Synthesis H. Watanabe et al. Special Topic

Custom-Made Pyrene Photocatalyst-Promoted Desulfonylation of Arylethenyl Sulfones Using Green-Light-Emitting Diodes

Hikaru Watanabe[a]
Kazuki Nakajima[a]
Kento Ekuni[a]
Ryota Edagawa[a]
Yuta Akagi[a]
Yasuhiro Okuda[a]
Kan Wakamatsu[b]
Akihiro Orita*[a]

[a] Department of Applied Chemistry and Biotechnology, Okayama University of Science, 1-1, Ridai-cho, Kita-ku, Okayama 700-0005, Japan
orita@dac.ous.ac.jp
[b] Department of Chemistry, Okayama University of Science, 1-1, Ridai-cho, Kita-ku, Okayama 700-0005, Japan

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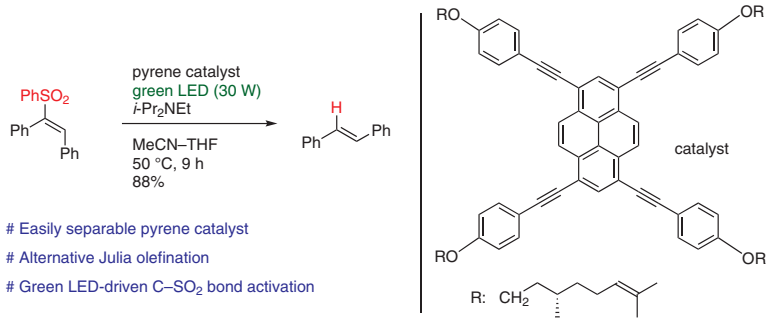

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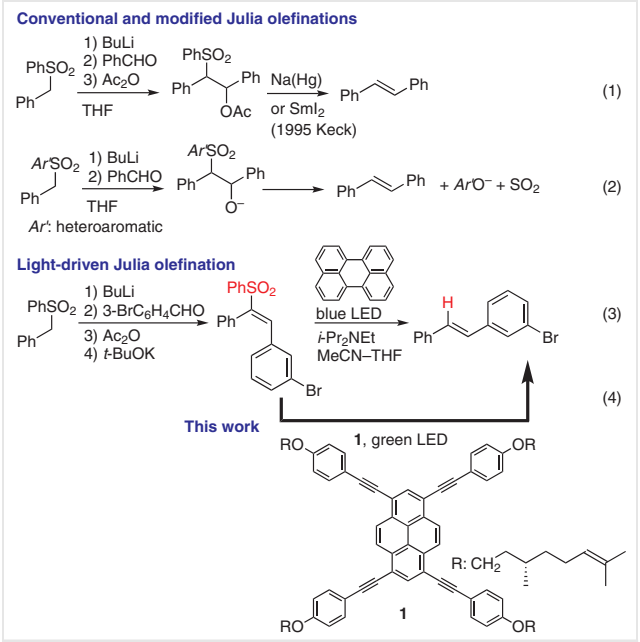
Abstract The Sonogashira coupling of 1,3,6,8-tetrabromopyrene with 4-[(–)-β-citronellyloxy]phenylethyne was employed to synthesize 1,3,6,8-tetra[4-(citronellyloxy)phenylethynyl]pyrene. The pyrene derivative catalyzed the reductive desulfonylation of ethenyl sulfones via visible-light irradiation (514 nm green light-emitting diodes) in the presence of *i*-Pr_2NEt. The β-citronellyloxy groups provided the sufficient solubility to the highly π-expanded pyrene catalyst, and their polar oxygen functionalities enabled the easy separation of the catalyst from the products via column chromatography.

Keywords desulfonylation, photocatalyst, pyrene, ethenyl sulfones, ethenes, green LED

Aryl sulfones have attracted considerable attention owing to their ability to exhibit potent biological activities[1] and to act as easily accessible air-stable reagents in organic syntheses.[2] The C–SO_2 bonds of sulfones can be activated using various methods,[3] and these protocols are used in the carbon–carbon (C–C) bond formations and/or the transformation of functional groups.[2,4,5] Recently, photoredox C–SO_2 bond activation has been extensively developed and utilized in organic syntheses.[6] In 1973, Julia reported the transformation of sulfones to olefins.[7] This olefination protocol comprised two types of transformation: (i) base-promoted C–C bond formation between sulfones and aldehydes followed by acetylation using Ac_2O and (ii) simultaneous reductive desulfonylation and deacetoxylation from the resulting β-acetoxysulfones (equation 1 in Scheme 1). Although Julia olefination was synthetically useful, it required the use of hazardous sodium amalgam as a reductant. In 1995, Keck developed an alternative to Julia olefination using SmI_2 rather than amalgam and demonstrated the usability of the former (equation 1 in Scheme 1).[8] However, the precious rare-earth metal reagent (SmI_2) was still required as a reductant, and high *E*-selectivity of the olefinic product was not achieved. To achieve operational compaction of this process, modified Julia olefinations were developed using heteroaromatic sulfones, which are widely utilized in organic syntheses (equation 2 in Scheme 1).[9,10]



Scheme 1 Conventional and light-driven Julia olefinations

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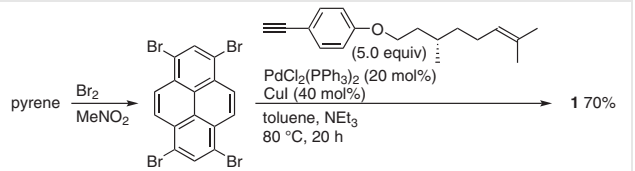
To avoid the use of hazardous and/or precious metal reagents for the reductive desulfonylation,[11] we developed a new technology by exploiting perylene/blue light-emitting diodes (LEDs) as a photocatalyst system (equation 3 in Scheme 1).[6c] This protocol worked well in the transformation of functionalized ethenyl sulfones to the corresponding ethenes with high *E*-selectivity. For example, in the desulfonylation of bromo-/chloro-substituted ethenyl sulfones, the desired halo-substituted stilbenes were obtained, whereas the halo groups remained untouched. Although this protocol is versatile in synthetic chemistry owing to its environmentally benign and mild reaction conditions, it was difficult or practically impossible to separate the perylene photocatalyst from less-polar ethene products, which had no polar functional groups due to a small difference in polarities. To solve this problem, we have developed pyrene catalyst **1** as a next-generation photocatalyst for reductive desulfonylation (equation 4 in Scheme 1). Catalyst **1** comprises a π-extended pyrene substituted at the 1, 3, 6, and 8 positions by four phenylethynes bearing long branched alkoxy groups.[12] Herein, we report that **1** promotes C–SO_2 bond cleavage via visible-light (green LEDs) irradiation. Furthermore, **1** was easily separated from the ethene products via column chromatography.

First, we designed the 'custom-made' pyrene photocatalyst **1**, which was featured in three contexts: (i) a visible-light-driven system; (ii) sufficient solubility; and (iii) polarity-assisted easy separation from the products (Scheme 2). Catalyst **1** bore an expanded π-system and long branched alkyl chains and possessed oxygen functionality; we expected these characters to satisfy all the requirements. The pyrene core of **1** is a thermally and photochemically stable polycyclic aromatic unit and has been widely used as a fluorescent optical material for organic LEDs (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and sensing.[13] Photocatalyst **1** was easily prepared by the consecutive bromination of commercially available pyrene and Sonogashira coupling of the resulting 1,3,6,8-tetrabromide with 4-[(*S*)-β-citronellyloxy]phenylethyne (Scheme 2).[14]



Scheme 2 Synthesis of photocatalyst **1**

When the ultraviolet/visible (UV/Vis) absorption of **1** was recorded in $CHCl_3$ (1.0×10^{-5} M), a broad absorption band was observed at 387–530 nm, and the longest-wavelength absorption maximum (λ_{max}) was at 478 nm (ε 70 300 L/mol·cm), indicating the highly expanded π-system of **1** (Figure 1). When UV light was irradiated to a $CHCl_3$ solution of **1** (1.0×10^{-7} M), the acetylenic pyrene **1** emitted strong fluorescence (E_{max} 499 nm, Φ_F 0.98), and the intersection of the normalized absorption and emission spectra indicated the energy of the lowest excited singlet state (E_{00}) at 491 nm. Due to its low-energy absorption band, we anticipated that **1** would be able to undergo photo-excitation via irradiation of visible light from green LEDs (514 nm) and drive the following photoreactions.

