Supporting Information For

CuI Promoted Sulfenylation of Organozinc Reagents with Arylsulfonyl Chlorides

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1. General Experimental Information

General remarks:

All the solvents and commercially available reagents were purchased from commercial suppliers. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz or a 600 MHz Bruker FT-NMR spectrometer. All chemical shifts are given as the δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J, are reported in hertz (Hz). Mass spectroscopy and high resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). The chemicals and solvents were purchased from commercial suppliers Aldrich, USA, or Beijing Ouhe Chemical Company, China. Products were purified by flash chromatography on 300–400 mesh silica gels, SiO_2.

Compound characterization: Tabulated ^{1}H and ^{13}C NMR data and copies of ^{1}H and ^{13}C spectra are given for all synthesized sulfide products. For new compounds, **3m-3o, 5s** and **5t**, HRMS data is provided. The other compounds have previously been reported in the literature. Spectral data obtained herein were in agreement with literature data.

2. Details of experimental procedures.

2.1 General procedure for the preparation and reaction of organozinc reagents and arylsulfonyl chlorides

General Procedure A1: preparation of organozinc reagents via Mg insertion reaction[1]

A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with magnesium turnings (0.14g, 6 mmol), $ZnCl_2$ (0.54g, 4 mmol) and LiCl (0.21g, 5 mmol). 8 ml of THF was added and the magnesium was activated with *i*Bu_2AlH (0.2 mL, 0.02 mmol). After 5 min of stirring, aryl bromide (5.0 mmol) was added dropwise at room temperature and was stirred for 3 h. The concentration of organozinc reagents was titrated to be no less than 4 mmol.

General Procedure A2: preparation of functionalized organozinc reagents by Mg/I exchange reaction[2]

Preparation of the reagent *i*PrMgCl·LiCl: Magnesium turnings (0.17g, 7.0 mmol) and anhydrous LiCl (0.21g, 5.0 mmol) were placed in an Ar-flushed flask, and THF (5 mL) was added. A solution of *i*PrCl (5.0 mmol) in THF (5 mL) was slowly added at room temperature. The reaction started within a few minutes. After the addition, the reaction mixture was stirred for 12 h at room temperature.

A dry and argon-flushed 10-mL flask equipped with a magnetic stirrer and a septum was charged with *i*PrMgCl·LiCl (3 mmol) and 2 ml of THF. The reaction mixture was cooled to -40 °C, and aryl halide (3.0 mmol) in 2 ml of THF was added in one portion. The reaction temperature was increased to -10 °C, and the I/Mg exchange was complete after 15 min. $ZnCl_2$ (409 mg, 3 mmol) in 5 ml of THF was then added and the reaction mixture was stirred for additional 0.5 h.

General Procedure A3: Zincation of polyfunctionalized aromatics and heterocycles with TMPZnCl·LiCl[3]

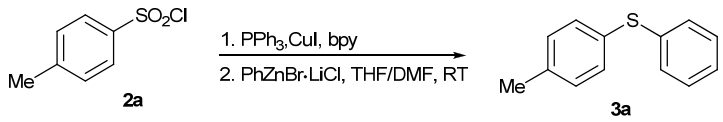
A dry and argon flushed 10 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum was charged with the TMPZnCl·LiCl[3](1.3 M in THF, 1.7 mL, 2.2 mmol). A solution of the corresponding arene or heteroarene (2.0 mmol) in dry THF (4 mL) was then added dropwise at room temperature and the reaction mixture was further stirred at 40 °C temperature for 1h.

General Procedure B: Reaction of Organozinc Reagents with sulfonyl chlorides

Diorganozinc (2.0 mmol, 2 ml in toluene) or organozinc reagent prepared above (2.0 mmol) was added slowly to a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing sulfonyl chlorides (1.0 mmol), triphenylphosphine (0.58g, 2.2 mmol), CuI (0.19g, 1 mmol) and 2,2'-bipyridyl (0.31g, 2 mmol) at room temperature and was then stirred at room temperature for 12 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The sulfide was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. All products were characterized by ^1H NMR, and ^{13}C NMR.

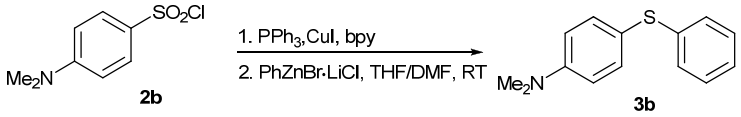
2.2 ^{1}H and ^{13}C NMR spectra of compounds

4-Tolyl phenyl sulfide (3a)[4]



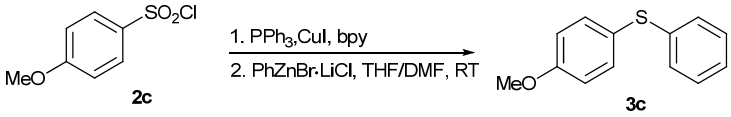
PhZnBr/LiCl prepared according to general procedure A1 was used and 176 mg of **3a** (88% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.33 (s, 3H), 7.12 (d, J = 7.8 Hz, 2H), 7.16-7.19 (m, 1H), 7.22-7.35 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.6, 137.2, 132.3, 131.4, 130.1, 129.8, 129.1 126.4, 21.2.

N,N-Dimethyl-4-(phenylthio)benzenamine (3b)[5]



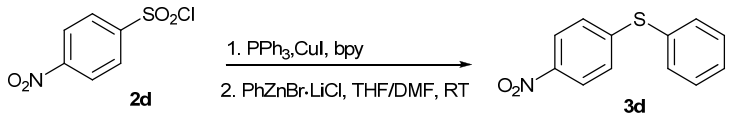
PhZnBr/LiCl prepared according to general procedure A1 was used and 156 mg of **3b** (84% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.98 (s, 6H), 6.72 (d, J = 8.8 Hz, 2H), 7.04-7.12 (m, 3H), 7.15-7.17 (m, 2H),7.40 (dd, J = 8.8, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 40.4, 113.1, 125.0, 127.0, 127.6, 128.7,136.0, 140.1, 150.4.

4-Methoxydiphenyl sulfide [4] (3c):



PhZnBr/LiCl prepared according to general procedure A1 was used and 197 mg of **3c** (91% yield) was obtained as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.81 (s, 3H), 6.89 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 6.8 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.27-7.20 (m, 2H), 7.41 (d, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 55.3, 115.0, 124.4, 125.7, 128.2, 128.9, 135.3, 138.6, 159.8.

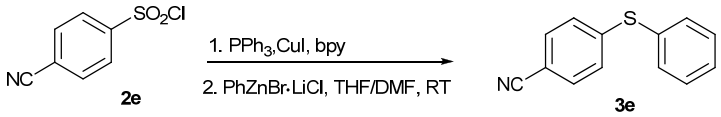
4-Nitrodiphenyl sulfide (3d)[6]



PhZnBr/LiCl prepared according to general procedure A1 was used and 178 mg of **3d** (77% yield) was

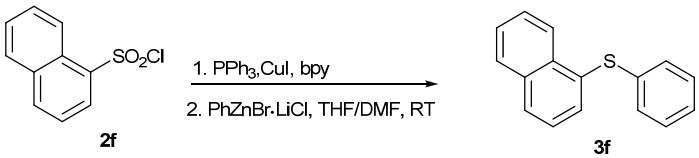
obtained as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (d, J = 8.7 Hz, 2H), 7.49-7.41 (m, 3H), 7.59-7.50 (m, 2H), 8.07 (d, J = 8.7 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 124.0, 126.7, 129.6, 130.0, 130.1, 134.7, 145.4, 148.4.

4-Cyanodiphenyl sulfide (3e)[7]



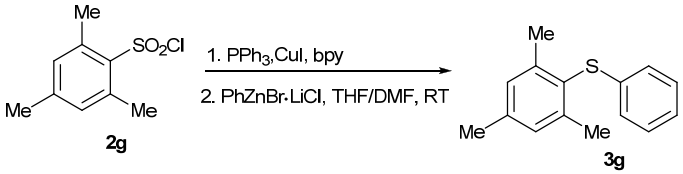
PhZnBr/LiCl prepared according to general procedure A1 was used and 139 mg of **3e** (66% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17 (d, J = 8.6 Hz, 2H), 7.40-7.46 (m, 4H), 7.46-7.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 108.6, 118.7, 127.2, 129.3, 129.8, 130.9, 132.4, 134.4, 145.6.

1-Naphthalenyl phenyl sulfide (3f)[4]



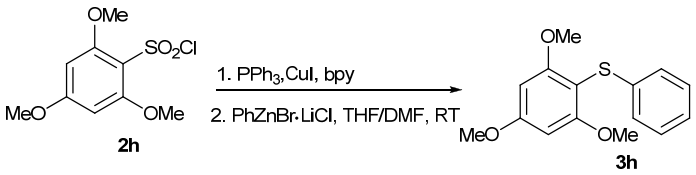
PhZnBr/LiCl prepared according to general procedure A1 was used and 132 mg of **3f** (56% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.10-7.24 (m, 5H), 7.42 (td, J = 7.2, 2.0 Hz, 1H), 7.46-7.55 (m, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.90-7.97 (m, 2H), 8.35-8.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 125.6, 125.8, 126.1, 126.4, 126.9, 128.5, 128.9, 129.0, 129.1, 131.2, 132.5, 133.6, 134.2, 136.9.

Mesityl phenyl sulfide (3g)[8]



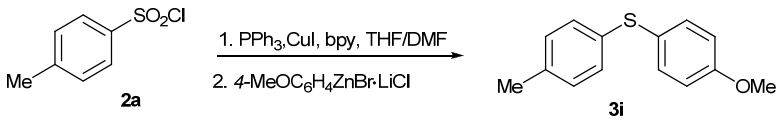
PhZnBr/LiCl prepared according to general procedure A1 was used and 162 mg of **3g** (71% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.28 (s, 3H), 2.34 (s, 3H), 2.45 (s, 6H), 6.85 (d, J = 8.0 Hz, 2H), 7.00 (brs, 1H), 7.03 (brs, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.9, 21.3, 21.9, 125.8, 127.6, 129.8, 134.9, 139.2, 143.8.

2,4,6-Trimethoxydiphenyl sulfide (3h)[8]



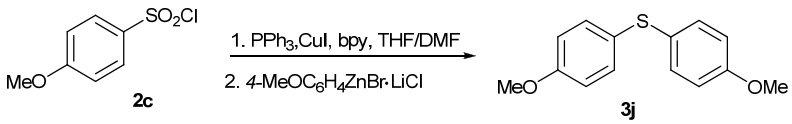
PhZnBr/LiCl prepared according to general procedure A1 and 2,4,6-trimethoxybenzene-1-sulfonyl chloride (267 mg, 1.0 mmol) were used and 199 mg of **3h** (72% yield) was obtained as a white solid. Mp 124-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.80 (s, 6H), 3.87 (3, 3H), 6.21 (s, 2H), 7.00-7.05 (m, 3H), 7.12-7.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm): 55.4, 56.2, 91.2, 98.6, 124.5, 125.7, 128.4, 138.7, 162.6, 163.0.

***4*-Methoxyphenyl *p*-tolyl sulfide (3i)**[9]



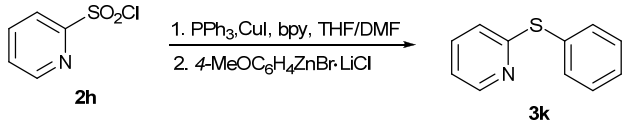
4-$MeOC_6H_4ZnBr$/LiCl prepared from 4-bromoanisole according to general procedure A1 was used and 191 mg of **3i** (83% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.29 (s, 3H), 3.79 (d, J = 1.8 Hz, 3H), 6.86 (d, J = 6.7 Hz, 2H), 7.05 (d, J = 6.9 Hz, 2H), 7.11 (t, J = 9.4 Hz, 2H), 7.35 (d, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.9, 55.3, 114.8, 125.7, 128.6, 129.4, 129.7, 134.2, 136.0, 159.4.

Bis(4-methoxyphenyl) sulfide (3j)[9]



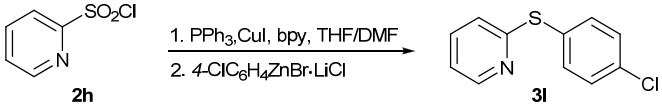
4-$MeOC_6H_4ZnBr$/LiCl prepared from 4-bromoanisole according to general procedure A1 was used and 207 mg of **3j** (84% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.80 (s, 6H), 6.85 (d, J = 6.8 Hz, 4H), 7.28 (d, J = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 55.2, 114.5, 127.6, 132.6, 158.5.

2-(Phenylthio)pyridine (3k)[4]



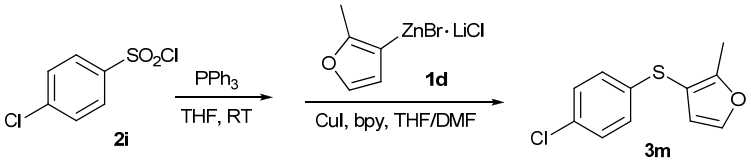
PhZnBr/LiCl prepared according to general procedure A1 and 2-pyridylsulfonyl chloride (178 mg, 1.0 mmol) were used. 131 mg of **3k** (70% yield) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.88 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 7.47-7.42 (m, 4H), 7.60 (t, J = 3.6 Hz, 2H), 8.43 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 119.8, 121.4, 129.0, 130.8, 134.9, 136.8, 149.2, 161.4.

2-(4-Chlorophenylthio)pyridine (3l)[10]



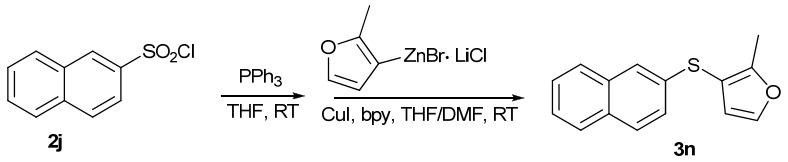
4-ClC_6H_4ZnI/LiCl prepared from 1-iodo-4-chlorobenzene according to general procedure A1 and 2-pyridylsulfonyl chloride (178 mg, 1.0 mmol) were used. 171 mg of **3l** (77% yield) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.94 (d, J = 7.6 Hz, 1H), 7.02 (t, J = 6.4 Hz, 1H), 7.38 (d, J = 7.6 Hz, 2H), 7.45-7.55 (m, 3H), 8.43 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 120.4, 121.9, 129.9, 130.0, 135.5, 136.2, 137.1, 149.9, 160.7.

3-(4-Chlorophenylthio)-2-methylfuran (3m)



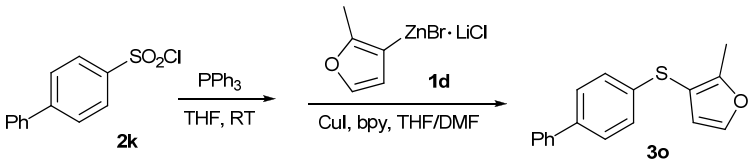
2-Methyl-3-furylzinc bromide prepared from 3-bromo-2-methylfuran according to general procedure A1 and 4-chlorobenzenesulfonyl chloride (211 mg, 1.0 mmol) were used. 150 mg of **3m** (67% yield) was obtained as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.34 (s, 3H), 6.35 (s, 1H), 7.02 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.8, 107.6, 115.2, 127.5, 128.9, 131.0, 136.6, 141.4, 156.9. IR (KBr) ν (cm^{-1}): 889, 939, 1011, 1090, 1126, 1196, 1226, 1296, 1388, 1438, 1475, 1514, 1633, 1697, 1886, 2852, 2920, 2953, 3076. HRMS-ESI: calcd for $C_{11}H_{10}ClOS$ $[M + H]^+$: 225.0141. Found: 225.0138.

2-methyl-3-(naphthalen-2-ylthio)furan (3n)



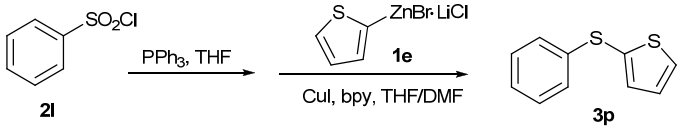
2-Methyl-3-furylzinc bromide prepared from 3-bromo-2-methylfuran according to general procedure A1 and naphthalene-2-sulfonyl chloride (227 mg, 1.0 mmol) were used. 149 mg of **3n** (62% yield) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.41 (s, 3H), 6.45 (s, 1H), 7.26-7.28 (m, 1H), 7.41-7.49 (m, 4H), 7.69 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.8, 107.8, 115.5, 123.9, 124.9, 125.3, 126.5, 126.9, 127.6, 128.4, 131.4, 133.7, 135.4, 141.2, 156.8. IR (KBr) ν (cm^{-1}): 850, 887, 940, 1016, 1088, 1128. 1196, 1224, 1267, 1342, 1384, 1512, 1324, 1699, 2855, 2920, 3052. HRMS-ESI: calcd for $C_{15}H_{13}OS$ $[M + H]^+$: 241.0687. Found: 241.0691.

3-(Biphenyl-4-ylthio)-2-methylfuran (3o)



2-Methyl-3-furylzinc bromide prepared from 3-bromo-2-methylfuran according to general procedure A1 and biphenyl-4-sulfonyl chloride (253 mg, 1.0 mmol) were used. 197 mg of **3o** (74% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 3H), 6.41 (s, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 6.8 Hz, 1H), 7.48-7.37 (m, 5H), 7.53 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.8, 107.8, 115.5, 126.6, 126.8, 127.2, 127.5, 128.8, 137.2, 138.2, 140.5, 141.2, 156.9. IR (KBr) ν (cm^{-1}): 887, 1004, 1084, 1122, 1222, 1338, 1475, 1512, 1591, 1651, 2857, 2924, 2951, 3026, 3070. HRMS-ESI: calcd for $C_{17}H_{15}OS$ $[M+H]^+$: 267.0844. Found: 267.0846.

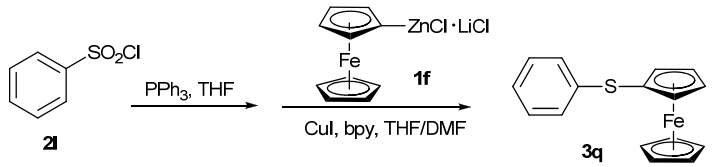
2-(Phenylthio)thiophene (3p)[11]



2-Thienylzinc bromide prepared from 2-bromothiophene according to general procedure A1 and benzenesulfonyl chloride (176 mg, 1.0 mmol) were used. 117 mg of **3p** (61% yield) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.03-7.07 (dd, J = 3.6, 5.4 Hz, 1H), 7.12-7.24(m, 5H),

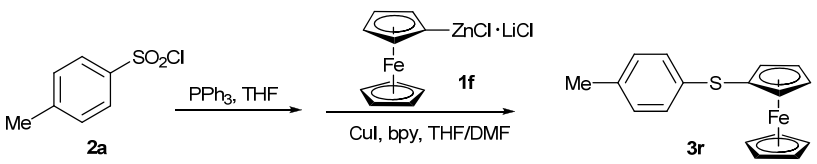
7.28 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 126.0, 127.2, 127.8. 128.7, 131.1, 131.3, 136.0, 138.3.

Phenylthioferrocene (3q)[12]



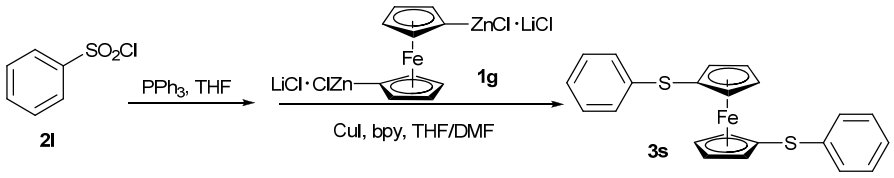
Monozincation of ferrocene was performed according to a literatured method.[13] typically, to a nitrogen-flushed three-necked flask with addition funnel, stirrer, and reflux condenser, ferrocene (0.47 g, 2.5 mmol) and potassium *t*-butoxide (0.13 g, 0.12 mmol) were dissolved in 10 ml of dry THF and the solution was cooled to 0°C. 1.67 ml (2.5 mmol) of 1.5 M *t*-BuLi in hexane were then added dropwise during a period of 10 min. The reaction mixture was stirred at this temperature for 30 min. $ZnCl_2$ (0.27g, 2 mmol) in THF (10 ml) was added and the solution was stirred for 30 min, allowing the reaction temperature raised to room temperature. The organozinc reagent thus prepared was transferred via syringe to a nitrogen protected flask containing CuI (0.19g, 1.0 mmol), 2,2'-bipyridyl (0.31g, 2 mmol), benzensulfonyl chloride (177 mg, 1.0 mmol), triphenylphosphine (0.58g, 2.2 mmol) in 5 ml THF-DMF (4:1, v/v). The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was quenched by aqueous NH_4Cl (20 mL). 20 mL of ethyl acetate was then added and the organic phase was separated, washed with 20 mL of water and then with 20 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The sulfide was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 212 mg of **3q** (72% yield) was obtained as a yellow solid. mp 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.30 (s, 5H), 4.40 (s, 2H), 4.46 (s, 2H), 7.03 (m, 3H), 7.17 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 69.8, 70.2, 74.9, 124.8, 125.9, 128.5, 140.6. IR (KBr) ν (cm^{-1}): 889, 999, 1022, 1072, 1105, 1169, 1473, 1575, 1649, 2852, 2924, 3064.

4-Tolyl ferrocenyl sulphide (3r)[14]



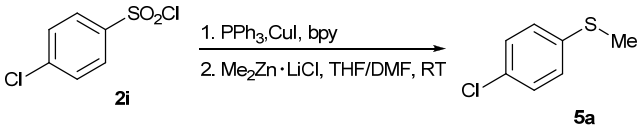
Compound **3r** was prepared using a similar method of compound **3o** and this afford 237 mg (77% yield) of **3r** as a yellow solid. Mp 110-112 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.25 (s, 3H), 4.27 (s, 5H), 4.33 (s, 2H), 4.41 (s, 2H), 6.98 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.8, 69.8, 70.1, 74.7, 126.5, 129.3, 134.8, 136.8. IR (KBr) ν (cm^{-1}): 889, 1105, 1249, 1521, 1558, 1651, 1699, 2854, 2924, 3649, 3674.

1,1'-Bis(phenylthio)ferrocene (3s)[12]



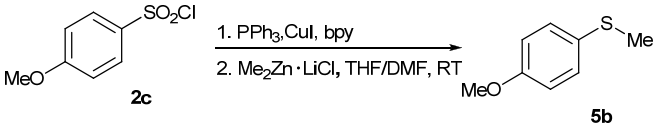
Biszincation of ferrocene was performed according to a literatured method.[15] typically, to a solution of ferrocene (0.19 g, 1.0 mmol) in THF (5 ml) was added tetramethylethylenediamine (TMEDA) (2.2 eq, 0.33 ml, 2.2 mmol) and the mixture was stirred for 5 min. To this suspension was added dropwise *n*-butyllithium (2.5 M in hexane, 2.2 eq, 0.88 ml, 2.2 mmol). The mixture was stirred at room temperature overnight. $ZnCl_2$ (0.27g, 2.0 mmol) in THF (5 ml) was added and the solution was stirred for a further hour. The organozinc reagent thus prepared was transferred via syringe to a nitrogen protected flask containing CuI (0.19g, 1.0 mmol), 2,2'-bipyridyl (0.31g, 2 mmol), *p*-tolylsulfonyl chloride (191 mg, 1.0 mmol), triphenylphosphine (0.58g, 2.2 mmol) in 5 ml THF-DMF (4:1, v/v). The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was quenched by aqueous NH_4Cl (20 mL). 20 mL of ethyl acetate was then added and the organic phase was separated, washed with 20 mL of water and then with 20 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The sulfide was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 205mg of **3s** (51% yield) was obtained as an orange solid. M.p 174-176 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.44 (d, J = 1.5 Hz, 4H), 4.48 (s, 4H), 7.02-7.12 (m, 6H), 7.18 (t, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 71.9, 76.3, 125.0, 126.2, 128.6, 140.1. IR (KBr) ν (cm^{-1}): 826, 1022, 1082, 1394, 1459, 1475, 1521, 1651, 1699, 2854, 2924, 3446.

Methyl 4-chlorophenyl sulfide (5a)[16]



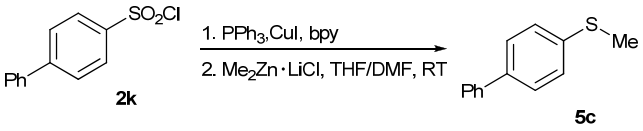
Compound **5a** was prepared using Me_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and *p*-chlorosulfonyl chloride (211mg, 1.0 mmol) according to general procedure B. 116 mg, 73% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.54 (s, 3H), 7.25 (dd, J = 8.8, 2.0 Hz, 2H), 7.32 (dd, J = 8.6, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 16.1, 128.0, 128.9, 130.9, 137.0.

***p*-Methylthioanisole (5b)**[17]



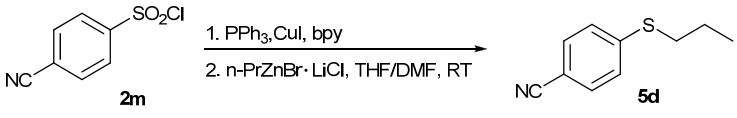
Compound **5b** was prepared using Me_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and 4-methoxybenzenesulfonyl chloride (190 mg, 1.0 mmol) according to general procedure B. 120 mg, 78% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 3.79 (3, 3H), 6.85 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 18.0, 55.3, 114.6, 128.8, 130.2, 158.2.

4-(Methylsulfanyl)biphenyl (5c)[18]



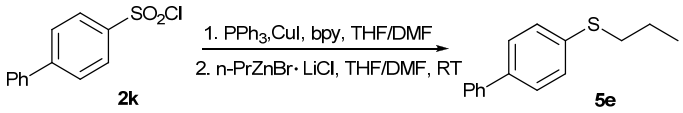
Compound **5c** was prepared using Me_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and 4-biphenylsulfonyl chloride (253 mg, 1.0 mmol) according to general procedure B. 142 mg, 71% yield of **5c** was obtained. white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.53 (s, 3H), 7.34 (dd, J = 7.6, 5.5 Hz, 3H), 7.43 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 15.9, 126.8, 127.0, 127.2, 127.5, 128.8, 137.6, 138.1, 140.5.

4-(Propylthio)benzonitrile (5d)[19]



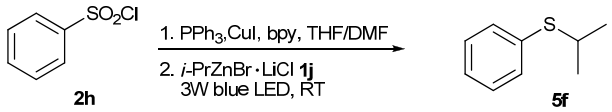
Compound **5d** was prepared using *n*-PrZnBr·LiCl (prepared according to general procedure A1) and 4-cyanobenzenesulfonyl chloride (202 mg, 1.0 mmol) according to general procedure B. 77 mg, 52% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.04 (t, J = 7.6 Hz, 3H), 1.65-1.77 (m, 2H), 2.94 (t, J = 7.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.7, 22.3, 34.1, 106.2, 119.2, 126.9, 132.4, 145.5.

