

Electronic supplementary information (ESI) for

Supporting Information

Iron-catalyzed intermolecular azidosulfonylation of alkenes from sulfur dioxide

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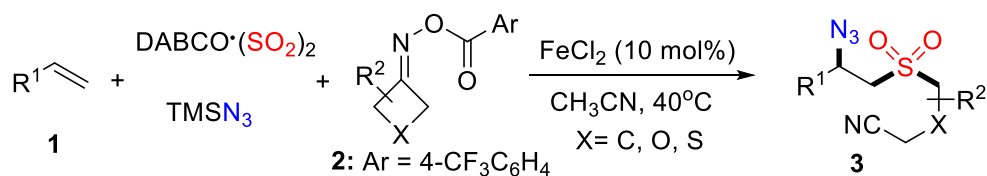
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1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S18).
3. ¹H and ¹³C NMR spectra of compounds **3**, **4**, **5**, **7** and **8** (S19-S97).

General experimental methods:

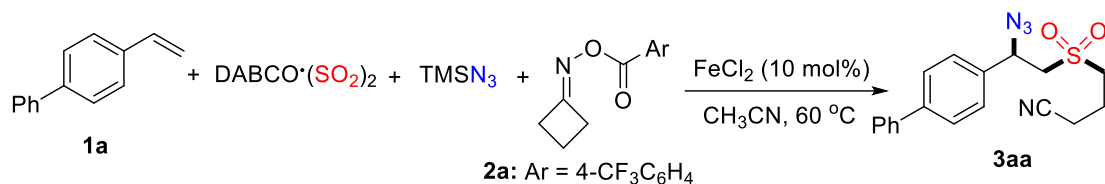
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using 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 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 reaction of alkenes 1, cycloketone oxime esters 2, TMSN₃ and DABCO·(SO₂)₂.



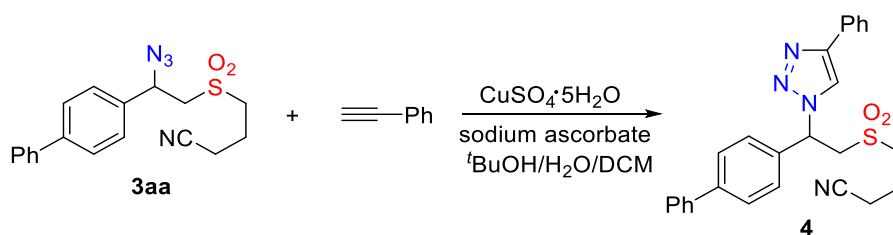
TMSN₃ (0.24 mmol) was added to a mixture of alkenes **1** (0.2 mmol), cycloketone oxime esters **2** (0.24 mmol), DABCO·(SO₂)₂ (0.2 mmol) and FeCl₂ (0.02 mmol, 10 mol%) in CH₃CN under N₂ atmosphere. The resulting mixture was stirred at 40 °C for 12 hours. After completion of reaction as monitored by TLC analysis, ethyl acetate and saturated sodium bicarbonate were added for extraction. Subsequently, the organic layer was washed with brine, and dried over anhydrous sodium sulfate. Finally, the solvent was concentrated under reduced pressure, and the crude product was purified directly by flash column chromatography (n-hexane/ethyl acetate = 4:1 – 1:1) to give the corresponding products **3**.

General experimental procedure for the reaction of 4-vinyl-1,1'-biphenyl 1a, O-(4-(trifluoromethyl)benzoyl) oxime 2a, TMSN₃ and DABCO·(SO₂)₂ on a scaled-up version.

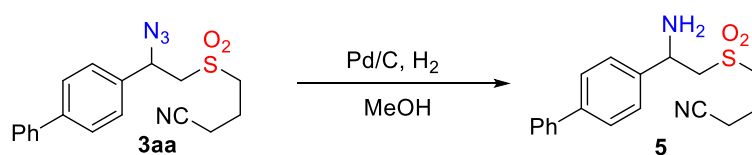


TMSN₃ (3.6 mmol, 414.8 mg) was added to a mixture of 4-vinyl-1,1'-biphenyl **1a** (3 mmol, 540.8 mg), *O*-(4-(trifluoromethyl)benzoyl) oxime **2a** (3.6 mmol, 926.0 mg), DABCO·(SO₂)₂ (3 mmol, 720.9 mg) and FeCl₂ (0.3 mmol, 38.0 mg) in CH₃CN (30 mL) under N₂ atmosphere. The resulting mixture was stirred at 40 °C for 18 hours. After completion of reaction as monitored by TLC analysis, ethyl acetate and saturated sodium bicarbonate were added for extraction. Subsequently, the organic layer was washed with brine, and dried over anhydrous sodium sulfate. Finally, the solvent was concentrated under reduced pressure, and the crude product was purified directly by flash column chromatography to give the corresponding product **3aa** (822.9 mg, 77% yield).

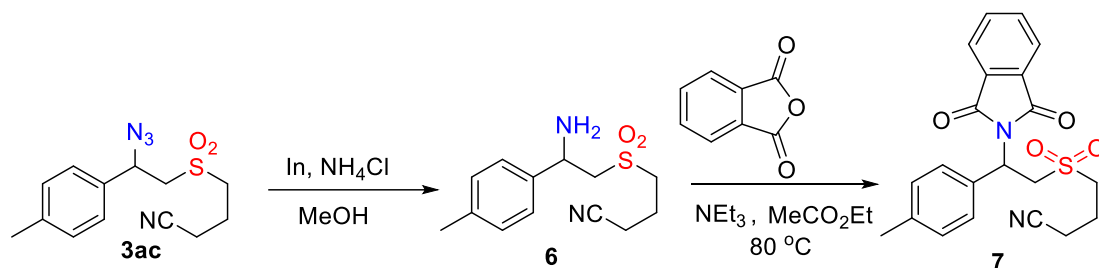
General experimental procedure for further transformation of β-azidosulfones.



