Supporting Information

Rhodium-catalyzed odorless synthesis of diaryl sulfides from borylarenes and *S*-aryl thiosulfonates

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Contents

General Remarks

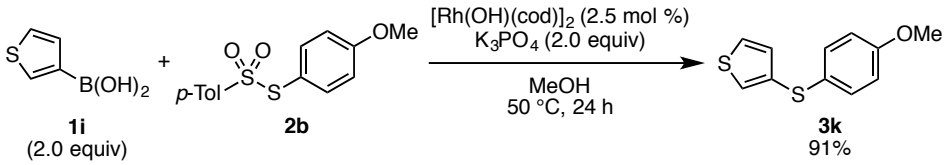
All reactions were performed with dry glassware under atmosphere of argon unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715) or NH TLC plates (Fuji Silysia Chemical Ltd., Chromatorex, NH-TLC plate). Column chromatography was conducted using Biotage® SNAP Ultra 50 g (Cat. No. FSUL-0442-0050), 100 g (Cat. No. FSUL-0442-0100), or 340 g (Cat. No. FSUL-0442-0340), or Purif-Pack NH 60 μm SIZE: 20 (Shoko Scientific Co., Ltd) with medium pressure liquid chromatography (Biotage, Isolera One). Preparative TLC was performed on silica-gel (Wako Pure Chemical Industries, Ltd., Wakogel® B-5F, Cat. No. 230-00043). High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC-2010CHT. 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), DMSO-d_6 (CIL, Cat. No. DLM-10), or deuterium oxide (CIL, Cat. No. DLM-4) 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^+).

Rhodium(II) trifluoroacetate dimer (Cat. No. 399191), chlorobis(cyclooctene)rhodium(I) dimer (Cat. No. 302473), chloro(1,5-hexadiene)rhodium(I) dimer (Cat. No. 259039), bicyclo[2.2.1]hepta-2,5-diene-rhodium(I) chloride dimer (Cat. No. 249939), chloro(1,5-cyclooctadiene)rhodium(I) dimer (Cat. No. 227951), bis(1,5-cyclooctadiene)rhodium(I) trifluoromethanesulfonate (Cat. No. 530840), bis(acetonitrile)(1,5-cyclooctadiene)-rhodium(I)tetrafluoroborate (Cat. No. 640360), tris(triphenylphosphine)rhodium(I) chloride (Cat. No. 199982), chloro(1,5-cyclooctadiene)iridium(I) dimer (Cat. No. 683094), 4-methoxyphenylboronic acid (**1b**) (Cat. No. 417599), *trans*-2-phenylvinylboronic acid (**1j**) (Cat. No. 473790), and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (Cat. No. 515477) were purchased from Sigma–Aldrich Japan. Copper(II) sulfate (Cat. No. 034-04445), cesium fluoride (Cat. No. 031-17162), tripotassium phosphate (Cat. No. 161-04325), 4-bromophenylboronic acid (**1e**) (Cat. No. 328-70463), 2-(pivaloylamino)phenylboronic acid (**1g**) (Cat. No. 327-57113), 2-benzofuranylboronic acid (**1h**) (Cat. No. 322-84371), 2-fluorobenzenethiol (Cat. No. 328-62332), magnesium oxide (Cat. No. 133-00281), 2,2,2-trifluoroacetamide (Cat. No. 206-09562), (diacetoxyiodo)benzene (Cat. No. 045-32963), cesium carbonate (Cat. No. 034-06542), and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (Cat. No. 042-31834) were purchased from Wako Pure Chemical Industries Ltd. 2-Thienylboronic acid (**1a**) (Cat. No. T1772), 4-hydroxyphenylboronic acid (**1c**) (Cat. No. H1228), 4-(dimethylamino)phenyl-boronic acid (**1d**) (Cat. No. D4428), 3-thienylboronic acid (**1i**) (Cat. No. T1975), sodium *p*-toluenesulfinate (**4**) (Cat. No. T0275), bis(4-hydroxyphenyl) disulfide (Cat. No. B3827), bis(3-hydroxyphenyl) disulfide (Cat. No. B3149), bis(4-aminophenyl) disulfide (Cat. No. D0291), bis(4-chlorophenyl) disulfide (Cat. No. D0360), bis(2-thienyl) disulfide (Cat. No. D3774), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (Cat. No. T1560), 18-crown-6 (Cat. No. C0860), bis(pinacolato)diboron (Cat. No. B1964), and 2-methylthiophene (**12**) (Cat. No. M0635) were purchased from Tokyo Chemical Industry Co., Ltd. Sodium bicarbonate (Cat. No. 37116), potassium carbonate (Cat. No. 32323), 4-(methoxycarbonyl)phenylboronic acid (**1f**) (Cat. No. 25810), and potassium hydroxide (Cat. No. 32344) were purchased from Kanto Chemical Co., Inc. Hydroxy(cyclooctadiene)rhodium(I) dimer (Cat. No. 45-1000) was purchased from Strem Chemicals, Inc. Rhodium(II) acetate dimer (Cat. No. 7016) was purchased from Colonial Metals Inc. Bis(4-methoxyphenyl) disulfide (Cat. No. SS-4201) was purchased from Combi-Blocks Inc. 4-(Methoxycarbonyl)benzenethiol (Cat. No. 113939) was purchased from Matrix Scientific. *S*-(4-Tolyl) 4-toluenethiosulfonate (**2a**)[S1] *S*-(4-toluenesulfonyl) 4-toluenethiosulfonate (**11**)[S2], bis(4-(*tert*-butoxycarbonylamino)phenyl) disulfide,[S3] and bis(3-thienyl) disulfide[S4] were prepared according to the reported methods. 3-Methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**7**) was prepared from 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate according to our reported method.[S5,S6] All other chemical reagents used were commercial grade and used as received.

Experimental Procedures

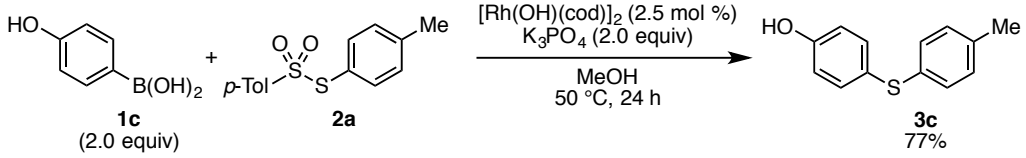
A typical procedure for rhodium-catalyzed thiolation of boronic acids with thiosulfonates



A mixture of *S*-(4-methoxyphenyl) 4-toluenethiosulfonate (**2b**) (74.0 mg, 0.251 mmol, 1.0 equiv), 3-thienylboronic acid (**1i**) (63.4 mg, 0.495 mmol, 2.0 equiv), $[Rh(OH)(cod)]_2$ (2.9 mg, 6.3 μmol, 2.5 mol %), and tripotassium phosphate (106 mg, 0.499 mmol, 2.0 equiv) suspended in MeOH (2.5 mL) was stirred for 24 h at 50 ºC. After cooling to room temperature, the mixture was filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. To the residue was added EtOAc (20 mL) and the mixture was washed with aqueous saturated solution of sodium bicarbonate (20 mL × 2) and brine (20 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc =20/1) to give 4-methoxyphenyl 3-thienyl sulfide (**3k**) (50.7 mg, 0.228 mmol, 90.8%) as a colorless oil.

According to the procedure for preparing 4-methoxyphenyl 3-thienyl sulfide (**3k**), 2-thienyl 4-tolyl sulfide (**3a**) (35.0 mg, 68.5%), 4-methoxyphenyl 4-tolyl sulfide (**3b**) (47.4 mg, 82.0%), 4-hydroxyphenyl 4-tolyl sulfide (**3c**) (45.0 mg, 83.3%), 4-(dimethylamino)phenyl 4-tolyl sulfide (**3d**) (49.3 mg, 81.4%), 4-bromophenyl 4-tolyl sulfide (**3e**) (47.4 mg, 67.3%), 4-(methoxycarbonyl)phenyl 4-tolyl sulfide (**3f**) (37.8 mg, 58.5%), 2-(*N*-pivaloylamino)phenyl 4-tolyl sulfide (**3g**) (45.8 mg, 60.5%), 2-benzo[*b*]furyl 4-tolyl sulfide (**3h**) (57.1 mg, 95.3%), 3-thienyl 4-tolyl sulfide (**3i**) (48.0 mg, 92.5%), (*E*)-2-(4-tolylthio)styrene (**3j**) (55.6 mg, quant), 4-hydroxyphenyl 3-thienyl sulfide (**3l**) (42.7 mg, 81.6%), 3-hydroxyphenyl 3-thienyl sulfide (**3m**) (46.5 mg, 89.9%), 4-aminophenyl 3-thienyl sulfide (**3n**) (42.1 mg, 82.1%), 4-(*tert*-butoxycarbonyl-amino)phenyl 3-thienyl sulfide (**3o**) (70.5 mg, 92.1%), 4-chlorophenyl 3-thienyl sulfide (**3p**) (41.7 mg, 73.6%), 4-(methoxycarbonyl)phenyl 3-thienyl sulfide (**3q**) (26.4 mg, 42.4%), 2-fluorophenyl 3-thienyl sulfide (**3r**) (27.2 mg, 52.0%), 2-thienyl 3-thienyl sulfide (**3s**) (72.6 mg, 73.1%), and bis(3-thienyl) sulfide (**3t**) (42.0 mg, 88.8%) were prepared from the corresponding organoboronic acid **1** and thiosulfonate **2**.

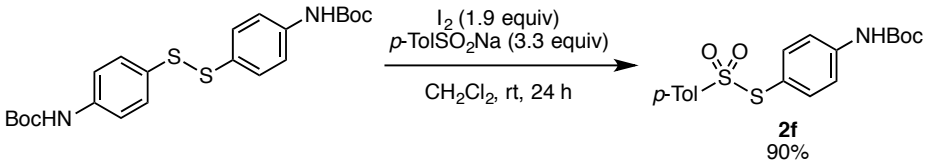
*A procedure for the rhodium-catalyzed deborylthiolation using 1.5 mmol of thiosulfonate **2a***



A mixture of *S*-(4-tolyl) 4-toluenethiosulfonate (**2a**) (419 mg, 1.51 mmol, 1.0 equiv), 4-hydroxyphenylboronic acid (**1c**) (422 mg, 3.06 mmol, 2.0 equiv), $[Rh(OH)(cod)]_2$ (17.4 mg, 38.1 μmol, 2.5 mol %), and tripotassium phosphate (643 mg, 3.03 mmol, 2.0 equiv) suspended in MeOH (15 mL) was stirred for 24 h at 50 ºC. After cooling to room temperature, the mixture was filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. To the residue was added EtOAc (50 mL) and the mixture was washed

with aqueous saturated solution of sodium bicarbonate (50 mL × 2) and brine (50 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® SNAP Ultra 50 g, *n*-heptane/EtOAc = 95/5 to 90/10) to give 4-hydroxyphenyl 4-tolyl sulfide (**3c**) (250 mg, 1.16 mmol, 76.8%) as a brown solid.

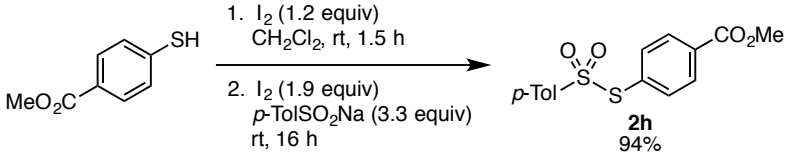
A typical procedure for the synthesis of thiosulfonates from disulfides



To a mixture of bis(4-(*tert*-butoxycarbonylamino)phenyl) disulfide (2.21 g, 4.93 mmol, 1.0 equiv) and sodium *p*-toluenesulfinate (**4**) (2.92 g, 16.4 mmol, 3.3 equiv) suspended in CH_2Cl_2 (88.0 mL) was added I_2 (2.34 g, 9.22 mmol, 1.9 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture were added ca. 5% aqueous solution of sodium bicarbonate (28 mL) and 10% aqueous solution of sodium thiosulfate (35 mL). The mixture was separated, and then the organic layer was washed two times with ca. 5% aqueous solution of sodium bicarbonate (55 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® SNAP Ultra 340 g, *n*-heptane/EtOAc = 90/10 to 80/20) to give *S*-(4-(*tert*-butoxycarbonylamino)phenyl) 4-toluenethiosulfonate (**2f**) (3.37 g, 8.88 mmol, 90.1%) as a colorless solid.

According to the procedure for preparing *S*-(4-(*tert*-butoxycarbonylamino)phenyl) 4-toluenethiosulfonate (**2f**), *S*-(4-methoxyphenyl) 4-toluenethiosulfonate (**2b**) (2.76 g, 93.1%), *S*-(4-hydroxyphenyl) 4-toluenethiosulfonate (**2c**) (1.52 g, 54.1%), *S*-(3-hydroxyphenyl) 4-toluenethiosulfonate (**2d**) (327 mg, 29.1%), *S*-(4-aminophenyl) 4-toluenethiosulfonate (**2e**) (294 mg, 47.5%), *S*-(4-chlorophenyl) 4-toluenethiosulfonate (**2g**) (1.07 g, 70.6%), *S*-(2-thienyl) 4-toluenethiosulfonate (**2j**) (2.33 g, 86.1%), and *S*-(3-thienyl) 4-toluenethiosulfonate (**2k**) (1.08 g, 81.7%) were prepared from bis(4-methoxyphenyl) disulfide, bis(4-hydroxyphenyl) disulfide, bis(3-hydroxyphenyl) disulfide, bis(4-aminophenyl) disulfide, bis(4-chlorophenyl) disulfide, bis(2-thienyl) disulfide, and bis(3-thienyl) disulfide, respectively.

A typical procedure for the synthesis of thiosulfonates from thiols

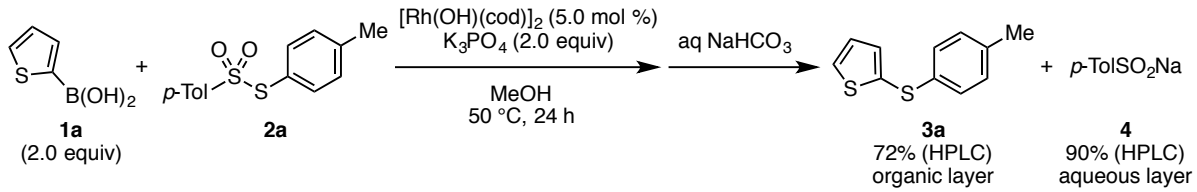


To a solution of 4-(methoxycarbonyl)benzenethiol (1.86 g, 11.1 mmol, 1.0 equiv) dissolved in CH_2Cl_2 (130 mL) was added I_2 (3.32 g, 13.1 mmol, 1.2 equiv) at room temperature. After stirring for 1.5 h at the same temperature, to the mixture were added I_2 (5.35 g, 21.1 mmol, 1.9 equiv) and sodium *p*-toluenesulfinate (**4**) (6.50 g, 36.5 mmol, 3.3

equiv) at room temperature. After stirring for 16 h at the same temperature, to the mixture were added ca. 5% aqueous solution of sodium bicarbonate (60 mL) and aqueous saturated solution of sodium thiosulfate (40 mL). The mixture was separated, and then the organic layer was washed with ca. 5% aqueous solution of sodium bicarbonate (200 mL) and H_2O (100 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 110 g, *n*-hexane/EtOAc = 10/1 to 5/1) to give *S*-(4-(methoxycarbonyl)phenyl) 4-toluenethiosulfonate (**2h**) (3.37 g, 10.4 mmol, 94.3%) as a colorless solid.

