

Supporting Information

Catalytic conversion of aryl triazenes into aryl sulfonamides using sulfur dioxide as the sulfonyl source

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1. General Methods and Materials

NMR spectra were recorded on Bruker Avance 300 (300 MHz). Chemical shifts (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H-NMR) and 77.00 ppm (¹³C-NMR); references for *d*₆-DMSO were 2.50 ppm (¹H-NMR) and 40.00 ppm (¹³C-NMR). The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

All reactions were carried out under argon atmosphere unless otherwise specified. 1,4-Dioxane (anhydrous, 99.8%), acetonitrile and other reagents were purchased from Sigma-Aldrich and used as received. The sulfur dioxide solution in MeCN was prepared as in the following set up (Fig.1). The concentration was ca. 0.5 mol/L according to the amount of sodium sulfate used.

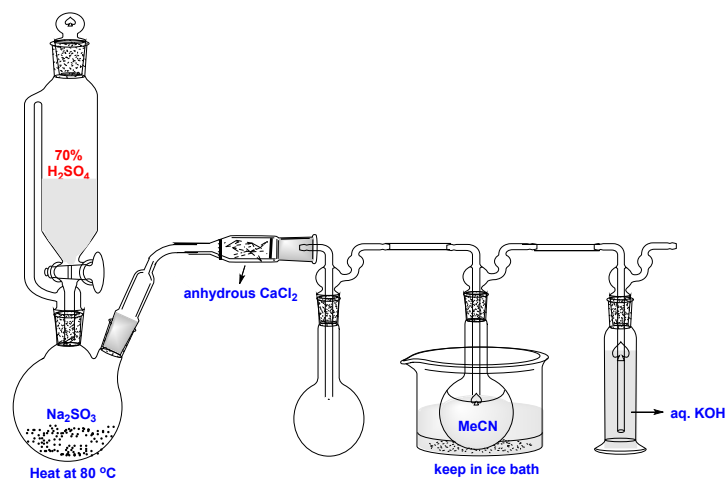
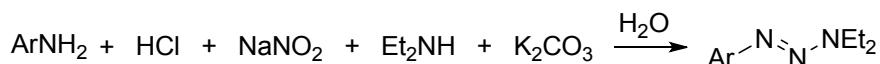


Fig 1. Set up for the preparation of SO₂(g) solution in MeCN

2. Preparation of triazenes

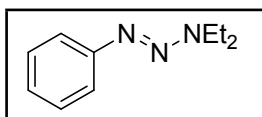
1-Aryl-3-diethyltriazene was prepared according the reported procedure as the following. The other triazenes was prepared with the similar procedure using MeCN-H₂O (2:1) as the solvent.



Aryl amine (21 mmol) was added to 12 mL of 6 M HCl at 0 °C, then sodium nitrite (1.63 g, 23.6 mmol) in 6 mL of H₂O was added dropwise. After stirring for 10 min, the mixture was added slowly to a solution of Et₂NH (3.3 mL, 56.7 mmol) and K₂CO₃ (4.5 g, 32 mmol) in ice water (30 mL). Stirring at room temperature for 0.5 hour and extracted with ethyl acetate (30 mL × 3). The combined organic phase was dried over Na₂SO₄ and the product was obtained by column chromatography.

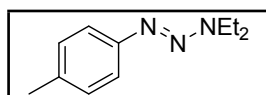
3. NMR data of the triazene substrates

(1a) 3,3-diethyl-1-phenyltriaz-1-ene¹



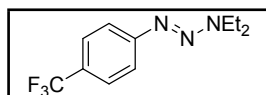
Yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.27 (m, 2H), 7.29 – 7.16 (m, 2H), 7.08 – 6.96 (m, 1H), 3.73 – 3.55 (m, 4H), 1.23 – 1.07 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 151.2, 128.7, 125.0, 120.4, 43.8, 12.8.

(1b) 3,3-diethyl-1-(p-tolyl)triaz-1-ene¹



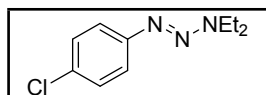
Brown liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.46 – 7.30 (m, 2H), 7.27 – 7.10 (m, 2H), 3.92 – 3.65 (m, 4H), 2.38 (s, 1H), 1.41 – 1.17 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.9, 134.5, 129.3, 120.2, 120.2, 44.5, 20.9, 12.9.

(1c) 3,3-diethyl-1-(4-(trifluoromethyl)phenyl)triaz-1-ene²



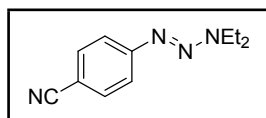
Yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.59 – 7.44 (m, 4H), 3.79 (q, *J* = 7.2 Hz, 4H), 1.27 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 153.9, 127.1, 126.7, 126, 125.8 (q, *J*_{F-C} = 3.9 Hz), 122.8, 120.4, 48.9, 41.3, 14.1, 10.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -61.4.

