Experimental Supporting Information

Visible-Light, Iodine-Promoted Formation of *N*-Sulfonyl Imines and *N*-Alkylsulfonamides from Aldehydes and Hypervalent Iodine Reagents

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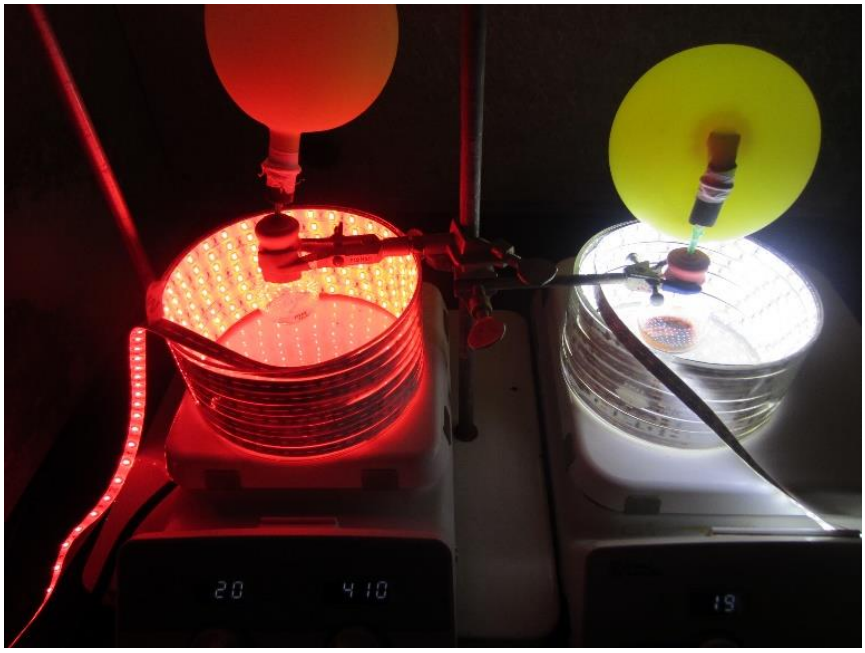


On the left – A red LED strip (620 nm) light bath reaction vessel

On the right – A white LED strip (cool white) light bath reaction vessel

Photocatalytic reactions were set up in a light bath which was constructed in our laboratory as follows. Waterproof 5050 LED strips (12V with power adapter, 18 LEDs/foot, approximately 0.24 Watt per LED – 72 Watt per strip) are coiled around the interior of evaporating dish (170mm x 90mm) using the adhesive backing of the LED strip. A Petri dish (150 x 20 mm) is placed upside down at the bottom of the dish to serve as an elevated glass "floor" to ensure that a round-bottom flask receives maximum light exposure. The temperature inside the dish is monitored and is generally maintained (air-cooled) between 19-22 ^{o}C (the temperature has not been observed above 25 ^{o}C).

δ imine C-H (ppm)

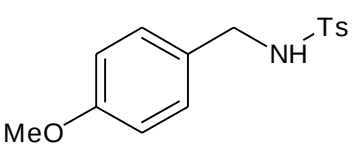
Product	NMR intgn crude	lit. (ref.)
2aa	8.92	8.91 (1)
2ba	8.97	8.96 (1)
2ca	9.02	9.01 (1)
2da	8.93	8.94 (1)
2ea	8.94	8.96 (1)
2fa	9.07	9.07 (1)
2ga	9.01	9.01 (1)
2ha	8.97	8.97 (1)
2ia	9.31	9.30 (1)
2ja	8.95	8.94 (1)
2ka	9.49	9.48 (1)
2la	8.92	8.92 (1)
2ma	9.35	9.37 (1)

δ imine C-H (ppm)

Product	NMR intgn crude	lit. (ref.)
2bb	9.04	9.03 (3)
2eb	9.01	9.02 (3)
2hb	9.36	9.38 (4)
2bc	8.98	8.93 (1)
2dc	8.99	8.95 (1)
2bd	9.13	-
2ae	8.97	8.98 (1)
2ee	9.04	9.04 (1)
2bf	9.06	-
2bg	8.98	9.04 (2)
2de	9.09	9.09 (1)

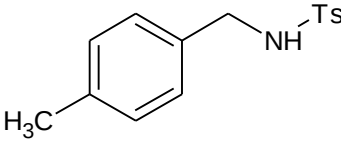
All values are reported in $CDCl_3$

_N_-(4-methoxybenzyl)-4-methylbenzenesulfonamide (3aa)[5]



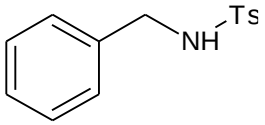
White solid (90 mg, 61% yield). M.p. 119-121 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz), 6.79 (d, *J* = 8.0 Hz, 2H), 4.72 (t, *J* = 4.0 Hz, 1H), 4.04 (d, *J* = 4.0 Hz, 2H), 3.77 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.4, 136.8, 129.7, 129.2, 128.2, 127.2, 114.0, 55.3, 46.8, 21.5 ppm. IR (neat): ν = 3248, 2922, 1612, 1513, 1320, 1251, 1155, 1029, 815, 553 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_3S_1$ $[M + H]^+$ requires *m/z* 292.10074, found *m/z* 292.07983.

