

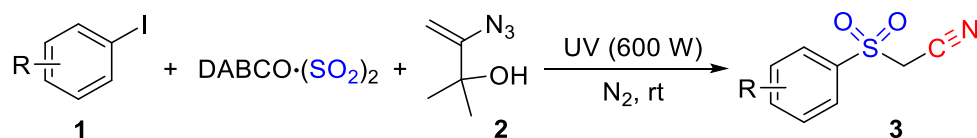
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S3-S9).
3. ^1H and ^{13}C NMR spectra of compounds **3** (S10–S61).

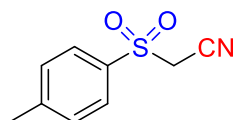
General experimental methods:

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, 32–63µm, 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 35–45°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 photo-induced three-component reaction of aryl iodides 1, sulfur dioxide, and 3-azido-2-methylbut-3-en-2-ol 2

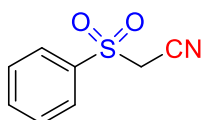


Aryl iodide **1** (0.4mmol) was added to a mixture of 3-azido-2-methylbut-3-en-2-ol **2** (0.2 mmol) and DABCO·(SO₂)₂ (0.6 mmol) in MeCN (4.0 mL) under N₂ atmosphere in a quartz tube. The mixture was then placed around the mercury lamp (purchased from Yuming, Shanghai) with a distance of 10 centimeters, was stirred under UV irradiation (0.67 W cm⁻¹) for 24 hours at room temperature. After the conversion was completed as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:4) to give the corresponding product **3**.



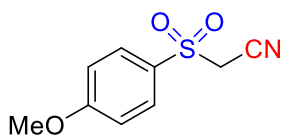
2-Tosylacetone nitrile (**3a**)¹

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.89 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 4.02 (s, 2H), 2.48 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 147.1, 133.9, 130.7, 129.1, 110.7, 46.1, 22.0.



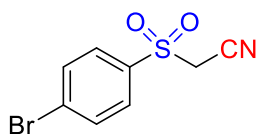
2-(Phenylsulfonyl)acetone nitrile (**3b**)²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.03 (d, *J* = 7.5 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 4.04 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 141.8, 135.7, 130.1, 129.1, 110.5, 46.0.



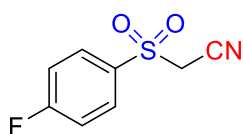
2-((4-Methoxyphenyl)sulfonyl)acetone nitrile (**3c**)²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.93 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 4.02 (s, 2H), 3.89 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 165.3, 131.5, 128.2, 115.2, 110.9, 56.1, 46.2.



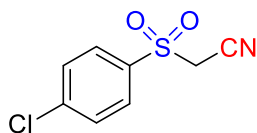
2-((4-Bromophenyl)sulfonyl)acetone nitrile (**3d**)

¹H NMR (400 MHz, DMSO) δ (ppm) 7.99 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 2H); ¹³C NMR (101 MHz, DMSO) δ (ppm) 138.7, 136.4, 132.9, 130.3, 112.1, 44.6.
HRMS (EI) calcd for C₈H₆BrNO₂S: 258.9303, found: 258.9306.



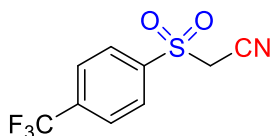
2-((4-Fluorophenyl)sulfonyl)acetonitrile (**3e**)²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.09 – 8.02 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 4.04 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 167.0 (d, *J* = 286 Hz), 132.3 (d, *J* = 10 Hz), 132.0 (d, *J* = 15 Hz), 117.6 (d, *J* = 22 Hz), 110.9, 46.1.



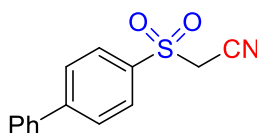
2-((4-Chlorophenyl)sulfonyl)acetonitrile (**3f**)

¹H NMR (400 MHz, DMSO) δ (ppm) 7.99 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 5.30 (s, 2H); ¹³C NMR (101 MHz, DMSO) δ (ppm) 140.4, 136.0, 130.3, 129.9, 112.1, 44.7. HRMS (EI) calcd for C₈H₆ClNO₂S: 214.9808, found: 214.9824.



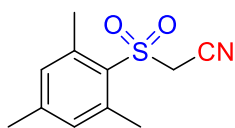
2-((4-(Trifluoromethyl)phenyl)sulfonyl)acetonitrile (**3g**)²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.18 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 4.10 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 140.2, 137.5, 129.92, 127.3 (d, *J* = 3 Hz), 123.6 (q, *J* = 158 Hz), 110.2, 45.9.



