**Supporting Information**

# $CO_2$-Promoted Oxidative Cross-Coupling Reaction for C-S Bond Formation *via* Masked Strategy in an Odourless Way

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## I. General information

### NMR spectrum:

$^{1}H$ and $^{13}C$ NMR spectra were collected on 300 MHz, 400 MHz, or 500 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

### Mass spectroscopy:

Mass spectra were in general recorded on a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector.

### Chromatography:

Column chromatography was performed with silica gel (300-400 mesh ASTM).

### IR:

TENSOR (27) Series FT-IR Spectrometers.

### TGA:

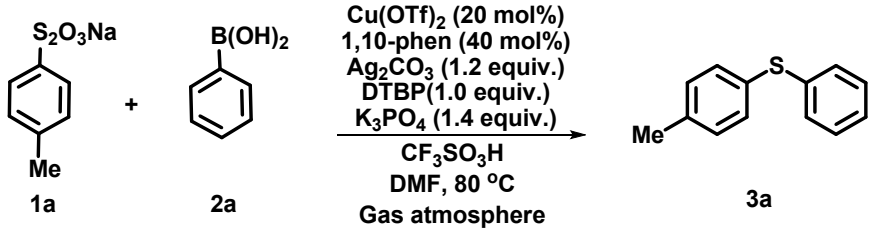
Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449 F3 instrument with a heating rate of 10 $^{o}C\ min^{-1}$ under $N_2$ atmosphere.

**II. General procedure for organic thiosulfate salt formation.**

A 25 mL flask equipped with a magnetic stirbar was charged with iodobenzene (10 mmol), anhydrous sodium thiosulfate (15 mmol) and CuI (1 mmol). The flask was sealed with a septum, evacuated and filled with nitrogen (3 times). DMSO (5 mL) was charged *via* syringe followed by N,N'-dimethylethylenediamine (2 mmol). The mixture was stirred at 80 °C for 10 h. When the reaction was finished, the mixture was add hot saturated aqueous NaCl (10 mL) was added, and the resultant slurry was stirred vigorously at rt for 10min. The mixture was filtered and the mixture of NaCl in saturated aqueous solution (90 mL) and n-hexane (100 mL) was added. The solid was obtained by recrystallization under vacuum (water pump) at rt.


**Figure 1. A set of organic thiosulfate salts**

## III. Selected condition optimization




| Entry | Variation from above | Gas atmosphere | 3a | Disulfide 4a |
|---|---|---|---|---|
| 1 | / | $CO_2$ | 85% | <2% |
| 2 | 4-MePhSH instead of 1a | $CO_2$ | 9% | 49% |
| 3 | without $CF_3SO_3H$ | $CO_2$ | 67% | 10% |
| 4 | without $Cu(OTf)_2$ | $CO_2$ | <2% | <2% |
| 5 | without 1,10-phen | $CO_2$ | <2% | <2% |
| 6 | without $K_3PO_4$ | $CO_2$ | 7% | 9% |
| 7 | without $Ag_2CO_3$ | $CO_2$ | 18% | 15% |
| 8 | / | $N_2$ | 40% | 20% |
| 9 | / | CO | 63% | 5% |
| 10 | / | $H_2$ | 31% | 24% |
| 11 | / | $O_2$ | 5% | 5% |

**Table 1 Condition optimization**

## IV. $^{1}H$ NMR and $^{13}C$ NMR spectra

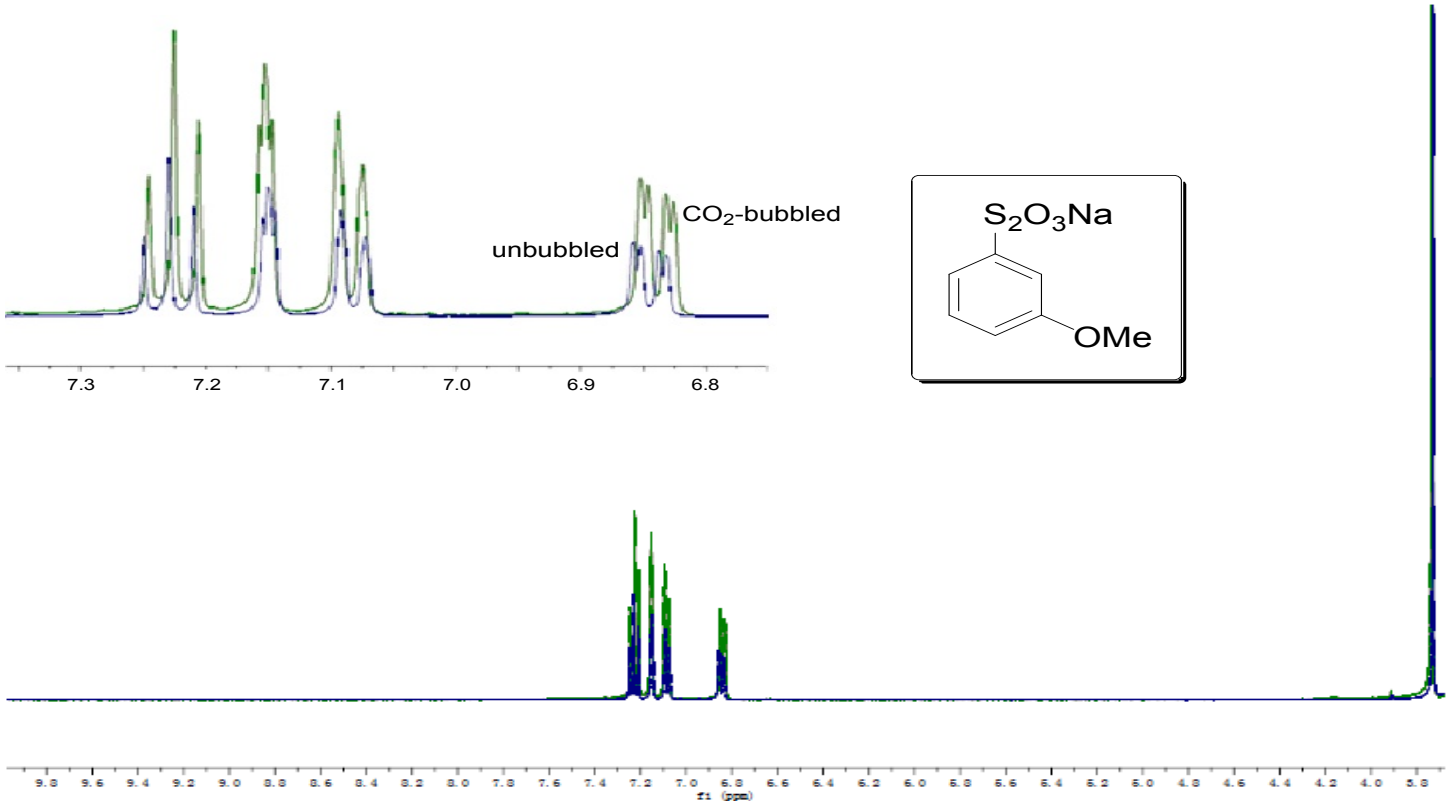



**Figure 2A. $^{1}H$ NMR spectra of $CO_2$-bubbled and unbubbled thiosulfate salts**

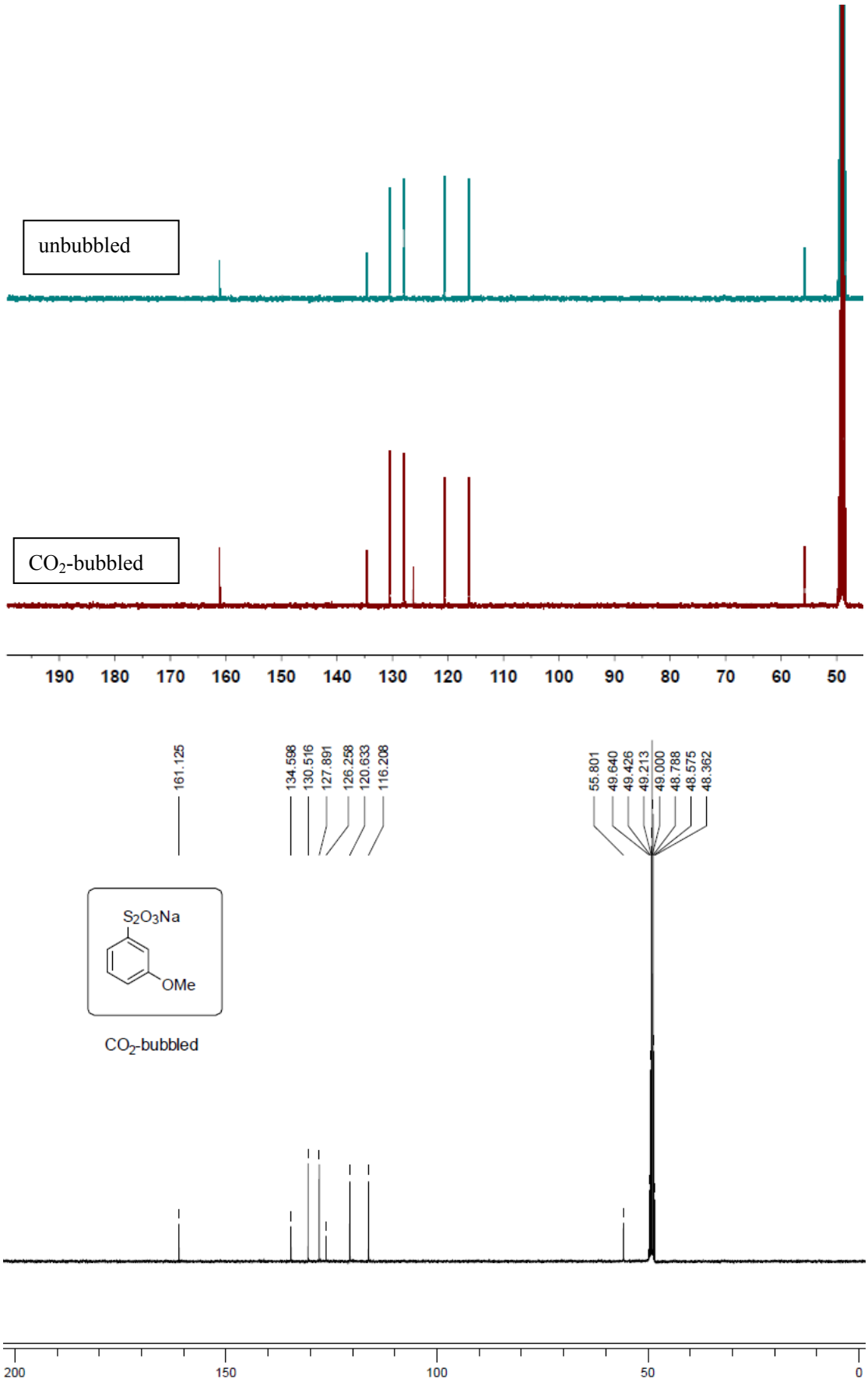
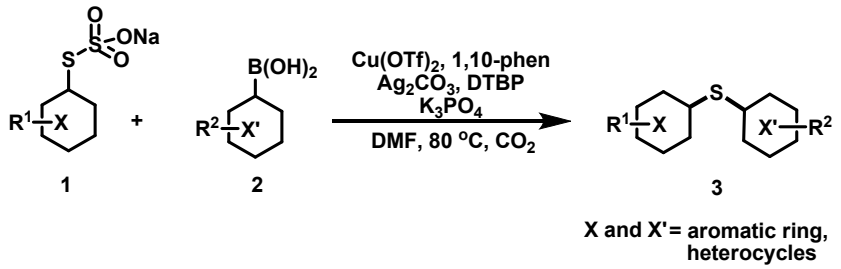
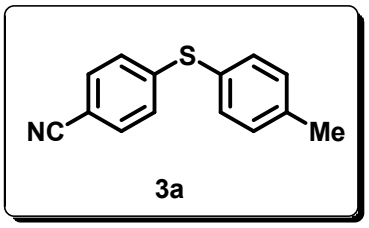



**Figure 2B. $^{13}C$ NMR spectra of $CO_2$-bubbled and unbubbled thiosulfate salt**

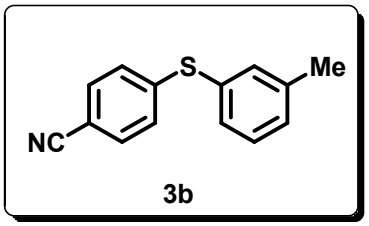
## V. The synthetic procedure and data for table 2, 3, and 4




To a 25mL Schlenk tube under carbon dioxide atmosphere were added sulfothioate **1** (0.1 mmol), boronic acid **2** (0.15-0.2 mmol), copper (0.02 mmol), 1,10-phenanthroline (0.04 mmol), $Ag_2CO_3$ (0.12 mmol), $K_3PO_4$ (0.14 mmol), DTBP (0.1 mmol), and DMF (2.0 mL). The system was heated to 80 °C. The reaction was monitored by TLC. When the reaction was finished, the mixture was cooled to rt., quenched by $NH_4Cl$ (aq.) and extracted with EA (3 * 10 mL). The combined extracts are dried over $Na_2SO_4$ and concentrated. Purification by column chromatography on silica gel affords product aromatic sulfide.

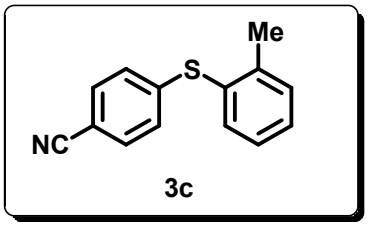



To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-cyanophenyl sulfothioate (0.1 mmol, 23.7 mg), *p*-tolylboronic acid (0.15 mmol, 20.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 4-(*p*-tolylthio)benzonitrile **3a** 13.7 mg (61 %). $R_f$ = 0.35 (Ethyl Acetate : Petroleum Ether = 20:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.41 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 146.6, 140.0, 134.9, 132.3, 130.7, 126.8, 126.7, 118.9, 108.2, 21.3; **IR (neat)** 3024, 2858, 2226, 1485, 1261, 1082, 731cm$^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{11}NS$ 225.0612, Found 225.0610.



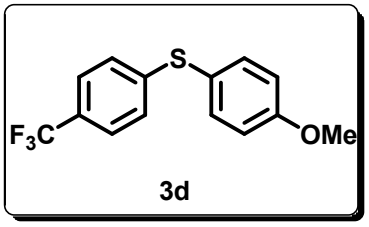
3b

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-cyanophenyl sulfothioate (0.1 mmol, 23.7 mg), *m*-tolylboronic acid (0.15 mmol, 20.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford **3e** 4-(*m*-tolylthio)benzonitrile **3b** 13.1 mg (58 %). $R_f$ = 0.35 (Ethyl Acetate : Petroleum Ether = 20:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.31-7.34 (m, 3H), 7.24-7.27 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 146.0, 139.9, 135.1, 132.3, 131.6, 130.3, 130.2, 129.7, 127.1, 118.8, 108.5, 21.2,; **IR (neat)** 2961, 2852, 2226, 1587, 1481, 1401, 1260, 1177, 829, 689 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{11}NS$ 225,0612, Found 225.0613.



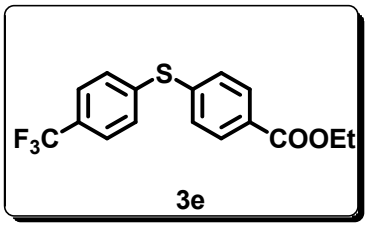
3c

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-cyanophenyl sulfothioate (0.1 mmol, 23.7 mg), *o*-tolylboronic acid (0.15 mmol, 20.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 4-(*o*-tolylthio)benzonitrile **3c** 9.3 mg (41 %). $R_f$ = 0.35 (Ethyl Acetate : Petroleum Ether = 20:1);**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35-7.40 (m, 2H), 7.24-7.28 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 145.6, 142.6, 136.4, 132.4, 131.3, 130.2, 129.2, 127.4, 126.4, 118.9, 108.2, 20.7; **IR (neat)** 2925, 2226, 1592, 1484, 1741, 1086, 1016, 755 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{11}NS$ 225.0612, Found 225.0611.



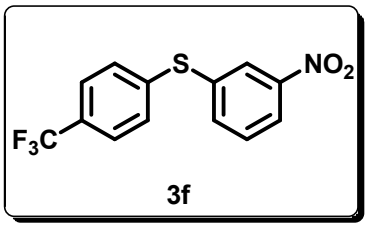
3d

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-(trifluoromethyl)phenyl sulfothioate (0.1 mmol, 28.0 mg), 4-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane **3d** 21.3 mg (75 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.43-7.48 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.6, 144.8, 136.7, 127.2 (q, $J^2$= 32.3 Hz), 126.4, 125.6 (q, $J^3$= 3.7 Hz), 124.2 (q, $J^1$ = 270.1 Hz), 121.6, 115.4, 55.4; **$^{19}$F NMR (376 MHz, CDCl3)**: δ -62.4 (s, 3F); **IR (neat)** 3029, 2847, 1492, 1460, 1251, 1060, 831, 699 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{11}OSF_3$ 284.0483, Found 284.0484.



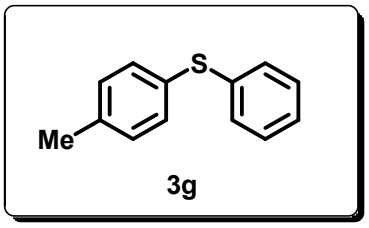
3e

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-(trifluoromethyl)phenyl sulfothioate (0.1 mmol, 28.0 mg), 4-(ethoxycarbonyl)phenylboronic acid (0.15 mmol, 29.1 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford ethyl 4-(4-(trifluoromethyl)phenylthio)benzoate **3e** 26.1 mg (80 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.38 (q, *J* = 0.8 Hz, 5.6Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 165.9, 140.5, 139.6, 131.0, 130.9, 130.4, 130.4, 129.5 (q, $J^2$ = 32.7 Hz), 126.2 (q, $J^3$= 3.6 Hz), 123.9 (q, $J^1$= 369.9 Hz), 61.2, 14.3; **$^{19}$F NMR (376 MHz, $CDCl_3$)**: δ -62.7 (s, 3F); **IR (neat)** 2984, 1718, 1440, 1399, 1270, 1063, 1014, 830, 702$cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{13}O_2F_3S$ 326.0588, Found 326.0586.



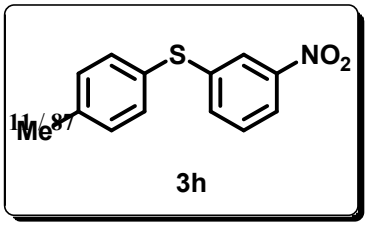
3f

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-(trifluoromethyl)phenyl sulfothioate (0.1 mmol, 28.0 mg), 3-nitrophenylboronic acid (0.15 mmol, 25.1 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford ethyl (3-nitrophenyl)(4-(trifluoromethyl)phenyl)sulfane **3f** 21.5 mg (72 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.21-8.22 (m, 1H), 8.13-8.16 (m, 1H), 7.64-7.67 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 148.8, 139.0, 137.2, 136.9, 130.9, 130.2, 129.6 (q, $J^2$= 32.7 Hz), 126.4 (q, $J^3$= 3.6 Hz), 125.8, 123.8 (q, $J^1$ = 270.6 Hz), 122.5; **$^{19}$F NMR (376 MHz, $CDCl_3$)**: δ -62.7 (s, 3F); **IR (neat)** 3086, 1401, 1348, 1123, 876, 829, 672 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_8NO_2SF_3$ 299.0228 Found 299.0227.



3g

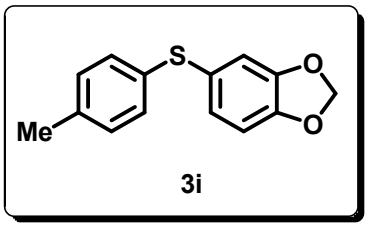
To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), phenylboronic acid (0.15 mmol, 18.3 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (3.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford phenyl(*p*-tolyl)sulfane **3g** 17.0 mg (85 %). $R_f$ = 0.80 (Petroleum Ether); **$^1$H NMR (400 MHz, CDCl3):** δ 7.18-7.24 (m, 6H), 7.11-7.13 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 137.6, 137.1, 132.3, 131.3, 130.0, 129.8, 129.0, 126.4, 21.1; **IR (neat)** 2950, 2851, 1896, 1492, 1477, 808, 739, 690$cm^{-1}$; **HRMS(EI)** Calcd for C13H12S 200.0660, Found 200.0661.



3h

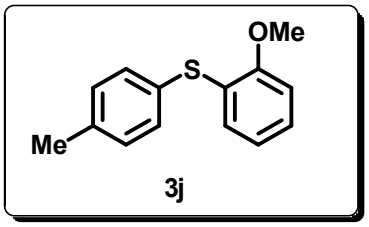
To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol,

22.6 mg), 3-nitrophenylboronic acid (0.15 mmol, 25.1 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 3 (3-nitrophenyl)(*p*-tolyl)sulfane **3h** 12.8 mg (52 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.95-7.97 (m, 2H), 7.36-7.45 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 148.6, 141.6, 139.6, 134.2, 133.3, 130.7, 129.5, 127.8, 122.2, 120.4, 21.3; **IR (neat)** 2956, 2930, 2872, 1591, 1480, 1409, 1304, 1214, 812, 684 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}NO_2S$ 245.0511, Found 245.0509.



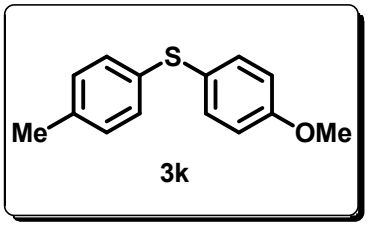
**3i**

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), benzo[*d*][1,3]dioxol-5-ylboronic acid (0.15 mmol, 24.9 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 5-(*p*-tolylthio)benzo[*d*][1,3]dioxole **3i** 17.3 mg (71 %). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 2.32 (s, 3H), 5.96 (s, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 1.6 Hz, 1H), 6.92-6.94 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 148.2, 147.5, 136.6, 133.5, 130.1, 129.8, 127.7, 126.1, 112.6, 108.8, 101.3, 21.0; **IR (neat)** 2853, 2922, 1714, 1477, 1235, 1039, 890, 806 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{12}NO_2S$ 244.0558, Found 244.0560.



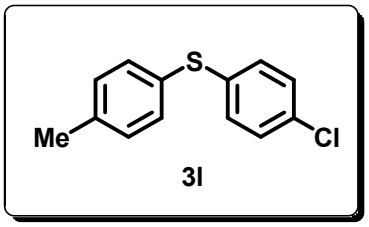
3j

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), 2-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (2-methoxyphenyl)(*p*-tolyl)sulfane **3j** 12.4 mg (54 %). $R_f$ = 0.50 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.32 (d, J = 8.0 Hz, 2H), 7.20-7.15 (m, 3H), 6.95-6.81 (m, 3H), 3.89 (s, 3H), 2.36 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 156.5, 137.7, 133.0, 130.0, 129.8, 129.7, 127.4, 125.7, 121.2, 110.6, 55.9, 21.2; **IR (neat)** 2856, 2038, 1578, 1475, 1432, 1274, 1242, 1025, 7489 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{14}SO$ 230.0765, Found 230.0762.



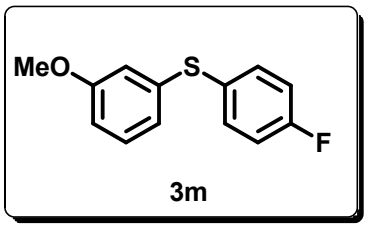
3k

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), 4-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-methoxyphenyl)(*p*-tolyl)sulfane **3k** 14.5 mg (63 %). $R_f$ = 0.80 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ7.36 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.30 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ159.5, 136.1, 134.3, 129.8, 129.4, 125.7, 114.9, 55.3, 21.0; **IR (neat)** 2852, 1482, 1390, 1267, 1077, 1009, 819 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{14}OS$ 230.0765, Found 230.0766.



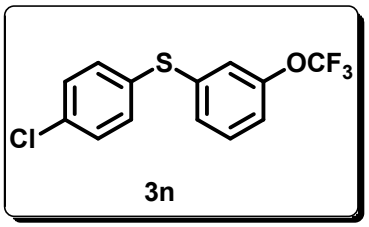
3l

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), 4-chlorophenylboronic acid (0.15 mmol, 23.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)(*p*-tolyl)sulfane **3l** 17.1 mg (73 %). $R_f$ = 0.80 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.14-7.18 (m, 6H), 2.35 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ138.0, 135.9, 132.5, 132.3, 130.8, 130.6, 130.2, 129.1, 21.1; **IR (neat)** 3023, 2854, 1742, 1491, 1475, 1090, 1011, 812cm$^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}S^{35}Cl$ 234.0270, Found 234.0271.



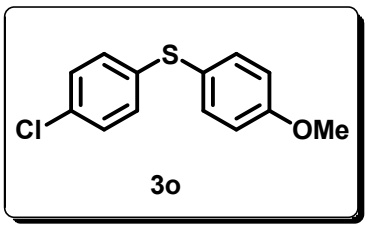
3m

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), 4-fluorophenylboronic acid (0.15 mmol, 21.0 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford ethyl (4-fluorophenyl)(3-methoxyphenyl)sulfane **3m** 19.7 mg (84 %). $R_f$ = 0.70 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.39-7.42 (m, 2H), 7.17-7.21 (m, 1H), 7.02-7.06 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.74-6.78 (m, 2H), 3.75 (s, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 162.5 (*J* = 122.2 Hz), 160.0, 138.1, 134.5 (*J* = 40.5 Hz), 129.9, 129.6 (*J* = 1.6 Hz), 121.8, 116.4 (*J* = 10.9 Hz), 114.9, 112.3, 55.3; **$^{19}$F NMR (376 MHz, $CDCl_3$)**: δ -113.7 (s, 1F); **IR (neat)** 3003, 2938, 2836, 1590, 1489, 1230, 1043, 831cm$^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}OSF$ 234.0515, Found 234.0517.



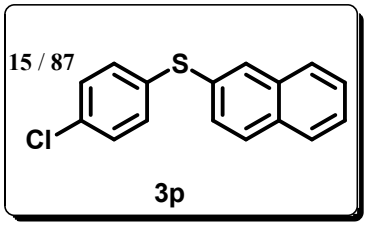
3n

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-chlorophenyl sulfothioate (0.1 mmol, 24.6 mg), 3-(trifluoromethoxy)phenylboronic acid (0.15 mmol, 30.9 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)(3-(trifluoromethoxy)phenyl)sulfane **3n** 15.4 mg (51 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.29-7.36 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.06-7.10 (m, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 149.7, 138.7, 134.3, 133.6, 132.2, 130.3, 129.7, 127.8, 122.0, 119.1; **IR (neat)** 2969, 2929, 1475, 1424, 1254, 1167, 822, 686cm$^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_8OF_3S^{35}Cl$ 303.9936, Found 303.9935.



3o

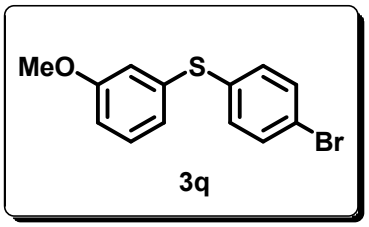
To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-chlorophenyl sulfothioate (0.1 mmol, 24.6 mg), 4-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)(4-methoxyphenyl)sulfane **3o** 15.3 mg (61 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.0, 137.3, 135.5, 131.6, 129.3, 129.0, 123.7, 115.1, 55.4; **IR (neat)** 3061, 2835, 1493, 1474, 1439, 1247, 1010, 742cm$^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}OS^{35}Cl$ 250.0219, Found 250.0217.



3p

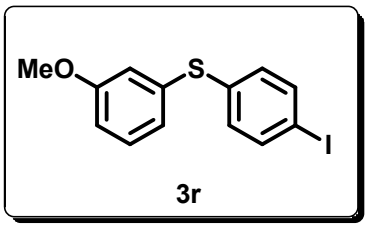
To a Schlenk tube under carbon dioxide atmosphere

were added sodium *S*-4-chlorophenyl sulfothioate (0.1 mmol, 24.6 mg), naphthalen-2-ylboronic acid (0.15 mmol, 25.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)(naphthalen-2-yl)sulfane **3p** 14.9 mg (55 %). $R_f$ = 0.50 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.85 (s, 1H), 7.74-7.83 (m, 3H), 7.48-7.51 (m, 2H), 7.40 (dd, *J* = 1.6 Hz, 8.4Hz, 1H), 7.28-7.32 (m, 4H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 126.4, 126.7, 127.4, 127.7, 128.7, 129.1, 129.3, 130.3, 131.9, 132.3, 132.4, 133.0, 133.8, 134.7; **IR (neat)** 3054, 2925, 1898, 1475, 1262, 1092, 908, 747 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{11}S^{35}Cl$ 270.0270, Found 270.0273.



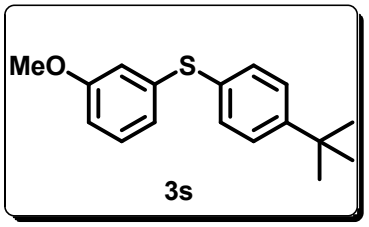
**3q**

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), 4-bromophenylboronic acid (0.15 mmol, 30.0 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-bromophenyl)(3-methoxyphenyl)sulfane **3q** 21.8 mg (74 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.11-7.18 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.1, 136.1, 135.0, 132.4, 132.2, 130.1, 123.4, 121.1, 116.4, 113.2, 55.3; **IR (neat)** 3003, 2933, 2834, 1589, 1472, 1247, 1069, 686 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}OS^{79}Br$ 293.9714, Found 293.9715.



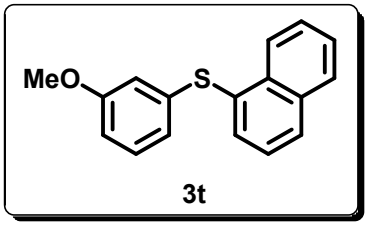
3r

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), 4-iodophenylboronic acid (0.15 mmol, 37.2 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-iodophenyl)(3-methoxyphenyl)sulfane **3r** 20.5 mg (60 %). $R_f$ = 0.50 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.56-7.60 (m, 2H), 7.20-7.24 (m, 1H), 7.02-7.05 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87-6.88 (m, 1H), 6.81 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H), 3.76 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.1, 138.1, 136.1, 135.8, 132.3, 130.1, 123.7, 116.7, 113.4, 92.1, 55.3; **IR (neat)** 3001, 2954, 2833, 1468, 1381, 1229, 1041, 686 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{11}OSI$ 341.9575, Found 341.9577.



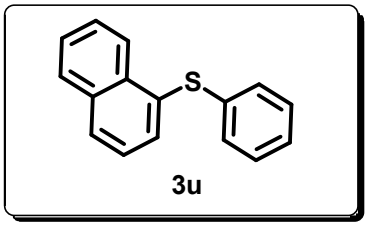
3s

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), 4-tert-butylphenylboronic acid (0.15 mmol, 37.2 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-tert-butylphenyl)(3-methoxyphenyl)sulfane **3s** 15.5 mg (57 %). $R_f$ = 0.50 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.32-7.37 (m, 4H), 7.17-7.21 (m, 1H), 6.84-6.89 (m, 2H), 6.75 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H), 3.76 (s, 3H), 1.32 (s, 9H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 159.9, 150.8, 138.1, 131.8, 131.0, 129.8, 126.3, 122.2, 115.2, 112.2, 55.2, 34.6, 31.2; **IR (neat)** 2961, 2868, 1479, 1363, 1246, 1229, 773, 686$cm^{-1}$; **HRMS(EI)** Calcd for $C_{17}H_{20}OS$ 272.1235, Found 272.1237.



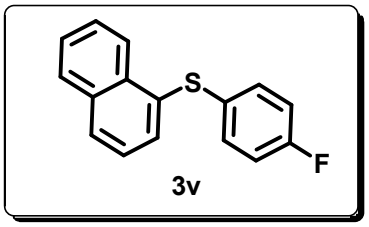

3t

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), naphthalen-1-ylboronic acid (0.15 mmol, 25.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), $CF_3SO_3H$ (5.0 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (3-methoxyphenyl)(naphthalen-1-yl)sulfane **3t** 16.2 mg (61 %). $R_f$ = 0.60 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.37-8.39 (m, 1H), 7.86-7.89 (m, 2H), 7.69-7.72 (m, 1H), 7.51-7.53 (m, 2H), 7.43-7.46 (m, 1H), 7.11-7.15 (m, 1H), 6.68-6.76 (m, 3H), 3.69 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.0, 138.3, 134.2, 133.7, 132.9, 130.7, 129.8, 129.4, 128.5, 127.0, 126.4, 125.8, 125.6, 121.1, 114.2, 111.7, 55.2; **IR (neat)** 3055, 2934, 2833, 1588, 1476, 1246, 971, 686 cm$^{-1}$; **HRMS(EI)** Calcd for $C_{17}H_{14}OS$ 266.0765, Found 266.0766.



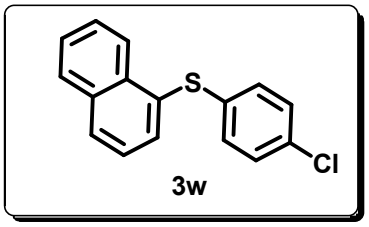

3u

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), phenylboronic acid (0.15 mmol, 18.3 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford naphthalen-1-yl(phenyl)sulfane **3u** 18.9 mg (80 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.31-8.28 (m, 1H), 7.81-7.78 (m, 2H), 7.59-7.57 (m, 1H), 7.45-7.41 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.15-7.04 (m, 5H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 136.9, 134.2, 133.5, 132.6, 131.1, 129.2, 129.0, 128.9, 128.5, 126.9, 126.4, 126.1, 125.8, 125.6; **IR (neat)** 2945, 1583, 1478, 1438, 1332, 1201, 1080, 860 cm$^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{12}S$ 236.0660, Found 236.0661.



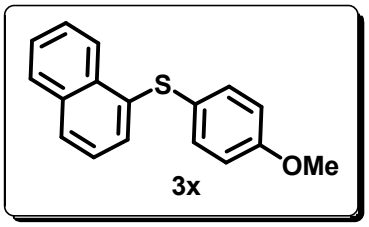
3v

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), 4-fluorophenylboronic acid (0.15 mmol, 21.0 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-fluorophenyl)(naphthalen-1-yl)sulfane **3v** 20.8 mg (82 %). $R_f$ = 0.30 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.27-8.24 (m, 1H), 7.78-7.71 (m, 2H), 7.46-7.41 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 2H) , 6.85 (t, *J* = 8.8 Hz, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.8 (*J* = 122.5 Hz), 134.1, 133.0, 132.1, 131.8, 131.8, 131.3, 131.2 (*J* = 1.2 Hz),128.8, 128.6, 126.7 (*J* = 22.2 Hz), 125.8, 125.2, 116.3 (*J* = 11.0 Hz); **$^{19}$F NMR (376 MHz, CDCl3)**: δ 115.3; **IR (neat)** 2992, 1589, 1488, 1292, 1228, 1085, 1012, 831 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{11}FS$ 254.0566, Found 254.0568.

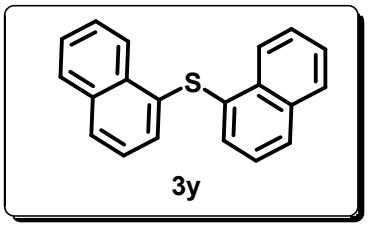


3w

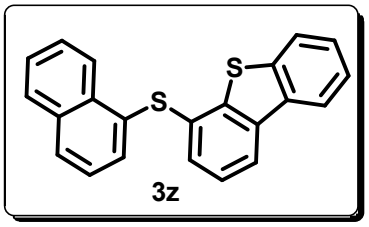
To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), 4-chlorophenylboronic acid (0.15 mmol, 23.4 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)(naphthalen-1-yl)sulfane **3w** 20.5 mg (76 %). $R_f$ = 0.25 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.35-8.32 (m, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.55-7.52 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.19-7.07 (m, 4H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 135.7, 134.2, 133.5, 133.1, 131.9, 130.4, 129.8, 129.7, 129.1, 128.6, 129.1, 126.5, 125.8, 125.5; **IR (neat)** 2932, 1639, 1475, 1092, 1011, 859, 814 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{12}ClS$ 270.0270, Found 270.0268.



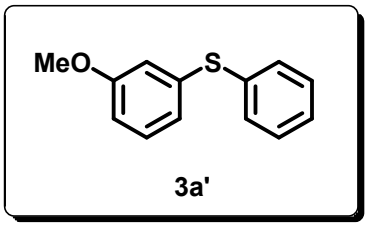

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), 4-methoxyphenylboronic acid (0.15 mmol, 22.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-methoxyphenyl)(naphthalen-1-yl)sulfane **3x** 22.6 mg (85 %). $R_f$ = 0.25 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.39-8.37 (m, 1H), 7.87-7.85 (m, 1H), 7.75-7.73 (m, 1H), 7.55-7.52 (m, 2H), 7.37-7.32 (m, 4H), 6.89-6.87 (m, 2H), 3.80 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 159.3, 134.6, 133.9, 133.8, 132.1, 128.5, 128.4, 127.3, 126.5, 126.3, 125.7, 125.0, 124.8, 115.0, 55.3; **IR (neat)** 3004, 2955, 1591, 1493, 1459, 1249, 1031, 832 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{17}H_{14}OS$ 266.0765, Found 266.0767.



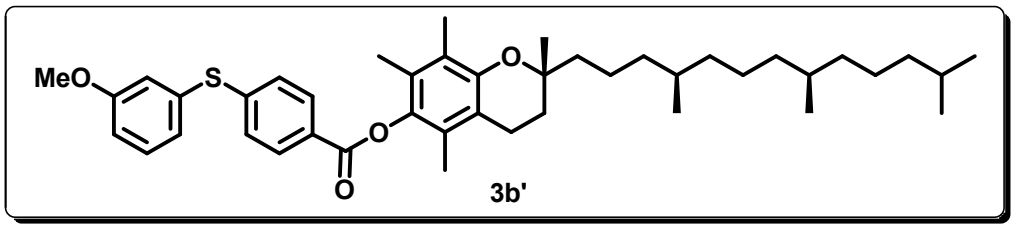

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), naphthalen-1-ylboronic acid (0.15 mmol, 25.8 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford dinaphthalen-1-ylsulfane **3y** 20.9 mg (73 %). $R_f$ = 0.25 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.91-7.89 (m, 2H), 7.81-7.78 (m, 2H), 7.56-7.54 (m, 4H), 7.33 (d, *J* = 8.8 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 134.1, 132.6, 132.4, 129.9, 128.6, 128.0, 126.7, 126.4, 125.8, 125.; **IR (neat)** 2943, 1624, 1422, 1275, 1204, 1057, 857, 797 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{20}H_{14}S$ 286.0816, Found 286.0819.



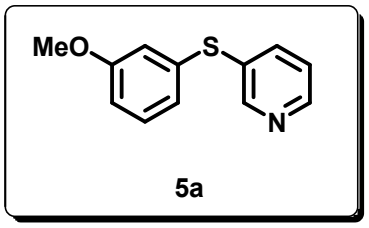

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-naphthalen-1-yl sulfothioate (0.1 mmol, 26.2 mg), dibenzo[*b,d*]thiophen-4-ylboronic acid (0.15 mmol, 34.2 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 4-(naphthalen-1-ylthio)dibenzo[*b,d*]thiophene **3z** 23.3 mg (68 %). $R_f$ = 0.22 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.46-8.43 (m, 1H), 8.16-8.14 (m, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.90-7.81 (m, 3H), 7.56-7.52 (m, 5H), 7.38-7.30 (m, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 142.1, 139.5, 136.3, 135.7, 134.1, 132.8, 131.0, 130.1, 129.7, 129.1, 128.6, 128.5, 127.0, 126.8, 126.4, 125.7, 125.3, 125.1, 124.5, 122.9, 121.9, 120.6; **IR (neat)** 2993, 1542, 1473, 1436, 1211, 1162, 861, 848 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{22}H_{14}S_2$ 342.0537, Found 342.0535.




To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), phenylboronic acid (0.15 mmol, 18.3 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (3-methoxyphenyl)(phenyl)sulfane **3a'** 14.9 mg (69 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.11-7.31 (m, 6H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.79-6.80 (m, 1H), 6.71 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 3.68 (s, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.0, 137.2, 135.2, 131.4, 129.9, 129.2, 127.2, 122.9, 115.9, 112.8, 55.3; **IR (neat)** 3061, 2833, 1590, 1477, 1439, 1247, 860, 775 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{12}OS$ 216.0609, Found 216.0607.

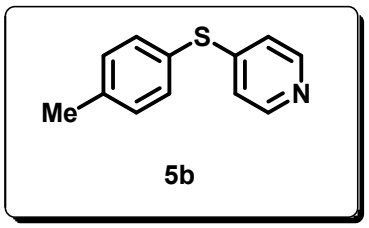



To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)benzoate (0.15 mmol, 18.3 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), MeOH (0.1 mL), and DMF (2.0 mL). The system was heated to 80 °C to afford (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(3-methoxyphenylthio)benzoate **3b'** 49.1 mg (73 %). $R_f$ = 0.40 (Petroleum Ether : Ethyl Acetate = 20:1 ); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.36-7.30 (m, 3H), 7.13-7.07 (m, 2H), 6.96-6.93 (m, 1H), 3.82 (s, 3H), 2.62 (t, *J* = 6.4 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.86-1.78 (m, 2H), 1.59-1.33 (m, 3H), 1.42-1.03 (m, 22H), 0.89-0.86 (m, 13H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 164.7, 160.3, 149.4, 144.9, 140.5, 133.2, 130.6, 130.4, 127.7, 126.9, 125.9, 125.1, 123.1, 118.8, 117.4, 114.7, 75.0, 55.4, 40.4, 39.6, 39.5, 37.4, 37.3, 32.8, 32.7, 32.7, 31.2, 31.0, 27.0, 26.9, 24.8, 24.4, 24.2, 23.7, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 13.0, 12.2, 11.8; **IR (neat)** 2928, 2867, 2358, 2340, 1463, 1232, 1014, 689 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{43}H_{60}O_4S$ 672.4212, Found 672.4207.



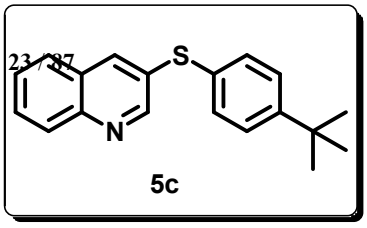

5a

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), pyridin-3-ylboronic acid (0.2 mmol, 24.4 mg), $CuCl_2$ (0.025 mmol, 3.4 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 3-(3-methoxyphenylthio)pyridine **5a** 13.4 mg (62 %). $R_f$ = 0.30 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.49 (d, *J* = 1.2 Hz, 1H), 8.41 (d, *J* = 4.0 Hz, 1H), 7.56-7.58 (m, 1H), 7.16-7.20 (m, 2H), 6.86-6.89 (m, 1H), 6.83 (d, *J* = 1.6 Hz, 1H), 6.76-6.78 (m, 1H), 3.71 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 160.2, 150.7, 147.5, 138.4, 134.9, 133.6, 130.3, 124.0, 123.8, 116.9, 113.7, 55.3; **IR (neat)** 3008, 2835, 1479, 1405, 1247, 1074, 859, 688 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{12}H_{11}NOS$ 217.0561, Found 217.0562.