According to the procedure for preparing *S*-(4-(methoxycarbonyl)phenyl) 4-toluenethiosulfonate (**2h**), *S*-(2-fluorophenyl) 4-toluenethiosulfonate (**2i**) (2.37 g, 85.4%) was prepared from 2-fluorobenzenethiol.

Confirmation of the formation of sodium p-toluenesulfinate (4)

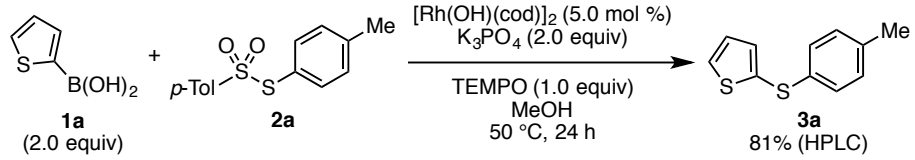


A mixture of *S*-(4-tolyl) 4-toluenethiosulfonate (**2a**) (69.7 mg, 0.250 mmol, 1.0 equiv), 2-thienylboronic acid (**1a**) (64.0 mg, 0.500 mmol, 2.0 equiv), $[Rh(OH)(cod)]_2$ (5.7 mg, 13 μmol, 5.0 mol %), and tripotassium phosphate (107 mg, 0.502 mmol, 2.0 equiv) suspended in MeOH (2.5 mL) was stirred for 24 h at 50 ºC. After cooling to room temperature, the mixture was concentrated under reduced pressure, and to the residue was added EtOAc (20 mL). The mixture was washed with aqueous saturated solution of sodium bicarbonate (20 mL ×2) and brine (20 mL).

Weight of the organic layer was measured (64.4 g), and 422 mg of the organic layer was sampled and diluted to 10 mL with MeCN to prepare a sample solution. Then, 10 μL of the sample solution was analyzed by HPLC, from which the yield of 2-thienyl 4-tolyl sulfide (**3a**) was calculated to be 72.1% from a calibration curve obtained separately. On the other hand, to the combined aqueous layer was added water until the inorganic salt completely dissolved, and the total weight of the solution was measured (145 g). The sample solution was prepared by diluting 522 mg of the solution to 10 mL with 50% aqueous MeCN solution. Then, 10 μL of the sample solution was analyzed by HPLC. The yield of sodium *p*-toluenesulfinate (**4**) was calculated to be 90.1% from a calibration curve obtained separately using commercial **4**. 2-Thienyl 4-tolyl sulfide (**3a**) and sodium *p*-toluenesulfinate (**4**) were detected at R*t* = 8.1 min and 3.5 min, respectively [column: YMC-Triart C18 plus TA12S03-L546PTH (4.6 mm i.d. × 75 mm, particle size: 3 μm, pore size: 12 nm); mobile phase: CH_3CN:10 mM aqueous H_3PO_4 = 5:95 (0 min), linear gradient from 5:95 to 80:20 (0 min to 6.7 min), 80:20 (6.7 min to 12 min), flow rate: 1.50 mL/min; detection: UV at 230 nm].

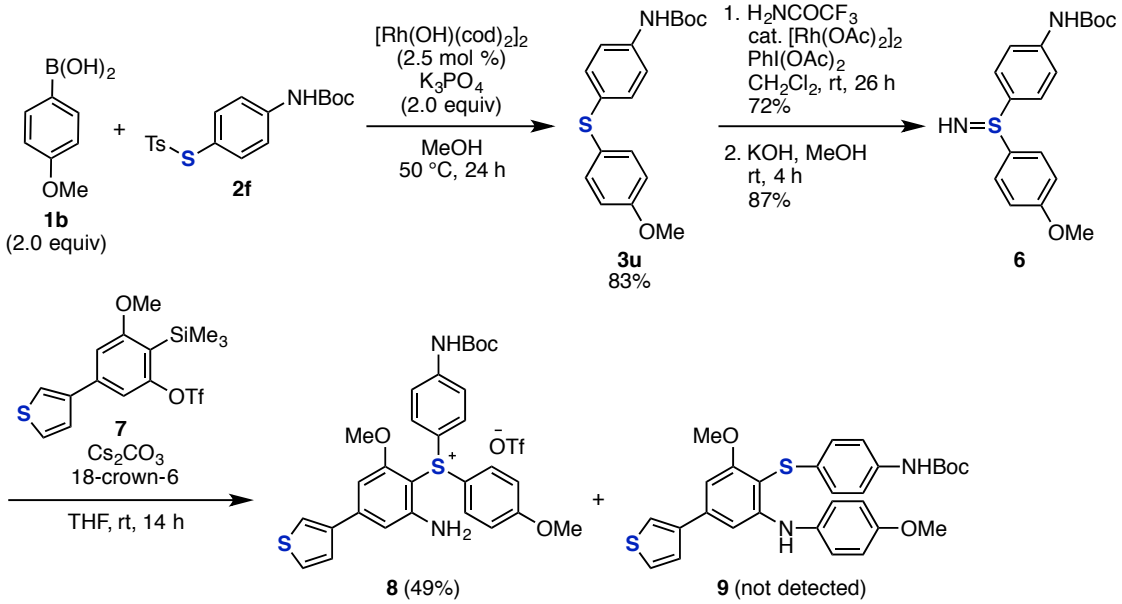
The formation of **4** was also confirmed by ^{1}H NMR analysis; after concentration of the aqueous layer under reduced pressure, the residue was dissolved in deuterium oxide and ^{1}H NMR analysis was conducted. The ^{1}H NMR spectrum obtained contained peaks identical to that of commercial **4**.

Rhodium-catalyzed deborylthiolation in the presence of TEMPO



A mixture of *S*-(4-tolyl) 4-toluenethiosulfonate (**2a**) (70.0 mg, 0.251 mmol, 1.0 equiv), 2-thienylboronic acid (**1a**) (64.3 mg, 0.503 mmol, 2.0 equiv), $[Rh(OH)(cod)]_2$ (5.9 mg, 13 μmol, 5.1 mol %), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (39.6 mg, 0.253 mmol, 1.0 equiv), and tripotassium phosphate (107 mg, 0.503 mmol, 2.0 equiv) suspended in MeOH (2.5 mL) was stirred for 24 h at 50 ºC. After cooling to room temperature, the mixture was filtered through a pad of Celite, washed with MeOH (ca. 65 mL). Weight of the filtrate solution was measured (53.2 g), and 266 mg of the solution was sampled and diluted to 10 mL with MeCN to prepare a sample solution. Then, 10 μL of the sample solution was analyzed by HPLC. The yield of 2-thienyl 4-tolyl sulfide (**3a**) was calculated to be 80.7% from a calibration curve obtained separately. 2-Thienyl 4-tolyl sulfide (**3a**) was detected at R*t* = 8.1 min [column: YMC-Triart C18 plus TA12S03-L546PTH (4.6 mm i.d. × 75 mm, particle size: 3 μm, pore size: 12 nm); mobile phase: CH_3CN:10 mM aqueous H_3PO_4 = 5:95 (0 min), linear gradient from 5:95 to 80:20 (0 min to 6.7 min), 80:20 (6.7 min to 12 min), flow rate: 1.50 mL/min; detection: UV at 230 nm].

*Modular synthesis of multisubstituted triaryl sulfonium salt **8***



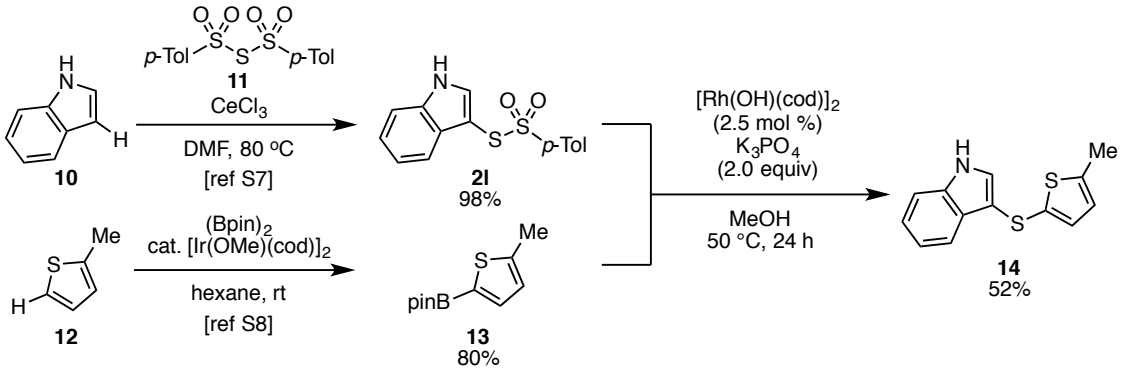
4-(*tert*-Butoxycarbonylamino)phenyl 4-methoxyphenyl sulfide (**3u**) was prepared in 82.8% yield from *S*-(4-(*tert*-butoxycarbonylamino)phenyl) 4-toluenethiosulfonate (**2f**) (240 mg, 0.633 mmol, 1.0 equiv) and 4-methoxyphenylboronic acid (**1b**) (194 mg, 1.28 mmol, 2.0 equiv) according to the typical procedure for rhodium-catalyzed thiolation of boronic acids with thiosulfonates.

To a mixture of 4-(*tert*-butoxycarbonylamino)phenyl 4-methoxyphenyl sulfide (**3u**) (998 mg, 3.01 mmol, 1.0 equiv), MgO (524 mg, 13.0 mmol, 4.3 equiv), H_2NCOCF_3 (723 mg, 6.40 mmol, 2.1 equiv), and $[Rh(OAc)_2]_2$ (36.2 mg, 81.9 μmol, 2.7 mol %) suspended in CH_2Cl_2 (16 mL) was added $PhI(OAc)_2$ (1.55 g, 4.81 mmol, 1.6 equiv) at room temperature. After stirring for 26 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® SNAP Ultra 100 g, heptane/EtOAc = 70/30 to 50/50) to give *S*-(4-(*tert*-butoxycarbonylamino)phenyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-methoxyphenyl)sulfilimine (957 mg, 2.16 mmol, 71.9%) as a brown solid.

To a solution of *S*-(4-(*tert*-butoxycarbonylamino)phenyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-methoxyphenyl)sulfilimine (452 mg, 1.02 mmol, 1.0 equiv) dissolved in MeOH (5.1 mL) was added KOH (299 mg, 5.32 mmol, 5.2 equiv) at room temperature. After stirring for 4 h at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3), and the combined organic extract was dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Purif-Pack NH 60 μm SIZE: 20, $CHCl_3$/MeOH = 100/0 to 98/2) to give *S*-(4-(*tert*-butoxycarbonylamino)phenyl)-*S*-(4-methoxyphenyl)sulfilimine (**6**) (309 mg, 0.892 mmol, 87.2%) as a colorless solid.

To a mixture of 3-methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**7**)[S5,S6] (41.2 mg, 0.100 mmol, 1.0 equiv) and *S*-(4-(*tert*-butoxycarbonylamino)phenyl)-*S*-(4-methoxyphenyl)-sulfilimine (**6**) (71.1 mg, 0.205 mmol, 2.0 equiv) suspended in THF (0.6 mL) were added cesium carbonate (68.2 mg, 0.209 mmol, 2.1 equiv) and 18-crown-6 (51.2 mg, 0.194 mmol, 1.9 equiv) at room temperature. After stirring for 14 h at room temperature, the mixture was filtered through a pad of Celite, and then the filtrate was concentrated under reduced pressure. To the residue was added EtOAc (20 mL) and the mixture was washed with aqueous saturated solution of sodium bicarbonate (20 mL × 2) and brine (20 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (CH_2Cl_2/MeOH = 10/1, then *n*-hexane/EtOAc = 5/1) to give (2-amino-6-methoxy-4-(3-thienyl)phenyl)(4-*tert*-butoxycarbonylaminophenyl)(4-methoxyphenyl)sulfonium triflate (**8**) (33.4 mg, 48.8 μmol, 48.6%) as a pale brown solid.

*Synthesis of 3-(2-(5-methylthienyl)thio)indole (**14**) via formal C–H thiolation*



S-(1*H*-Indol-3-yl) 4-toluenethiosulfonate (**2l**) (408 mg, 67.3%) was prepared from 1*H*-indole (**10**) and *S*-(4-toluenesulfonyl) 4-toluenethiosulfonate (**11**) according to the reported method.[S7]

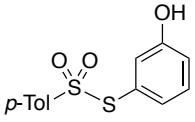
2-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**13**) was prepared according to the reported method with some modifications for the purification process.[S8] To a mixture of bis(pinacolato)diboron (2.55 g, 10.1 mmol, 1.0 equiv), $[Ir(OMe)(cod)]_2$ (99.8 mg, 0.151 mmol, 1.5 mol %), and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (80.5 mg, 0.300 mmol, 3.0 mol %) dissolved in hexane (60 mL) was added 2-methylthiophene (**12**) (1.97 g, 20.1 mmol, 2.0 equiv) at room temperature. After stirring for 2 h at room temperature, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (Biotage® SNAP Ultra 50 g, *n*-heptane/EtOAc = 30/1) to give 2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**13**) (1.81 g, 8.06 mmol, 80.1%) as a colorless oil.

1*H*-Indol-3-yl 2-(5-methyl)thienyl sulfide (**14**) (31.6 mg, 51.6%) was prepared from *S*-(1*H*-indol-3-yl) 4-toluenethiosulfonate (**2l**) and 2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**13**) according to the typical procedure for rhodium-catalyzed thiolation of boronic acids with thiosulfonates.

Characterization Data of New Compounds

Thiosulfonates (**2a**,[S9] **2b,**[S10] **2c**,[S11] **2e**,[S11] **2g**,[S11] and **2i**[S12]), diaryl sulfides (**3a**,[S13] **3b**,[S14] **3c**,[S15] **3d**,[S16] **3e**,[S15] **3f**,[S1] **3h**,[S17] **3i**,[S1] **3j**,[S18] **3k**,[S19] **3s**,[S20] and **3t**[S21]), 3-methoxy-5-(3-thienyl)-2-(trimethylsilyl)phenyl triflate (**7**),[S6] *S*-(1*H*-indol-3-yl) 4-toluenethiosulfonate (**2l**),[S7] and 2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**13**)[S8] were identical in spectra data with those reported in the literature.

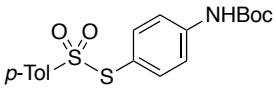
S-(3-Hydroxyphenyl) 4-toluenethiosulfonate (**2d**)



Colorless solid; Mp 114–115 ºC; TLC R_f 0.30 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 6.87 (ddd, 1H, J = 7.9, 1.4, 0.9 Hz), 6.93 (dd, 1H, J = 2.5, 1.4 Hz), 6.96 (ddd, 1H, J = 7.9, 2.5, 0.9 Hz), 7.19 (dd, 1H, J = 7.9, 7.9 Hz), 7.21–7.24 (AA′BB′, 2H), 7.47–7.50 (AA′BB′, 2H); ^{13}C NMR (DMSO-d_6, 126 MHz) δ 22.1 (1C), 119.8 (1C), 123.2 (1C), 127.4 (1C), 128.1 (2C), 128.4 (1C), 130.8 (2C), 131.5 (1C), 140.5 (1C), 146.1 (1C),

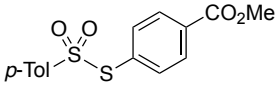
158.9 (1C); IR (KBr, cm^{-1}) 574, 590, 658, 747, 1141, 1259, 1303, 1440, 1584, 1594, 3448; HRMS (ESI^+) *m*/*z* 303.0127 ($[M+Na]^+$, $C_{13}H_{12}NaO_3S_2^+$ requires 303.0120).

