Supporting Information for

Asymmetric Dearomatization of Naphthols *via* a Rh-Catalyzed $C(sp^2)$−H Functionalization/Annulation Reaction

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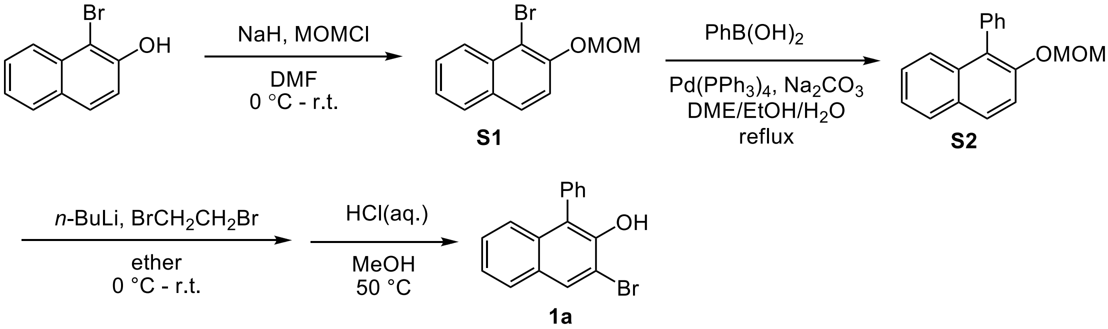
General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (400, 600 MHz and 100, 151 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on a Varian instrument or Agilent instrument (376 MHz) and internally referenced to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm).

Chiral rhodium catalysts **K1-K4**[1], substituted naphthol derivatives **1e**[2] and substituted alkynes **2c**[3], **2e-2i**[4] were prepared according to published procedures.

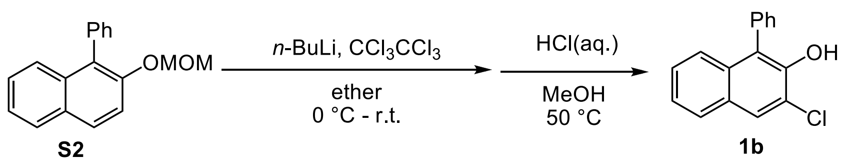
Synthesis and Characterization of Starting Materials



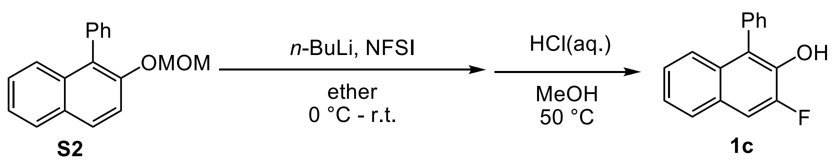
A flame-dried reaction flask was cooled to room temperature and filled with argon. To the flask were added NaH (1.6 g, 1.8 equiv.) and DMF (150 mL). The resulting reaction mixture was stirred at 0 ℃. To the flask was added 1-bromo-2-naphthol (5.0 g, 22.4 mmol) slowly. After the reaction mixture was reacted at this temperature for 30 minutes, chloromethyl methyl ether (1.7 mL, 1.1 equiv.) was slowly added. After stirring overnight at room temperature, the reaction was quenched by water. The mixture was extracted with EtOAc, washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product **S1** (5.98 g, 99% yield) for further use. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.80-7.74 (m, 2H), 7.55 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.42-7.38 (M, 2H), 5.34 (s, 2H), 3.56 (s, 3H). Spectral data were in agreement with those reported in the literature.[5]

S1, $Pd(PPh_3)_4$ (3 mol%, 780 mg), Na_2CO_3 (11.2 g), $PhB(OH)_2$ (4.1 g, 1.5 equiv.) were dissolved in DME/EtOH/H_2O (4/1/1, 60 mL) under argon atmosphere and this reaction mixture was heated to reflux. After stirring for overnight, the reaction mixture was cooled to rt and extracted with EtOAc, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and filtered through short column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 = 10/1/1). The filtrate was concentrated and the residue **S2** was used for the next step without further purification.

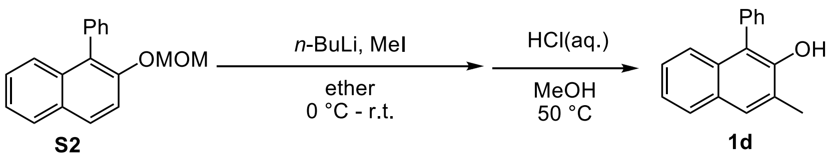
The crude **S2** (1.32 g, 5.0 mmol) was dissolved in ether (60 mL) under argon atmosphere and cooled to 0 ^{o}C. *n*-BuLi (4.2 mL, 2.4 M in *n*-hexane, 2 equiv.) was slowly added and warmed to room temperature. After stirring for 2 h, 1,2-dibromoethane (1.7 mL, 4 equiv.) was slowly added. After stirring for another 1 h, the reaction was quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give a crude product for further use. The residue was dissolved in MeOH (20 mL) and conc. HCl (aq.) (35%, 0.2 mL) was added at 50 °C. After stirring for 1 h, the reaction mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum/CH_2Cl_2 = 10:1) and recrystallized from hexane/DCM to afford **1a** (441.4 mg, 29% yield, from **S2**). **1a**: White solid, m.p. = 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.73-7.70 (m, 1H), 7.58-7.54 (m, 2H), 7.51-7.47 (m, 1H), 7.42-7.30 (m, 5H), 5.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 134.4, 132.7, 131.3, 130.8, 129.4, 129.2, 128.4, 127.0, 126.7, 125.0, 124.3, 122.8, 111.9; IR (thin film): ν_{max}(cm^{-1}) = 2987, 2901, 1376, 1066, 749; Anal. calcd for $C_{16}H_{11}BrO$: C, 64.24; H, 3.71; Found: C, 64.30; H, 3.73.



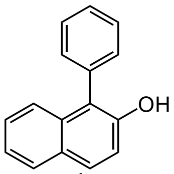
1b was prepared from **S2** by the same procedure as the synthesis of **1a**, except that hexachloroethane was used instead of 1,2-dibromoethane. **1b**: (0.7 g, 55% yield, from **S2**), colorless solid, m.p. = 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72-7.70 (m, 1H), 7.57-7.53 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.38 (m, 3H), 7.35-7.30 (m, 2H), 5.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 134.3, 132.2, 130.8, 129.1, 128.8, 128.3, 127.7, 127.1, 126.6, 125.0, 124.3, 123.1, 121.9; IR (thin film): ν_{max}(cm^{-1}) = 3517, 3472, 3057, 1504, 1454, 1380, 1150, 776; HRMS (EI) calcd for $C_{16}H_{11}ClO$ $[M]^+$: 254.0498; Found: 254.0502.



1c was prepared from **S2** by the same procedure as the synthesis of **1a**, except that NFSI was used instead of 1,2-dibromoethane. **1c**: (0.8 g, 67% yield, from **S2**), pale yellow solid, m.p. = 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.60-7.49 (m, 4H), 7.44-7.42 (m, 3H), 7.39-7.30 (m, 2H), 5.243-5.237 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (d, *J* = 244.3 Hz), 140.4 (d, *J* = 15.4 Hz), 133.7 (d, *J* = 3.0 Hz), 130.8, 130.1, 129.2, 128.5, 128.3 (d, *J* = 8.6 Hz), 127.4 (d, *J* = 5.3 Hz), 125.7 (d, *J* = 2.6 Hz), 124.9 (d, *J* = 2.0 Hz), 124.5, 124.2 (d, *J* = 2.2 Hz), 111.6 (d, *J* = 17.4 Hz); ^{19}F NMR (376 Hz, $CDCl_3$) δ -135.8 (m); IR (thin film): ν_{max}(cm^{-1}) = 3674, 3504, 3057, 2987, 2901, 1592, 1509, 1465, 777; HRMS (EI) calcd for $C_{16}H_{11}FO$ $[M]^+$: 238.0794; Found: 238.0790.

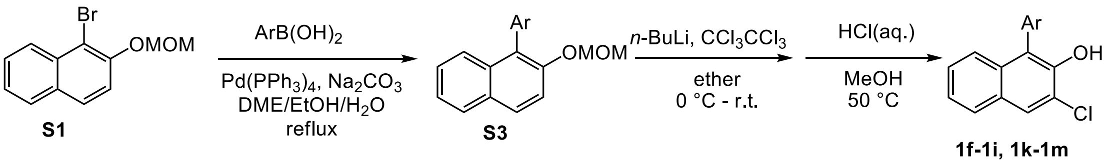


1d was prepared from **S2** by the same procedure as the synthesis of **1a**, except that iodomethane was used instead of 1,2-dibromoethane. **1d**: (0.81 g, 69% yield, from **S2**), White solid, m.p. = 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 1H), 7.63 (s, 1H), 7.59-7.55 (m, 2H), 7.51-7.47 (m, 1H), 7.42 -7.40 (m, 2H), 7.33-7.24 (m, 3H), 5.19 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 134.4, 132.0, 131.2, 129.6, 128.9, 128.8, 128.4, 127.2, 126.5, 125.4, 124.4, 123.2, 120.4, 17.0; IR (thin film): ν_{max}(cm^{-1}) = 3674, 3514, 2973, 2901, 1428, 1210, 1126, 748; HRMS (EI) calcd for $C_{17}H_{14}O$ $[M]^+$: 234.1045; Found: 234.1039.



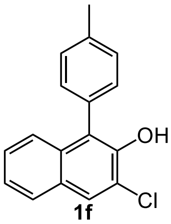
1e

1e[2]. Colorless solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.59-7.55 (m, 2H), 7.53-7.36 (m, 4H), 7.36-7.28 (m, 2H), 7.26-7.22 (m, 1H), 5.14 (s, 1H).



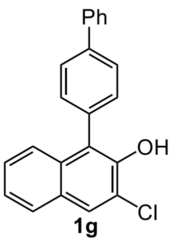
S1 (8 mmol, 2.1 g), $Pd(PPh_3)_4$ (184.8 mg, 0.16 mmol, 2 mol%), Na_2CO_3 (3.4 g, 32 mmol, 4 equiv.), and $ArB(OH)_2$ (12 mmol, 1.5 equiv.) were dissolved in DME/EtOH/H_2O (5/1/1, 70 mL) under argon atmosphere and this mixture was heated to reflux. After stirring for overnight, the reaction mixture was cooled to rt and extracted with EtOAc, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and filtered through short column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 = 10/1/1)]. The filtrate was concentrated and the residue **S3** was used for next step without further purification.

1f-1i, 1k-1m was prepared from **S3** in the same procedure as **1b**.



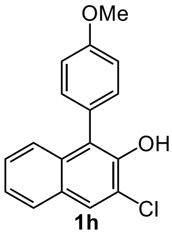
1f

1f: (1.13 g, 53% yield, from **S1**), colorless solid, m.p. = 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.76-7.66 (m, 1H), 7.44-7.25 (m, 7H), 5.56 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 138.2, 132.3, 131.1, 130.6, 129.9, 128.8, 127.6, 127.1, 126.5, 125.0, 124.3, 123.1, 121.9, 21.3; IR (thin film): $\nu_{max}(cm^{-1})$ = 3519, 3474, 3058, 2918, 2856, 1618, 1584, 1514, 1451, 1376, 749; HRMS (EI) calcd for $C_{17}H_{13}ClO$ $[M]^+$: 268.0655; Found: 268.0658.



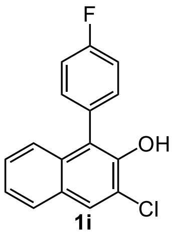
1g

1g: (1.3 g, 49% yield, from **S1**), colorless solid, m.p. = 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81-7.75 (m, 2H), 7.75-7.71 (m, 1H), 7.70-7.69 (m, 2H), 7.53-7.44 (m, 5H), 7.41-7.32 (m, 3H), 5.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 141.1, 140.5, 133.3, 132.3, 131.2, 128.9, 128.8, 127.78, 127.77, 127.5, 127.1, 126.7, 125.0, 124.4, 122.8, 121.9; IR (thin film): $\nu_{max}(cm^{-1})$ = 3502, 3073, 3027, 2987, 1927, 1584, 1502, 763; HRMS (EI) calcd for $C_{22}H_{15}ClO$ $[M]^+$: 330.0811; Found: 330.0812.



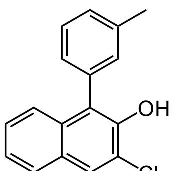
1h

1h: (1.5 g, 65% yield, from **S1**), white solid, m.p. = 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.74-7.67 (m, 1H), 7.46-7.39 (m, 1H), 7.34-7.30 (m, 4H), 7.09-7.07 (m, 2H), 5.59 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.1, 132.5, 131.9, 128.8, 127.6, 127.1, 126.5, 126.0, 125.0, 124.2, 122.8, 121.9, 114.6, 55.3; IR (thin film): $\nu_{max}(cm^{-1})$ = 3674, 3503, 3476, 2987, 2901, 2834, 1604, 1511, 1454, 1382, 1036, 752; HRMS (EI) calcd for $C_{17}H_{13}ClO_2$ $[M]^+$: 284.0604; Found: 284.0599.



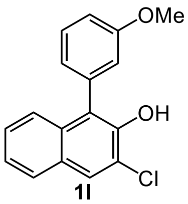
1i

1i: (0.54 g, 25% yield, from **S1**), white solid, m.p. = 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.75-7.68 (m, 1H), 7.42-7.31 (m, 5H), 7.26-7.22 (m, 2H), 5.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.3 Hz), 145.9, 132.5 (d, *J* = 8.0 Hz), 132.4, 128.8, 127.8, 127.2, 126.8, 126.6, 124.8, 124.4, 122.1, 121.8, 116.0 (d, *J* = 21.3 Hz); ^{19}F NMR (376 Hz, $CDCl_3$) δ -113.5 (m); IR (thin film): $\nu_{max}(cm^{-1})$ = 3502, 2987, 1600, 1509, 1455, 1371, 747.8; HRMS (EI) calcd for $C_{16}H_{10}ClFO$ $[M]^+$: 272.0404; Found: 272.0408.



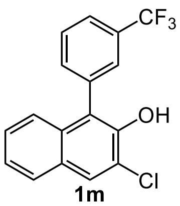
1k

1k: (1.55 g, 72% yield, from **S1**), red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.74-7.67 (m, 1H), 7.48-7.36 (m, 2H), 7.36-7.27 (m, 3H), 7.23-7.15 (m, 2H), 5.56 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 138.9, 134.1, 132.2, 131.3, 129.2, 129.1, 128.8, 127.72, 127.71, 127.0, 126.5, 125.0, 124.3, 123.2, 121.9, 21.5; IR (thin film): ν_{max}(cm^{-1}) = 3518, 3055, 3017, 2980, 1727, 1586, 1380, 1194, 747; HRMS (EI) calcd for $C_{17}H_{13}ClO$ $[M]^+$: 268.0655; Found: 268.0652.



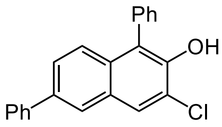
1l

1l: (1.4 g, 49% yield, from **S1**), white solid, m.p. = 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (s, 1H), 7.58-7.27 (m, 4H), 7.04-6.94 (m, 3H), 5.62 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 145.8, 135.5, 132.1, 130.3, 128.7, 127.9, 127.1, 126.6, 125.0, 124.3, 122.9, 121.9, 116.0, 114.2, 55.3; IR (thin film): ν_{max}(cm^{-1}) = 3380, 2987, 2945, 2901, 1585, 1451, 1383, 1081, 751; HRMS (EI) calcd for $C_{17}H_{13}ClO_2$ $[M]^+$: 284.0604; Found: 284.0598.



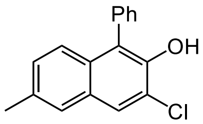
1m

1m: (1.4 g, 49% yield, from **S1**), yellow solid, m.p. = 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.78-7.72 (m, 2H), 7.70-7.66 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.40-7.38 (m, 3H), 5.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 135.8, 134.3, 132.2, 131.2 (q, *J* = 32.3 Hz), 129.2, 128.8, 128.0, 127.7 (q, *J* = 3.7 Hz), 127.3, 127.1, 124.8 (q, *J* = 3.7 Hz), 124.62, 124.56, 124.1 (q, *J* = 271.0 Hz), 121.8, 121.7; ^{19}F NMR (376 Hz, $CDCl_3$) δ -62.5; IR (thin film): ν_{max}(cm^{-1}) = 3529, 2987, 2901, 1591, 1504, 1458, 1324, 1070; HRMS (EI) calcd for $C_{17}H_{10}ClF_3O$ $[M]^+$: 322.0372; Found: 322.0371.



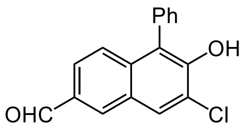
1n

1n: (0.5 g, 30% yield), white solid, m.p. = 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 13.6 Hz, 2H), 7.68-7.33 (m, 12H), 5.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 140.6, 137.1, 134.3, 131.4, 130.8, 129.2, 129.1, 128.9, 128.4, 128.0, 127.4, 127.2, 126.3, 125.6, 124.9, 123.1, 122.4; IR (thin film): ν_{max}(cm^{-1}) = 3510, 2969, 2923, 2901, 1590, 1487, 1434, 1257, 752; HRMS (EI) calcd for $C_{22}H_{15}ClO$ $[M]^+$: 330.0811; Found: 330.0809.



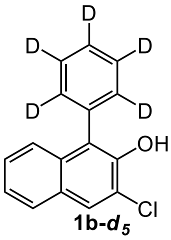
1o

1o: (0.48 g, 27% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.55-7.51 (m, 2H), 7.48-7.45 (m, 2H), 7.38-7.36 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.5, 133.9, 130.7, 130.4, 129.02, 128.98, 128.9, 128.2, 127.0, 126.0, 124.8, 123.0, 121.9, 21.3; IR (thin film): ν_{max}(cm^{-1}) = 3523, 2920, 1590, 1492, 1454, 1259, 1151, 700; HRMS (EI) calcd for $C_{17}H_{13}ClO$ $[M]^+$: 268.0655; Found: 268.0654.



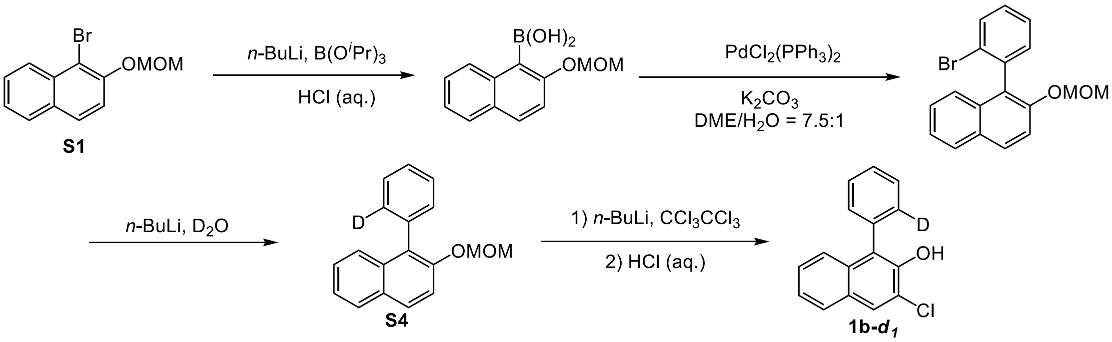
1p

1p: (0.22 g, 38% yield), red solid, m.p. = 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.20 (s, 1H), 8.04 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.69-7.44 (m, 4H), 7.42-7.33 (m, 2H), 6.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 148.7, 135.4, 133.4, 132.6, 130.6, 129.4, 129.3, 128.7, 127.8, 126.0, 123.7, 123.6, 123.3; IR (thin film): ν_{max}(cm^{-1}) = 3349, 3059, 2851, 1684, 1606, 1458, 1144, 693; HRMS (EI) calcd for $C_{17}H_{11}ClO_2$ $[M]^+$: 282.0448; Found: 282.0452.



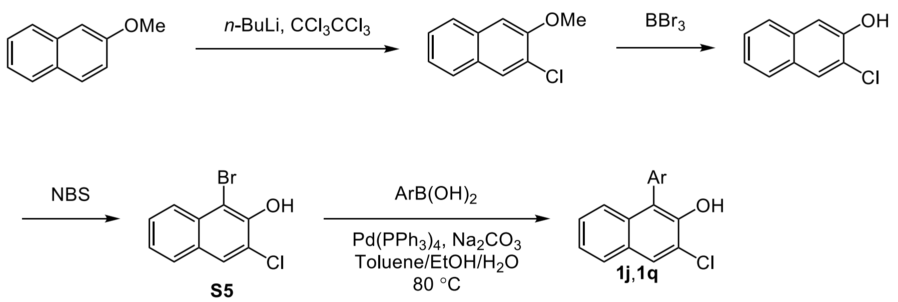
1b-*d*$_5$

1b-*d*$_5$: (0.66 g, 51% yield, from **S1**), pale brown solid, m.p. = 114-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74-7.65 (m, 1H), 7.42-7.36 (m, 1H), 7.36-7.27 (m, 2H), 5.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 134.1, 132.2, 130.3 (t, J = 24.1 Hz), 128.8, 128.6 (t, J = 24.5 Hz), 127.7, 127.1, 126.6, 124.9, 124.3, 123.1, 121.9; IR (thin film): ν_{max}(cm^{-1}) = 3517, 3470, 3057, 2987, 2901, 1585, 1502, 1199, 752; HRMS (EI) calcd for $C_{16}H_6D_5ClO$ $[M]^+$: 259.0812; Found: 259.0817.



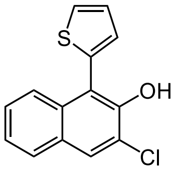
A solution of **S1** (2.7 g, 2.1 mmol) in THF (25 mL) under Ar was treated dropwise at -78 ^{o}C with *n*-butyllithium (8.0 mL, 2.5 M in hexane, 20 mmol). The reaction was stirred at -78 ℃ for 45 min, and then triisopropylborate (4.7 mL, 20 mmol) was added in one portion. The resulting mixture was stirred at -78 ℃ for 30 min and then at room temperature for 1 h. 5 mL of 10% HCl (aq.) and ether (50 mL) were added and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. After concentrating in vacuum, the residue was added to round-bottomed flask, fitted with a condenser. K_2CO_3 (2.5 g, 18 mmol), 1-bromo-2-iodobenzene (1.68 g, 6 mmol), bis(triphenylphosphine)palladium(II) chloride (420 mg, 0.6 mmol), DME (30 mL) and H_2O (4 mL) were added, and the resulting mixture was stirred at 80 ℃ for 9 h. The reaction mixture was allowed to cool to room temperature, DME was evaporated, and water (40.0 mL) and EtOAc (20.0 mL) were added. The layers were separated and the aqueous layer was extracted. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After concentrating in vacuum, the residue was added to a round-bottomed flask. THF (20 mL) was added under Ar to the mixture dropwise at -78 °C with *n*-butyllithium (1.4 mL, 2.5 M in hexane, 3.4 mmol). The reaction was stirred at -78 °C for 2 h, and then deuterium oxide (0.5 mL, 3.5 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 5 h. 5 mL of 10% HCl aqueous solution and ether (50 mL) were added and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After concentrating in vacuum, the residue **S4** was used directly without purification. **1b-*d₁*** was prepared from **S4** by the same procedure as the synthesis of **1b**.

1b-d_1: (0.25 g, 12% yield, from **S1**), white solid, m.p. = 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.77-7.70 (m, 1H), 7.61-7.54 (m, 2H), 7.54-7.47 (m, 1H), 7.44-7.30 (m, 4H), 5.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 134.2, 132.2, 130.7, 130.4 (t, J = 24.3 Hz), 129.0, 128.9, 128.7, 128.2, 127.7, 127.0, 126.5, 124.9, 124.2, 123.0, 121.9; IR (thin film): ν_{max}(cm^{-1}) = 3517, 3471, 3056, 2987, 2901, 1586, 1502, 1471, 749; HRMS (EI) calcd for $C_{16}H_{10}DClO$ $[M]^+$: 255.0561; Found: 255.0556.



To a solution of 2-methoxynaphthalene (4.75 g, 30 mmol) in THF (50 mL) was added *n*-butyllithium (15 mL, 2.5 M in hexane, 36 mmol) at –78 °C. After the mixture was stirred for 1 h at room temperature, hexachloroethane (8.5 g, 36 mmol) in THF (20 mL) was added to the solution at –78 °C, and the resulting mixture was stirred for 4 h at room temperature. The mixture was poured into a saturated aqueous ammonium chloride solution (10 mL) and was extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was dissolved in dichloromethane (50 mL). To this mixture was added dropwise a dichloromethane solution of BBr_3 (ca. 0.5 M 90 mL, 45 mmol) at –78 °C. After the stirring was maintained for 20 h at room temperature, the mixture was added ice at 0 °C. The aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic layer was washed with brine (30 mL), dried (Na_2SO_4) and concentrated in vacuo. To a solution of this residue in DMF (40 mL) was added NBS (5.6 g, 31.5 mmol). The mixture was stirred at room temperature for 7 h. Water was added, and the mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with water (30 mL × 3), dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on a silica gel column using CH_2Cl_2/PE 1:10 as eluent. A white solid **S5** was obtained (1.71 g, 22% for three steps); m.p. = 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.39-7.35 (m, 1H), 6.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 131.3, 129.0, 127.98, 127.97, 127.3, 125.7, 125.2, 121.5, 106.8; IR (thin film): $\nu_{max}(cm^{-1})$ = 3403, 3053, 2961, 1620, 1588, 1462, 1497, 739; HRMS (EI) calcd for $C_{10}H_6OClBr$ $[M]^+$: 255.9291; Found: 255.9292.

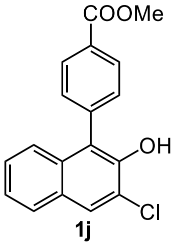
S5 (2 mmol), $Pd(PPh_3)_4$ (10 mol%, 231 mg), Na_2CO_3 (445 mg), $ArB(OH)_2$ (2 equiv.) were dissolved in Toluene/EtOH/H_2O (5/1/1, 14 mL) under argon atmosphere and this reaction mixture was heated to 80 °C. After stirring for 3 h, the reaction mixture was cooled to rt and extracted with EtOAc, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and filtered through short column chromatography (*n*-hexane/EtOAc = 10/1).



1q

1q: (0.48 g, 24% yield), brown solid, m.p. = 63-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.69-7.60 (m, 1H), 7.60-7.49 (m, 2H), 7.41-7.26 (m, 2H), 7.22 (dd, *J* =

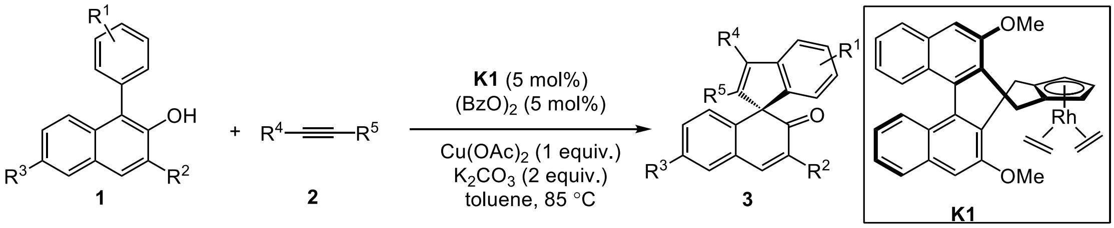
5.2, 3.6 Hz, 1H), 7.12 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 133.9, 133.0, 129.6, 129.0, 128.5, 128.0, 127.8, 127.0, 126.95, 124.7, 124.5, 121.7, 115.1; IR (thin film): ν_{max}(cm^{-1}) = 3455, 3061, 2923, 2853, 1699, 1587, 1502, 1451, 1191, 727; HRMS (EI) calcd for $C_{14}H_9ClOS$ [M]$^+$: 260.0063; Found: 260.0060.



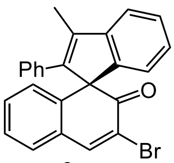
1j

1j: (0.28 g, 45% yield), white solid, m.p. = 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.79-7.72 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41-7.35 (m, 3H), 5.63 (s, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.6, 139.9, 131.9, 130.9, 130.0, 129.7, 128.8, 128.0, 127.2, 126.9, 124.7, 124.5, 122.2, 121.9, 52.2; IR (thin film): ν_{max}(cm^{-1}) = 3391, 2953, 1702, 1606, 1496, 1401, 765; HRMS (ESI) calcd for $C_{18}H_{14}ClO_3$ [M + H]$^+$: 313.0626; Found: 313.0624.

General Procedure for Enantioselective Dearomatization of Naphthols

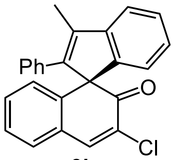


To a Schlenk tube were added **K1** (10 μmol, 5.6 mg), $(BzO)_2$ (10 μmol, 2.4 mg) and toluene (1 mL) successively. After the mixture was stirred at room temperature for 30 min, **1** (0.2 mmol), $Cu(OAc)_2$ (36.4 mg, 0.2 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), **2** (0.4 mmol) and toluene (1 mL) were added successively. The mixture was stirred at 85℃ under air (open flask). After the reaction was complete (monitored by TLC), the mixture was concentrated under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/40, v/v) to afford desired product **3**.



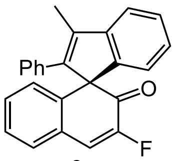
3aa

Yellow solid, m.p. = 163-165 °C, 33.6 mg, 81% yield (0.1 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.39 (d, *J* = 4.0 Hz, 1H), 7.36-7.27 (m, 2H), 7.26-7.11 (m, 5H), 7.10-7.02 (m, 1H), 7.01-6.89 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 147.4, 147.0, 146.2, 144.1, 140.3, 140.0, 134.7, 130.6, 130.3, 129.2, 128.7, 128.2, 128.1, 127.8, 127.2, 127.1, 126.4, 122.5, 121.6, 120.6, 72.8, 12.5; IR (thin film): ν_{max}(cm^{-1}) = 3061, 2921, 1681, 1595, 1337, 1220, 752; HRMS (ESI) calcd for $C_{25}H_{18}BrO$ $[M + H]^+$: 413.0536; Found: 413.0537; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 15.90 min, t (minor) = 12.05 min], 95:5 e.r.; $[\alpha]_D^{20}$ = -177.3 (c = 0.20, $CHCl_3$).



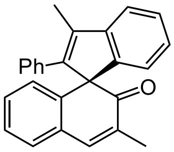
3ba

Yellow solid, m.p. = 163-165 °C, 61.2 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33-7.23 (m, 2H), 7.22-7.01 (m, 6H), 7.01-6.96 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 147.1, 146.2, 144.0, 143.3, 140.1, 139.8, 134.6, 130.7, 130.4, 129.6, 129.2, 128.6, 128.2, 128.0, 127.8, 127.2, 127.0, 126.4, 121.5, 120.6, 73.0, 12.2; IR (thin film): ν_{max}(cm^{-1}) = 3674, 2987, 2901, 1668, 1610, 1439, 1406, 1394, 1066; HRMS (ESI) calcd for $C_{25}H_{18}ClO$ $[M + H]^+$: 369.1041; Found: 369.1042; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 12.58 min, t (minor) = 15.55 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -227.5 (c = 0.20, $CHCl_3$).



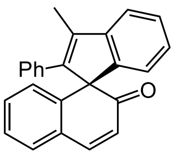
3ca

Yellow solid, m.p. = 158-160 °C, 50.9 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.34-7.28 (m, 2H), 7.2-7.05 (m, 7H), 7.01-6.96 (m, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6 (d, *J* = 17.2 Hz), 153.0 (d, *J* = 266.4 Hz), 147.2, 146.4, 143.8, 140.3, 138.5 (d, *J* = 0.9 Hz), 134.6, 129.7 (d, *J* = 2.7 Hz), 129.3 (d, *J* = 5.9 Hz), 128.7 (d, *J* = 6.0 Hz), 128.6, 128.2, 128.1, 127.8, 127.3, 127.1 (d, *J* = 1.2 Hz), 126.5, 124.9 (d, *J* = 17.3 Hz), 121.5, 120.6, 73.7 (d, *J* = 4.0 Hz), 12.2; ^{19}F NMR (376 Hz, $CDCl_3$) δ -130.8 (d, *J* = 11.3 Hz); IR (thin film): ν_{max}(cm^{-1}) = 3674, 2987, 2902, 1673, 1406, 1258, 1066; HRMS (ESI) calcd for $C_{25}H_{18}FO$ $[M + H]^+$: 353.1336; Found: 353.1346; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 20.58 min, t (minor) = 18.86 min], 86:14 e.r.; $[\alpha]_D^{20}$ = -87.2 (c = 0.20, $CHCl_3$).



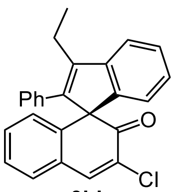
3da

White solid, m.p. = 159-160 °C, 34.6 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.31-7.23 (m, 2H), 7.22-7.08 (m, 4H), 7.05-7.00 (m, 4H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 147.9, 146.4, 144.5, 142.4, 140.2, 139.5, 135.2, 134.1, 130.5, 129.1, 128.67, 128.65, 128.1, 127.6, 127.3, 126.9, 126.7, 126.1, 121.3, 120.4, 71.8, 16.3, 12.3; IR (thin film): $\nu_{max}(cm^{-1})$ = 3674, 2987, 2901, 1655, 1595, 1075, 1051, 696; HRMS (ESI) calcd for $C_{26}H_{21}O$ $[M + H]^+$: 349.1587; Found: 349.1589; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.03 min, t (minor) = 16.64 min], 95:5 e.r.; $[\alpha]_D^{20}$ = -169.8 (c = 0.20, $CHCl_3$).



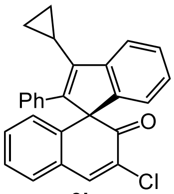
3ea

White solid, 25.2 mg, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 10.0 Hz, 1H), 7.47-6.96 (m, 11H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H), spectral data were in agreement with those reported in the literature;[6] [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 31.83 min, t (minor) = 40.57 min], 89:11 e.r.; $[\alpha]_D^{20}$ = -123.5 (c = 0.20, $CHCl_3$).



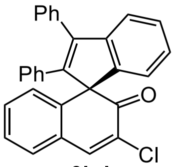
3bb

White solid, m.p. = 139-141 °C, 67.7 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.36-7.12 (m, 7H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.95-6.91 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 147.7, 146.0, 145.4, 144.2, 143.1, 139.7, 134.8, 130.8, 130.4, 129.9, 129.1, 128.6, 128.2, 128.0, 127.7, 127.4, 127.2, 126.3, 122.0, 120.8, 73.2, 19.6, 13.7; IR (thin film): ν_{max}(cm^{-1}) = 2972, 1668, 1608, 1558, 1274, 752; HRMS (ESI) calcd for $C_{26}H_{20}ClO$ $[M + H]^+$: 383.1197; Found: 383.1196; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (major) = 19.47 min, t (minor) = 26.89 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -150.9 (c = 1.00, $CHCl_3$).



3bc

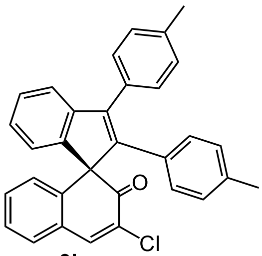
Pale yellow solid, m.p. = 160-162 °C, 58.8 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.31-7.26 (m, 2H), 7.25-7.06 (m, 7H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 1.98 (dq, *J* = 8.4, 5.6 Hz, 1H), 1.02-0.90 (m, 2H), 0.67-0.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 146.9, 146.0, 145.1, 144.8, 143.1, 140.1, 134.4, 130.7, 130.5, 129.6, 129.2, 129.0, 128.0, 127.9, 127.7, 127.2, 126.9, 126.2, 121.5, 72.7, 8.9, 7.4, 7.2; IR (thin film): ν_{max}(cm^{-1}) = 2999, 1680, 1606, 1493, 1225, 1062, 757; HRMS (ESI) calcd for $C_{27}H_{20}ClO$ $[M + H]^+$: 395.1197; Found: 395.1196; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL · min^{-1}, λ = 254 nm, t (minor) = 40.14 min, t (major) = 44.14 min], 97:3 e.r.; $[\alpha]_D^{20}$ = -126.3 (c = 1.00, $CHCl_3$).



3bd

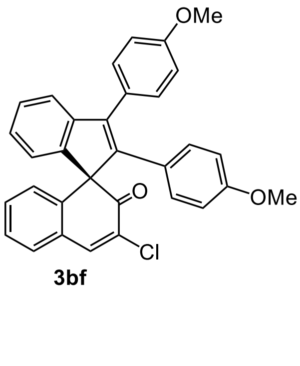
Yellow solid, m.p. = 126-128 °C, 73.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.54-7.48 (m, 2H), 7.47-7.34 (m, 4H), 7.31-7.21 (m, 3H), 7.17 (td, J =

7.6, 1.2 Hz, 1H), 7.07 (td, J = 7.6, 1.2 Hz, 1H), 7.03-6.93 (m, 5H), 6.84-6.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 146.8, 145.3, 144.9, 144.3, 143.3, 140.0, 134.8, 133.9, 130.8, 130.7, 129.45, 129.43, 129.4, 129.0, 128.8, 128.1, 128.0, 127.95, 127.92, 127.2, 126.8, 126.6, 122.1, 121.6, 72.7; IR (thin film): ν_{max}(cm^{-1}) = 3065, 2923, 1675, 1607, 1487, 1226, 751, 688; HRMS (ESI) calcd for $C_{30}H_{23}ClNO$ [M + NH_4]$^+$: 448.1463; Found: 448.1460; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 15.63 min, t (major) = 17.69 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -197.5 (c = 0.20, $CHCl_3$).



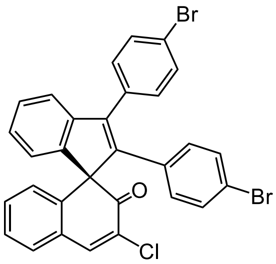
3be

Yellow foam, m.p. = 88-89 °C, 57.0 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.41-7.35 (m, 3H), 7.29-7.20 (m, 5H), 7.16-7.12 (m, 1H), 7.05-7.01 (m, 1H), 7.00-6.92 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 146.6, 145.5, 144.2, 143.9, 143.2, 140.3, 137.6, 137.9, 132.0, 131.0, 130.8, 130.7, 129.5, 129.4, 129.3, 129.2, 128.81, 128.77, 128.0, 127.8, 126.8, 126.3, 121.9, 121.5, 72.6, 21.4, 21.0; IR (thin film): ν_{max}(cm^{-1}) = 2987, 2917, 1676, 1608, 1558, 1226, 1020, 751; HRMS (ESI) calcd for $C_{32}H_{27}ClNO$ [M + NH_4]$^+$: 476.1776; Found: 476.1774; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 17.15 min, t (major) = 27.73 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -207.0 (c = 0.20, $CHCl_3$).



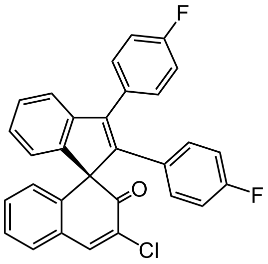
3bf

Yellow foam, m.p. = 89-90 °C, 84.4 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.30-7.20 (m, 3H), 7.16-7.12 (m, 1H), 7.07-6.90 (m, 5H), 6.76 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 159.1, 158.4, 146.5, 145.6, 143.4, 143.3, 143.0, 140.4, 130.8, 130.7, 130.6, 130.2, 129.4, 129.3, 128.0, 127.8, 127.1, 126.7, 126.5, 126.1, 121.7, 121.4, 114.3, 113.5, 72.6, 55.2, 54.9; IR (thin film): ν_{max}(cm^{-1}) = 2999, 2930, 2835, 1675, 1607, 1502, 1461, 1245, 1028, 732; HRMS (ESI) calcd for $C_{32}H_{27}ClNO_3$ [M + NH_4]$^+$: 508.1674; Found: 508.1672; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 22.16 min, t (major) = 30.93 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -199.4 (c = 0.20, $CHCl_3$).



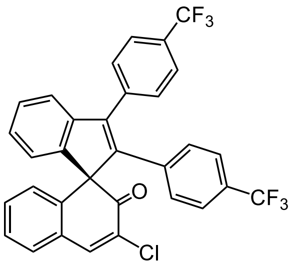
3bg

Yellow foam, m.p. = 108-110 °C, 70.4 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.61-7.54 (m, 2H), 7.40-7.35 (m, 3H), 7.32-7.23 (m, 3H), 7.21-7.05 (m, 4H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.92-6.86 (m, 1H), 6.68-6.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 146.7, 144.4, 144.3, 143.7, 143.5, 139.2, 133.2, 132.6, 132.2, 131.4, 131.0, 130.9, 130.6, 130.4, 129.6, 129.4, 128.3, 128.2, 127.1, 126.8, 122.8, 121.9, 121.8, 121.6, 72.7; IR (thin film): ν_{max}(cm^{-1}) = 2987, 2901, 1675, 1481, 1452, 1068, 752; HRMS (ESI) calcd for $C_{30}H_{21}Br_2ClNO$ [M + NH_4]$^+$: 603.9673; Found: 603.9670; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 15.93 min, t (major) = 22.97 min], 97:3 e.r.; $[\alpha]_D^{20}$ = -140.2 (c = 0.20, $CHCl_3$).



3bh

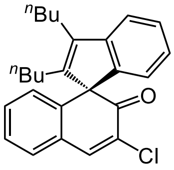
Pale yellow solid, m.p. = 174-176 °C, 60.6 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.49-7.42 (m, 2H), 7.39 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.31-7.27 (m, 3H), 7.22-7.07 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 7.6, 0.4 Hz, 1H), 6.79-6.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 162.4 (d, *J* = 246.4 Hz), 161.7 (d, *J* = 247.2 Hz), 146.7, 144.8, 143.8, 143.7, 143.4, 139.5, 131.2, 131.1, 130.8, 130.74, 130.68, 130.66, 130.3 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 3.4 Hz), 128.2, 128.1, 126.8, 121.9, 121.8, 116.0 (d, *J* = 21.3 Hz), 115.2 (d, *J* = 21.3 Hz), 72.8; ^{19}F NMR (376 Hz, $CDCl_3$) δ -113.1 (m), -113.5 (m); IR (thin film): ν_{max}(cm^{-1}) = 2987, 2901, 1675, 1601, 1499, 1451, 1065, 753; HRMS (ESI) calcd for $C_{30}H_{21}ClF_2NO$ [M + NH_4]$^+$: 484.1274; Found: 484.1274; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 13.42 min, t (major) = 16.97 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -189.5 (c = 1.00, $CHCl_3$).



3bi

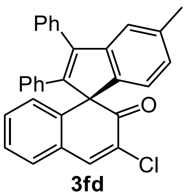
Pale yellow solid, m.p. = 145-147 °C, 61.2 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35-7.18 (m, 6H), 7.17-7.11 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 146.9, 145.5, 144.1, 144.0, 143.5, 138.9, 138.0, 137.2, 131.0, 130.7, 130.3, 129.79, 129.77, 129.5, 129.6, 128.5, 128.4, 127.5, 126.8, 126.1 (q, *J* = 3.7 Hz), 125.4, 125.2 (q, *J* = 3.8 Hz), 122.7, 122.5, 122.2, 122.0, 73.0; ^{19}F NMR (376 Hz, $CDCl_3$) δ -154.5, -154.8; IR (thin film): ν_{max}(cm^{-1}) = 2970, 2901, 1680, 1613, 1563, 1453, 1318, 1065, 753;

HRMS (ESI) calcd for $C_{32}H_{21}ClF_6NO$ $[M + NH_4]^+$: 584.1210; Found: 584.1208; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 15.16 min, t (major) = 21.53 min], 97:3 e.r.; $[\alpha]_D^{20}$ = -135.5 (c = 0.20, $CHCl_3$).



3bj

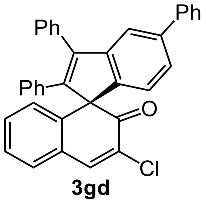
Yellow oil, 76.6 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.30-7.22 (m, 3H), 7.17-7.13 (m, 1H), 7.01-6.95 (m, 1H), 6.83 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 2.62 (t, J = 7.6 Hz, 2H), 2.29-2.22 (m, 1H), 2.09-1.99 (m, 1H), 1.74-1.58 (m, 2H), 1.54-1.41 (m, 2H), 1.22-1.02 (m, 4H), 0.98 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 148.0, 146.4, 146.1, 143.0, 142.6, 140.0, 130.9, 130.2, 129.7, 129.1, 127.64, 127.63, 127.2, 125.4, 121.7, 119.7, 72.0, 30.9, 27.0, 25.4, 23.0, 22.8, 14.1, 13.6; IR (thin film): ν_{max}(cm^{-1}) = 2955, 2930, 2859, 1677, 1610, 1559, 1465, 1227, 750; HRMS (ESI) calcd for $C_{26}H_{31}ClNO$ $[M + NH_4]^+$: 408.2089; Found: 408.2087; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 9.42 min, t (major) = 10.69 min], 92:8 e.r.; $[\alpha]_D^{20}$ = -116.9 (c = 1.00, $CHCl_3$).



3fd

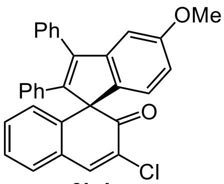
Yellow foam, m.p. = 86-87 °C, 68.5 mg, 77% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.54-7.47 (m, 2H), 7.45-7.33 (m, 4H), 7.24-7.20 (m, 1H), 7.15-7.12 (m, 1H), 7.08 (s, 1H), 7.01-6.93 (m, 4H), 6.91-6.85 (m, 2H), 6.81-6.79 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 145.4, 144.9, 144.5, 144.0, 143.2, 140.2, 138.0, 134.9, 133.9, 130.7, 130.6, 129.4, 129.3, 129.0, 128.9, 128.0, 127.9, 127.8, 127.3, 127.1, 126.7, 122.7, 121.3, 72.3, 21.5; IR (thin film): ν_{max}(cm^{-1}) = 3053, 3021, 2920, 1676, 1607, 1558, 1343, 1226, 745; HRMS (ESI) calcd for $C_{31}H_{25}ClNO$ [M +

$NH_4]^+$: 462.1619; Found: 462.1617; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 13.74 min, t (major) = 16.29 min], 92:8 e.r.; $[\alpha]_D^{20}$ = -159.3 (c = 0.20, $CHCl_3$).



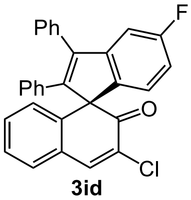
3gd

Yellow solid, m.p. = 227-229 °C, 87.4 mg, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.55-7.25 (m, 14H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09-6.97 (m, 5H), 6.82 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 145.9, 145.7, 145.0, 144.8, 143.4, 141.6, 141.1, 139.9, 134.7, 133.8, 130.8, 130.7, 129.5, 129.42, 129.40, 129.0, 128.9, 128.6, 128.04, 128.02, 127.98, 127.3, 126.9, 125.8, 121.8, 120.9, 72.5; IR (thin film): ν_{max}(cm^{-1}) = 2923, 1681, 1597, 1557, 1499, 1227, 751; HRMS (ESI) calcd for $C_{36}H_{27}ClNO$ $[M + NH_4]^+$: 524.1776; Found: 524.1774; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 9.05 min, t (major) = 10.12 min], 92:8 e.r.; $[\alpha]_D^{20}$ = -181.1 (c = 0.20, $CHCl_3$).



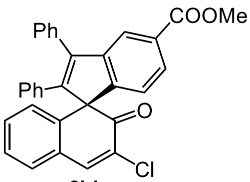
3hd

Yellow foam, m.p. = 76-78 °C, 75.8 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51-7.49 (m, 2H), 7.45-7.28 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.00-6.92 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.83-6.75 (m, 3H), 6.59 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 160.0, 146.8, 145.4, 144.6, 143.2, 140.2, 138.9, 134.7, 133.8, 130.7, 130.5, 129.4, 129.3, 128.9, 128.8, 127.9, 127.8, 127.2, 126.7, 122.2, 111.9, 108.0, 71.9, 55.4; IR (thin film): ν_{max}(cm^{-1}) = 3019, 1675, 1595, 1472, 1223, 746; HRMS (ESI) calcd for $C_{31}H_{25}ClNO_2$ $[M + NH_4]^+$: 478.1568; Found: 478.1567; [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 13.54 min, t (minor) = 17.43 min], 90:10 e.r.; $[\alpha]_D^{20}$ = -158.2 (c = 0.20, $CHCl_3$).



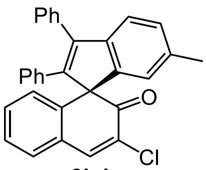
3id

Yellow solid, m.p. = 169-170 °C, 64.4 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.52-7.34 (m, 6H), 7.29-7.25 (m, 1H), 7.20-7.16 (m, 1H), 7.06-6.89 (m, 6H), 6.82-6.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 164.3, 161.9, 147.6 (d, *J* = 8.8 Hz), 146.4, 144.0 (d, *J* = 3.0 Hz), 143.4, 142.2 (d, *J* = 2.5 Hz), 139.5, 134.2, 133.5, 130.9, 130.6, 129.5, 129.4, 129.2, 129.0, 128.2, 128.09, 128.07, 127.5, 126.8, 122.8 (d, *J* = 9.2 Hz), 113.2 (d, *J* = 23.4 Hz), 109.3 (d, *J* = 23.2 Hz), 72.0; ^{19}F NMR (376 Hz, $CDCl_3$) δ -113.5 (m); IR (thin film): $\nu_{max}(cm^{-1})$ = 2987, 1672, 1594, 1558, 1487, 1464, 1138, 747; HRMS (ESI) calcd for $C_{30}H_{22}ClFNO$ $[M + NH_4]^+$: 466.1368; Found: 466.1365; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 7.83 min, t (major) = 8.91 min], 94:6 e.r.; $[\alpha]_D^{20}$ = -154.2 (c = 0.20, $CHCl_3$).



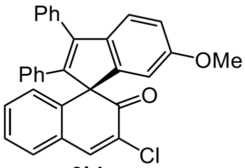
3jd

Yellow foam, m.p. = 94-95 °C, 70.0 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.51-7.39 (m, 6H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.11-6.96 (m, 4H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.80-6.78 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 166.7, 151.4, 145.8, 145.7, 144.2, 143.5, 138.9, 134.1, 133.5, 130.9, 130.6, 130.3, 129.6, 129.4, 129.3, 129.0, 128.96, 128.4, 128.3, 128.2, 128.1, 127.5, 126.8, 122.9, 121.7, 72.6, 52.1; IR (thin film): $\nu_{max}(cm^{-1})$ = 2988, 2917, 1718, 1676, 1436, 1344, 1286, 699; HRMS (ESI) calcd for $C_{32}H_{25}ClNO_3$ $[M + NH_4]^+$: 506.1517; Found: 506.1516; [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL ·min^{-1}, λ = 254 nm, t (major) = 11.00 min, t (minor) = 16.59 min], 91:9 e.r.; $[\alpha]_D^{20}$ = -132.3 (c = 1.00, $CHCl_3$).



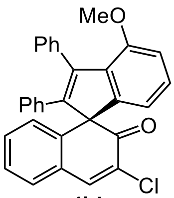
3kd

Yellow foam, m.p. = 99-100 °C, 72.3 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.50-7.48 (m, 2H), 7.44-7.33 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.19-7.11 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.01-6.91 (m, 4H), 6.80-6.78 (m, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 147.1, 144.8, 143.5, 143.3, 142.6, 140.2, 136.6, 135.0, 134.0, 130.8, 130.7, 129.4, 129.35, 129.33, 128.9, 128.82, 128.76, 128.0, 127.9, 127.8, 127.0, 126.9, 122.3, 121.8, 72.5, 21.4; IR (thin film): ν_{max}(cm^{-1}) = 3021, 2919, 1676, 1608, 1558, 1486, 1227, 823, 743; HRMS (ESI) calcd for $C_{31}H_{25}ClNO$ [M + NH_4]$^+$: 462.1619; Found: 462.1617; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 9.46 min, t (major) = 19.64 min], 93:7 e.r.; $[\alpha]_D^{20}$ = -155.2 (c = 0.20, $CHCl_3$).



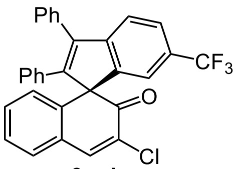
3ld

Yellow solid, m.p. = 176-177 °C, 74.1 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.50-7.35 (m, 6H), 7.31-7.10 (m, 3H), 6.99-6.96 (m, 4H), 6.78-6.76 (m, 3H), 6.58 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 158.8, 148.4, 144.4, 143.3, 142.5, 140.2, 138.1, 135.0, 134.0, 130.8, 130.6, 129.4, 129.3, 128.81, 128.76, 128.0, 127.90, 127.86, 126.94, 126.89, 122.6, 112.6, 108.9, 72.4, 55.5; IR (thin film): ν_{max}(cm^{-1}) = 2934, 1672, 1593, 1577, 1477, 1029, 701; HRMS (ESI) calcd for $C_{31}H_{25}ClNO_2$ [M + NH_4]$^+$: 478.1568; Found: 478.1566; [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 25.29 min, t (minor) = 28.26 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -156.5 (c = 0.20, $CHCl_3$).



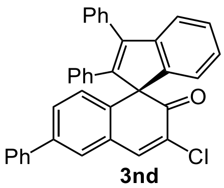
4ld

Yellow solid, m.p. = 187-189 °C, 7.1 mg, 8% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.47-7.45 (m, 2H), 7.37-7.30 (m, 4H), 7.23-7.15 (m, 2H), 7.07-7.01 (m, 2H), 6.98-6.89 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.69-6.68 (m, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 3.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.3, 155.0, 148.7, 144.9, 143.9, 143.2, 140.1, 136.7, 134.2, 132.3, 130.8, 130.7, 129.8, 129.5, 129.3, 129.1, 128.1, 127.9, 127.8, 127.5, 127.1, 127.0, 126.8, 114.6, 111.9, 72.7, 55.5; IR (thin film): ν_{max}(cm^{-1}) = 2919, 2850, 1672, 1592, 1475, 1346, 1263, 1065, 747; HRMS (ESI) calcd for $C_{31}H_{25}ClNO_2$ [M + NH_4]$^+$: 478.1568; Found: 478.1566; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 25.67 min, t (major) = 31.16 min], 97:3 e.r.; $[\alpha]_D^{20}$ = -108.8 (c = 0.10, $CHCl_3$).



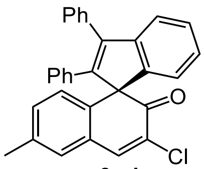
3md

Pale brown solid, m.p. = 179-180 °C, 32.8 mg, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.50-7.36 (m, 7H), 7.34-7.30 (m, 1H), 7.24-7.17 (m, 2H), 7.06-6.98 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.81-6.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 149.0, 147.6, 147.3, 143.8, 143.7, 138.5, 134.0, 133.2, 131.0, 130.6, 129.8, 129.5, 129.3, 129.0, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 126.9, 125.7 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.9 Hz), 122.0, 118.6 (q, *J* = 3.7 Hz), 72.5; ^{19}F NMR (376 Hz, $CDCl_3$) δ -61.6; IR (thin film): ν_{max}(cm^{-1}) = 2922, 1676, 1611, 1562, 1486, 1319, 1123, 698; HRMS (ESI) calcd for $C_{31}H_{22}ClF_3NO$ [M + NH_4]$^+$: 516.1337; Found: 516.1335; [Phenomenex Lux 5u Amylose-2 PA-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 8.48 min, t (major) = 11.14 min], 93:7 e.r.; $[\alpha]_D^{20}$ = -109.1 (c = 0.20, $CHCl_3$).



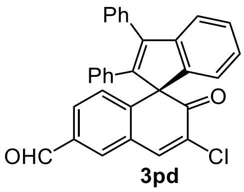
3nd

Yellow solid, m.p. = 205-206 °C, 83.5 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.63-7.47 (m, 5H), 7.47-7.17 (m, 9H), 7.16-6.92 (m, 6H), 6.91-6.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 146.7, 145.2, 144.9, 144.2, 143.3, 140.8, 139.3, 138.7, 134.7, 133.9, 131.1, 129.8, 129.4, 129.0, 128.9, 128.8, 128.13, 128.06, 128.0, 127.9, 127.8, 127.3, 127.2, 126.8, 126.6, 122.1, 121.6, 72.5; IR (thin film): ν_{max}(cm^{-1}) = 3028, 1681, 1596, 1553, 1484, 753; HRMS (ESI) calcd for $C_{36}H_{27}ClNO$ $[M + NH_4]^+$: 524.1776; Found: 524.1772; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 20.57 min, t (major) = 28.33 min], 97:3 e.r.; $[\alpha]_D^{20}$ = -154.0 (c = 0.20, $CHCl_3$).



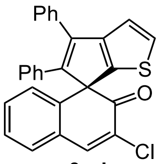
3od

Yellow foam, m.p. = 73-74 °C, 57.7 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.56-7.33 (m, 5H), 7.32-7.15 (m, 3H), 7.12-6.92 (m, 6H), 6.94-6.76 (m, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 147.0, 145.2, 144.8, 144.4, 143.5, 137.7, 136.9, 134.9, 133.9, 131.7, 130.6, 130.0, 129.4, 129.3, 129.0, 128.8, 128.0, 127.9, 127.1, 126.7, 126.5, 122.0, 121.5, 72.4, 20.9; IR (thin film): ν_{max}(cm^{-1}) = 2993, 2849, 1677, 1598, 1558, 1488, 755, 699; HRMS (ESI) calcd for $C_{31}H_{25}ClNO$ $[M + NH_4]^+$: 462.1619; Found: 462.1617; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 16.28 min, t (major) = 19.86 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -181.1 (c = 1.00, $CHCl_3$).



3pd

Yellow foam, m.p. = 94-96 °C, 63.3 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.94-7.90 (m, 2H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.57-7.36 (m, 5H), 7.34-7.25 (m, 2H), 7.14-6.94 (m, 6H), 6.80-6.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 188.4, 146.5, 145.8, 145.4, 145.3, 143.7, 141.8, 135.9, 134.4, 133.4, 132.3, 131.4, 130.1, 130.0, 129.3, 128.9, 128.8, 128.5, 128.20, 128.17, 127.7, 127.5, 126.8, 122.4, 121.6, 72.7; IR (thin film): ν_{max}(cm^{-1}) = 2987, 2924, 1681, 1609, 1488, 1151, 756, 699; HRMS (ESI) calcd for $C_{31}H_{23}ClNO_2$ [M + NH_4]$^+$: 476.1412; Found: 476.1408; [Daicel Chiralpak AD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 15.57 min, t (minor) = 17.47 min], 95:5 e.r.; $[\alpha]_D^{20}$ = -157.8 (c = 1.00, $CHCl_3$).

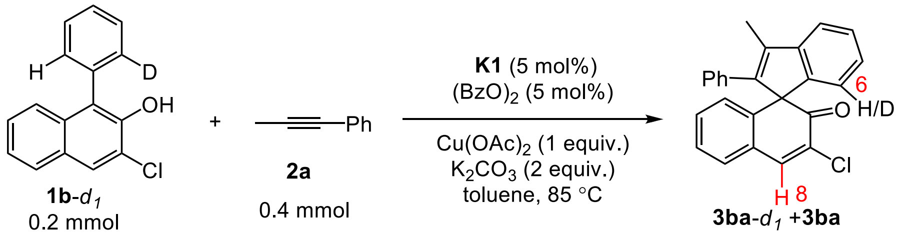


3qd

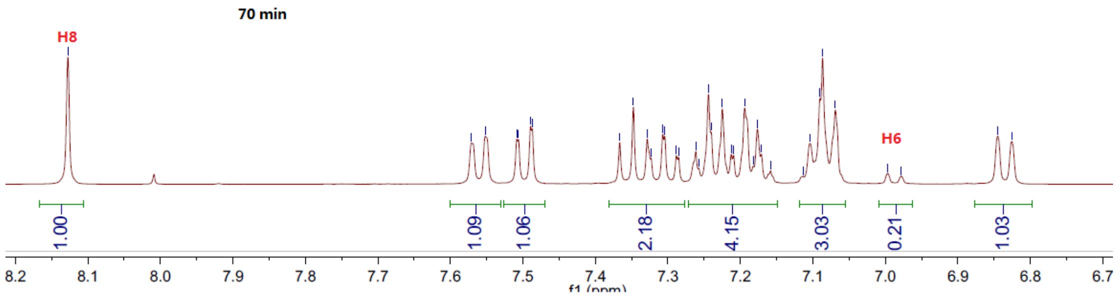
Yellow foam, m.p. = 188-189 °C, 9.5 mg, 11% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.45-7.43 (m, 2H), 7.36 (d, J = 5.2 Hz, 1H), 7.33-7.24 (m, 6H), 7.13-7.06 (m, 2H), 7.04-6.99 (m, 3H), 6.73-6.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 151.6, 148.2, 145.9, 142.8, 139.9, 138.8, 134.6, 134.4, 130.7, 130.5, 129.7, 129.4, 129.1, 129.0, 128.8, 128.4, 128.2, 128.0, 127.98, 127.4, 127.2, 120.1, 70.8; IR (thin film): ν_{max}(cm^{-1}) = 2988, 2969, 2922, 1678, 1611, 1593, 1227, 696; HRMS (ESI) calcd for $C_{28}H_{18}ClOS$ [M + H]$^+$: 437.0761; Found: 437.0754; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 11.12 min, t (major) = 14.30 min], 95:5 e.r.; $[\alpha]_D^{20}$ = -18.1 (c = 0.20, $CHCl_3$).

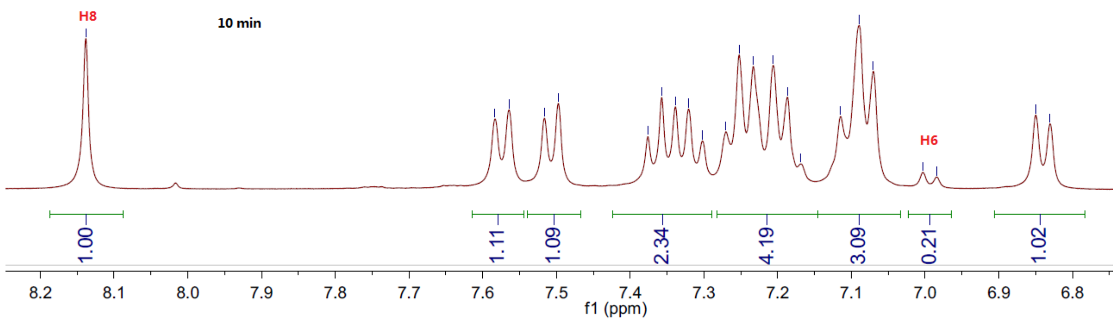
Deuterium-labeling Experiments:

a) Intramolecular kinetic isotope effect experiment.

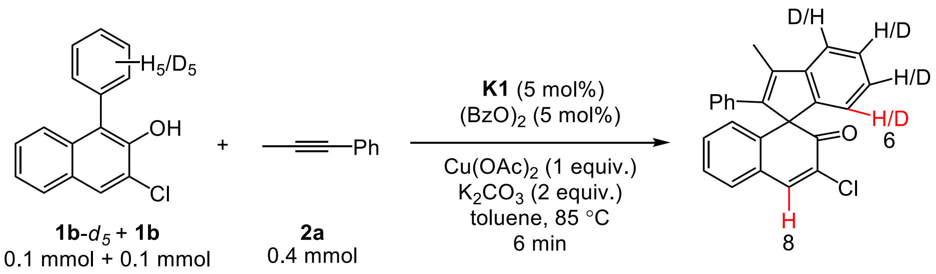


To a Schlenk tube were added **K1** (10 μmol, 5.6 mg), $(BzO)_2$ (10 μmol, 2.4 mg) and toluene (1 mL) successively. After the mixture was stirred at room temperature for 30 min, **1b-*d₁*** (51.1 mg, 0.2 mmol), $Cu(OAc)_2$ (36.4 mg, 0.2 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), **2a** (46.5 mg, 0.4 mmol) and toluene (1 mL) were added successively. The mixture was stirred at 85 °C under air (open flask). After 70 min and 10 min respectively, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/50, v/v) to afford a mixture of **3ba** and **3ba-d_1** in 63% yield (46.5 mg) and 32% yield (23.9 mg), respectively. The KIE value (approx 3.8) was obtained by integrating the H8 of the spiro **3ba** and the H6 of the spiro **3ba** and **3ba-d_1**.

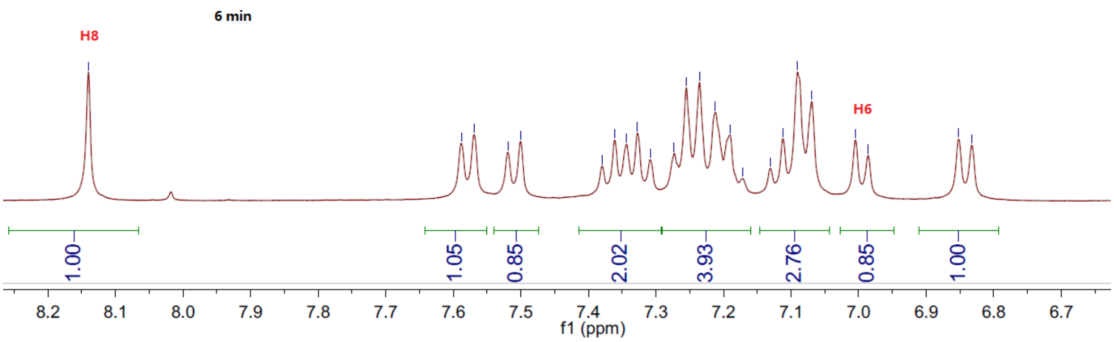




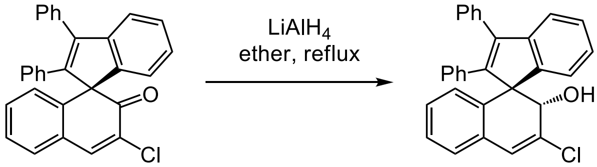
b) Intermolecular kinetic isotope effect experiment.



To a Schlenk tube were added **K1** (10 μmol, 5.6 mg), $(BzO)_2$ (10 μmol, 2.4 mg) and toluene (1 mL) successively. After the mixture was stirred at room temperature for 30 min, **1b** (25.5 mg, 0.1 mmol), **1b-*d*₅** (26.0 mg, 0.1 mmol), $Cu(OAc)_2$ (36.4 mg, 0.2 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), **2a** (46.5 mg, 0.4 mmol) and toluene (1 mL) were added successively. The mixture was stirred at 85 °C under air (open flask). After 6 min, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/50, v/v) to afford a mixture of **3ba** and **3ba-d_5** in 21% yield (16.0 mg). The KIE value (approx 5.7) was obtained by integrating the H8 of the spiro **3ba** and the H6 of the spiro **3ba** and **3ba-d_5**. The ratio between **3ba** and **3ba-d_5** was also determined to be 6.5 by the analysis of HRMS.



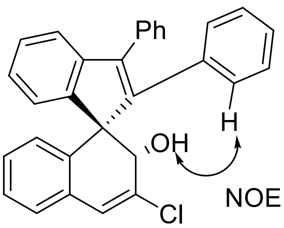
Procedure for the Synthesis of Alcohol 5bd:



3bd, 95:5 e.r. **5bd**, 97% yield > 19:1 dr 95:5 e.r.

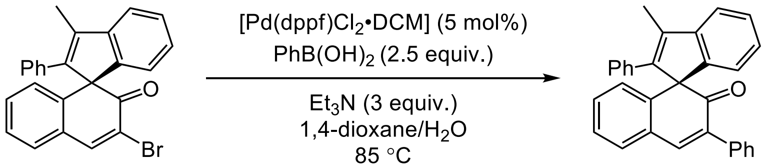
To a stirred mixture of lithium aluminum hydride (3.8 mg, 0.1 mmol) in anhydrous diethyl ether (1 mL) at 0 ℃ was added **3bd** (43.1 mg, 0.1 mmol). The mixture was refluxed for 10 min, then cold to 0 ℃, and treated successively with water (4 μL), 15% NaOH aqueous solution (8 μL), and water (12 μL). After stirring for 20 min, Na_2SO_4 was added and the slurry was filtered through celite. After concentration under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/15, v/v) to afford **5bd** (41.8 mg, 97% yield). **5bd**, colorless foam, m.p. = 63-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.18 (m, 10H), 7.10-7.05 (m, 2H), 7.02-6.99 (m, 2H), 6.93 (d, J = 7.2 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 7.6 Hz, 2H), 6.17 (d, J = 1.6 Hz, 1H), 5.18 (d, J = 2.4 Hz, 1H), 1.98 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.0, 145.5, 141.0, 136.1, 134.8, 134.18, 134.15, 134.1, 129.5, 125.4, 128.2, 128.05, 127.99, 127.9, 127.2, 127.1, 126.9, 126.6, 126.55, 126.53, 125.5, 123.0, 121.0, 74.0, 66.4; IR (thin film): ν_{max}(cm^{-1}) = 3540, 3055, 3024, 2923, 1634, 1597, 1096, 741, 698; HRMS (ESI) calcd for $C_{30}H_{21}ClO$ $[M]^+$: 432.1281; Found: 432.1276; [Daicel Chiralpak AD-H (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 17.30 min, t (major) = 21.22 min], 95:5 e.r.; $[\alpha]_D^{20}$ = -46.2 (c = 0.16, $CHCl_3$).

Assignment of the structure.



The structure was assigned based on the HMBC, COSY, ^{13}C NMR experiments, as well as by the observation of noe between the alcohol hydrogen and the benzene hydrogen of the spiro unit.

Procedure for the Synthesis of Compound 5aa:



3aa, 96:4 e.r. **5aa**, 99% yield 96:4 e.r.

A flame-dried sealed tube was cooled to room temperature and filled with argon. To this tube were added **3aa** (41.3 mg, 0.1 mmol, 96:4 e.r.), Pd(dppf)Cl_2•DCM (4.1 mg, 0.005 mmol, 5 mol%), PhB$(OH)_2$ (30.5 mg, 0.25 mmol), and Et_3N (30.4 mg, 0.3 mmol). The tube was evacuated and refilled with argon and placed under an argon atmosphere. To this mixture were added freshly distilled dioxane (1.0 mL) and deionized water (0.1 mL). After the reaction flask was degassed twice, the reaction mixture was stirred at 80 ℃. After the reaction was complete (monitored by TLC), the solvents were removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 40/1, v/v) to afford the desired product **5aa** (41.0 mg, 99% yield). **5aa**, light yellow solid, m.p. = 159-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.44-7.38 (m, 4H), 7.36-7.26 (m, 4H), 7.26-7.06 (m, 9H), 6.86 (d, J = 7.2 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 147.0, 146.3, 144.1, 143.0, 140.6, 139.7, 136.8, 135.6, 135.2, 130.6, 130.0, 129.8, 128.9, 128.5, 128.1, 128.07, 127.8, 127.6, 127.0, 126.8, 126.2, 121.4, 120.6, 73.0, 12.4; IR (thin film): ν_{max}(cm^{-1}) = 3055, 3020, 1660, 1597, 1492, 1466, 817, 694; HRMS (ESI) calcd for $C_{31}H_{23}O$ $[M+H]^+$: 411.1743; Found: 411.1749; [Phenomenex Lux 5u Celluloxe-4 PC-4 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.33 min, t (minor) = 15.43 min], 96:4 e.r.; $[\alpha]_D^{20}$ = -517.8 (c = 1.00, $CHCl_3$).

References:

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2. Truong, T.; Daugulis, O. *Chem. Sci.* **2013**, *4*, 531.
3. Wender, P. A.; Deschamps, N. M.; Williams, T. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3076.
4. Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*. **2002**, *4*, 3199.
5. T. Oguma, T. Katsuki, *J. Am. Chem. Soc.* **2012**, *134*, 20017.
6. Nan, J.; Zuo, Z.; Luo, L.; Bai, L.; Zheng, H.; Yuan, Y.; Liu, J.; Luan, X.; Wang, Y. *J. Am. Chem. Soc.* **2013**, *135*, 17306.

