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Electronic Supplementary Information for

Redox-active benzimidazolium sulfonamides as cationic thiolating reagent for reductive cross-coupling of organic halides

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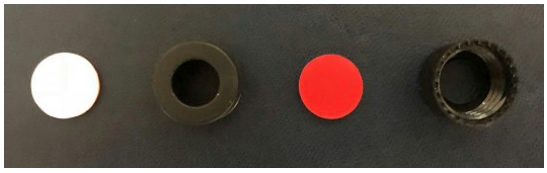
I. General Methods

All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or submersion in $KMnO_4$ solution or in I_2. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out in chloroform-*d* ($CDCl_3$) or acetonitrile-d_3 (CD_3CN). ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers, respectively.^{19}F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ^1H NMR), chloroform (δ 7.26 for ^1H NMR), acetonitrile (δ 1.94 for ^1H NMR), chloroform (δ 77.00 for ^{13}C NMR), and acetonitrile (δ 1.32 or 118.26 for ^{13}C NMR) in parts per million (ppm). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (*J*) are reported in Hertz (Hz). Melting points were uncorrected. Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker miccOTOF-Q111. GC-MS spectra were performed on Agilent 5977B.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C)

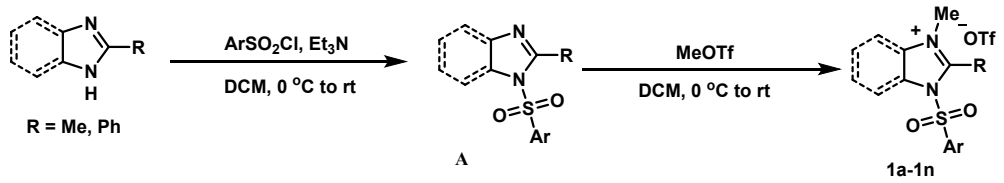
Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



II. Synthesis of Starting Materials

Unless otherwise noted, all halides were purchased from commercial source. Starting materials of products **10a-10d** were prepared according to the literature[1a].

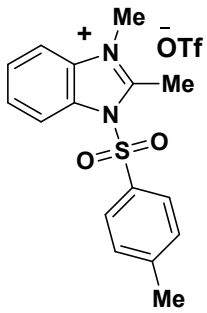
III. Synthesis of Imidazolium Sulfonamides (1a-1n)



1) To a one-necked 100 mL flask equipped with a magnetic stirrer, the corresponding imidazole (10 mmol), NEt_3 (150 mmol) and 40 mL DCM were added. The flask was then cooled in a ice bath, and about 13 mmol corresponding arylsulfonyl chloride was added into it slowly. Then, The mixture was stirred at room temperature for 2 hours. After the reaction was completed by TLC monitoring, the reaction mixture was evaporated in vacuo. Then, the reaction mixture was quenched with water and extracted with ethyl acetate (60 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding intermediate **A**.

2) Under argon, to a solution of the corresponding intermediate **A** in dried DCM (40 mL) was added dropwise MeOTf (13 mmol) at 0 °C. Then, the mixture was stirred at room temperature for 12 hours, while monitoring by TLC. After that time, the mixture was concentrated under rotary evaporation to give a white solid (or a viscous liquid) crude product, to which Et_2O (30 mL) was added. With vigorous stirring, a solid precipitate was formed. The precipitate was washed with Et_2O (30 mL × 3) and dried in vacuo to yield the title compound (**1a-1n**) as a white solid.

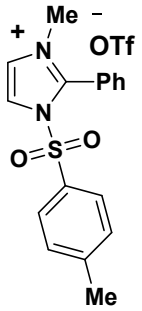
2,3-dimethyl-1-tosyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1a)



87%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.34 – 8.31 (m, 1H), 8.12 – 8.09 (m, 2H), 7.85 – 7.82 (m, 1H), 7.78 – 7.69 (m, 2H), 7.54 – 7.51 (m, 2H), 3.94 (s, 3H), 3.10 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 155.1, 150.4, 132.9, 132.6, 132.0, 129.9, 129.6, 129.5, 128.8, 122.1 (q, J = 320.9 Hz), 116.0, 114.5, 33.5, 21.9, 13.7. ^{19}F NMR (377 MHz, CD_3CN) δ -79.23. IR (neat) ν (cm^{-1}): 3095.6, 2968.8,

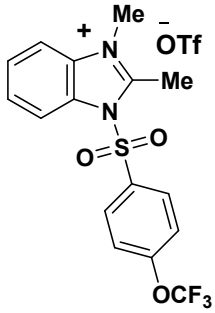
1597.2, 1559.9, 1463.0, 1388.4, 1258.0, 1144.3, 1086.5, 1028.7, 961.7, 892.7, 810.7, 752.9, 635.5; HRMS (ESI): caled for $C_{16}H_{17}N_2O_2S^+$ $[M]^+$ 301.1005; found 301.1009.

3-methyl-2-phenyl-1-tosyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (1b)



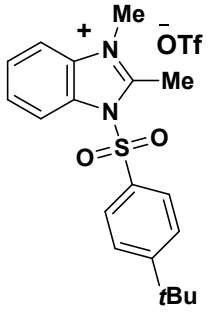
82%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.3 Hz, 1H), 7.82 (d, *J* = 2.3 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.54 – 7.49 (m, 2H), 7.39 – 7.32 (m, 4H), 7.24 – 7.20 (m, 2H), 3.72 (s, 4H), 2.42 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 145.3, 133.1, 131.0, 130.5, 130.4, 129.1, 129.0, 124.1, 120.6 (q, *J* = 320.6 Hz), 120.4, 119.5, 36.6, 21.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.36. IR (neat) ν (cm^{-1}): 3183.1, 3123.5, 3067.6, 1587.8, 1442.5, 1405.2, 1254.2, 1153.6, 1026.9, 984.0, 810.7, 769.7, 633.6, 538.6; HRMS (ESI): caled for $C_{17}H_{17}N_2O_2S^+$ $[M]^+$ 313.1005; found 313.1012.

2,3-dimethyl-1-((4-(trifluoromethoxy)phenyl)sulfonyl)-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1c)



93%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.36 – 8.32 (m, 3H), 7.88 – 7.72 (m, 3H), 7.60 – 7.56 (m, 2H), 3.96 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 155.86 (s), 155.35 (s), 134.22 (s), 132.61 (s), 132.49 (s), 129.9, 129.8, 129.1, 123.1, 122.1 (q, *J* = 320.7 Hz), 121.1 (q, *J* = 259.2 Hz), 116.0, 114.6, 33.6, 13.9. ^{19}F NMR (377 MHz, CD_3CN) δ -58.51, -79.31. IR (neat) ν (cm^{-1}): 3116.1, 1589.7, 1466.7, 1410.8, 1261.7, 1161.1, 1028.7, 965.4, 896.4, 758.5, 572.1, 516.2; HRMS (ESI): caled for $C_{16}H_{14}F_3N_2O_3S^+$ $[M]^+$ 371.0672; found 371.0678.

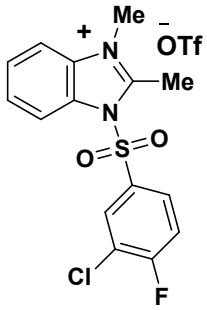
1-((4-(tert-butyl)phenyl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1d)



89%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.36 – 8.33 (m, 1H), 8.17 – 8.12 (m, 2H), 7.85 – 7.83 (m, 1H), 7.77 – 7.72 (m, 4H), 3.94 (s, 3H), 3.10 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ 162.7, 155.1, 133.0, 132.6, 129.9, 129.6, 129.4, 128.9, 128.6, 116.0, 114.5, 36.4, 33.5, 31.0, 13.8. ^{19}F NMR (377 MHz, CD_3CN) δ -79.28.

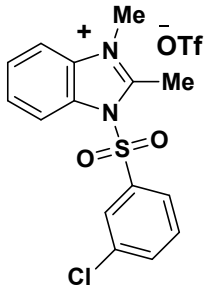
IR (neat) ν (cm^{-1}): 3065.7, 2972.6, 1591.6, 1464.8, 1399.6, 1259.8, 1153.6, 1082.8, 1026.9, 959.8, 840.5, 762.2, 622.5, 577.7; HRMS (ESI): caled for $C_{19}H_{23}N_2O_2S^+$ $[M]^+$ 343.1475; found 343.1483.

1-((3-chloro-4-fluorophenyl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1e)



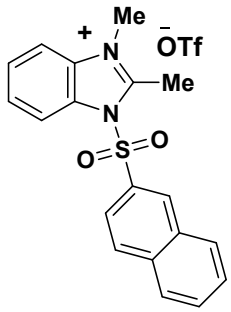
87%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.37 – 8.31 (m, 2H), 8.25 – 8.20 (m, 1H), 7.88 – 7.85 (m, 1H), 7.81 – 7.72 (m, 2H), 7.57 (t, *J* = 8.8 Hz, 1H), 3.96 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 164.1 (d, *J* = 260.7 Hz), 155.5, 133.0 (d, *J* = 3.6 Hz), 132.6, 132.5 (d, *J* = 1.9 Hz), 131.3 (d, *J* = 10.1 Hz), 129.9, 129.9, 129.1, 124.5 (d, *J* = 19.3 Hz), 122.0 (q, *J* = 320.6 Hz), 120.0 (d, *J* = 23.4 Hz), 116.0, 114.6, 33.7, 13.9. ^{19}F NMR (377 MHz, CD_3CN) δ -79.30, -102.18 – -102.23. IR (neat) ν (cm^{-1}): 3088.1, 1578.5, 1466.7, 1410.8, 1254.2, 1161.1, 1097.7, 1028.7, 963.5, 894.6, 862.9, 758.5, 635.5, 574.0; HRMS (ESI): caled for $C_{15}H_{13}ClFN_2O_2S^+$ $[M]^+$ 339.0365; found 339.0371.

1-((3-chlorophenyl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1f)



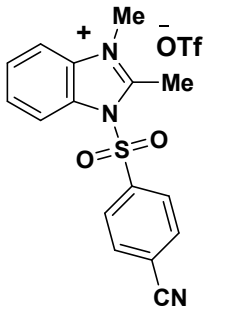
85%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.35 – 8.32 (m, 1H), 8.21 – 8.15 (m, 2H), 7.89 – 7.84 (m, 2H), 7.80 – 7.68 (m, 4H), 3.95 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 155.4, 138.1, 137.6, 137.0, 133.2, 132.6, 129.9, 129.8, 129.1, 128.9, 128.1, 122.1 (q, *J* = 320.7 Hz), 116.0, 114.6, 33.6, 13.9. ^{19}F NMR (377 MHz, CD_3CN) δ -79.28. IR (neat) ν (cm^{-1}): 3099.3, 3069.5, 1571.1, 1466.7, 1395.9, 1258.0, 1161.1, 1030.6, 967.2, 889.0, 799.5, 754.8, 669.1, 635.5, 553.5; HRMS (ESI): caled for $C_{15}H_{14}ClN_2O_2S^+$ $[M]^+$ 321.0459; found 321.0460.

2,3-dimethyl-1-(naphthalen-2-ylsulfonyl)-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1g)



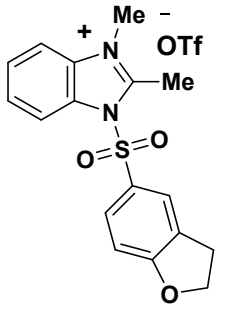
93%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.96 (d, *J* = 1.7 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 8.06 – 8.02 (m, 2H), 7.83 – 7.69 (m, 5H), 3.92 (s, 3H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 155.2, 137.4, 132.9, 132.8, 132.6, 132.5, 132.3, 132.0, 131.0, 130.0, 129.8, 129.7, 129.1, 128.9, 122.5, 122.1 (q, *J* = 320.7 Hz), 116.1, 114.5, 33.5, 13.8. ^{19}F NMR (377 MHz, CD_3CN) δ -79.22. IR (neat) ν (cm^{-1}): 3114.2, 3063.9, 1559.9, 1464.8, 1401.5, 1261.7, 1146.2, 1071.6, 1028.7, 963.5, 894.6, 859.2, 818.2, 758.5, 631.8; HRMS (ESI): caled for $C_{19}H_{17}N_2O_2S^+$ $[M]^+$ 337.1005; found 337.1012.

1-((4-cyanophenyl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1h)



83%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.37 – 8.31 (m, 3H), 8.06 – 8.03 (m, 2H), 7.88 – 7.85 (m, 1H), 7.81 – 7.72 (m, 2H), 3.96 (s, 1H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 155.6, 139.6, 135.3, 132.6, 132.6, 130.2, 129.9, 129.9, 129.2, 122.0 (q, *J* = 320.7 Hz), 120.8, 117.6, 115.9, 114.7, 33.7, 13.9. ^{19}F NMR (377 MHz, CD_3CN) δ -79.23. IR (neat) ν (cm^{-1}): 3103.0, 3045.2, 2238.3, 1559.9, 1466.7, 1397.8, 1258.0, 1159.2, 1026.9, 965.4, 894.6, 846.1, 756.6, 684.0, 626.2, 574.0, 512.5; HRMS (ESI): caled for $C_{16}H_{14}N_3O_2S^+$ $[M]^+$ 312.0801; found 312.0808.

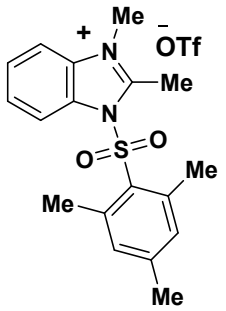
1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1i)



88%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.32 – 8.29 (m, 1H), 8.04 – 8.01 (m, 2H), 7.84 – 7.82 (m, 1H), 7.77 – 7.69 (m, 2H), 6.98 – 6.95 (m, 1H), 4.70 (t, *J* = 8.9 Hz, 2H), 3.94 (s, 3H), 3.27 (t, *J* = 8.9 Hz, 2H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 168.6, 154.8, 132.5, 132.3, 132.3, 130.0, 129.4, 128.7, 127.1, 126.3, 122.1 (q, *J* = 320.9 Hz), 116.1, 114.4, 111.3, 74.7, 33.4, 29.2, 13.7. ^{19}F NMR (377 MHz, CD_3CN) δ -79.3. IR (neat) ν (cm^{-1}): 3103.0, 1600.9, 1466.7, 1384.7, 1248.7, 1151.7,

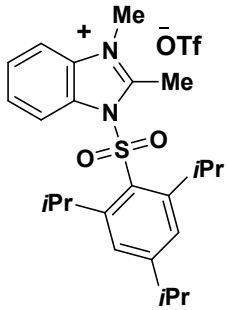
1030.6, 954.2, 890.8, 829.3, 754.8, 635.5, 583.3, 516.2; HRMS (ESI): caled for $C_{17}H_{17}N_2O_3S^+$ $[M]^+$ 329.0954; found 329.0961.

1-(mesitylsulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1j)



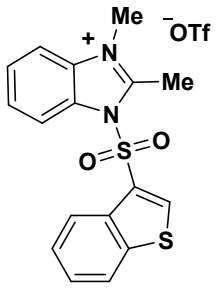
79%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.12 – 8.09 (m, 1H), 7.90 – 7.87 (m, 1H), 7.76 – 7.70 (m, 2H), 7.24 (s, 2H), 3.94 (s, 3H), 2.73 (s, 3H), 2.53 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 154.5, 149.1, 142.5, 134.2, 132.0, 131.2, 129.6, 128.6, 122.1 (q, J = 320.9 Hz), 116.2, 114.6, 33.5, 22.9, 21.4, 13.0. ^{19}F NMR (377 MHz, CD_3CN) δ -79.29. IR (neat) ν (cm^{-1}): 3127.2, 3037.8, 2980.0, 2939.0, 1602.8, 1567.3, 1459.3, 1392.2, 1261.7, 1140.6, 1028.7, 959.8, 754.8, 635.5, 572.1; HRMS (ESI): caled for $C_{18}H_{21}N_2O_2S^+$ $[M]^+$ 329.1318; found 329.1326.

2,3-dimethyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1k)



75%; white solid; ^{1}H NMR (400 MHz, CD_3CN) δ 7.96 – 7.90 (m, 2H), 7.77 – 7.69 (m, 2H), 7.46 (s, 2H), 3.98 (s, 3H), 3.92 – 3.85 (m, 3H), 2.73 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H), 1.08 (d, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, CD_3CN) δ 159.7, 153.2, 129.8, 128.7, 127.4, 126.9, 126.6, 122.0 (q, J = 320.5 Hz), 118.3, 115.5, 114.8, 113.3, 35.2, 33.7, 30.9, 24.2, 23.5, 13.1. ^{19}F NMR (377 MHz, CD_3CN) δ -79.25. IR (neat) ν (cm^{-1}): 2968.8, 2935.3, 2875.6, 1597.2, 1559.9. 1463.0, 1388.4, 1258.0, 1151.7, 1030.6, 959.8, 885.2, 754.8, 637.4, 555.4; HRMS (ESI): caled for $C_{24}H_{33}N_2O_2S^+$ $[M]^+$ 413.2257; found 413.2261.

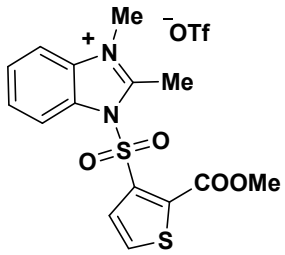
1-(benzo[b]thiophen-3-ylsulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1l)



93%; white solid; ^{1}H NMR (500 MHz, CD_3CN) δ 9.20 (s, 1H), 8.57 – 8.55 (m, 1H), 8.23 – 8.20 (m, 1H), 8.13 – 8.10 (m, 1H), 7.86 – 7.83 (m, 2H), 7.80 – 7.76 (m, 1H), 7.61 – 7.56 (m, 2H), 3.91 (s, 3H), 3.08

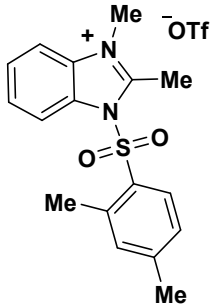
(s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.33. ^{13}C NMR (126 MHz, CD_3CN) δ 155.2, 145.4, 141.3, 133.7, 132.3, 130.4, 129.7, 128.9, 128.2, 128.0, 127.8, 124.9, 122.9, 122.1 (q, J = 321.0 Hz), 116.3, 114.5, 33.5, 13.8. IR (neat) ν (cm^{-1}): 3117.9, 3069.5, 1604.6, 1559.9, 1453.7, 1407.1, 1259.8, 1144.3, 1028.7, 974.7, 751.1; HRMS (ESI): caled for $C_{17}H_{15}N_2O_2S_2^+$ $[M]^+$ 343.0569; found 343.0568.

1-((2-(methoxycarbonyl)thiophen-3-yl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1m)



87%; white solid; ^{1}H NMR (500 MHz, CD_3CN) δ 8.03 – 7.99 (m, 3H), 7.90 – 7.88 (m, 1H), 7.76 – 7.68 (m, 2H), 4.02 (s, 3H), 3.75 (s, 3H), 3.11 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -79.31. ^{13}C NMR (126 MHz, CD_3CN) δ 159.8, 156.3, 138.9, 137.1, 134.0, 132.8, 132.1, 130.6, 129.3, 128.6, 122.0 (q, J = 320.9 Hz), 116.2, 114.5, 54.2, 33.6, 14.1. IR (neat) ν (cm^{-1}): 3114.2, 3076.9, 1727.6, 1466.7, 1390.3, 1265.4, 1198.3, 1146.2, 1028.7, 965.4, 758.5; HRMS (ESI): caled for $C_{15}H_{15}N_2O_4S_2^+$ $[M]^+$ 351.0468; found 351.0467.

1-((2,4-dimethylphenyl)sulfonyl)-2,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (1n)



94%; white solid; ^{1}H NMR (500 MHz, CD_3CN) δ 8.25 – 8.19 (m, 2H), 7.90 – 7.86 (m, 1H), 7.75 – 7.70 (m, 2H), 7.42 (d, J = 8.2 Hz, 1H), 7.33 (s, 1H), 3.95 (s, 3H), 2.90 (s, 3H), 2.42 – 2.41 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 154.9, 150.1, 141.0, 135.5, 132.5, 132.3, 131.7, 131.0, 129.4, 129.0, 128.7, 122.0 (q, J = 320.8 Hz), 116.3, 114.5, 33.5, 21.7, 20.7, 13.6. ^{19}F NMR (471 MHz, CD_3CN) δ -79.27. IR (neat) ν (cm^{-1}): 3129.1, 1567.3, 1464.8, 1364.2, 1271.0, 1224.4, 1149.9, 1028.7, 963.5, 894.6, 751.1; HRMS (ESI): caled for $C_{17}H_{19}N_2O_2S^+$ $[M]^+$ 315.1162; found 315.1160.

IV. General Procedures

IV-1. General Procedure for the synthesis of the products 3, 5, 7, 10, 12.

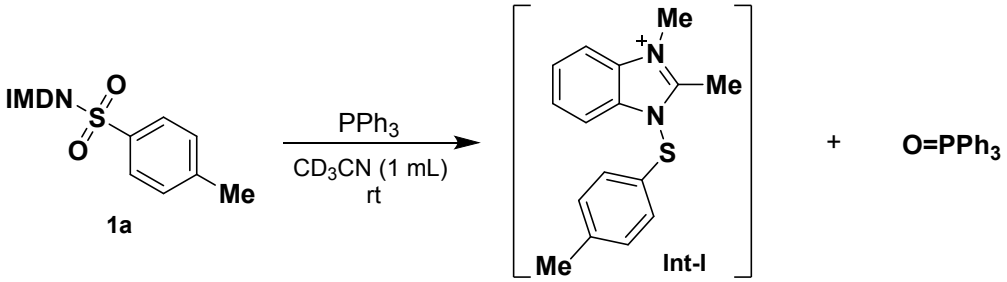
Under argon, to a suspension of $Ni(OTf)_2$ (0.04 mmol, 20 mol%), 4,4'-di-tert-butyl-2,2'-bipyridine (0.04 mmol, 20 mol%), $MgCl_2$ (0.4 mmol, 2.0 equiv), Zn powder (0.6 mmol, 3.0 equiv), benzimidazolium sulfonamides **1** (0.40 mmol, 2.0 equiv) and PPh_3 (0.5 mmol, 2.5 equiv) in DMA (2 mL) was added corresponding halide (0.2 mmol) at room temperature. After that, the reaction mixture was stirred at 60 ºC until the reaction was completed as monitored by TLC or GC-MS analysis. Then, distilled water (40 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **3**, **5**, **7**, **10**, **12**.

IV-2. **General Procedure for the synthesis of the products 9a-9i.**

Under argon, to a suspension of $Ni(OTf)_2$ (0.04 mmol, 20 mol%), 4-(trifluoromethyl)pyridine (0.2 mmol, 1.0 equiv), $MgCl_2$ (0.4 mmol, 2.0 equiv), Zn powder (0.6 mmol, 3.0 equiv), benzimidazolium sulfonamides **1** (0.40 mmol, 2.0 equiv) and PPh_3 (0.5 mmol, 2.5 equiv) in THF (2 mL) was added the corresponding halide (0.2 mmol) at room temperature. After that, the reaction mixture was stirred at 60 ºC until the reaction was completed as monitored by TLC or GC-MS analysis. Then, distilled water (30 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **9a-9i**.

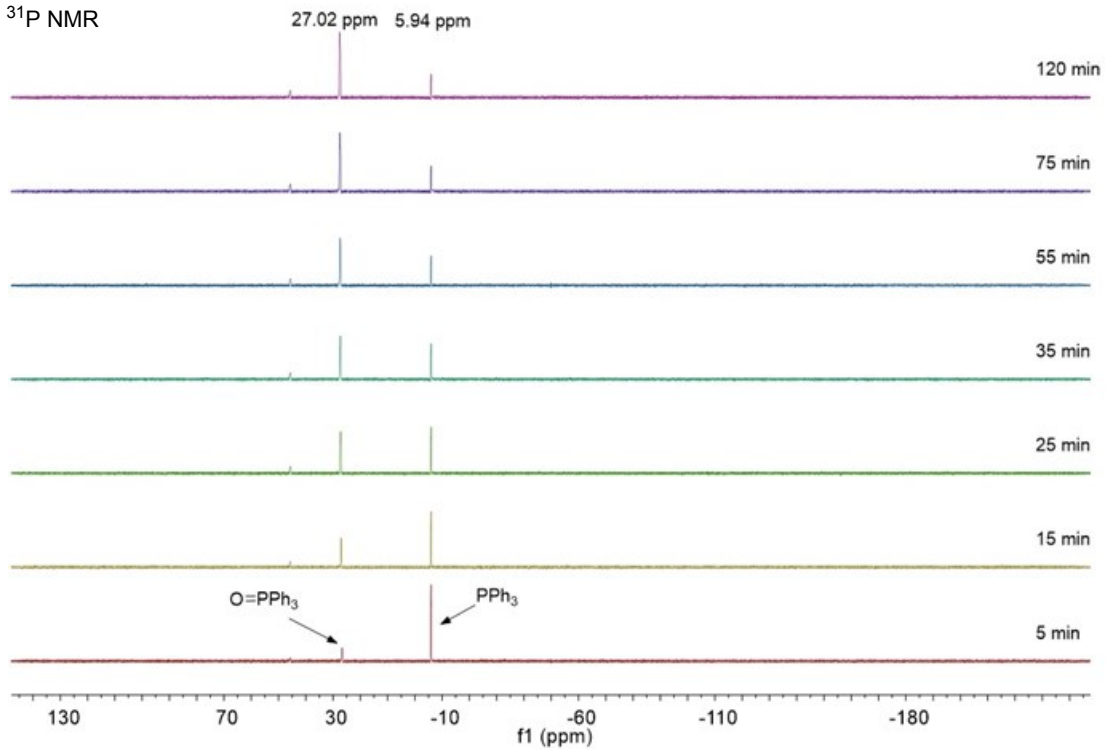
V. Mechanistic Studies

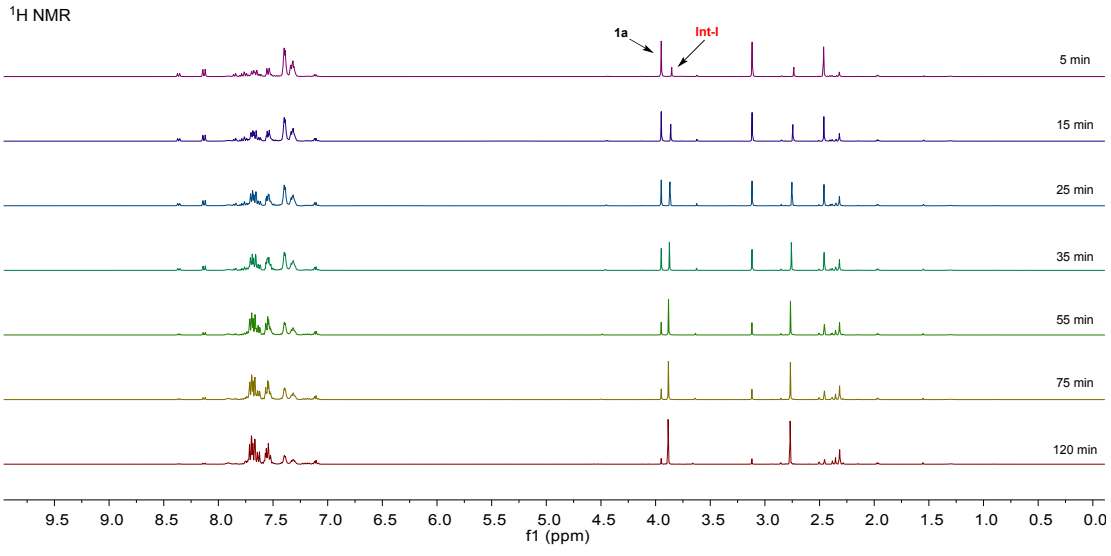
Control Experiment (a):

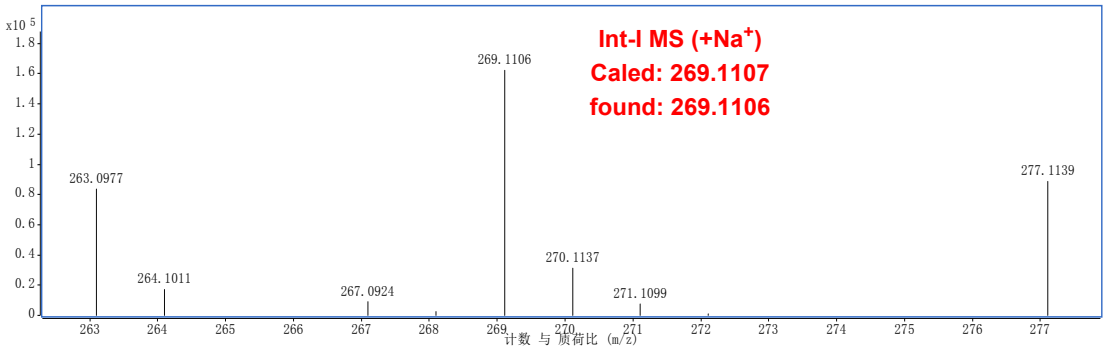


Under argon, to a solution of benzimidazolium sulfonamide **1a** (0.20 mmol, 2.0 equiv) in CD_3CN (1 mL) was added PPh_3 (0.4 mmol, 2 equiv) at room temperature. Then, the reaction mixture was immediately monitored by ^1H NMR and ^{31}P NMR for 2 h. The

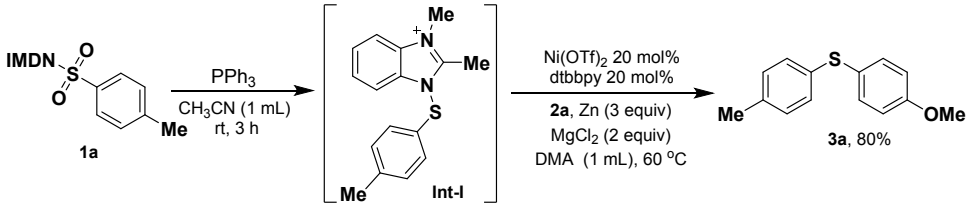
intermediate **Int-I** and $O{=}PPh_3$ were detected by ^{1}H NMR and ^{31}P NMR, respectively. Meanwhile, the intermediate **Int-I** was detected by HRMS.







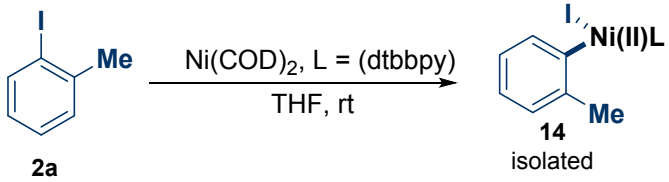
Control Experiment (b):



Under argon, to a solution of benzimidazolium sulfonamide **1a** (0.20 mmol, 2.0 equiv) in CH_3CN (1 mL) was added PPh_3 (0.4 mmol, 2 equiv) at room temperature. After 3 hours, $Ni(OTf)_2$ (0.02 mmol, 20 mol%), 4,4'-di-tert-butyl-2,2'-bipyridine (0.02 mmol, 20 mol%), $MgCl_2$ (0.2 mmol, 2.0 equiv), Zn powder (0.3 mmol, 3.0 equiv), 1-iodo-4-methoxybenzene **2a** (0.10 mmol) and DMA (1 mL) were added to the reaction mixture. After that, the reaction mixture was stirred at 60 ºC for 8 h. Then, distilled water (40 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **3a** in 80% yield.

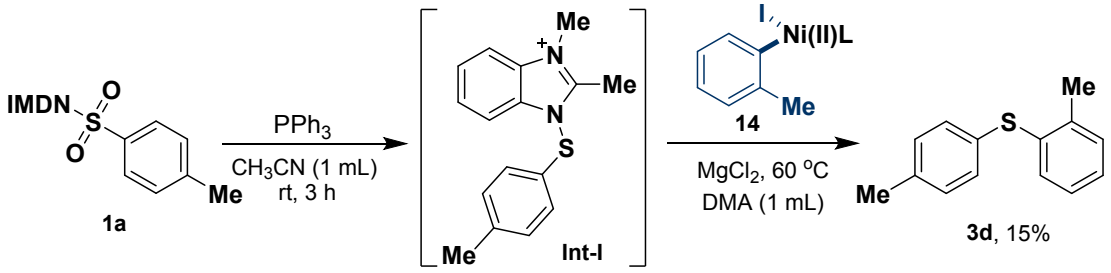
Control Experiment (c):

The synthesis of nickel-complex 14



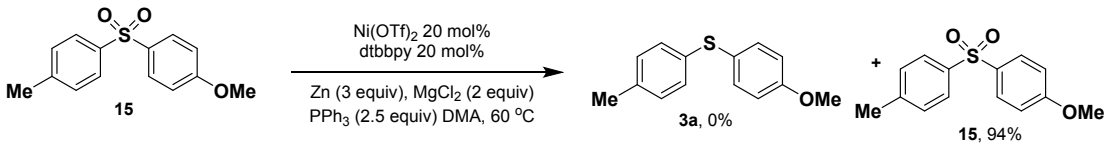
A solution of (dtbbpy)Ni(cod) was generated by stirring 138 mg of $Ni(cod)_2$ (0.5 mmol) and 134 mg of 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.5 mmol) in 5 mL of THF overnight at room temperature in an argon-filled glovebox. Upon dissolution of the solids, the reaction mixture became dark purple. To this purple mixture was added 0.076 mL of 2-iodotoluene **2a** (131 mg, 0.6 mmol) and the color rapidly changed to red, indicating

formation of **14**. The solution was stirred for an additional 2 h before the solvent was removed under vacuum. The solid was triturated with dry, degassed pentane three times to remove residual cyclooctadiene and 2-iodotoluene and then dried under vacuum overnight to provide 236 mg of **14** (87% yield) [1b]. ^{1}H NMR (400 MHz, Acetone) δ 9.56 (d, *J* = 5.5 Hz, 1H), 8.40 (d, *J* = 12.7 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.38 (d, *J* = 4.9 Hz, 1H), 6.85 – 6.60 (m, 4H), 2.95 (s, 3H), 1.42 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Acetone) δ 164.5, 164.1, 156.7, 154.2, 154.1, 149.9, 149.0, 143.5, 138.5, 127.8, 124.4, 124.3, 123.6, 122.6, 119.7, 119.3, 36.2 (2C), 30.4, 27.2.



Under argon, to a solution of benzimidazolium sulfonamide **1a** (0.20 mmol, 2.0 equiv) in CH_3CN (1 mL) was added PPh_3 (0.4 mmol, 2 equiv) at room temperature. After 3 hours, the nickel-complex **14** (0.1 mmol, 54.4 mg), $MgCl_2$ (0.2 mmol, 2.0 equiv) and DMA (1 mL) were added to the reaction mixture. After that, the reaction mixture was stirred at 60 ºC for 8 h. Then, distilled water (40 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **3d** in 15% yield.

Control Experiment (d):

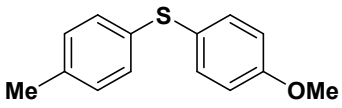


Under argon, to a suspension of $Ni(OTf)_2$ (0.04 mmol, 20 mol%), 4,4'-di-tert-butyl-2,2'-bipyridine (0.04 mmol, 20 mol%), $MgCl_2$ (0.4 mmol, 2.0 equiv), Zn powder (0.6 mmol, 3.0 equiv) and PPh_3 (0.5 mmol, 2.5 equiv) in DMA (2 mL) was added 1-methoxy-4-tosylbenzene **15** (0.2 mmol) at room temperature. After that, the reaction mixture was stirred at 60 ºC for 8 h. Then, distilled water (40 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15mL). The combined organic layers were

dried over Na_2SO_4, filtered and concentrated. Experimental results show that the desired product **3a** was not formed and substrate **15** was recovered in 94% yield.

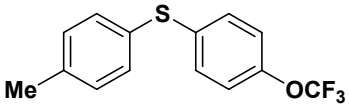
VI. Characteristic Data

(4-methoxyphenyl)(*p*-tolyl)sulfane (3a)



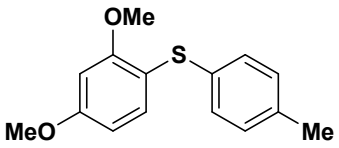
92% (42.4 mg, X = I); Gram-scale: 60% (685 mg, X = I); 81% (37.2 mg, X = Br); white solid; mp 41-42 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.14 – 7.11 (m, 2H), 7.07 – 7.04 (m, 2H), 6.88 – 6.84 (m, 2H), 3.80 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 136.1, 134.3, 129.7, 129.3, 128.5, 125.6, 114.8, 55.3, 21.0. IR (neat) ν (cm^{-1}): 3067.6, 3002.4, 2920.4, 2834.6, 1589.7, 1489.1, 1241.2, 1172.2, 1030.6, 801.4; HRMS (ESI): caled for $C_{14}H_{15}OS^+$ $[M + H]^+$ 231.0838; found 231.0833.

***p*-tolyl(4-(trifluoromethoxy)phenyl)sulfane (3b)**



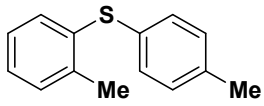
72% (20.4 mg); white solid; mp 37-38 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.23 (m, J = 5.1, 3.8 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.11 – 7.08 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 138.3, 136.4, 132.8, 130.3, 130.3, 121.6, 120.4 (q, J = 257.3 Hz), 21.2. IR (neat) ν (cm^{-1}): 3022.9, 2929.7, 2873.8, 1595.3, 1487.2, 1217.0, 1157.3, 1080.9, 1015.7, 803.2; HRMS (ESI): caled for $C_{14}H_{12}F_3OS^+$ $[M + H]^+$ 285.0555; found 285.0568.

(2,4-dimethoxyphenyl)(*p*-tolyl)sulfane (3c)



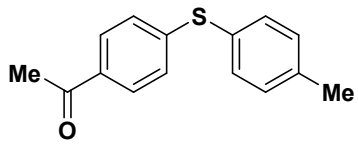
82% (42.6 mg); white solid; mp 64-65 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 1H), 7.11 – 7.08 (m, 2H), 7.05 – 7.04 (m, 2H), 6.50 (d, J = 2.5 Hz, 1H), 6.47 – 6.45 (m, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 159.7, 135.7, 135.4, 133.3, 129.6, 128.9, 113.5, 105.2, 99.1, 55.9, 55.4, 21.0. IR (neat) ν (cm^{-1}): 3071.3, 3002.4, 2937.1, 2834.6, 1591.6, 1459.3, 1299.0, 1207.7, 1161.1, 1073.5, 1028.7, 803.2; HRMS (ESI): caled for $C_{15}H_{16}O_2SNa^+$ $[M + Na]^+$ 283.0763; found 283.0761.

***o*-tolyl(*p*-tolyl)sulfane (3d)**



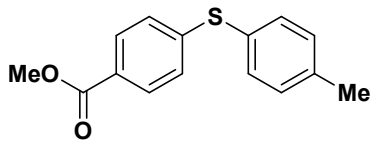
89% (38.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 8H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.9, 135.2, 131.6, 131.3, 131.0, 130.4, 130.0, 127.1, 126.6, 21.1, 20.5. IR (neat) ν (cm^{-1}): 3058.3, 3013.6, 2920.4, 2860.7, 1589.7, 1490.9, 1466.7, 1060.4, 1015.7, 803.2, 743.6; HRMS (ESI): caled for $C_{14}H_{15}S^+$ $[M + H]^+$ 215.0889; found 215.0888.

1-(4-(*p*-tolylthio)phenyl)ethan-1-one (3e)



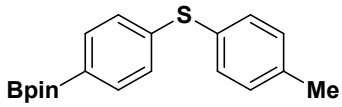
63% (30.5 mg); white solid; mp 89-90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.42 – 7.39 (m, 2H), 7.24 (t, J = 9.2 Hz, 2H), 7.17 – 7.13 (m, 2H), 2.54 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 145.9, 139.3, 134.5, 134.1, 130.5, 128.8, 127.9, 126.6, 26.4, 21.3. IR (neat) ν (cm^{-1}): 3324.8, 3080.6, 2922.2, 2851.4, 1671.7, 1578.5, 1395.9, 1261.7, 1088.4, 959.8, 814.4; HRMS (ESI): caled for $C_{15}H_{15}OS^+$ $[M + H]^+$ 243.0838; found 243.0839.

methyl 4-(*p*-tolylthio)benzoate (3f)



84% (43.3 mg); white solid; mp 73-74 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.42 – 7.39 (m, 2H), 7.23 – 7.20 (m, 2H), 7.16 – 7.12 (m, 2H), 3.88 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 145.4, 139.2, 134.4, 130.5, 130.0, 128.1, 127.0, 126.7, 52.0, 21.3. IR (neat) ν (cm^{-1}): 3017.3, 2946.5, 2922.2, 2849.5, 1705.3, 1589.7, 1431.3, 1272.9, 1183.4, 1112.6, 814.4, 762.2; HRMS (ESI): caled for $C_{15}H_{15}O_2S^+$ $[M + H]^+$ 259.0787; found 259.0785.

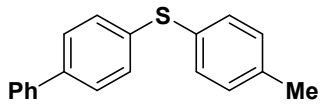
4,4,5,5-tetramethyl-2-(4-(*p*-tolylthio)phenyl)-1,3,2-dioxaborolane (3g)



89% (58.2 mg); white solid; mp 122-123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.13 (m, 2H), 2.35 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.1, 135.2, 133.0, 130.1, 130.1, 127.8, 83.8, 24.8, 21.2.

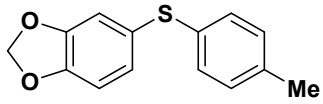
IR (neat) ν (cm^{-1}): 3000.5, 2980.0, 2924.1, 1593.4, 1354.9, 1142.4, 1015.7, 857.3, 812.6, 650.4; HRMS (ESI): caled for $C_{19}H_{24}BO_2S^+$ $[M + H]^+$ 327.1585; found 327.1587.

[1,1'-biphenyl]-4-yl(*p*-tolyl)sulfane (3h)



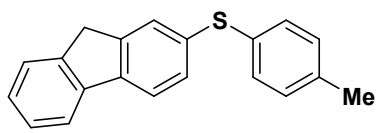
94% (52.2 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.50 – 7.47 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 – 7.30 (m, 5H), 7.16 – 7.14 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.3, 137.7, 136.3, 132.4, 131.1, 130.1, 130.0, 128.8, 127.7, 127.3, 126.9, 21.1. IR (neat) ν (cm^{-1}): 3028.5, 2918.5, 2853.3, 1904.7, 1654.9, 1591.6, 1474.2, 1395.9, 1207.7, 1084.7, 810.7, 752.9, 687.7; HRMS (ESI): caled for $C_{19}H_{17}S^+$ $[M + H]^+$ 277.1045; found 277.1035.

5-(*p*-tolylthio)benzo[*d*][1,3]dioxole (3i)



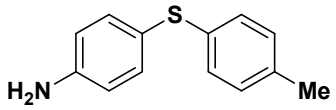
91% (44.4 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.93 (dd, J = 8.0, 1.8 Hz, 2H), 6.84 (d, J = 1.8 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.5, 136.6, 133.5, 130.1, 129.8, 127.7, 126.1, 112.6, 108.8, 101.3, 21.0. IR (neat) ν (cm^{-1}): 3069.5, 3013.6, 2888.7, 2775.0, 1474.2, 1230.0, 1036.2, 933.7, 889.0, 801.4, 603.8; HRMS (ESI): caled for $C_{14}H_{13}O_2S^+$ $[M + H]^+$ 245.0631; found 245.0629.

(9*H*-fluoren-2-yl)(*p*-tolyl)sulfane (3j)



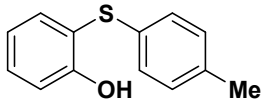
82% (47.4 mg); white solid; mp 108-109 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 3H), 7.14 – 7.11 (m, 2H), 3.84 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.1, 141.0, 140.7, 137.2, 134.6, 132.4, 131.4, 130.0, 129.4, 127.3, 126.8, 126.8, 125.0, 120.3, 119.9, 36.8, 21.1. IR (neat) ν (cm^{-1}): 3047.1, 2924.1, 2853.3, 1654.9, 1559.9, 1444.3, 954.2, 810.7, 732.4, 631.8, 572.1; HRMS (EI): caled for $C_{20}H_{16}S$ [M] 288.0973; found 288.0974.

4-(*p*-tolylthio)aniline (3k)



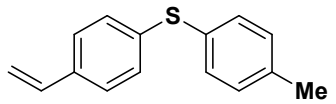
57% (24.7 mg); white solid; mp 66-67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.09 – 7.01 (m, 4H), 6.66 – 6.63 (m, 2H), 3.76 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 135.5, 135.4, 135.3, 129.6, 128.2, 121.7, 115.8, 20.9. IR (neat) ν (cm^{-1}): 3464.6, 3358.3, 3199.9, 3030.3, 2914.8, 1597.2, 1489.1, 1299.0, 1176.0, 1082.8, 1015.7, 797.7; HRMS (ESI): caled for $C_{13}H_{14}NS^+$ $[M + H]^+$ 216.0841; found 216.0839.

2-(*p*-tolylthio)phenol (3l)



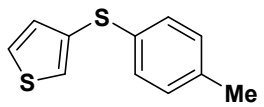
60% (26.3 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.7, 1.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.06 – 7.00 (m, 4H), 6.95 – 6.91 (m, 1H), 6.53 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 136.6, 136.3, 132.1, 132.0, 130.0, 127.4, 121.2, 117.2, 115.4, 20.9. IR (neat) ν (cm^{-1}): 3419.8, 3021.0, 2920.4, 2862.6, 1572.9, 1468.6, 1338.1, 1289.7, 1181.6, 1026.9, 803.2, 751.1; HRMS (ESI): caled for $C_{13}H_{12}OS^+$ $[M + Na]^+$ 239.0501; found 239.0500.

***p*-tolyl(4-vinylphenyl)sulfane (3m)**



49% (22.2 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.23 – 7.19 (m, 2H), 7.15 – 7.12 (m, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.71 (dd, J = 17.6, 0.7 Hz, 1H), 5.23 (dd, J = 10.9, 0.7 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.6, 136.1, 135.9, 132.2, 130.1, 129.9, 129.9, 126.8, 113.9, 21.1. IR (neat) ν (cm^{-1}): 3069.5, 3022.9, 2965.1, 2920.4, 2860.7, 1489.1, 1395.9, 1082.8, 987.7, 905.7, 807.0; HRMS (ESI): caled for $C_{15}H_{15}S^+$ $[M + H]^+$ 227.0889; found 227.0887.

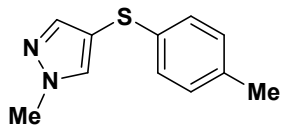
3-(*p*-tolylthio)thiophene (3n)



74% (30.7 mg); white solid; mp 30-31 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 5.0, 3.0 Hz, 1H), 7.28 (dd, J = 3.0, 1.3 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.10 – 7.07 (m, 2H), 7.00 (dd, J = 5.0, 1.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 133.1, 130.7, 130.6, 129.8, 129.5, 126.6,

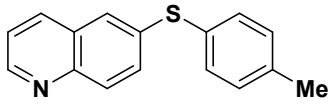
126.5, 21.0. IR (neat) ν (cm^{-1}): 3393.7, 3103.0, 3019.1, 2918.5, 2849.5, 1489.1, 1351.2, 1198.3, 1086.5, 1015.7, 851.7, 803.2, 775.3, 613.1; HRMS (ESI): caled for $C_{11}H_{11}S_2^+$ $[M + H]^+$ 207.0297; found 207.0292.

1-methyl-4-(*p*-tolylthio)-1*H*-pyrazole (3o)



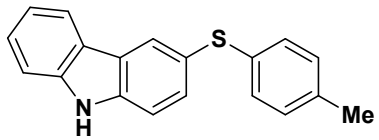
56% (22.6 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.49 (s, 1H), 7.06 – 7.01 (m, 4H), 3.91 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 135.3, 135.1, 134.9, 129.5, 126.8, 108.3, 39.3, 20.8. IR (neat) ν (cm^{-1}): 3117.9, 3017.3, 2920.4, 2866.3, 1490.9, 1438.8, 1116.3, 974.7, 803.2, 704.5, 657.9, 622.5; HRMS (ESI): caled for $C_{11}H_{13}N_2S^+$ $[M + H]^+$ 205.0794; found 205.0793.

6-(*p*-tolylthio)quinolone (3p)



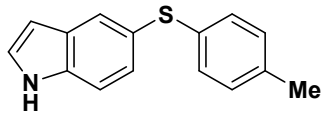
38% (19.3 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, J = 4.2, 1.7 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.61 – 7.52 (m, 2H), 7.41 – 7.34 (m, 3H), 7.21 – 7.18 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 146.9, 138.4, 136.5, 135.2, 133.1, 130.6, 130.3, 130.0, 130.0, 128.6, 126.5, 121.6, 21.2. IR (neat) ν (cm^{-1}): 3021.0, 2920.4, 2858.9, 1586.0, 1485.3, 1179.7, 1121.9, 943.0, 864.7, 807.0, 766.0, 605.7; HRMS (ESI): caled for $C_{16}H_{14}NS^+$ $[M + H]^+$ 252.0841; found 252.0843.

3-(*p*-tolylthio)-9*H*-carbazole (3q)



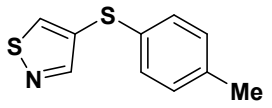
70% (40.0 mg); white solid; mp 194-195 ℃; ^1H NMR (400 MHz, DMSO) δ 11.49 (s, 1H), 8.33 (d, J = 1.7 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.56 – 7.40 (m, 4H), 7.20 – 7.15 (m, 1H), 7.11 – 7.05 (m, 4H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 140.2, 139.7, 135.4, 135.3, 131.5, 129.8, 127.9, 126.4, 126.2, 123.6, 121.9, 121.3, 120.6, 119.1, 112.3, 111.2, 20.5. IR (neat) ν (cm^{-1}): 3397.5, 2916.6, 2849.5, 1891.6, 1597.2, 1449.9, 1332.5, 1239.3, 1088.4, 1015.7, 939.3, 883.4, 803.2, 726.8; HRMS (ESI): caled for $C_{19}H_{16}NS^+$ $[M + H]^+$ 290.0998; found 290.0994.

5-(*p*-tolylthio)-1*H*-indole (3r)



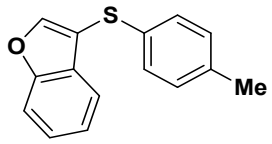
85% (40.7 mg); white solid; mp 51-53 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.80 – 7.79 (m, 1H), 7.35 – 7.32 (m, 1H), 7.28 (dd, J = 8.5, 1.6 Hz, 1H), 7.21 – 7.19 (m, 1H), 7.13 – 7.11 (m, 2H), 7.04 – 7.01 (m, 1H), 6.52 – 6.50 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 135.5, 135.4, 129.6, 128.8, 128.7, 127.5, 126.4, 125.0, 124.2, 112.0, 102.7, 20.9. IR (neat) ν (cm^{-1}): 3412.4, 3017.3, 2918.5, 2860.7, 1489.1, 1451.8, 1410.8, 1308.3, 1084.7, 1015.7, 799.5, 762.2, 723.1, 598.2; HRMS (ESI): caled for $C_{15}H_{14}NS^+$ [M + H]$^+$ 240.0841; found 240.0840.

4-(*p*-tolylthio)isothiazole (3s)



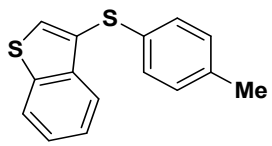
58% (24.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.36 (s, 1H), 7.22 – 7.19 (m, 2H), 7.12 – 7.10 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 147.9, 137.5, 131.5, 130.3, 130.1, 129.6, 21.0. IR (neat) ν (cm^{-1}): 3049.0, 2916.6, 2860.7, 1490.9, 1347.4, 1300.8, 1207.7, 1086.5, 1015.7, 920.7, 801.4, 616.9; HRMS (ESI): caled for $C_{10}H_{10}NS_2^+$ [M + H]$^+$ 208.0249; found 208.0247.

3-(*p*-tolylthio)benzofuran (3t)



The product **3t** was prepared at 80 °C in 77% yield (37.3 mg); white solid; mp 46-47 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.53 – 7.45 (m, 2H), 7.34 – 7.30 (m, 1H), 7.24 – 7.19 (m, 1H), 7.15 – 7.12 (m, 2H), 7.04 – 7.01 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 148.2, 135.9, 132.2, 129.7, 128.1, 127.9, 125.0, 123.3, 120.3, 111.8, 111.2, 20.9. IR (neat) ν (cm^{-1}): 3131.0, 3021.0, 2920.4, 2862.6, 1490.9, 1448.1, 1250.5, 1161.1, 1090.2, 1015.7, 803.2, 747.3; HRMS (ESI): caled for $C_{15}H_{13}OS^+$ [M + H]$^+$ 241.0682; found 241.0670.

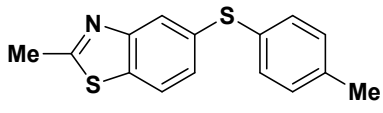
3-(*p*-tolylthio)benzo[*b*]thiophene (3u)



The product **3u** was prepared at 80 °C in 83% yield (42.7 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.77 (m, 2H), 7.60 (s, 1H), 7.39 – 7.32 (m, 2H), 7.12 – 7.09 (m, 2H), 7.03

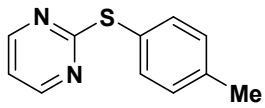
– 7.00 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.8, 136.1, 132.5, 130.8, 129.8, 128.4, 125.0, 124.9, 124.7, 123.0, 122.8, 20.9. IR (neat) ν (cm^{-1}): 3095.6, 3054.6, 3019.1, 2918.5, 2860.7, 1489.1, 1420.1, 1310.2, 1252.4, 1086.5, 1015.7, 803.2, 754.8, 702.6; HRMS (ESI): caled for $C_{15}H_{13}S_2^+$ $[M + H]^+$ 257.0453; found 257.0443.

2-methyl-5-(*p*-tolylthio)benzo[*d*]thiazole (3v)



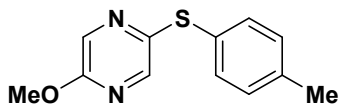
56% (30.2 mg); white solid; mp 70-71 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.15 – 7.13 (m, 2H), 2.80 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 154.0, 137.9, 135.5, 133.7, 132.6, 130.8, 130.2, 126.3, 123.2, 121.6, 21.1, 20.1. IR (neat) ν (cm^{-1}): 3049.0, 2916.6, 2587.0, 1891.6, 1522.6, 1489.1, 1407.1, 1295.2, 1168.5, 1058.6, 1017.6, 903.9, 797.7, 635.5; HRMS (ESI): caled for $C_{15}H_{14}NS_2^+$ $[M + H]^+$ 272.0562; found 272.0564.

2-(*p*-tolylthio)pyrimidine (3w)



39% (X = Br, 15.8 mg); 25% (X = Cl, 10.0 mg); white solid; mp 49-50 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.26 – 7.24 (m, 2H), 6.94 (t, *J* = 4.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 157.5, 139.6, 135.3, 130.1, 125.8, 116.8, 21.4. IR (neat) ν (cm^{-1}): 3356.5, 2918.5, 2851.4, 1545.0, 1490.9, 1369.8, 1170.4, 1103.3, 1015.7, 807.0, 769.7, 516.2; HRMS (ESI): caled for $C_{11}H_{11}N_2S^+$ $[M + H]^+$ 203.0637; found 203.0639.

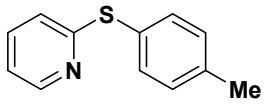
2-methoxy-5-(*p*-tolylthio)pyrazine (3x)



94% (43.8 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.4 Hz, 1H), 7.92 (d, *J* = 1.4 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.18 – 7.15 (m, 2H), 3.92 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 146.6, 140.7, 138.6, 135.1, 133.2, 130.3, 128.8, 53.8, 21.2. IR (neat) ν (cm^{-1}): 3019.1, 2980.0, 2942.7, 2857.0, 1565.5, 1528.2, 1455.5, 1420.1,

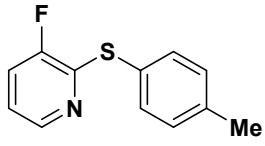
1328.8, 1267.3, 1161.1, 1019.4, 890.8, 807.0, 676.5; HRMS (ESI): caled for $C_{12}H_{13}N_2OS^+$ $[M + H]^+$ 233.0743; found 233.0745.

2-(*p*-tolylthio)pyridine (3y)



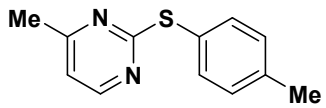
88% (35.4 mg); white solid; mp 31-32 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.39 (m, 1H), 7.50 – 7.47 (m, 2H), 7.44 – 7.39 (m, 1H), 7.25 – 7.22 (m, 2H), 6.98 – 6.94 (m, 1H), 6.85 – 6.82 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 149.4, 139.4, 136.5, 135.2, 130.4, 127.2, 120.8, 119.5, 21.3. IR (neat) ν (cm^{-1}): 3043.4, 2920.4, 2864.5, 1571.1, 1492.8, 1446.2, 1414.5, 1278.5, 1123.8, 1043.7, 1017.6, 985.9, 808.8, 754.8, 721.2, 616.9; HRMS (ESI): caled for $C_{12}H_{12}NS^+$ $[M + H]^+$ 202.0685; found 202.0687.

3-fluoro-2-(*p*-tolylthio)pyridine (3z)



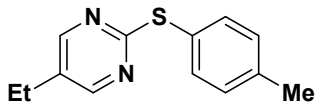
74% (32.7 mg); colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.30 – 7.20 (m, 3H), 7.06 – 7.01 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (d, *J* = 257.2 Hz), 145.3 (d, *J* = 5.2 Hz), 139.0, 134.9, 130.0, 125.4, 121.9, 121.7, 121.2 (d, *J* = 2.9 Hz), 21.3. IR (neat) ν (cm^{-1}): 3356.5, 3177.6, 3058.3, 2920.4, 2849.5, 1586.0, 1492.8, 1446.2, 1410.8, 1259.8, 1205.8, 1077.2, 1017.6, 792.1, 725.0, 674.6; HRMS (ESI): caled for $C_{12}H_{11}FNS^+$ $[M + H]^+$ 220.0591; found 220.0590.

4-methyl-2-(*p*-tolylthio)pyrimidine (3aa)



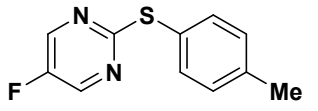
42% (18.4 mg); white solid; mp 40-42 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 5.1 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.24 – 7.22 (m, 2H), 6.80 (d, *J* = 5.1 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 167.7, 157.1, 139.3, 135.2, 130.0, 126.1, 116.6, 24.1, 21.4. IR (neat) ν (cm^{-1}): 3356.5, 3073.2, 3017.3, 2955.8, 2920.4, 2851.4, 1535.7, 1412.7, 1321.3, 1202.1, 1015.7, 807.0, 702.6, 581.5; HRMS (ESI): caled for $C_{12}H_{13}N_2S^+$ $[M + H]^+$ 217.0794; found 217.0792.

5-ethyl-2-(*p*-tolylthio)pyrimidine (3bb)



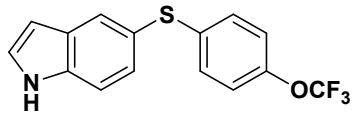
26% (12.1 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2H), 7.52 – 7.50 (m, 2H), 7.25 – 7.23 (m, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 157.1, 139.4, 135.2, 132.0, 130.1, 126.2, 23.0, 21.4, 15.0. IR (neat) ν (cm^{-1}): 3017.3, 2967.0, 2924.1, 2871.9, 1578.5, 1537.5, 1492.8, 1388.4, 1233.7, 1155.5, 1017.6, 930.0, 807.0, 629.9; HRMS (ESI): caled for $C_{13}H_{15}N_2S^+$ [M + H]$^+$ 231.0950; found 231.0953.

