Supplementary Information

Molybdenum-catalyzed carbonyl-carbonyl olefination reaction for heterocycle syntheses

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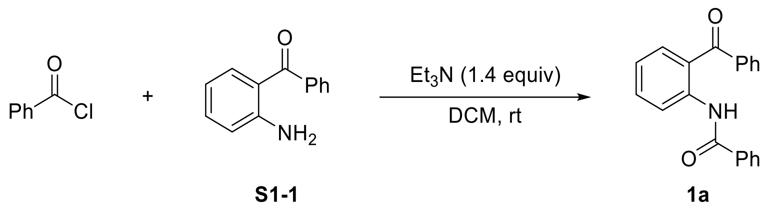
Table of Contents

I. Experimental details and characterization data.

General information. Unless stated otherwise, all reactions were carried out in oven-dried (oven temperature ≥ 110 °C) glassware using anhydrous solvents under argon or N_2 atmosphere. The solvents were purified by distillation over the following drying agents and were transferred under argon or N_2 atmosphere: THF, toluene (Na); anhydrous 1,3,5-trimethylbenzene (mesitylene), CH_2Cl_2 and DMF were purchased from Energy Chemical and kept in a sealed bottle containing 4 Å molecular sieve under argon. General-Reagent silica gel (300-400 mesh) was used for the flash column chromatography. Unless stated otherwise, all commercially available compounds (Energy Chemical, Bidepharmatech, TCI, J&K Chemical, and Strem Chemicals) were used as received. The substituted anilines **S1** were synthesized according to a reported procedure.[1]

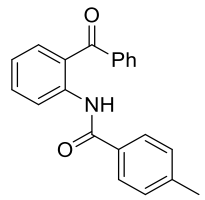
NMR spectra were recorded on Bruker AV-400 MHz, Quantum-IPlus 400 MHz or Bruker AV-500 MHz spectrometers in the solvents indicated; chemical shifts (δ =) are given in ppm, coupling constants (*J*) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; C_3D_6O: δ_C = 206.26, 29.84 ppm; residual C_3D_5HO: δ_H = 2.05 ppm; dimethyl sulfoxide-D_6: δ_C = 39.52 ppm; residual dimethyl sulfoxide-D_5H: δ_H = 2.50 ppm). Infrared (IR) spectra were measured on a Nicolet AVATER FTIR330 spectrometer. High-resolution mass spectra (ESI) were recorded on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer.

1. Representative procedure for the syntheses of substrates 1 (RP1).[2]

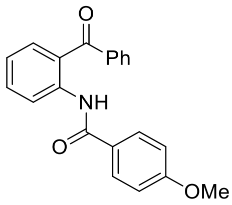


Preparation of compound 1a. Benzoyl chloride (984.0 mg, 0.81 mL, 7.0 mmol, 1.4 equiv) was added dropwise to a stirred solution of 2-aminophenyl-(phenyl)methanone **S1-1** (986.0 mg, 5.0 mmol, 1.0 equiv) and Et_3N (708.3 mg, 0.97 mL, 7.0 mmol, 1.4 equiv) in CH_2Cl_2 (15 mL) at room temperature. Stirring was continued at this temperature until the reaction was complete (monitored by TLC). The reaction mixture was quenched with H_2O, and extracted with DCM (20 mL × 3). The combined organic layers were washed with saturated aqueous sodium bicarbonate and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) gave **1a**[3] as a white solid (1.35 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.98 (s, 1H), 8.91 (d, *J* = 8.2 Hz, 1H), 8.10 – 8.05 (m, 2H), 7.74 – 7.69 (m, 2H), 7.65 – 7.45 (m, 8H), 7.15 – 7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 165.7, 141.0, 138.7, 134.54, 134.45, 133.9, 132.3, 131.9, 129.7, 128.7, 128.2, 127.3, 123.0, 122.1, 121.3. IR (thin film): ν_{max} (cm^{-1}) = 3285, 3062, 1682, 1615, 1582, 1449, 1267, 941, 700, 643; HRMS (ESI) calcd for $C_{20}H_{15}NNaO_2$ $[M+Na]^+$: 324.1000. Found: 324.0990.

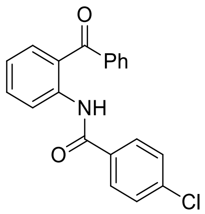
The following substrates **1b**–**1z** & **1ak-1an** were prepared analogously.



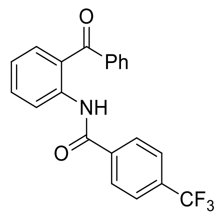
1b.[3] White solid, 1.43 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.94 (s, 1H), 8.91 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.74 – 7.70 (m, 2H), 7.66 – 7.57 (m, 3H), 7.52 – 7.47 (m, 2H), 7.33 – 7.29 (m, 2H), 7.15 – 7.08 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 165.8, 142.5, 141.3, 138.8, 134.6, 134.0, 132.3, 131.7, 129.7, 129.4, 128.3, 127.4, 123.0, 121.9, 121.3, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 3305, 2919, 1679, 1529, 1447, 1267, 752, 700, 642; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1152. Found: 338.1152.



1c.[3] White solid, 1.65 g, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.92 (s, 1H), 8.89 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.64 – 7.54 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 165.2, 162.5, 141.3, 138.7, 134.5, 134.0, 132.2, 129.7, 129.2, 128.2, 126.7, 122.8, 121.7, 121.2, 113.9, 55.3. IR (thin film): ν_{max} (cm^{-1}) = 3307, 2918, 1677, 1507, 1255, 1175, 700, 643; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_3$ [M+Na]$^+$: 354.1101. Found: 354.1100.

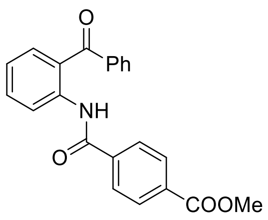


1d.[3] White solid, 1.61 g, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.01 (s, 1H), 8.87 (dd, *J* = 8.8, 1.1 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.73 – 7.69 (m, 2H), 7.67 – 7.57 (m, 3H), 7.52 – 7.45 (m, 4H), 7.13 (td, *J* = 7.8, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 164.6, 141.0, 138.6, 138.3, 134.7, 134.1, 132.9, 132.4, 129.8, 129.0, 128.8, 128.3, 122.9, 122.3, 121.3. IR (thin film): ν_{max} (cm^{-1}) = 3284, 1683, 1584, 1267, 1111, 753, 710, 643; HRMS (ESI) calcd for $C_{20}H_{14}ClNNaO_2$ [M+Na]$^+$: 358.0605. Found: 358.0610.

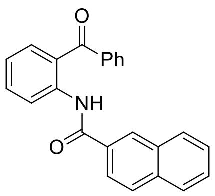


1e. Yellow solid, 1.39 g, 94% yield, mp 81.1-81.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.11 (s, 1H), 8.88 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.58 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 164.3, 140.7, 138.5, 137.8, 134.7, 134.1, 133.5 (q, *J* = 32.6 Hz), 132.5, 129.8, 128.3, 127.8, 125.8 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 271.0 Hz), 123.0, 122.5, 121.3. ^{19}F NMR (376

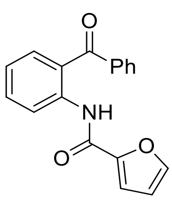
MHz, $CDCl_3$): δ = -62.99. IR (thin film): ν_{max} (cm^{-1}) = 3278, 1686, 1604, 1531, 1327, 1296, 1128, 941, 768, 643; HRMS (ESI) calcd for $C_{21}H_{14}F_3NNaO_2$ $[M+Na]^+$: 392.0869. Found: 392.0874.



1f. Yellow solid, 1.66 g, 92% yield, mp 143.4-143.6 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.05 (s, 1H), 8.86 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.20 – 8.08 (m, 4H), 7.74 – 7.68 (m, 2H), 7.66 – 7.55 (m, 3H), 7.49 – 7.45 (m, 2H), 7.15 – 7.10 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 166.1, 164.7, 140.7, 138.5, 138.3, 134.6, 134.0, 133.0, 132.4, 129.9, 129.7, 128.3, 127.3, 123.0, 122.4, 121.3, 52.3. IR (thin film): ν_{max} (cm^{-1}) = 3288, 2920, 1725, 1603, 1529, 1268, 1108, 723, 704, 643; HRMS (ESI) calcd for $C_{22}H_{17}NNaO_4$ $[M+Na]^+$: 382.1050. Found: 382.1052.

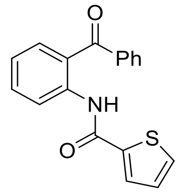


1g.[3] White solid, 1.35 g, 96% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.15 (s, 1H), 8.96 (d, *J* = 8.1 Hz, 1H), 8.61 (d, *J* = 1.3 Hz, 1H), 8.13 (dd, *J* = 8.6, 1.9 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.77 – 7.73 (m, 2H), 7.70 – 7.62 (m, 2H), 7.62 – 7.55 (m, 3H), 7.53 – 7.48 (m, 2H), 7.17 – 7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 165.9, 141.2, 138.8, 135.0, 134.6, 134.1, 132.7, 132.4, 131.8, 129.8, 129.4, 128.7, 128.4, 128.3, 127.9, 127.7, 126.7, 123.6, 123.1, 122.2, 121.5. IR (thin film): ν_{max} (cm^{-1}) = 3059, 2921, 1679, 1598, 1526, 1448, 1259, 1198, 773, 700; HRMS (ESI) calcd for $C_{24}H_{17}NNaO_2$ $[M+Na]^+$: 374.1152. Found: 374.1151.

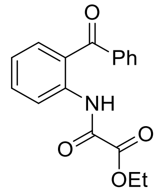


1h. White solid, 1.27 g, 87% yield, mp 116.2-116.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.87 (s, 1H), 8.82 (dd, *J* = 8.9, 0.9 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.65 – 7.57 (m, 4H), 7.53 – 7.47 (m, 2H), 7.29 – 7.27 (m, 1H), 7.16 – 7.10 (m, 1H), 6.57 – 6.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$):

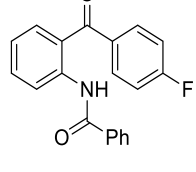
δ = 199.6, 156.6, 147.9, 144.8, 140.2, 138.5, 134.2, 133.7, 132.3, 129.7, 128.2, 123.2, 122.1, 121.3, 115.3, 112.2. IR (thin film): $ν_{max}$ (cm^{-1}) = 3298, 2918, 1682, 1637, 1525, 1449, 1274, 923, 753, 713, 643; HRMS (ESI) calcd for $C_{18}H_{13}NNaO_3$ $[M+Na]^+$: 314.0788. Found: 314.0785.



1i. Yellow solid, 1.40 g, 91% yield, mp 141.9-143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.99 (s, 1H), 8.80 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 3.4 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.61 – 7.51 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 160.2, 140.8, 139.8, 138.5, 134.5, 133.9, 132.2, 131.2, 129.6, 128.6, 128.1, 127.8, 122.4, 121.9, 120.9. IR (thin film): $ν_{max}$ (cm^{-1}) = 3298, 2918, 1670, 1603, 1530, 1447, 1269, 939, 752, 711, 642; HRMS (ESI) calcd for $C_{18}H_{13}NNaO_2S$ $[M+Na]^+$: 330.0559. Found: 330.0560.

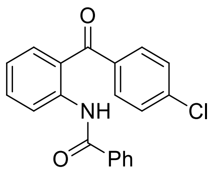


1j. White solid, 1.32 g, 89% yield, mp 124.6-125.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.23 (s, 1H), 8.71 – 8.66 (m, 1H), 7.74 – 7.68 (m, 2H), 7.63 – 7.55 (m, 3H), 7.50 – 7.44 (m, 2H), 7.18 (td, *J* = 7.8, 1.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 160.2, 154.8, 138.5, 138.2, 134.2, 133.5, 132.6, 129.9, 128.2, 124.1, 123.5, 121.3, 63.5, 13.9. IR (thin film): $ν_{max}$ (cm^{-1}) = 3274, 2985, 1715, 1600, 1523, 1263, 1178, 946, 711, 643; HRMS (ESI) calcd for $C_{17}H_{15}NNaO_4$ $[M+Na]^+$: 320.0893. Found: 320.0892.

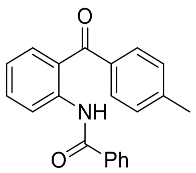


1k. White solid, 0.65 g, 81% yield, mp 117.5-118.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.80 (s, 1H), 8.87 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.07 – 8.03 (m, 2H), 7.80 – 7.74 (m, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.57 (m, 1H), 7.56 – 7.49 (m, 3H), 7.20 – 7.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 165.7, 165.3 (d, *J* = 253.1 Hz), 140.9, 134.8 (d, *J* = 3.1 Hz), 134.6, 134.5, 133.5, 132.5 (d, *J* = 9.1 Hz), 132.0, 128.8, 127.3, 123.1, 122.2, 121.6, 115.5 (d, *J* = 21.8 Hz). ^{19}F NMR (376

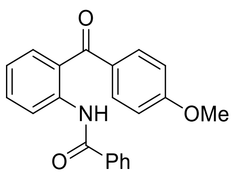
MHz, $CDCl_3$): δ = -105.5. IR (thin film): ν_{max} (cm^{-1}) = 3305, 3066, 1682, 1598, 1449, 1267, 1156, 933, 759, 703; HRMS (ESI) calcd for $C_{20}H_{14}FNNaO_2$ $[M+Na]^+$: 342.0901. Found: 342.0899.



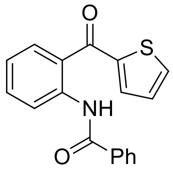
1l.[4] White solid, 0.78 g, 93% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.85 (s, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.70 – 7.63 (m, 3H), 7.60 – 7.45 (m, 6H), 7.17 – 7.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 165.8, 141.1, 138.9, 137.0, 134.8, 134.5, 133.6, 132.1, 131.2, 128.8, 128.7, 127.4, 122.9, 122.2, 121.6. IR (thin film): ν_{max} (cm^{-1}) = 3301, 2918, 1682, 1604, 1528, 1448, 1294, 932, 758, 702; HRMS (ESI) calcd for $C_{20}H_{14}ClNNaO_2$ $[M+Na]^+$: 358.0611. Found: 358.0608.



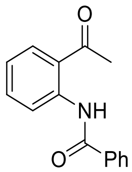
1m. White solid, 0.87 g, 92% yield, mp 88.0-89.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.90 (s, 1H), 8.88 (dd, J = 8.8, 1.0 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.65 – 7.59 (m, 4H), 7.55 – 7.47 (m, 3H), 7.28 (d, J = 7.9 Hz, 2H), 7.11 (td, J = 7.9, 1.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.8, 165.7, 143.3, 140.8, 135.9, 134.5, 134.2, 133.7, 131.9, 130.0, 128.9, 128.7, 127.3, 123.4, 122.0, 121.3, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 3280, 3063, 1682, 1582, 1495, 1268, 1183, 933, 782, 704; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1152. Found: 338.1150.



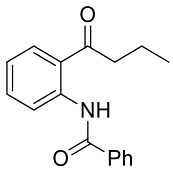
1n.[5] White solid, 0.82 g, 82% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.73 (s, 1H), 8.83 (dd, J = 8.8, 0.8 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.59 (t, J = 7.3 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.11 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 165.5, 163.2, 140.3, 134.4, 133.7, 133.2, 132.4, 131.8, 130.8, 128.6, 127.2, 123.8, 122.0, 121.4, 113.5, 55.3. IR (thin film): ν_{max} (cm^{-1}) = 3319, 2917,1678, 1598, 1581, 1257, 1176, 933, 760, 703; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_3$ $[M+Na]^+$: 354.1101. Found: 354.1099.



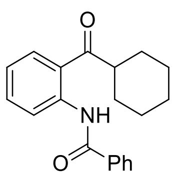
1o.[3] Yellow solid, 0.22 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.41 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.88 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.73 (d, *J* = 4.9 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.56 – 7.46 (m, 3H), 7.22 – 7.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 165.5, 143.8, 139.8, 135.6, 134.7, 134.4, 133.9, 132.0, 131.9, 128.7, 128.0, 127.2, 124.1, 122.4, 121.7. IR (thin film): ν_{max} (cm^{-1}) = 3319, 1678, 1599, 1581, 1409, 1270, 758, 703, 651; HRMS (ESI) calcd for $C_{18}H_{13}NNaO_2S$ $[M+Na]^+$: 330.0559. Found: 330.0565.



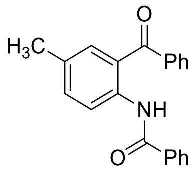
1p.[6] White solid, 1.09 g, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.70 (s, 1H), 8.98 (d, *J* = 8.5 Hz, 1H), 8.10 – 8.05 (m, 2H), 7.95 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.57 – 7.49 (m, 3H), 7.18 – 7.13 (m, 1H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 165.9, 141.3, 135.2, 134.7, 131.8, 131.7, 128.7, 127.3, 122.3, 121.8, 120.6, 28.4.



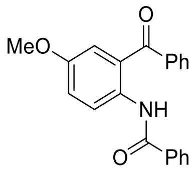
1q. Yellow solid, 0.32 g, 60% yield, mp 92.8-93.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.74 (s, 1H), 8.97 (d, *J* = 8.5 Hz, 1H), 8.11 – 8.05 (m, 2H), 8.00 – 7.95 (m, 1H), 7.63 – 7.50 (m, 4H), 7.18 – 7.12 (m, 1H), 3.04 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.3, 166.0, 141.3, 134.9, 134.8, 131.8, 130.9, 128.7, 127.4, 122.4, 121.8, 120.9, 41.9, 18.1, 13.8. IR (thin film): ν_{max} (cm^{-1}) = 2692, 1680, 1607, 1584, 1450, 1303, 753, 703; HRMS (ESI) calcd for $C_{17}H_{17}NNaO_2$ $[M+Na]^+$: 290.1152. Found: 290.1156.



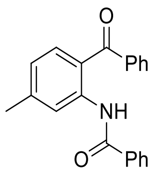
1r. Yellow solid, 1.09 g, 81% yield, mp 120.4-121.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.74 (s, 1H), 8.97 (d, *J* = 8.4 Hz, 1H), 8.11 – 8.05 (m, 2H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.44 – 3.33 (m, 1H), 1.96 – 1.82 (m, 4H), 1.80 – 1.71 (m, 1H), 1.61 – 1.50 (m, 2H), 1.48 – 1.36 (m, 2H), 1.32 – 1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.8, 166.0, 141.7, 134.9, 134.8, 131.8, 130.6, 128.7, 127.4, 122.4, 121.2, 121.1, 46.7, 29.8, 25.8, 25.76. IR (thin film): ν_{max} (cm^{-1}) = 2962, 2854, 1679, 1583, 1526, 1450, 1306, 972, 753, 704; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$: 330.1464. Found: 330.1472.



