

Supporting Information

Copper-Catalyzed Thiolation of Di- or Trimethoxybenzene Arene C-H Bond with Disulfides

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Table of contents

1. General experimental details	S2
2. Experimental characterization data for compounds	S3-S8
3. Copies of product ¹ H NMR and ¹³ C NMR	S9-S27

1. General experimental details

Chemicals were either purchased or purified by standard techniques without special instructions. ^1H NMR and ^{13}C NMR spectra were measured on a 300 (^1H 300 MHz, ^{13}C 75 MHz) or 500 MHz (^1H 500 MHz, ^{13}C 125 MHz) spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. All reactions were conducted under air atmosphere. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

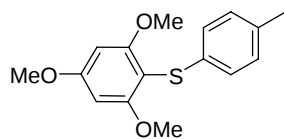
1.1 Preparation of *CuSPh*:¹

To an ice-cold mixture of 25 mL conc. aq. NH_3 and 100 mL H_2O was added $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (6.26 g, 25.1 mmol) forming a royal blue-colored solution. Over a period of 45 min., solid $\text{NH}_2\text{OH} \cdot \text{HCl}$ (3.89 g, 56.0 mmol) was added. Stirring overnight at 25 °C under N_2 purge produced a colorless solution of $[\text{Cu}(\text{NH}_3)_2]^+$. Using a syringe, a solution of PhSH (2.84 g, 25.8 mmol) in 125 mL of EtOH was added. A pale yellow solid formed immediately. The solid product was collected via filtration and was washed with H_2O , EtOH, and ether in succession and vacuum-dried (3.89 g, 22.5 mmol, 89.6%). Yellowish solid; ^1H NMR (CDCl_3 , 300 MHz): δ 7.50 (d, $J = 7.2$ Hz, 2H), 7.33-7.20 (m, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 137.0, 129.1, 127.5, 127.2.

1. Nguyen, L. M.; Dellinger, M. E.; Lee, J. T.; Quinlan, R. A.; Rheingold, A. L.; Pike, R. D. *Inorg. Chim. Acta* **2005**, 358, 1331.

2. Experimental characterization data for compounds

4-tolyl(2,4,6-trimethoxyphenyl)sulfane 3b

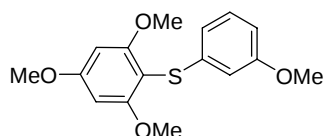


White solid; R_f 0.60 (cyclohexane-EtOAc, 20:1); m.p. 112-113 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 6.99-6.92 (m, 4H), 6.20 (s, 2H), 3.86 (s, 3 H), 3.81 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 162.7, 162.5, 135.0, 134.1, 129.2, 126.0, 99.3, 91.1, 56.3, 55.4, 20.8.

IR (prism, cm^{-1}): 3005, 1716, 1592, 1456, 1227, 1124, 743.

MS(EI) 290 (M^+); HRMS Calcd. for $\text{C}_{16}\text{H}_{18}\text{SO}_3$ (M) $^+$ 290.0977, found 290.0982.

(3-Methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane 3c



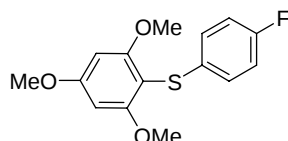
Brownish solid; R_f 0.60 (cyclohexane-EtOAc, 20:1); m.p. 55-56 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.09-7.04 (m, 1H), 6.62-6.59 (m, 3H), 6.21 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H), 3.71 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.0, 162.6, 159.7, 140.2, 129.2, 118.0, 111.2, 110.0, 98.6, 91.3, 56.3, 55.4, 55.1.

IR (prism, cm^{-1}): 2956, 1714, 1593, 1457, 1125, 741.

MS(EI) 306 (M^+); HRMS Calcd. for $\text{C}_{16}\text{H}_{18}\text{SO}_4$ (M) $^+$ 306.0926, found 306.0920.

(4-Fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane 3d



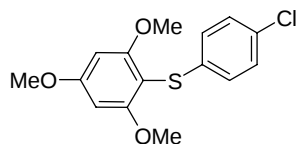
Yellowish solid; R_f 0.50 (cyclohexane-EtOAc, 15:1); m.p. 80-81 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.01 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 6.20 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 162.9, 162.4, 160.7 (d, $J_{\text{C-F}} = 241.8$ Hz), 133.6, 127.9 (d, $J_{\text{C-F}} = 7.7$ Hz), 115.5 (d, $J_{\text{C-F}} = 21.9$ Hz), 99.4, 91.3, 56.3, 55.4.

IR (prism, cm^{-1}): 2968, 1715, 1593, 1457, 1125, 742.

MS(EI) 294 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{FSO}_3$ (M) $^+$ 294.0726, found 294.0728.

(4-Chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane 3e



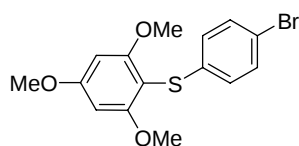
White solid; R_f 0.60 (cyclohexane-EtOAc, 20:1); m.p. 93-94 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.11 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.21 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.1, 162.4, 137.3, 130.0, 128.5, 126.9, 98.2, 91.2, 56.2, 55.4.

IR (prism, cm^{-1}): 2966, 1733, 1715, 1593, 1456, 1125, 742.

MS(EI) 310 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{ClSO}_3$ (M^+) 310.0430, found 310.0427.

(4-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane 3f



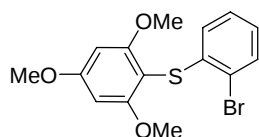
Brown solid; R_f 0.60 (cyclohexane-EtOAc, 20:1); m.p. 114-115 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.25 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.21 (s, 2H), 3.87 (s, 6H), 3.81 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.1, 162.4, 138.1, 131.4, 127.2, 117.8, 98.1, 91.2, 56.3, 55.4.

IR (prism, cm^{-1}): 2964, 1715, 1593, 1456, 1124, 742.

MS(EI) 353 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{BrSO}_3$ (M^+) 353.9925, found 353.9922.

(2-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane 3g



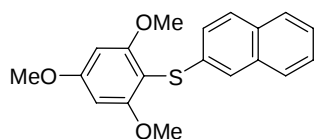
Brown solid; R_f 0.60 (cyclohexane-EtOAc, 20:1); m.p. 148-149 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.46 (d, J = 8.0 Hz, 1H), 7.05-7.00 (m, 1H), 6.91-6.89 (m, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.23 (s, 2H), 3.88 (s, 3H), 3.80 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.3, 162.6, 139.8, 132.5, 127.2, 125.4, 125.1, 120.1, 97.8, 91.3, 56.3, 55.4.

IR (prism, cm^{-1}): 3005, 1716, 1594, 1456, 1125, 743.

MS(EI) 353 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{BrSO}_3$ (M^+) 353.9925, found 353.9921.

Naphthalen-2-yl(2,4,6-trimethoxyphenyl)sulfane 3h



Brown oil; R_f 0.60 (cyclohexane-EtOAc, 20:1); ^1H NMR (CDCl_3 , 500 MHz): δ 7.72

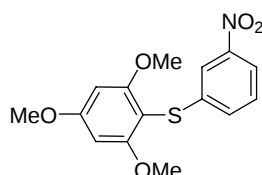
(d, $J = 8.0$ Hz, 1H), 7.65-7.38 (m, 2H), 7.38-7.32 (m, 3H), 7.21 (dd, $J = 9.0, 7.0$ Hz, 1H), 6.25 (s, 2H), 3.90 (s, 3H), 3.81 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.0, 162.6, 136.3, 133.8, 131.2, 127.9, 127.6, 126.8, 126.1, 124.9, 124.7, 123.0, 98.8, 91.3, 56.3, 55.4.

IR (prism, cm^{-1}): 2968, 1593, 1456, 1227, 1124, 743.

MS(EI) 326 (M^+); HRMS Calcd. for $\text{C}_{19}\text{H}_{18}\text{SO}_3$ (M^+) 326.0977, found 326.0974.

(3-Nitrophenyl)(2,4,6-trimethoxyphenyl)sulfane 3i



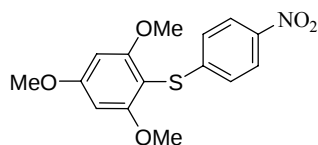
Yellow solid; R_f 0.45 (cyclohexane-EtOAc, 15:1); m.p. 130-131 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.87 (d, $J = 7.5$ Hz, 1H), 7.77 (s, 1H), 7.34-7.27 (m, 2H), 6.24 (s, 2H), 3.89 (s, 3H), 3.82 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 162.4, 148.6, 142.0, 131.3, 129.0, 120.0, 119.2, 96.6, 91.4, 56.3, 55.5.

IR (prism, cm^{-1}): 2930, 1716, 1592, 1457, 1123, 741.

MS(EI) 321 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{NSO}_5$ (M^+) 321.0671, found 321.0677.

(4-Nitrophenyl)(2,4,6-trimethoxyphenyl)sulfane 3j



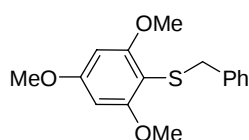
Yellowish solid; R_f 0.40 (cyclohexane-EtOAc, 15:1); m.p. 125-126 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.13 (d, $J = 9.0$ Hz, 2H), 7.83 (d, $J = 9.0$ Hz, 2H), 6.10 (s, 2H), 3.82 (s, 6H), 3.81 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 163.6, 162.3, 148.8, 145.6, 126.6, 123.4, 123.4, 97.0, 55.5, 55.2.

IR (prism, cm^{-1}): 2967, 1734, 1716, 1593, 1456, 1124, 742.

MS(EI) 321 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{NSO}_5$ (M^+) 321.0671, found 321.0672.