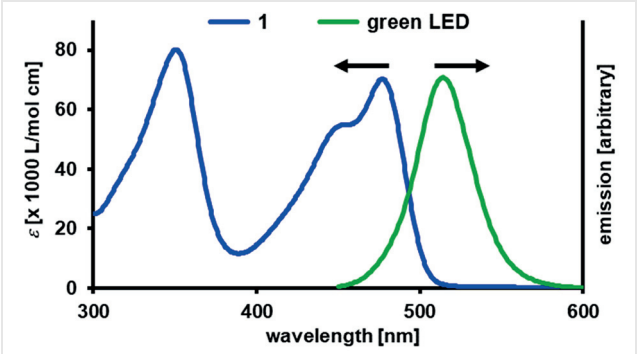


Figure 1 Spectral profiles of UV/Vis absorption of **1** ($CHCl_3$, 1.0×10^{-5} M) and the emission of green LEDs (arbitrary unit)

We estimated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of **1** using the density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory. The DFT simulations demonstrated HOMO and LUMO at –4.60 and –2.13 eV, respectively, as presented in Figure 2.[15] To evaluate the reduction potential of **1** in the photo-promoted desulfonylation, we also simulated the singly occupied molecular orbital (SOMO) level of radical anion $\mathbf{1}^{\bullet-}$, which formed through a single-electron transfer (SET) from a sacrificing reagent, *i*-Pr_2NEt, to photo-excited pyrene $\mathbf{1}^*$. The DFT calculations indicated that radical anion $\mathbf{1}^{\bullet-}$ bore the SOMO level at –0.44 eV, which enabled a single-electron transfer to ethenyl sulfone **2a** with –1.65 eV of LUMO under irradiation of green LEDs (Figure 2). Since the SOMO level of $\mathbf{1}^{\bullet-}$ (–0.44 eV) was significantly lower compared with that of perylene radical anion (+0.83 eV), which was used as a photocatalyst in the existing research,[16] we anticipated that pyrene **1** would serve as a somewhat mild photo-driven reductant. In parallel with these DFT calculations, we also investigated electrochemical reduction of **1** and **2a** using the cyclic voltammetry swept in CH_2Cl_2 (1.0 mM) by using $Ag/AgNO_3$ as a reference electrode. In the reduction process, **1** demonstrated a finely reversible profile diagnosing its electrochemical stability, while **2a** did quasi-reversible. Their half-wave reduction potentials $E_{1/2}^{red}$ (in CH_2Cl_2) were observed at –1.40 V and –1.81 V (Fc^+/Fc), and the LUMO energy levels of **1** and **2a** was estimated as –3.40 eV and –2.99 eV, respectively.[17] The (*S*)-β-citronellyloxy groups attached to the four terminus points of phenylethynyl moieties improved the solubility of the π-system expanded pyrene **1** to implement a

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practical solubility at room temperature (20 °C) in common organic solvents such as EtOAc, $CHCl_3$, toluene, THF, and acetone. However, in hexane, MeCN, MeOH, and EtOH, **1** was insoluble at room temperature and even at 50 °C. When linear alkyl chains were attached instead of (*S*)-β-citronellyloxy groups, insoluble or sparingly soluble pyrenes were synthesized. The oxygen functionality of the (*S*)-β-citronellyloxy group plays a significant role in the tuning of the polarity of **1** to enable its easy separation from olefinic products via column chromatography on silica gel; for example, the retardation factor (R_f) values developed by 20% CH_2Cl_2/hexane was 0.17 for **1** and 0.70 for *trans*-stilbene (0.57 for perylene).

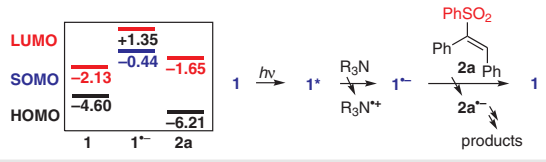
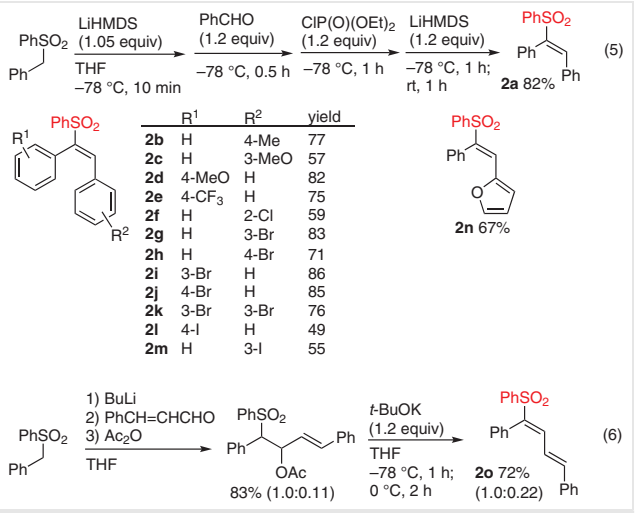


Figure 2 The calculated potentials of **1**, radical anion **1**$^{\bullet-}$, and **2a** at the B3LYP/6-31G(d) level of theory and a partial mechanism of reductive desulfonylation

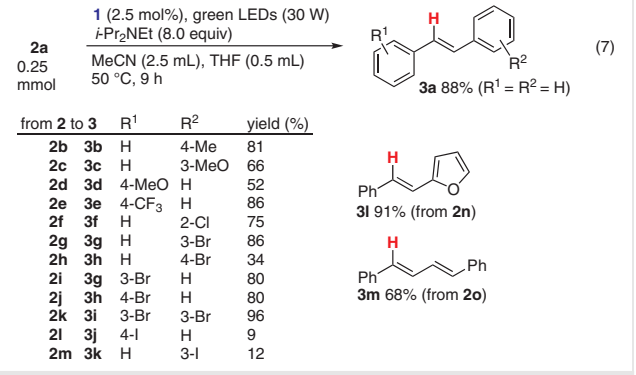
The ethenyl sulfones subjected to reductive desulfonylation were prepared from the corresponding benzyl sulfones and arylaldehydes in the lithium hexamethyldisilazide (LiHMDS)-promoted one-pot synthesis (Scheme 3). When a THF solution of benzyl sulfone was successively treated with LiHMDS (1.05 equiv), benzaldehyde, $ClP(O)(OEt)_2$, and LiHMDS (1.2 equiv), ethenyl sulfone **2a** was obtained in an 82% yield with high geometrical selectivity (equation 5 in Scheme 3). Although the *E*/*Z* geometry of **2a** was not determined, we assumed it would be an *E*-isomer.[18] The one-pot process was useful for the syntheses of other functionalized ethenyl sulfones **2**. The substituted sulfones bearing methyl **2b**, methoxy **2c** and **2d**, and trifluoromethyl **2e** were produced via this synthetic process. Halogen-substituted derivatives chloride **2f**; bromides **2g**, **2h**, **2i**, **2j**, and **2k**; and iodides **2l** and **2m** were also successfully synthesized in a range of 49–86% yields, without a loss of halo groups.

