Supporting Information

A mild and facile synthesis of aryl and alkenyl sulfides via copper-catalyzed deborylthiolation of organoborons with thiosulfonates

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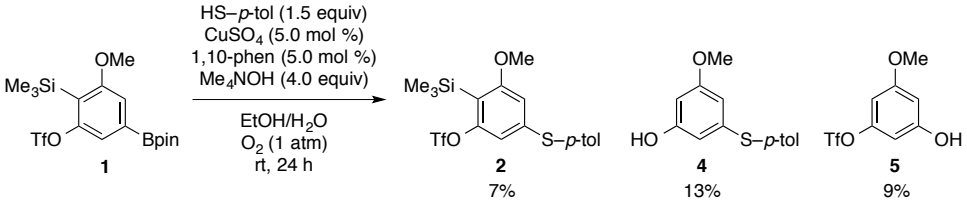
Contents

General Remarks

All reactions were performed in dry glasswares 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). Column chromatography was conducted using Biotage ZIP® sphere cartridge [silica] 5 g (Cat. No. 445-0500-DZ-20), 10 g (Cat. No. 445-1000-FZ-20), or 80 g (Cat. No. 445-8000-JZ-20) with medium pressure liquid chromatography (Yamazen, W-Prep 2XY A-type). Preparative thin-layer chromatography was performed on silica-gel (Wako Pure Chemical Industries, Ltd., Wakogel® B5-F, Cat. No. 230-00043). 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 500 spectrometer at 500 MHz. ^{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 23 ºC unless otherwise noted. $CDCl_3$ (Acros Organics, Cat. No. 368651000) 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 and ^{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, q, sept, m, and br signify singlet, doublet, triplet, quartet, septet, 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}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions or negative electrospray ionization (ESI^-). Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd.. All chemical reagents used were commercial grade and used as received unless otherwise noted.

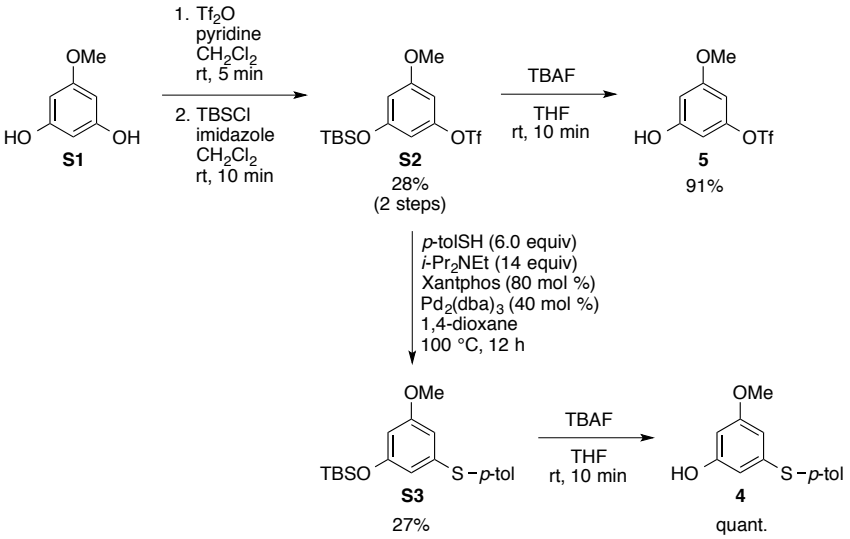
Experimental Procedures

*Chan–Lam–Evans-type thiolation of borylated aryne precursor **1** with 4-toluenethiol*



To a solution of copper(II) sulfate (1.62 mg, 10.2 μmol), 1,10-phenanthroline (1.84 mg, 10.2 μmol), 4-toluenethiol (35.4 mg, 0.285 mmol), and 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) (90.1 mg, 0.198 mmol) dissolved in ethanol (0.30 mL) was added aqueous tetramethylammonium hydroxide (25%, 0.30 mL, 0.82 mmol) at room temperature under oxygen atmosphere. After stirring for 24 h at the same temperature, to this was added an aqueous saturated solution of ammonium chloride (5 mL). The mixture was extracted with EtOAc, and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methoxy-5-(4-tolylthio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) (6.3 mg, 14 μmol, 7.1%) and a 1.4:1 mixture (8.3 mg) of 3-hydroxy-5-methoxyphenyl 4-tolyl sulfide (**4**) (13%) and 3-hydroxy-5-methoxyphenyl trifluoromethanesulfonate (**5**) (9.4%). The NMR spectra of two byproducts **4** and **5** were identical to those of authentic samples that were prepared as shown below.

*Preparation of **4** and **5** for characterization purpose*



To a solution of 5-methoxyresorcinol (**S1**) (140 mg, 0.999 mmol) dissolved in dichloromethane (2.0 mL) were added pyridine (40 μL, 0.50 mmol) and trifluoromethanesulfonic anhydride (50 μL, 0.30 mmol). After stirring for 5 min at room temperature, to this was added hydrochloric acid (1 M, 2 mL). The mixture was extracted with dichloromethane (1 mL × 2), and the combined organic extract was dried (Na_2SO_4), and after filtration, the

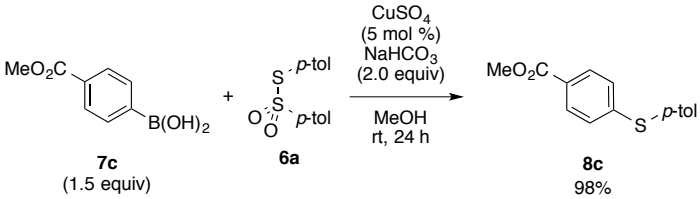
filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 7/3) to give a mixture containing 3-hydroxy-5-methoxyphenyl trifluoromethanesulfonate (**5**). To a solution of crude **5** dissolved in dichloromethane (0.30 mL) were added imidazole (50 mg, 0.73 mmol) and *tert*-butyldimethylchlorosilane (50 mg, 0.33 mmol) at room temperature. After stirring for 10 min at the same temperature, to this was added an aqueous saturated solution of ammonium chloride (1 mL). The mixture was extracted with dichloromethane (1 mL × 2), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/toluene = 9/1) to give 3-(*tert*-butyldimethylsilyloxy)-5-methoxyphenyl trifluoromethanesulfonate (**S2**) (32.6 mg, 84.4 μmol, 28.3% in 2 steps from **S1**) as a colorless oil.

To a solution of **S2** (5.8 mg, 15 μmol) dissolved in THF (0.50 mL) was added tetrabutylammonium fluoride (1.0 M, THF solution, 40 μL, 40 mmol) at room temperature. After stirring for 10 min at the same temperature, to this was added an aqueous saturated solution of sodium bicarbonate (1 mL). The mixture was extracted with diethyl ether (1 mL × 2), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 7/3) to give 3-hydroxy-5-methoxyphenyl trifluoromethanesulfonate (**5**) (3.7 mg, 9.6 μmol, 91%) as a colorless oil.

To a solution of **S2** (5.8 mg, 15 μmol) dissolved in 1,4-dioxane (0.60 mL) were added *N*,*N*-diisopropylethylamine (21 μL, 0.12 mmol), tris(dibenzylideneacetone)dipalladium(0) (5.5 mg, 6.0 μmol), Xantphos (7.0 mg, 12 μmol), and 4-toluenethiol (11 mg, 89 μmol) at room temperature.[S1] The mixture was heated at 100 °C for 12 h. After cooling to room temperature, to this was added an aqueous saturated solution of sodium bicarbonate (2 mL). The mixture was extracted with EtOAc (1 mL × 2), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/toluene = 4/1) to give 3-(*tert*-butyldimethylsilyloxy)-5-methoxyphenyl 4-tolyl sulfide (**S3**) (5.9 mg, 16 μmol, 27%) as a colorless oil.

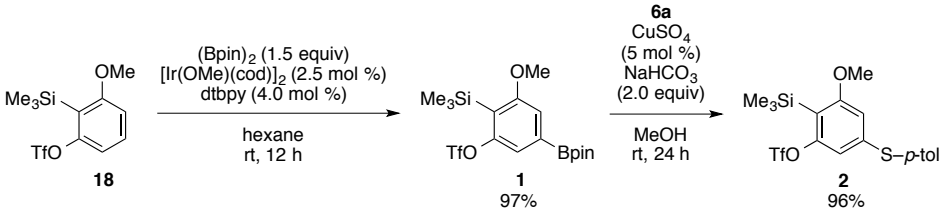
To a solution of **S3** (5.1 mg, 14 μmol) dissolved in THF (0.50 mL) was added tetrabutylammonium fluoride (1.0 M, THF solution, 40 μL) at room temperature. After stirring for 10 min at the same temperature, to this was added an aqueous saturated solution of sodium bicarbonate (1 mL). The mixture was extracted with diethyl ether (1 mL × 2), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 7/3) to give 3-hydroxy-5-methoxyphenyl 4-tolyl sulfide (**4**) (3.8 mg, 15 μmol, quant.) as a colorless oil.

A typical procedure for copper-catalyzed thiolation of boronic acids and thiosulfonates



To a mixture of copper(II) sulfate (1.63 mg, 10.2 μmol) and sodium bicarbonate (34.5 mg, 0.411 mmol) was added a solution of *S*-(4-tolyl) 4-toluenethiosulfonate (**6a**) (54.7 mg, 0.196 mmol) and 4-methoxycarbonylphenylboronic acid (**7c**) (53.7 mg, 0.298 mmol) dissolved in methanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, the mixture was passed through a short pad of silica gel with EtOAc and then concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 95/5) to give 4-methoxycarbonylphenyl 4-tolyl sulfide (**8c**) (49.8 mg, 0.193 mmol, 98.1%) as a white solid.

*Formal C–H thiolation of aryne precursor **18***

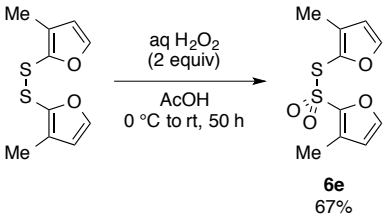


3-Methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) was prepared from 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**18**) according to our previously reported method.[S2]

3-Methoxy-5-(4-tolylthio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) was prepared from 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)-phenyl trifluoromethanesulfonate (**1**) according to the typical procedure for copper-catalyzed thiolation of boronic acids and thiosulfonates.

A typical procedure for the synthesis of thiosulfonates via oxidation of disulfides[S3]

S-(3-Methylfuran-2-yl) 2-(3-methylfuran)thiosulfonate (**6e**)

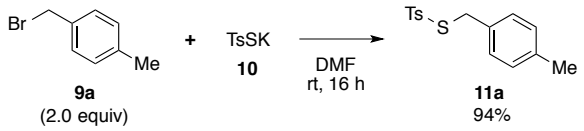


To a solution of bis(3-methylfuran-2-yl) disulfide (1.15 g, 5.08 mmol) dissolved in acetic acid (4.0 mL) was added dropwise aqueous hydrogen peroxide (30%, 1.1 mL, 10 mmol) at 0 °C. After gradually warming to room temperature, the mixture was stirred for 50 h, and to this was added water (4 mL). The mixture was extracted with dichloromethane (10 mL × 3), and the combined organic extract was washed with an aqueous saturated solution of sodium bicarbonate (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-

hexane/EtOAc = 90/10) to give *S*-(3-methylfuran-2-yl) 2-(3-methylfuran)thiosulfonate (**6e**) (885 mg, 3.43 mmol, 67.4%) as a pale yellow oil.

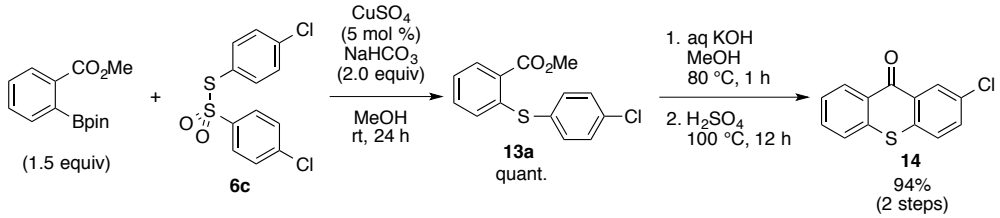
According to the procedure for preparing **6e**, *S*-(4-tolyl) 4-toluenethiosulfonate (**6a**), *S*-(4-methoxyphenyl) 4-methoxybenzenethiosulfonate (**6b**), *S*-(4-chlorophenyl) 4-chlorobenzenethiosulfonate (**6c**), *S*-(2-benzamidophenyl) 2-benzamidobenzenethiosulfonate (**6d**), and *S*-benzyl phenylmethanethiosulfonate (**6f**) were prepared from bis(4-tolyl) disulfide, bis(4-methoxyphenyl) disulfide, bis(4-chlorophenyl) disulfide, bis(2-benzamidophenyl) disulfide, and dibenzyl disulfide, respectively.

*A typical procedure for the synthesis of thiosulfonates from alkyl halides and potassium thiosulfonate **10***



A solution of α-bromo-4-xylene (**9a**) (1.85 g, 10.0 mmol) and potassium 4-toluenethiosulfonate (**10**) (1.13 g, 5.00 mmol) dissolved in DMF (10 mL) was stirred for 16 h at room temperature, and to this was added water (10 mL). The mixture was extracted with EtOAc (30 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 120/1 to 95/5) to give *S*-(4-methylbenzyl) 4-toluenethiosulfonate (**11a**) (1.37 g, 4.69 mmol, 93.9%) as a white solid.

*Synthesis of thioxanthone **14***



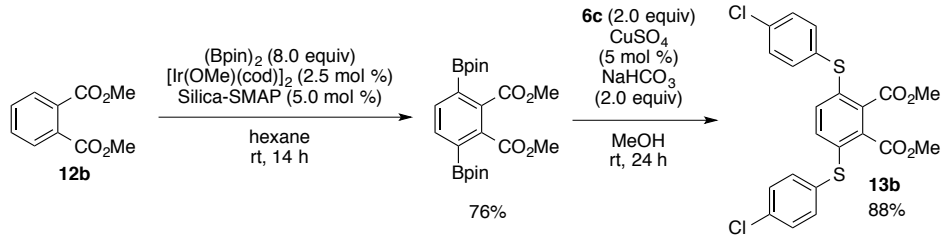
To a mixture of copper(II) sulfate (1.56 mg, 9.77 μmol) and sodium bicarbonate (34.4 mg, 0.409 mmol) was added a solution of *S*-(4-chlorophenyl) 4-chlorobenzenethiosulfonate (**6c**) (61.7 mg, 0.193 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid methyl ester[S4] (76.8 mg, 0.293 mmol) dissolved in methanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, the mixture was passed through a short pad of silica gel with EtOAc and then concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 95/5) to give 4-chlorophenyl 2-methoxycarbonylphenyl sulfide (**13a**) (54.1 mg, 0.194 mmol, quant.) as a colorless oil.

To a solution of 4-chlorophenyl 2-methoxycarbonylphenyl sulfide (**13a**) (9.7 mg, 35 μmol) dissolved in methanol (1.0 mL) was added aqueous potassium hydroxide (1.0 M, 1.0 mL, 1.0 mmol) at room temperature, and the resulting mixture was heated at 80 °C for 1 h. After cooling to room temperature, to this was added hydrochloric acid (1 M, 5 mL). The

mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue containing 2-carboxyphenyl 4-chlorophenyl sulfide was used in the next step without further purification.

To the crude 2-carboxyphenyl 4-chlorophenyl sulfide prepared as above was added concentrated sulfuric acid (2.0 mL) at room temperature, and the resulting mixture was heated at 100 °C for 12 h. After cooling to room temperature, to this was carefully added an aqueous saturated solution of sodium bicarbonate (20 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give 2-chloro-9*H*-thioxanthen-9-one (**14**) (8.1 mg, 33 μmol, 94% in 2 steps from **13a**) as a pale yellow solid.

A typical procedure for the double formal C–H thiolation

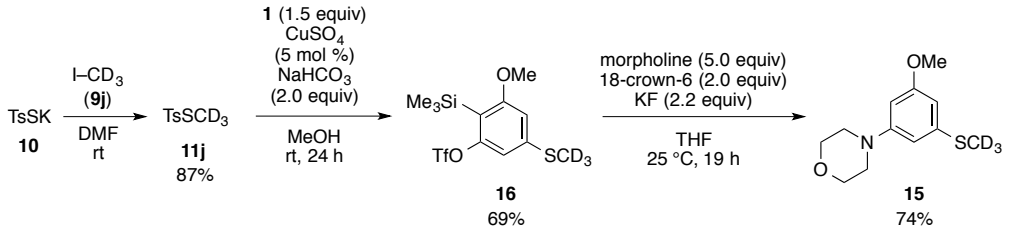


To a mixture of bis(pinacolato)diboron (946 mg, 4.01 mmol), $[Ir(OMe)(cod)]_2$ (8.4 mg, 13 μmol), and Silica-SMAP (64 μmol/g, 392 mg, 25 μmol) were added *n*-hexane (7.5 mL) and dimethyl phthalate (**12b**) (82.0 μL, 0.503 mmol) at room temperature. After stirring for 14 h at the same temperature, the mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 80 g, *n*-hexane/EtOAc = 70/30 to 15/85) to give a 72:28 mixture (238 mg) of dimethyl 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phthalate (171 mg, 0.383 mmol, 76.2% yield) and bis(pinacolato)diboron (67 mg, 0.26 mmol) as a white solid, a part of which was used in the next step without further purification.

To a mixture of copper(II) sulfate (1.69 mg, 10.6 μmol) and sodium bicarbonate (49.8 mg, 0.593 mmol) was added a solution of *S*-(4-chlorophenyl) 4-chlorobenzenethiosulfonate (**6c**) (95.7 mg, 0.300 mmol) and dimethyl 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phthalate (92.6 mg, purity: 72%, 0.15 mmol) dissolved in methanol (2.0 mL) at room temperature. After stirring for 36 h at the same temperature, the mixture was passed through a short pad of silica gel with EtOAc and then concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 10 g, *n*-hexane/EtOAc = 95/5) to give 3,6-bis((4-chlorophenyl)thio)phthalic acid dimethyl ester (**13b**) (63.0 mg, 0.131 mmol, 88%) as a colorless oil.

According to the procedure for preparing **13b**, 4,6-bis((4-methoxyphenyl)thio)isophthalic acid dimethyl ester (**13c**) was prepared from dimethyl isophthalate (**12c**) and *S*-(4-methoxyphenyl) 4-methoxybenzenethiosulfonate (**6b**).

*Copper-catalyzed thiolation of borylated aryne precursor **1** and its transformation through generation of aryne*



S-(Methyl-d_3) 4-toluenethiosulfonate (**11j**) was prepared from iodomethane-d_3 (**9j**) according to the typical procedure for the synthesis of thiosulfonates from alkyl halides and potassium thiosulfonate **10**.

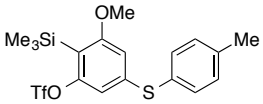
3-Methoxy-5-((methyl-d_3)thio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**16**) was prepared from *S*-(methyl-d_3) 4-toluenethiosulfonate (**11j**) and 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) according to the typical procedure for copper-catalyzed thiolation of boronic acids and thiosulfonates.

To a mixture of 3-methoxy-5-((methyl-d_3)thio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**16**) (77.5 mg, 0.205 mmol), morpholine (91.5 mg, 1.05 mmol), and 18-crown-6 (107 mg, 0.405 mmol) dissolved in THF (1.0 mL) was added potassium fluoride (25.6 mg, 0.441 mmol) at 25 °C. After stirring for 19 h at the same temperature, to this was added water (1 mL). The mixture was extracted with EtOAc (3 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 preparative TLC (*n*-hexane/EtOAc = 3/1) to give *N*-(3-methoxy-5-((methyl-d_3)thio)phenyl)morpholine (**15**) (37.0 mg, 0.153 mmol, 74.3%) as a white solid.

Characterization Data of New Compounds

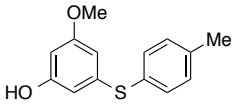
S-(4-Tolyl) 4-toluenethiosulfonate (**6a**),[S5] *S*-(4-methoxyphenyl) 4-methoxybenzenethiosulfonate (**6b**),[S5] *S*-(4-chlorophenyl) 4-chlorobenzenethiosulfonate (**6c**),[S5] phenyl 4-tolyl sulfide (**8a**),[S4] 4-methoxyphenyl 4-tolyl sulfide (**8b**),[S6] 2-bromophenyl 4-tolyl sulfide (**8d**),[S7] 2-hydroxyphenyl 4-tolyl sulfide (**8e**),[S8] (*E*)-styryl 4-tolyl sulfide (**8i**),[S9] 4-methoxycarbonylphenyl 4-methoxyphenyl sulfide (**8k**),[S10] 4-chlorophenyl 4-methoxycarbonylphenyl sulfide (**8l**),[S11] benzyl 4-methoxycarbonylphenyl sulfide (**8o**),[S12] 4-methoxycarbonylphenyl methyl sulfide (**8q**),[S13] *S*-methyl 4-toluenethiosulfonate (**11b**),[S14] *S*-isopropyl 4-toluenethiosulfonate (**11c**),[S15] and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid methyl ester[S2] were identical in the spectrum data with those reported in the literatures.

3-Methoxy-5-(4-tolylthio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**)



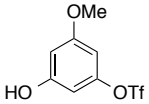
White solid; Mp 63–65 °C; R_f 0.44 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.32 (s, 9H), 2.38 (s, 3H), 3.71 (s, 3H), 6.54 (d, 1H, *J* = 1.0 Hz), 6.62 (d, 1H, *J* = 1.0 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.7 (3C), 21.2 (1C), 55.6 (1C), 108.3 (1C), 111.5 (q, 1C, *J* = 1.4 Hz), 118.5 (q, 1C, $J^1_{C–F}$ = 321.7 Hz), 117.8 (1C), 127.6 (1C), 130.4 (2C), 134.3 (2C), 139.4 (1C), 143.8 (1C), 154.9 (1C), 165.4 (1C); IR (KBr, cm^{-1}) 938, 1046, 1140, 1213, 1250, 1420, 1587, 2957; ^{19}F NMR (376 MHz) δ –73.0 (s); Anal. calcd for $C_{18}H_{21}F_3O_4S_2Si$: C, 47.98; H, 4.70; N, 0.00%. Found: C, 47.97; H, 4.78; N, 0.00%.

3-Hydroxy-5-methoxyphenyl 4-tolyl sulfide (**4**)



Colorless oil; TLC R_f 0.55 (*n*-hexane/EtOAc = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H), 3.72 (s, 3H), 4.84 (s, 1H), 6.21 (dd, 1H, *J* = 2.8, 2.8 Hz), 6.23 (dd, 1H, *J* = 2.8, 2.8 Hz), 6.38 (dd, 1H, *J* = 2.8, 2.8 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.1 (1C), 55.3 (1C), 99.5 (1C), 106.8 (1C), 107.9 (1C), 129.8 (1C), 130.1 (2C), 133.3 (2C), 138.2 (1C), 140.0 (1C), 156.8 (1C), 161.1 (1C); IR (KBr, cm^{-1}) 808, 973, 1053, 1154, 1193, 1427, 1491, 1586, 3353; HRMS (ESI^+) m/z 247.0784 ($[M+H]^+$, $C_{14}H_{15}O_2S^+$ requires 247.0787).

3-Hydroxy-5-methoxyphenyl trifluoromethanesulfonate (**5**)



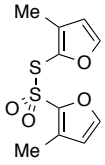
Colorless oil; TLC R_f 0.55 (*n*-hexane/EtOAc = 7/3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.79 (s, 3H), 6.36–6.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.7 (1C), 100.1 (1C), 101.4 (1C), 101.5 (1C), 118.5 (q, 1C, $J^1_{C–F}$ = 321.3 Hz), 150.5 (1C), 157.5 (1C), 161.5 (1C); ^{19}F NMR

($CDCl_3$, 376 MHz) δ –73.1 (s); IR (KBr, cm^{-1}) 845, 991, 1141, 1213, 1419, 1622, 3392; HRMS (ESI^-) m/z 270.9896 ($[M–H]^-$, $C_8H_6F_3O_5S^-$ requires 270.9894).

S-(2-Benzamidophenyl) 2-benzamidobenzenethiosulfonate (**6d**)

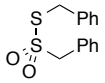
White solid; Mp 139–142 ºC; TLC R_f 0.48 (*n*-hexane/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.87 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.02 (d, 1H, *J* = 7.6 Hz), 7.07 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.37 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.48 (dd, 2H, *J* = 7.6, 7.6 Hz), 7.52–7.64 (m, 6H), 7.88 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 7.6 Hz), 8.29 (d, 1H, *J* = 8.3 Hz), 8.70 (d, 1H, *J* = 8.3 Hz), 9.07 (br s, 1H), 10.04 (br s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 115.2 (1C), 122.1 (1C), 122.3 (1C), 123.4 (1C), 124.9 (1C), 127.2 (2C+2C, two signals overlapped), 128.2 (1C), 128.9 (2C), 129.0 (2C), 129.8 (1C), 132.3 (1C), 132.5 (1C), 133.4 (1C), 134.0 (1C), 134.1 (1C), 136.2 (1C), 137.2 (1C), 138.1 (1C), 141.1 (1C), 164.8 (1C), 165.0 (1C); IR (KBr, cm^{-1}) 1126, 1217, 1366, 1431, 1514, 1580, 1690, 1715, 1736; HRMS (ESI^+) m/z 511.0750 ($[M+Na]^+$, $C_{26}H_{20}N_2NaO_4S_2^+$ requires 511.0757).

S-(3-Methylfuran-2-yl) 2-(3-methylfuran)thiosulfonate (**6e**)



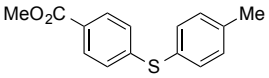
Pale yellow oil; TLC R_f 0.22 (*n*-hexane/EtOAc = 10/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.16 (s, 3H), 2.22 (s, 3H), 6.31 (d, 1H, *J* = 2.0 Hz), 6.52 (d, 1H, *J* = 2.0 Hz), 7.28 (d, 1H, *J* = 2.0 Hz), 7.34 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 11.4 (1C), 12.2 (1C), 105.6 (1C), 109.6 (1C), 115.4 (1C), 124.1 (1C), 140.9 (1C), 141.3 (1C), 158.2 (1C), 160.4 (1C); IR (KBr, cm^{-1}) 908, 1020, 1089, 1121, 1212, 1229, 1324, 1385, 1518, 1572; Anal. calcd. for $C_{10}H_{10}O_4S_2$: C, 46.50; H, 3.90; N, 0.00%; Found: C, 46.28; H, 3.81, N, 0.00%.

S-Benzyl phenylmethanethiosulfonate (**6f**)



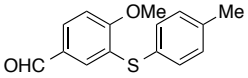
White solid; Mp 107–108 ºC; TLC R_f 0.22 (*n*-hexane/EtOAc = 10/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.02 (s, 2H), 4.20 (s, 2H), 7.24–7.33 (m, 5H), 7.33–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 41.0 (1C), 69.1 (1C), 127.7 (1C), 128.4 (1C), 128.8 (2C), 129.0 (2C), 129.38 (1C), 129.40 (2C), 131.4 (2C), 134.9 (1C); IR (KBr, cm^{-1}) 873, 918, 1030, 1072, 1200, 1254, 1332, 1455, 1495; Anal. calcd. for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07; N, 0.00%; Found: C, 60.51; H, 4.97; N, 0.00%.

4-Methoxycarbonylphenyl 4-tolyl sulfide (**8c**)



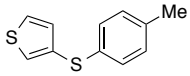
White solid; Mp 45–47 °C; R_f 0.51 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.88 (s, 3H), 7.13–7.16 (AA'BB', 2H), 7.22 (d, 2H, *J* = 8.0 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.85–7.88 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (1C), 52.1 (1C), 126.7 (2C), 127.0 (1C), 128.1 (1C), 130.0 (2C), 130.5 (2C), 134.4 (2C), 139.2 (1C), 145.4 (1C), 166.8 (1C); IR (KBr, cm^{-1}) 1113, 1276, 1288, 1433, 1593, 1715, 2947, 3017; Anal. calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; N, 0.00%; Found: C, 69.77; H, 5.26; N, 0.00%.

3-Formyl-6-methoxyphenyl 4-tolyl sulfide (**8f**)



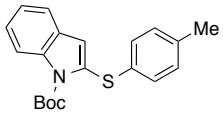
White solid; Mp 94–96 °C; R_f 0.38 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.00 (s, 3H), 6.97 (d, 1H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 7.35 (d, 1H, *J* = 2.0 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 7.68 (dd, 1H, *J* = 8.4, 2.0 Hz), 9.72 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (1C), 56.3 (1C), 110.1 (1C), 127.5 (1C), 128.8 (1C), 129.4 (1C), 129.6 (1C), 130.3 (1C), 130.6 (2C), 134.2 (2C), 139.0 (1C), 160.5 (1C), 190.5 (1C); IR (KBr, cm^{-1}) 1017, 1196, 1251, 1488, 1570, 1586, 1693, 2839, 3022; Anal. calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; N, 0.00%; Found: C, 69.93; H, 5.37; N, 0.00%.

3-Thienyl 4-tolyl sulfide (**8g**)



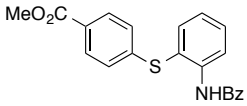
Colorless oil; R_f 0.67 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H, CH_3), 7.00 (d, 1H, *J* = 4.9 Hz), 7.08 (d, 2H, *J* = 8.0 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 2.9 Hz), 7.34 (dd, 1H, *J* = 4.9, 2.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0 (1C), 126.5 (1C), 126.6 (1C), 129.4 (2C), 129.8 (2C), 130.5 (1C), 130.6 (1C), 133.1 (1C), 136.5 (1C); IR (KBr, cm^{-1}) 805, 852, 1016, 1197, 1351, 1491, 2919, 3019, 3102; HRMS (ESI^+) m/z 207.0306 ($[M+H]^+$, $C_{11}H_{11}S_2^+$ requires 207.0297).

1-(*tert*-Butoxycarbonyl)indol-2-yl 4-tolyl sulfide (**8h**)



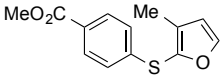
Colorless oil; R_f 0.59 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (s, 9H), 2.40 (s, 3H), 5.77 (s, 1H), 7.09–7.19 (m, 2H), 7.21–7.26 (m, 3H), 7.51 (d, 2H, *J* = 8.0 Hz), 8.02 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4 (1C), 28.3 (3C), 85.1 (1C), 107.3 (1C), 115.1 (1C), 118.9 (1C), 122.88 (1C), 122.90 (1C), 129.1 (1C), 129.7 (1C), 130.5 (2C), 134.8 (2C), 136.7 (1C), 138.2 (1C), 139.4 (1C), 150.5 (1C); IR (KBr, cm^{-1}) 1016, 1160, 1247, 1328, 1446, 1598, 1731, 2929, 2979; HRMS (ESI^+) m/z 340.1382 ($[M+H]^+$, $C_{20}H_{22}NO_2S^+$ requires 340.1366).

2-Benzamidophenyl 4-methoxycarbonylphenyl sulfide (**8m**)



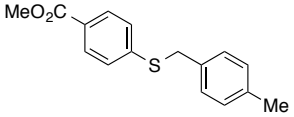
White solid; Mp 103–105 °C; R_f 0.44 (*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.10–7.13 (AA'BB', 2H), 7.21 (ddd, 1H, *J* = 7.6, 7.6, 1.3 Hz), 7.38–7.42 (AA'BB'C, 2H), 7.48–7.52 (AA'BB'C, 1H), 7.58 (ddd, 1H, *J* = 7.6, 7.6, 1.3 Hz), 7.61–7.64 (AA'BB'C, 2H), 7.66 (dd, 1H, *J* = 7.6, 1.3 Hz), 7.87–7.91 (AA'BB', 2H), 8.74 (dd, 1H, *J* = 7.6, 1.3 Hz), 8.99 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.1 (1C), 118.2 (1C), 120.8 (1C), 124.8 (1C), 125.8 (2C), 126.9 (2C), 127.8 (1C), 128.8 (2C), 130.4 (2C), 131.96 (1C), 132.04 (1C), 134.5 (1C), 137.1 (1C), 140.4 (1C), 142.2 (1C), 165.2 (1C), 166.4 (1C); IR (KBr, cm^{-1}) 1109, 1285, 1513, 1578, 1683, 1719, 2950, 3061, 3366; HRMS (ESI^+) m/z 386.0817 ($[M+Na]^+$, $C_{21}H_{17}NNaO_3S^+$ requires 386.0821).

4-Methoxycarbonylphenyl 3-methylfuran-2-yl sulfide (**8n**)



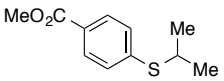
White solid; Mp 37–38 °C; R_f 0.48 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.88 (s, 3H), 6.39 (d, 1H, *J* = 2.0 Hz), 7.08–7.12 (AA'BB', 2H), 7.42 (d, 1H, *J* = 2.0 Hz), 7.86–7.89 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 11.8 (1C), 52.0 (1C), 106.3 (1C), 115.3 (1C), 124.9 (2C), 126.6 (1C), 130.0 (2C), 141.6 (1C), 144.9 (1C), 157.5 (1C), 166.8 (1C); IR (KBr, cm^{-1}) 1109, 1274, 1435, 1594, 1719, 2951, 3120; HRMS (ESI^+) m/z 249.0569 ($[M+H]^+$, $C_{13}H_{13}O_3S^+$ requires 249.0580).