X-ray crystal structure of **3aa** (CCDC 1049299)

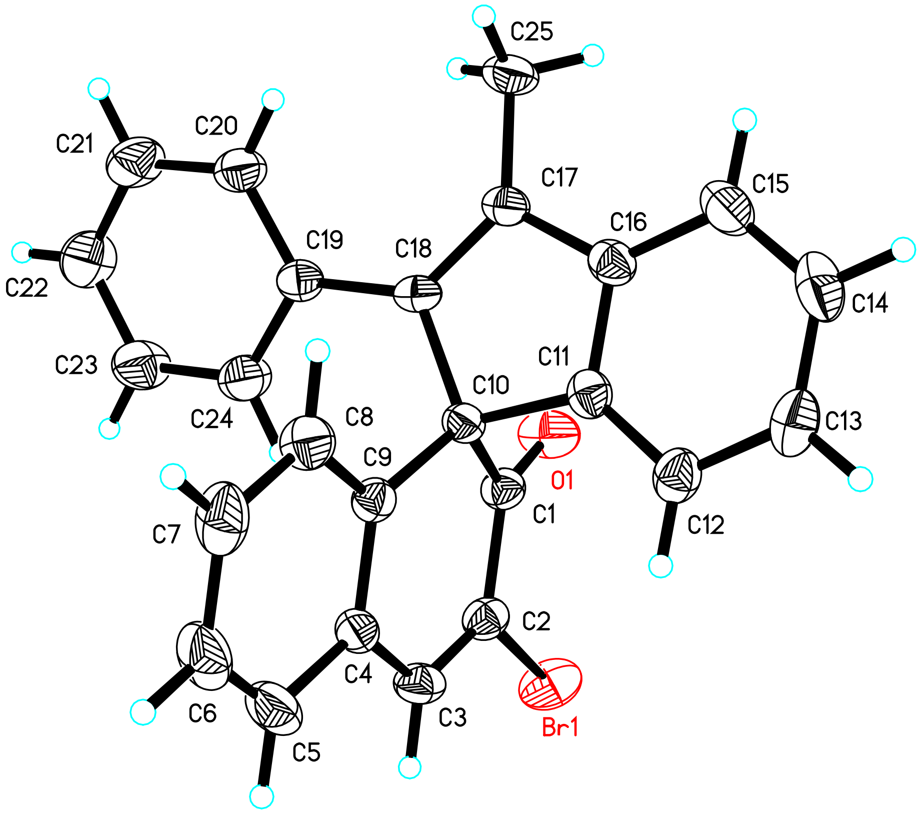
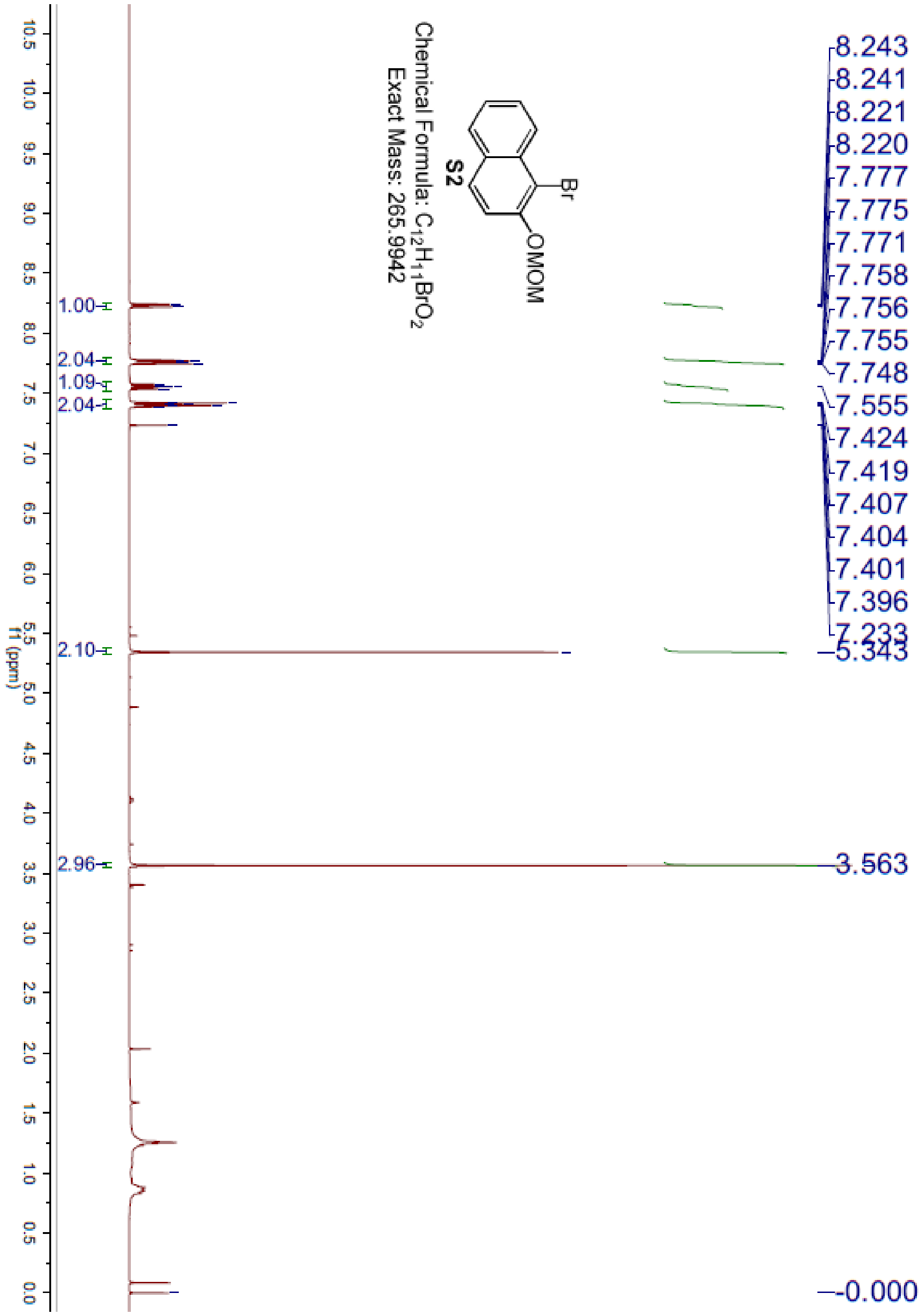


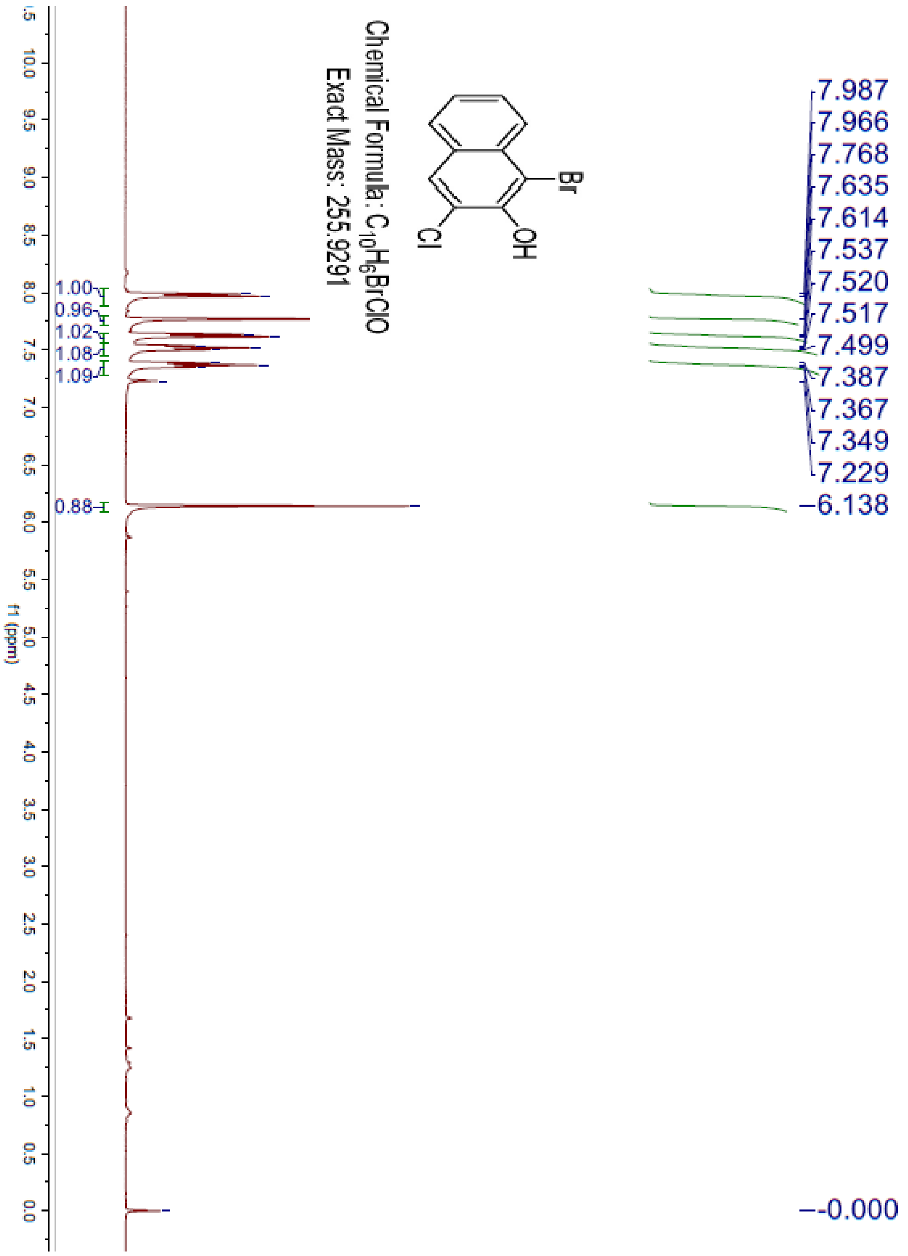
Table 1. Crystal data and structure refinement for cd214620.

Identification code	cd214620	
Empirical formula	C25 H17 Br O	
Formula weight	413.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 14.7015(17) Å	a= 90°.
	b = 8.9613(10) Å	b= 114.880(2)°.
	c = 15.8849(18) Å	g = 90°.
Volume	1898.5(4) $Å^3$	
Z	4	
Density (calculated)	1.446 Mg/m^3	

Absorption coefficient	2.177 mm^{-1}
F(000)	840
Crystal size	0.211 x 0.134 x 0.112 mm^3
Theta range for data collection	2.479 to 25.999 °.
Index ranges	-16<=h<=18, -11<=k<=9, -19<=l<=18
Reflections collected	11507
Independent reflections	6635 [R(int) = 0.0263]
Completeness to theta = 25.242 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5664
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6635 / 1 / 489
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0945
R indices (all data)	R1 = 0.0515, wR2 = 0.0995
Absolute structure parameter	0.006(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.790 and -0.481 e.$Å^{-3}$

Copies of NMR Spectra and HPLC Chromatographs





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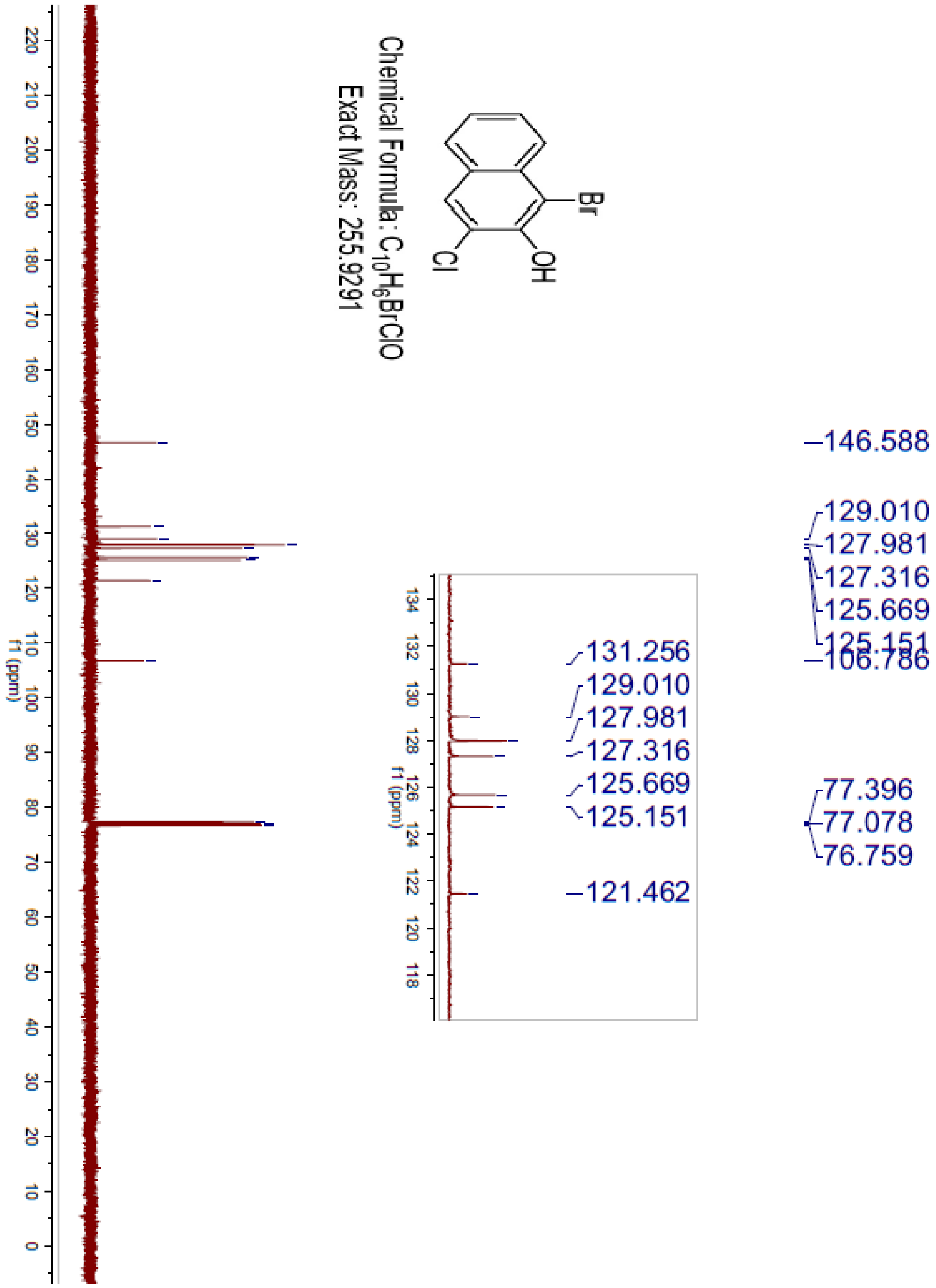
7.520
7.517
7.499
7.387
7.367
7.349
7.229
6.138
-0.000
1.00
0.96
1.02
1.08
1.09
0.88
f1 (ppm)


Br
OH
Cl
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125.151
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77.396
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129.010
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127.316
125.669
125.151
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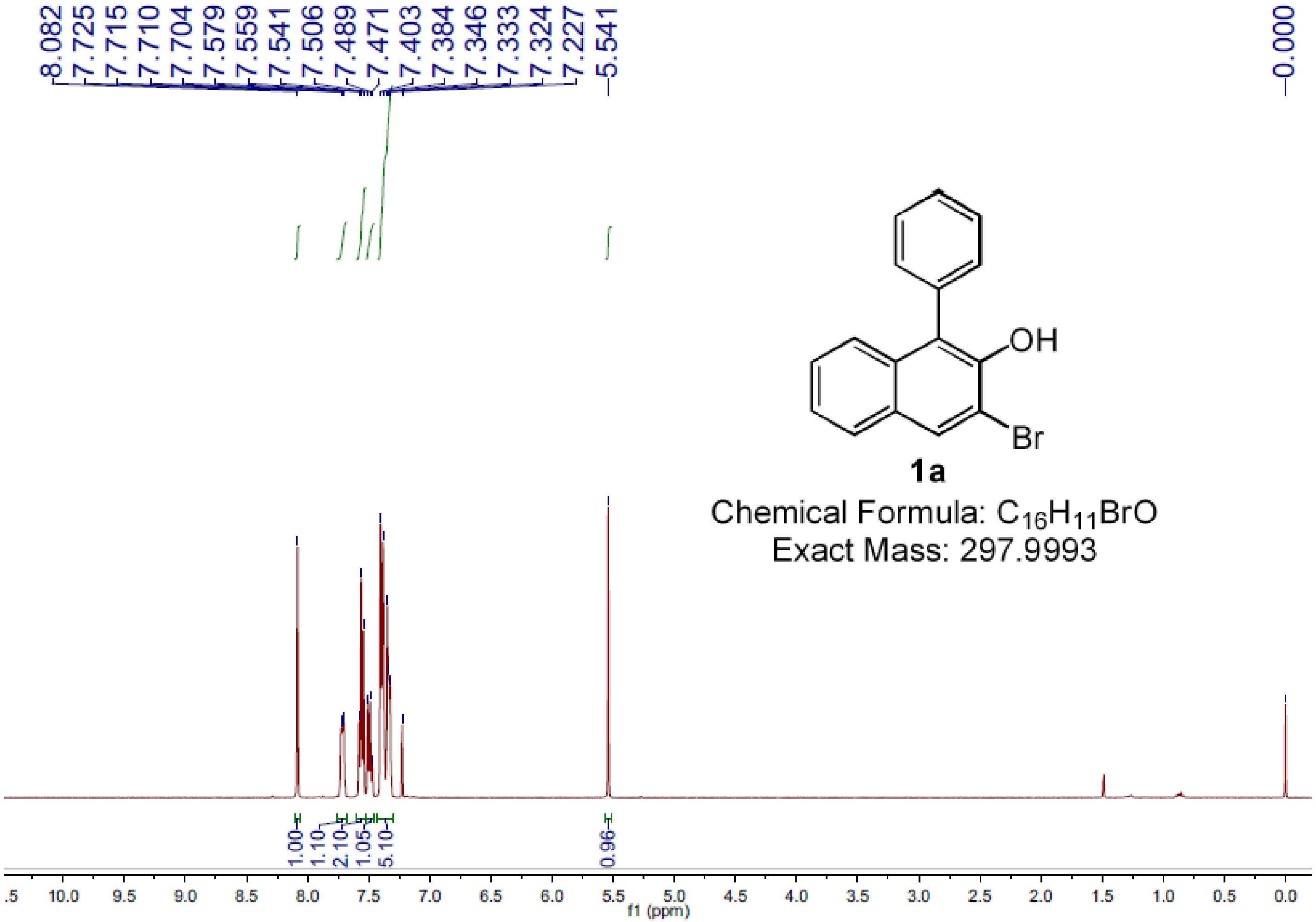
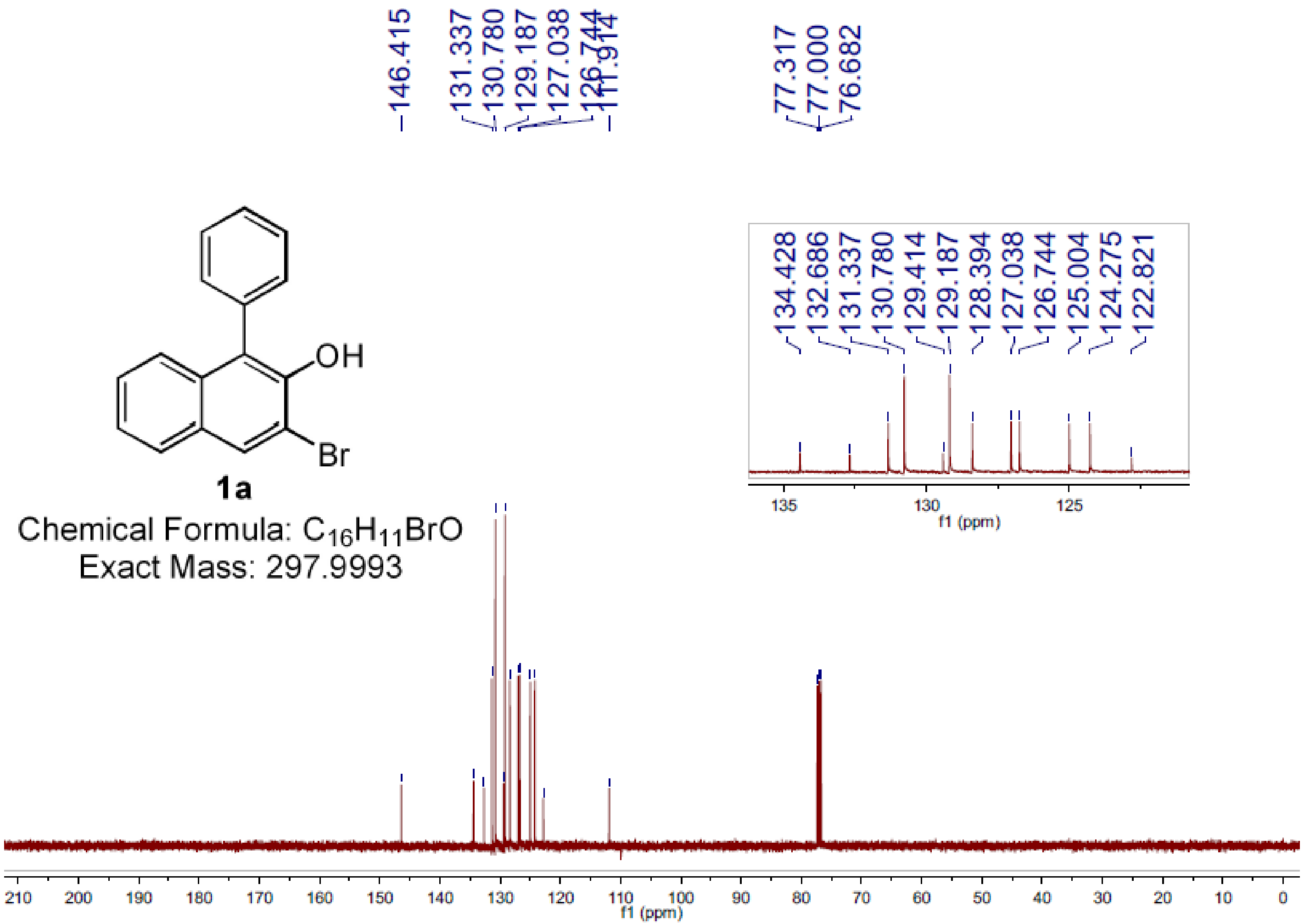
f1 (ppm)
f1 (ppm)



1a

Chemical Formula: $C_{16}H_{11}BrO$

Exact Mass: 297.9993



1a
Chemical Formula: C16H11BrO
Exact Mass: 297.9993
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111.914
77.317
77.000
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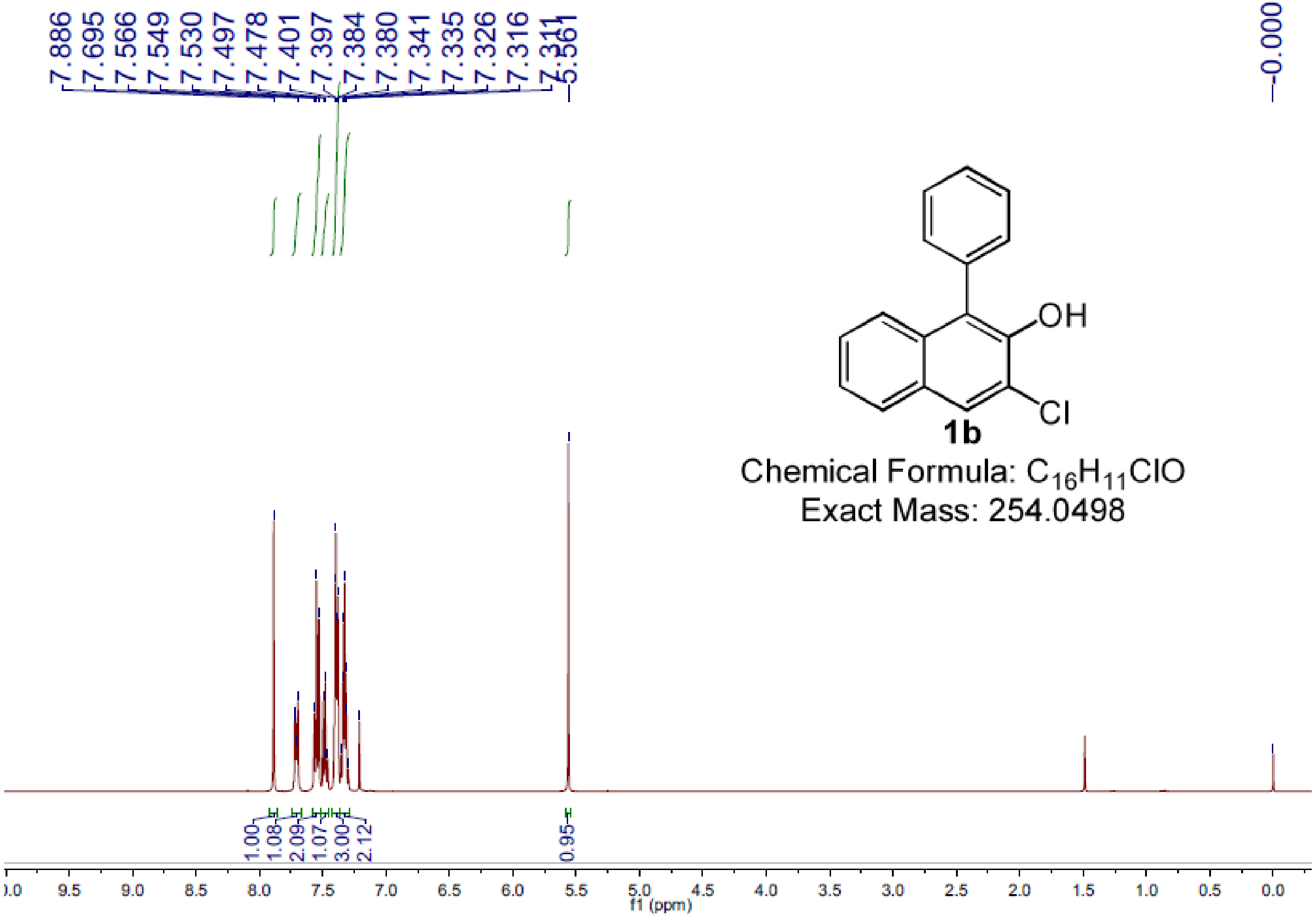
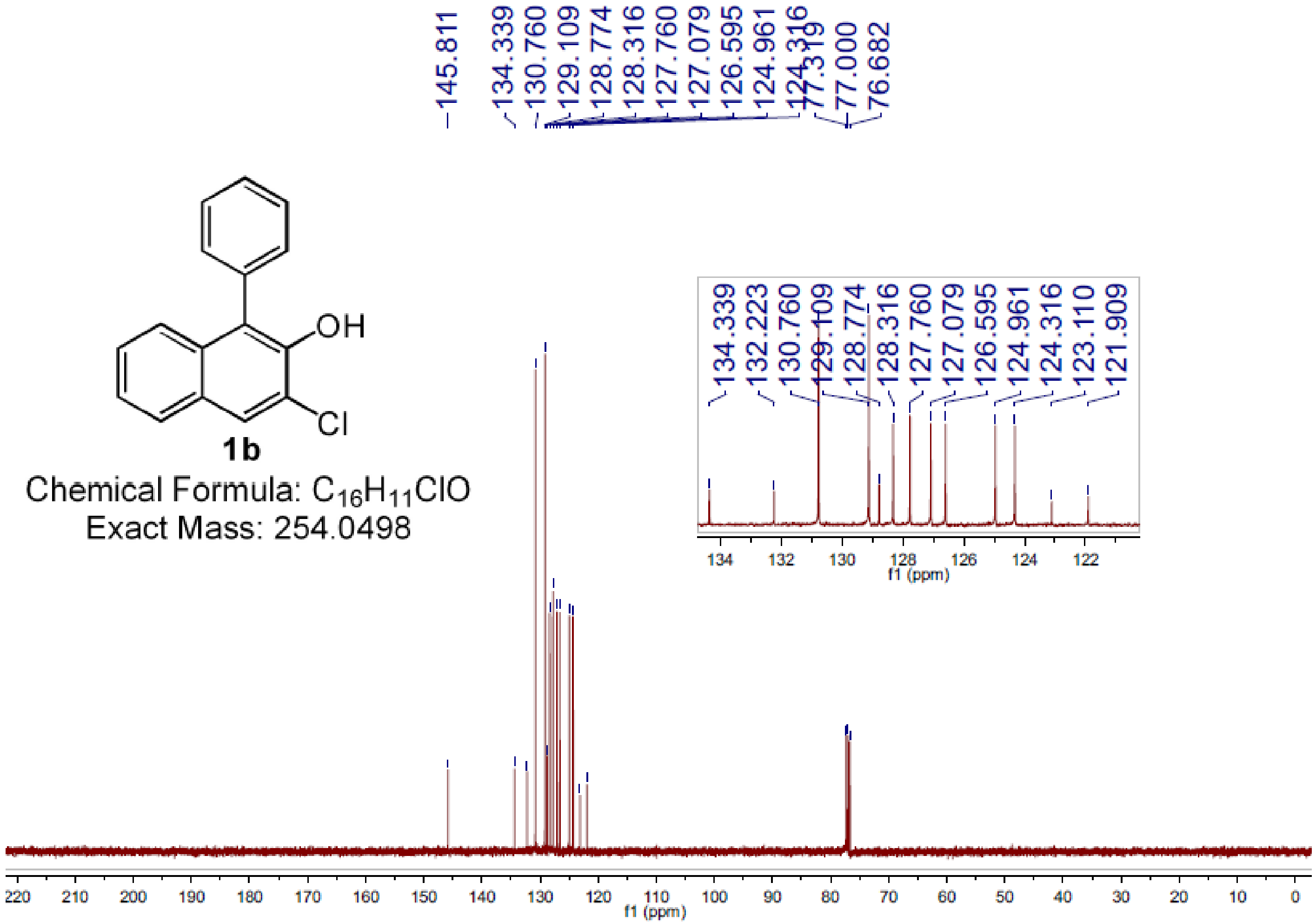
129.414
129.187
128.394
127.038
126.744
125.004
124.275
122.821
135
130
125
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

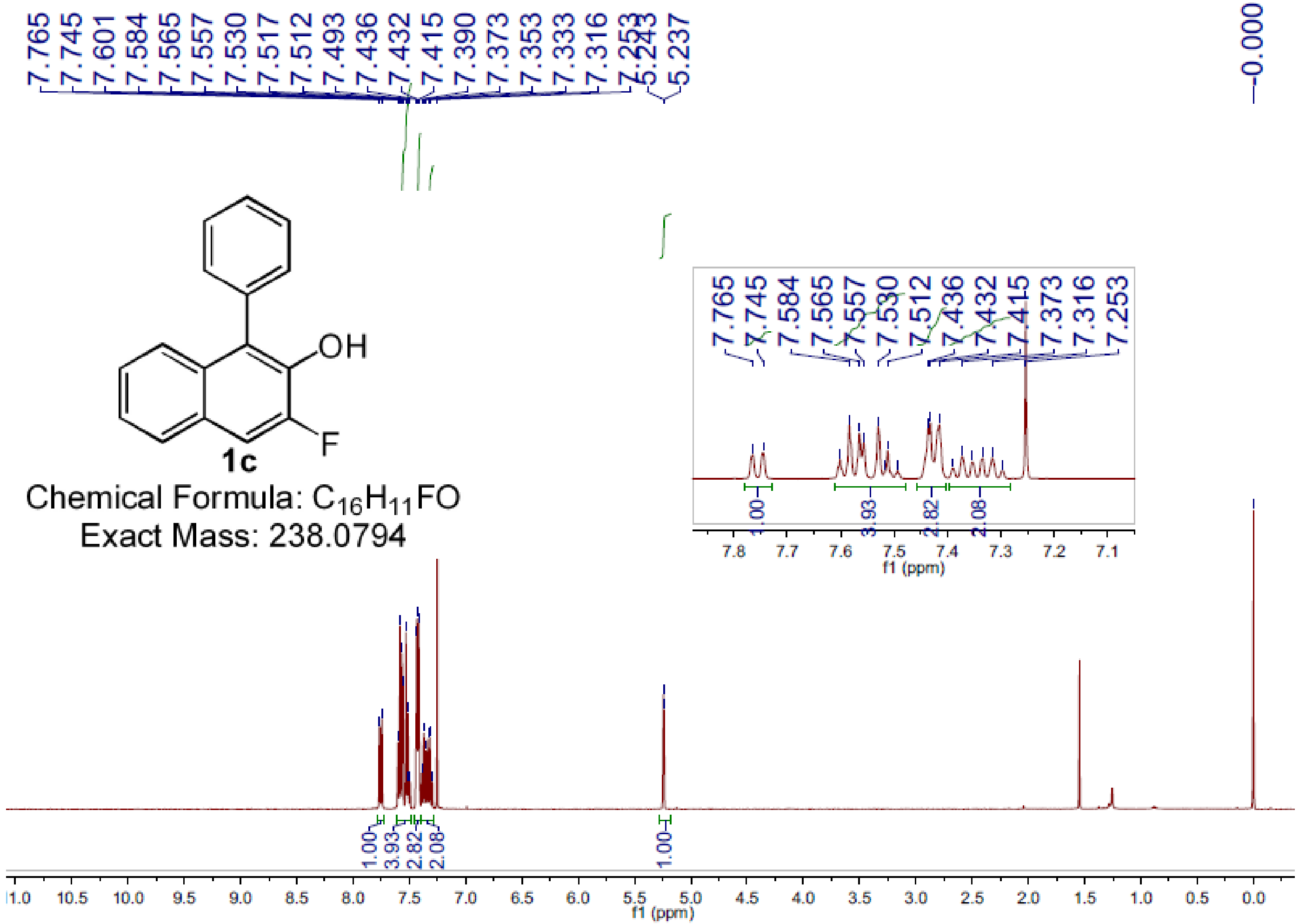

7.886
7.695
7.566
7.549
7.530
7.497
7.478
7.401
7.397
7.384
7.380
7.341
7.335
7.326
7.316
7.311
5.561
-0.000
OH
Cl
1b
Chemical Formula: C16H11ClO
Exact Mass: 254.0498
1.00
1.08
2.09
1.07
3.00
2.12
0.95
f1 (ppm)

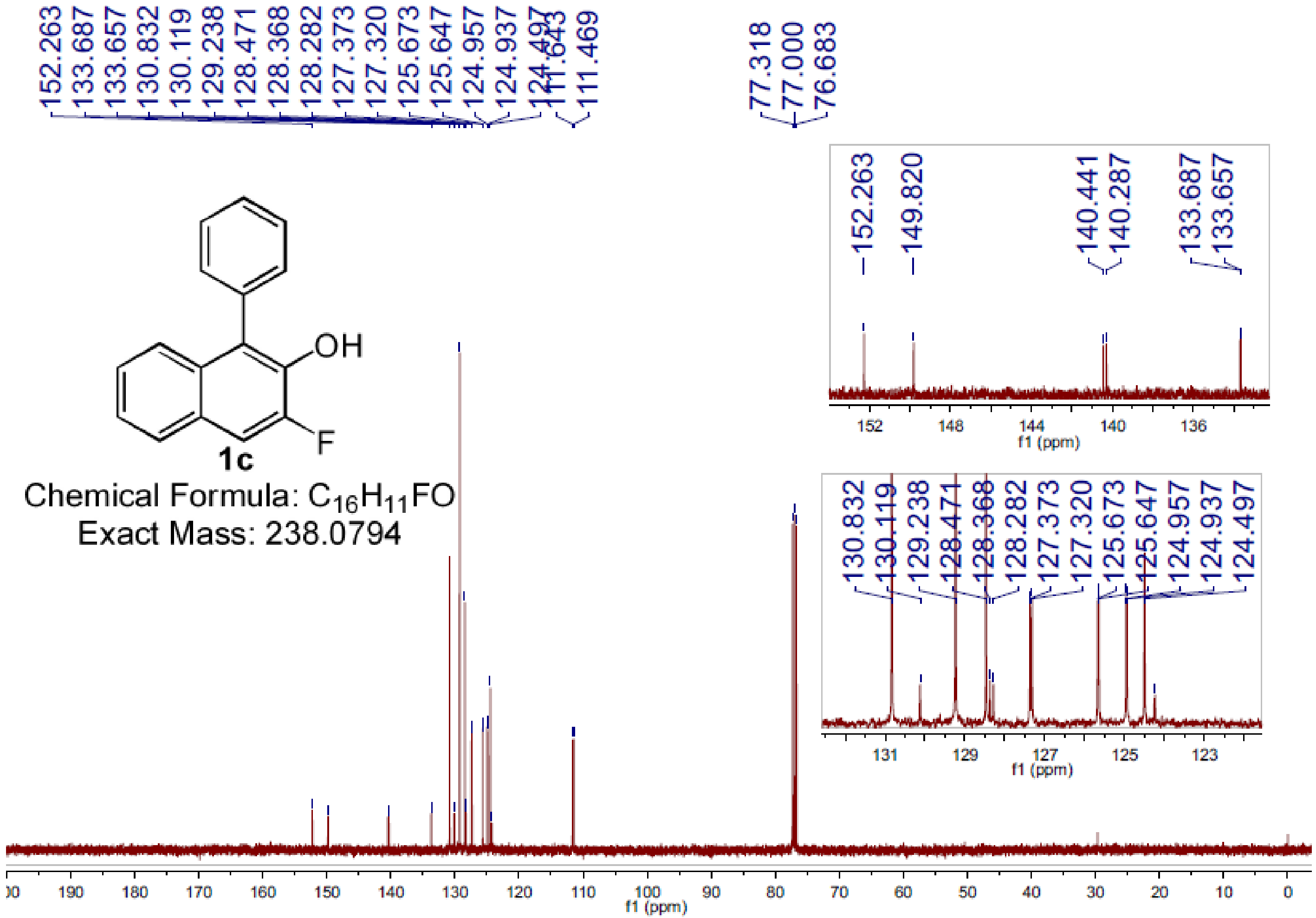


1b

Chemical Formula: $C_{16}H_{11}ClO$

Exact Mass: 254.0498

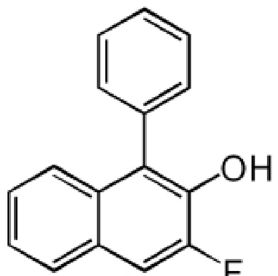

7.765 7.745 7.601 7.584 7.565 7.557 7.530 7.517 7.512 7.493 7.436 7.432 7.415 7.390 7.373 7.353 7.333 7.316 7.253 5.243 5.237
-0.000
OH
F
1c
Chemical Formula: C16H11FO
Exact Mass: 238.0794
7.765 7.745 7.584 7.565 7.557 7.530 7.512 7.436 7.432 7.415 7.373 7.316 7.253
1.00 3.93 2.82 2.08
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.00 3.93 2.82 2.08 1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



1c

Chemical Formula: $C_{16}H_{11}FO$

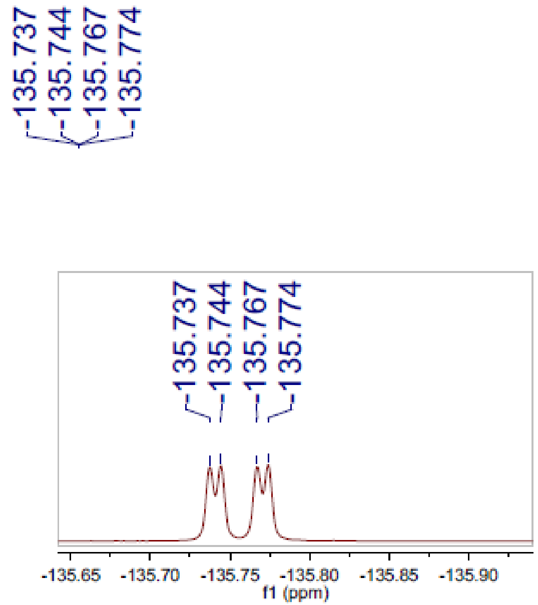
Exact Mass: 238.0794

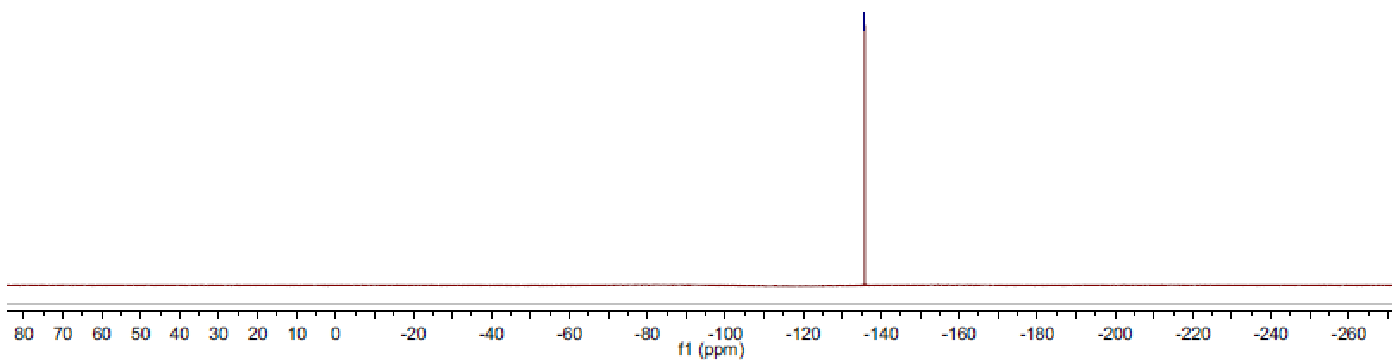


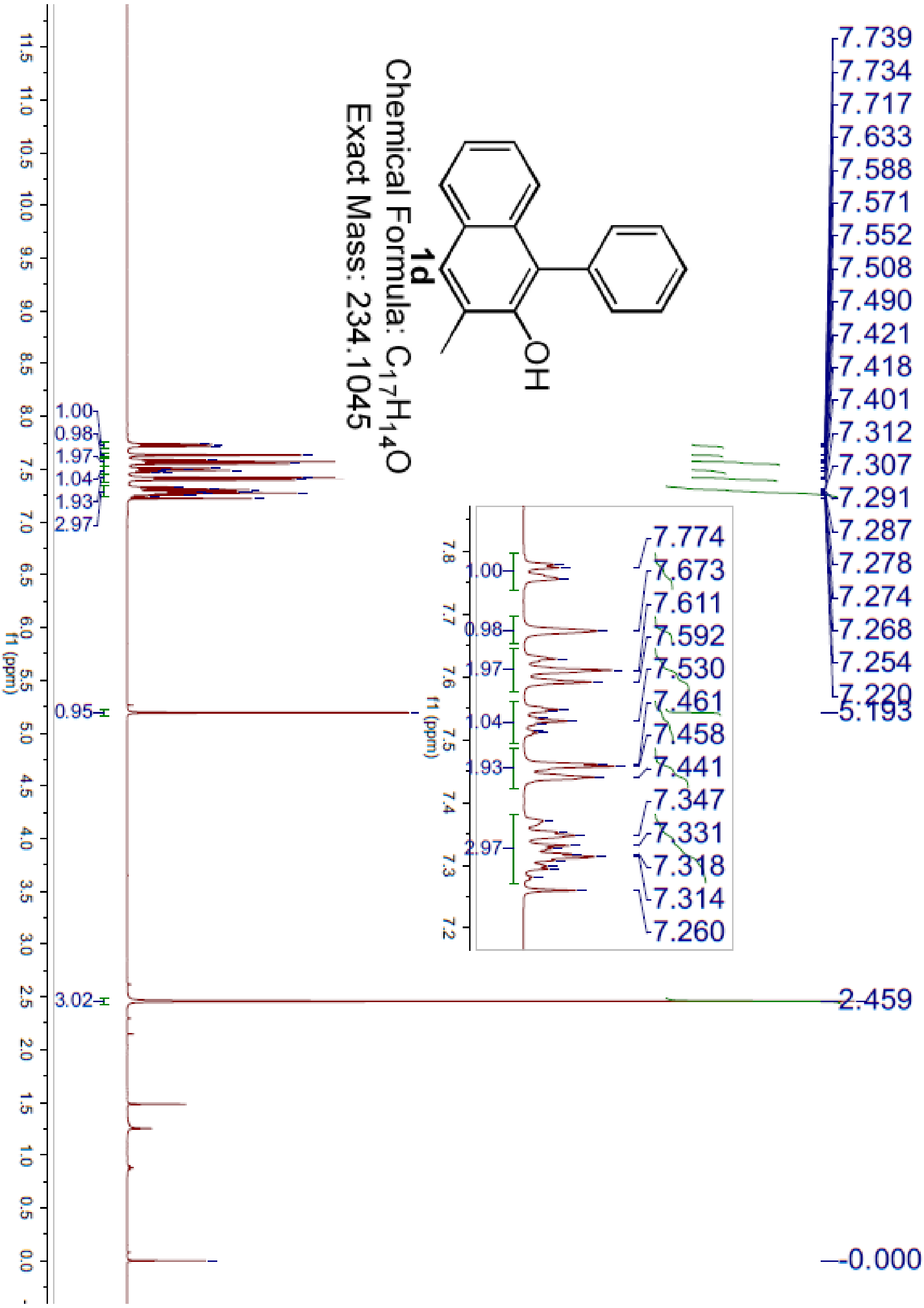
1c

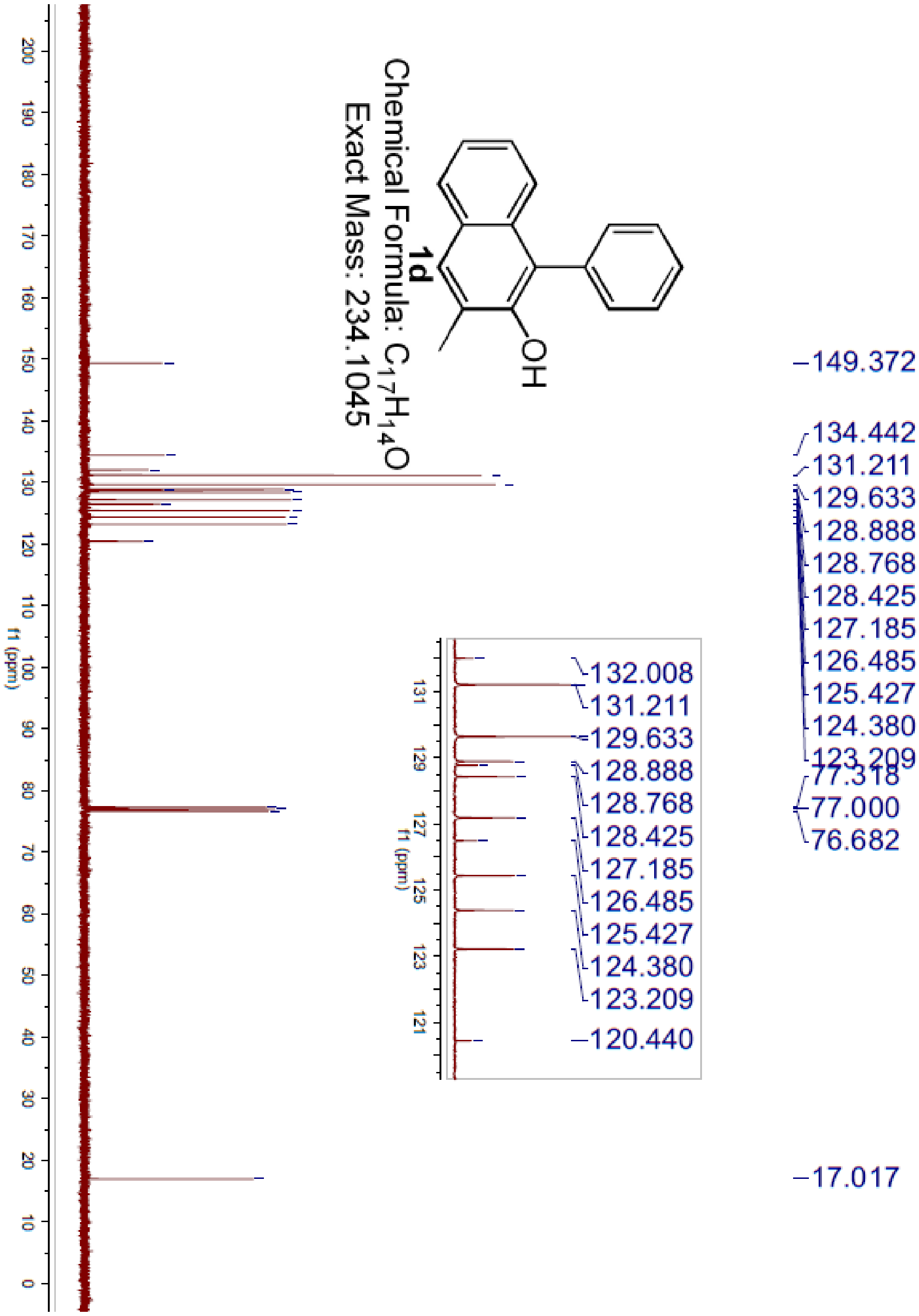
Chemical Formula: $C_{16}H_{11}FO$

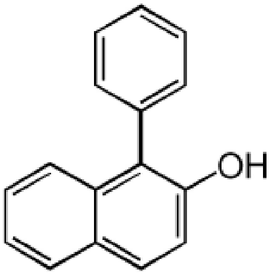
Exact Mass: 238.0794






1d
Chemical Formula: C17H14O
Exact Mass: 234.1045
OH
7.739
7.734
7.717
7.633
7.588
7.571
7.552
7.508
7.490
7.421
7.418
7.401
7.312
7.307
7.291
7.287
7.278
7.274
7.268
7.254
7.220
5.193
2.459
0.000
7.774
7.673
7.611
7.592
7.530
7.461
7.458
7.441
7.347
7.331
7.318
7.314
7.260
1.00
0.98
1.97
1.04
1.93
2.97
0.95
3.02
f1 (ppm)

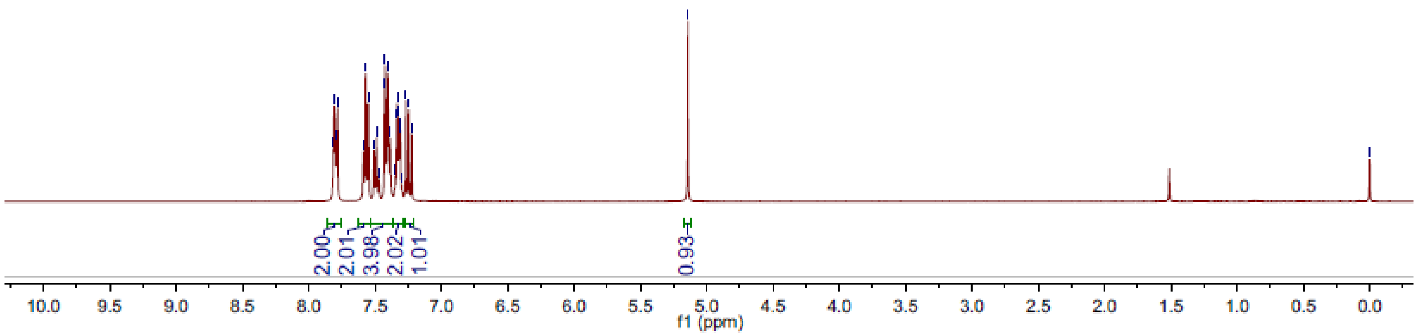

1d
Chemical Formula: C17H14O
Exact Mass: 234.1045
OH
149.372
134.442
131.211
129.633
128.888
128.768
128.425
127.185
126.485
125.427
124.380
123.209
77.318
77.000
76.682
17.017
132.008
131.211
129.633
128.888
128.768
128.425
127.185
126.485
125.427
124.380
123.209
120.440
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
131 129 127 125 123 121
f1 (ppm)

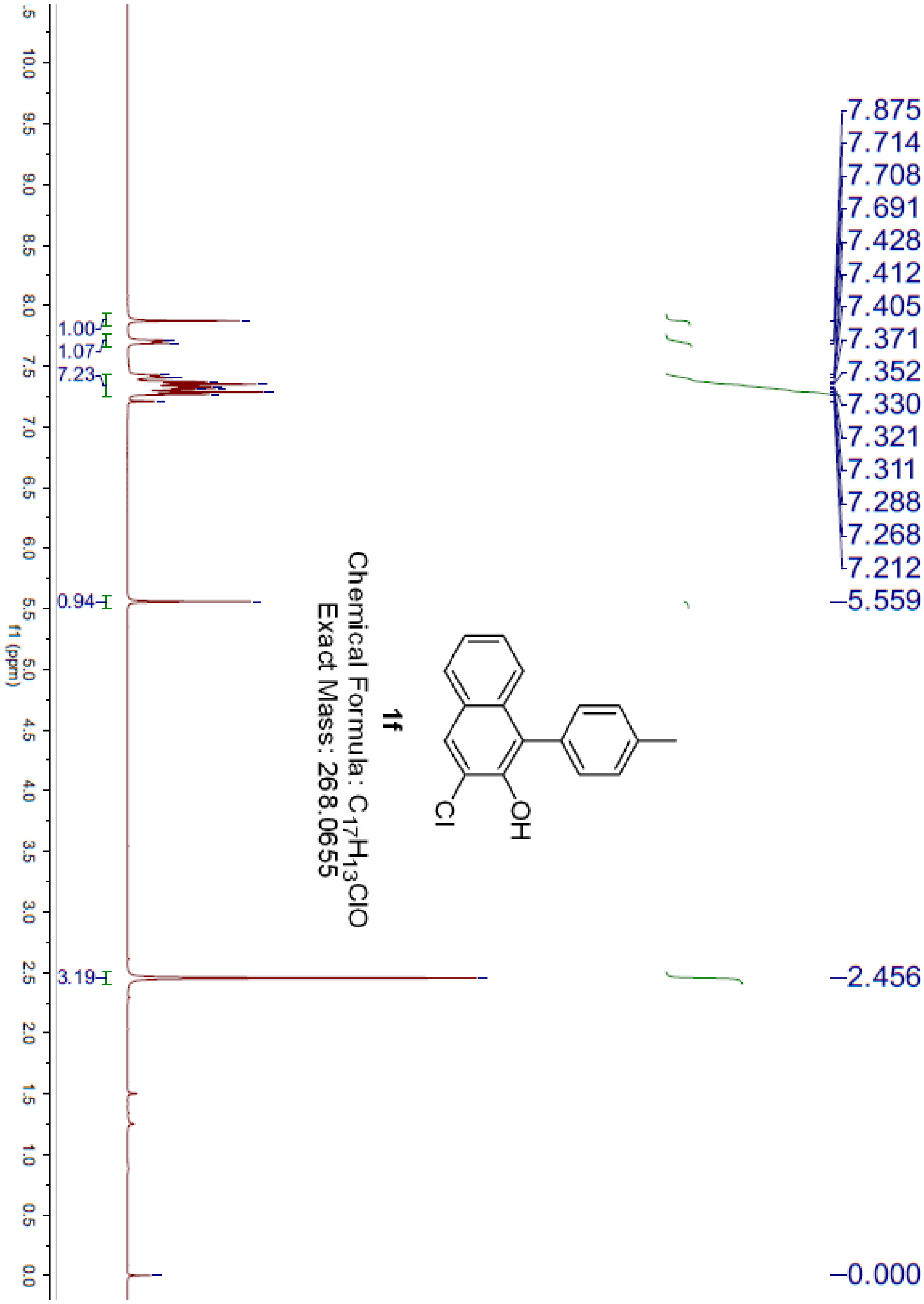


1e

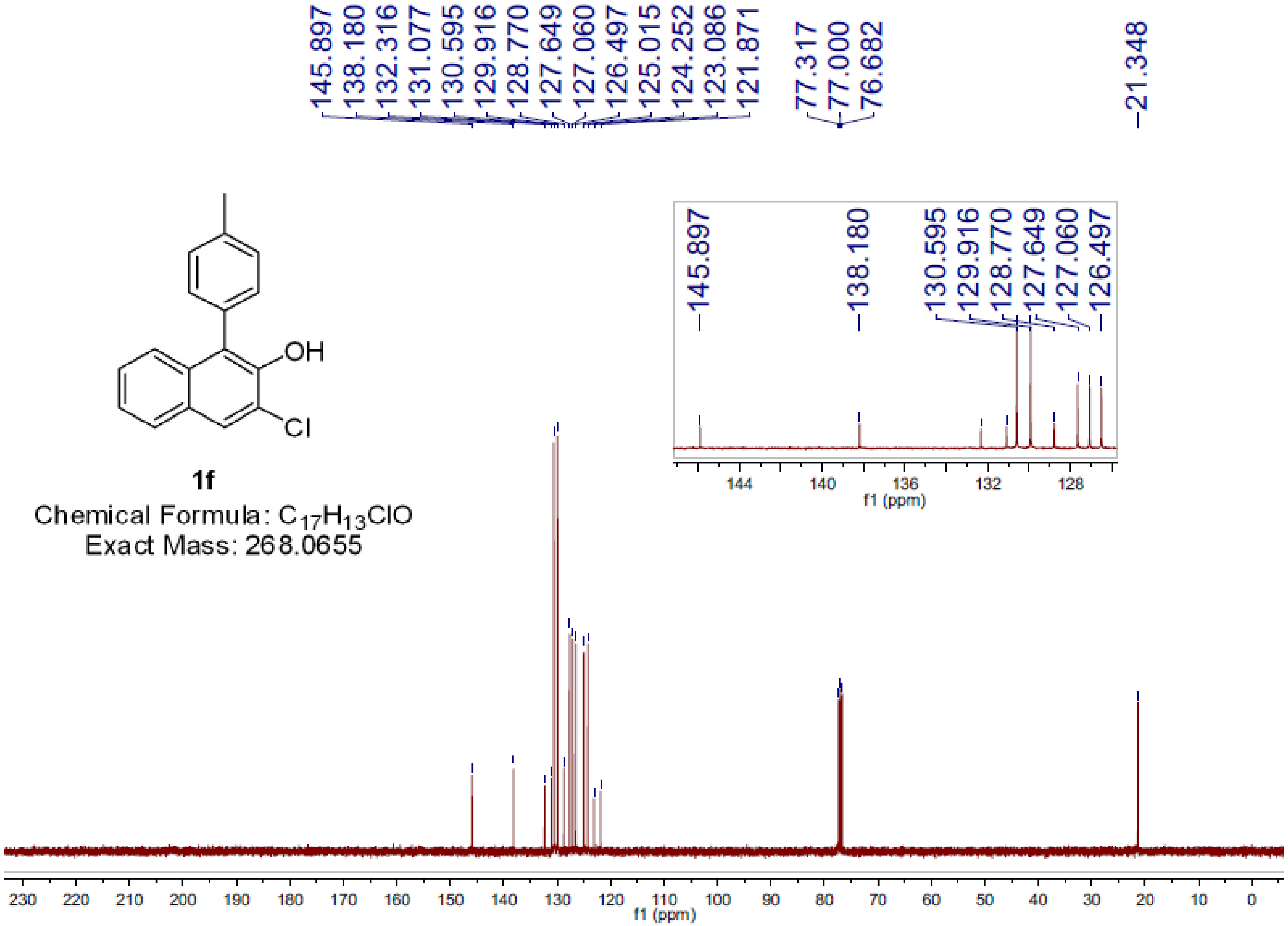
Chemical Formula: $C_{16}H_{12}O$

Exact Mass: 220.0888

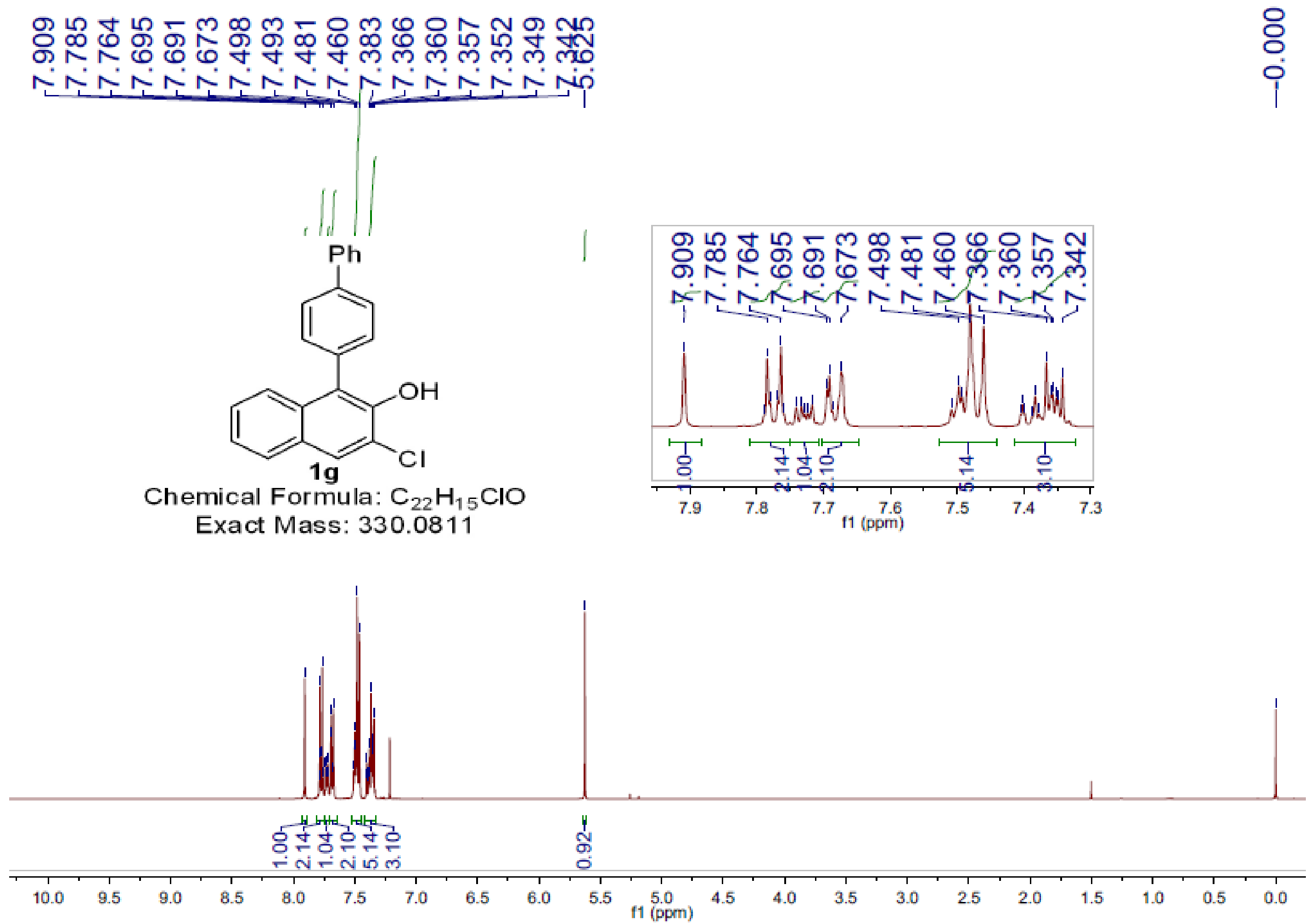


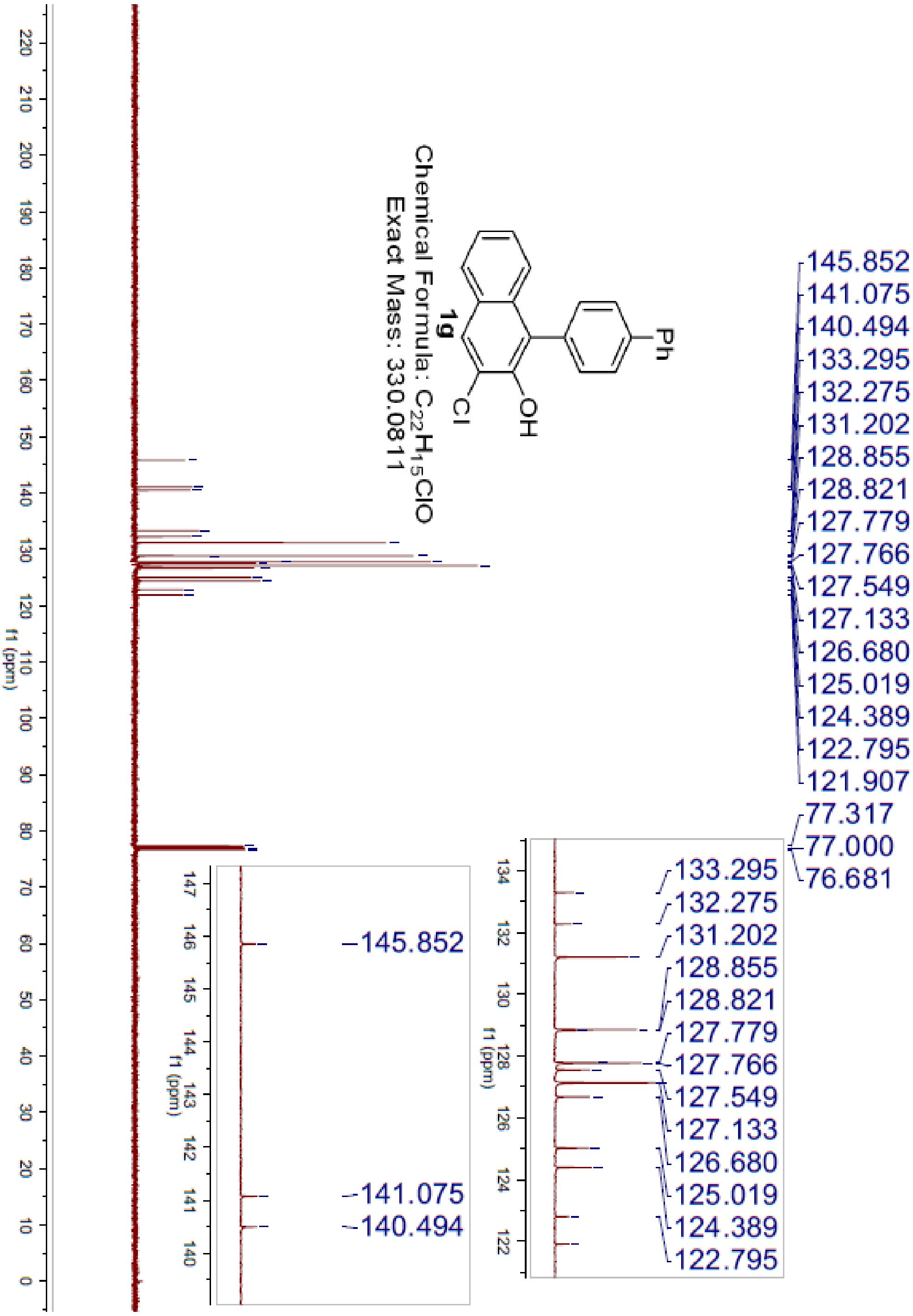


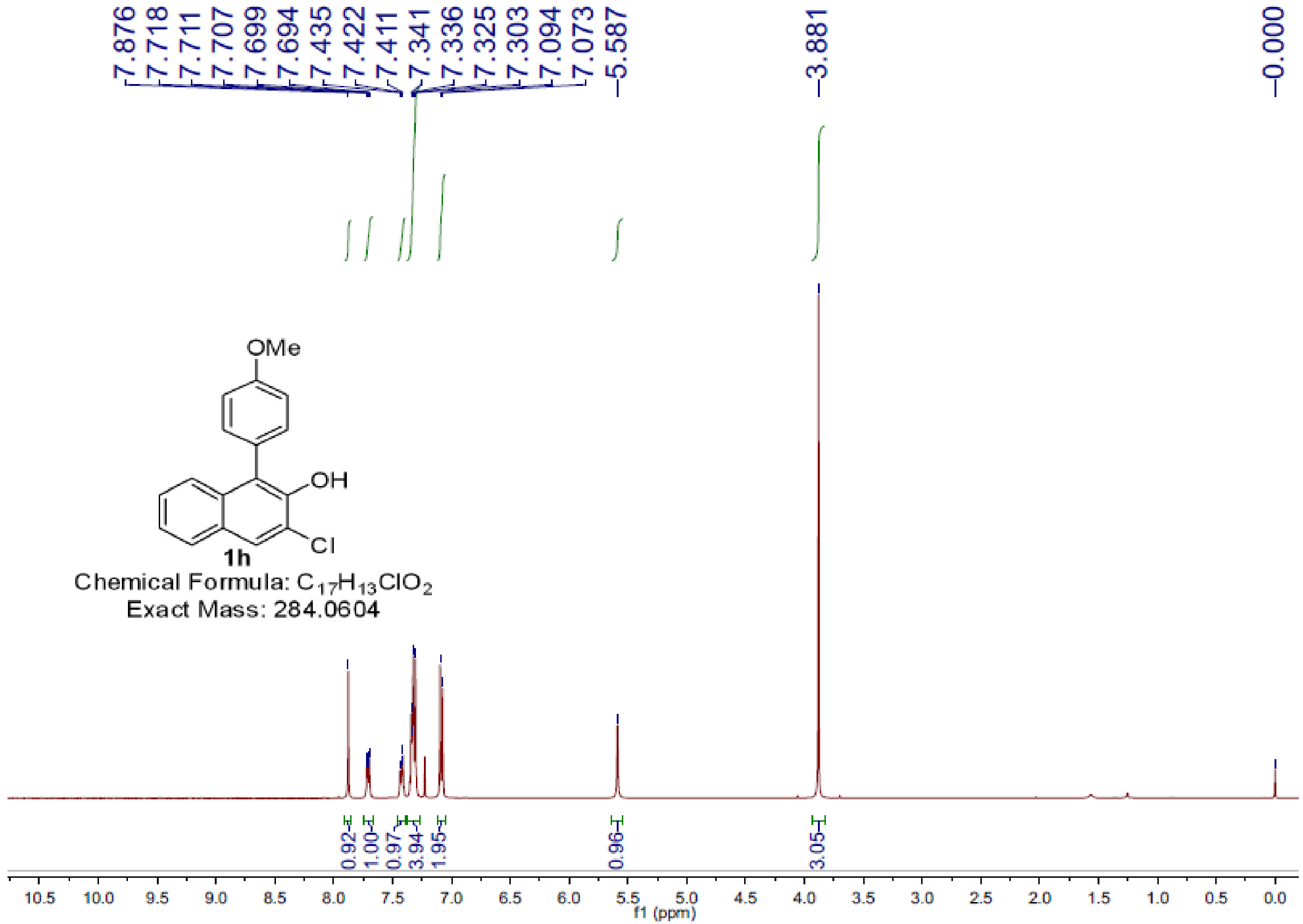
7.875
7.714
7.708
7.691
7.428
7.412
7.405
7.371
7.352
7.330
7.321
7.311
7.288
7.268
7.212
5.559
2.456
0.000
1.00
1.07
7.23
0.94
3.19
OH
Cl
1f
Chemical Formula: C17H13ClO
Exact Mass: 268.0655
f1 (ppm)

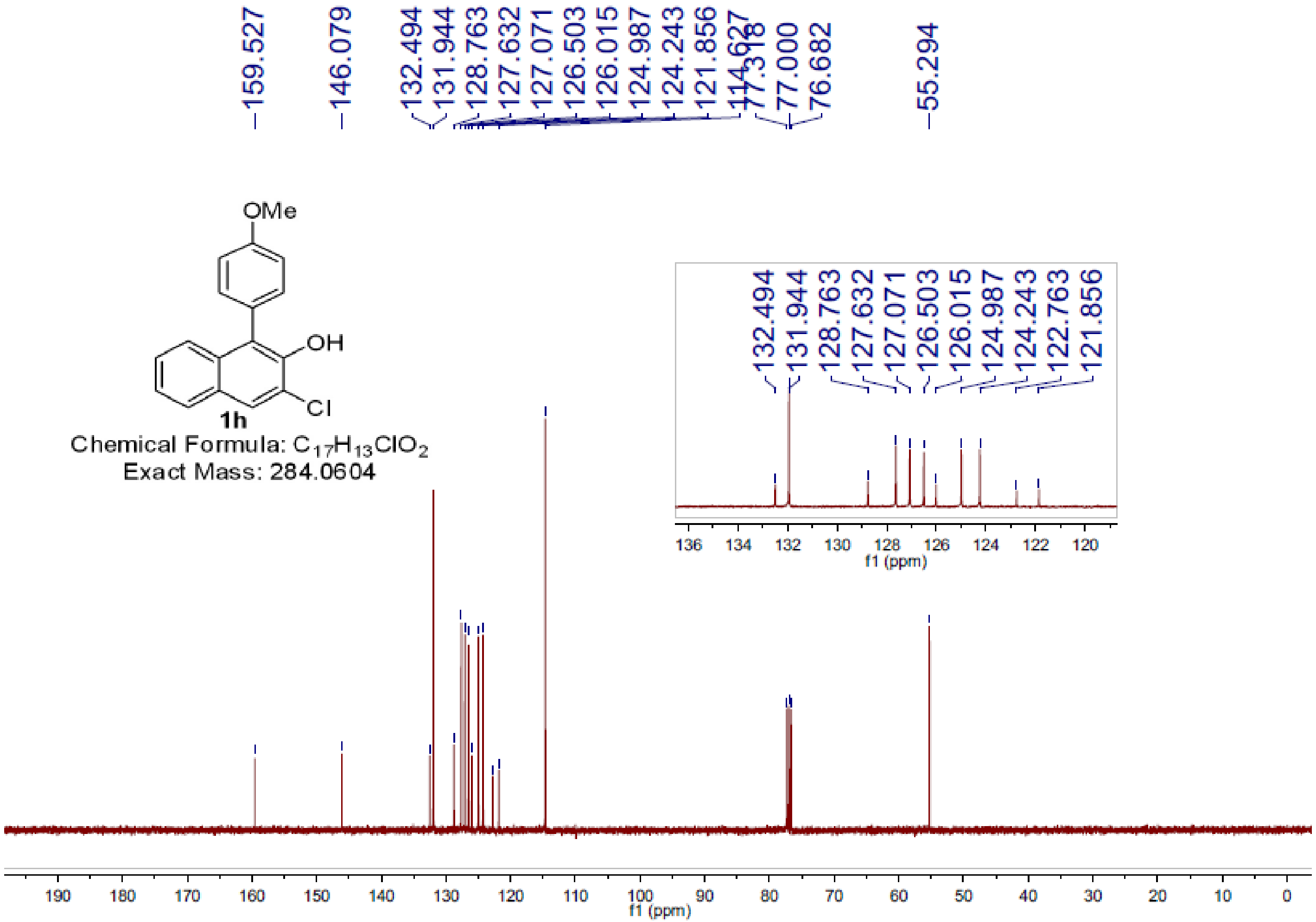


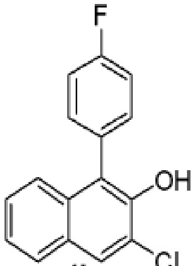
1f
Chemical Formula: $C_{17}H_{13}ClO$
Exact Mass: 268.0655


7.909
7.785
7.764
7.695
7.691
7.673
7.498
7.493
7.481
7.460
7.383
7.366
7.360
7.357
7.352
7.349
7.342
5.625
0.000
Ph
OH
Cl
1g
Chemical Formula: $C_{22}H_{15}ClO$
Exact Mass: 330.0811
1.00
2.14
1.04
2.10
5.14
3.10
0.92
f1 (ppm)


Ph
OH
Cl
1g
Chemical Formula: $C_{22}H_{15}ClO$
Exact Mass: 330.0811
145.852
141.075
140.494
133.295
132.275
131.202
128.855
128.821
127.779
127.766
127.549
127.133
126.680
125.019
124.389
122.795
121.907
77.317
77.000
76.681
f1 (ppm)


7.876
7.718
7.711
7.707
7.699
7.694
7.435
7.422
7.411
7.341
7.336
7.325
7.303
7.094
7.073
5.587
3.881
0.000
OMe
OH
Cl
1h
Chemical Formula: $C_{17}H_{13}ClO_2$
Exact Mass: 284.0604
0.92
1.00
0.97
3.94
1.95
0.96
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

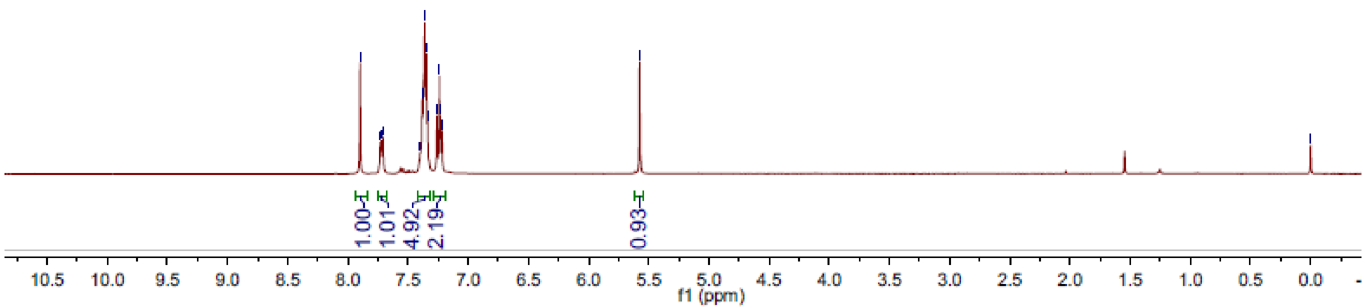

159.527
146.079
132.494
131.944
128.763
127.632
127.071
126.503
126.015
124.987
124.243
121.856
114.627
77.318
77.000
76.682
55.294
OMe
OH
Cl
1h
Chemical Formula: $C_{17}H_{13}ClO_2$
Exact Mass: 284.0604
132.494
131.944
128.763
127.632
127.071
126.503
126.015
124.987
124.243
122.763
121.856
f1 (ppm)
f1 (ppm)

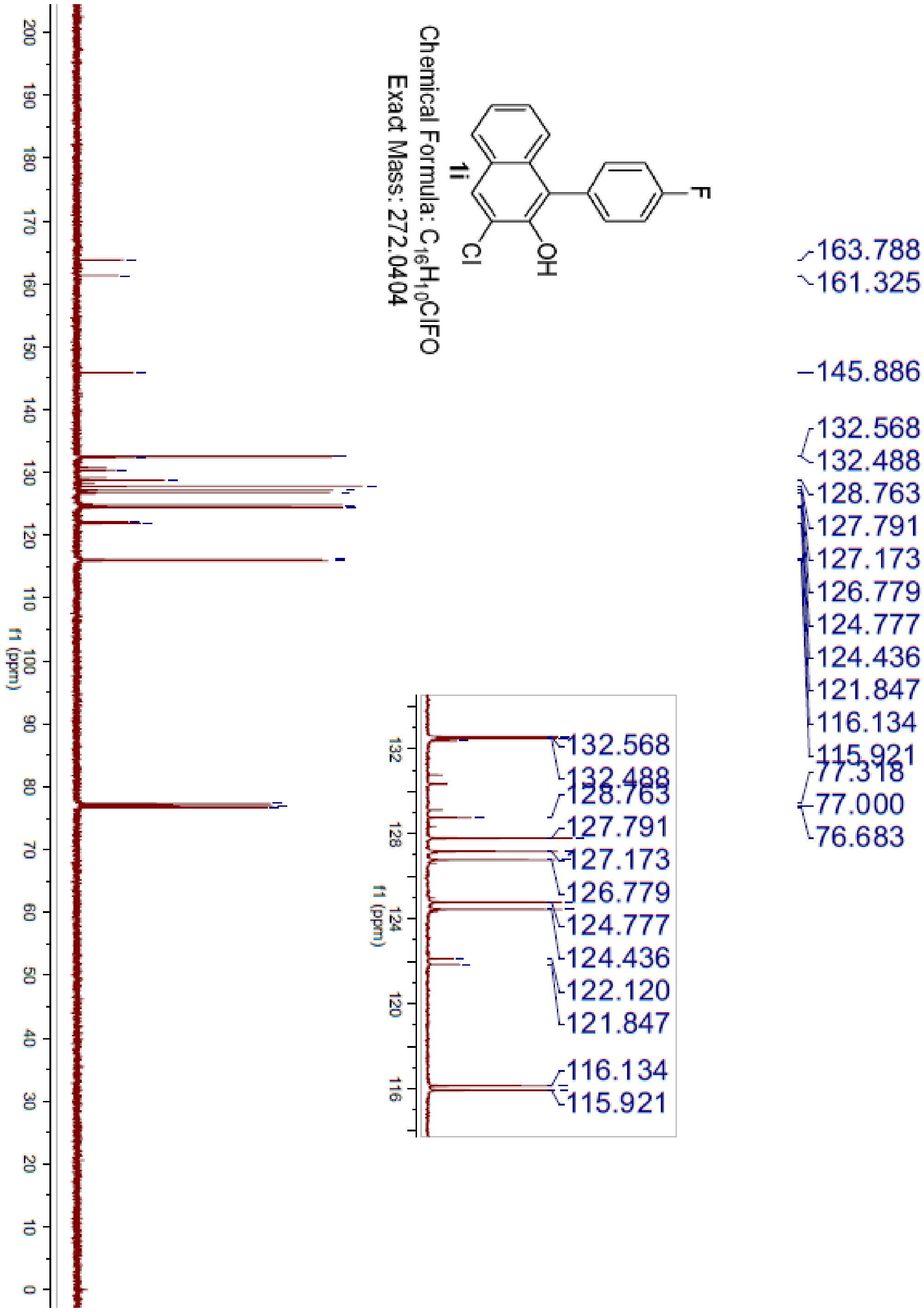


1i

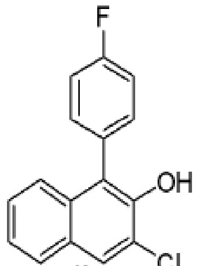
Chemical Formula: $C_{16}H_{10}ClFO$

Exact Mass: 272.0404





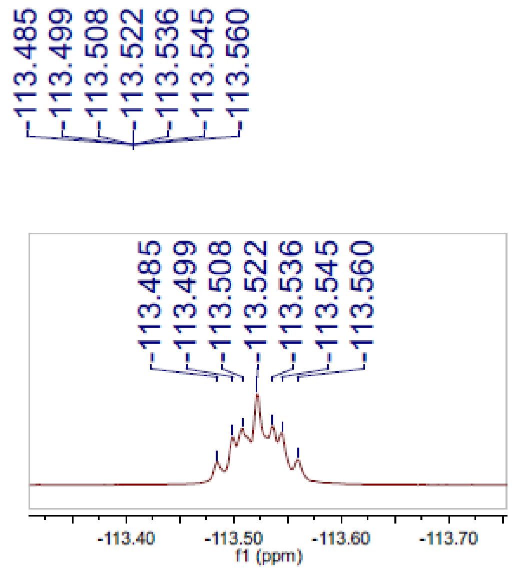
1i
Chemical Formula: C16H10ClFO
Exact Mass: 272.0404
OH
Cl
F
163.788
161.325
145.886
132.568
132.488
128.763
127.791
127.173
126.779
124.777
124.436
121.847
116.134
115.921
77.318
77.000
76.683
132.568
132.488
128.763
127.791
127.173
126.779
124.777
124.436
122.120
121.847
116.134
115.921
f1 (ppm)

