SUPPORTING INFORMATION

Palladium-Catalyzed Direct Alpha Arylation of Methyl Sulfones with Aryl Bromides

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General Methods. All reactions were carried out under an atmosphere of dry nitrogen. Anhydrous CPME, dioxane, and 2-MeTHF were purchased from Sigma-Aldrich and used as solvent without purification, Toluene was dried through activated alumina columns. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were obtained from Sigma-Aldrich, Acros, or Matrix Scientific, and solvents were purchased from Fisher Scientific. Flash chromatography was performed with Silica gel (230–400 mesh, Silicycle). The NMR spectra were obtained using a Brüker 500 MHz Fourier-transform NMR spectrometer. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 1600 Series spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of Sulfones.

Sulfones were prepared according to literature procedures.[1,2]

1-Methyl-2-(methylsulfonyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz ,1H), 7.54−7.51 (m, 1H), 7.40−7.27 (m, 2H), 3.08 (s, 3H), 2.72 (s, 3H) ppm. This data matches the reported spectral data.[3]

1-Methoxy-3-(methylsulfonyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52−7.43 (m, 3H), 7.18−7.16 (m, 1H), 3.87 (s, 3H), 3.07 (s, 3H) ppm. This data matches the reported spectral data.[4]

1-Methoxy-4-(methylsulfonyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88−7.85 (m, 2H), 7.04−7.01 (m, 2H), 3.89 (s, 3H), 3.03 (s, 3H) ppm. This data matches the reported spectral data.[5]

1-Fluoro-4-(methylsulfonyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00−7.97 (m, 2H), 7.28−7.25 (m, 2H), 3.09 (s, 3H) ppm. This data matches the reported spectral data.[6]

1-Chloro-4-(methylsulfonyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 9.0 Hz 2H), 3.08 (s, 3H) ppm. This data matches the reported spectral data.[7]

1-(Methylsulfonyl)-4-(trifluoromethyl)benzene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz ,2H), 7.86 (d, J = 8.0 Hz ,2H), 3.10 (s, 3H) ppm. This data matches the reported spectral data.[8]

1-(Methylsulfonyl)naphthalene: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, J = 8.5 Hz ,1H), 8.31 (d, J = 7.5 Hz ,1H), 8.10 (d, J = 8.5 Hz ,1H), 7.95 (d, J = 8.0 Hz ,1H), 7.71−7.67 (m, 1H), 7.61−7.55 (m, 2H), 3.19 (s, 3H) ppm. This data matches the reported spectral data.[9]

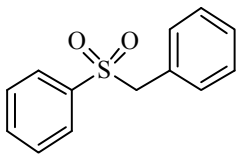
3-(Methylsulfonyl)pyridine: 1H NMR (500 MHz, CDCl3): δ 9.17 (d, J = 1.5 Hz ,1H), 8.91 (dd, J = 5.0 Hz, 1.5 Hz ,1H), 8.27–8.24 (m, 1H), 7.56-7.29 (m, 1H), 3.13 (s, 3H) ppm. This data matches the reported spectral data.[3]

2-Methyl-2-(methylsulfonyl)propane: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.82 (s, 3H), 1.43 (s, 9H) ppm. This data matches the reported spectral data.[10]

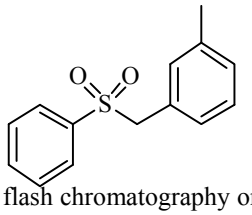
(Methylsulfonyl)cyclohexane: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88–2.84 (m, 1H), 2.83 (s, 3H), 2.22–2.19 (m, 2H), 1.96–1.92 (m, 2H), 1.77–1.73 (m, 1H), 1.55–1.46 (m, 2H), 1.37–1.28 (m, 2H), 1.27–1.18 (m, 1H) ppm. This data matches the reported spectral data.[11]

Procedure and Characterization for the Pd-Catalyzed Arylation of Alkylsulfones.

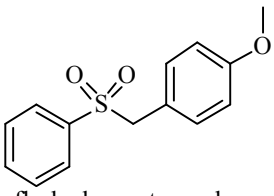
General Procedure: A flame-dried microwave vial equipped with a stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and ligand **L** (16.1 mg, 0.04 mmol) under a nitrogen atmosphere. The LiO^tBu (48.3 mg, 0.60 mmol, 3 equiv) was added to the reaction vial, followed by 1 mL dry toluene via syringe. After the catalyst solution stirred for 30 min at 25 °C, methyl phenyl sulfone (31.2 mg, 0.20 mmol, 1.0 equiv) was added to the mixture. The microwave vial was sealed and bromobenzene (42.4 μL, 0.40 mmol, 2.0 equiv) was added by syringe under nitrogen atmosphere. The reaction mixture was stirred until TLC indicated complete consumption of the starting sulfone. The reaction mixture was quenched with H_2O (2 mL) and extracted with ethyl acetate (3 mL x 3). The organic layer was dried over anhydrous Na_2SO_4 and the volatile materials were removed under reduced pressure. The resulting product was purified by flash column chromatography on silica gel to give purified product.



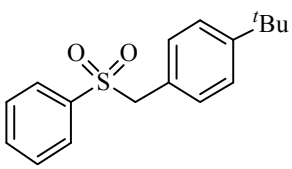
(Benzylsulfonyl)benzene (3a): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^tBu (48.3 mg, 0.60 mmol) and **2a** (42.4 µL, 0.40 mmol). The crude product was purified by flashchromatography on silica gel (eluted with EtOAc:hexanes = 1:5) to give the product (39.9 mg, 86% yield) as a white solid; R_f = 0.40 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.58 (m, 3H), 7.43 (t, J = 7.5 Hz, 2H), 7.31–7.29 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.31 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.8, 133.7, 130.8, 128.8, 128.7, 128.5, 128.5, 128.0, 62.8 ppm; These spectroscopic data correspond to previously reported data.[7]



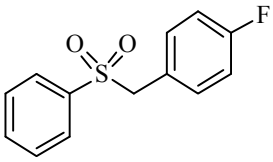
1-Methyl-3-((phenylsulfonyl)methyl)benzene (3b): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^tBu (48.3 mg, 0.60 mmol) and **2b** (48.0 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:5) to give the product (40.4 mg, 82% yield) as a white solid; R_f = 0.42 (hexanes:EtOAc = 4:1); m.p. = 120–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.0 Hz, 2H), 7.61–7.58 (m, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 6.5 Hz, 2H), 6.90 (s, 1H), 6.84 (d, J = 6.0 Hz, 1H), 4.26 (s, 2H), 2.26 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.2, 137.9, 133.6, 131.5, 129.4, 128.8, 128.6, 128.3, 127.8, 127.8, 62.8, 21.2 ppm; IR (thin film): 3010, 2963, 2903, 2868, 1312, 1156, 1117, 777, 697 cm^{-1}; HRMS calc'd for $C_{14}H_{15}O_2S^+$ 247.0793, found 247.0790 $[M+H]^+$.



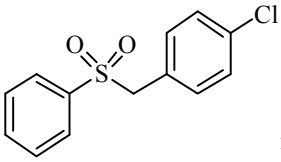
1-Methoxy-4-((phenylsulfonyl)methyl)benzene (3c): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2c** (50.0 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (40.8 mg, 78% yield) as a white solid; R_f = 0.32 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.63 (m, 3H), 7.59 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.00–6.98 (m, 2H), 6.78 (dd, J = 6.5 Hz, 2.0 Hz, 2H), 4.25 (s, 2H), 3.78 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.9, 137.8, 133.6, 131.9, 128.8, 128.6, 119.9, 113.9, 62.1, 55.2.ppm; These spectroscopic data correspond to previously reported data.[12]



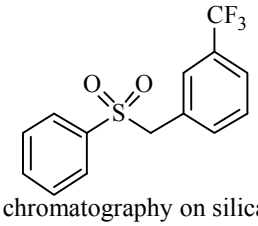
1-(*tert*-Butyl)-4-((phenylsulfonyl)methyl)benzene (3d): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2d** (69.0 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (51.8 mg, 90% yield) as a white solid; R_f = 0.47 (hexanes:EtOAc = 4:1); m.p. = 162–165 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 8.5 Hz, 1.5 Hz, 2H), 7.61–7.58 (m, 1H), 7.46–7.42 (m, 2H), 7.29–7.27 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 4.28 (s, 2H), 1.28 (s, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.9, 138.1, 133.6, 130.5, 128.8, 128.5, 125.5, 124.8, 62.4, 34.5, 31.2 ppm; IR (thin film): 2962, 1447, 1290, 1147, 1136, 1084, 733, 598, 548 cm^{-1}; HRMS calc'd for $C_{17}H_{20}O_2NaS^+$ 311.1082, found 311.1089 $[M+Na]^+$.



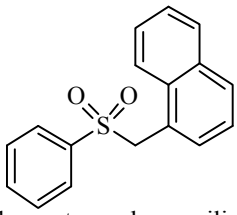
1-Fluoro-4-((phenylsulfonyl)methyl)benzene (3e): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2e** (44.6 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (41.5 mg, 83% yield) as a white solid; R_f = 0.40 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, J = 16.0 Hz, 8.0 Hz, 3H), 7.48–7.45 (m, 2H), 7.08–7.05 (m, 2H), 6.97–6.93 (m, 2H), 4.28 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $J_{C\text{-}F}$ = 247 Hz), 137.6, 133.8, 132.5 (d, $J_{C\text{-}F}$ = 8 Hz), 128.9, 128.5, 123.9 (d, $J_{C\text{-}F}$ = 4 Hz), 115.6 (d, J = 22 Hz), 61.9 ppm; These spectroscopic data correspond to previously reported data.[13]



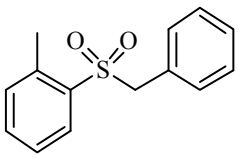
1-Chloro-4-((phenylsulfonyl)methyl)benzene (3f): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2f** (76.0 mg, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (43.1 mg, 81% yield) as a white solid; R_f = 0.42 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66–7.64 (m, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 4.27 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.6, 135.0, 133.9, 132.0, 129.0, 128.8, 128.5, 126.6, 62.0 ppm; These spectroscopic data correspond to previously reported data.[14]



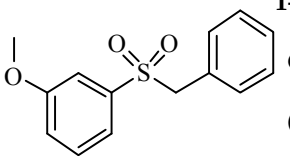
1-((Phenylsulfonyl)methyl)-3-(trifluoromethyl)benzene (3g): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2g** (56.0 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (48.0 mg, 80% yield) as a white solid; R_f = 0.42 (hexanes:EtOAc = 4:1); m.p. = 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.61 (m, 3H), 7.57 (d, J = 7.5 Hz, 1H), 7.48–7.44 (m, 2H), 7.39 (dd, J = 19.0 Hz, 7.5 Hz, 2H), 7.21 (s, 1H), 4.36 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.3 , 134.2, 134.0, 131.2, 130.7 (q, $J_{C\text{-}F}$ = 33 Hz), 129.2, 129.1, 129.0, 128.5, 127.5, 127.4, 126.8, 125.5, 125.4, 124.6, 122.5, 120.3, 62.2 ppm; IR (thin film): 2951, 1449, 1334, 1309, 1142, 1119, 1073, 813, 701, 685, 544 cm^{-1}; HRMS calc'd for $C_{14}H_{11}O_2F_3NaS^+$ 322.0330, found 323.0345 $[M+Na]^+$.