5b

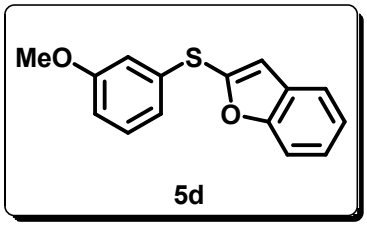
To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-*p*-tolyl sulfothioate (0.1 mmol, 22.6 mg), pyridin-4-ylboronic acid (0.2 mmol, 24.4 mg), $CuCl_2$ (0.025 mmol, 3.4 mg), 1,10-phenanthroline(0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 4-(p-tolylthio)pyridine **5b** 16.3 mg (81 %). $R_f$ = 0.30 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.25 (s, 2H), 7.37(d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 5.6 Hz, 2H), 2.34 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 151.2, 149.2, 140.2, 135.4, 130.7, 125.5, 120.5, 21.3; **IR (neat)** 2944, 2828, 1631, 1479, 1442, 1220, 1018, 703$cm^{-1}$; **HRMS(EI)** Calcd for $C_{12}H_{11}NS$ 201.0612, Found 201.0613.




5c

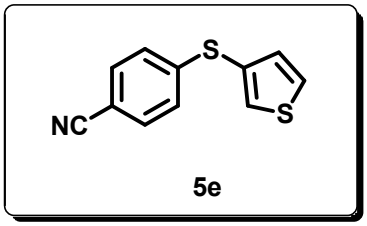
To a Schlenk tube under carbon dioxide atmosphere

were added sodium *S*-quinolin-3-yl sulfothioate (0.1 mmol, 26.3 mg), 4-tert-butylphenylboronic acid (0.2 mmol, 35.6 mg), $CuCl_2$ (0.025 mmol, 3.4 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 3-(4-tert-butylphenylthio)quinoline **5c** 23.4 mg (80 %). $R_f$ = 0.2 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.78 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.66-7.71 (m, 2H), 7.53-7.55 (m, 1H), 7.37 (s, 4H), 1.32 (s, 9H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 151.7, 151.4, 146.4, 136.2, 131.9, 131.0, 130.1, 129.2, 128.2, 127.2, 127.2, 126.7, 34.6, 31.2; **IR (neat)** 3027, 2868, 1490, 1363, 1267, 1013, 828, 750 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{19}H_{19}NS$ 293.1238, Found 293.1241.



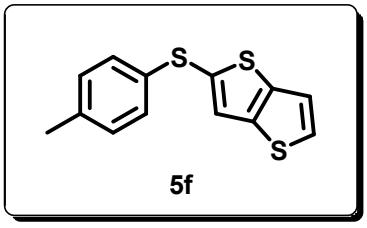
**5d**

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), benzofuran-2-ylboronic acid (0.2 mmol, 32.4 mg), $CuCl_2$ (0.025 mmol, 3.4 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 2-(3-methoxyphenylthio)benzofuran **5d** 14.8 mg (58 %). $R_f$ = 0.4 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30-7.34 (m, 1H), 7.18-7.26 (m, 2H), 7.06 (s, 1H), 6.87-6.91 (m, 2H), 6.75-6.78 (m, 1H), 3.76 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 60.0, 156.8, 147.6, 135.5, 130.0, 128.3, 125.2, 123.1, 121.2, 121.0, 114.6, 114.4, 112.8, 111.4, 55.3; **IR (neat)** 2931, 2855, 1477, 1443, 1230, 1041, 857, 686 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{15}H_{12}O_2S$ 256.0558, Found 256.0560.



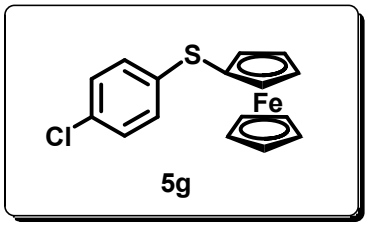

5e

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-cyanophenyl sulfothioate (0.1 mmol, 23.7 mg), thiophen-3-ylboronic acid (0.2 mmol, 25.6 mg), $Cu(OTf)_2$ (0.02 mmol, 7.2 mg), 1,10-phenanthroline(0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 4-(thiophen-3-ylthio)benzonitrile **5e** 13.5 mg (62 %). $R_f$ = 0.5 (Ethyl Acetate : Petroleum Ether = 20:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.58-7.59 (m, 1H), 7.46-7.49 (m, 3H), 7.09-7.12 (m, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 146.0, 132.3, 131.9, 127.7, 126.3, 125.4, 118.8, 108.5; **IR (neat)** 3094, 2856, 1484, 1401, 1200, 1080, 855, 730 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{11}H_7NS_2$ 217.0020, Found 217.0019.




5f

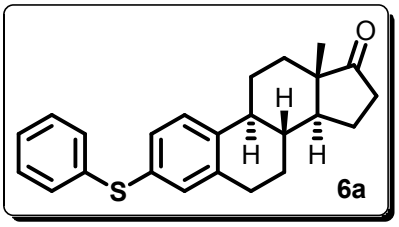
To a Schlenk tube under carbon dioxide atmosphere were added sodium S-p-tolyl sulfothioate (0.1 mmol, 22.6 mg), thieno[3,2-*b*]thiophen-2-ylboronic acid (0.2 mmol, 36.8 mg), $Cu(OTf)_2$ (0.1 mmol, 36.3 mg), 1,10-phenanthroline(0.1 mmol, 10.0 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford 2-(*p*-tolylthio)thieno[3,2-*b*]thiophene **5f** 13.1 mg (51 %). $R_f$ = 0.5 (Ethyl Acetate : Petroleum Ether = 20:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.44 (m, 2H), 7.22-7.20 (m, 3H), 7.09-7.07 (m, 2H), 2.30 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 142.9, 138.4, 136.7, 134.6, 134.3, 129.8, 128.4, 128.1, 127.4, 119.5, 21.0; **IR (neat)** 2337. 1492, 1442, 1343, 1229, 1189, 656, 616 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{13}H_{10}S_3$ 261.9945, Found 216.9943.



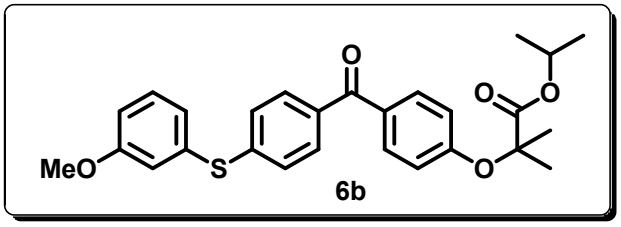
5g

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-4-chlorophenyl sulfothioate (0.1 mmol, 24.6 mg), ferroceneboronic acid (0.2 mmol, 45.8 mg), $CuCl_2$ (0.025 mmol, 3.4 mg), 1,10-phenanthroline (0.04 mmol, 7.2 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 20.2 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (4-chlorophenyl)( ferrocenyl)sulfane **5g** 15.3 mg (62 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.38 (d, *J* = 9.2 Hz, 4H), 4.27 (s, 5H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 139.4, 130.6, 128.6, 127.0, 74.8, 70.3, 69.7; **IR (neat)** 3104, 3023, 2849, 1645, 1475, 1219, 892, 740 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{13}S^{35}ClFe$ 327.9776, Found 327.9778.

**III. The Synthetic Procedure and Data for Scheme 2.**



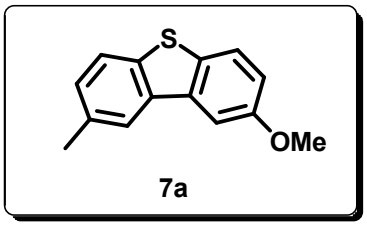

To a Schlenk tube under carbon dioxide atmosphere were added sodium *S*-(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl sulfothioate (0.1 mmol, 38.8 mg), phenylboronic acid (0.15 mmol, 18.3 mg), $Cu(OTf)_2$ (0.03 mmol, 10.8 mg), 1,10-phenanthroline (0.05 mmol, 9 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford (8R,9S,13S,14S)-13-methyl-3-(phenylthio)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one **6a** 24.2 mg (67 %). $R_f$ = 0.40 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.33-7.30 (m, 4H), 7.25-7.14 (m, 4H), 2.87 (dd, J = 4.0 Hz, 8.8Hz, 2H), 2.54-2.48 (m, 1H), 2.41-2.38 (m, 1H), 2.30-2.29 (m, 1H), 2.17-1.96 (m, 4H), 1.68-1.41 (m, 6H); **$^{13}$C NMR (100 MHz, $CDCl_3$)**: δ 139.2, 137.7, 136.5, 132.1, 132.1, 130.3, 129.1, 129.1, 126.6, 126.3, 50.5, 47.9, 44.3, 38.0, 35.8, 31.5, 29.2, 26.3, 25.6, 21.6, 13.8; **IR (neat)** 2928, 2918, 1740, 1713, 1480, 1440, 1082, 1023, 803cm$^{-1}$; **HRMS(EI)** Calcd for $C_{24}H_{26}OS$ 362.1704, Found 362.1703.



6b

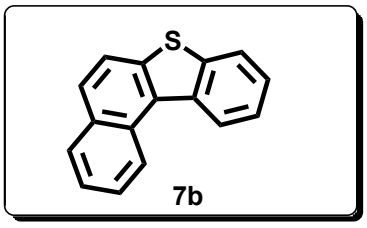
To a Schlenk tube under carbon dioxide atmosphere were added sodium sodium sodium sodium *S*-3-methoxyphenyl sulfothioate (0.1 mmol, 24.2 mg), isopropyl 2-methyl-2-(4-(4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)benzoyl)phenoxy)propanoate (0.2 mmol, 90.8 mg), $Cu(OTf)_2$ (0.03 mmol, 10.8 mg), 1,10-phenanthroline (0.05 mmol, 9 mg), $Ag_2CO_3$ (0.12 mmol, 33.1 mg), $K_3PO_4$ (0.14 mmol, 29.7 mg), DTBP (0.1 mmol, 18.5 μL), and DMF (2.0 mL). The system was heated to 80 °C to afford isopropyl 2-(4-(4-(3-methoxyphenylthio)benzoyl)phenoxy)-2-methylpropanoate **6b** 35.0 mg (75 %). $R_f$ = 0.20 (Petroleum Ether); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.32-7.26 (m, 3H), 7.07-7.03 (m, 2H), 7.92-6.89 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.11-5.05 (m, 1H), 3.80 (s, 3H), 1.65 (s, 6H), 1.20 (s, 3H), 1.19 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 194.5, 173.1, 160.2, 159.4, 142.9, 135.5, 133.6, 131.8, 130.5, 130.5, 130.4, 127.7, 125.5, 118.4, 117.1, 114.4, 79.3, 69.3, 55.3, 25.3, 21.5; **IR (neat)** 3134, 3066, 2922, 1477, 1420, 1375, 1335, 1039, 890, 805cm$^{-1}$; **HRMS(EI)** Calcd for $C_{27}H_{28}O_5S$ 464.1657, Found 464.1655.

## III. The Synthetic Procedure and Data for Table 4



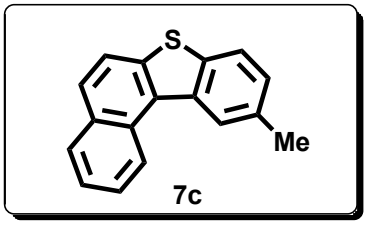
**7a**

To a Schlenk tube were added (4-methoxyphenyl)(*p*-tolyl)sulfane (0.1 mmol, 23.0 mg), $Pd(tfa)_2$ (0.02 mmol, 6.6 mg), AgOAc (41.8 mmol ), $K_2CO_3$ (0.1 mmol), and PivOH (0.5 mL), then closed after $CO_2$ completely released, the mixture had been stirred at 130 °C for 24 h to afford **7a** 2-methoxy-8-methyldibenzo[*b,d*]thiophene 13.8mg (61%). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.82 (s, 1H), 7.63-7.60 (m, 2H), 7.52 (d, *J* = 2.8 Hz, 1H), 7.20-7.17 (m, 1H), 7.00-6.98 (m, 1H), 3.86 (s, 3H), 2.45 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 157.6, 137.6, 136.5, 135.6, 133.9, 131.7, 128.2, 123.4, 122.6, 121.7, 115.7, 104.8, 55.7, 21.4; **IR (neat)** 2834 1447, 1424, 1323, 1343, 1164, 1014, 872, 742 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{12}OS$ 228.0609, Found 228.0611.



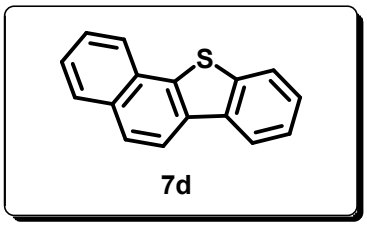
**7b**

To a Schlenk tube were added naphthalen-2-yl(phenyl)sulfane (0.1 mmol, 23.6 mg), *t*BuOK (0.12 mmol, 13.4 mg), diethyl ether (0.5 mL), and THF (1.0 mL), then added *n*BuLi (0.12 mmol), the mixture had been stirred at rt for 0.5 h to afford **7b** benzo[*d*]naphtho[2,1-*b*]thiophene 9.4 mg (40%). $R_f$ = 0.50 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 9.03 (d, *J* = 8.8 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.03 (t, *J* = 8.8 Hz, 2H), 7.94-7.89 (m, 1H), 7.77-7.73 (m, 1H), 7.63-7.57 (m, 2H), 7.53-7.47 (m, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 139.7, 138.6, 136.7, 131.9, 130.7, 129.5, 129.0, 127.9, 127.1, 125.2, 124.9, 124.8, 124.7, 123.2, 123.2, 121.1; **IR (neat)** 2355, 1588, 1462, 1397, 803, 738, 705 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_{10}S$ 234.0503, Found 234.0502.



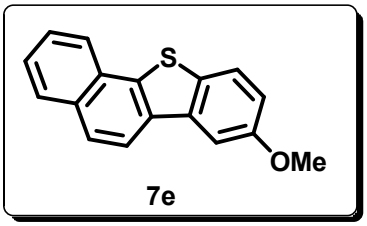
7c

To a Schlenk tube were added naphthalen-2-yl(*p*-tolyl)sulfane (0.1 mmol, 25.0 mg), *t*BuOK (0.12 mmol, 13.4 mg), diethyl ether (0.5 mL), and THF (1.0 mL), then added *n*BuLi (0.12 mmol), the mixture had been stirred at rt for 0.5 h to afford **7c** 10-methylbenzo[*d*]naphtho[2,1-*b*]thiophene 10.4 mg (40%). $R_f$ = 0.50 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.67 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.92-7.88 (m, 3H), 7.77-7.73 (m, 1H), 7.60-7.57 (m, H), 7.35 (d, *J* = 8.4Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 139.0, 137.0, 136.8, 134.5, 131.9, 130.7, 129.4, 128.9, 127.7, 127.0, 126.8, 125.0, 124.8, 123.2, 122.8, 121.2; **IR (neat)** 2949, 1688, 1657, 1453, 1360, 1069, 587, 572 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{17}H_{12}S$ 248.0660, Found 248.0661.



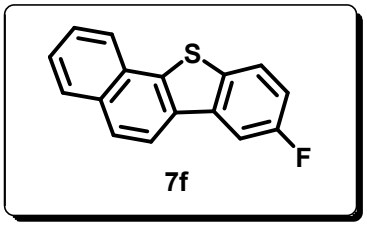
7d

To a Schlenk tube were added naphthalen-1-yl(phenyl)sulfane (0.1 mmol, 23.6 mg), $Pd(tfa)_2$ (0.02 mmol, 6.6 mg), AgOAc (41.8 mmol ), $K_2CO_3$ (0.1 mmol), and PivOH (0.5 mL), then closed after $CO_2$ completely released, the mixture had been stirred at 130 °C for 24 h to afford **7d** benzo[d]naphtho[1,2-*b*]thiophene 14.1mg (60%). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.24-8.14 (m, 3H), 8.00-7.97 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.65-7.47 (m, 4H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 139.1, 137.3, 136.6, 132.6, 132.4, 129.0, 128.9, 126.3, 126.2, 125.5, 124.5, 124.5, 123.0, 121.6, 119.7; **IR (neat)** 2861, 1554, 1469, 1423, 1189, 1062, 614, 600 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{14}H_{10}S$ 234.0503, Found 234.0504.



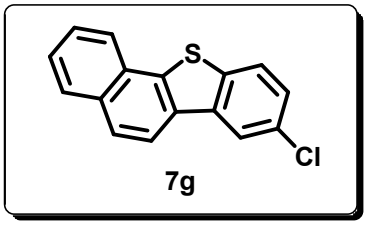
7e

To a Schlenk tube were added (4-methoxyphenyl)(naphthalen-1-yl)sulfane (0.1 mmol, 26.6 mg), $Pd(tfa)_2$ (0.02 mmol, 6.6 mg), AgOAc (41.8 mmol ), $K_2CO_3$ (0.1 mmol), and PivOH (0.5 mL), then closed after $CO_2$ completely released, the mixture had been stirred at 130 °C for 24 h to afford **7e** 8-methoxybenzo[*d*]naphtho[1,2-*b*]thiophene 18.7 mg (71%). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.64-7.55 (m, 2H), 7.13 (dd, *J* = 2.8 Hz, 8.8 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 157.9, 138.6, 137.7, 132.5, 132.4, 131.1, 129.1, 128.9, 126.7, 126.3, 125.3, 124.5, 123.6, 119.6, 115.5, 104.8, 55.7; **IR (neat)** 2367, 1601, 1472, 1457, 1423, 1222, 806, 747 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{17}H_{12}OS$ 264.0609, Found 264.0607.



7f

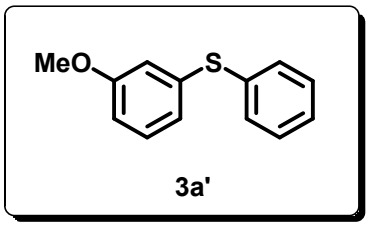
To a Schlenk tube were added (4-fluorophenyl)(naphthalen-1-yl)sulfane (0.1 mmol, 25.4 mg), $Pd(tfa)_2$ (0.02 mmol, 6.6 mg), AgOAc (41.8 mmol ), $K_2CO_3$ (0.1 mmol), and PivOH (0.5 mL), then closed after $CO_2$ completely released, the mixture had been stirred at 130 °C for 24 h to afford **7f** 8-fluorobenzo[*d*]naphtho[1,2-*b*]thiophene 12.3 mg (46%). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.17 (d, *J* = 1.6 Hz, 1H), 8.13-8.09 (m, 2H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.88-7.86 (m, 2H), 7.46-7.43 (m, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.2 (*J* = 122.5 Hz), 139.0, 137.9 (*J* = 35.5 Hz), 134.1, 132.5, 132.2 (*J* = 15.5 Hz), 129.0, 128.9, 126.6, 126.9, 125.6, 124.5, 124.0 (*J* = 36.5 Hz), 119.6, 114.5 (*J* = 9.8 Hz), 107.7; **$^{19}$F NMR (376 MHz, $CDCl_3$)**: δ -118.0; **IR (neat)** 2962 1451, 1410, 1262, 1100, 1022, 690, 643 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_7SF$ 252.0409, Found 252.0408.



7g

To a Schlenk tube were added (4-chlorophenyl)(naphthalen-1-yl)sulfane (0.1 mmol, 27.0 mg), $Pd(tfa)_2$ (0.02 mmol, 6.6 mg), AgOAc (41.8 mmol ), $K_2CO_3$ (0.1 mmol), and PivOH (0.5 mL), then closed after $CO_2$ completely released, the mixture had been stirred at 130 $^oC$ for 24 h to afford **7g** 8-chlorobenzo[*d*]naphtho[1,2-*b*]thiophene 11.6 mg (51%). $R_f$ = 0.40 (Ethyl Acetate : Petroleum Ether = 50:1); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.14-8.08 (m, 2H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.90-7.85 (m, 3H), 7.65-7.57 (m, 3H), 7.26-7.21 (m, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ138.4, 137.9, 137.1, 132.6, 131.7, 130.9, 129.0, 128.8, 127.0, 126.7, 126.4, 125.8, 124.5, 123.9, 121.5, 119.5; **IR (neat)** 2926, 2855, 1453, 1424, 1349, 1282, 806, 772 $cm^{-1}$; **HRMS(EI)** Calcd for $C_{16}H_9S_{35}Cl$ 268.0133, Found 252.0115.

## VI.Scalable Process

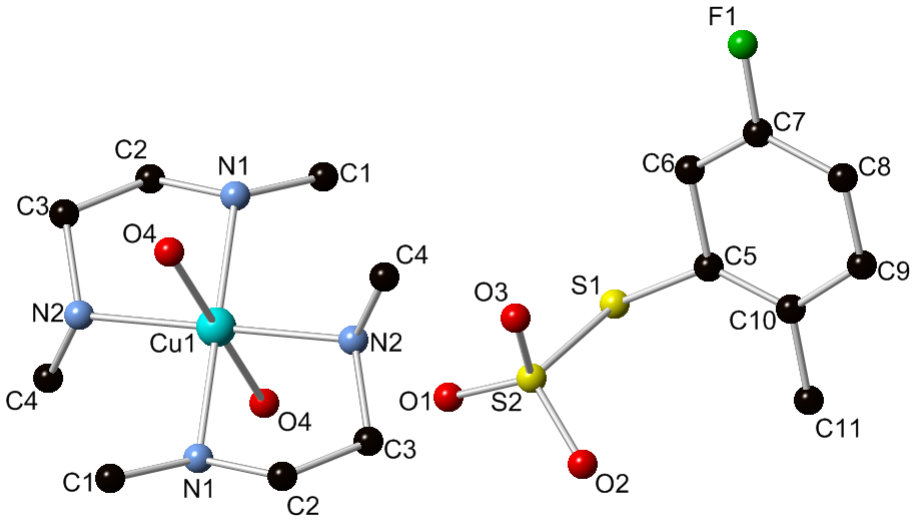



**3a'**

To a 100 mL Schlenk tube under carbon dioxide atmosphere were added sodium *S*-3-methoxyphenyl sulfothioate (5 mmol, 1.2 g), phenylboronic acid (7.5 mmol, 0.9 g), $Cu(OTf)_2$ (0.5 mmol, 182 mg), 1,10-phenanthroline (1 mmol, 180 mg), $Ag_2CO_3$ (6 mmol, 1.6 g), $K_3PO_4$ (7 mmol, 1.5 g), DTBP (5 mmol, 0.9 mL), and DMF (8 mL). The system was heated to 80 $^oC$ to afford (3-methoxyphenyl)(phenyl)sulfane **3a'** 0.91g (84 %).

## VII. X-ray Crystallography of Compound

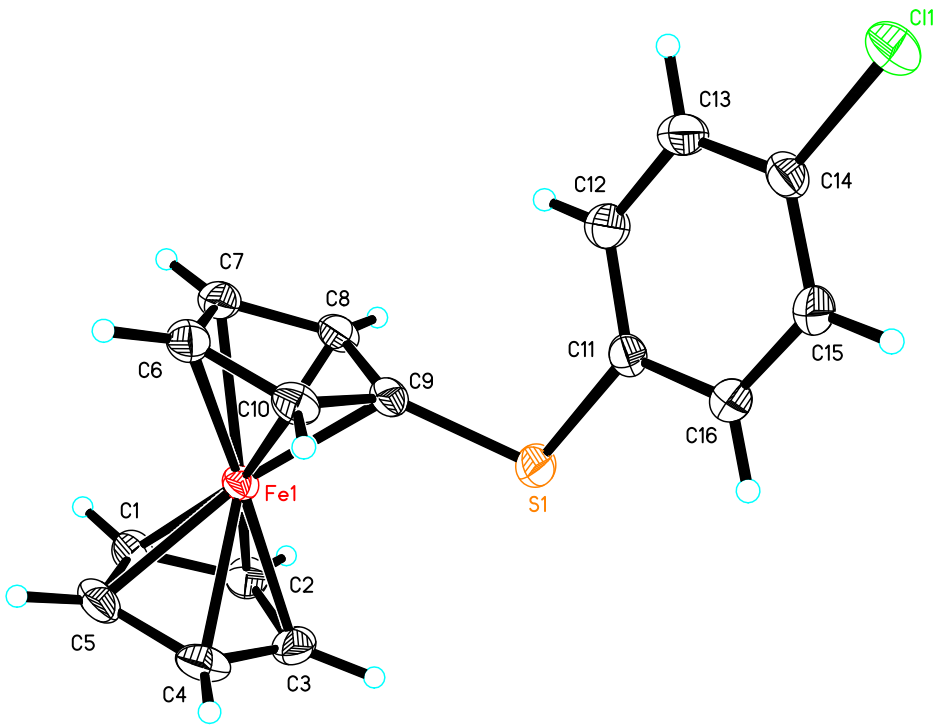
### *X-ray Crystallography of Compound I[a]*




[a]One of the two symmetry-equivalent sulfthioate anions is removed for clarity.

CCDC-1034136: $C_{22}H_{40}CuF_2N_4O_8S_4$, MW = 718.36, triclinic, space group *P* -1, final R indices [I > 2 σ (*I*)], $R_1$ = 0.0619, *w*$R_2$ = 0.1716, R indices (all data), $R_1$ = 0.0688, *w*$R_2$ = 0.1777, *a* = 7.5312(15) Å, *b* = 8.2038 (16) Å, *c* = 13.344(3) Å, *α* = 92.852(3)°, *β* = 93.152(4)°, *γ* = 107.116(3)°, *V* = 784.9(3) Å$^3$, *T* = 130 K, *Z* = 1, reflections collected/unique: 5492/3094 (R(int) = 0.0249). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci.

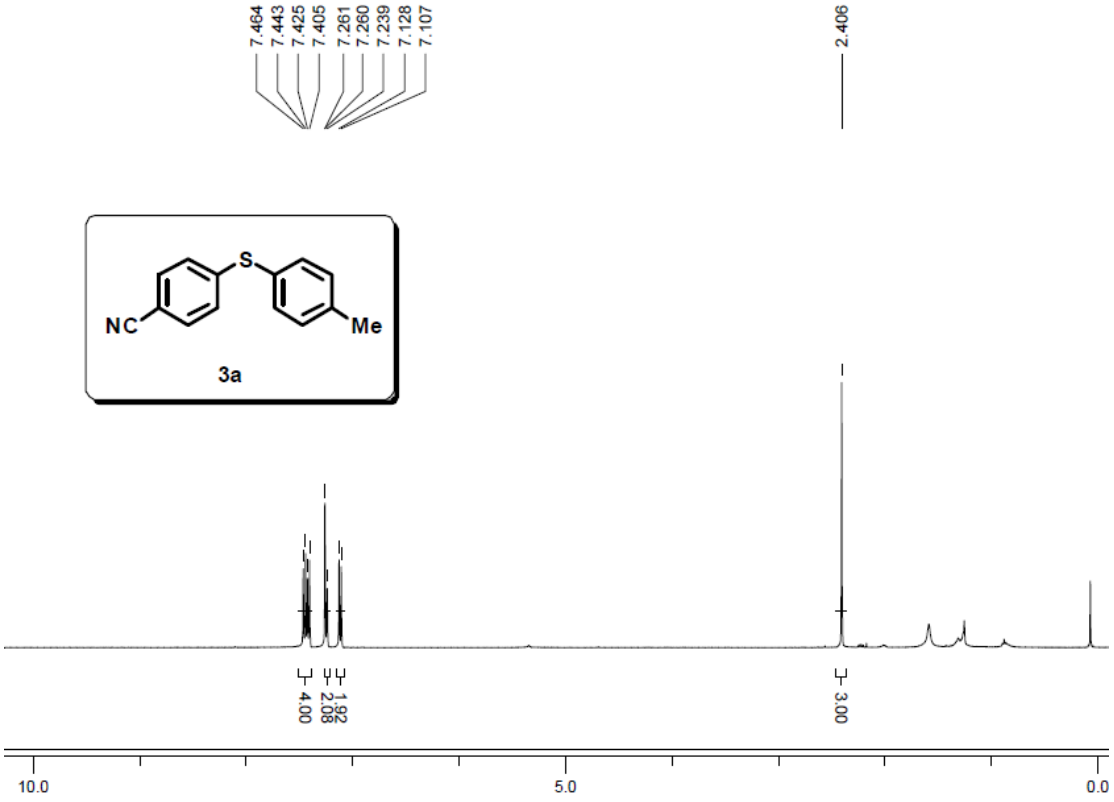
*X-ray Crystallography of Compound 5g*

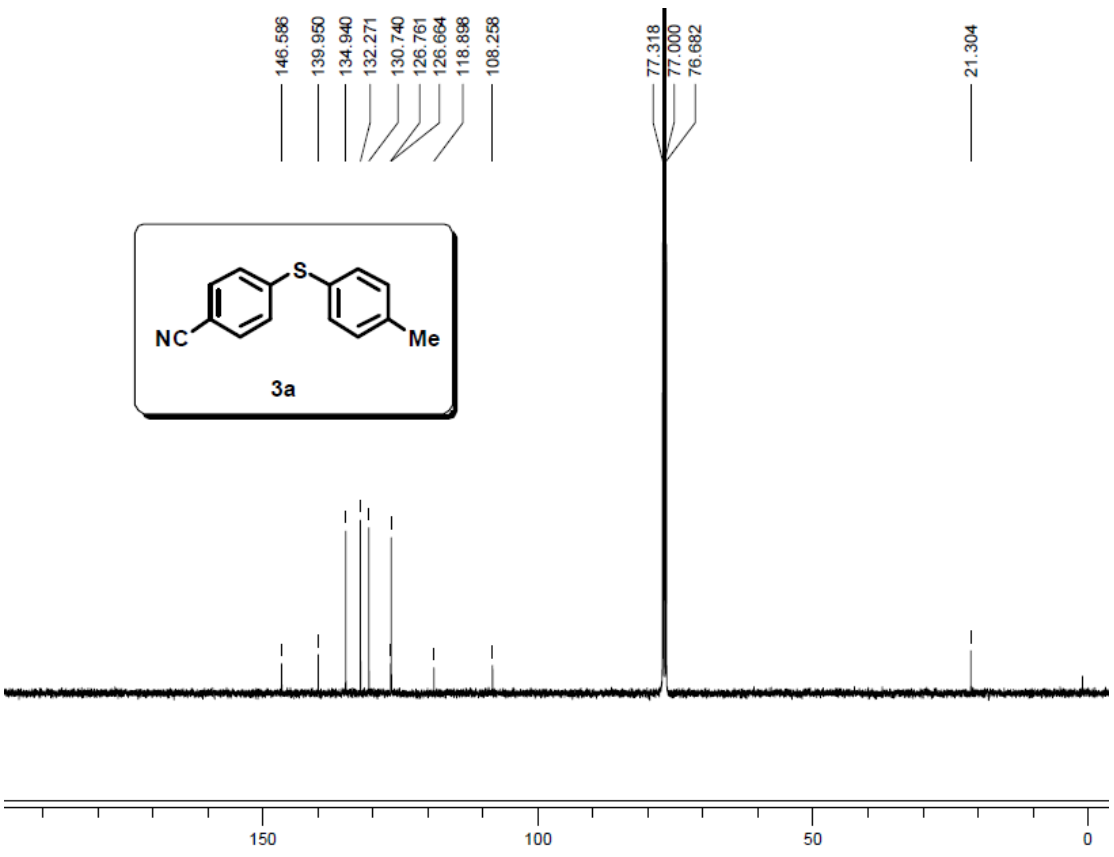


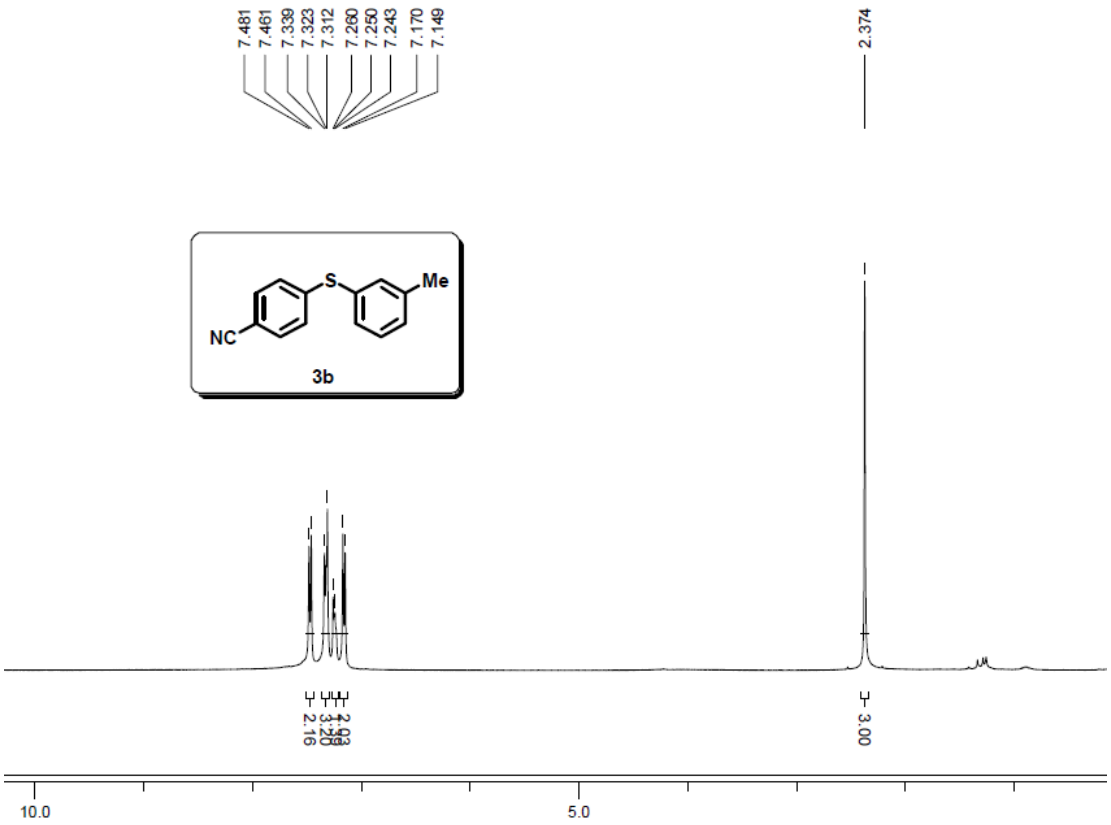

CCDC-1034135 (5g): $C_{16}H_{13}ClFeS$, MW = 328.62, triclinic, space group *P* -1, final R indices [I > 2 σ (*I*)], $R_1$ = 0.0280, $wR_2$ = 0.0755, R indices (all data), $R_1$ = 0.0300, $wR_2$ = 0.0773, *a* = 5.7825(6) Å, *b* = 8.6085(9) Å, *c* = 14.0430(14) Å, $\alpha$ = 99.114(2)°, $\beta$ = 99.532(2)°, $\gamma$ = 94.734(2)°, *V* = 676.43(12) Å$^3$, *T* = 293(2) K, *Z* = 2, reflections collected/unique: 4135/2653 (R(int) = 0.0172). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci.