4-Biphenyl propyl sulfide (5e)[19]



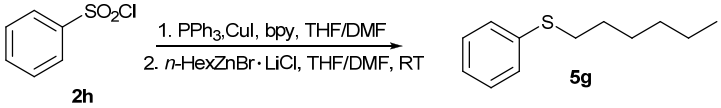
Compound **5e** was prepared using *n*-PrZnBr·LiCl (prepared according to general procedure A1) and 4-biphenylsulfonyl chloride (253 mg, 1.0 mmol) according to general procedure B. 167 mg, 73% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.05 (t, J = 7.6 Hz, 3H), 1.65-1.78 (m, 2H), 2.94 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.36-7.44 (m, 4H), 7.51 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.4, 22.6, 35.7, 126.8, 127.2, 127.4, 128.8, 129.3, 136.1, 138.6, 140.5.

Isopropyl phenyl sulfide (5f)[19]



Compound **5f** was prepared using *i*-PrZnBr·LiCl (prepared according to general procedure A1) and phenylsulfonyl chloride (177 mg, 1.0 mmol) according to general procedure B. 110 mg, 72% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.28 (d, J = 6.8 Hz, 6H), 3.30-3.42 (m, 1H), 7.22 (dd, J = 7.8, 6.8 Hz, 2H), 7.39 (d, J = 6.8 Hz, 1H), 7.49 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 23.1, 38.2, 127.4, 129.0, 131.8, 137.0.

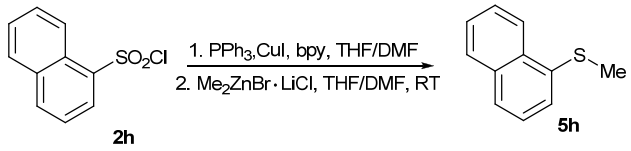
***n*-Hexyl phenyl sulfide (5g)**[20]



Compound **5g** was prepared using *n*-HexZnBr·LiCl (prepared according to general procedure A1) and phenylsulfonyl chloride (177 mg, 1.0 mmol) according to general procedure B. 144 mg, 74% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, J = 6.8 Hz, 3H), 1.29 (brs, 4H), 1.39-1.46

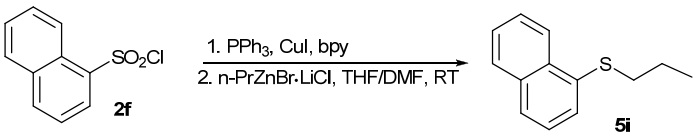
(m, 2H), 1.58-1.73 (m, 2H), 2.91 (t, J = 7.2 Hz, 2H), 7.16 (t, J = 6.8 Hz, 1H), 7.23-7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.0, 22.5, 28.5, 29.1, 31.3, 33.6, 125.6, 128.7, 128.8, 137.1.

Methyl 1-naphthyl sulfide (5h)[21]



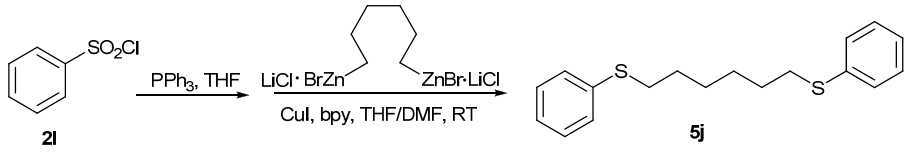
Compound **5h** was prepared using Me_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and 1-naphthalene sulfonylchloride (227 mg, 1.0 mmol) according to general procedure B. 117 mg, 67% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.57 (s, 3H), 7.36-7.46 (m, 2H), 7.48-7.57 (m, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 16.2, 123.7, 124.2, 125.6, 125.8, 126.1, 126.2, 128.5, 131.7, 133.6, 135.8.

1-Propyl naphthyl sulfide (5i)[22]



Compound **5i** was prepared using *n*-PrZnBr·LiCl (prepared according to general procedure A1) and 1-naphthalene sulfonylchloride (227 mg, 1.0 mmol) according to general procedure B. 131 mg, 65% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):1.04 (t, J = 7.3 Hz, 3H), 1.64-1.73 (m, 2H), 2.96 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1 H,), 7.50-7.59 (m, 3H), 7.71 (d, J = 8.4 Hz, 1 H), 7.83 (d, J = 8.0 Hz 1H,), 8.41 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.5, 22.6, 36.3, 125.3, 125.8, 125.9, 126.5, 127.8, 127.9, 128.1, 132.9, 133.5, 138.5.

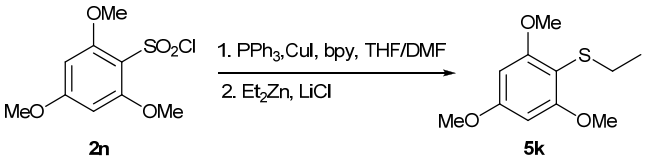
1,6-bis(phenylthio)hexane (5j)[20]



Compound **5j** was prepared by reaction of 1,6-dibromozinc hexane (prepared from 1,6-dibromohexane (146 mg, 0.6 mmol), Mg (36 mg, 1.5 mmol), $ZnCl_2$ (136 mg, 1.0 mmol) and LiCl (42 mg, 1.0 mmol)) according to general procedure A1) and phenylsulfonyl chloride (177 mg, 1.0 mmol) according to general procedure B. 92 mg, 61% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.44 (brs,

4H), 1.64 (brs, 4H), 2.91 (t, J = 7.3 Hz, 4H), 7.16 (t, J = 7.2 Hz, 2H), 7.25-7.32 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 28.3, 29.0, 33.5, 125.7, 128.8, 129.0, 136.9.

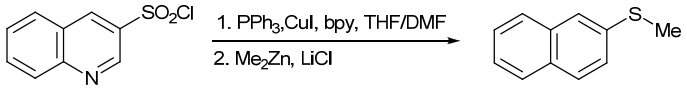
Ethyl 2,4,6-trimethoxyphenyl sulfide (5k)[23]



2n **5k**

Compound **5k** was prepared using Et_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and 2,4,6-trimethoxybenzenesulfonyl chloride (267 mg, 1.0 mmol) according to general procedure B. 173 mg, 76% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.13 (t, J = 7.6 Hz, 3H), 2.73 (q, J = 6.8 Hz, 2H), 3.87 (s, 9H), 6.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.4, 28.9, 55.6, 56.2, 91.3, 101.9, 161.3, 162.4.

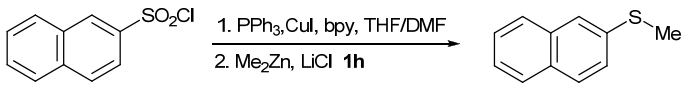
3-(Methylthio)quinoline (5l)[24]



2n **5l**

Compound **5l** was prepared using Me_2Zn (1.0 M in toluene, 2.0 ml, 2.0 mmol) and 3-quinolinesulfonyl chloride (228 mg, 1.0 mmol) according to general procedure B. 126 mg, 72% yield, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.57 (s, 3H), 7.39-7.44 (m, 1 H), 7.55-7.62 (m, 2 H), 7.78 (d, J = 8.2 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 8.77 (d, J = 4.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 16.2, 126.5, 127.6, 128.5, 128.8, 129.7, 131.2, 132.6, 145.7, 150.2.

Allyl 2-naphthyl sulfide (5m)[25]

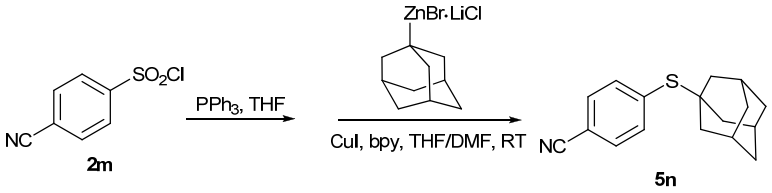


2j **5m**

A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with zinc powder (130 mg, 2 mmol), LiCl (83g, 2 mmol). A small piece of iodine was added and the mixture was stirred until brown color faded. Allyl bromide (0.24g, 2.0 mmol) in 2 ml of THF was then added at melting ice temperature. Formation of allylzinc bromide was indicated by complete dissolution of zinc in the mixture. After bringing to room temperature, it was then transferred via

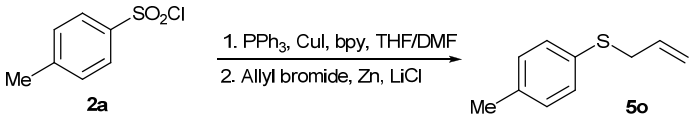
syringe to a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing 2-naphthylsulfonyl chloride (227 mg, 1.0 mmol), triphenylphosphine (0.58g, 2.2 mmol), CuI (0.19g, 1 mmol) and 2,2'-bipyridyl (0.31g, 2 mmol) and the mixture was then stirred at room temperature for 12 hours. After usual workup, compound **5m** was obtained as a colorless oil. 126 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.40 (d, *J* = 7.6 Hz, 2H), 5.12 (d, *J* = 9.2 Hz, 1H), 5.15 (d, *J* = 15.2 Hz, 1H), 5.78-5.87 (m, 1H), 7.45-7.51 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.76-7.86 (m, 3H), 7.98 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):41.7, 119.0, 125.9, 126.0, 126.4, 126.7, 127.3, 1227.7, 128.7, 128.8, 132.5, 133.5, 134.5.

1-Adamantyl 4-cyanophenyl sulfide (5n)[26]



Compound **5n** was prepared using adamantylzinc bromide (6 ml, 0.5 M in THF, 3 mmol) and 4-cyanobenzenesulfonyl chloride (202 mg, 1.0 mmol) according to general procedure B. 121 mg, 45% yield, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.58-1.72 (m 6H), 1.84 (br s, 6H), 2.04 (br s, 3H), 7.61 (br s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) 30.6, 36.3, 44.0, 49.8, 112.4, 118.8, 132.0, 137.8, 138.0.

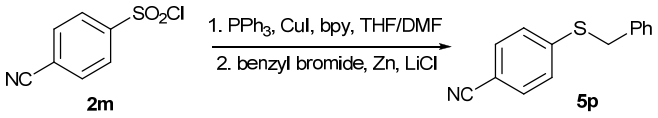
Allyl *p*-tolyl sulfide (5o)[27]



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with zinc powder (130 mg, 2 mmol), LiCl (83g, 2 mmol). A small piece of iodine was added and the mixture was stirred until brown color faded. Allyl bromide (0.24g, 2.0 mmol) in 2 ml of THF was then added at melting ice temperature. Formation of allylzinc bromide was indicated by complete dissolution of zinc in the mixture. After bringing to room temperature, it was then transferred via syringe to a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing 4-tolylsulfonyl chlorides (191 mg, 1.0 mmol), triphenylphosphine (0.58g, 2.2 mmol), CuI (0.19g, 1 mmol) and 2,2'-bipyridyl (0.31g, 2 mmol) and the mixture was then stirred at room temperature for 12 hours. After usual workup,

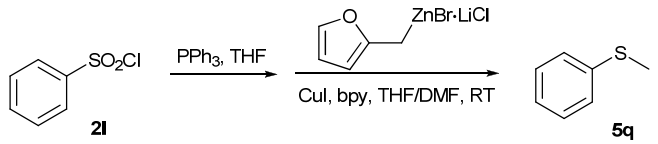
compound **5o** was obtained as a colorless oil. 116 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.31 (s, 3H), 3.50 (dd, *J* = 6.8 Hz, 2H), 5.06 (dd, *J* = 18.8, 11.6 Hz, 2H), 5.81-5.91 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.0, 37.9, 117.3, 129.5, 130.7, 132.1, 133.8, 136.4.

4-(Benzylthio)benzonitrile (5p)[28]



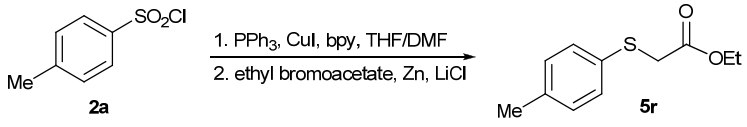
Compound **5p** was prepared using benzylzinc bromide (0.5 M in THF, 6.0 ml, 3.0 mmol) and 4-cyanobenzenesulfonyl chloride (202 mg, 1.0 mmol) according to general procedure B. White solid (113 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.15 (s, 2H), 7.15-7.33 (m, 7H), 7.47 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 37.1, 108.6, 118.8, 127.4, 127.7, 128.6, 128.7, 132.2, 134.2, 144.4.

2-(Phenylthio)methyl)furan (5q)[29]



Compound **5q** was prepared using 2-(chlorozincmethyl)furan (0.5 M in THF, 6.0 ml, 3.0 mmol) and 2-thiophenesulfonyl chloride (183 mg, 1.0 mmol) according to general procedure B. Brown oil (126 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 4.10 (s, 2H), 6.09 (s, 1H), 6.27 (s, 1H), 7.22 (d, *J* = 6.4 Hz, 1H), 7.25-7.32 (m, 2H), 7.32-7.40 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* (ppm): 31.6, 107.8, 110.4, 126.7, 128.8, 130.6, 135.5, 142.1, 152.0.

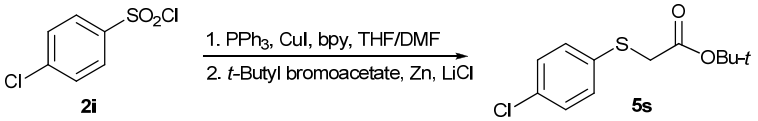
Ethyl 2-(*p*-tolylthio)acetate (5r)[30]



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with zinc powder (130 mg, 2 mmol), LiCl (83g, 2 mmol). Ethyl bromoacetate (0.33 g, 2.0 mmol) in 2 ml of THF was then added at melting ice temperature. CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2

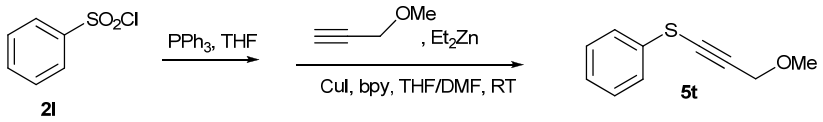
mmol) and a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing 4-tolylsulfonyl chlorides (191 mg, 1.0 mmol) and triphenylphosphine (0.58g, 2.2 mmol) were added succesively. The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **5r** was obtained as a colorless oil (174 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 1.22 (t, J = 7.2 Hz, 3H), 2.32 (s, 3H), 3.58 (s, 2H) , 4.15 (q, J = 7.2 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 14.1, 21.0, 37.4, 61.4, 129.8, 130.9, 137.3, 169.8. IR (KBr) ν (cm^{-1}): 940, 1010, 1153, 1246, 1375, 1464, 1620, 2852, 2920, 3030.

***tert*-Butyl 2-((4-chlorophenyl)thio)acetate (5s)**[24]



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with zinc powder (130 mg, 2 mmol), LiCl (83g, 2 mmol). A small piece of iodine was added and the mixture was stirred until the brown color faded. *tert*-Butyl bromoacetate (0.40 g, 2.0 mmol) in 2 ml of THF was then added at melting ice temperature. CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol) and a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing 4-chlorobenzenesulfonyl chlorides (211 mg, 1.0 mmol) and triphenylphosphine (0.58g, 2.2 mmol) were added succesively. The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **5s** was obtained as a colorless oil (210 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.43 (s, 9 H), 3.59 (s, 2 H), 7.23-7.28 (m, 2 H), 7.33-7.37 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 28.2, 38.0, 82.4, 129.2, 131.2, 132.9, 134.0, 168.5.

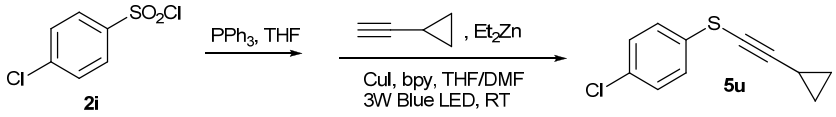
3-Methoxyprop-1-ynyl phenyl sulfide (5t)



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with methoxyacetylene (112 mg, 2 mmol), LiCl (83g, 2 mmol) and 2 ml of THF. Et_2Zn (1.0 M in hexane, 2 ml, 2.0 mmol) was then added at melting ice temperature. After stirring at same temperature for 30 min, CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol) and a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing phenylsulfonyl chlorides (177 mg, 1.0 mmol) and triphenylphosphine (0.58g, 2.2 mmol) were added succesively. The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **5t** was obtained as a colorless oil (135 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.48 (s, 3H), 4.36 (s, 2H), 7.16-7.22 (m, 1 H), 7.26-7.36 (m, 4 H); ^{13}C

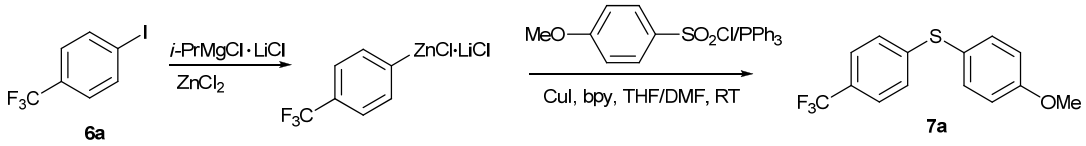
NMR (100 MHz, $CDCl_3$) δ (ppm): 56.3, 60.7, 73.5, 95.7, 125.6, 128.7, 128.8, 137.1. HRMS-ESI: calcd for $C_{10}H_{11}OS$ $[M+H]^+$: 179.0531. Found: 179.0524.

Cyclopropylethynyl 4-chlorophenyl sulfide (5u)



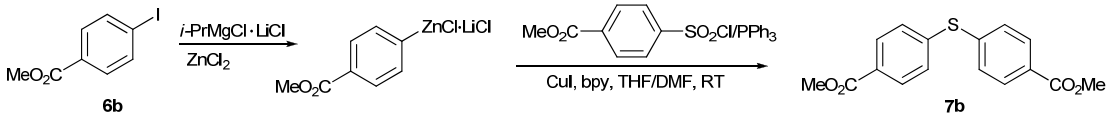
A solution of cyclopropylacetylene (133 mg, 2 mmol) in THF (2 mL) was treated at rt with Et_2Zn (2.0mL, 2 mmol, 1.0M in hexane). The reaction mixture was stirred at rt for 30 min. CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol) and a mixture solution of THF-DMF (5 ml, 4:1 v/v) containing 4-chlorobenzenesulfonyl chlorides (211 mg, 1.0 mmol) and triphenylphosphine (0.58g, 2.2 mmol) were added succesively. The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **5u** was obtained as a colorless oil (142 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.82-0.98 (m, 4 H), 1.47-1.70 (m, 1 H), 7.18 (d, J = 8.8 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): -1.0, 8.6, 58.6, 94.6, 128.0, 128.9, 131.0, 137.0. HRMS-ESI: calcd for $C_{11}H_{10}ClS$ $[M+H]^+$: 209.0192. Found: 209.0184.

4-Methoxyphenyl 4-(trifluoromethyl)phenyl sulfide (7a)[16]



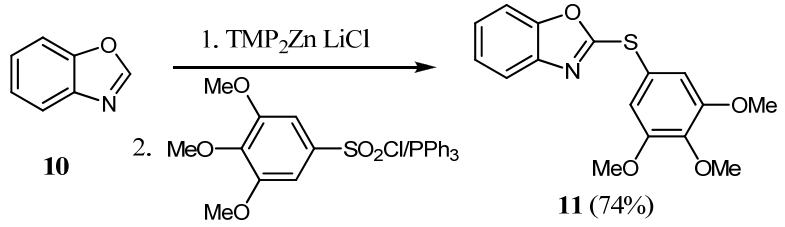
The 3-trifluoromethylphenylzinc iodide prepared from 1-iodo-3-(trifluoromethyl)benzene by general procedure A2 (about 3.0 mmol) was added slowly to a THF/DMF solution (5 ml, 4:1,v/v) containing CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol), 4-methoxybenzenesulfonyl chloride (207 mg, 1.0 mmol) and PPh_3 (0.52g, 2.0 mmol). The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **7a** was obtained as a colorless oil (210 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*): 3.85 (s, 3H), 6.95 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.42-7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 55.4, 115.4, 120.1, 121.8 (q, J = 271.0 Hz), 125.7 (q, J = 4.2 Hz), 126.4, 127.4 (q, J = 31.6 Hz), 136.7, 144.8, 160.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.8 (s, 3F). IR (KBr) ν (cm^{-1}): 835, 1020, 1054, 1062, 1337, 1465, 1494, 2856, 3028.

Di(4-methylcorboxylphenyl) sulfide (7b)[31]



Methyl 4-iodobenzoate (786 mg, 3 mmol) was converted into corresponding organozinc reagent according to general procedure A2 and was added slowly to a THF/DMF solution (5 ml, 4:1(v/v)) containing CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol), methyl 4-(chlorosulfonyl)benzoate (235 mg, 1.0 mmol) and PPh_3 (0.52g, 2.0 mmol). The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **7b** was obtained as a white solid (245 mg, 81% yield).7.98 (d, *J* = 7.8 Hz, 4H), 7.39 (d, *J* = 8.0 Hz, 4H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.3, 128.8, 130.3, 130.4, 140.9, 166.5.

2-(3,4,5-Trimethoxyphenylthio)benzoxazole (9)[32]



10 **11** (74%)

Benzoxazole (357 mg, 3 mmol) was converted into corresponding organozinc reagent according to general procedure A3 and was added slowly to a THF/DMF solution (5 ml, 4:1(v/v)) containing CuI (0.19g, 1 mmol), 2,2'-bipyridyl (0.31g, 2 mmol), 3,4,5-trimethoxybenzenesulfonyl chloride (267 mg, 1.0 mmol) and PPh_3 (0.52g, 2.0 mmol). The reaction mixture was then stirred at room temperature for 12 hours. After usual workup, compound **9** was obtained as a white solid (235 mg, 74% yield). M.p. 128-130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.87 (s, 6H), 3.91 (s, 3H), 6.94 (s, 2H), 7.24-7.29 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 56.3, 61.0, 110.3, 121.1, 119.2, 121.4, 124.4, 124.5, 140.1, 142.2, 152.0, 153.7, 163.5.

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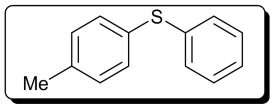
3. Copies of NMR Spectra

4-Tolyl phenyl sulfide (3a)



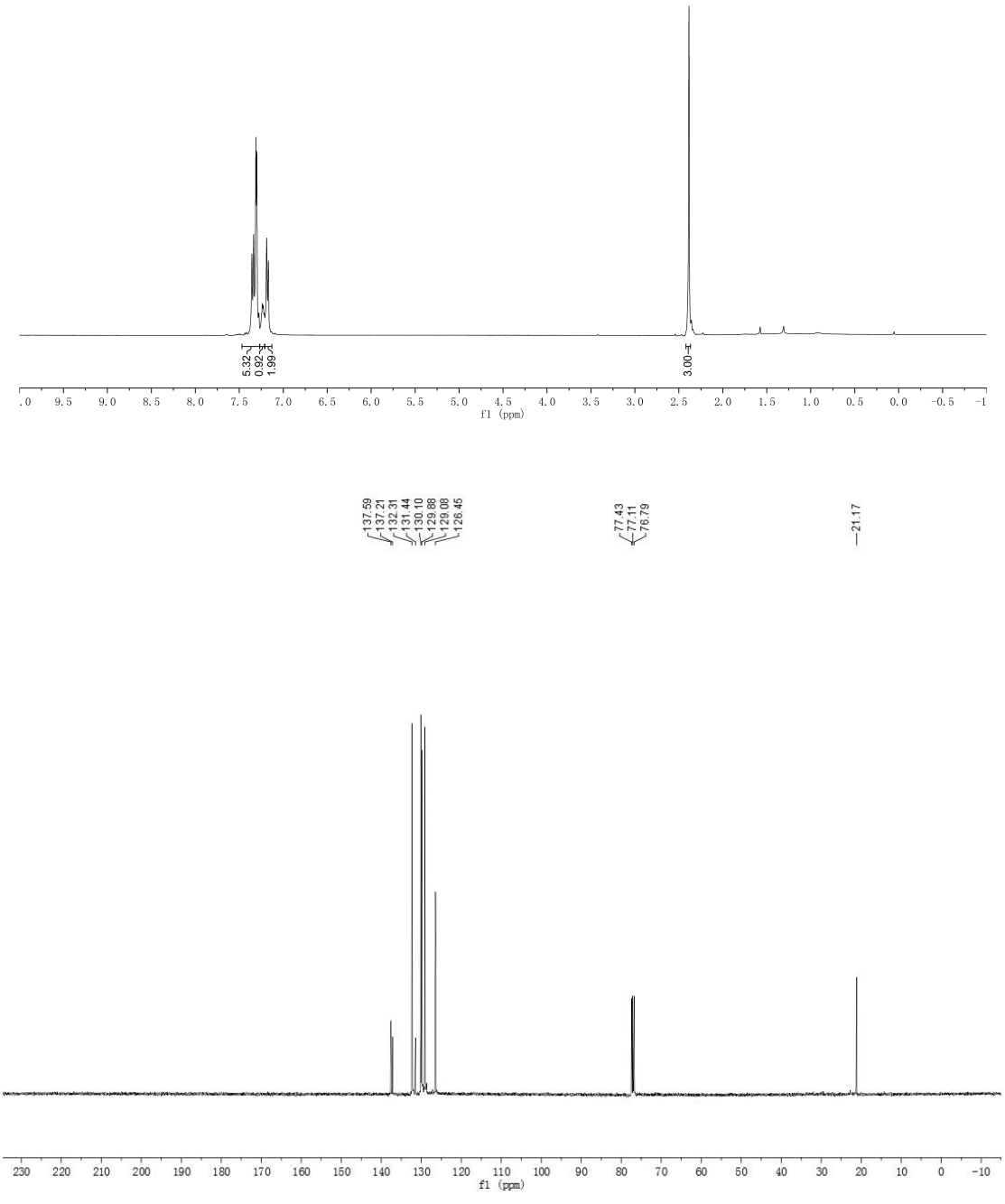
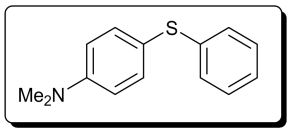


Figure S1. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3a in $CDCl_3$.