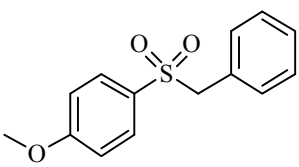
1-((Phenylsulfonyl)methyl)naphthalene (3h): The reaction was performed following the General Procedure with **1a** (31.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2h** (56.0 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (41.2 mg, 73% yield) as a white solid; R_f = 0.40 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 1.5 Hz, 3H), 7.59–7.57 (m, 2H), 7.50–7.46 (m, 1H), 7.43–7.38 (m, 2H), 7.33–7.29 (m, 3H), 7.18 (d, J = 7.0 Hz, 1H), 4.79 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.9, 133.7, 133.6, 132.0, 130.6, 129.7, 128.8, 128.6, 126.6, 125.9, 125.0, 124.4, 123.5, 59.8 ppm; These spectroscopic data correspond to previously reported data.[15]



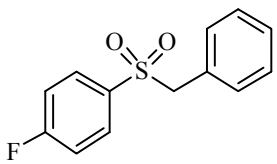
1-(Benzylsulfonyl)-2-methylbenzene (4b): The reaction was performed following the General Procedure with **1b** (34.0 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (42.3 mg, 86% yield) as a white solid; R_f = 0.47 (hexanes:EtOAc = 4:1); m.p. = 90–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 1.0 Hz, 1H), 7.45–7.42 (m, 1H), 7.27–7.18 (m, 5H), 7.05 (d, J = 7.5 Hz, 2H), 4.31 (s, 2H), 2.50 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.6, 135.9, 133.7, 132.4, 130.8, 130.7, 128.7, 128.5, 127.9, 126.4, 62.1, 20.3 ppm; IR (thin film): 3063, 1456, 1309, 1290, 1154, 1120, 763, 700, 526 cm^{-1}; HRMS calc'd for $C_{14}H_{14}O_2NaS^+$ 269.0612, found 269.0615 [M+Na]$^+$.



1-(Benzylsulfonyl)-3-methoxybenzene (4c): The reaction was performed following the General Procedure with **1c** (37.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (44.5 mg, 85% yield) as a white solid; R_f = 0.42 (hexanes:EtOAc = 4:1); m.p. = 105–107 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.30 (m, 2H), 7.27–7.24 (m, 3H), 7.11–7.09 (m, 3H), 7.02 (d, J = 1.5Hz, 1H), 4.30 (s, 2H), 3.69 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.6, 138.8, 130.8, 129.9, 128.7, 128.5, 128.2, 120.7, 120.6, 112.7, 62.8, 55.5 ppm; IR (thin film): 1597, 1480, 1308, 1149, 780, 699, 512 cm^{-1}; HRMS calc'd for $C_{14}H_{14}O_3NaS^+$ 285.0561, found 285.0560 [M+Na]$^+$.

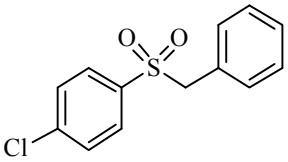


1-(Benzylsulfonyl)-4-methoxybenzene (4d): The reaction was performed following the General Procedure with **1d** (37.2mg, 0.20mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (42.5 mg, 81% yield) as a white solid; R_f = 0.40 (hexanes:EtOAc = 4:1); m.p. = ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.51 (m, 2H), 7.30–7.29 (m, 1H), 7.27–7.24 (m, 2H), 7.09–7.07 (m, 2H), 6.89–6.87 (m, 2H), 4.28 (s, 2H), 3.83 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.6, 130.8, 130.7, 129.3, 128.6, 128.5, 128.4, 114.0, 63.0, 55.6 ppm; These spectroscopic data correspond to previously reported data.[16]

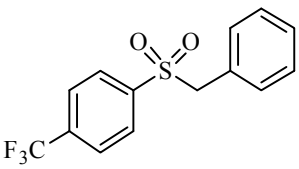


1-(Benzylsulfonyl)-4-fluorobenzene (4e): The reaction was performed following the General Procedure with **1e** (34.8 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and

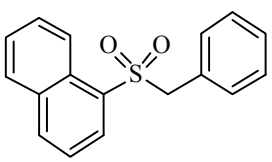
2a (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:5) to give the product (41.1 mg, 82% yield) as a white solid; R_f = 0.45 (hexanes:EtOAc = 4:1); m.p. = 152–154 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.60 (m, 2H), 7.33–7.31 (m, 1H), 7.29–7.26 (m, 2H), 7.13–7.07(m, 4H), 4.31 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (d, $J_{C\text{-}F}$ = 255 Hz), 133.7 (d, $J_{C\text{-}F}$ = 3 Hz), 131.5, 131.4, 130.7, 128.8, 128.6, 127.9, 116.1 (d, $J_{C\text{-}F}$ = 23 Hz), 62.9 ppm; IR (thin film): 2932, 1598, 1315, 1290, 1150, 1086, 845, 775, 696, 547, 509 cm^{-1}; HRMS calc'd for $C_{13}H_{12}O_2SF^+$ 251.0542, found 251.0548 $[M+H]^+$.



1-(Benzylsulfonyl)-4-chlorobenzene (4f): The reaction was performed following the General Procedure with **1f** (38.0 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:5) to give the product (43.1 mg, 81% yield) as a white solid; R_f = 0.53 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.40–7.38 (m, 2H), 7.33–7.30 (m, 1H), 7.27–7.24 (m, 2H), 7.09–7.07 (m, 2H), 4.31 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.4, 136.2, 130.8, 130.1, 129.1, 128.9, 128.6, 127.8, 62.8 ppm; These spectroscopic data correspond to previously reported data.[17]

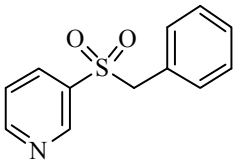


1-(Benzylsulfonyl)-4-(trifluoromethyl)benzene (4g): The reaction was performed following the General Procedure with **1g** (44.8 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (50.4 mg, 84% yield) as a white solid; R_f = 0.53 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H), 4.35 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.3, 135.4 (q, $J_{C\text{-}F}$ = 33 Hz), 134.9, 130.8, 129.3, 129.0, 128.7, 127.4, 126.3, 125.9 (q, $J_{C\text{-}F}$ = 4 Hz), 124.1, 121.9, 119.8, 62.7 ppm; These spectroscopic data correspond to previously reported data.[16]

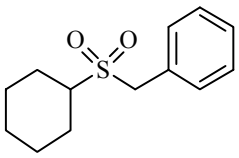


1-(Benzylsulfonyl)naphthalene (4h): The reaction was performed following the General Procedure with **1h** (41.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash

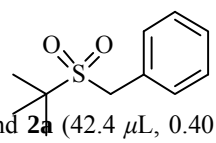
chromatography on silica gel (eluted with EtOAc:hexanes = 1:5) to give the product (46.8 mg, 83% yield) as a white solid; R_f = 0.32 (hexanes:EtOAc = 4:1); m.p. = 110–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.97–7.94 (m, 2H), 7.70–7.66 (m, 1H), 7.63–7.60 (m, 1H), 7.43–7.40 (m, 1H), 7.25-7.21 (m, 1H), 7.16–7.13 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.49 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 135.1, 133.9, 132.9, 131.4, 130.6, 129.2, 129.1, 128.6, 128.6, 128.4, 127.9, 126.9, 124.1, 124.0, 62.3 ppm; IR (thin film): 1507, 1456, 1312, 1156, 1117, 777, 698, 497 cm^{-1}; HRMS calc'd for $C_{17}H_{15}O_2S^+$ 283.0793, found 283.0782 $[MH]^+$.



3-(Benzylsulfonyl)pyridine (4i): The reaction was performed following the General Procedure with **1i** (31.4 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (32.6 mg, 70% yield) as a white solid; R_f = 0.45 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80-8.79 (m, 2H), 7.85–7.83 (m, 1H), 7.39–7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 4.38 (s, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.2, 149.4, 136.4, 134.1, 130.8, 129.1, 128.8, 127.4, 123.4, 63.1 ppm; These spectroscopic data correspond to previously reported data.[17]

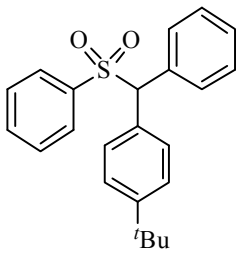


((Cyclohexylsulfonyl)methyl)benzene (4j): The reaction was performed following the General Procedure with **1j** (32.4 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (39.5 mg, 83% yield) as a white solid; R_f = 0.36 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.37 (m, 5H), 4.18 (s, 2H), 2.77–2.70 (m, 1H), 2.12 (d, *J* = 12.5 Hz, 2H), 1.89 (dd, *J* = 9.5 Hz, 4.0 Hz, 2H), 1.69–1.67 (m, 1H), 1.61–1.53 (m, 2H), 1.26–1.20 (m, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 130.6, 128.9, 128.7, 127.9, 59.2, 56.1, 25.0, 24.9 ppm; These spectroscopic data correspond to previously reported data.[18]



((*tert*-Butylsulfonyl)methyl)benzene (4k): The reaction was performed following the General Procedure with **1k** (27.2 mg, 0.20 mmol), LiO^{t}Bu (48.3 mg, 0.60 mmol) and **2a** (42.4 μL, 0.40 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product (35.6 mg, 84% yield) as a white solid; R_f = 0.4 (hexanes:EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.39 (m, 2H), 7.34–7.33 (m, 3H), 4.15 (s, 2H), 1.39 (s, 9H) ppm; ^{13}C{^{1}H} NMR

(125 MHz, $CDCl_3$): δ 131.2, 128.6, 127.3, 59.8, 52.7, 23.6 ppm;. These spectroscopic data correspond to previously reported data.[19]



1-(*tert*-Butyl)-4-(phenyl(phenylsulfonyl)methyl)benzene (5a): The reaction was performed following the General Procedure with **3a** (46.4 mg, 0.20 mmol), KO^{t}Bu (67.4 mg, 0.60 mmol) and **2d** (69.0 μL, 0.40 mmol) in 1 mL dioxane. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (59.0 mg, 81% yield) as a white solid; R_f = 0.5 (hexanes:EtOAc = 4:1); m.p. = 172–174 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.59 (m, 2H), 7.52–7.47 (m, 5H), 7.35–7.32 (m, 4H), 7.29–7.28 (m, 3H), 5.26 (s, 1H), 1.28 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 151.7, 138.2, 133.3, 133.1, 129.9, 129.6, 129.5, 129.0, 128.6, 128.5, 128.4, 125.6, 76.2, 34.5, 31.2 ppm; IR (thin film): 2945, 1308, 1142, 1083 cm^{-1}; HRMS calc'd for $C_{23}H_{24}O_2NaS^+$ 387.1395, found 387.1394 $[MNa]^+$.

