


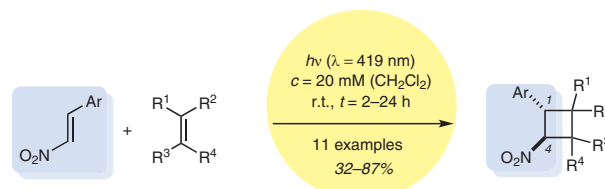
Intermolecular [2+2] Photocycloaddition of β -Nitrostyrenes to Olefins upon Irradiation with Visible Light

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



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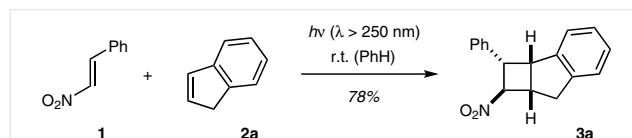
Abstract The title compounds were found to undergo a [2+2] photocycloaddition with olefins at $\lambda = 419$ nm in CH_2Cl_2 as the solvent. The resulting cyclobutanes were isolated in yields of 32–87% (11 examples) and showed a defined relative configuration at C1/C4 in the major diastereoisomer (nitro 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.

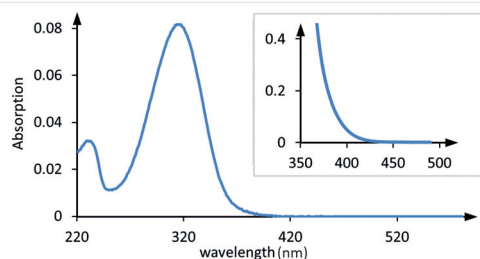


Figure 1 UV-Vis spectrum of *trans*- β -nitrostyrene in CH_2Cl_2 solution ($c = 0.05 \text{ mM}$), the inset shows the long-wavelength absorption measured at $c = 5 \text{ mM}$

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 $\lambda = 300, 350,$ and 366 nm , but also at $\lambda = 419 \text{ nm}$ (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 $\lambda = 350 \text{ nm}$ (Table 1, entry 2) and $\lambda = 419 \text{ nm}$ (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 $\lambda = 457 \text{ nm}$ and at $\lambda = 470 \text{ nm}$ (Table 1, entries 5, 6). At $\lambda = 517 \text{ nm}$, there was essentially no conversion after 23 hours (Table 1, entry 7).

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

Entry	$\lambda \text{ (nm)}^a$	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	–

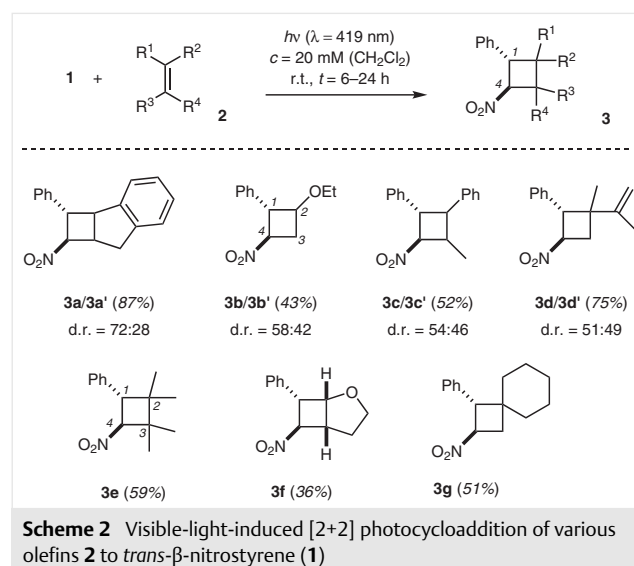
^a For the emission spectra of the light sources, see ref.²⁰

^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.

