Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2016

Metal-Free O-H/C-H Difunctionalization of Phenols by *o*-Hydroxyarylsulfonium Salts in Water

Dengfeng Chen, Qingyuan Feng, Yunqin Yang, Xumin Cai, Fei Wang, and Shenlin Huang*

College of Chemical Engineering, Jiangsu Key Lab of Biomass-Based Green Fuels and Chemicals, Nanjing Forestry University, Nanjing, 210037, P. R. China

Email: shuang@njfu.edu.cn

Supporting Information

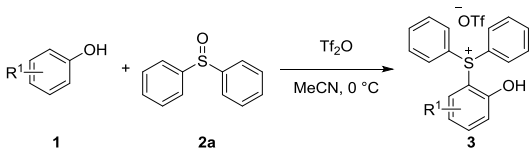
Table of Contents

I.	General Information	S2
II.	General procedure A for the preparation of sulfonium salts	S2
III.	General procedure B for rearrangement of sulfonium salts	S6
IV.	Procedure C for one-pot oxidation to sulfoxide in water	S20
V.	Procedure D for one-pot oxidation to sulfone in water	S21
VI.	Crossover experiment	S22
VII.	Recycle Study and E Factor Calculation	S23
VIII.	Reference for Sulfoxide Synthesis and compound data from Literature	S24
IX.	^{1}H and ^{13}C NMR Spectral data	S25

I. General Information

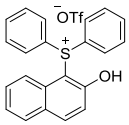
Unless otherwise stated, all glassware was oven dried and all reactions were carried out under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise indicated. A 2 wt% TPGS-750-M/H_2O solution was prepared by dissolving TPGS-750-M in water (degassed with argon prior to mixing, HPLC grade), followed by degassing with argon. TPGS-750-M was made as previously described.[1] Sulfoxides were prepared according to the procedures reported in the literature.[2, 3] Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent and High Performance Liquid Chromatography (HPLC) with UV detection at 254 nm. For HPLC yields, UV response factors relative to an internal standard (nitrobenzene). Flash column chromatography was performed using silica gel 60 (230-400 mesh). High resolution mass spectra were acquired by Agilent 6500 QTOFMS (ESI) or Waters GCT Premier TOFMS (EI). All ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker DRX-600 or AMX-400 instruments. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 (^{1}H NMR), defined at δ = 77.16 (^{13}C NMR). Coupling constants were quoted in Hz (J). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

II. General Procedure A for the Preparation of Sulfonium Salts



An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf_2O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel with EtOAc to afford desired sulfonium salts.

(2-Hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3a)



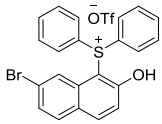
Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3a** (91 mg, 0.19 mmol, 95%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.37 (br s, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.65 (m, 8H), 7.65 – 7.58 (m, 4H), 7.54 – 7.48 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 139.4, 133.9, 131.1, 130.3, 130.3, 129.9, 129.0, 125.2, 123.9, 120.5, 120.3, 96.5.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{22}H_{17}OS$ 329.0995, found 329.0985.

(7-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3b)



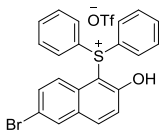
Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 7-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3b** (102.6 mg, 0.185 mmol, 92%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (br s, 1H), 8.47 (s, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.74 – 7.68 (m, 7H), 7.66 – 7.58 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 139.3, 135.2, 134.1, 131.4, 131.2, 130.4, 128.7, 127.4, 125.2, 123.4, 122.9, 120.8, 95.4.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{22}H_{16}BrOS$ 407.0100, found 407.0083.

(6-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3c)



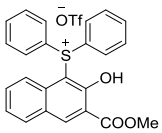
Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 6-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3c** (100.3 mg, 0.18 mmol, 90%) as a purple oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (br s, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.77 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.73 – 7.68 (m, 7H), 7.65 – 7.59 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.2, 134.1, 133.4, 132.6, 131.8, 131.2, 130.3, 130.0, 123.5, 122.3, 121.7, 118.8, 96.8.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{22}H_{16}BrOS$ 407.0100, found 407.0085.

(2-Hydroxy-3-(methoxycarbonyl)naphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3d)



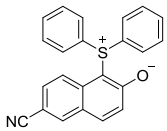
Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and methyl-3-hydroxy-2-naphthoate (40.5 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3d** (93 mg, 0.174 mmol, 87%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.37 (br s, 1H), 8.99 (s, 1H), 8.77 – 8.59 (m, 1H), 8.06 (d, J = 7.3 Hz, 1H), 8.01 – 7.92 (m, 1H), 7.87 – 7.53 (m, 11H), 4.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 160.3, 142.1, 136.6, 134.4, 134.1, 131.8, 131.6, 131.2, 131.1, 130.7, 127.5, 126.9, 123.1, 122.0, 114.7, 100.4, 54.1.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{24}H_{19}O_3S$ 387.1049, found 387.1035.

6-Cyano-1-(diphenylsulfonio)naphthalen-2-olate (3e)



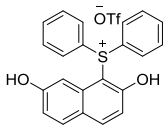
Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 6-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3e** (63.6 mg, 0.18 mmol, 90%) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 8.7 Hz, 1H), 8.26 (s, 1H), 8.17 (d, J = 9.1 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.77 – 7.70 (m, 7H), 7.63 (t, J = 7.7 Hz, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.75, 139.28, 136.06, 135.13, 134.25, 131.30, 131.04, 130.40, 127.89, 123.20, 122.35, 122.19, 121.47, 119.35, 118.19, 108.77, 97.62.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{23}H_{16}NOS$ 354.0947, found 354.0935.

(2,7-Dihydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3f)



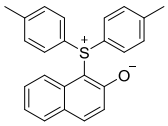
Following the general procedure **A**, diphenyl sulfoxide (44.5 mmol, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and naphthalene-2,7-diol (32.1 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3f** (80.1 mg, 0.162 mmol, 81%) as a red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.93 (s, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 4H), 7.53 (t, *J* = 7.3 Hz, 3H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.96 (d, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 159.3, 138.7, 136.3, 133.5, 131.3, 130.8, 130.5, 124.5, 123.5, 117.5, 115.8, 104.1, 95.9.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{22}H_{17}O_2S$ 345.0944, found 345.0932.

1-(Di-p-tolylsulfonio)naphthalen-2-olate (3g)



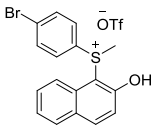
Following the general procedure **A**, 4,4'-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3g** (64.1 mg, 0.18 mmol, 90%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.63 – 7.57 (m, 4H), 7.53 – 7.44 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 4H), 2.44 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 138.8, 134.1, 131.7, 130.2, 129.9, 129.8, 128.6, 124.7, 122.2, 120.8, 120.8, 120.4, 119.0, 96.7, 21.7.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{24}H_{21}OS$ 357.1308, found 357.1298.

(4-Bromophenyl)(2-hydroxynaphthalen-1-yl)(methyl)sulfonium trifluoromethanesulfonate (3h)



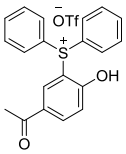
Following the general procedure **A**, 1-bromo-4-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3h** (92.1 mg, 0.186 mmol, 93%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (br s, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.61 (m, 5H), 7.54 (d, *J* = 9.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 138.9, 134.1, 133.5, 130.4, 130.3, 129.70, 128.8, 128.7, 125.4, 124.6, 122.1, 121.0, 119.6, 118.9, 97.0, 26.4.

HRMS-ESI (m/z) $[M-OTf]^+$ calculated for $C_{17}H_{14}BrOS$ 344.9943, found 344.9930.

(5-Acetyl-2-hydroxyphenyl)diphenylsulfonium trifluoromethanesulfonate (3i)



Following the general procedure **A**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 1-(4-hydroxycyclohexa-2,4-dien-1-yl)ethan-1-one (27.6 mg, 0.2 mmol) were

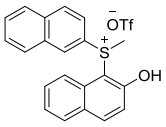
used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3i** (24.4 mg, 0.052 mmol, 26%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.75 – 7.68 (m, 4H), 7.64 – 7.55 (m, 6H), 2.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 161.6, 137.4, 135.0, 131.9, 130.9, 130.8, 122.9, 119.1, 110.2, 77.5, 77.2, 76.8, 26.4.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{20}H_{17}O_2S$ 321.0944, found 321.0932.

(2-Hydroxynaphthalen-1-yl)(methyl)(naphthalen-2-yl)sulfonium trifluoromethanesulfon-ate (3j)



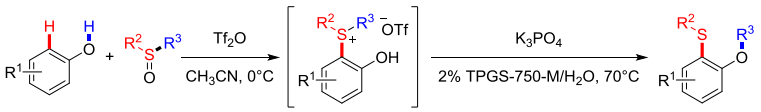
Following the general procedure **A**, 2-(methylsulfinyl)naphthalene (41.9 mg, 0.22 mmol), Tf_2O (40.8 µL, 0.24 mmol) and 2-naphthol (28.9 mg, 0.2 mmol) were used. The crude mixture was purified by flash column chromatography (100% ethyl acetate) to give **3j** (88.6 mg, 0.19 mmol, 95%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (br s, 1H), 8.35 (d, *J* = 1.8 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 9.1 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.76 – 7.66 (m, 2H), 7.63 – 7.52 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 138.6, 134.8, 133.5, 133.0, 131.5, 130.6, 130.2, 129.8, 129.7, 123.0, 128.8, 128.5, 128.1, 125.2, 123.0, 122.2, 121.0, 119.8, 97.5, 26.4.

HRMS-ESI (m/z) $[M\text{-}OTf]^+$ calculated for $C_{21}H_{17}OS$ 317.0995, found 317.0993.

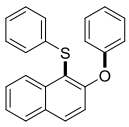
III. General Procedure B for rearrangement of sulfonium salts



An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf_2O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated *in vacuo*. K_3PO_4 (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H_2O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was allowed to cool to room temperature and extracted with EtOAc (1 mL x 3), dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude

mixture was purified by flash column chromatography (100% petroleum ether to 10% EtOAc/petroleum ether) to afford desired products.

(2-Phenoxynaphthalen-1-yl)(phenyl)sulfane (4aa)



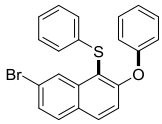
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4aa** (57 mg, 0.172 mmol, 86%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.57 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.23 (d, J = 8.9 Hz, 1H), 7.19 – 7.03 (m, 5H), 6.94 – 6.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 156.8, 137.8, 136.2, 131.9, 131.3, 129.8, 128.9, 128.5, 127.9, 127.5, 126.2, 125.5, 125.4, 123.3, 120.1, 119.0, 118.4.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{22}H_{16}OS$ 328.0922, found 328.0910.

(7-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ba)



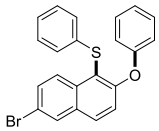
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 7-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ba** (66.9 mg, 0.164 mmol, 82%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.55 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.03 (m, 7H), 6.87 (dd, *J* = 8.6, 0.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 157.0, 137.7, 137.2, 131.7, 130.1, 129.9, 129.5, 129.0, 128.9, 128.4, 127.8, 125.8, 123.7, 122.8, 112.0, 118.8, 118.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{22}H_{15}BrOS$ 406.0027, found 406.0029.

(6-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ca)



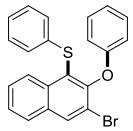
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 6-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ca** (61.3 mg, 0.15 mmol, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.1 Hz, 1H), 8.01 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.19 – 7.04 (m, 6H), 6.88 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 157.1, 137.4, 134.8, 132.2, 131.1, 130.8, 130.4, 129.9, 129.0, 128.2, 127.6, 125.7, 123.6, 120.9, 119.5, 119.3, 118.6.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{22}H_{15}BrOS$ 406.0027, found 406.0001.

(3-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4da)



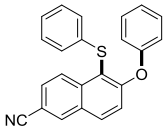
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3-bromonaphthalen-2-ol (44.6 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4da** (59.5 mg, 0.146 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.45 (m, 1H), 8.29 (s, 1H), 7.88 – 7.80 (m, 1H), 7.61 – 7.51 (m, 2H), 7.26 – 7.21 (m, 2H), 7.17 – 6.99 (m, 6H), 6.74 (dd, *J* = 8.7, 0.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 150.8, 136.8, 135.1, 134.9, 132.8, 129.6, 129.0, 128.1, 128.0, 127.7, 127.0, 126.8, 125.9, 125.4, 122.2, 117.4, 115.4.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{22}H_{15}BrOS$ 406.0027, found 406.0028.

6-Phenoxy-5-(phenylthio)-2-naphthonitrile (4ea)



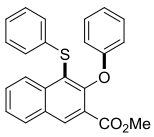
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 6-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ea** (57.3 mg, 0.162 mmol, 81%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.8 Hz, 1H), 8.22 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.04 (m, 6H), 6.90 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 156.4, 138.0, 136.9, 134.4, 132.1, 130.1, 129.8, 129.1, 128.4, 127.8, 127.5, 126.0, 124.4, 120.8, 119.3, 119.1, 119.0, 108.8.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{15}NOS$ 353.0874, found 353.0880.

Methyl 3-phenoxy-4-(phenylthio)-2-naphthoate (4fa)



Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), methyl 3-hydroxy-2-naphthoate (40.4 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4fa** (38.6 mg, 0.1 mmol, 50%) as a white solid and the hydrolysis product **4fa'** (25.3 mg, 34%) as a pale yellow solid.

4fa:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.02 (m, 5H), 6.99 – 6.93 (m, 1H), 6.73 (dd, *J* = 8.7, 0.9 Hz, 2H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.2, 152.9, 137.7, 137.0, 135.5, 130.9, 129.8, 129.7, 129.5, 128.9, 127.9, 126.8, 126.7, 125.7, 125.1, 125.0, 121.8, 115.4, 52.5.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{24}H_{18}NaO_3S$ 409.0869, found 409.0851.

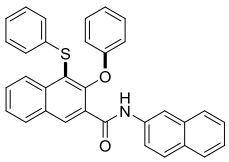
4fa':

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.99 (dd, *J* = 15.3, 7.6 Hz, 3H), 6.73 (d, *J* = 8.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 158.7, 153.0, 138.4, 137.0, 136.7, 131.0, 130.4, 130.1, 129.6, 129.0, 127.8, 127.1, 126.7, 125.9, 125.3, 123.3, 122.5, 115.7.

HRMS-ESI (m/z) $[M-H]^-$ calculated for $C_{23}H_{15}O_3S$ 371.0747, found 371.0738.

N-(Naphthalen-2-yl)-3-phenoxy-4-(phenylthio)-2-naphthamide (4ga)



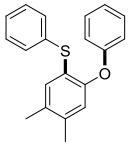
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3-hydroxy-N-(naphthalen-2-yl)-2-naphthamide (62.7 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ga** (15 mg, 0.03 mmol, 15%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 9.02 (s, 1H), 8.52 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.65 (dtd, *J* = 14.6, 6.9, 1.3 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.32 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.18 – 7.08 (m, 3H), 7.05 – 6.97 (m, 3H), 6.84 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 157.9, 151.4, 137.8, 136.9, 136.2, 135.4, 134.0, 131.7, 131.0, 130.20, 130.16, 129.9, 129.1, 128.9, 127.9, 127.7, 127.6, 127.4, 127.2, 126.6, 125.9, 125.3, 124.7, 123.3, 120.3, 117.4, 115.5.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{33}H_{23}NO_2S$ 497.1449, found 497.1455.

(4,5-Dimethyl-2-phenoxyphenyl)(phenyl)sulfane (4ha)



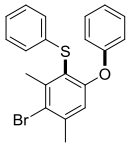
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3,4-dimethylphenol (24.5 mmol, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ha** (36.8 mg, 60%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (s, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 2.21 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.6, 138.3, 136.0, 134.8, 133.1, 130.5, 129.7, 129.1, 126.7, 123.5, 122.8, 121.5, 117.9, 19.8, 19.2.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{20}H_{18}OS$ 306.1078, found 306.1094.

(3-Bromo-2,4-dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ia)



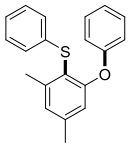
Following the general procedure **B**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 4-bromo-3,5-dimethylphenol (40.2 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ia** (58.6 mg, 0.12 mmol, 60%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 2.68 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 157.2, 144.6, 141.3, 137.6, 129.8, 129.0, 127.2, 125.5, 123.4, 122.8, 122.6, 119.3, 118.6, 24.7, 23.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{20}H_{17}BrOS$ 384.0183, found 384.0185.

(2,4-Dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ja)



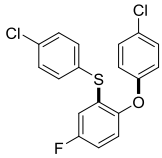
Following the general procedure **2**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 3,5-dimethylphenol (24.5 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ja** (41.7 mg, 0.136 mmol, 68%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.09 – 7.03 (m, 4H), 6.95 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 2.44 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 157.6, 145.05, 140.9, 138.1, 129.7, 128.8, 126.93, 126.89, 125.1, 123.1, 120.1, 118.7, 118.1, 21.5, 21.4.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{20}H_{18}OS$ 306.1078, found 306.1069.

(2-(4-Chlorophenoxy)-5-fluorophenyl)(4-chlorophenyl)sulfane (4kb)



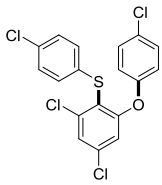
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-fluorophenol (22.5 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4kb** (25.6 mg, 0.07 mmol, 35%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 6.93 – 6.86 (m, 2H), 6.85 – 6.83 (m, 1H), 6.83 – 6.81 (m, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ159.6 (d, *J* = 245.7 Hz), 156.2, 149.2 (d, *J* = 2.8 Hz), 135.1, 135.0, 131.9 (d, *J* = 8.1 Hz), 130.6, 130.0, 129.9, 128.3, 121.5 (d, *J* = 8.7 Hz), 118.7, 116.9 (d, *J* = 25.8 Hz), 114.6 (d, *J* = 23.5 Hz).

HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{11}Cl_2FOS$ 363.9892, found 363.9884.

(4-Chlorophenyl)(2,4-dichloro-6-(4-chlorophenoxy)phenyl)sulfane (4lb)



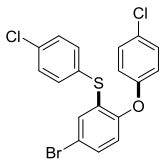
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 3,5-dichlorophenol (32.6 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4lb** (25 mg, 0.06 mmol, 30%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 3H), 7.22 – 7.16 (m, 2H), 7.14 – 7.09 (m, 2H), 6.79 – 6.71 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 154.3, 141.7, 136.6, 134.2, 132.6, 130.3, 130.1, 130.0, 129.2, 125.4, 122.8, 120.5, 117.7.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{10}Cl_4OS$ 415.9177, found 415.9165.

(5-Bromo-2-(4-chlorophenoxy)phenyl)(4-chlorophenyl)sulfane (4mb)



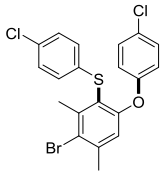
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-bromophenol (34.6 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4mb** (28.1 mg, 33%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 3H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.77 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 153.2, 134.8, 134.4, 133.4, 131.2, 131.1, 131.0, 130.0, 129.9, 128.9, 121.1, 119.5, 117.4.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{11}BrCl_2OS$ 423.9091, found 423.9083.

(3-Bromo-6-(4-chlorophenoxy)-2,4-dimethylphenyl)(4-chlorophenyl)sulfane (4ib)



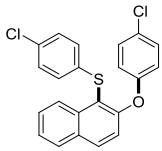
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 4-bromo-3,5-dimethylphenol (40.2mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ib** (70 mg, 0.154 mmol, 77%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.00 – 6.93 (m, 2H), 6.76 (s, 1H), 6.75 – 6.70 (m, 2H), 2.67 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 155.8, 144.7, 141.8, 135.9, 131.6, 129.8, 129.1, 128.5, 123.4, 122.5, 119.7, 119.5, 100.1, 24.7, 23.05.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{20}H_{15}BrCl_2OS$ 451.9404, found 451.9415.

(2-(4-Chlorophenoxy)naphthalen-1-yl)(4-chlorophenyl)sulfane (4ab)



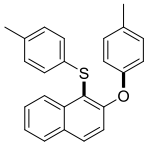
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford 4ab (58 mg, 0.146 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.59 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.51 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.13 – 7.07 (m, 2H), 7.05 – 6.97 (m, 2H), 6.83 – 6.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 156.2, 136.1, 136.0, 132.4, 131.50, 131.47, 129.8, 129.0, 128.9, 128.7, 128.4, 128.2, 126.0, 125.9, 120.1, 119.3, 119.2.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{22}H_{14}Cl_2OS$ 396.0142, found 396.0156.

p-Tolyl(2-(p-tolyloxy)naphthalen-1-yl)sulfane (4ac)



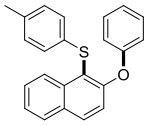
Following the general procedure **B**, 4,4'-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ac** (48.5 mg, 0.136 mmol, 68%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.5 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.56 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.47 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.13 – 7.03 (m, 4H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.85 – 6.76 (m, 2H), 2.32 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.3, 136.2, 135.3, 134.3, 132.8, 131.6, 131.1, 130.3, 129.7, 128.5, 127.9, 127.8, 126.2, 125.3, 119.8, 119.1, 118.5, 21.0, 20.8.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{24}H_{20}OS$ 356.1235, found 356.1236.

(2-Phenoxynaphthalen-1-yl)(p-tolyl)sulfane (4ad)



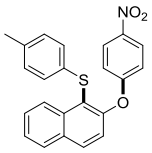
Following the general procedure **B**, 1-methyl-4-(phenylsulfinyl)benzene (47.6 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ad** (49.5 mg, 0.144 mmol, 72%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.09 – 7.03 (m, 3H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 156.6, 136.2, 135.4, 134.1, 131.7, 131.3, 129.8, 129.7, 128.5, 128.0, 127.8, 126.3, 125.5, 123.2, 120.2, 119.9, 118.3, 21.0.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{18}OS$ 342.1078, found 342.1071.

(2-(4-Nitrophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ae)



Following the general procedure **B**, 1-methyl-4-((4-nitrophenyl)sulfinyl)benzene (57.5 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ae** (50.4 mg, 0.13 mmol, 65%) as a pale yellow oil.

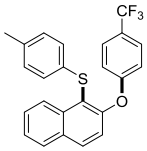
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.29

(d, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 154.1, 142.6, 136.13, 136.10, 133.1, 132.24, 132.23, 129.8, 128.7, 128.5, 128.2, 126.6, 126.5, 125.9, 122.8, 121.2, 116.6, 21.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{17}NO_3S$ 387.0929, found 387.0920.

p-Tolyl(2-(4-(trifluoromethyl)phenoxy)naphthalen-1-yl)sulfane (4af)



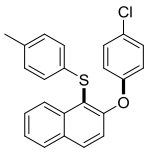
Following the general procedure **B**, 1-methyl-4-((4-(trifluoromethyl)phenyl)sulfinyl)benzene (62.6 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4af** (67.3 mg, 0.164 mmol, 82%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.94 – 6.89 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.0, 136.2, 135.9, 133.5, 132.0, 131.9, 129.7, 128.6, 128.5, 128.0, 127.05 (q, *J* = 3.7 Hz), 126.5, 126.1, 124.7 (q, *J* = 32.7 Hz), 124.4 (q, *J* = 271.3 Hz), 122.1, 121.0, 117.1, 21.0.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{24}H_{17}F_3OS$ 410.0952, found 410.0943.

(2-(4-Chlorophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ag)



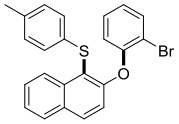
Following the general procedure **B**, 1-chloro-4-(p-tolylsulfinyl)benzene (55.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ag** (45.2 mg, 0.12 mmol, 60%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.53 – 7.47 (m, 1H), 7.23 – 7.17 (m, 3H), 7.04 – 6.99 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.81 – 6.74 (m, 2H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 156.0, 136.2, 135.6, 133.9, 131.8, 131.6, 129.71, 129.67, 128.5, 128.2, 128.0, 127.9, 126.4, 125.7, 120.7, 120.3, 119.2, 21.0.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{17}ClOS$ 376.0689, found 376.0665.

(2-(2-Bromophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ah)



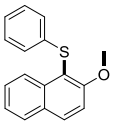
Following the general procedure **B**, 1-bromo-2-(p-tolylsulfinyl)benzene (65.0 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ah** (67.4 mg, 0.16 mmol, 80%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 9.2 Hz, 2H), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.18 – 7.08 (m, 4H), 7.00 – 6.92 (m, 3H), 6.68 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 154.1, 136.3, 135.5, 133.9, 133.8, 131.8, 131.4, 129.7, 128.61, 128.54, 128.51, 127.9, 126.4, 125.5, 124.7, 119.6, 119.5, 119.1, 114.3, 21.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{17}BrOS$ 420.0183, found 420.0195.

(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (4ai)



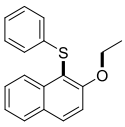
Following the general procedure **B**, (methylsulfinyl)benzene (30.8 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ai** (48 mg, 0.18 mmol, 90%) as a color-less oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.17 – 7.10 (m, 2H), 7.07 – 6.99 (m, 3H), 3.97 (s, 3H).

HRMS-EI (m/z) $[M]^+$ calculated for $C_{17}H_{14}OS$ 266.0765, found 266.0775.

Spectroscopic data matches that reported in the literature.[4]

(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (4aj)



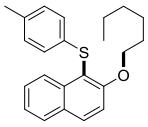
Following the general procedure **B**, (ethylsulfinyl)benzene (34.0 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4aj** (47.6 mg, 0.17 mmol, 85%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.51 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.11 – 7.02 (m, 3H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H).

HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{16}OS$ 280.0922, found 280.0933.

Spectroscopic data matches that reported in the literature.[4]

(2-(Hexyloxy)naphthalen-1-yl)(p-tolyl)sulfane (4ak)



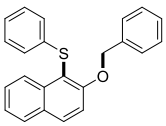
Following the general procedure **B**, 1-(hexylsulfinyl)-4-methylbenzene (49.4 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ak** (53.3 mg, 0.152 mmol, 76%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 2.23 (s, 3H), 1.74 – 1.65 (m, 2H), 1.37 – 1.29 (m, 2H), 1.29 – 1.21 (m, 4H), 0.86 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 136.6, 135.1, 134.7, 131.6, 129.6, 129.5, 128.3, 127.6, 127.1, 125.7, 124.1, 115.0, 114.8, 70.0, 31.7, 29.5, 25.6, 22.7, 21.0, 14.2.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{26}OS$ 350.1704, found 350.1694.

(2-(Benzyloxy)naphthalen-1-yl)(phenyl)sulfane (4al)



Following the general procedure **B**, (benzylsulfinyl)benzene (47.6 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4al** (49.5 mg, 0.144 mmol, 72%) as a colorless oil.

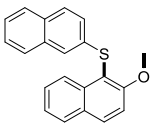
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.08 – 7.03 (m, 3H), 5.23 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 138.5, 136.9, 136.6, 131.8, 129.9, 128.8, 128.6, 128.4, 127.9, 127.8, 127.2, 126.8, 125.7, 125.0, 124.4, 115.3, 114.7, 71.5.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{23}H_{18}OS$ 342.1078, found 342.1094.

Spectroscopic data matches that reported in the literature.[2]

(2-Methoxynaphthalen-1-yl)(naphthalen-2-yl)sulfane (4am)



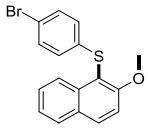
Following the general procedure **B**, 2-(methylsulfinyl)naphthalene (41.9 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4am** (55.7 mg, 0.176 mmol, 88%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.4, 3.4 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.21 (dd, *J* = 8.6, 1.6 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 136.5, 135.9, 133.9, 132.3, 131.4, 129.8, 128.5, 128.4, 128.0, 127.8, 127.0, 126.4, 125.6, 125.3, 125.1, 124.3, 124.0, 113.6, 113.0, 57.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{21}H_{16}OS$ 316.0922, found 316.0935.

(4-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4an)



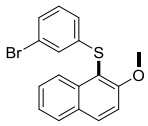
Following the general procedure **B**, 1-bromo-4-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4an** (47.7 mg, 0.138 mmol, 69%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.97 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 137.7, 136.2, 132.5, 131.8, 129.7, 128.5, 128.1, 128.0, 125.3, 124.4, 118.5, 113.5, 112.6, 57.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{17}H_{13}BrOS$ 343.9870, found 343.9874.

(3-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ao)



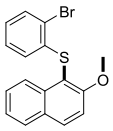
Following the general procedure **B**, 1-bromo-3-(methylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ao** (58 mg, 84%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.52 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.19 – 7.13 (m, 2H), 7.01 – 6.95 (m, 1H), 6.93 – 6.88 (m, 1H), 3.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 140.8, 136.3, 132.7, 130.1, 129.7, 128.9, 128.5, 128.1, 128.0, 125.3, 124.9, 124.4, 122.9, 113.5, 112.1, 57.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{17}H_{13}BrOS$ 343.9870, found 343.9865.

(2-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ap)



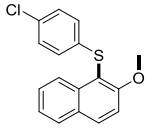
Following the general procedure **B**, 1-methyl-4-(phenylsulfinyl)benzene (48.2 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ap** (42.8 mg, 0.124 mmol, 62%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 9.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.44 – 7.36 (m, 2H), 6.95 – 6.85 (m, 2H), 6.36 – 6.29 (m, 1H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 139.4, 136.3, 132.8, 129.8, 128.5, 128.1, 127.6, 126.4, 125.7, 125.4, 124.4, 120.7, 113.6, 112.2, 57.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{17}H_{13}BrOS$ 343.9870, found 343.9878.

(4-Chlorophenyl)(2-methoxynaphthalen-1-yl)sulfane (4aq)



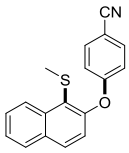
Following the general procedure **B**, 1-chloro-4-(methylsulfinyl)benzene (38.5 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4aq** (46.4 mg, 0.154 mmol, 77%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.51 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.97 – 6.91 (m, 2H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 137.0, 136.3, 132.5, 130.7, 129.8, 128.9, 128.5, 128.1, 127.8, 125.4, 124.4, 113.6, 112.8, 57.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{17}H_{13}ClOS$ 300.0376, found 300.0381.

4-((1-(Methylthio)naphthalen-2-yl)oxy)benzonitrile (4ar)



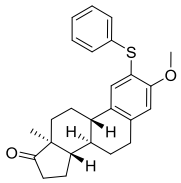
Following the general procedure **B**, 4-(methylsulfinyl)benzonitrile (36.4 mg, 0.22 mmol), 2-naphthanol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ar** (40.8 mg, 0.14 mmol, 70%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8, 153.6, 135.6, 134.3, 132.1, 131.2, 128.7, 127.8, 126.3, 126.2, 125.6, 121.0, 119.0, 117.3, 105.9, 19.1.

HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{13}NOS$ 291.0718, found 291.0733.

(8R,9S,13S,14S)-3-Methoxy-13-methyl-2-(phenylthio)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4ni)



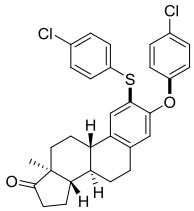
Following the general procedure **B**, (methylsulfinyl)benzene (30.9 mg, 0.22 mmol), estrone (54.1 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4ni** (53.4 mg, 0.136 mmol, 68%) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 5H), 7.19 – 7.15 (m, 1H), 6.66 (s, 1H), 3.80 (s, 3H), 2.96 – 2.88 (m, 2H), 2.49 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.23-2.18 (m, 2H), 2.16 – 2.10 (m, 1H), 2.10 – 2.05 (m, 1H), 2.03 – 1.98 (m, 1H), 1.92 – 1.86 (m, 1H), 1.67-1.56 (m, 2H), 1.55 – 1.49 (m, 1H), 1.46 – 1.38 (m, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 156.7, 138.4, 136.5, 132.9, 131.5, 129.4, 129.0, 126.2, 119.4, 111.8, 56.1, 50.5, 48.1, 44.0, 38.4, 36.0, 31.6, 29.8, 26.6, 25.9, 21.7, 14.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{25}H_{28}NaO_2S$ 415.1702, found 415.1720.

(8R,9S,13S,14S)-3-(4-Chlorophenoxy)-2-((4-chlorophenyl)thio)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4nb)



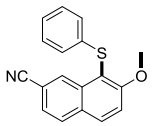
Following the general procedure **B**, 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), estrone (54.1 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4nb** (71.2 mg, 68%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.24 – 7.18 (m, 4H), 7.18 – 7.13 (m, 2H), 6.78 – 6.73 (m, 2H), 6.68 (s, 1H), 2.84 (dd, *J* = 8.6, 3.9 Hz, 2H), 2.51 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.28 (dt, *J* = 16.8, 8.9 Hz, 2H), 2.16 (dd, *J* = 18.5, 9.4 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.95 (dd, *J* = 9.1, 2.0 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.54 – 1.48 (m, 2H), 1.47 – 1.37 (m, 2H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 220.5, 156.0, 153.8, 139.4, 136.9, 134.8, 132.5, 132.1, 131.1, 129.7, 129.2, 128.1, 122.8, 120.4, 119.2, 50.5, 48.0, 44.2, 38.1, 35.9, 31.6, 29.4, 26.4, 25.9, 21.7, 14.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{30}H_{28}Cl_2NaO_2S$ 545.1079, found 545.1062.

7-Methoxy-8-(phenylthio)-2-naphthonitrile (4oi)



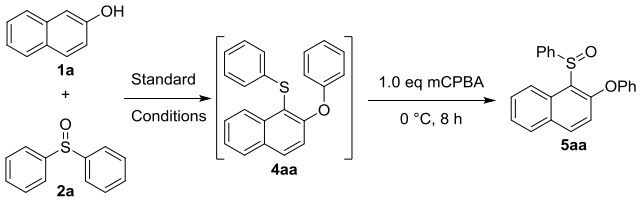
Following the general procedure **B**, (methylsulfinyl)benzene (30.9 mg, 0.22 mmol), 7-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol) and K_3PO_4 (188.7 mg, 0.88 mmol) were used to afford **4oi** (51 mg, 88%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.89 (m, 1H), 8.01 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.19 – 7.13 (m, 2H), 7.11 – 7.06 (m, 1H), 7.04 – 6.99 (m, 2H), 3.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 137.2, 135.8, 132.1, 132.0, 130.8, 129.7, 129.1, 126.9, 125.6, 124.8, 119.5, 116.4, 114.7, 111.4, 57.1.

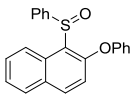
HRMS-EI (m/z) $[M]^+$ calculated for $C_{18}H_{13}NOS$ 291.0718, found 291.0732.

IV. Procedure C for one-pot oxidation to sulfoxide in water



An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf_2O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated *in vacuo*. K_3PO_4 (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H_2O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was allowed to cooled to room temperature. mCPBA (0.2 mmol, 1.0 eq) was slowly added to the resulting mixture at 0 °C. After stirred for 8 h at 0 °C, the aqueous phase was exacted with EtOAc (1 mL x 3), dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (10% ethyl acetate in petroleum ether) to afford desired products.

2-Phenoxy-1-(phenylsulfinyl)naphthalene (5aa)



Following the general procedure **C**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol), K_3PO_4 (188.7 mg, 0.88 mmol) and mCPBA (40.6 mg, 0.2 mmol) were used to afford **5aa** (55.1 mg, 0.16 mmol, 80%) as a colourless oil.

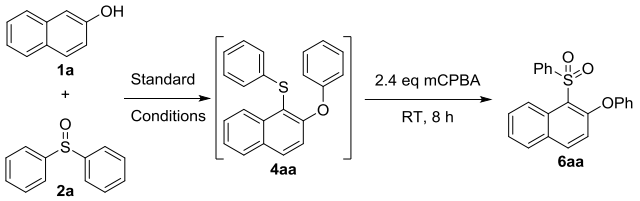
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.42 (dt, *J* = 23.3, 7.5 Hz, 3H),

7.38 – 7.32 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.4, 144.9, 134.6, 131.7, 131.2, 130.0, 129.9, 129.0, 128.9, 128.2, 127.8, 125.8, 124.6, 124.1, 123.8, 118.9, 118.8.

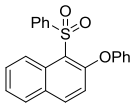
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{22}H_{17}O_2S$ 345.0944, found 345.0929; $[M+Na]^+$ calculated for $C_{22}H_{16}NaO_2S$ 367.0763, found 367.0749.

V. Procedure D for one-pot oxidation to sulfone in water



An oven-dried vial was charged with sulfoxide (0.22 mmol, 1.1 eq) and anhydrous MeCN (2 mL, 0.1 M) under argon. Tf_2O (0.24 mmol, 1.2 eq) was then added to the resulting mixture at 0 °C, followed by addition of phenol (0.2 mmol, 1 eq). The reaction mixture was stirred for 3 h at 0 °C and then concentrated *in vacuo*. K_3PO_4 (0.88 mmol, 4.4 eq) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H_2O (0.27 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After completion, the solution was cooled to room temperature, followed by mCPBA (0.48 mmol, 2.4 eq). After stirred for 8 h at room temperature, the aqueous phase was exacted with EtOAc (1 mL x 3), dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (10% ethyl acetate in petroleum ether) to afford desired products.

2-Phenoxy-1-(phenylsulfonyl)naphthalene (6aa)



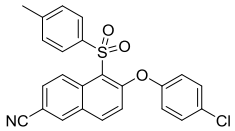
Following the general procedure **D**, diphenyl sulfoxide (44.5 mg, 0.22 mmol), 2-naphthol (28.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol), K_3PO_4 (188.7 mg, 0.88 mmol) and mCPBA (40.6 mg, 0.2 mmol) were used to afford **6aa** (59.9 mg, 0.166 mmol, 83%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 8.9 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.73 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.49 – 7.43 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.15 – 7.06 (m, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.3, 143.8, 136.4, 132.8, 131.4, 130.7, 129.9, 129.2, 128.9, 128.6, 127.7, 125.8, 125.7, 124.6, 124.4, 119.2, 118.8.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{22}H_{16}NaO_3S$ 383.0712, found 383.0707.