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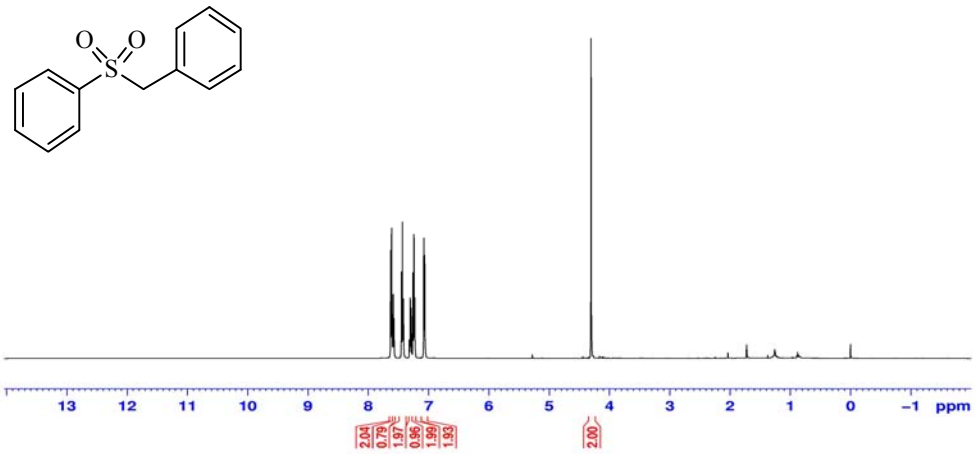
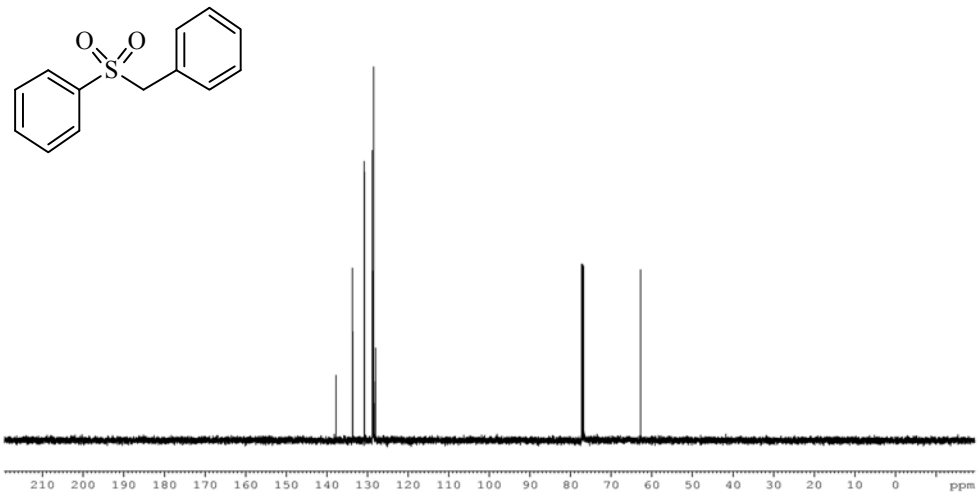
NMR Spectra.

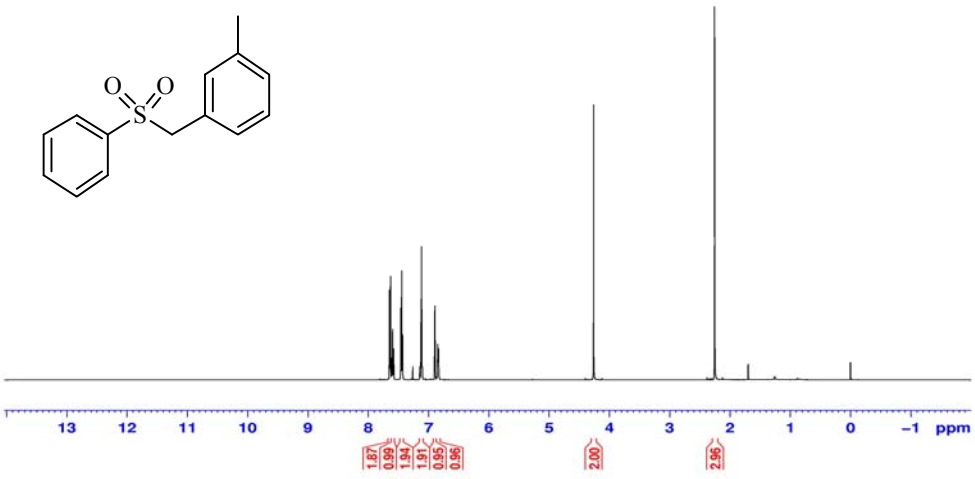
(Benzylsulfonyl)benzene (3a)



(Benzylsulfonyl)benzene (3a)



1-Methyl-3-((phenylsulfonyl)methyl)benzene (3b)



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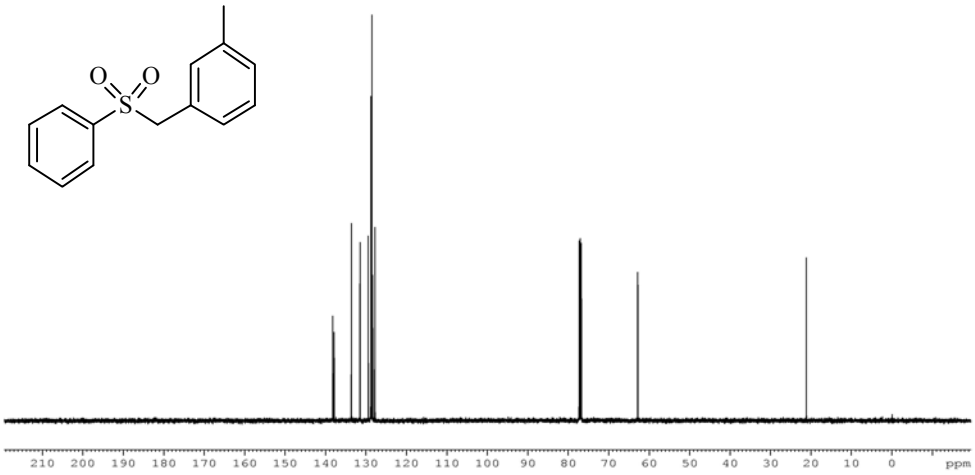

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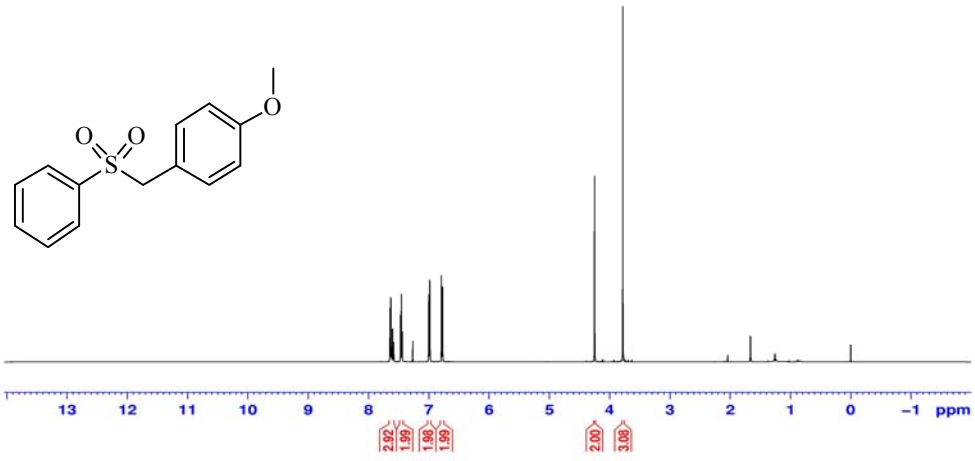

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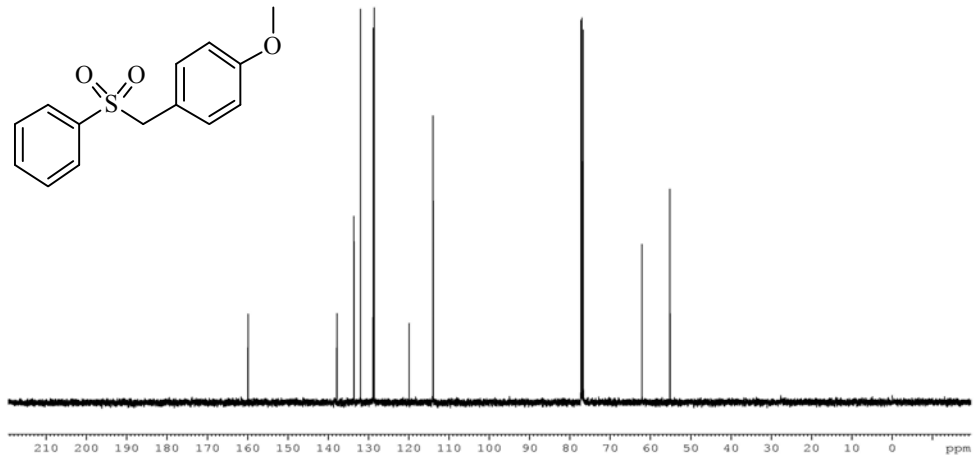