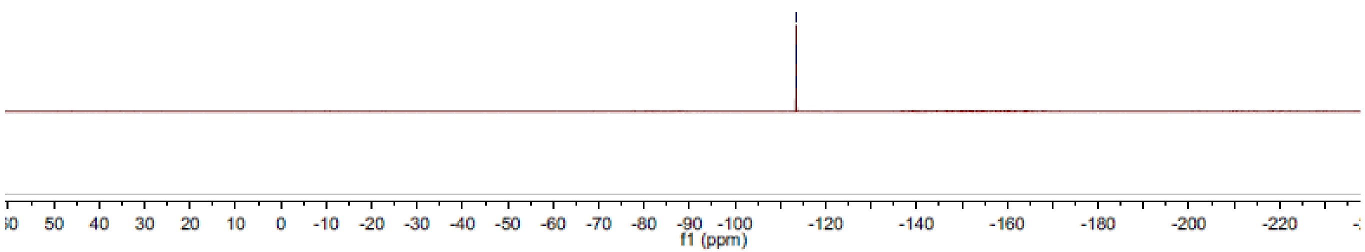


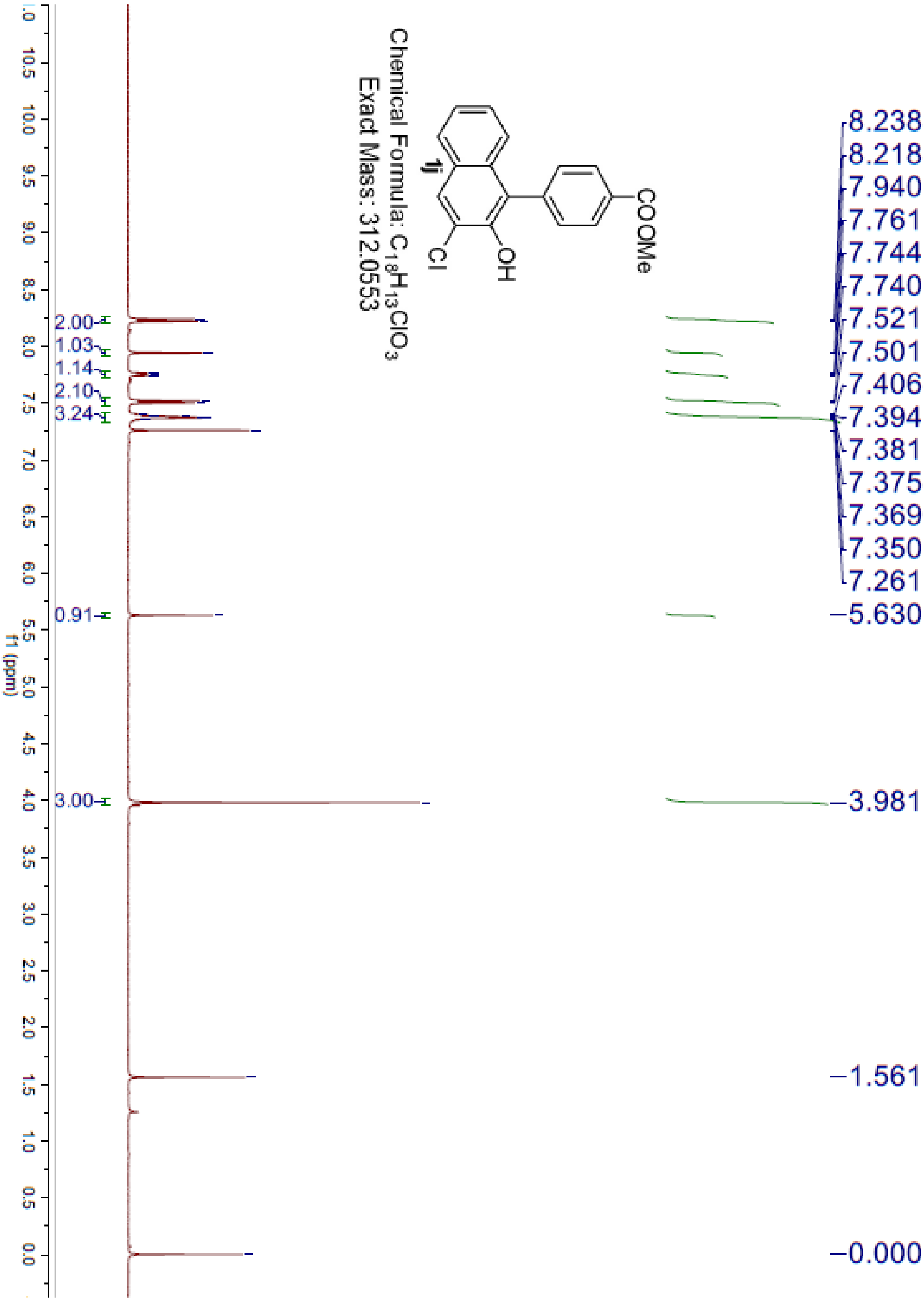
1i

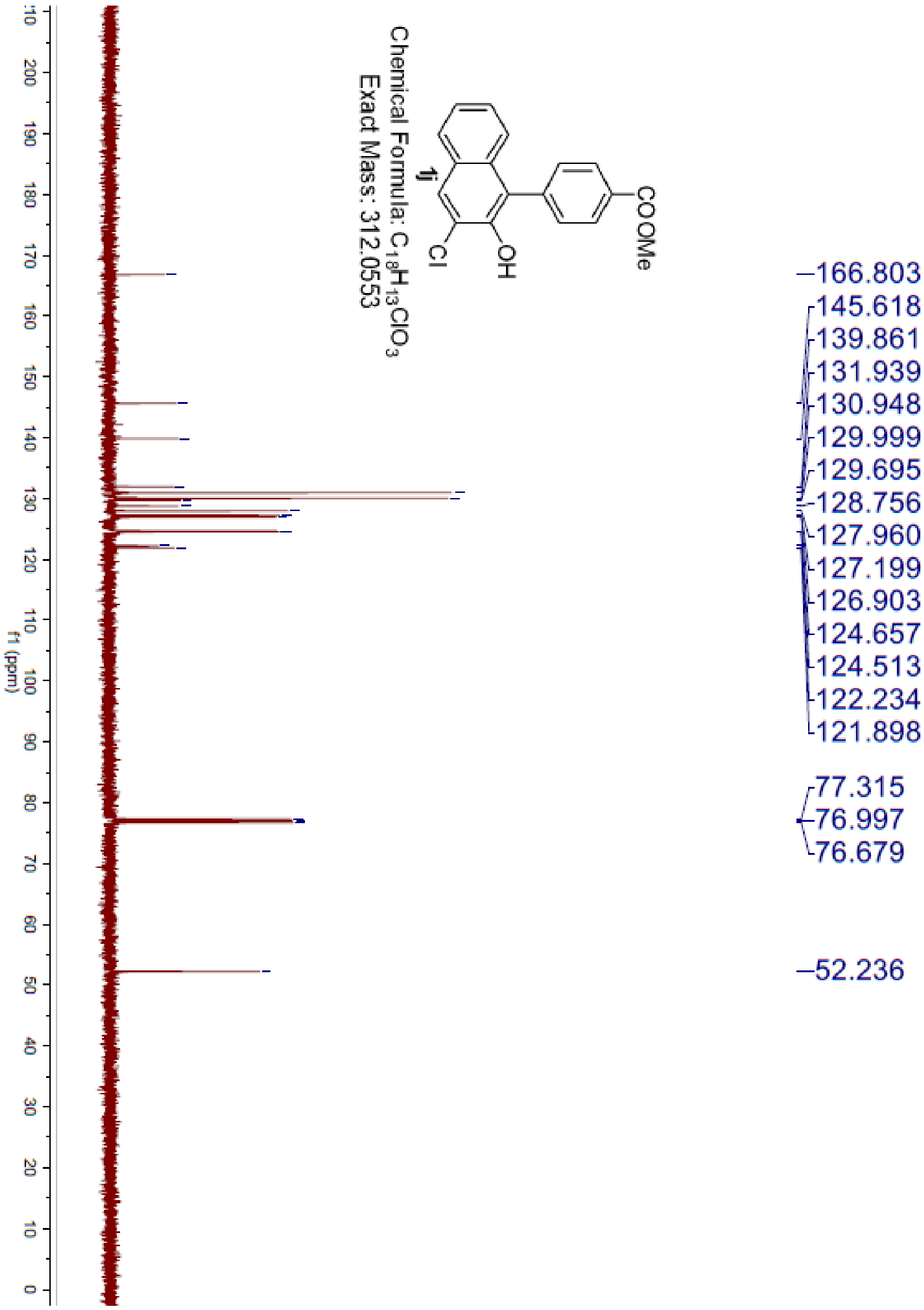
Chemical Formula: $C_{16}H_{10}ClFO$

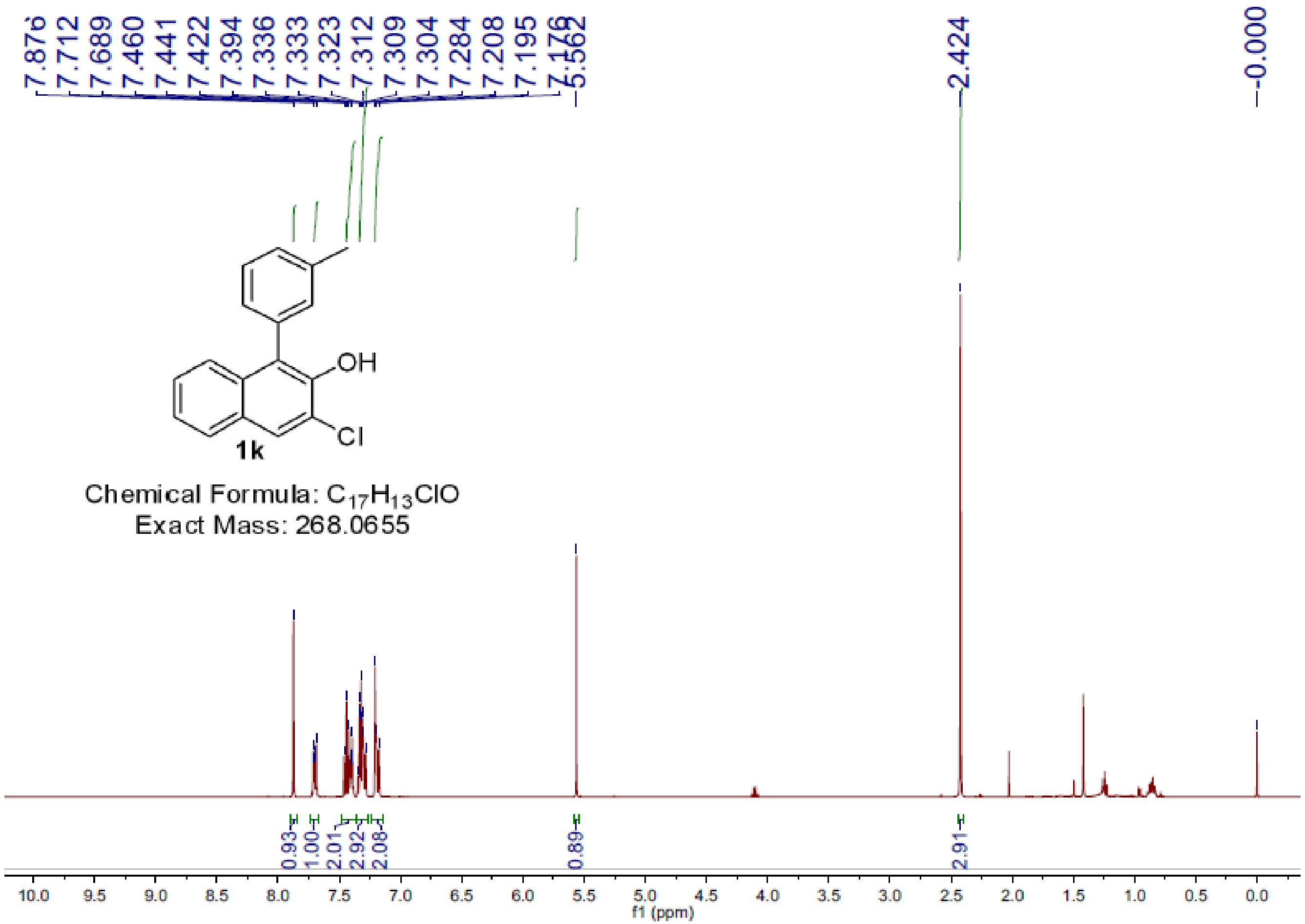
Exact Mass: 272.0404

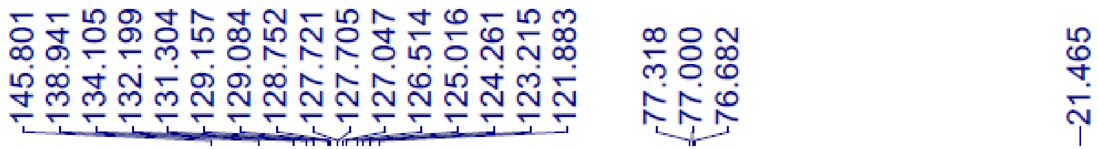


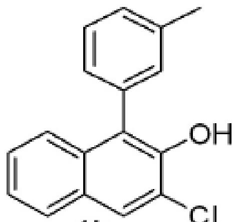



8.238
8.218
7.940
7.761
7.744
7.740
7.521
7.501
7.406
7.394
7.381
7.375
7.369
7.350
7.261
5.630
3.981
1.561
0.000
COOMe
OH
Cl
1j
Chemical Formula: $C_{18}H_{13}ClO_3$
Exact Mass: 312.0553
2.00
1.03
1.14
2.10
3.24
0.91
3.00
f1 (ppm)


COOMe
OH
Cl
1j
Chemical Formula: C18H13ClO3
Exact Mass: 312.0553
166.803
145.618
139.861
131.939
130.948
129.999
129.695
128.756
127.960
127.199
126.903
124.657
124.513
122.234
121.898
77.315
76.997
76.679
52.236
f1 (ppm)

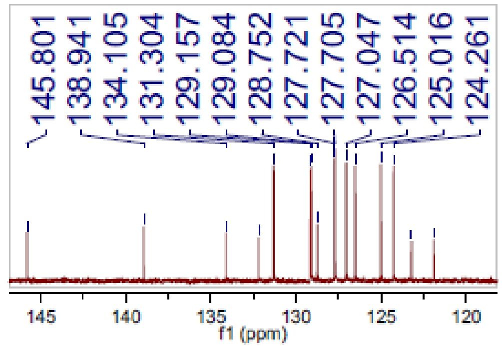

7.876
7.712
7.689
7.460
7.441
7.422
7.394
7.336
7.333
7.323
7.312
7.309
7.304
7.284
7.208
7.195
7.176
5.562
2.424
-0.000
OH
Cl
1k
Chemical Formula: $C_{17}H_{13}ClO$
Exact Mass: 268.0655
0.93
1.00
2.01
2.92
2.08
0.89
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

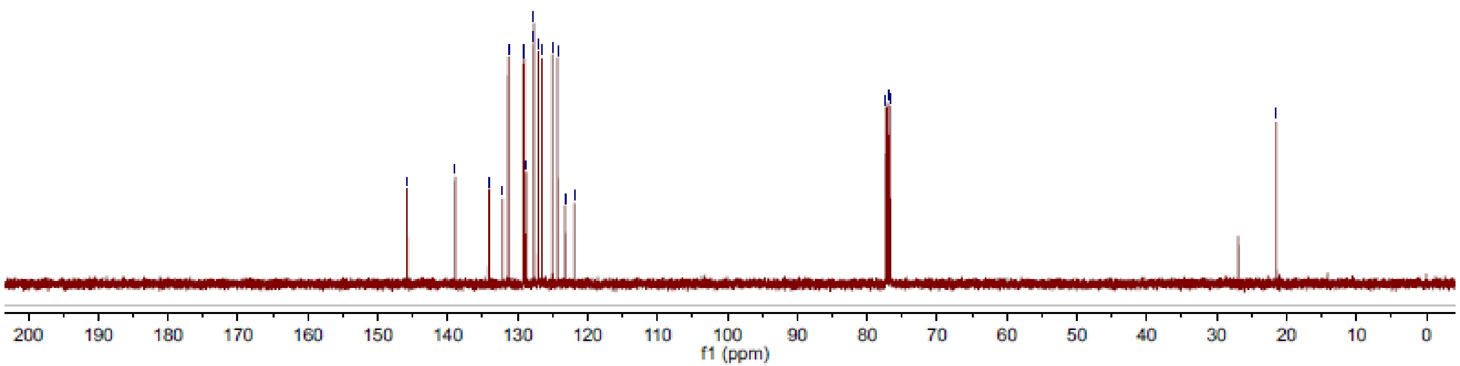


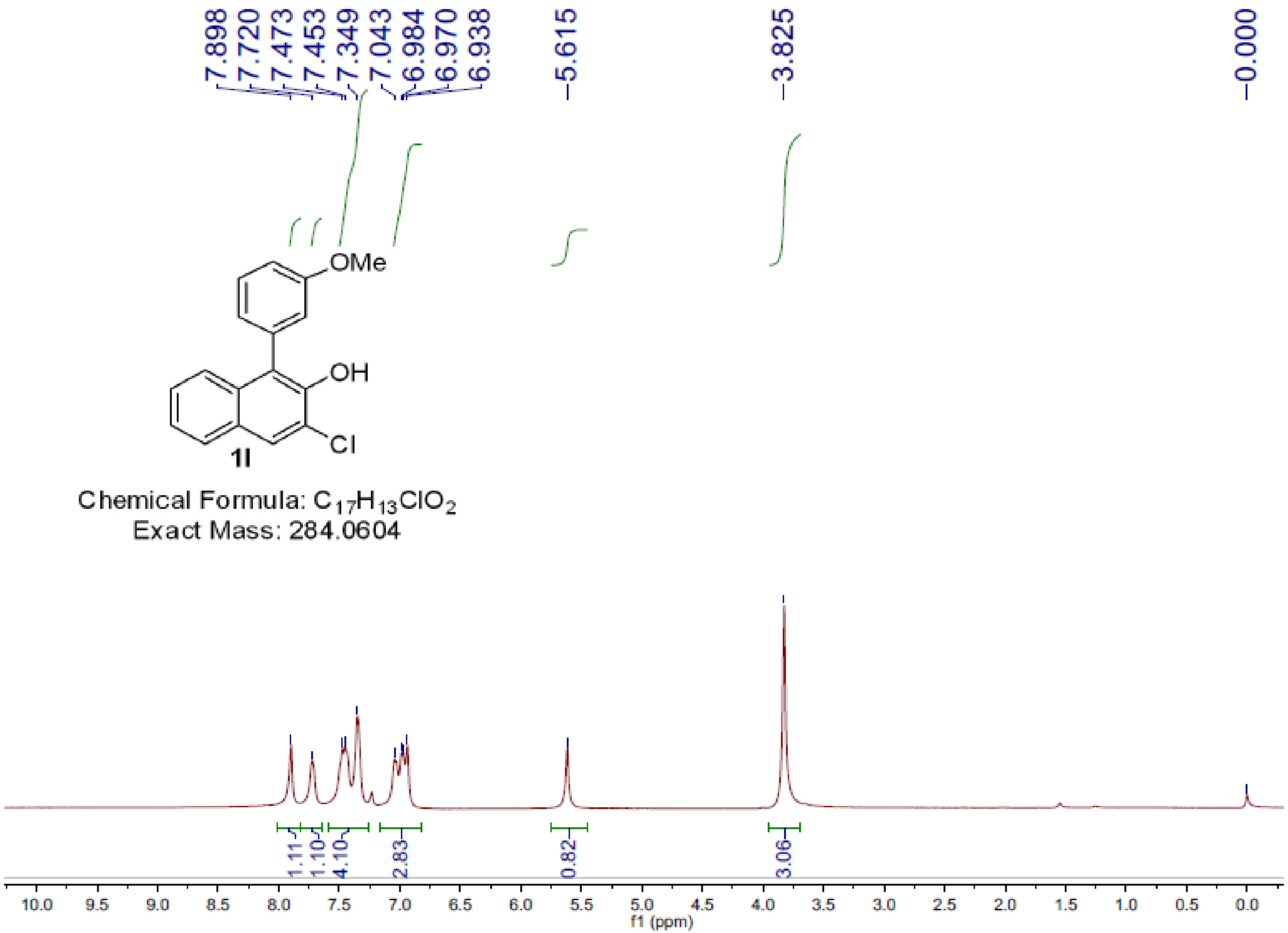


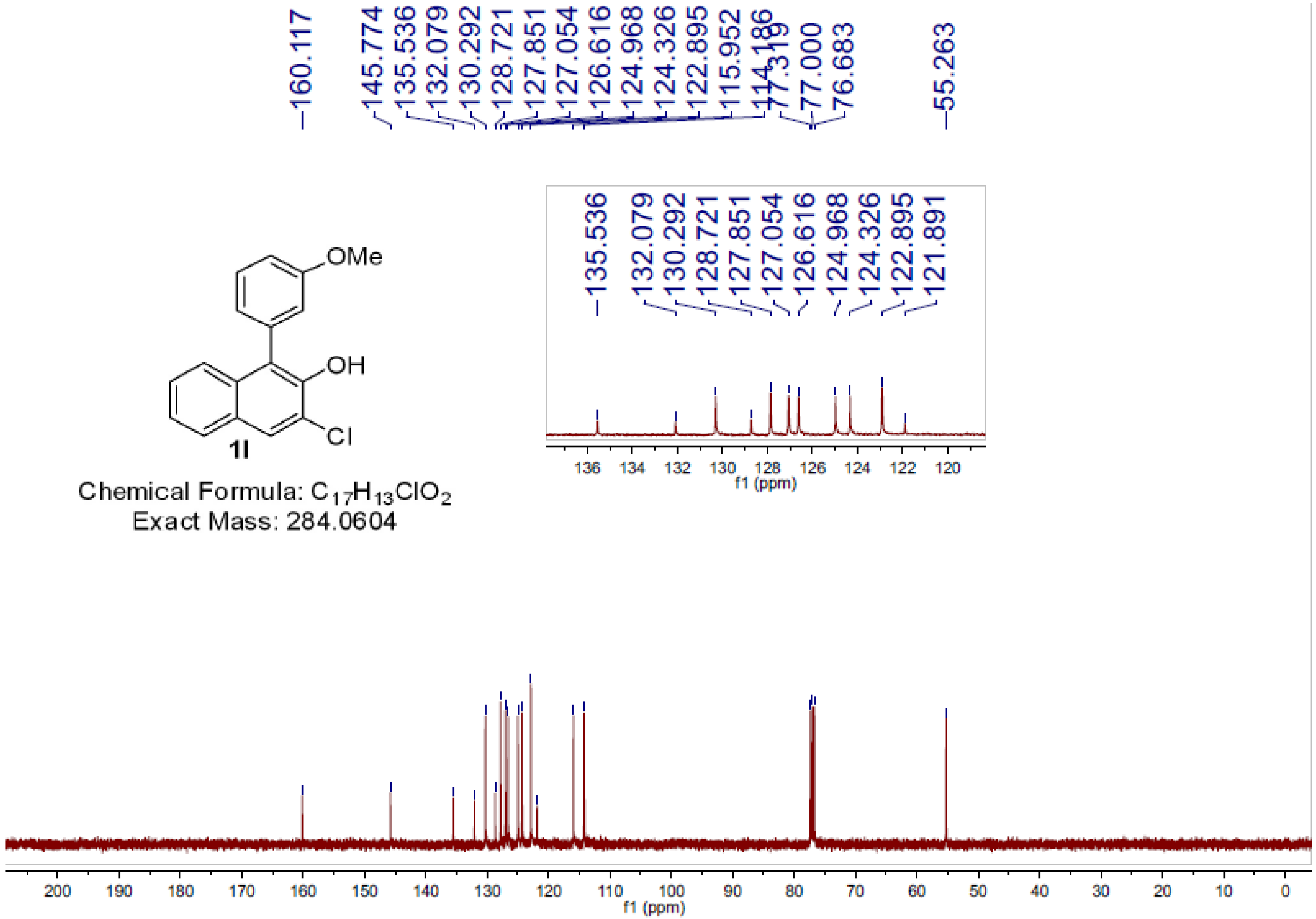
1k

Chemical Formula: $C_{17}H_{13}ClO$
Exact Mass: 268.0655



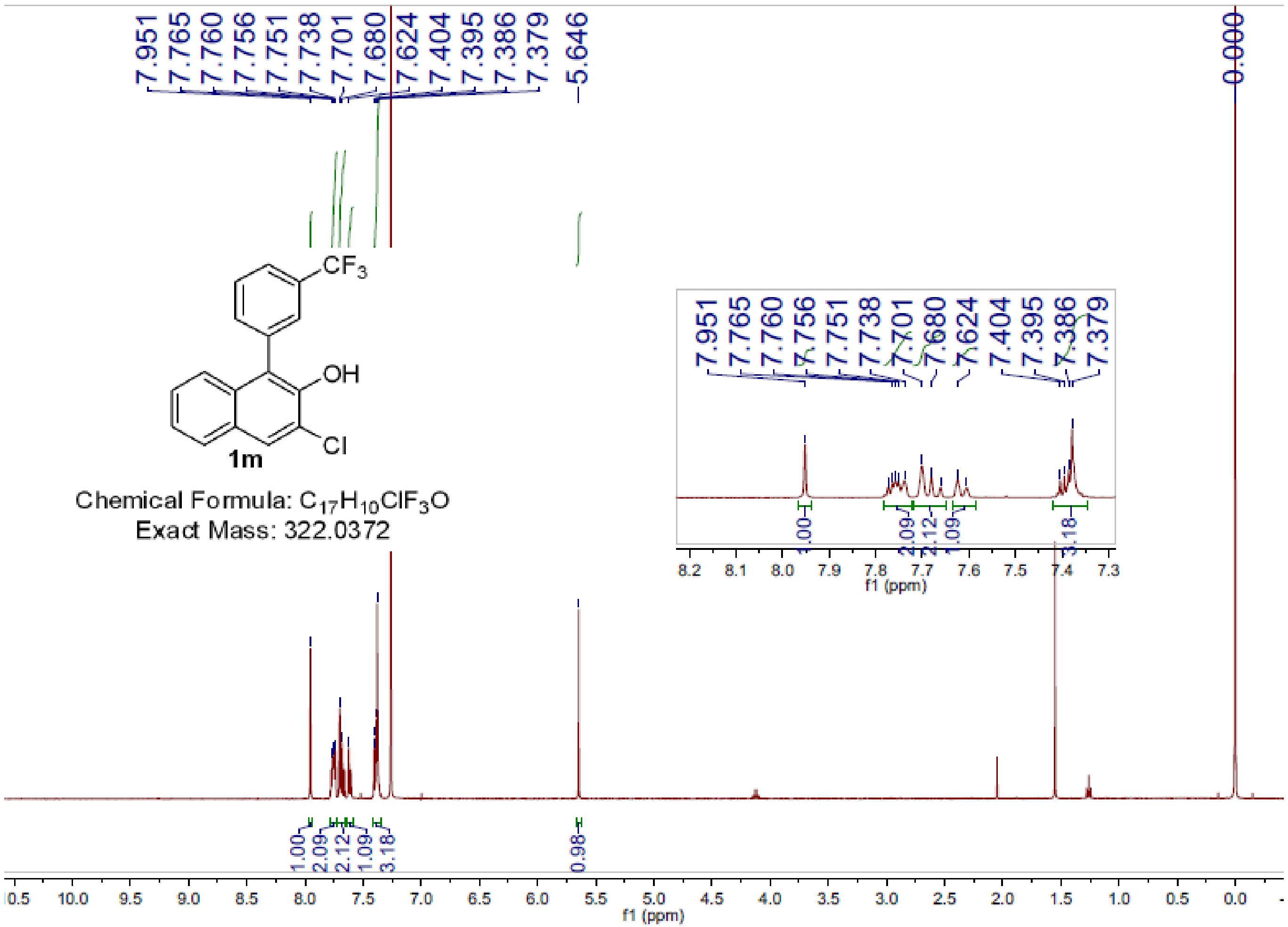


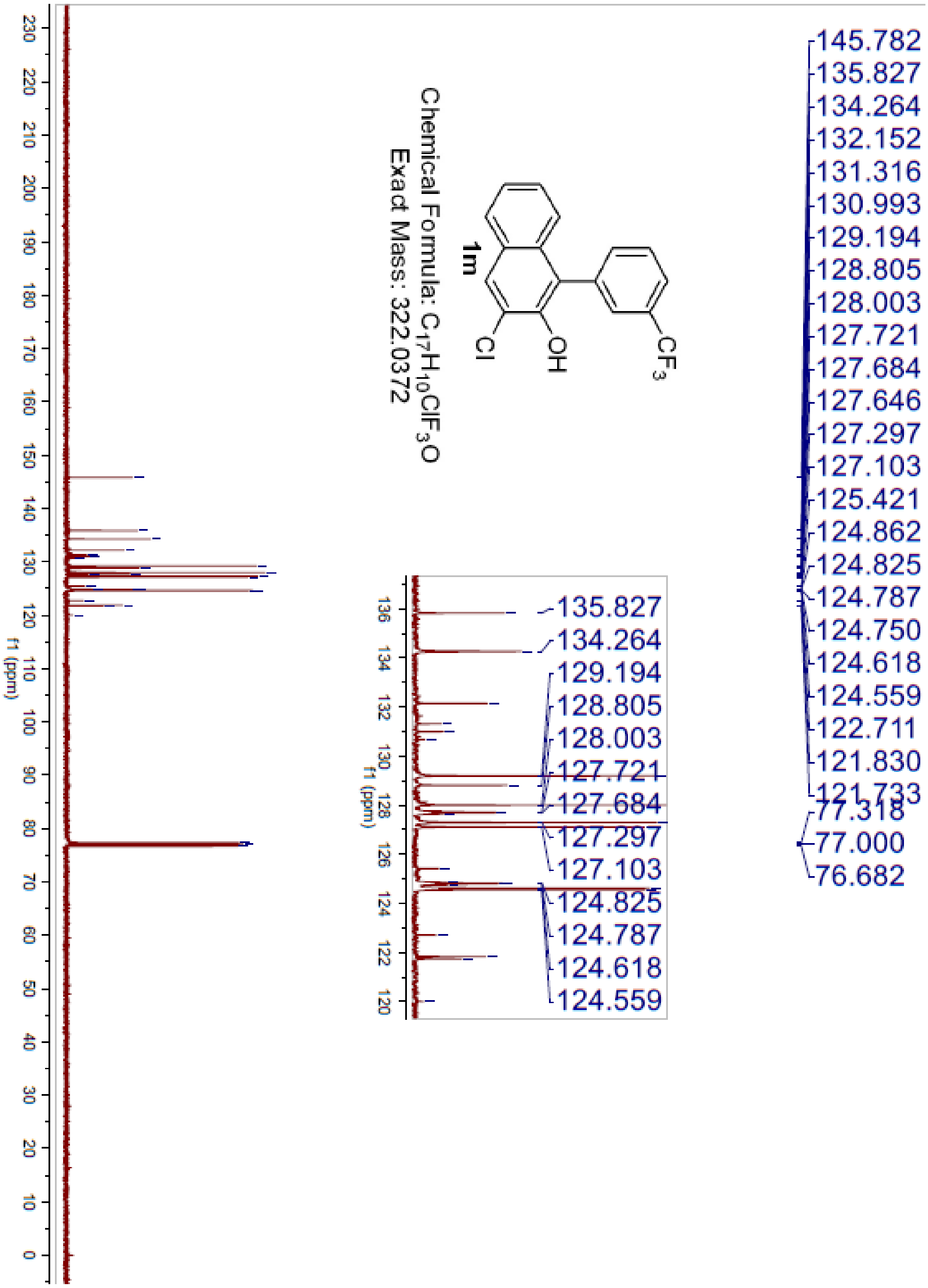

7.898
7.720
7.473
7.453
7.349
7.043
6.984
6.970
6.938
5.615
3.825
0.000
OMe
OH
Cl
1l
Chemical Formula: $C_{17}H_{13}ClO_2$
Exact Mass: 284.0604
1.11
1.10
4.10
2.83
0.82
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

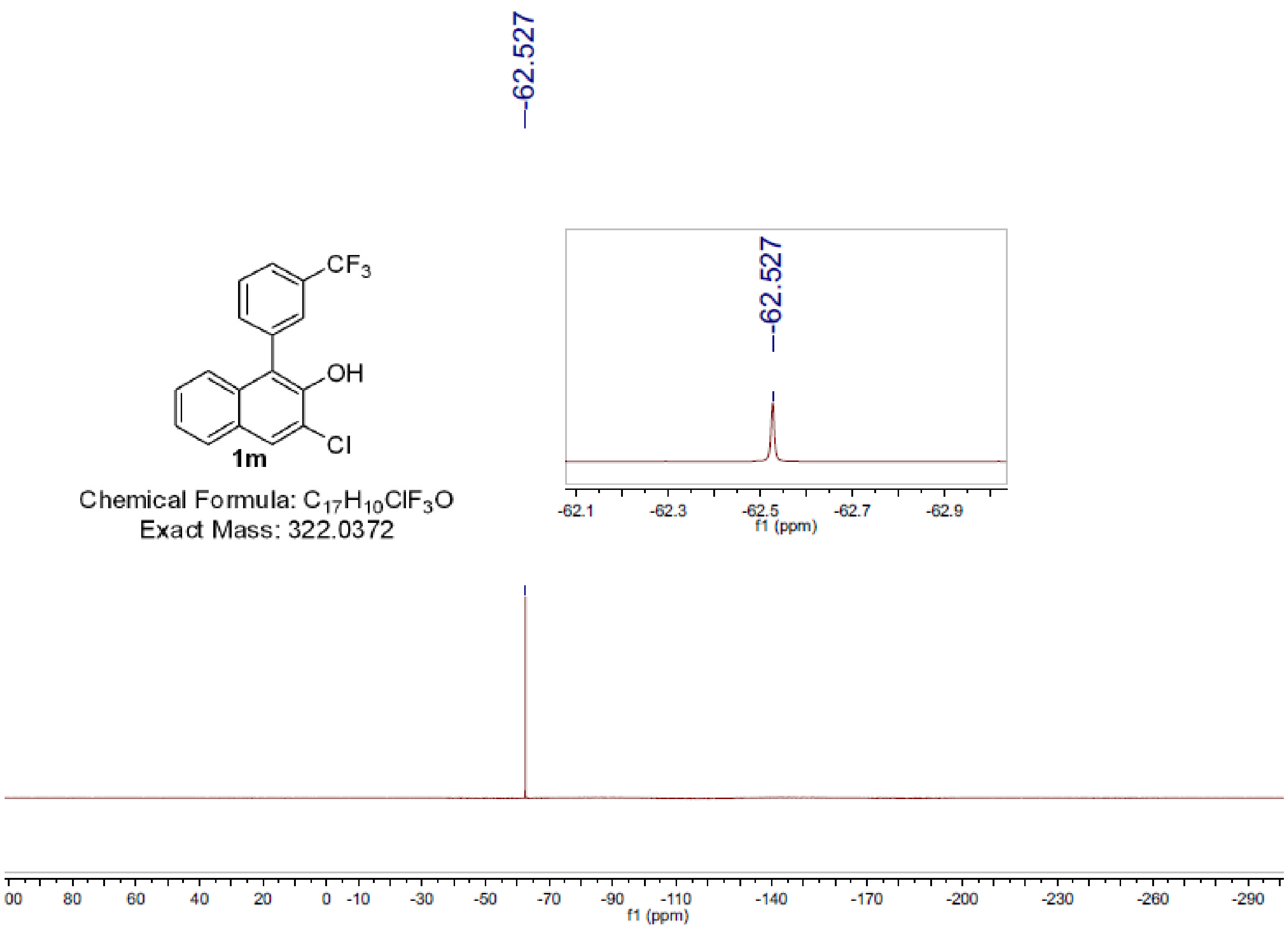


1l

Chemical Formula: $C_{17}H_{13}ClO_2$
Exact Mass: 284.0604

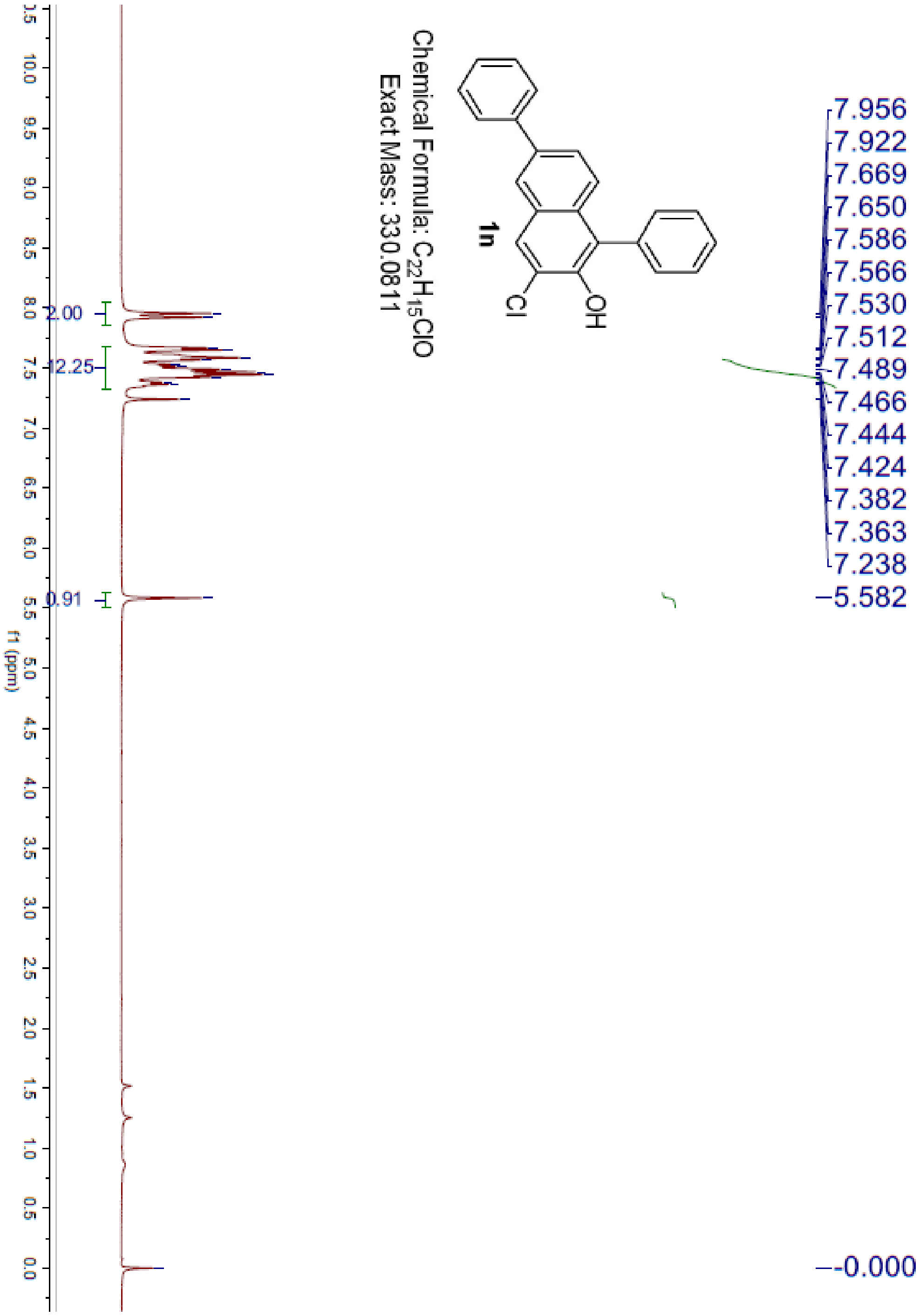

7.951
7.765
7.760
7.756
7.751
7.738
7.701
7.680
7.624
7.404
7.395
7.386
7.379
5.646
0.000
CF3
OH
Cl
1m
Chemical Formula: C17H10ClF3O
Exact Mass: 322.0372
1.00
2.09
2.12
1.09
3.18
0.98
f1 (ppm)

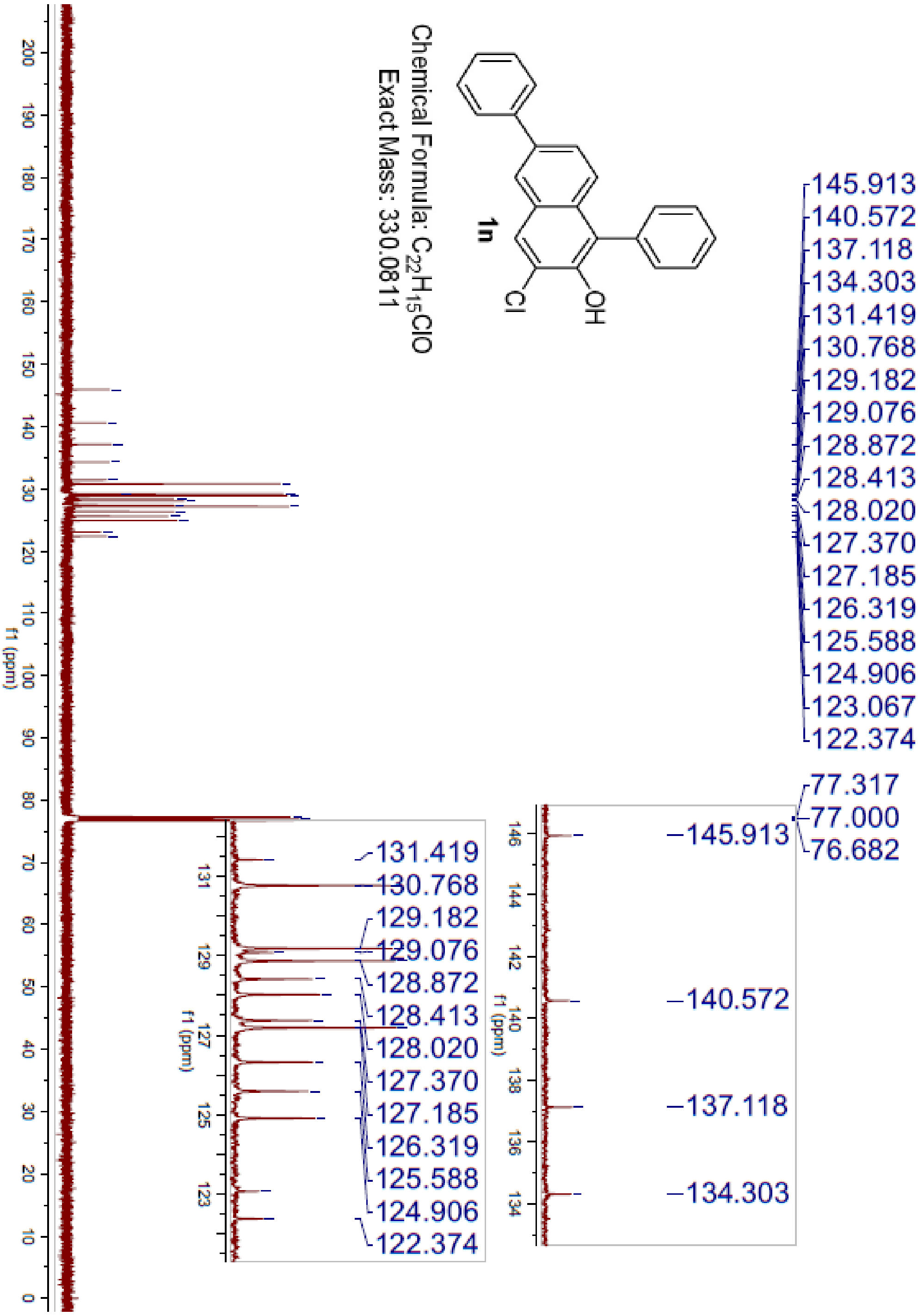

1m
CF3
OH
Cl
Chemical Formula: C17H10ClF3O
Exact Mass: 322.0372
145.782
135.827
134.264
132.152
131.316
130.993
129.194
128.805
128.003
127.721
127.684
127.646
127.297
127.103
125.421
124.862
124.825
124.787
124.750
124.618
124.559
122.711
121.830
121.733
77.318
77.000
76.682
135.827
134.264
129.194
128.805
128.003
127.721
127.684
127.297
127.103
124.825
124.787
124.618
124.559
f1 (ppm)
f1 (ppm)

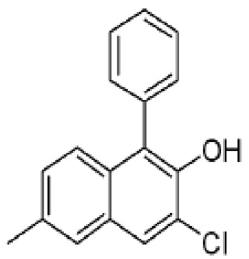


1m

Chemical Formula: $C_{17}H_{10}ClF_3O$
Exact Mass: 322.0372

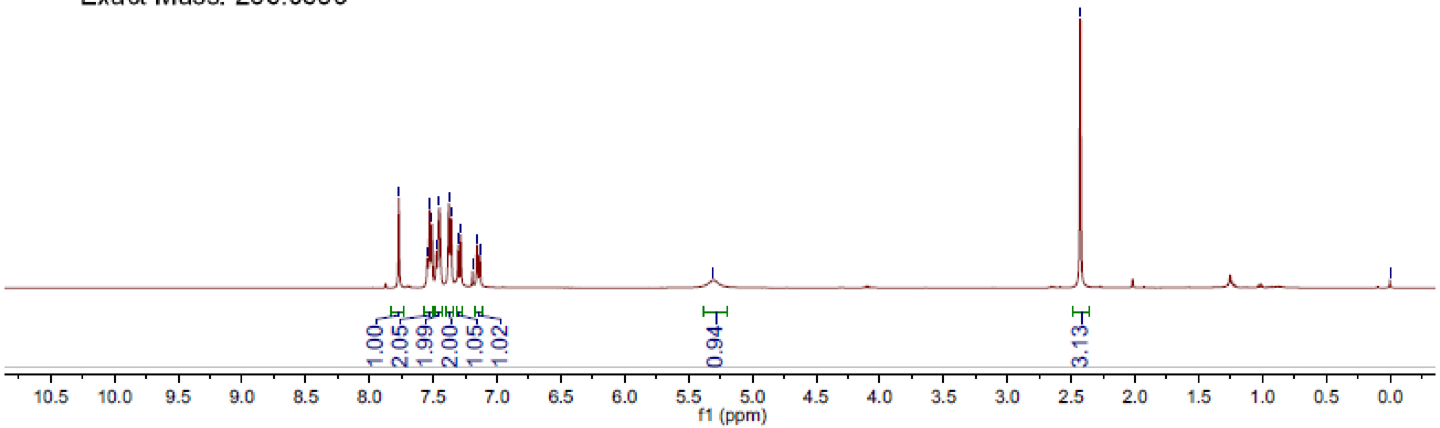

1n
OH
Cl
Chemical Formula: $C_{22}H_{15}ClO$
Exact Mass: 330.0811
7.956
7.922
7.669
7.650
7.586
7.566
7.530
7.512
7.489
7.466
7.444
7.424
7.382
7.363
7.238
5.582
-0.000
2.00
12.25
0.91
f1 (ppm)

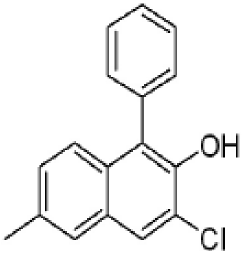

1n
Cl
OH
Chemical Formula: $C_{22}H_{15}ClO$
Exact Mass: 330.0811
145.913
140.572
137.118
134.303
131.419
130.768
129.182
129.076
128.872
128.413
128.020
127.370
127.185
126.319
125.588
124.906
123.067
122.374
77.317
77.000
76.682
f1 (ppm)



1o

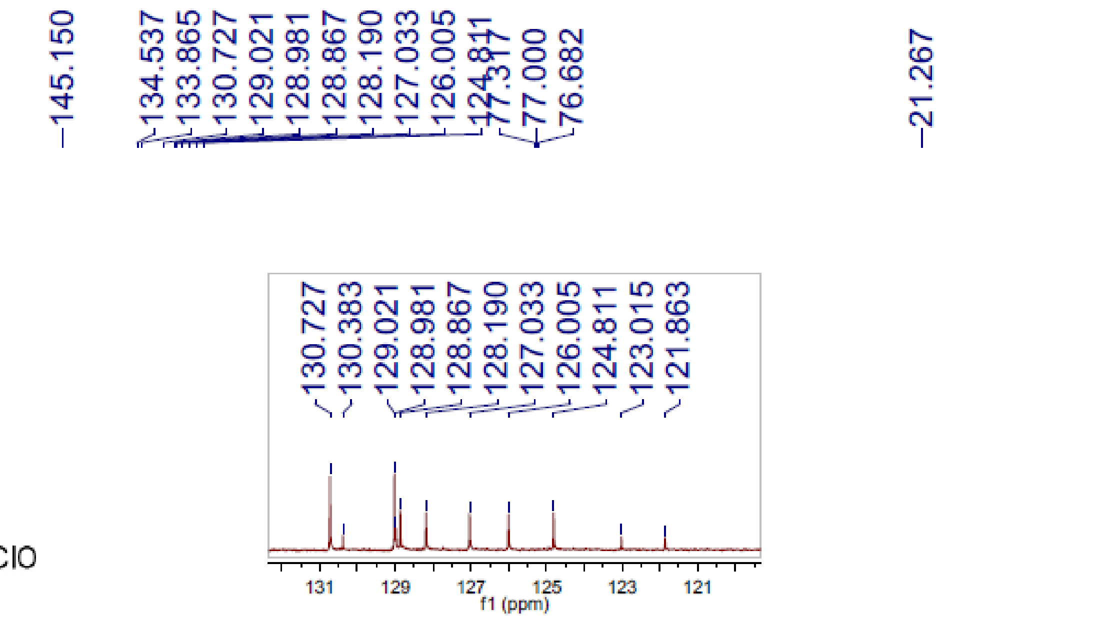
Chemical Formula: $C_{17}H_{13}ClO$
Exact Mass: 268.0655

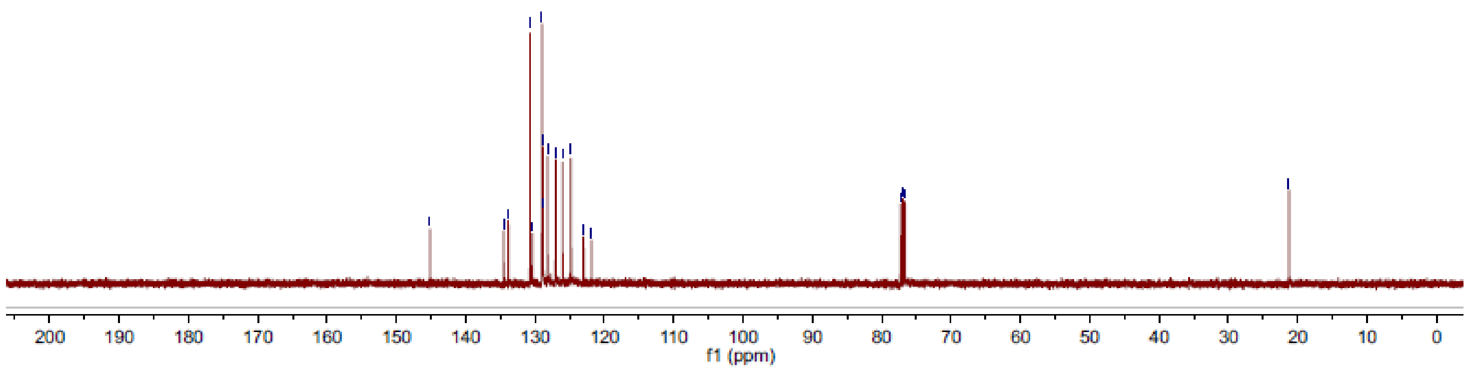


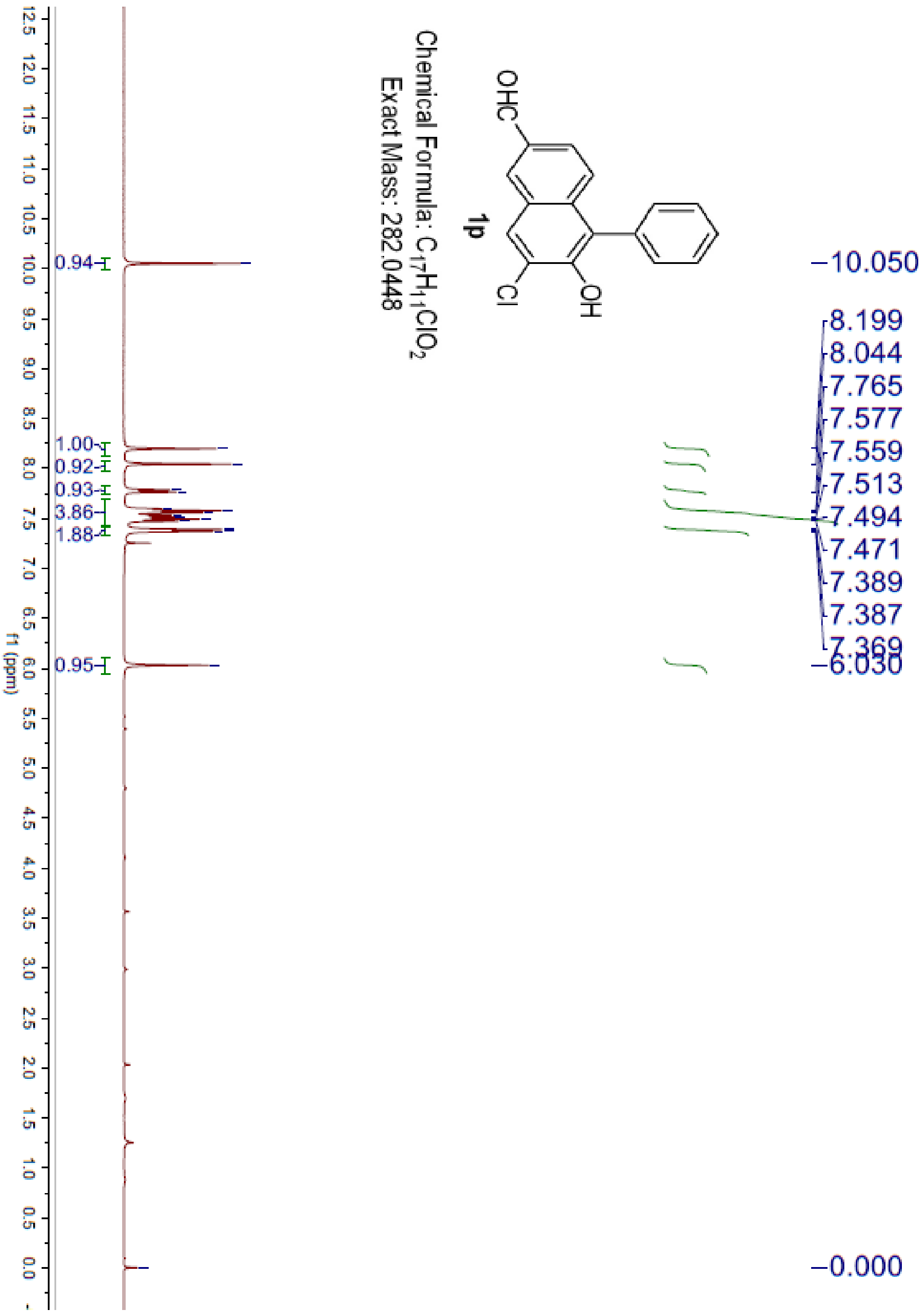


1o

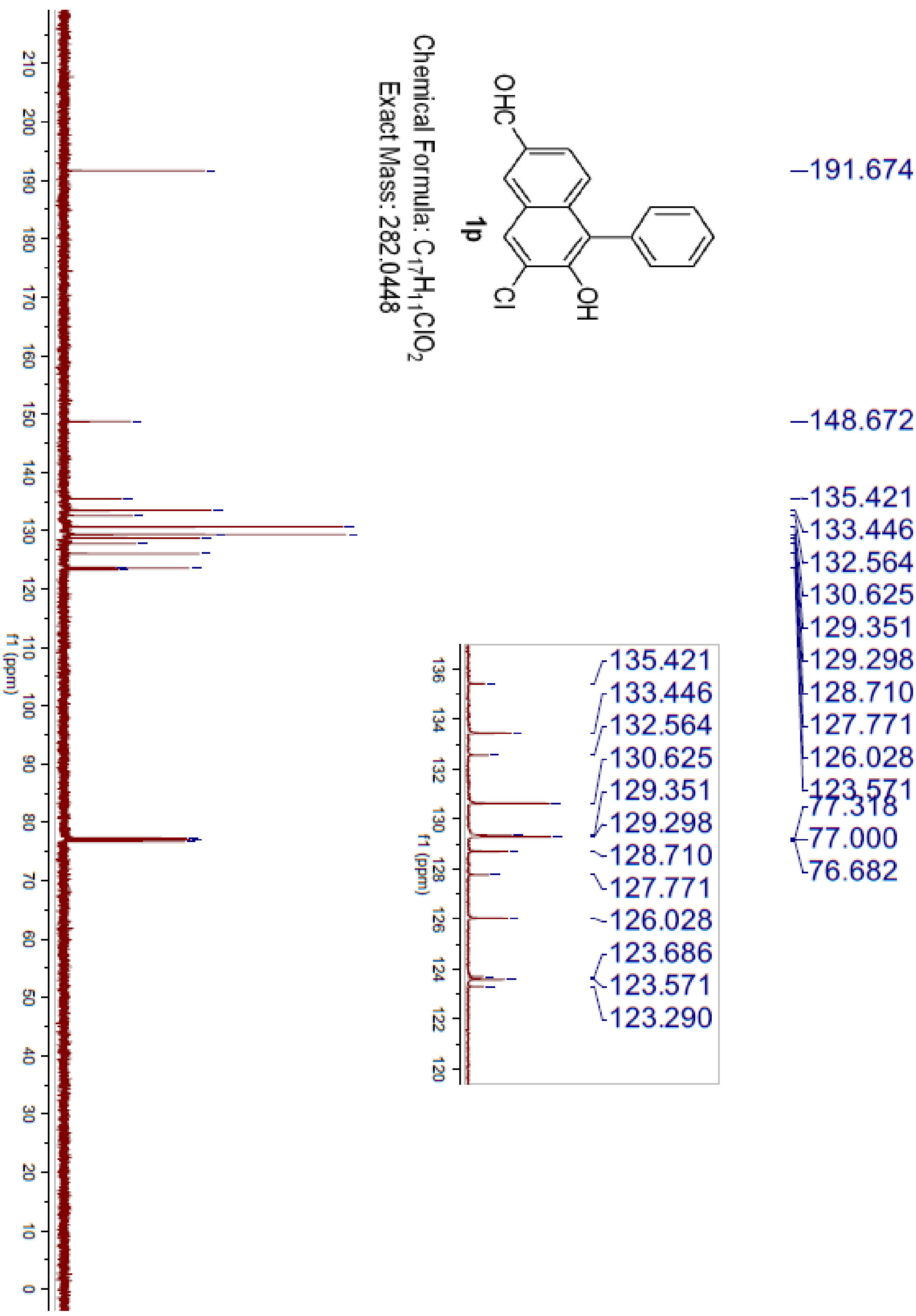
Chemical Formula: $C_{17}H_{13}ClO$
Exact Mass: 268.0655

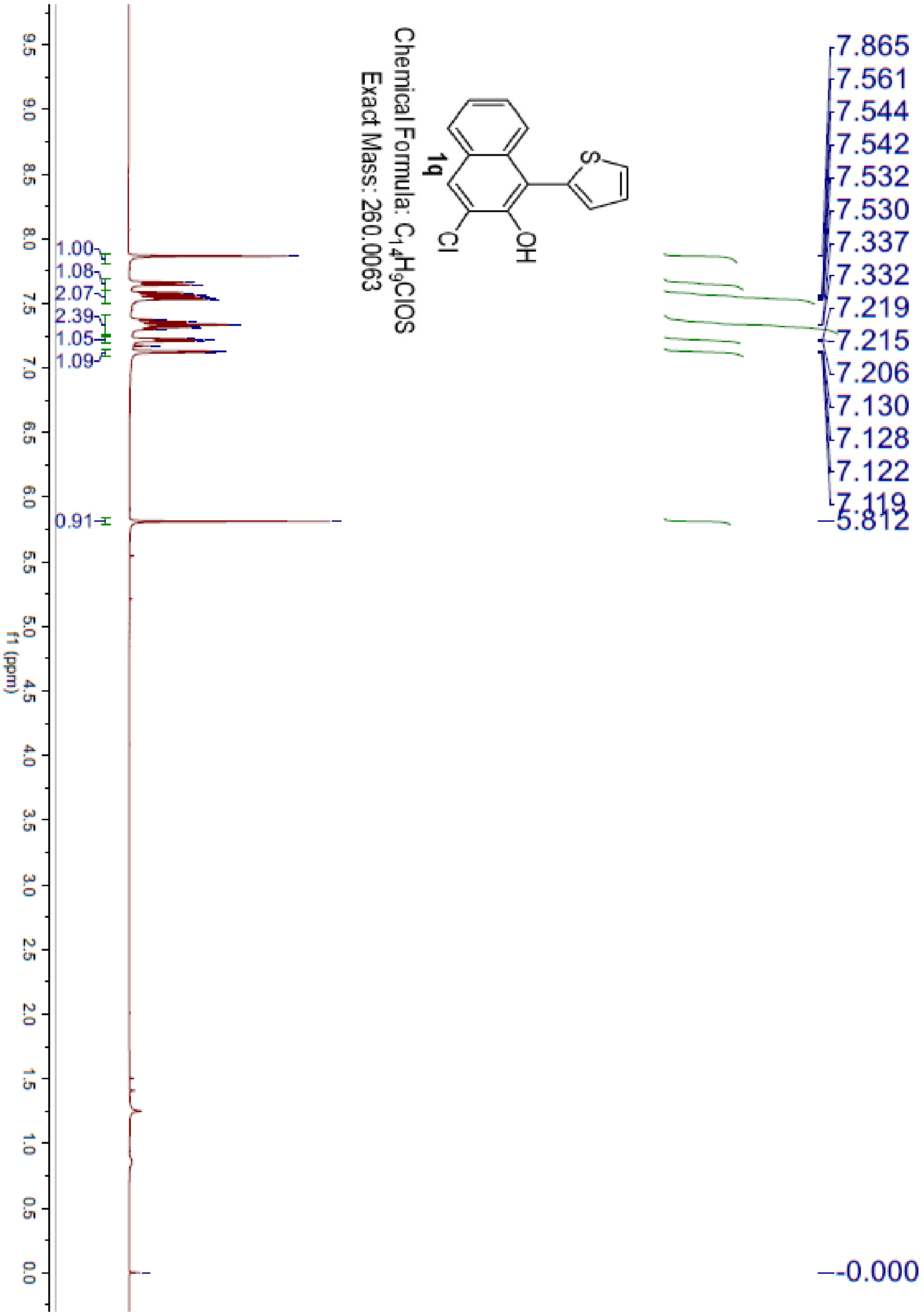




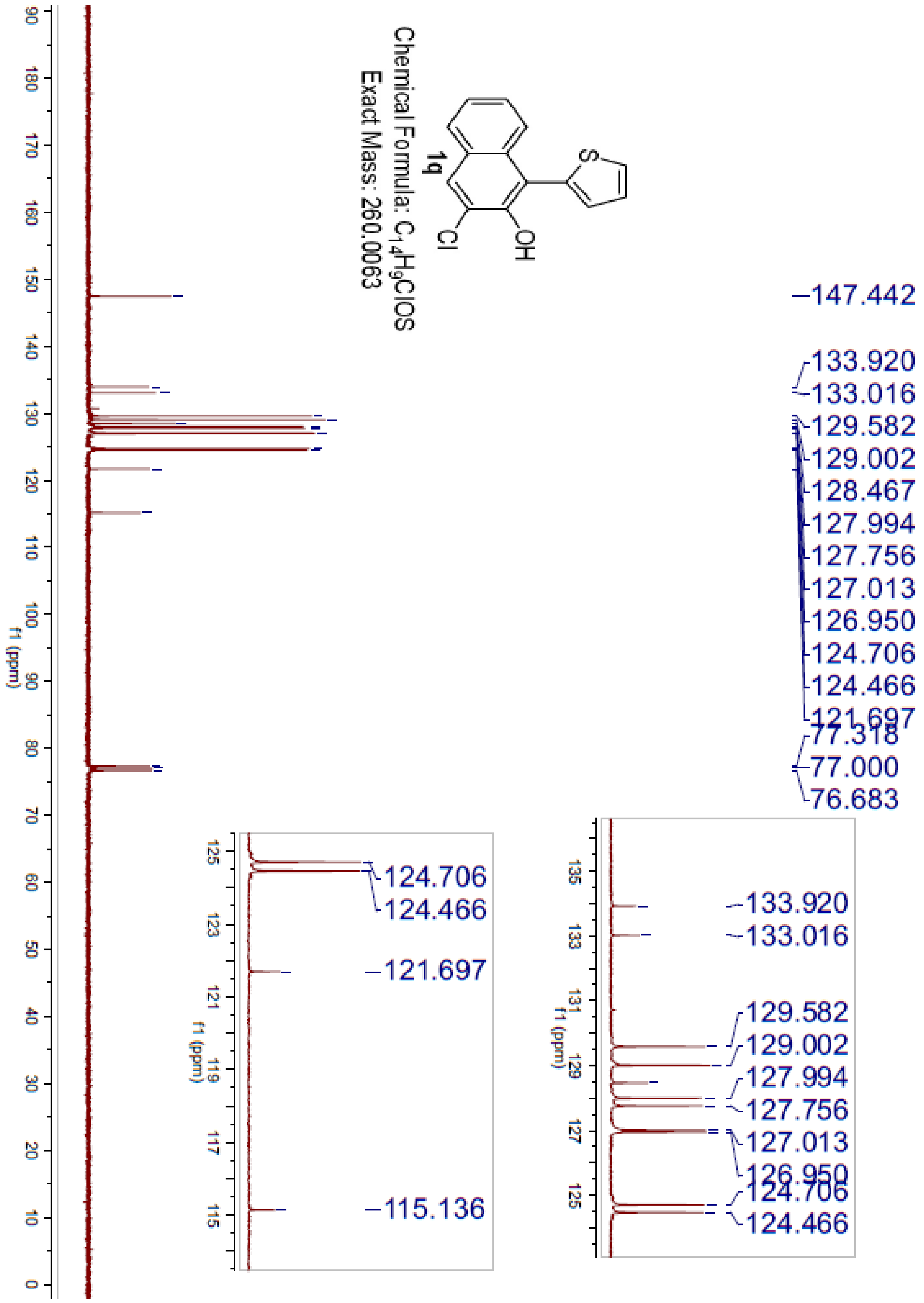


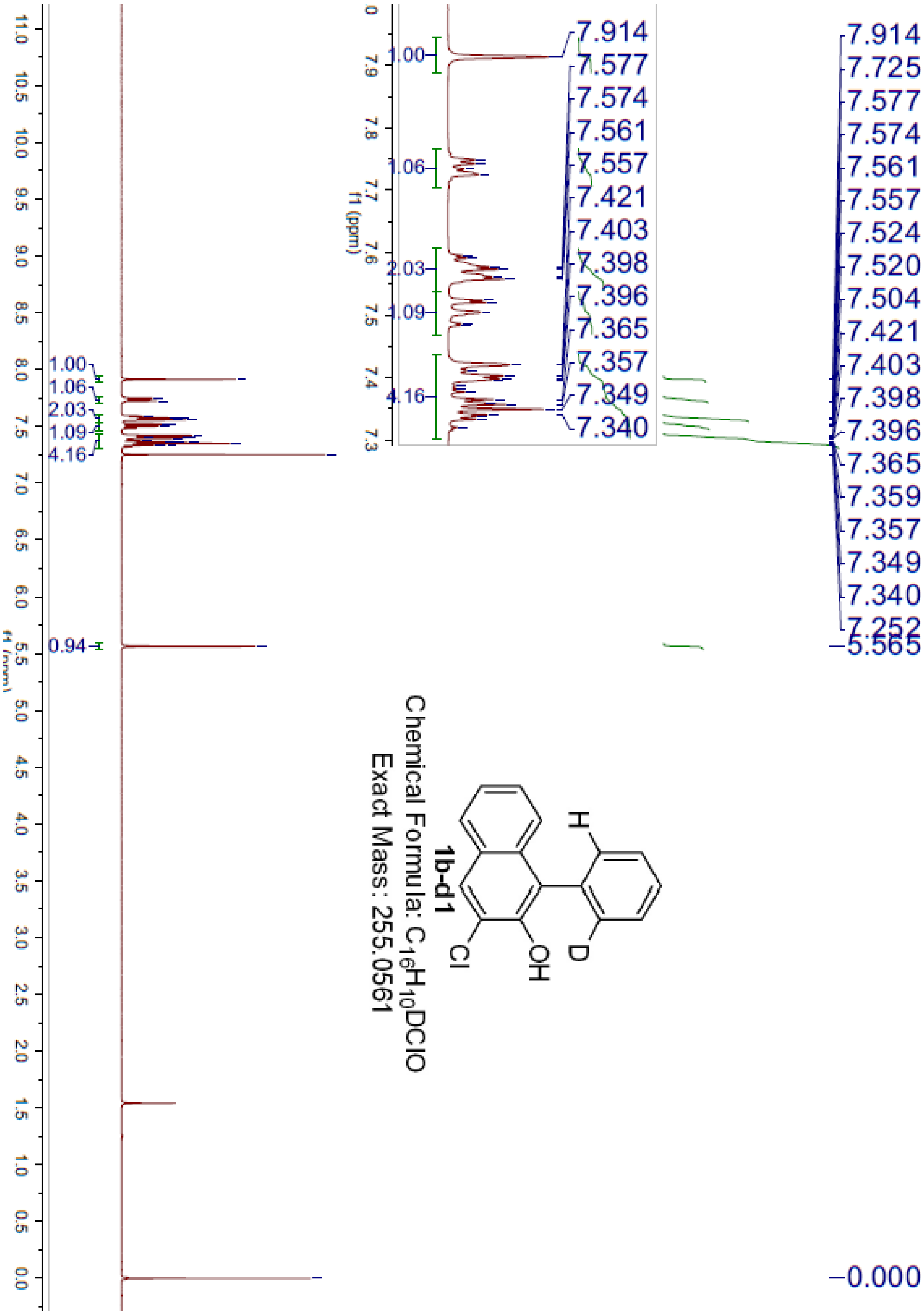
1p
Chemical Formula: C17H11ClO2
Exact Mass: 282.0448
OHC
OH
Cl
10.050
8.199
8.044
7.765
7.577
7.559
7.513
7.494
7.471
7.389
7.387
7.369
6.030
0.000
0.94
1.00
0.92
0.93
3.86
1.88
0.95
f1 (ppm)

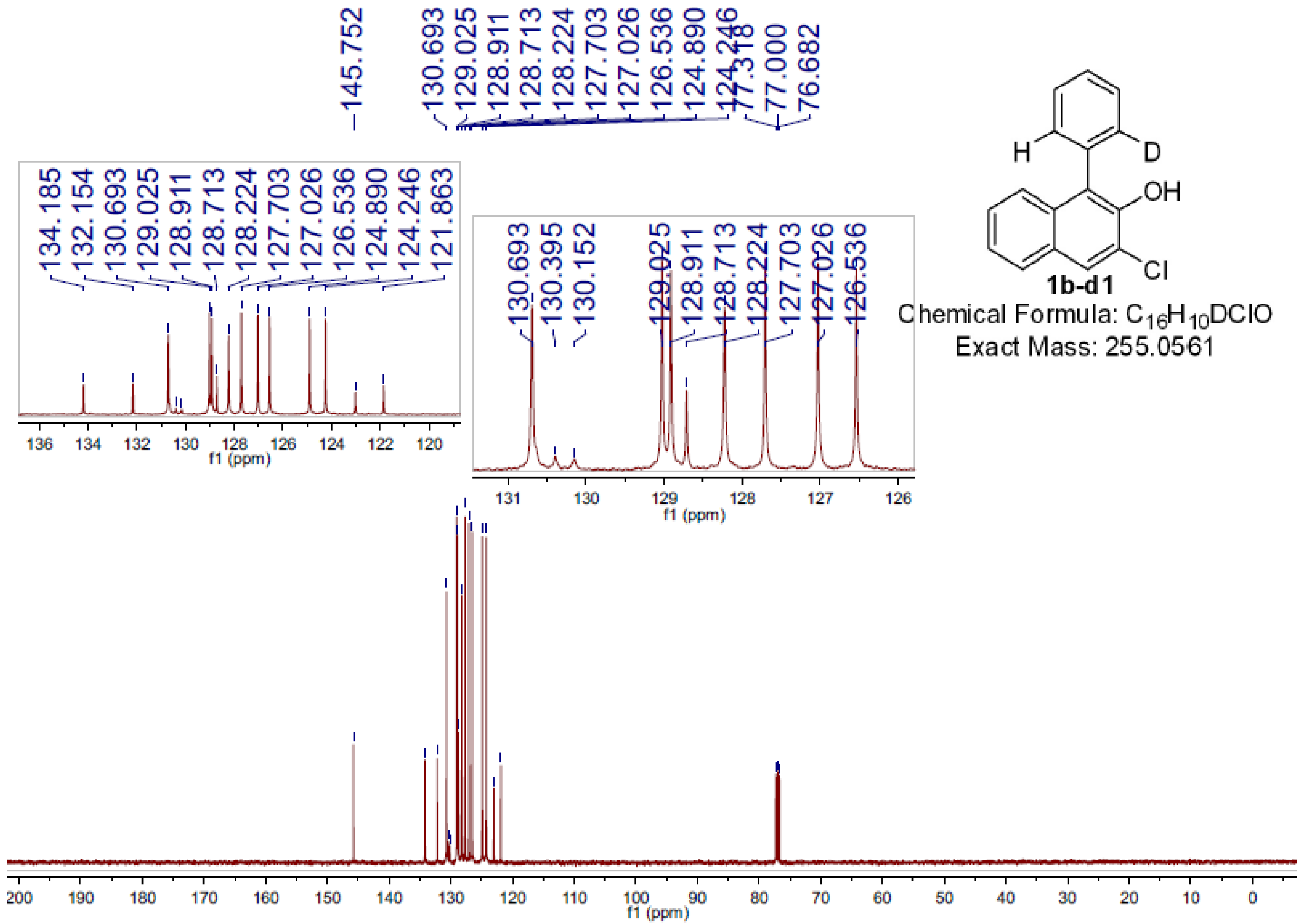

OHC
Cl
OH
1p
Chemical Formula: $C_{17}H_{11}ClO_2$
Exact Mass: 282.0448
191.674
148.672
135.421
133.446
132.564
130.625
129.351
129.298
128.710
127.771
126.028
123.571
77.318
77.000
76.682
135.421
133.446
132.564
130.625
129.351
129.298
128.710
127.771
126.028
123.686
123.571
123.290
f1 (ppm)



