Supporting Information

Direct Thioamination of Arynes via Reaction with Sulfilimines and Migratory *N*-Arylation

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Contents

General Remarks

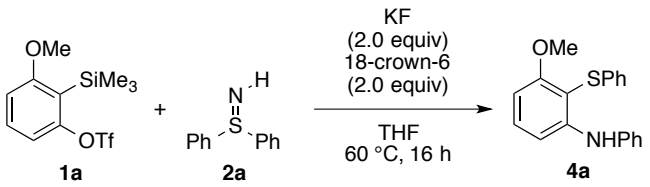
All reactions were performed with dry glassware under atmosphere of argon unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715) or NH TLC plates (Fuji Silysia Chemical Ltd., Chromatorex, NH-TLC plate). Column chromatography was conducted using Biotage® ZIP sphere cartridge [silica] 5 g (Cat. No. 445-0500-DZ-20), 30 g (Cat. No. 445-3000-FZ-20), or 45 g (Cat. No. 445-4500-SZ-20), or Biotage® SNAP Ultra 50 g (Cat. No. FSUL-0442-0050), or Cromatorex Q-PACK NH30 with medium pressure liquid chromatography (Yamazen, W-Prep 2XY A-type). Recycling preparative HPLC was conducted using YMC-GPC T2000 and T2000-40 columns (600 mm × 20 ϕ, YMC Co., Ltd.) with a recycling preparative HPLC (SHIMADZU, eluent: $CHCl_3$). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer or a Bruker AVANCE 500 spectrometer at 400 or 500 MHz, respectively. ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 ºC unless otherwise noted. $CDCl_3$ (Acros Organics, Cat. No. 368651000) or DMSO-d_6 (CIL, Cat. No. DLM-10) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 2.49 for ^{1}H NMR and δ 39.5 for ^{13}C NMR in DMSO-d_6 or δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, m, and br signify singlet, doublet, triplet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. Elemental analyses were carried out at A

Rabbit Science Japan Co. Ltd. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) or negative electrospray ionization (ESI^-) conditions. X-ray crystallographic data were collected on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54187 Å) at 123 K for CCDC 1428753 (compound **4p**) and 296 K for CCDC 1428752 (compound **4t**), or a Rigaku Saturn724 diffractometer with multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71075 Å) at 143 K for CCDC 1428754 (compound **4a**). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

3-Methoxy-2-(trimethylsilyl)phenyl triflate (**1a**) (Cat. No. M1884), 2-(trimethylsilyl)-phenyl triflate (**1b**) (Cat. No. T2089), 2-methyl-6-(trimethylsilyl)phenyl triflate (**1c**) (Cat. No. M1883), 4-methyl-2-(trimethylsilyl)phenyl triflate (**1d**) (Cat. No. M1882), 1-(trimethylsilyl)-2-naphthyl triflate (**1j**) (Cat. No. T2465), and *S*,*S*-diphenylsulfilimine monohydrate (**2a**·H_2O) (Cat. No. D2002), were purchased from Tokyo Chemical Industry Co., Ltd. *S*,*S*-Diphenyl-sulfilimine monohydrate (**2a**·H_2O) was purified by flash column chromatography (NH-silica gel, Cromatorex Q-PACK NH30, CH_2Cl_2/MeOH = 100/0 to 98/2) before use. 5-Bromo-3-methoxy-2-(trimethylsilyl)phenyl triflate (**1e**),[S1] 2,6-bis(trimethylsilyl)phenyl triflate (**1g**),[S2] 4-methoxy-2,6-bis(trimethylsilyl)phenyl triflate (**1h**),[S2] 1-methyl-4-(trimethylsilyl)-1*H*-indol-5-yl triflate (**1k**),[S3] 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethyl-silyl)phenyl triflate,[S1] and *S*-4-tolyl 4-toluenethiosulfonate (**7**)[S4] were prepared according to the reported methods. All other chemical reagents used were commercial grade and used as received.

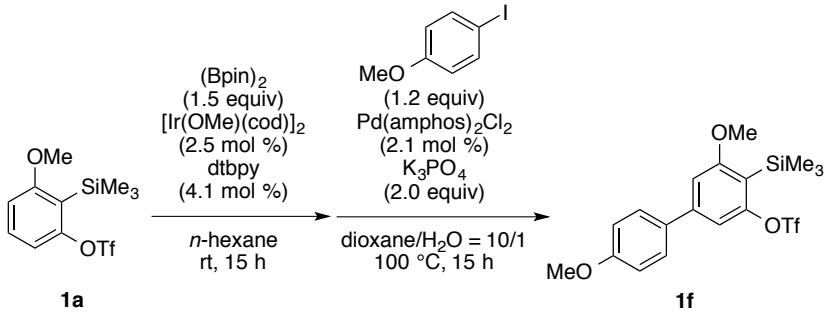
Experimental Procedures

*A typical procedure for the synthesis of o-sulfanylanilines **4***



To a mixture of 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1a**) (162 mg, 0.493 mmol) and *S*,*S*-diphenylsulfilimine (**2a**) (202 mg, 1.00 mmol, 2.03 equiv) dissolved in THF (3.0 mL) were added potassium fluoride (57.0 mg, 0.981 mmol, 1.99 equiv) and 18-crown-6-ether (261 mg, 0.987 mmol, 2.00 equiv) at room temperature. After stirring for 16 h at 60 ºC, the mixture was cooled to room temperature, filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® ZIP sphere cartridge 5 g, *n*-hexane/EtOAc = 100/0 to 95/5) to give 3-methoxy-*N*-phenyl-2-(phenylthio)aniline (**4a**) (117 mg, 0.381 mmol, 77.3%) as a colorless solid.

Synthesis of 5-aryl-3-methoxy-2-(trimethylsilyl)phenyl triflate



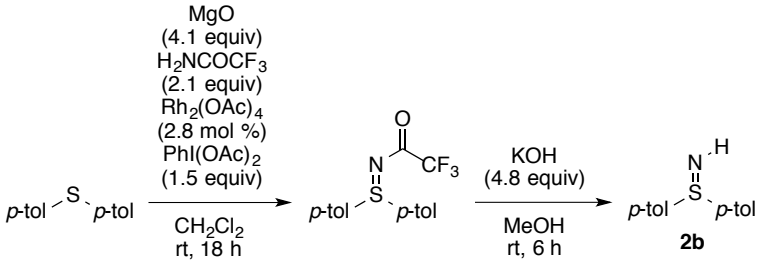
To a mixture of bis(pinacolato)diboron (1.91 g, 7.52 mmol, 1.50 equiv), $[Ir(OMe)(cod)]_2$ (83.0 mg, 0.125 mmol, 2.50 mol %), and 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy) (55.3 mg, 0.206 mmol, 4.12 mol %) dissolved in *n*-hexane (40 mL) was added 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1a**) (1.25 mL, 5.00 mmol) at room temperature. After stirring for 15 h at the same temperature, the mixture was concentrated under reduced pressure to afford a crude mixture containing 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl triflate.

To the crude mixture were added 4-iodoanisole (1.41 g, 6.02 mmol, 1.20 equiv), $Pd(amphos)_2Cl_2$ (74.0 mg, 0.105 mmol, 2.09 mol %), $K_3PO_4{\cdot}nH_2O$ (2.68 g, 10.1 mmol, 2.02 equiv), 1,4-dioxane (50 mL), and H_2O (5 mL) at room temperature. After stirring for 15 h at 100 ºC, the mixture was cooled to room temperature and then concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® SNAP Ultra cartridge 50 g, *n*-hexane/EtOAc = 85/15) and recycling preparative HPLC to give 3-methoxy-

5-(4-methoxyphenyl)-2-(trimethylsilyl)phenyl triflate (**1f**) (1.35 g, 3.26 mmol, 65.3% in 2 steps) as a colorless oil.

Similarly, 4-(3,4-dichlorophenyl)-2,6-bis(trimethylsilyl)phenyl triflate (**1i**) was prepared from 2,6-bis(trimethylsilyl)phenyl triflate (**1g**) and 1,2-dichloro-4-iodobenzene.

A typical procedure for the preparation of sulfilimines ***2***[S5]

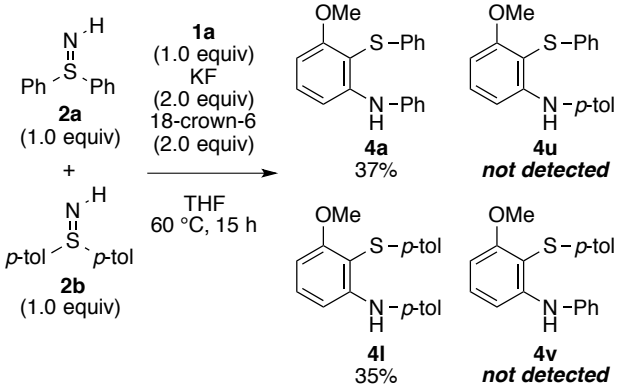


To a mixture of di(4-tolyl) sulfide (5.01 g, 23.4 mmol), MgO (3.87 g, 96.0 mmol, 4.10 equiv), H_2NCOCF_3 (5.45 g, 48.2 mmol, 2.06 equiv), and $Rh_2(OAc)_4$ (284 mg, 0.641 mmol, 2.75 mol %) in CH_2Cl_2 (100 mL) was added $PhI(OAc)_2$ (11.4 g, 35.4 mmol, 1.51 equiv) at room temperature. After stirring for 18 h at the same temperature, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage® SNAP Ultra cartridge 50 g, *n*-hexane/EtOAc = 84/16 to 63/37) to give *N*-(2,2,2-trifluoroacetyl)-*S*,*S*-di(4-tolyl)sulfilimine (4.84 g, 14.9 mmol, 63.6%) as a colorless solid.

To a solution of *N*-(2,2,2-trifluoroacetyl)-*S*,*S*-di(4-tolyl)sulfilimine (1.33 g, 4.09 mmol) in MeOH (20 mL) was added KOH (1.15 g, 19.8 mmol, 4.8 equiv) at room temperature. After stirring for 6 h at the same temperature, to the mixture was added water (200 mL). The mixture was extracted with CH_2Cl_2 (200 mL × 5), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Cromatorex Q-PACK NH30 cartridge 30 g, CH_2Cl_2/MeOH = 100/0 to 98/2) to give *S*,*S*-di(4-tolyl)sulfilimine (**2b**) (825 mg, 3.60 mmol, 87.8%) as a colorless solid.

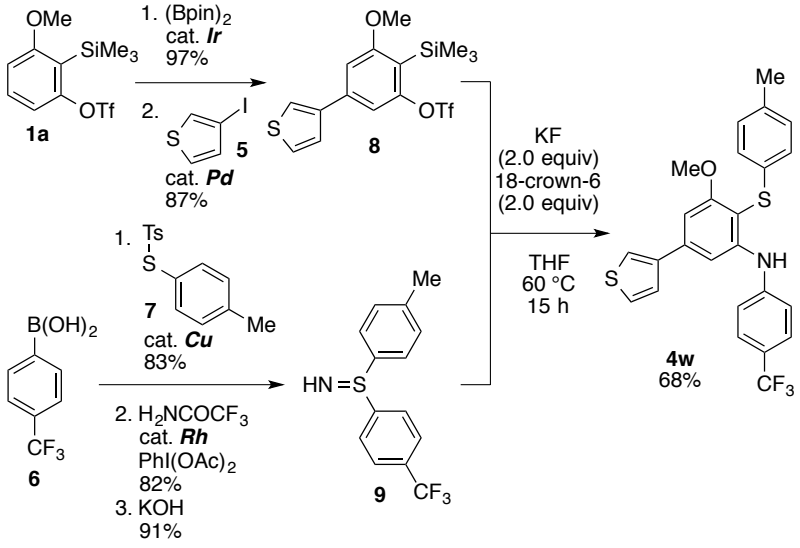
Sulfilimines **2c**–**2j** and **9** were prepared similarly.

*Crossover experiment: reaction of 3-methoxybenzyne with a mixture of sulfilimines **2a** and **2b***



To a mixture of 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1a**) (164 mg, 0.500 mmol), *S*,*S*-diphenylsulfilimine (**2a**) (101 mg, 0.500 mmol, 1.00 equiv), and *S*,*S*-di(4-tolyl)sulfilimine (**2b**) (115 mg, 0.500 mmol, 1.00 equiv) dissolved in THF (3.0 mL) were added potassium fluoride (58.1 mg, 1.00 mmol, 2.00 equiv) and 18-crown-6-ether (265 mg, 1.00 mmol, 2.00 equiv) at room temperature. After stirring for 15 h at 60 ºC, the mixture was cooled to room temperature, filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. To the residue was added dibenzyl ether (74.4 mg, 0.375 mmol) as an internal standard and the mixture was dissolved in $CDCl_3$. The yields of **4a** and **4l** were determined by ^{1}H NMR analysis to be 37.1% and 35.0%, respectively, by comparing the relative values of integration for the peaks observed at 6.46 ppm (for **4a**), and 6.41 ppm (for **4l**) with that of dibenzyl ether observed at 4.56 ppm. Crossovered products **4u** and **4v** were not detected.

*Modular synthesis of multi-arylated o-sulfanylaniline **4w***



A mixture of 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl triflate[S1] (908 mg, 2.00 mmol), 3-iodothiophene (**5**) (841 mg, 4.01 mmol, 2.00

equiv), $Pd(amphos)_2Cl_2$ (28.3 mg, 40.0 μmol, 2.00 mol %), and K_2CO_3 (830 mg, 6.00 mmol, 3.00 equiv) dissolved in 1,4-dioxane (18 mL) and H_2O (2.0 mL) was stirred for 16 h at 100 ºC. After cooling to room temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® ZIP sphere cartridge 45 g, *n*-hexane/CH_2Cl_2 = 84/16; then Biotage® SNAP Ultra cartridge 50 g, *n*-hexane/CH_2Cl_2 = 90/10 to 80/20) to give 3-methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**8**) (717 mg, 1.76 mmol, 87.3%) as a colorless solid.

To a mixture of $NaHCO_3$ (841 mg, 10.0 mmol, 2.0 equiv) and $CuSO_4$ (40.3 mg, 0.252 mmol, 5.04 mol %) was added a solution of *S*-4-tolyl 4-toluenethiosulfonate (**7**) (1.39 g, 5.01 mmol) and 4-(trifluoromethyl)phenylboronic acid (**6**) (1.43 g, 7.54 mmol, 1.51 equiv) dissolved in MeOH (140 mL) at room temperature. After stirring for 17 h at the same temperature, the mixture was concentrated under reduced pressure. To the residue was added aqueous saturated $NaHCO_3$ (50 mL), and the mixture was extracted with EtOAc (30 mL× 3). The combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® SNAP Ultra cartridge 50 g, *n*-hexane) to give 4-tolyl 4-(trifluoromethyl)phenyl sulfide (1.31 g, 4.89 mmol, 97.7%) as a colorless solid, which contained a small amount of impurity. Further purification by recrystallization from *n*-hexane afforded 4-tolyl 4-(trifluoromethyl)phenyl sulfide (1.11 g, 4.14 mmol, 82.8%) as a colorless crystal.

To a mixture of 4-tolyl 4-(trifluoromethyl)phenyl sulfide (504 mg, 1.88 mmol), MgO (323 mg, 8.01 mmol, 4.27 equiv), H_2NCOCF_3 (452 mg, 4.00 mmol, 2.13 equiv), $Rh_2(OAc)_4$ (22.6 mg, 0.511 mmol, 2.72 mol %) dissolved in CH_2Cl_2 (10 mL) was added $PhI(OAc)_2$ (966 mg, 3.00 mmol, 1.60 equiv) at room temperature. After stirring for 21 h at the same temperature, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® ZIP-sphere cartridge 45 g, CH_2Cl_2/EtOAc =99/1 to 95/5) to give *S*-(4-tolyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (584 mg, 1.54 mmol, 81.9%) as a colorless oil.

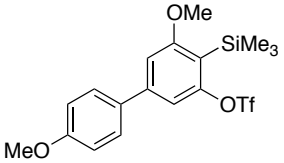
To a solution of *S*-(4-tolyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-(trifluoromethyl)phenyl)-sulfilimine (190 mg, 0.500 mmol) dissolved in MeOH (2.5 mL) was added KOH (146 mg, 2.61 mmol, 5.22 equiv) at room temperature. After stirring for 75 min at the same temperature, to the mixture was added water (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3), and the combined organic extract was washed with brine, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Chromatorex Q-PACK NH30 SIZE10, CH_2Cl_2) to give *S*-(4-tolyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (**9**) (128 mg, 0.453 mmol, 90.7%) as a colorless solid.

To a mixture of 3-methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**8**) (82.0 mg, 0.200 mmol) and *S*-(4-tolyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (**9**) (113 mg, 0.400 mmol, 2.00 equiv) dissolved in THF (1.2 mL) were added potassium fluoride (23.3 mg, 0.401 mmol, 2.00 equiv) and 18-crown-6 (106 mg, 0.400 mmol, 2.00 equiv) at room temperature.

After stirring for 15 h at 60 ºC, the mixture was cooled to room temperature, filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® ZIP-sphere cartridge 30 g, *n*-hexane/CH_2Cl_2 = 88/12 to 80/20) to give 3-methoxy-5-(3-thienyl)-2-(4-tolylthio)-*N*-(4-(trifluoromethyl)phenyl)aniline (**4w**) (63.7 mg, 0.135 mmol, 67.6%) as a colorless solid.

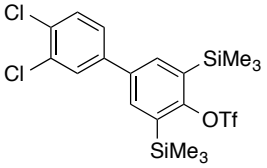
Characterization Data of New Compounds

3-Methoxy-5-(4-methoxyphenyl)-2-(trimethylsilyl)phenyl triflate (**1f**)



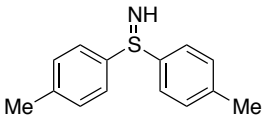
Colorless oil; TLC R_f 0.40 (*n*-hexane/CH_2Cl_2 = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.38 (s, 9H, $SiCH_3$), 3.86 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.97 (d, 1H, J = 1.0 Hz, aromatic), 6.98–7.00 (AA′BB′, 2H, aromatic), 7.09 (d, 1H, J = 1.0 Hz, aromatic), 7.48–7.51 (AA′BB′, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.8 (3C), 55.4 (1C), 55.6 (1C), 107.9 (1C), 111.2 (1C), 114.4 (2C), 118.5 (1C), 118.6 (q, 1C, $^1J_{C–F}$ = 321.4 Hz), 128.2 (2C), 131.9 (1C), 144.9 (1C), 155.0 (1C), 160.0 (1C), 165.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 828, 845, 1046, 1058, 1142, 1210, 1252, 1394, 1418, 1518, 1606; HRMS (ESI^+) m/z 457.0728 ($[M+Na]^+$, $C_{18}H_{21}F_3NaO_5SSi^+$ requires 457.0723).

4-(3,4-Dichlorophenyl)-2,6-bis(trimethylsilyl)phenyl triflate (**1i**)



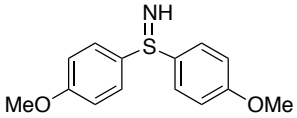
Colorless solid; Mp 97–98 ºC; TLC R_f 0.37 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.40 (s, 18H, $SiCH_3$), 7.36 (dd, 1H, J = 8.3, 2.2 Hz, aromatic), 7.53 (d, 1H, J = 8.3 Hz, aromatic), 7.59 (d, 1H, J = 2.2 Hz, aromatic), 7.64 (s, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.4 (6C), 118.4 (q, 1C, $^1J_{C–F}$ = 320.6 Hz), 126.7 (1C), 129.1 (2C), 130.9 (1C), 132.2 (1C), 133.0 (1C), 135.9 (1C), 136.7 (2C), 137.9 (1C), 140.1 (1C), 154.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.5 (s); IR (KBr, cm^{-1}) 843, 894, 1138, 1214, 1254, 1397; HRMS (ESI^+) m/z 537.0138 ($[M+Na]^+$, $C_{19}H_{23}Cl_2F_3NaO_3SSi_2^+$ requires 537.0128).

S,*S*-Di(4-tolyl)sulfilimine (**2b**)



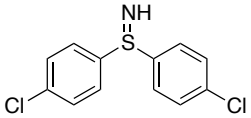
Colorless solid; Mp 46−48 °C; TLC (Amino) R_f 0.24 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 6H, CH_3), 7.22−7.24 (AA′BB′, 4H, aromatic), 7.42−7.44 (AA′BB′, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.3 (2C), 125.8 (4C), 129.9 (4C), 140.6 (2C), 142.6 (2C); IR (KBr, cm^{-1}) 807, 915, 1016, 1078, 1397, 1491, 2920, 3042, 3179; HRMS (ESI^+) m/z 230.0995 ($[M+H]^+$, $C_{14}H_{16}NS^+$ requires 230.0998).

S,*S*-Di(4-methoxyphenyl)sulfilimine (**2c**)



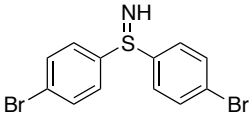
Colorless solid; Mp 49−51 °C; TLC (Amino) R_f 0.46 (EtOAc/MeOH = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.82 (s, 6H, CH_3), 6.92−6.95 (AA′BB′, 4H, aromatic), 7.45−7.48 (AA′BB′, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.5 (2C), 114.6 (4C), 127.6 (4C), 137.0 (2C), 161.2 (2C); IR (KBr, cm^{-1}) 827, 913, 1026, 1173, 1257, 1303, 1495, 1592, 3172; HRMS (ESI^+) *m*/*z* 262.0894 ($[M+H]^+$, $C_{14}H_{16}NO_2S^+$ requires 262.0896).

S,*S*-Di(4-chlorophenyl)sulfilimine (**2d**)



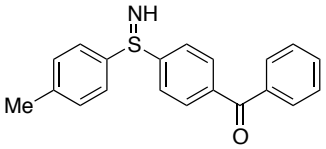
Colorless solid; Mp 103–104 ºC; TLC (Amino) R_f 0.43 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41−7.44 (AA′BB′, 4H, aromatic), 7.50−7.53 (AA′BB′, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 127.2 (4C), 129.6 (4C), 136.9 (2C), 143.6 (2C); IR (KBr, cm^{-1}) 821, 921, 1011, 1090, 1391, 1474, 1572, 3053, 3077, 3181; Anal. calcd. for $C_{12}H_9Cl_2NS$: C, 53.35; H, 3.36; N, 5.18%; Found: C, 53.22; H, 3.32; N, 5.20%.

S,*S*-Di(4-bromophenyl)sulfilimine (**2e**)



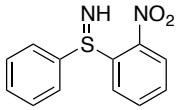
Colorless solid; Mp 107–108 ºC; TLC (Amino) R_f 0.43 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43−7.46 (AA′BB′, 4H, aromatic), 7.57−7.60 (AA′BB′, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 125.2 (2C), 127.4 (4C), 132.6 (4C), 144.2 (2C); IR (KBr, cm^{-1}) 813, 919, 1006, 1065, 1386, 1470, 1567, 3049, 3077, 3180; HRMS (ESI^+) *m*/*z* 357.8883 ($[M+Na]^+$, $C_{12}H_{10}Br_2NS^+$ requires 357.8895).

S-(4-Benzoylphenyl)-*S*-(4-tolyl)sulfilimine (**2f**)



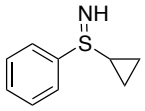
Colorless solid; Mp 139 ºC (decomp.); TLC (Amino) R_f 0.33 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.39 (s, 3H, CH_3), 7.27–7.29 (m, 2H, aromatic), 7.48–7.50 (m, 4H, aromatic), 7.59–7.63 (m, 1H, aromatic), 7.67−7.70 (AA′BB′, 2H, aromatic), 7.76–7.79 (AA′BB′, 2H, aromatic), 7.83−7.86 (AA′BB′, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.3 (1C), 125.6 (2C), 126.1 (2C), 128.4 (2C), 130.0 (2C), 130.2 (2C), 130.6 (2C), 132.9 (1C), 136.9 (1C), 139.0 (1C), 141.4 (1C), 141.7 (1C), 150.0 (1C), 195.6 (1C); IR (KBr, cm^{-1}) 920, 1277, 1659, 3054, 3179; HRMS (ESI^+) *m*/*z* 320.1100 ($[M+H]^+$, $C_{20}H_{18}NOS^+$ requires 320.1104).

S-(2-Nitrophenyl)-*S*-phenylsulfilimine (**2g**)



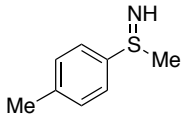
Yellow solid; Mp 82 ºC (decomp.); TLC (Amino) R_f 0.26 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36–7.41 (m, 3H, aromatic), 7.47–7.52 (m, 2H, aromatic), 7.69 (ddd, 1H, *J* = 7.7, 7.7, 1.3 Hz, aromatic), 8.02 (ddd, 1H, *J* = 7.7, 7.7, 1.1 Hz, aromatic), 8.24 (dd, 1H, *J* = 7.7, 1.1 Hz, aromatic), 8.50 (dd, 1H, *J* = 7.7, 1.3 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 125.2 (1C), 126.8 (2C), 127.3 (1C), 129.5 (2C), 130.8 (1C), 131.1 (1C), 135.0 (1C), 143.4 (1C), 145.20 (1C), 145.24 (1C); IR (KBr, cm^{-1}) 853, 913, 1343, 1442, 1527, 3158; HRMS (ESI^+) *m*/*z* 247.0536 ($[M+H]^+$, $C_{12}H_{11}N_2O_2S^+$ requires 247.0536).

S-Cyclopropyl-*S*-phenylsulfilimine (**2h**)



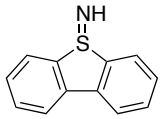
Colorless oil; TLC (Amino) R_f 0.37 (EtOAc/MeOH = 19/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.77–0.83 (m, 1H, aliphatic), 0.92–0.98 (m, 1H, aliphatic), 1.00–1.05 (m, 1H, aliphatic), 1.09–1.14 (m, 1H, aliphatic), 2.26 (dddd, 1H, *J* = 7.9, 7.9, 4.8, 4.8 Hz, aliphatic), 7.43–7.47 (m, 1H, aromatic), 7.48–7.51 (m, 2H, aromatic), 7.67–7.69 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 1.1 (1C), 4.1 (1C), 32.9 (1C), 124.6 (2C), 129.1 (2C), 130.1 (1C), 145.2 (1C); IR (KBr, cm^{-1}) 878, 913, 1042, 1321, 1444, 1478, 1503, 3201; HRMS (ESI^+) *m*/*z* 166.0681 ($[M+H]^+$, $C_9H_{12}NS^+$ requires 166.0685).

S-Methyl-*S*-(4-tolyl)sulfilimine (**2i**)



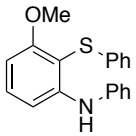
Colorless oil; TLC (Amino) R_f 0.22 (tailing) (EtOAc/MeOH = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.40 (s, 3H, CH_3), 2.68 (s, 3H, SCH_3), 7.30–7.31 (AA′BB′, 2H, aromatic), 7.52–7.55 (AA′BB′, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.2 (1C), 43.5 (1C), 123.9 (2C), 129.9 (2C), 140.5 (1C), 142.9 (1C); IR (KBr, cm^{-1}) 812, 911, 966, 1048, 1325, 1419, 1496, 3042; HRMS (ESI^+) *m*/*z* 154.0683 ($[M+H]^+$, $C_8H_{12}NS^+$ requires 154.0685).

5*H*-5λ^4-Dibenzo[*b*,*d*]thiophen-5-imine (**2j**)



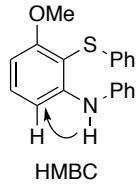
Pale brown solid; Mp 113 ºC (decomp.); TLC (Amino) R_f 0.23 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (ddd, 2H, *J* = 7.5, 7.5, 1.0 Hz, aromatic), 7.59 (ddd, 2H, *J* = 7.5, 7.5, 1.0 Hz, aromatic), 7.85 (dd, 2H, *J* = 7.5, 1.0 Hz, aromatic), 7.60 (dd, 2H, *J* = 7.5, 1.0 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 121.7 (2C), 126.3 (2C), 129.4 (2C), 131.4 (2C), 135.8 (2C), 146.9 (2C); IR (KBr, cm^{-1}) 911, 1057, 1122, 1445, 3066, 3168, 3246; HRMS (ESI^+) *m*/*z* 200.0521 ($[M+H]^+$, $C_{12}H_{10}NS^+$ requires 200.0528).

3-Methoxy-*N*-phenyl-2-(phenylthio)aniline (**4a**)

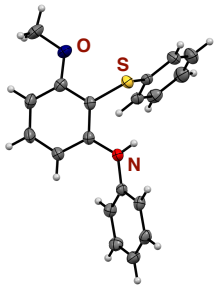


Colorless solid; Mp 92–94 °C; TLC R_f 0.43 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.73 (s, 3H, OCH_3), 6.37 (dd, 1H, J = 8.5, 0.8 Hz, aromatic), 6.84 (dd, 1H, J = 8.5, 0.8 Hz, aromatic), 6.91–6.95 (AA′BB′C, 1H, aromatic), 6.96 (br s, 1H, NH), 6.98–7.06 (m, 5H, aromatic), 7.08–7.13 (AA′B ′C, 2H, aromatic), 7.14–7.22 (m, 3H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.2 (1C), 101.9 (1C), 103.9 (1C), 106.8 (1C), 121.5 (2C), 123.0 (1C), 125.2 (1C), 126.0 (2C), 128.9 (2C), 129.3 (2C), 131.5 (1C), 136.5 (1C), 141.6 (1C), 147.9 (1C), 161.7 (1C); IR (KBr, cm^{-1}) 1078, 1260, 1467, 1505, 1589, 2836, 3057, 3353; HRMS (ESI^+) *m*/*z* 330.0917 ($[M+Na]^+$, $C_{19}H_{17}NNaOS^+$ requires 330.0923).

The structure of **4a** was confirmed by the X-ray crystallographic analysis. The regiochemistry of **4a** was also determined by the HMBC experiment.

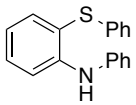


Crystallographic analysis



Selected crystal data: Crystal System; monoclinic, Space Group; $P2_1/c$ (No. 14), a = 6.0234(8) Å, b = 25.185(4) Å, c = 10.524(2) Å, β = 90.087(3)°, V = 1596.4(4) Å^3, Z = 4, R_1 = 0.0659, wR_2 = 0.1624. CCDC 1428754 contains the supplementary crystallographic data for this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

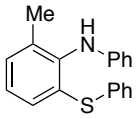
N-Phenyl-2-(phenylthio)aniline (**4b**)



Colorless solid; Mp 93–94 °C; TLC R_f 0.71 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (br s, 1H, NH), 6.82–6.86 (m, 1H, aromatic), 6.96–7.02 (m, 1H, aromatic), 7.06–7.17 (m, 5H, aromatic), 7.20–7.31 (m, 6H, aromatic), 7.53 (dd, 1H, J = 7.8, 1.5 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 114.4 (1C), 117.2 (1C), 119.9 (1C), 120.7 (2C), 122.6 (1C), 125.7 (1C), 126.9 (2C), 129.1 (2C), 129.3 (2C), 130.7 (1C), 136.5 (1C), 137.4

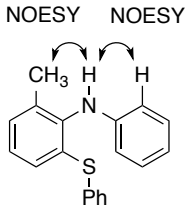
(1C), 141.6 (1C), 145.8 (1C); IR (KBr, cm^{-1}) 1024, 1312, 1504, 1584, 3060, 3359; HRMS (ESI^+) *m*/*z* 278.0989 ($[M+H]^+$, $C_{18}H_{16}NS^+$ requires 278.0998).

