SUPPORTING INFORMATION

Palladium-Catalyzed Arylation of Alkyl Sulfenate Anions

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General Methods: All reactions were carried out under dry nitrogen. Anhydrous cyclopentyl methyl ether **(**CPME), dioxane and 2-Me-THF were purchased from Sigma-Aldrich and directly used without further purification. Toluene and THF were dried through activated alumina columns. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar Matrix Scientific or Frontier Scientific, and solvents were purchased from Fisher Scientific and Sigma-Aldrich. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with I_2. 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. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were taken with KBr plates with 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 Mel-Temp melting point apparatus and were uncorrected.

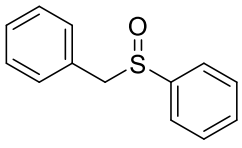
Preparation of sulfoxides: Sulfoxides were prepared according to the literature procedures.[1,2]

Procedure and Characterization for Formation of Diaryl Sulfoxides by Cross-Coupling Reactions.

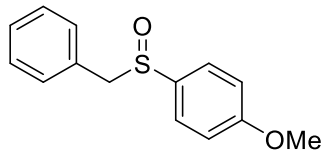
General Procedure for catalysis A: To an oven-dried microwave vial equipped with a stir bar was added $[(allyl)PdCl]_2$ (4.6 mg, 0.0125 mmol) and SPhos (20.6 mg, 0.05 mmol) inside a nitrogen filled glove box, followed by 1.0 mL dry 2-Me-THF. After the catalyst/ligand solution was stirred for 2 h at 24 ℃, CsF (227.9 mg, 1.5 mmol, 3 equiv) was added to the reaction vial followed by benzyl 2-(trimethylsilyl)ethyl sulfoxide (**1a**) (120.0 mg, 0.5 mmol, 1.0 equiv). The microwave vial was sealed with a rubber septum and an aluminium cap, and moved out of the glove box. Bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv)

was added by syringe a under nitrogen atmosphere. Note that if the aryl bromide was a solid, it was added to the reaction vial right after CsF inside the glove box (unless otherwise stated). The reaction mixture was heated to 80 ℃ in an oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and the reaction mixture was passed through a short pad of Celite packed in a glass Pasteur pipet. The pad was then rinsed with 5 mL ethyl acetate. The solvent was removed under reduced pressure to yield a white solid. The residue was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (103.8 mg, 96% yield) as a white solid.

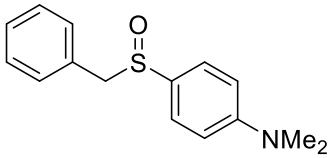
General Procedure for catalysis B: To an oven-dried microwave vial equipped with a stir bar was added $Pd(dba)_2$ (14.4 mg, 0.025 mmol) and Cy-CarPhos (22.0 mg, 0.05 mmol) inside a nitrogen filled glove box, followed by 1.0 mL dry DME. After the catalyst/ligand solution was stirred for 2 h at 24 ℃, CsF (227.9 mg, 1.5 mmol, 3 equiv) was added to the reaction vial followed by 2-thienyl 2-(trimethylsilyl)ethyl sulfoxide (**1t**) (123.2 mg, 0.5 mmol, 1.0 equiv). The microwave vial was sealed with a rubber septum and an aluminium cap, and moved out of glove box. Bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv) was added by syringe under a nitrogen atmosphere. Note that if the aryl bromide was a solid, it was added to the reaction vial right after CsF inside the glove box (unless otherwise stated). The reaction mixture was heated to 80 ℃ in an oil bath and stirred for 24 h. The sealed vial was cooled to room temperature, opened to air, and the reaction mixture was passed through a short pad of Celite packed in a glass Pasteur pipet. The pad was then rinsed with 5 mL ethyl acetate. The solvent was removed under reduced pressure to yield a white solid. The residue was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (94.5 mg, 85% yield) as a white solid.



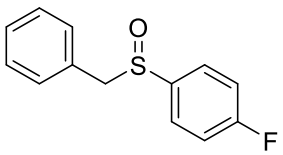
Benzylsulfinyl)benzene (3a): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (103.8 mg, 96% yield) as a white solid. The spectroscopic data match the previously reported data.[3]



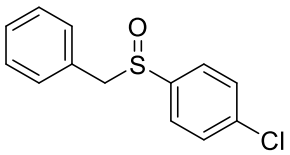
1-(Benzylsulfinyl)-4-methoxybenzene (3b): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-bromoanisole (**2b**) (125.2 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (121.9 mg, 99% yield) as a white solid. R_f = 0.2 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[4]



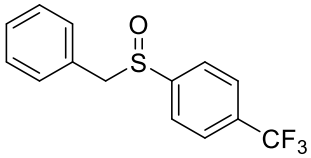
4-(Benzylsulfinyl)-*N*,*N*-dimethylaniline (3c): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-bromo-*N*,*N*-dimethylaniline (**2c**) (200.1 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (111.5 mg, 86% yield) as a white solid. R_f = 0.2 (hexanes:EtOAc = 1:1); m.p. = 140–141 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 5H), 7.02 (dd, *J* = 7, 1.5 Hz, 2H), 6.66 (d, *J* = 9 Hz, 2H), 4.12 (d, *J* = 12.5 Hz, 1H), 3.94 (d, *J* = 12.5 Hz, 1H), 3.00 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 152.4, 130.4, 130.0, 128.4, 127.9, 127.6, 126.2, 111.6, 63.9, 40.2 ppm; IR (thin film): 2903, 1597, 1513, 1365, 1088, 1031, 803, 701 cm^{-1}; HRMS calculated for $C_{15}H_{17}OSNNa$ 282.0929, found 282.0928 $[M+Na]^+$.



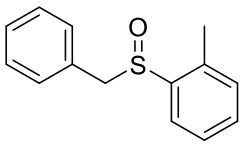
1-(Benzylsulfinyl)-4-fluorobenzene (3d): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 1-bromo-4-fluorobenzene (**2d**) (110.0 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (105.4 mg, 90% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[5]



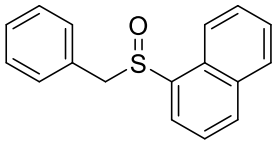
1-(Benzylsulfinyl)-4-chlorobenzene (3e): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 1-bromo-4-chlorobenzene (**2e**) (116.0 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (115.3 mg, 92% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[5]



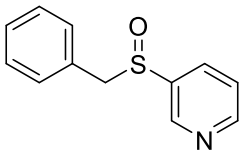
1-(Benzylsulfinyl)-4-(trifluoromethyl)benzene (3f): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-bromobenzotrifluoride (**2f**) (140.0 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (122.2 mg, 86% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[6]



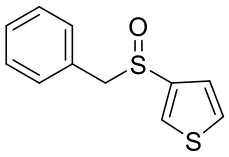
1-(Benzylsulfinyl)-2-methylbenzene (3g): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 2-bromotoluene (**2g**) (120.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (103.6 mg, 90% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[5]



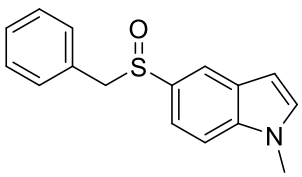
1-(Benzylsulfinyl)naphthalene (3h): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 1-bromonaphthalene (**2h**) (139.9 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (123.9 mg, 93% yield) as a white solid. R_f = 0.5 (hexanes:EtOAc = 2:1). The spectroscopic data match the previously reported data.[7]



3-(Benzylsulfinyl)pyridine (3i): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 3-bromopyridine (**2i**) (96.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (92.4 mg, 85% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 1:1); m.p. = 120–124 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, *J* = 4.5 Hz, 1H), 8.43 (t, *J* = 2 Hz, 1H), 7.69 (t, *J* = 1.5 Hz, 1H), 7.36 – 7.24 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 2H), 4.16 (d, *J* = 13 Hz, 1H), 4.06 (d, *J* = 13 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 152.1, 146.0, 139.2, 132.4, 130.4, 128.7, 128.6, 128.2, 123.9, 63.2 ppm; IR (thin film): 2959, 1572, 1454, 1416,1039, 1016, 800, 765, 708, 696 cm^{-1}; HRMS calculated for $C_{12}H_{11}OSNNa$ 240.0459, found 240.0463 $[M+Na]^+$.

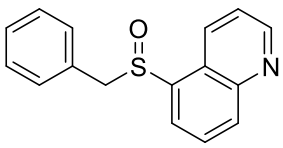


3-(Benzylsulfinyl)thiophene (3j): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 3-bromothiophene (**2j**) (93.7 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (96.7 mg, 87% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1); m.p. = 85–86 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.24 (m, 5H), 7.21 (d, *J* = 5 Hz, 1H), 6.91 (dd, *J* = 5, 2.5 Hz, 1H), 6.71 (d, *J* = 2.5 Hz, 1H), 4.23 (d, *J* = 14 Hz, 1H), 4.20 (d, *J* = 14 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.7, 131.3, 129.8, 129.1, 129.0, 127.2, 126.7, 124.2, 57.7 ppm; IR (thin film): 3059, 2922, 1475, 1443, 1086,1045, 850, 752, 745, 691 cm^{-1}; HRMS calculated for $C_{11}H_{10}OS_2Na$ 245.0071, found 245.0081 $[M+Na]^+$.

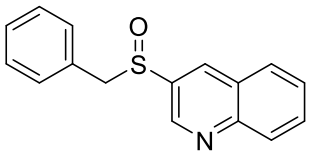


5-(Benzylsulfinyl)-1-methyl-1*H*-indole (3k): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 5-bromo-1-methyl-1*H*-indole (**2k**) (210.1 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (115.8 mg, 86% yield) as a white solid. R_f = 0.3

(hexanes:EtOAc = 2:1); m.p. = 130–133 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 1.5 Hz, 1H), 7.36 (d, *J* = 14 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.13 (d, *J* = 3 Hz, 1H), 6.99 (t, *J* = 6.5 Hz, 2H), 6.50 (d, *J* = 3 Hz, 1H), 4.14 (d, *J* = 13 Hz, 1H), 4.01 (d, *J* = 13 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.1, 132.9, 130.5, 130.4, 130.0, 128.4, 128.2, 128.0, 118.4, 117.3, 109.8, 101.9, 64.3, 33.1 ppm; IR (thin film): 2922, 1511, 1477, 1440, 1422,1339, 1279, 1243, 1055, 1036, 762, 698 cm^{-1}; HRMS calculated for $C_{16}H_{16}OSN$ 270.0953, found 270.0948 $[M+H]^+$.

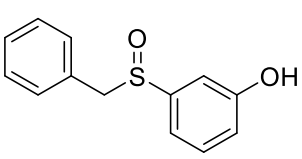


5-(Benzylsulfinyl)quinoline (3l): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 5-bromoquinoline (**2l**) (208.1 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (113.6 mg, 85% yield) as a white solid; m.p. = 132–135 ℃; R_f = 0.3 (hexanes:EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (d, *J* = 3 Hz, 1H), 8.21 (d, *J* = 8 Hz, 2H), 7.88 (d, *J* = 7 Hz, 1H), 7.78 (t, *J* = 8 Hz, 1H), 7.34 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.11 (m, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 4.22 (d, *J* = 7.5 Hz, 1H), 4.18 (d, *J* = 7.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.0, 147.6, 139.1, 132.7, 130.2, 129.8, 128.8, 128.7, 128.4, 128.3, 125.1, 124.4, 121.5, 62.8 ppm; IR (thin film): 2923, 1561, 1493, 1454, 1316, 1047, 803, 766, 699 cm^{-1}; HRMS calculated for $C_{16}H_{14}OSN$ 268.0796, found 268.0790 $[M+H]^+$.

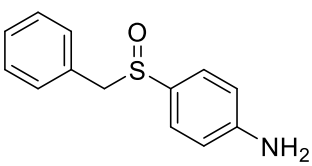


3-(Benzylsulfinyl)quinoline (3m): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 3-bromoquinoline (**2m**) (208.1 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:1) to give the product (121.6 mg, 91% yield) as a while solid. R_f = 0.3 (hexanes:EtOAc = 2:1); m.p. = 134–136 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (d, *J* = 2Hz, 1H), 8.21 (s, 1H), 8.16 (d, *J* = 8 Hz, 1H), 7.82 (t, *J* = 8 Hz, 2H), 7.62 (t, *J* = 8 Hz, 1H), 7.30 – 7.21 (m, 3H), 6.98 (d, *J* = 7.5 Hz, 2H), 4.25 (d, *J* = 13 Hz, 1H), 4.16 (d, *J* = 13 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ

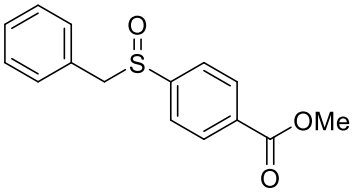
149.0, 145.1, 136.0, 133.5, 131.2, 130.4, 130.3, 129.5, 128.6, 128.2, 128.1, 127.8, 127.1, 63.2 ppm; IR (thin film): 2955, 1566, 1495, 1454, 1357, 1077, 1041, 958, 910, 786, 766, 749, 697 cm^{-1}; HRMS calculated for $C_{16}H_{14}OSN$ 268.0796, found 268.0798 $[M+H]^+$.



3-(Benzylsulfinyl)phenol (3n): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (379.8 mg, 2.5 mmol, 5 equiv) and 3-bromophenol (**2n**) (137.0 mg, 1.0 mmol, 2.0 equiv) in additional 1 mL 2-Me-THF was added to the reaction. The reaction was stirred at 110 ^oC for 24 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:MeOH = 5:1) to give the product (87.1 mg, 75% yield) as a vicious oil. R_f = 0.2 (EtOAc:MeOH = 10:1); ^1H NMR (500 MHz, $CDCl_3$): δ 8.81 (br s, 1H), 7.48 (s, 1H), 7.29 – 7.17 (m, 4H), 7.02 (d, *J* = 7 Hz, 2H), 6.96 (dd, *J* = 8, 1.5 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 4.15 (d, *J* = 12.5 Hz, 1H), 4.00 (d, *J* = 12.5 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 158.6, 142.1, 130.4, 129.7, 128.8, 128.5, 128.4, 119.4, 115.8, 111.0, 63.5 ppm; IR (thin film): 3167, 1602, 1587, 1495, 1476, 1448, 1260, 1227, 1020, 992, 766, 698, 687 cm^{-1}; HRMS calculated for $C_{13}H_{12}O_2SNa$ 255.0456, found 255.0459 $[M+Na]^+$.

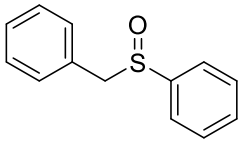


4-(Benzylsulfinyl)aniline (3o): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (551.7 mg, 3.5 mmol, 7 equiv) and 4-bromoaniline (**2o**) (172.0 mg, 1.0 mmol, 2.0 equiv) in additional 2 mL 2-Me-THF was added to the reaction. The reaction was stirred at 110 ^oC for 24 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:MeOH = 2:1) to give the product (89.1 mg, 77% yield) as a brown solid. R_f = 0.2 (EtOAc:MeOH = 2:1). The spectroscopic data match the previously reported data.[8]

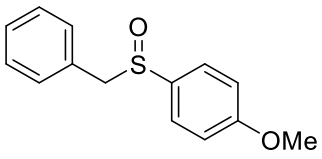


Methyl 4-(benzylsulfinyl)benzoate (3p): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and methyl 4-bromobenzoate

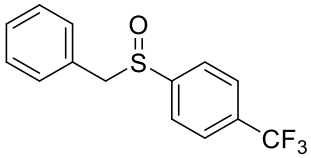
(**2p**) (215.0 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes= 1:2) to give the product (87.1 mg, 75% yield) as a white solid. R_f = 0.3 (EtOAc:hexanes = 1:2); m.p. = 164–165 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 2, 6.5 Hz, 2H), 7.38 (dd, *J* = 2, 6.5 Hz, 2H), 7.26 – 7.20 (m, 3H), 6.92 (d, *J* = 2 Hz, 2H), 4.07 (d, *J* = 12.5 Hz, 1H), 3.95 (d, *J* = 12.5 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.0, 147.9, 132.6, 130.3, 129.8, 128.5, 128.4(6), 128.4(2), 124.4, 63.2, 52.4 ppm; IR (thin film): 2961, 1722, 1437, 1279, 1116, 1038, 1117, 759, 701, 693 cm^{-1}; HRMS calculated for $C_{15}H_{14}O_3SNa$ 297.0561, found 297.0567 $[M+Na]^+$.



Benzylsulfinyl)benzene (3a) (from chlorobenzene): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and chlorobenzene (**4a**) (101.4 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (89.7 mg, 83% yield) as a white solid. The spectroscopic data match the previously reported data.[3]

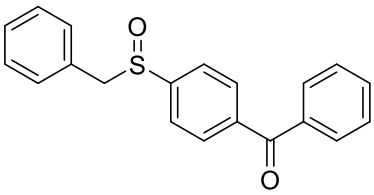


1-(Benzylsulfinyl)-4-methoxybenzene (3b) (from 4-chloroanisole): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-chloroanisole (**4b**) (122.5 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (75.1 mg, 61% yield) as a white solid. R_f = 0.2 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[4]

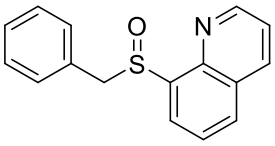


1-(Benzylsulfinyl)-4-(trifluoromethyl)benzene (3f) (from 4-chlorobenzotrifluoride): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-chlorobenzotrifluoride (**4f**) (133.5 μL, 1.0 mmol, 2.0 equiv). The crude product was

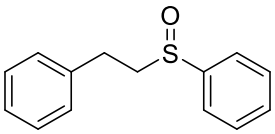
purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (132.2 mg, 93% yield) as a white solid. R_f = 0.3 (hexanes:EtOAc = 2:1).The spectroscopic data match the previously reported data.[6]



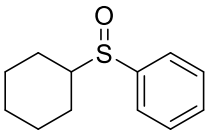
(4-(Benzylsulfinyl)phenyl)(phenyl)methanone (3q): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-chlorobenzophenone (**4q**) (216.7 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes= 1:4) to give the product (137.8 mg, 86% yield) as a white solid. R_f = 0.2 (EtOAc:hexanes = 1:4); m.p. = 140–141 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 13.5 Hz, 2H), 7.71 (d, *J* = 18 Hz, 2H), 7.58 (t, *J* = 7 Hz, 1H), 7.48–7.43 (m, 3H), 7.28–7.22 (m, 3H), 6.98 (d, *J* = 7 Hz, 2H), 4.09 (d, *J* = 12.5 Hz, 1H), 4.04 (d, *J* = 12.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 195.6, 147.3, 139.9, 136.9, 130.0, 130.4, 130.2, 130.1, 128.7, 128.6, 128.5,128.4,124.4, 63.3 ppm; IR (thin film): 3453, 1658, 1596, 1275, 1041, 731, 699, 661 cm^{-1}; HRMS calculated for $C_{20}H_{16}O_2SNa$ 343.0796, found 343.0778 $[M+Na]^+$.



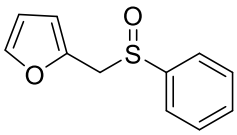
8-(Benzylsulfinyl)quinoline (3r): The reaction was performed following the General Procedure A with **1a** (120.0 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 8-chloroquinoline (**4r**) (163.6 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes= 1:2) to give the product (108.3 mg, 81% yield) as a white solid. R_f = 0.2 (EtOAc:hexanes = 1:2); m.p. = 94–95 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (dd, *J* = 8, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.84 (dd, *J* = 8, 1 Hz, 1H), 7.79 (dd, *J* = 7, 1 Hz, 1H), 7.53–7.46 (m, 2H), 7.19–7.10 (m, 3H), 6.88 (d, *J* = 7 Hz, 2H), 4.55 (d, *J* = 13 Hz, 1H), 4.22 (d, *J* = 13 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.2, 144.1, 140.5, 136.5, 130.3, 130.2, 130.1, 128.0, 127.9, 127.8,127.3,126.4, 122.0, 59.6 ppm; IR (thin film): 3469, 3030, 1612, 1593, 1562, 1494, 1455, 1072, 1045, 831, 789, 764, 699 cm^{-1}; HRMS calculated for $C_{16}H_{13}NOSNa$ 290.0616, found 290.0617 $[M+Na]^+$.



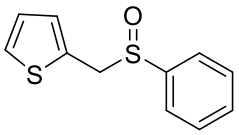
(Phenethylsulfinyl)benzene (3s): The reaction was performed following the General Procedure A with **1s** (127.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (108.3 mg, 94% yield) as a white solid. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 143.5, 138.6, 130.9, 129.1, 128.6, 128.4, 126.6, 123.9, 58.2, 28.0 ppm. Other spectroscopic data were previously reported.[9]



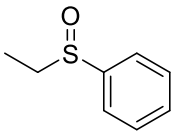
(Cyclohexylsulfinyl)benzene (3t): The reaction was performed following the General Procedure A with **1t** (116.3 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (95.8 mg, 92% yield) as a white solid. The spectroscopic data match the previously reported data.[9]



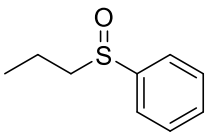
2-((Phenylsulfinyl)methyl)furan (3u): The reaction was performed following the General Procedure A with **1u** (115.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (91.8 mg, 89% yield) as a colorless vicious oil; R_f = 0.3 (EtOAc:hexanes = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.44 (m, 5H), 7.30 (d, *J* = 1 Hz, 1H), 6.28 (dd, *J* = 1, 3 Hz, 1H), 6.12 (d, *J* = 3 Hz, 1H), 4.15 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 143.8, 143.4, 143.1, 131.3, 129.0, 124.1, 111.4, 111.0, 56.4 ppm; IR (thin film): 3057, 1497, 1477, 1443, 1149, 1085, 1046, 1012, 937, 745, 721, 690 cm^{-1}; HRMS calculated for $C_{11}H_{11}O_2S$ 207.0480, found 207.0478 $[M+H]^+$.