The 2-furylethenyl **2n** and dienyl sulfones **2o** were also synthesized from furfural and cinnamaldehyde, respectively (equation 6 in Scheme 3).

Since a variety of ethenyl sulfones **2** were obtained in the one-pot process, we performed reductive desulfonylation of **2** using pyrene **1** as a photocatalyst. When the green LED light (514 nm, 30 W) was irradiated in a THF/MeCN solution of **2a** in the presence of 2.5 mol% **1** and eight equivalents of *i*-Pr_2NEt at 50 °C for 9 hours, the desired desulfonylation smoothly proceeded to provide *trans*-stilbene (**3a**) in an 88% yield (equation 7 in Scheme 4). It is noted that **3a** could be easily purified via column chromatography on silica gel without any contamination of **1** as was expected. When **2a** was subjected to the **1**-catalyzed desulfonylation in the presence of four equivalents of *i*-Pr_2NEt, **3a** was provided in an 83% yield, and a 13% of **2a** was recovered. In the presence of an equimolar amount of *i*-Pr_2NEt, the desired desulfonylation proceeded only sluggishly to result in a 90% recovery of **2a**. Although this reaction proceeded in mixed solvents MeCN/THF,[19] no **3a** formation was observed in other solvents, such as THF, DMF, DMSO, and toluene/THF.



Scheme 3 One-pot synthesis of ethenyl sulfones from benzyl sulfones and aldehydes



Scheme 4 Photocatalyst **1**-promoted reductive desulfonylation of **2** using green LEDs

When this reaction was conducted using perylene rather than **1**, desulfonylation did not occur due to the small overlap between its absorption band and the emission band of the green LEDs.[20] In the desulfonylation of 4-methylsulfone **2b**, the desired methylstilbene **3b** was produced in an 81% yield via the green LED irradiation for 9 hours. The reductive desulfonylation of methoxy-substituted sulfones **2c** and **2d** successfully proceeded, and the corresponding methoxyethenes **3c** and **3d** were obtained in 66% and 52% yields, respectively. The 4-CF_3-substituted sulfone **2e** underwent a somewhat more rapid desulfonylation compared

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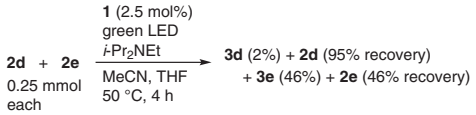
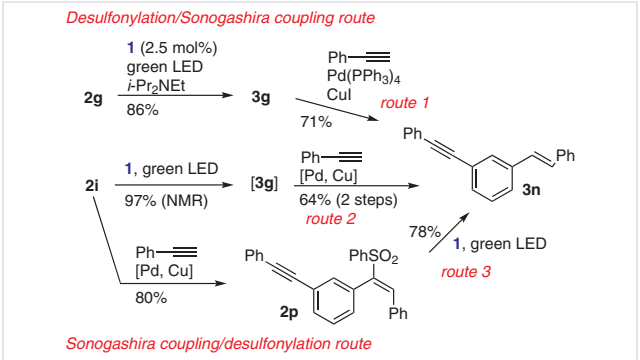
with the corresponding 4-MeO derivative **2d**, likely due to an electron-withdrawing effect on the part of the CF_3 group. In the competitive desulfonylation between **2d** and **2e** assisted by the green LED irradiation, **3e** was selectively present in a 46% yield, whereas 95% of **2d** was recovered intact (Scheme 5).[21]



Scheme 5 Competitive photo-catalyzed desulfonylation between **2d** and **2e**

In the **1**-catalyzed photo-desulfonylation of halo-substituted ethenyl sulfones **2f–m**, the significant effects of halogens and/or their substitution positions were observed in the chemical yields and chemoselectivities. Chloro-substituted ethenyl sulfone **2f** provided the desired chloroethene **3f** in a 75% yield. Ethenyl sulfones bearing the bromo group at 3-positions of benzene rings **2g** and **2i** underwent desulfonylation to provide **3g** in 86% and 80% yield, respectively. In the desulfonylation of 4-bromide **2h**, the desire product **3h** (34%), as well as debrominated compounds **2a** (25%) and **3a** (2%), were produced alongside the recovery of **2h** (44%). In contrast, 4-bromo sulfone **2j** underwent reductive desulfonylation to provide **3h** in an 80% yield, despite the use of 5 mL of MeCN and 2 mL of THF being required because of poor solubility. In 2.5 mL of MeCN and 2 mL of THF, the chemical yield of **3h** was significantly decreased to a 30% yield. In the reductive desulfonylation of dibromoethenyl sulfone **2k**, the desired 3,3′-dibromo-substituted stilbene **3i** was obtained in a 96% yield, and no loss of bromo functionality was observed. In this reduction, iodine functionality was labile. Iodo sulfones **2l** and **2m** yielded only small amounts of the desired ethenes **3j** (9%) and **3k** (12%), and in both reactions, the formation of deiodinated ethenyl sulfone **2a** (27% and 35%, respectively) and the recovery of staring sulfones **2l** (57%) and **2m** (31%) were observed. The **1**/green LED-promoted desulfonylation occurred in heteroaromatic ethenyl sulfone **2n** to provide **3l** in a 91% yield. In the reductive desulfonylation of dienyl sulfone **2o**, the desired diene **3m** was successfully obtained in 68% yield. In sharp contrast, when the desulfonylation of **2o** was performed using perylene/blue LED light, a complicated mixture was obtained, and **3m** was not synthesized. Although 1,2-diarylethenyl sulfones successfully underwent **1**-catalyzed reductive desulfonylation, 2-alkyl-1-phenylethenyl sulfones did not due to their higher LUMO levels.

We found that consecutive process, which comprised **1**/green LED light-promoted desulfonylation and Sonogashira coupling of the resulting bromostilbene was versatile to synthesize additionally expanded π-system. For instance, when **2g** was subjected to reductive desulfonylation, and Sonogashira coupling of the resulting 3-bromostilbene (**3g**) with phenylethyne was consecutively performed, enyne **3n** was obtained in a 61% yield (86% × 71%; route 1 in Scheme 6). In similar two-step reactions, **2i** was transformed into **3n** in a 64% yield (route 2 in Scheme 6).[22] In this process, **2i** was converted into **3g** by reductive desulfonylation in a 97% NMR yield, and the crude bromostilbene **3g** was used in the subsequent Sonogashira coupling without any purification. Alternatively, the consecutive Sonogashira coupling–reductive desulfonylation protocol also functioned well, and **2i** was transformed into **3n** through **2p** in a stepwise manner (62% yield, 80% × 78%; route 3 in Scheme 6).[23]



Scheme 6 Two alternative syntheses of expanded π-system enyne **3n**

We applied this consecutive coupling–desulfonylation protocol to the π-system expansion using photo-labile haloethenyl sulfones such as **2h** and **2l** (Scheme 7). In this route, the direct photoreduction of **2h** and **2l** was avoided; as such, we expect that the photochemically labile ethenyl sulfones can also be used as stilbene equivalents for new π-systems. When bromo- **2h** and iodoethenyl sulfones **2l** were treated with 4-MeO- and 4-Ph_2N-substituted phenylethynes in the presence of $Pd(PPh_3)_4$ and CuI, the desired ethyne adducts **2q** and **2r** were obtained in 48% and 66% yield, respectively, via successive column chromatography and recrystallization. The consecutive desulfonylation of **2q** and **2r** using the **1**/green LED protocol smoothly proceeded to afford MeO- and Ph_2N-substituted enynes **3o** and **3p** in 75% and 77% yield, respectively. During their purification, pyrene photocatalyst **1** could be easily separated from enyne products **3o** and **3p** via column chromatography on silica gel, where the R_f values (CH_2Cl_2/hexane 1:4 as eluent) were 0.23 for **3o**, 0.26 for **3p**, and 0.17 for **1**. Figure 3 presents the UV/Vis absorption and fluorescence spectra of **3o** and **3p**, and their optical properties are summarized in Table 1. The amino-substituted enyne **3p** demonstrated 29–48 nm longer wavelengths than methoxy derivative **3o** in the UV-Vis absorption and photoluminescence spectra. In photoluminescence, **3p** exhibited a larger emission quantum yield than **3o** in $CHCl_3$, but **3o** did the larger than **3p** in a powdery state (Figure 3, inset), that is, Φ_F **3o** 0.74 vs **3p** 0.87 in $CHCl_3$ and Φ_F **3o** 0.40 versus **3p** 0.08 in powdery states. Interestingly, **3p** indicated an emission profile at