## VIII.Copies of the Fig. 3 in manuscript

## IX. Copies of the NMR

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3b
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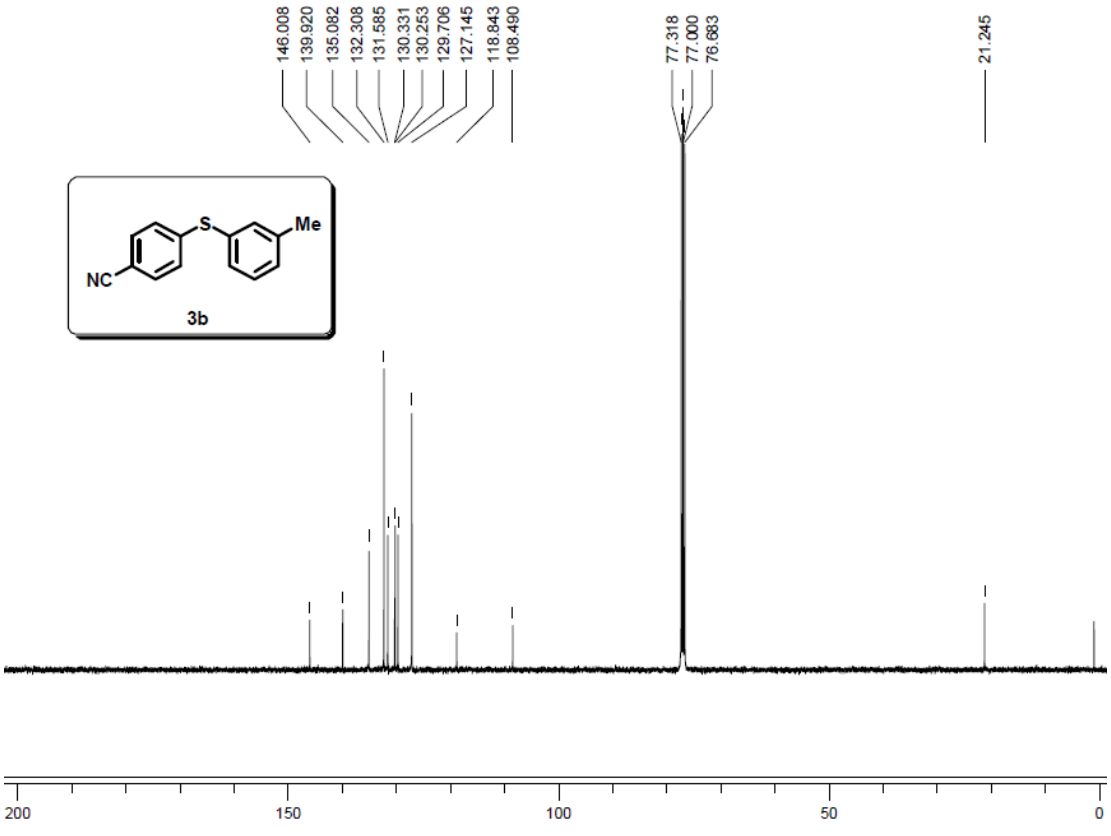
3.00
10.0
5.0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3b
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50
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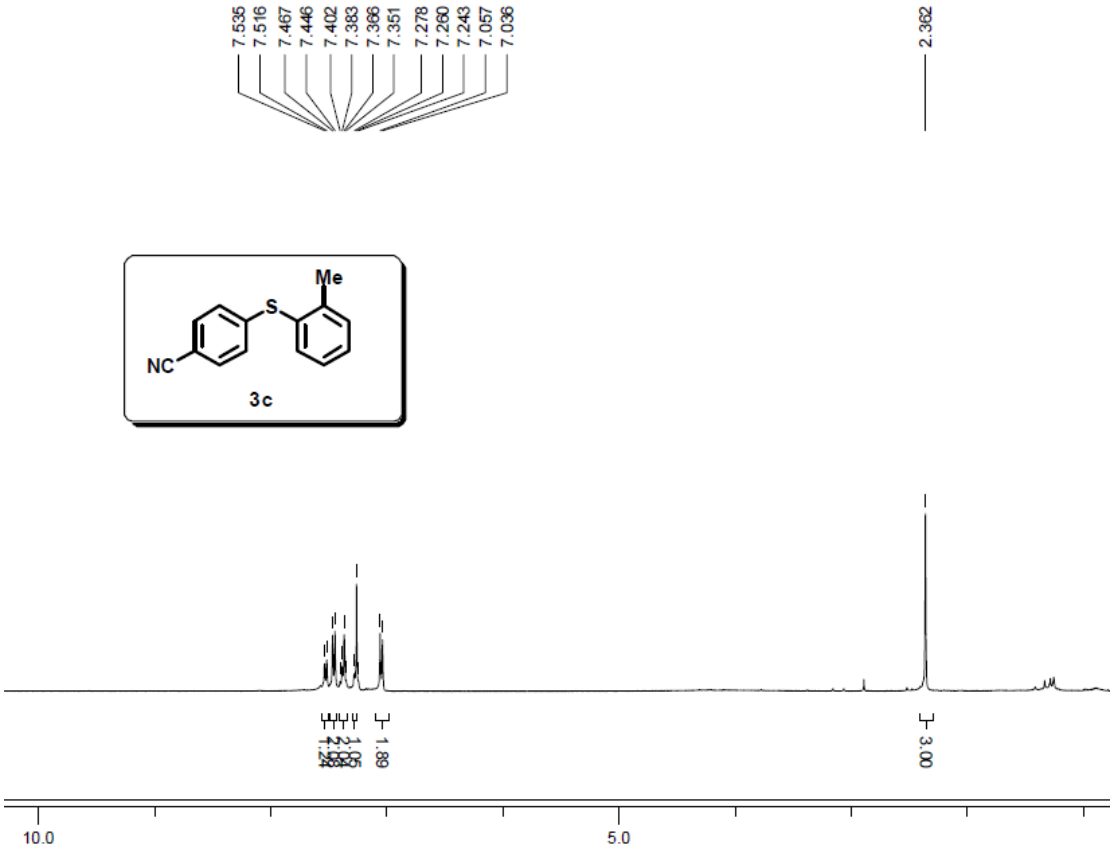
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3c
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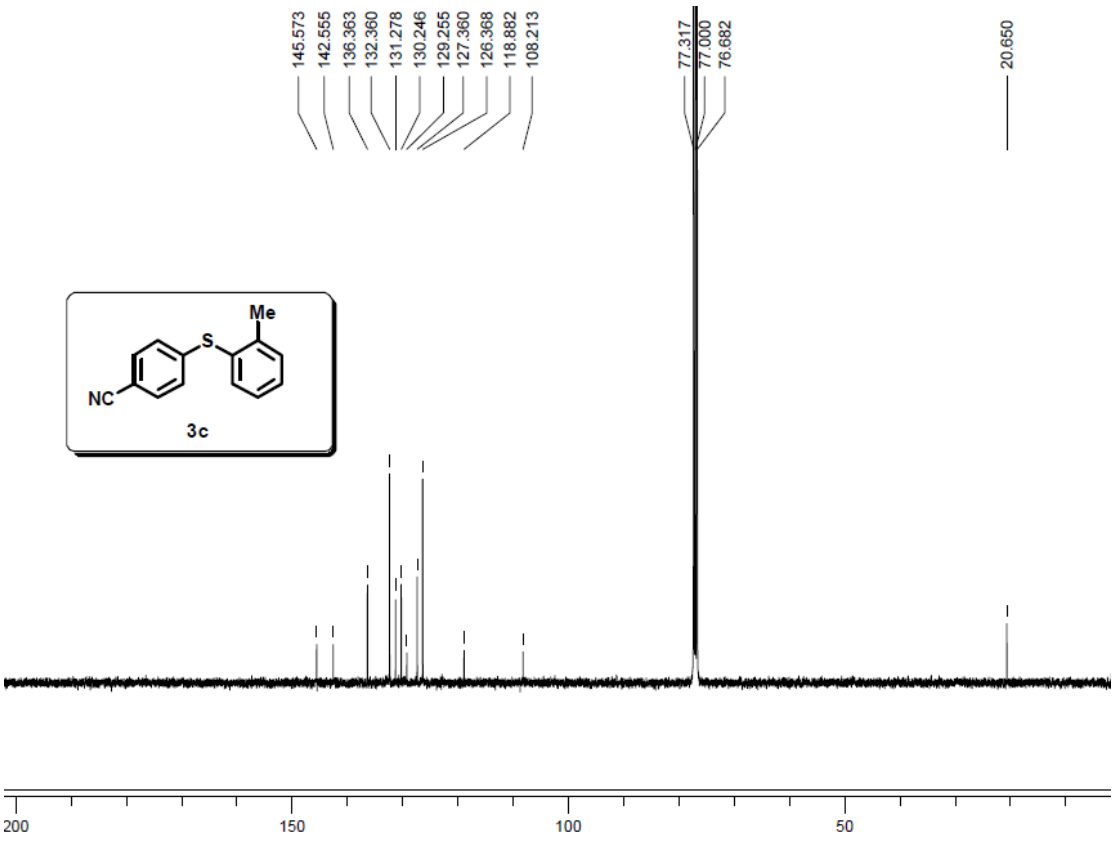
3.00
10.0
5.0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Me
S
NC
3c
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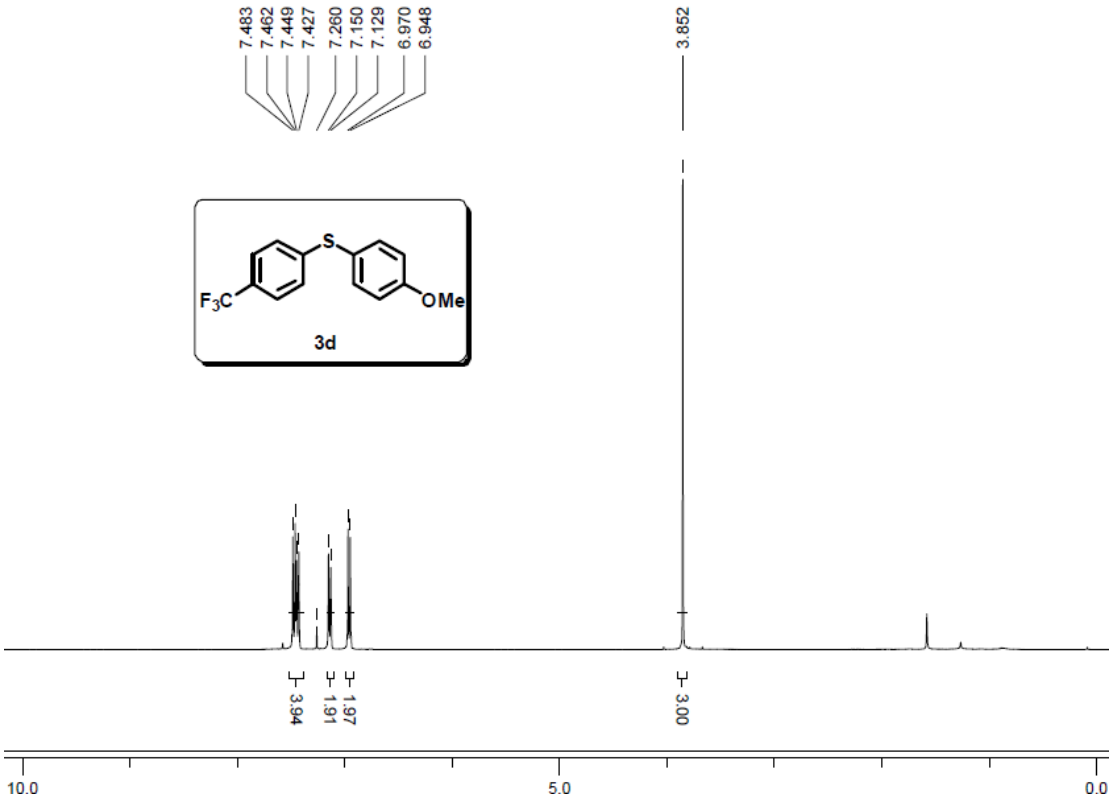
100
50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7.129
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S
F3C
OMe
3d
3.94
1.91
1.97
3.00
10.0
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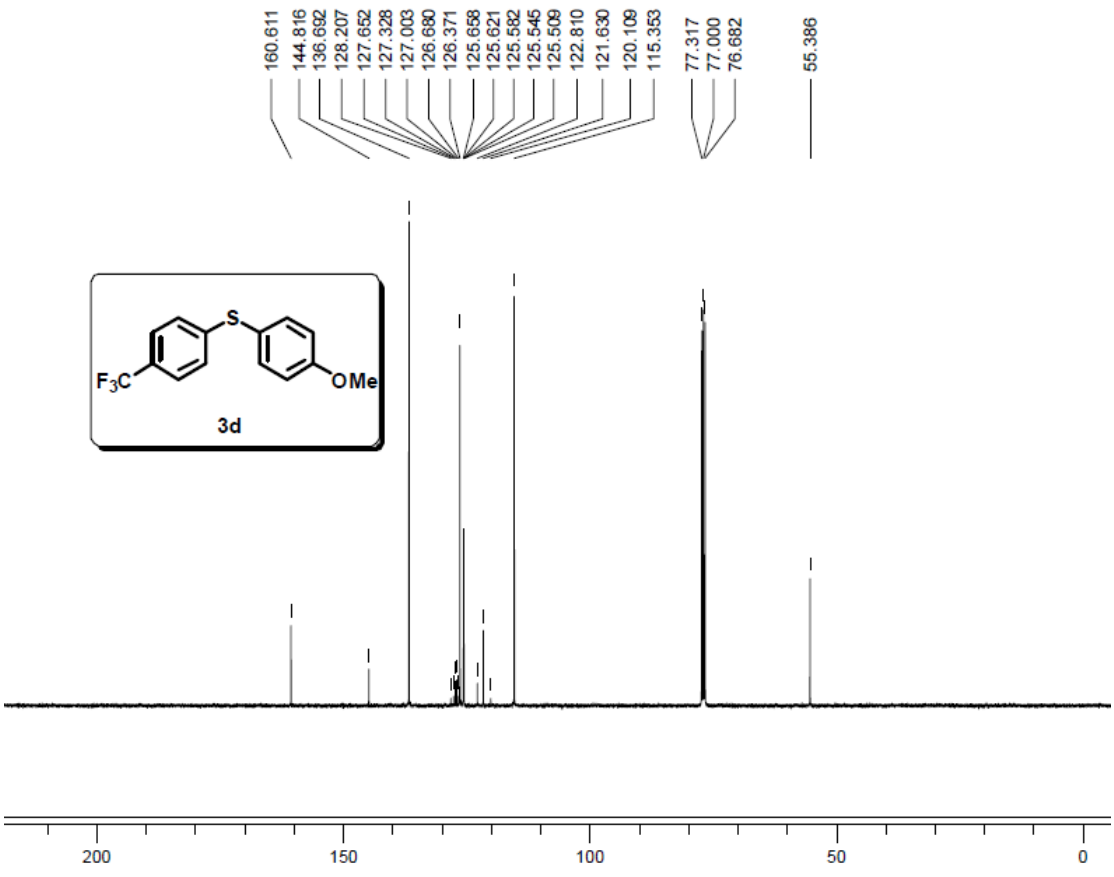
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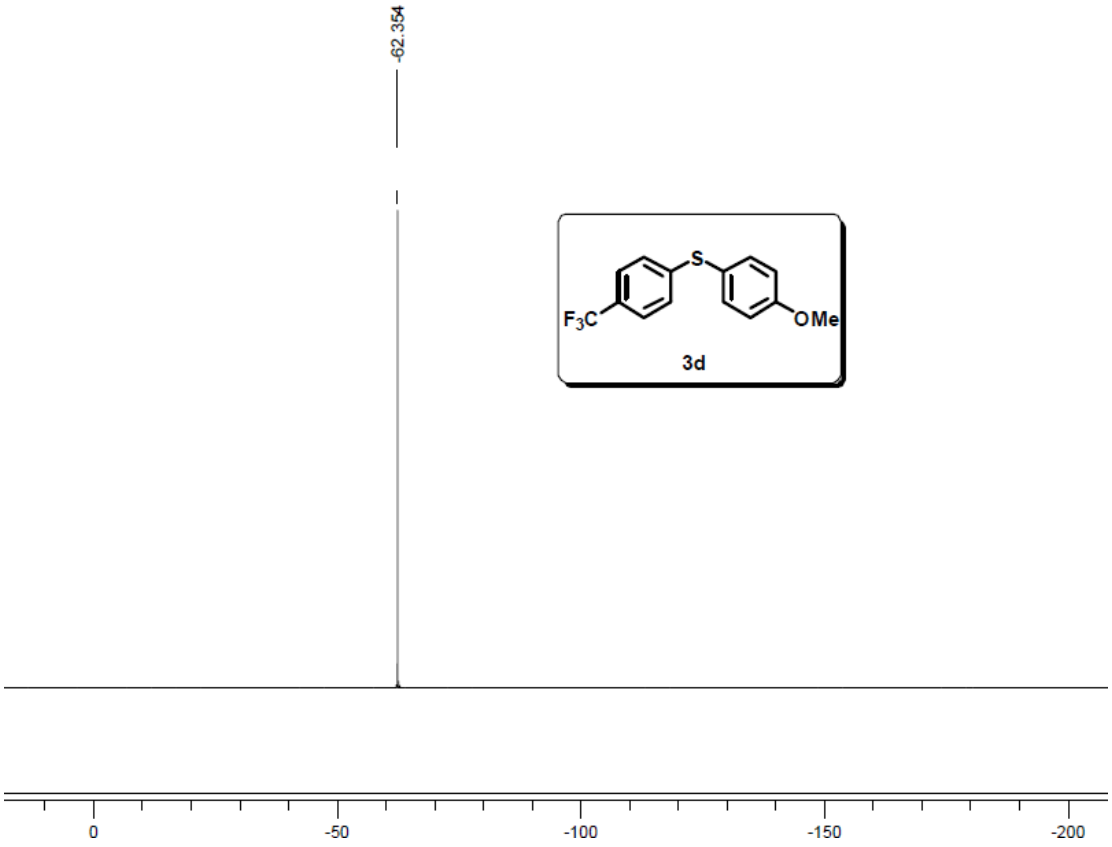
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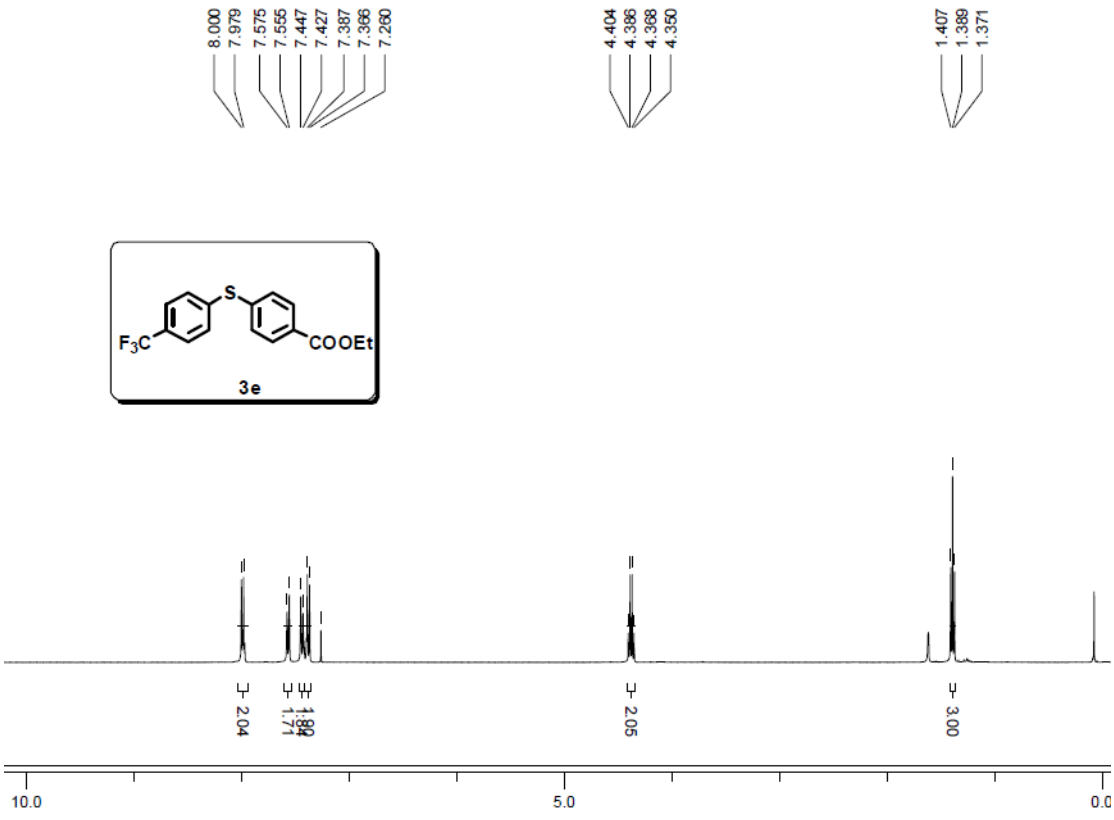
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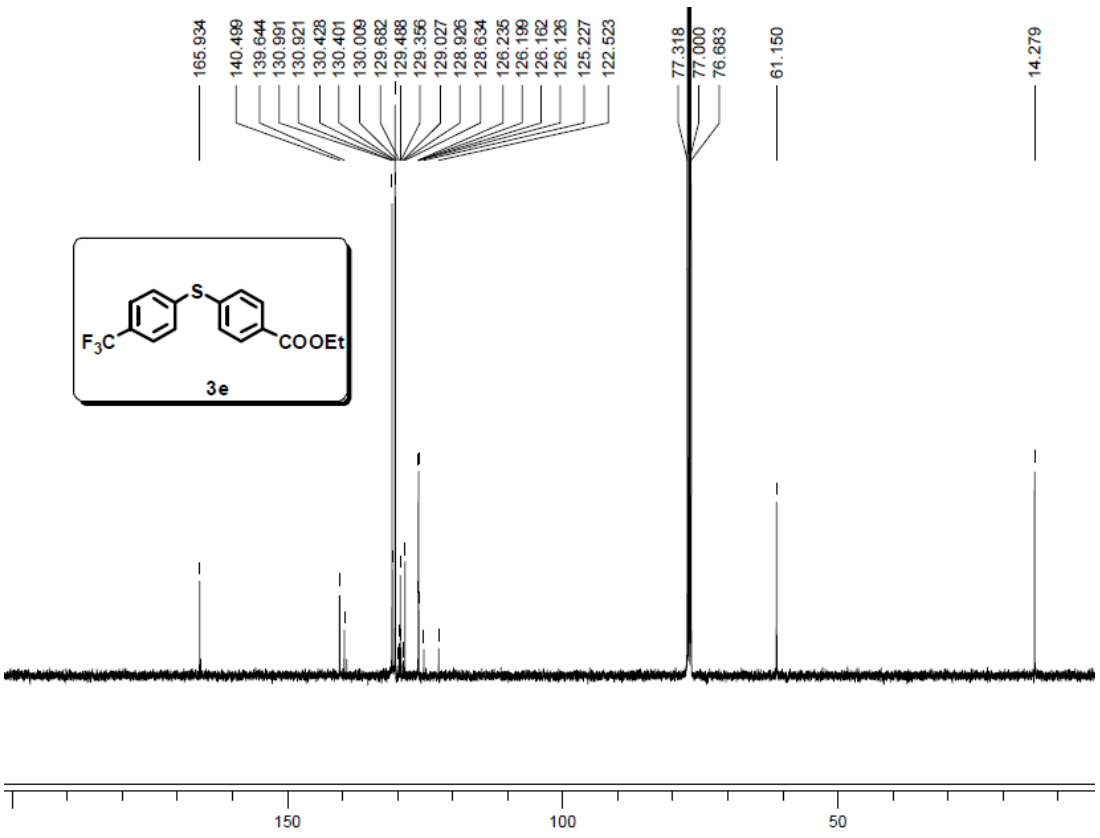
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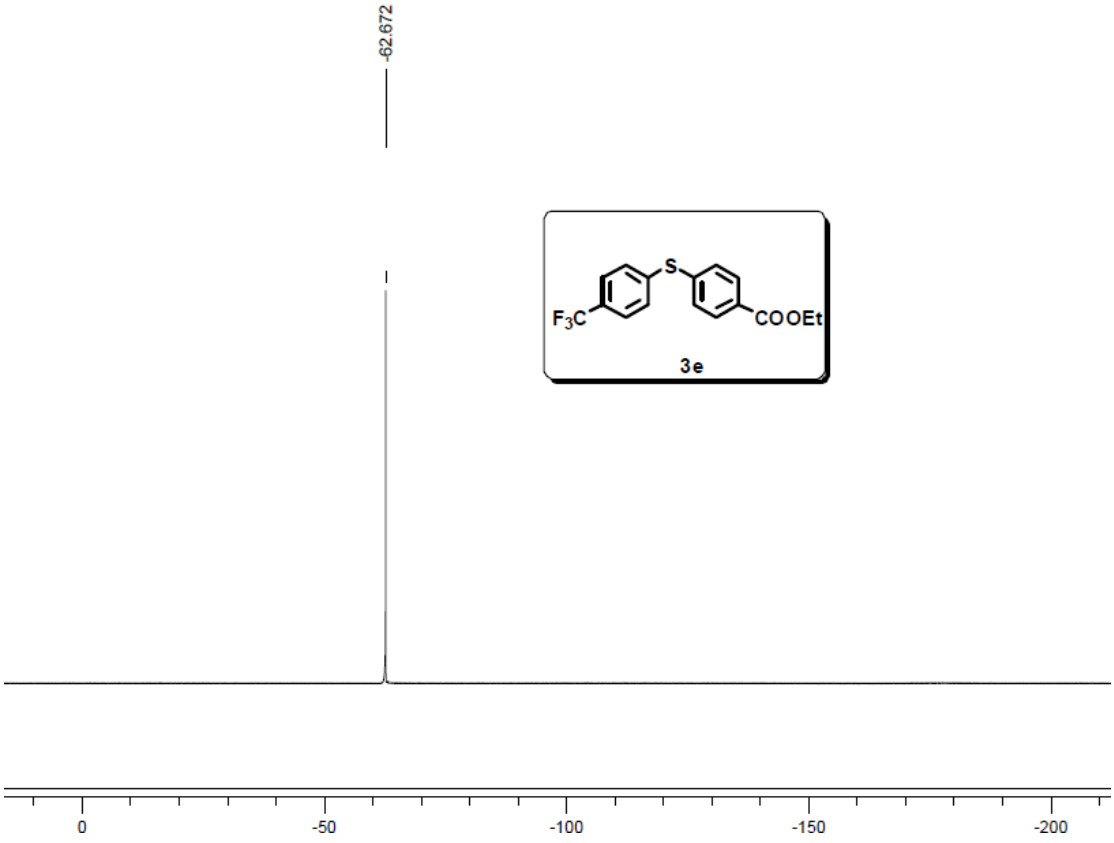
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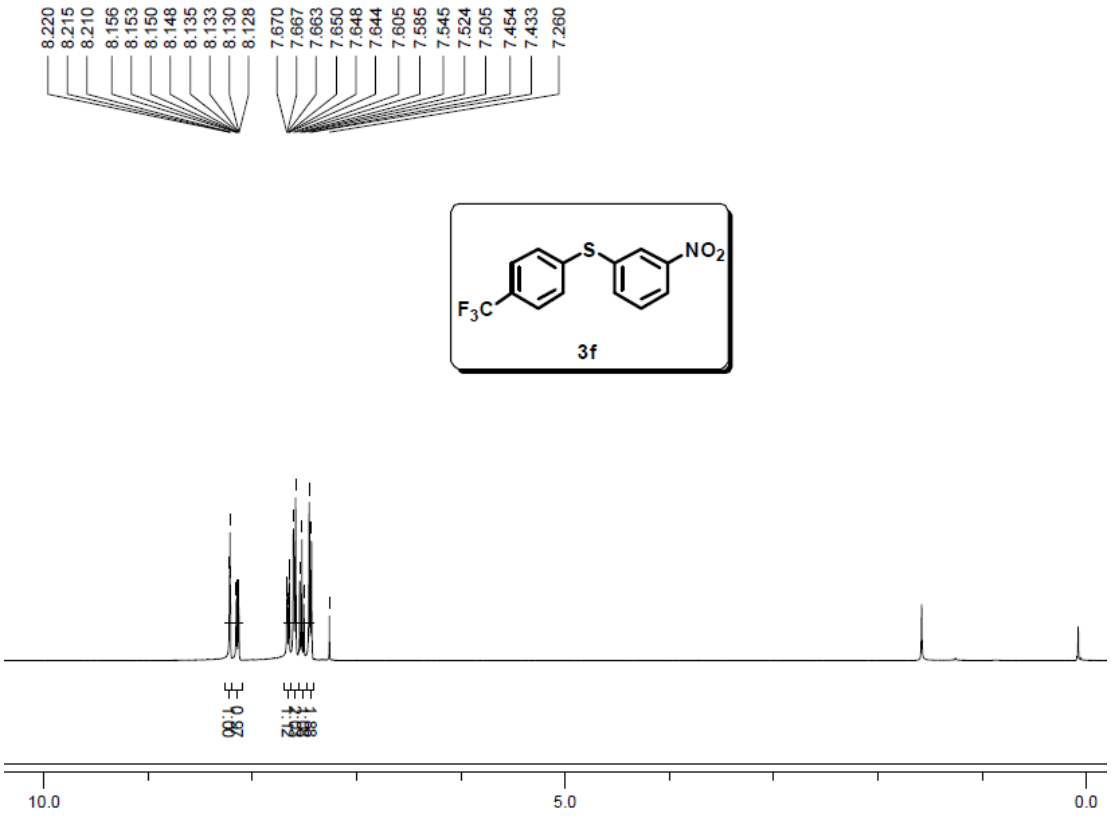
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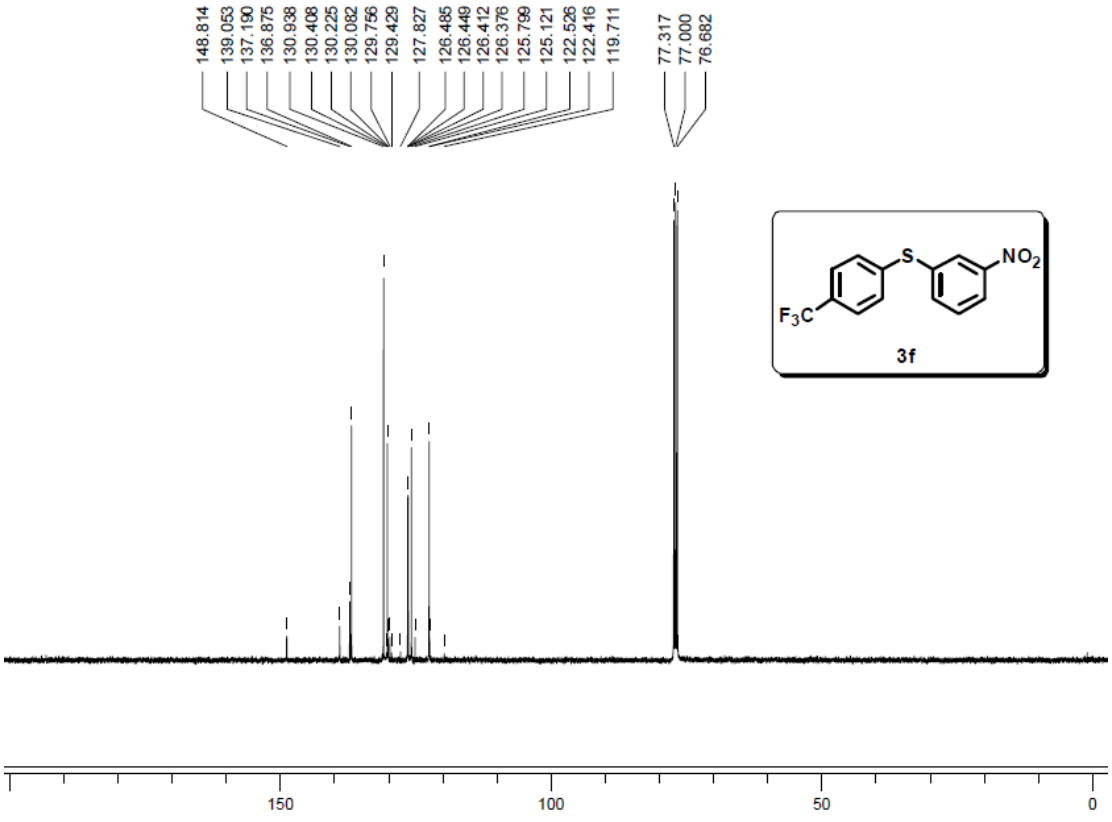