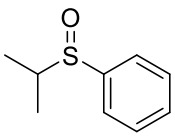
2-((Phenylsulfinyl)methyl)thiophene (3v): The reaction was performed following the General Procedure B with **1v** (123.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (94.5 mg, 85% yield) as a white solid; R_f = 0.3 (EtOAc:hexanes = 1:2); m.p. = 85–86 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.07 (dd, *J* = 2, 4 Hz, 1H), 7.03 (m, 2H), 4.19 (d, *J* = 12.5 Hz, 1H), 4.07 (d, *J* = 12.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.2, 130.3, 129.2, 128.5, 128.3, 127.8, 126.4, 123.2, 63.1 ppm; IR (thin film): 2962, 1493, 1453, 1403, 1197, 1072, 1035, 781, 763, 696, 605 cm^{-1}; HRMS calculated for $C_{11}H_{11}OS_2$ 223.0251, found 223.0254 $[M+H]^+$.



(Ethylsulfinyl)benzene (3w): The reaction was performed following the General Procedure B with **1w** (89.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (67.1 mg, 87% yield) as a colorless oil. R_f = 0.3 (EtOAc:hexanes = 1:1). The spectroscopic data match the previously reported data.[10]

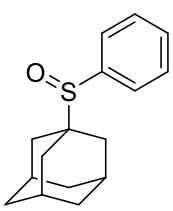


(Propylsulfinyl)benzene (3x): The reaction was performed following the General Procedure B with **1x** (96.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (80.1 mg, 86% yield) as a colorless oil. R_f = 0.3 (EtOAc:hexanes = 1:1).The spectroscopic data match the previously reported data.[11]

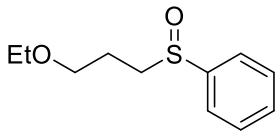


(*iso*-Propylsulfinyl)benzene (3y): The reaction was performed following the General Procedure B with **1y** (96.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv)

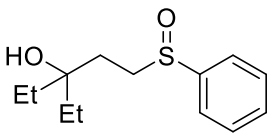
and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The reaction was heated for 48 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product (76.4 mg, 82% yield) as a colorless oil. R_f = 0.3 (EtOAc:hexanes = 1:1).The spectroscopic data match the previously reported data.[10]



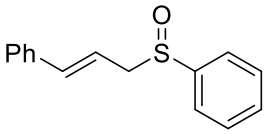
1-(Phenylsulfinyl)adamantane (3z): The reaction was performed following the General Procedure B with **1z** (142.3 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The reaction was heated to 48 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (115.9 mg, 87% yield) as a white solid; R_f = 0.5 (EtOAc:hexanes = 1:10); m.p. = 96–98 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 5H), 2.12 – 2.05 (m, 3H), 1.76 – 1.51 (m, 12H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.4, 131.0, 128.3, 126.4, 57.6, 38.2, 34.9, 28.8 ppm; IR (thin film): 2906, 2851, 1454, 1443, 1300, 1084, 1050, 1029, 750, 700, 692 cm^{-1}; HRMS calculated for $C_{16}H_{19}OS$ 259.1157, found 259.1157 $[M+H]^+$.



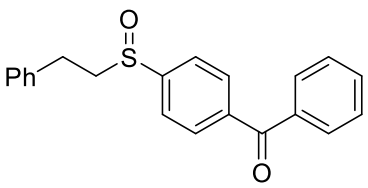
((3-Ethoxypropyl)sulfinyl)benzene (3aa): The reaction was performed following the General Procedure B with **1aa** (138.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:1) to give the product (98.7 mg, 93% yield) as a colorless vicious oil; R_f = 0.4 (EtOAc:hexanes = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 3, 1 Hz, 2H), 7.49 – 7.43 (m, 3H), 3.51 – 3.49 (m, 1H), 3.48 – 3.35 (m, 3H), 2.93 – 2.87 (m, 1H), 2.82 – 2.76 (m, 1H), 2.02 – 1.93 (m, 1H), 1.86 – 1.81 (m, 1H), 1.11 (t, *J* = 7 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.8, 130.8, 129.1, 123.9, 68.5, 66.1, 54.1, 22.5, 15.0 ppm; IR (thin film): 2974, 2866, 1478, 1443, 1378, 1109, 1088, 1046, 1024, 749, 693 cm^{-1}; HRMS calculated for $C_{11}H_{17}O_2S$ 213.0949, found 213.0949 $[M+H]^+$.



3-Ethyl-1-(phenylsulfinyl)pentan-3-ol (3ab): The reaction was performed following the General Procedure B with **1ab** (132.3 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with 100% EtOAc) to give the product (115.4 mg, 96% yield) as a white solid; R_f = 0.4 (100% EtOAc); m.p. = 70–72 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 3, 1.5 Hz, 2H), 7.49 – 7.44 (m, 3H), 2.99 – 2.92 (m, 1H), 2.81 – 2.75 (m, 1H), 2.22 (br s, 1H), 1.82 – 1.76 (m, 1H), 1.71 – 1.65 (m, 1H), 1.46 – 1.39 (m, 4H), 0.76 (dt, *J* = 13, 7.5 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.4, 130.9, 129.1, 124.1, 73.4, 51.4, 30.9, 30.6, 30.4, 7.7, 7.6 ppm; IR (thin film): 3400, 2966, 2938, 1460, 1444, 1172, 1086, 1029, 997, 918, 748, 692 cm^{-1}; HRMS calculated for $C_{13}H_{21}O_2S$ 241.1262, found 241.1263 $[M+H]^+$.

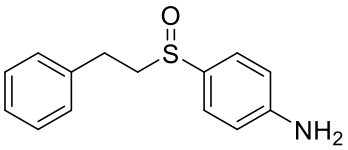


(Cinnamylsulfinyl)benzene (3ac): The reaction was performed following the General Procedure A with **1ac** (133.3 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (48.5 mg, 40% yield) as a white solid. IR (thin film): 2961, 1475, 1442, 1402, 1303, 1086, 1034, 998, 965, 750, 689 cm^{-1}; HRMS calculated for $C_{15}H_{14}OSNa$ 265.0663, found 265.0651 $[M+Na]^+$.Other spectroscopic data were previously reported.[12]

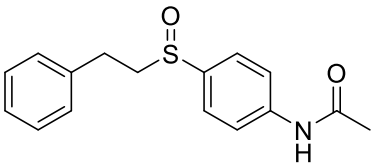


(4-(Phenethylsulfinyl)phenyl)(phenyl)methanone (3ad): The reaction was performed following the General Procedure A with **1s** (127.2 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and 4-bromobenzophenone (**2ad**) (261.1 mg, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (135.5 mg, 81% yield) as a colorless vicious oil; R_f = 0.4 (EtOAc:hexanes = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (apparent t, 2H), 7.29 (apparent t, 2H), 7.23 – 7.18 (m, 3H), 3.19 – 3.04 (m, 3H), 2.96 – 2.89 (m, 1H) 1 1H) ppm;

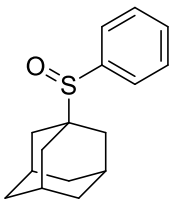
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 195.6, 148.2, 139.9, 138.5, 136.9, 133.0, 130.6, 130.1, 128.8, 128.6, 128.5, 126.8, 124.0, 58.2, 28.1 ppm; IR (thin film): 3469, 1659, 1594, 1496,1447, 1395, 1317, 1305, 1276, 1046, 924, 732, 699, 661 cm^{-1}; HRMS calculated for $C_{21}H_{19}O_2S$ 335.1106, found 335.1104 $[M+H]^+$.



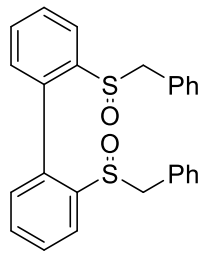
4-(Phenethylsulfinyl)aniline (3ae): The reaction was performed following the General Procedure A with **1s** (127.2 mg, 0.5 mmol, 1.0 equiv), CsF (551.7 mg, 3.5 mmol, 7 equiv) and 4-bromoanline (**2o**) (172.0 µL, 1.0 mmol, 2.0 equiv) at 80 °C for 48 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:MeOH = 2:1) to give the product (74.8 mg, 61% yield) as a colorless vicious oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22– 7.15 (m, 3H), 6.74 (d, *J* = 9 Hz, 2H), 4.06 (br s, 2H), 3.08– 2.91 (m, 3H), 2.90– 2.87 (m, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 149.6, 139.0, 128.6, 128.4, 126.5, 126.1, 115.0, 58.3, 28.5 ppm; IR (thin film): 3342, 1632, 1595, 1500, 1297, 1088, 1015, 827, 752, 701 cm^{-1}; HRMS calculated for $C_{14}H_{15}OSNNa$ 268.0772, found 268.0772 $[M+Na]^+$.



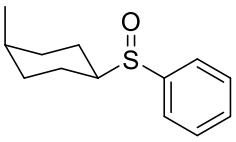
***N*-(4-(phenethylsulfinyl)phenyl)acetamide (3af):** The reaction was performed following the General Procedure A with **1s** (127.2 mg, 0.5 mmol, 1.0 equiv), CsF (379.8 mg, 2.5 mmol, 5 equiv) and 4-bromoacetanilide (**2af**) (214.1 m, 1.0 mmol, 2.0 equiv) at 80 °C for 48 h. The crude product was purified by flash chromatography on silica gel (eluted with 100% EtOAc) to give the product (206.9 mg, 72% yield) as a colorless vicious oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (br s, 1H), 7.74 (d, *J* = 9 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.29– 7.26 (m, 2H), 7.21 (t, *J* = 7 Hz, 1H), 7.15 (d, *J* = 7 Hz, 2H), 3.08– 3.00 (m, 3H), 2.93– 2.85 (m, 1H), 2.18 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 169.2, 141.4, 138.4, 137.1, 128.7, 128.4, 126.7, 125.1, 120.2, 58.2, 28.3, 24.5 ppm; IR (thin film): 3435, 1677, 1591, 1536, 1496, 1398, 1316, 1263, 1088, 1028, 1010, 833, 752, 701 cm^{-1}; HRMS calculated for $C_{16}H_{18}O_2SN$ 288.1058, found 288.1062 $[M+H]^+$.



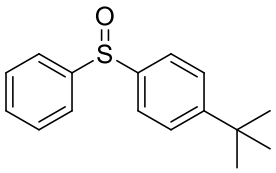
1-(Phenylsulfinyl)adamantane (3z) (Gram scale): To an oven-dried Schlenk flask equipped with a stir bar was added $Pd(dba)_2$ (230.0 mg, 0.40 mmol) and Cy-CarPhos (352.0 mg, 0.80 mmol) inside a nitrogen filled glove box, followed by 16.0 mL dry DME via syringe. After the catalyst/ligand solution was stirred for 2 h at 24 ℃, CsF (3.6 g, 24 mmol, 3 equiv) was added to the reaction vial followed by **1z** (2.3 g, 8 mmol, 1.0 equiv). The Schlenk flask was sealed by rubber sputum, and moved out of glove box. Bromobenzene (**2a**) (1.7 mL, 16 mmol, 2.0 equiv) was added by syringe under nitrogen atmosphere. The Schlenk flask was equipped with condenser, whose top was connected to a nitrogen line and the reaction mixture was heated to 80 ℃ in an oil bath and stirred for 48 h. The flask was cooled to room temperature, opened to air, and the reaction mixture was passed through a short pad of Celite packed in a 15 mL Buchner funnel. The pad was then rinsed with 30 mL ethyl acetate. The solvent was removed under reduced pressure to yield a residue. The residue was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (1.8 g, 86% yield) as a white solid; R_f = 0.5 (EtOAc:hexanes = 1:10). The spectra data were previously described.



2,2'-Bis(benzylsulfinyl)-1,1'-biphenyl (3ag, mixture of two diasteromers): The reaction was performed following the General Procedure A with **1a** (480.0 mg, 2.0 mmol, 4.0 equiv), CsF (445.8 mg, 3.0 mmol, 6 equiv) and 2,2'-dibromobiphenyl (**2ag**) (156.0 mg, 0.5 mmol, 1.0 equiv). The reaction was heated for 48 h. The crude product was purified by flash chromatography on silica gel (eluted with 100% EtOAc) to give the products of a pair of diasteromers (176.5 mg, overall 82% yield) as a white solid. R_f = 0.3 (100% EtOAc). According to ^{1}H NMR, dr = 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 – 6.12 (m, 36H), 4.22 (d, *J* = 12.5 Hz, 1H), 4.15 (d, *J* = 12.5 Hz, 1H), 3.99 (d, *J* = 13 Hz, 1H), 3.75 (d, *J* = 13 Hz, 2H), 3.70 (d, *J* = 13 Hz, 1H), 3.55 (d, *J* = 13 Hz, 2H).



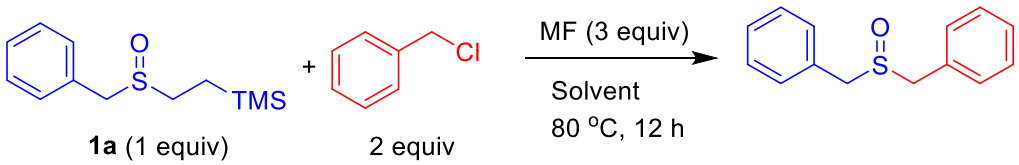
((*cis*-4-Methylcyclohexyl)sulfinyl)benzene (3ah): The reaction was performed following the General Procedure A with **1ah** (123.3 mg, 0.5 mmol, 1.0 equiv), CsF (227.9 mg, 1.5 mmol, 3 equiv) and bromobenzene (**2a**) (105.3 μL, 1.0 mmol, 2.0 equiv). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product (115.4 mg, 89% yield) as a colorless vicious oil; R_f = 0.4 (EtOAc:hexanes = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.62 (m, 2H), 7.53 – 7.48 (m, 3H), 2.71 – 2.66 (m, 1H), 2.22 – 2.15 (m, 1H), 1.75 – 1.36 (m, 8H), 0.96 (d, *J* = 7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.7, 131.1, 128.9, 125.1, 63.6, 30.8, 30.2, 29.6, 23.6, 21.8, 20.0 ppm; IR (thin film): 3464, 2921, 2852, 1443, 1086, 1040, 1022, 998, 750, 692 cm^{-1}; HRMS calculated for $C_{13}H_{19}OS$ 223.1157, found 223.1155 $[M+H]^+$.



1-(*tert*-Butyl)-4-(phenylsulfinyl)benzene (5a): To an oven-dried microwave vial equipped with a stir bar was added $[(allyl)PdCl]_2$ (4.6 mg, 0.0125 mmol) and SPhos (20.6 mg, 0.05 mmol) inside a nitrogen filled glove box, followed by 1.0 mL dry 2-Me-THF. After the catalyst/ligand solution was stirred for 2 h at 24 ℃, NaO^{t}Bu (144.2 mg, 1.5 mmol, 3 equiv) was added to the reaction vial followed by (phenethylsulfinyl)benzene (**3s**) (115.2 mg, 0.5 mmol, 1.0 equiv). The microwave vial was sealed with a rubber septum and an aluminium cap, and moved out of glove box. 4-*tert*-Butyl bromobenzene (**2ai**) (173.4 μL, 1.0 mmol, 2.0 equiv) was added by syringe under nitrogen atmosphere. The reaction mixture was heated to 80 ℃ in an oil bath and stirred for 12 h. The sealed vial was cooled to room temperature, opened to air, and the reaction mixture was passed through a short pad of Celite packed in a glass Pasteur pipet. The pad was then rinsed with 5 mL ethyl acetate. The solvent was removed under reduced pressure to yield a white solid. The residue was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product (127.9 mg, 99% yield) as a white solid. R_f = 0.4 (hexanes:EtOAc = 2:1). The spectroscopic data match the previously reported data.[13]

High-throughput Experimentation Screenings.

Base and Solvent Screening



1a (1 equiv) 2 equiv

Set up:

Experiments were set up in a glove box under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials was dosed with fluoride salts (30 μmol) in THF. The solvent was removed to dryness using a GeneVac. Next, 2-(trimethylsilyl)ethyl benzyl sulfoxide (10 μmol) in THF was added to the vials. The solvent was again removed to dryness using a GeneVac and a parylene stir bar was then added to each reaction vial. Benzyl chloride (20 μmol/reaction) was then dosed together into each reaction vial as a solution in each solvent (100 μL, 0.2 M). The 24-well plate was then sealed and stirred for 10 h at 80 °C.

Work up:

The plate was cooled to room temperature. Upon opening the plate to air, 500 μL of acetonitrile containing biphenyl (1 μmol, used as an internal standard to measure HPLC yields) was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate 24-well LC block was added 700 μL of acetonitrile, followed by 40 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

MF: LiF, NaF, KF, CsF.

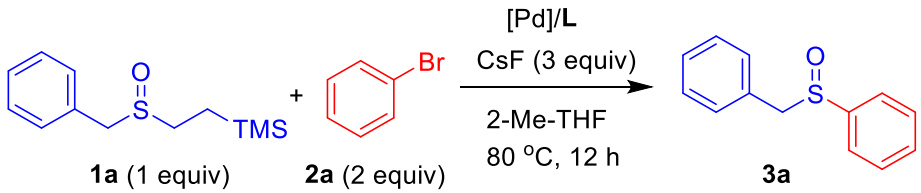
Solvent: THF, toluene, 2-Me-THF, DME (dimethoxyethane), CPME (cyclopentyl methyl ether), dioxane.

Well	Solvent	MF	Prod/IS[a]
A01	THF	LiF	0
B01		NaF	0
C01		KF	0
D01		CsF	0.10
A02	Toluene	LiF	0
B02		NaF	0
C02		KF	0
D02		CsF	0
A03	2-Me-THF	LiF	0
B03		NaF	0
C03		KF	0
D03		CsF	0.21
A04	DME	LiF	0
B04		NaF	0
C04		KF	0
D04		CsF	0.17

A05	CPME	LiF	0
B05		NaF	0
C05		KF	0
D05		CsF	0.06
A06	Dioxane	LiF	0
B06		NaF	0
C06		KF	0
D06		CsF	0.05

[a]Product-internal standard radio.

Ligand Screening



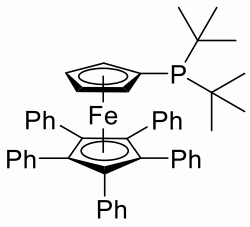
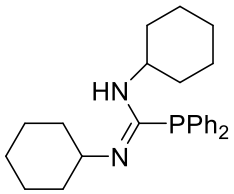
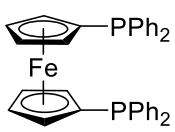
Set up:

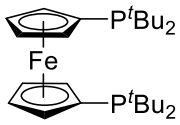
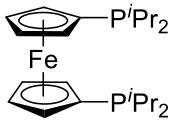
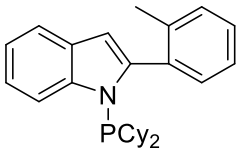
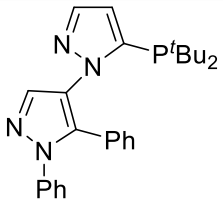
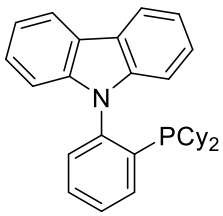
Experiments were set up in a glove box under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials was predosed with $Pd(dba)_2$ (1 μmol) and the phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and CsF (60 μmol) in THE was added to the ligand/catalyst mixture. The solvent was again removed to dryness using a GeneVac and a parylene stir bar was then added to each reaction vial. 2-(trimethylsilyl)ethyl benzyl sulfoxide (20 μmol/reaction) and bromobenzene (40 μmol/reaction) were

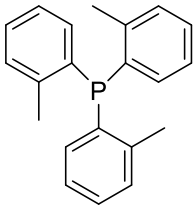
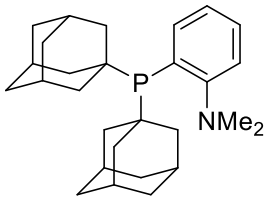
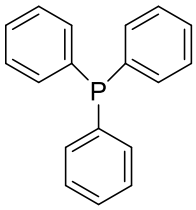
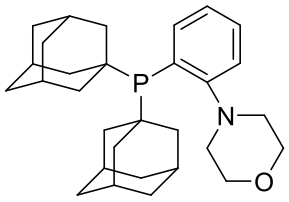
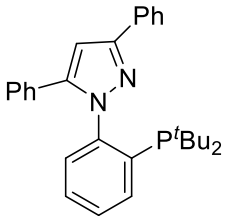
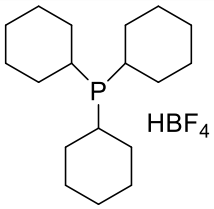
then dosed together into each reaction vial as a solution in each 2-Me-THF (200 μL, 0.1 M). The 24-well plate was then sealed and stirred for 10 h at 80 ^{o}C.