4-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)butanenitrile **3aa** (0.2 mmol) and phenylacetylene (0.4 mmol) were suspended in *t*BuOH/H₂O/DCM (2:1:0.2 v/v, 3.2 mL). Then, CuSO₄ (0.04 mmol) and sodium ascorbate (0.08 mmol) were added and the reaction mixture was stirred for 24 hours at room temperature. After completion of reaction as monitored by TLC analysis, water and DCM were added for extraction. The combined organic layer was dried over anhydrous sodium sulfate. Finally, the solvent was concentrated under reduced pressure, and the crude product was purified directly by flash column chromatography to give the corresponding product **4** in 92% yield.¹

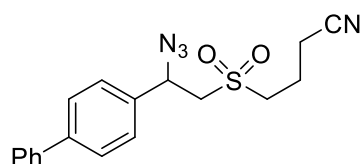


To a flame-dried flask equipped with a magnetic stir bar was added 4-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)butanenitrile **3aa** (0.2 mmol), 10 % Pd on carbon (10 mol%) in MeOH (4 mL). The flask was allowed to stir at room temperature with a H₂ balloon overnight. Then, the reaction mixture was filtered through Celite. Finally, the solvent was concentrated under reduced pressure, and the crude product was purified directly by flash column chromatography to give the corresponding product **5** in 91% yield.²



A sealed tube was charged with 4-((2-azido-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile **3ac** (0.4 mmol), followed by NH₄Cl (0.6 mmol), indium powder (0.6 mmol) and MeOH (2 mL). The resulting solution heated to reflux for 6 hours under N₂ atmosphere. After completion (TLC), the solvent was evaporated and the crude product was purified directly by flash column chromatography to give the corresponding product **6** in 80% yield.²

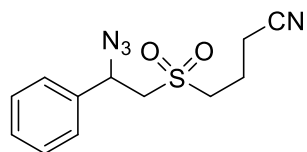
In a sealed tube, 4-((2-amino-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (0.2 mmol) and isobenzofuran-1,3-dione (0.3 mmol) were dissolved in ethyl acetate (5 mL), then triethylamine (0.3 mmol) was added. The mixture was stirred at 80 °C for 24 hours. After that, the solvent was evaporated and the crude product was purified directly by flash column chromatography to give the corresponding product **7** in 78% yield.³



4-((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)butanenitrile (**3aa**)

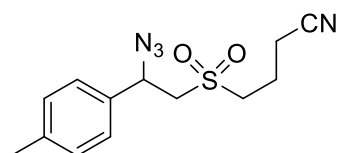
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.66 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.49 – 7.35 (m, *J* = 14.9, 7.2 Hz, 5H), 5.19 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.51 (dd, *J* = 15.1, 10.3 Hz, 1H), 3.41 – 3.31 (m, 1H), 3.25 (dd, *J* = 14.1, 7.1 Hz, 1H), 3.19 (dd, *J* = 15.1, 3.1 Hz, 1H), 2.68 – 2.59 (m, 2H), 2.32 – 2.21 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.5, 139.8, 135.0, 128.9, 128.1, 127.8,

127.3, 127.0, 118.1, 60.3, 59.0, 52.8, 18.2, 16.3. HRMS (ESI) calcd for $C_{18}H_{18}N_4NaO_2S^+$: 377.1043 ($M + Na^+$), found: 377.1054.



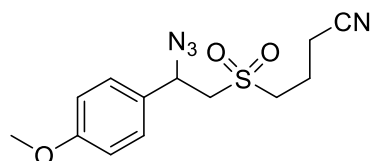
4-((2-Azido-2-phenylethyl)sulfonyl)butanenitrile (**3ab**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 – 7.39 (m, 3H), 7.38 – 7.34 (m, 2H), 5.14 (dd, $J = 10.2, 3.3$ Hz, 1H), 3.49 (dd, $J = 15.1, 10.2$ Hz, 1H), 3.32 (dt, $J = 14.6, 7.4$ Hz, 1H), 3.22 (dd, $J = 14.2, 7.1$ Hz, 1H), 3.16 (dd, $J = 14.9, 3.4$ Hz, 1H), 2.71 – 2.55 (m, 2H), 2.25 (p, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 136.1, 129.6, 129.5, 126.8, 118.1, 60.5, 59.0, 52.7, 18.1, 16.3. HRMS (ESI) calcd for $C_{12}H_{14}N_4NaO_2S^+$: 301.0730 ($M + Na^+$), found: 301.0735.



4-((2-Azido-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (**3ac**)

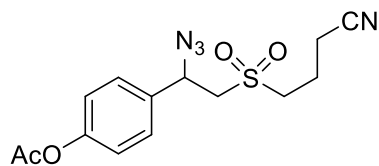
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 – 7.22 (m, 4H), 5.10 (dd, $J = 10.2, 3.4$ Hz, 1H), 3.48 (dd, $J = 15.1, 10.2$ Hz, 1H), 3.35 – 3.27 (m, 1H), 3.24 – 3.11 (m, 2H), 2.69 – 2.55 (m, 2H), 2.37 (s, 3H), 2.29 – 2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.6, 133.0, 130.1, 126.7, 118.1, 60.3, 58.9, 52.7, 21.1, 18.1, 16.3. HRMS (ESI) calcd for $C_{13}H_{16}N_4NaO_2S^+$: 315.0886 ($M + Na^+$), found: 315.0896.



4-((2-Azido-2-(4-methoxyphenyl)ethyl)sulfonyl)butanenitrile (**3ad**)

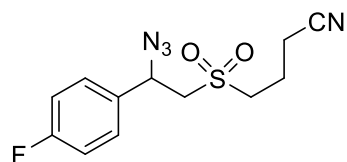
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31 – 7.26 (m, 2H), 6.98 – 6.93 (m, 2H), 5.09 (dd, $J = 10.0, 3.5$ Hz, 1H), 3.83 (s, 3H), 3.48 (dd, $J = 15.0, 10.0$ Hz, 1H), 3.34 – 3.25 (m, 1H), 3.23 – 3.11 (m, 2H), 2.70 – 2.54 (m, 2H), 2.29 – 2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.3, 128.2,

128.0, 118.1, 114.7, 60.0, 58.9, 55.3, 52.6, 18.1, 16.2. HRMS (ESI) calcd for $C_{13}H_{16}N_4NaO_3S^+$: 331.0835 (M + Na⁺), found: 331.0839.