5-fluoro-2-(*p*-tolylthio)pyrimidine (3cc)



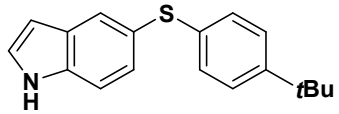
34% (14.9 mg); white solid; mp 38-39 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 7.51 – 7.48 (m, 2H), 7.26 – 7.24 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (d, *J* = 261.1 Hz), 145.6, 145.4, 139.8, 135.3, 130.2, 125.9, 21.4. IR (neat) ν (cm^{-1}): 3035.9, 2922.2, 2862.6, 1554.3, 1492.8, 1384.7, 1239.3, 1174.1, 1017.6, 922.5, 807.0, 760.4, 648.6; HRMS (ESI): caled for $C_{11}H_{10}FN_2S^+$ [M + H]$^+$ 221.0543; found 221.0542.

5-((4-(trifluoromethoxy)phenyl)thio)-1*H*-indole (3dd)



89% (55.3 mg); white solid; mp 54-56 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.86 – 7.86 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.25 – 7.23 (m, 1H), 7.15 – 7.10 (m, 2H), 7.03 (dd, *J* = 8.9, 0.8 Hz, 2H), 6.56 – 6.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 138.8, 135.8, 129.0, 128.4, 128.3, 127.7, 125.3, 122.2, 121.5, 120.4 (q, *J* = 257.0 Hz), 112.3, 102.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.0. IR (neat) ν (cm^{-1}): 3397.5, 1485.3, 1455.5, 1217.0, 1155.5, 1084.7, 1013.8, 887.1, 803.2, 728.7, 663.5, 607.6; HRMS (ESI): caled for $C_{15}H_{11}F_3NOS^+$ [M + H]$^+$ 310.0508; found 310.0509.

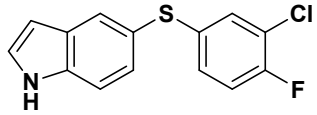
5-((4-(*tert*-butyl)phenyl)thio)-1*H*-indole (3ee)



87% (48.9 mg); white solid; mp 95-96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.83 – 7.82 (m, 1H), 7.35 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 7.14 – 7.11 (m, 2H), 6.52 – 6.51 (m, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 135.8, 135.5, 128.8, 127.9, 127.9, 126.9,

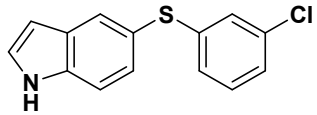
125.9, 125.0, 123.6, 112.0, 102.7, 34.3, 31.3. IR (neat) ν (cm^{-1}): 3330.4, 2957.6, 2866.3, 1449.9, 1306.4, 1116.3, 1064.2, 885.2, 805.1, 719.4, 603.8; HRMS (ESI): caled for $C_{18}H_{20}NS^+$ $[M + H]^+$ 282.1311; found 282.1312.

5-((3-chloro-4-fluorophenyl)thio)-1*H*-indole (3ff)



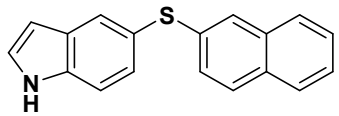
83% (46.2 mg); white solid; mp 76-78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.83 – 7.83 (m, 1H), 7.41 – 7.38 (m, 1H), 7.30 – 7.27 (m, 1H), 7.27 – 7.25 (m, 1H), 7.17 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.99 – 6.94 (m, 1H), 6.57 – 6.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (d, *J* = 247.4 Hz), 136.3 (d, *J* = 3.8 Hz), 135.8, 129.6, 128.9, 128.0, 127.5 (d, *J* = 6.9 Hz), 127.4, 125.3, 122.5, 121.4 (d, *J* = 18.3 Hz), 116.8 (d, *J* = 21.6 Hz), 112.3, 102.9. IR (neat) ν (cm^{-1}): 3408.7, 2920.4, 2849.5, 1720.2, 1571.1, 1477.9, 1410.8, 1313.9, 1231.9, 1097.7, 1053.0, 885.2, 810.7, 760.4, 730.6, 600.1; HRMS (ESI): caled for $C_{14}H_{10}ClFNS^+$ $[M + H]^+$ 278.0201; found 278.0200.

5-((3-chlorophenyl)thio)-1*H*-indole (3gg)



88% (45.9 mg); white solid; mp 57-58 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.87 – 7.86 (m, 1H), 7.40 – 7.37 (m, 1H), 7.31 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.11 – 6.97 (m, 4H), 6.56 – 6.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 135.9, 134.7, 129.7, 128.9, 128.5, 128.0, 126.6, 125.3, 125.2, 125.1, 121.5, 112.3, 102.9. IR (neat) ν (cm^{-1}): 3421.7, 3054.6, 2920.4, 2853.2, 1574.8, 1453.7, 1407.1, 1308.3, 1080.9, 889.0, 762.2, 725.0, 676.5, 598.2; HRMS (ESI): caled for $C_{14}H_{11}ClNS^+$ $[M + H]^+$ 260.0295; found 260.0293.

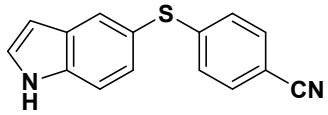
5-(naphthalen-2-ylthio)-1*H*-indole (3hh)



92% (50.8 mg); white solid; mp 130-131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.89 – 7.88 (m, 1H), 7.75 – 7.72 (m, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.40 – 7.35 (m, 4H), 7.30 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.23 – 7.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 135.6, 133.8, 131.5, 128.9, 128.3, 128.1, 127.6, 127.1, 127.1, 126.5, 126.4, 125.7,

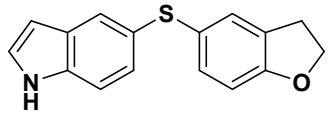
125.4, 125.1, 123.1, 112.1, 102.8. IR (neat) ν (cm^{-1}): 3356.5, 3054.6, 1586.0, 1453.7, 1338.1, 1310.2, 1196.5, 1066.0, 957.9, 861.0, 807.0, 732.4, 598.2; HRMS (ESI): caled for $C_{18}H_{14}NS^+$ $[M + H]^+$ 276.0841; found 276.0839.

4-((1*H*-indol-5-yl)thio)benzonitrile (3ii)



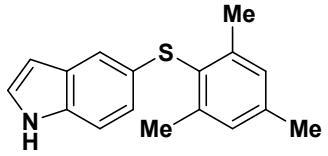
81% (40.4 mg); white solid; mp 141-143 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.89 – 7.88 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.08 – 7.04 (m, 2H), 6.60 – 6.58 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 136.2, 132.1, 129.2, 128.9, 128.8, 125.8, 125.6, 119.3, 119.1, 112.7, 107.4, 102.9. IR (neat) ν (cm^{-1}): 3421.7, 2227.1, 1587.8, 1483.5, 1401.5, 1310.2, 1243.1, 1179.7, 1079.1, 887.1, 807.0, 736.1, 616.9, 581.5; HRMS (ESI): caled for $C_{15}H_{11}N_2S^+$ $[M + H]^+$ 251.0637; found 251.0636.

5-((2,3-dihydrobenzofuran-5-yl)thio)-1*H*-indole (3jj)



81% (43.2 mg); white solid; mp 72-74 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.69 – 7.68 (m, 1H), 7.32 – 7.29 (m, 1H), 7.25 – 7.14 (m, 4H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.50 – 6.48 (m, 1H), 4.54 (t, *J* = 8.7 Hz, 2H), 3.12 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 135.0, 131.3, 128.6, 128.2, 128.1, 127.9, 126.7, 126.0, 124.9, 124.3, 111.8, 109.8, 102.5, 71.4, 29.6. IR (neat) ν (cm^{-1}): 3352.7, 2968.8, 2892.4, 1584.1, 1477.9, 1313.9, 1237.5, 1164.8, 1107.0, 877.8, 808.8, 725.0, 609.4; HRMS (ESI): caled for $C_{16}H_{14}NOS^+$ $[M + H]^+$ 268.0791; found 268.0792.

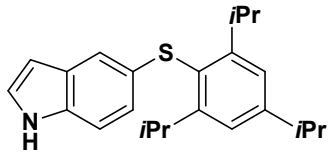
5-(mesitylthio)-1*H*-indole (3kk)



82% (44.1 mg); white solid; mp 115-116 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.21 – 7.18 (m, 2H), 7.11 – 7.10 (m, 1H), 6.99 (s, 2H), 6.90 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.37 – 6.36 (m, 1H), 2.42 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.6, 134.0, 129.2, 129.0, 128.7, 128.2, 124.6, 121.5, 118.4, 111.5, 102.1, 21.9, 21.1. IR (neat) ν (cm^{-1}): 3371.4, 2916.6, 1569.2, 1451.8, 1418.3, 1312.0, 1243.1, 1053.0,

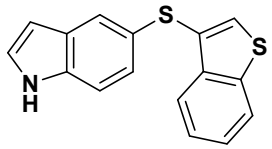
866.6, 799.5, 760.4, 736.1, 598,2; HRMS (ESI): caled for $C_{17}H_{18}NS^+$ $[M + H]^+$ 268.1154; found 268.1156.

5-((2,4,6-triisopropylphenyl)thio)-1*H*-indole (3ll)



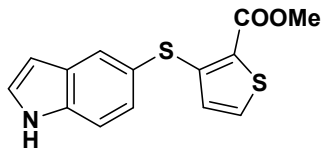
78% (54.5 mg); white solid; mp 94-95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.19 – 7.17 (m, 2H), 7.11 (s, 2H), 7.08 – 7.07 (m, 1H), 6.86 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.37 – 6.35 (m, 1H), 3.87 – 3.79 (m, 2H), 2.98 – 2.90 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 150.2, 133.8, 130.1, 128.6, 126.5, 124.6, 122.1, 120.9, 117.8, 111.4, 102.0, 34.3, 31.6, 24.3, 23.9. IR (neat) ν (cm^{-1}): 3404.9, 2957.6, 2866.3, 1597.2, 1565.5, 1449.9, 1306.4, 1099.6, 1056.7, 937.4, 874.1, 805.1, 721.2; HRMS (ESI): caled for $C_{23}H_{29}NSNa^+$ $[M + Na]^+$ 352.2093; found 352.2092.

5-(benzo[*b*]thiophen-3-ylthio)-1*H*-indole (3mm)



80% (45.0 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92 – 7.84 (m, 2H), 7.73 – 7.72 (m, 1H), 7.40 (s, 1H), 7.38 – 7.35 (m, 2H), 7.30 – 7.28 (m, 1H), 7.25 – 7.23 (m, 1H), 7.18 – 7.17 (m, 1H), 6.48 – 6.47 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 138.6, 135.0, 128.7, 127.8, 127.5, 125.0, 125.0, 124.7, 124.6, 124.4, 123.4, 122.9, 122.8, 111.8, 102.5. IR (neat) ν (cm^{-1}): 3418.0, 3095.6, 3056.4, 1567.3, 1451.8, 1410.8, 1306.4, 1252.4, 1196.5, 1060.4, 1017.6, 954.2, 889.0; HRMS (ESI): caled for $C_{16}H_{12}NS_2^+$ $[M + H]^+$ 282.0406; found 282.0404.

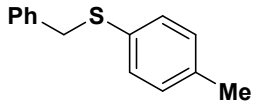
methyl 3-((1*H*-indol-5-yl)thio)thiophene-2-carboxylate (3nn)



61% (35.3 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.97 – 7.91 (m, 1H), 7.47 – 7.38 (m, 2H), 7.30 – 7.28 (m, 1H), 7.20 (d, *J* = 5.3 Hz, 1H), 6.59 – 6.57 (m, 1H), 6.25 (d, *J* = 5.3 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 148.1, 136.1, 130.2, 129.0, 128.9, 128.5, 128.1, 125.4, 121.9, 119.8, 112.3, 103.0, 52.0. IR (neat) ν (cm^{-1}): 3254.0, 2950.2, 1656.8, 1492.8, 1436.9, 14.5.2, 1349.3,

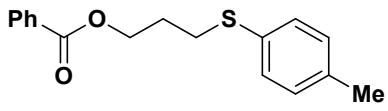
1250.5, 1190.9, 1075.3, 889.0; HRMS (ESI): caled for $C_{14}H_{12}NO_2S_2^+$ $[M + H]^+$ 290.0304; found 290.0303.

benzyl(*p*-tolyl)sulfane (5a)



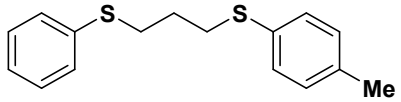
73% (31.4 mg); white solid; mp 35-36 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 3H), 7.24 – 7.19 (m, 3H), 7.07 – 7.04 (m, 2H), 4.06 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.5, 132.4, 130.7, 129.6, 128.8, 128.4, 127.0, 39.8, 21.0. IR (neat) ν (cm^{-1}): 3062.0, 3028.5, 2920.4, 2864.5, 1599.0, 1492.8, 1451.8, 1235.6, 1090.2, 799.5, 695.1, 564.7; HRMS (EI): caled for $C_{14}H_{14}S$ [M] 214.0816; found 214.0811.

3-(*p*-tolylthio)propyl benzoate (5b)



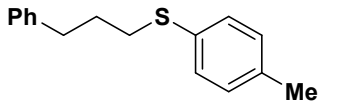
81% (42.6 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.41 (m, 2H), 7.30 – 7.27 (m, 2H), 7.11 – 7.08 (m, 2H), 4.42 (t, J = 6.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.10 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 136.4, 132.9, 132.0, 130.4, 130.2, 129.7, 129.5, 128.3, 63.3, 31.1, 28.5, 21.0. IR (neat) ν (cm^{-1}): 3062.0, 2955.8, 2920.4, 1716.4, 1600.9, 1492.8, 1449.9, 1313.9, 1267.3, 1176.0, 1110.7, 1026.9, 803.2, 708.2; HRMS (ESI): caled for $C_{17}H_{18}O_2SNa^+$ $[M + Na]^+$ 309.0920; found 309.0917.

phenyl(3-(*p*-tolylthio)propyl)sulfane (5c)



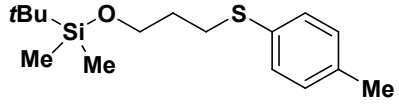
86% (47.4 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.22 (m, 3H), 7.19 – 7.14 (m, 1H), 7.09 – 7.06 (m, 2H), 3.04 – 2.97 (m, 4H), 2.31 (s, 3H), 1.95 – 1.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 136.1, 132.1, 130.3, 129.7, 129.3, 128.9, 126.0, 33.2, 32.3, 28.3, 21.0. IR (neat) ν (cm^{-1}): 3054.6, 3017.3, 2918.5, 2855.1, 1582.3, 1492.8, 1436.9, 1246.8, 1090.2, 1025.0, 801.4, 736.1, 689.6, 542.3; HRMS (ESI): caled for $C_{16}H_{18}S_2Na^+$ $[M + Na]^+$ 297.0742; found 297.0745.

(3-phenylpropyl)(*p*-tolyl)sulfane (5d)



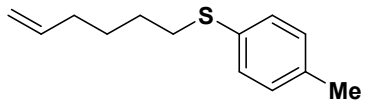
83% (40.3 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 7.20 – 7.15 (m, 3H), 7.09 – 7.06 (m, 2H), 2.92 – 2.82 (m, 2H), 2.78 – 2.69 (m, 2H), 2.31 (s, 3H), 1.96 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.0, 132.6, 130.0, 129.6, 128.5, 128.4, 125.9, 34.6, 33.6, 30.7, 21.0. IR (neat) ν (cm^{-1}): 3062.0, 3024.7, 2920.4, 2855.1, 1602.8, 1492.8, 1451.8, 1092.1, 799.5, 743.6, 698.9, 566.6; HRMS (ESI): caled for $C_{16}H_{19}S^+$ $[M + H]^+$ 243.1202; found 243.1203.

tert-butyldimethyl(3-(_p_-tolylthio)propoxy)silane (5e)



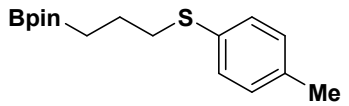
75% (44.3 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.13 – 7.11 (m, 2H), 3.73 (t, J = 6.0 Hz, 2H), 3.06 – 2.92 (m, 2H), 2.34 (s, 3H), 1.87 – 1.81 (m, 2H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 132.8, 129.7, 129.6, 61.4, 32.2, 30.6, 25.9, 21.0, 18.3, -5.4. IR (neat) ν (cm^{-1}): 2953.9, 2927.8, 2857.0, 1492.8, 1254.2, 1092.1, 948.6, 833.1, 803.2, 773.4, 661.6, 542.3; HRMS (ESI): caled for $C_{16}H_{29}OSSi^+$ $[M + H]^+$ 297.1703; found 297.1708.

hex-5-en-1-yl(_p_-tolyl)sulfane (5f)



84% (34.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 2H), 7.10 – 7.07 (m, 2H), 5.84 – 5.72 (m, 1H), 5.02 – 4.92 (m, 2H), 2.90 – 2.84 (m, 2H), 2.31 (s, 3H), 2.09 – 2.02 (m, 2H), 1.68 – 1.59 (m, 2H), 1.55 – 1.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 135.9, 133.0, 129.8, 129.6, 114.7, 34.2, 33.2, 28.7, 28.0, 21.0. IR (neat) ν (cm^{-1}): 3075.1, 2924.1, 2855.1, 1640.0, 1492.8, 1436.9, 1209.5, 1092.1, 991.5, 909.5, 799.5, 631.8; HRMS (ESI): caled for $C_{13}H_{19}S^+$ $[M + H]^+$ 207.1202; found 207.1202.

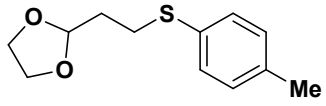
4,4,5,5-tetramethyl-2-(3-(_p_-tolylthio)propyl)-1,3,2-dioxaborolane (5g)



57% (33.2 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 2H), 7.08 – 7.07 (m, 2H), 2.90 – 2.87 (m, 2H), 2.31 (s, 3H), 1.77 – 1.71 (m, 2H), 1.24 (s, 12H), 0.90 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 133.2, 129.5, 129.4, 83.0, 36.3, 24.8, 24.0, 20.9.

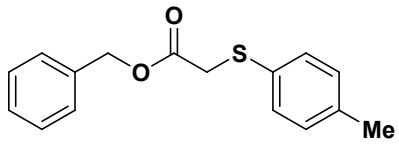
IR (neat) ν (cm^{-1}): 2978.1, 2924.1, 1492.8, 1369.8, 1313.9, 1224.4, 1142.4, 1092.1, 967.2, 848.0, 801.4, 672.8; HRMS (ESI): caled for $C_{16}H_{25}BO_2SNa^+$ $[M + Na]^+$ 315.1561; found 315.1559.

2-(2-(*p*-tolylthio)ethyl)-1,3-dioxolane (5h)



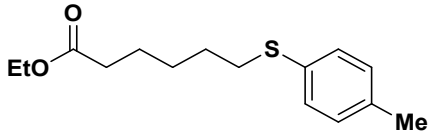
76% (34.0 mg); colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 2H), 7.10 – 7.08 (m, 2H), 4.97 (t, *J* = 4.5 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.88 – 3.81 (m, 2H), 2.99 – 2.96 (m, 2H), 2.31 (s, 3H), 1.99 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 132.3, 130.0, 129.7, 103.1, 64.9, 33.6, 28.6, 21.0. IR (neat) ν (cm^{-1}): 2950.2, 2879.4, 1492.8, 1436.9, 1397.8, 1211.4, 1129.4, 1015.7, 943.0, 875.9, 803.2, 697,0; HRMS (ESI): caled for $C_{12}H_{16}O_2SNa^+$ $[M + Na]^+$ 247.0763; found 247.0767.

benzyl 2-(*p*-tolylthio)acetate (5i)



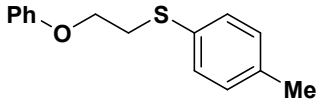
72% (39.2 mg); colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 7H), 7.08 – 7.05 (m, 2H), 5.12 (s, 2H), 3.61 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 137.4, 135.4, 131.1, 130.9, 129.8, 128.5, 128.3, 128.2, 67.1, 37.4, 21.0. IR (neat) ν (cm^{-1}): 3065.7, 3032.2, 2553.9, 2922.2, 1731.3, 1492.8, 1407.1, 1265.4, 1120.1, 971.0, 805.1, 736.1, 695.1, 575.9; HRMS (ESI): caled for $C_{16}H_{16}O_2SNa^+$ $[M + Na]^+$ 295.0763; found 295.0764.

ethyl 6-(*p*-tolylthio)hexanoate (5j)



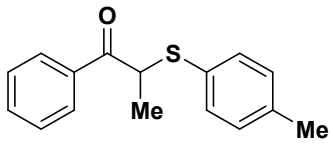
93% (49.6 mg); colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.10 – 7.08 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.90 – 2.82 (m, 2H), 2.31 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.59 (m, 4H), 1.48 – 1.41 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 135.9, 132.8, 129.9, 129.6, 60.2, 34.1, 28.8, 28.2, 24.5, 20.9, 14.2. IR (neat) ν (cm^{-1}): 2980.0, 2929.7, 2860.7, 1731.3, 1492.8, 1459.3, 1371.7, 1254.2, 1177.8, 1092.1, 1017.6, 801.4; HRMS (ESI): caled for $C_{15}H_{22}O_2SNa^+$ $[M + Na]^+$ 289.1233; found 289.1237.

(2-phenoxyethyl)(*p*-tolyl)sulfane (5k)



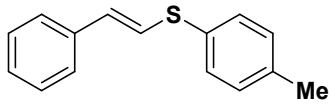
81% (39.6 mg); white solid; mp 39-41 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 2H), 7.27 – 7.23 (m, 2H), 7.12 – 7.10 (m, 2H), 6.95 – 6.92 (m, 1H), 6.86 – 6.83 (m, 2H), 4.11 (t, *J* = 7.1 Hz, 2H), 3.23 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 136.8, 131.5, 130.7, 129.8, 129.4, 121.0, 114.5, 66.5, 33.5, 21.0. IR (neat) ν (cm^{-1}): 3062.0, 3043.4, 2918.5, 2868.2, 2728.4, 1599.0, 1489.1, 1422.0, 1377.3, 1239.3, 1170.4, 1080.9, 1012.0, 879.7, 799.5, 747.3, 687.7; HRMS (ESI): caled for $C_{15}H_{16}OSNa^+$ [M + Na]$^+$ 267.0814; found 267.0827.

1-phenyl-2-(*p*-tolylthio)propan-1-one (5l)



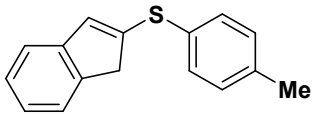
$Ni(PCy_3)_2Cl_2$ was used for the preparation of **5l** in the absence of dtbbpy. 27% (13.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 7.24 – 7.22 (m, 2H), 7.09 – 7.07 (m, 2H), 4.56 (q, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 139.0, 135.8, 135.2, 133.0, 129.7, 128.6, 128.5, 127.7, 46.1, 21.2, 16.8. IR (neat) ν (cm^{-1}): 2972.2, 2925.3, 1677.3, 1595.5, 1491.1, 1447.3, 1371.2, 1329.2, 1230.2, 1176.6, 1000.7, 949.0, 811.1, 798.1, 716.1, 686.2. HRMS (ESI): caled for $C_{16}H_{16}NaOS^+$ [M + Na]$^+$ 279.0814; found 279.0817.

(*E*)-styryl(p-tolyl)sulfane (7a)



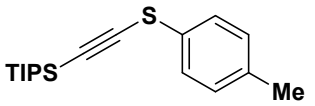
68% (38.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.26 (m, 6H), 7.23 – 7.13 (m, 3H), 6.87 – 6.43 (m, 2H), 2.35 – 2.30 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4*, 137.3, 136.6, 136.5*, 131.1*, 130.6, 130.5*, 130.5, 129.9, 129.9*, 128.7*, 128.6, 128.3*, 127.4, 127.0*, 127.0, 126.5*, 126.4*, 125.9, 124.4, 21.1. IR (neat) ν (cm^{-1}): 3056.4, 3021.0, 2920.4, 2862.6, 1597.2, 1490.9, 1090.2, 937.4, 803.2, 736.1, 689.6. HRMS (EI): caled for $C_{15}H_{14}S$ [M] 226.0816; found 226.0811.

(1*H*-inden-2-yl)(*p*-tolyl)sulfane (7b)



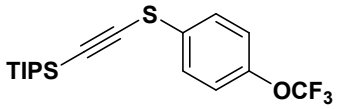
92% (43.7 mg); white solid; mp 51-52 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.30 – 7.28 (m, 1H), 7.20 – 7.15 (m, 4H), 7.10 – 7.06 (m, 1H), 6.56 (s, 1H), 3.42 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 143.3, 143.0, 138.2, 132.9, 130.0, 129.8, 129.1, 126.5, 124.0, 123.2, 119.7, 41.9, 21.2. IR (neat) ν (cm^{-1}): 3065.7, 3021.0, 2918.5, 2864.5, 1604.6, 1537.5, 1490.9, 1455.5, 1390.3, 1269.2, 1015.7, 807.0, 749.2, 713.8; HRMS (ESI): caled for $C_{16}H_{15}S^+$ $[M + H]^+$ 239.0889; found 239.0890.

triisopropyl((*p*-tolylthio)ethynyl)silane (9a)



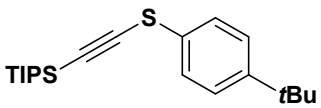
71% (43.4 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.16 – 7.13 (m, 2H), 2.33 (s, 3H), 1.13 – 1.10 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 129.9, 129.1, 126.2, 102.5, 91.8, 20.9, 18.6, 11.4. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2091.0, 1490.9, 1459.3, 1082.8, 995.2, 859.2, 801.4, 676.5, 590.8; HRMS (ESI): caled for $C_{18}H_{29}SSi^+$ $[M + H]^+$ 305.1754; found 305.1751.

triisopropyl(((4-(trifluoromethoxy)phenyl)thio)ethynyl)silane (9b)



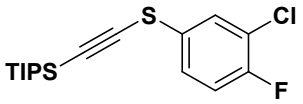
39% (28.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.21 – 7.18 (m, 2H), 1.32 – 0.91 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 131.7, 127.2, 121.9, 120.4 (q, *J* = 257.4 Hz), 104.1, 90.3, 18.6, 11.3. IR (neat) ν (cm^{-1}): 2944.6, 2866.3, 2092.9, 1489.1, 1463.0, 1254.2, 1205.8, 1162.9, 1080.9, 1015.7, 918.8, 857.3, 659.7, 590.8; HRMS (ESI): caled for $C_{18}H_{26}F_3OSSi^+$ $[M + H]^+$ 375.1420; found 375.1422.

(((4-(*tert*-butyl)phenyl)thio)ethynyl)triisopropylsilane (9c)



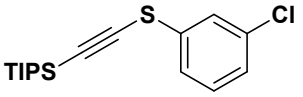
50% (34.8 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 1.31 (s, 3H), 1.19 – 1.00 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 129.1, 126.3, 125.8, 102.7, 91.5, 34.5, 31.3, 18.6, 11.4. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2091.0, 1459.3, 1364.2, 1116.3, 1012.0, 859.2, 821.9, 736.1, 676.5, 592.6; HRMS (ESI): caled for $C_{21}H_{34}SSiNa^+$ $[M + Na]^+$ 369.2043; found 369.2045.

(((3-chloro-4-fluorophenyl)thio)ethynyl)triisopropylsilane (9d)



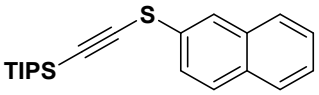
68% (46.4 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 6.6, 2.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.11 (t, J = 8.6 Hz, 1H), 1.22 – 0.94 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, J = 248.9 Hz), 129.4 (d, J = 3.8 Hz), 128.1, 125.7 (d, J = 7.2 Hz), 122.2 (d, J = 18.7 Hz), 117.2 (d, J = 22.2 Hz), 104.5, 90.2, 18.6, 11.3. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2092.9, 1479.8, 1261.7, 1094.0, 1056.7, 995.2, 857.3, 810.7, 713.8, 676.5, 592.6; HRMS (EI): caled for $C_{17}H_{24}ClFSSi$ [M] 342.1041; found 342.1043.

(((3-chlorophenyl)thio)ethynyl)triisopropylsilane (9e)



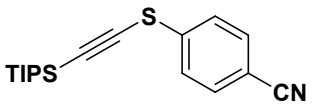
87% (56.6 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, 1H), 7.27 – 7.24 (m, 2H), 7.18 (dt, J = 7.0, 1.9 Hz, 1H), 1.16 – 1.08 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 135.0, 130.0, 126.5, 125.7, 123.9, 104.8, 89.8, 18.6, 11.3. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2092.9, 1576.7, 1459.3, 1408.9, 1071.6, 995.2, 857.3, 769.7, 672.8, 590.8; HRMS (ESI): caled for $C_{17}H_{26}ClSSi^+$ $[M + H]^+$ 325.1208; found 325.1205.

triisopropyl((naphthalen-2-ylthio)ethynyl)silane (9f)



51% (34.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.79 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 1.22 – 1.09 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 132.0, 130.2, 128.8, 127.8, 127.0, 126.8, 125.9, 124.3, 123.9, 103.6, 91.2, 18.7, 11.4. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2091.0, 1589.7, 1459.3, 1133.1, 1064.2, 995.2, 881.5, 849.8, 807.0, 739.9, 676.5, 590.8; HRMS (ESI): caled for $C_{21}H_{28}SSiNa^+$ $[M + Na]^+$ 363.1573; found 363.1571.

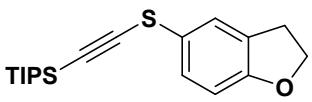
4-(((triisopropylsilyl)ethynyl)thio)benzonitrile (9g)



61% (38.2 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.53 – 7.51 (m, 2H), 1.29 – 0.89 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 132.5, 125.9, 118.4, 109.7, 106.4, 88.2, 18.6, 11.2. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2228.9, 2094.8, 1591.6, 1459.3,

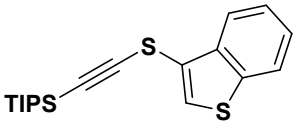
1401.5, 1079.1, 995.2, 881.5, 855.4, 821.9, 676.5, 590.8, 542.3; HRMS (ESI): caled for $C_{18}H_{25}NSSiNa^+$ $[M + Na]^+$ 338.1369; found 338.1368.

(((2,3-dihydrobenzofuran-5-yl)thio)ethynyl)triisopropylsilane (9h)



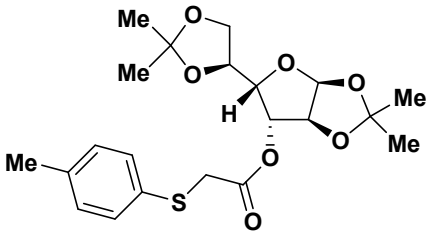
48% (31.9 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.31 (m, 1H), 7.20 – 7.17 (m, 1H), 6.75 (d, J = 8.4 Hz, 1H), 4.58 (t, J = 8.7 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H), 1.13 – 1.04 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 128.6, 127.3, 124.2, 122.4, 110.1, 101.2, 93.2, 71.5, 29.6, 18.6, 11.4. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2089.2, 1466.7, 1231.9, 982.2, 943.0, 855.4, 810.7, 676.5, 594.5; HRMS (ESI): caled for $C_{19}H_{29}OSSi^+$ $[M + H]^+$ 333.1703; found 333.1707.

((benzo[*b*]thiophen-3-ylthio)ethynyl)triisopropylsilane (9i)



64% (44.3 mg); colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.53 (s, 1H), 7.44 – 7.37 (m, 2H), 1.07 (s, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 137.0, 125.0, 124.8, 124.5, 122.9, 122.2, 100.6, 91.1, 18.6, 11.3. IR (neat) ν (cm^{-1}): 2942.7, 2864.5, 2092.9, 1459.3, 1422.0, 1315.8, 1256.1, 1062.3, 995.2, 881.5; HRMS (ESI): caled for $C_{19}H_{27}S_2Si^+$ $[M + H]^+$ 347.1318; found 347.1317.

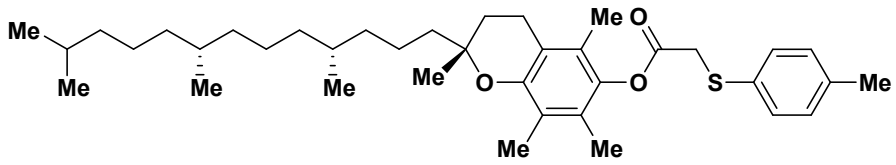
(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 2-(*p*-tolylthio)acetate (10a)



52% (43.4 mg); white solid; mp 77-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.14 – 7.11 (m, 2H), 5.69 (d, J = 3.7 Hz, 1H), 5.23 (d, J = 2.3 Hz, 1H), 4.22 (d, J = 3.7 Hz, 1H), 4.18 – 4.12 (m, 2H), 4.06 – 3.96 (m, 2H), 3.65 – 3.56 (m, 2H), 2.33 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 137.7, 131.3, 130.6, 129.9, 112.3, 109.4, 105.0, 83.1, 79.7, 76.8, 72.2, 67.2, 37.3, 26.8, 26.6, 26.1, 25.2, 21.1. IR (neat) ν (cm^{-1}): 2991.2, 2922.2, 1735.1, 1492.8, 1371.7, 1211.4, 1123.8,

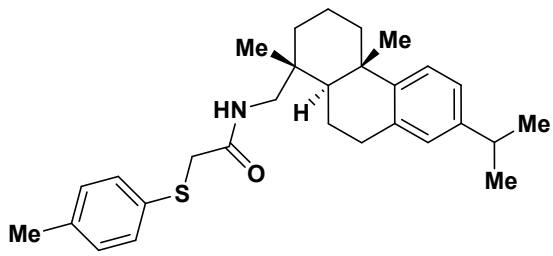
1079.1, 1015.7, 941.2, 810.7, 643.0; HRMS (ESI): caled for $C_{21}H_{29}O_7S^+$ $[M + H]^+$ 425.1629; found 425.1631.

(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 2-(*p*-tolylthio)acetate (10b)



75% (88.5 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.12 – 7.09 (m, 2H), 3.84 (s, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.31 (s, 3H), 2.09 – 1.90 (m, 9H), 1.83 – 1.68 (m, 2H), 1.58 – 1.48 (m, 3H), 1.43 – 1.02 (m, 21H), 0.88 – 0.83 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 149.5, 140.3, 137.3, 131.2, 130.7, 129.8, 126.6, 124.9, 123.0, 117.3, 75.0, 39.3, 37.4, 37.4, 37.3, 37.0, 32.8, 32.7, 27.9, 24.8, 24.4, 22.7, 22.6, 21.0, 21.0, 20.5, 19.7, 19.6, 12.8, 12.0, 11.8. IR (neat) ν (cm^{-1}): 2924.1, 2866.3, 1751.8, 1459.3, 1377.3, 1241.2, 1105.2, 1064.2, 922.5, 803.2, 736.1; HRMS (ESI): caled for $C_{38}H_{59}O_3S^+$ $[M + H]^+$ 595.4179; found 595.4176.

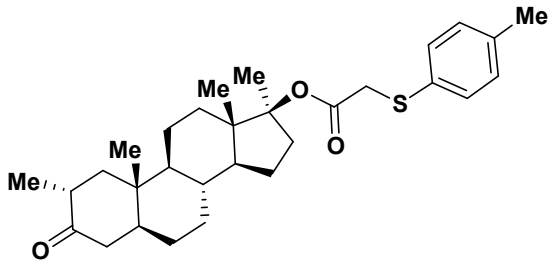
***N*-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2-(*p*-tolylthio)acetamide (10c)**



48% (42.4 mg); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 1H), 7.03 – 6.95 (m, 4H), 6.89 (s, 1H), 6.71 – 6.68 (m, 2H), 3.68 – 3.56 (m, 2H), 3.26 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.01 – 2.71 (m, 4H), 2.14 – 2.08 (m, 4H), 1.86 – 1.78 (m, 1H), 1.71 – 1.57 (m, 2H), 1.52 – 1.45 (m, 1H), 1.29 – 1.11 (m, 11H), 1.04 – 0.82 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 147.1, 145.5, 136.3, 134.7, 130.3, 129.9, 127.3, 126.7, 124.3, 123.7, 49.6, 44.6, 37.8, 37.5, 37.3, 36.9, 35.8, 33.4, 30.4, 25.3, 24.0, 20.8, 18.8, 18.8, 18.4. IR (neat) ν (cm^{-1}): 3313.6, 2924.1, 2868.2, 1653.1, 1528.2, 1492.8, 1457.4, 1382.8, 1090.2,

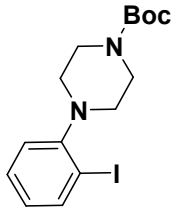
1015.7, 909.5, 801.4, 730.6, 620.6; HRMS (ESI): caled for $C_{29}H_{40}NOS^+$ $[M + H]^+$ 450.2825; found 450.2827.

(2R,5S,8R,9S,10S,13S,14S,17S)-2,10,13,17-tetramethyl-3-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-(*p*-tolylthio)acetate (10d)



73% (70.1 mg); white solid; mp 115-116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.11 – 7.08 (m, 2H), 3.53 (s, 2H), 2.46 (m, 1H), 2.35 – 2.27 (m, 4H), 2.11 – 1.95 (m, 4H), 1.72 – 1.17 (m, 14H), 1.14 – 0.98 (m, 8H), 0.93 – 0.64 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 168.8, 136.7, 131.5, 130.2, 129.6, 92.1, 53.7, 48.8, 48.5, 47.9, 46.5, 44.6, 41.0, 37.9, 36.4, 36.2, 35.6, 31.8, 31.4, 28.5, 23.5, 21.1, 21.0, 20.9, 14.5, 14.3, 12.3. IR (neat) ν (cm^{-1}): 2914.8, 2860.7, 1710.8, 1492.8, 1442.5, 1371.7, 1293.4, 1179.7, 1133.1, 1039.9, 900.2, 808.8, 734.3; HRMS (ESI): caled for $C_{30}H_{43}O_3S^+$ $[M + H]^+$ 483.2927; found 483.2924.

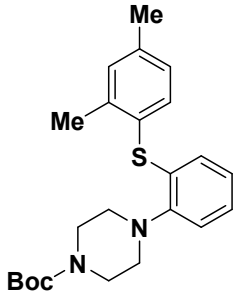
***tert*-butyl 4-(2-iodophenyl)piperazine-1-carboxylate (11)**



Under argon, to a suspension of $Pd_2(dba)_3$ (0.025 mmol, 2.5 mol%), BINAP (0.075 mmol, 7.5 mol%), *tert*-butyl piperazine-1-carboxylate (1.0 mmol, 1.0 equiv) and *t*-BuONa (1.2 mmol, 1.2 equiv) in toluene (2.5 mL) was added 1,2-diiodobenzene (2.0 mmol, 2.0 equiv) at room temperature. After that, the reaction mixture was stirred at 80 ℃ for 24 h. Then, distilled water (40 mL) was added and the aqueous layer was extracted with Et_2O (3 × 15mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **9** in 40% yield; light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.9, 1.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.00 (dd, J = 8.0, 1.5 Hz, 1H), 6.83 – 6.79 (m, 1H), 3.62 (s, 4H), 2.92 (s, 4H), 1.49 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 153.1, 140.0, 129.2, 125.6, 121.0, 98.3, 79.7, 52.2, 44.5, 28.4. IR (neat) ν (cm^{-1}): 3054.6, 2974.4, 2929.7, 2860.7, 2816.0,

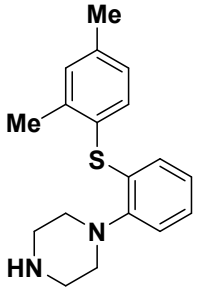
1686.6, 1578.5, 1468.6, 1412.7, 1364.2, 1332.5, 1244.9, 1164.8, 1120.1, 1032.5, 998.9, 862.9, 758.5; HRMS (ESI): caled for $C_{15}H_{22}IN_2O_2^+$ $[M + H]^+$ 389.0720; found 389.0718.

***tert*-butyl 4-(2-((2,4-dimethylphenyl)thio)phenyl)piperazine-1-carboxylate (12)**



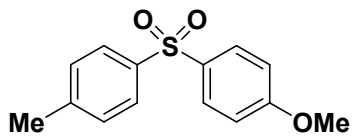
56%; Viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.09 – 7.00 (m, 3H), 6.89 – 6.85 (m, 1H), 6.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.62 – 3.60 (m, 4H), 3.02 – 2.99 (m, 4H), 2.36 (s, 3H), 2.32 (s, 3H), 1.49 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 148.9, 142.3, 139.2, 136.1, 134.6, 131.6, 127.8, 127.7, 126.2, 125.4, 124.5, 119.8, 79.6, 51.6, 44.7, 28.4, 21.2, 20.6. This compound has been previously reported in the literature.[2]

1-(2-((2,4-dimethylphenyl)thio)phenyl)piperazine (13)



A glass vial was charged with N-Boc vortioxetine 10 (79.7 mg, 0.2 mmol) and a magnetic stirer. Dry CH_2Cl_2 (0.5 mL) and trifluoroacetic acid (0.5 mL) were added and the solution was stirred for 1h at room temperature. The solvent was removed, the residue was disolved in CH_2Cl_2 (20 mL) and extracted with sat. $NaHCO_3$ aq (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed in vacuo to afford vortioxetine (54.1 mg, 90%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.10 – 7.01 (m, 3H), 6.88 – 6.84 (m, 1H), 6.52 – 6.50 (m, 1H), 3.09 – 3.06 (m, 8H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 142.4, 139.2, 136.2, 134.6, 131.6, 127.9, 127.7, 126.1, 125.4, 124.3, 119.8, 52.8, 46.3, 21.2, 20.6. This compound has been previously reported in the literature.[3]

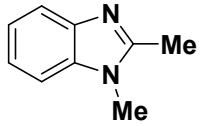
1-methoxy-4-tosylbenzene (15)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.80 – 7.78 (m, 2H), 7.28 – 7.26 (m, 2H), 6.96 – 6.93 (m, 2H), 3.83 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

163.2, 143.7, 139.4, 133.5, 129.8, 129.6, 127.3, 114.4, 55.6, 21.5. This compound has been previously reported in the literature.[4]

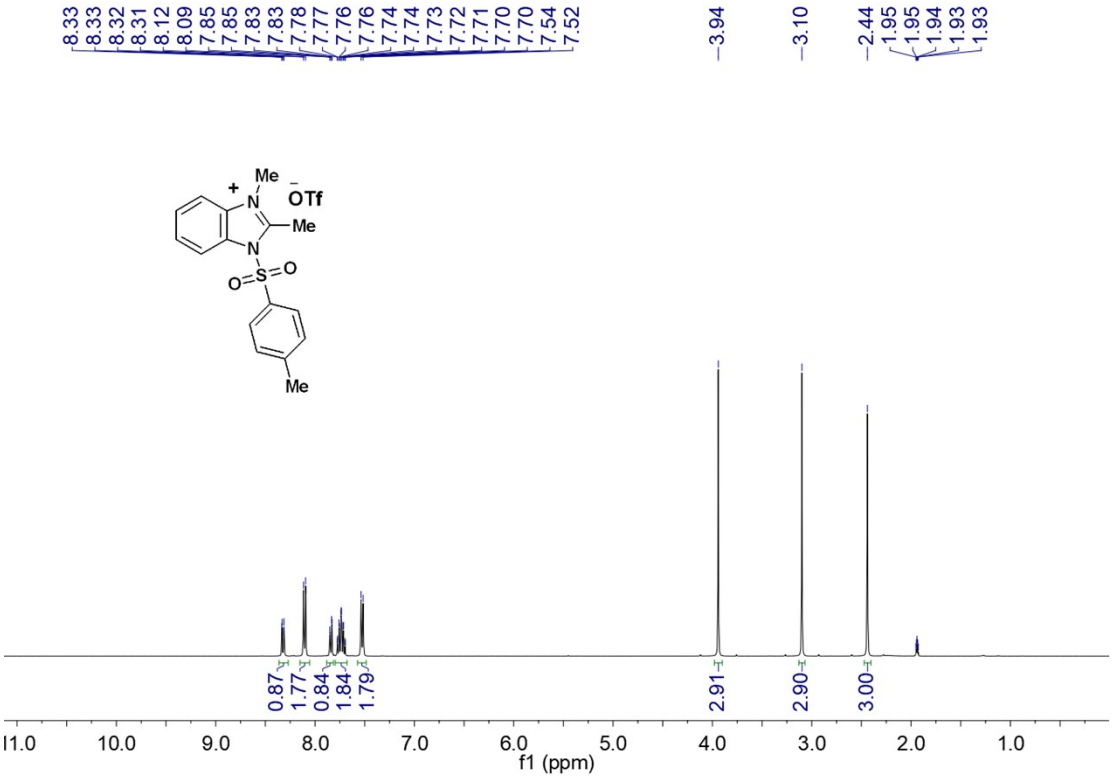
1,2-dimethyl-1*H*-benzo[*d*]imidazole (16)

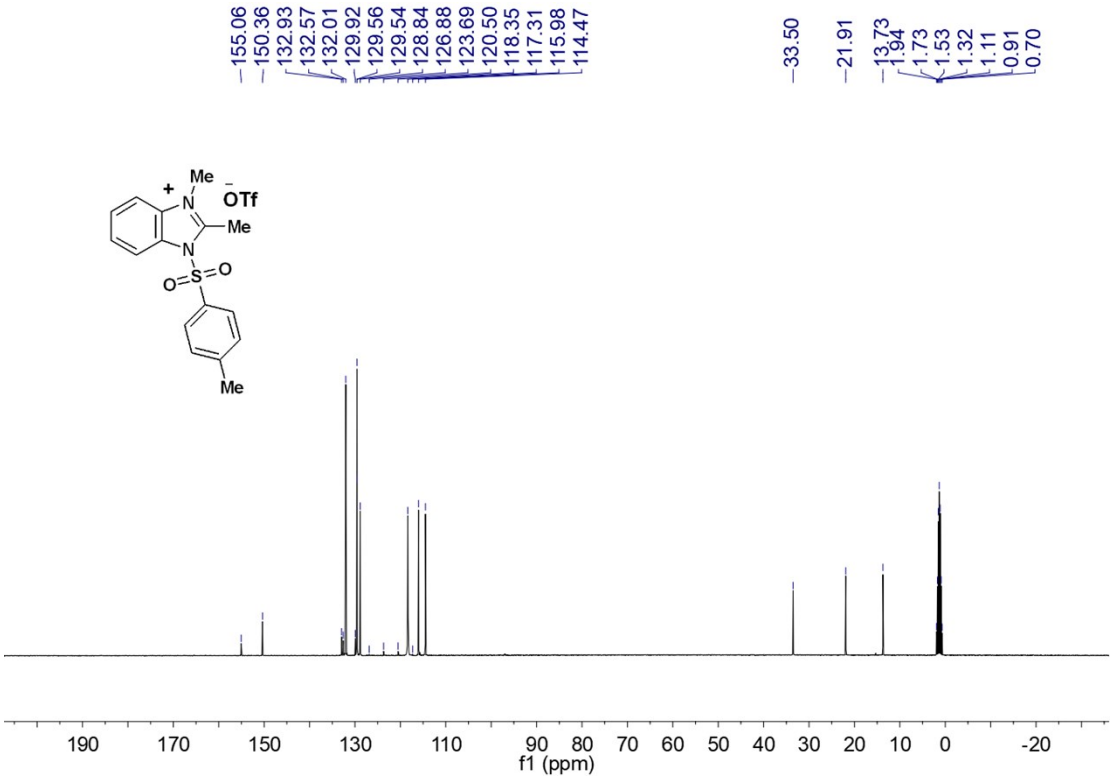


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 1H), 7.32 – 7.23 (m, 3H), 3.75 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 142.5, 135.8, 121.9, 121.8, 119.0, 108.8, 29.8, 13.8. This compound has been previously reported in the literature.[5]

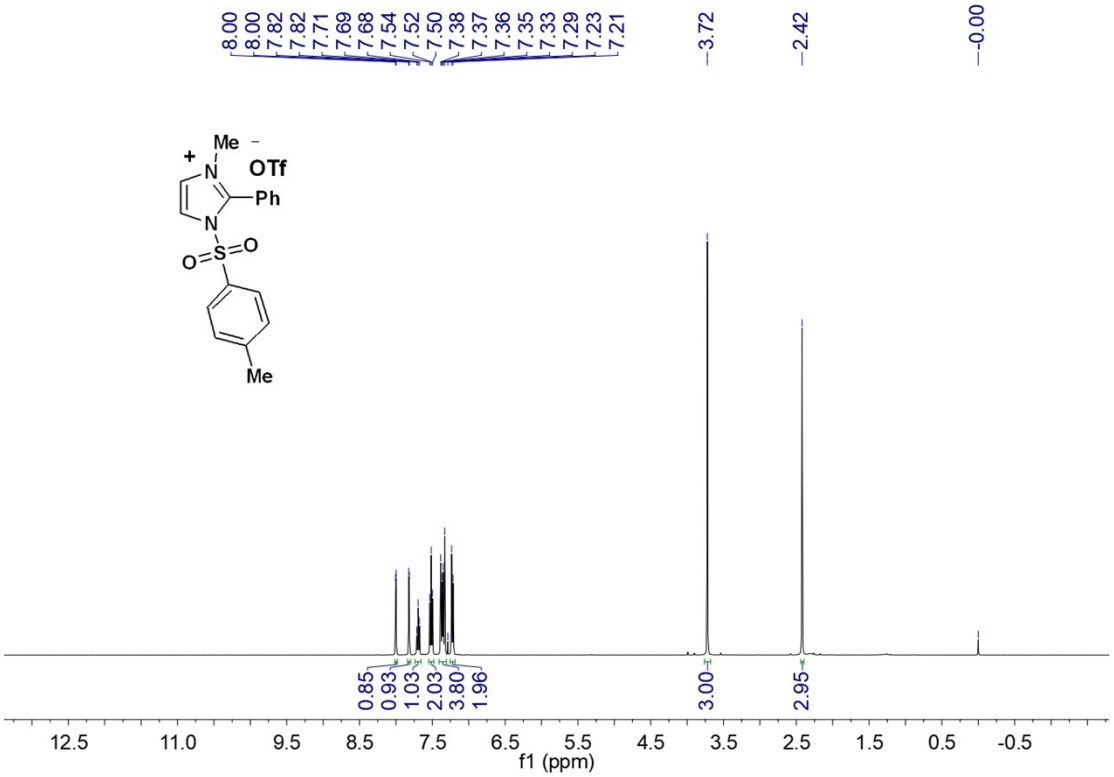
VII. NMR Spectra for Compounds

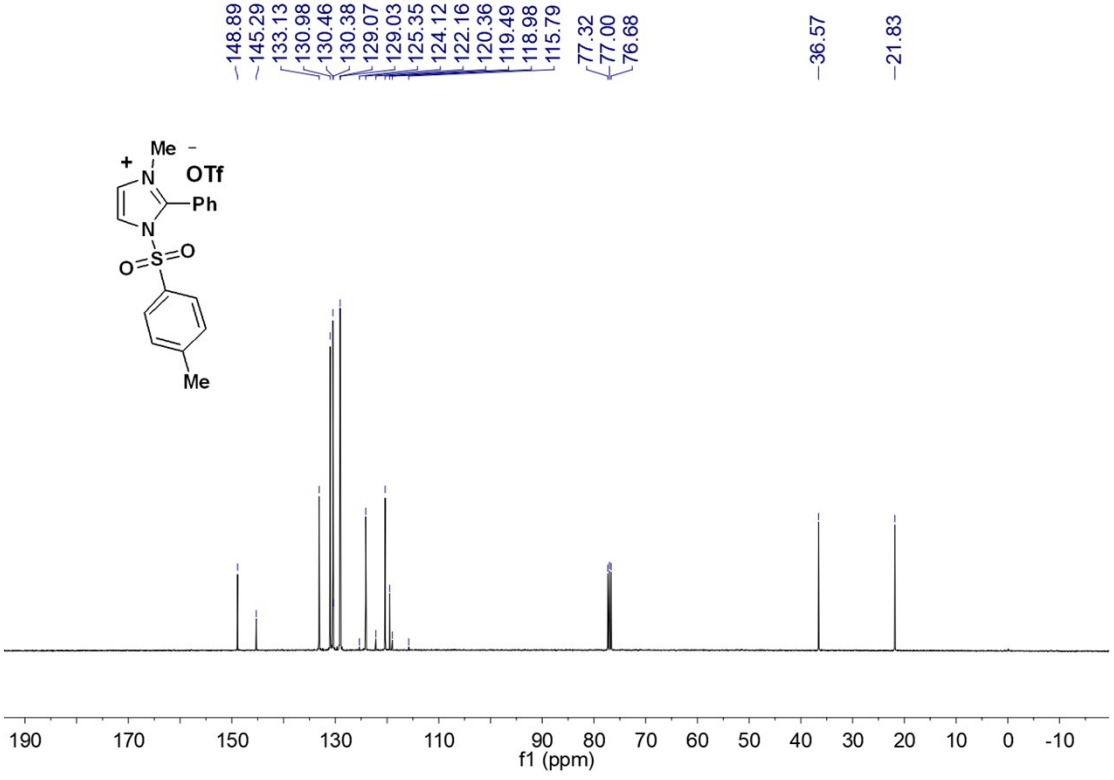
NMR Spectra of product **1a**:



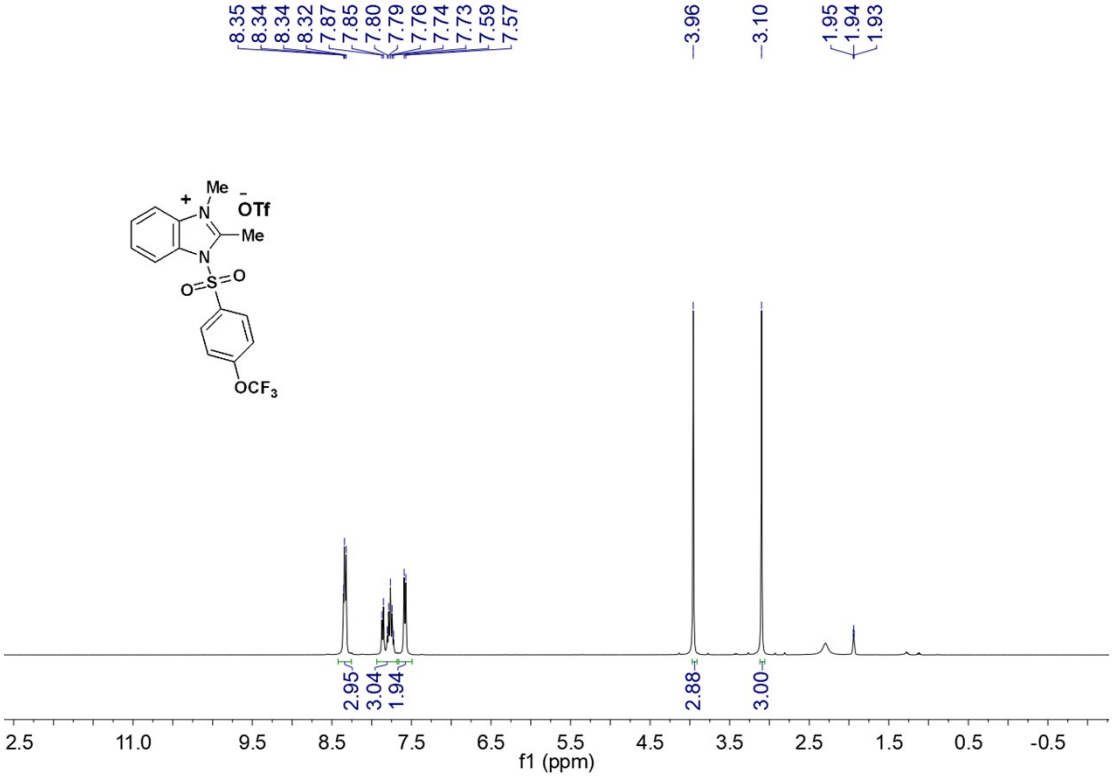


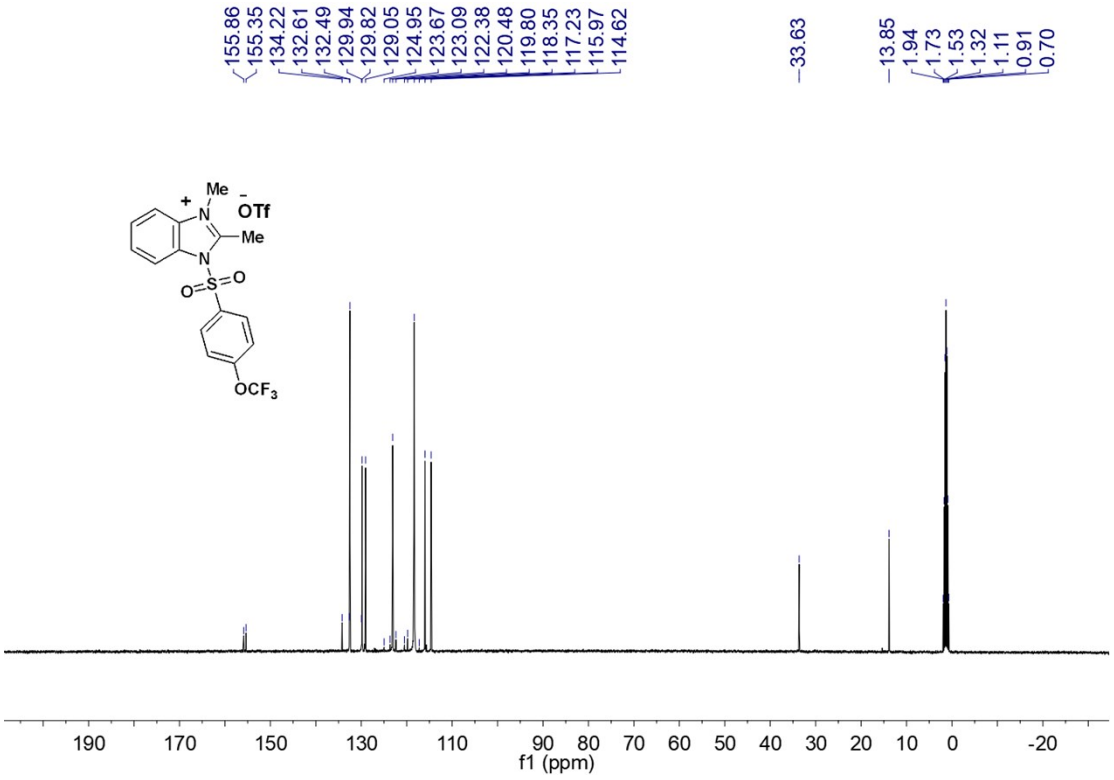
NMR Spectra of product **1b**:



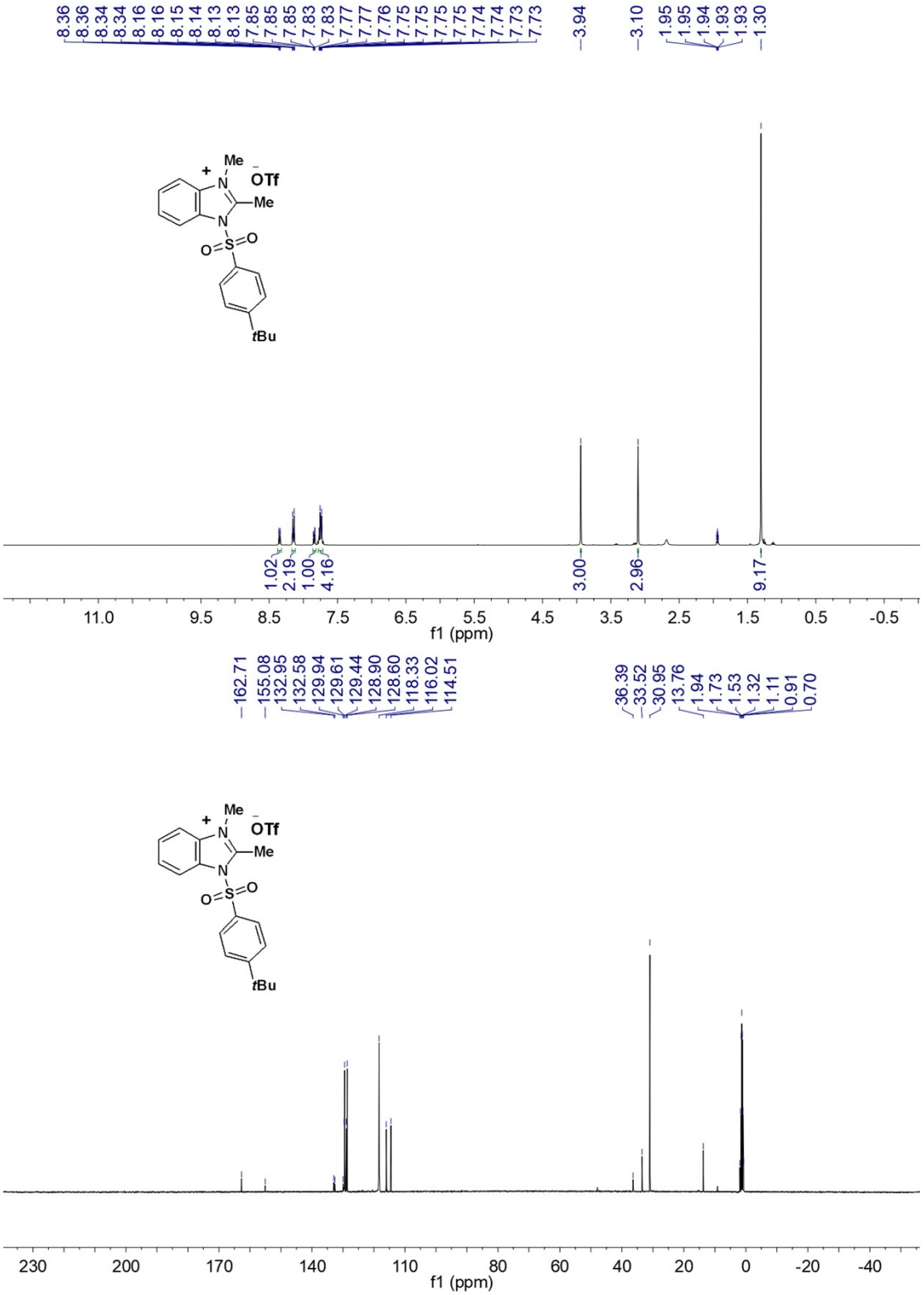


NMR Spectra of product **1c**:

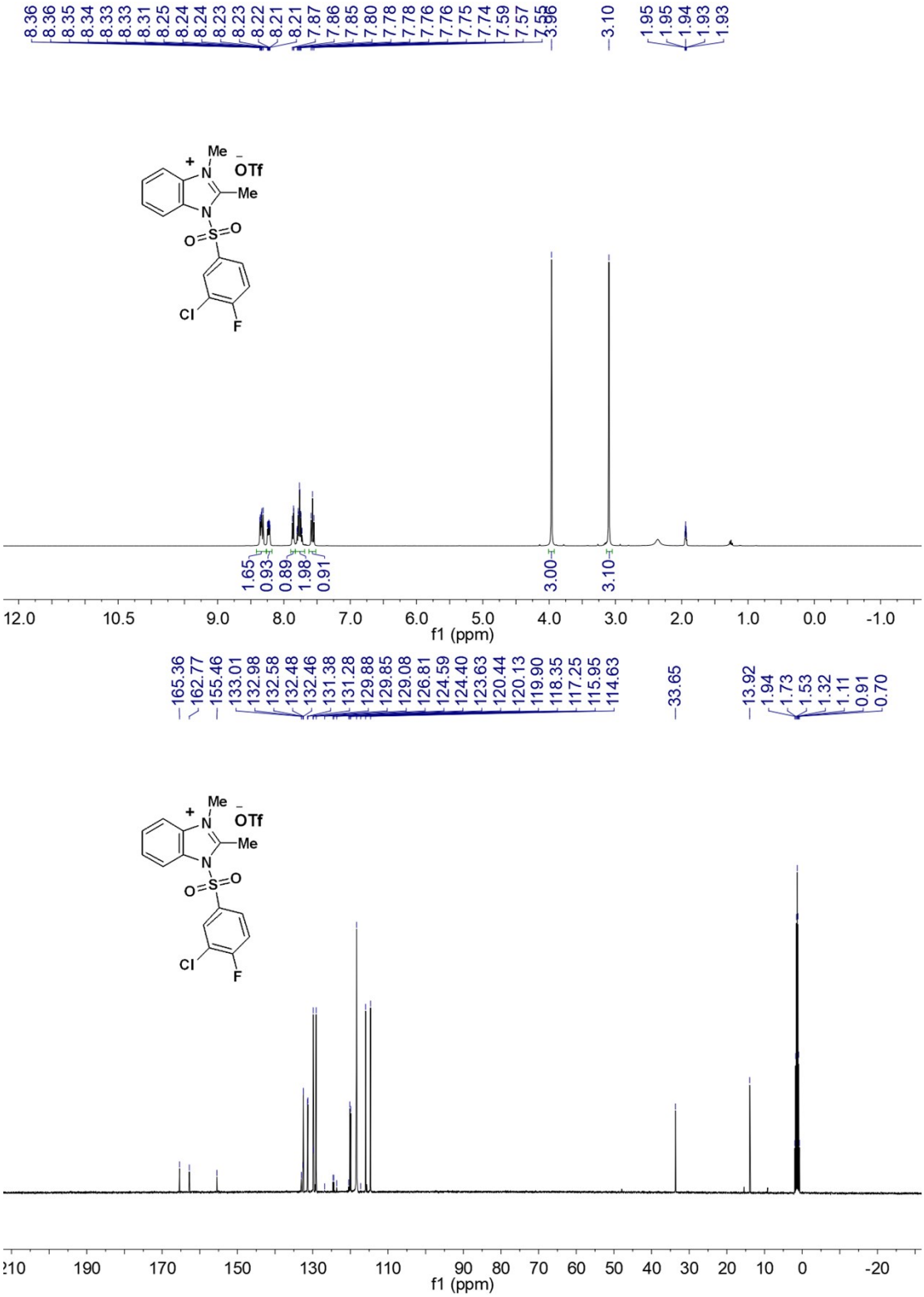




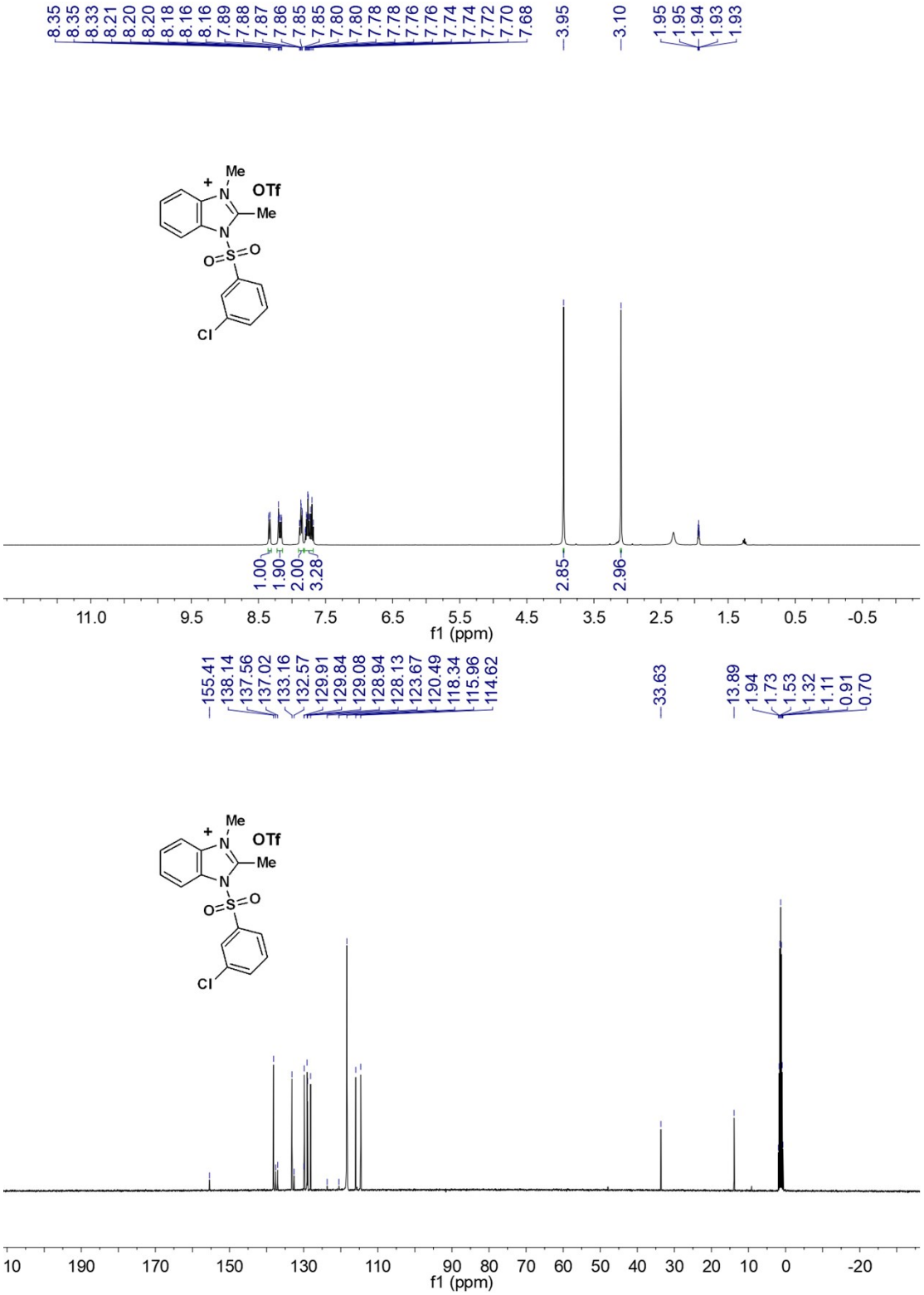
NMR Spectra of product **1d**:



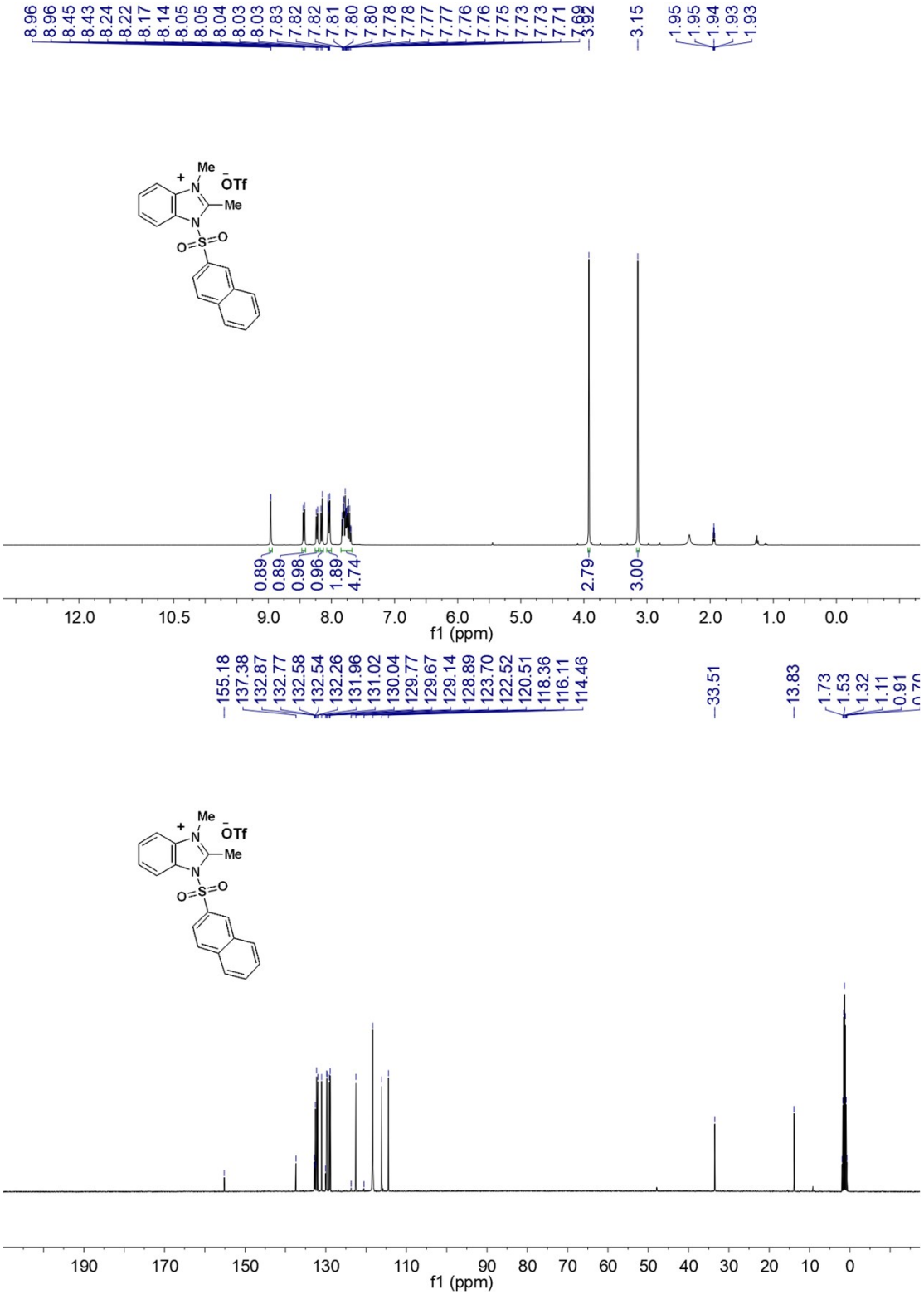
NMR Spectra of product **1e**:



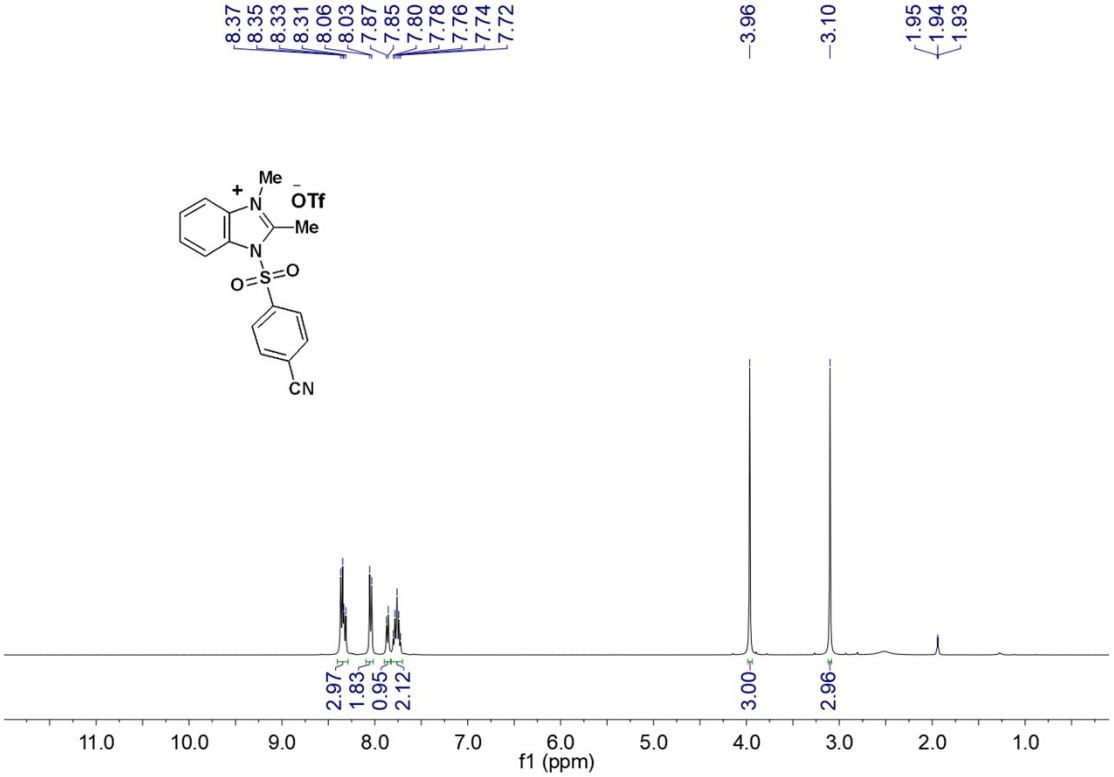
NMR Spectra of product **1f**:

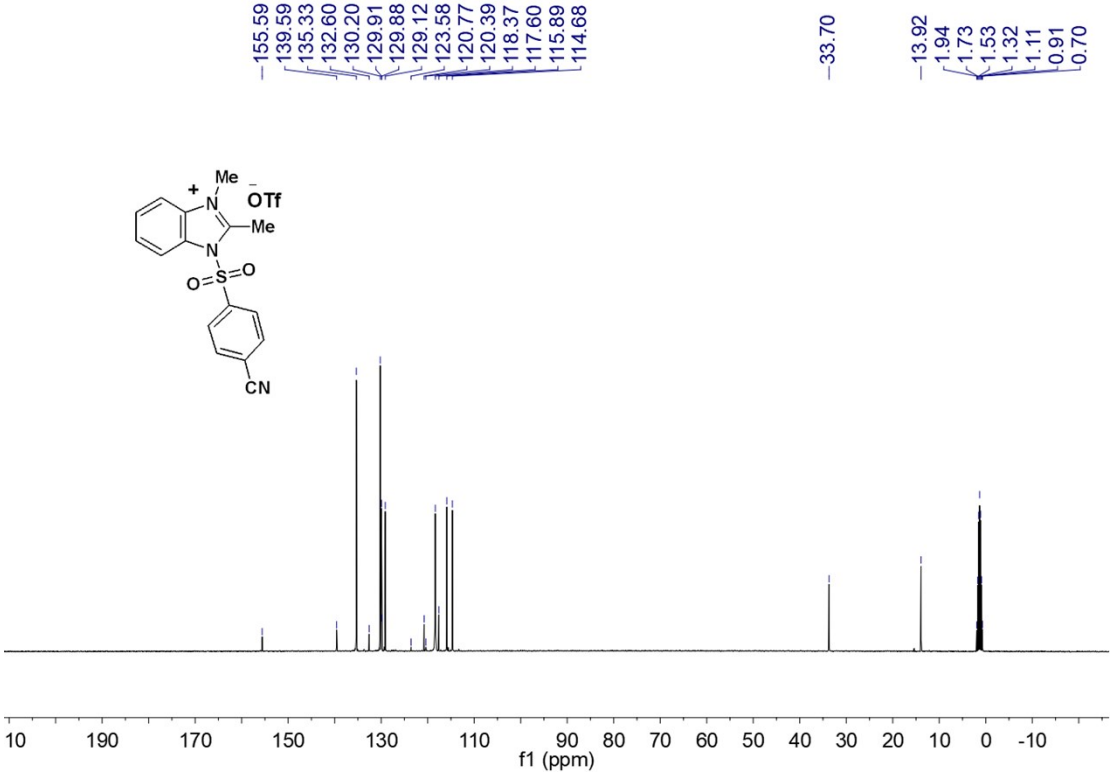


NMR Spectra of product **1g**:

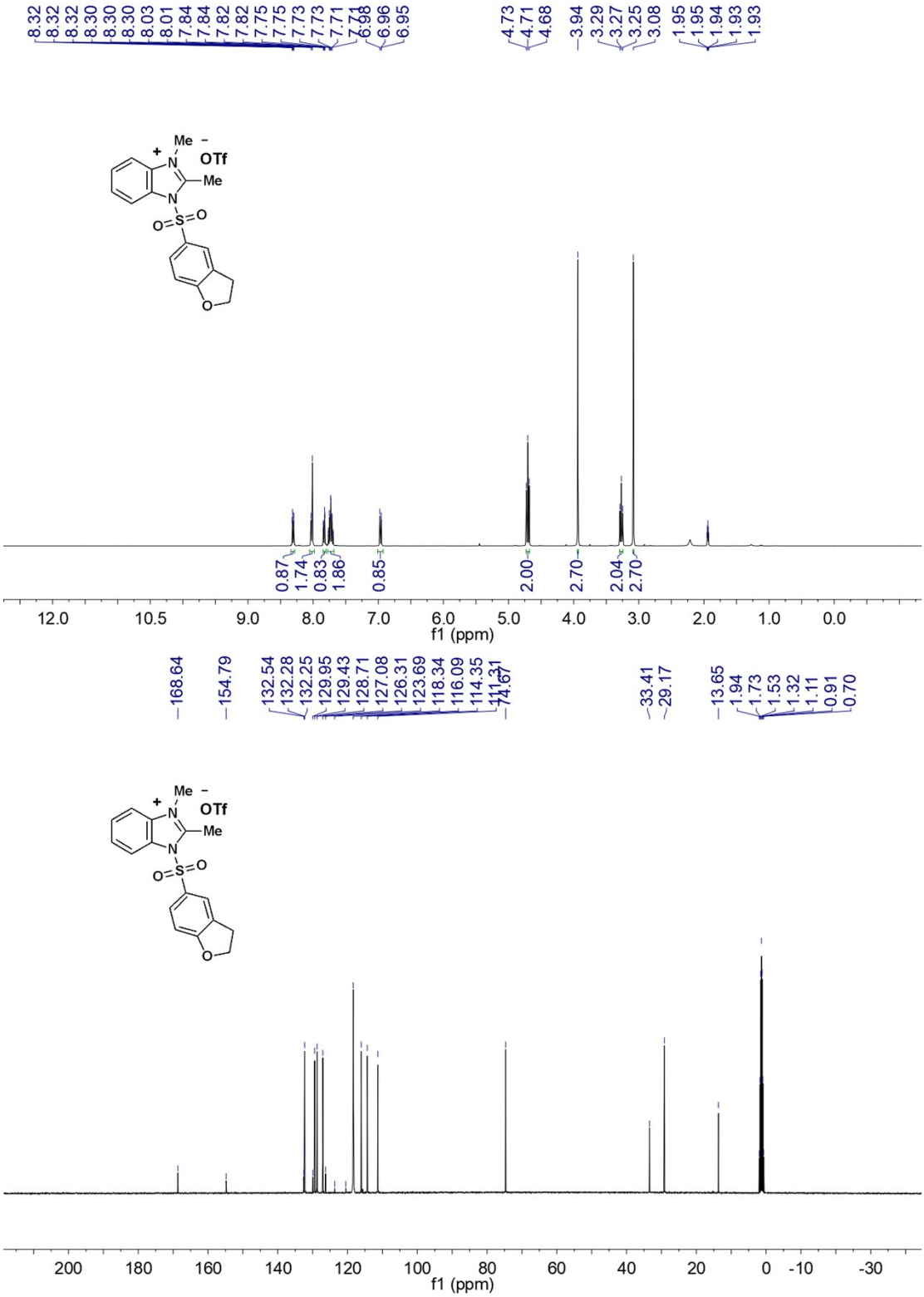


NMR Spectra of product **1h**:

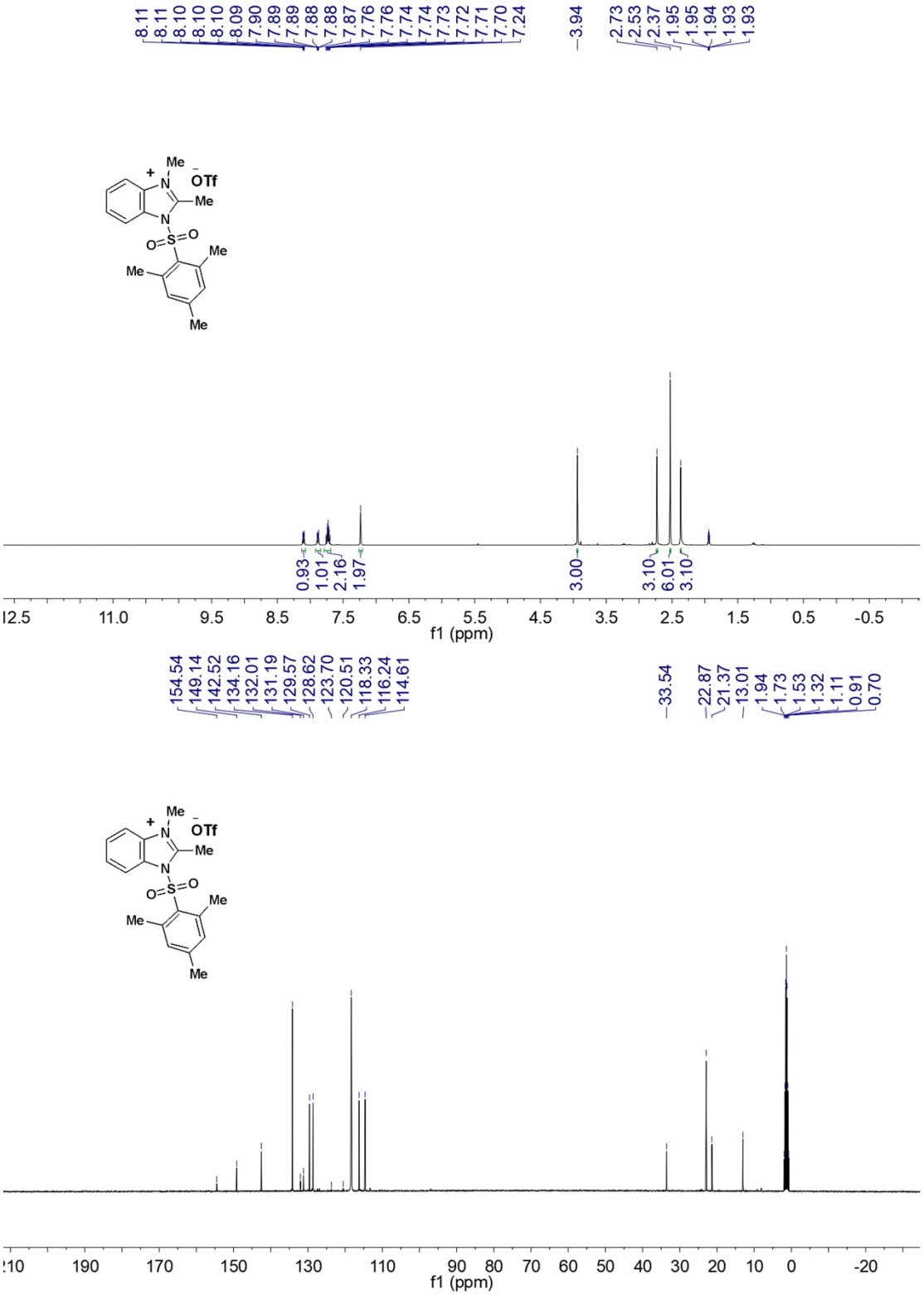




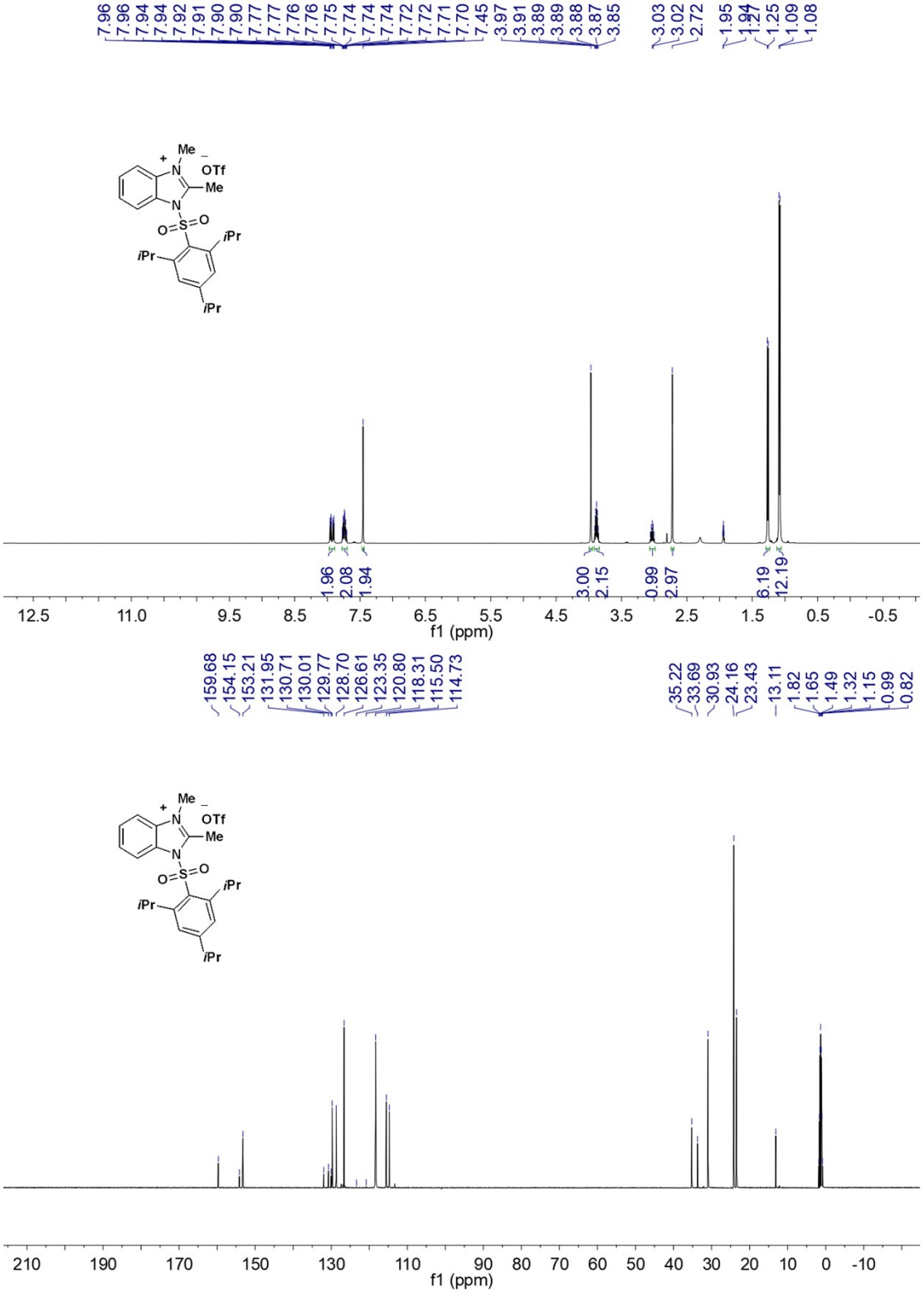
NMR Spectra of product **1i**:



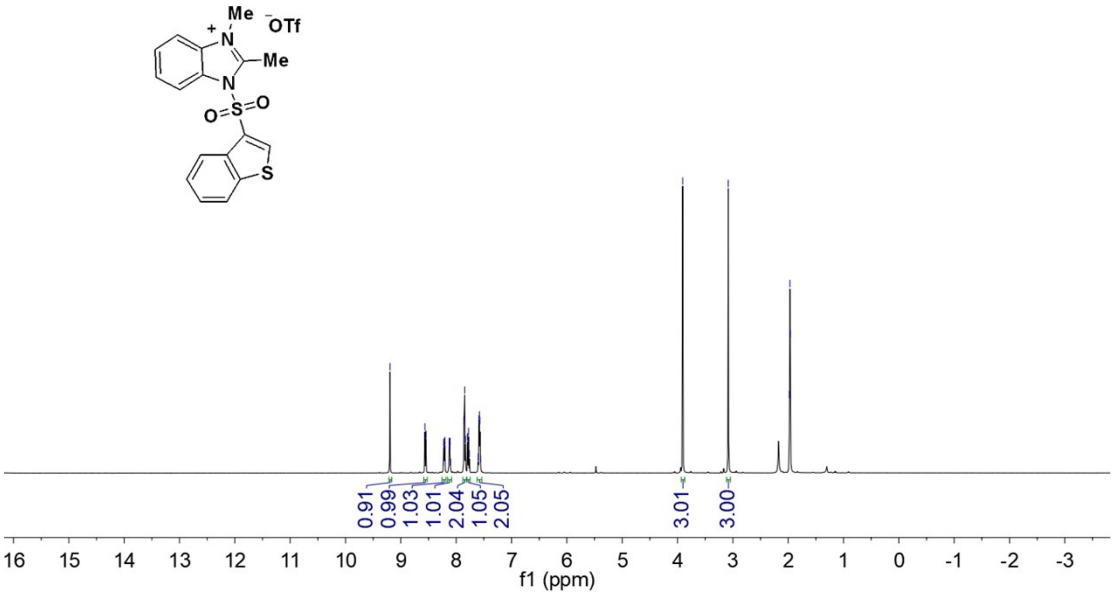
NMR Spectra of product **1j**:

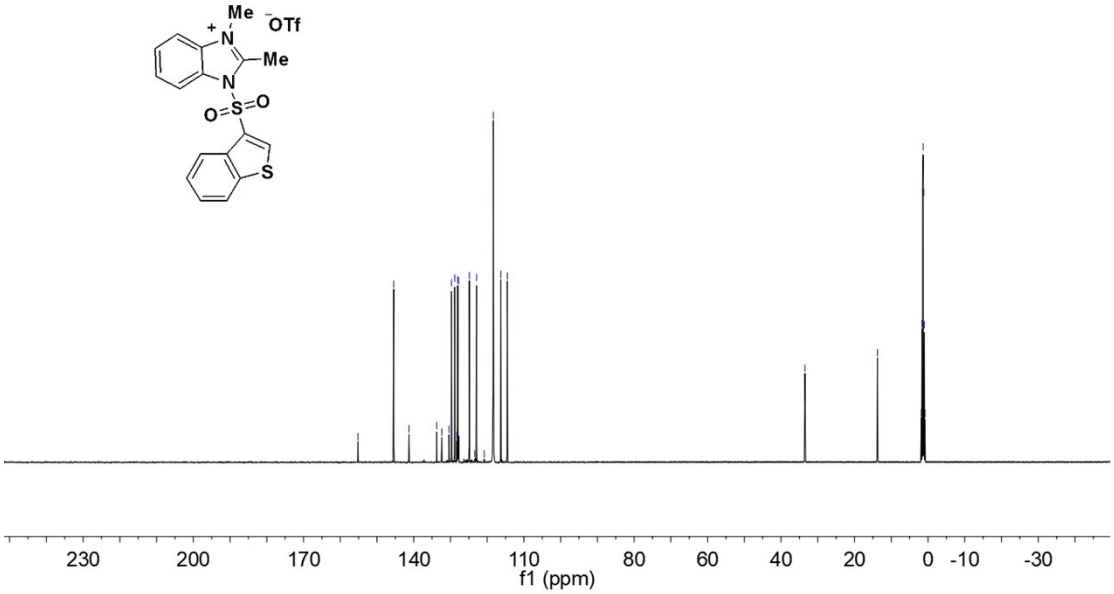


NMR Spectra of product **1k**:

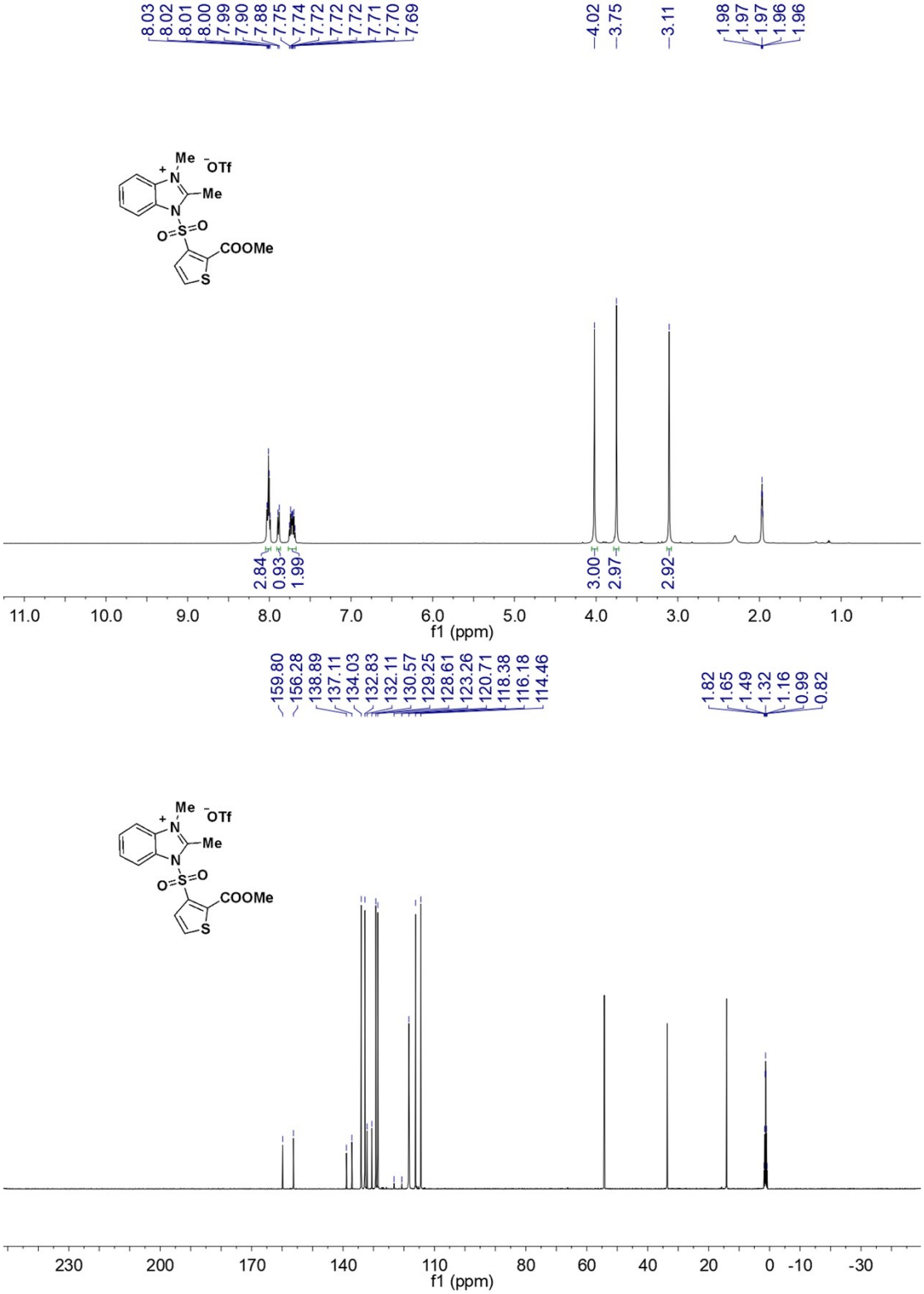


NMR Spectra of product **1l**:

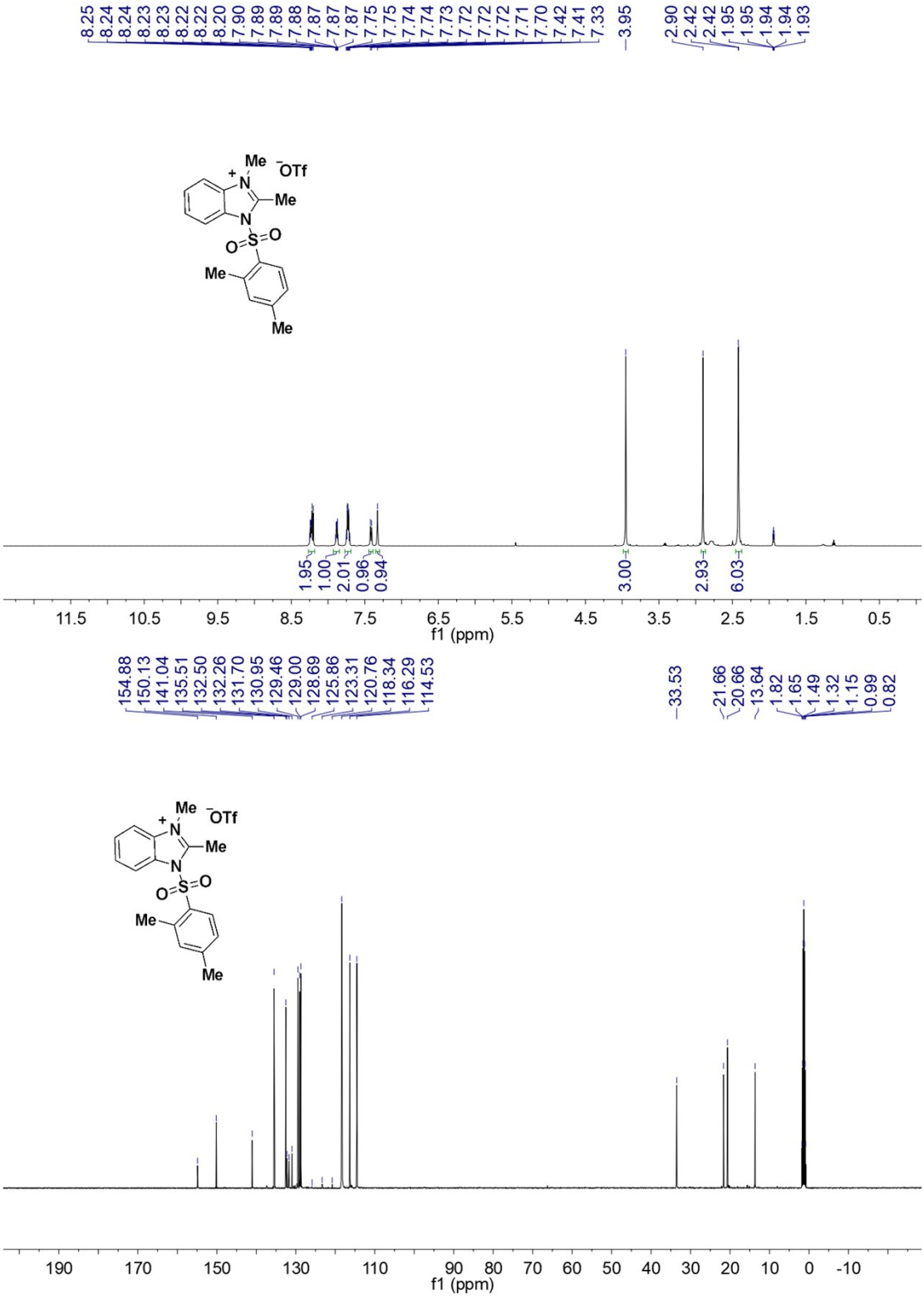




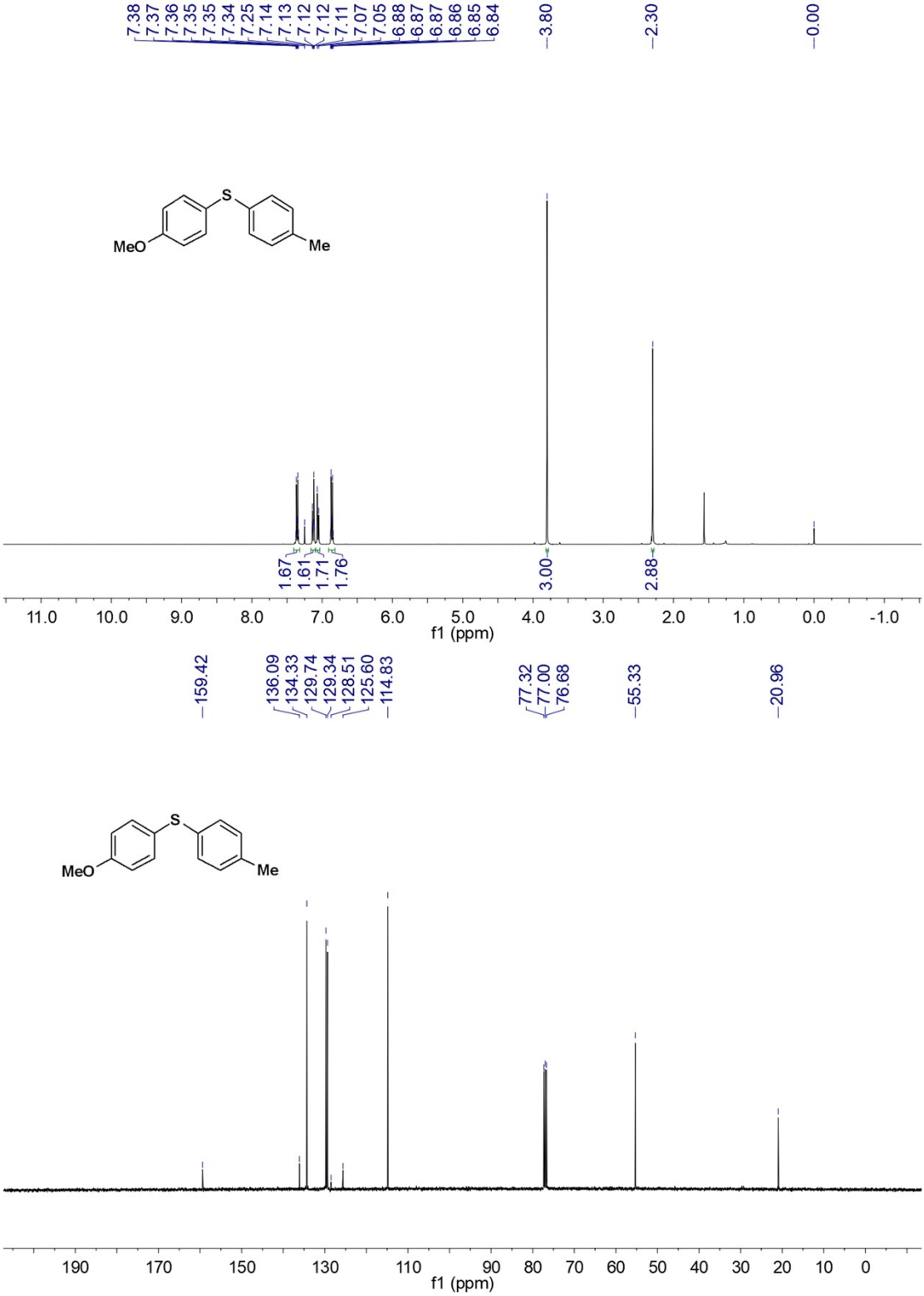
NMR Spectra of product **1m**:



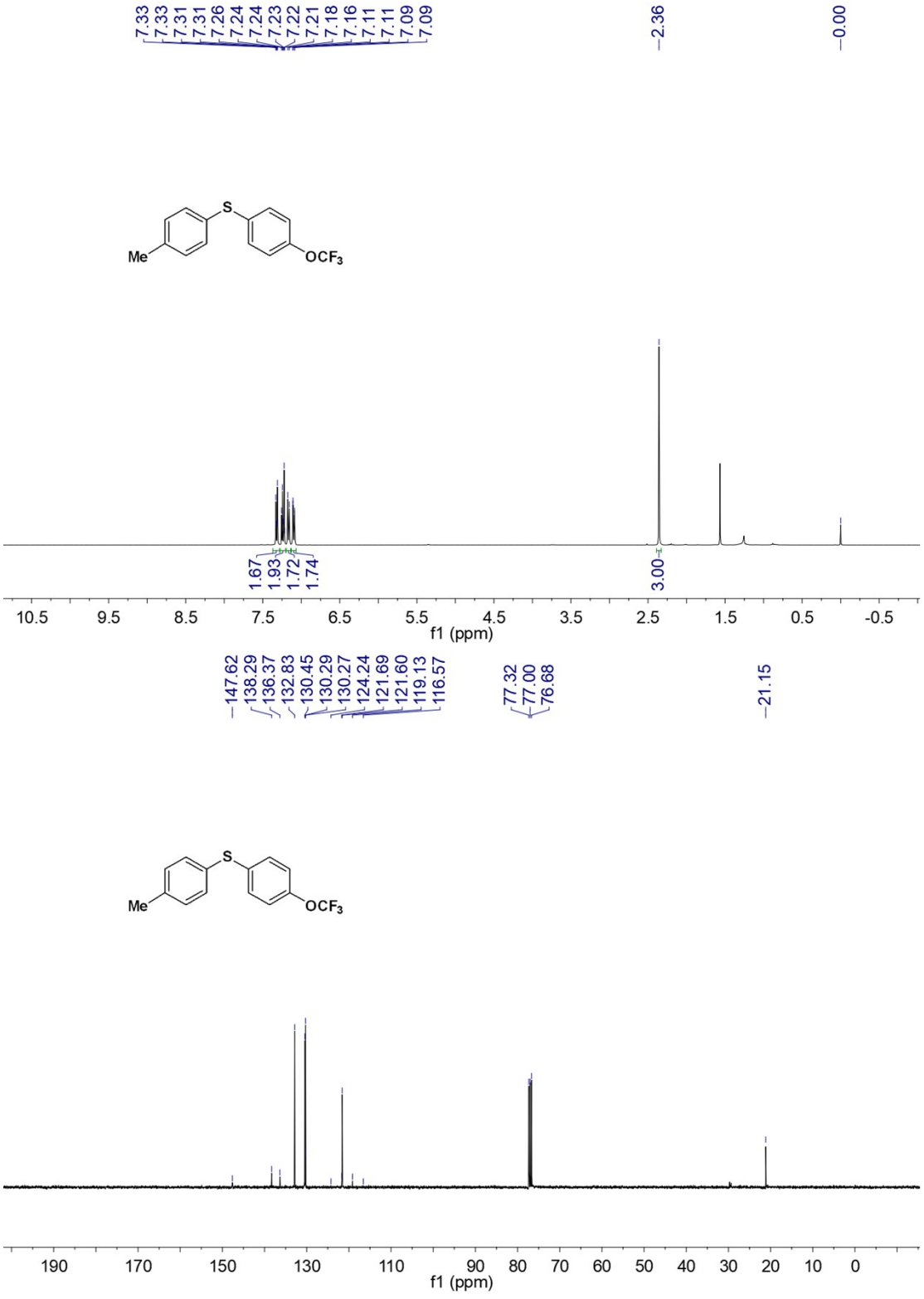
NMR Spectra of product **1n**:



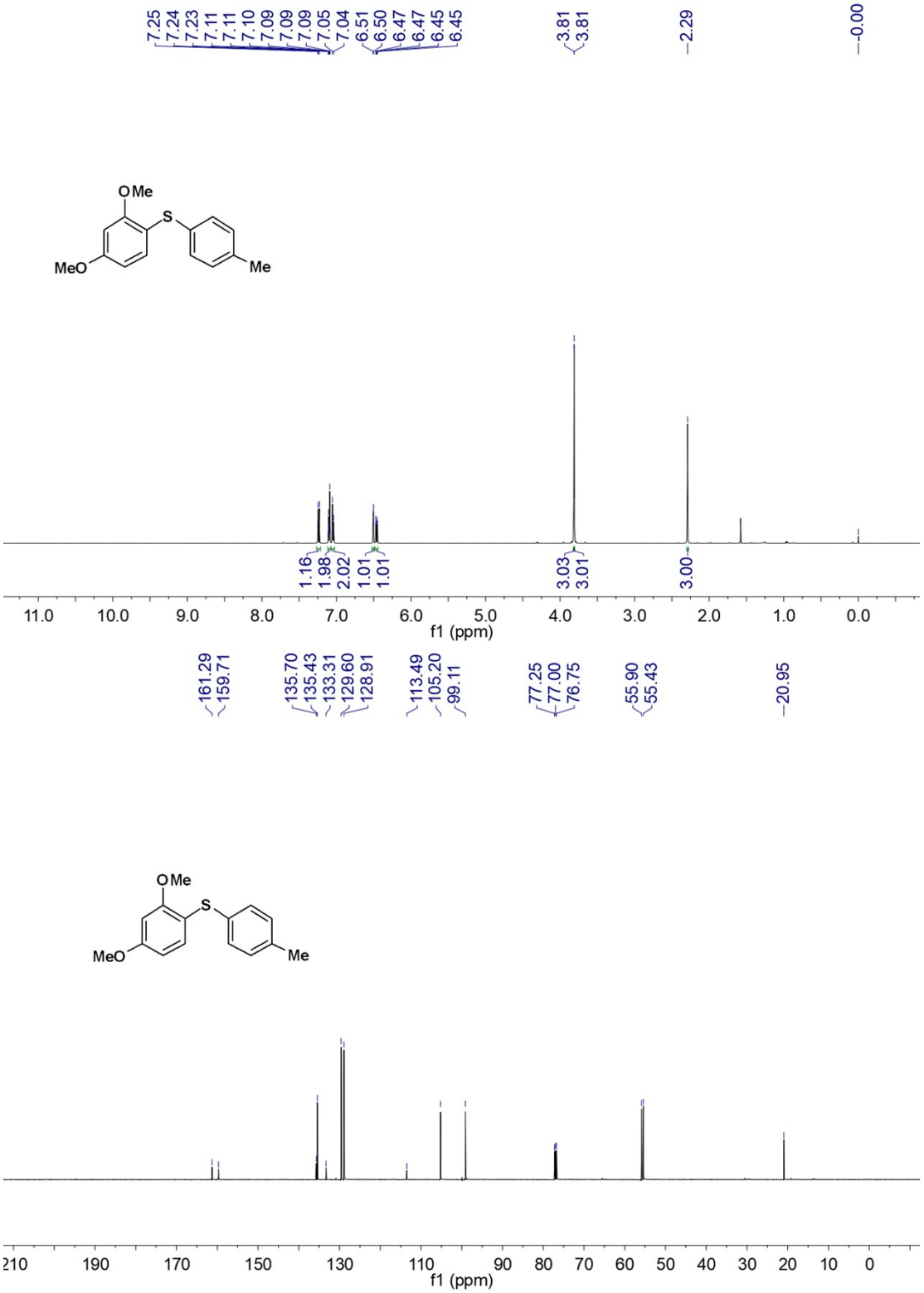
NMR Spectra of product **3a**:



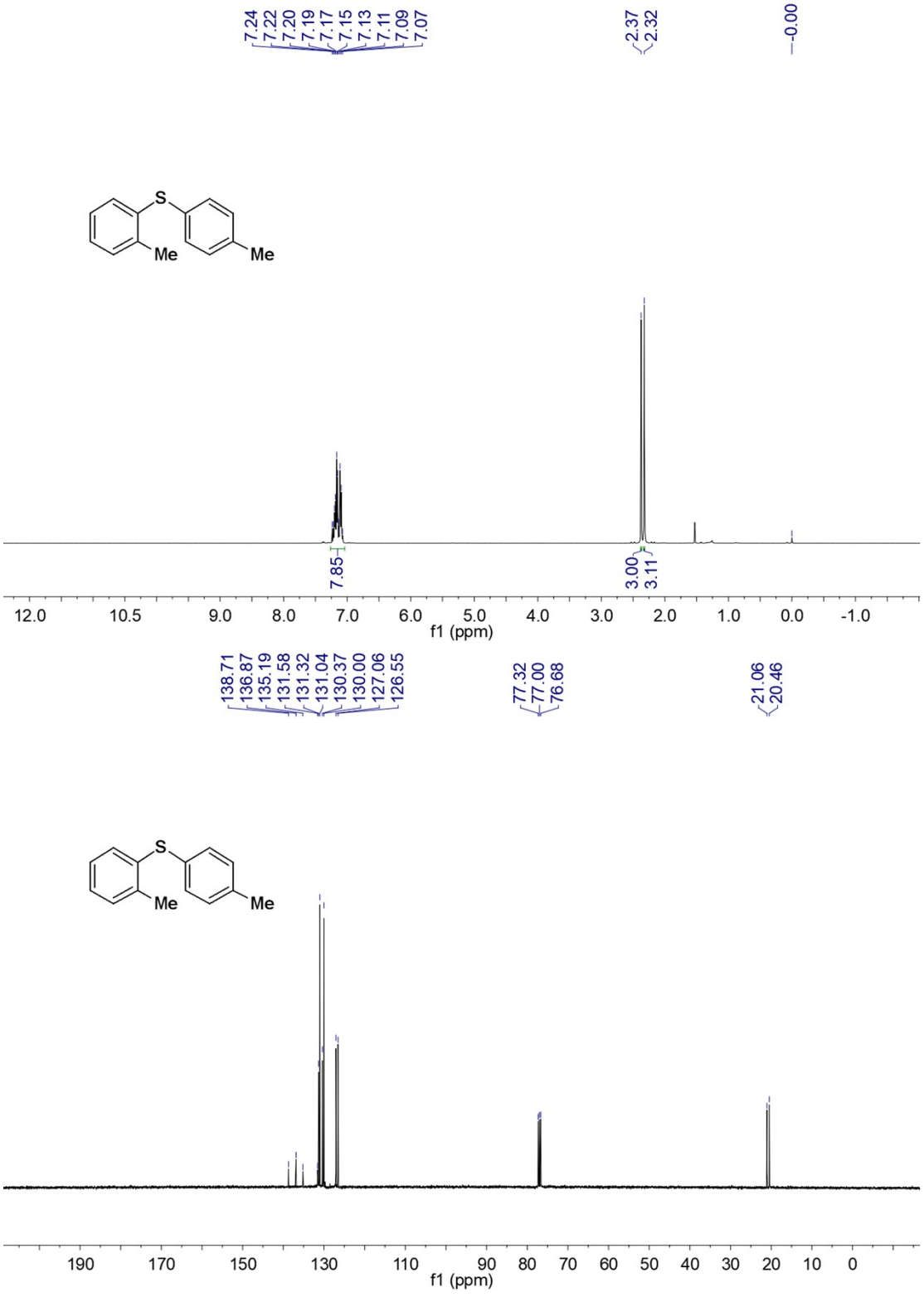
NMR Spectra of product **3b**:



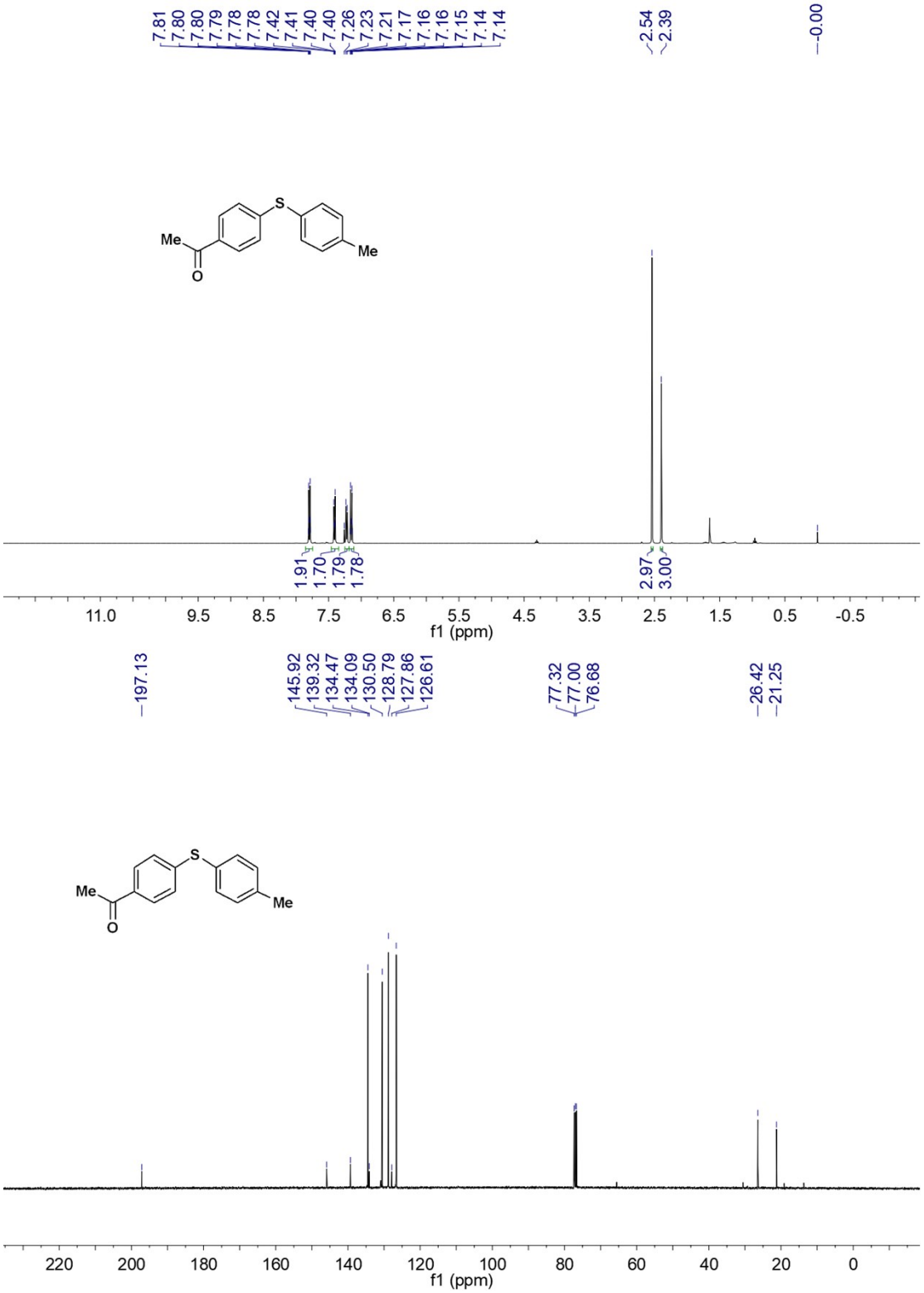
NMR Spectra of product **3c**:



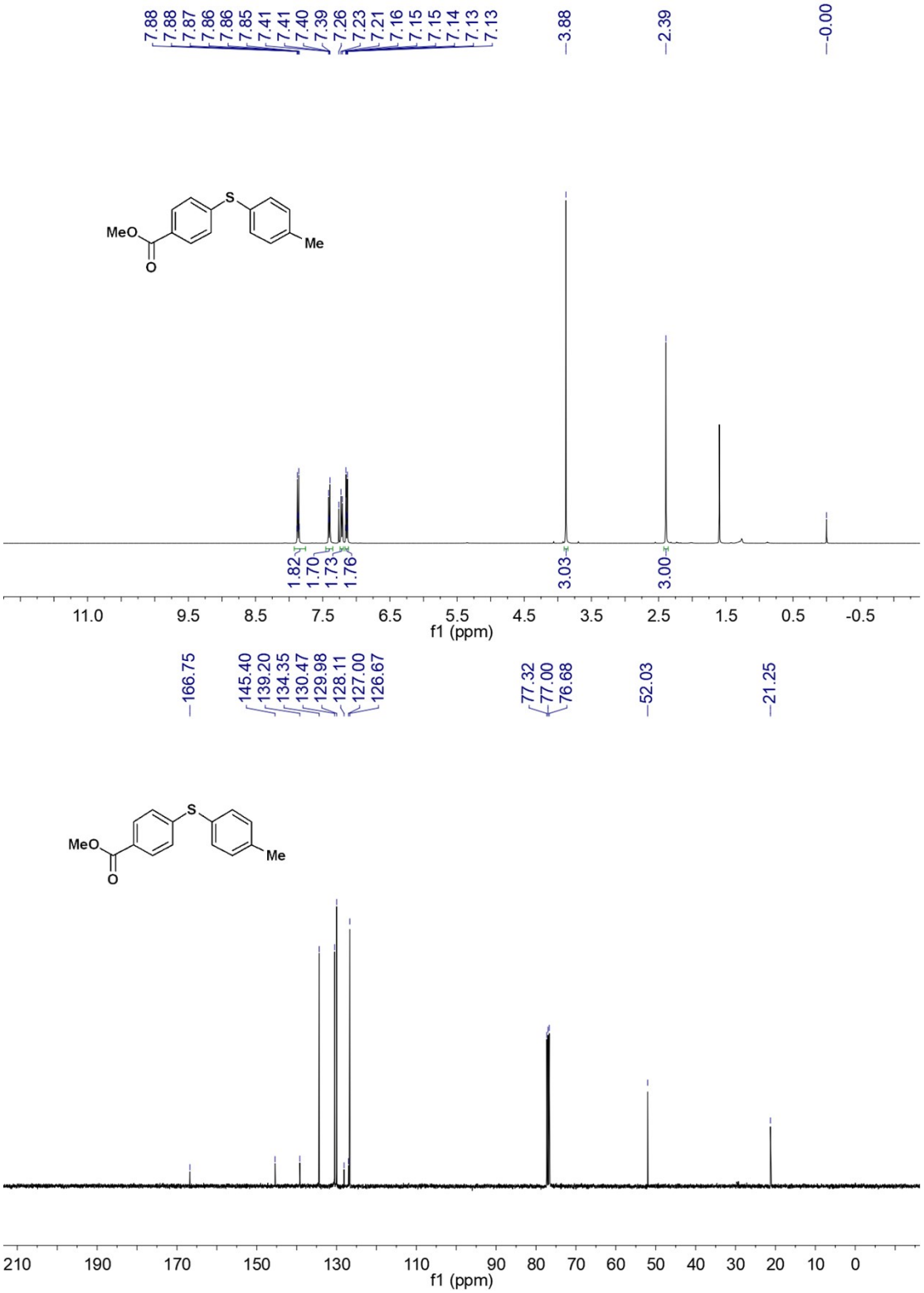
NMR Spectra of product **3d**:



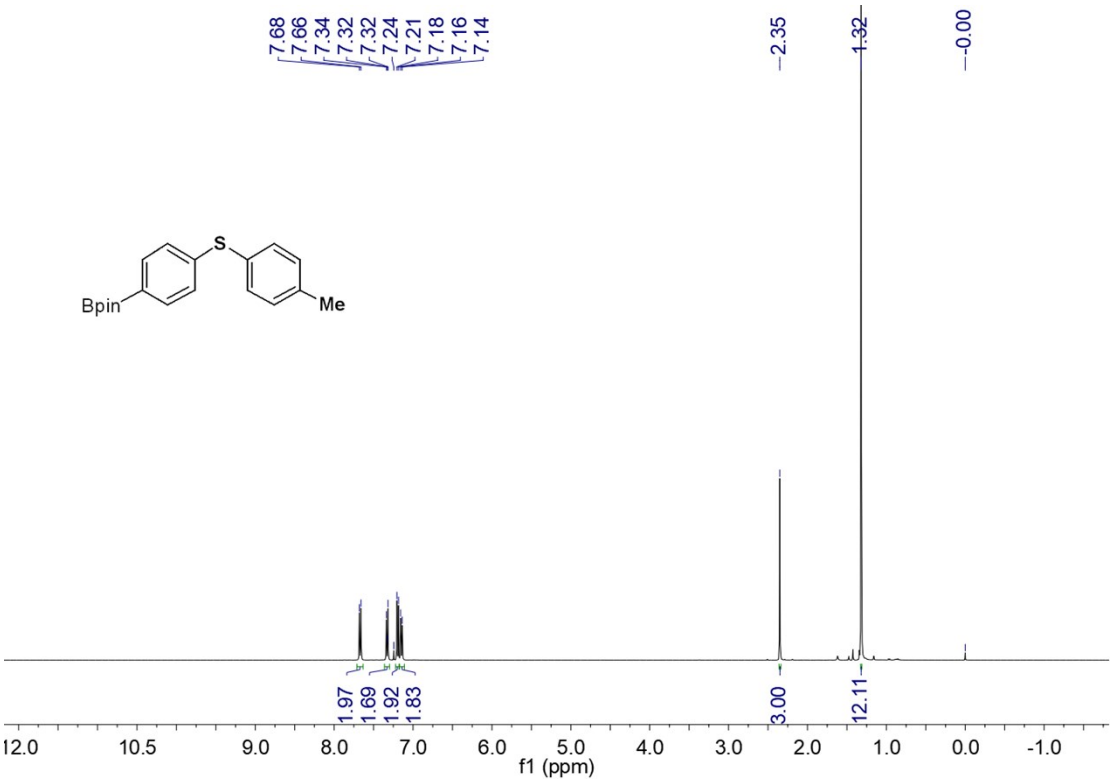
NMR Spectra of product **3e**:

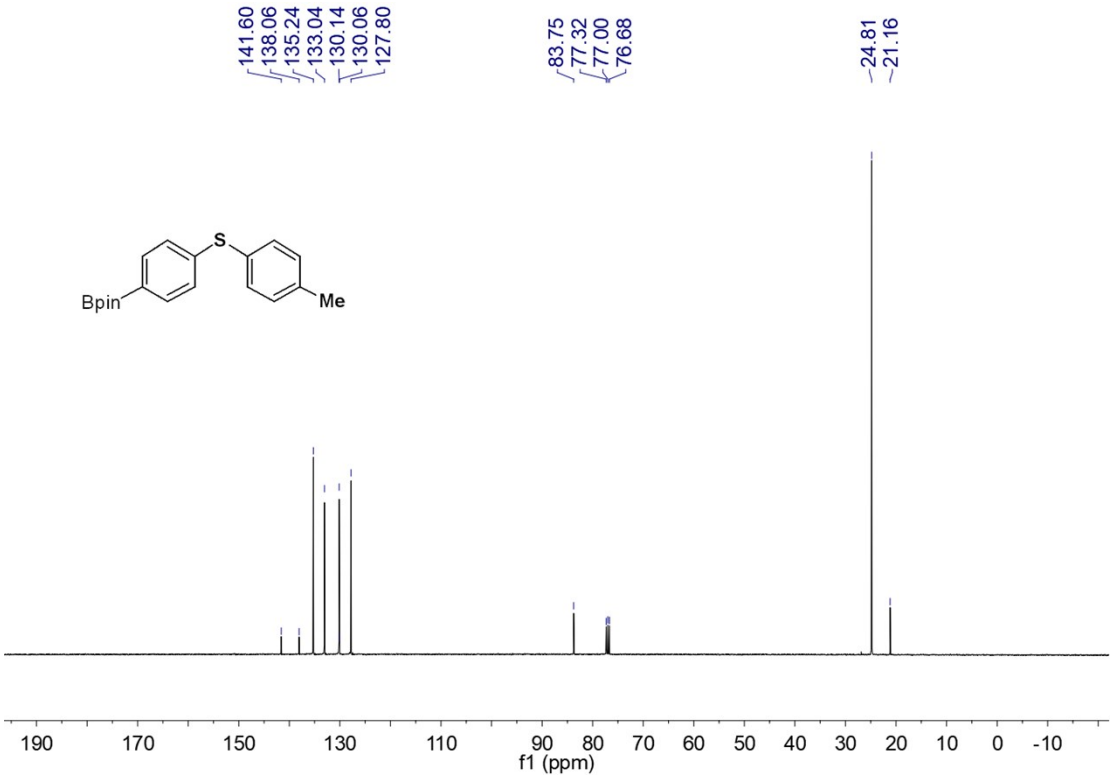


NMR Spectra of product **3f**:

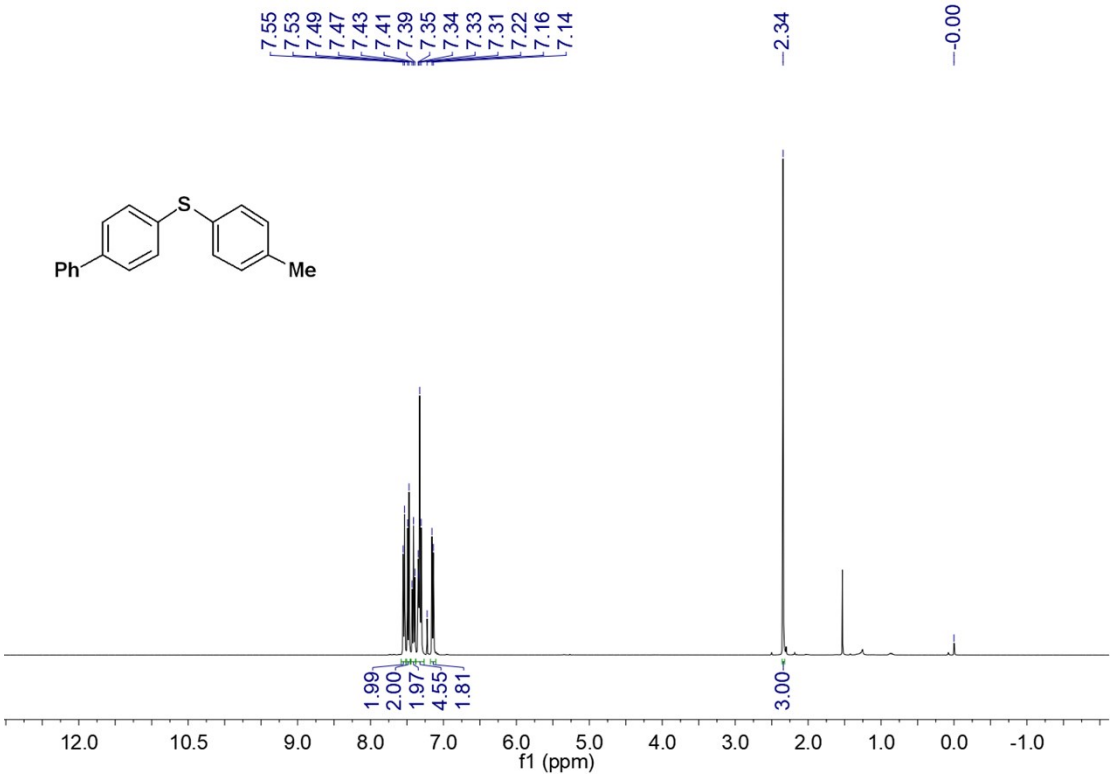


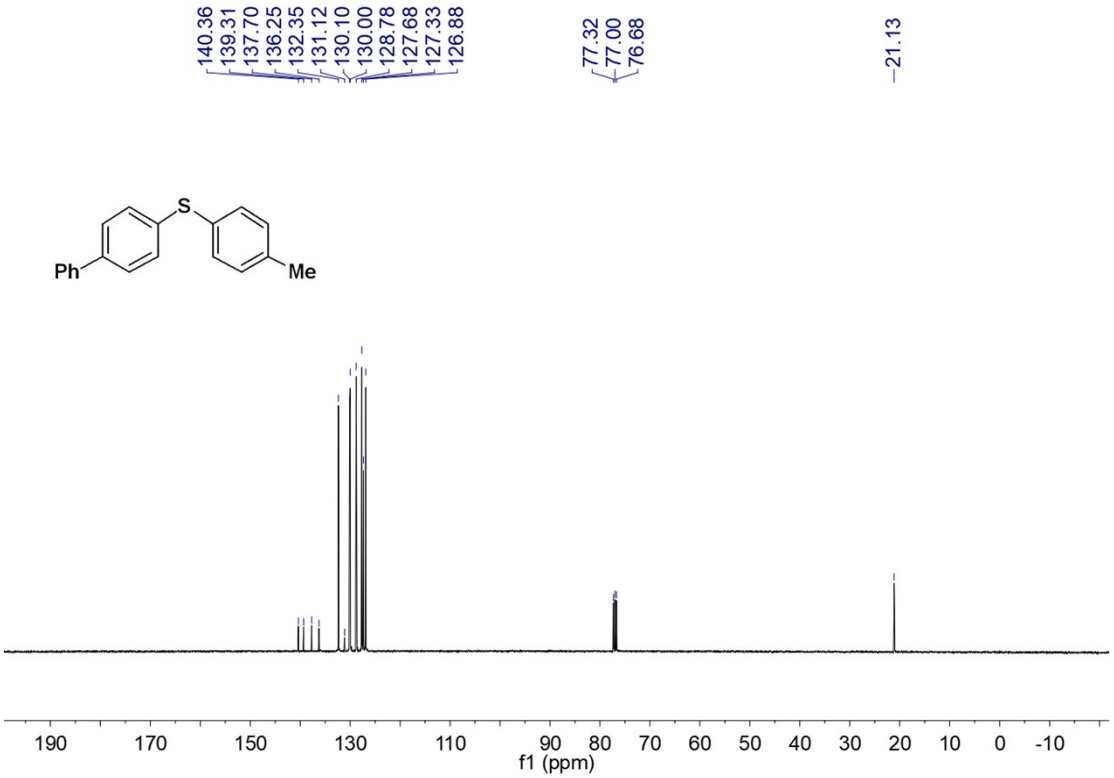
NMR Spectra of product **3g**:



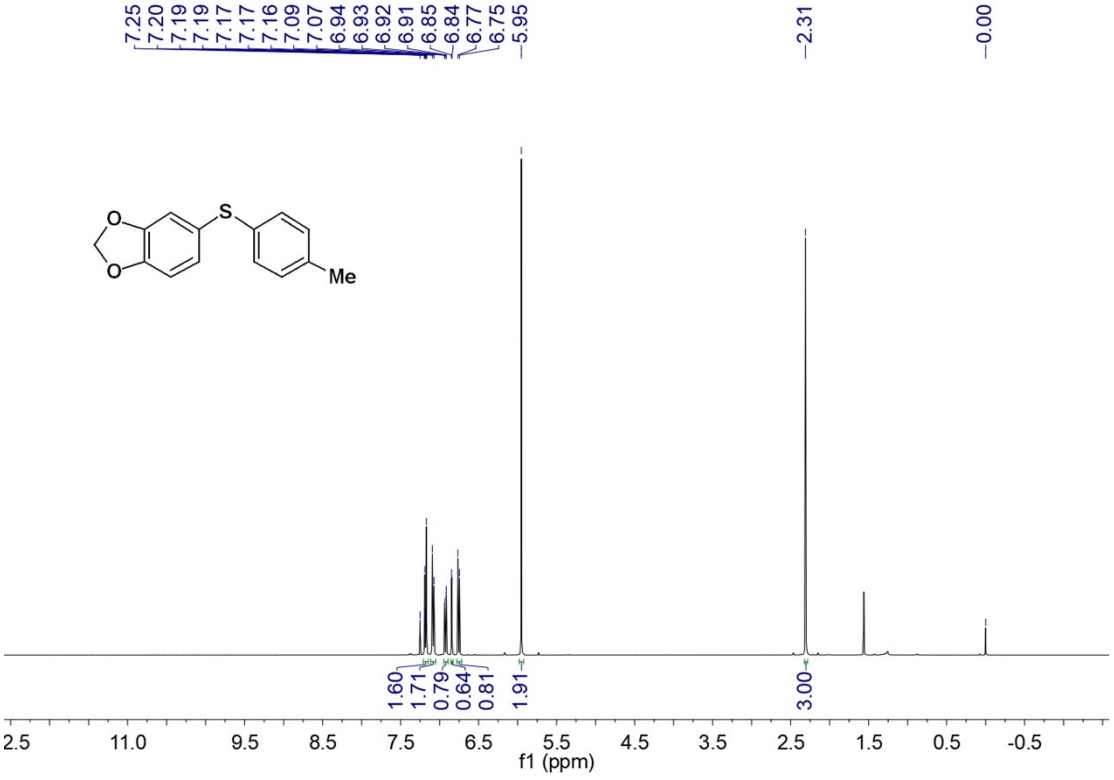


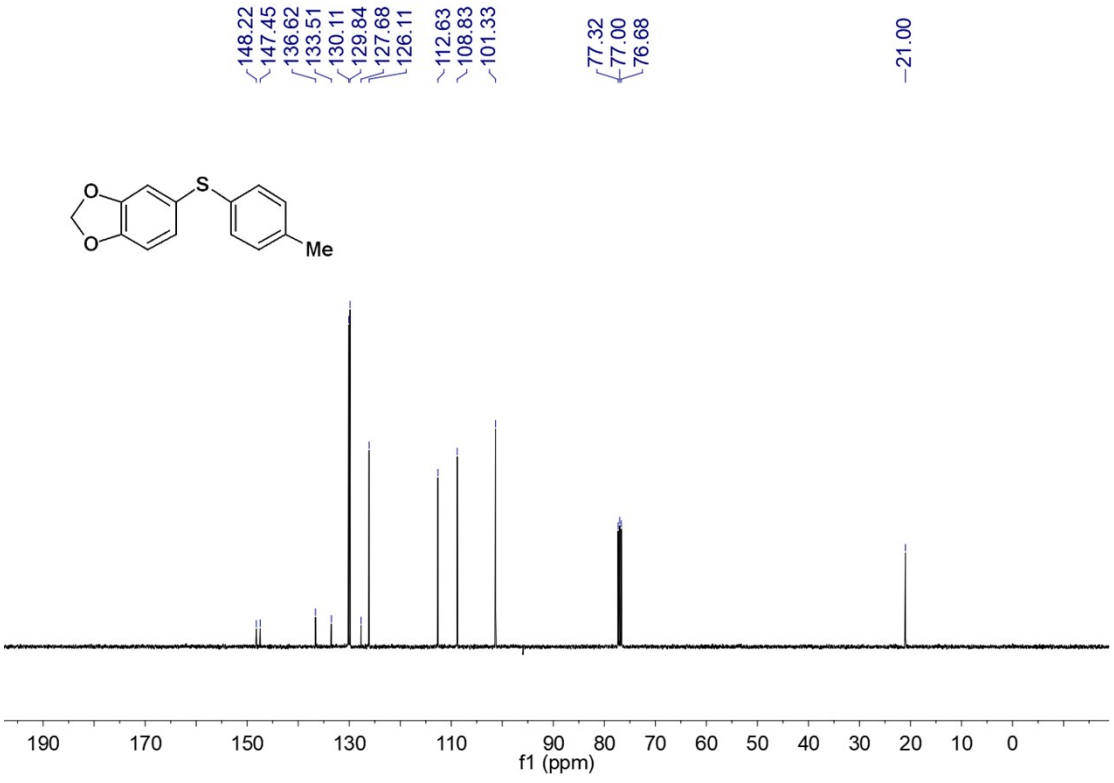
NMR Spectra of product **3h**:



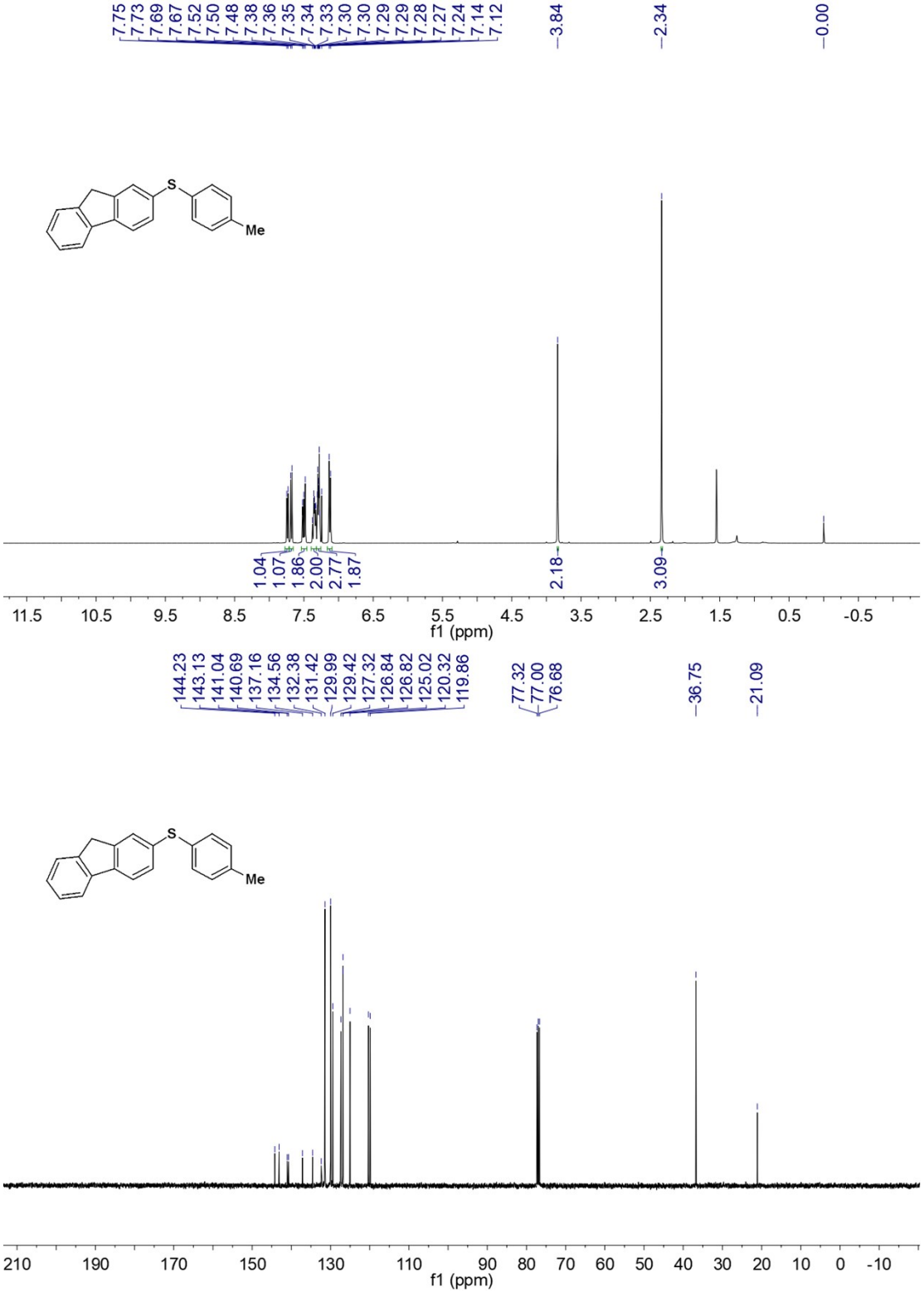


NMR Spectra of product **3i**:

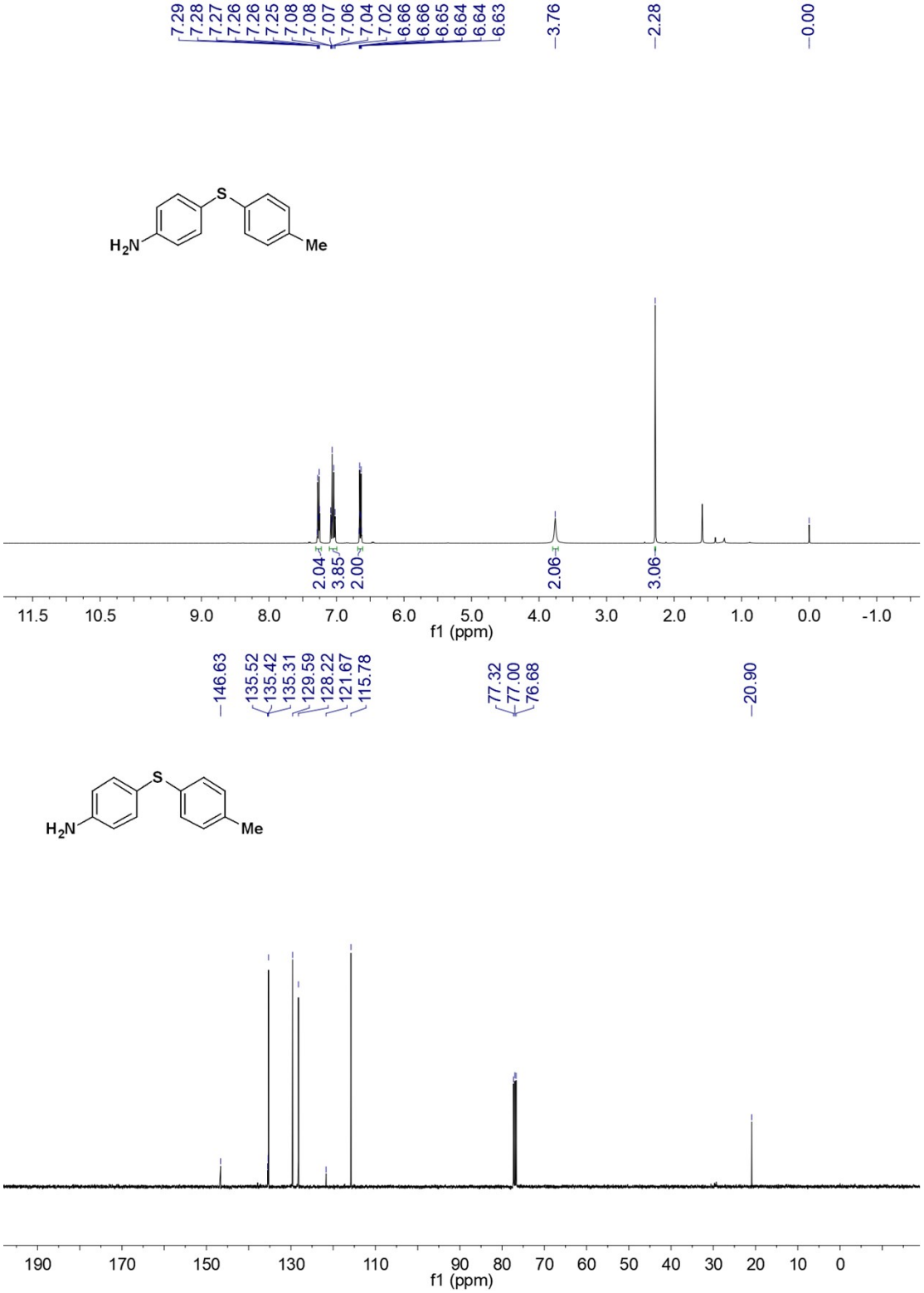




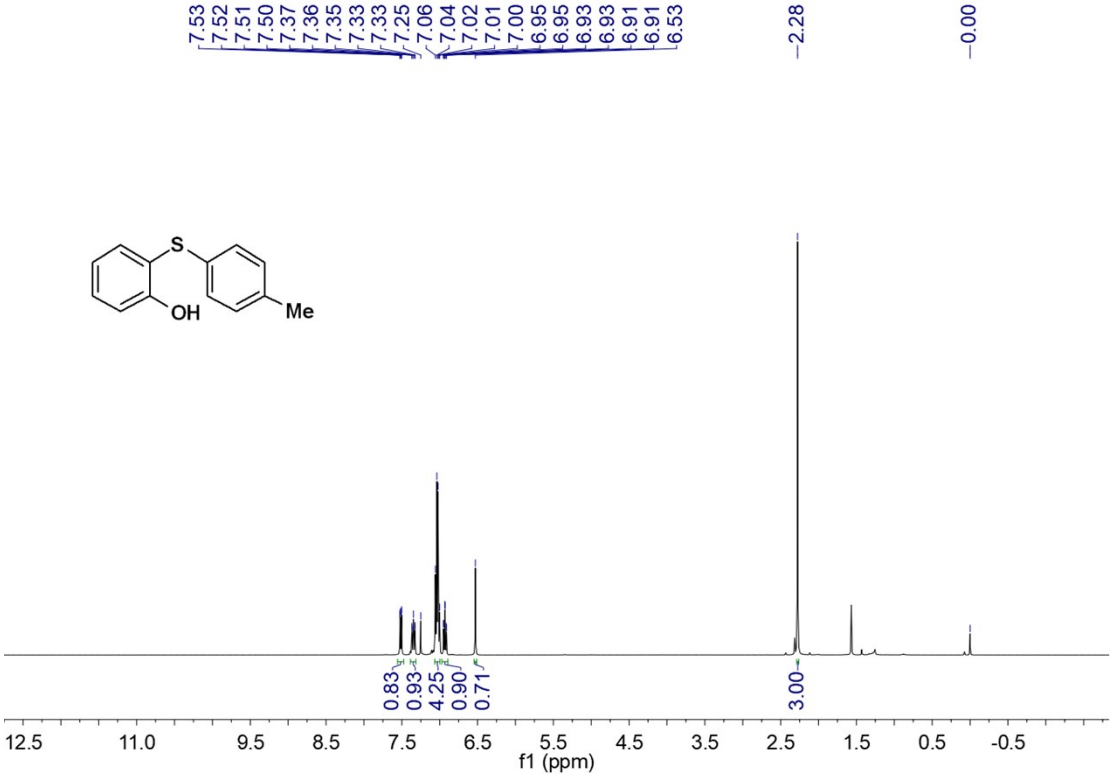
NMR Spectra of product **3j**:

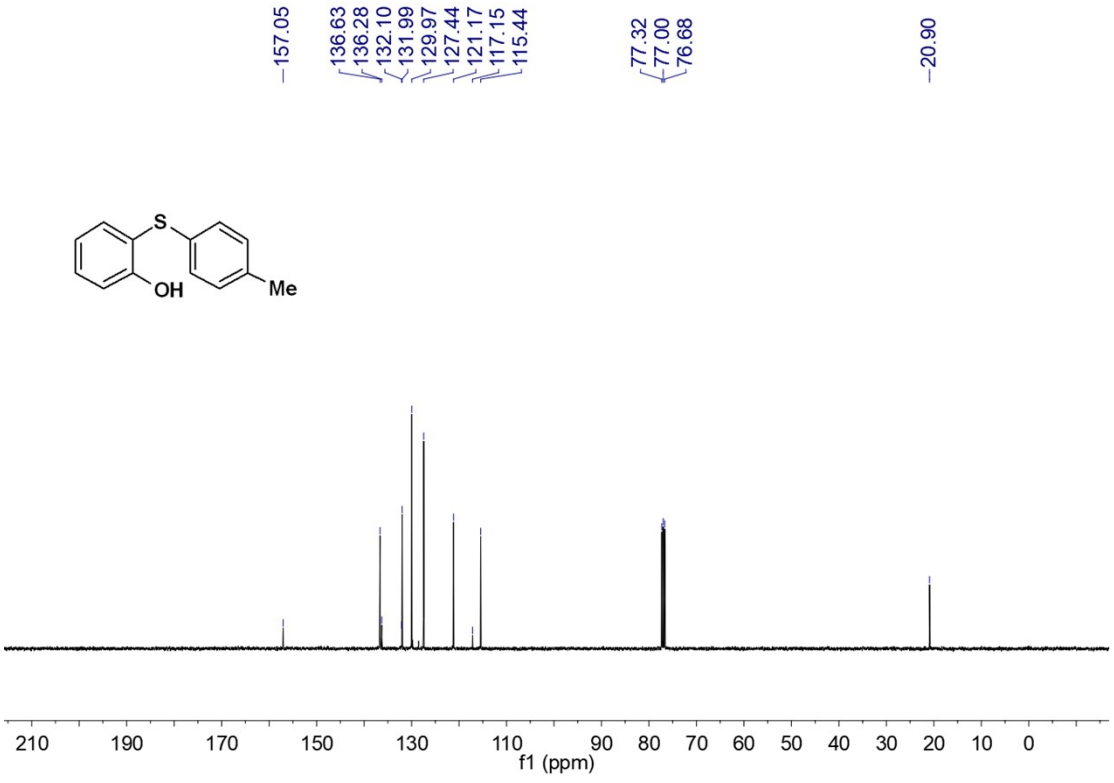


NMR Spectra of product **3k**:

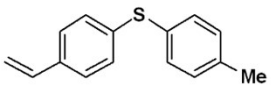


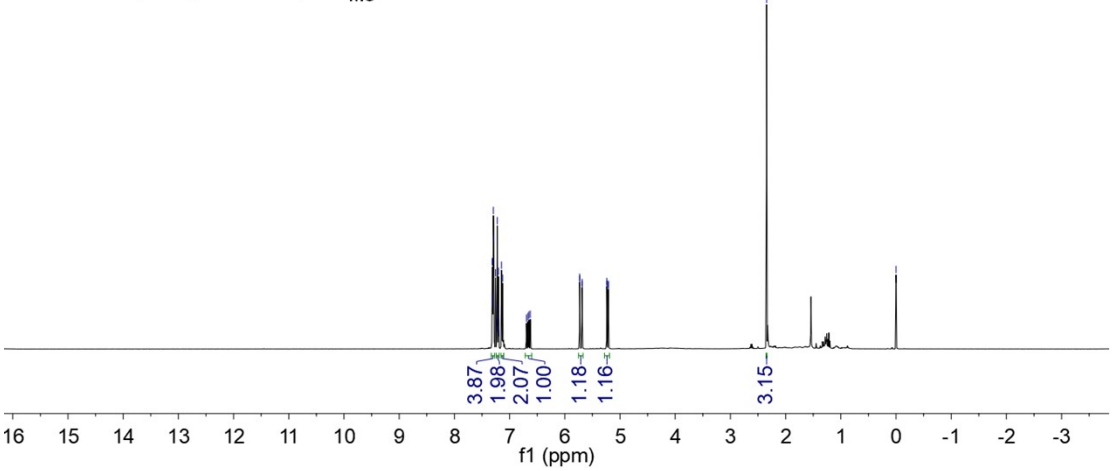
NMR Spectra of product **3l**:

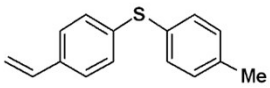


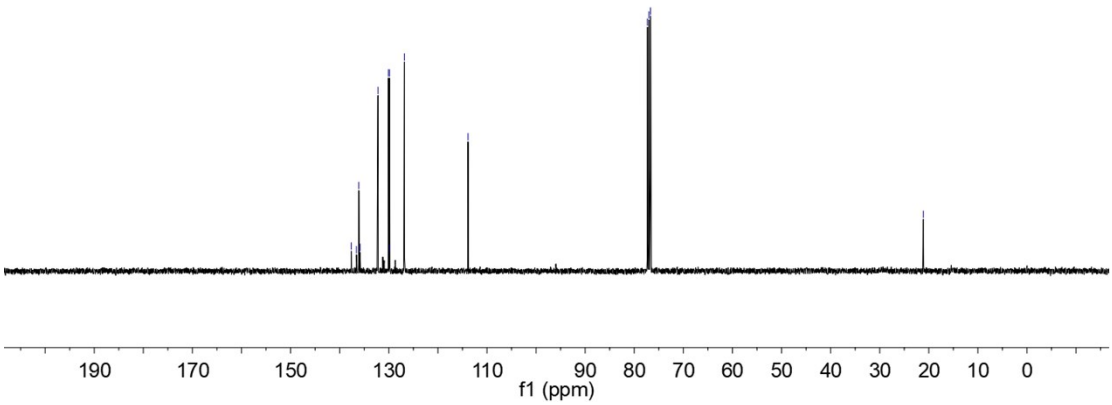


NMR Spectra of product **3m**:

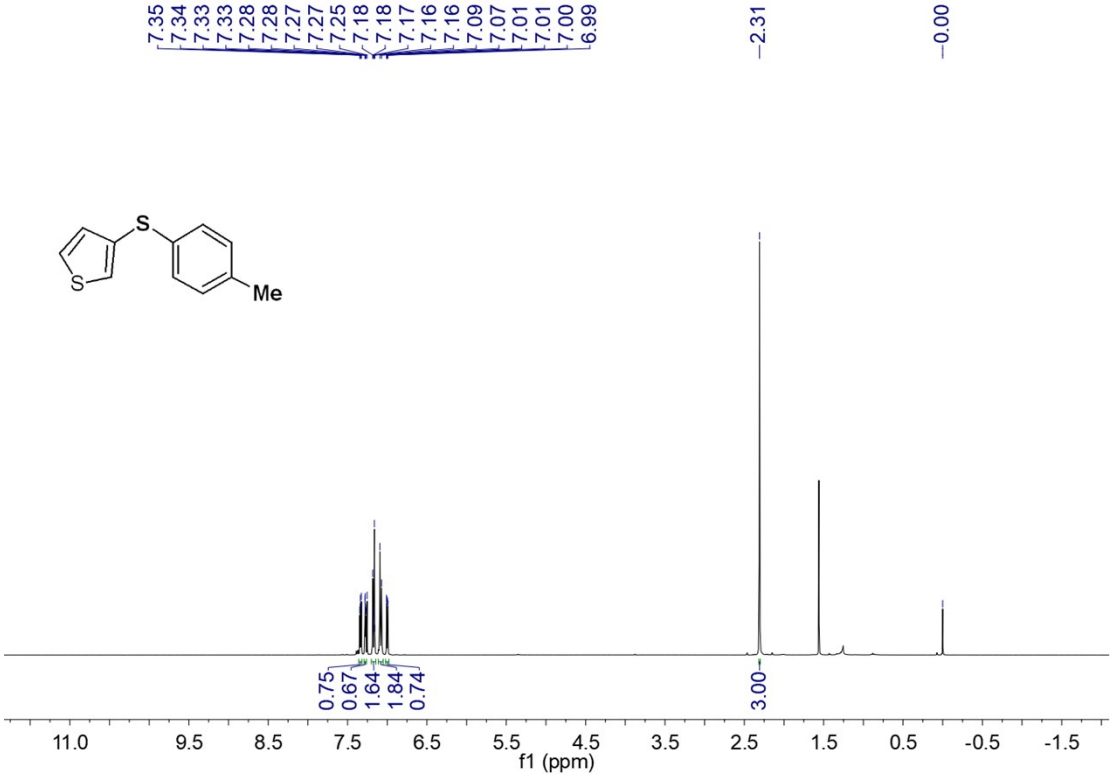


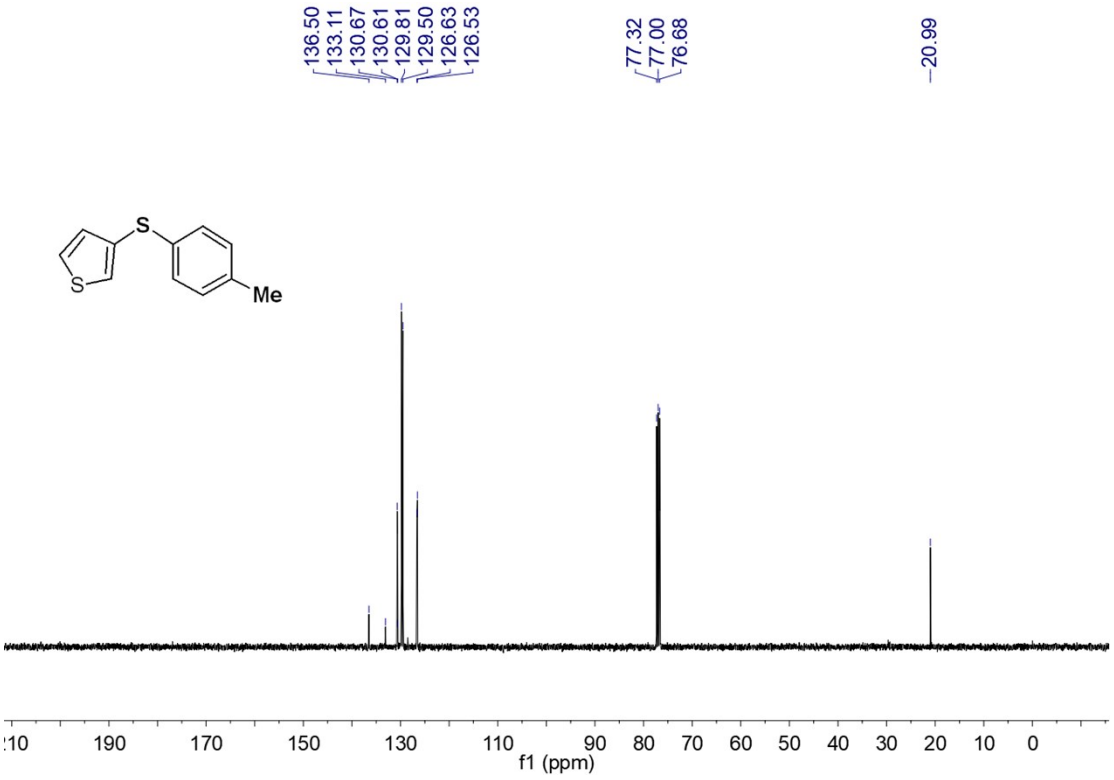




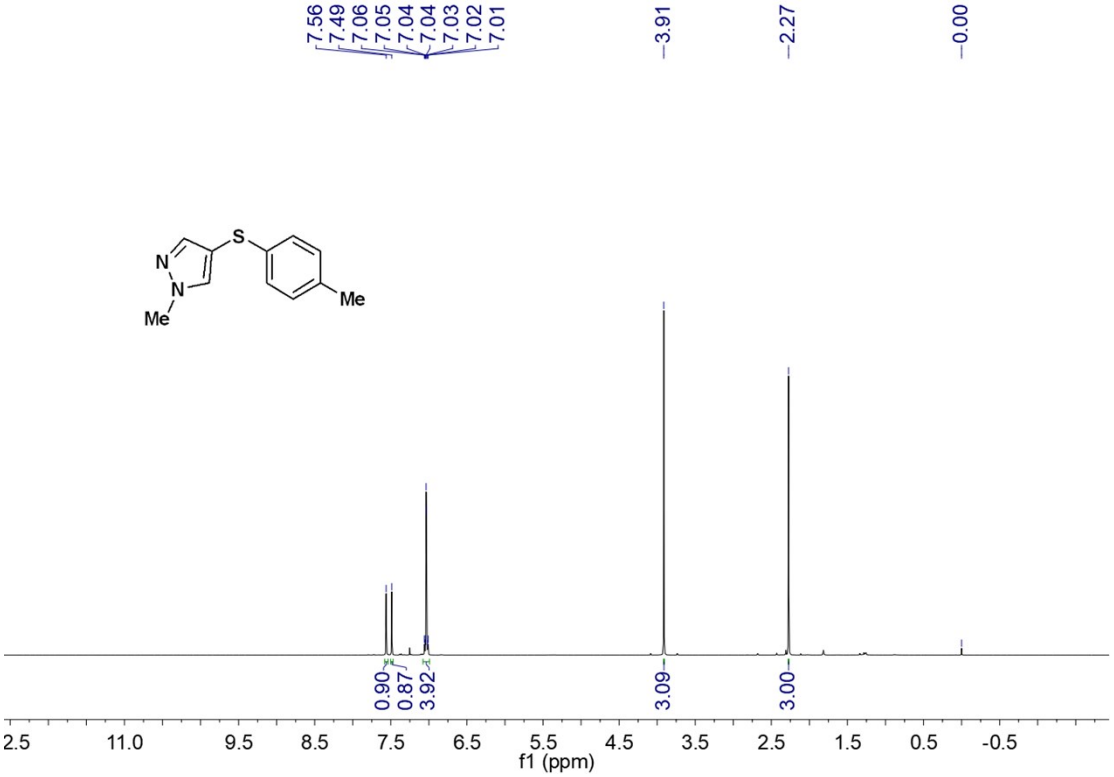


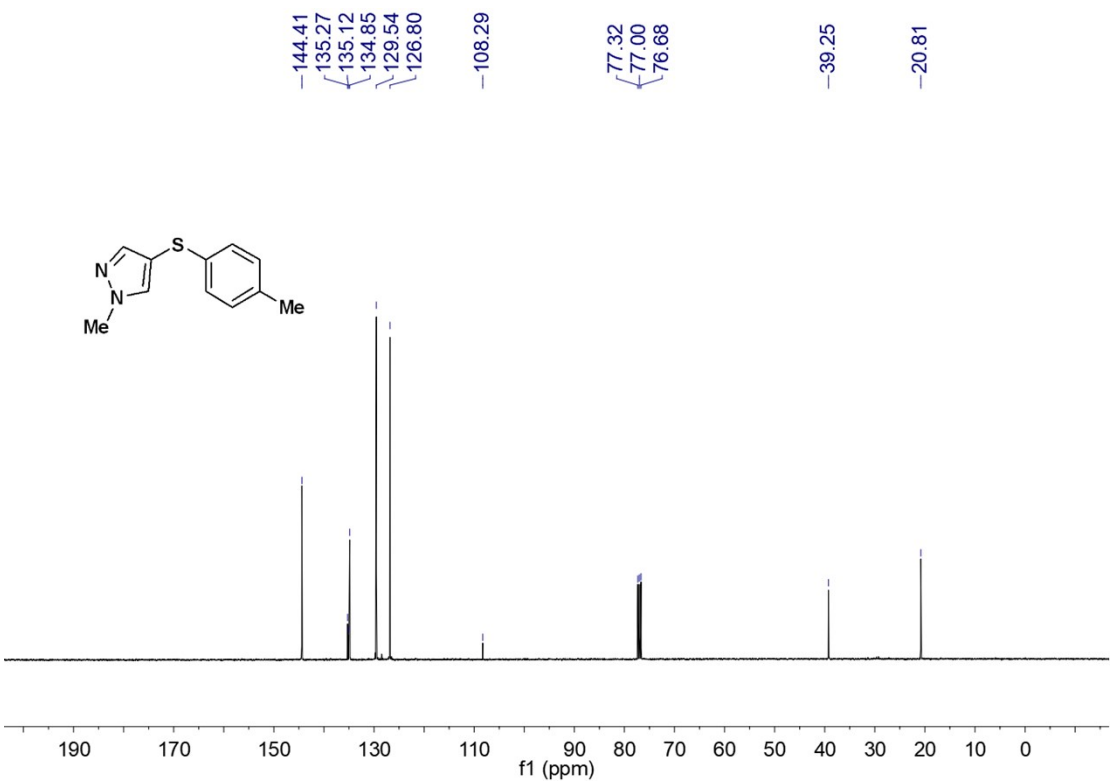
NMR Spectra of product **3n**:



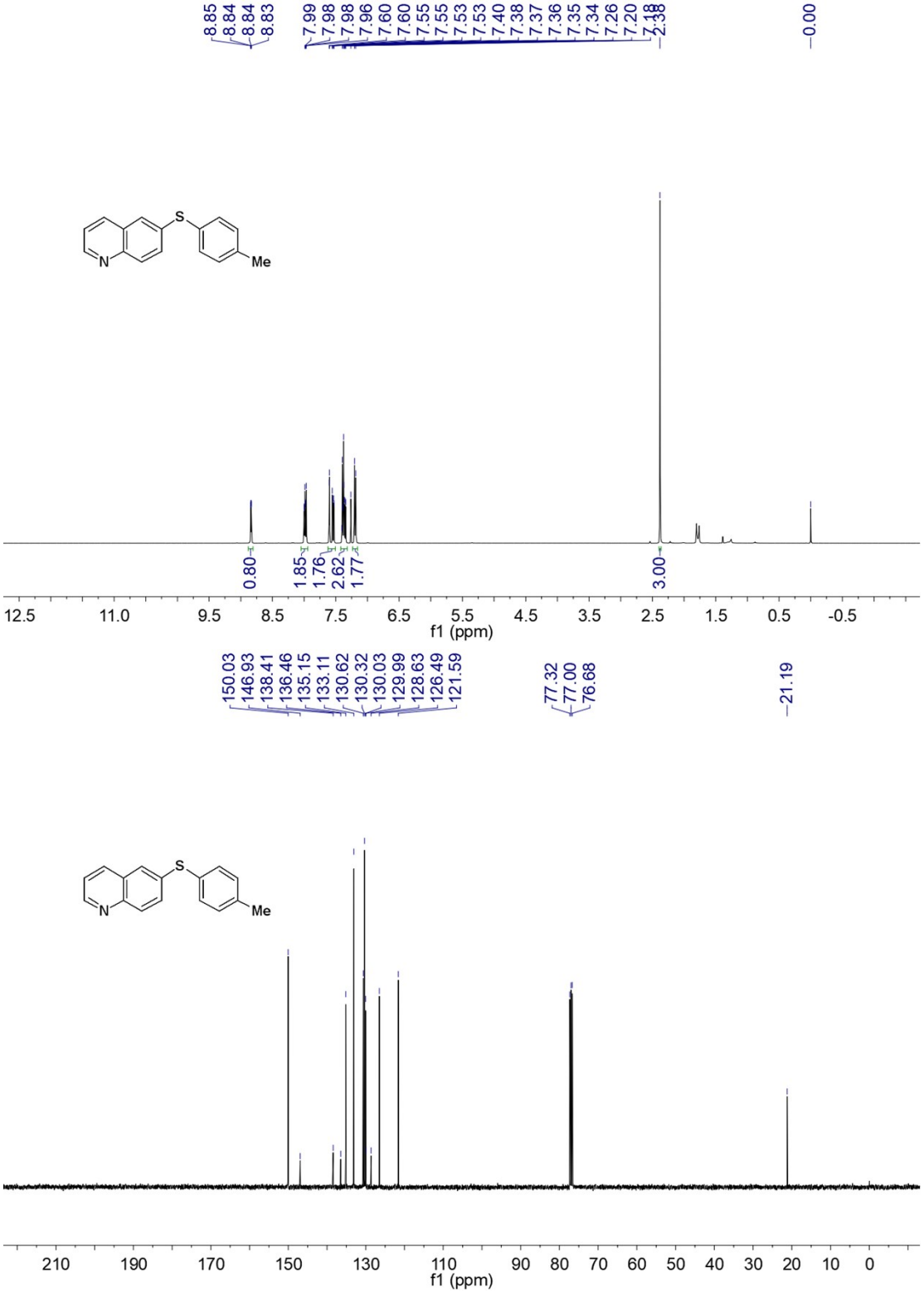


NMR Spectra of product **3o**:

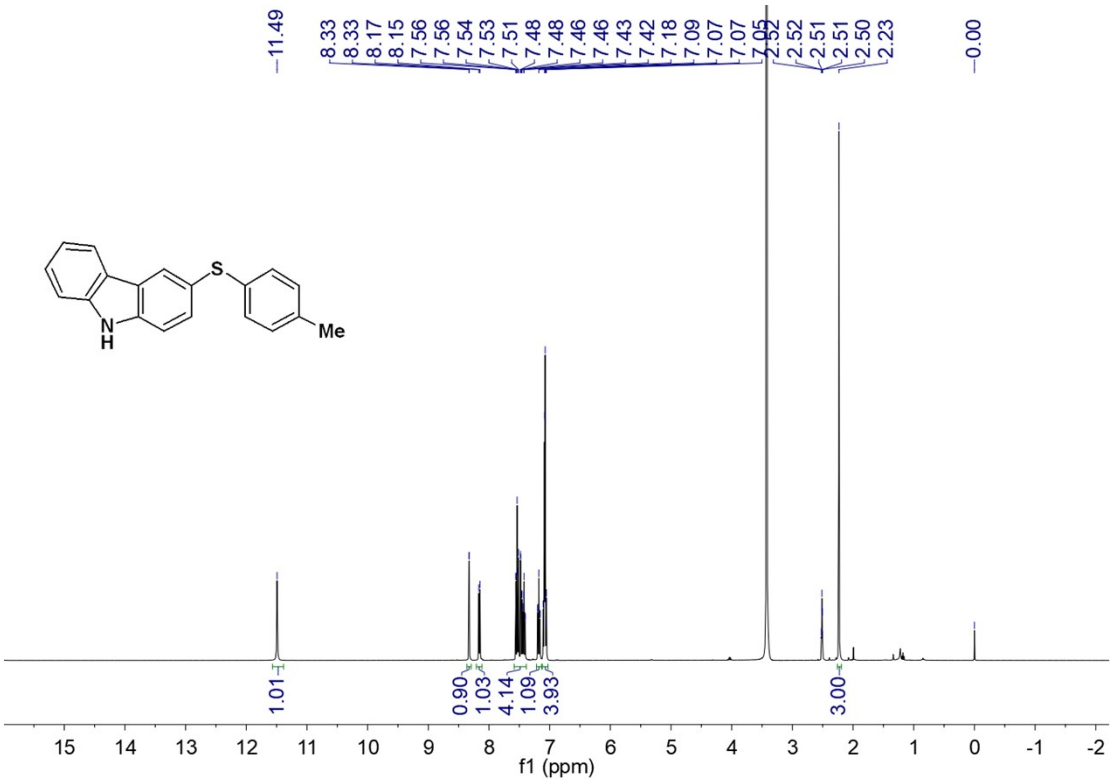


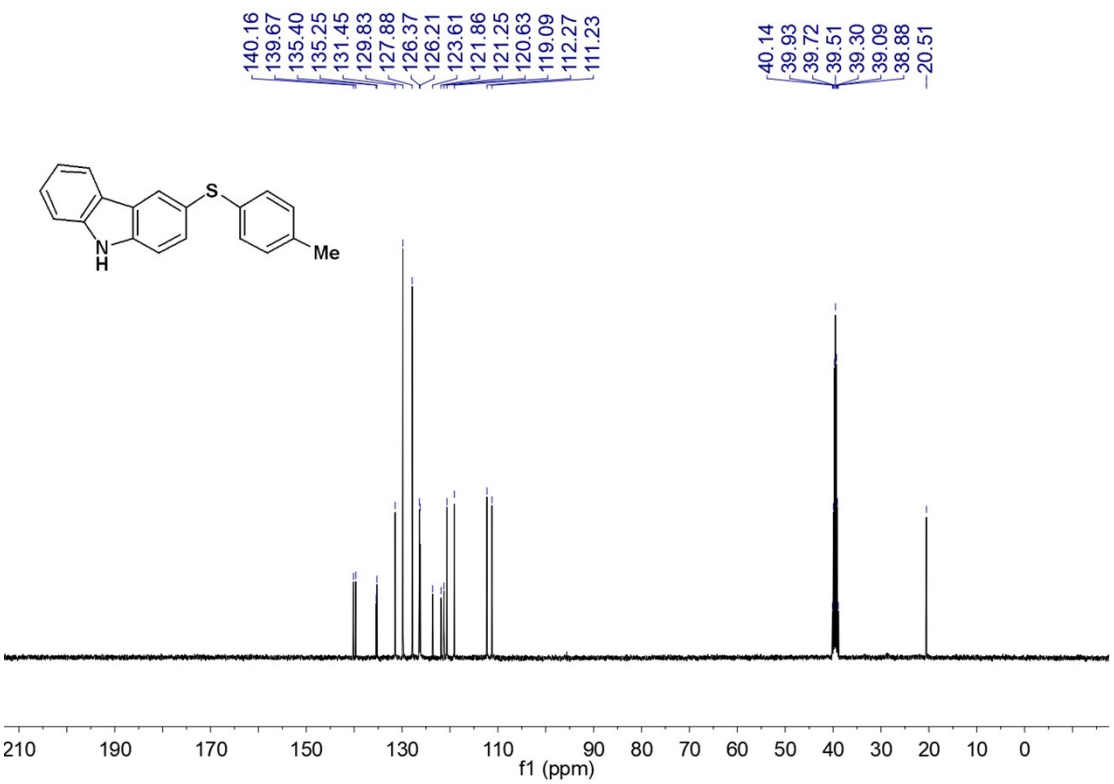


NMR Spectra of product **3p**:

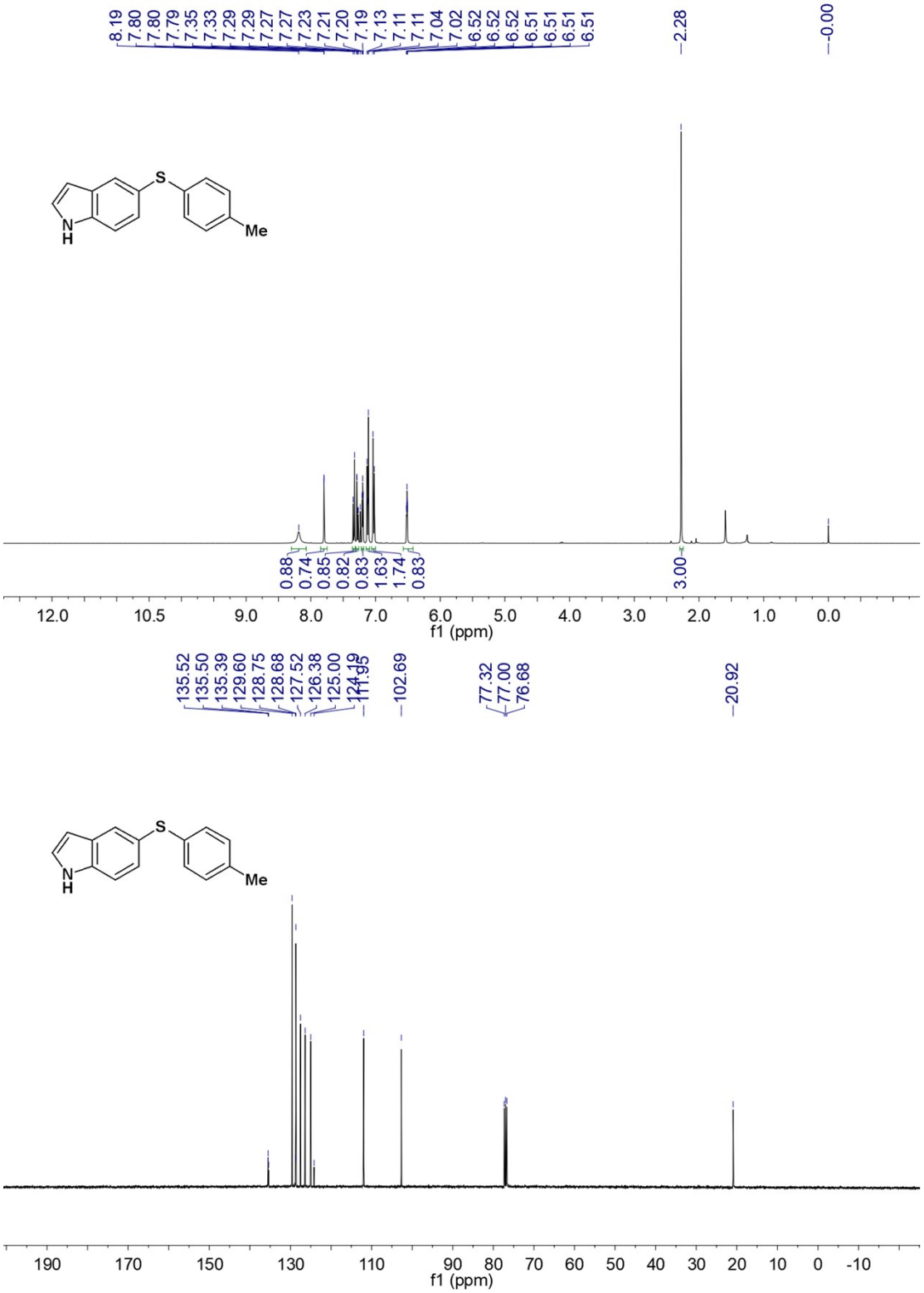


NMR Spectra of product **3q**:

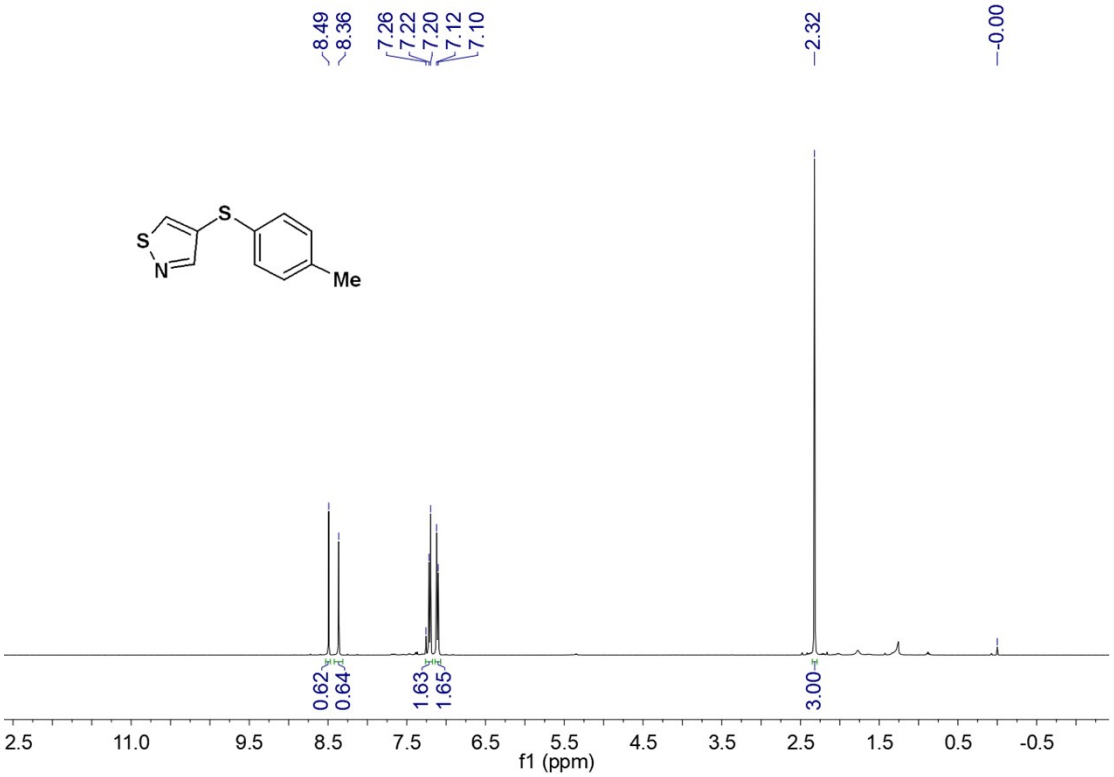


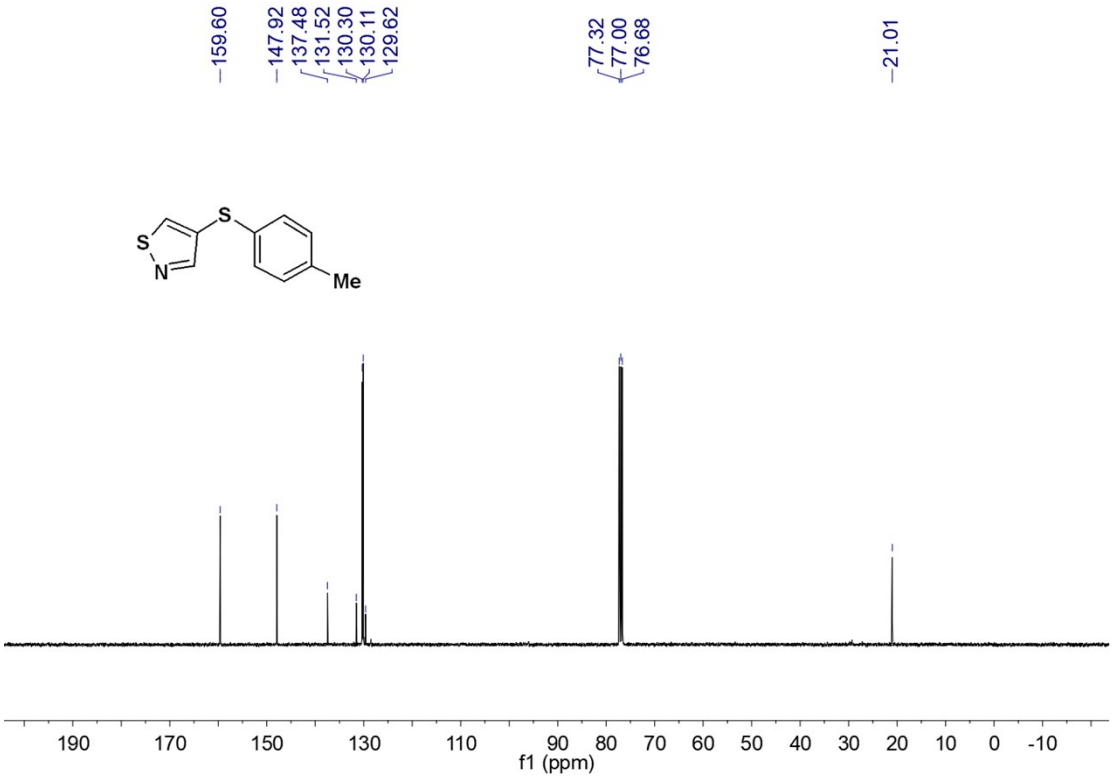


NMR Spectra of product **3r**:

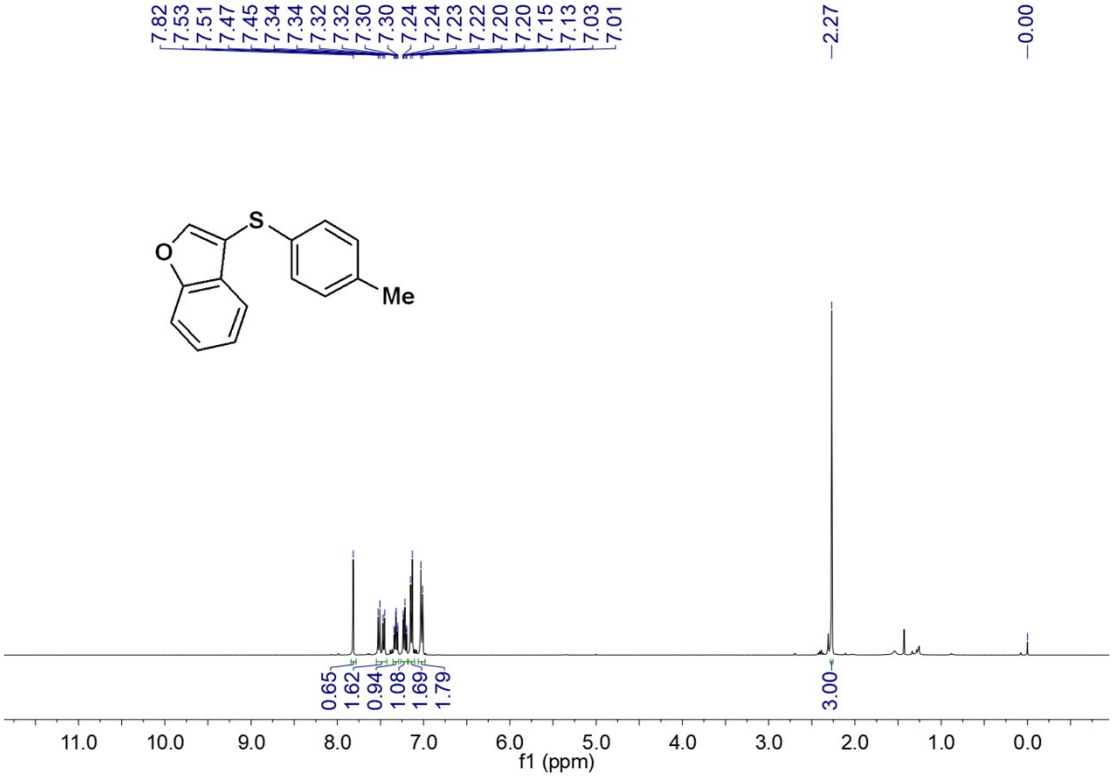


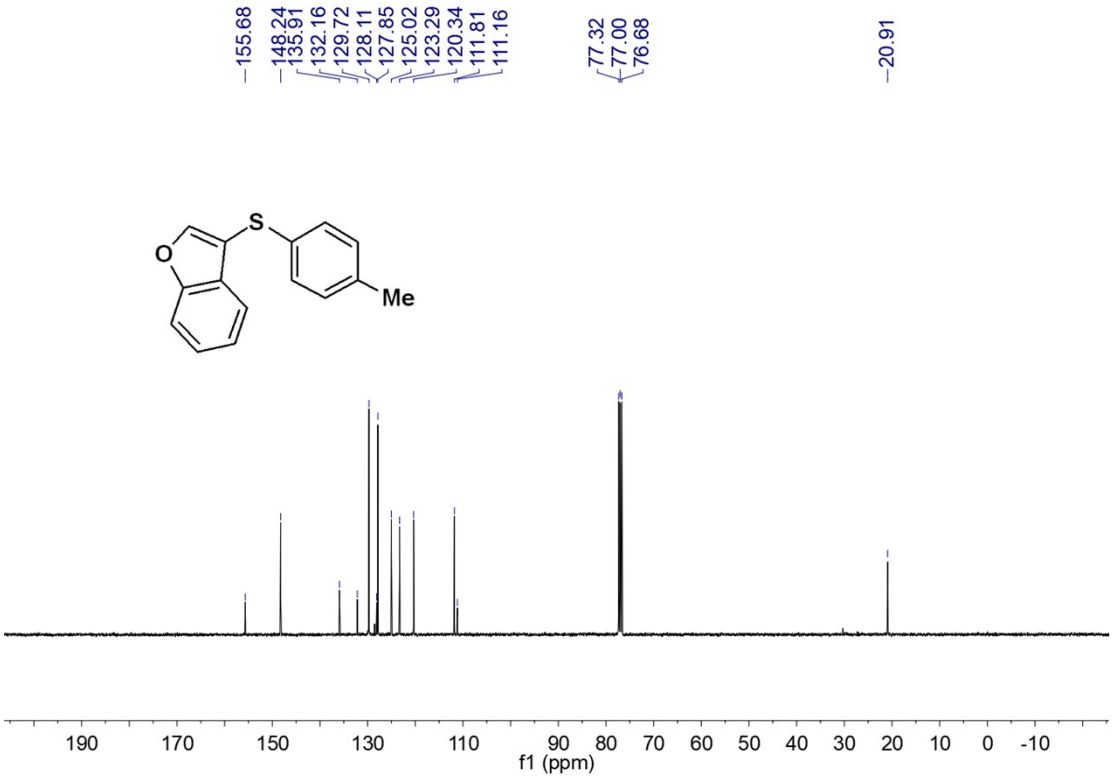
NMR Spectra of product **3s**:



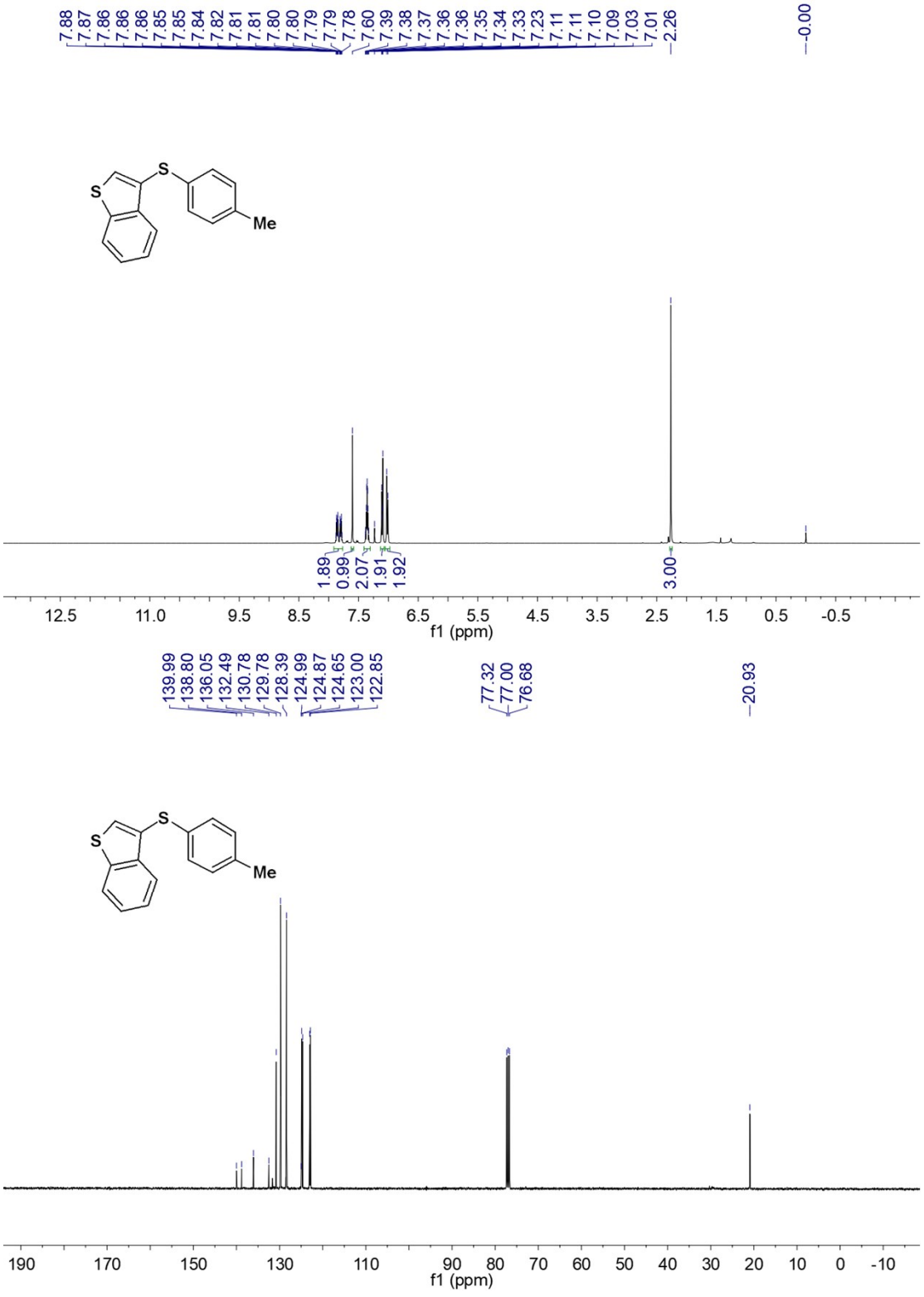


NMR Spectra of product **3t**:

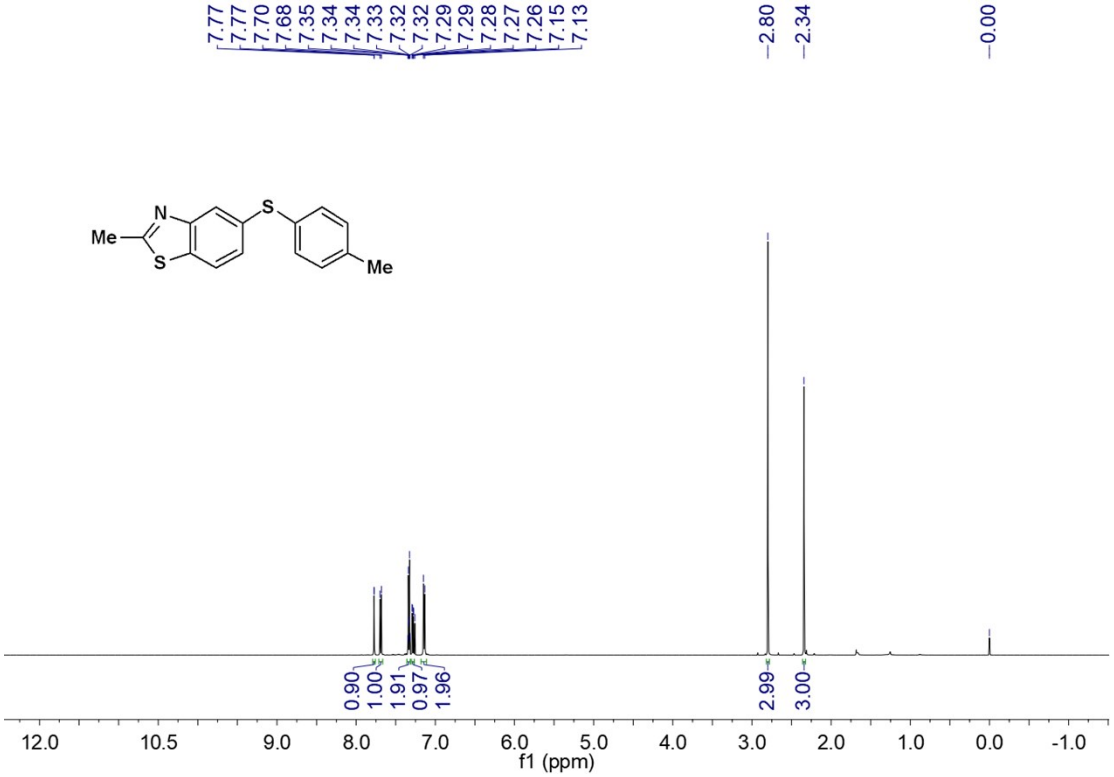


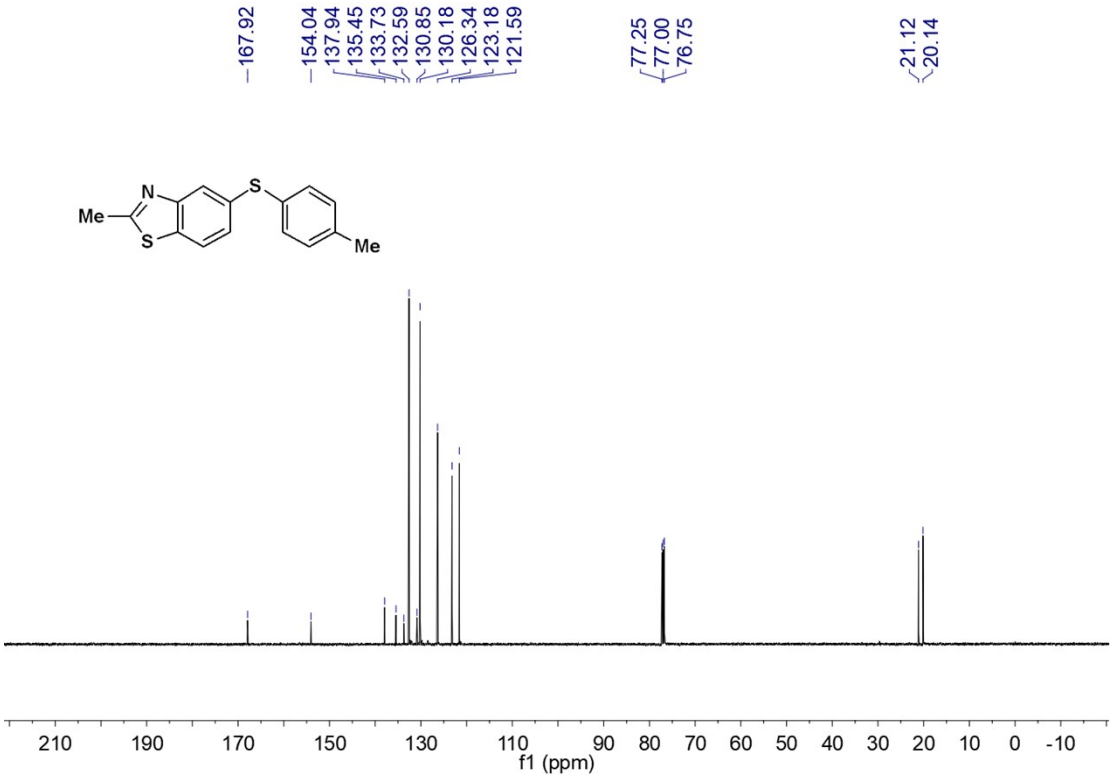


NMR Spectra of product **3u**:

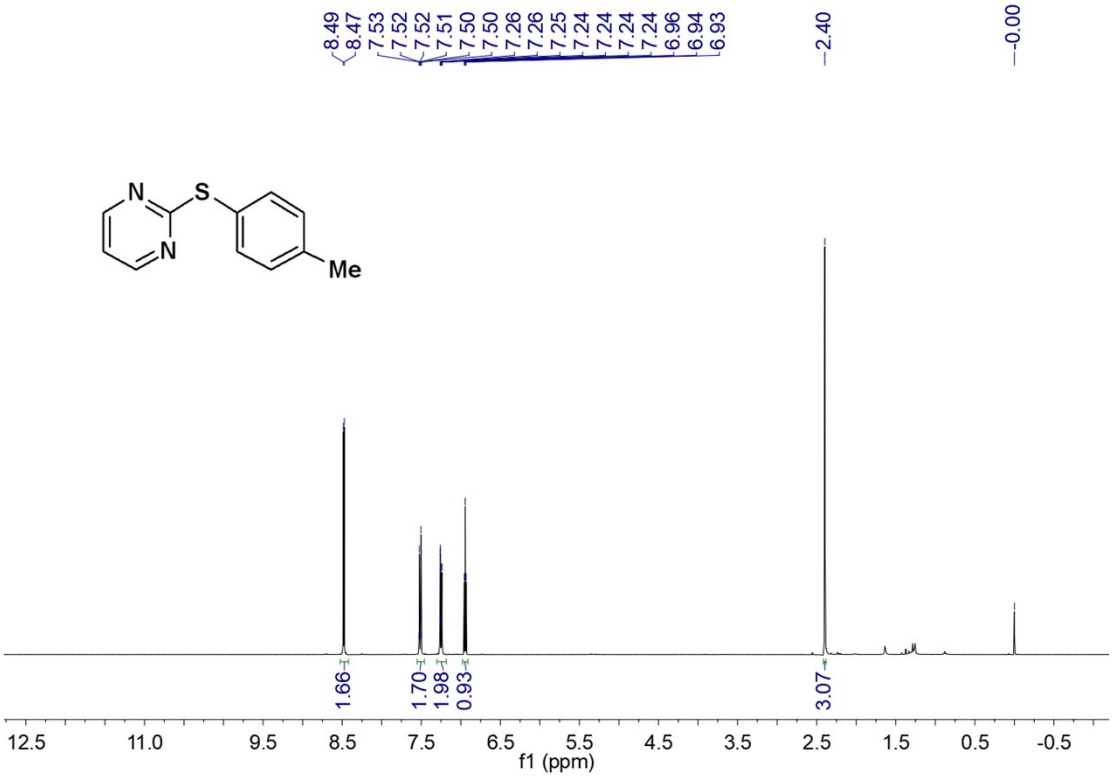


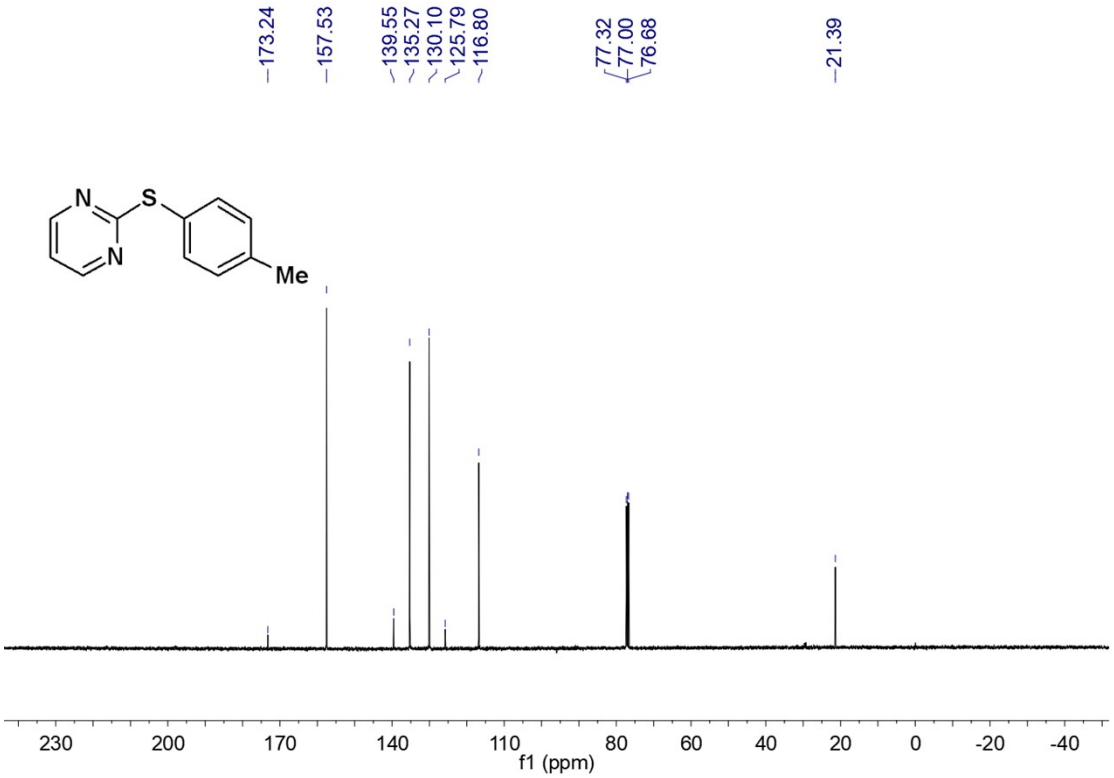
NMR Spectra of product **3v**:



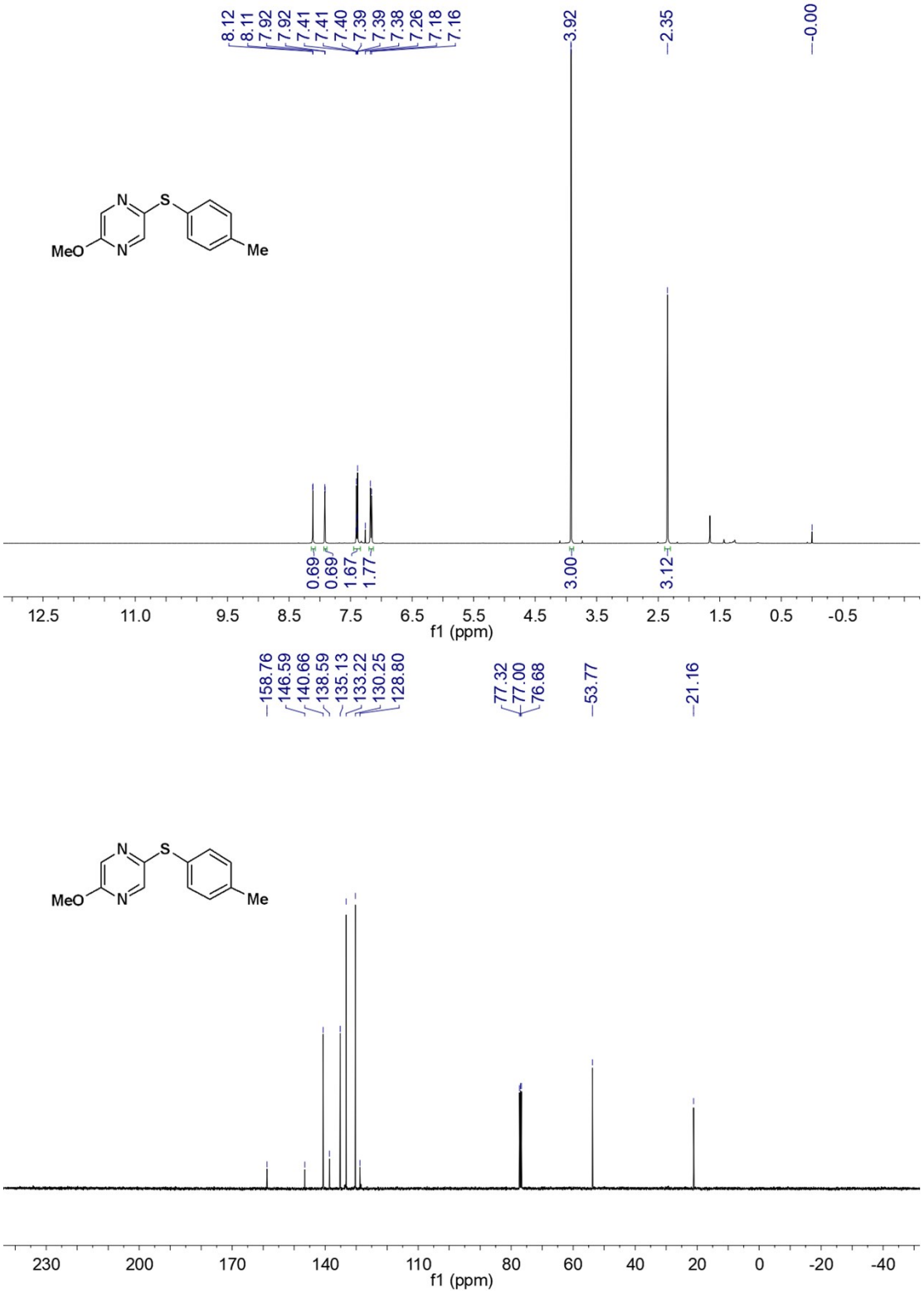


NMR Spectra of product **3w**:

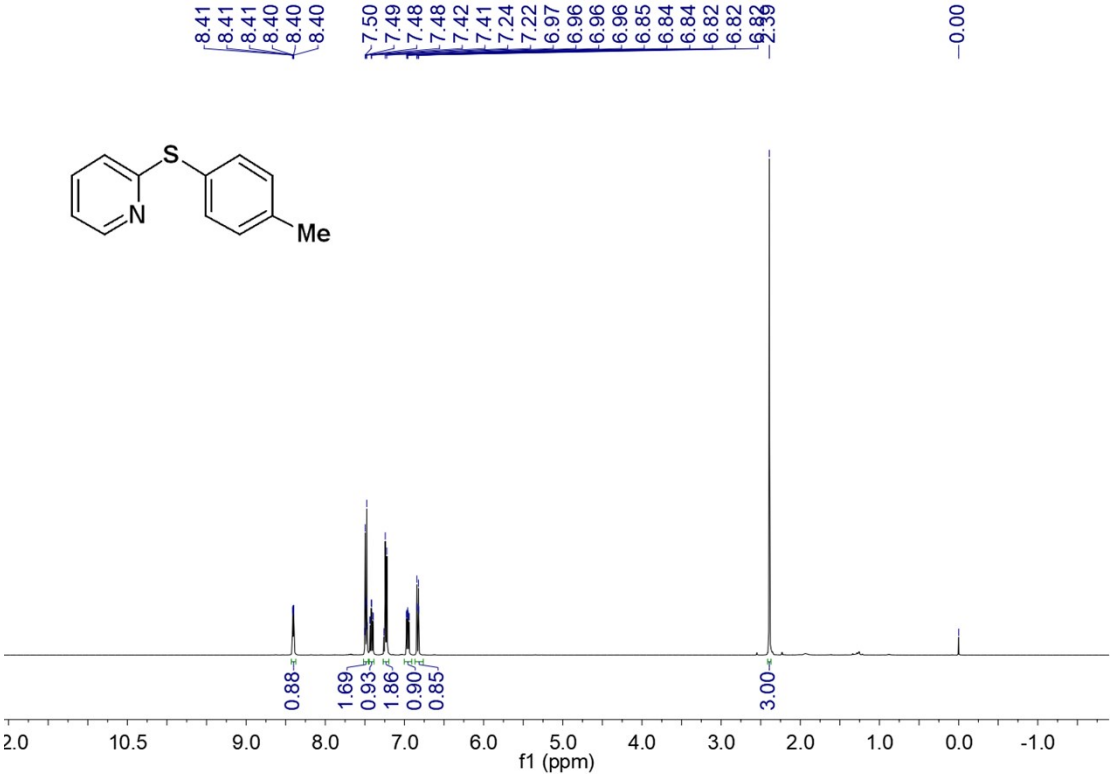


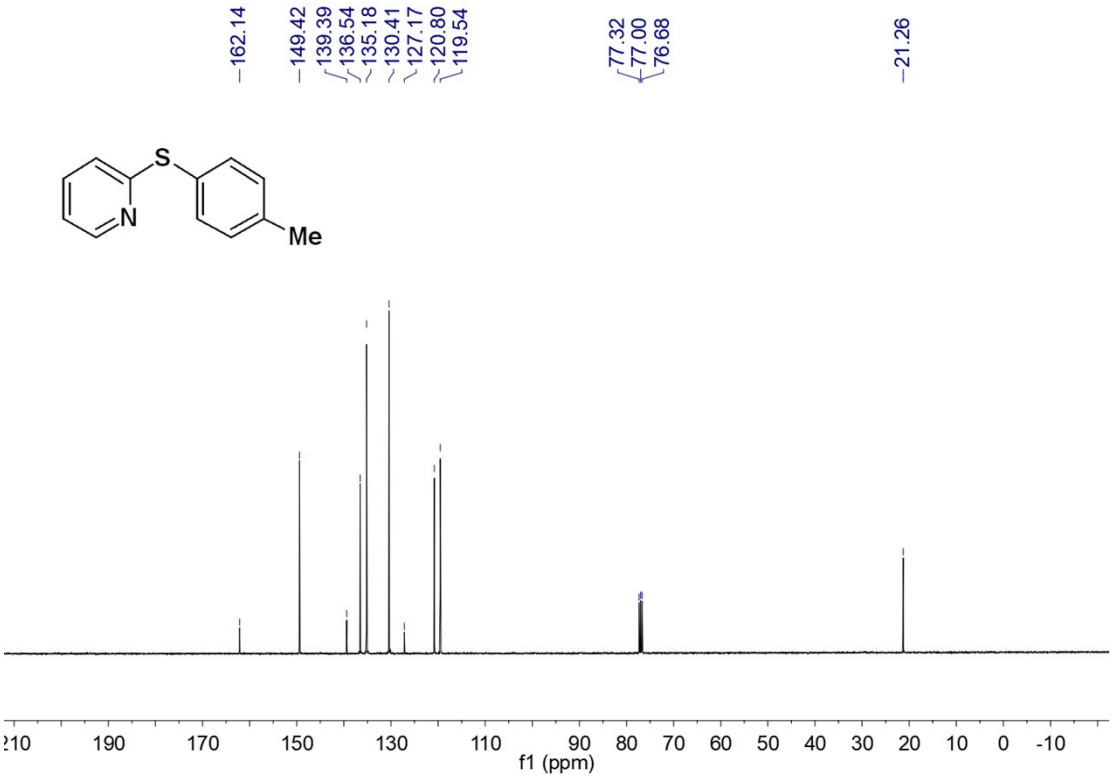


NMR Spectra of product **3x**:

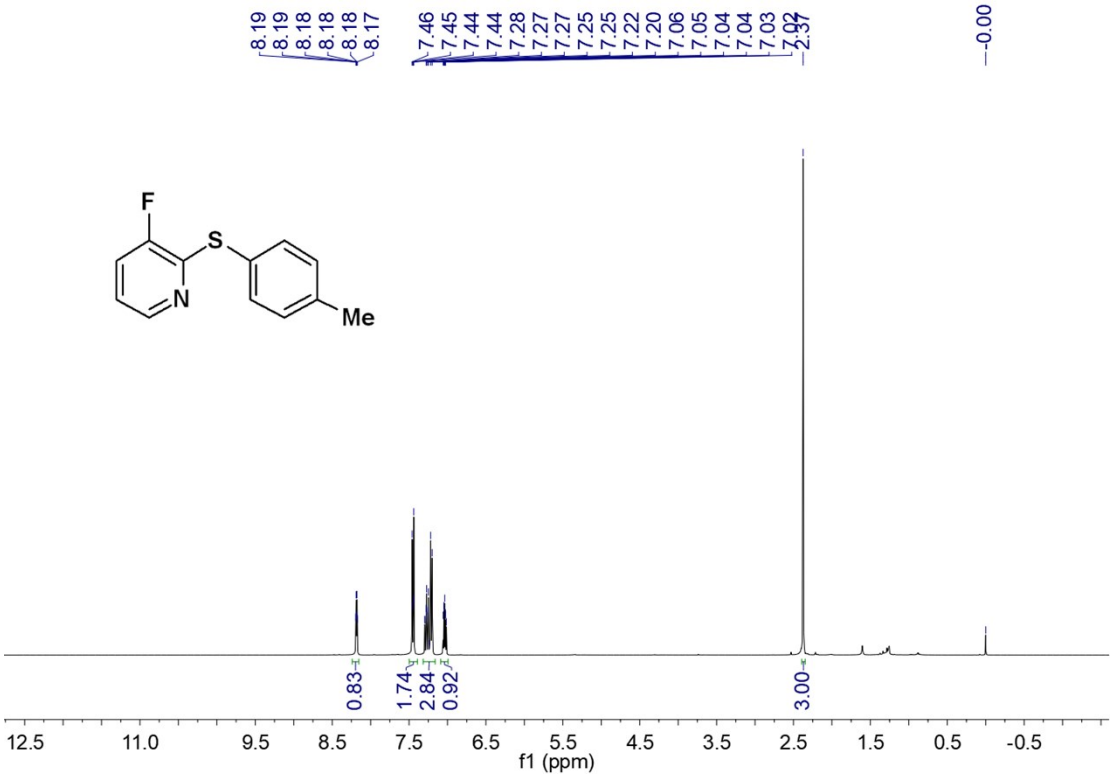


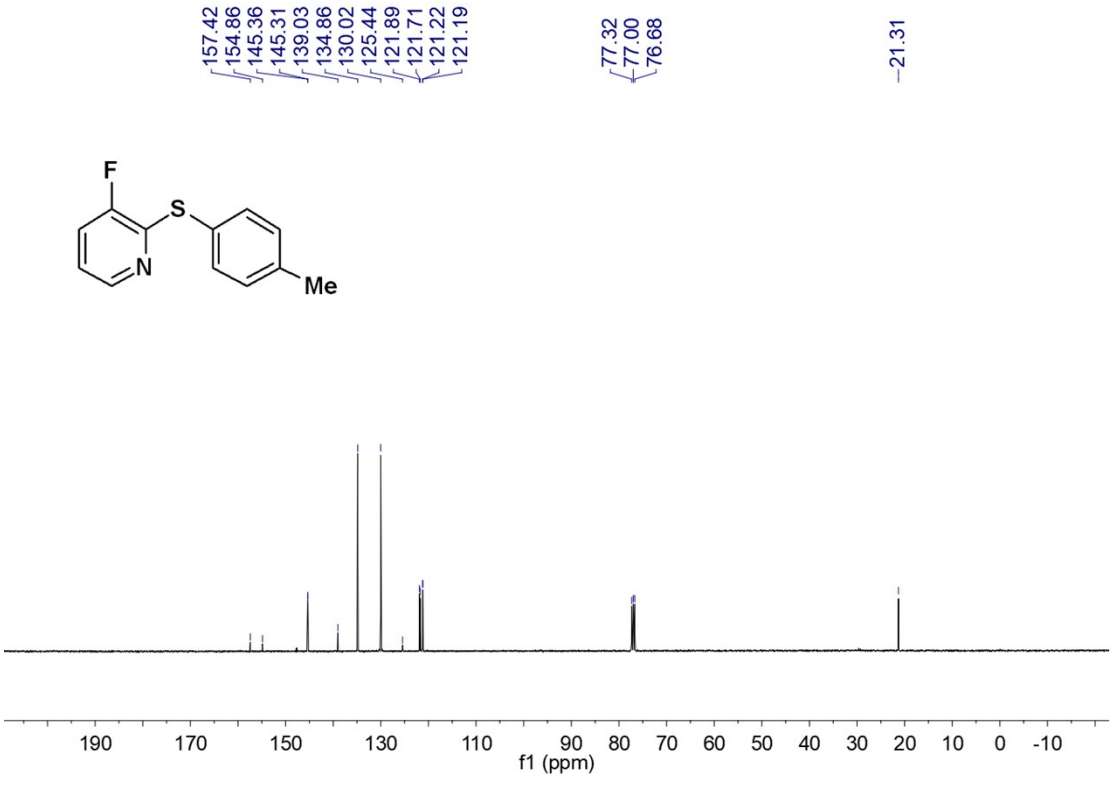
NMR Spectra of product **3y**:



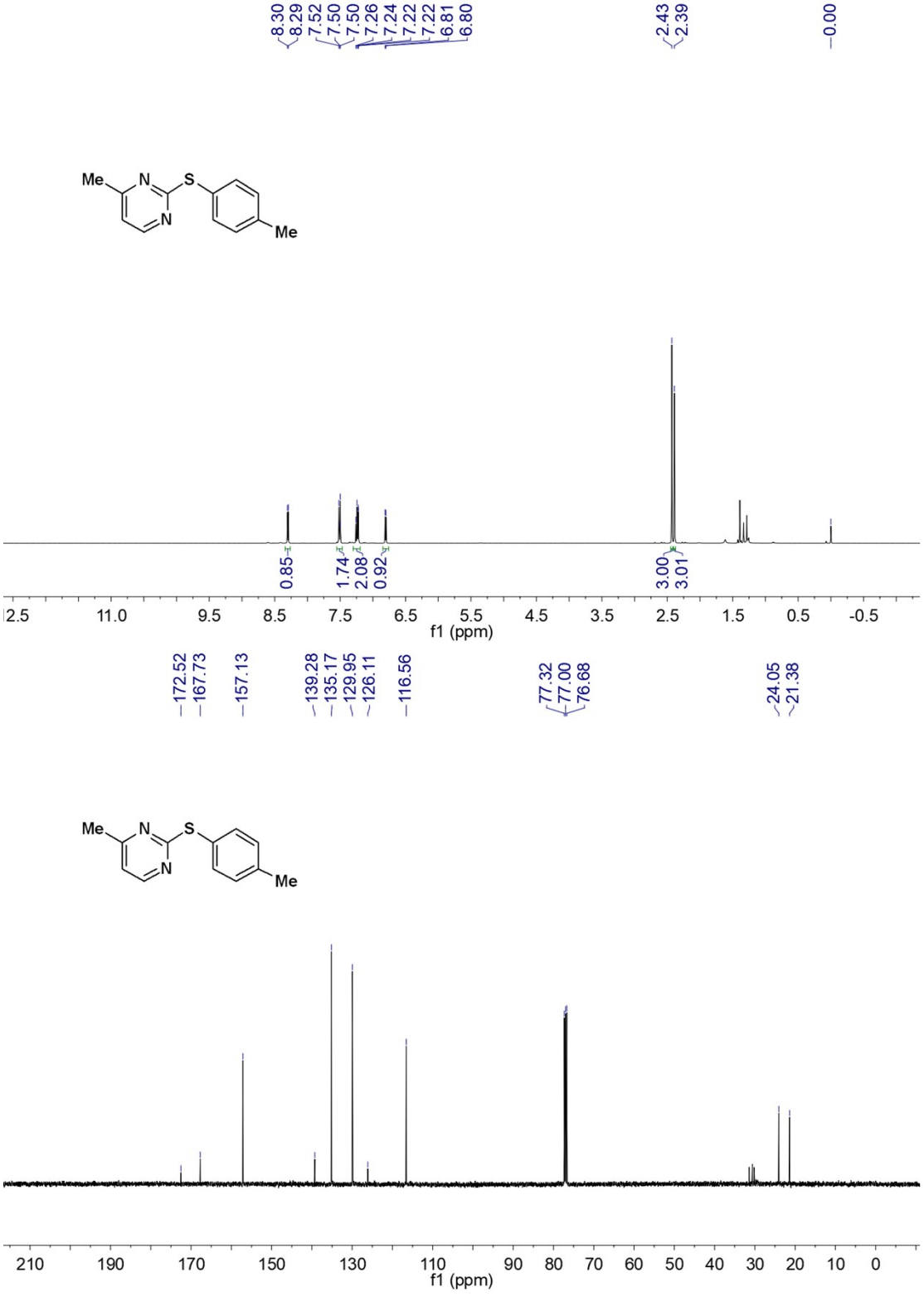


NMR Spectra of product **3z**:

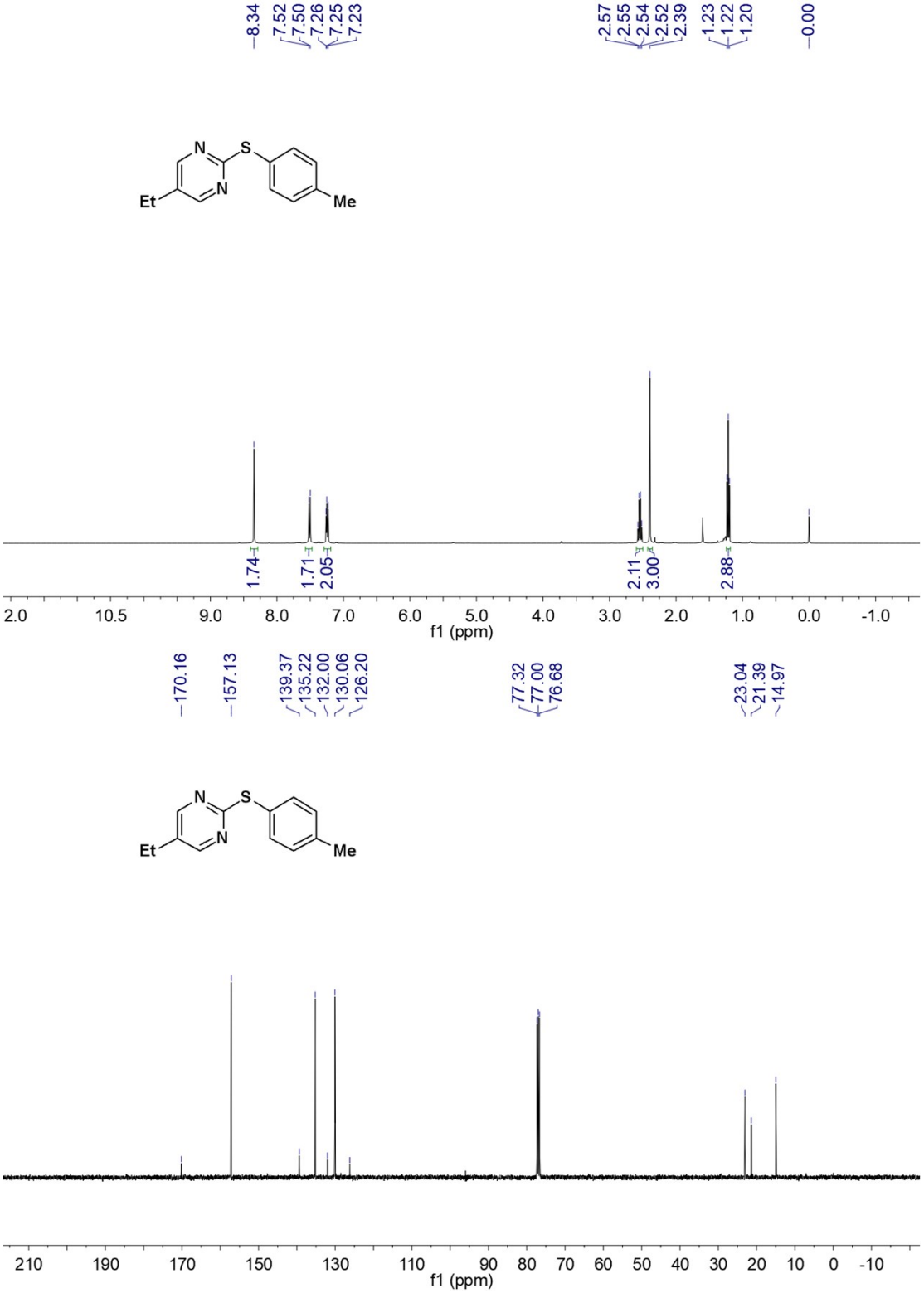




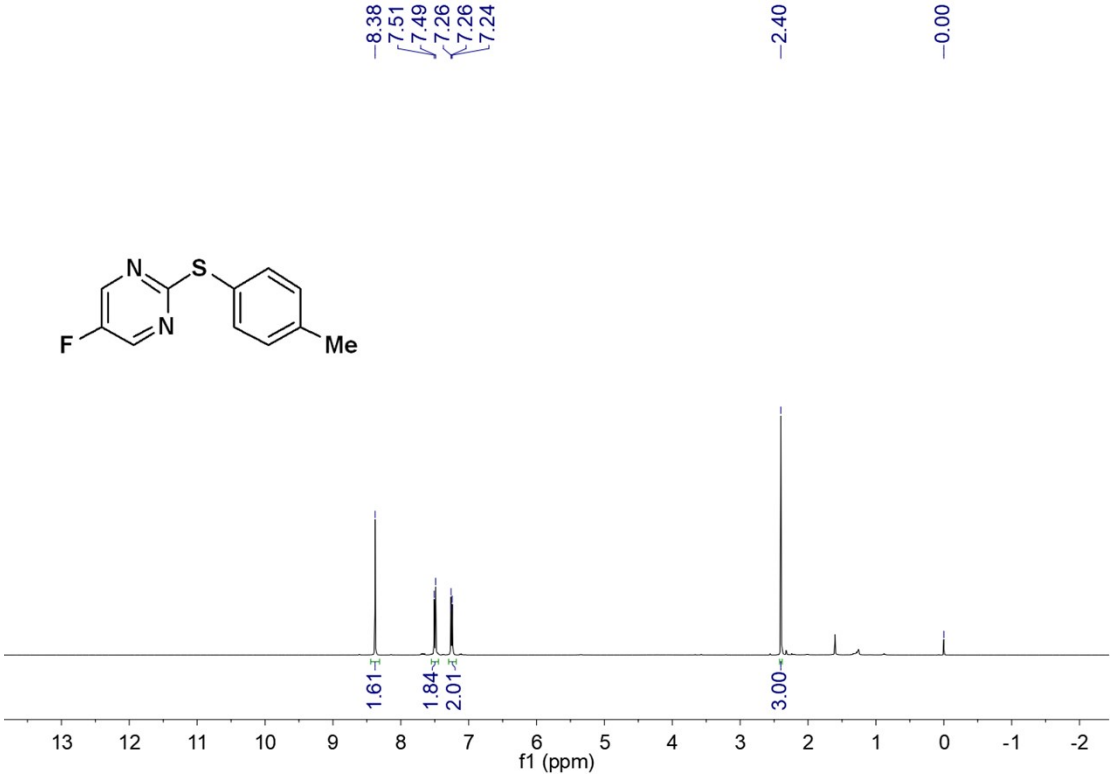
NMR Spectra of product **3aa**:

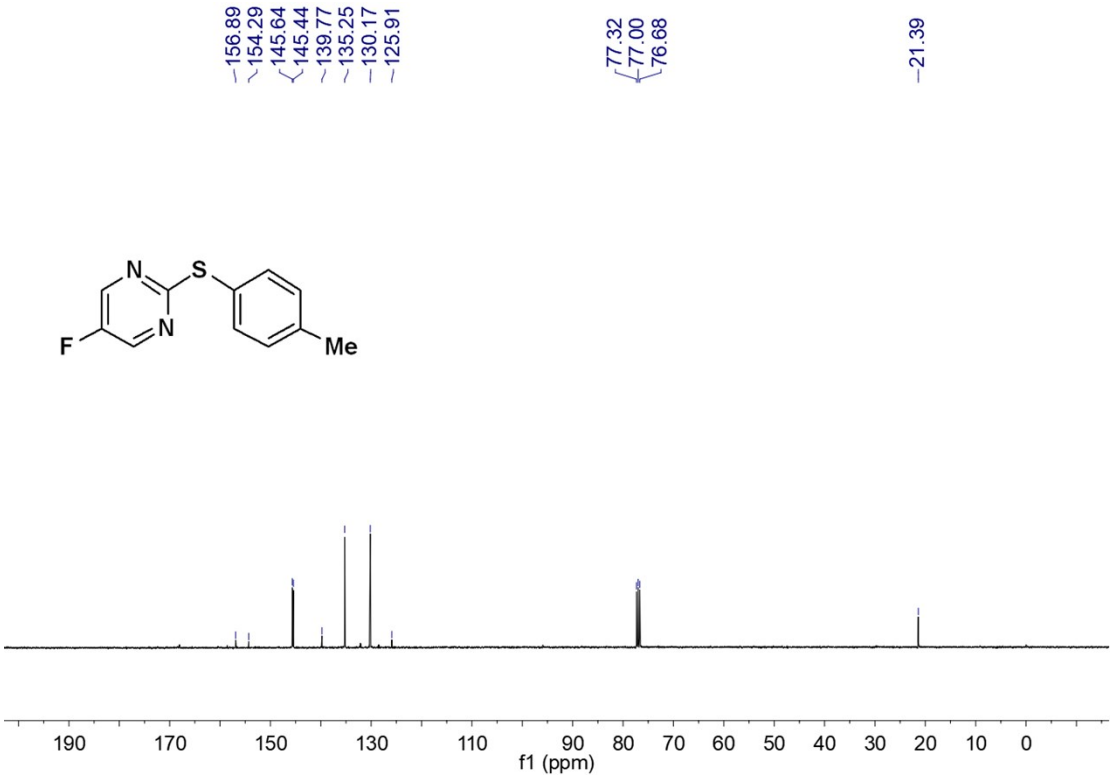


NMR Spectra of product **3bb**:

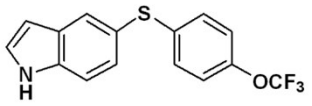


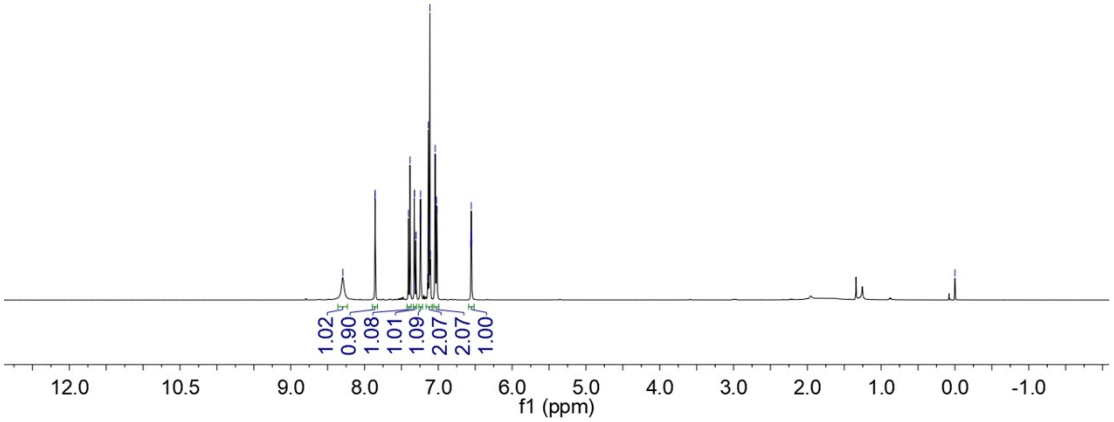
NMR Spectra of product **3cc**:

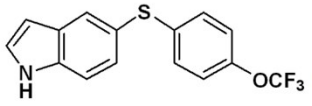


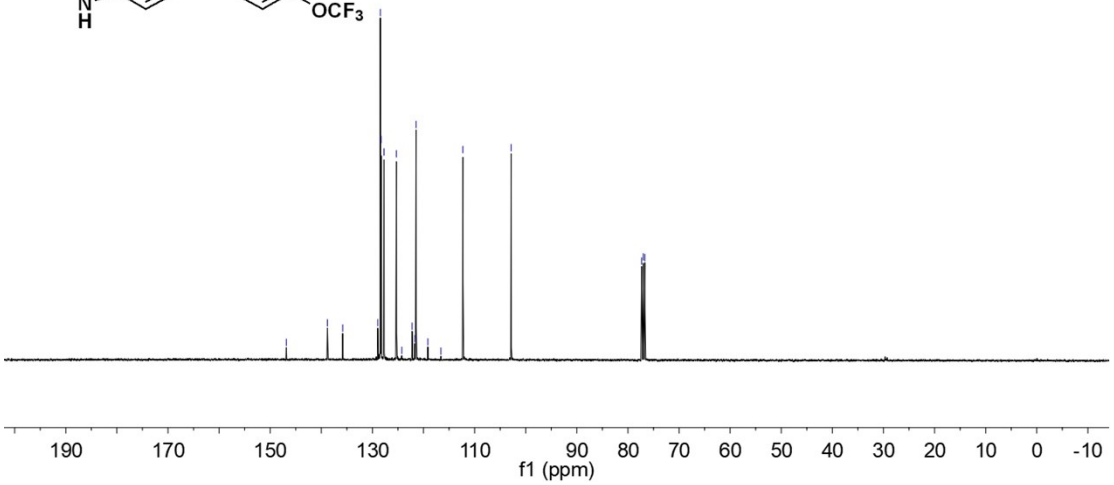


NMR Spectra of product **3dd**:

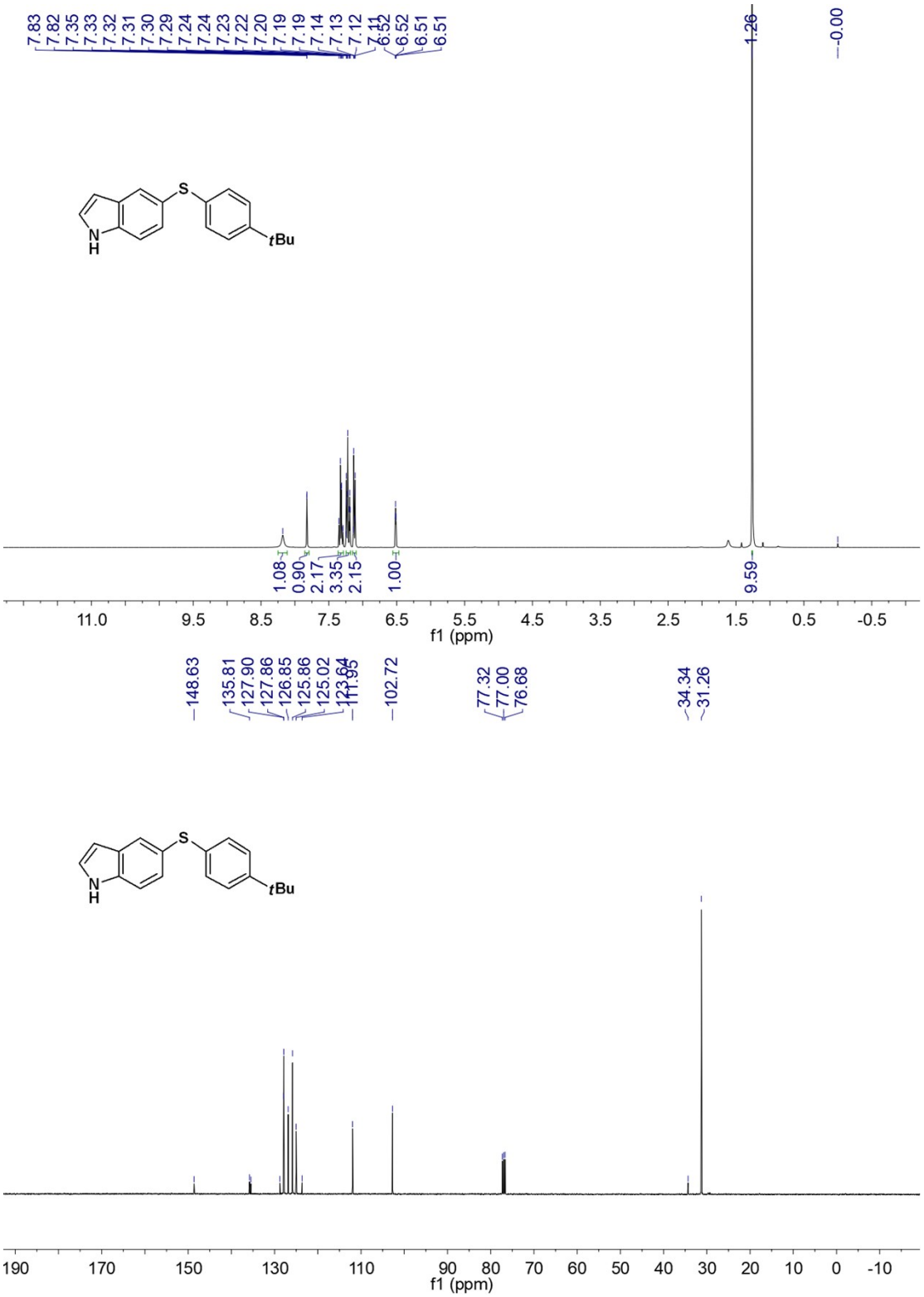




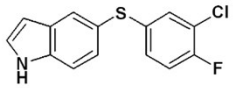


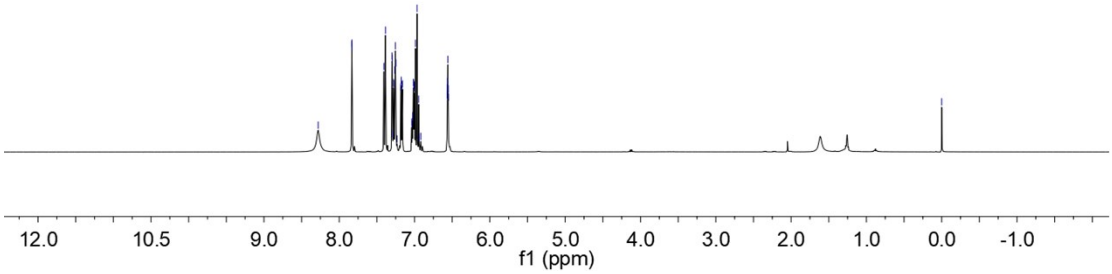


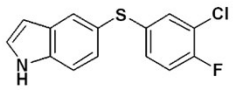
NMR Spectra of product **3ee**:

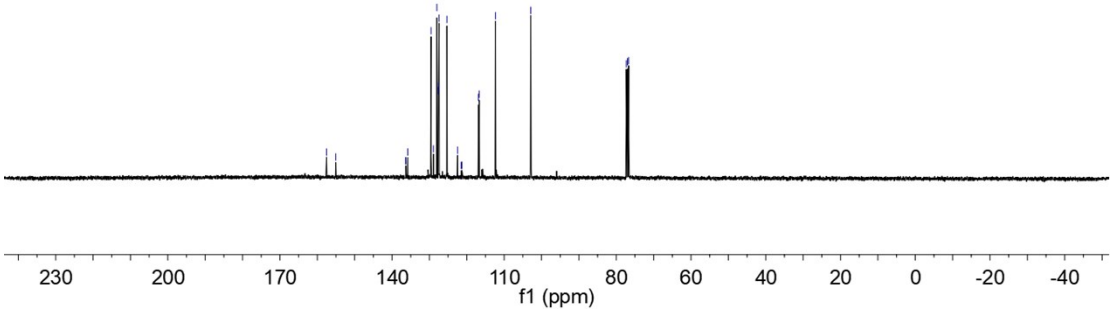


NMR Spectra of product **3ff**:

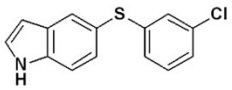


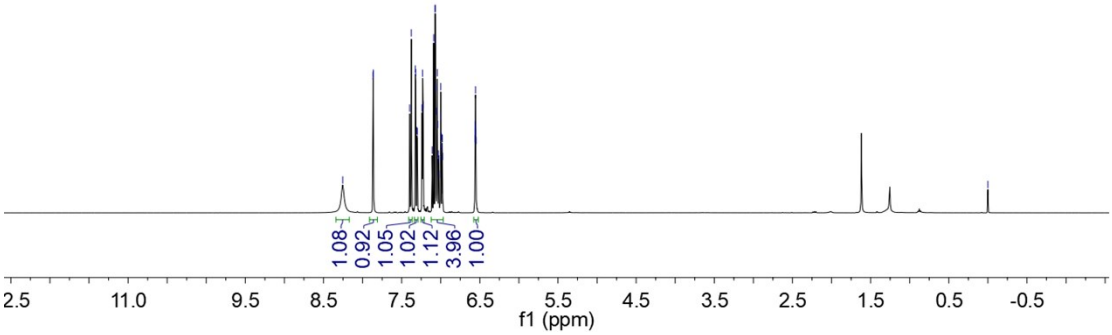


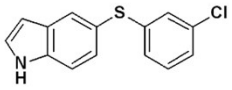


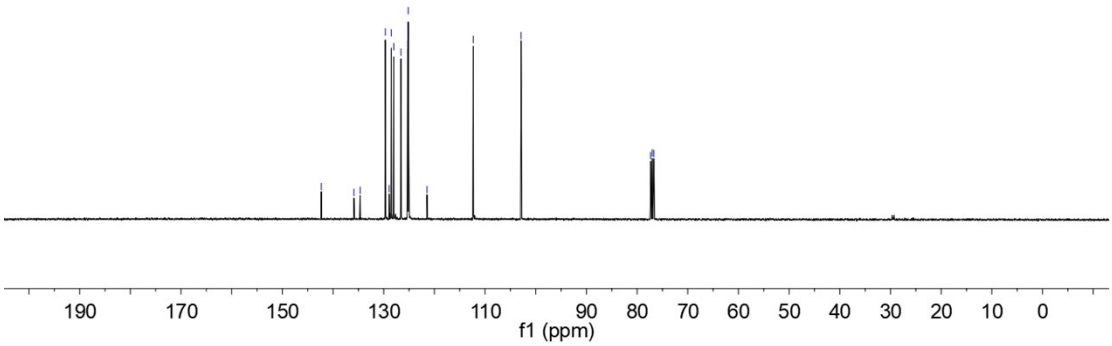


NMR Spectra of product **3gg**:

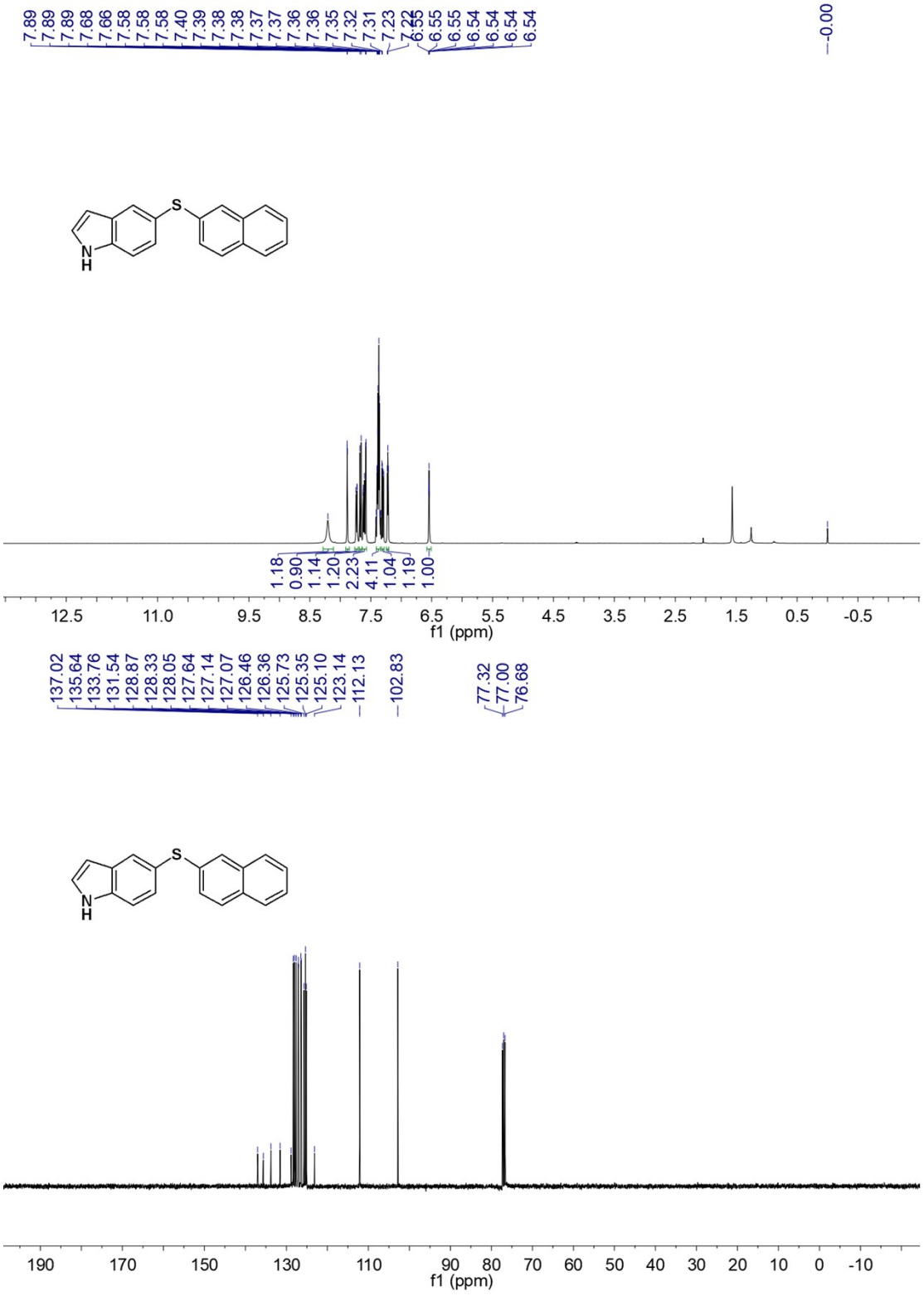








NMR Spectra of product **3hh**:



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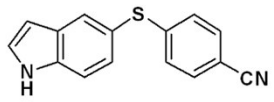

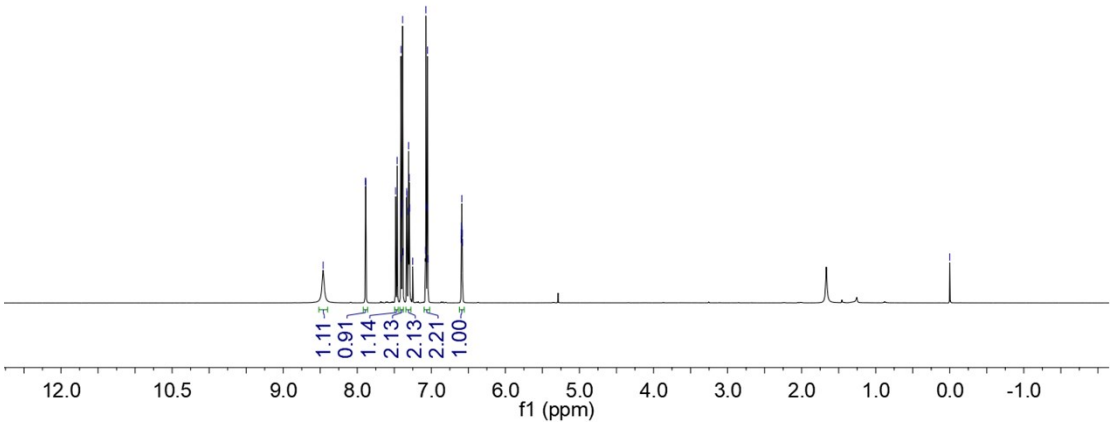

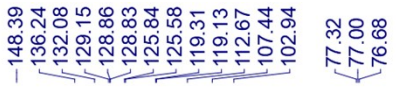

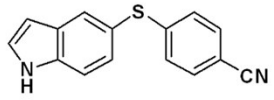

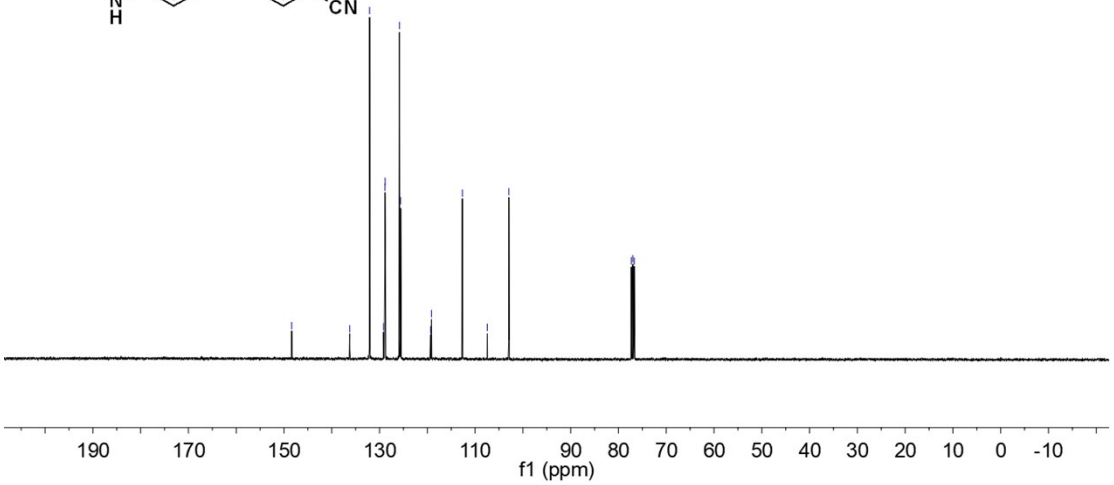

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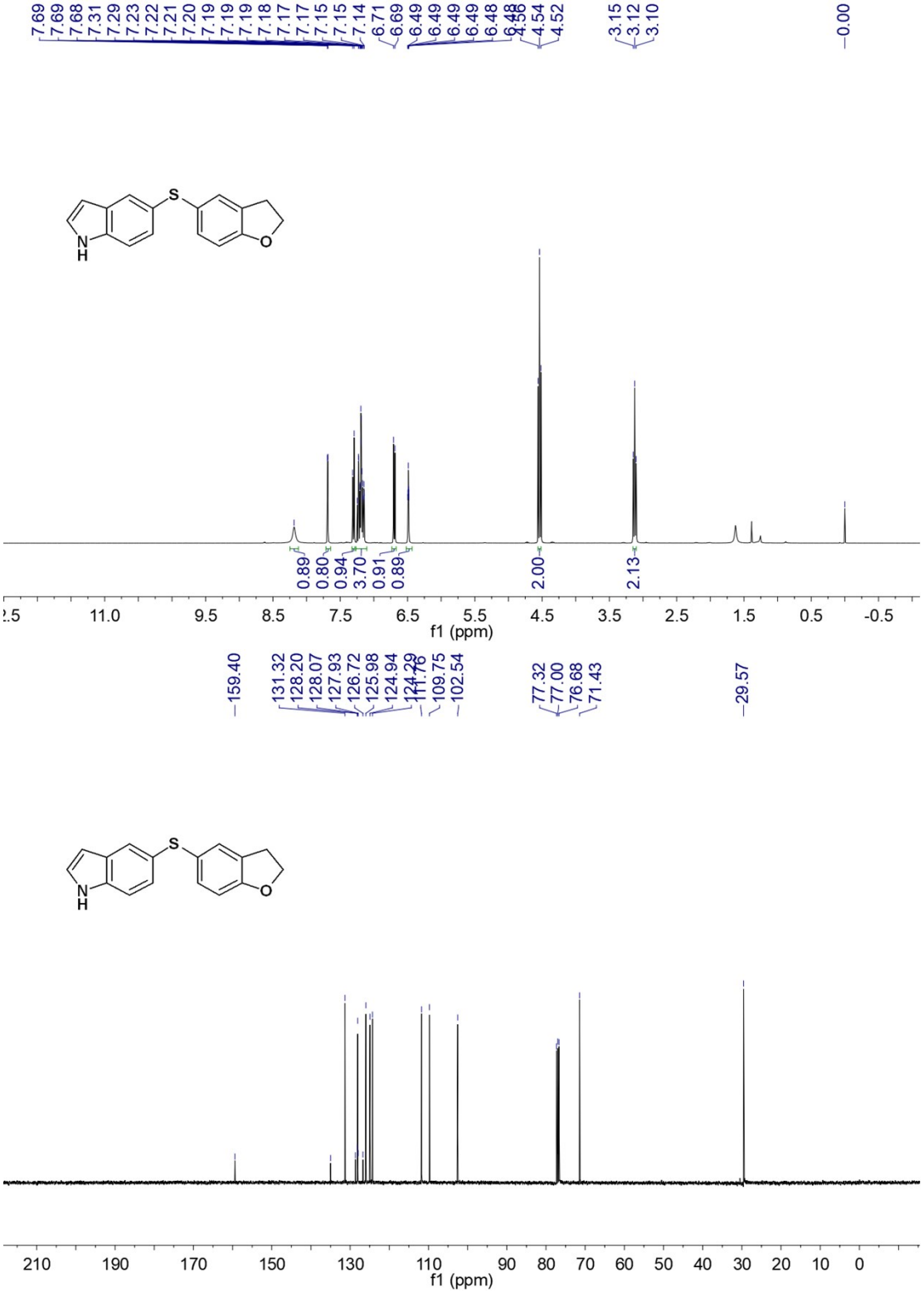

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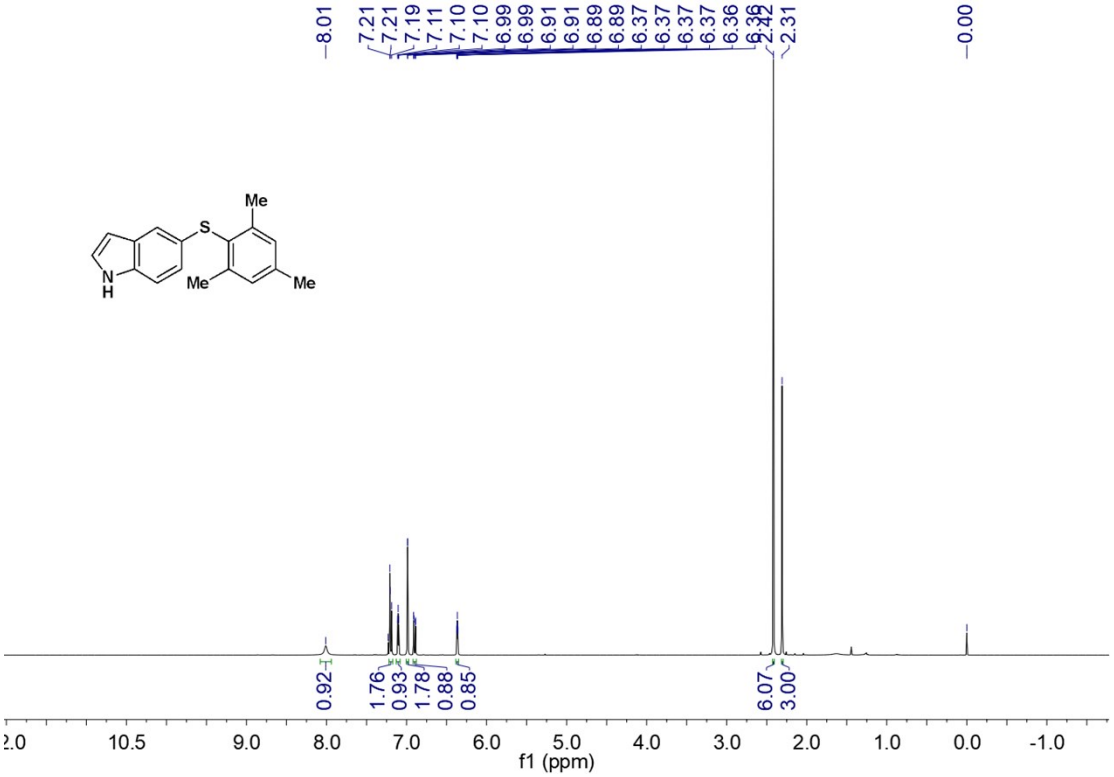

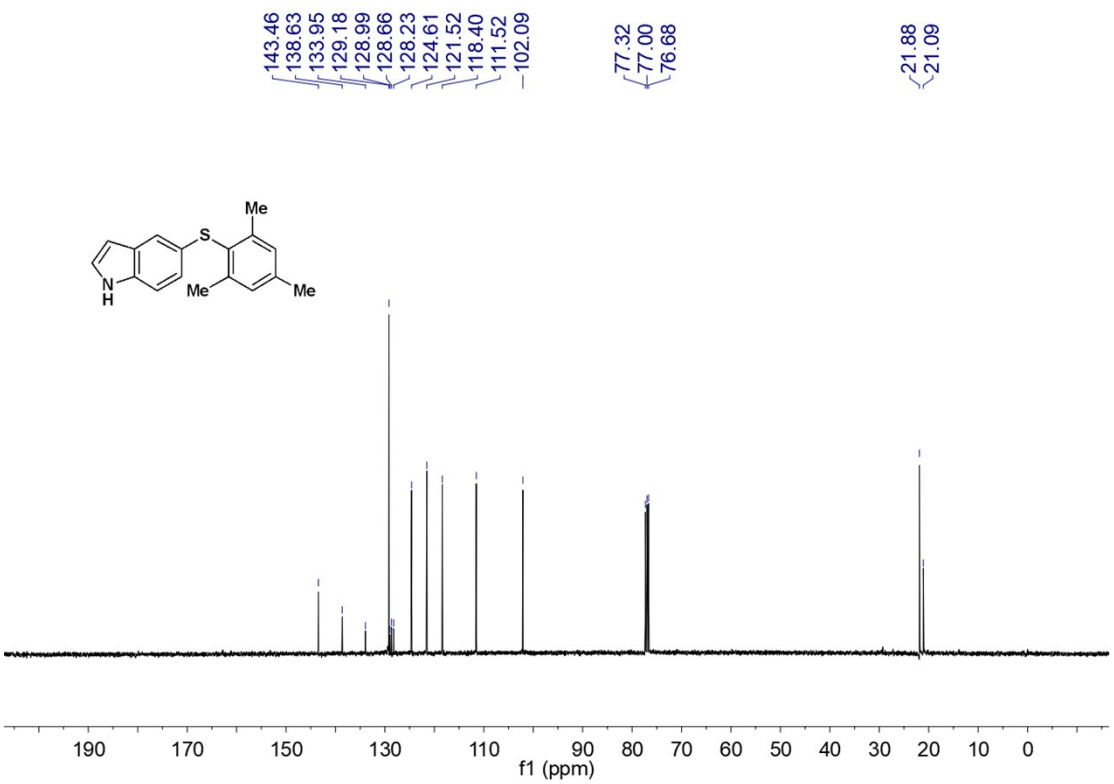

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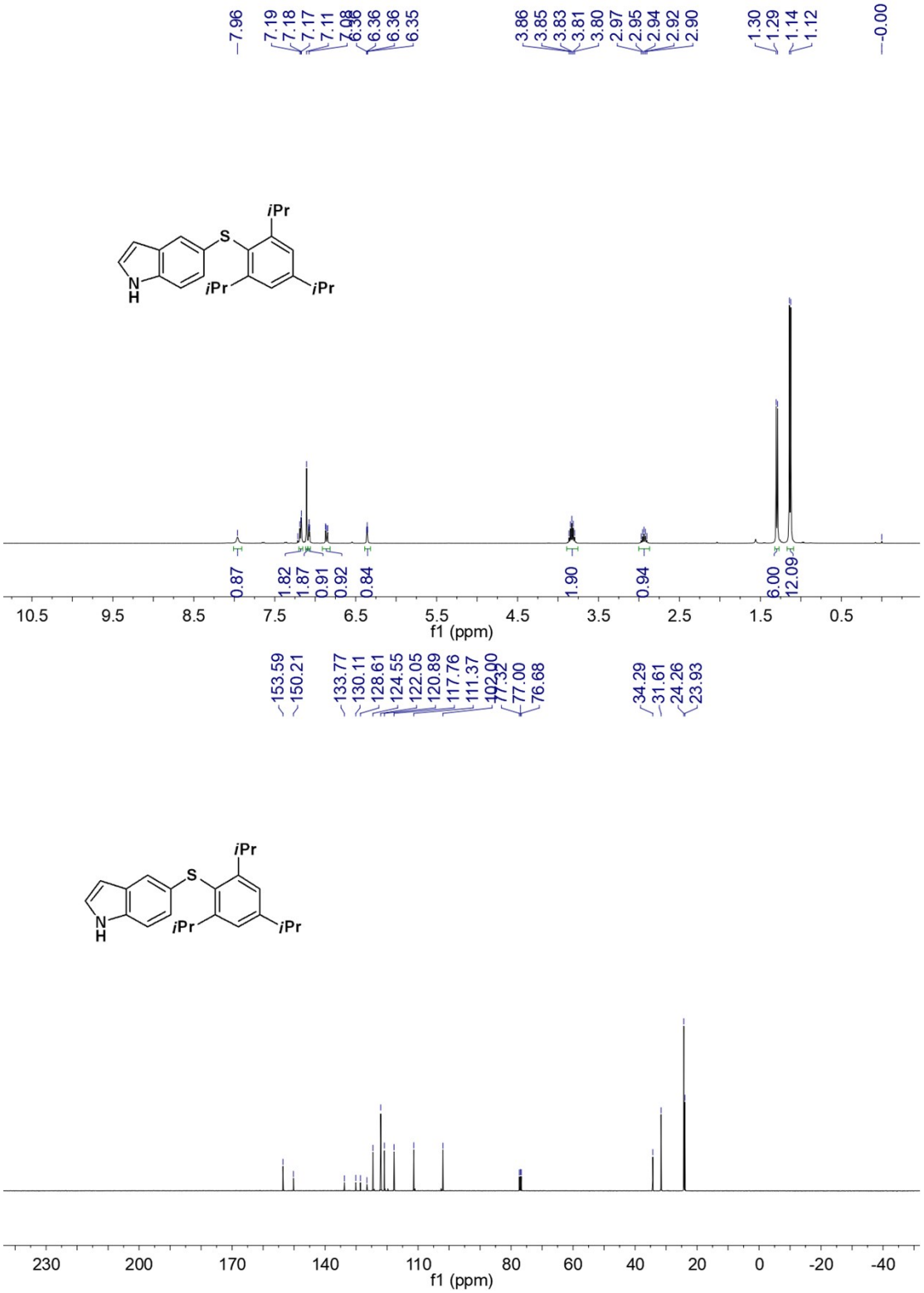

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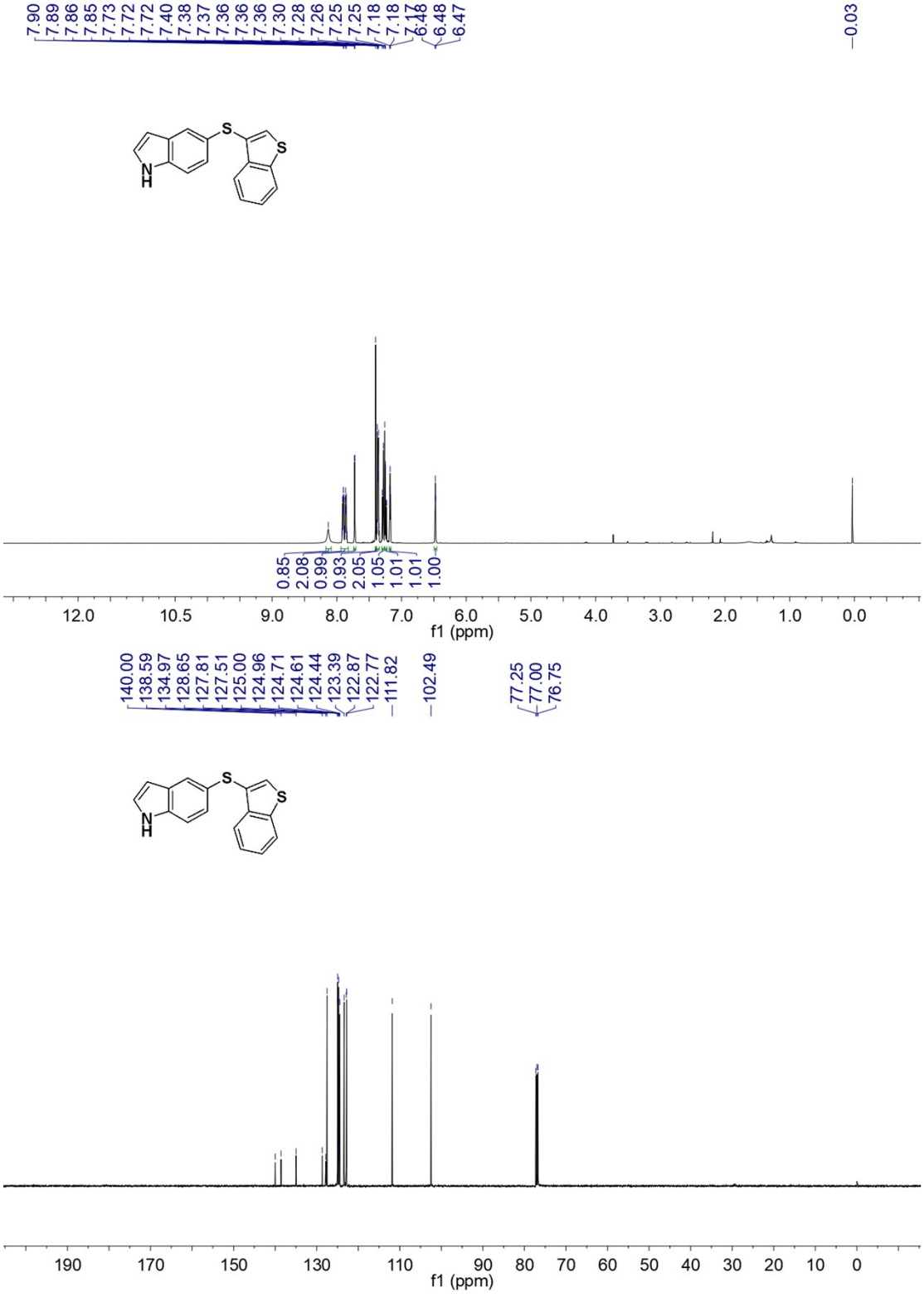

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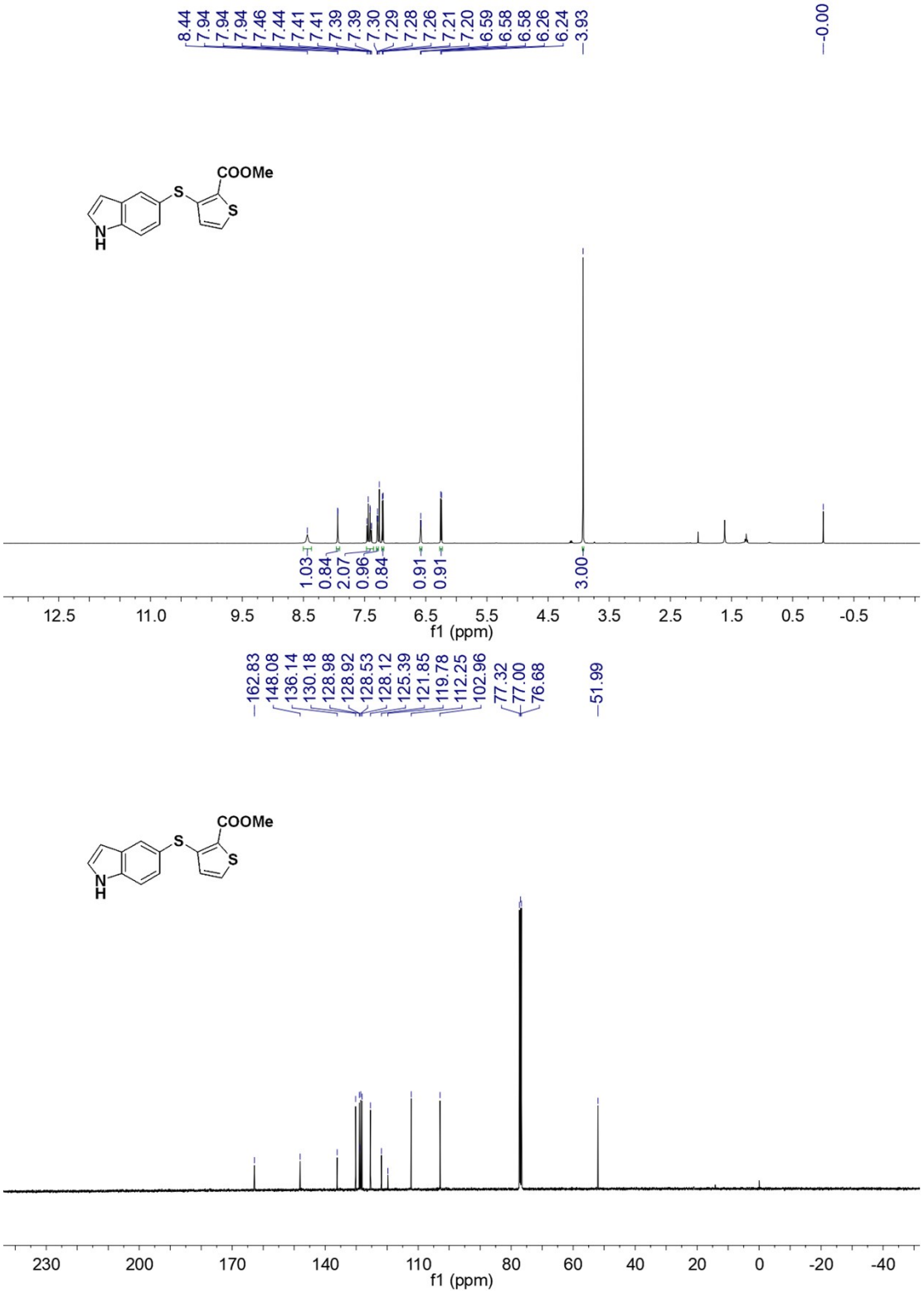

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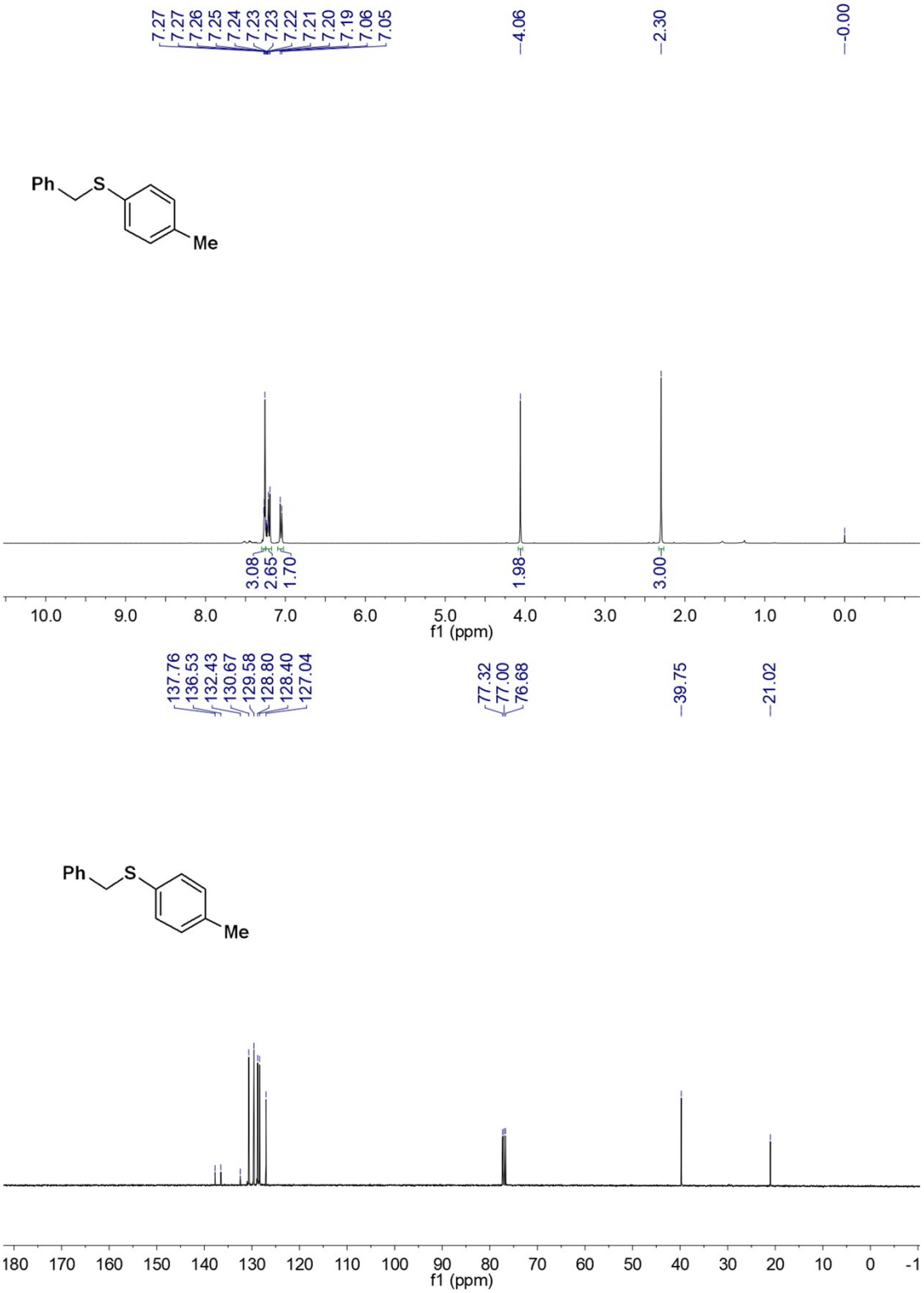

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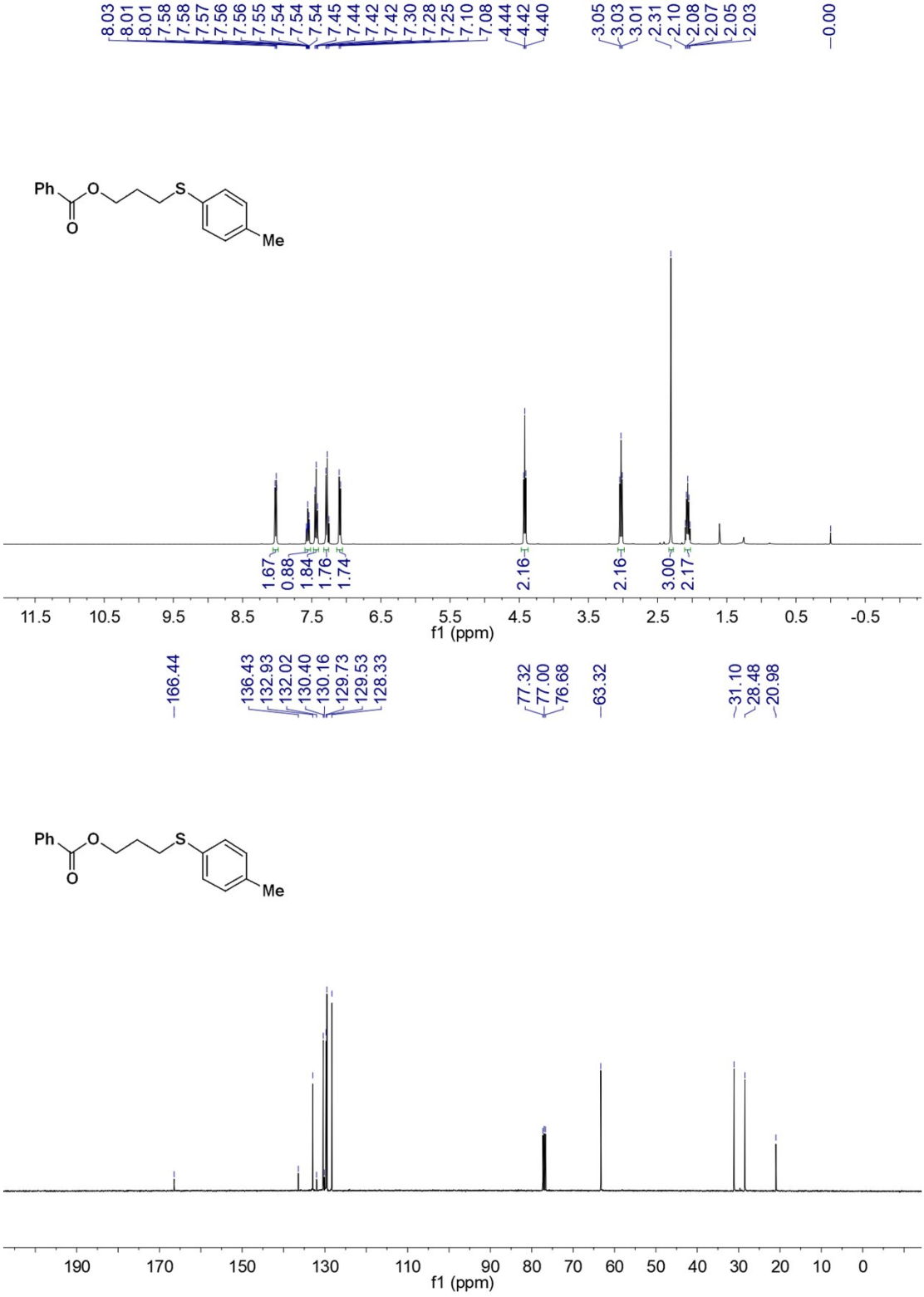

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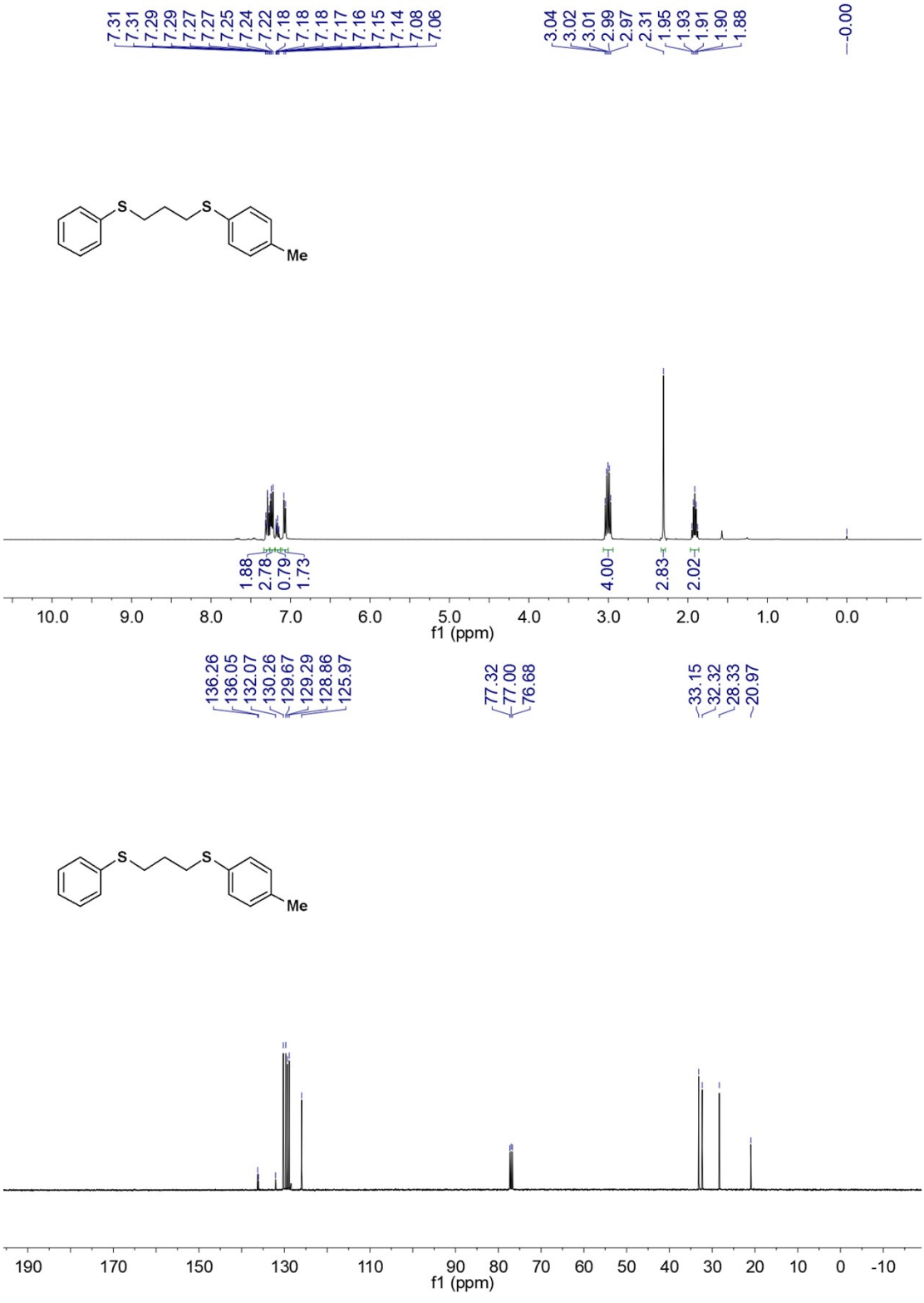

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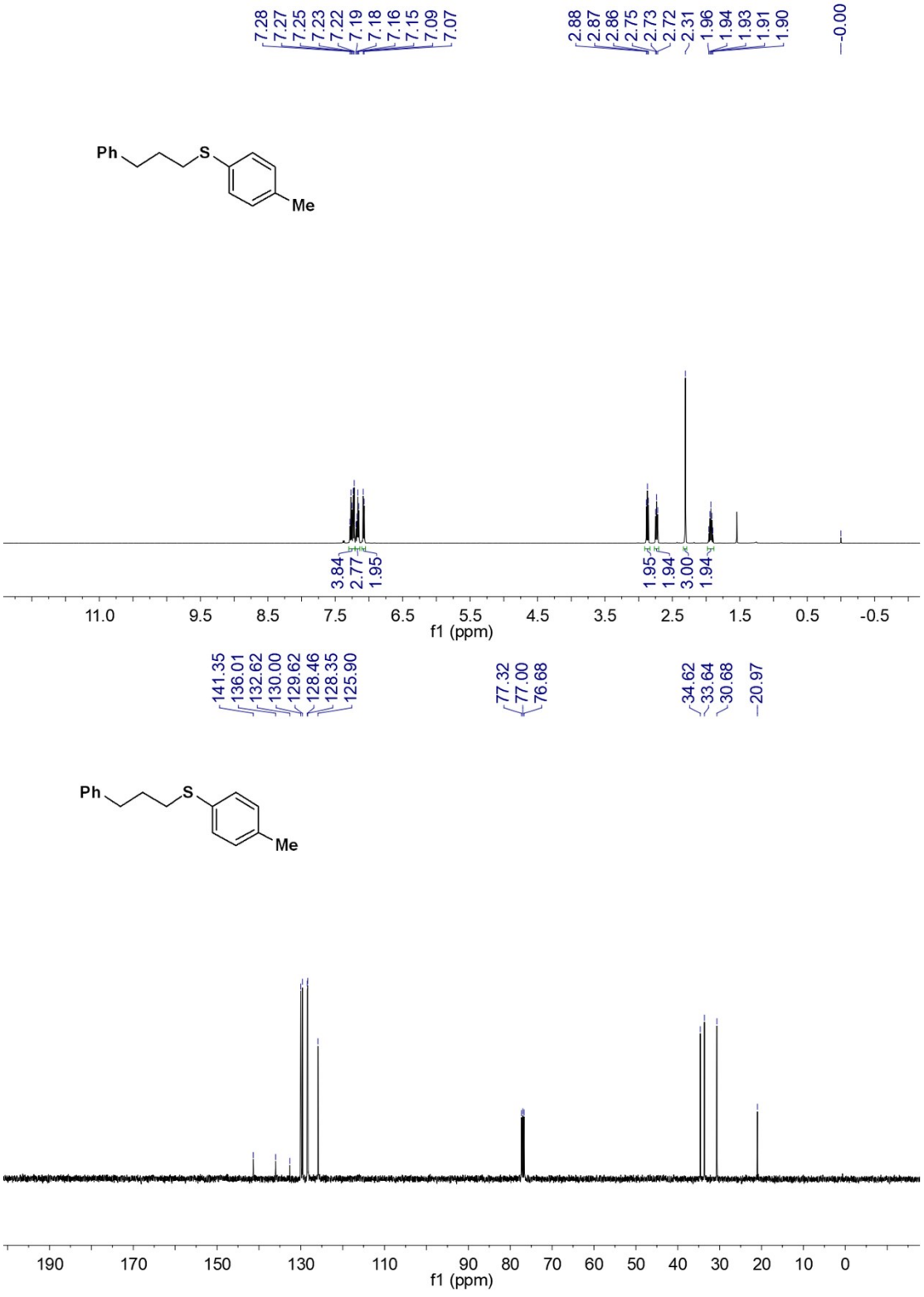

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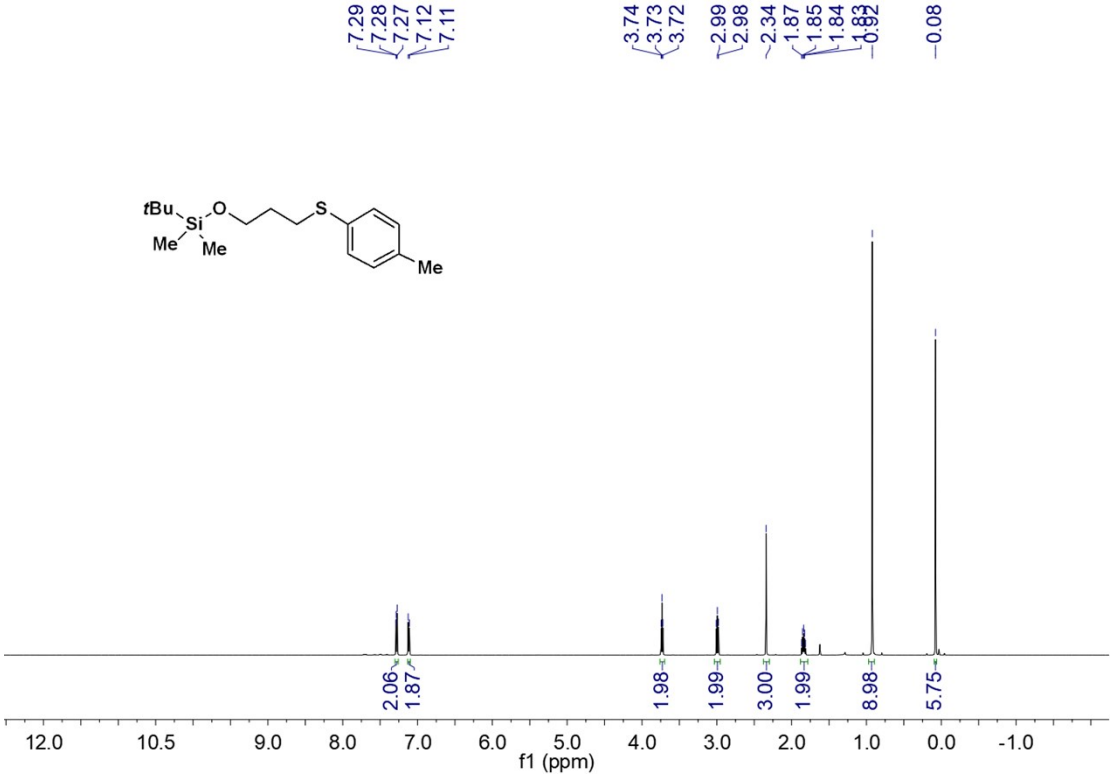

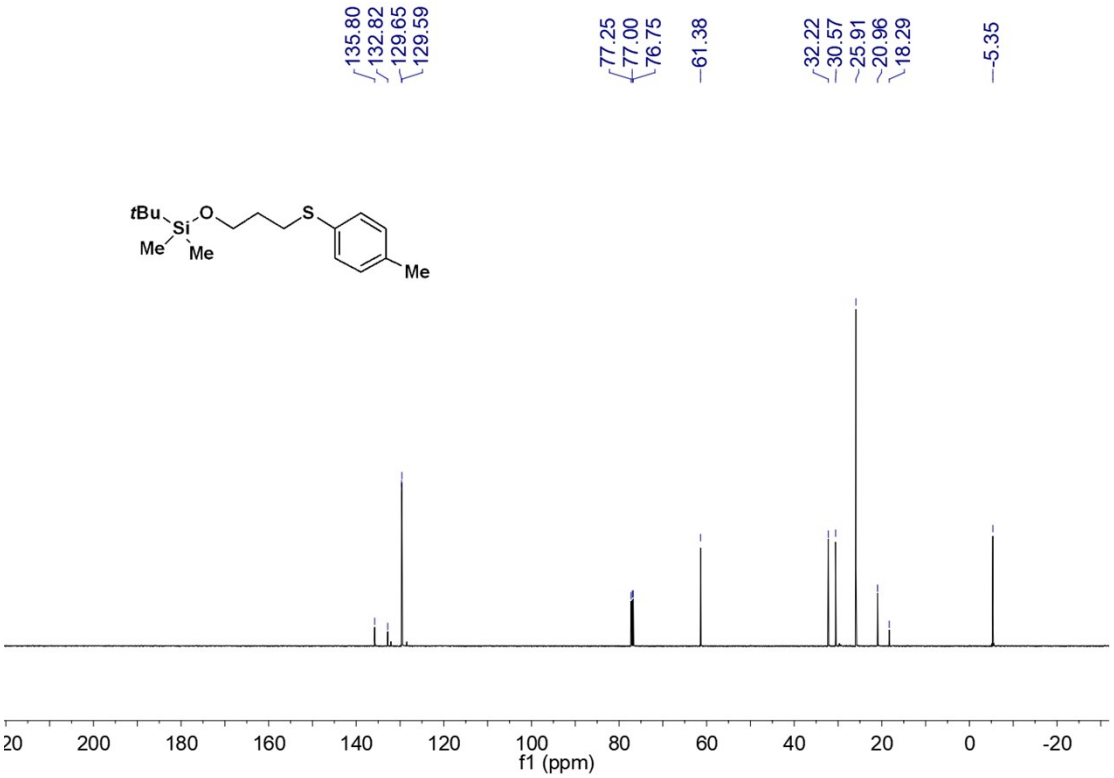

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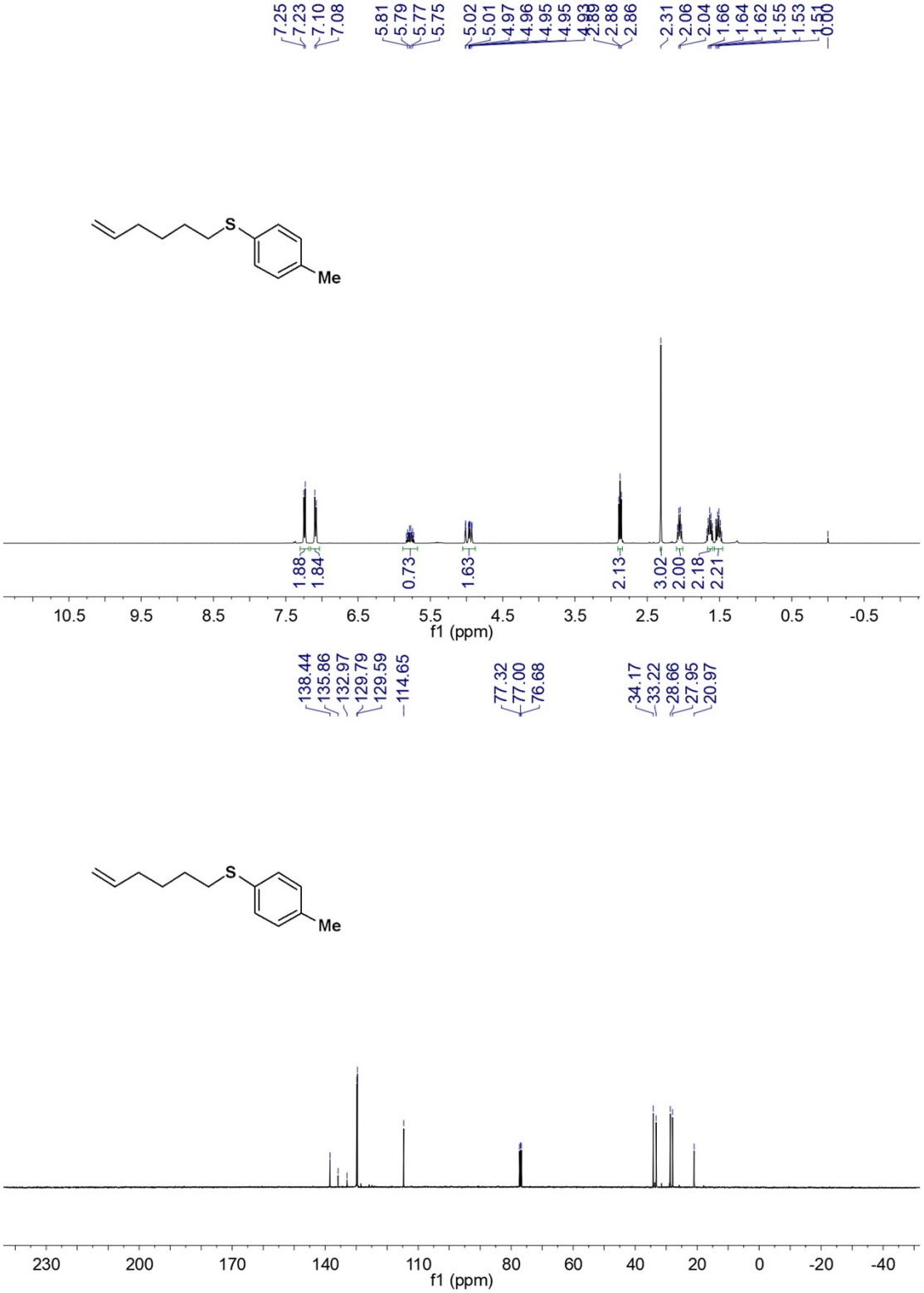