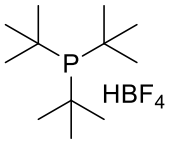
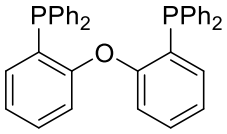
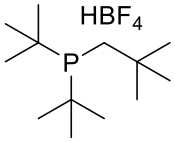
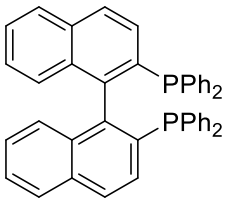
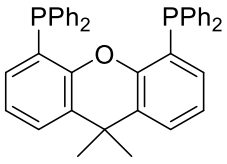
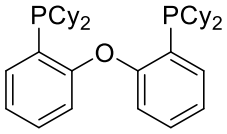
Work up:

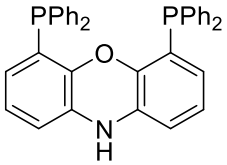
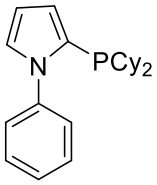
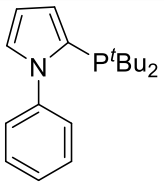
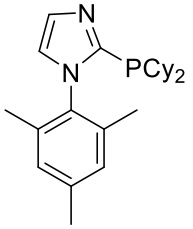
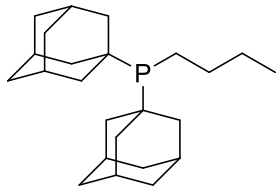
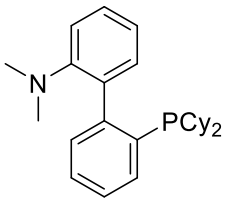
The plate was cooled to room temperature. Upon opening the plate to air, 500 μL of acetonitrile containing biphenyl (1 μmol, used as an internal standard to measure HPLC yields) was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate 24-well LC block was added 700 μL of acetonitrile, followed by 40 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

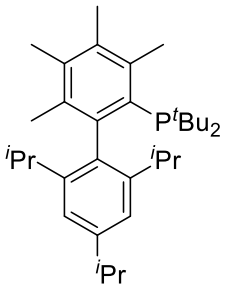
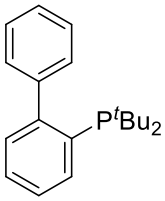
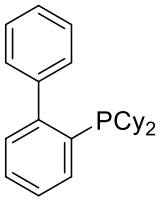
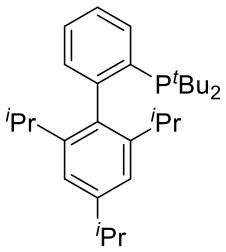
	Ligand
1	1,2,3,4,5-Pentaphenyl-1′-(di-*tert*-butylphosphino)ferrocene (QPhos) 
2	*N*,*N*'-dicyclohexyl-1-diphenylphosphanyl-formamidine (DCyF) 
3	1,1'-Bis(diphenylphosphino)ferrocene (DPPF) 

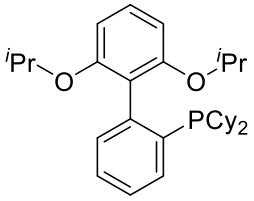
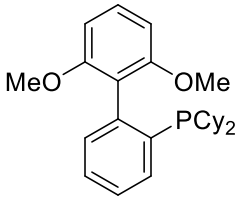
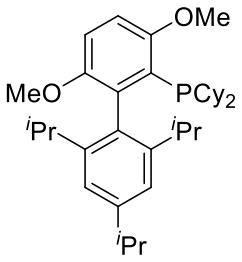
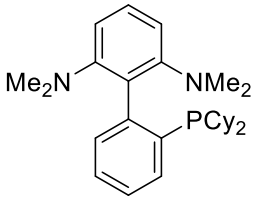
4	1,1'-Bis(di-*tert*-butylphosphino)ferrocene (D*t*BPF) 
5	1,1'-Bis(di-*i*-propylphosphino)ferrocene (D*i*PPF) 
6	N-(dicyclohexylphosphino)-2-(2′-tolyl)indole 
7	5-(Di-*tert*-butylphosphino)-1′, 3′, 5′-triphenyl-1′*H*-[1,4′]bipyrazole (BippyPhos) 
8	9-[2-(Dicyclohexylphosphino)phenyl]-9H-carbazole (Cy CarPhos) 
9	Tri(*o*-tolyl)phosphine

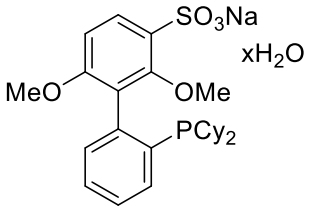
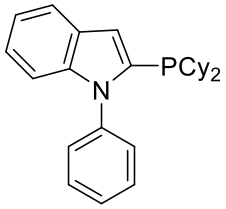
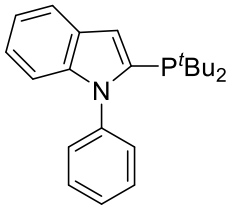
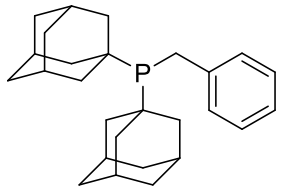
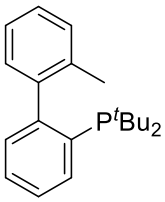
	
10	Di(1-adamantyl)-2-dimethylaminophenylphosphine (MeDal Phos) 
11	Triphenylphosphine 
12	Di(1-adamantyl)-2-morpholinophenylphosphine (MorDal Phos) 
13	1-[2-[Bis(*tert*-butyl)phosphino]phenyl]-3,5-diphenyl-1*H*-pyrazole (TrippyPhos) 
14	Tricyclohexylphosphine tetrafluoroborate (PCy_3 HBF_4) 

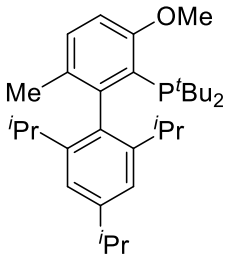
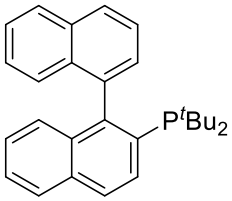
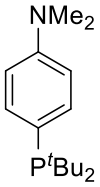
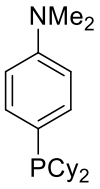
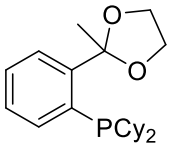
15	Tri-*tert*-butylphosphonium tetrafluoroborate ($PtBu_3$ HBF_4) 
16	Bis(diphenylphosphinophenyl)ether (DPEPhos) 
17	Di-*tert*-butylneopentylphosphonium tetrafluoroborate 
18	(2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (Binap) 
19	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos) 
20	Bis(dicyclohexylphosphinophenyl) ether (DCEPhos) 
21	4,6-Bis (diphenylphosphino)phenoxazine (NiXantPhos)

	
22	2-(Dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole (cataCXium PCy) 
23	2-(Di-*tert*-butyl-phosphino)-1-phenyl-1*H*-pyrrole (cataCXium PtB) 
24	2-(Dicyclohexylphosphino)-1-(2,4,6-trimethyl-phenyl)-1*H*-imidazole (cataCXium PICy) 
25	Di(1-adamantyl)-*n*-butylphosphine (cataCXium A) 
26	2-Dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos) 

27	2-Di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropyl-1,1′-biphenyl (Me_4*t*BuXPhos) 
28	(2-Biphenyl)di-*tert*-butylphosphine (JohnPhos) 
29	(2-Biphenyl)dicyclohexylphosphine (CyJohnPhos) 
30	2-Di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl (*t*BuXPhos) 

31	2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos) 
32	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) 
33	2-(Dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl (BrettPhos) 
34	2-(2-dicyclohexylphosphanylphenyl)-N1,N1,N3,N3-tetramethyl-benzene-1,3-diamine (CPhos) 
35	Sodium 2′-dicyclohexylphosphino-2,6-dimethoxy-1,1′-biphenyl-3-sulfonate hydrate (^{S}SPhos)

	
36	2-(Dicyclohexylphosphino)-1-phenylindole (cataCXium PInCy) 
37	2-(Di-*tert*-butylphosphino)-1-phenylindole (cataCXium PIntB) 
38	Di(1-adamantyl)benzylphosphine (cataCXium ABn) 
39	2-Di-*tert*-butylphosphino-2′-methylbiphenyl (*t*BuMePhos) 
40	Di-*tert*-butyl(2′,4′,6′-triisopropyl-3-methoxy-6-methyl-[1,1′-biphenyl]-2-yl)phosphine (RockPhos)

	
41	2-Di-*tert*-butylphosphino-1,1'-binaphthyl (TrixiePhos) 
42	*N*,*N*-Dimethyl 4-(Di(*tert*-butyl)phosphino)aniline (A^{ta} Phos) 
43	Dicyclohexyl(4-(*N*,*N*-dimethylamino)phenyl)phosphine (A^{ca} Phos) 
44	2′-(Dicyclohexylphosphino)acetophenone ethylene ketal (SymPhos) 

Best results from screening:

Ligand	**Prod/IS**[a]

SPhos	0.95
Cy-CarPhos	2.70
DPEPhos	1.23
DCEPhos	1.99

[a]Product-internal standard radio.

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2. Schwan, A. L.; Strickler, R. R.; Dunn-Dufault, R.; Brillon, D. *Eur. J. Org. Chem.* **2001**, *2001*, 1643.
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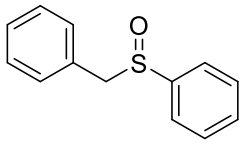
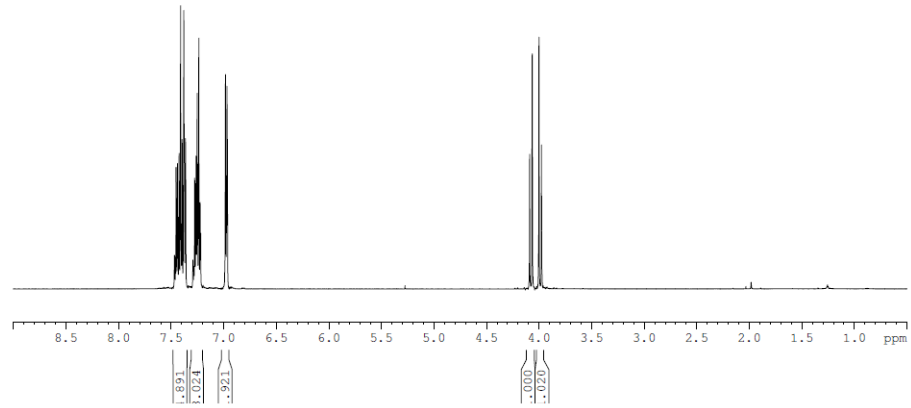
5. Wang, B.; Liu, Y.; Lin, C.; Xu, Y.; Liu, Z.; Zhang, Y. *Org. Lett.* **2014**, *16*, 4574.
6. Samanta, R.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 5217.
7. O'Mahony, G. E.; Eccles, K. S.; Morrison, R. E.; Ford, A.; Lawrence, S. E.; Maguire, A. R. *Tetrahedron* **2013**, *69*, 10168.
8. Capozzi, M. A. M.; Fracchiolla, G.; Cardellicchio, C. *J. Sulfur. Chem.* **2013**, *34*, 646.
9. Fabretti, A.; Gheifi, F.; Grandi, R.; Pagnoni, U. M. *Synth. Commun.* **1994**, *24*, 2393.
10. Hendriks, C. M. M.; Lamers, P.; Engel, J.; Bolm, C. *Adv. Syn. Catal.* **2013**, *353*, 3363.
11. Imada, Y.; Iida, H.; Naota, T. *J. Am. Chem. Soc.* **2005**, *127*, 14544.
12. Linden, A. A.; Johansson, M.; Hermanns, N.; Backvall, J.-E. *J. Org. Chem.* **2006**, *71*, 3849.
13. Jia, T.; Bellomo, A.; Montel, S.; Zhang, M.; El Baina, K.; Zheng, B.; Walsh, P. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 260.

NMR Spectra

Benzylsulfinyl)benzene (3a)





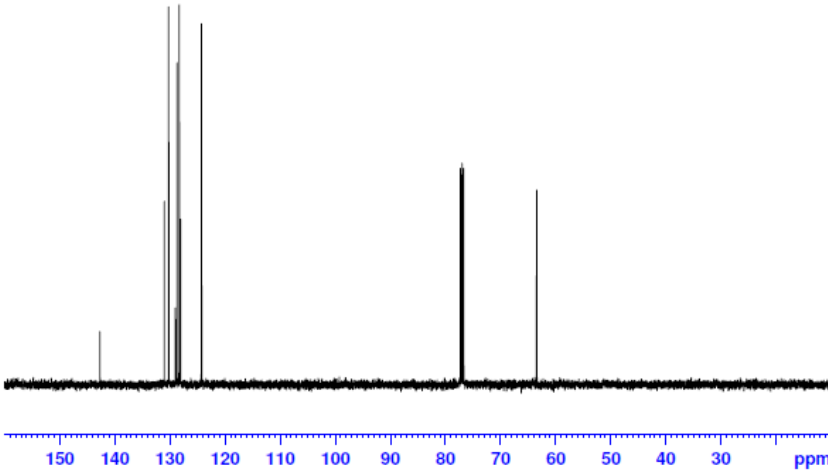
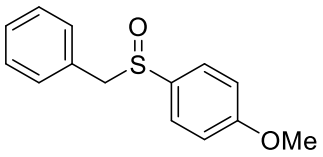


Figure S1. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3a in $CDCl_3$.

1-(Benzylsulfinyl)-4-methoxybenzene (3b)



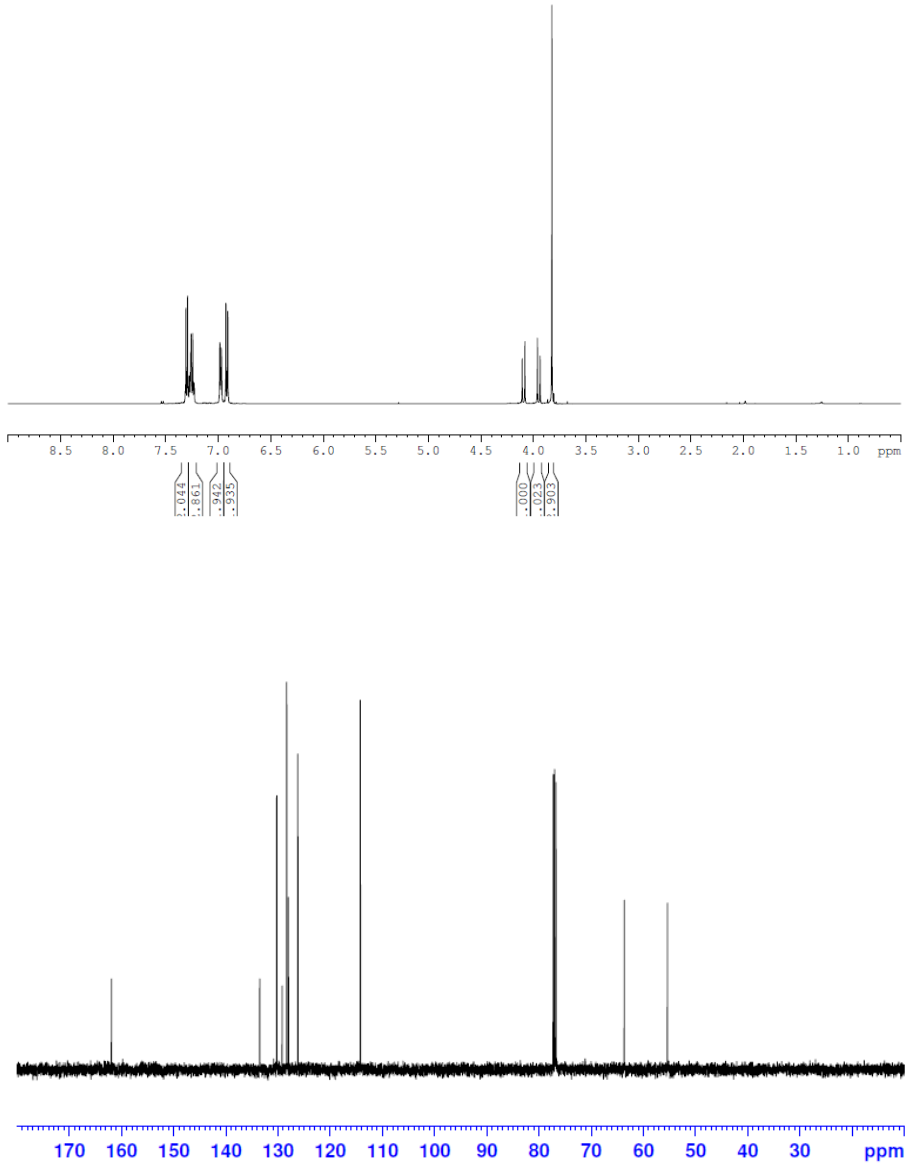


Figure S2. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3b in $CDCl_3$.

4-(Benzylsulfinyl)-*N*,*N*-dimethylaniline (3c)

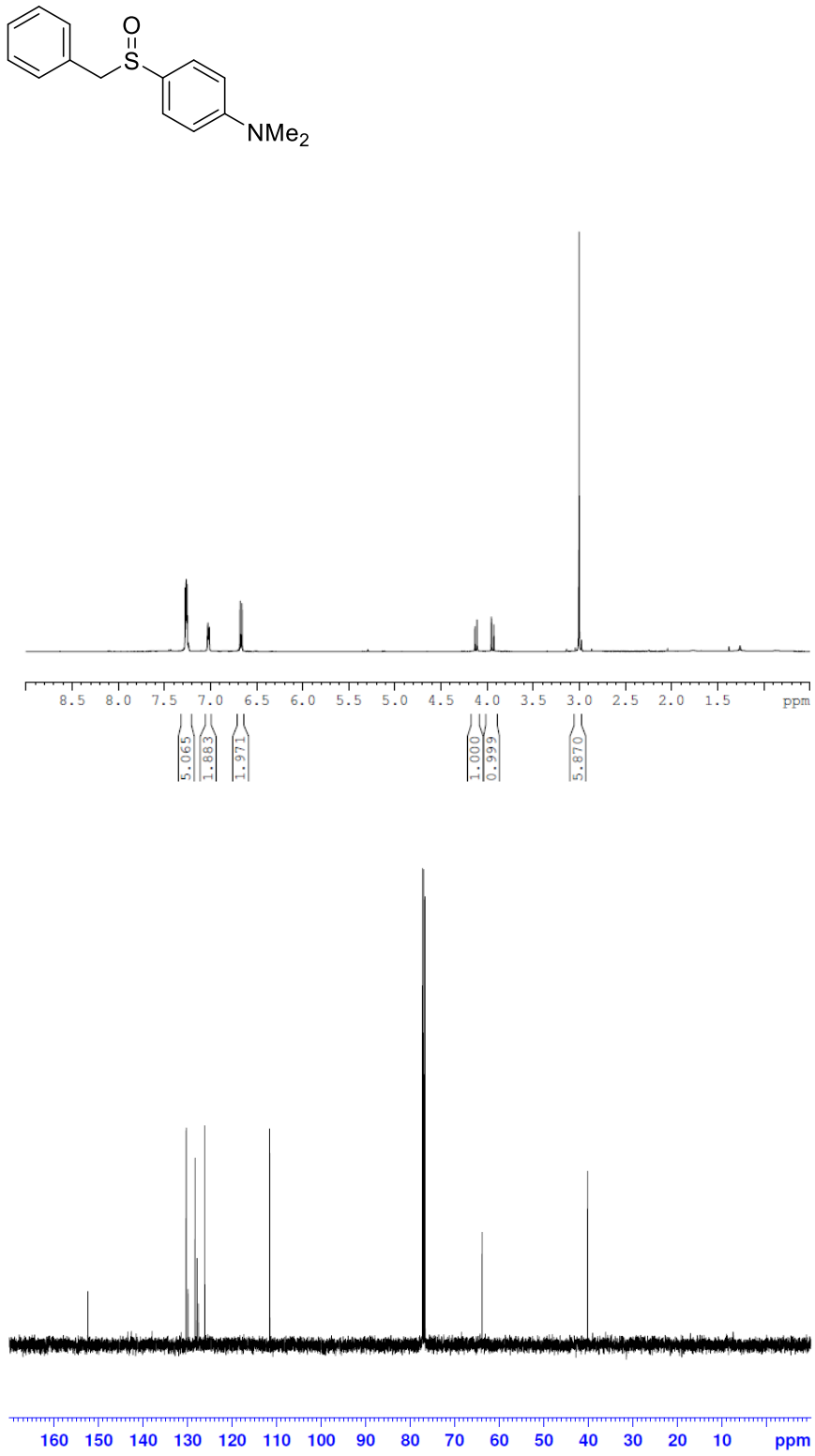
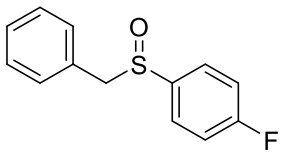


Figure S3. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3c in $CDCl_3$.