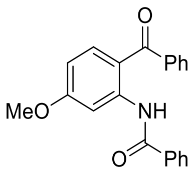
1s. White solid, 0.55 g, 44% yield, mp 115.0-117.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.82 (s, 1H), 8.78 (d, *J* = 8.5 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.74 – 7.70 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.43 (m, 6H), 7.42 – 7.39 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 165.6, 138.8, 138.6, 135.3, 134.6, 134.0, 132.3, 131.9, 131.7, 129.7, 128.7, 128.3, 127.3, 123.2, 121.4, 20.7. IR (thin film): ν_{max} (cm^{-1}) = 3291, 2922, 1679, 1590, 1522, 1297, 1270, 964, 701, 674; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1152. Found: 338.1149.



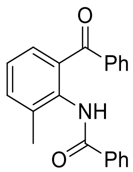
1t. Yellow solid, 0.28 g, 85% yield, mp 94.5-94.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.53 (s, 1H), 8.78 (d, *J* = 9.1 Hz, 1H), 8.03 (d, *J* = 6.9 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.46 (m, 5H), 7.23 – 7.10 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 165.5, 154.1, 138.4, 134.6, 134.2, 132.6, 131.8, 129.8, 128.7, 128.3, 127.2, 124.6, 123.1, 119.6, 118.8, 55.6. IR (thin film): ν_{max} (cm^{-1}) = 2923, 1675, 1593, 1522, 1284, 1217, 960, 701; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_3$ $[M+Na]^+$: 354.1101. Found: 354.1100.



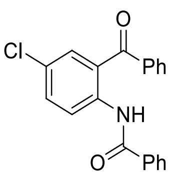
1u. White solid, 0.76 g, 80% yield, mp 134.5-135.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.16 (s, 1H), 8.79 (d, *J* = 0.6 Hz, 1H), 8.12 – 8.05 (m, 2H), 7.71 – 7.67 (m, 2H), 7.61 – 7.46 (m, 7H), 6.95 – 6.90 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 165.8, 146.2, 141.4, 139.1, 134.6, 134.3, 132.1, 131.9, 129.6, 128.8, 128.2, 127.4, 123.0, 121.6, 120.5, 22.2. IR (thin film): ν_{max} (cm^{-1}) = 3280, 3061, 2926, 1682, 1599, 1530, 1293, 1270, 935, 798, 700; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1152. Found: 338.1158.



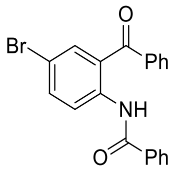
1v.[7] White solid, 0.40 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.68 (s, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.13 – 8.07 (m, 2H), 7.65 – 7.60 (m, 2H), 7.57 – 7.43 (m, 7H), 6.58 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 166.0, 164.7, 144.3, 139.4, 136.4, 134.4, 131.9, 131.5, 129.1, 128.7, 128.1, 127.3, 115.4, 109.2, 104.5, 55.5.



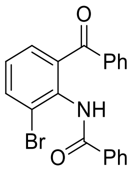
1w. White solid, 0.49 g, 86% yield, mp 85.3-86.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 7.93 – 7.89 (m, 2H), 7.83 – 7.79 (m, 2H), 7.58 – 7.40 (m, 7H), 7.34 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 165.4, 137.6, 136.5, 135.8, 134.8, 134.1, 133.0, 132.4, 131.8, 130.4, 129.1, 128.6, 128.2, 127.4, 125.1, 19.2. IR (thin film): ν_{max} (cm^{-1}) = 3303, 1664, 1509, 1486, 1317, 778, 741, 706, 668; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1150. Found: 338.1147.



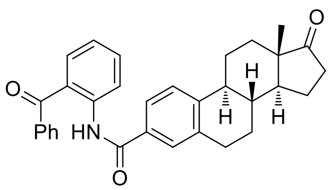
1x. Yellow solid, 0.61 g, 60% yield, mp 119.0-121.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.78 (s, 1H), 8.88 (d, *J* = 9.7 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.75 – 7.70 (m, 2H), 7.64 – 7.47 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.0, 165.7, 139.5, 138.0, 134.2, 134.1, 133.0, 132.8, 132.2, 129.8, 128.8, 128.5, 127.3, 127.2, 124.3, 122.9. IR (thin film): ν_{max} (cm^{-1}) = 3303, 3062, 1684, 1637, 1512, 1396, 1288, 1244, 951, 700; HRMS (ESI) calcd for $C_{20}H_{14}ClNNaO_2$ $[M+Na]^+$: 358.0605. Found: 358.0610.



1y. Yellow solid, 1.06 g, 70% yield, mp 117.4-118.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.78 (s, 1H), 8.84 – 8.80 (m, 1H), 8.06 – 8.01 (m, 2H), 7.76 – 7.70 (m, 4H), 7.66 – 7.61 (m, 1H), 7.57 – 7.48 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 165.7, 140.0, 138.0, 137.1, 135.9, 134.2, 132.9, 132.2, 129.8, 128.8, 128.5, 127.3, 124.7, 123.2, 114.6. IR (thin film): ν_{max} (cm^{-1}) = 3299, 2917, 2926, 1683, 1577, 1511, 1492, 1287, 1259, 948, 833, 699; HRMS (ESI) calcd for $C_{20}H_{14}BrNNaO_2$ $[M+Na]^+$: 404.0080. Found: 404.0083.

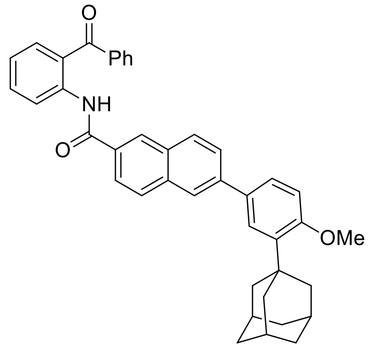


1z. White solid, 0.28 g, 73% yield, mp 158.0-160.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.35 (m, 6H), 7.16 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8, 165.4, 136.5, 135.6, 135.3, 134.0, 133.6, 133.0, 132.0, 130.3, 129.3, 128.5, 128.2, 127.3, 126.2, 120.8. IR (thin film): ν_{max} (cm^{-1}) = 3291, 3062, 1667, 1597, 1509, 1485, 1316, 1283, 751, 703, 655; HRMS (ESI) calcd for $C_{20}H_{14}BrNNaO_2$ $[M+Na]^+$: 404.0081. Found: 404.0083.

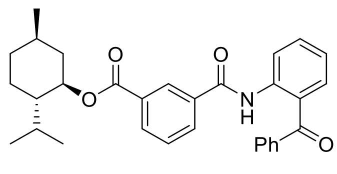


The corresponding substituted benzoyl chloride was prepared according to the literature procedure.[8–9] **1ak**. Yellow solid, 295.2 mg, 87% yield, mp 114.9-116.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.89 (s, 1H), 8.88 (d, *J* = 8.2 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.73 – 7.71 (m, 2H), 7.63 – 7.58 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.09 (m, 1H), 3.08 – 2.94 (m, 2H), 2.56 – 2.42 (m, 2H), 2.40 – 2.31 (m, 1H), 2.18 – 2.13 (m, 1H), 2.11 – 2.04 (m, 2H), 2.02 – 1.96 (m, 1H), 1.70 – 1.61 (m, 2H), 1.60 – 1.45 (m, 4H), 0.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):

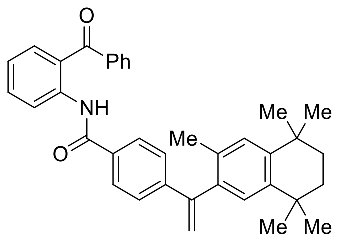
δ = 220.4, 200.1, 165.8, 144.1, 141.1, 138.7, 137.1, 134.5, 133.9, 132.2, 131.9, 129.7, 128.2, 125.7, 124.3, 122.9, 121.9, 121.3, 50.4, 47.8, 44.4, 37.7, 35.7, 31.4, 29.3, 26.2, 25.5, 21.5, 13.7. IR (thin film): ν_{max} (cm^{-1}) = 3289, 2925, 1738, 1526, 1447, 1261, 715, 701; HRMS (ESI) calcd for $C_{32}H_{31}NNaO_3$ $[M+Na]^+$: 500.2202. Found: 500.2195.



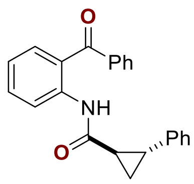
The corresponding substituted benzoyl chloride was prepared according to the literature procedure.[9] **1al**. Yellow solid, 0.32 g, 54% yield, mp 146.0-148.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.16 (s, 1H), 8.98 (d, *J* = 8.2 Hz, 1H), 8.62 (s, 1H), 8.14 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.09 – 7.99 (m, 3H), 7.82 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.71 – 7.59 (m, 4H), 7.57 – 7.49 (m, 3H), 7.17 – 7.13 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.21 (d, *J* = 1.8 Hz, 6H), 2.12 (s, 3H), 1.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 165.7, 158.8, 141.2, 141.0, 138.8, 138.75, 135.4, 134.6, 134.0, 132.4, 132.2, 131.4, 131.1, 129.7, 129.6, 128.7, 128.2, 128.1, 126.4, 125.8, 125.6, 124.5, 123.8, 122.9, 122.0, 121.4, 112.0, 55.0, 40.5, 37.1, 37.0, 29.0. IR (thin film): ν_{max} (cm^{-1}) = 3303, 2904, 2849, 1679, 1602, 1582, 1448, 1238, 700, 643; HRMS (ESI) calcd for $C_{41}H_{37}NNaO_3$ $[M+Na]^+$: 614.2671. Found: 614.2668.



The corresponding substituted benzoyl chloride was prepared according to the literature procedure.[9–10] **1am**. White solid, 0.58 g, 60% yield, mp 105.7-107.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.08 (s, 1H), 8.88 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.76 (s, 1H), 8.24 – 8.22 (m, 2H), 7.74 – 7.69 (m, 2H), 7.67 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 7.50 – 7.46 (m, 2H), 7.14 (td, *J* = 7.6, 0.9 Hz, 1H), 4.98 (td, *J* = 10.8, 4.4 Hz, 1H), 2.16 – 2.13 (m, 1H), 2.06 – 1.95 (m, 1H), 1.74 – 1.71 (m, 2H), 1.65 – 1.51 (m, 2H), 1.21 – 1.05 (m, 2H), 0.95 – 0.87 (m, 7H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 165.1, 164.8, 140.8, 138.6, 134.9, 134.5, 133.9, 132.8, 132.3, 131.6, 131.1, 129.8, 128.9, 128.7, 128.2, 123.1, 122.3, 121.3, 75.2, 47.0, 40.8, 34.2, 31.4, 26.3, 23.4, 22.0, 20.7, 16.3. IR (thin film): ν_{max} (cm^{-1}) = 3287, 2956, 2927, 1717, 1584, 1449, 1262, 705, 643; HRMS (ESI) calcd for $C_{31}H_{33}NNaO_4$ $[M+Na]^+$: 506.2307. Found: 506.2309.

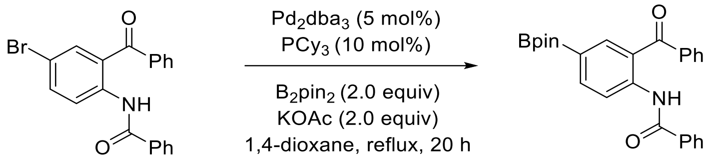


The corresponding substituted benzoyl chloride was prepared according to the literature procedure.[9] **1an**. Yellow solid, 412.0 mg, 94% yield, mp 89.0-90.3 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.52 (m, 3H), 7.44 – 7.40 (m, 2H), 7.39 – 7.32 (m, 4H), 7.17 – 7.09 (m, 3H), 5.84 (s, 1H), 5.35 (s, 1H), 1.98 (s, 3H), 1.73 (s, 4H), 1.33 (s, 6H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 149.0, 144.8, 144.4, 142.4, 139.2, 138.0, 133.7, 132.7, 131.5, 131.4, 129.9, 128.9, 128.6, 128.1, 128.0, 127.1, 127.0, 123.5, 122.3, 119.1, 116.6, 112.2, 97.0, 84.6, 35.22, 35.20, 34.0, 33.9, 31.9, 31.88, 19.9. IR (thin film): ν_{max} (cm^{-1}) = 3319, 2958, 2924, 1683, 1583, 1448, 1294, 700, 643; HRMS (ESI) calcd for $C_{37}H_{37}NNaO_2$ $[M+Na]^+$: 550.2722. Found: 550.2721.



The corresponding acid chloride was prepared according to the literature procedure.[9] **1ao**. White solid, 1.2 g, 91% yield, mp 127.0-128.3 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.19 (s, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.62 – 7.55 (m, 3H), 7.52 – 7.46 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.12 (m, 2H), 7.09 (td, *J* = 7.9, 1.1 Hz, 1H), 2.65 (ddd, *J* = 9.3, 6.5, 4.1 Hz, 1H), 1.92 (ddd, *J* = 8.3, 5.1, 4.1 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.39 (ddd, *J* = 8.2, 6.5, 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 171.0, 140.6, 140.2, 138.5, 134.3, 133.5, 132.4, 129.8, 128.4, 128.2, 126.3, 126.0, 122.8, 121.8, 121.3, 28.1, 26.1, 16.9. IR (thin film): ν_{max} (cm^{-1}) = 3312, 3061, 1690, 1521, 1448, 1262, 955, 754, 642; HRMS (ESI) calcd for $C_{23}H_{19}NNaO_2$ $[M+Na]^+$: 364.1308. Found: 364.1365.

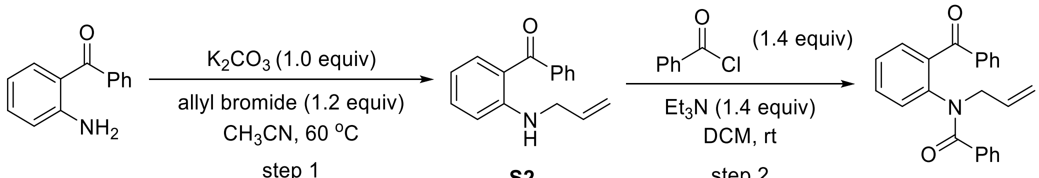
2. Procedure for the synthesis of substrate 1aa.[11]



1y **1aa**

To an oven-dried Schlenk tube were added compound **1y** (380.0 mg, 1.0 mmol, 1.0 equiv), B_2pin_2 (508.0 mg, 2.0 mmol, 2.0 equiv), Pd_2dba_3 (46.0 mg, 0.05 mmol, 5 mol%), tricyclohexylphosphine (28.1 mg, 0.1 mmol, 10 mol%), potassium acetate (197.0 mg, 2.0 mmol, 2.0 equiv) and 1,4-dioxane (10 mL). Then the mixture was heated to reflux and stirred for 20 h under argon. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, filtered through a short pad of silica gel, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) gave **1aa** as a white solid (0.25 g, 58% yield, mp 170.4-171.1 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.04 (s, 1H), 8.92 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 4H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.48 (m, 5H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 165.8, 143.3, 141.0, 140.3, 138.8, 134.5, 132.5, 132.1, 130.0, 128.8, 128.4, 127.4, 122.5, 120.3, 84.0, 24.8. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.4 (s). IR (thin film): ν_{max} (cm^{-1}) = 2978, 2927, 1685, 1582, 1362, 1294, 1144, 703, 649; HRMS (ESI) calcd for $C_{26}H_{26}BNNaO_4$ $[M+Na]^+$: 450.1852. Found: 450.1848.

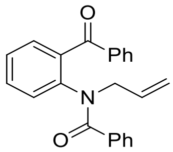
3. Procedure for the synthesis of substrate 1ab.[12]



S2 **1ab**

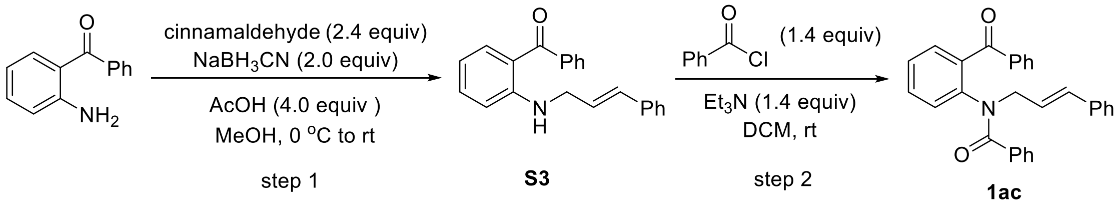
Step 1: To a solution of 2-aminophenyl-(phenyl)methanone (986.0 mg, 5.0 mmol, 1.0 equiv) and K_2CO_3 (691.1 mg, 5.0 mmol, 1.0 equiv) in CH_3CN (10 mL) was added allyl bromide (726.0 mg, 6.0 mmol, 1.2 equiv) at rt. The mixture was stirred at 60 °C for 24 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a short pad of silica gel, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) gave product **S2** as yellow oil (0.95 g, 80% yield), which was directly used for the next step.

Step 2: compound **1ab** was prepared according to **RP1** (page S-3).



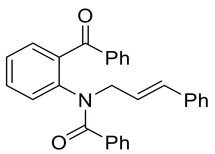
1ab. White solid, 0.91 g, 66% yield, mp 105.5-106.4 °C. ^{1}H NMR (400 MHz, DMSO-D$_6$): δ = 7.81 – 6.96 (m, 14H), 6.08 – 5.90 (m, 1H), 5.19 – 5.01 (m, 2H), 4.76 (d, J = 12.8 Hz, 1H), 4.20 – 3.75 (m, 1H). ^{13}C NMR (100 MHz, DMSO-D$_6$): δ = 194.5, 168.5, 142.1, 136.2, 135.5, 135.0, 133.7, 133.3, 131.9, 130.3, 129.6, 129.58, 128.5, 128.4, 127.6, 126.7, 117.6, 52.9. IR (thin film): ν_{max} (cm^{-1}) = 3061, 2920, 1663, 1595, 1340, 1265, 927, 702, 636; HRMS (ESI) calcd for $C_{23}H_{19}NNaO_2$ [M+Na]$^+$: 364.1308. Found: 364.1308.