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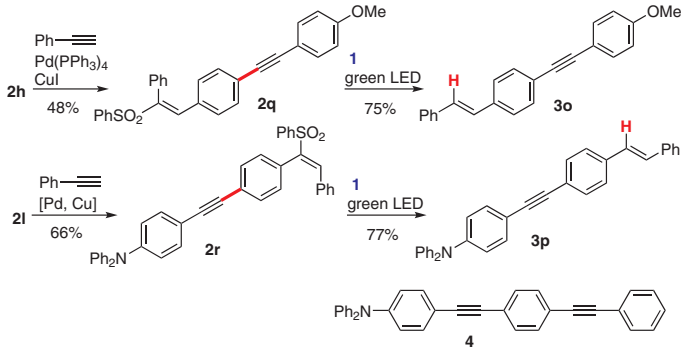


Scheme 7 The Sonogashira coupling/desulfonylation protocol using photo-labile halo-substituted ethenyl sulfones

Table 1 Optical Properties of **3o** and **3p** in $CHCl_3$ and as a Powdery State

	Ultraviolet/visible absorption (1.0×10^{-5} M) [nm] [ε (10^4) L/mol·cm]	Photoluminescence In $CHCl_3$ (1.0×10^{-7} M) [nm] (Φ_F)[a]	Powdery state [nm] (Φ_F)[a]
3o	343 (5.1)	404 (0.74)	419 (0.40)
3p	372 (4.8)	452 (0.87)	448 (0.08)

[a] Absolute fluorescence quantum yield measured by integrated sphere system (Hamamatsu photonics C9920-02).

approximately 450 nm in both the $CHCl_3$ solution and the powdery state. In sharp contrast, aminodiyne **4** demonstrated a 20 nm difference of emission wavelengths between in $CHCl_3$ solution and powdery state and a moderate fluorescence quantum yield in the powdery state: fluorescence, 442 nm in $CHCl_3$ (Φ_F 0.92) and 462 nm (0.53).[24]

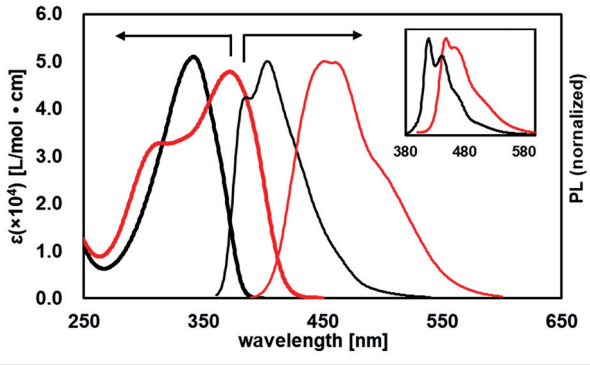
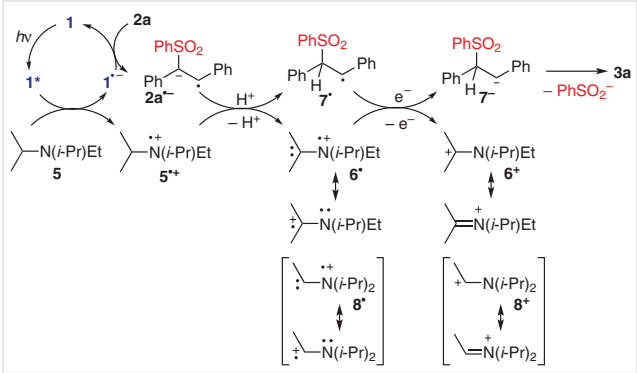


Figure 3 The UV/Vis absorption of **3o** (thick, black) and **3p** (thick, red) ($CHCl_3$, 1.0×10^{-5} M) and photoluminescence spectra of **3o** (thin, black) and **3p** (thin, red) [$CHCl_3$, 1.0×10^{-7} M, powdery state (inset)].

Finally, a plausible mechanism for **1**-catalyzed reductive desulfonylation is presented in Scheme 8.[6c] Pyrene catalyst **1** was photochemically excited by irradiation of green LEDs and transformed to anionic radical $\mathbf{1}^{\bullet-}$ via SET from *i*-Pr_2NEt (**5**). Highly reactive anionic radical $\mathbf{1}^{\bullet-}$ converted ethenyl sulfone **2** into anionic radical $\mathbf{2}^{\bullet-}$ through SET, with $\mathbf{1}^{\bullet-}$ being converted into **1**: –0.44 eV for the SOMO of anionic radical $\mathbf{1}^{\bullet-}$ and –1.65 eV for the LUMO of ethenyl sulfone **2**. Radical anion $\mathbf{2}^{\bullet-}$ underwent protonation by cationic radical $\mathbf{5}^{\bullet+}$, and the resulting radical $\mathbf{7}^{\bullet}$ consecutively effected SET from $\mathbf{6}^{\bullet}$ to provide anion $\mathbf{7}^{-}$. The subsequent elimination of the $PhSO_2$ anion consequently furnished stilbene (**3a**).



Scheme 8 A plausible mechanism of **1**/green-LED-promoted reductive desulfonylation of **2a**

In Table 2 are summarized the heats of formation, which were simulated for all the intermediates derived from **2a** at the B3LYP/6-31G(d) level of theory. Based on the simulation, an energy diagram for the transformation of $\mathbf{2a}^{\bullet-}$ to **3a** was depicted in Figure 4, and the substantially downhill reaction pathway would consistently support the reaction mechanism proposed in Scheme 8. Although, in this reaction, an α-proton of ethyl group in cationic radical $\mathbf{5}^{\bullet+}$ could be alternatively transferred to $\mathbf{2a}^{\bullet-}$ to produce radical $\mathbf{8}^{\bullet}$ and

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subsequently cation **8**$^{+}$, we tentatively employed **6**$^{\cdot}$ and **6**$^{+}$ because they were thermodynamically more stable than **8**$^{\cdot}$ and **8**$^{+}$.[25]

Table 2 The Heats of Formation (HOFs) Simulated for **2**$^{\cdot-}$, **7**$^{\cdot}$, **7**$^{-}$, **3a**, and $PhSO_2^-$ at the B3LYP/6-31G(d) Level of Theory

Stage	Chemical species	HOF [kcal/mol]	Δ(ΣHOF) [kcal/mol][a]
1	**2**$^{\cdot-}$	–828523.2	0.0
2	**7**$^{\cdot}$	–828879.7	–356.5
3	**7**$^{-}$	–828904.4	–381.2
4	**3a**, $PhSO_2^-$	–339300.6, –489627.7	–405.1

[a] Δ(ΣHOF) was calculated by the following equation: Δ(ΣHOF) = ΣHOF(stage x) – HOF(stage 1).