1-(Benzylsulfinyl)-4-fluorobenzene (3d)



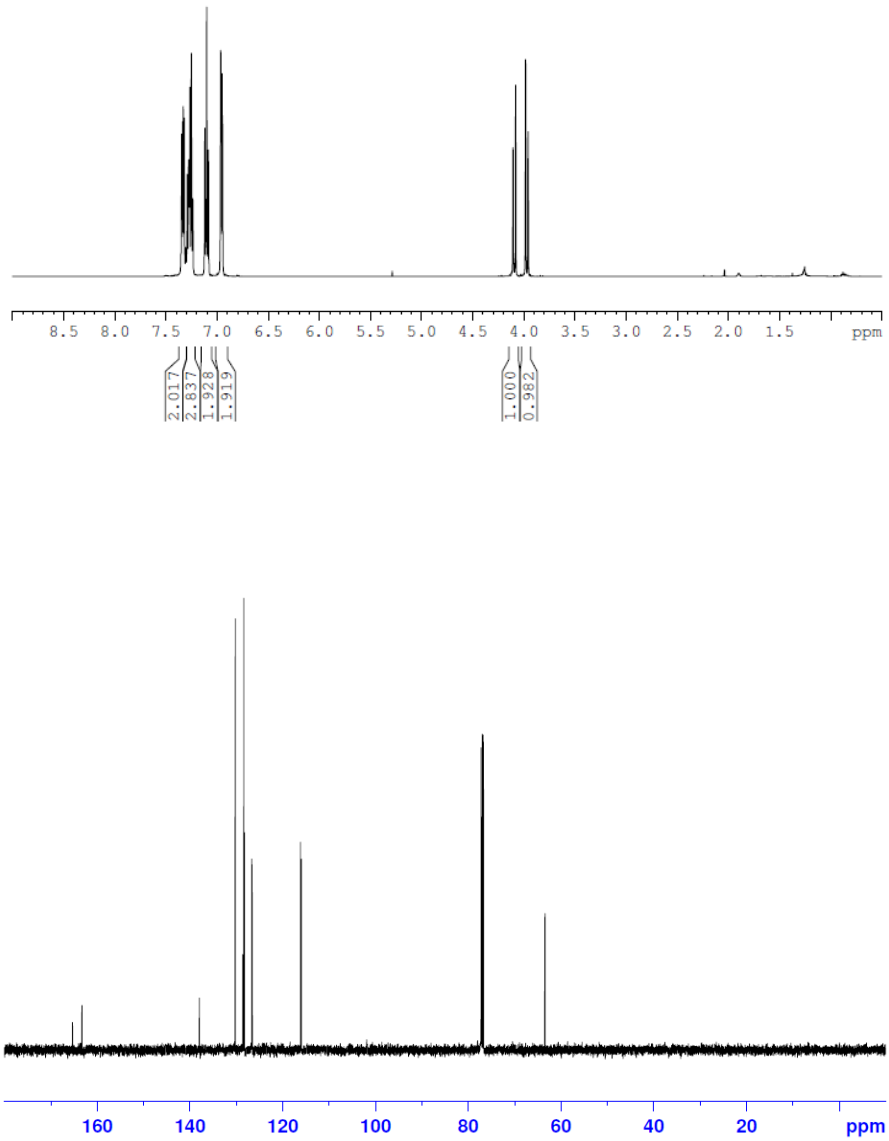
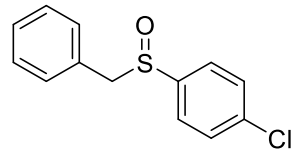
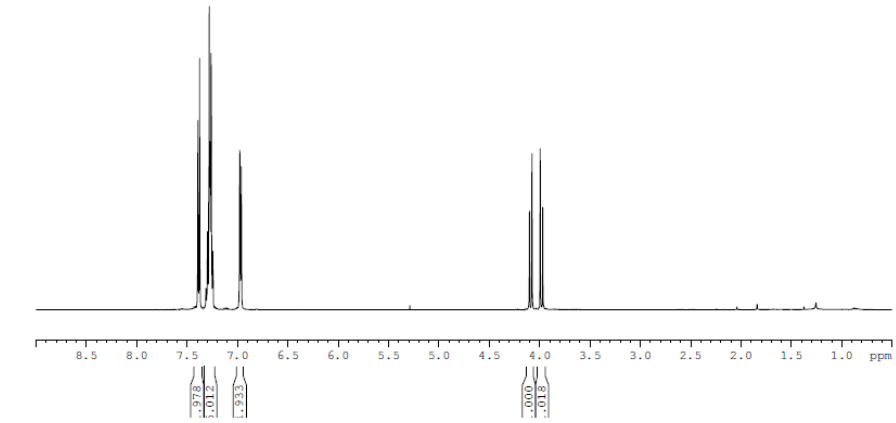


Figure S4. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3d in $CDCl_3$.

1-(Benzylsulfinyl)-4-chlorobenzene (3e)





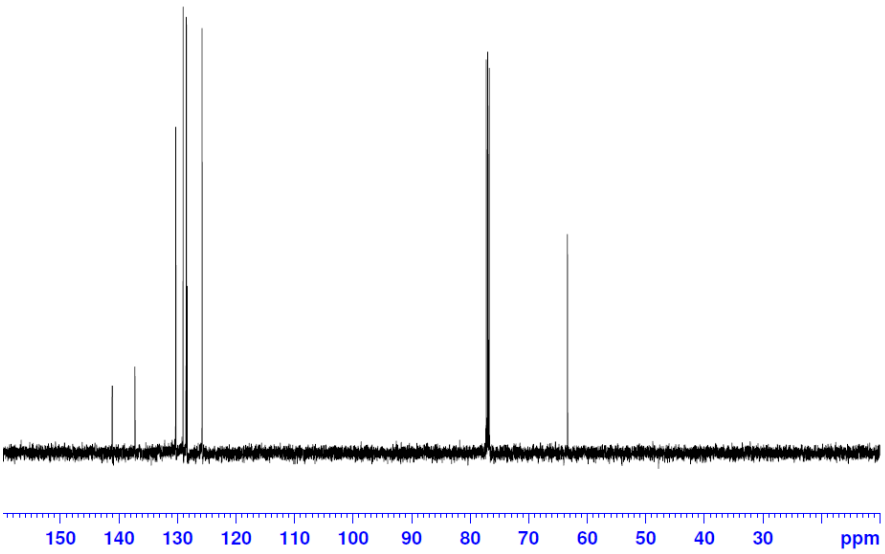
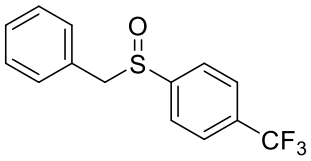


Figure S5. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3e in $CDCl_3$.

1-(Benzylsulfinyl)-4-(trifluoromethyl)benzene (3f)



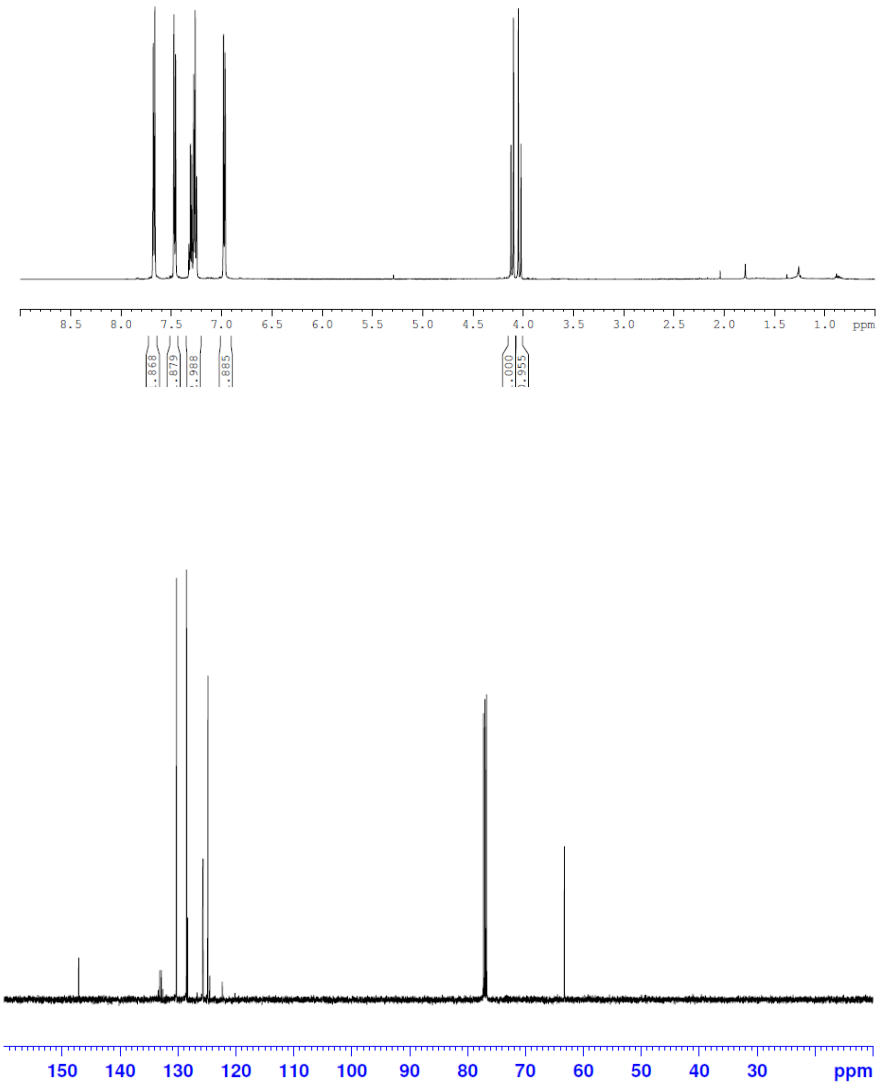
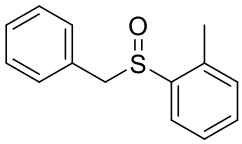


Figure S6. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3f in $CDCl_3$.

1-(Benzylsulfinyl)-2-methylbenzene (3g)



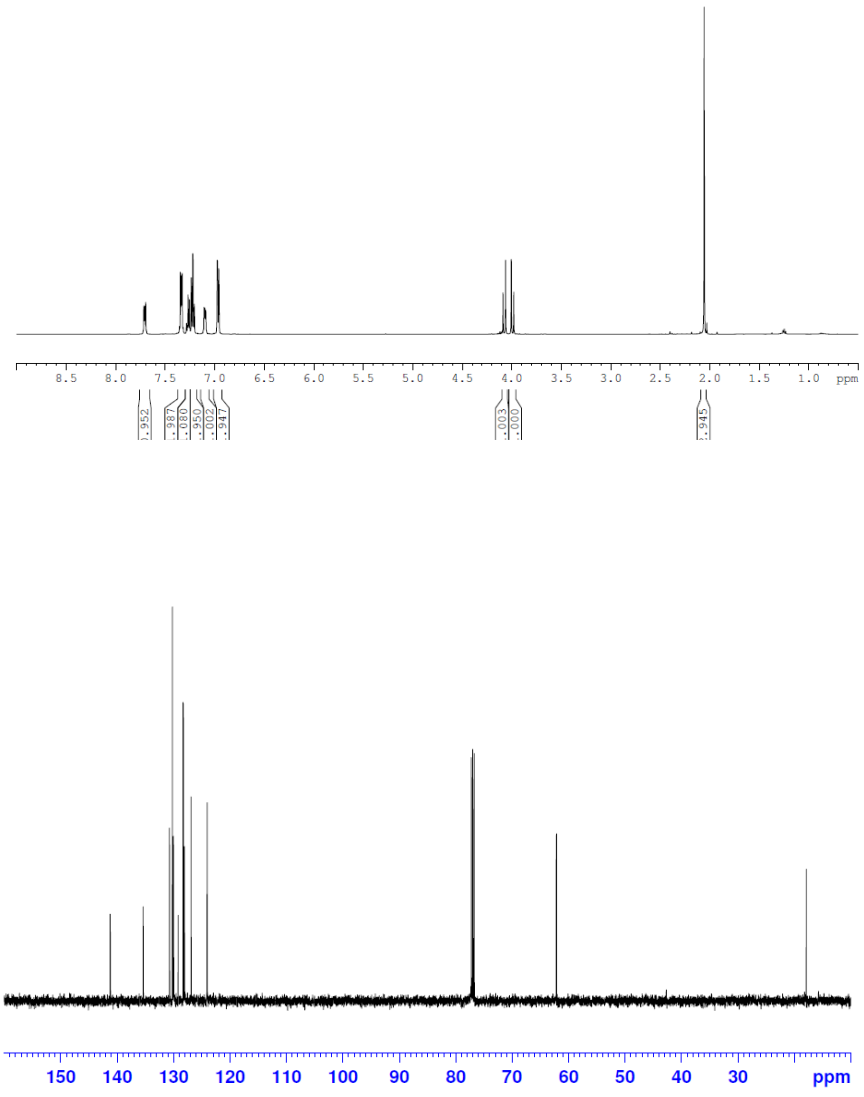
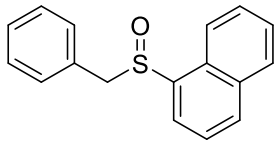
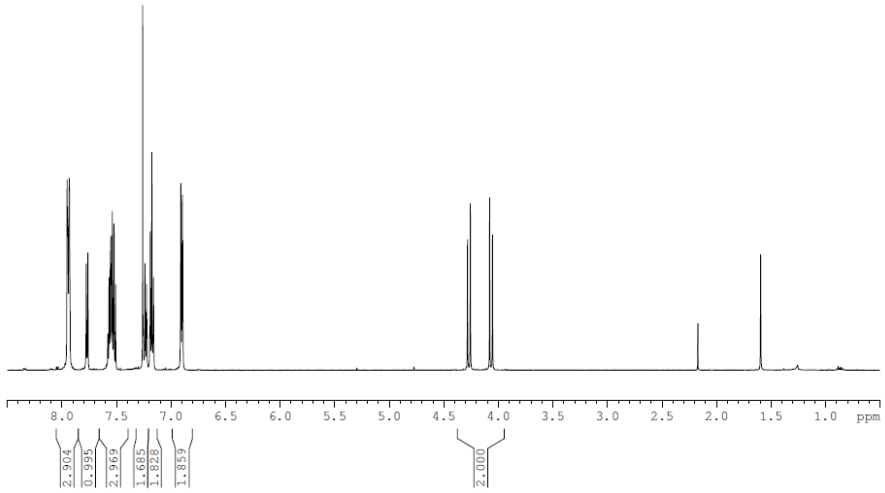


Figure S7. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3g in $CDCl_3$.

1-(Benzylsulfinyl)naphthalene (3h)





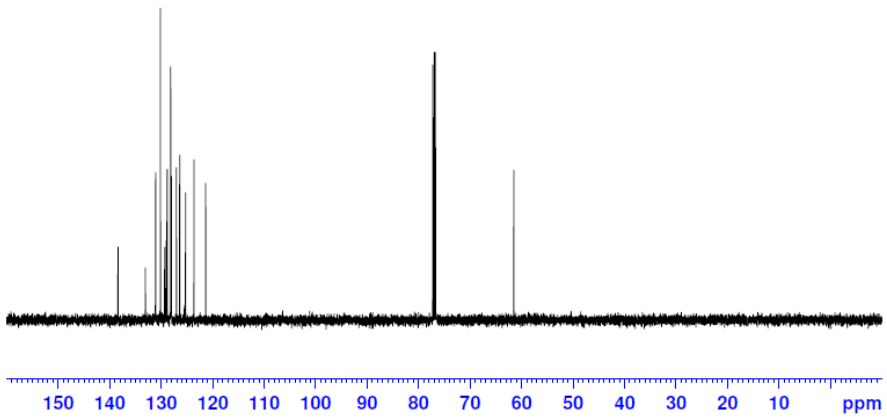
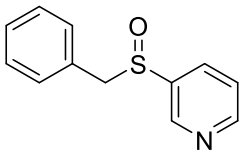


Figure S8. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3h in $CDCl_3$.

3-(Benzylsulfinyl)pyridine (3i)



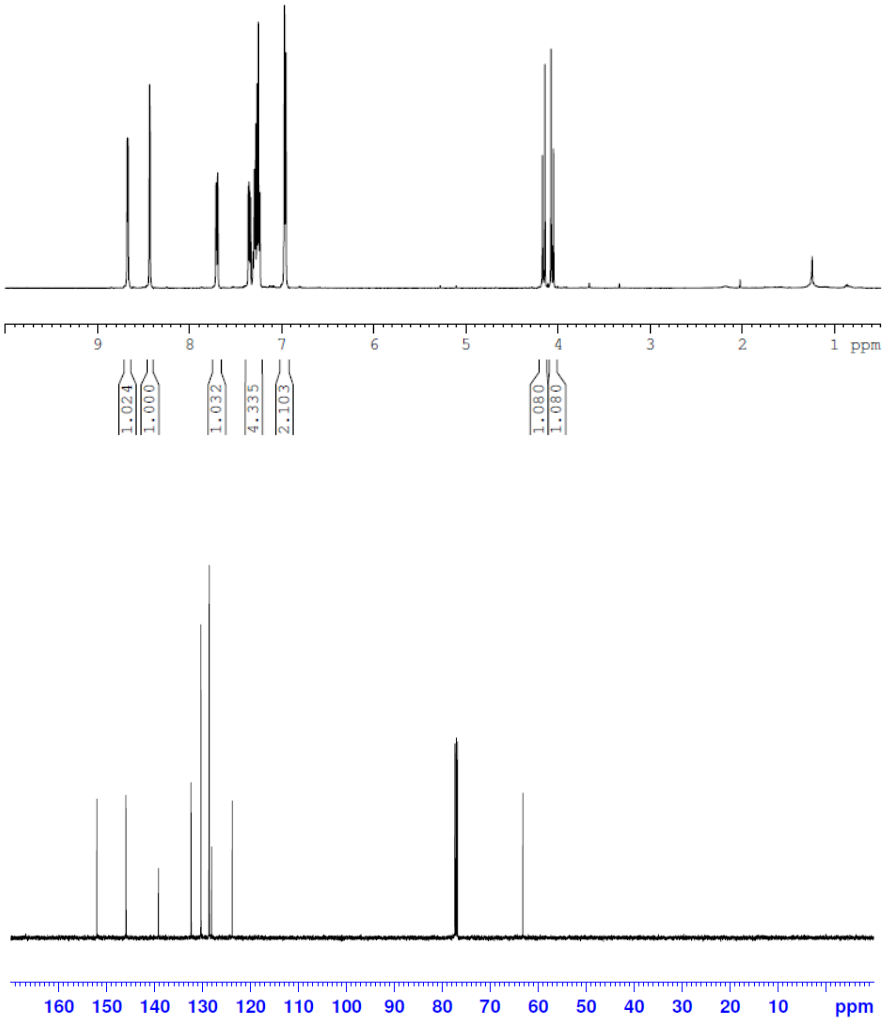
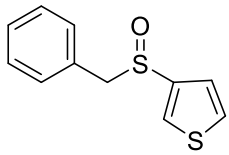


Figure S9. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3i in $CDCl_3$.

3-(Benzylsulfinyl)thiophene (3j)



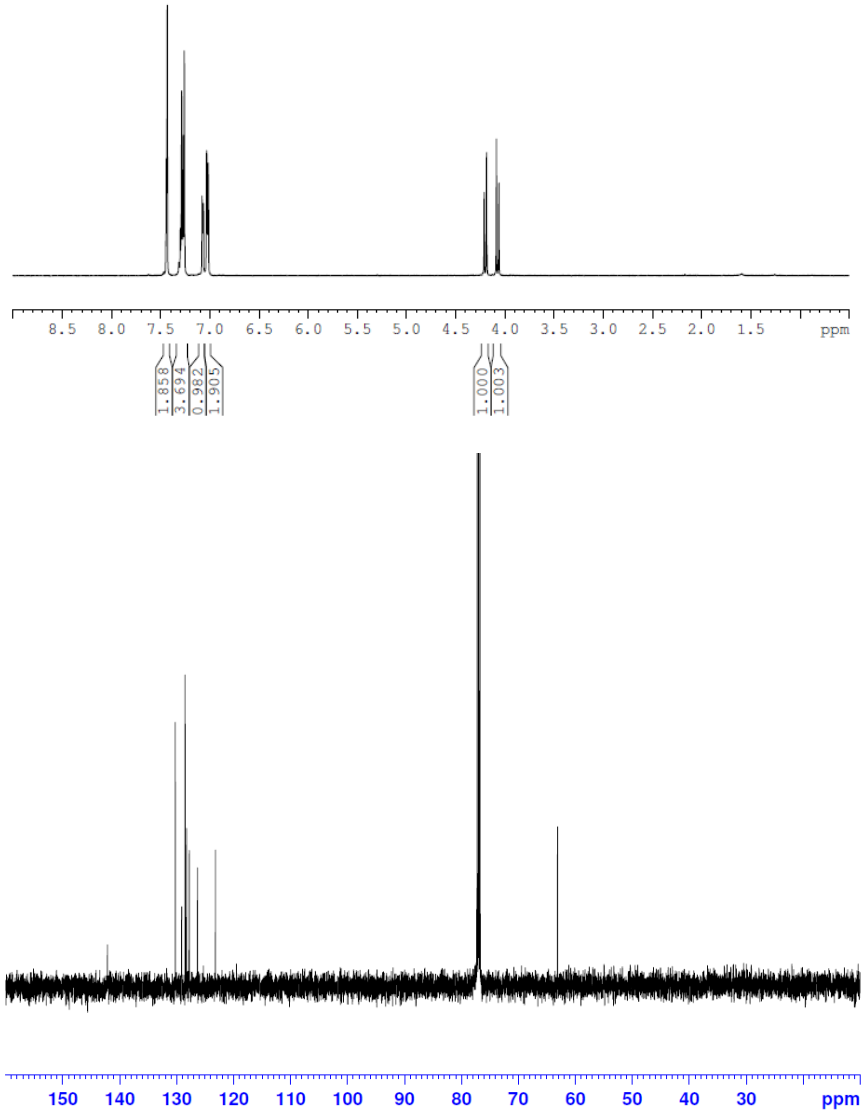


Figure S10. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3j in $CDCl_3$.