4. Procedure for the synthesis of substrate 1ac.[13]



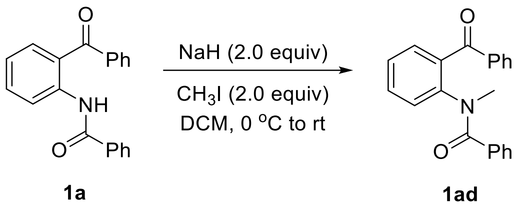
Step 1: To a solution of 2-aminophenyl-(phenyl)methanone (986.0 mg, 5.0 mmol, 1.0 equiv) in methanol (10 mL), acetic acid (1.21 g, 1.1 mL, 20.0 mmol, 4.0 equiv) was added dropwise at 0 °C. $NaBH_3CN$ (628.4 mg, 10.0 mmol, 2.0 equiv) was added subsequently and stirred for 5 min at this temperature. Then cinnamaldehyde (1.59 g, 12.0 mmol, 2.4 equiv) was added to the reaction mixture, which was then allowed to stir for 22 h at rt. After the reaction was complete (monitored by TLC), the crude reaction mixture was quenched with ice cold water, extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) afforded the product **S3** as yellow solid (0.95 g, 61% yield), which was directly used for the next step.

Step 2: compound **1ac** was prepared according to **RP1** (page S-3).



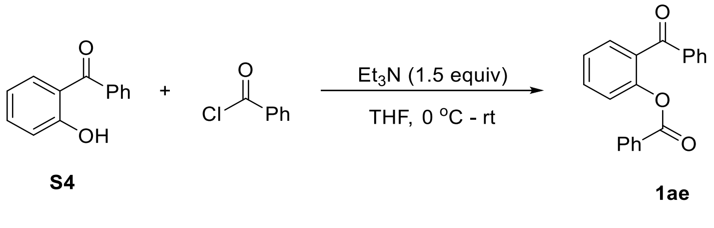
1ac. White solid, 0.70 g, 84% yield, mp 57.2-59.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 7.0 Hz, 1H), 7.45 – 6.99 (m, 18H), 6.54 – 6.13 (m, 2H), 5.18 – 5.04 (m, 1H), 4.42 – 4.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6, 169.8, 142.8, 136.6, 136.5, 135.6, 133.1, 133.0, 131.4, 130.5, 130.4, 130.1, 129.5, 129.0, 128.4, 128.1, 127.6, 126.4, 125.0, 53.4. IR (thin film): ν_{max} (cm^{-1}) = 3059, 2923, 1663, 1647, 1313, 1265, 967, 763, 702; HRMS (ESI) calcd for $C_{29}H_{23}NNaO_2$ $[M+Na]^+$: 440.1621. Found: 440.1620.

5. Procedure for the synthesis of substrate 1ad.[14]



To a solution of NaH (80.0 mg, 2.0 mmol, 2.0 equiv) in DCM (3 mL) at 0 °C, **1a** (301.0 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 0.5 h at this temperature before iodomethane (283.9 mg, 2.0 mmol, 2.0 equiv) was added. Then the reaction mixture was warmed to rt and stirred for 10 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was quenched with water and extracted with DCM (10 mL x 3). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) afforded the desired product **1ad** as colorless oil (283.5mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.41 (m, 2H), 7.38 – 7.08 (m, 10H), 7.00 – 6.90 (m, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 169.8, 144.2, 136.3, 135.7, 135.2, 132.9, 131.7, 130.3, 129.8, 129.4, 129.3, 128.9, 128.0, 127.4, 126.2, 39.0. IR (thin film): ν_{max} (cm^{-1}) = 3060, 2925, 1663, 1596, 1486, 1367, 765, 703, 654; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1152. Found: 338.1149.

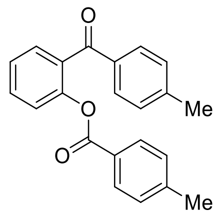
6. Representative procedure for the synthesis of substrates 1ae–1ai.



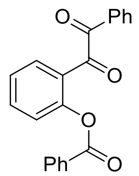
Preparation of compound 1ae. To a solution of (2-hydroxyphenyl)(phenyl)methanone **S4**

(1.98 g, 10 mmol, 1.0 equiv) in dry THF (20 mL) was added Et_3N (2.09 mL, 15 mmol, 1.5 equiv) and benzoyl chloride (13.5 mmol, 1.56 mL, 1.35 equiv) at 0 °C. The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). Then, the reaction mixture was quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford compound **1ae**[15] as a colorless oil (1.89 g, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 – 7.81 (m, 2H), 7.80 – 7.72 (m, 2H), 7.62 – 7.60 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.33 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8, 164.6, 148.8, 137.6, 133.5, 132.9, 132.2, 131.9, 130.4, 130.0, 129.7, 128.8, 128.31, 128.27, 125.8, 123.3.

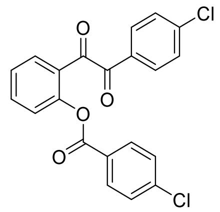
The following substrates **1af**–**1aj** were prepared analogously.



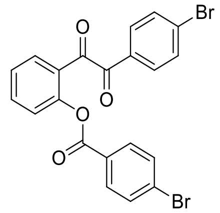
1af. Yellow solid, 373 mg, 66% yield, mp 99.4-99.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.56 (m, 2H), 7.38 – 7.35 (m, 2H), 7.17– 7.13 (m, 4H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5, 164.6, 148.8, 144.3, 143.8, 135.0, 132.2, 131.8, 130.2, 130.1, 130.0, 128.99, 128.95, 126.2, 125.6, 123.3, 21.7, 21.6. IR (thin film): ν_{max} (cm^{-1}) = 2920, 1732, 1659, 1603, 1446, 1297, 1262, 1197, 1176, 1100, 1061, 1017, 929; HRMS (ESI) calcd for $C_{22}H_{18}O_3Na$ $[M+Na]^+$: 353.1148. Found: 353.1146.



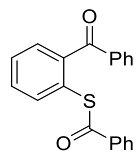
1ag. Yellow solid, 946 mg, 95% yield, mp 73.0-74.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.78 – 7.72 (m, 5H), 7.55 – 7.47 (m, 3H), 7.33 – 7.27 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 192.6, 164.3, 151.3, 135.7, 134.4, 133.7, 131.9, 131.1, 130.0, 129.9, 128.6, 128.2, 128.1, 127.1, 126.6, 124.0. IR (thin film): ν_{max} (cm^{-1}) = 2921, 2851, 1742, 1663, 1599, 1449, 1247, 1192, 1177, 1104, 1047, 1019, 702, 633; HRMS (ESI) calcd for $C_{21}H_{14}O_4Na$ [M+Na]$^+$: 353.0784. Found: 353.0779.



1ah. White solid, 251 mg, 41% yield, mp 130.0-130.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.77 – 7.65 (m, 5H), 7.49 (td, *J* = 7.9, 0.9 Hz, 1H), 7.33 – 7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 191.2, 163.5, 150.9, 141.4, 140.5, 135.9, 131.3, 131.2, 130.2, 129.0, 128.6, 127.0, 126.8, 126.6, 123.9. IR (thin film): ν_{max} (cm^{-1}) = 2920, 2850, 1634, 1470, 1384, 1092, 1015; HRMS (ESI) calcd for $C_{21}H_{12}Cl_2O_4Na$ [M+Na]$^+$: 421.0005. Found: 421.0006.

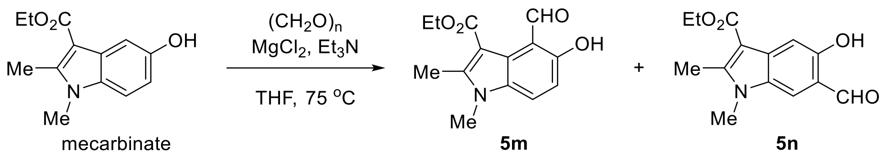


1ai. White solid, 250 mg, 21% yield, mp 113.6-114.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.63 – 7.56 (m, 4H), 7.52 – 7.43 (m, 5H), 7.28 – 7.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 191.4, 163.7, 150.9, 135.9, 132.1, 131.7, 131.33, 131.3, 131.2, 130.6, 130.3, 129.2, 127.1, 127.0, 126.9, 123.9. IR (thin film): ν_{max} (cm^{-1}) = 2921, 2851, 1741, 1654, 1586, 1398, 1255, 1195, 1132, 1072, 1052, 1009, 748, 632; HRMS (ESI) calcd for $C_{21}H_{12}Br_2O_4Na$ [M+Na]$^+$: 510.8974. Found: 510.8984.



1aj. Colorless oil, 50 mg, 16% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.76 (m, 4H), 7.67 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.60 (td, *J* = 7.6, 1.6 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.42 – 7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.2, 189.2, 144.0, 137.5, 137.0, 136.3, 133.6, 133.3, 130.6, 130.2, 129.3, 129.0, 128.6, 128.4, 127.5, 125.9. IR (thin film): ν_{max} (cm^{-1}) = 2961, 2924, 2853, 1668, 1596, 1447, 1262, 1023, 801; HRMS (ESI) calcd for $C_{20}H_{14}O_2SNa$ $[M+Na]^+$: 341.0607. Found: 341.0607.

7. Procedure for the syntheses of substrates 5m-5n.

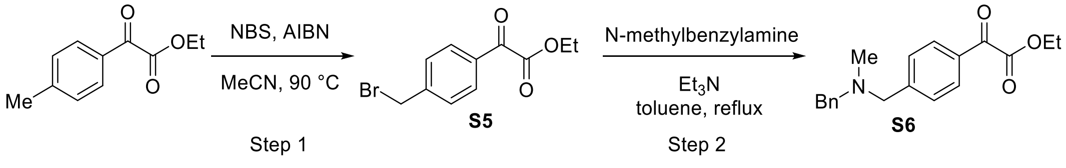


The compounds **5m** and **5n** were prepared according to the known procedure.[16] To a solution of anhydrous magnesium dichloride (1.9 g, 20 mmol) and solid paraformaldehyde (0.9 g, 30 mmol) in dry THF (30 mL), triethylamine (2.8 mL, 20 mmol) was added dropwise by syringe under N_2 atmosphere and the mixture is stirred for 10 min. Mecarbinate (2.3 g, 10 mmol) was added and the reaction mixture was heated under reflux for 24 h. The reaction mixture was cooled to room temperature, and quenched with 1N HCl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford product **5m**.[16] Product **5n** was obtained when the eluent was switched to petroleum ether/ethyl acetate = 2:1.

5m.[16] Pale yellow solid, 1.23 g, 47% yield, mp 146.1-147.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.56 (s, 1H), 10.94 (s, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.69 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 166.2, 160.6, 145.7, 130.6, 125.5, 118.3, 112.5, 111.4, 105.0, 60.1, 29.9, 14.3, 12.7.

5n. Pale yellow solid, 1.23 g, 47% yield, mp 174.8-175.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (s, 1H), 9.88 (s, 1H), 7.60 (s, 1H), 7.36 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 2.78 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 165.1, 156.3, 151.3, 133.6, 131.0, 116.4, 114.4, 107.0, 104.1, 59.6, 29.7, 14.5, 12.2. IR (thin film): ν_{max} (cm^{-1}) = 2960, 2930, 2859, 1728, 1689, 1634, 1469, 1382, 1277, 1188, 1099, 756; HRMS (ESI) calcd for $C_{14}H_{15}NNaO_4$ $[M+Na]^+$: 284.0893. Found: 284.0898.

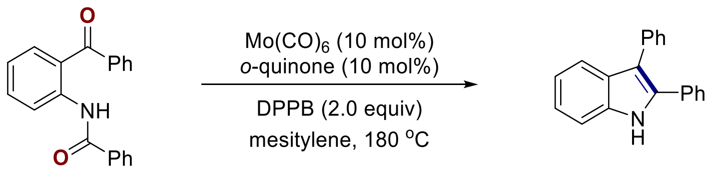
8. Procedure for the synthesis of substrate S6.



Step 1: Ethyl 2-oxo-2-(p-tolyl)acetate (780 mg, 4.06 mmol, 1.0 equiv) was dissolved in acetonitrile (10 mL) under N_2 atmosphere. NBS (801 mg, 4.5 mmol, 1.1 equiv) and AIBN (66 mg, 0.4 mmol, 0.1 equiv) were added and the reaction mixture was stirred for 1.5 h at 90°C to give a yellow solution. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt. The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel to afford the title compound **S5** as a white solid (897 mg, 82%).

Step 2: To a Young Schlenk tube were added compound **S5** (1.2 g, 4.5 mmol, 1.0 equiv), N-methylbenzylamine (0.7 mL, 5.4 mmol, 1.2 equiv), Et_3N (0.75 mL, 5.4 mmol, 1.2 equiv) and toluene (10 mL). The tube was sealed and the reaction mixture was stirred at 110 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt. The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel to afford the title compound **S6** as a pale yellow oil (1.26 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.92 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 2H), 3.55 (s, 2H), 2.20 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.1, 163.9, 147.6, 138.8, 131.3, 130.1, 129.1, 128.8, 128.3, 127.1, 62.2, 62.0, 61.3, 42.3, 14.1. IR (thin film): ν_{max} (cm^{-1}) = 2927, 2790, 1737, 1683, 1606, 1454, 1369, 1316, 1200, 1172, 1015, 982, 876, 741, 699; HRMS (ESI) calcd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594. Found: 312.1594.

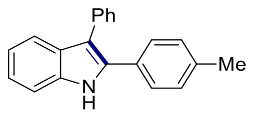
9. Representative procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction for the syntheses of indoles 2.



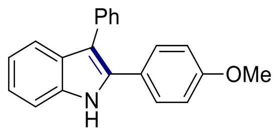
1a **2a**

Preparation of compound 2a. To an oven-dried Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (2.7 mg, 0.01 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (2.2 mg, 0.01 mmol, 10 mol%), and mesitylene (0.5 mL) under argon. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **1a** (30.1 mg, 0.1 mmol, 1.0 equiv) and DPPB (85.3 mg, 0.2 mmol, 2.0 equiv) were added to the reaction mixture under argon. The tube was sealed and the reaction mixture was stirred at 180 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, and passed through a short pad of silica gel (DCM/EtOAc = 1:1). The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether/*tert*-butyl methyl ether = 80:1 to 40:1) to afford the title compound **2a**[17] as a white solid (25.3 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.47 (m, 5H), 7.45 – 7.36 (m, 5H), 7.30 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8, 135.0, 134.0, 132.6, 130.1, 128.7, 128.6, 128.5, 128.1, 127.6, 126.2, 122.6, 120.4, 119.6, 114.9, 110.9.

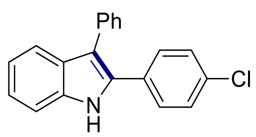
The following compounds **2b–2ad** were prepared analogously.



2b.[18] Colorless oil, 26.0 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.47 – 7.43 (m, 3H), 7.39 – 7.28 (m, 4H), 7.25 – 7.15 (m, 3H) , 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 135.8, 135.2, 134.2, 130.1, 129.7, 129.4, 128.8, 128.5, 128.0 , 126.1, 122.5, 120.3, 119.5, 114.6, 110.8, 21.2.

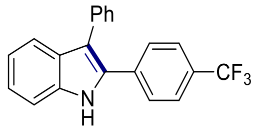


In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (2.0 mL, 0.4 mmol scale) at 160 °C. **2c.**[19] White solid, 101.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.46 – 7.25 (m, 7H), 7.22 – 7.18 (m, 1H), 6.92 – 6.88 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 135.7, 135.2, 134.1, 130.1, 129.4, 128.8, 128.5, 126.0, 125.2, 122.3, 120.3, 119.4, 114.1, 110.8, 55.2.

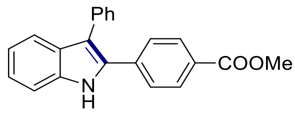


2d.[18] White solid, 24.5 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.40 (m, 5H), 7.39 – 7.27 (m, 6H), 7.23 – 7.16 (m, 1H). ^{13}C NMR (100 MHz,

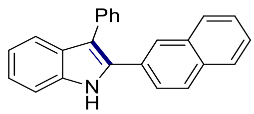
$CDCl_3$): δ = 136.0, 134.7, 133.6, 132.8, 131.1, 130.1, 129.3, 128.9, 128.7, 128.6, 126.5, 123.0, 120.6, 119.8, 115.6, 110.9.



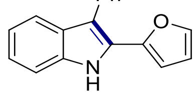
2e.[20] White solid, 29.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.29 (m, 7H), 7.24 – 7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.2, 134.5, 132.2, 130.1, 129.3 (q, *J* = 32.5 Hz), 128.74, 128.7, 128.1, 126.7, 125.6 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.3 Hz), 123.4, 120.7, 120.0, 116.6, 111.1. ^{19}F NMR (377 MHz, $CDCl_3$): δ = – 62.5.



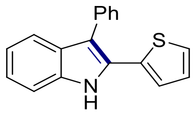
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene/dioxane (3/2, 1.25 mL, 0.2 mmol scale) at 160 °C. **2f.**[21] White solid, 45.8 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 7.99 – 7.95 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.37 (m, 5H), 7.35 – 7.31 (m, 1H), 7.31 – 7.25 (m, 1H), 7.18 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 137.1, 136.2, 134.6, 132.7, 130.1, 129.9, 128.8, 128.7, 128.67, 127.8, 126.6, 123.4, 120.7, 120.0, 116.7, 111.0, 52.2. IR (thin film): ν_{max} (cm^{-1}) = 3346, 2921, 1721, 1699, 1607, 1281, 1111, 771, 744, 702; HRMS (ESI) calcd for $C_{22}H_{17}NNaO_2$ $[M+Na]^+$: 350.1157. Found: 350.1152.



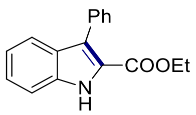
2g.[22] White solid, 29.1 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.96 (s, 1H), 7.84 – 7.72 (m, 4H), 7.52 – 7.44 (m, 6H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 135.0, 134.0, 133.4, 132.6, 130.3, 130.2, 128.8, 128.5, 128.1, 128.0, 127.7, 126.6, 126.4, 126.3, 126.26, 122.8, 120.5, 119.7, 115.5, 110.9. IR (thin film): ν_{max} (cm^{-1}) = 3410, 3055, 1602, 1496, 1453, 1330, 773, 749, 701; HRMS (ESI) calcd for $C_{24}H_{17}NNa$ $[M+Na]^+$: 342.1259. Found: 342.1254.



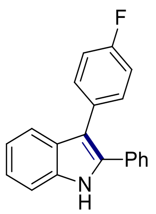
2h.[18] Yellow oil, 22.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.68 – 7.63 (m, 3H), 7.58 – 7.53 (m, 2H), 7.49 – 7.43 (m, 3H), 7.31 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.43 – 6.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 141.3, 135.4, 134.6, 130.2, 128.7, 128.6, 126.9, 125.1, 122.9, 120.4, 119.5, 114.4, 111.8, 110.8, 106.8.