4-Methoxycarbonylphenyl 4-methylbenzyl sulfide (**8p**)



White solid; Mp 94–98 ºC; TLC R_f 0.19 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.33 (s, 3H), 3.89 (s, 3H), 4.17 (s, 2H), 7.12 (d, 2H, *J* = 7.9 Hz), 7.25 (d, 2H, *J* = 7.9 Hz), 7.27–7.31 (AA'BB', 2H), 7.88–7.92 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 36.9 (1C), 52.0 (1C), 126.8 (2C), 126.9 (1C), 128.6 (2C), 129.3 (2C), 129.8 (2C), 133.1 (1C), 137.2 (1C), 143.9 (1C), 166.7 (1C); IR (KBr, cm^{-1}) 824, 847, 1013, 1112, 1184, 1276, 1400, 1435, 1513, 1711; HRMS (ESI^+) m/z 295.0750 ($[M+Na]^+$, $C_{16}H_{16}NaO_2S^+$ requires 295.0763).

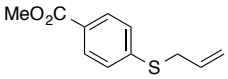
Isopropyl 4-methoxycarbonylphenyl sulfide (**8r**)



Colorless oil; TLC R_f 0.28 (*n*-hexane/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35 (d, 6H, *J* = 6.7 Hz), 3.55 (sept, 1H, *J* = 6.7 Hz), 3.90 (s, 3H), 7.32–7.36 (AA'BB', 2H), 7.91–7.95 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 22.9 (2C), 36.7 (1C), 52.0 (1C), 127.1 (1C), 128.5 (2C), 129.8 (2C), 143.2 (1C), 166.8 (1C); IR (KBr, cm^{-1}) 826, 844, 1015, 1111,

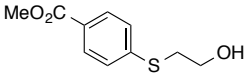
1180, 1286, 1435, 1490, 1595, 1722; Anal. calcd. for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; N, 0.00%; Found: C, 62.90; H, 6.56; N, 0.00%.

Allyl 4-methoxycarbonylphenyl sulfide (**8s**)



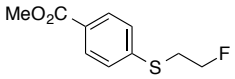
White solid; Mp 36–37 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.63 (d, 2H, *J* = 6.2 Hz), 3.90 (s, 3H), 5.15 (dd, 1H, *J* = 10.1, 1.1 Hz), 5.26 (dd, 1H, *J* = 17.0, 1.1 Hz), 5.89 (ddt, 1H, *J* = 17.0, 10.1, 6.2 Hz), 7.29–7.32 (AA'BB', 2H), 7.91–7.94 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 52.0 (1C), 118.4 (1C), 126.97 (1C), 127.04 (2C), 129.8 (2C), 132.6 (1C), 143.2 (1C), 166.7 (1C); IR (KBr, cm^{-1}) 826, 844, 926, 1015, 1108, 1182, 1284, 1434, 1595, 1718; Anal. calcd. for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81; N, 0.00%; Found: C, 63.40; H, 5.87; N, 0.00%.

2-Hydroxyethyl 4-methoxycarbonylphenyl sulfide (**8t**)



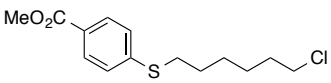
White solid; Mp 59–61 °C; R_f 0.37 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (t, 1H, *J* = 6.0 Hz), 3.21 (t, 2H, *J* = 6.0 Hz), 3.84 (dt, 2H, *J* = 6.0, 6.0 Hz), 3.91 (s, 3H), 7.36 (d, 2H, *J* = 8.5 Hz), 7.94 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 35.5 (1C), 52.1 (1C), 60.4 (1C), 127.3 (2C), 127.4 (1C), 130.1 (2C), 142.3 (1C), 166.7 (1C); IR (KBr, cm^{-1}) 1013, 1114, 1288, 1436, 1598, 1719, 2877, 2955, 3318; HRMS (ESI^+) m/z 235.0398 ($[M+Na]^+$, $C_{10}H_{12}NaO_3S^+$ requires 235.0399).

2-Fluoroethyl 4-methoxycarbonylphenyl sulfide (**8u**)



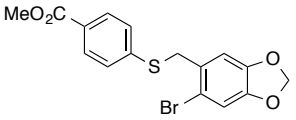
Colorless oil; TLC R_f 0.57 (*n*-hexane/CH_2Cl_2 = 3/7); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.30 (dt, 2H, *J* = 17.8, 6.7 Hz), 3.91 (s, 3H), 4.60 (dt, 2H, *J* = 46.9, 6.7 Hz), 7.34–7.38 (AA'BB', 2H), 7.93–7.97 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 32.1 (d, 1C, J^2_{C-F} = 22.3 Hz), 52.1 (1C), 81.3 (d, 1C, J^1_{C-F} = 173.5 Hz), 127.2 (2C), 127.6 (1C), 130.1 (2C), 141.9 (1C), 166.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –212.8 (tt, *J* = 46.9, 17.8 Hz); IR (KBr, cm^{-1}) 1013, 1113, 1183, 1287, 1435, 1595, 1717; HRMS (ESI^+) m/z 237.0357 ($[M+Na]^+$, $C_{10}H_{11}FNaO_2S^+$ requires 237.0356).

6-Chlorohexyl 4-methoxycarbonylphenyl sulfide (**8v**)



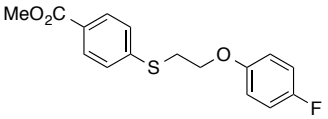
White solid; Mp 45–46 °C; R_f 0.24 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45–1.53 (m, 4H), 1.66–1.82 (m, 4H), 2.99 (t, 2H, *J* = 7.2 Hz), 3.53 (t, 2H, *J* = 6.6 Hz), 3.90 (s, 3H), 7.27–7.30 (AA'BB', 2H), 7.91–7.94 (AA'BB', 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.4 (1C), 28.1 (1C), 28.5 (1C), 31.9 (1C), 32.4 (1C), 44.9 (1C), 52.0 (1C), 126.3 (2C), 126.6 (1C), 129.9 (2C), 144.2 (1C), 166.8 (1C); IR (KBr, cm^{-1}) 1110, 1285, 1434, 1595, 1717, 2858, 2934; HRMS (ESI^+) m/z 309.0683 ($[M+Na]^+$, $C_{14}H_{19}ClNaO_2S^+$ requires 309.0686).

(6-Bromobenzo[*d*][1,3]dioxol-5-yl)methyl 4-methoxycarbonylphenyl sulfide (**8w**)



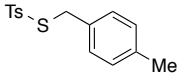
White solid; Mp 104–107 ºC; TLC R_f 0.34 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.90 (s, 3H), 4.23 (s, 2H), 5.96 (s, 2H), 6.89 (s, 1H), 7.01 (s, 1H), 7.29–7.33 (AA'BB', 2H), 7.90–7.94 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 37.7 (1C), 52.0 (1C), 101.8 (1C), 110.0 (1C), 112.8 (1C), 114.9 (1C), 127.3 (1C), 127.4 (2C), 128.6 (1C), 129.9 (2C), 143.0 (1C), 147.5 (1C), 147.8 (1C), 166.7 (1C); IR (KBr, cm^{-1}) 827, 934, 1039, 1112, 1286, 1472, 1594, 1714; HRMS (ESI^+) m/z 402.9607 ($[M+Na]^+$, $C_{16}H_{13}BrNaO_4S^+$ requires 402.9610).

2-(4-Fluorophenoxy)ethyl 4-methoxycarbonylphenyl sulfide (**8x**)



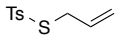
White solid; Mp 82–83 ºC; TLC R_f 0.59 (*n*-hexane/CH_2Cl_2 = 3/7); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.36 (t, 2H, J = 6.9 Hz), 3.90 (s, 3H), 4.15 (t, 2H, J = 6.9 Hz), 6.76–6.84 (m, 2H), 6.96 (dd, 2H, J = 8.6, 8.6 Hz), 7.37 (d, 2H, J = 8.5 Hz), 7.95 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 31.4 (1C), 52.1 (1C), 67.0 (1C), 115.6 (d, 2C, $J^3_{C–F}$ = 7.7 Hz), 115.8 (d, 2C, $J^2_{C–F}$ = 23.1 Hz), 127.0 (2C), 127.3 (1C), 130.0 (2C), 142.6 (1C), 154.3 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 157.5 (d, 1C, $J^1_{C–F}$ = 239 Hz), 166.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –123.5 (m); IR (KBr, cm^{-1}) 827, 959, 1115, 1227, 1398, 1437, 1597, 1723; HRMS (ESI^+) m/z 329.0618 ($[M+Na]^+$, $C_{16}H_{15}FNaO_3S^+$ requires 329.0618).

S-(4-Methylbenzyl) 4-toluenethiosulfonate (**11a**)



White solid; Mp 58–59 ºC; TLC R_f 0.35 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 3H), 2.47 (s, 3H), 4.24 (s, 2H), 7.05–7.08 (AA'BB', 2H), 7.08–7.11 (AA'BB', 2H), 7.29–7.33 (AA'BB', 2H), 7.75–7.78 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.0 (1C), 21.6 (1C), 40.0 (1C), 127.0 (2C), 129.0 (2C), 129.4 (2C), 129.7 (2C), 130.4 (1C), 137.8 (1C), 142.0 (1C), 144.5 (1C); IR (KBr, cm^{-1}) 813, 1017, 1077, 1140, 1327, 1515, 1593, 2921; HRMS (ESI^+) m/z 315.0478 ($[M+Na]^+$, $C_{15}H_{16}NaO_2S_2^+$ requires 315.0484).

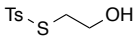
S-Allyl 4-toluenethiosulfonate (**11d**)



Pale yellow oil; TLC R_f 0.40 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 3.67 (d, 2H, J = 7.2 Hz), 5.11 (dd, 1H, J = 10.0, 1.0 Hz), 5.21 (dd, 1H, J = 16.9, 1.0 Hz), 5.71 (ddt, 1H, J = 16.9, 10.0, 7.2 Hz), 7.34 (d, 2H, J = 8.2 Hz), 7.81 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 38.8 (1C), 119.9 (1C), 127.1 (2C), 129.8 (2C), 130.6

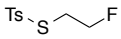
(1C), 142.0 (1C), 144.7 (1C); IR (KBr, cm^{-1}) 813, 929, 988, 1017, 1076, 1293, 1326, 1402, 1492; HRMS (ESI^+) m/z 251.0165 ($[M+Na]^+$, $C_{10}H_{12}NaO_2S_2^+$ requires 251.0171).

S-(2-Hydroxyethyl) 4-toluenethiosulfonate (**11e**)



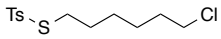
Pale yellow oil; TLC R_f 0.30 (*n*-hexane/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.92 (br s, 1H), 2.46 (s, 3H), 3.17 (t, 2H, J = 5.9 Hz), 3.86 (t, 2H, J = 5.9 Hz), 7.36 (d, 2H, J = 8.3 Hz), 7.83 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 38.7 (1C), 60.9 (1C), 127.1 (2C), 129.9 (2C), 141.5 (1C), 145.1 (1C); IR (KBr, cm^{-1}) 814, 1076, 1139, 1322, 1403, 1491, 1593, 2879, 2926, 3538 (br); HRMS (ESI^+) m/z 255.0116 ($[M+Na]^+$, $C_9H_{12}NaO_3S_2^+$ requires 255.0120).

S-(2-Fluoroethyl) 4-toluenethiosulfonate (**11f**)



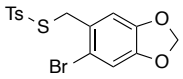
Colorless oil; TLC R_f 0.39 (*n*-hexane/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 3.28 (dt, 2H, J = 20.5, 6.2 Hz), 4.56 (dt, 2H, J = 46.5, 6.2 Hz), 7.37 (d, 2H, J = 8.2 Hz), 7.82 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 35.3 (d, 1C, $J^2_{C–F}$ = 22.9 Hz), 80.9 (d, 1C, $J^1_{C–F}$ = 172.7 Hz), 127.0 (2C), 130.0 (2C), 141.6 (1C), 145.2 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –213.4 (m); IR (KBr, cm^{-1}) 813, 1016, 1078, 1144, 1184, 1325, 1402, 1492, 1593, 2960; Anal. calcd. for $C_9H_{11}FO_2S_2$: C, 46.14; H, 4.73; N, 0.00%; Found: C, 45.87; H, 4.91; N, 0.00%.

S-(6-Chlorohexyl) 4-toluenethiosulfonate (**11g**)



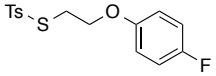
Yellow oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.29–1.41 (m, 4H), 1.62 (tt, 2H, J = 7.3, 7.3 Hz), 1.71 (tt, 2H, J = 7.3, 7.3 Hz), 2.46 (s, 3H), 2.99 (t, 2H, J = 7.3 Hz), 3.49 (t, 2H, J = 7.3 Hz), 7.35 (d, 2H, J = 8.2 Hz), 7.81 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 26.1 (1C), 27.6 (1C), 28.4 (1C), 32.1 (1C), 35.8 (1C), 44.8 (1C), 127.0 (2C), 129.8 (2C), 142.0 (1C), 144.7 (1C); IR (KBr, cm^{-1}) 813, 1077, 1292, 1324, 1455, 1594, 2860, 2934; HRMS (ESI^+) m/z 329.0392 ($[M+Na]^+$, $C_{13}H_{19}ClNaO_2S_2^+$ requires 329.0407).

S-((6-Bromobenzo[*d*][1,3]dioxol-5-yl)methyl) 4-toluenethiosulfonate (**11h**)



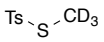
White solid; Mp 107–109 ºC; TLC R_f 0.23 (*n*-hexane/EtOAc = 20/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 4.26 (s, 2H), 5.94 (s, 2H), 6.69 (s, 1H), 6.92 (s, 1H), 7.31 (d, 2H, J = 8.3 Hz), 7.79 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 40.7 (1C), 101.9 (1C), 110.6 (1C), 112.8 (1C), 115.4 (1C), 126.5 (1C), 127.1 (2C), 129.7 (2C), 141.8 (1C), 144.7 (1C), 147.3 (1C), 148.3 (1C); IR (KBr, cm^{-1}) 813, 933, 1037, 1077, 1140, 1247, 1324, 1480, 1505, 1594; Anal. calcd. for $C_{15}H_{13}BrO_4S_2$: C, 44.90; H, 3.27; N, 0.00%; Found: C, 44.93; H, 3.26; N, 0.00%.

S-(2-(4-Fluorophenoxy)ethyl) 4-toluenethiosulfonate (**11i**)



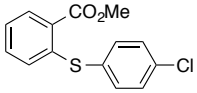
White solid; Mp 74–75 ºC; TLC R_f 0.26 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 3.33 (t, 2H, *J* = 6.3 Hz), 4.12 (t, 2H, *J* = 6.3 Hz), 6.75 (dd, 2H, *J* = 9.1, 4.3 Hz), 6.94 (dd, 2H, *J* = 9.1, 9.1 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 7.82 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6 (1C), 34.8 (1C), 66.6 (1C), 115.7 (d, 2C, $J^3_{C–F}$ = 8.2 Hz), 115.8 (d, 2C, $J^2_{C–F}$ = 23.3 Hz), 127.0 (2C), 129.9 (2C), 141.7 (1C), 145.0 (1C), 154.0 (d, 1C, $J^4_{C–F}$ = 2.5 Hz), 157.5 (d, 1C, $J^1_{C–F}$ = 240.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –123.2 (m); IR (KBr, cm^{-1}) 828, 1025, 1076, 1141, 1207, 1247, 1326, 1466, 1505, 1593; Anal. calcd. for $C_{15}H_{15}FO_3S_2$: C, 55.20; H, 4.63; N, 0.00%; Found: C, 55.11; H, 4.68; N, 0.00%.

S-(Methyl-d_3) 4-toluenethiosulfonate (**11j**)



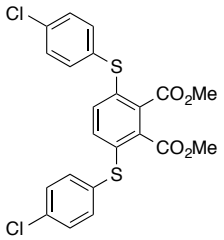
White solid; Mp 56–57 ºC; TLC R_f 0.26 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 7.35 (d, 2H, *J* = 8.2 Hz), 7.81 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.4 (sept, 1C, *J* = 21.7 Hz), 21.6 (1C), 127.1 (2C), 129.8 (2C), 140.8 (1C), 144.8 (1C); IR (KBr, cm^{-1}) 814, 1043, 1077, 1143, 1322, 1403, 1448, 1492, 1595; HRMS (ESI$^+$) m/z 206.0373 ([M+H]$^+$, $C_8H_8D_3O_2S_2^+$ requires 206.0383).

4-Chlorophenyl 2-methoxycarbonylphenyl sulfide (**13a**)



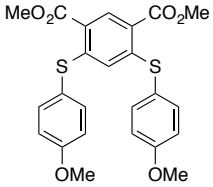
White solid; Mp 79–80 °C; R_f 0.37 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 3H), 6.80 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.14 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.26 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.38–7.41 (AA'BB', 2H), 7.46–7.50 (AA'BB', 2H), 7.98 (dd, 1H, *J* = 7.8, 1.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.2 (1C), 124.6 (1C), 126.8 (1C), 127.4 (1C), 129.9 (2C), 131.0 (1C), 131.2 (1C), 132.4 (1C), 135.4 (1C), 136.6 (2C), 142.5 (1C), 166.8 (1C); IR (KBr, cm^{-1}) 822, 1058, 1251, 1475, 1714, 2950, 3062; HRMS (ESI$^+$) m/z 301.0061 ([M+Na]$^+$, $C_{14}H_{11}ClNaO_2S^+$ requires 301.0060).

3,6-Di((4-chlorophenyl)thio)phthalic acid dimethyl ester (**13b**)



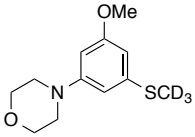
Colorless oil; TLC R_f 0.23 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 6H), 6.97 (s, 2H), 7.27–7.35 (m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.8 (2C), 129.8 (4C), 132.0 (2C), 132.8 (2C+2C, two signals overlapped), 134.4 (4C), 134.8 (2C), 135.9 (2C), 166.6 (2C); IR (KBr, cm^{-1}) 823, 1014, 1093, 1235, 1273, 1476, 1729; HRMS (ESI$^+$) m/z 500.9752 ([M+Na]$^+$, $C_{22}H_{16}Cl_2NaO_4S_2^+$ requires 500.9759).

4,6-Di((4-methoxyphenyl)thio)isophthalic acid dimethyl ester (**13c**)



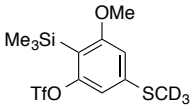
White solid; Mp 187–189 °C; R_f 0.35 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 6H), 3.95 (s, 6H), 6.35 (s, 1H), 6.70 (d, 4H, J = 8.5 Hz), 7.15 (d, 4H, J = 8.5 Hz), 8.63 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.2 (2C), 55.1 (2C), 115.3 (4C), 120.4 (2C), 120.9 (2C), 123.9 (1C), 134.0 (1C), 137.3 (4C), 150.4 (2C), 160.6 (2C), 166.0 (2C); IR (KBr, cm^{-1}) 1075, 1251, 1277, 1493, 1591, 1710, 2956, 3008; HRMS (ESI$^+$) m/z 493.0739 ([M+Na]$^+$, $C_{24}H_{22}NaO_6S_2^+$ requires 493.0750).

N-(3-Methoxy-5-((methyl-d_3)thio)phenyl)morpholine (**15**)



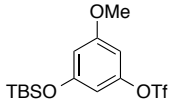
White solid; Mp 123–124 ºC; TLC R_f 0.42 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.12–3.15 (AA'BB', 4H), 3.78 (s, 3H), 3.82–3.85 (AA'BB', 4H), 6.23 (dd, 1H, J = 2.0, 2.0 Hz), 6.35 (dd, 1H, J = 2.0, 2.0 Hz), 6.42 (dd, 1H, J = 2.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 15.1 (sept, 1C, J = 21.3 Hz), 49.2 (2C), 55.2 (1C), 66.8 (2C), 99.2 (1C), 103.3 (1C), 106.7 (1C), 140.2 (1C), 152.7 (1C), 160.8 (1C); IR (KBr, cm^{-1}) 816, 888, 993, 1051, 1121, 1201, 1270, 1448, 1581; HRMS (ESI$^+$) m/z 243.1245 ([M+H]$^+$, $C_{12}H_{15}D_3NO_2S^+$ requires 243.1241).

3-Methoxy-5-((methyl-d_3)thio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**16**)



Colorless oil; TLC R_f 0.35 (*n*-hexane/EtOAc = 50/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.81 (s, 3H), 6.67 (d, 1H, J = 1.2 Hz), 6.75 (d, 1H, J = 1.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.9 (3C), 14.6 (sept, 1C, J = 21.5 Hz), 55.7 (1C), 107.4 (1C), 109.7 (1C), 117.1 (1C), 118.7 (q, 1C, $J^1_{C–F}$ = 321.4 Hz), 143.8 (1C), 155.1 (1C), 165.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 812, 843, 938, 1140, 1211, 1419, 1538, 1591; HRMS (ESI$^+$) m/z 400.0362 ([M+Na]$^+$, $C_{12}H_{14}D_3F_3NaO_4S_2Si^+$ requires 400.0370).

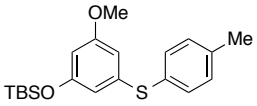
3-(*tert*-Butyldimethylsilyloxy)-5-methoxyphenyl trifluoromethanesulfonate (**S2**)



Colorless oil; TLC R_f 0.50 (*n*-hexane/toluene = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.22 (s, 6H), 0.98 (s, 9H), 3.78 (s, 3H), 6.36 (dd, 1H, J = 1.7, 1.7 Hz), 6.39 (dd, 1H, J = 1.7, 1.7 Hz), 6.44 (dd, 1H, J = 1.7, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –4.6 (2C), 18.1 (1C), 25.5 (3C), 55.6 (1C), 100.6 (1C), 105.8 (1C), 106.1 (1C), 118.6 (q, 1C, $J^1_{C–F}$ = 321.8 Hz), 150.3 (1C),

157.5 (1C), 161.1 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.1 (s); IR (KBr, cm^{-1}) 840, 954, 1018, 1100, 1164, 1209, 1425, 1615; HRMS (ESI^+) m/z 387.0889 ($[M+H]^+$, $C_{14}H_{22}F_3O_5SSi^+$ requires 387.0904).

3-(*tert*-Butyldimethylsilyloxy)-5-methoxyphenyl 4-tolyl sulfide (**S3**)



Colorless oil; TLC R_f 0.58 (*n*-hexane/toluene = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 6H), 0.93 (s, 9H), 2.35 (s, 3H), 3.70 (s, 3H), 6.22 (dd, 1H, J = 2.8, 2.8 Hz), 6.29 (dd, 1H, J = 2.8, 2.8 Hz), 6.41 (dd, 1H, J = 2.8, 2.8 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –4.6 (2C), 18.1 (1C), 21.1 (1C), 25.6 (3C), 55.2 (1C), 104.4 (1C), 107.6 (1C), 113.3 (1C), 130.0 (2C), 130.4 (1C), 132.8 (2C), 137.8 (1C), 139.0 (1C), 156.9 (1C), 160.8 (1C); IR (KBr, cm^{-1}) 831, 1000, 1159, 1194, 1423, 1586; HRMS (ESI^+) m/z 361.1635 ($[M+H]^+$, $C_{20}H_{29}O_2SSi^+$ requires 361.1652).

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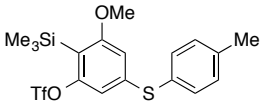
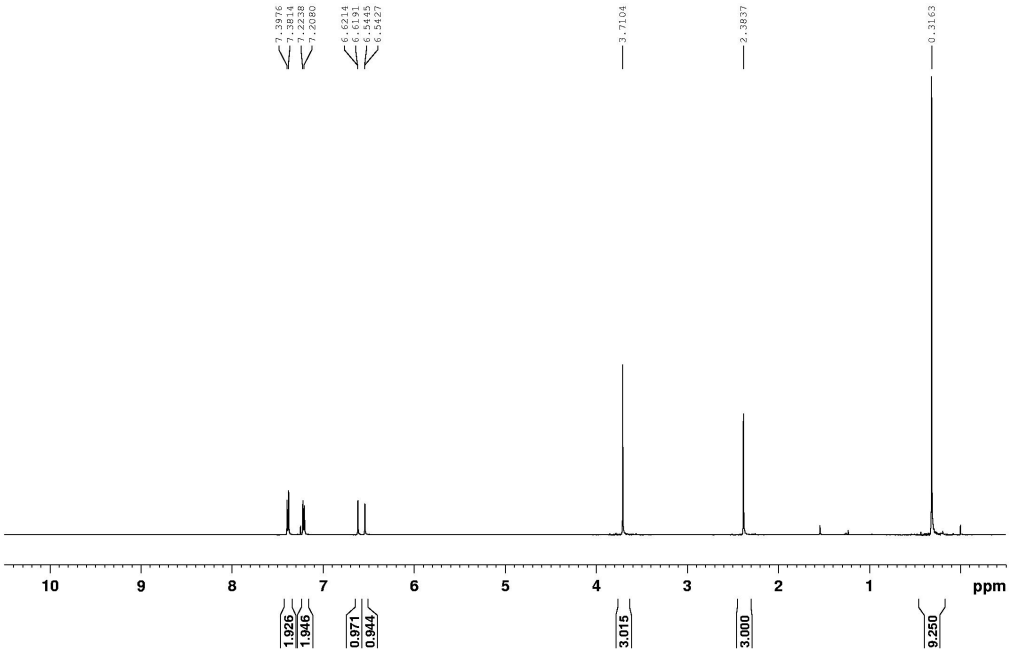
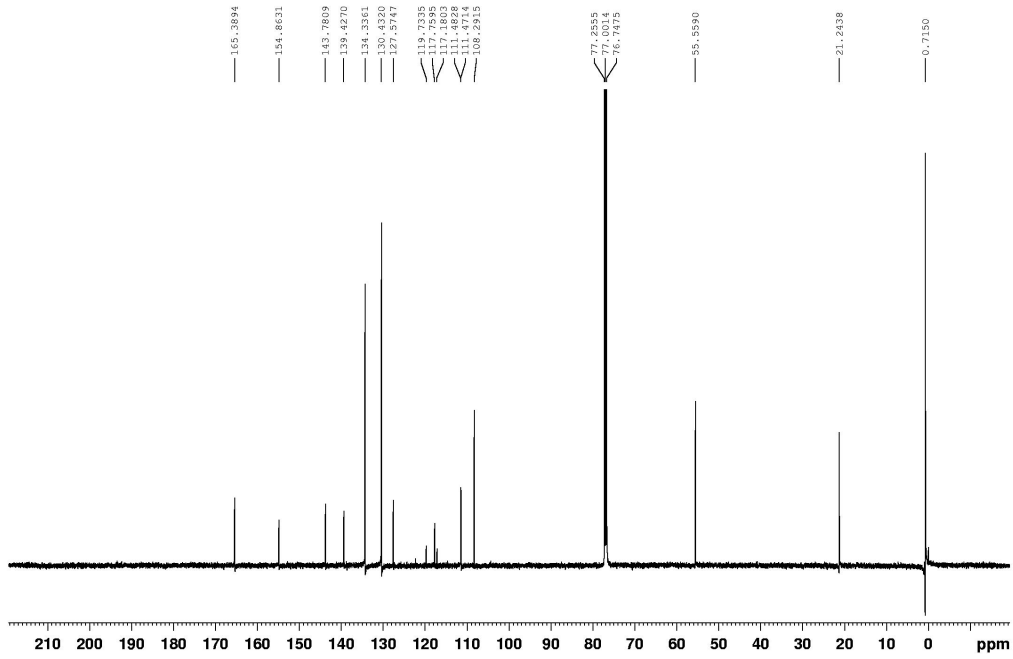
^{1}H and ^{13}C NMR Spectra of Compounds

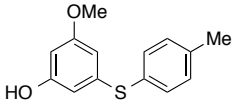
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2** ($CDCl_3$)

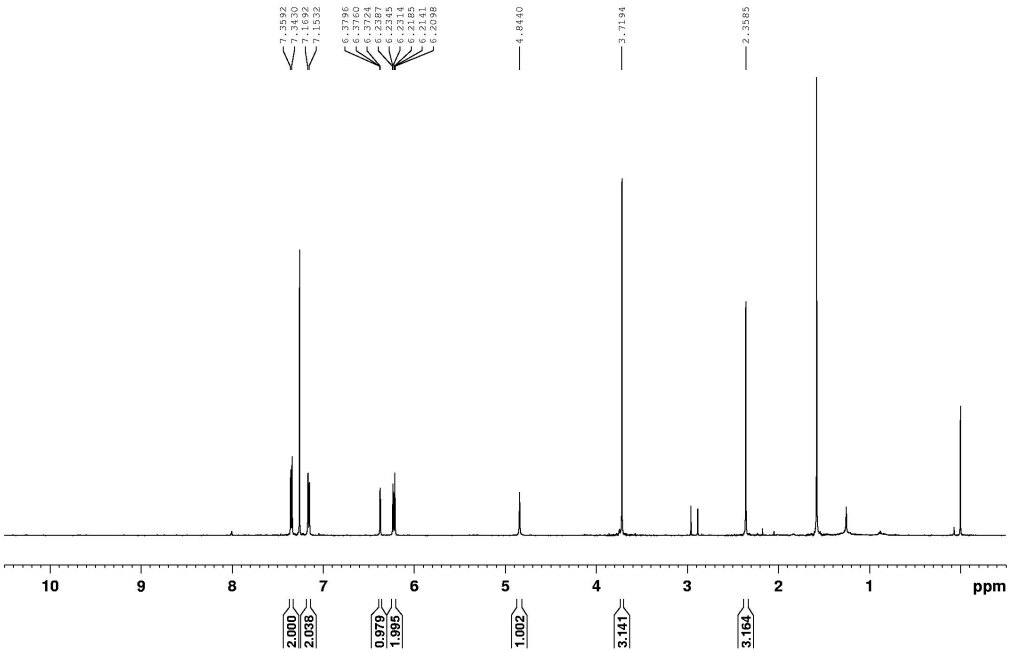


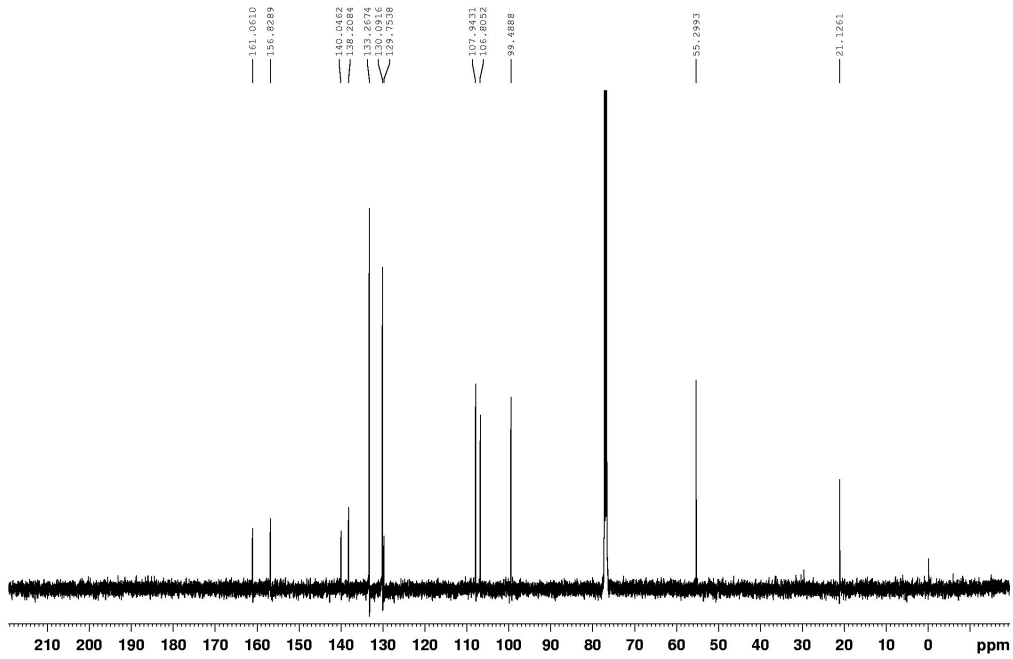




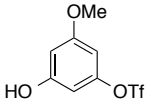
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **4** ($CDCl_3$)