Benzyl(2,4,6-trimethoxyphenyl)sulfane 3k



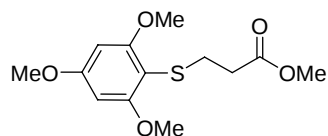
Yellow oil; R_f 0.70 (cyclohexane-EtOAc, 20:1); ^1H NMR (CDCl_3 , 300 MHz): δ 7.18-7.15 (m, 5H), 6.08 (s, 2H), 3.86 (s, 2H), 3.81 (s, 3H), 3.74 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 162.2, 161.9, 138.9, 128.9, 127.9, 126.5, 101.5, 91.0, 56.1, 55.3, 39.2.

IR (prism, cm^{-1}): 2935, 1579, 1454, 1226, 1092, 737.

MS(EI) 290 (M^+); HRMS Calcd. for $C_{16}H_{18}SO_3$ (M) $^+$ 290.0977, found 290.0971.

Methyl 3-(2,4,6-trimethoxyphenylthio)propanoate 3l



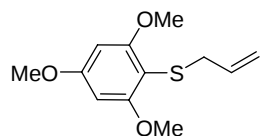
Colorless oil; R_f 0.45 (cyclohexane-EtOAc, 15:1); 1H NMR ($CDCl_3$, 500 MHz): δ 6.13 (s, 2H), 3.85 (s, 6H), 3.82 (s, 3H), 3.62 (s, 3H), 2.93 (t, J = 7.5 Hz, 2H), 2.50 (t, J = 7.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.5, 172.6, 162.2, 100.3, 90.9, 56.1, 55.3, 51.5, 34.6, 29.2.

IR (prism, cm^{-1}): 2944, 1733, 1716, 1592, 1267, 1124, 742.

MS(EI) 286 (M^+); HRMS Calcd. for $C_{13}H_{18}SO_5$ (M) $^+$ 286.0875, found 286.0872.

Allyl(2,4,6-trimethoxyphenyl)sulfane 3m



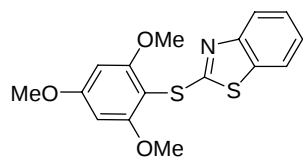
Yellow oil; R_f 0.55 (cyclohexane-EtOAc, 20:1); 1H NMR ($CDCl_3$, 500 MHz): δ 6.14 (s, 2H), 5.84-5.76 (m, 1H), 4.88-4.84 (m, 2H), 3.86 (s, 6H), 3.82 (s, 3H), 3.36 (d, J = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.1, 161.7, 134.6, 116.3, 93.3, 91.0, 56.1, 55.3, 37.6.

IR (prism, cm^{-1}): 2954, 1716, 1592, 1456, 1227, 1123, 743.

MS(EI) 240 (M^+); HRMS Calcd. for $C_{12}H_{16}SO_3$ (M) $^+$ 240.0820, found 240.0817.

2-(2,4,6-Trimethoxyphenylthio)benzo[d]thiazole 3n



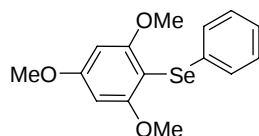
Yellowish solid; R_f 0.45 (cyclohexane-EtOAc, 10:1); m.p. 88-89 °C. 1H NMR ($CDCl_3$, 300 MHz): δ 8.02 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.47-7.42 (m, 1H), 7.32 (d, J = 8.5 Hz, 1H), 6.23 (s, 2H), 3.91 (s, 3H), 3.84 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.4, 162.6, 154.5, 140.3, 135.4, 127.1, 125.8, 121.4, 121.3, 97.3, 91.3, 56.3, 55.5.

IR (prism, cm^{-1}): 2968, 1594, 1456, 1411, 1227, 1124, 741.

MS(EI) 333 (M^+); HRMS Calcd. for $C_{16}H_{15}NS_2O_3$ (M) $^+$ 333.0493, found 333.0499.

Phenyl(2,4,6-trimethoxyphenyl)sulfane 3o



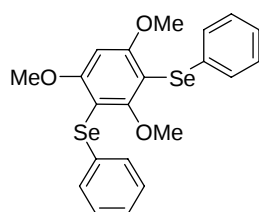
Yellowish oil; R_f 0.60 (cyclohexane-EtOAc, 20:1); ^1H NMR (CDCl_3 , 500 MHz): δ 7.20-7.18 (m, 2H), 7.15-7.07 (m, 3H), 6.21 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 163.0, 162.0, 133.6, 128.9, 128.7, 125.3, 93.0, 91.3, 56.3, 55.4.

IR (prism, cm^{-1}): 2964, 1716, 1582, 1456, 1226, 1123, 742.

MS(EI) 324 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{16}\text{SeO}_3$ (M) $^+$ 324.0265, found 324.0262.

1,3,5-Trimethoxy-2,4-bis(phenylselanyl)benzene 3p



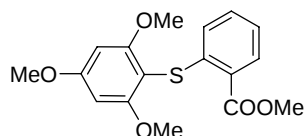
White solid; R_f 0.50 (cyclohexane-EtOAc, 15:1); m.p. 112-113 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 7.25-7.24 (m, 4H), 7.17-7.10 (m, 6H), 6.41 (s, 1H), 3.83 (s, 6H), 3.77 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 164.8, 163.1, 133.3, 129.4, 128.8, 125.7, 104.6, 92.5, 62.1, 56.4.

IR (prism, cm^{-1}): 2931, 1715, 1578, 1457, 1228, 1125, 737.

MS(EI) 479 (M^+); HRMS Calcd. for $\text{C}_{21}\text{H}_{20}\text{Se}_2\text{O}_3$ (M) $^+$ 479.9743, found 479.9746.

Methyl 2-(2,4,6-trimethoxyphenylthio)benzoate 3q



Yellowish solid; R_f 0.35 (cyclohexane-EtOAc, 6:1); m.p. 133-134 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 7.98 (dd, J = 7.8, 6.5 Hz, 1H), 7.18-7.16 (m, 1H), 7.06-7.03 (m, 1H), 6.69 (d, J = 8.2 Hz, 1H), 6.23 (s, 2H), 3.95 (s, 3H), 3.89 (s, 3H), 3.77 (s, 6H).

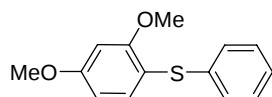
^{13}C NMR (CDCl_3 , 125 MHz): 167.0, 163.2, 162.8, 143.7, 132.0, 131.3, 125.4, 123.2, 98.8, 91.3, 56.3, 55.4, 52.0.

IR (prism, cm^{-1}): 2944, 1712, 1580, 1456, 1227, 1144, 1123, 742.

MS(EI) 334 (M^+); HRMS Calcd. for $\text{C}_{17}\text{H}_{18}\text{SO}_5$ (M) $^+$ 334.0875, found 334.0877.

(2,4-Dimethoxyphenyl)(phenyl)sulfane² 3r

2. Matsugi, M.; Murata, K.; Gotanda, K.; Nambu, H.; Auilkumar, G.; Matsumoto, K.; Kita, Y. *J. Org. Chem.* **2001**, 66, 2434.



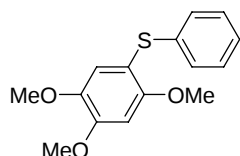
Yellowish oil; R_f 0.60 (cyclohexane-EtOAc, 20:1); ^1H NMR (CDCl_3 , 500 MHz): δ 7.54-7.10 (m, 5H), 6.53-6.47 (m, 3H), 3.81 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): δ 161.9, 160.9, 136.7, 129.9, 129.1, 128.8, 127.8, 125.4, 106.2, 100.5, 55.5, 55.3.

IR (prism, cm^{-1}): 1715, 1636, 1594, 1457, 1227, 1125, 742.

MS(EI) 246 (M^+); HRMS Calcd. for $\text{C}_{14}\text{H}_{14}\text{SO}_2$ (M^+) 246.0715, found 246.0717.