2-Methyl-*N*-phenyl-6-(phenylthio)aniline (**4c**)

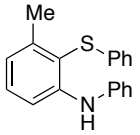


Pale brown solid; Mp 40–41 ºC; TLC R_f 0.21 (*n*-hexane/CH_2Cl_2 = 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 3H, CH_3), 5.84 (br s, 1H, NH), 6.54–6.57 (AA′BB′C, 2H, aromatic), 6.78–6.82 (AA′BB′C, 1H, aromatic), 7.05 (dd, 1H, *J* = 7.7, 7.7 Hz, aromatic), 7.12–7.24 (m, 9H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 19.0 (1C), 115.3 (2C), 119.6 (1C), 125.2 (1C), 126.8 (1C), 129.0 (2C), 129.2 (2C), 130.3 (2C), 130.9 (1C), 131.0 (1C), 131.3 (1C), 135.36 (1C), 135.43 (1C), 140.4 (1C), 145.1 (1C); IR (KBr, cm^{-1}) 1024, 1305, 1456, 1496, 1601, 3051, 3379; HRMS (ESI^+) *m*/*z* 292.1155 ($[M+H]^+$, $C_{19}H_{18}NS^+$ requires 292.1154).

The regiochemistry of **4c** was determined by the NOESY experiment.

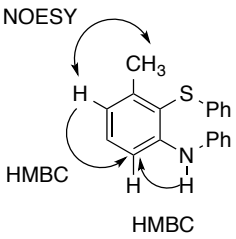


3-Methyl-*N*-phenyl-2-(phenylthio)aniline (**4c′**)



Pale brown solid; Mp 68–70 ºC; TLC R_f 0.33 (*n*-hexane/CH_2Cl_2 = 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H, CH_3), 6.81 (dd, 1H, *J* = 6.7, 1.4 Hz, aromatic), 6.98–7.01 (m, 1H, aromatic), 7.02 (br s, 1H, NH), 7.03–7.06 (m, 2H, aromatic), 7.08–7.13 (m, 3H, aromatic), 7.15–7.23 (m, 4H, aromatic), 7.25–7.29 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.8 (1C), 111.8 (1C), 115.9 (1C), 120.9 (2C), 121.2 (1C), 122.6 (1C), 125.2 (1C), 125.8 (2C), 129.1 (2C), 129.3 (2C), 130.3 (1C), 136.4 (1C), 141.9 (1C), 145.0 (1C), 146.8 (1C); IR (KBr, cm^{-1}) 1024, 1316, 1463, 1503, 1578, 3057, 3360; HRMS (ESI^+) *m*/*z* 292.1157 ($[M+H]^+$, $C_{19}H_{18}NS^+$ requires 292.1154).

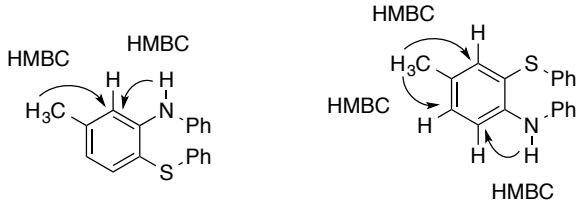
The regiochemistry of **4c′** was determined by the NOESY and the HMBC experiments.



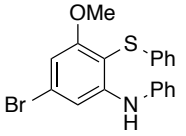
5-Methyl-*N*-phenyl-2-(phenylthio)aniline (**4d**) and 4-methyl-*N*-phenyl-2-(phenylthio)aniline (**4d′**) (analyzed as a mixture of isomers (**4d**/**4d′** = 55/45))

Pale brown oil; TLC R_f 0.29 (*n*-hexane/CH_2Cl_2 = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 3H of **4d′**, CH_3), 2.30 (s, 3H of **4d**, CH_3), 6.52 (br s, 1H of **4d′**, NH), 6.64–6.69 (m, 2H of **4d**, NH and aromatic), 6.95 (tt, 1H of **4d′**, *J* = 7.4, 1.0 Hz, aromatic), 7.00 (tt, 1H of **4d**, *J* = 7.4, 1.0 Hz, aromatic), 7.03–7.05 (m, 2H of **4d′**, aromatic), 7.07–7.14 (m, 6H of **4d**, 4H of **4d′**, aromatic), 7.19–7.30 (m, 4H of **4d**, 5H of **4d′**, aromatic), 7.36 (d, 1H of **4d′**, *J* = 1.9 Hz, aromatic), 7.43 (d, 1H of **4d**, *J* = 7.8 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.3 (1C, **4d′**), 21.8 (1C, **4d**), 113.5 (1C, **4d**), 114.8 (1C, **4d**), 115.3 (1C, **4d′**), 117.8 (1C, **4d′**), 119.7 (2C, **4d′**), 120.8 (2C, **4d**), 121.0 (1C, **4d**), 121.9 (1C, **4d′**), 122.6 (1C, **4d**), 125.5 (1C, **4d**), 125.7 (1C, **4d′**), 126.4 (2C, **4d**), 126.9 (2C, **4d′**), 129.0 (2C, **4d**), 129.1 (2C, **4d′**), 129.2 (2C, **4d′**), 129.3 (2C, **4d**), 129.7 (1C, **4d′**), 131.3 (1C, **4d′**), 136.6 (1C, **4d′**), 137.0 (1C, **4d**), 137.46 (1C, **4d′**), 137.55 (1C, **4d**), 141.3 (1C, **4d**), 141.7 (1C, **4d**), 142.3 (1C, **4d′**), 143.1 (1C, **4d′**), 145.8 (1C, **4d**); IR (KBr, cm^{-1}) 1311, 1478, 1508, 1566, 1595, 3049, 3366; HRMS (ESI$^+$) *m*/*z* 292.1154 ([M+H]$^+$, $C_{19}H_{18}NS^+$ requires 292.1154).

The regiochemistries of the isomers **4d** and **4d′** were determined by the HMBC experiments.

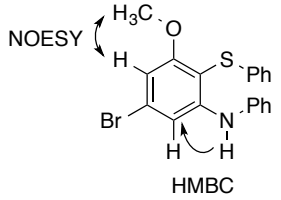


5-Bromo-3-methoxy-*N*-phenyl-2-(phenylthio)aniline (**4e**)

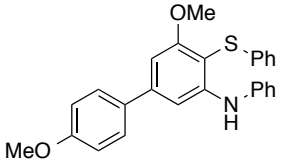


Colorless solid; Mp 113–115 ºC; TLC R_f 0.54 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H, OCH_3), 6.58 (d, 1H, *J* = 2.0 Hz, aromatic), 7.00 (d, 1H, *J* = 2.0 Hz, aromatic), 7.07 (br s, 1H, NH), 7.08–7.14 (m, 6H, aromatic), 7.20–7.24 (AA′BB′C, 2H, aromatic), 7.30–7.34 (AA′BB′C, 2H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.5 (1C), 102.5 (1C), 105.5 (1C), 109.3 (1C), 122.5 (2C), 124.0 (1C), 125.5 (1C), 126.0 (1C), 126.1 (2C), 129.0 (2C), 129.5 (2C), 135.8 (1C), 140.6 (1C), 148.9 (1C), 162.0 (1C); IR (KBr, cm^{-1}) 1094, 1241, 1417, 1568, 2935, 3058, 3346; HRMS (ESI^+) *m*/*z* 386.0199 ($[M+H]^+$, $C_{19}H_{17}BrNOS^+$ requires 386.0209).

The regiochemistry of **4e** was determined by the NOESY and the HMBC experiments.

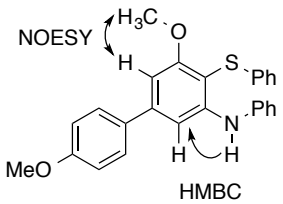


3-Methoxy-5-(4-methoxyphenyl)-*N*-phenyl-2-(phenylthio)aniline (**4f**)

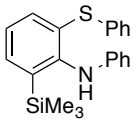


Pale brown solid; Mp 148–149 °C; TLC R_f 0.31 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.63 (d, 1H, *J* = 2.0 Hz, aromatic), 6.93–6.98 (AA′BB′, 2H, aromatic), 7.02 (t, 1H, *J* = 7.5 Hz, aromatic), 7.07 (br s, 1H, NH), 7.08–7.11 (AA′BB′C, 1H, aromatic), 7.12 (d, 1H, *J* = 2.0 Hz, aromatic), 7.14–7.19 (m, 4H, aromatic), 7.20–7.23 (AA′BB′C, 2H, aromatic), 7.27–7.31 (AA′BB′C, 2H, aromatic), 7.49–7.53 (AA′BB′, 2H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.4 (1C), 56.3 (1C), 100.9 (1C), 102.4 (1C), 105.3 (1C), 114.2 (2C), 121.4 (2C), 122.9 (1C) 125.2 (1C), 126.0 (2C), 128.2 (2C), 128.9 (2C), 129.4 (2C), 133.6 (1C), 136.6 (1C), 141.7 (1C), 144.2 (1C), 147.8 (1C), 159.6 (1C), 161.8 (1C); IR (KBr, cm^{-1}) 1251, 1428, 1516, 1604, 2835, 2933, 3057, 3353; HRMS (ESI^+) *m*/*z* 436.1327 ($[M+Na]^+$, $C_{26}H_{23}NNaO_2S^+$ requires 436.1342).

The regiochemistry of **4f** was determined by the NOESY and the HMBC experiments.

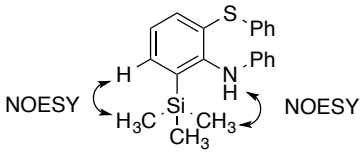


N-Phenyl-2-(phenylthio)-6-(trimethylsilyl)aniline (**4g**)

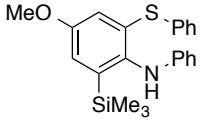


Colorless oil; TLC R_f 0.32 (*n*-hexane/CH_2Cl_2 = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.17 (s, 9H, CH_3), 5.45 (br s, 1H, NH), 6.46–6.49 (AA′BB′C, 2H, aromatic), 6.75–6.79 (AA′BB′C, 1H, aromatic), 7.13–7.18 (m, 4H, aromatic), 7.24–7.34 (m, 5H, aromatic), 7.39–7.43 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.2 (3C), 114.3 (2C), 118.8 (1C), 126.7 (1C), 127.6 (1C), 129.0 (2C), 129.3 (2C), 131.9 (1C), 132.5 (2C), 133.7 (1C), 134.3 (1C), 137.2 (1C), 140.9 (1C), 144.2 (1C), 147.2 (1C); IR (KBr, cm^{-1}) 839, 1249, 1415, 1497, 1601, 2952, 3050, 3362; HRMS (ESI$^+$) *m*/*z* 372.1200 ([M+Na]$^+$, $C_{21}H_{23}NNaSSi^+$ requires 372.1213).

The regiochemistry of **4g** was determined by the NOESY experiment.

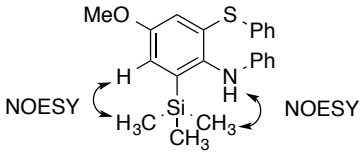


4-Methoxy-*N*-phenyl-2-(phenylthio)-6-(trimethylsilyl)aniline (**4h**)

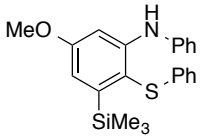


Pale brown solid; Mp 89–91 ºC; TLC R_f 0.29 (*n*-hexane/CH_2Cl_2 = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 9H, $SiCH_3$), 3.67 (s, 3H, OCH_3), 5.21 (br s, 1H, NH), 6.44 (d, 2H, *J* = 8.0 Hz, aromatic), 6.62 (d, 1H, *J* = 2.9 Hz, aromatic), 6.74 (t, 1H, *J* = 7.0 Hz, aromatic), 6.91 (d, 1H, *J* = 2.9 Hz, aromatic), 7.12–7.17 (AA′BB′C, 2H, aromatic), 7.26–7.38 (m, 5H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ –0.3 (3C), 55.3 (1C), 113.8 (2C), 115.9 (1C), 118.4 (1C), 118.9 (1C), 128.0 (1C), 129.1 (2C), 129.4 (2C), 133.1 (2C), 133.9 (1C), 136.6 (1C), 139.6 (1C), 143.0 (1C), 147.9 (1C), 158.0 (1C); IR (KBr, cm^{-1}) 840, 1047, 1247, 1421, 1496, 1600, 2954, 3049, 3368; HRMS (ESI$^+$) *m*/*z* 402.1300 ([M+Na]$^+$, $C_{22}H_{25}NNaOSSi^+$ requires 402.1318).

The regiochemistry of **4h** was determined by the NOESY experiment.

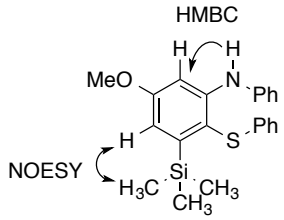


5-Methoxy-*N*-phenyl-2-(phenylthio)-3-(trimethylsilyl)aniline (**4h′**)

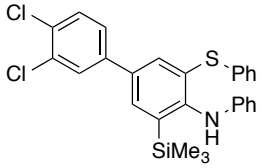


Pale brown solid; Mp 129–131 ºC TLC R_f 0.38 (*n*-hexane/CH_2Cl_2 = 7/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9H, $SiCH_3$), 3.77 (s, 3H, OCH_3), 6.65 (d, 1H, *J* = 2.6 Hz, aromatic), 6.77 (br s, 1H, NH), 6.84 (d, 1H, *J* = 2.6 Hz, aromatic), 6.97–7.03 (m, 3H, aromatic), 7.04–7.09 (m, 3H, aromatic), 7.16–7.21 (AA′BB′C, 2H, aromatic), 7.23–7.28 (AA′BB′C, 2H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.0 (3C), 54.9 (1C), 99.7 (1C), 111.9 (1C), 112.2 (1C), 121.2 (2C), 122.7 (1C), 124.7 (1C), 124.8 (2C), 128.7 (2C), 129.0 (2C), 137.6 (1C), 141.2 (1C), 147.7 (1C), 150.2 (1C), 161.0 (1C); IR (KBr, cm^{-1}) 839, 1246, 1499, 1575, 2953, 3059, 3359; HRMS (ESI^+) *m*/*z* 380.1481 ($[M+H]^+$, $C_{22}H_{26}NOSSi^+$ requires 380.1499).

The regiochemistry of **4h′** was determined by the NOESY and the HMBC experiments.

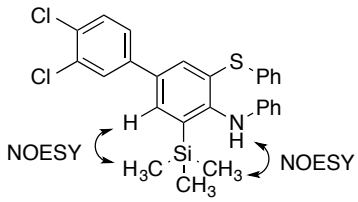


4-(3,4-Dichlorophenyl)-*N*-phenyl-2-(phenylthio)-6-(trimethylsilyl)aniline (**4i**)

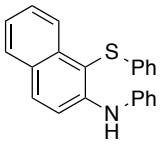


Colorless solid; Mp 147–149 °C; TLC R_f 0.59 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 9H, $SiCH_3$), 5.49 (br s, 1H, NH), 6.50–6.53 (AA′BB′C, 2H, aromatic), 6.78–6.82 (AA′BB′C, 1H, aromatic), 7.15–7.19 (AA′BB′C, 2H, aromatic), 7.25 (dd, 1H, *J* = 8.0, 2.0 Hz, aromatic), 7.26–7.35 (m, 6H, aromatic), 7.44 (d, 1H, *J* = 8.0 Hz, aromatic), 7.51 (d, 1H, *J* = 1.0 Hz, aromatic), 7.52 (d, 1H, *J* = 1.0 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.0 (3C), 114.8 (2C), 119.4 (1C), 126.4 (1C), 128.0 (1C), 129.0 (1C), 129.3 (2C), 129.6 (2C), 130.8 (1C), 130.9 (1C), 131.7 (1C), 132.5 (2C), 132.6 (1C), 133.0 (1C), 134.3 (1C), 137.1 (1C), 137.6 (1C), 140.7 (1C), 141.6 (1C), 144.7 (1C), 147.1 (1C); IR (KBr, cm^{-1}) 840, 1028, 1248, 1427, 1495, 1600, 2895, 2953, 3047, 3350; HRMS (ESI^+) *m*/*z* 516.0725 ($[M+Na]^+$, $C_{27}H_{25}Cl_2NNaSSi^+$ requires 516.0746).

The regiochemistry of **4i** was determined by the NOESY experiment.

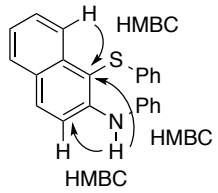


2-Phenylamino-1-(phenylthio)naphthalene (**4j**)

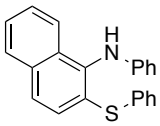


Colorless oil; TLC R_f 0.69 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02–7.08 (m, 4H, aromatic), 7.12–7.18 (m, 4H, aromatic), 7.26–7.34 (m, 4H, aromatic + NH), 7.42–7.46 (m, 1H, aromatic), 7.54 (d, 1H, J = 9.0 Hz, aromatic), 7.73 (d, 1H, J = 8.3 Hz, aromatic), 7.79 (d, 1H, J = 9.0 Hz, aromatic), 8.31 (d, 1H, J = 8.3 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 108.0 (1C), 116.4 (1C), 121.5 (2C), 123.3 (1C), 123.4 (1C), 124.8 (1C), 125.3 (1C), 126.0 (2C), 127.9 (1C), 128.4 (1C), 129.10 (1C), 129.14 (2C), 129.5 (2C), 131.5 (1C), 136.63 (1C), 136.64 (1C), 141.6 (1C), 146.0 (1C); IR (KBr, cm^{-1}) 813, 1024, 1306, 1417, 1497, 1594, 1618, 3052, 3352; HRMS (ESI$^-$) m/z 326.1006 ([M–H]$^+$, $C_{22}H_{16}NS^-$ requires 326.1009).

The regiochemistry of **4j** was determined by the HMBC experiment.

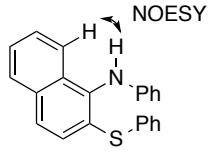


1-Phenylamino-2-(phenylthio)naphthalene (**4j′**)

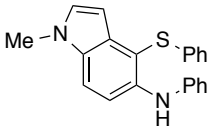


Pale brown solid; Mp 105–107 °C; TLC R_f 0.44 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.54 (d, 2H, J = 7.5 Hz, aromatic), 6.65 (t, 1H, J = 7.5 Hz, aromatic), 7.09 (dd, 2H, J = 7.5, 7.5 Hz, aromatic), 7.15 (d, 1H, J = 8.5 Hz, aromatic), 7.32–7.43 (m, 5H, aromatic), 7.46–7.52 (m, 2H, aromatic), 7.76 (d, 1H, J = 8.5 Hz, aromatic), 7.86–7.93 (m, 2H, aromatic), 8.03 (br s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d_6) δ 113.4 (2C), 117.4 (1C), 123.6 (1C), 126.0 (1C), 126.6 (1C), 126.7 (1C), 127.0 (1C), 127.9 (1C), 128.3 (1C), 128.9 (2C), 129.6 (2C), 131.1 (1C), 132.2 (2C), 132.3 (1C), 132.9 (1C), 133.9 (1C), 135.3 (1C), 147.3 (1C); IR (KBr, cm^{-1}) 810, 1024, 1247, 1300, 1380, 1498, 1564, 1599, 3052, 3360; HRMS (ESI$^-$) m/z 326.1003 ([M–H]$^+$, $C_{22}H_{16}NS^-$ requires 326.1009).

The regiochemistry of **4j′** was determined by the NOESY experiment.

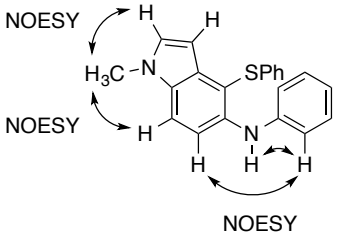


1-Methyl-5-(phenylamino)-4-(phenylthio)-1*H*-indole (**4k**)

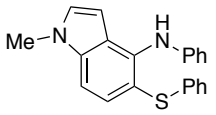


Pale brown solid; Mp 80–82 ºC TLC R_f 0.32 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H, CH_3), 6.46 (d, 1H, *J* = 2.8 Hz, aromatic), 6.56 (br s, 1H, NH), 6.83–6.89 (AA′BB′C, 1H, aromatic), 6.97 (d, 1H, *J* = 2.8 Hz, aromatic), 6.99–7.22 (m, 9H, aromatic), 7.26–7.34 (m, 2H, aromatic); ^{13}C NMR (101 MHz, $CDCl_3$) δ 33.1 (1C), 100.8 (1C), 109.4 (1C), 111.6 (1C), 114.1 (1C), 118.0 (2C), 120.8 (1C), 125.2 (1C), 126.6 (2C), 129.0 (2C), 129.2 (2C), 130.0 (1C), 132.4 (1C), 133.2 (1C), 137.2 (1C), 139.2 (1C), 144.6 (1C); IR (KBr, cm^{-1}) 911, 1080, 1249, 1302, 1503, 1599, 2908, 3055, 3368; HRMS (ESI^-) *m*/*z* 329.1124 ($[M–H]^+$, $C_{21}H_{17}N_2S^-$ requires 329.1118).

The regiochemistry of **4k** was determined by the NOESY experiment.

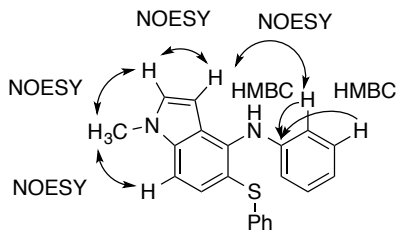


1-Methyl-4-(phenylamino)-5-(phenylthio)-1*H*-indole (**4k′**)

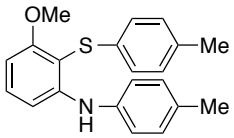


Pale brown solid; Mp 141–143 ºC; TLC R_f 0.62 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (s, 3H, CH_3), 5.96 (dd, 1H, *J* = 3.2, 0.4 Hz, aromatic), 6.87 (br s, 1H, NH), 6.88 (d, 1H, *J* = 3.2 Hz, aromatic), 6.91–6.96 (m, 3H, aromatic), 7.01 (dd, 1H, *J* = 8.5, 0.4 Hz, aromatic), 7.03–7.07 (m, 3H, aromatic), 7.13–7.21 (m, 4H, aromatic), 7.44 (d, 1H, *J* = 8.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 33.0 (1C), 102.2 (1C), 104.1 (1C), 108.6 (1C), 119.9 (2C), 120.0 (1C), 121.6 (1C), 125.0 (1C), 126.0 (2C), 127.4 (1C), 128.6 (2C), 128.8 (2C), 130.6 (1C), 138.8 (1C), 139.1 (1C), 139.4 (1C), 143.6 (1C); IR (KBr, cm^{-1}) 1293, 1497, 1600, 2917, 3057, 3348; HRMS (ESI^-) *m*/*z* 329.1109 ($[M–H]^+$, $C_{21}H_{17}N_2S^-$ requires 329.1118).

The regiochemistry of **4k′** was determined by the NOESY and the HMBC experiments.

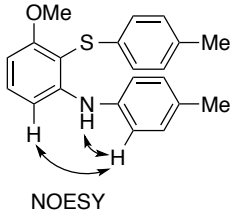


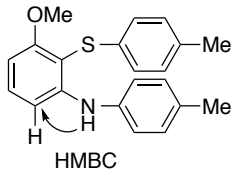
3-Methoxy-*N*-(4-tolyl)-2-(4-tolylthio)aniline (**4l**)



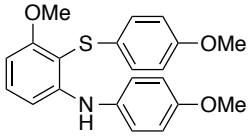
Colorless solid; Mp 105–106 °C; TLC R_f 0.51 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.40 (d, 1H, J = 8.0 Hz, aromatic), 6.81 (d, 1H, J = 8.0 Hz, aromatic), 6.95–7.04 (m, 7H, NH & aromatic), 7.08 (d, 2H, J = 8.5 Hz, aromatic), 7.20 (dd, 1H, J = 8.0, 8.0 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.85 (1C), 20.94 (1C), 56.2 (1C), 101.4 (1C), 103.8 (1C), 106.4 (1C), 122.3 (2C), 126.3 (2C), 129.7 (2C), 129.8 (2C), 131.3 (1C), 132.8 (1C), 132.9 (1C), 135.0, (1C), 139.0 (1C), 148.5 (1C), 161.7 (1C); IR (KBr, cm^{-1}) 1079, 1260, 1467, 1516, 1588, 2919, 3016, 3353; HRMS (ESI$^+$) *m*/*z* 358.1226 ([M+Na]$^+$, $C_{21}H_{21}NNaOS^+$ requires 358.1236).

The regiochemistry of **4l** was determined by the NOESY and the HMBC experiments.



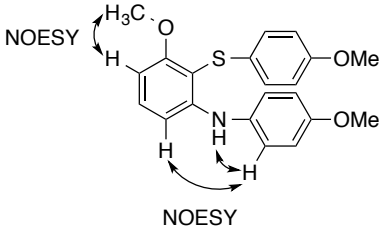


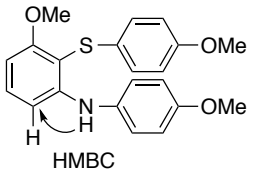
3-Methoxy-*N*-(4-methoxyphenyl)-2-(4-methoxyphenylthio)aniline (**4m**)



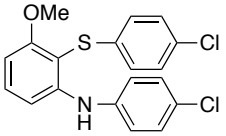
Colorless oil; TLC R_f 0.24 (*n*-hexane/CH_2Cl_2 = 3/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.36 (dd, 1H, J = 8.4, 1.2 Hz, aromatic), 6.62 (dd, 1H, J = 8.4, 1.2 Hz, aromatic), 6.74–6.78 (AA′BB′, 2H, aromatic), 6.82–6.86 (AA′BB′, 2H, aromatic), 6.94 (br s, 1H, NH), 7.03–7.08 (AA′BB′, 2H, aromatic), 7.09–7.13 (AA′BB′, 2H, aromatic), 7.15 (dd, 1H, J = 8.4, 8.4 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3 (1C), 55.5 (1C), 56.2 (1C), 100.9 (1C), 104.2 (1C), 105.8 (1C), 114.6 (2C), 114.7 (2C), 125.2 (2C), 127.2 (1C), 128.5 (2C), 131.2 (1C), 134.5 (1C), 149.3 (1C), 156.4 (1C), 158.0 (1C), 161.5 (1C); IR (KBr, cm^{-1}) 1032, 1245, 1463, 1511, 1591, 2834, 2937, 2999, 3346; HRMS (ESI$^+$) *m*/*z* 390.1115 ([M+Na]$^+$, $C_{21}H_{21}NNaO_3S^+$ requires 390.1134).

The regiochemistry of **4m** was determined by the NOESY and the HMBC experiments.



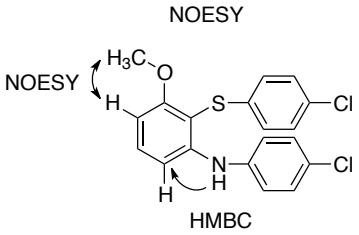


N-(4-Chlorophenyl)-2-(4-chlorophenylthio)-3-methoxyaniline (**4n**)

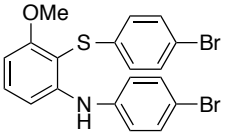


Colorless solid; Mp 148–149 °C; TLC R_f 0.47 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H, OCH_3), 6.48 (d, 1H, *J* = 8.0 Hz, aromatic), 6.85 (d, 1H, *J* = 8.0 Hz, aromatic), 6.93 (br s, 1H, NH), 6.98–7.03 (AA′BB′, 2H, aromatic), 7.04–7.08 (AA′BB′, 2H, aromatic), 7.14–7.18 (AA′BB′, 2H, aromatic), 7.22–7.26 (AA′BB′, 2H, aromatic), 7.27 (dd, 1H, *J* = 8.0, 8.0 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.2 (1C), 102.3 (1C), 103.9 (1C), 106.9 (1C), 122.6 (2C), 127.3 (2C), 127.9 (1C), 129.0 (2C), 129.4 (2C), 131.1 (1C), 131.8 (1C), 135.0 (1C), 140.1 (1C), 147.5 (1C), 161.6 (1C); IR (KBr, cm^{-1}) 1077, 1260, 1468, 1502, 1585, 2837, 3002, 3352; HRMS (ESI^-) *m*/*z* 374.0174 ($[M–H]^+$, $C_{19}H_{14}Cl_2NOS^-$ requires 374.0179).

The regiochemistry of **4n** was determined by the HMBC and the NOESY experiments.

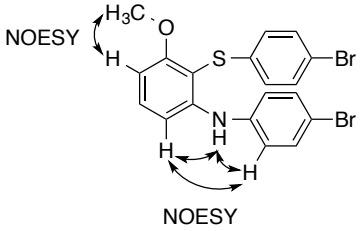


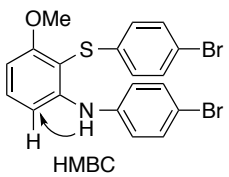
N-(4-Bromophenyl)-2-(4-bromophenylthio)-3-methoxyaniline (**4o**)



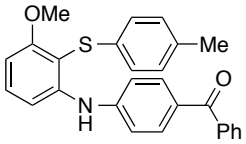
Pale brown solid; Mp 148–150 °C; TLC R_f 0.46 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H, OCH_3), 6.48 (dd, 1H, *J* = 8.5, 0.5 Hz, aromatic), 6.87 (dd, 1H, *J* = 8.5, 0.5 Hz, aromatic), 6.92 (br s, 1H, NH), 6.93–6.96 (AA′BB′, 2H, aromatic), 6.99–7.02 (AA′BB′, 2H, aromatic), 7.28 (dd, 1H, *J* = 8.5, 8.5 Hz, aromatic), 7.28–7.31 (AA′BB′, 2H, aromatic), 7.36–7.39 (AA′BB′, 2H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.2 (1C), 102.5 (1C), 103.9 (1C), 107.1 (1C), 115.3 (1C), 118.9 (1C), 122.7 (2C), 127.6 (2C), 131.8 (1C), 131.9 (2C), 132.3 (2C), 135.7 (1C), 140.6 (1C), 147.3 (1C), 161.6 (1C); IR (KBr, cm^{-1}) 1071, 1260, 1468, 1504, 1581, 2837, 2938, 3349; HRMS (ESI^-) *m*/*z* 461.9166 ($[M–H]^+$, $C_{19}H_{14}Br_2NOS^-$ requires 461.9168).

The regiochemistry of **4o** was determined by the NOESY experiment.