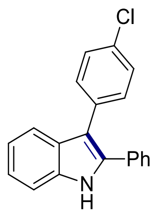
2i.[18] Brown oil, 22.3 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.40 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.04 (dd, *J* = 4.9, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 134.4, 130.5, 129.0, 128.5, 128.2, 127.4, 126.8, 125.3, 125.25, 123.0, 120.5, 119.6, 115.7, 110.7.



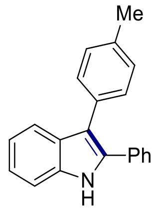
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (2.0 mL, 0.4 mmol scale) at 160 °C. **2j**.[17] White solid, 88.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 7.67 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.36 (m, 2H), 7.18 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 135.8, 133.5, 130.6, 127.9, 127.7, 127.1, 125.7, 124.2, 122.8, 121.7, 120.8, 111.7, 60.9, 14.0.



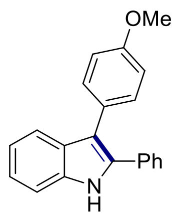
2k.[20] White solid, 25.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.35 (m, 5H), 7.34 – 7.28 (m, 3H), 7.27 – 7.22 (m, 1H), 7.19 – 7.14 (m, 1H), 7.10 – 7.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 243.5 Hz), 135.8, 134.1, 132.4, 131.6 (d, *J* = 7.8 Hz), 130.9 (d, *J* = 3.3 Hz), 128.7, 128.66, 128.1, 127.8, 122.7, 120.5, 119.4, 115.4 (d, *J* = 21.1 Hz), 113.9, 110.9. ^{19}F NMR (377 MHz, $CDCl_3$): δ = – 116.3.



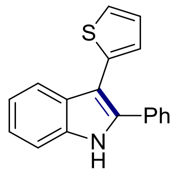
2l.[20] White solid, 27.0 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.37 (m, 10H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8, 134.3, 133.6, 132.3, 131.9, 131.3, 128.73, 128.7, 128.4, 128.2, 127.9, 122.8, 120.6, 119.3, 113.7, 111.0.



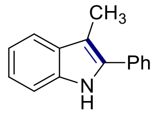
2m.[23] White solid, 24.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.36 – 7.27 (m, 5H), 7.25 – 7.17 (m, 3H), 7.18 – 7.13 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9 , 135.7, 133.8, 132.8, 132.0, 130.0, 129.3, 128.9, 128.6, 128.1, 127.5, 122.6, 120.3, 119.7, 115.0, 110.9, 21.2. IR (thin film): ν_{max} (cm^{-1}) = 3407, 2920, 1602, 1515, 1456, 1329, 1250, 836, 759, 696; HRMS (ESI) calcd for $C_{21}H_{18}N$ [M+H]$^+$: 284.1434. Found: 284.1433.



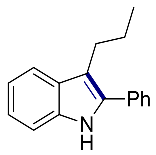
2n.[20] White solid, 24.8 mg, 83% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.57 (s, 1H), 7.56 – 7.47 (m, 4H), 7.36 – 7.24 (m, 5H), 7.20 – 7.15 (m, 1H), 7.09 – 7.05 (m, 1H), 7.00 – 6.95 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 158.4, 136.6, 133.9, 133.2, 131.1, 129.0, 128.5, 128.1, 127.8, 127.3, 122.1, 119.7, 119.0, 114.1, 114.0, 111.3, 54.6. IR (thin film): ν_{max} (cm^{-1}) = 3419, 2923, 1603, 1513, 1244, 1178, 1026, 771, 696; HRMS (ESI) calcd for $C_{21}H_{18}NO$ [M+H]$^+$: 300.1388. Found: 300.1384.



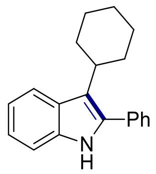
2o.[23] White solid, 22.6 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.46 – 7.40 (m, 4H), 7.38 – 7.25 (m, 3H), 7.18 – 7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 135.6, 135.2, 132.2, 128.8, 128.6, 128.4, 128.1, 127.2, 126.2, 124.5, 122.9, 120.6, 119.8, 110.9, 107.9.



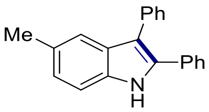
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (1.0 mL, 0.2 mmol scale) at 180 °C. **2p.**[24] White solid, 36.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.20 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8, 134.0, 133.3, 130.0, 128.8, 127.7, 127.3, 122.3, 119.5, 119.0, 110.7, 108.7, 9.6.



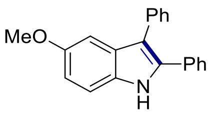
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (2.0 mL, 0.4 mmol scale) at 180 °C. **2q.**[24] Yellow oil, 60.2 mg, 64% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.22 (s, 1H), 7.71 – 7.66 (m, 2H), 7.65 – 7.61 (m, 1H), 7.53 – 7.46 (m, 2H), 7.44 – 7.41 (m, 1H), 7.39 – 7.33 (m, 1H), 7.17 – 7.11 (m, 1H), 7.09 – 7.04 (m, 1H), 2.96 – 2.89 (m, 2H), 1.82 – 1.72 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 137.4, 135.0, 134.6, 130.3, 129.5, 128.7, 128.0, 122.5, 119.71, 119.7, 113.7, 111.9, 27.5, 25.0, 14.6. IR (thin film): ν_{max} (cm^{-1}) = 3409, 3057, 2958, 1539, 1457, 1306, 757, 741, 696; HRMS (ESI) calcd for $C_{17}H_{18}N$ $[M+H]^+$: 236.1439. Found: 236.1434.



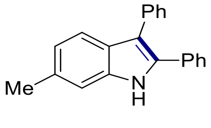
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (1.0 mL, 0.2 mmol scale) at 180 °C. **2r.** White solid, 28.2 mg, 51% yield, mp 149.8-151.4 °C. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.14 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.09 (t, *J* = 7.1 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.19 – 2.07 (m, 2H), 1.89 – 1.73 (m, 5H), 1.45 – 1.34 (m, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 137.8, 134.8, 134.7, 129.6, 129.4, 128.5, 128.3, 122.0, 121.6, 119.3, 118.6, 112.2, 37.4, 34.0, 27.9, 27.0. IR (thin film): ν_{max} (cm^{-1}) = 3399, 2922, 2852, 1455, 1447, 1309, 761, 743, 696; HRMS (ESI) calcd for $C_{20}H_{22}N$ $[M+H]^+$: 276.1747. Found: 276.1749.



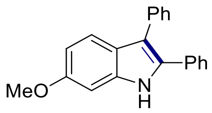
2s.[25] Yellow oil, 26.3 mg, 93% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.51 (s, 1H), 7.51 – 7.47 (m, 2H), 7.42 – 7.36 (m, 6H), 7.34 – 7.25 (m, 4H), 7.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 136.8, 135.9, 135.2, 134.0, 131.0, 129.9, 129.6, 129.4, 129.3, 129.1, 128.2, 126.9, 124.7, 119.4, 114.7, 111.9, 21.7. IR (thin film): ν_{max} (cm^{-1}) = 3416, 2923, 2851, 1464, 1432, 764, 698; HRMS (ESI) calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1439. Found: 284.1435.



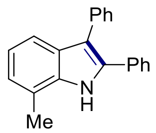
2t.[24] White solid, 25.5 mg, 85% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.47 (s, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.36 (m, 5H), 7.34 – 7.23 (m, 4H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 155.6, 136.8, 135.8, 133.9, 132.6, 130.9, 129.9, 129.4, 129.3, 129.0, 128.2, 126.9, 115.0, 113.4, 112.9, 101.4, 55.9. IR (thin film): ν_{max} (cm^{-1}) = 3409, 2923, 1621, 1506, 1488, 1160, 1033, 761, 699; HRMS (ESI) calcd for $C_{21}H_{17}NNaO$ $[M+Na]^+$: 322.1208. Found: 322.1203.



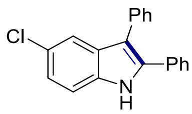
2u.[25] Colorless oil, 24.9 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.49 – 7.40 (m, 4H), 7.39 – 7.31 (m, 4H), 7.23 (s, 1H), 7.06 (dd, *J* = 8.1, 0.6 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 135.2, 133.4, 132.8, 132.6, 130.1, 128.6, 128.5, 128.0, 127.4, 126.6, 126.1, 122.2, 119.3, 114.9, 110.8, 21.7.



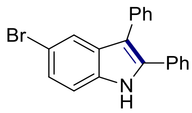
2v.[26] White solid, 23.4 mg, 78% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.45 (s, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.42 (m, 1H), 7.42 – 7.36 (m, 4H), 7.34 – 7.23 (m, 4H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 157.9, 138.3, 136.8, 134.0, 133.8, 130.8, 129.4, 129.3, 128.8, 128.0, 126.9, 124.0, 120.5, 115.0, 111.0, 95.2, 55.7. IR (thin film): ν_{max} (cm^{-1}) = 3331, 2923, 2852, 1601, 1457, 1197, 1029, 814, 763, 697; HRMS (ESI) calcd for $C_{21}H_{18}NO$ $[M+H]^+$: 300.1388. Found: 300.1383.



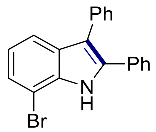
2w.[17] White solid, 25.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.50 – 7.35 (m, 6H), 7.23 – 7.14 (m, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4, 135.2, 133.9, 132.8, 130.1, 128.6, 128.5, 128.3, 128.2, 127.6, 126.1, 123.2, 120.7, 120.0, 117.4, 115.6, 16.6.



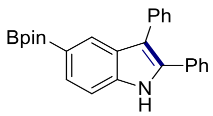
2x.[18] Yellow oil, 27.2mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.45 – 7.39 (m, 6H), 7.37 – 7.30 (m, 5H), 7.22 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4, 134.3, 134.1, 132.1, 130.0, 129.8, 128.69, 128.6, 128.1, 128.0, 126.5, 126.1, 122.9, 119.0, 114.7, 111.9.



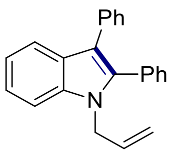
2y.[25] Yellow oil, 28.5 mg, 82% yield. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.85 (s, 1H), 7.68 (s, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.38 (m, 4H), 7.37 – 7.28 (m, 5H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 136.7, 136.0, 135.8, 133.2, 131.3, 130.9, 129.5, 129.4, 129.2, 128.7, 127.3, 125.7, 122.1, 114.6, 114.1, 113.6. IR (thin film): ν_{max} (cm^{-1}) = 3407, 2918, 1601, 1507, 1449, 1307, 1071, 762, 698; HRMS (ESI) calcd for $C_{20}H_{15}BrN$ $[M+H]^+$: 348.0388. Found: 348.0386.



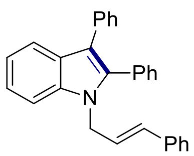
2z. White solid, 28.5 mg, 82% yield, mp 109.0-110.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.32 (m, 11H), 7.08 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.7, 134.6, 134.5, 132.1, 130.1, 129.9, 128.7, 128.6, 128.2, 128.1, 126.5, 124.8, 121.5, 118.9, 116.0, 104.5. IR (thin film): ν_{max} (cm^{-1}) = 3429, 3059, 2921, 1602, 1505, 1449, 1305, 783, 723, 607; HRMS (ESI) calcd for $C_{20}H_{15}BrN$ $[M+H]^+$: 348.0382. Found: 348.0384.



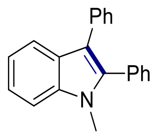
2aa. White solid, 30.5 mg, 77% yield, mp 210.1-213.2 °C. ^{1}H NMR (400 MHz, C_3D_6O): δ = 10.76 (s, 1H), 8.05 (s, 1H), 7.64 – 7.59 (m, 1H), 7.55 – 7.41 (m, 7H), 7.37 – 7.27 (m, 4H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, C_3D_6O): δ = 139.4, 136.5, 135.2, 133.6, 131.1, 129.5, 129.43, 129.4, 129.0, 128.4, 127.6, 127.2, 115.6, 111.5, 84.0, 25.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.1 (s). IR (thin film): ν_{max} (cm^{-1}) = 3309, 2925, 2853, 1602, 1430, 1353, 1144, 1070, 858, 699; HRMS (ESI) calcd for $C_{26}H_{27}BNO_2$ $[M+H]^+$: 396.2134. Found: 396.2132.



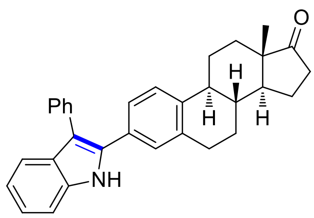
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (1.0 mL, 0.2 mmol scale) at 160 °C. **2ab.**[27] White solid, 51.6 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 8H), 7.42 – 7.36 (m, 3H), 7.34 – 7.26 (m, 2H), 6.12 – 5.99 (m, 1H), 5.29 (dd, *J* = 10.4, 1.1 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.1 Hz, 1H), 4.81 – 4.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 136.8, 135.1, 133.7, 131.8, 131.0, 129.8, 128.3, 128.12, 128.1, 127.2, 125.5, 122.2, 120.3, 119.7, 116.6, 115.4, 110.3, 46.4. IR (thin film): ν_{max} (cm^{-1}) = 3058, 2921, 1602, 1461, 1363, 1215, 743 700; HRMS (ESI) calcd for $C_{23}H_{19}NNa$ $[M+Na]^+$: 332.1415. Found: 332.1412.



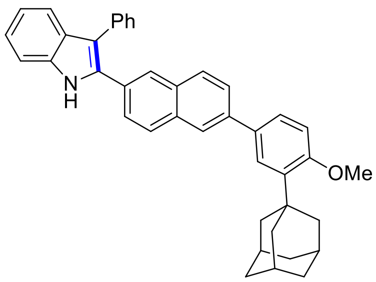
2ac. White solid, 32.7 mg, 85% yield, mp 76.2-76.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 7.93 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.42 (m, 7H), 7.40 – 7.34 (m, 7H), 7.32 – 7.23 (m, 3H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.37 (dt, *J* = 15.9, 4.3 Hz, 1H), 4.90 (d, *J* = 4.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 136.9, 136.4, 135.1, 131.9, 131.6, 131.1, 129.8, 128.5, 128.4, 128.1, 127.7, 127.3, 126.4, 125.5, 125.3, 122.3, 120.4, 119.7, 115.5, 110.3, 46.1. IR (thin film): ν_{max} (cm^{-1}) = 3058, 2924, 2853, 1602, 1461, 1362, 1264, 966, 741, 700; HRMS (ESI) calcd for $C_{29}H_{23}NNa$ $[M+Na]^+$: 408.1723. Found: 408.1728.



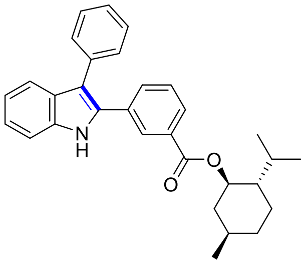
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (1.0 mL, 0.2 mmol scale) at 160 °C. **2ad.**[28] White solid, 46.4 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.89 (m, 1H), 7.53 – 7.33 (m, 11H), 7.32 – 7.24 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 137.3, 135.2, 131.9, 131.1, 129.8, 128.4, 128.1, 128.0, 127.0, 125.5, 122.2, 120.2, 119.6, 115.1, 109.5, 30.9.



In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone in mesitylene (1.0 mL, 0.05 mmol scale) at 180 °C. **2ak**. White solid, 20.1 mg, 90% yield, mp 145.4-147.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.36 – 7.31 (m, 1H), 7.29 – 7.17 (m, 5H), 2.88 – 2.87 (m, 2H), 2.57 – 2.52 (m, 1H), 2.42 – 2.33 (m, 2H), 2.23 – 2.14 (m, 1H), 2.13 – 1.95 (m, 3H), 1.73 – 1.45 (m, 6H), 0.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 220.7, 139.3, 136.8, 135.8, 135.2, 134.0, 130.2, 130.1, 128.9, 128.4, 128.2, 126.1, 125.6, 125.57, 122.5, 120.3, 119.5, 114.7, 110.8, 50.5, 47.9, 44.4, 38.0, 35.8, 31.5, 29.3, 26.4, 25.6, 21.5, 13.8. IR (thin film): ν_{max} (cm^{-1}) = 3354, 2926, 2855, 1732, 1456, 1250, 742, 701; HRMS (ESI) calcd for $C_{32}H_{32}NO$ $[M+H]^+$: 446.2484. Found: 446.2471.

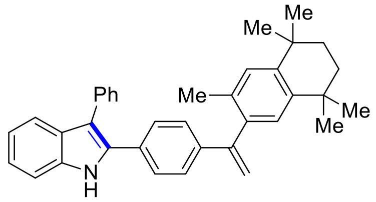


In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone, PCy_3 (2.4 equiv) in mesitylene/dioxane (1/1, 1.0 mL, 0.05 mmol scale) at 180 °C. **2al**. White solid, 26.3 mg, 94% yield, mp 260.0-263.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.95 (s, 2H), 7.83 – 7.73 (m, 4H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.54 – 7.46 (m, 5H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.21 (s, 6H), 2.13 (s, 3H), 1.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 139.4, 138.9, 136.1, 135.0, 134.2, 133.0, 132.9, 132.2, 130.2, 129.9, 128.8, 128.5, 128.3, 128.25, 126.7, 126.3, 125.9, 125.5, 124.8, 122.8, 120.5, 119.7, 115.4, 112.1, 110.9, 55.1, 40.6, 37.2, 37.1, 29.1. IR (thin film): ν_{max} (cm^{-1}) = 3407, 2904, 2850, 1603, 1489, 1238, 1029, 742, 701; HRMS (ESI) calcd for $C_{41}H_{38}NO$ [M+H]$^+$: 560.2953. Found: 560.2936.



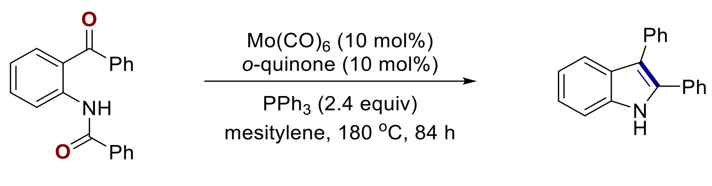
In lieu of the standard conditions, the reaction was performed with 30 mol% of $Mo(CO)_6$ and 30 mol% of *o*-quinone, PCy_3 (2.4 equiv) in mesitylene/dioxane (1/1, 1.0 mL, 0.05 mmol scale) at 180 °C. **2am**. White solid, 22.0 mg, 98% yield, mp 126.1-128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 8.19 – 8.15 (m, 1H), 7.96 – 7.94 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.48 – 7.24 (m, 8H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 2.10 – 2.07 (m, 1H), 1.94 – 1.83 (m, 1H), 1.75 – 1.72 (m, 2H), 1.59 – 1.45 (m, 2H), 1.18 – 1.01 (m, 2H), 0.98 – 0.88 (m, 7H), 0.78 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 136.0, 134.8, 132.9, 132.88, 132.5, 131.4, 130.2, 128.7, 128.67, 128.63, 128.61, 128.56, 126.5, 123.0, 120.5, 119.8, 115.8, 111.0, 75.1, 47.1, 40.9, 34.3, 31.4, 26.4, 23.5, 22.0, 20.8, 16.4. IR (thin film): ν_{max}

(cm^{-1}) = 3345, 2956, 2925, 1714, 1694, 1289, 1275, 742; HRMS (ESI) calcd for $C_{31}H_{33}NNaO_2$ [M+Na]$^+$: 474.2409. Found: 474.2408.



