively with short-wavelength light. Chapman et al. mentioned in a review on the photochemistry of unsaturated nitro compounds the reaction with olefins but did not provide any experimental details.^{12,13}



Scheme 1 [2+2] Photocycloaddition of *trans*- β -nitrostyrene (**1**) and indene (**2a**) as reported by Majima et al.¹⁴

Later, Majima et al. employed the reaction of *trans*- β -nitrostyrene (**1**) and indene (**2a**) to form cyclobutane **3a** (Scheme 1).¹⁴ A high-pressure mercury lamp was employed as the light source in this transformation. In more recent work, pyrex-filtered irradiation was used to study the reaction of nitrostyrenes with silyl enol ethers.^{15,16}

Inspection of the UV-Vis spectrum¹⁷ of *trans*- β -nitrostyrene in CH_2Cl_2 (Figure 1) reveals a strong absorption centered at $\lambda = 312$ nm ($\epsilon = 16500 \text{ M}^{-1} \text{ cm}^{-1}$). This band has been previously assigned to an allowed $\pi\pi^*$ -transition with significant charge-transfer character.^{18,19} At high concentration it is evident that the absorption continues into the visible region of the electromagnetic spectrum in line with the fact that *trans*- β -nitrostyrene (**1**) is a yellow-colored solid.

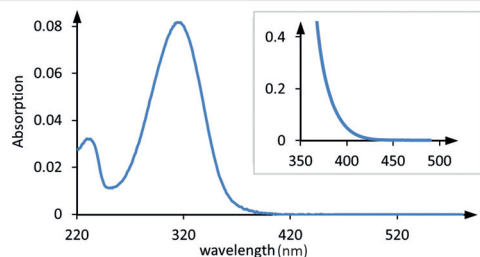


Figure 1 UV-Vis spectrum of *trans*-β-nitrostyrene in CH₂Cl₂ solution (*c* = 0.05 mM), the inset shows the long-wavelength absorption measured at *c* = 5 mM

In view of the apparent long-wavelength absorption of *trans*-β-nitrostyrene (**1**), its reaction with indene was revisited. The concentration, the solvent, and the stoichiometry (3.1 equiv indene) were taken from previous work,¹⁴ and the reaction was run for 23 hours (Table 1). We were pleased to find that conversion was not only complete when the mixture was irradiated with fluorescent lamps²⁰ at λ = 300, 350, and 366 nm, but also at λ = 419 nm (Table 1, entries 1–4). In all cases, it was observed that major diastereoisomer **3a** was accompanied by a minor diastereoisomer to which structure **3a'** was assigned based on NOESY experiments. The diastereomeric ratio (d.r.) varied at around 3:1. Best yields were recorded at λ = 350 nm (Table 1, entry 2) and λ = 419 nm (Table 1, entry 4). Clearly, the [2+2] photocycloaddition was promoted by visible light as even long-wavelength light-emitting diodes (LEDs) led to a significant conversion at λ = 457 nm and at λ = 470 nm (Table 1, entries 5, 6). At λ = 517 nm, there was essentially no conversion after 23 hours (Table 1, entry 7).

Table 1 Conversion, Yield, and Diastereomeric Ratio in the Inter-molecular [2+2] Photocycloaddition Reaction to Products **3a/3a'** in Correlation to the Irradiation Wavelength

Entry	λ (nm) ^a	Conv. (%)	Yield (%) ^b	d.r. (3a/3a') ^c
1	300	100	49	77:23
2	350	100	83	80:20
3	366	100	64	77:23
4	419	100	75	75:25
5	457	71	50	75:25
6	470	42	18	73:27
7	517	<5	– ^d	–

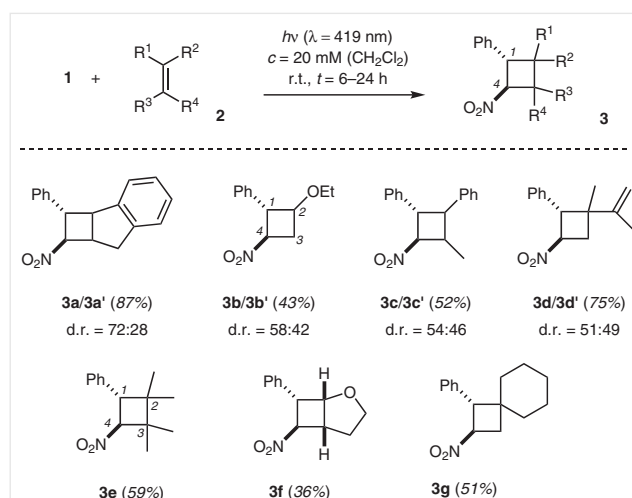
^a For the emission spectra of the light sources, see ref.²⁰

^b Yield of isolated products **3a** and **3a'** as a mixture of diastereoisomers.