Phenyl(2,4,5-trimethoxyphenyl)sulfane² 3s

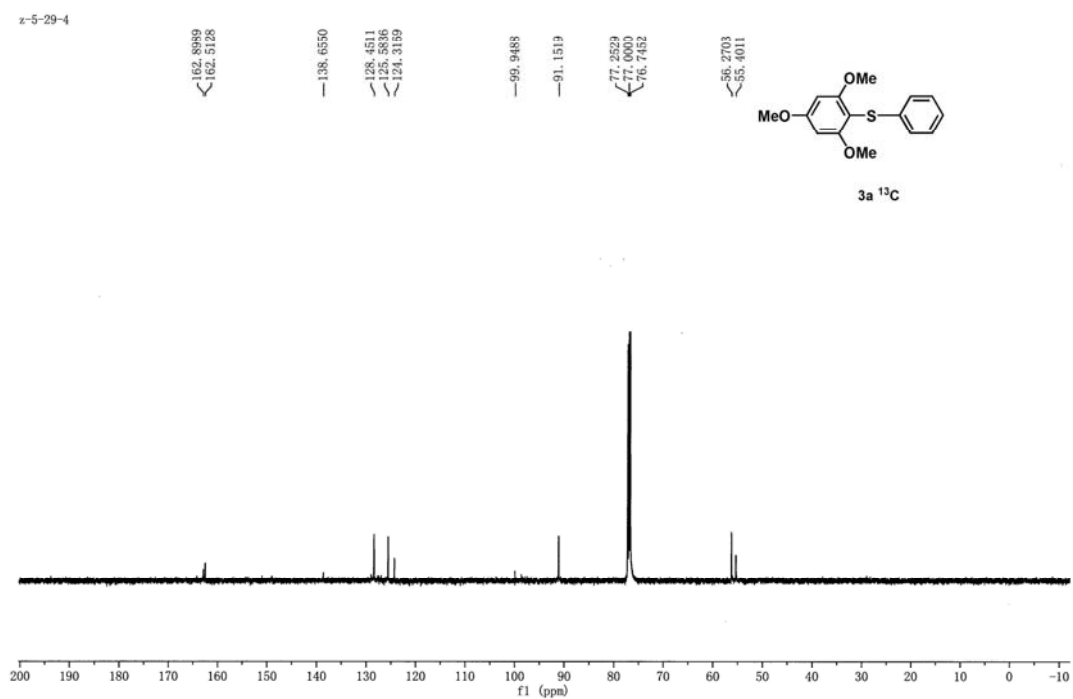
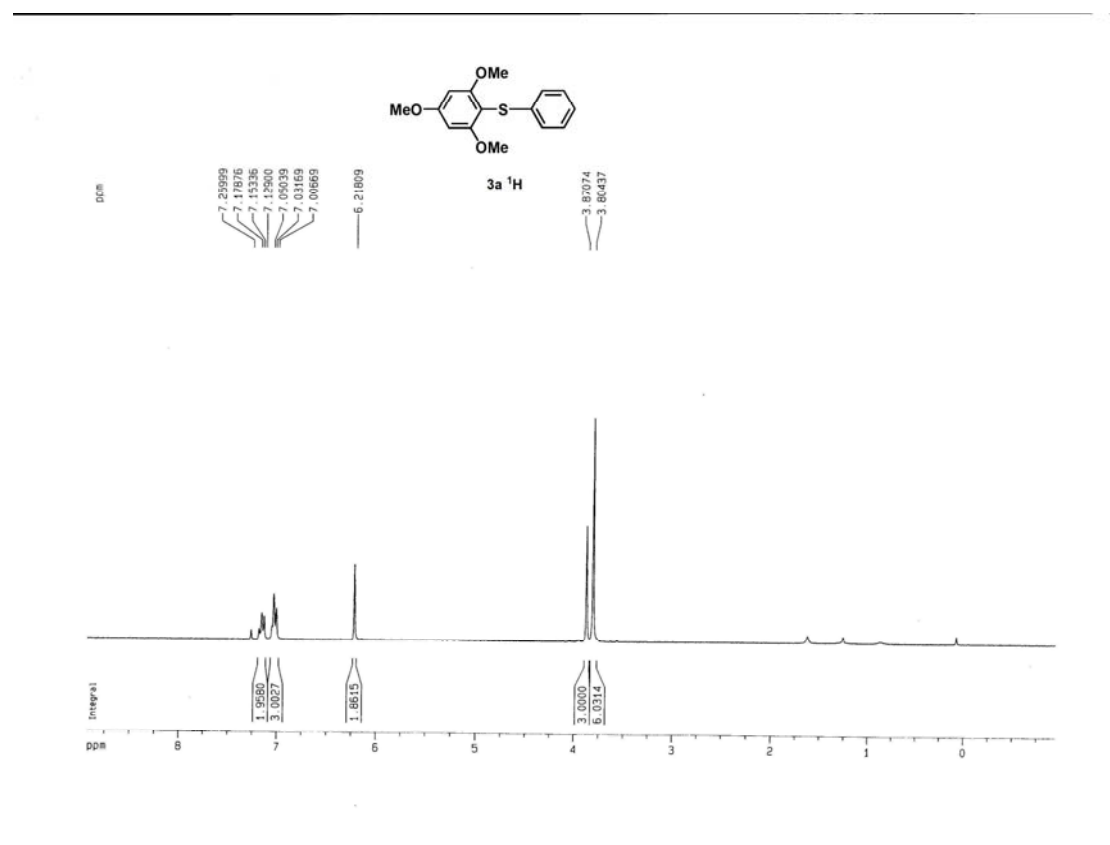


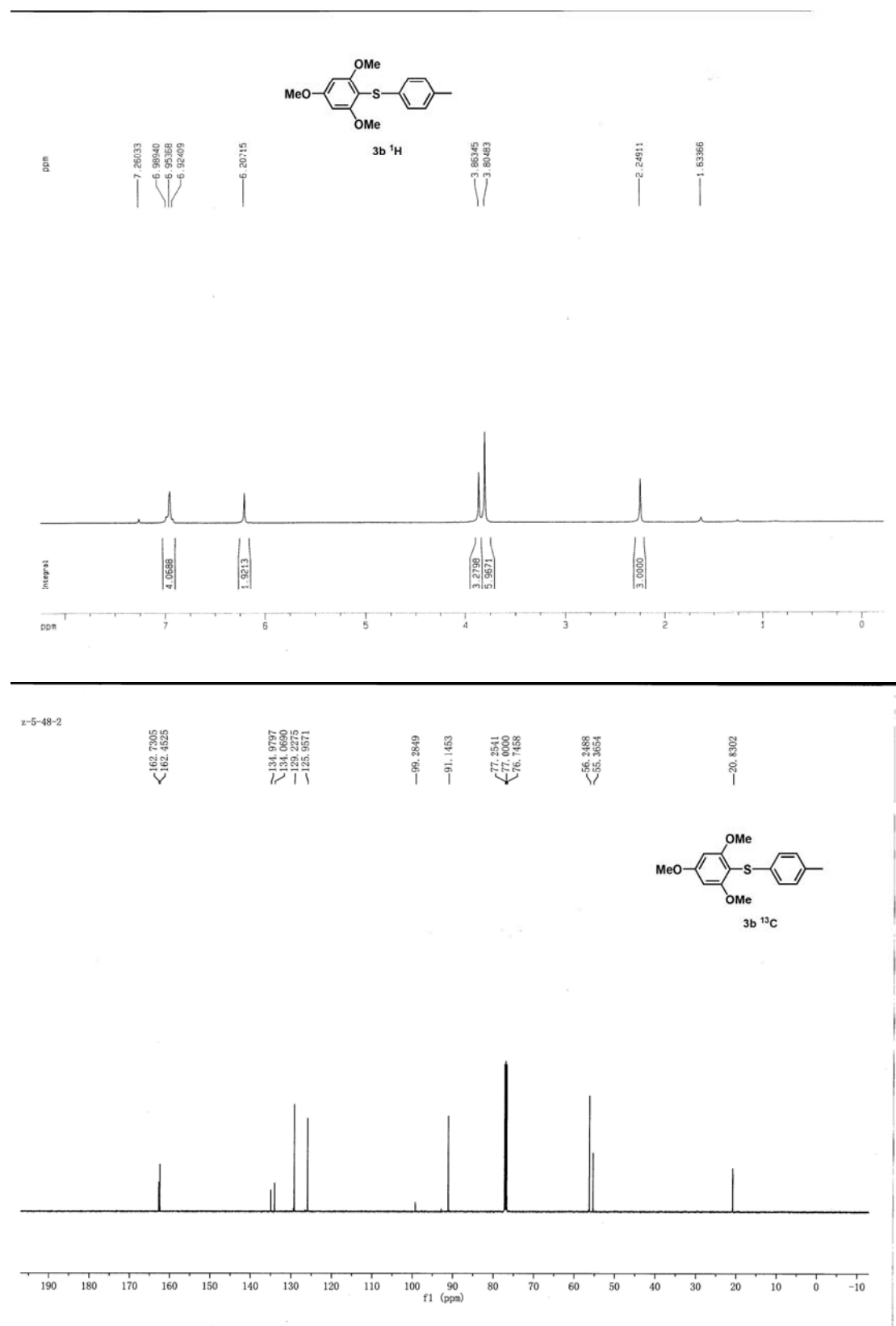
Yellowish oil; R_f 0.65 (cyclohexane-EtOAc, 20:1); ^1H NMR (CDCl_3 , 500 MHz): δ 7.24-7.21 (m, 2H), 7.15-7.12 (m, 3H), 7.11 (s, 1H), 6.95 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H).