N,N-Dimethyl-4-(phenylthio)benzenamine (3b)



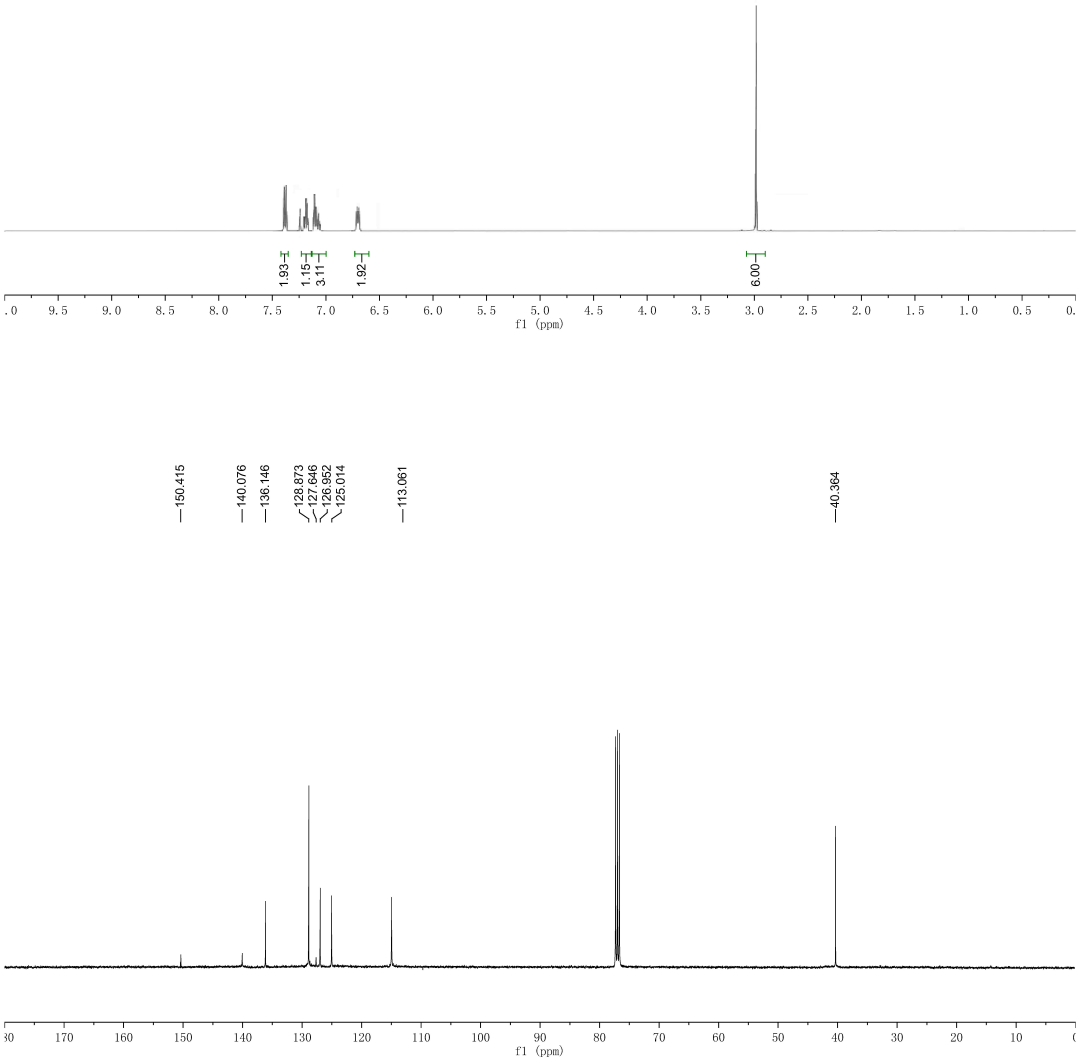
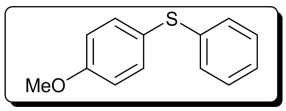


Figure S2. ^{1}H (400 MHz) and ^{13}C {1H} (150 MHz) NMR spectra of 3b in $CDCl_3$.

4-Methoxydiphenyl sulphide (3c)



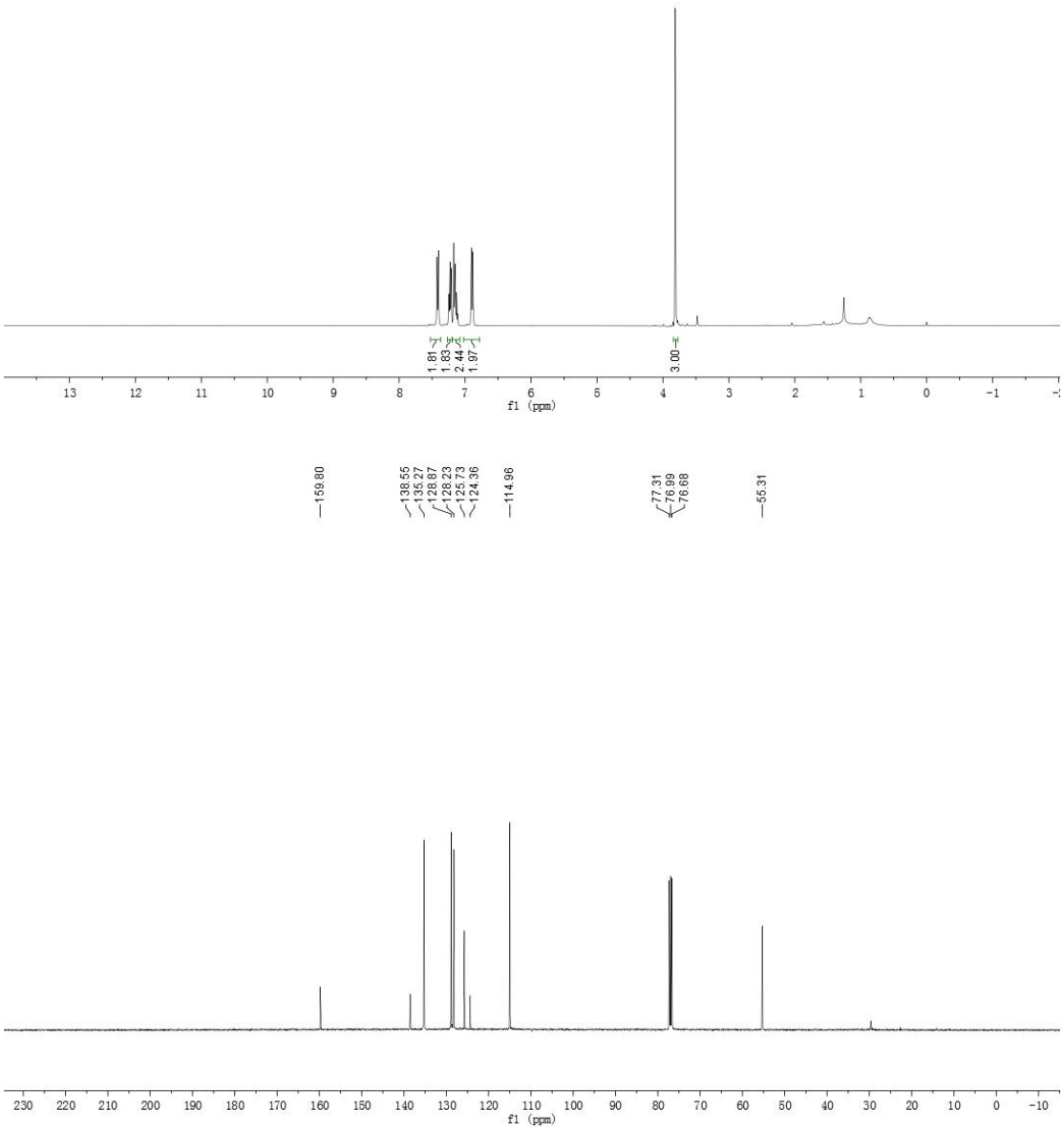
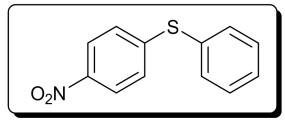


Figure S3. ^{1}H (400 MHz) and ^{13}C {1H} (150 MHz) NMR spectra of 3c in $CDCl_3$.

4-Nitrodiphenyl sulphide (3d)



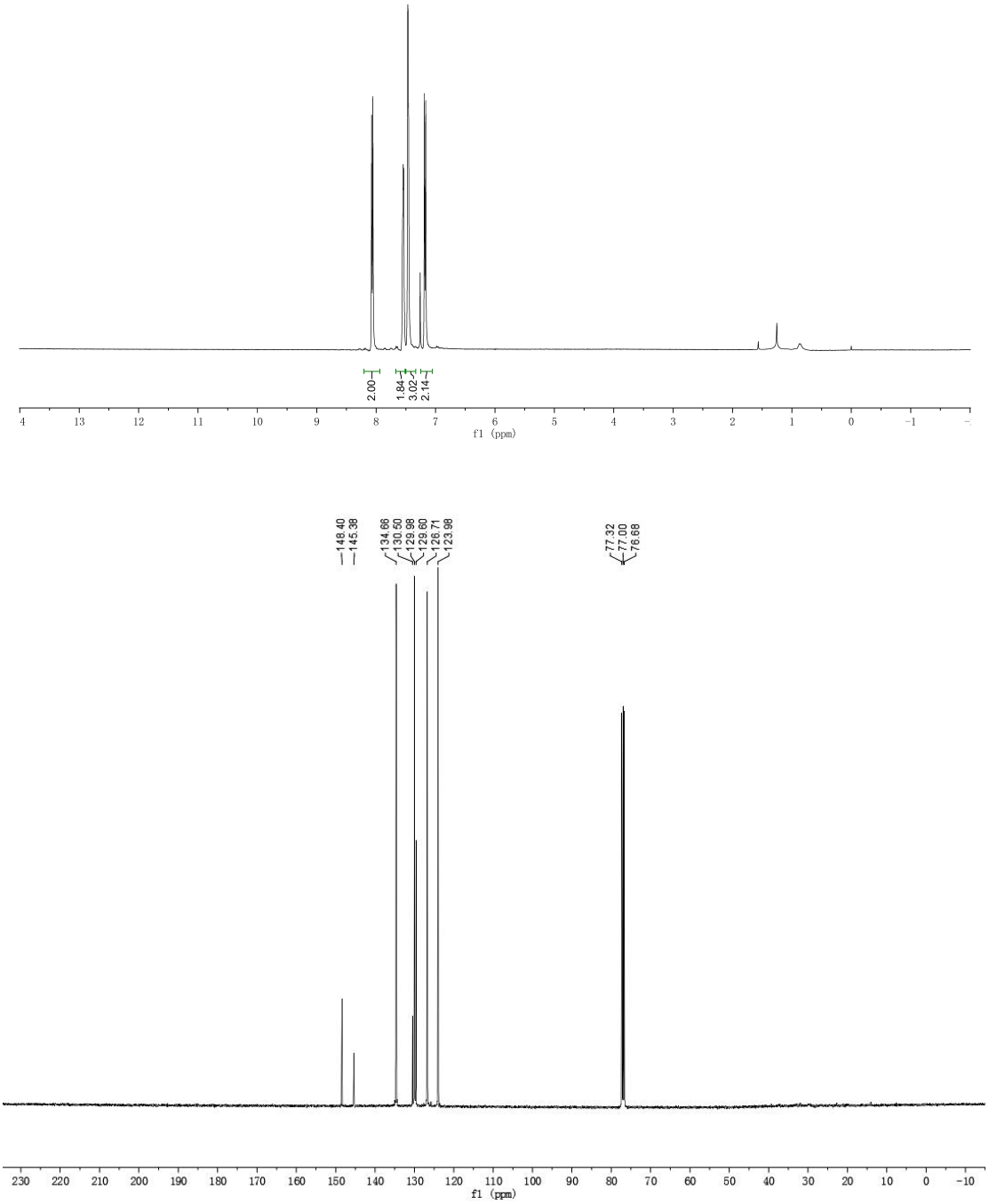
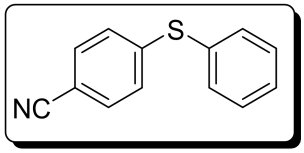


Figure S4. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3d in $CDCl_3$.

4-Cyanodiphenyl sulphide (3e)



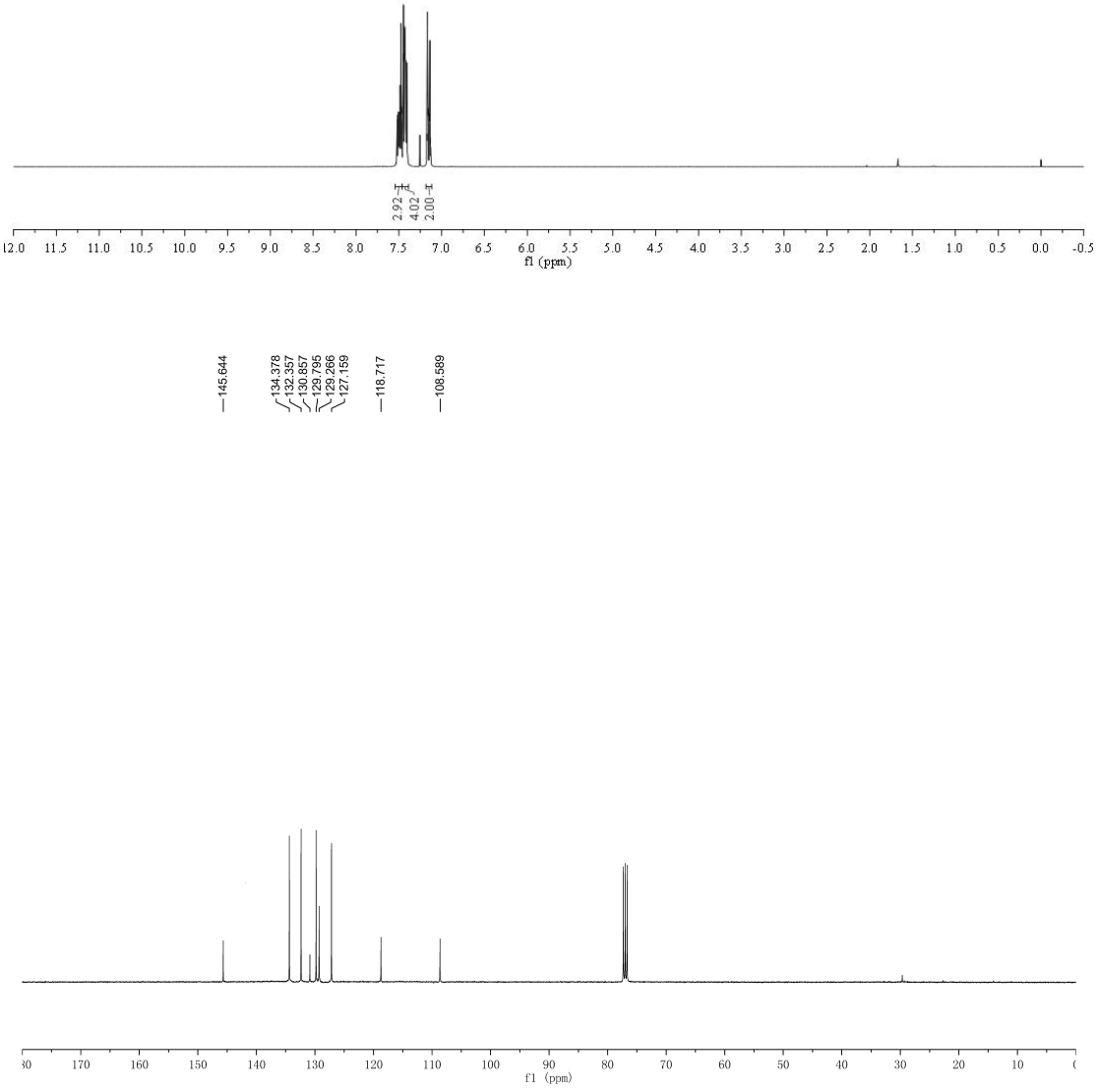
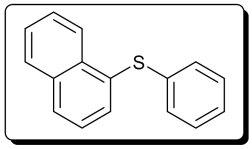
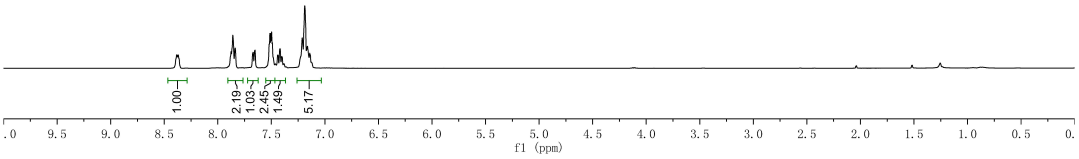


Figure S5. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3e in $CDCl_3$.

1-Naphthalenyl phenyl sulfide (3f)





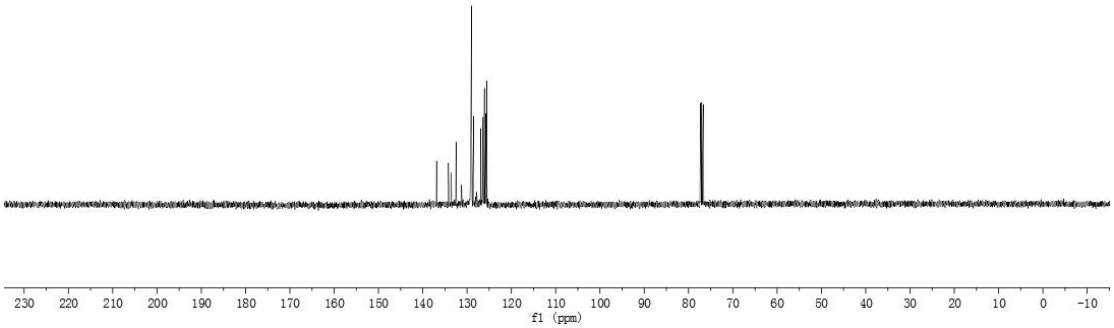
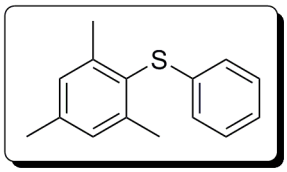
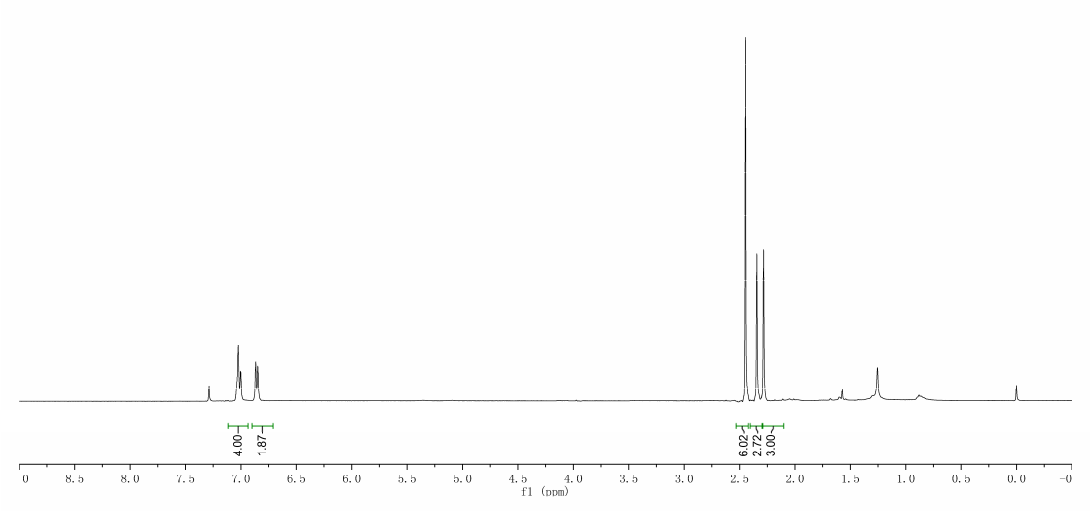


Figure S6. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3f in $CDCl_3$.

Mesityl phenyl sulfide (3g)





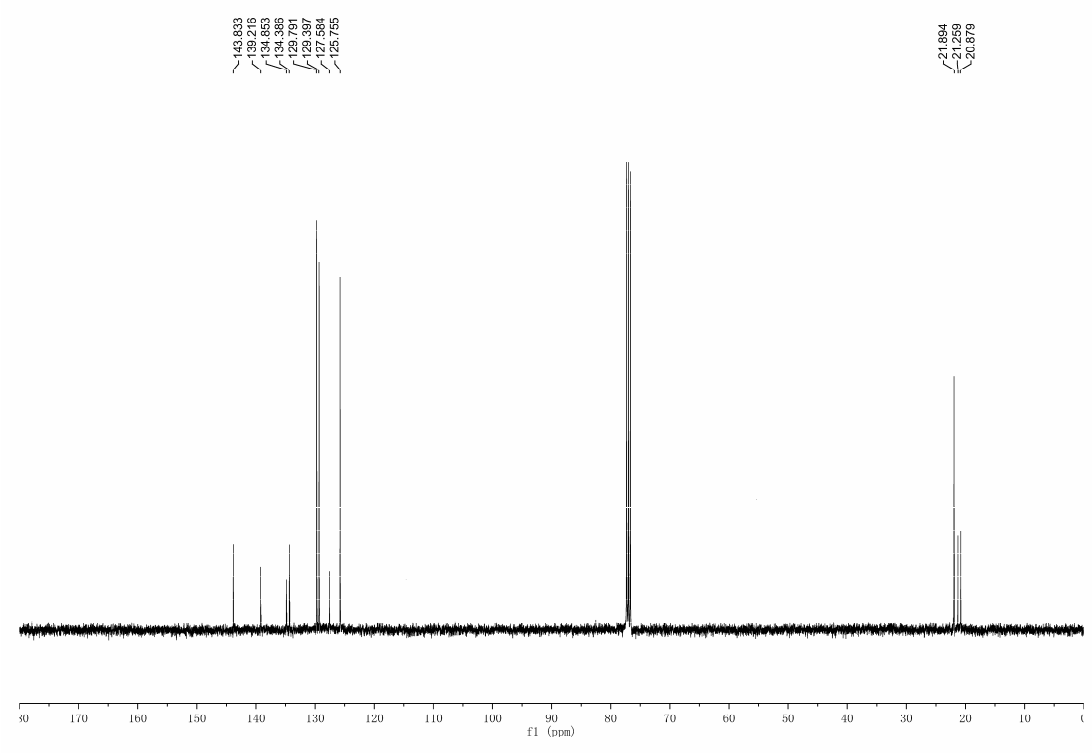
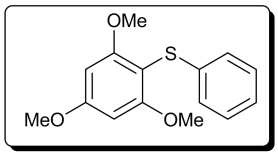


Figure S7. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3g in $CDCl_3$.

2,4,6-Trimethoxyphenyl phenyl sulfane (3h)



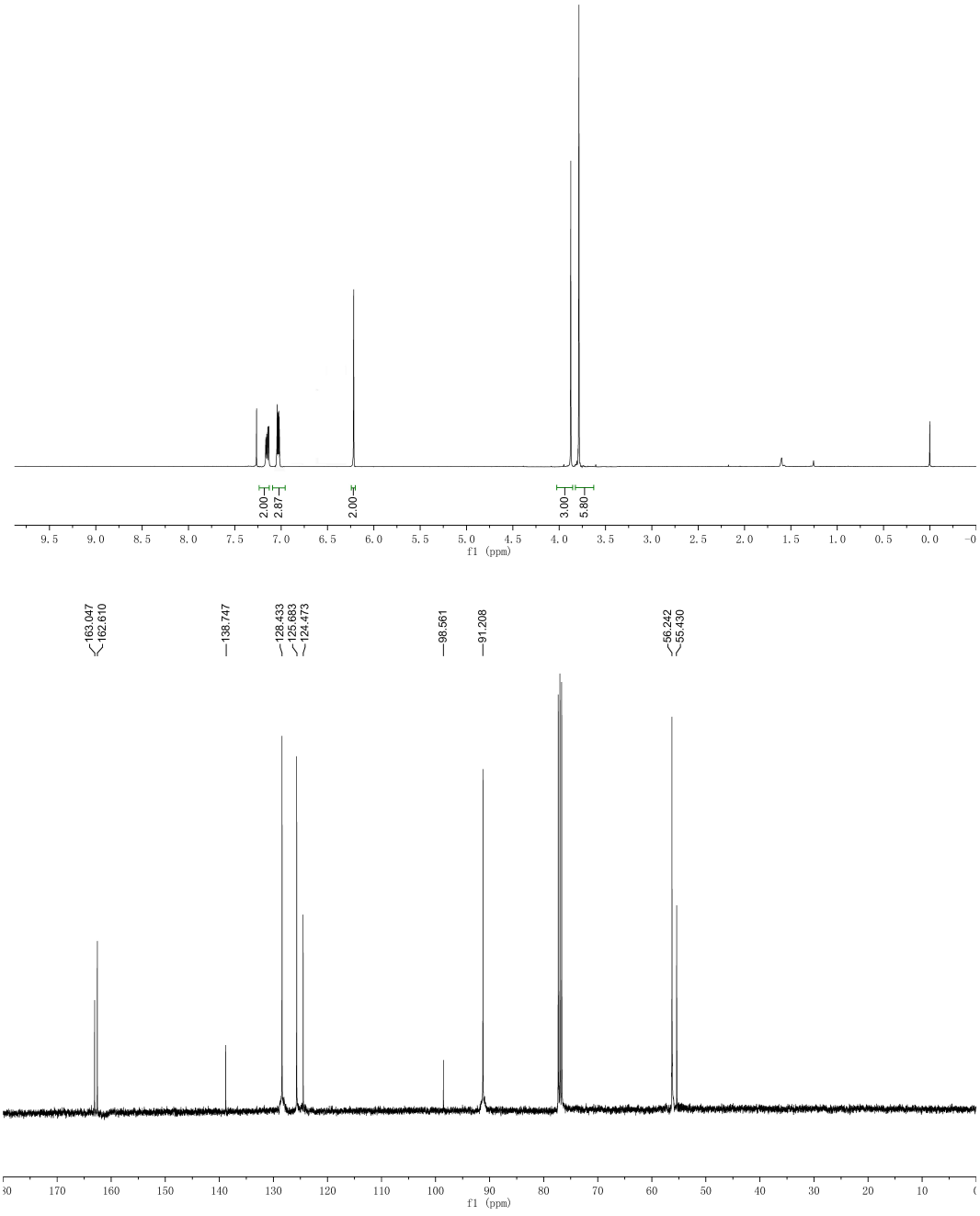
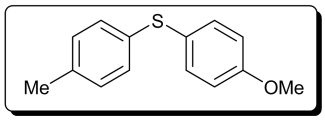
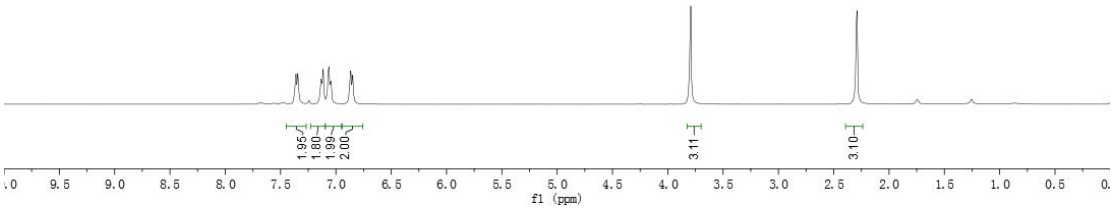


Figure S8. ^{1}H (600 MHz) and ^{13}C {1H} (150 MHz) NMR spectra of 3h in $CDCl_3$.