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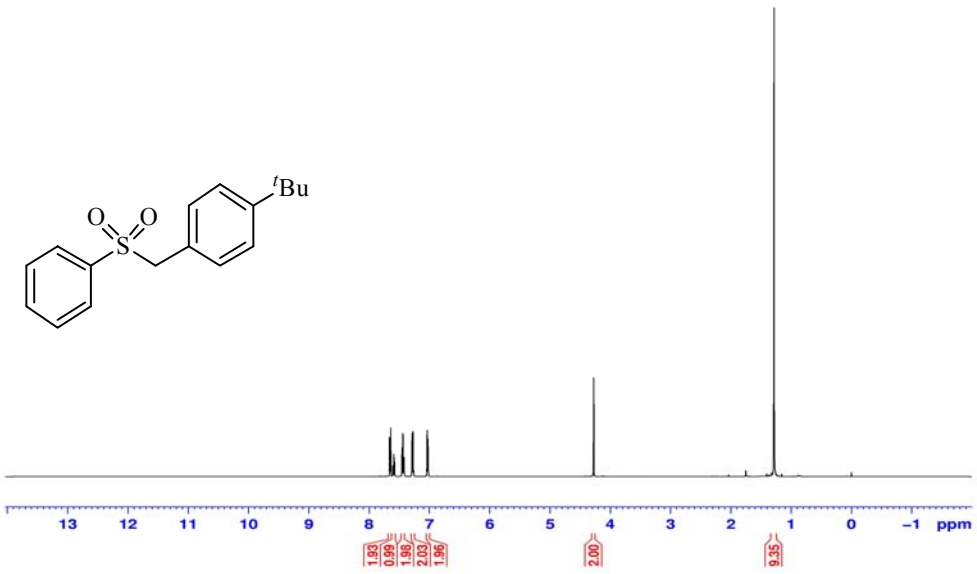

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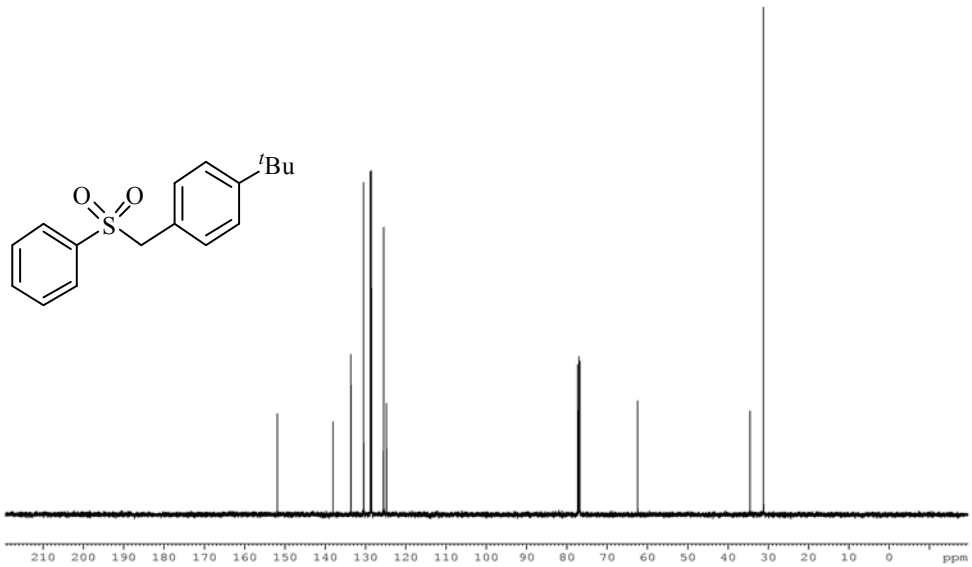
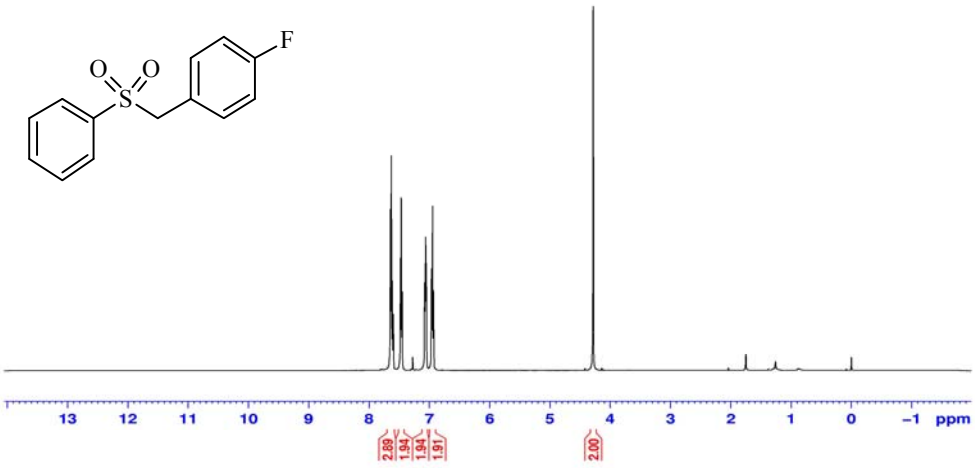
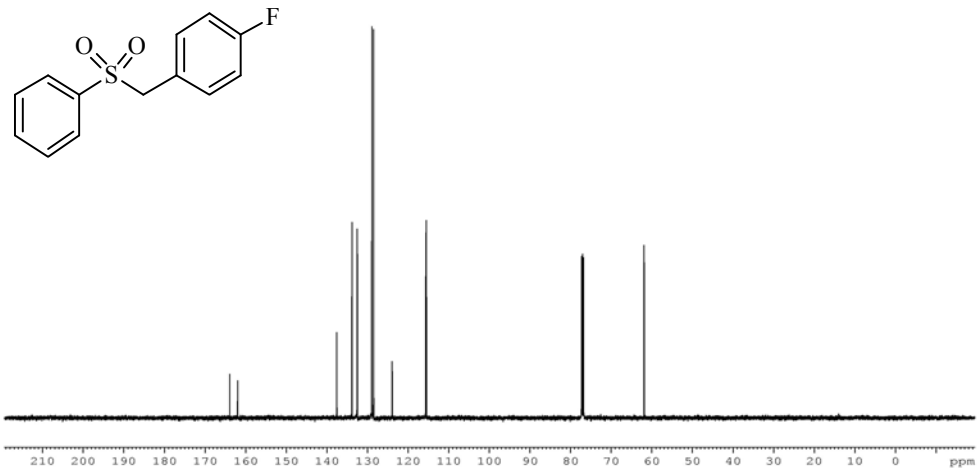


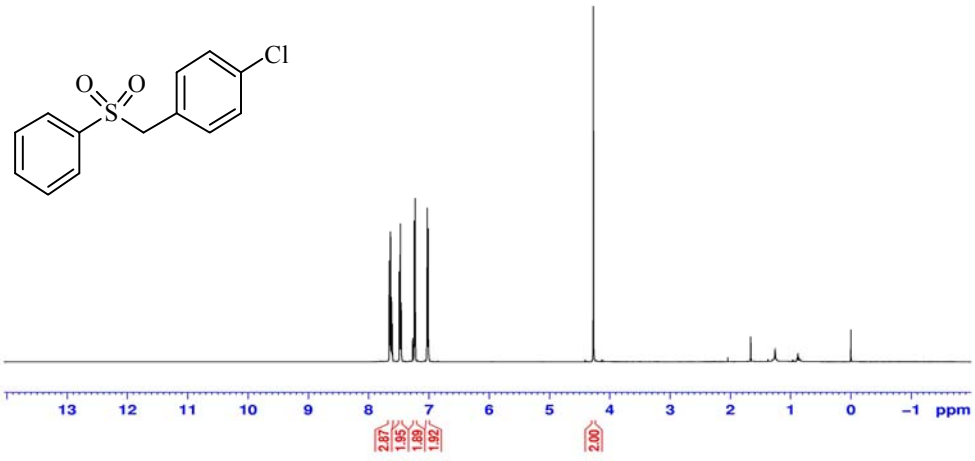
1-Fluoro-4-((phenylsulfonyl)methyl)benzene (3e)



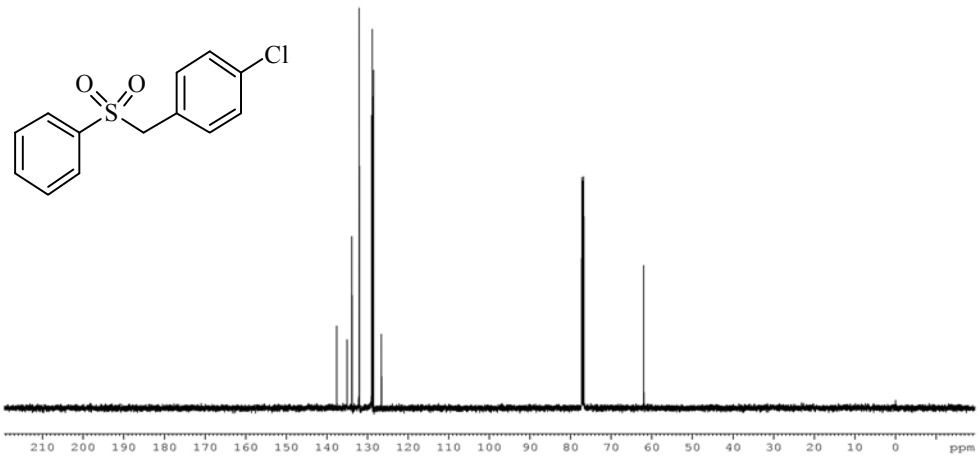
1-Fluoro-4-((phenylsulfonyl)methyl)benzene (3e)



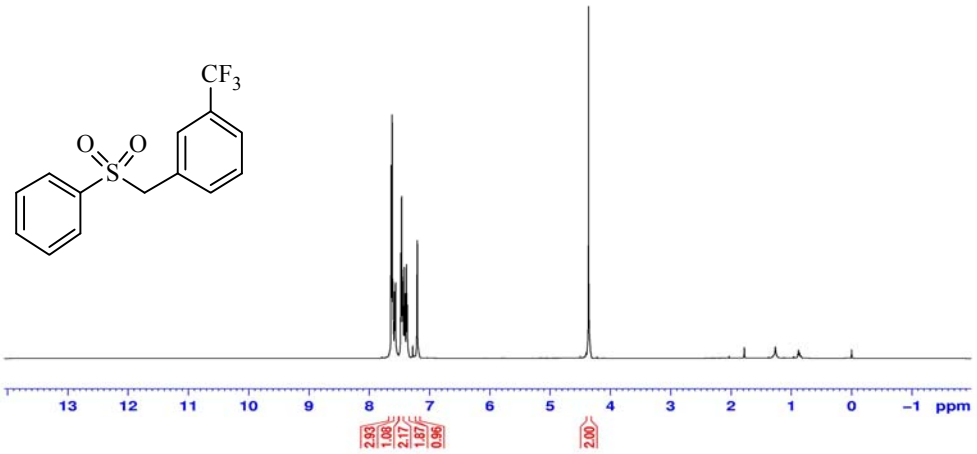
1-Chloro-4-((phenylsulfonyl)methyl)benzene (3f)