4-methyl-_N_-(4-methylbenzyl)benzenesulfonamide (smaller scale, 0.125 mmol) (3ba)[5]



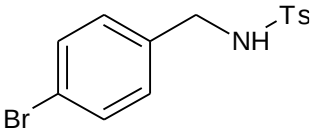
White solid (21 mg, 60%). M.p. 88-90 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 4H), 4.62 (t, *J* = 6.0 Hz, 1H), 4.07 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.7, 136.8, 133.1, 129.7, 129.3, 127.8, 127.2, 47.0, 21.5, 21.1 ppm. IR (neat): ν = 3261, 2921, 1597, 1323, 1151, 1093, 748, 665 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 276.10583, found *m/z* 276.10449.

***N*-benzyl-4-methylbenzenesulfonamide (3ca)[5]**



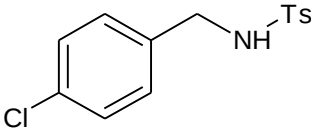
White solid (66 mg, 50%). M.p. 114-116 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.30-7.24 (m, 3H), 7.20-7.18 (m, 2H), 4.84 (t, *J* = 4.0 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.8, 136.2, 129.7, 128.7, 127.9, 127.8, 127.2, 47.2, 21.5 ppm. IR (neat): ν = 3268, 3064, 1598, 1453, 1321, 1160, 1058, 874, 805, 741 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{16}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 262.09018, found *m/z* 262.08948.

***N*-(4-bromobenzyl)-4-methylbenzenesulfonamide (3da)[6]**



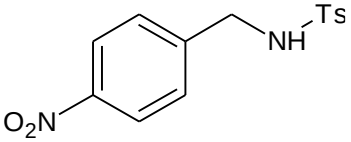
White solid (78 mg, 45%). M.p. 113-115 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.17 (t, *J* = 4.0 Hz, 1H), 4.06 (d, *J* = 4.0 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.7, 135.4, 131.7, 129.7, 129.5, 127.1, 121.7, 46.5, 21.5 ppm. IR (neat): ν = 3269, 2920, 1597, 1317, 1155, 1072, 1013, 878, 802, 544 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Br_1$ $[M + H]^+$ requires *m/z* 342.00069, found *m/z* 341.99771.

***N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (smaller scale, 0.125 mmol) (3ea)[5]**



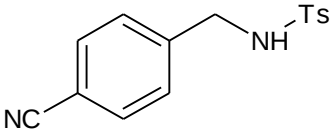
White solid (27 mg, 74%). M.p. 105-107 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 4.0 Hz, 1H), 4.08 (d, *J* = 4.0 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.7, 134.8, 133.7, 129.8, 129.2, 128.8, 127.1, 46.5, 21.5 ppm. IR (neat): ν = 3226, 2920, 1597, 1304, 1183, 816 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Cl_1$ $[M + H]^+$ requires *m/z* 296.05120, found *m/z* 296.05054.

4-methyl-*N*-(4-nitrobenzyl)benzenesulfonamide (3fa)



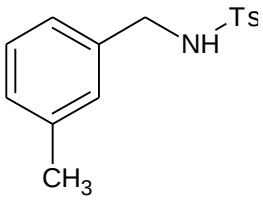
Yellow solid (62 mg, 40%). M.p. 111-113 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.13 (t, *J* = 4.0 Hz, 1H), 4.24 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.9, 136.6, 129.9, 128.4, 127.1, 123.8, 46.4, 27.5, 21.6 ppm. IR (neat): ν = 3252, 2855, 1516, 1309, 1150, 1109, 814 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_2O_4S_1$ $[M + H]^+$ requires *m/z* 307.07525, found *m/z* 307.07452.