4-Methoxyphenyl *p*-tolyl sulfane (3i)





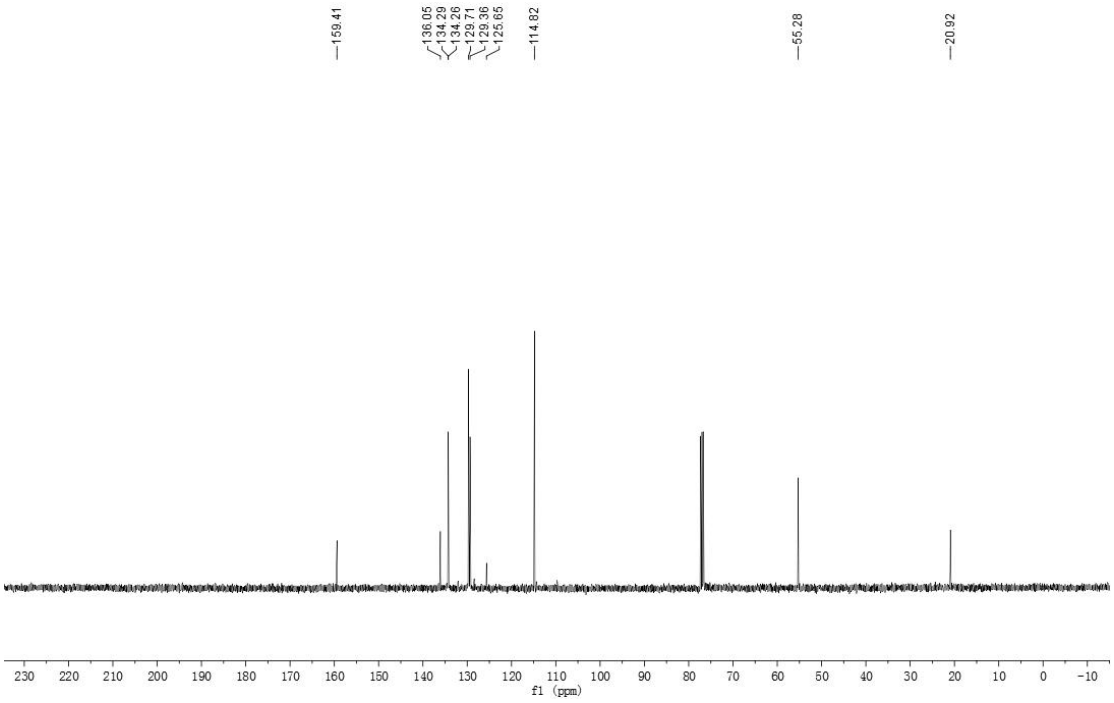
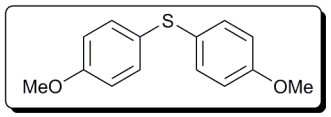


Figure S9. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3i in $CDCl_3$.

Bis(4-methoxyphenyl) sulfane (3j)



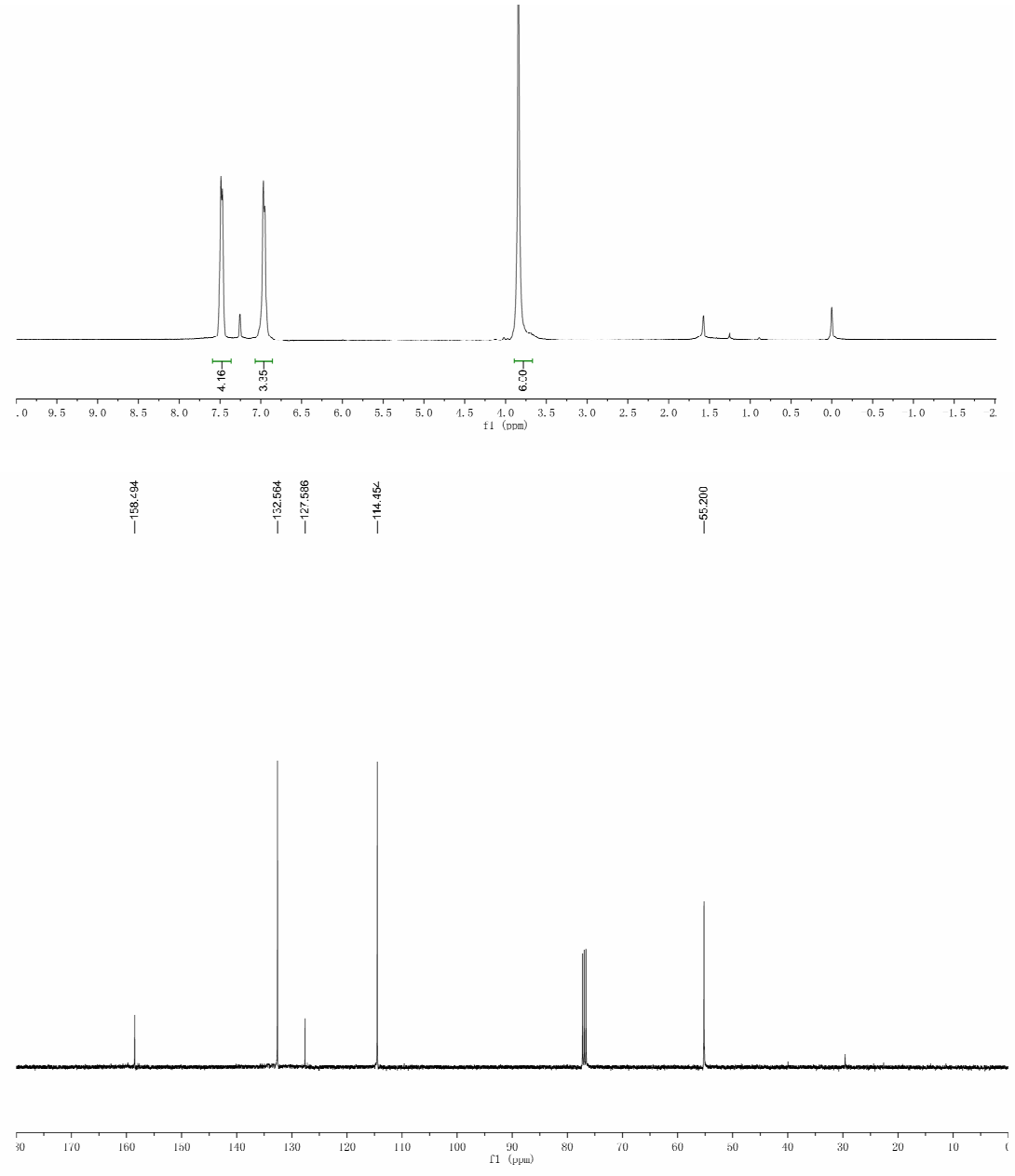
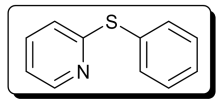


Figure S10. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3j in $CDCl_3$

2-(Phenylthio)pyridine (3k)



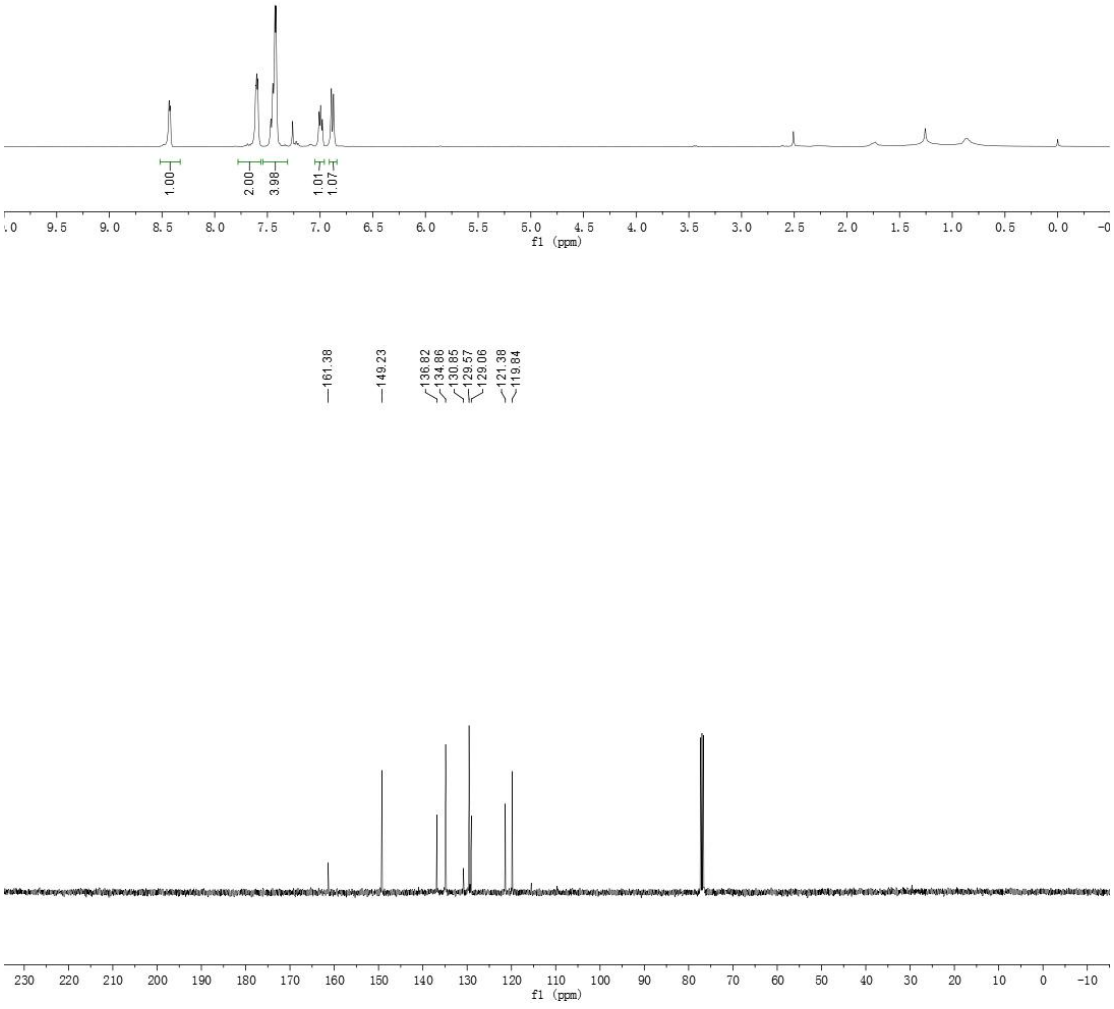
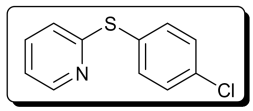


Figure S11. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3k in $CDCl_3$

2-(4-Chlorophenylthio)pyridine (3l)



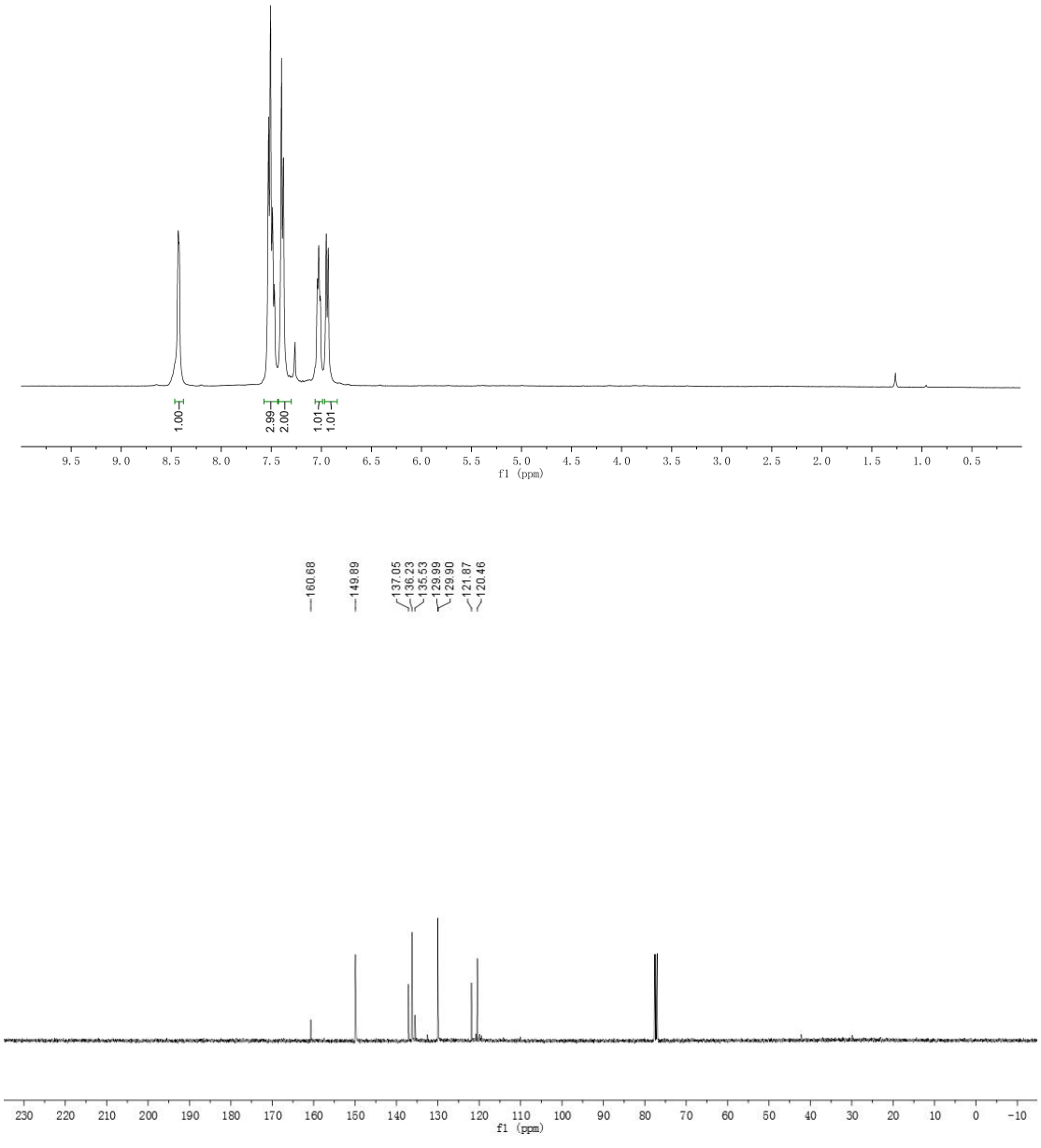
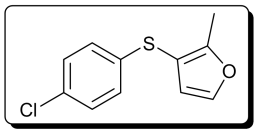


Figure S12. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3l in $CDCl_3$

3-(4-Chlorophenylthio)-2-methylfuran (3m)



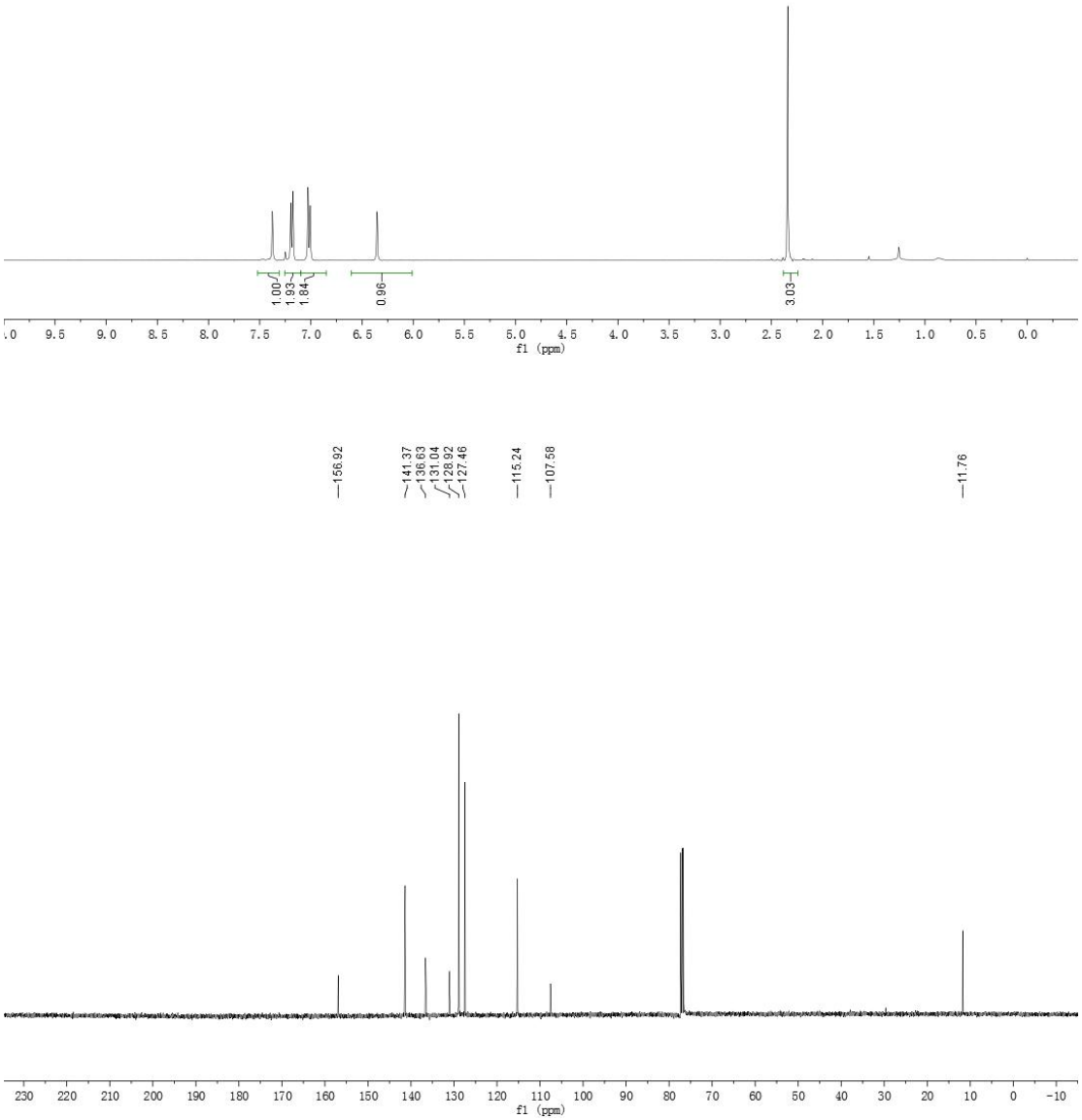
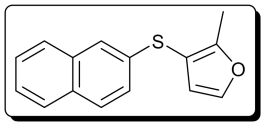


Figure S13. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3m in $CDCl_3$

2-Methyl-3-(naphthalen-2-ylthio)furan (3n)



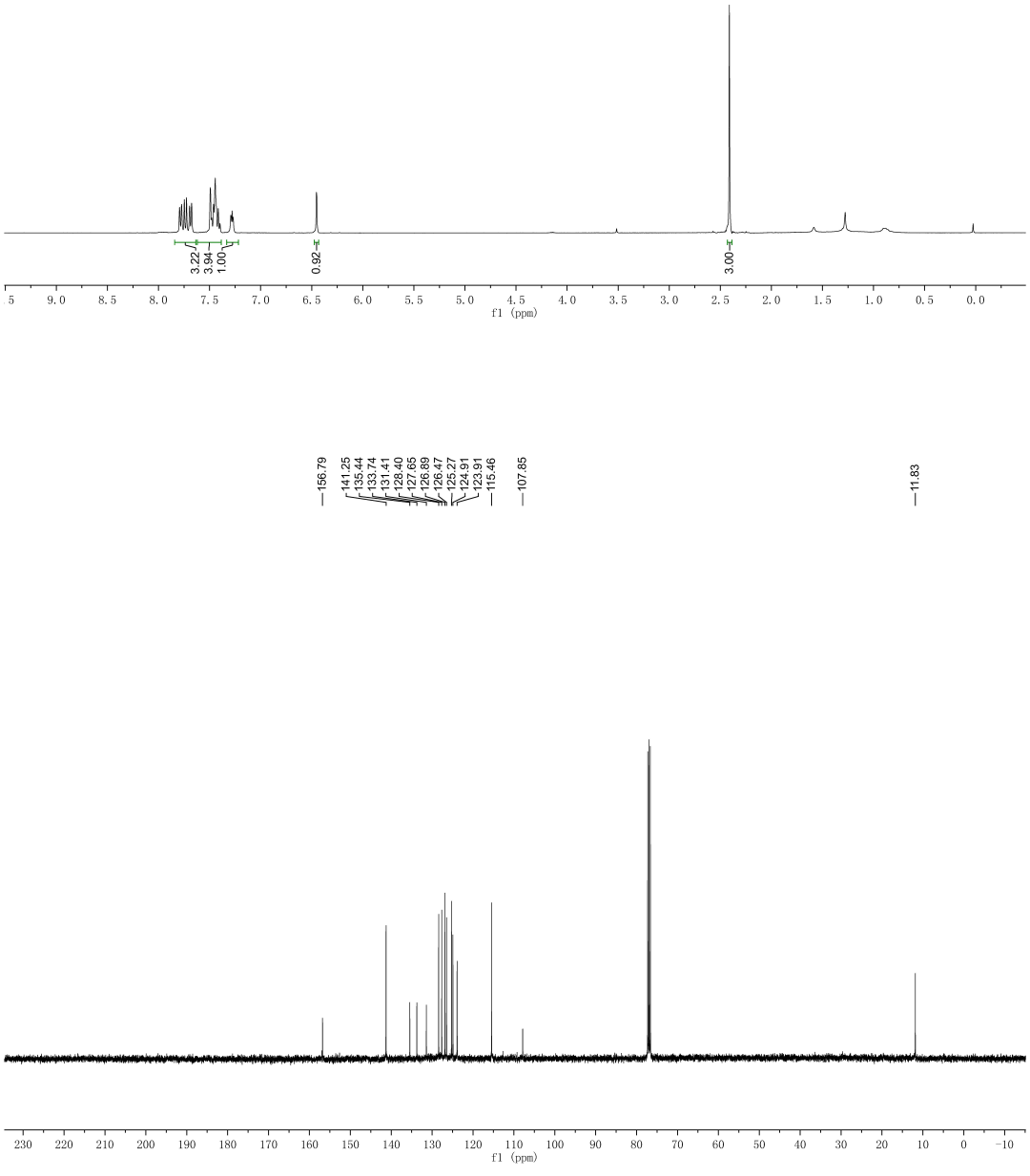
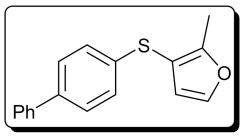


Figure S14. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 3n in $CDCl_3$

3-(Biphenyl-4-ylthio)-2-methylfuran (3o)



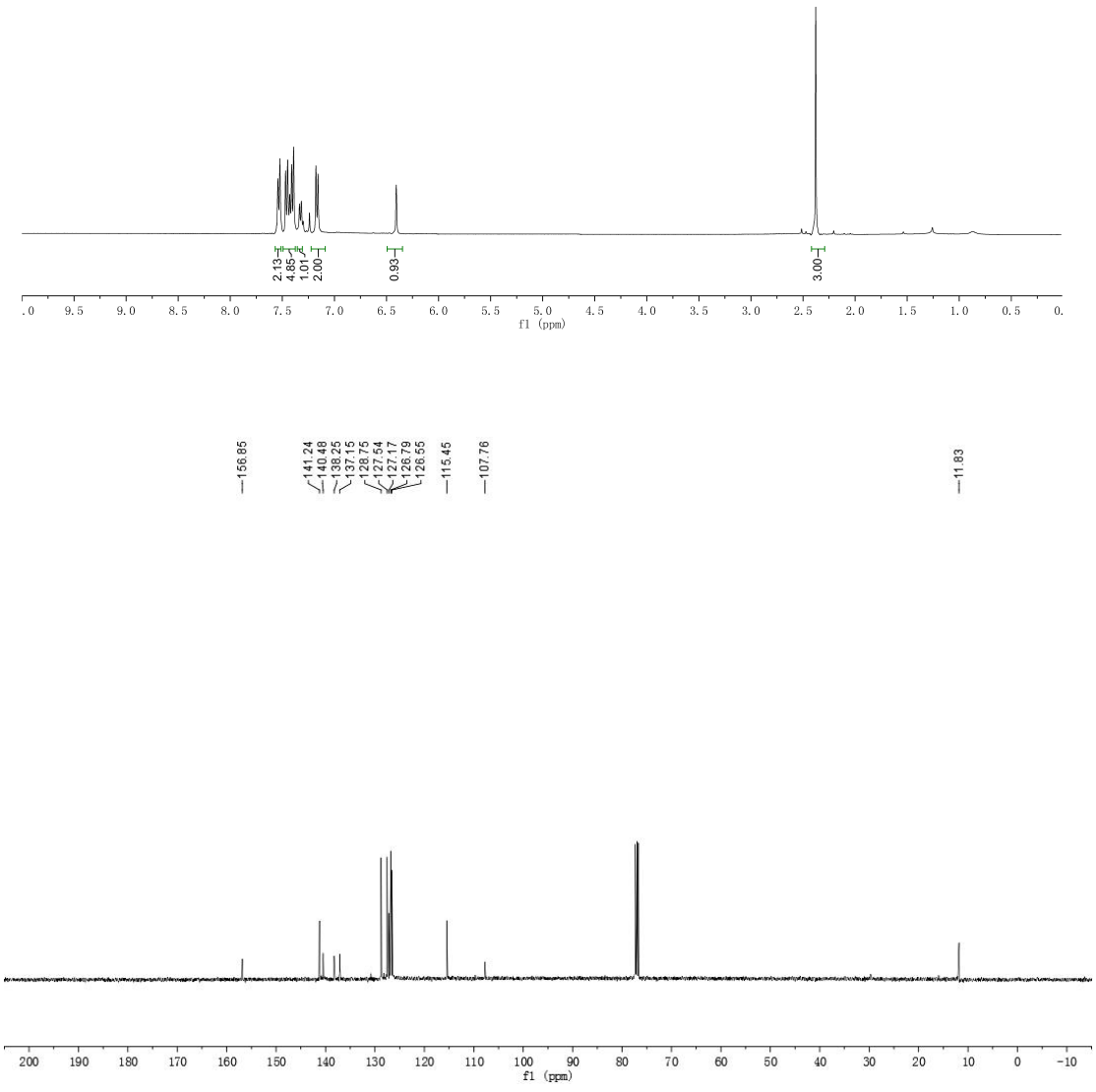
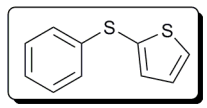
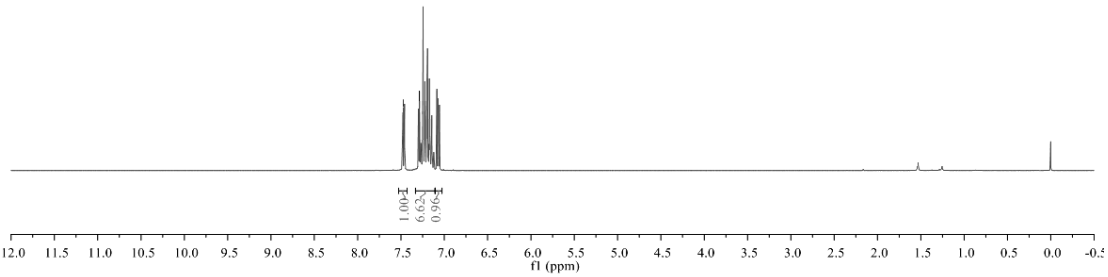


Figure S15. ^{1}H (400 MHz) and ^{13}C {1H} (100 MHz) NMR spectra of 3o in $CDCl_3$

2-(Phenylthio)thiophene (3p)