S-(4-(*tert*-Butoxycarbonylamino)phenyl) 4-toluenethiosulfonate (**2f**)



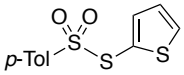
Colorless solid; Mp 164–166 ºC; TLC R_f 0.23 (*n*-hexane/EtOAc = 5/1); ^1H NMR (DMSO-d_6, 500 MHz) δ 1.52 (s, 9H), 2.44 (s, 3H), 7.22–7.26 (AA′BB′, 2H), 7.41–7.45 (AA′BB′, 2H), 7.46–7.50 (AA′BB′, 2H), 7.51–7.56 (AA′BB′, 2H), 9.79 (br s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 22.1 (1C), 29.0 (3C), 80.8 (1C), 119.4 (2C), 119.7 (1C), 128.1 (2C), 130.8 (2C), 138.0 (2C), 140.6 (1C), 143.9 (1C), 146.0 (1C), 153.4 (1C); IR (KBr, cm^{-1}) 750, 1141, 1261, 1510, 1586, 1731, 2306, 2981, 3055; HRMS (ESI^+) *m*/*z* 402.0811 ($[M+Na]^+$, $C_{18}H_{21}NNaO_4S_2^+$ requires 402.0804).

S-(4-(Methoxycarbonyl)phenyl) 4-toluenethiosulfonate (**2h**)



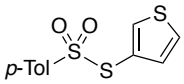
Colorless solid; Mp 71–72 ºC; TLC R_f 0.20 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 3.94 (s, 3H), 7.20–7.24 (AA′BB′, 2H), 7.43–7.48 (m, 4H), 7.97–8.01 (AA′BB′, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.7 (1C), 52.5 (1C), 127.6 (2C), 129.5 (2C), 130.3 (2C), 132.5 (1C), 133.2 (1C), 136.3 (2C), 140.3 (1C), 145.1 (1C), 166.1 (1C); IR (KBr, cm^{-1}) 519, 583, 764, 1016, 1078, 1115, 1144, 1277, 1331, 1396, 1435, 1539, 1726; Anal. calcd for $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.38; N, 0.00%. Found: C, 55.74; H, 4.35; N, 0.00%.

S-(2-Thienyl) 4-toluenethiosulfonate (**2j**)



Brown solid; Mp 50–51 ºC; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 7.07 (dd, 1H, *J* = 5.3, 3.7 Hz), 7.16 (dd, 1H, *J* = 3.7, 1.3 Hz), 7.23–7.27 (AA′BB′, 2H), 7.51–7.55 (AA′BB′, 2H), 7.61 (dd, 1H, *J* = 5.3, 1.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.7 (1C), 125.3 (1C), 127.9 (2C), 128.3 (1C), 129.5 (2C), 135.1 (1C), 139.4 (1C), 139.5 (1C), 145.1 (1C); IR (KBr, cm^{-1}) 520, 582, 655, 716, 1077, 1143, 1328, 1396; HRMS (ESI^+) *m*/*z* 292.9746 ($[M+Na]^+$, $C_{11}H_{10}NaO_2S_3^+$ requires 292.9735).

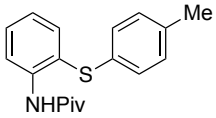
S-(3-Thienyl) 4-toluenethiosulfonate (**2k**)



Pale brown solid; Mp 58–60 ºC; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.43 (s, 3H), 7.01 (dd, 1H, *J* = 5.0, 1.3 Hz), 7.21–7.25 (AA′BB′, 2H), 7.34 (dd, 1H, *J* = 5.0, 3.1 Hz), 7.43 (dd, 1H, *J* = 3.1, 1.3 Hz), 7.46–7.50 (AA′BB′, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.7 (1C), 123.3 (1C), 126.7 (1C), 127.6 (2C), 129.4 (2C), 132.6 (1C), 135.2

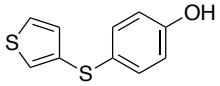
(1C), 140.2 (1C), 144.8 (1C); IR (KBr, cm^{-1}) 519, 577, 656, 782, 1078, 1143, 1326; HRMS (ESI^+) *m*/*z* 292.9745 ($[M+Na]^+$, $C_{11}H_{10}NaO_2S_3^+$ requires 292.9735).

2-(*N*-Pivaloylamino)phenyl 4-tolyl sulfide (**3g**)



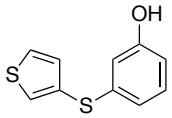
Pale yellow oil; TLC R_f 0.40 (*n*-hexane/EtOAc = 10/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.13 (s, 9H), 2.27 (s, 3H), 6.94–6.98 (AA′BB′, 2H), 7.02–7.06 (AA′BB′, 2H), 7.10 (ddd, 1H, *J* = 7.7, 7.7, 1.4 Hz), 7.44 (ddd, 1H, *J* = 7.7, 7.7, 1.6 Hz), 7.59 (dd, 1H, *J* = 7.7, 1.6 Hz), 8.51 (dd, 1H, *J* = 7.7, 1.4 Hz), 8.61 (br s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.9 (1C), 27.3 (3C), 40.0 (1C), 120.1 (1C), 120.4 (1C), 124.0 (1C), 126.8 (2C), 130.0 (2C), 130.9 (1C), 131.7 (1C), 136.1 (1C), 136.4 (1C), 139.9 (1C), 176.7 (1C); IR (KBr, cm^{-1}) 749, 802, 917, 1158, 1302, 1505, 1580, 1683, 2960, 3375; HRMS (ESI^+) *m*/*z* 322.1233 ($[M+Na]^+$, $C_{18}H_{21}NNaOS^+$ requires 322.1236).

4-Hydroxyphenyl 3-thienyl sulfide (**3l**)



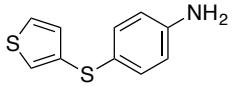
Brown oil; TLC R_f 0.19 (*n*-hexane/EtOAc = 5:1); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.94 (br s, 1H), 6.75–6.80 (AA'BB', 2H), 6.95 (dd, 1H, *J* = 5.1, 1.3 Hz), 7.14 (dd, 1H, *J* = 3.1, 1.3 Hz), 7.24 (AA'BB', 2H), 7.31 (dd, 1H, *J* = 5.1, 3.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 116.2 (2C), 124.6 (1C), 126.5 (1C), 126.7 (1C), 129.8 (1C), 132.2 (1C), 132.9 (2C), 155.1 (1C); IR (KBr, cm^{-1}) 773, 828, 1169, 1200, 1223, 1258, 1493, 1584, 1599, 3296; HRMS (ESI^+) *m*/*z* 209.0092 ($[M+H]^+$, $C_{10}H_9OS_2^+$ requires 209.0089).

3-Hydroxyphenyl 3-thienyl sulfide (**3m**)



Brown oil; TLC R_f 0.23 (*n*-hexane/EtOAc = 5:1); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.83 (br s, 1H), 6.60–6.64 (m, 2H), 6.77 (ddd, 1H, *J* = 7.9, 2.5, 1.0 Hz), 7.07 (dd, 1H, *J* = 4.9, 1.3 Hz), 7.12 (dd, 1H, *J* = 8.5, 7.9 Hz), 7.39 (dd, 1H, *J* = 4.9, 3.1 Hz), 7.10–7.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 113.1 (1C), 114.5 (1C), 120.3 (1C), 126.8 (1C), 128.4 (1C), 129.2 (1C), 130.0 (1C), 131.6 (1C), 139.3 (1C), 155.9 (1C); IR (KBr, cm^{-1}) 617, 683, 772, 853, 1198, 1246, 1296, 1350, 1435, 1472, 1582, 2924, 3101, 3342; HRMS (ESI^+) *m*/*z* 209.0089 ($[M+H]^+$, $C_{10}H_9OS_2^+$ requires 209.0089).

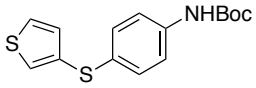
4-Aminophenyl 3-thienyl sulfide (**3n**)



Brown oil; TLC R_f 0.44 (*n*-hexane/EtOAc = 2/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.74 (br s, 2H), 6.60–6.65 (AA′BB′, 2H), 6.91 (dd, 1H, *J* = 5.0, 1.3 Hz), 7.00 (dd, 1H, *J* = 3.1, 1.3 Hz),

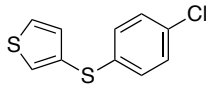
7.22–7.26 (AA′BB′, 2H), 7.27 (dd, 1H, J = 5.0, 3.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 115.7 (2C), 122.56 (1C), 122.59 (1C), 126.2 (1C), 129.1 (1C), 133.80 (1C), 133.83 (2C), 146.3 (1C); IR (KBr, cm^{-1}) 765, 825, 1284, 1495, 1595, 1618, 3344; Anal. calcd for $C_{10}H_9NS_2$: C, 57.94; H, 4.38; N, 6.76%. Found: C, 57.79; H, 4.10; N, 6.59%.

4-(*tert*-Butoxycarbonylamino)phenyl 3-thienyl sulfide (**3o**)



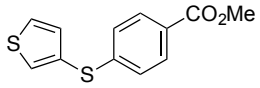
Pale yellow solid; Mp 95–97 ºC; TLC R_f 0.27 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (s, 9H), 6.45 (br s, 1H), 6.96 (dd, 1H, J = 5.0, 1.3 Hz), 7.21 (dd, 1H, J = 3.1, 1.3 Hz), 7.23–7.27 (AA′BB′, 2H), 7.27–7.31 (AA′BB′, 2H), 7.32 (dd, 1H, J = 5.0, 3.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 28.3 (3C), 80.8 (1C), 119.2 (1C), 125.7 (1C), 126.5 (2C), 129.7 (1C), 130.2 (1C), 131.2 (2C), 131.2 (1C), 137.4 (1C), 152.6 (1C); IR (KBr, cm^{-1}) 767, 828, 1053, 1157, 1231, 1311, 1368, 1397, 1513, 1588, 1697, 2977, 3330; HRMS (ESI$^+$) m/z 330.0599 ([M+Na]$^+$, $C_{15}H_{17}NNaO_2S_2^+$ requires 330.0593).

4-Chlorophenyl 3-thienyl sulfide (**3p**)



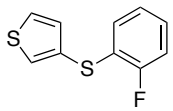
Pale yellow solid; Mp 38–39 ºC; TLC R_f 0.32 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.03 (dd, 1H, J = 4.9, 1.4 Hz), 7.10–7.14 (AA′BB′, 2H), 7.20–7.24 (AA′BB′, 2H), 7.37–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 127.1 (1C), 128.75 (1C), 128.76 (1C), 129.1 (2C), 129.6 (2C), 131.2 (1C), 132.1 (1C), 136.1 (1C); IR (KBr, cm^{-1}) 780, 815, 1011, 1091, 1475; Anal. calcd for $C_{10}H_7ClS_2$: C, 52.97; H, 3.11; N, 0.00%. Found: C, 53.24; H, 3.15; N, 0.00%.

4-(Methoxycarbonyl)phenyl 3-thienyl sulfide (**3q**)



Pale yellow solid; Mp 72–73 ºC; TLC R_f 0.30 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.89 (s, 3H), 7.10 (dd, 1H, J = 5.0, 1.2 Hz), 7.11–7.14 (AA′BB′, 2H), 7.45 (dd, 1H, J = 5.0, 3.1 Hz), 7.55 (dd, 1H, J = 3.1, 1.2 Hz), 7.86–7.90 (AA′BB′, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.1 (1C), 126.0 (2C), 126.6 (1C), 127.1 (1C), 127.3 (1C), 130.0 (2C), 131.0 (1C), 131.9 (1C), 145.0 (1C), 166.7 (1C); IR (KBr, cm^{-1}) 619, 689, 758, 783, 852, 1015, 1109, 1178, 1275, 1400, 1433, 1489, 1593, 1714; HRMS (ESI$^+$) m/z 273.0021 ([M+Na]$^+$, $C_{12}H_{10}NaO_2S_2^+$ requires 273.0014).

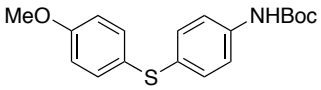
2-Fluorophenyl 3-thienyl sulfide (**3r**)



Colorless oil; TLC R_f 0.28 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99–7.08 (m, 4H), 7.15–7.20 (m, 1H), 7.38 (dd, 1H, J = 5.0, 3.0 Hz), 7.42 (dd, 1H, J = 3.0, 1.2 Hz); ^{13}C NMR

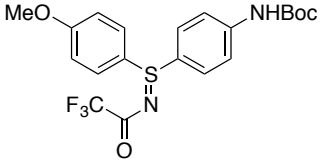
($CDCl_3$, 126 MHz) δ 115.6 (d, 1C, $J_{C–F}$ = 21.9 Hz), 124.5 (1C), 124.6 (d, 1C, $J_{C–F}$ = 3.6 Hz), 126.9 (1C), 127.5 (1C), 128.1 (d, 1C, $J_{C–F}$ = 7.5 Hz), 128.9 (1C), 130.7 (1C), 131.3 (1C), 159.9 (d, 1C, $J_{C–F}$ = 246.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –111.3 to –111.2 (m); IR (KBr, cm^{-1}) 750, 781, 1220, 1259, 1470; HRMS (ESI^+) *m*/*z* 211.0048 ($[M+H]^+$, $C_{10}H_8FS_2^+$ requires 211.0046).

4-(*tert*-Butoxycarbonylamino)phenyl 4-methoxyphenyl sulfide (**3u**)



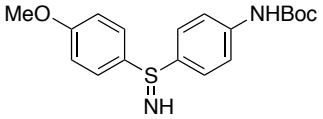
Colorless solid; Mp 155–157 ºC; TLC R_f 0.18 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.50 (s, 9H), 3.78 (s, 3H), 6.95–7.00 (AA′BB′, 2H), 7.19–7.25 (AA′BB′, 2H), 7.28–7.33 (AA′BB′, 2H), 7.43–7.49 (AA′BB′, 2H), 9.47 (br s, 1H); ^{13}C NMR (DMSO-d_6, 126 MHz) δ 29.0 (3C), 56.2 (1C), 80.2 (1C), 116.0 (2C), 119.9 (2C), 126.8 (1C), 129.2 (1C), 132.1 (2C), 133.9 (2C), 139.8 (1C), 153.6 (1C), 159.8 (1C); IR (KBr, cm^{-1}) 826, 1160, 1244, 1493, 1310, 1398, 1515, 1591, 1700, 1727, 3371; HRMS (ESI^+) *m*/*z* 354.1127 ($[M+Na]^+$, $C_{18}H_{21}NNaO_3S^+$ requires 354.1134).