***N*-(4-cyanobenzyl)-4-methylbenzenesulfonamide (3ga)**



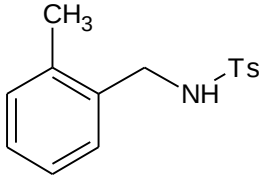
White solid (63 mg, 44%). M.p. 120-126 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.43 (t, *J* = 4.0 Hz, 1H), 4.17 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.0, 136.6, 132.3, 129.8, 128.3, 127.0, 118.5, 111.5, 46.6, 21.5 ppm. IR (neat): ν = 3234, 2922, 2857, 2230, 1594, 1324, 1152, 1069, 842, 815, 548 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{15}N_2O_2S_1$ $[M + H]^+$ requires *m/z* 287.08543, found *m/z* 287.08475.

4-methyl-*N*-(3-methylbenzyl)benzenesulfonamide (3ha)[8]



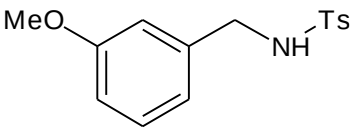
White solid (46 mg, 33%). M.p. 64-66 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.81. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.98 (m, 2H), 4.60 (t, *J* = 4.0 Hz, 1H), 4.09 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.4, 136.8, 136.1, 129.7, 128.62, 128.59, 128.56, 127.2, 124.9, 47.3, 21.5, 21.2 ppm. IR (neat): ν = 3294, 3029, 2922, 1596, 1320, 1153, 1065, 908, 811, 664, 537 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 276.10583, found *m/z* 276.10513.

4-methyl-*N*-(2-methylbenzyl)benzenesulfonamide (smaller scale, 0.125 mmol) (3ia)[7]



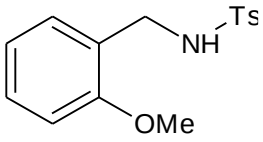
White solid (23 mg, 33%). M.p. 113-117 °C. Purification (hexanes: EtOAc, 60:40). R_f = 0.74. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21-7.10 (m, 4H), 4.46 (t, *J* = 4.0 Hz, 1H), 4.09 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 3H), 2.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.7, 136.6, 133.8, 130.6, 129.7, 128.8, 128.2, 127.2, 126.2, 45.4, 21.5, 18.8 ppm. IR (neat): ν = 3260, 3023, 2925, 1597, 1489, 1423, 1318, 1152, 1091, 1041, 879, 806, 702, 654 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 276.10583, found *m/z* 276.10483.

***N*-(3-methoxybenzyl)-4-methylbenzenesulfonamide (smaller scale, 0.125 mmol) (3ja)[8]**



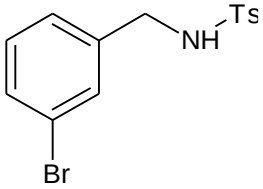
Clear oil (15 mg, 40%). Purification (hexanes:EtOAc, 60:40). R_f = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.80-6.75 (m, 2H), 6.73 (s, 1H), 4.65 (m, 1H), 4.10 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.6, 137.8, 136.8, 129.8, 129.7, 127.2, 120.0, 113.7, 113.1, 55.2, 47.3, 21.5 ppm. IR (neat): ν = 3279, 2922, 1597, 1586, 1490, 1455, 1436, 1320, 1288, 1262, 1152, 1091, 1040, 864, 812, 780, 660 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_3S_1$ $[M + H]^+$ requires *m/z* 292.10074, found *m/z* 292.09961.

***N*-[(2-Methoxyphenyl)methyl]-4-methylbenzenesulfonamide (3ka)[8]**



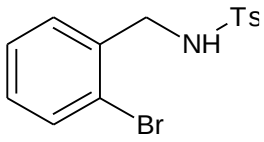
White solid (57 mg, 40%). M.p. 79-81 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.0 Hz, 2H), 7.21-7.16 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.09 (t, *J* = 4.0 Hz, 1H), 4.14 (d, *J* = 4.0 Hz, 2H), 3.73 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 143.0, 129.8, 129.4, 129.2, 127.03, 126.99, 124.3, 120.5, 110.1, 55.1, 44.0, 21.5 ppm. IR (neat): ν = 3304, 3254, 3014, 2949, 2837, 1602, 1404, 1325, 1148, 1024, 756, 663 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{18}N_1O_3S_1$ $[M + H]^+$ requires *m/z* 292.10074, found *m/z* 292.09958.

***N*-(3-bromobenzyl)-4-methylbenzenesulfonamide (3la)[6]**



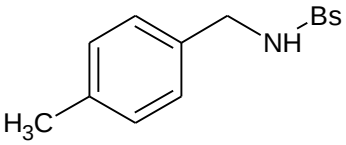
White solid (36 mg, 22%). M.p. 78-80 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.73 (d, *J* = 8.0 Hz, 2H), 7.37 (td, *J* = 4.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 (m, 1H), 7.15 (d, *J* = 4.0 Hz, 2H), 4.72 (t, *J* = 4.0 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.5, 136.7, 131.0, 130.8, 130.2, 129.8, 127.1, 126.4, 122.7, 46.6, 21.5 ppm. IR (neat): ν = 3259, 3067, 2918, 2852, 1570, 1435, 1316, 1149, 1052, 921, 814, 692, 529 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Br_1$ $[M + H]^+$ requires *m/z* 342.00069, found *m/z* 341.99731.