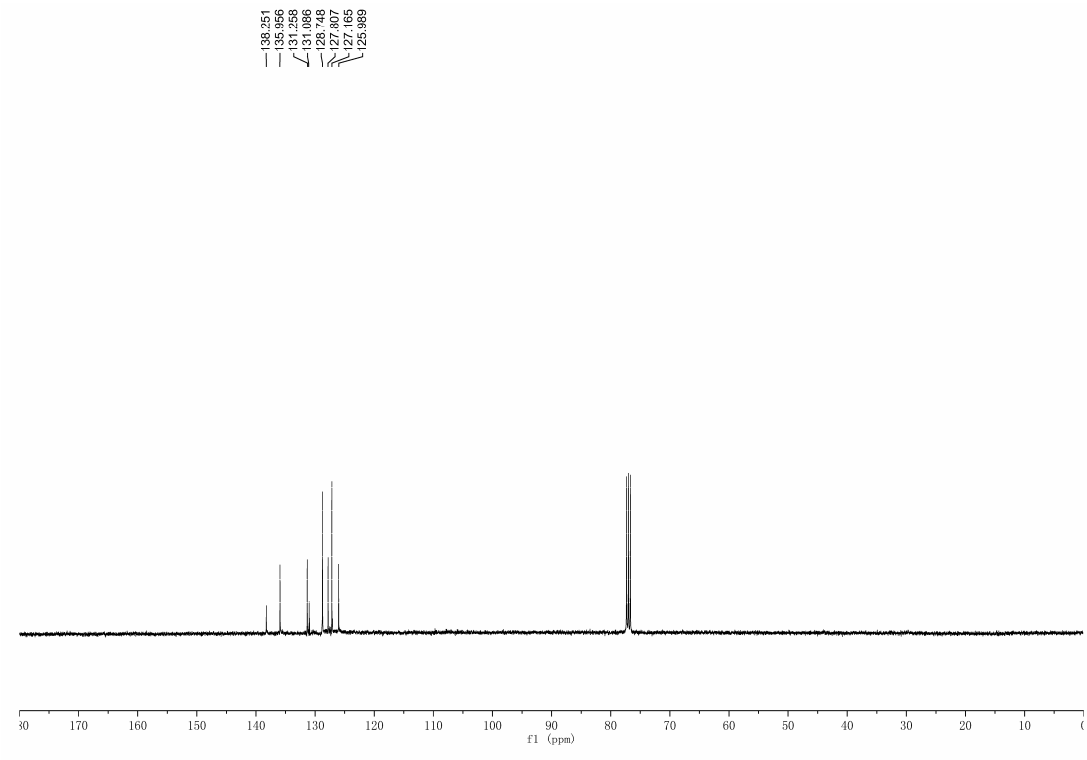


Figure S16. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 3p in $CDCl_3$

Phenylthioferrocene (3q)

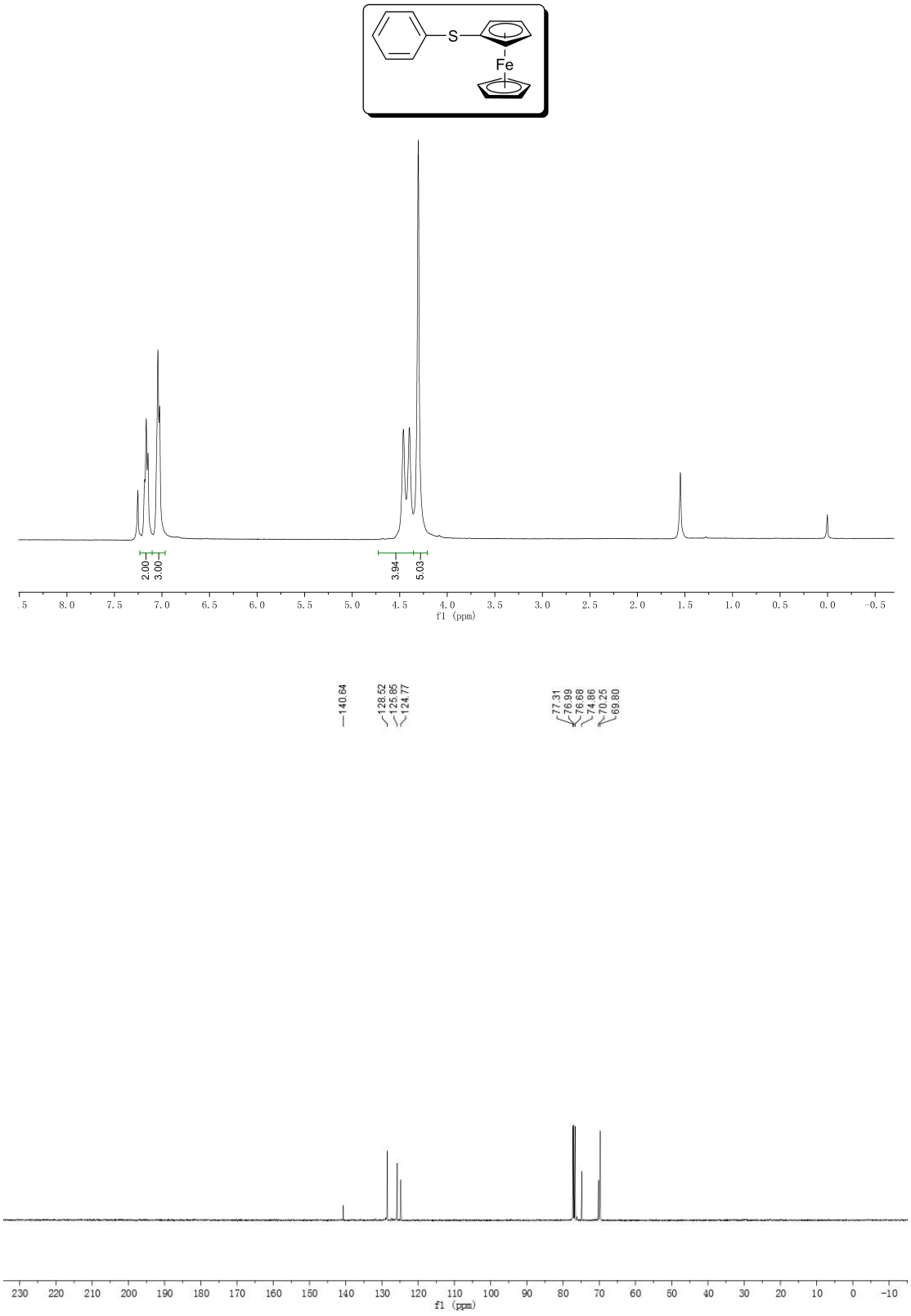
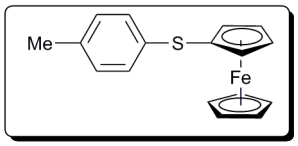


Figure S17. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 3q in $CDCl_3$

4-Tolyl ferrocenyl sulphide (3r)



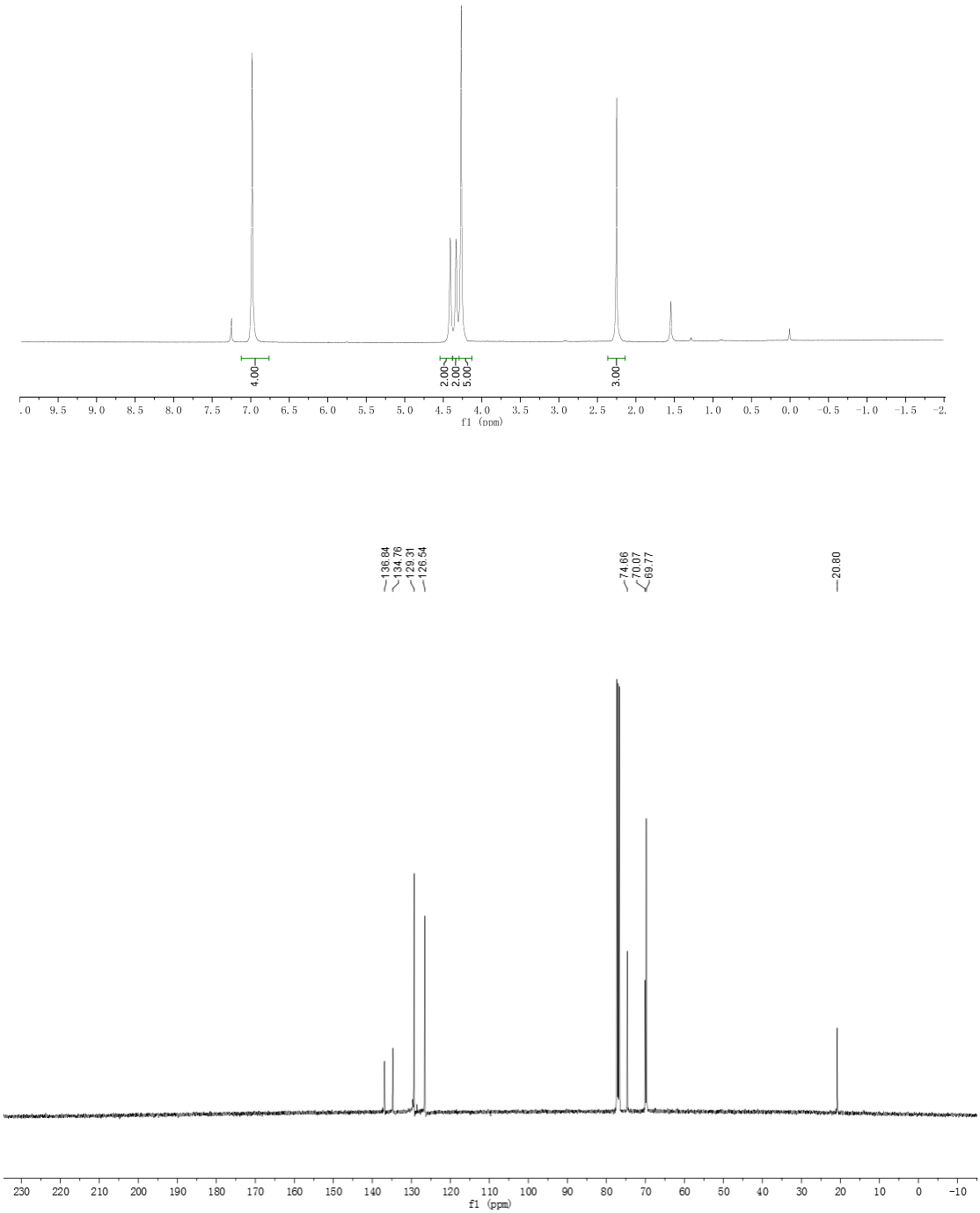
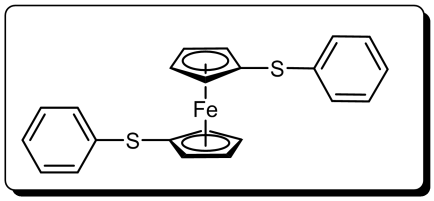


Figure S18. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 3r in $CDCl_3$

1,1’-Bis(phenylthio)ferrocene (3s)



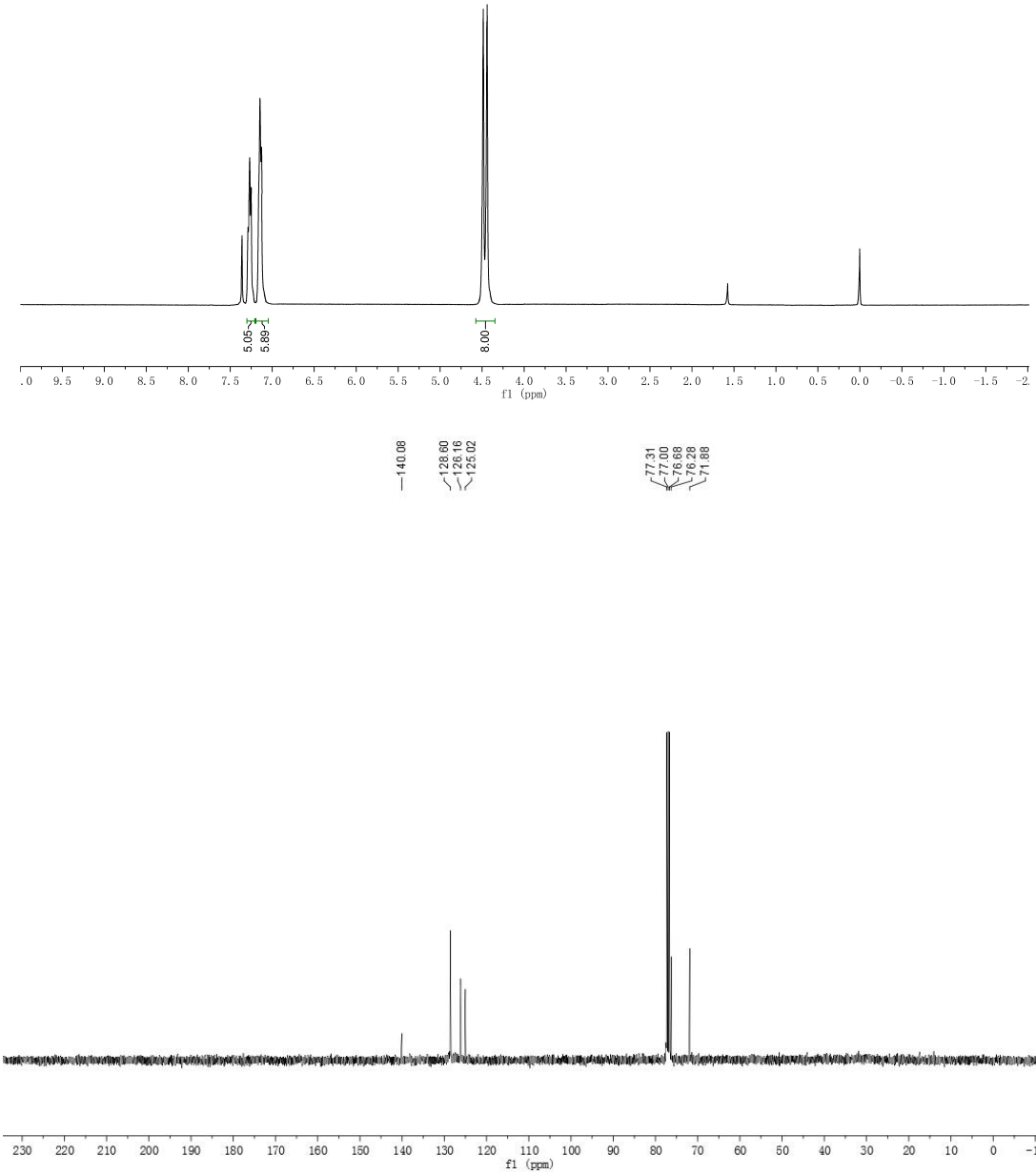
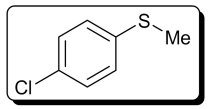


Figure S19. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 3s in $CDCl_3$

Methyl 4-chlorophenyl sulfide (5a)



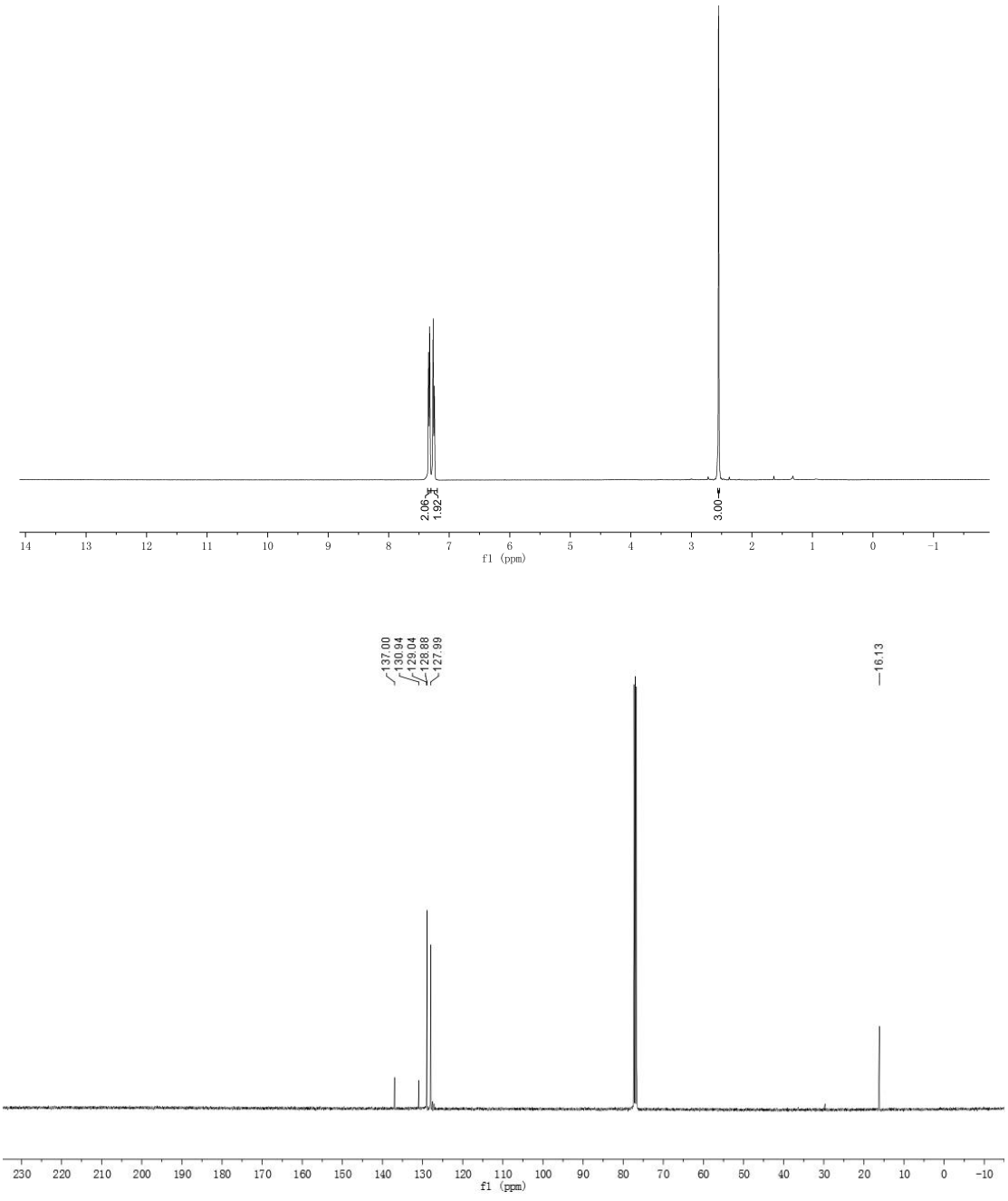
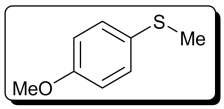


Figure S20. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5a in $CDCl_3$

***p*-Methylthioanisole (5b)**



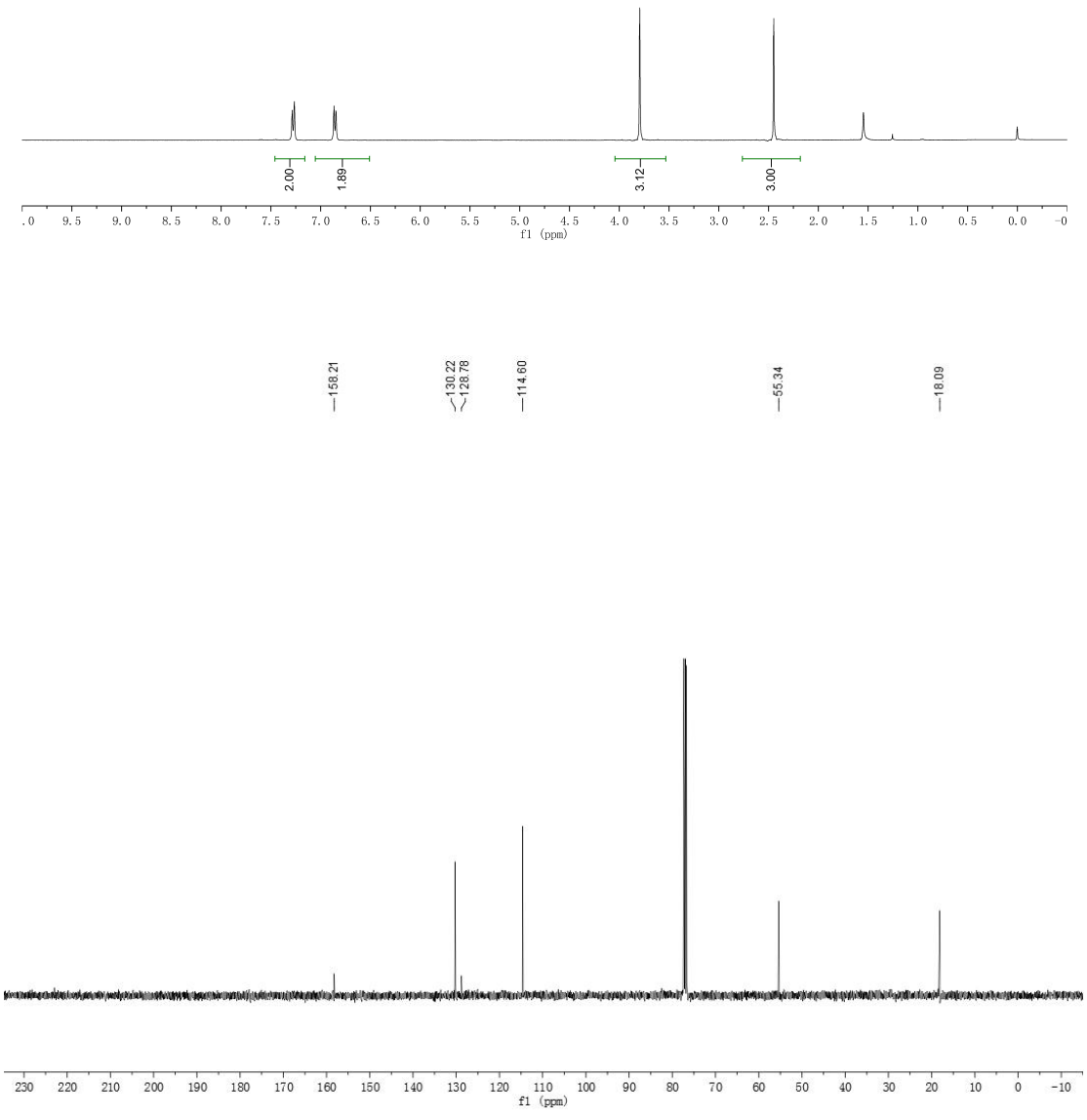
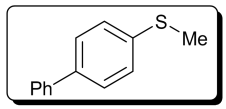


Figure S21. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5b in $CDCl_3$

4-(Methylsulfanyl)biphenyl (5c)



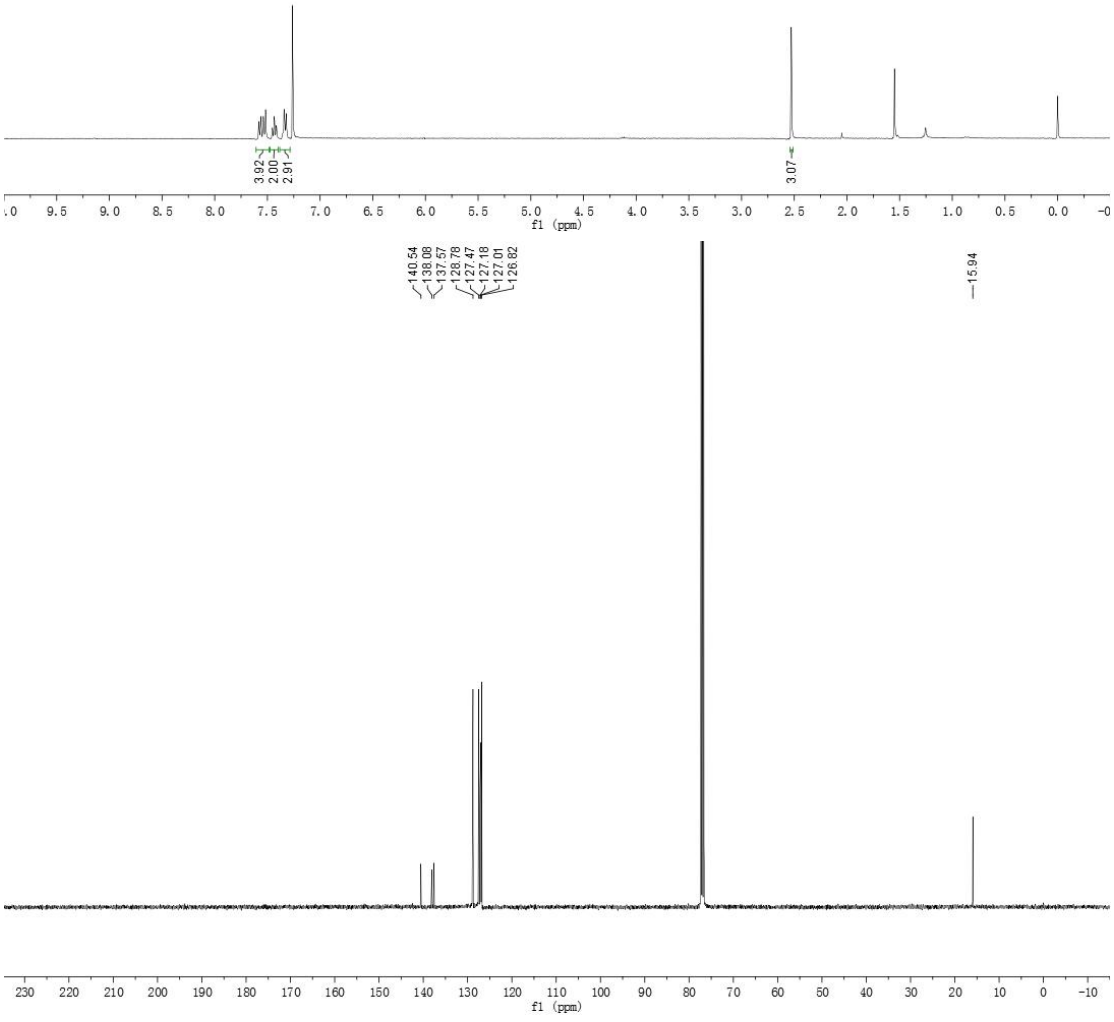
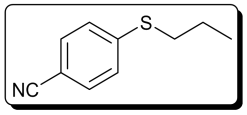


Figure S22. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5h in $CDCl_3$

4-(Propylthio)benzonitrile (5d)