(1d) 1-(4-chlorophenyl)-3,3-diethyltriaz-1-ene³



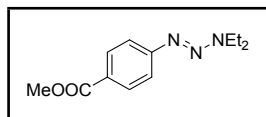
Brown liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.20 (m, 4H), 3.84 – 3.66 (m, 4H), 1.34 – 1.20 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 149.8, 130.0, 128.7, 121.5, 47.8, 40.9, 14.1, 12.6.

(1e) 4-(3,3-diethyltriaz-1-en-1-yl)benzonitrile¹



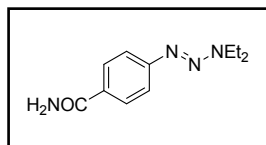
Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.64 – 7.55 (m, 2H), 7.50 – 7.43 (m, 2H), 3.81 (q, *J* = 7.2 Hz, 4H), 1.38 – 1.19 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 154.5, 132.9, 120.8, 119.6, 107.2, 49.3, 41.5, 14.3, 11.1.

(1f) Methyl 4-(3,3-diethyltriaz-1-en-1-yl)benzoate



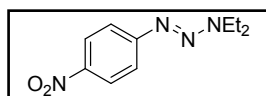
Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 8.07 – 7.93 (m, 2H), 7.55 – 7.37 (m, 2H), 3.89 (s, 3H), 3.79 (q, *J* = 7.2 Hz, 4H), 1.43 – 1.11 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 166.6, 154.6, 130.2, 125.8, 119.8, 51.4, 48.7, 41.0, 14.0, 13.8, 10.9.

(1g) 4-(3,3-diethyltriaz-1-en-1-yl)benzamide⁴



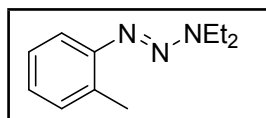
White solid. ¹H NMR (300 MHz, CDCl₃) δ 7.87 – 7.73 (m, 2H), 7.54 – 7.41 (m, 2H), 6.13 (s, 1H), 5.64 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 4H), 1.40 – 1.14 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 154.2, 129.2, 128.3, 120.3, 41.3, 14.2.

(1h) 3,3-diethyl-1-(4-nitrophenyl)triaz-1-ene¹



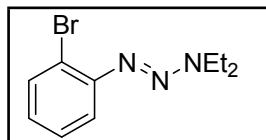
Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 8.19 (d, *J* = 9.1 Hz, 2H), 7.49 (d, *J* = 9.1 Hz, 2H), 3.83 (q, *J* = 7.2 Hz, 4H), 1.36 – 1.24 (m, 3H), 1.24 – 1.12 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 156.3, 144.3, 124.7, 120.3, 49.5, 41.7, 14.3, 11.1.

(1i) 3,3-diethyl-1-(o-tolyl)triaz-1-ene³



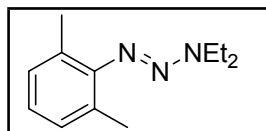
Brown oil. ¹H NMR (300 MHz, CDCl₃) δ 7.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.22 – 7.08 (m, 2H), 7.04 (dd, *J* = 7.3, 1.4 Hz, 1H), 3.76 (q, *J* = 7.1 Hz, 4H), 2.42 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 149.0, 132.4, 130.4, 126.2, 124.9, 116.4, 45.7, 17.7, 12.8.

(1j) 1-(2-bromophenyl)-3,3-diethyltriaz-1-ene²



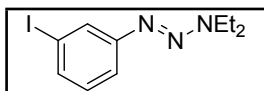
Brown liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.31 – 7.17 (m, 1H), 7.05 – 6.91 (m, 1H), 3.80 (q, *J* = 7.1 Hz, 4H), 1.31 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.5, 132.9, 127.7, 125.9, 119.7, 118.5, 49.1, 41.9, 14.5, 10.9.

(1k) 1-(2,6-dimethylphenyl)-3,3-diethyltriaz-1-ene⁵



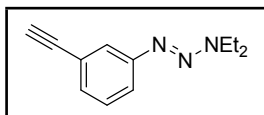
Yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.11 – 6.87 (m, 3H), 3.75 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 130.0, 128.3, 124.4, 44.5, 18.5, 12.9.

(1l) 3,3-diethyl-1-(3-iodophenyl)triaz-1-ene⁶



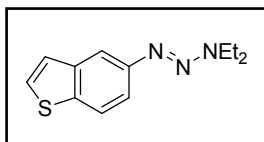
Yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.87 – 7.74 (m, 1H), 7.52 – 7.31 (m, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 3.76 (q, *J* = 7.1 Hz, 4H), 1.26 (t, *J* = 7.0 Hz, 6H).