1q
Chemical Formula: C14H9ClOS
Exact Mass: 260.0063
OH
Cl
S
7.865
7.561
7.544
7.542
7.532
7.530
7.337
7.332
7.219
7.215
7.206
7.130
7.128
7.122
7.119
5.812
-0.000
1.00
1.08
2.07
2.39
1.05
1.09
0.91
f1 (ppm)


1q
Chemical Formula: C14H9ClOS
Exact Mass: 260.0063
147.442
133.920
133.016
129.582
129.002
128.467
127.994
127.756
127.013
126.950
124.706
124.466
121.697
77.318
77.000
76.683
115.136
f1 (ppm)

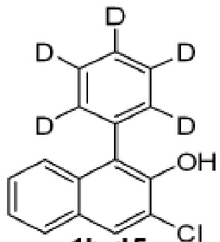

1b-d1
Chemical Formula: C16H10DClO
Exact Mass: 255.0561
H
D
OH
Cl
7.914
7.725
7.577
7.574
7.561
7.557
7.524
7.520
7.504
7.421
7.403
7.398
7.396
7.365
7.359
7.357
7.349
7.340
7.252
5.565
0.000
1.00
1.06
2.03
1.09
4.16
0.94
f1 (ppm)



1b-d1

Chemical Formula: $C_{16}H_{10}DClO$

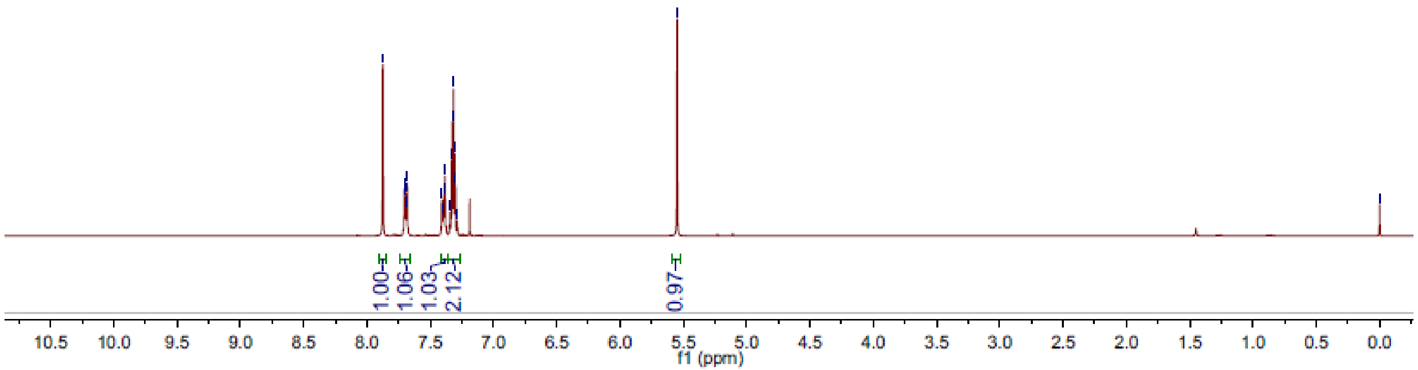
Exact Mass: 255.0561

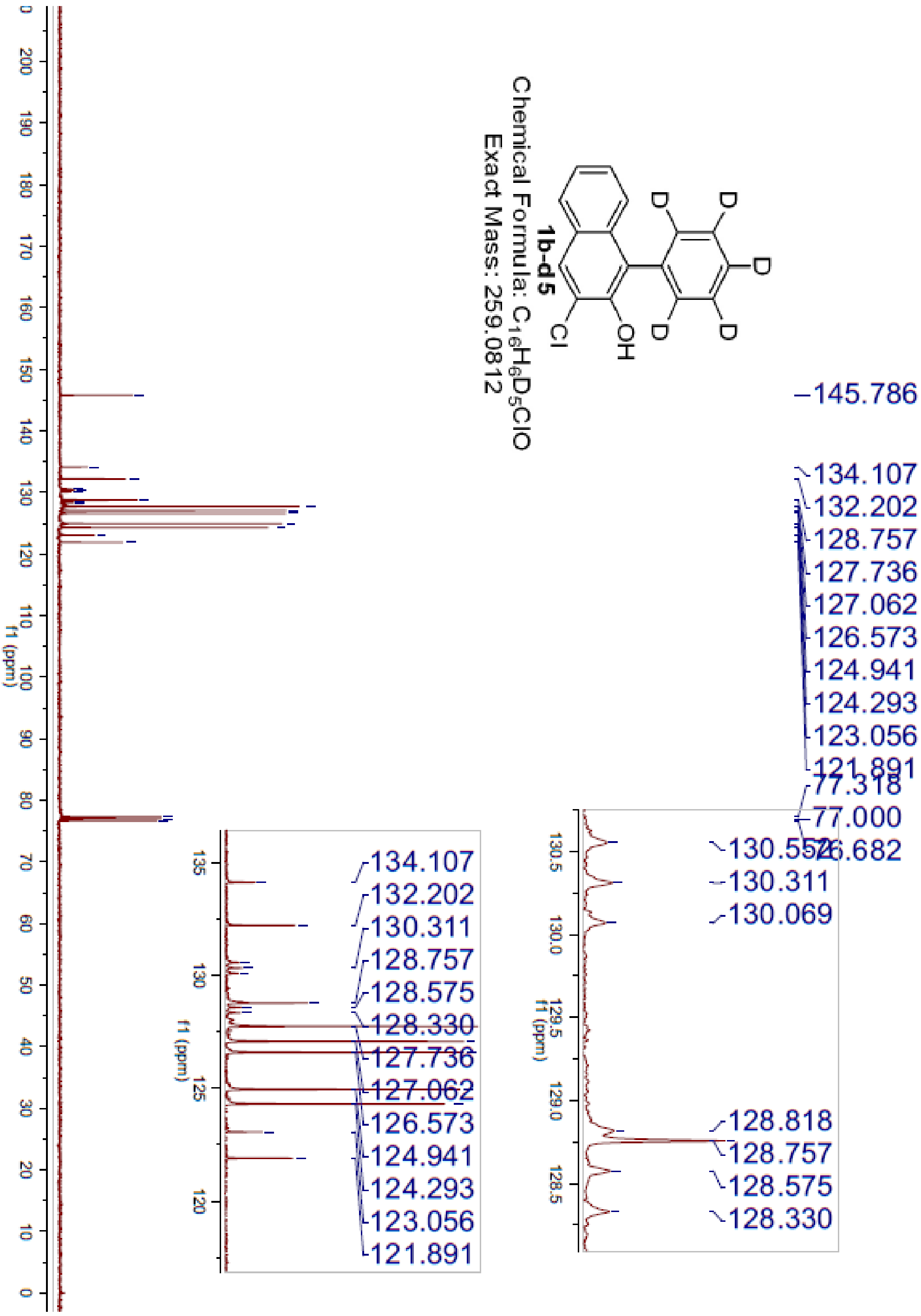


1b-d5

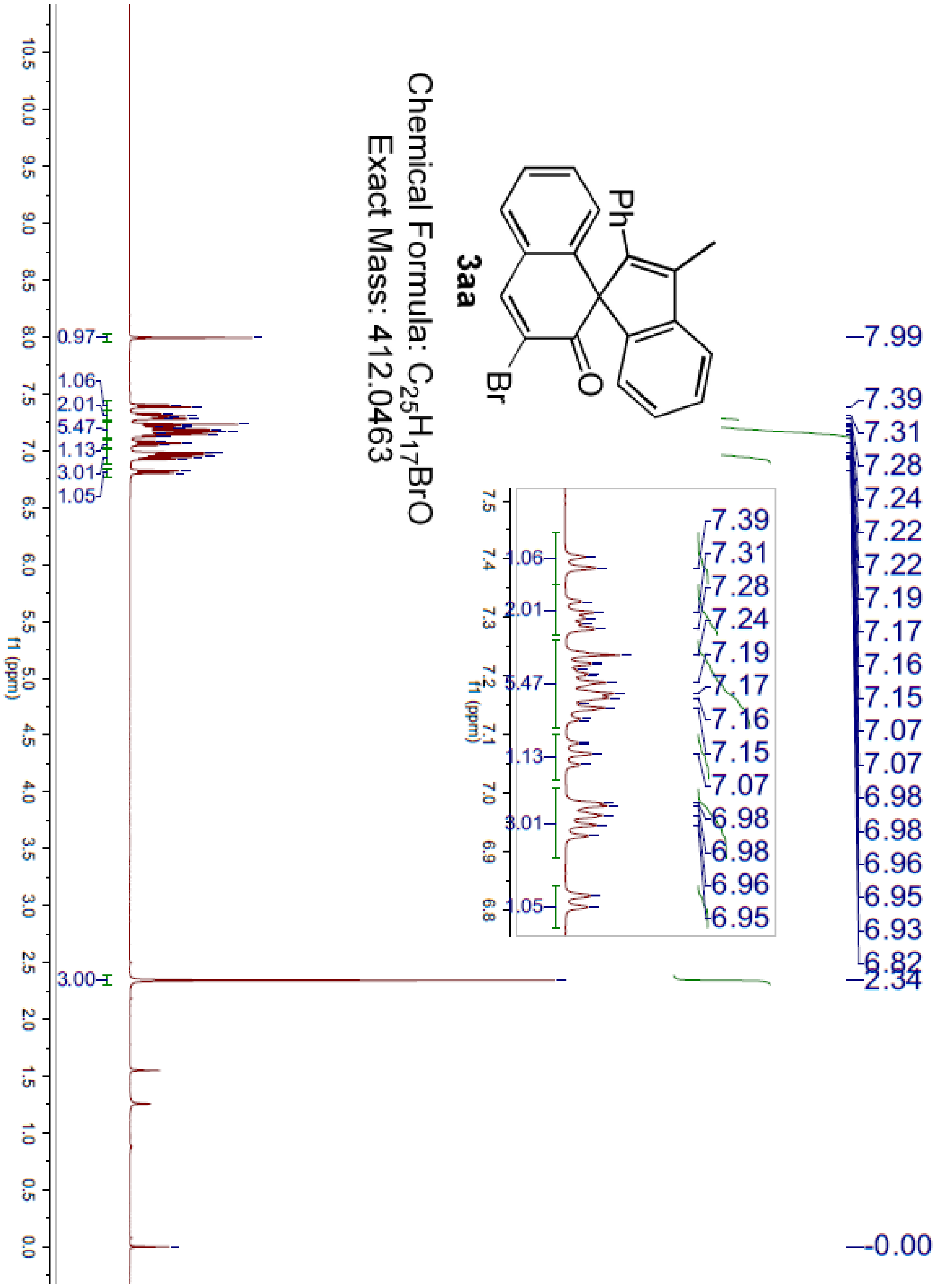
Chemical Formula: $C_{16}H_6D_5ClO$

Exact Mass: 259.0812





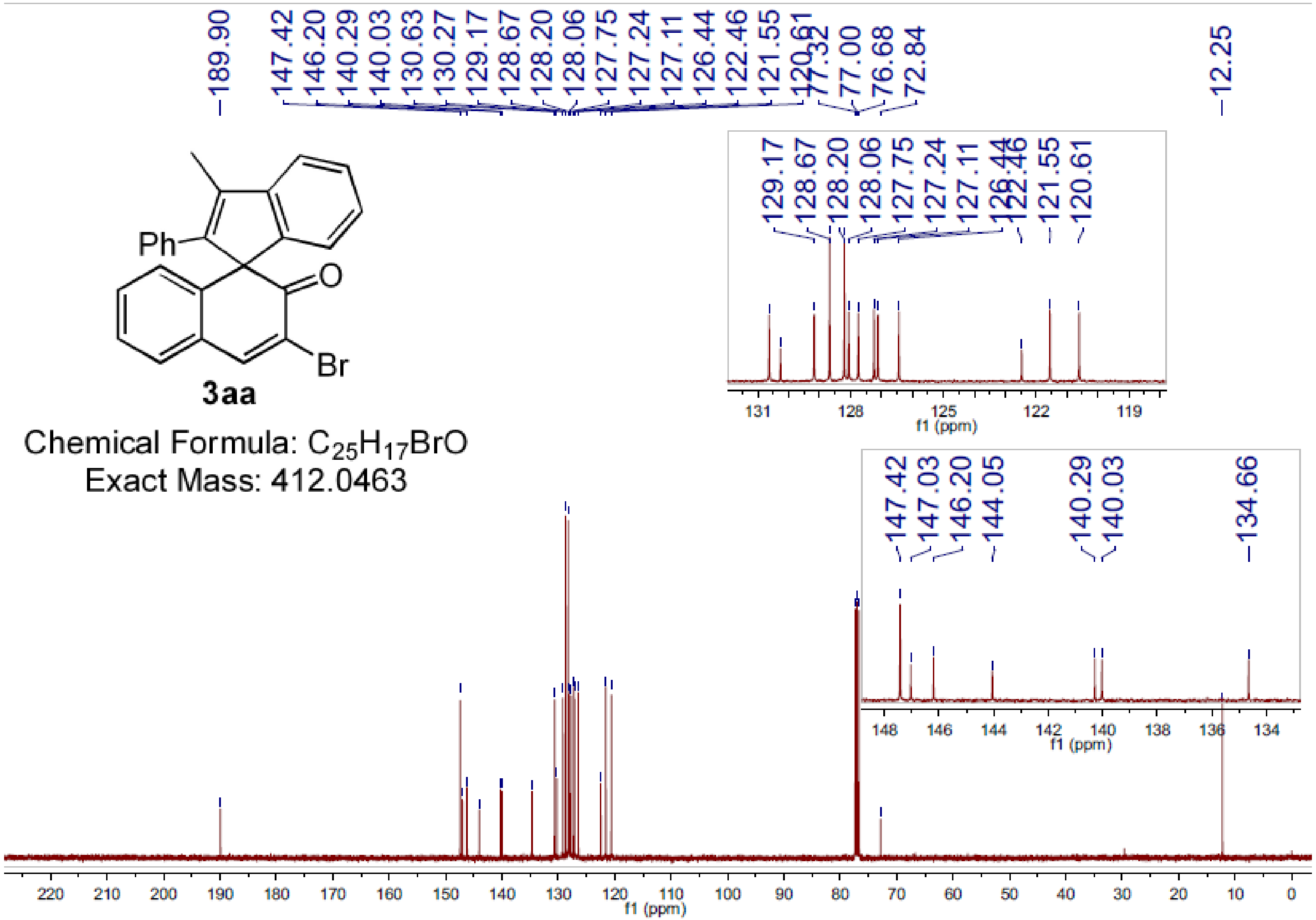
1b-d5
Chemical Formula: $C_{16}H_6D_5ClO$
Exact Mass: 259.0812
D
D
D
D
D
OH
Cl
145.786
134.107
132.202
128.757
127.736
127.062
126.573
124.941
124.293
123.056
121.891
77.318
77.000
76.682
130.552
130.311
130.069
128.818
128.757
128.575
128.330
134.107
132.202
130.311
128.757
128.575
128.330
127.736
127.062
126.573
124.941
124.293
123.056
121.891
f1 (ppm)

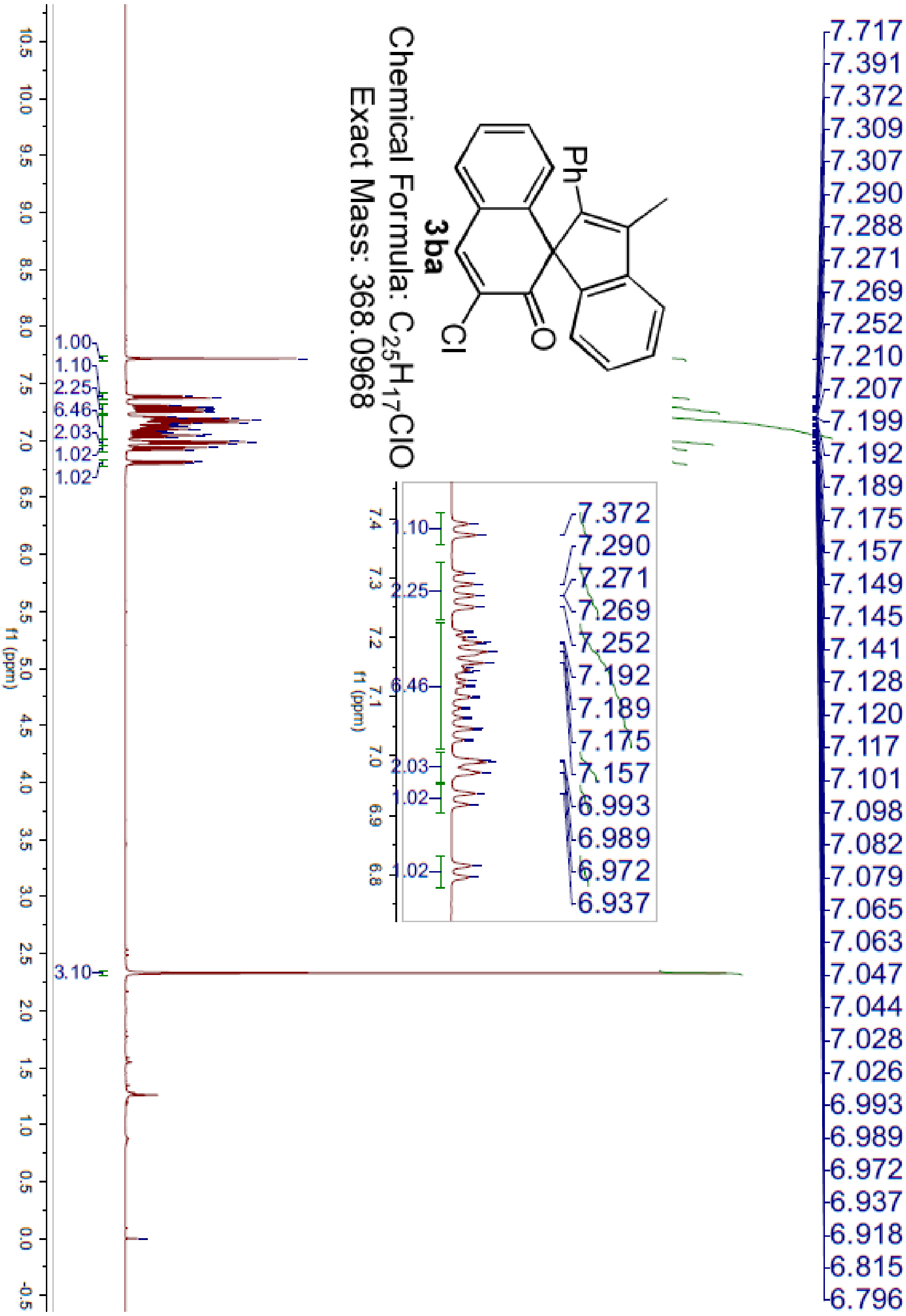

3aa
Chemical Formula: C25H17BrO
Exact Mass: 412.0463
Ph
Br
O
f1 (ppm)

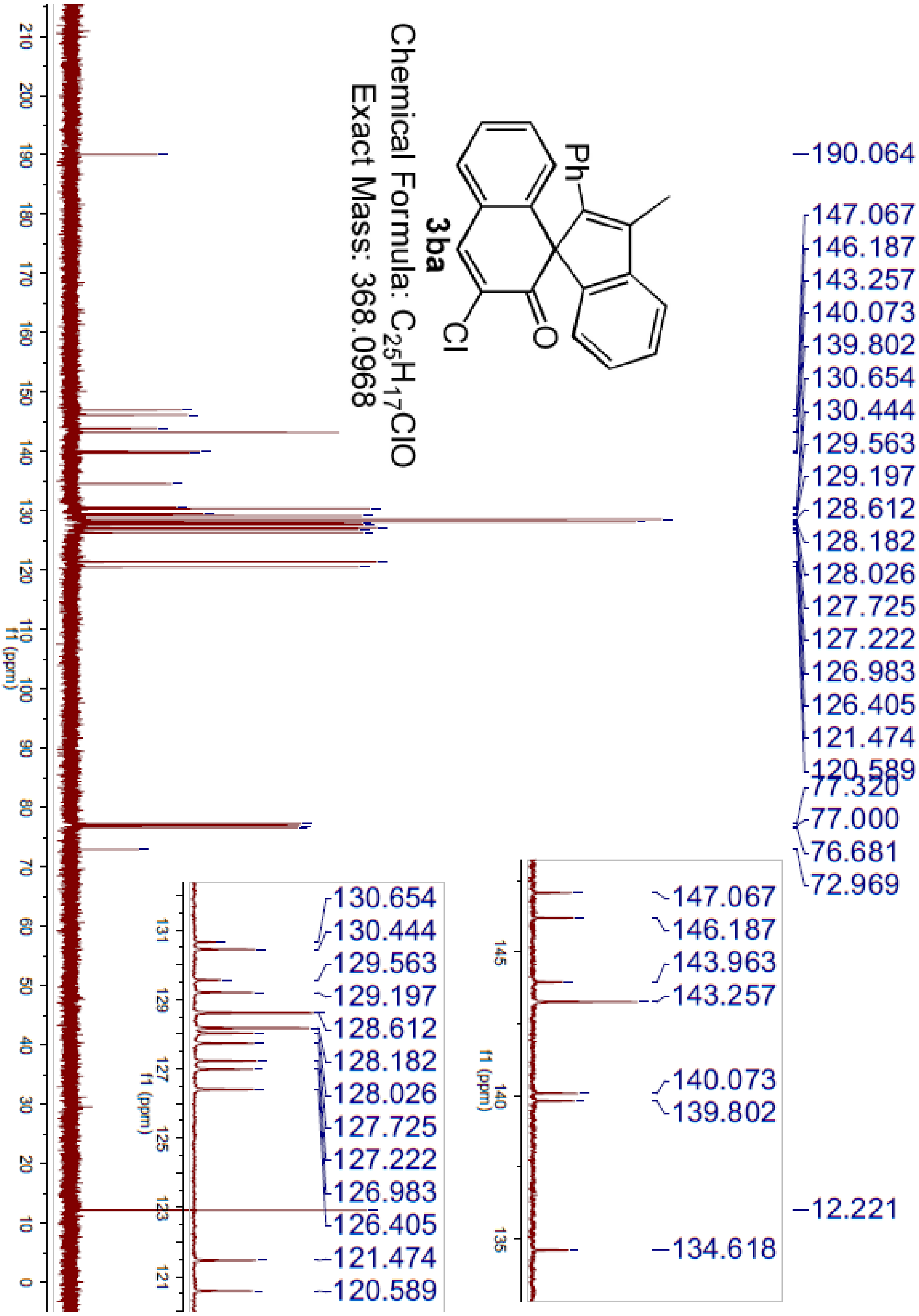
3aa

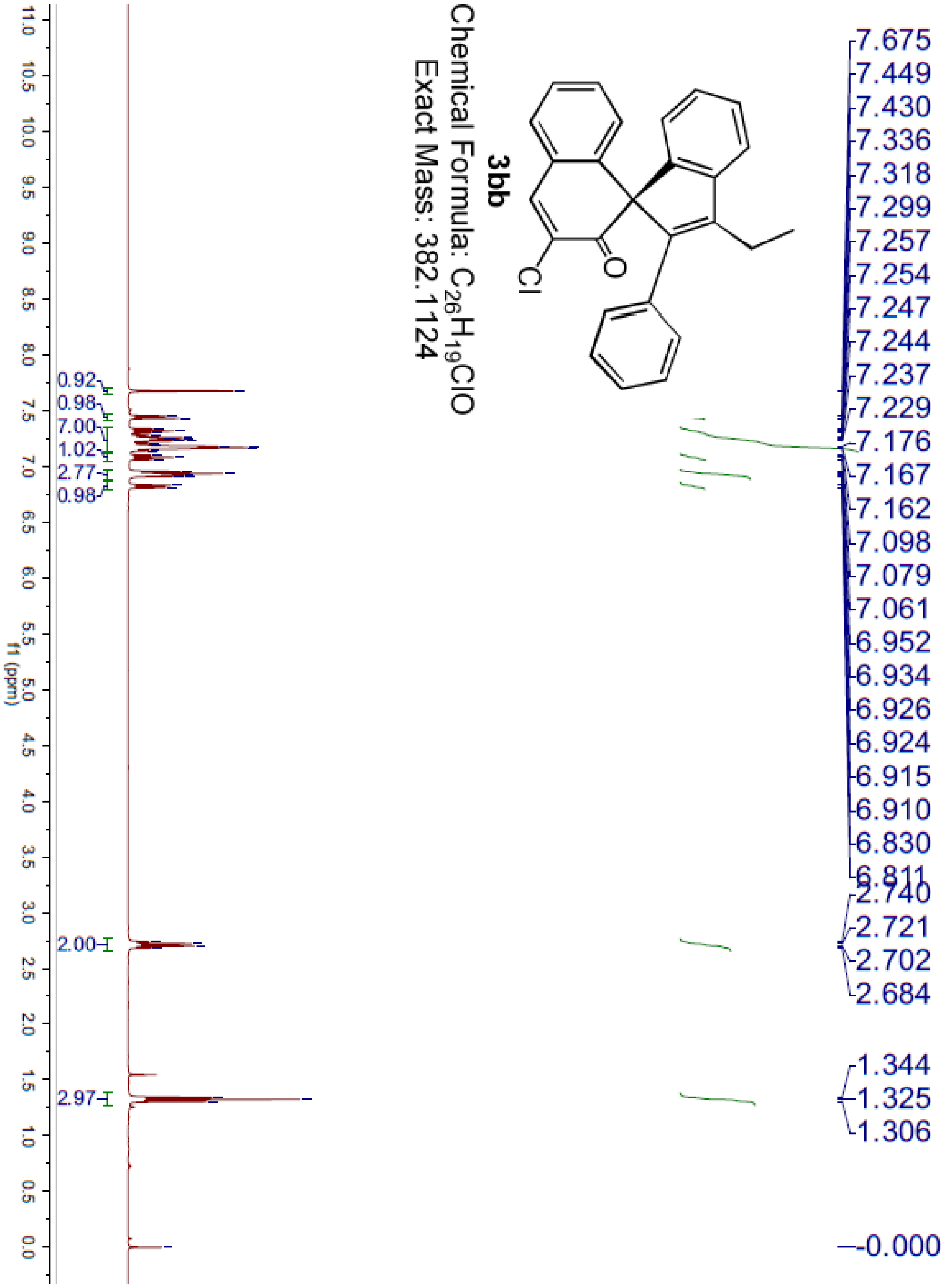
Chemical Formula: $C_{25}H_{17}BrO$

Exact Mass: 412.0463

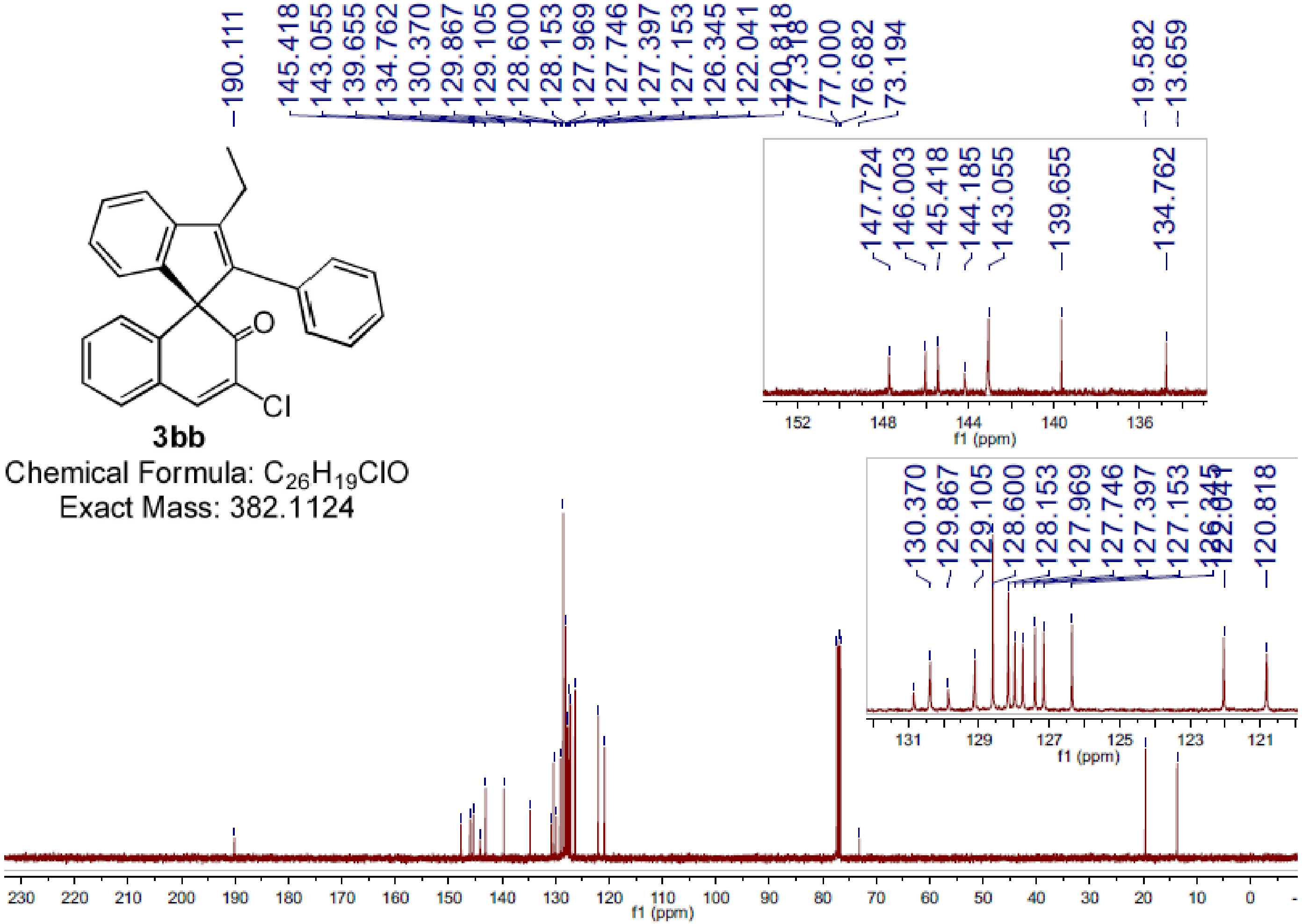



7.717
7.391
7.372
7.309
7.307
7.290
7.288
7.271
7.269
7.252
7.210
7.207
7.199
7.192
7.189
7.175
7.157
7.149
7.145
7.141
7.128
7.120
7.117
7.101
7.098
7.082
7.079
7.065
7.063
7.047
7.044
7.028
7.026
6.993
6.989
6.972
6.937
6.918
6.815
6.796
Ph
Cl
O
3ba
Chemical Formula: C25H17ClO
Exact Mass: 368.0968
f1 (ppm)


Ph
O
Cl
3ba
Chemical Formula: C25H17ClO
Exact Mass: 368.0968
190.064
147.067
146.187
143.257
140.073
139.802
130.654
130.444
129.563
129.197
128.612
128.182
128.026
127.725
127.222
126.983
126.405
121.474
120.589
77.320
77.000
76.681
72.969
12.221
143.963
134.618
f1 (ppm)



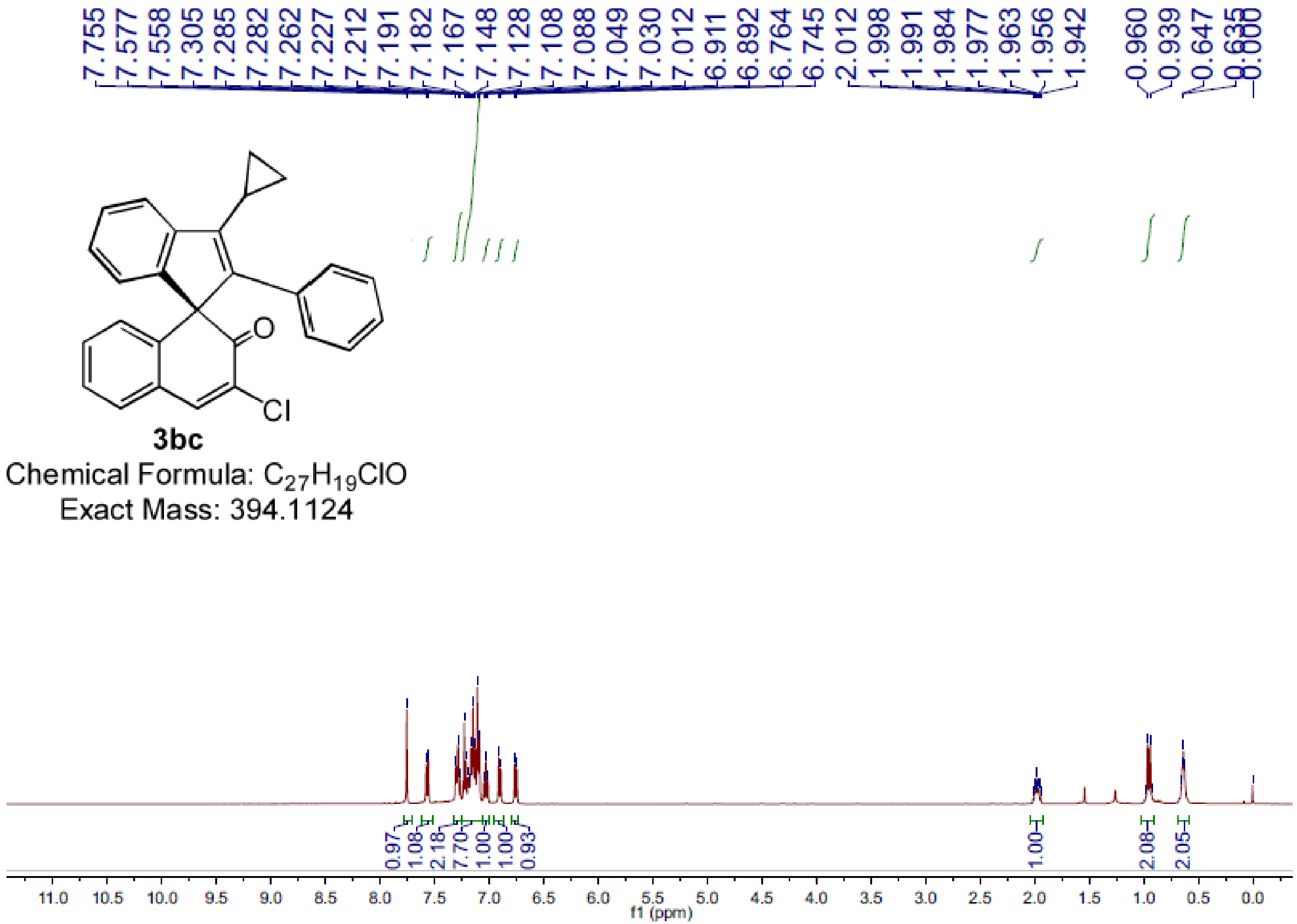
3bb
Chemical Formula: $C_{26}H_{19}ClO$
Exact Mass: 382.1124
O
Cl
7.675
7.449
7.430
7.336
7.318
7.299
7.257
7.254
7.247
7.244
7.237
7.229
7.176
7.167
7.162
7.098
7.079
7.061
6.952
6.934
6.926
6.924
6.915
6.910
6.830
6.811
2.740
2.721
2.702
2.684
1.344
1.325
1.306
-0.000
0.92
0.98
7.00
1.02
2.77
0.98
2.00
2.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



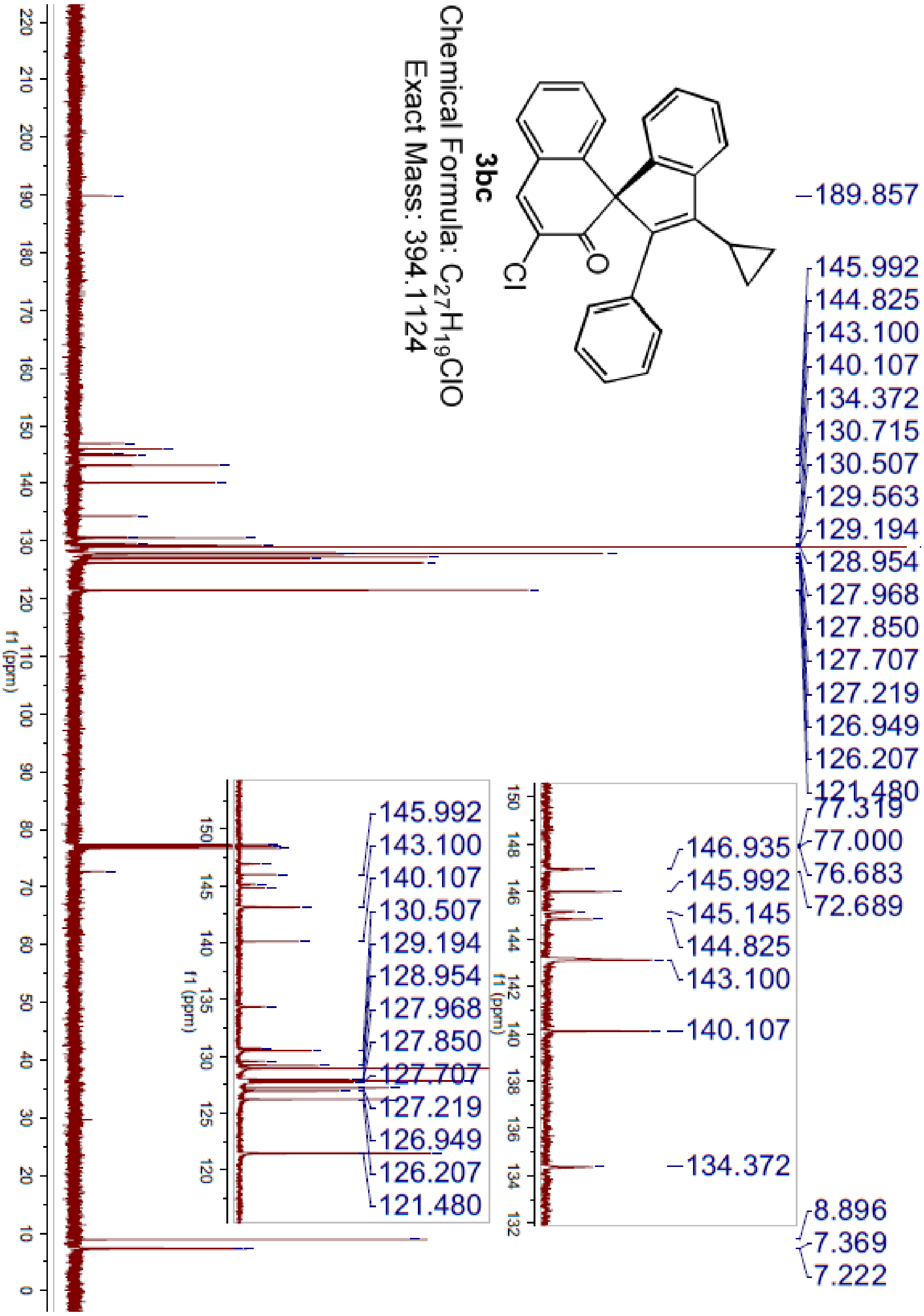
3bb

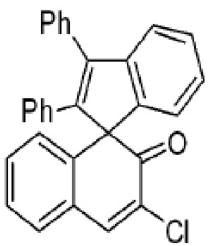
Chemical Formula: $C_{26}H_{19}ClO$

Exact Mass: 382.1124



3bc
Chemical Formula: $C_{27}H_{19}ClO$
Exact Mass: 394.1124

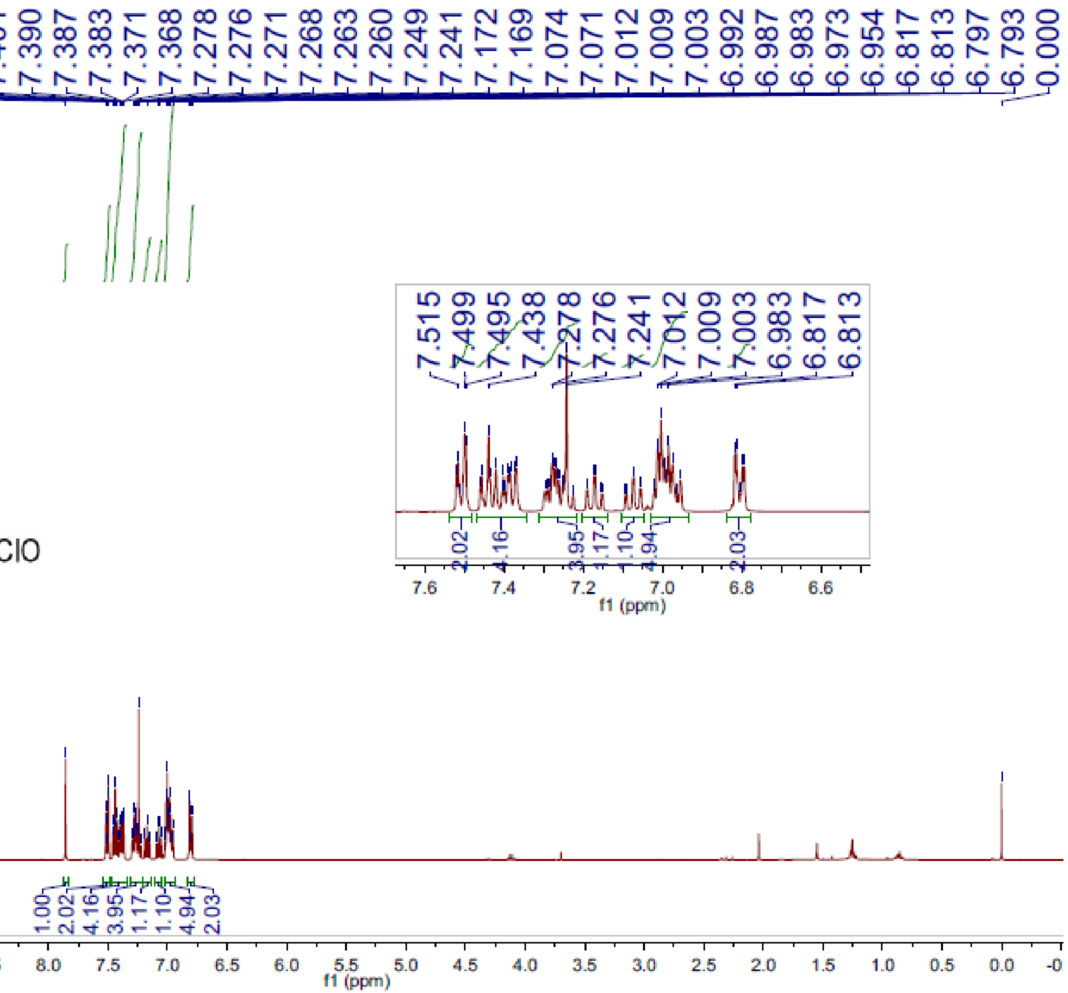

3bc
Chemical Formula: $C_{27}H_{19}ClO$
Exact Mass: 394.1124
189.857
145.992
144.825
143.100
140.107
134.372
130.715
130.507
129.563
129.194
128.954
127.968
127.850
127.707
127.219
126.949
126.207
121.480
77.319
77.000
76.683
72.689
8.896
7.369
7.222
146.935
145.992
145.145
144.825
143.100
140.107
134.372
f1 (ppm)

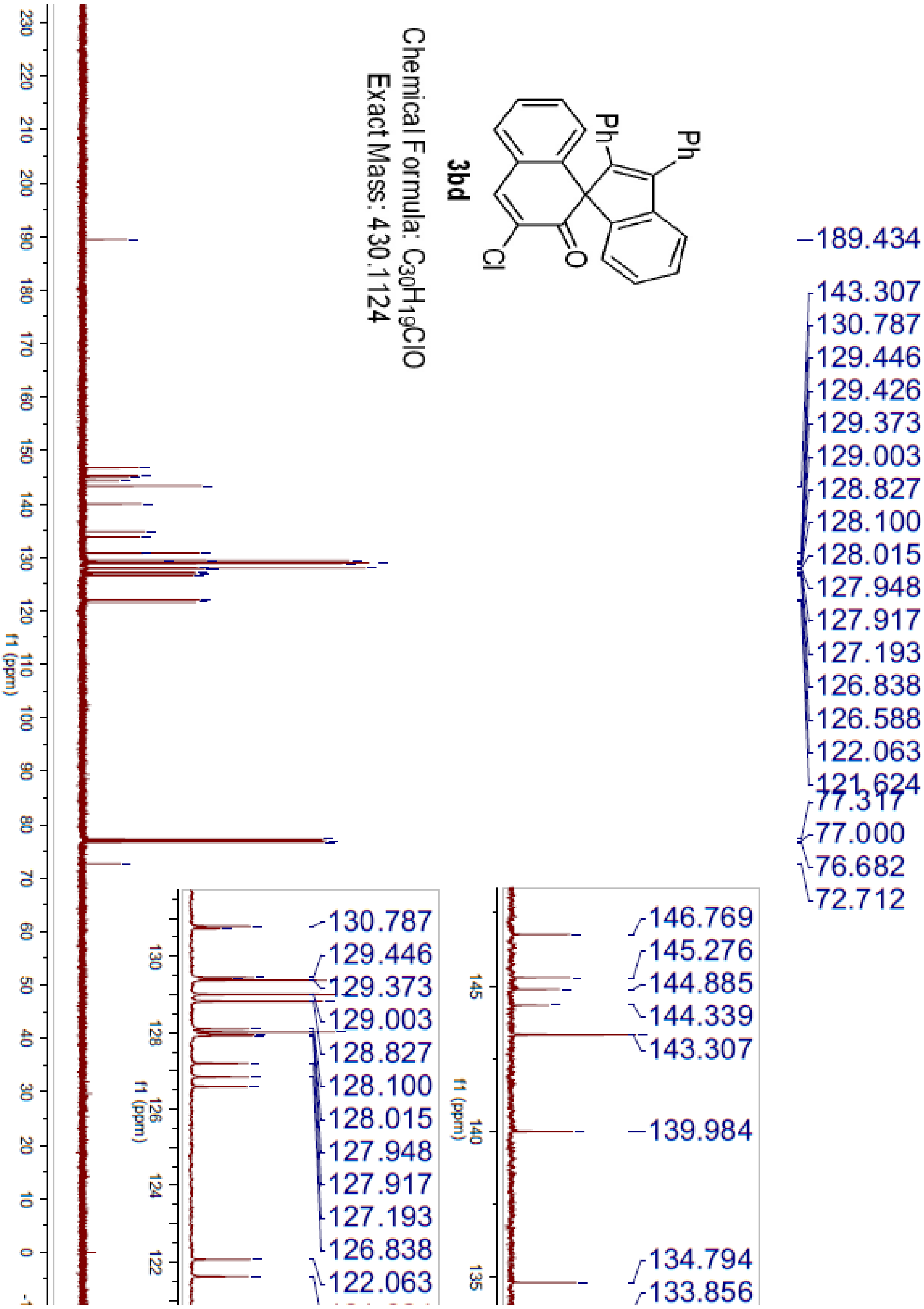


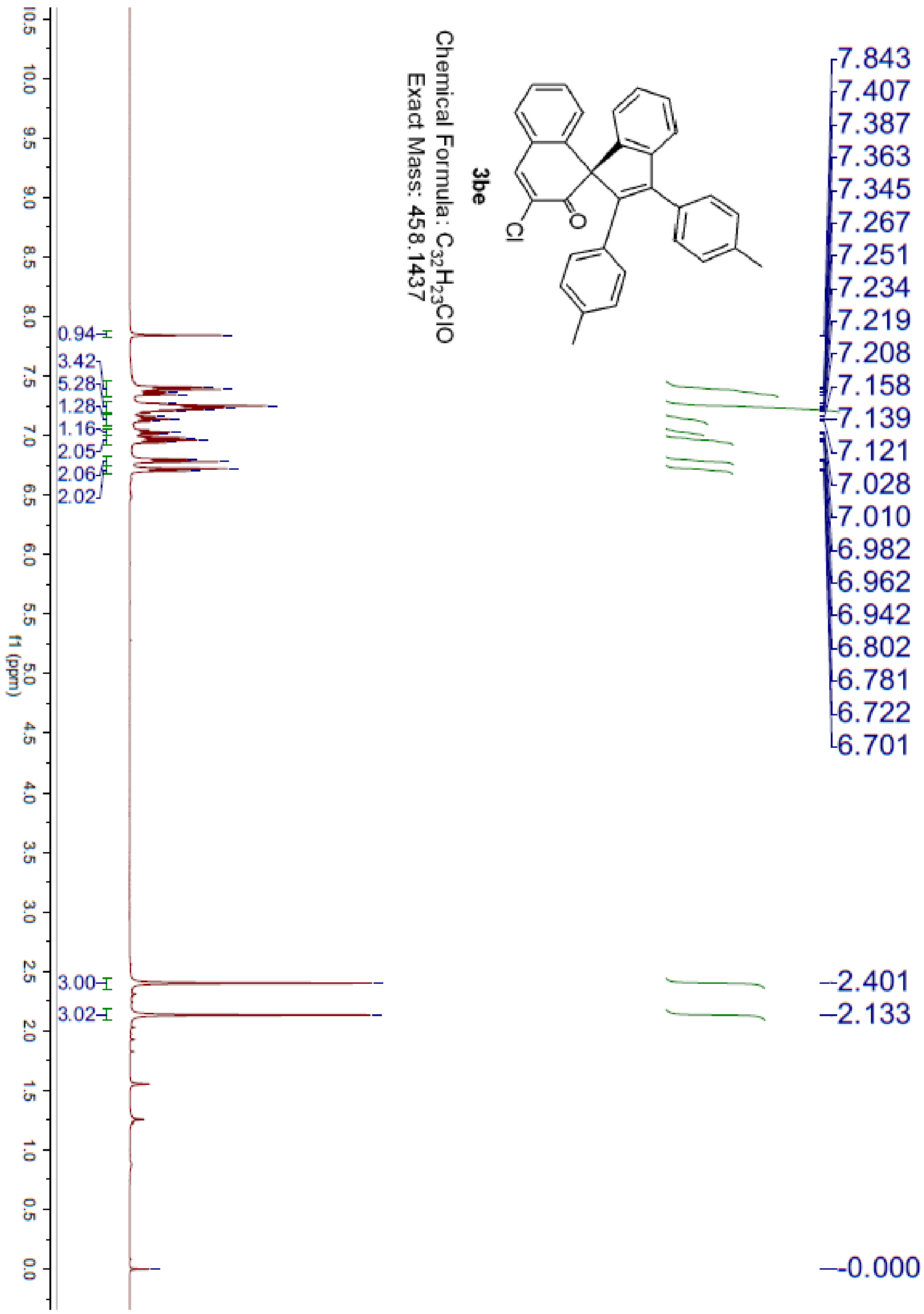
3bd

Chemical Formula: $C_{30}H_{19}ClO$

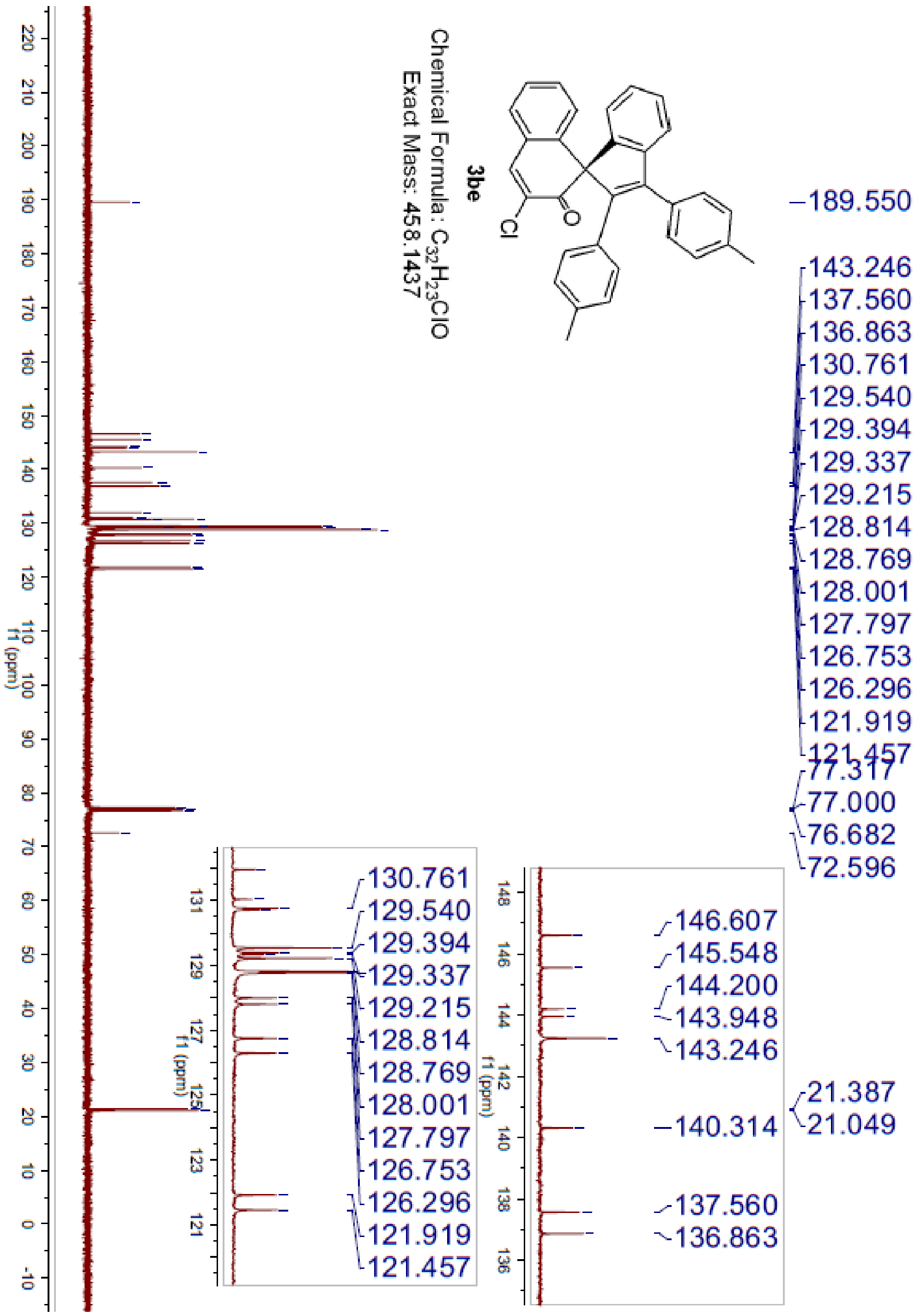
Exact Mass: 430.1124



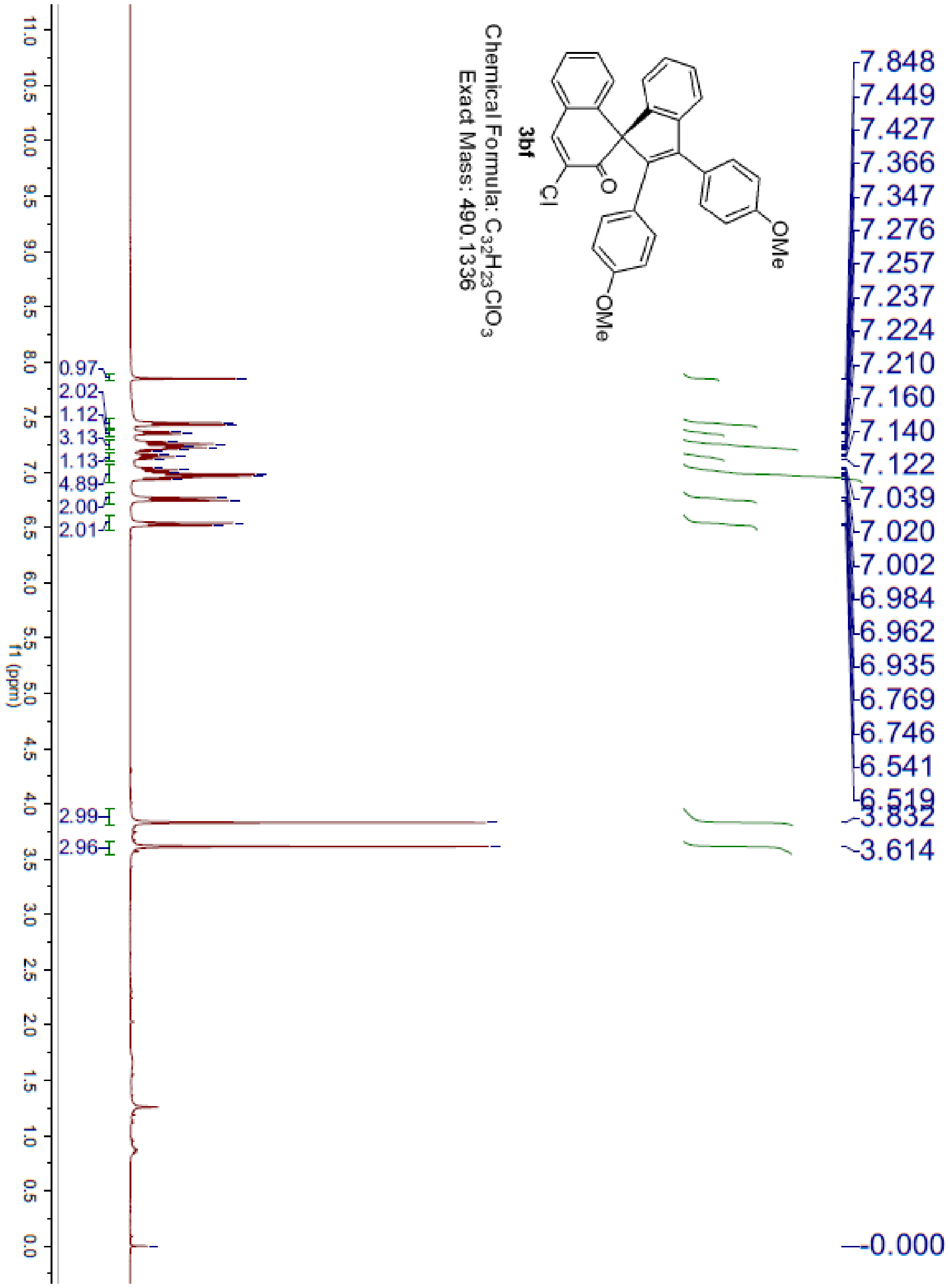

3bd
Chemical Formula: $C_{30}H_{19}ClO$
Exact Mass: 430.1124
Ph
Ph
O
Cl
189.434
143.307
130.787
129.446
129.426
129.373
129.003
128.827
128.100
128.015
127.948
127.917
127.193
126.838
126.588
122.063
121.624
77.317
77.000
76.682
72.712
146.769
145.276
144.885
144.339
143.307
139.984
134.794
133.856
f1 (ppm)



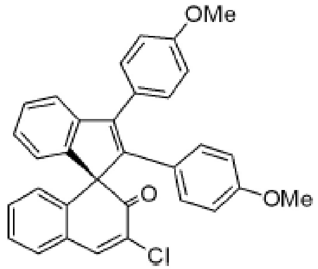
3be
Chemical Formula: C32H23ClO
Exact Mass: 458.1437
Cl
O
7.843
7.407
7.387
7.363
7.345
7.267
7.251
7.234
7.219
7.208
7.158
7.139
7.121
7.028
7.010
6.982
6.962
6.942
6.802
6.781
6.722
6.701
2.401
2.133
-0.000
0.94
3.42
5.28
1.28
1.16
2.05
2.06
2.02
3.00
3.02
f1 (ppm)



3be
Chemical Formula: $C_{32}H_{23}ClO$
Exact Mass: 458.1437
O
Cl
189.550
143.246
137.560
136.863
130.761
129.540
129.394
129.337
129.215
128.814
128.769
128.001
127.797
126.753
126.296
121.919
121.457
77.317
77.000
76.682
72.596
21.387
21.049
146.607
145.548
144.200
143.948
143.246
140.314
137.560
136.863
f1 (ppm)

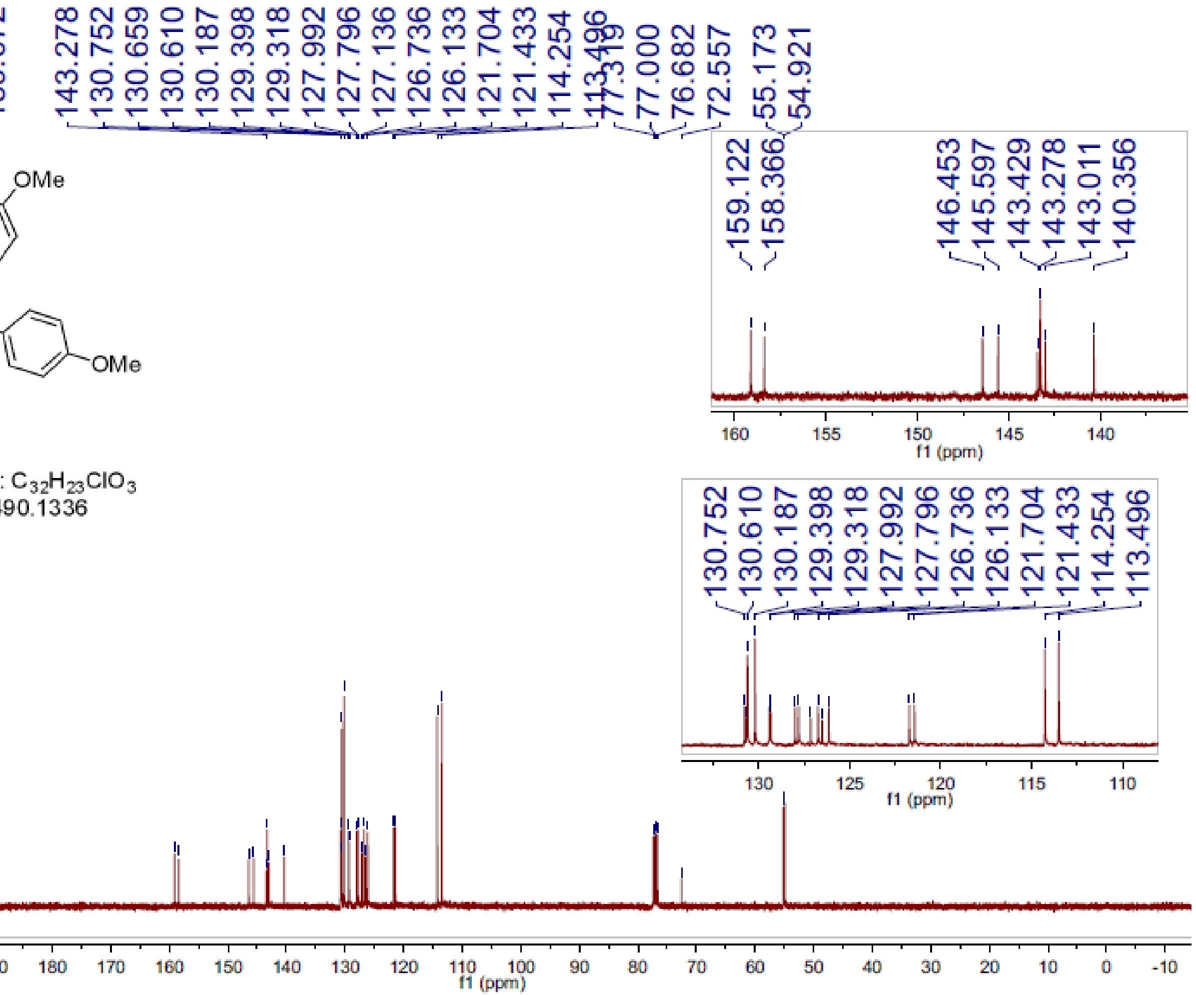


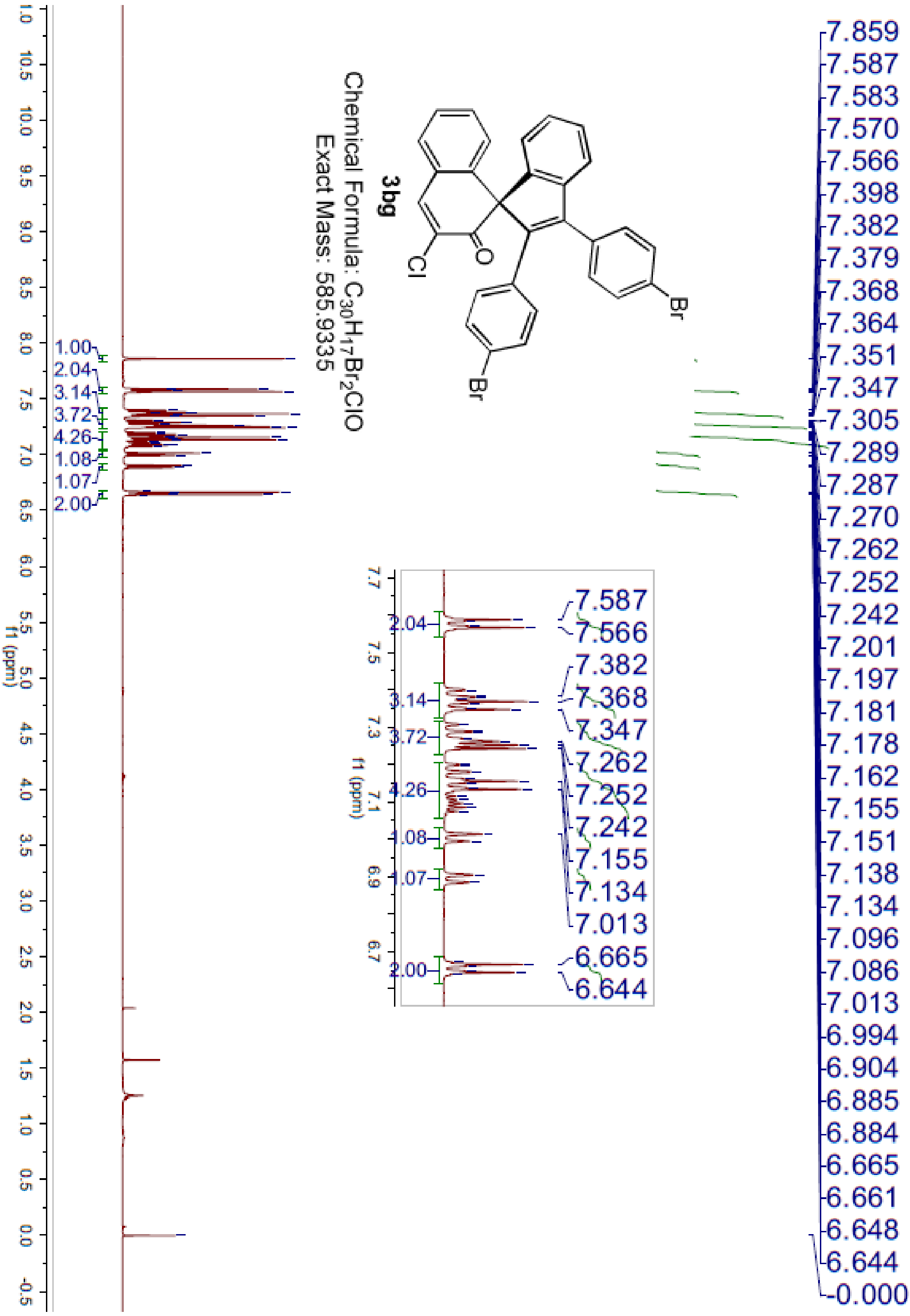
3bf
Chemical Formula: $C_{32}H_{23}ClO_3$
Exact Mass: 490.1336
7.848
7.449
7.427
7.366
7.347
7.276
7.257
7.237
7.224
7.210
7.160
7.140
7.122
7.039
7.020
7.002
6.984
6.962
6.935
6.769
6.746
6.541
6.519
3.832
3.614
-0.000
0.97
2.02
1.12
3.13
1.13
4.89
2.00
2.01
2.99
2.96
f1 (ppm)

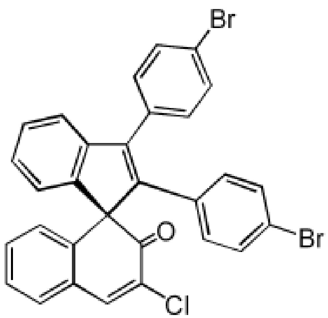


3bf

Chemical Formula: $C_{32}H_{23}ClO_3$
Exact Mass: 490.1336



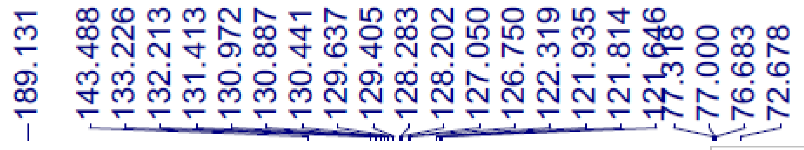
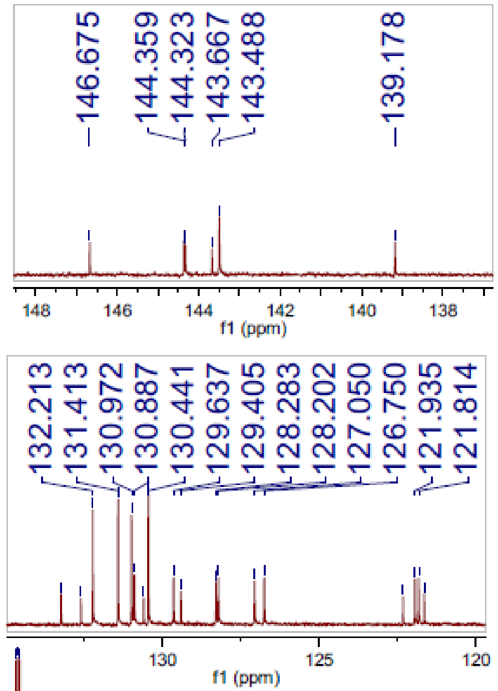
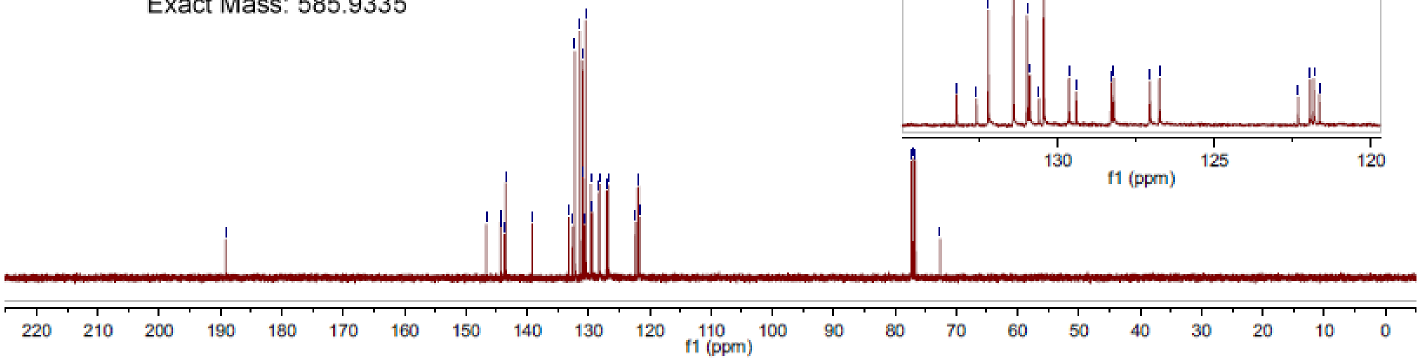

3bg
Chemical Formula: C30H17Br2ClO
Exact Mass: 585.9335
Br
Br
Cl
O
7.859
7.587
7.583
7.570
7.566
7.398
7.382
7.379
7.368
7.364
7.351
7.347
7.305
7.289
7.287
7.270
7.262
7.252
7.242
7.201
7.197
7.181
7.178
7.162
7.155
7.151
7.138
7.134
7.096
7.086
7.013
6.994
6.904
6.885
6.884
6.665
6.661
6.648
6.644
-0.000
1.00
2.04
3.14
3.72
4.26
1.08
1.07
2.00
f1 (ppm)