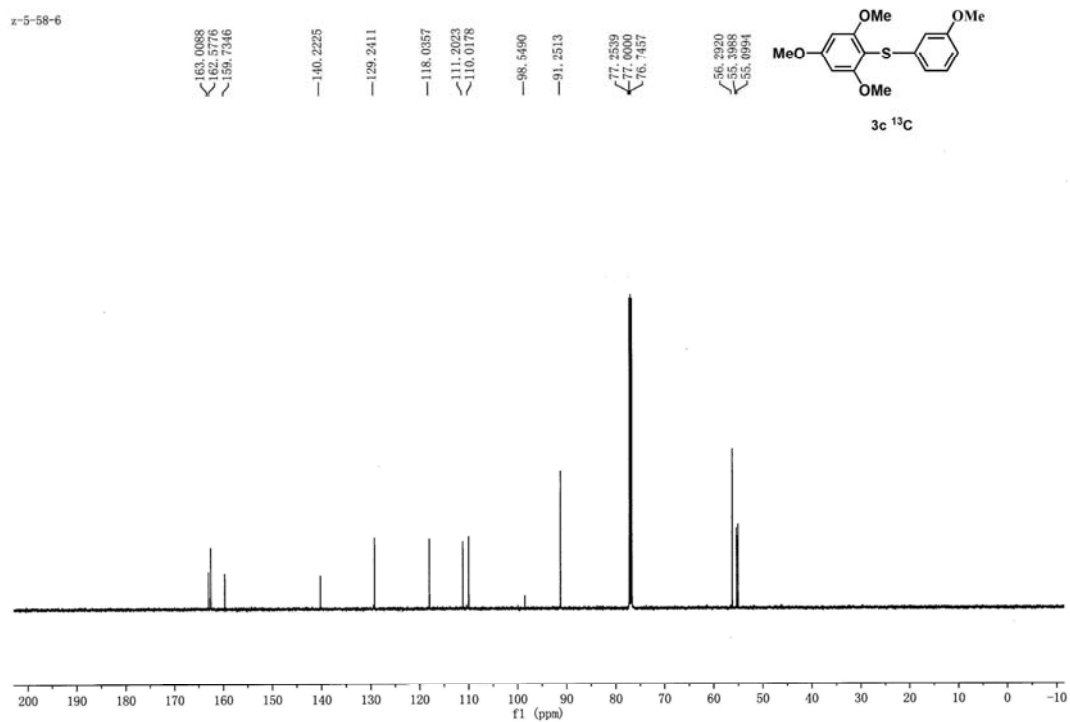
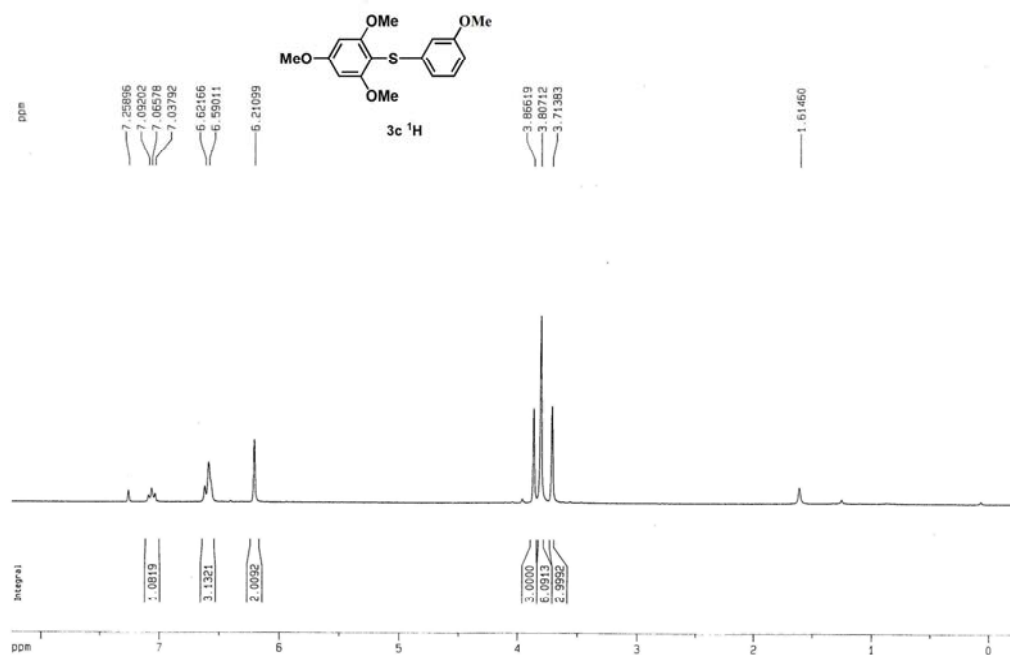
^{13}C NMR (CDCl_3 , 125 MHz): δ 154.4, 150.4, 143.6, 138.1, 128.9, 127.2, 125.7, 119.0, 110.9, 98.2, 57.0, 56.3, 55.9.

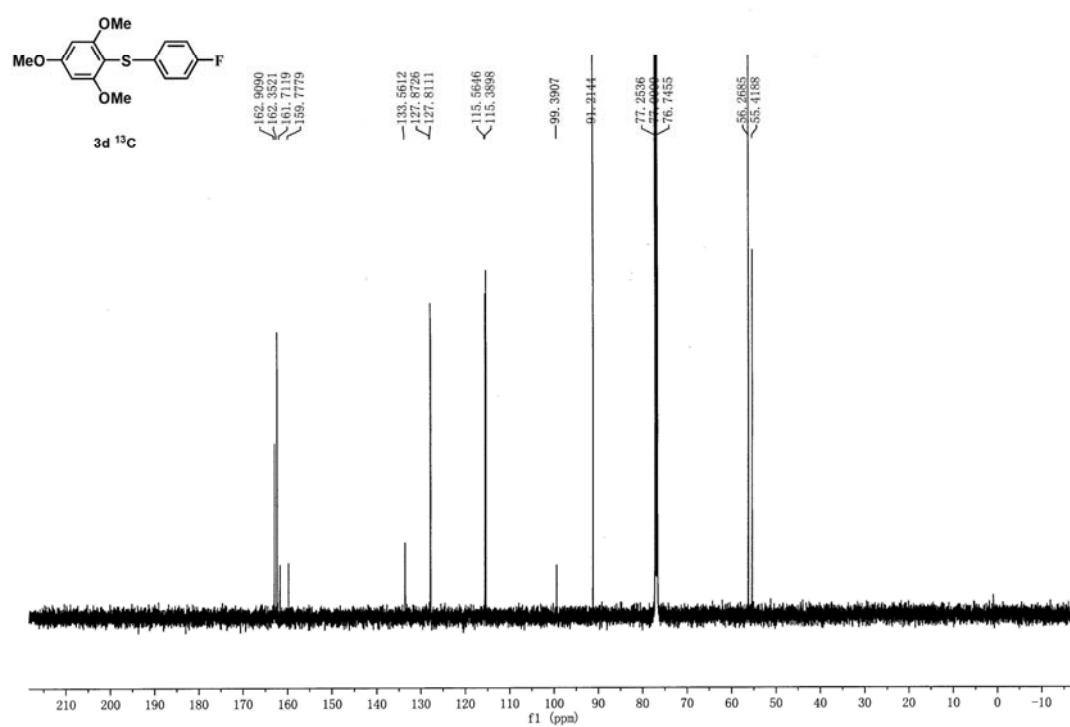
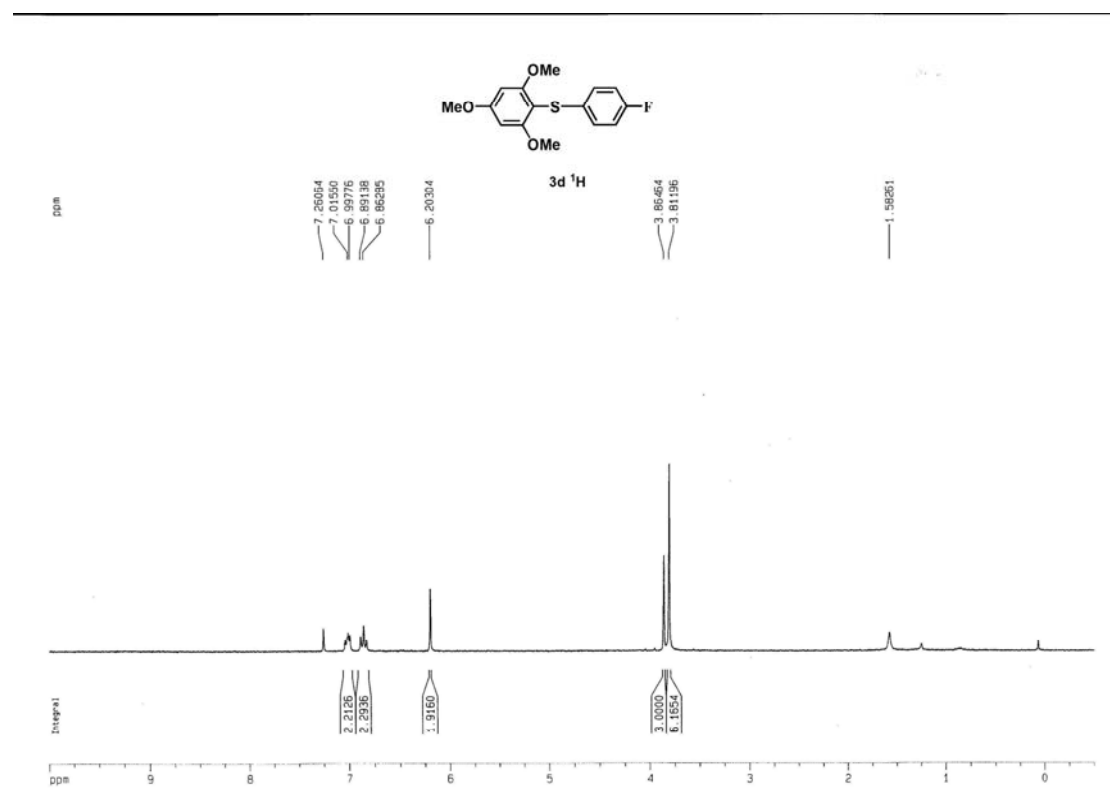
IR (prism, cm^{-1}): 2968, 1716, 1507, 1457, 1227, 1162, 1125, 743.