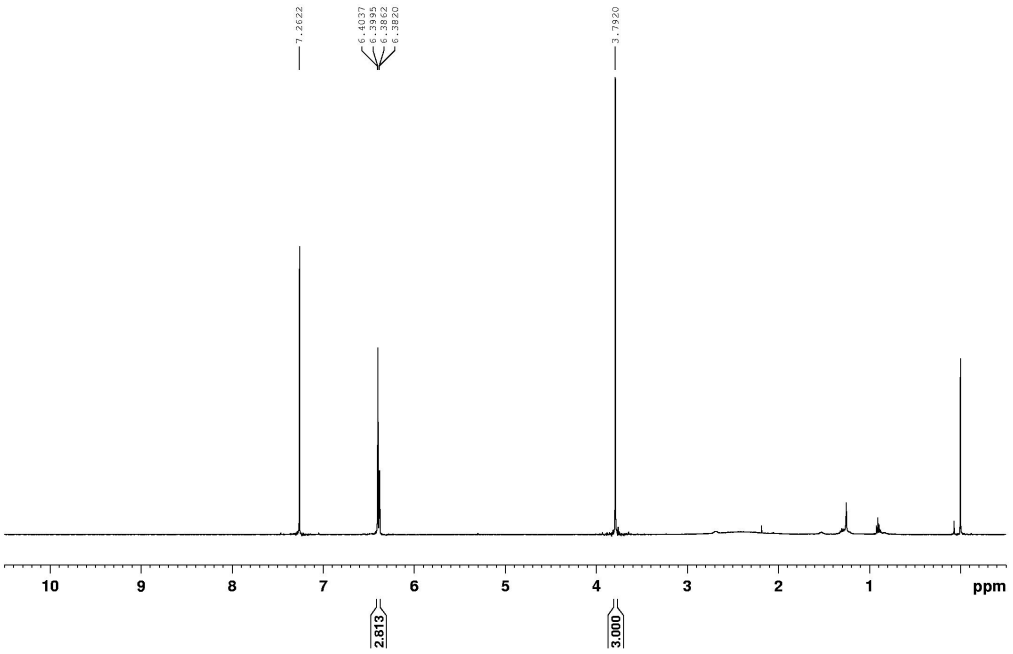


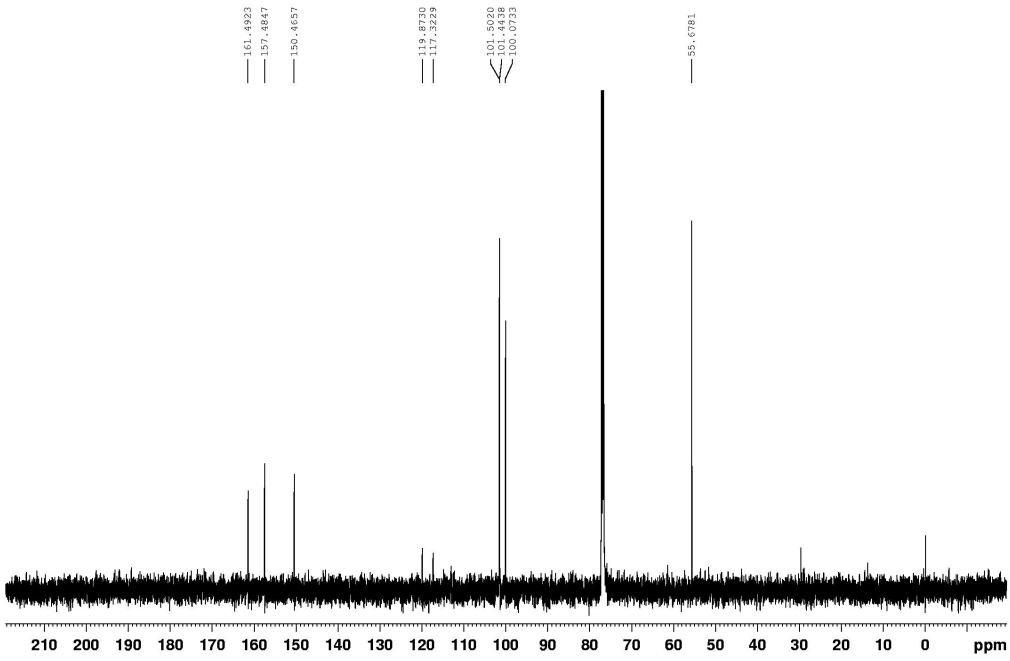




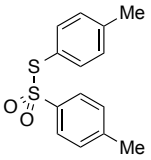
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **5** ($CDCl_3$)

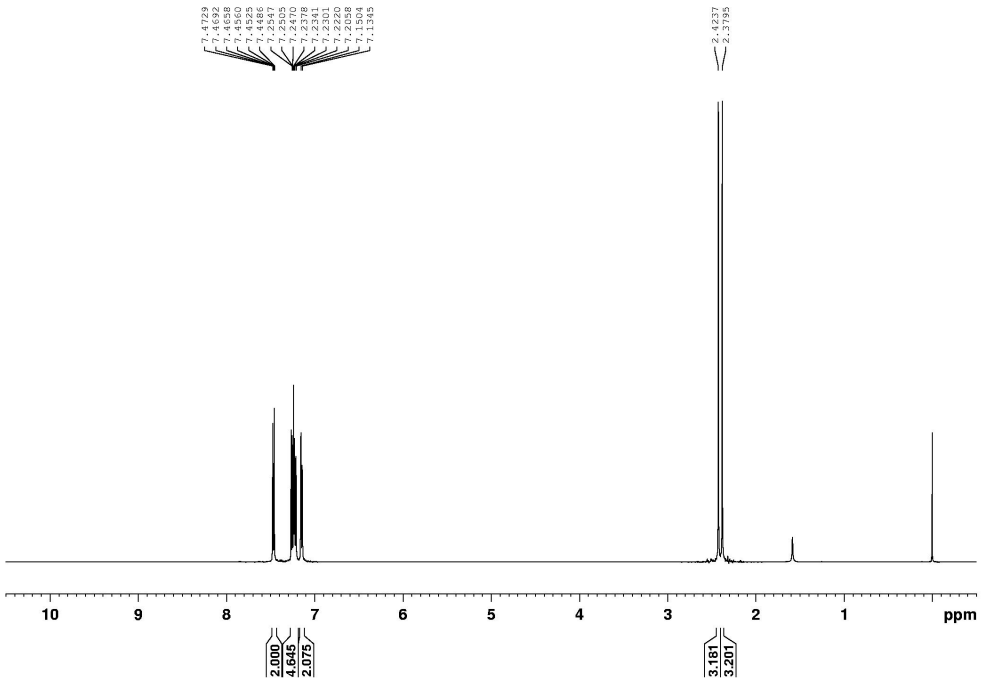


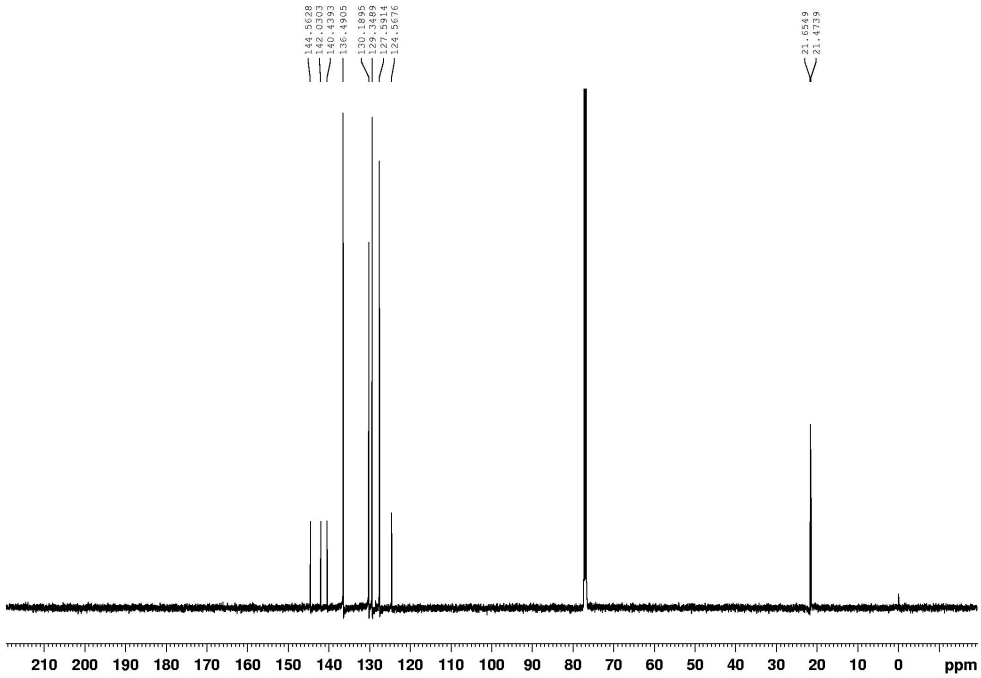




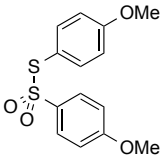
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6a** ($CDCl_3$)

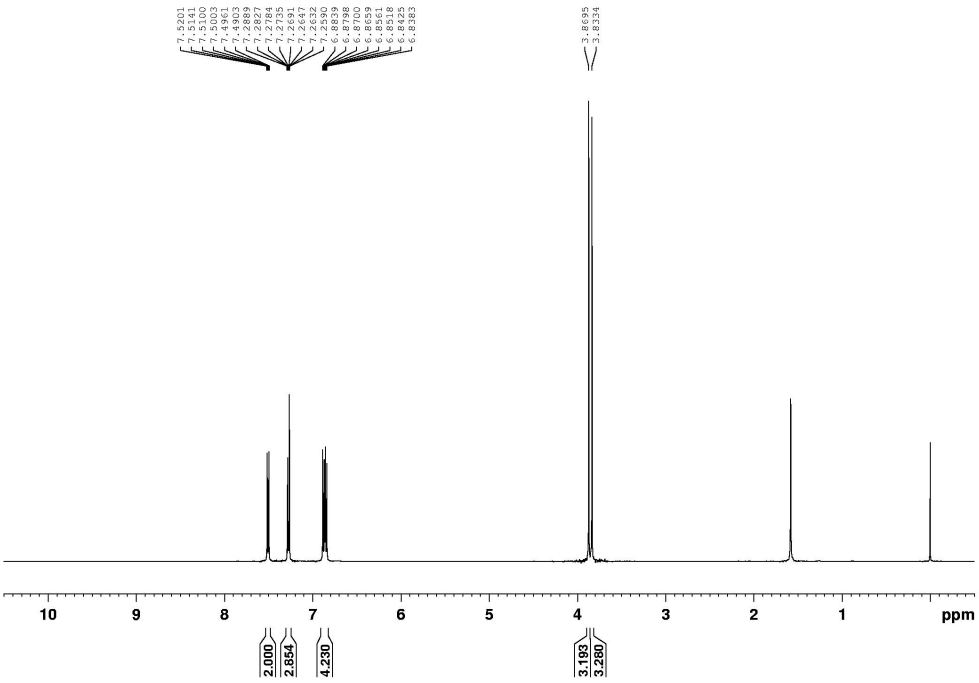


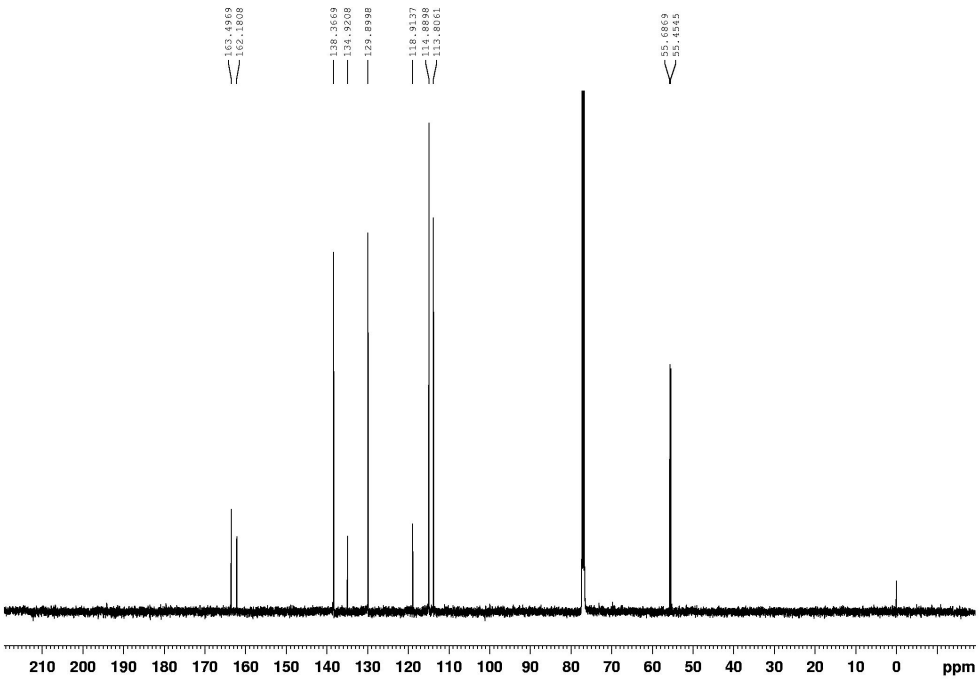




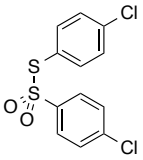
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6b** ($CDCl_3$)

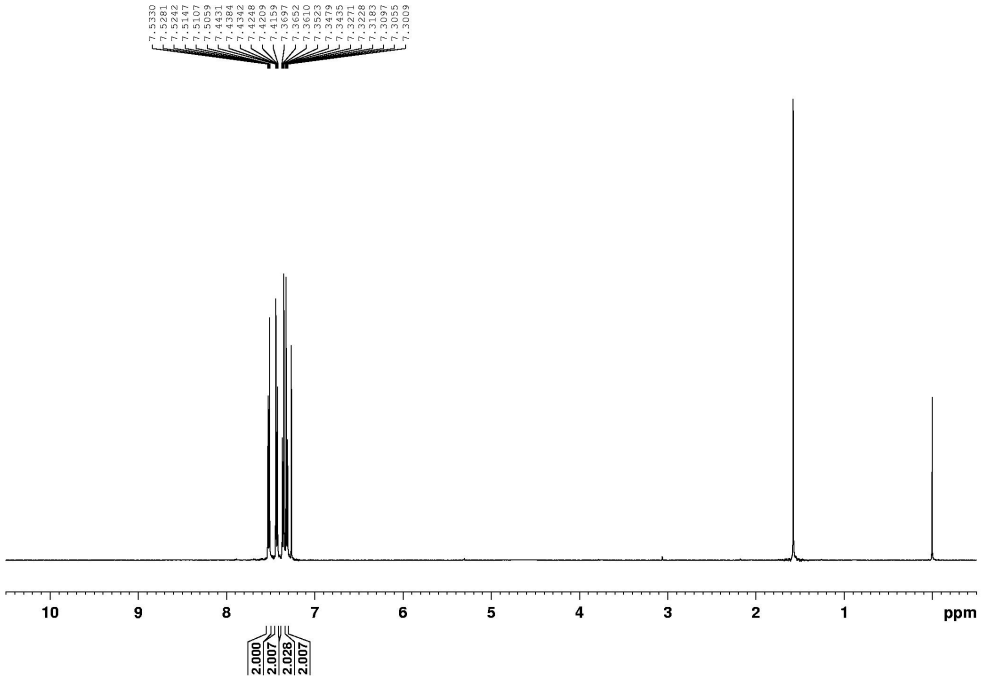


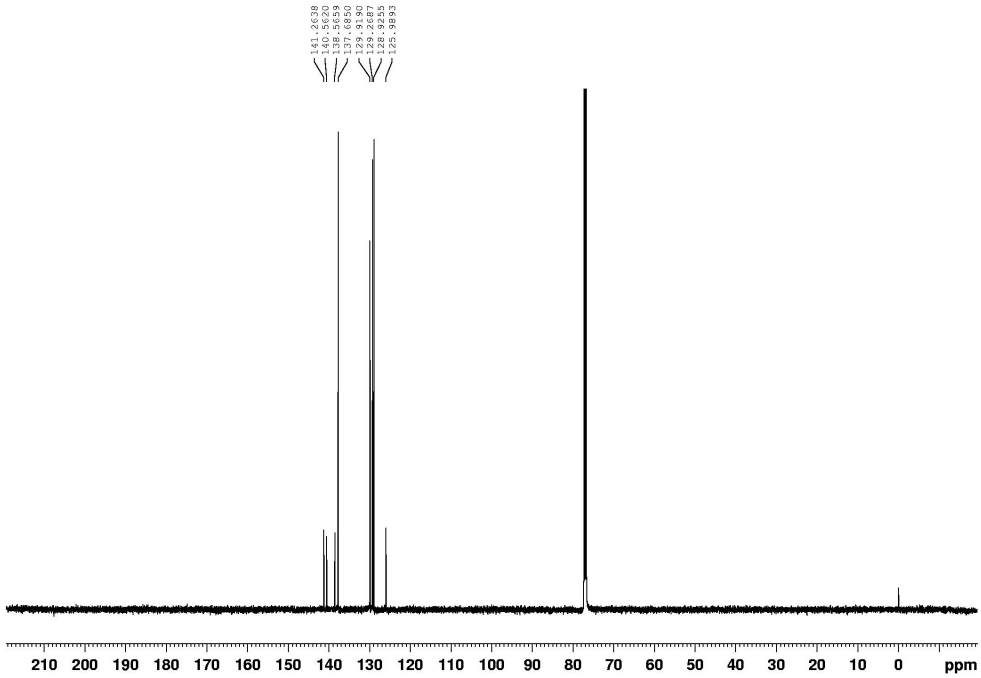




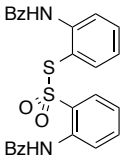
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6c** ($CDCl_3$)

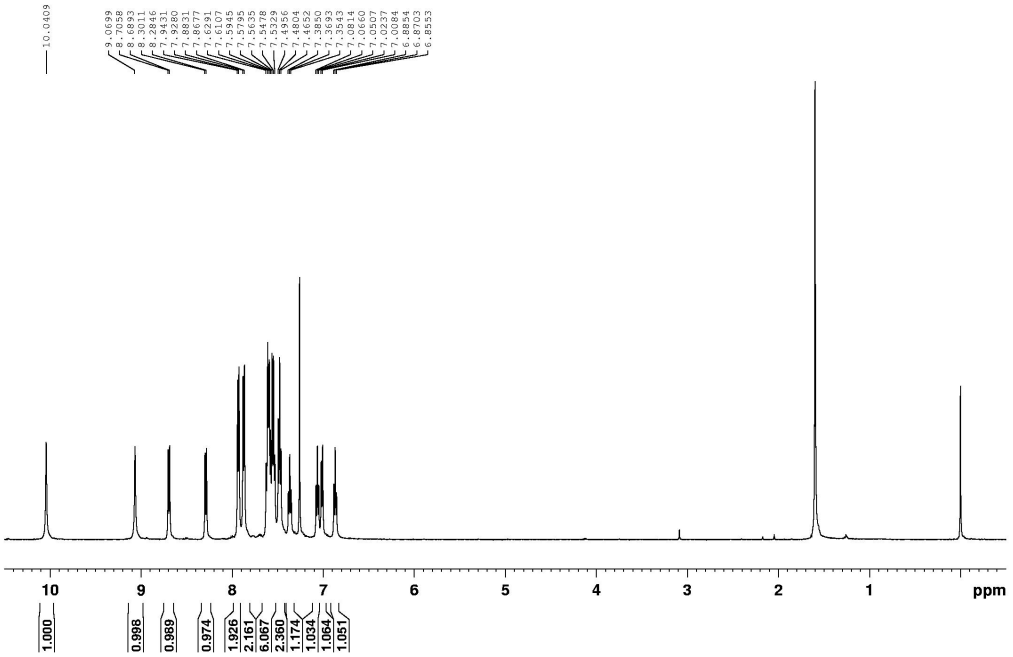


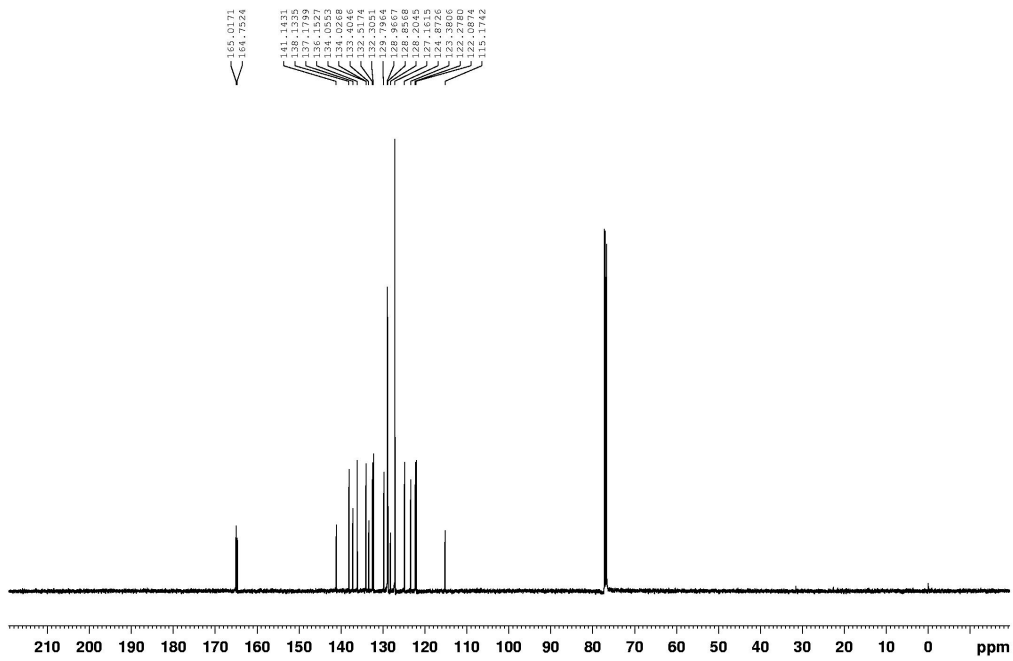




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6d** ($CDCl_3$)







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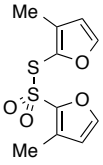
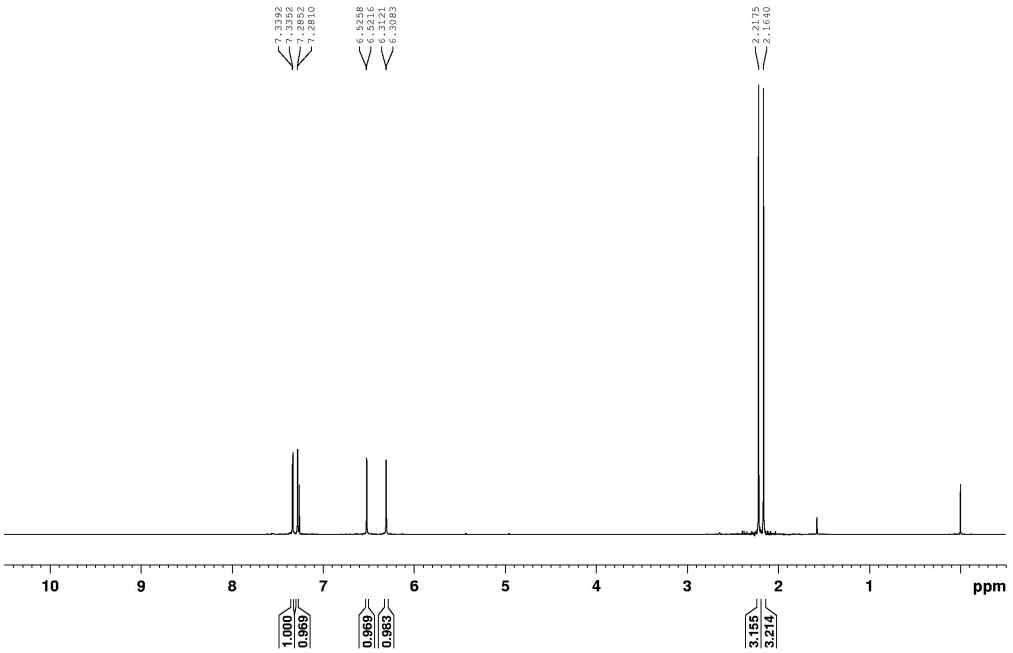
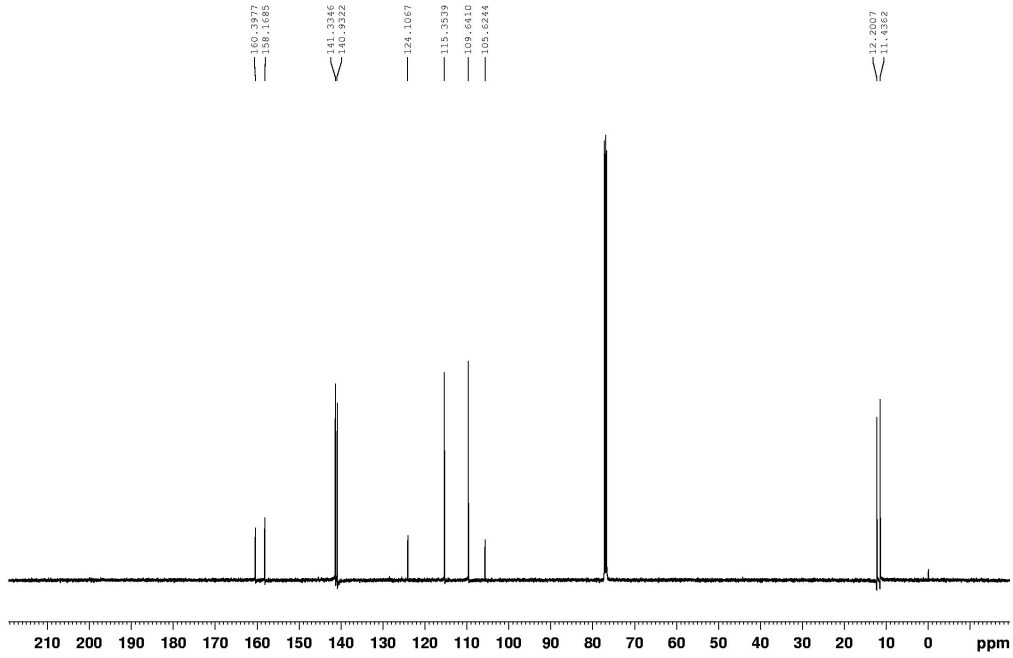
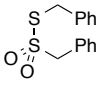
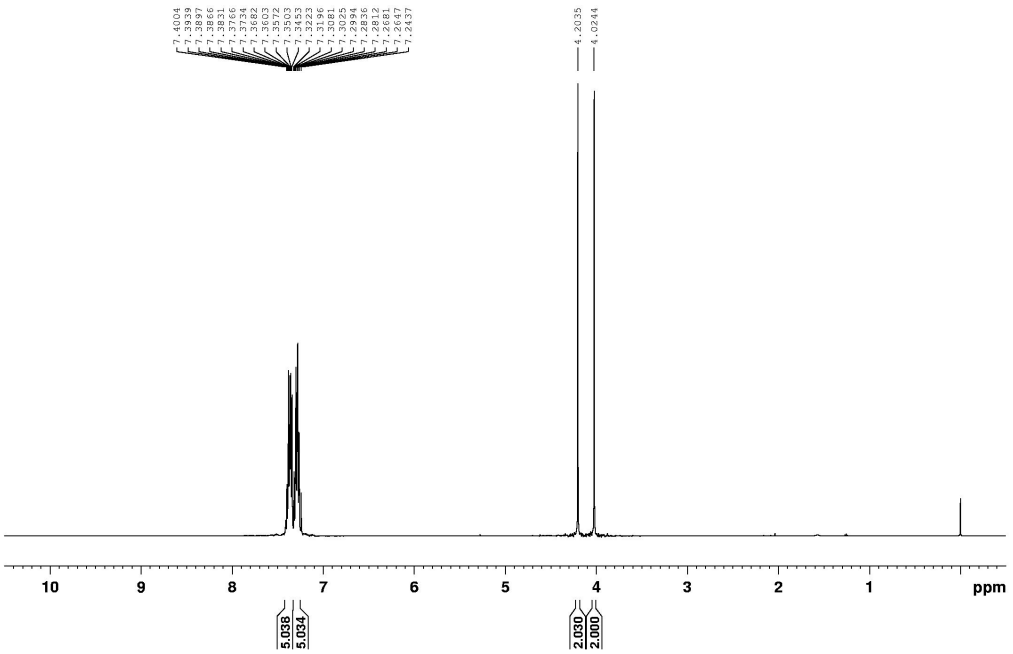


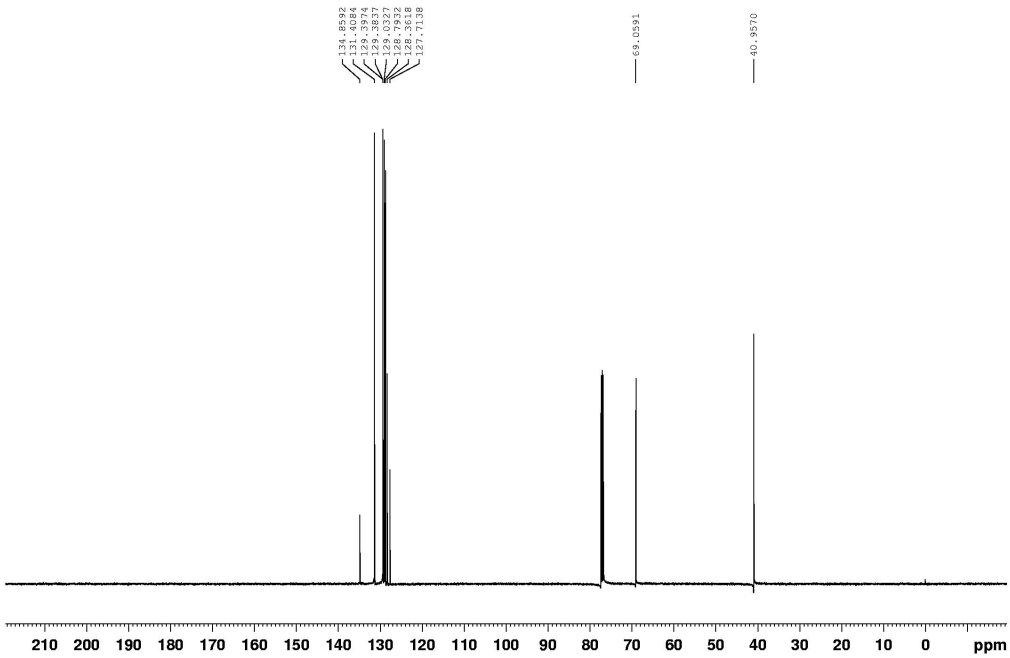




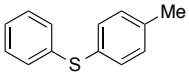
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **6f** ($CDCl_3$)

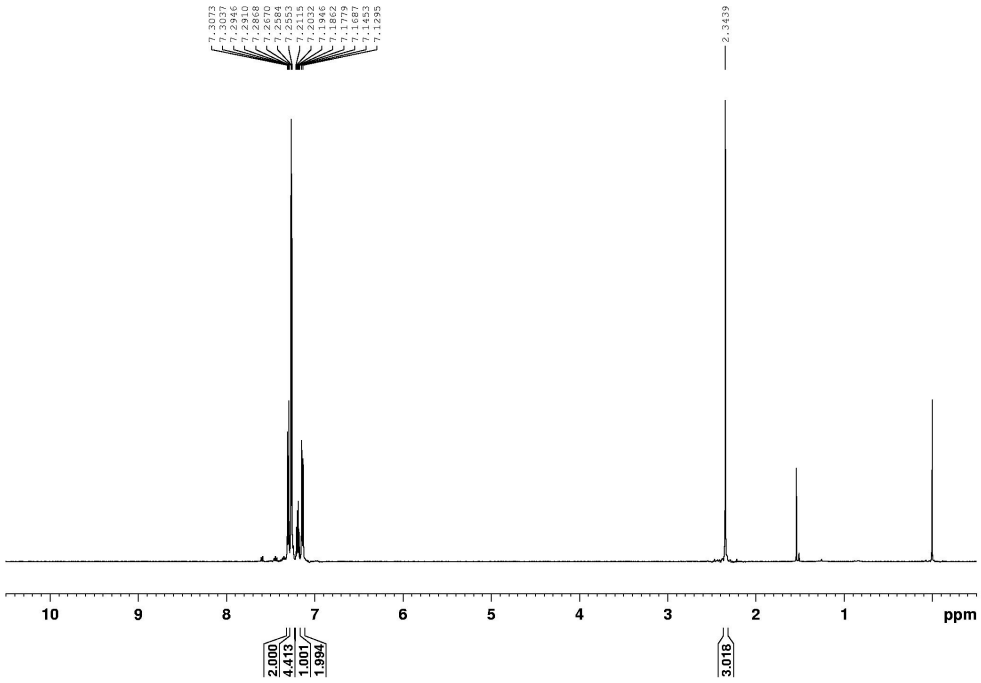


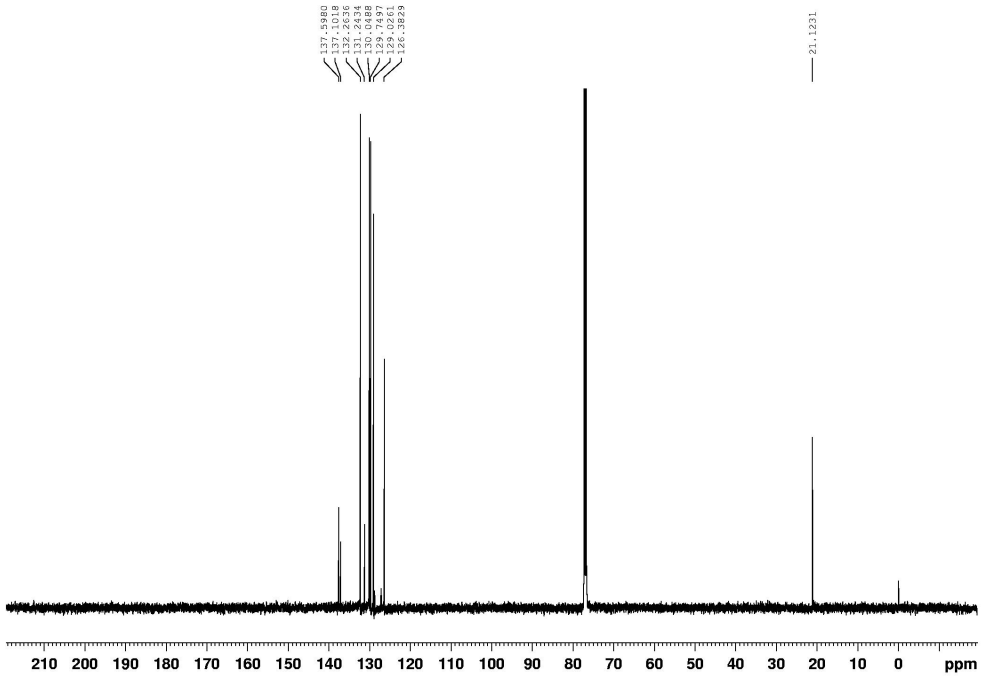




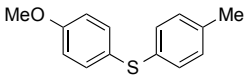
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8a** ($CDCl_3$)