6-(4-Chlorophenoxy)-5-tosyl-2-naphthonitrile (6eg)



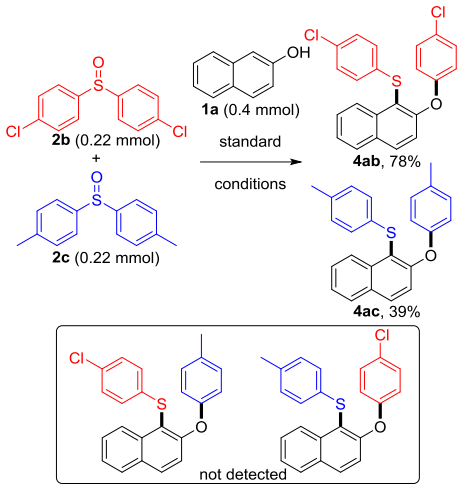
Following the general procedure **D**, 1-chloro-4-(p-tolylsulfinyl)benzene (55.2 mg, 0.22 mmol), 6-hydroxy-2-naphthonitrile (33.9 mg, 0.2 mmol), Tf_2O (40.8 µL, 0.2 mmol), K_3PO_4 (188.7 mg, 0.88 mmol) and mCPBA (97.5 mg, 0.48 mmol) were used to afford **6eg** (67.7 mg, 0.156 mmol, 78%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.76 (d, *J* = 9.2 Hz, 1H), 8.20 (d, *J* = 1.4 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.85 (dd, *J* = 8.8, 2.1 Hz, 3H), 7.27 – 7.24 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 1H), 6.70 – 6.65 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 153.8, 144.4, 140.1, 136.6, 134.4, 133.1, 130.4, 130.2, 129.6, 129.4, 127.9, 126.7, 126.2, 120.7, 120.3, 118.5, 109.7, 21.7.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{24}H_{17}ClNO_3S$ 434.0612, found 434.0618.

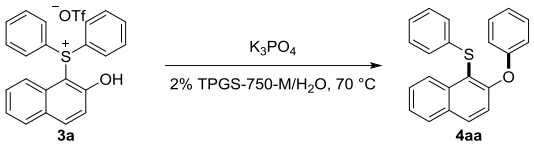
VI. Crossover experiment



An oven-dried vial was charged with **2b** 4,4'-sulfinylbis(chlorobenzene) (59.7 mg, 0.22 mmol), **2c** 4,4'-sulfinylbis(methylbenzene) (50.7 mg, 0.22 mmol) and anhydrous MeCN (4 mL, 0.1 M) under argon. Tf_2O (81.6 µL, 0.48 mmol) was then added to the resulting mixture at 0 °C, followed by addition of **1a** naphthalen-2-ol (57.8 mg, 0.4 mmol). The reaction mixture was stirred for 3 h at 0 °C and then concentrated in *vacuo*. K_3PO_4 (377.4 mg, 1.76 mmol) was added to the residue, followed by addition of 2 wt% TPGS-750-M/H2O (0.53 mL, 0.75 M). The reaction vial was capped with a rubber septum and the mixture was stirred vigorously for 24 h at 70 °C. After cooled to room temperature, the mixture was extracted with EtOAc (3 x 1 mL) and the combined organic layers was dried over anhydrous $MgSO_4$, concentrated in *vacuo*. The crude product was purified by flash column chromatography (1% to 5% ethyl acetate in petroleum ether) to afford afford **4ab** (68 mg, 78%) as a white solid and **4ac** (31 mg, 39%) as a colorless oil

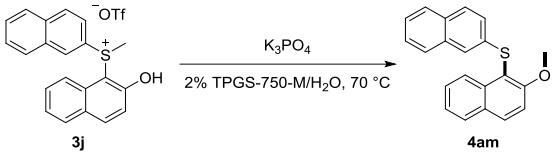
VII. Recycle Study and E Factor Calculation

Initial reaction:



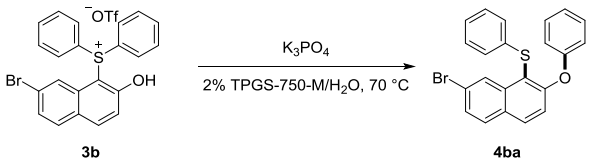
To a 2 mL vial, sulfonium salt **3a** (179.5 mg, 0.375 mmol) was added followed by K_3PO_4 (241.2 mg, 1.125 mmol), and 2 wt% TPGS-750-M/H_2O (0.5 mL, 0.75 M). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in *vacuo*. The crude product was purified by flash column chromatography (2% ethyl acetate in petroleum ether) to afford the desired product **4aa** (111 mg, 0.18 mmol, 90%).

***Re-use of surfactant solution* (1st *recycle*):**



The septum was removed quickly and the vial was charged with sulfonium salt **3j** (175.0 mg, 0.375 mmol) and capped, followed by K_3PO_4 (241.2 mg, 1.125 mmol). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in *vacuo*. The crude product was purified by flash column chromatography (3% ethyl acetate in petroleum ether) to afford the desired product **4am** (108 mg, 0.182 mmol, 91%).

***Re-use of surfactant solution* (2ed *recycle*)**



The septum was removed quickly and the vial was charged with sulfonium salt **3b** (209.0 mg, 0.375 mmol) and capped, followed by K_3PO_4 (241.2 mg, 1.125 mmol). The solution was heated at 70 °C for 24 h and then allowed to cool to room temperature. The mixture was extracted two times with EtOAc (0.2 mL + 0.2 mL), placed in a round bottom flask and concentrated in *vacuo*. The crude product was purified by flash column chromatography (3% ethyl acetate in petroleum ether) to afford the desired product **4ba** (134 mg, 0.176 mmol, 88%).

E Factor calculation

Note: Density of each liquid at 25 °C; ethyl acetate = 0.897 g/mL; water = 1.00 g/mL.

Initial Reaction:

Water Not included as waste

Solvents:
0.5 mL EtOAc (449 mg)

initial reaction

$$\frac{449 \text{ mg waste}}{111 \text{ mg product}} = 4.0 \text{ E Factor}$$

Waster included as waste

Solvents:
0.5 mL EtOAc (449 mg)
0.5 mL H_2O (500 mg)

initial reaction

$$\frac{949 \text{ mg waste}}{111 \text{ mg product}} = 8.6 \text{ E Factor}$$

1st recycle

Solvents:
0.5 mL EtOAc (449 mg)

1st recycle:

$$\frac{449 \text{ mg waste}}{108 \text{ mg product}} = 4.2 \text{ E Factor}$$

2ed recycle

Solvents:
0.5 mL EtOAc (449 mg)

2nd recycle:

$$\frac{449 \text{ mg waste}}{134 \text{ mg product}} = 3.4 \text{ E Factor}$$

VIII. Reference:

1. Lipshutz. B. H.; Ghorai, S.; Abela, A. R.; Moser, R.; Nishikata, T.; Duplais, C.; Krasovskiy, A. *J. Org. Chem.*, **2011**, *76*, 4379

2. She, J.; Jiang, Z.; Wang, Y.-G. *Tetrahedron Letters*, **2009**, *50*, 593.

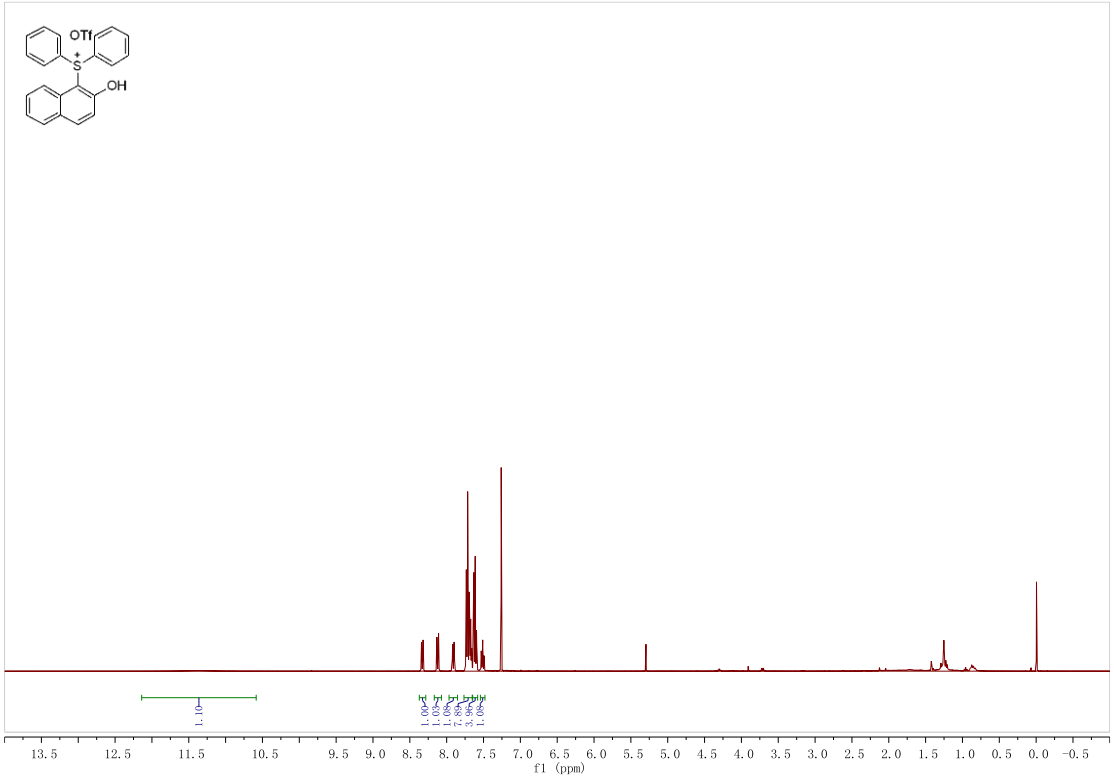
3. Padalaa, K.; Jeganmohan, M. *Chem. Commun.*, **2014**, *50*, 14573.

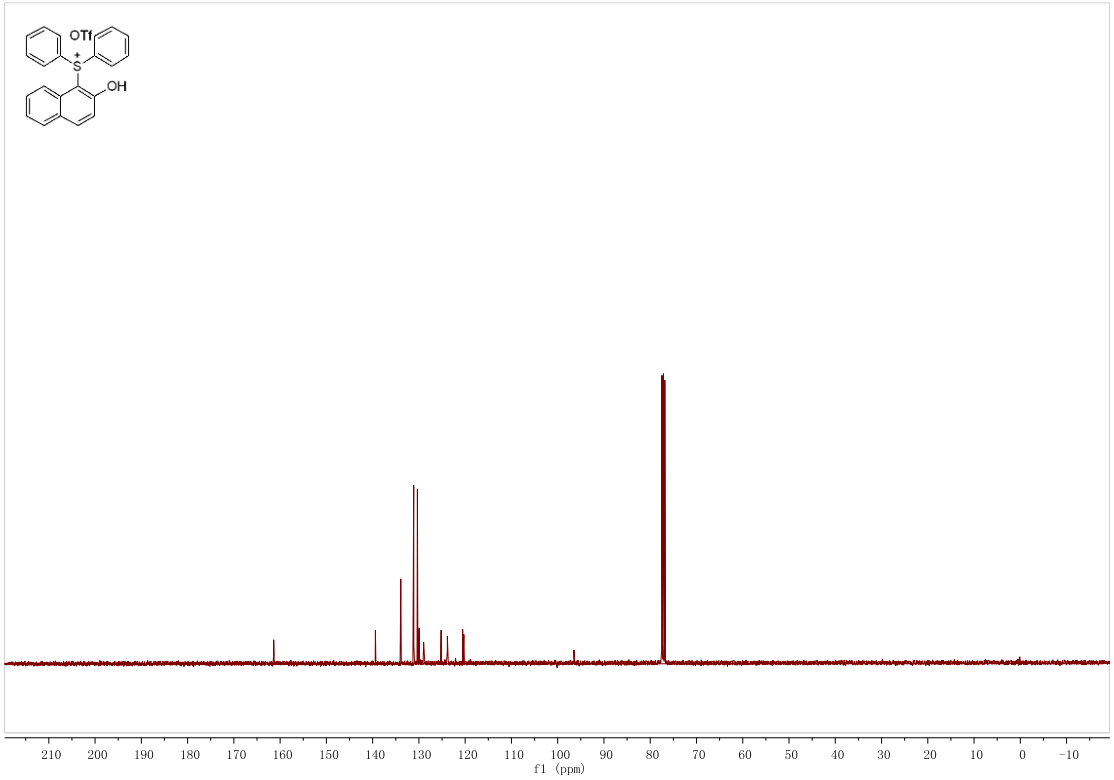
4. Xiao, F.-L.; Chen, S.-Q; Tian, J.-X.; Huang, H.-W.; Liu, Y.-J.; Deng, G.-J. *Green Chemistry*, **2016**, *18*, 1538.

5. Mahmoud, S.; Organ, Michael G. *Chemistry - A European Journal*, **2011**, *17*, 11719.

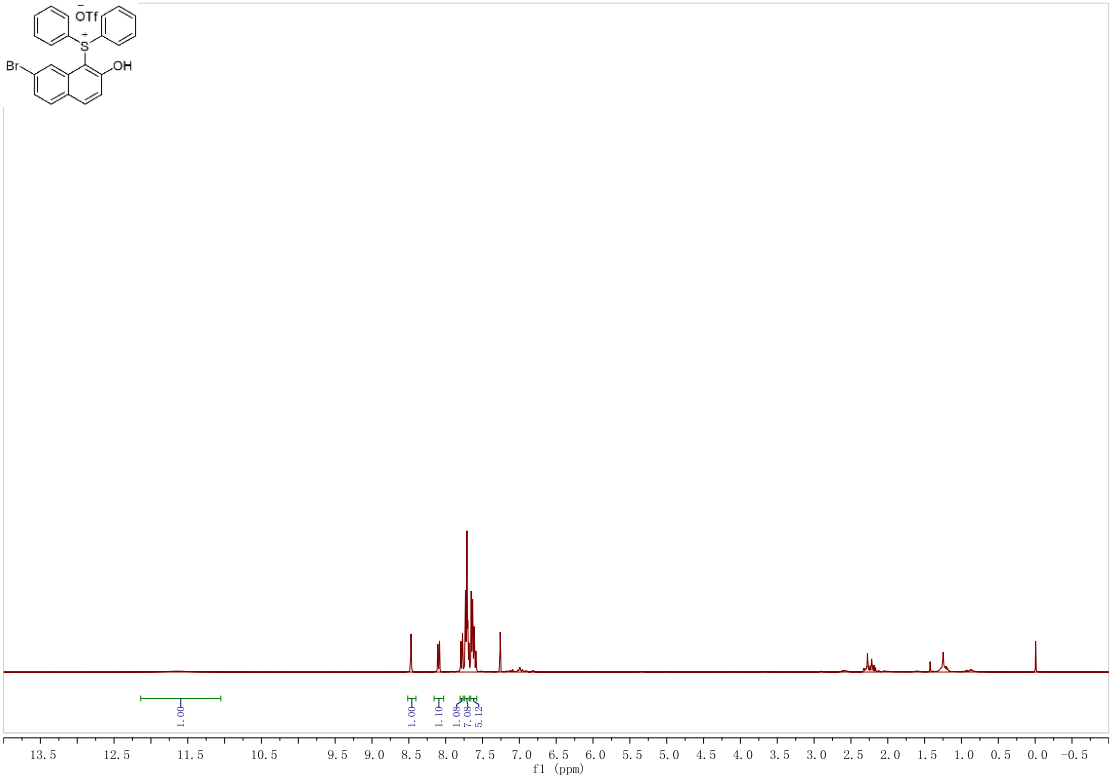
IX. ^{1}H and ^{13}C NMR Spectral data:

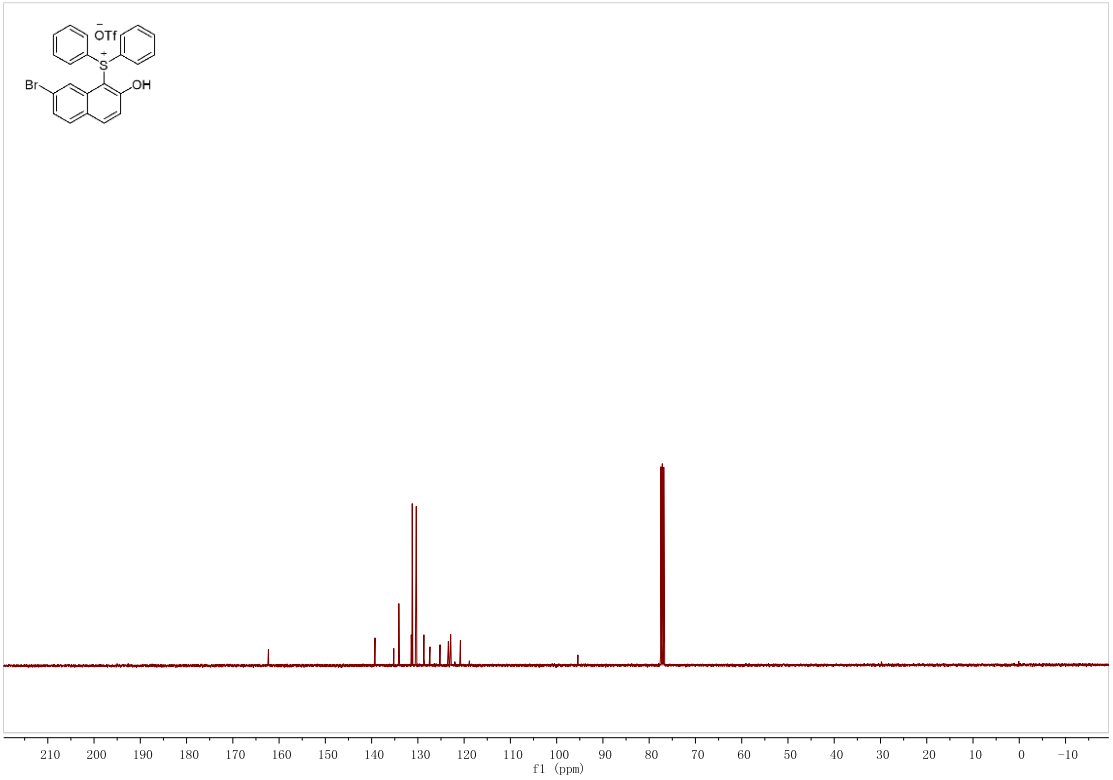
(2-Hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3a)



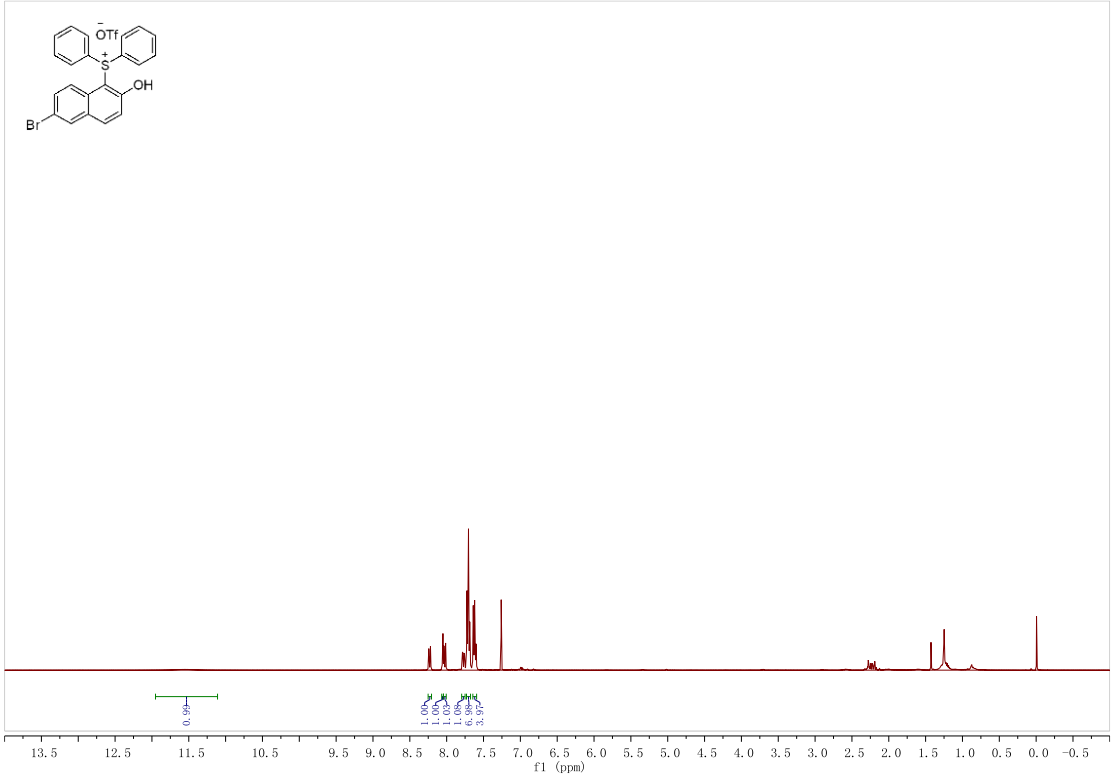


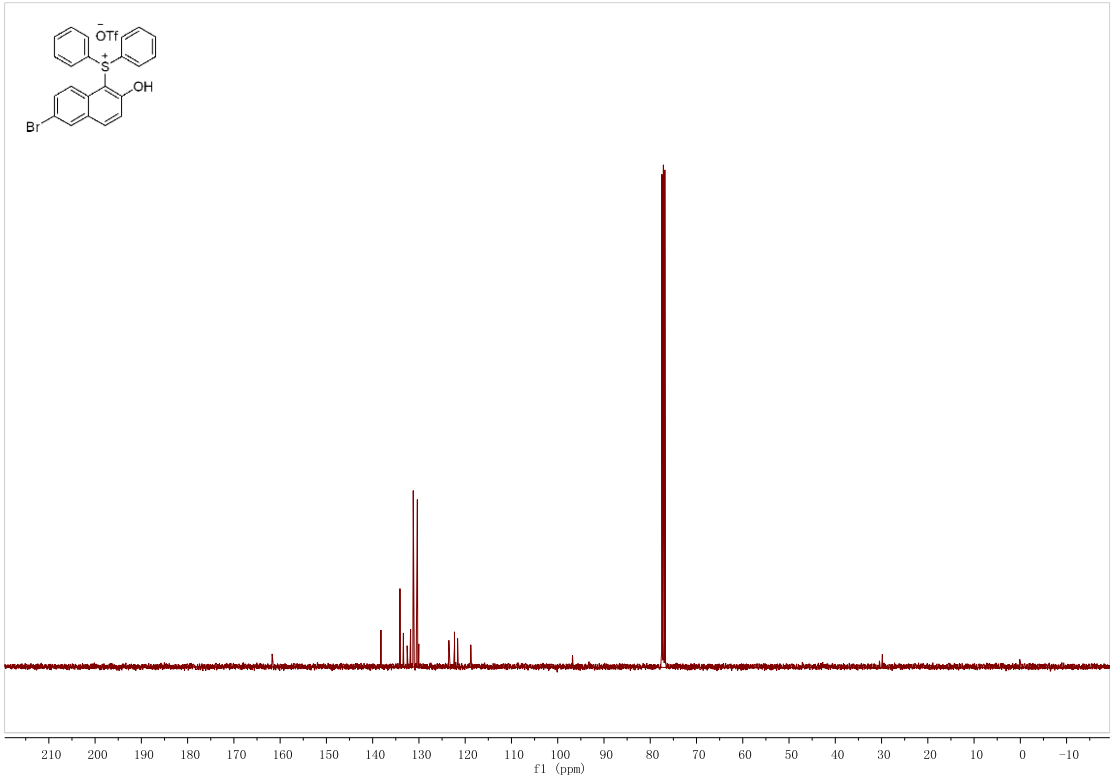
(7-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3b)



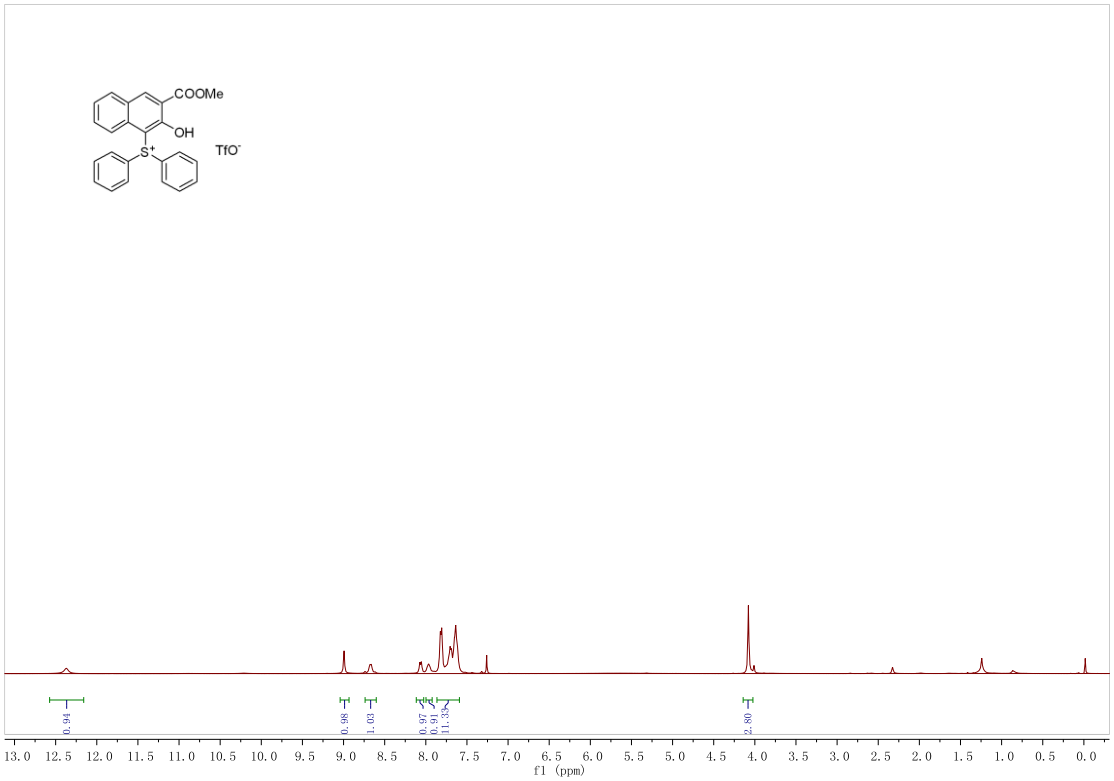


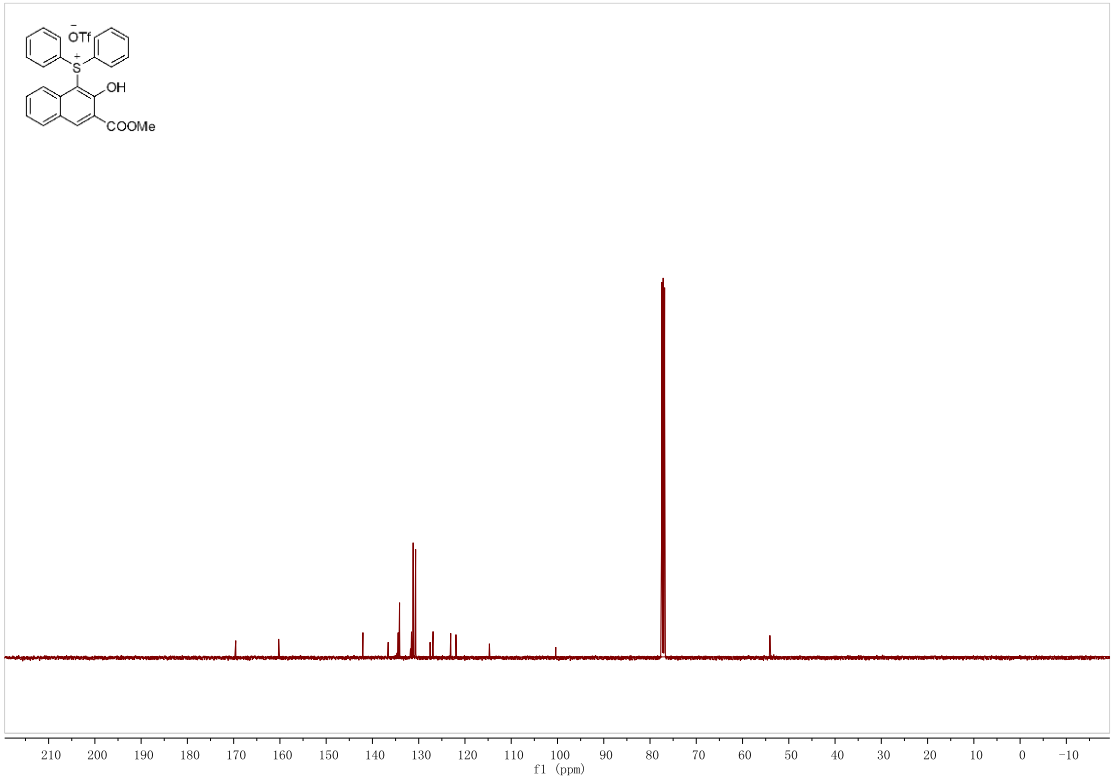
(6-Bromo-2-hydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3c)



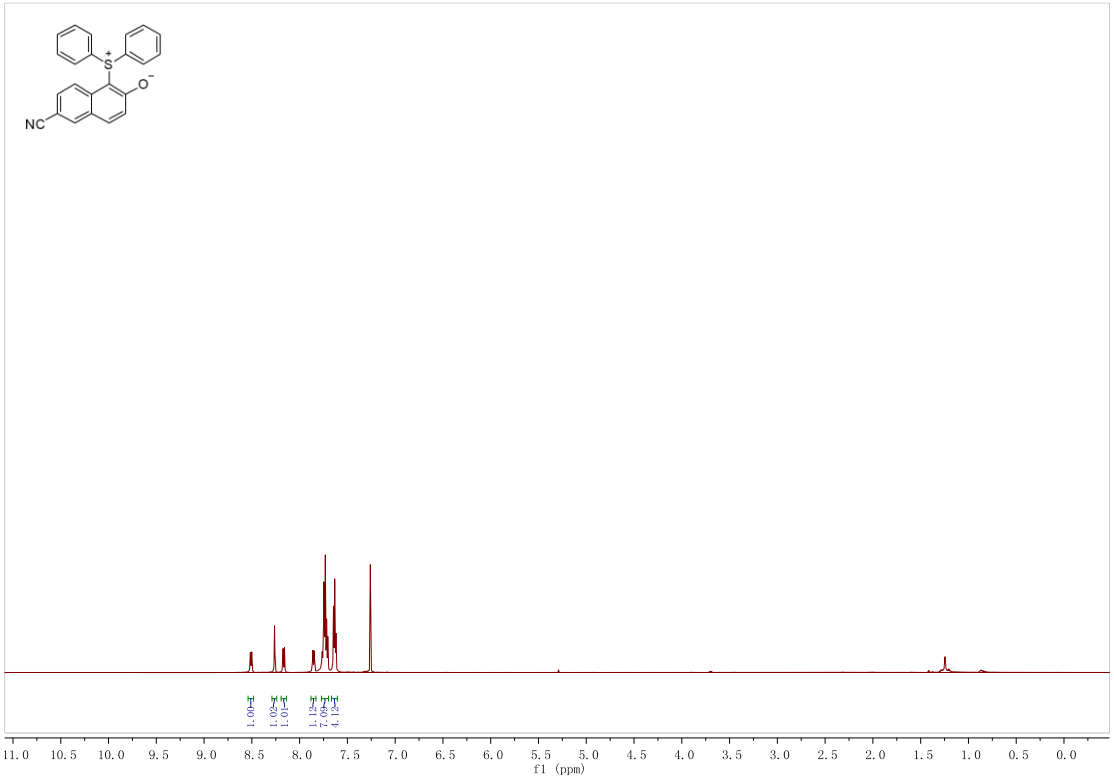


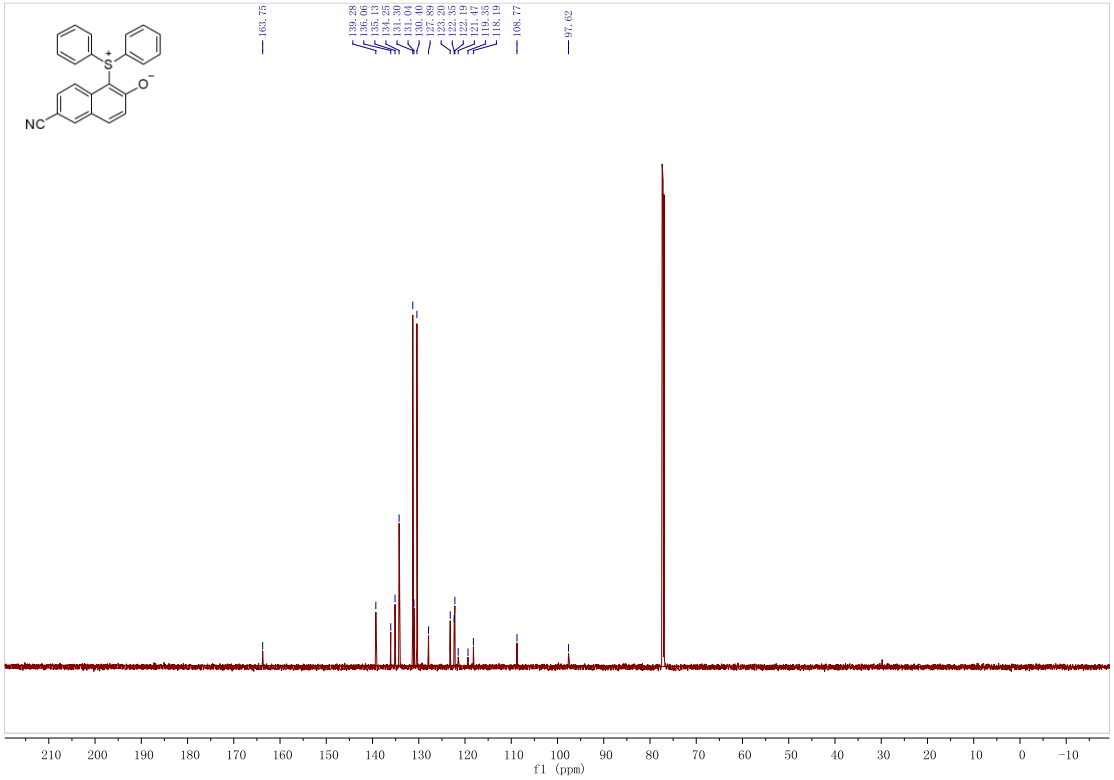
(2-Hydroxy-3-(methoxycarbonyl)naphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3d)



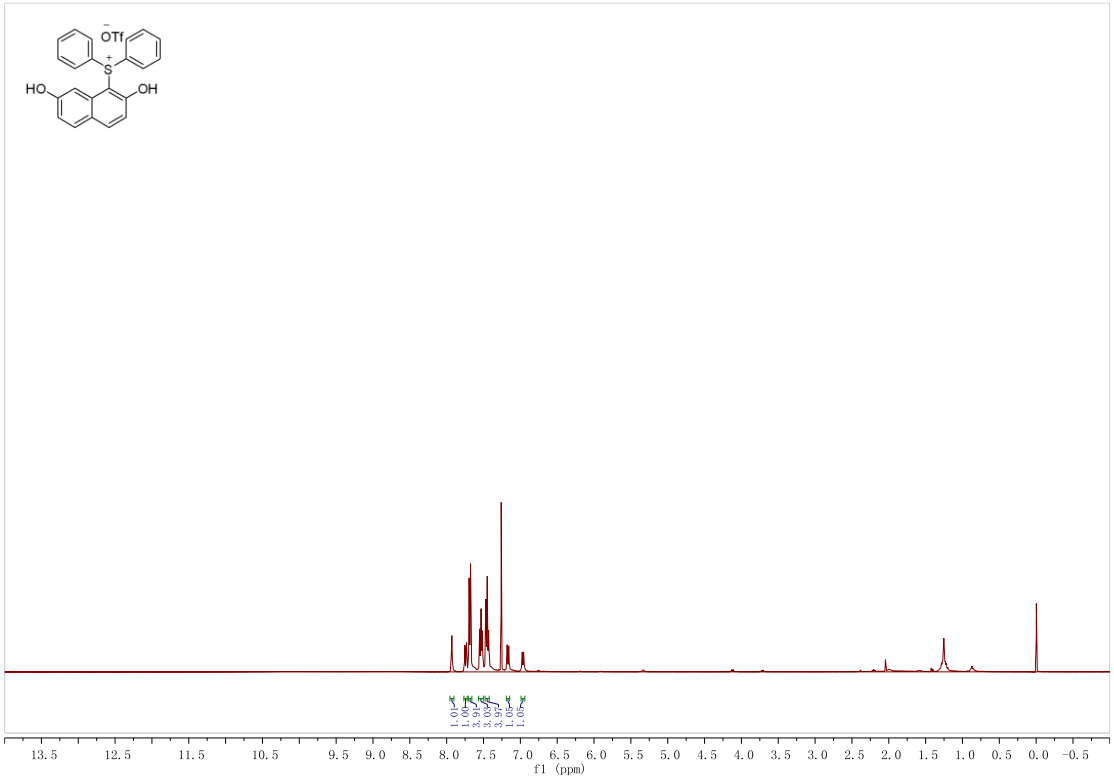


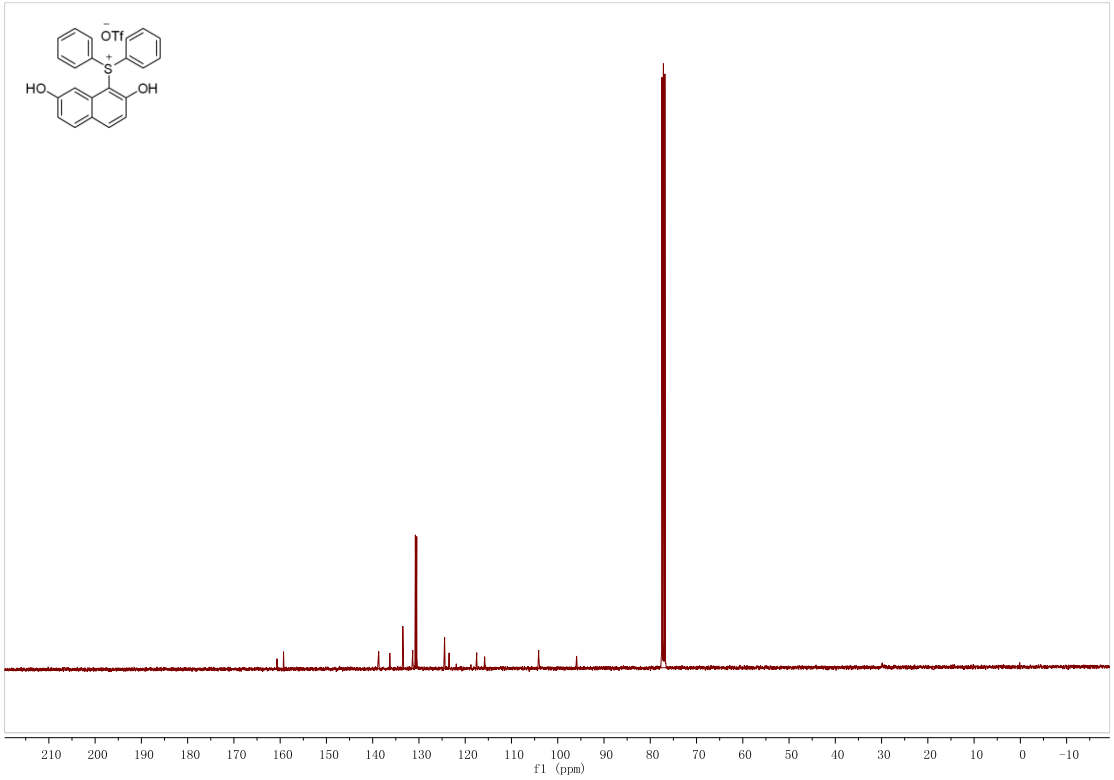
6-Cyano-1-(diphenylsulfonio)naphthalen-2-olate (3e)