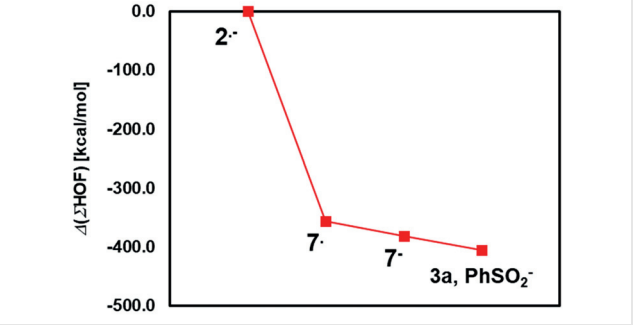

Figure 4 An energy diagram in the transformation of **2a**$^{\cdot-}$ to **3a**

In summary, a new photocatalyst **1** was developed. An expanded π-system of pyrene catalyst **1** triggered the desired photoreaction, even by low-energy green light irradiation, which resulted in carbon–sulfur (C–SO_2) bond cleavage in ethenyl sulfones. Due to the long branched alkoxy groups attached to the π-system, **1** demonstrated sufficient solubility in common organic solvents, and the proper polarity of oxygen functionalities enabled the easy separation of ethene products from **1** via column chromatography. This desulfonylation protocol worked well in halo-substituted ethenyl sulfones and, in combination with the Sonogashira coupling, achieved the syntheses of π-expanded enynes. Further application of the reductive desulfonylation using **1**/green LEDs and other pyrene derivatives/visible light to synthesize functionalized expanded π-systems is in progress.

Unless otherwise stated, all the reactions were carried out under a N_2 atmosphere. Glassware were oven-dried (70 °C) and heated under reduced pressure before use. Solvents were employed as eluents for all other routine operations. Anhydrous solvents (THF, DMF, and DMSO) were purchased from commercial suppliers and used without any further purification. Toluene and MeCN were distilled from CaH_2 before use. For TLC analyses, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used throughout this work. Silica gel column chromatography was performed using DAISOGEL. All NMR spectra were recorded on JEOL ECS400 and ECZ400S spectrometers and referenced to the internal standard TMS (δ = 0.0) for ^{1}H NMR, $CDCl_3$ (δ = 77.16) for ^{13}C NMR. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded on a Bruker Autoflex Speed instrument. UV/Vis absorption and fluorescence spectra were recorded using JASCO V-650 and FP-6500, respectively. The reduction and oxidation potentials (vs Fc/Fc^+) were measured in CH_2Cl_2 (1.0×10^{-4} M, 100 mV/s scan rate, 0.1 M Bu_4NPF_6) using a glassy carbon as the working electrode, a platinum (Pt) counter electrode, and a silver/silver ion (Ag/Ag^+) reference electrode (0.01 M $AgNO_3$ and 0.1 M tetrabutylammonium perchlorate in MeCN) in 0.1 M $LiClO_4$/MeCN.

(*E*)-1,2-Diphenyl-1-phenylsulfonylethene (2a);[18a] Typical Procedure

To benzyl sulfone (232 mg, 1.0 mmol) in THF (8.0 mL) was added LiHMDS (1.3 M in THF, 0.81 mL, 1.05 mmol) at –78 °C, and the mixture was stirred for 10 min. To the solution was added benzaldehyde (127 mg, 1.2 mmol), and the mixture was stirred for 30 min. Diethyl chlorophosphate (207 mg, 1.2 mmol) was added, and the mixture was stirred for 1 h. Then, LiHMDS (1.3 M in THF, 0.92 mL, 1.2 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 1 h. To this mixture were added EtOAc (20 mL) and sat. aq NH_4Cl (20 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine. The organic layer was dried ($MgSO_4$) and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc 8:2) and to recrystallization (MeOH) to afford **2a** as a white solid; yield: 263 mg (82%); mp 191–192 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.01–7.09 (m, 4 H), 7.17 (t, *J* = 7.4 Hz, 2 H), 7.23–7.32 (m, 3 H), 7.34–7.41 (m, 3 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.62–7.64 (m, 2 H), 7.97 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 128.6, 128.77, 128.82, 129.0, 129.3, 130.2, 130.7, 130.9, 131.4, 132.9, 133.3, 137.8, 138.8, 141.4.

Other ethenyl sulfones **2b–n** were synthesized according to the same procedure. A synthetic procedure for **2o** is described in the Supporting Information.

(*E*)-2-(4-Methylphenyl)-1-phenyl-1-phenylsulfonylethene (2b)[18a]

Isolated by column chromatography (hexane/EtOAc 8:2); yield: 515 mg (77%, 2.0 mmol scale); white solid; mp 209–210 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.27 (s, 3 H), 6.94–7.03 (m, 6 H), 7.26–7.30 (m, 2 H), 7.34–7.41 (m, 3 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.94 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 21.5, 128.7, 128.8, 128.9, 129.2, 129.4, 130.1, 130.7, 130.9, 131.6, 133.2, 137.8, 138.9, 140.2, 140.7.

(*E*)-2-(3-Methoxyphenyl)-1-phenyl-1-phenylsulfonylethene (2c)

Isolated by column chromatography (hexane/EtOAc 8:2); yield: 200 mg (57%, 1.0 mmol scale); white solid; mp 152–153 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.45 (s, 3 H), 6.50–6.51 (m, 1 H), 6.76–6.82 (m, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.12 (t, *J* = 8.0 Hz, 1 H), 7.27–7.42 (m, 5 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.64 (d, *J* = 6.8 Hz, 2 H), 7.94 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 54.9, 114.2, 117.1, 123.9, 128.7, 128.8, 129.0, 129.3, 129.6, 130.9, 131.5, 133.3, 134.0, 137.7, 138.7, 141.5, 159.3.

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HRMS (MALDI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{18}O_3SNa$: 373.0874; found: 373.0901.

(*E*)-1-(4-Methoxyphenyl)-2-phenyl-1-phenylsulfonylethene (2d)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 573 mg (82%, 2.0 mmol scale); white solid; mp 150.5–151.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.82 (s, 3 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 6.95 (d, *J* = 8.6 Hz, 2 H), 7.11 (d, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.26 (t, *J* = 7.6 Hz, 2 H), 7.40 (t, *J* = 7.5 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 2 H), 7.94 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 55.3, 114.4, 123.0, 128.5, 128.6, 128.7, 130.0, 130.6, 132.1, 133.0, 133.2, 137.7, 138.9, 141.1, 160.3.

(*E*)-2-Phenyl-1-(4-trifluoromethyphenyl)-1-phenylsulfonylethene (2e)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 583 mg (75%, 2.0 mmol scale); white solid; mp 174–175 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.05 (d, *J* = 7.6 Hz, 2 H), 7.17–7.22 (m, 4 H), 7.27–7.31 (m, 1 H), 7.42 (t, *J* = 7.8 Hz, 2 H), 7.54–7.59 (m, 3 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 8.03 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 123.9 (q, $^1J_{C,F}$ = 272.3 Hz), 125.9 (q, $^3J_{C,F}$ = 3.9 Hz), 128.7, 128.8, 129.1, 130.59, 130.63, 131.36 (q, $^2J_{C,F}$ = 32.8 Hz), 131.41, 132.3, 133.6, 135.5, 138.5, 138.8, 140.1.

^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ = –63.2.

(*E*)-2-(2-Chlorophenyl)-1-phenyl-1-phenylsulfonylethene (2f)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 419 mg (59%, 2.0 mmol scale); white solid; mp 159–160 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.77 (d, *J* = 8.0 Hz, 1 H), 6.88 (t, *J* = 7.6 Hz, 1 H), 7.04–7.06 (m, 2 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.21 (t, *J* = 7.6 Hz, 2 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 7.37–7.42 (m, 3 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.66–7.68 (m, 2 H), 8.29 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 126.5, 128.7, 128.9, 129.3, 129.8, 130.56, 130.60, 130.9, 131.6, 133.4, 134.9, 135.5, 138.6, 144.0. Two carbon signals are missing probably due to overlapping.