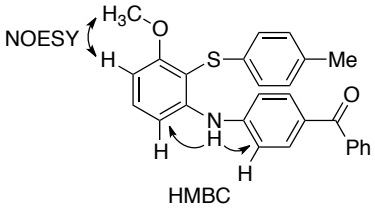


N-(4-Benzoylphenyl)-3-methoxy-2-(4-tolylthio)aniline (**4p**)

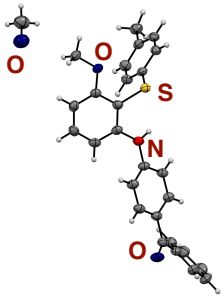


Pale brown solid; Mp 75 °C (decomp.); TLC R_f 0.17 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.60 (d, 1H, *J* = 8.5 Hz, aromatic), 6.98–7.02 (m, 4H, aromatic), 7.11–7.17 (m, 4H, aromatic), 7.29 (br s, 1H, NH), 7.34 (dd, 1H, *J* = 8.5, 8.5 Hz, aromatic), 7.44–7.48 (AA′BB′C, 2H, aromatic), 7.54 (AA′BB′C, 1H, aromatic), 7.73–7.78 (m, 4H, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9 (1C), 56.3 (1C), 104.2 (1C), 107.7 (1C), 109.4 (1C), 117.0 (2C), 125.6 (2C), 128.2 (2C), 129.7 (2C), 129.8 (2C), 130.2 (1C), 131.2 (1C), 131.8 (1C), 132.36 (2C), 132.43 (1C), 135.5 (1C), 138.4 (1C), 145.2 (1C), 146.5 (1C), 161.7 (1C), 195.3 (1C); IR (KBr, cm^{-1}) 1078, 1261, 1467, 1581, 1647, 2924, 3017, 3337; HRMS (ESI^-) *m*/*z* 424.1383 ($[M–H]^+$, $C_{27}H_2NO_2S^-$ requires 424.1377).

The structure of **4p** was confirmed by the X-ray crystallographic analysis. The regiochemistry of **4p** was also determined by the NOESY and the HMBC experiments.

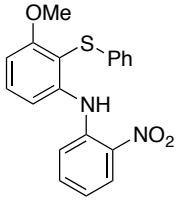


Crystallographic analysis



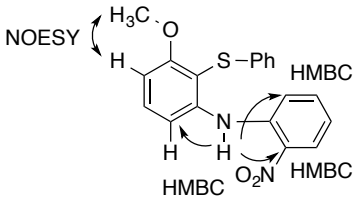
Selected crystal data: Crystal System; monoclinic, Space Group; $P2_1/n$ (No. 14), *a* = 14.4735(7) Å, *b* = 9.4794(4) Å, *c* = 17.0411(8) Å, β = 98.528(7)°, *V* = 2312/20(19) Å^3, *Z* = 4, R_1 = 0.0683, wR_2 = 0.2149. CCDC 1428753 contains the supplementary crystallographic data for this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-Methoxy-*N*-(2-nitrophenyl)-2-(phenylthio)aniline (**4q**)

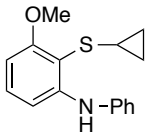


Red solid; Mp 134–135 ºC; TLC R_f 0.24 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.88 (s, 3H, CH_3), 6.76–6.81 (m, 2H, aromatic), 7.02–7.06 (m, 1H, aromatic), 7.10–7.14 (m, 5H, aromatic), 7.33–7.34 (m, 2H, aromatic), 7.38 (dd, 1H, *J* = 8.3, 8.3 Hz, aromatic), 8.10 (d, 1H, *J* = 8.5 Hz, aromatic), 9.75 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 56.4 (1C), 106.9 (1C), 113.5 (1C), 114.2 (1C), 117.0 (1C), 118.6 (1C), 125.7 (1C), 126.6 (1C), 127.3 (2C), 128.9 (2C), 130.8 (1C), 134.9 (1C), 135.1 (1C), 136.1 (1C), 140.8 (1C), 143.4 (1C), 161.7 (1C); IR (KBr, cm^{-1}) 1074, 1150, 1255, 1346, 1439, 1469, 1504, 1577, 1613, 3330; Anal. calcd. for $C_{19}H_{16}N_2O_3S$: C, 64.76; H, 4.58; N, 7.95%; Found: C, 64.85; H, 4.61; N, 7.80%.

The regiochemistry of **4q** was determined by the NOESY and the HMBC experiments.

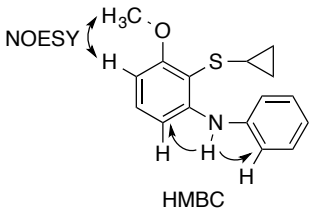


2-(Cyclopropylthio)-3-methoxy-*N*-phenylaniline (**4r**)

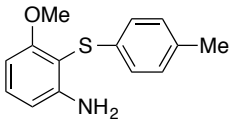


Colorless oil; TLC R_f 0.66 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63–0.70 (m, 2H, CH_2), 0.71–0.79 (m, 2H, CH_2), 2.21–2.29 (m, 1H, CH), 3.89 (s, 3H, OCH_3), 6.42 (dd, 1H, *J* = 8.2, 1.0 Hz, aromatic), 6.89 (dd, 1H, *J* = 8.2, 1.0 Hz, aromatic), 6.98–7.03 (AA'BB'C, 1H, aromatic), 7.12 (br s, 1H, NH), 7.13–7.19 (m, 3H, aromatic), 7.27–7.33 (AA'BB'C, 2H, aromatic); ^{13}C NMR (101 MHz, $CDCl_3$) δ 8.3 (2C), 15.5 (1C), 56.0 (1C), 102.0 (1C), 107.2 (1C), 108.8 (1C), 120.6 (2C), 122.4 (1C), 129.3 (2C), 130.1 (1C), 142.3 (1C), 146.9 (1C), 161.3 (1C); IR (KBr, cm^{-1}) 912, 1081, 1256, 1436, 1507, 1589, 2835, 3007, 3346; HRMS (ESI^-) *m*/*z* 270.0953 ($[M–H]^+$, $C_{16}H_{16}NOS^-$ requires 270.0958).

The regiochemistry of **4r** was determined by the NOESY the HMBC experiments.

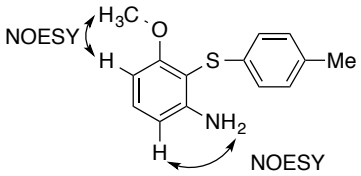


3-Methoxy-2-(4-tolylthio)aniline (**4s**)

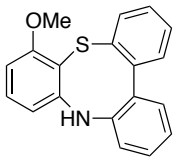


colorless oil; TLC R_f 0.24 (*n*-hexane/CH_2Cl_2 = 2/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 4.44 (br s, 2H, NH_2), 6.33 (dd, 1H, *J* = 8.0, 1.0 Hz, aromatic), 6.42 (dd, 1H, *J* = 8.0, 1.0 Hz, aromatic), 6.95–7.01 (m, 4H, aromatic), 7.17 (dd, 1H, *J* = 8.0, 8.0 Hz, aromatic); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.9 (1C), 56.1 (1C), 100.6 (1C), 102.8 (1C), 108.0 (1C), 126.2 (2C), 129.6 (2C), 131.3 (1C), 133.1 (1C), 134.8 (1C), 150.7 (1C), 161.6 (1C); IR (KBr, cm^{-1}) 1060, 1127, 1260, 1467, 1604, 2836, 2938, 3363, 3470; HRMS (ESI^+) *m*/*z* 268.0769 ($[M+Na]^+$, $C_{14}H_{15}NNaOS^+$ requires 268.0767).

The regiochemistry of **4s** was determined by the NOESY experiment.



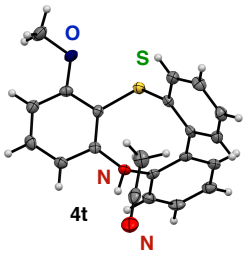
6-Methoxy-10*H*-tribenzo[*b*,*e*,*g*][1,4]thiazocine (**4t**)



Pale yellow solid; Mp 84−86 ºC; TLC (Amino) R_f 0.29 (*n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.88 (s, 3H, CH_3), 5.01 (br s, 1H, NH), 6.45–6.49 (m, 2H, aromatic), 7.00 (dd, 1H, *J* = 8.1, 8.1 Hz, aromatic), 7.21 (dd, 1H, *J* = 7.6, 0.8 Hz, aromatic), 7.33–7.43 (m, 4H, aromatic), 7.46–7.50 (m, 2H, aromatic), 7.77–7.78 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 56.3 (1C), 103.6 (1C), 111.4 (1C), 113.5 (1C), 126.6 (1C), 127.2 (1C), 127.28 (1C), 127.32 (1C), 128.0 (1C), 129.1 (1C), 129.51 (1C), 129.54 (1C), 129.7 (1C), 136.7 (1C), 139.0 (1C), 142.8 (1C), 147.7 (1C), 148.4 (1C), 158.5 (1C); IR (KBr, cm^{-1}) 910, 1089, 1250, 1435, 1445, 1463, 1488, 1579, 3066, 3246, 3352; HRMS (ESI^+) *m*/*z* 328.0765 ($[M+Na]^+$, $C_{19}H_{15}NNaOS^+$ requires 328.0767).

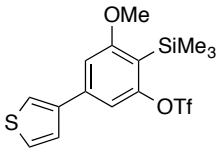
The structure of **4t** was confirmed by the X-ray crystallographic analysis.

Crystallographic analysis



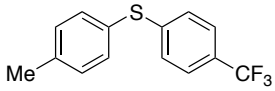
Selected crystal data: Crystal System; orthorhombic, Space Group; *Pbca* (No. 61), a = 14.654(3) Å, b = 7.559(2) Å, c = 31.389(5) Å, V = 3476.7(13) Å^3, Z = 8, R_1 = 0.0458, wR_2 = 0.0890. CCDC 1428752 contains the supplementary crystallographic data for this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-Methoxy-5-(thienyl)-2-(trimethylsilyl)phenyl triflate (**8**)



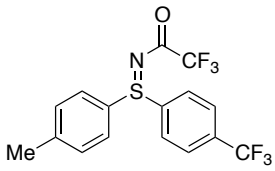
Colorless solid; Mp 59−60 °C; TLC R_f 0.40 (*n*-hexane/CH_2Cl_2 = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.37 (s, 9H, $SiCH_3$), 3.88 (s, 3H, OCH_3), 7.00 (d, 1H, J = 1.0 Hz, aromatic), 7.14 (d, 1H, J = 1.0 Hz, aromatic), 7.34 (dd, 1H, J = 5.0, 1.3 Hz, heteroaromatic), 7.42 (dd, 1H, J = 5.0, 3.0 Hz, heteroaromatic), 7.49 (dd, 1H, J = 3.0, 1.3 Hz, heteroaromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.8 (3C), 55.6 (1C), 107.5 (1C), 111.0 (1C), 118.6 (q, 1C, $^1J_{C–F}$ = 320.8 Hz), 119.2 (1C), 121.8 (1C), 126.1 (1C), 126.8 (1C), 139.7 (1C), 140.7 (1C), 155.0 (1C), 165.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 825, 852, 931, 954, 1046, 1059, 1141, 1214, 1246, 1416, 1608; Anal. calcd. for $C_{15}H_{17}F_3O_4S_2Si$: C, 43.89; H, 4.17; N, 0.00%; Found: C, 43.74; H, 4.20; N, 0.00%.

4-(Trifluoromethyl)phenyl 4-tolyl sulfide



Colorless crystal; Mp 104−105 °C; TLC R_f 0.36 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.39 (s, 3H, CH_3), 7.19−7.23 (m, 4H, aromatic) 7.38−7.41 (AA′BB′, 2H, aromatic), 7.44−7.46 (AA′BB′, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.2 (1C), 124.1 (q, 1C, $^1J_{C–F}$ = 271.4 Hz), 125.7 (q, 2C, $^3J_{C–F}$ = 3.7 Hz), 127.3 (2C), 127.5 (q, 1C, $^2J_{C–F}$ = 32.6 Hz), 128.2 (1C), 130.5 (2C), 134.3 (2C), 139.2 (1C), 143.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.7 (s); IR (KBr, cm^{-1}) 812, 830, 1014, 1064, 1087, 1107, 1172, 1333, 1404, 1605; Anal. calcd. for $C_{14}H_{11}F_3S$: C, 62.67; H, 4.13; N, 0.00%; Found: C, 62.61; H, 4.16; N, 0.00%.

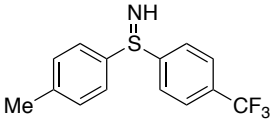
S-(4-Tolyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine



Colorless oil; TLC R_f 0.33 (CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H, CH_3), 7.35−7.37 (AA′BB′, 2H, aromatic), 7.66−7.69 (AA′BB′, 2H, aromatic), 7.77−7.79 (AA′BB′, 2H, aromatic), 7.88−7.89 (AA′BB′, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 116.9 (q, 1C, $^1J_{C–F}$ = 287.3 Hz), 123.0 (q, 1C, $^1J_{C–F}$ = 273.0 Hz), 127.0 (q, 2C, $^3J_{C–F}$ = 3.6 Hz), 128.1 (2C), 128.3 (2C), 129.7 (1C), 131.2 (2C), 134.3 (q, 1C, $^2J_{C–F}$ = 33.3 Hz), 138.6 (1C), 144.6 (1C), 166.9 (q, 1C, $^2J_{C–F}$ = 35.5 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.7 (s, 3F), –

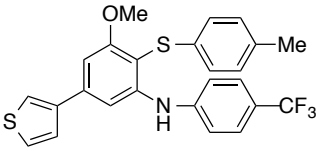
63.5 (s, 3F); IR (KBr, cm^{-1}) 1014, 1063, 1138, 1173, 1324, 1403, 1640; Anal. calcd. for $C_{16}H_{11}F_6NOS$: C, 50.66; H, 2.92; N, 3.69%; Found: C, 50.76; H, 2.97; N, 3.71%.

S-(4-Tolyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (**2k**)



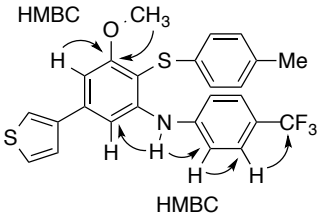
Colorless solid; Mp 64−66 °C; TLC (Amino) R_f 0.44 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.39 (s, 3H, CH_3), 7.26−7.28 (m, 2H, aromatic), 7.45−7.48 (AA′BB′, 2H, aromatic), 7.68−7.72 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.3 (1C), 123.5 (q, 1C, $^1J_{C–F}$ = 272.8 Hz), 126.0 (2C), 126.077 (q, 2C, $^3J_{C–F}$ = 3.6 Hz), 126.084 (2C), 130.3 (2C), 132.1 (q, 1C, $^2J_{C–F}$ = 32.8 Hz), 141.5 (1C), 141.6 (1C), 150.0 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –63.0 (s); IR (KBr, cm^{-1}) 914, 1014, 1059, 1127, 1166, 1323, 1399, 3042, 3178; HRMS (ESI^+) m/z 284.0712 ($[M+H]^+$, $C_{14}H_{13}F_3NS^+$ requires 284.0715).

3-Methoxy-5-(3-thienyl)-2-(4-tolylthio)-*N*-(4-(trifluoromethyl)phenyl)aniline (**4w**)



Colorless solid; Mp 129–131 °C; TLC R_f 0.24 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.77 (d, 1H, *J* = 2.0 Hz, aromatic), 6.98–7.05 (m, 4H, AA′BB′, aromatic), 7.18 (br s, 1H, NH), 7.19 (d, 2H, *J* = 8.5 Hz, aromatic), 7.27 (d, 1H, *J* = 2.0 Hz, aromatic), 7.35 (dd, 1H, *J* = 5.0, 1.5 Hz, aromatic), 7.40 (dd, 1H, *J* = 5.0, 3.0 Hz, aromatic), 7.49 (dd, 1H, *J* = 3.0, 1.5 Hz, aromatic), 7.50 (d, 2H, *J* = 8.5 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9 (1C), 56.4 (1C), 102.2 (1C), 105.8 (1C), 106.7 (1C), 118.6 (2C), 121.5 (1C), 123.5 (q, 1C, *J* = 32.8 Hz, aromatic), 124,4 (q, 1C, $^1J_{C–F}$ = 271.0 Hz), 126.3 (1C), 126.5 (2C), 126.6 (1C), 126.6 (q, 2C, *J* = 3.8 Hz, aromatic), 129.8 (2C), 132.5 (1C), 135.5 (1C), 138.9 (1C), 141.9 (1C), 145.3 (1C), 145.9 (1C), 161.9 (1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2 (s); IR (KBr, cm^{-1}) 1066, 1113, 1324, 1452, 1565, 1592, 2937, 3015, 3349; HRMS (ESI^+) *m/z* 494.0816 ($[M+Na]^+$, $C_{25}H_{20}F_3NNaOS_2^+$ requires 494.0831).

The regiochemistry of **4w** was determined by the HMBC experiment.



References for Supporting Information

S1 Yoshida, S.; Shimomori, K.; Nonaka, T.; Hosoya, T. *Chem. Lett.* **2015**, *44*, 1324.

S2 Ikawa, T.; Nishiyama, T.; Shigeta, T.; Mohri, S.; Morita, S.; Takayanagi, S.; Terauchi, Y.; Morikawa, Y.; Takagi, A.; Ishikawa, Y.; Fujii, S.; Kita, Y.; Akai, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5674.

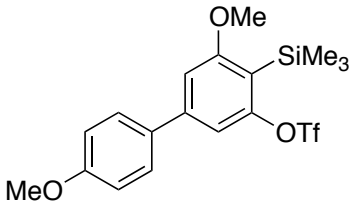
S3 Bronner, S. M.; Garg, N. K. *J. Org. Chem.* **2009**, *74*, 8842.

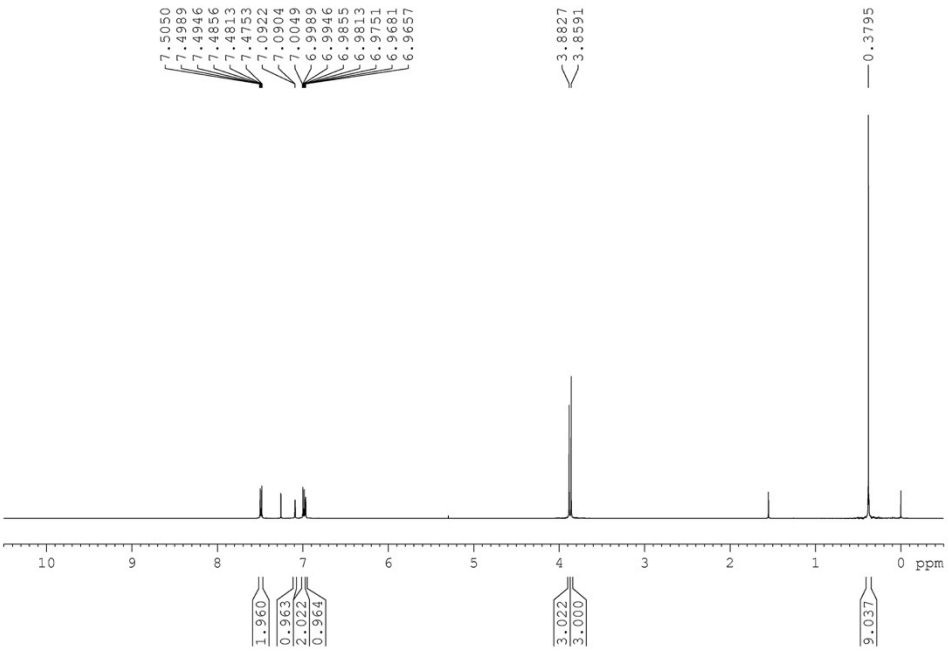
S4 Abdo M.; Knapp, S. *J. Org. Chem.* **2012**, *77*, 3433.

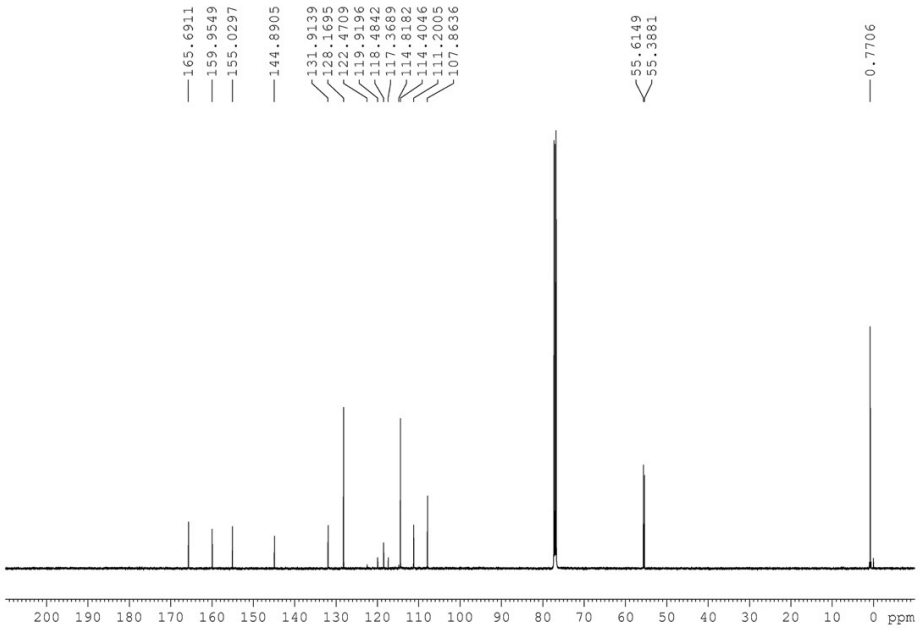
S5 Okamura, H.; Bolm, C. *Org. Lett.* **2004**, *6*, 1305.

^{1}H and ^{13}C NMR Spectra of Compounds

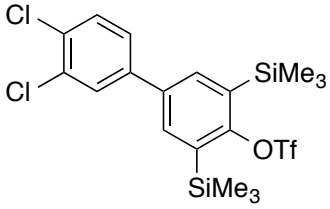
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **1f** ($CDCl_3$)

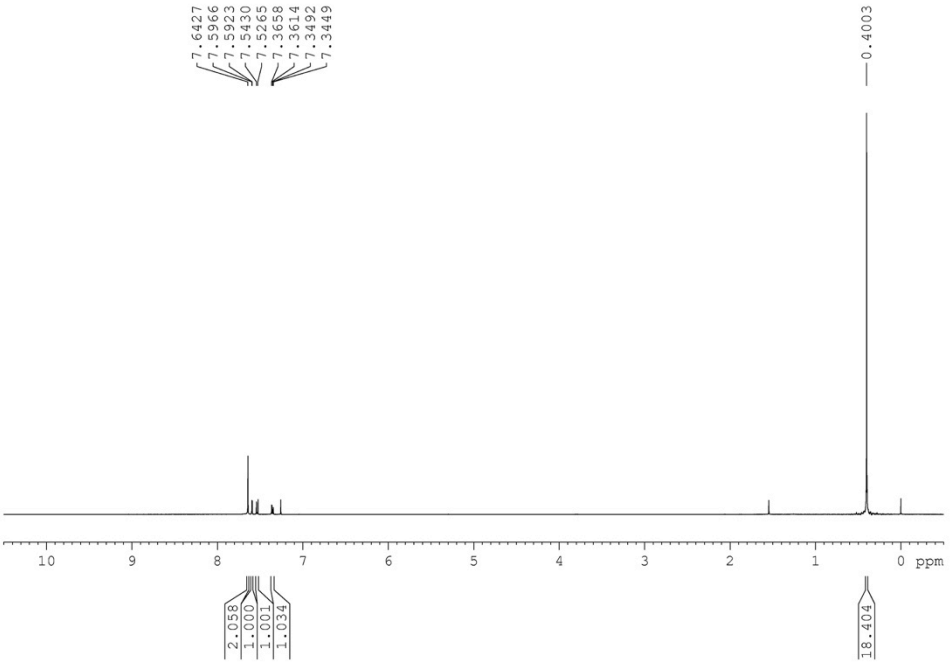


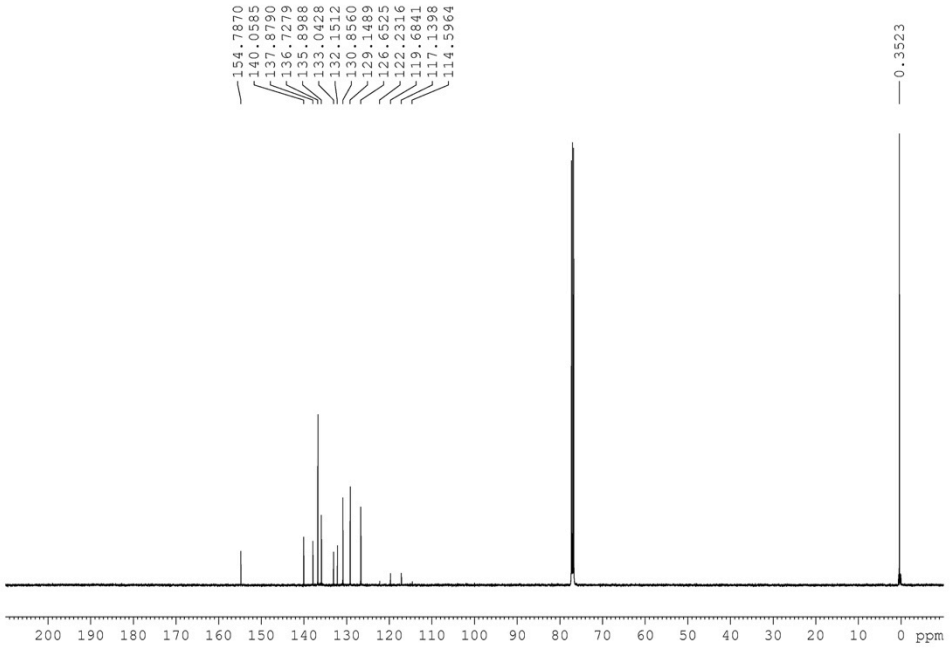




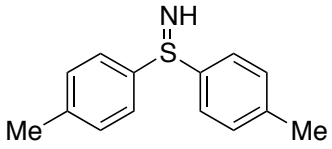
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **1i** ($CDCl_3$)

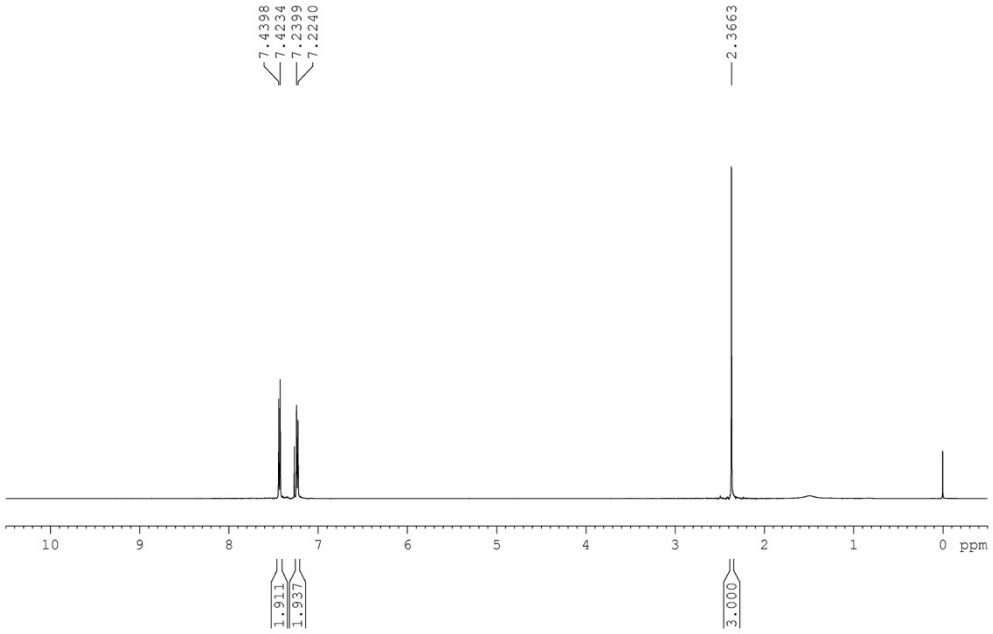


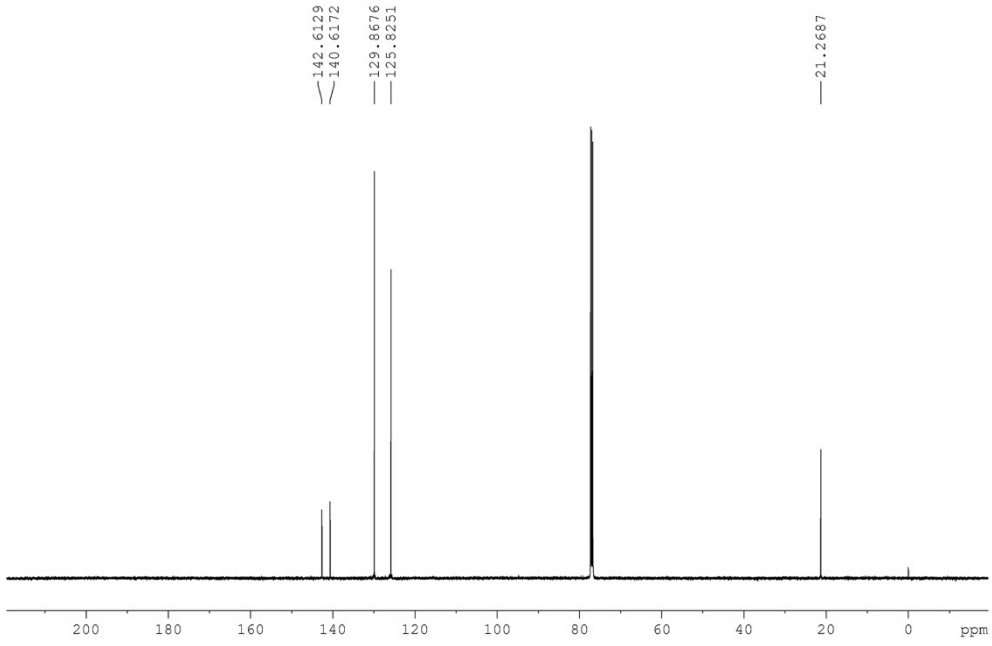




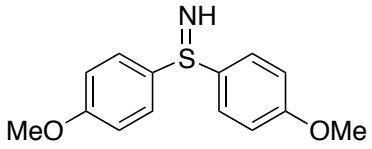
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2b** ($CDCl_3$)