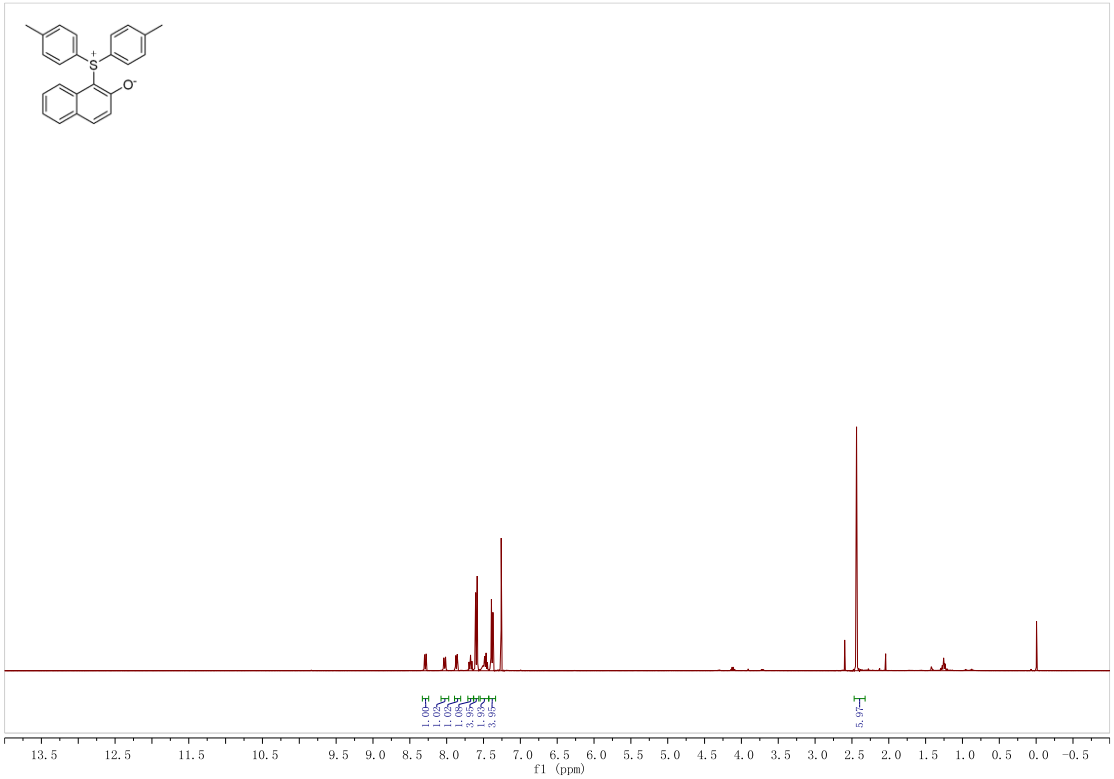


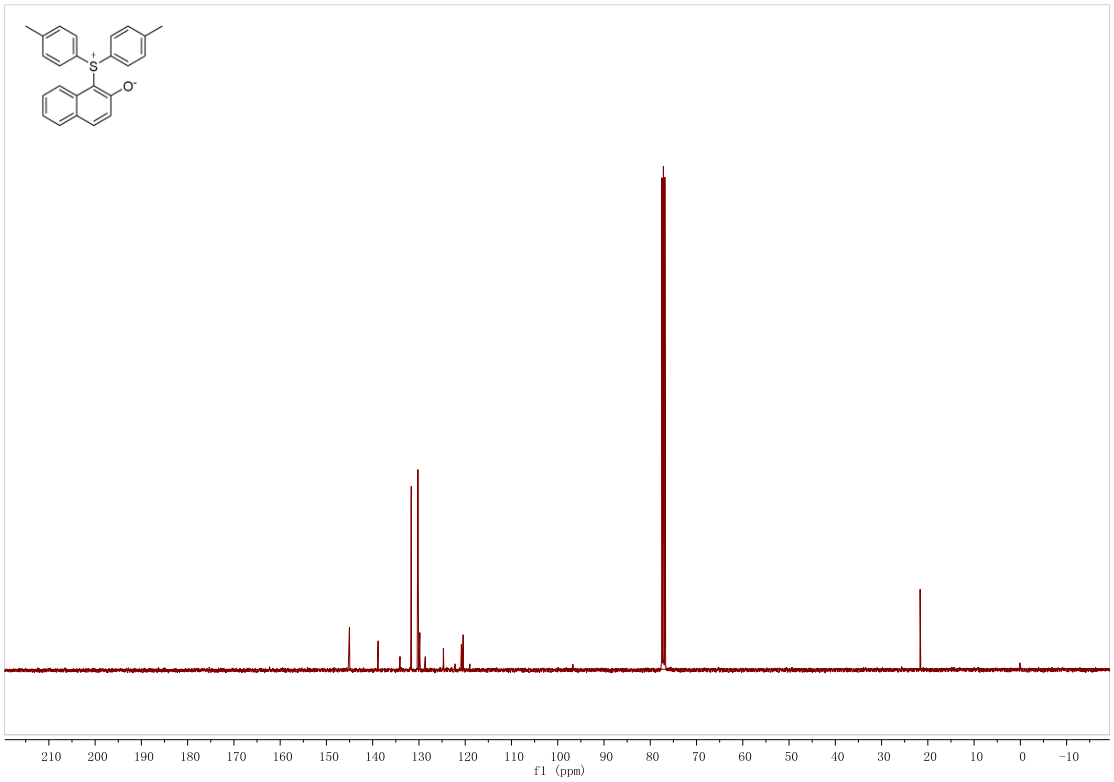
(2,7-Dihydroxynaphthalen-1-yl)diphenylsulfonium trifluoromethanesulfonate (3f)



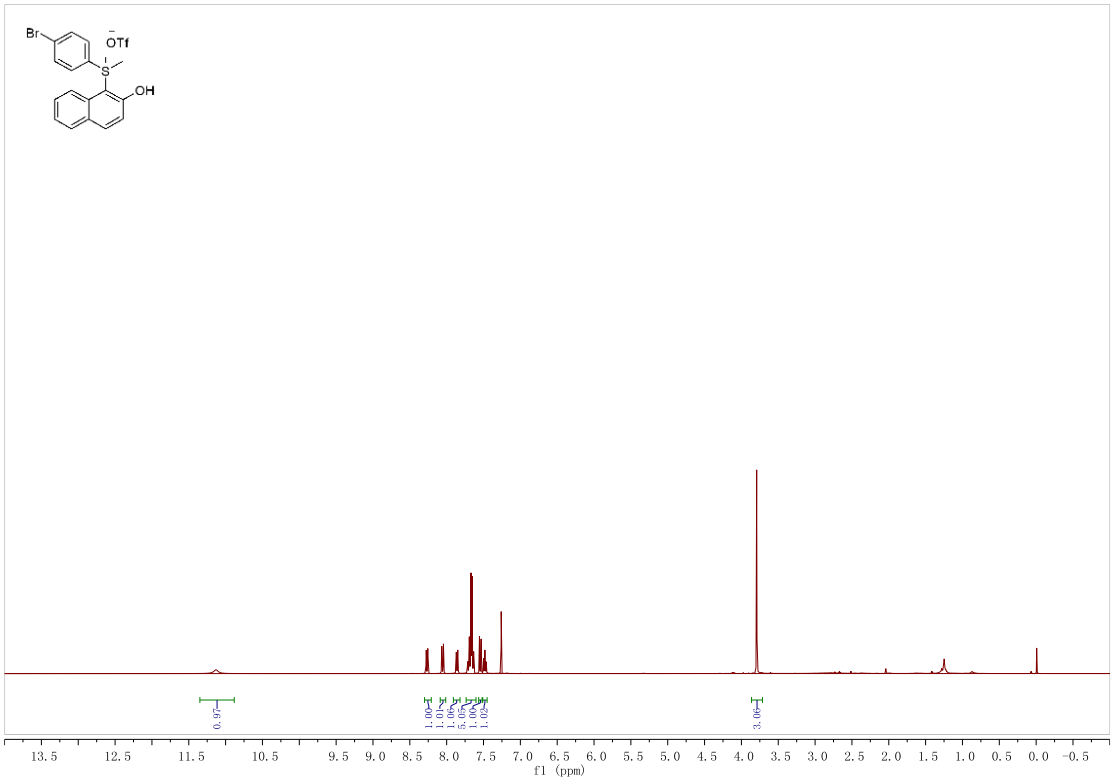


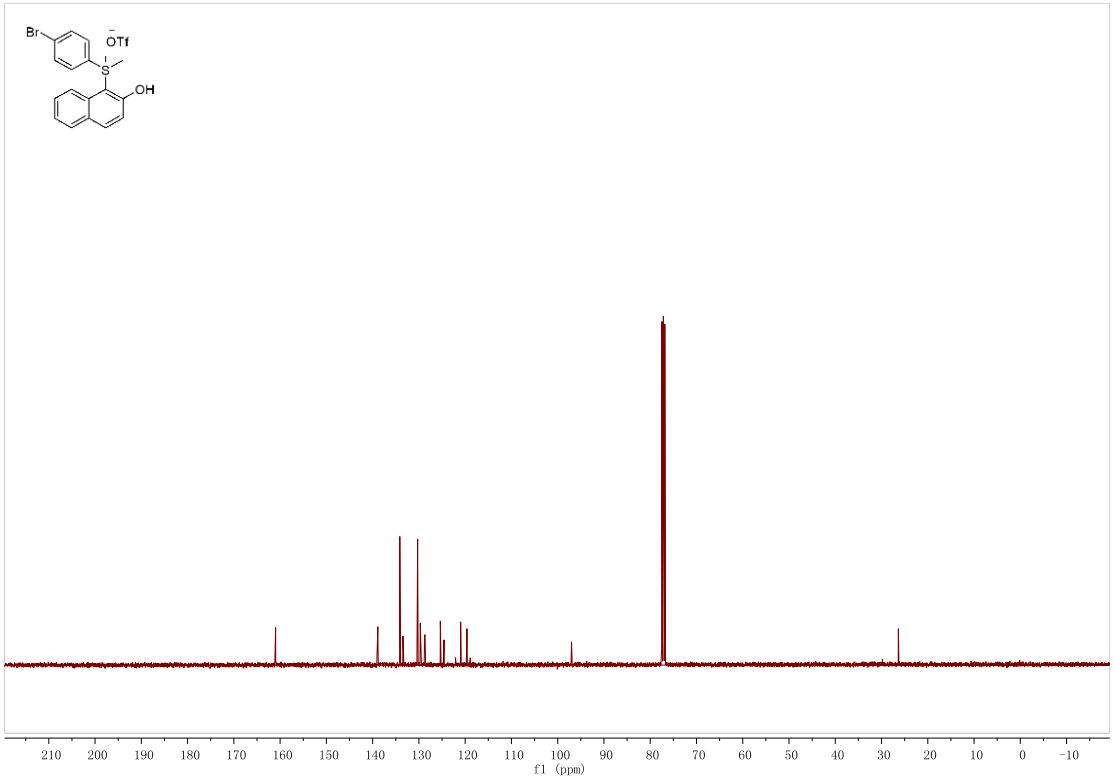
1-(Di-p-tolylsulfonio)naphthalen-2-olate (3g)



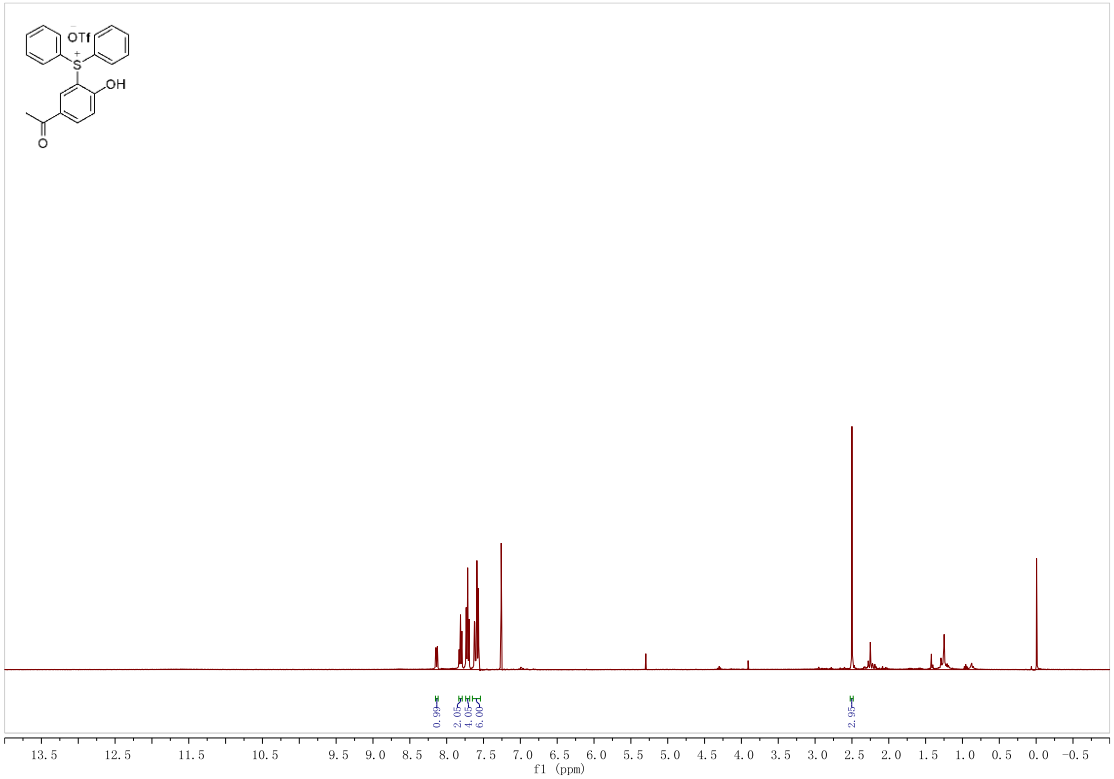


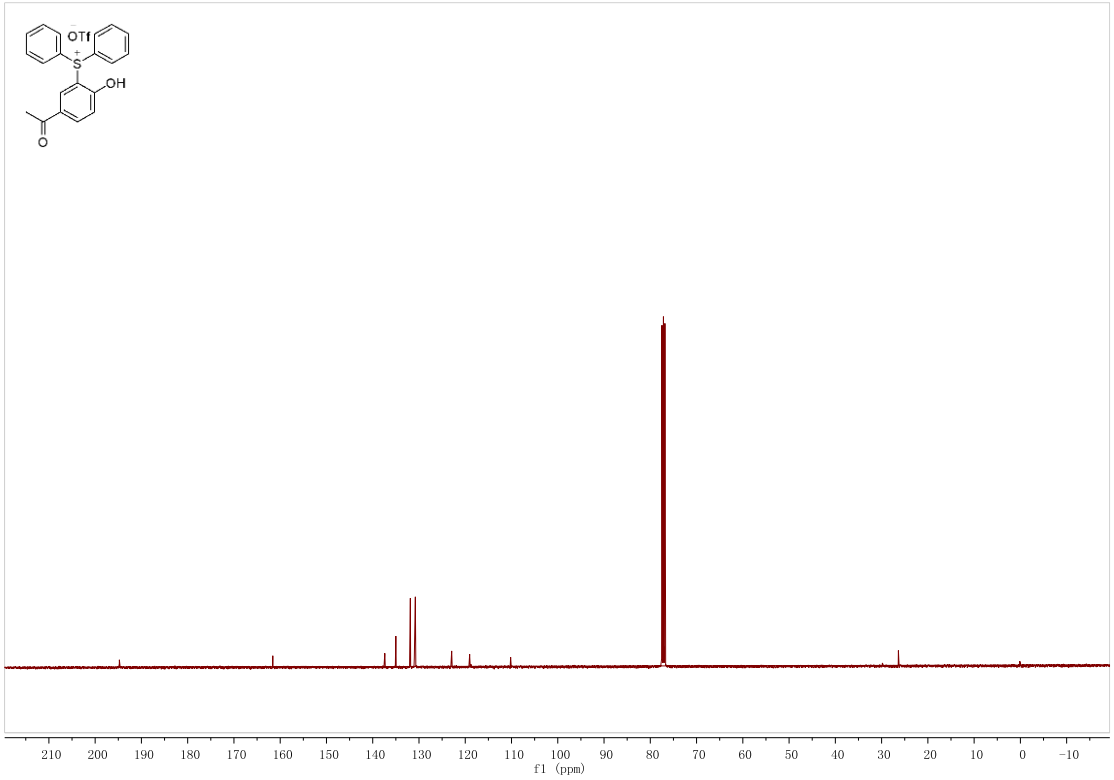
(4-Bromophenyl)(2-hydroxynaphthalen-1-yl)(methyl)sulfonium trifluoromethanesulfonate (3h)



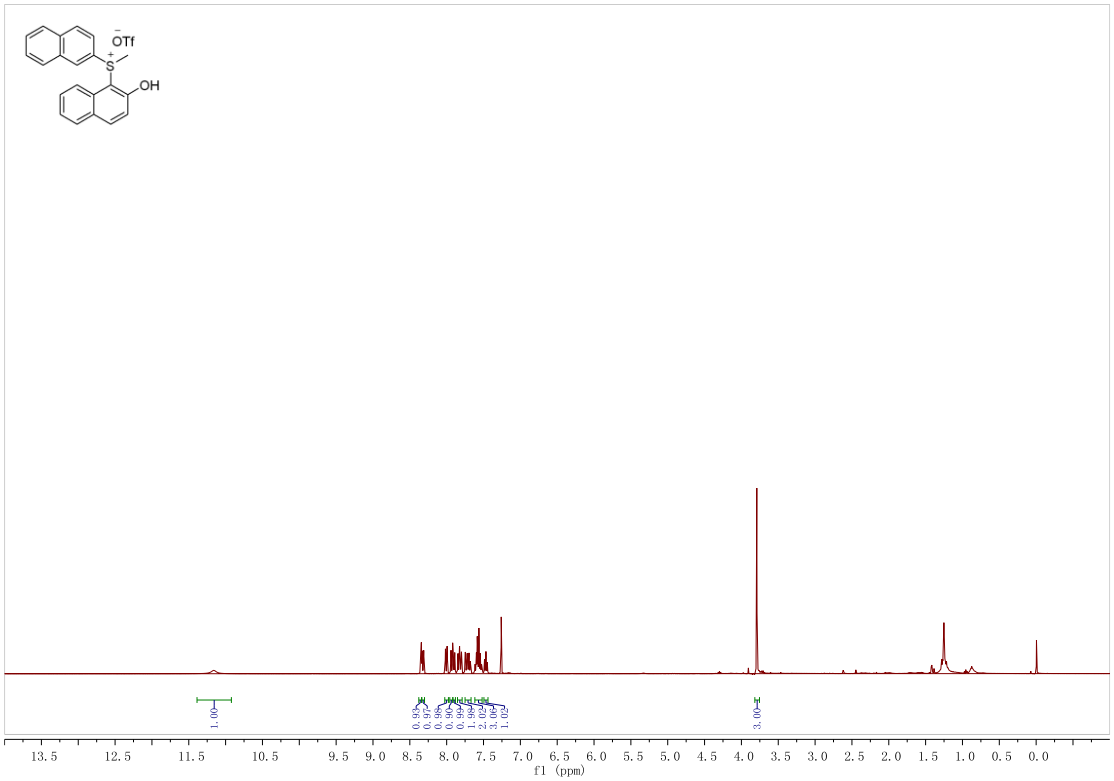


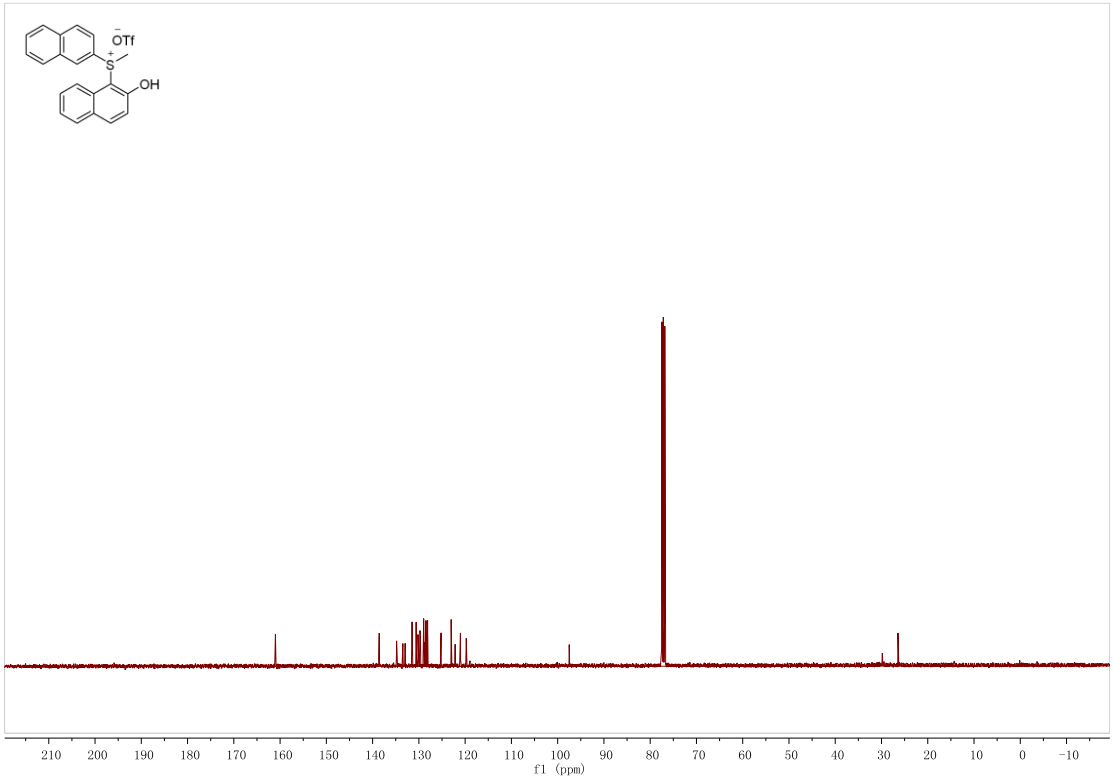
(5-Acetyl-2-hydroxyphenyl)diphenylsulfonium trifluoromethanesulfonate (3i)



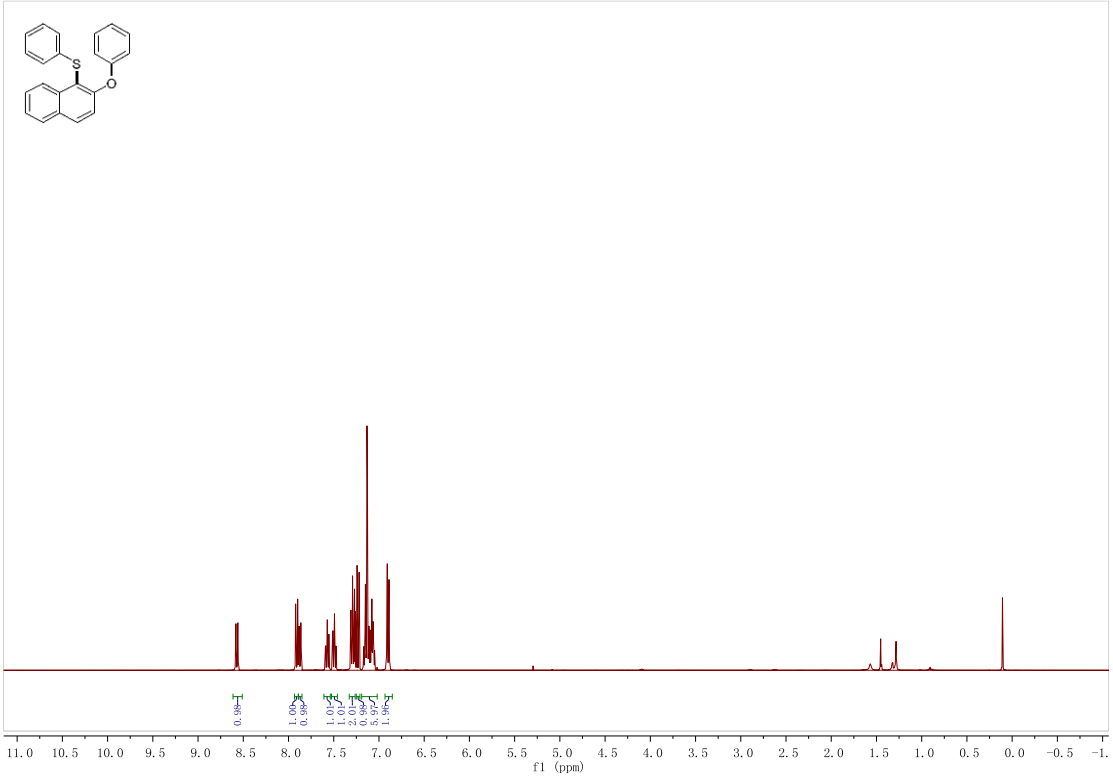


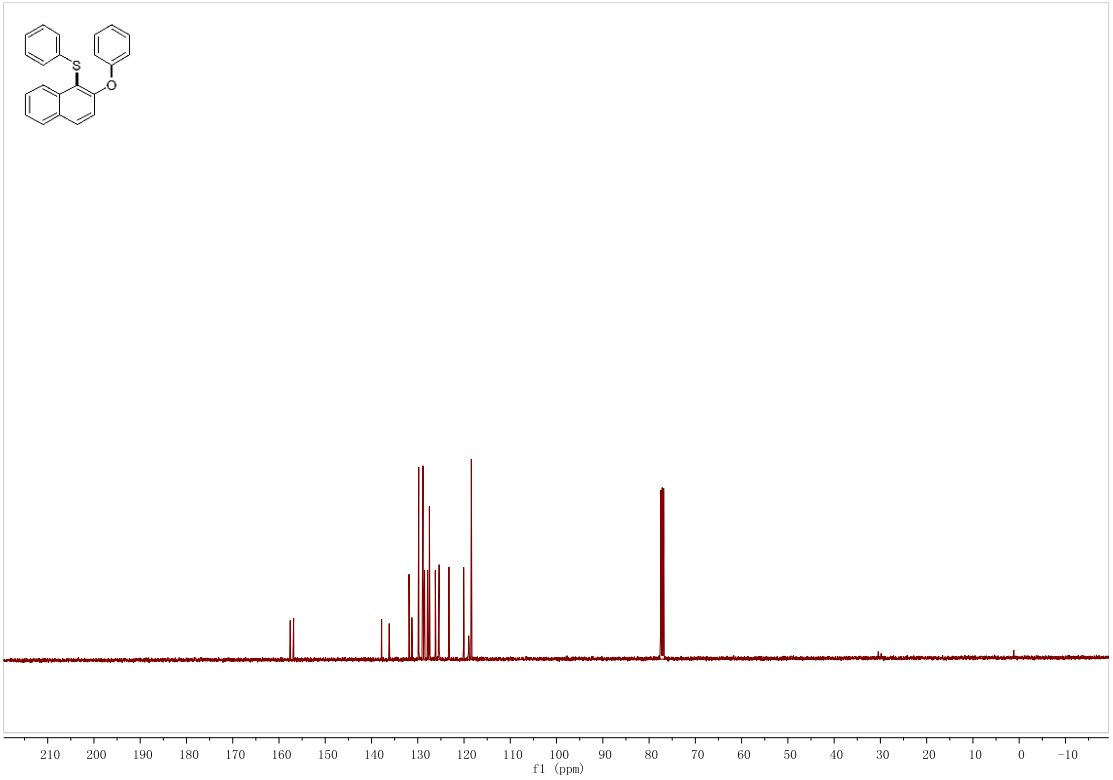
(2-Hydroxynaphthalen-1-yl)(methyl)(naphthalen-2-yl)sulfonium trifluoromethanesulfonate (3j)



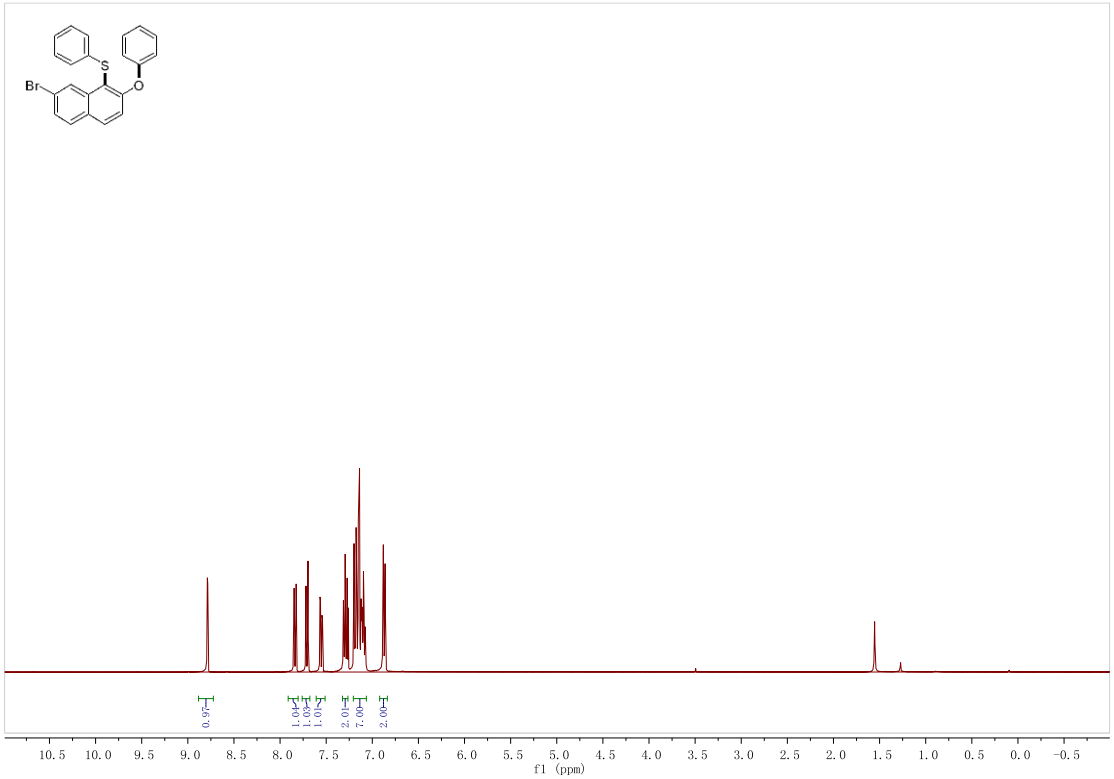


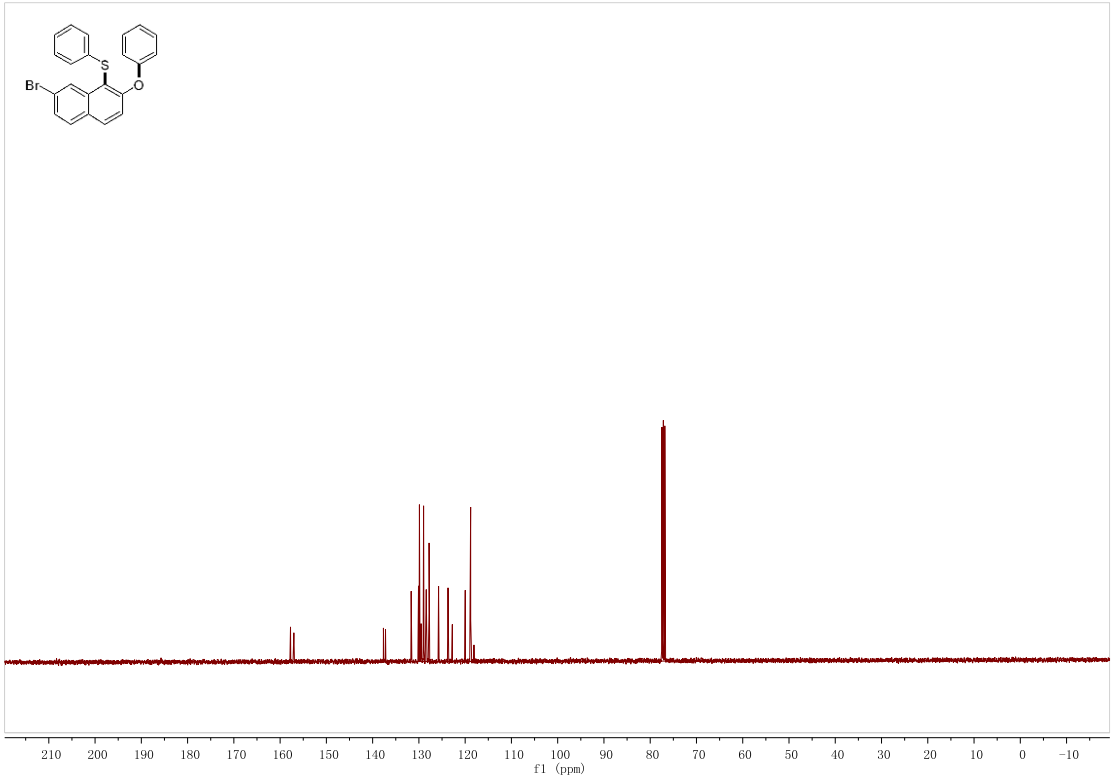
(2-Phenoxynaphthalen-1-yl)(phenyl)sulfane (4aa)



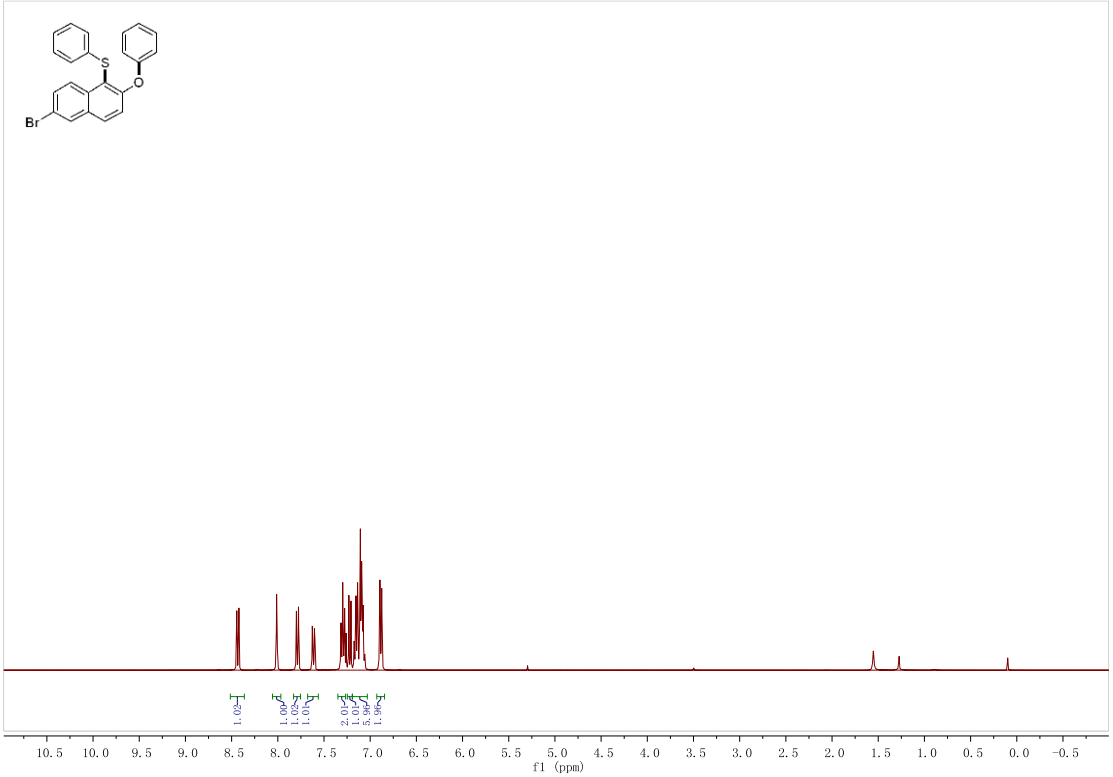


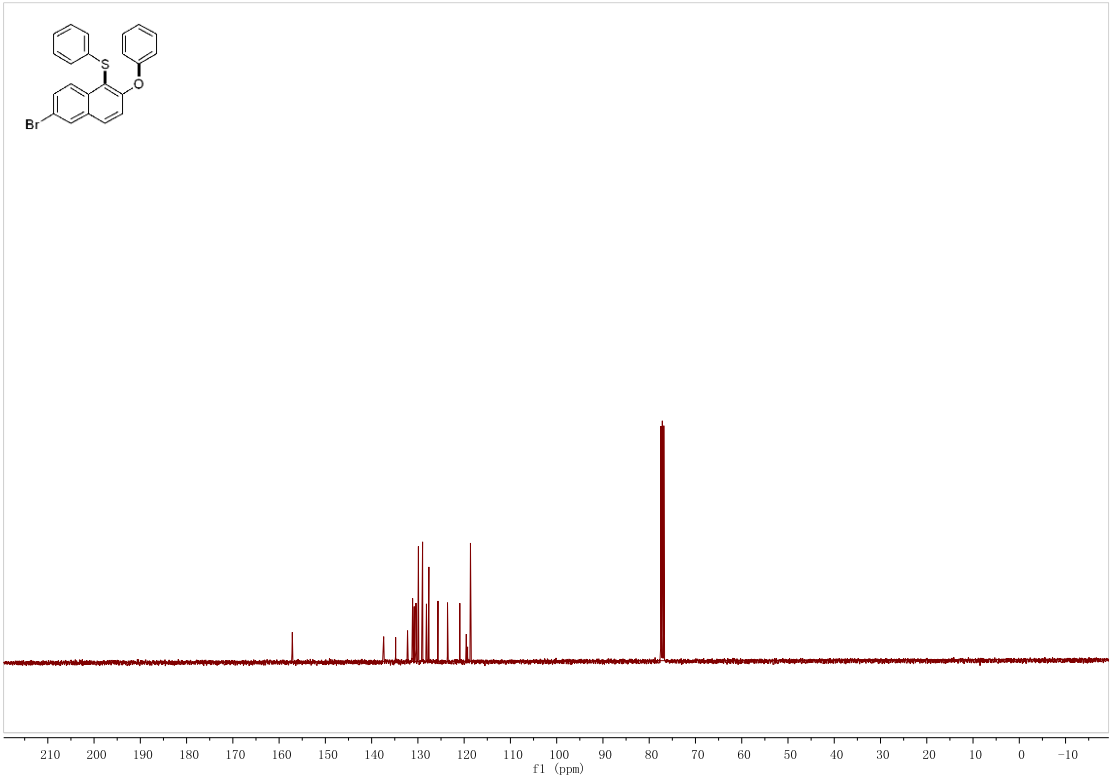
(7-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ba)