1-Chloro-4-((phenylsulfonyl)methyl)benzene (3f)



1-((Phenylsulfonyl)methyl)-3-(trifluoromethyl)benzene **(3g)**



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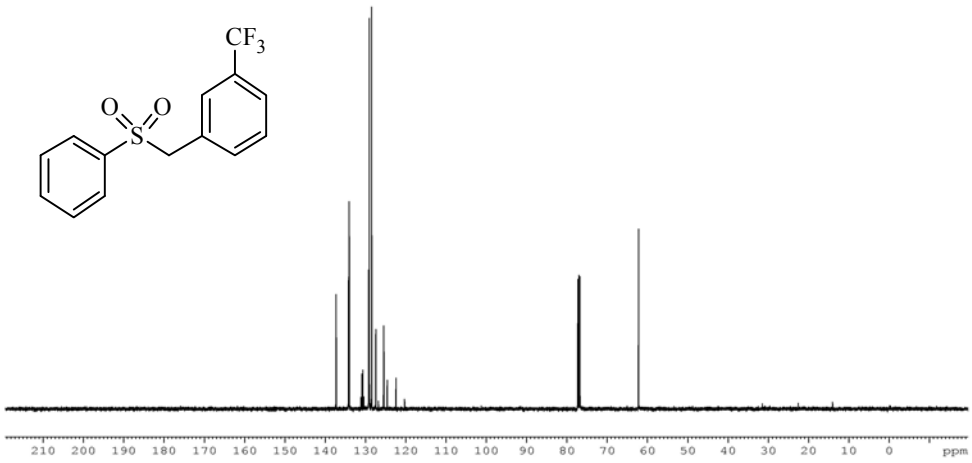
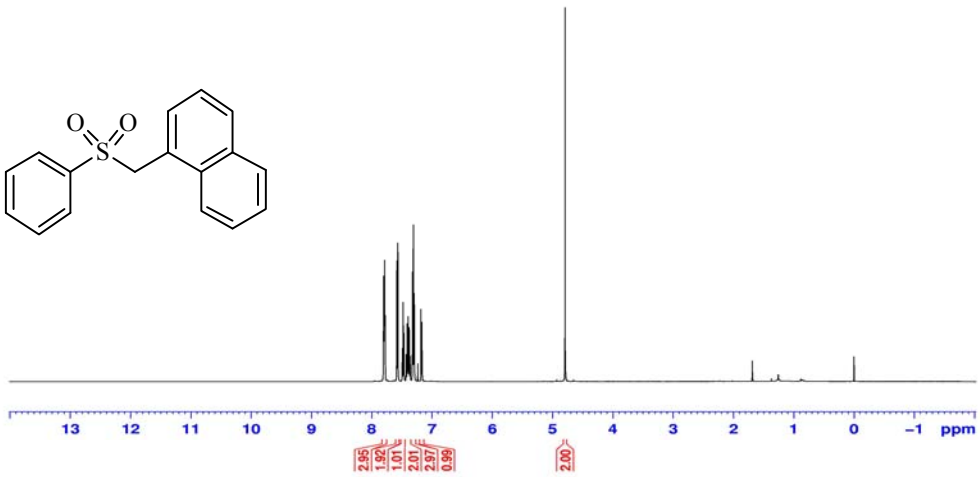
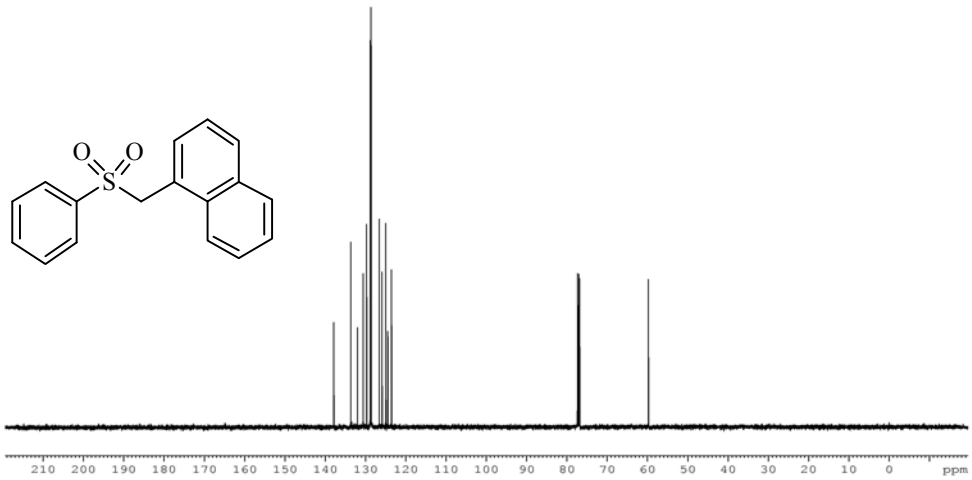


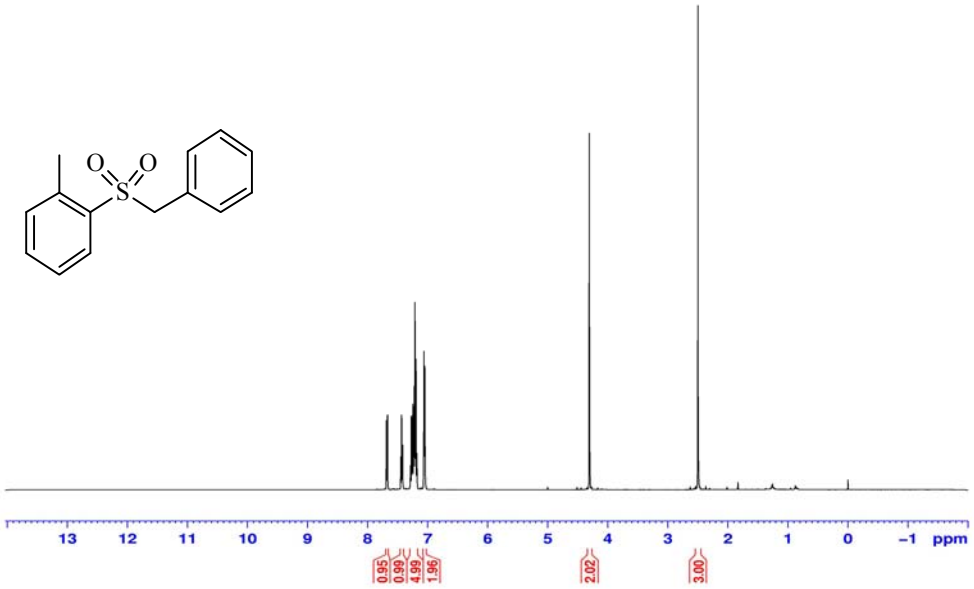
1-((Phenylsulfonyl)methyl)naphthalene (3h)



1-((Phenylsulfonyl)methyl)naphthalene (3h)



1-(Benzylsulfonyl)-2-methylbenzene (4b)



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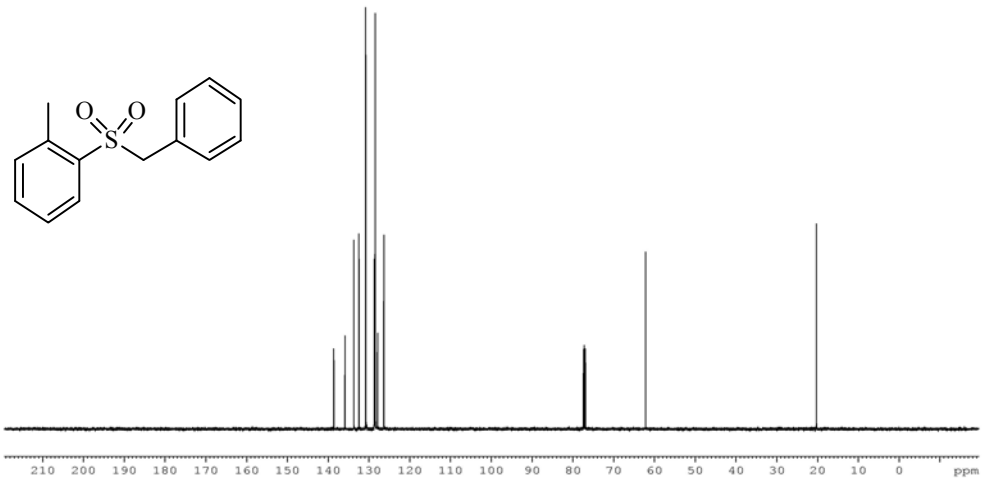

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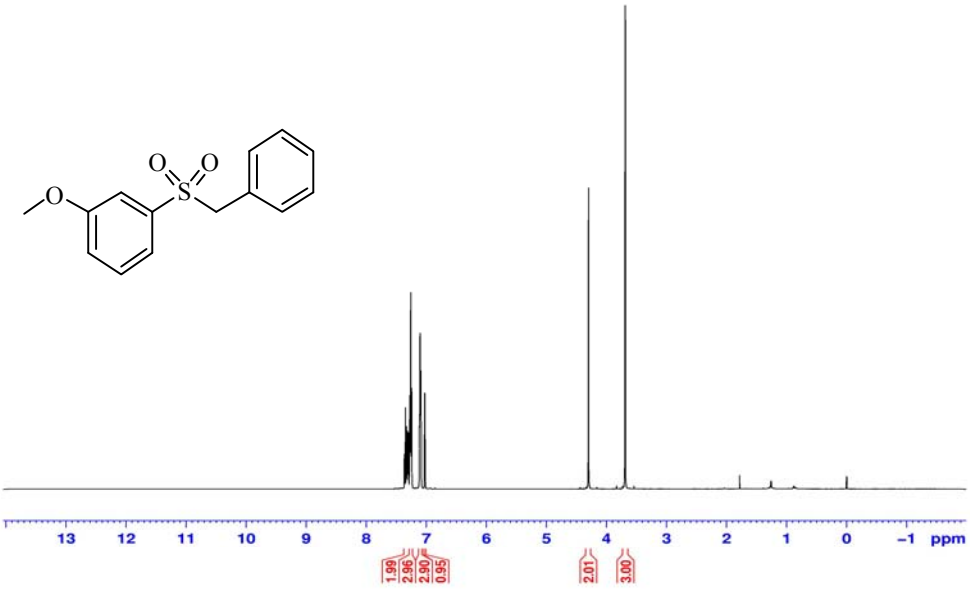