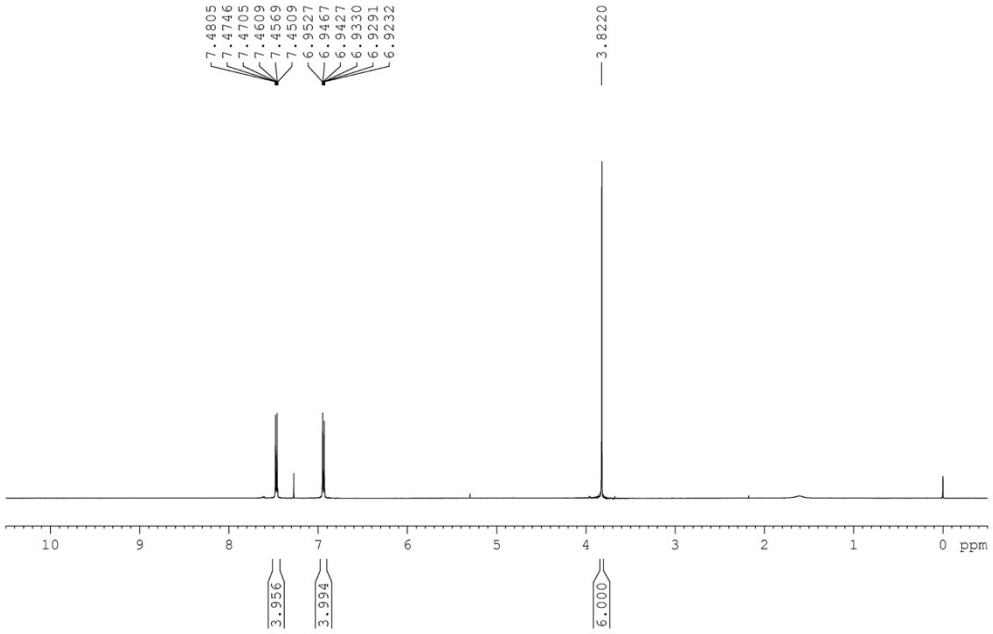


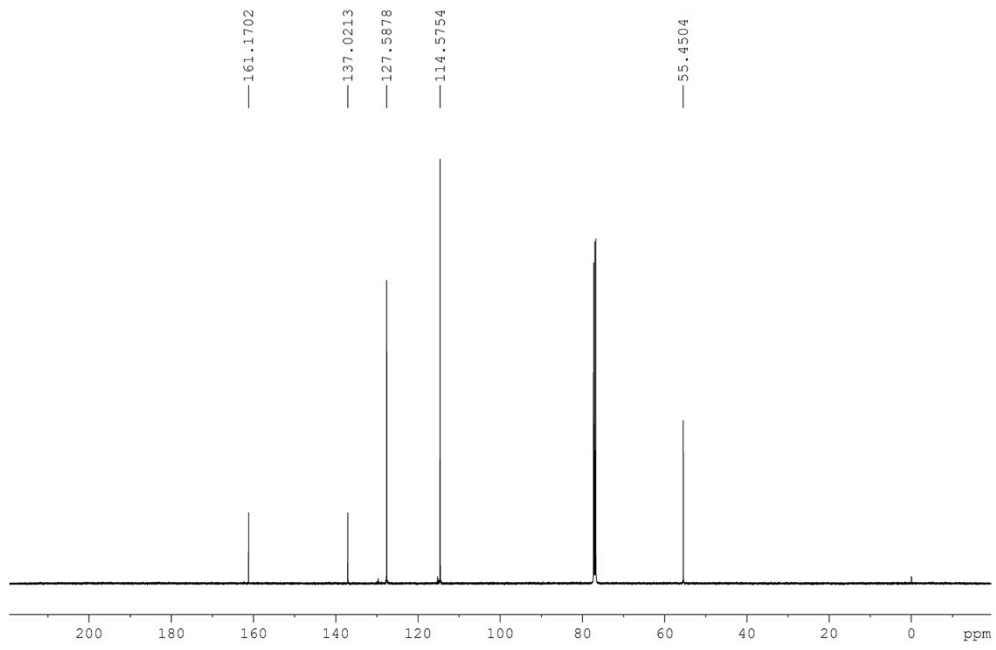




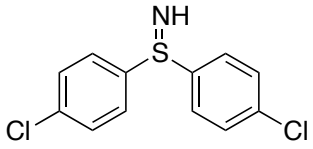
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2c** ($CDCl_3$)

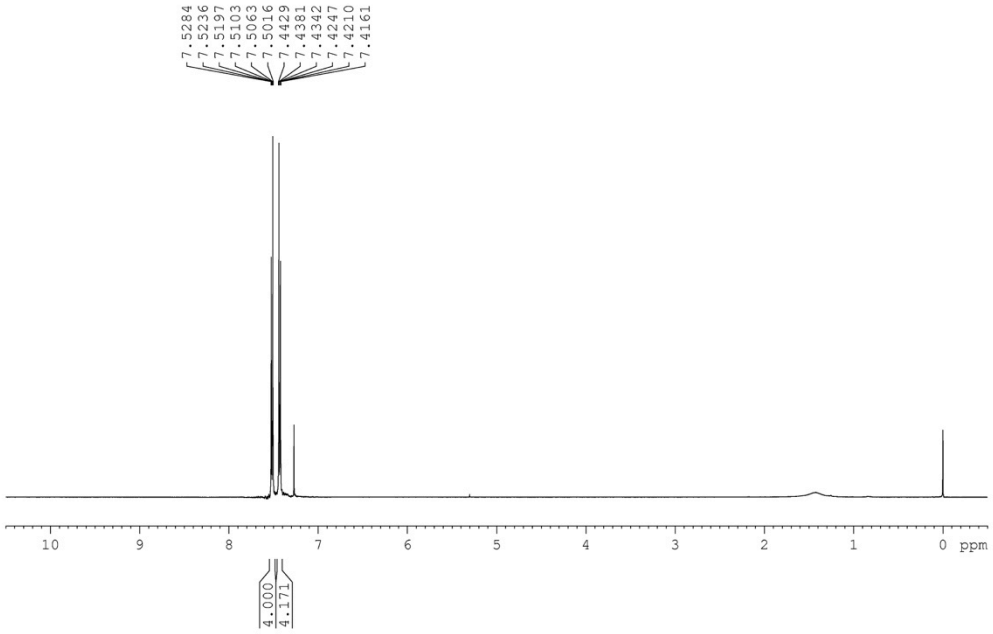


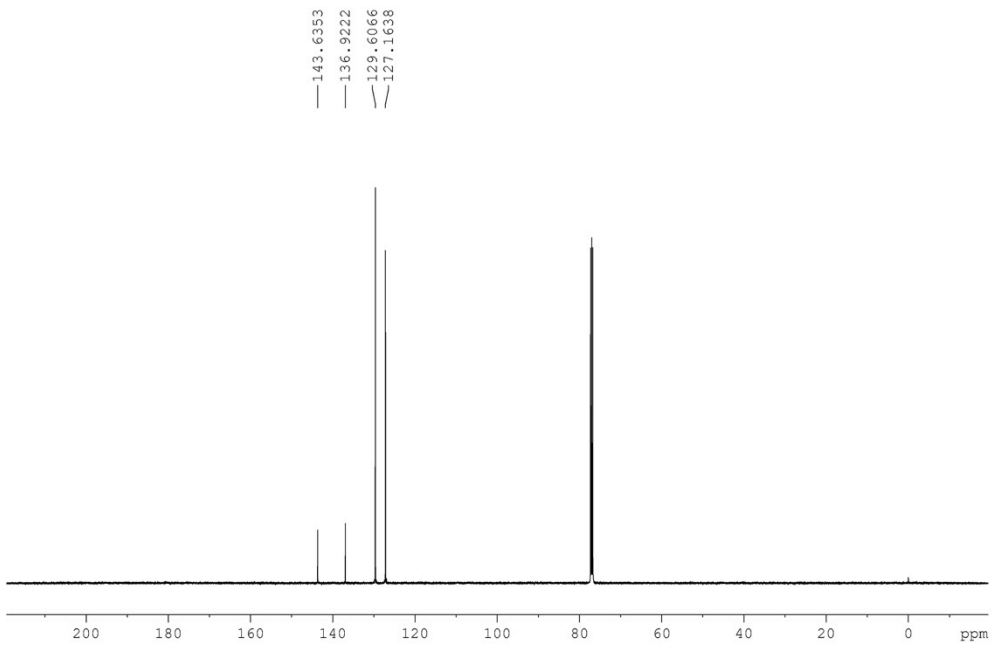




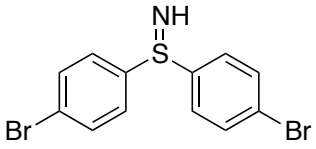
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2d** ($CDCl_3$)

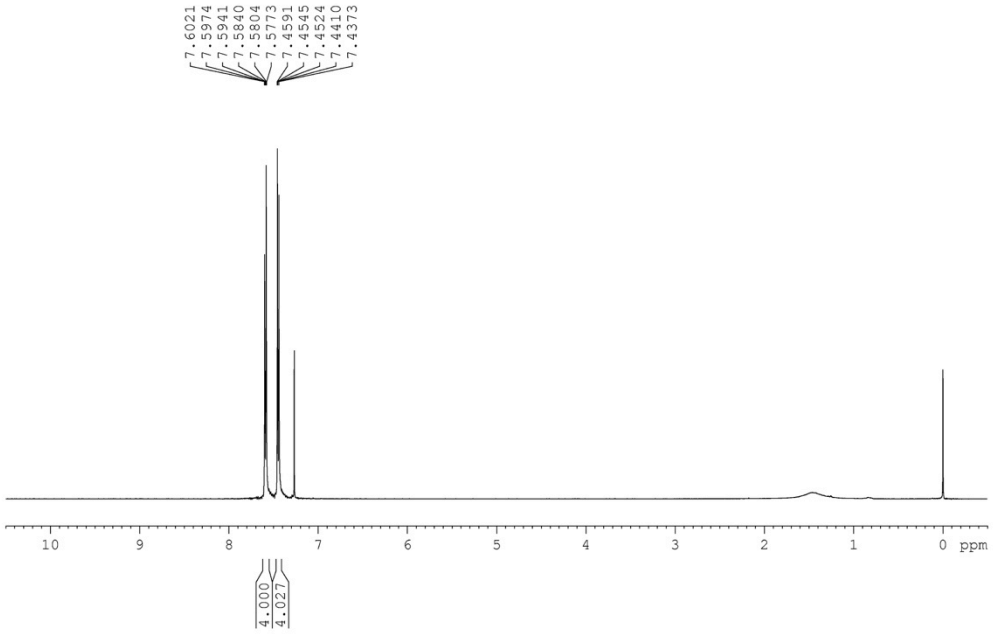


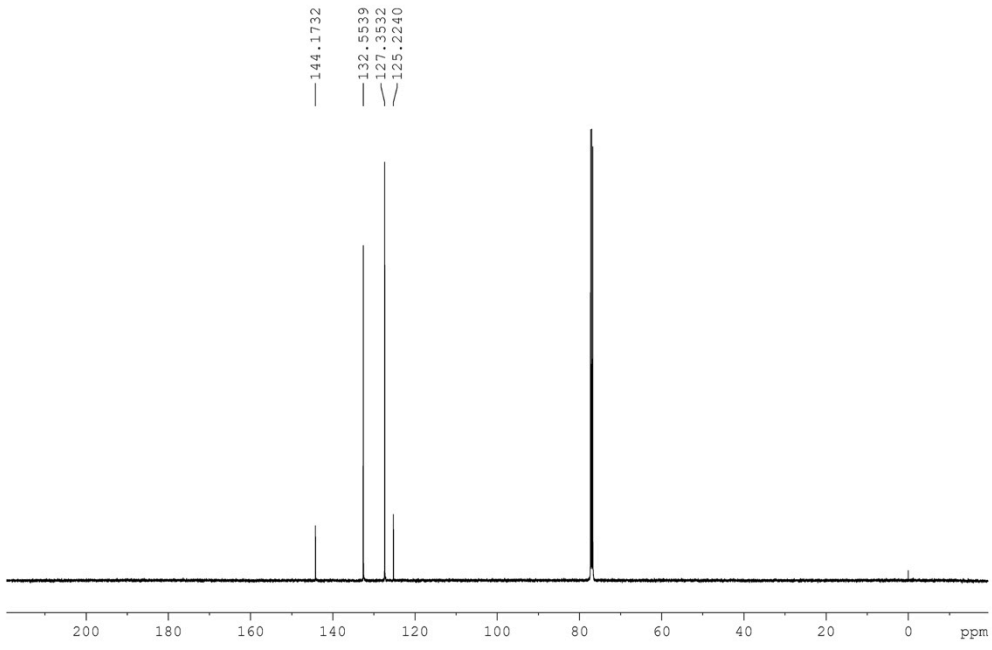




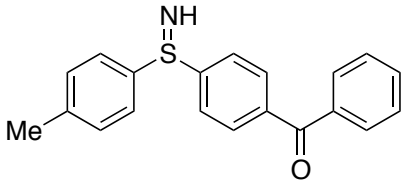
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2e** ($CDCl_3$)

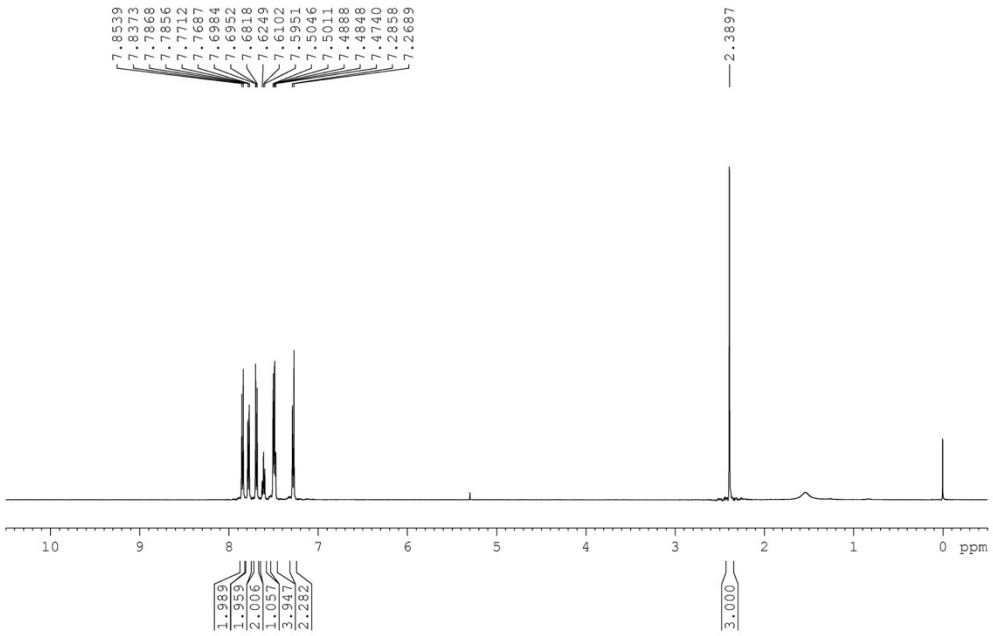


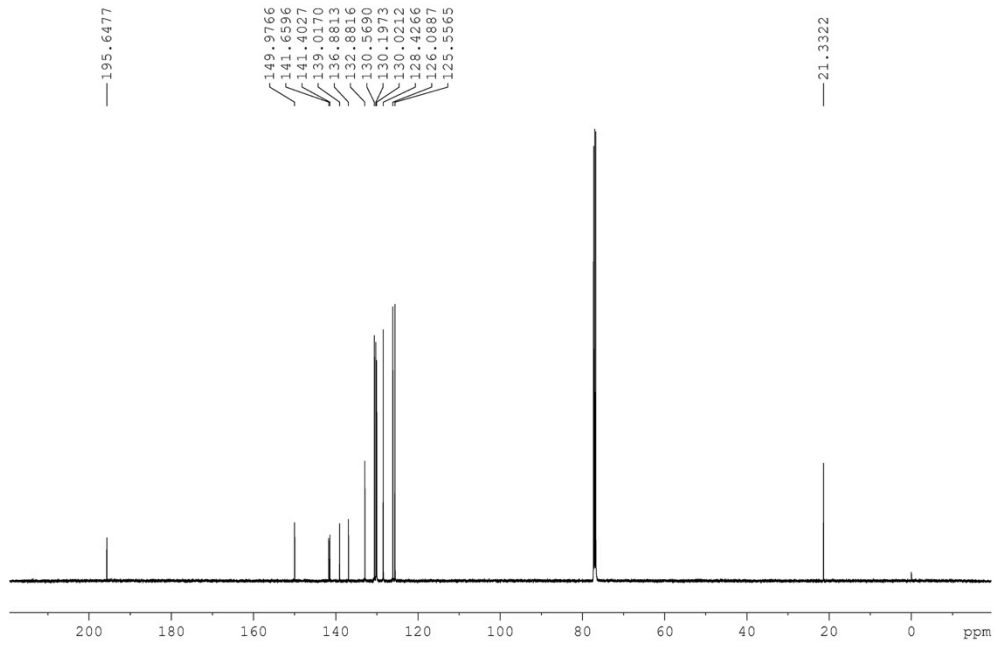




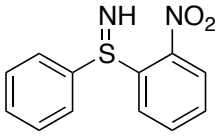
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2f** ($CDCl_3$)

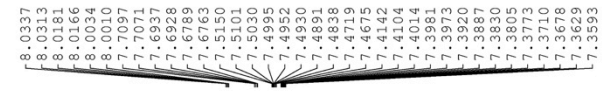


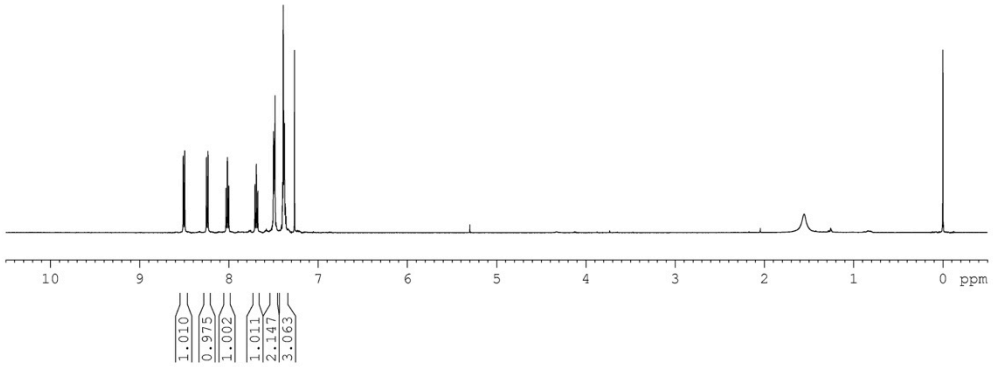


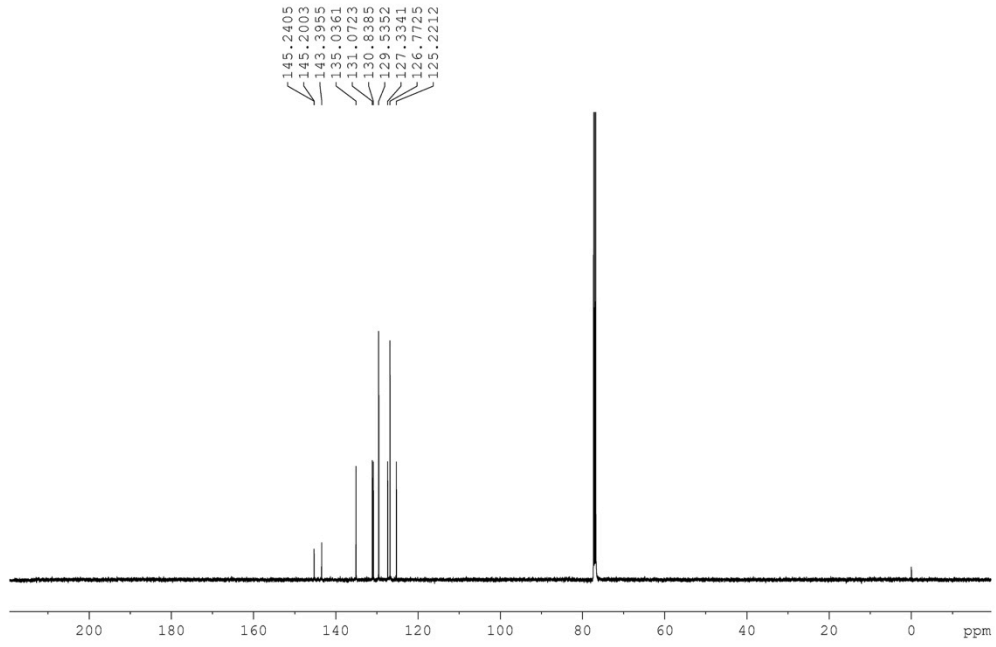


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2g** ($CDCl_3$)

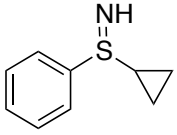


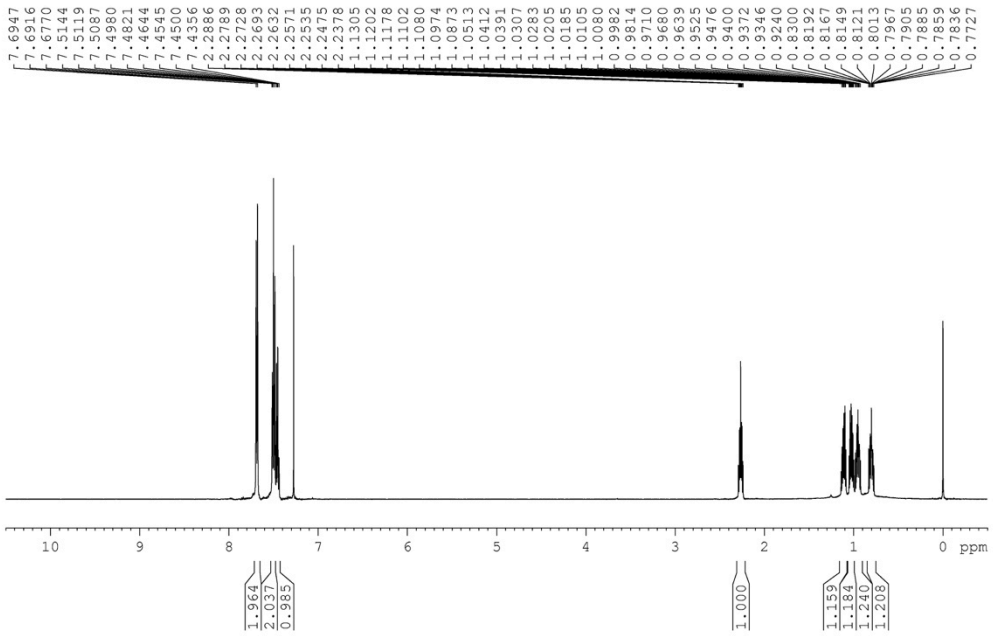


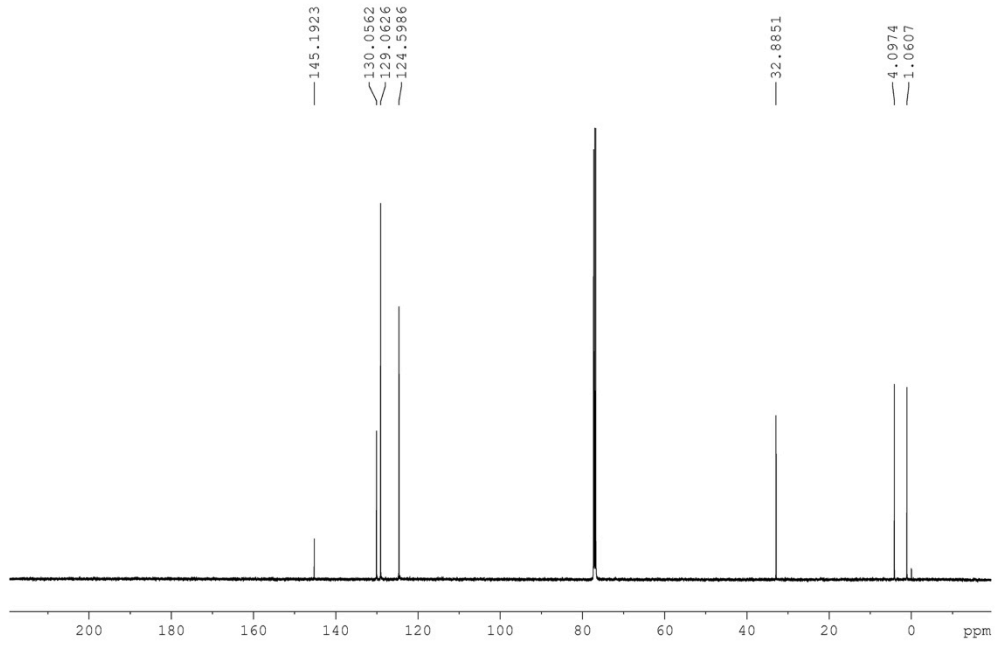




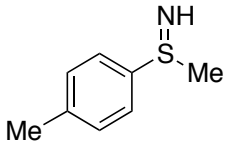
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2h** ($CDCl_3$)

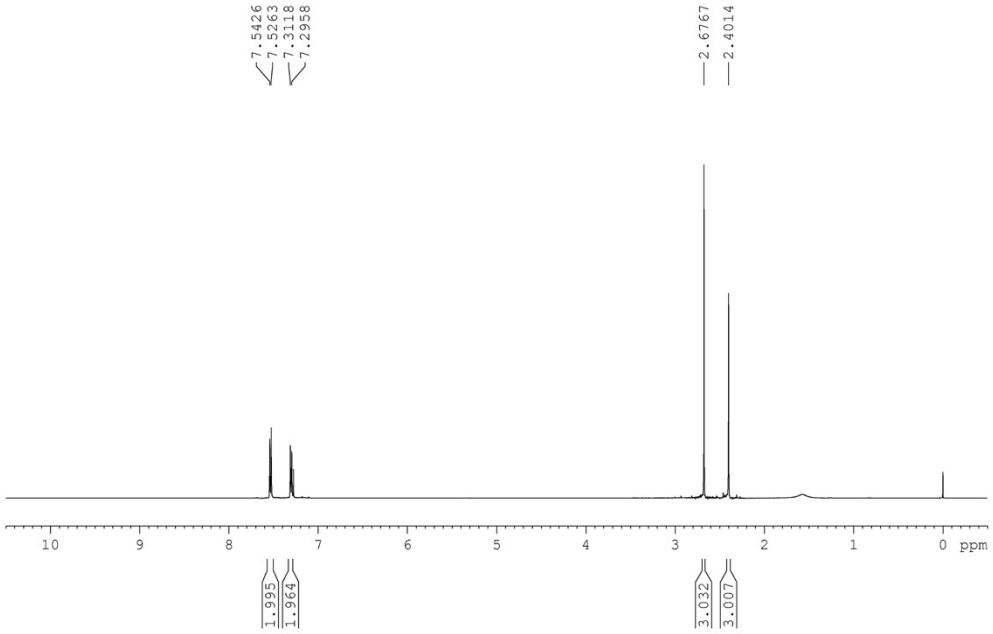


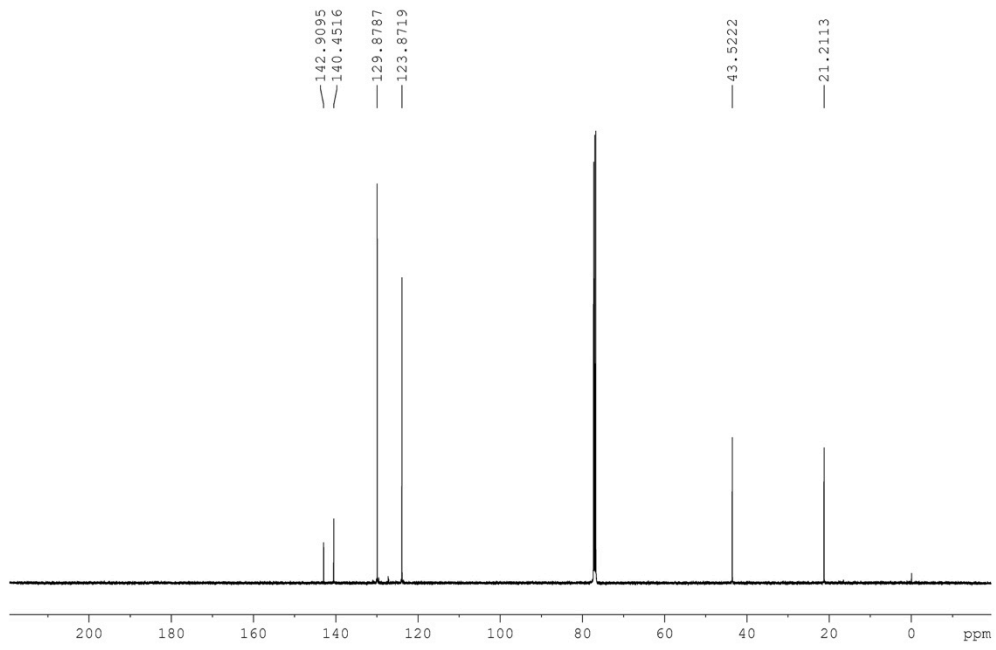




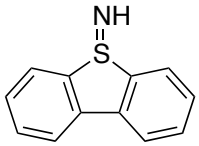
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2i** ($CDCl_3$)

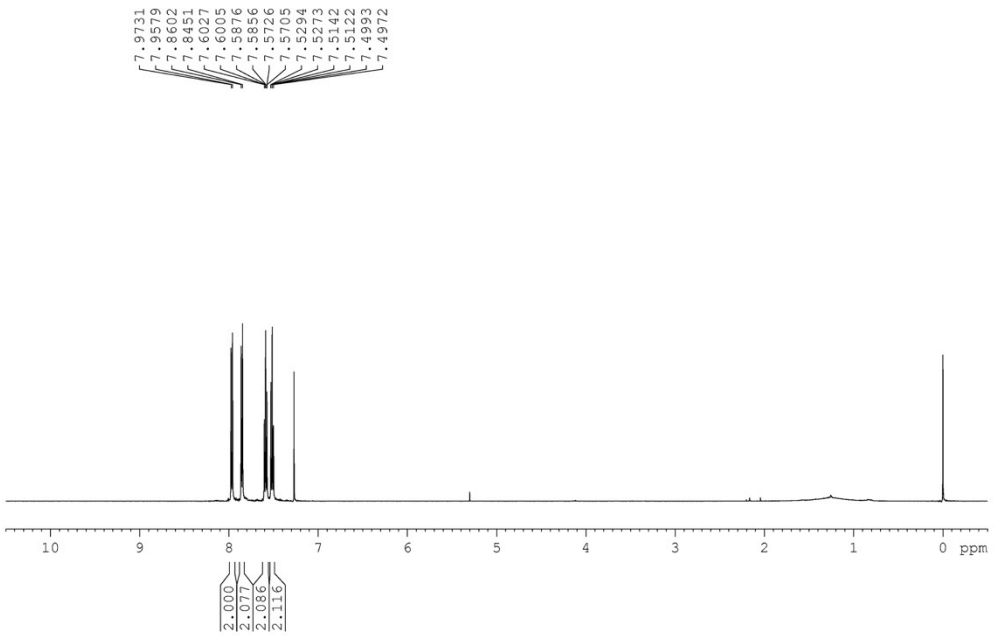


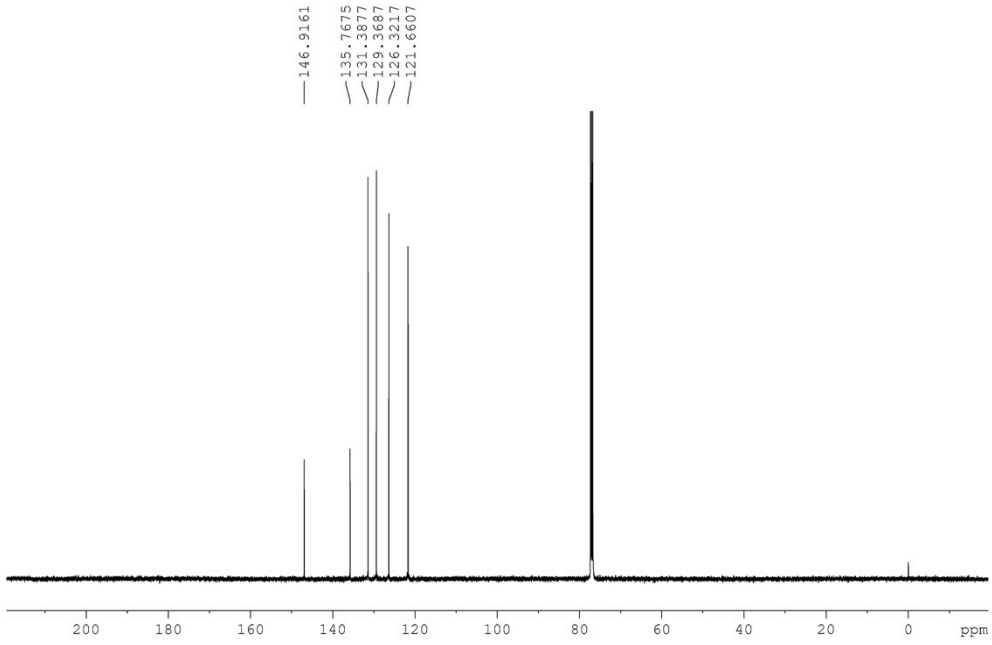




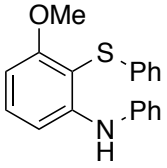
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2j** ($CDCl_3$)