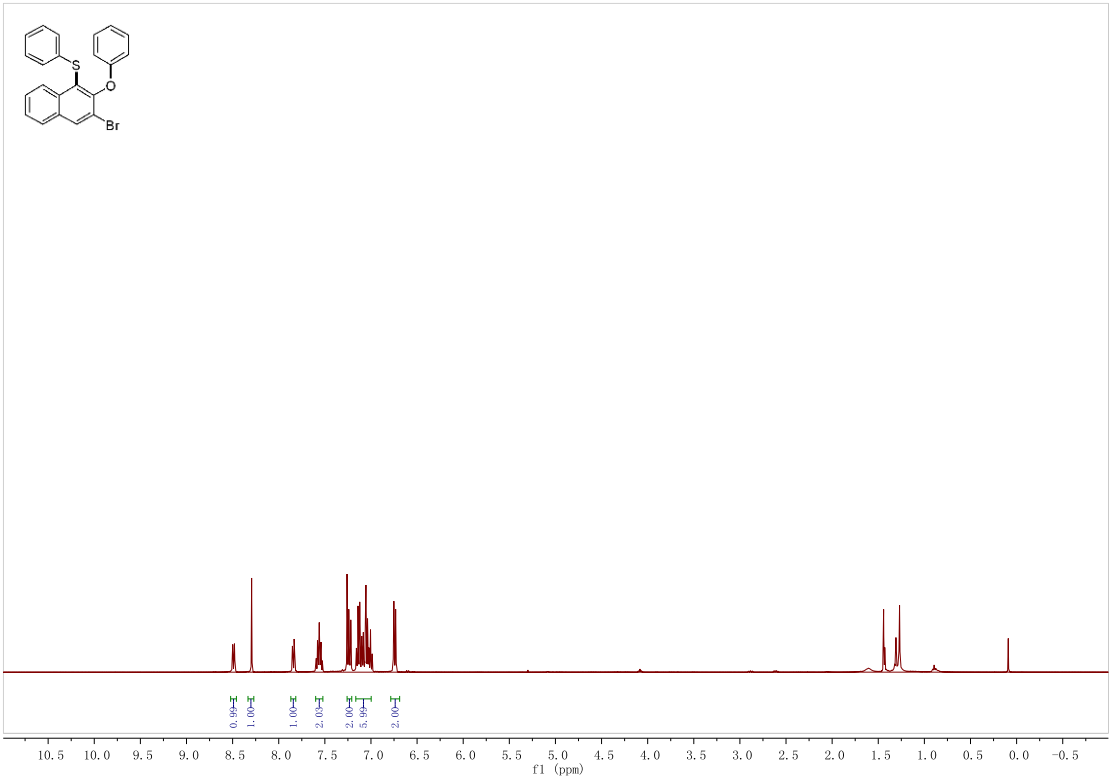


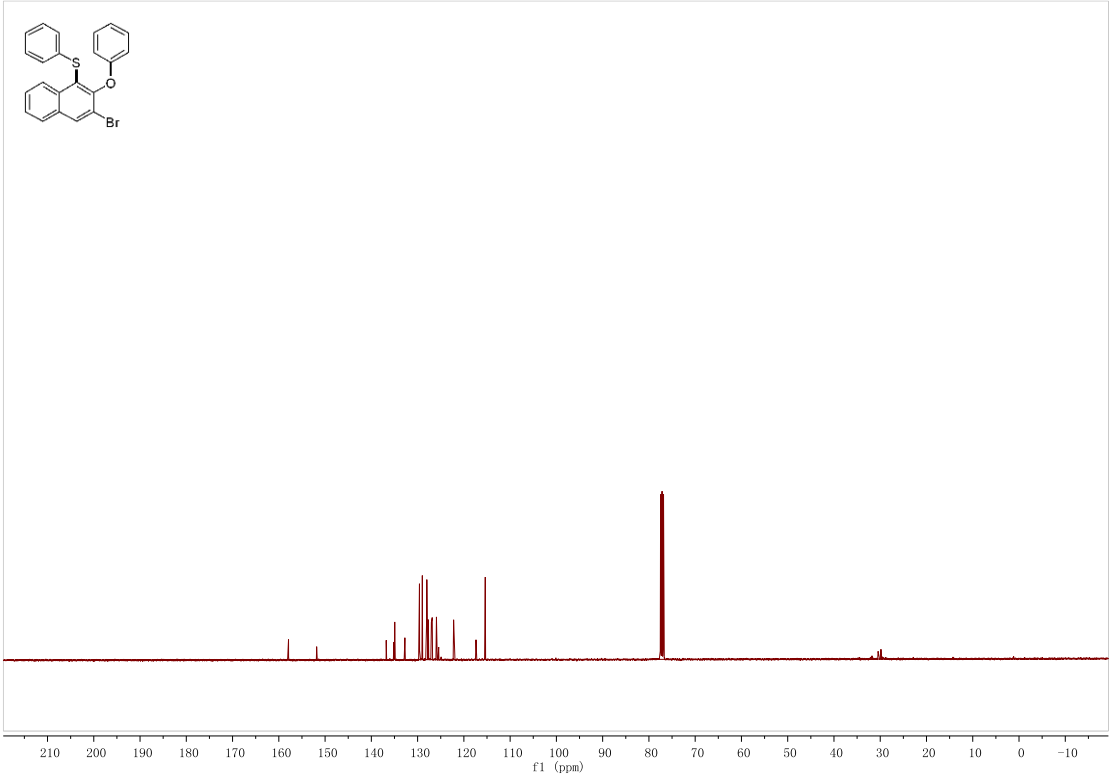
(6-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4ca)



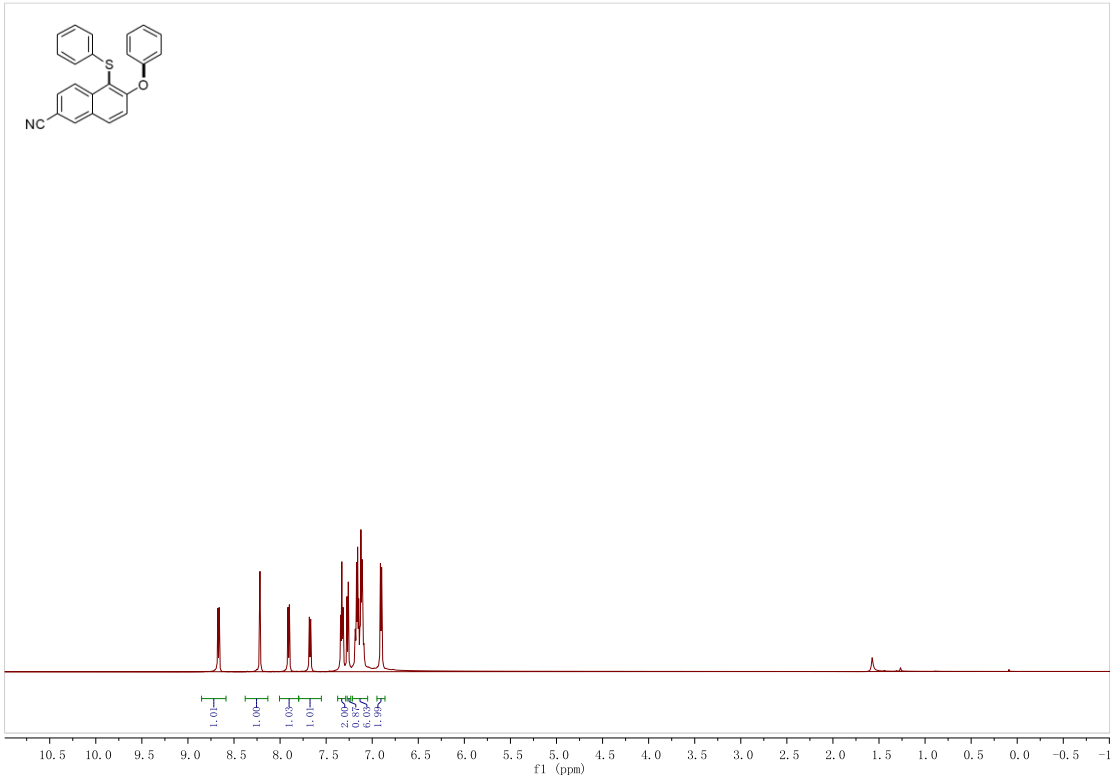


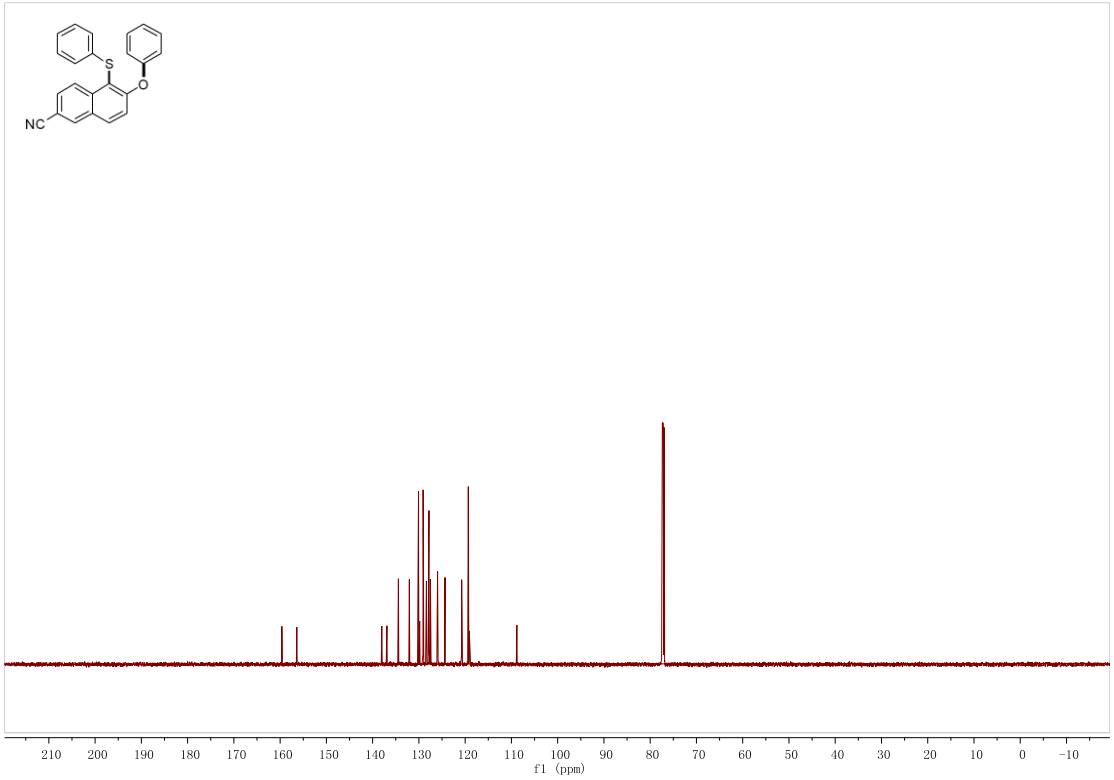
(3-Bromo-2-phenoxynaphthalen-1-yl)(phenyl)sulfane (4da)



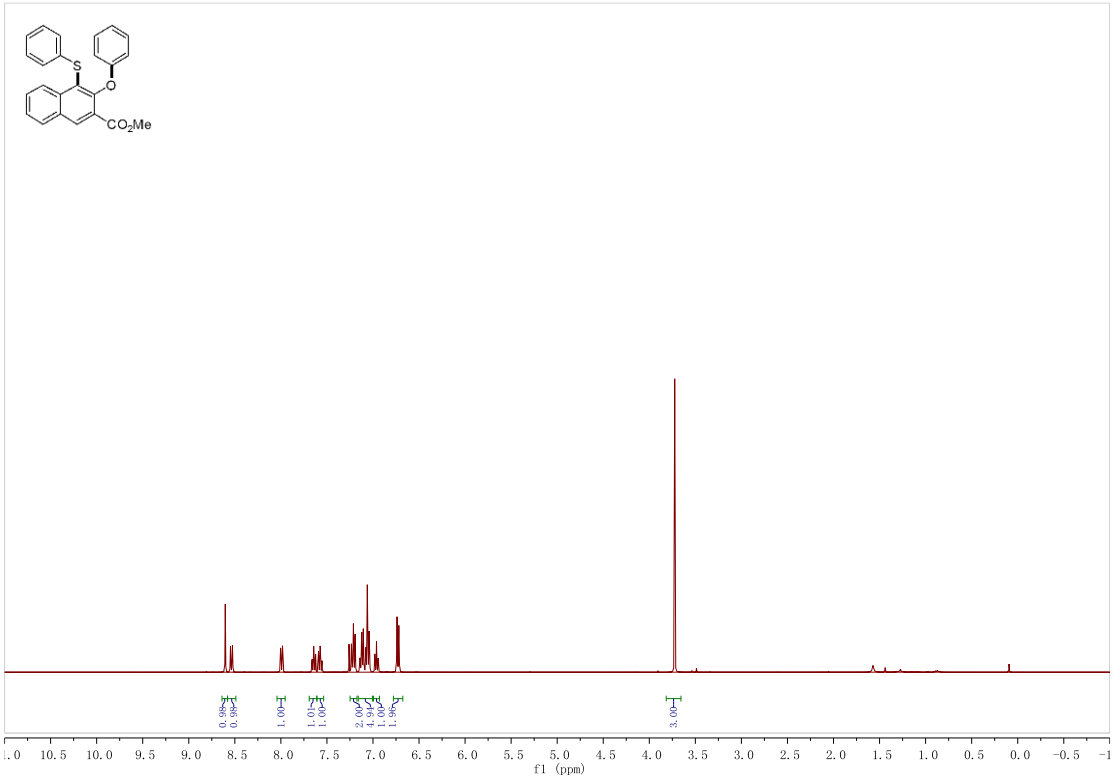


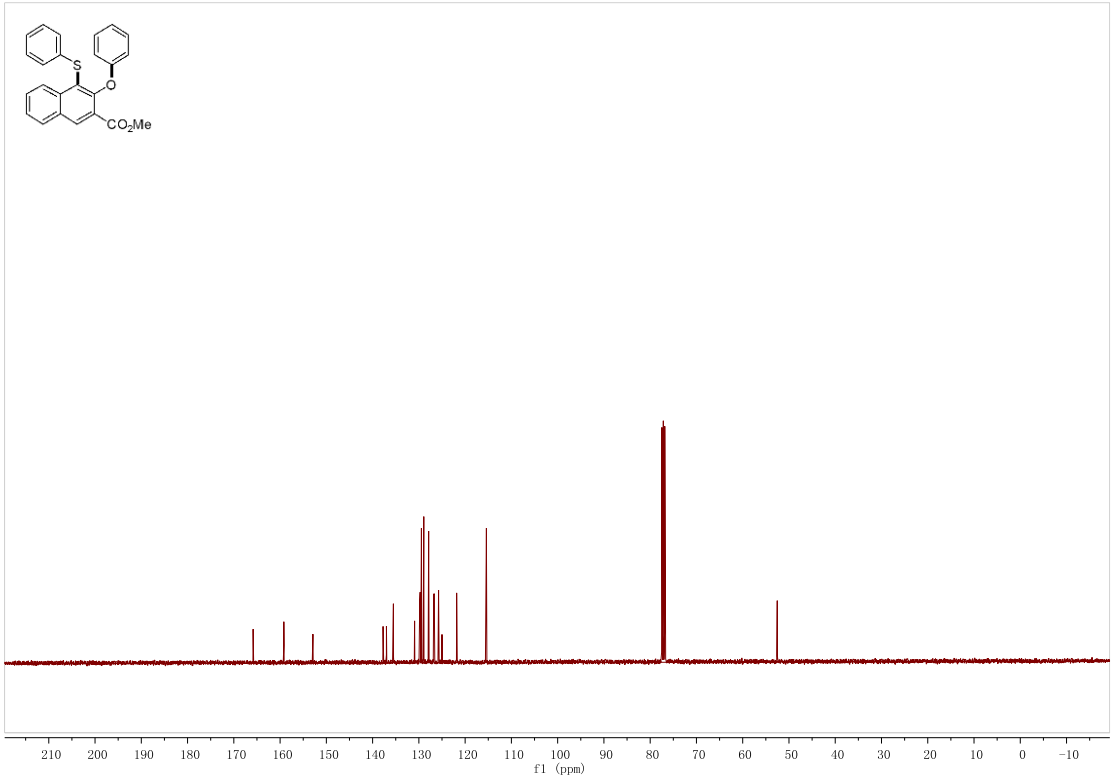
6-Phenoxy-5-(phenylthio)-2-naphthonitrile (4ea)



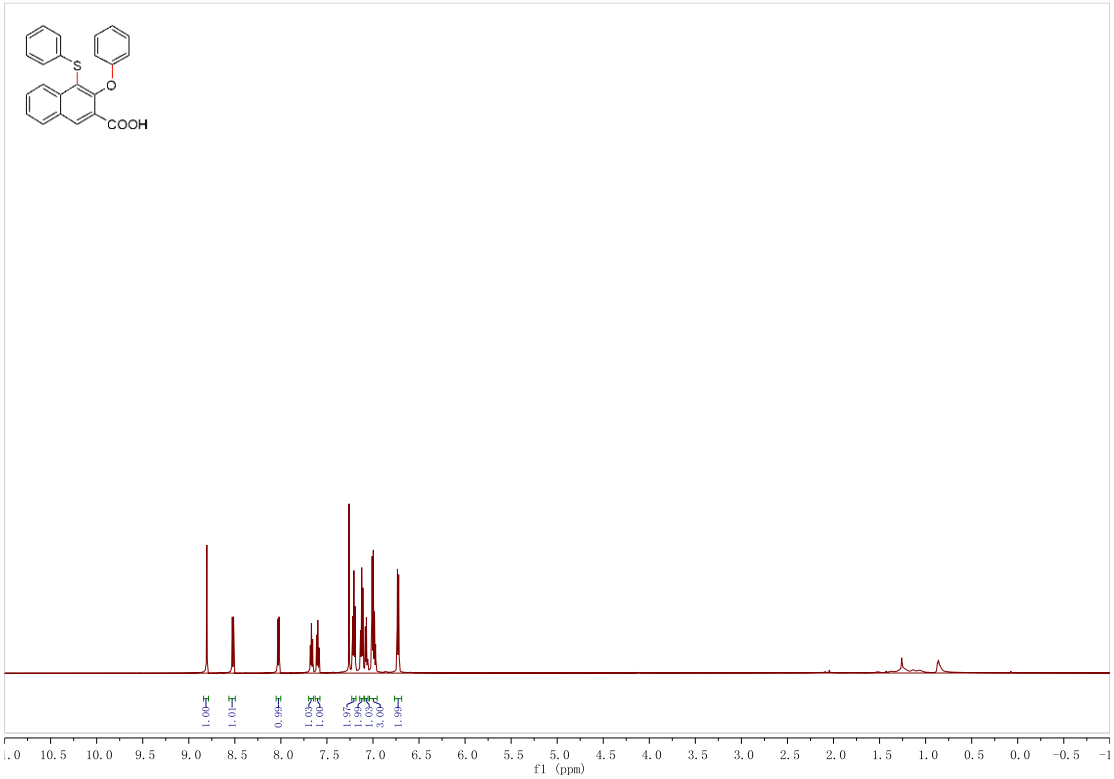


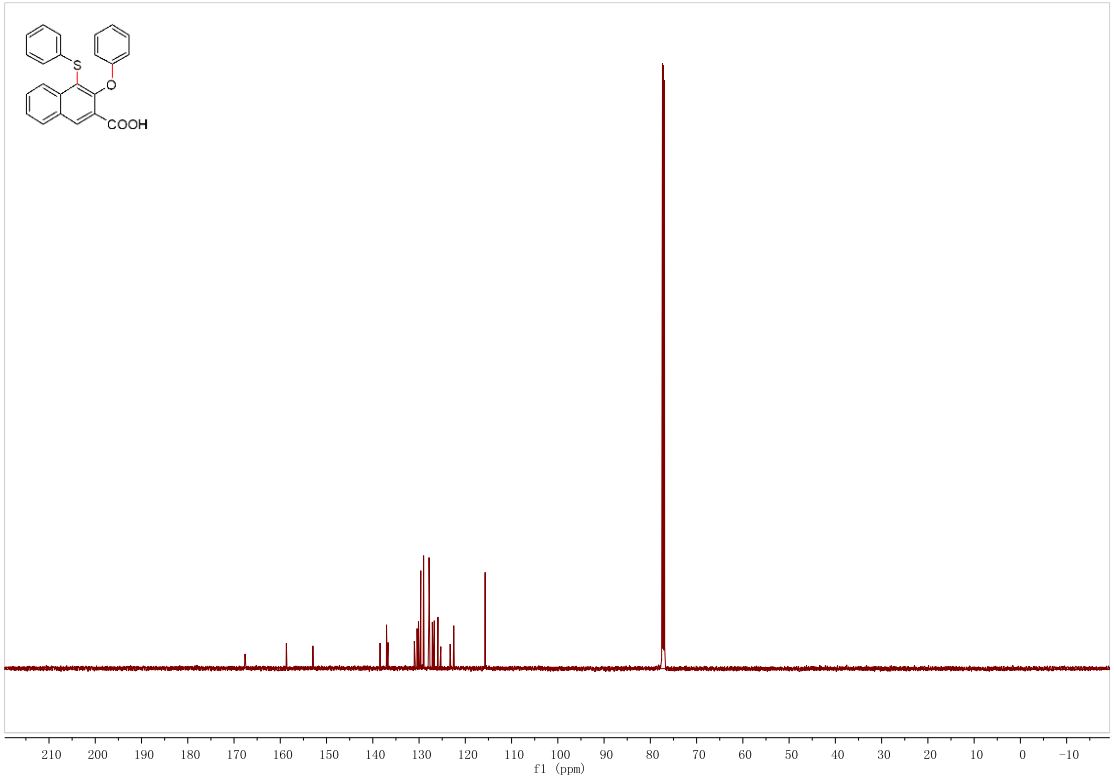
Methyl 3-phenoxy-4-(phenylthio)-2-naphthoate (4fa)



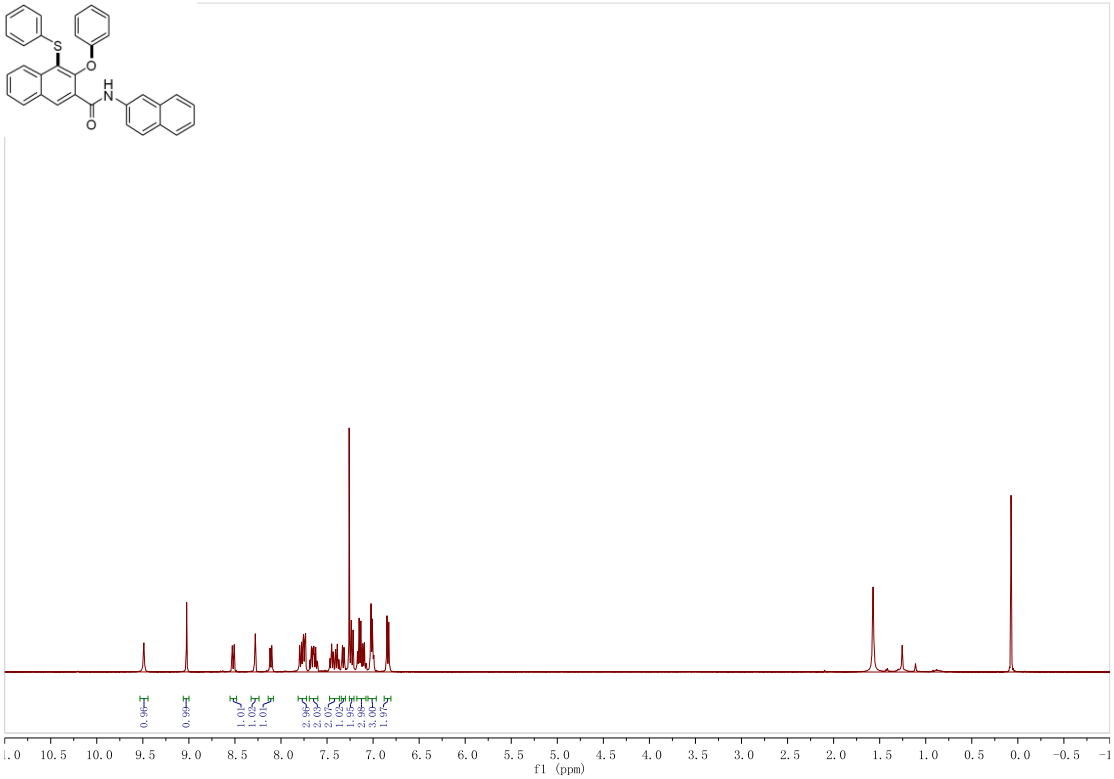


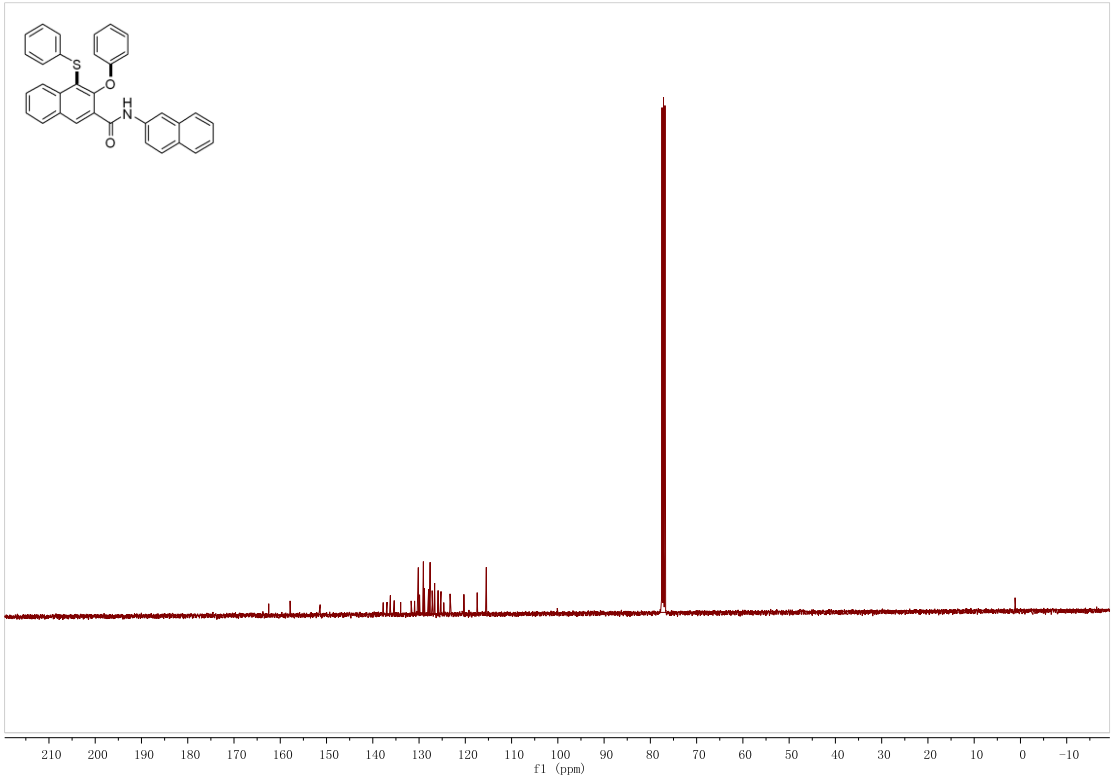
3-Phenoxy-4-(phenylthio)-2-naphthoic acid (4fa')



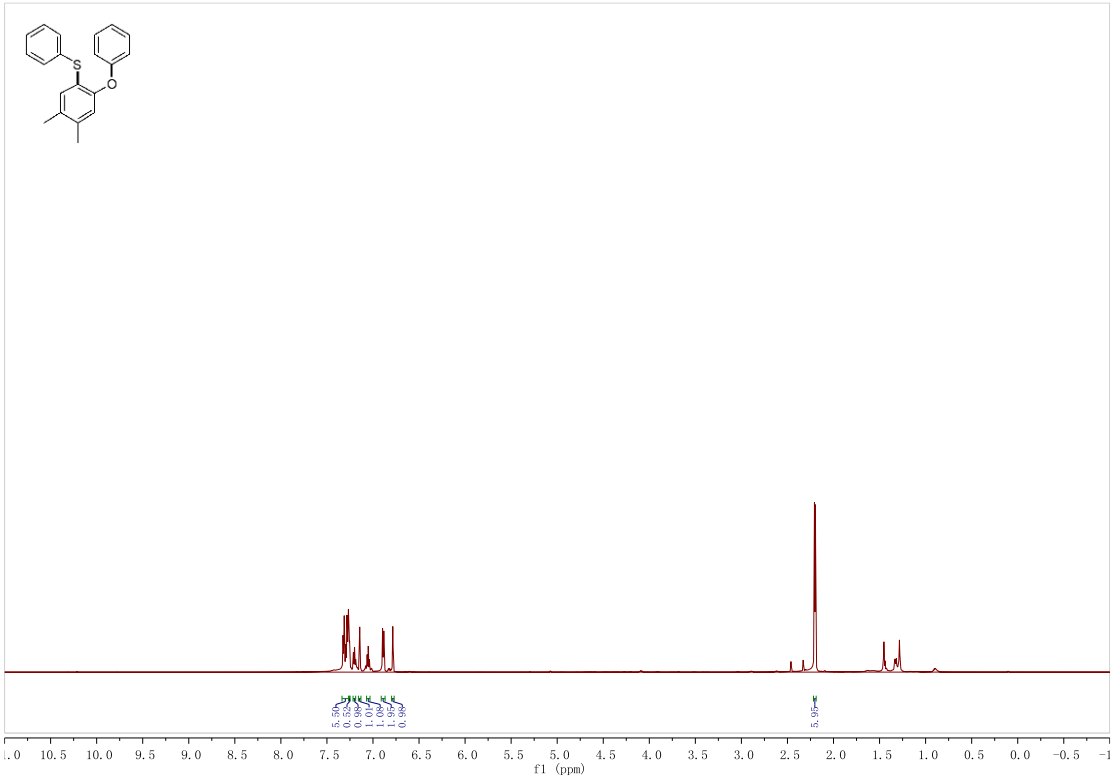


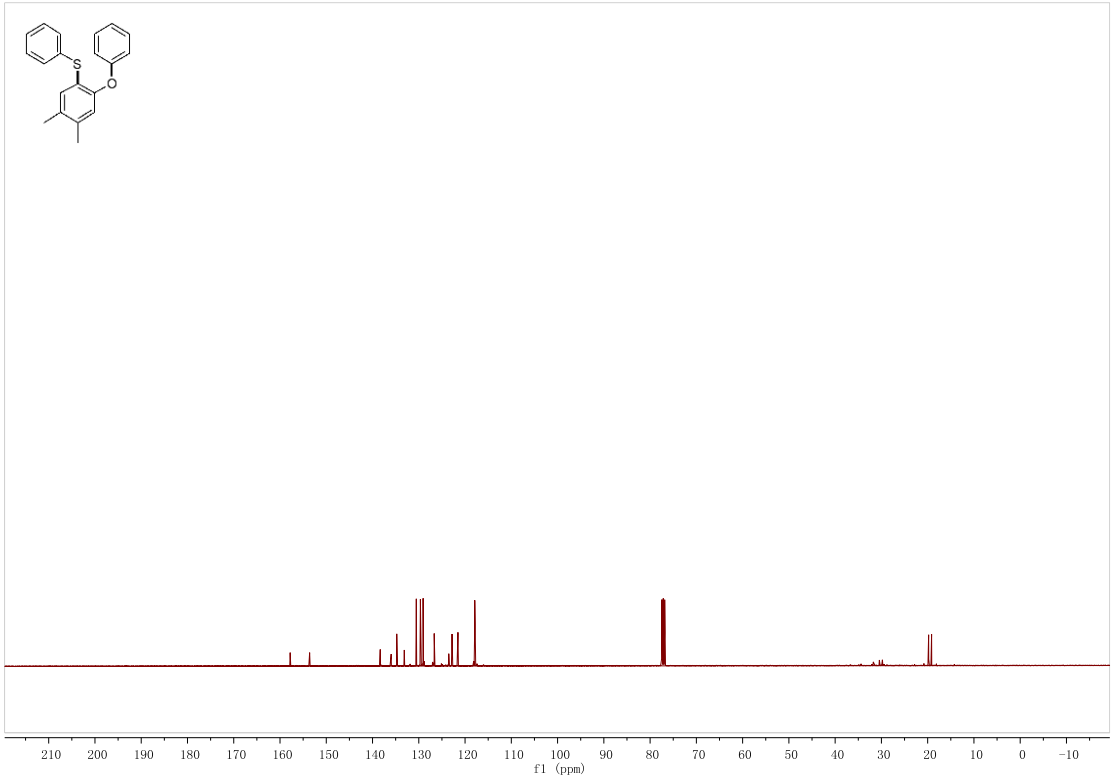
N-(Naphthalen-2-yl)-3-phenoxy-4-(phenylthio)-2-naphthamide (4ga)