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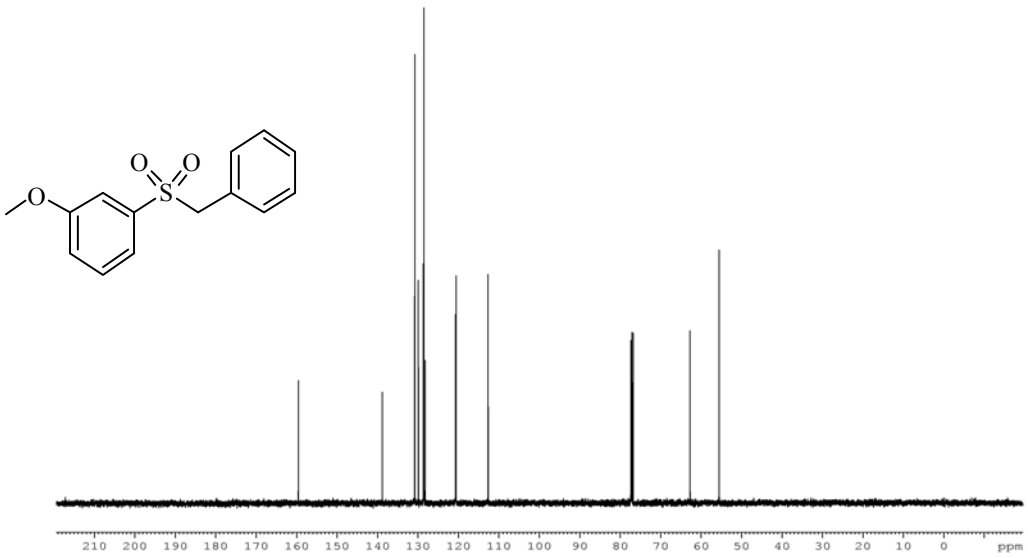

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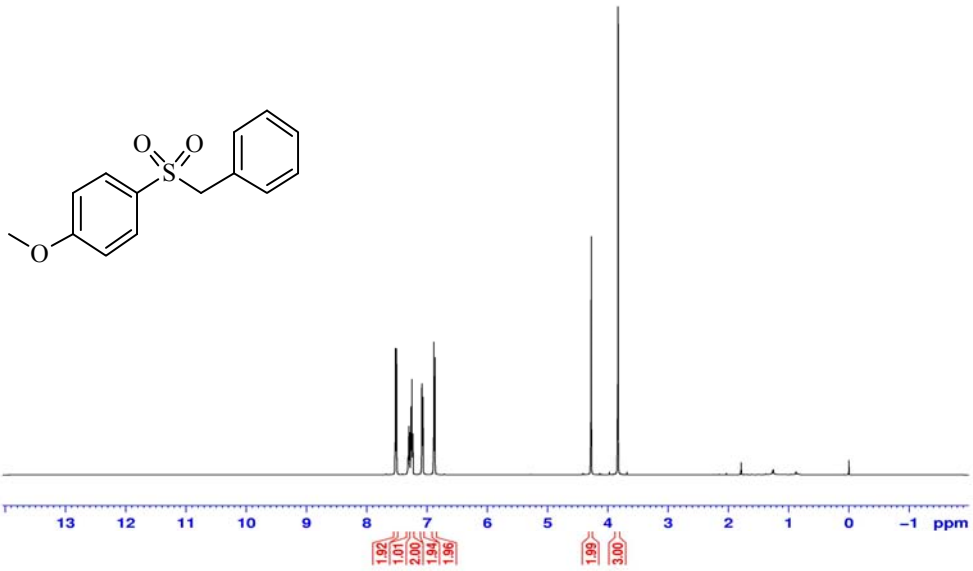

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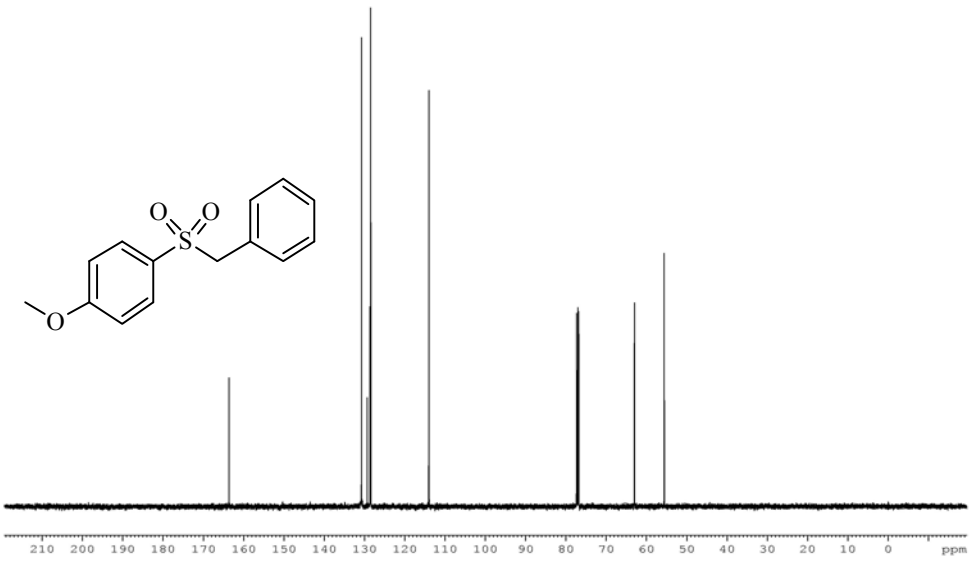

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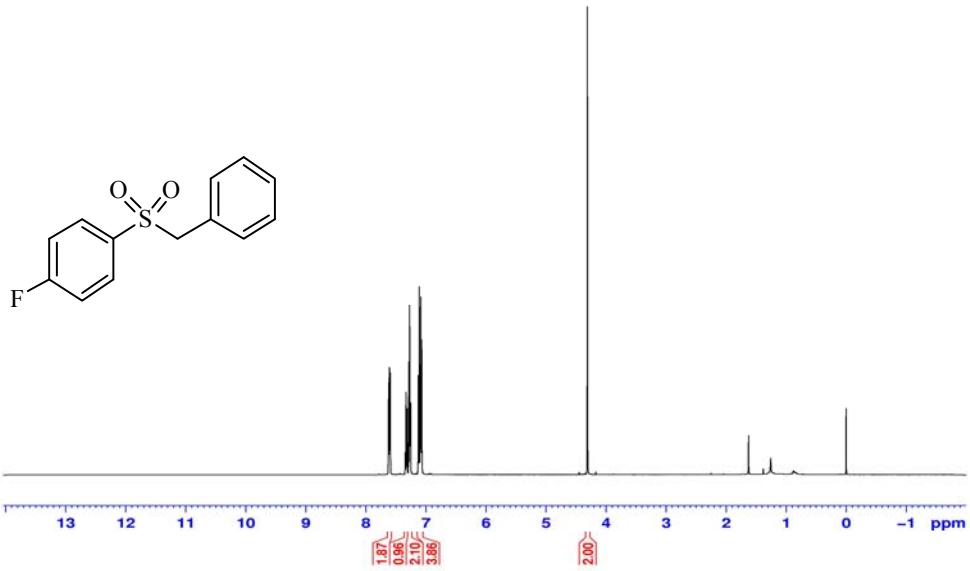

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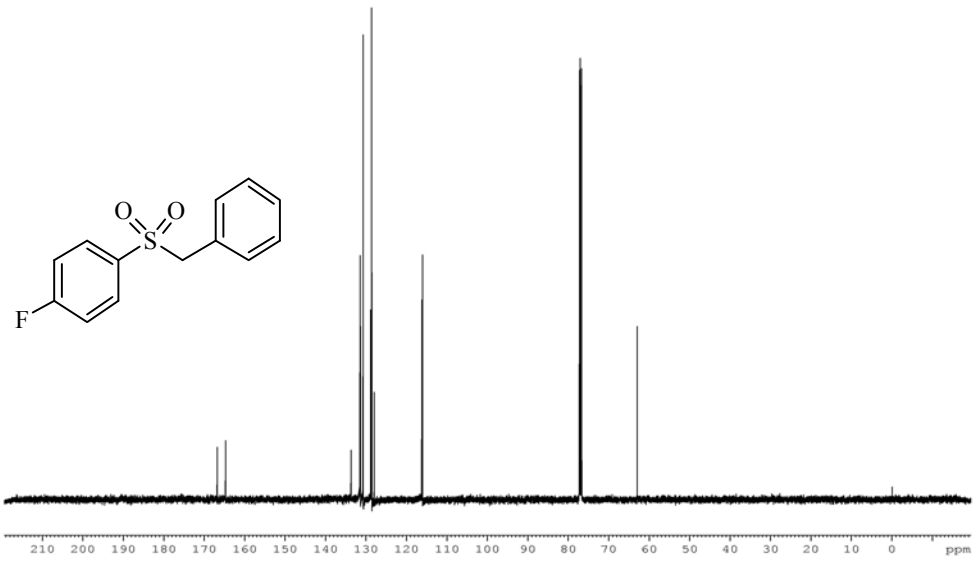