(1m) 3,3-diethyl-1-(3-ethynylphenyl)triaz-1-ene⁶



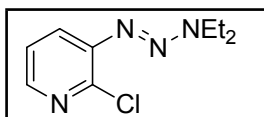
Yellow liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.57 – 7.48 (m, 1H), 7.43 – 7.29 (m, 1H), 7.29 – 7.18 (m, 2H), 3.72 (q, *J* = 7.2 Hz, 3H), 3.01 (s, 1H), 1.23 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 151.1, 128.6, 128.5, 123.8, 122.3, 122.3, 121.2, 83.9, 76.5, 47.7, 41.3, 12.6.

(1n) 1-(benzo[b]thiophen-5-yl)-3,3-diethyltriaz-1-ene



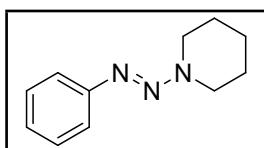
Red thick oil. ¹H NMR (300 MHz, CDCl₃) δ 7.83 – 7.81 (m, 1H), 7.80 (dd, *J* = 8.6, 0.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.41 (d, *J* = 5.4 Hz, 1H), 7.31 (dd, *J* = 5.4, 0.8 Hz, 1H), 3.79 (q, *J* = 7.1 Hz, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.5, 140.3, 136.4, 126.7, 124.1, 122.4, 117.7, 115.0, 44.8, 12.9. HRMS (ESI) Calc. for C₁₂H₁₅N₃S (M)⁺: 233.09812; found: 233.09803.

(1o) 2-chloro-3-(3,3-diethyltriaz-1-en-1-yl)pyridine²



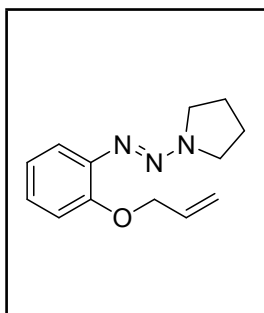
¹H NMR (300 MHz, CDCl₃) δ 8.13 (dd, *J* = 4.6, 1.8 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.17 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 4H), 1.42 – 1.22 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 146.1, 144.5, 143.7, 125.5, 122.5, 49.1, 41.8, 14.1, 10.3.

(1p) 1-(phenyldiazenyl)piperidine⁷



Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.39 (m, 2H), 7.38 – 7.28 (m, 2H), 7.20 – 7.11 (m, 1H), 3.83 – 3.72 (m, 4H), 1.78 – 1.66 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 150.8, 128.8, 125.6, 120.5, 48.0, 25.2, 24.4.

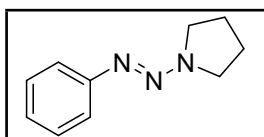
(1q) 1-((2-(allyloxy)phenyl)diazenyl)pyrrolidine



1q was prepared from 2-(allyloxy)aniline, which was prepared by the literature procedure:⁸
2-(allyloxy)aniline: ¹H NMR (300 MHz, CDCl₃) δ 6.86 – 6.64 (m, 4H), 6.23 – 5.95 (m, 1H), 5.41 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.57 (dt, *J* = 5.4, 1.5 Hz, 2H), 3.81 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 145.9, 136.3, 133.3, 121.1, 118.0, 117.0, 114.9, 111.8, 68.9.

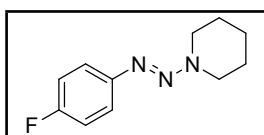
(1q): ¹H NMR (300 MHz, CDCl₃) δ 7.35 – 7.30 (m, 1H), 7.12 – 7.04 (m, 1H), 6.97 – 6.89 (m, 2H), 6.19 – 6.04 (m, 1H), 5.45 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.25 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.64 (dt, *J* = 5.1, 1.6 Hz, 2H), 3.83 (s, 4H), 2.08 – 1.96 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 151.8, 141.4, 133.8, 125.6, 121.4, 118.4, 116.7, 114.7, 70.1, 23.6. HRMS (ESI) Calc. for C₁₃H₁₇O₃N (M)⁺: 231.13661; found: 231.13612.

(1-3j) 1-(phenyldiazenyl)pyrrolidine



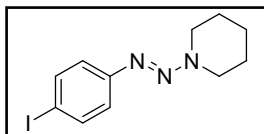
Pale yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.57 – 7.26 (m, 4H), 7.19 – 7.07 (m, 1H), 4.12 – 3.52 (m, 4H), 2.25 – 1.92 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 151.3, 128.7, 125.0, 120.3, 47.3, 23.7.

(1-3l) 1-((4-fluorophenyl)diazenyl)piperidine



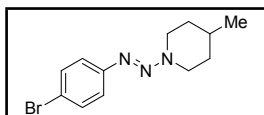
Pale yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.50 – 7.34 (m, 2H), 7.10 – 6.94 (m, 1H), 3.87 – 3.68 (m, 3H), 1.79 – 1.65 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 162.4, 159.2, 147.1 (d, *J* = 2.9 Hz), 128.8, 121.6 (d, *J* = 8.1 Hz), 116.4, 115.2 (d, *J* = 22.5 Hz), 50.5, 25.7, 25.1, 24.2.