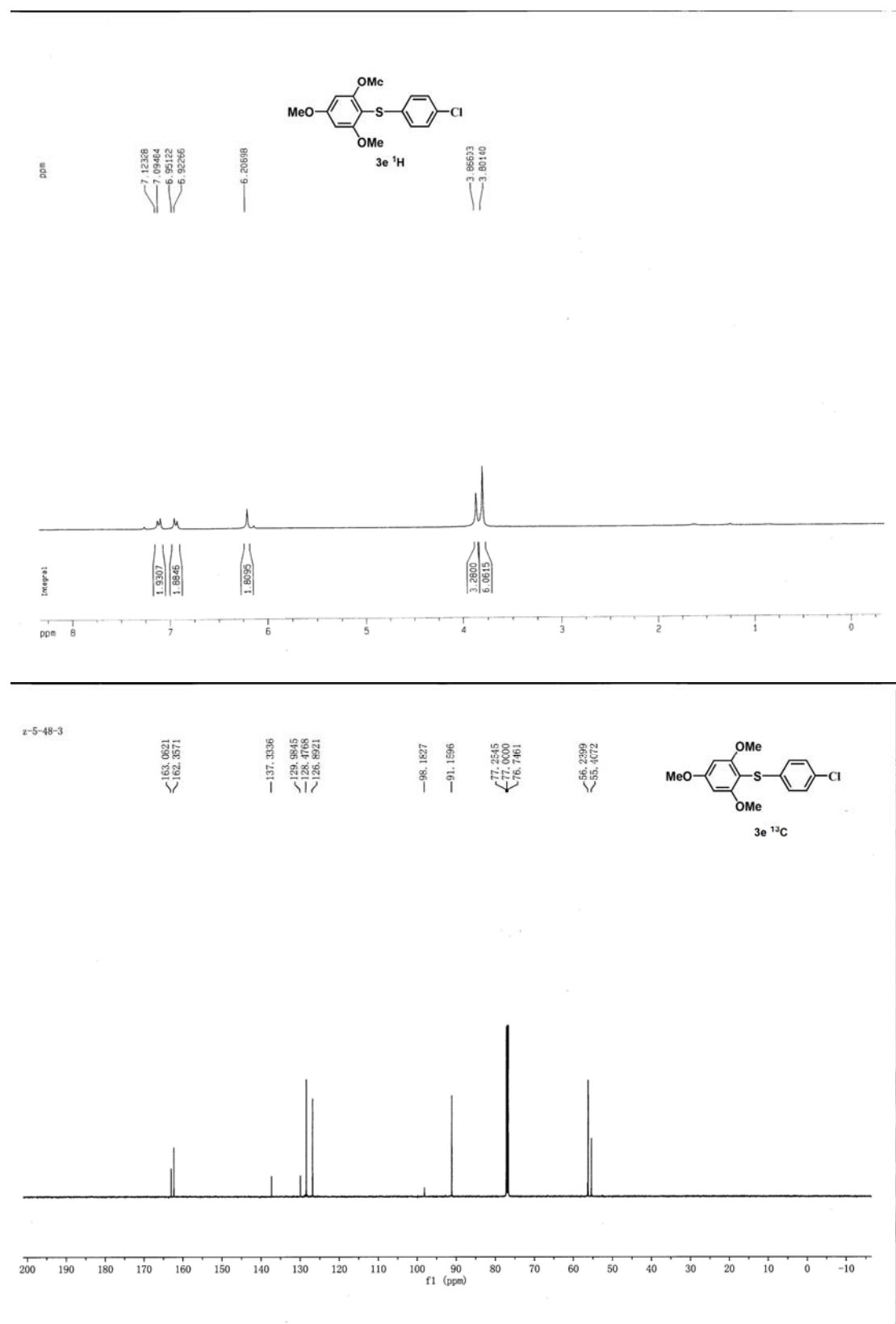
MS(EI) 276 (M^+); HRMS Calcd. for $\text{C}_{15}\text{H}_{16}\text{SO}_3$ (M^+) 276.0820, found 276.0814.