^c The diastereomeric ratio (d.r.) was determined by integration of appropriate ¹H NMR signals.

^d No significant amounts of the respective products were isolated.

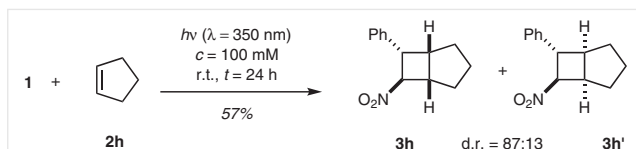
Further experiments were undertaken to identify a less problematic solvent but benzene and to optimize the reaction conditions at λ = 419 nm. While toluene was found less suited to substitute benzene, dichloromethane turned out to be an excellent solvent. A larger excess of the olefin led to higher product yields and the concentration was lowered to 20 mM in order to allow for small-scale reactions with more precious, not commercially available nitrostyrenes (vide infra). At optimized conditions²¹ the [2+2] photocycloaddition products **3a/3a'** were obtained in a yield of 87% after 24 hours of irradiation at λ = 419 nm. A variety of other olefins was employed in the reaction, and the results are summarized in Scheme 2.



Scheme 2 Visible-light-induced [2+2] photocycloaddition of various olefins **2** to *trans*-β-nitrostyrene (**1**)

It should be noted that the reactions were not always complete and that in some cases substantial amounts (up to 22%) of starting material were recovered, mostly as *cis*-β-nitrostyrene. Yields refer to isolated products, however, and are not corrected for conversion. With olefins **2b,d,f,g**, the fact that the polarity of the excited state is opposite to the ground state polarity (photochemical *umpolung*) becomes particularly apparent. C–C bond formation occurs formally between two – in the ground state – electrophilic centers (C1–C2) and between two nucleophilic centers (C3–C4). The reactions with olefins **2b–d** led to a mixture of diastereoisomers the relative configuration of which could be in most cases elucidated by NOESY experiments (see Supporting Information for further details). Cyclobutanes **3e–g** were obtained as single products. For the reaction of the electron rich olefin **2b**, it was checked that there was no reaction in the absence of irradiation.²²

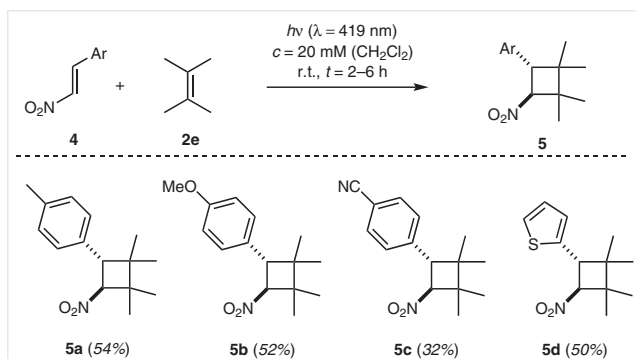
Contrary to unsaturated hydrocarbons **2e** and **2g**, cyclopentene **2h** did not react with a sufficient rate at λ = 419 nm. The [2+2] photocycloaddition could, however, be successively conducted if nitrostyrene **1** was irradiated in a



Scheme 3 Intermolecular [2+2] photocycloaddition of cyclopentene (**2h**) to *trans*- β -nitrostyrene (**1**)

solution of cyclopentene at $\lambda = 350$ nm (Scheme 3). The products were found to be a mixture of diastereoisomers in which product **3h** with the nitro group in *exo* position to the cyclopentyl ring prevailed (d.r. = 87:13).

