

A metal-free route to alkynyl sulfones under photoinduced conditions with the insertion of sulfur dioxide

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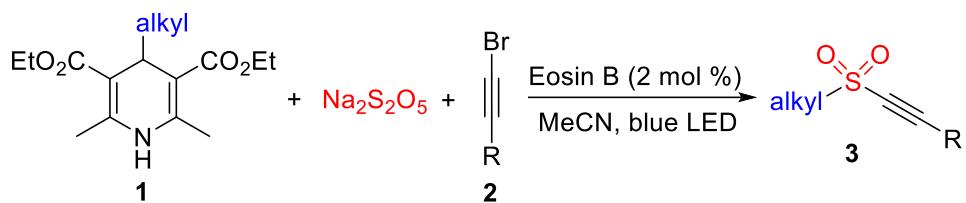
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S6).
3. ^1H and ^{13}C NMR spectra of compounds **3** and **4** (S7-S20).

General experimental methods:

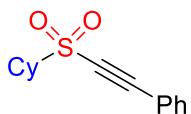
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μ m, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the photoinduced reaction of 4-alkyl Hantzsch esters **1**, sodium metabisulfite, and alkynyl bromides **2***



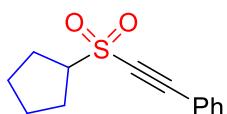
4-Alkyl Hantzsch ester **1** (0.3 mmol), sodium metabisulfite (0.4 mmol) and Eosin B (2 mol %) were combined in a tube. The tube was evacuated and backfilled with N_2 three times, then alkynyl bromide **2** (0.2 mmol) in MeCN (2.0 mL) was added in the tube under N_2 atmosphere. The mixture was then placed around a blue LED with a distance of 6 centimeters, and was stirred under light irradiation for 48 hours at room temperature. After completion of reaction as indicated by TLC, the mixture was purified directly by flash column chromatography ($\text{EtOAc}/n\text{-hexane}$, 1:8 - 1:2) to

provide the desired product **3**.



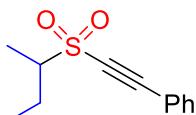
((Cyclohexylsulfonyl)ethynyl)benzene (**3a**)

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.52 (m, 1H), 7.42 (m, 2H), 3.04 (t, *J* = 11.9 Hz, 1H), 2.36 (d, *J* = 12.5 Hz, 2H), 1.97 (d, *J* = 12.6 Hz, 2H), 1.76 – 1.54 (m, 4H), 1.46 – 1.30 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 132.8, 131.5, 128.7, 117.7, 93.0, 81.7, 65.1, 25.4, 24.9, 24.8. HRMS (ESI) calcd for C₁₄H₁₆O₂S⁺: 249.0944 (M+H⁺), found: 249.0943.



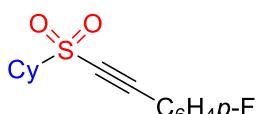
((Cyclopentylsulfonyl)ethynyl)benzene (**3b**)

¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (m, 1H), 7.42 (m, 2H), 3.87 – 3.59 (m, 1H), 2.44 – 2.07 (m, 4H), 1.79 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 132.7, 131.5, 128.7, 117.7, 92.6, 82.5, 66.1, 27.3, 26.0. HRMS (ESI) calcd for C₁₃H₁₄O₂S⁺: 235.0787 (M+H⁺), found: 235.0781.



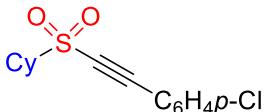
((sec-Butylsulfonyl)ethynyl)benzene (**3c**)

¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.42 (m, 2H), 3.07 (m, 1H), 2.37 – 2.19 (m, 1H), 1.79 – 1.62 (m, 1H), 1.52 (m, 3H), 1.11 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 132.7, 131.5, 128.7, 117.7, 93.0, 81.7, 63.4, 22.6, 12.7, 11.0. HRMS (ESI) calcd for C₁₂H₁₄O₂S⁺: 223.0787 (M+H⁺), found: 223.0771.