***N*-(2-bromobenzyl)-4-methylbenzenesulfonamide (3ma)[6]**



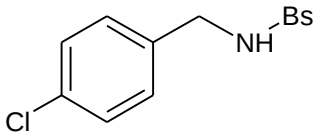
Yellow oil (50 mg, 30%). Purification (hexanes:EtOAc, 80:20). R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 5.03 (t, *J* = 6.0 Hz, 1H), 4.22 (d, *J* = 6.0 Hz, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 135.5, 132.7, 130.5, 129.6, 129.5, 129.1, 127.7, 127.1, 123.4, 47.4, 21.5 ppm. IR (neat): ν = 3282, 2922, 1597, 1441, 1325, 1154, 1024, 811, 658 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Br_1$ $[M + H]^+$ requires *m/z* 342.00069, found *m/z* 341.99728.

***N*-(4-methylbenzyl)benzenesulfonamide (3bb)[11]**



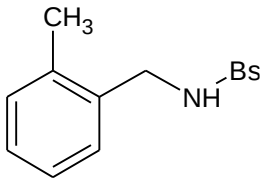
White solid (52 mg, 40%). M.p. 76-79 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.0 Hz, 2H), 7.59 (tt, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.51 (m, 2H), 7.06 (s, 4H), 4.75 (t, *J* = 4.0 Hz, 1H), 4.09 (d, *J* = 4.0 Hz, 2H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.7, 133.1, 132.7, 129.3, 129.1, 127.8, 127.1, 47.1, 21.1 ppm. IR (neat): ν = 3264, 2920, 1615, 1445, 1318, 1156, 1038, 907, 805 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{16}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 262.09018, found *m/z* 262.08905.

***N*-(4-chlorobenzyl)benzenesulfonamide (smaller scale, 0.125 mmol) (3eb)[9]**



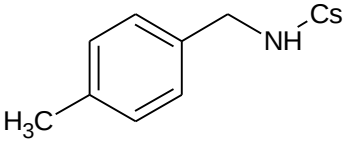
White solid (51 mg, 70%). M.p. 109-112 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.61-7.57 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.87 (t, *J* = 4.0 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 134.7, 133.8, 132.8, 129.2, 128.8, 127.0, 46.6, 29.7 ppm. IR (neat): ν = 3255, 3059, 1598, 1490, 1320, 1181, 1091, 817 cm^{-1}. HRMS (ESI): calculated for $C_{13}H_{13}N_1O_2S_1Cl_1$ $[M + H]^+$ requires *m/z* 282.03555, found *m/z* 282.03458.

***N*-(2-methylbenzyl)benzenesulfonamide (smaller scale, 0.125 mmol) (3hb)[12]**



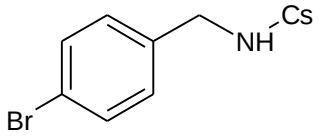
White solid (25 mg, 38%). M.p. 117-123 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.0 Hz, 2H), 7.61-7.57 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.21-7.09 (m, 4H), 4.56 (t, *J* = 4.0 Hz, 1H), 4.12 (d, *J* = 4.0 Hz, 2H), 2.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 133.7, 132.7, 130.6, 129.3, 129.1, 128.9, 128.3, 127.1, 126.2, 45.4, 18.8 ppm. IR (neat): ν = 3274, 3068, 1448, 1323, 1159, 1092, 1036, 886, 722, 686 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{16}N_1O_2S_1$ $[M + H]^+$ requires *m/z* 262.09018, found *m/z* 262.08923.

4-chloro-*N*-(4-methylbenzyl)benzenesulfonamide (3bc)



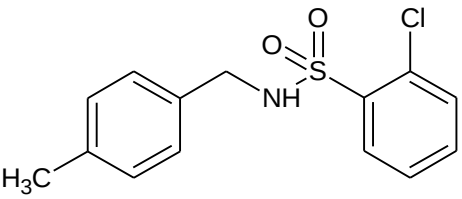
White solid (59 mg, 40%). M.p. 120-122 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.06 (m, 4H), 4.86 (t, *J* = 4.0 Hz, 1H), 4.10 (d, *J* = 4.0Hz, 2H), 2.31 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.5, 137.9, 132.8, 129.4, 129.3, 128.6, 127.8, 47.1, 21.1 ppm. IR (neat): ν = 3245, 2923, 1586, 1325, 1158, 1092, 1058, 757, 565 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Cl_1$ $[M + H]^+$ requires *m/z* 296.05120, found *m/z* 296.05029.