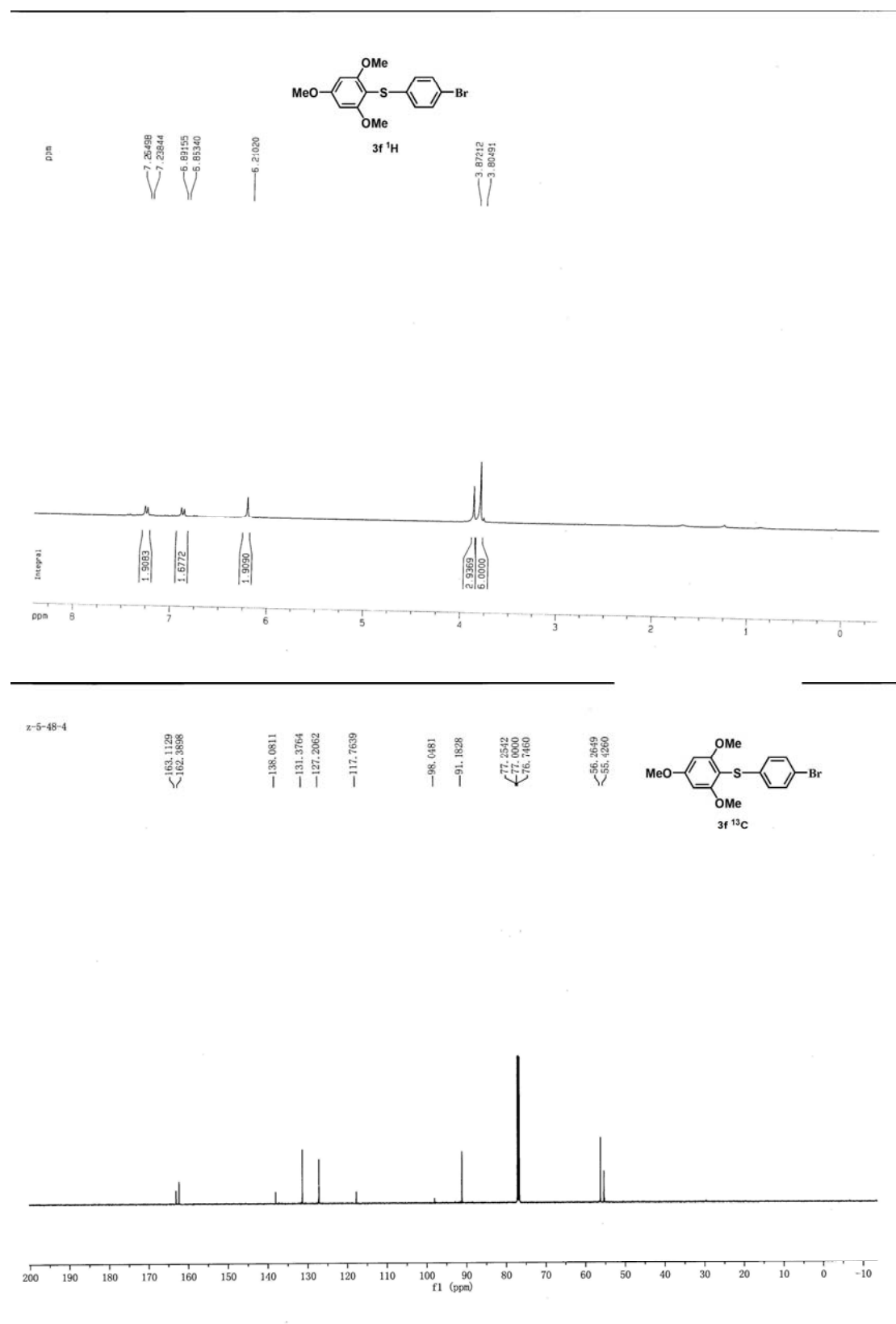


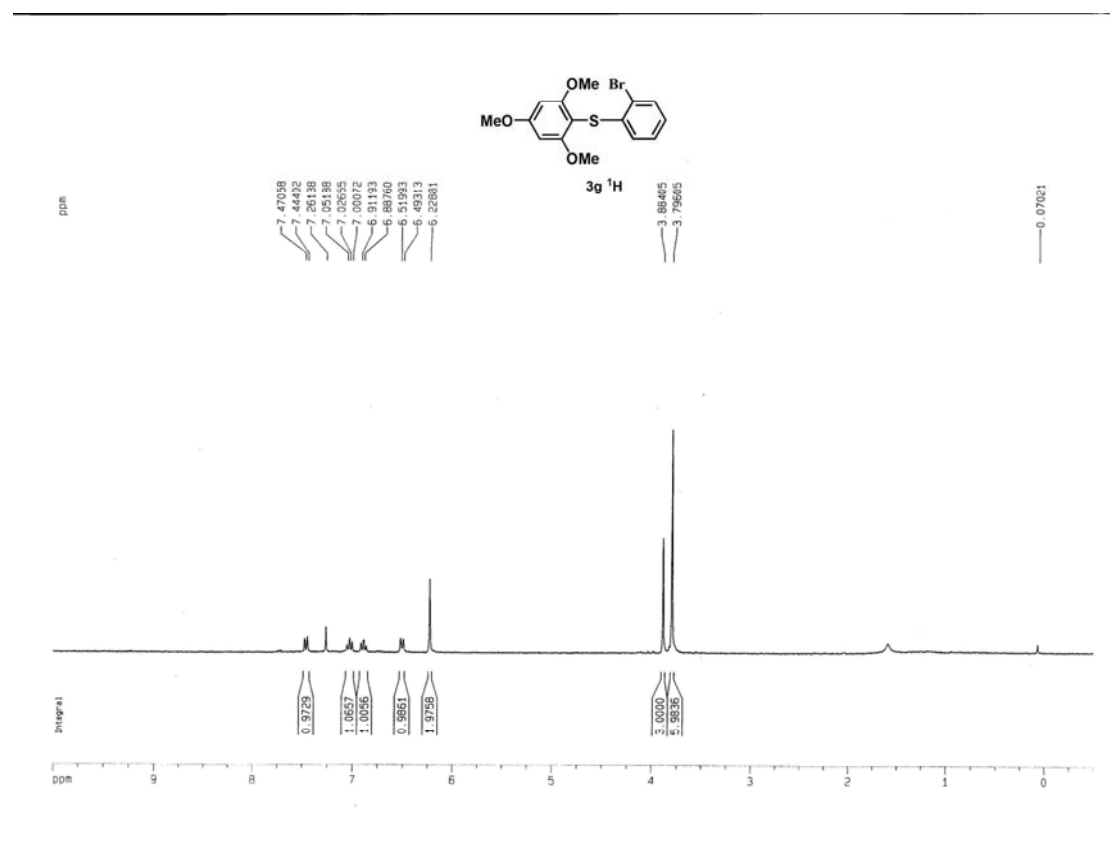




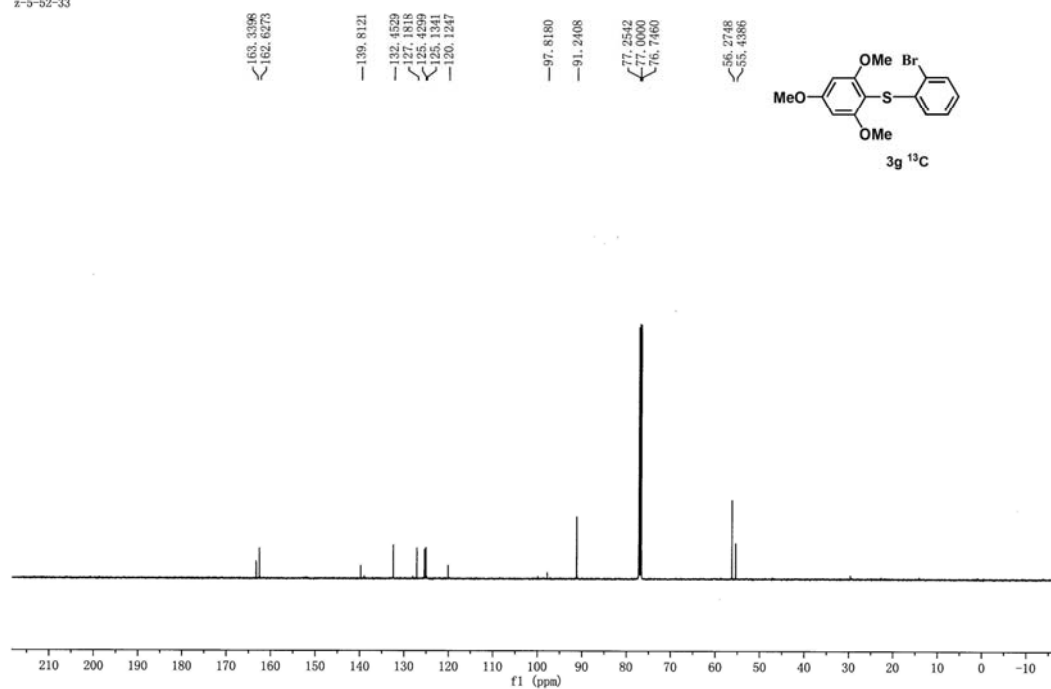


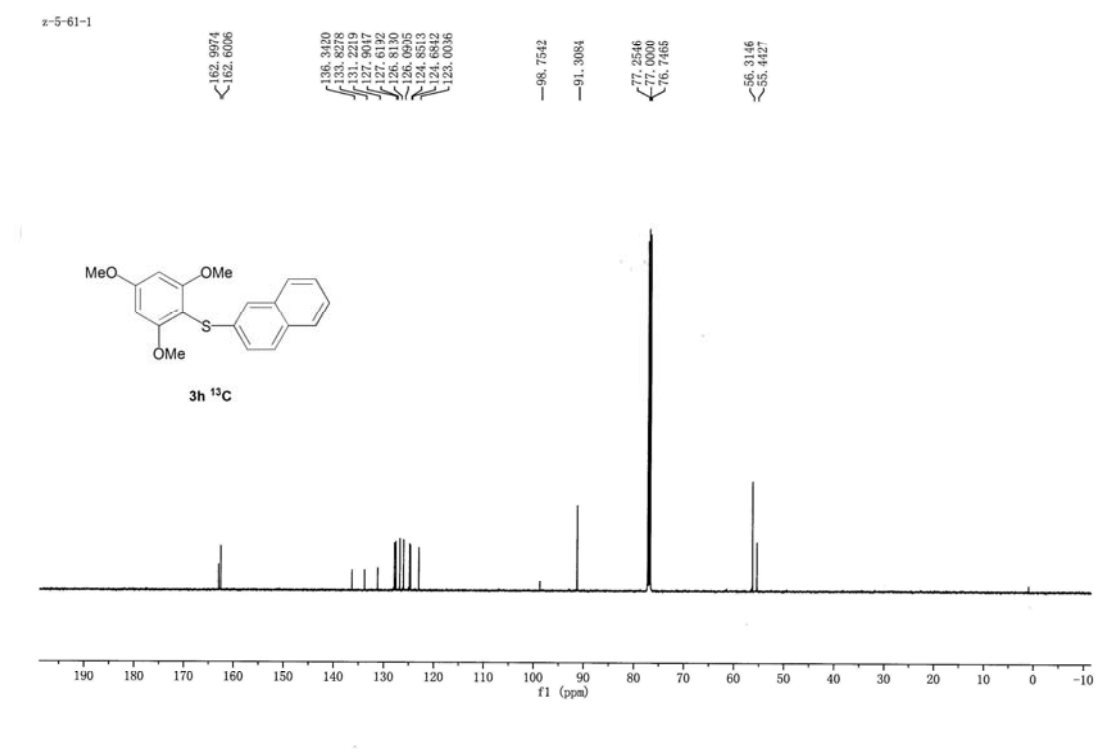
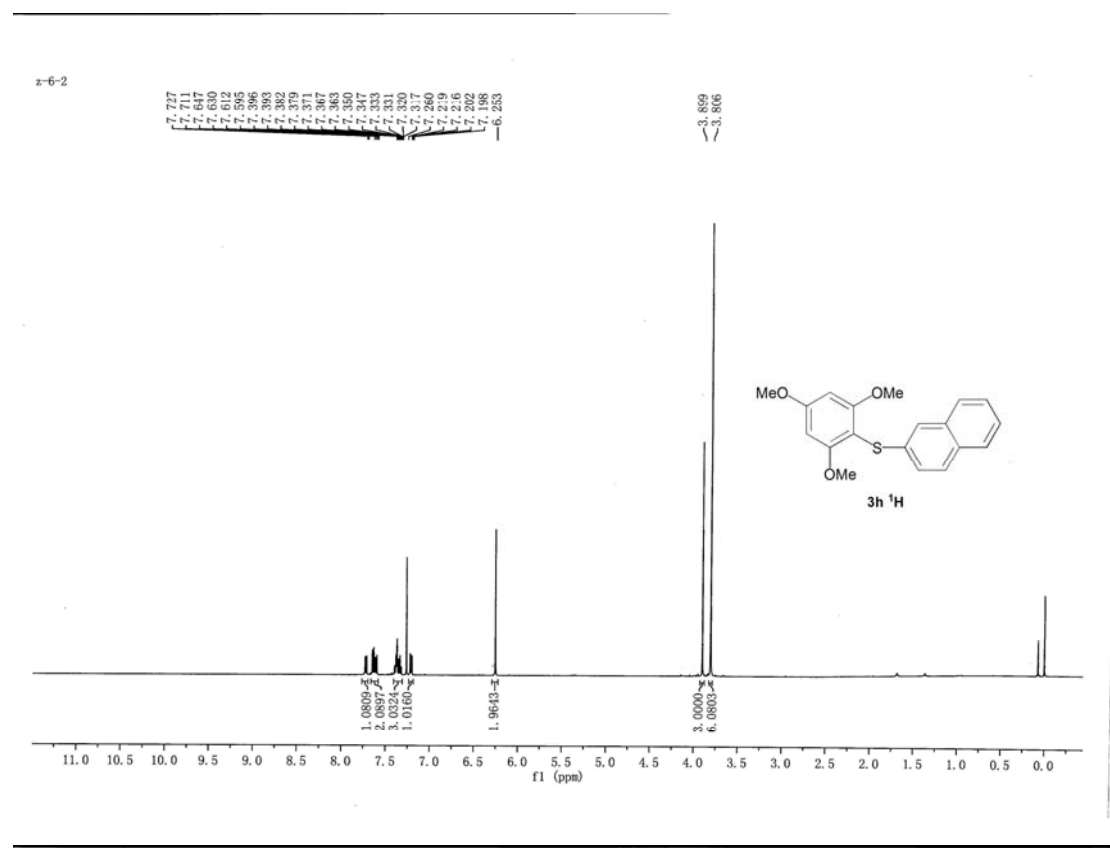