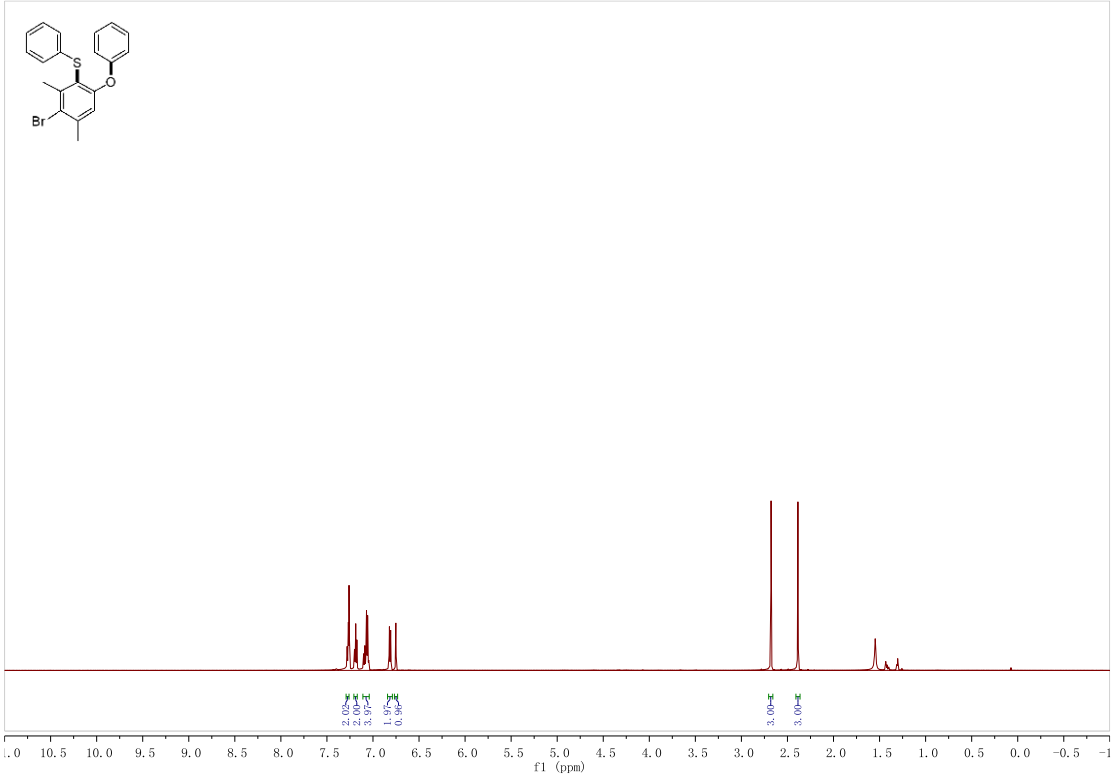


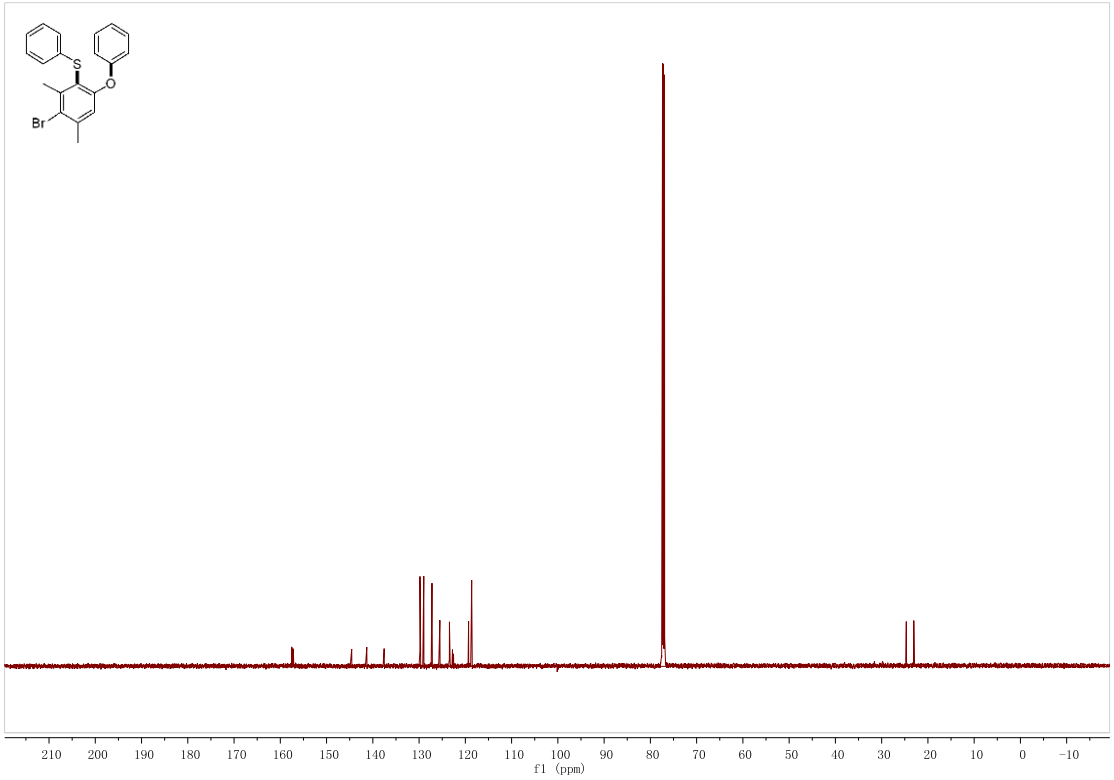
(4,5-Dimethyl-2-phenoxyphenyl)(phenyl)sulfane (4ha)



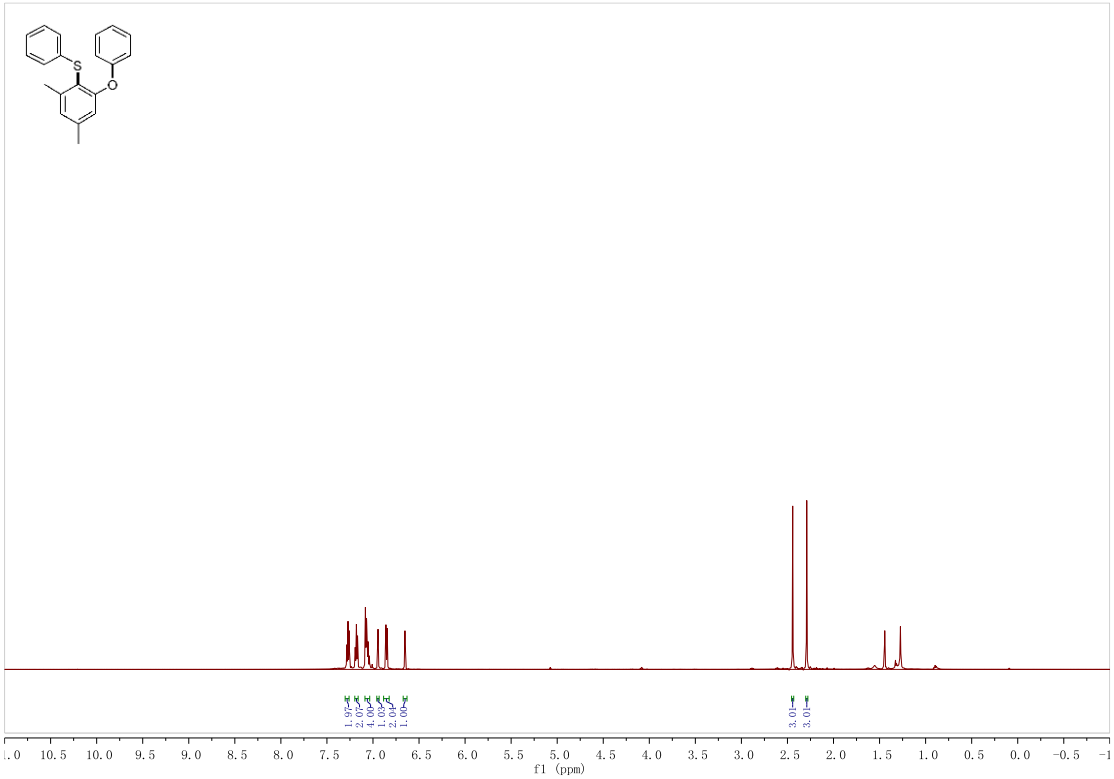


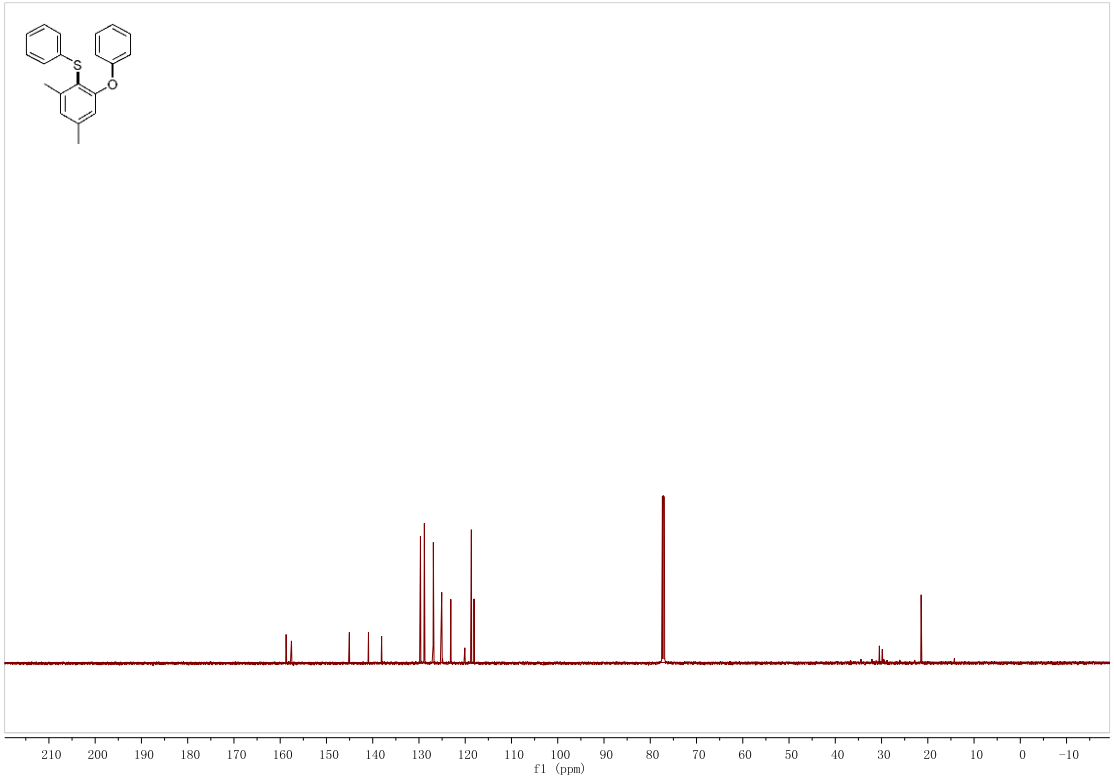
(3-Bromo-2,4-dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ia)



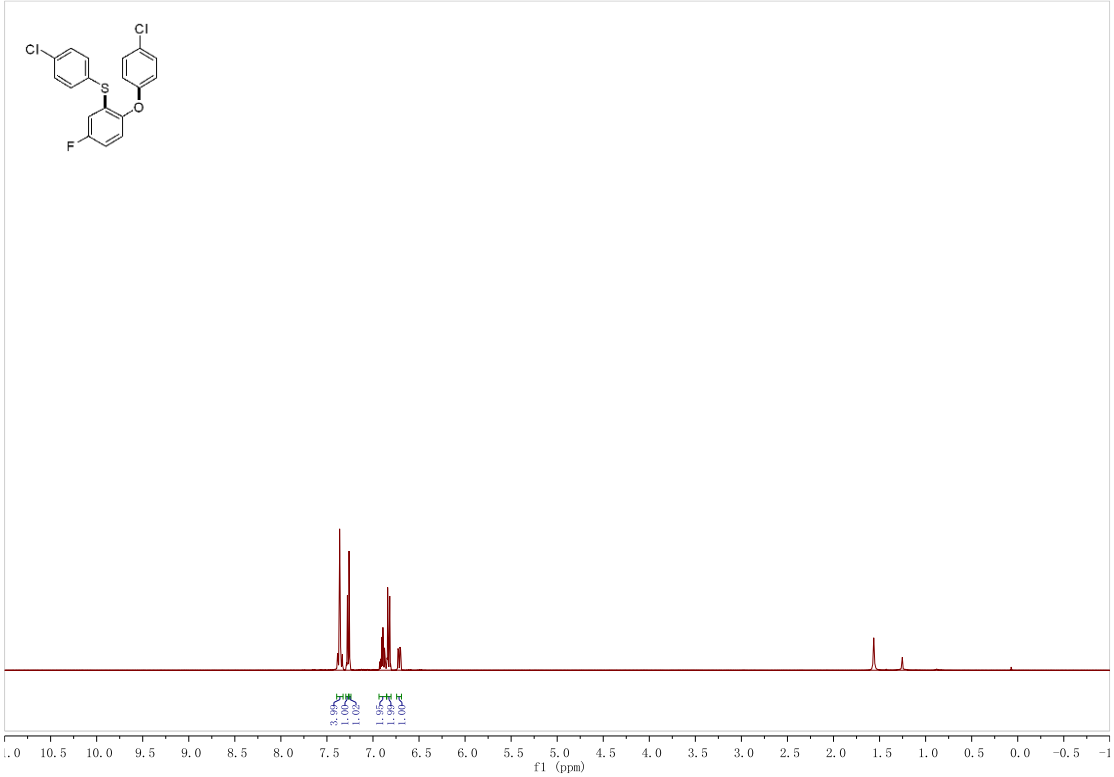


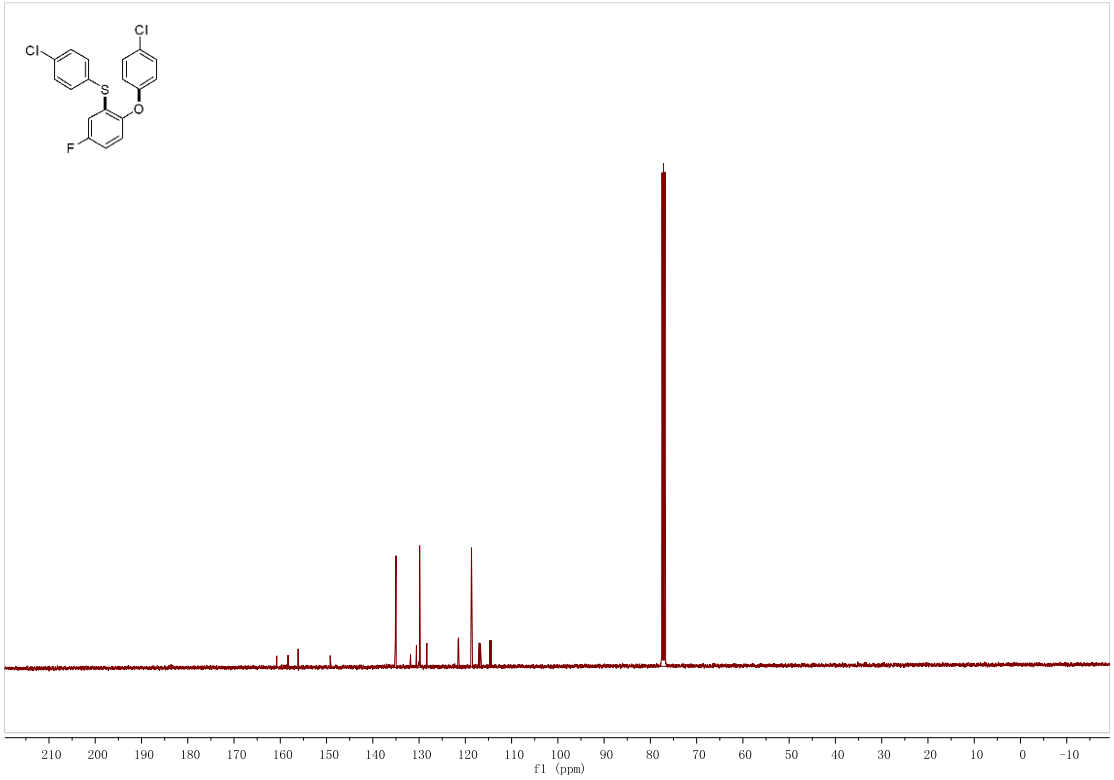
(2,4-Dimethyl-6-phenoxyphenyl)(phenyl)sulfane (4ja)



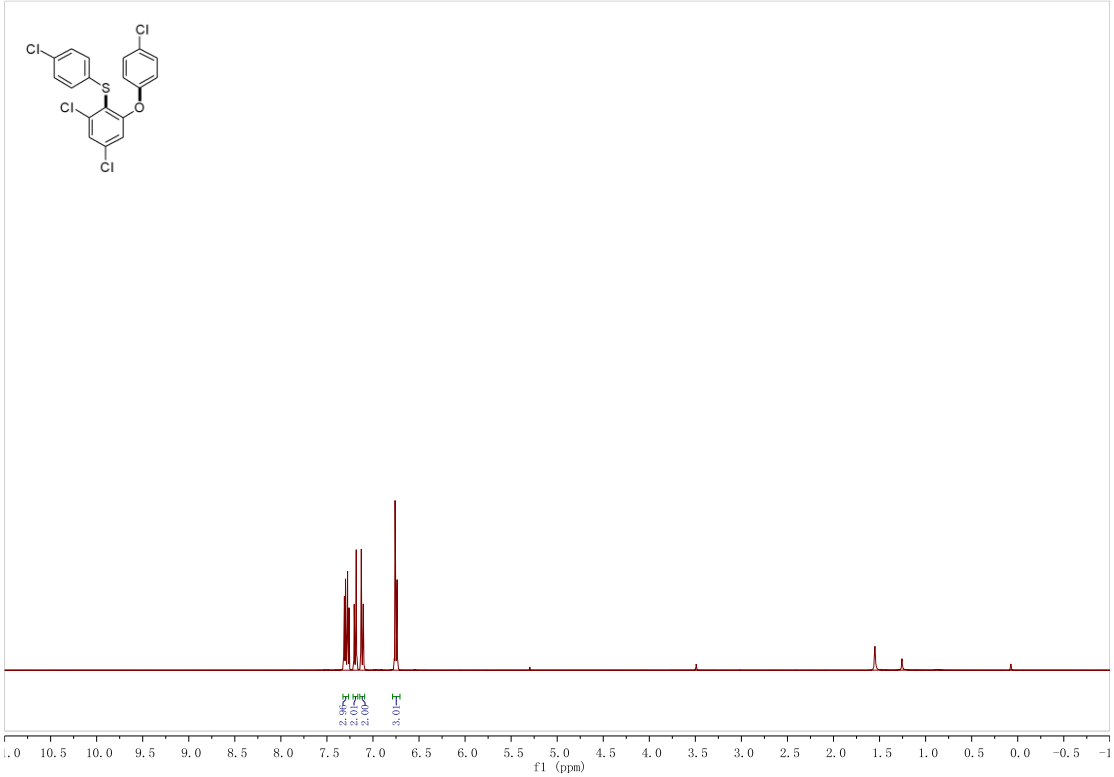


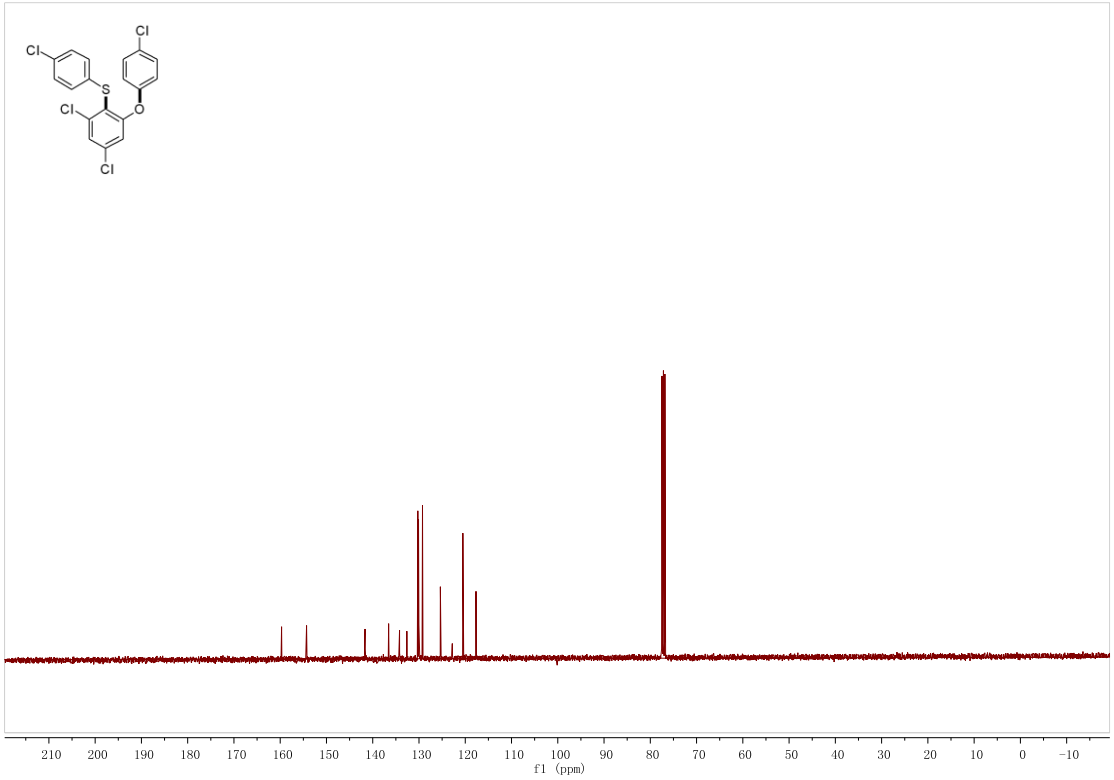
(2-(4-Chlorophenoxy)-5-fluorophenyl)(4-chlorophenyl)sulfane (4kb)



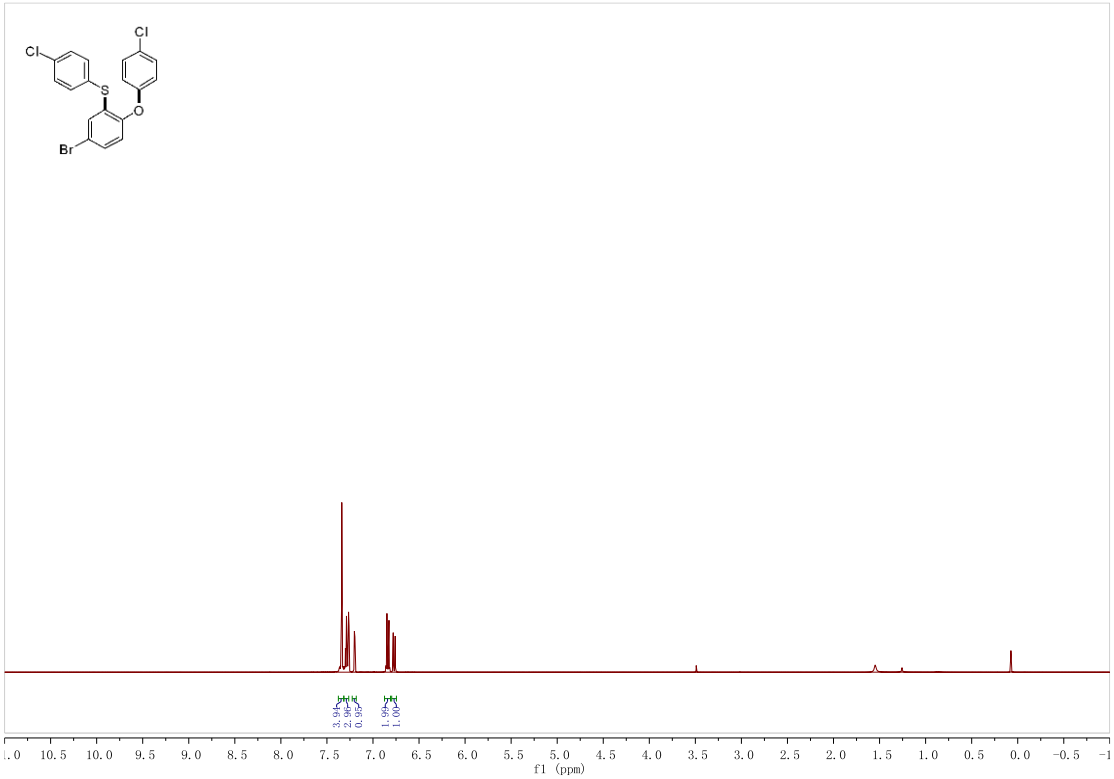


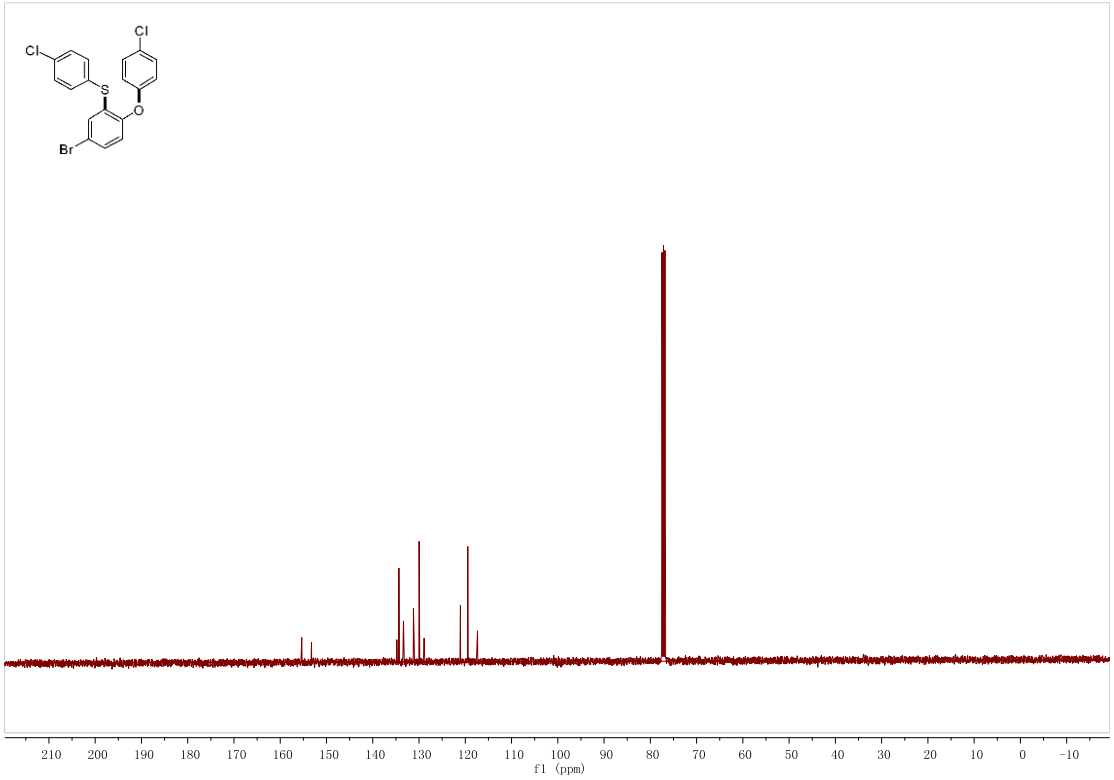
(4-Chlorophenyl)(2,4-dichloro-6-(4-chlorophenoxy)phenyl)sulfane (4lb)



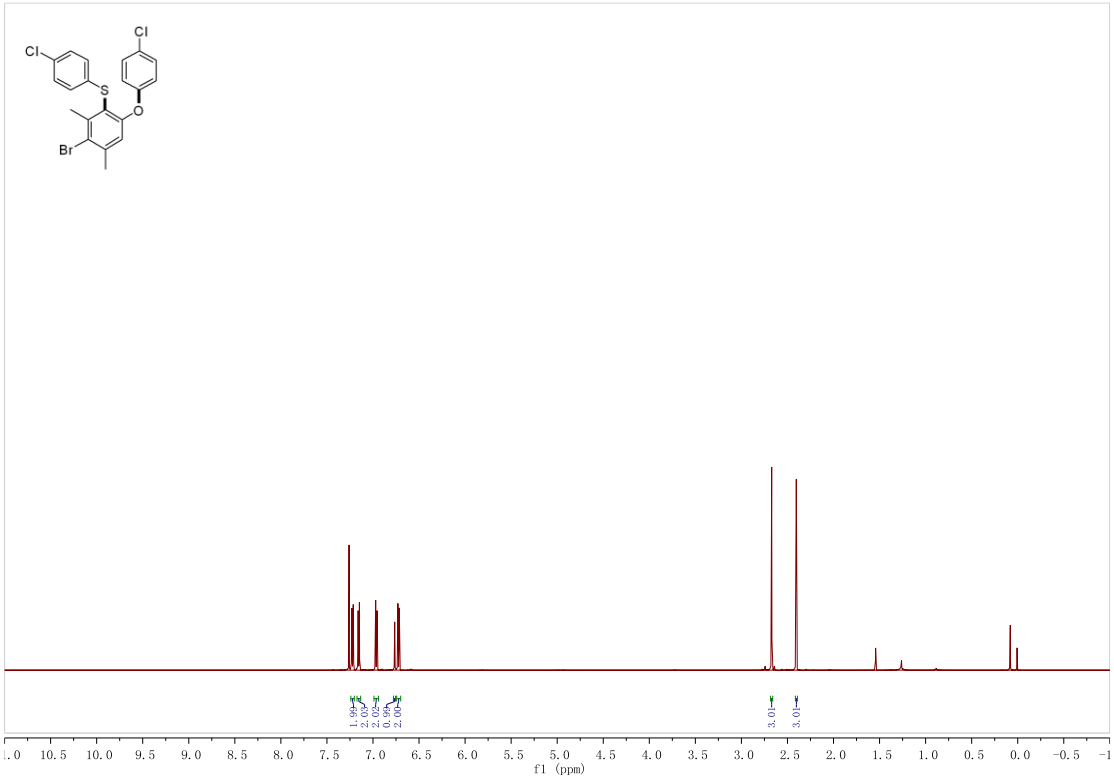


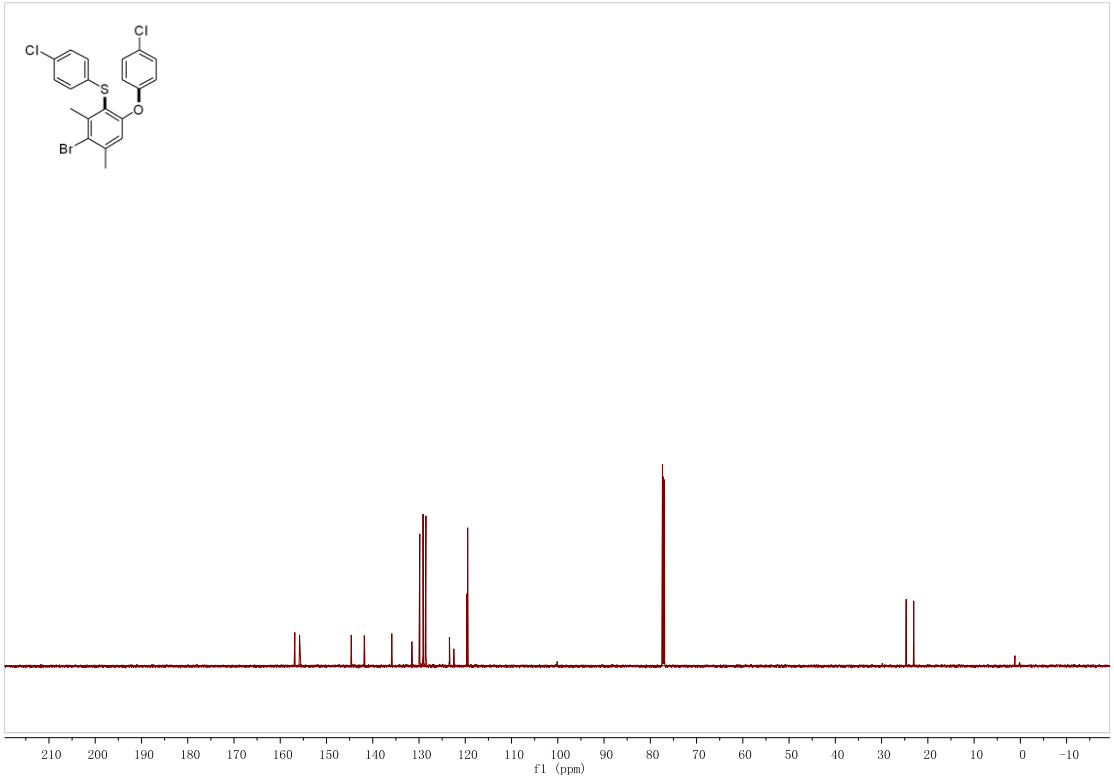
(5-Bromo-2-(4-chlorophenoxy)phenyl)(4-chlorophenyl)sulfane (4mb)



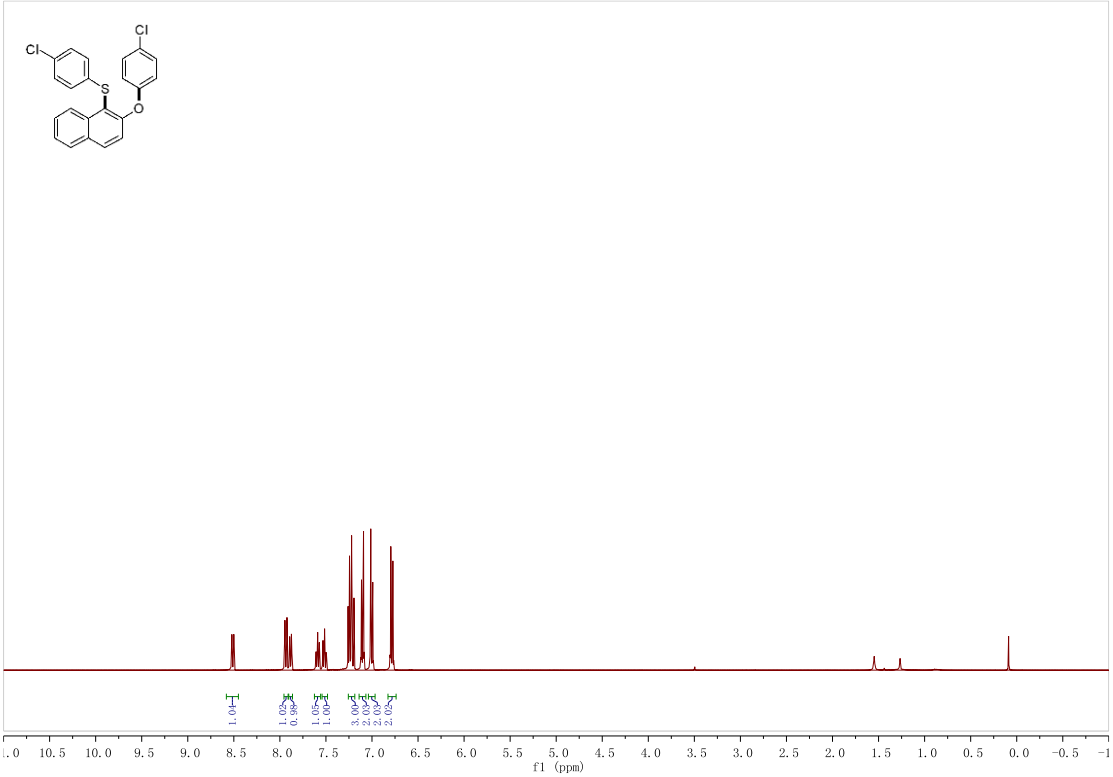


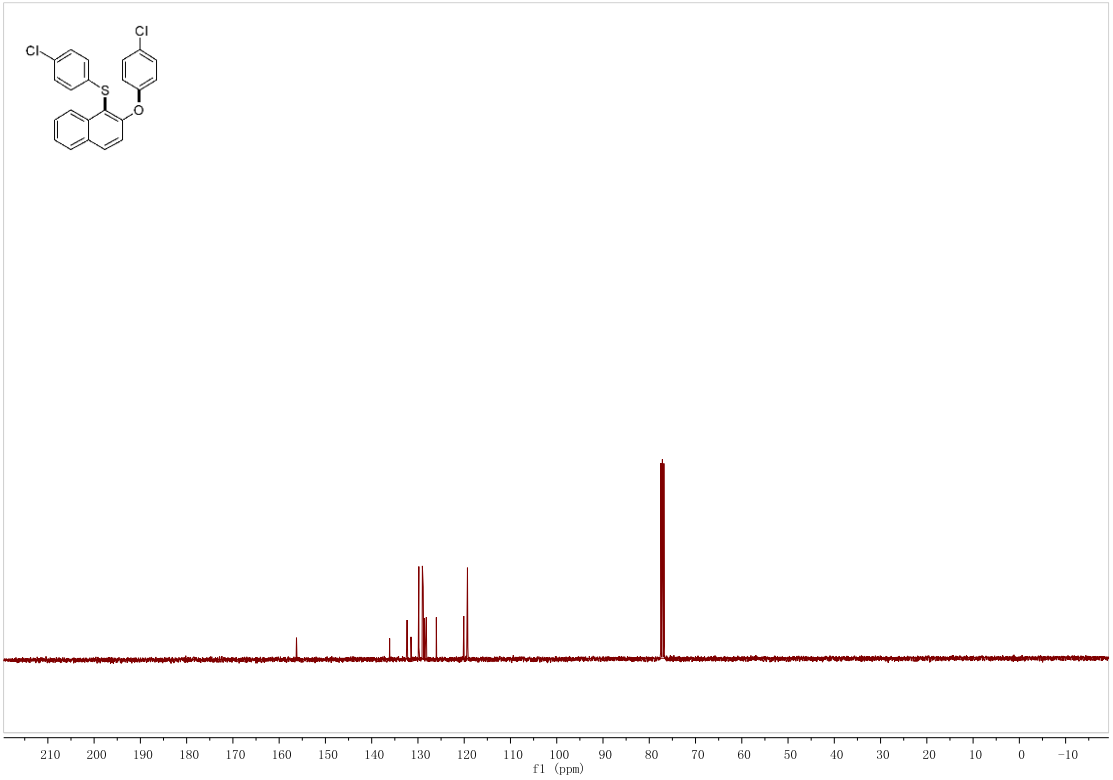
(3-Bromo-6-(4-chlorophenoxy)-2,4-dimethylphenyl)(4-chlorophenyl)sulfane (4ib)