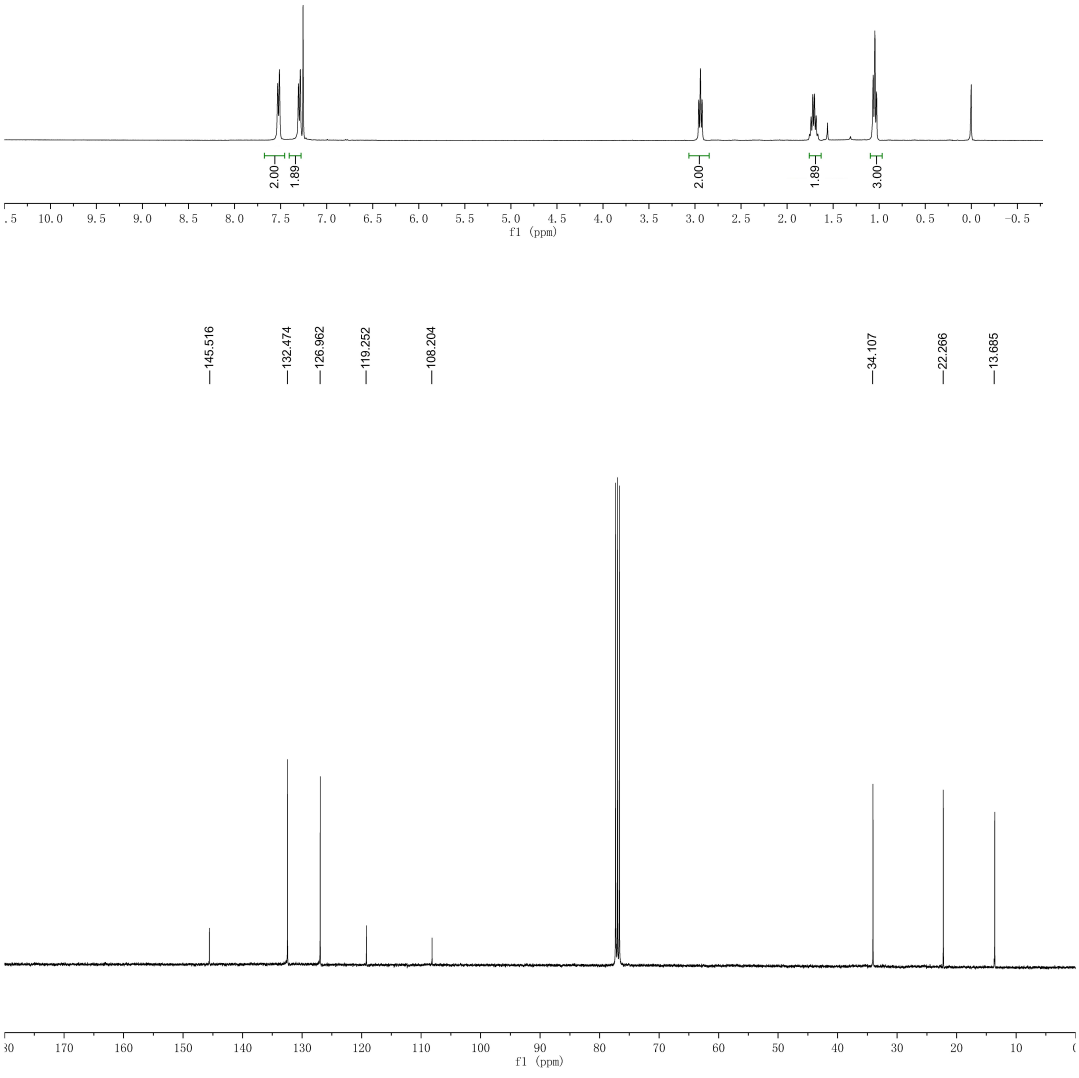
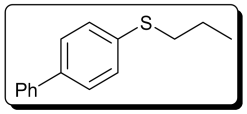


Figure S23. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5d in $CDCl_3$

4-Biphenyl propyl sulfide (5e)



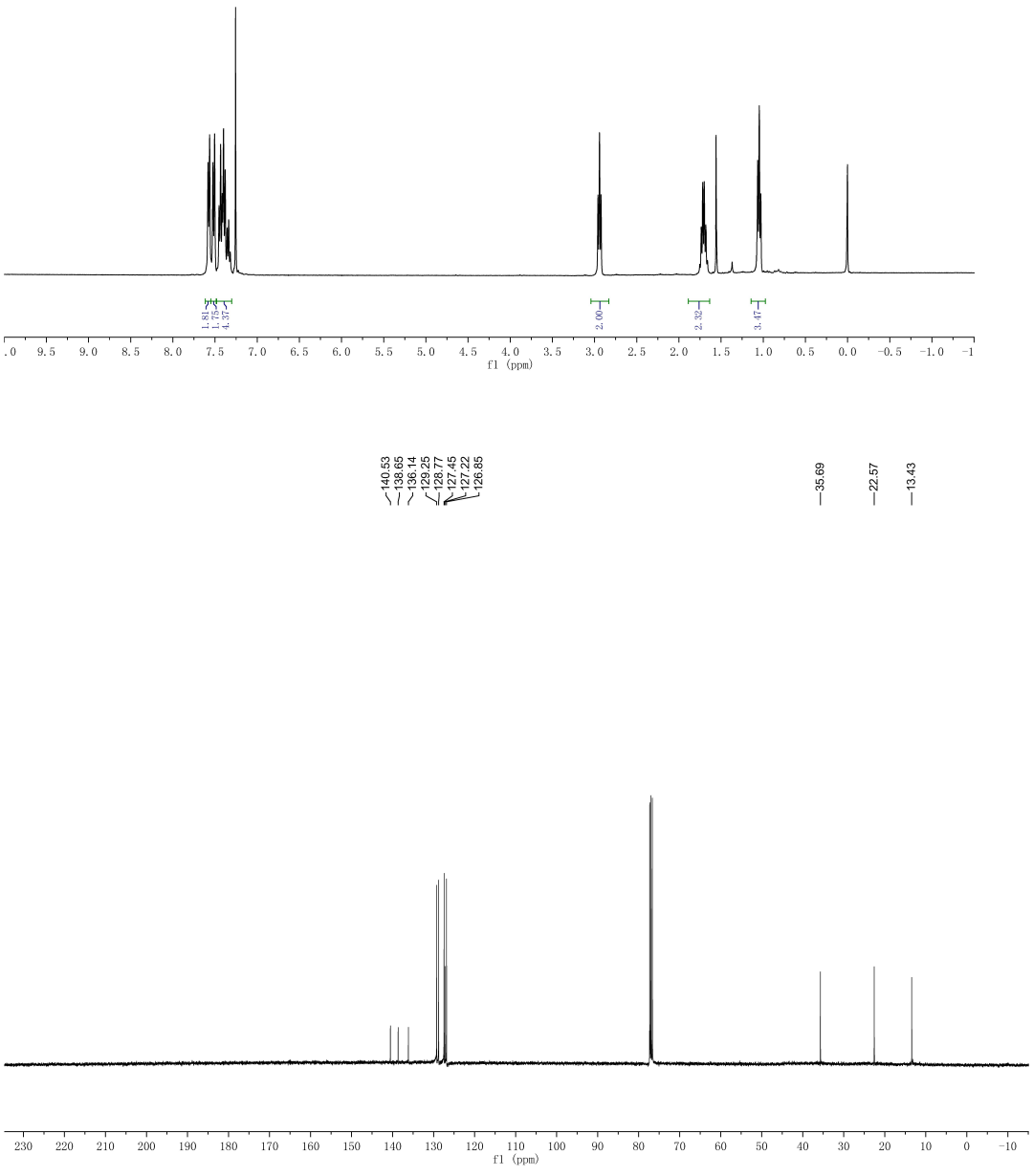
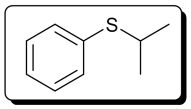


Figure S24. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5e in $CDCl_3$

Isopropyl phenyl sulfide (5f)



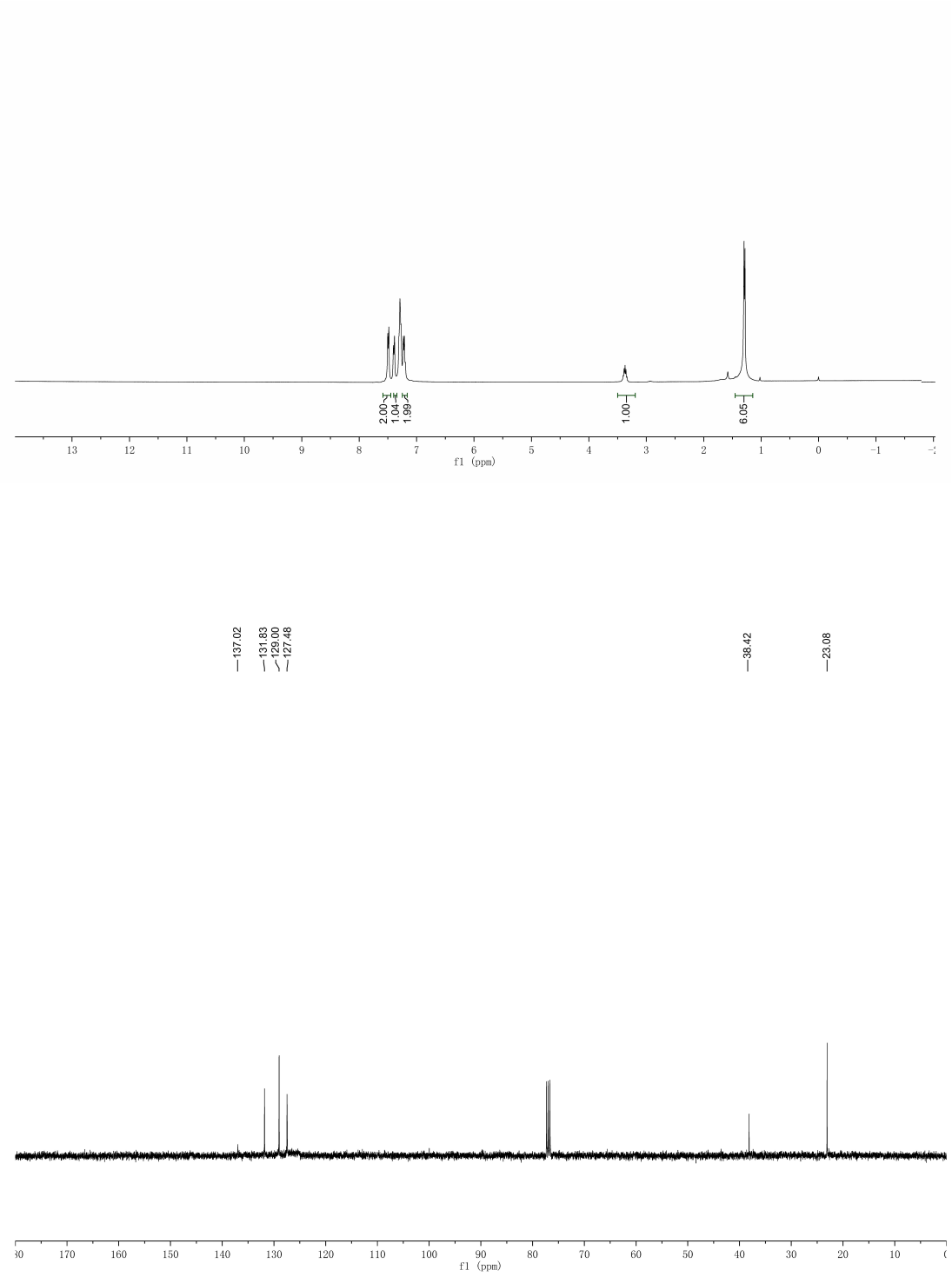
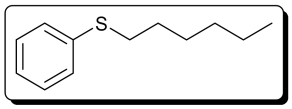
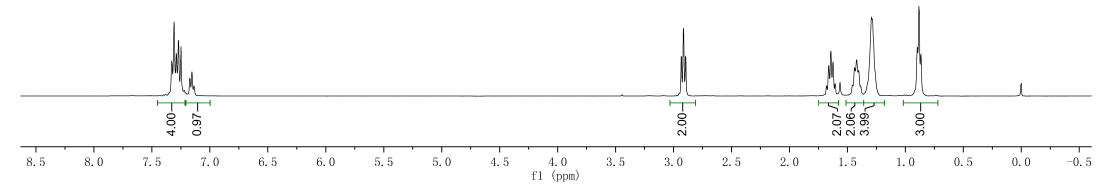


Figure S25. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5f in $CDCl_3$

n-Hexyl phenyl sulfide (5g)





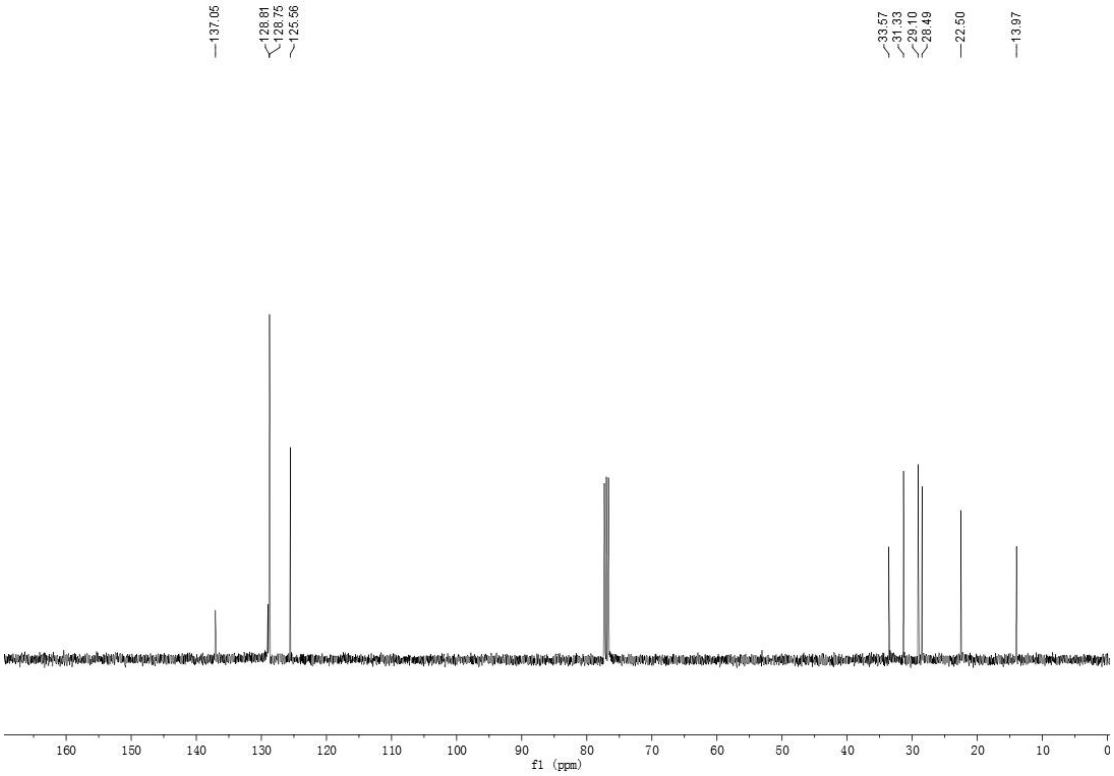
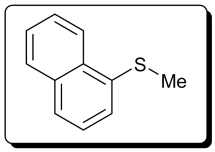


Figure S26. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5g in $CDCl_3$

Methyl 1-naphthyl sulfide (5h)



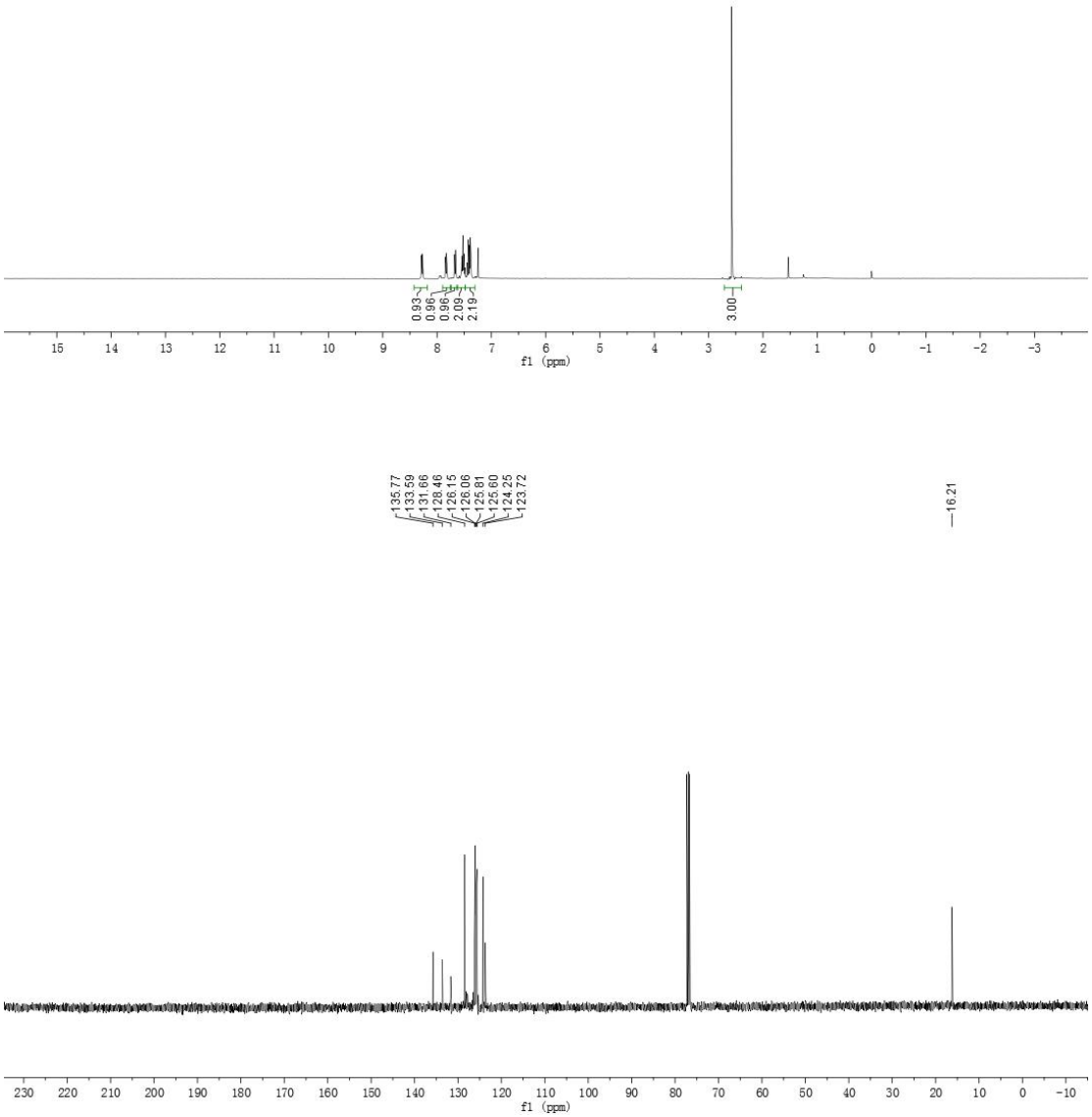
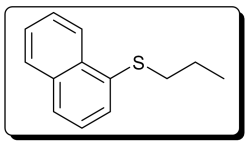


Figure S27. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5h in $CDCl_3$

1-Propyl naphthyl sulfide (5i)



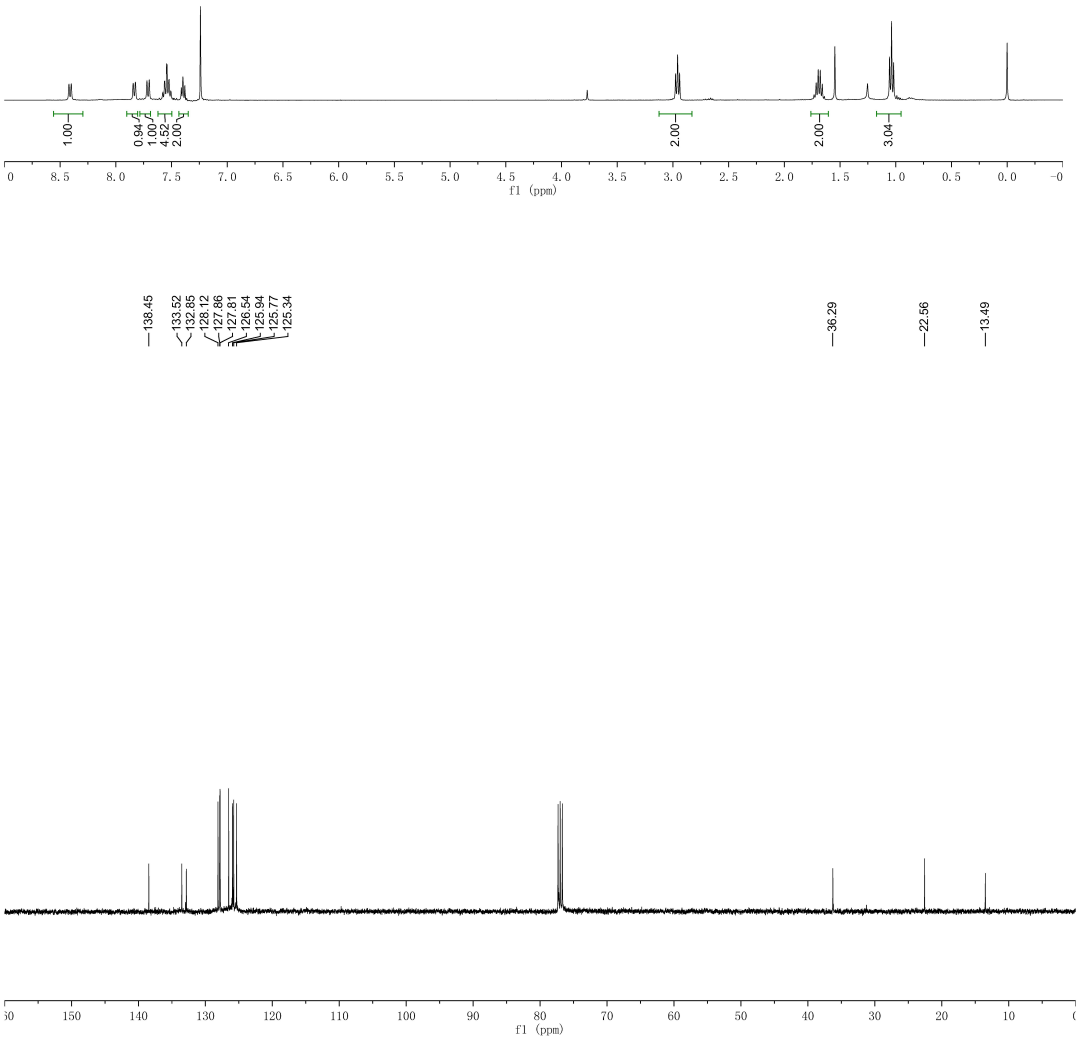
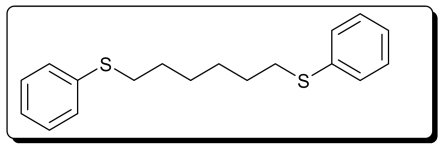


Figure S28. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5i in $CDCl_3$

1,6-Bis(phenylthio)hexane (5j):



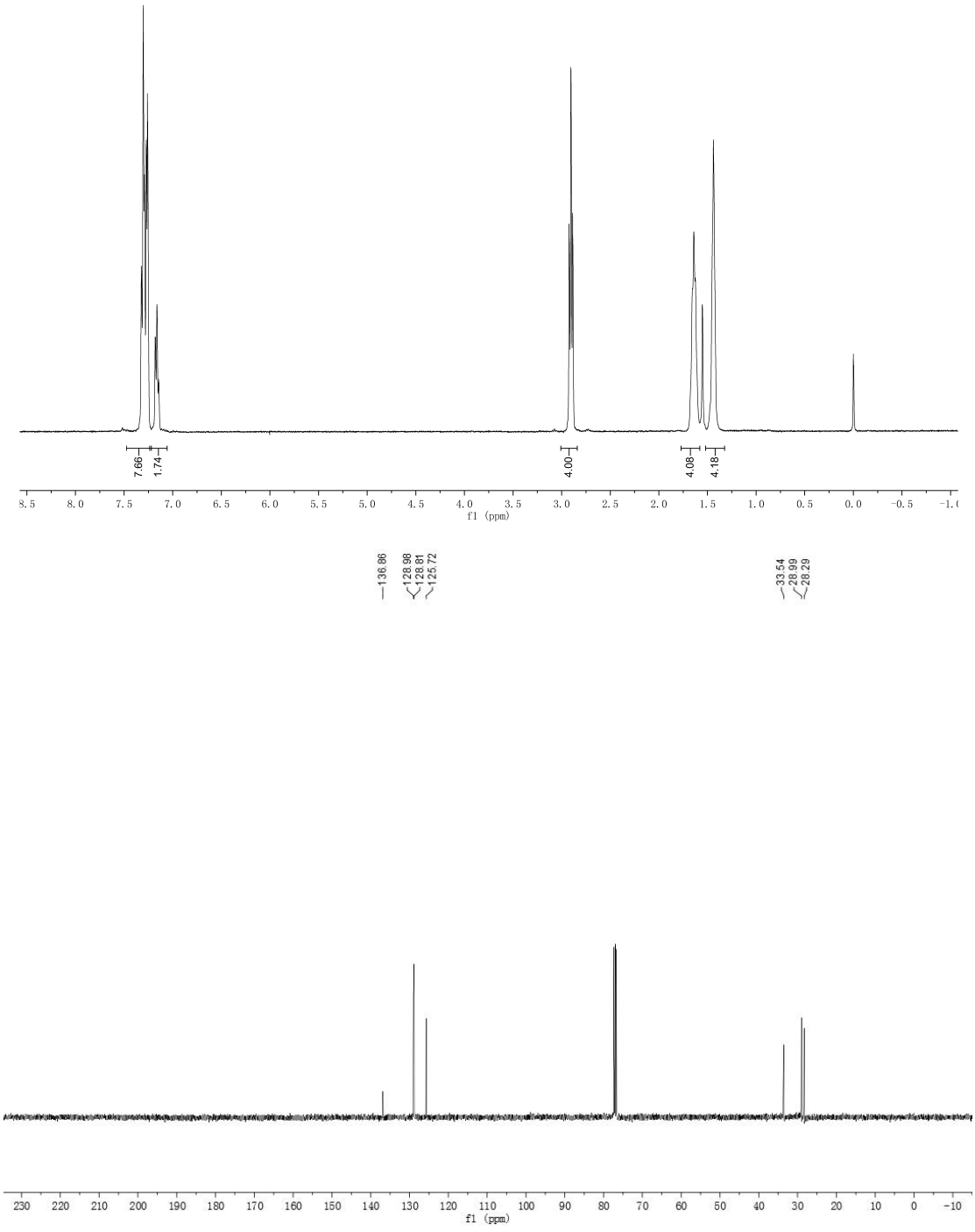
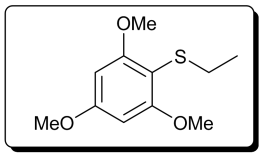


Figure S29. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5j in $CDCl_3$

Ethyl 2,4,6-trimethoxyphenyl sulfide (5k)