***N*-(4-bromobenzyl)-4-chlorobenzenesulfonamide (smaller scale, 0.125 mmol) (3dc)**



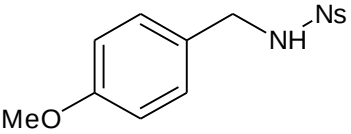
White solid (25 mg, 54%). M.p. 126-128 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.82 (t, *J* = 4.0 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.3, 135.0, 131.8, 129.50, 129.45, 128.5, 122.0, 46.6 ppm. IR (neat): ν = 3246, 3087, 1573, 1320, 1153, 826 cm^{-1}. HRMS (ESI): calculated for $C_{13}H_{12}N_1O_2S_1Cl_1Br_1$ $[M + H]^+$ requires *m/z* 361.94607, found *m/z* 361.94302.

2-chloro-*N*-(4-methylbenzyl)benzenesulfonamide (3bd)



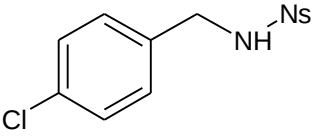
White solid (25 mg, 17%). M.p. 64-66 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.0 Hz, 1H), 7.50-7.49 (m, 2H), 7.42-7.38 (m, 1H), 7.06 (s, 4H), 5.21 (t, *J* = 4.0 Hz, 1H), 4.07 (d, *J* = 4.0 Hz, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.1, 133.6, 132.6, 131.5, 131.4, 131.3, 129.3, 127.9, 127.2, 47.3, 21.1 ppm. IR (neat): ν = 3277, 3094, 2924, 1426, 1327, 1163, 1042, 760, 585 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_1O_2S_1Cl_1$ $[M + H]^+$ requires *m/z* 296.05120, found *m/z* 296.05140.

***N*-(4-methoxybenzyl)-4-nitrobenzenesulfonamide (3ae)[9]**



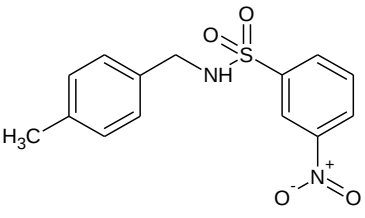
Tan solid (19 mg, 11%). M.p. 126-130 °C. Purification (hexanes:EtOAc, 60:40). R_f = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.82 (t, *J* = 4.0 Hz, 1H), 4.16 (d, *J* = 4.0 Hz, 2H), 3.76 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 129.3, 128.6, 128.3, 127.4, 124.3, 121.0, 114.2, 55.3, 47.0 ppm. IR (neat): ν = 3269, 3110, 29`5, 2840, 1512, 1245, 1151, 1030, 817 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_2O_5S_1$ $[M + H]^+$ requires *m/z* 323.07017, found *m/z* 323.22165.

***N*-(4-chlorobenzyl)-4-nitrobenzenesulfonamide (smaller scale, 0.125 mmol) (3ee)[11]**



Oil (9 mg, 21%). Purification (hexanes:EtOAc, 60:40). R_f = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.84 (t, *J* = 4.0 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 134.3, 134.0, 129.2, 129.0, 128.3, 124.4, 46.7, 29.7 ppm. IR (neat): ν = 3265, 2921, 1606, 1341, 1156, 837 cm^{-1}. HRMS (ESI): calculated for $C_{13}H_{12}N_2O_4S_1Cl_1$ $[M + H]^+$ requires *m/z* 327.02063, found *m/z* 327.07776.

***N*-(4-methylbenzyl)-3-nitrobenzenesulfonamide (3bf)[10]**



White solid (12 mg, 8%). M.p. 110-113 °C. Purification (hexanes:EtOAc, 70:30). R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (t, *J* = 4.0 Hz, 1H), 8.38 (ddd, *J* = 4.0 Hz, 8.0 Hz, 1H), 8.13 (dt, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.04 (s, 4H), 4.93 (t, *J* = 4.0 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.1, 132.5, 130.3, 129.4, 127.9, 127.1, 126.9, 122.4, 47.2, 21.0 ppm. IR (neat): ν = 3250, 3089, 2921, 1607, 1526, 1428, 1331, 1163 cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{15}N_2O_4S_1$ $[M + H]^+$ requires *m/z* 307.07525, found *m/z* 307.07416.

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