(*E*)-2-(3-Bromophenyl)-1-phenyl-1-phenylsulfonylethene (2g)[6c]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 663 mg (83%, 2.0 mmol scale); white solid; mp 117–118 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.95–7.05 (m, 4 H), 7.20–7.21 (m, 1 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.35–7.42 (m, 4 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.61–7.64 (m, 2 H), 7.88 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 122.5, 128.7, 128.8, 129.0, 129.5, 130.0, 130.6, 130.7, 132.9, 133.35, 133.45, 134.87, 135.90, 138.3, 143.0. One carbon signal is missing due to overlapping.

(*E*)-2-(4-Bromophenyl)-1-phenyl-1-phenylsulfonylethene (2h)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 567 mg (71%, 2.0 mmol scale); white solid; mp 245–246 °C

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.92 (d, *J* = 8.8 Hz, 2 H), 7.00 (d, *J* = 6.8 Hz, 2 H), 7.27–7.31 (m, 4 H), 7.35–7.42 (m, 3 H), 7.52–7.56 (m, 1 H), 7.60–7.63 (m, 2 H), 7.89 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 124.7, 128.8, 128.9, 129.1, 129.5, 130.7, 131.0, 131.8, 131.9, 132.0, 133.4, 136.3, 138.5, 142.3.

(*E*)-1-(3-Bromophenyl)-2-phenyl-1-phenylsulfonylethene (2i)[6c]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 344 mg (86%, 1.0 mmol scale); white solid; mp 147.5–148.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.95–6.97 (m, 1 H), 7.08 (d, *J* = 7.2 Hz, 2 H), 7.15–7.23 (m, 4 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.49–7.52 (m, 1 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.63–7.66 (m, 2 H), 7.97 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 122.7, 128.7, 128.8, 129.0, 129.6, 130.45, 130.52, 130.7, 132.40, 132.43, 133.5, 133.6, 138.36, 138.40, 140.0. One carbon signal is missing due to overlapping.

(*E*)-1-(4-Bromophenyl)-2-phenyl-1-phenylsulfonylethene (2j)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 339 mg (85%, 1.0 mmol scale); white solid; mp 180–181 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.91 (d, *J* = 8.6 Hz, 2 H), 7.08 (d, *J* = 7.3 Hz, 2 H), 7.21 (t, *J* = 7.3 Hz, 2 H), 7.28 (t, *J* = 7.3 Hz, 1 H), 7.41–7.44 (m, 4 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.5 Hz, 2 H), 7.98 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 124.0, 128.7, 128.8, 129.0, 130.4, 130.5, 130.7, 132.3, 132.52, 132.55, 133.5, 138.4, 138.6, 140.2.

(*E*)-1,2-Bis(3-bromophenyl)-1-phenylsulfonylethene (2k)

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 727 mg (76%, 2.0 mmol scale); white solid; mp 123–124 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.95 (d, *J* = 8.0 Hz, 2 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 7.14–7.19 (m, 2 H), 7.25 (s, 1 H), 7.39–7.48 (m, 3 H), 7.50–7.53 (m, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.88 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 122.8, 122.9, 128.7, 128.8, 129.1, 129.4, 130.2, 130.6, 132.7, 132.9, 133.3, 133.4, 133.6, 133.8, 134.5, 136.6, 138.1, 141.7.

HRMS (MALDI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{14}Br_2O_2SNa$: 498.8979; found: 498.8937.

(*E*)-1-(4-Iodophenyl)-2-phenyl-1-phenylsulfonylethene (2l)

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 656 mg (49%, 3.0 mmol scale); white solid; mp 199–200 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.77 (d, *J* = 8.4 Hz, 2 H), 7.08 (d, *J* = 7.2 Hz, 2 H), 7.21 (t, *J* = 7.4 Hz, 2 H), 7.29 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.61–7.65 (m, 4 H), 7.97 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 95.9, 128.7, 128.8, 129.0, 130.4, 130.6, 131.0, 132.5, 132.6, 133.5, 138.2, 138.3, 138.6, 140.3.

HRMS (MALDI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{15}IO_2SNa$: 468.9735; found: 468.9766.

(*E*)-2-(3-Iodophenyl)-1-phenyl-1-phenylsulfonylethene (2m)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 491 mg (55%, 2.0 mmol scale); white solid; mp 140.0–140.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.88 (t, *J* = 7.8 Hz, 1 H), 6.98–7.01 (m, 3 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 7.36–7.42 (m, 4 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 6.8 Hz, 2 H), 7.85 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 94.2, 128.8, 128.9, 129.0, 129.3, 129.5, 130.1, 130.6, 130.8, 133.5, 135.0, 135.9, 138.4, 138.8, 139.5, 142.9.

(*E*)-2-(2-Furyl)-1-phenyl-1-phenylsulfonylethene (2n)[18a]

Isolated by flash chromatography (hexane/EtOAc 8:2); yield: 208 mg (67%, 1.0 mmol scale); white solid mp 134.5–135.0 °C.

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^{1}H NMR($CDCl_3$, 400 MHz): δ = 5.89 (d, *J* = 3.4 Hz, 1 H), 6.27 (dd, *J* = 3.4, 1.8 Hz, 1 H), 7.02 (d, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.35–7.42 (m, 4 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.63 (d, *J* = 6.8 Hz, 2 H), 7.83 (s, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 112.4, 115.5, 126.1, 128.6, 128.77, 128.83, 129.3, 130.5, 131.4, 133.3, 138.1, 138.9, 145.2, 149.3.

(*1E,3E*)-1,4-Diphenyl-1-phenylsulfonyl-1,3-butadiene (2o)

Isolated by column chromatography (hexane/EtOAc 8:2) and then recrystallization (MeOH); yield: 62 mg [60% (83% × 72%)] [(1*E*,3*E*)/(1*Z*,3*E*) = 1.0:0.22]; white solid; mp 115–116 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.54–8.34 (dd, *J* = 15.6, 15.5, 10.8, 11.5 Hz, 1 H), 7.06–6.85 (d, *J* = 15.6, 15.5 Hz, 1 H), 7.13–7.58 (d, *J* = 6.8, 7.4 Hz, 2 H), 7.27–7.42 (m, 10 H), 7.49–7.54 (m, 1 H), 7.62–7.70 (d, *J* = 7.6, 7.4 Hz, 2 H), 7.74–6.77 (d, *J* = 10.8, 11.5 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 122.8, 123.2, 127.5, 127.7, 127.9, 128.2, 128.4, 128.5, 128.78, 128.85, 128.87, 128.92, 129.0, 129.2, 129.48, 129.55, 130.2, 130.8, 131.1, 133.2, 135.76, 135.82, 136.2, 138.6, 139.5, 141.0, 141.1, 142.1, 142.9, 143.4.

HRMS (MALDI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{18}O_2SNa$: 369.0925; found: 369.0918.