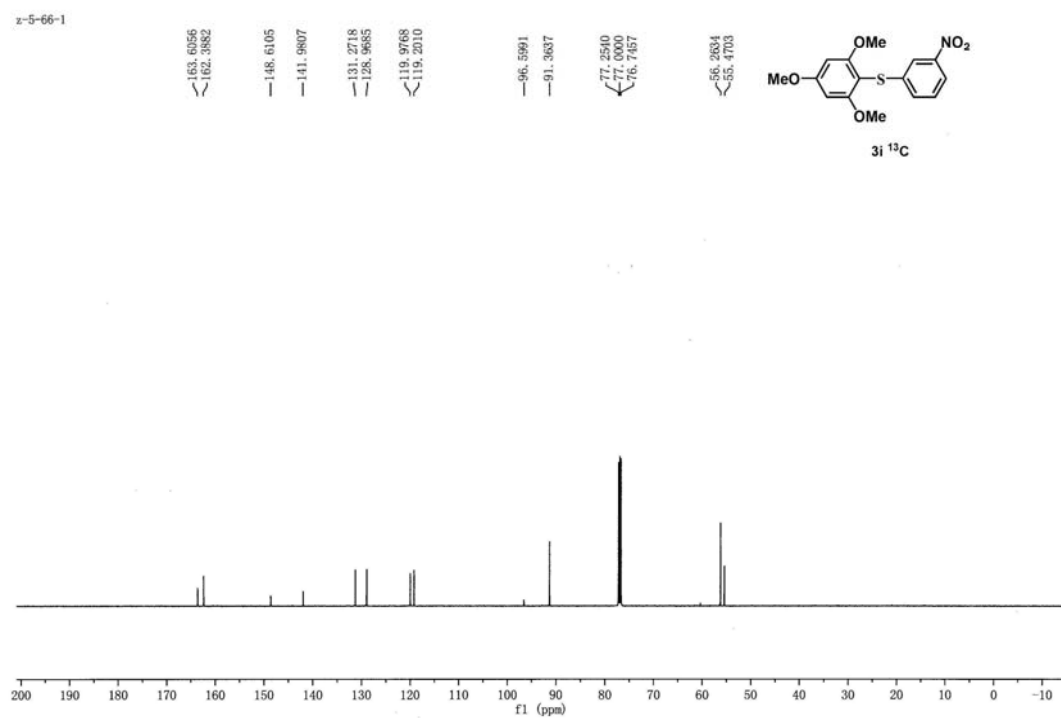
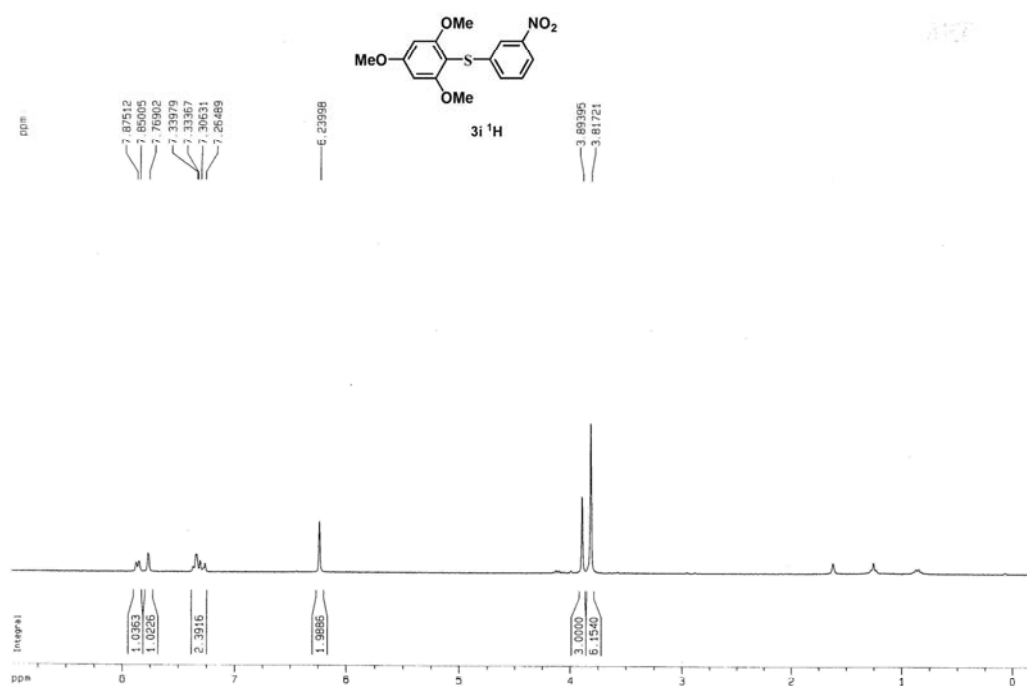


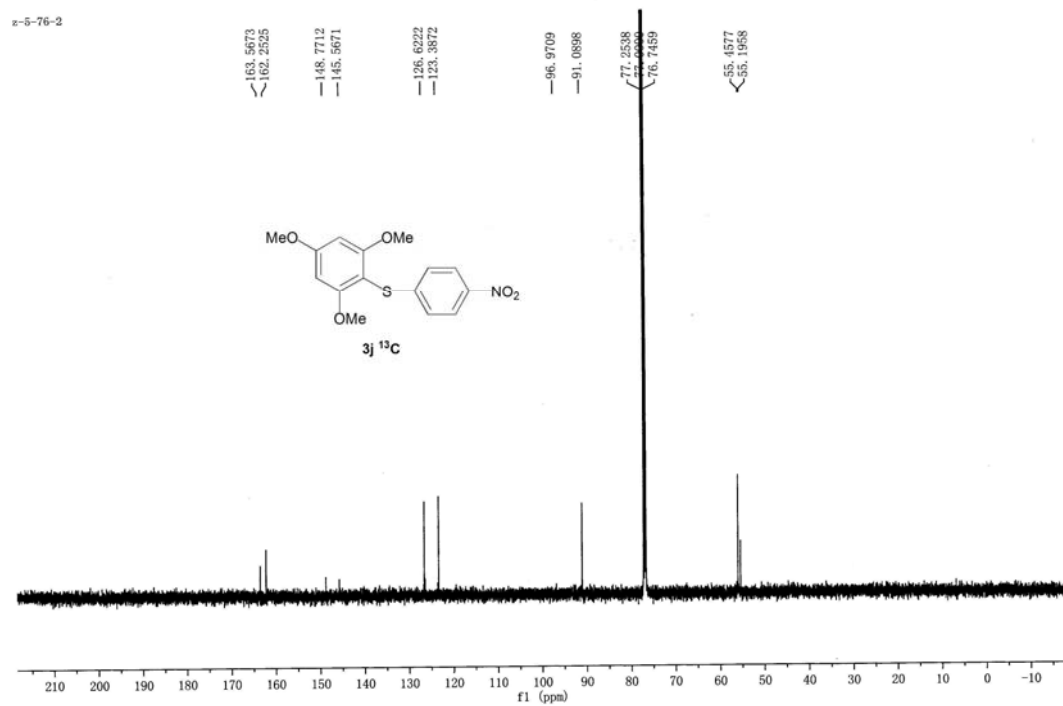
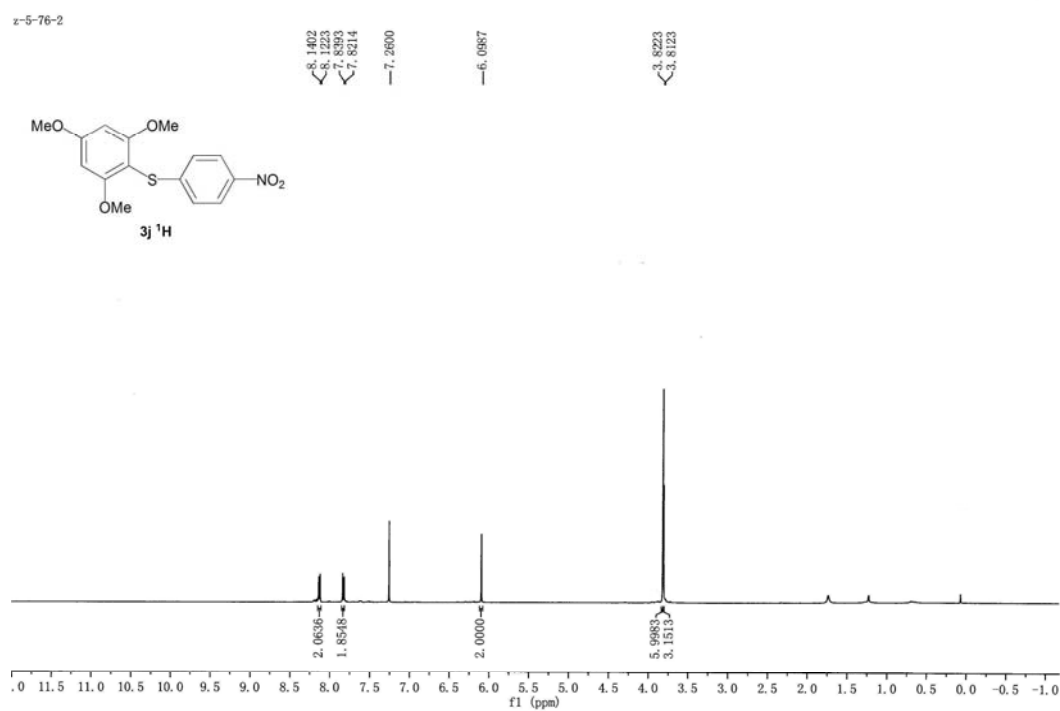