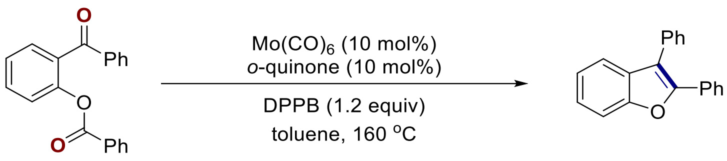
2an. White solid, 40.2 mg, 81% yield, mp 134.0-134.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.43 – 7.38 (m, 4H), 7.32 – 7.25 (m, 4H), 7.21 – 7.16 (m, 2H), 7.12 (s, 1H), 5.80 (s, 1H), 5.26 (s, 1H), 2.03 (s, 3H), 1.74 (s, 4H), 1.35 (s, 6H), 1.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 144.1, 142.2, 140.2, 138.4, 135.9, 135.1, 133.8, 132.8, 131.6, 130.2, 128.9, 128.5, 128.1, 127.9, 127.8, 126.9, 126.2, 122.7, 120.4, 119.7, 115.2, 114.9, 110.8, 35.23, 35.22, 34.0, 33.9, 31.9, 31.89, 19.9. IR (thin film): ν_{max} (cm^{-1}) = 3411, 2957, 2925, 1602, 1456, 849, 773, 701; HRMS (ESI) calcd for $C_{37}H_{38}N$ [M+H]$^+$: 496.3004. Found: 496.2984.

10. Procedure for the gram-scale reaction of substrate 1a.



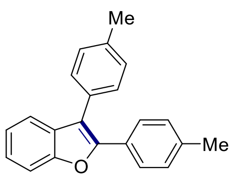
To a Young Schlenk tube (100 mL) was added $Mo(CO)_6$ (132.0 mg, 0.5 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (110.0 mg, 0.5 mmol, 10 mol%), and mesitylene (20 mL) under argon. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to rt, compound **1a** (1.51 g, 5.0 mmol, 1.0 equiv) and PPh_3 (3.15 g, 12.0 mmol, 2.4 equiv) were added to the reaction mixture under argon. The tube was sealed and the reaction mixture was stirred at 180 °C for 84 h (***Caution***: a protective shield should be installed around the Young Schlenk tube when the reaction was carried out in big scale because of the risk of explosion due to CO release). After the reaction was complete (monitored by TLC), the mixture was cooled to rt, and passed through a short pad of silica gel (DCM/EtOAc = 1:1). The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether/*tert*-butyl methyl ether = 80:1 to 40:1) to afford the compound **2a** as a white solid (1.21 g, 90% yield).

11. Representative procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction for the syntheses of benzofurans 2.

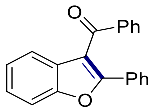


Preparation of compound 2ae. In a glovebox, $Mo(CO)_6$ (5.3 mg, 0.02 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (4.4 mg, 0.02 mmol, 10 mol%) and toluene (1.0 mL) were added to a Young Schlenk tube (10 mL) equipped with a stirring bar. The tube was sealed and transferred out of the glovebox and the mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, the tube was transferred to the glovebox and compound **1ae** (60.4 mg, 0.2 mmol, 1.0 equiv), DPPB (102.2 mg, 0.24 mmol, 1.2 equiv) and toluene (1.0 mL) were added to the reaction mixture. Then, the tube was sealed and transferred out of the glovebox and the mixture was stirred at 160 °C until the reaction was complete (monitored by TLC). The reaction mixture was cooled to rt, and concentrated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether) to give compound **2ae**[29] as a white solid (52.4 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 – 7.70 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.50 (m, 5H), 7.47 – 7.45 (m, 1H), 7.40 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 150.5, 132.8, 130.6, 130.2, 129.8, 129.0, 128.4, 128.3, 127.6, 127.0, 124.7, 122.9, 120.0, 117.5, 111.1.

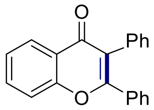
The following compounds **2af–2aj** were prepared analogously.



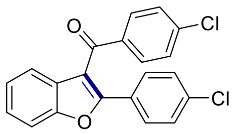
2af.[29] Colorless oil, 55.0 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.40 – 7.28 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 150.6, 138.2, 137.2, 130.4, 129.9, 129.63, 129.6, 129.1, 128.0, 126.9, 124.4, 122.7, 119.9, 116.7, 111.0, 21.3.



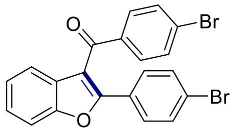
In lieu of the standard conditions, the reaction was performed with 2.4 equiv of PPh_3 instead of DPPB in toluene at 160 °C. **2ag.**[30] Yellow solid, 44.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.7 Hz, 2H), 7.72 – 7.70 (m, 2H), 7.66 – 7.55 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.24 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 157.7, 153.8, 137.8, 133.1, 129.8, 129.7, 129.4, 128.44, 128.4, 128.38, 125.3, 123.8, 121.5, 116.1, 111.2.



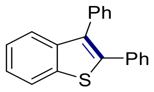
2ag'.[31] Minor isomer. Yellow solid, 7.0 mg, 11% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 7.0 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.24 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 161.5, 156.1, 133.7, 133.3, 132.8, 131.2, 130.1, 129.6, 128.3, 128.1, 127.6, 126.4, 125.1, 123.5, 123.0, 118.0.



In lieu of the standard conditions, the reaction was performed with 2.4 equiv of PPh_3 in toluene at 160 °C. **2ah**. White solid, 31.6 mg, 67% yield, mp 158.0-158.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 – 7.76 (m, 2H), 7.69 – 7.64 (m, 2H), 7.60 – 7.58 (m, 1H), 7.49 – 7.43 (m, 1H), 7.41 – 7.28 (m, 5H), 7.27 – 7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 156.3, 153.8, 139.9, 136.1, 136.0, 131.2, 129.5, 128.92, 128.85, 128.1, 127.7, 125.7, 124.1, 121.4, 116.2, 111.3. IR (thin film): ν_{max} (cm^{-1}) = 2920, 2850, 1747, 1671, 1587, 1488, 1453, 1402, 1255, 1193, 1173, 1091, 1054, 1013, 751; HRMS (ESI) calcd for $C_{21}H_{12}Cl_2O_2Na$ $[M+Na]^+$: 389.0107. Found: 389.0108.

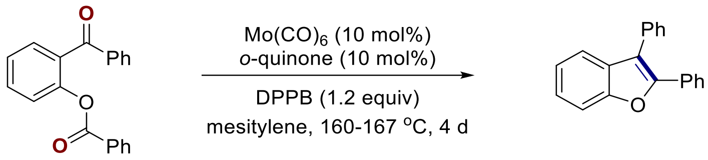


In lieu of the standard conditions, the reaction was performed with 2.4 equiv of PPh_3 in toluene at 160 °C. **2ai.**[32] White solid, 56.0 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.68 (m, 2H), 7.63 – 7.57 (m, 3H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 3H), 7.43 – 7.39 (m, 1H), 7.29 – 7.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 156.3, 153.8, 136.4, 131.9, 131.8, 131.3, 129.7, 128.7, 128.2, 128.1, 125.8, 124.5, 124.1, 121.4, 116.2, 111.4.



In lieu of the standard conditions, the reaction was performed on 0.1 mmol scale. **2aj.**[33] White solid, 21.0 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.86 (m, 1H), 7.67 – 7.57 (m, 1H), 7.46 – 7.33 (m, 9H), 7.29 – 7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 139.6, 138.9, 135.6, 134.3, 133.3, 130.5, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.4, 122.1.

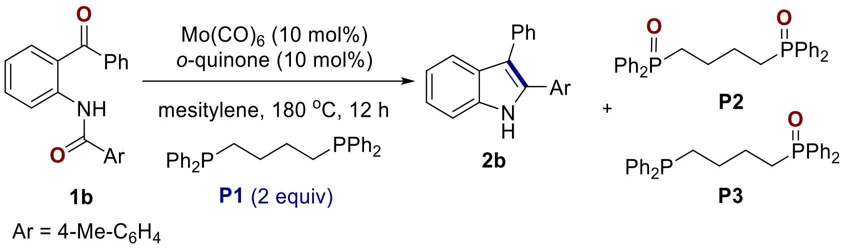
12. Procedure for the gram-scale reaction of substrate 1ae.



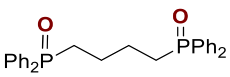
1ae **2ae**

In a glovebox, $Mo(CO)_6$ (87.1 mg, 0.33 mmol, 10 mol %), 3,5-di-*tert*-butyl-*o*-benzoquinone (72.6 mg, 0.33 mmol, 10 mol %) and mesitylene (10 mL) were added to a Young Schlenk tube (100 mL) equipped with a stirring bar. The tube was sealed and transferred out of the glovebox and the mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, the tube was transferred to the glovebox and compound **1ae** (1.0 g, 3.31 mmol, 1.0 equiv), DPPB (1.7 g, 3.98 mmol, 1.2 equiv) and mesitylene (15 mL) were added to the reaction mixture. Then, the tube was sealed and transferred out of the glovebox and the mixture was stirred at 160 °C for 2 days and at 167 °C for another 2 days (***Caution***: a protective shield should be installed around the Young Schlenk tube when the reaction was carried out in big scale because of the risk of explosion due to CO release). Then the reaction mixture was cooled to rt, and concentrated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether) to give compound **2ae** as a white solid (831 mg, 93% yield).

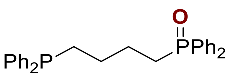
13. Procedure for the syntheses of compounds 2b, P2 and P3.



To an oven-dried Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (2.7 mg, 0.01 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (2.2 mg, 0.01 mmol, 10 mol%), and mesitylene (0.5 mL) under argon. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **1b** (31.5 mg, 0.1 mmol, 1.0 equiv) and DPPB (85.3 mg, 0.2 mmol, 2.0 equiv) were added to the reaction mixture under argon. The tube was sealed and the reaction mixture was stirred at 180 °C for 12 h. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, and concentrated under reduced pressure to give the crude residue, which was purified by flash column chromatography on silica gel (petroleum ether/*tert*-butyl methyl ether = 60:1 to 40:1) to afford the title compounds **2b** as a colorless oil (26.1 mg, 92% yield). Diphosphine monoxide **P3** was obtained as a white solid (26.5 mg, 60% yield) when the eluent was switched to petroleum ether/ethyl acetate = 1:1. Diphosphine oxide **P2** was obtained as a white solid (28.0 mg, 61% yield) when the eluent was switched to petroleum ether/ethyl acetate/methanol = 2:2:1.

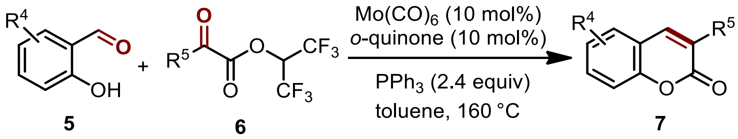


P2.[34] White solid, 28.0 mg, 61% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.62 (m, 8H), 7.51 – 7.34 (m, 12H), 2.35 – 2.14 (m, 4H), 1.78 – 1.60 (m, 4H). ^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.9.

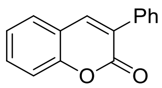


P3.[35] White solid, 26.5 mg, 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.18 (m, 20H), 2.28 – 2.18 (m, 2H), 2.06 – 1.97 (m, 2H), 1.78 – 1.66 (m, 2H), 1.58 – 1.46 (m, 2H). ^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.7, –16.8.

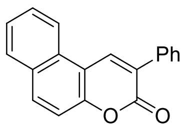
14. Representative procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction for the syntheses of coumarin derivatives 7.



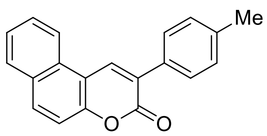
To a Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (5.3 mg, 0.02 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (4.4 mg, 0.02 mmol, 10 mol%), and toluene (1.0 mL) under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **5** (0.2 mmol, 1.0 equiv), compound **6** (0.3 mmol, 1.5 equiv), and PPh_3 (125.9 mg, 0.48 mmol, 2.4 equiv) were added to the reaction mixture under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 160 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt. The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel to afford the coumarin derivatives **7**.



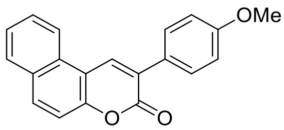
7a.[36] White solid, 31.2 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.73 – 7.68 (m, 2H), 7.57 – 7.50 (m, 2H), 7.48 – 7.38 (m, 3H), 7.38 – 7.35 (m, 1H), 7.30 (td, *J* = 7.5, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 153.5, 139.8, 134.7, 131.4, 128.8, 128.5, 128.44, 128.36, 127.9, 124.5, 119.7, 116.4.



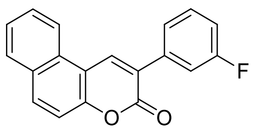
7b.[36] White solid, 47.9 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.69 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.54 – 7.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 153.2, 135.7, 135.1, 132.7, 130.4, 129.14, 129.10, 128.9, 128.59, 128.55, 128.2, 127.3, 126.0, 121.4, 116.7, 113.8.



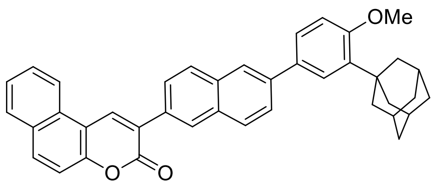
7c.[37] Yellow solid, 54.4 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.63 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 152.9, 138.8, 134.9, 132.4, 132.1, 130.2, 129.2, 129.0, 128.4, 128.0, 127.0, 125.9, 121.4, 116.6, 113.7, 21.3.



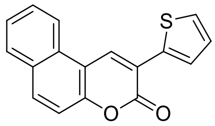
7d.[37] Yellow solid, 58.6 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.65 (td, *J* = 8.2, 1.1 Hz, 1H), 7.55 – 6.52 (m, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.03 – 6.95 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 160.1, 152.6, 134.1, 132.1, 130.2, 129.8, 128.9, 128.0, 127.3, 126.6, 125.9, 121.3, 116.5, 113.9, 113.7, 55.3.



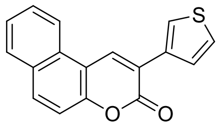
7e. Yellow solid, 36.0 mg, 62% yield, mp 174.8-176.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.70 (td, *J* = 8.2, 1.1 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.52 – 7.40 (m, 2H), 7.13 (td, *J* = 8.4, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 246.0 Hz), 160.2, 153.3, 137.0 (d, *J* = 8.2 Hz), 136.1, 133.1, 130.0 (d, *J* = 8.4 Hz), 130.0, 129.1, 129.0, 128.3, 126.1, 125.8 (d, *J* = 1.9 Hz), 124.2 (d, *J* = 2.7 Hz), 121.3, 116.6, 115.73 (d, *J* = 21.1 Hz), 115.7 (d, *J* = 23.0 Hz), 113.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -113.4. IR (thin film): ν_{max} (cm^{-1}) = 2928, 1724, 1581, 1444, 1267, 1072, 746; HRMS (ESI) calcd for $C_{19}H_{11}FNaO_2$ $[M+Na]^+$: 313.0635. Found: 313.0635.



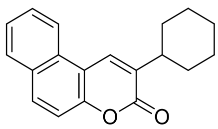
7f. Yellow solid, 100.2 mg, 89% yield, mp 206.0-207.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.38 – 8.23 (m, 2H), 8.02 – 7.84 (m, 6H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.64 (s, 1H), 7.60 – 7.51 (m, 2H), 7.45 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H), 2.24 (s, 6H), 2.15 (s, 3H), 1.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 158.6, 153.0, 139.6, 138.8, 135.5, 133.6, 132.7, 132.5, 131.9, 130.2, 129.0, 128.99, 128.8, 128.12, 128.1, 127.8, 126.8, 126.1, 126.0, 125.9, 125.7, 125.5, 124.5, 121.5, 116.5, 113.8, 112.1, 55.1, 40.6, 37.2, 37.1, 29.1. IR (thin film): ν_{max} (cm^{-1}) = 2903, 2848, 1724, 1569, 1493, 1463, 1237, 1101, 1029, 811, 734; HRMS (ESI) calcd for $C_{40}H_{34}NaO_3$ [M+Na]$^+$: 585.2400. Found: 585.2395.



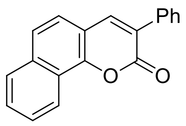
7g.[37] Pale yellow solid, 39.7 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.72 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.18 (dd, *J* = 5.1, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 152.3, 136.5, 132.5, 131.3, 130.4, 129.1, 128.9, 128.2, 127.7, 127.1, 126.1, 121.4, 120.8, 116.6, 113.6.



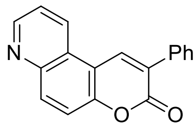
7h. Yellow solid, 45.6 mg, 82% yield, mp 207.0-208.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.33 – 8.16 (m, 2H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.62 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 – 7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 152.4, 134.8, 132.9, 132.4, 130.3, 129.1, 128.9, 128.1, 126.2, 126.0, 125.8, 121.6, 121.3, 116.6, 113.5. IR (thin film): ν_{max} (cm^{-1}) = 2926, 1717, 1465, 1273, 1124, 1072, 798, 744; HRMS (ESI) calcd for $C_{17}H_{10}NaO_2S$ [M+Na]$^+$: 301.0294. Found: 301.0291.



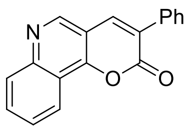
7i.[38] Yellow solid, 23.4 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 7.91 (d, *J* = 6.7 Hz, 1H), 7.89 (d, *J* = 5.3 Hz, 1H), 7.67 (td, *J* = 8.2, 1.1 Hz, 1H), 7.55 (td, *J* = 7.8, 0.7 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 2.94 – 2.82 (m, 1H), 2.06 (d, *J* = 11.1 Hz, 2H), 1.92 – 1.80 (m, 3H), 1.53 – 1.38 (m, 4H), 1.37 – 1.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 152.0, 134.0, 131.9, 131.6, 130.3, 128.9, 127.8, 125.7, 121.4, 116.7, 113.5, 38.6, 32.2, 26.5, 26.2.