(1-3m)-1-((4-fluorophenyl)diazenyl)piperidine



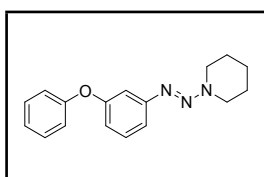
Yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.62 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 2H), 3.77 (t, $J = 4.4$ Hz, 4H), 1.79 – 1.64 (m, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 150.4, 137.7, 122.4, 89.6, 48.3, 25.2, 24.2.

(1-3n)-1-((4-bromophenyl)diazenyl)-4-methylpiperidine



Yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.72 – 7.56 (m, 4H), 3.74 (d, $J = 11.5$ Hz, 2H), 2.33 – 2.19 (m, 2H), 1.72 – 1.62 (m, 2H), 1.35 – 1.26 (m, 2H), 1.30 – 1.22 (m, 1H), 0.92 (d, $J = 5.5$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 149.8, 131.7, 122.0, 118.6, 47.0, 33.4, 30.9, 21.6. HRMS (ESI) Calc. for $\text{C}_{12}\text{H}_{16}\text{N}_3\text{Br}$ (M, M+2) $^+$: 281.05221 and 283.05017; found: 283.05236 and 283.05056.

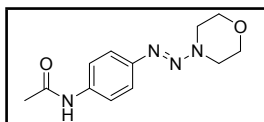
(1-3o)-1-((3-phenoxyphenyl)diazenyl)piperidine



Thick yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.38 – 7.28 (m, 3H), 7.18 (ddd, $J = 7.9, 1.8, 1.1$ Hz, 1H), 7.13 – 7.00 (m, 4H), 6.81 (ddd, $J = 8.0, 2.4, 1.1$ Hz, 1H), 3.81 – 3.71 (m, 4H), 1.75 – 1.64 (m, 6H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 157.6, 157.4, 152.5, 129.7, 129.6, 122.9, 122.9, 118.7, 118.7, 116.1, 115.9, 110.8, 47.9, 25.2, 24.3. HRMS (ESI) Calc. for $\text{C}_{17}\text{H}_{19}\text{ON}_3$ (M) $^+$: 281.15226; found: 281.15234.

(1-3p) N-(4-(morpholinodiazenyl)phenyl)acetamide

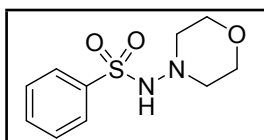


White solid. $^1\text{H NMR}$ (300 MHz, DMSO) δ 9.96 (s, 1H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.32 (d, $J = 8.8$ Hz, 2H), 3.80 – 3.71 (m, 4H), 3.69 – 3.62 (m, 4H), 2.03 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 168.6, 145.5, 138.2, 121.2, 119.8, 66.0, 48.3, 24.5. HRMS (ESI) Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_4$ (M) $^+$: 248.12678; found: 248.12663.

4. NMR data of products 2a-q

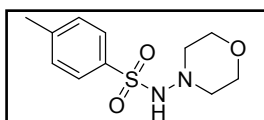
General procedure for the reaction: To an oven dried Schlenk tube (10 ml), triazene substrate (0.2 mmol) was added under Ar, then 1 mL of SO_2 solution in MeCN was added. After which the hydrazine (0.3 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (0.3 mmol) were added through syringe. The mixture was stirring at 60 $^\circ\text{C}$ for the indicated time. Cooled to room temperature and column chromatography gave the desired products.

(2a) N-morpholinobenzenesulfonamide⁹



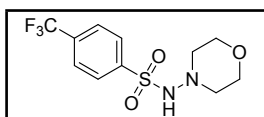
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.09 – 7.84 (m, 1H), 7.77 – 7.37 (m, 2H), 5.48 (s, 0H), 3.77 – 3.39 (m, 2H), 2.82 – 2.42 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 138.5, 133.1, 128.8, 128.1, 66.5, 56.6.

(2b) 4-methyl-N-morpholinobenzenesulfonamide⁹



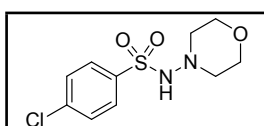
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.84 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.52 (s, 1H), 3.67 – 3.47 (m, 4H), 2.68 – 2.56 (m, 4H), 2.43 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.9, 135.6, 129.4, 128.0, 66.5, 56.5, 21.5.

(2c) N-morpholino-4-(trifluoromethyl)benzenesulfonamide¹⁰



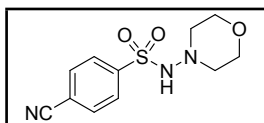
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.11 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 5.48 (s, 1H), 3.79 – 3.54 (m, 4H), 2.83 – 2.56 (m, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 142.3, 135.1, 134.6, 128.7, 126.1, 126.0, 126.0, 125.9, 125.0, 121.4, 66.6. $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -62.7.