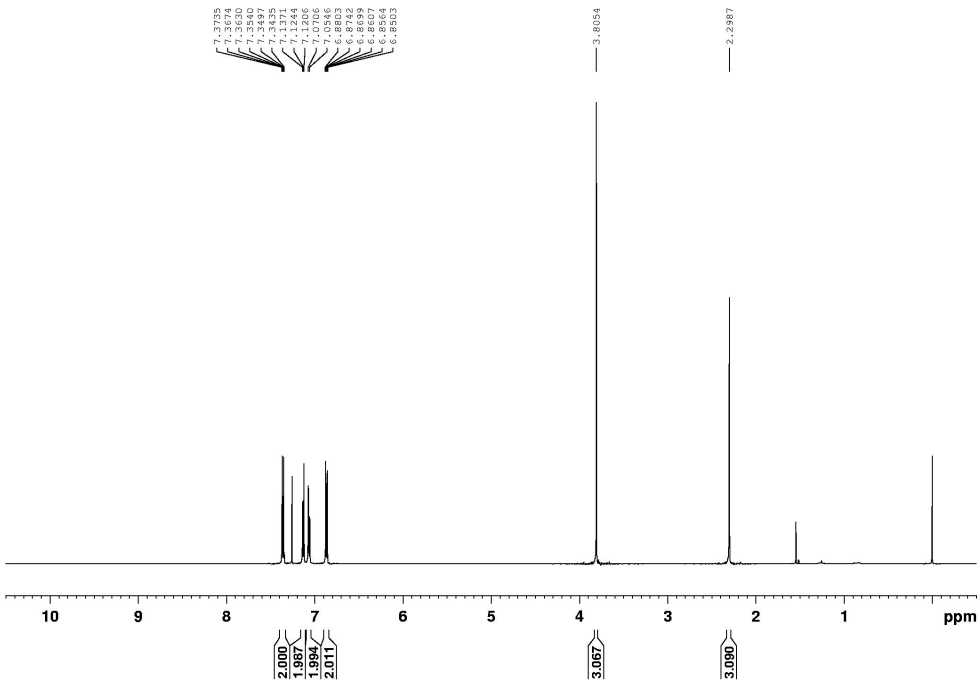


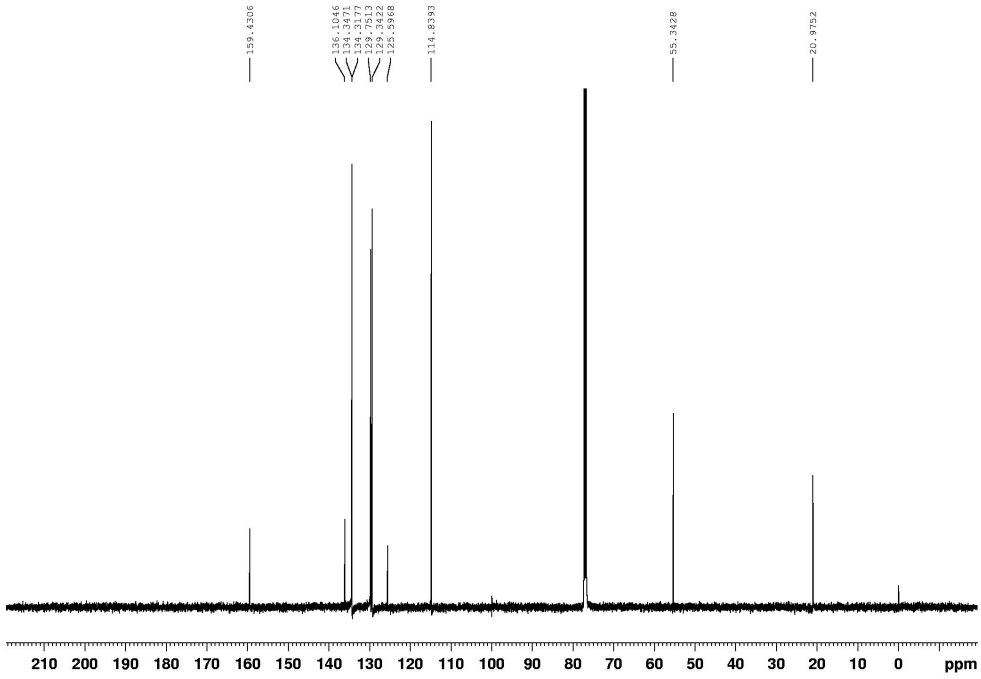




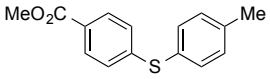
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8b** ($CDCl_3$)

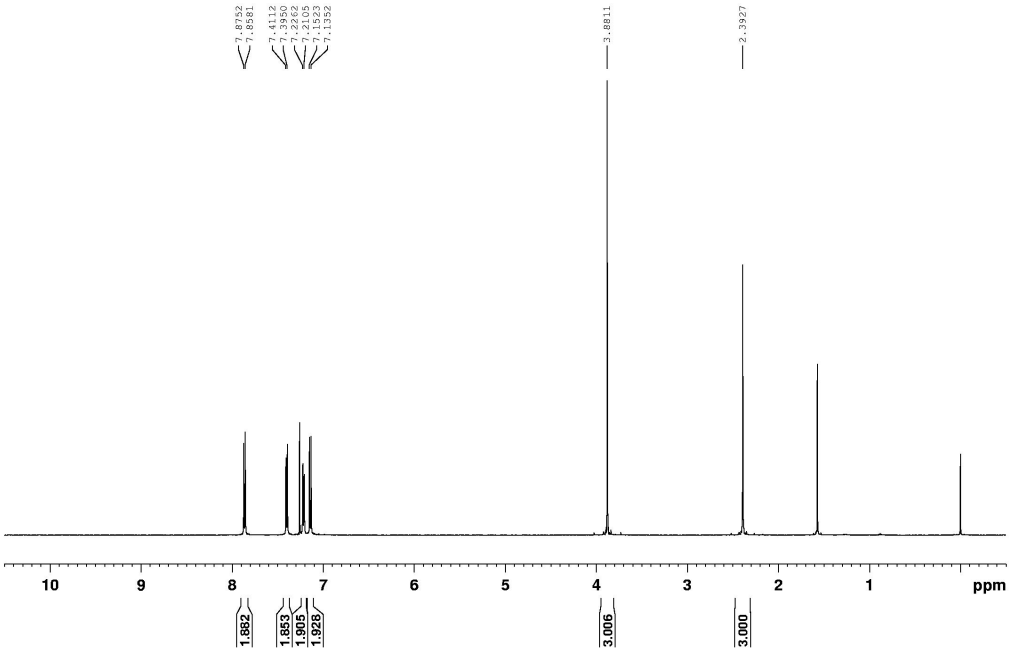


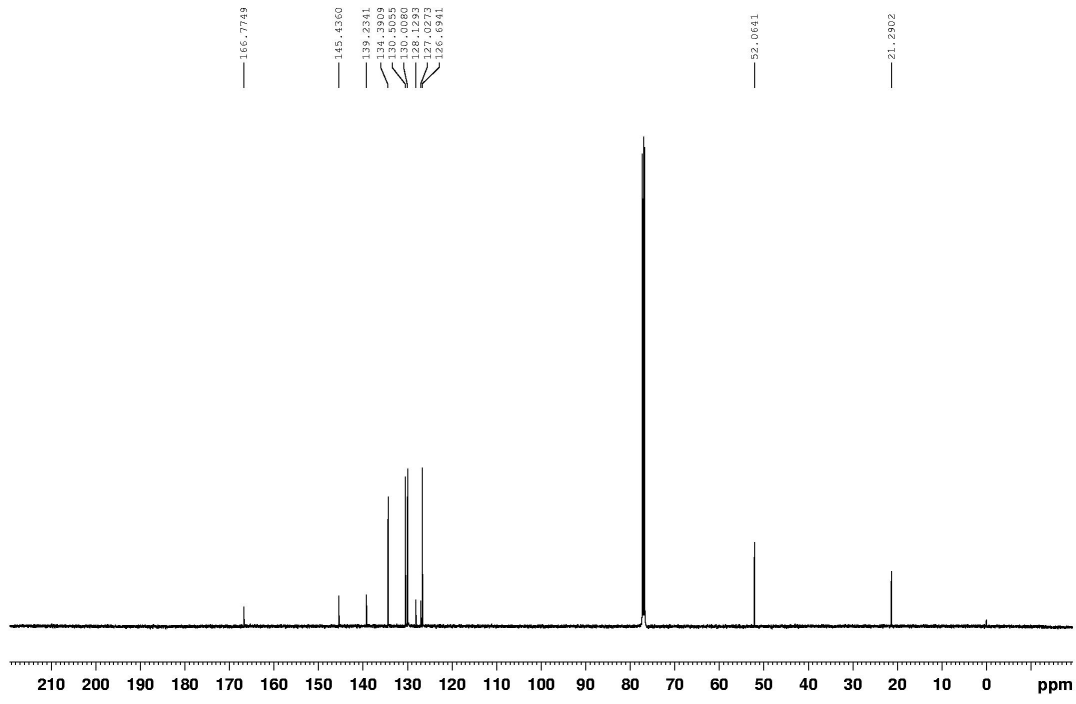




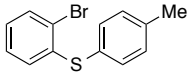
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8c** ($CDCl_3$)

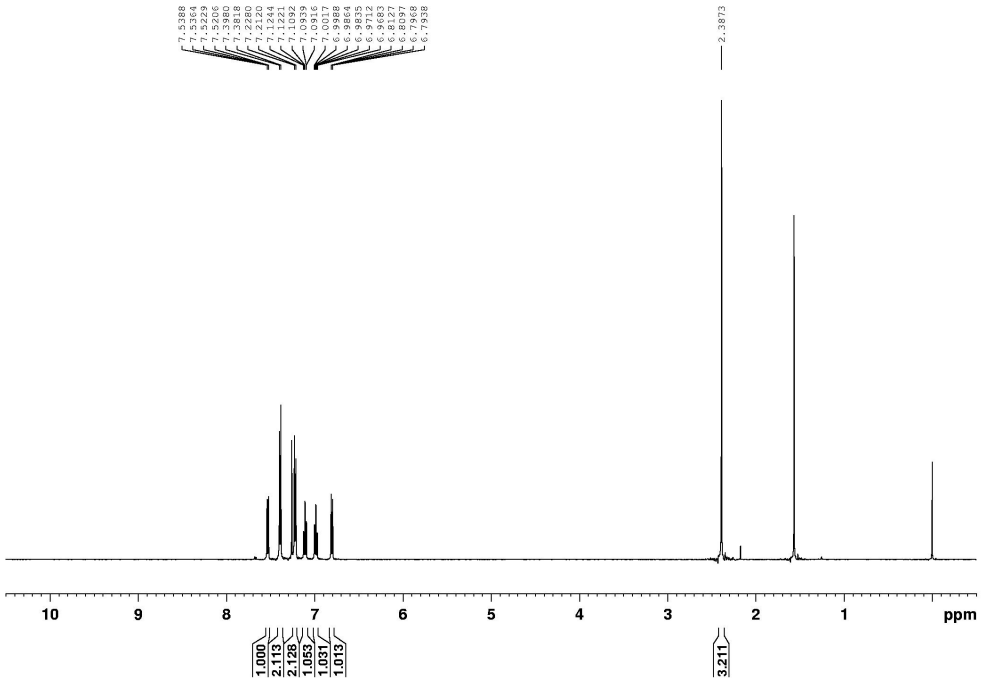


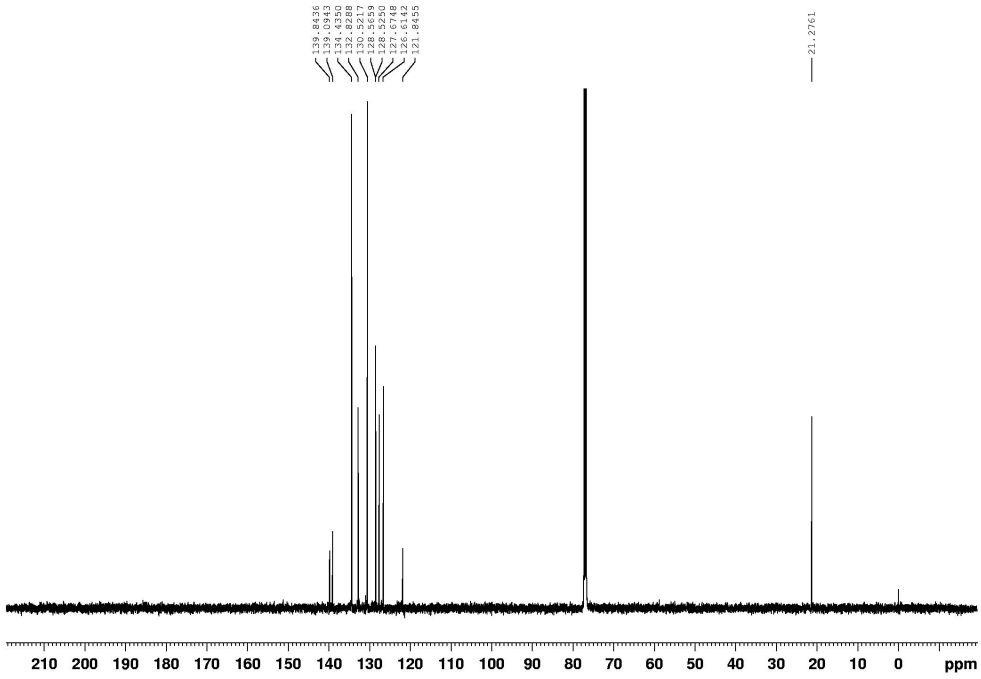




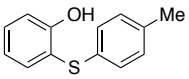
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8d** ($CDCl_3$)

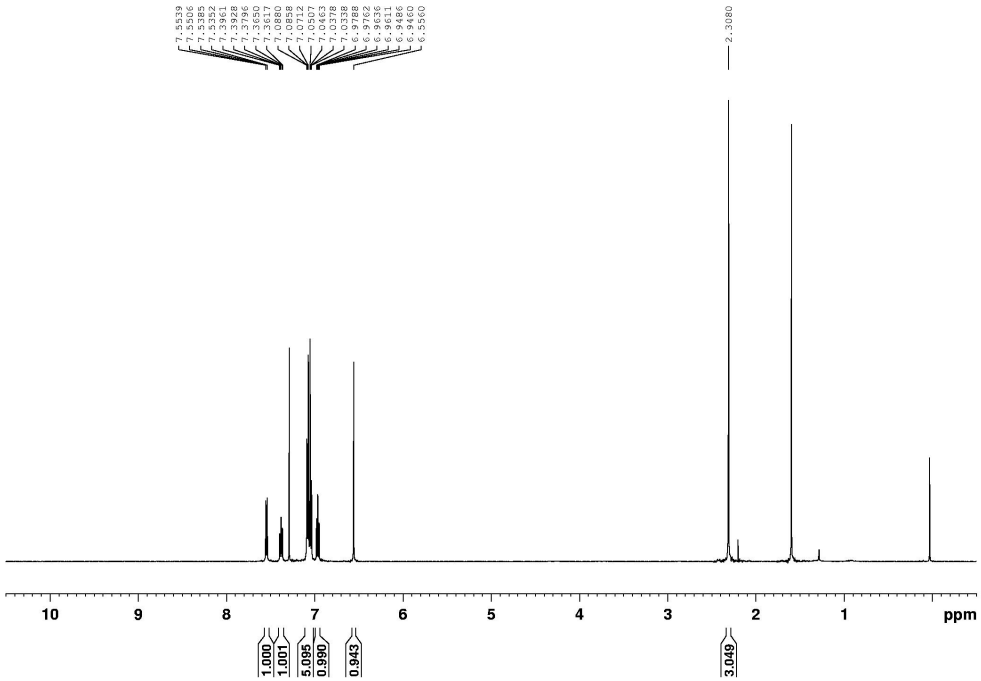


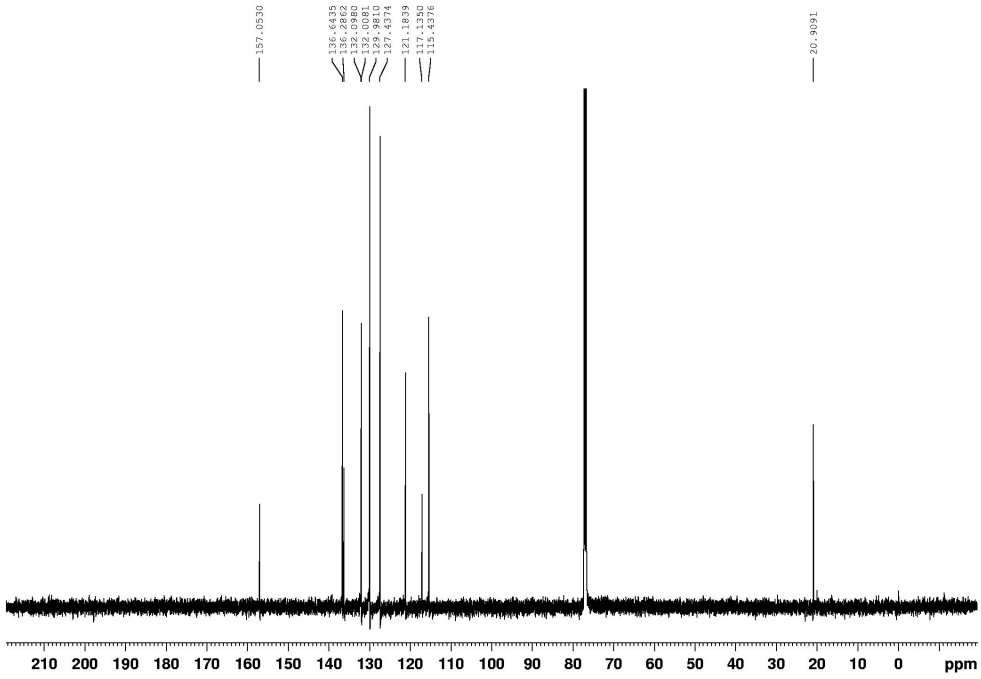




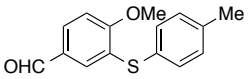
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8e** ($CDCl_3$)

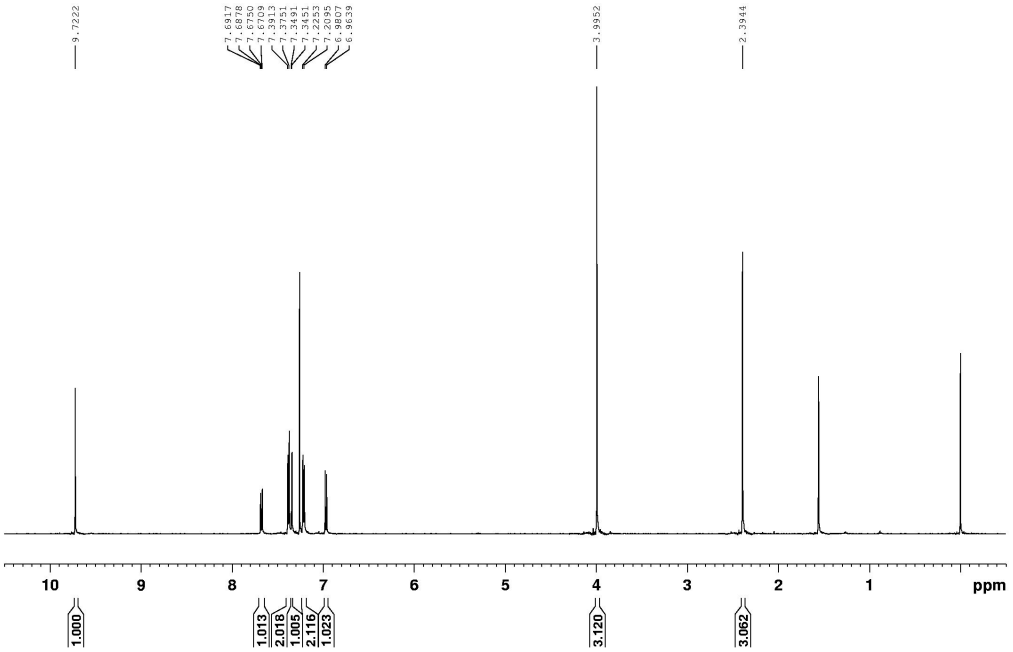


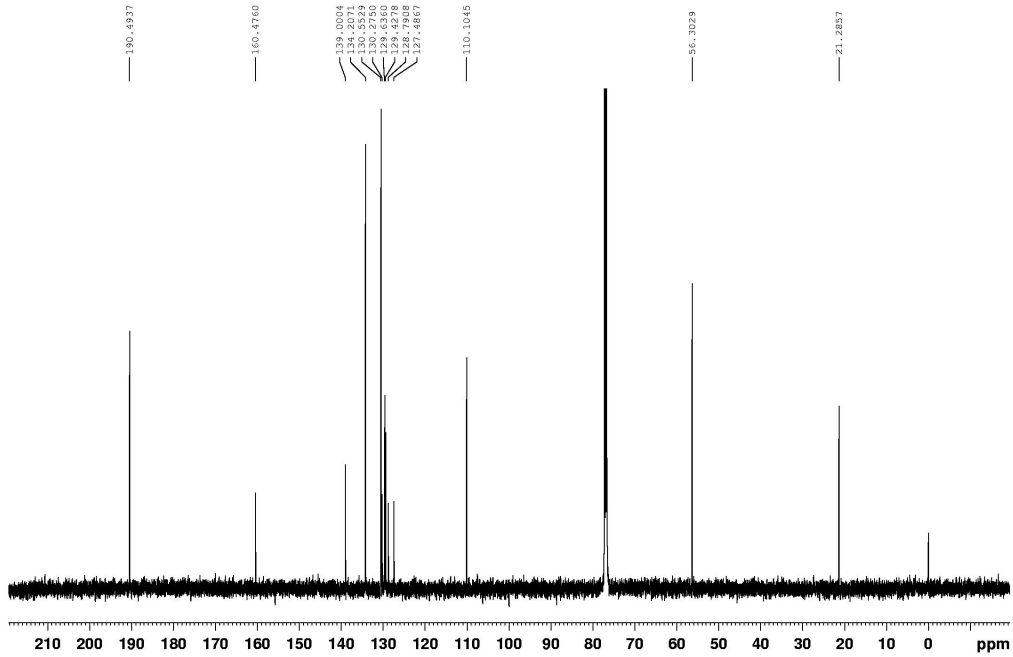




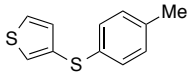
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8f** ($CDCl_3$)

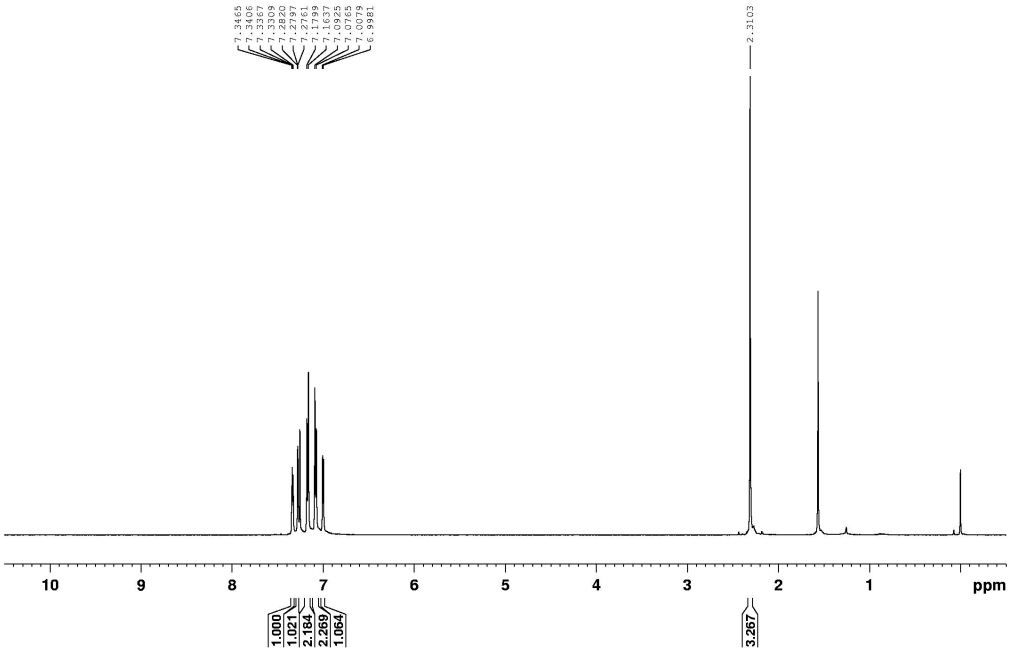


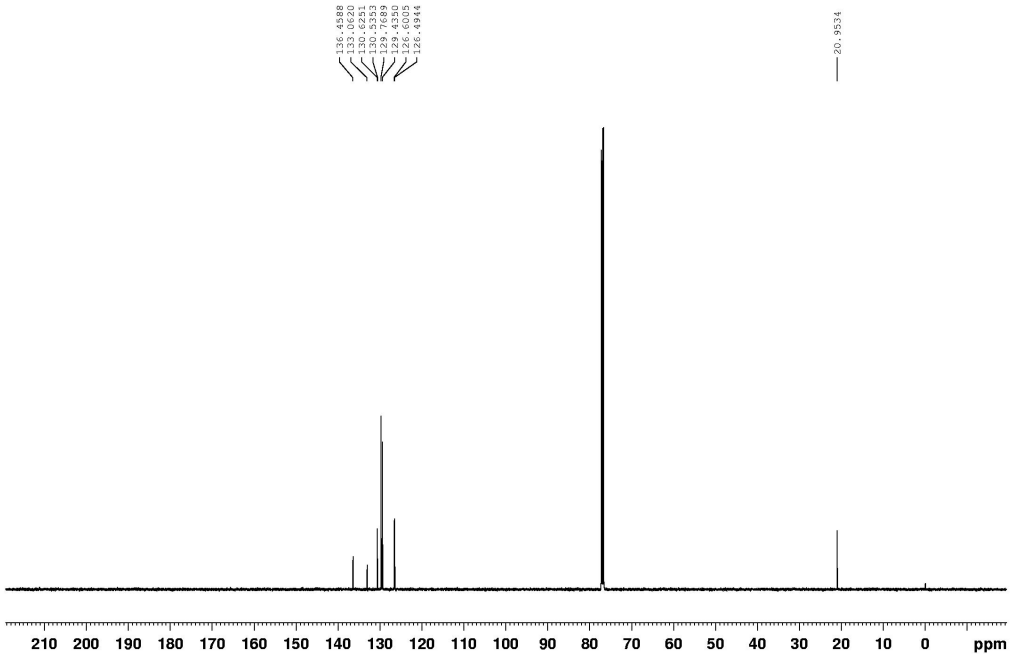




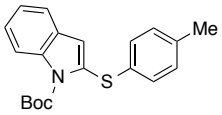
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8g** ($CDCl_3$)

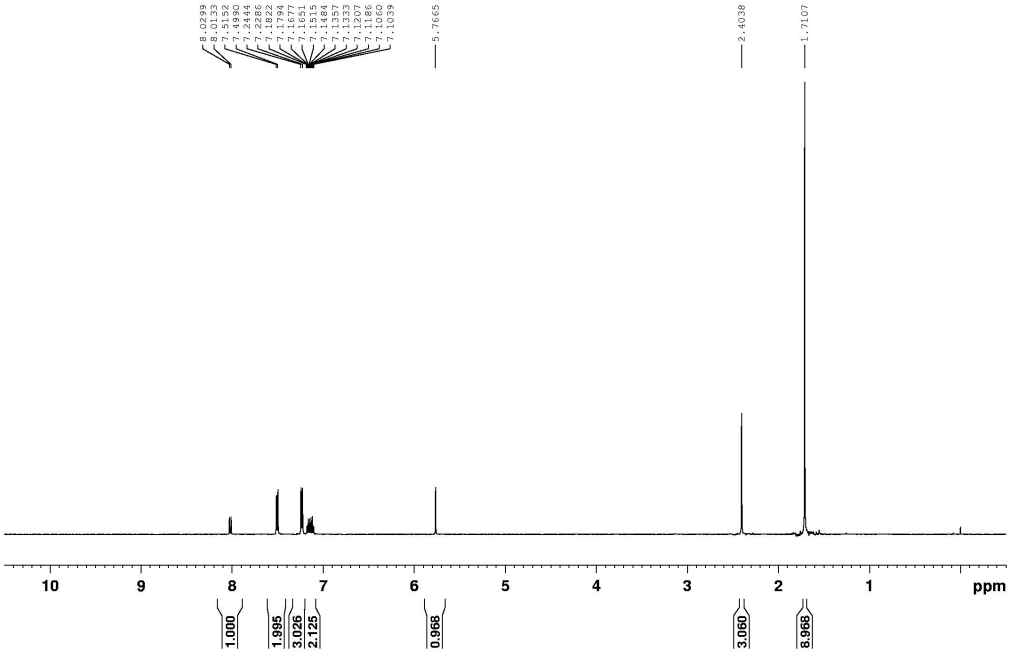


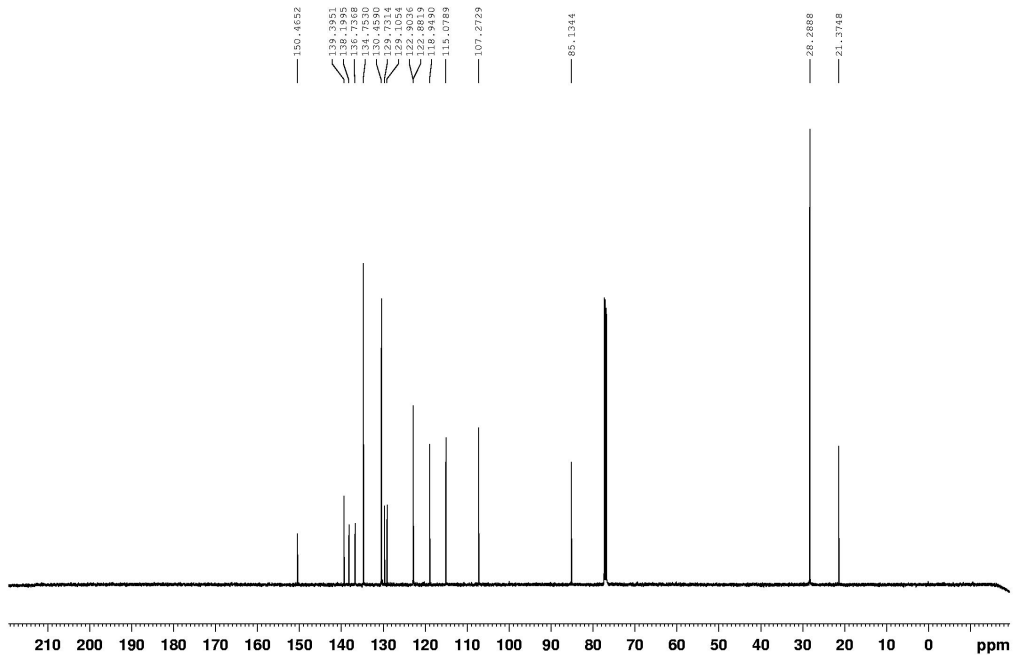




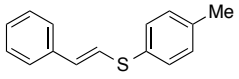
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8h** ($CDCl_3$)