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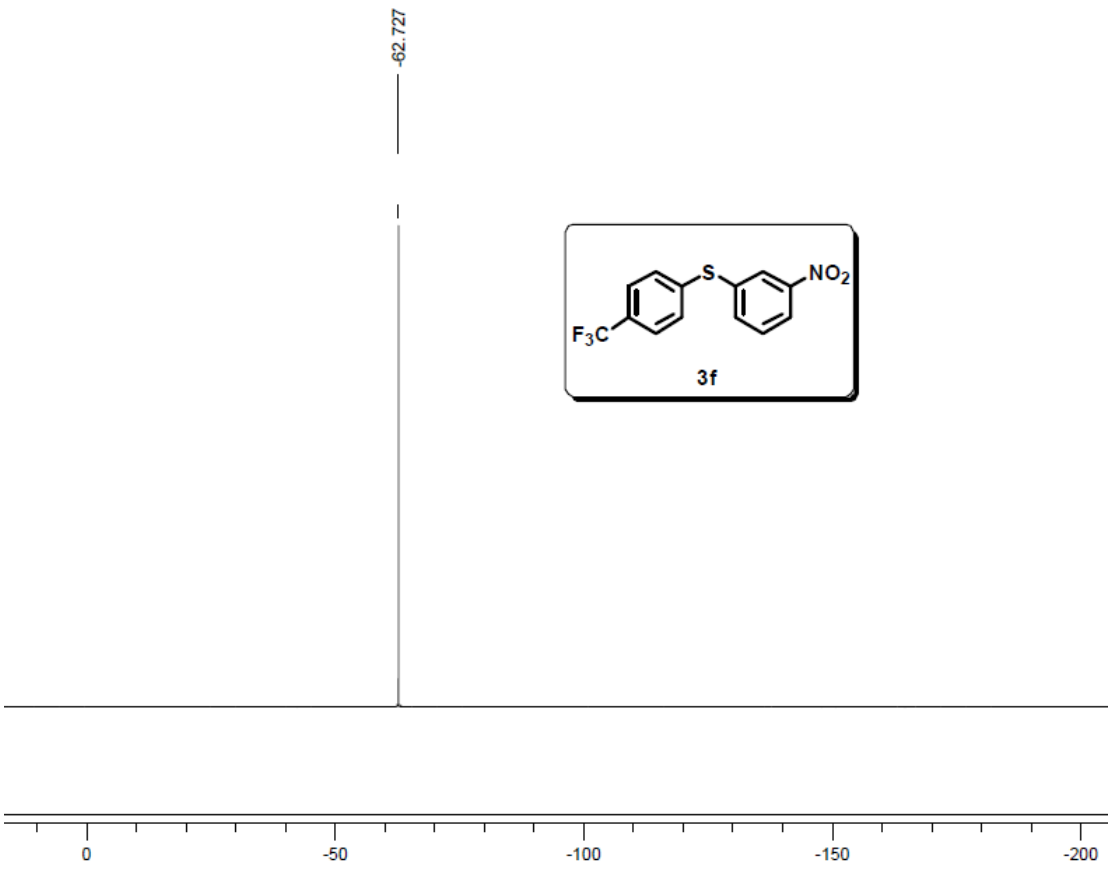
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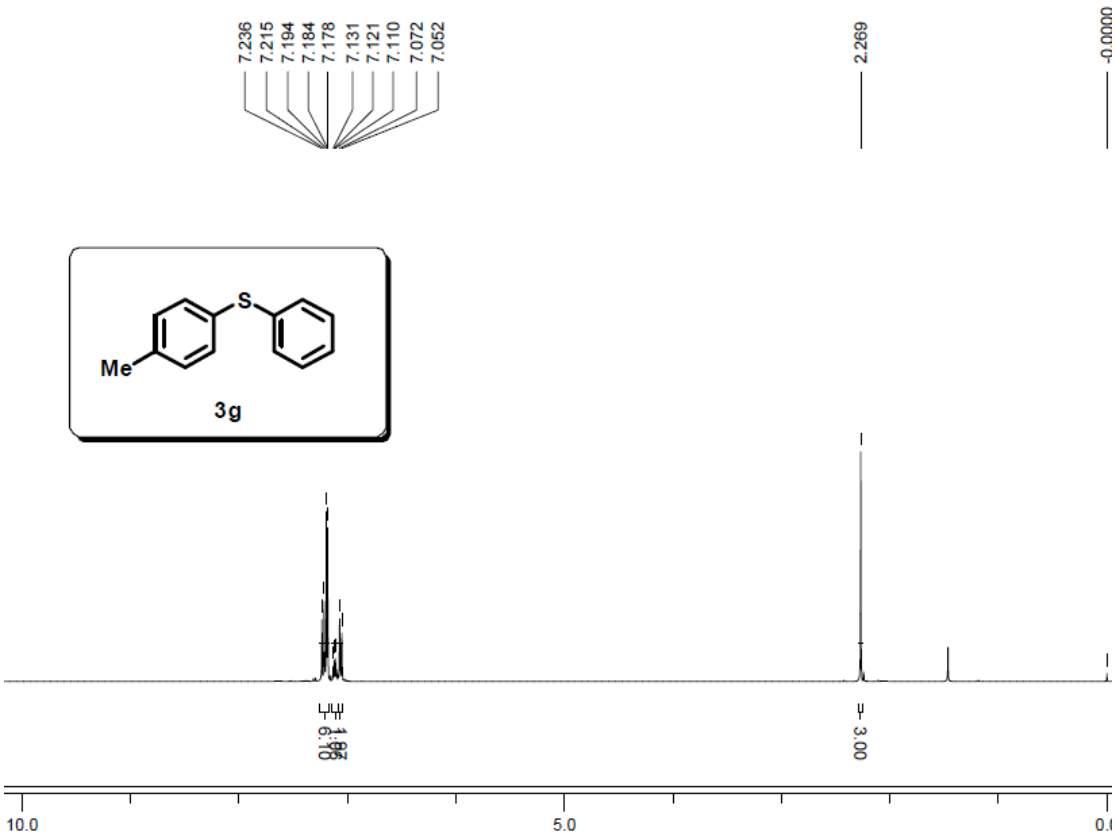
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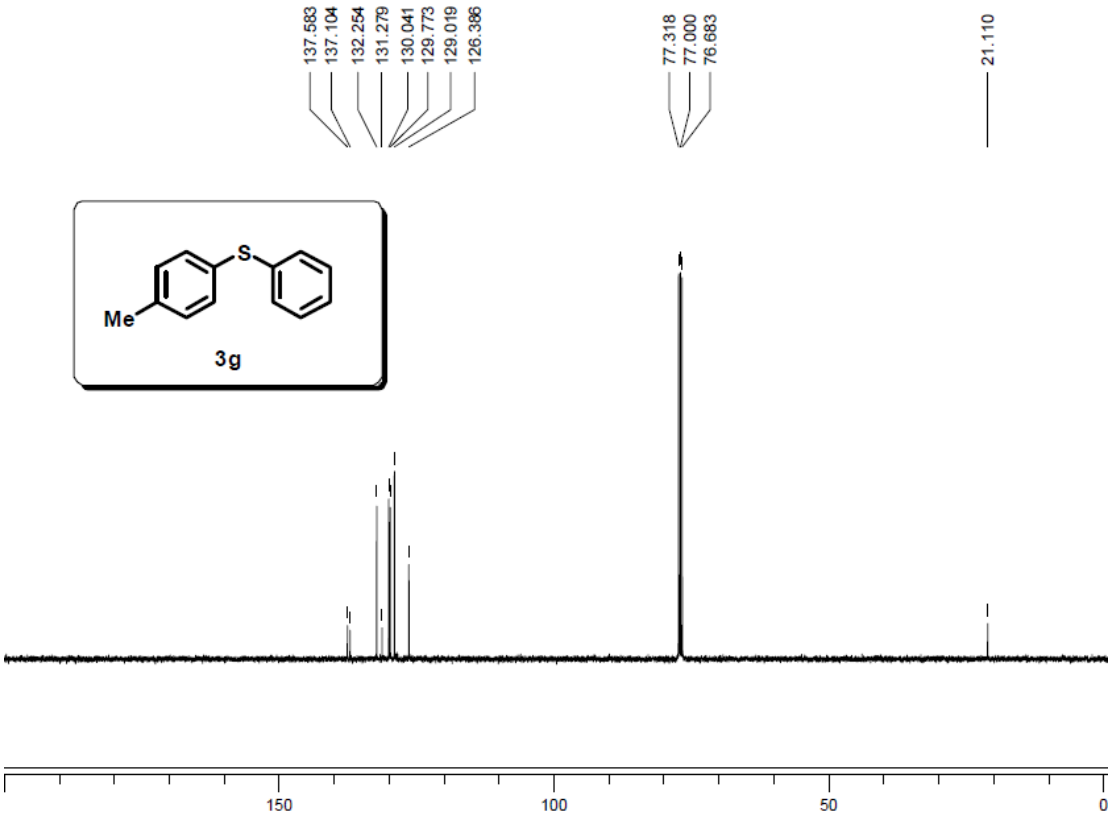
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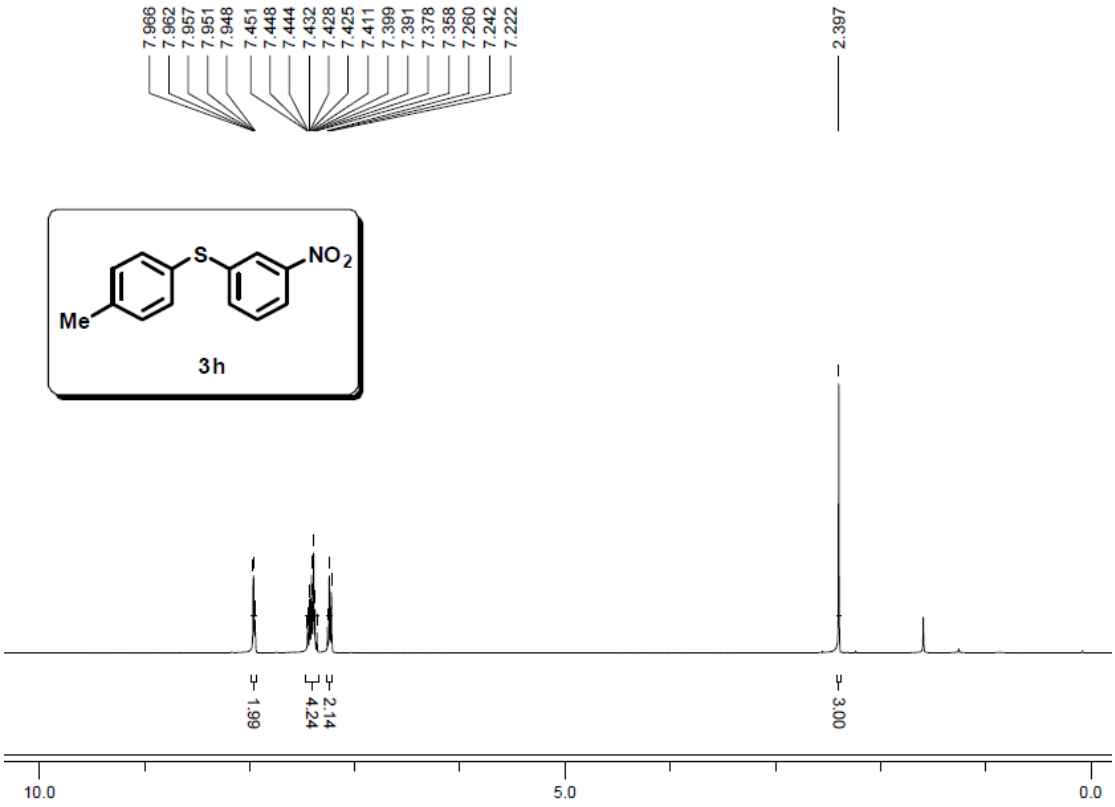
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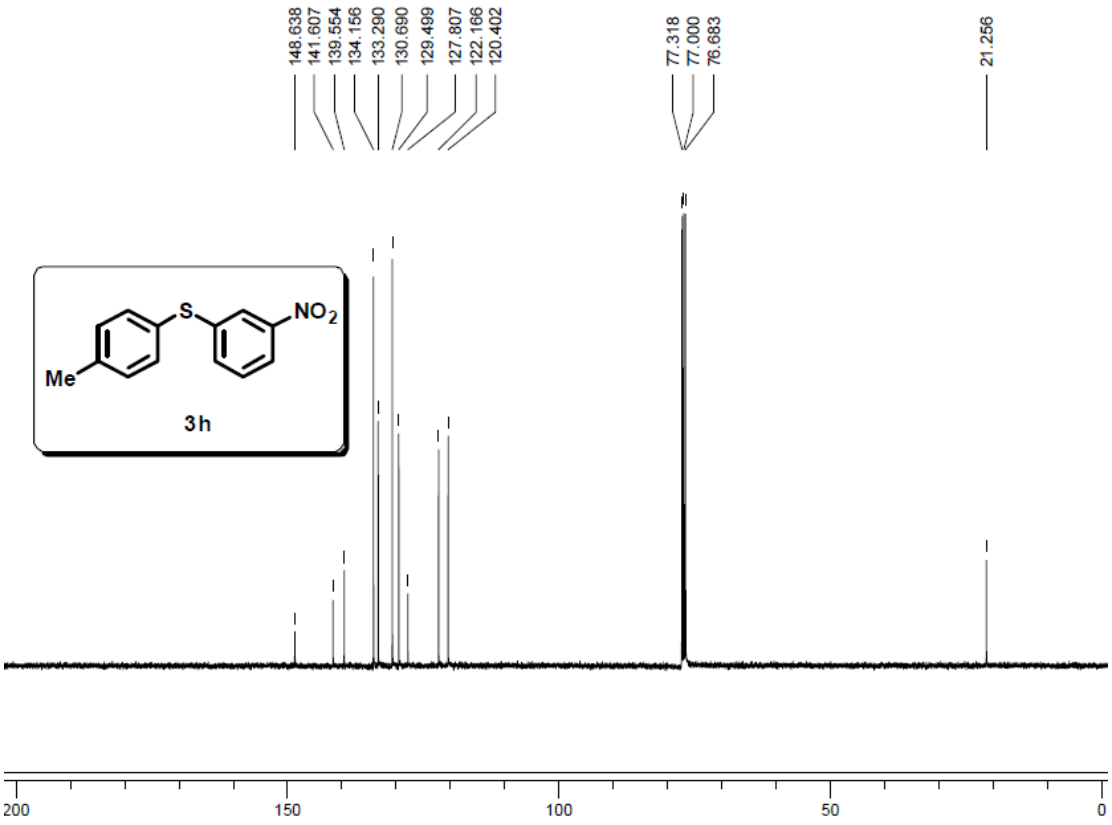
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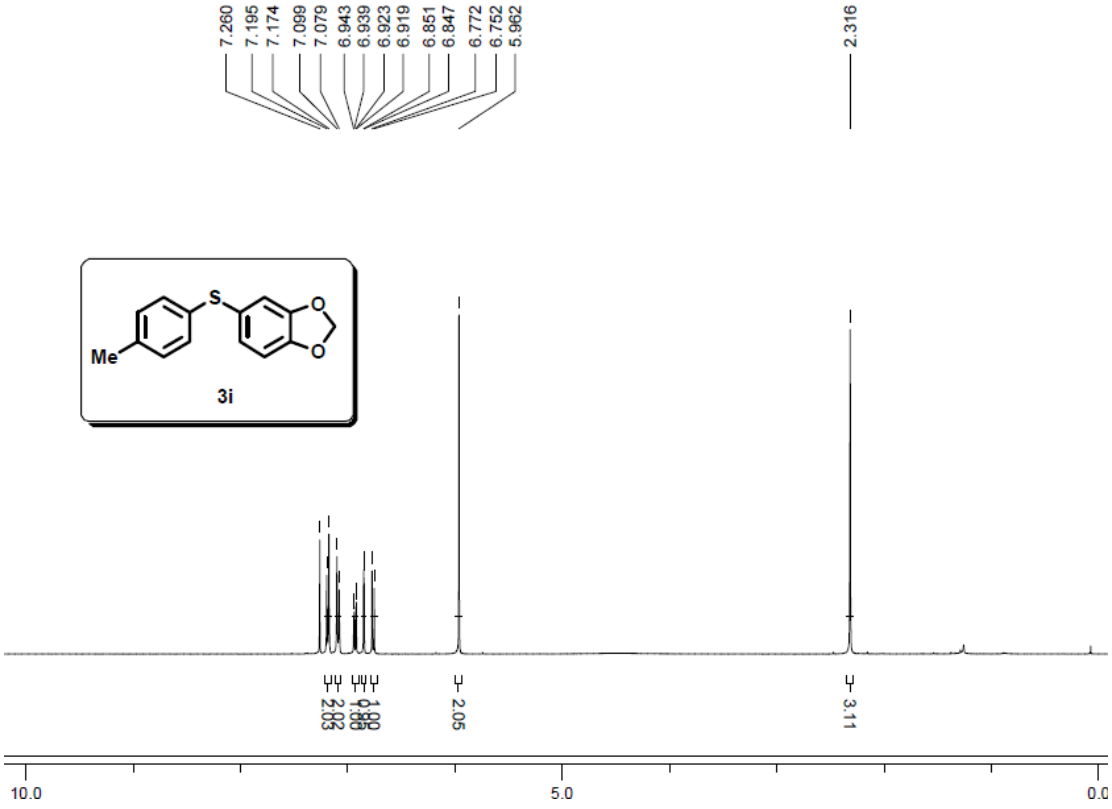
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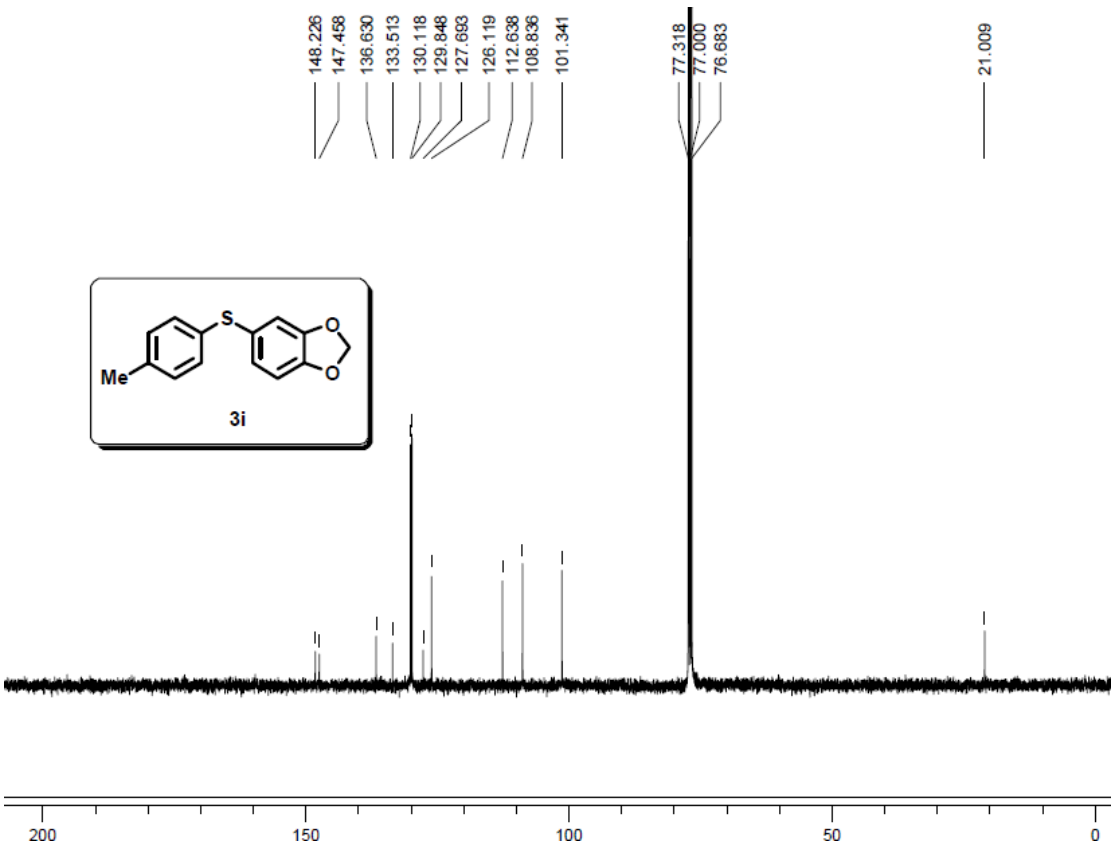
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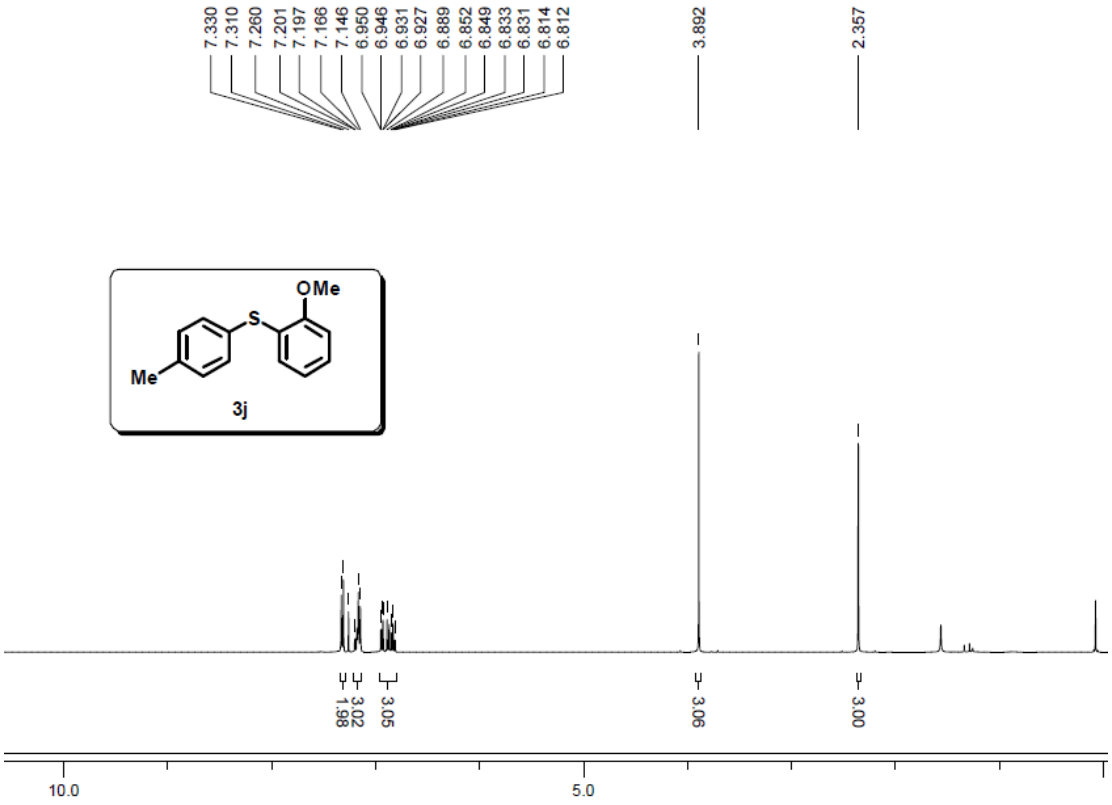
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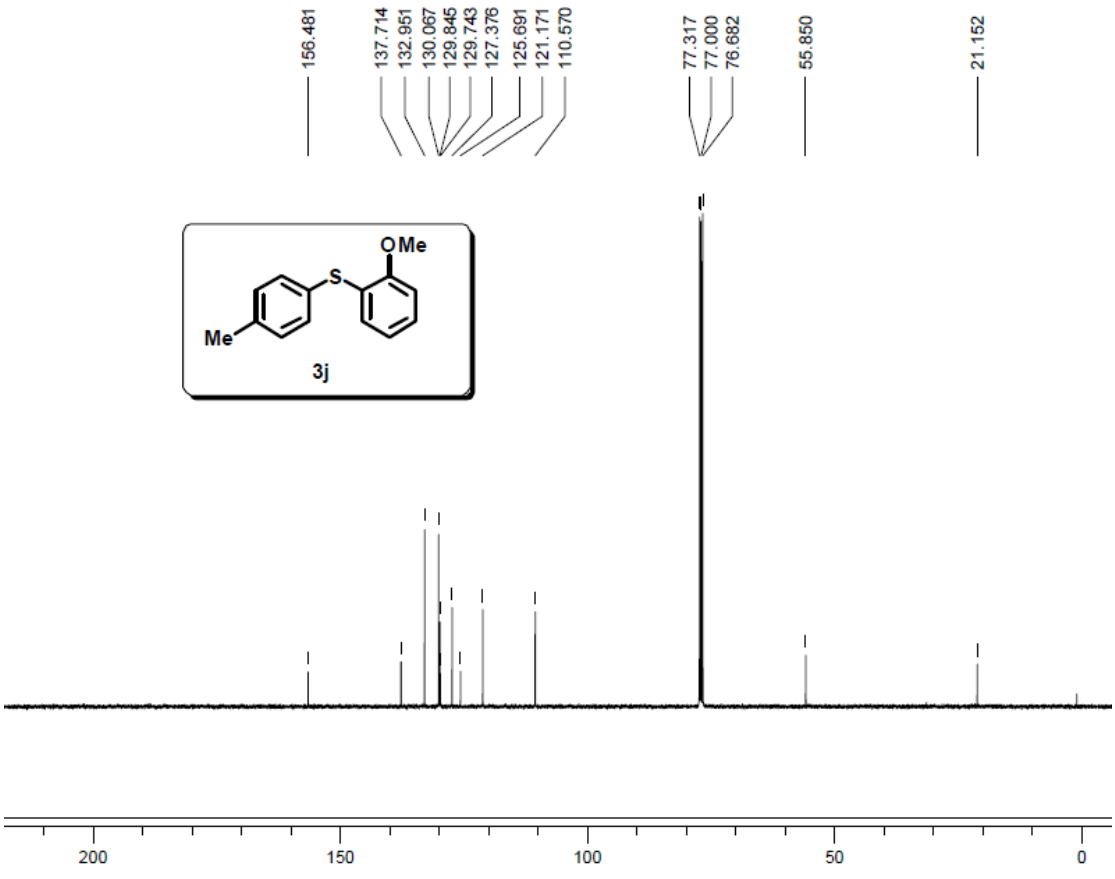
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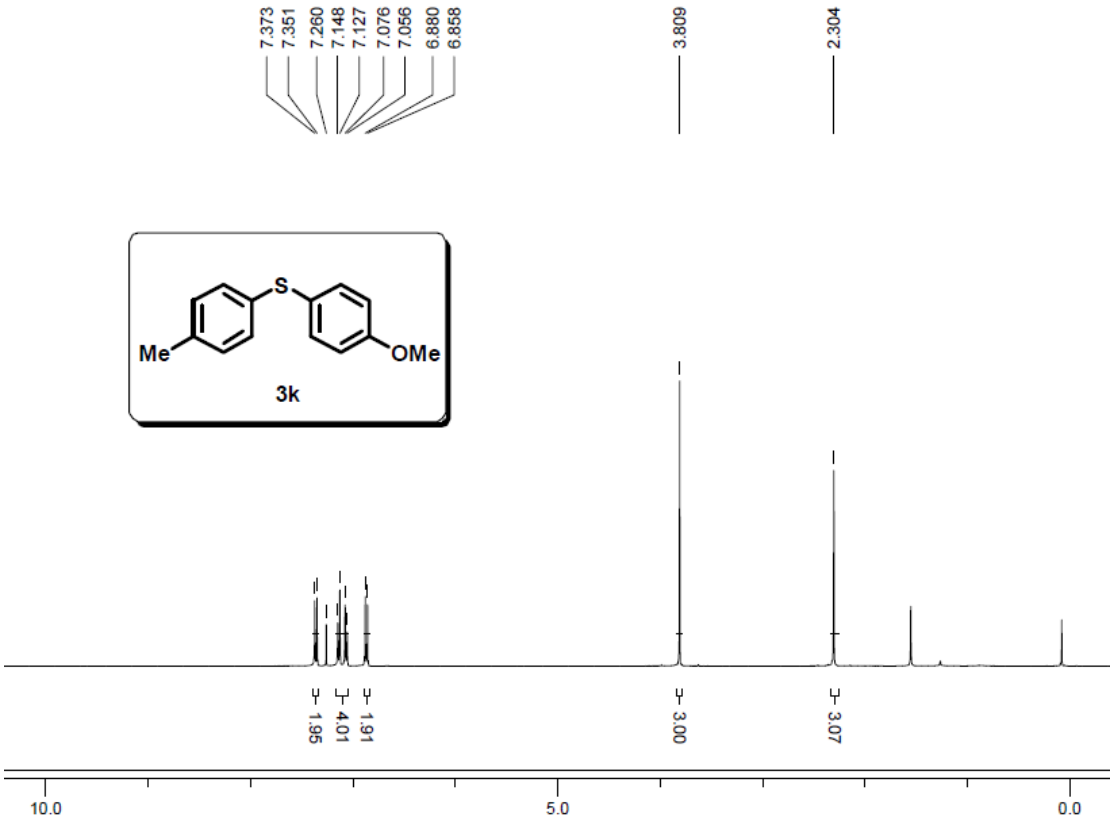
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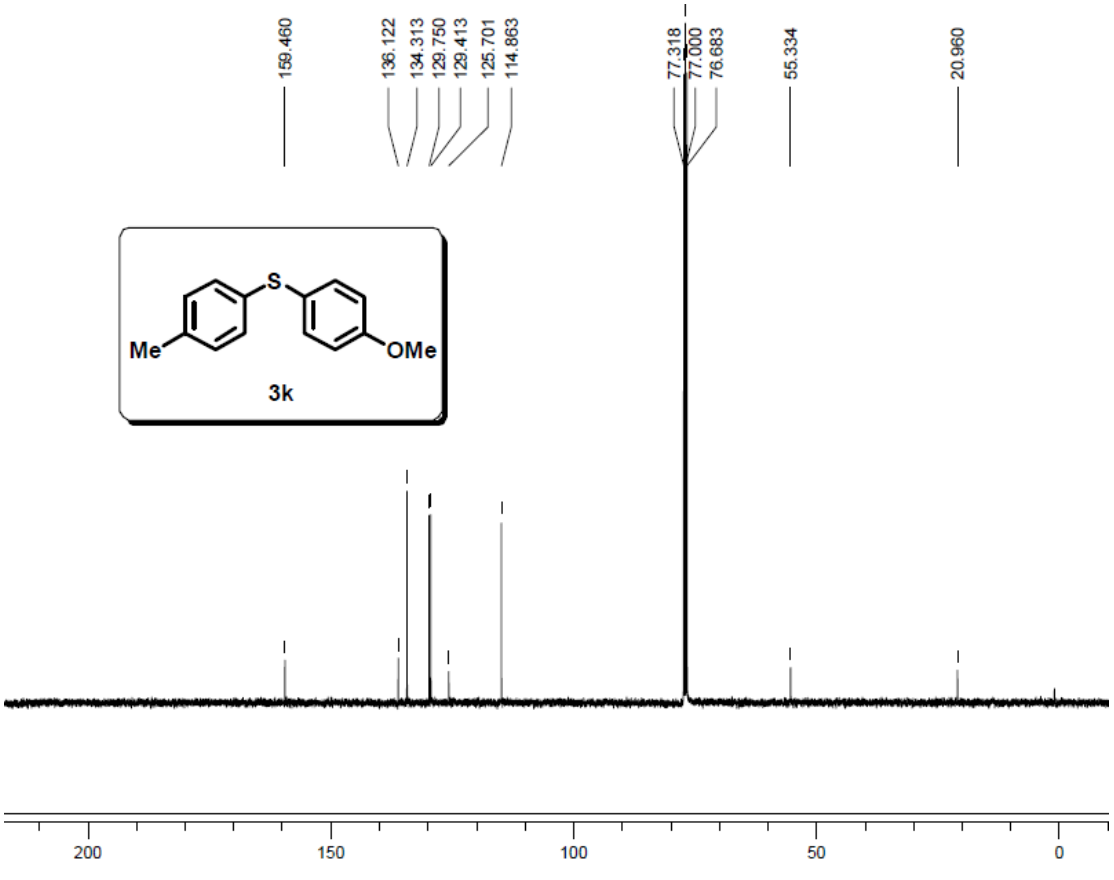
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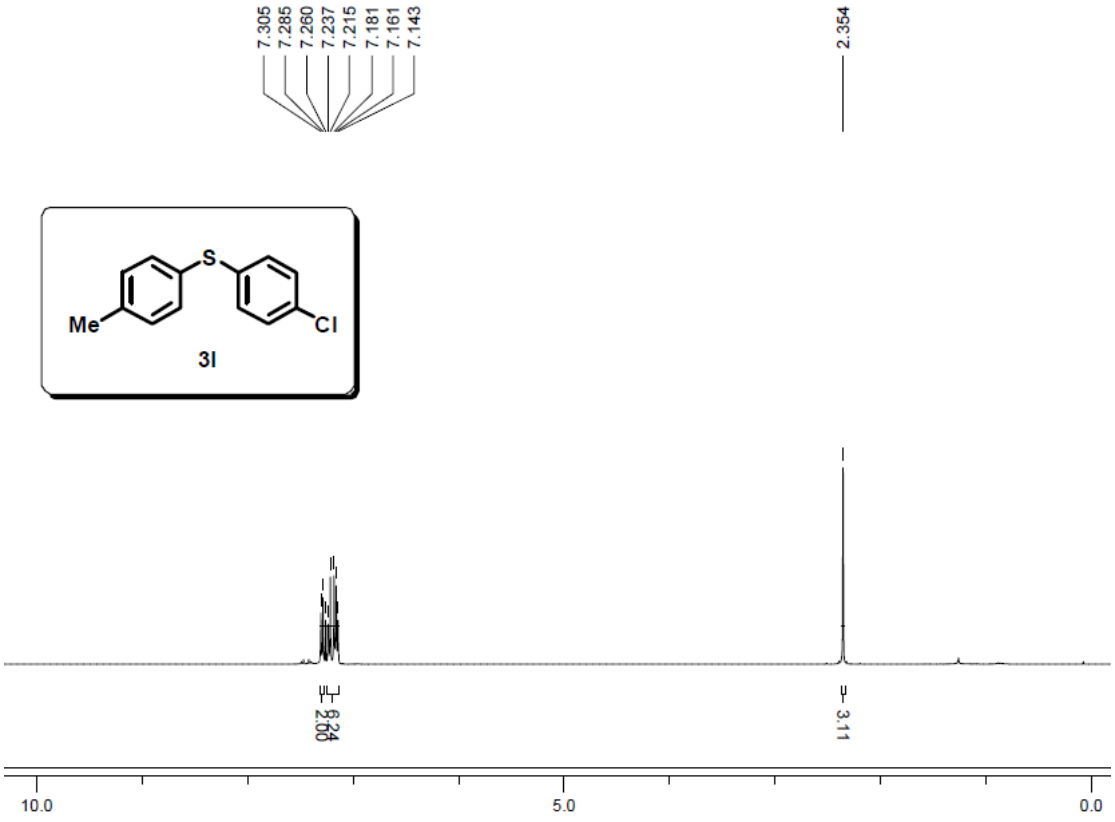
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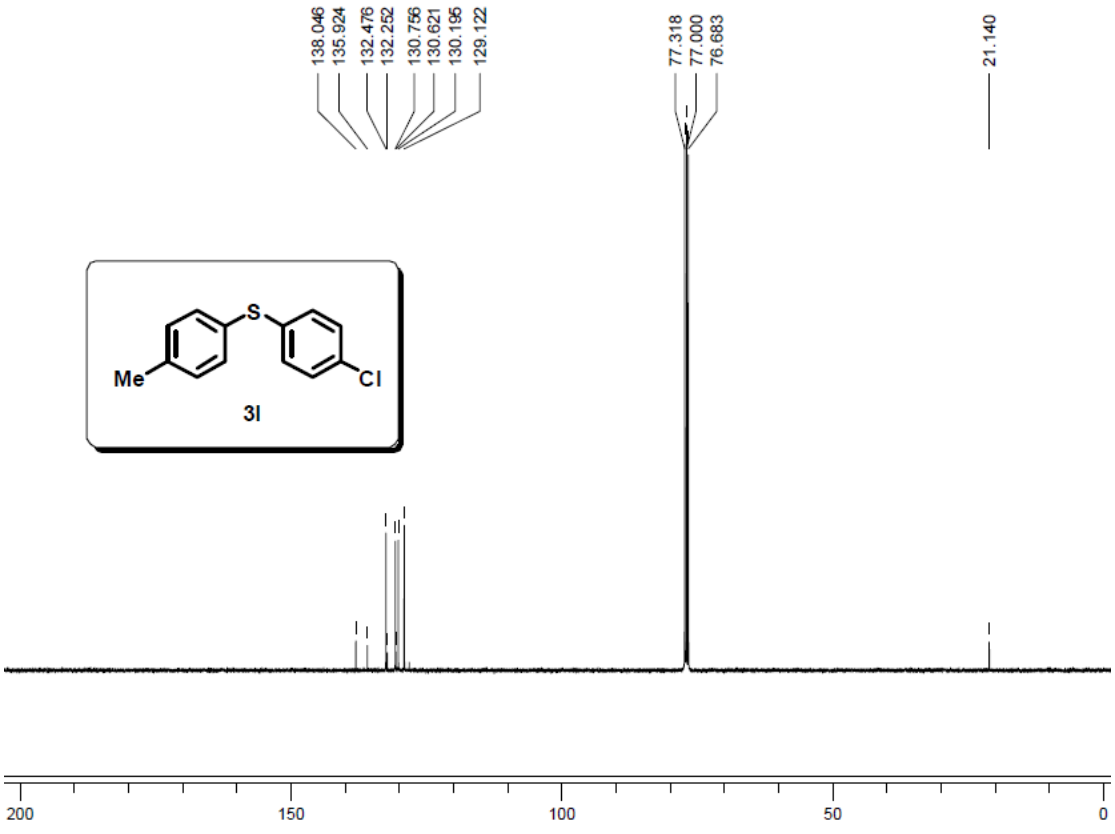
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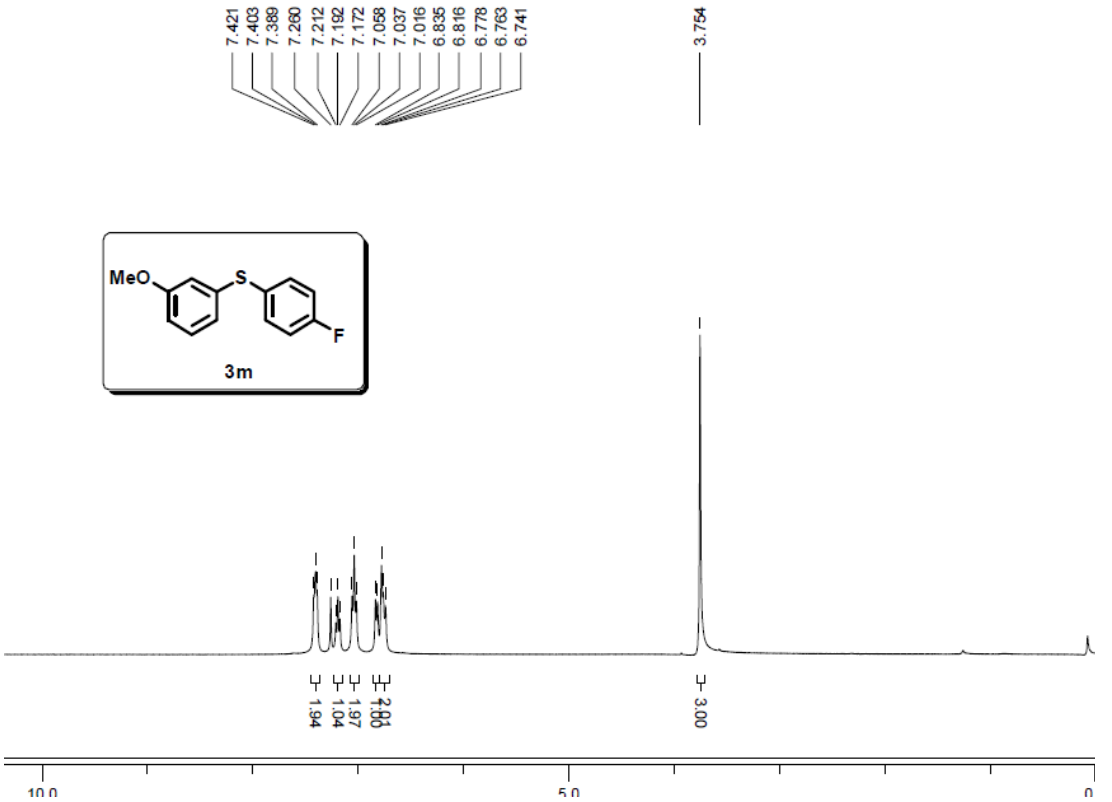
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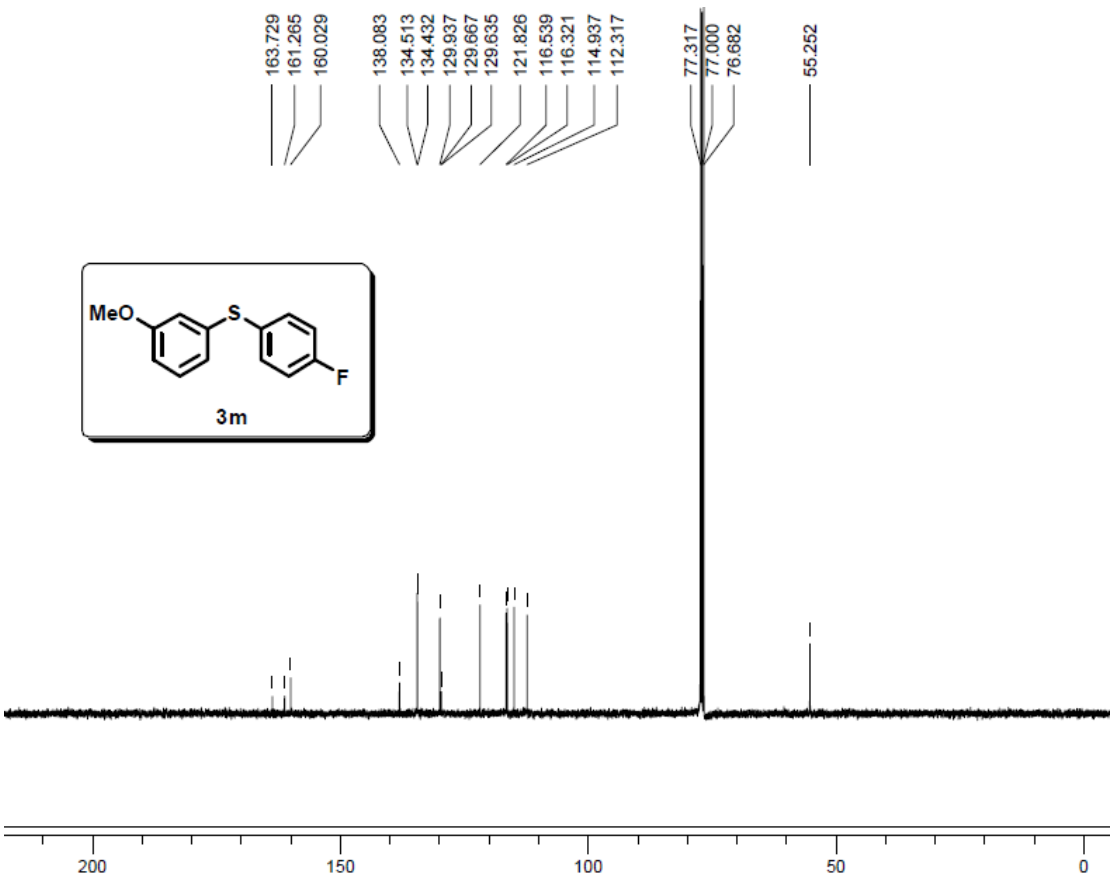
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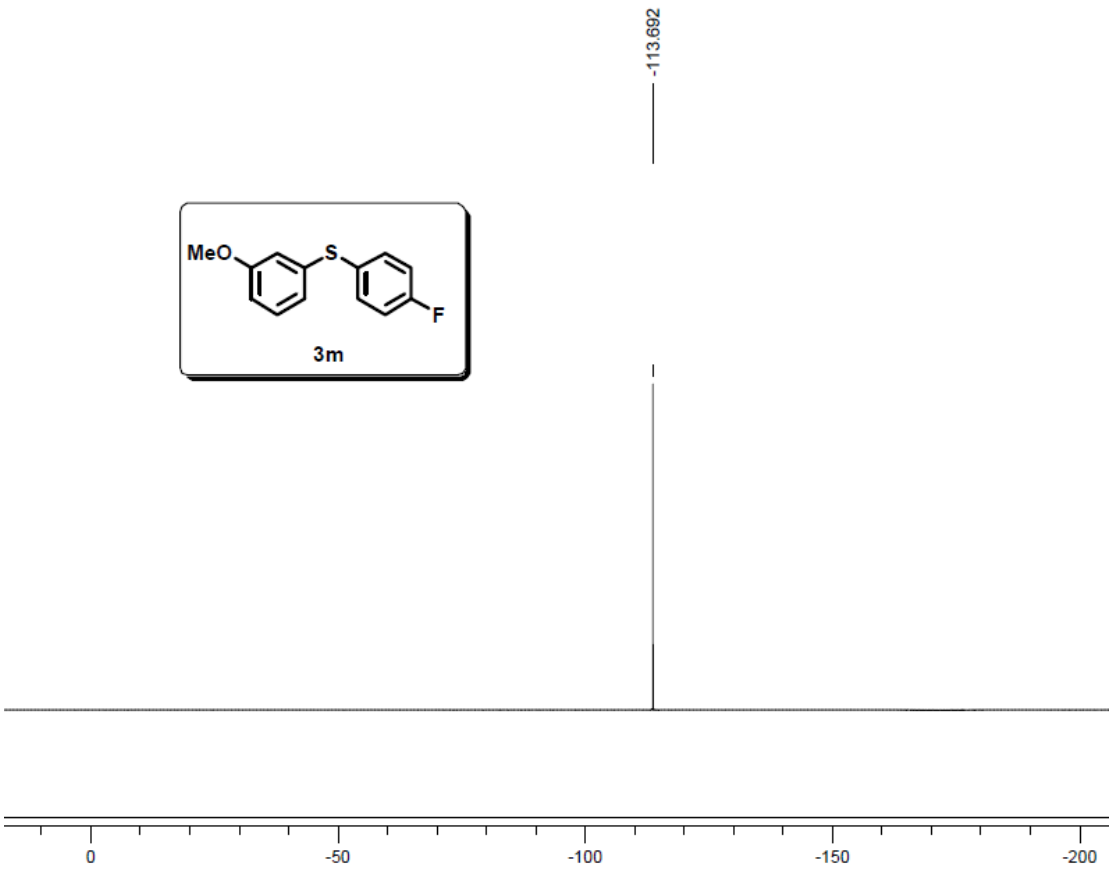