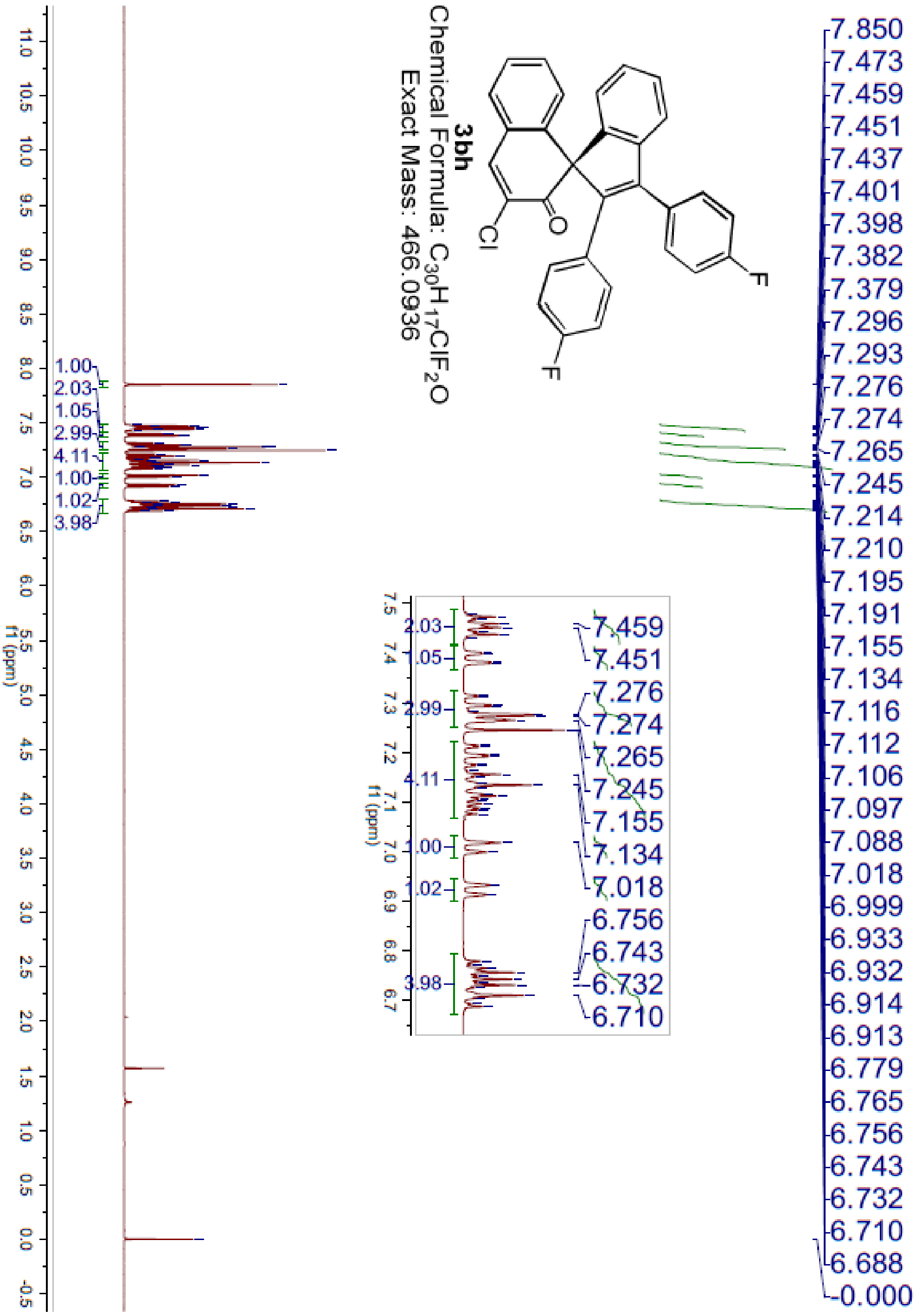


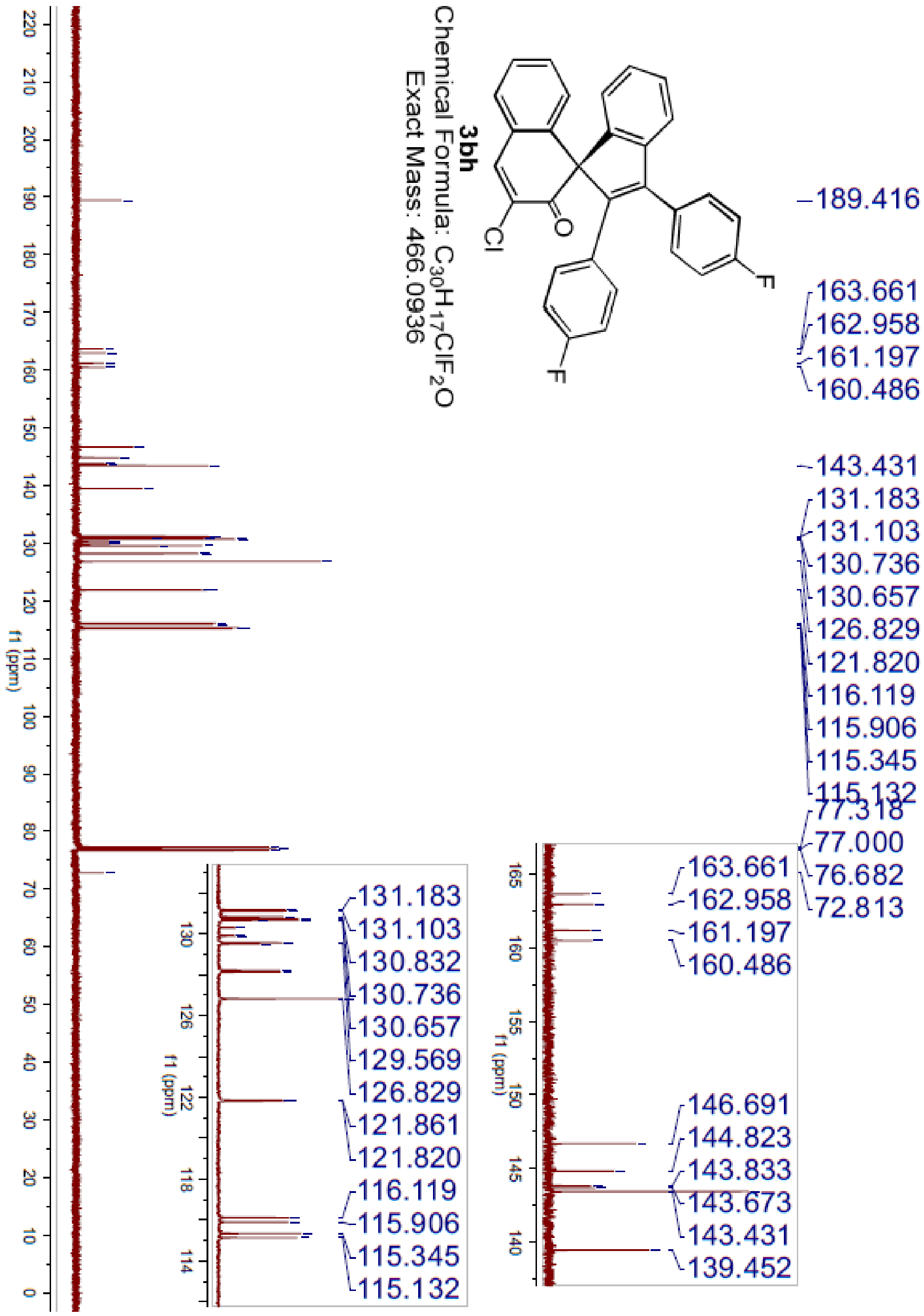
3bg

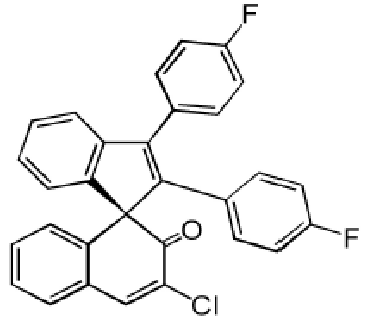
Chemical Formula: $C_{30}H_{17}Br_2ClO$

Exact Mass: 585.9335

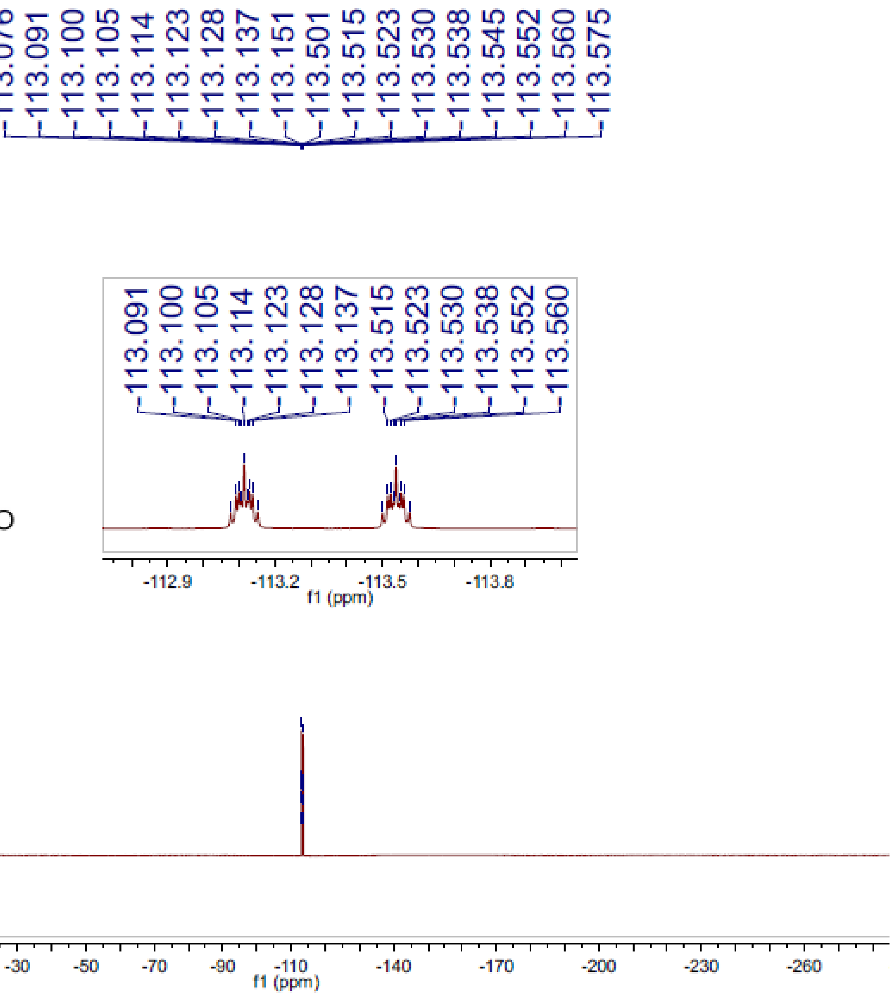




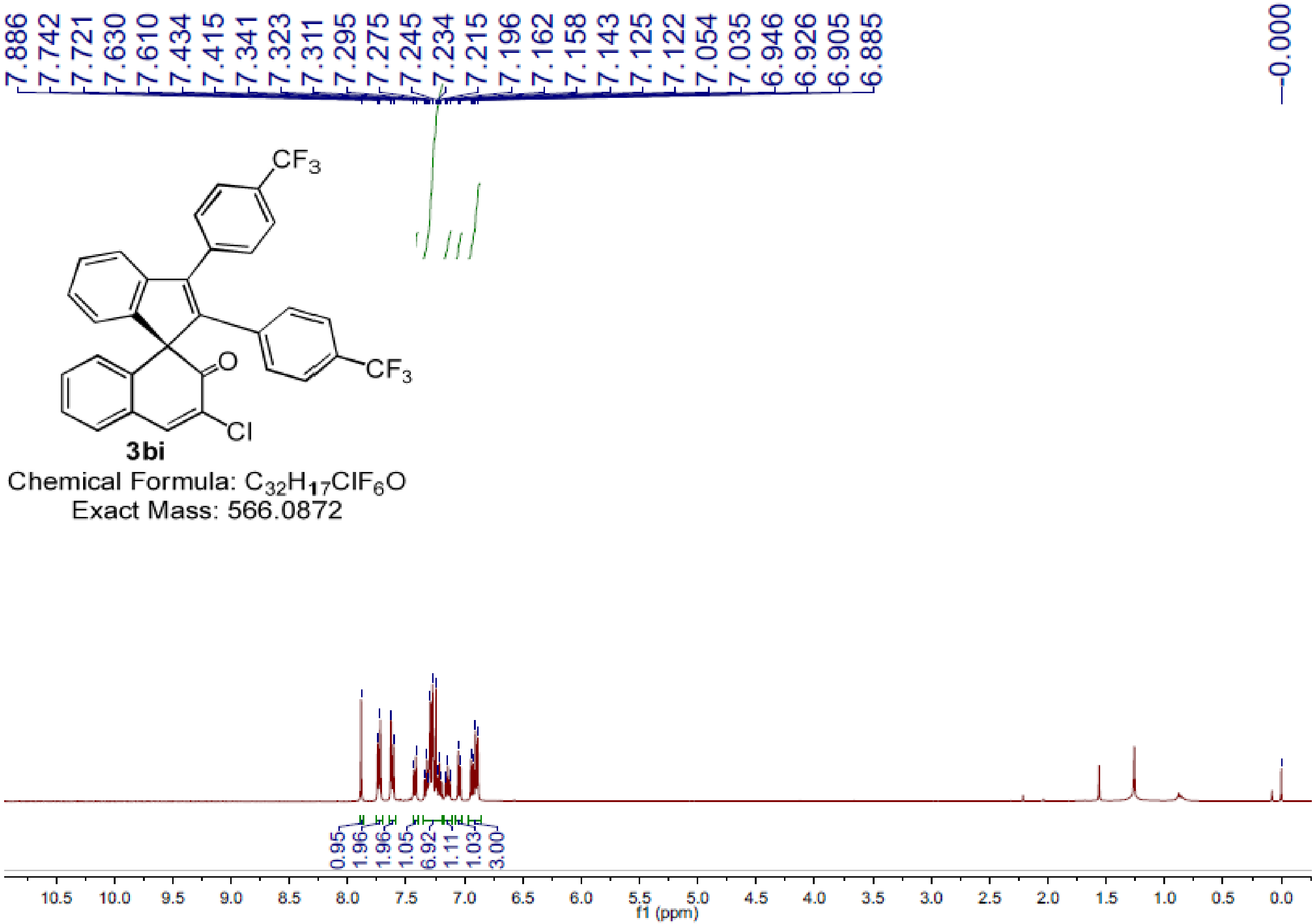

3bh
Chemical Formula: C30H17ClF2O
Exact Mass: 466.0936
7.850
7.473
7.459
7.451
7.437
7.401
7.398
7.382
7.379
7.296
7.293
7.276
7.274
7.265
7.245
7.214
7.210
7.195
7.191
7.155
7.134
7.116
7.112
7.106
7.097
7.088
7.018
6.999
6.933
6.932
6.914
6.913
6.779
6.765
6.756
6.743
6.732
6.710
6.688
-0.000
f1 (ppm)

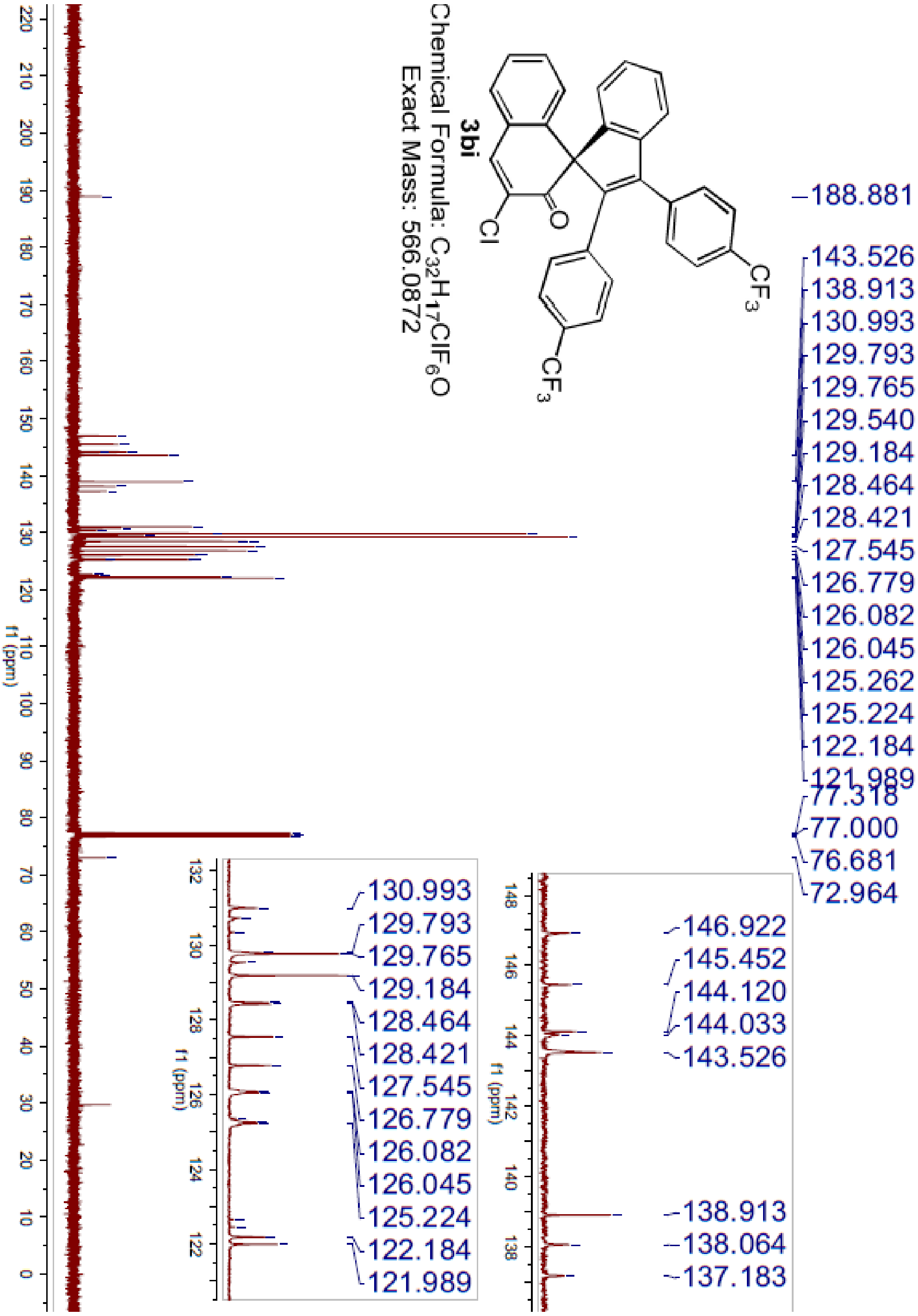

3bh
Chemical Formula: C30H17ClF2O
Exact Mass: 466.0936
189.416
163.661
162.958
161.197
160.486
143.431
131.183
131.103
130.736
130.657
126.829
121.820
116.119
115.906
115.345
115.132
77.318
77.000
76.682
72.813
131.183
131.103
130.832
130.736
130.657
129.569
126.829
121.861
121.820
116.119
115.906
115.345
115.132
163.661
162.958
161.197
160.486
146.691
144.823
143.833
143.673
143.431
139.452
f1 (ppm)



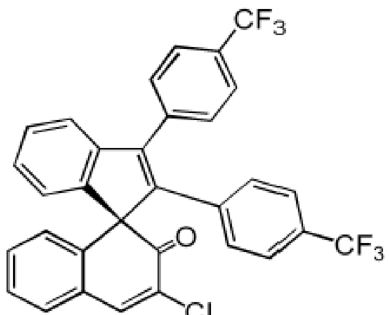
3bh
Chemical Formula: $C_{30}H_{17}ClF_2O$
Exact Mass: 466.0936



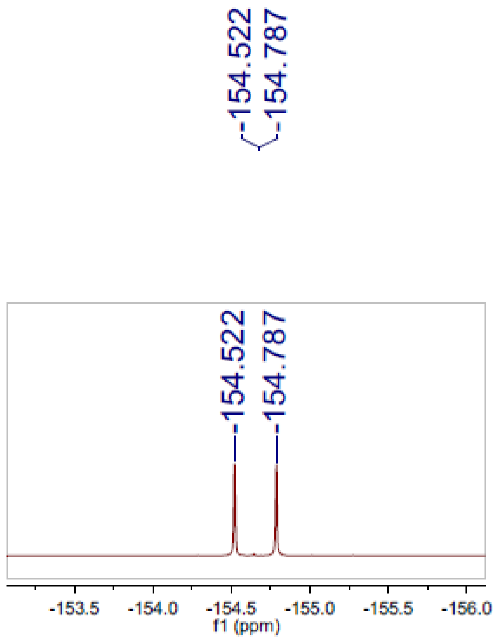

7.886
7.742
7.721
7.630
7.610
7.434
7.415
7.341
7.323
7.311
7.295
7.275
7.245
7.234
7.215
7.196
7.162
7.158
7.143
7.125
7.122
7.054
7.035
6.946
6.926
6.905
6.885
0.000
CF3
CF3
Cl
O
3bi
Chemical Formula: C32H17ClF6O
Exact Mass: 566.0872
0.95
1.96
1.96
1.05
6.92
1.11
1.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

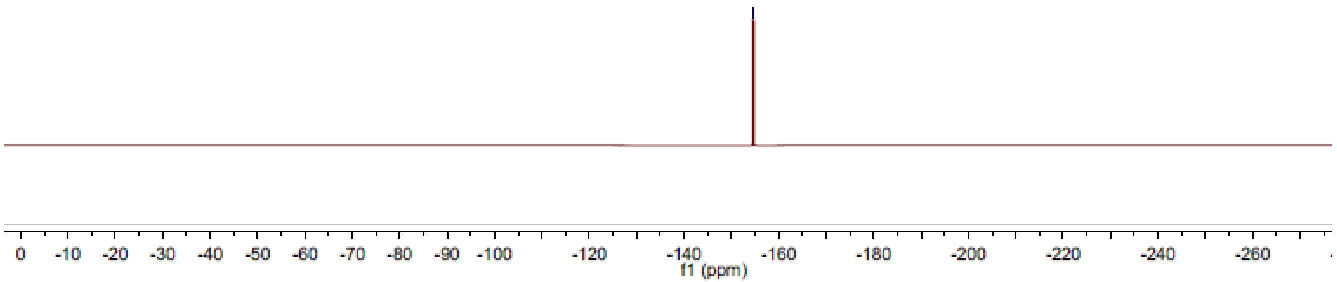


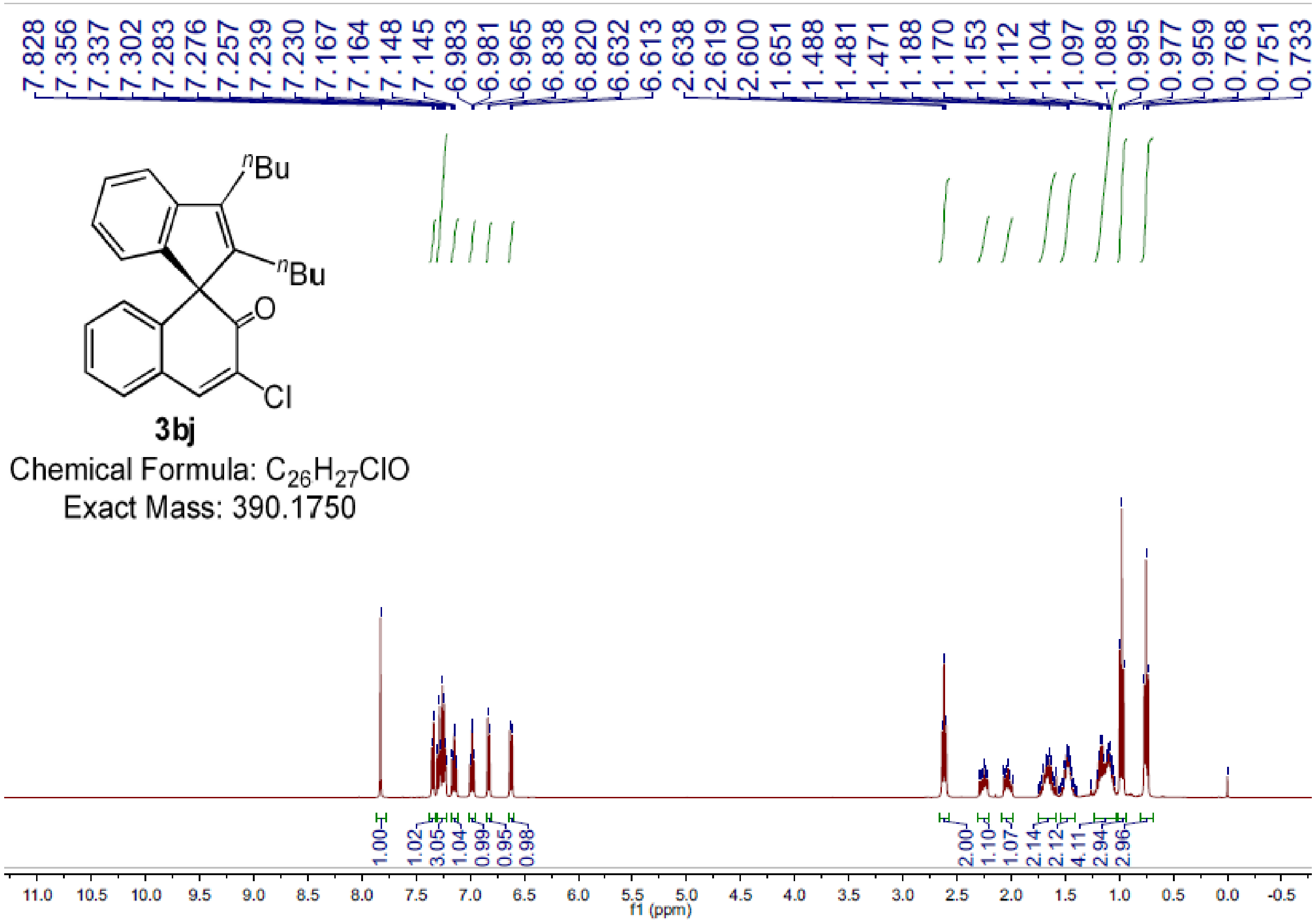
3bi
Chemical Formula: $C_{32}H_{17}ClF_6O$
Exact Mass: 566.0872
188.881
143.526
138.913
130.993
129.793
129.765
129.540
129.184
128.464
128.421
127.545
126.779
126.082
126.045
125.262
125.224
122.184
121.989
77.318
77.000
76.681
72.964
146.922
145.452
144.120
144.033
143.526
138.913
138.064
137.183
f1 (ppm)

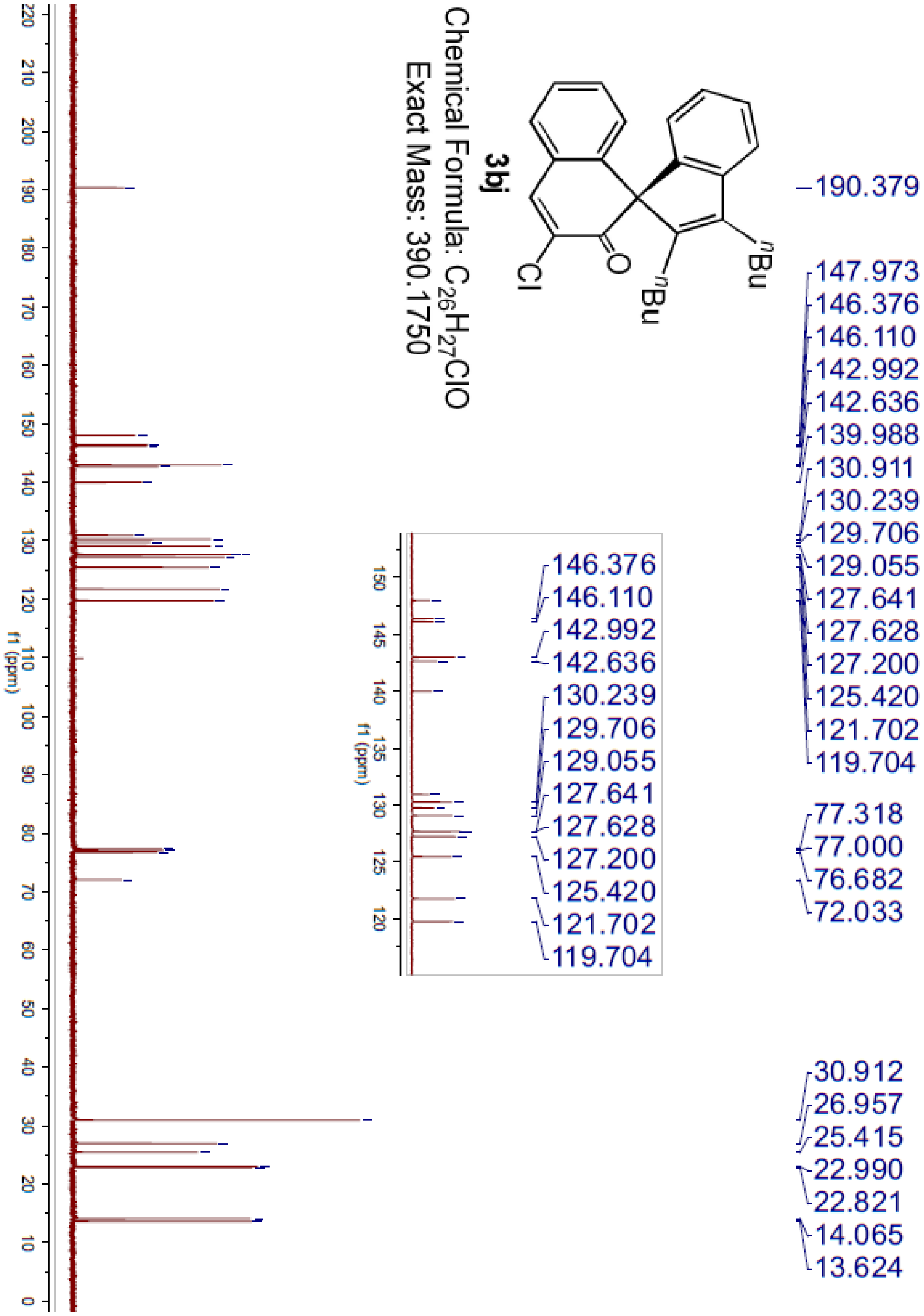


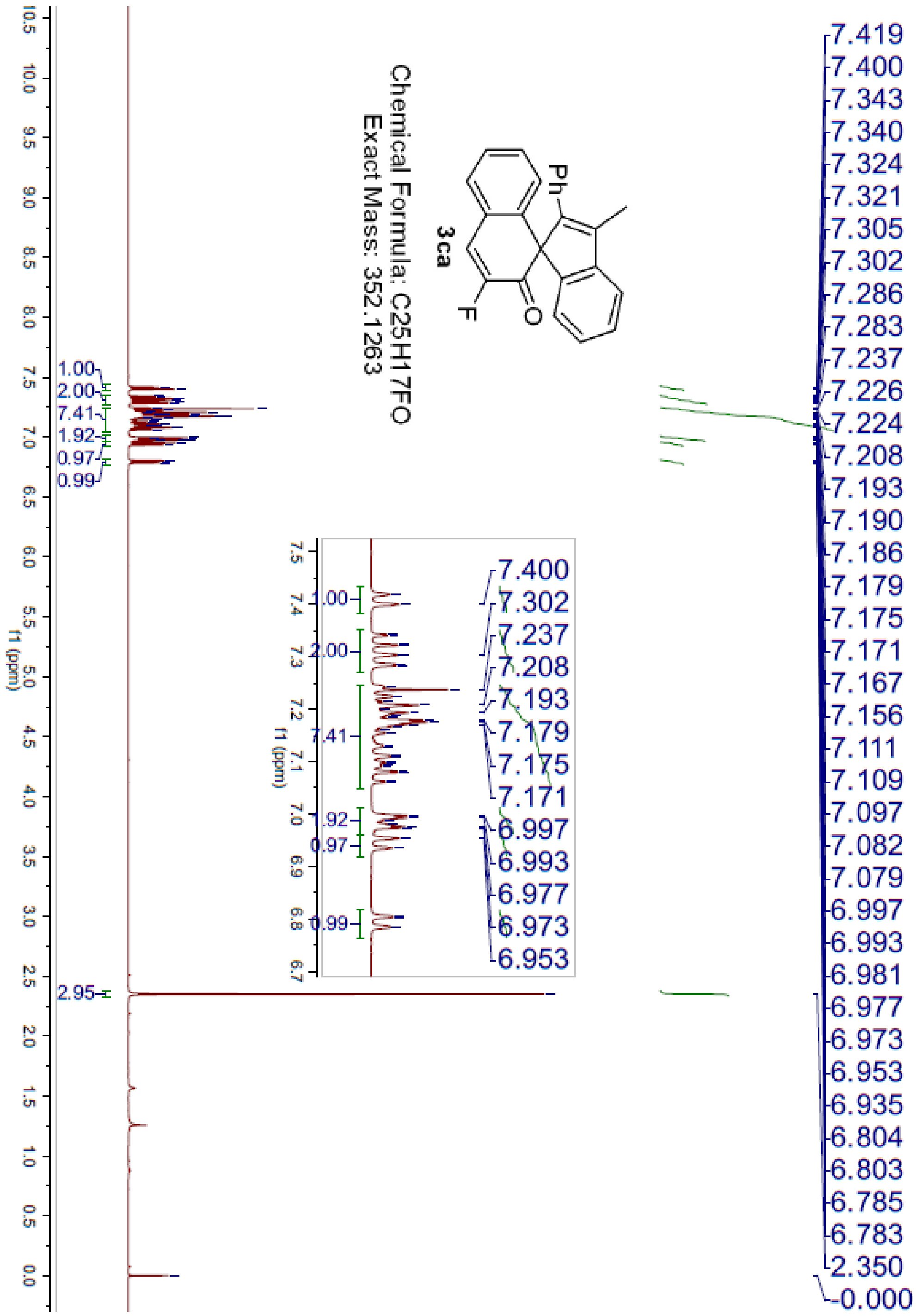
3bi
Chemical Formula: $C_{32}H_{17}ClF_6O$
Exact Mass: 566.0872



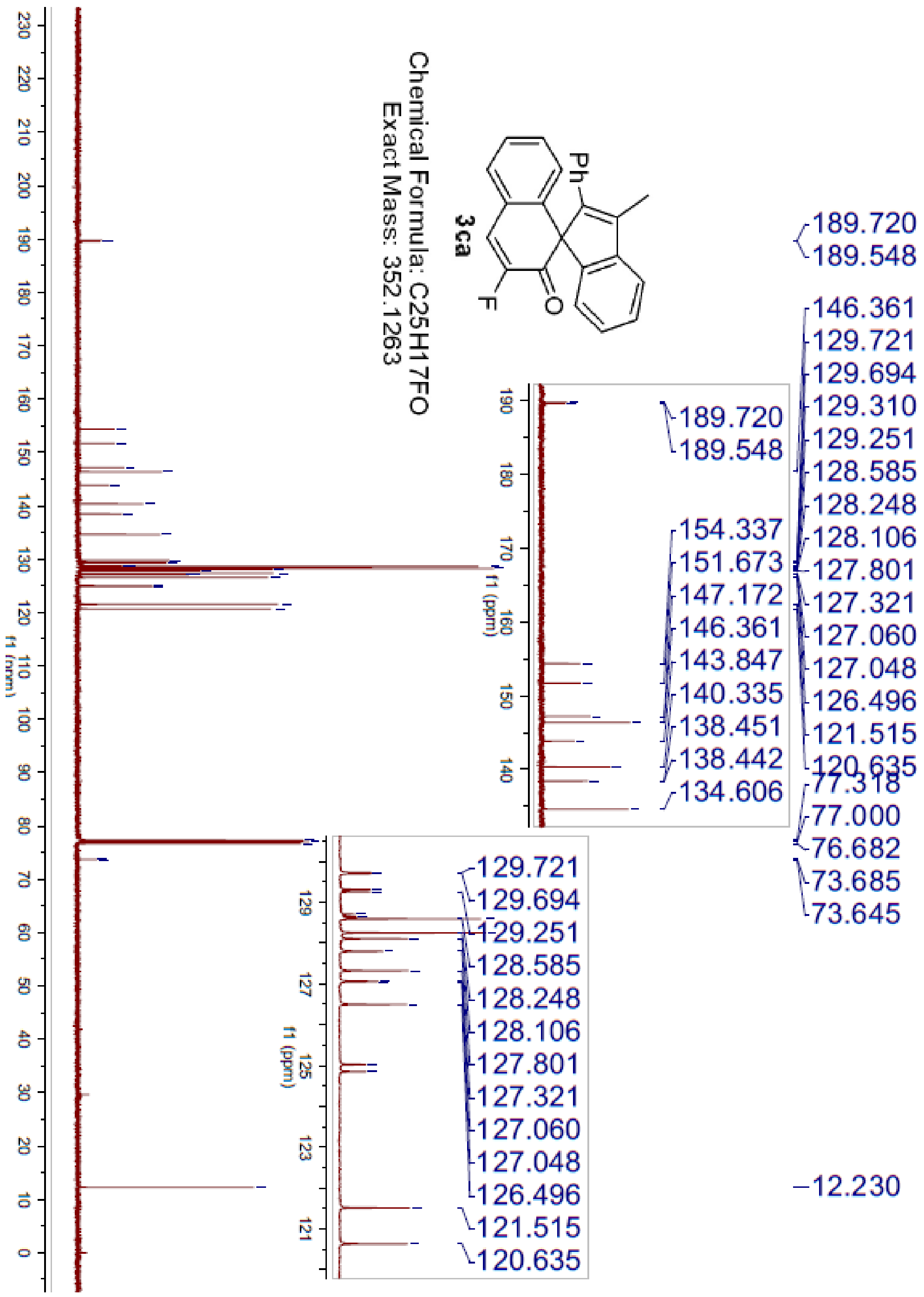


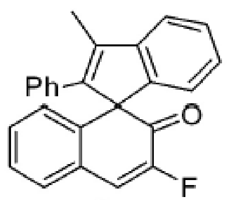

7.828 7.356 7.337 7.302 7.283 7.276 7.257 7.239 7.230 7.167 7.164 7.148 7.145 6.983 6.981 6.965 6.838 6.820 6.632 6.613 2.638 2.619 2.600 1.651 1.488 1.481 1.471 1.188 1.170 1.153 1.112 1.104 1.097 1.089 0.995 0.977 0.959 0.768 0.751 0.733
ⁿBu
ⁿBu
O
Cl
3bj
Chemical Formula: C26H27ClO
Exact Mass: 390.1750
1.00 1.02 3.05 1.04 0.99 0.95 0.98 2.00 1.10 1.07 2.14 2.12 4.11 2.94 2.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


3bj
Chemical Formula: $C_{26}H_{27}ClO$
Exact Mass: 390.1750
190.379
147.973
146.376
146.110
142.992
142.636
139.988
130.911
130.239
129.706
129.055
127.641
127.628
127.200
125.420
121.702
119.704
77.318
77.000
76.682
72.033
30.912
26.957
25.415
22.990
22.821
14.065
13.624
f1 (ppm)



3ca
Chemical Formula: C25H17FO
Exact Mass: 352.1263
7.419
7.400
7.343
7.340
7.324
7.321
7.305
7.302
7.286
7.283
7.237
7.226
7.224
7.208
7.193
7.190
7.186
7.179
7.175
7.171
7.167
7.156
7.111
7.109
7.097
7.082
7.079
6.997
6.993
6.981
6.977
6.973
6.953
6.935
6.804
6.803
6.785
6.783
2.350
-0.000
f1 (ppm)

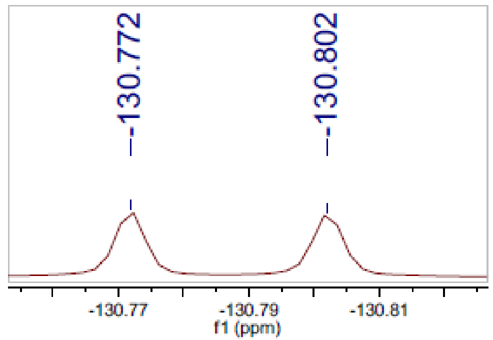

Chemical Formula: C25H17FO
Exact Mass: 352.1263
3ca
Ph
O
F
189.720
189.548
146.361
129.721
129.694
129.310
129.251
128.585
128.248
128.106
127.801
127.321
127.060
127.048
126.496
121.515
120.635
77.318
77.000
76.682
73.685
73.645
12.230
154.337
151.673
147.172
143.847
140.335
138.451
138.442
134.606
f1 (ppm)

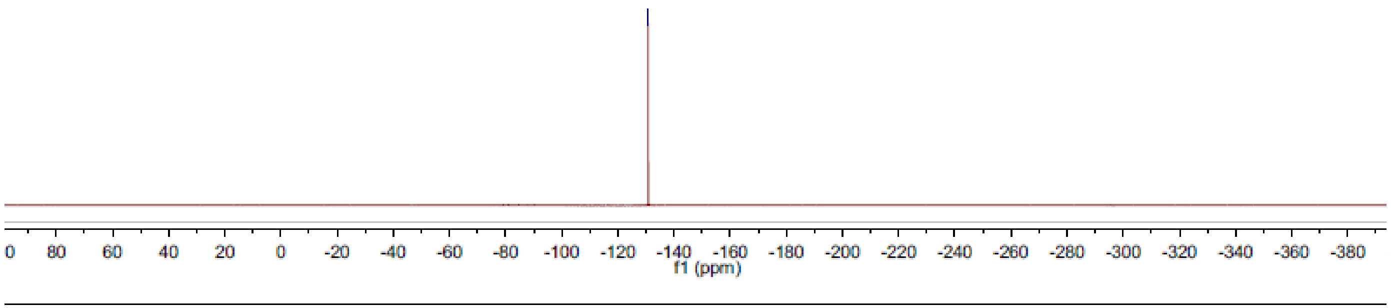


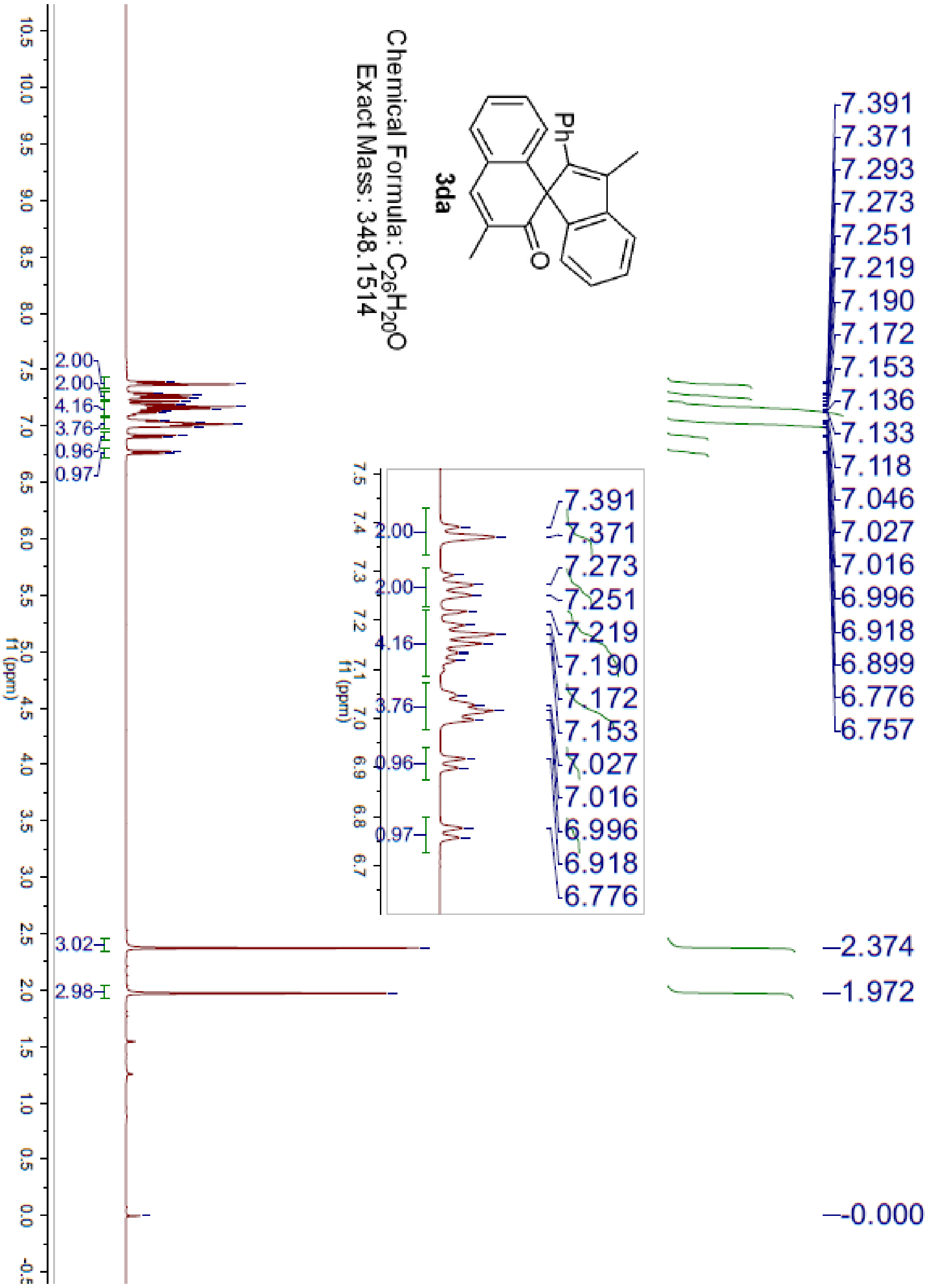
3ca

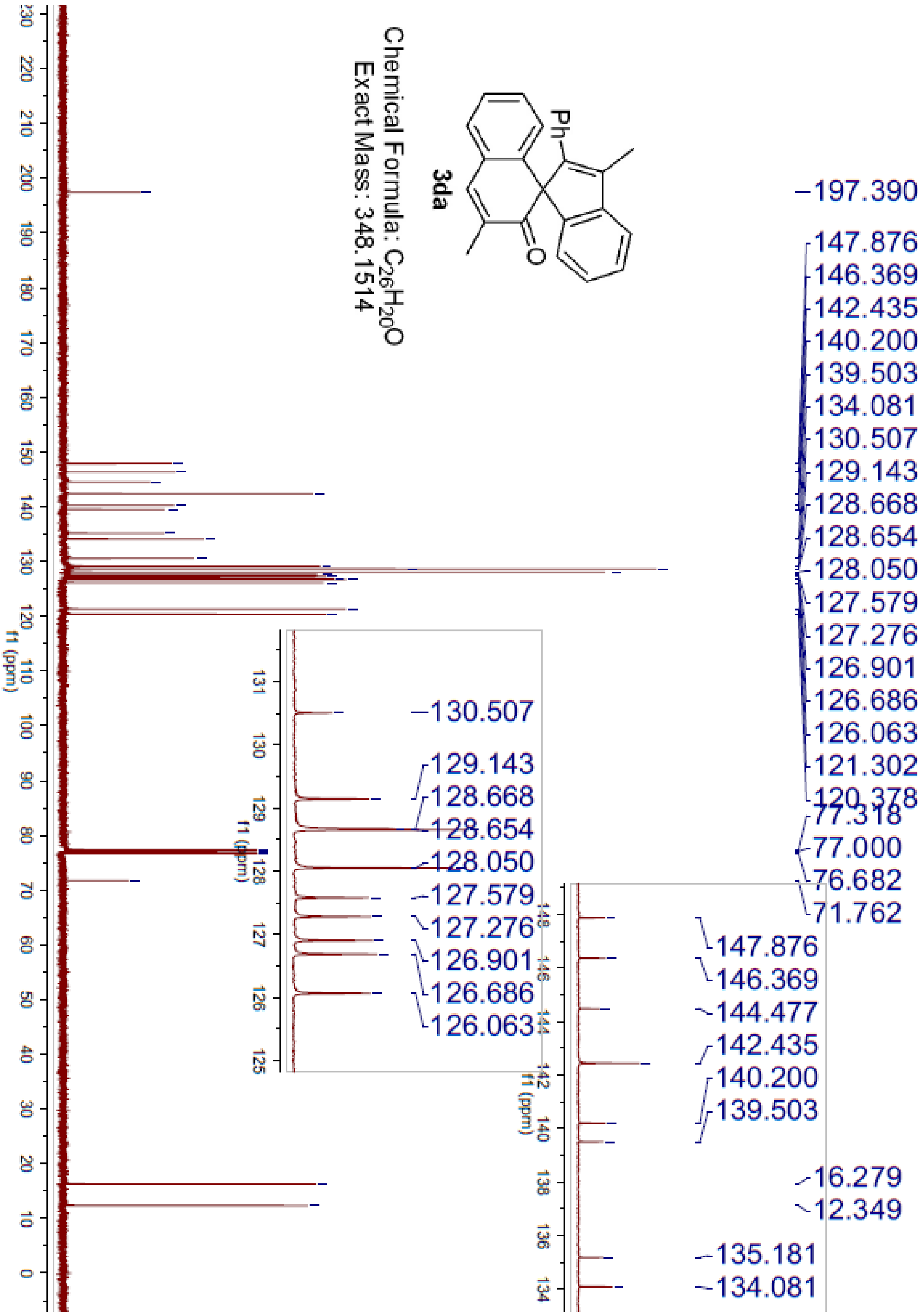
Chemical Formula: C25H17FO
Exact Mass: 352.1263

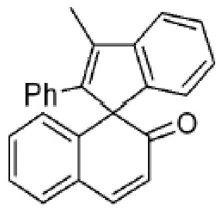
-130.772
-130.802





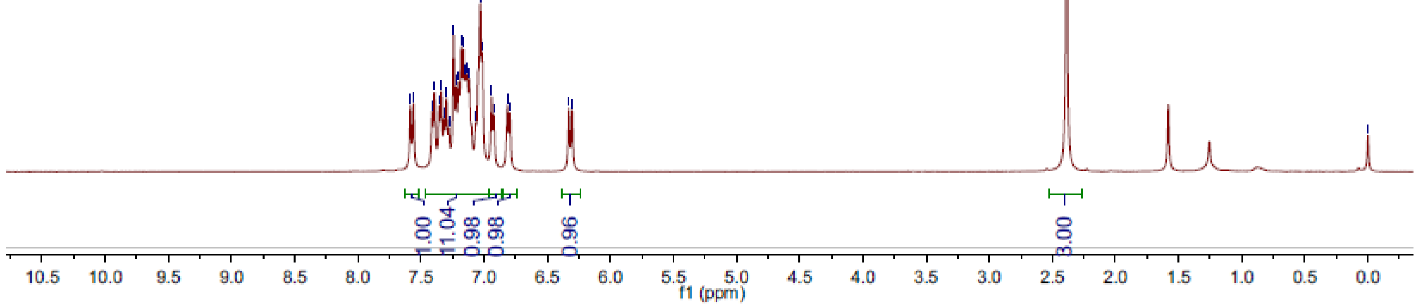

3da
Chemical Formula: $C_{26}H_{20}O$
Exact Mass: 348.1514
Ph
O
7.391
7.371
7.293
7.273
7.251
7.219
7.190
7.172
7.153
7.136
7.133
7.118
7.046
7.027
7.016
6.996
6.918
6.899
6.776
6.757
2.374
1.972
0.000
2.00
2.00
4.16
3.76
0.96
0.97
3.02
2.98
f1 (ppm)

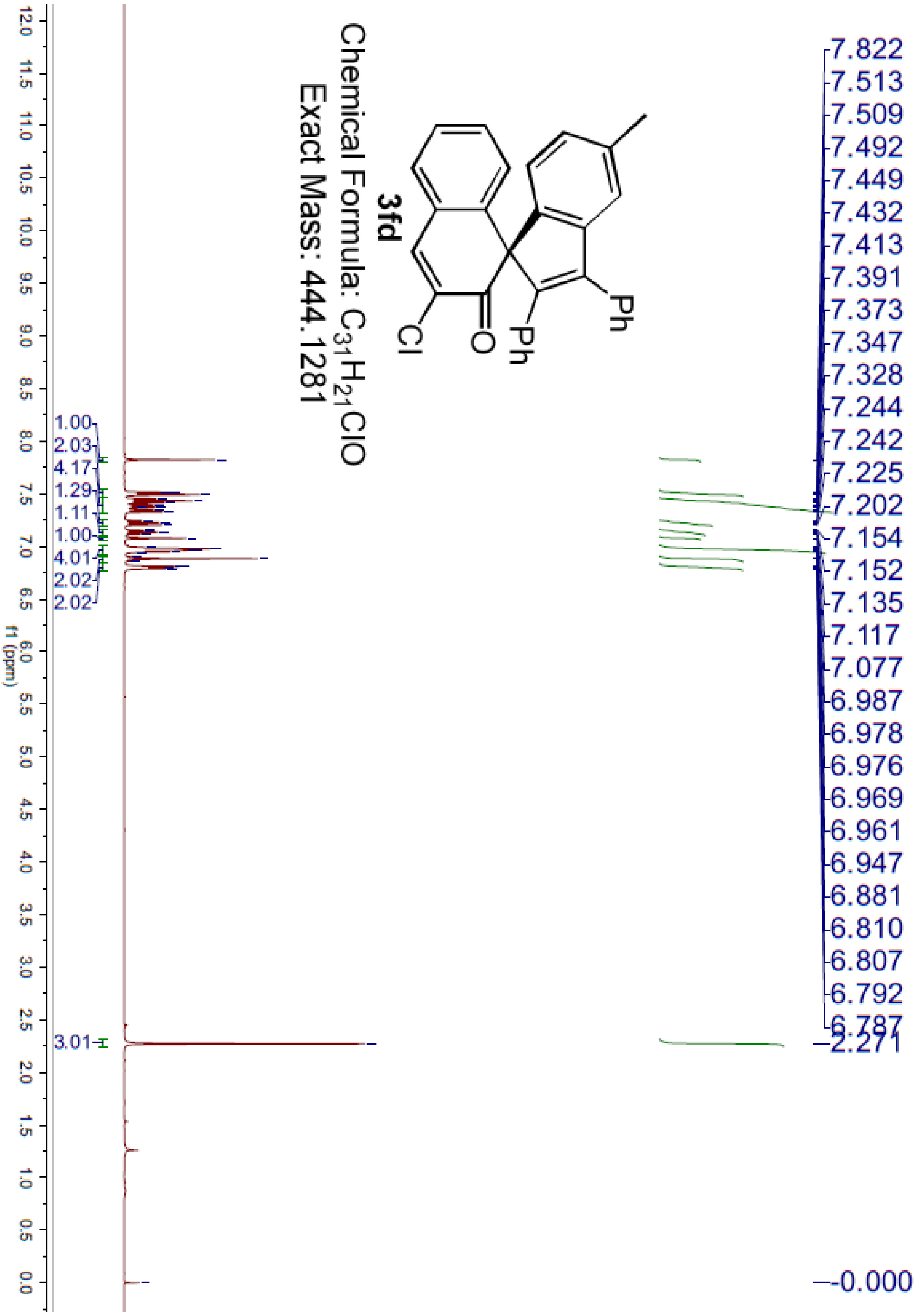

3da
Chemical Formula: C26H20O
Exact Mass: 348.1514
Ph
O
197.390
147.876
146.369
142.435
140.200
139.503
134.081
130.507
129.143
128.668
128.654
128.050
127.579
127.276
126.901
126.686
126.063
121.302
120.378
77.318
77.000
76.682
71.762
16.279
12.349
144.477
135.181
f1 (ppm)



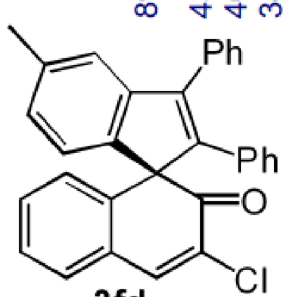
3ea

Chemical Formula: $C_{25}H_{18}O$
Exact Mass: 334.1358





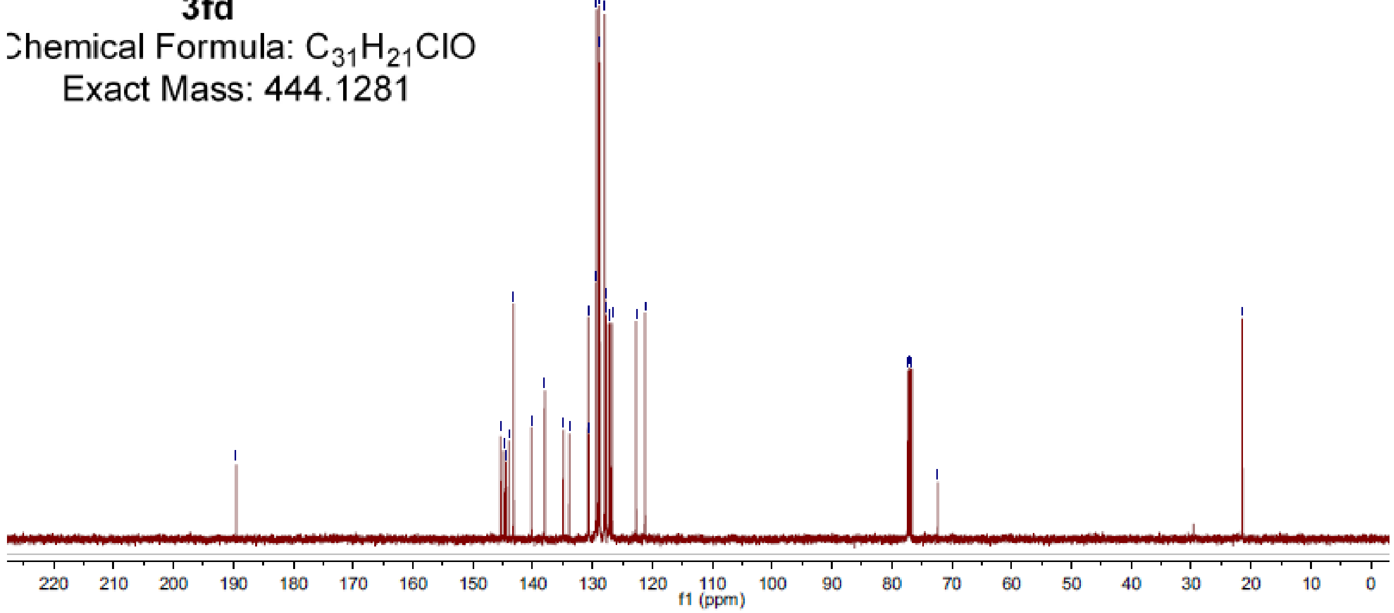
Ph
Ph
O
Cl
3fd
Chemical Formula: C31H21ClO
Exact Mass: 444.1281
7.822
7.513
7.509
7.492
7.449
7.432
7.413
7.391
7.373
7.347
7.328
7.244
7.242
7.225
7.202
7.154
7.152
7.135
7.117
7.077
6.987
6.978
6.976
6.969
6.961
6.947
6.881
6.810
6.807
6.792
6.787
2.271
-0.000
1.00
2.03
4.17
1.29
1.11
1.00
4.01
2.02
2.02
3.01
f1 (ppm)

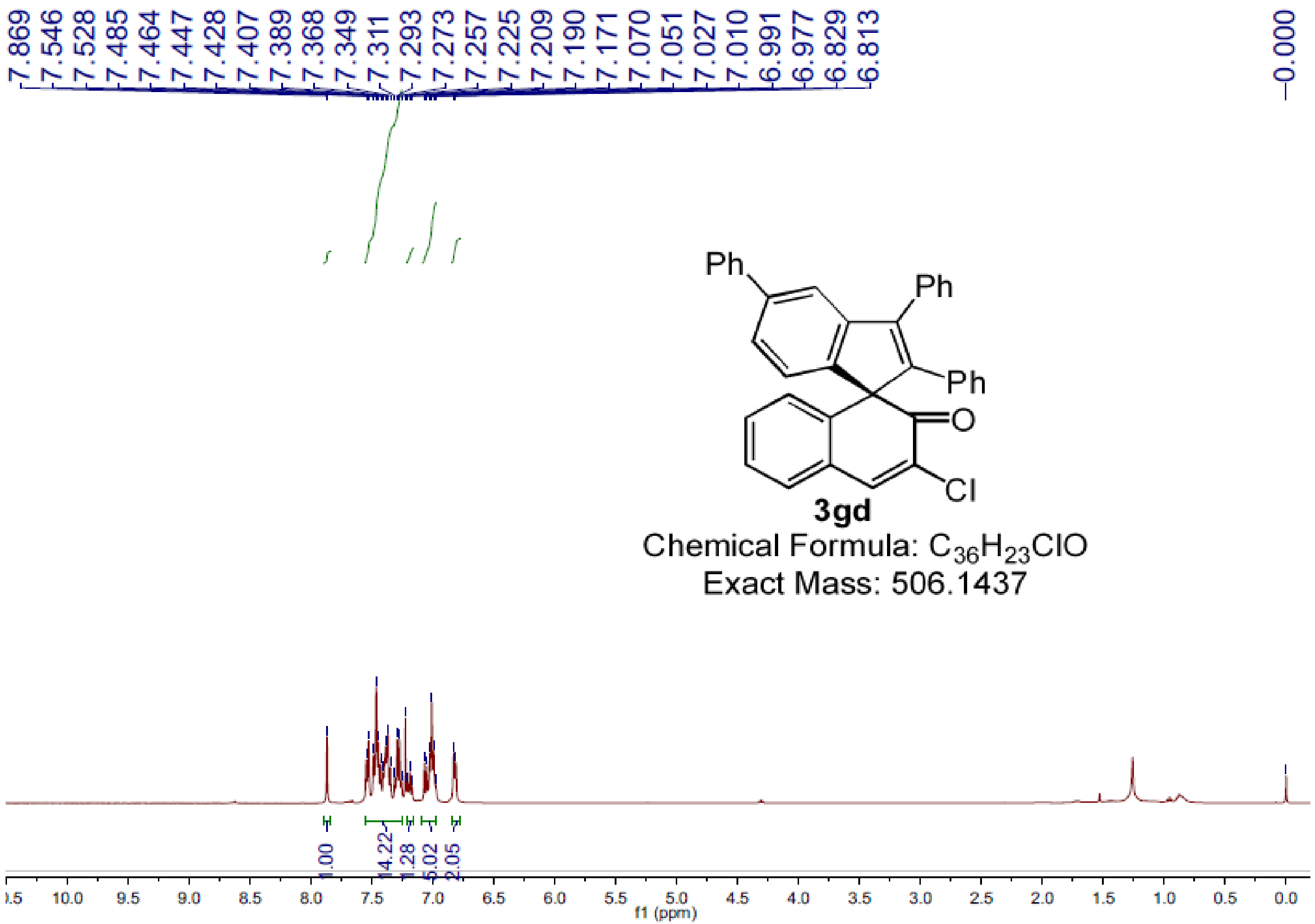


3fd

Chemical Formula: $C_{31}H_{21}ClO$

Exact Mass: 444.1281

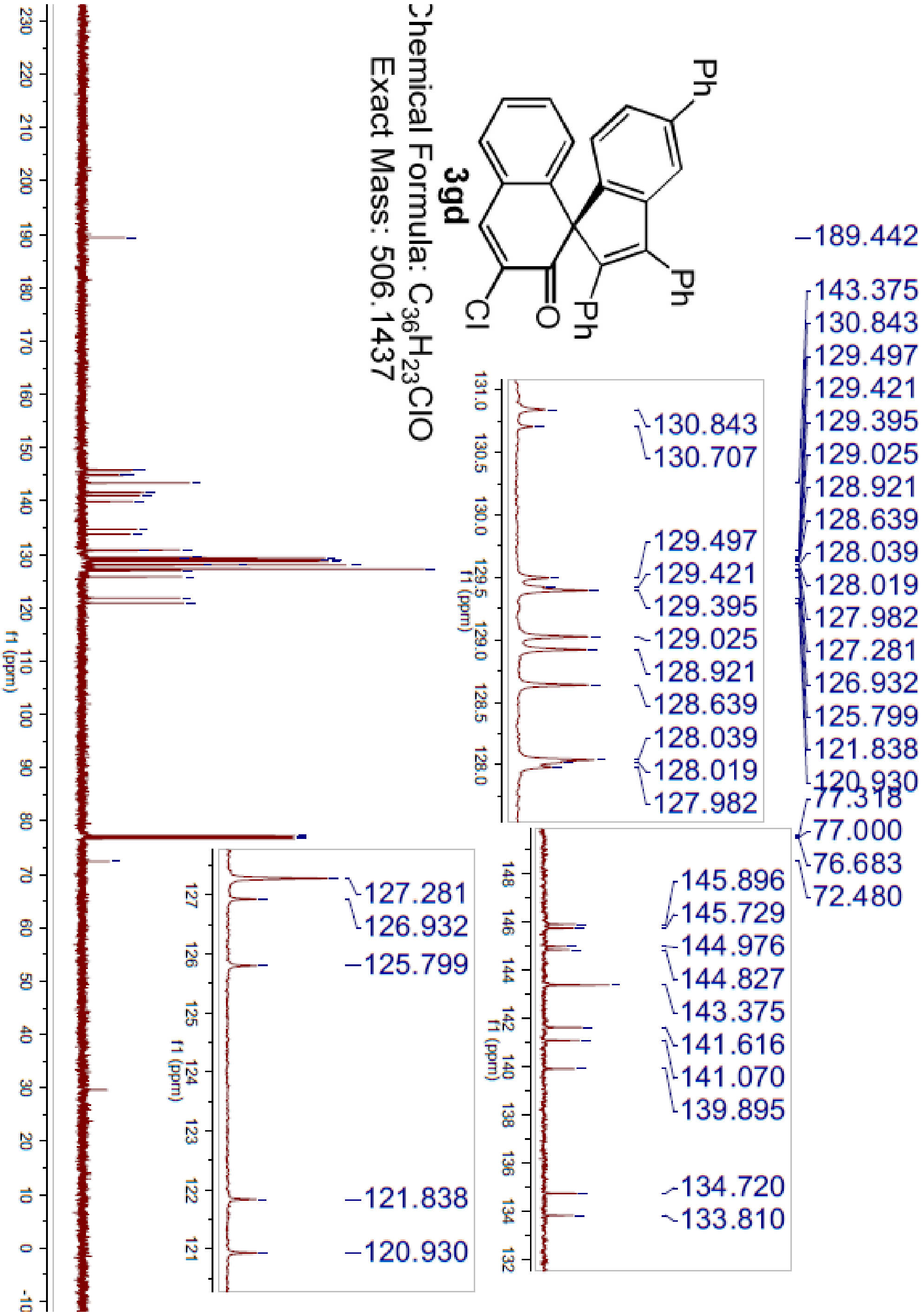


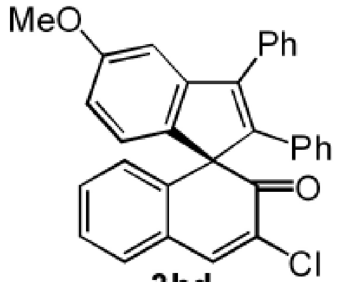


3gd

Chemical Formula: $C_{36}H_{23}ClO$

Exact Mass: 506.1437

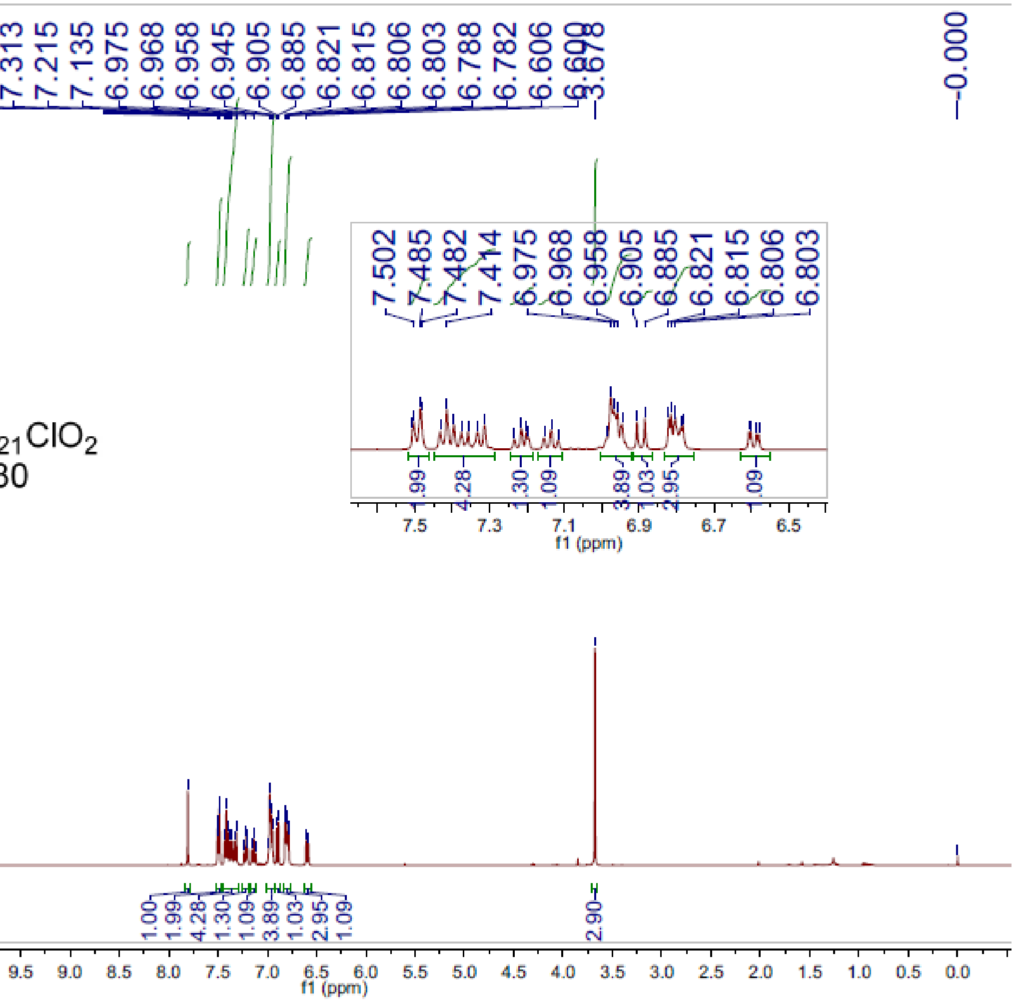

3gd
Chemical Formula: C36H23ClO
Exact Mass: 506.1437
Ph
Ph
Ph
O
Cl
189.442
143.375
130.843
129.497
129.421
129.395
129.025
128.921
128.639
128.039
128.019
127.982
127.281
126.932
125.799
121.838
120.930
77.318
77.000
76.683
72.480
130.843
130.707
129.497
129.421
129.395
129.025
128.921
128.639
128.039
128.019
127.982
145.896
145.729
144.976
144.827
143.375
141.616
141.070
139.895
134.720
133.810
127.281
126.932
125.799
121.838
120.930
f1 (ppm)

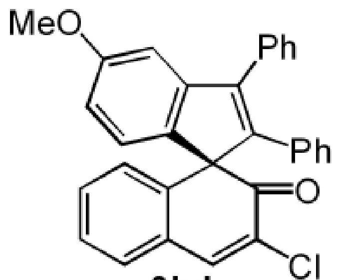


3hd

Chemical Formula: $C_{31}H_{21}ClO_2$

Exact Mass: 460.1230

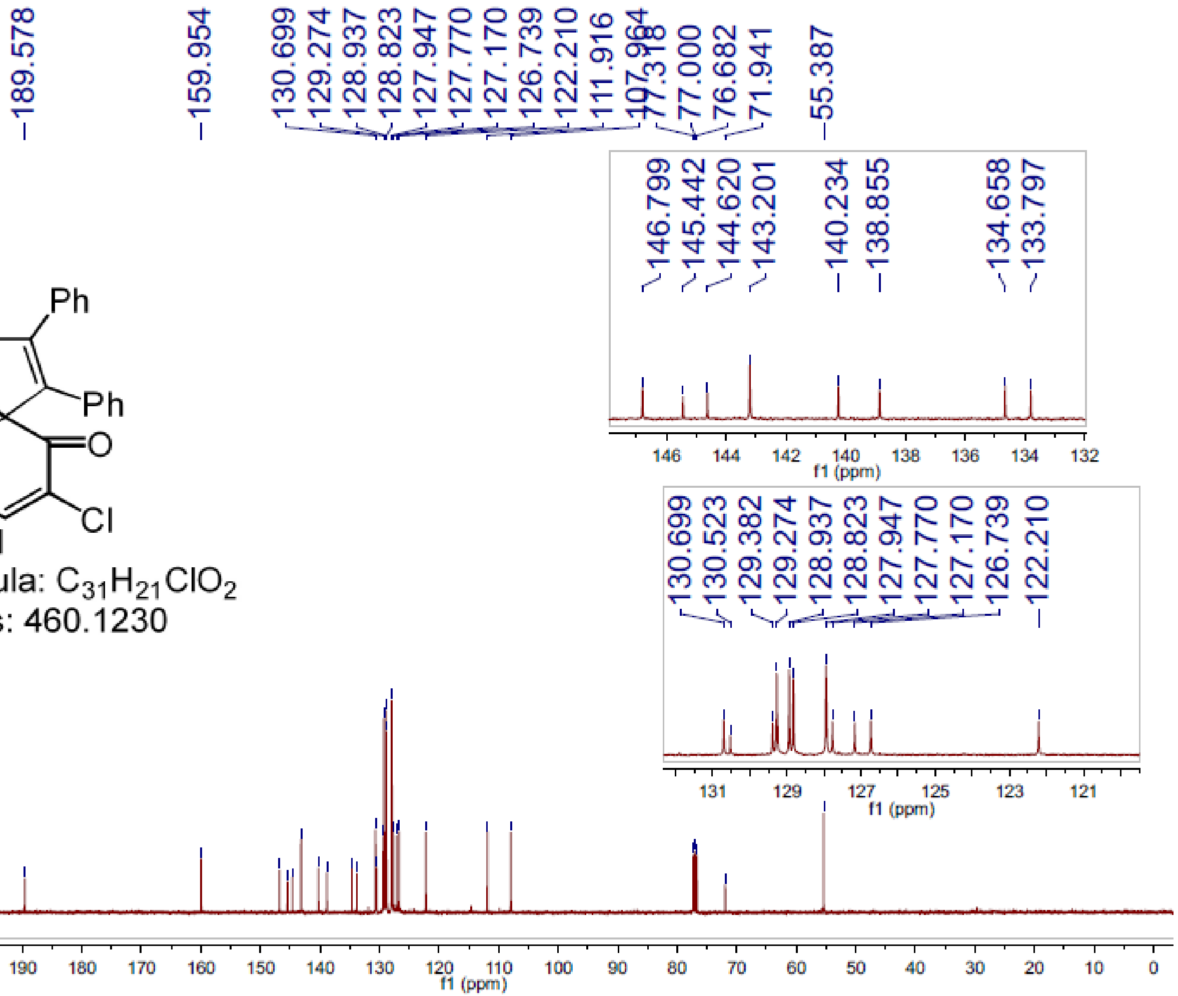


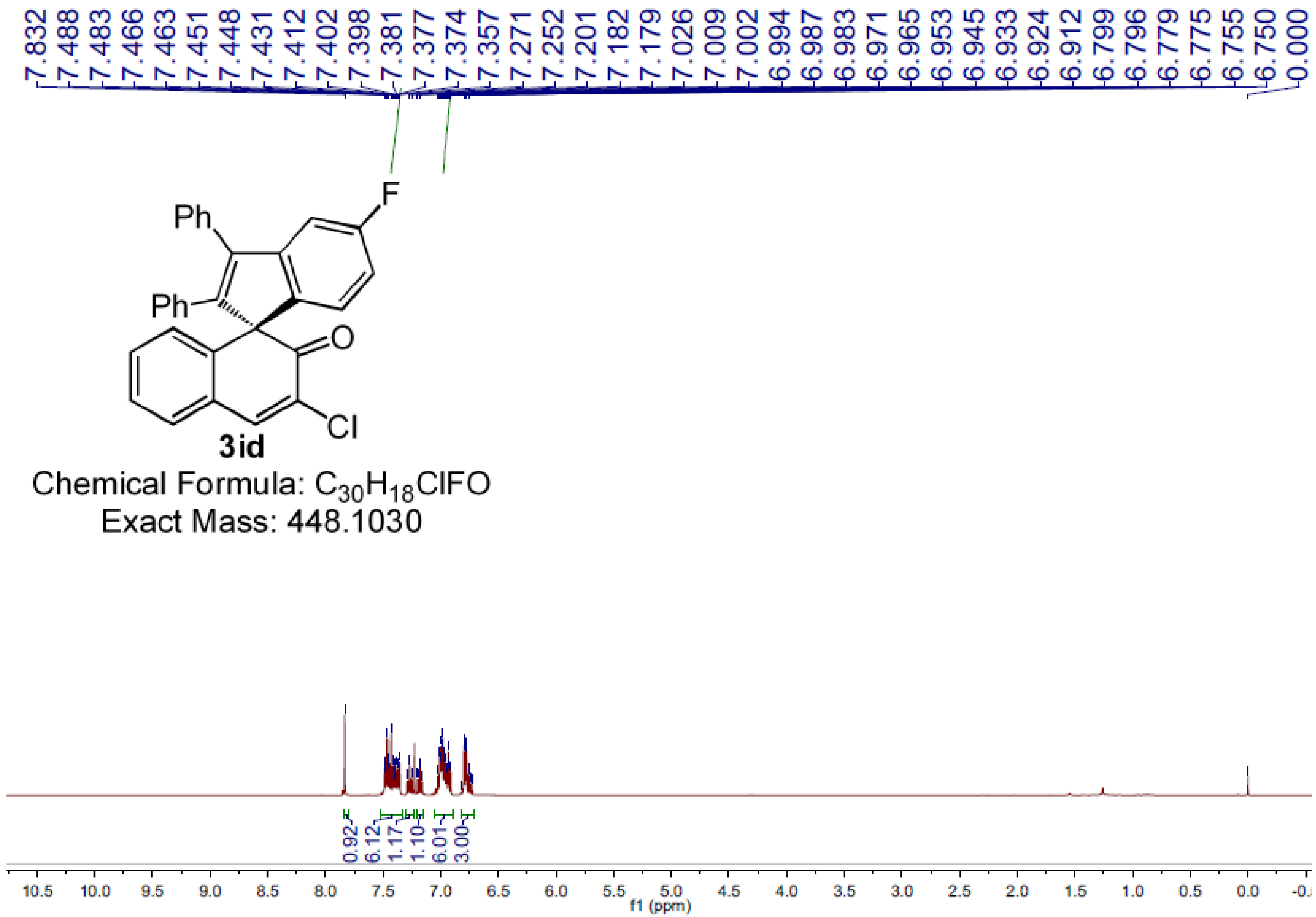


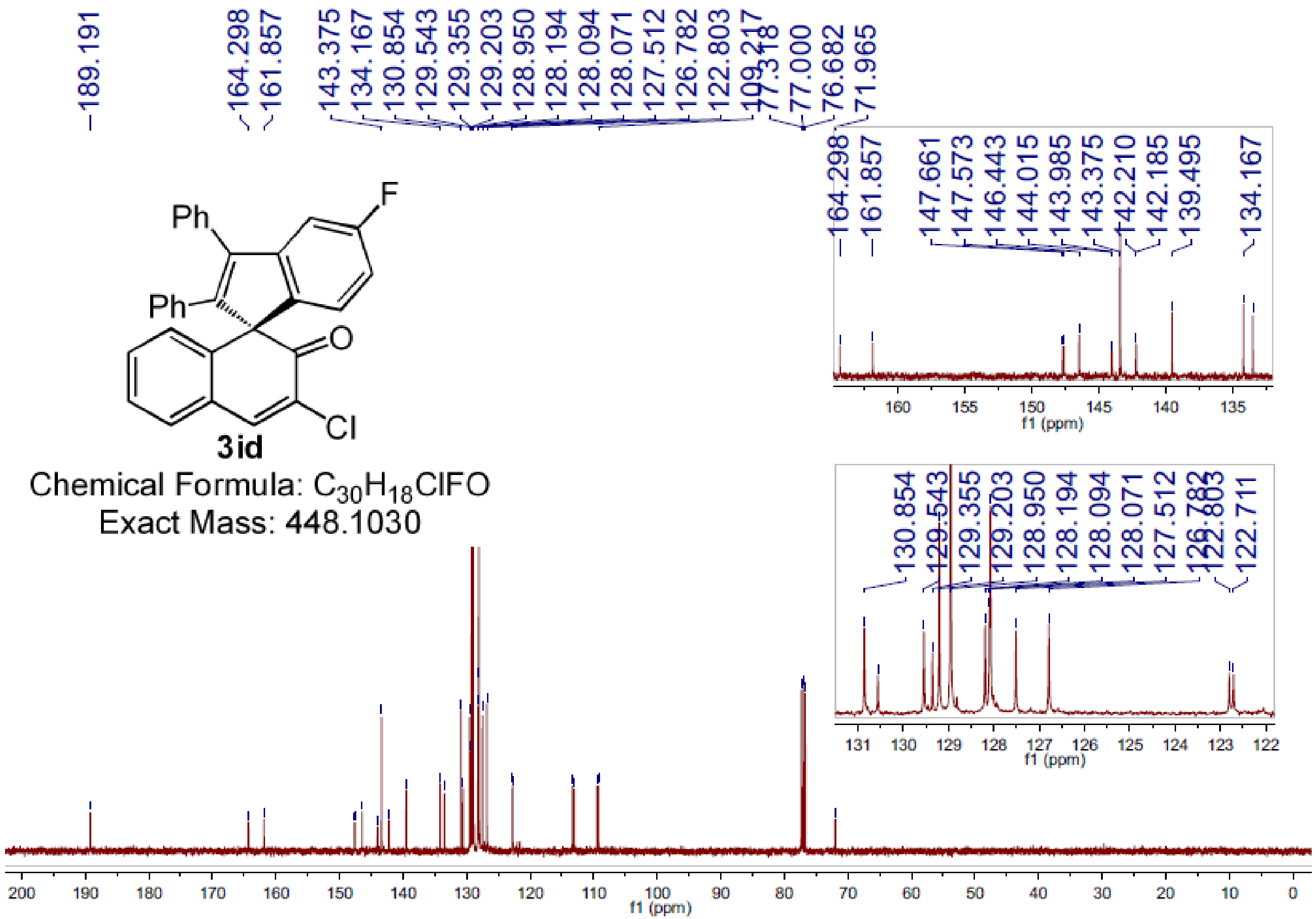
3hd

Chemical Formula: $C_{31}H_{21}ClO_2$

Exact Mass: 460.1230



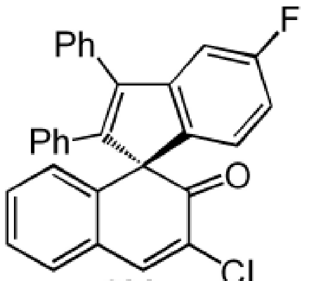

7.832
7.488
7.483
7.466
7.463
7.451
7.448
7.431
7.412
7.402
7.398
7.381
7.377
7.374
7.357
7.271
7.252
7.201
7.182
7.179
7.026
7.009
7.002
6.994
6.987
6.983
6.971
6.965
6.953
6.945
6.933
6.924
6.912
6.799
6.796
6.779
6.775
6.755
6.750
0.000
Ph
Ph
F
O
Cl
3id
Chemical Formula: C30H18ClFO
Exact Mass: 448.1030
0.92
6.12
1.17
1.10
6.01
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3id