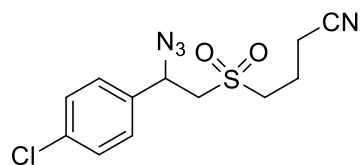
4-(1-Azido-2-((3-cyanopropyl)sulfonyl)ethyl)phenyl acetate (**3ae**)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.41 – 7.36 (m, 2H), 7.22 – 7.13 (m, 2H), 5.15 (dd, *J* = 10.2, 3.3 Hz, 1H), 3.45 (dd, *J* = 15.1, 10.2 Hz, 1H), 3.35 – 3.25 (m, 1H), 3.22 – 3.11 (m, 2H), 2.69 – 2.54 (m, 2H), 2.31 (s, 3H), 2.27 – 2.18 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 169.1, 151.3, 133.8, 128.0, 122.7, 118.1, 60.0, 58.9, 52.8, 21.0, 18.1, 16.2. HRMS (ESI) calcd for $C_{14}H_{16}N_4NaO_4S^+$: 359.3784 (M + Na⁺), found: 359.3793.



4-((2-Azido-2-(4-fluorophenyl)ethyl)sulfonyl)butanenitrile (**3af**)

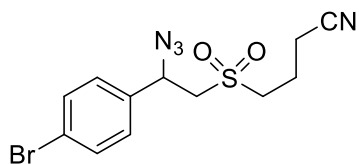
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.40 – 7.33 (m, 2H), 7.18 – 7.11 (m, 2H), 5.15 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.47 (dd, *J* = 15.0, 10.3 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.29 – 3.20 (m, 1H), 3.14 (dd, *J* = 15.0, 3.2 Hz, 1H), 2.72 – 2.57 (m, 2H), 2.31 – 2.22 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -111.98 - -111.07 (m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.0 (d, ¹*J*_{CF} = 249.4 Hz), 161.8, 132.1, 132.1, 128.7 (d, ³*J*_{CF} = 8.5 Hz), 118.1, 116.5 (d, ²*J*_{CF} = 21.9 Hz), 59.8, 58.9, 52.8, 18.1, 16.3. HRMS (ESI) calcd for $C_{12}H_{13}FN_4NaO_2S^+$: 319.0635 (M + Na⁺), found: 319.0646.



4-((2-Azido-2-(4-chlorophenyl)ethyl)sulfonyl)butanenitrile (**3ag**)

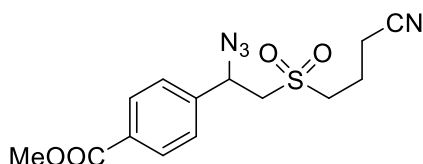
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46 – 7.41 (m, 2H), 7.34 – 7.29 (m, 2H), 5.14 (dd, *J* = 10.4, 3.1 Hz, 1H), 3.46 (dd, *J* = 15.0, 10.4 Hz, 1H), 3.41 – 3.33 (m, 1H), 3.30 – 3.21 (m, 1H), 3.12 (dd, *J* = 15.0, 3.1 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.31 – 2.21 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ

(ppm) 135.5, 134.7, 129.7, 128.2, 118.1, 59.9, 58.8, 52.8, 18.1, 16.3. HRMS (ESI) calcd for $C_{12}H_{13}ClN_4NaO_2S^+$: 335.0340 ($M + Na^+$), found: 335.0340.



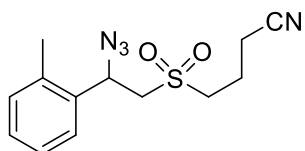
4-((2-Azido-2-(4-bromophenyl)ethyl)sulfonyl)butanenitrile (**3ah**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 – 7.57 (m, 2H), 7.27 – 7.23 (m, 2H), 5.13 (dd, $J = 10.3, 3.1$ Hz, 1H), 3.45 (dd, $J = 15.0, 10.4$ Hz, 1H), 3.40 – 3.32 (m, 1H), 3.29 – 3.21 (m, 1H), 3.12 (dd, $J = 15.1, 3.1$ Hz, 1H), 2.71 – 2.58 (m, 2H), 2.31–2.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.4, 132.8, 128.5, 123.7, 118.2, 60.1, 58.9, 52.9, 18.2, 16.4. HRMS (ESI) calcd for $C_{12}H_{13}BrN_4NaO_2S^+$: 378.9835 ($M + Na^+$), found: 378.9869.



Methyl 4-(1-azido-2-((3-cyanopropyl)sulfonyl)ethyl)benzoate (**3ai**)

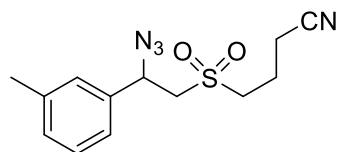
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 5.22 (dd, $J = 10.4, 3.0$ Hz, 1H), 3.94 (s, 3H), 3.49 (dd, $J = 15.0, 10.4$ Hz, 1H), 3.42 – 3.34 (m, 1H), 3.32 – 3.23 (m, 1H), 3.16 (dd, $J = 15.1, 3.0$ Hz, 1H), 2.73 – 2.59 (m, 2H), 2.33 – 2.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.1, 141.0, 131.3, 130.7, 126.9, 118.1, 60.2, 58.8, 52.9, 52.3, 18.2, 16.3. HRMS (ESI) calcd for $C_{14}H_{16}N_4NaO_4S^+$: 359.0784 ($M + Na^+$), found: 359.0785.



4-((2-Azido-2-(*o*-tolyl)ethyl)sulfonyl)butanenitrile (**3aj**)

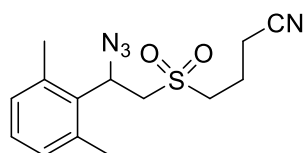
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 – 7.33 (m, 1H), 7.32 – 7.23 (m, 3H), 5.41 (dd, $J = 10.1, 3.0$ Hz, 1H), 3.46 (dd, $J = 15.2, 10.1$ Hz, 1H), 3.37 – 3.28 (m, 1H), 3.27 – 3.19 (m, 1H), 3.09 (dd, $J = 15.2, 3.0$ Hz, 1H), 2.70 – 2.56 (m, 2H), 2.30 – 2.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

(ppm) 135.4, 134.3, 131.4, 129.1, 127.0, 126.3, 118.1, 58.2, 57.0, 52.6, 19.1, 18.1, 16.2. HRMS (ESI) calcd for $C_{13}H_{16}N_4NaO_2S^+$: 315.0886 ($M + Na^+$), found: 315.0895.