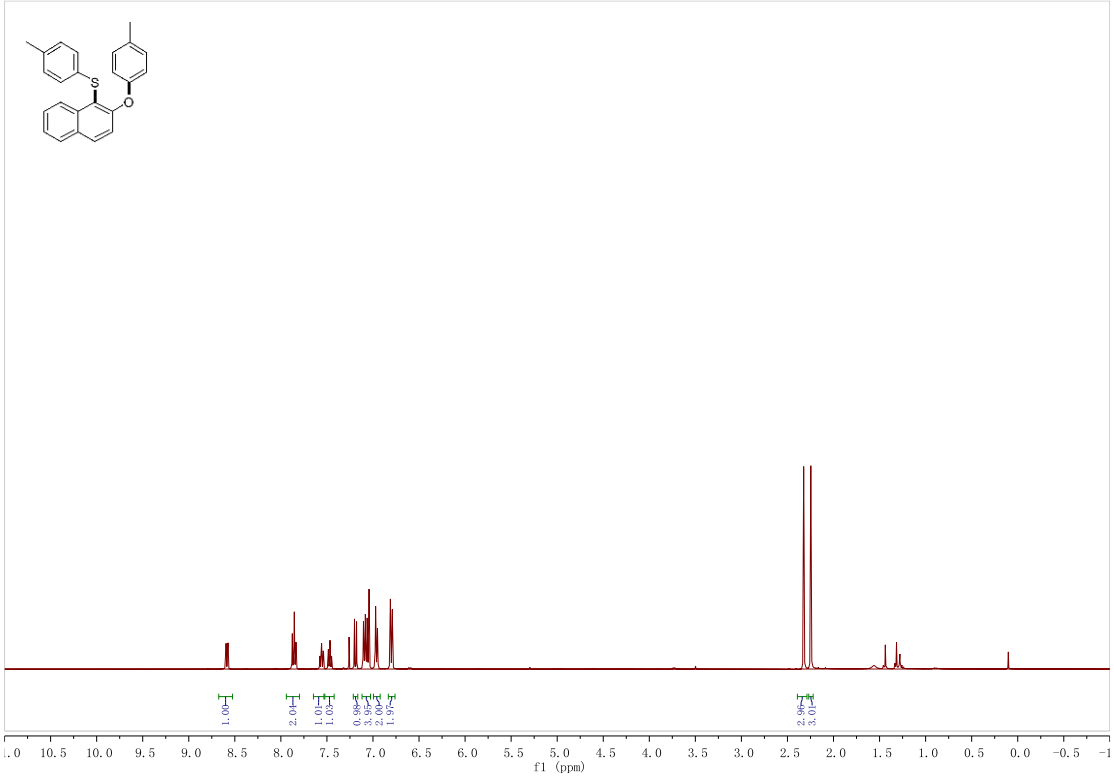


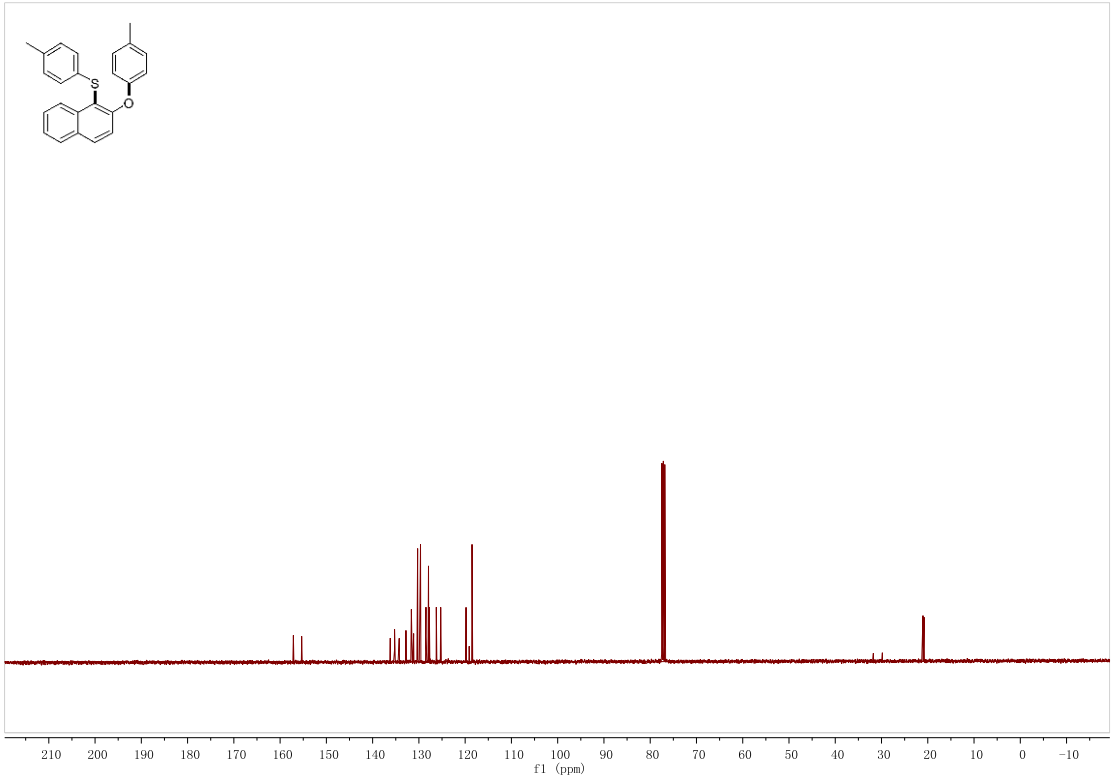
(2-(4-Chlorophenoxy)naphthalen-1-yl)(4-chlorophenyl)sulfane (4ab)



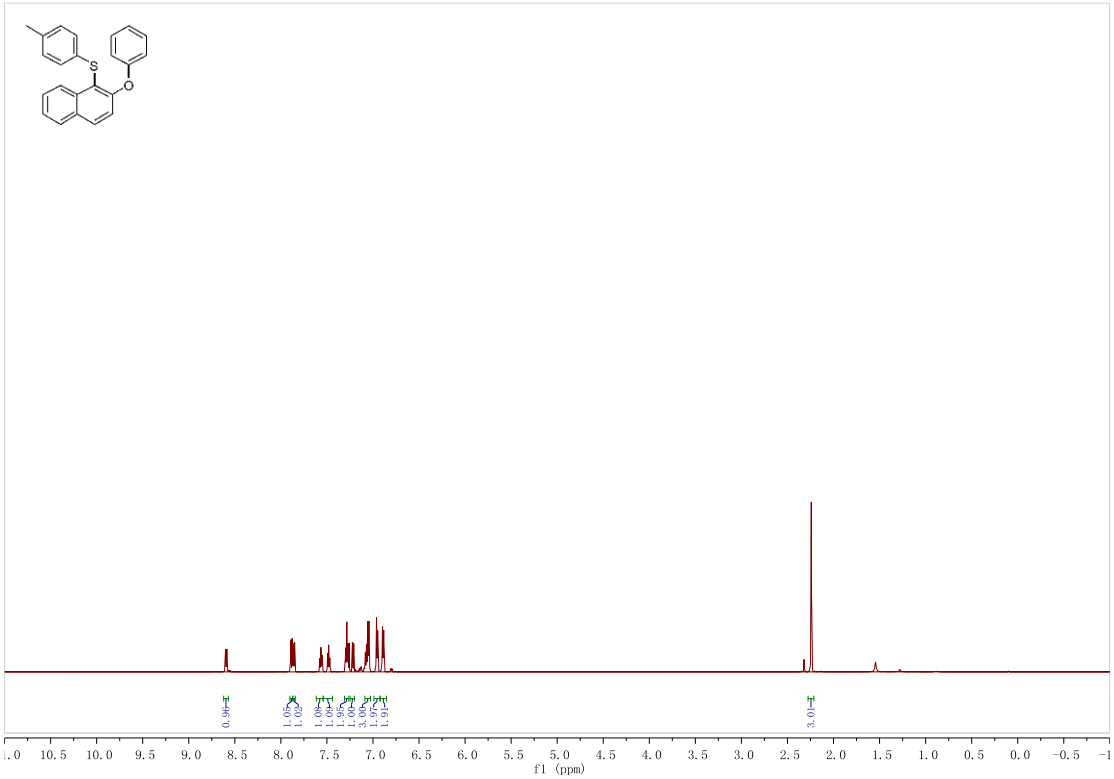


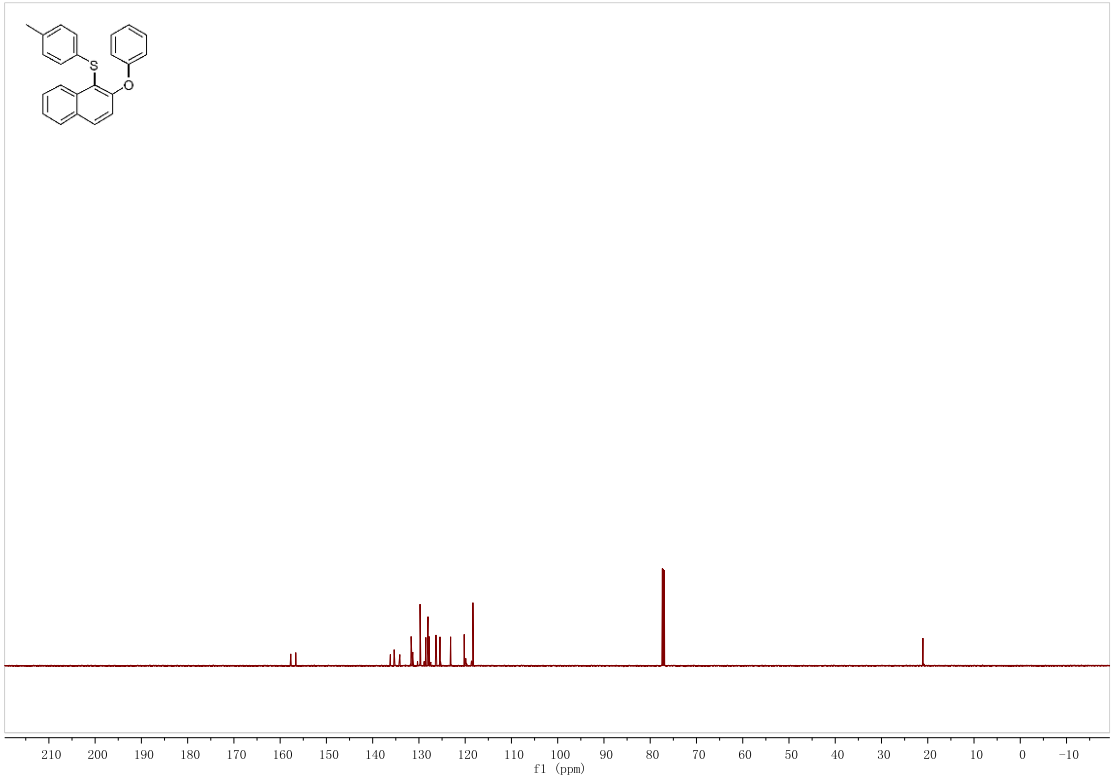
p-Tolyl(2-(p-tolyloxy)naphthalen-1-yl)sulfane (4ac)



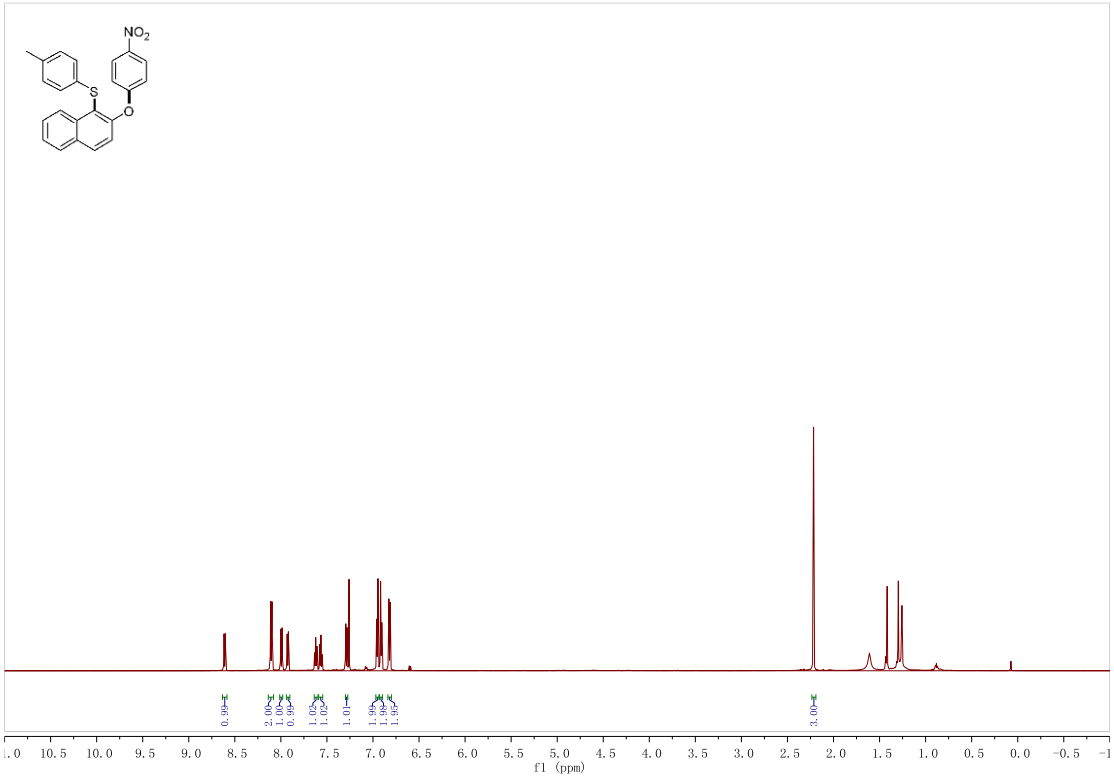


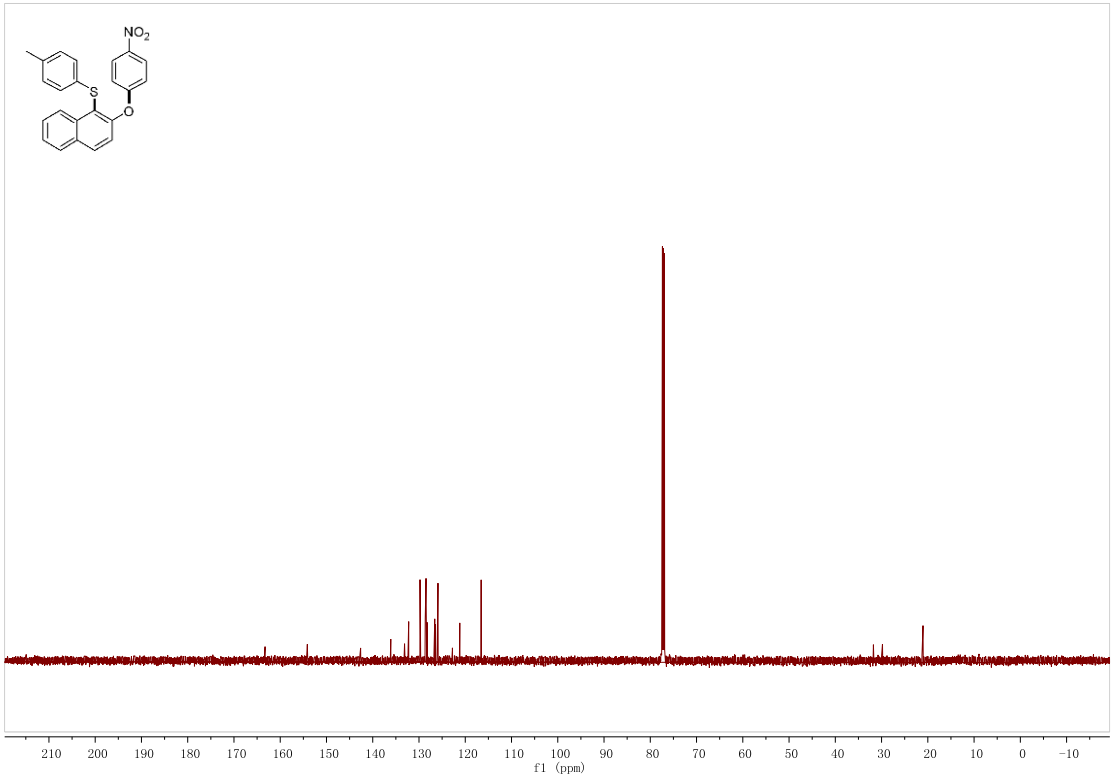
(2-Phenoxynaphthalen-1-yl)(p-tolyl)sulfane (4ad)



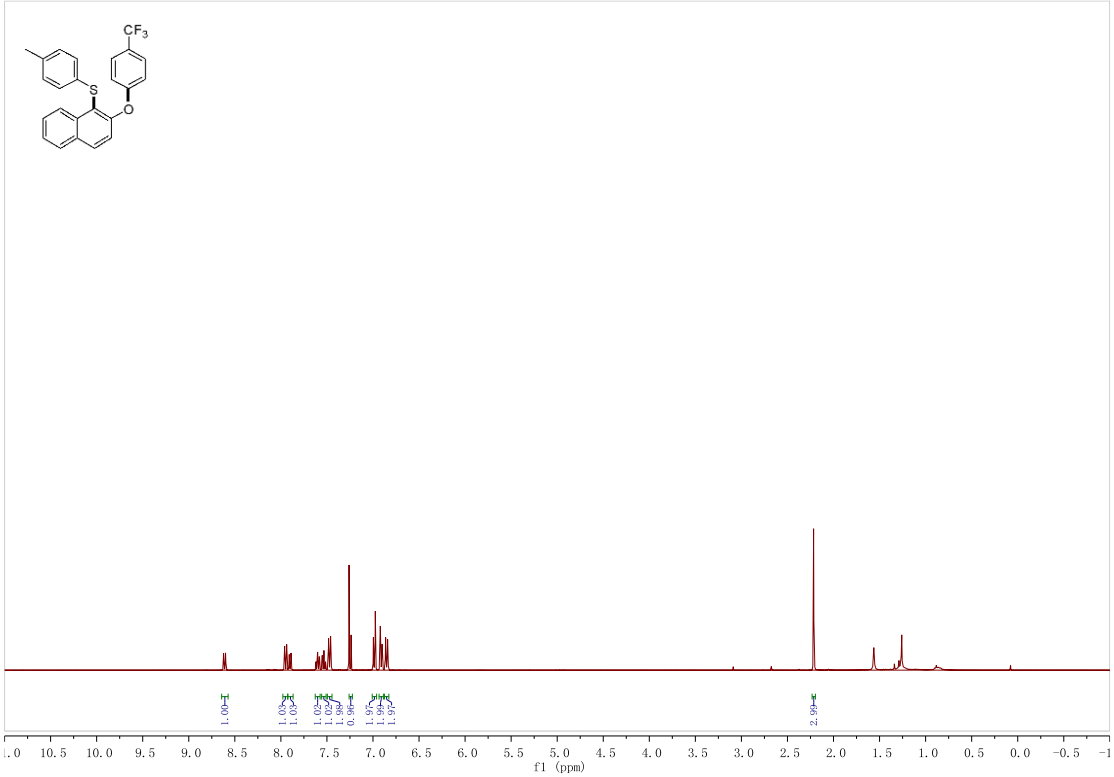


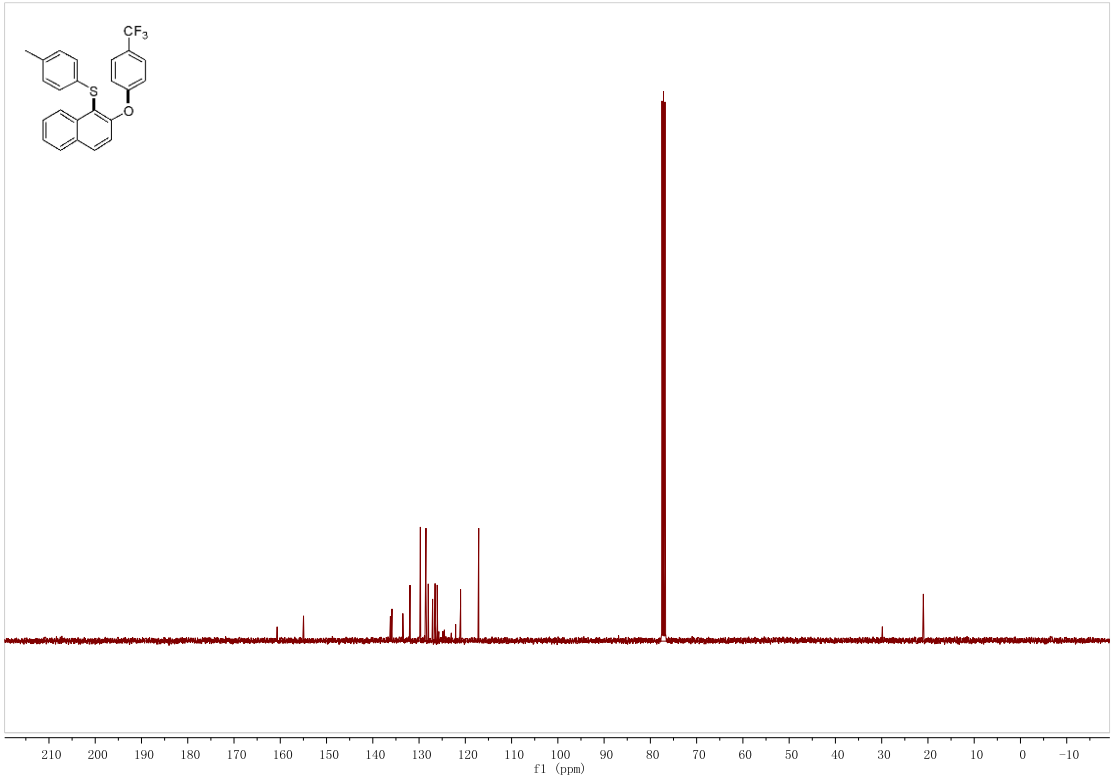
(2-(4-Nitrophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ae)



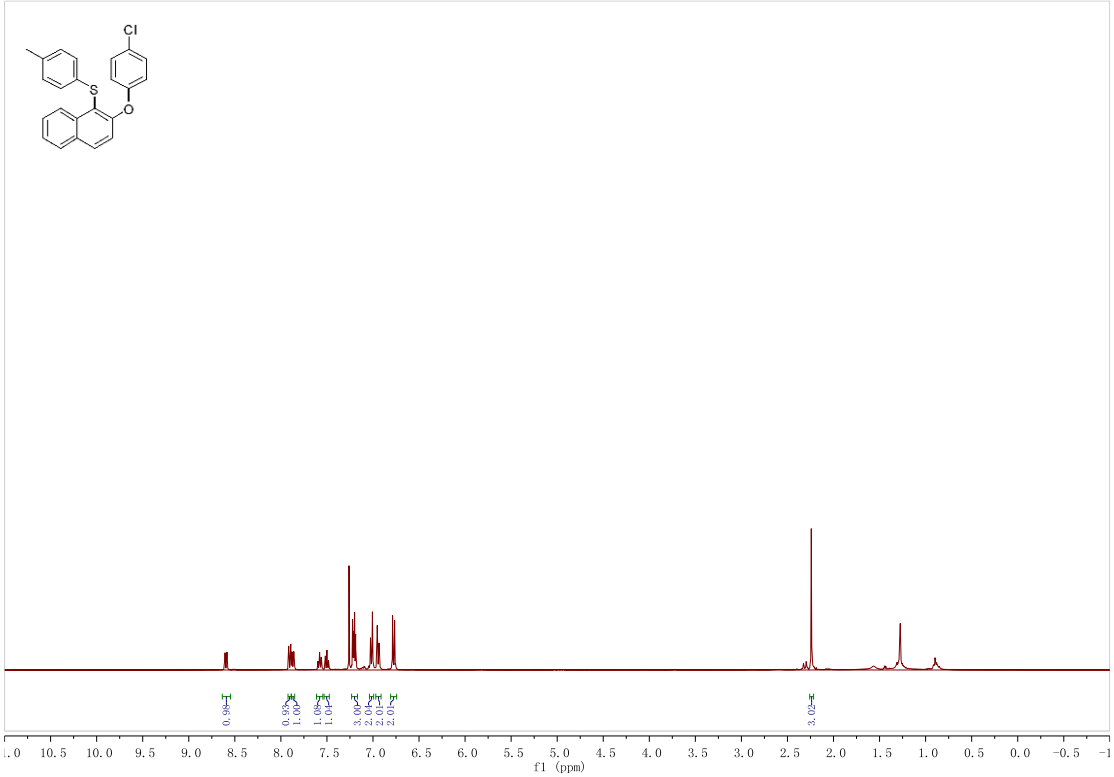


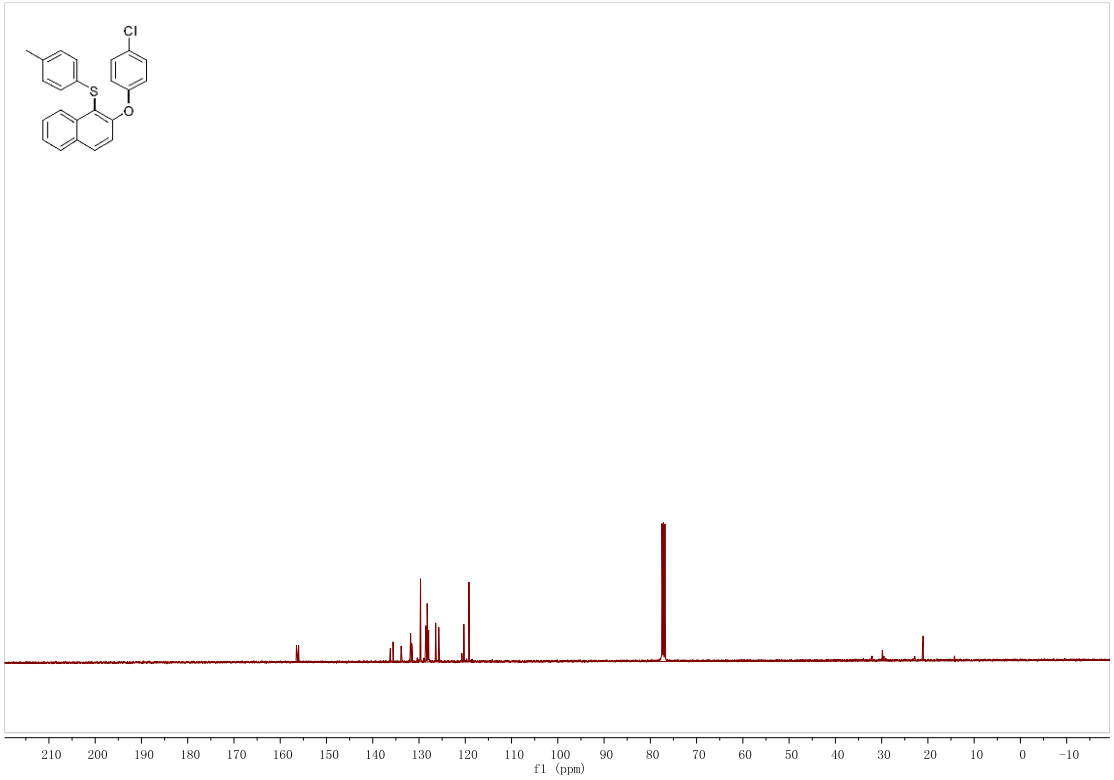
p-Tolyl(2-(4-(trifluoromethyl)phenoxy)naphthalen-1-yl)sulfane (4af)



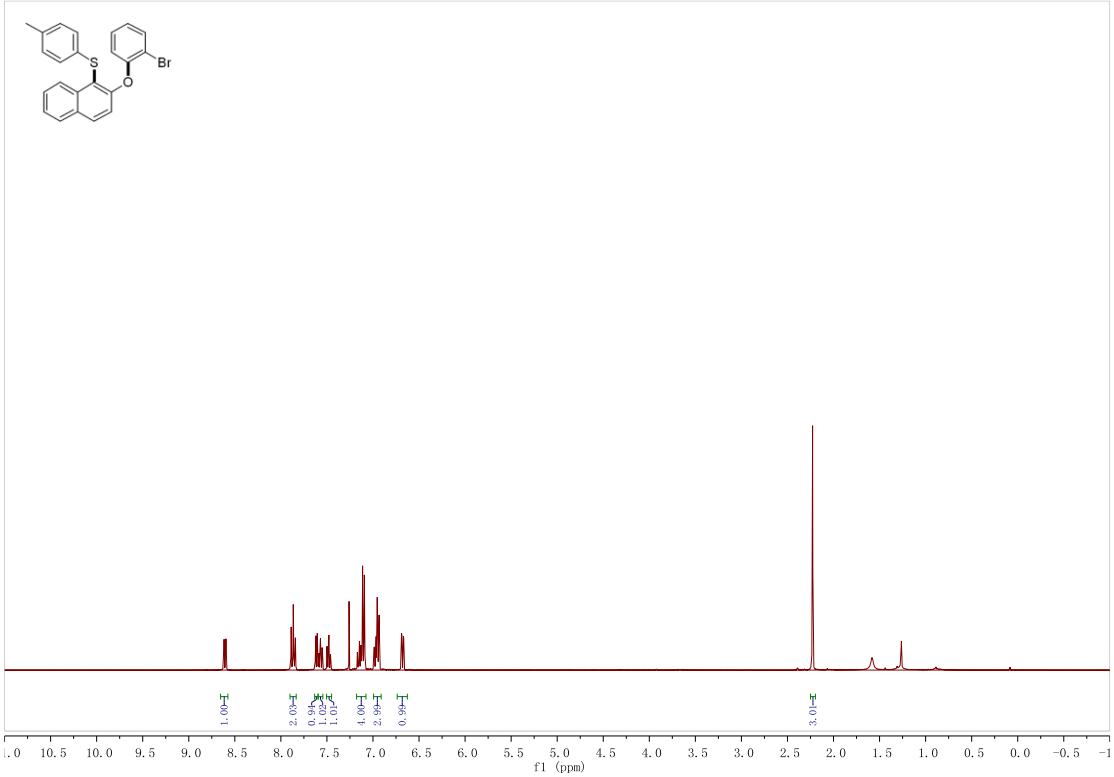


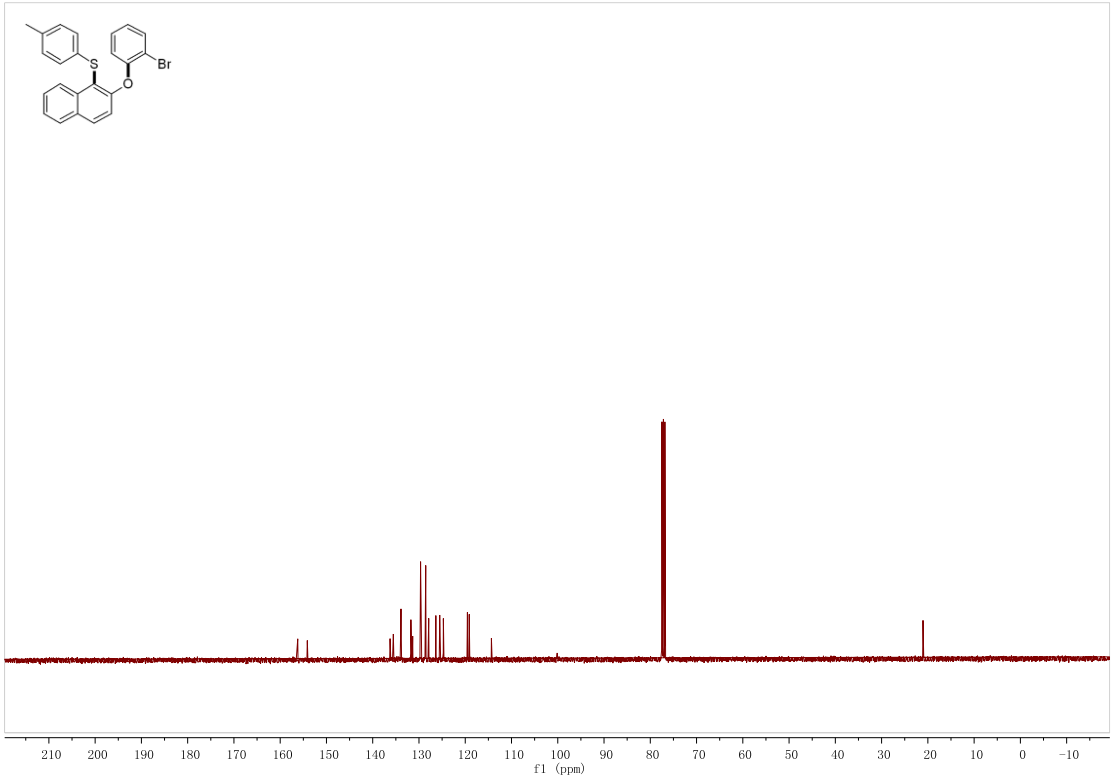
(2-(4-Chlorophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ag)



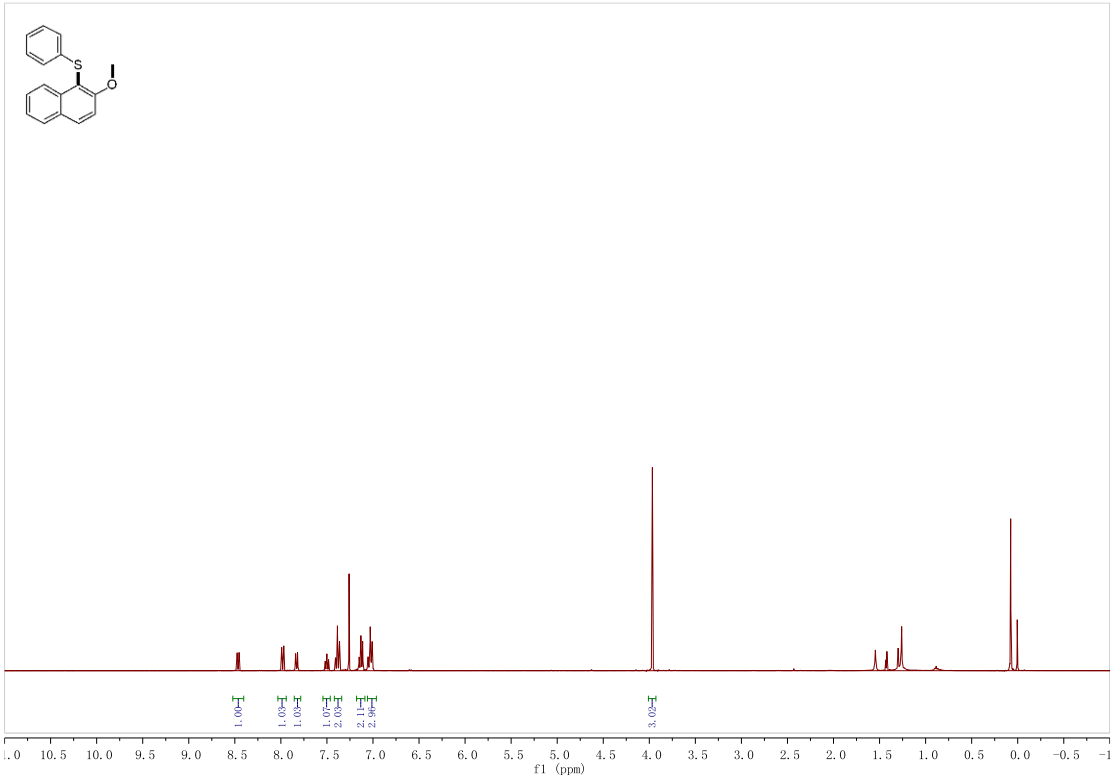


(2-(2-Bromophenoxy)naphthalen-1-yl)(p-tolyl)sulfane (4ah)

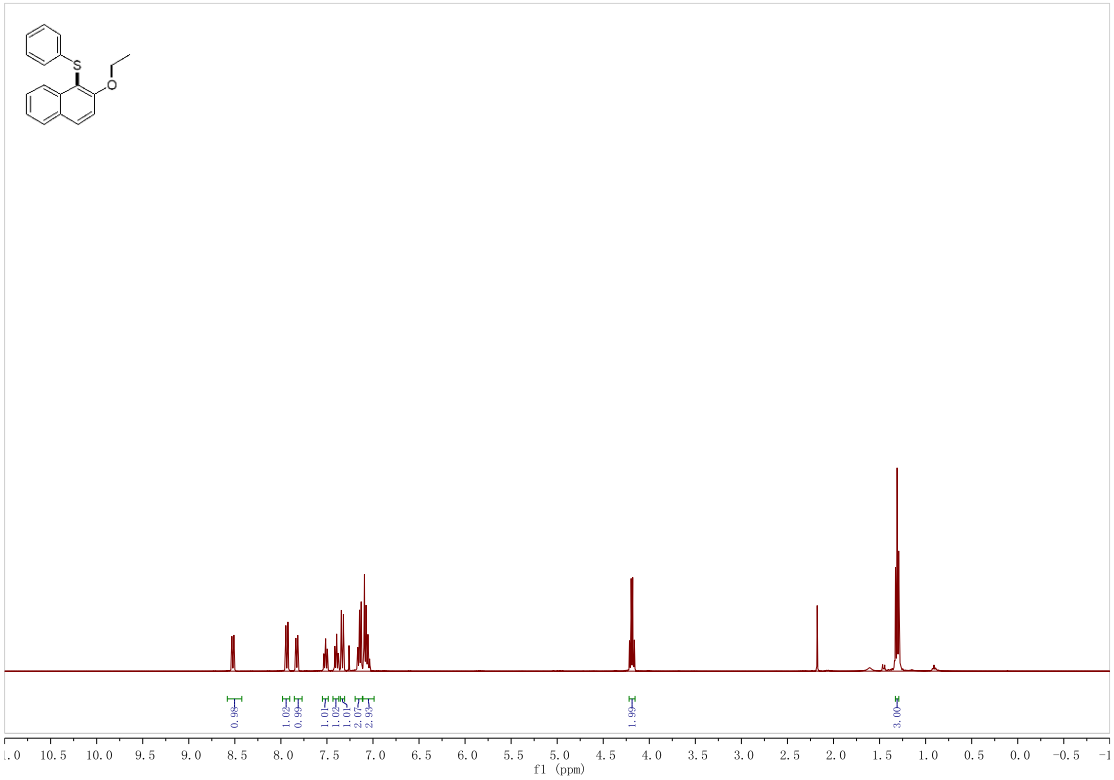




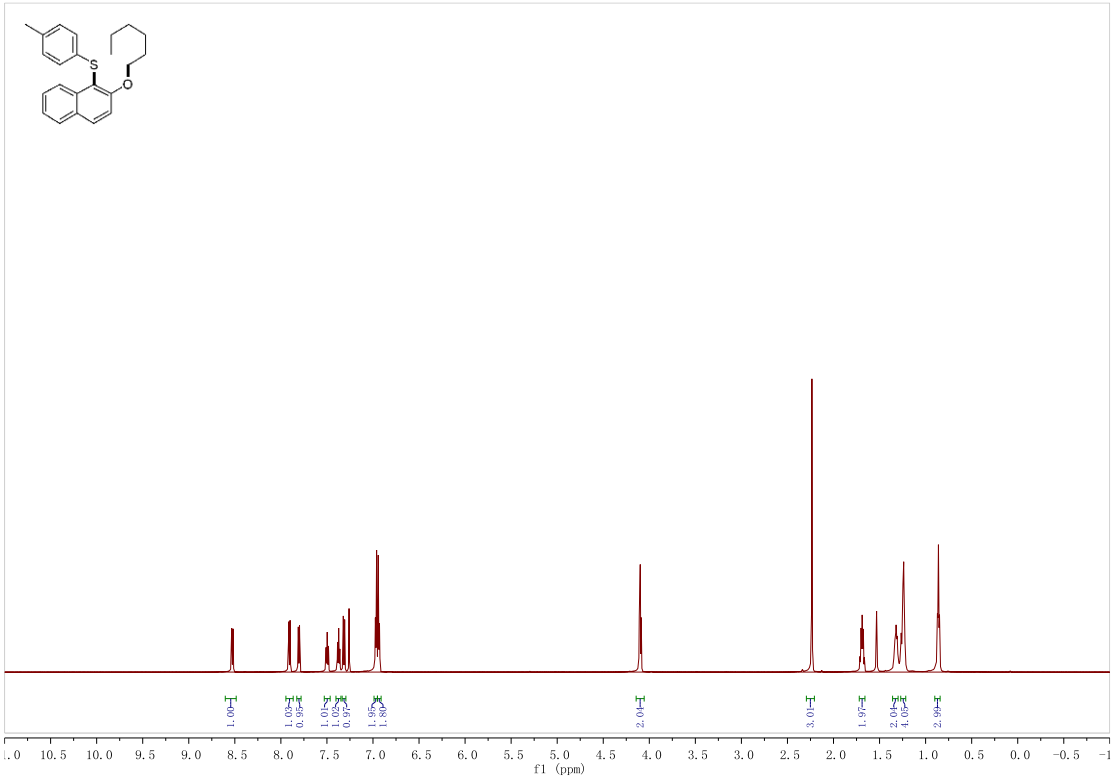
(2-Methoxynaphthalen-1-yl)(phenyl)sulfane (4ai)