S-(4-(*tert*-Butoxycarbonylamino)phenyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-methoxyphenyl)sulfilimine



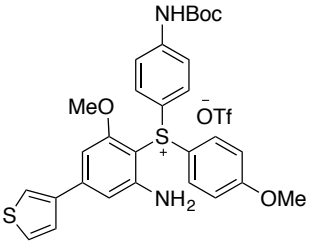
Brown solid; Mp 68–71 ºC; TLC R_f 0.31 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (s, 9H), 3.83 (s, 3H), 6.96–7.01 (AA′BB′, 2H), 7.25 (br s, 1H), 7.48–7.53 (AA′BB′, 2H), 7.56–7.61 (AA′BB′, 2H), 7.62–7.67 (AA′BB′, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 28.1 (3C), 55.6 (1C), 81.3 (1C), 115.6 (2C), 117.1 (q, 1C, $^1J_{C–F}$ = 288.6 Hz), 119.1 (2C), 124.3 (1C), 126.2 (1C), 128.9 (2C), 129.9 (2C), 143.0 (1C), 152.2 (1C), 163.0 (1C), 166.4 (q, 1C, $^2J_{C–F}$ = 35.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.5 (s); IR (KBr, cm^{-1}) 648, 742, 913, 1154, 1173, 1496, 1593, 1634, 2253; HRMS (ESI^+) *m*/*z* 465.1080 ($[M+Na]^+$, $C_{20}H_{21}F_3N_2NaO_4S^+$ requires 465.1066).

S-(4-(*tert*-Butoxycarbonylamino)phenyl)-*S*-(4-methoxyphenyl)sulfilimine (**6**)



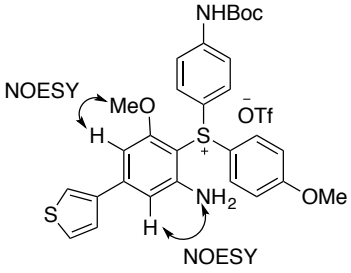
Colorless solid; Mp 150–151 ºC; TLC (Amino) R_f 0.32 ($CHCl_3$/MeOH = 50/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (s, 9H), 3.82 (s, 3H), 6.76–6.83 (br s, 1H), 6.91–6.95 (AA′BB′, 2H), 7.43–7.48 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 28.3 (3C), 55.5 (1C), 81.1 (1C), 114.7 (2C), 118.7 (2C), 126.9 (2C), 127.7 (2C), 137.0 (1C), 139.2 (1C), 140.5 (1C), 152.4 (1C), 161.3 (1C); IR (KBr, cm^{-1}) 743, 748, 913, 1161, 1246, 1315, 1496, 1539, 1593, 1717, 2356, 2977; HRMS (ESI^+) *m*/*z* 347.1430 ($[M+H]^+$, $C_{18}H_{23}N_2O_3S^+$ requires 347.1424).

(2-Amino-6-methoxy-4-(3-thienyl)phenyl)(4-*tert*-butoxycarbonylaminophenyl)(4-methoxyphenyl)sulfonium triflate (**8**)

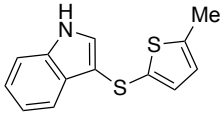


Pale brown solid; Mp 102–105 ºC; TLC R_f 0.17 (CH_2Cl_2/MeOH = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.52 (s, 9H), 3.66 (s, 3H), 3.88 (s, 3H), 5.71 (br s, 2H), 6.40 (d, 1H, J = 1.5 Hz), 6.74 (d, 1H, J = 1.5 Hz), 7.04–7.08 (AA′BB′, 2H), 7.28 (br s, 1H), 7.34 (dd, 1H, J = 5.1, 1.4 Hz), 7.41 (dd, 1H, J = 5.1, 3.0 Hz), 7.48–7.53 (AA′BB′, 2H), 7.58 (dd, 1H, J = 3.0, 1.4 Hz), 7.63–7.68 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 28.2 (3C), 55.8 (1C), 55.9 (1C), 81.6 (1C), 89.4 (1C), 98.9 (1C), 108.5 (1C), 114.7 (1C), 116.1 (2C), 116.4 (1C), 119.5 (2C), 120.7 (q, 1C, $^1J_{C–F}$ = 320.6 Hz), 123.4 (1C), 126.0 (1C), 127.0 (1C), 130.8 (2C), 132.3 (2C), 140.3 (1C), 143.6 (1C), 144.9 (1C), 152.3 (1C), 153.0 (1C), 160.2 (1C), 163.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –78.4 (s); IR (KBr, cm^{-1}) 525, 1030, 1154, 1258, 1495, 1532, 1591, 3330; HRMS (ESI$^+$) *m*/*z* 535.1730 ([M–OTf]$^+$, $C_{29}H_{31}N_2O_4S_2^+$ requires 535.1720).

The regiochemistry of **8** was determined by the NOESY experiment.



1*H*-Indol-3-yl 2-(5-methyl)thienyl sulfide (**14**)



Brown solid; Mp 106–108 ºC; TLC R_f 0.26 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.34 (s, 3H), 6.64–6.66 (m, 1H), 7.02 (d, 1H, J = 2.7 Hz), 7.13 (ddd, 1H, J = 7.5, 7.5, 1.0 Hz), 7.19 (ddd, 1H, J = 7.5, 7.5, 1.0 Hz), 7.46 (dd, 1H, J = 7.5, 1.0 Hz), 7.65 (dd, 1H, J = 7.5, 1.0 Hz), 7.72 (d, 1H, J = 2.7 Hz), 11.56 (br s, 1H); ^{13}C NMR (DMSO-d_6, 126 MHz) δ 16.1 (1C), 104.8 (1C), 113.1 (1C), 119.2 (1C), 120.9 (1C), 122.9 (1C), 126.7 (1C), 129.1 (1C), 131.5 (1C), 131.7 (1C), 135.3 (1C), 137.2 (1C), 142.9 (1C); IR (KBr, cm^{-1}) 747, 762, 1452, 2921, 3401; Anal. calcd for $C_{13}H_{11}NS_2$: C, 63.64; H, 4.52; N, 5.71%. Found: C, 63.40; H, 4.47; N, 5.70%.

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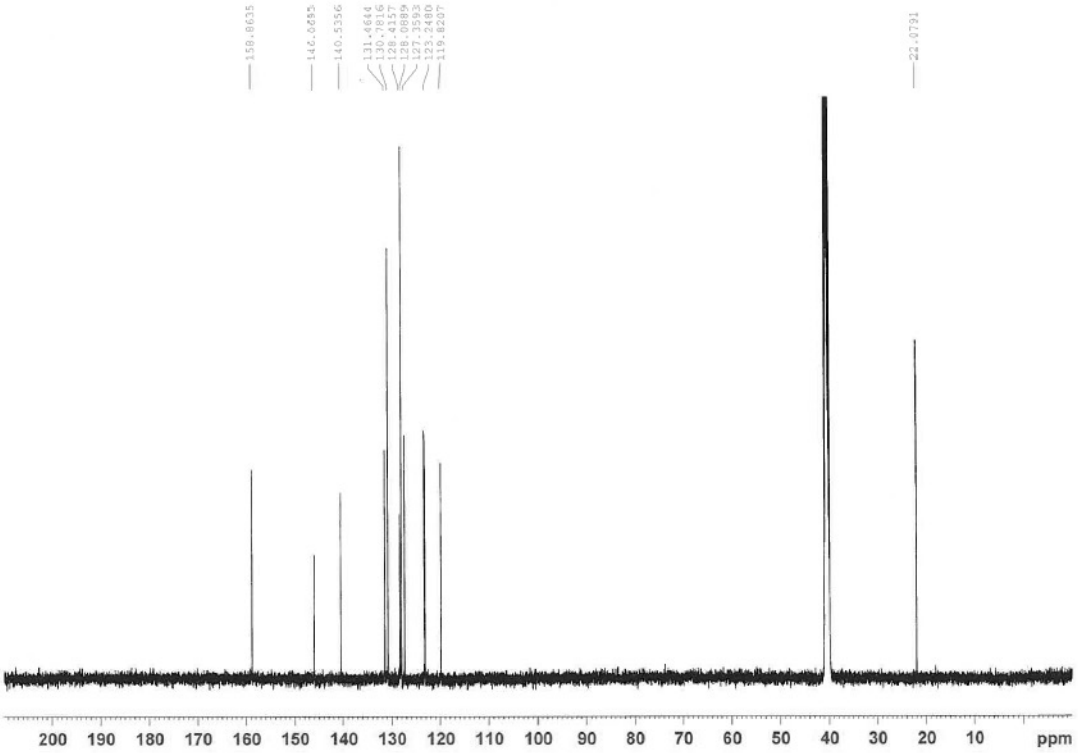
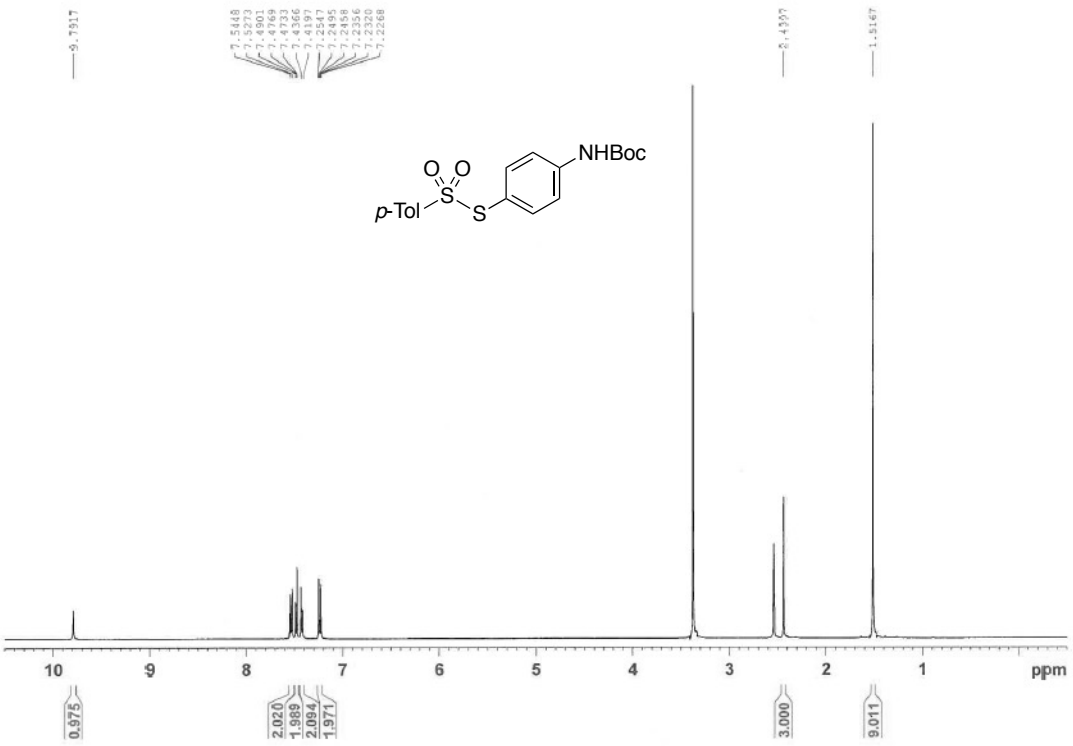
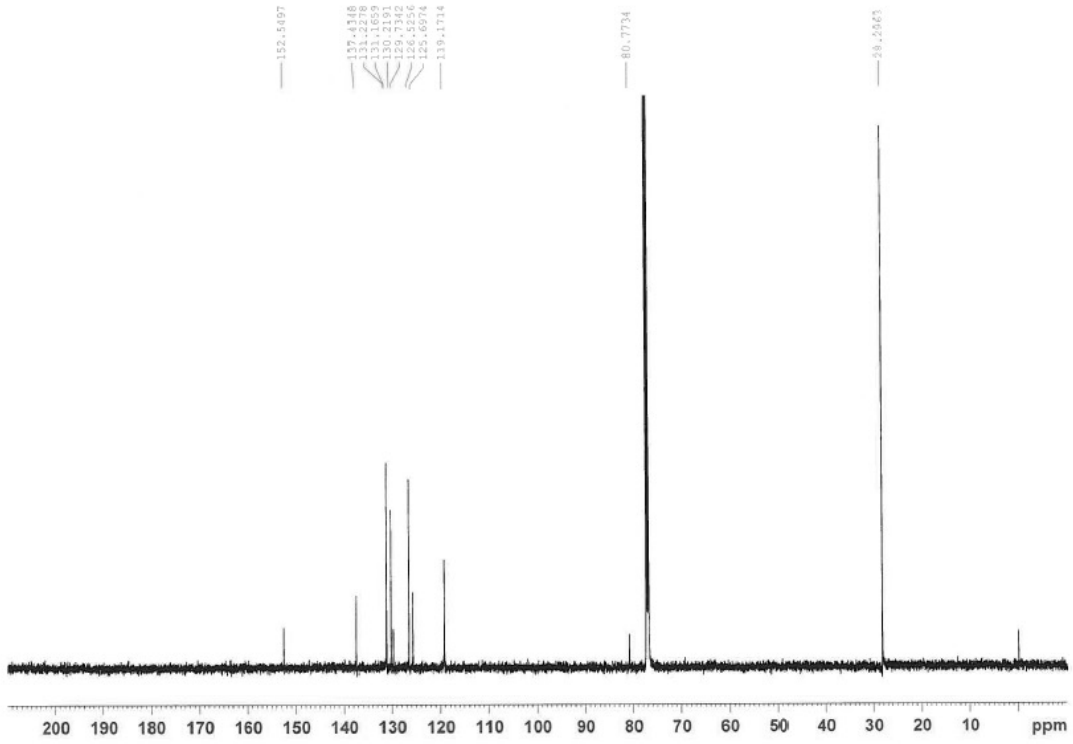
^{1}H and ^{13}C NMR Spectra of Compounds