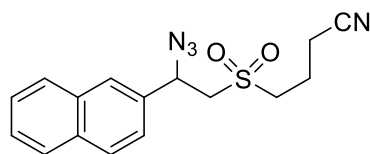
4-((2-Azido-2-(*m*-tolyl)ethyl)sulfonyl)butanenitrile (**3ak**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 – 7.31 (m, 1H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.19 – 7.14 (m, 2H), 5.11 (dd, $J = 10.2, 3.3$ Hz, 1H), 3.49 (dd, $J = 15.1, 10.3$ Hz, 1H), 3.37 – 3.28 (m, 1H), 3.27 – 3.13 (m, 2H), 2.71 – 2.57 (m, 2H), 2.40 (s, 3H), 2.30 – 2.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.3, 136.0, 130.2, 129.2, 127.4, 123.8, 118.1, 60.5, 58.9, 52.7, 21.3, 18.1, 16.2. HRMS (ESI) calcd for $C_{13}H_{16}N_4NaO_2S^+$: 315.0886 ($M + Na^+$), found: 315.0887.



4-((2-Azido-2-(2,6-dimethylphenyl)ethyl)sulfonyl)butanenitrile (**3al**)

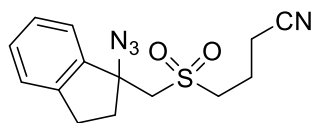
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 – 7.08 (m, 3H), 5.38 (dd, $J = 10.1, 3.0$ Hz, 1H), 3.51 – 3.43 (m, 1H), 3.38 – 3.20 (m, 2H), 3.14 – 3.05 (m, 1H), 2.68 – 2.58 (m, 2H), 2.39 (s, 3H), 2.36 (s, 3H), 2.32 – 2.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 136.6, 134.1, 132.1, 131.3, 129.9, 126.8, 118.1, 58.2, 57.0, 52.6, 20.9, 18.6, 18.2, 16.2. HRMS (ESI) calcd for $C_{14}H_{18}N_4NaO_2S^+$: 329.1043 ($M + Na^+$), found: 329.1043.



4-((2-Azido-2-(naphthalen-2-yl)ethyl)sulfonyl)butanenitrile (**3am**)

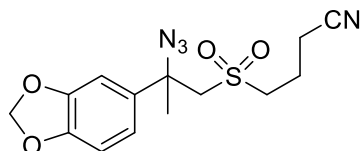
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, $J = 8.6$ Hz, 1H), 7.89 – 7.82 (m, 3H), 7.58 – 7.51 (m, 2H), 7.42 (dd, $J = 8.5, 1.8$ Hz, 1H), 5.31 (dd, $J = 10.3, 3.1$ Hz, 1H), 3.57 (dd, $J = 15.1, 10.3$ Hz, 1H), 3.40 – 3.31 (m, 1H), 3.30 – 3.19 (m, 2H), 2.68 – 2.53 (m, 2H), 2.30 – 2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.4, 133.4, 133.0, 129.7, 128.1, 127.8, 127.1, 127.0, 126.6, 123.4,

118.1, 60.7, 58.9, 52.8, 18.2, 16.3. HRMS (ESI) calcd for $C_{16}H_{16}N_4NaO_2S^+$: 351.0886 ($M + Na^+$), found: 351.0886.



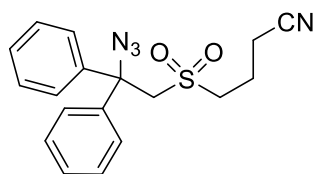
4-(((1-Azido-2,3-dihydro-1H-inden-1-yl)methyl)sulfonyl)butanenitrile (**3an**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 – 7.31 (m, 4H), 3.69 (d, $J = 15.1$ Hz, 1H), 3.49 – 3.29 (m, 2H), 3.17 (d, $J = 15.1$ Hz, 1H), 3.15 – 3.07 (m, 1H), 3.04 – 2.86 (m, 2H), 2.72 – 2.53 (m, 3H), 2.28 (p, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.1, 140.8, 130.0, 127.4, 125.6, 122.8, 118.2, 71.5, 60.51, 53.4, 36.5, 30.0, 18.2, 16.3. HRMS (ESI) calcd for $C_{14}H_{16}N_4NaO_2S^+$: 327.0886 ($M + Na^+$), found: 327.0898.



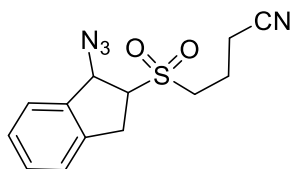
4-((2-Azido-2-(benzo[d][1,3]dioxol-5-yl)propyl)sulfonyl)butanenitrile (**3ao**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.97 – 6.92 (m, 2H), 6.84 (dd, $J = 7.8, 0.7$ Hz, 1H), 6.01 (s, 2H), 3.38 (d, $J = 15.2$ Hz, 1H), 3.26 (d, $J = 15.2$ Hz, 1H), 3.13 – 3.04 (m, 1H), 3.01 – 2.92 (m, 1H), 2.60 – 2.52 (m, 2H), 2.20 – 2.12 (m, 2H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.5, 147.9, 135.0, 119.3, 118.3, 108.5, 106.4, 101.7, 64.0, 63.8, 53.0, 23.6, 18.2, 16.3. HRMS (ESI) calcd for $C_{14}H_{16}N_4NaO_4S^+$: 359.0784 ($M + Na^+$), found: 359.0791.



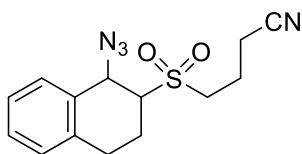
4-((2-Azido-2,2-diphenylethyl)sulfonyl)butanenitrile (**3ap**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 – 7.33 (m, 10H), 4.11 (s, 2H), 2.68 (t, $J = 7.3$ Hz, 2H), 2.42 (t, $J = 7.0$ Hz, 2H), 2.07 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.2, 128.9, 128.8, 127.1, 118.2, 69.4, 62.6, 52.9, 18.1, 16.3. HRMS (ESI) calcd for $C_{18}H_{18}N_4NaO_2S^+$: 377.1043 ($M + Na^+$), found: 377.1052.



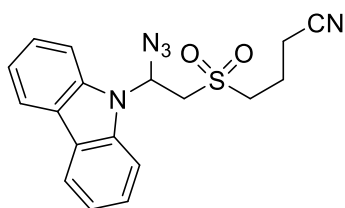
4-((1-Azido-2,3-dihydro-1*H*-inden-2-yl)sulfonyl)butanenitrile (**3aq**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.44 – 7.27 (m, 4H), 5.37 (d, $J = 6.6$ Hz, 1H), 3.84 (td, $J = 8.6$, 6.7 Hz, 1H), 3.43 (d, $J = 9.0$ Hz, 2H), 3.28 – 3.16 (m, 2H), 2.65 (t, $J = 7.1$ Hz, 2H), 2.29 (p, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 138.4, 137.6, 129.8, 128.1, 125.0, 124.4, 118.1, 67.4, 65.4, 50.2, 30.9, 17.8, 16.3. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}_4\text{NaO}_2\text{S}^+$: 313.0730 ($\text{M} + \text{Na}^+$), found: 313.0735.