(2d) 4-chloro-N-morpholinobenzenesulfonamide¹¹



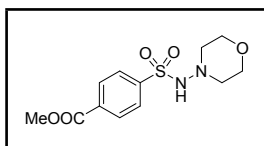
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.06 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.48 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.39 – 7.25 (m, 2H), 5.63 (d, $J = 4.7$ Hz, 1H), 3.63 – 3.52 (m, 4H), 2.69 – 2.58 (m, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 139.7, 137.0, 129.6, 129.1, 66.6, 56.6.

(2e) 4-cyano-*N*-morpholinobenzenesulfonamide¹⁰



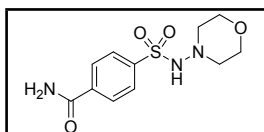
¹H NMR (300 MHz, DMSO) δ 9.24 (s, 1H), 8.14 – 8.04 (m, 2H), 8.04 – 7.96 (m, 2H), 3.49 – 3.39 (m, 4H), 2.49 – 2.45 (m, 5H). ¹³C NMR (75 MHz, DMSO) δ 144.0, 133.7, 128.7, 125.0, 118.3, 115.8, 66.4, 56.3.

(2f) methyl 4-(*N*-morpholinofamoyl)benzoate¹⁰



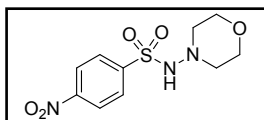
¹H NMR (300 MHz, DMSO) δ 9.13 (s, 1H), 8.38 – 8.10 (m, 2H), 8.12 – 7.92 (m, 2H), 3.89 (s, 3H), 3.62 – 3.40 (m, 4H), 2.62 – 2.44 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 165.7, 144.0, 133.7, 130.3, 128.4, 66.4, 56.3, 53.1.

(2g) 4-(*N*-morpholinofamoyl)benzamide



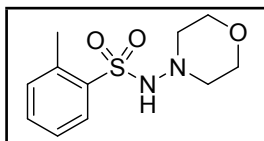
¹H NMR (300 MHz, DMSO) δ 9.03 (s, 1H), 8.18 (s, 1H), 8.09 – 7.97 (m, 2H), 7.97 – 7.87 (m, 2H), 7.62 (s, 1H), 3.49 – 3.40 (m, 4H), 2.55 – 2.43 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 167.3, 142.3, 138.5, 128.6, 128.0, 66.4, 56.4.

(2h) 4-nitro-*N*-morpholinobenzenesulfonamide¹²



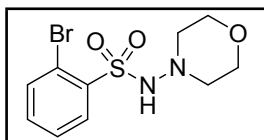
¹H NMR (300 MHz, DMSO) δ 9.1 (s, 1H), 8.2 – 8.1 (m, 2H), 8.1 – 8.0 (m, 2H), 4.14 – 3.74 (m, 4H), 3.5 – 3.4 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 150.3, 145.4, 129.5, 124.9, 66.4, 56.4.

(2i) 2-methyl-*N*-morpholinobenzenesulfonamide⁹



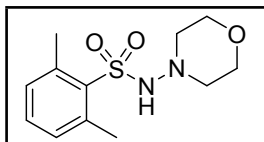
¹H NMR (300 MHz, CDCl₃) δ 8.07 (dd, J = 8.0, 1.4 Hz, 1H), 7.47 (dd, J = 7.4, 1.5 Hz, 1H), 7.38 – 7.27 (m, 2H), 5.40 (brs, 1H), 3.63 – 3.49 (m, 4H), 2.69 (s, 3H), 2.68 – 2.58 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 137.9, 136.4, 133.2, 132.2, 131.0, 126.0, 66.5, 56.6, 20.6.

(2j) 2-bromo-*N*-morpholinobenzenesulfonamide



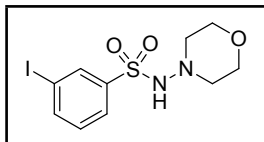
¹H NMR (300 MHz, CDCl₃) δ 8.29 – 8.22 (m, 1H), 7.77 – 7.70 (m, 1H), 7.55 – 7.41 (m, 2H), 6.08 (s, 1H), 3.62 – 3.53 (m, 4H), 2.76 – 2.67 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 137.8, 134.9, 134.1, 133.2, 127.7, 120.0, 66.4, 56.4. HRMS (ESI) Calc. for C₁₀H₁₃O₃N₂BrS (M)⁺: 319.98248; found: 319.98302.

(2k) 2,6-dimethyl-*N*-morpholinobenzenesulfonamide



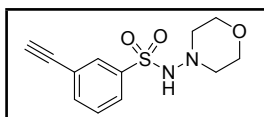
¹H NMR (300 MHz, CDCl₃) δ 7.31 (dd, J = 8.1, 7.0 Hz, 1H), 7.19 – 7.10 (m, 2H), 5.49 (s, 1H), 3.62 – 3.52 (m, 4H), 2.73 (s, 6H), 2.70 – 2.60 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 135.4, 132.2, 130.9, 66.7, 56.5, 23.2. HRMS (ESI) Calc. for C₁₂H₁₈O₃N₂S (M)⁺: 270.10326; found: 270.10294.