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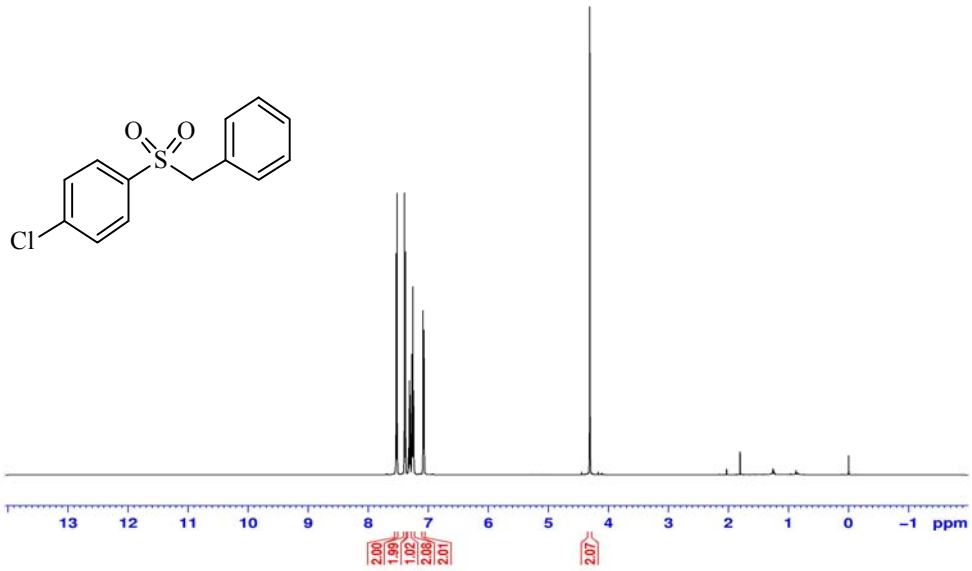
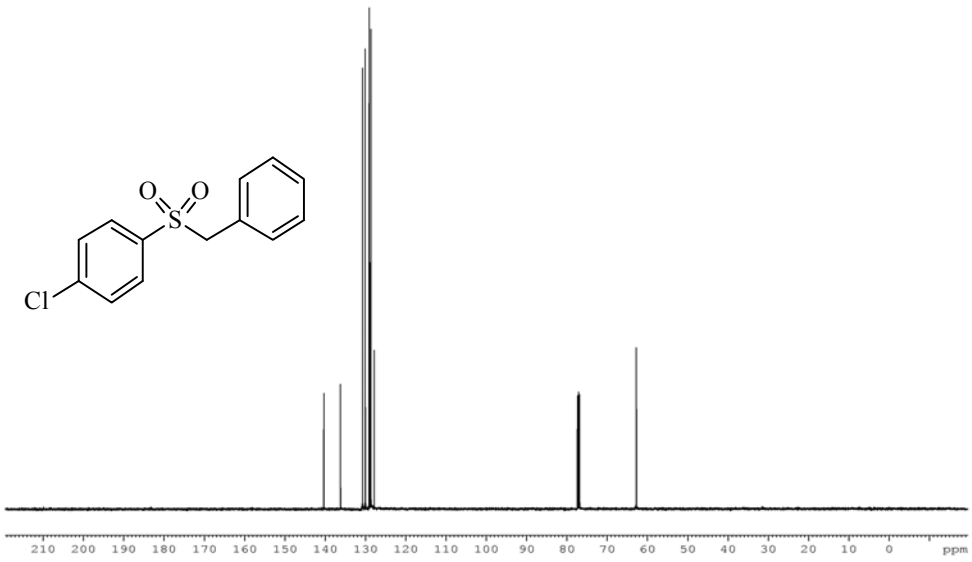
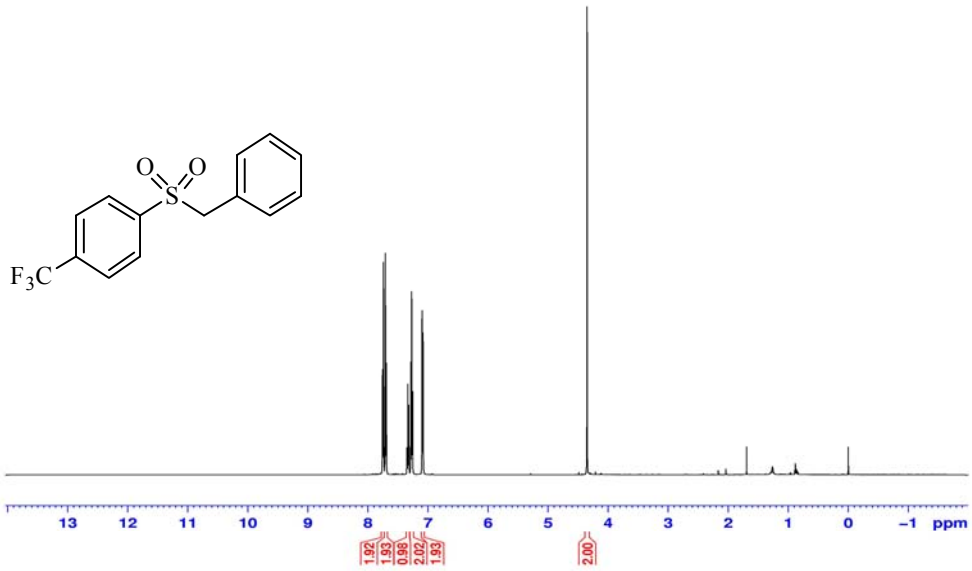


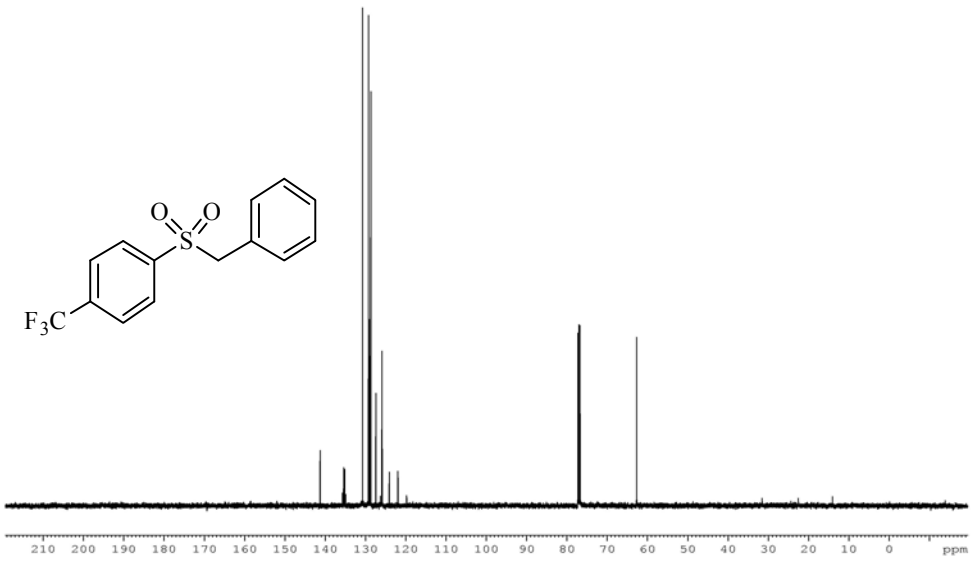
1-(Benzylsulfonyl)-4-chlorobenzene (4f)



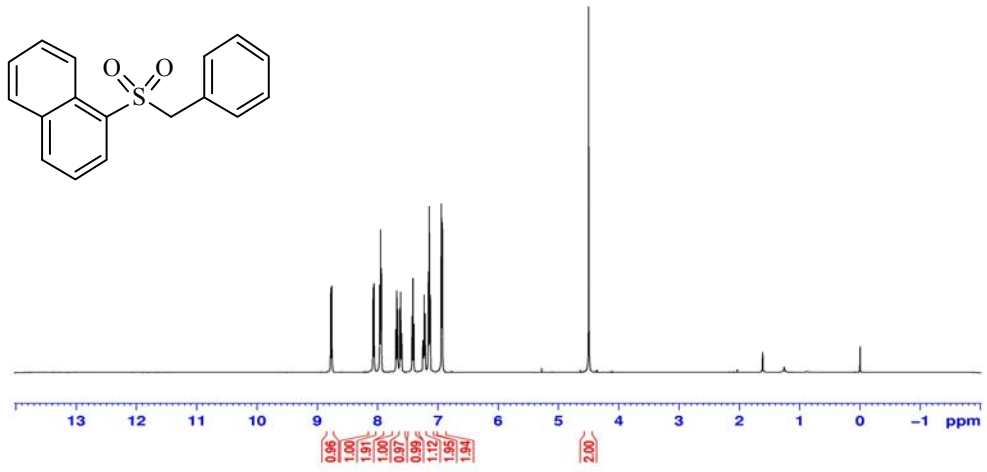
1-(Benzylsulfonyl)-4-(trifluoromethyl)benzene (4g)



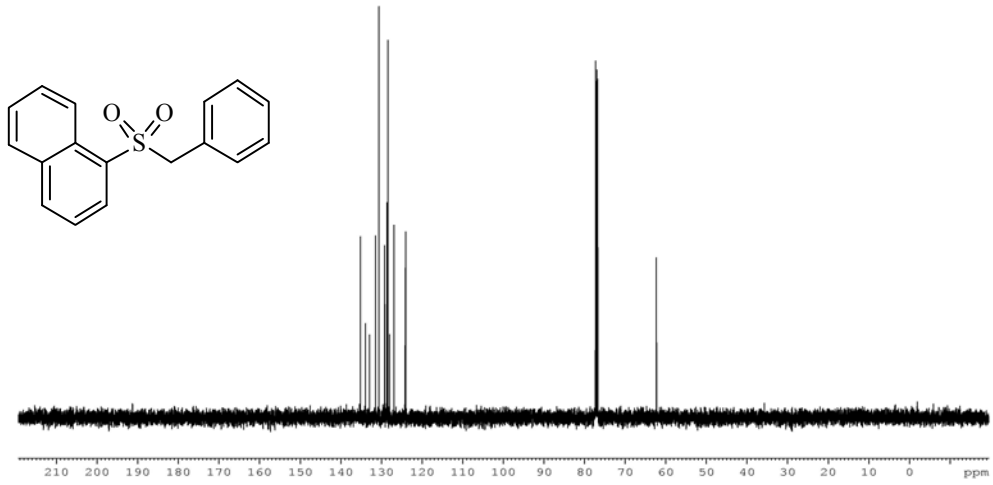
1-(Benzylsulfonyl)-4-(trifluoromethyl)benzene (4g)



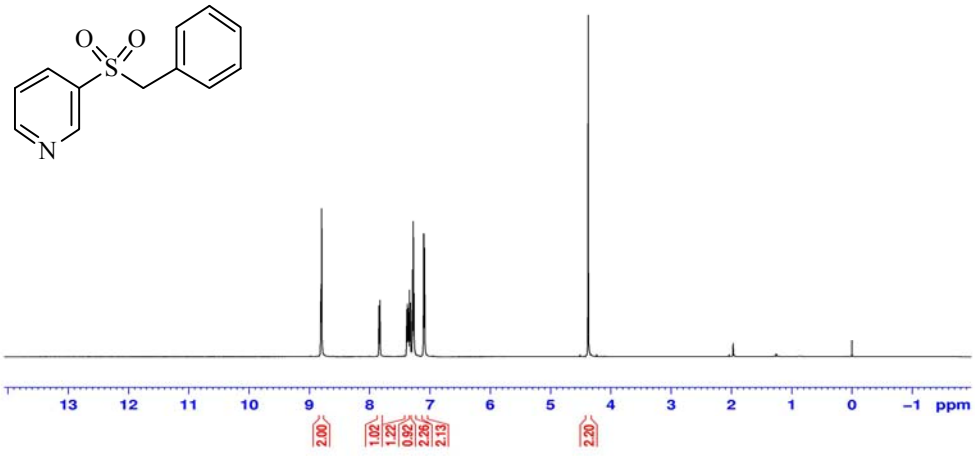
1-(Benzylsulfonyl)naphthalene (4h)