^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra of **2d**

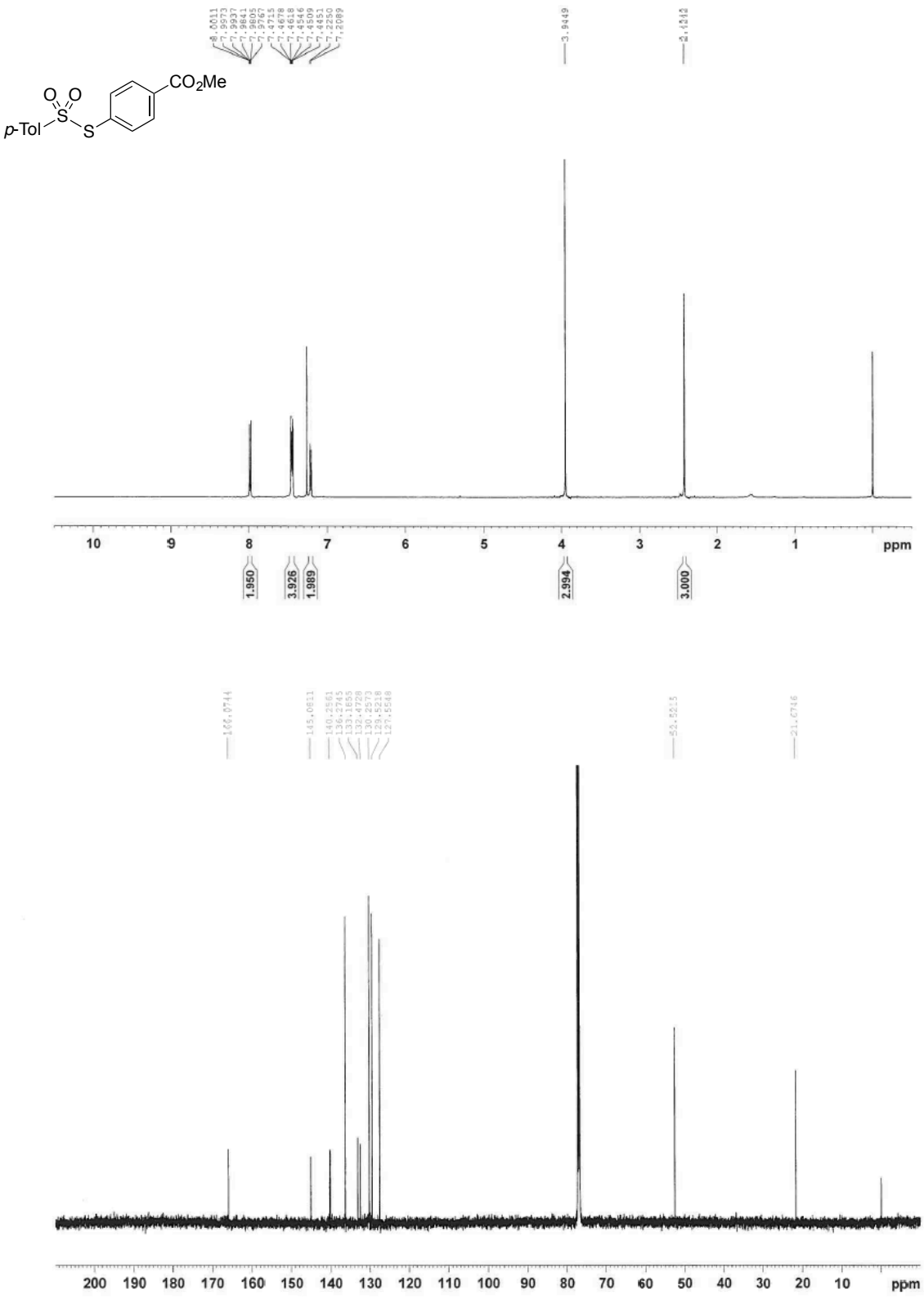


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of **2f**

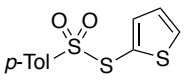


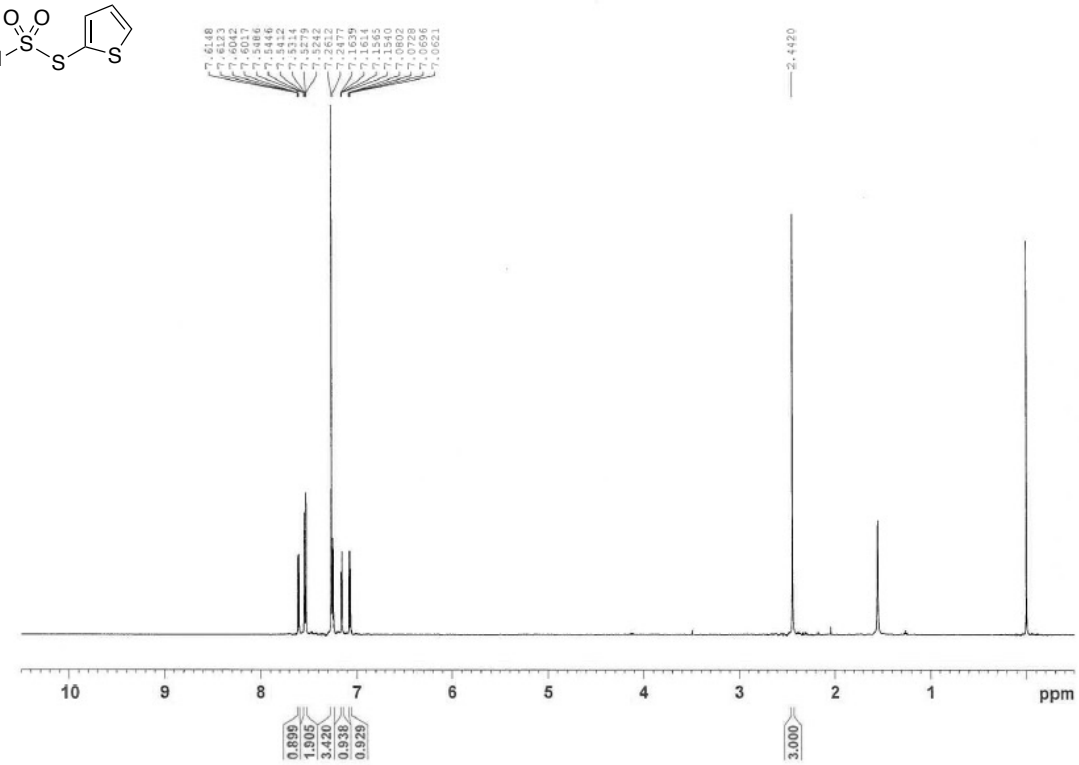


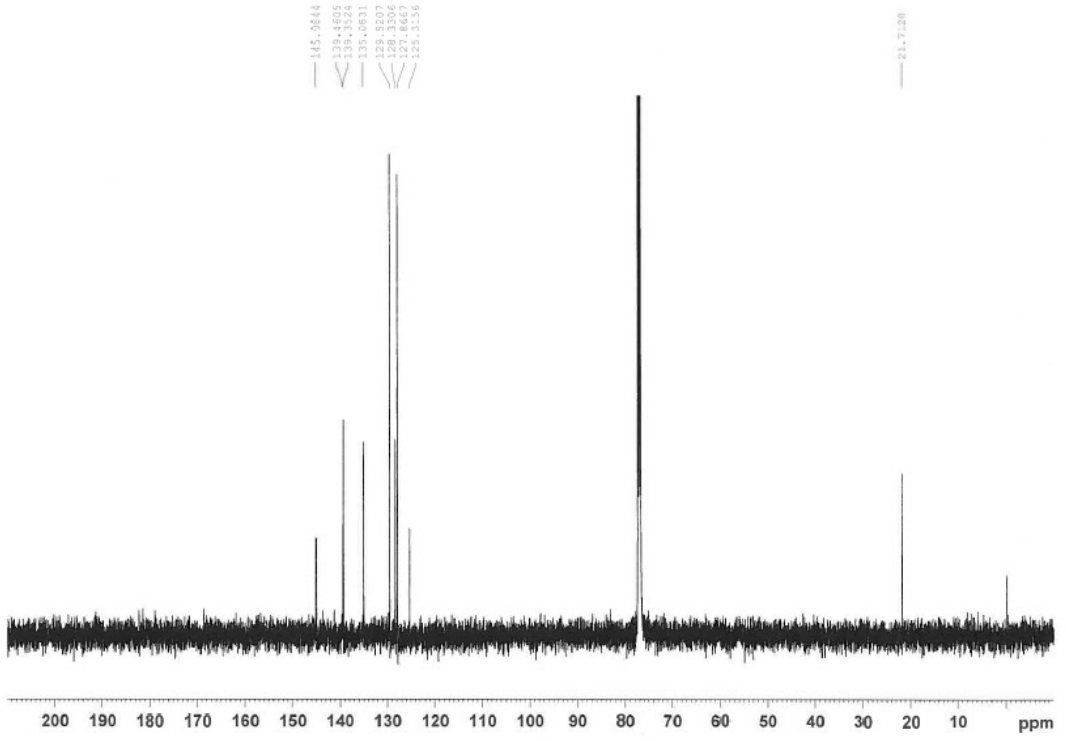
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2h** ($CDCl_3$)



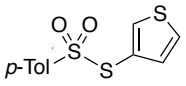
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2j** ($CDCl_3$)

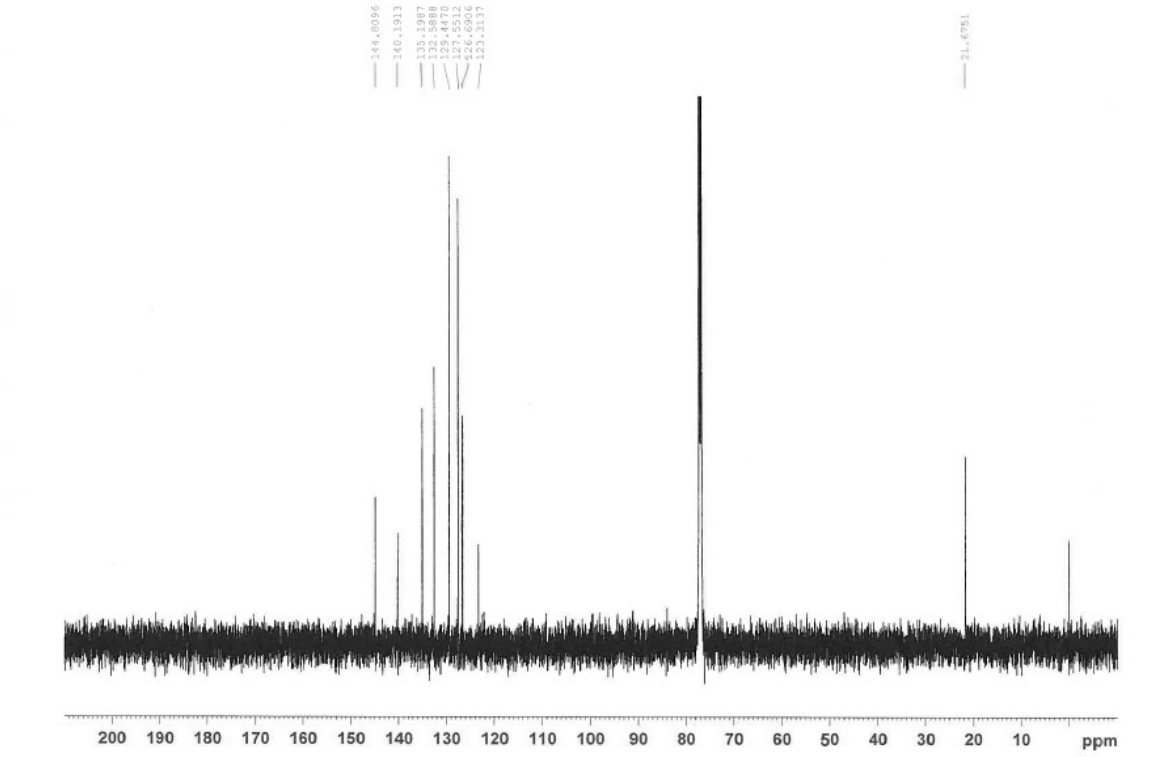




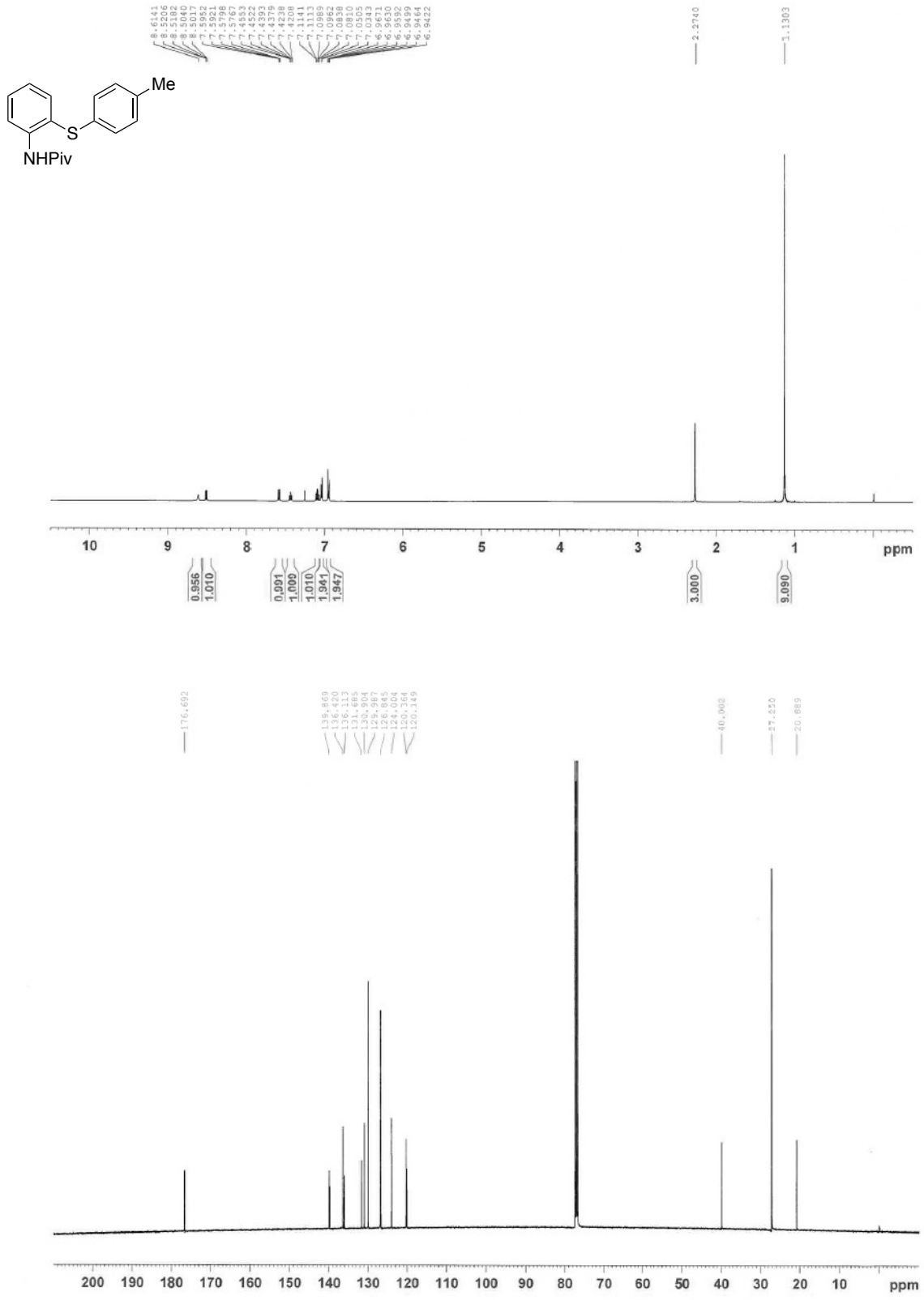


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2k** ($CDCl_3$)