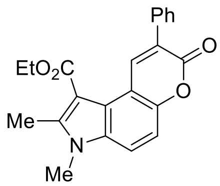
7j.[39] White solid, 46.6 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 – 8.57 (m, 1H), 7.95 (s, 1H), 7.92 – 7.85 (m, 1H), 7.81 – 7.75 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 150.6, 140.5, 134.8, 134.6, 128.8, 128.53, 128.49, 128.4, 127.8, 127.6, 127.2, 124.5, 123.7, 122.9, 122.3, 115.1.



7k. Pale yellow solid, 48.4 mg, 89% yield, mp 200.3-202.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 8.24 (d, *J* = 9.3 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.59 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.52 – 7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 152.8, 150.0, 145.5, 134.6, 134.5, 133.9, 129.7, 129.1, 128.6, 128.5, 128.1, 124.3, 122.5, 120.2, 113.5. IR (thin film): ν_{max} (cm^{-1}) = 2927, 1728, 1601, 1468, 1282, 830, 812, 745, 702; HRMS (ESI) calcd for $C_{18}H_{11}NNaO_2$ $[M+Na]^+$: 296.0682. Found: 296.0685.

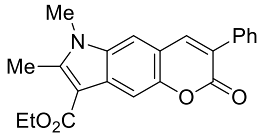


7l.[40] Pale yellow solid, 25.4 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 155.9, 149.0, 148.9, 137.6, 134.1, 131.7, 129.5, 129.3, 128.7, 128.6, 128.4, 127.8, 122.0, 117.6, 111.4.

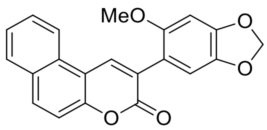


7m. Pale yellow solid, 58.1 mg, 80% yield, mp 177.4-178.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (s, 1H), 7.87 – 7.80 (m, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 2.67 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100

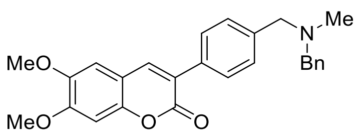
MHz, $CDCl_3$): δ = 165.6, 160.8, 151.1, 145.6, 140.8, 135.7, 133.0, 128.5, 128.3, 128.1, 124.8, 122.1, 112.7, 112.3, 111.4, 106.3, 60.3, 30.1, 14.4, 13.1. IR (thin film): ν_{max} (cm^{-1}) = 3087, 2932, 1709, 1588, 1440, 1376, 1287, 1184, 1149, 1098, 960, 787, 704, 619; HRMS (ESI) calcd for $C_{22}H_{19}NNaO_4$ $[M+Na]^+$: 384.1206. Found: 384.1200.



7n. Pale yellow solid, 44.8 mg, 62% yield, mp 215.9-217.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.78 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.26 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.75 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 161.2, 149.6, 149.1, 140.5, 135.0, 133.8, 129.2, 128.3, 125.6, 115.0, 107.6, 107.1, 104.4, 59.7, 29.9, 14.5, 12.1. IR (thin film): ν_{max} (cm^{-1}) = 2929, 1715, 1630, 1467, 1418, 1178, 1094, 967, 784, 695; HRMS (ESI) calcd for $C_{22}H_{19}NNaO_4$ $[M+Na]^+$: 384.1206. Found: 384.1208.



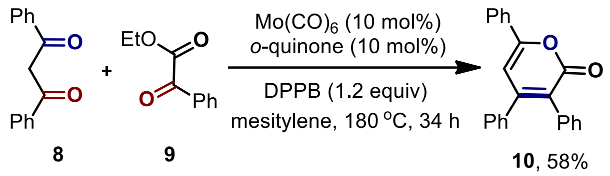
7o. Pale yellow solid, 39.5 mg, 57% yield, mp 190.9-192.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 6.97 (s, 1H), 6.66 (s, 1H), 5.98 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 153.1, 153.0, 148.9, 141.3, 137.7, 132.3, 130.3, 129.1, 128.9, 128.0, 125.8, 125.0, 121.5, 116.8, 116.3, 113.6, 110.3, 101.5, 95.5, 56.9. IR (thin film): ν_{max} (cm^{-1}) = 2933, 2787, 1718, 1617, 1572, 1508, 1452, 1386, 1282, 1236, 1199, 1150, 1009, 737, 700; HRMS (ESI) calcd for $C_{21}H_{14}NaO_5$ $[M+Na]^+$: 369.0733. Found: 369.0729.



7p.[41] Viscous yellow oil, 64.5 mg, 78% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.69 – 7.64 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 6.91 (s, 1H), 6.87 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.57 (s, 2H), 3.56 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 152.6, 149.4, 146.4, 139.7, 139.6, 139.1, 133.7, 128.9, 128.2, 127.0, 125.0, 112.3, 107.9, 99.6, 61.8, 61.4, 56.4, 56.3, 42.2. IR (thin film): ν_{max} (cm^{-1}) =

2918, 1714, 1578, 1491, 1439, 1370, 1266, 1195, 1042, 1012, 928, 814, 736; HRMS (ESI) calcd for $C_{26}H_{25}NNaO_4$ $[M+Na]^+$: 438.1676. Found: 438.1673.

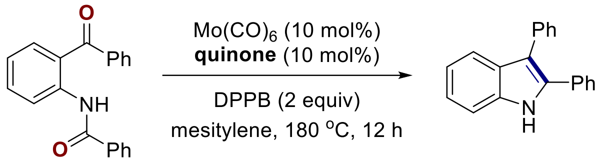
15. Procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction for the synthesis of 2-pyrone 10.



To a Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (5.3 mg, 0.02 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (4.4 mg, 0.02 mmol, 10 mol%), and mesitylene (1.0 mL) under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **8** (44.8 mg, 0.2 mmol, 1.0 equiv), compound **9** (53.4 mg, 0.3 mmol, 1.5 equiv) and DPPB (102.4 mg, 0.24 mmol, 1.2 equiv) were added to the reaction mixture under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 180 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, and passed through a short pad of silica gel (DCM/EtOAc = 1:1). The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 60:1 to 30:1) to afford the title compound **10**[42] as a yellow solid (37.6 mg, 58% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.88 (m, 2H), 7.55 – 7.45 (m, 3H), 7.34 – 7.16 (m, 10H), 6.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 158.2, 152.6, 137.7, 133.7, 131.3, 130.8, 130.7, 128.9, 128.64, 128.6, 128.3, 127.9, 127.6, 125.5, 123.0, 104.9. IR (thin film): ν_{max} (cm^{-1}) = 2922, 2852, 1708, 1627, 1532, 1449, 1350, 766, 701; HRMS (ESI) calcd for $C_{23}H_{16}NaO_2$ $[M+Na]^+$: 347.1043. Found: 347.1067.

II. Investigation of other quinones and transition-metal carbonyl complexes.

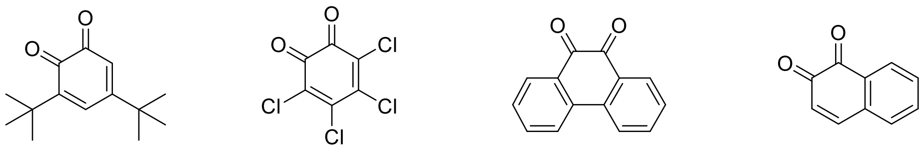
Table S1. Investigation of other quinones.[a]



1a **2a**

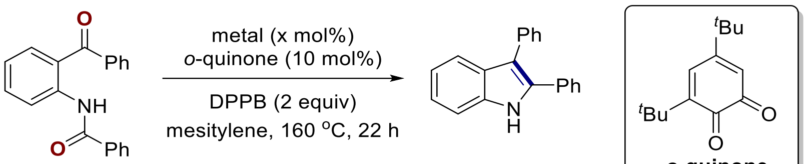
entry	quinone	yield[b] (%)	conv.[b] (%)
1	***o*-quinone**	>95	>95
2	**Q1**	trace	22
3	**Q2**	54	57
4	**Q3**	15	16

[a] Reaction conditions: the reaction was performed with $Mo(CO)_6$/quinone, DPPB (2 equiv) on 0.1 mmol scale in mesitylene (0.5 mL) at 180 °C. [b] Yield and conversion were determined by ^1H NMR using CH_2Br_2 as internal standard.



o-quinone **Q1** **Q2** **Q3**

Table S2. Investigation of other transition-metal carbonyl complexes.[a]



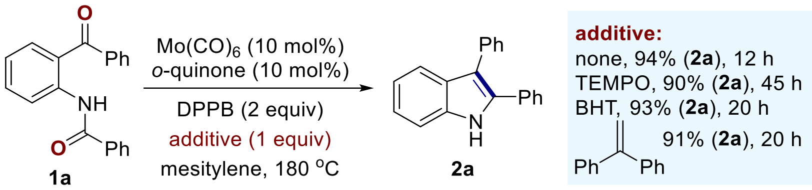
1a **2a**

entry	metal	x (mol%)	yield[b] (%)
1	$Cr(CO)_6$	10	n.r.[c]
2	$W(CO)_6$	10	n.r.[c]
3	$Fe_2(CO)_9$	5	n.r.[c]
4	$Ru_3(CO)_{12}$	3.3	n.r.[c]
5	$Mn_2(CO)_{12}$	5	n.r.[c]

[a] Reaction conditions: the reaction was performed with metal/*o*-quinone, DPPB (2 equiv) on 0.1 mmol scale in mesitylene (0.5 mL) at 160 °C. [b] Yield was determined by ^1H NMR using CH_2Br_2 as internal standard. [c] No reaction.

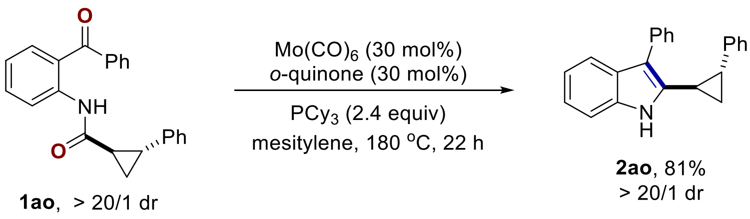
III. Mechanistic studies.

1. General procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction of compound 1a in the presence of radical scavengers.



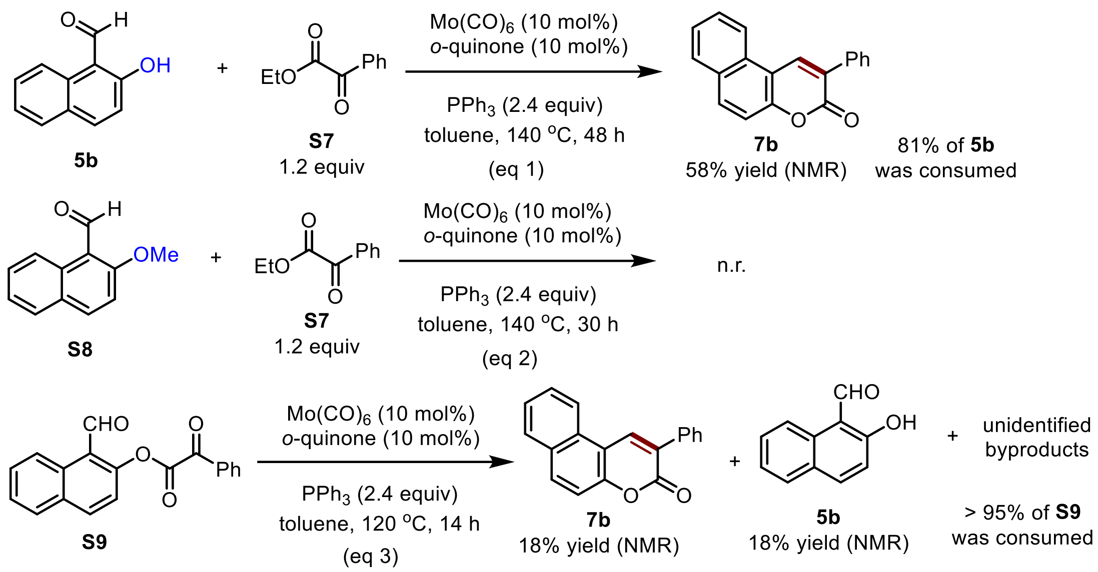
To a Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (2.7 mg, 0.01 mmol, 10 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (2.2 mg, 0.01 mmol, 10 mol%), and mesitylene (0.5 mL) under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **1a** (30.1 mg, 0.1 mmol, 1.0 equiv), the corresponding additive (0.1 mmol, 1.0 equiv) and DPPB (85.3 mg, 0.2 mmol, 2.0 equiv) were added to the reaction mixture under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 180 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, and passed through a short pad of silica gel (DCM/EtOAc = 1:1). The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether/*tert*-butyl methyl ether = 80:1 to 40:1) to afford the title compound **2a** as a white solid.

2. Procedure for the Mo-catalyzed carbonyl-carbonyl olefination reaction of compound 1ao.

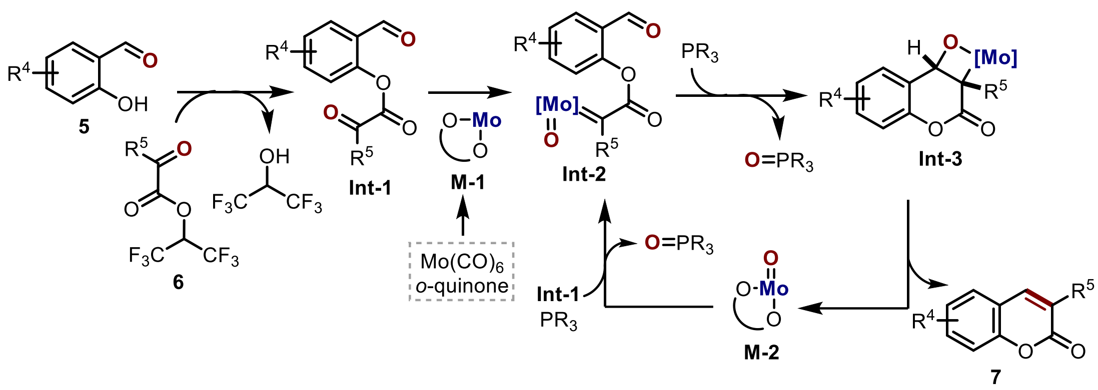


To a Young Schlenk tube (10 mL) were added $Mo(CO)_6$ (7.9 mg, 0.03 mmol, 30 mol%), 3,5-di-*tert*-butyl-*o*-benzoquinone (6.6 mg, 0.03 mmol, 30 mol%), and mesitylene (2.0 mL) under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 160 °C for 15 min. After cooling to ambient temperature, compound **1ao** (34.1 mg, 0.1 mmol, 1.0 equiv), PCy_3 (67.3 mg, 0.24 mmol, 2.4 equiv) were added to the reaction mixture under N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 180 °C. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to rt, and passed through a short pad of silica gel (DCM/EtOAc = 1:1). The solvents were evaporated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate= 80:1 to 30:1) to afford the title compound **2ao** as a white solid (25.1 mg, 81% yield, mp 114.9-115.5 °C). The relative configuration of product **2ao** was determined by 2D-NMR analysis. For details, see the NMR spectra in Page S-228 to S-235. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.31 – 7.25 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 2.58 – 2.50 (m, 1H), 2.28 (dt, *J* = 9.1, 5.5 Hz, 1H), 1.50 (dt, *J* = 8.9, 5.6 Hz, 1H), 1.44 (dt, *J* = 8.9, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 135.0, 134.9, 134.87, 129.6, 128.4, 128.37, 127.9, 126.0, 125.8, 125.77, 121.9, 120.2, 118.9, 115.5, 110.5, 26.0, 20.3, 16.7. IR (thin film): ν_{max} (cm^{-1}) = 3419, 2925, 1603, 1460, 1075, 772, 697; HRMS (ESI) calcd for $C_{23}H_{20}N$ $[M+H]^+$: 310.1590. Found: 310.1587.

IV. A proposed reaction pathway for the formation of coumarins.



Preliminary mechanistic experiments were performed to gain some insights to the reaction mechanism of the coumarin forming reaction. First, the the reaction of ethyl 2-oxo-2-phenylacetate **S7** with O−methyl protected substrate **S8** was performed to probe whether the transesterification or carbonyl-carbonyl olefination occurred first (eq 2). Under the Mo-catalytic conditions, no reaction was occurred while 58% yield of product **7b** could be detected when the 2-hydroxy-1-naphthaldehyde **5b** was used as the substrate (eq 1). In contrast, reaction of transesterification product **S9** which was considered as one of the possible reaction intermediates, proceeded and afforded product **3g** in 18% yield (eq 3). The low yield of this reaction might be due to the low stability of substrate **S9** under the reaction conditions. These experimental results suggested that the coumarin forming reaction might be initiated via the transesterification and followed by the intramolecular carbonyl-carbonyl olefination. Accordingly, a possible reaction pathway was proposed (Scheme S1).



Scheme S1. Plausible reaction mechanism.