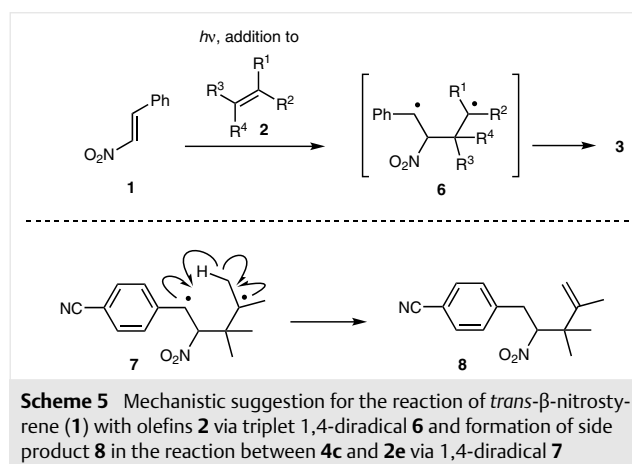
Some preliminary experiments were conducted with other aromatic nitroolefins **4** (Scheme 4). 2,3-Dimethyl-2-butene (**2e**) was employed as the reaction partner since its use avoids the formation of regio- or diastereomeric cyclobutane products. It was found that electron-rich aryl groups (*para*-tolyl, *para*-anisyl, 2-thiophenyl) in 2-position of the respective nitroethenes (**4a**,²³ **4b**,²³ **4d**²⁴) led in their [2+2] photocycloaddition to results similar to those of *trans*- β -nitrostyrene. Reaction times were short (2–4 h) and cyclobutanes **5a**, **5b**, and **5d** were obtained in yields of 50–54%. The reaction with the *para*-cyano-substituted nitrostyrene **4c**²⁵ was less chemoselective and gave product **5c** in a yield of only 32% after a longer reaction time (6 h). A side product could be isolated (vide infra).



Scheme 4 Visible-light-induced [2+2] photocycloaddition of some 2-aryl-substituted nitroethenes **4** and 2,3-dimethyl-2-butene (**2e**)

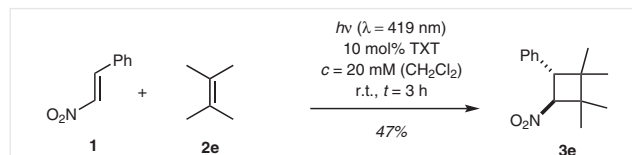
If 2,3-dimethyl-2-butene was subjected to [2+2] photocycloaddition with *cis*- β -nitrostyrene instead of *trans*- β -nitrostyrene the reaction was slower. The reaction product was exclusively the *trans*-substituted cyclobutane **3e** that was isolated in 43% yield. Irradiation of *trans*- β -nitrostyrene at $\lambda = 419$ nm in the absence of an olefin established an equilibrium²⁶ between the *cis* and the *trans* diastereoisomer in a ratio of 86:14.²⁷ This finding is in accord with the higher extinction coefficient of the *trans* diastereoisomer within the wavelength range of the light source.^{20c} The absorption maximum of *cis*- β -nitrostyrene is centered at $\lambda = 309$ nm ($\epsilon = 5200 \text{ M}^{-1} \text{ cm}^{-1}$) in CH_2Cl_2 solution.^{26b}

Mechanistically, there is no indication for a reaction course which would deviate from the pathway of typical [2+2] photocycloaddition reactions.¹ In this regard, it seems likely that olefin **2** adds to the excited substrate, for example, *trans*- β -nitrostyrene (**1**), most likely on the triplet hypersurface (Scheme 5). A 1,4-diradical **6** is formed as intermediate which collapses after intersystem crossing to product **3**. Evidence for the postulated structure of diradical **6** is based on the constitution of the products and side products. Indeed, olefins such as **8** were isolated in a few instances and their formation is readily explained by a hydrogen abstraction in the intermediate 1,4-diradical. In the reaction of olefin **2e** with styrene **4c**, byproduct **8** was obtained in 5% yield and is putatively formed via intermediate **7**.