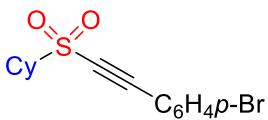
1-((Cyclohexylsulfonyl)ethynyl)-4-fluorobenzene (**3d**)

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.53 (m, 1H), 7.12 (t, J = 8.6 Hz, 2H), 3.11 – 2.96 (m, 1H), 2.34 (d, J = 11.7 Hz, 2H), 1.97 (d, J = 13.5 Hz, 2H), 1.76 (d, J = 12.6 Hz, 1H), 1.66–1.56 (m, 2H), 1.44 – 1.20 (m, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 164.4 (d, J = 255.4 Hz), 135.3 (d, J = 9.6 Hz), 116.5 (d, J = 22.8 Hz), 114.0, 92.0, 81.9, 65.2, 25.5, 25.0, 24.9. HRMS (ESI) calcd for C₁₄H₁₅FO₂SNa⁺: 289.0669 (M+ Na⁺), found: 289.0675.



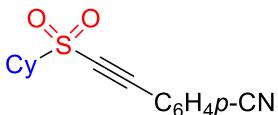
1-Chloro-4-((cyclohexylsulfonyl)ethynyl)benzene (3e)

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.18 – 2.94 (m, 1H), 2.36 (d, J = 11.7 Hz, 2H), 1.99 (d, J = 13.3 Hz, 2H), 1.78 (d, J = 12.6 Hz, 1H), 1.67–1.57 (m, 2H), 1.47 – 1.18 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.2, 134.1, 129.3, 116.3, 91.7, 82.8, 65.2, 25.5, 25.0, 24.9. HRMS (ESI) calcd for C₁₄H₁₅ClO₂SNa⁺: 305.0373 (M+Na⁺), found: 305.0381.



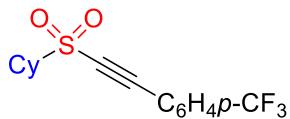
1-Bromo-4-((cyclohexylsulfonyl)ethynyl)benzene (3f)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 3.11 – 2.99 (m, 1H), 2.35 (d, J = 11.7 Hz, 2H), 1.99 (d, J = 13.4 Hz, 2H), 1.77 (d, J = 12.6 Hz, 1H), 1.67–1.57 (m, 2H), 1.40 – 1.22 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 134.2, 132.3, 126.6, 116.8, 91.8, 82.9, 65.2, 25.5, 25.0, 24.9. HRMS (ESI) calcd for C₁₄H₁₅BrO₂SNa⁺: 348.9868 (M+Na⁺), found: 348.9883.



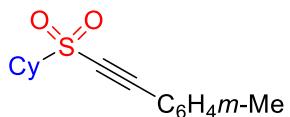
4-((Cyclohexylsulfonyl)ethynyl)benzonitrile (3g)

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 1.9 Hz, 4H), 3.08 (t, J = 3.2 Hz, 1H), 2.35 (d, J = 11.8 Hz, 2H), 2.00 (d, J = 13.3 Hz, 2H), 1.79 (d, J = 12.5 Hz, 1H), 1.62 (dt, J = 12.2, 9.3 Hz, 2H), 1.36 (dt, J = 23.5, 11.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 133.3, 132.4, 122.6, 117.6, 115.0, 89.9, 85.2, 65.2, 25.4, 25.0, 24.9. HRMS (ESI) calcd for C₁₅H₁₅NO₂S⁺: 274.0896 (M+H⁺), found: 274.0890.



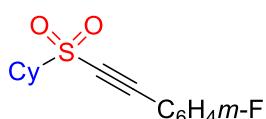
1-((Cyclohexylsulfonyl)ethynyl)-4-(trifluoromethyl)benzene (3h**)**

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.1 Hz, 4H), 3.15 – 2.99 (m, 1H), 2.37 (d, *J* = 11.8 Hz, 2H), 2.00 (d, *J* = 13.4 Hz, 2H), 1.79 (d, *J* = 12.6 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.43 – 1.25 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 133.2, 133.0, 125.8, 125.8, 121.7, 90.6, 83.8, 65.2, 25.5, 25.0, 24.9. HRMS (ESI) calcd for C₁₅H₁₅FO₂S⁺: 317.0818 (M+H⁺), found: 317.0804.



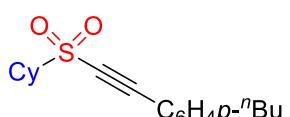
1-((Cyclohexylsulfonyl)ethynyl)-3-methylbenzene (3i**)**

¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 2H), 7.34 (s, 2H), 3.17 – 2.98 (m, 1H), 2.39–2.36 (m, 5H), 1.99 (d, *J* = 13.3 Hz, 2H), 1.78 (d, *J* = 12.4 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.34 (dd, *J* = 24.0, 11.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.7, 133.3, 132.5, 130.0, 128.7, 117.7, 93.5, 81.6, 65.2, 25.5, 25.1, 25.0. HRMS (ESI) calcd for C₁₅H₁₈O₂S⁺: 263.1100 (M+H⁺), found: 263.1115.