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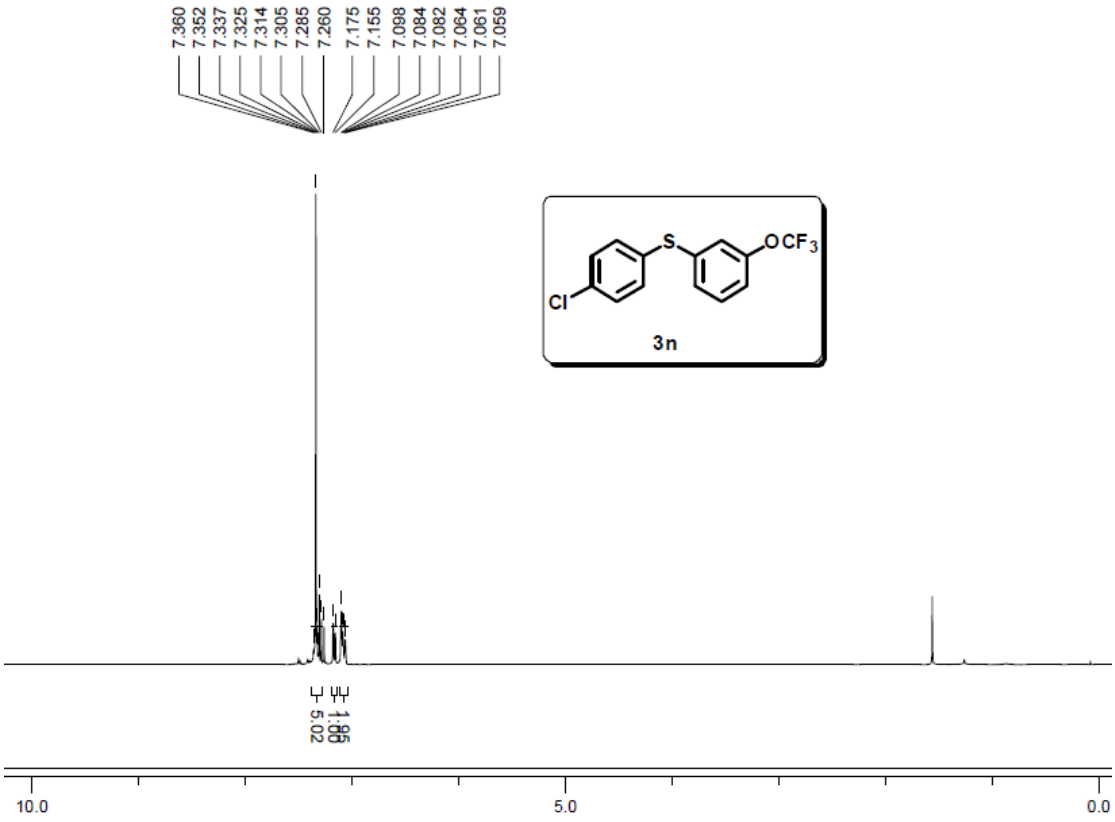
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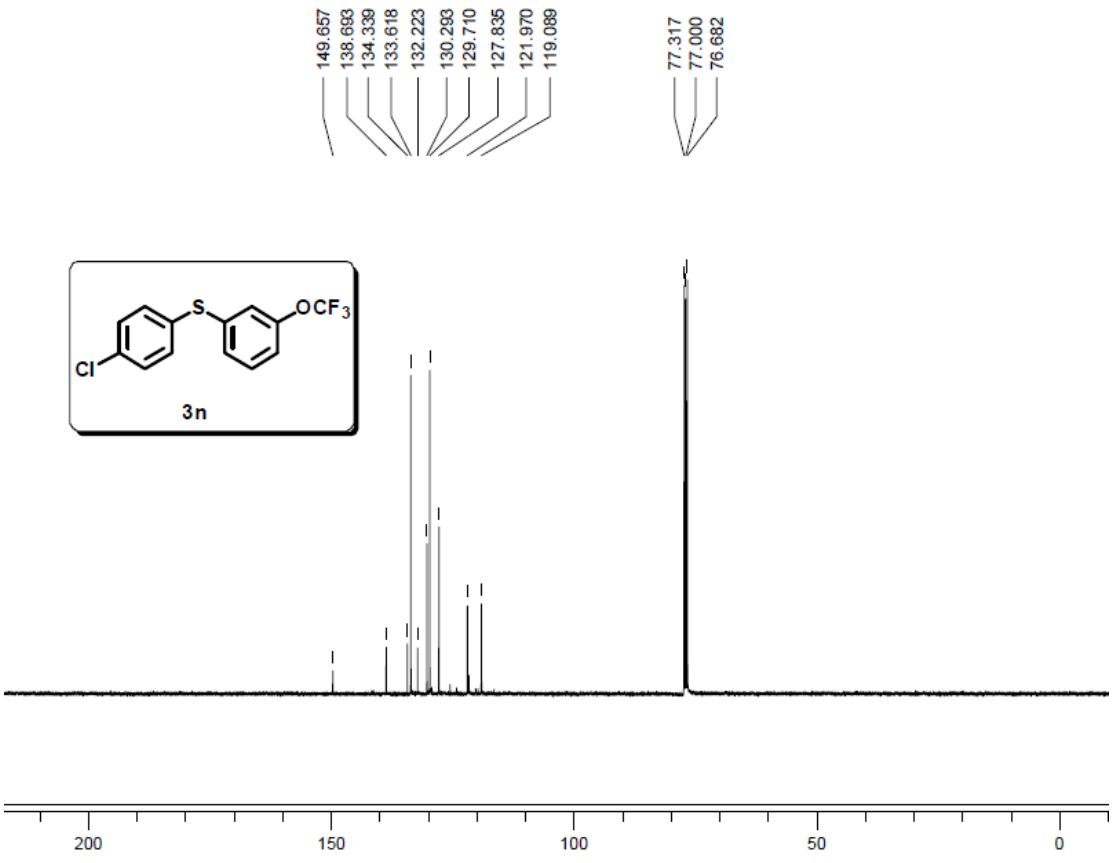
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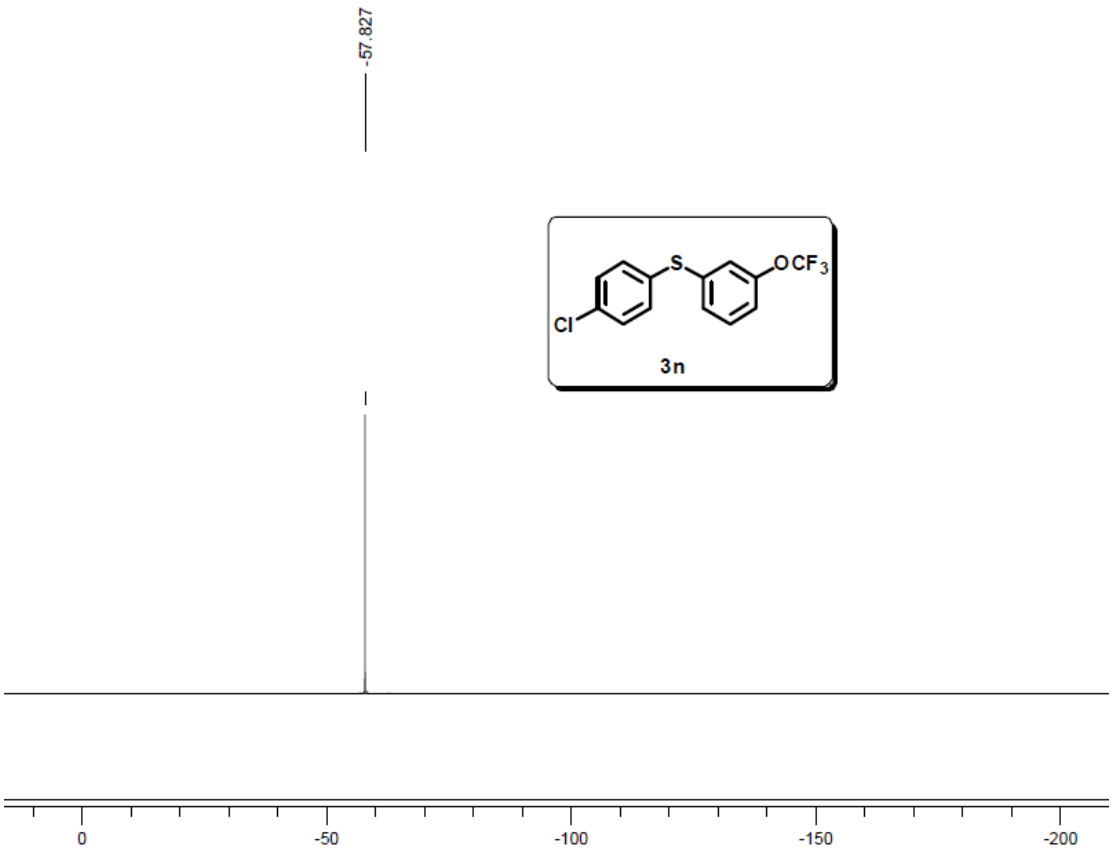
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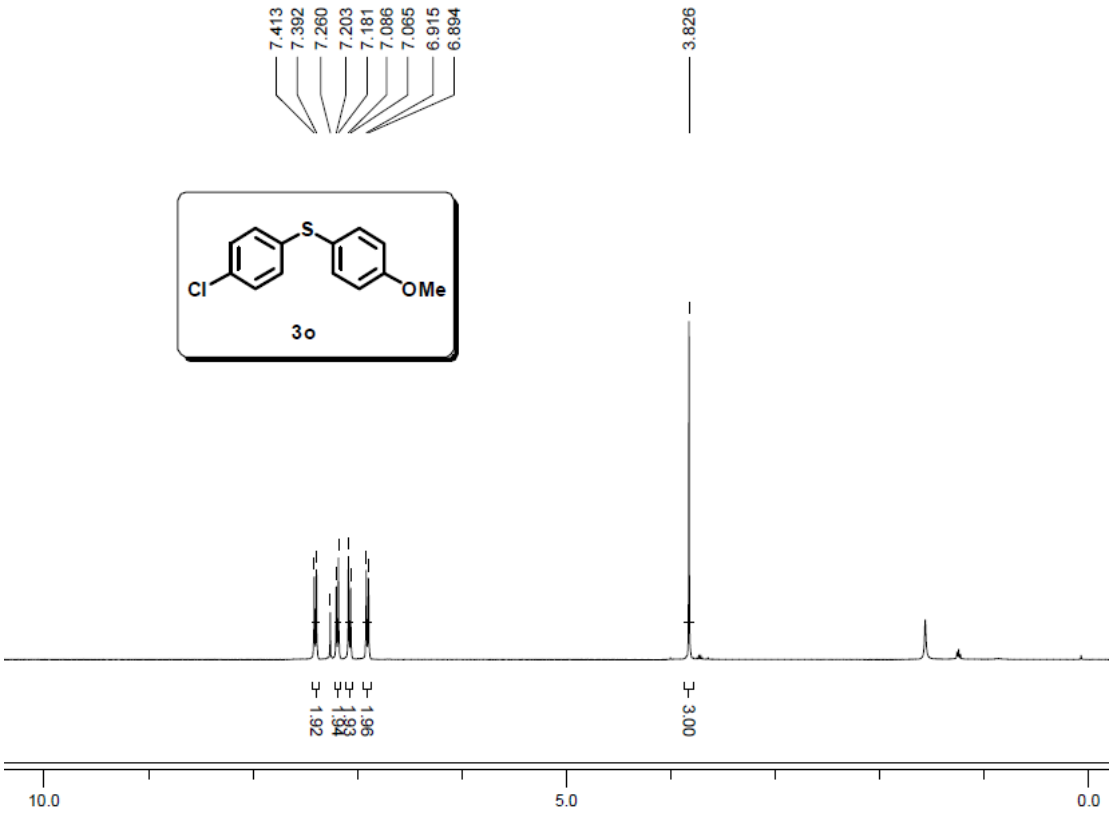
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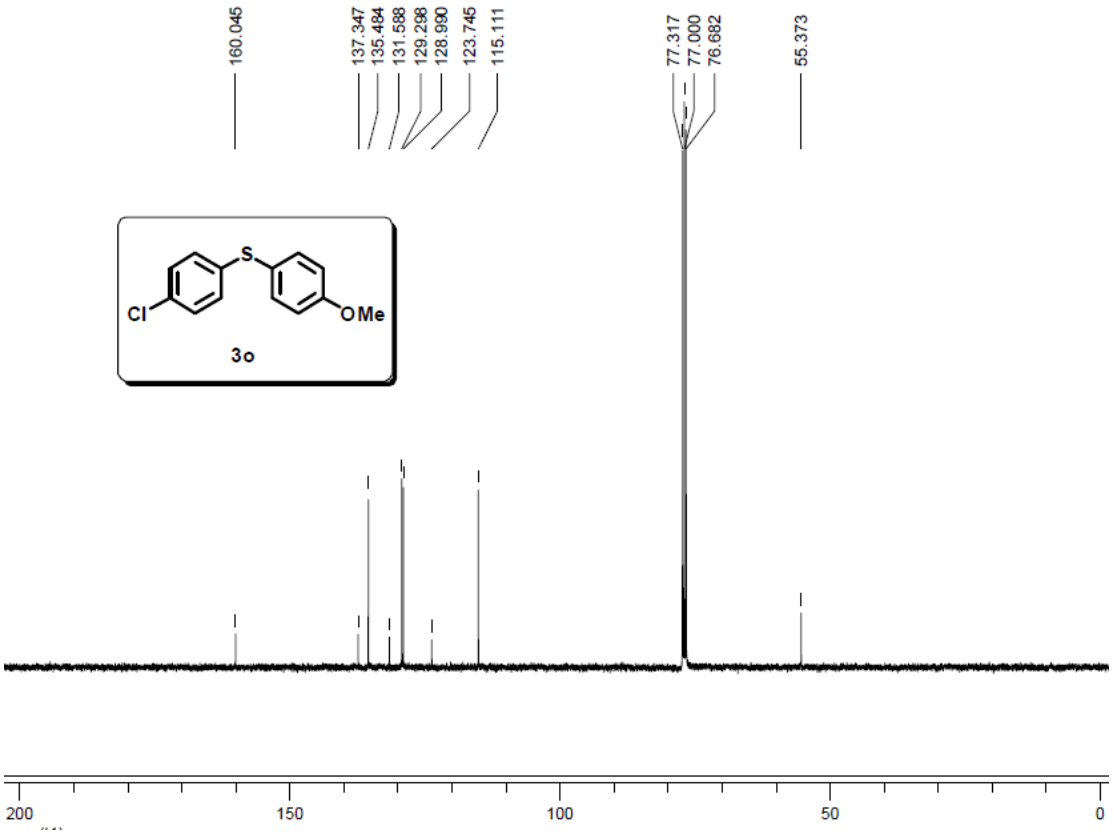
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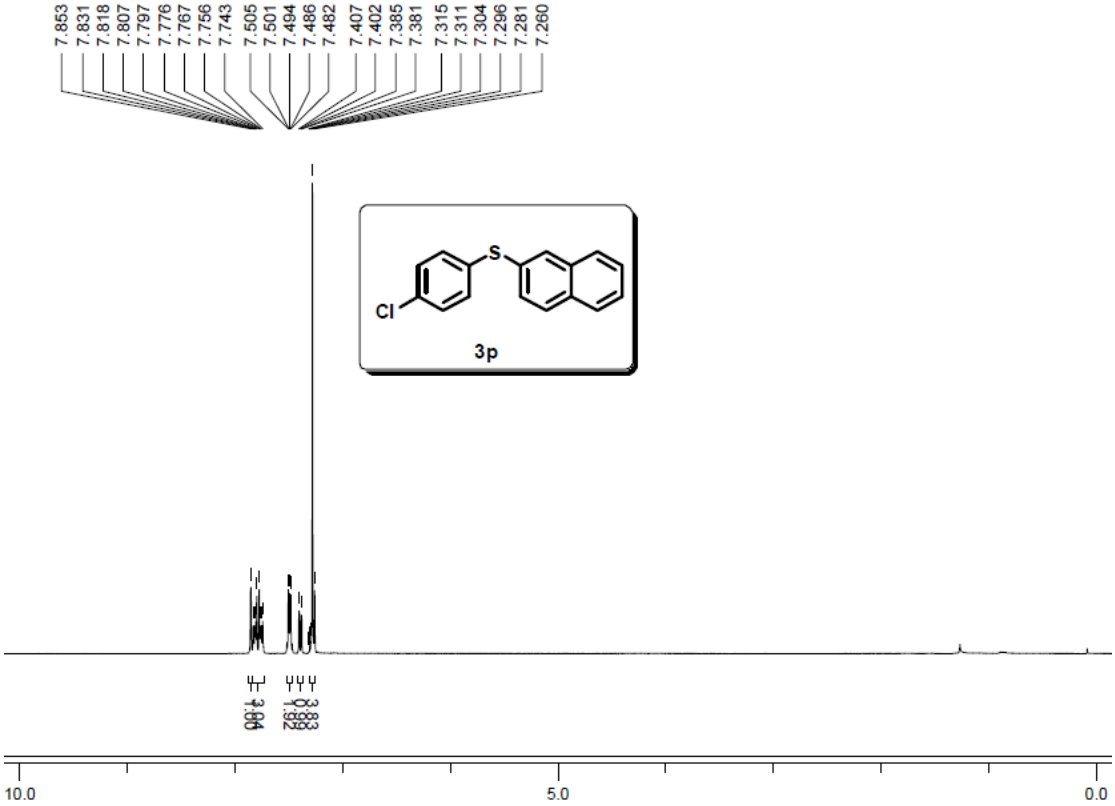
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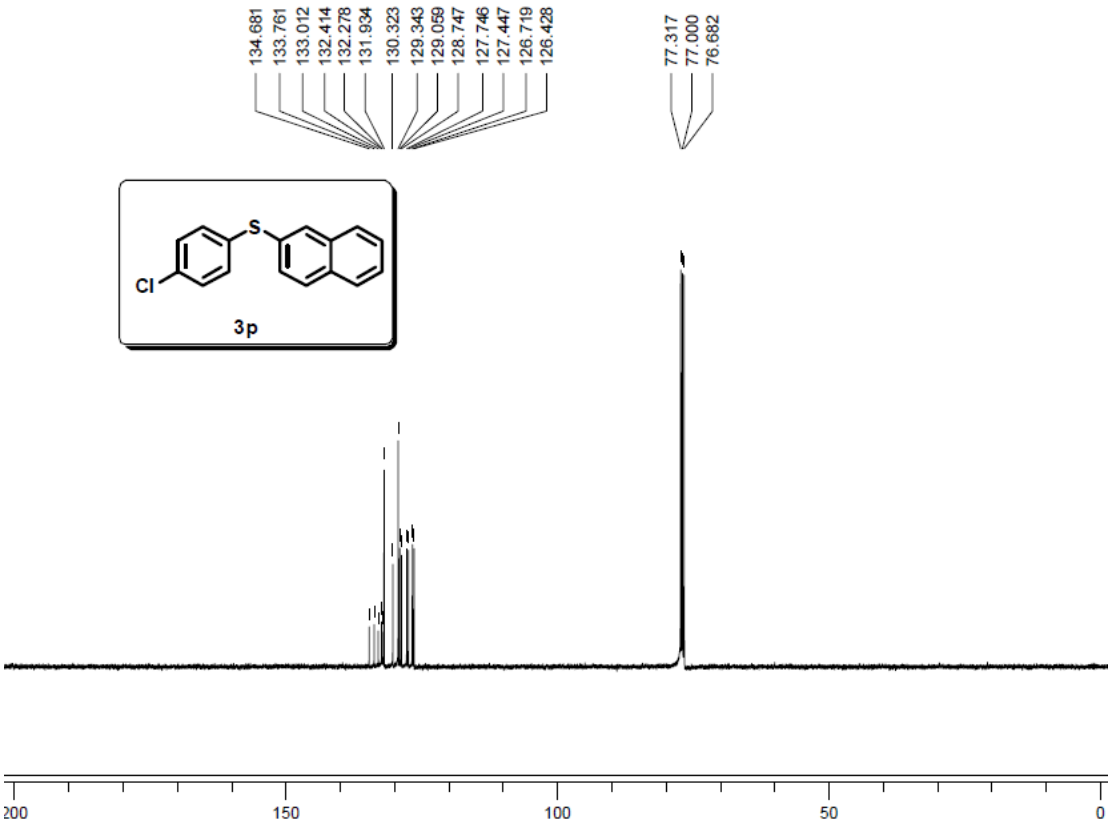
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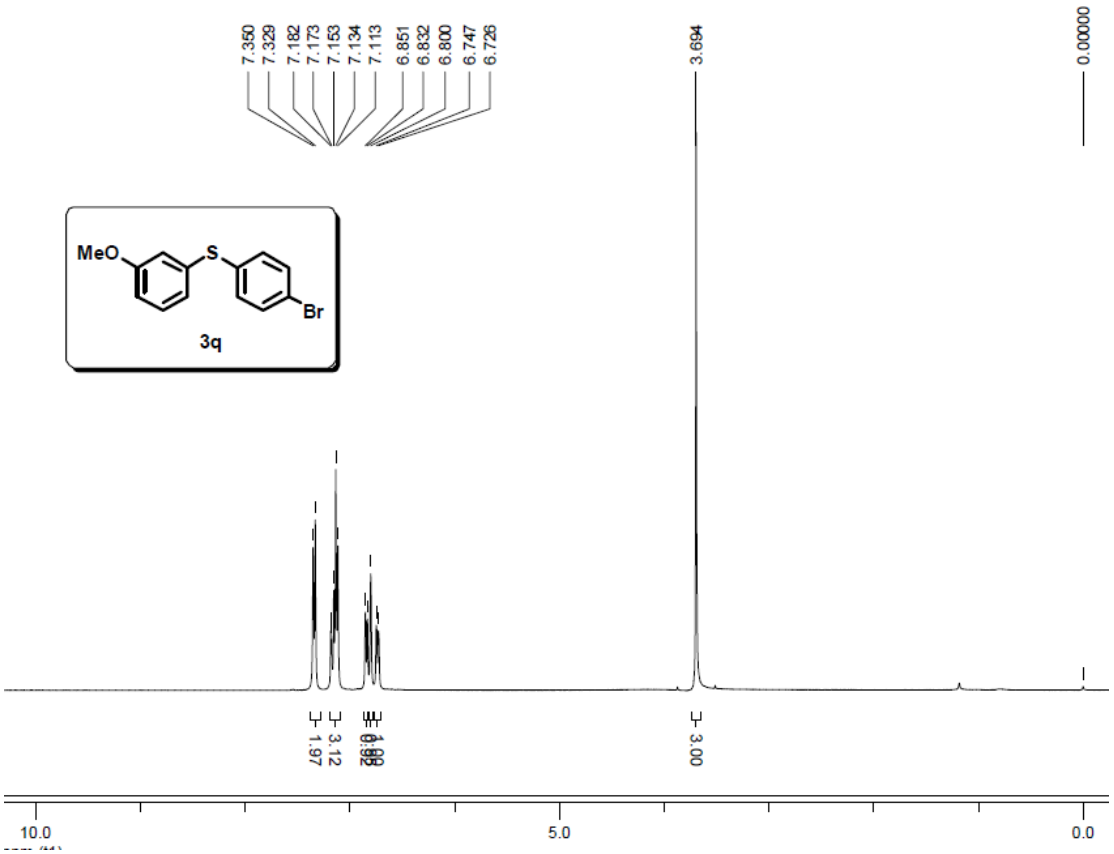
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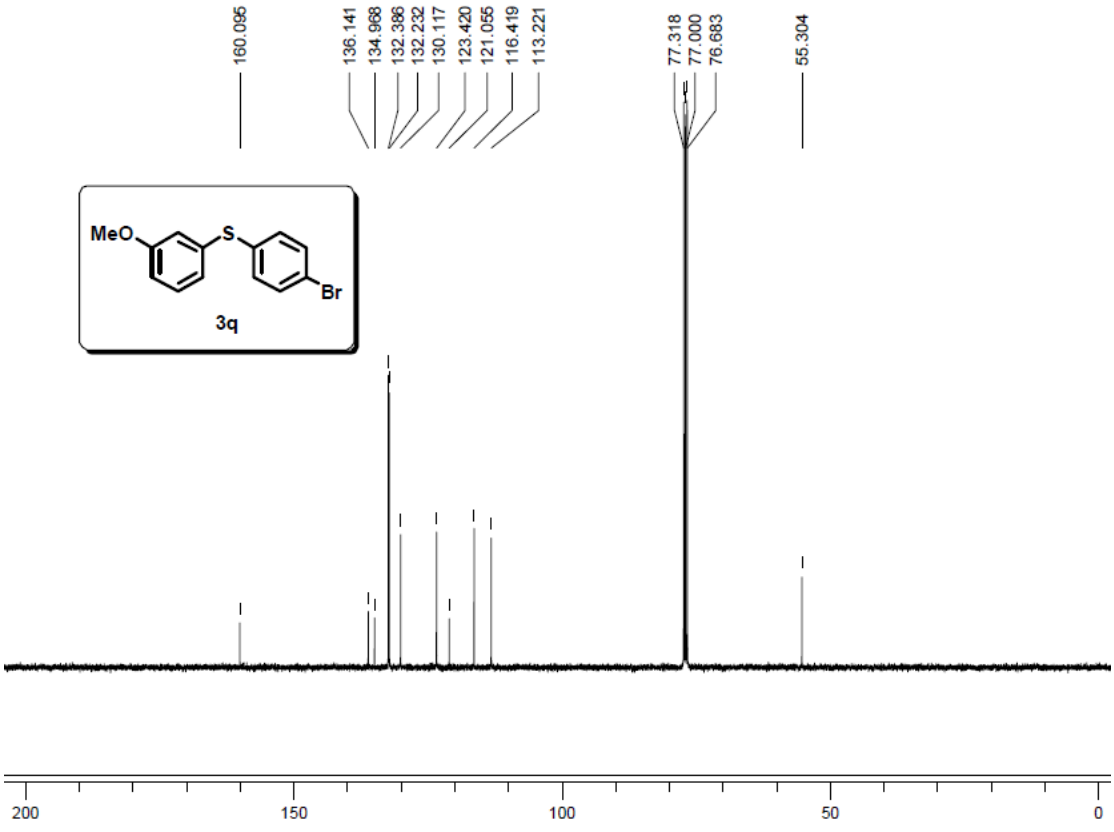
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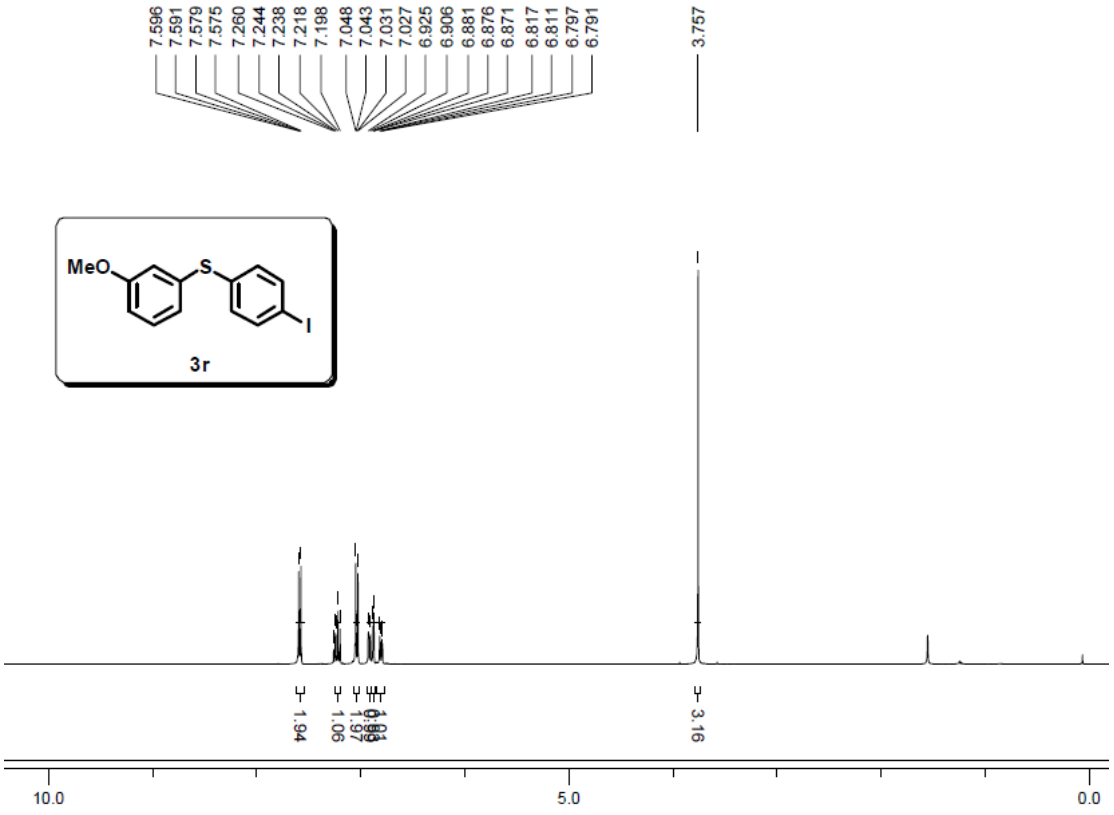
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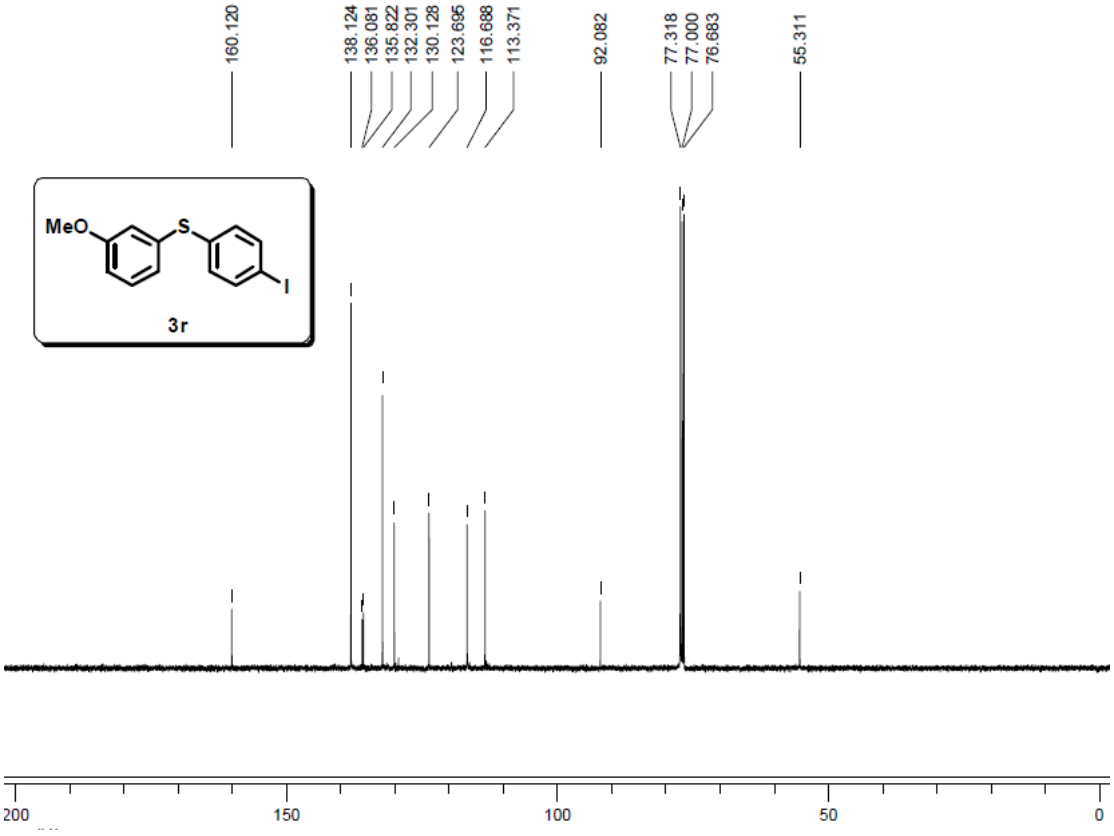
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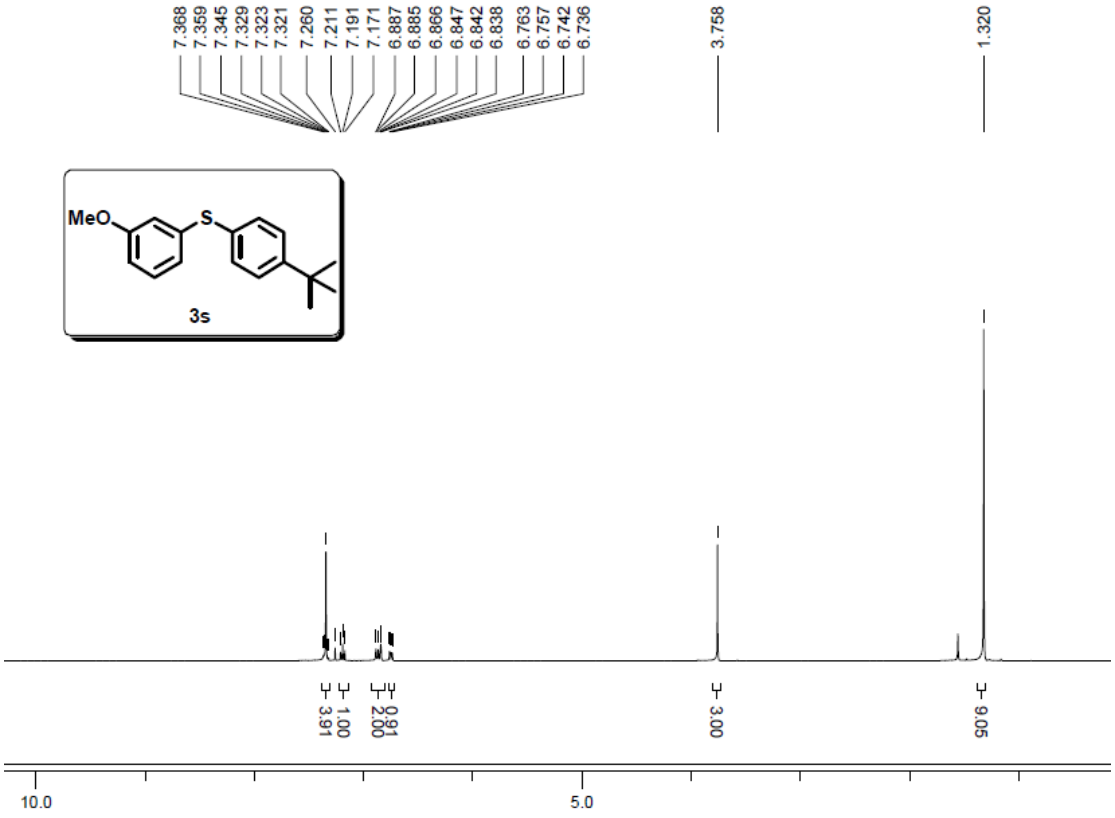
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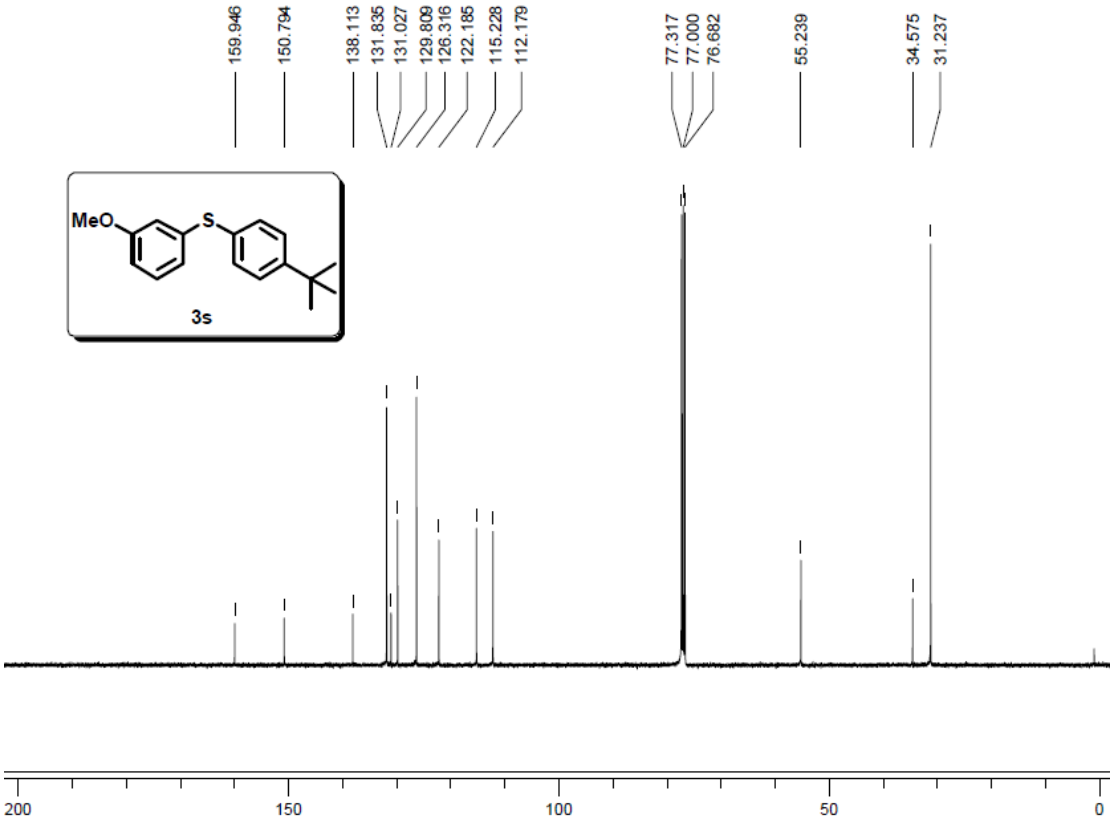
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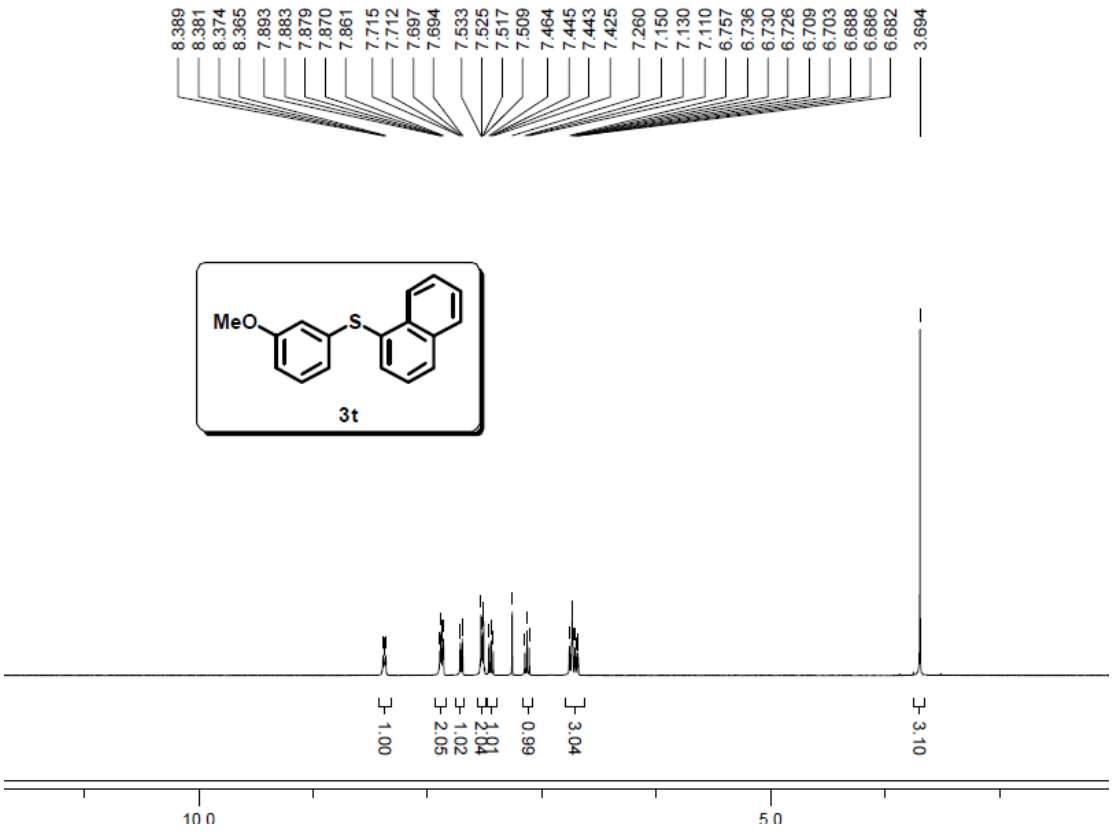
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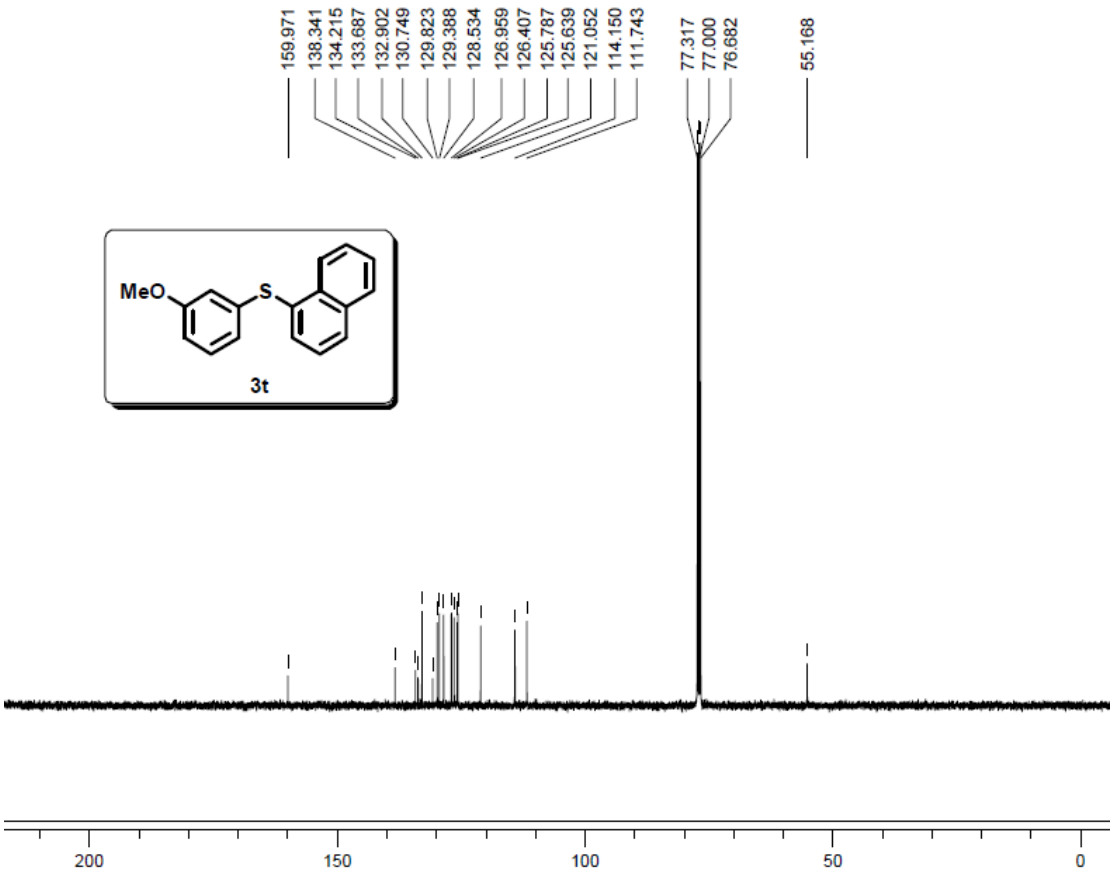
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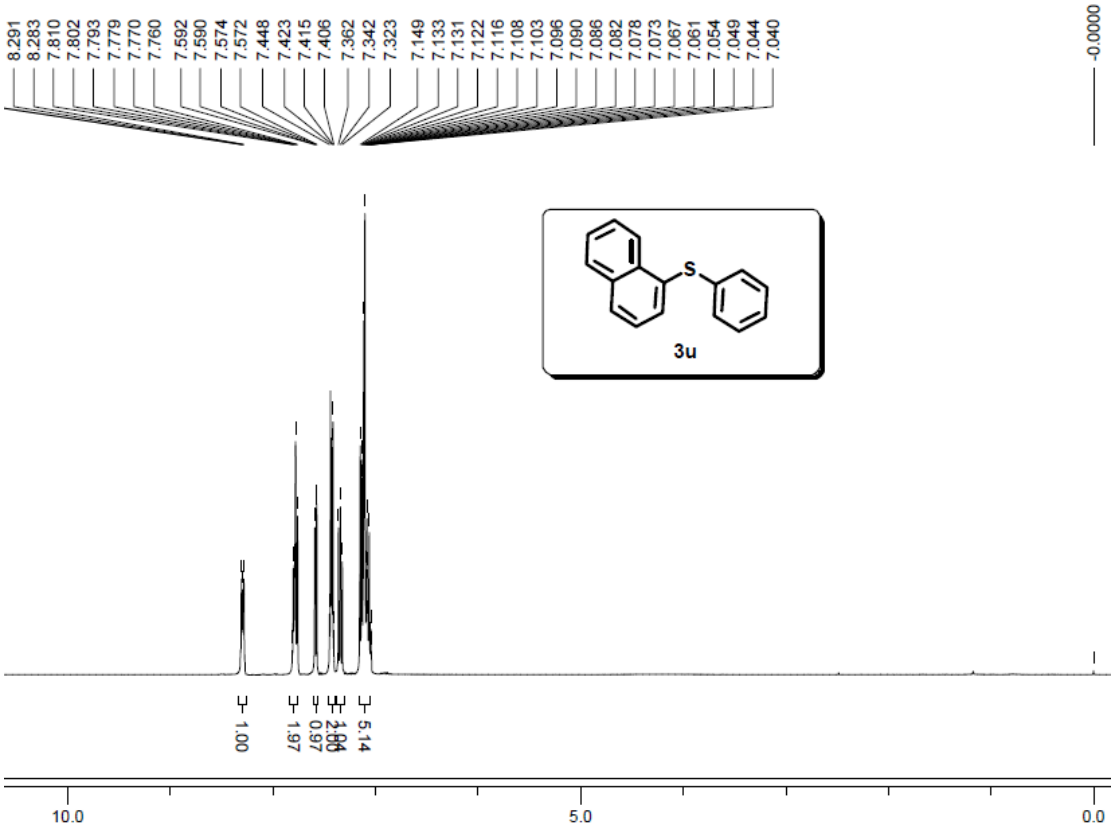