(2l) 3-iodo-*N*-morpholinobenzenesulfonamide



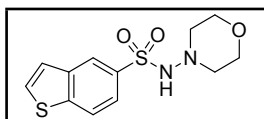
¹H NMR (300 MHz, DMSO) δ 9.02 (s, 1H), 8.15 (t, J = 1.7 Hz, 1H), 8.09 – 7.99 (m, 1H), 7.91 – 7.81 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H), 3.46 (s, 5H), 2.53 – 2.42 (m, 5H). ¹³C NMR (75 MHz, DMSO) δ 141.9, 141.5, 136.0, 131.6, 127.2, 95.2, 66.4, 56.3. HRMS (ESI) Calc. for C₁₀H₁₃O₃N₂IS (M)⁺: 367.96861; found: 367.96935.

(2m) 3-ethynyl-*N*-morpholinobenzenesulfonamide



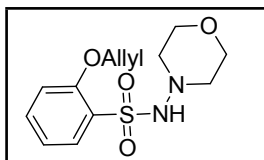
¹H NMR (300 MHz, CDCl₃) δ 8.10 (t, J = 1.8 Hz, 1H), 7.99 – 7.89 (m, 1H), 7.70 (dt, J = 7.7, 1.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 5.47 (s, 1H), 3.62 (t, J = 4.7 Hz, 4H), 2.77 – 2.53 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 136.4, 131.5, 128.9, 128.1, 123.3, 81.6, 79.5, 66.5, 56.6. HRMS (ESI) Calc. for C₁₂H₁₄O₃N₂S (M)⁺: 266.07196; found: 266.07261.

(2n) N-morpholinobenzo[b]thiophene-5-sulfonamide



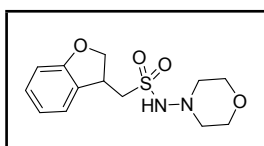
¹H NMR (300 MHz, DMSO) δ 8.91 (s, 1H), 8.42 (d, *J* = 1.8 Hz, 1H), 8.22 (d, *J* = 0.7 Hz, 1H), 7.96 (d, *J* = 5.4 Hz, 1H), 7.79 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.69 (d, *J* = 5.5 Hz, 1H), 3.43 – 3.40 (m, 4H), 2.52 – 2.42 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 143.6, 139.5, 136.3, 130.6, 125.1, 123.9, 123.8, 122.8, 66.4, 56.4. HRMS (ESI) Calc. for C₁₂H₁₄O₃N₂S₂ (M)⁺: 298.04404; found: 98.04382.

(2qa) 1-((2-(allyloxy)phenyl)sulfonyl)pyrrolidine



¹H NMR (300 MHz, CDCl₃) δ 8.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.15 – 6.95 (m, 2H), 6.19 – 6.02 (m, 1H), 5.91 (s, 1H), 5.58 – 5.34 (m, 2H), 4.71 (dt, *J* = 5.4, 1.5 Hz, 2H), 3.61 – 3.51 (m, 4H), 2.71 – 2.60 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 155.3, 134.9, 131.8, 127.4, 121.1, 119.3, 113.4, 70.1, 66.4, 56.6. HRMS (ESI): Calc. for C₁₃H₁₈O₄N₂S (M)⁺: 298,09818; found: 298,09816.

(2qb) 1-(2,3-Dihydrobenzofuran-3-yl)-N-morpholinomethanesulfonamide¹³

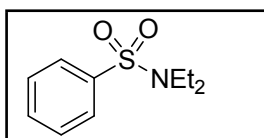


¹H NMR (300 MHz, CDCl₃) δ 7.23 – 7.16 (m, 2H), 6.91 (t, *J* = 7.5, 1H), 6.87 – 6.81 (m, 1H), 5.14 (s, 1H), 4.75 (dd, *J* = 9.7, 8.7 Hz, 1H), 4.61 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.10 – 3.97 (m, 1H), 3.78 (t, *J* = 4.7 Hz, 4H), 3.60 (dd, *J* = 14.2, 3.1 Hz, 1H), 3.34 (dd, *J* = 14.2, 10.8 Hz, 1H), 2.90 (tt, *J* = 10.8, 6.1 Hz, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 159.8, 129.4, 127.0, 124.2, 120.9, 110.2, 75.9, 66.6, 57.5, 54.2, 37.4.

5. NMR data of products 3a-q

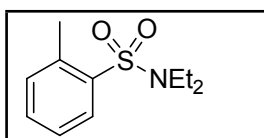
General procedure for the reaction: To an oven dried Schlenk tube (10 ml), triazene substrate (0.2 mmol) and CuCl₂ (0.02 mmol) was added under Ar, then 1 mL of SO₂ solution in MeCN was added. The mixture was stirring at 70 °C for 18 h. Cooled to room temperature and column chromatography gave the desired products.