4-((1-Azido-1,2,3,4-tetrahydronaphthalen-2-yl)sulfonyl)butanenitrile (**3ar**)

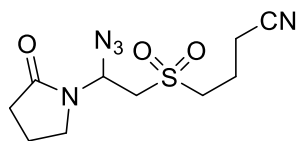
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.43 – 7.39 (m, 1H), 7.34 – 7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 5.01 (d, $J = 7.7$ Hz, 1H), 3.42 – 3.22 (m, 3H), 3.03 – 2.84 (m, 2H), 2.72 – 2.58 (m, 2H), 2.57 – 2.48 (m, 1H), 2.34 – 2.24 (m, 2H), 2.07 – 1.96 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 136.3, 131.7, 128.9, 128.7, 128.2, 127.2, 118.1, 63.4, 59.1, 51.3, 27.3, 20.6, 18.0, 16.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}^+$: 327.0886 ($\text{M} + \text{Na}^+$), found: 327.0887.



4-((2-Azido-2-(9*H*-carbazol-9-yl)ethyl)sulfonyl)butanenitrile (**3as**)

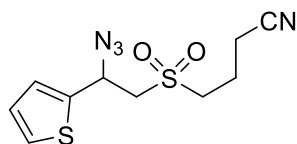
^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.13 (d, $J = 7.7$ Hz, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.57 – 7.51 (m, 2H), 7.40 – 7.34 (m, 2H), 6.83 (t, $J = 6.5$ Hz, 1H), 3.83 (dd, $J = 15.1$, 6.8 Hz, 1H), 3.67 (dd, $J = 15.1$, 6.1 Hz, 1H), 2.84 – 2.66 (m, 2H), 2.37 – 2.20 (m, 2H), 2.08 – 1.95 (m, 1H), 1.95 – 1.82 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 138.4, 126.8, 124.1, 121.4, 121.0, 117.9, 110.2,

66.9, 55.2, 52.0, 18.1, 16.1. HRMS (ESI) calcd for $C_{18}H_{17}N_5NaO_2S^+$: 390.0995 ($M + Na^+$), found: 390.0994.



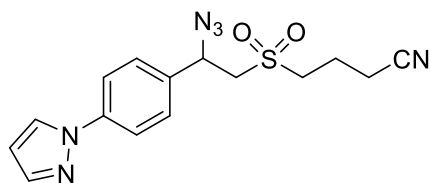
4-((2-Azido-2-(2-oxopyrrolidin-1-yl)ethyl)sulfonyl)butanenitrile (**3at**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.20 – 6.15 (m, 1H), 3.56 – 3.41 (m, 3H), 3.38 – 3.22 (m, 3H), 2.73 – 2.57 (m, 2H), 2.52 – 2.46 (m, 2H), 2.25 (p, $J = 7.2$ Hz, 2H), 2.14 (p, $J = 7.7$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.9, 118.2, 63.4, 54.4, 52.0, 42.7, 30.6, 18.1, 17.9, 16.2. HRMS (ESI) calcd for $C_{10}H_{15}N_5NaO_3S^+$: 308.0788 ($M + Na^+$), found: 308.0797.



4-((2-Azido-2-(thiophen-2-yl)ethyl)sulfonyl)butanenitrile (**3au**)

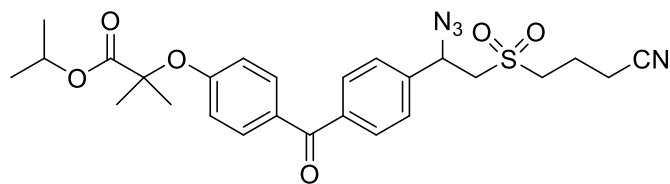
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.16 – 7.13 (m, 1H), 7.06 (dd, $J = 5.1, 3.6$ Hz, 1H), 5.44 (dd, $J = 10.0, 3.6$ Hz, 1H), 3.54 (dd, $J = 15.0, 10.0$ Hz, 1H), 3.37 – 3.26 (m, 2H), 3.25 – 3.16 (m, 1H), 2.70 – 2.56 (m, 2H), 2.30 – 2.21 (p, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.5, 127.3, 127.1, 118.0, 59.3, 56.2, 52.8, 18.2, 16.4. HRMS (ESI) calcd for $C_{10}H_{12}N_4NaO_2S_2^+$: 307.0294 ($M + Na^+$), found: 307.0299.



4-((2-(4-(1H-pyrazol-1-yl)phenyl)-2-azidoethyl)sulfonyl)butanenitrile (**3av**)

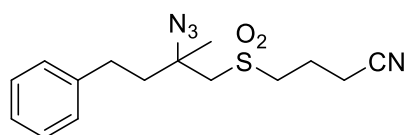
1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, $J = 2.3$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 2H), 7.75 (d, $J = 1.2$ Hz, 1H), 7.46 (d, $J = 8.5$ Hz, 2H), 6.57 – 6.47 (m, 1H), 5.20 (dd, $J = 10.2, 3.1$ Hz, 1H), 3.49 (dd, $J = 15.0, 10.3$ Hz, 1H), 3.42 – 3.33 (m, 1H), 3.30 – 3.13 (m, 2H), 2.76 – 2.59 (m, 2H), 2.33 – 2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.7, 141.0, 134.1, 128.1, 126.7, 119.9,

118.0, 108.2, 60.1, 59.1, 52.9, 18.2, 16.4. HRMS (ESI) calcd for $C_{15}H_{16}N_6NaO_2S^+$: 367.0948 (M + Na⁺), found: 367.0954.