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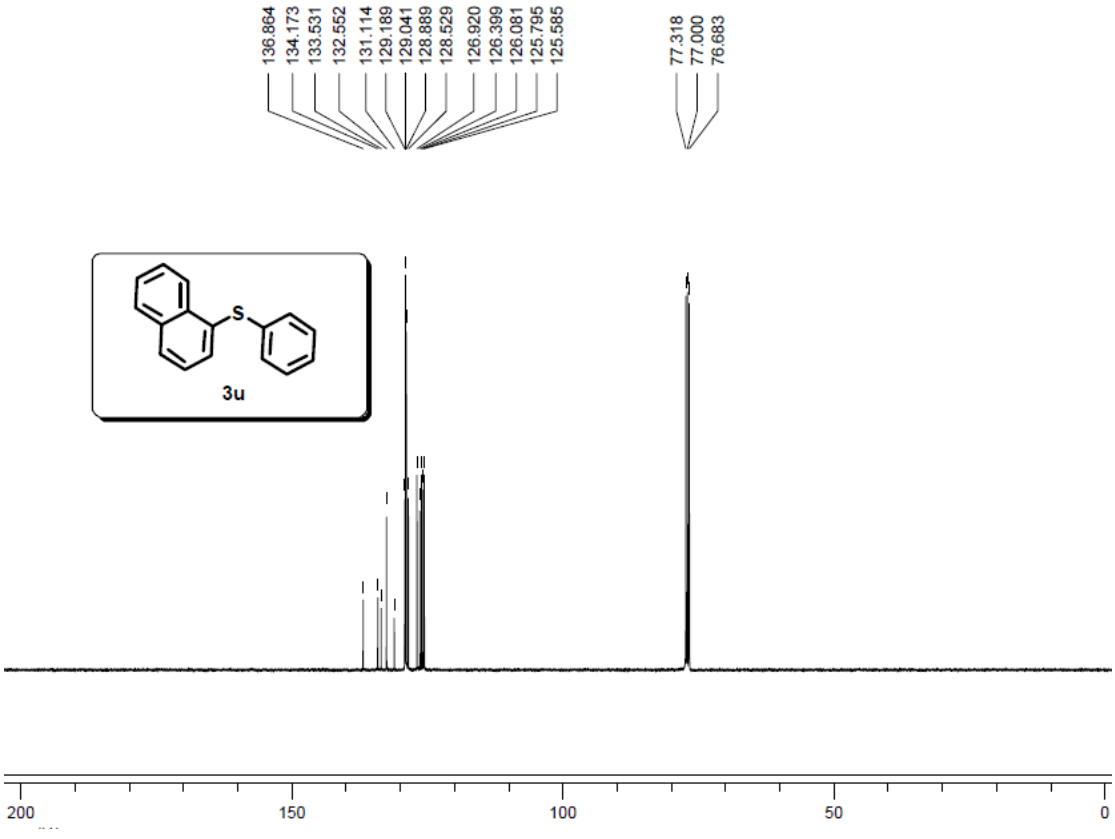
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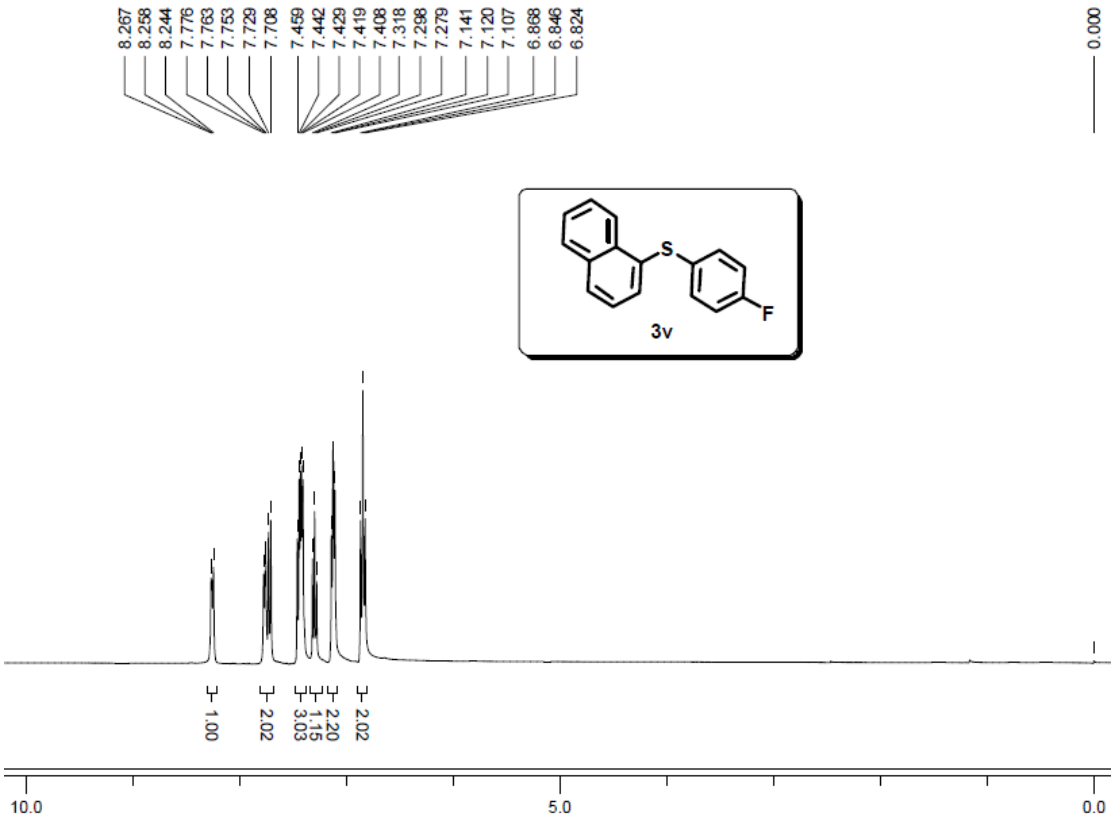
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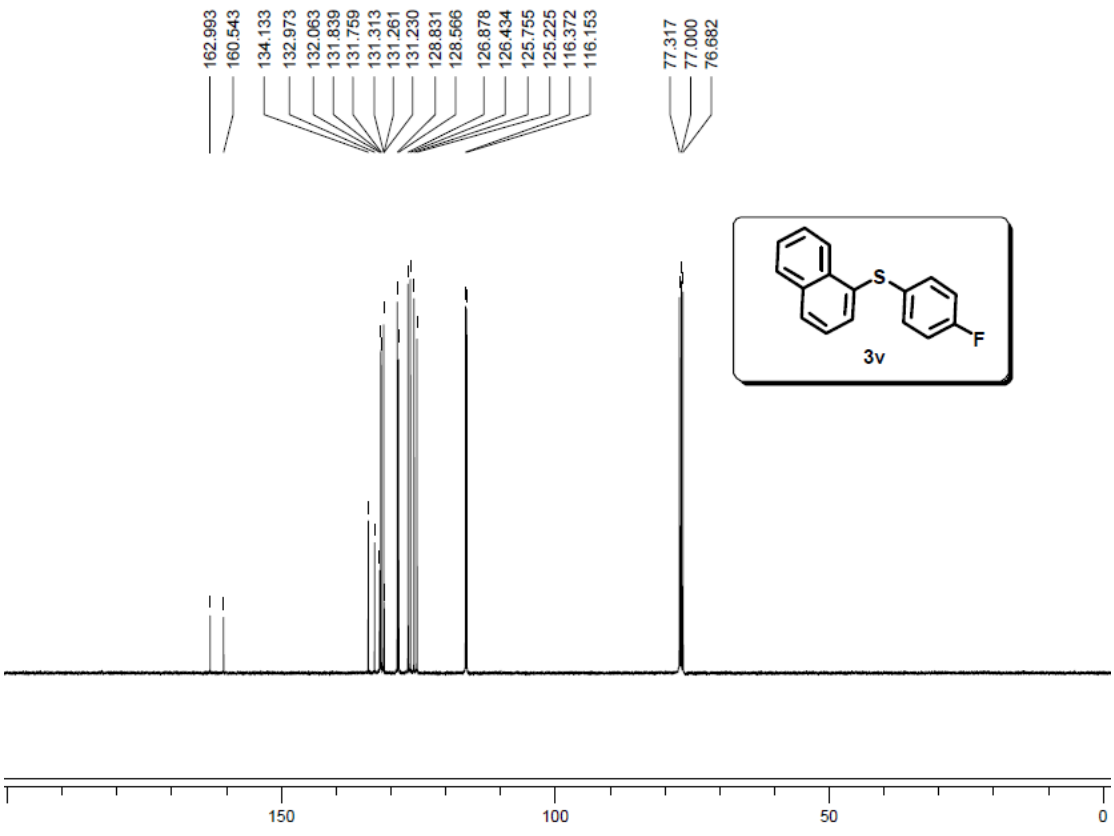
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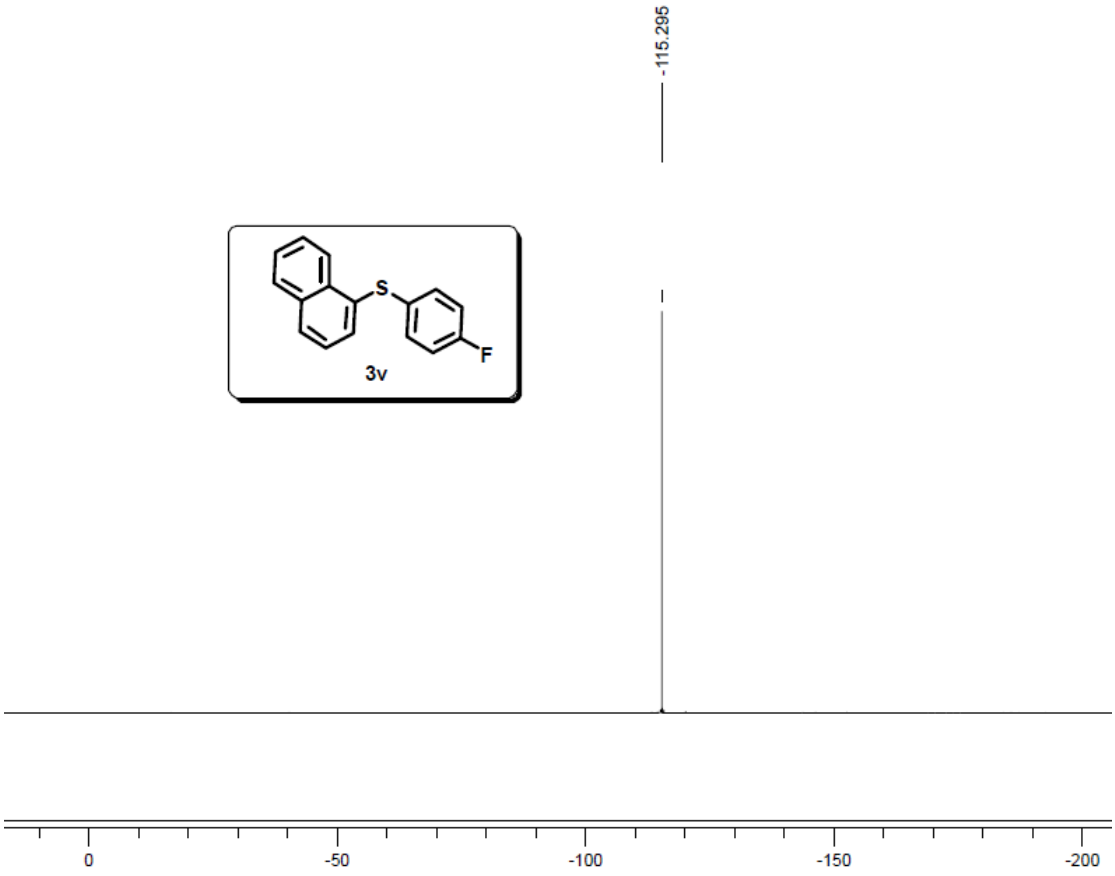
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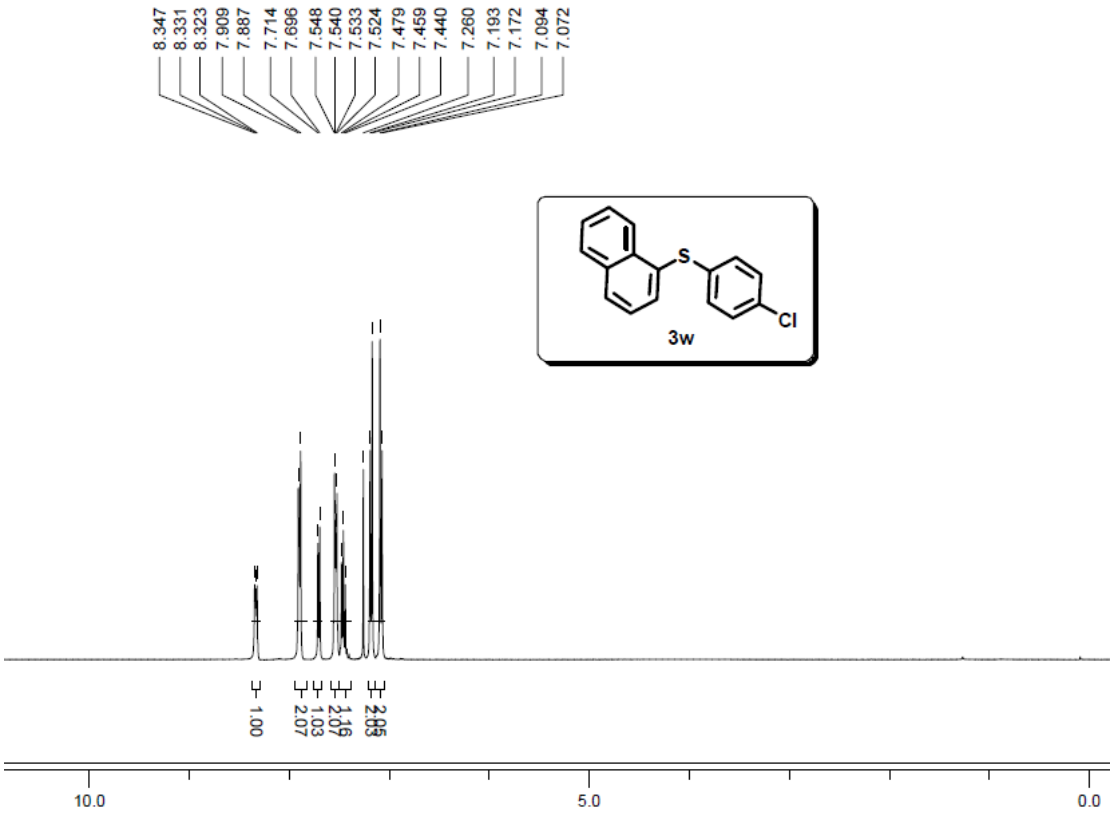
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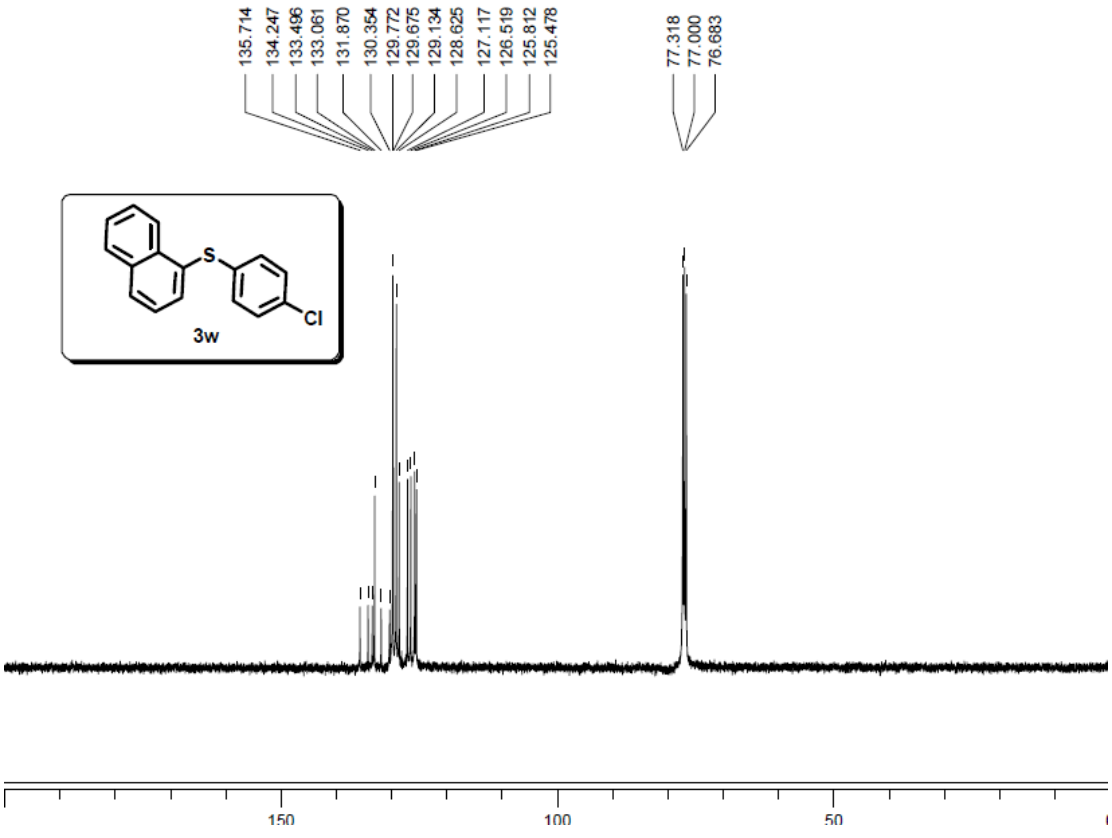
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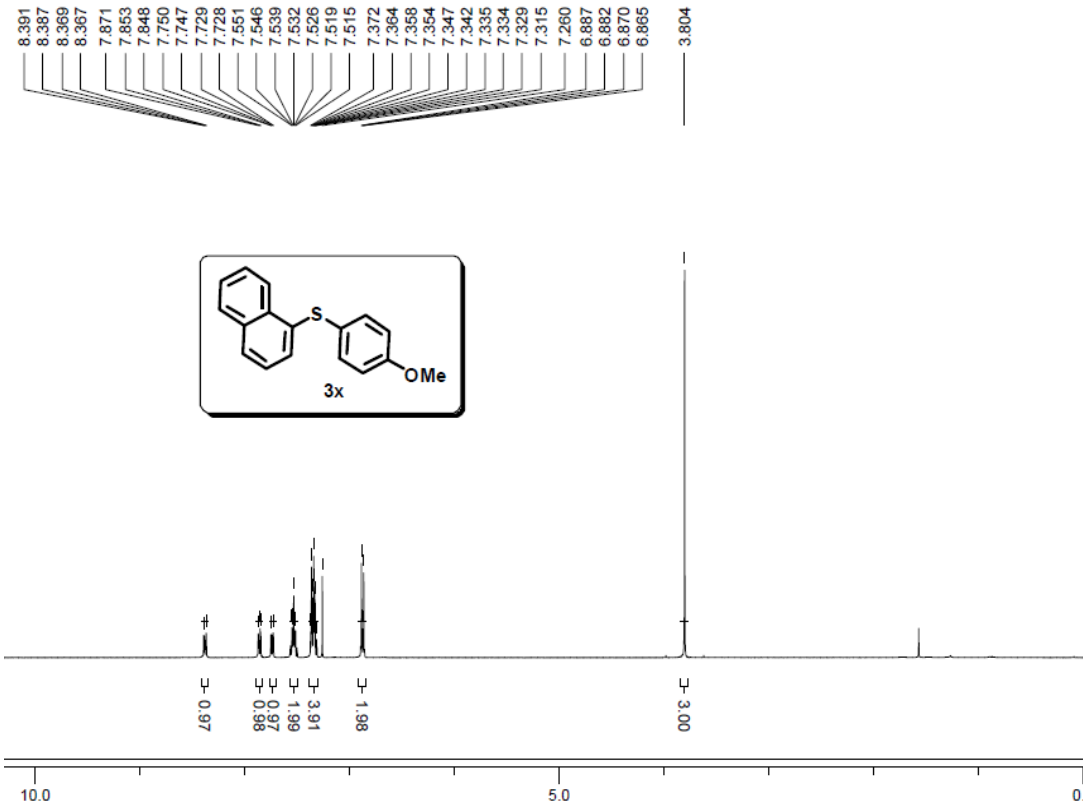
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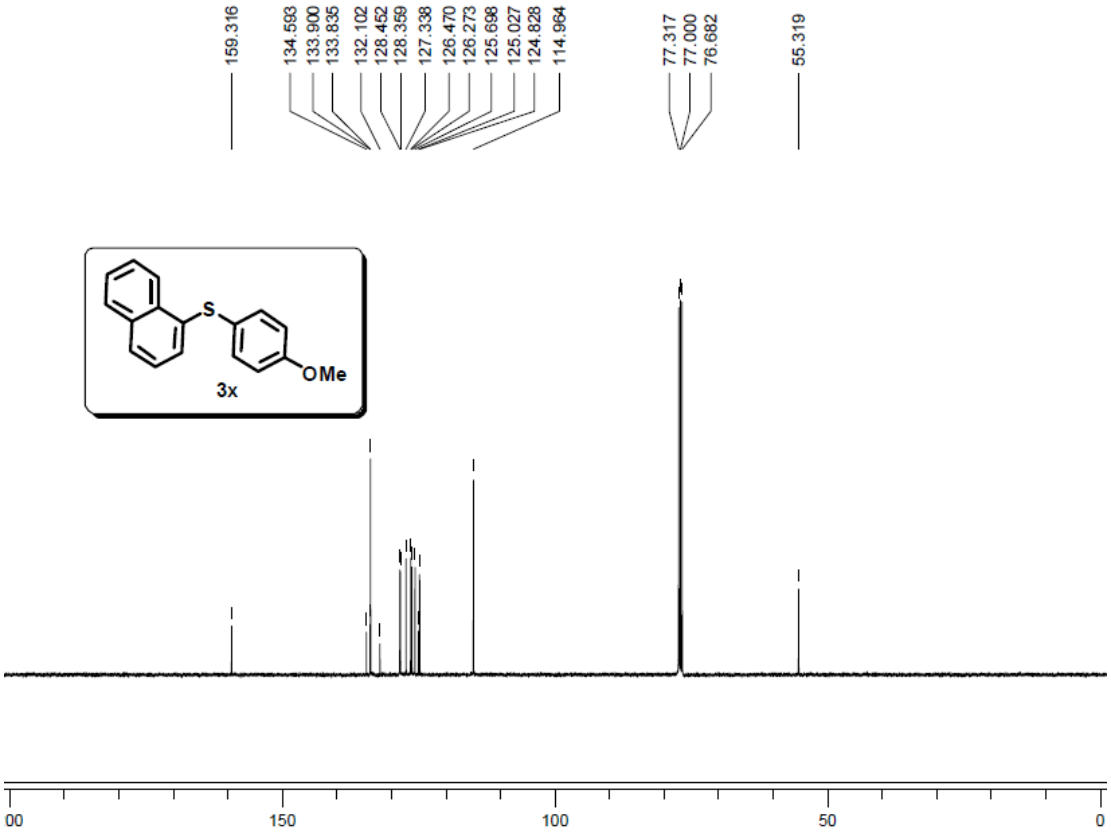
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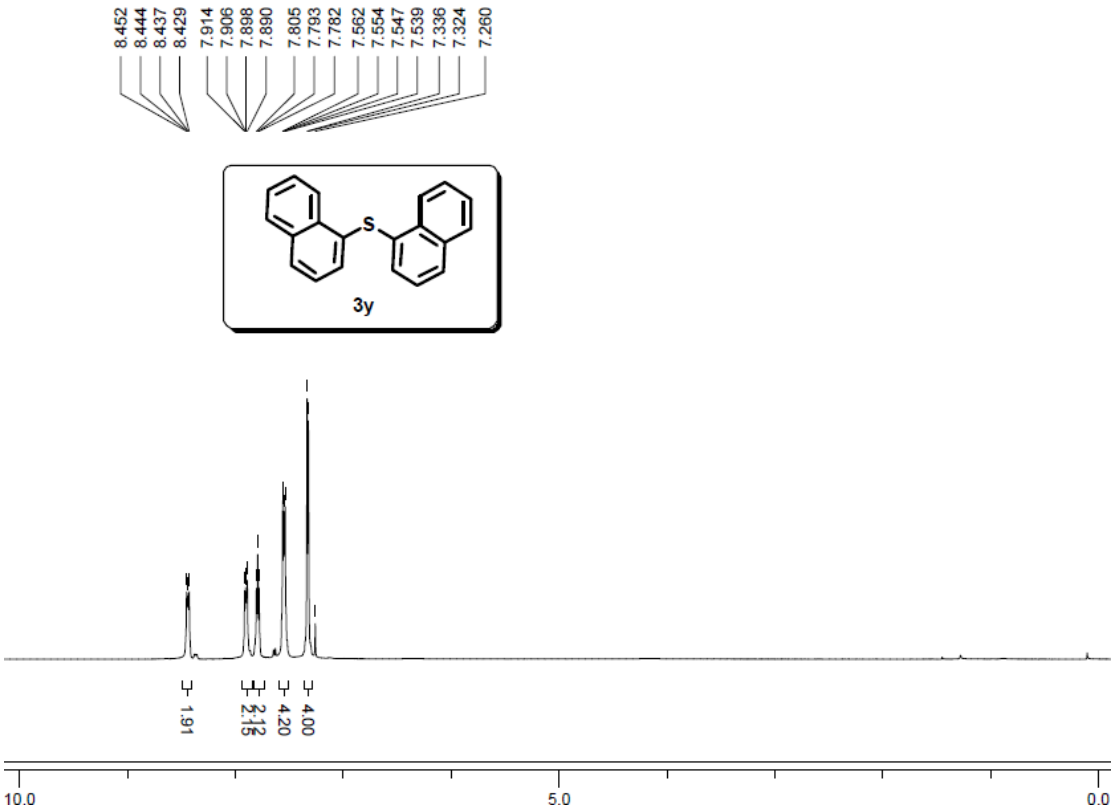
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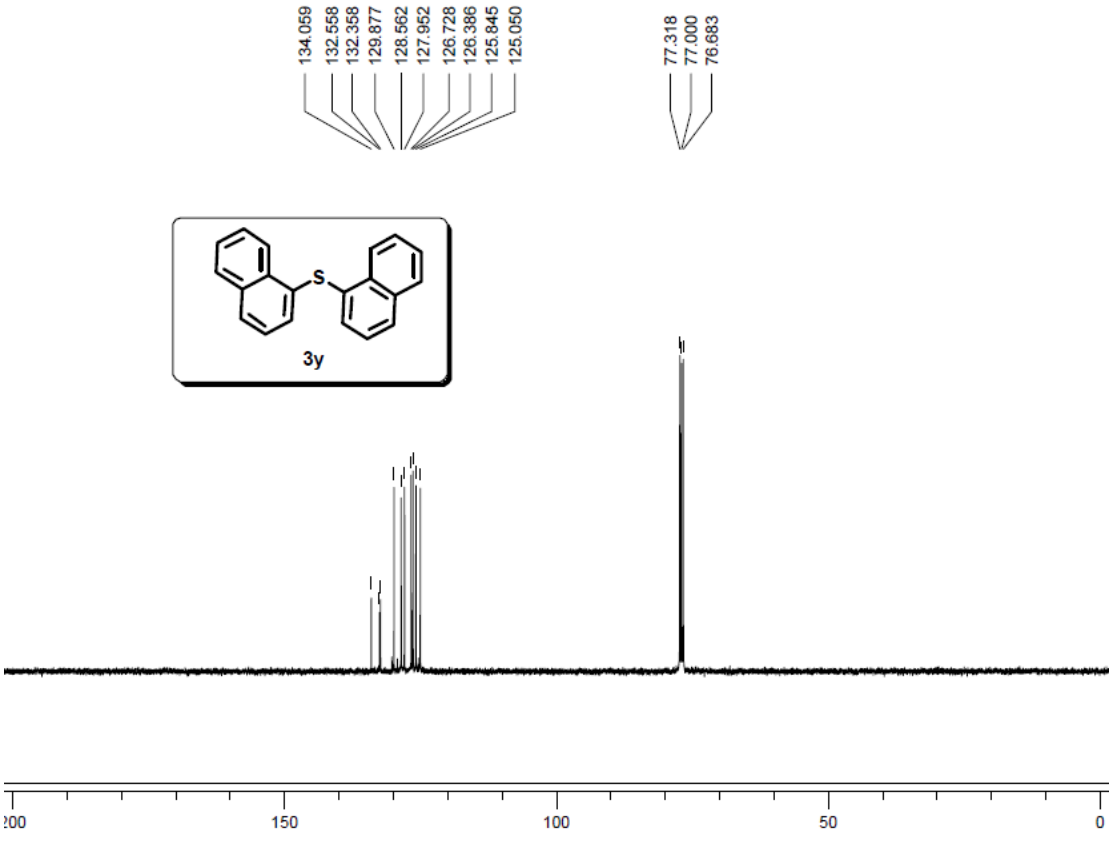
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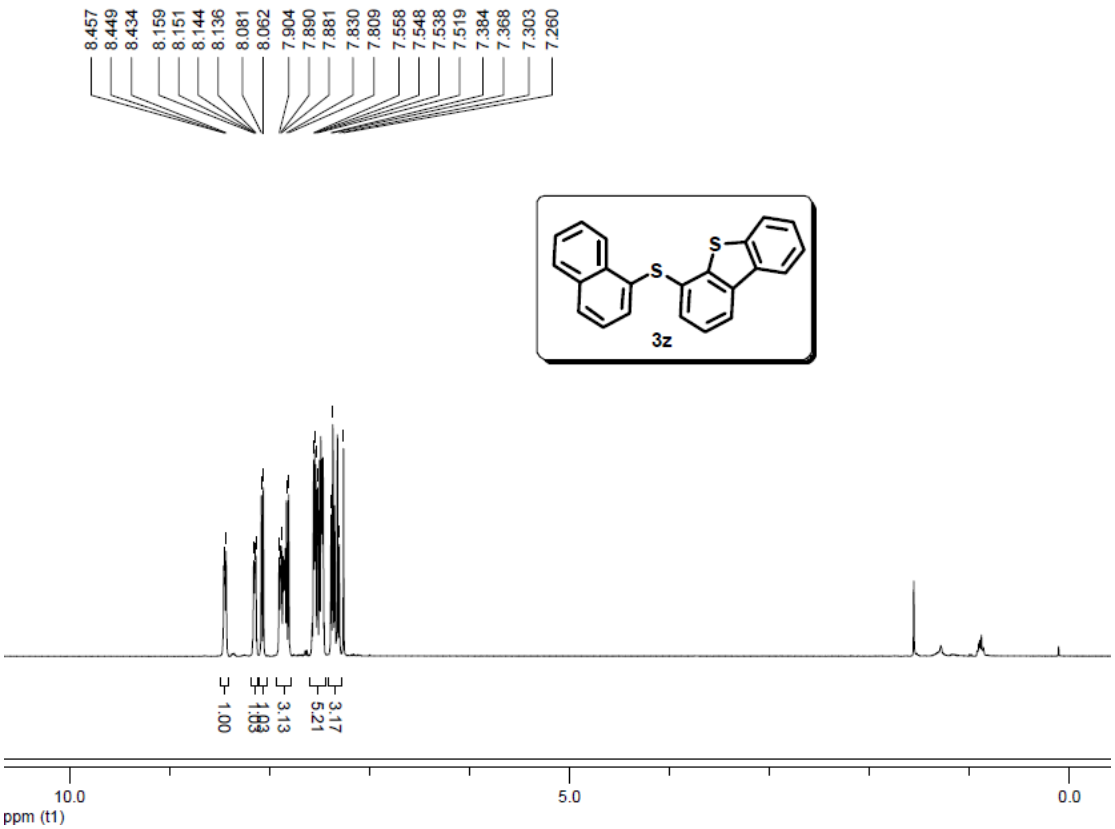
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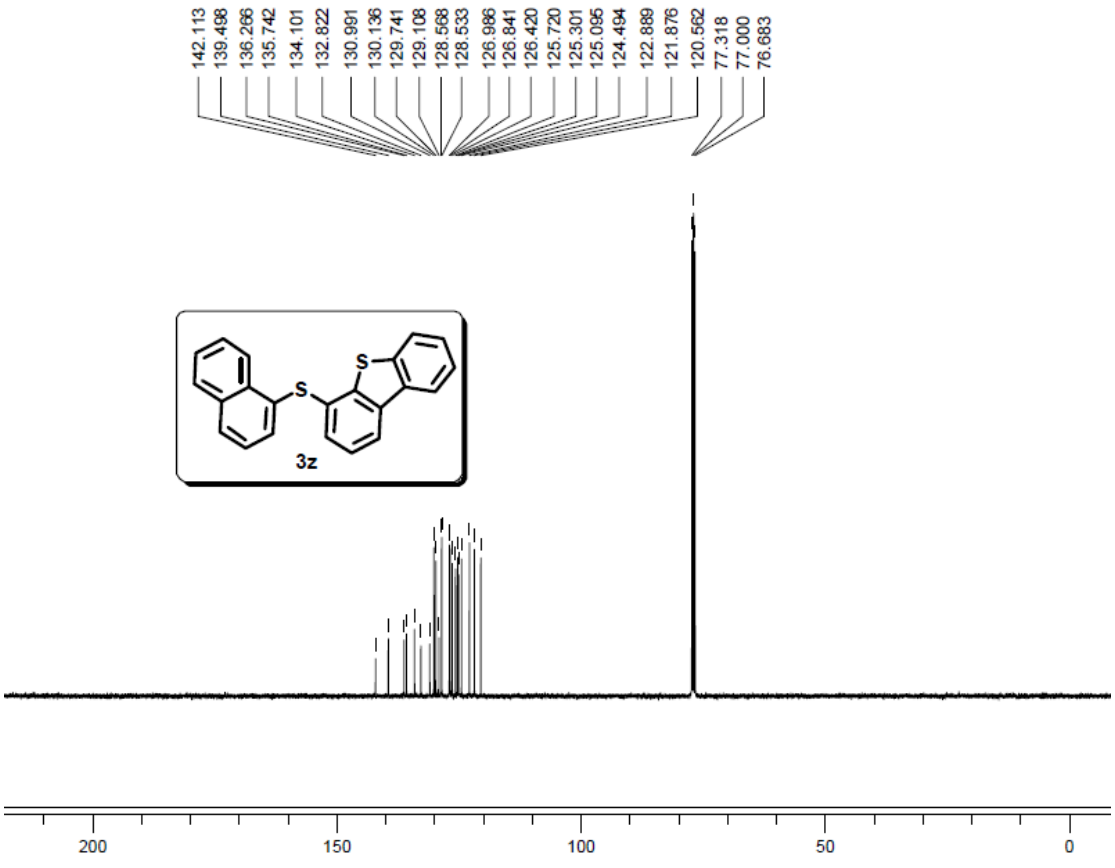
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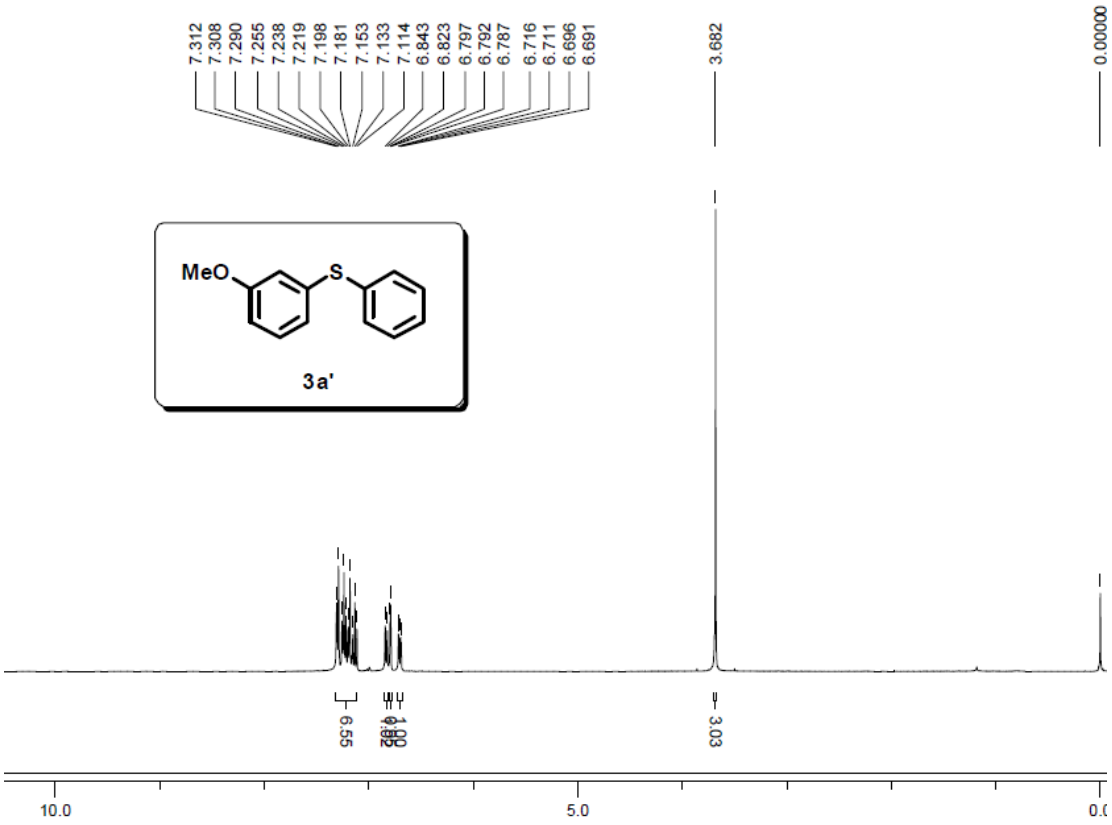
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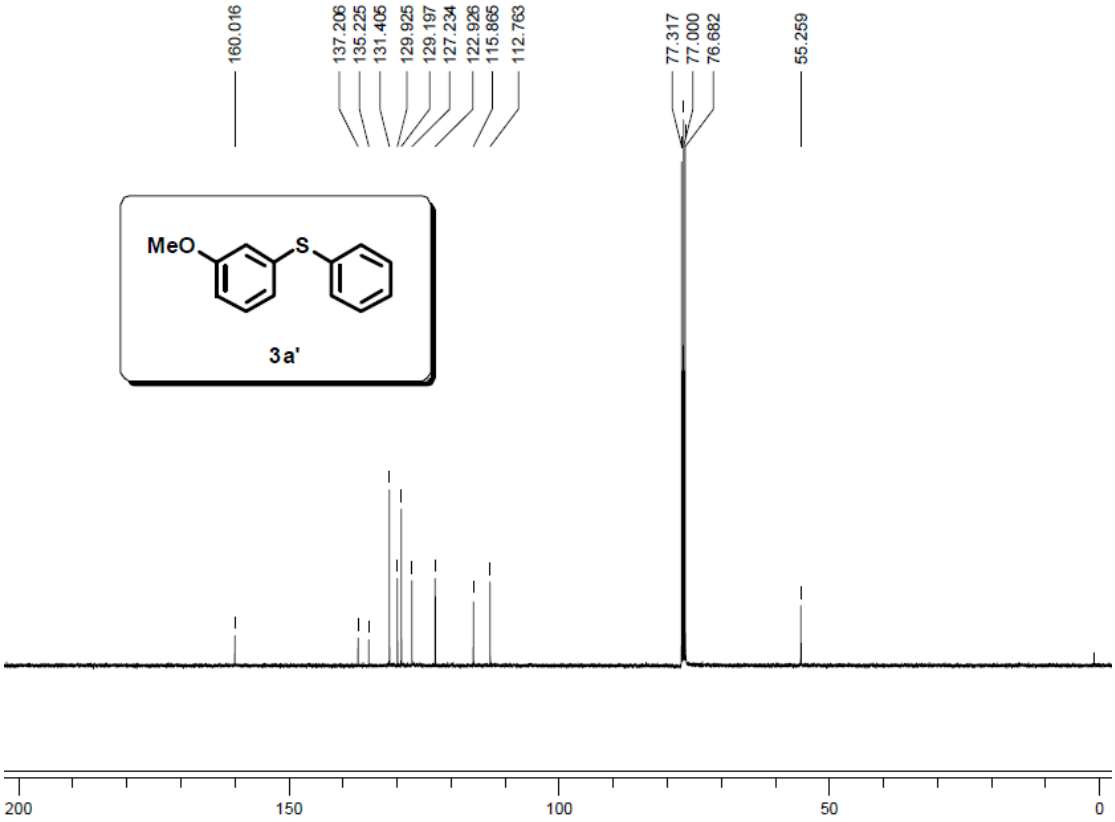
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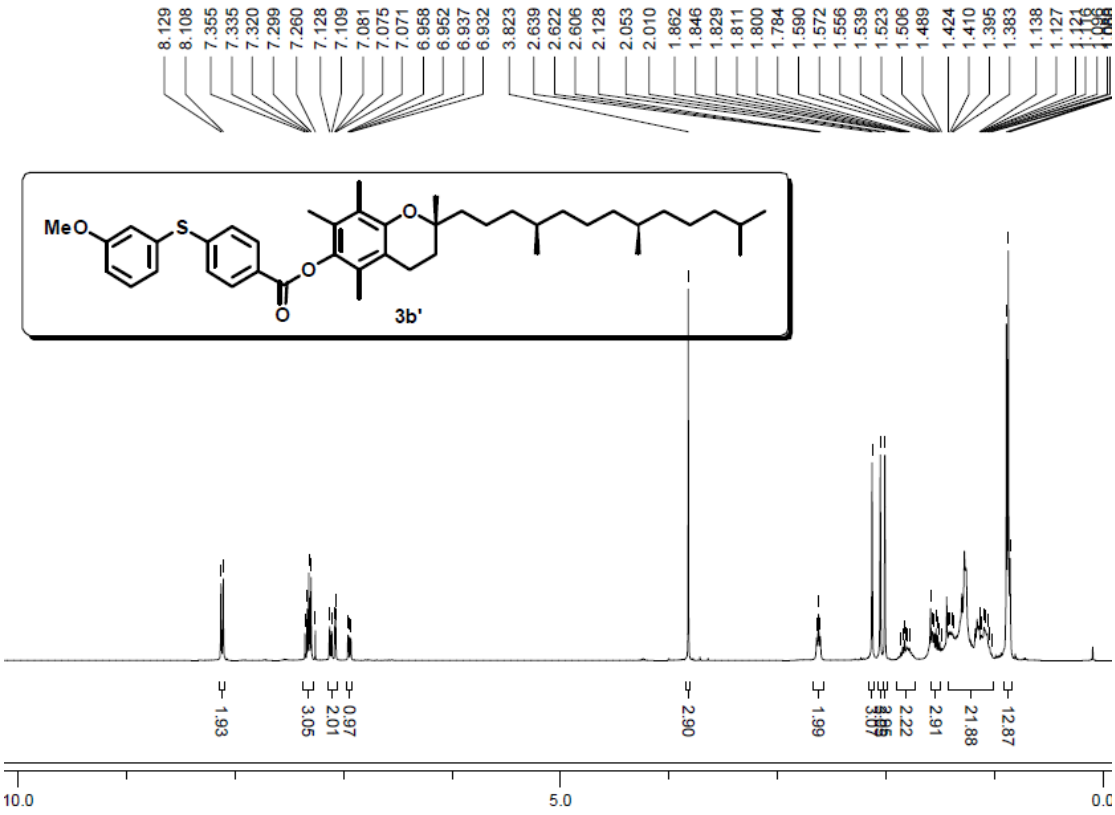
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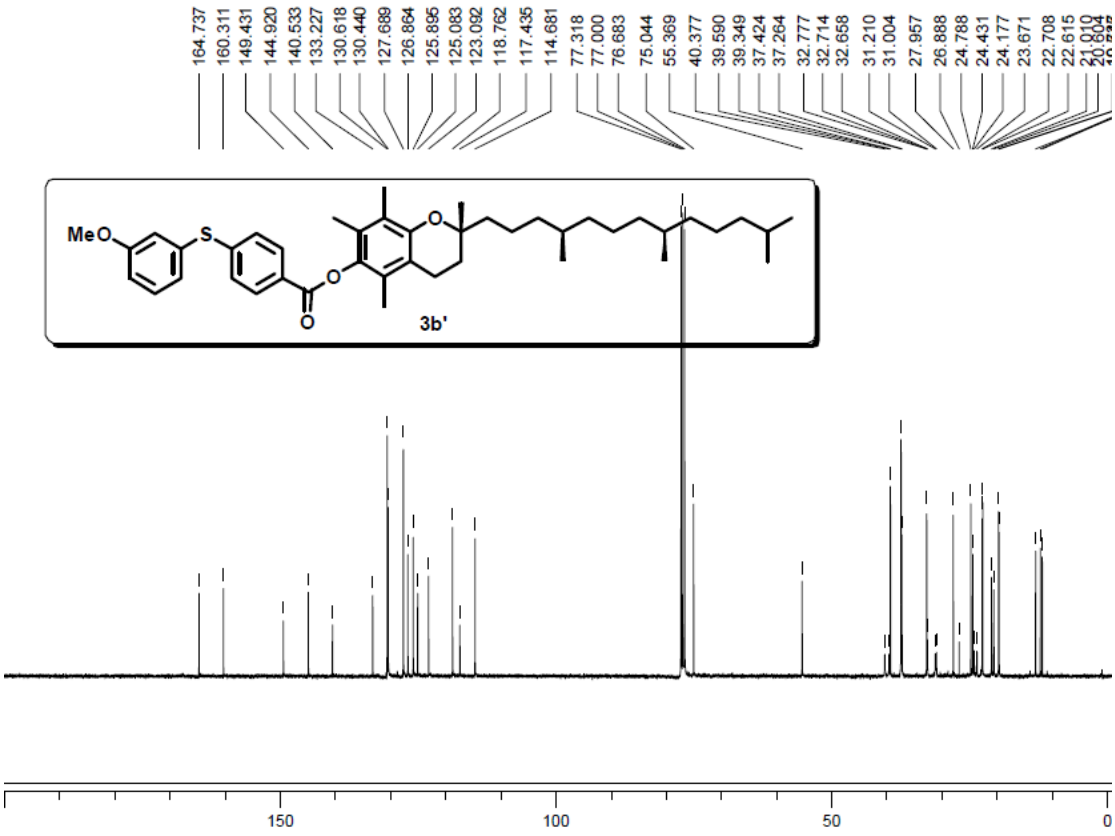
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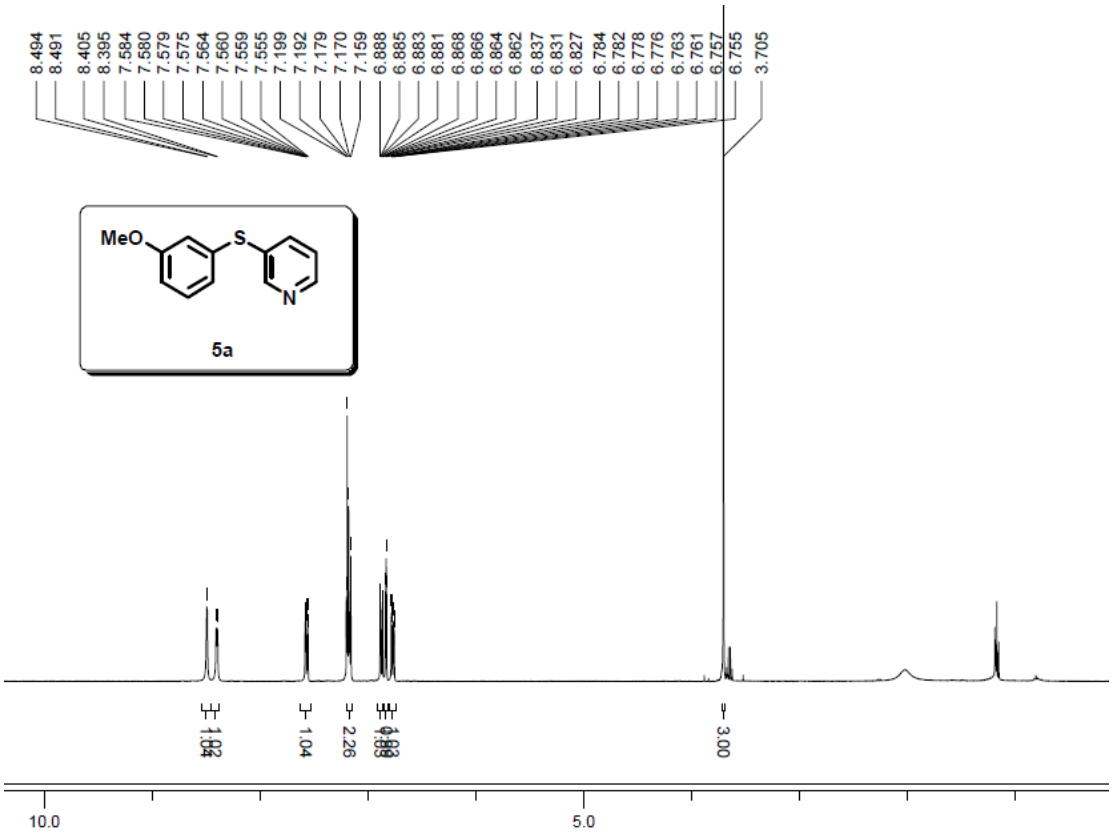