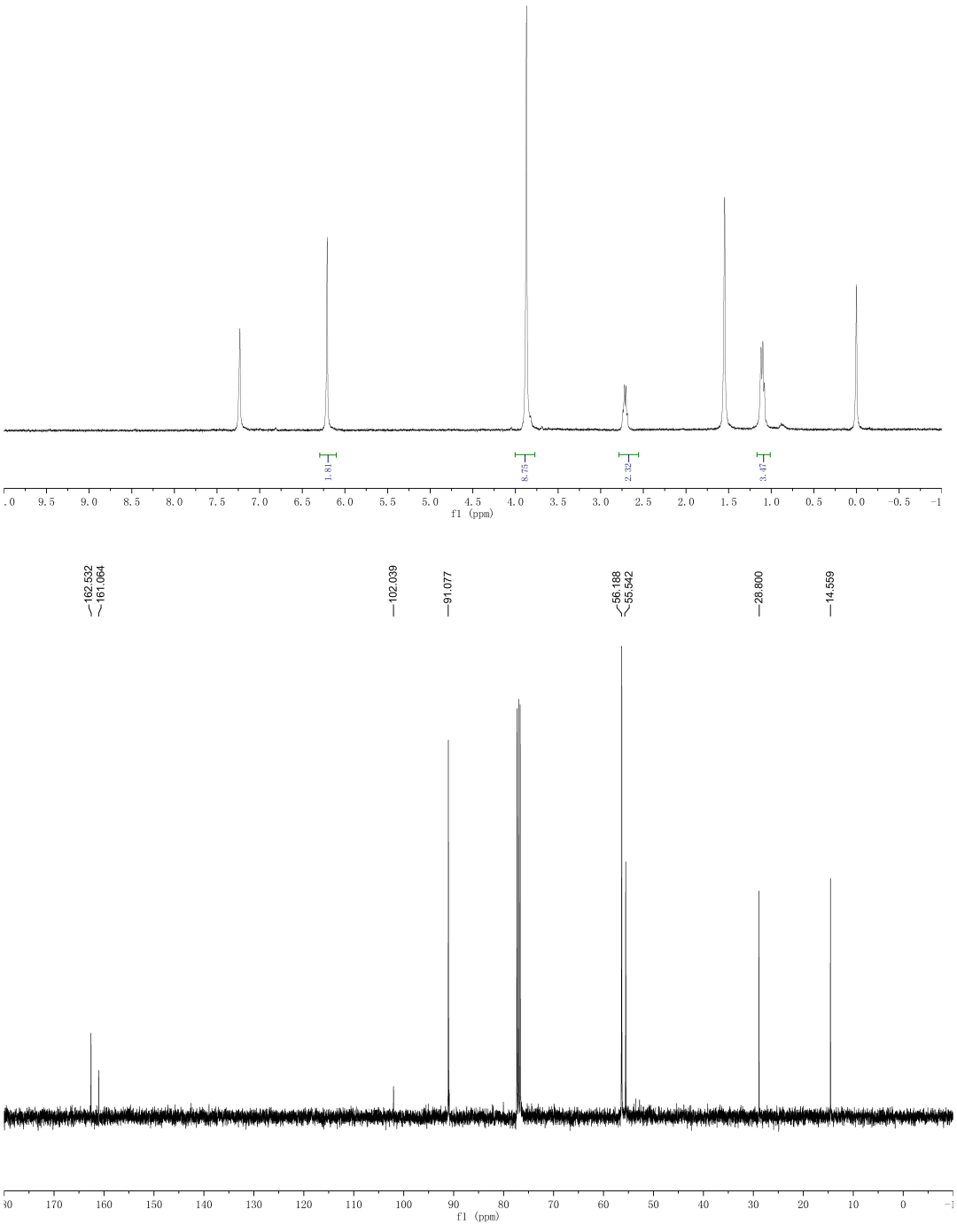
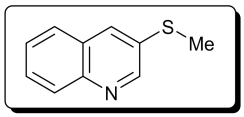


Figure S30. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5k in $CDCl_3$

3-(Methylthio)quinoline (5l)



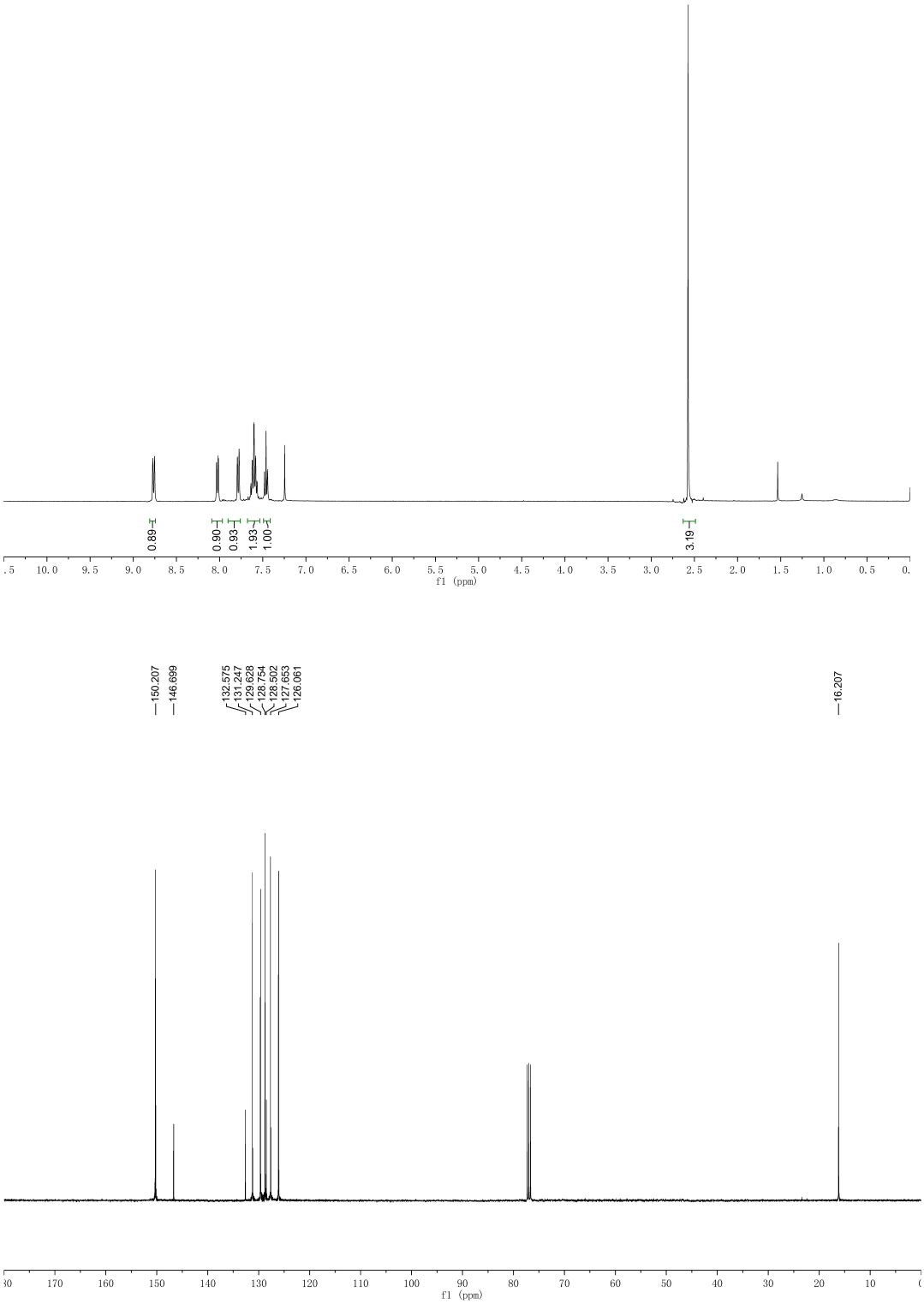
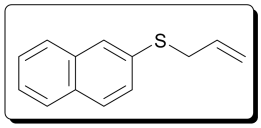


Figure S31. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5l in $CDCl_3$

Allyl 2-naphthyl sulfide (5m)



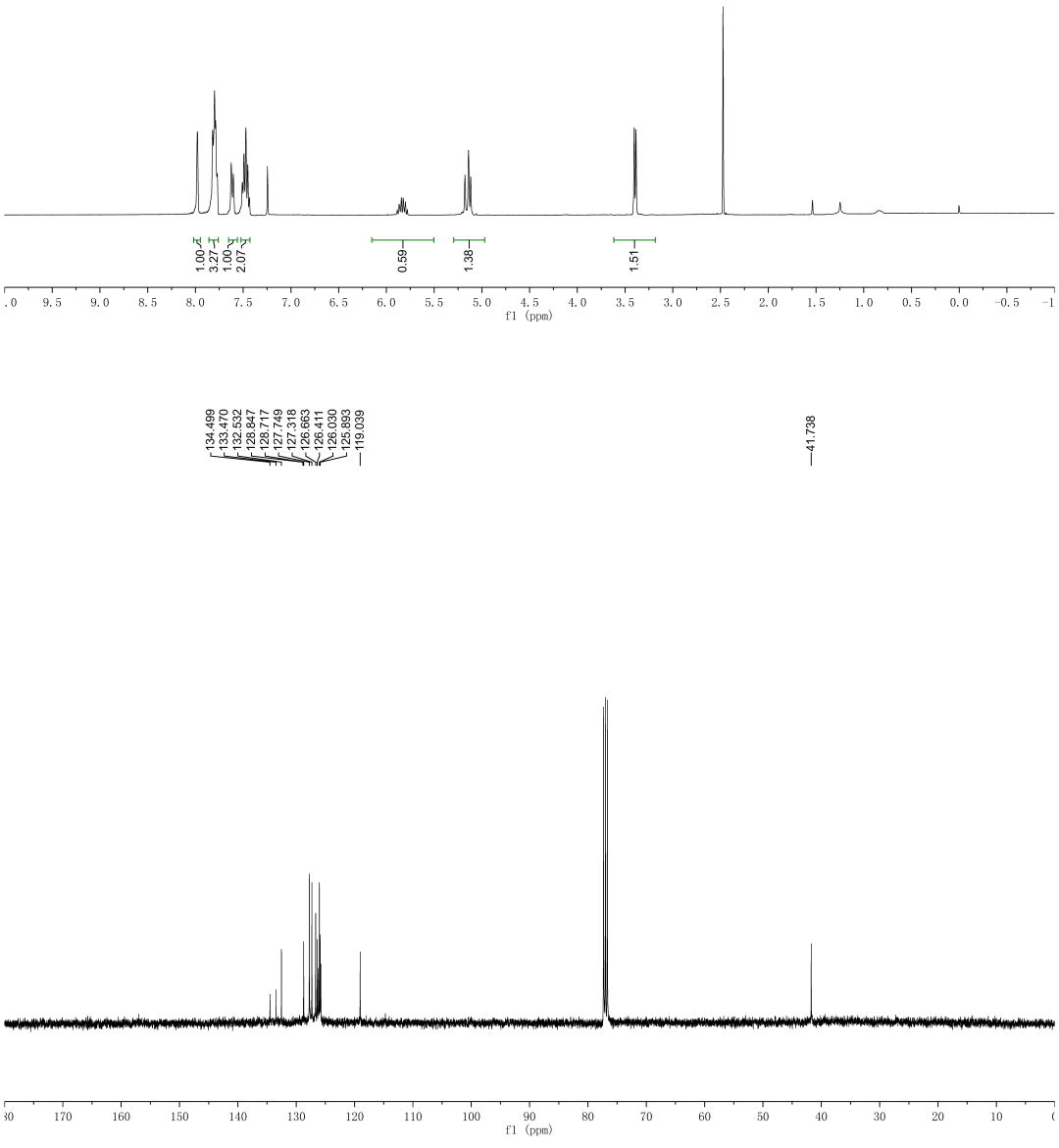
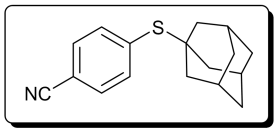


Figure S32. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5m in $CDCl_3$

1-Adamantyl 4-cyanophenyl sulfide (5n)



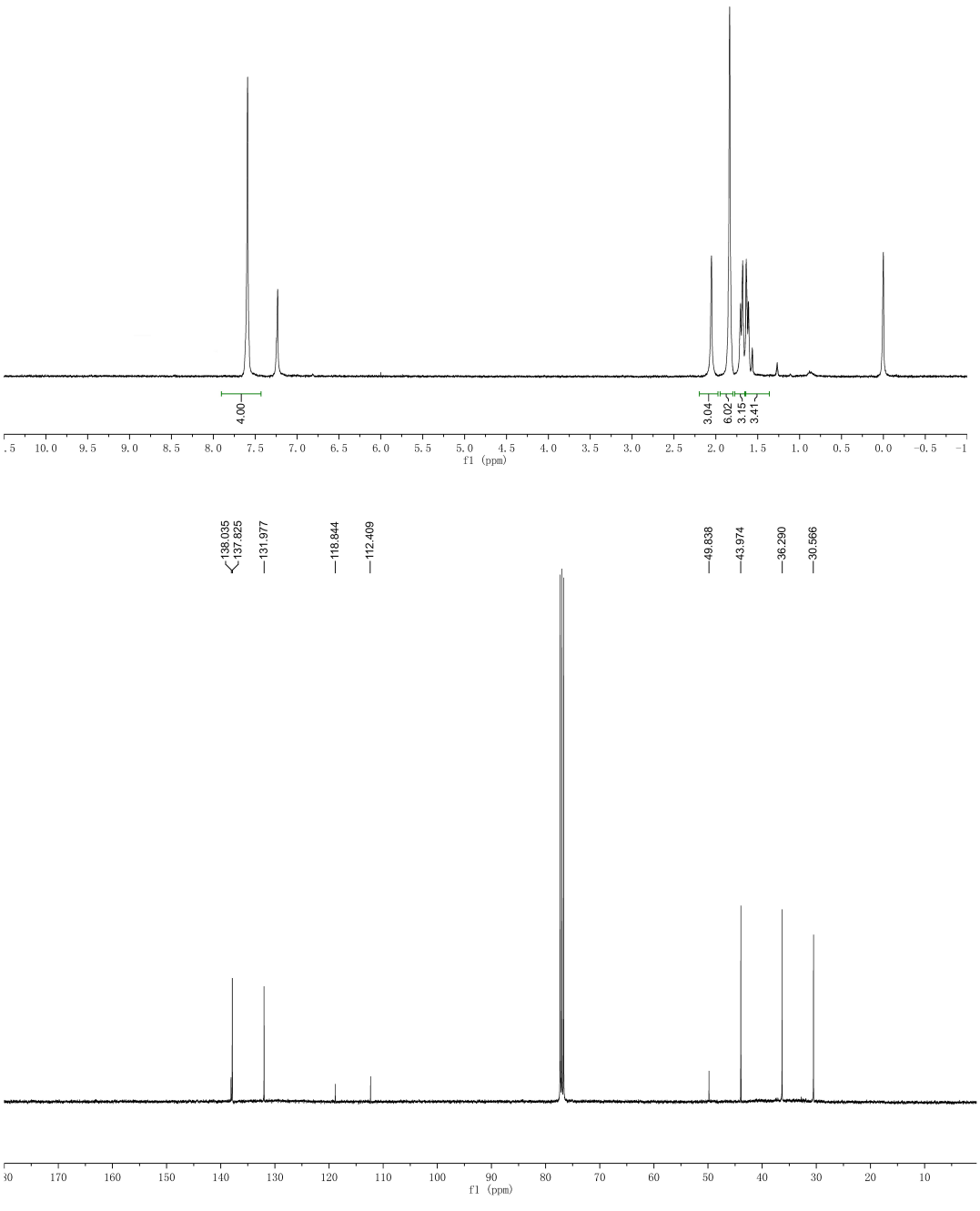
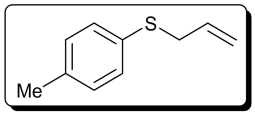


Figure S33. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5n in $CDCl_3$

Allyl *p*-tolyl sulfide (5o)



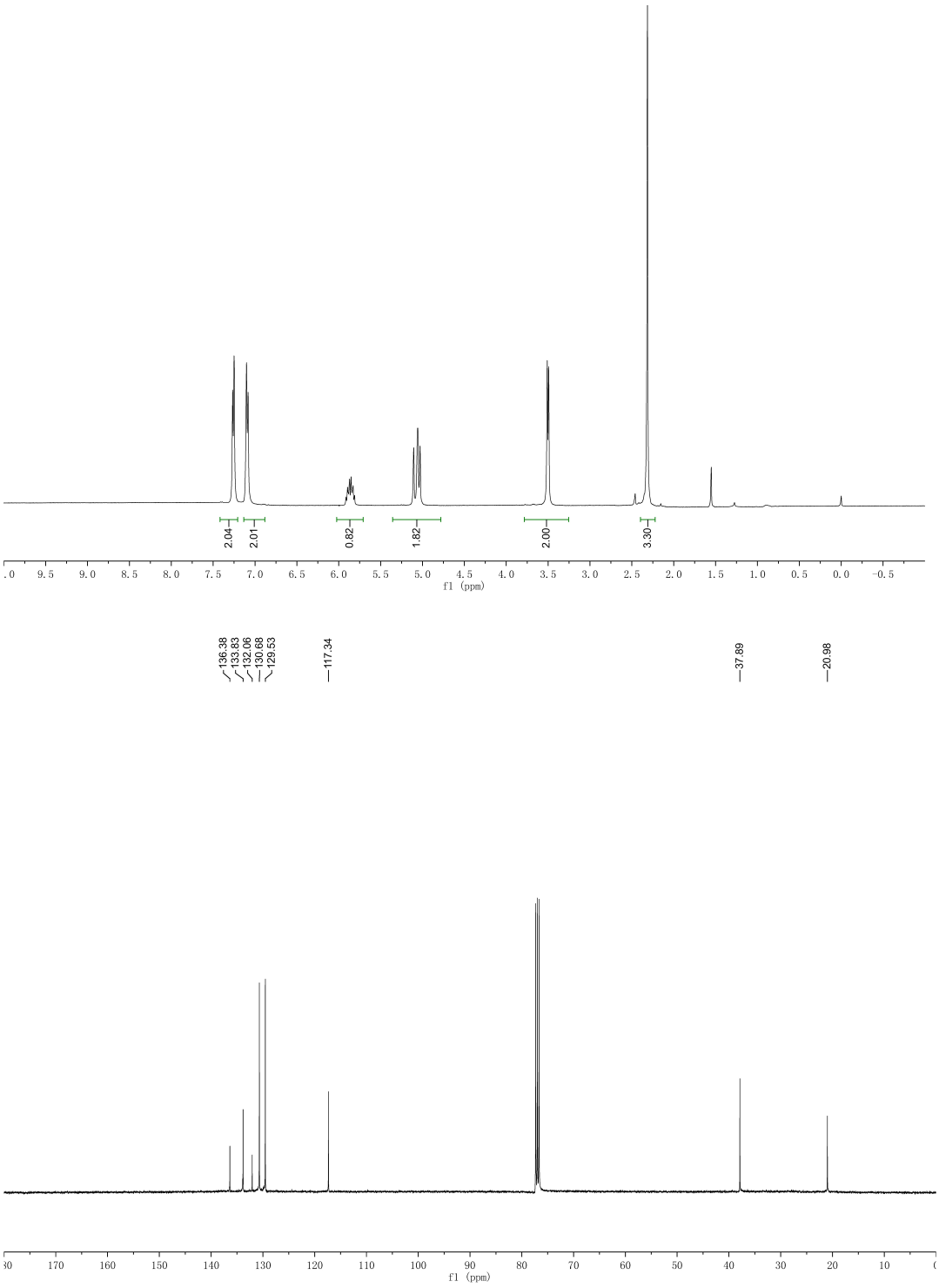
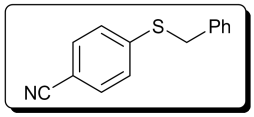


Figure S34. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5o in $CDCl_3$

4-(Benzylthio)benzonitrile (5p)



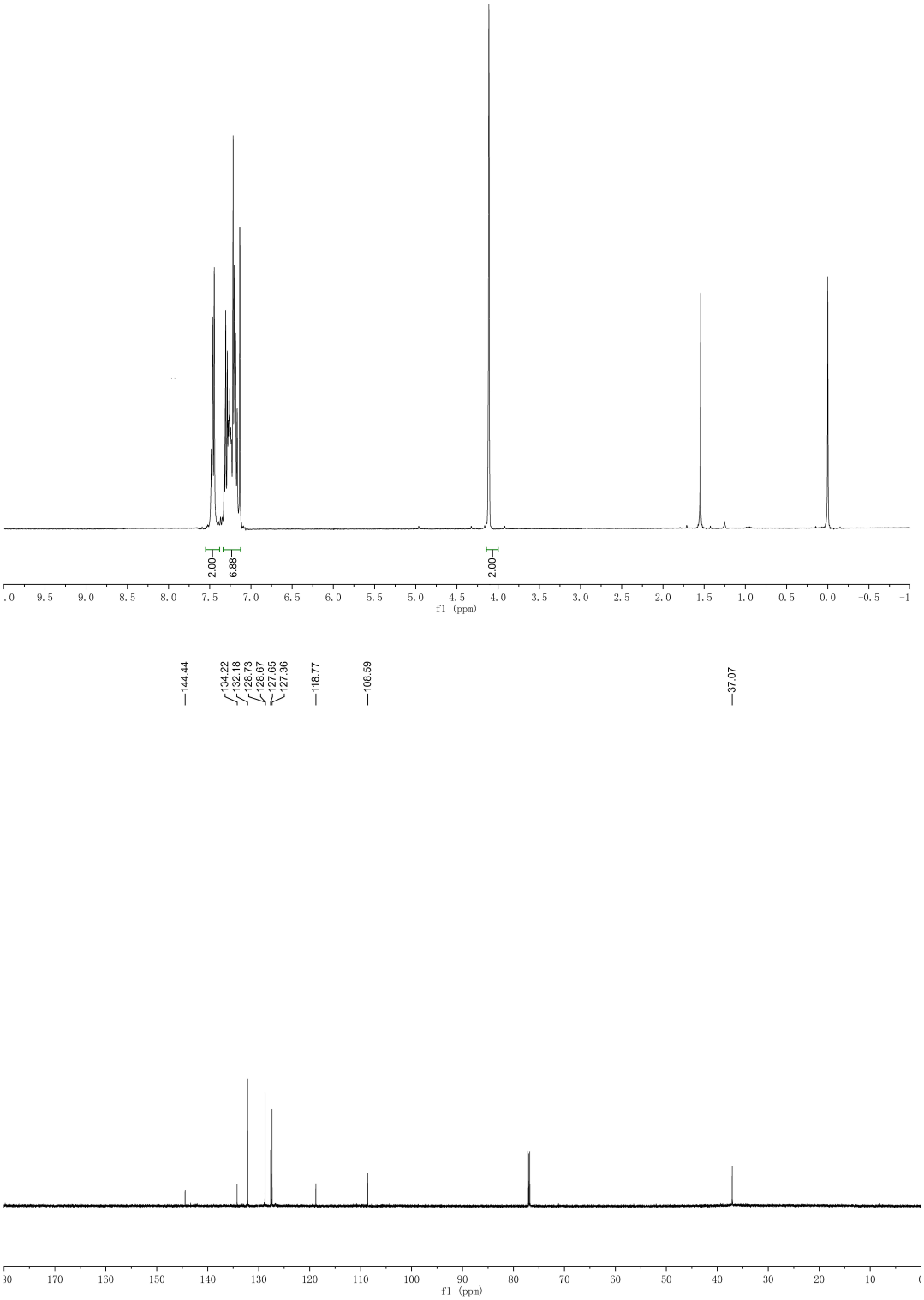
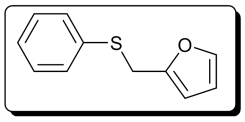


Figure S35. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5p in $CDCl_3$

2-(Phenylthio)methyl)furan (5q)



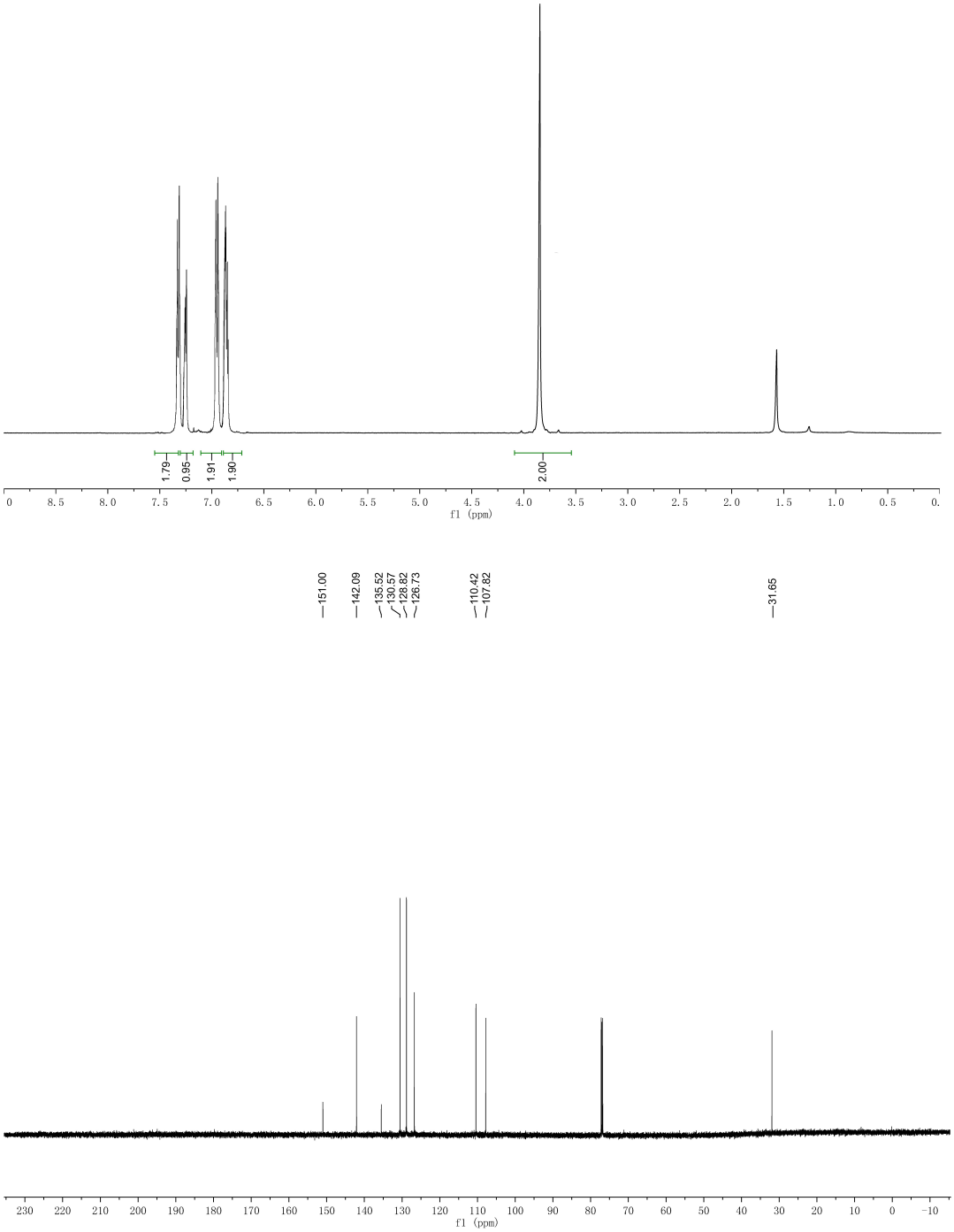
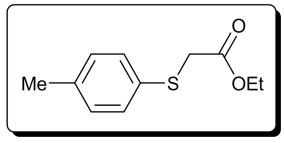


Figure S36. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5q in $CDCl_3$

Ethyl 2-(*p*-tolylthio)acetate (5r)