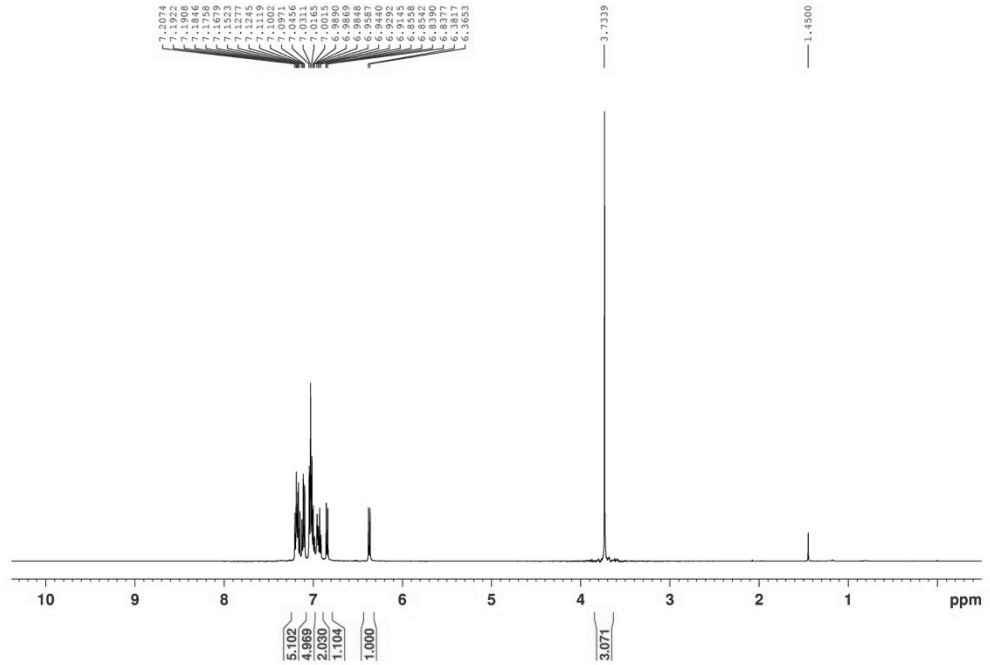


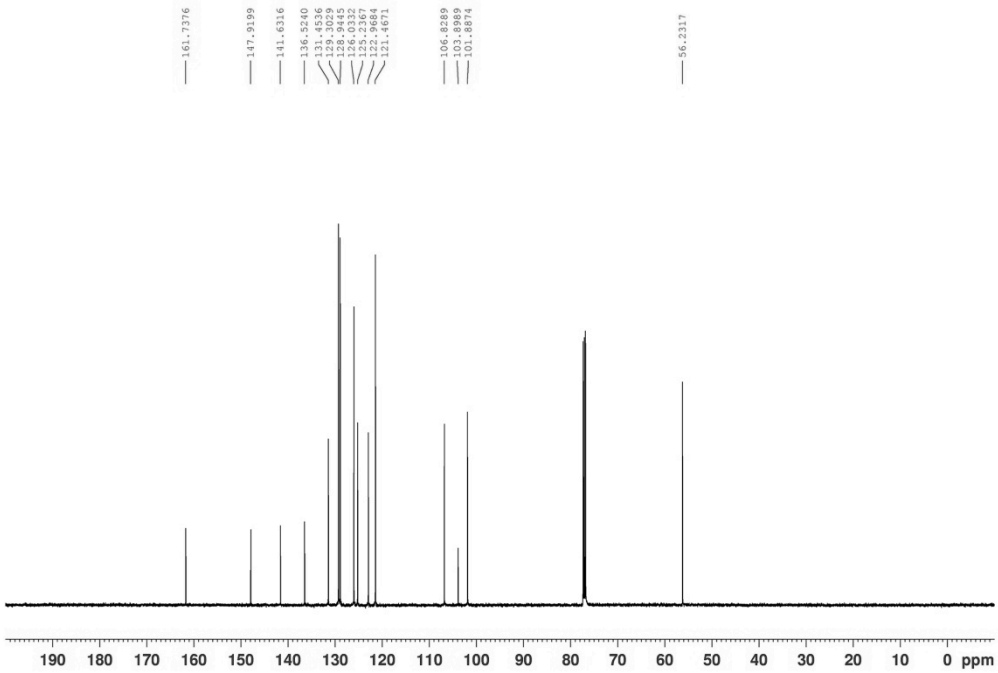




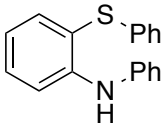
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4a** ($CDCl_3$)

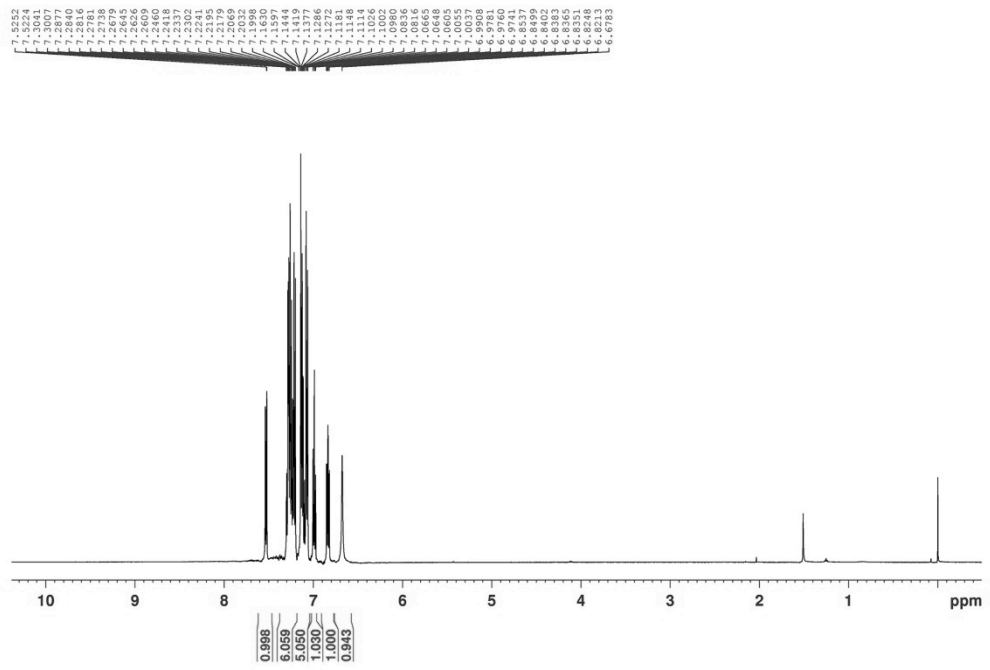


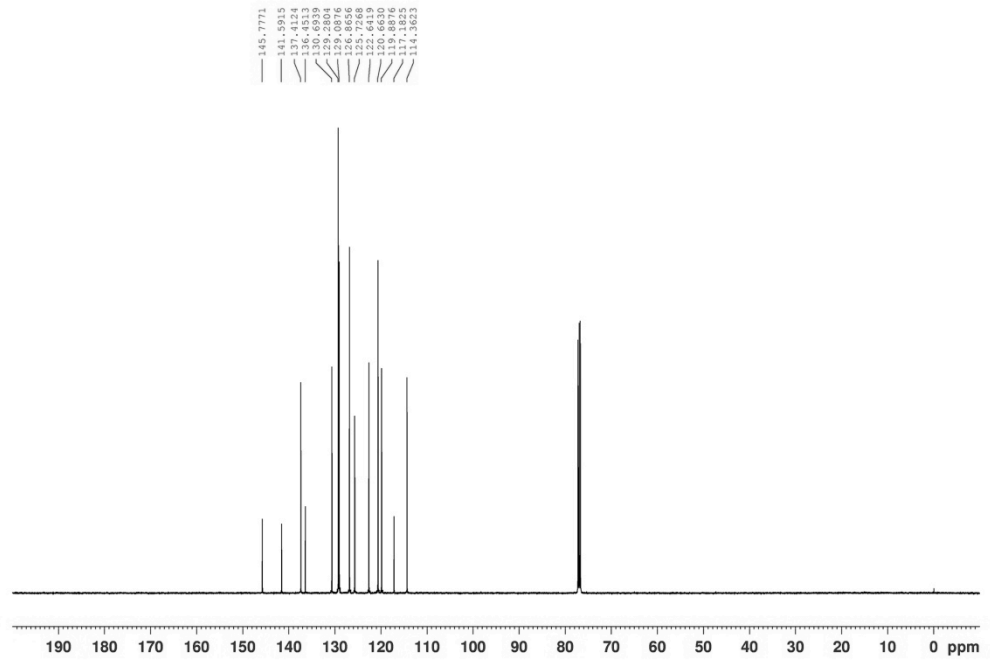




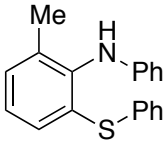
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4b** ($CDCl_3$)

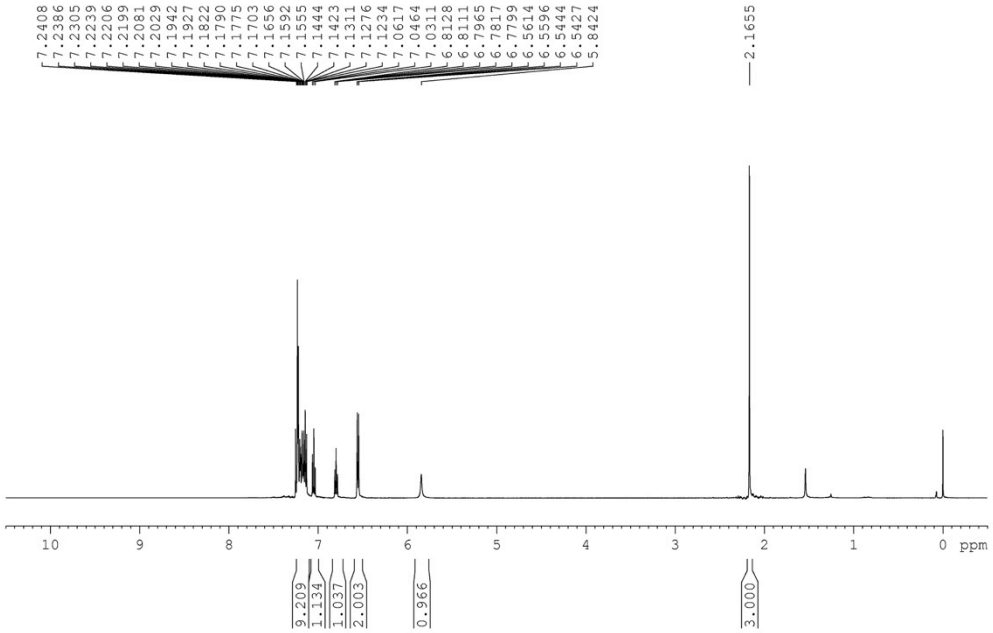


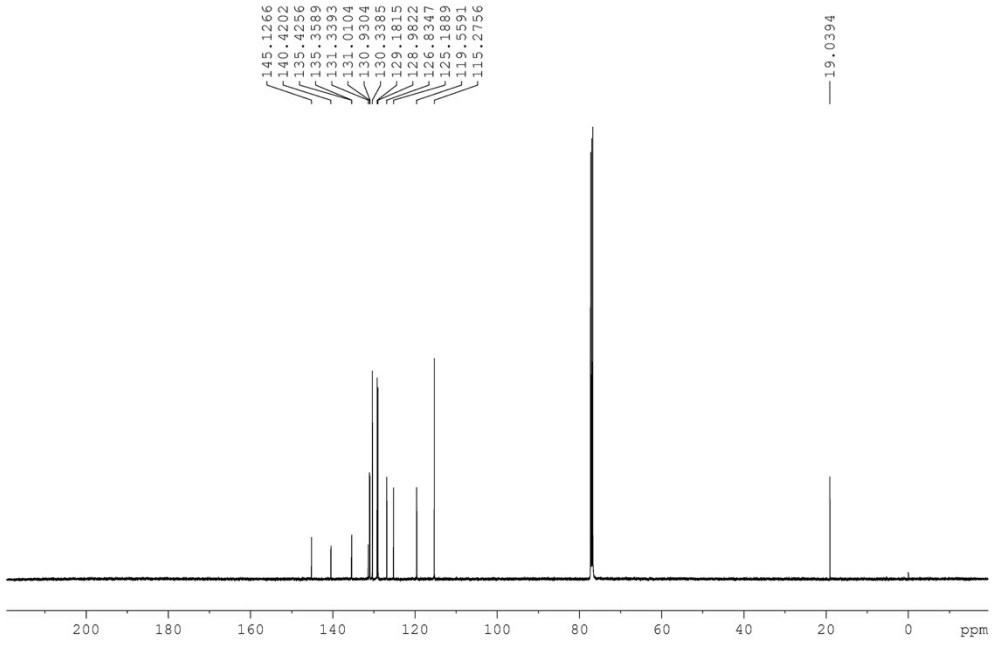




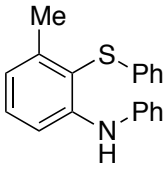
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4c** ($CDCl_3$)

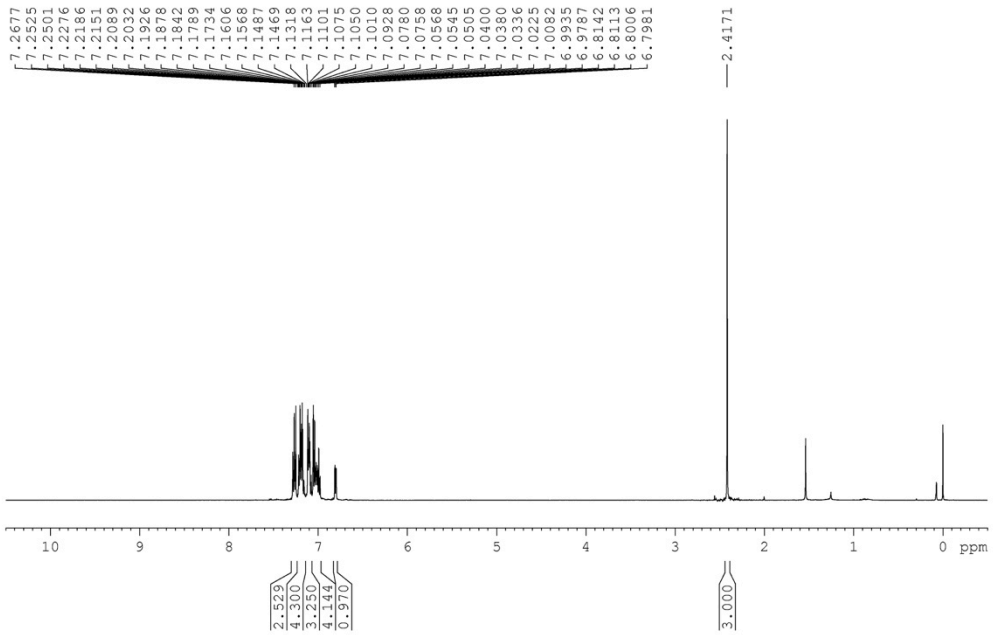


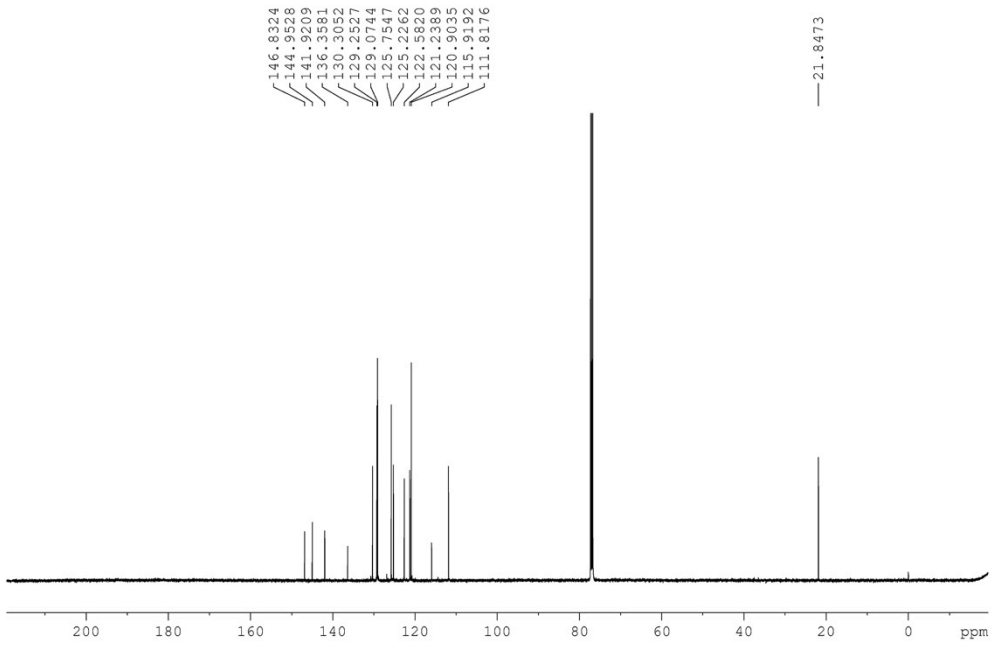




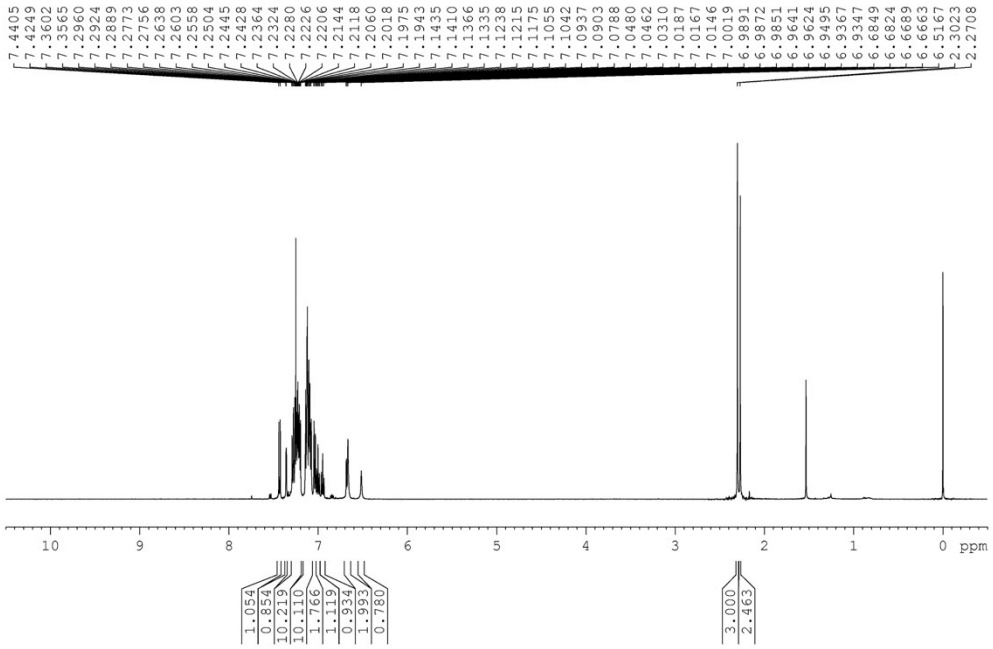
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4c′** ($CDCl_3$)

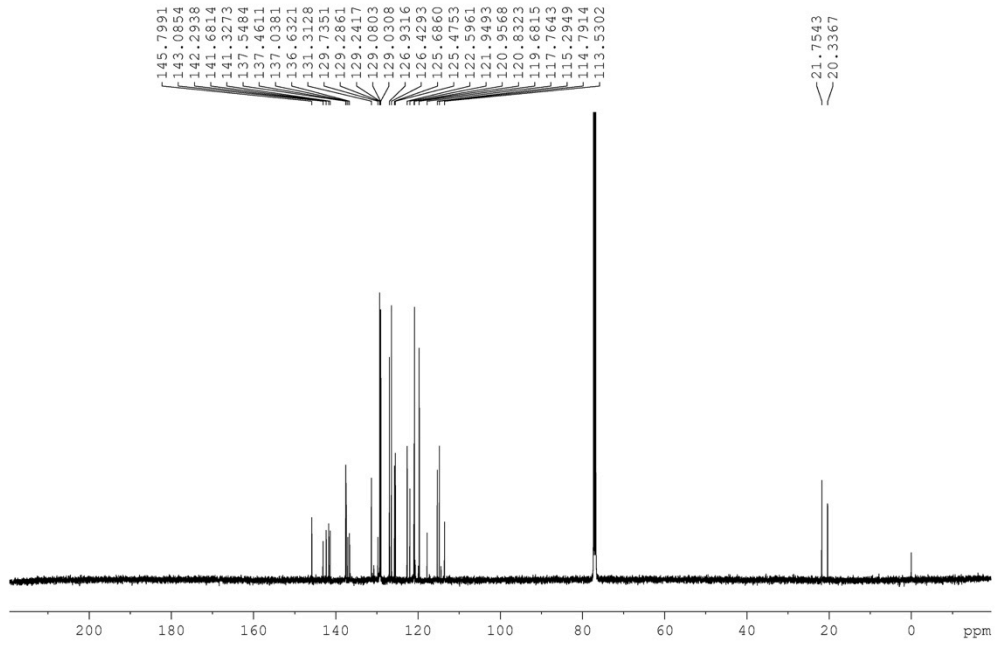




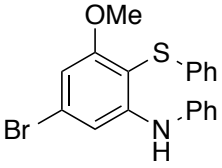


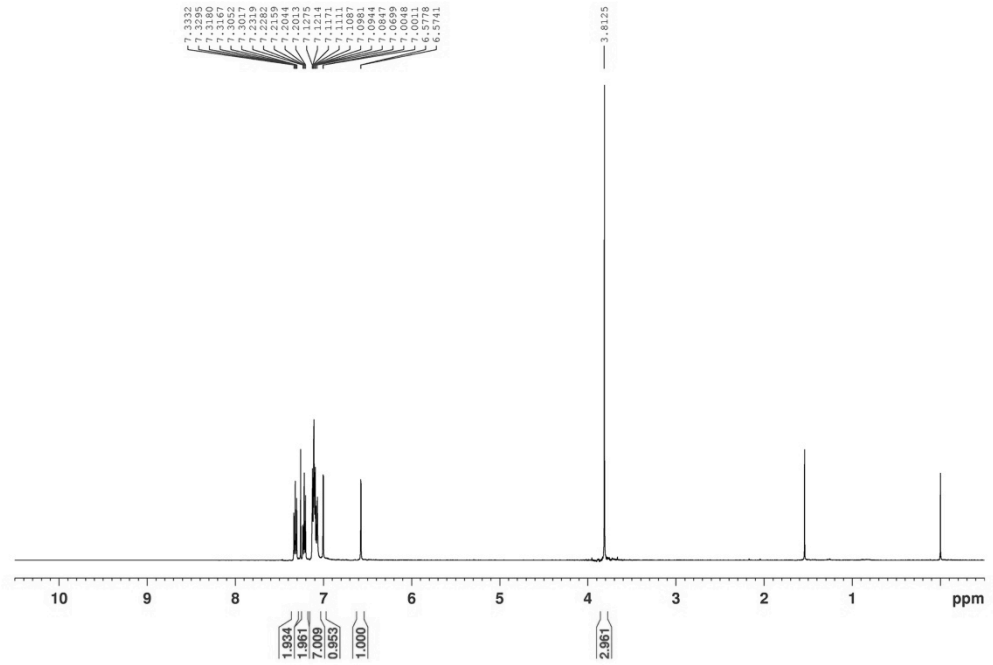
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of a mixture of **4d** and **4d′** (55:45) ($CDCl_3$)

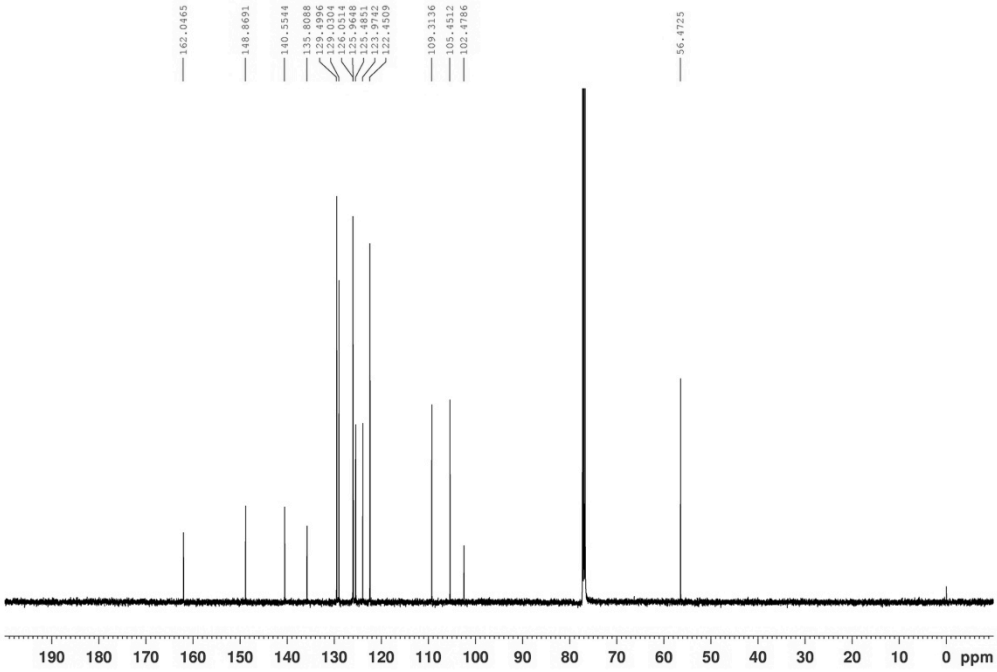




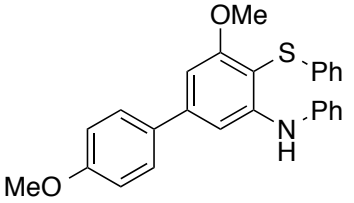
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4e** ($CDCl_3$)

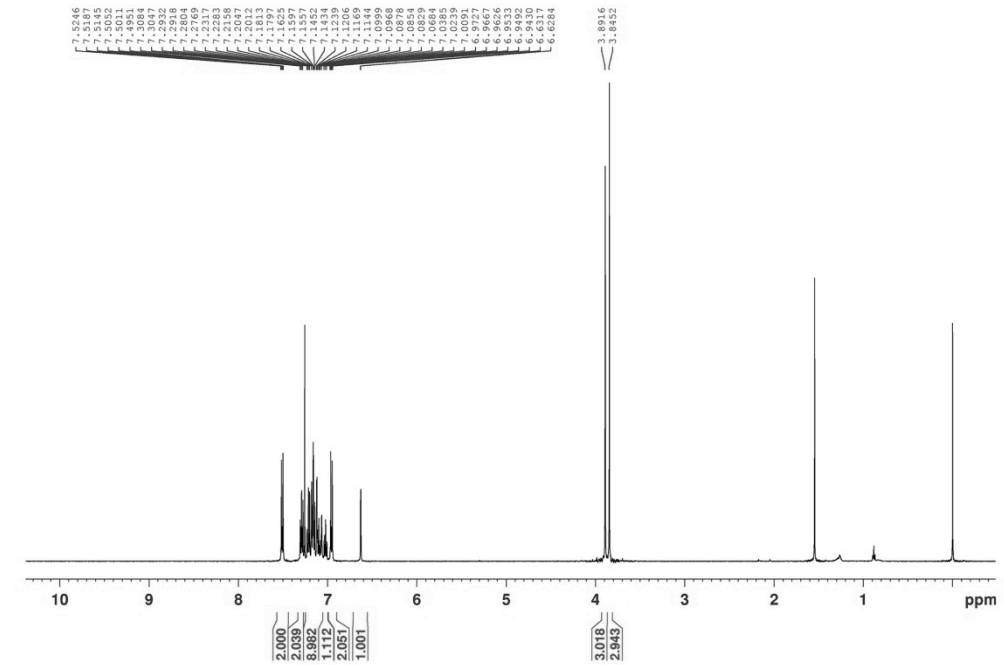


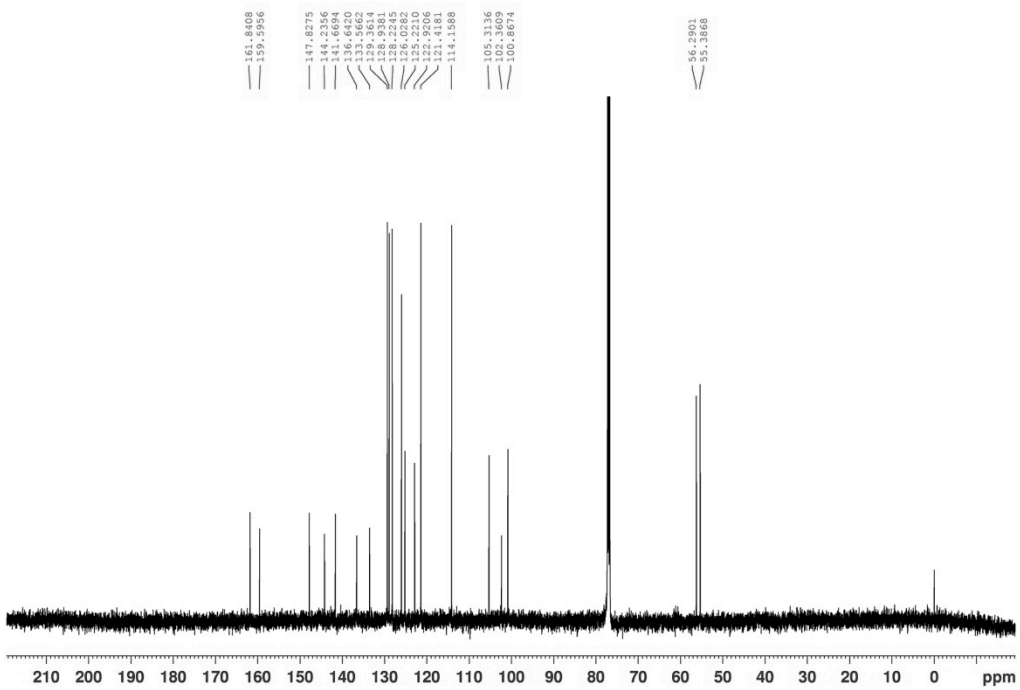




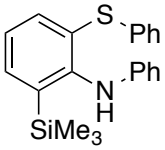
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4f** ($CDCl_3$)