2-([1,1'-Biphenyl]-4-ylsulfonyl)acetonitrile (**3h**)

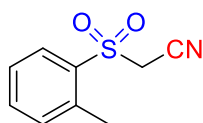
¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.07 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.40 (m, 3H), 4.10 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 148.7, 138.8, 135.2, 129.6, 129.4, 129.3, 128.6, 127.7, 110.7, 46.1. HRMS (EI) calcd for C₁₄H₁₁NO₂S: 257.0510, found: 257.0516.



2-(Mesitylsulfonyl)acetonitrile (**3i**)

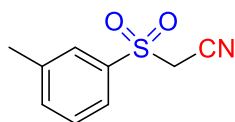
¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.03 (s, 2H), 4.03 (s, 2H), 2.69 (s, 6H), 2.33 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 145.6, 141.2, 133.0, 110.6, 45.5, 23.3, 21.4. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2\text{S}$: 223.0667, found: 223.0681.



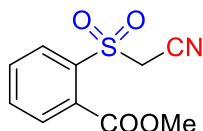
2-(*o*-Tolylsulfonyl)acetonitrile (**3j**)²

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.07 (d, $J = 8.0$ Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 4.07 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 138.9, 135.4, 135.0, 133.4, 131.4, 127.3, 110.1, 45.2, 20.7.



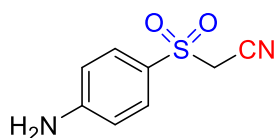
2-(*m*-Tolylsulfonyl)acetonitrile (**3k**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81 (s, 2H), 7.59 – 7.48 (m, 2H), 4.03 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 140.6, 136.8, 136.5, 129.9, 129.2, 126.2, 110.6, 46.0, 21.6. HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{NO}_2\text{S}$: 195.0354, found: 195.0368.



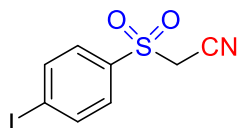
Methyl 2-((cyanomethyl)sulfonyl)benzoate (**3l**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.24 (d, $J = 7.4$ Hz, 1H), 7.85 – 7.69 (m, 3H), 4.69 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 165.2, 135.5, 135.1, 132.9, 132.3, 131.8, 130.6, 110.6, 53.6, 46.1. HRMS (EI) calcd for $\text{C}_{10}\text{H}_9\text{NO}_4\text{S}$: 239.0252, found: 239.0256.



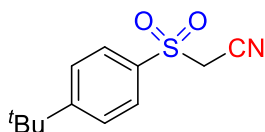
2-((4-Aminophenyl)sulfonyl)acetonitrile (**3m**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.75 (d, $J = 7.9$ Hz, 2H), 6.73 (d, $J = 7.8$ Hz, 2H), 4.37 (s, 2H), 3.97 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 150.3, 136.7, 131.5, 114.4, 109.4, 46.3. HRMS (EI) calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{S}$: 196.0306, found: 196.0312.



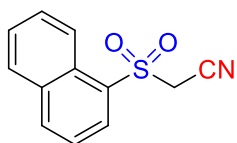
2-((4-Iodophenyl)sulfonyl)acetonitrile (**3n**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.02 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 4.03 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 139.5, 130.3, 126.8, 116.4, 110.4, 46.0. HRMS (EI) calcd for $\text{C}_8\text{H}_6\text{INO}_2\text{S}$: 306.9164, found: 306.9172.



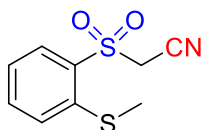
2-((4-(*tert*-Butyl)phenyl)sulfonyl)acetonitrile (**3o**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, $J = 7.7$ Hz, 2H), 7.63 (d, $J = 7.7$ Hz, 2H), 4.02 (s, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 160.0, 133.9, 129.0, 127.1, 110.7, 46.0, 35.7, 31.2. HRMS (EI) calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S}$: 237.0823, found: 237.0832.



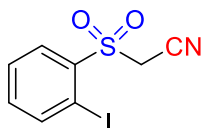
2-(Naphthalen-1-ylsulfonyl)acetonitrile (**3p**)²

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.68 (d, $J = 8.6$ Hz, 1H), 8.43 (d, $J = 7.3$ Hz, 1H), 8.23 (d, $J = 8.1$ Hz, 1H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.76 (t, $J = 7.8$ Hz, 1H), 7.67 (t, $J = 7.8$ Hz, 2H), 4.25 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 137.3, 134.6, 132.9, 131.7, 130.0, 129.9, 128.8, 127.8, 124.7, 123.4, 110.3, 45.5.



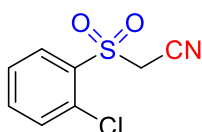
2-((2-(Methylthio)phenyl)sulfonyl)acetonitrile (**3q**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.11 (d, $J = 7.9$ Hz, 1H), 7.65 (t, $J = 7.7$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 4.47 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 142.6, 140.6, 135.5, 132.5, 127.5, 125.6, 110.5, 42.4, 16.5. HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{BrNO}_2\text{S}_2$: 227.0075, found: 227.0084.