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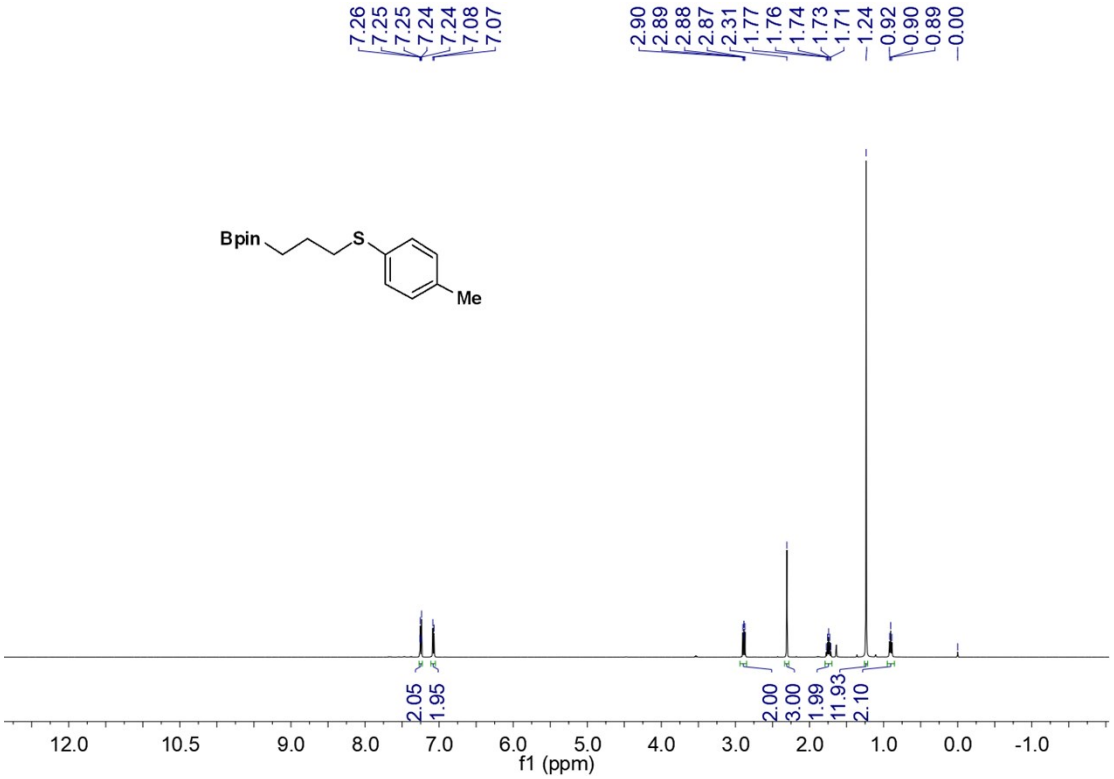

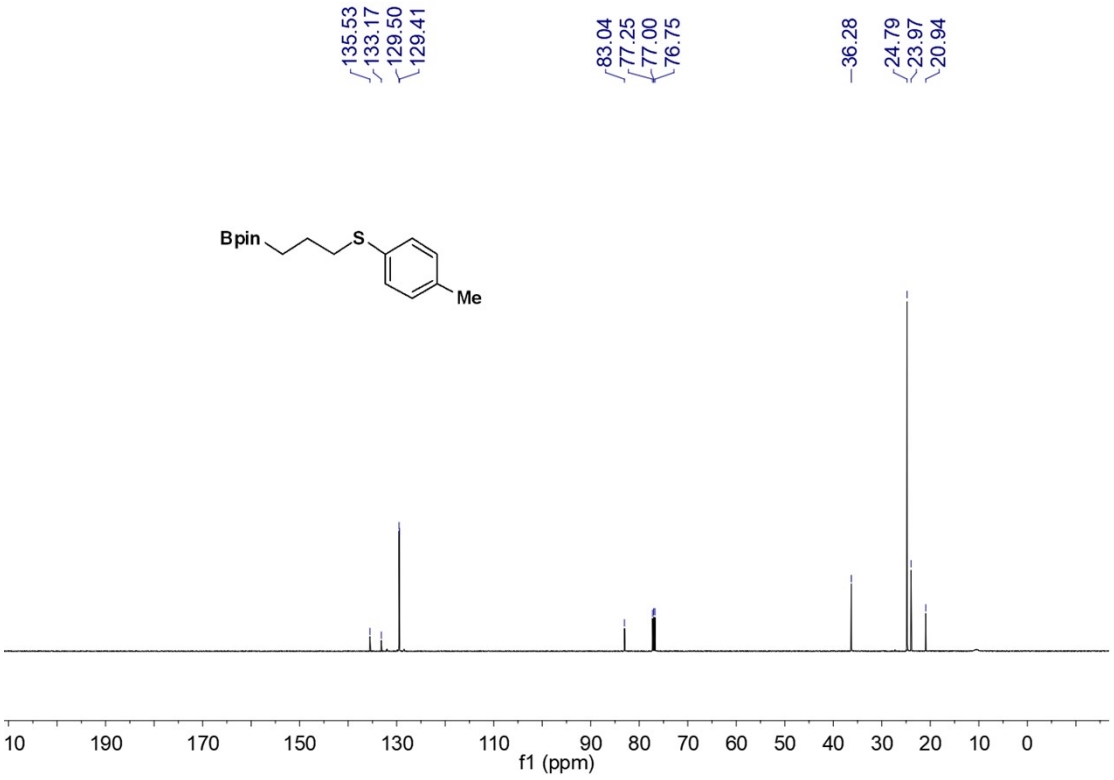

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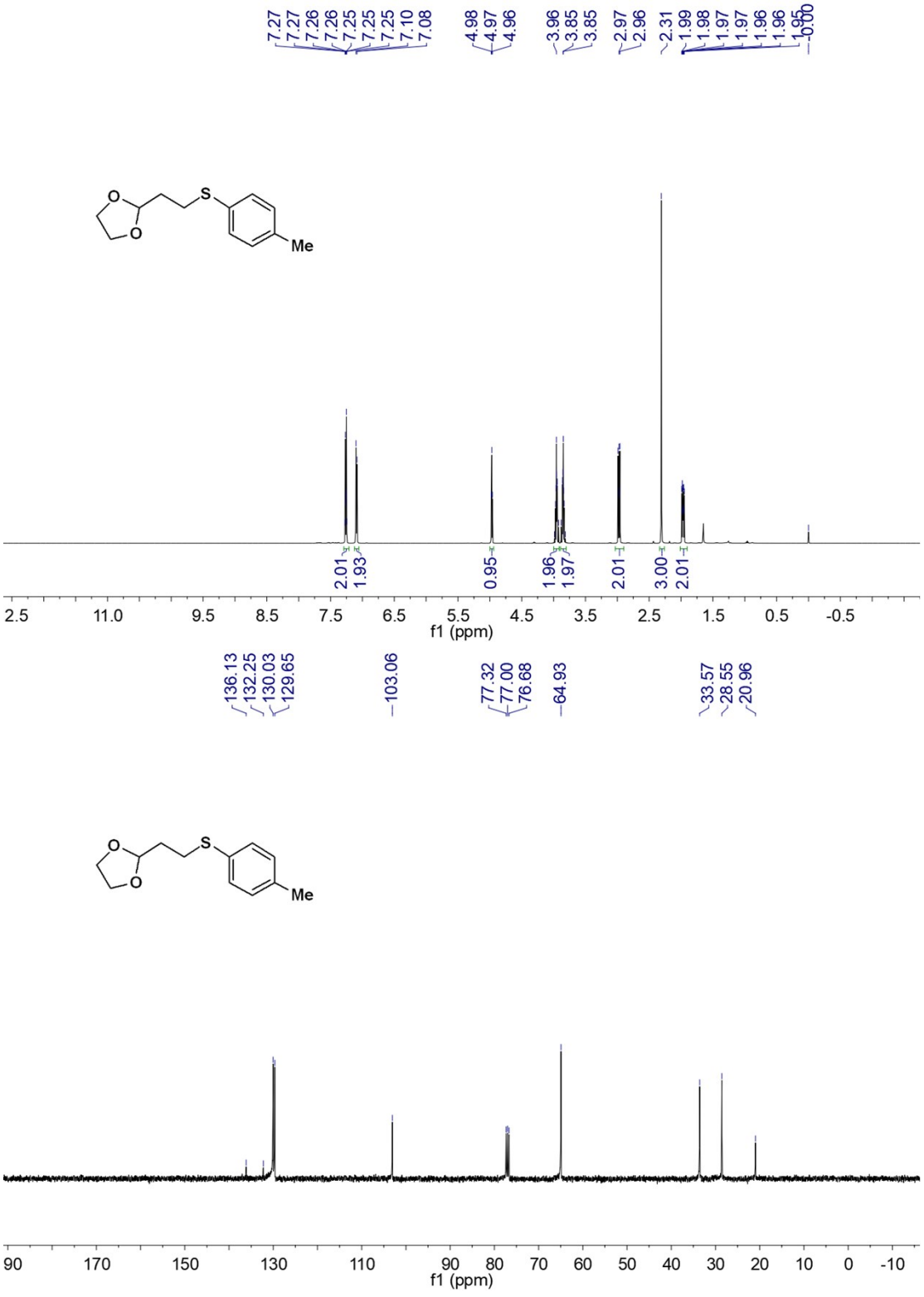

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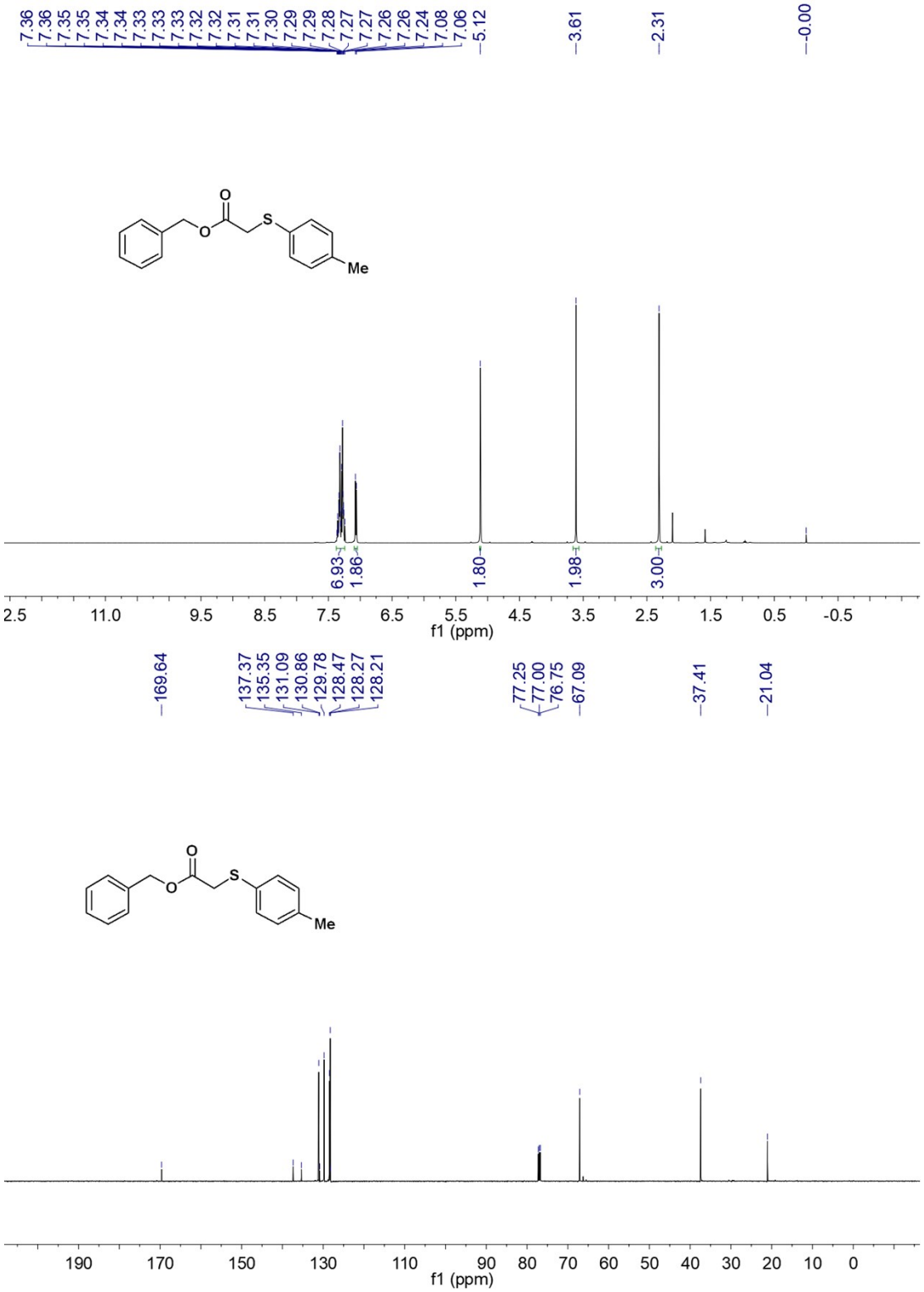

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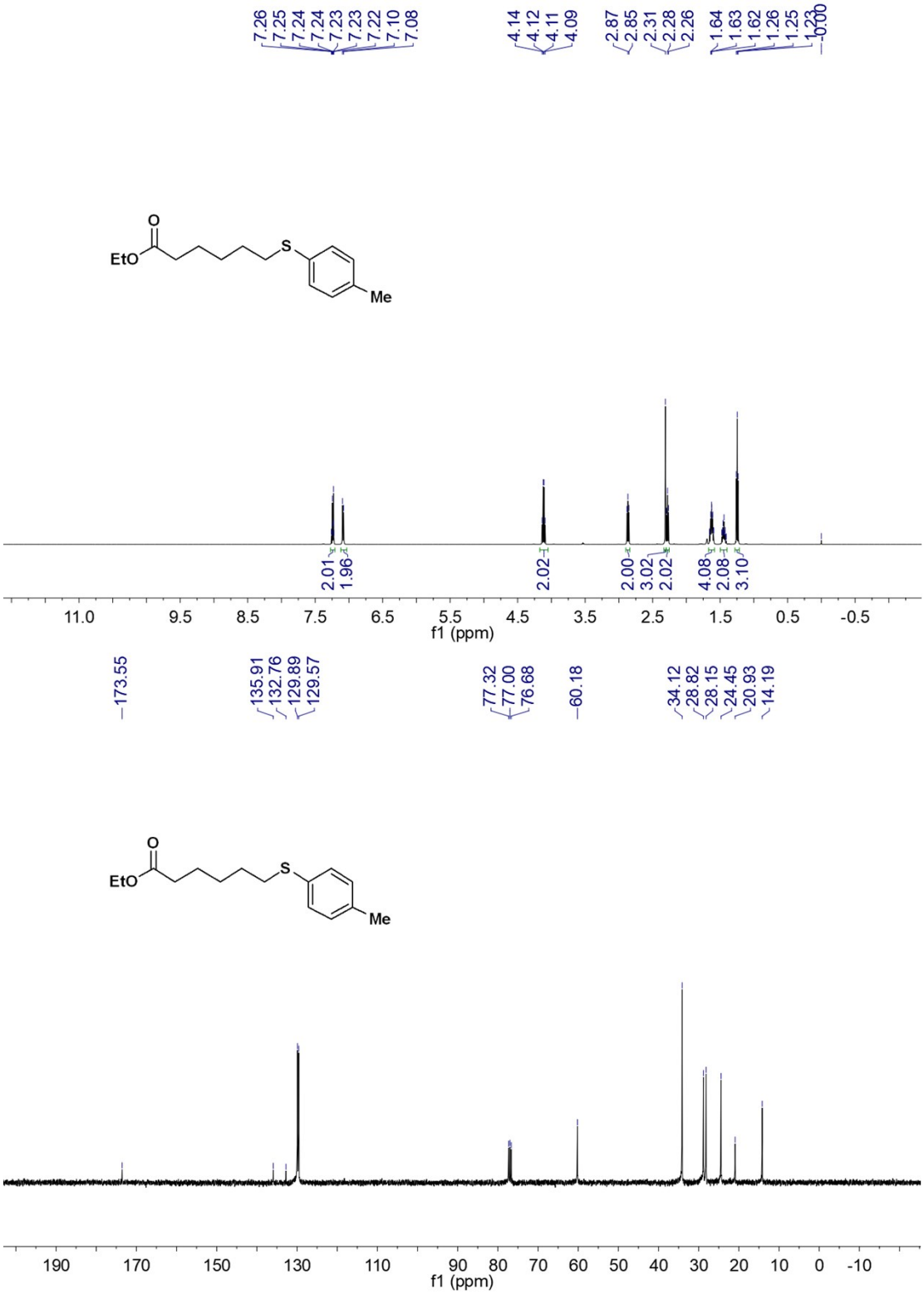

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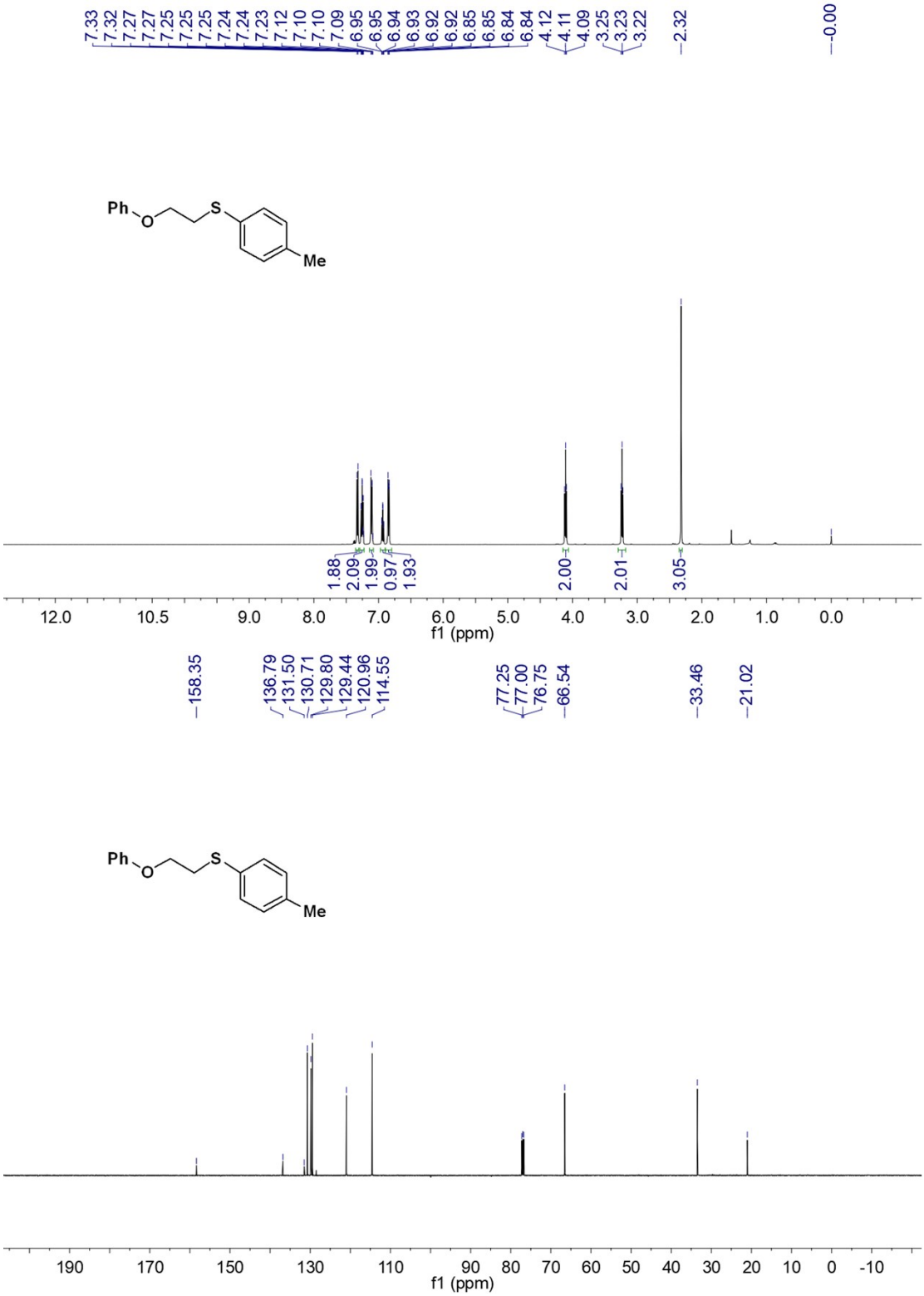

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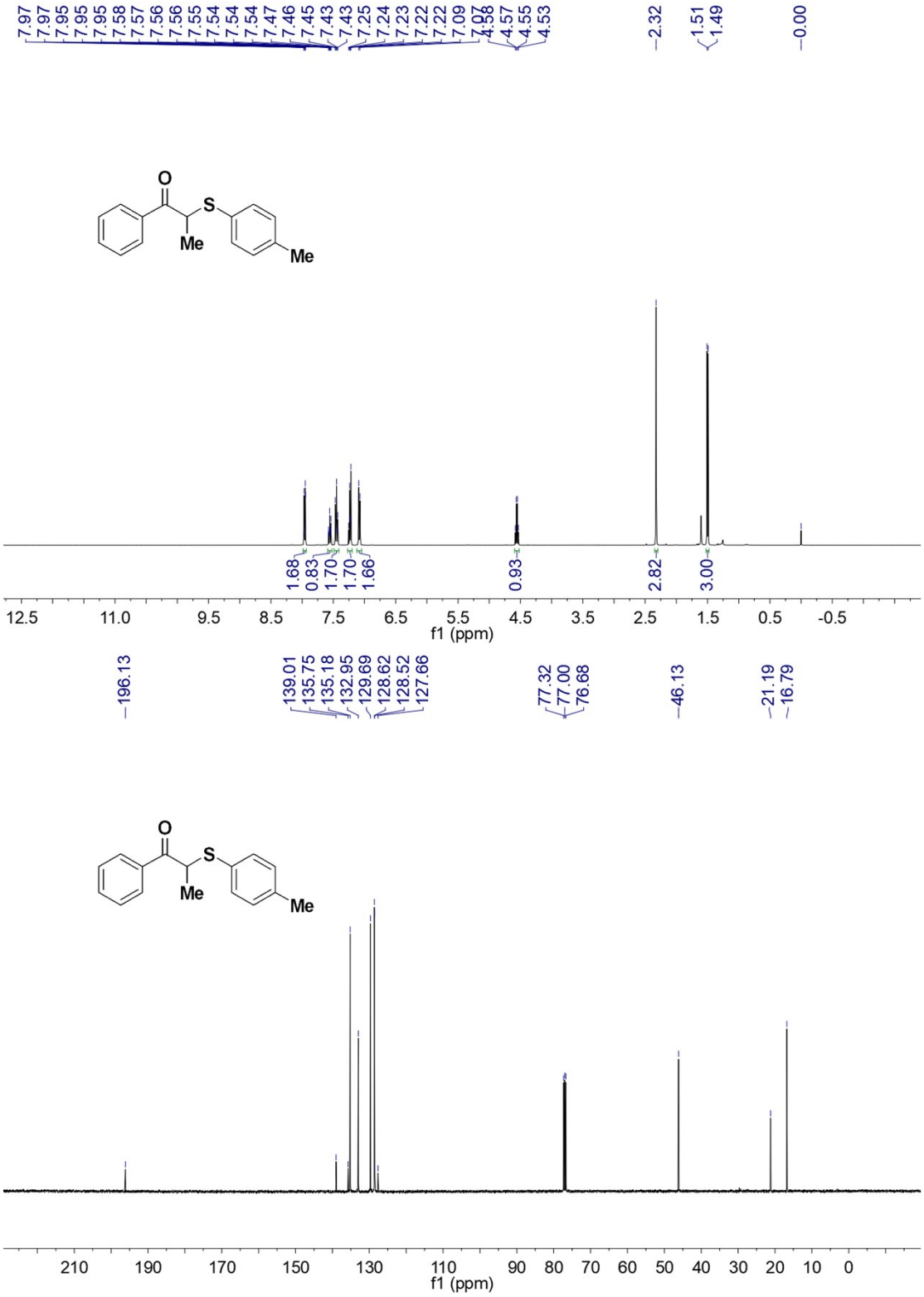

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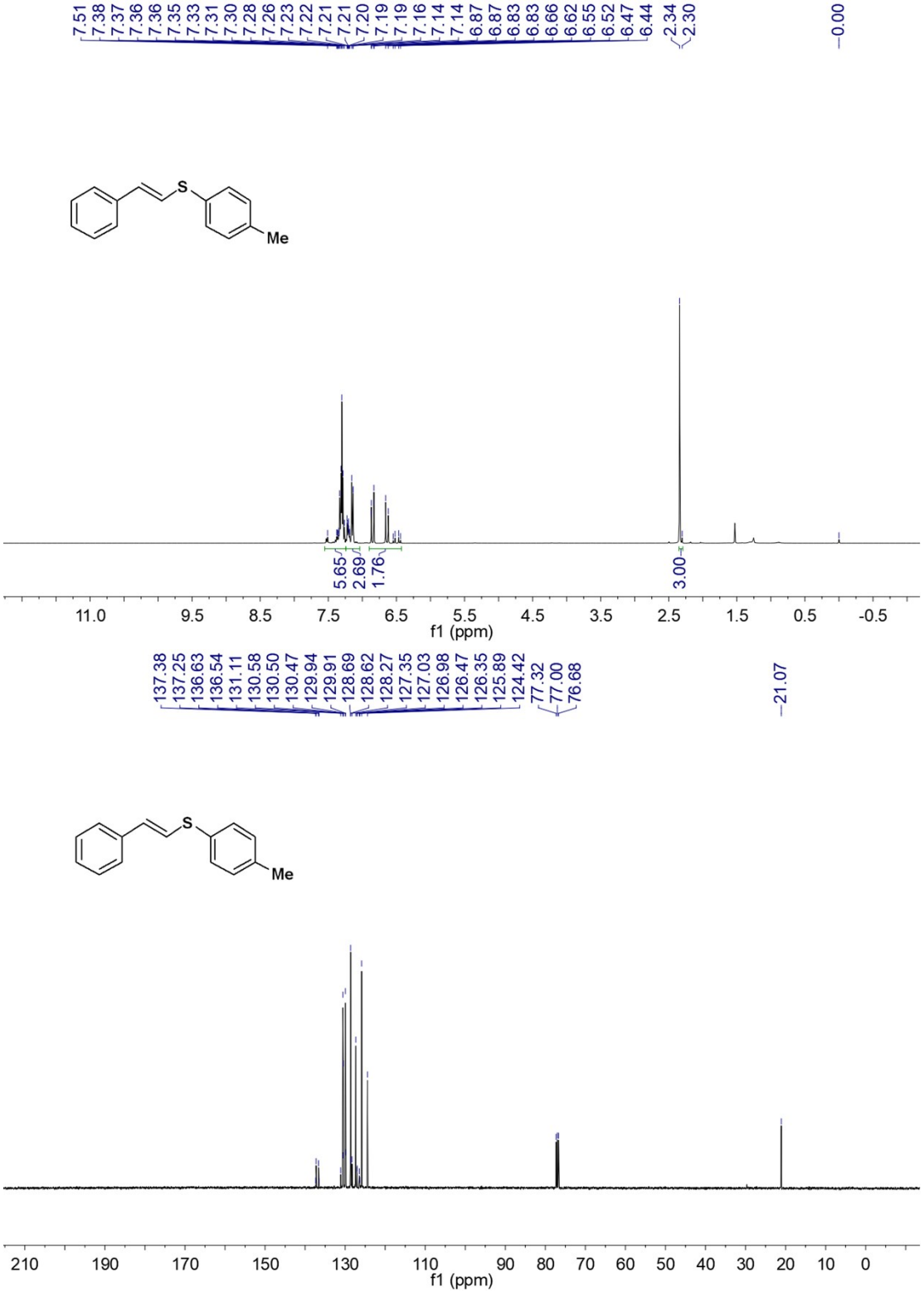

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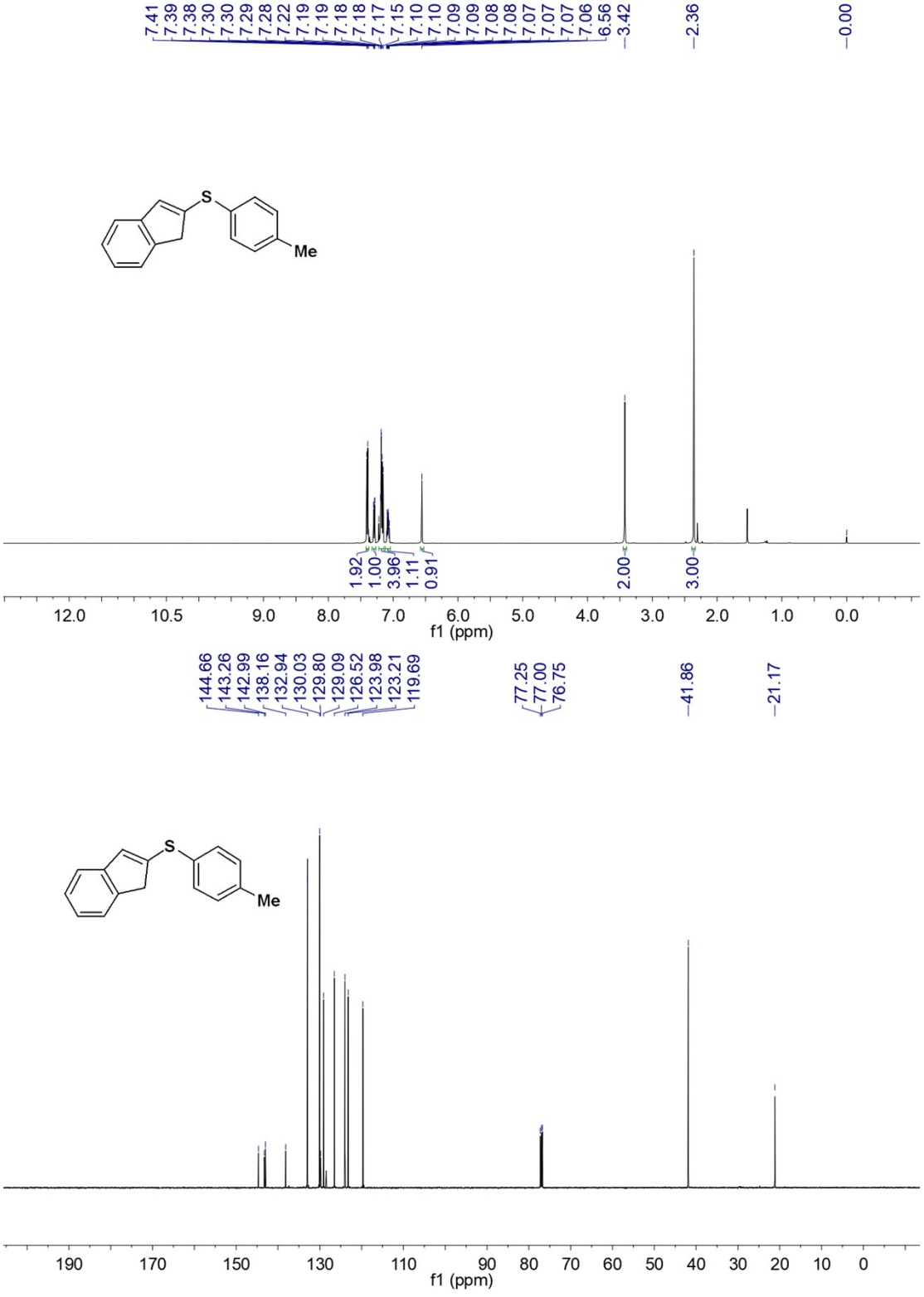

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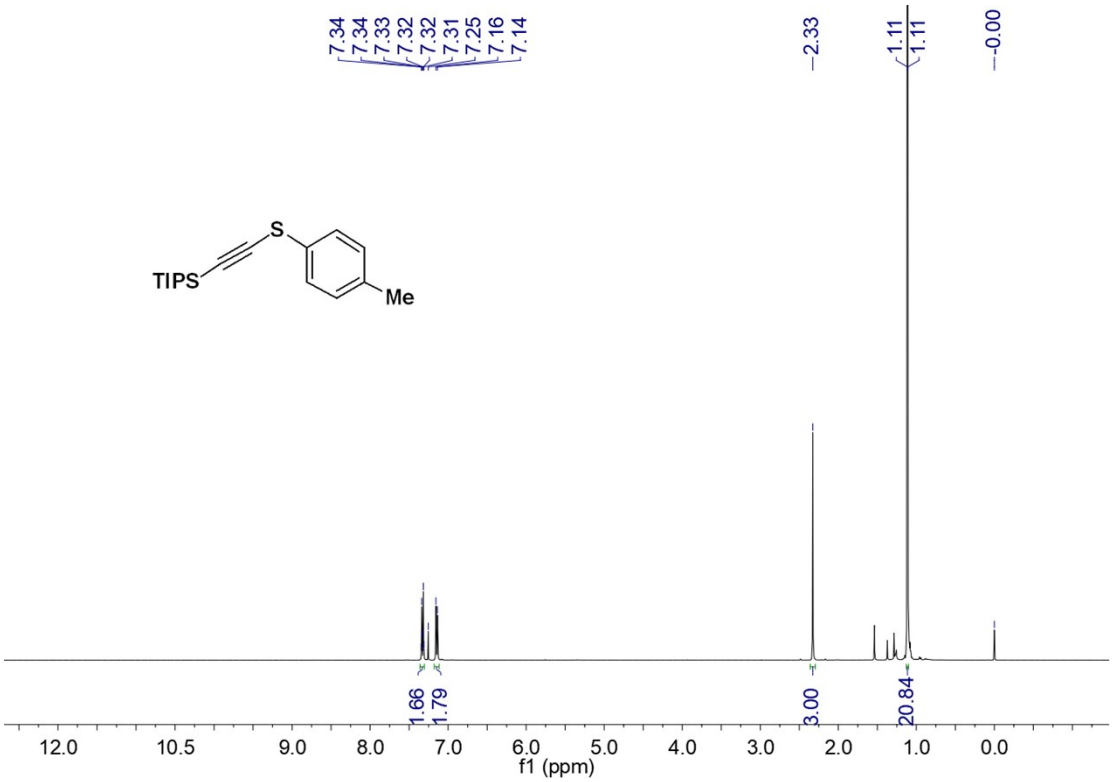

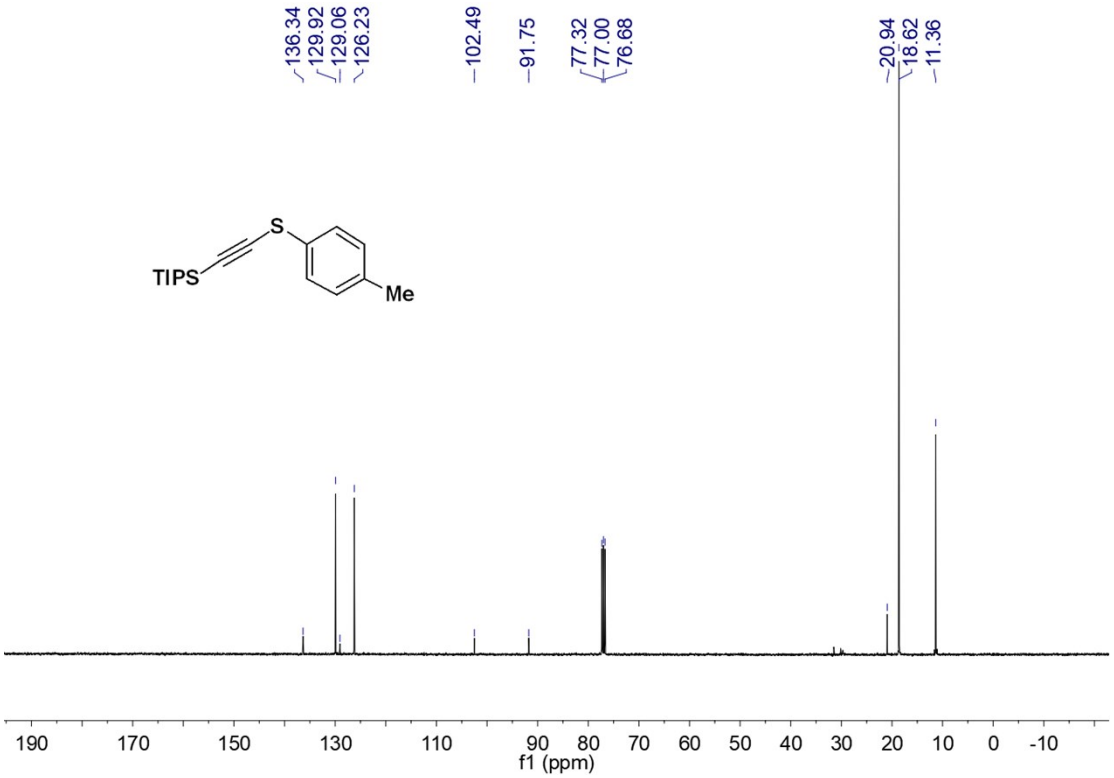

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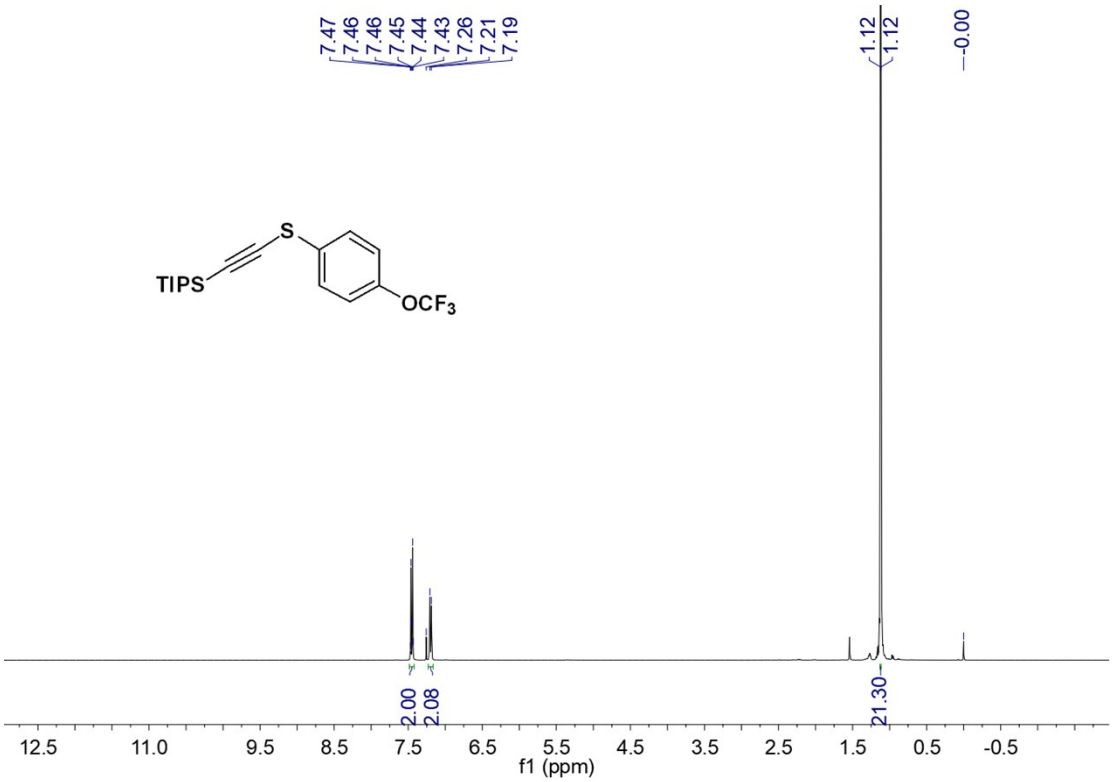

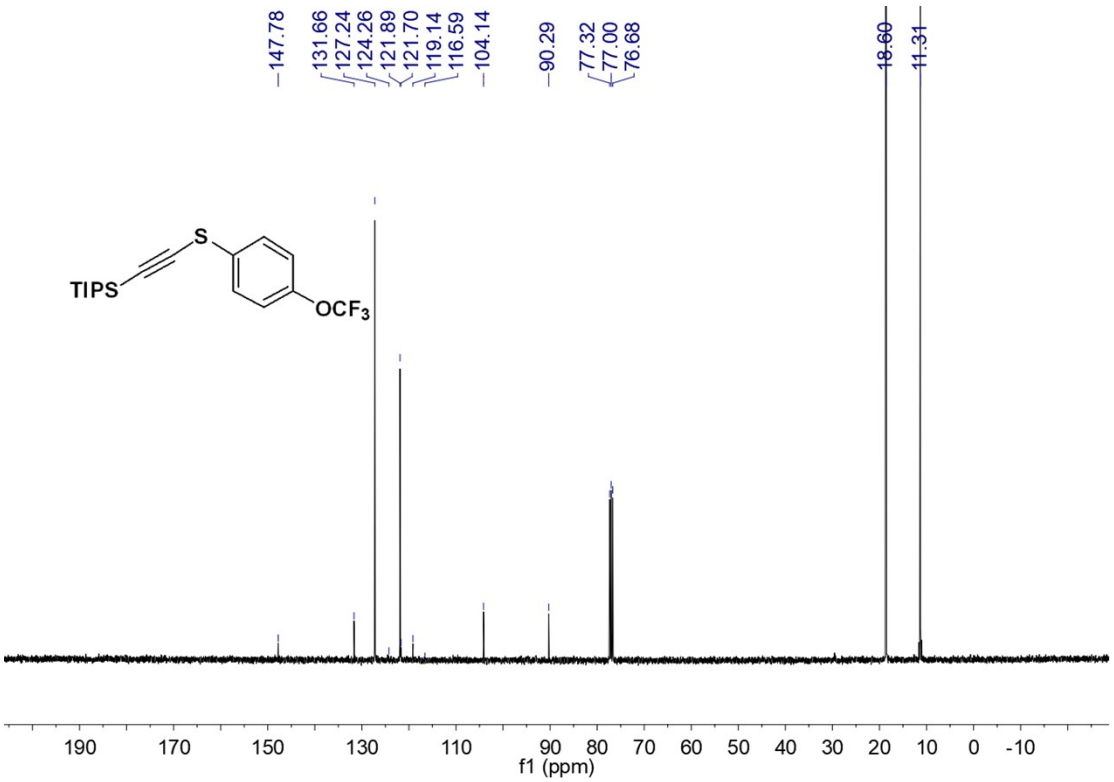

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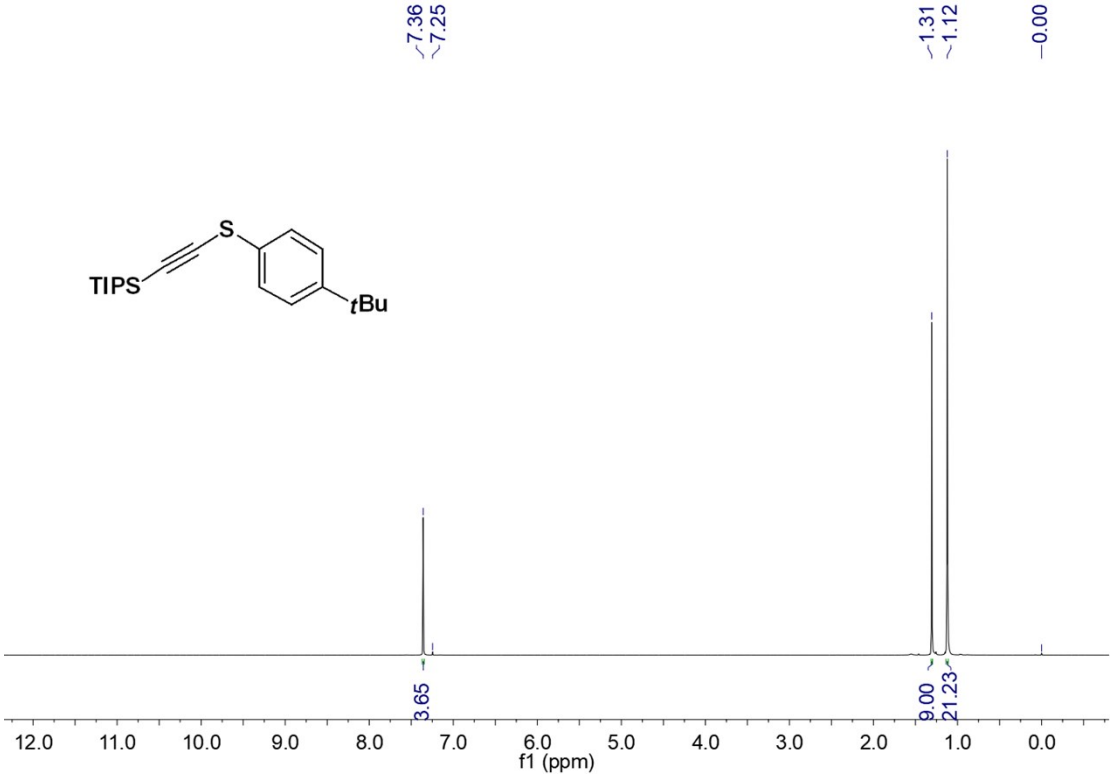

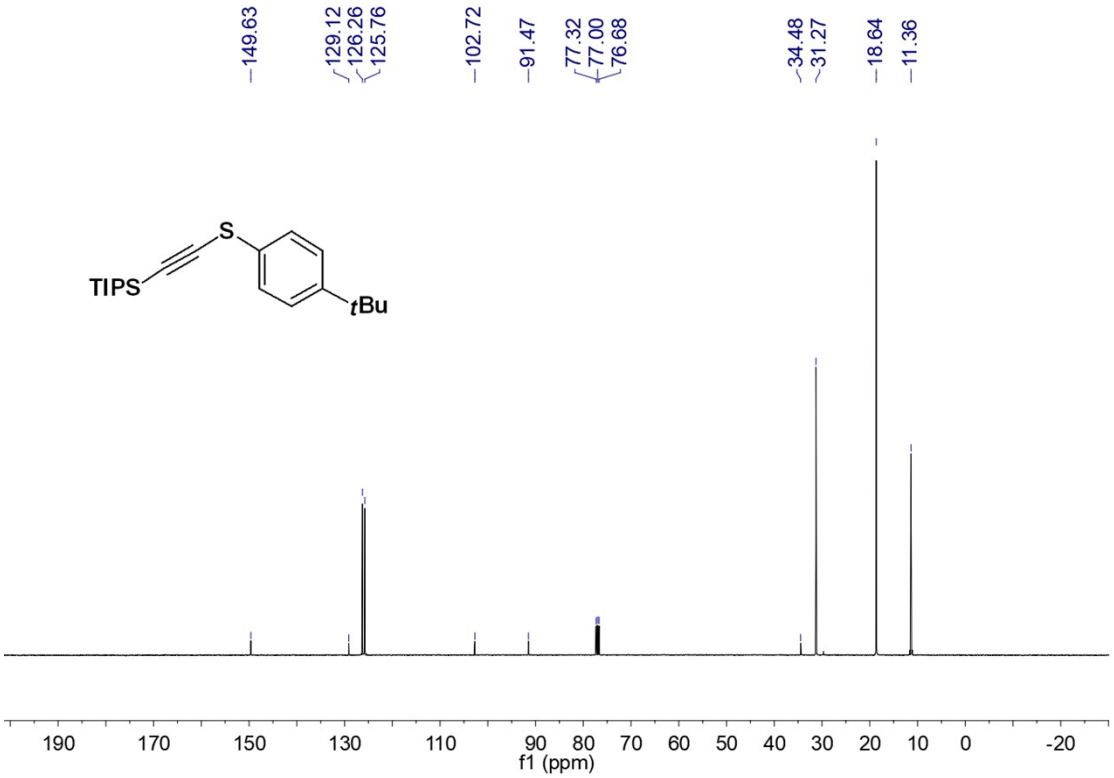

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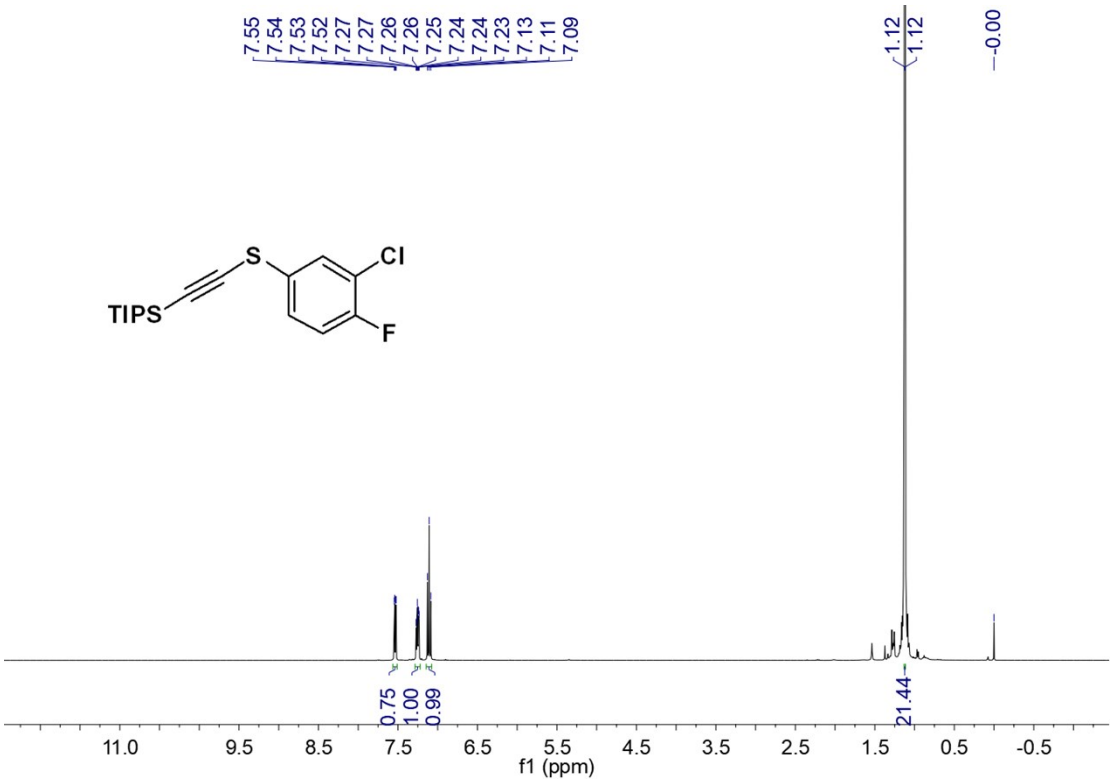

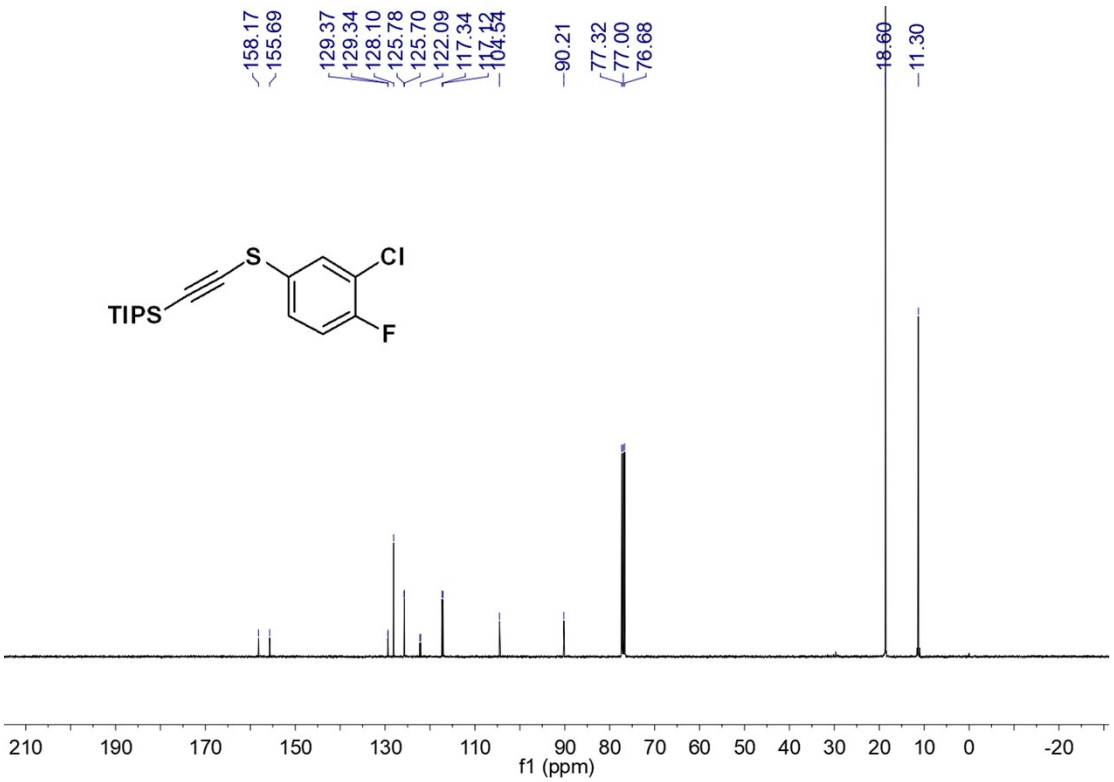

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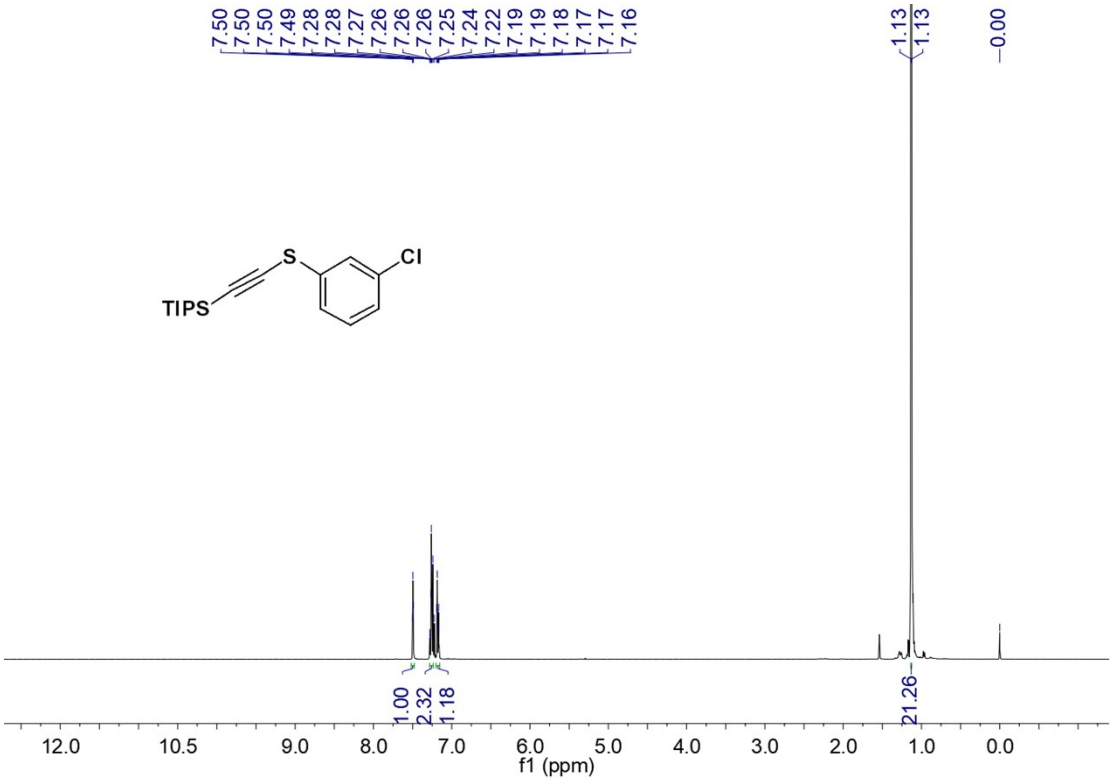

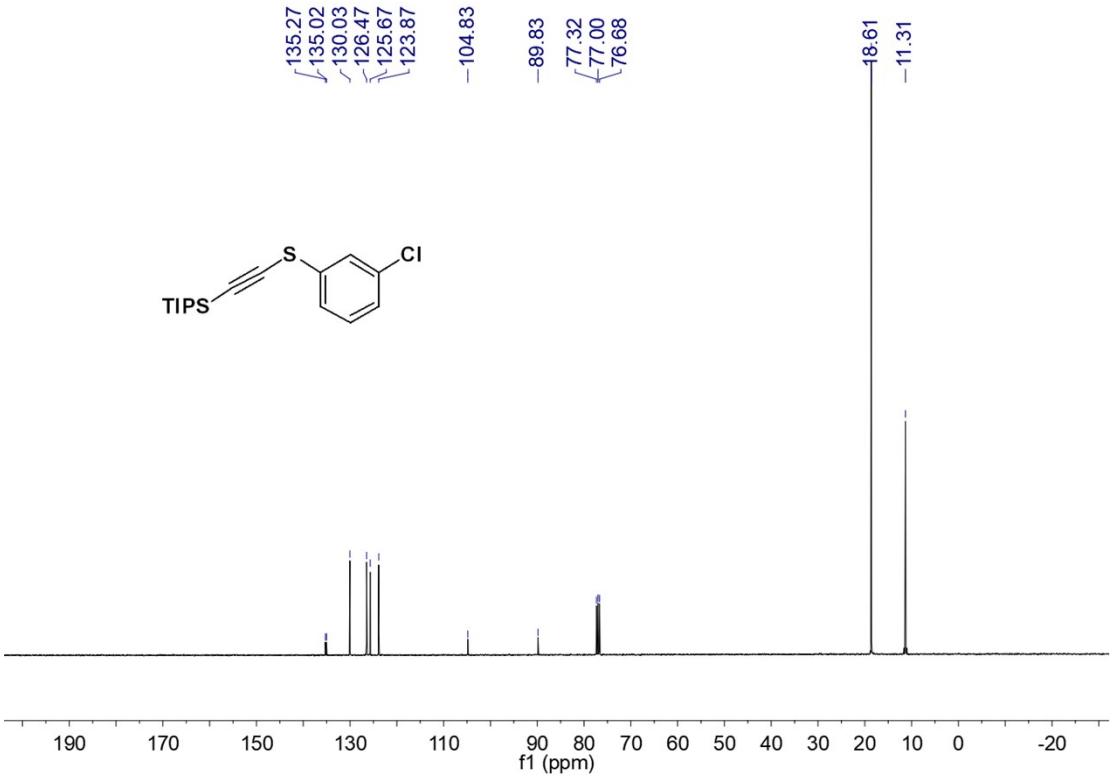

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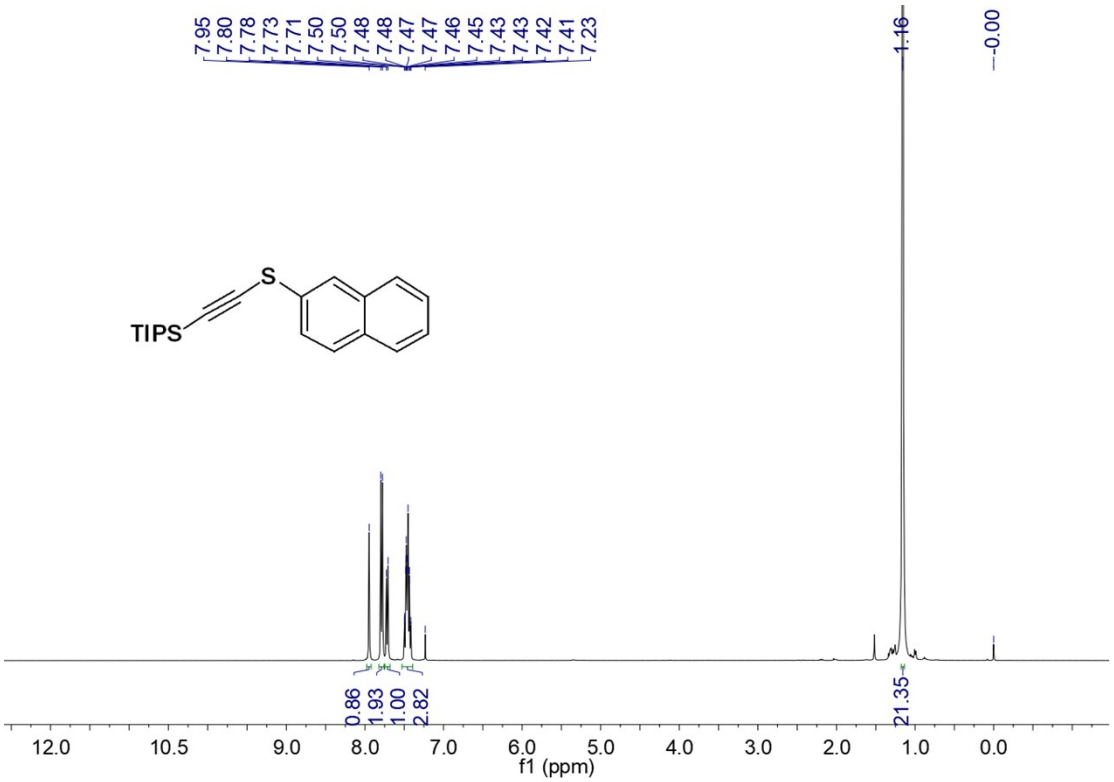