Scheme 5 Mechanistic suggestion for the reaction of *trans*- β -nitrostyrene (**1**) with olefins **2** via triplet 1,4-diradical **6** and formation of side product **8** in the reaction between **4c** and **2e** via 1,4-diradical **7**

Further support for the hypothesis that the reaction proceeds via a triplet intermediate was obtained from the reaction of styrene **1** and olefin **2e**. In the absence of an additive the reaction was complete after 12 hours (Scheme 2), while a significant rate increase was noted upon addition of the triplet sensitizer 9*H*-thioxanthen-9-one (thioxanthone).²⁸ No β -nitrostyrene was detected after three hours and product **3e** was obtained in 47% yield (Scheme 6).



Scheme 6 Rate increase of the reaction between *trans*- β -nitrostyrene (**1**) and **2e** in the presence of a triplet sensitizer (TXT = thioxanthone)

In summary, we have shown that nitro-substituted cyclobutanes can be accessed by a visible-light-induced [2+2] photocycloaddition of various 2-arylnitroethenes and olefins. The yields are moderate to good (32–87%) and can possibly be further improved by adjusting the wavelength and the reaction temperature. Given the straightforward reduc-

tion of nitro compounds to amines,^{11c,14,29} the method offers also access to various aminocyclobutanes. Mechanistically, it remains open to what degree a charge transfer³⁰ occurs upon encounter of the photoexcited nitro compound and the olefin. In addition, it might be worth to study whether other nitroethenes but nitrostyrenes are equally suited for [2+2] photocycloaddition reactions. Work along these lines is in progress in our laboratories and will be reported in due course.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0036-1588524>.