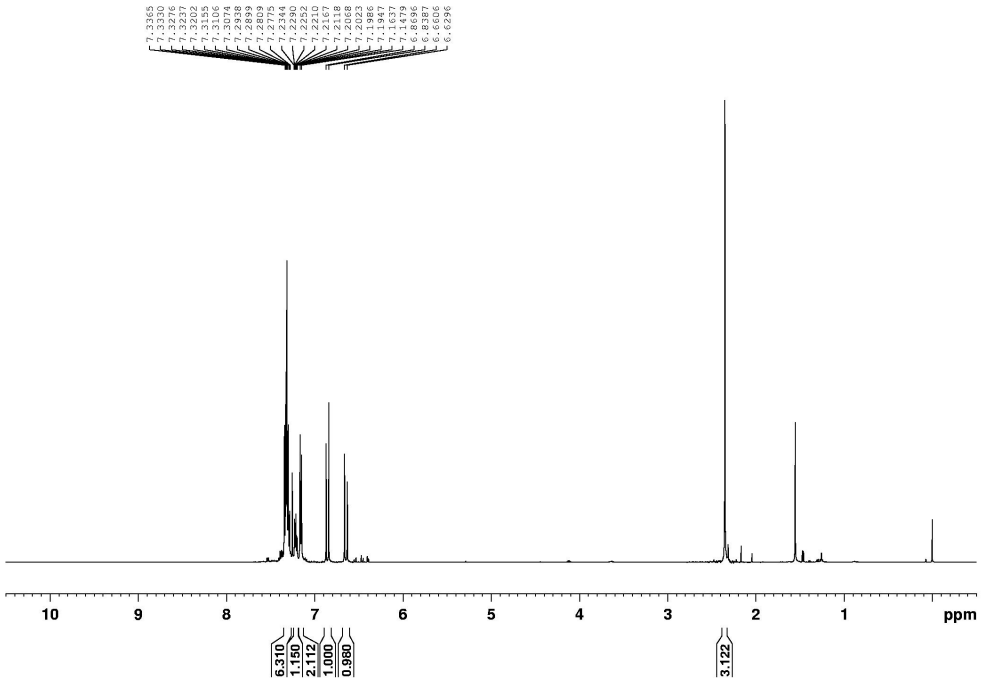


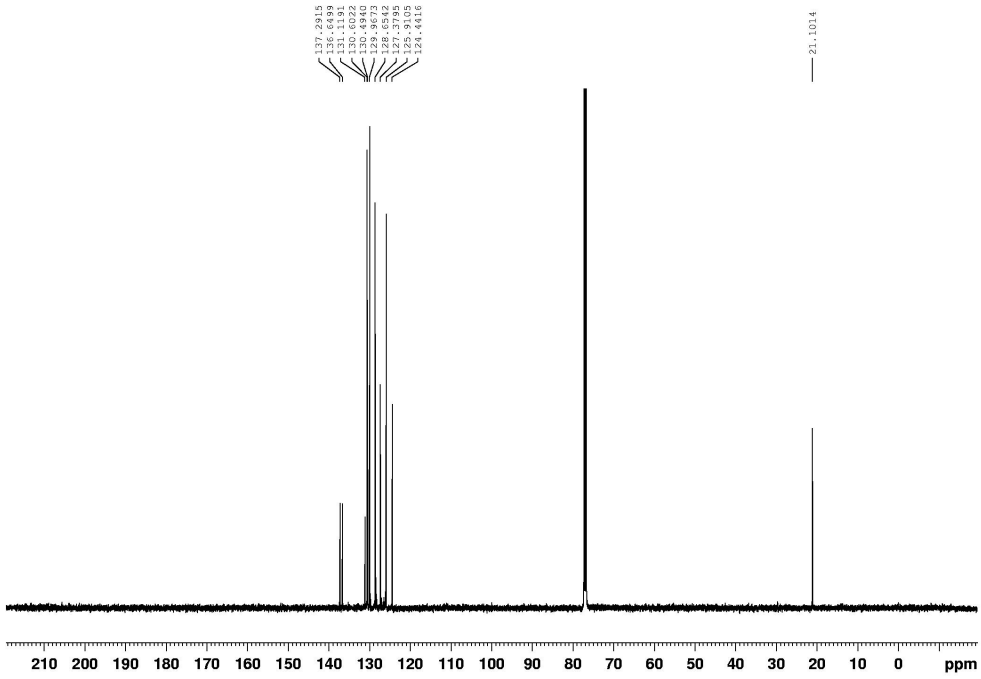




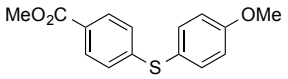
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8i** ($CDCl_3$)

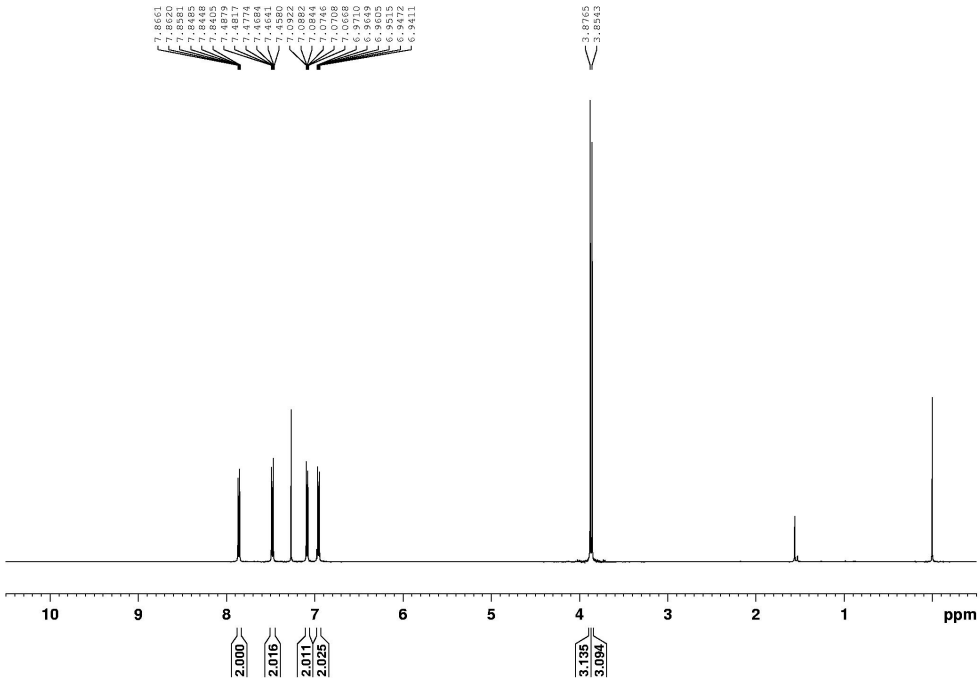


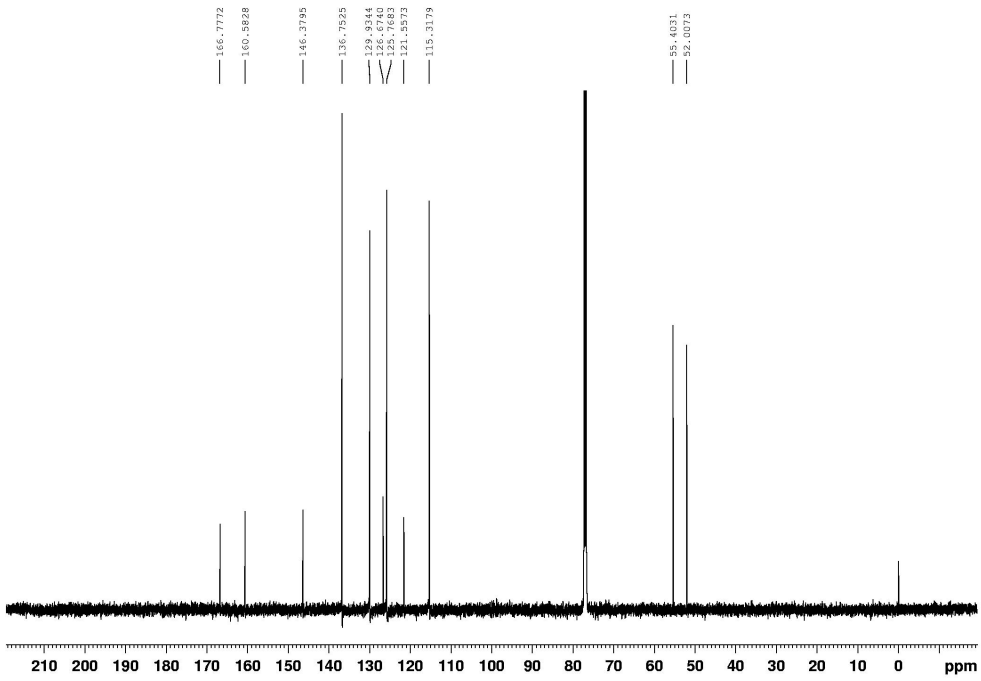




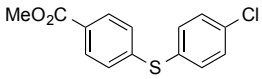
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8k** ($CDCl_3$)

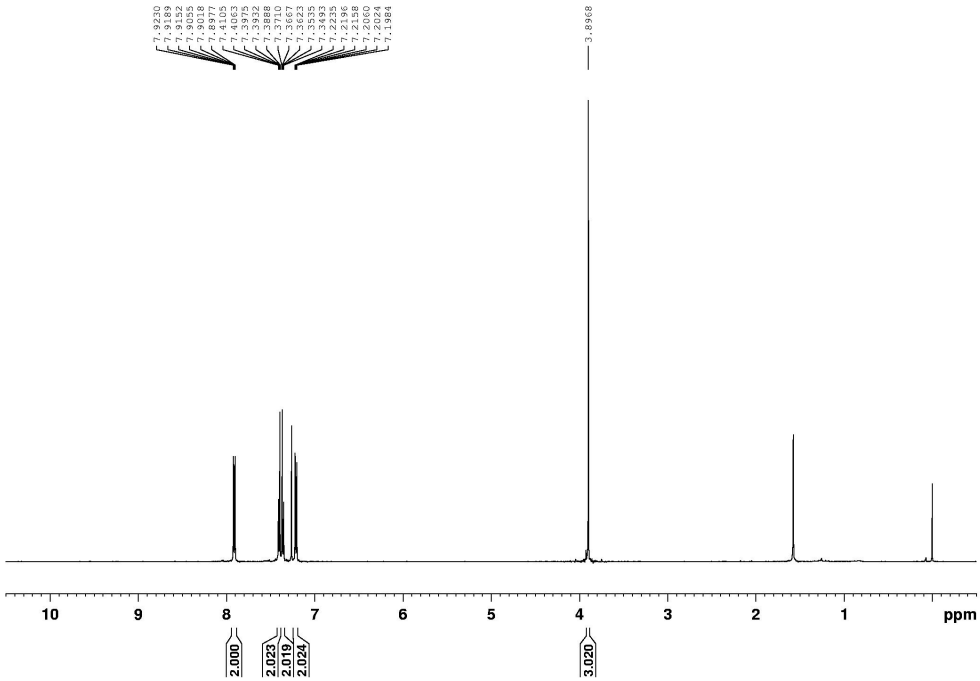


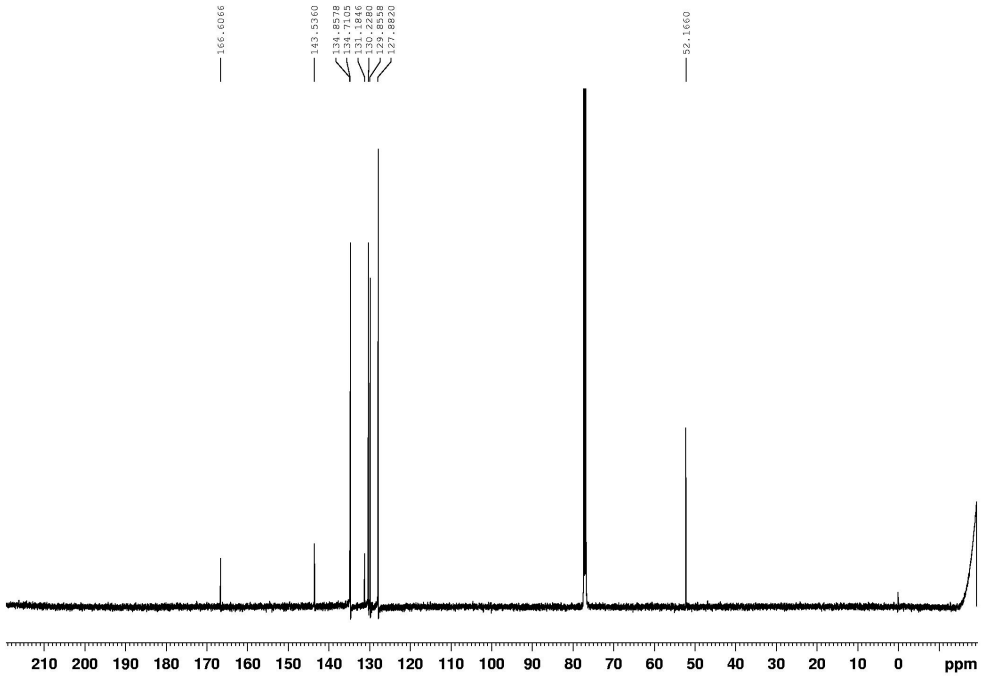




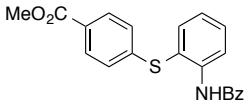
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8l** ($CDCl_3$)

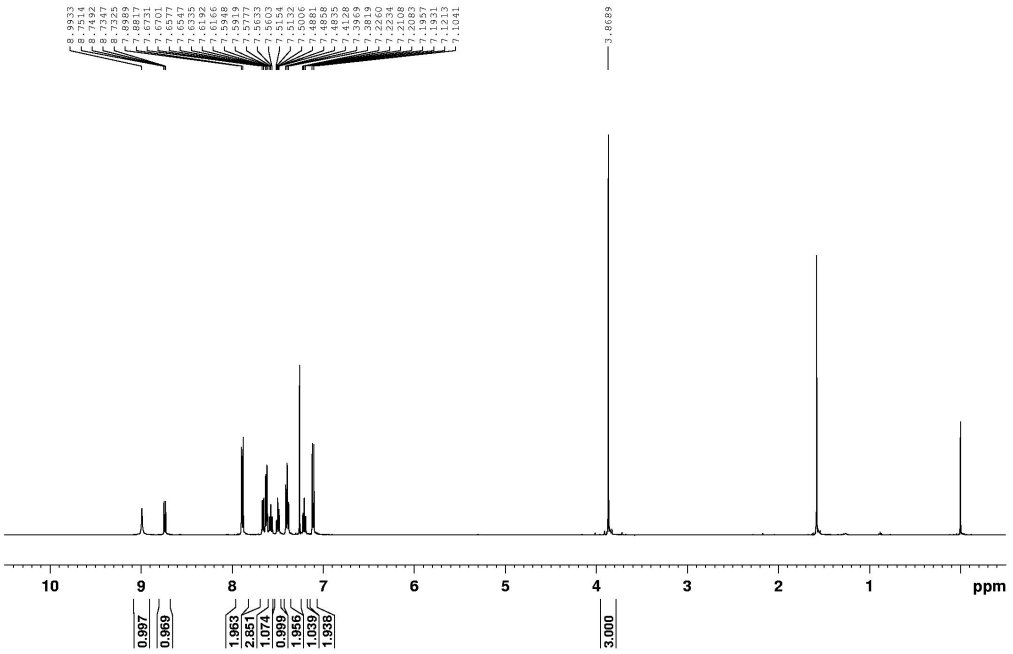


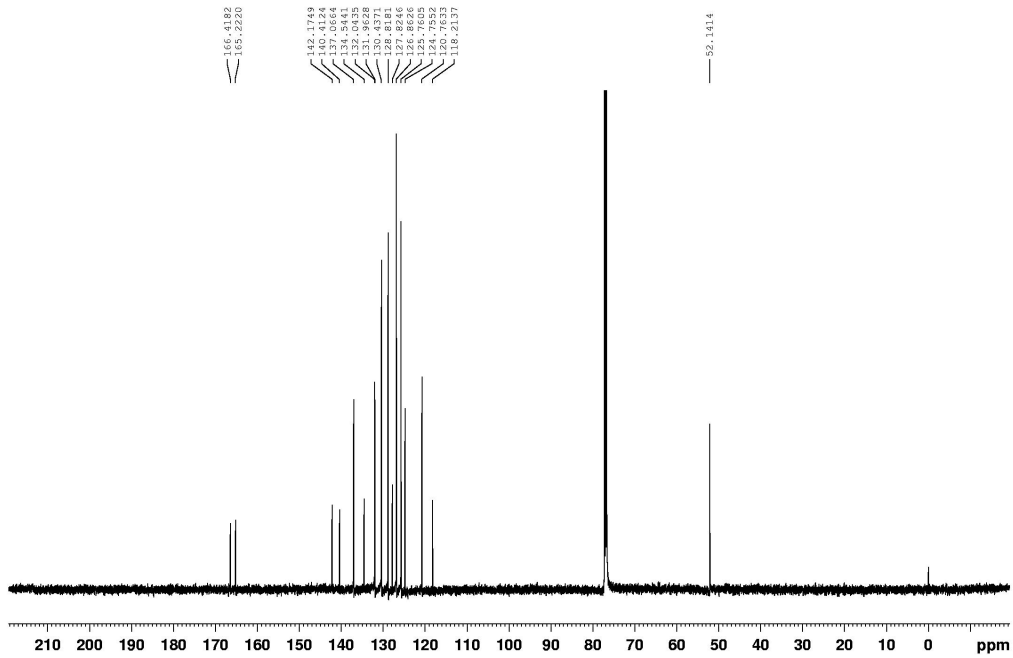




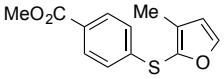
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8m** ($CDCl_3$)

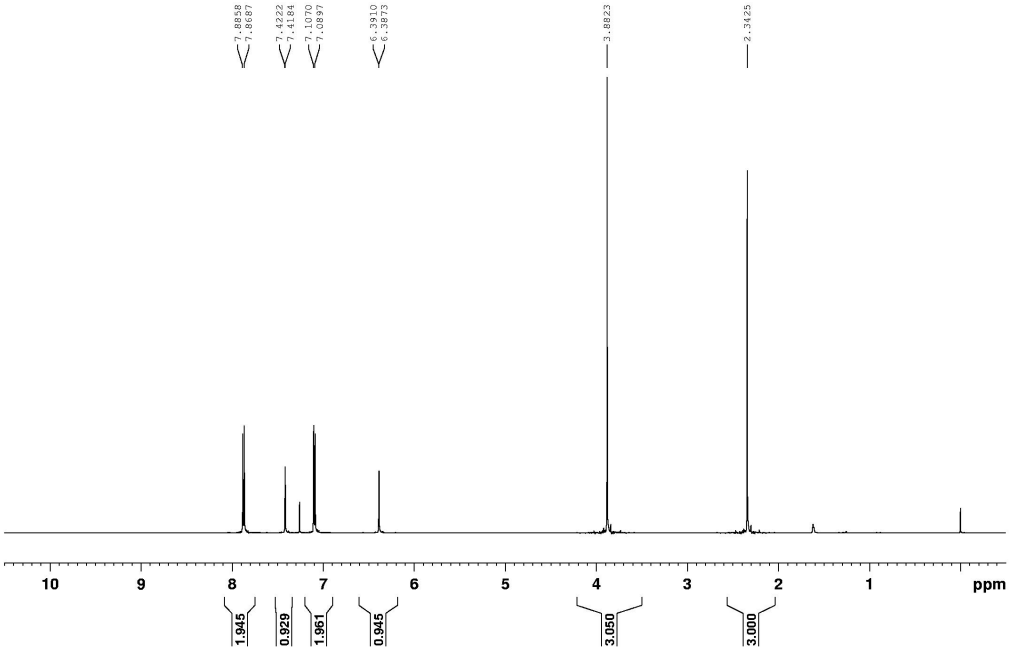


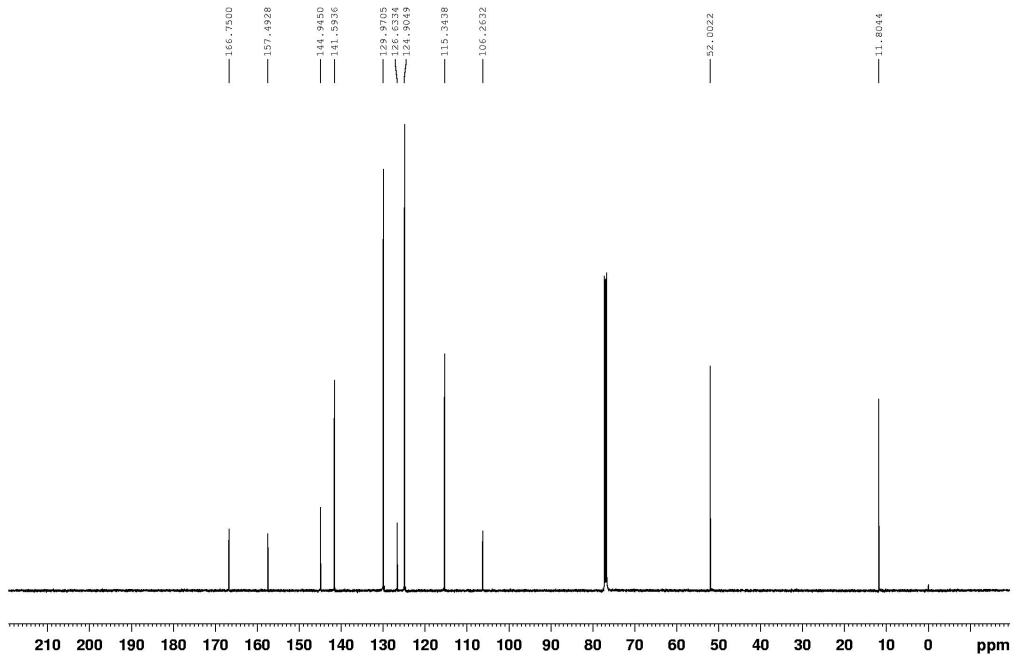




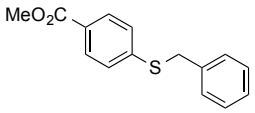
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8n** ($CDCl_3$)

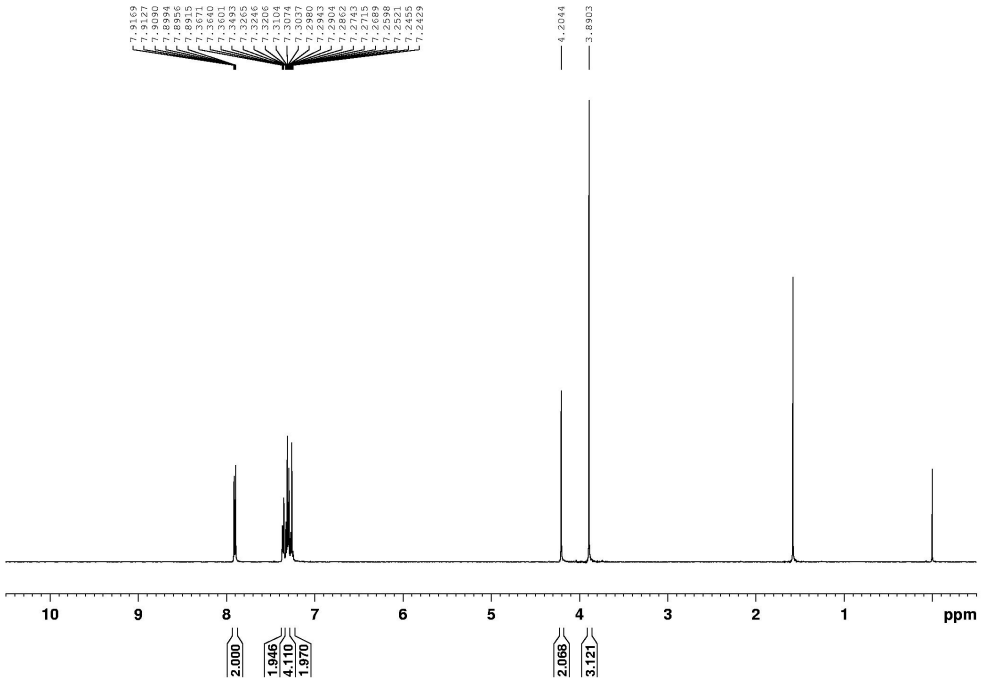


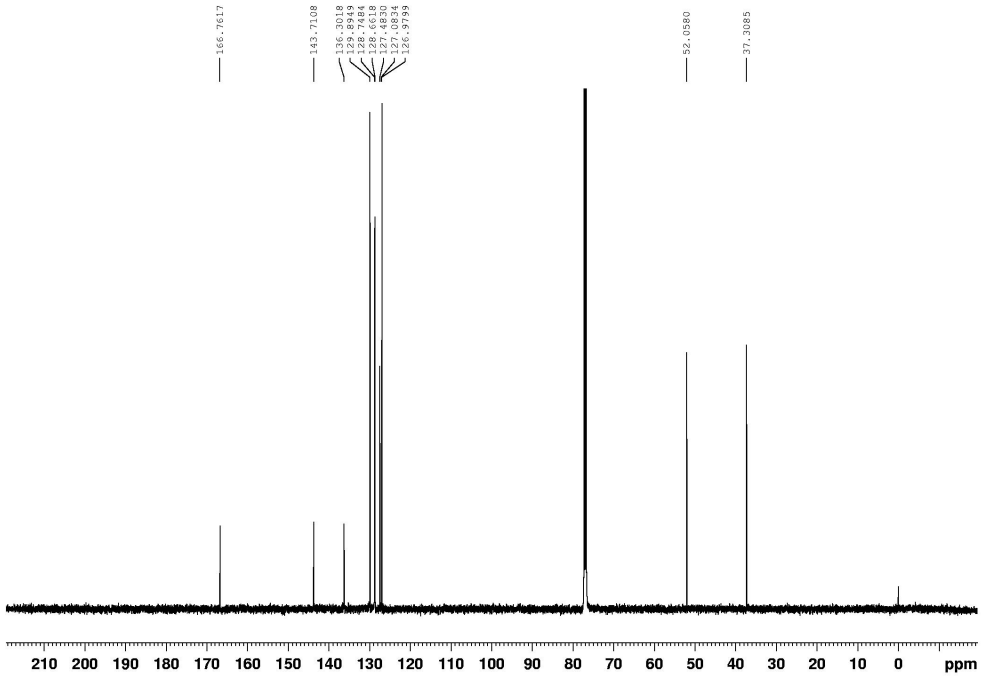




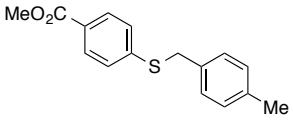
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8o** ($CDCl_3$)

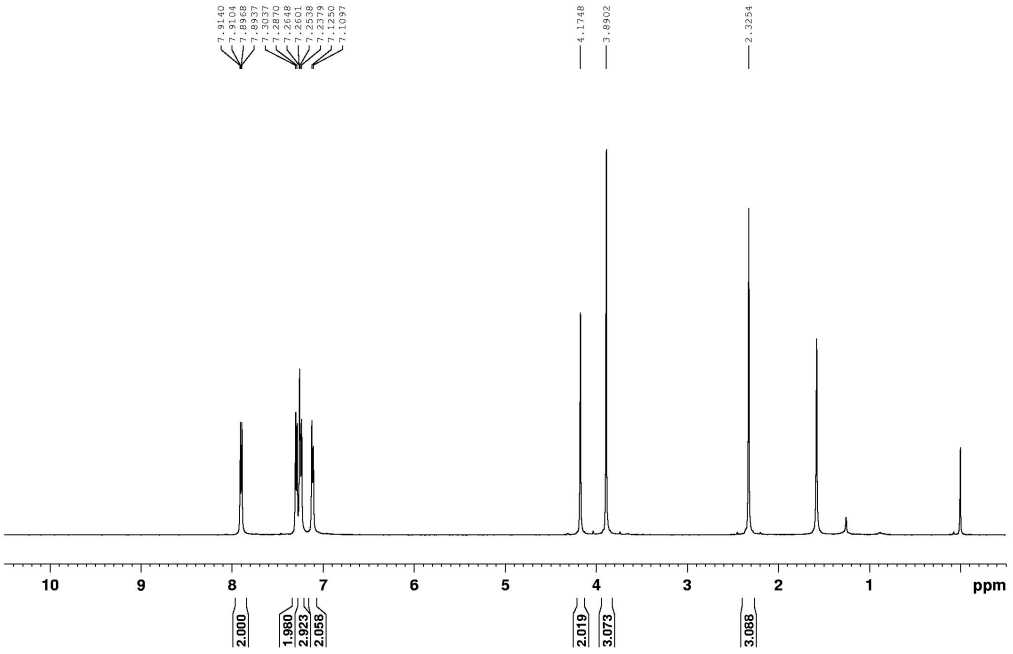


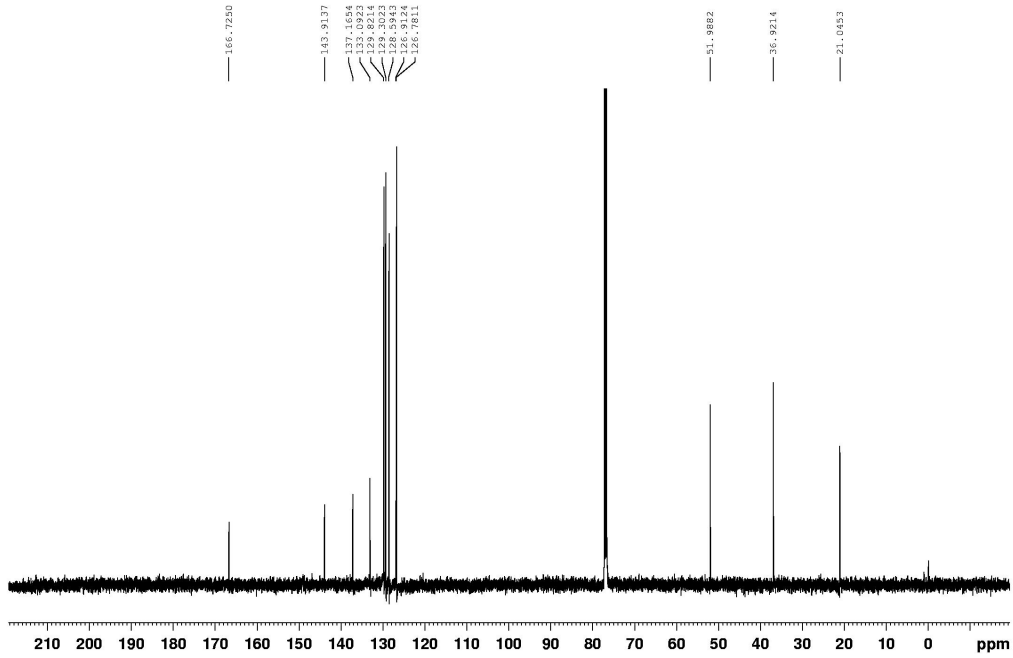




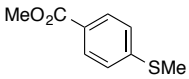
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8p** ($CDCl_3$)

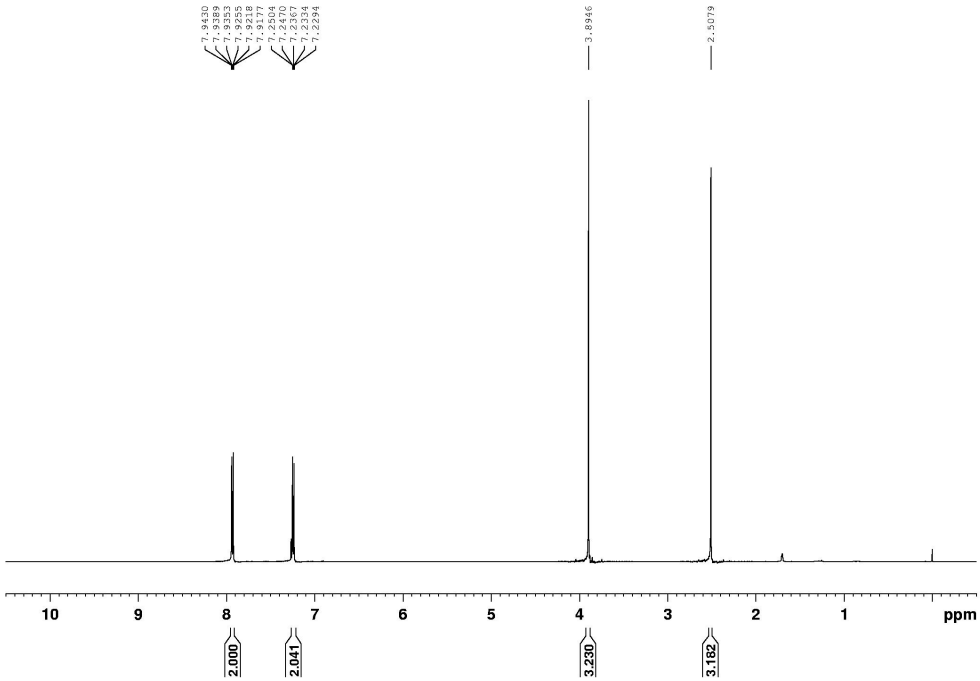


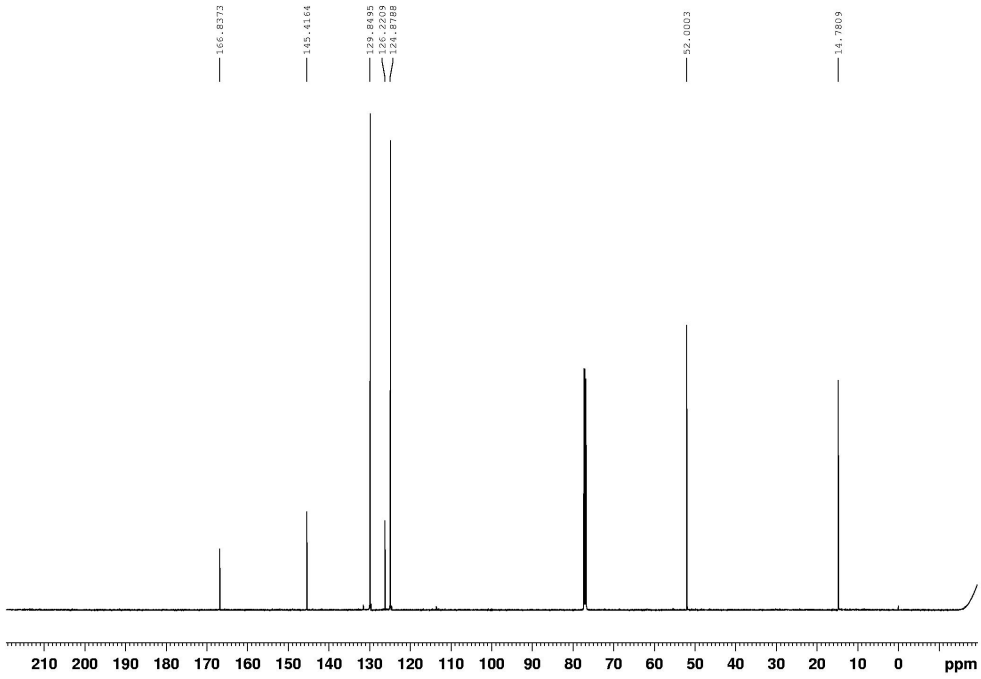




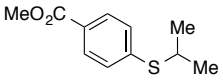
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8q** ($CDCl_3$)