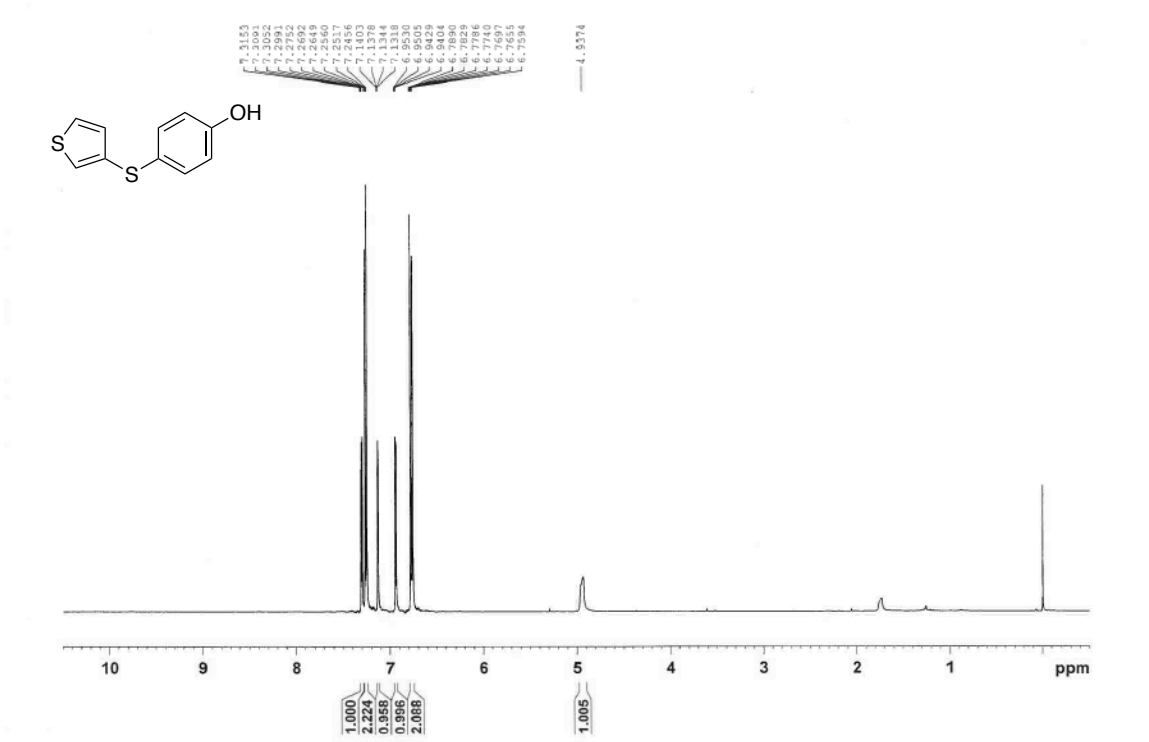


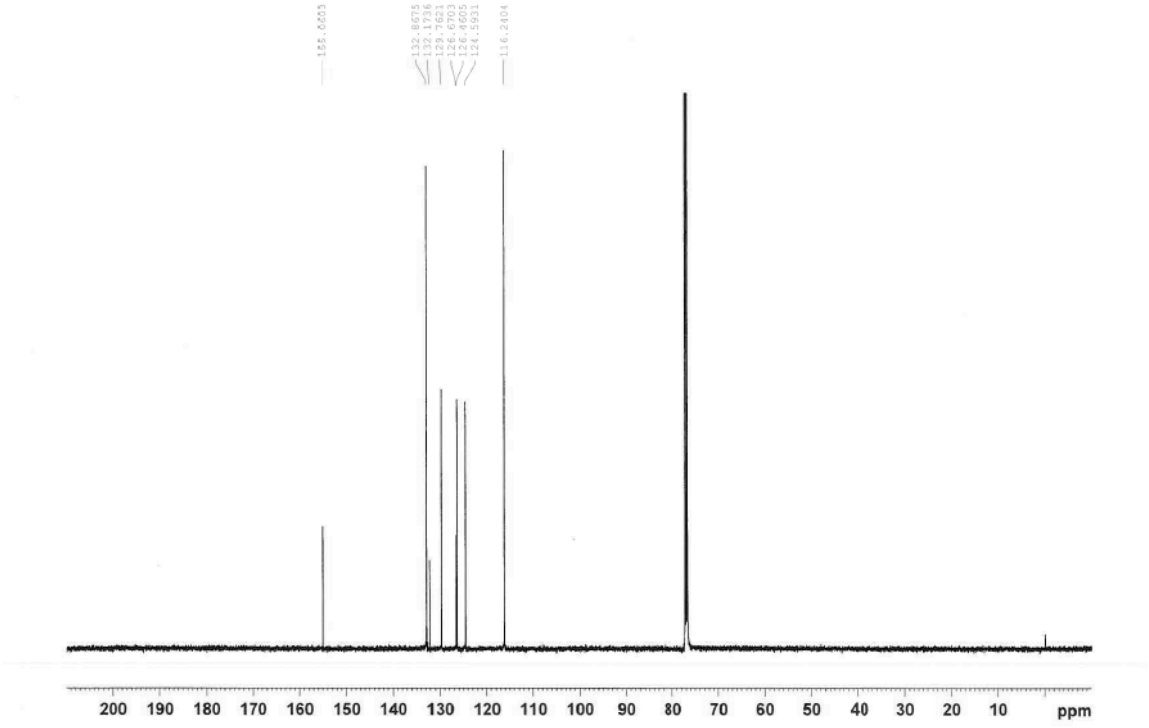


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3g** ($CDCl_3$)

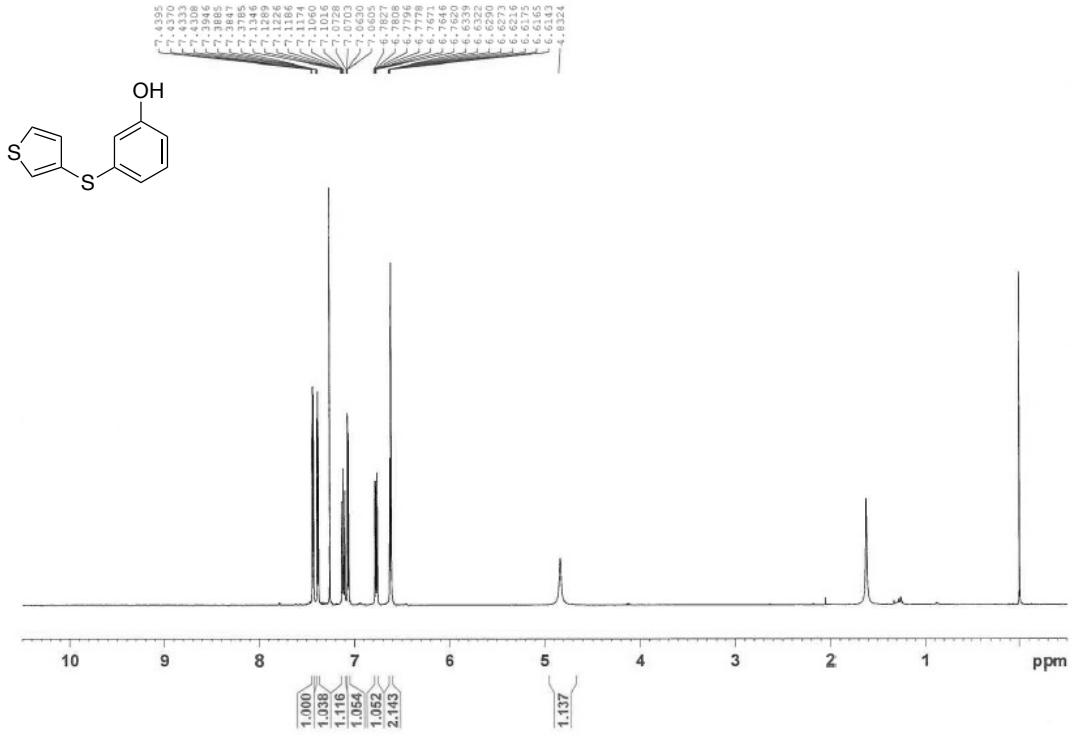


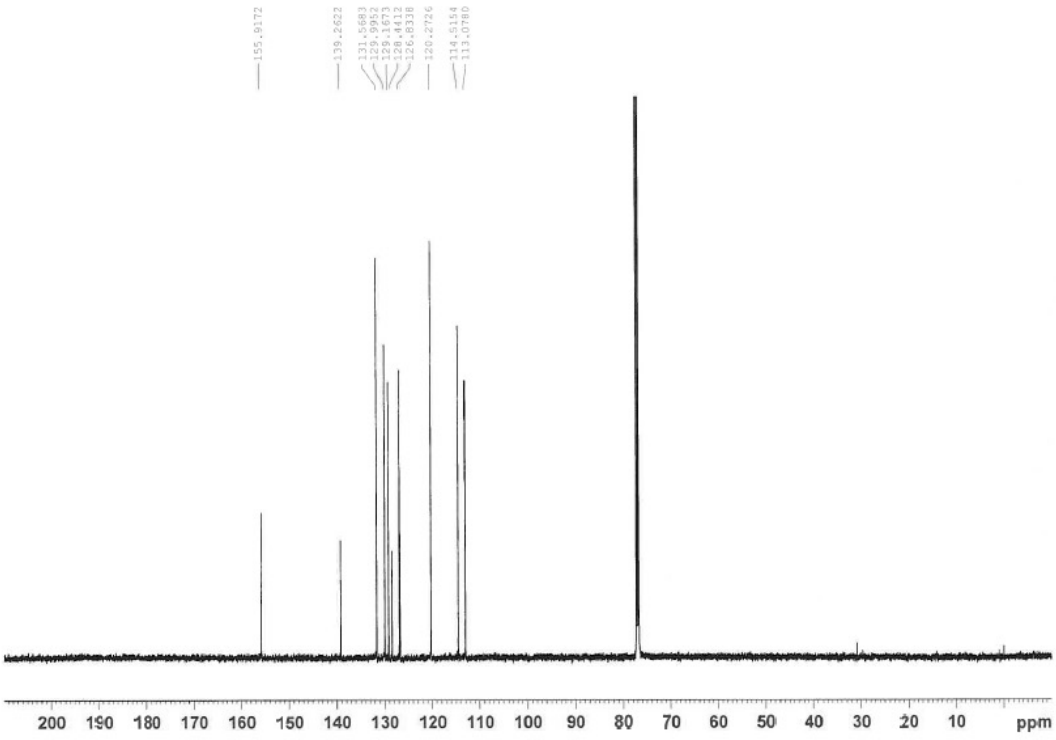
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3l** ($CDCl_3$)



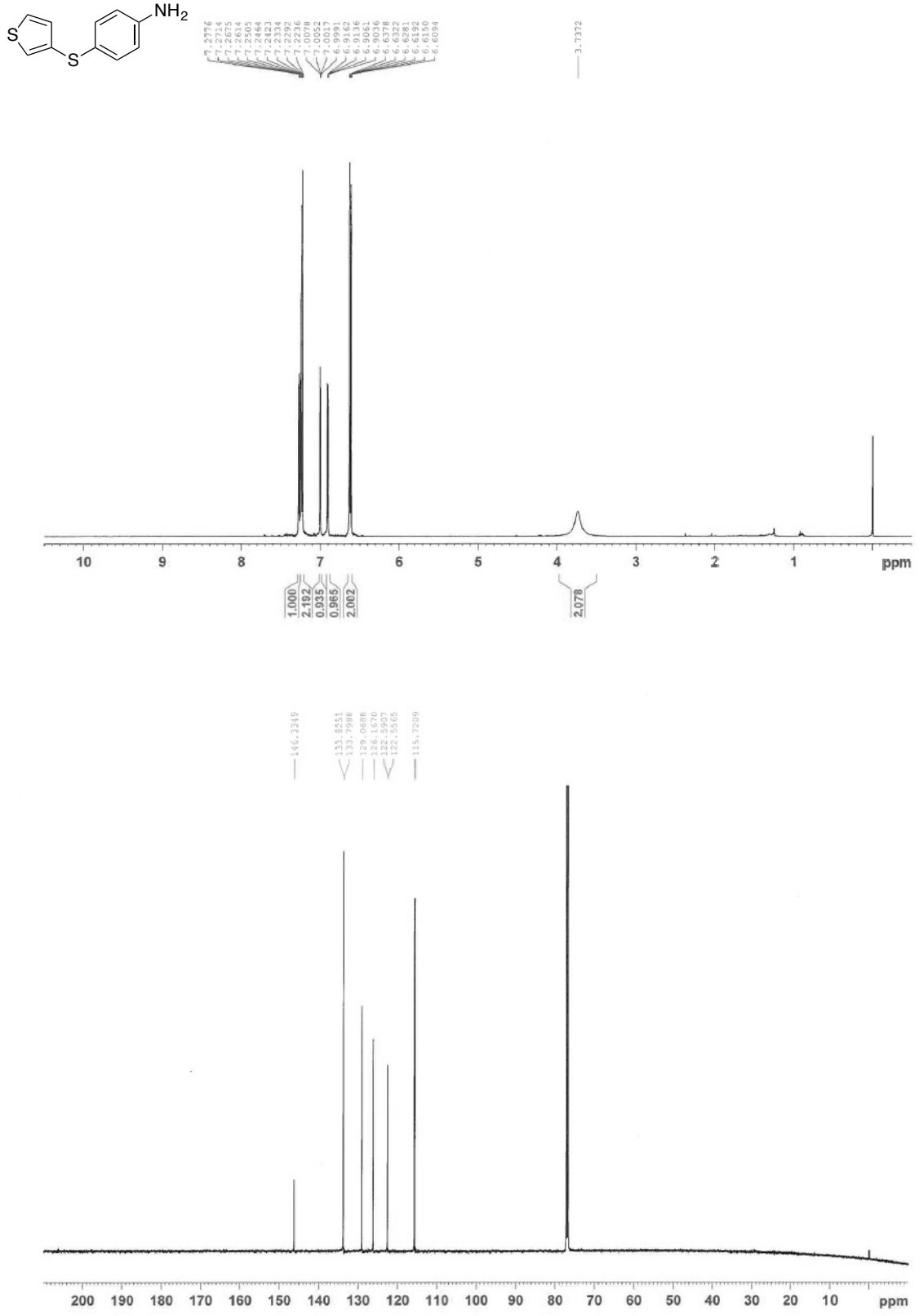


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3m** ($CDCl_3$)

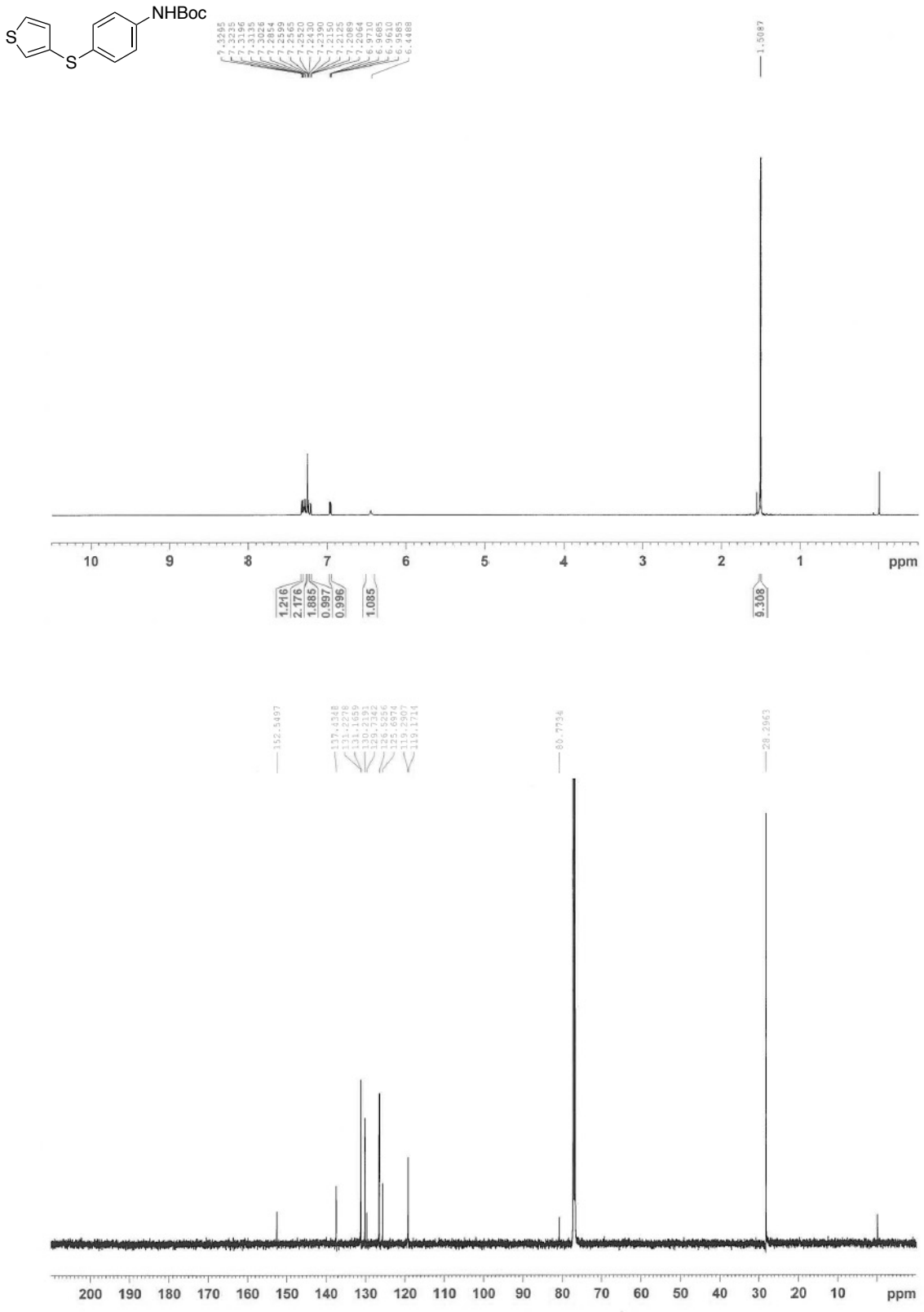




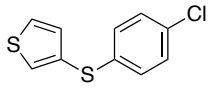
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3n** ($CDCl_3$)