1-((Cyclohexylsulfonyl)ethynyl)-3-fluorobenzene (3j**)**

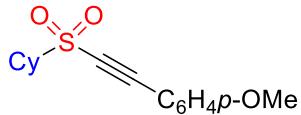
¹H NMR (400 MHz, CDCl₃) δ 7.42 (t, *J* = 5.1 Hz, 2H), 7.35 – 7.25 (m, 2H), 3.15 – 3.01 (m, 1H), 2.36 (d, *J* = 11.6 Hz, 2H), 2.00 (d, *J* = 13.5 Hz, 2H), 1.79 (d, *J* = 12.6 Hz, 1H), 1.63 (dd, *J* = 12.4, 3.4 Hz, 2H), 1.36 – 1.28 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.4, 130.7 (d, *J* = 9.1 Hz), 128.8, 119.6 (d, *J* = 24.0 Hz), 119.2 (d, *J* = 21.5 Hz), 91.1, 82.6, 65.2, 25.5, 25.0, 24.9. HRMS (ESI) calcd for C₁₄H₁₆FO₂S⁺: 267.0850 (M+H⁺), found: 267.0847.



1-Butyl-4-((cyclohexylsulfonyl)ethynyl)benzene (3k**)**

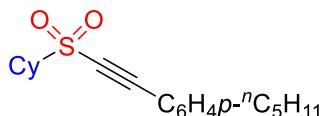
¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.13 – 2.97 (m, 1H), 2.75 – 2.61 (m, 2H), 2.37 (d, *J* = 11.8 Hz, 2H), 1.98 (d, *J* = 13.3 Hz, 2H), 1.77 (d,

$J = 12.5$ Hz, 1H), 1.63 (dd, $J = 12.0, 3.2$ Hz, 3H), 1.41-1.20 (m, 6H), 0.95 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.4, 132.9, 128.9, 114.9, 93.8, 81.4, 65.2, 35.8, 33.2, 25.6, 25.1, 25.0, 22.3, 13.9. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{25}\text{BrO}_2\text{S}^+$: 305.1570 ($\text{M}+\text{H}^+$), found: 305.1570.



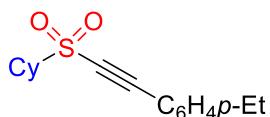
1-((Cyclohexylsulfonyl)ethynyl)-4-methoxybenzene (3l)

^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 3.07-3.00 (m, 1H), 2.44 – 2.30 (m, 2H), 1.98 (d, $J = 13.4$ Hz, 2H), 1.76 (d, $J = 12.5$ Hz, 1H), 1.67 – 1.58 (m, 2H), 1.39 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.2, 134.8, 114.5, 110.0, 94.2, 81.1, 65.2, 55.5, 25.6, 25.1, 25.0. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}^+$: 279.1049 ($\text{M}+\text{H}^+$), found: 279.1048.



1-((Cyclohexylsulfonyl)ethynyl)-4-pentylbenzene (3m)

^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 3.06-2.99 (m, 1H), 2.68 – 2.60 (m, 2H), 2.35 (d, $J = 11.8$ Hz, 2H), 1.96 (d, $J = 13.4$ Hz, 2H), 1.77 – 1.58 (m, 6H), 1.34 – 1.28 (m, 6H), 0.88 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 132.9, 128.9, 114.9, 93.8, 81.4, 65.2, 36.1, 31.4, 30.7, 25.6, 25.1, 25.0, 22.5, 14.0. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{27}\text{O}_2\text{S}^+$: 319.1726 ($\text{M}+\text{H}^+$), found: 319.1723.



1-((Cyclohexylsulfonyl)ethynyl)-4-ethylbenzene (3n)

^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.18 (m, 2H), 3.03 (s, 1H), 2.69 (q, $J = 7.6$ Hz, 2H), 2.35 (d, $J = 11.5$ Hz, 2H), 1.96 (d, $J = 13.5$ Hz, 2H), 1.61 (m, 2H), 1.35 – 1.22 (m, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 132.9, 128.3, 114.8, 93.7, 81.3, 65.1, 28.9, 25.4, 24.9, 24.8, 15.0. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{SNa}^+$: 299.1076 ($\text{M}+\text{Na}^+$), found: 299.1069.