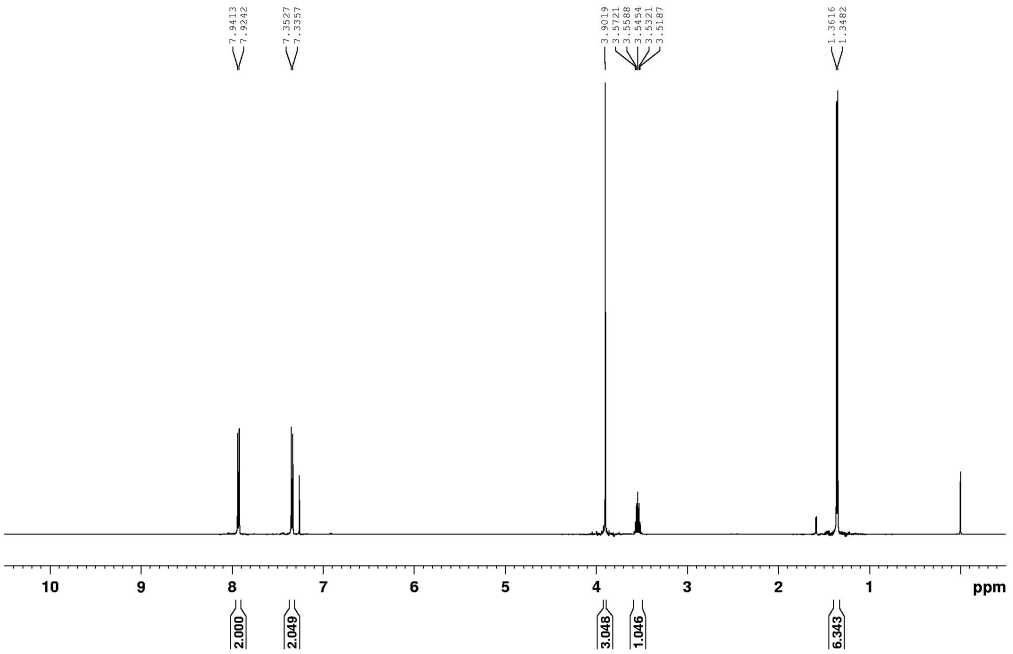


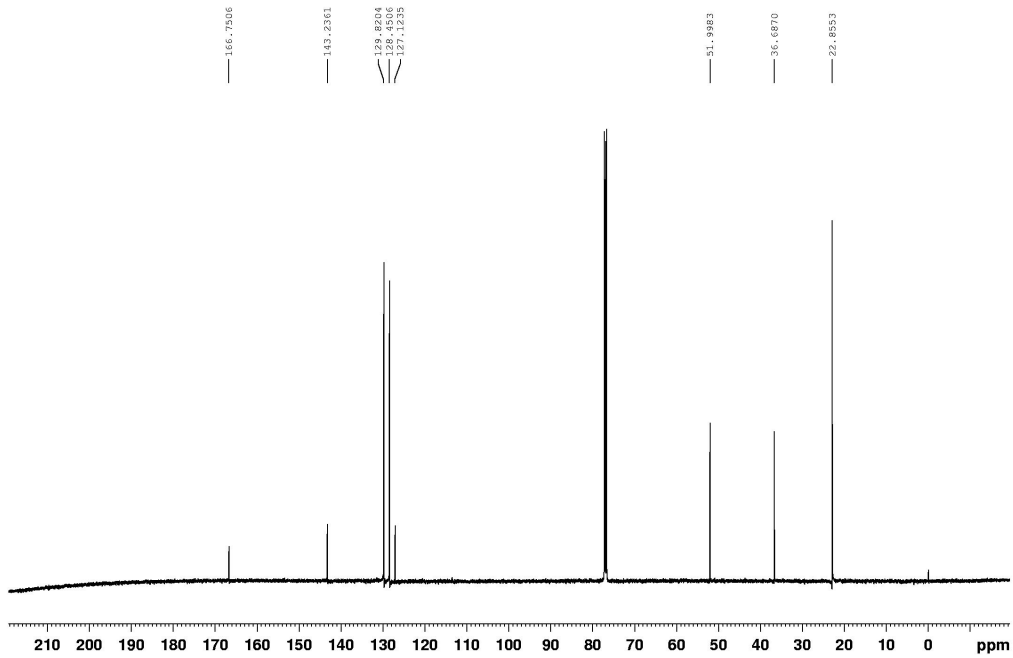




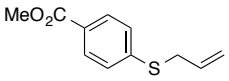
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8r** ($CDCl_3$)

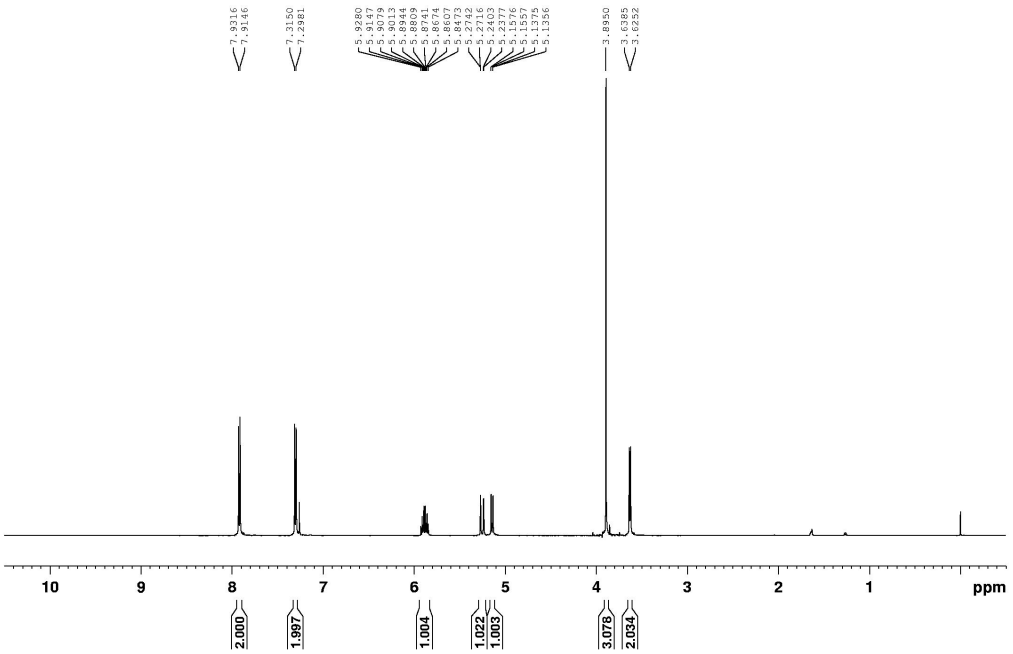


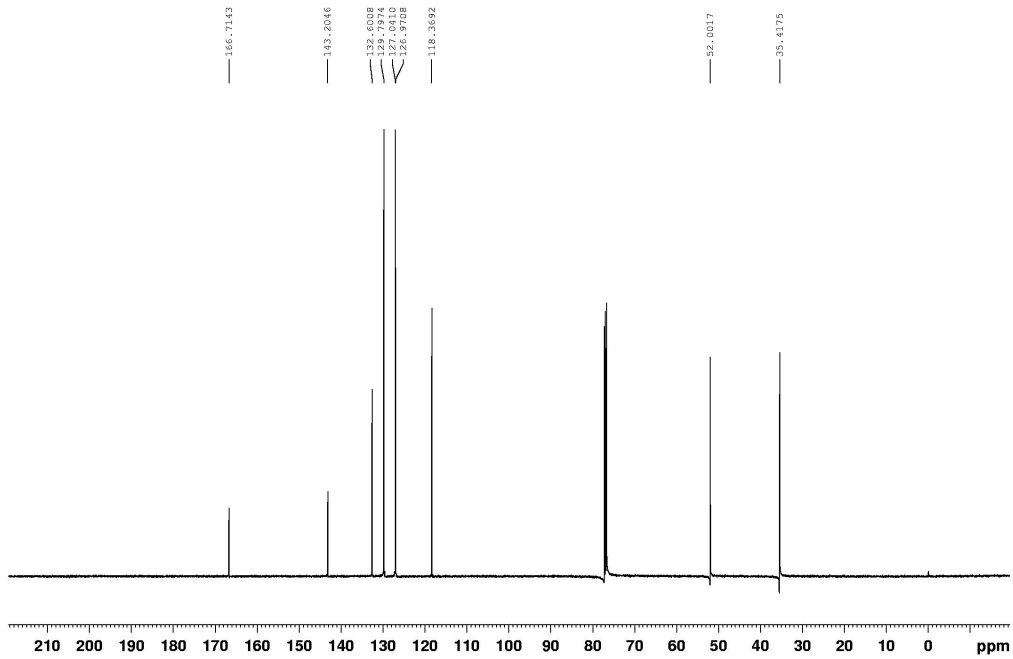




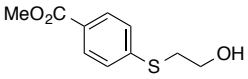
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8s** ($CDCl_3$)

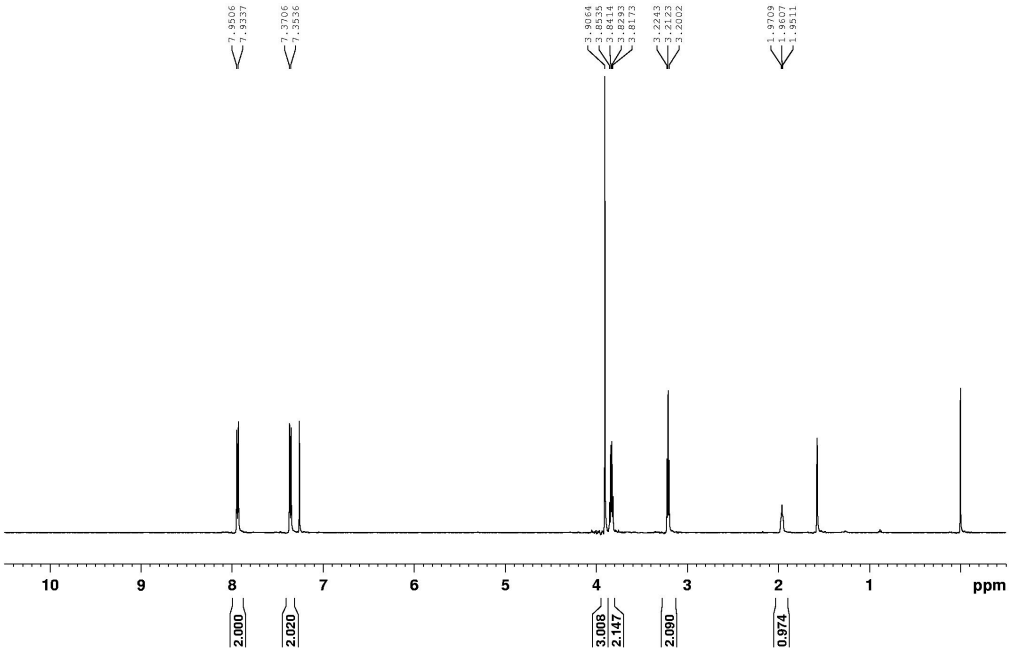


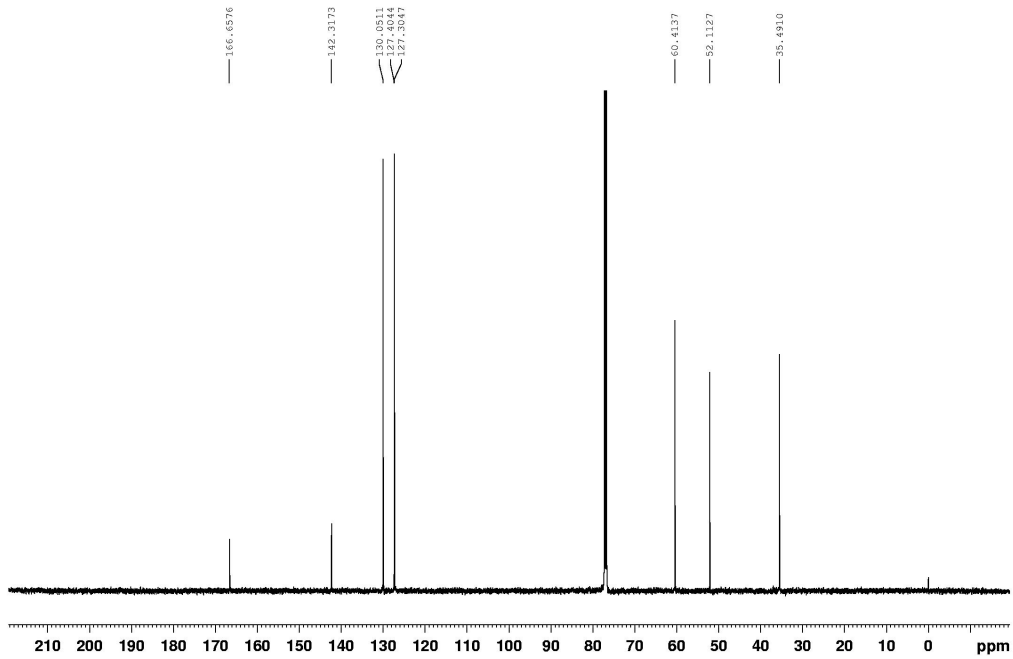




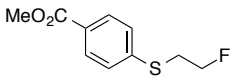
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8t** ($CDCl_3$)

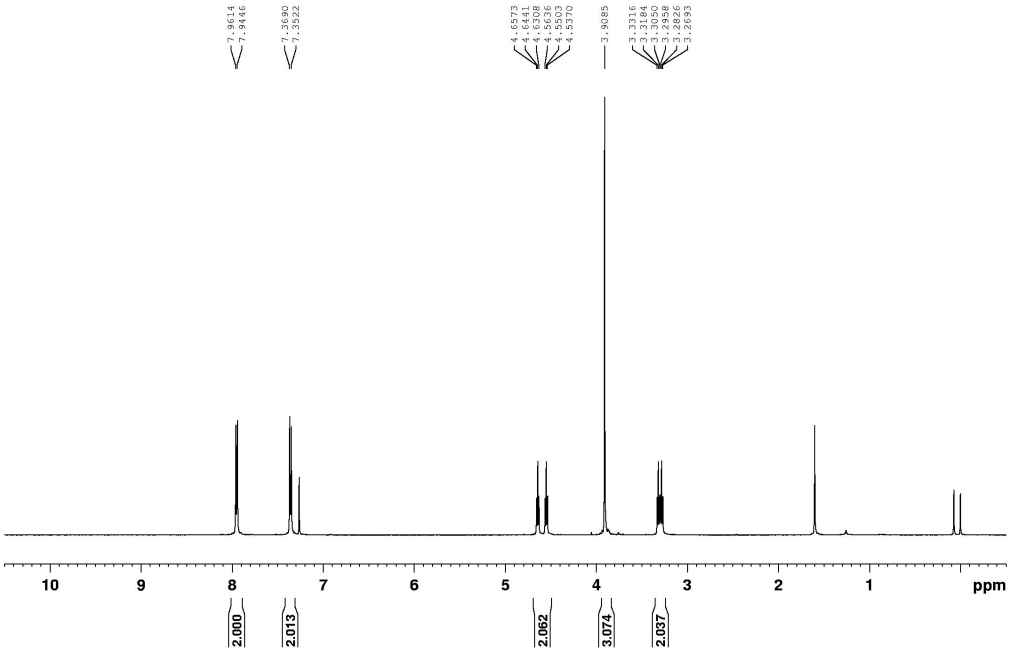


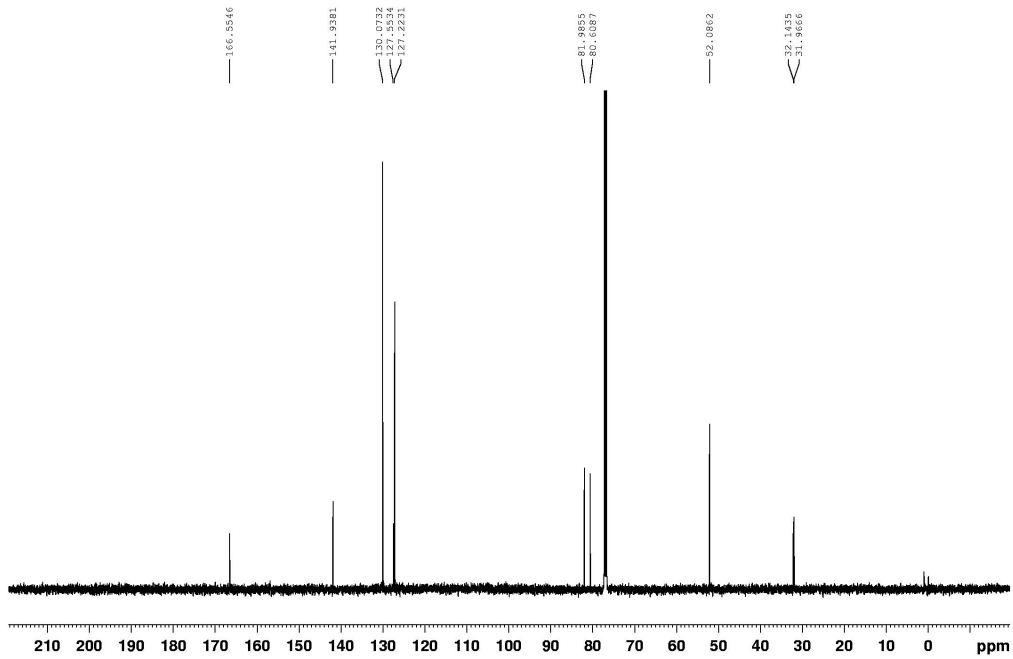




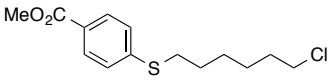
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8u** ($CDCl_3$)

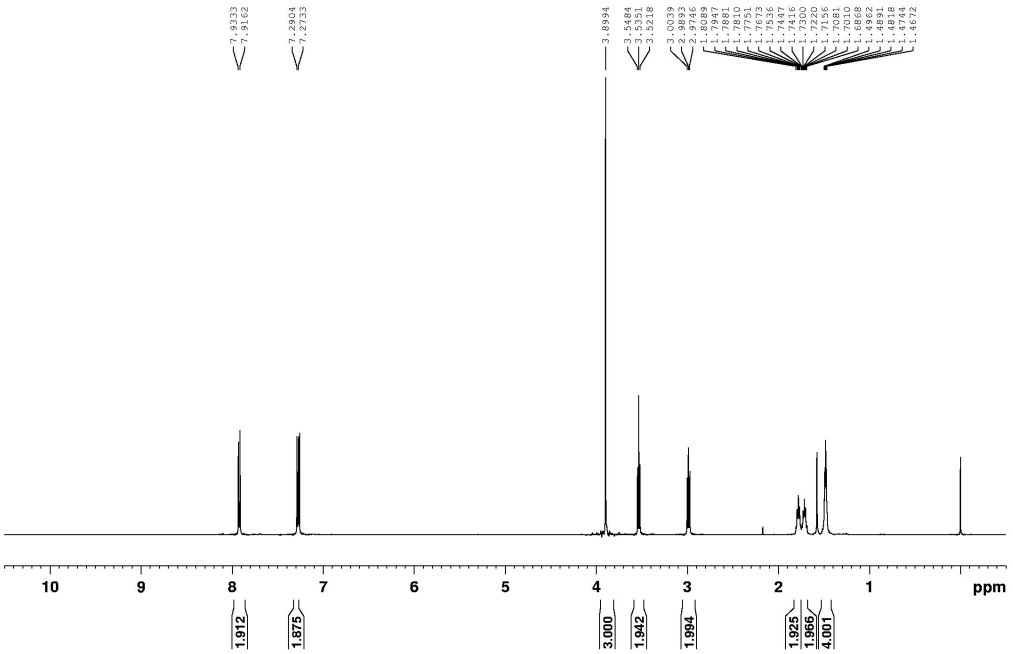


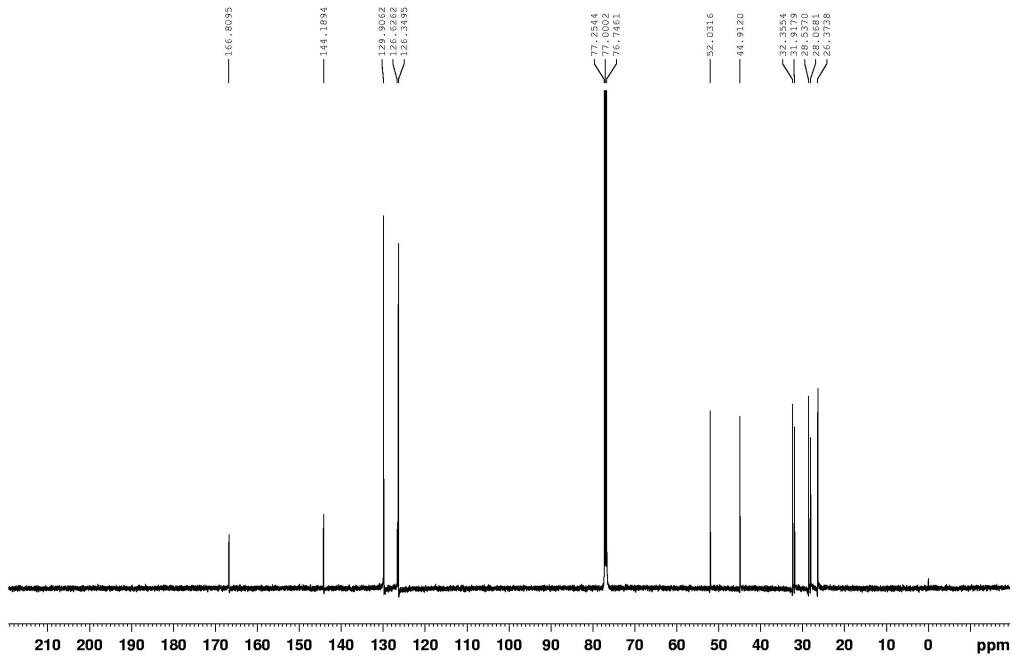




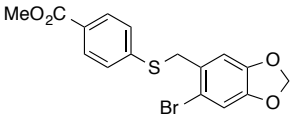
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8v** ($CDCl_3$)

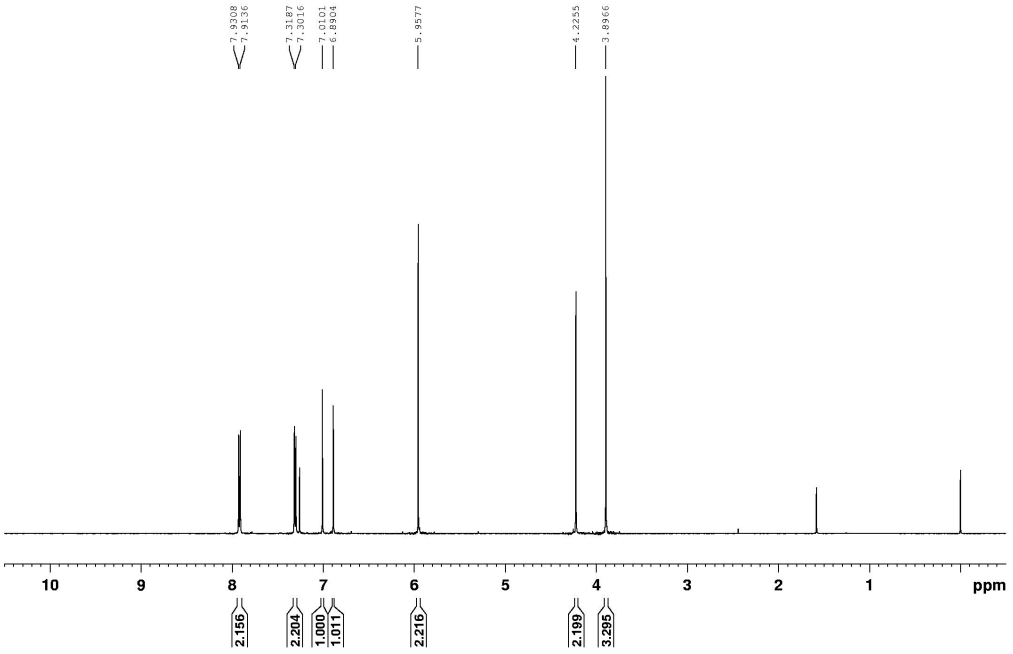


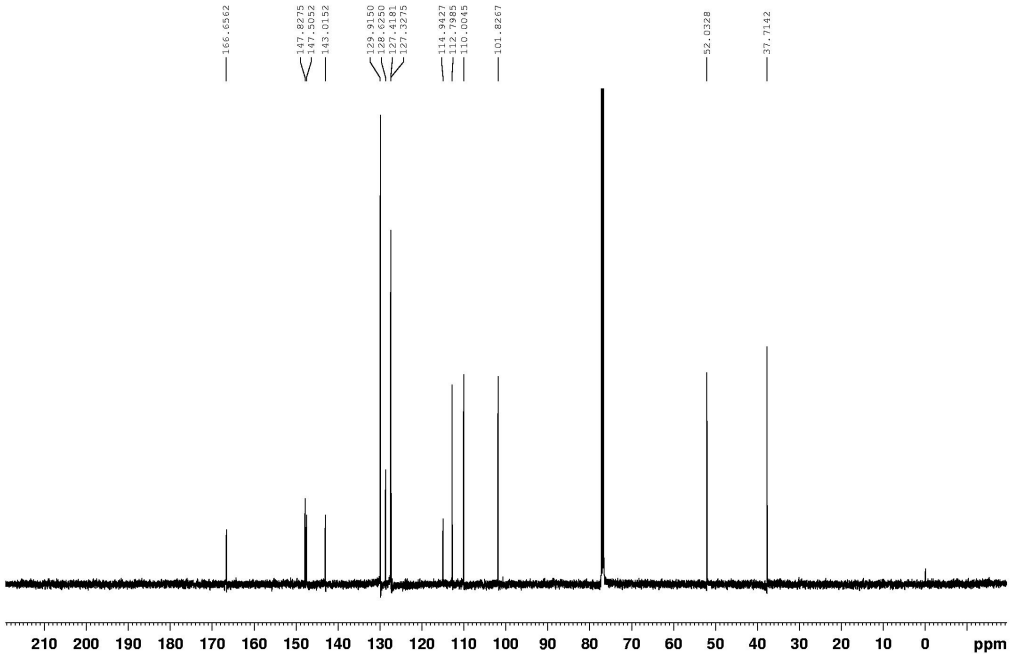




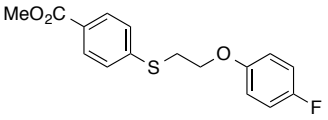
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8w** ($CDCl_3$)

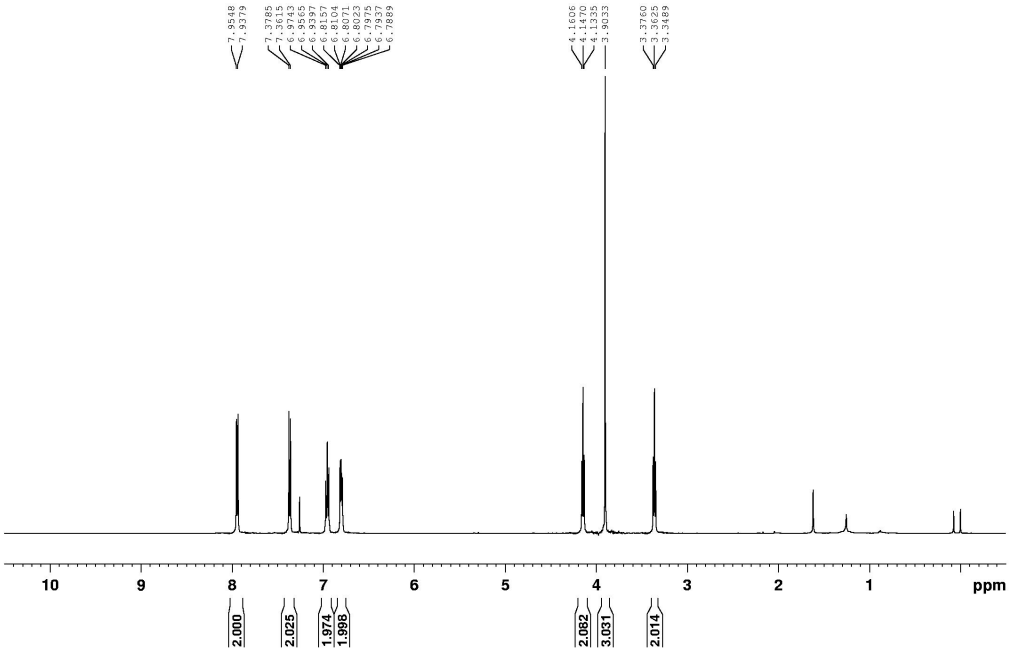


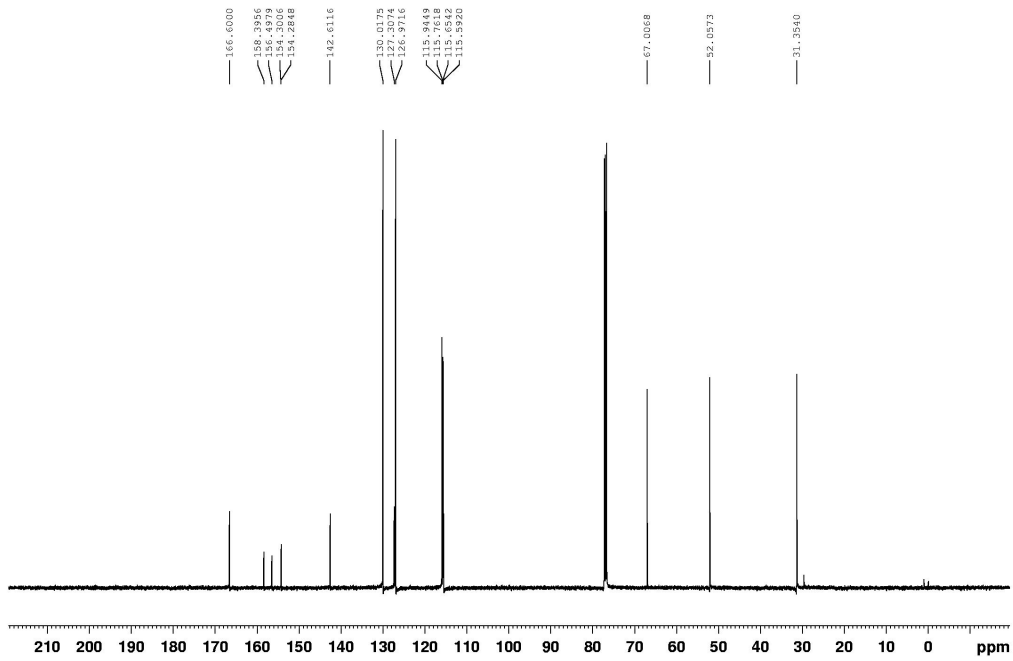




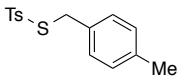
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **8x** ($CDCl_3$)