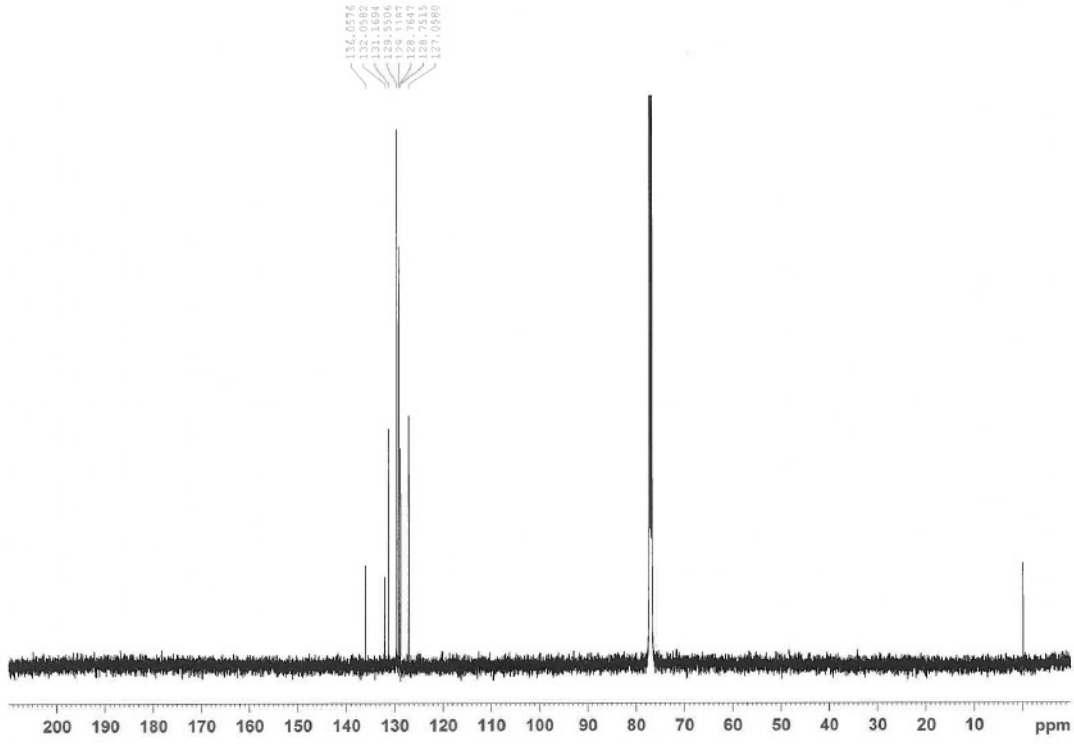


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3o** ($CDCl_3$)

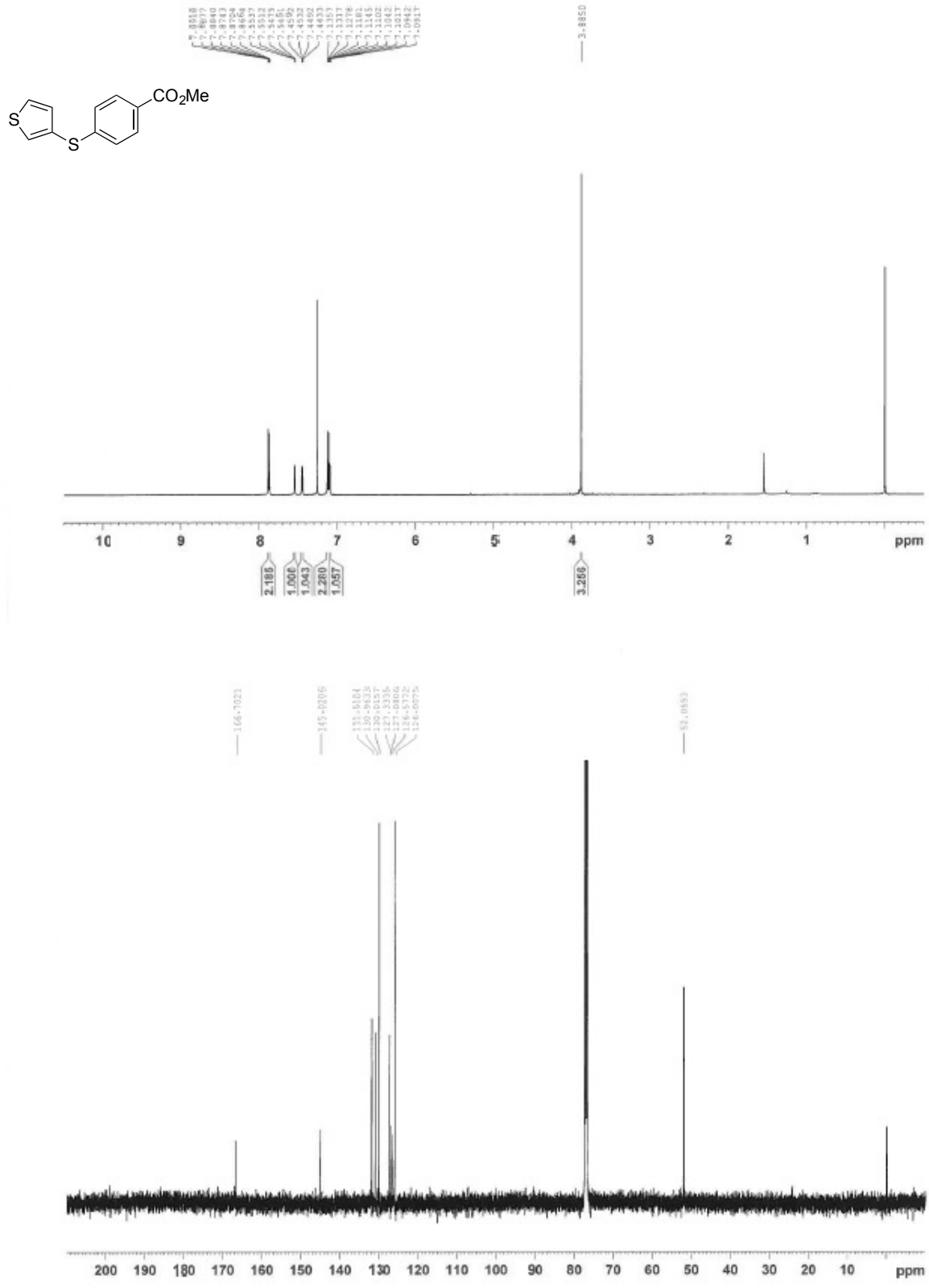


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3p** ($CDCl_3$)

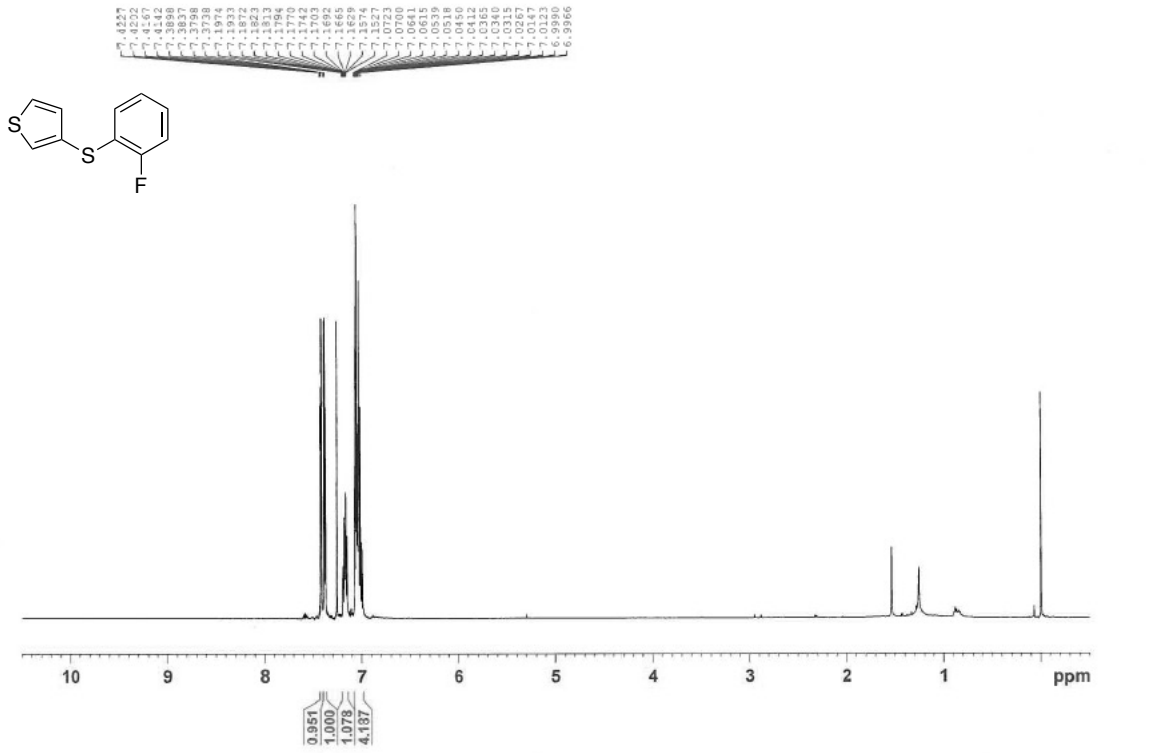


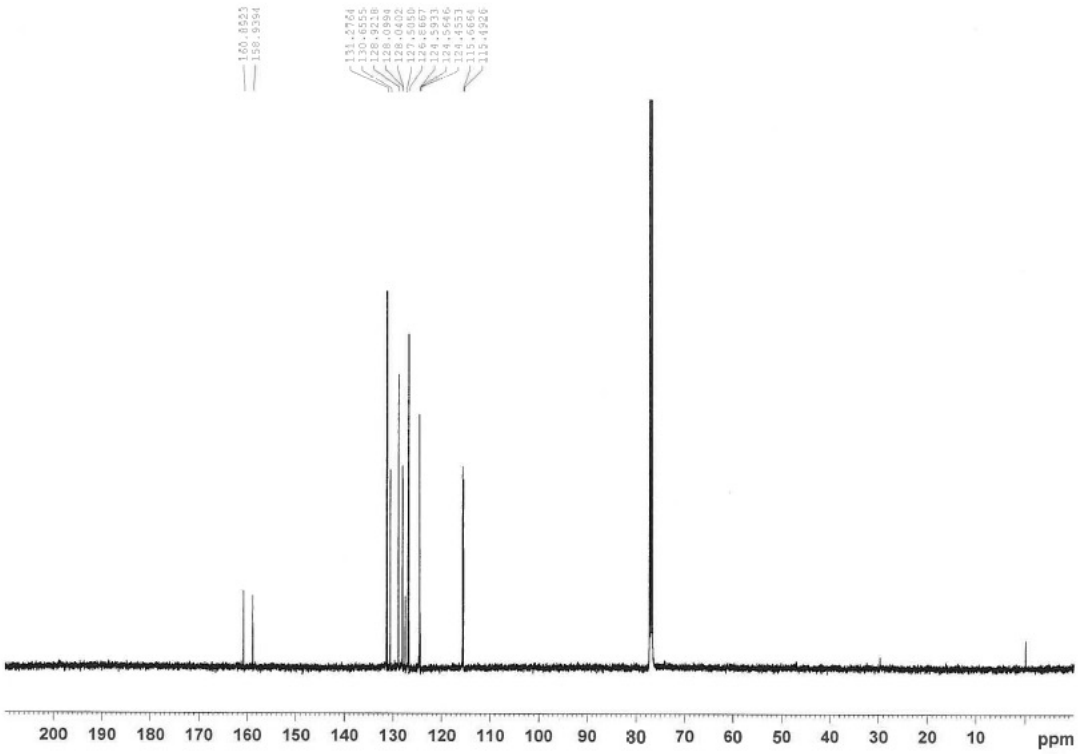


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3q** ($CDCl_3$)

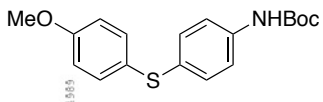


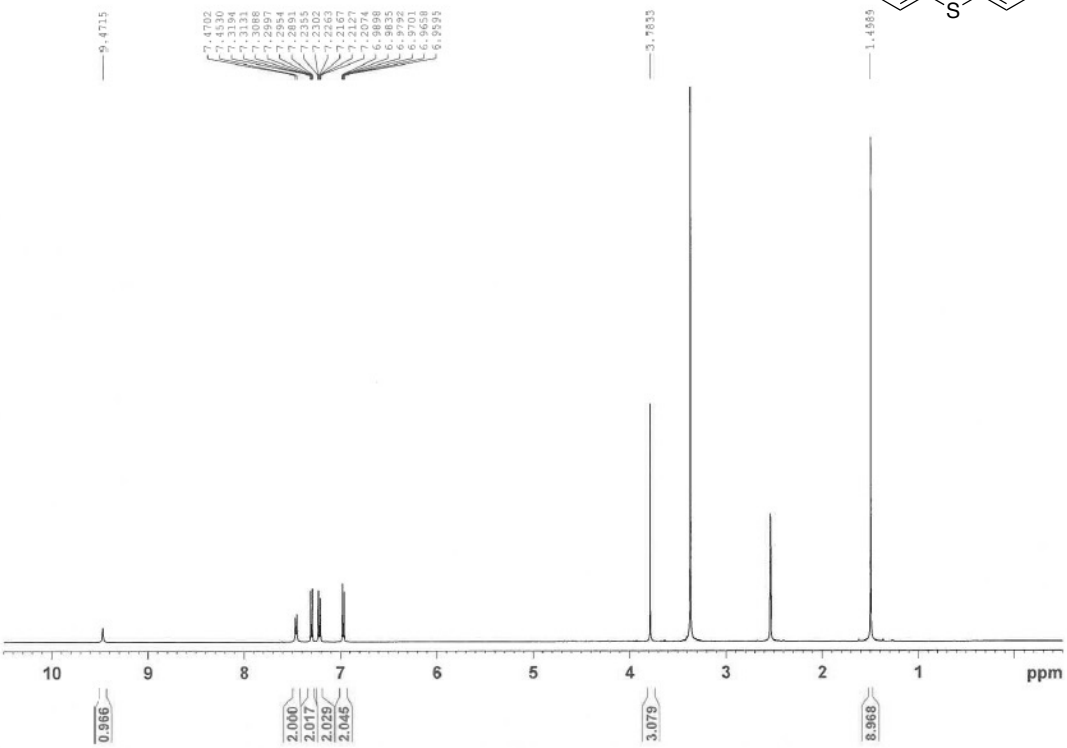
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3r** ($CDCl_3$)