(3a) N,N-diethylbenzenesulfonamide¹⁴



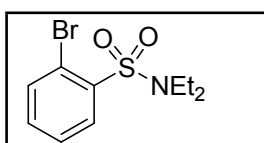
¹H NMR (300 MHz, CDCl₃) δ 7.79 – 7.71 (m, 2H), 7.54 – 7.40 (m, 3H), 3.19 (q, *J* = 7.1 Hz, 4H), 1.07 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 140.1, 132.1, 128.8, 126.7, 41.9, 13.9.

(3b) 2-methyl-N,N-diethylbenzenesulfonamide¹⁵



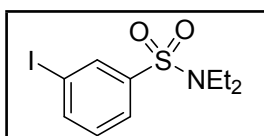
¹H NMR (300 MHz, CDCl₃) δ 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.43 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 3.32 (q, *J* = 7.1 Hz, 4H), 2.60 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 138.4, 137.6, 132.6, 132.4, 129.4, 125.9, 40.7, 20.2, 13.7.

(3c) 2-bromo-N,N-diethylbenzenesulfonamide¹⁶



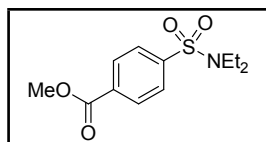
¹H NMR (300 MHz, CDCl₃) δ 8.12 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.50 – 7.30 (m, 2H), 3.38 (q, *J* = 7.2 Hz, 4H), 1.12 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 139.8, 135.5, 133.2, 132.1, 127.4, 120.4, 41.2, 13.6.

(3d) N,N-diethyl-3-iodobenzenesulfonamide



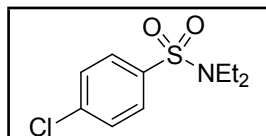
¹H NMR (300 MHz, CDCl₃) δ 8.15 (t, *J* = 1.7 Hz, 1H), 7.92 – 7.82 (m, 1H), 7.82 – 7.72 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 3.25 (q, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 142.2, 141.1, 135.5, 130.6, 126.0, 94.2, 42.1, 14.1. HRMS (ESI) Calc. for C₁₀H₁₄O₂NIS (M)⁺: 338.97844; found: 338.97817.

(3e) methyl 4-(N,N-diethylsulfamoyl)benzoate¹⁷



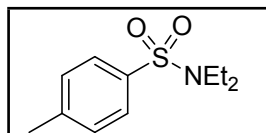
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.15 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 8.6$ Hz, 2H), 3.96 (s, 3H), 3.27 (q, $J = 7.1$ Hz, 4H), 1.13 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 165.7, 144.4, 130.2, 126.9, 52.6, 42.0, 14.0.

(3f) 4-chloro-N,N-diethylbenzenesulfonamide¹⁸



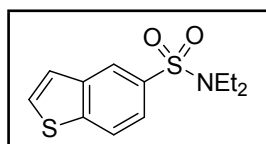
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.81 – 7.71 (m, 2H), 7.54 – 7.43 (m, 2H), 3.32 – 3.18 (m, 4H), 1.22 – 1.09 (m, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 139.0, 138.6, 129.2, 128.4, 42.0, 14.1.

(3g) N,N-diethyl-4-methylbenzenesulfonamide¹⁹



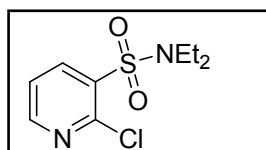
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.74 – 7.64 (m, 2H), 7.33 – 7.23 (m, 2H), 3.22 (q, $J = 7.1$ Hz, 4H), 2.41 (s, 3H), 1.12 (t, $J = 7.2$ Hz, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 142.8, 137.2, 129.5, 126.9, 41.9, 21.4, 14.0.

(3h) N,N-diethylbenzo[*b*]thiophene-5-sulfonamide



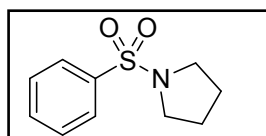
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.36 – 8.25 (m, 1H), 7.98 (d, $J = 8.7, 0.9$ Hz, 1H), 7.73 (d, $J = 8.5, 1.4$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.47 – 7.41 (m, 1H), 3.27 (q, $J = 7.2, 1.0$ Hz, 4H), 1.14 (t, $J = 7.2, 1.0$ Hz, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.2, 139.2, 136.5, 128.8, 124.2, 123.1, 122.9, 121.8, 42.1, 14.2. HRMS (ESI) Calc. for $\text{C}_{12}\text{H}_{15}\text{O}_2\text{NS}_2$ (M)⁺: 269.05387; found: 269.05370.

(3i) 2-chloro-N,N-diethylpyridine-3-sulfonamide²⁰



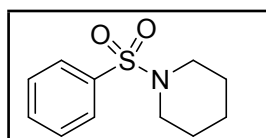
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.12 (dd, $J = 4.6, 1.8$ Hz, 1H), 7.70 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.16 (dd, $J = 7.9, 4.6$ Hz, 1H), 3.80 (q, $J = 7.2$ Hz, 4H), 1.43 – 1.19 (m, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 146.5, 145.0, 144.1, 125.9, 122.8, 49.4, 42.1, 14.4, 10.7.