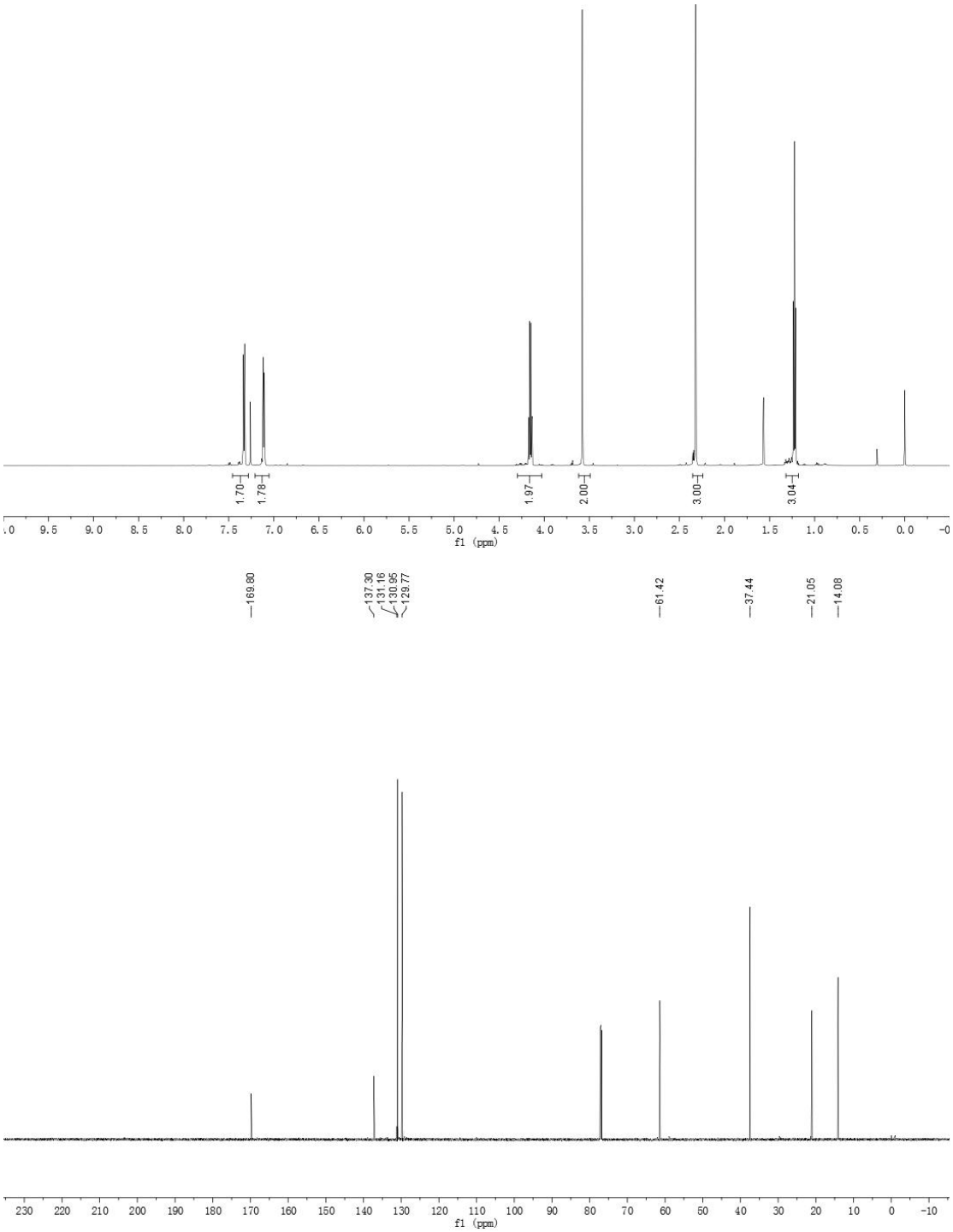
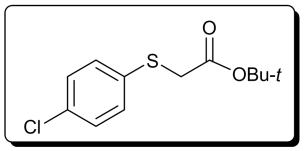


Figure S37. ^{1}H (600 MHz) and ^{13}C {^{1}H} (150 MHz) NMR spectra of 5r in $CDCl_3$

***tert*-Butyl 2-((4-chlorophenyl)thio)acetate (5s)**



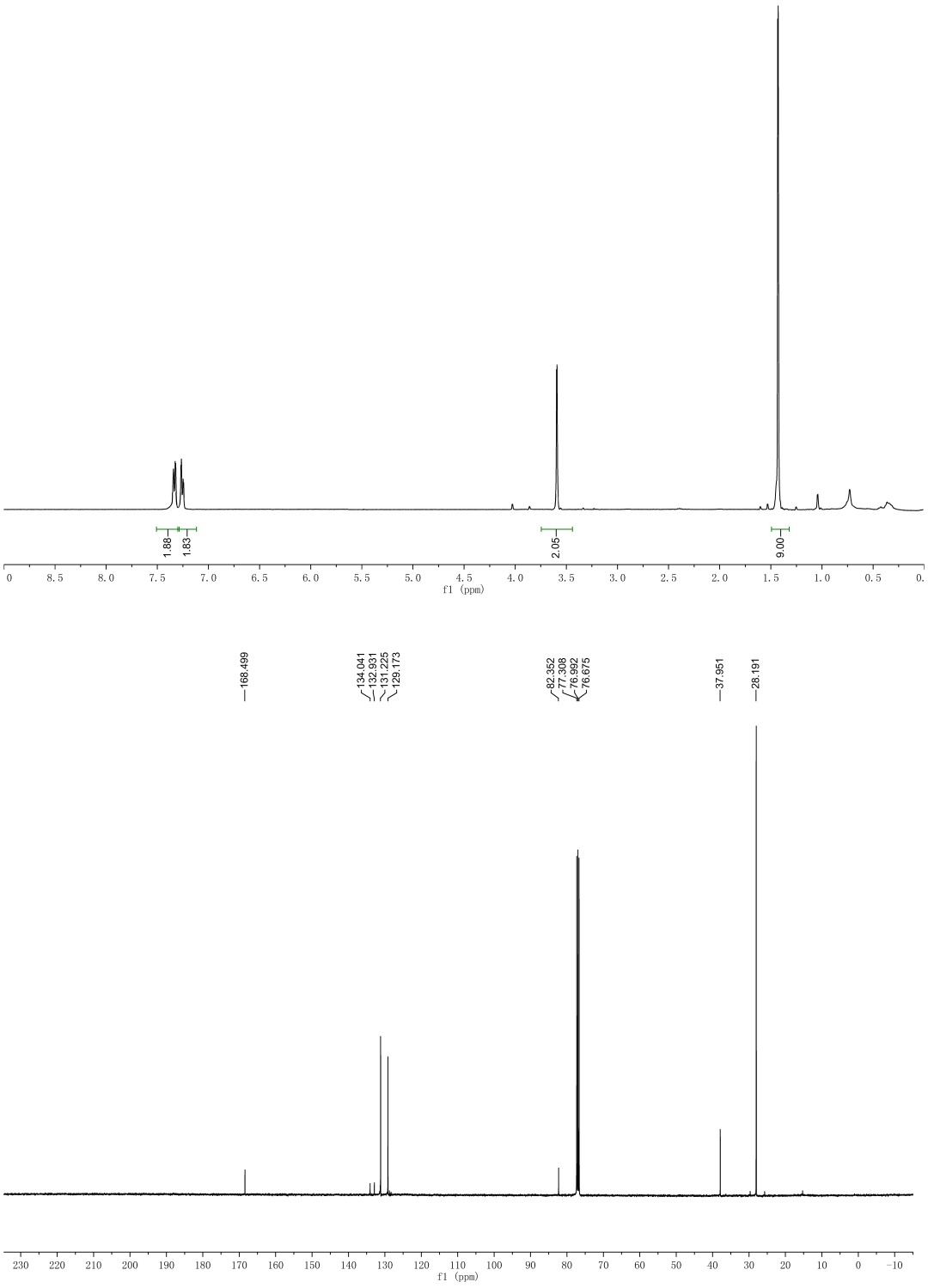
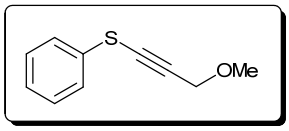


Figure S38. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5s in $CDCl_3$

3-Methoxyprop-1-ynyl phenyl sulfide (5t)



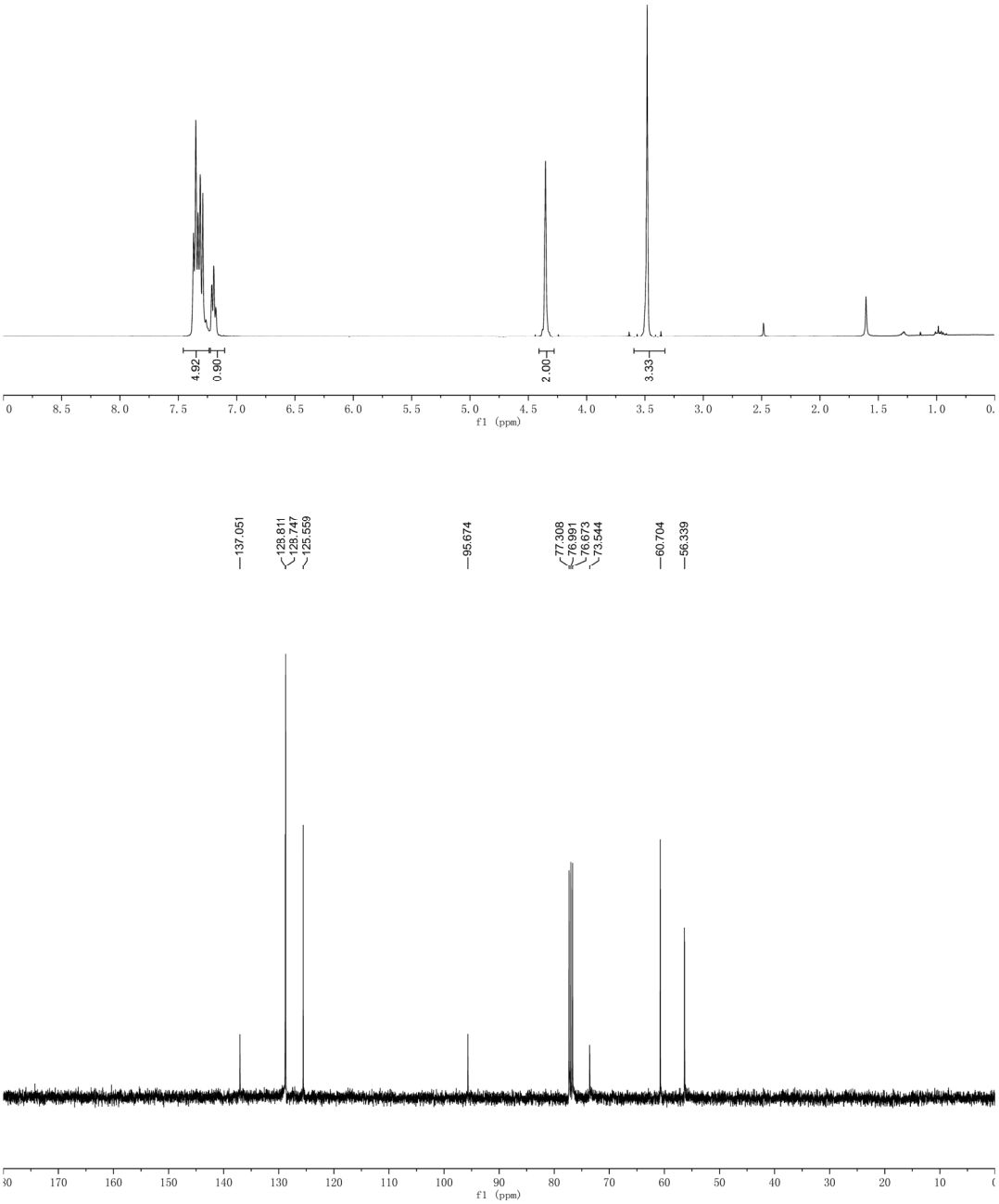
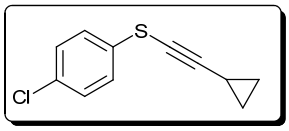


Figure S39. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5t in $CDCl_3$

Cyclopropylethynyl 4-chlorophenyl sulfide (5u)



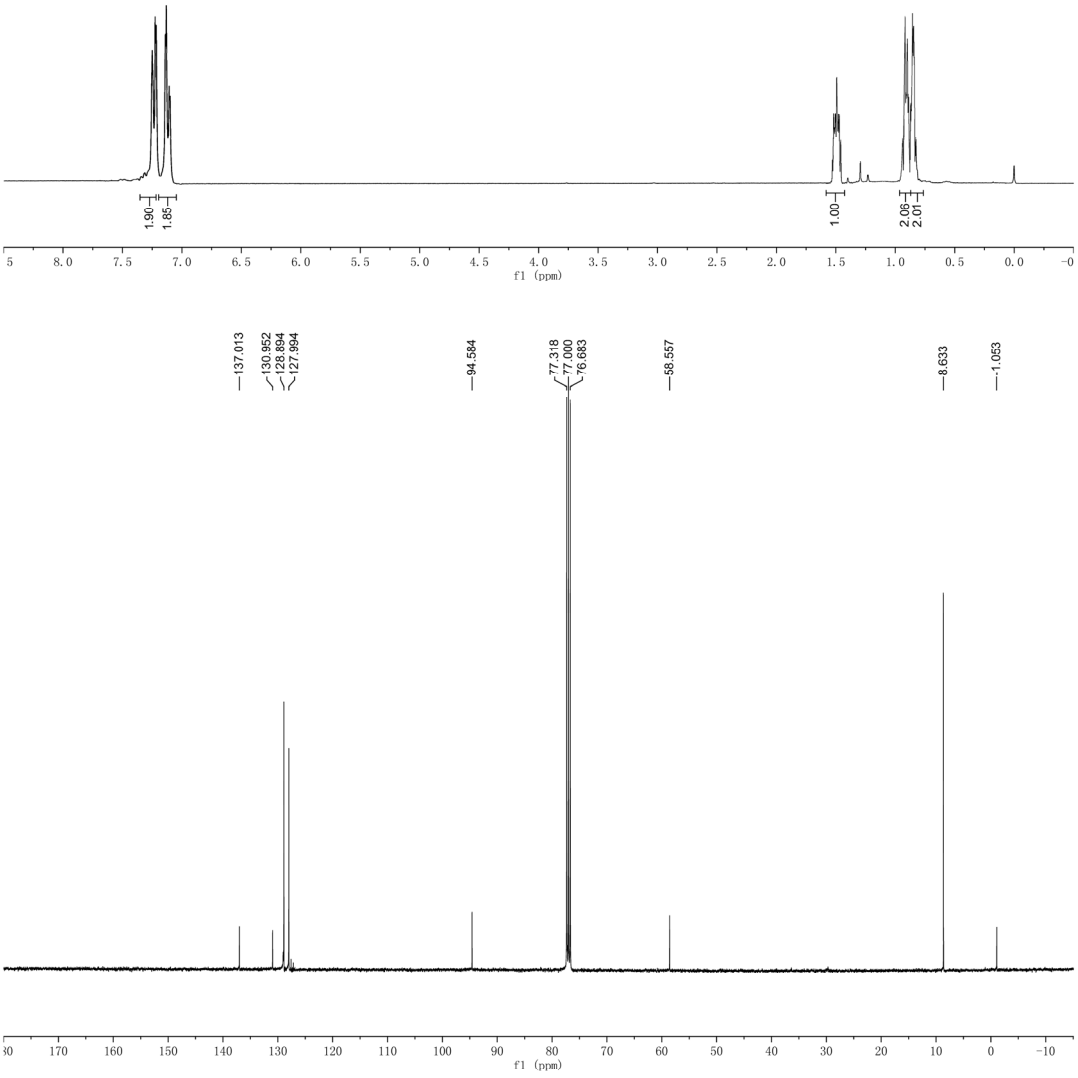


Figure S40. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 5u in $CDCl_3$

4-Methoxyphenyl 4-(trifluoromethyl)phenyl sulfide (7a)

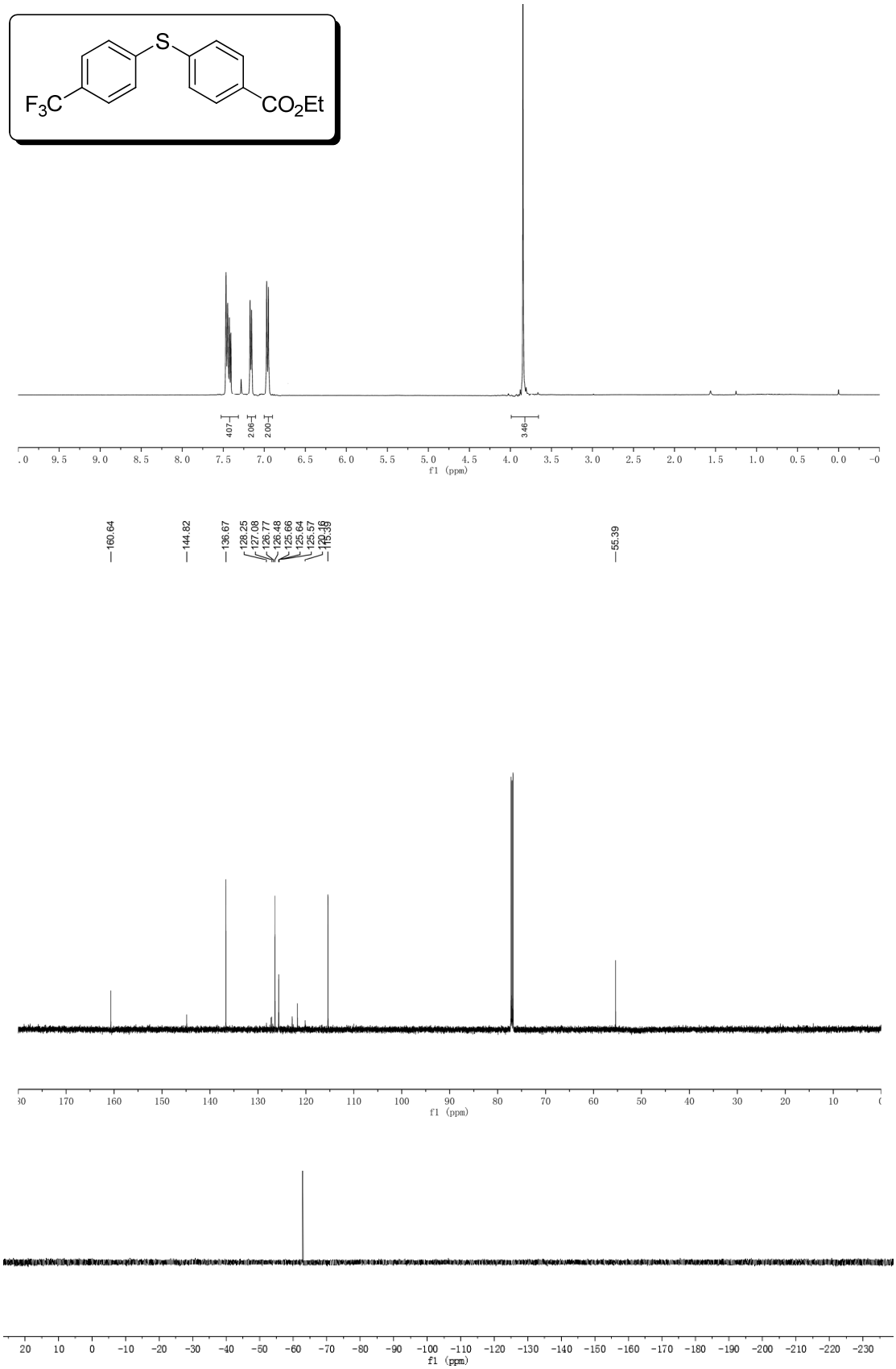
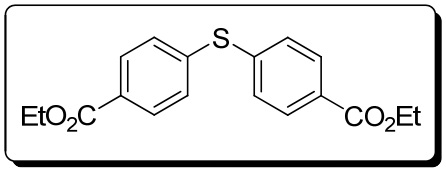


Figure S41. ^{1}H (400 MHz), ^{13}C {^{1}H} (100 MHz) and 19F (375 MHz) NMR spectra of 7a in $CDCl_3$

Di(4-methylcorboxylphenyl) sulfide (7b)



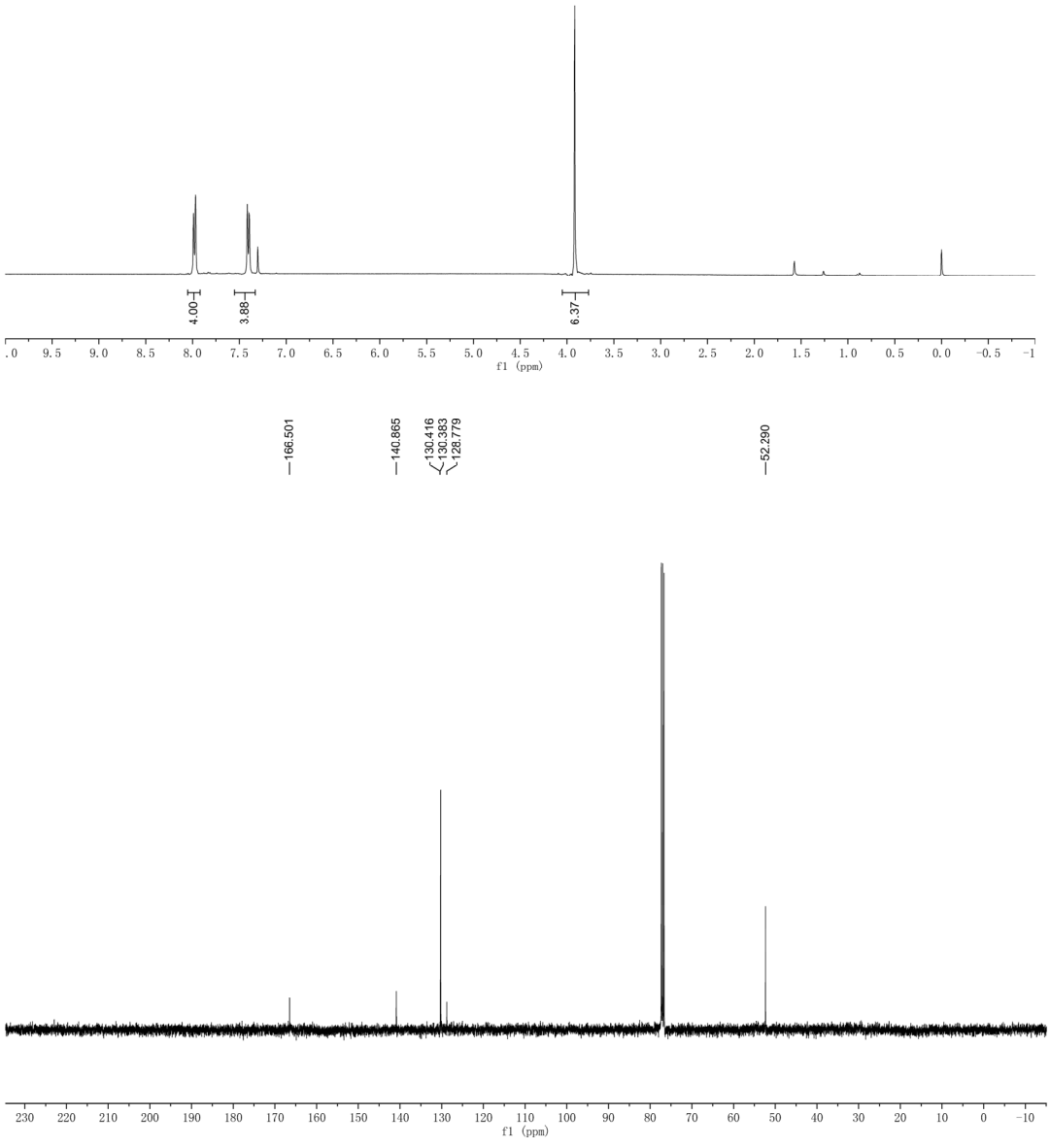
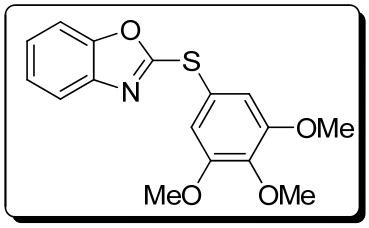


Figure S42. ^{1}H (400 MHz) and ^{13}C {^{1}H} (100 MHz) NMR spectra of 7b in $CDCl_3$

2-(3,4,5-Trimethoxyphenylthio)benzoxazole (9)



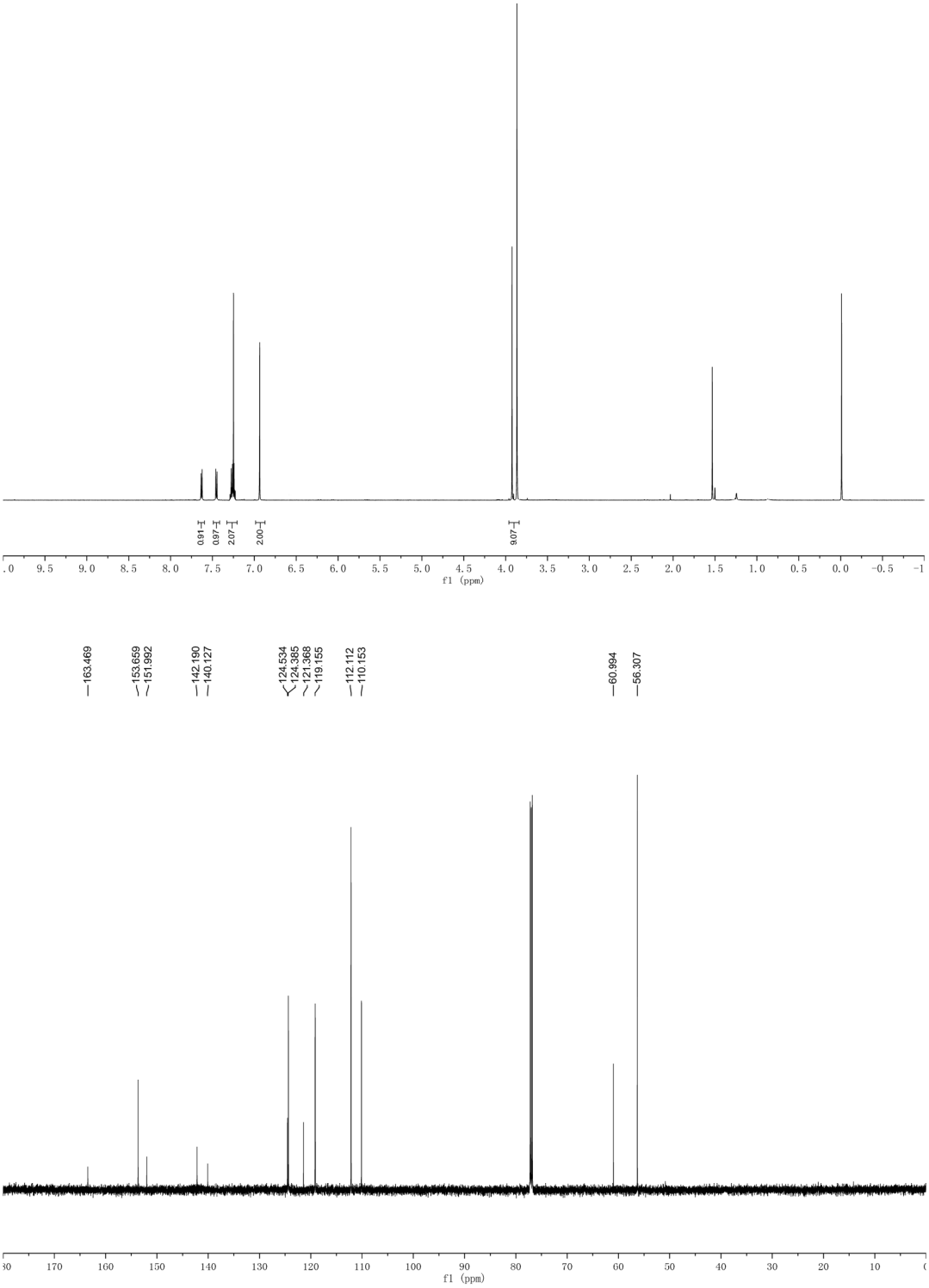


Figure S43. ^{1}H (600 MHz) and ^{13}C {^{1}H} (150 MHz) NMR spectra of 9 in $CDCl_3$