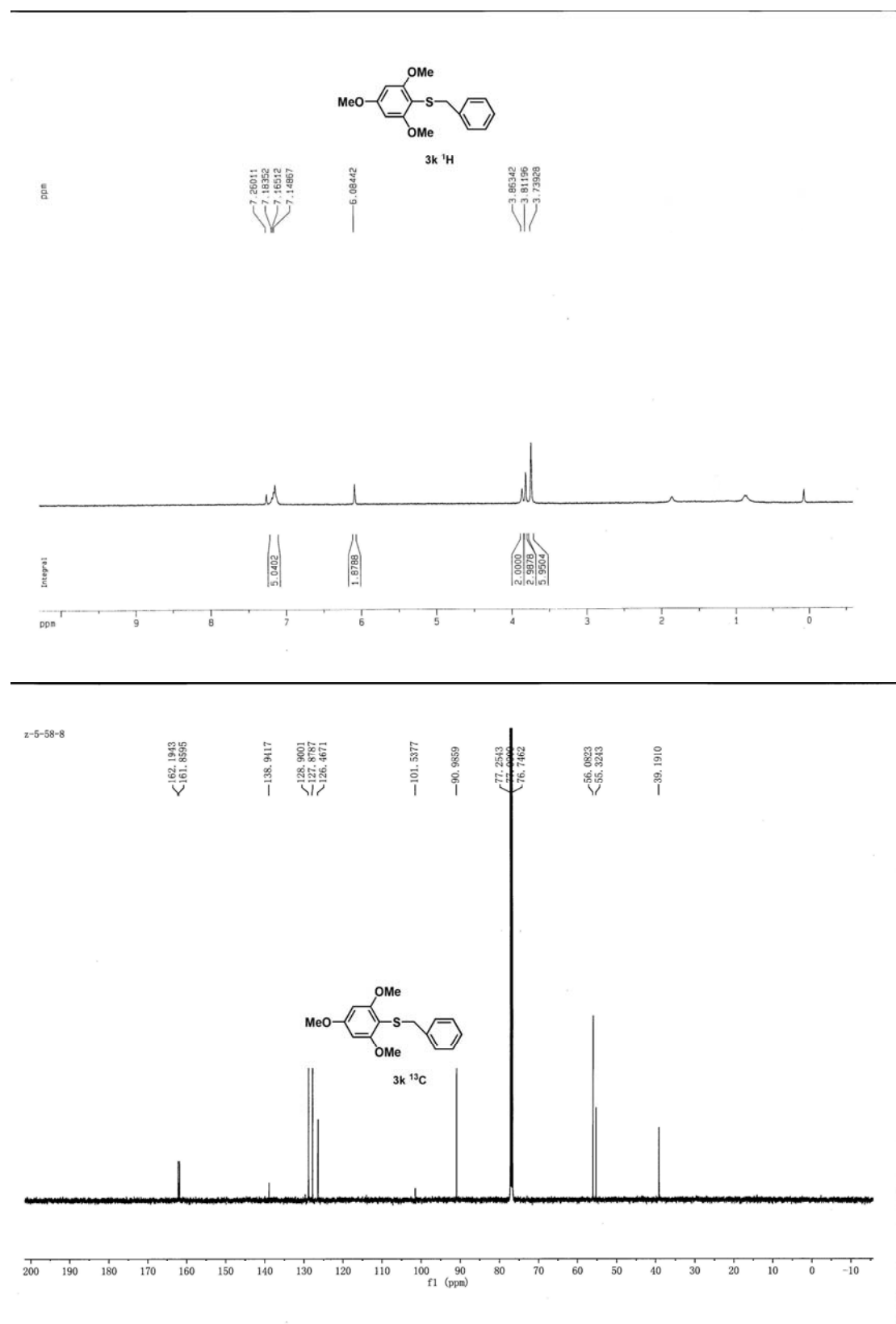
x-5-52-33

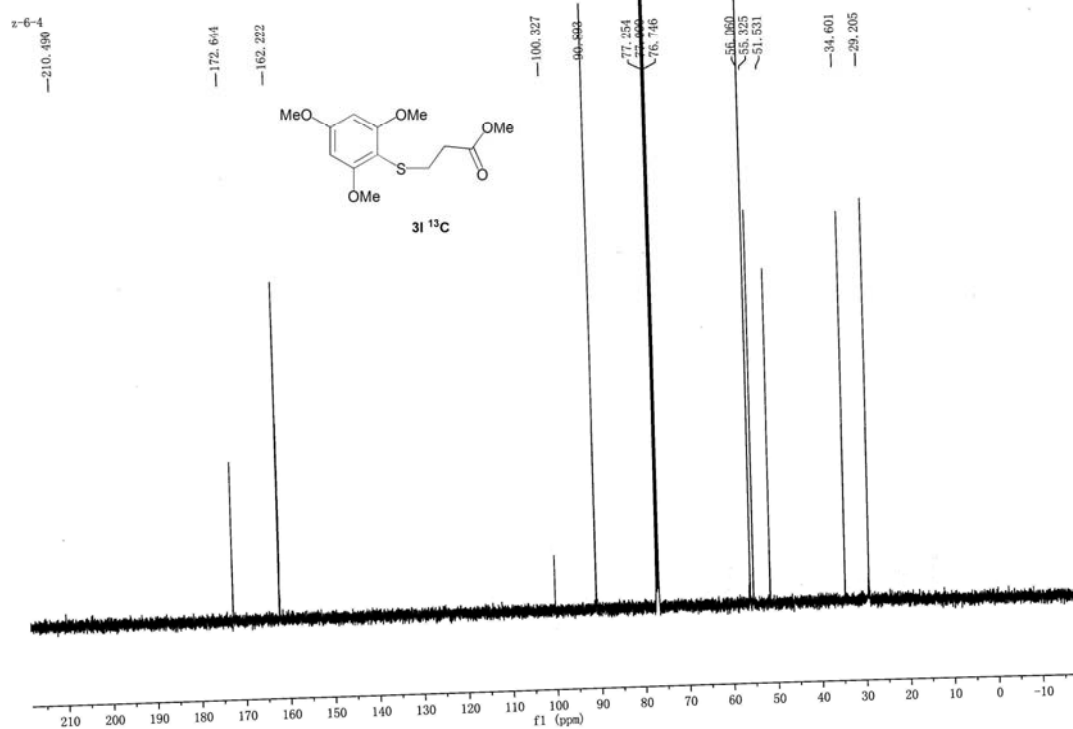
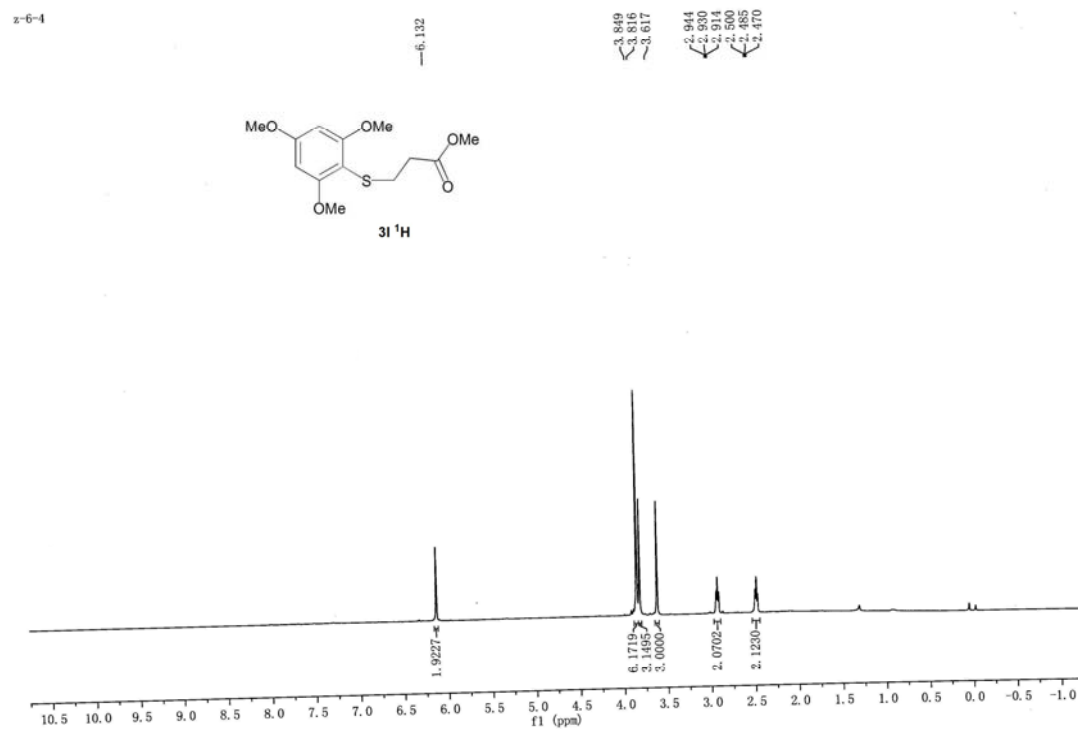




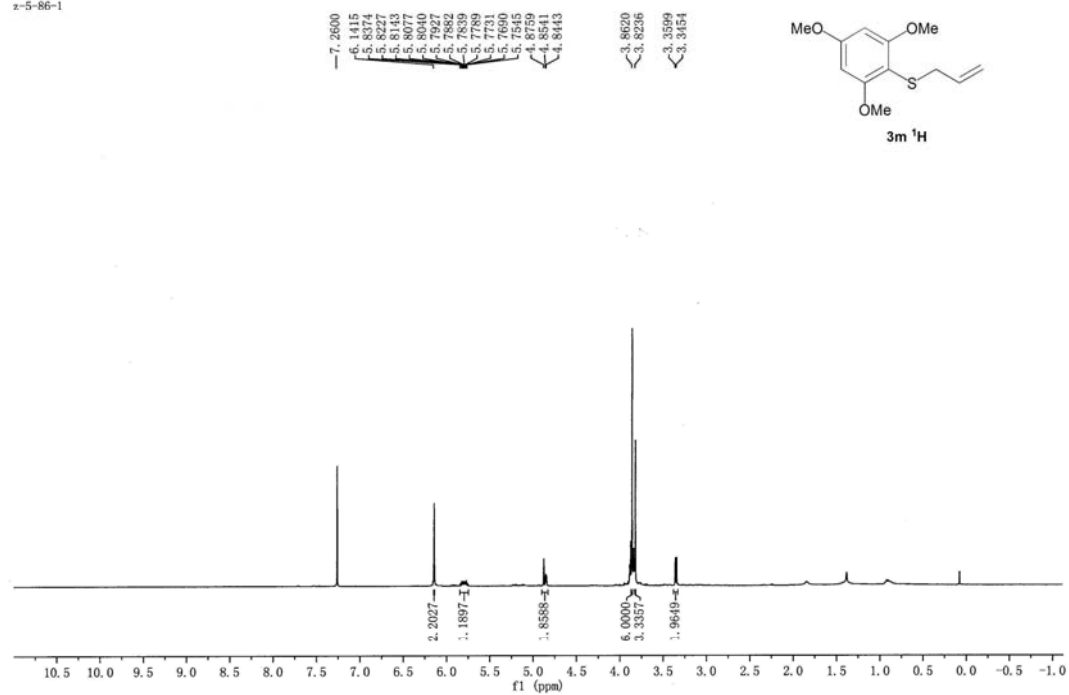








z-5-86-1



z-5-86-1