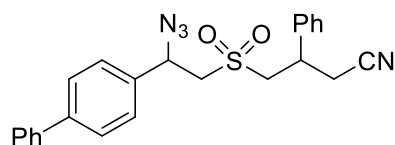
Isopropyl 2-(4-(4-(1-azido-2-((3-cyanopropyl)sulfonyl)ethyl)benzoyl)phenoxy)-2-methylpropanoate (**3aw**)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.82 (d, *J* = 7.9 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 6.92 – 6.85 (m, 2H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.15 – 5.03 (m, 1H), 3.57 – 3.15 (m, 4H), 2.67 (t, *J* = 6.7 Hz, 2H), 2.36 – 2.24 (m, 2H), 1.67 (s, 6H), 1.21 (d, *J* = 6.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 194.4, 173.1, 159.9, 140.0, 139.3, 132.1, 130.8, 130.0, 126.8, 118.2, 117.3, 79.5, 69.4, 60.4, 58.9, 53.0, 25.4, 21.5, 18.2, 16.4. HRMS (ESI) calcd for $C_{26}H_{30}N_4NaO_6S^+$: 549.1778 (M + Na⁺), found: 549.1777.



4-((2-Azido-2-methyl-4-phenylbutyl)sulfonyl)butanenitrile (**3ax**)

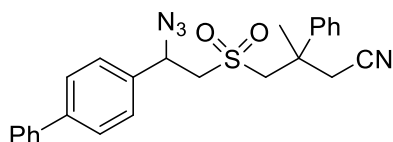
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.37 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 3.40 – 3.12 (m, 4H), 2.83 – 2.63 (m, 4H), 2.28 (p, *J* = 7.2 Hz, 2H), 2.22 – 2.02 (m, 2H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 140.3, 128.7, 128.3, 126.4, 118.1, 61.6, 60.6, 53.5, 42.1, 30.4, 23.4, 18.2, 16.4. HRMS (ESI) calcd for $C_{15}H_{20}N_4NaO_2S^+$: 343.1199 (M + Na⁺), found: 343.1198.



4-((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-3-phenylbutanenitrile (**3ba**)

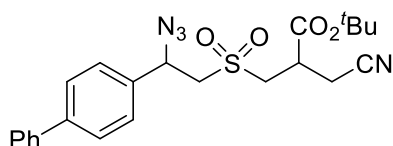
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.70 – 7.57 (m, 4H), 7.53 – 7.38 (m, 8H), 7.33 – 7.24 (m, 2H), 5.22 – 5.08 (m, 1H), 3.86 – 3.64 (m, 2H), 3.60 – 3.14 (m, 2H), 3.07 – 2.91 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.4, 142.3, 139.8, 138.9, 138.5, 134.9, 134.8, 129.4, 129.3, 128.8,

128.6, 128.4, 128.0, 127.9, 127.8, 127.8, 127.5, 127.3, 127.2, 127.0, 127.0, 117.3, 60.4, 60.1, 59.9, 58.9, 58.6, 57.9, 36.6, 35.6, 24.4, 24.4. HRMS (ESI) calcd for $C_{24}H_{22}N_4NaO_2S^+$: 453.1356 ($M + Na^+$), found: 453.1352.



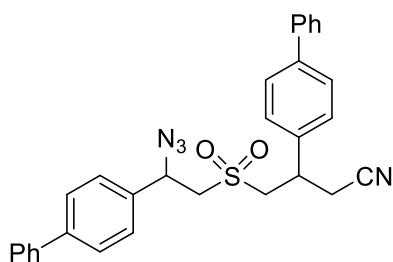
4-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-3-methyl-3-phenylbutanenitrile (**3ca**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 – 7.59 (m, 4H), 7.53 – 7.36 (m, 8H), 7.32 (d, $J = 8.3$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 1H), 5.17 – 5.03 (m, 1H), 3.83 – 3.67 (m, 1H), 3.62 – 3.54 (m, 1H), 3.37 – 3.27 (m, 1H), 3.26 – 3.15 (m, 1H), 3.06 – 2.82 (m, 1H), 2.75 – 2.66 (m, 1H), 1.88 (s, 1H), 1.90 – 1.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.2, 141.3, 140.7, 139.8, 135.0, 134.9, 129.1, 128.8, 128.0, 127.9, 127.8, 127.8, 127.2, 127.0, 126.0, 125.8, 117.5, 117.2, 64.0, 63.7, 60.3, 60.2, 60.1, 59.5, 40.0, 39.9, 29.6, 28.2, 27.1, 25.5. HRMS (ESI) calcd for $C_{25}H_{24}N_4NaO_2S^+$: 467.1512 ($M + Na^+$), found: 467.1507.



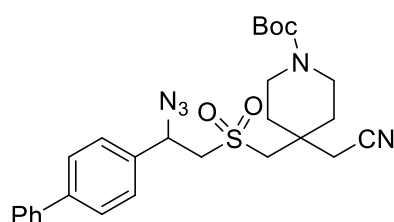
tert-Butyl 3-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-2-(cyanomethyl)propanoate (**3da**)

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (d, $J = 7.7$ Hz, 2H), 7.60 – 7.56 (m, 2H), 7.47 – 7.34 (m, 5H), 5.20 (dd, $J = 10.3, 3.2$ Hz, 1H), 3.90 – 3.71 (m, 1H), 3.66 – 3.20 (m, 4H), 2.94 (dd, $J = 5.4, 4.3$ Hz, 2H), 1.53 – 1.48 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.4, 168.3, 142.4, 142.4, 139.8, 135.0, 128.8, 128.1, 128.0, 127.8, 127.3, 127.0, 116.6, 83.8, 60.3, 60.2, 59.9, 59.7, 54.2, 54.0, 36.6, 36.5, 27.7, 19.7, 19.6. HRMS (ESI) calcd for $C_{23}H_{26}N_4NaO_4S^+$: 477.1567 ($M + Na^+$), found: 477.1566.



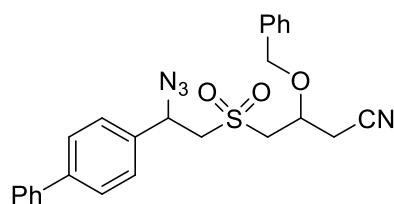
3-([1,1'-Biphenyl]-4-yl)-4-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)butanenitrile (**3ea**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.72 – 7.68 (d, $J = 8.3$ Hz, 1H), 7.66– 7.57 (m, 5H), 7.56 – 7.35 (m, 11 H), 7.22 (d, $J = 8.3$ Hz, 1H), 5.24 – 5.07 (m, 1H), 3.89 – 3.63 (m, 2H), 3.63 – 3.49 (m, 1H), 3.46 – 3.37 (m, 0.5H), 3.22 – 3.14 (m, 0.5H), 3.12 – 2.90 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 142.5, 142.3, 141.6, 141.4, 140.0, 139.9, 139.8, 137.8, 137.3, 134.9, 134.8, 128.9, 128.8, 128.1, 128.0, 128.0, 127.8, 127.8, 127.6, 127.5, 127.4, 127.2, 127.0, 117.3, 117.2, 60.4, 60.1, 59.9, 59.0, 58.8, 57.9, 36.5, 35.4, 24.4, 24.4. HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{26}\text{N}_4\text{NaO}_2\text{S}^+$: 529.1669 (M + Na^+), found: 529.1671.