Stilbene (3a)[26] by Reductive Desulfonylation of Ethenyl Sulfone 2a Using 1/Green LED; Typical Procedure

To a round-bottomed flask were added **2a** (80 mg, 0.25 mmol), photocatalyst **1** (7.6 mg, 6.3 μmol), *i*-Pr_2NEt (2.0 mmol, 0.35 mL), MeCN (2.5 mL), and THF (0.5 mL). The flask was placed in a glass water-bath surrounded by a green LED strip lighting, and the green light was irradiated at the mixture for 9 h. During the photoreaction, the bath temperature was maintained at 50–60 °C due to heat radiation from the photoreactor. The solvents were evaporated, and the crude product was subjected to column chromatography on silica gel (hexane) to give **3a** as a white solid; yield: 40 mg (88%); mp 129–130 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (s, 2 H), 7.26 (t, *J* = 7.4 Hz, 2 H), 7.36 (t, *J* = 7.4 Hz, 4 H), 7.52 (d, *J* = 7.4 Hz, 4 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 126.6, 127.7, 128.8, 137.4. One carbon signal is missing due to overlapping).

Other stilbenes **3b–m** were synthesized according to the same procedure.

***trans*-4-Methylstilbene (3b)[26]**

Isolated by flash chromatography (hexane); yield: 39 mg (81%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.36 (s, 3 H), 7.05 (d, *J* = 16.4 Hz, 1 H), 7.10 (d, *J* = 16.4 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.22–7.27 (m, 1 H), 7.35 (t, *J* = 7.3 Hz, 2 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.50 (d, *J* = 7.3 Hz, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 21.4, 126.5, 126.6, 127.5, 127.8, 128.8, 129.5, 134.7, 137.6. Two carbon signals are missing due to overlapping.

***trans*-3-Methoxystilbene (3c)[27]**

Isolated by flash chromatography (hexane); yield: 35 mg (66%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.85 (s, 3 H), 6.81–6.84 (m, 1 H), 7.05–7.13 (m, 4 H), 7.24–7.29 (m, 2 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.51 (d, *J* = 7.6 Hz, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 55.3, 111.9, 113.4, 119.3, 126.7, 127.8, 128.7, 128.8, 129.1, 129.7, 137.3, 138.9, 160.0.

***trans*-4-Methoxystilbene (3d)[27]**

Isolated by flash chromatography (hexane); yield: 27 mg (52%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.83 (s, 3 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.97 (d, *J* = 16.4 Hz, 1 H), 7.07 (d, *J* = 16.4 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.49 (d, *J* = 7.5 Hz, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 55.5, 114.3, 126.4, 126.8, 127.3, 127.9, 128.4, 128.8, 130.3, 137.8, 159.4.

***trans*-4-Trifluoromethylstilbene (3e)[27]**

Isolated by flash chromatography (hexane); yield: 54 mg (86%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.12 (d, *J* = 16.6 Hz, 1 H), 7.20 (d, *J* = 16.6 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 7.5 Hz, 2 H), 7.61 (s, 4 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 123.9 (q, *J* = 240.3 Hz), 125.8 (q, *J* = 3.8 Hz), 126.7, 126.9, 127.3, 128.4, 128.9, 129.4 (q, *J* = 32.8 Hz), 131.4, 136.8, 141.0.

^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ = –62.9 (s, 3 F).

***trans*-2-Chlorostilbene (3f)[28]**

Isolated by flash chromatography (hexane); yield: 40 mg (75%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.08 (d, *J* = 18.0 Hz, 1 H), 7.17–7.22 (m, 1 H), 7.25–7.31 (m, 2 H), 7.38 (t, *J* = 7.6 Hz, 3 H), 7.52 (d, *J* = 18.0 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.69 (d, *J* = 7.8 Hz, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 124.9, 126.6, 127.0, 128.2, 128.6, 128.8, 129.9, 131.4, 133.6, 135.5, 137.2. One carbon signal is missing due to overlapping.

***trans*-3-Bromostilbene (3g)[6c]**

Isolated by flash chromatography (hexane); yield: 56 mg, from **2g** (86%), 52 mg, from **2i** (80%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.02 (d, *J* = 16.6 Hz, 1 H), 7.11 (d, *J* = 16.6 Hz, 1 H), 7.22 (t, *J* = 7.9 Hz, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.35–7.39 (m, 3 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.66–7.67 (m, 1 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 123.0, 125.3, 126.8, 127.2, 128.1, 128.8, 129.3, 130.2, 130.5, 136.9, 139.6. One carbon signal is missing due to overlapping.

***trans*-4-Bromostilbene (3h)[6c]**

Isolated by flash chromatography (hexane); yield: 22 mg, from **2h** (34%), 52 mg, from **2j** (80%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.03 (d, *J* = 16.2 Hz, 1 H), 7.10 (d, *J* = 16.2 Hz, 1 H), 7.27–7.30 (m, 1 H), 7.34–7.39 (m, 4 H), 7.46–7.52 (m, 4 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 121.4, 126.7, 127.5, 128.0, 128.1, 128.9, 129.5, 131.9, 136.4, 137.1.

***trans*-3,3′-Dibromostilbene (3i)[29]**

Isolated by flash chromatography (hexane); yield: 81 mg (96%); white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.02 (s, 2 H), 7.23 (t, *J* = 7.8 Hz, 2 H), 7.39–7.42 (m, 4 H), 7.66 (t, *J* = 1.8 Hz, 2 H).

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$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 123.0, 125.4, 128.6, 129.5, 130.3, 130.9, 139.0.

***trans*-4-Iodostilbene (3j)**[26]

NMR yield by using CH_2Br_2 as an internal standard: 9%.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.01 (d, *J* = 16.2 Hz, 1 H), 7.11 (d, *J* = 16.2 Hz, 1 H), 7.24–7.30 (m, 3 H), 7.36 (t, *J* = 7.4 Hz, 2 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.68 (d, *J* = 8.8 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 92.9, 126.7, 127.6, 128.1, 128.4, 128.9, 129.6, 136.99, 137.04, 137.9.

***trans*-3-Iodostilbene (3k)**[6c]

NMR yield by using 1,4-dioxane as an internal standard: 12%.

1H NMR ($CDCl_3$, 400 MHz): δ = 6.98 (d, *J* = 16.0 Hz, 1 H), 7.07–7.11 (m, 2 H), 7.26–7.30 (m, 1 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.58 (d, *J* = 7.2 Hz, 1 H), 7.87 (t, *J* = 1.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 94.9, 125.9, 126.8, 127.1, 128.1, 128.8, 130.1, 130.4, 135.4, 136.4, 136.9, 139.7.

***trans*-1-(2-Furyl)-2-phenylethene (3l)**[6c]

Isolated by flash chromatography (hexane); yield: 39 mg (91%); white solid.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.35 (d, *J* = 3.2 Hz, 1 H), 6.42 (dd, *J* = 3.2, 1.8 Hz, 1 H), 6.89 (d, *J* = 16.2 Hz, 1 H), 7.04 (d, *J* = 16.2 Hz, 1 H), 7.22–7.24 (m, 1 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 1.8 Hz, 1 H), 7.46 (d, *J* = 7.2 Hz, 2 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 108.7, 111.7, 116.6, 126.4, 127.2, 127.7, 128.8, 137.1, 142.2, 153.4.

***trans,trans*-1,4-Diphenyl-1,3-butadiene (3m)**[6c]

Isolated by flash chromatography (hexane); yield: 35 mg (68%); white solid.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.64–6.71 (m, 2 H), 6.93–7.00 (m, 2 H), 7.23 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 4 H), 7.45 (d, *J* = 7.6 Hz, 4 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 126.5, 127.7, 128.8, 129.4, 133.0, 137.5.