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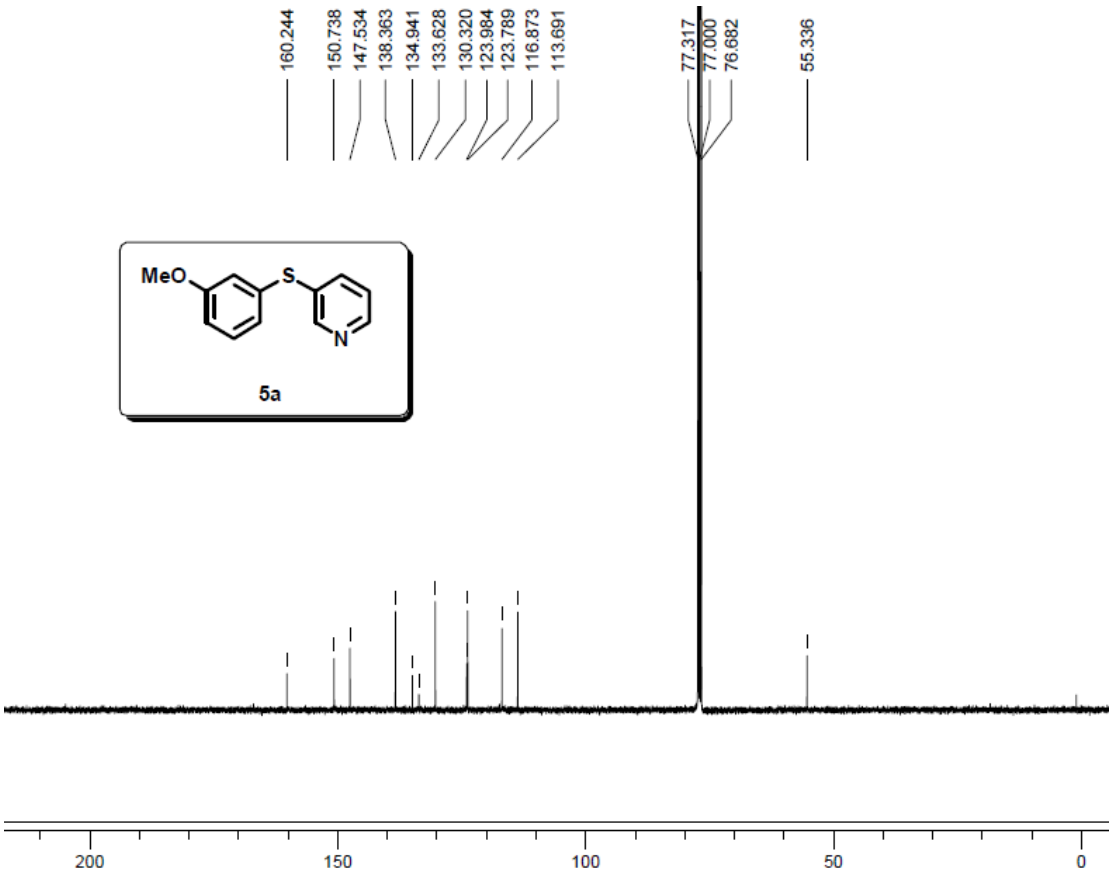
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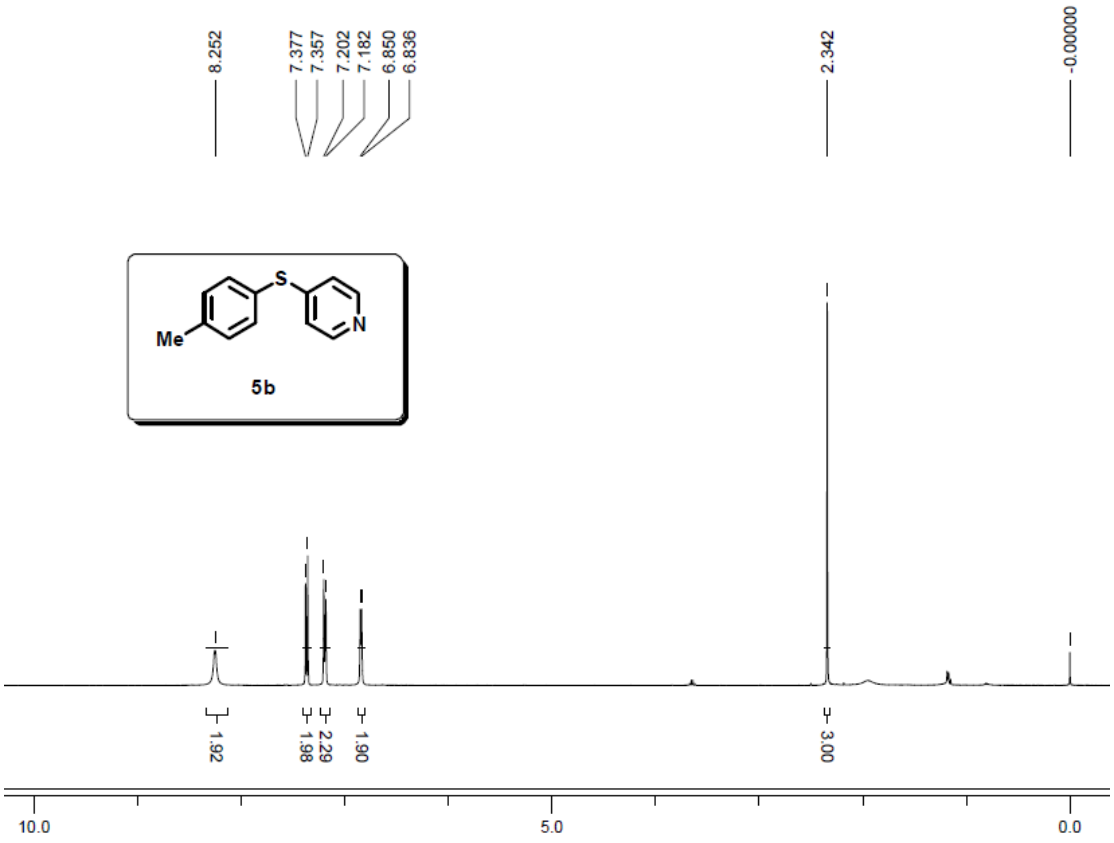
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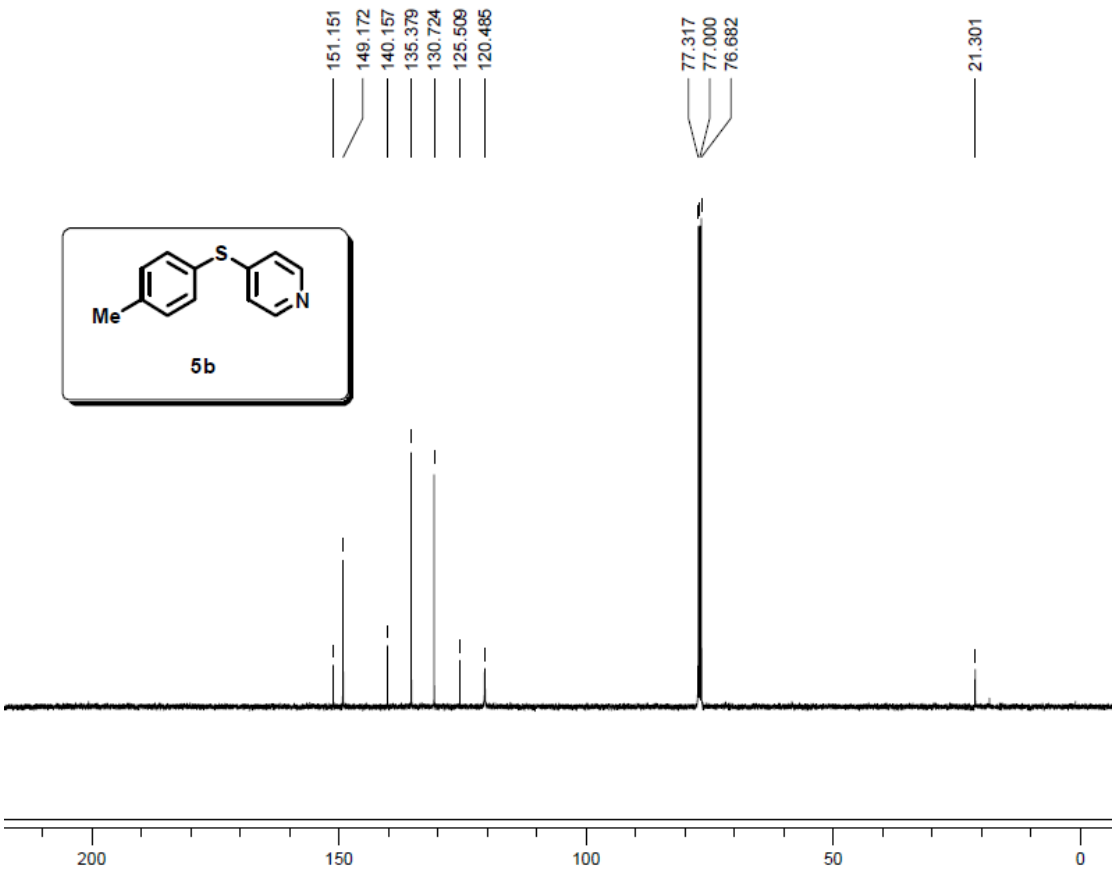
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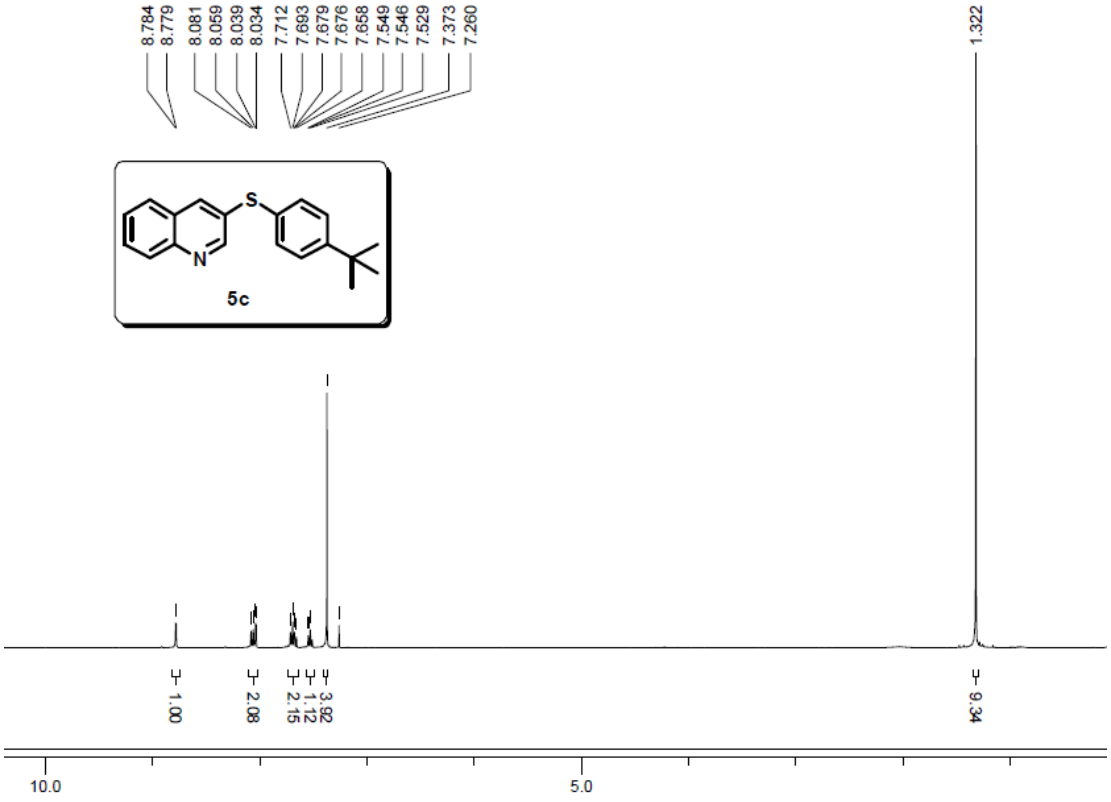
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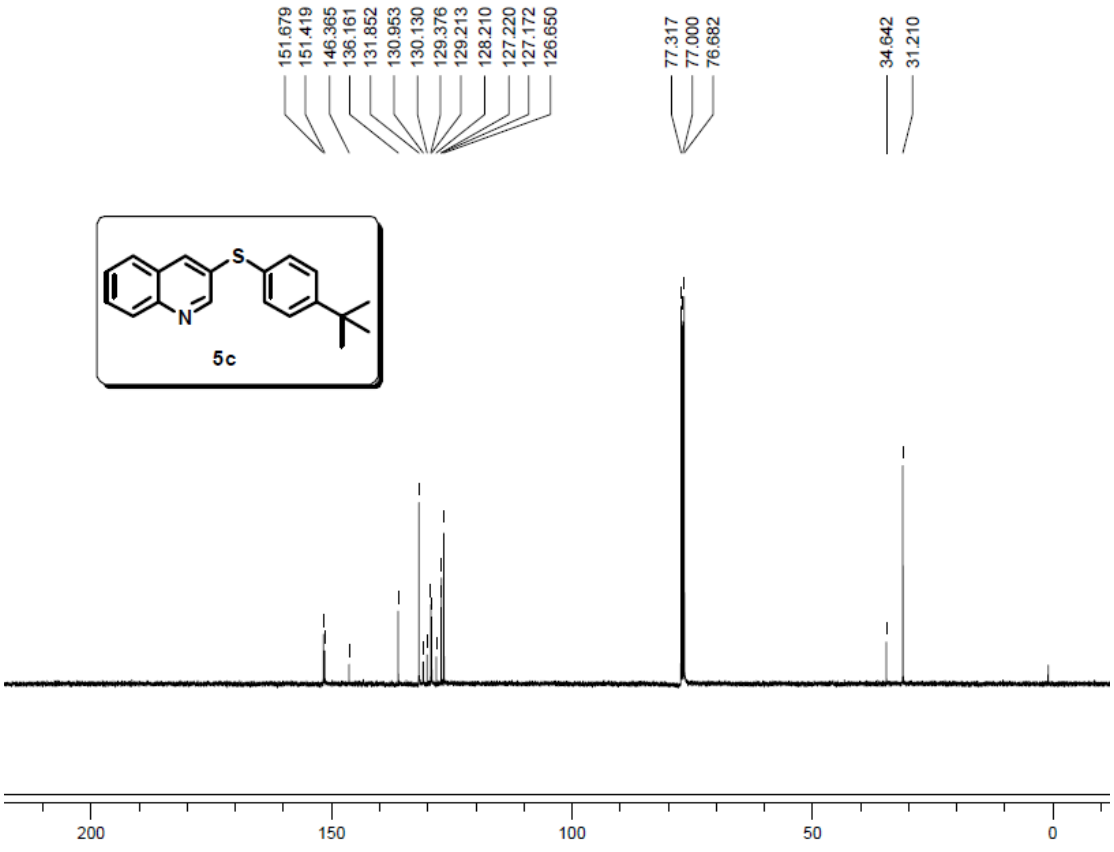
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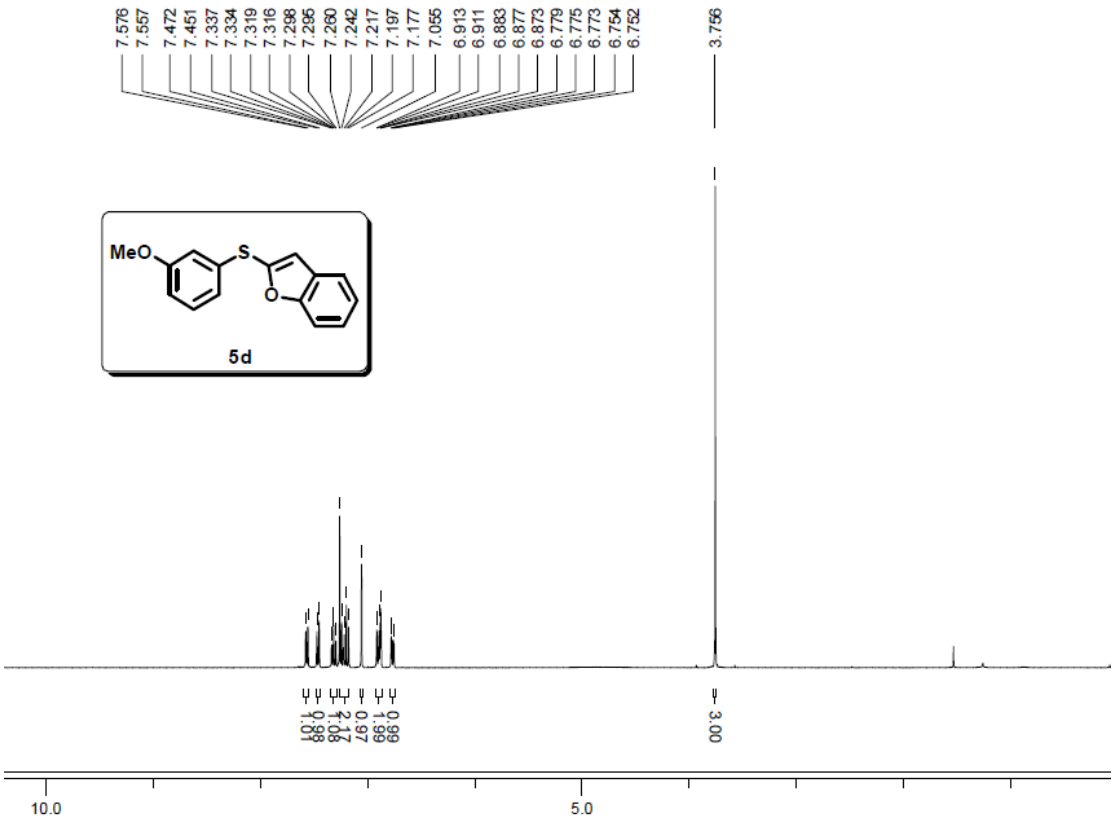
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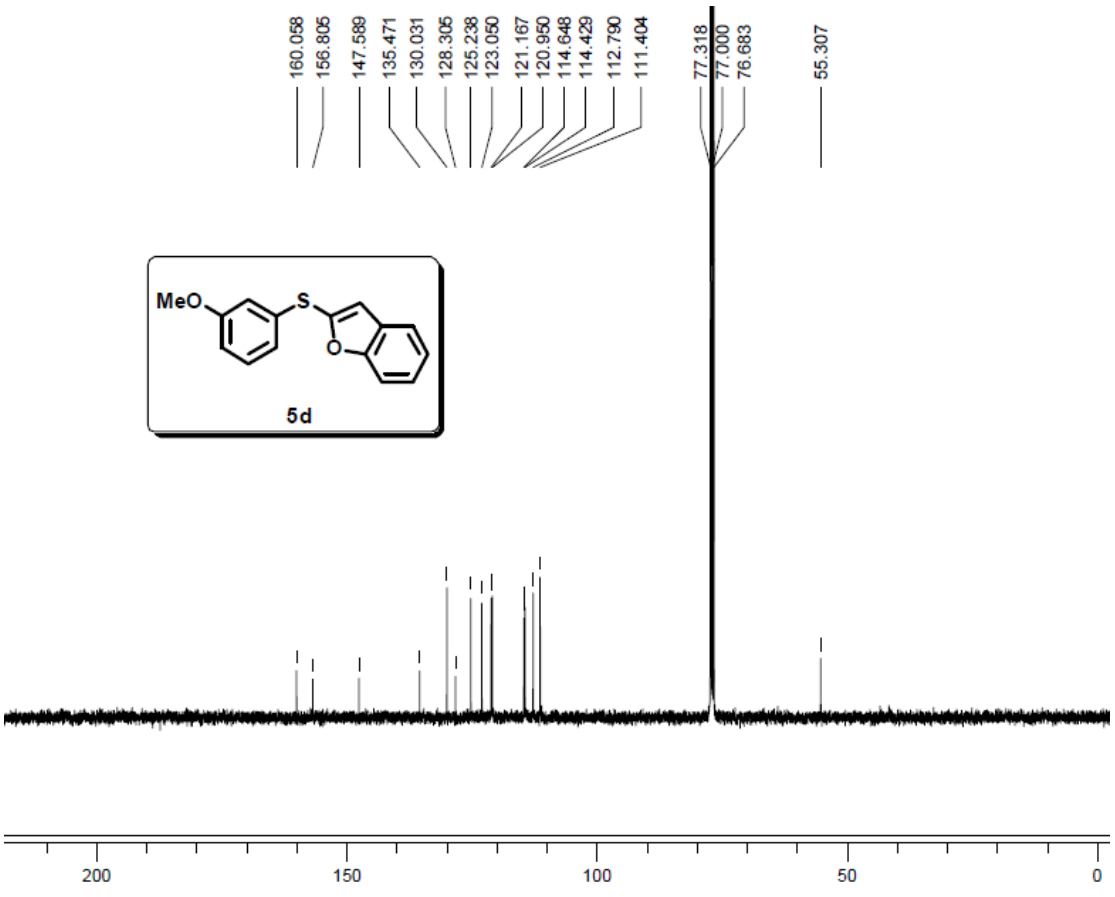
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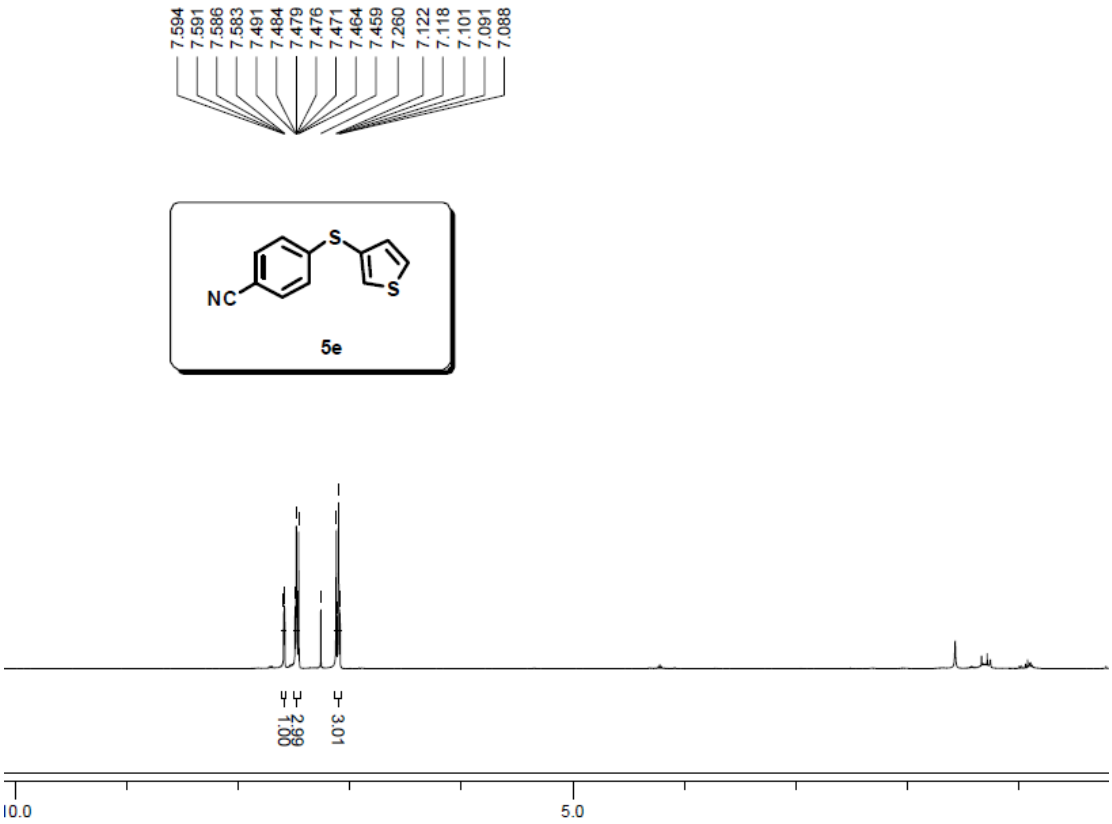
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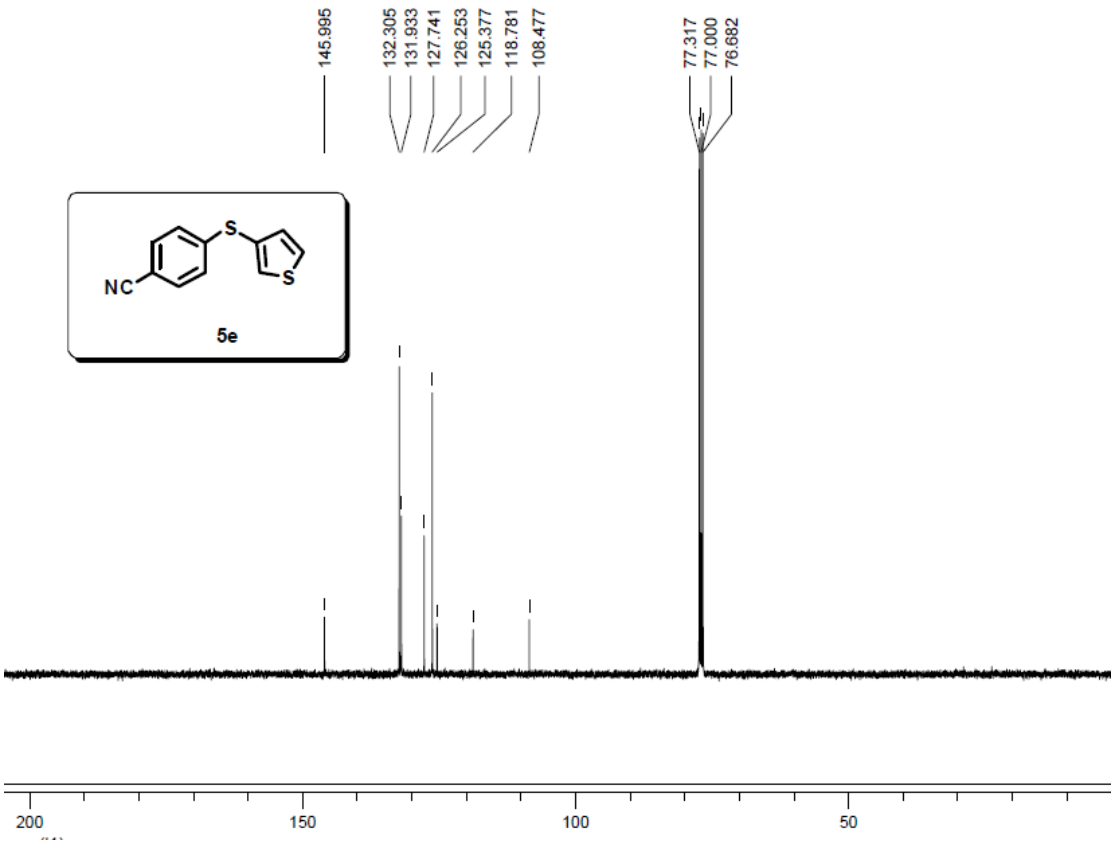
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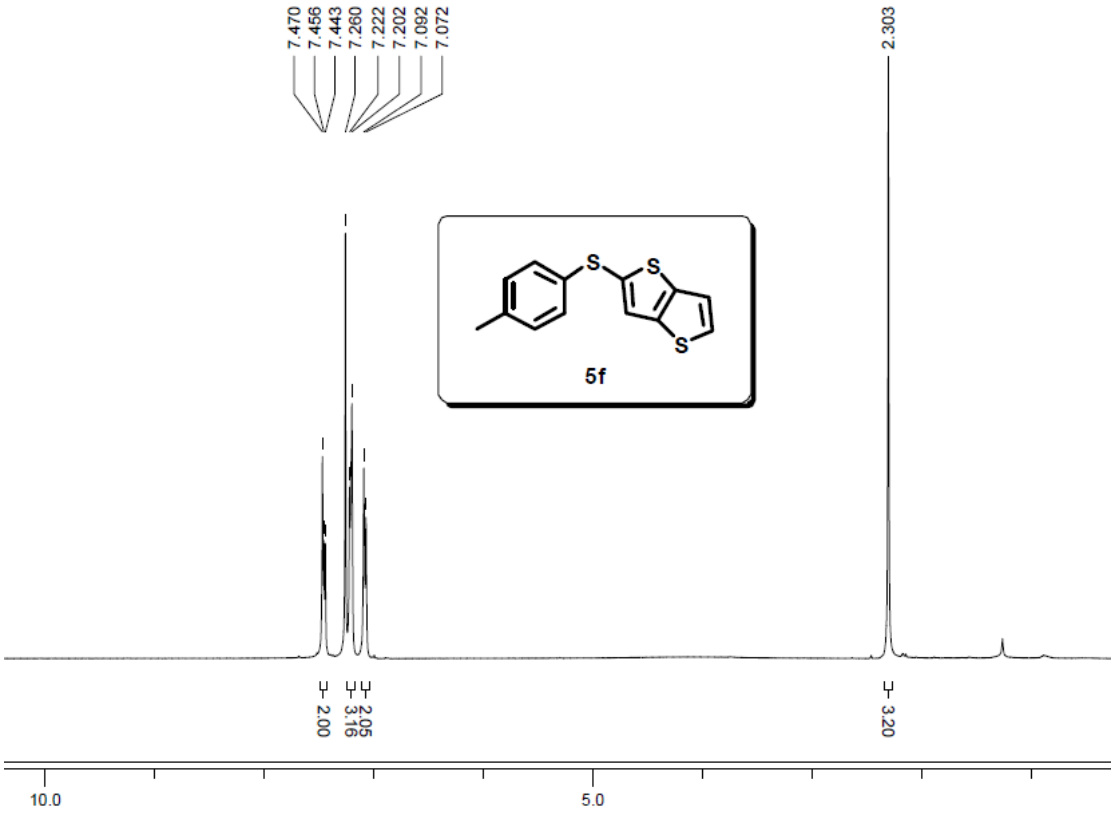
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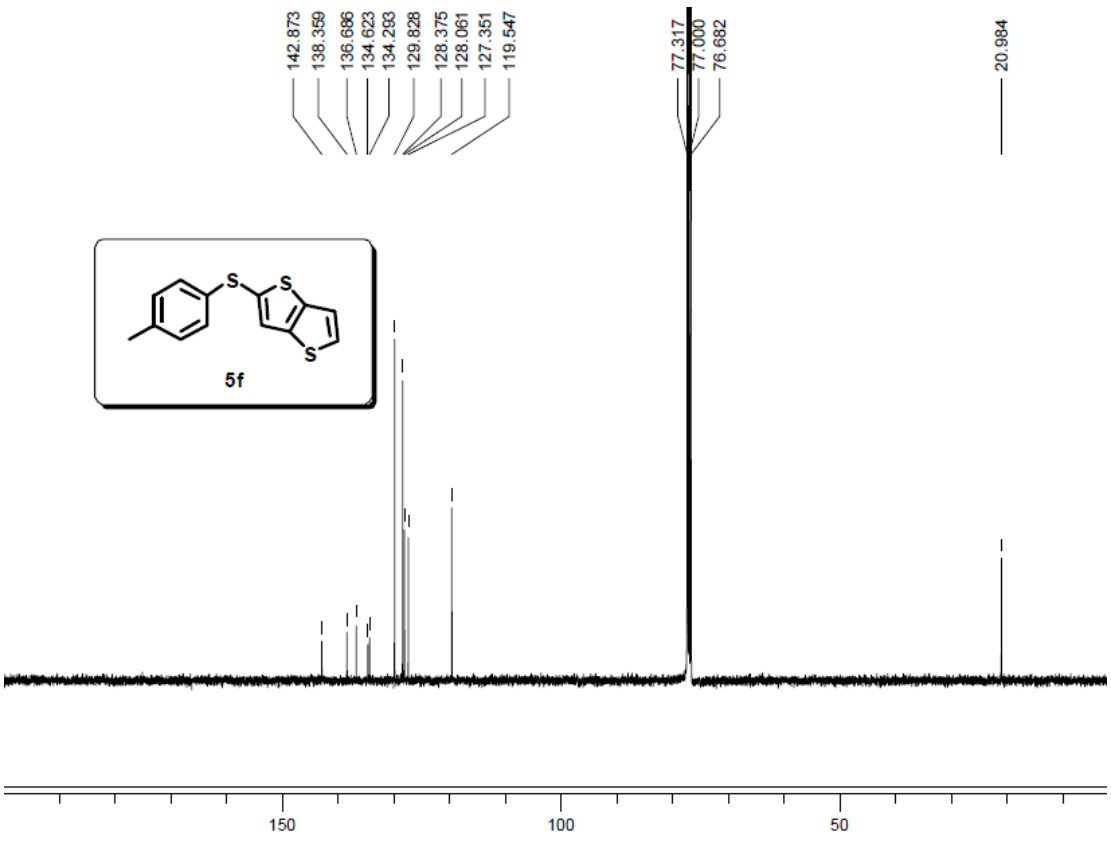
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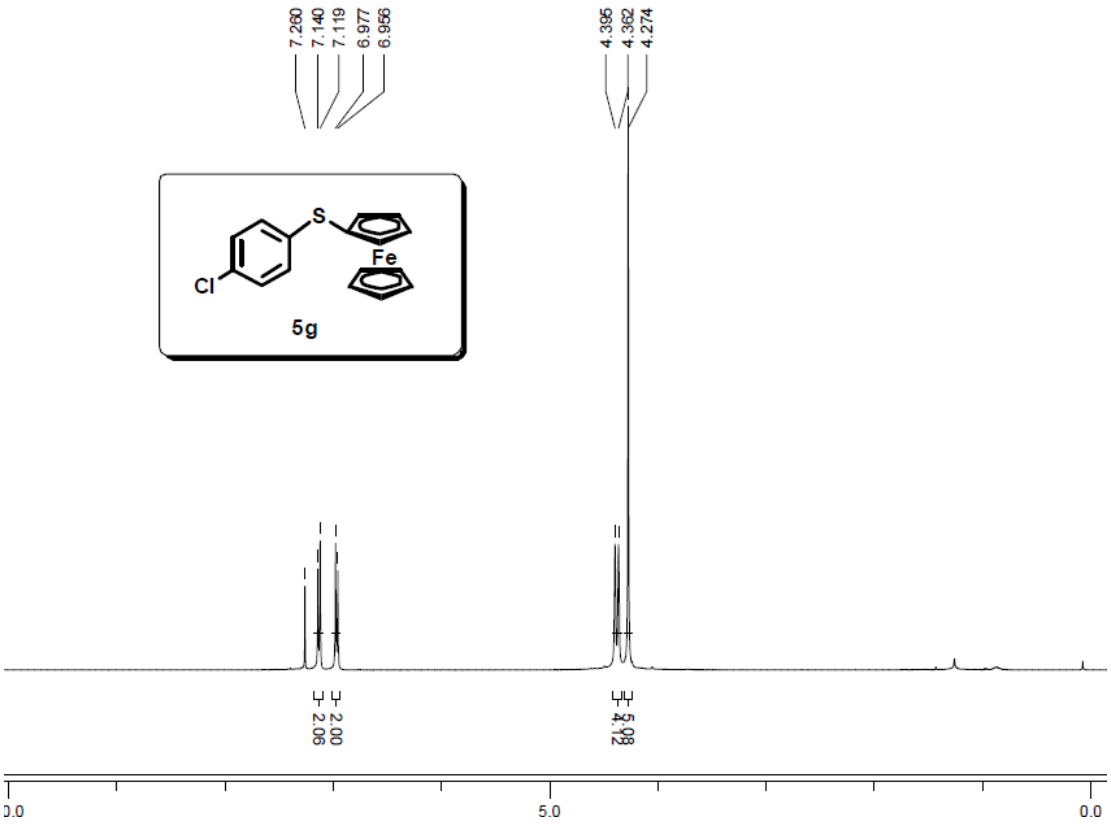
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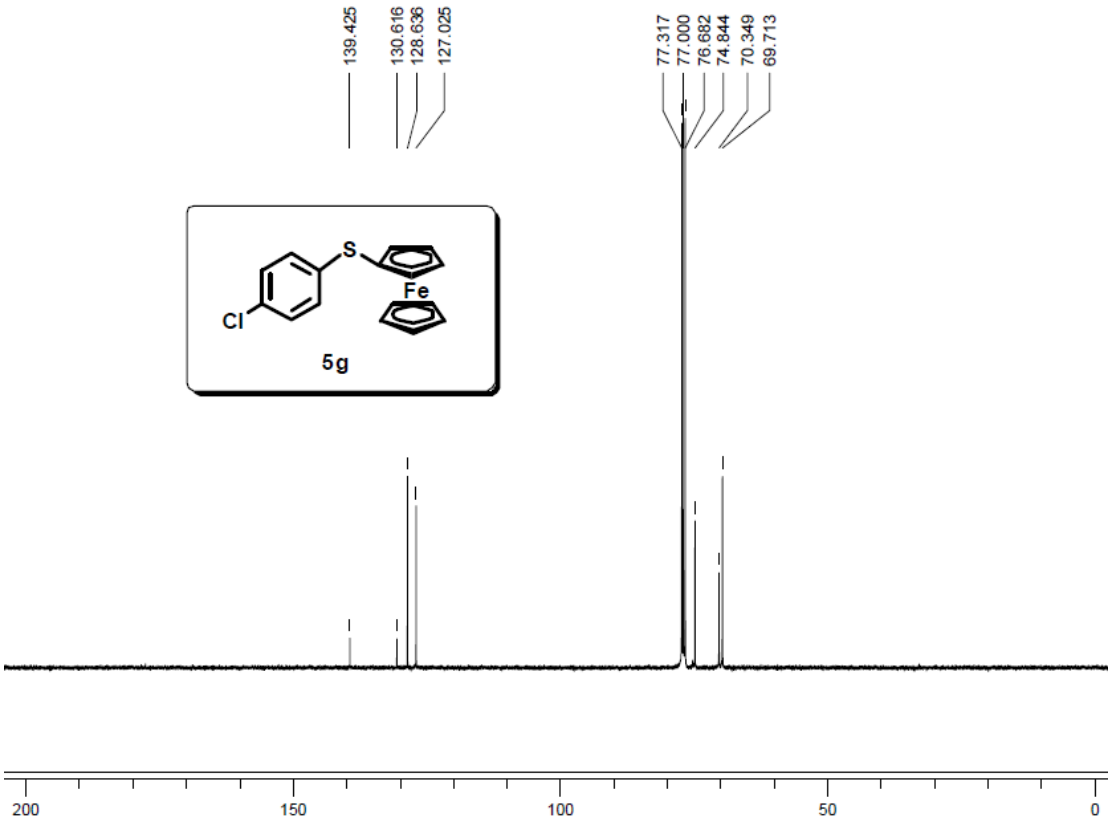
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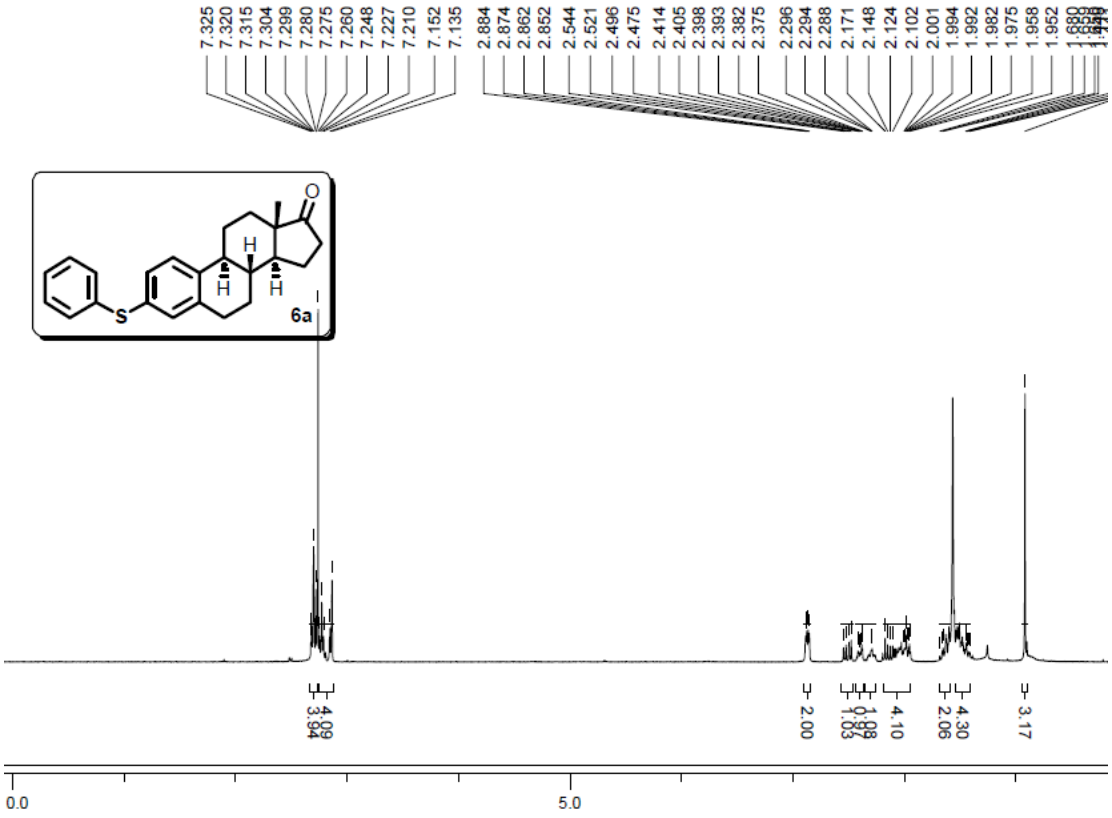
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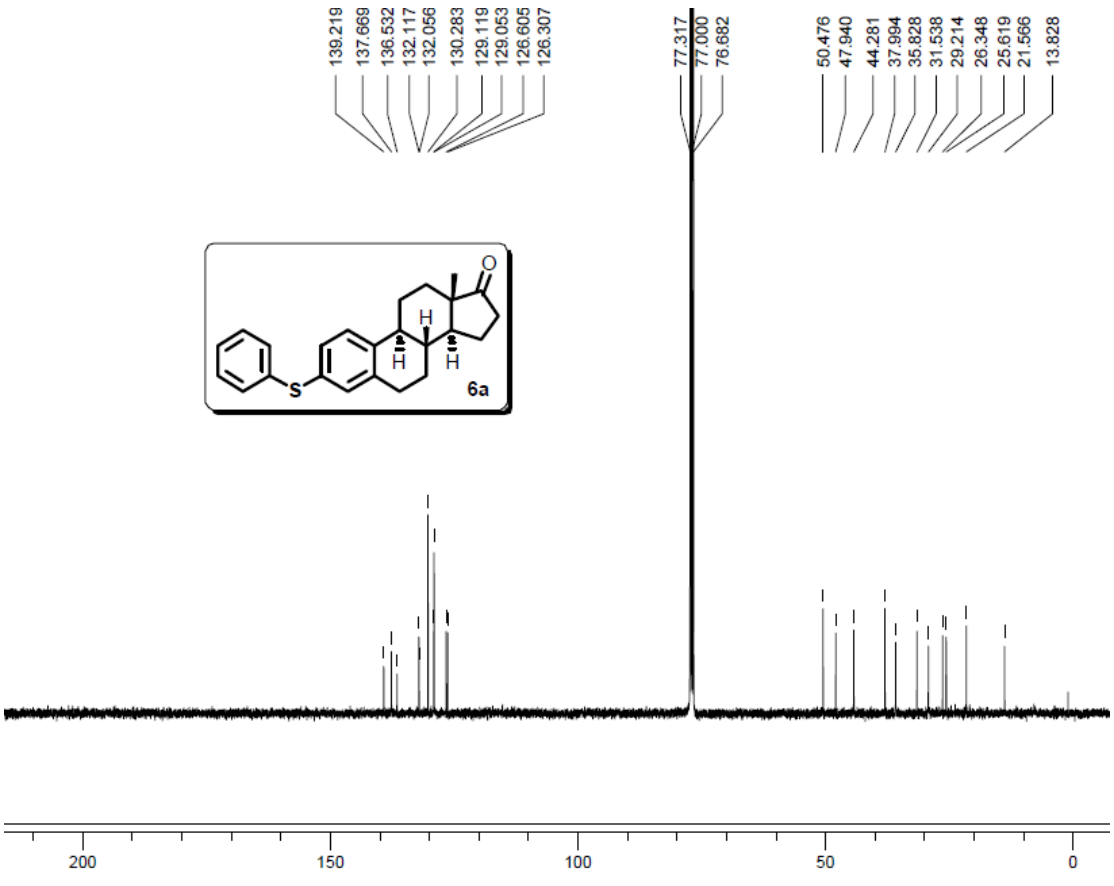
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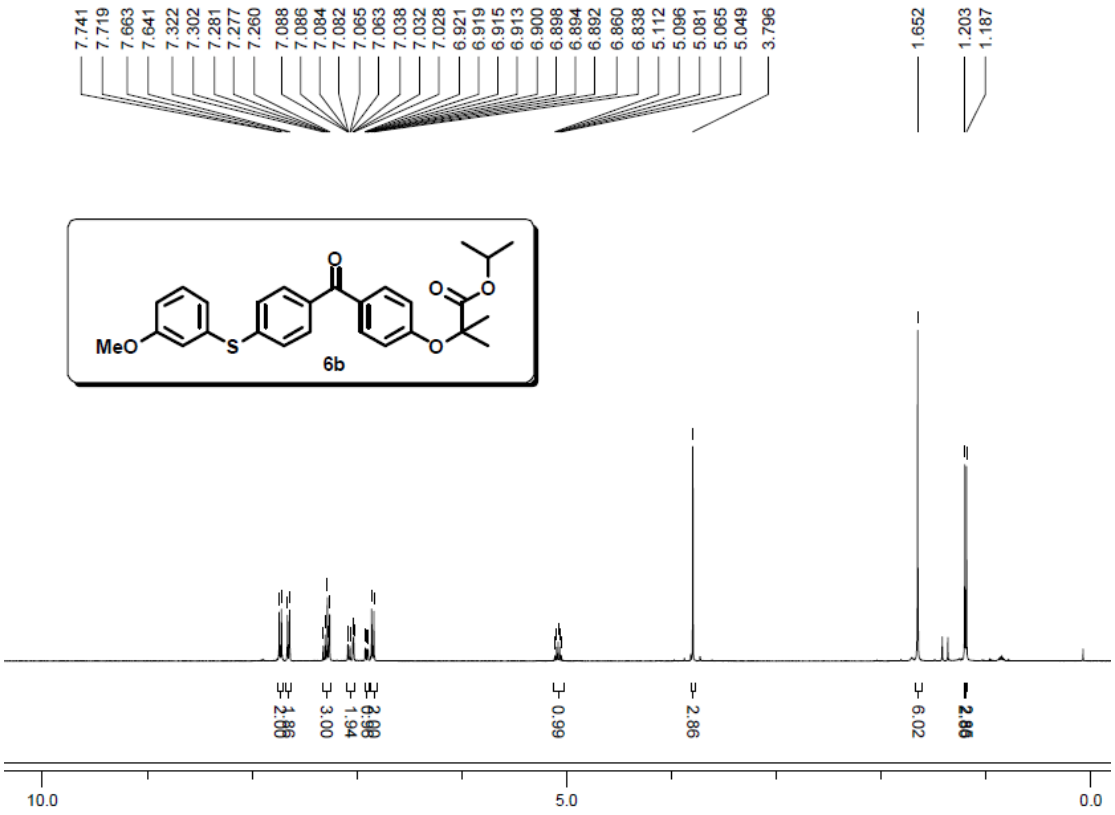