tert-Butyl 4-(((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)methyl)-4-(cyanomethyl)piperidine-1-carboxylate (**3fa**)

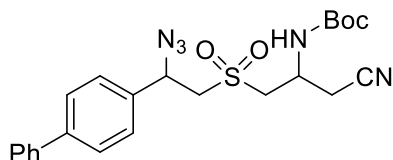
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.66 (d, $J = 8.3$ Hz, 2H), 7.60 – 7.56 (m, 2H), 7.49 – 7.35 (m, 5H), 5.20 (dd, $J = 10.2, 3.4$ Hz, 1H), 3.68 – 3.58 (m, 3H), 3.56 – 3.49 (m, 1H), 3.38 – 3.23 (m, 2H), 3.21 – 3.11 (m, 2H), 3.05 – 2.84 (m, 2H), 2.01 – 1.85 (m, 2H), 1.77 – 1.59 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 154.5, 142.6, 139.9, 135.1, 129.0, 128.2, 127.9, 127.4, 127.1, 117.1, 80.2, 61.8, 60.6, 57.6, 36.1, 34.7, 34.5, 28.4, 26.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{33}\text{N}_5\text{NaO}_4\text{S}^+$: 546.2145 (M + Na^+), found: 546.2142.



4-((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-3-(benzyloxy)butanenitrile (**3ga**)

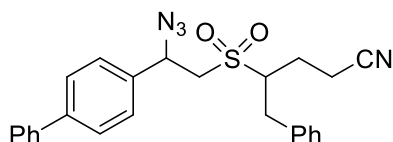
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.61 – 7.53 (m, 4H), 7.49 – 7.43 (m, 2H), 7.41 – 7.33 (m, 6H), 7.27 – 7.22 (m, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 5.16 – 5.04 (m, 1H), 4.82 – 4.55 (m, 2H), 4.45 – 4.32 (m, 1H), 3.96 – 3.40 (m, 2H), 3.36 – 3.04 (m, 2H), 2.87 – 2.65 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 142.4, 142.4, 140.1, 136.1, 135.1, 135.0, 129.0, 128.8, 128.6, 128.5,

128.4, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 116.2, 115.9, 73.0, 70.7, 70.0, 60.4, 60.0, 59.9, 58.4, 57.8, 22.9, 22.8. HRMS (ESI) calcd for $C_{25}H_{24}N_4NaO_3S^+$: 483.1461 ($M + Na^+$), found: 483.1461.



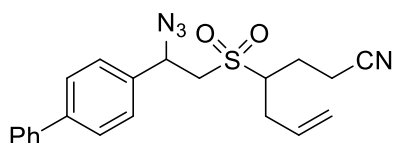
tert-Butyl (1-((2-([1,1'-biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-3-cyanopropan-2-yl)carbamate
(3ha)

1H NMR (400 MHz, $DMSO-d_6$): δ (ppm) 7.74 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 7.4$ Hz, 2H), 7.58 (d, $J = 7.9$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 1H), 5.37 – 5.26 (m, 1H), 4.40 – 4.26 (m, 1H), 4.01 – 3.88 (m, 1H), 3.72 – 3.49 (m, 2H), 3.45 – 3.37 (m, 1H), 2.95 – 2.74 (m, 2H), 1.44 - 1.35 (m, 9H). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ (ppm) 155.2, 155.1, 141.2, 139.9, 136.9, 136.8, 129.5, 128.4, 128.4, 128.2, 127.6, 127.2, 118.3, 79.2, 79.2, 59.2, 57.5, 57.4, 57.2, 57.04, 43.4, 28.5, 23.7, 23.7. HRMS (ESI) calcd for $C_{23}H_{27}N_5NaO_4S^+$: 492.1676 ($M + Na^+$), found: 492.1661.



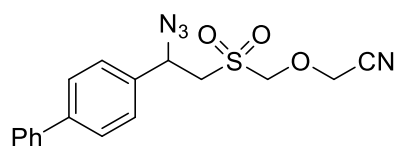
4-((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)-5-phenylpentanenitrile **(3ia)**

1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 – 7.69 (m, 1H), 7.67 – 7.60 (m, 3H), 7.53 – 7.29 (m, 9H), 7.12 (d, $J = 6.3$ Hz, 1H), 5.28 – 5.15 (m, 1H), 4.01 – 3.91 (m, 0.5H), 3.50 – 3.19 (m, 3H), 3.00 – 2.71 (m, 2H), 2.64 – 2.51 (m, 1H), 2.48 – 2.22 (m, 1.5H), 2.14 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.6, 142.5, 140.0, 139.9, 135.9, 135.5, 135.4, 135.1, 129.4, 129.3, 129.3, 129.0, 129.0, 128.3, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 127.3, 127.2, 127.2, 118.7, 118.6, 62.9, 62.6, 60.7, 60.0, 57.4, 57.3, 35.8, 34.1, 23.4, 23.1, 15.7, 15.3. HRMS (ESI) calcd for $C_{25}H_{24}N_4NaO_2S^+$: 467.1512 ($M + Na^+$), found: 467.1504.



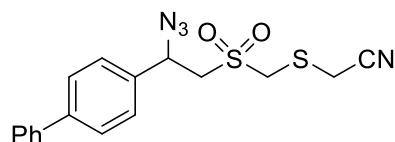
4-((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)hept-6-enenitrile (**3ja**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.69 – 7.63 (m, 2H), 7.60 – 7.56 (m, 2H), 7.48 – 7.34 (m, 5H), 5.91 – 5.62 (m, 1H), 5.33 – 5.15 (m, 3H), 3.70 – 3.48 (m, 1.5H), 3.30 – 3.21 (m, 0.5H), 3.18 – 3.04 (m, 1H), 2.88 – 2.50 (m, 3H), 2.49 – 2.20 (m, 2H), 2.18 – 2.01 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 142.6, 142.5, 140.0, 140.0, 135.4, 135.3, 132.3, 132.2, 129.0, 128.2, 128.2, 127.9, 127.5, 127.3, 127.2, 120.2, 120.1, 118.7, 118.6, 60.7, 60.7, 60.5, 60.0, 57.1, 33.5, 31.7, 23.3, 22.6, 15.6, 15.0. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{22}\text{N}_4\text{NaO}_2\text{S}^+$: 417.1356 ($\text{M} + \text{Na}^+$), found: 417.1363.