(3j) 1-(phenylsulfonyl)pyrrolidine¹⁹



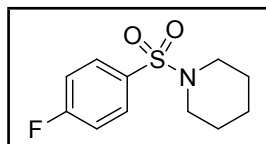
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88 – 7.80 (m, 2H), 7.63 – 7.49 (m, 3H), 3.25 (t, $J = 6.8$ Hz, 4H), 1.79 – 1.71 (m, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 136.8, 132.5, 128.9, 127.4, 47.9, 25.2.

(3k) 1-(phenylsulfonyl)piperidine²¹



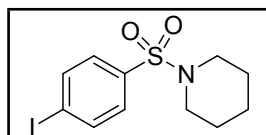
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.85 – 7.71 (m, 2H), 7.65 – 7.48 (m, 3H), 3.10 – 2.92 (m, 4H), 1.75 – 1.55 (m, 4H), 1.53 – 1.34 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 136.1, 132.5, 128.8, 127.5, 46.8, 25.0, 23.3.

(3l) 1-((4-fluorophenyl)sulfonyl)piperidine²²



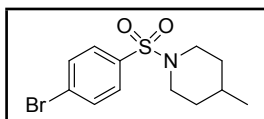
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.77 (dd, $J = 8.8, 5.1$ Hz, 2H), 7.22 (dd, $J = 17.0, 8.4$ Hz, 2H), 3.04 – 2.92 (m, 4H), 1.64 (q, $J = 5.7$ Hz, 4H), 1.44 (d, $J = 5.7$ Hz, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 165.0 (d, $J = 254.4$ Hz), 132.4 (d, $J = 3.2$ Hz), 130.2 (d, $J = 9.2$ Hz), 116.1 (d, $J = 22.4$ Hz), 46.9, 25.1, 23.4.

(3m) 1-((4-iodophenyl)sulfonyl)piperidine²³



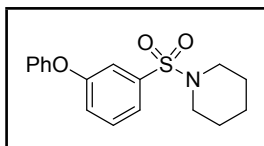
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.6$ Hz, 2H), 3.02 – 2.93 (m, 4H), 1.64 (p, $J = 5.8$ Hz, 4H), 1.49 – 1.38 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 138.1, 136.0, 128.9, 99.9, 46.8, 25.1, 23.4.

(3n) 1-((4-bromophenyl)sulfonyl)-4-methylpiperidine²⁴



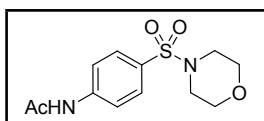
¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.56 (m, 4H), 3.77 – 3.67 (m, 2H), 2.32 – 2.18 (m, 2H), 1.72 – 1.61 (m, 2H), 1.43 – 1.21 (m, 4H), 0.92 (d, *J* = 5.5 Hz, 3H), 0.91 – 0.80 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 135.4, 132.2, 129.1, 127.5, 46.3, 33.2, 30.0, 21.4.

(3o) 1-((3-phenoxyphenyl)sulfonyl)piperidine



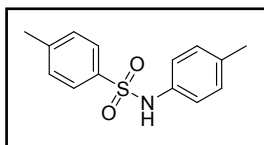
¹H NMR (300 MHz, CDCl₃) δ 7.51 – 7.30 (m, 5H), 7.24 – 7.11 (m, 2H), 7.09 – 6.97 (m, 2H), 3.04 – 2.92 (m, 4H), 1.64 (p, *J* = 5.7 Hz, 5H), 1.51 – 1.37 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 157.9, 155.9, 137.9, 130.2, 130.0, 124.3, 122.2, 121.8, 119.3, 117.2, 46.9, 25.1, 23.4. HRMS (ESI) Calc. for C₁₇H₁₉O₃NS (M)⁺: 317.10802; found: 317.10712.

(3p) *N*-(4-(morpholinylsulfonyl)phenyl)acetamide²⁵



¹H NMR (300 MHz, CDCl₃) δ 7.70 (s, 4H), 7.46 (s, 1H), 3.79 – 3.69 (m, 3H), 3.04 – 2.93 (m, 3H), 2.23 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 168.9, 142.5, 129.5, 129.0, 119.3, 66.0, 46.0, 24.7.

(3q) 4-methyl-*N*-(*p*-tolyl)benzenesulfonamide²⁶



The 1,3-di-*p*-tolyltriaz-1-ene was prepared by the literature procedure²⁷ and used as crude starting material for the reaction. ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.08 – 6.90 (m, 4H), 6.35 (s, 1H), 2.38 (s, 3H), 2.27 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 143.7, 136.1, 135.3, 133.7, 129.8, 129.6, 127.3, 122.2, 21.5, 20.8.

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