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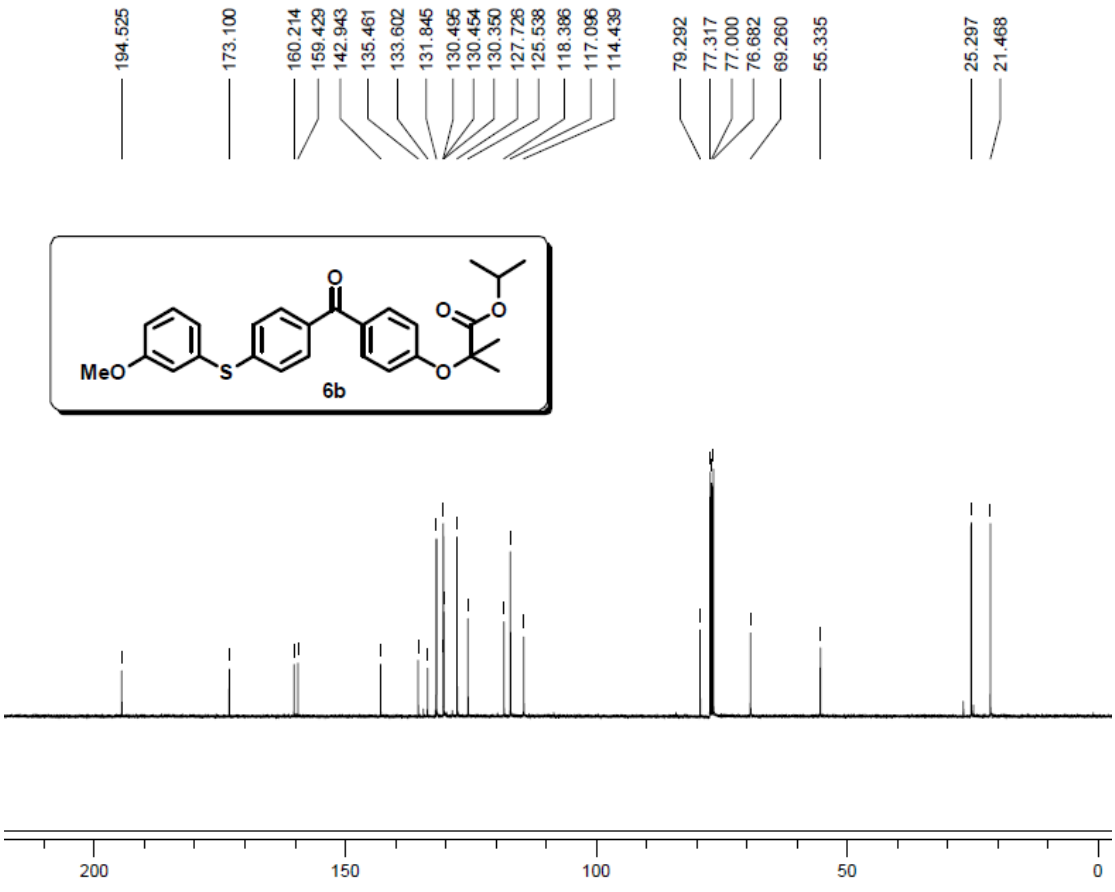
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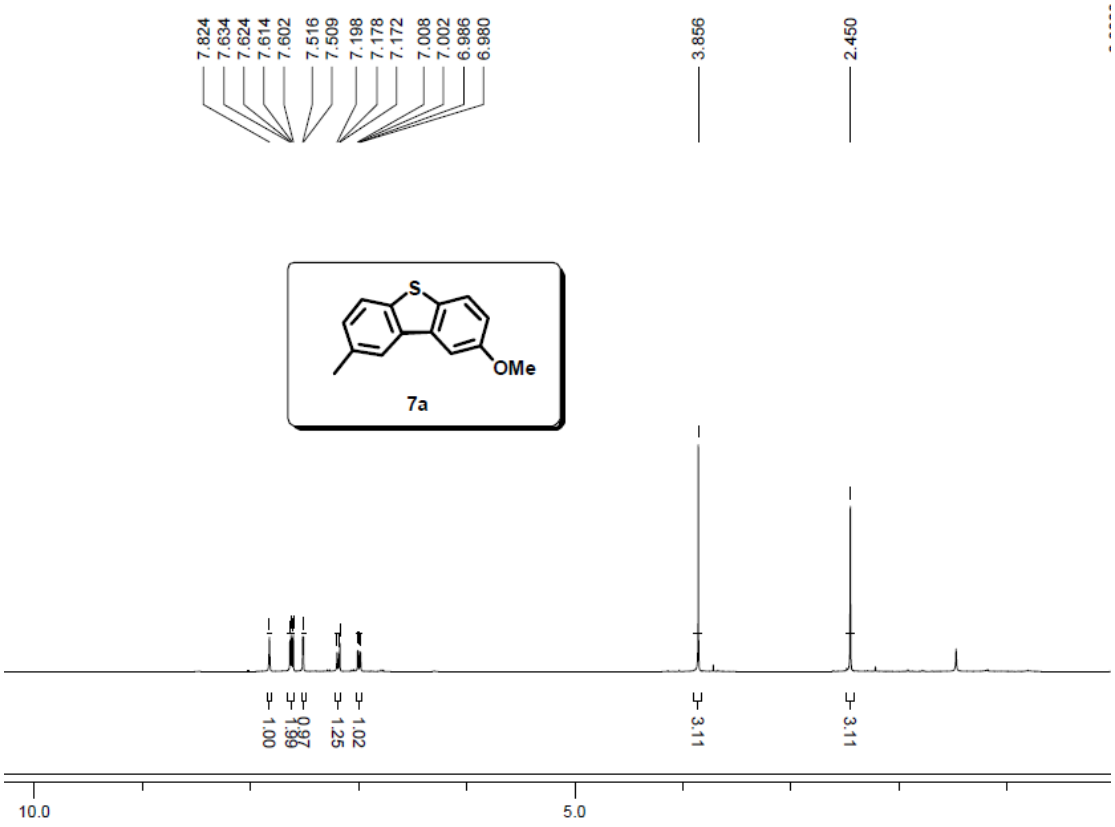
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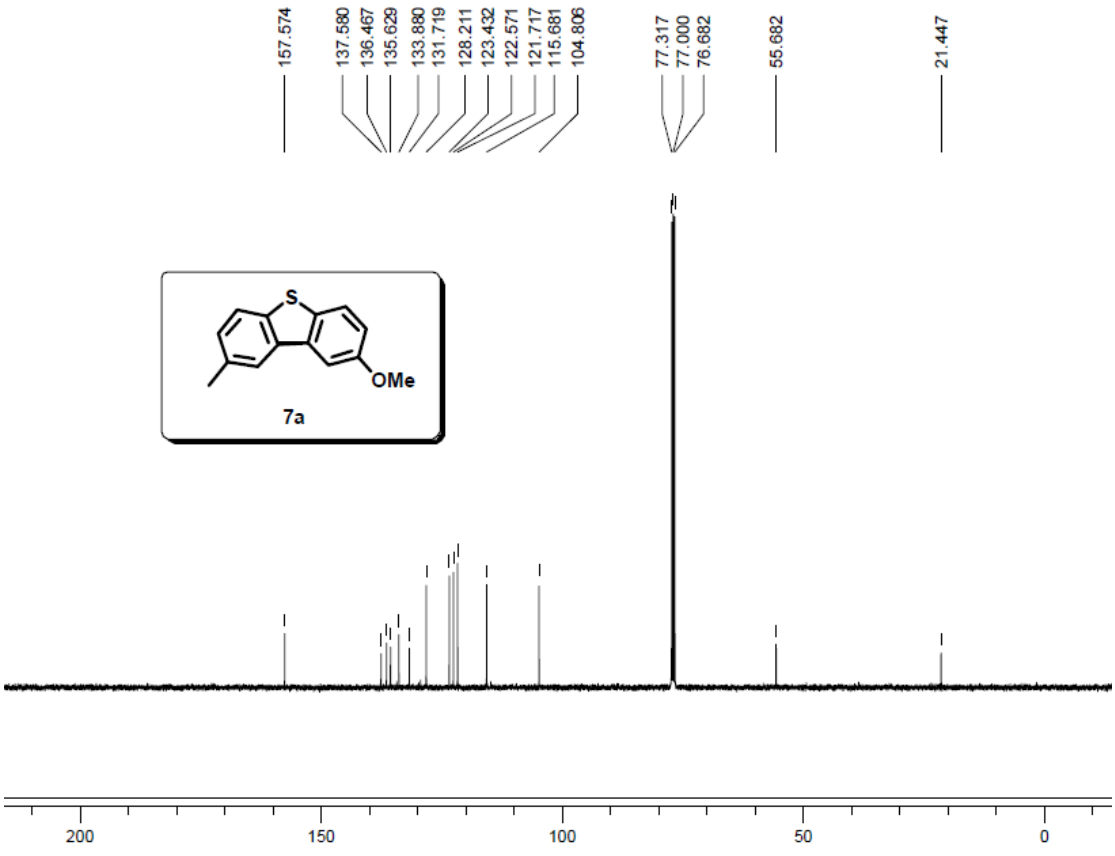
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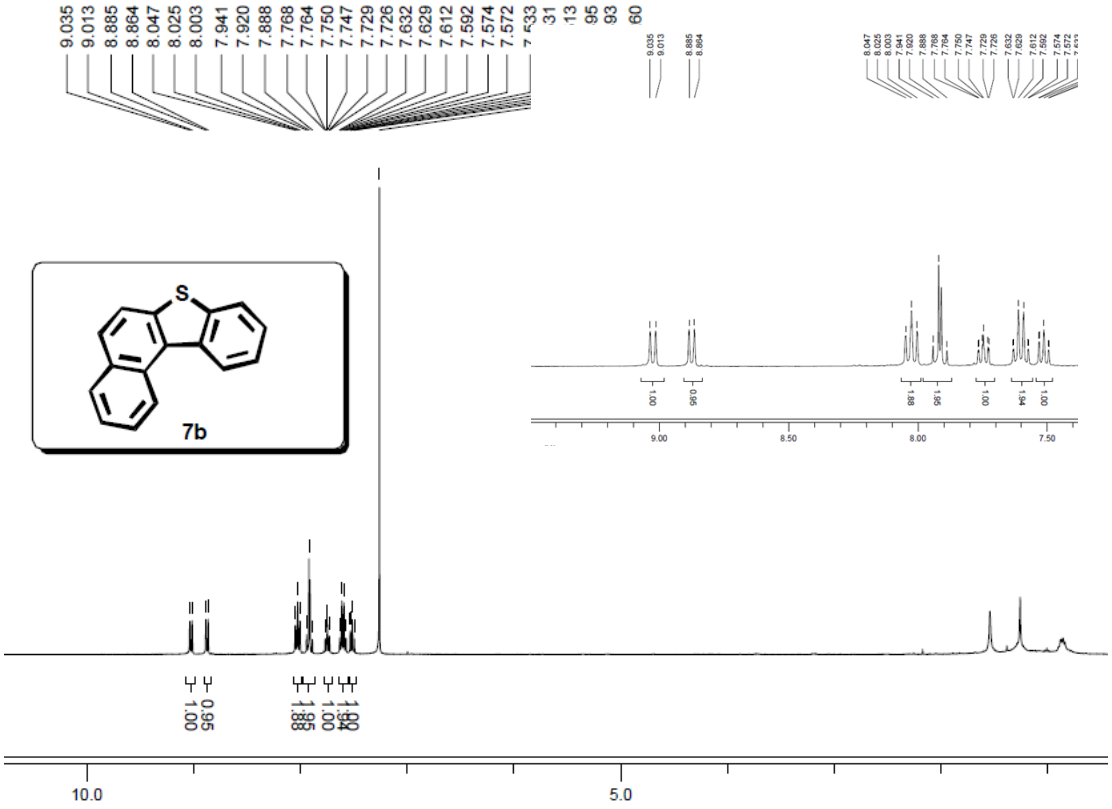
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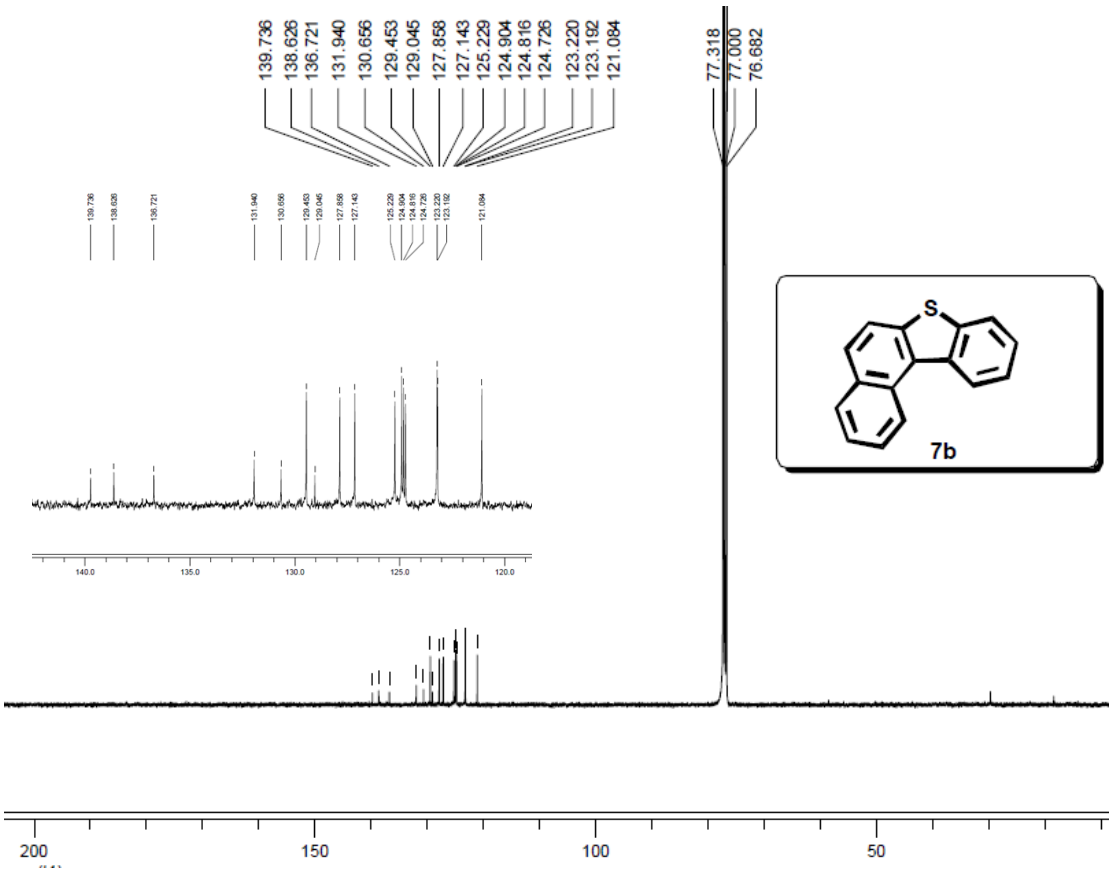
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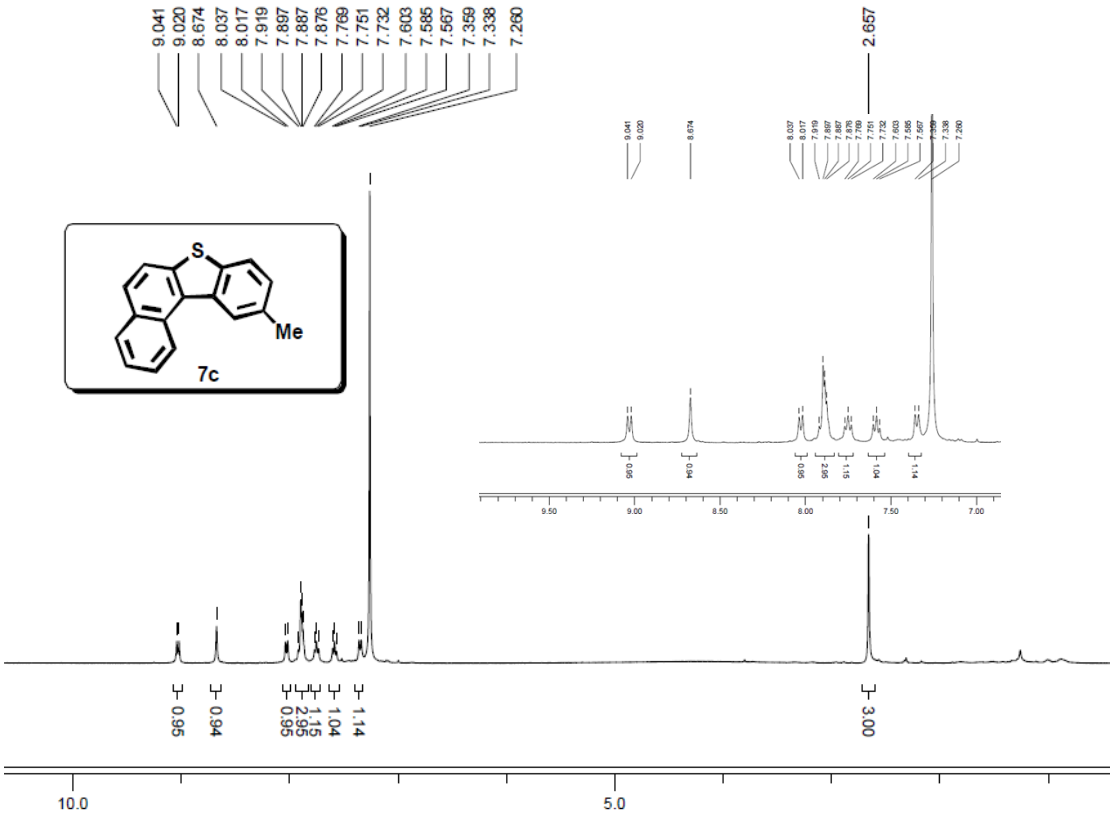
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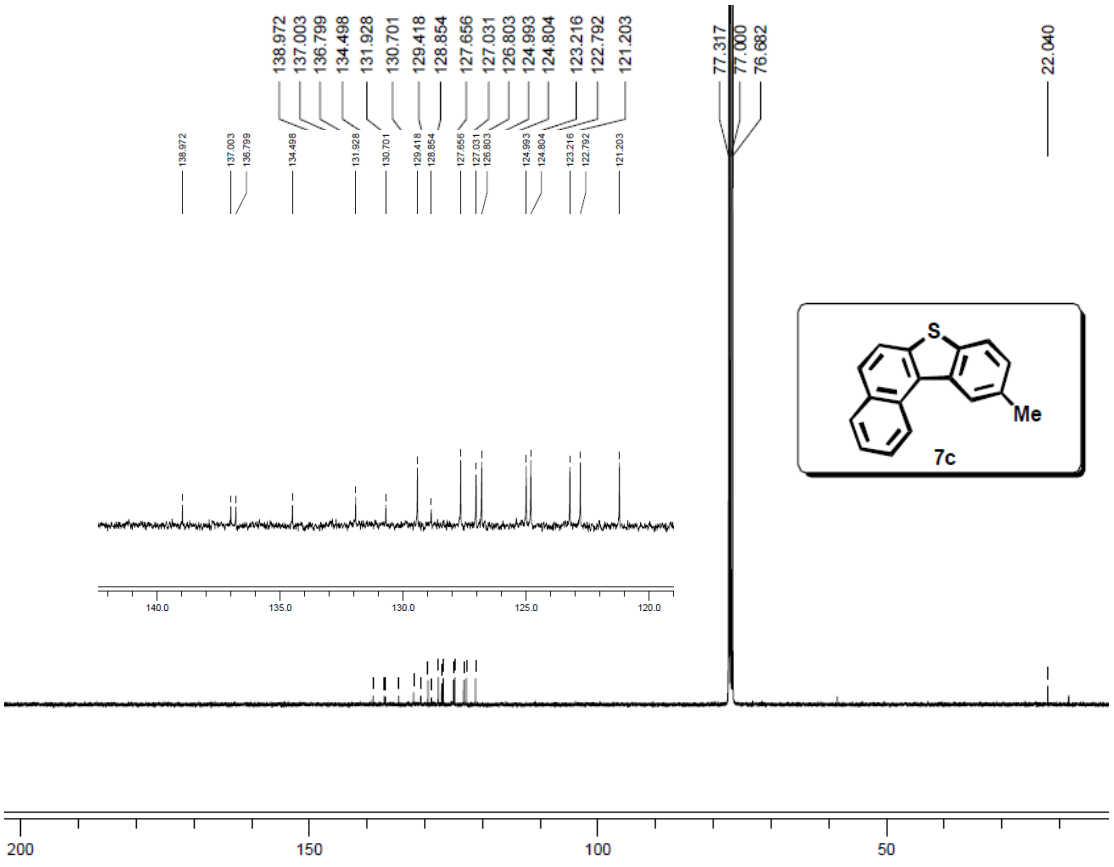
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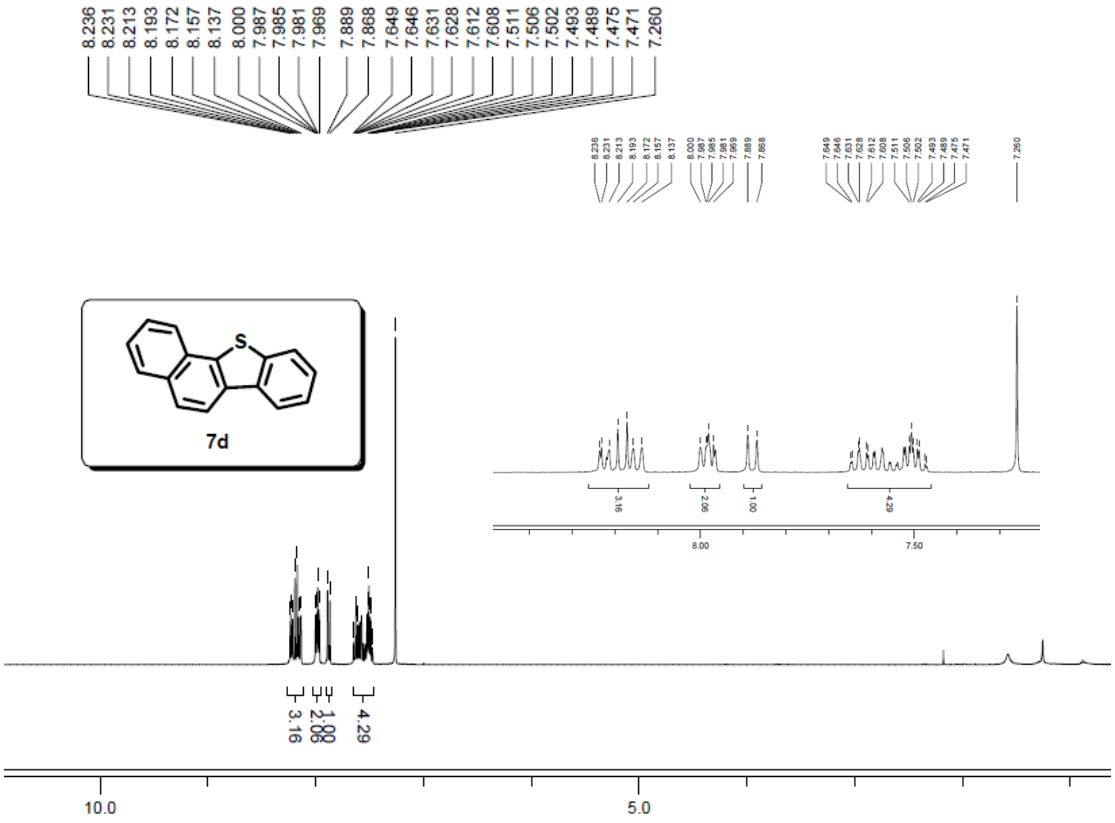
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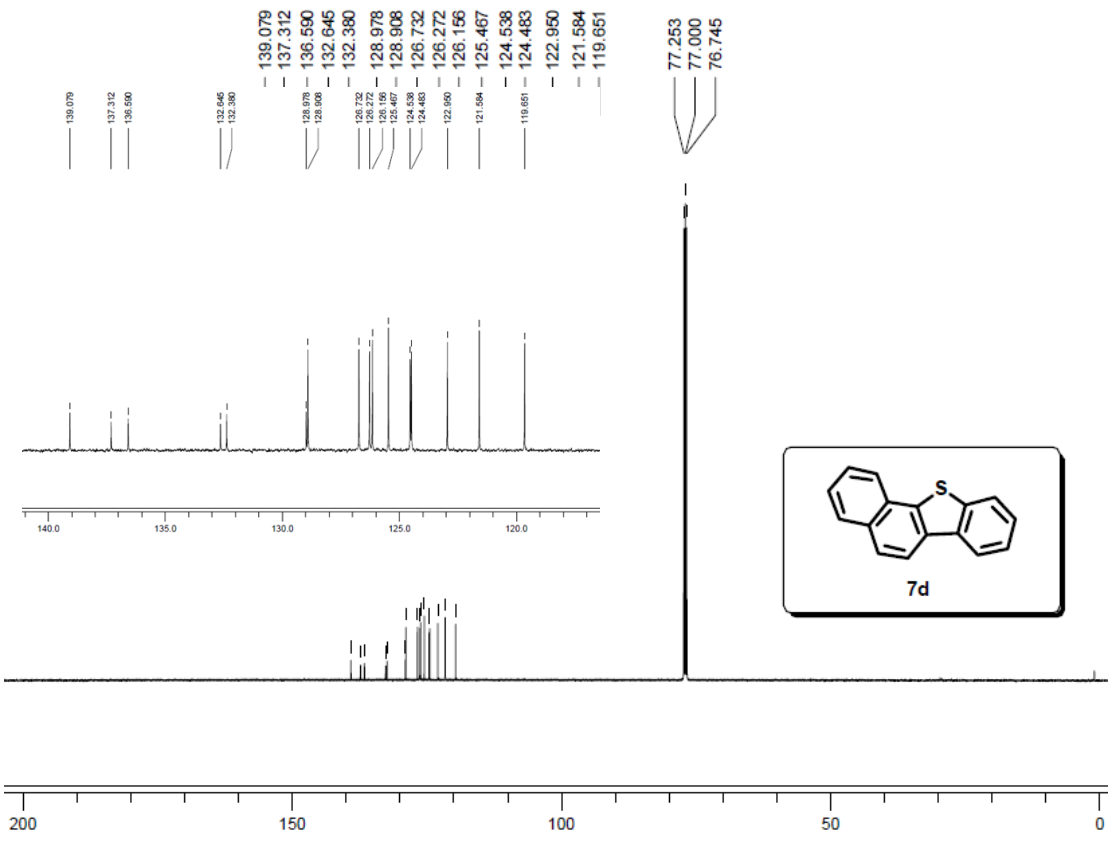
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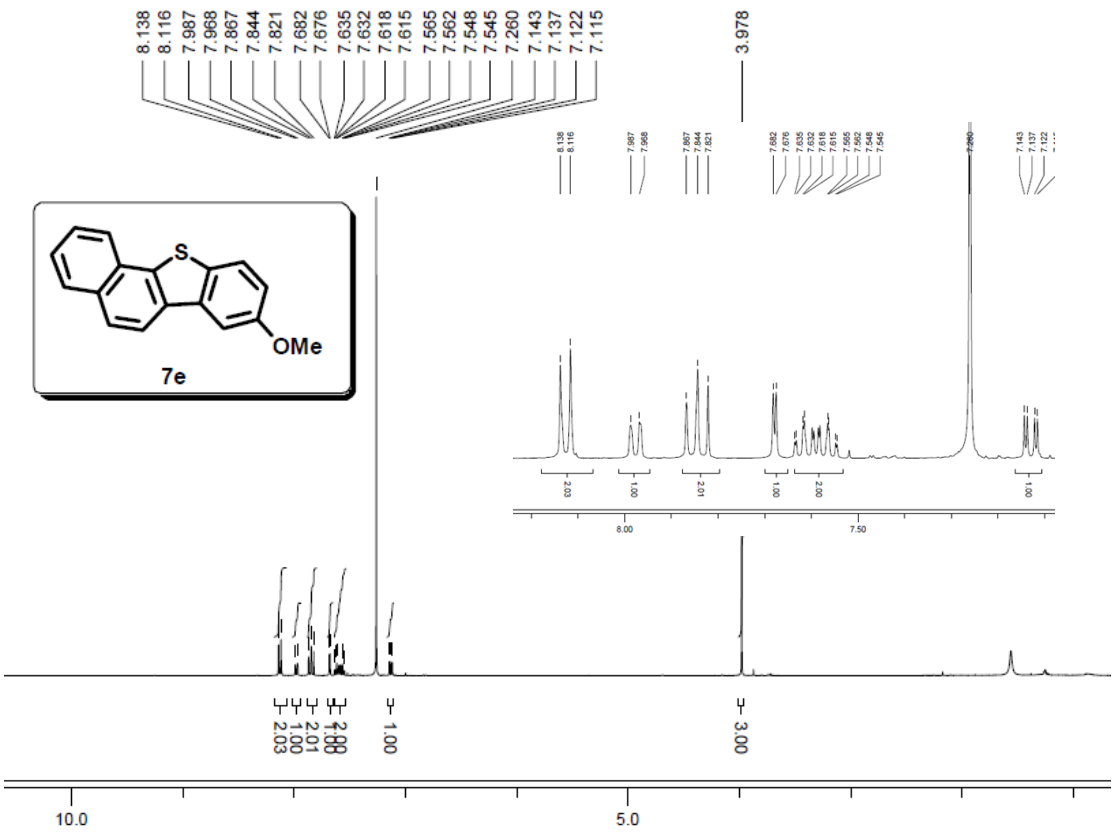
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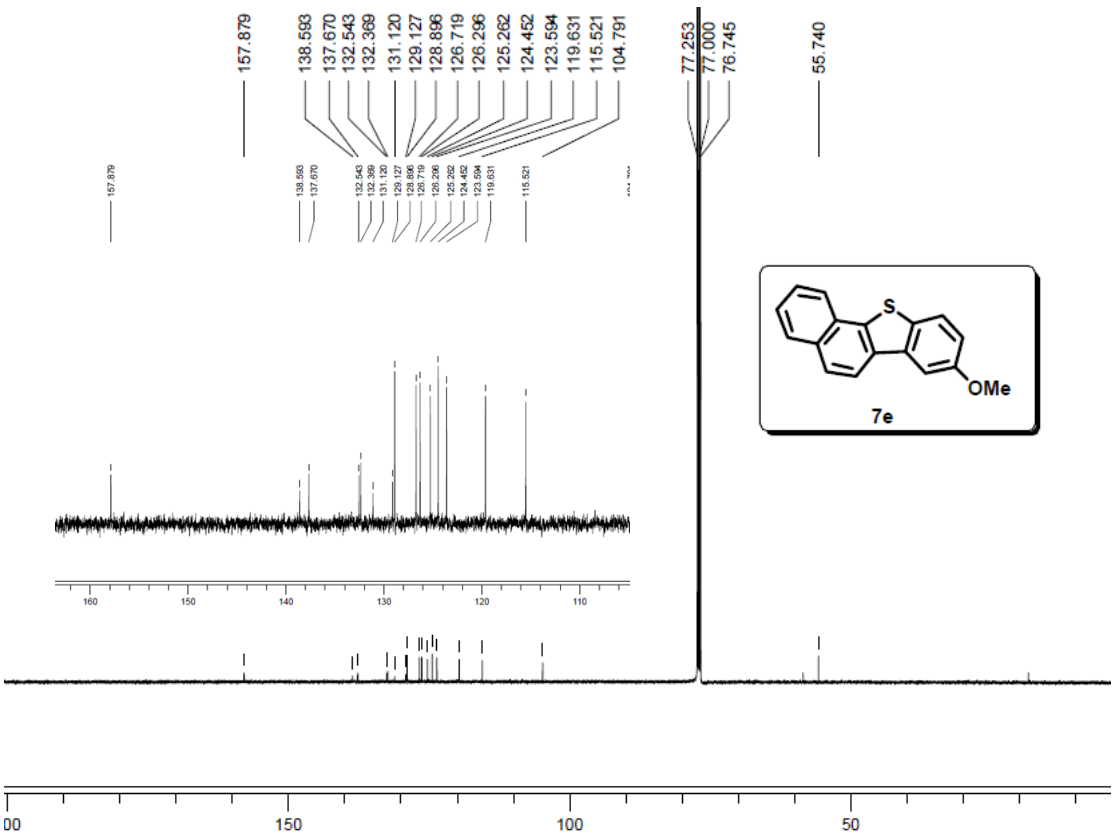
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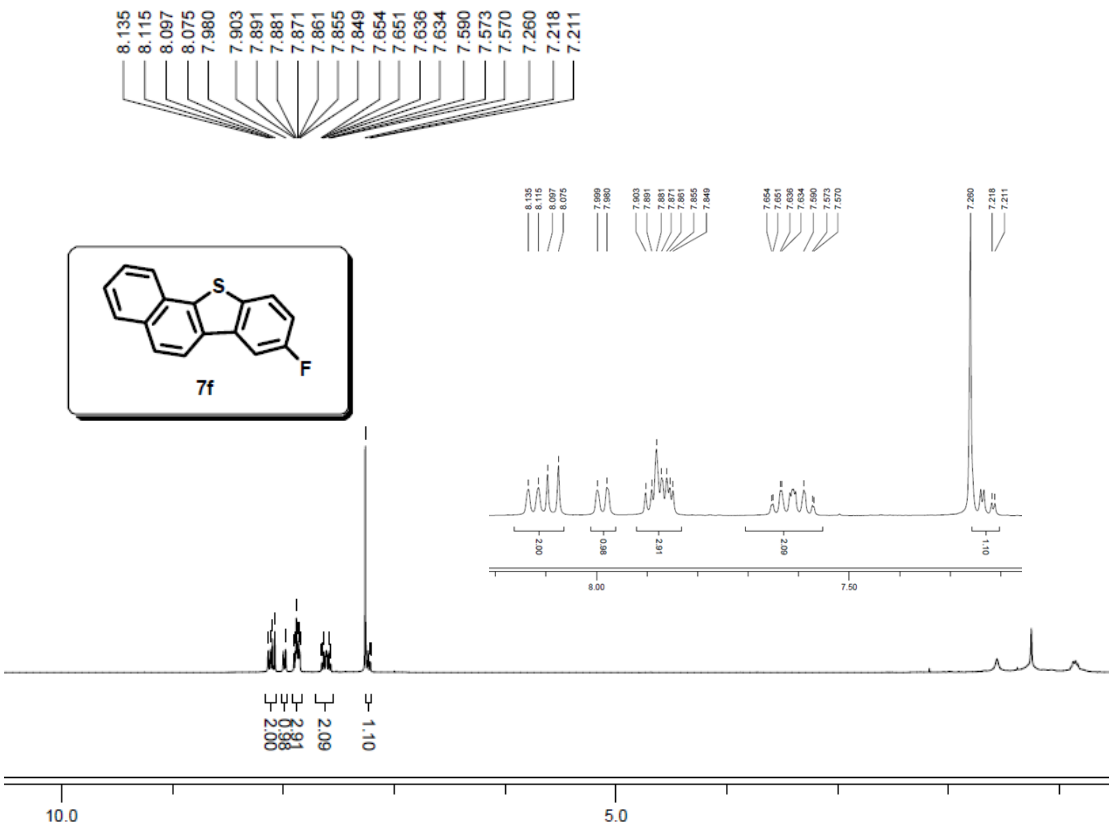
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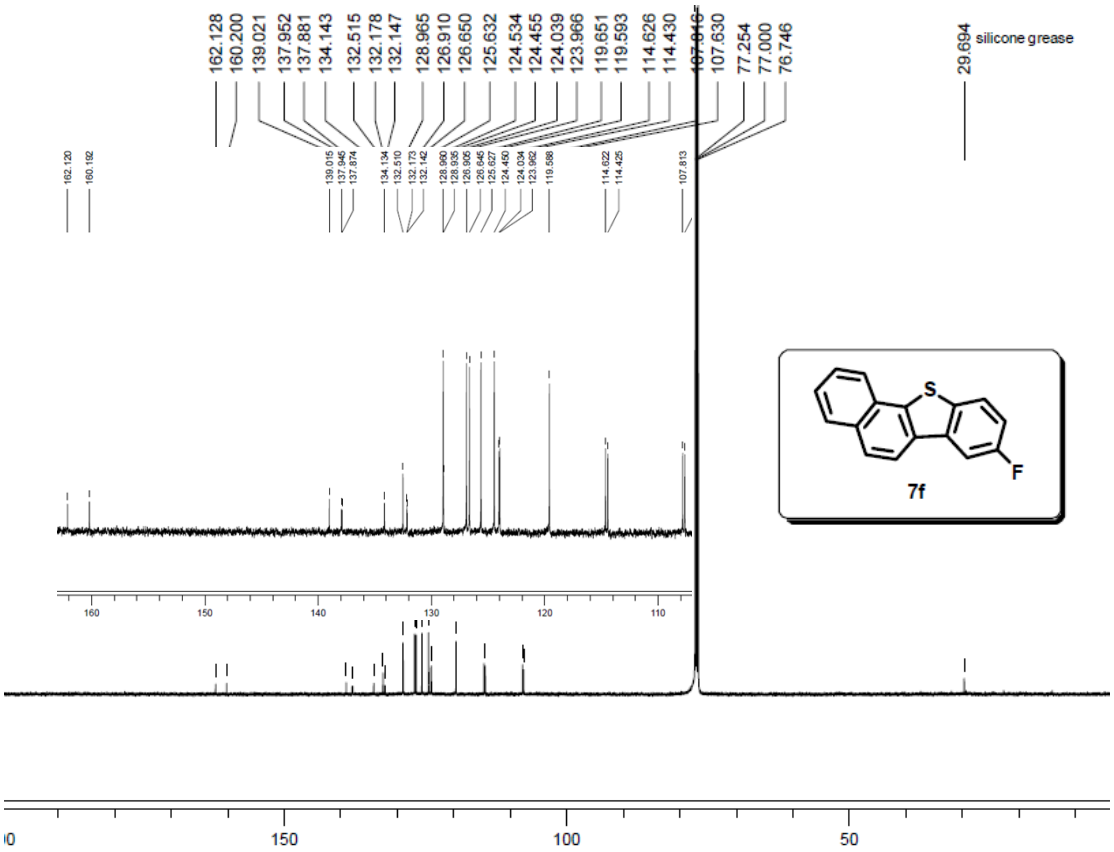
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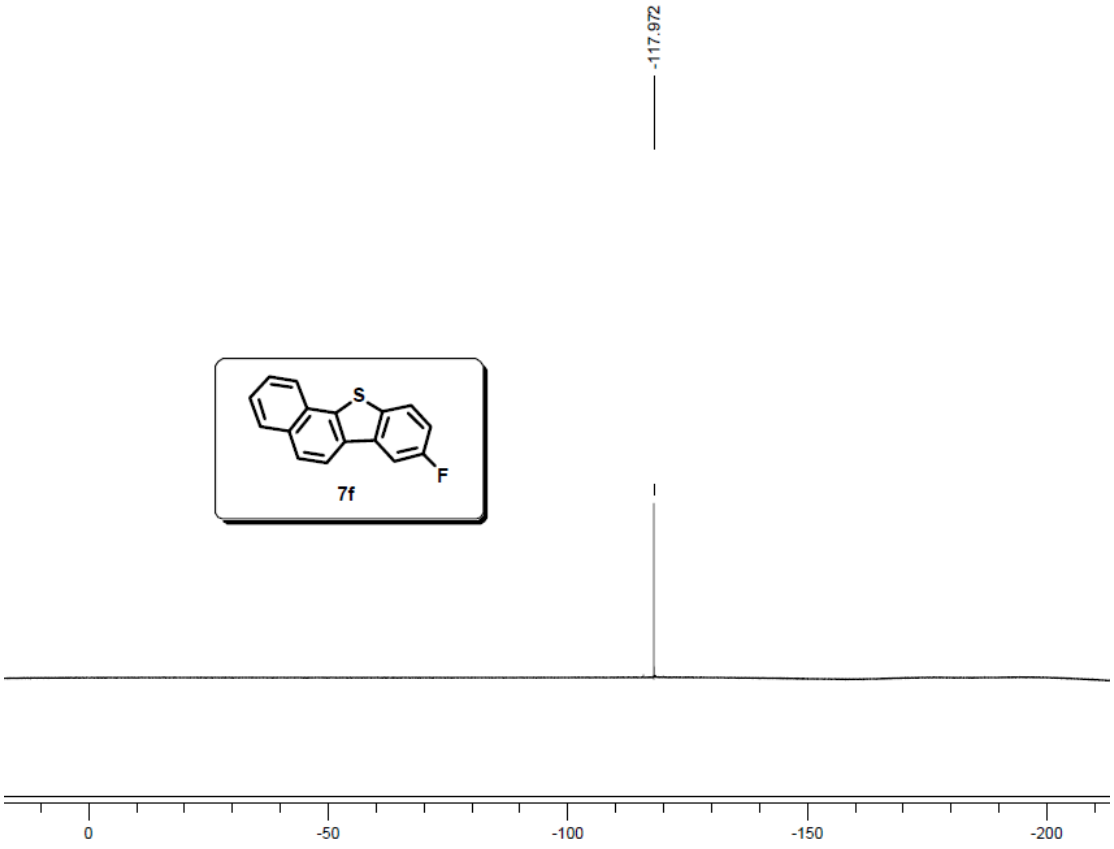
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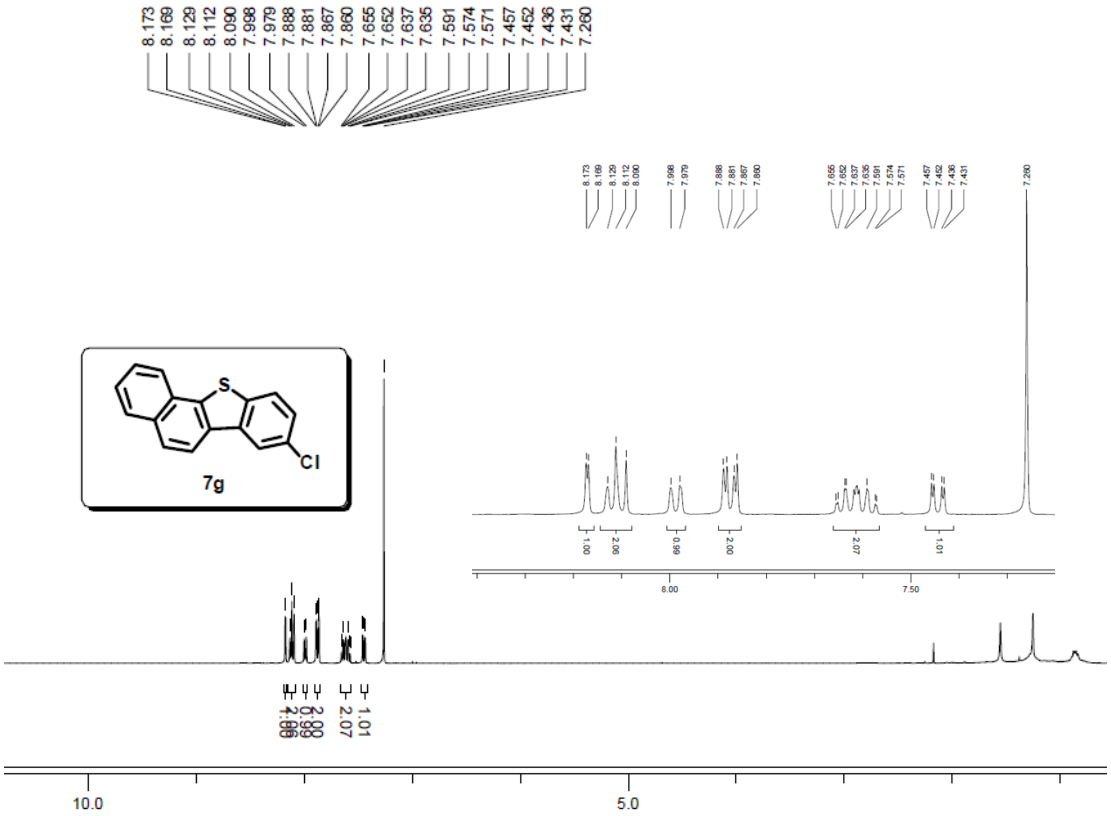
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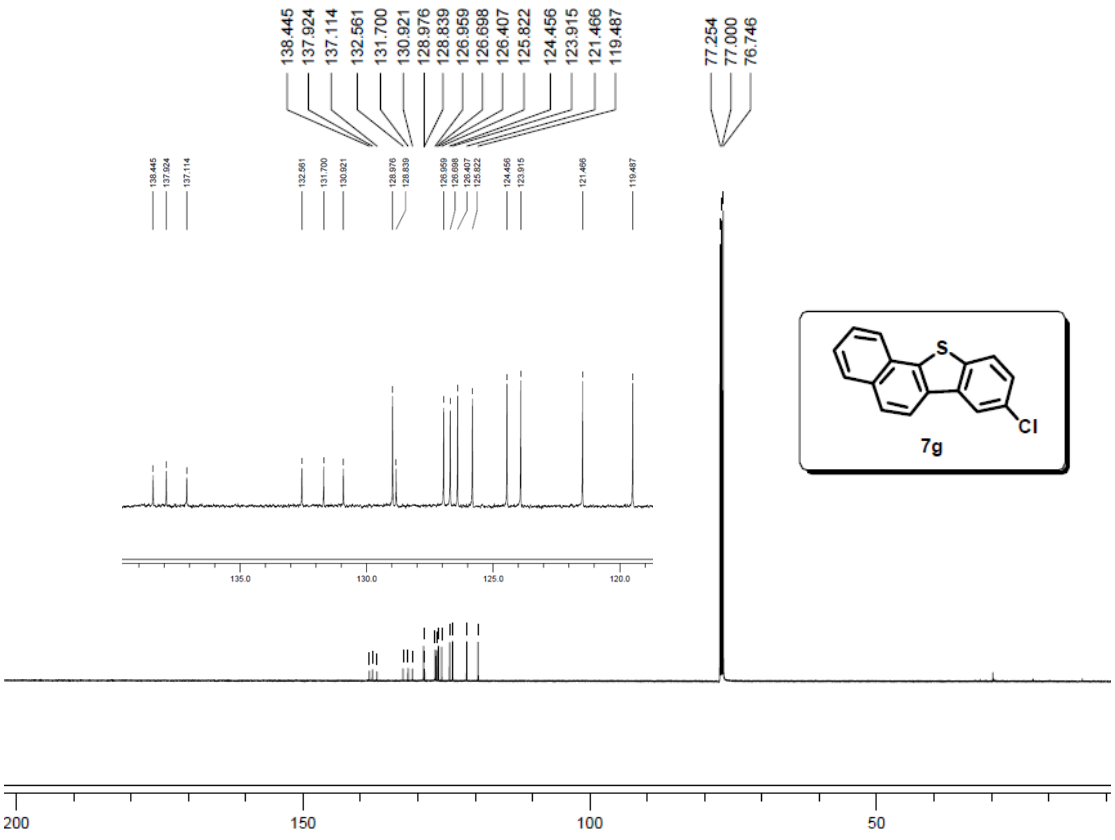
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