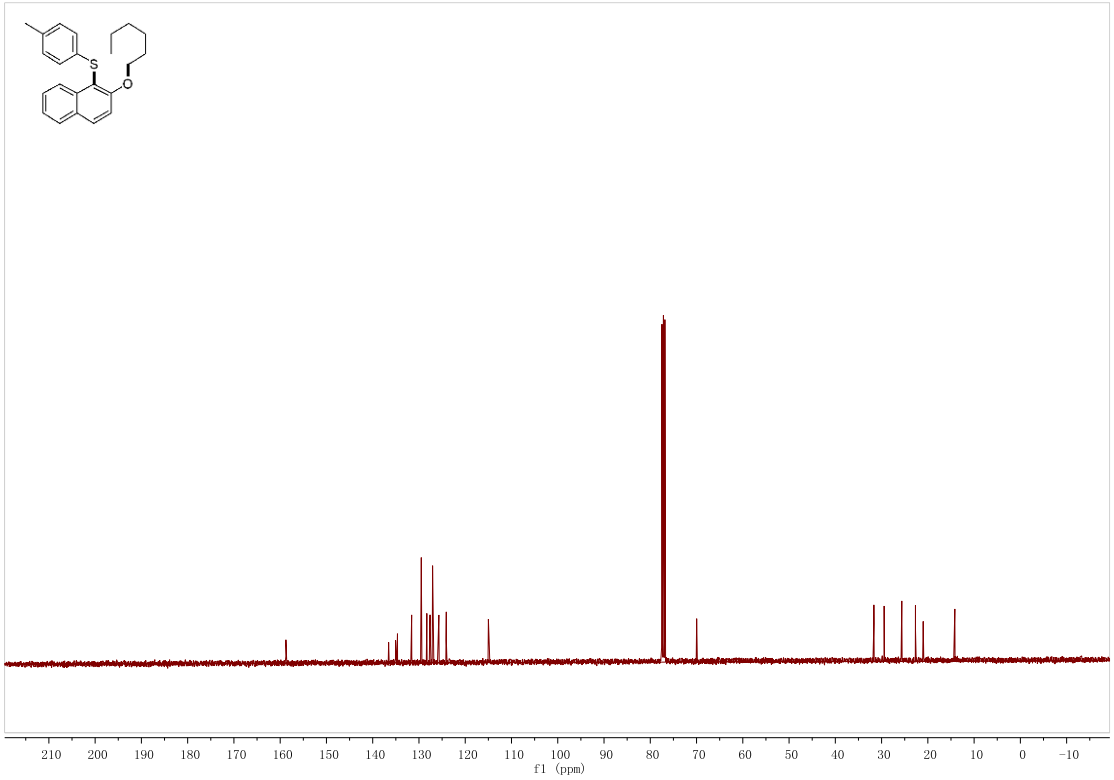


(2-Ethoxynaphthalen-1-yl)(phenyl)sulfane (4aj)

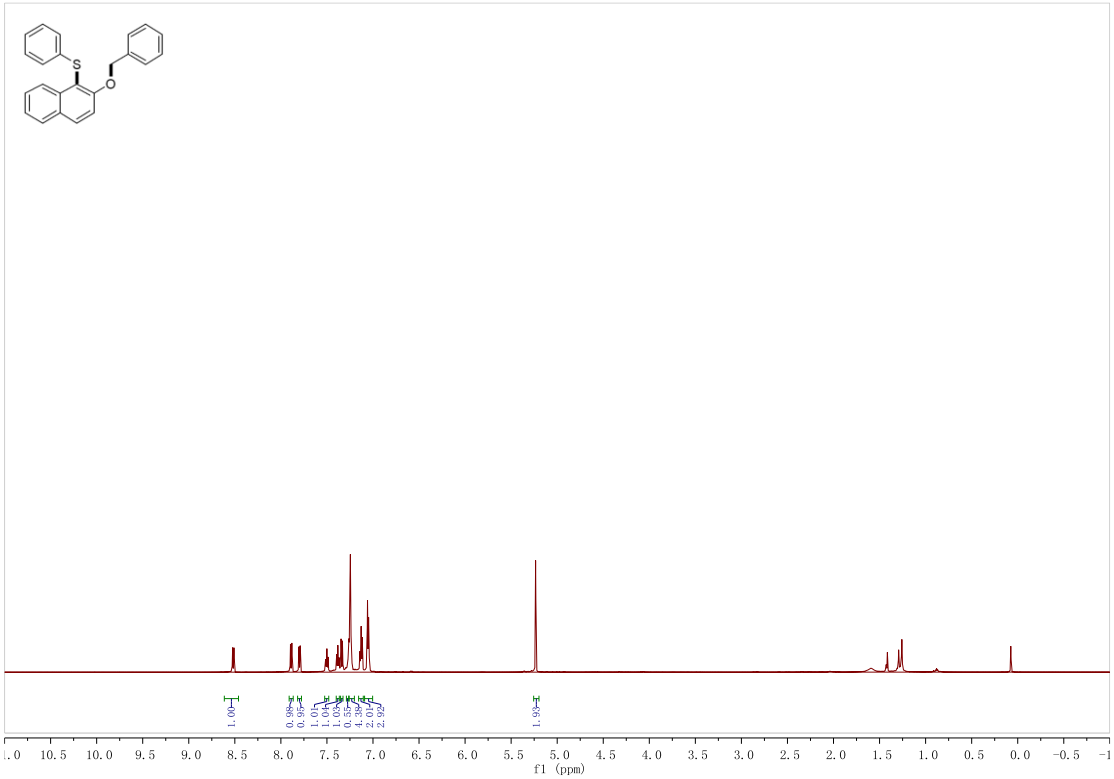


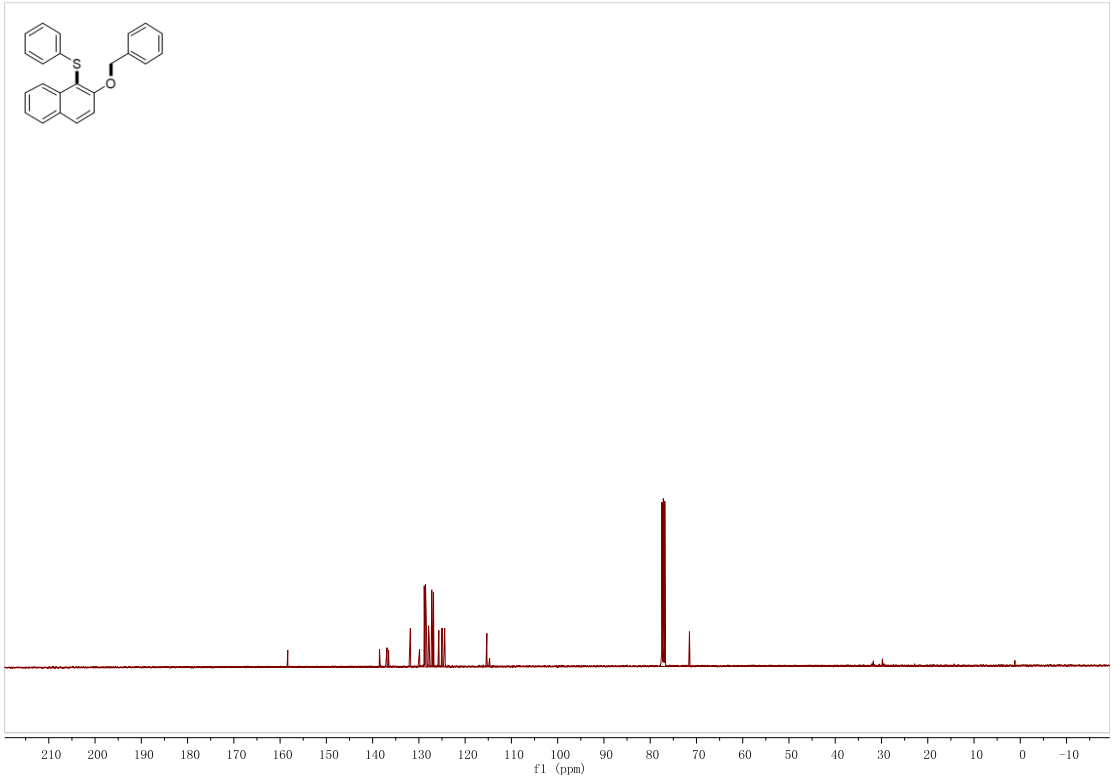
(2-(Hexyloxy)naphthalen-1-yl)(p-tolyl)sulfane (4ak)



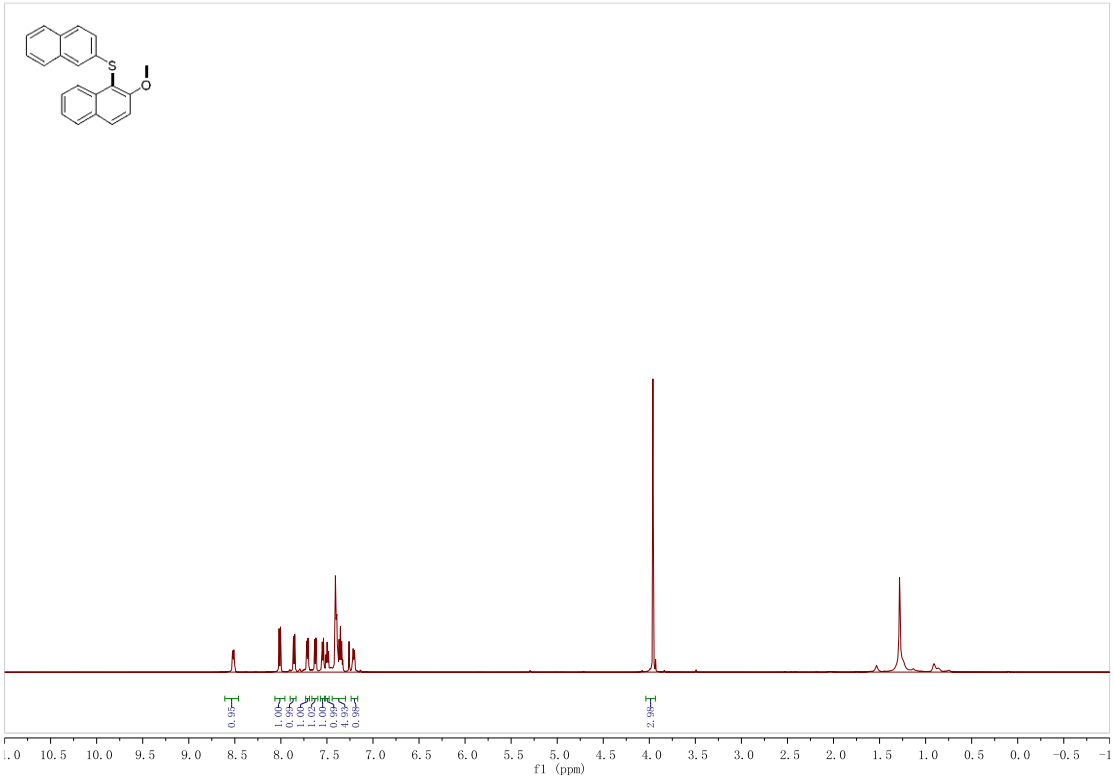


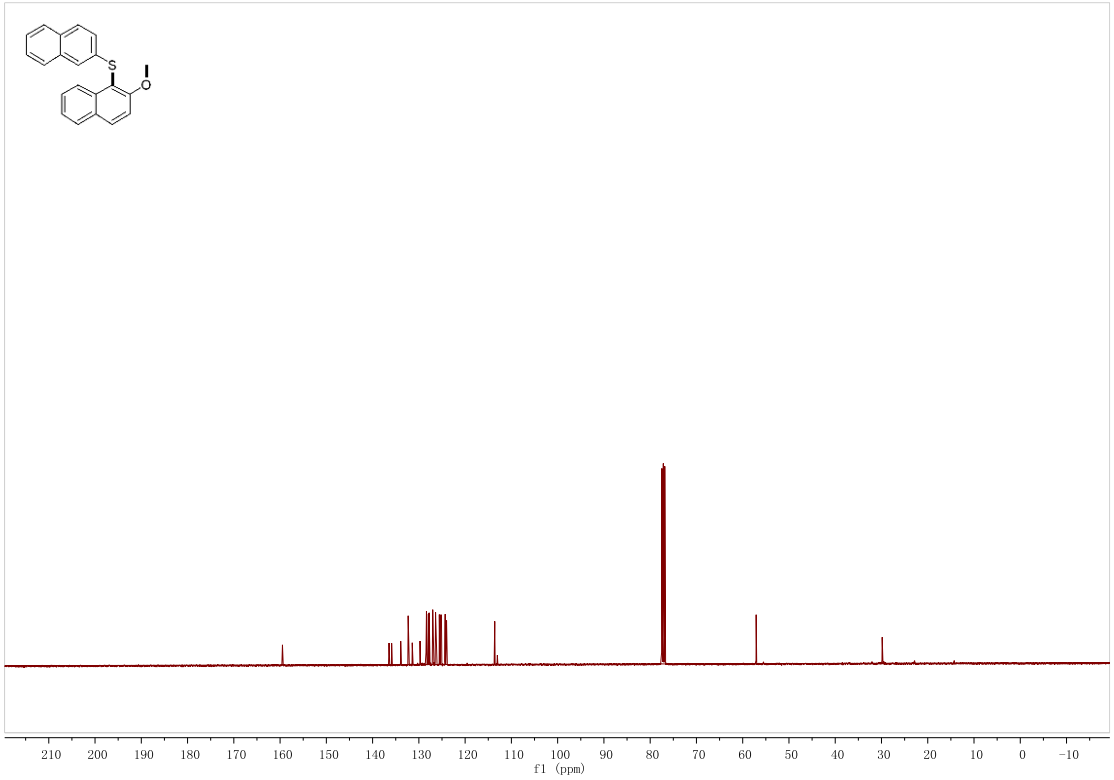
(2-(Benzyloxy)naphthalen-1-yl)(phenyl)sulfane (4al)



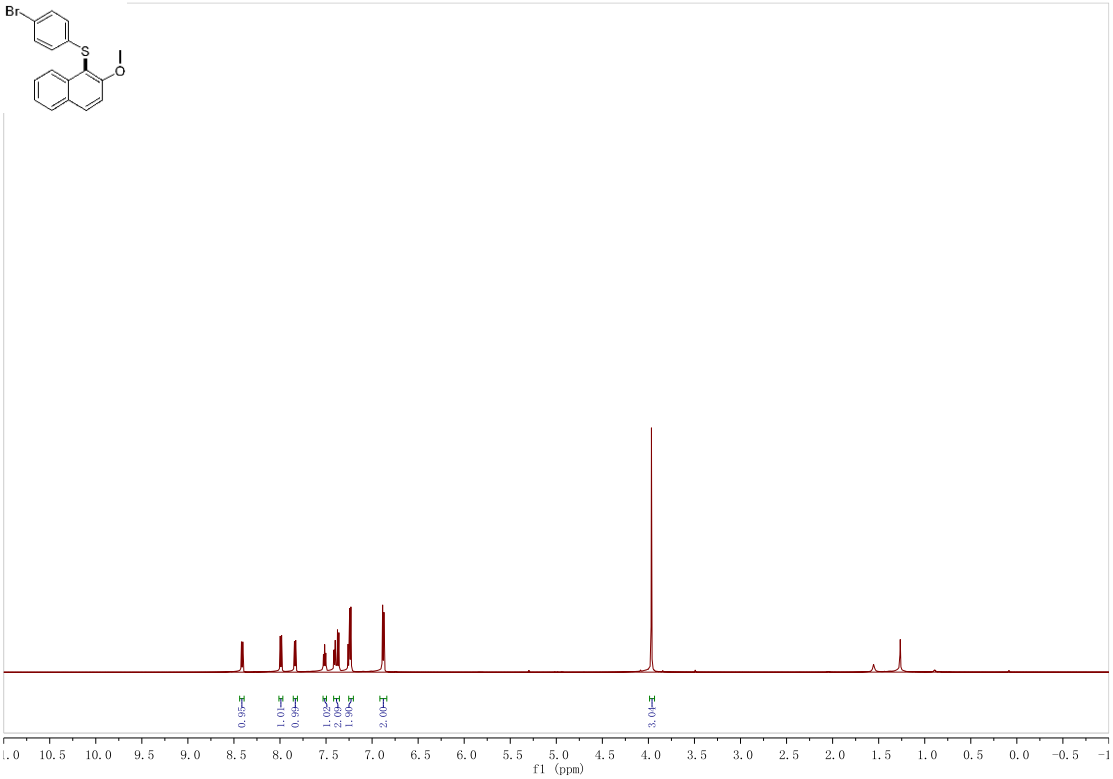


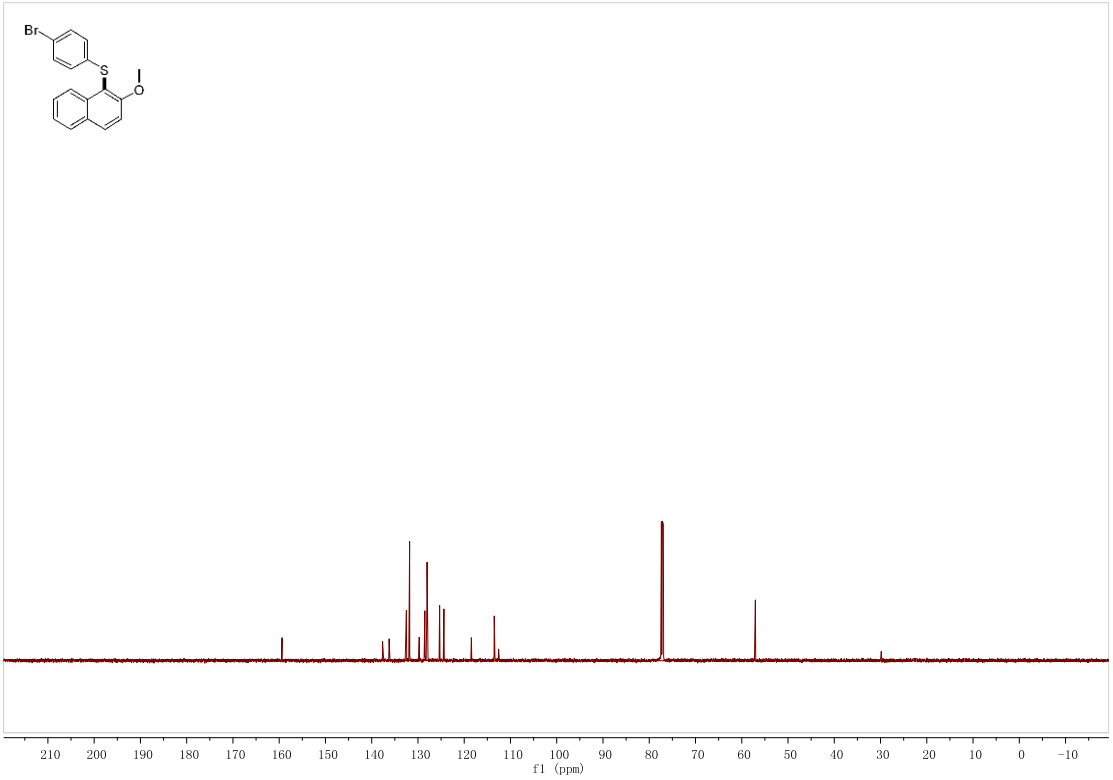
(2-Methoxynaphthalen-1-yl)(naphthalen-2-yl)sulfane (4am)



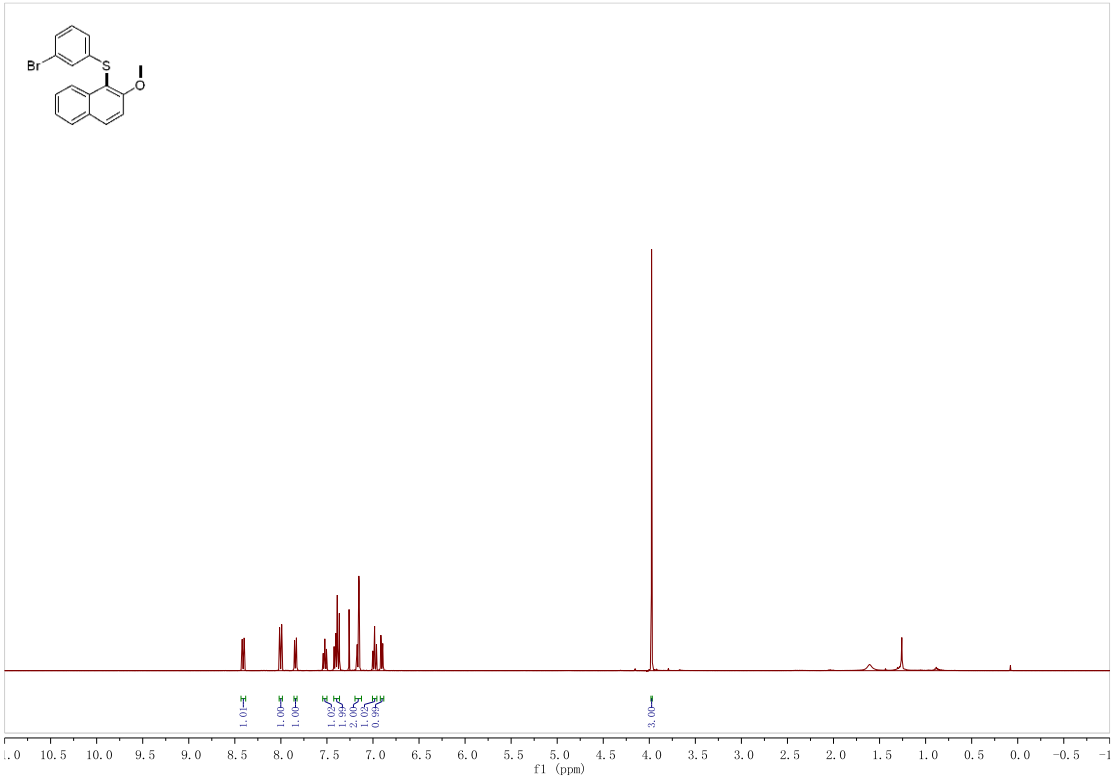


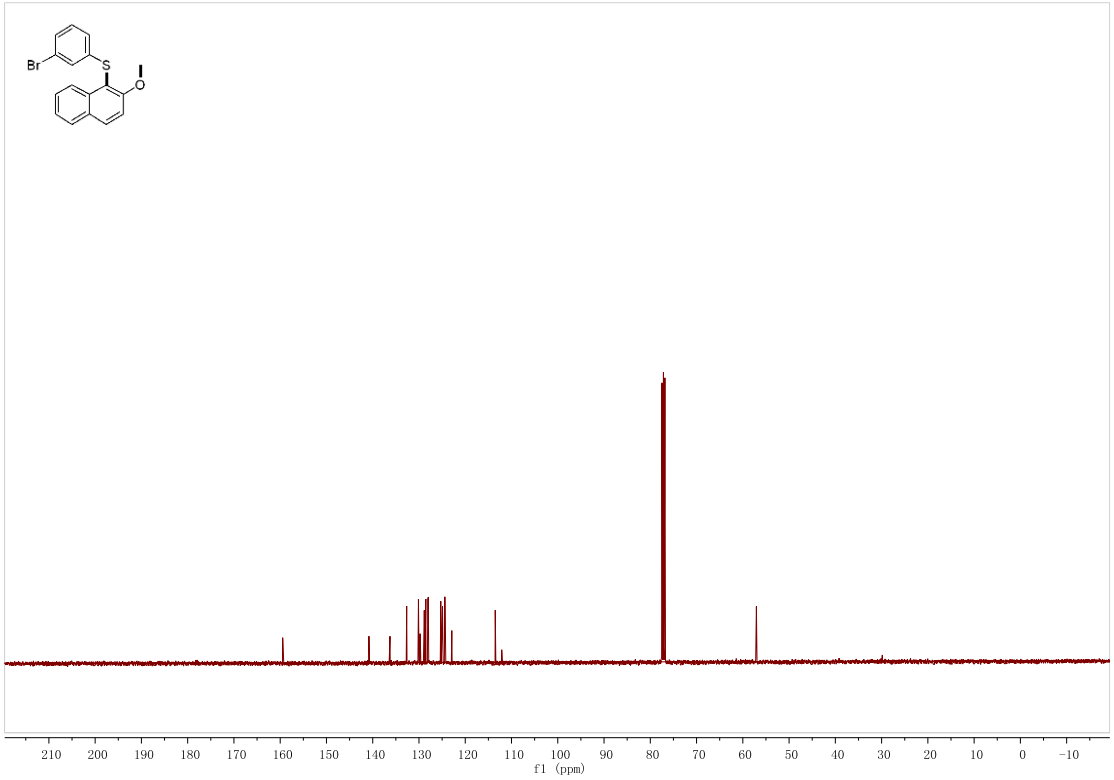
(4-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4an)



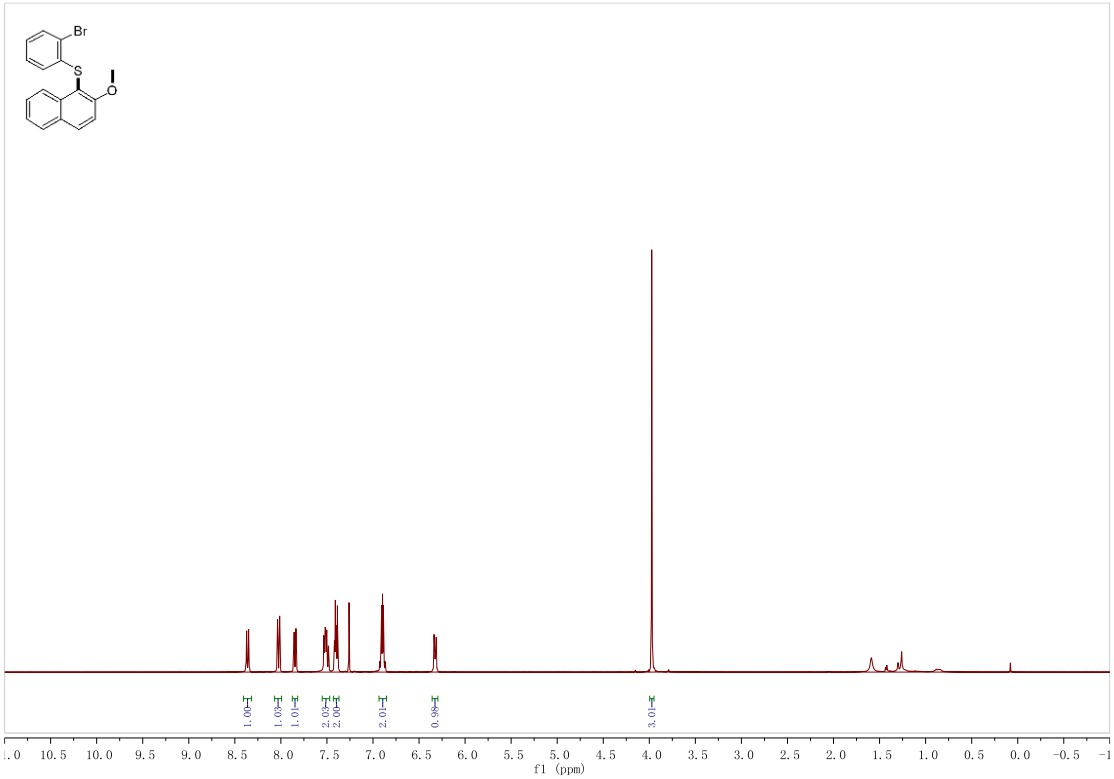


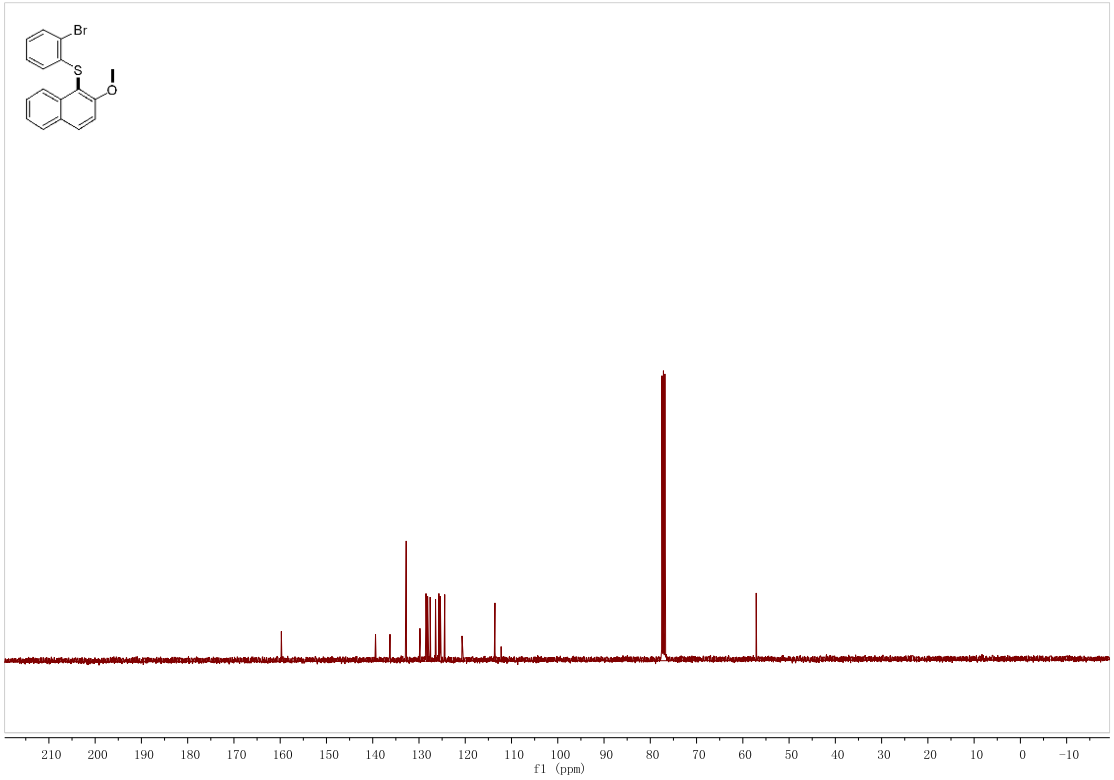
(3-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ao)



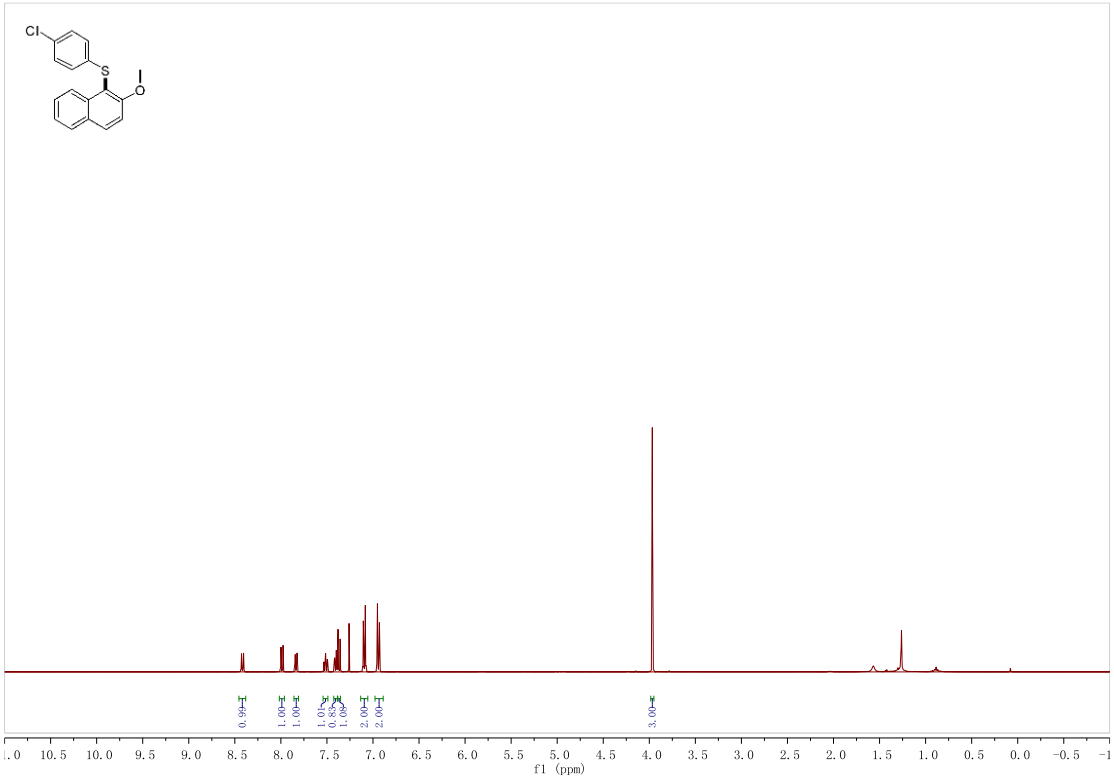


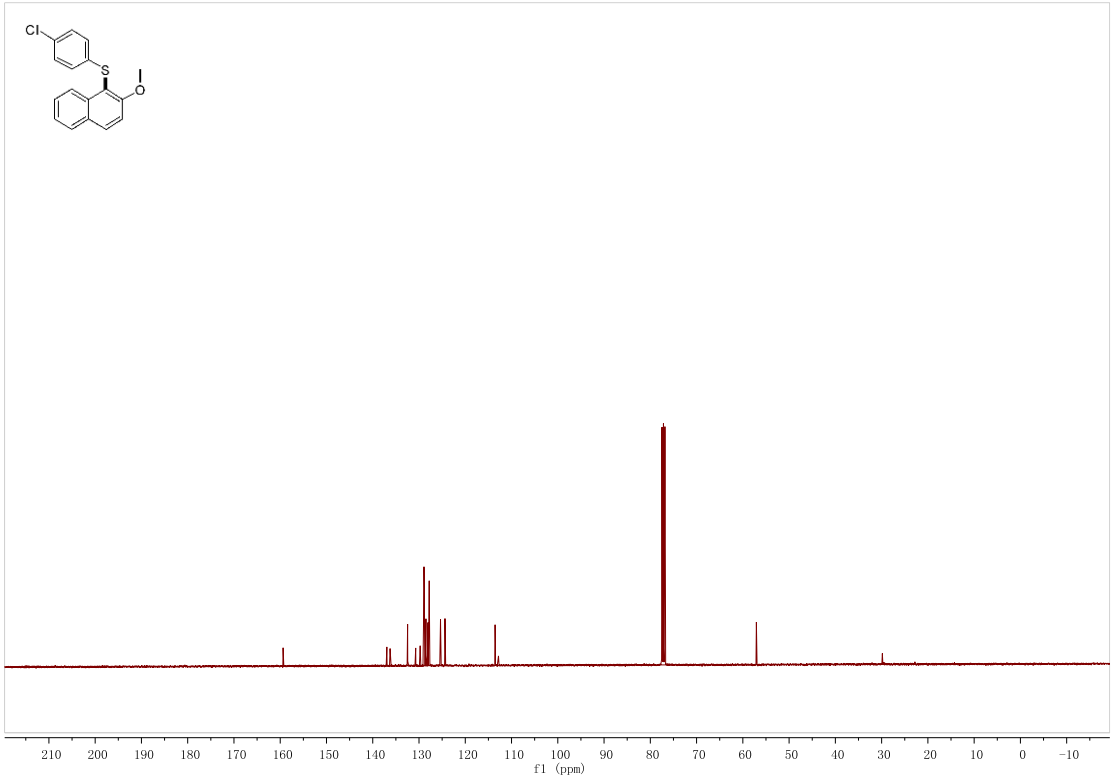
(2-Bromophenyl)(2-methoxynaphthalen-1-yl)sulfane (4ap)