5-(Benzylsulfinyl)-1-methyl-1*H*-indole (3k)

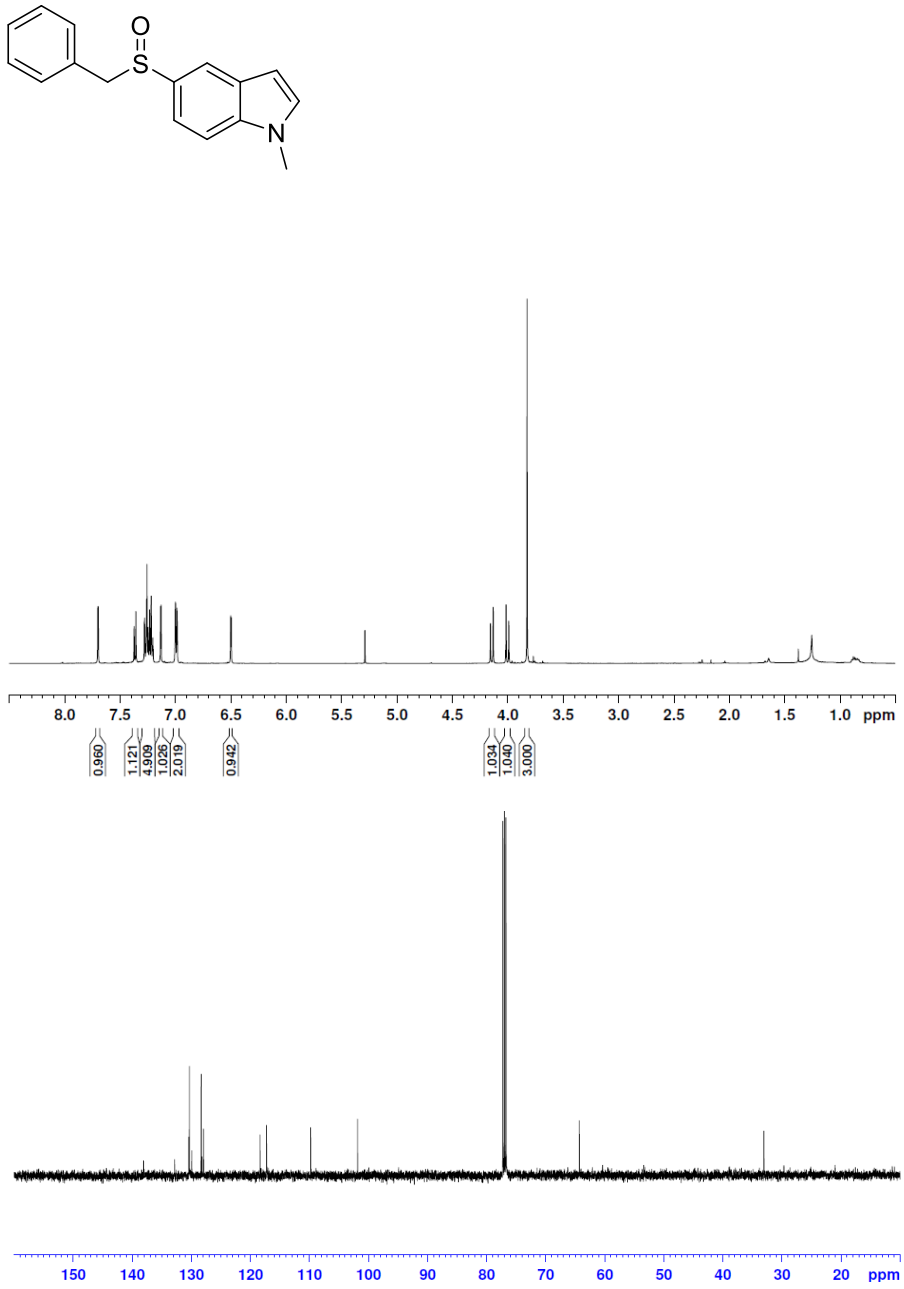
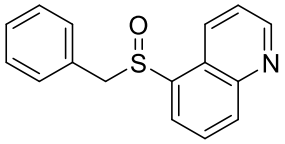


Figure S11. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3k in $CDCl_3$.

5-(Benzylsulfinyl)quinoline (3l)



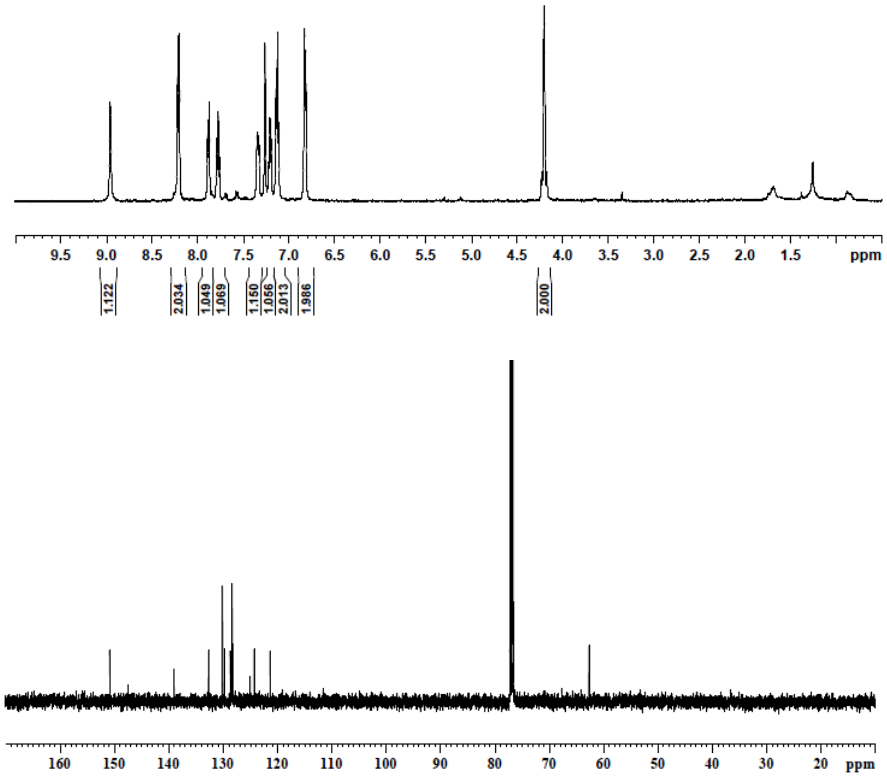
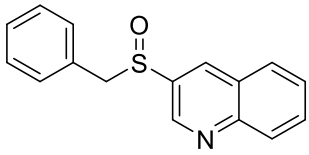
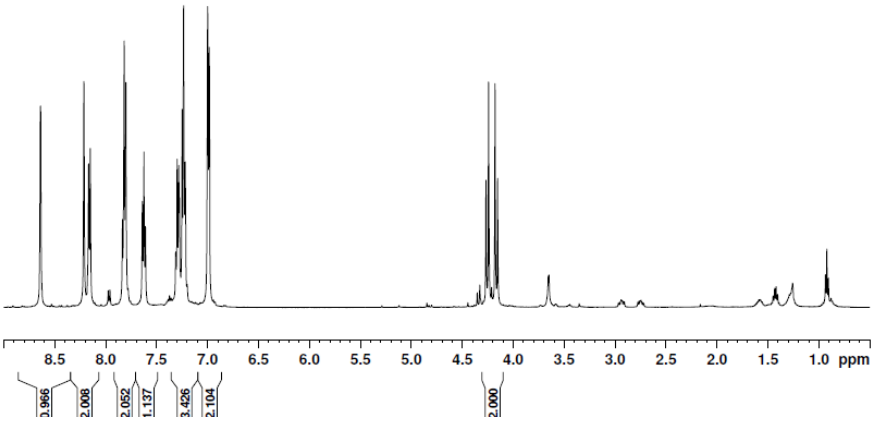


Figure S12. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3l in $CDCl_3$.

3-(Benzylsulfinyl)quinoline (3m)





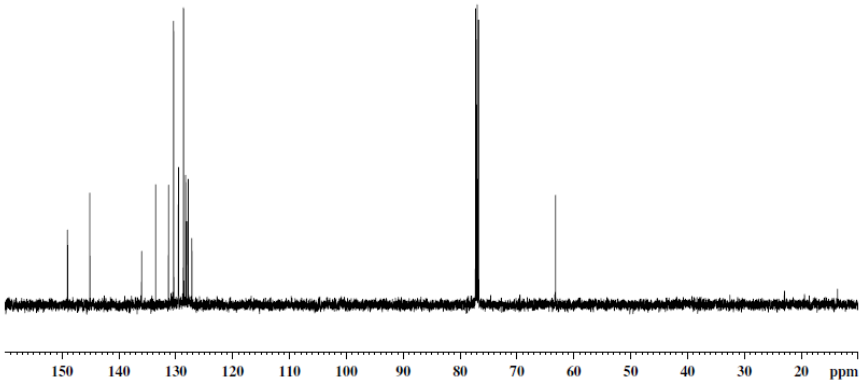
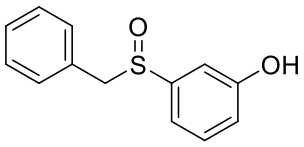


Figure S13. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3m in $CDCl_3$.

3-(Benzylsulfinyl)phenol (3n)



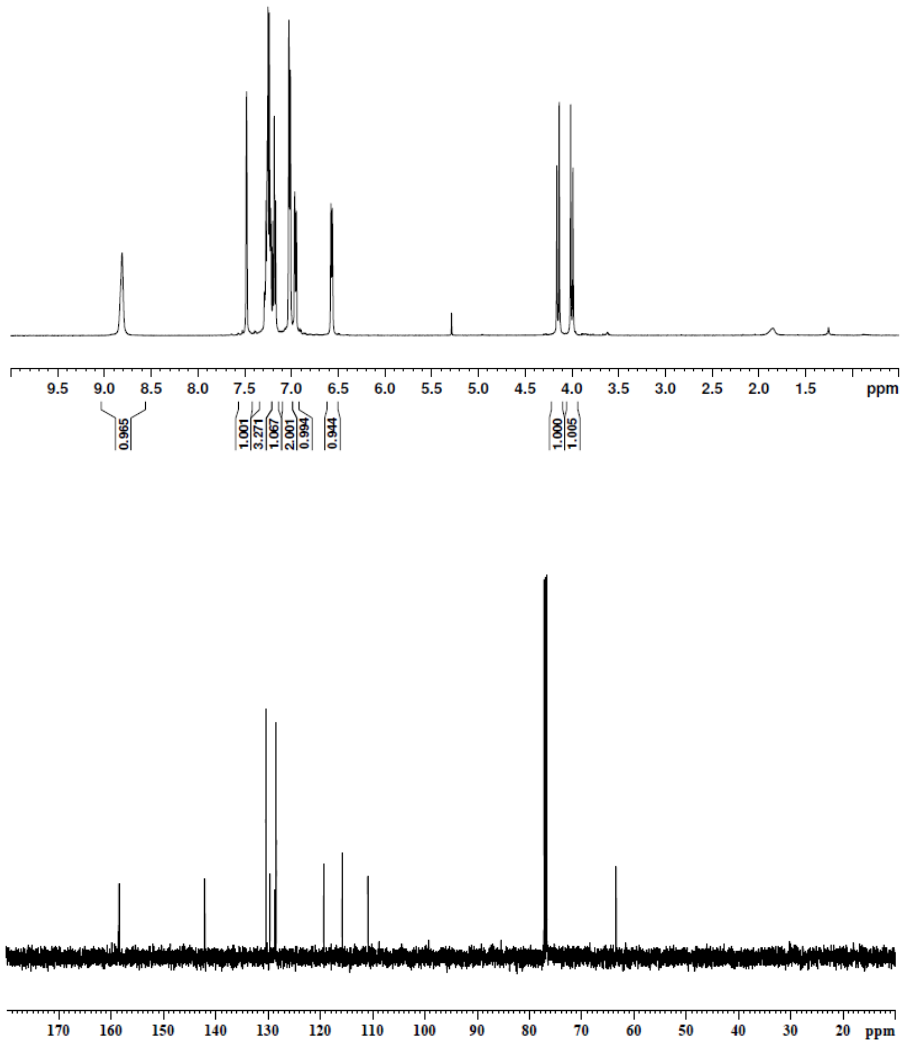


Figure S14. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3n in $CDCl_3$.

4-(Benzylsulfinyl)aniline (3o)

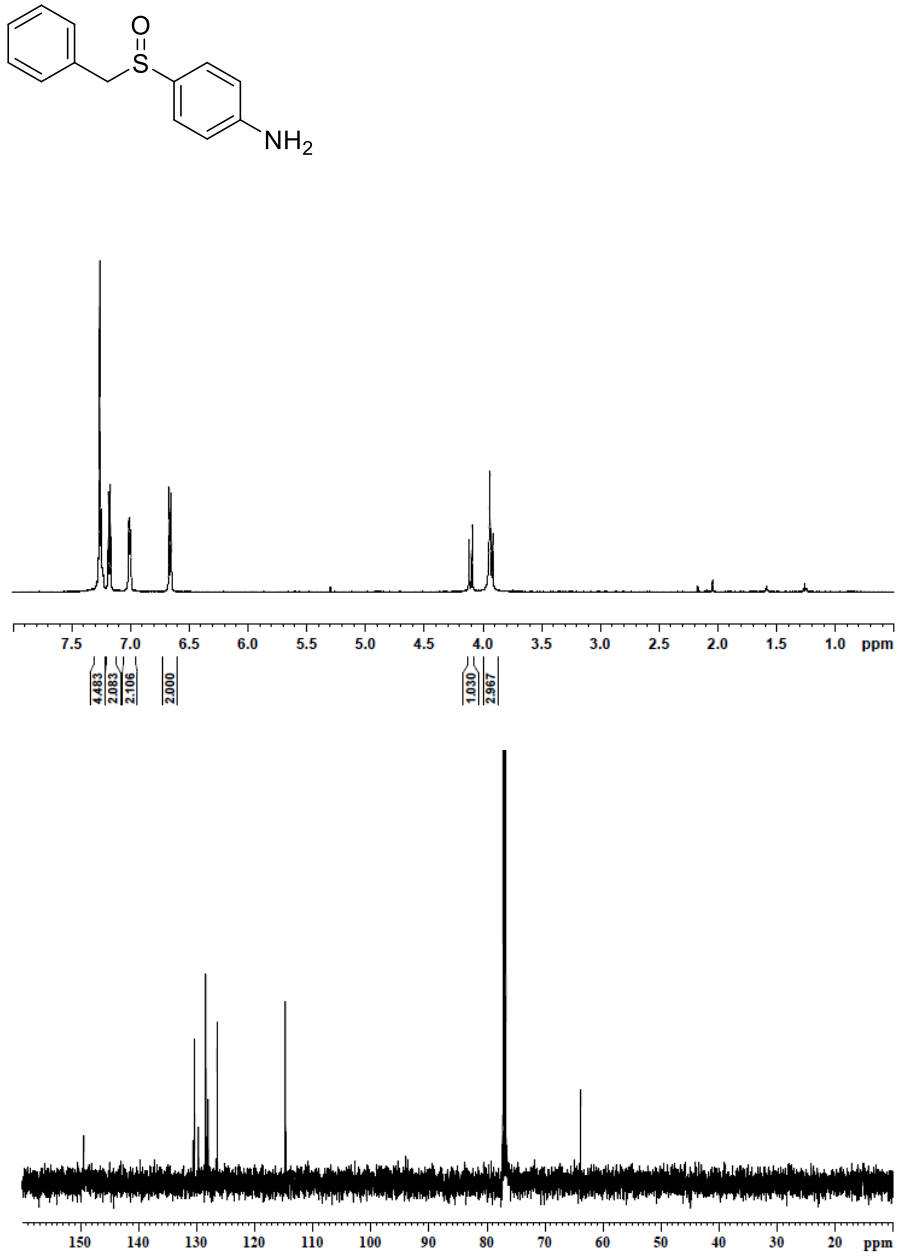
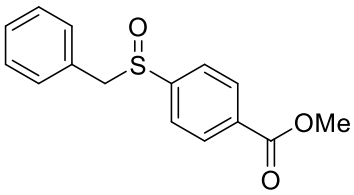


Figure S15. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3o in $CDCl_3$.

Methyl 4-(benzylsulfinyl)benzoate (3p)



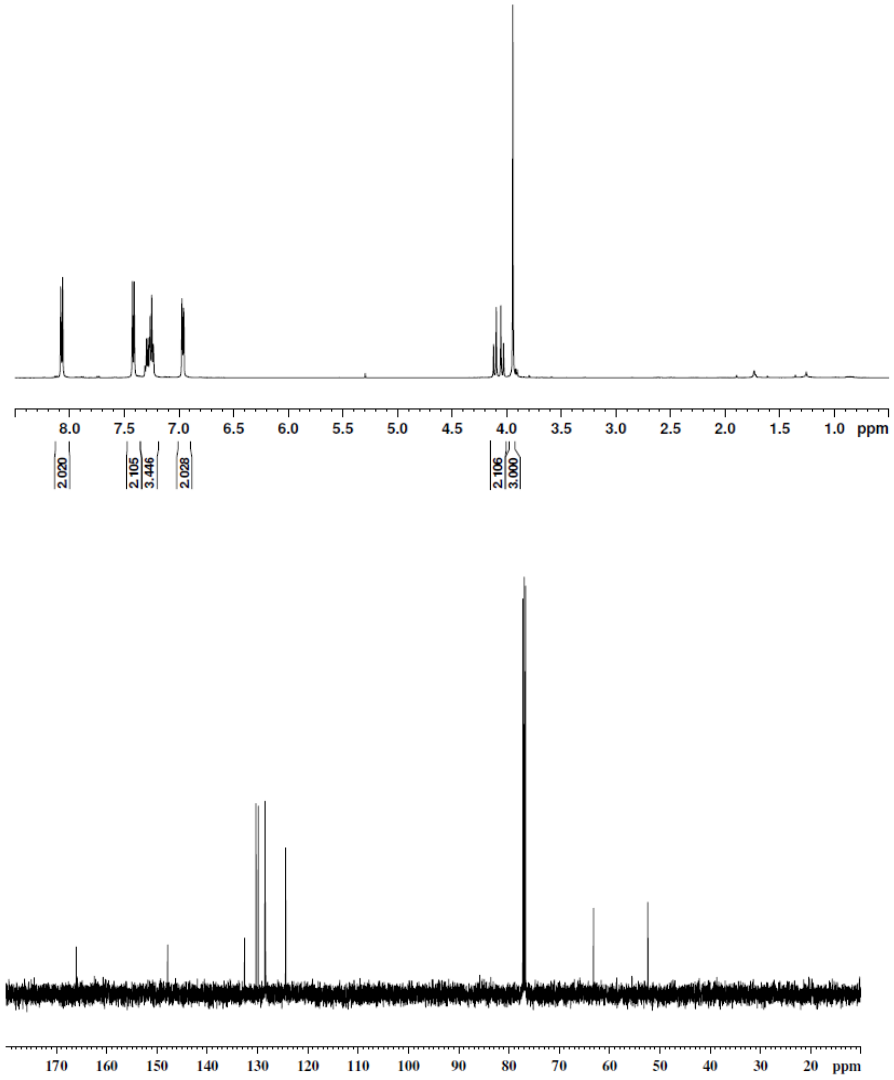
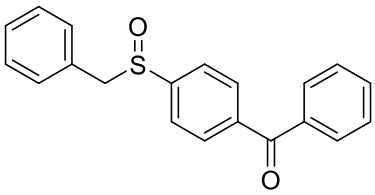
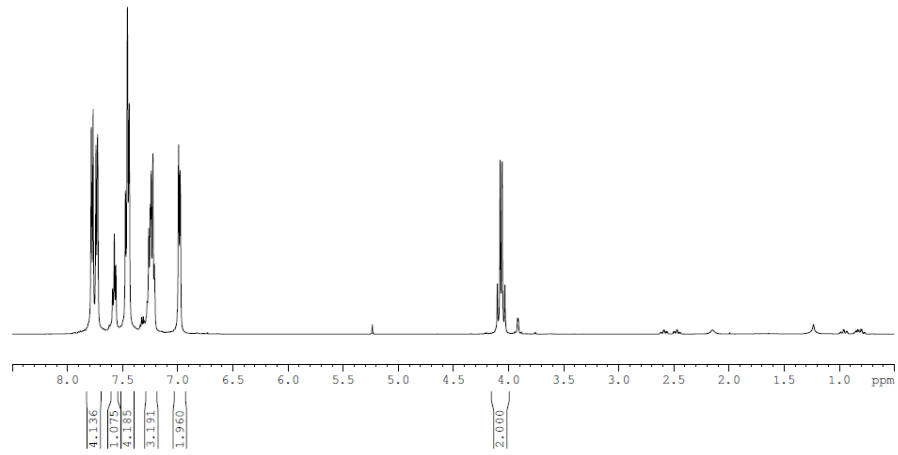


Figure S16. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3p in $CDCl_3$.

(4-(Benzylsulfinyl)phenyl)(phenyl)methanone (3q)





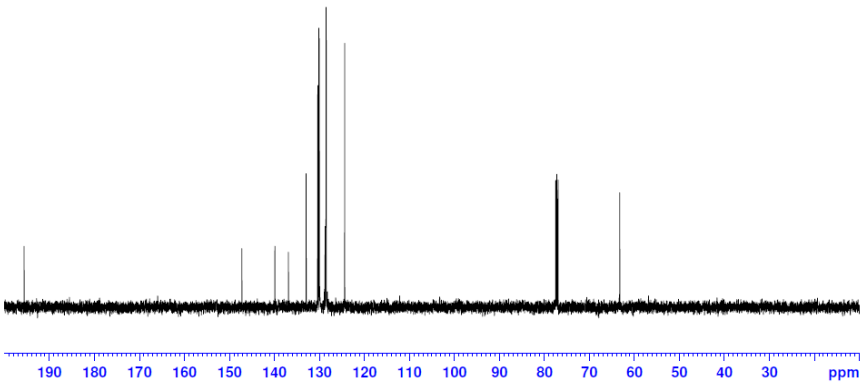


Figure S17. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3q in $CDCl_3$.