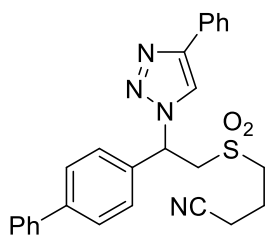
2-(((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)methoxy)acetonitrile (**3ka**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.68 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.5$ Hz, 2H), 7.51 – 7.38 (m, 5H), 5.17 (dd, $J = 10.4, 2.9$ Hz, 1H), 4.99 (d, $J = 12.9$ Hz, 1H), 4.71 (s, 2H), 4.42 (d, $J = 12.9$ Hz, 1H), 3.70 (dd, $J = 15.1, 10.5$ Hz, 1H), 3.18 (d, $J = 15.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 142.5, 139.8, 134.7, 128.9, 128.1, 127.8, 127.3, 127.0, 114.5, 83.1, 60.0, 57.3, 55.2. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{NaO}_3\text{S}^+$: 379.0835 ($\text{M} + \text{Na}^+$), found: 379.0835.



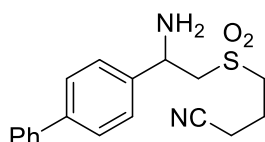
2-(((2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)sulfonyl)methylthio)acetonitrile (**3la**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.69 – 7.65 (m, 2H), 7.61 – 7.57 (m, 2H), 7.49 – 7.36 (m, 5H), 5.18 (dd, $J = 10.5, 3.3$ Hz, 1H), 4.28 (d, $J = 15.2$ Hz, 1H), 4.13 (dd, $J = 15.2, 1.2$ Hz, 1H), 3.95 – 3.82 (m, 2H), 3.62 (d, $J = 17.0$ Hz, 1H), 3.28 – 2.18 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 142.8, 139.9, 134.7, 129.0, 128.3, 128.0, 127.4, 127.2, 115.3, 60.5, 55.6, 53.0, 17.8. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}_2^+$: 395.0607 ($\text{M} + \text{Na}^+$), found: 395.0603.



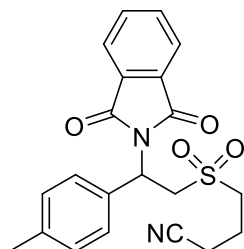
4-((2-((1,1'-Biphenyl)-4-yl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)sulfonyl)butanenitrile (**4**)

^1H NMR (400 MHz, $\text{DMSO-}d^6$): δ (ppm) 8.92 (s, 1H), 7.85 (d, $J = 7.3$ Hz, 2H), 7.76 – 7.63 (m, 6H), 7.46 (t, $J = 7.7$ Hz, 4H), 7.40 – 7.32 (m, 2H), 6.50 (dd, $J = 9.6, 4.3$ Hz, 1H), 4.76 (dd, $J = 14.8, 9.7$ Hz, 1H), 4.37 (dd, $J = 14.8, 4.4$ Hz, 1H), 3.28 – 3.18 (m, 2H), 2.65 (t, $J = 7.2$ Hz, 2H), 2.12 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $\text{DMSO-}d^6$): δ (ppm) 147.1, 141.2, 139.8, 137.3, 131.0, 129.4, 128.5, 128.3, 128.2, 127.7, 127.3, 125.6, 121.5, 120.1, 58.2, 55.4, 52.2, 18.4, 15.8. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_2\text{S}^+$: 351.1138 ($\text{M} + \text{Na}^+$), found: 351.1135. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{NaO}_2\text{S}^+$: 479.1512 ($\text{M} + \text{Na}^+$), found: 479.1510.



4-((2-((1,1'-Biphenyl)-4-yl)-2-aminoethyl)sulfonyl)butanenitrile (**5**)

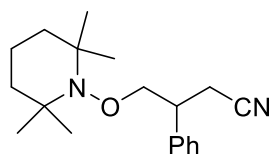
^1H NMR (400 MHz, CD_3CN): δ (ppm) 7.71 – 7.62 (m, 4H), 7.54 – 7.46 (m, 4H), 7.43 – 7.36 (m, 1H), 4.56 (dd, $J = 9.8, 3.2$ Hz, 1H), 3.46 (dd, $J = 14.5, 9.8$ Hz, 1H), 3.34 – 3.22 (m, 3H), 2.60 (t, $J = 7.2$ Hz, 2H), 2.21 – 2.11 (m, 2H), 2.05 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 143.7, 140.4, 140.1, 128.9, 127.5, 127.2, 127.0, 126.9, 119.2, 60.4, 52.4, 51.1, 18.3, 15.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_2\text{S}^+$: 351.1138 ($\text{M} + \text{Na}^+$), found: 351.1135.



4-((2-(1,3-Dioxoisindolin-2-yl)-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (**7**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.86 – 7.79 (m, 2H), 7.75 – 7.66 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 5.98 (dd, $J = 10.3, 4.5$ Hz, 1H), 4.61 (dd, $J = 14.4, 10.4$ Hz, 1H), 3.76

(dd, $J = 14.4, 4.5$ Hz, 1H), 3.06 (t, $J = 7.3$ Hz, 2H), 2.56 (dd, $J = 10.5, 4.1$ Hz, 2H), 2.32 (s, 3H), 2.26 – 2.13 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 167.8, 139.0, 134.3, 134.1, 131.6, 129.8, 127.8, 123.6, 118.1, 53.4, 51.6, 48.2, 21.1, 18.1, 16.3. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}^+$: 419.1036 ($\text{M} + \text{Na}^+$), found: 419.1039.



3-Phenyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (**8**)⁴

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 4.01 (d, $J = 6.4$ Hz, 2H), 3.32 – 3.21 (m, 1H), 2.94 (dd, $J = 16.7, 5.9$ Hz, 1H), 2.77 (dd, $J = 16.7, 8.0$ Hz, 1H), 1.60 – 1.28 (m, 6H), 1.18 – 1.07 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 139.2, 128.7, 127.6, 127.5, 118.7, 78.2, 60.0, 42.0, 39.7, 39.6, 33.0, 21.1, 20.2, 20.1, 17.0.

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