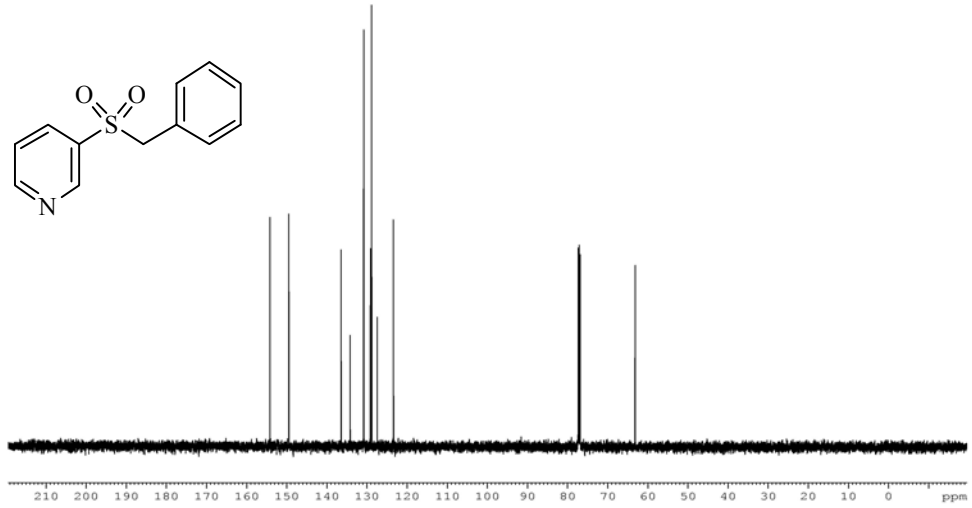
1-(Benzylsulfonyl)naphthalene (4h)



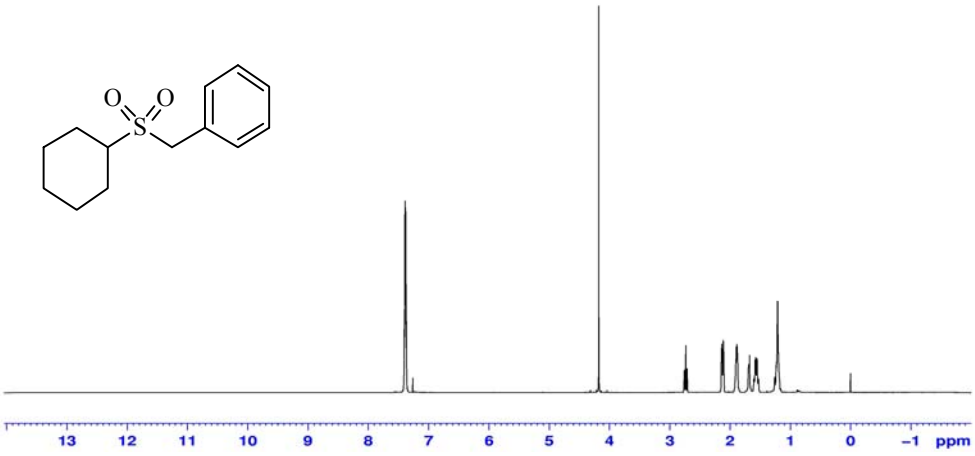
3-(Benzylsulfonyl)pyridine (4i)



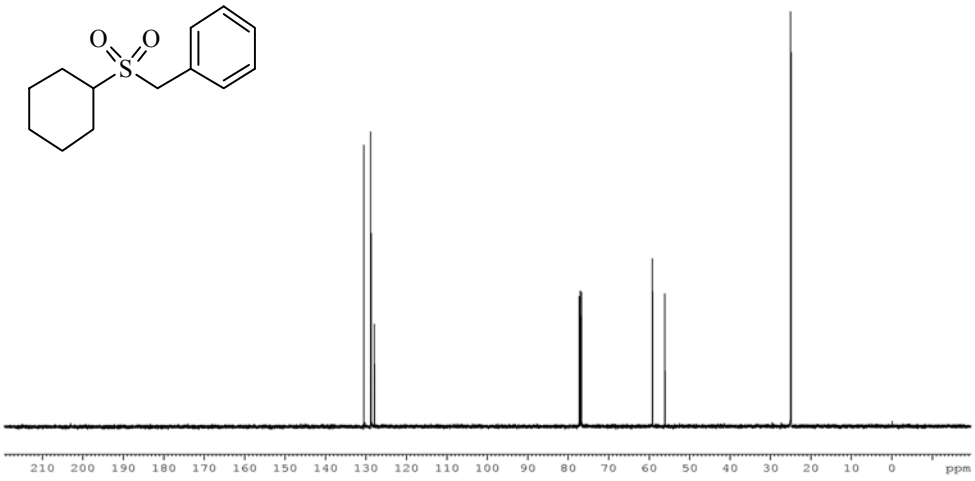
3-(Benzylsulfonyl)pyridine (4i)



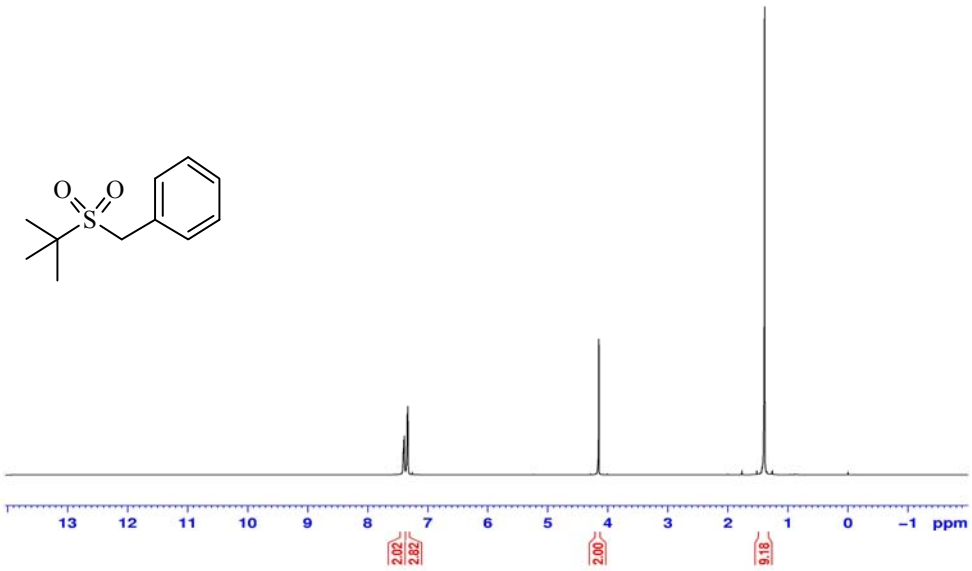
((Cyclohexylsulfonyl)methyl)benzene (4j)



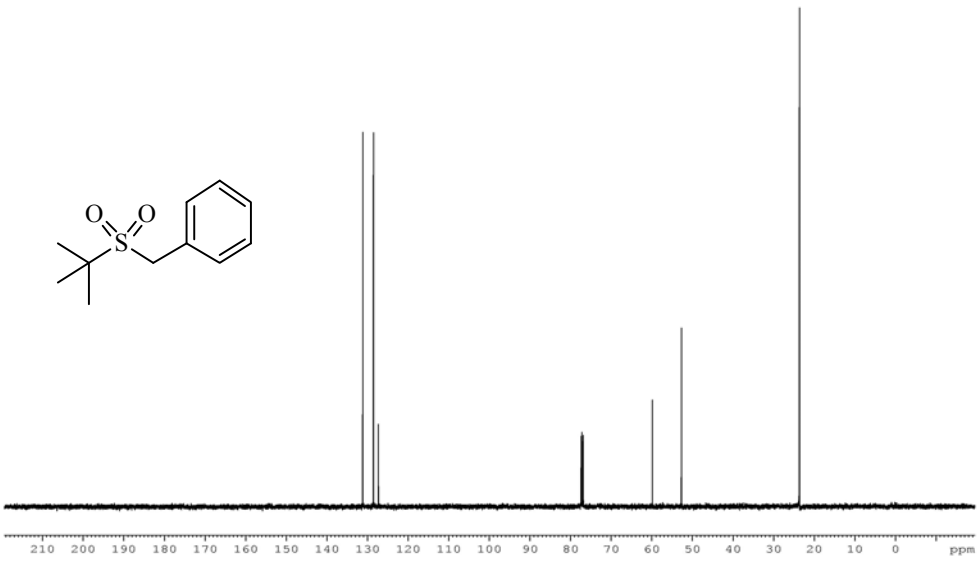
((Cyclohexylsulfonyl)methyl)benzene (4j)



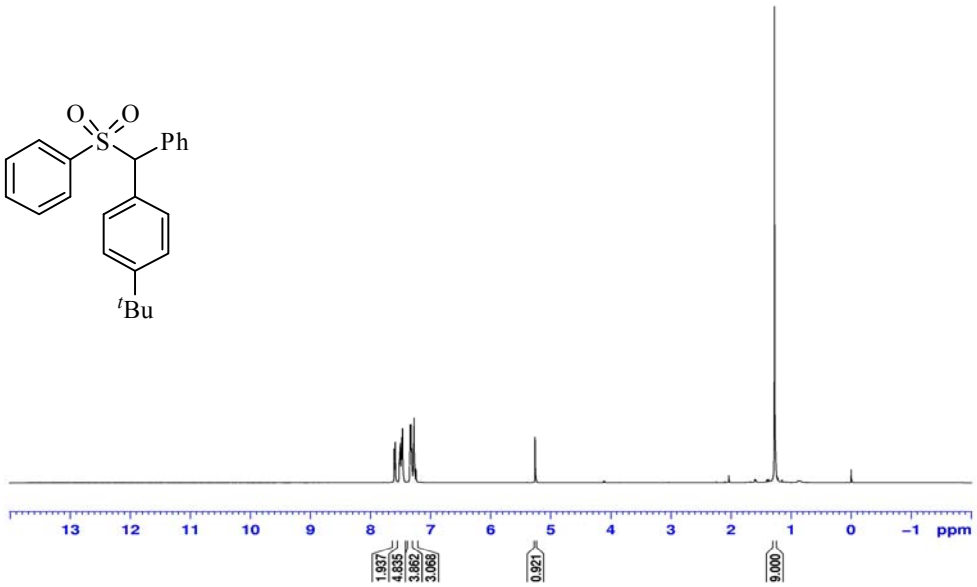
((*tert*-Butylsulfonyl)methyl)benzene (4k)



((*tert*-Butylsulfonyl)methyl)benzene (4k)



1-(*tert*-Butyl)-4-(phenyl(phenylsulfonyl)methyl)benzene (5a)



1-(*tert*-Butyl)-4-(phenyl(phenylsulfonyl)methyl)benzene (5a)