Primary Data

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References and Notes

- (1) Poplata, S.; Tröster, A.; Zou, Y.-Q.; Bach, T. *Chem. Rev.* **2016**, *116*, 9748.
- (2) Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1193.
- (3) (a) Lennartson, A.; Roffey, A.; Moth-Poulsen, K. *Tetrahedron Lett.* **2015**, *56*, 1457. (b) Dubonosov, A. D.; Bren, V. A.; Chernoiivanov, V. A. *Russ. Chem. Rev.* **2002**, *71*, 917.
- (4) (a) Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814. (b) Jones, G. II.; Chiang, S.-H.; Xuan, P. T. J. *Photochem.* **1979**, *10*, 1.
- (5) (a) Ikezawa, H.; Kutal, C.; Yasufuku, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 1589. (b) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1986**, *108*, 3108. (c) Sluggett, G. W.; Turro, N. J.; Roth, H. D. *J. Phys. Chem. A* **1997**, *101*, 8834.
- (6) (a) Brimiouille, R.; Lenhart, D.; Maturi, M. M.; Bach, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 3872. (b) Meggers, E. *Chem. Commun.* **2015**, *51*, 3290.
- (7) (a) Zou, Y.-Q.; Duan, S.-W.; Meng, X.-G.; Hu, X.-Q.; Gao, S.; Chen, J.-R.; Xiao, W.-J. *Tetrahedron* **2012**, *68*, 6914. (b) Lu, Z.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329. (c) Kumarasamy, E.; Raghunathan, R.; Jockusch, S.; Ugrinov, A.; Sivaguru, J. *J. Am. Chem. Soc.* **2014**, *136*, 8729. (d) Hurtley, A. E.; Lu, Z.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2014**, *53*, 8991. (e) Liu, Q.; Zhu, F.-P.; Jin, X.-L.; Wang, X.-J.; Chen, H.; Wu, L.-Z. *Chem. Eur. J.* **2015**, *21*, 10326. (f) Mojz, V.; Svobodová, E.; Straková, K.; Neveselý, T.; Chudoba, J.; Dvořáková, H.; Cibulka, R. *Chem. Commun.* **2015**, *51*, 12036.
- (8) (a) Alonso, R.; Bach, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 4368. (b) Tröster, A.; Alonso, R.; Bauer, A.; Bach, T. *J. Am. Chem. Soc.* **2016**, *138*, 7808. (c) Blum, T. R.; Miller, Z. D.; Bates, D. M.; Guzei, I. A.; Yoon, T. P. *Science* **2016**, *354*, 1391.
- (9) (a) Guo, H.; Herdtweck, E.; Bach, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 7782. (b) Brimiouille, R.; Bach, T. *Science* **2013**, *342*, 840. (c) Brimiouille, R.; Bauer, A.; Bach, T. *J. Am. Chem. Soc.* **2015**, *137*, 5170. (d) Brenninger, C.; Pöthig, A.; Bach, T. *Angew. Chem. Int. Ed.* **2017**, *56*, 4337.
- (10) Reviews on the photochemistry of nitro compounds: (a) Ho, T.-I.; Chow, Y. L. *Photochemistry of Nitro and Nitroso Compounds, In The Chemistry of Functional Groups, Supplement F2: The Chemistry of Amino, Nitroso, Nitro and Related Groups*; Patai, S., Ed.; Wiley: Chichester, **1996**, 747. (b) Döpp, D. *Photochemical Reactivity of the Nitro Group, In CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M.; Song, P.-S., Eds.; CRC Press: Boca Raton, **1995**, 1019.
- (11) (a) Priebis, B. *Justus Liebigs Ann. Chem.* **1884**, *225*, 319. (b) Meisenheimer, J.; Heim, F. *Justus Liebigs Ann. Chem.* **1907**, *355*, 260. (c) Miller, D. B.; Flanagan, P. W.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 3912.
- (12) Chapman, O. L.; Griswold, A. A.; Hoganson, E.; Lenz, G.; Reasoner, J. *Pure Appl. Chem.* **1964**, *9*, 585.
- (13) In a later paper, the reaction of *trans*- β -nitrostyrene (**1**) and 2,3-dimethylbutadiene (**2d**) was reported to be performed at $\lambda = 300$ nm: Magner, J. T.; Selke, M.; Russell, A. A.; Chapman, O. L. *J. Chem. Ed.* **1996**, *73*, 854.
- (14) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265.
- (15) Ramkumar, D.; Sankararaman, S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 939.
- (16) For a Cr-photocatalytic [4+2] cycloaddition of *trans*- β -nitro-*para*-methoxystyrene and 1,3-dienes, see: Stevenson, S. M.; Higgins, R. F.; Shores, M. P.; Ferreira, E. M. *Chem. Sci.* **2017**, *8*, 654.
- (17) (a) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643. (b) Aboskalova, N. I.; Smirnova, N. N.; Kataeva, O. N.; Baichurin, R. I.; Fel'gendler, A. V.; Berkova, G. A.; Berestovitskaya, V. A. *Russ. J. Gen. Chem.* **2008**, *78*, 1711.
- (18) (a) Cowley, D. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1576. (b) Zhang, S.-Q.; Wang, H.-G.; Pei, K.-M.; Zheng, X. *J. Chem. Phys.* **2007**, *126*, 194505.
- (19) For further references to the photochemistry of nitroolefins, see: (a) Ried, W.; Wilk, M. *Justus Liebigs Ann. Chem.* **1954**, 590, 111. (b) Zimmerman, H. E.; Roberts, L. C.; Arnold, R. J. *Org. Chem.* **1977**, *42*, 621. (c) Humphry-Baker, R. A.; Salisbury, K.; Wood, G. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 659. (d) Grant, R. D.; Pinhey, J. T.; Rizzardo, E.; Smith, G. C. *Aust. J. Chem.* **1985**, *38*, 1505. (e) Kassaei, M. Z.; Nassari, M. A. *J. Photochem. Photobiol. A* **2000**, *136*, 41.
- (20) For the emission spectra of the lamps, see for $\lambda = 300$ nm, 366 nm: (a) Maturi, M. M.; Wenninger, M.; Alonso, R.; Bauer, A.; Pöthig, A.; Riedle, E.; Bach, T. *Chem. Eur. J.* **2013**, *19*, 7461. $\lambda = 350$ nm: (b) Rimböck, K.-H.; Pöthig, A.; Bach, T. *Synthesis* **2015**, *47*, 2869. $\lambda = 419$ nm: (c) Alonso, R.; Bach, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 4368. $\lambda = 457$ nm, 470 nm: (d) Lenhart, D.; Bauer, A.; Pöthig, A.; Bach, T. *Chem. Eur. J.* **2016**, *22*, 6519.
- (21) **Representative Procedure**
29.8 mg of nitrostyrene **1** (199 μ mol, 1.00 equiv) and 10.0 equiv of olefin **2e** (168 mg, 2.00 mmol) were dissolved in degassed, dry CH_2Cl_2 ($c = 20$ mM). The reaction solution was irradiated at