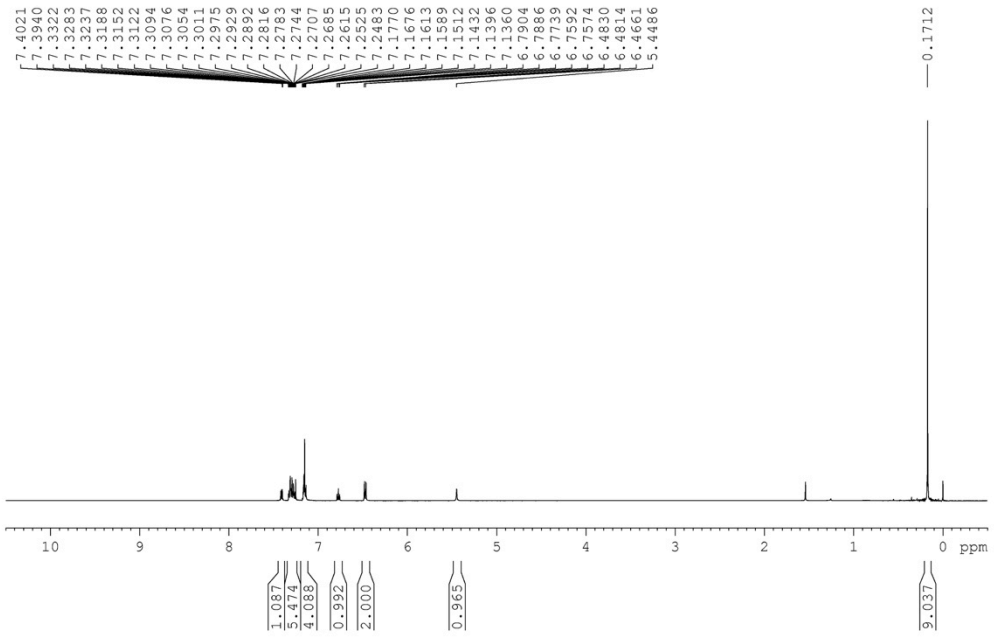


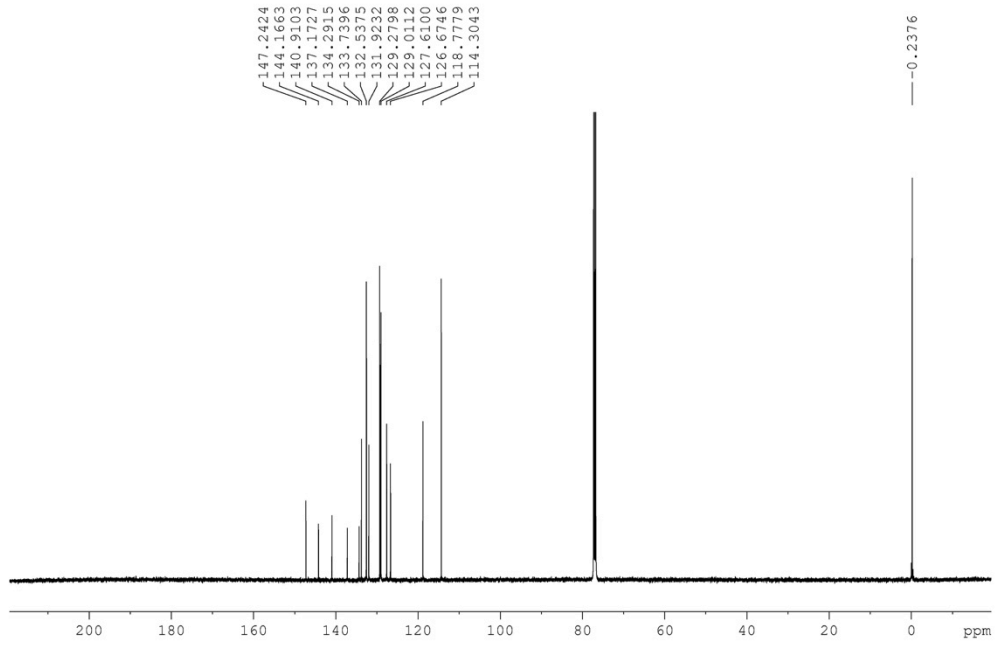




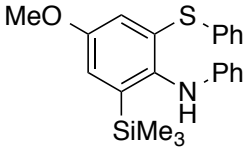
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4g** ($CDCl_3$)

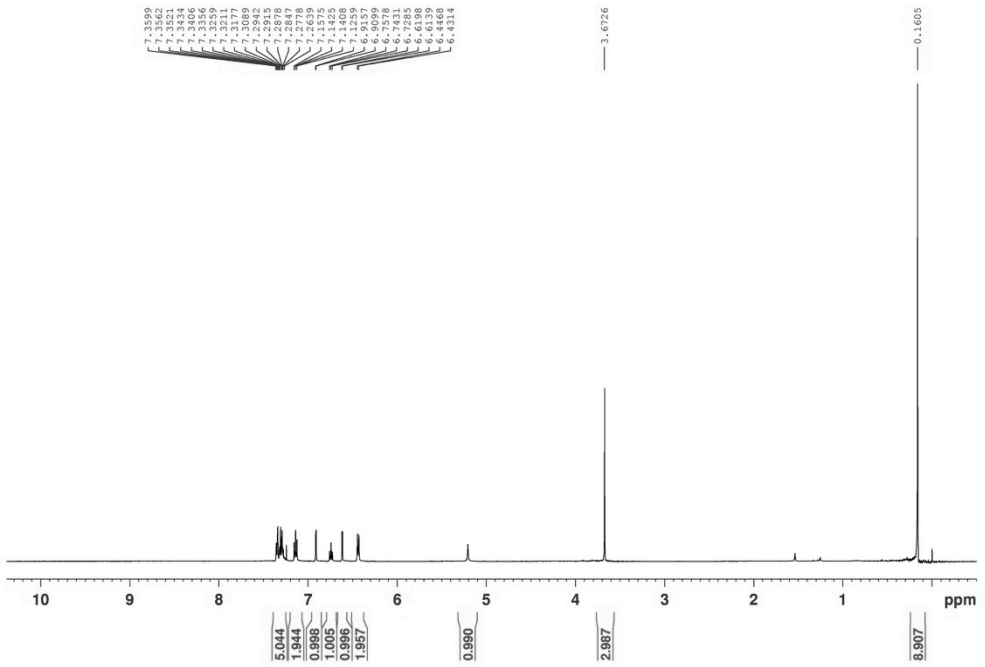


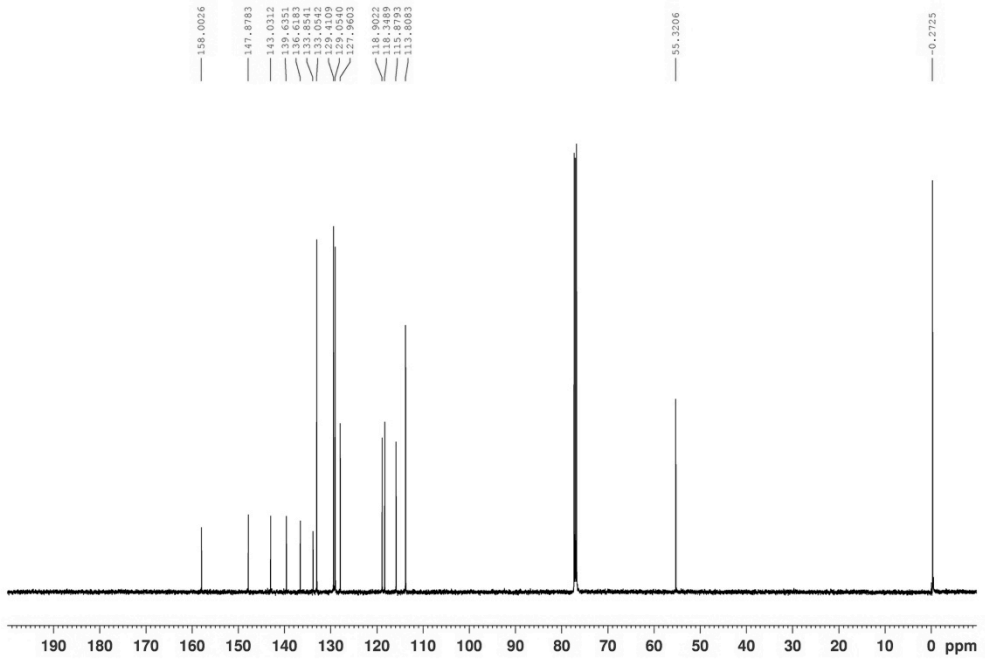




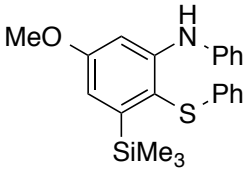
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4h** ($CDCl_3$)

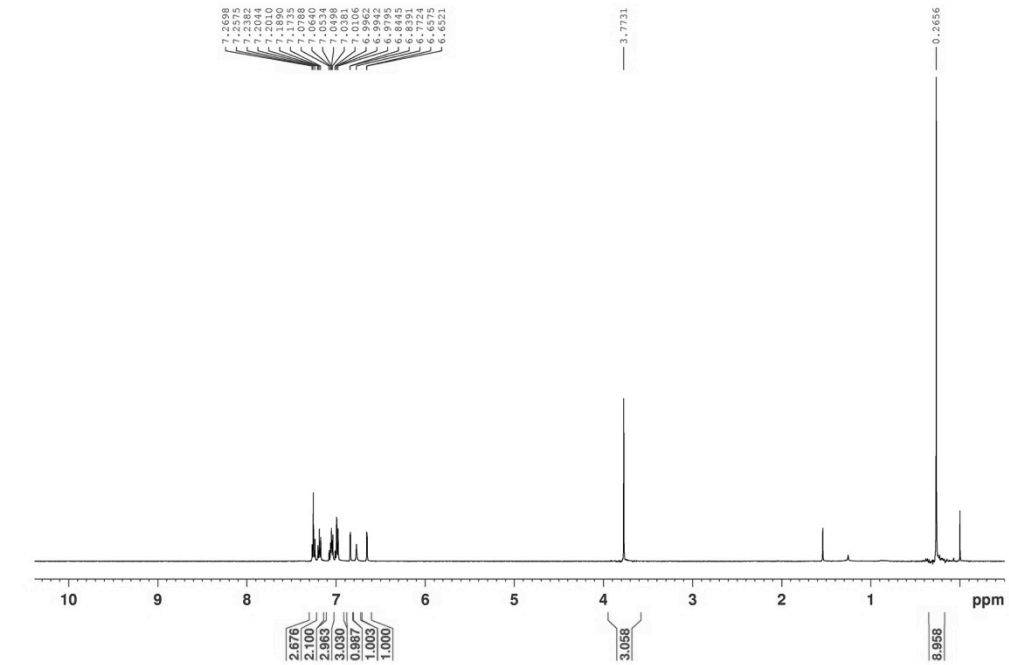


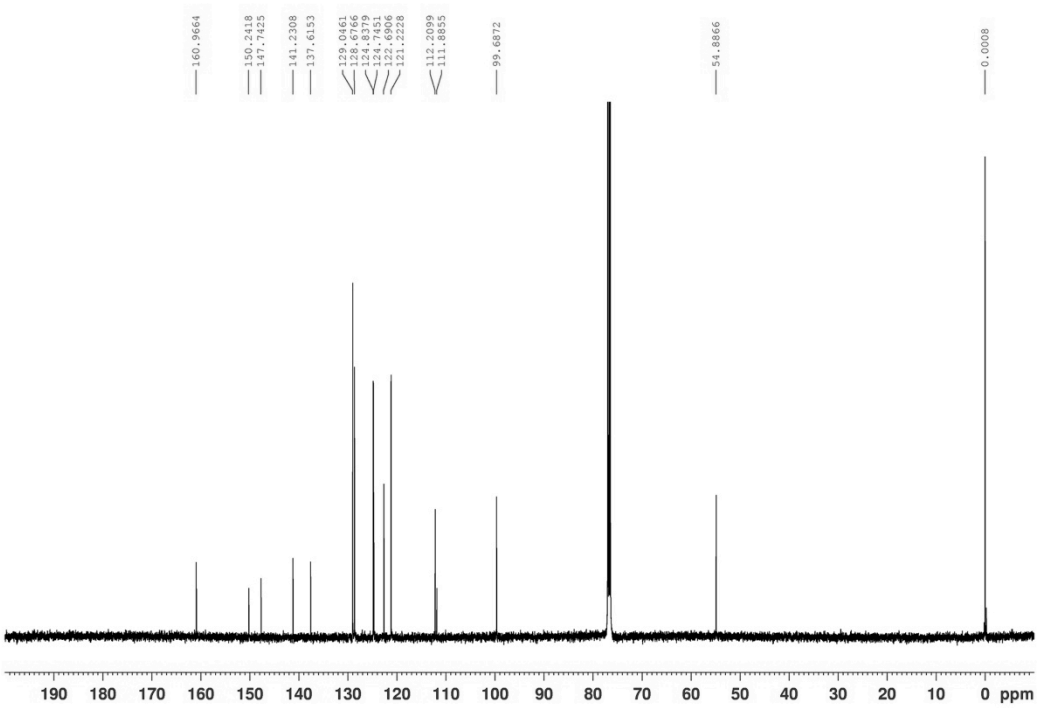




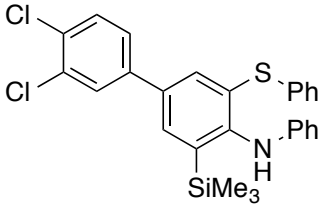
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4h′** ($CDCl_3$)

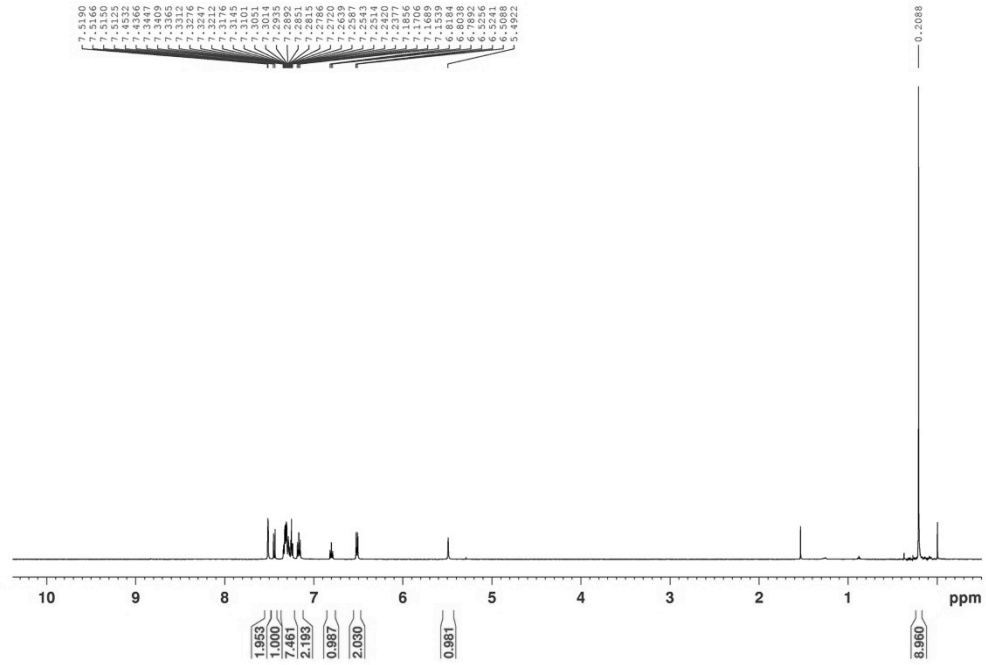


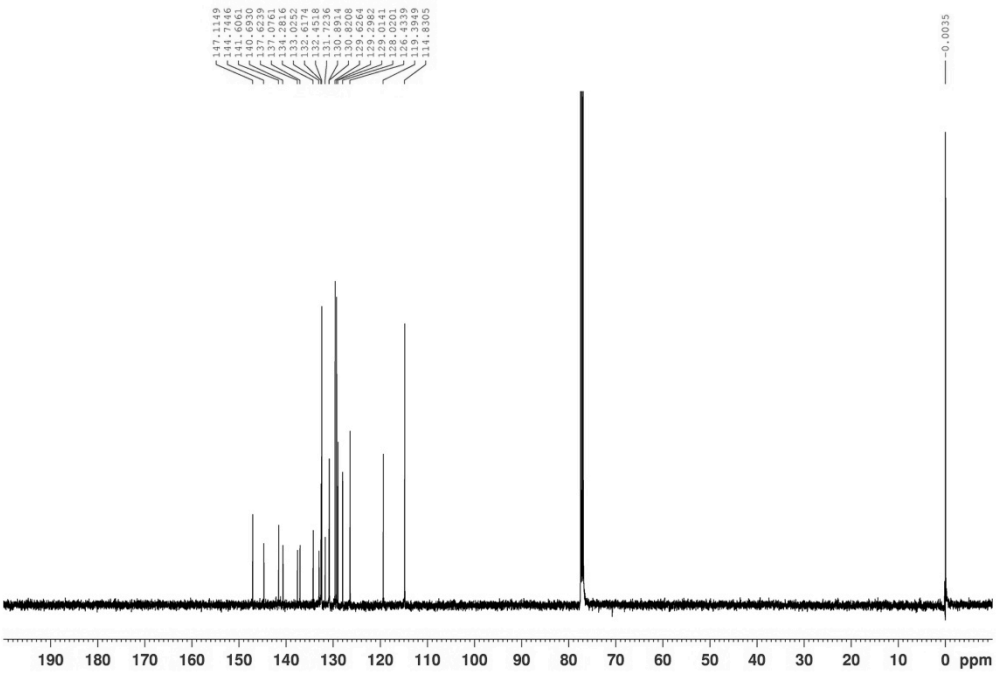




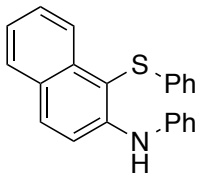
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4i** ($CDCl_3$)

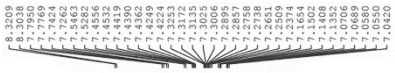


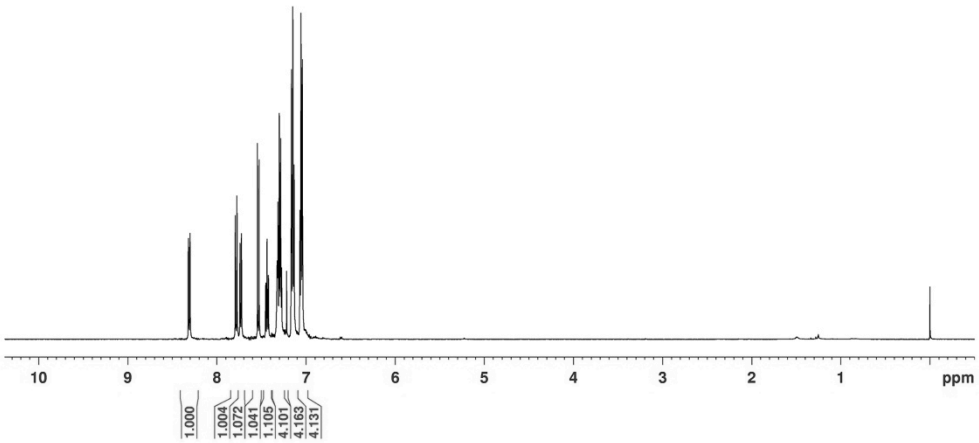


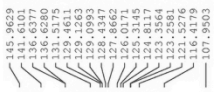


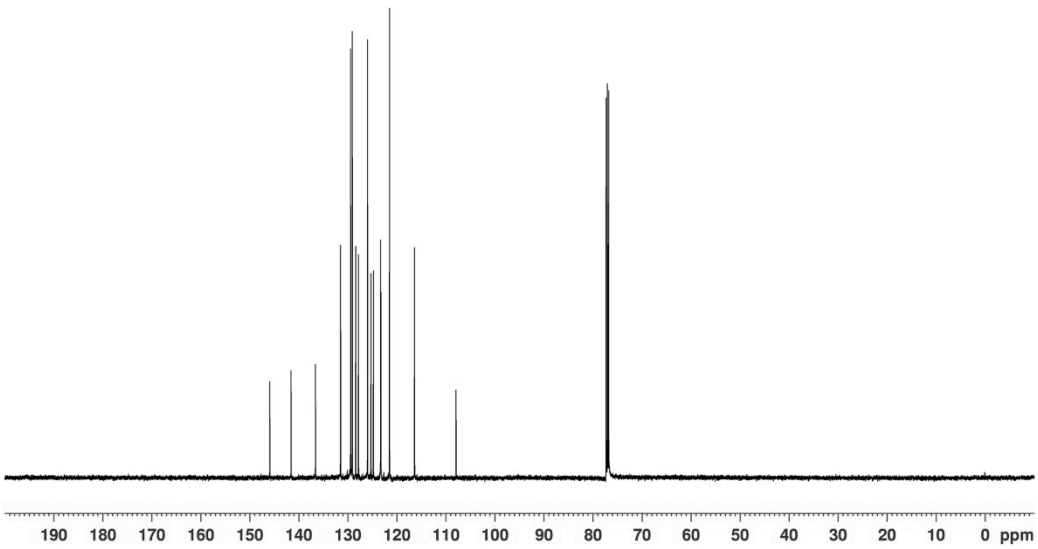
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4j** ($CDCl_3$)



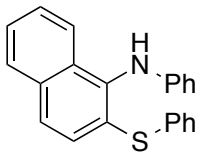


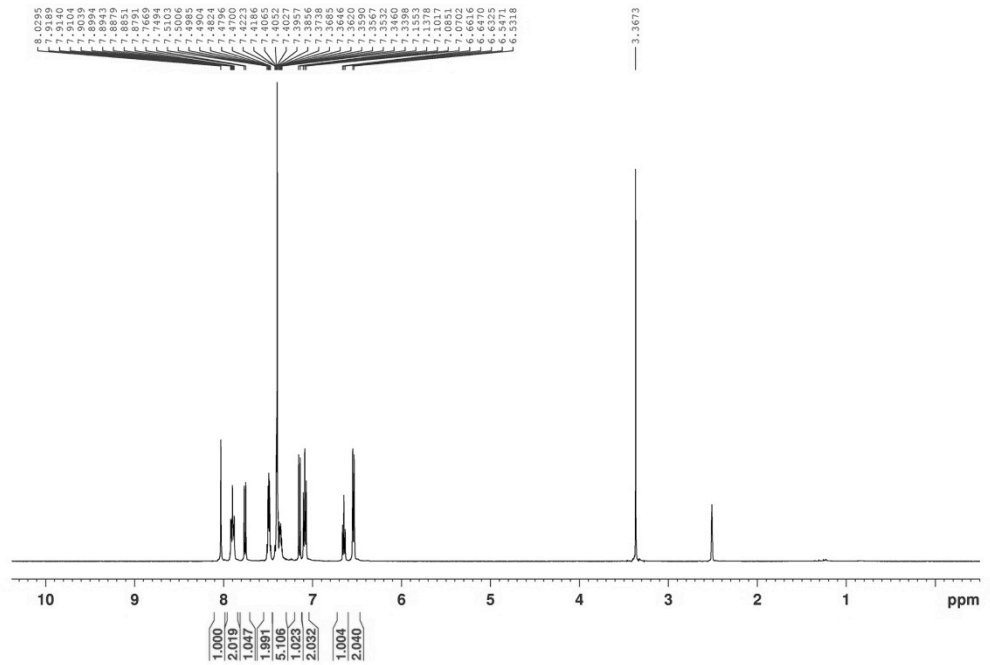


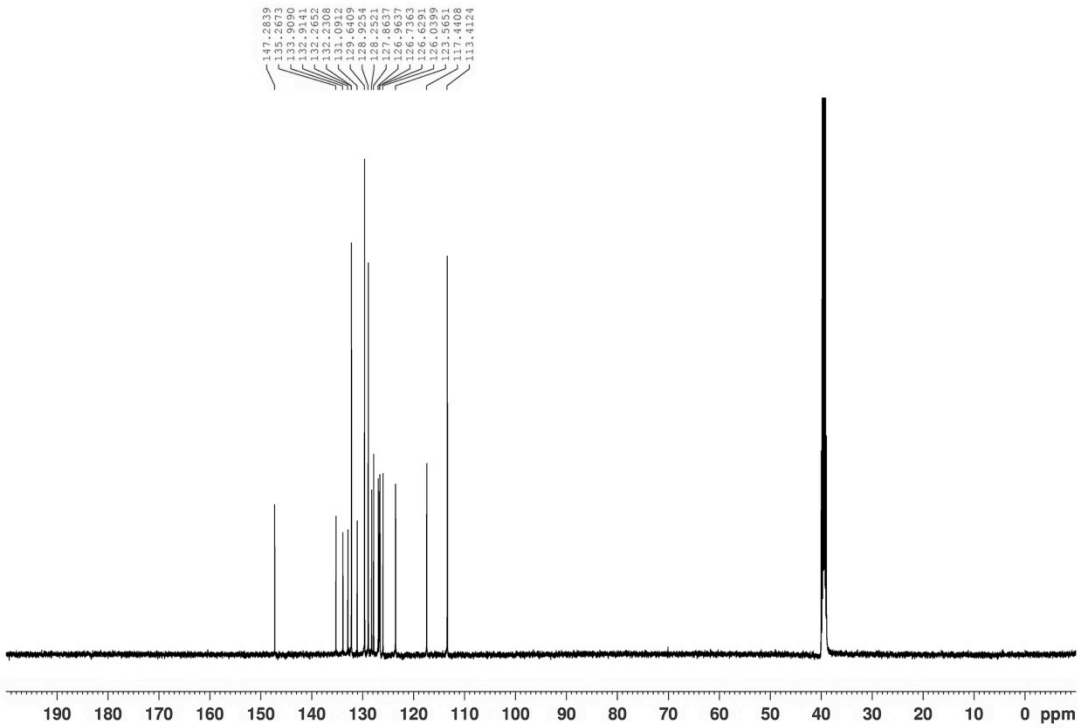




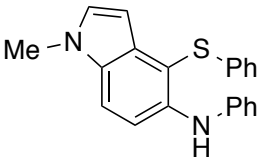
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4j′** (DMSO-d_6)

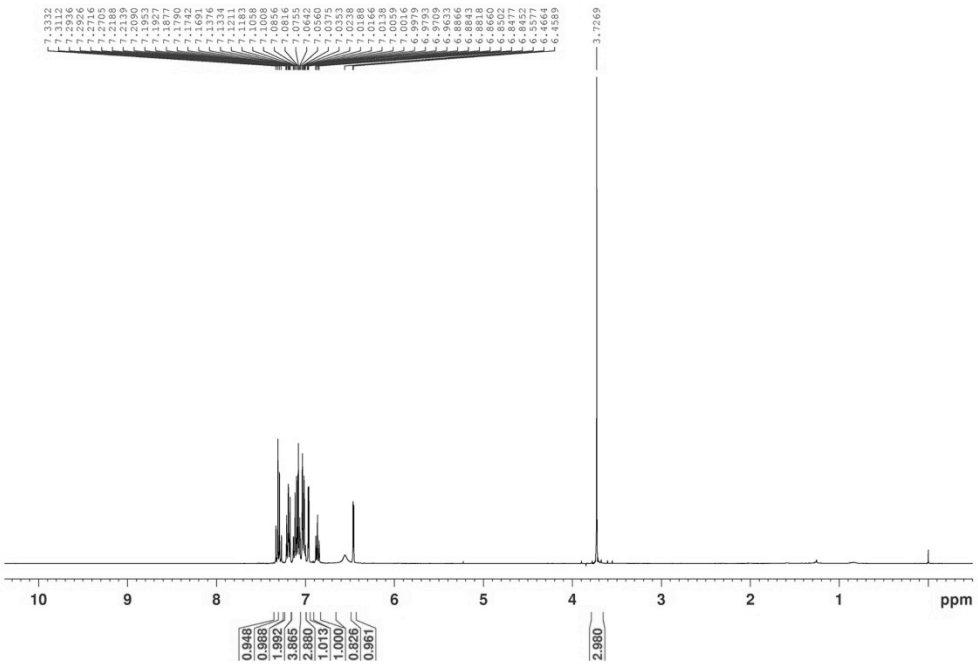


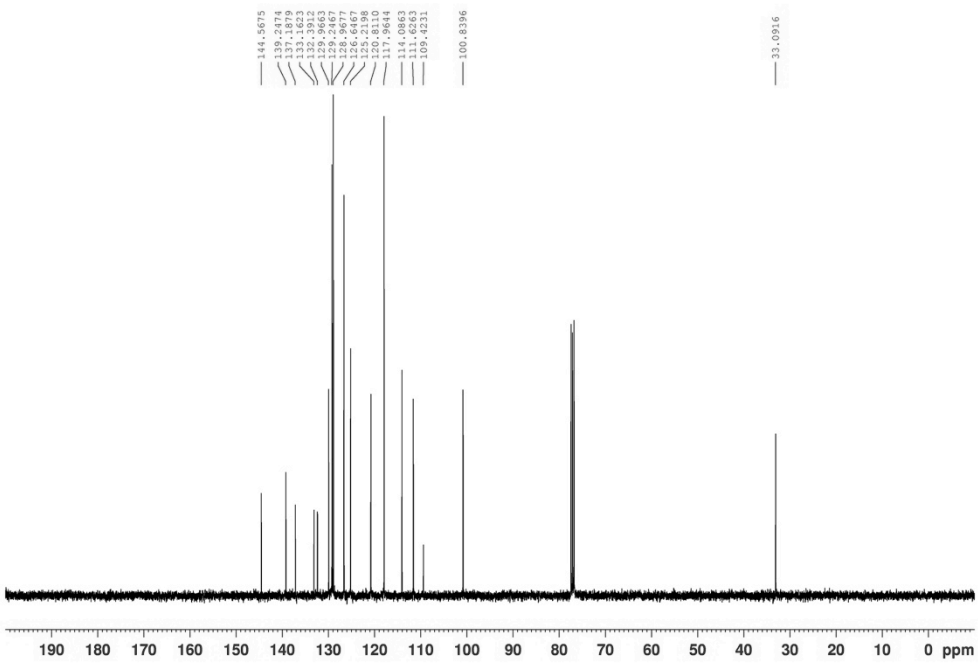




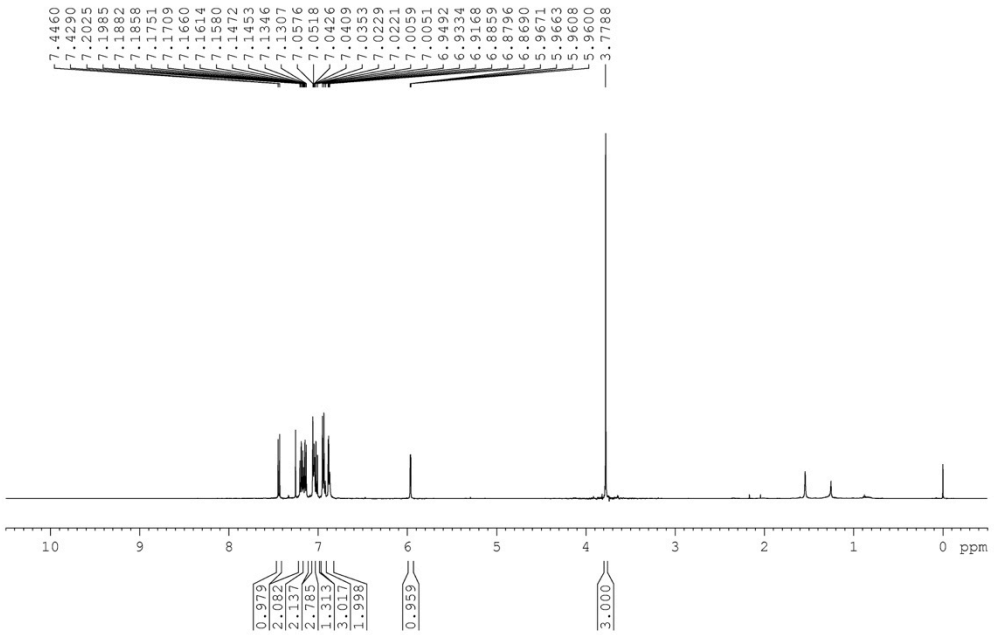
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **4k** ($CDCl_3$)