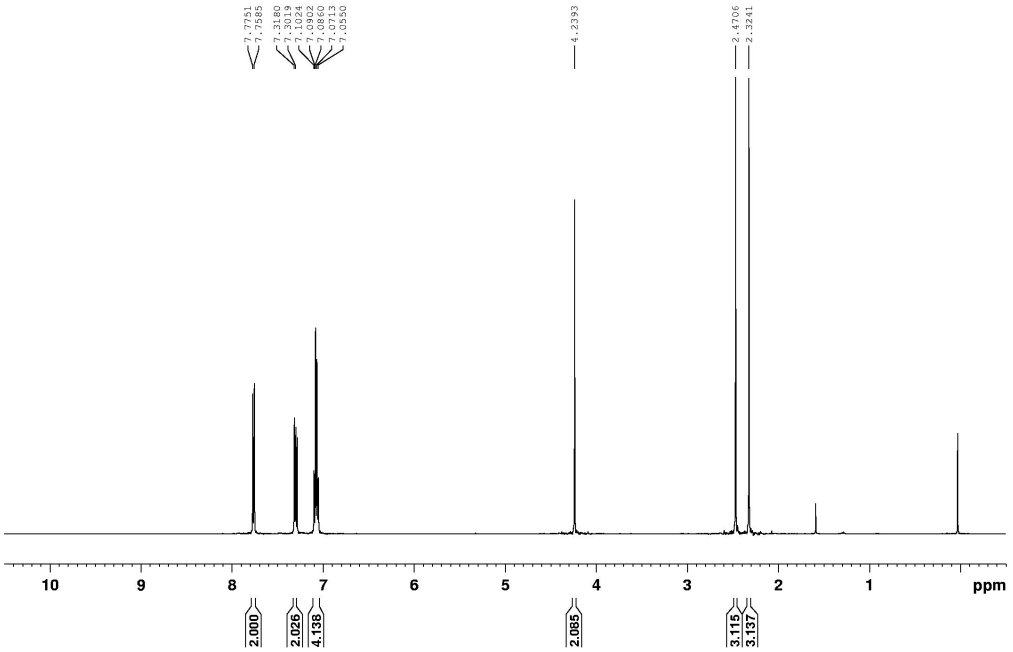


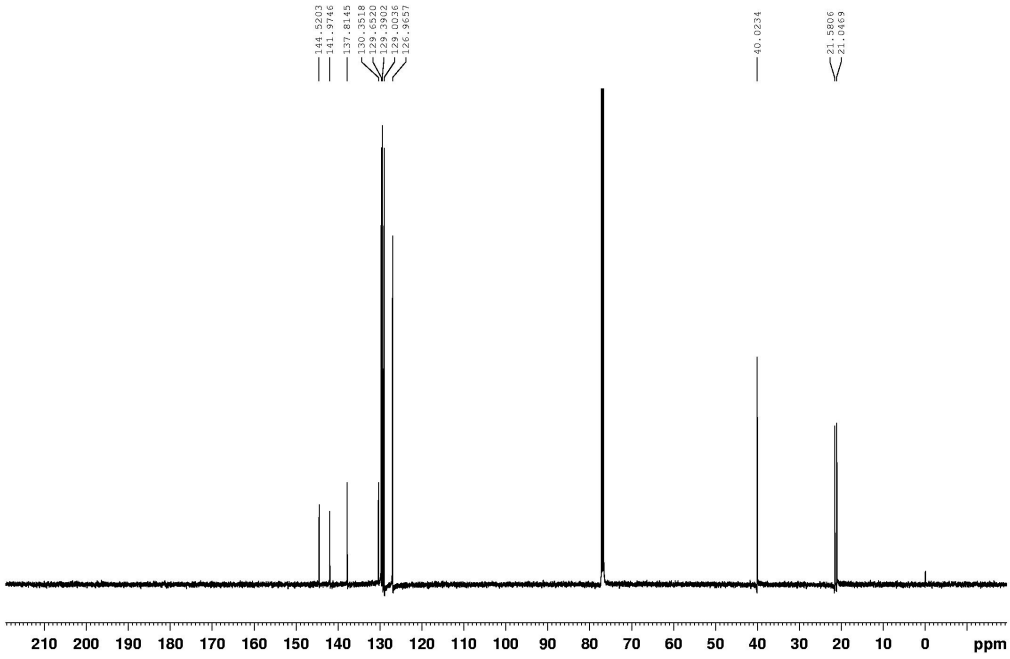




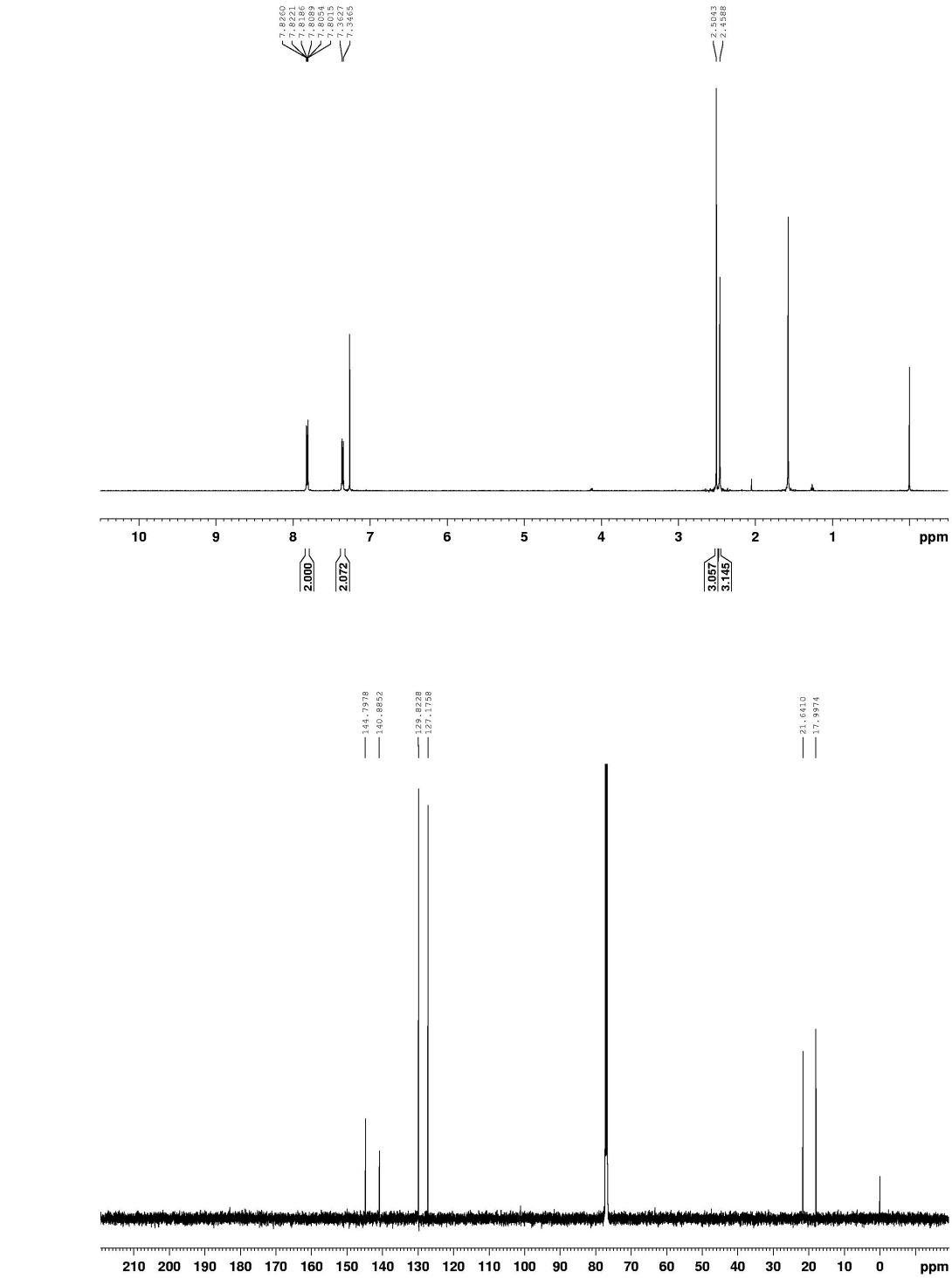
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11a** ($CDCl_3$)



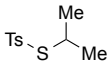


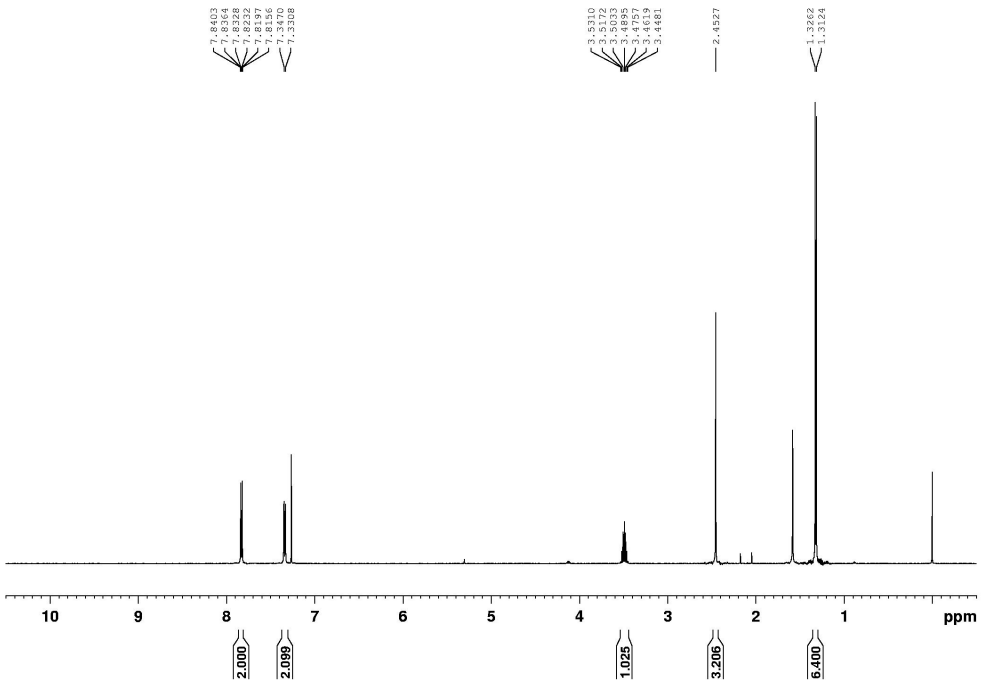


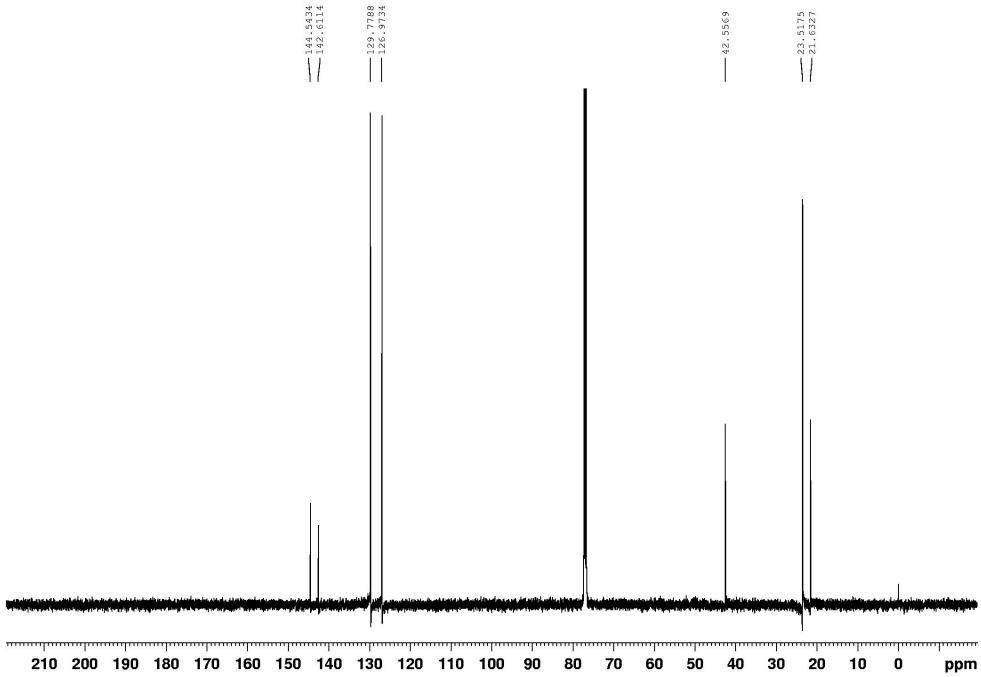
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11b** ($CDCl_3$)



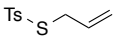
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11c** ($CDCl_3$)

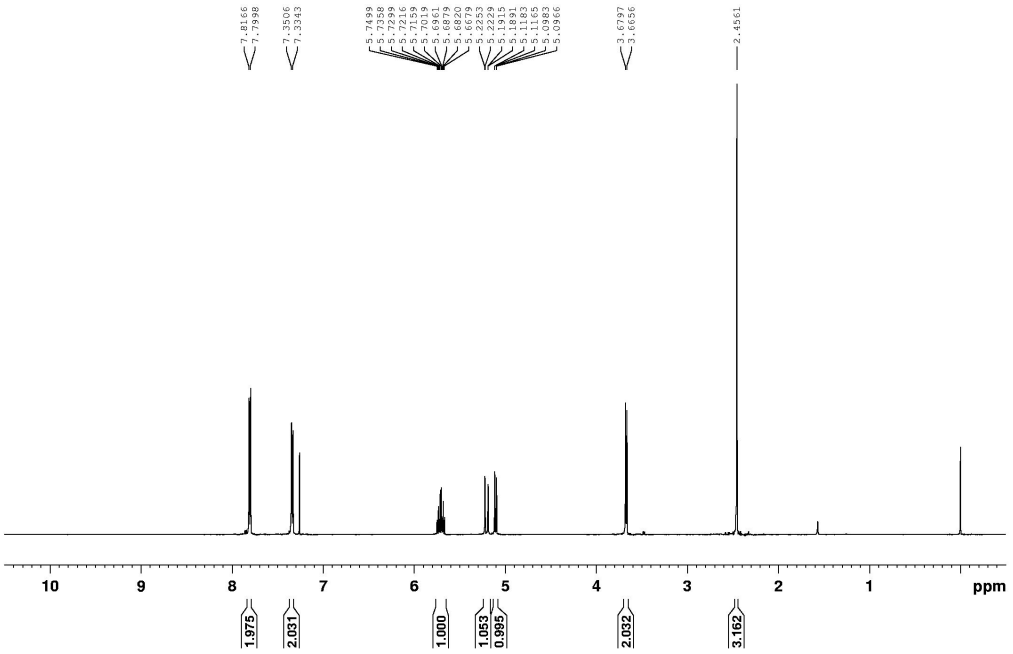


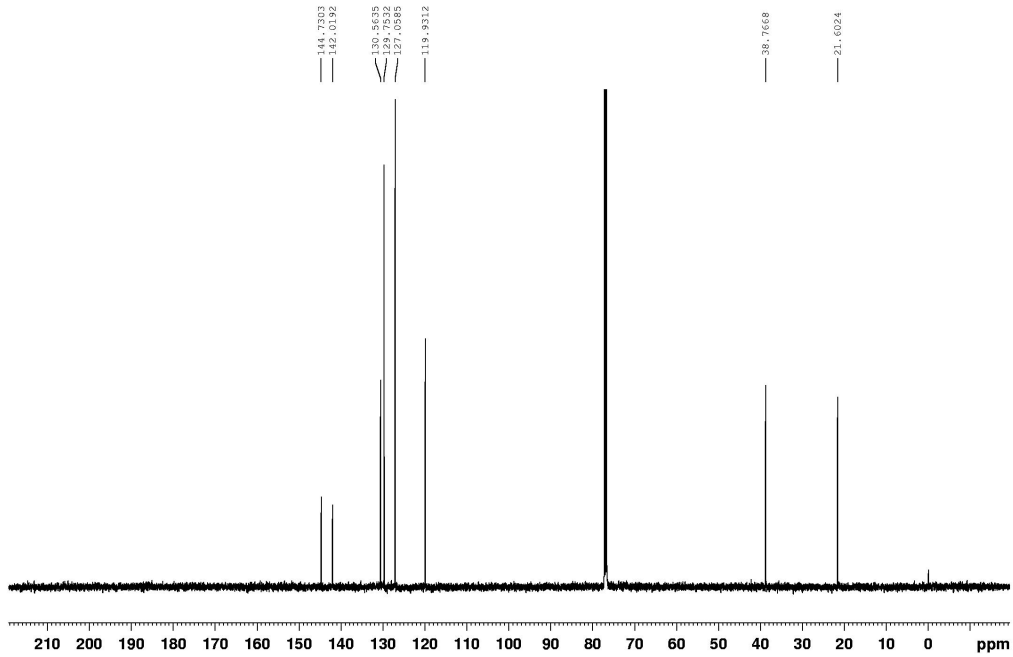




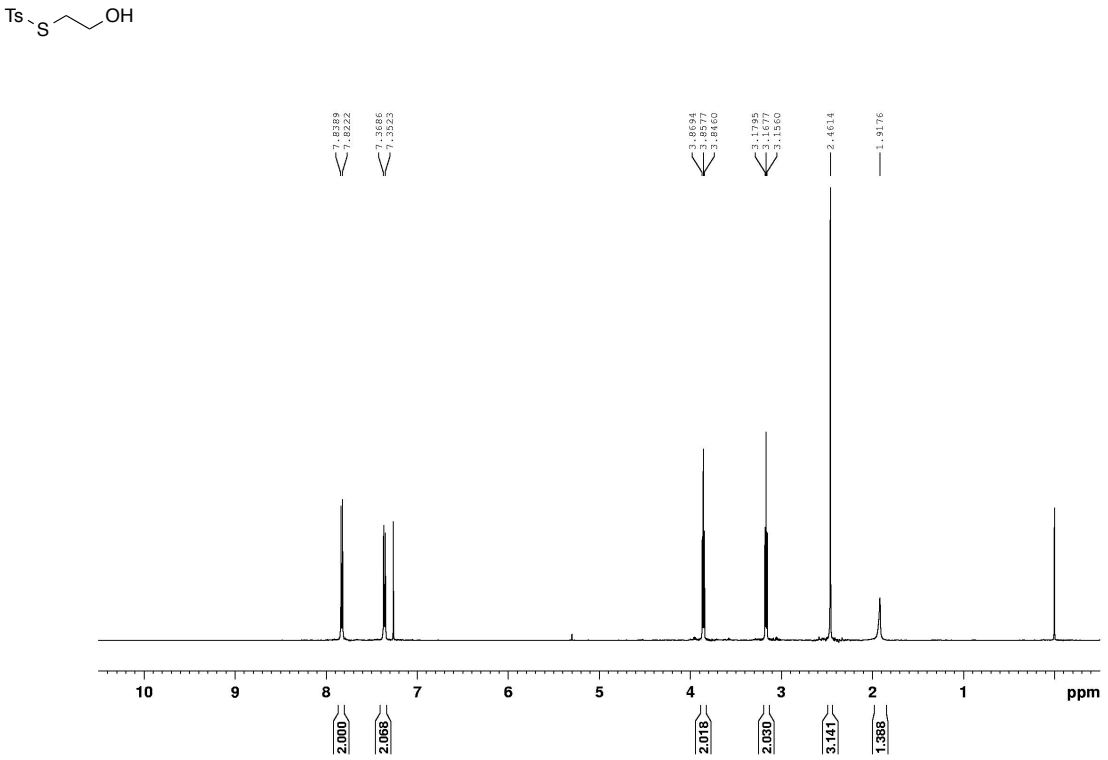
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11d** ($CDCl_3$)

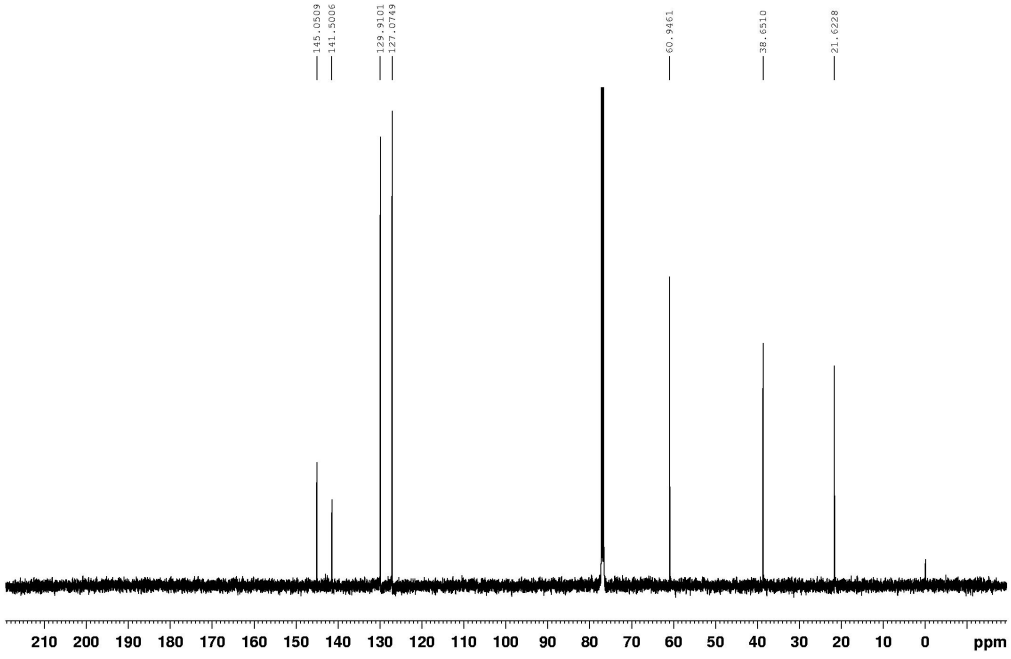




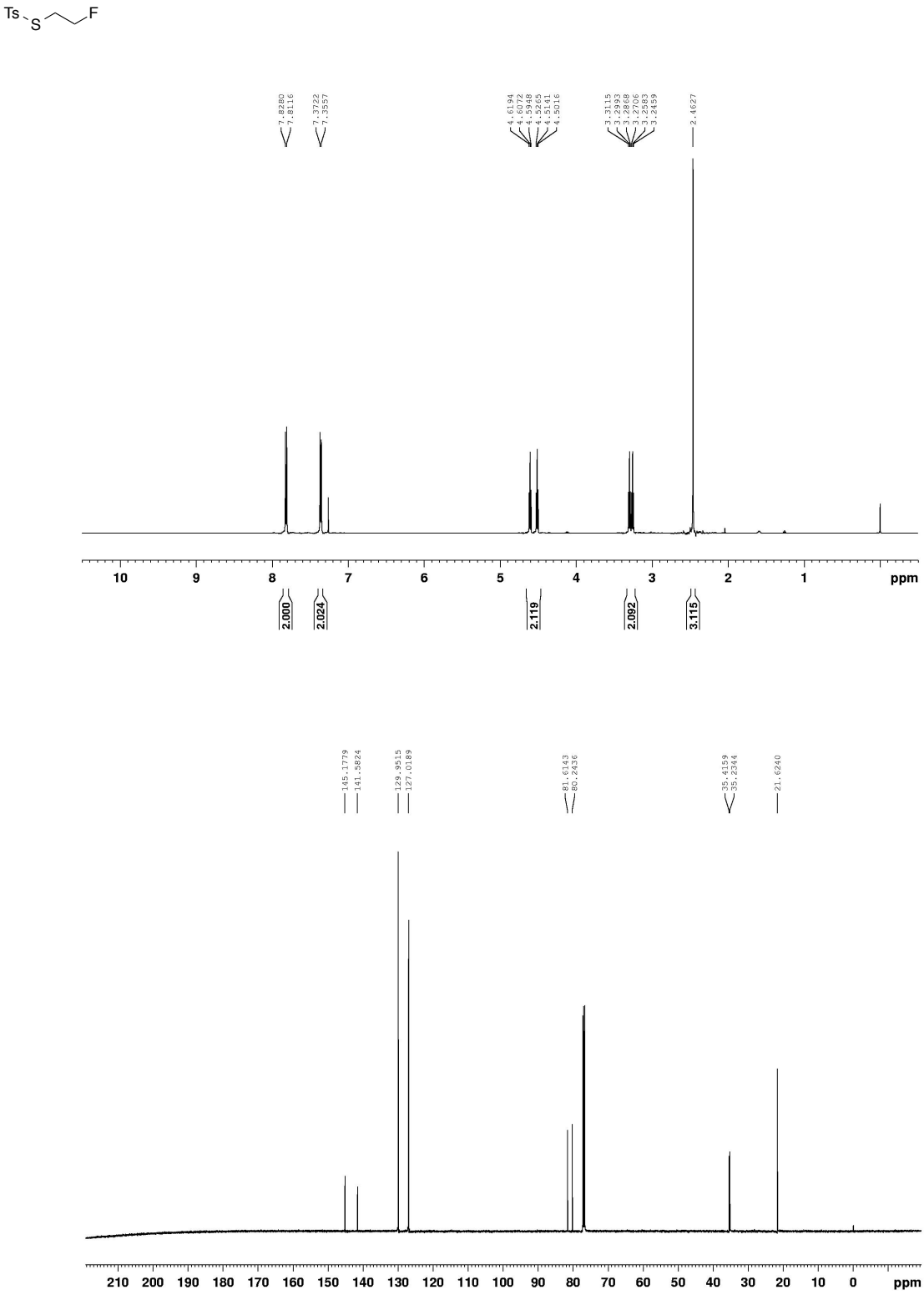


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11e** ($CDCl_3$)

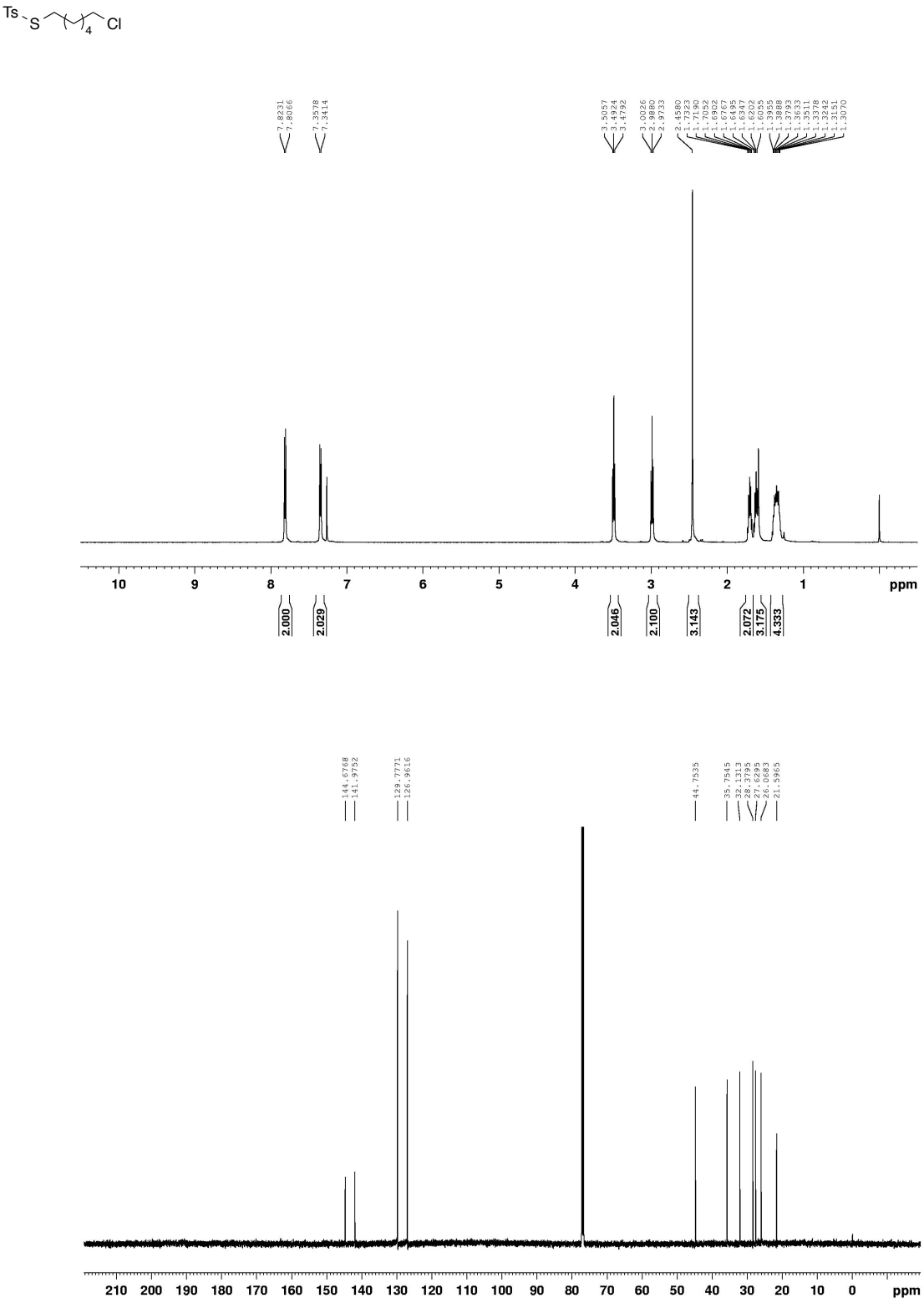




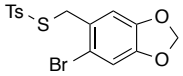
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11f** ($CDCl_3$)

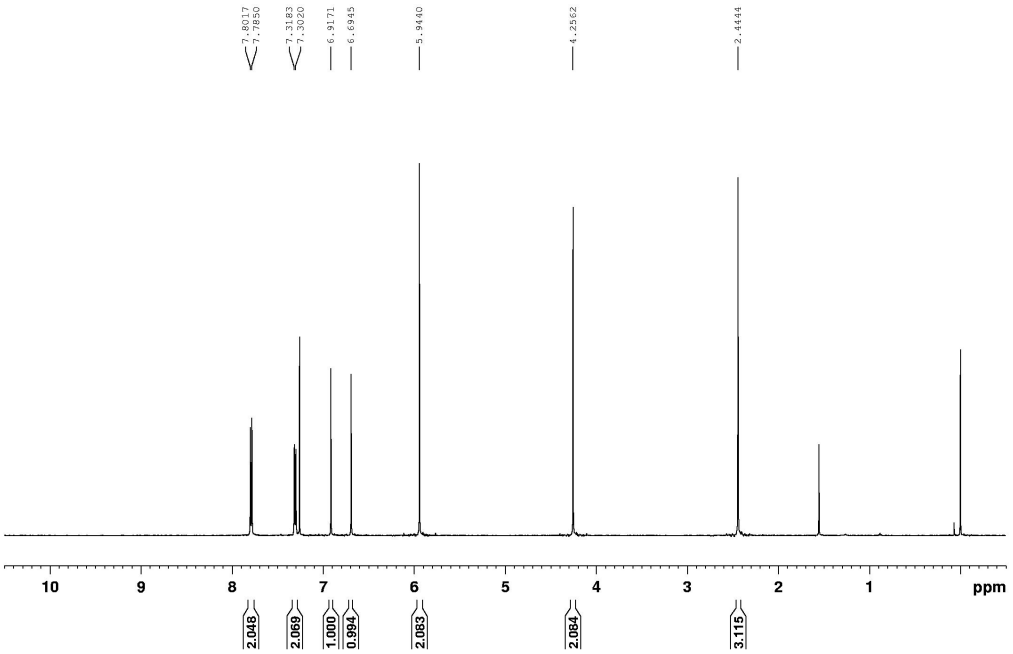


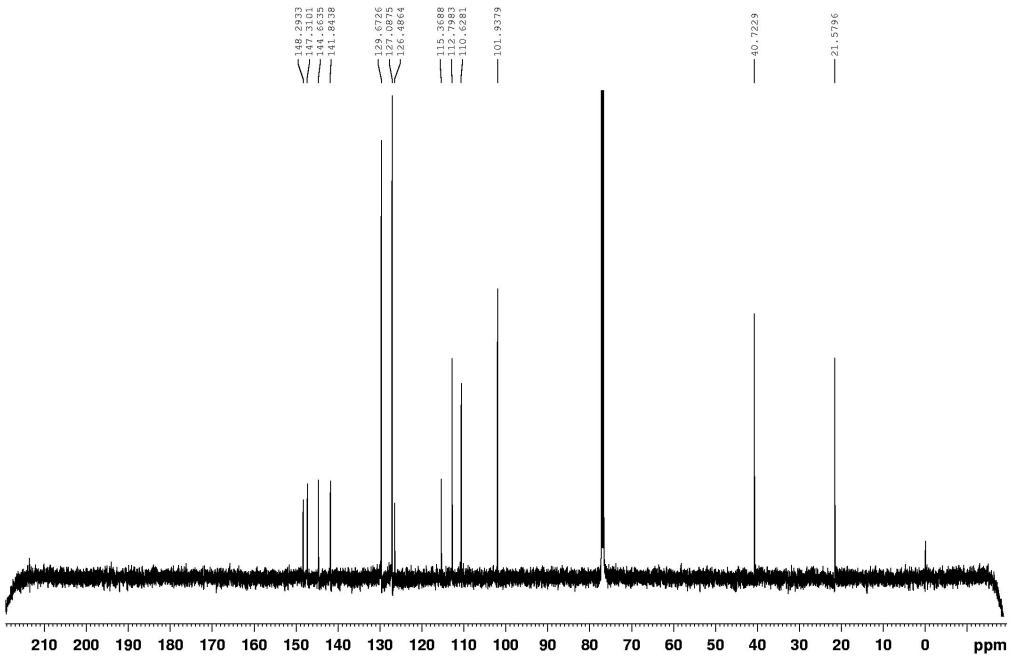
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11g** ($CDCl_3$)



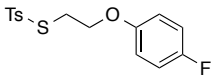
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11h** ($CDCl_3$)