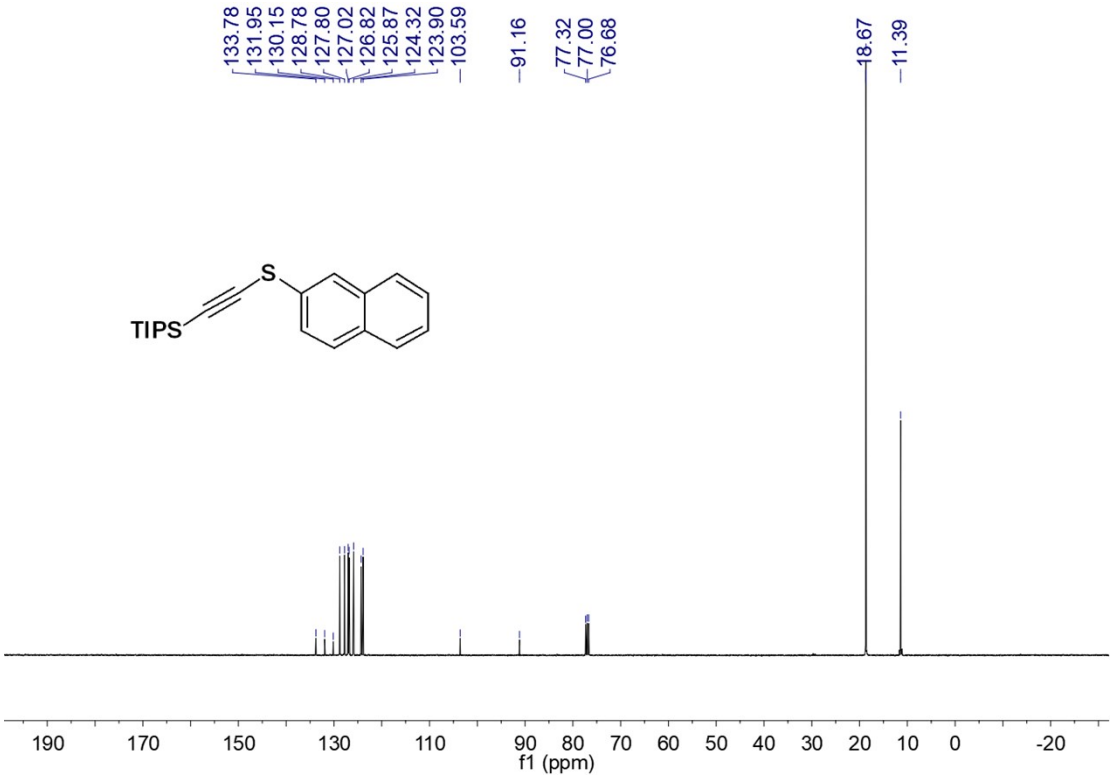

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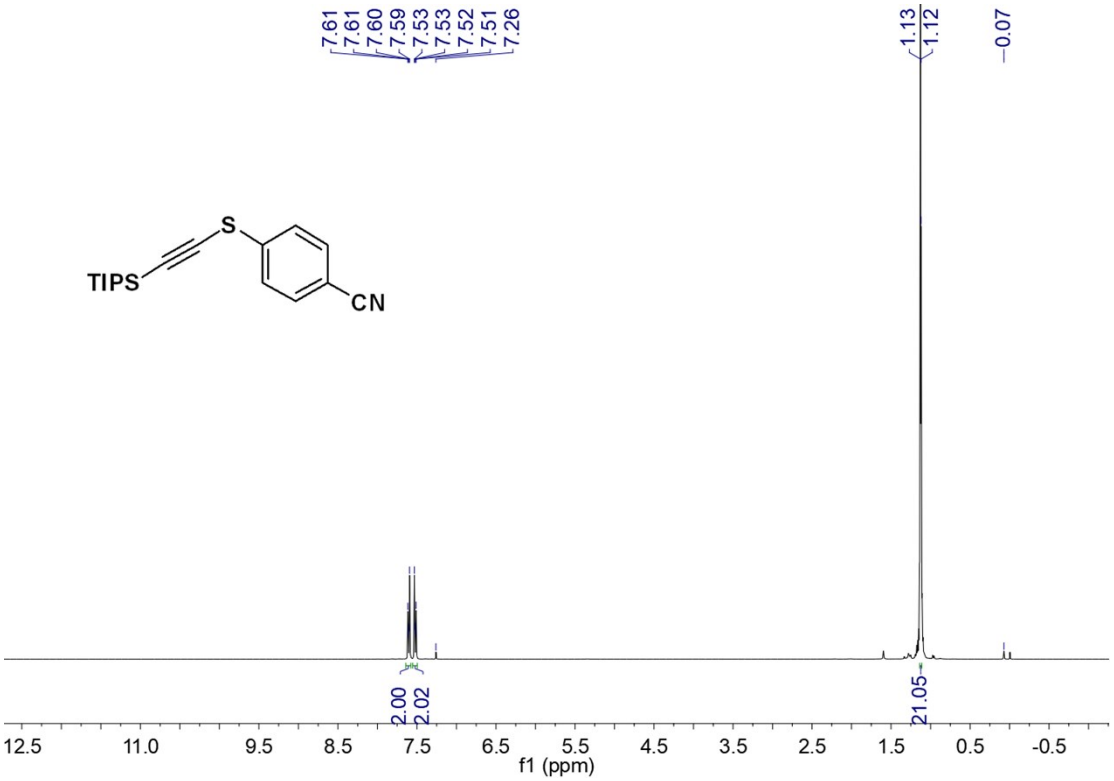

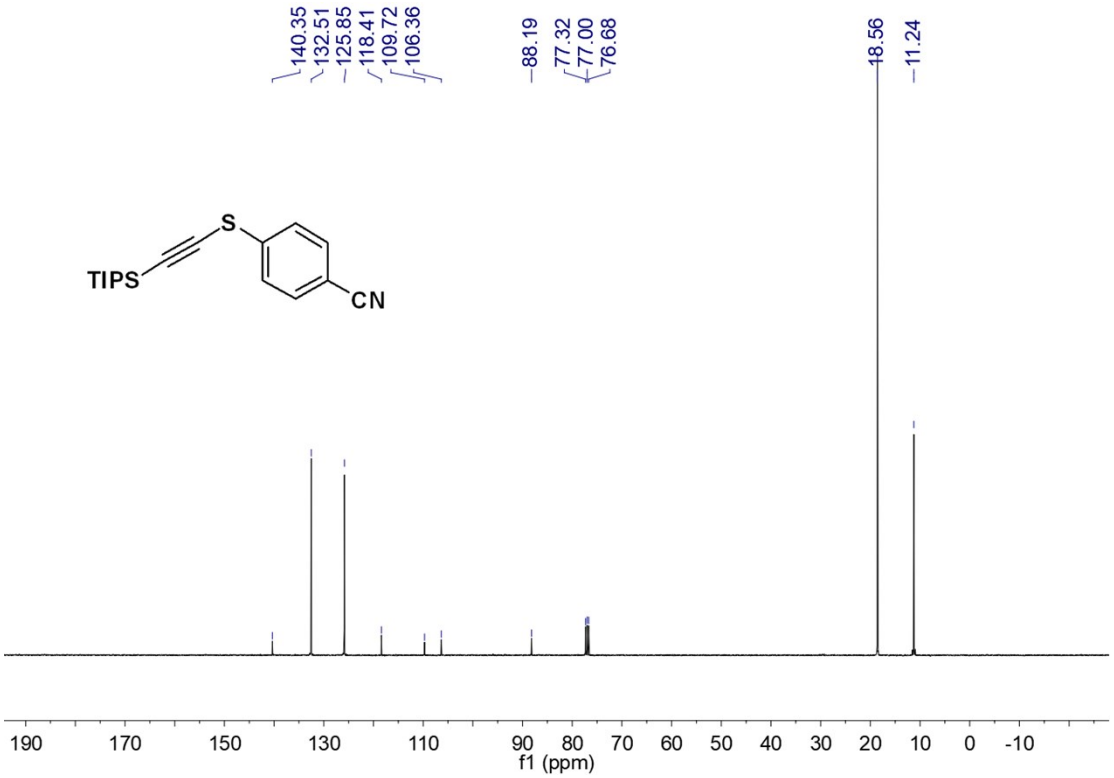

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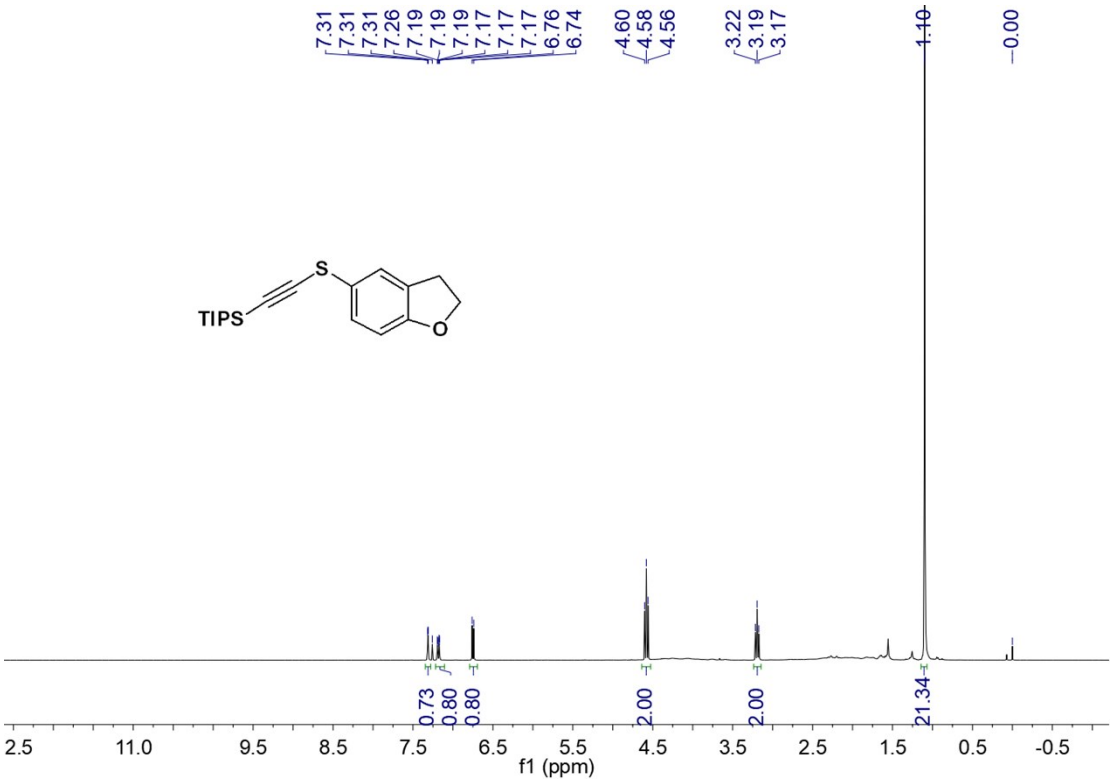

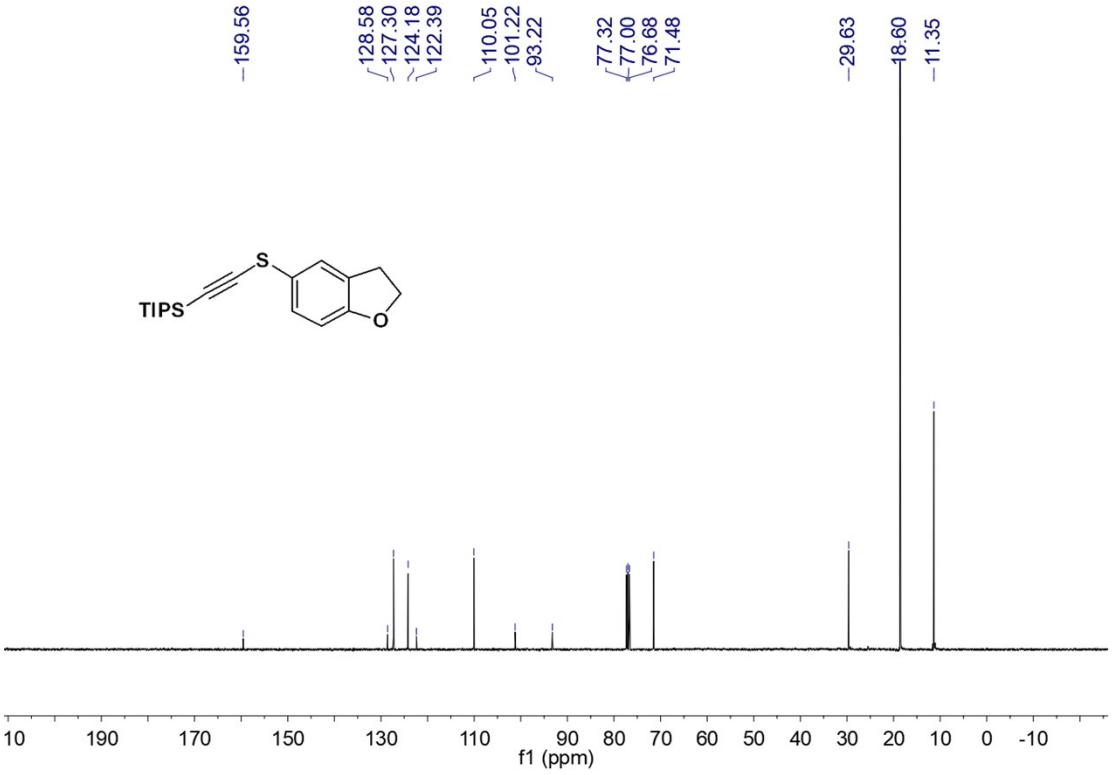

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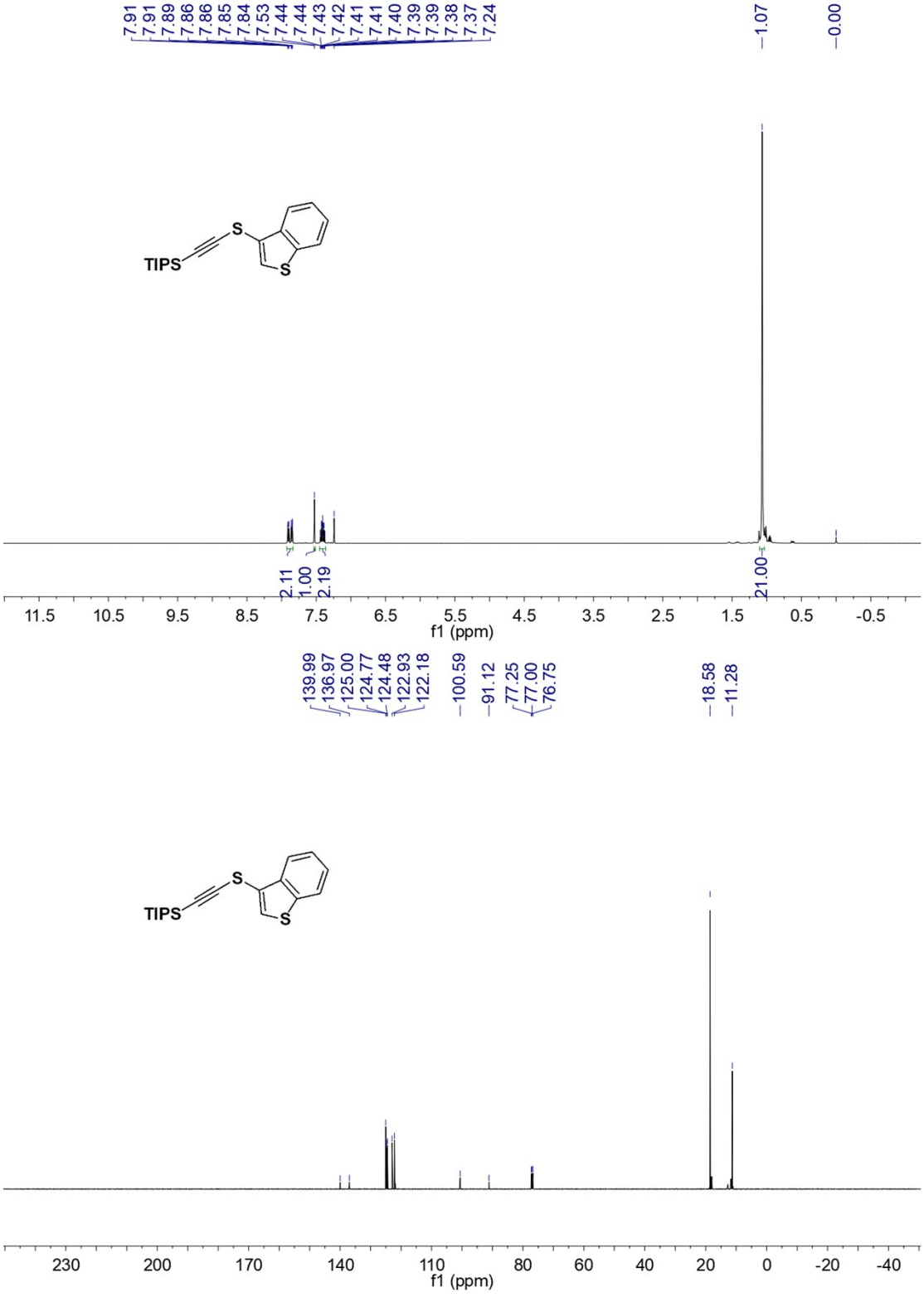

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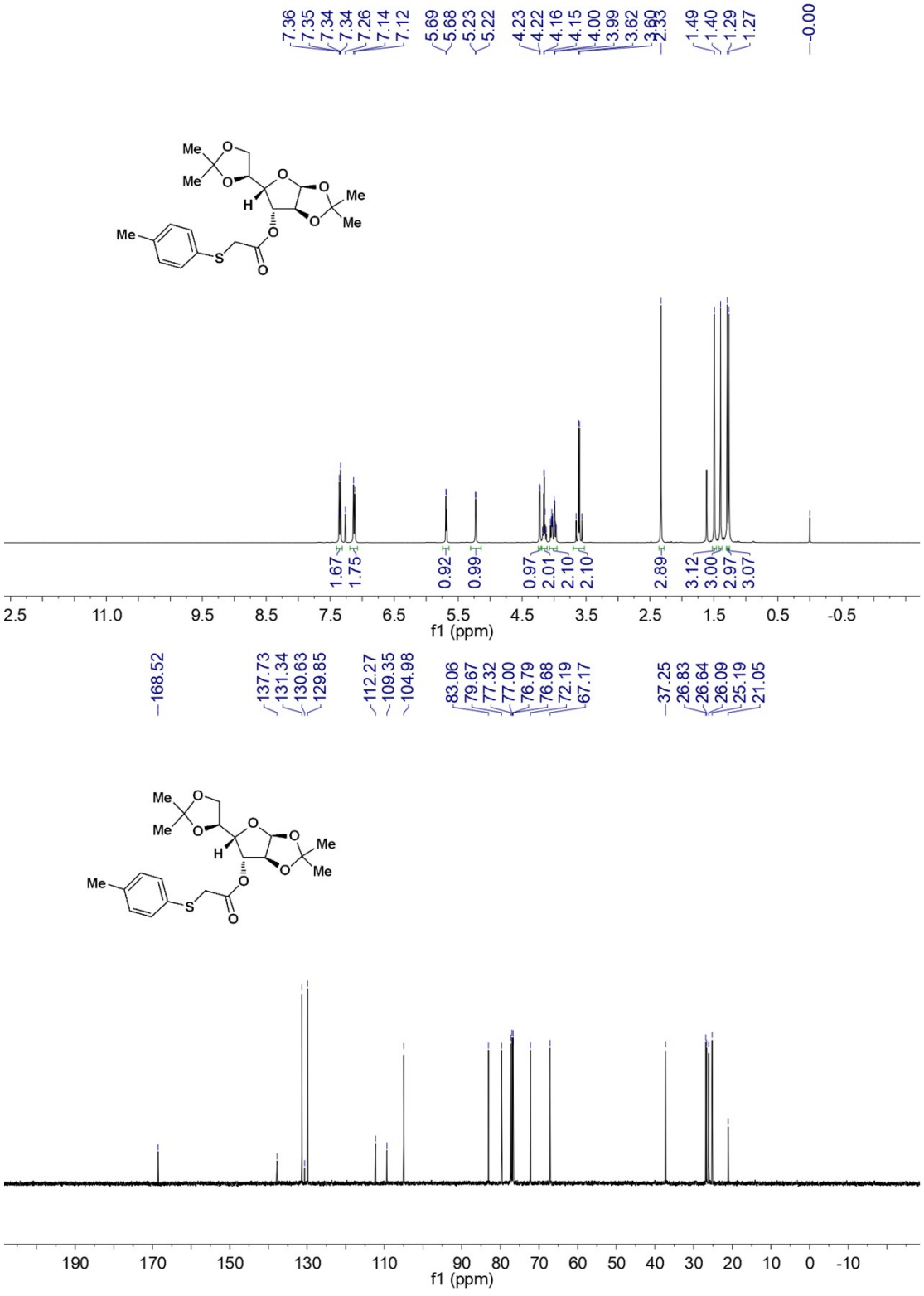

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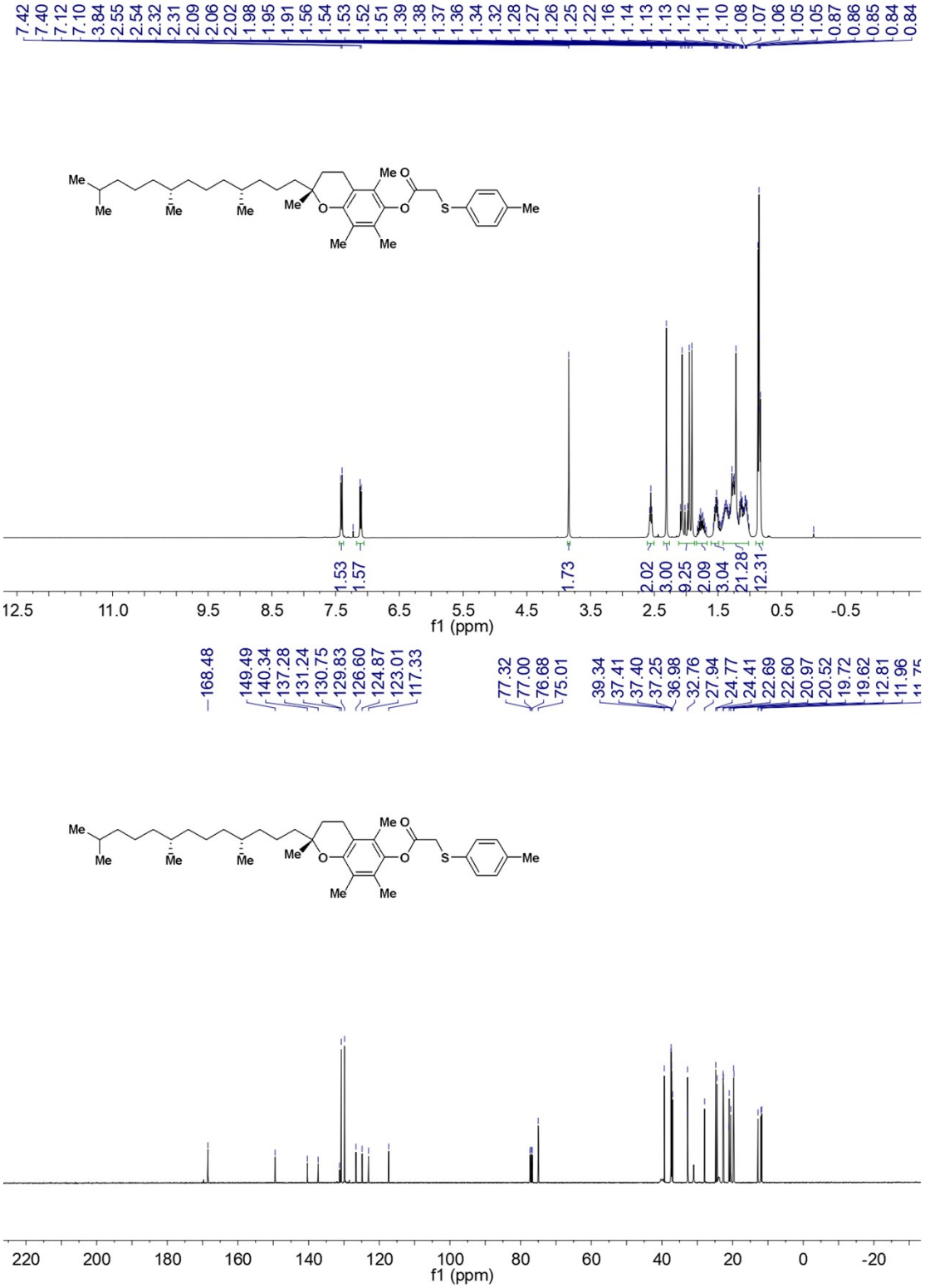

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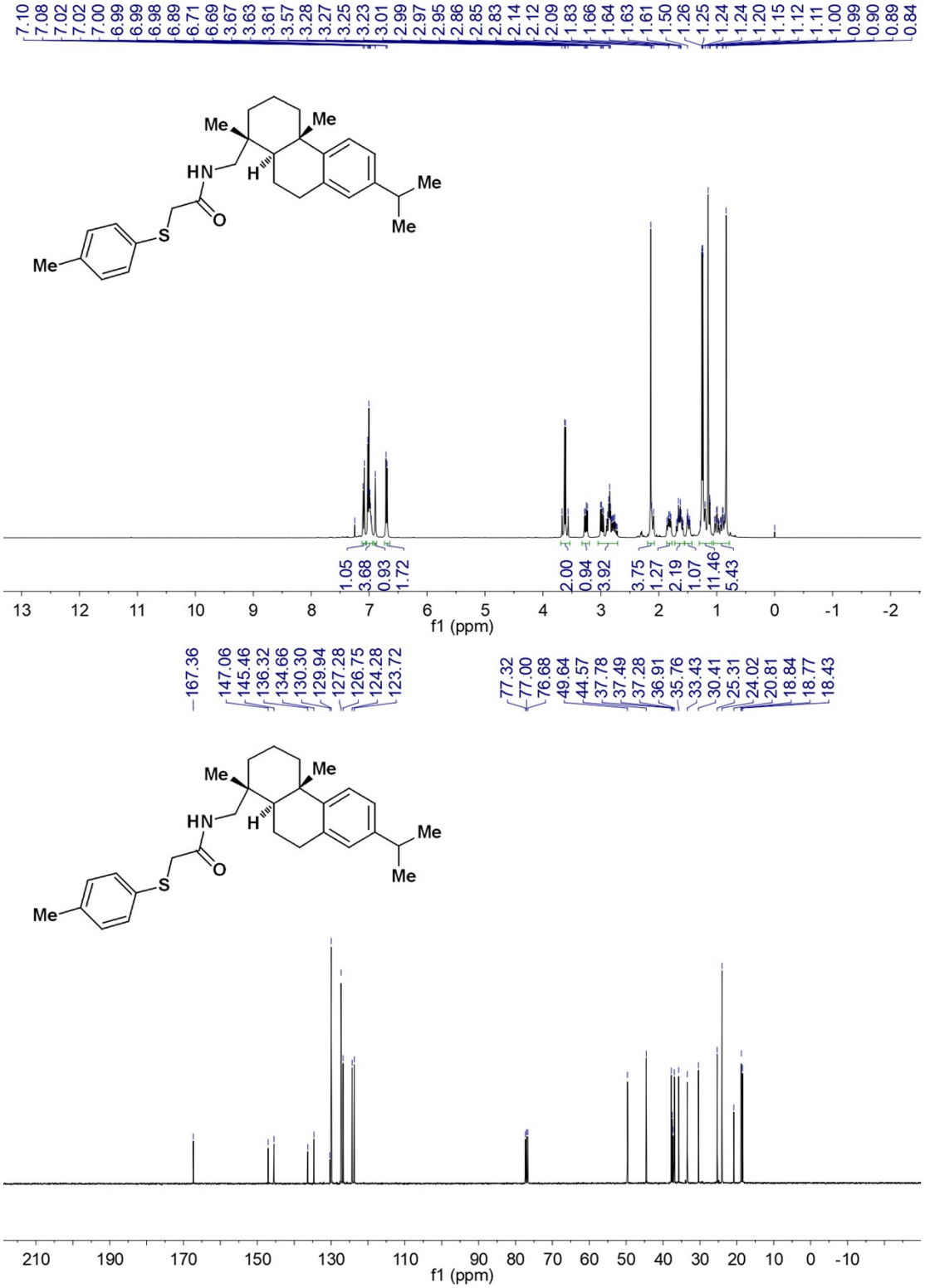

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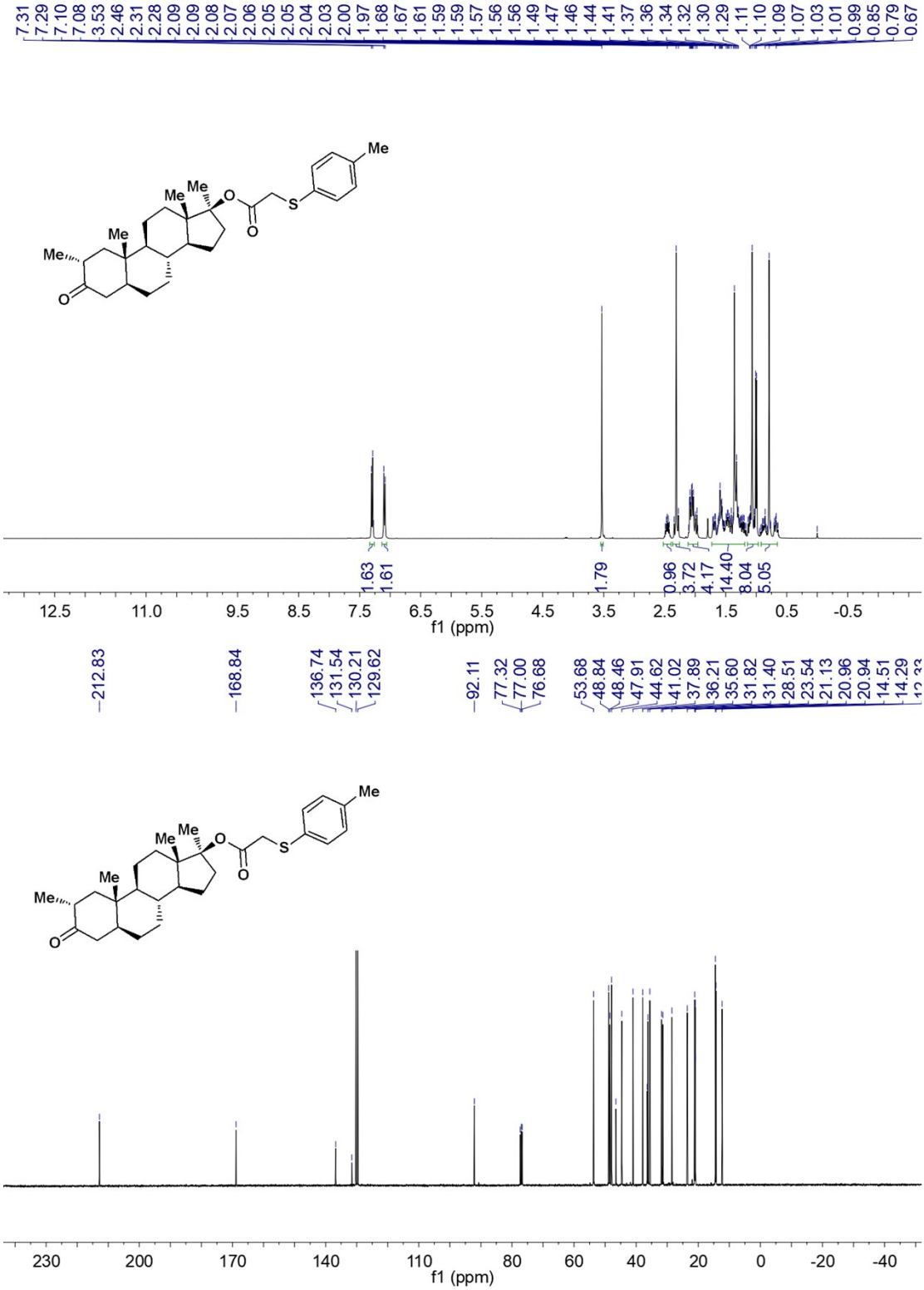

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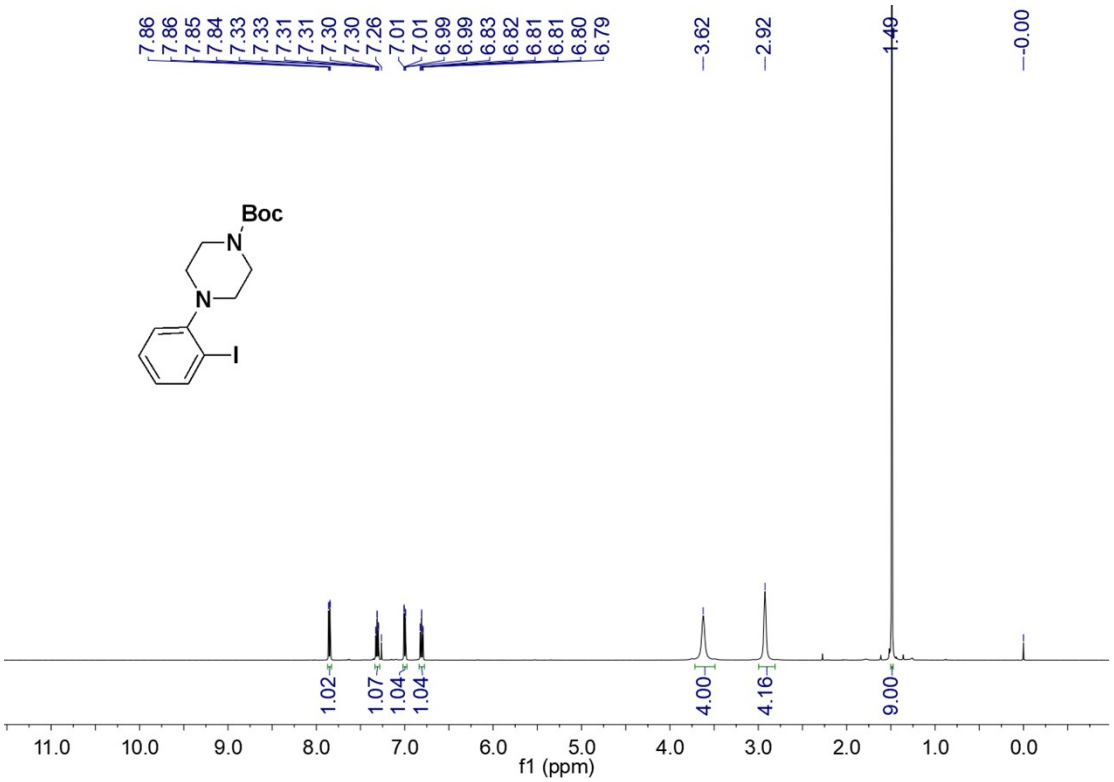

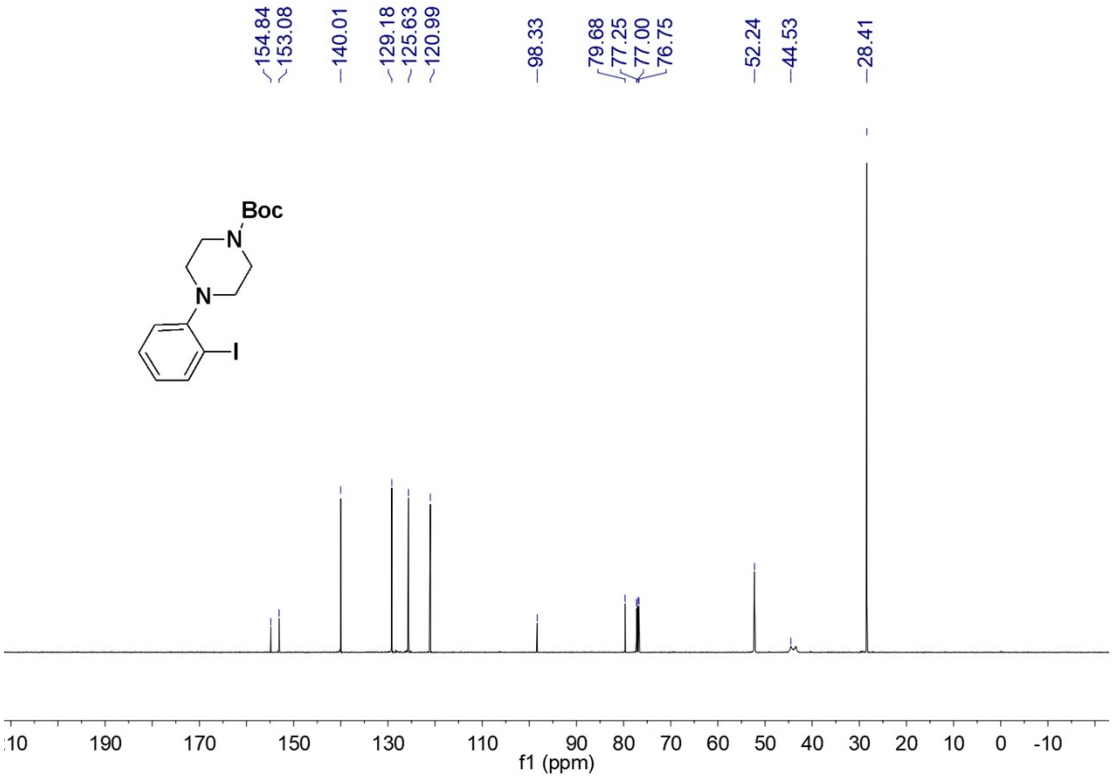

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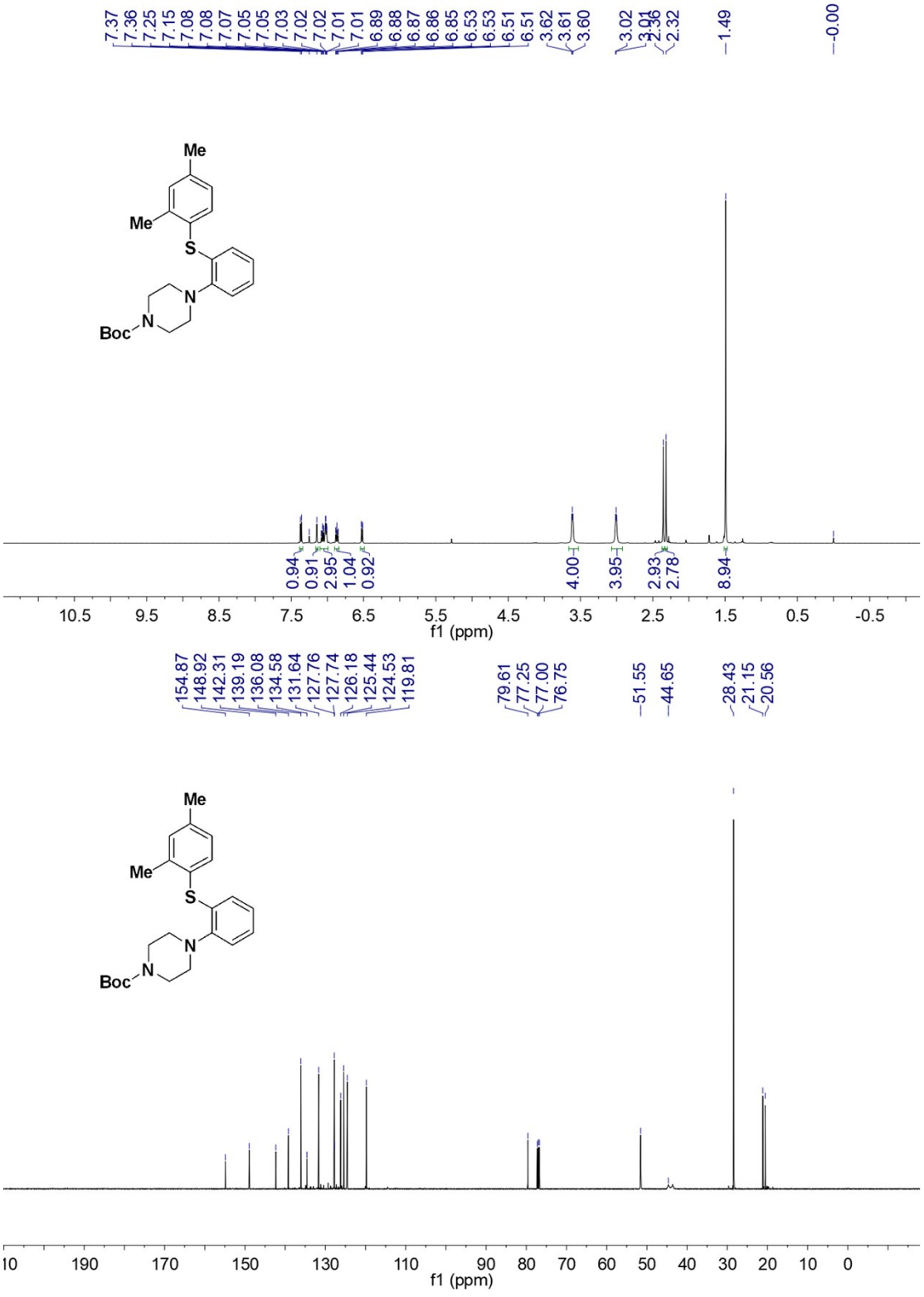

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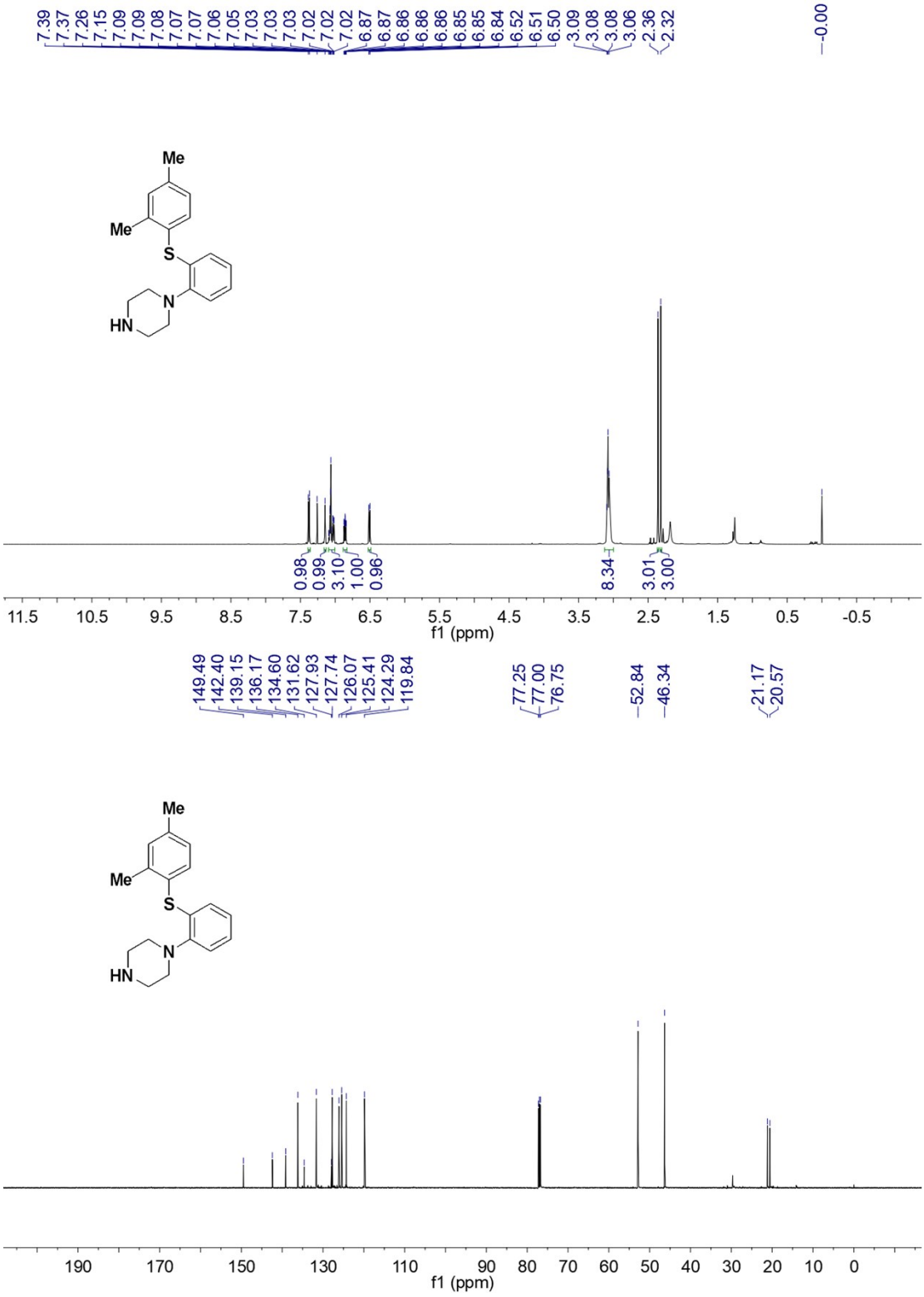

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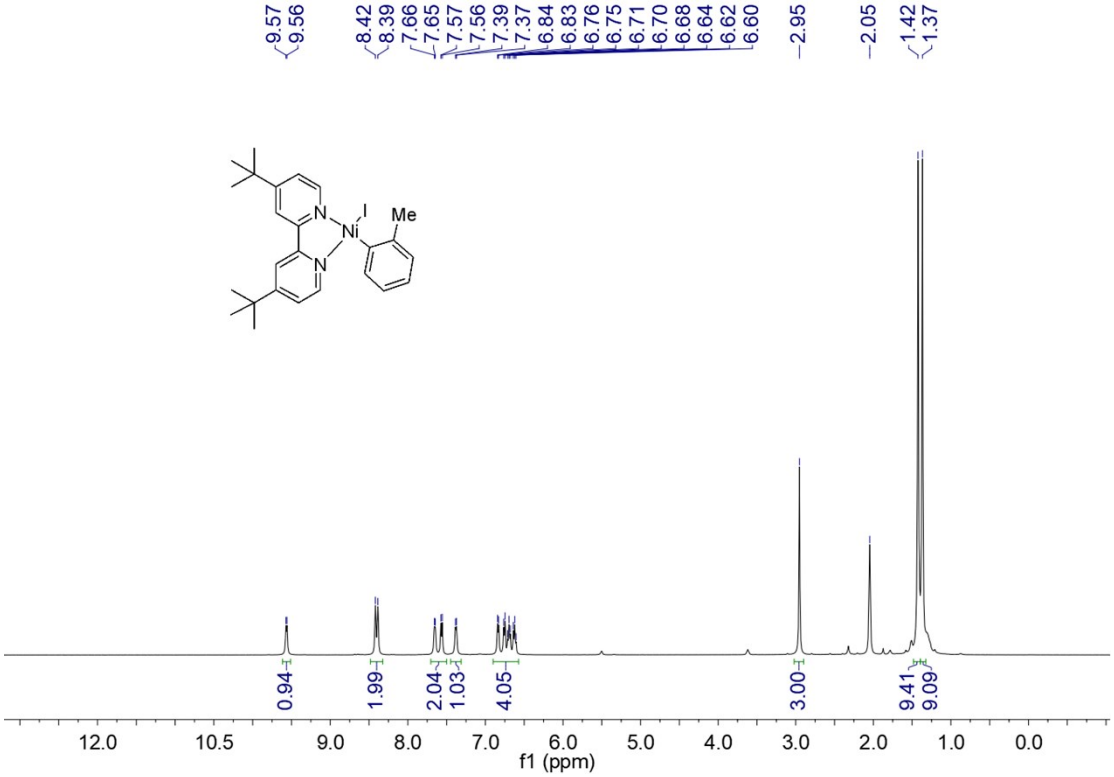

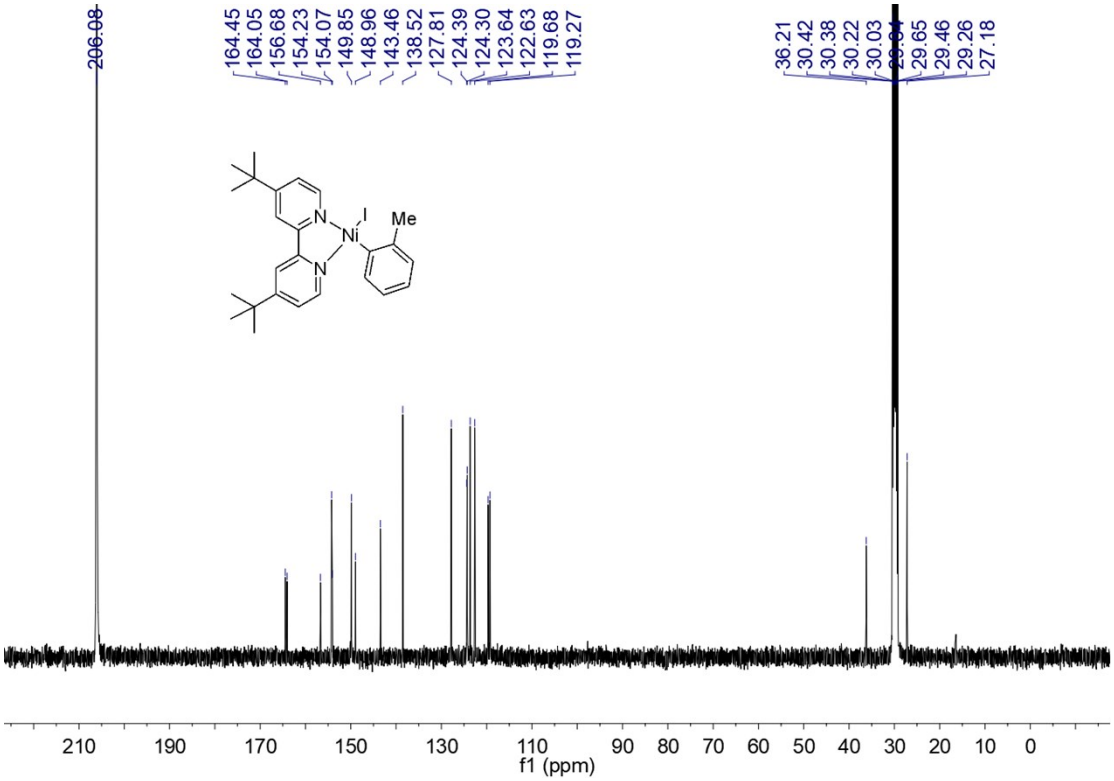

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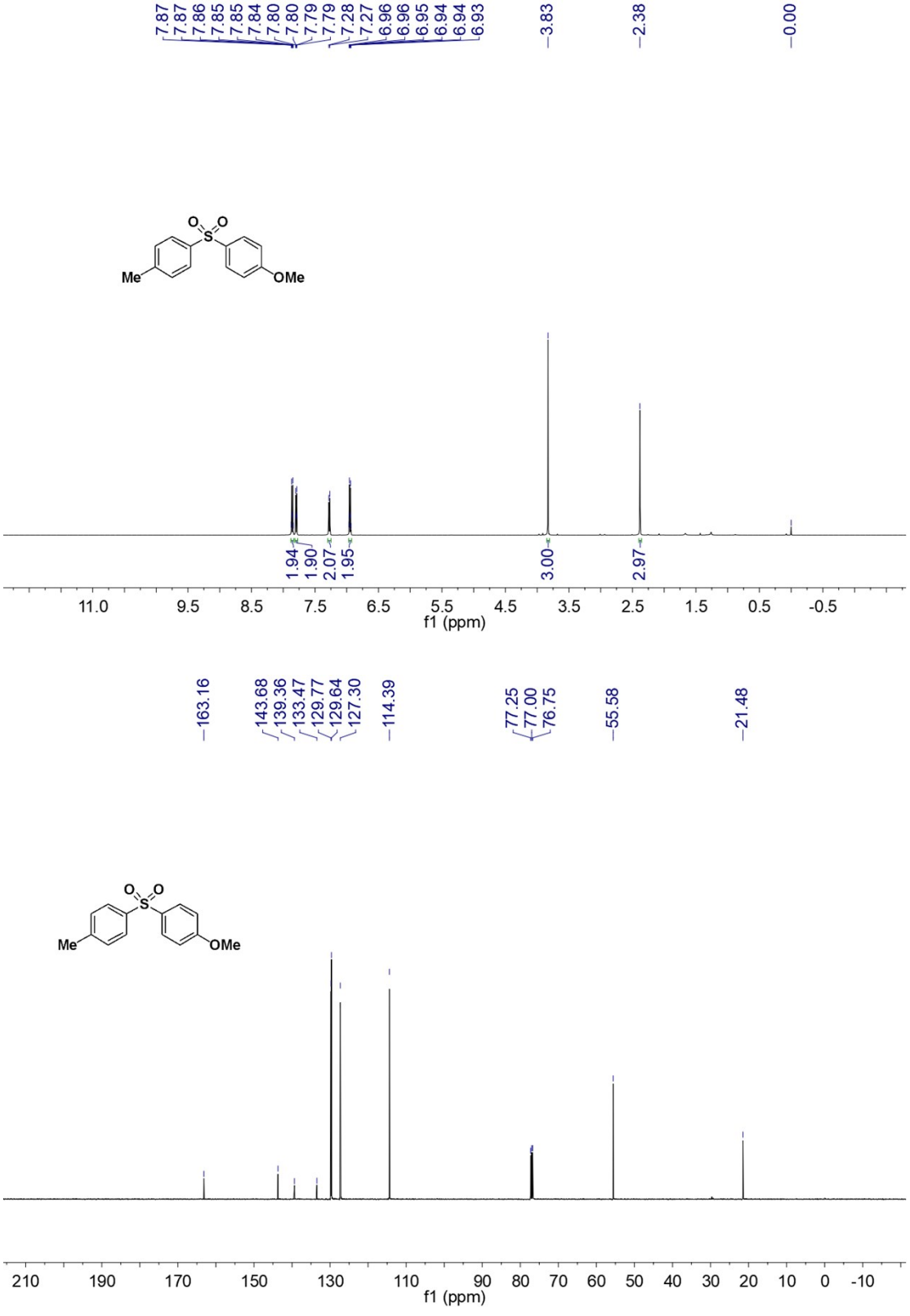

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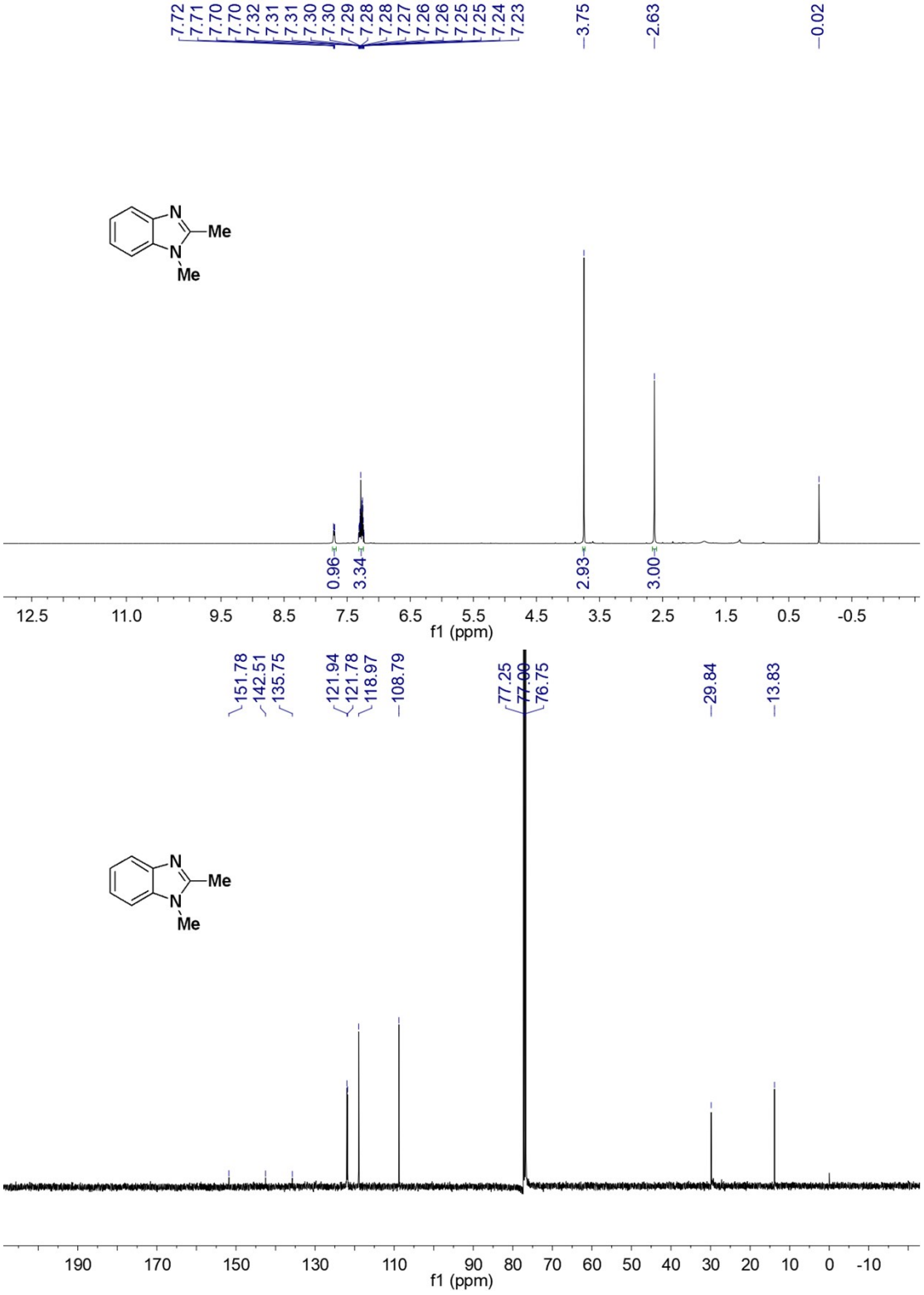

VIII. References

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