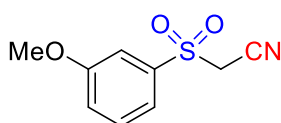
2-((2-Iodophenyl)sulfonyl)acetonitrile (**3r**)¹

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.34 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 4.50 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.4, 139.1, 136.2, 136.0, 133.5, 129.5, 110.0, 42.8.



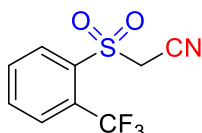
2-((2-Chlorophenyl)sulfonyl)acetonitrile (**3s**)

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.22 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 4.42 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 136.6, 134.4, 133.16, 133.0, 132.6, 128.2, 109.9, 44.1. HRMS (EI) calcd for C₈H₆ClNO₂S: 214.9808, found: 214.9820.



2-((3-Methoxyphenyl)sulfonyl)acetonitrile (**3t**)²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.59 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.48 (s, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 4.04 (s, 2H), 3.88 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 160.4, 137.8, 130.9, 122.1, 120.9, 113.0, 110.4, 55.9, 45.8.



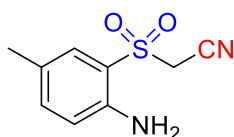
2-((2-(Trifluoromethyl)phenyl)sulfonyl)acetonitrile (**3u**)

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.41 (d, *J* = 7.1 Hz, 1H), 7.93 – 7.84 (m, 1H), 7.89 (p, *J* = 8.1 Hz, 2H), 4.25 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 152.1 (d, *J* = 105Hz), 139.3, 135.8, 134.9, 133.3, 129.2 (d, *J* = 6Hz), 123.1 (q, *J* = 194Hz), 110.1, 46.3. HRMS (EI) calcd for C₉H₆F₃NO₂S: 249.0071, found: 249.0076.



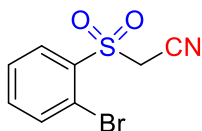
2-((2-Fluorophenyl)sulfonyl)acetonitrile (**3v**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.03 (t, $J = 7.2$ Hz, 1H), 7.81 – 7.73 (m, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 9.1$ Hz, 1H), 4.28 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 138.0 (d, $J = 9\text{Hz}$), 131.6, 125.7, 125.4 (d, $J = 3\text{Hz}$), 122.9, 117.6 (d, $J = 21\text{Hz}$), 110.0, 45.1. HRMS (EI) calcd for $\text{C}_8\text{H}_6\text{FNO}_2\text{S}$: 199.0103, found: 199.0109.



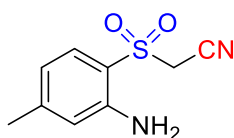
2-((2-Amino-5-methylphenyl)sulfonyl)acetonitrile (**3w**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.56 (s, 1H), 7.26 (s, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 4.88 (s, 2H), 4.14 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 144.7, 138.2, 130.4, 128.5, 127.5, 118.6, 110.5, 43.3, 20.4. HRMS (EI) calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: 210.0463, found: 210.0472.



2-((2-Bromophenyl)sulfonyl)acetonitrile (**3x**)

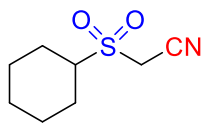
^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.26 (d, $J = 7.0$ Hz, 1H), 7.83 (d, $J = 6.9$ Hz, 1H), 7.64 – 7.56 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 143.9, 136.3, 135.9, 133.3, 128.5, 126.0, 109.7, 43.3. HRMS (EI) calcd for $\text{C}_8\text{H}_6\text{BrNO}_2\text{S}$: 258.9303, found: 258.9324.



2-((2-Amino-4-methylphenyl)sulfonyl)acetonitrile (**3y**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.64 (d, $J = 8.1$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 6.59 (s, 1H), 4.98 (s, 2H), 4.10 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 147.0, 131.1, 126.4, 121.7, 120.1, 118.5, 110.6, 43.6, 22.0. HRMS (EI) calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{S}$:

210.0463, found: 210.0466.



2-(Cyclohexylsulfonyl)acetonitrile (**3z**)¹

¹H NMR (400 MHz, CDCl₃) δ (ppm) 2.20 (d, *J* = 12.3 Hz, 2H), 1.97 (d, *J* = 13.2 Hz, 2H), 1.76 (d, *J* = 12.9 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.42 – 1.29 (m, 2H), 1.27 (d, *J* = 14.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 110.6, 62.5, 39.7, 25.4, 25.0, 22.6.

Reference:

1. J. R. Donald and S. L. Berrell, *Chem. Sci.*, 2019, **10**, 5832.
2. G. C. Tsui, Q. Glenadel, C. Lau and M. Lautens, *Org. Lett.*, 2011, **13**, 208.