- $\lambda = 419$ nm in a Duran tube at r.t., and the reaction progress was monitored by TLC. When no further conversion was observed by TLC ($t = 12$ h), the reaction was stopped and all volatiles were removed. Purification by column chromatography (pentane/Et₂O = 20:1) gave product **3e** as a yellow oil (27.5 mg, 118 μ mol, 59%). When performed on a mmol scale (150 mg **1**), product **3e** was obtained in 56% yield (132 mg). ¹H NMR (500 MHz, CDCl₃, 300 K): $\delta = 0.71$ (s, 3 H, CH₃-2), 1.15 (s, 3 H, CH₃-3), 1.19 (s, 3 H, CH₃-2), 1.24 (s, 3 H, CH₃-3), 3.97 (d, ³J = 10.1 Hz, 1 H, H-1), 4.91 (d, ³J = 10.1 Hz, 1 H, H-4), 7.08–7.13 (m, 2 H, *ortho*-H_{Ar}), 7.23–7.28 (m, 1 H, *para*-H_{Ar}), 7.30–7.37 (m, 2 H, *meta*-H_{Ar}) ppm. ¹³C NMR (101 MHz, CDCl₃, 300 K): $\delta = 19.5$ (q, CH₃-3), 21.5 (q, CH₃-2), 22.8 (q, CH₃-3), 24.3 (q, CH₃-2), 39.3 (s, C-2), 44.9 (s, C-3), 49.4 (d, C-1), 84.9 (d, C-4), 127.0 (*ortho*-C_{Ar}H), 127.1 (d, *para*-C_{Ar}H), 128.6 (d, *meta*-C_{Ar}H), 136.4 (s, C_{Ar}) ppm.
- (22) For thermal [2+2] cycloaddition reactions of *trans*- β -nitrostyrene (**1**) and olefins, see: (a) Brannock, K. C.; Bell, A.; Burpitt, R. D.; Kelly, C. A. *J. Org. Chem.* **1964**, 29, 801. (b) Scheeren, H. W.; Frissen, A. E. *Synthesis* **1983**, 794. (c) Albrecht, L.; Dickmeiss, G.; Acosta, F. C.; Rodríguez-Escrich, C.; Davis, R. L.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2012**, 134, 2543. (d) Seebach, D.; Sun, X.; Ebert, M.-O.; Schweizer, W. B.; Purkayastha, N.; Beck, A. K.; Duschmalé, J.; Wennemers, H.; Mukaiyama, T.; Benohoud, M.; Hayashi, Y.; Reiher, M. *Helv. Chim. Acta* **2013**, 96, 799. (e) Dobi, Z.; Holczbauer, T.; Soós, T. *Eur. J. Org. Chem.* **2017**, 1391.
- (23) Yan, Q.; Liu, M.; Kong, D.; Zi, G.; Hou, G. *Chem. Commun.* **2014**, 50, 12870.
- (24) Quan, X.-J.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Org. Lett.* **2014**, 16, 5728.
- (25) Keene, C.; Kürti, L. *Synthesis* **2013**, 45, 1719.
- (26) (a) Bluhm, A. L.; Weinstein, J. *J. Am. Chem. Soc.* **1965**, 87, 5511. (b) Miller, D. B.; Flanagan, P. W.; Shechter, H. *J. Org. Chem.* **1976**, 41, 2112. (c) Desiraju, G. R.; Pedireddi, V. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1112.
- (27) The reaction time was 6 h. If the isomerization was performed starting from *cis*- β -nitrostyrene under otherwise identical conditions, the *cis/trans* ratio was 82:18.
- (28) The tabulated triplet energy (E_T) of thioxanthone is $E_T = 265$ kJ mol⁻¹: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, **1993**, 80.
- (29) Xiong, H.; Foulk, M.; Aschenbrenner, L.; Fan, J.; Tiong-Yip, C.-L.; Johnson, K. D.; Moustakas, D.; Fleming, P. R.; Brown, D. G.; Zhang, M.; Ferguson, D.; Wu, D.; Yu, Q. *Bioorg. Med. Chem. Lett.* **2013**, 23, 6789.
- (30) (a) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, 93, 99. (b) Mori, T.; Inoue, Y. *Chem. Soc. Rev.* **2013**, 42, 8122.