***trans*-3-(Phenylethynyl)stilbene (3n);[30] Stepwise Desulfonylation/Sonogashira Coupling (Scheme 6, route 1)**

3-Bromostilbene (**3g**) was prepared from **2g** by **1**/green LED-assisted reductive desulfonylation. To a round-bottomed flask were added **3g** (259 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), ethynylbenzene (123 mg, 1.2 mmol), *i*-Pr_2NH (1.0 mL, 7.1 mmol), and toluene (10 mL), and the mixture was stirred at 80 °C for 24 h. The reaction was quenched with sat. aq NH_4Cl, and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine. The organic layer was dried ($MgSO_4$) and evaporated. The crude product was subjected to flash chromatography on silica gel (hexane/CH_2Cl_2 9:1) to afford **3n**; yield: 199 mg (71%); white solid.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.08 (d, *J* = 16.4 Hz, 1 H), 7.16 (d, *J* = 16.4 Hz, 1 H), 7.28–7.30 (m, 1 H), 7.33–7.39 (m, 6 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 7.52–7.57 (m, 4 H), 7.71 (t, *J* = 1.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 89.4, 89.6, 123.3, 123.8, 126.6, 126.7, 127.9, 128.0, 128.4, 128.5, 128.8, 129.6, 130.7, 131.8, 137.2, 137. Two carbon signals are missing due to overlapping.

Stepwise Sonogashira Coupling/Desulfonylation; Typical Procedure (Scheme 6, route 3)

(i) (*E*)-2-Phenyl-1-(3-phenylethynyl)phenyl-1-phenylsulfonylethene (2p)

To a round-bottomed flask were added **2i** (799 mg, 2.0 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), ethynylbenzene (245 mg, 2.4 mmol), *i*-Pr_2NH (2.0 mL, 14 mmol), and toluene (20 mL), and the mixture was stirred at 80 °C for 24 h. The reaction was quenched with sat. aq NH_4Cl, and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layers were washed with H_2O and brine. The organic layer was dried ($MgSO_4$) and evaporated. The crude product was subjected to flash chromatography (hexane/EtOAc 8:2) and recrystallized from MeOH to afford **2p**; yield: 673 mg (80%); white solid; mp 191–192 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.92 (dt, *J* = 8.0, 1.4 Hz, 1 H), 7.11 (d, *J* = 7.2 Hz, 2 H), 7.18–7.25 (m, 3 H), 7.27–7.29 (m, 2 H), 7.32–7.36 (m, 3 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.46–7.58 (m, 4 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.99 (s, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 88.6, 90.5, 123.0, 124.3, 128.5, 128.6, 128.76, 128.81, 129.0, 129.1, 130.4, 130.7, 130.8, 131.7, 131.8, 132.4, 132.6, 133.5, 133.8, 138.1, 138.6, 140.6.

HRMS (MALDI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{20}O_2SNa$: 443.1082; found: 443.1045.

Other π-expanded ethenyl sulfones **2q** and **2r** were synthesized according to the same procedure.

(*E*)-2-[4-(4-Methyoxyphenylethynyl)phenyl]-1-phenyl-1-phenylsulfonylethene (2q)

Isolated by flash chromatography (hexane/EtOAc 8:2) and recrystallized from EtOH; yield: 216 mg (48%); white solid; mp 225–226 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ = 3.82 (s, 3 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 4 H), 7.27–7.31 (m, 4 H), 7.35–7.43 (m, 5 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.94 (s, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 55.4, 87.8, 92.0, 114.2, 115.0, 125.5, 128.7, 128.8, 129.0, 129.4, 130.5, 130.8, 131.2, 131.5, 132.3, 133.3, 133.4, 136.9, 138.7, 141.8, 160.0.

HRMS (MALDI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{22}O_3SNa$: 473.1187; found: 473.1221.

(*E*)-1-[4-(4-Diphenylaminophenylethynyl)phenyl]-2-phenyl-1-phenylsulfonylethene (2r)

Isolated by flash chromatography (hexane/EtOAc 8:2) and recrystallized from EtOH; yield: 194 mg (66%); yellow solid; mp 168–169 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.99–7.03 (m, 4 H), 7.05–7.13 (m, 8 H), 7.19 (t, *J* = 7.6 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 5 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.39–7.43 (m, 4 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.64 (d, *J* = 6.8 Hz, 2 H), 7.97 (s, 1 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ = 88.1, 91.6, 115.4, 122.1, 123.8, 124.7, 125.2, 128.7, 128.9, 129.5, 130.3, 130.7, 130.9, 132.0, 132.7, 133.4, 138.0, 138.7, 140.9, 147.2, 148.3. Three carbon signals are missing probably due to overlapping.

HRMS (MALDI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{22}O_3SNa$: 610.1817; found: 610.1847.

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(ii) *trans*-3-(Phenylethynyl)stilbene (3n); Typical Procedure

To a round-bottomed flask were added **2p** (105 mg, 0.25 mmol), **1** (7.6 mg, 6.3 μmol), *i*-Pr_2NEt (0.35 mL, 2.0 mmol), MeCN (2.5 mL), and THF (0.5 mL). The flask was placed in a glass water-bath surrounded by green LED strip lighting, and green light was irradiated at the mixture for 9 h. During the photoreaction, the bath temperature was maintained at 50–60 °C due to heat radiation from the photoreactor. After the solvents were evaporated, the crude product was subject to column chromatography on silica gel (hexane/CH_2Cl_2 9:1) to afford **3n**; yield: 55 mg (78%).

Other ethynyl-substituted stilbenes **3o** and **3p** were synthesized according to the same procedure.

***trans*-4-(4-Methoxyphenylethynyl)stilbene (3o)**

Isolated by column chromatography on silica gel (hexane/CH_2Cl_2 9:1); yield: 58 mg (75%); white solid; mp 224–225 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.83 (s, 3 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 16.4 Hz, 1 H), 7.14 (d, *J* = 16.4 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.37 (t, *J* = 7.4 Hz, 2 H), 7.47–7.53 (m, 8 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 55.5, 88.4, 90.5, 114.2, 115.5, 122.8, 126.5, 126.7, 128.0, 128.2, 128.9, 129.5, 131.9, 133.2, 137.1, 137.3, 159.8.

HRMS (MALDI-TOF): *m*/*z* [M]$^+$ calcd for $C_{23}H_{18}O$: 310.1358; found: 310.1310.

***trans*-4-(4-Diphenylaminophenylethynyl)stilbene (3p)**

Isolated by column chromatography on silica gel (hexane/CH_2Cl_2 8:2); yield: 34 mg (77%); yellow solid; mp 200–201 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.01 (d, *J* = 8.4 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 2 H), 7.10–7.16 (m, 6 H), 7.26–7.30 (m, 5 H), 7.35–7.40 (m, 4 H), 7.49–7.53 (m, 6 H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 89.0, 90.8, 116.2, 122.4, 122.7, 123.7, 125.1, 126.5, 126.7, 127.9, 128.1, 128.8, 129.48, 129.52, 131.9, 132.6, 137.0, 137.2, 147.3, 148.0.

HRMS (MALDI-TOF): *m*/*z* [M]$^+$ calcd for $C_{34}H_{25}N$: 447.1987; found: 447.2032.

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Supporting Information

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(19) Because of the poor solubility of **1** in MeCN, the addition of a small amount of THF was crucial. See the Supporting Information for more detail of the solubility of **1**.

(20) An absorption terminus of perylene was observed at 460 nm. See also the Supporting Information for details.

(21) DFT calculations (B3LYP/6-31G(d)) indicated the LUMO levels of **2d** and **2e** at –1.57 and –1.87 eV, respectively. The lower LUMO level of **2e** could explain its more rapid desulfonylation in the competitive reaction. See also the Supporting Information for details.

(22) (a) We also attempted a three-step integration in the transformations of benzyl sulfone to **3n**, namely, in the synthesis of **2g**/desulfonylation/Sonogashira coupling. Unfortunately, the desired enyne **3n** was contaminated with a trace amount of 1,3-di(phenylethynyl)benzene, which was produced at the synthesis of **2g** by the unexpected further elimination of sulfinic acid. (b) See ref. 5c.

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