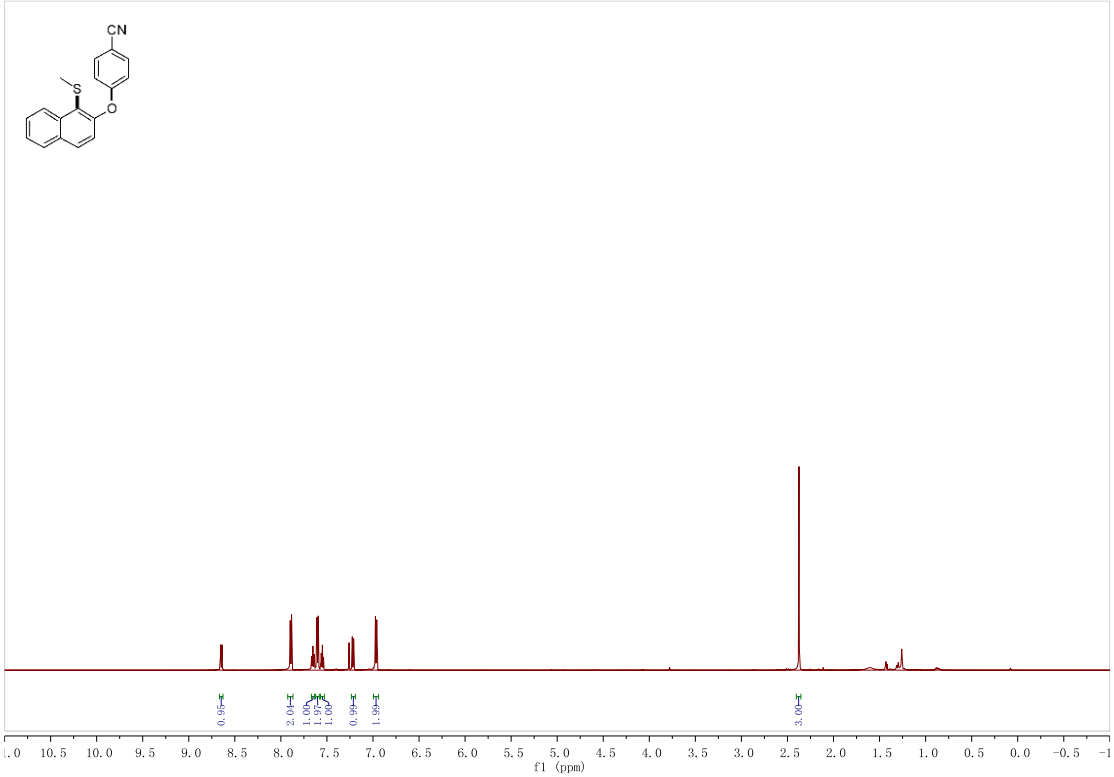


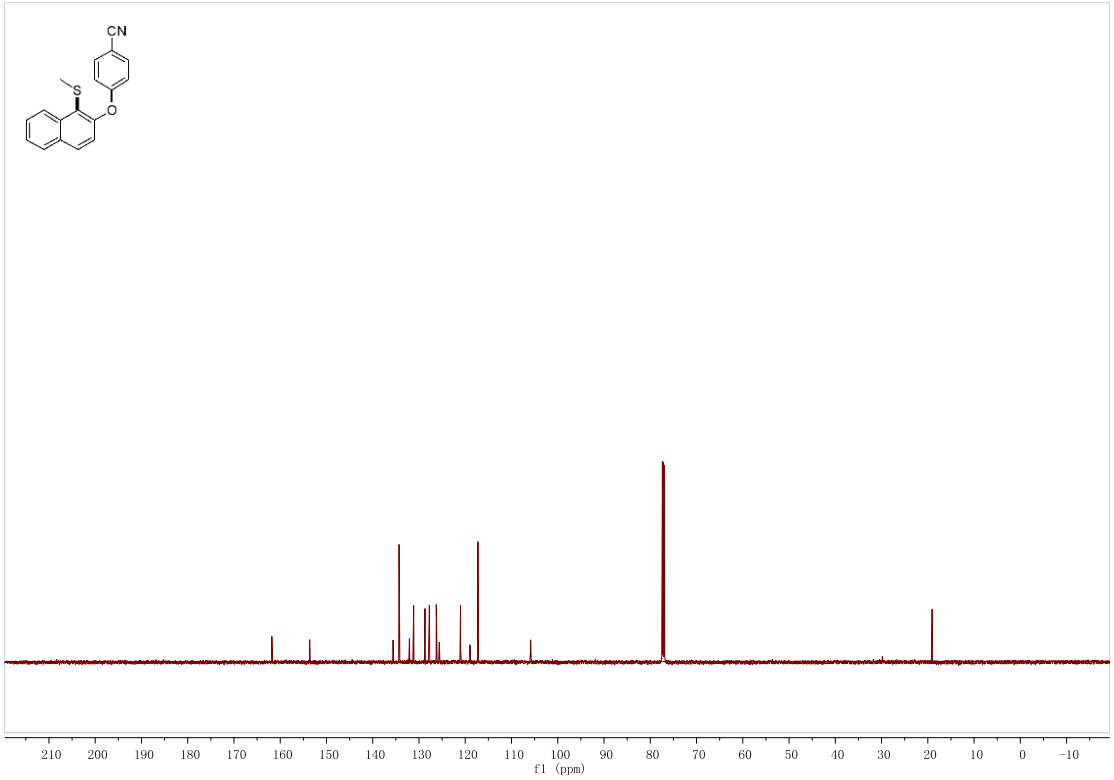
(4-Chlorophenyl)(2-methoxynaphthalen-1-yl)sulfane (4aq)



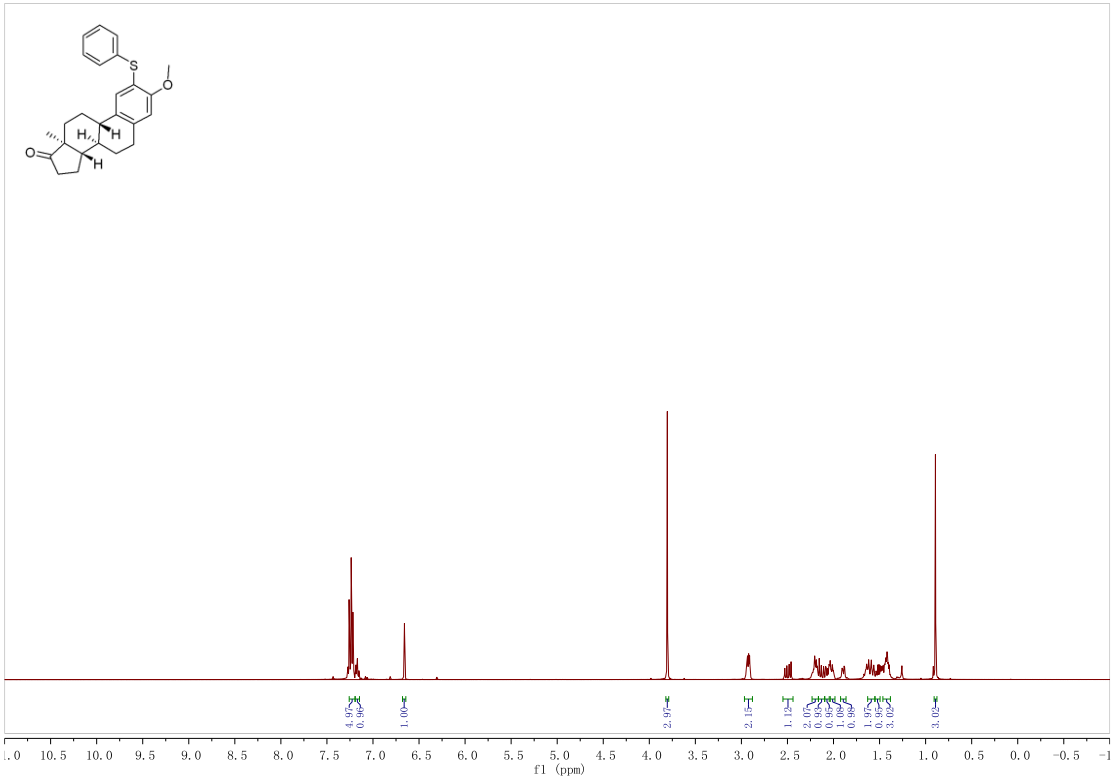


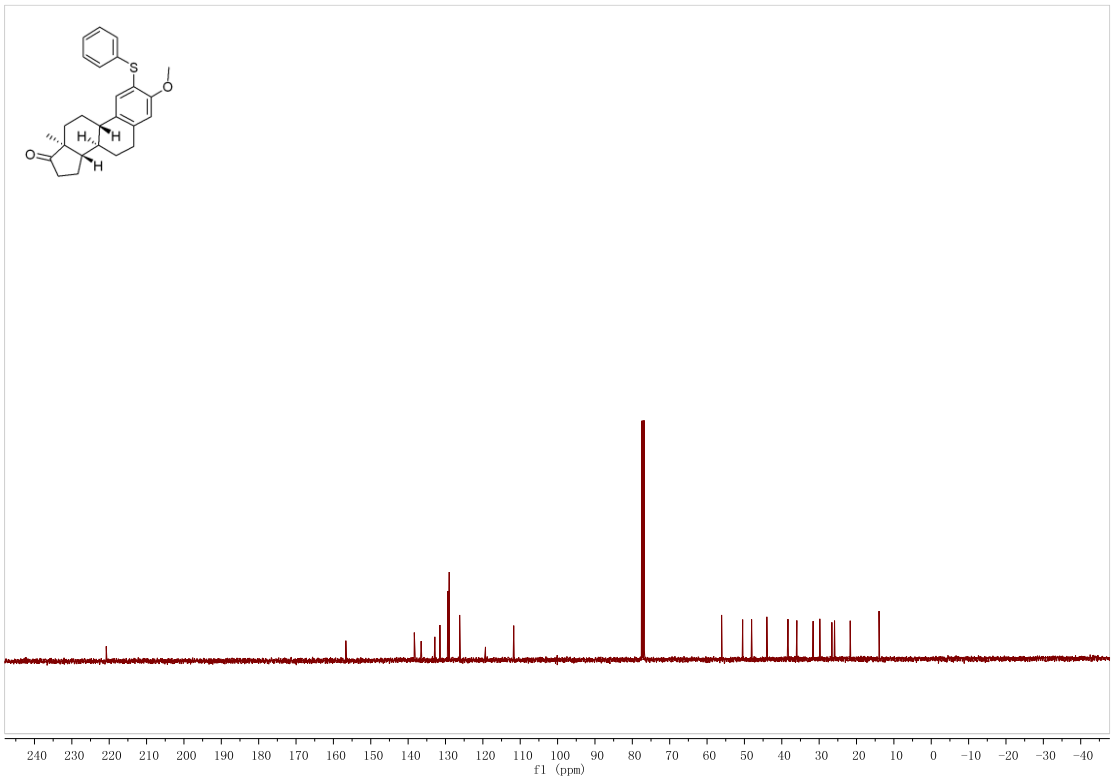
4-((1-(Methylthio)naphthalen-2-yl)oxy)benzonitrile (4ar)



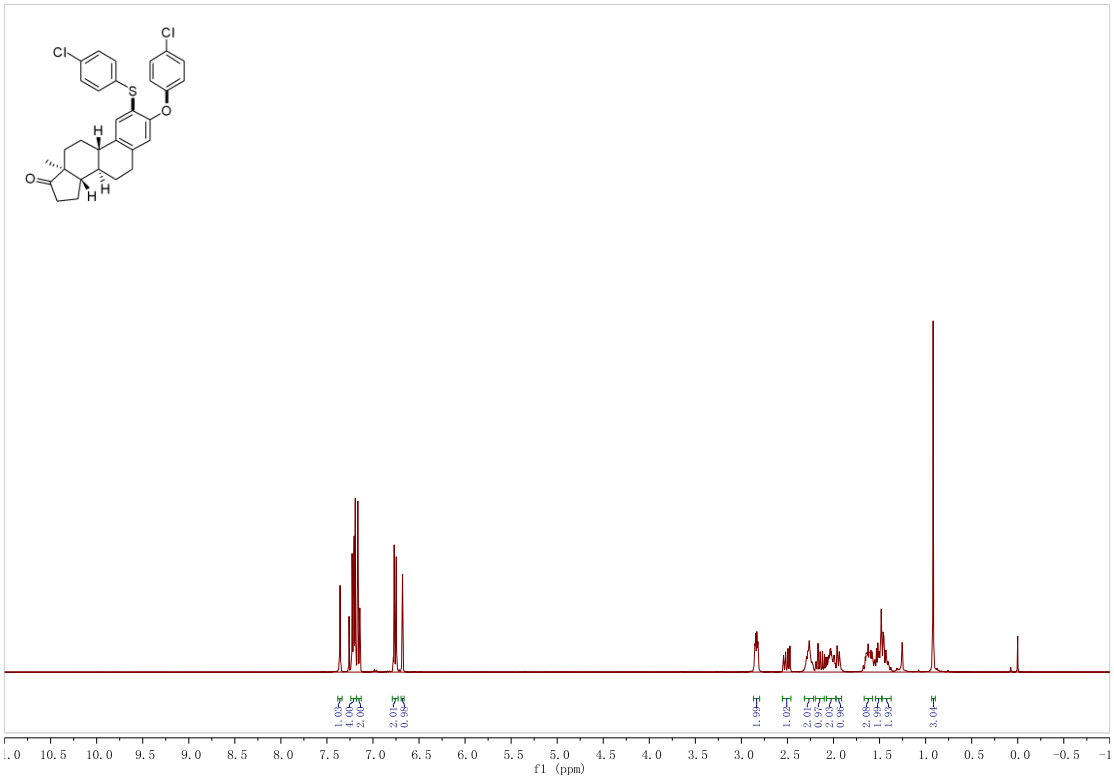


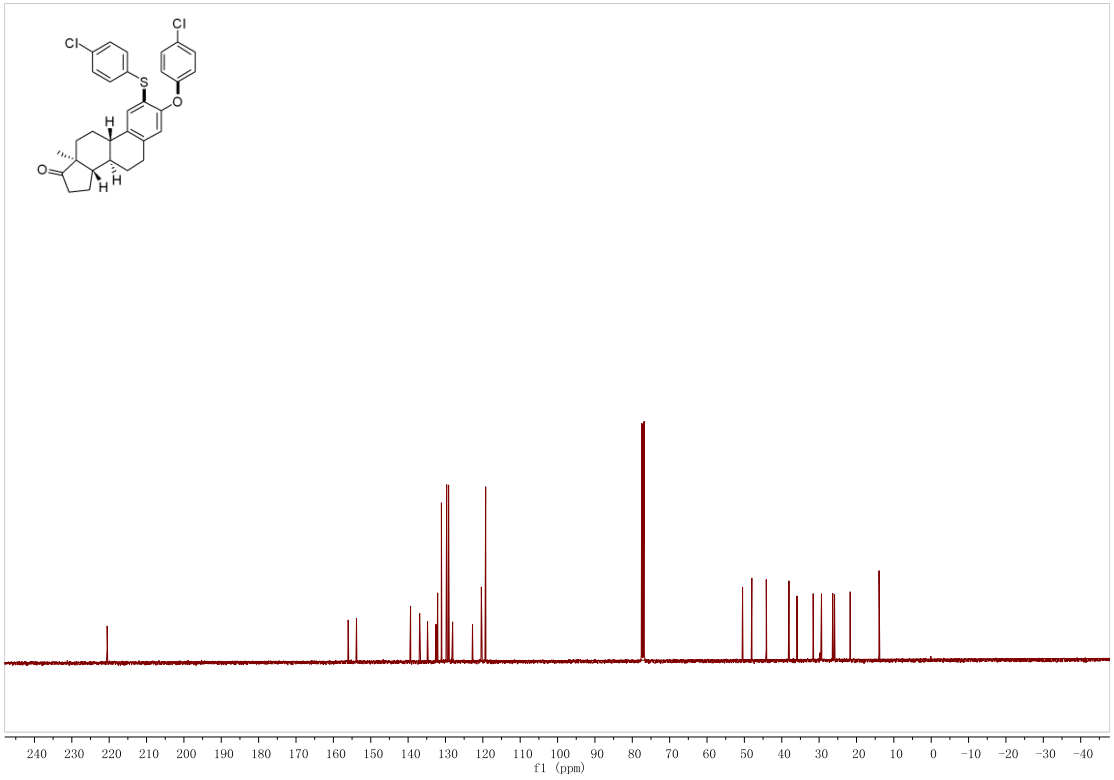
(8R,9S,13S,14S)-3-Methoxy-13-methyl-2-(phenylthio)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4ni)



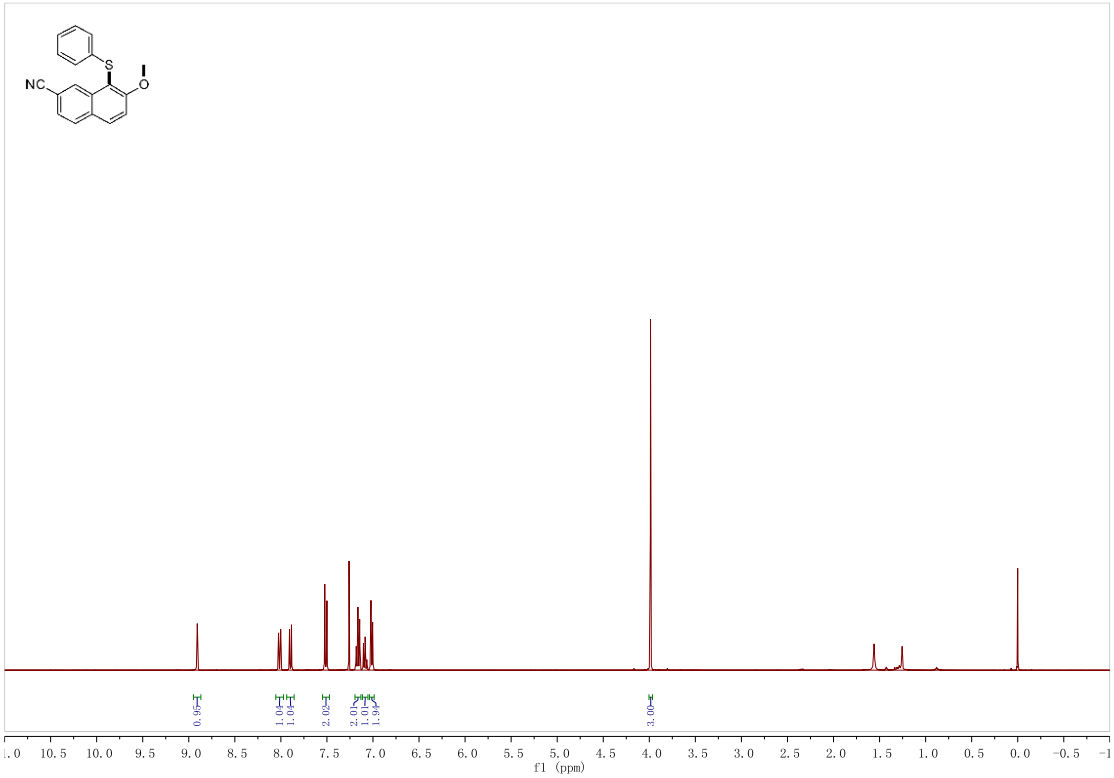


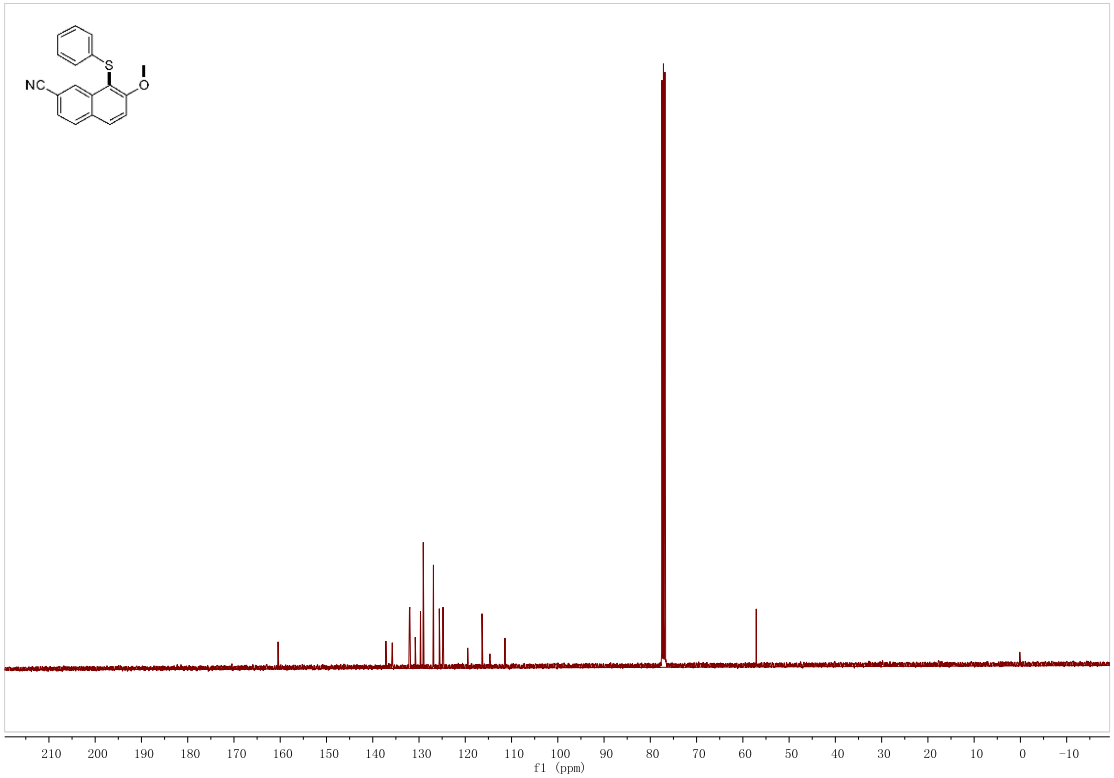
(8R,9S,13S,14S)-3-(4-Chlorophenoxy)-2-((4-chlorophenyl)thio)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4nb)



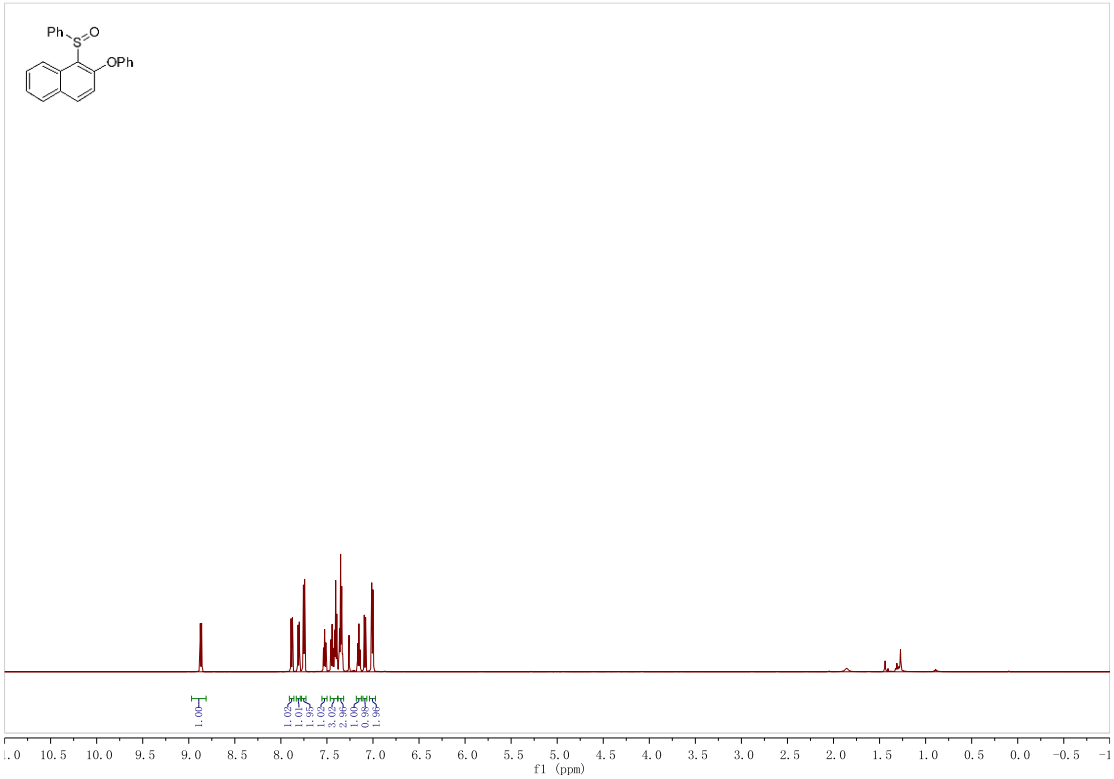


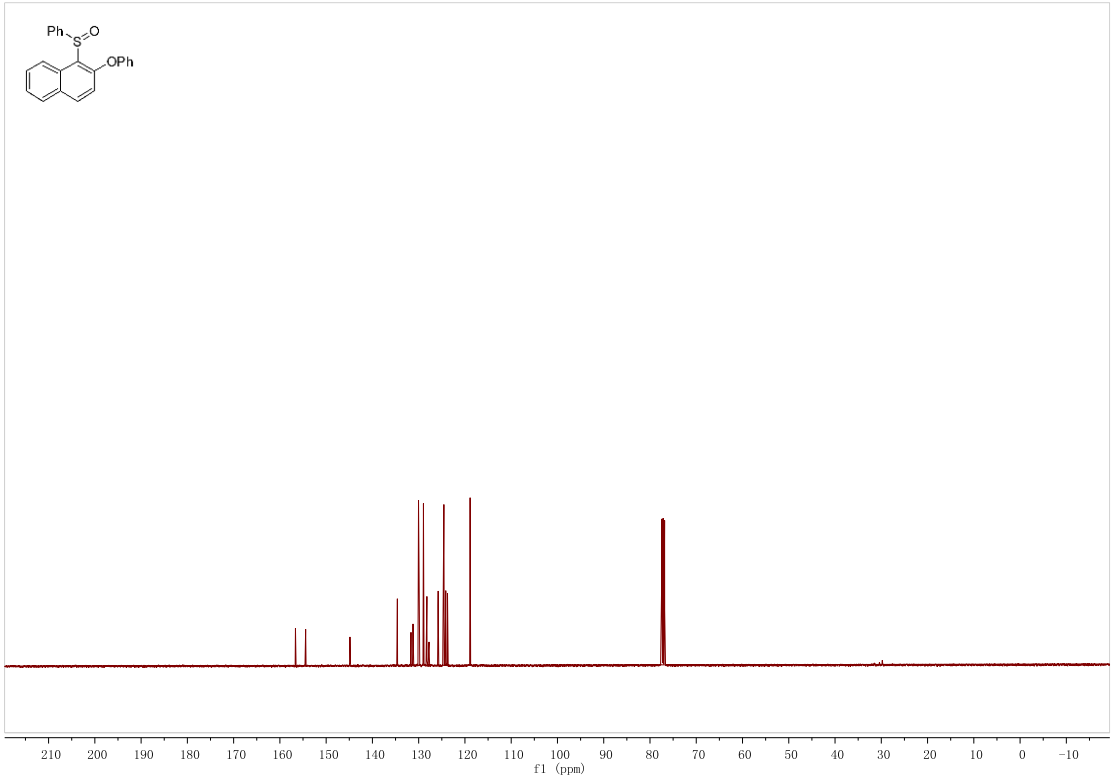
7-Methoxy-8-(phenylthio)-2-naphthonitrile (4oi)



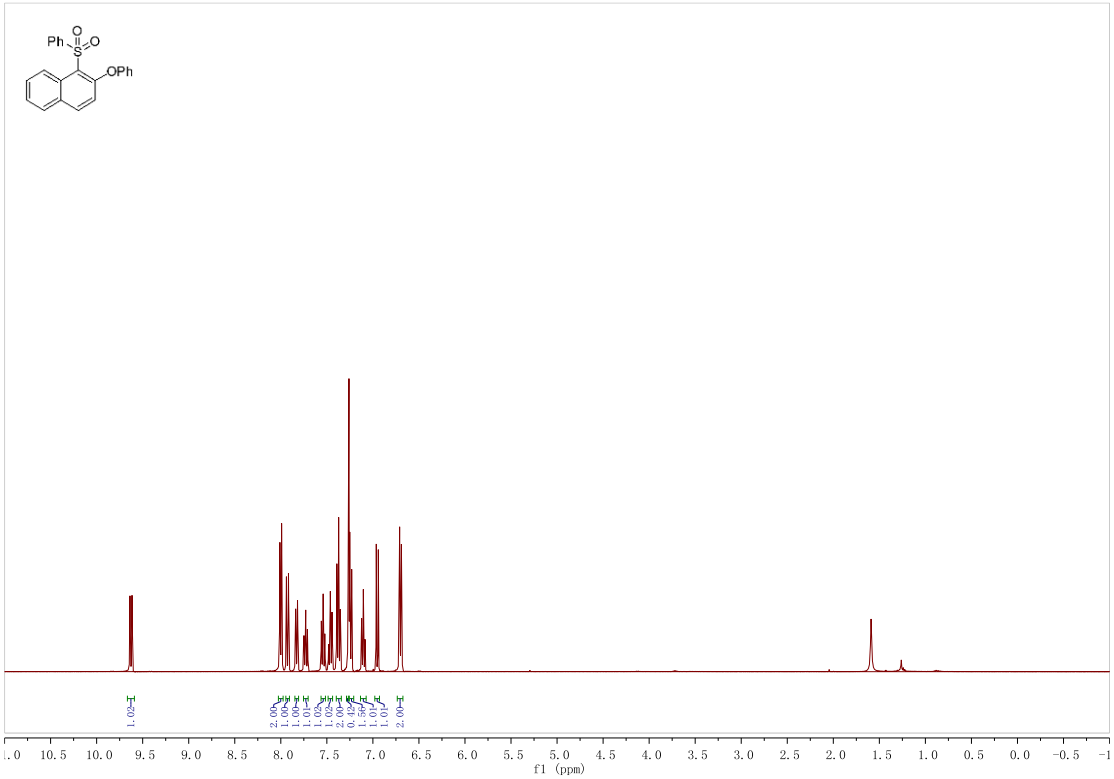


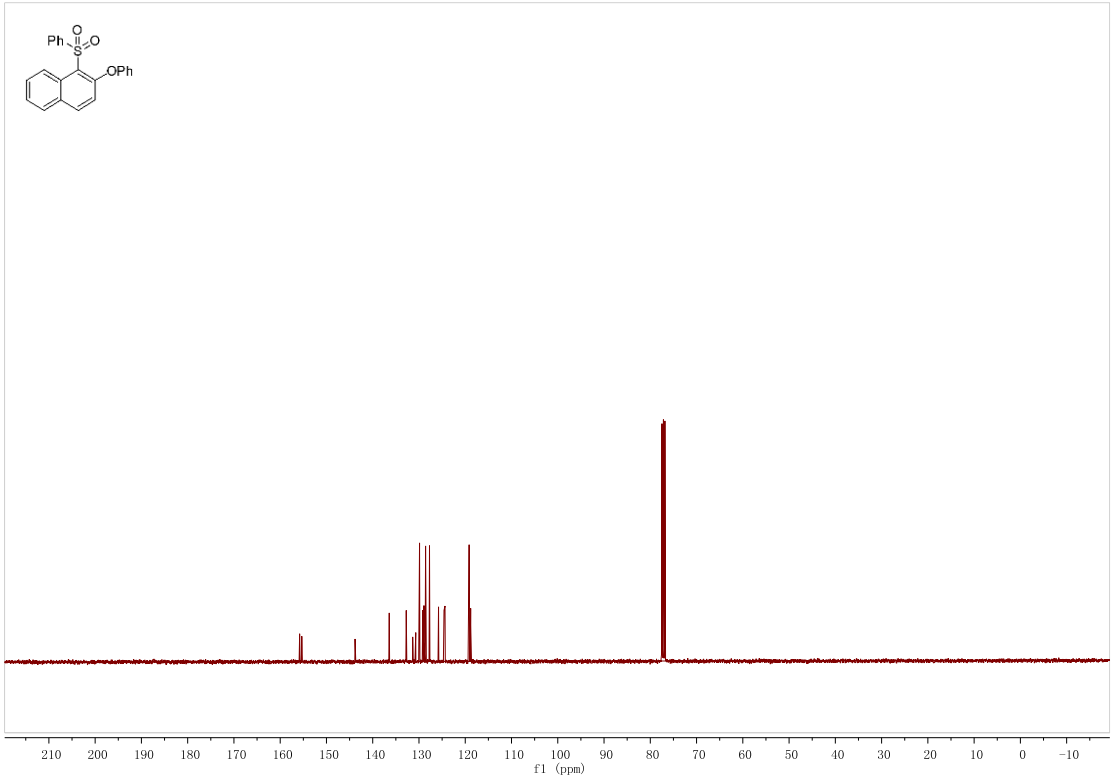
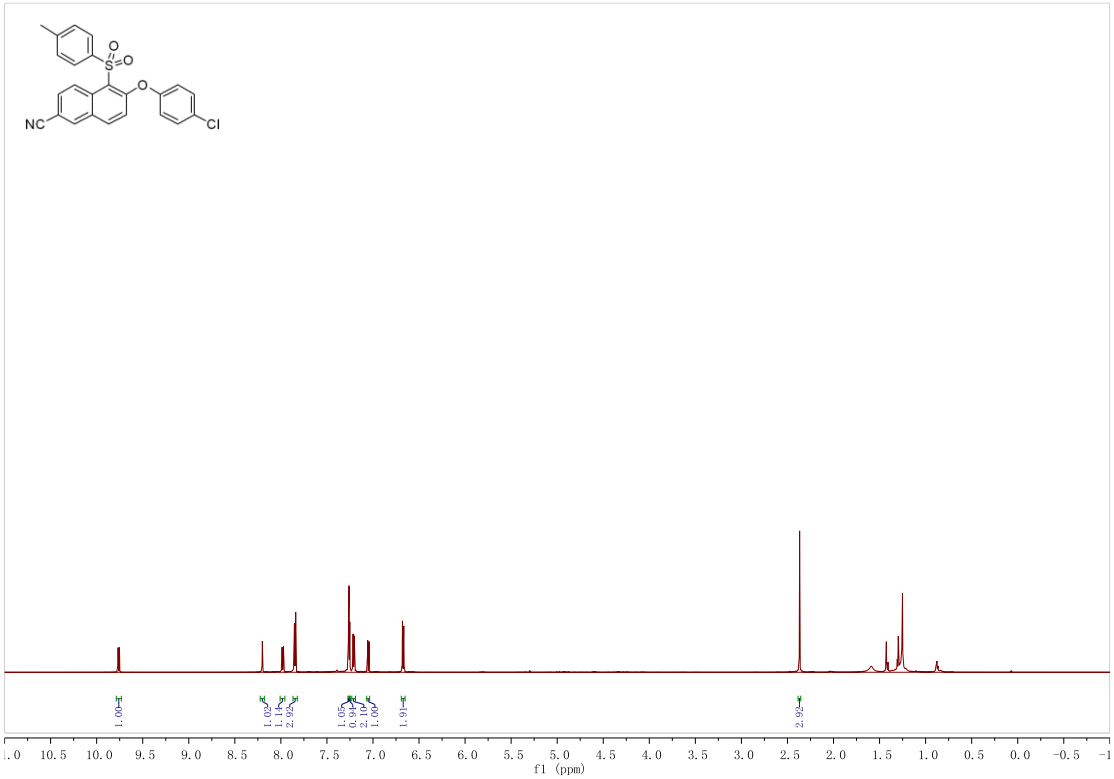
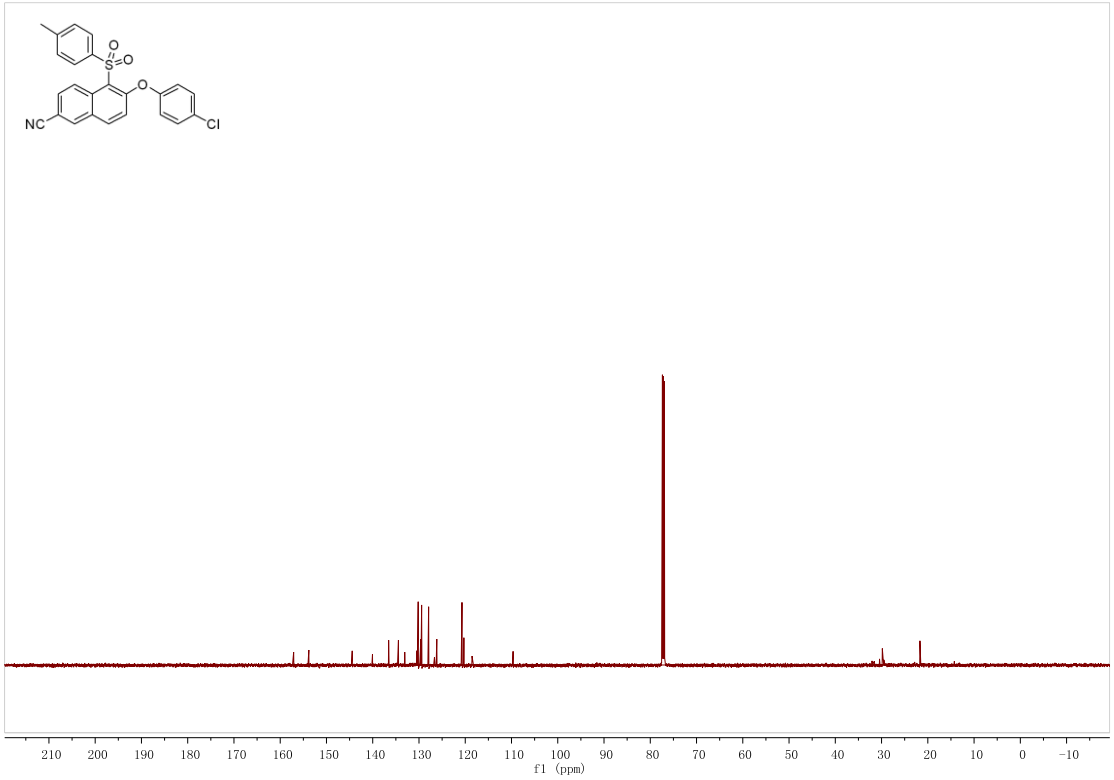
2-Phenoxy-1-(phenylsulfinyl)naphthalene (5aa)





2-Phenoxy-1-(phenylsulfonyl)naphthalene (6aa)





6-(4-Chlorophenoxy)-5-tosyl-2-naphthonitrile (6eg)