8-(Benzylsulfinyl)quinoline (3r)

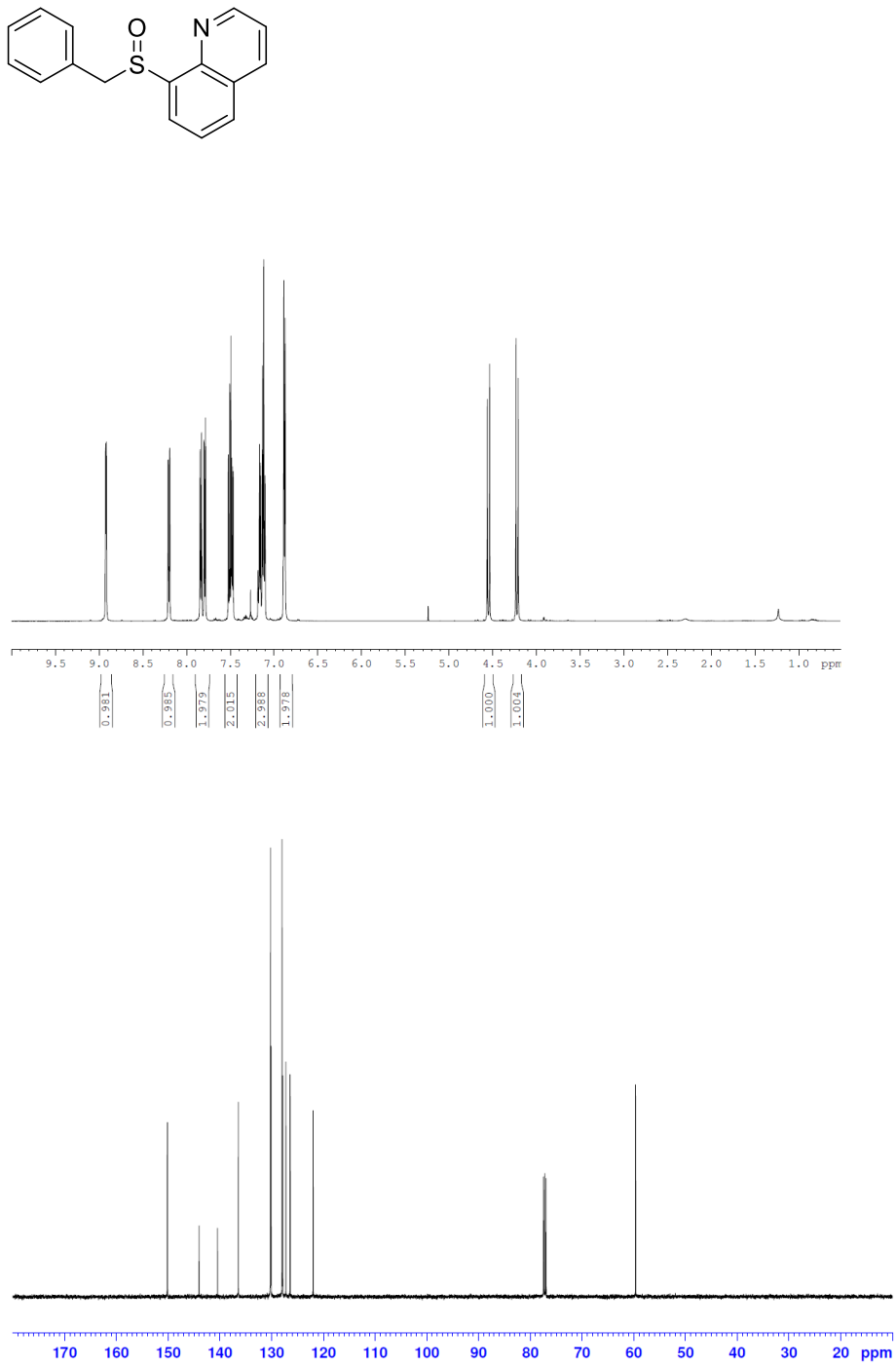
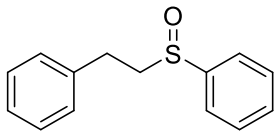


Figure S18. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3r in $CDCl_3$.

(Phenethylsulfinyl)benzene (3s)



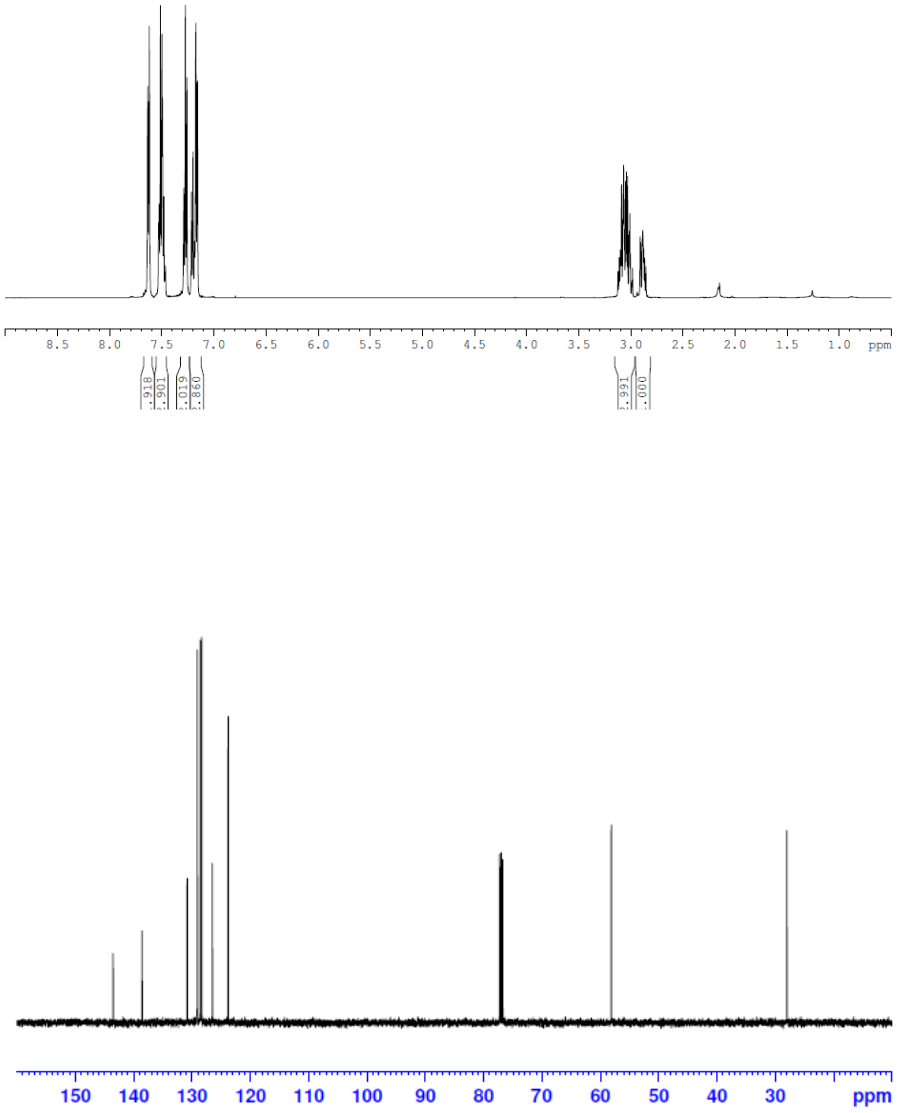
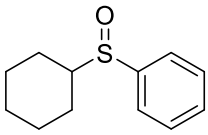


Figure S19. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3s in $CDCl_3$.

(Cyclohexylsulfinyl)benzene (3t)



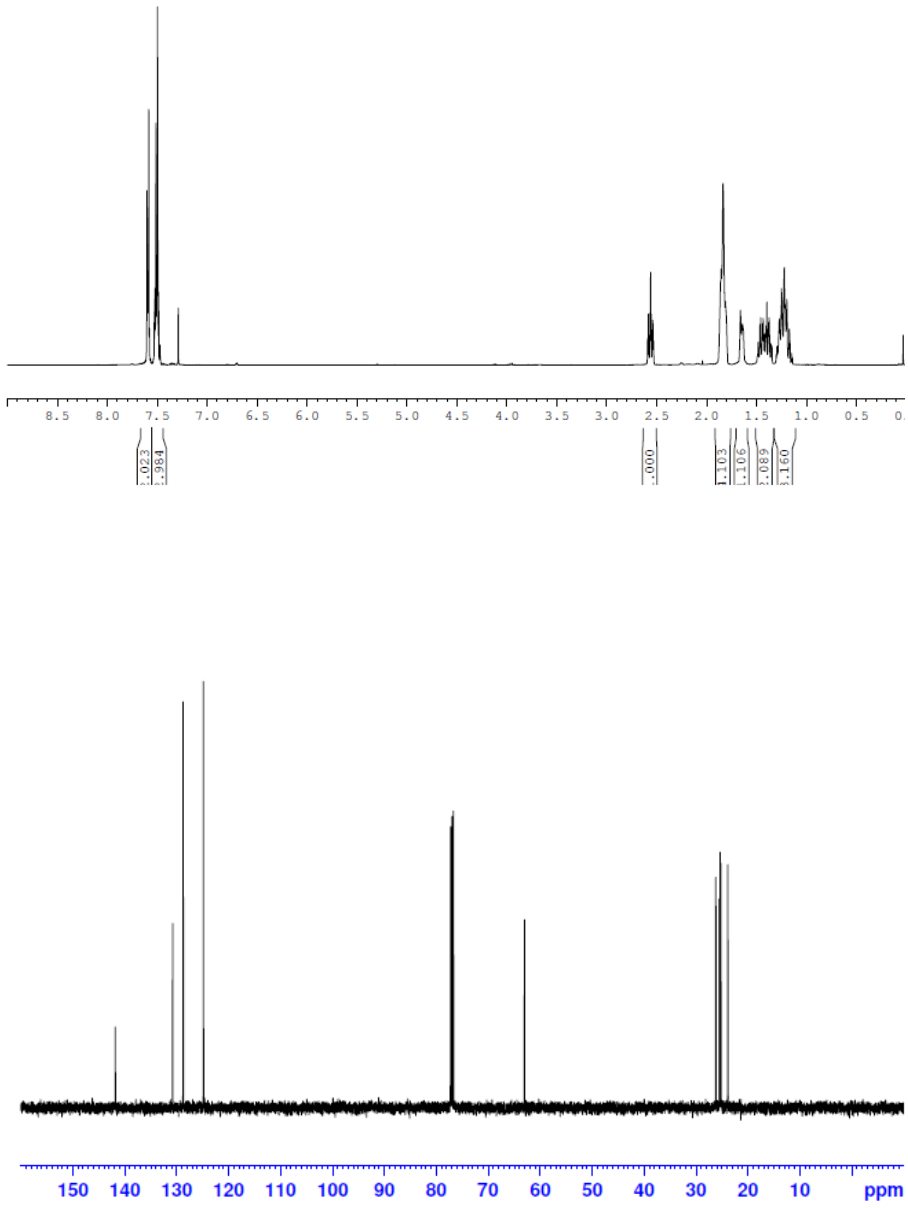
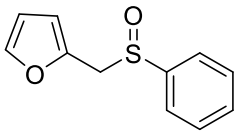


Figure S20. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3t in $CDCl_3$.

2-((Phenylsulfinyl)methyl)furan (3u)



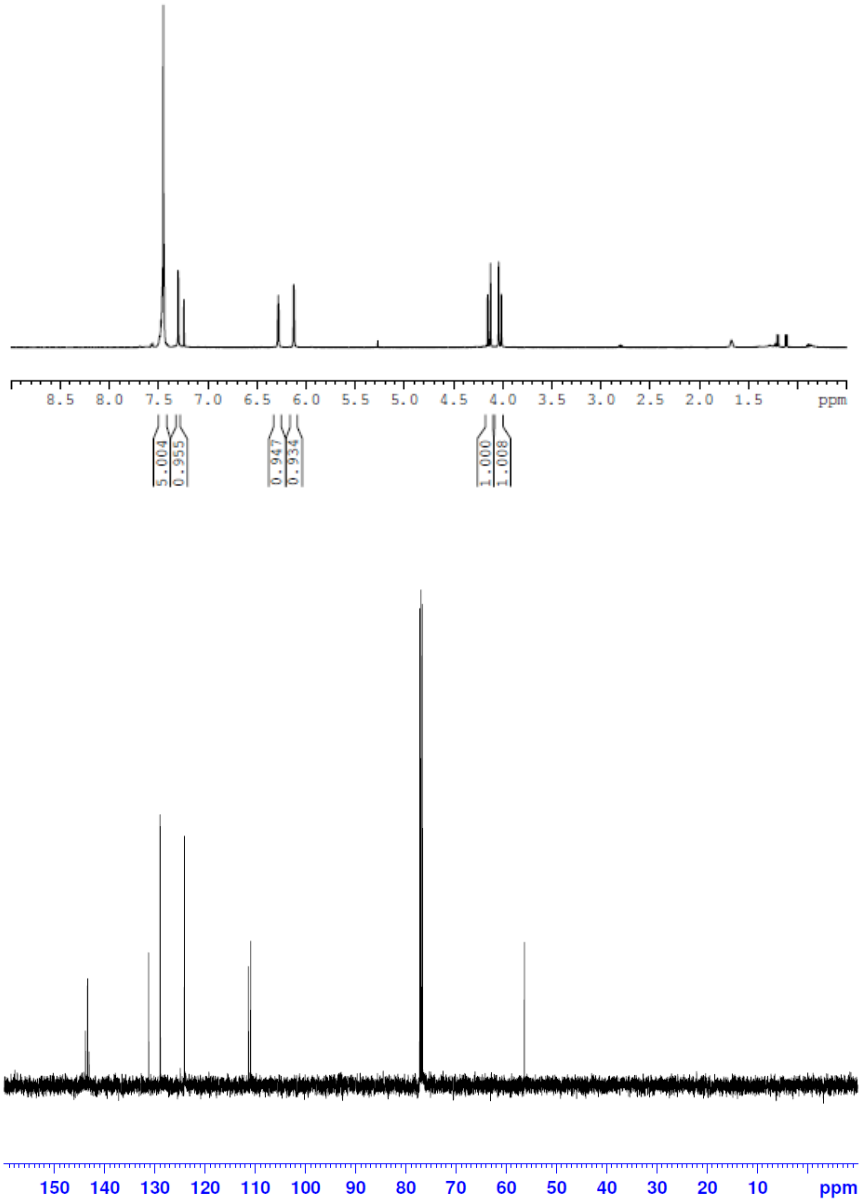
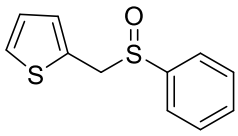


Figure S21. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3u in $CDCl_3$.

2-((Phenylsulfinyl)methyl)thiophene (3v)



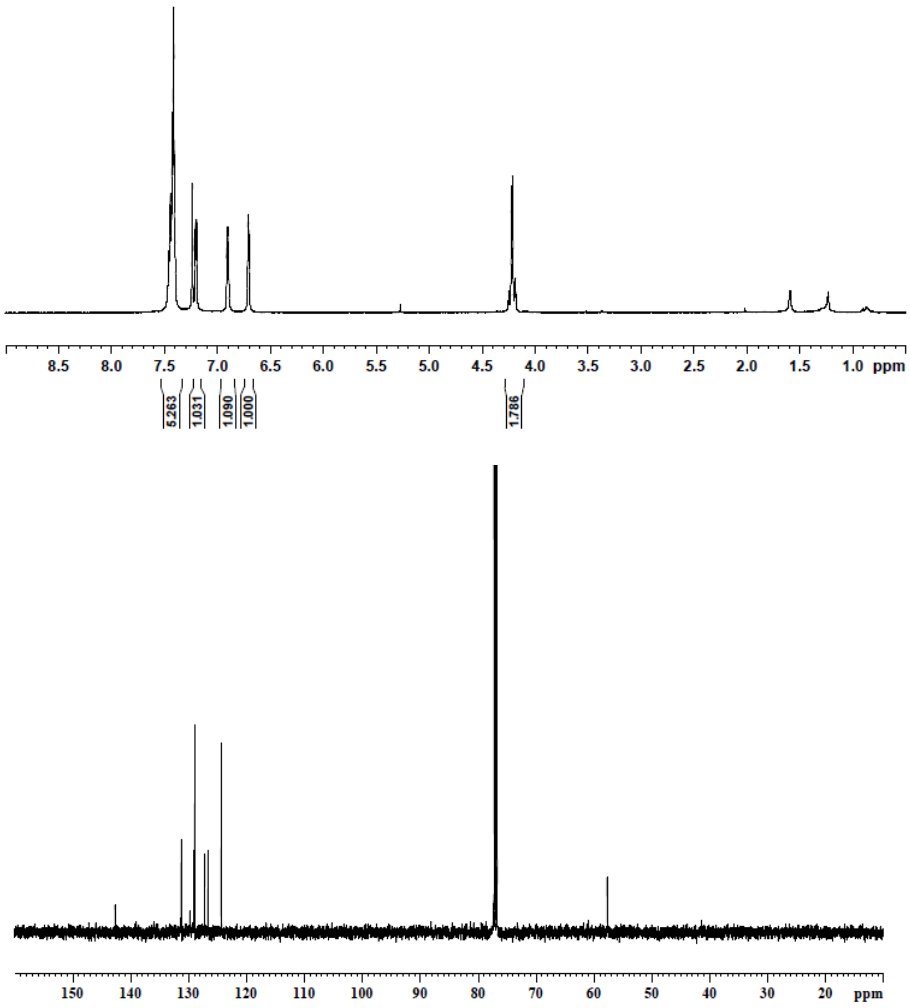
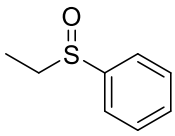
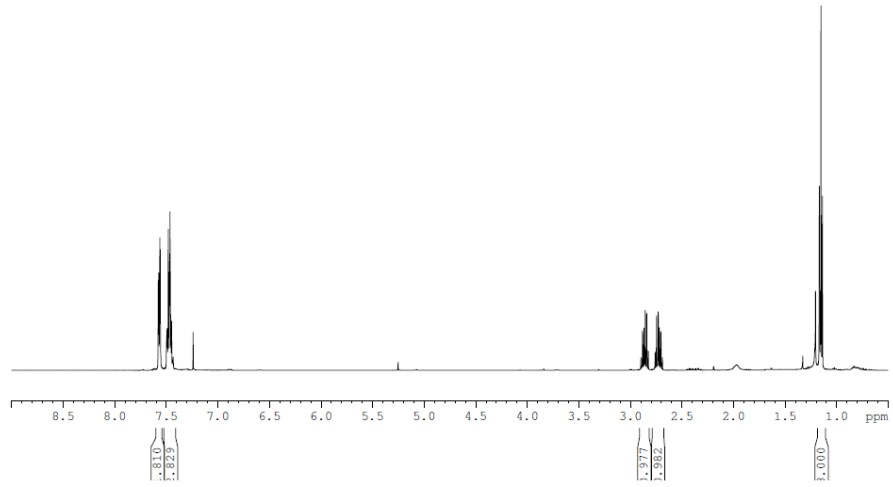


Figure S22. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3v in $CDCl_3$.

(Ethylsulfinyl)benzene (3w)





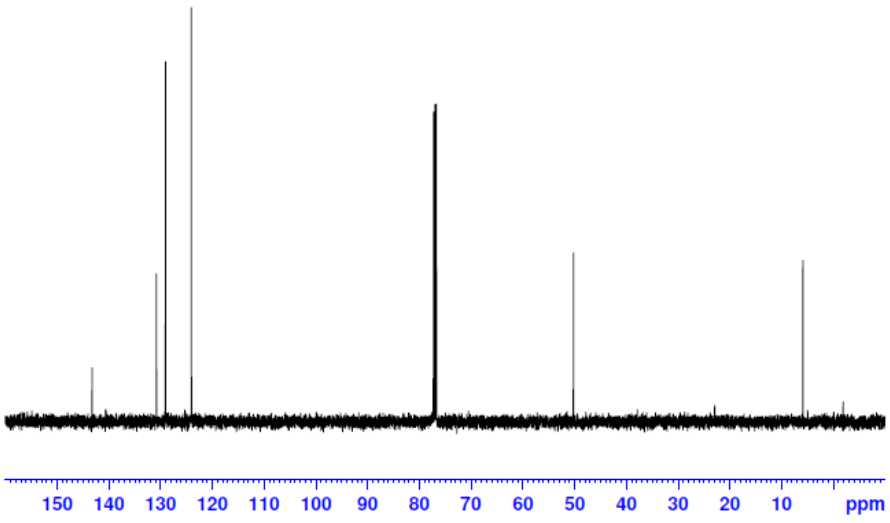
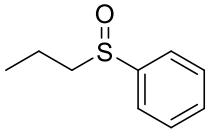
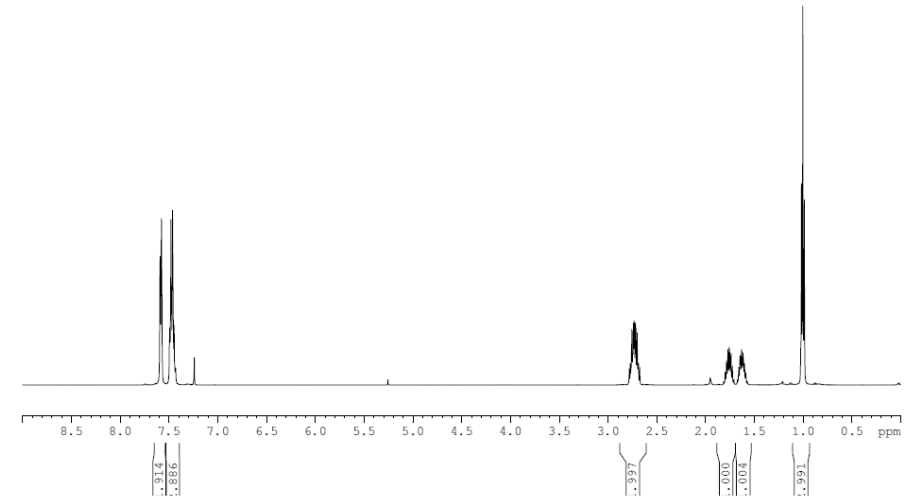


Figure S23. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3w in $CDCl_3$.

(Propylsulfinyl)benzene (3x)





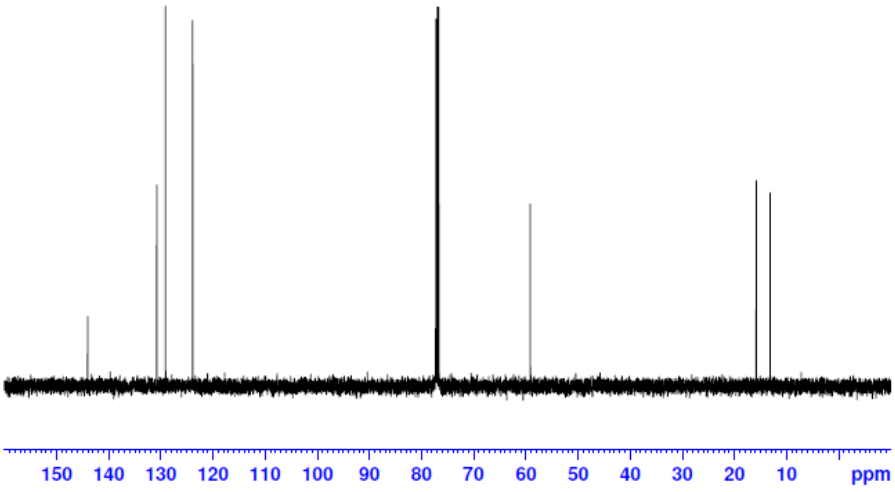
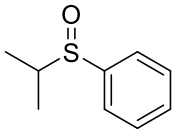


Figure S24. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3x in $CDCl_3$.