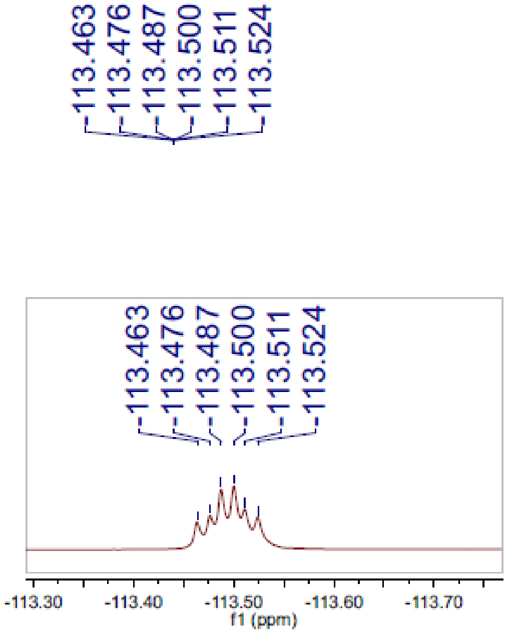
Chemical Formula: $C_{30}H_{18}ClFO$

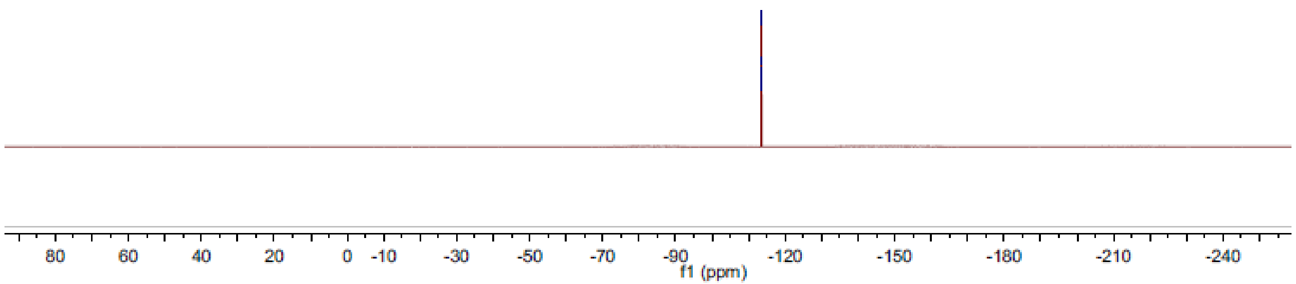
Exact Mass: 448.1030

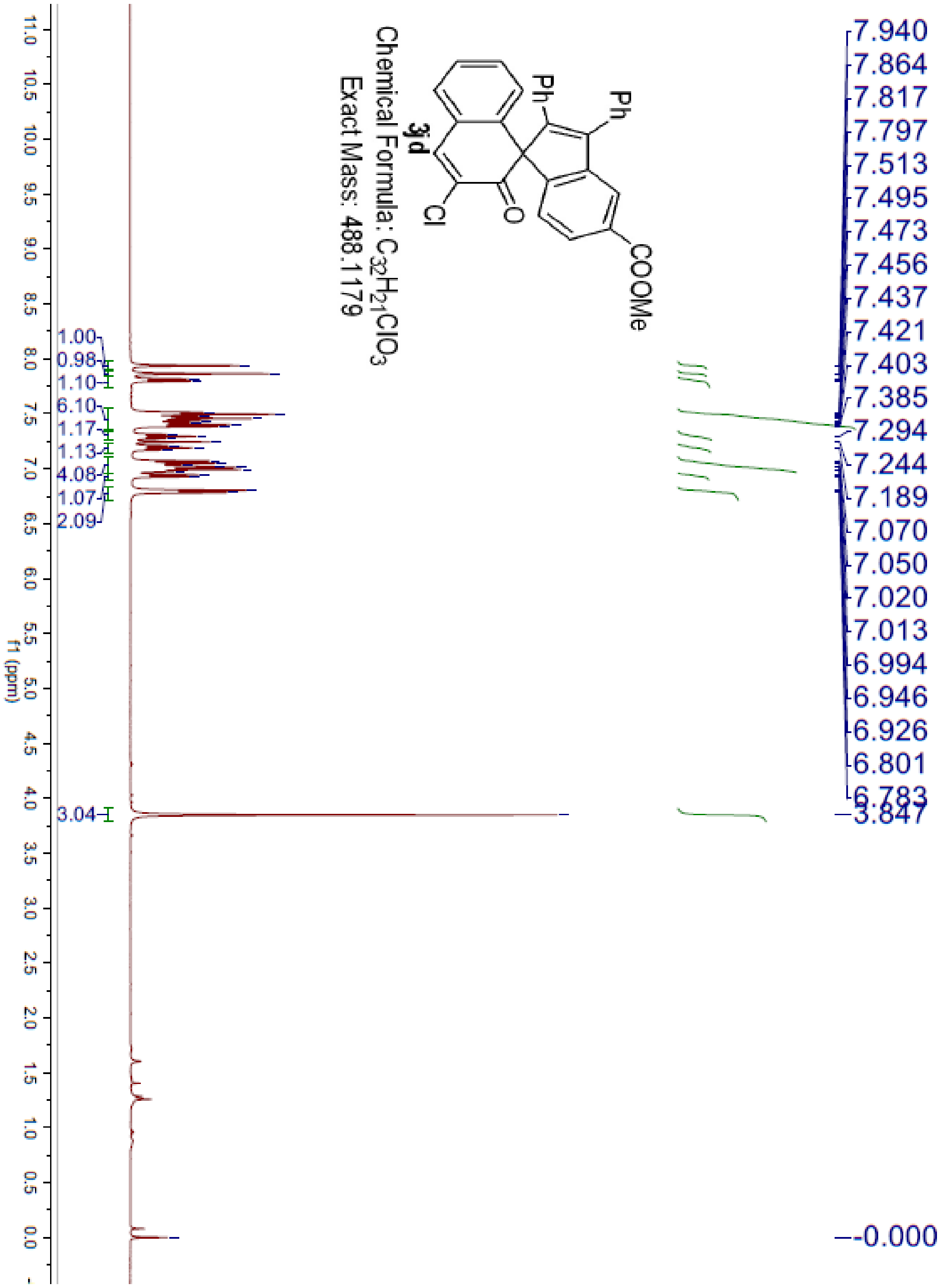


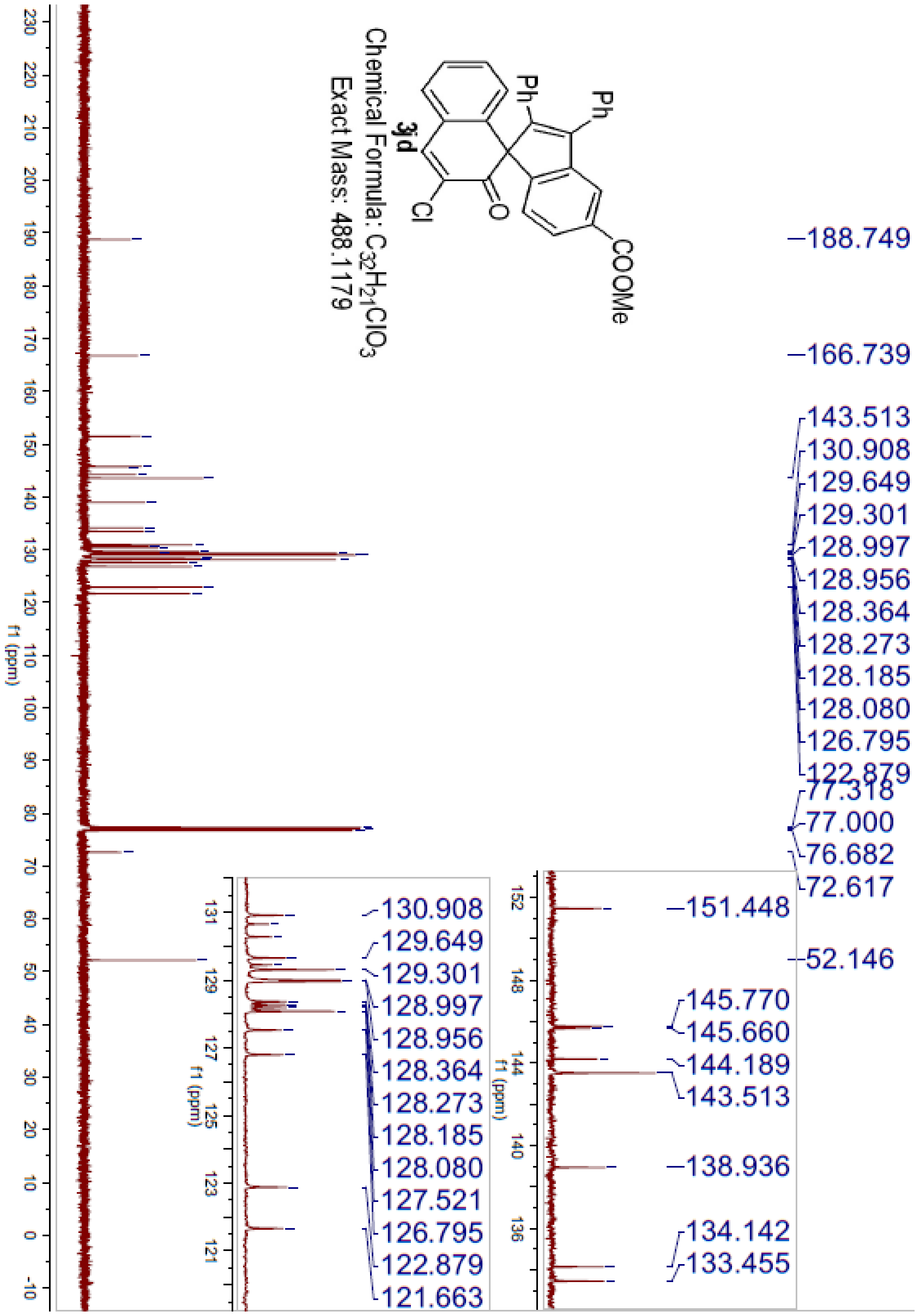
3id

Chemical Formula: $C_{30}H_{18}ClFO$
Exact Mass: 448.1030






7.940
7.864
7.817
7.797
7.513
7.495
7.473
7.456
7.437
7.421
7.403
7.385
7.294
7.244
7.189
7.070
7.050
7.020
7.013
6.994
6.946
6.926
6.801
6.783
3.847
-0.000
Ph
Ph
COOMe
O
Cl
3jd
Chemical Formula: C32H21ClO3
Exact Mass: 488.1179
1.00
0.98
1.10
6.10
1.17
1.13
4.08
1.07
2.09
3.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


3d
Chemical Formula: $C_{32}H_{21}ClO_3$
Exact Mass: 488.1179
Ph
Ph
COOMe
O
Cl
188.749
166.739
143.513
130.908
129.649
129.301
128.997
128.956
128.364
128.273
128.185
128.080
126.795
122.879
77.318
77.000
76.682
72.617
52.146
151.448
145.770
145.660
144.189
143.513
138.936
134.142
133.455
130.908
129.649
129.301
128.997
128.956
128.364
128.273
128.185
128.080
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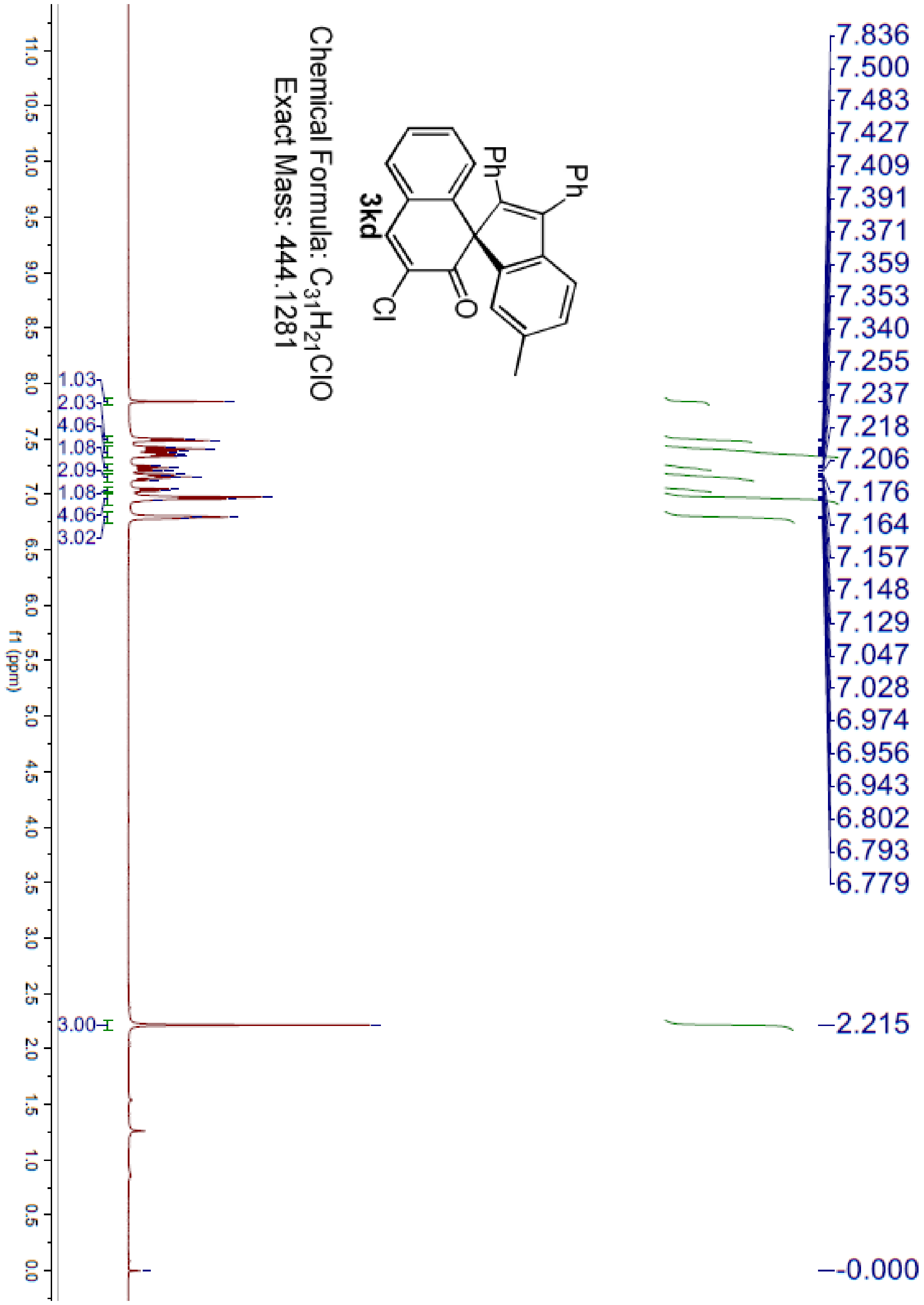
126.795
122.879
121.663
f1 (ppm)



3kd
Ph
Ph
O
Cl
Chemical Formula: C31H21ClO
Exact Mass: 444.1281
7.836
7.500
7.483
7.427
7.409
7.391
7.371
7.359
7.353
7.340
7.255
7.237
7.218
7.206
7.176
7.164
7.157
7.148
7.129
7.047
7.028
6.974
6.956
6.943
6.802
6.793
6.779
2.215
-0.000
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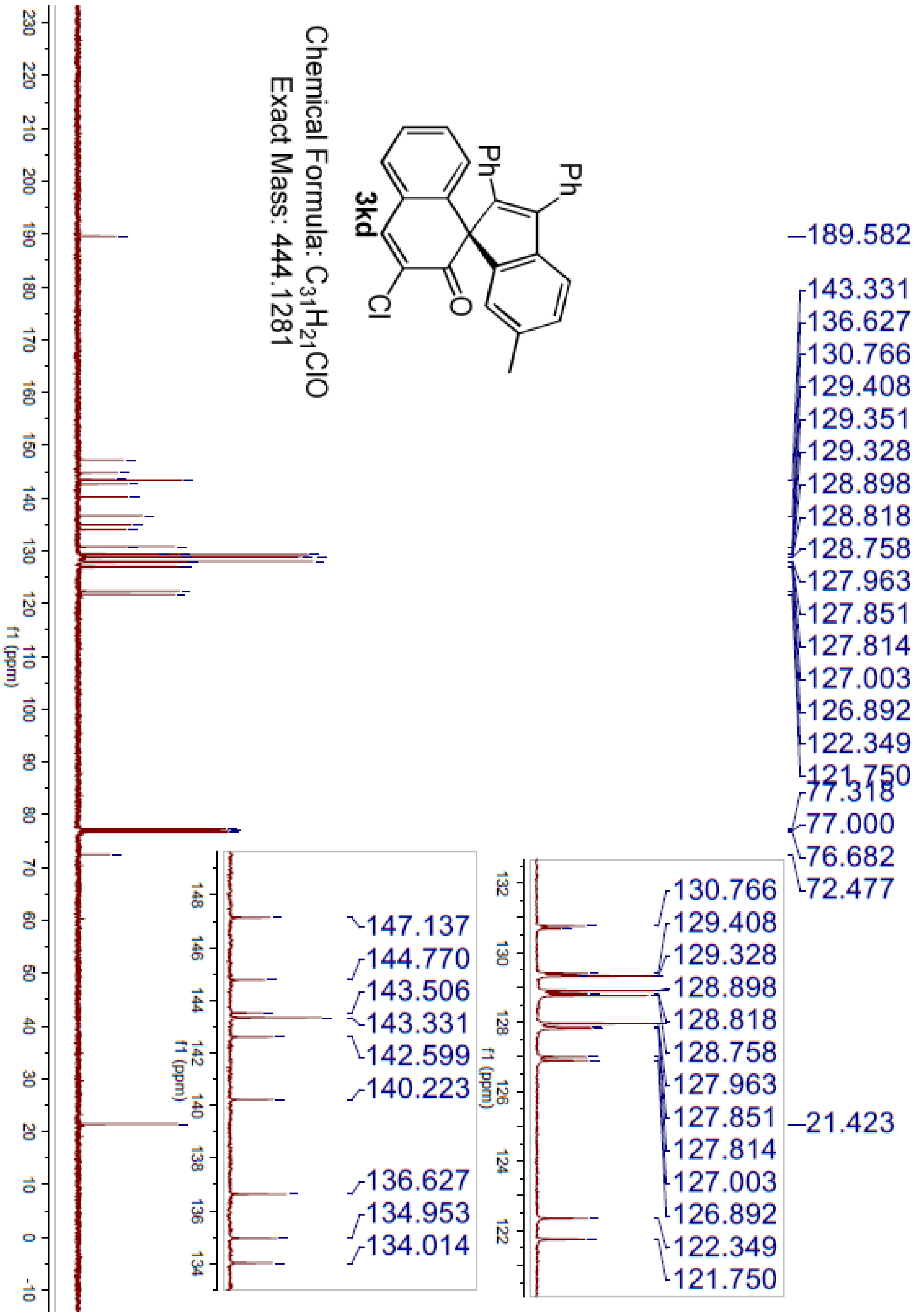
2.03
4.06
1.08
2.09
1.08
4.06
3.02
3.00
f1 (ppm)



Chemical Formula: $C_{31}H_{21}ClO$
Exact Mass: 444.1281
3kd
Ph
Ph
O
Cl
189.582
143.331
136.627
130.766
129.408
129.351
129.328
128.898
128.818
128.758
127.963
127.851
127.814
127.003
126.892
122.349
121.750
77.318
77.000
76.682
72.477
21.423
147.137
144.770
143.506
143.331
142.599
140.223
136.627
134.953
134.014
130.766
129.408
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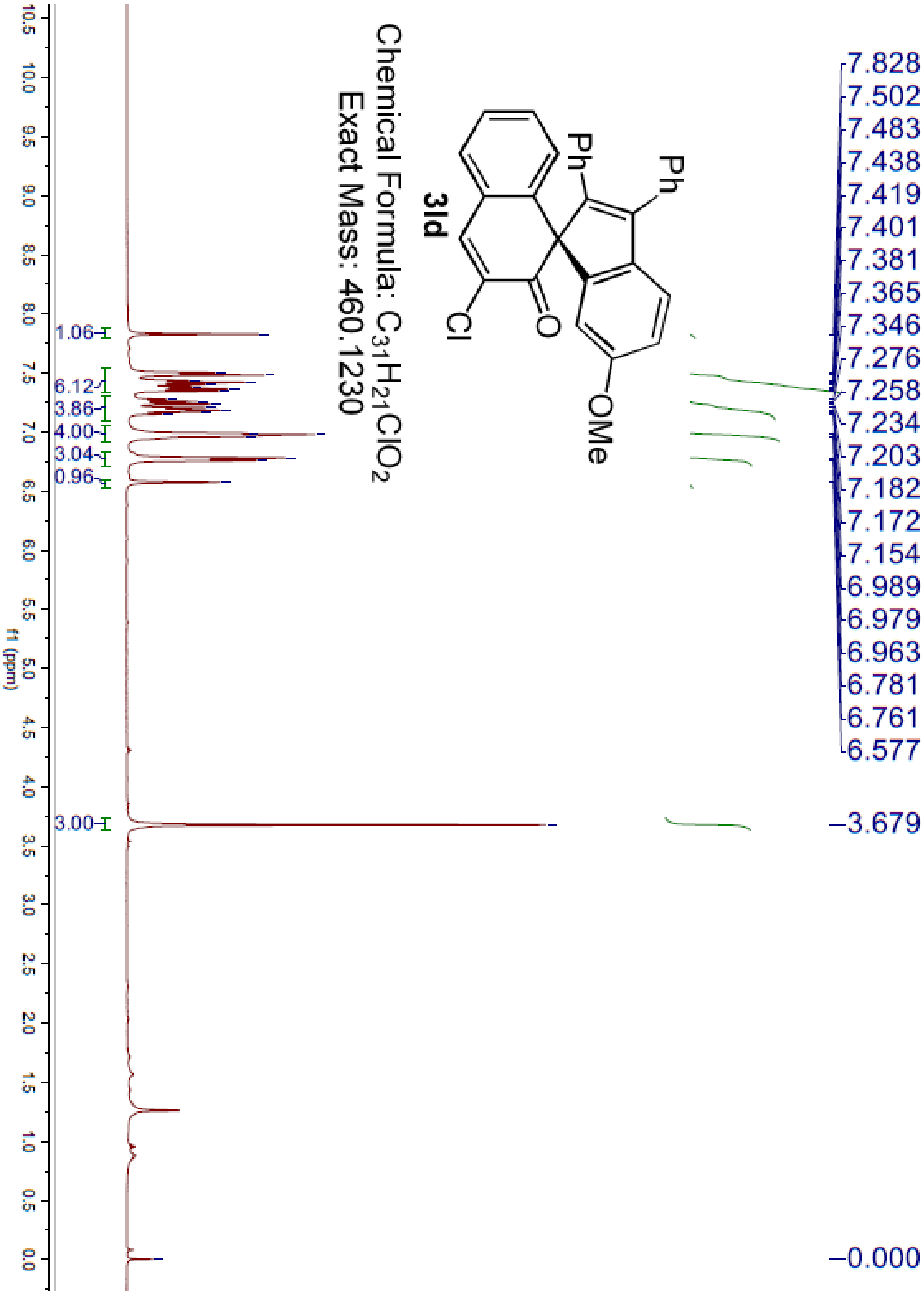
128.818
128.758
127.963
127.851
127.814
127.003
126.892
122.349
121.750
f1 (ppm)



7.828
7.502
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7.438
7.419
7.401
7.381
7.365
7.346
7.276
7.258
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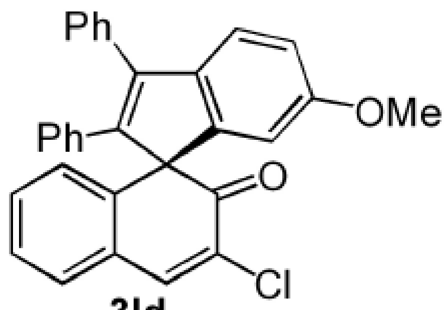
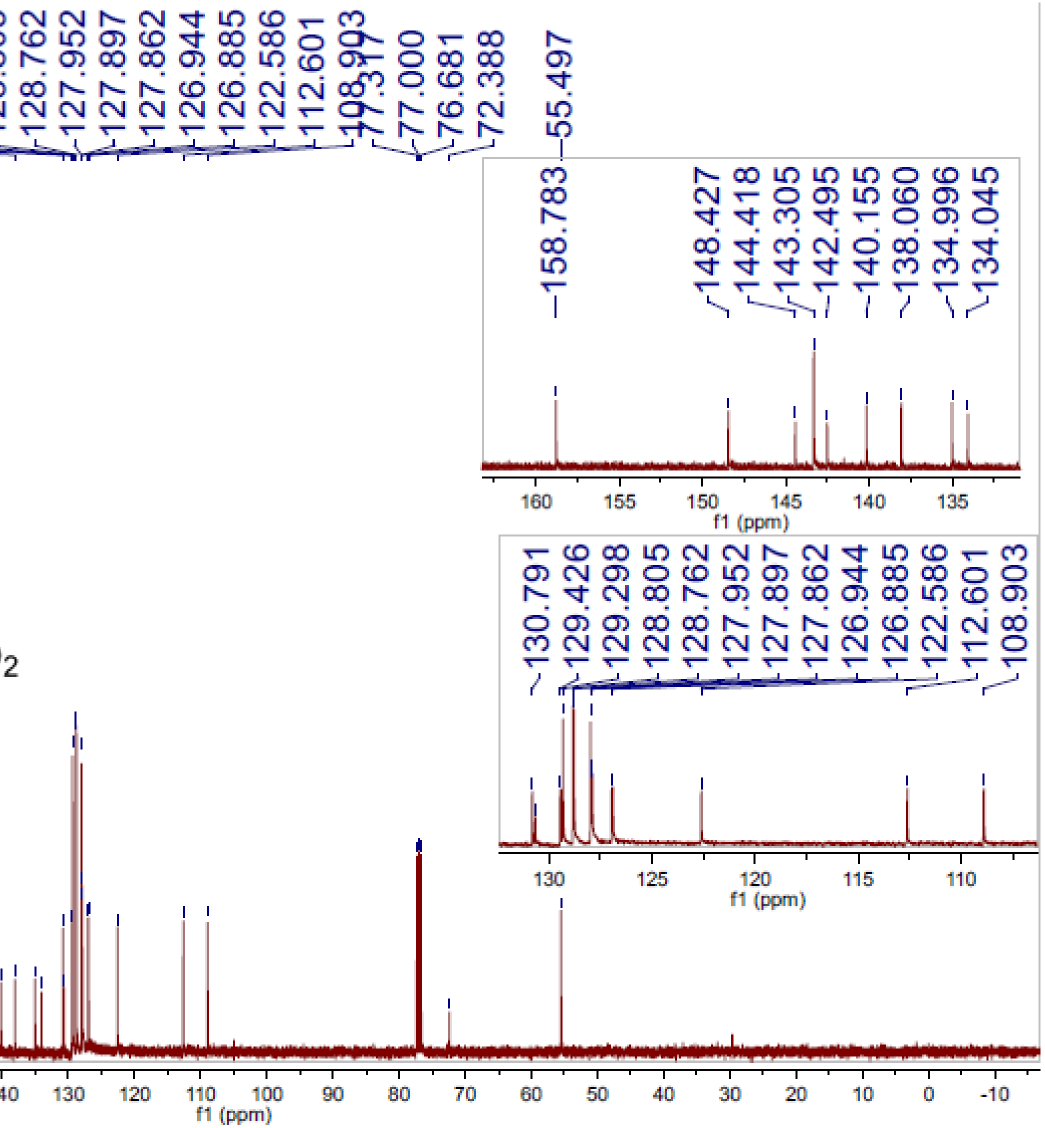
7.203
7.182
7.172
7.154
6.989
6.979
6.963
6.781
6.761
6.577
3.679
0.000
Ph
Ph
O
Cl
OMe
3ld
Chemical Formula: $C_{31}H_{21}ClO_2$
Exact Mass: 460.1230
1.06
6.12
3.86
4.00
3.04
0.96
3.00
f1 (ppm)

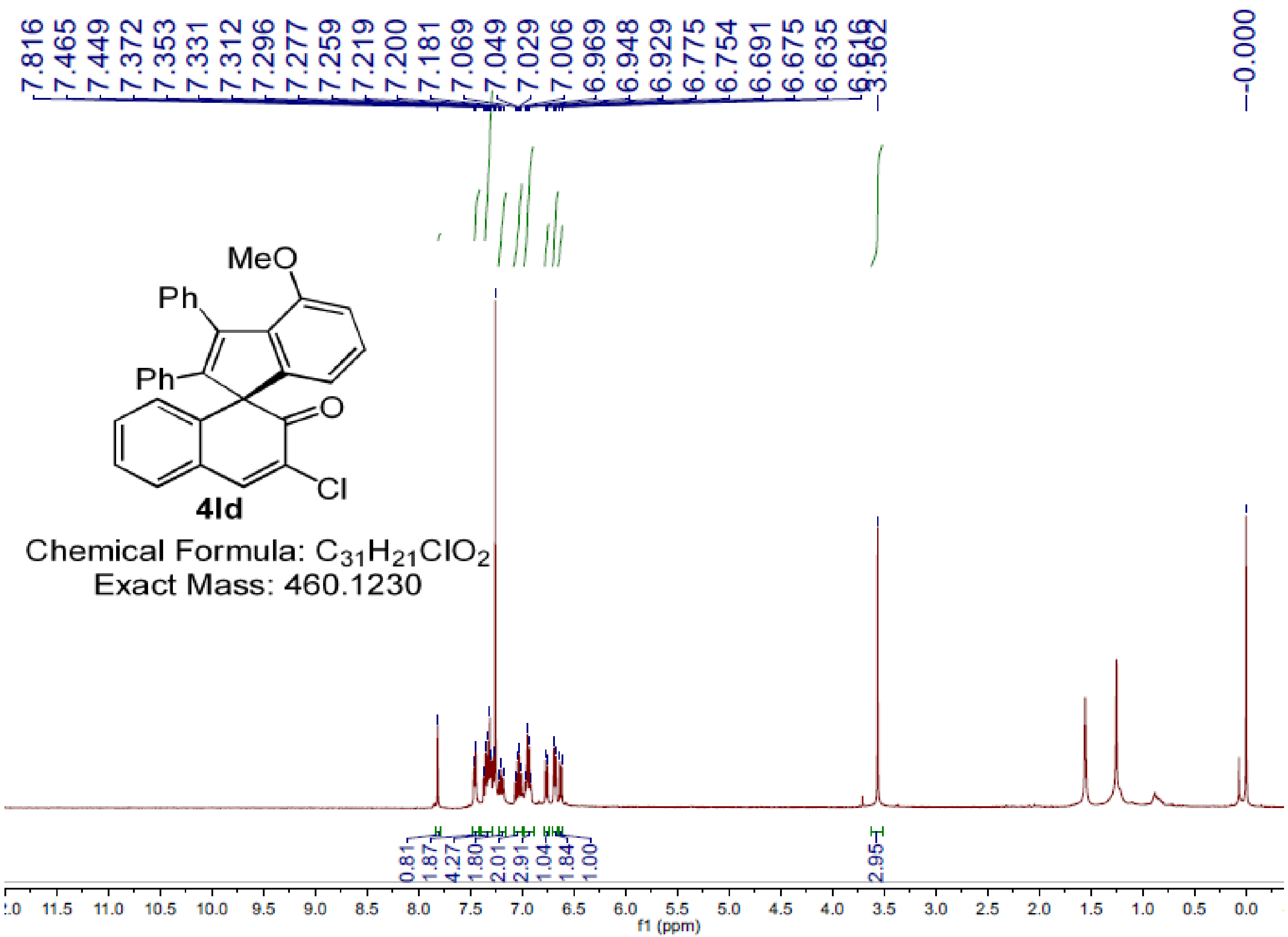


3ld

Chemical Formula: $C_{31}H_{21}ClO_2$

Exact Mass: 460.1230

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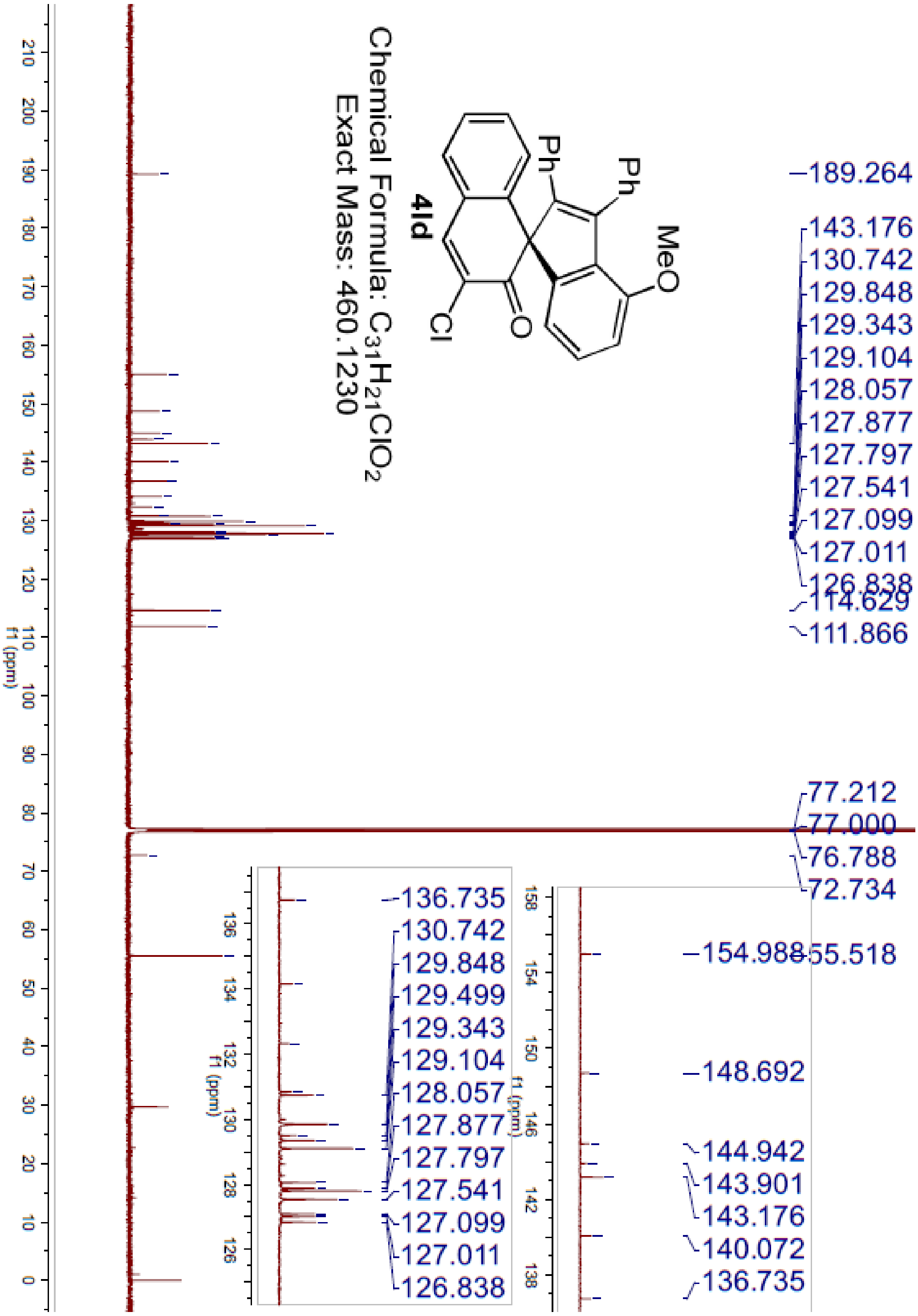
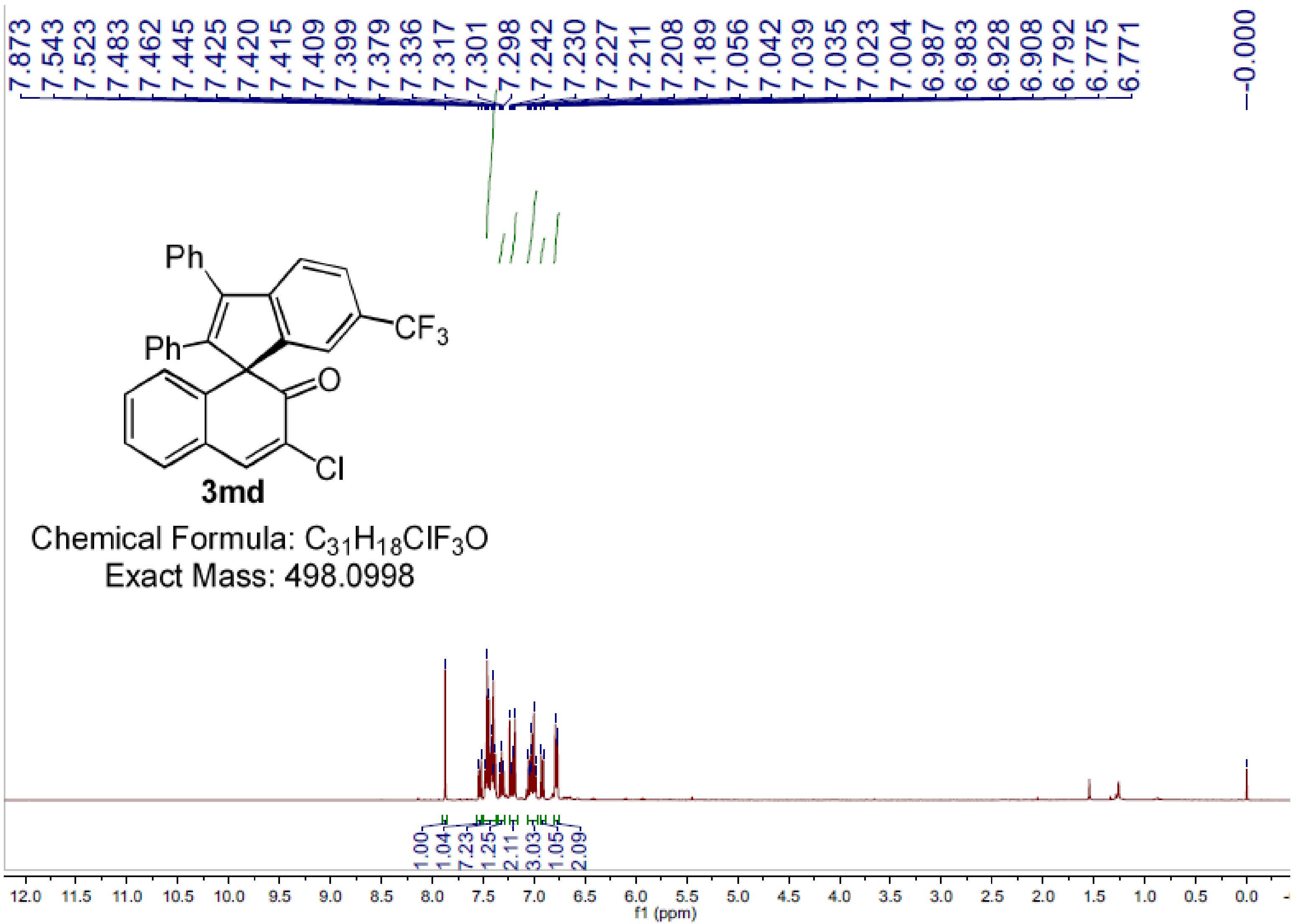
7.449
7.372
7.353
7.331
7.312
7.296
7.277
7.259
7.219
7.200
7.181
7.069
7.049
7.029
7.006
6.969
6.948
6.929
6.775
6.754
6.691
6.675
6.635
6.616
3.562
-0.000
MeO
Ph
Ph
O
Cl
4ld
Chemical Formula: $C_{31}H_{21}ClO_2$
Exact Mass: 460.1230
0.81
1.87
4.27
1.80
2.01
2.91
1.04
1.84
1.00
2.95
f1 (ppm)



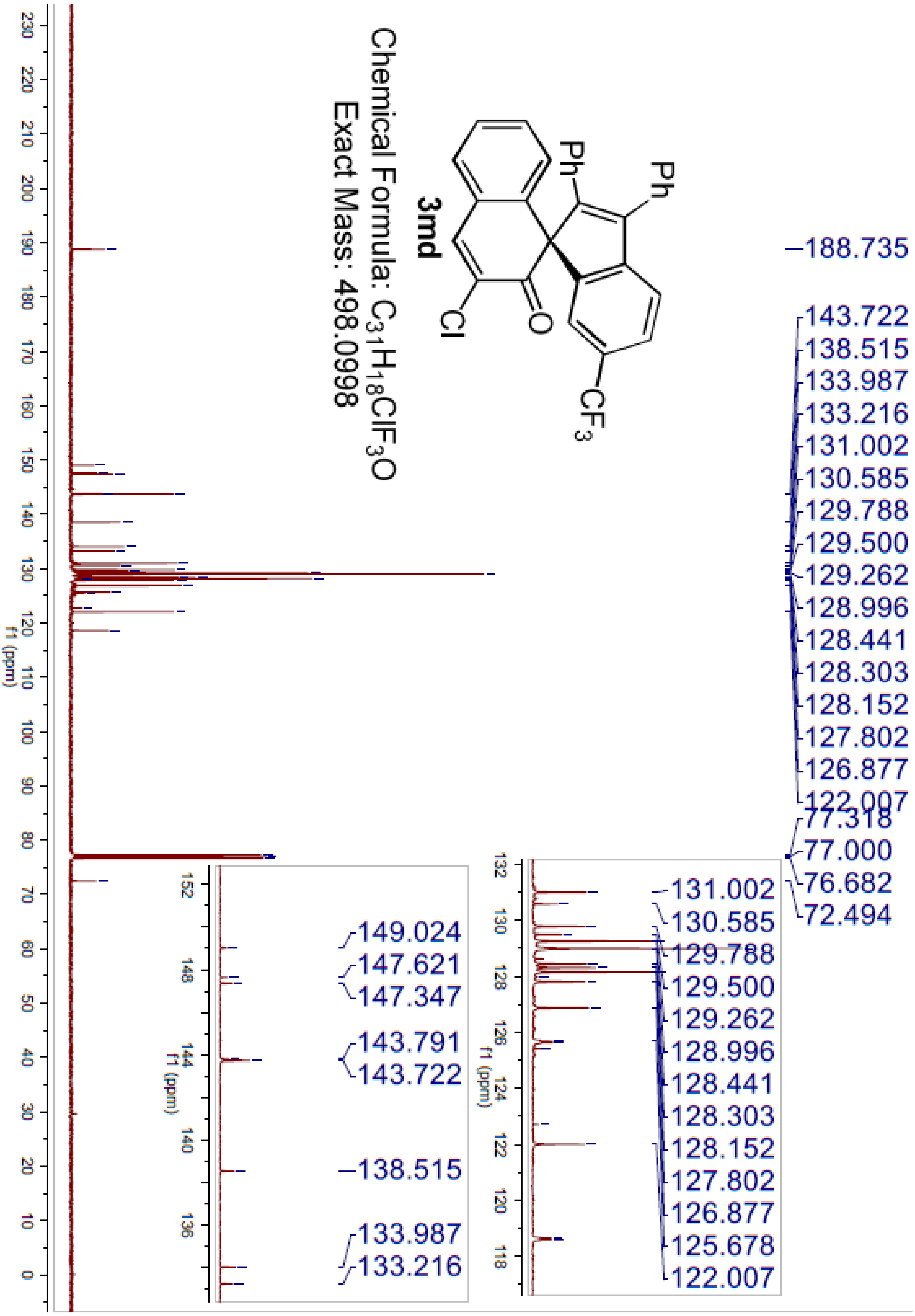
4ld
MeO
Ph
Ph
O
Cl
Chemical Formula: $C_{31}H_{21}ClO_2$
Exact Mass: 460.1230
189.264
143.176
130.742
129.848
129.343
129.104
128.057
127.877
127.797
127.541
127.099
127.011
126.838
114.629
111.866
77.212
77.000
76.788
72.734
55.518
154.988
148.692
144.942
143.901
143.176
140.072
136.735
136.735
130.742
129.848
129.499
129.343
129.104
128.057
127.877
127.797
127.541
127.099
127.011
126.838
f1 (ppm)



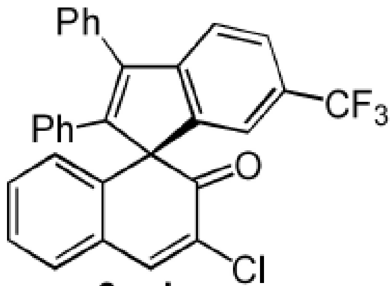
3md

Chemical Formula: $C_{31}H_{18}ClF_3O$

Exact Mass: 498.0998

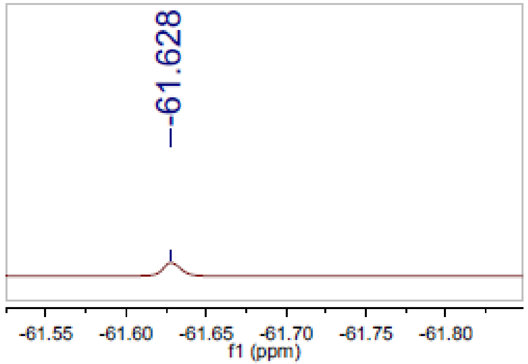

3md
Chemical Formula: C31H18ClF3O
Exact Mass: 498.0998
Ph
Ph
O
Cl
CF3
188.735
143.722
138.515
133.987
133.216
131.002
130.585
129.788
129.500
129.262
128.996
128.441
128.303
128.152
127.802
126.877
122.007
77.318
77.000
76.682
72.494
149.024
147.621
147.347
143.791
143.722
138.515
133.987
133.216
131.002
130.585
129.788
129.500
129.262
128.996
128.441
128.303
128.152
127.802
126.877
125.678
122.007
f1 (ppm)

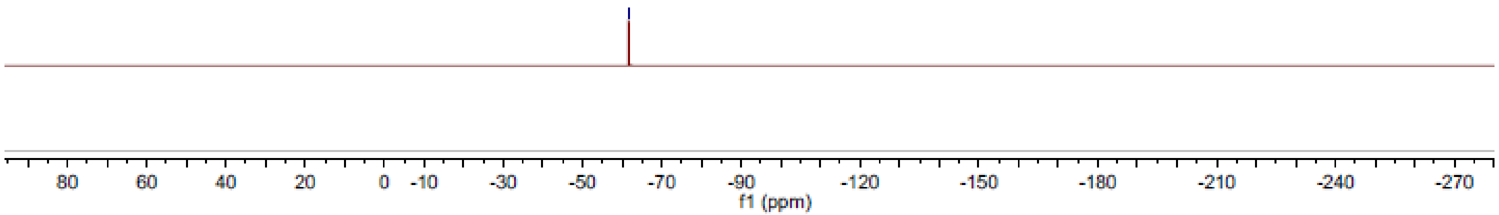
—-61.628

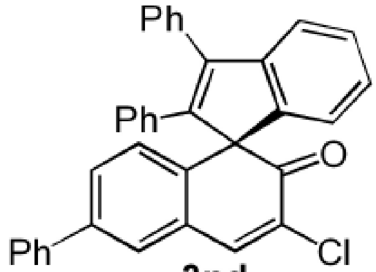


3md

Chemical Formula: $C_{31}H_{18}ClF_3O$
Exact Mass: 498.0998

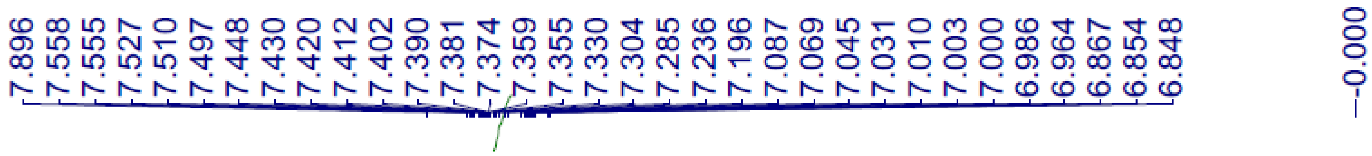


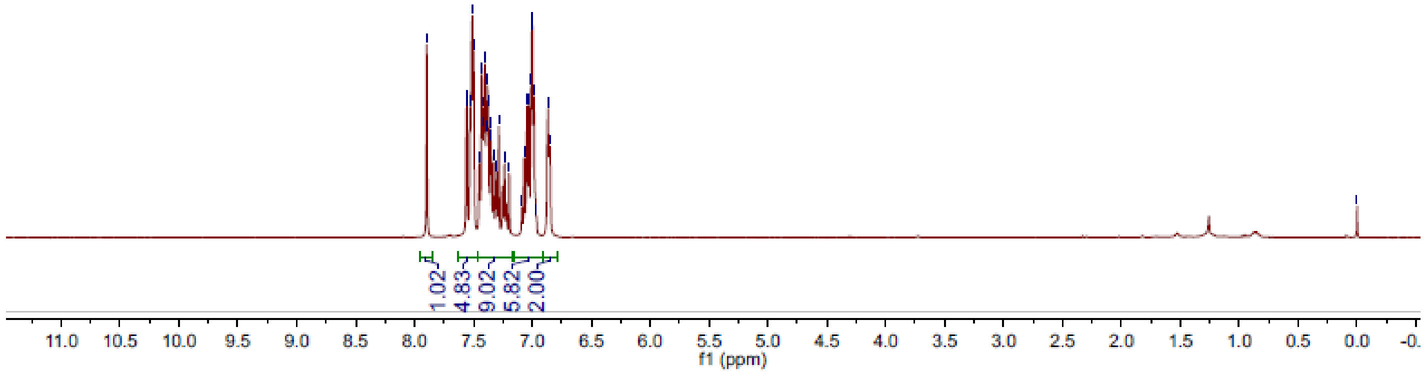


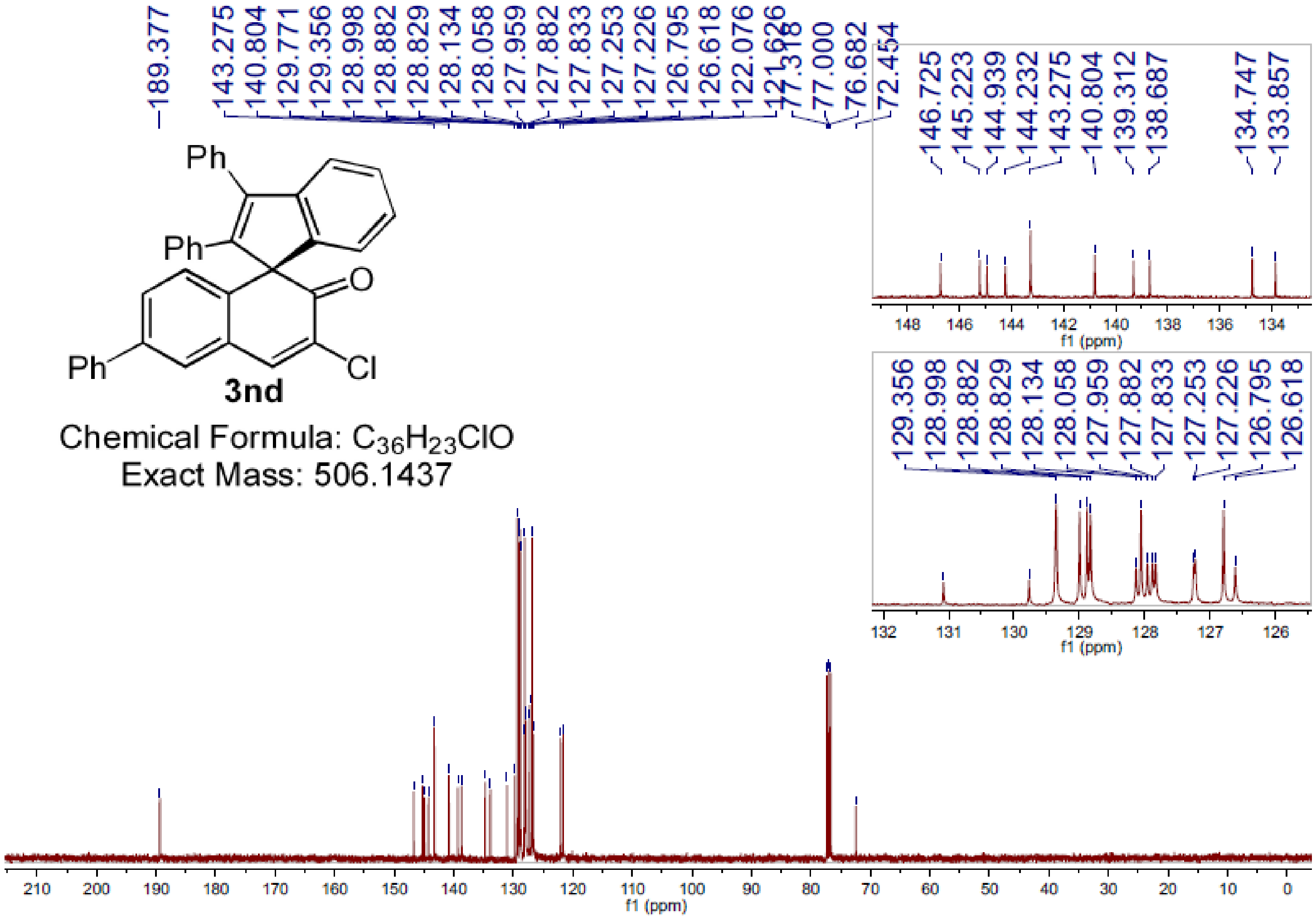


3nd

Chemical Formula: $C_{36}H_{23}ClO$
Exact Mass: 506.1437

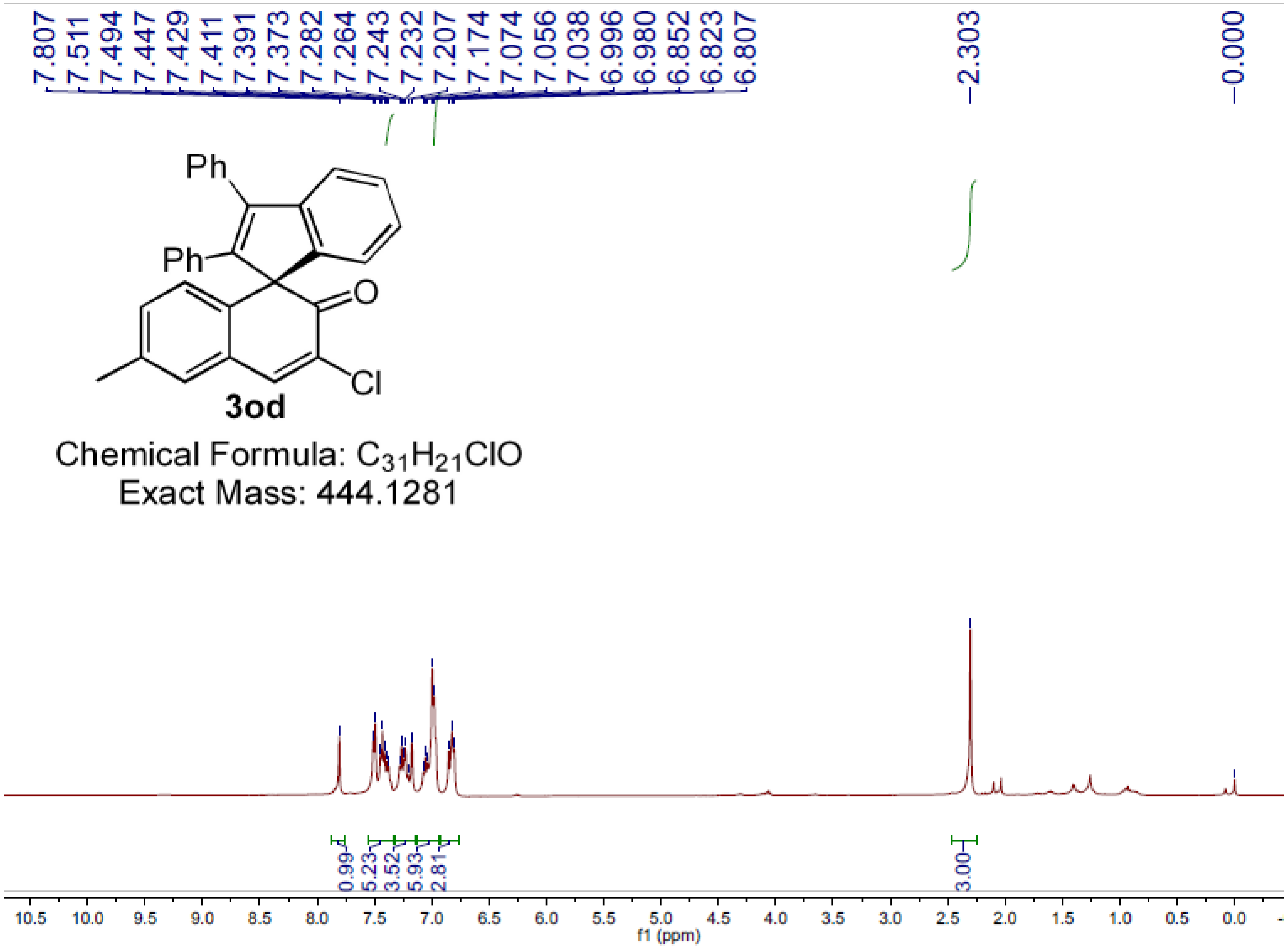


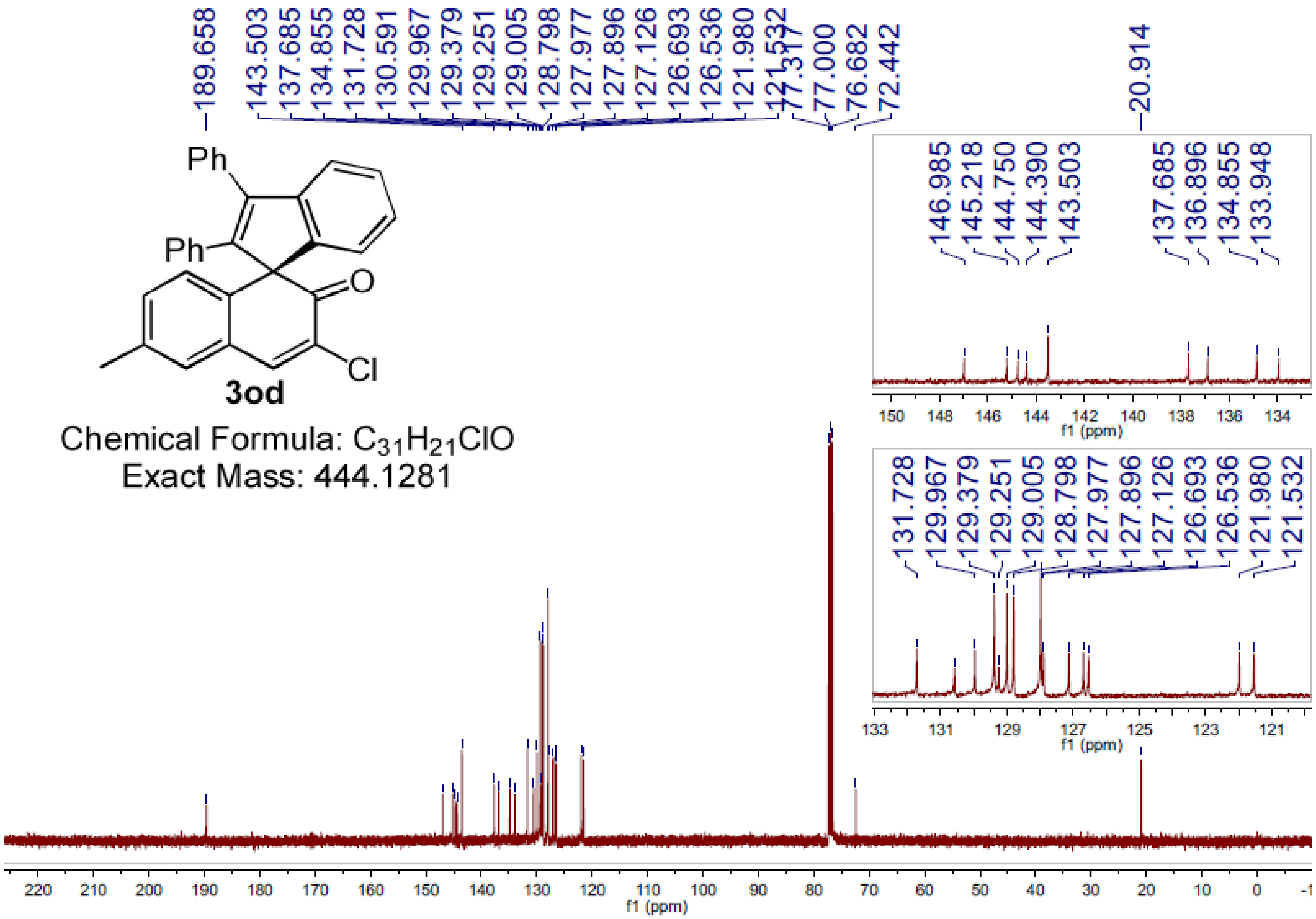




3nd

Chemical Formula: $C_{36}H_{23}ClO$
Exact Mass: 506.1437

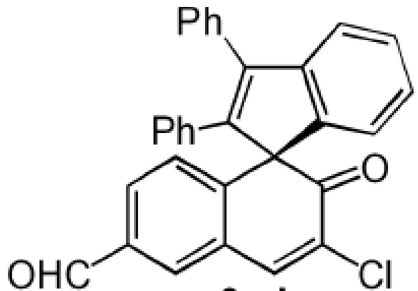

7.807
7.511
7.494
7.447
7.429
7.411
7.391
7.373
7.282
7.264
7.243
7.232
7.207
7.174
7.074
7.056
7.038
6.996
6.980
6.852
6.823
6.807
2.303
0.000
Ph
Ph
O
Cl
3od
Chemical Formula: $C_{31}H_{21}ClO$
Exact Mass: 444.1281
0.99
5.23
3.52
5.93
2.81
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3od

Chemical Formula: $C_{31}H_{21}ClO$

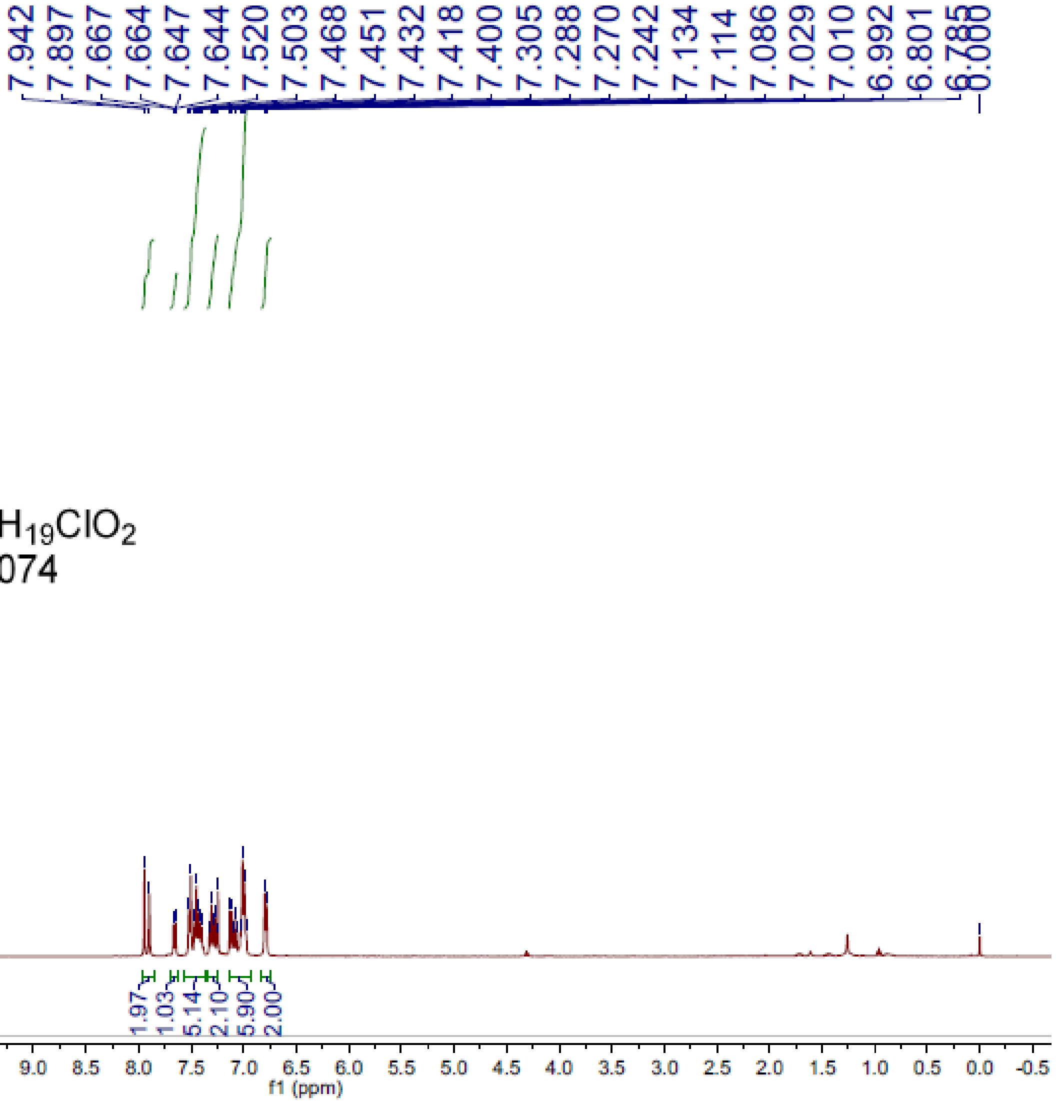
Exact Mass: 444.1281

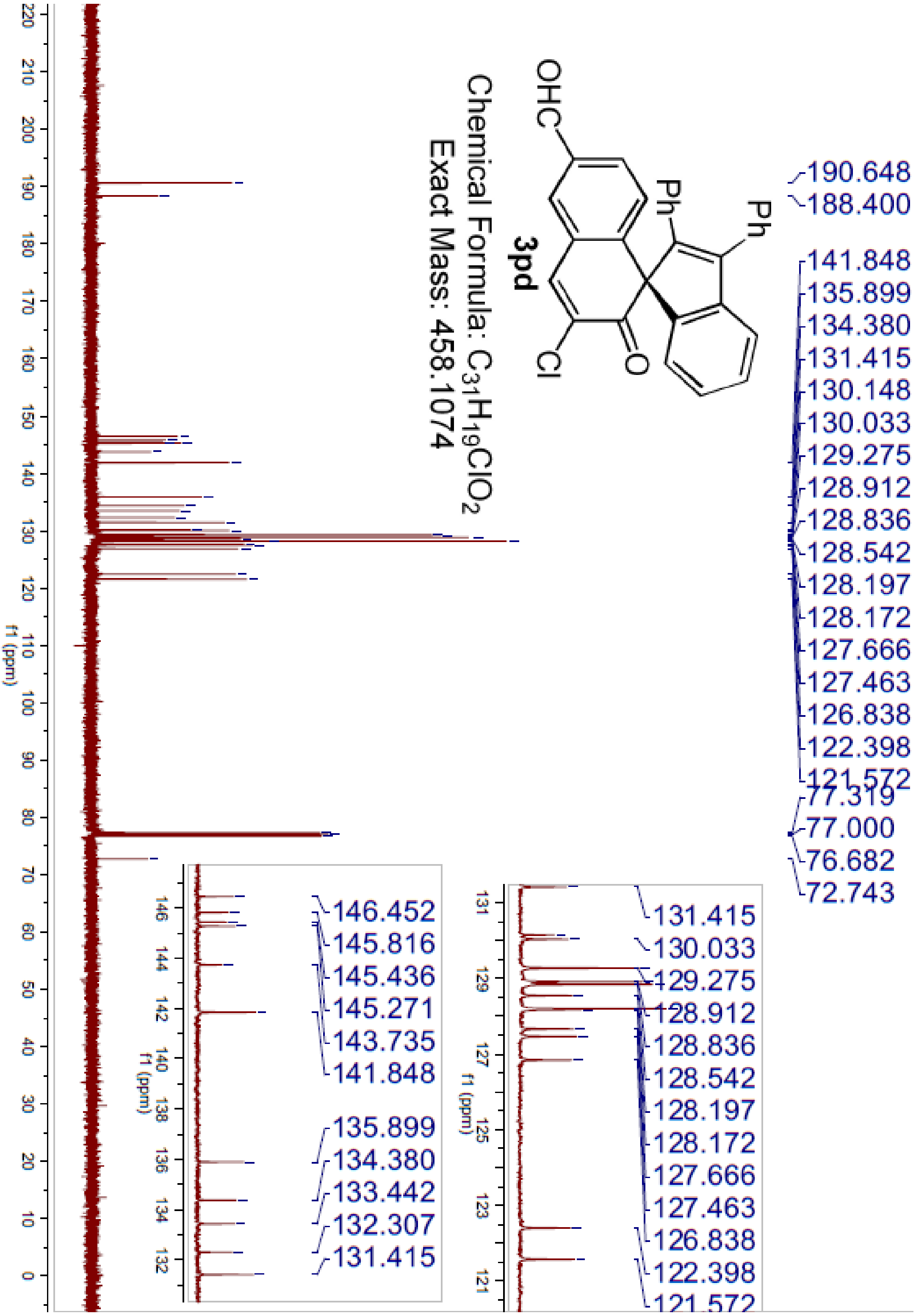


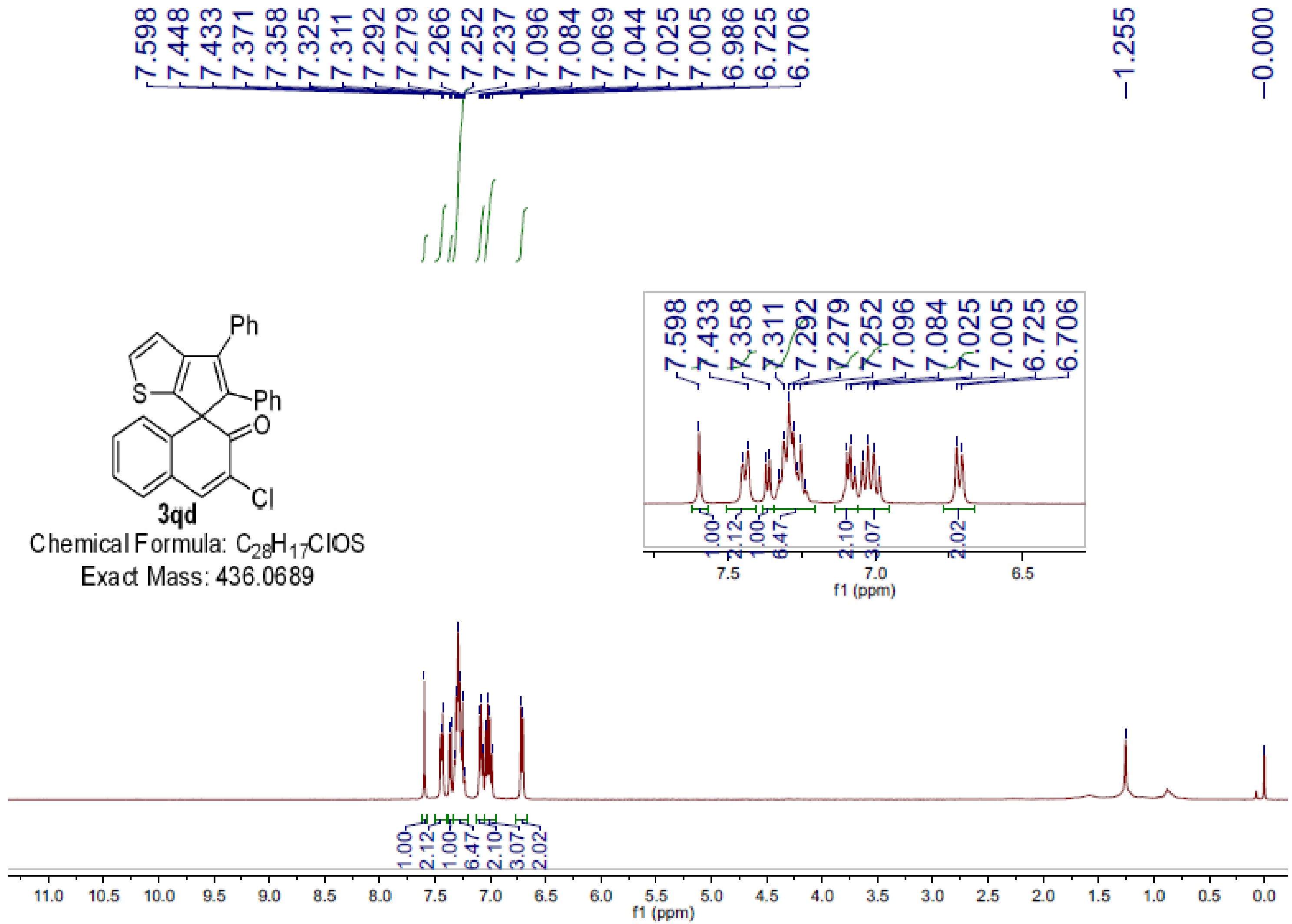
3pd

Chemical Formula: $C_{31}H_{19}ClO_2$

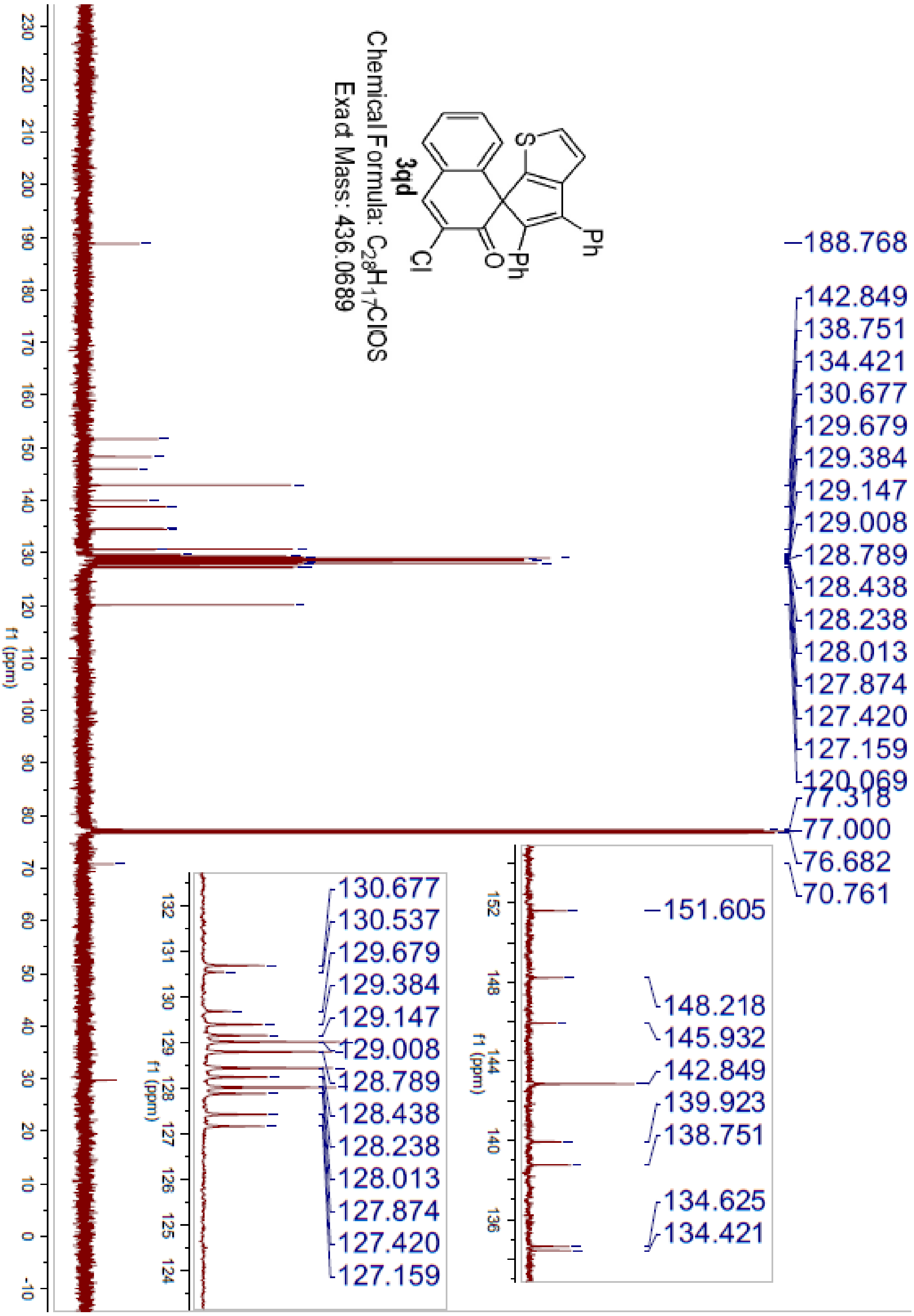
Exact Mass: 458.1074




3pd
Chemical Formula: $C_{31}H_{19}ClO_2$
Exact Mass: 458.1074
OHC
Ph
Ph
O
Cl
190.648
188.400
141.848
135.899
134.380
131.415
130.148
130.033
129.275
128.912
128.836
128.542
128.197
128.172
127.666
127.463
126.838
122.398
121.572
77.319
77.000
76.682
72.743
146.452
145.816
145.436
145.271
143.735
141.848
135.899
134.380
133.442
132.307
131.415
131.415
130.033
129.275
128.912
128.836
128.542
128.197
128.172
127.666
127.463
126.838
122.398
121.572
f1 (ppm)