V. References.

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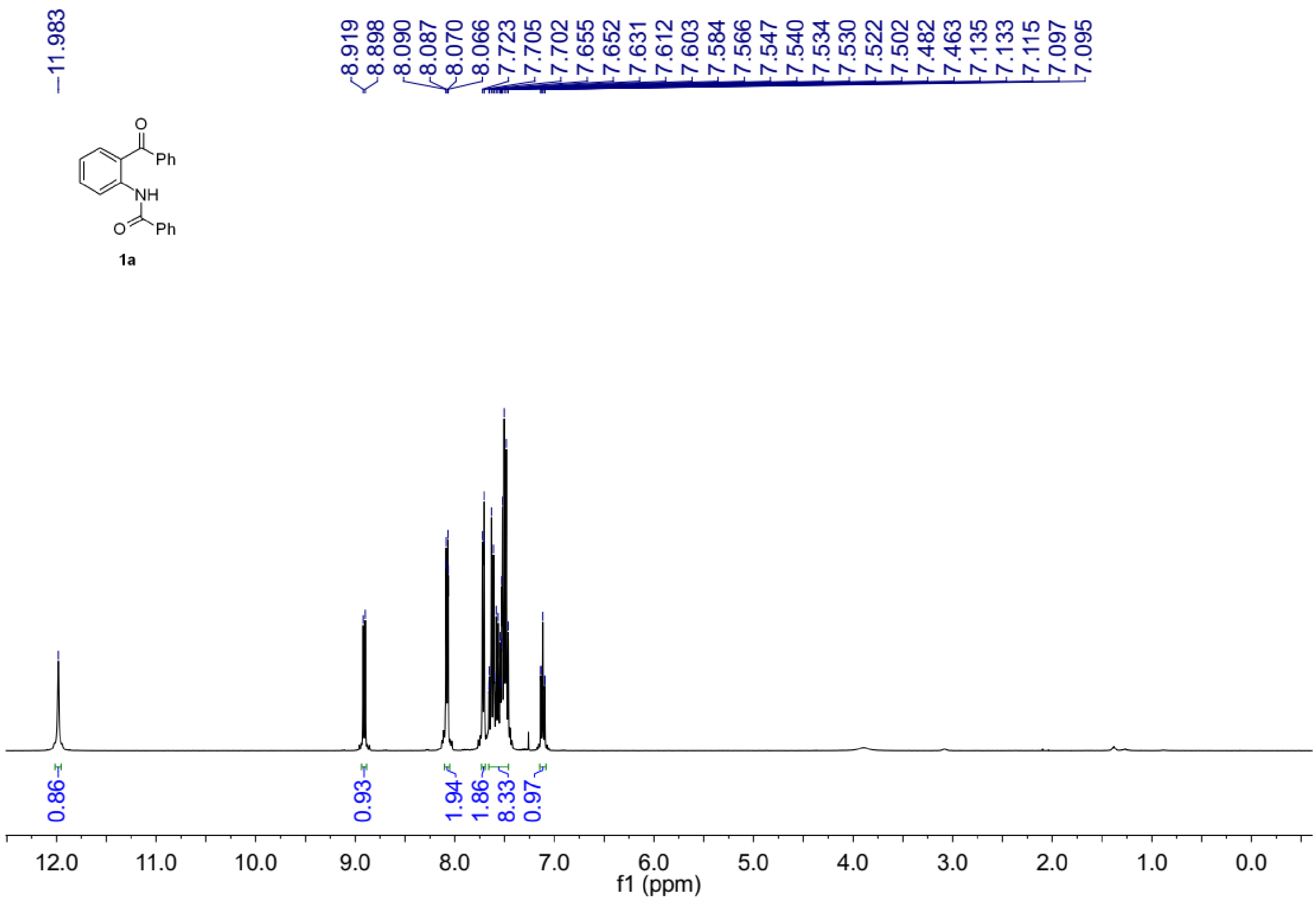
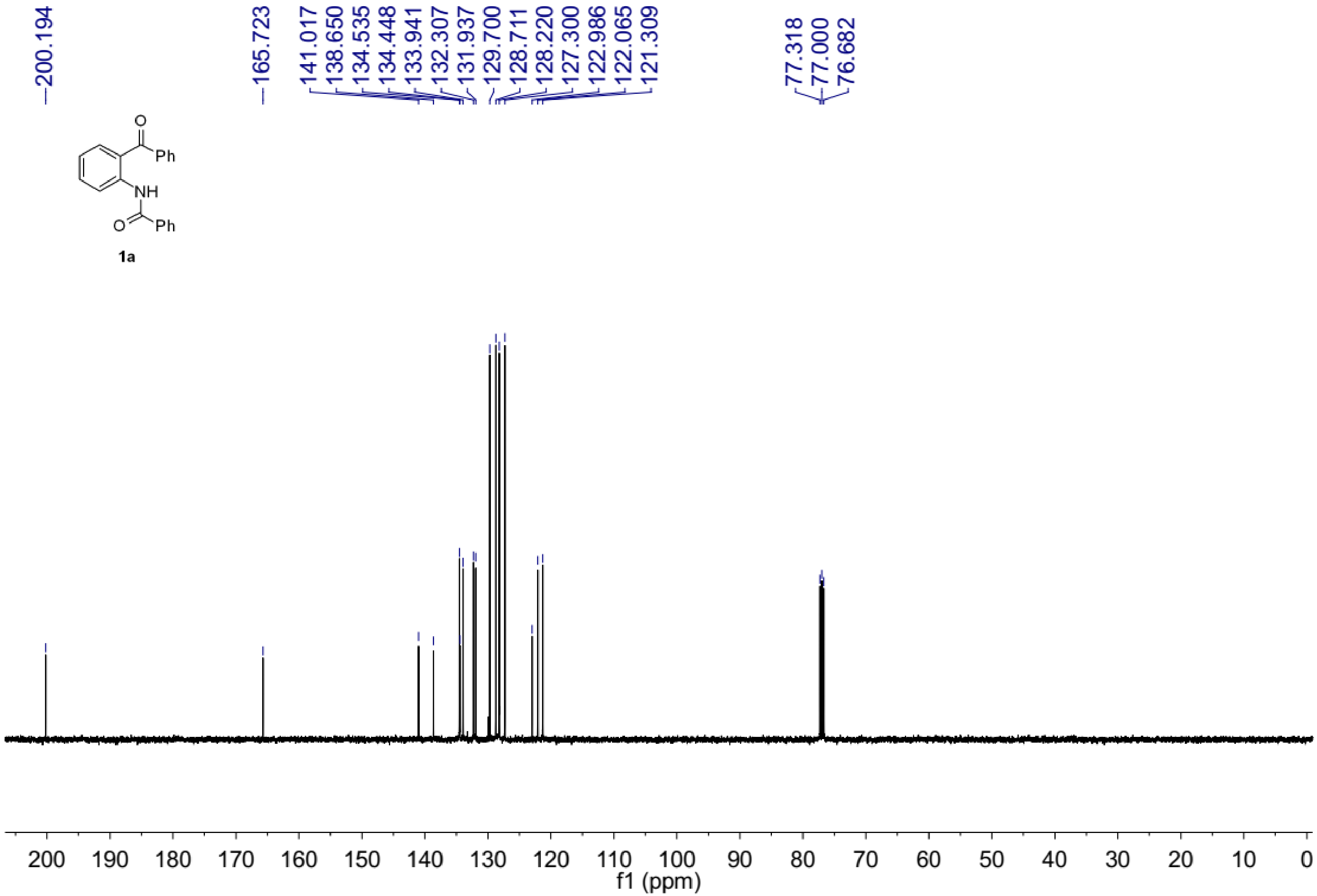
VI. Copies of NMR spectra.





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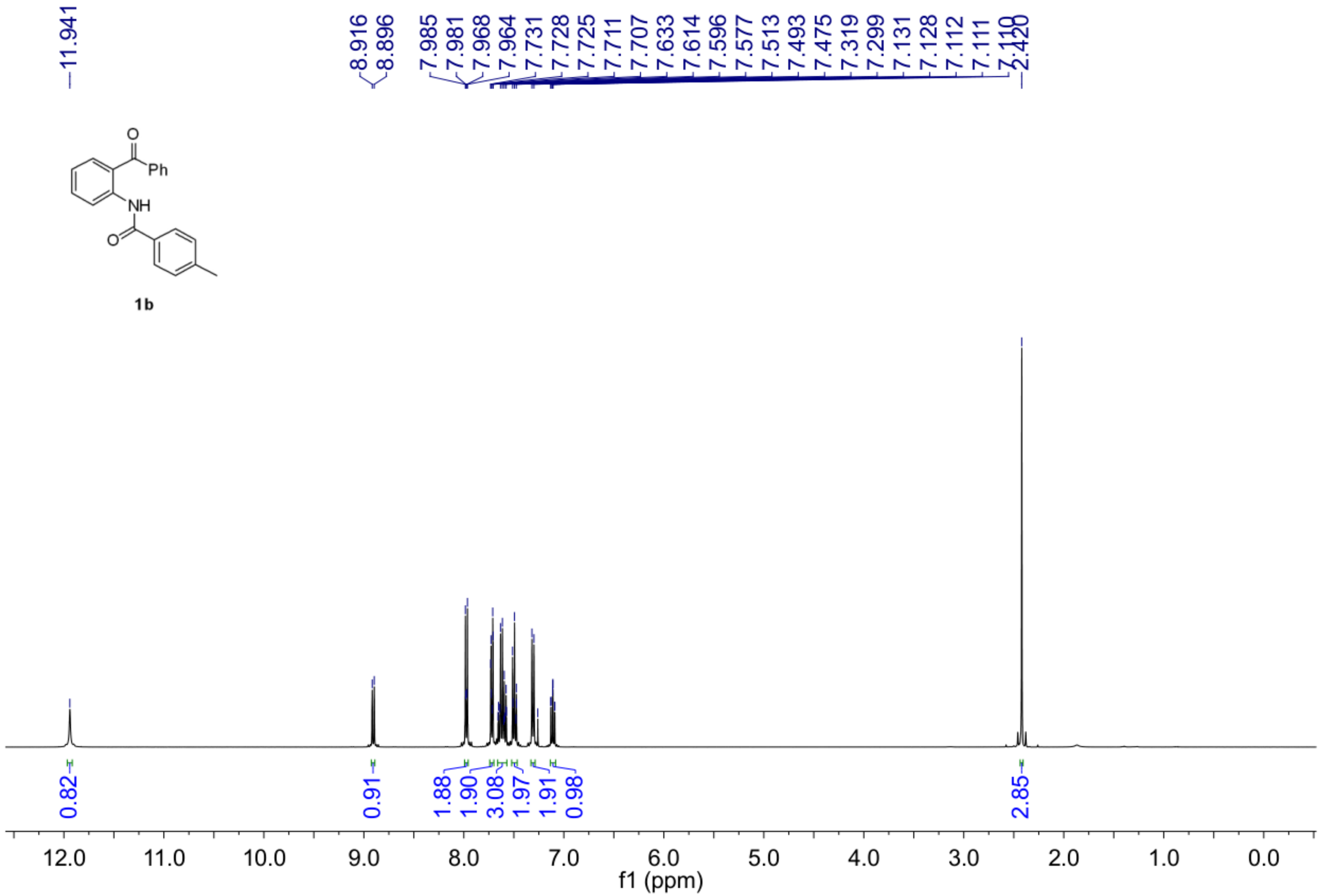
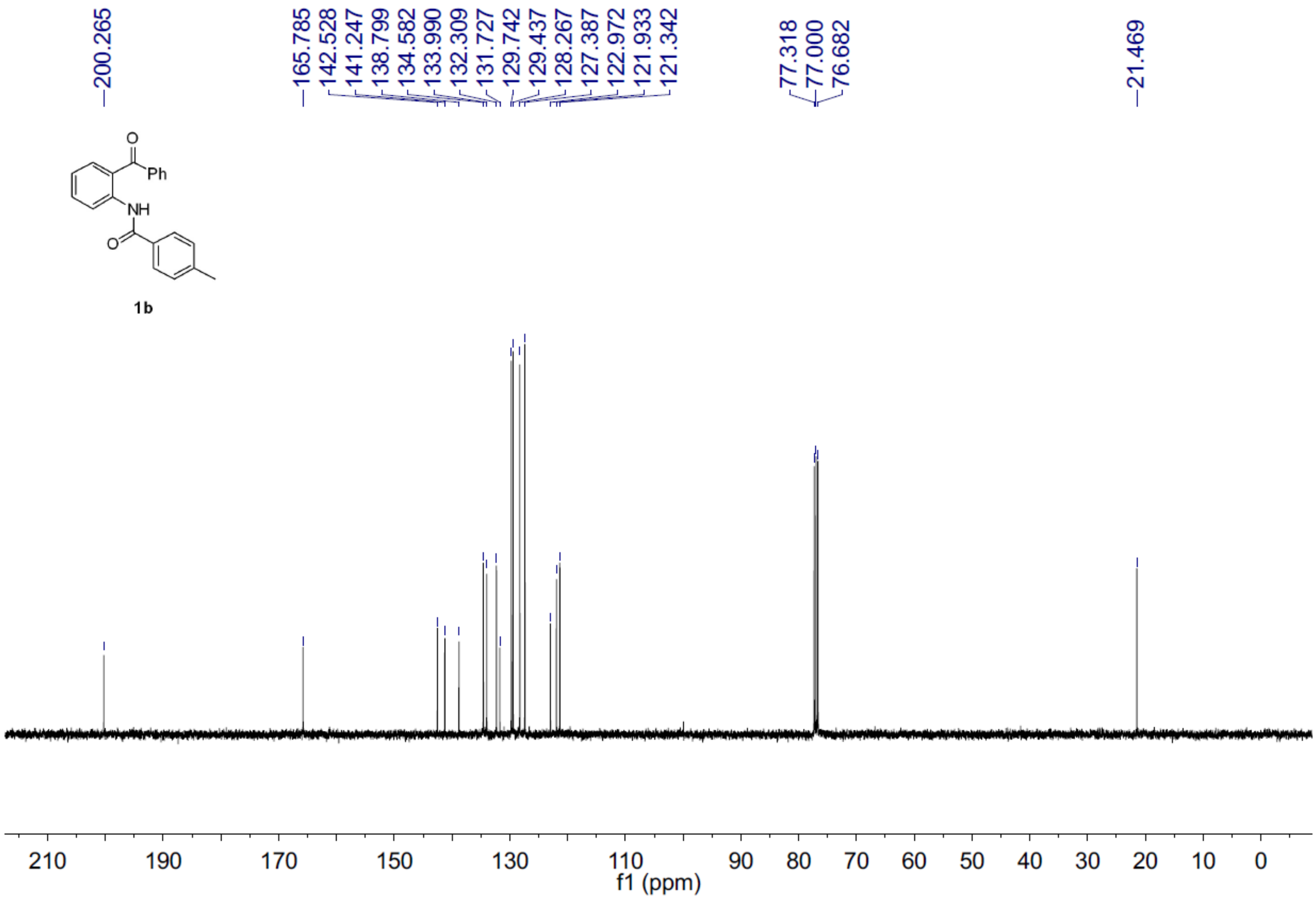
f1 (ppm)

1a

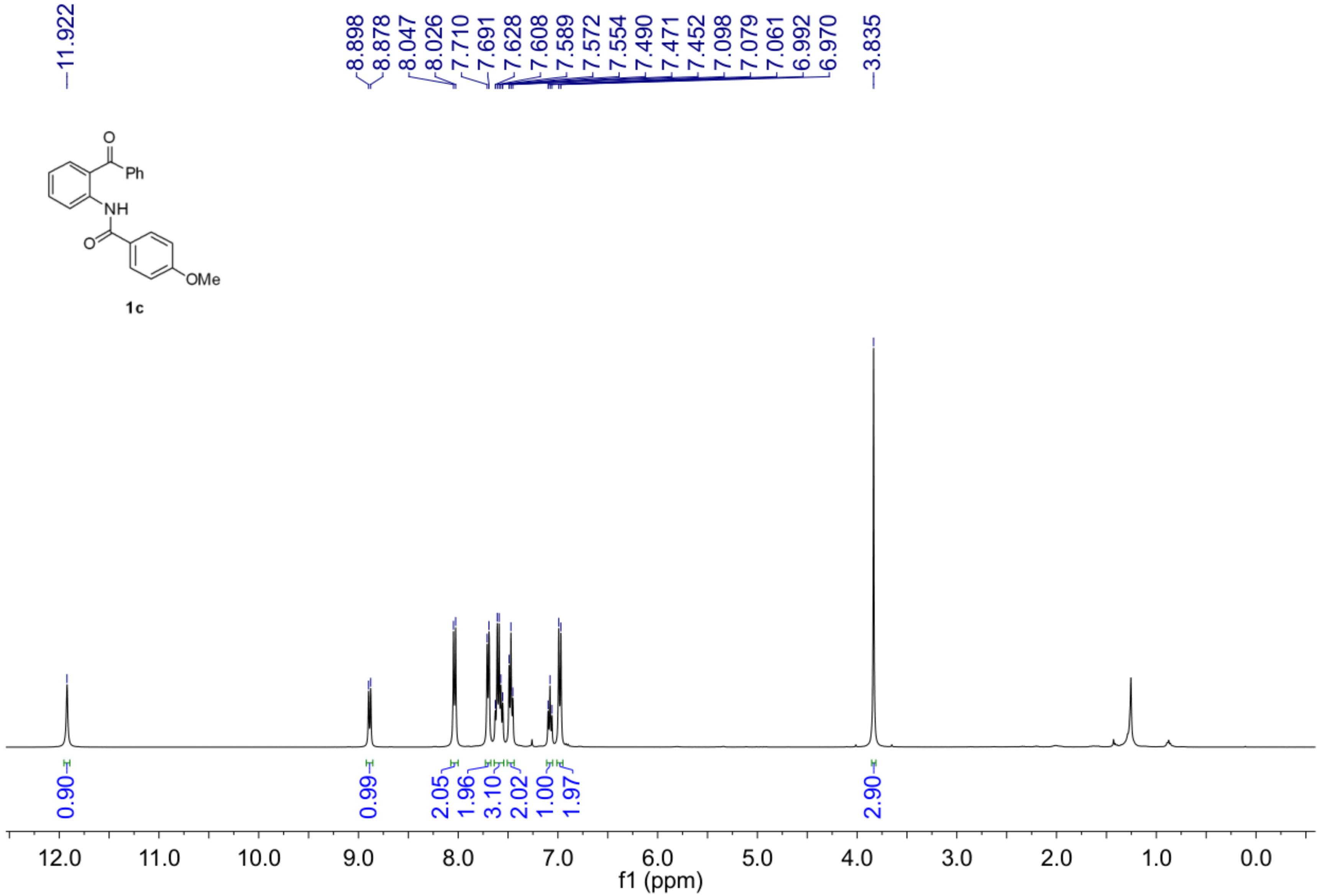


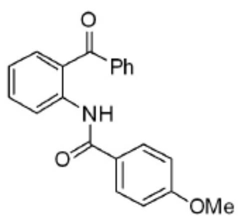
1b
11.941
8.916
8.896
7.985
7.981
7.968
7.964
7.731
7.728
7.725
7.711
7.707
7.633
7.614
7.596
7.577
7.513
7.493
7.475
7.319
7.299
7.131
7.128
7.112
7.111
7.110
2.420
0.82
0.91
1.88
1.90
3.08
1.97
1.91
0.98
2.85
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