(*iso*-Propylsulfinyl)benzene (3y)



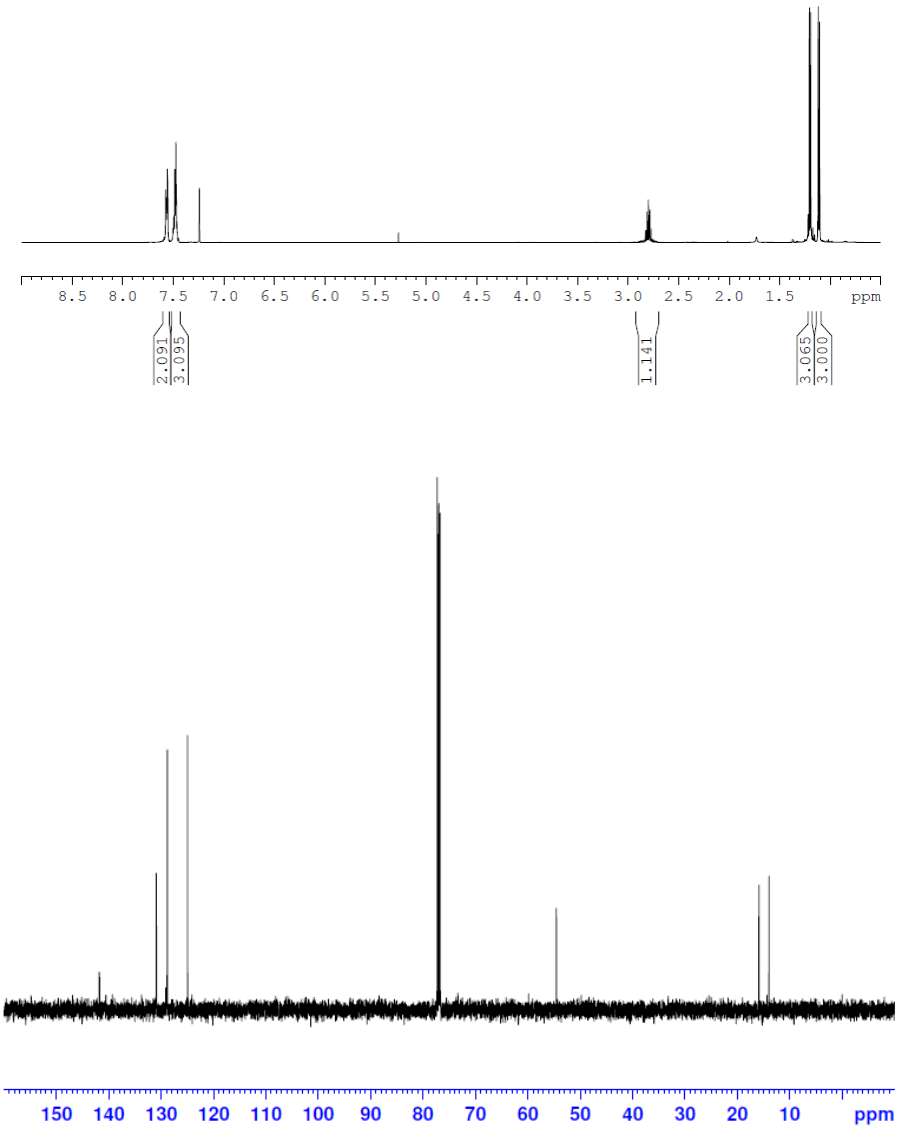
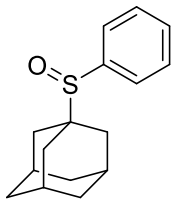


Figure S25. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3y in $CDCl_3$.

1-(Phenylsulfinyl)adamantane (3z)



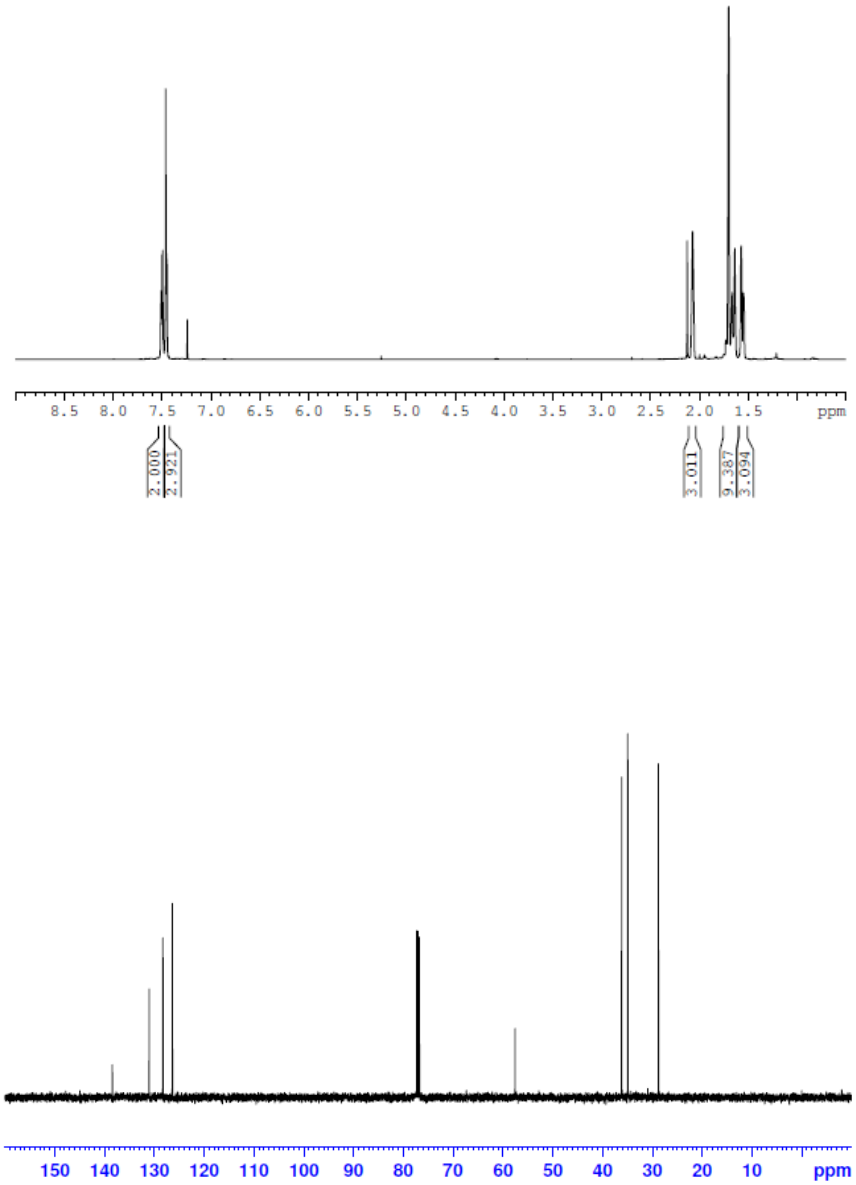


Figure S26. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3z in $CDCl_3$.

((3-Ethoxypropyl)sulfinyl)benzene (3aa)

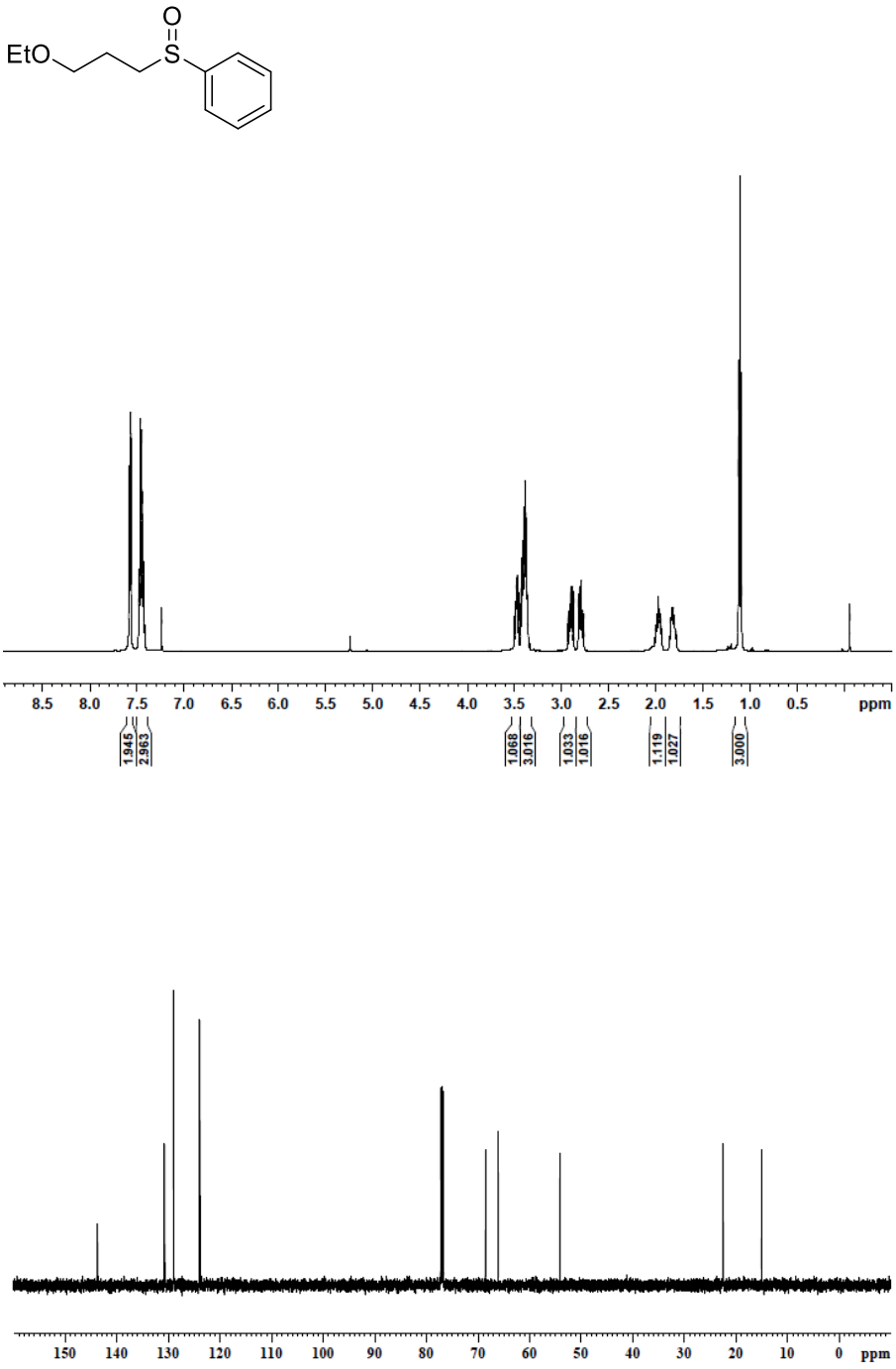
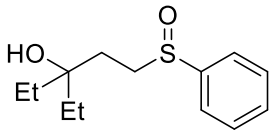


Figure S27 ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3aa in $CDCl_3$.

Ethyl-1-(phenylsulfinyl)pentan-3-ol (3ab)



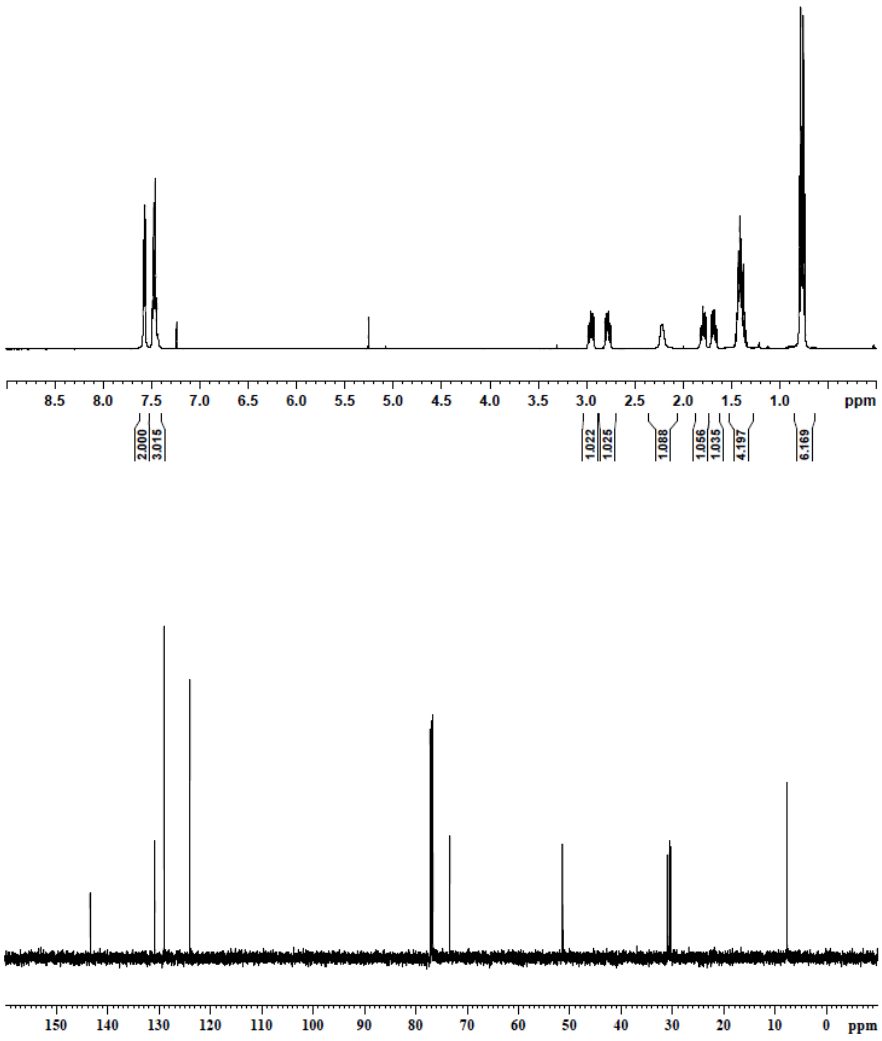


Figure S28. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3ab in $CDCl_3$.

Cinnamylsulfinyl)benzene (3ac)

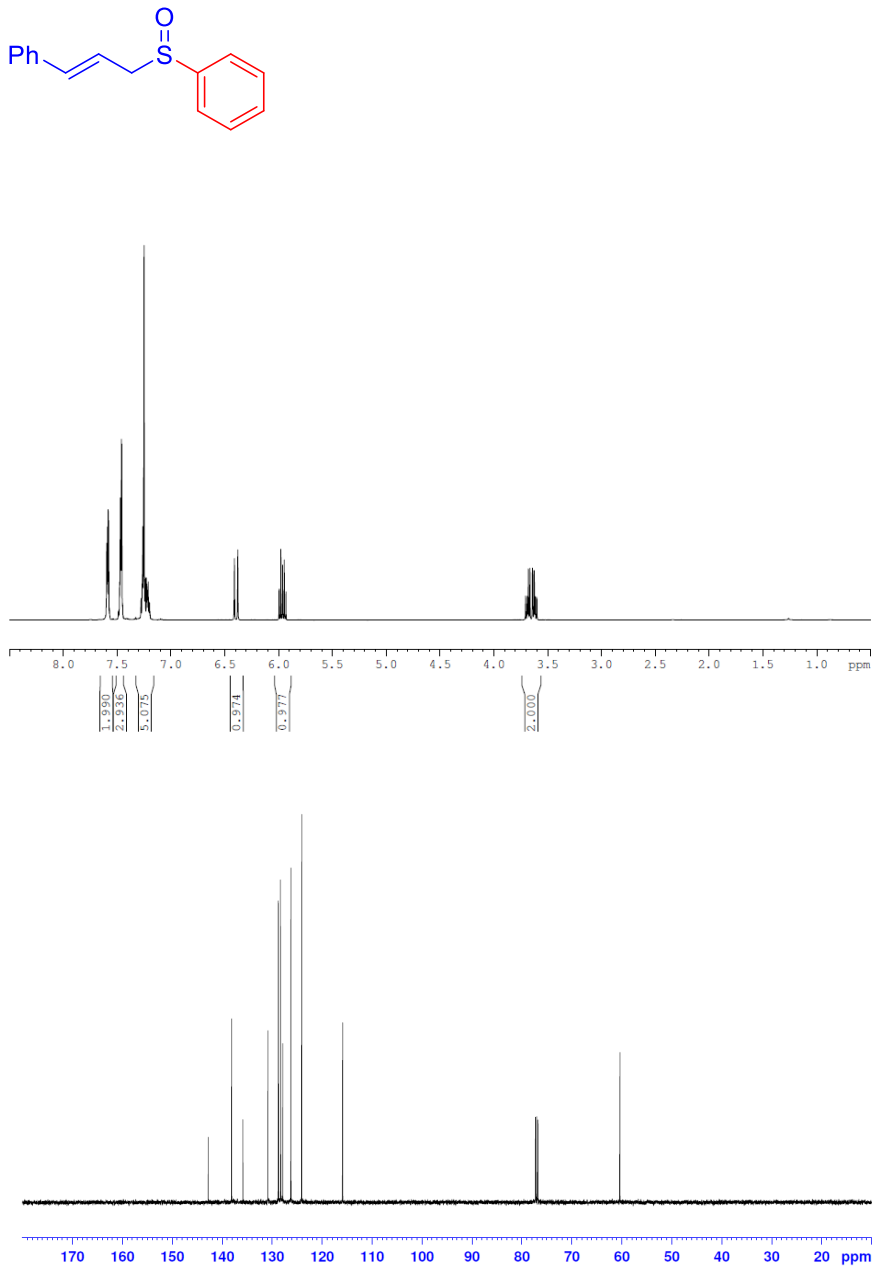
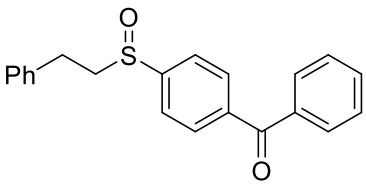
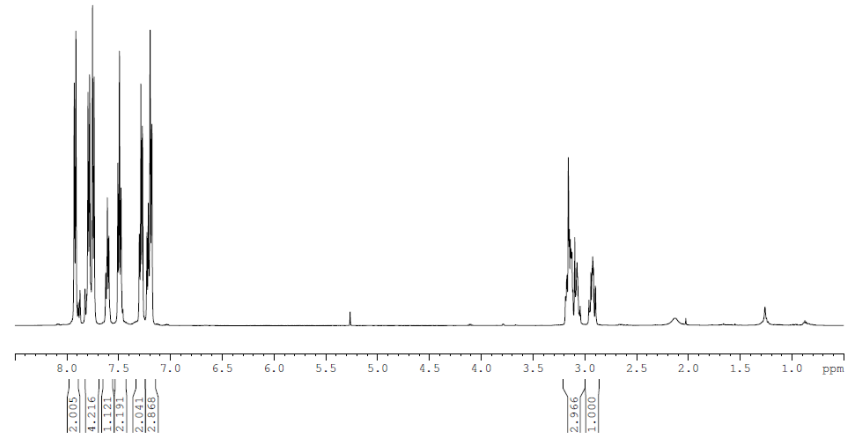


Figure S29. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3ac in $CDCl_3$.

(4-(Phenethylsulfinyl)phenyl)(phenyl)methanone (3ad)





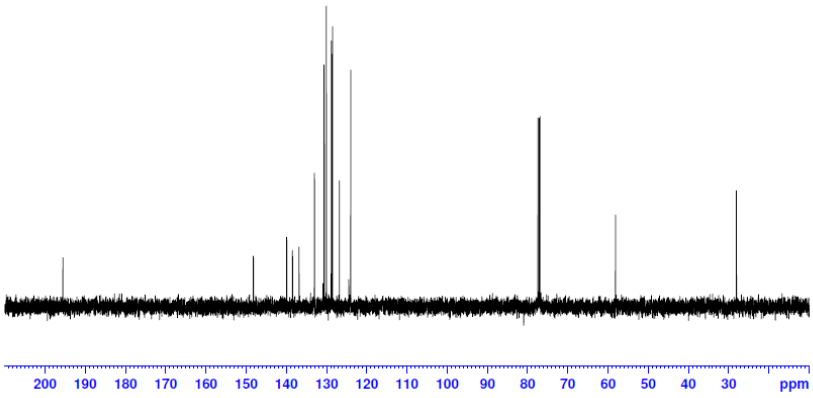
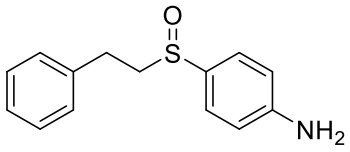


Figure S30. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3ad in $CDCl_3$.