7.598 7.448 7.433 7.371 7.358 7.325 7.311 7.292 7.279 7.266 7.252 7.237 7.096 7.084 7.069 7.044 7.025 7.005 6.986 6.725 6.706
1.255
0.000
Ph
S
Ph
O
Cl
3qd
Chemical Formula: $C_{28}H_{17}ClOS$
Exact Mass: 436.0689
7.598 7.433 7.358 7.311 7.292 7.279 7.252 7.096 7.084 7.025 7.005 6.725 6.706
1.00 2.12 1.00 6.47 2.10 3.07 2.02
7.5 7.0 6.5
f1 (ppm)
1.00 2.12 1.00 6.47 2.10 3.07 2.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


3qd
Chemical Formula: C28H17ClOS
Exact Mass: 436.0689
Ph
Ph
S
O
Cl
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142.849
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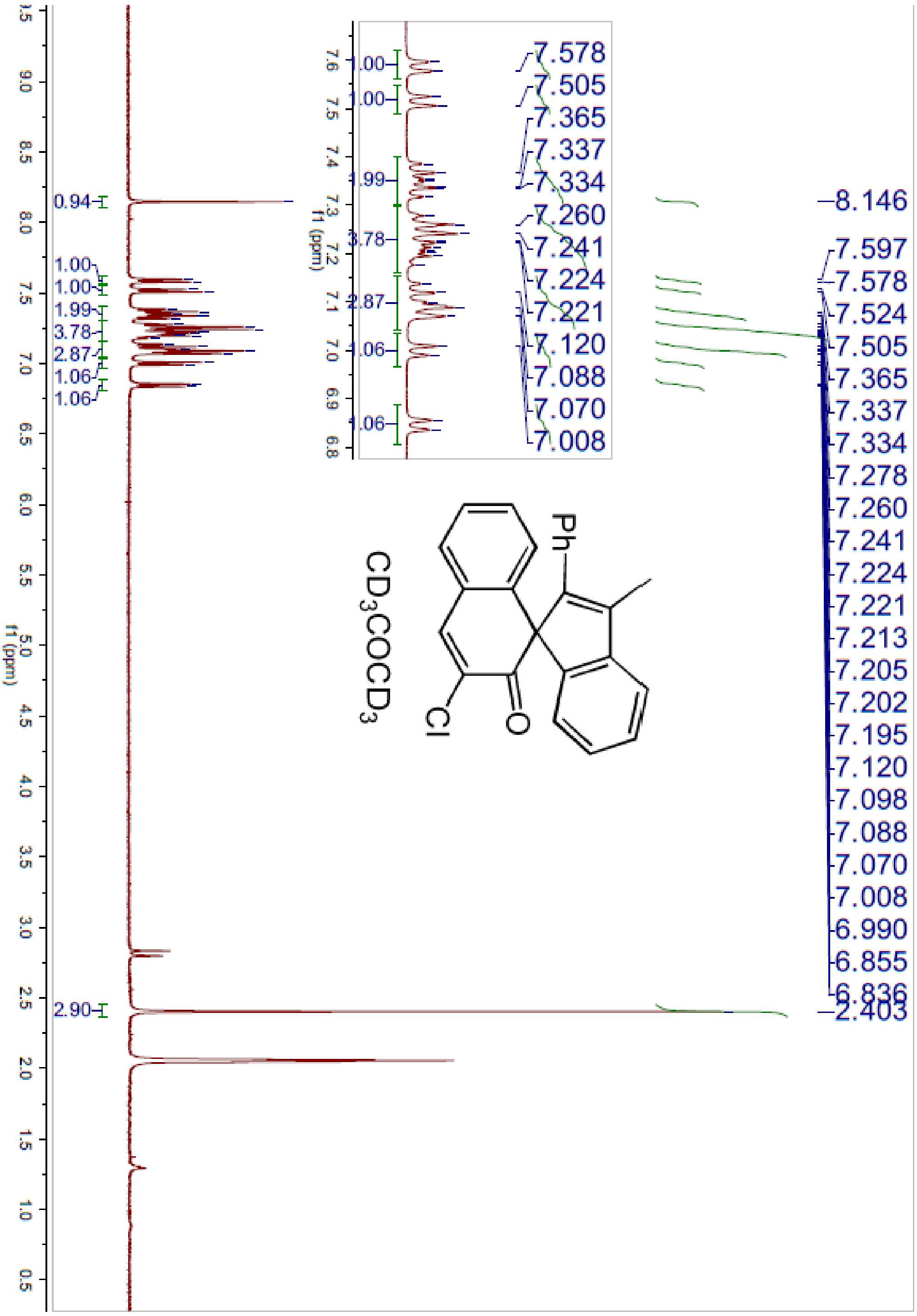
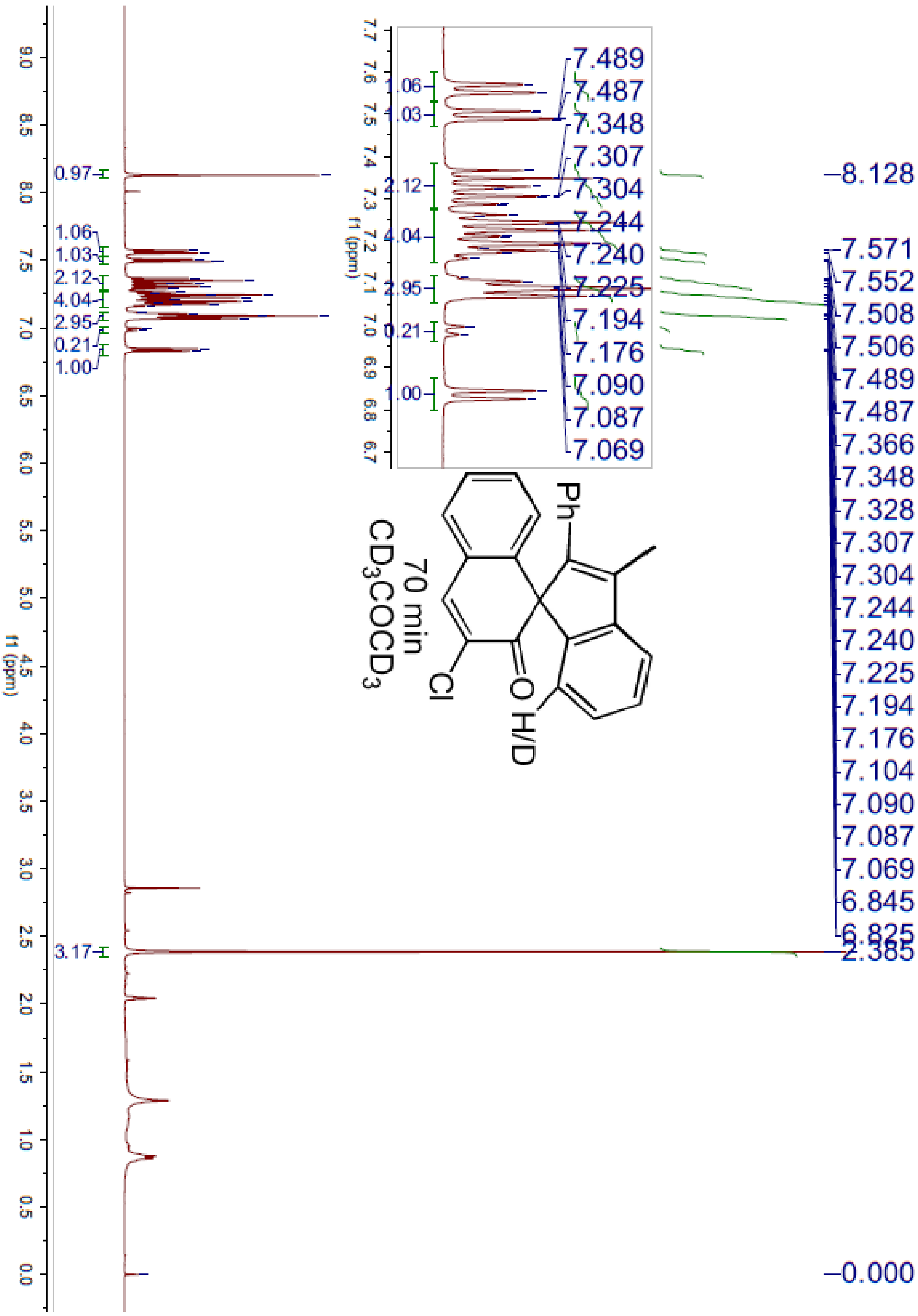
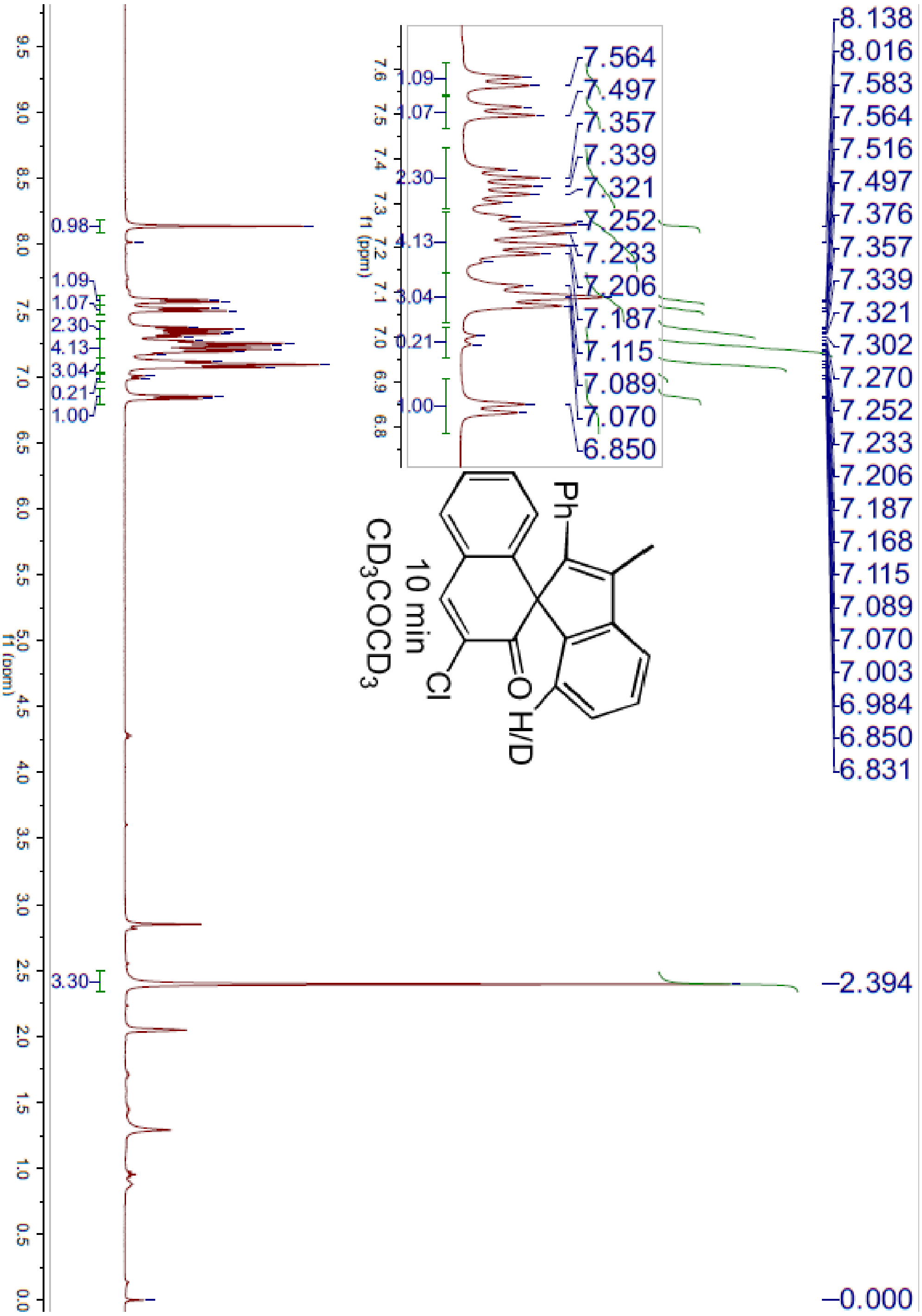
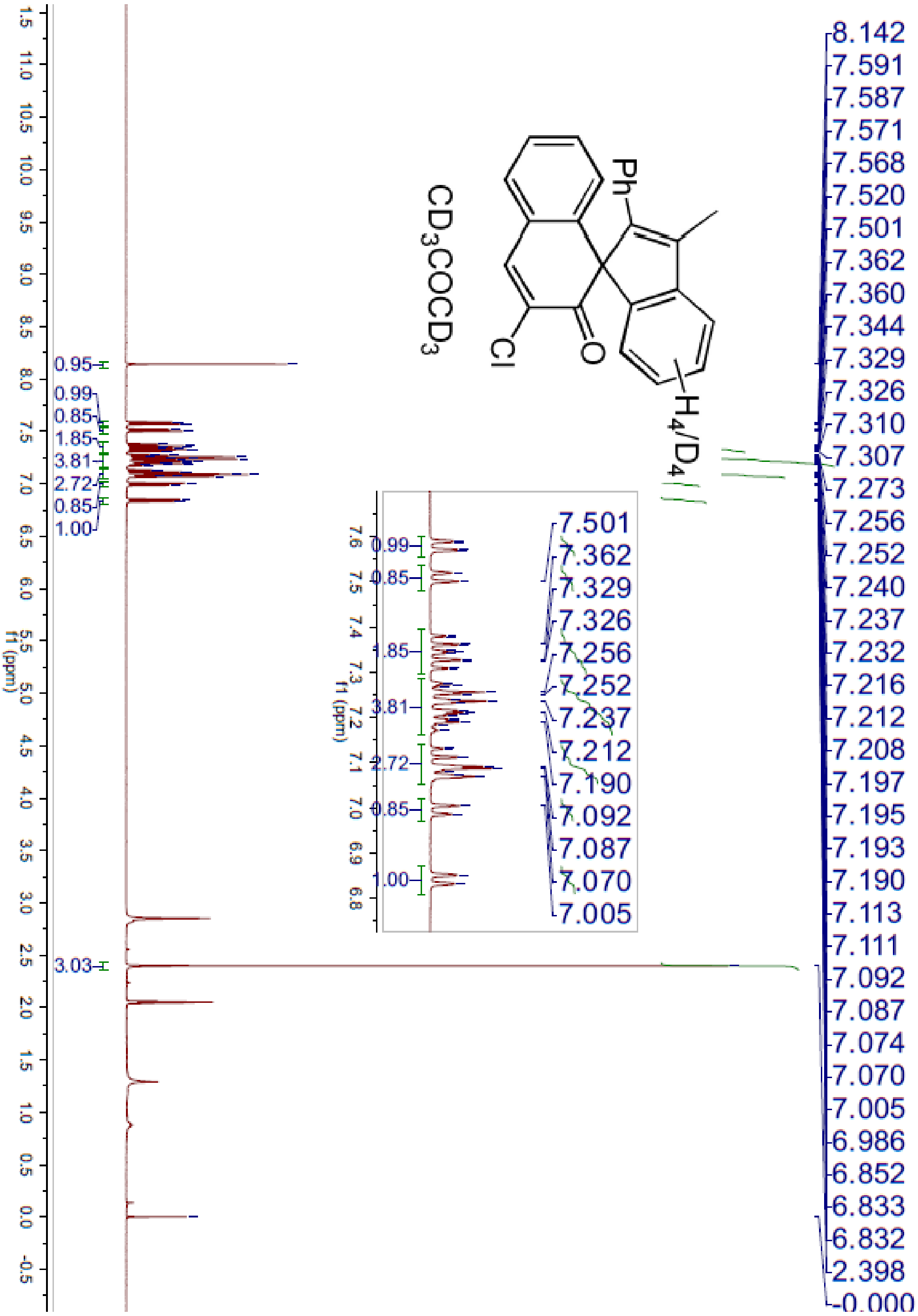
134.421
130.677
129.679
129.384
129.147
129.008
128.789
128.438
128.238
128.013
127.874
127.420
127.159
120.069
77.318
77.000
76.682
70.761
151.605
148.218
145.932
142.849
139.923
138.751
134.625
134.421
130.677
130.537
129.679
129.384
129.147
129.008
128.789
128.438
128.238
128.013
127.874
127.420
127.159
f1 (ppm)



8.146
7.597
7.578
7.524
7.505
7.365
7.337
7.334
7.278
7.260
7.241
7.224
7.221
7.213
7.205
7.202
7.195
7.120
7.098
7.088
7.070
7.008
6.990
6.855
6.836
2.403
0.94
1.00
1.00
1.99
3.78
2.87
1.06
1.06
2.90
f1 (ppm)
Ph
Cl
O
CD3COCD3


Ph
O H/D
Cl
70 min
CD3COCD3
f1 (ppm)
8.128
7.571
7.552
7.508
7.506
7.489
7.487
7.366
7.348
7.328
7.307
7.304
7.244
7.240
7.225
7.194
7.176
7.104
7.090
7.087
7.069
6.845
6.825
2.385
0.000


8.138
8.016
7.583
7.564
7.516
7.497
7.376
7.357
7.339
7.321
7.302
7.270
7.252
7.233
7.206
7.187
7.168
7.115
7.089
7.070
7.003
6.984
6.850
6.831
2.394
0.000
7.564
7.497
7.357
7.339
7.321
7.252
7.233
7.206
7.187
7.115
7.089
7.070
6.850
Ph
O H/D
Cl
10 min
CD_3COCD_3
f1 (ppm)



8.142
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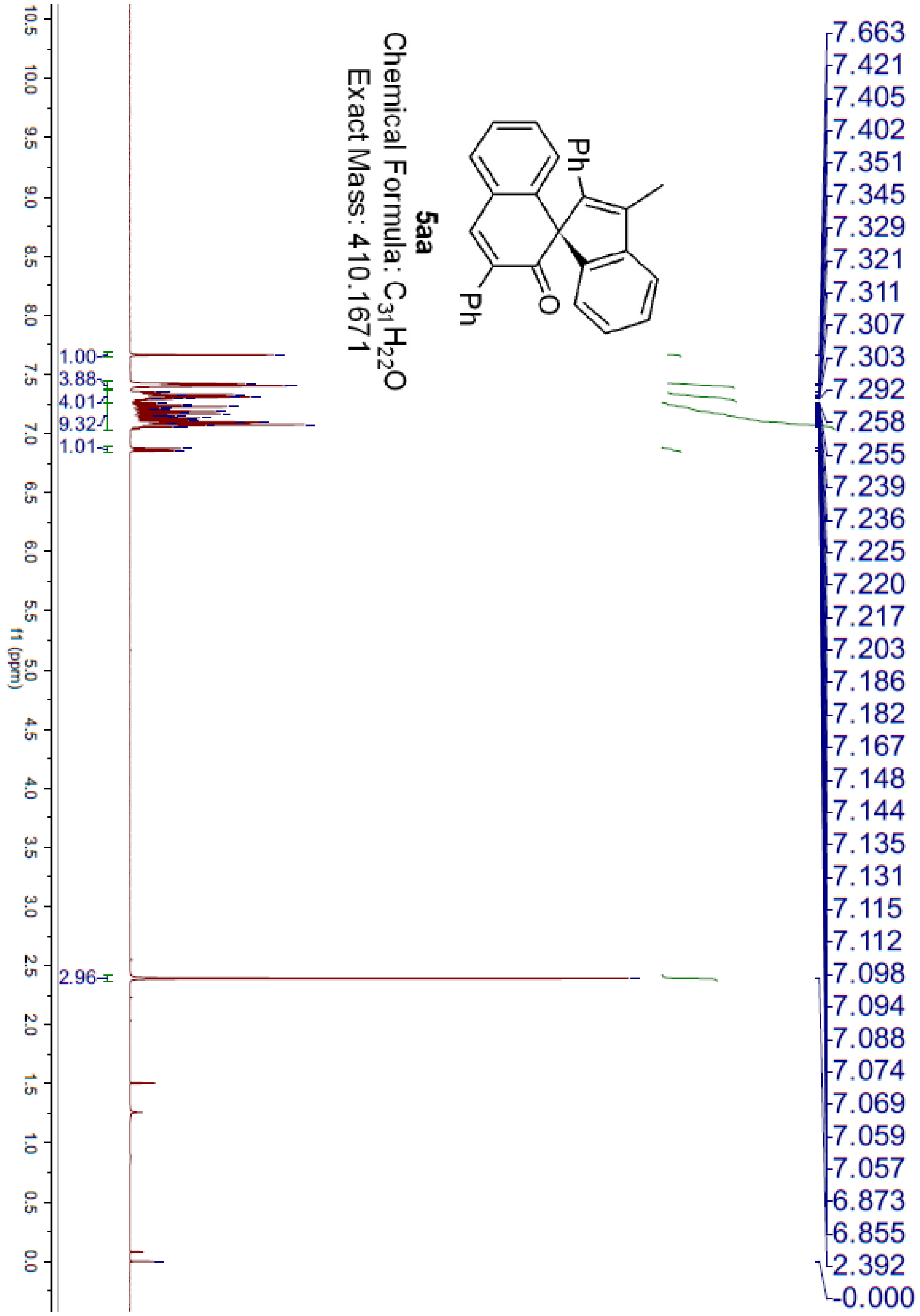
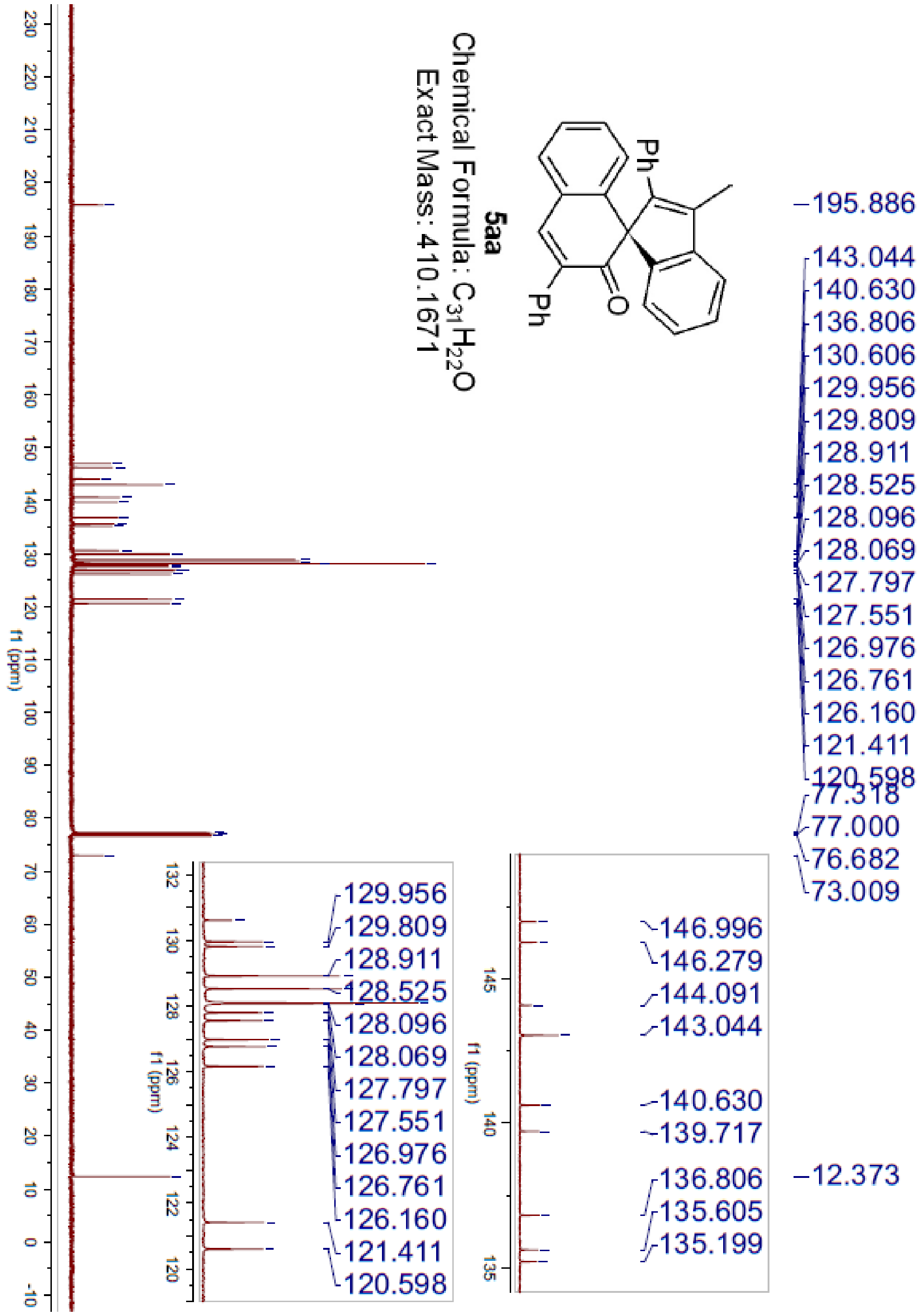
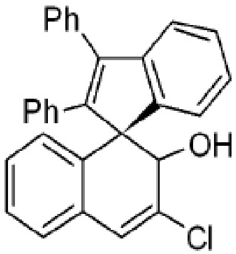
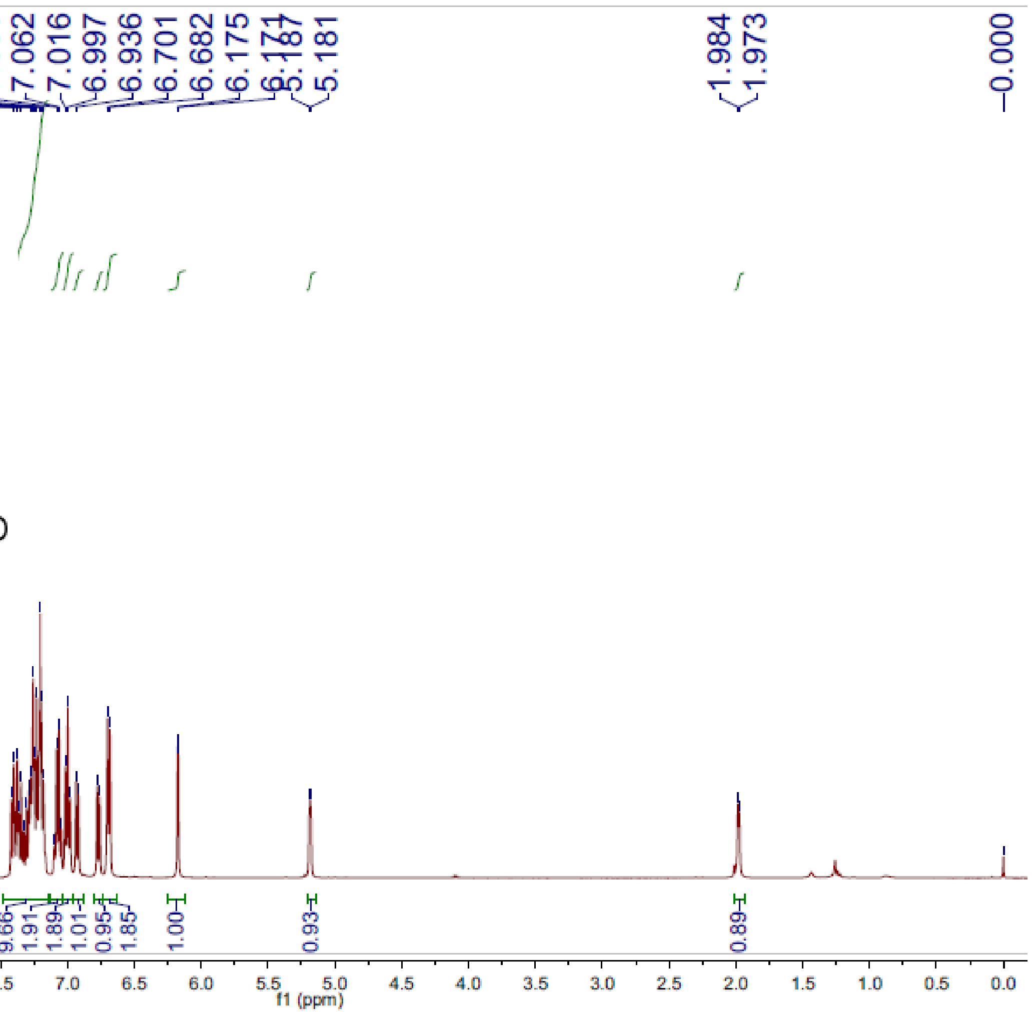
7.587
7.571
7.568
7.520
7.501
7.362
7.360
7.344
7.329
7.326
7.310
7.307
7.273
7.256
7.252
7.240
7.237
7.232
7.216
7.212
7.208
7.197
7.195
7.193
7.190
7.113
7.111
7.092
7.087
7.074
7.070
7.005
6.986
6.852
6.833
6.832
2.398
-0.000
Ph
Cl
O
H4/D4
CD3COCD3
f1 (ppm)

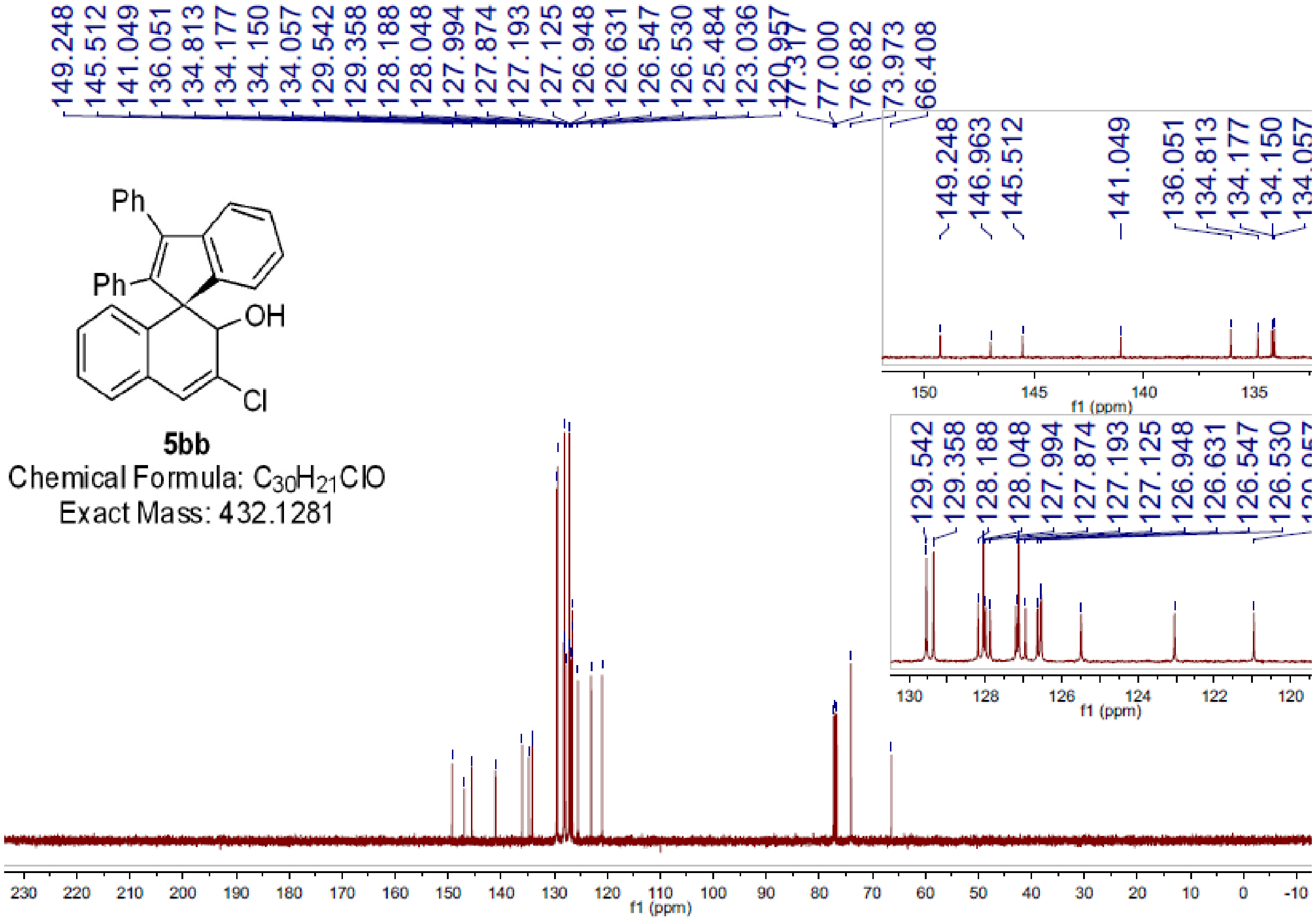

5aa
Chemical Formula: $C_{31}H_{22}O$
Exact Mass: 410.1671
Ph
Ph
O
f1 (ppm)

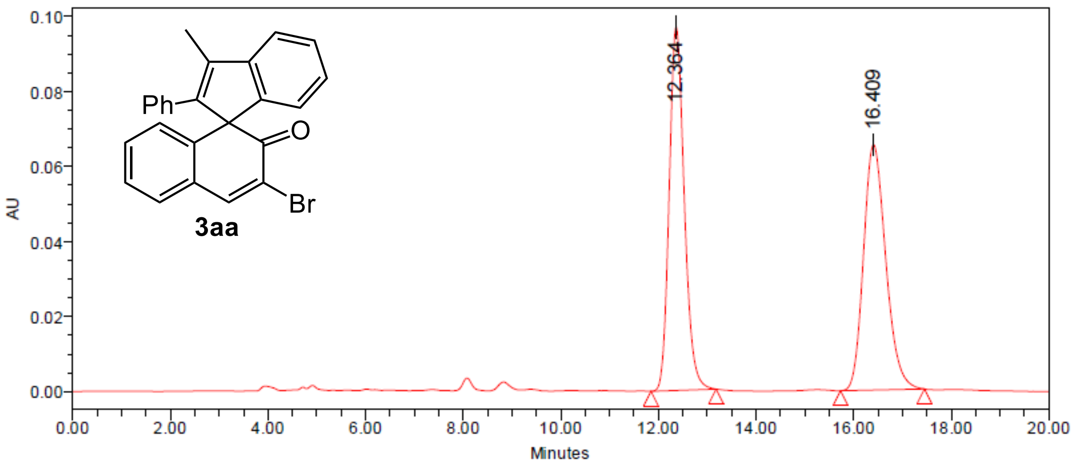

5aa
Chemical Formula: C31H22O
Exact Mass: 410.1671
Ph
Ph
O
195.886
143.044
140.630
136.806
130.606
129.956
129.809
128.911
128.525
128.096
128.069
127.797
127.551
126.976
126.761
126.160
121.411
120.598
77.318
77.000
76.682
73.009
12.373
146.996
146.279
144.091
143.044
140.630
139.717
136.806
135.605
135.199
f1 (ppm)



5bb
Chemical Formula: $C_{30}H_{21}ClO$
Exact Mass: 432.1281

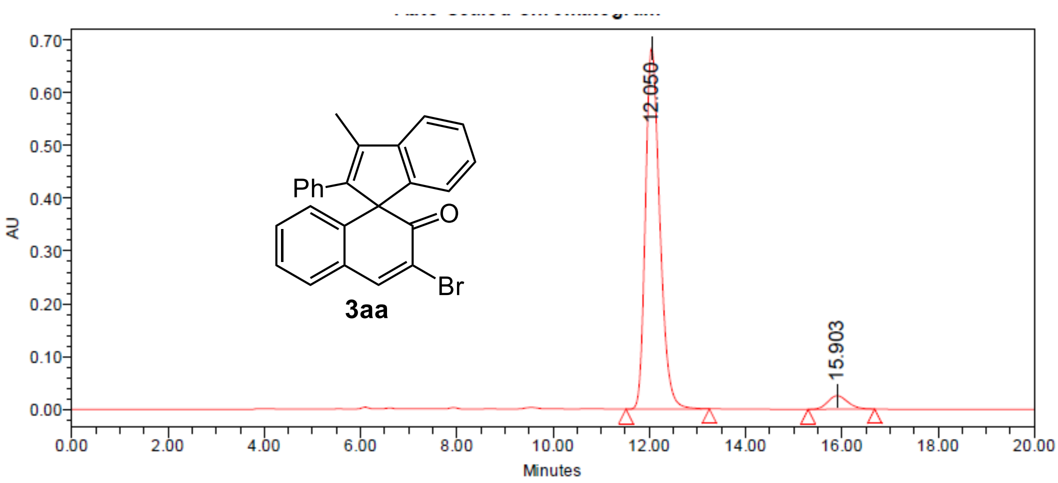



149.248
145.512
141.049
136.051
134.813
134.177
134.150
134.057
129.542
129.358
128.188
128.048
127.994
127.874
127.193
127.125
126.948
126.631
126.547
126.530
125.484
123.036
120.957
77.317
77.000
76.682
73.973
66.408
Ph
Ph
OH
Cl
5bb
Chemical Formula: $C_{30}H_{21}ClO$
Exact Mass: 432.1281
149.248
146.963
145.512
141.049
136.051
134.813
134.177
134.150
134.057
f1 (ppm)
129.542
129.358
128.188
128.048
127.994
127.874
127.193
127.125
126.948
126.631
126.547
126.530
f1 (ppm)
f1 (ppm)



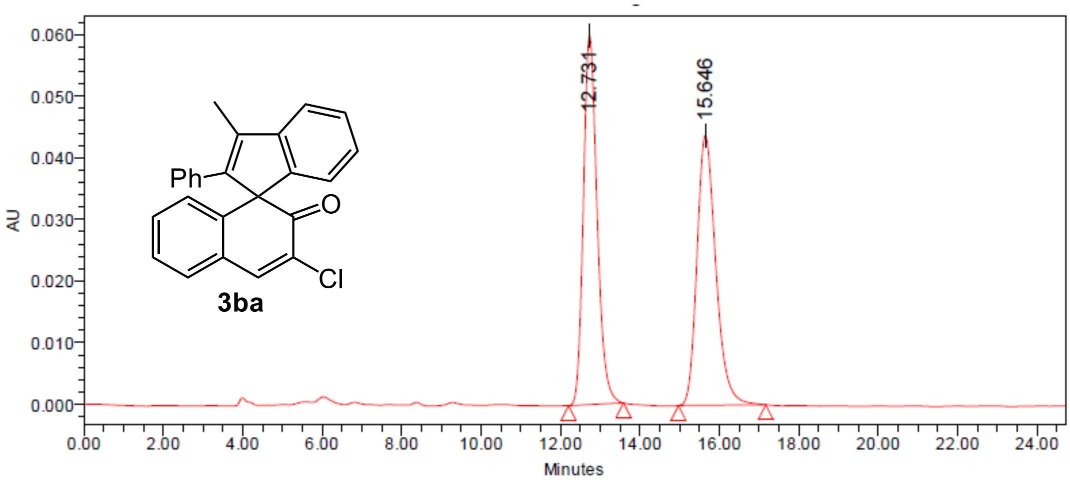
Peak Results

	Name	RT	Area	Height	% Area
1		12.364	2083097	96989	50.10
2		16.409	2074558	65496	49.90



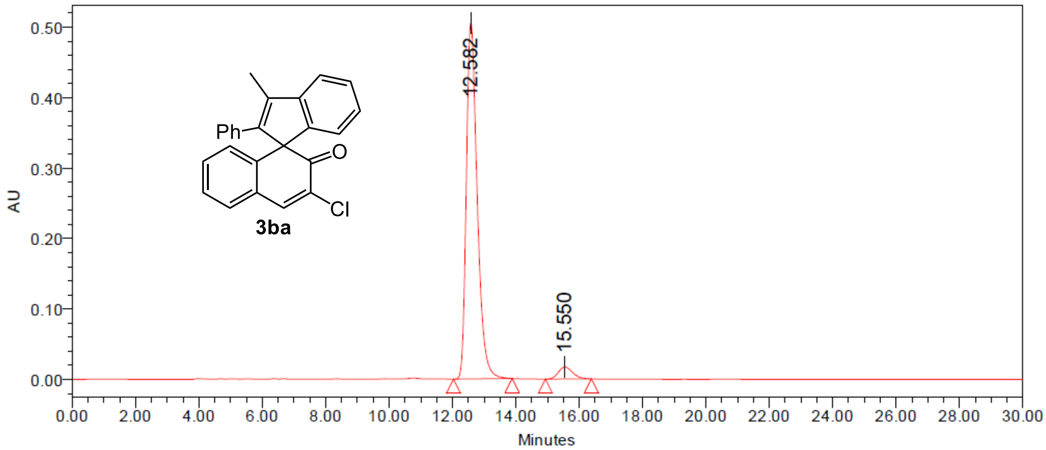
Peak Results

	Name	RT	Area	Height	% Area
1		12.050	14203815	684099	95.11
2		15.903	730044	25499	4.89



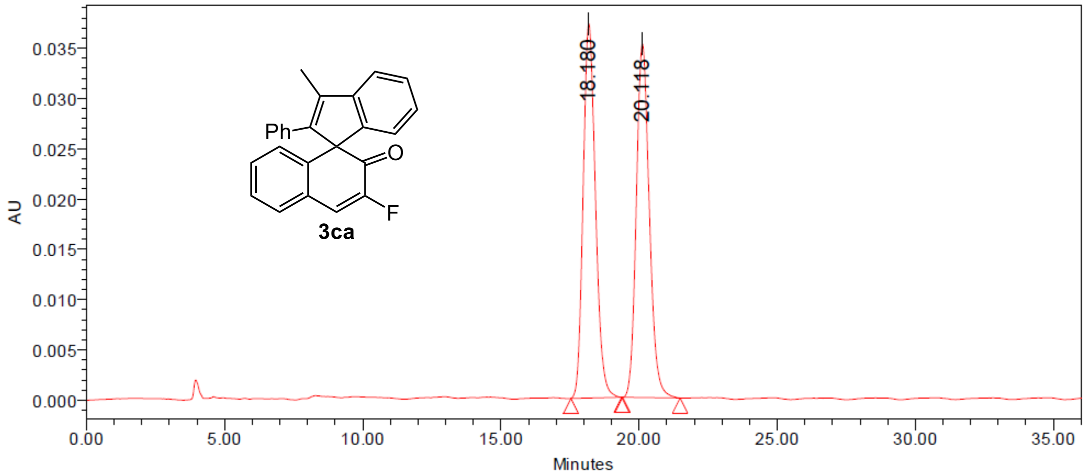
Peak Results

	Name	RT	Area	Height	% Area
1		12.731	1433558	59935	49.83
2		15.646	1443323	43800	50.17



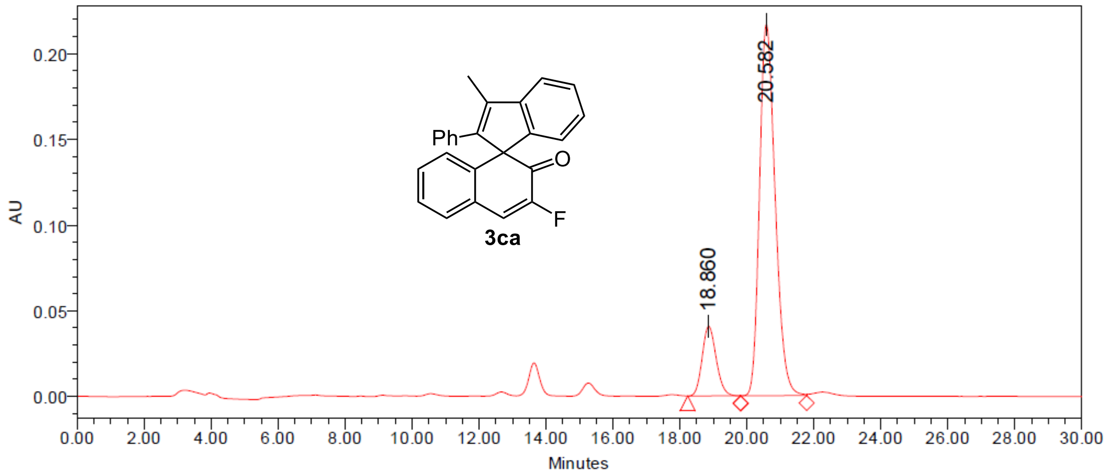
Peak Results

	Name	RT	Area	Height	% Area
1		12.582	12030642	505434	95.73
2		15.550	537208	17103	4.27



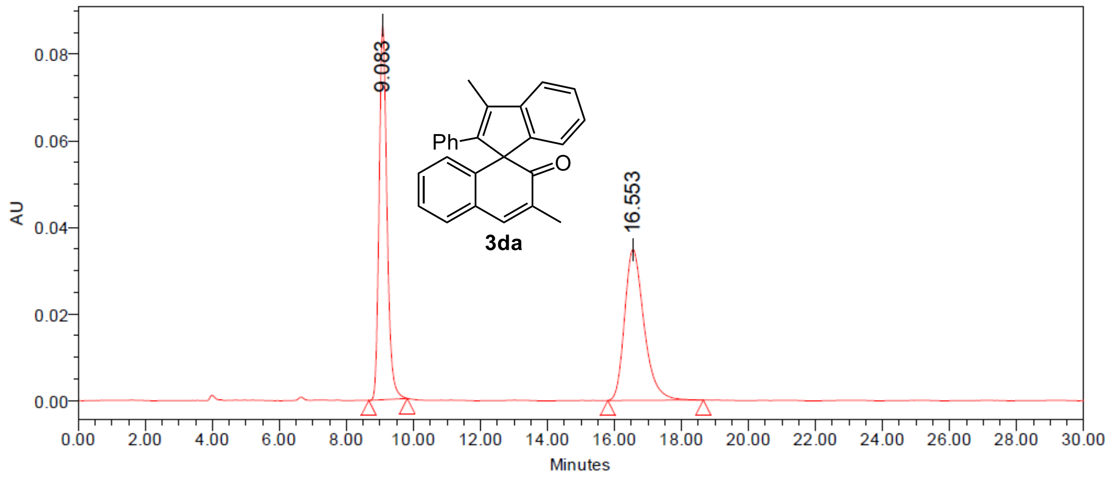
Peak Results

	Name	RT	Area	Height	% Area
1		18.180	1149914	37207	50.00
2		20.118	1150021	35168	50.00



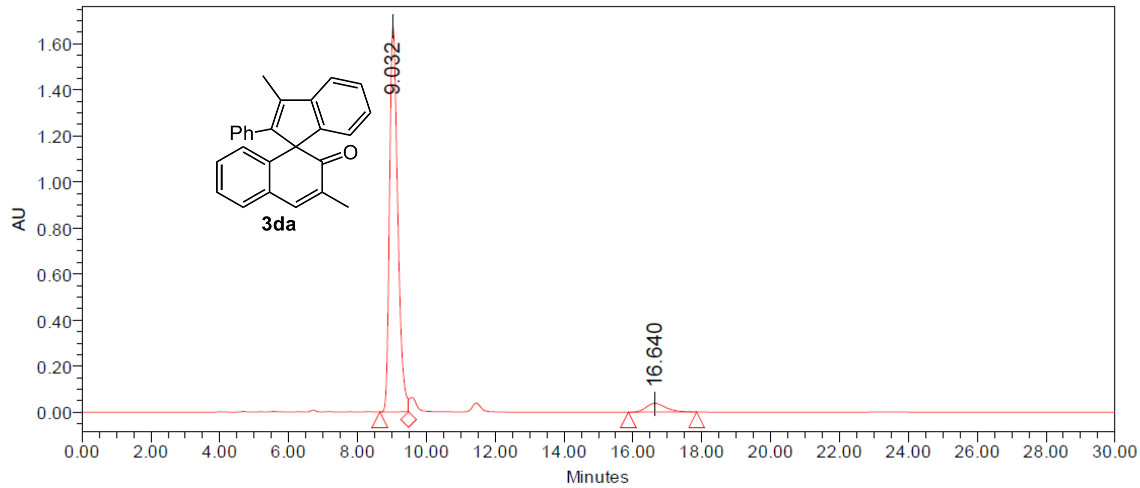
Peak Results

	Name	RT	Area	Height	% Area
1		18.860	1182566	40674	14.37
2		20.582	7048669	216766	85.63



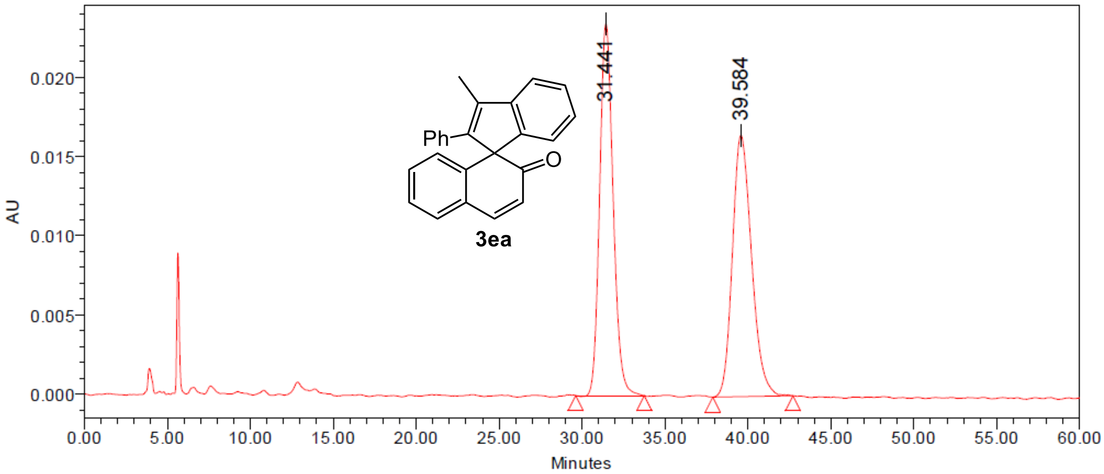
Peak Results

	Name	RT	Area	Height	% Area
1		9.083	1412916	86457	50.18
2		16.553	1402851	34823	49.82



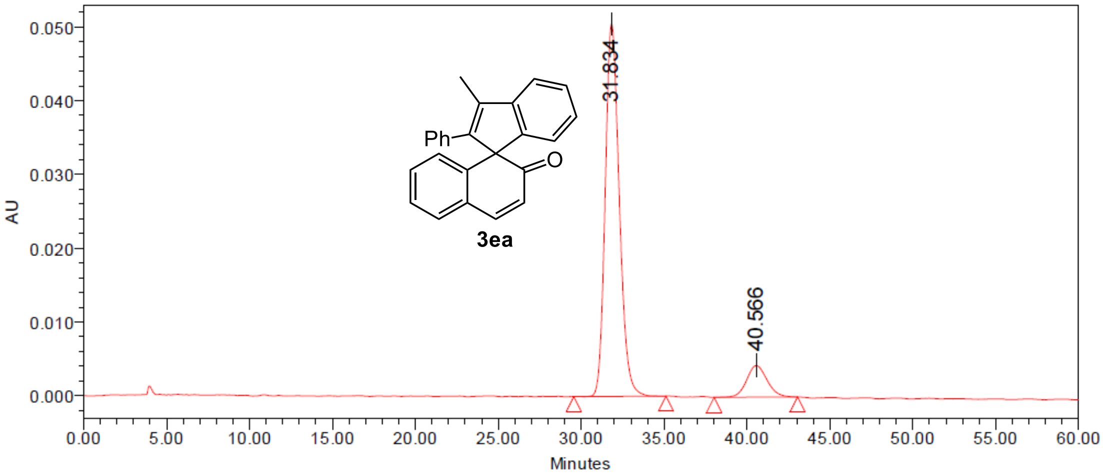
Peak Results

	Name	RT	Area	Height	% Area
1		9.032	27712565	1675591	94.88
2		16.640	1496787	37599	5.12



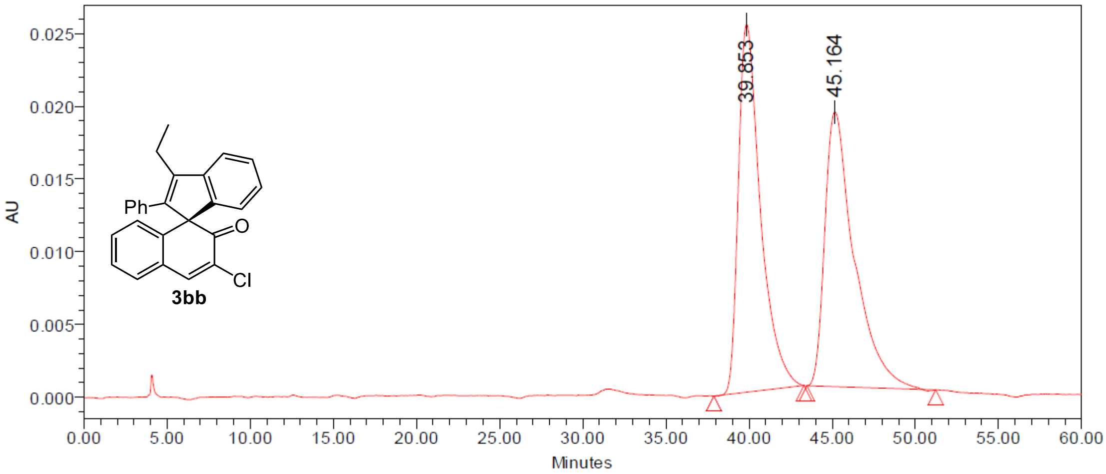
Peak Results

	Name	RT	Area	Height	% Area
1		31.441	1326367	23463	50.04
2		39.584	1324418	16485	49.96



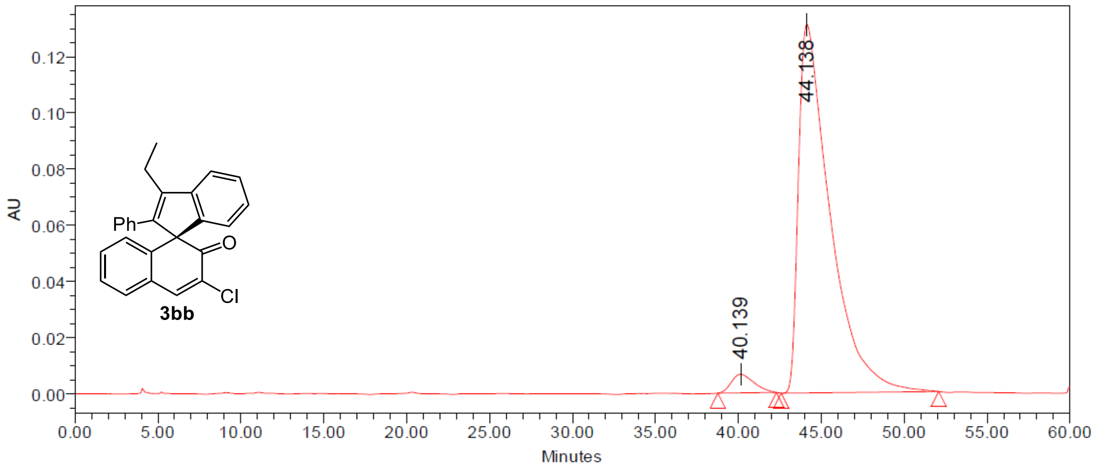
Peak Results

	Name	RT	Area	Height	% Area
1		31.834	2979129	50506	89.00
2		40.566	368343	4278	11.00



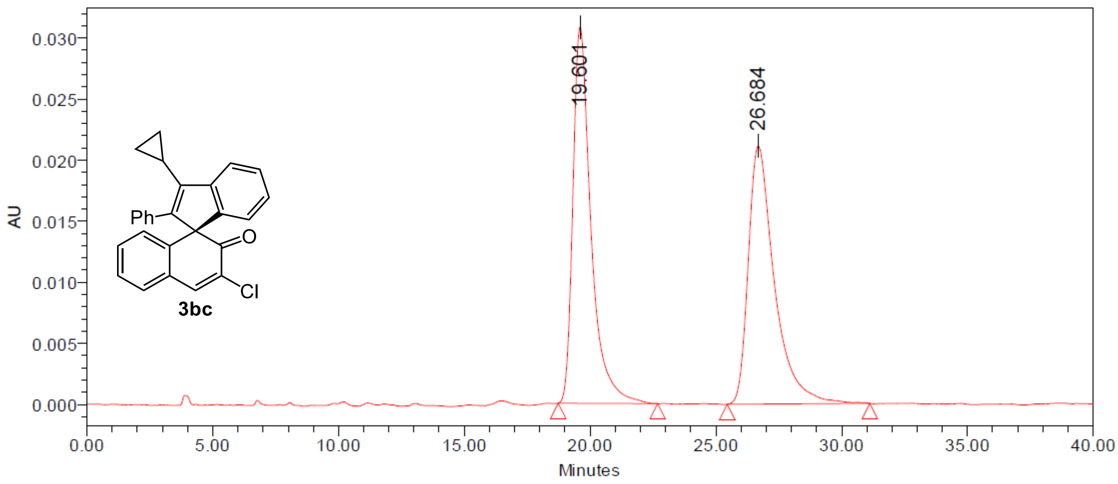
Peak Results

	Name	RT	Area	Height	% Area
1		39.853	2347077	25284	50.21
2		45.164	2327279	18882	49.79



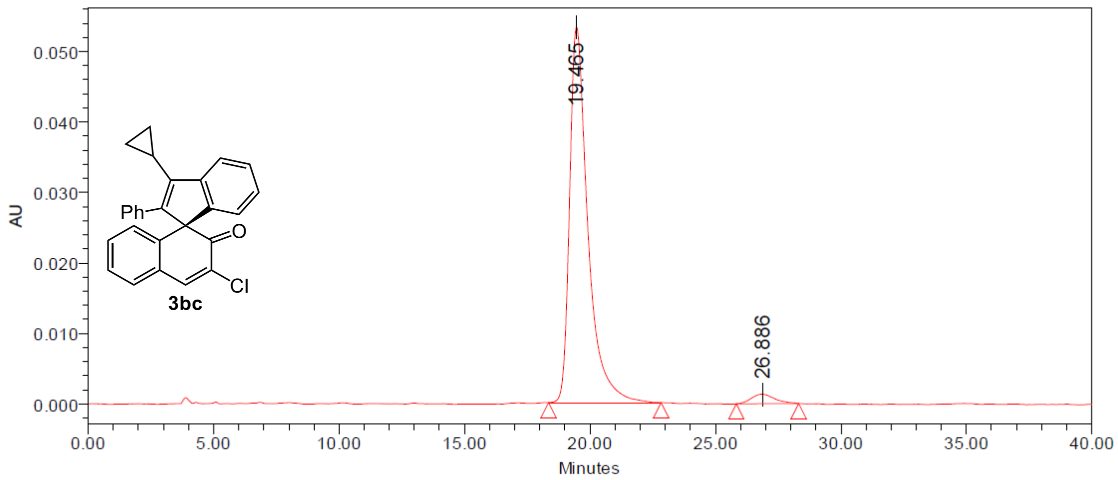
Peak Results

	Name	RT	Area	Height	% Area
1		40.139	631448	6624	3.51
2		44.138	17379831	131169	96.49



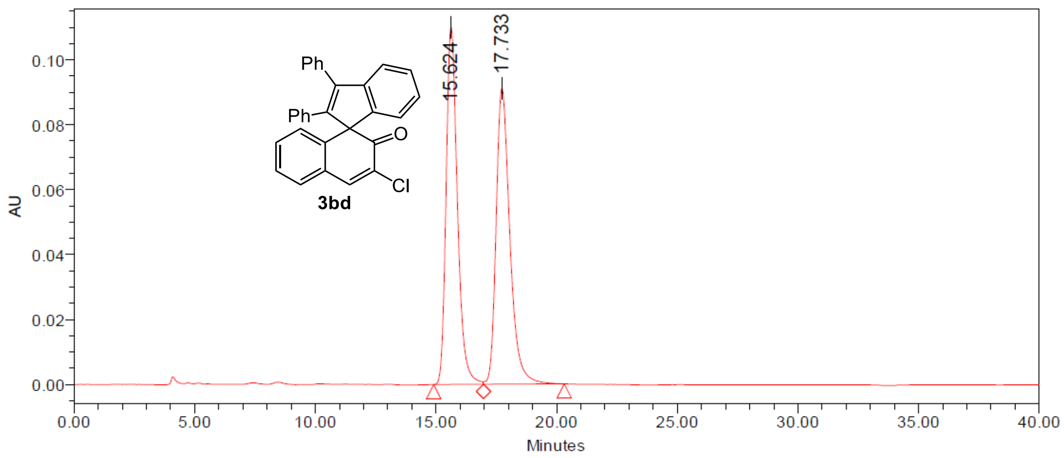
Peak Results

	Name	RT	Area	Height	% Area
1		19.601	1541003	30803	50.20
2		26.684	1528432	21127	49.80



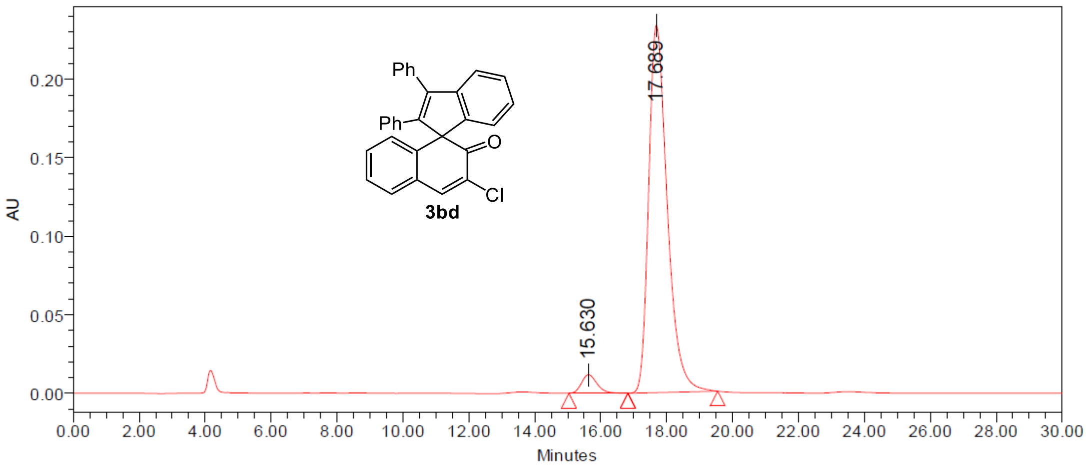
Peak Results

	Name	RT	Area	Height	% Area
1		19.465	2687122	53276	96.85
2		26.886	87256	1337	3.15



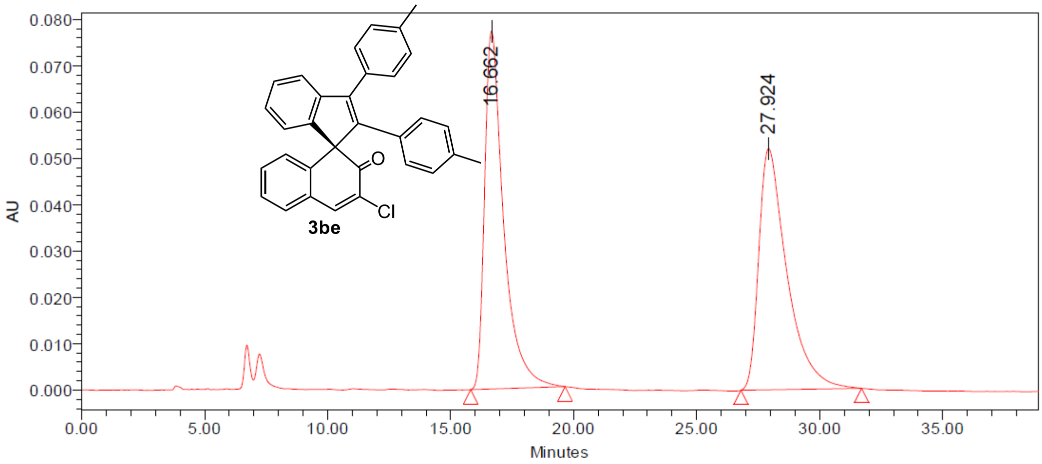
Peak Results

	Name	RT	Area	Height	% Area
1		15.624	3578463	110130	49.82
2		17.733	3604795	91162	50.18



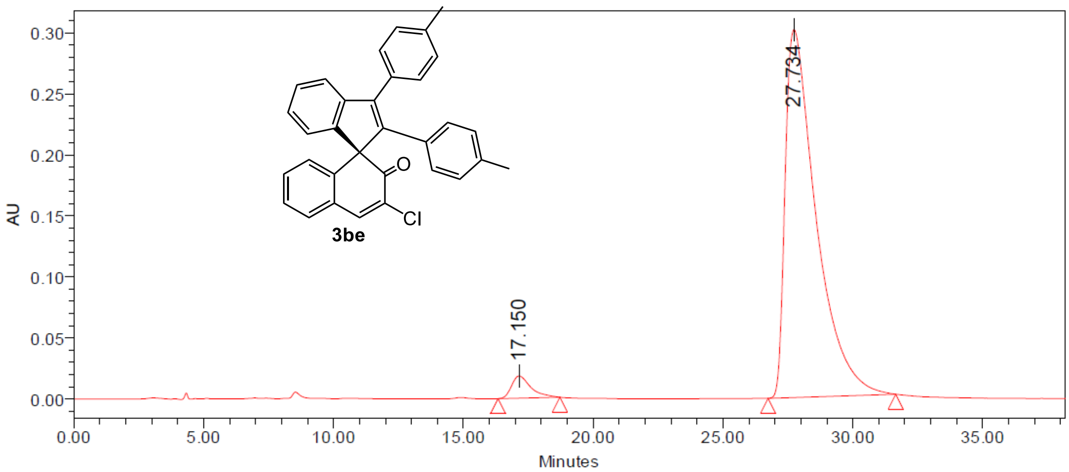
Peak Results

	Name	RT	Area	Height	% Area
1		15.630	383736	11865	4.02
2		17.689	9164351	234042	95.98



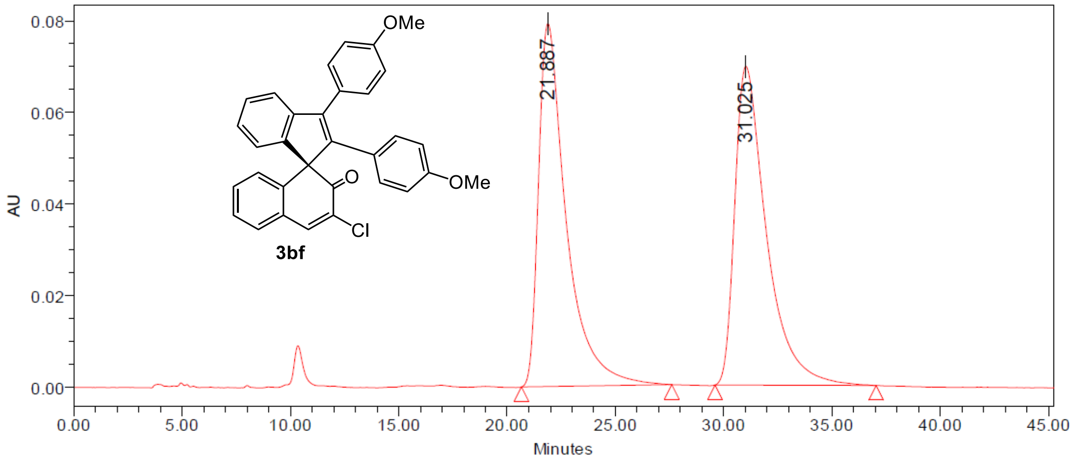
Peak Results

	Name	RT	Area	Height	% Area
1		16.662	4157293	77206	50.09
2		27.924	4141871	52047	49.91



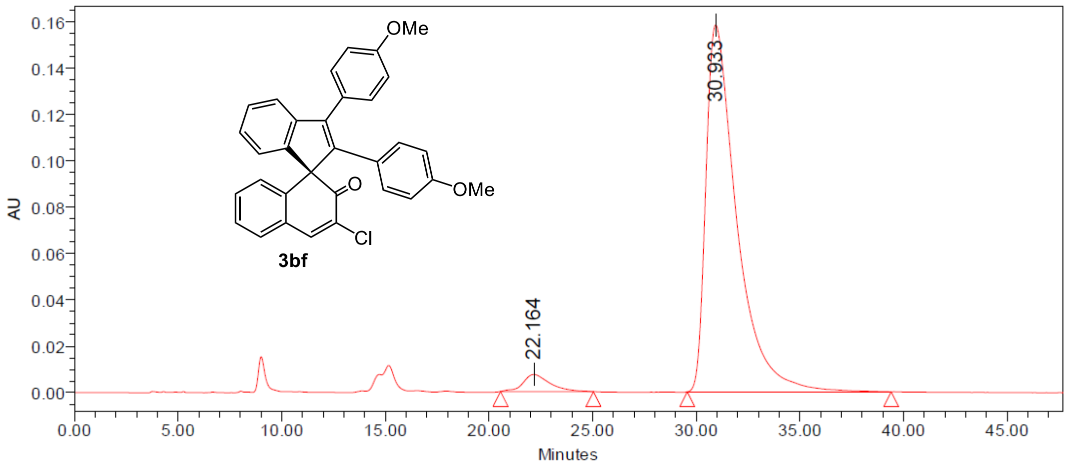
Peak Results

	Name	RT	Area	Height	% Area
1		17.150	937445	18138	3.62
2		27.734	24953906	301491	96.38



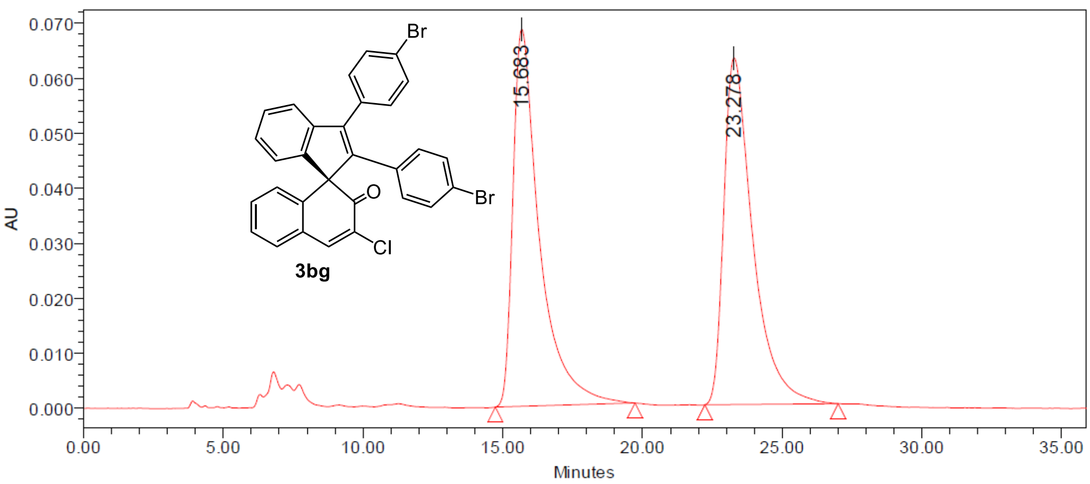
Peak Results

	Name	RT	Area	Height	% Area
1		21.887	7060075	79207	49.94
2		31.025	7076305	69558	50.06



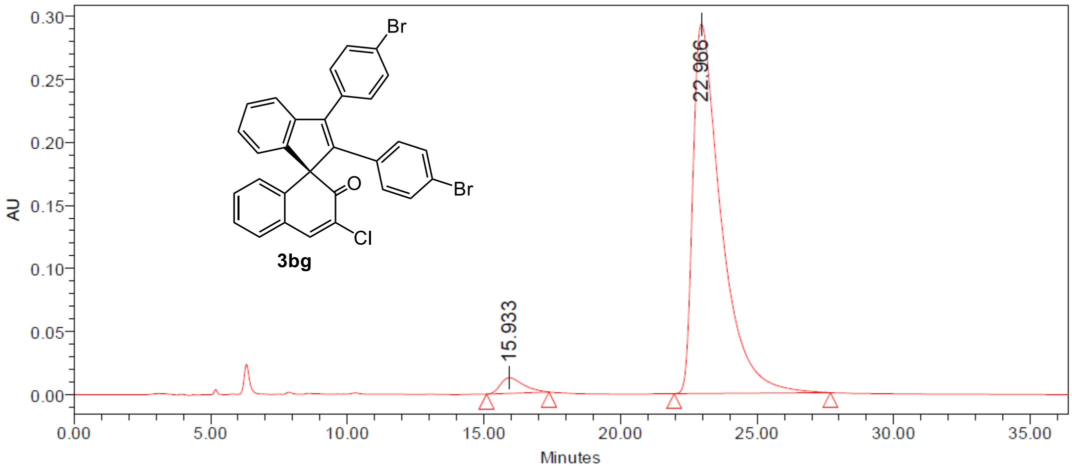
Peak Results

	Name	RT	Area	Height	% Area
1		22.164	663468	7374	3.89
2		30.933	16385456	158378	96.11