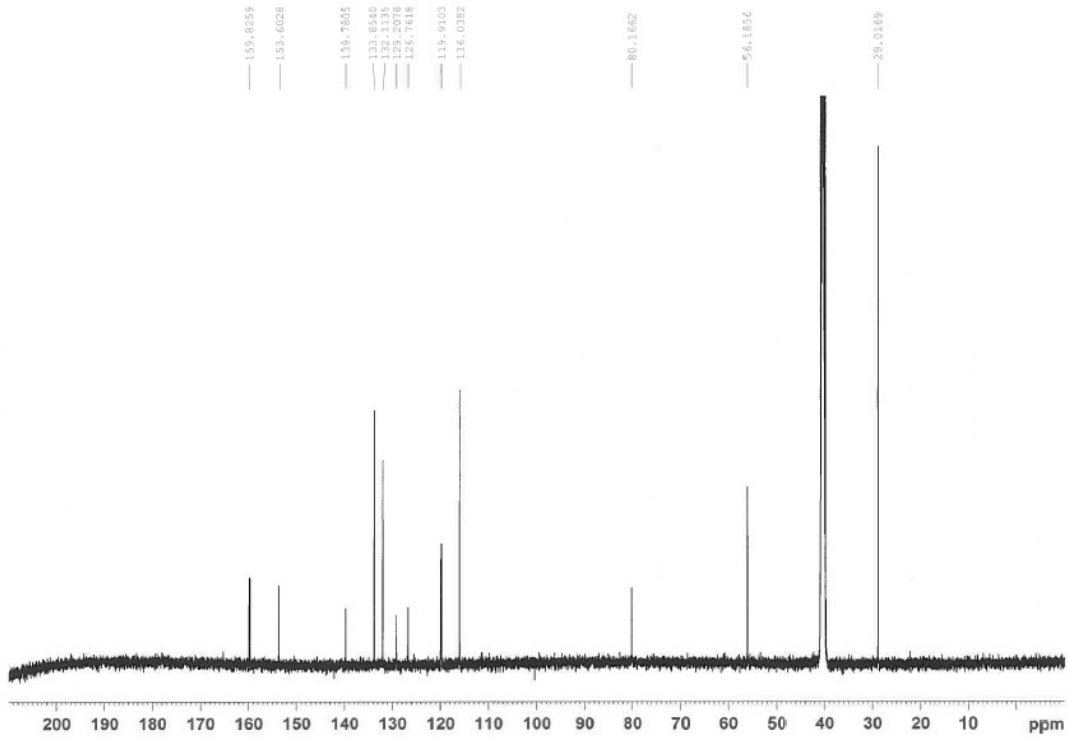




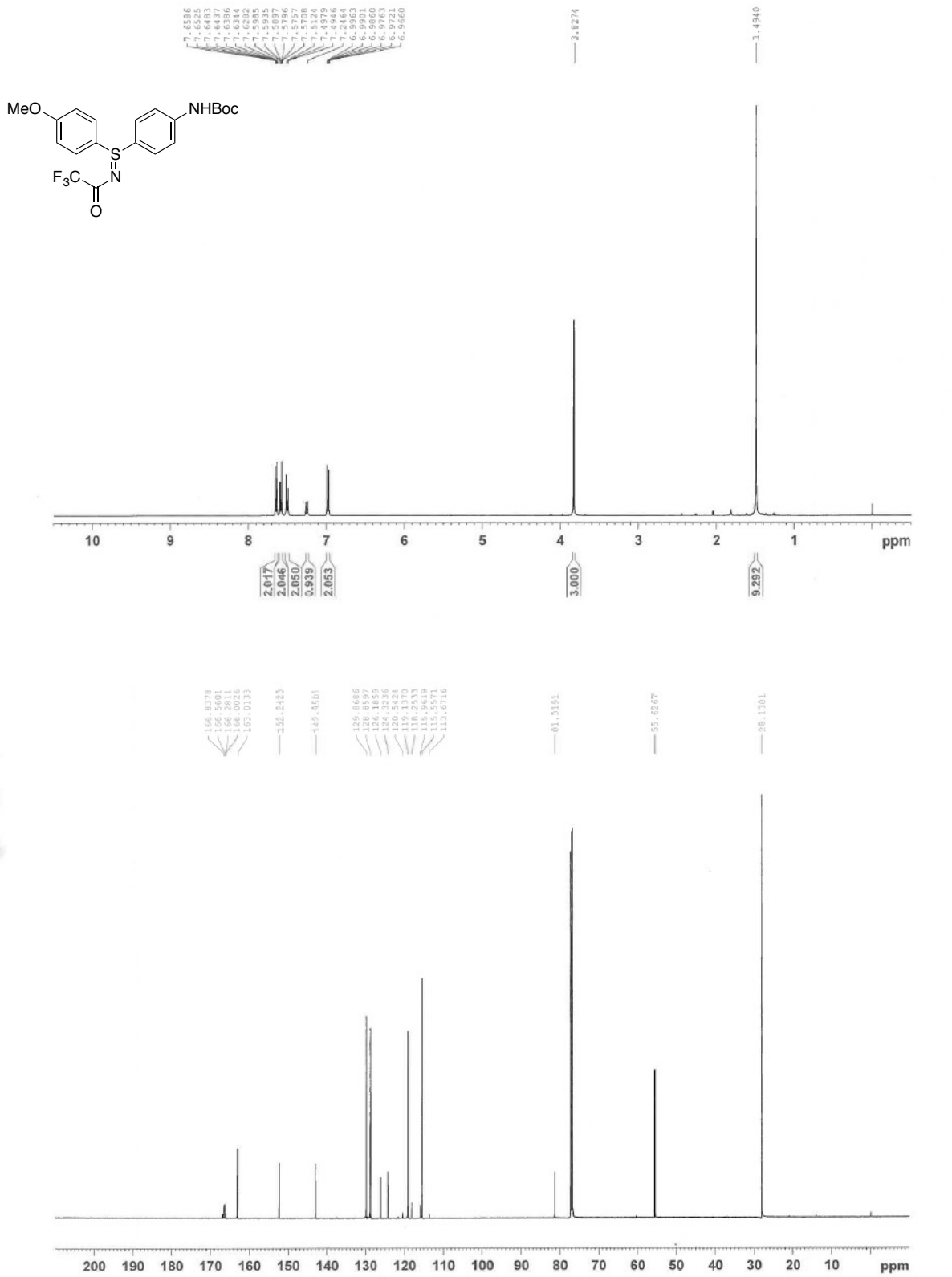
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(*tert*-butoxycarbonylamino)-phenyl 4-methoxyphenyl sulfide (**3u**) (DMSO-d_6)



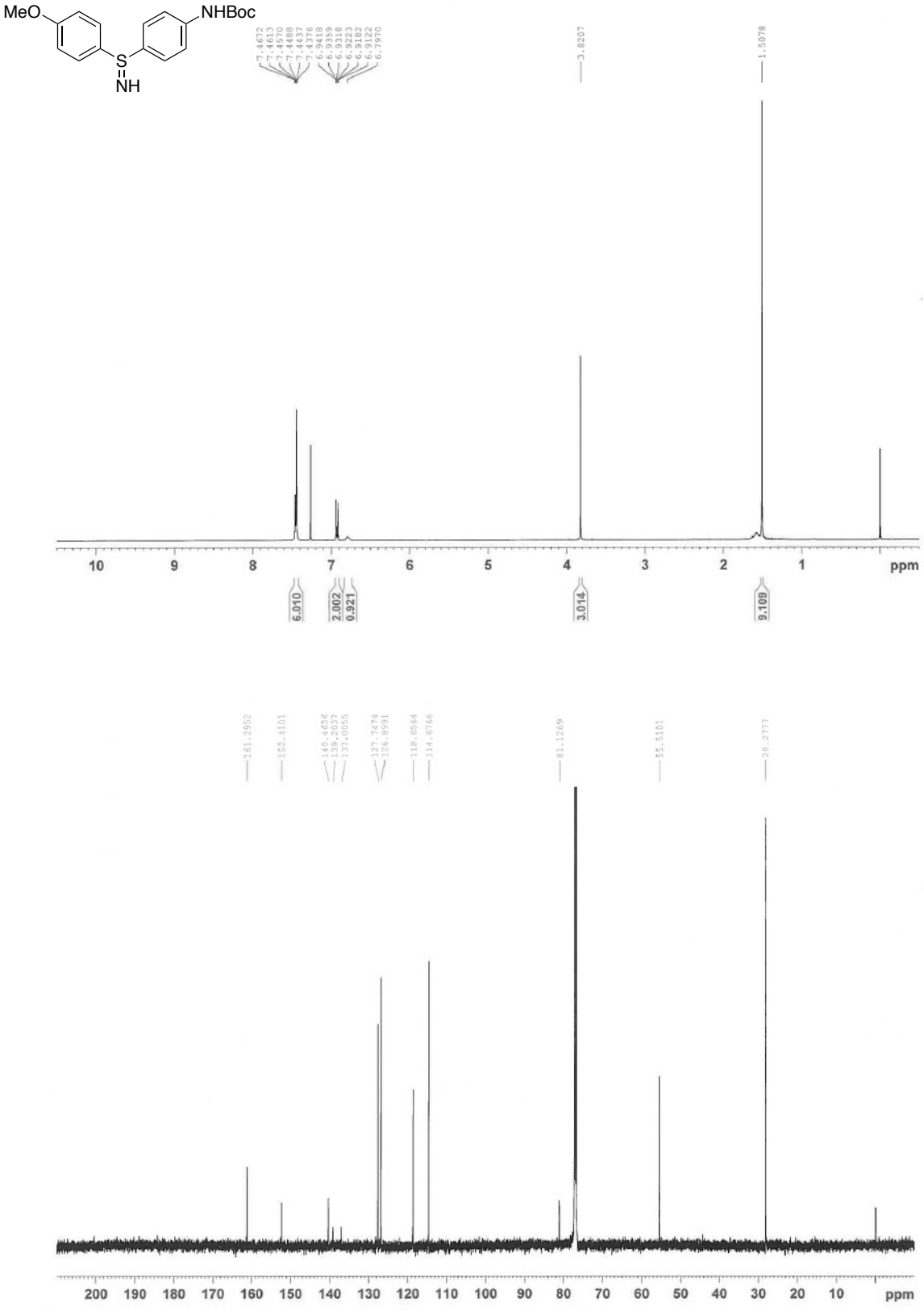




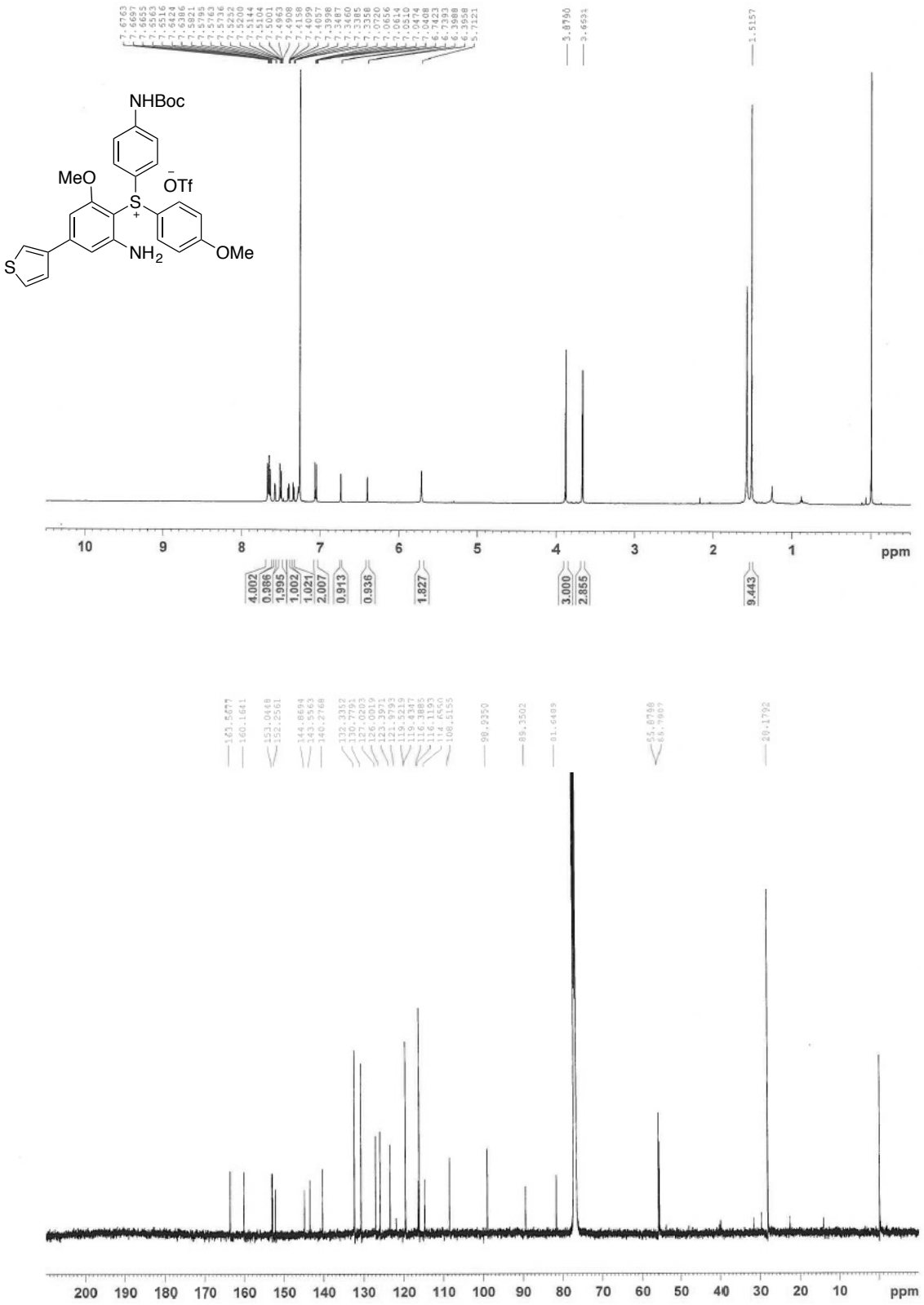
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *S*-(4-(*tert*-butoxycarbonylamino)-phenyl)-*N*-(2,2,2-trifluoroacetyl)-*S*-(4-methoxyphenyl)sulfilimine ($CDCl_3$)



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



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



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **14** (DMSO-d_6)