4-(Phenethylsulfinyl)aniline (3ae)



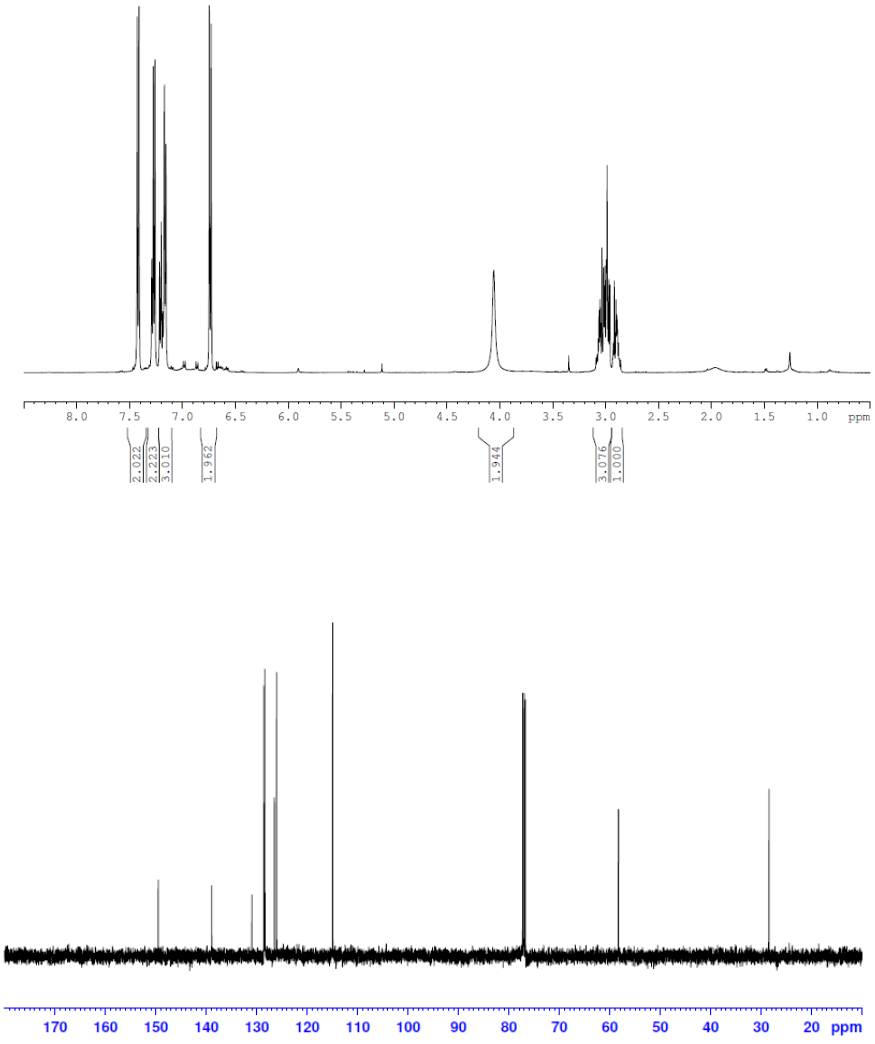
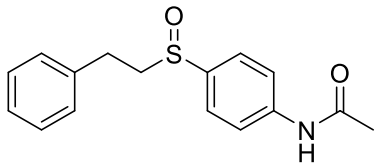


Figure S31. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3ae in $CDCl_3$.

***N*-(4-(phenethylsulfinyl)phenyl)acetamide (3af)**



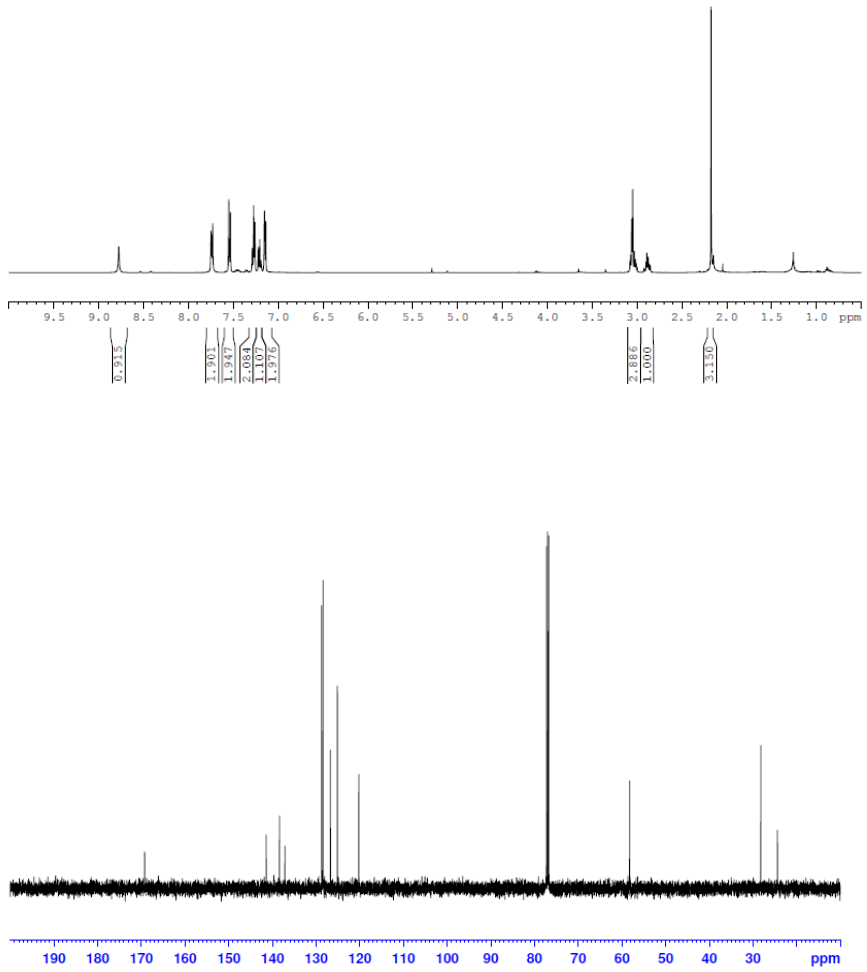
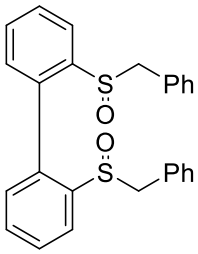


Figure S32. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3af in $CDCl_3$.

2,2'-Bis(benzylsulfinyl)-1,1'-biphenyl (3ag, mixture of two diasteromers)



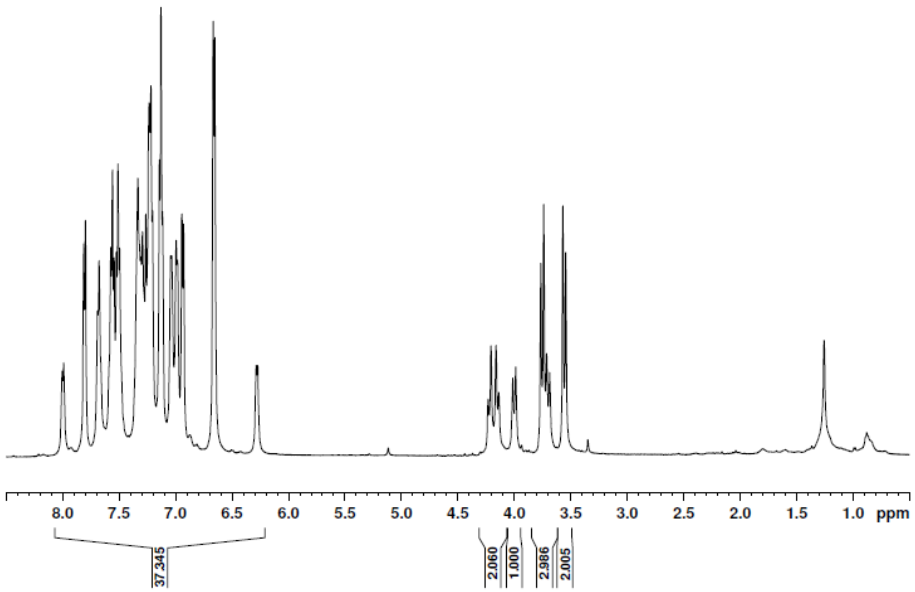
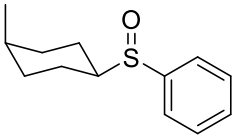
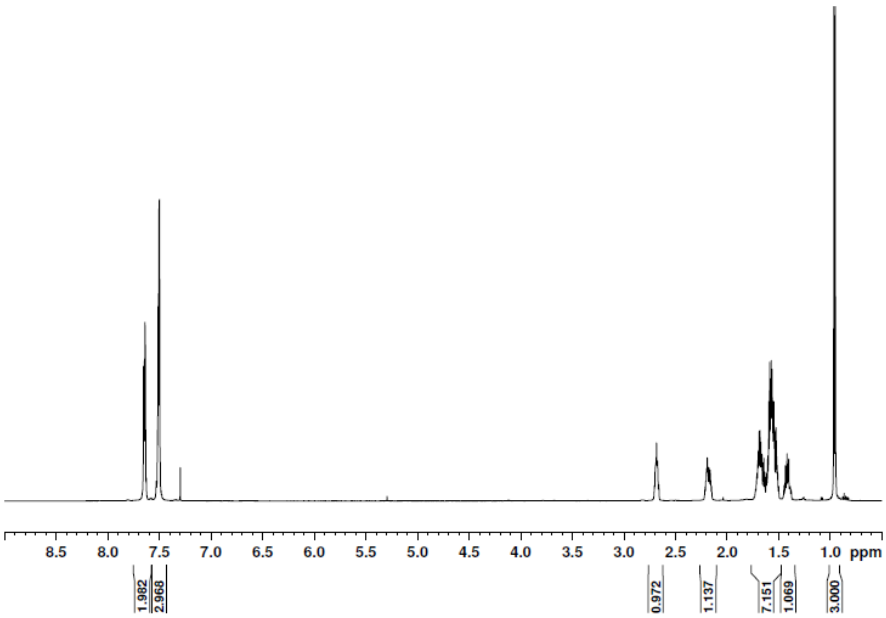


Figure S33. ^{1}H (500 MHz) NMR spectrum of 3ag (a pair of diasteromers) in $CDCl_3$.

((*cis*-4-Methylcyclohexyl)sulfinyl)benzene (3ah)





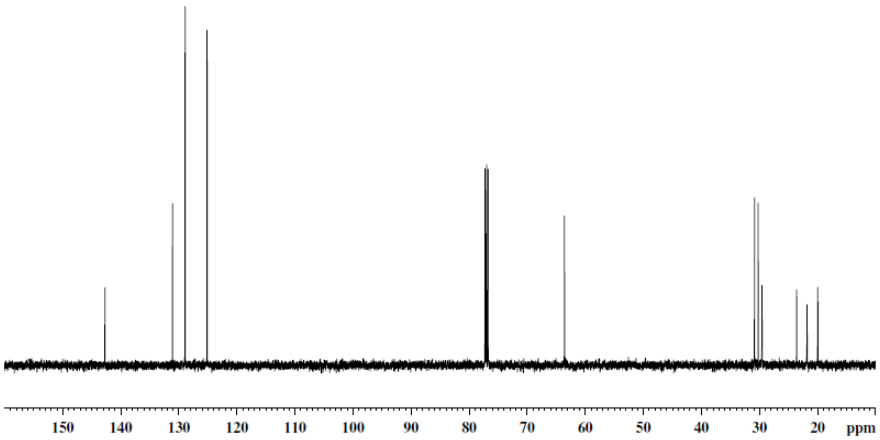


Figure S34. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 3ah in $CDCl_3$.

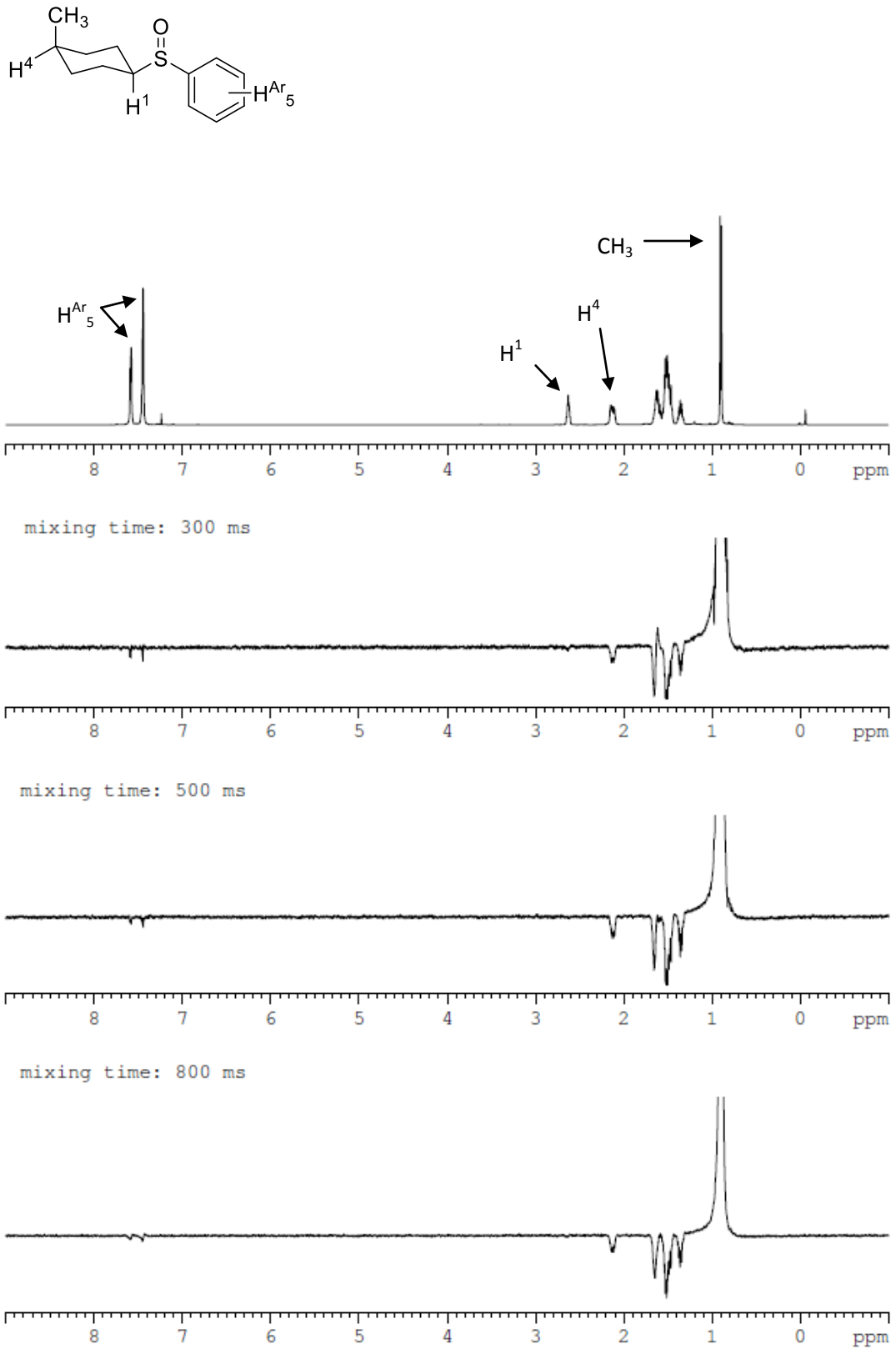


Figure S35. Nuclear Overhauser Effect (NOE) between CH_3 and H_{Ar}^5 by ^1H NMR (500 MHz)

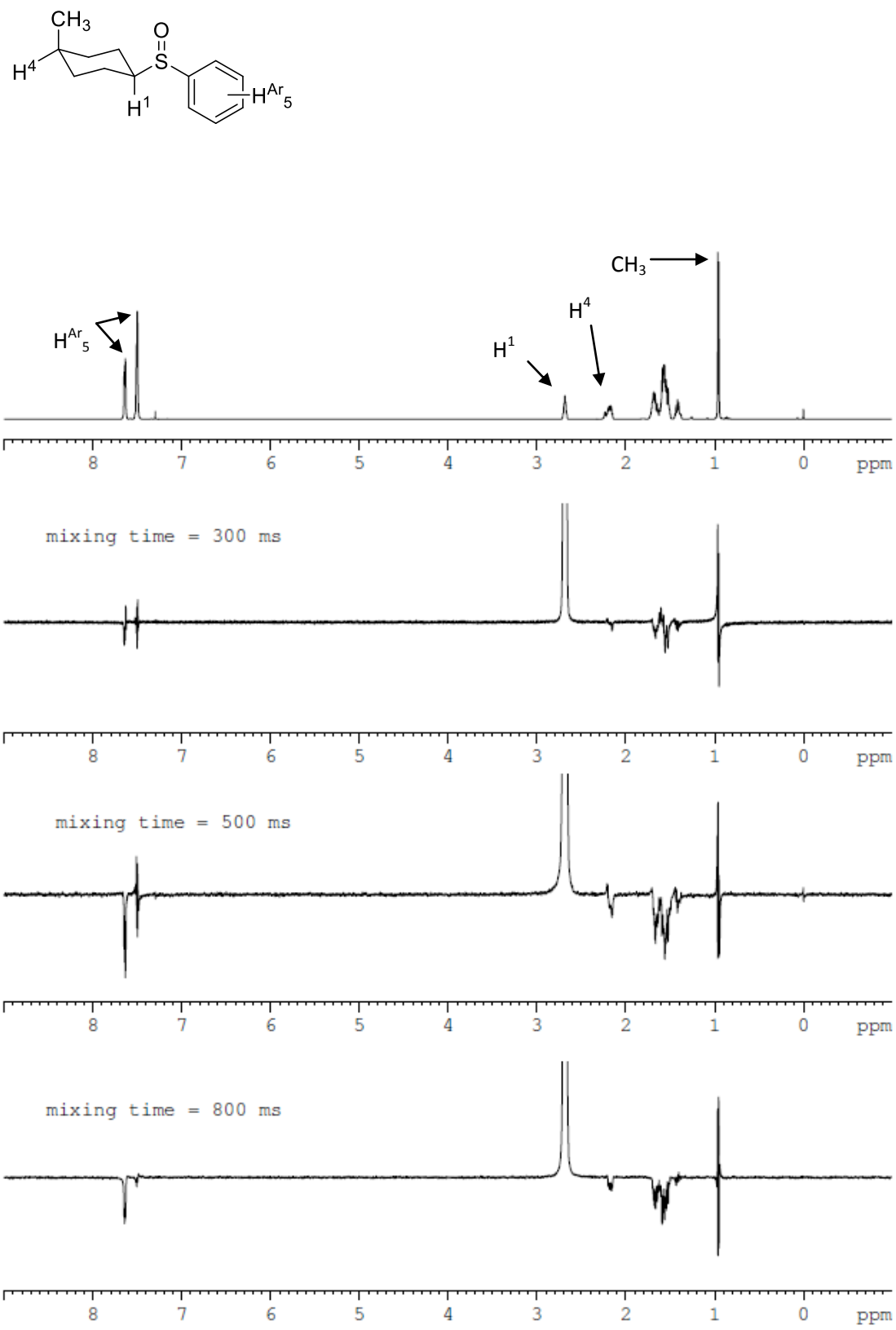
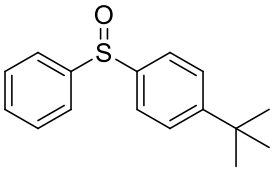


Figure S36. NOE between H^1 and $H_{Ar}{}^5$ by ^1H NMR (500 MHz)

1-(*tert*-Butyl)-4-(phenylsulfinyl)benzene (5a)



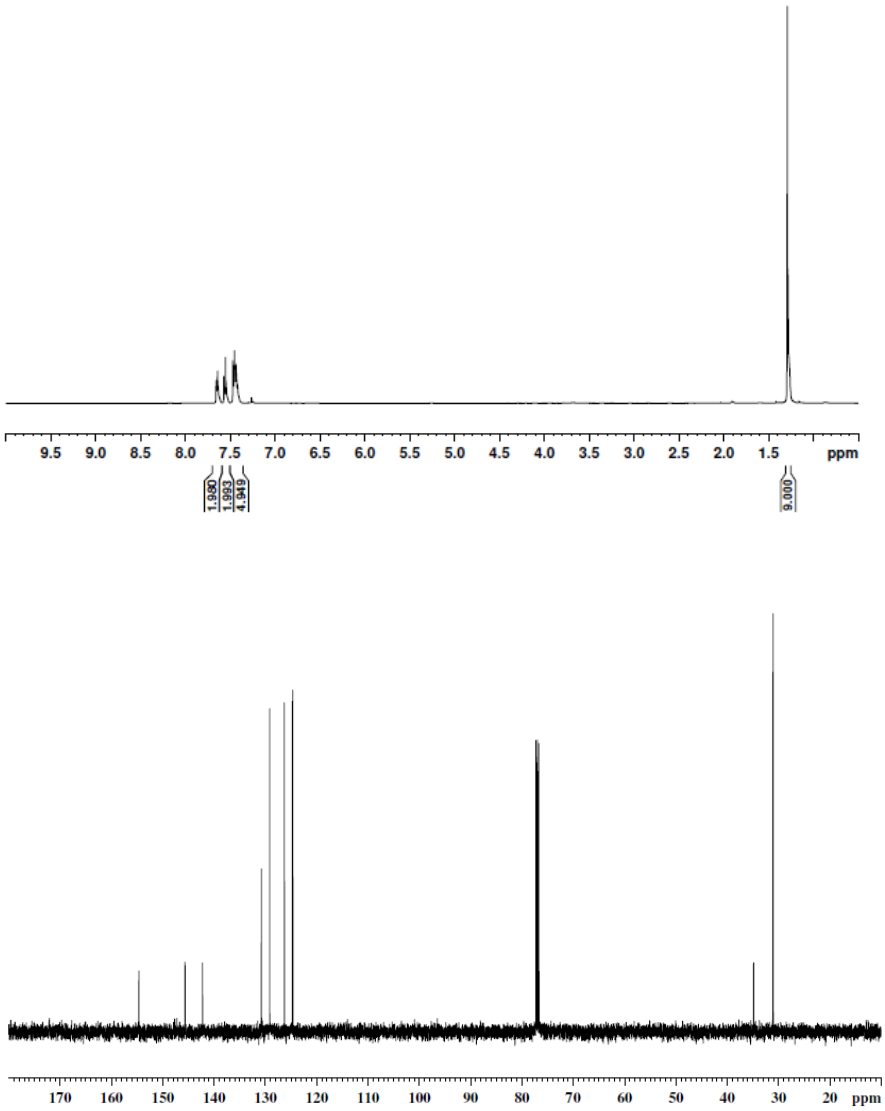


Figure S37. ^{1}H (500 MHz) and ^{13}C {1H} (125 MHz) NMR spectra of 5a in $CDCl_3$.