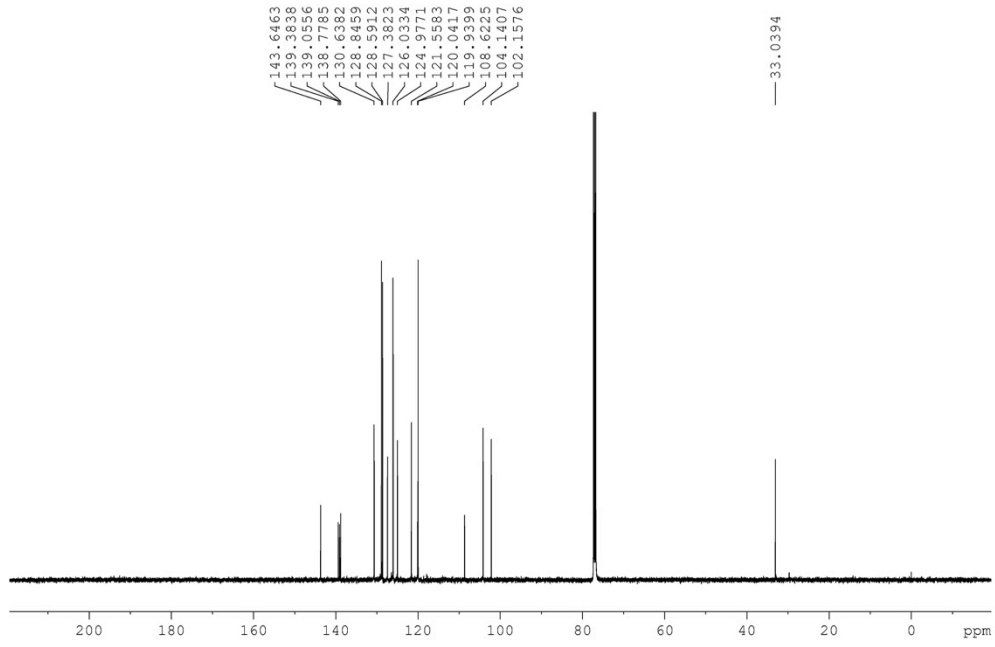




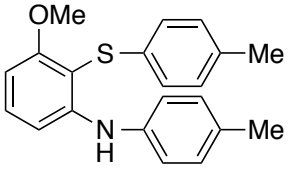


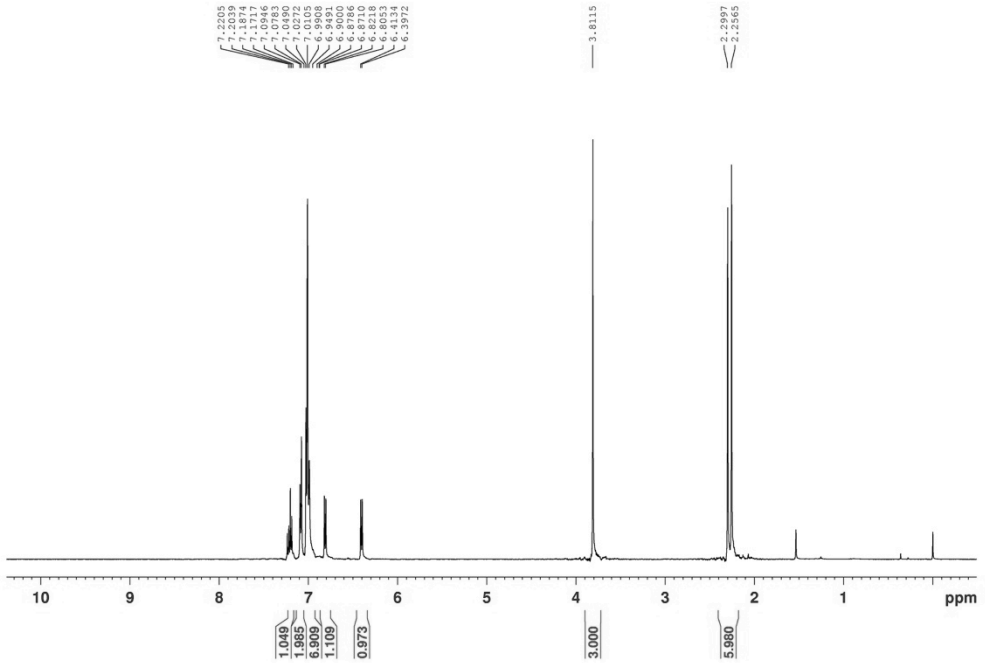
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4k′** ($CDCl_3$)

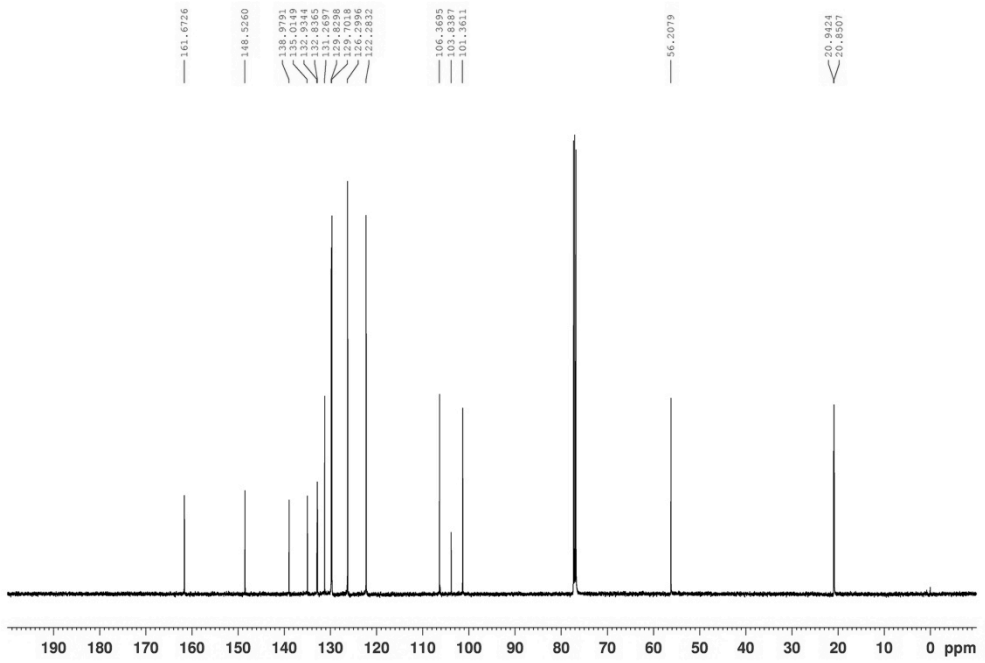




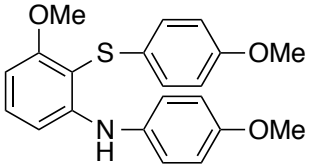
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4l** ($CDCl_3$)

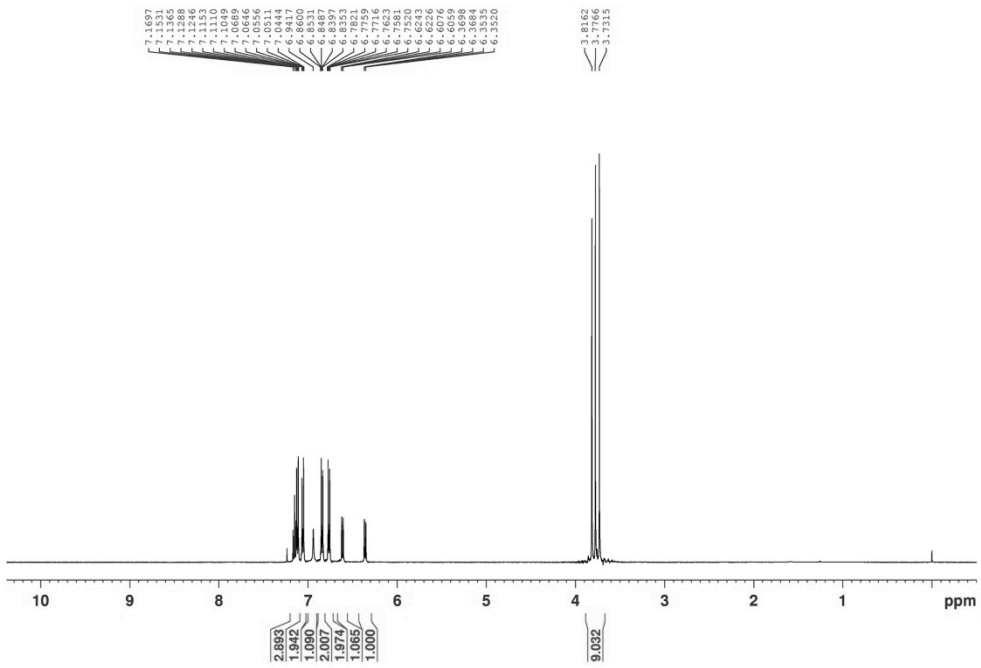


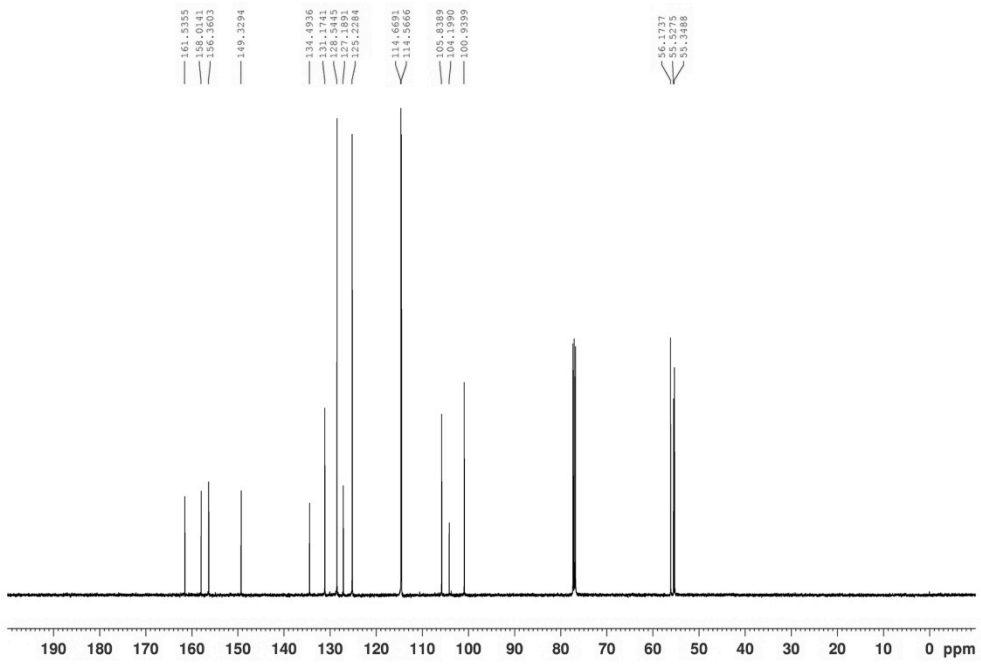




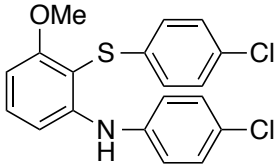
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4m** ($CDCl_3$)

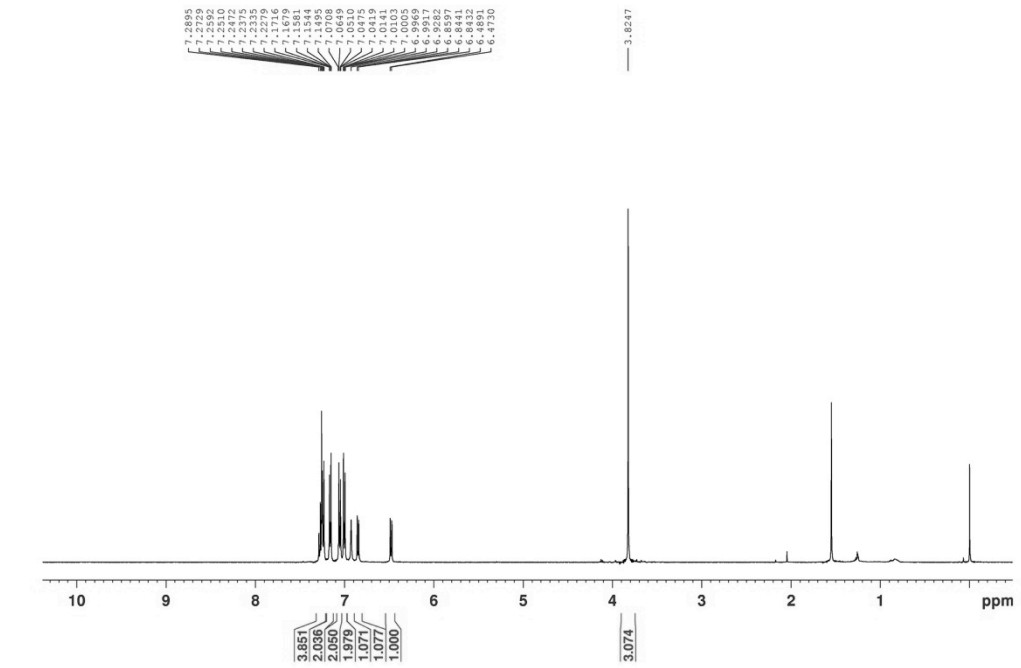


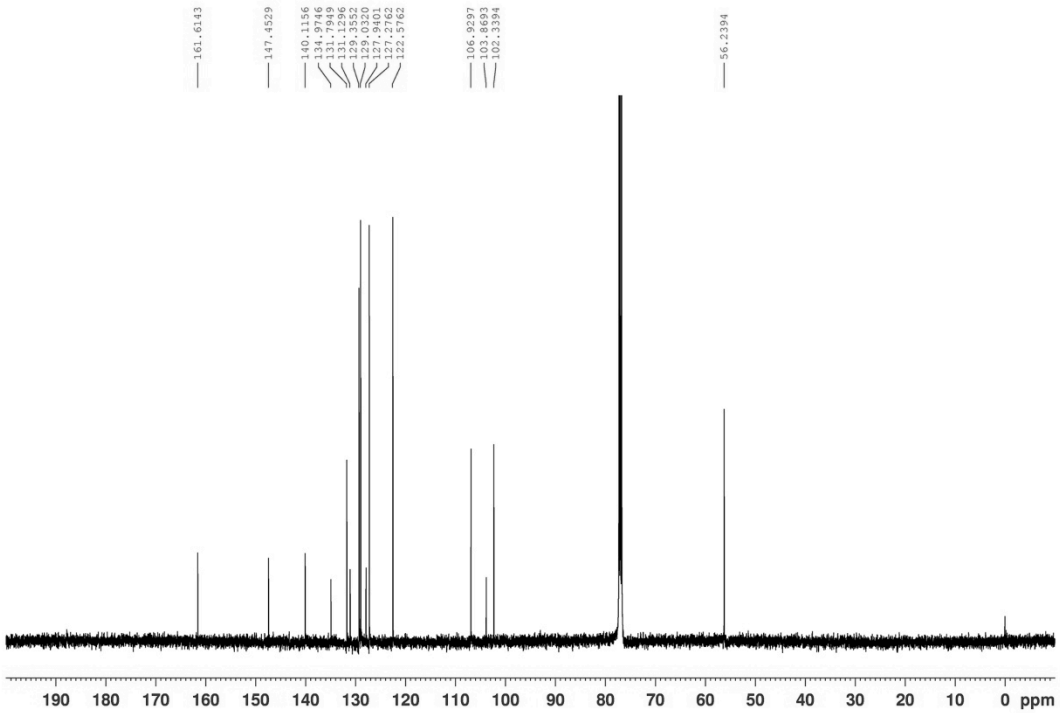




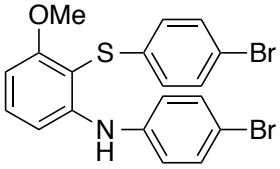
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4n** ($CDCl_3$)

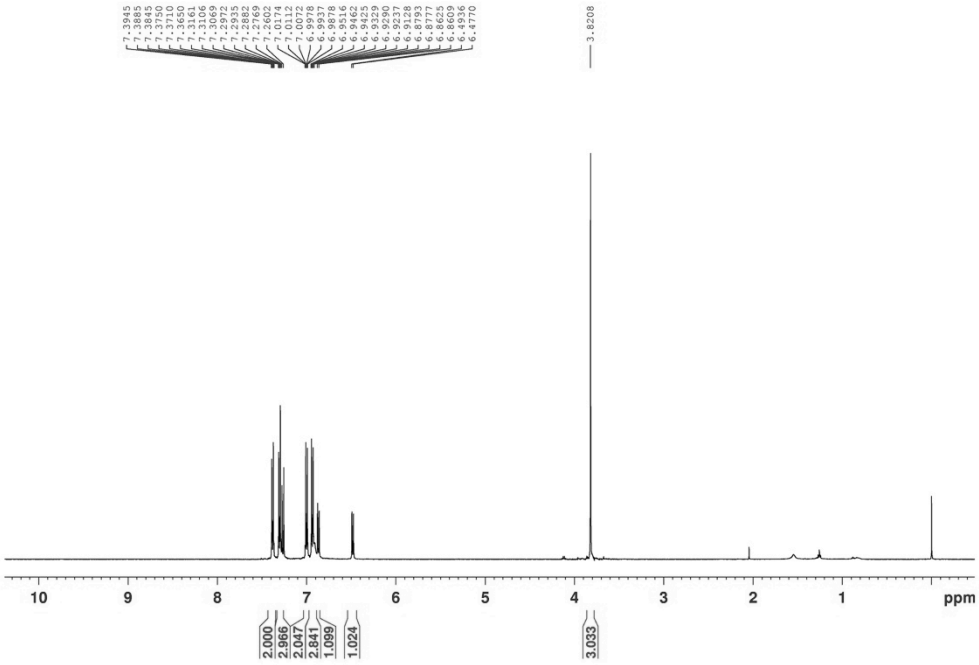


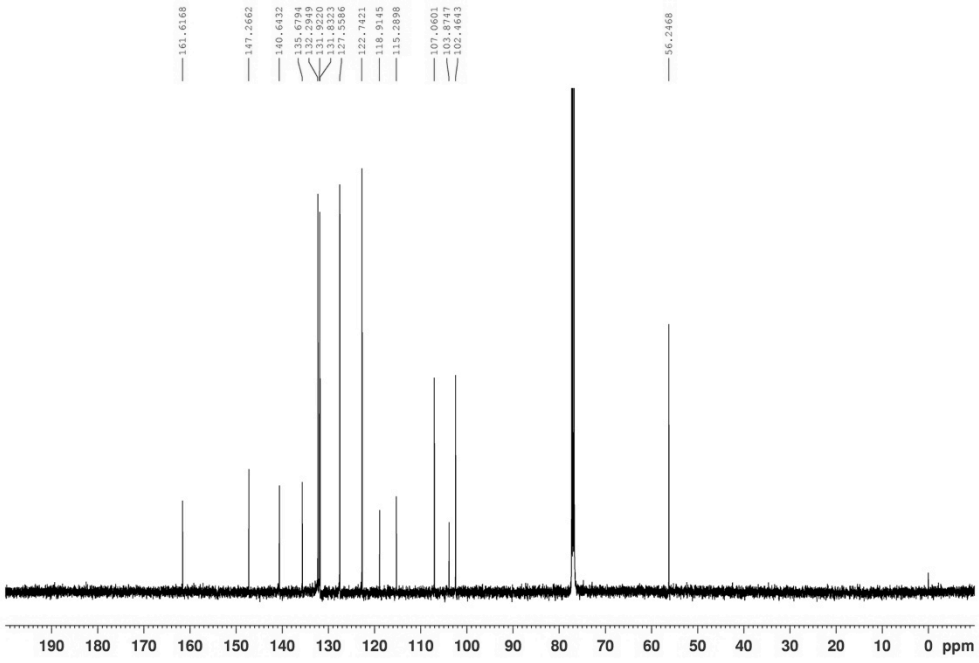




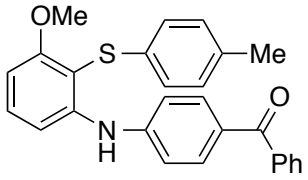
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4o** ($CDCl_3$)

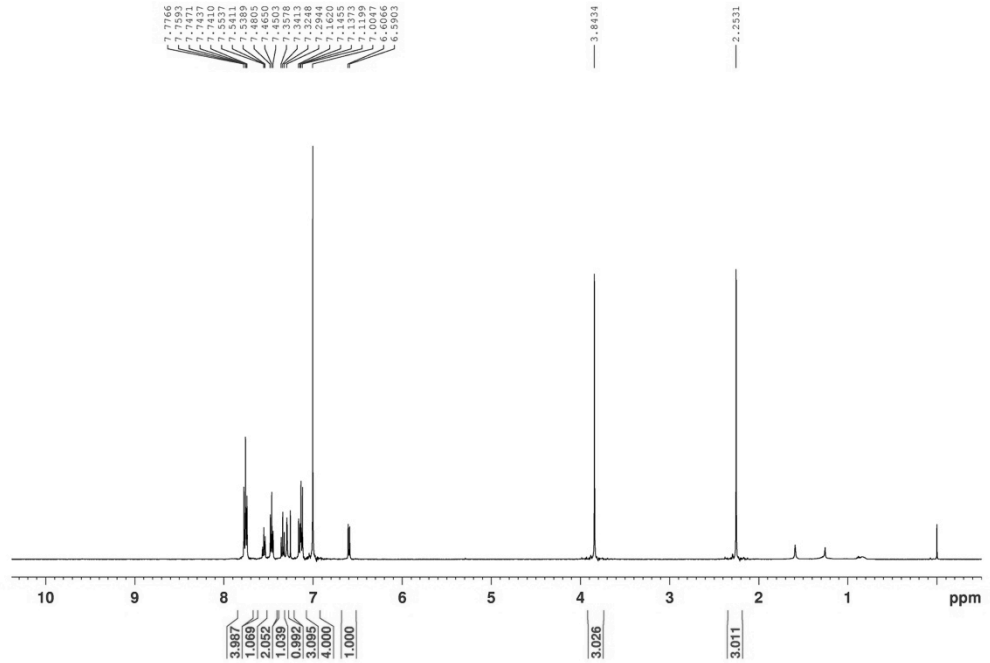


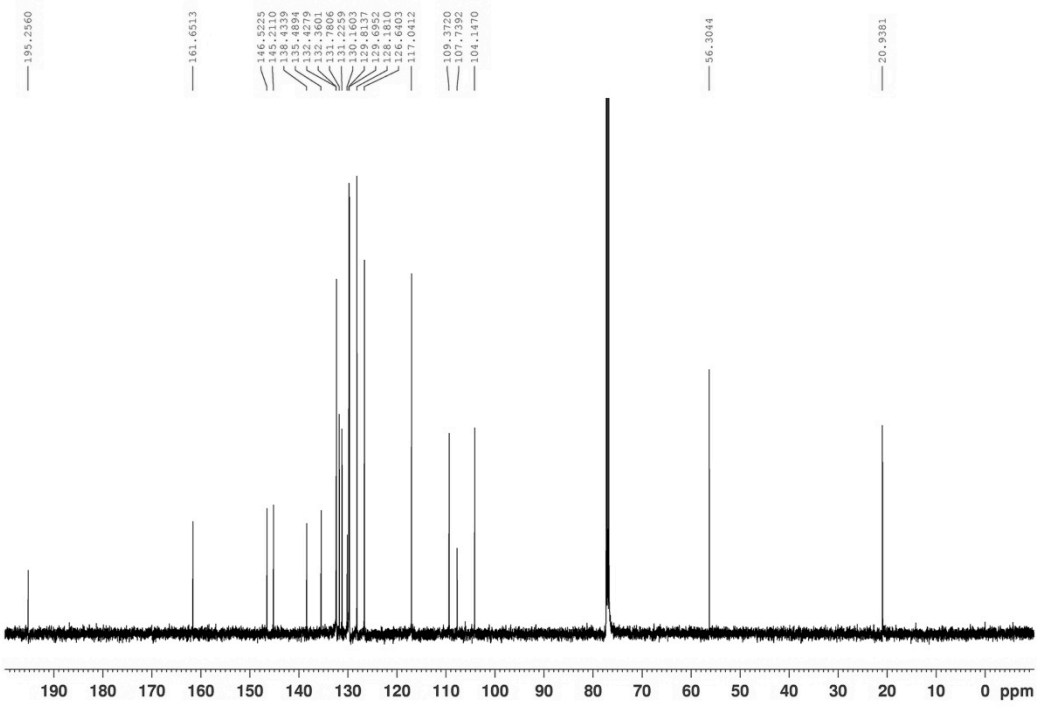




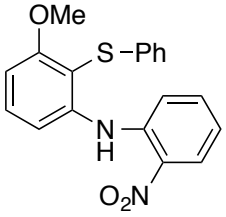
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4p** ($CDCl_3$)

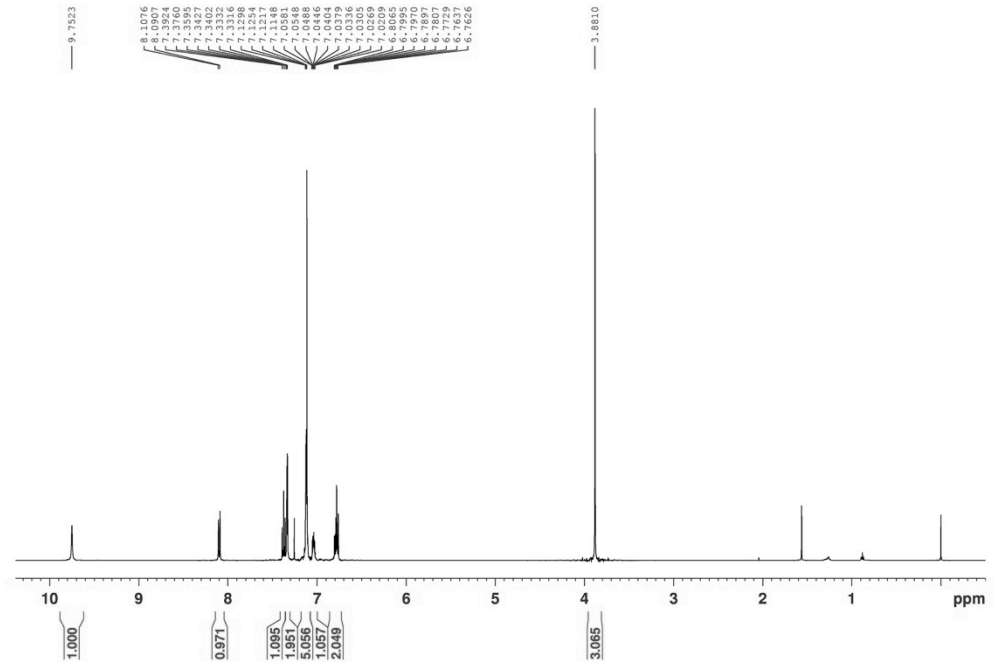


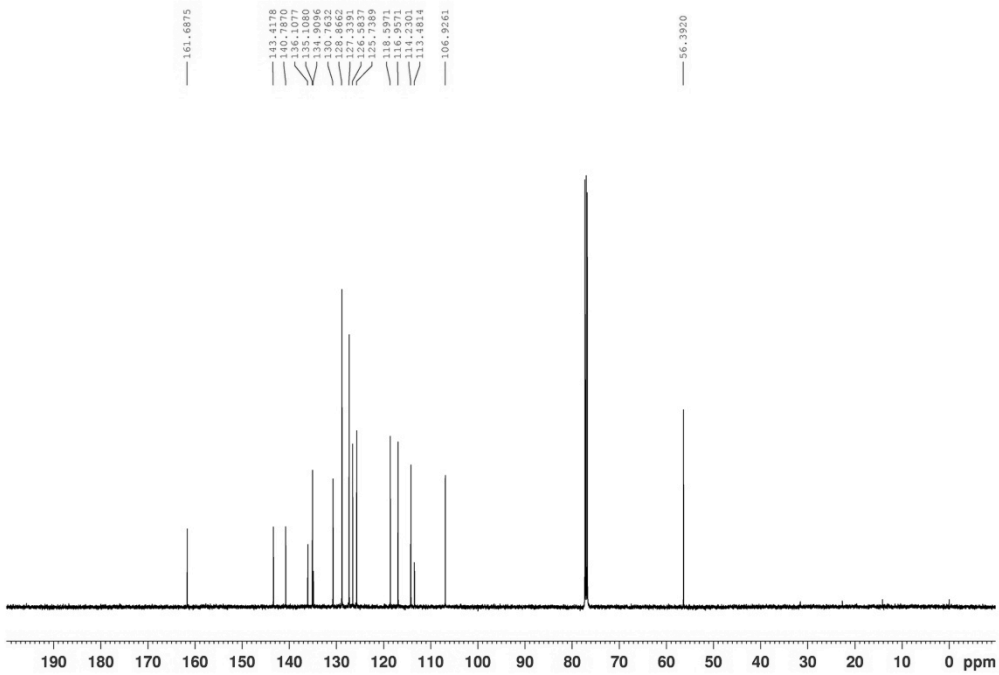




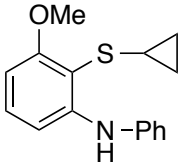
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4q** ($CDCl_3$)