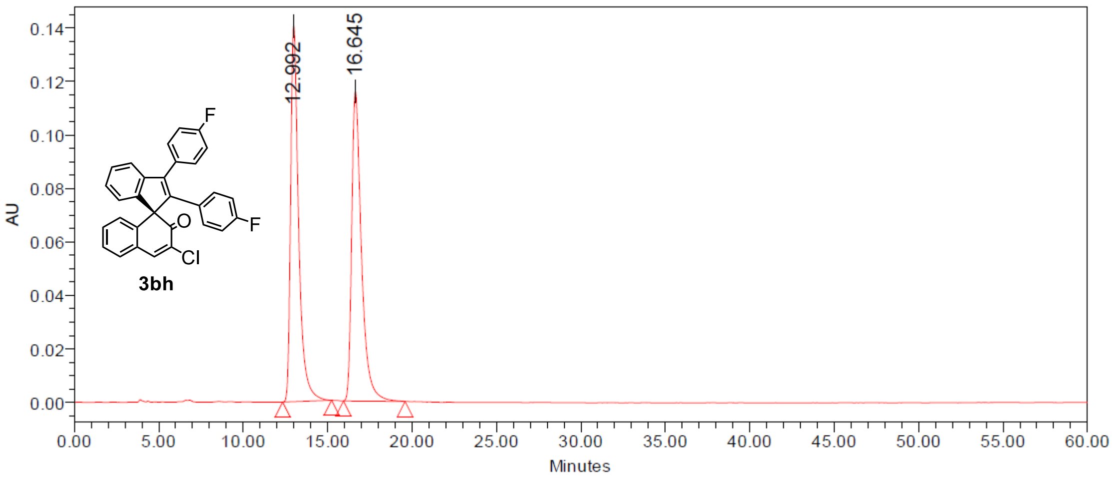
Peak Results

	Name	RT	Area	Height	% Area
1		15.683	4531738	68562	49.92
2		23.278	4546914	63048	50.08



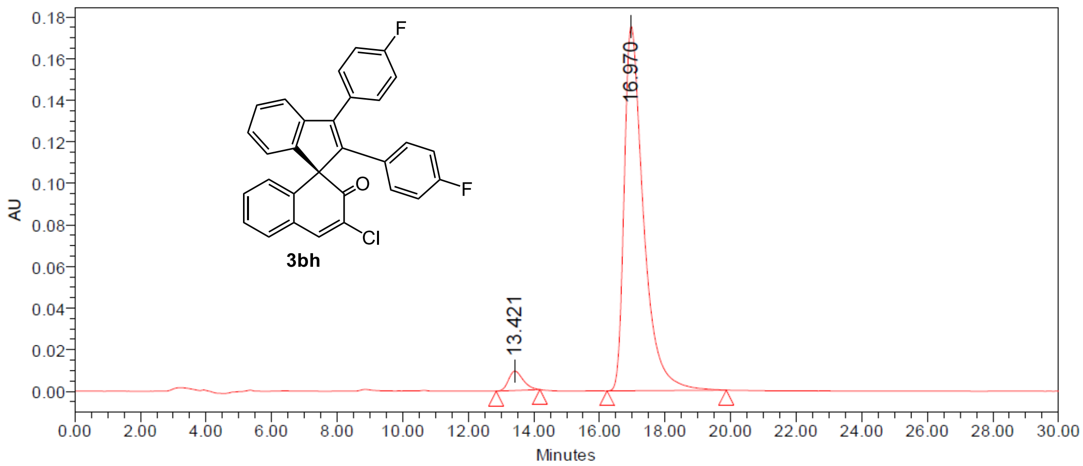
Peak Results

	Name	RT	Area	Height	% Area
1		15.933	720699	12341	3.31
2		22.966	21044641	292859	96.69



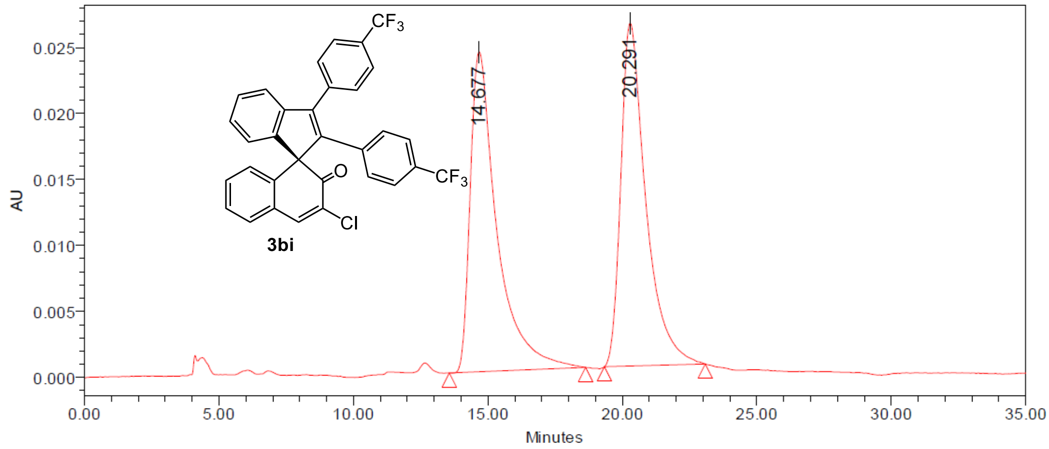
Peak Results

	Name	RT	Area	Height	% Area
1		12.992	4631143	140632	49.92
2		16.645	4645663	115734	50.08



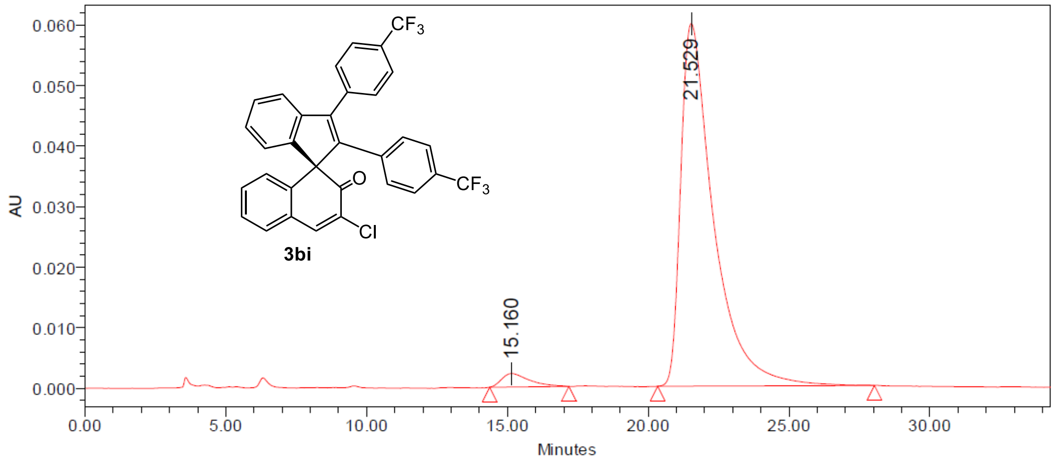
Peak Results

	Name	RT	Area	Height	% Area
1		13.421	289554	9366	3.89
2		16.970	7153291	175267	96.11



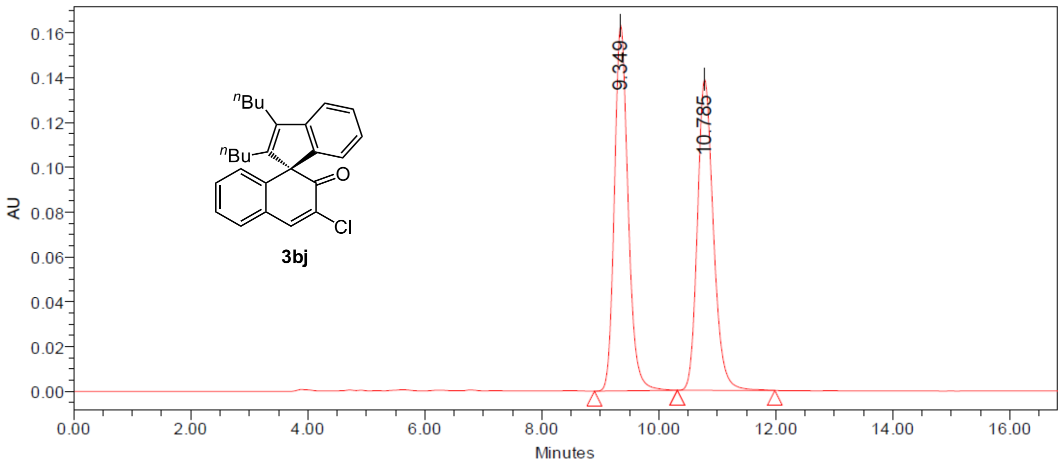
Peak Results

	Name	RT	Area	Height	% Area
1		14.677	1675777	24240	49.91
2		20.291	1681804	25996	50.09



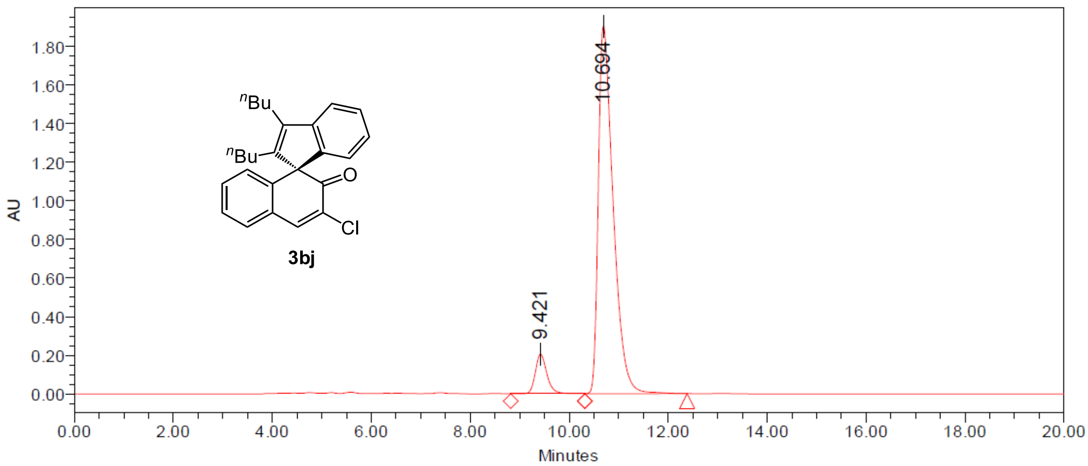
Peak Results

	Name	RT	Area	Height	% Area
1		15.160	151467	2207	3.03
2		21.529	4852417	59826	96.97



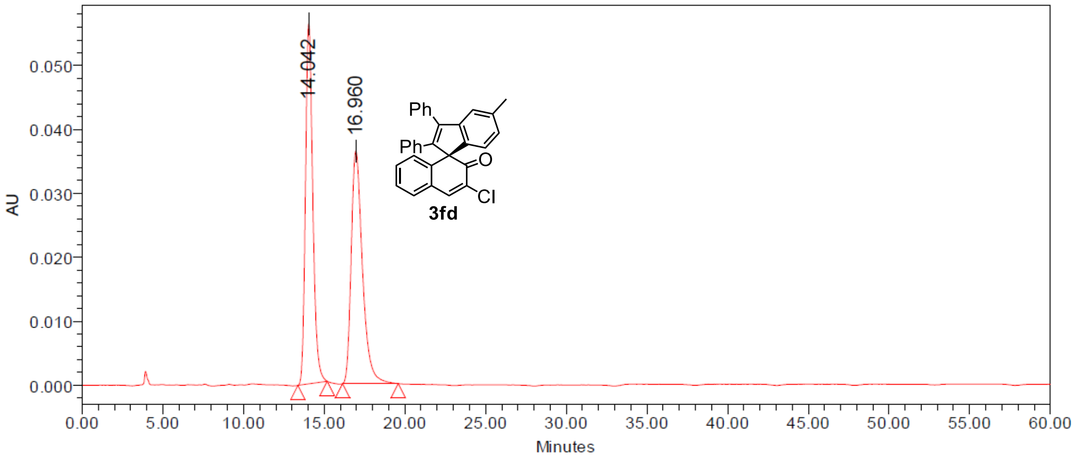
Peak Results

	Name	RT	Area	Height	% Area
1		9.349	2657598	163155	50.20
2		10.785	2636173	138791	49.80



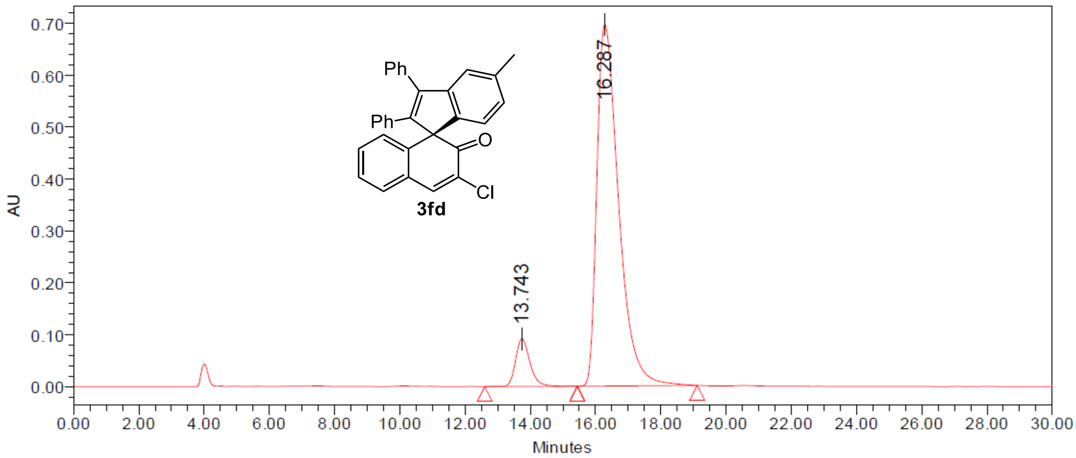
Peak Results

	Name	RT	Area	Height	% Area
1		9.421	3318771	205163	7.72
2		10.694	39652553	1902179	92.28



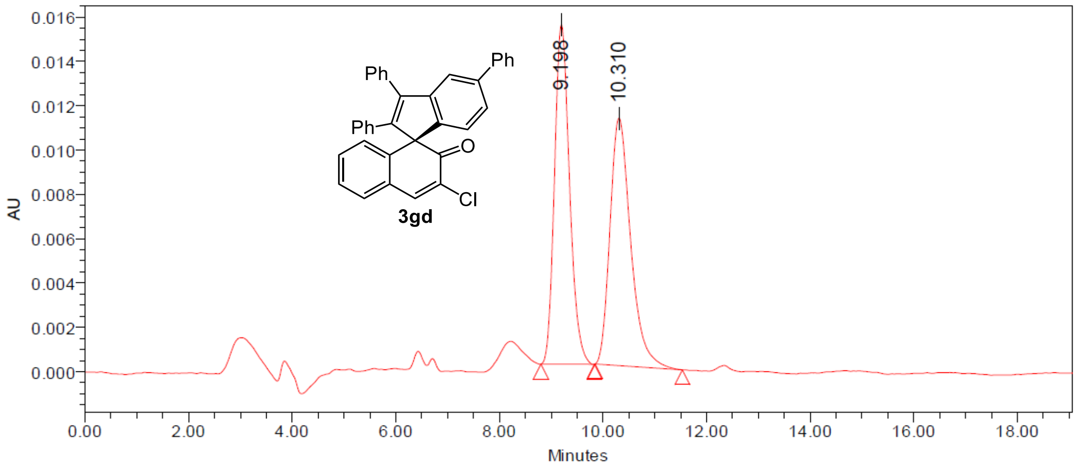
Peak Results

	Name	RT	Area	Height	% Area
1		14.042	1769119	56382	50.14
2		16.960	1759560	36406	49.86



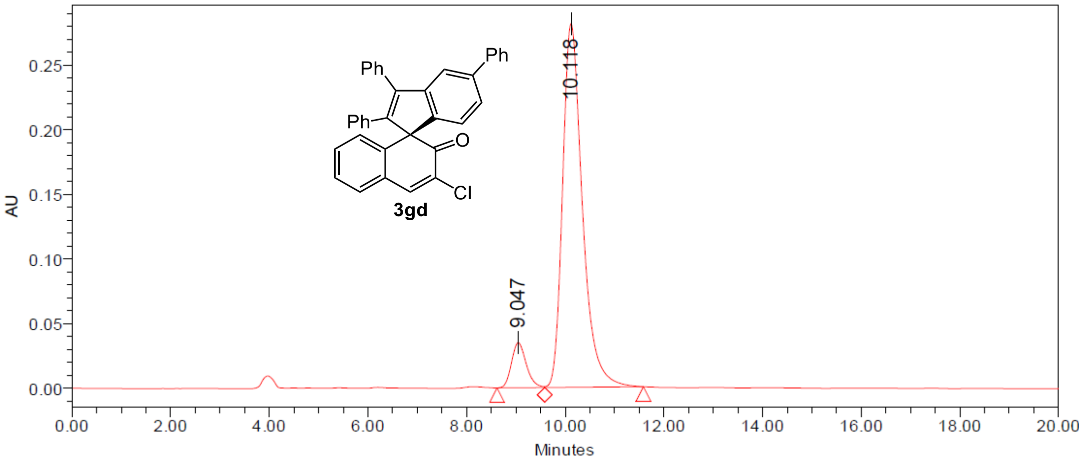
Peak Results

	Name	RT	Area	Height	% Area
1		13.743	2800020	91847	7.98
2		16.287	32278665	697018	92.02



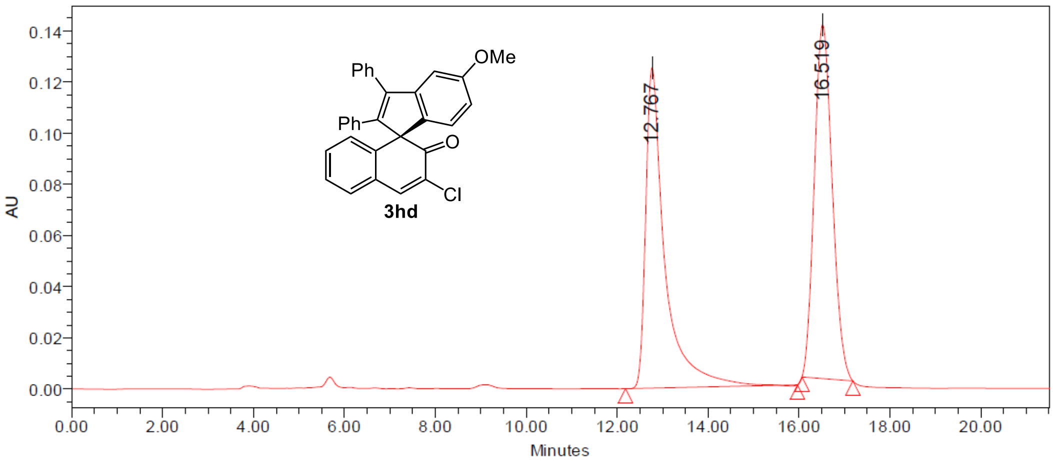
Peak Results

	Name	RT	Area	Height	% Area
1		9.198	310197	15333	50.00
2		10.310	310165	11173	50.00



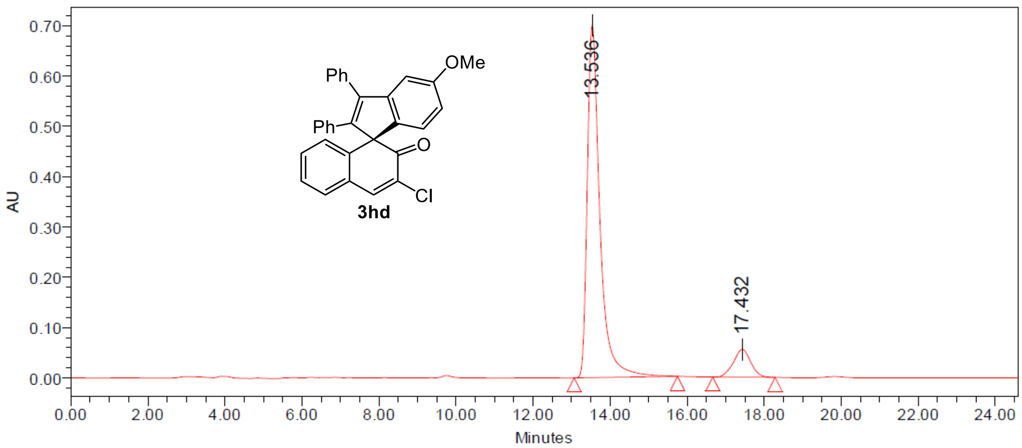
Peak Results

	Name	RT	Area	Height	% Area
1		9.047	722550	34874	8.44
2		10.118	7838037	281317	91.56



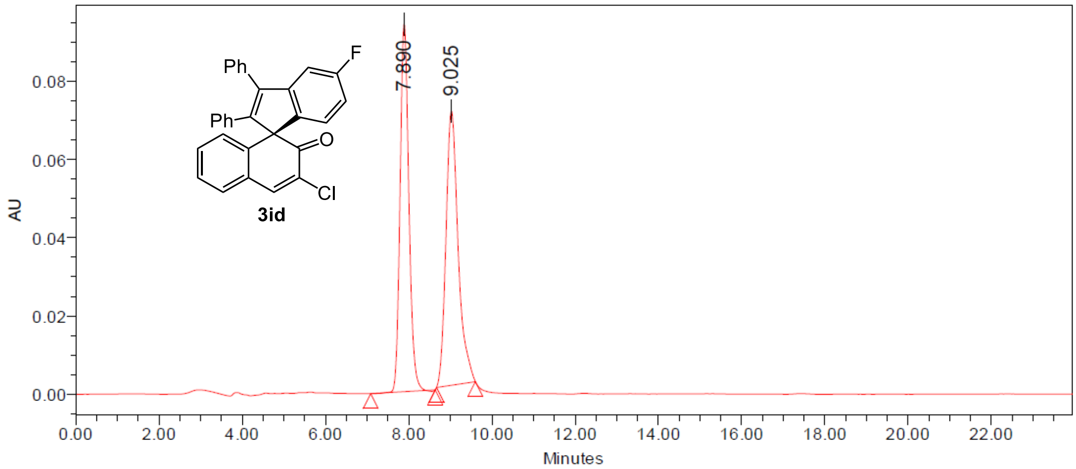
Peak Results

	Name	RT	Area	Height	% Area
1		12.767	3677498	125297	49.25
2		16.519	3788977	138376	50.75



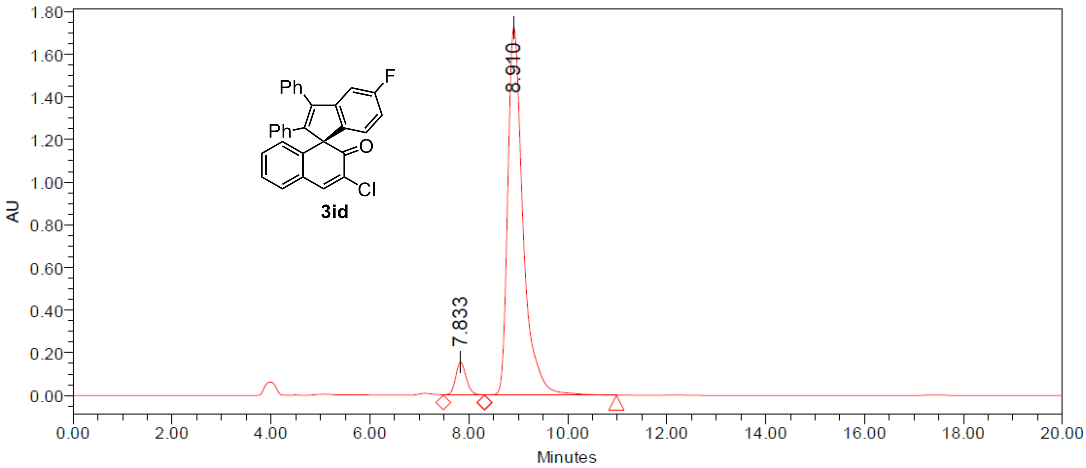
Peak Results

	Name	RT	Area	Height	% Area
1		13.536	15937226	700420	90.18
2		17.432	1734727	55363	9.82



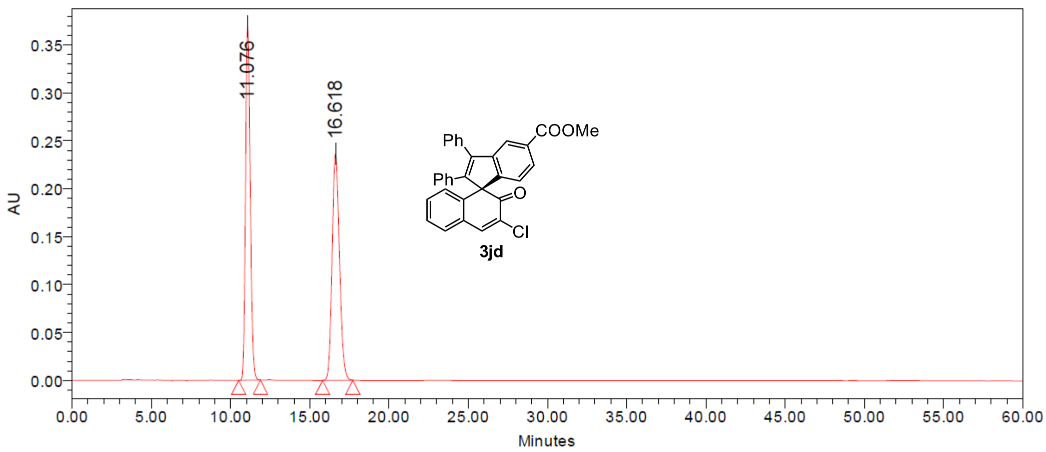
Peak Results

	Name	RT	Area	Height	% Area
1		7.890	1385545	94102	49.24
2		9.025	1428390	70095	50.76



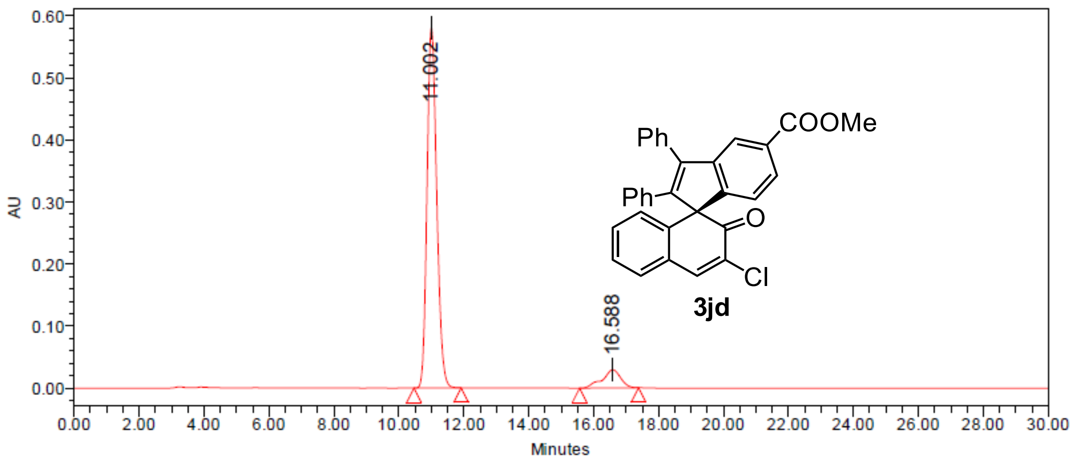
Peak Results

	Name	RT	Area	Height	% Area
1		7.833	2328241	155391	5.92
2		8.910	36998634	1725109	94.08



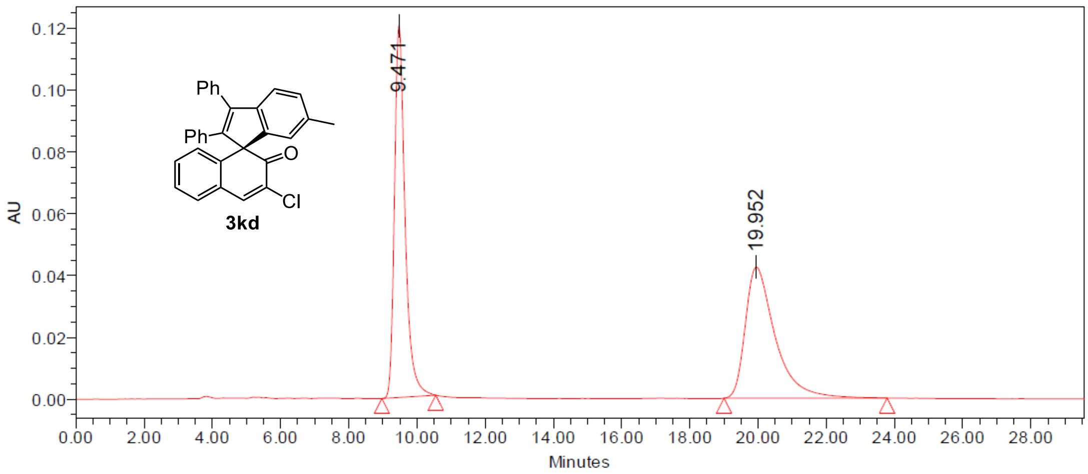
Peak Results

	Name	RT	Area	Height	% Area
1		11.076	7620995	369659	49.94
2		16.618	7638328	236355	50.06



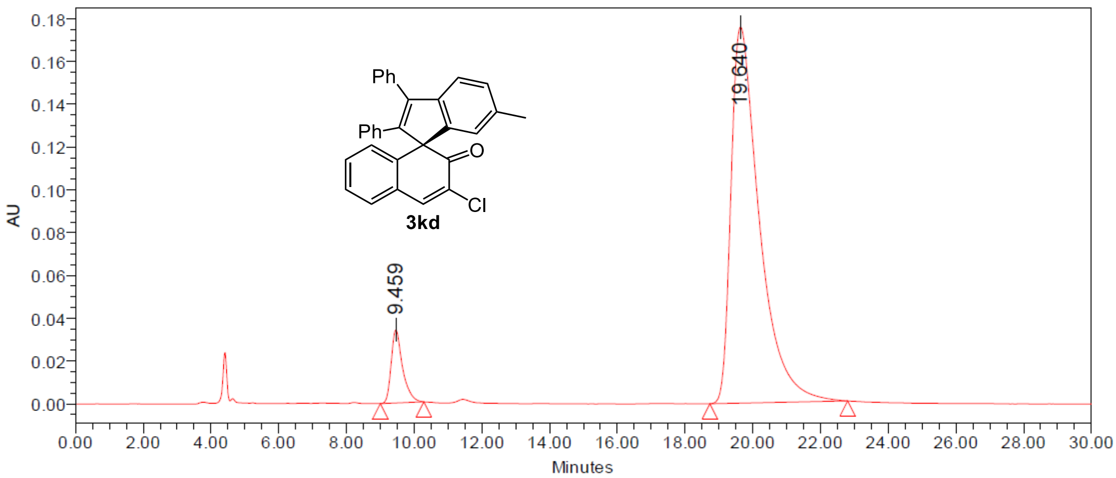
Peak Results

	Name	RT	Area	Height	% Area
1		11.002	12028787	581185	91.24
2		16.588	1154498	29261	8.76



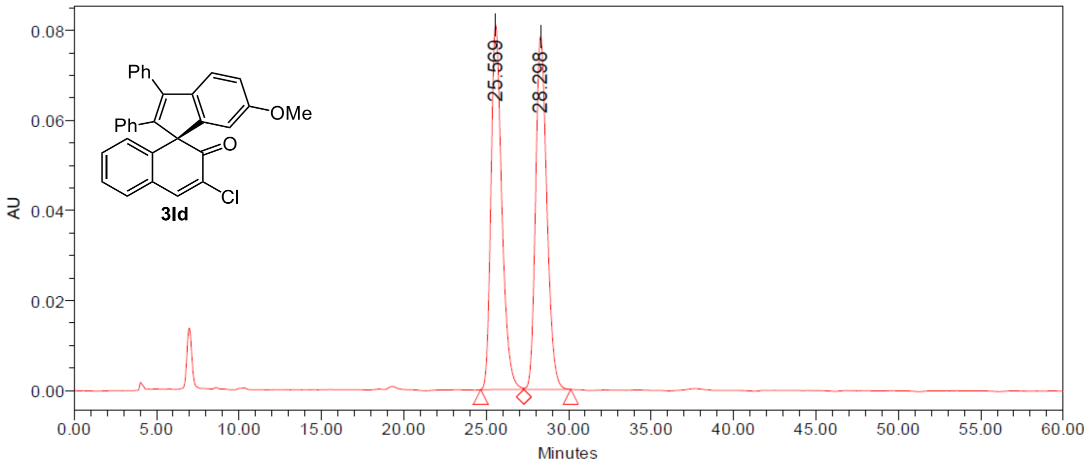
Peak Results

	Name	RT	Area	Height	% Area
1		9.471	2580088	120194	50.07
2		19.952	2572435	42363	49.93



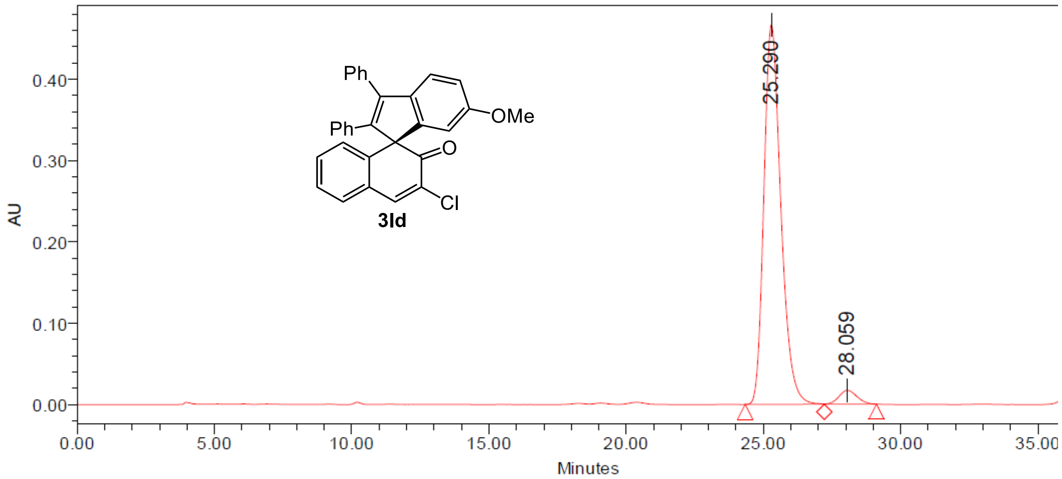
Peak Results

	Name	RT	Area	Height	% Area
1		9.459	796737	34113	7.21
2		19.640	10259087	175762	92.79



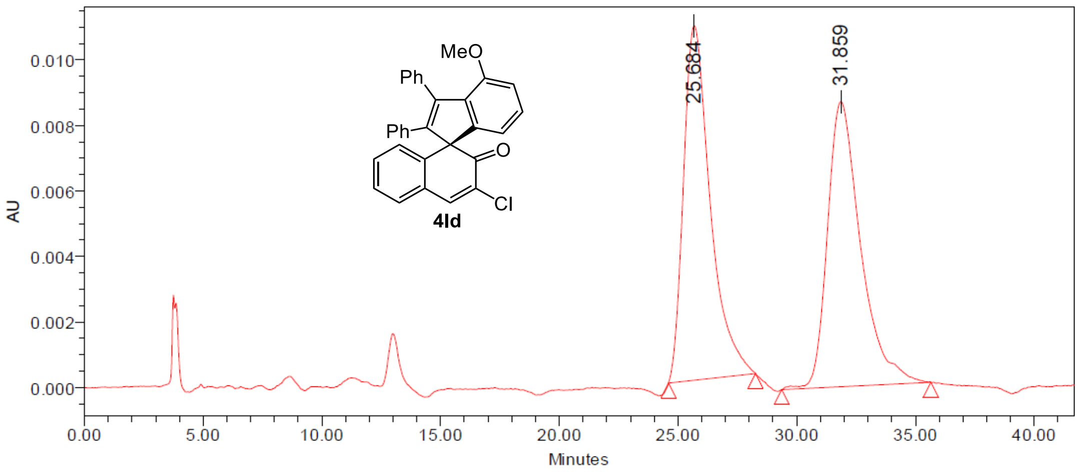
Peak Results

	Name	RT	Area	Height	% Area
1		25.569	3710189	81035	49.92
2		28.298	3721382	78439	50.08



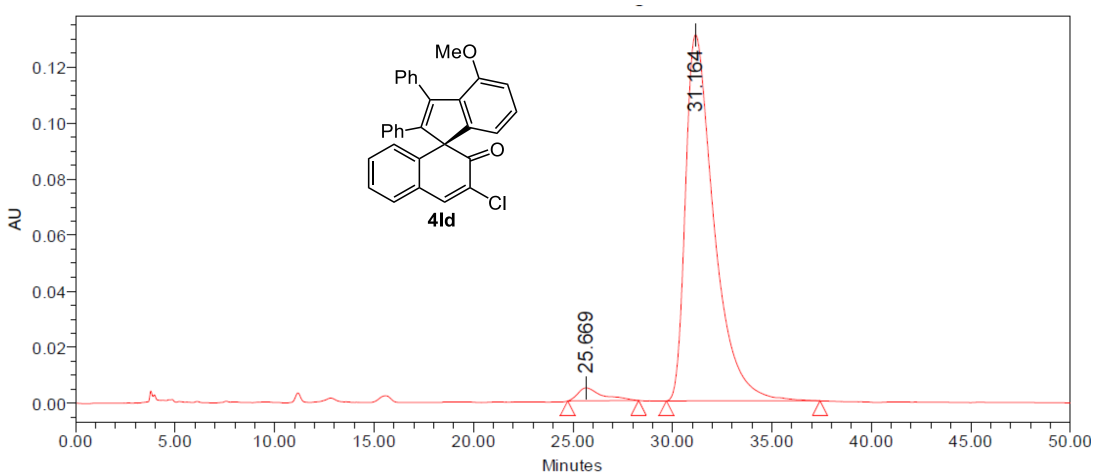
Peak Results

	Name	RT	Area	Height	% Area
1		25.290	20082534	466735	96.24
2		28.059	784162	17078	3.76



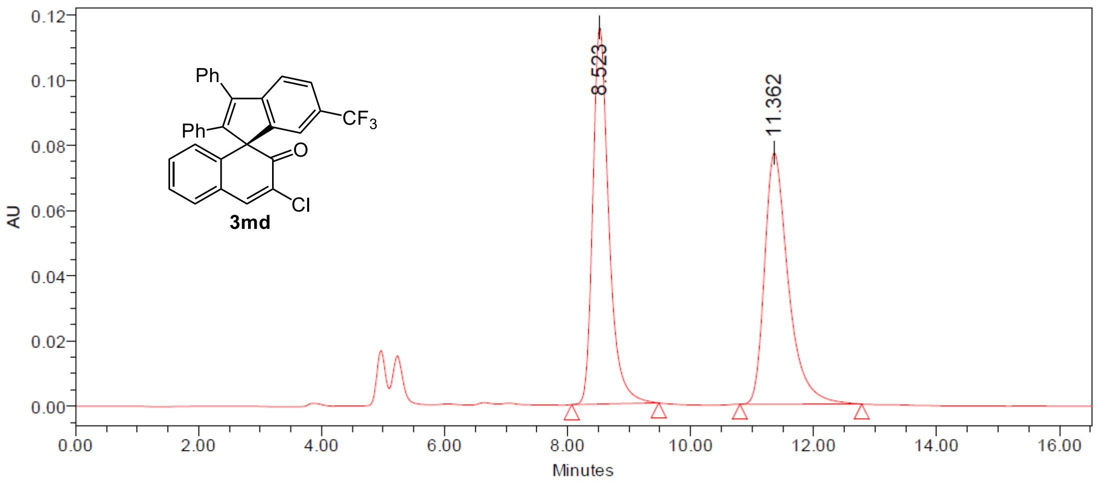
Peak Results

	Name	RT	Area	Height	% Area
1		25.684	848629	10818	50.08
2		31.859	845791	8702	49.92



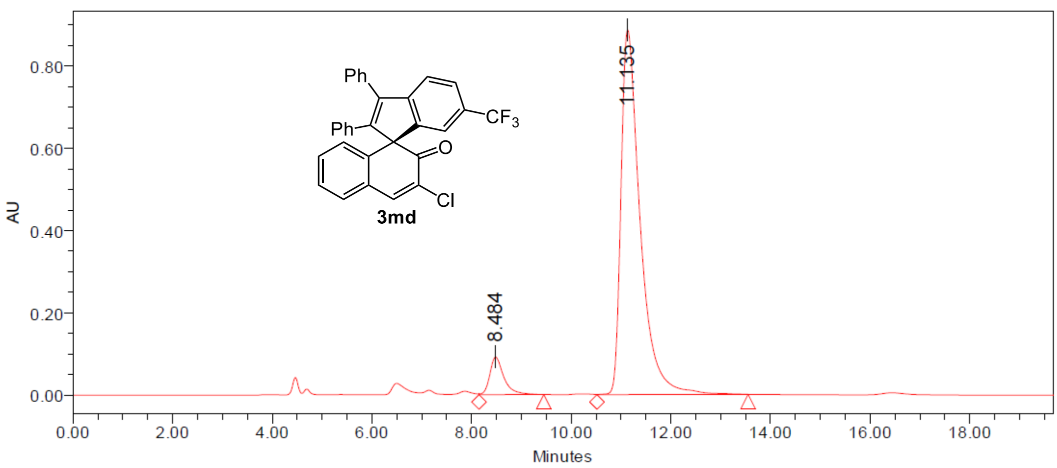
Peak Results

	Name	RT	Area	Height	% Area
1		25.669	397133	4591	2.97
2		31.164	12995138	130590	97.03



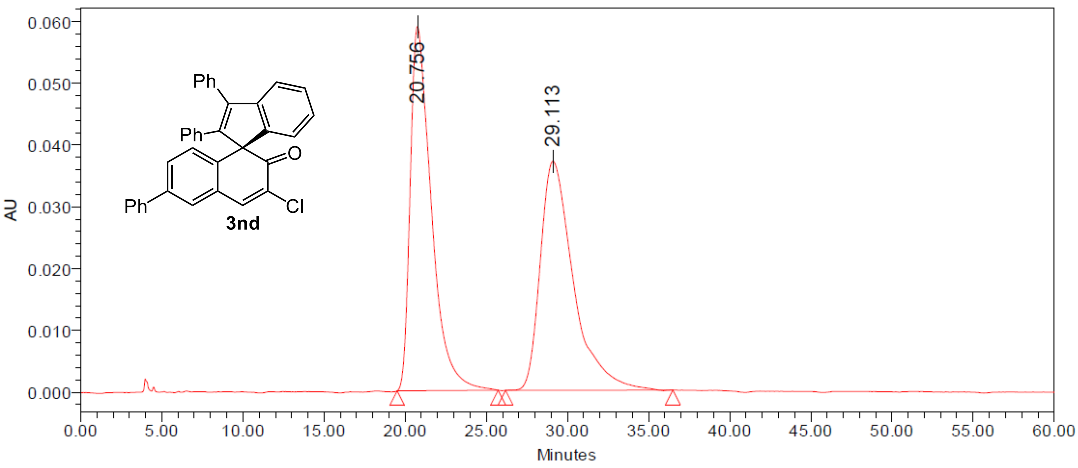
Peak Results

	Name	RT	Area	Height	% Area
1		8.523	2095313	115686	50.30
2		11.362	2070596	77020	49.70



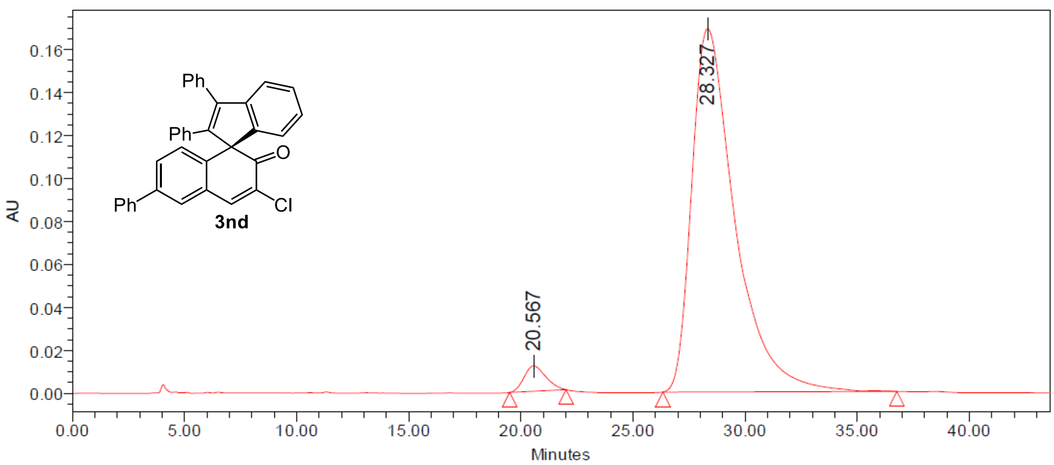
Peak Results

	Name	RT	Area	Height	% Area
1		8.484	1778448	91213	6.99
2		11.135	23671160	886780	93.01



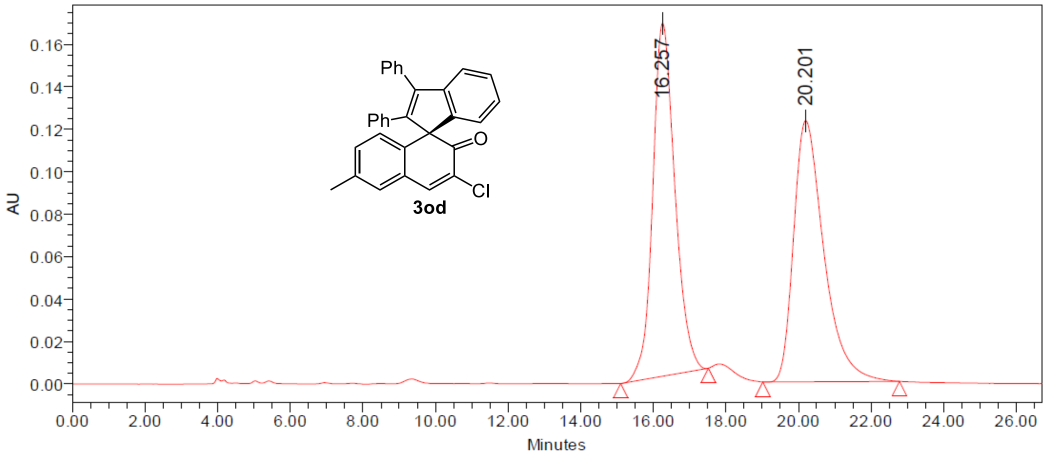
Peak Results

	Name	RT	Area	Height	% Area
1		20.756	5338067	58919	50.32
2		29.113	5270757	37059	49.68



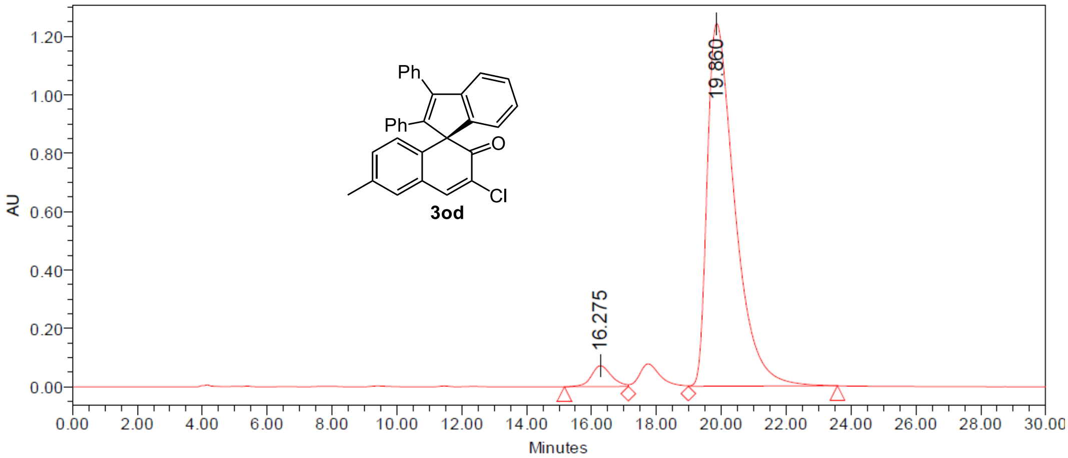
Peak Results

	Name	RT	Area	Height	% Area
1		20.567	794446	11748	3.39
2		28.327	22619814	169043	96.61



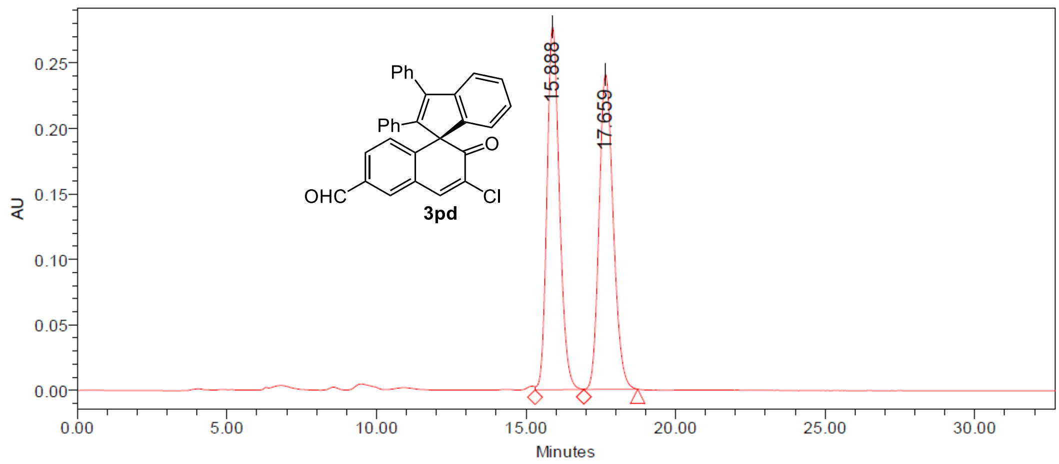
Peak Results

	Name	RT	Area	Height	% Area
1		16.257	7056968	166302	49.76
2		20.201	7124065	122984	50.24



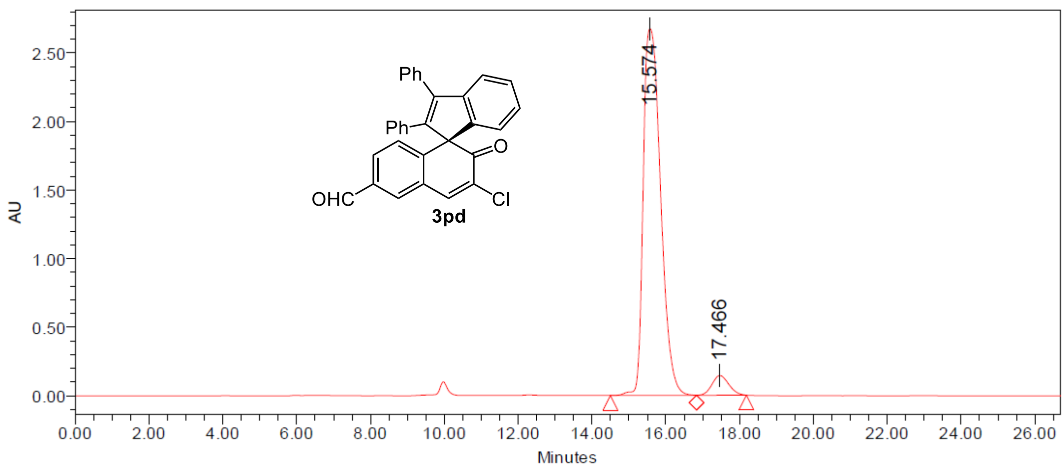
Peak Results

	Name	RT	Area	Height	% Area
1		16.275	3057735	71402	3.99
2		19.860	73481571	1241445	96.01



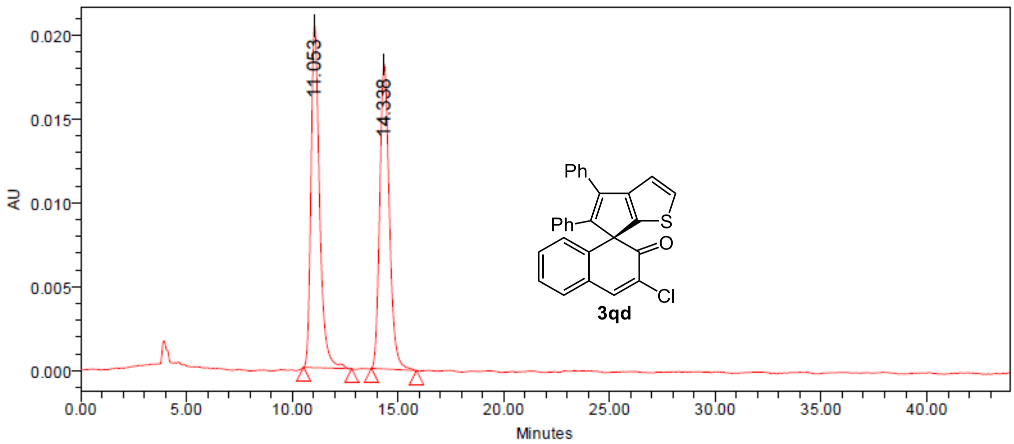
Peak Results

	Name	RT	Area	Height	% Area
1		15.888	7996752	277258	50.23
2		17.659	7921962	240487	49.77



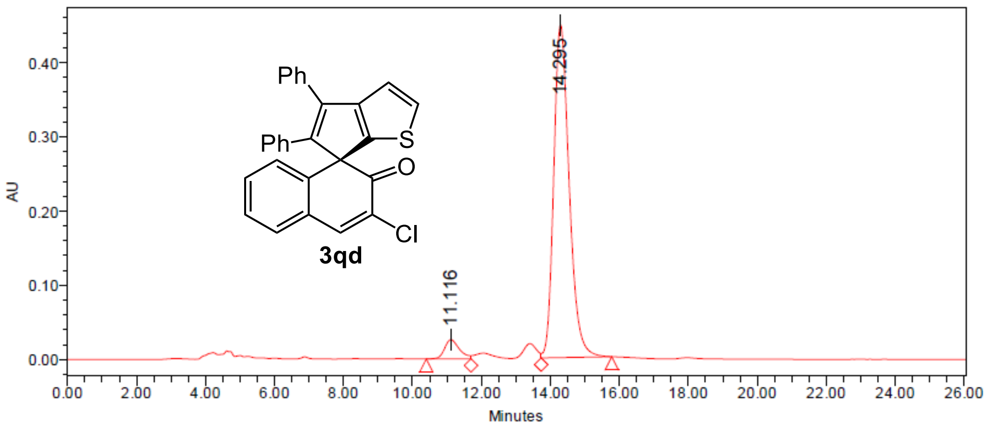
Peak Results

	Name	RT	Area	Height	% Area
1		15.574	87542380	2673266	95.08
2		17.466	4533561	143287	4.92



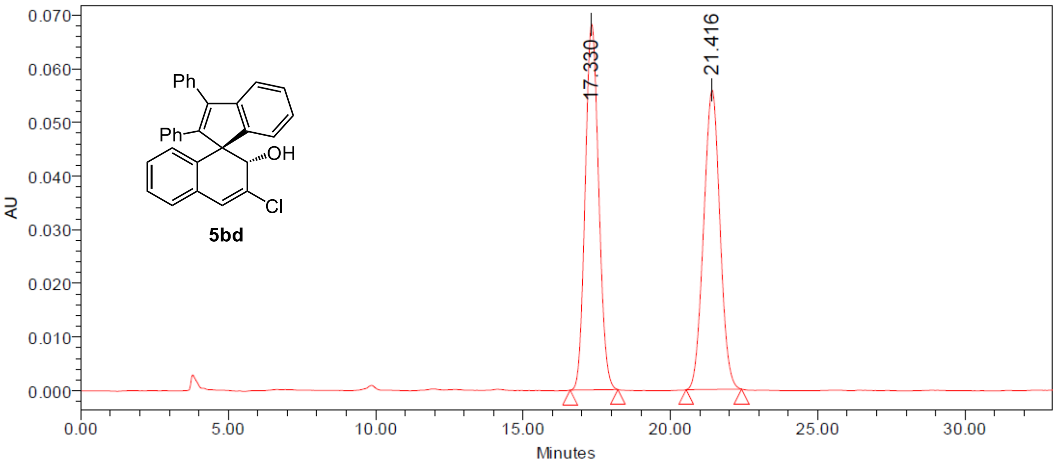
Peak Results

	Name	RT	Area	Height	% Area
1		11.053	576251	20410	50.05
2		14.338	575202	18176	49.95



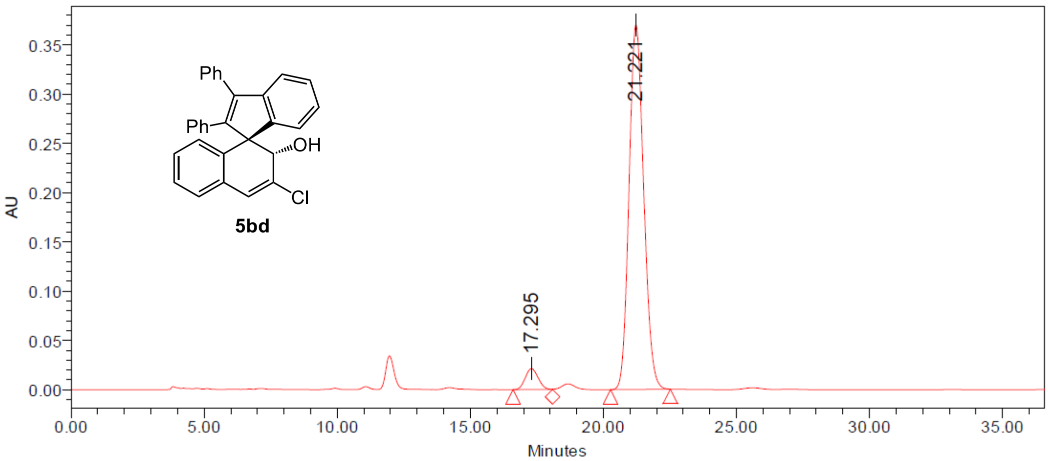
Peak Results

	Name	RT	Area	Height	% Area
1		11.116	770040	25951	5.23
2		14.295	13959245	448308	94.77



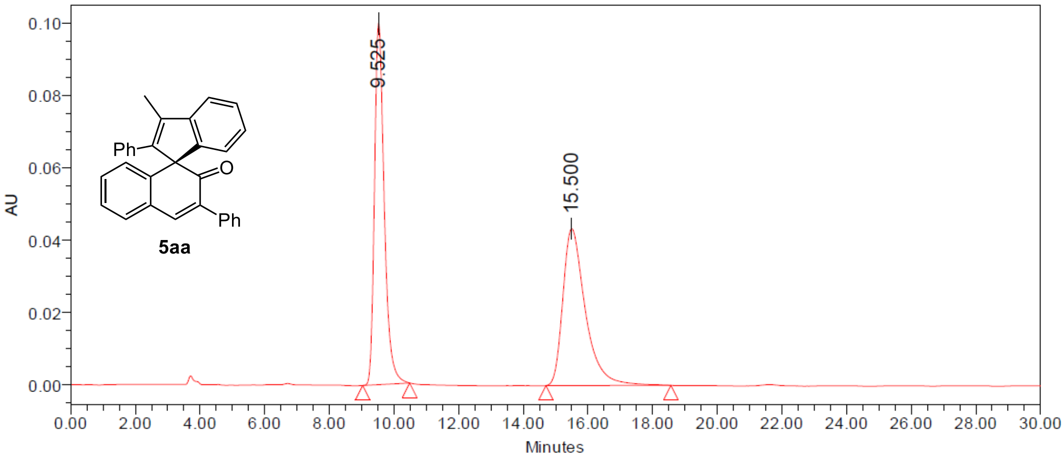
Peak Results

	Name	RT	Area	Height	% Area
1		17.330	2168853	68151	50.23
2		21.416	2149130	55805	49.77



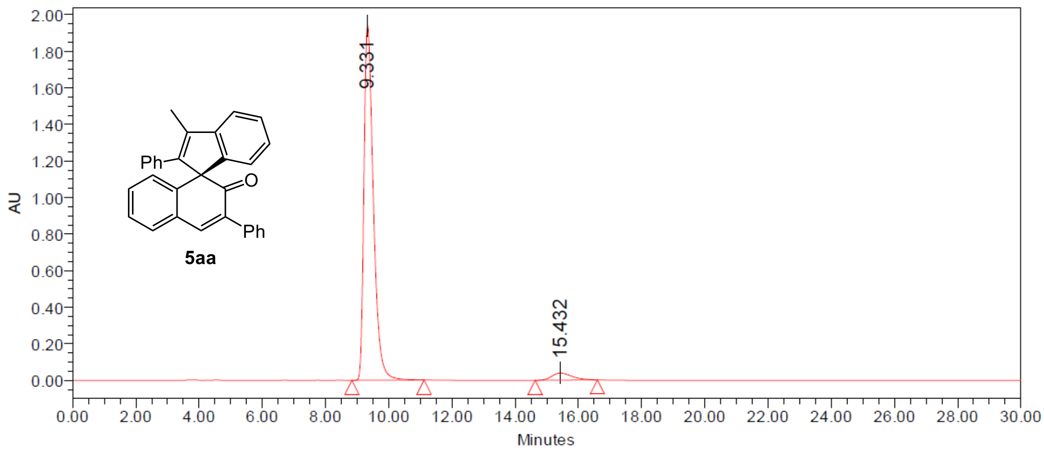
Peak Results

	Name	RT	Area	Height	% Area
1		17.295	715406	21241	4.80
2		21.221	14195999	370198	95.20



Peak Results

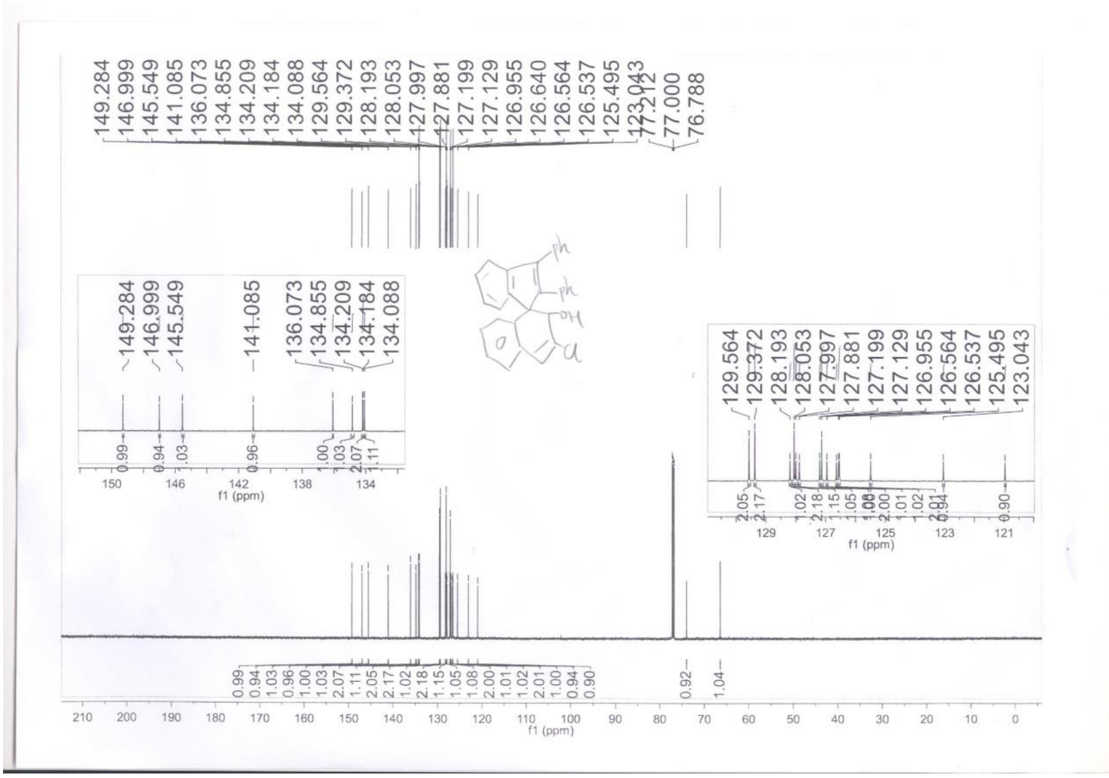
	Name	RT	Area	Height	% Area
1		9.525	2089251	100023	49.90
2		15.500	2097559	43362	50.10

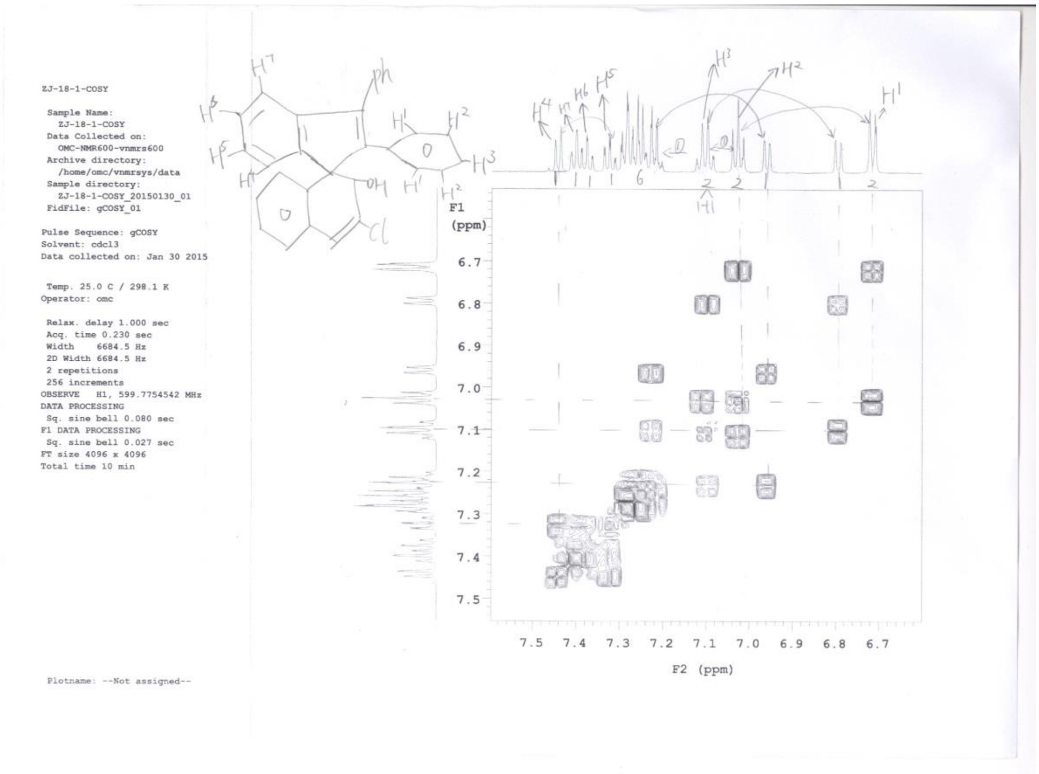


Peak Results

	Name	RT	Area	Height	% Area
1		9.331	40270830	1939539	95.93
2		15.432	1707999	38747	4.07

Copies of HSQC, COSY, 1D-NOESY of 5bb





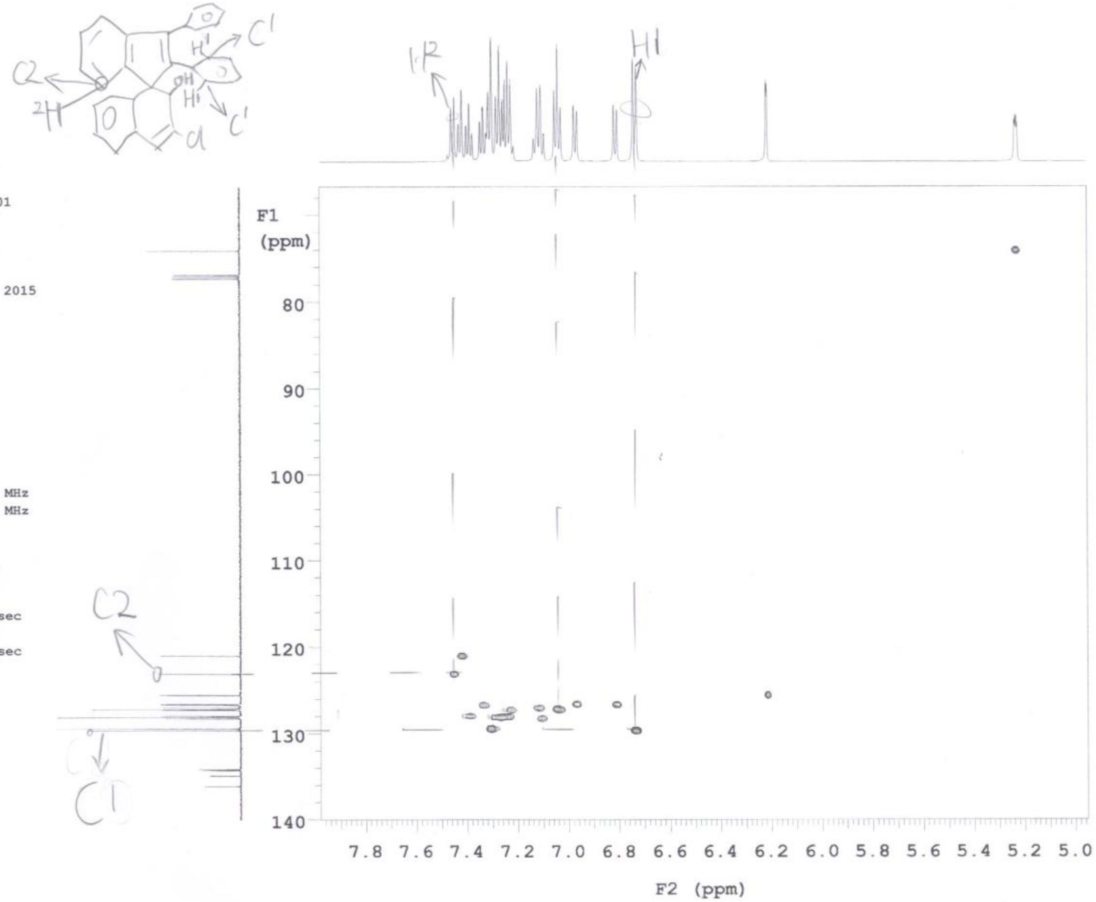
ZJ-18-1-HSQC

Sample Name:
ZJ-18-1-HSQC
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
ZJ-18-1-HSQC_20150129_01
FidFile: gHSQCAD_01

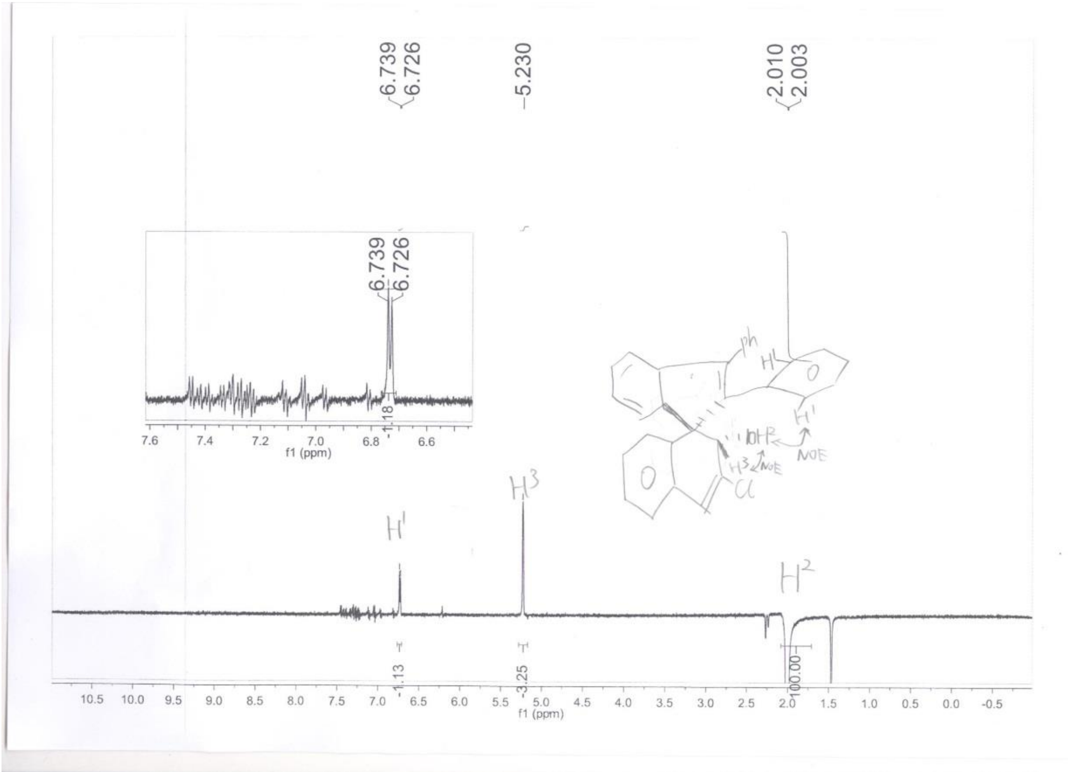
Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Jan 29 2015

Temp. 25.0 C / 298.1 K
Operator: omc

Relax. delay 1.000 sec
Acq. time 0.233 sec
Width 6613.8 Hz
2D Width 30165.9 Hz
4 repetitions
2 x 256 increments
OBSERVE H1, 599.7754542 MHz
DECOUPLE C13, 150.8272311 MHz
Power 44 dB
on during acquisition
off during delay
W40_OneProbe modulated
DATA PROCESSING
Gauss apodization 0.074 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 4096 x 2048
Total time 41 min



Plotname: --Not assigned--


6.739
6.726
5.230
2.010
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H1
H3
H2
NOE
Cl
Ph
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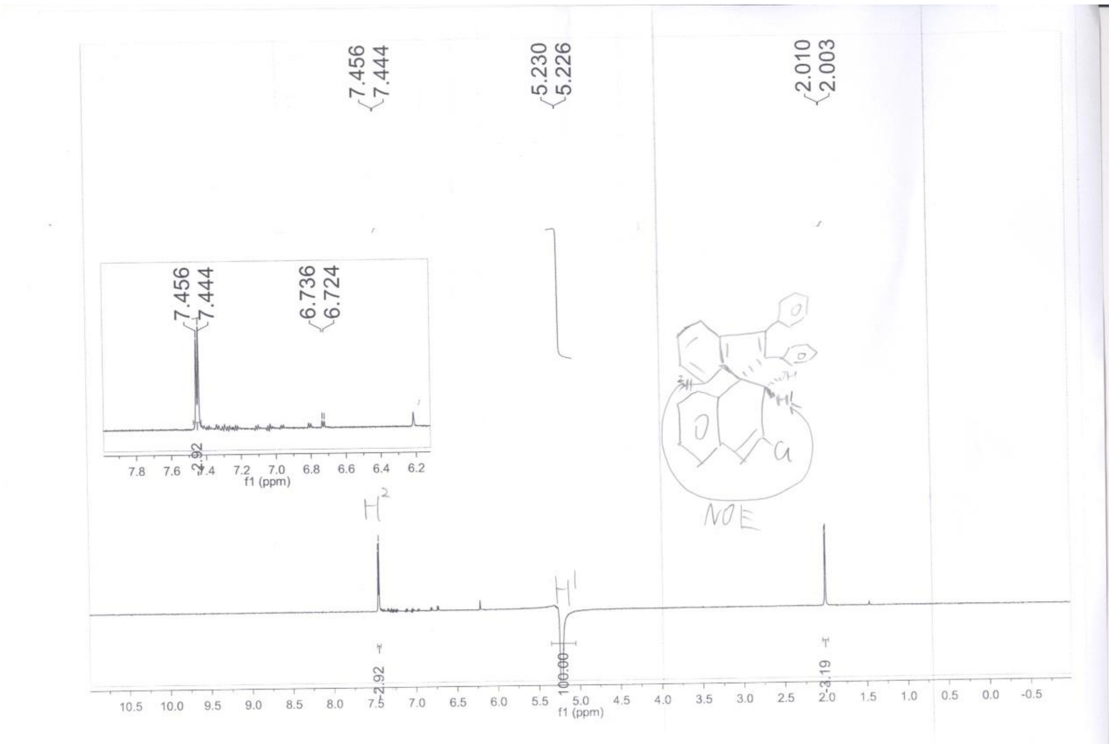
3.25
100.00
1.18
f1 (ppm)


7.456
7.444
5.230
5.226
2.010
2.003
6.736
6.724
H2
H1
NOE
Cl
2.92
100.00
3.19
f1 (ppm)