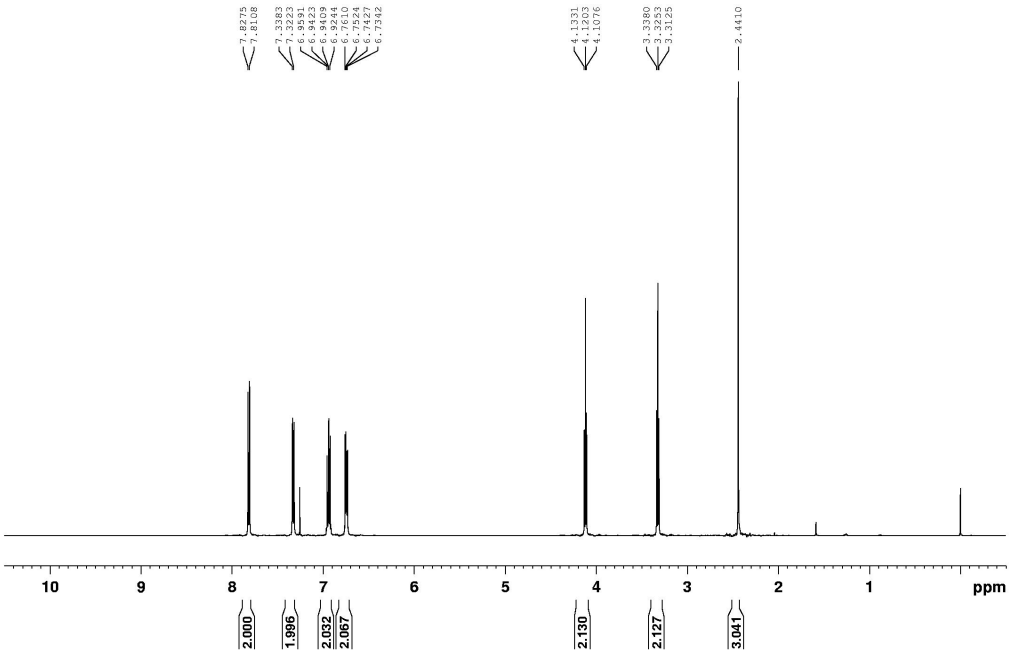


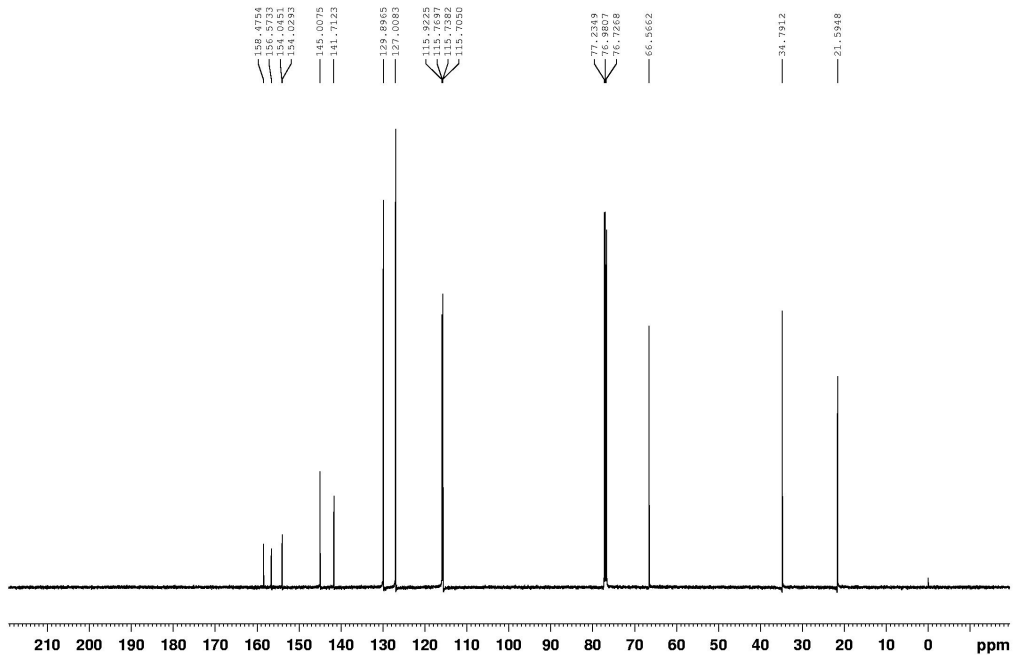




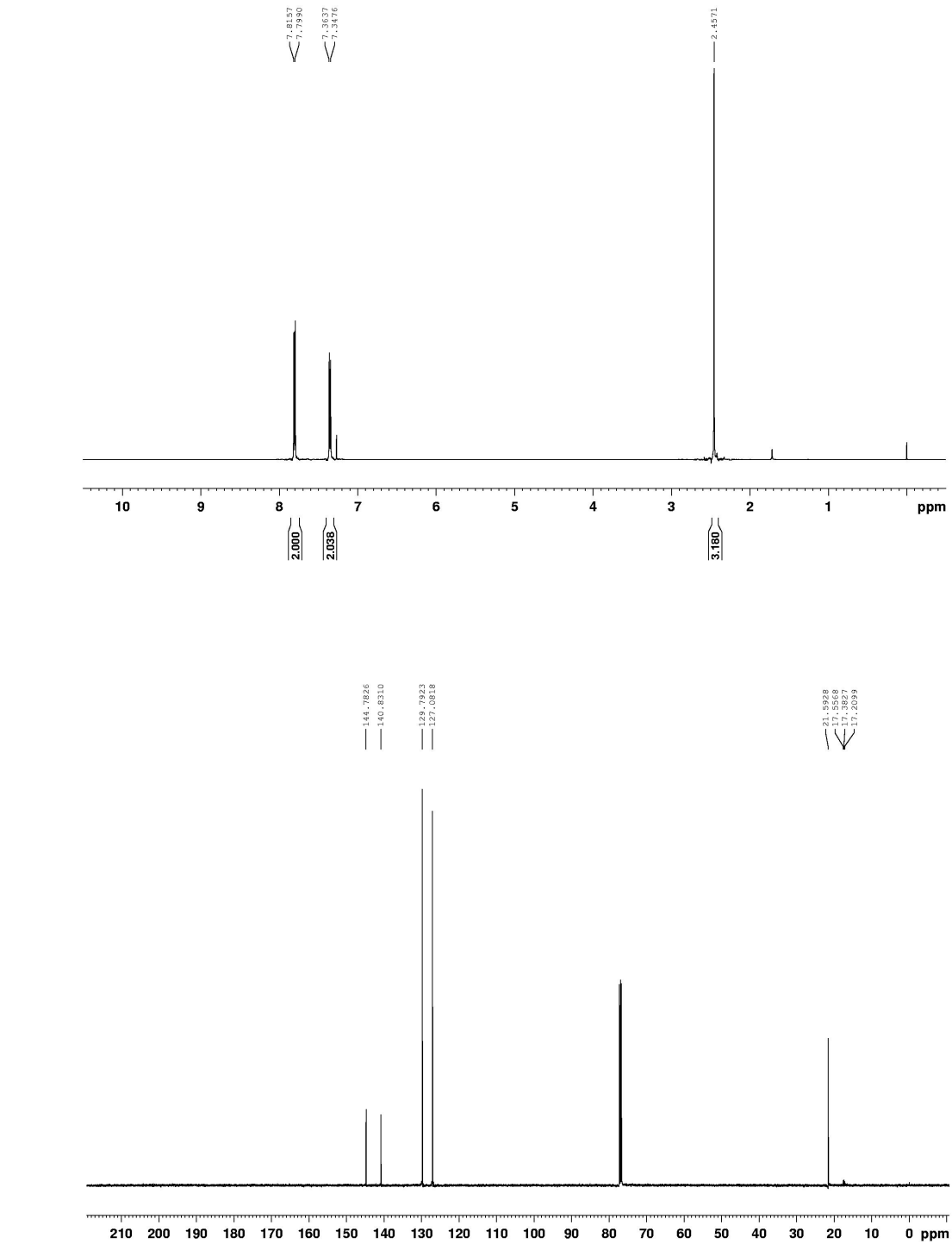
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11i** ($CDCl_3$)



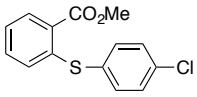


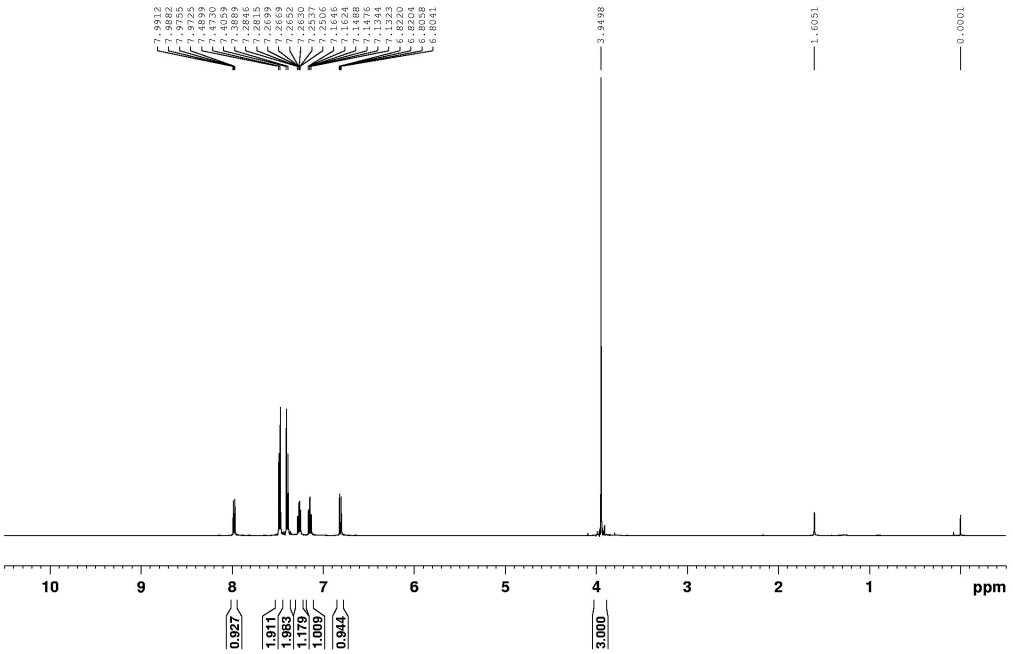


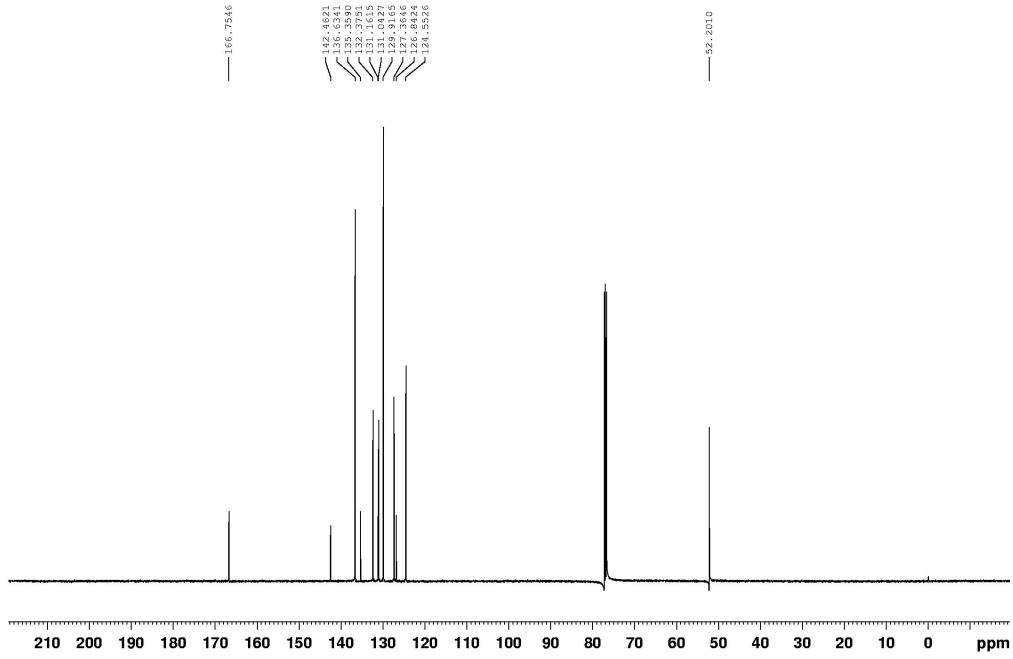
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11j** ($CDCl_3$)



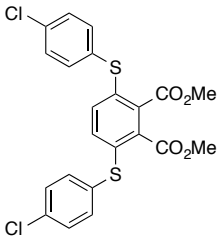
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13a** ($CDCl_3$)

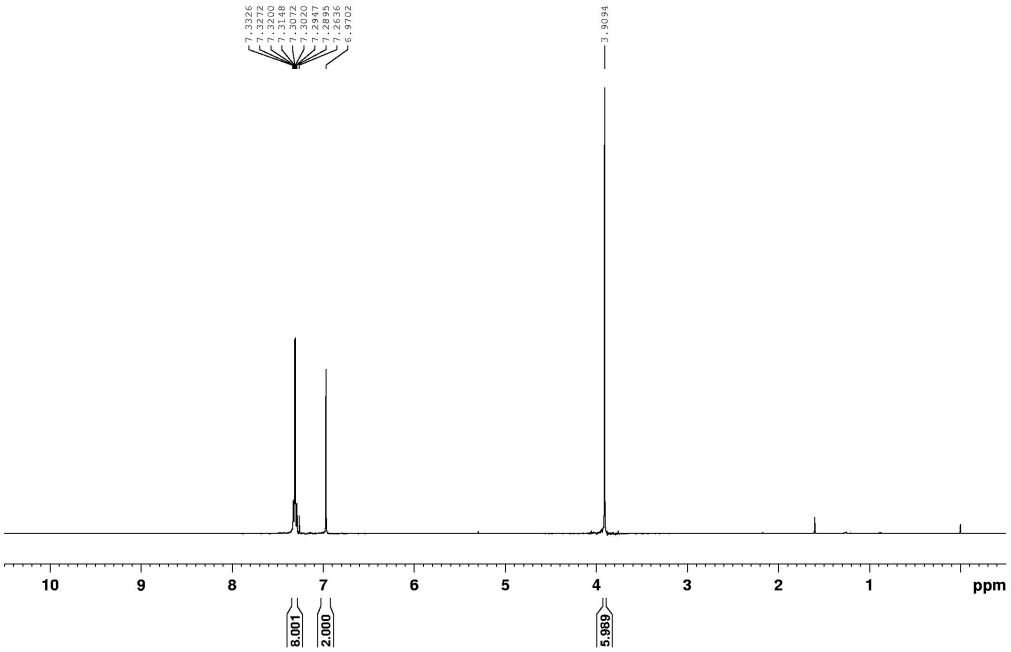


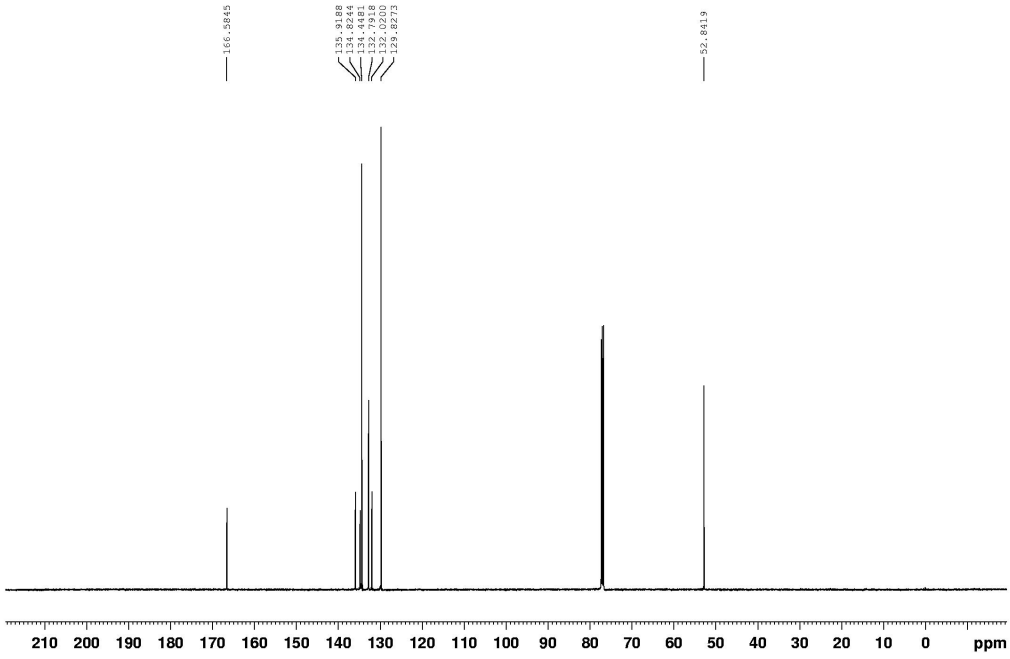




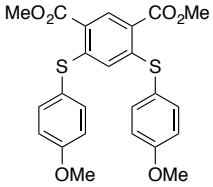
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13b** ($CDCl_3$)

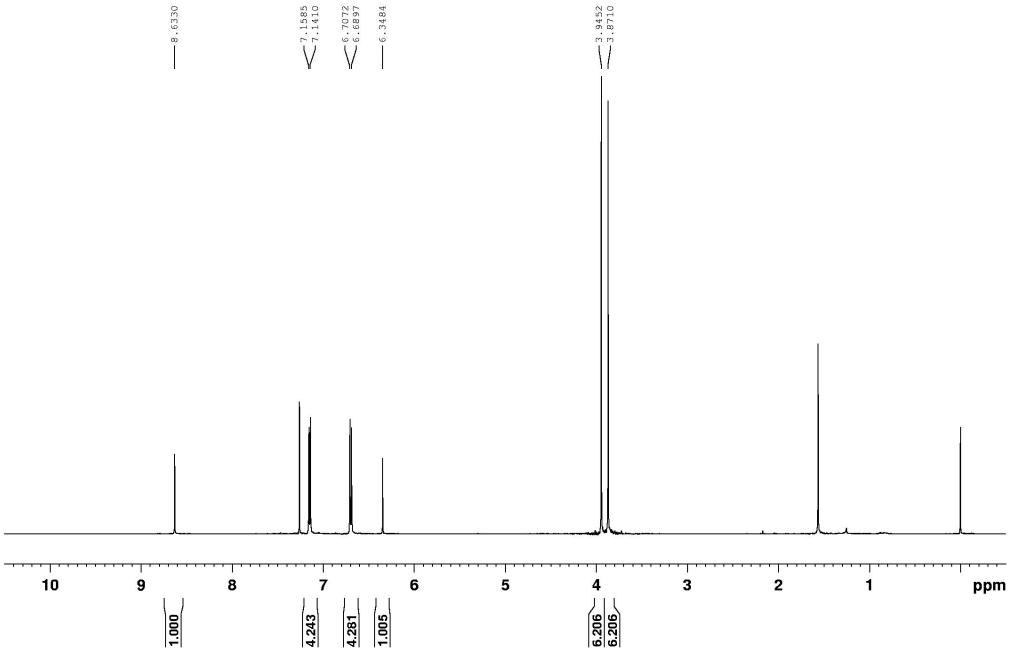


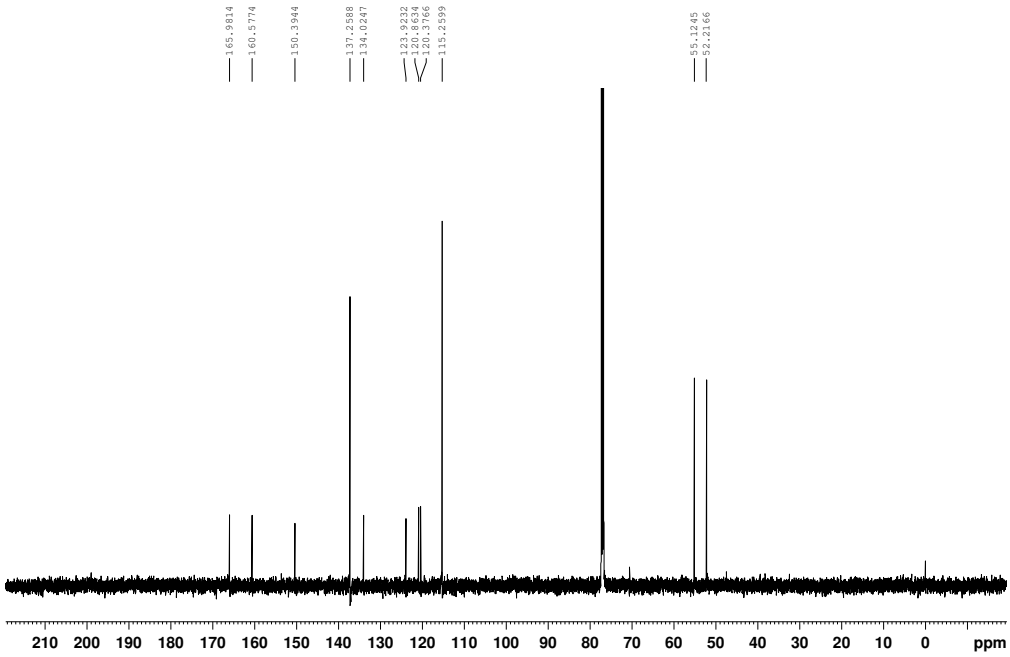




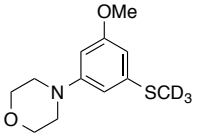
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13c** ($CDCl_3$)

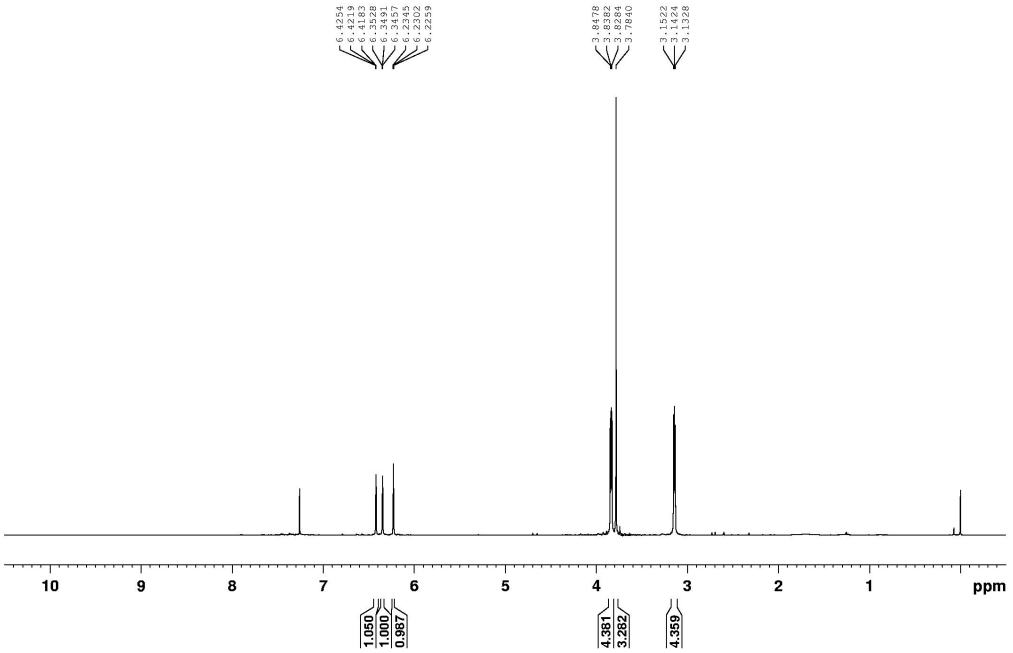


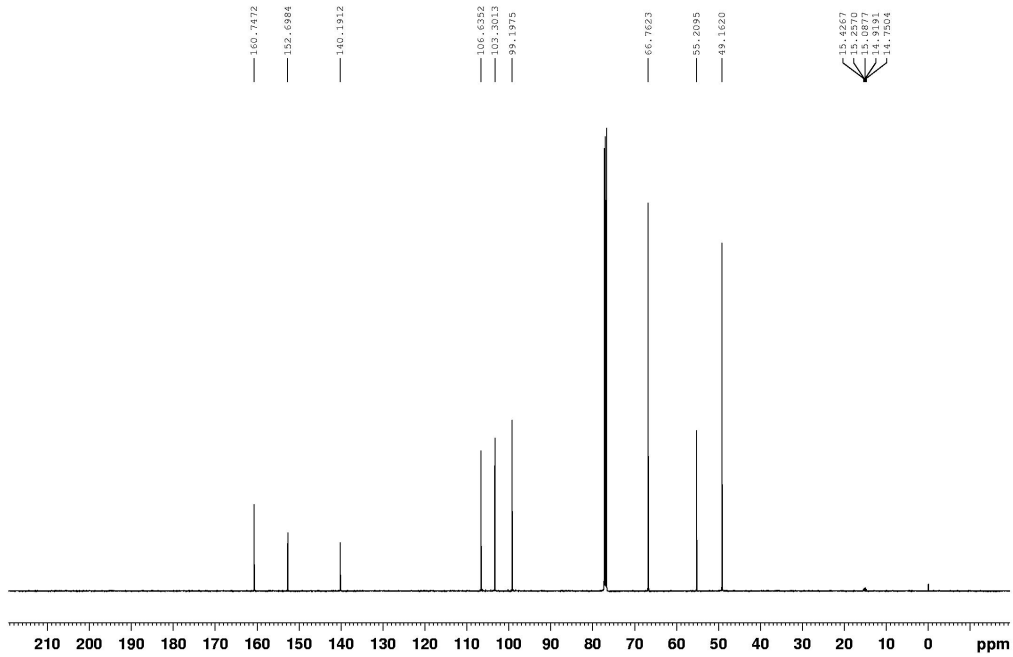




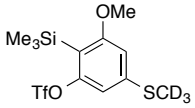
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **15** ($CDCl_3$)

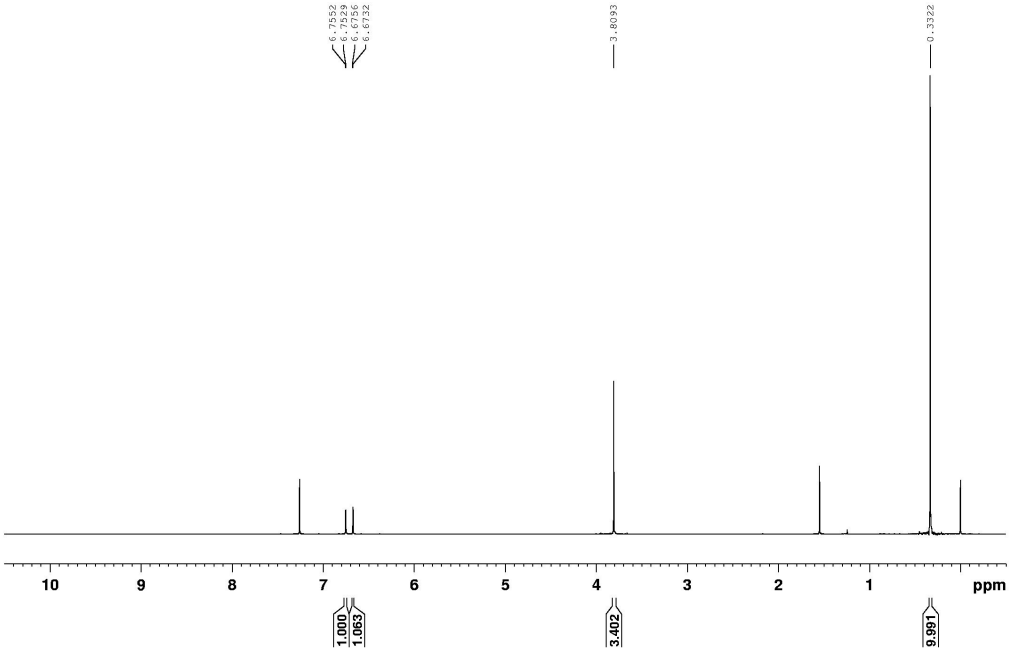


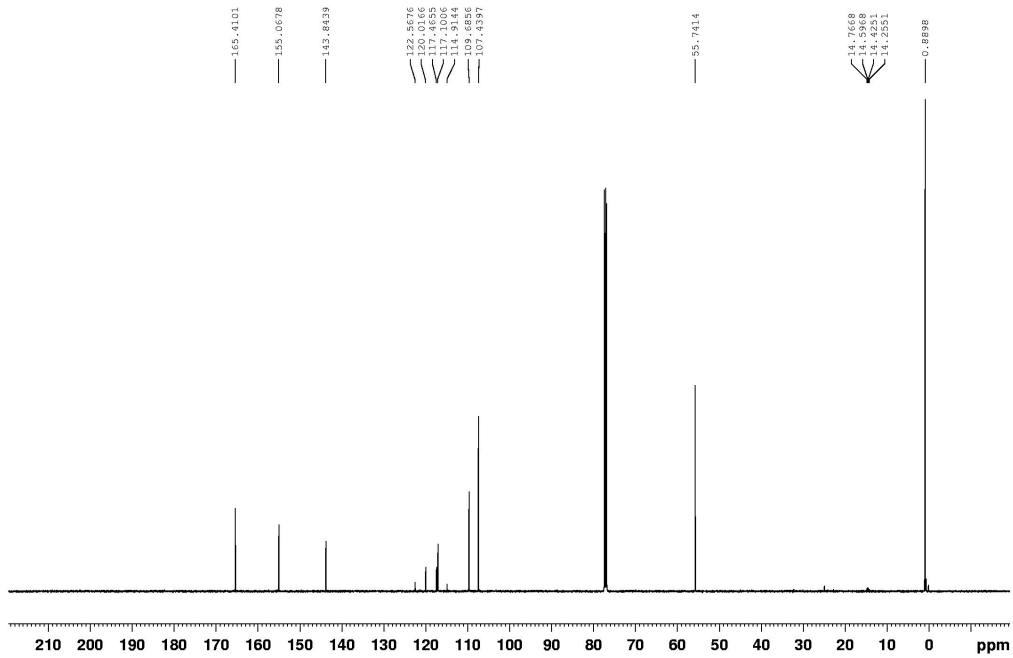




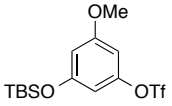
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **16** ($CDCl_3$)

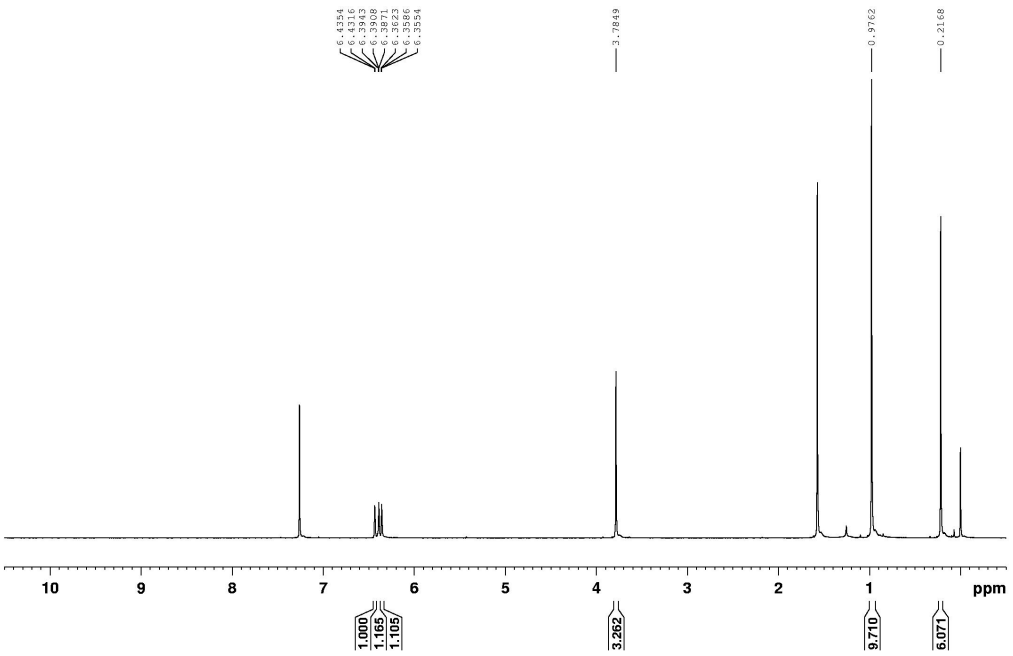


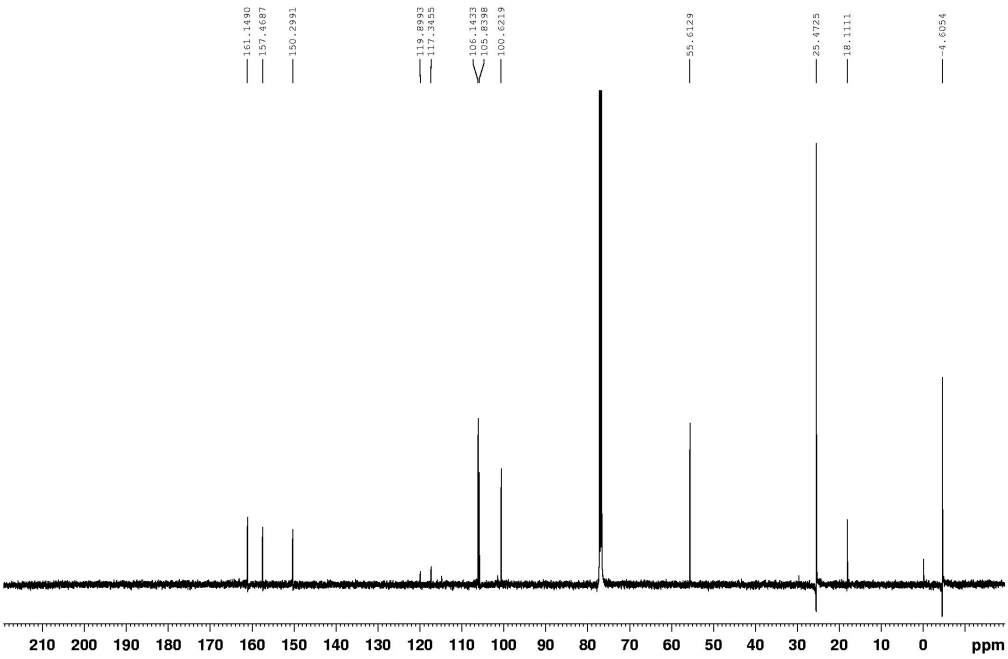




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **S2** ($CDCl_3$)







^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **S3** ($CDCl_3$)