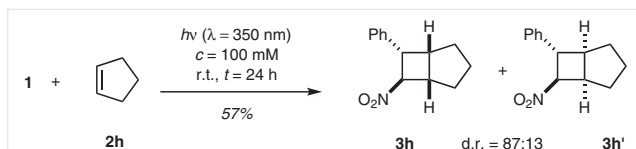
^d No significant amounts of the respective products were isolated.

Further experiments were undertaken to identify a less problematic solvent but benzene and to optimize the reaction conditions at $\lambda = 419 \text{ nm}$. 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 $\lambda = 419 \text{ nm}$. A variety of other olefins was employed in the reaction, and the results are summarized in Scheme 2.



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

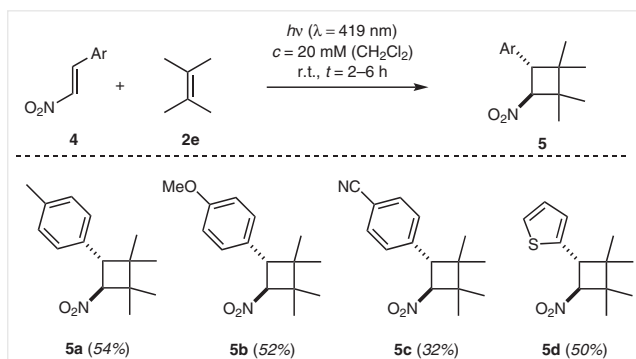
Contrary to unsaturated hydrocarbons **2e** and **2g**, cyclopentene **2h** did not react with a sufficient rate at $\lambda = 419 \text{ nm}$. The [2+2] photocycloaddition could, however, be successively conducted if nitrostyrene **1** was irradiated in a



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).

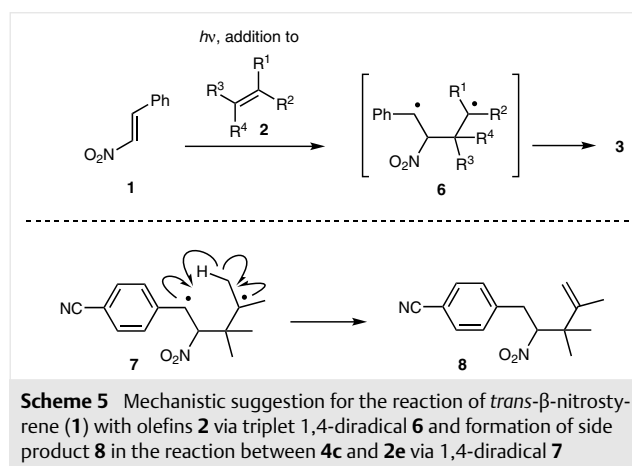
Some preliminary experiments were conducted with other aromatic nitroolefins **4** (Scheme 4). 2,3-Dimethyl-2-butene (**2e**) was employed as the reaction partner since its use avoids the formation of regio- or diastereomeric cyclobutane products. It was found that electron-rich aryl groups (*para*-tolyl, *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**)

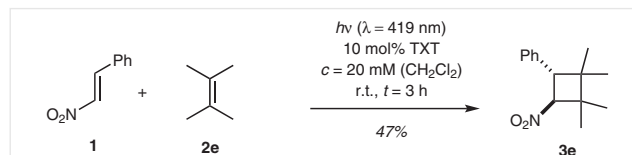
If 2,3-dimethyl-2-butene was subjected to [2+2] photocycloaddition with *cis*- β -nitrostyrene instead of *trans*- β -nitrostyrene the reaction was slower. The reaction product was exclusively the *trans*-substituted cyclobutane **3e** that was isolated in 43% yield. Irradiation of *trans*- β -nitrostyrene 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 ($\epsilon = 5200$ M⁻¹ cm⁻¹) in CH₂Cl₂ 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.

Funding Information

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Supporting Information

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Primary Data

for this article are available online at <http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083> and can be cited using the following DOI: 10.4125/pd0095th.

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.; Chernoiyanov, 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.; Stieglman, 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) Kassae, 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.