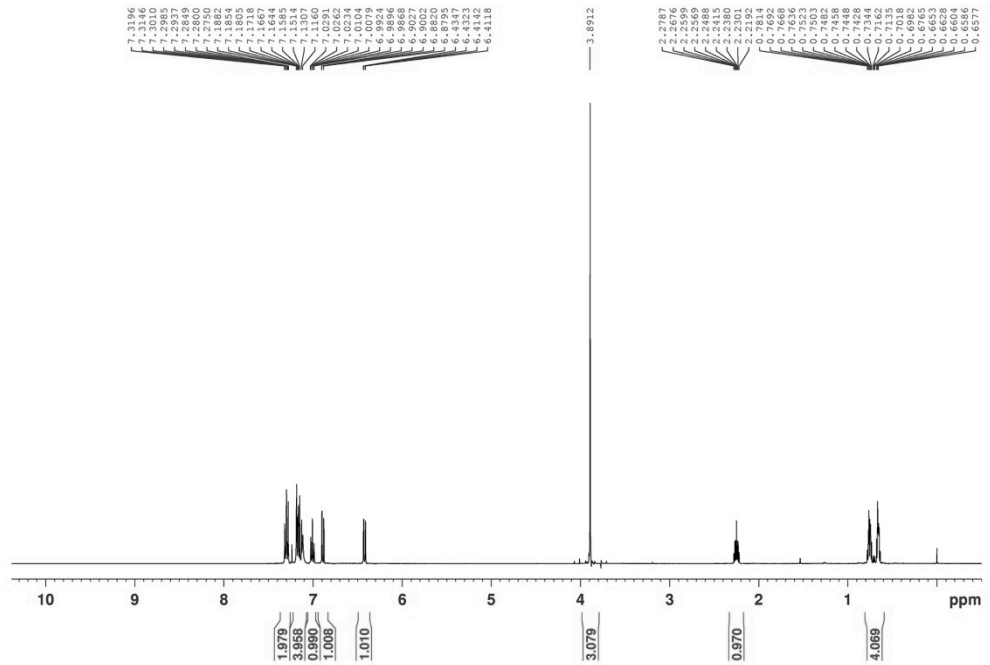


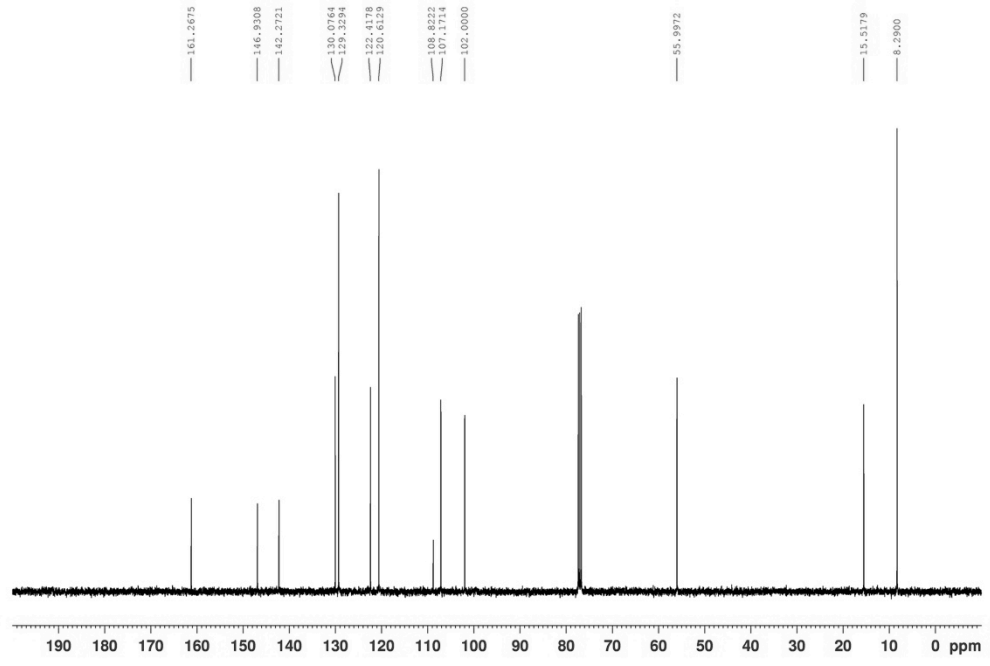




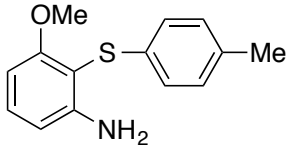
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **4r** ($CDCl_3$)

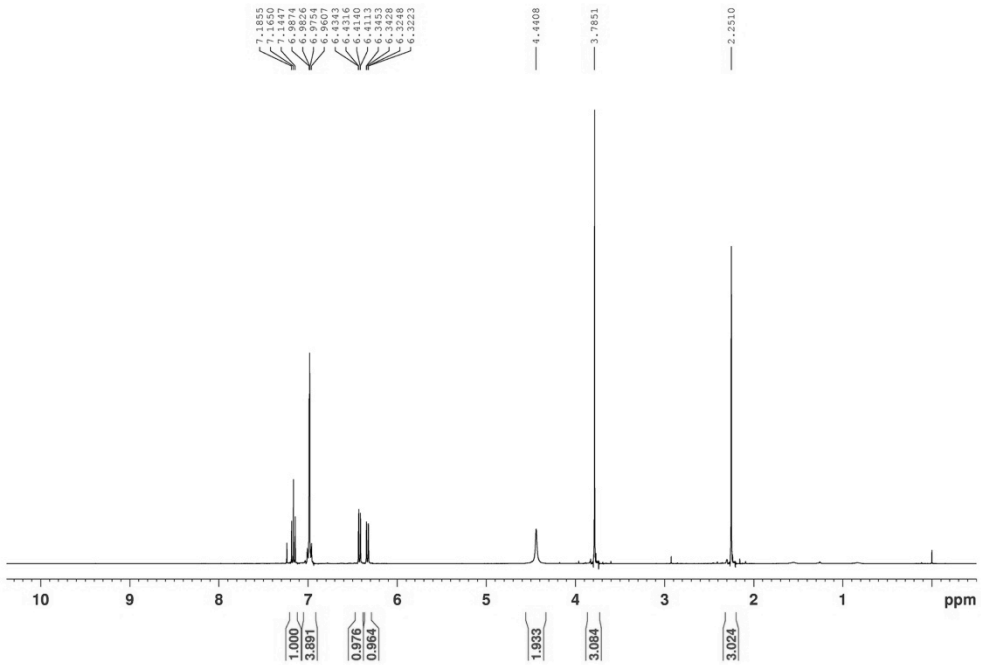


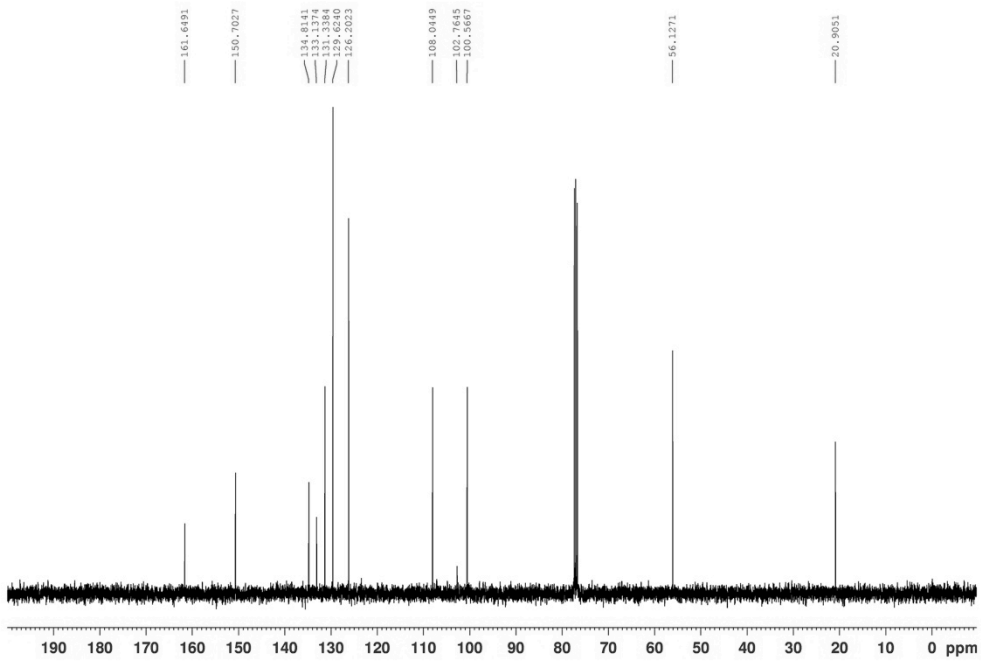




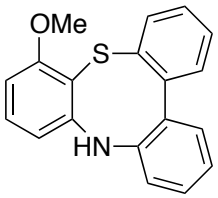
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **4s** ($CDCl_3$)

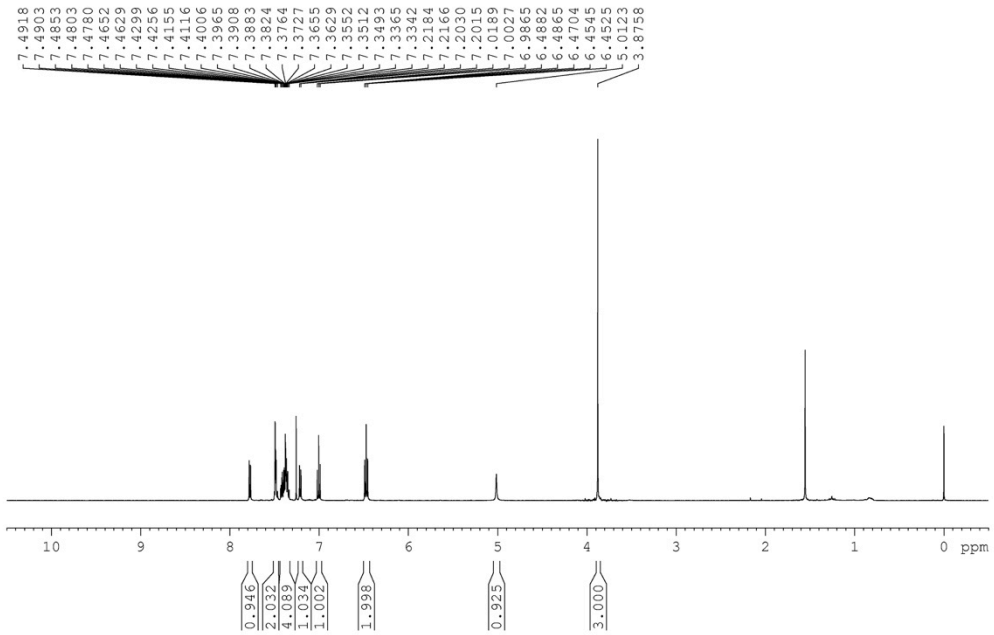


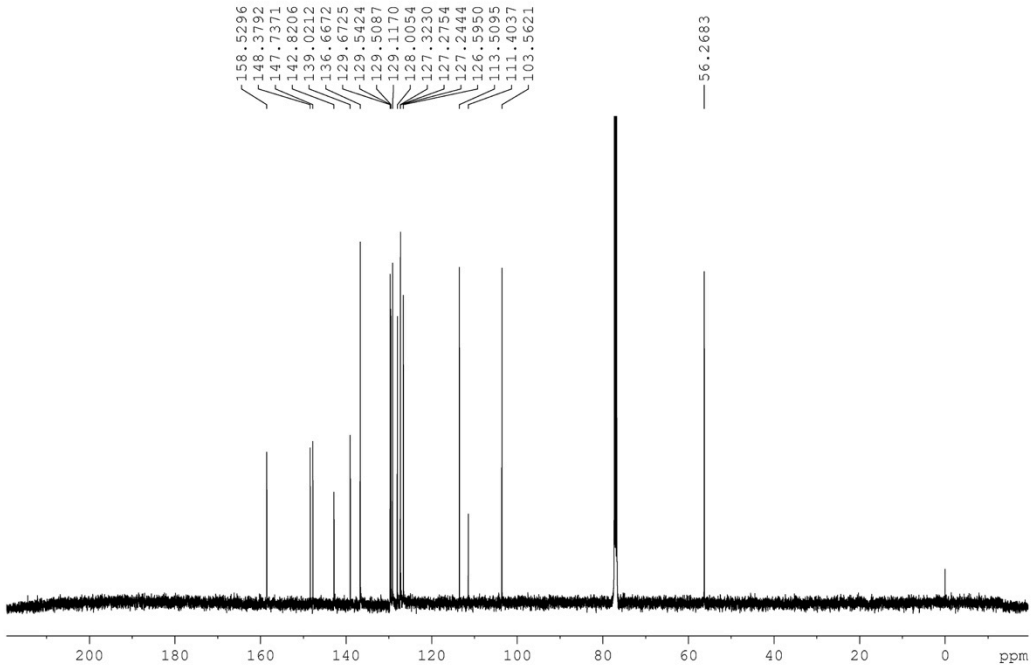




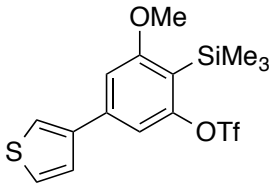
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4t** ($CDCl_3$)

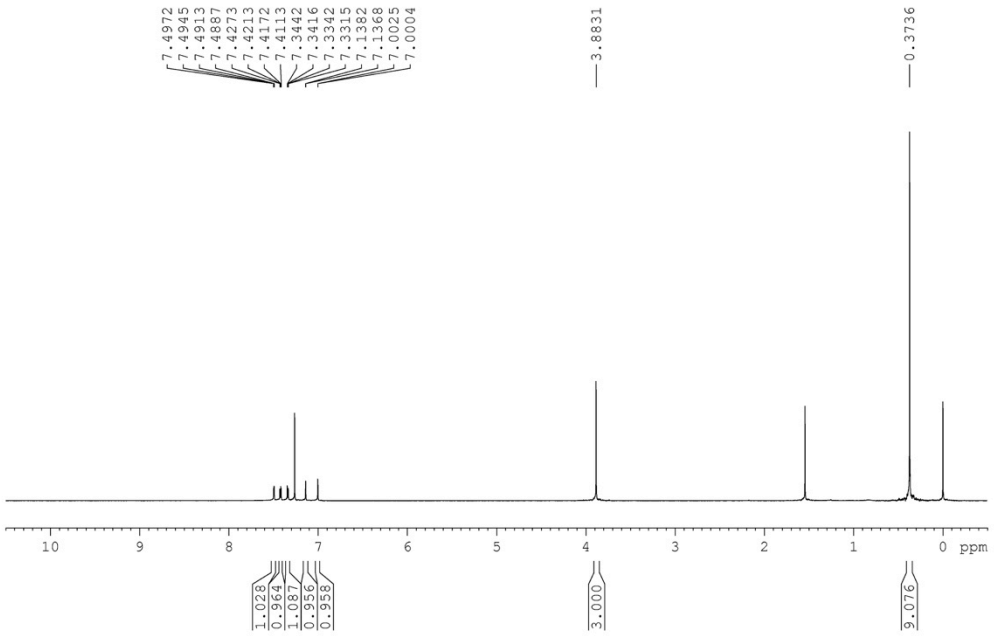


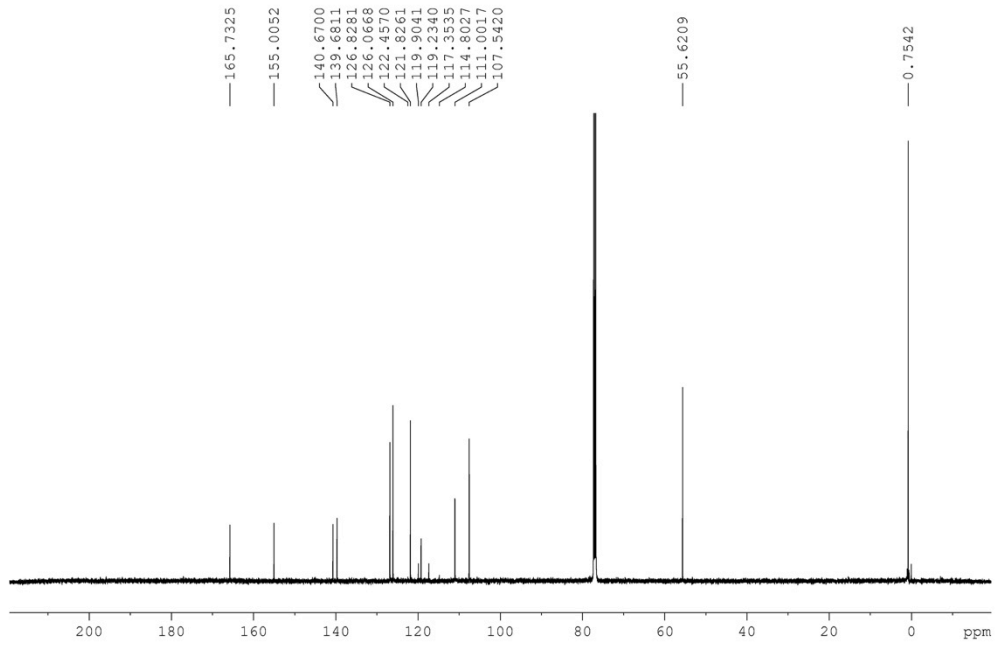




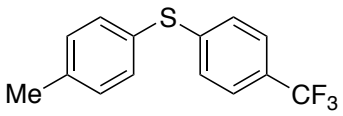
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**8**) ($CDCl_3$)

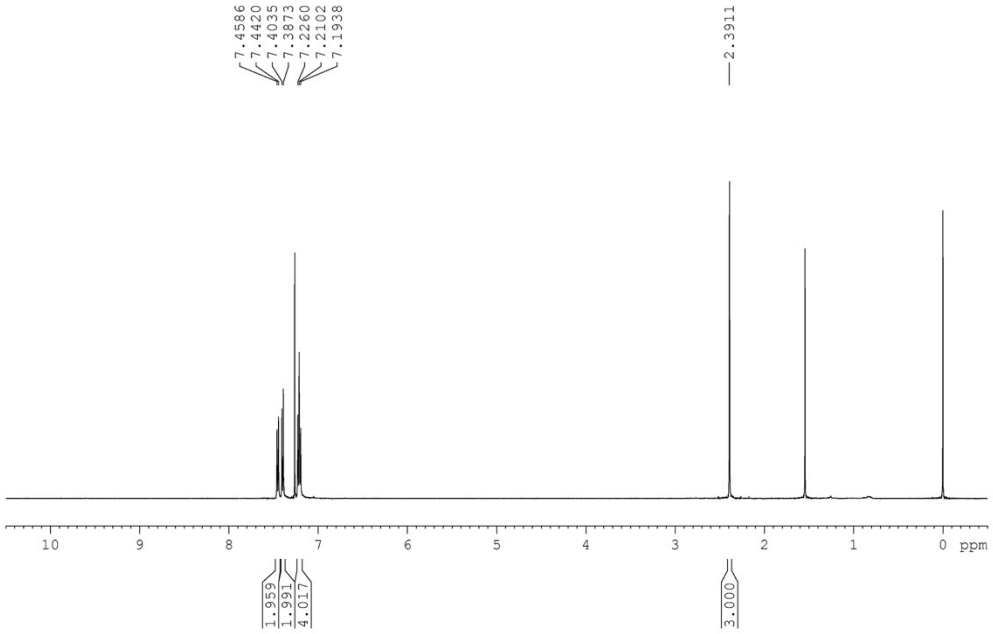


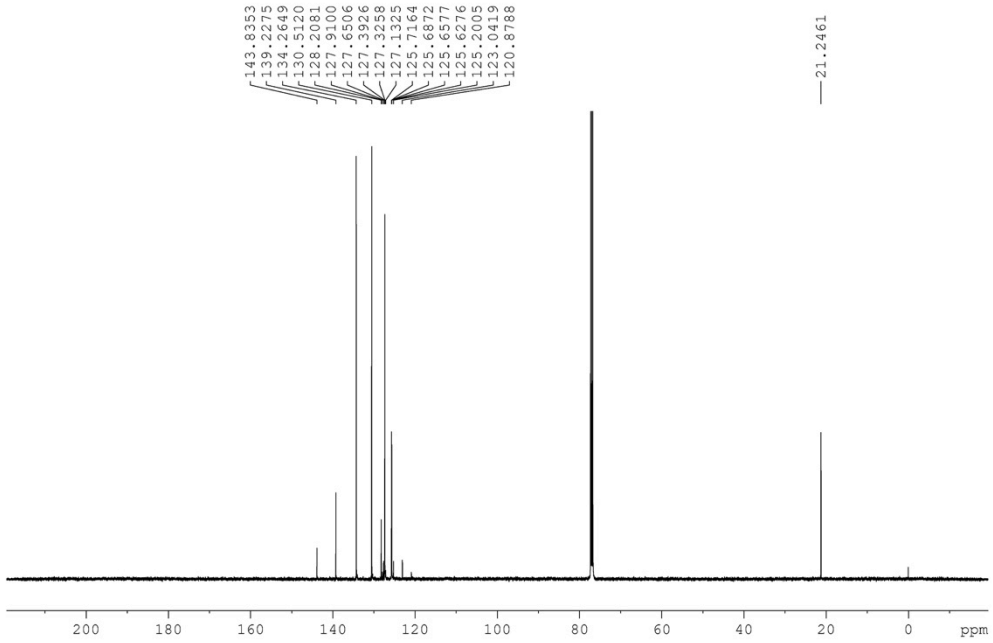




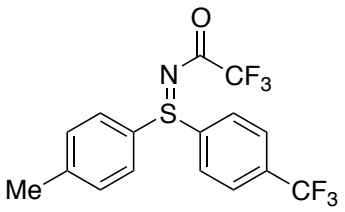
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-tolyl 4-(trifluoromethyl)phenyl sulfide ($CDCl_3$)

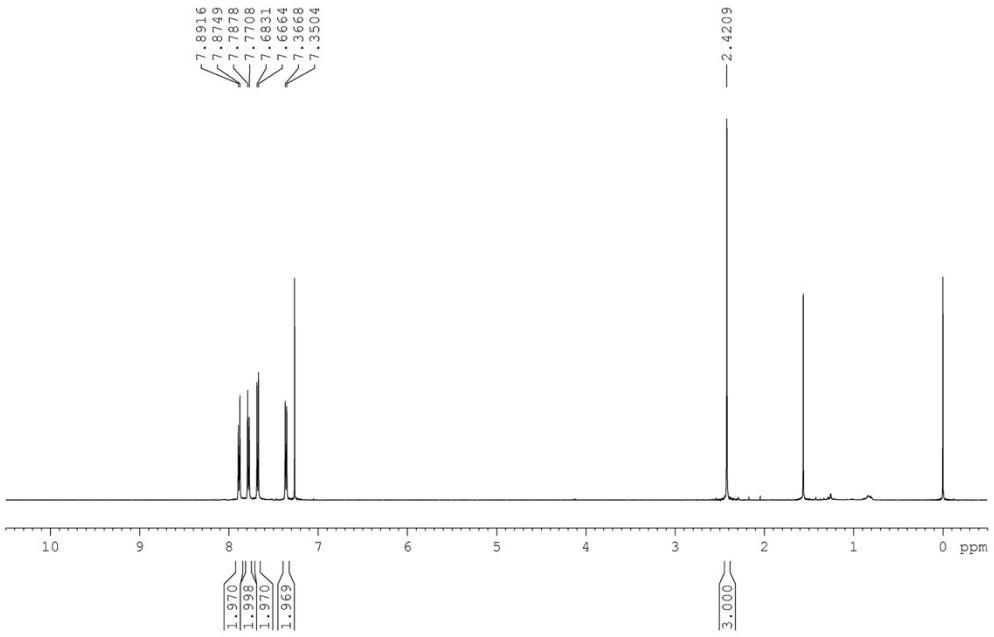


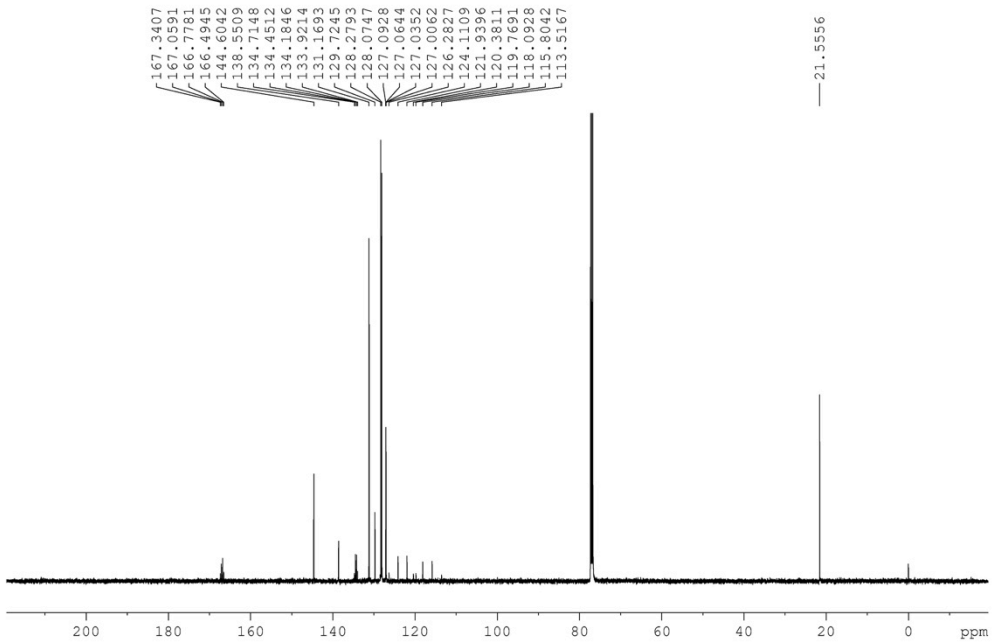




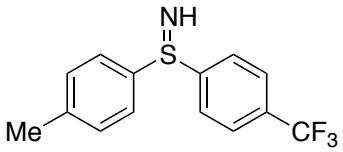
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *S*-(4-tolyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine ($CDCl_3$)

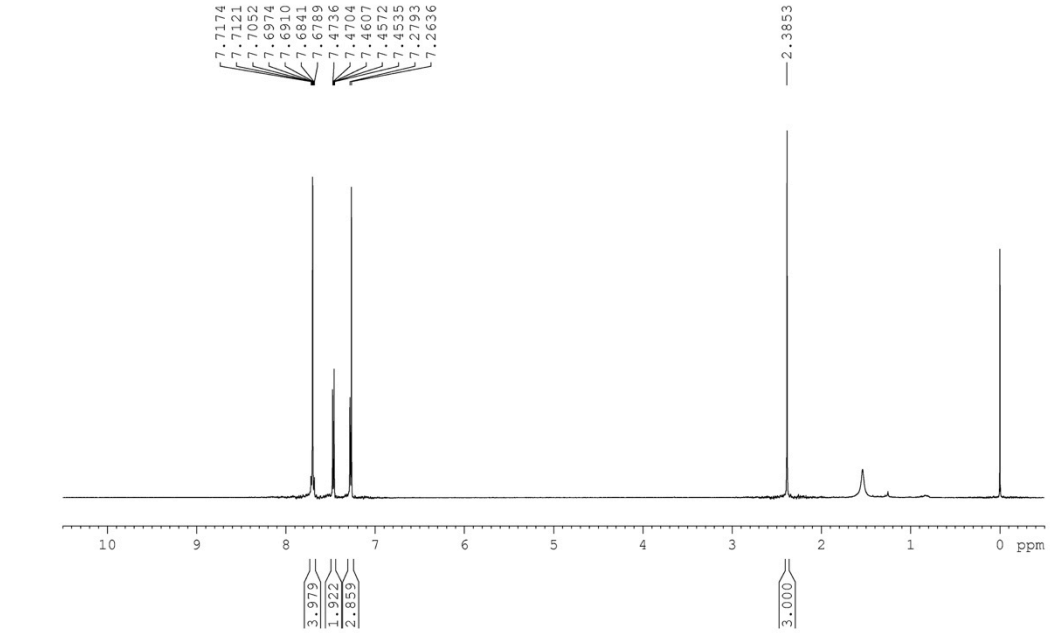


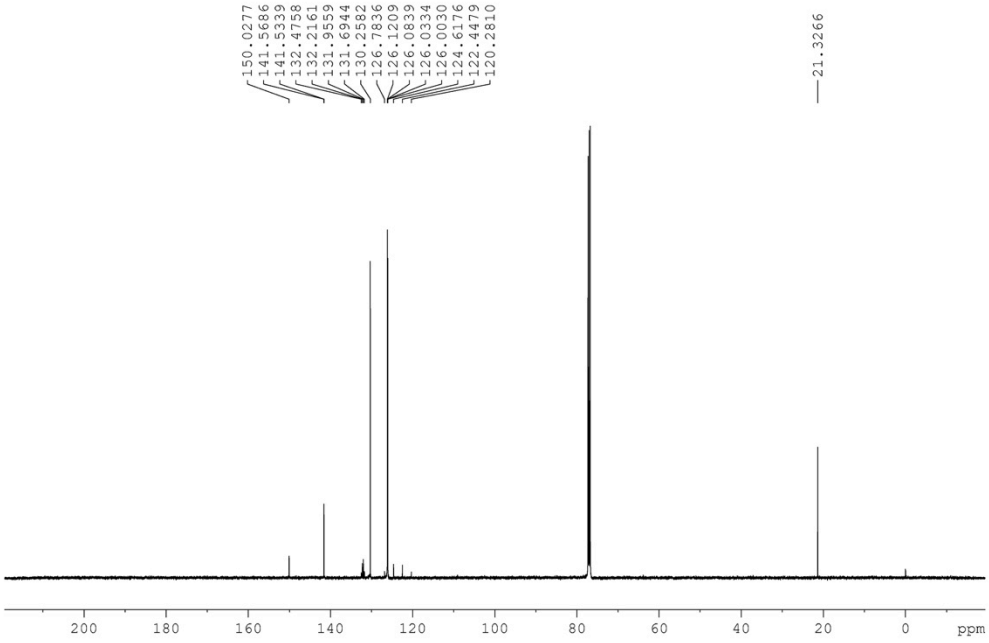




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *S*-(4-tolyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (**2k**) ($CDCl_3$)







^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4w** ($CDCl_3$)