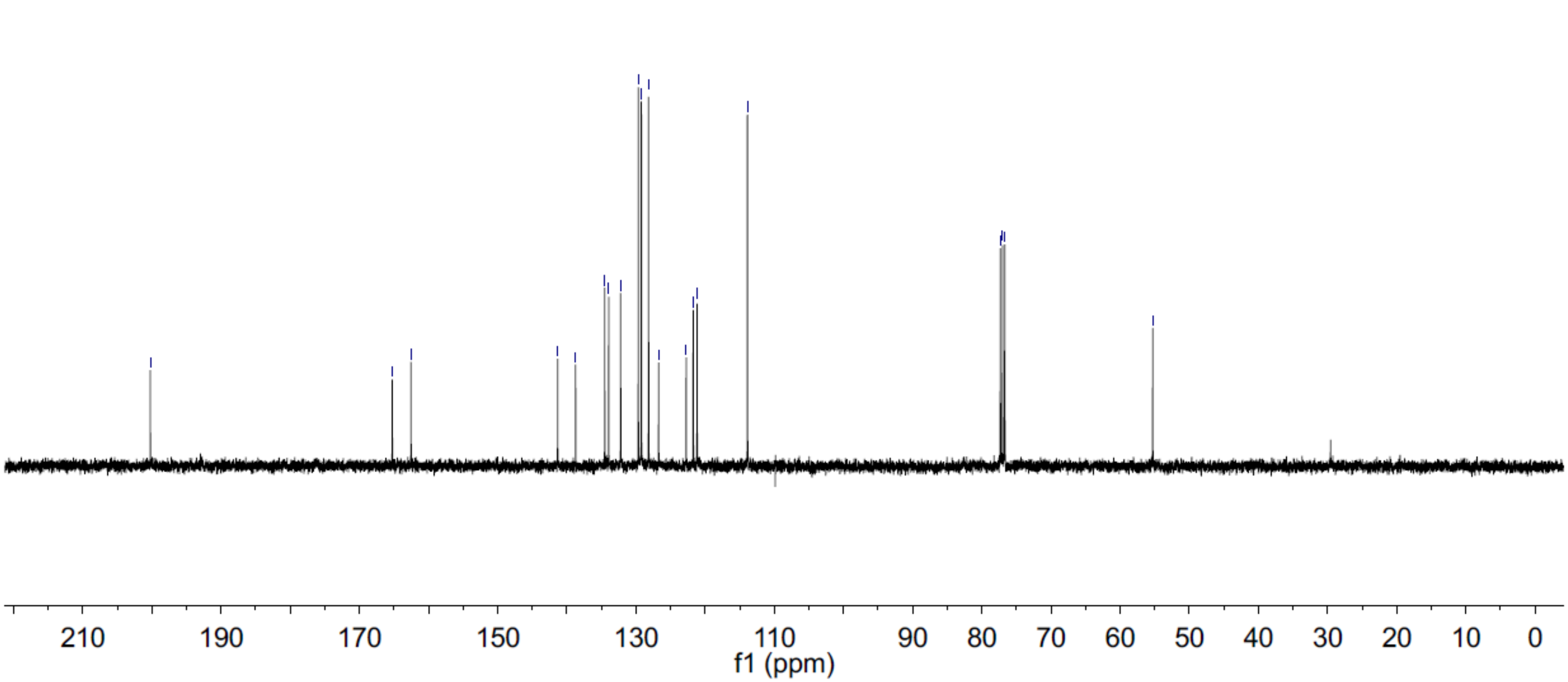
200.265
165.785
142.528
141.247
138.799
134.582
133.990
132.309
131.727
129.742
129.437
128.267
127.387
122.972
121.933
121.342
77.318
77.000
76.682
21.469
Ph
NH
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

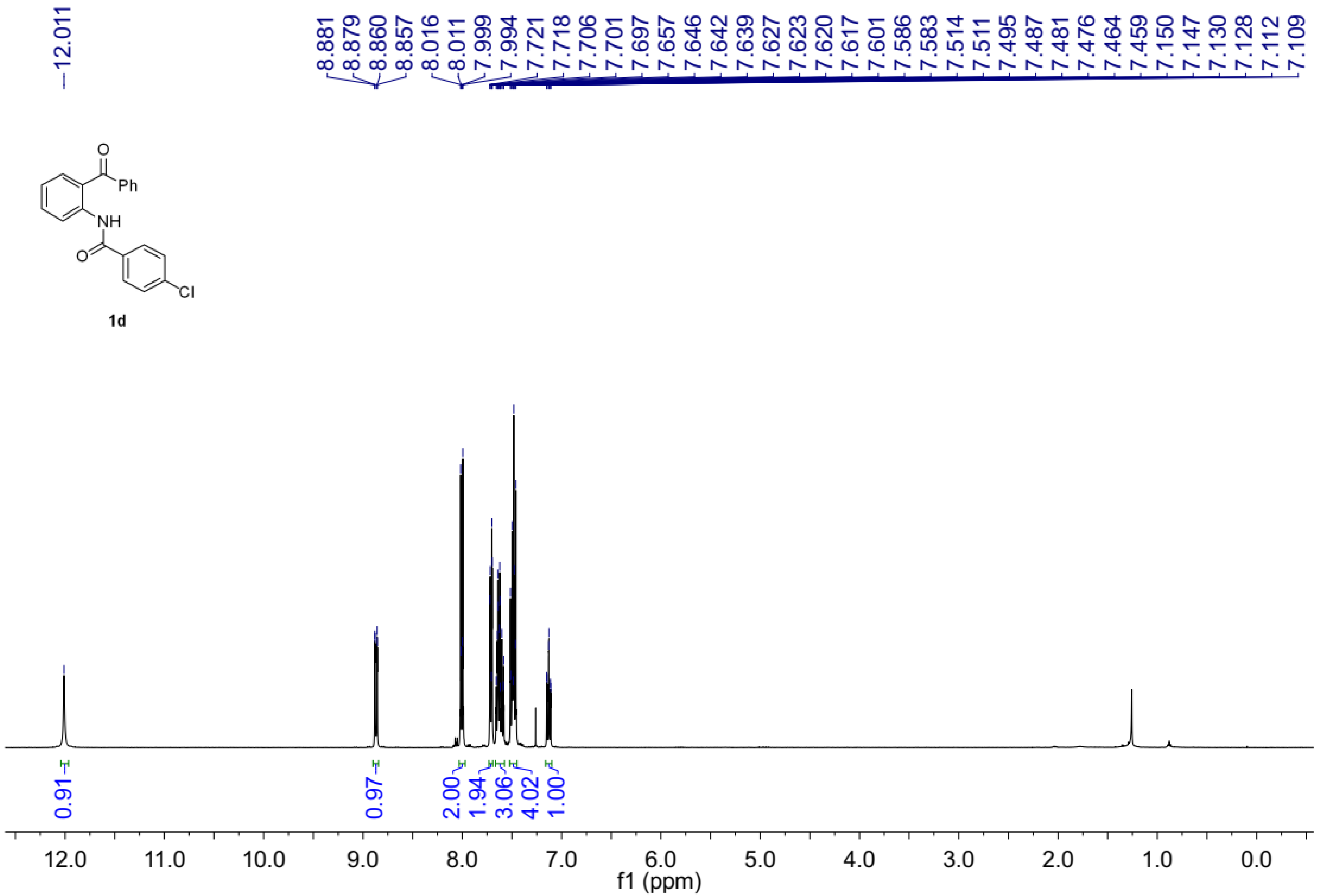
1b


O
Ph
NH
O
OMe
1c
11.922
8.898
8.878
8.047
8.026
7.710
7.691
7.628
7.608
7.589
7.572
7.554
7.490
7.471
7.452
7.098
7.079
7.061
6.992
6.970
3.835
0.90
0.99
2.05
1.96
3.10
2.02
1.00
1.97
2.90
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

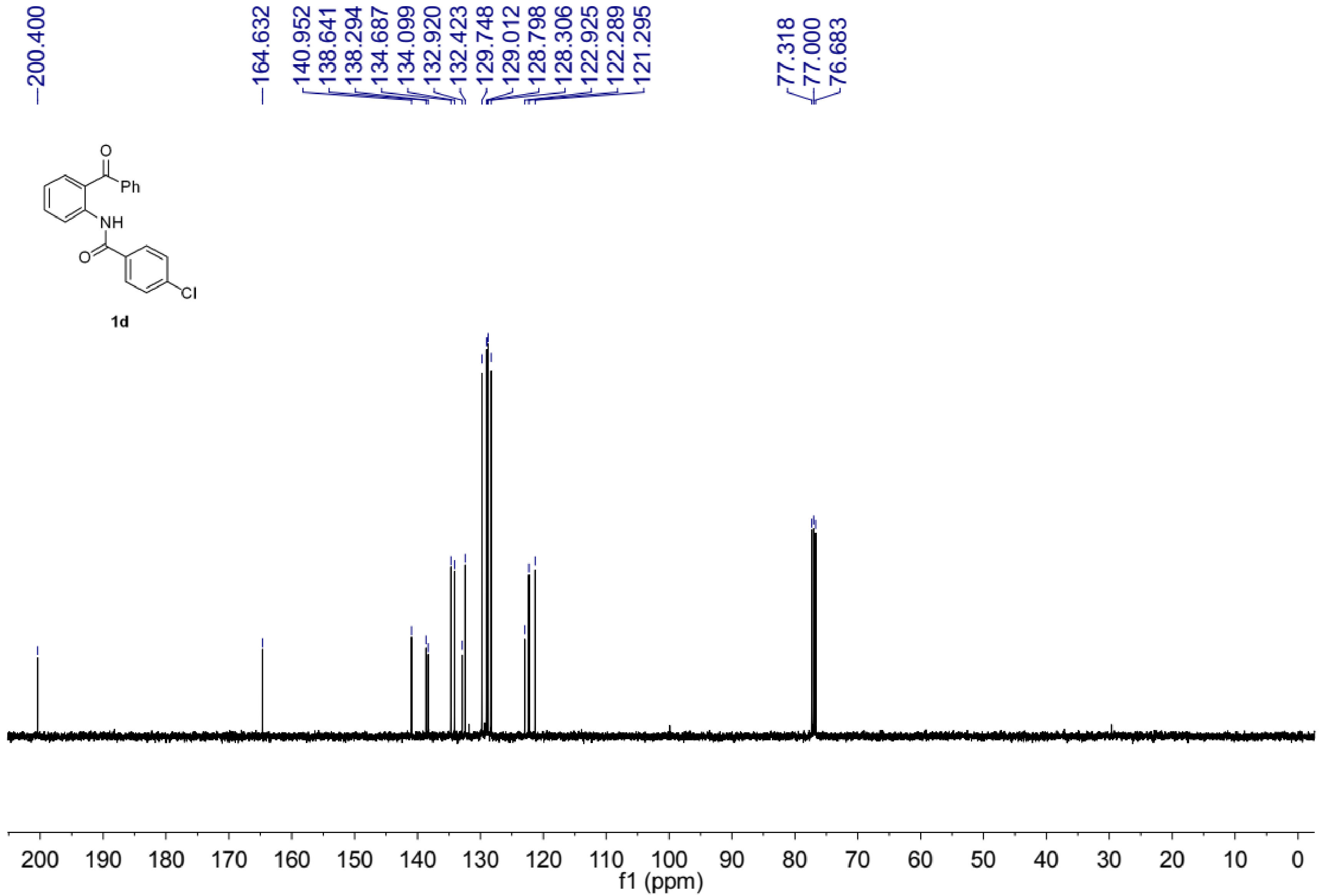

O
Ph
NH
O
OMe

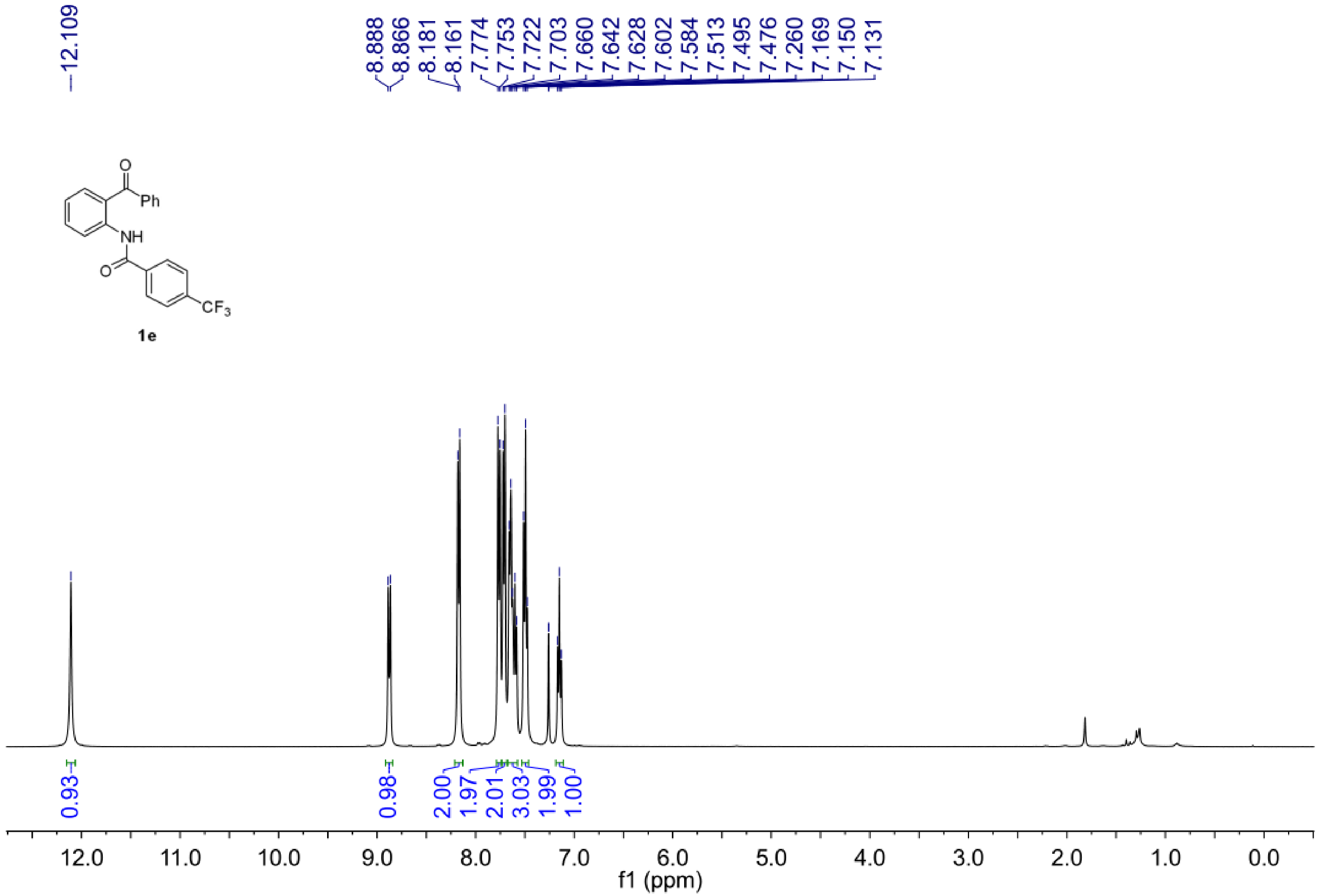
1c

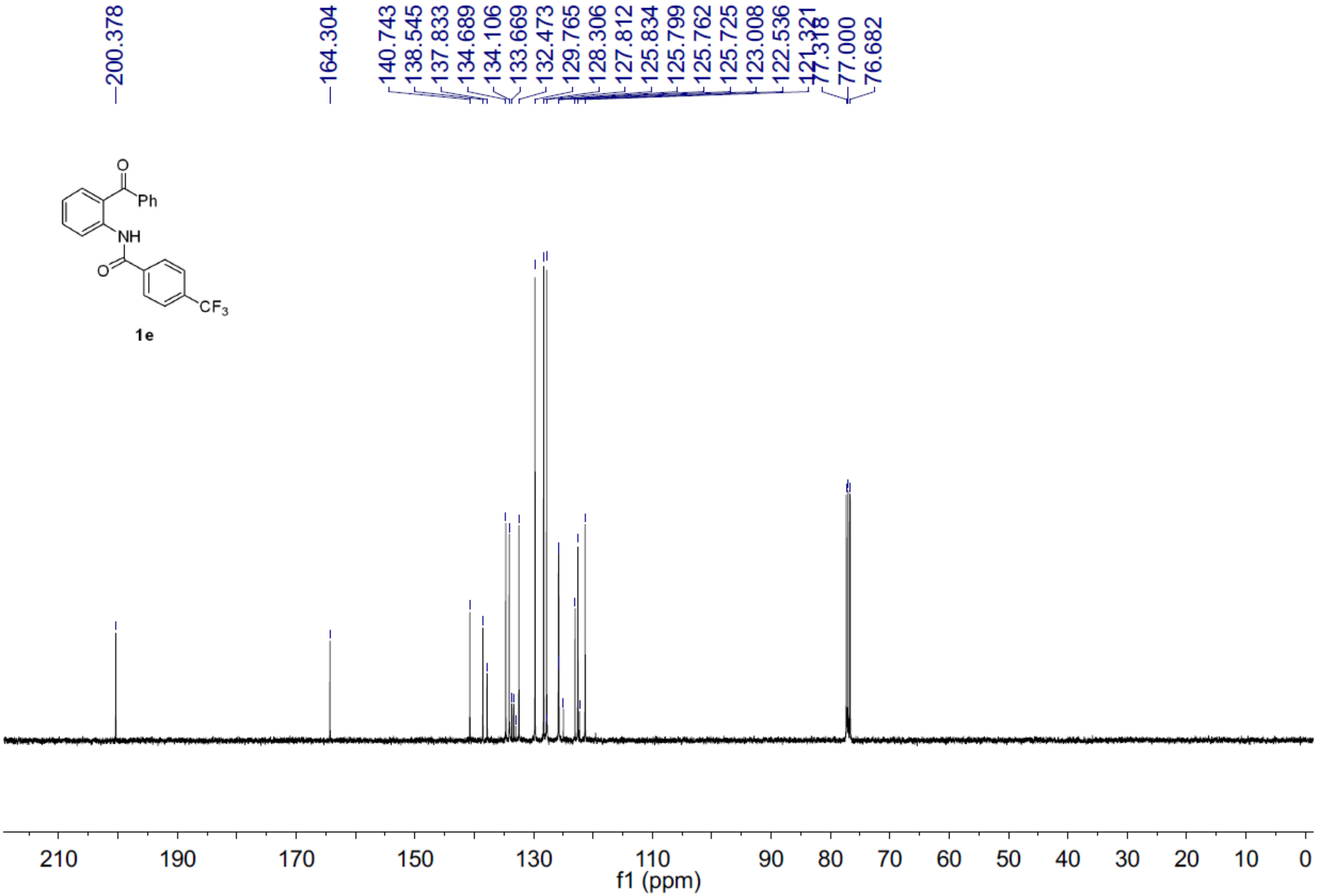

200.221
165.238
162.533
141.326
138.733
134.519
133.948
132.221
129.666
129.225
128.185
126.731
122.746
121.733
121.167
113.887
77.318
77.000
76.681
55.289
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



12.011
8.881
8.879
8.860
8.857
8.016
8.011
7.999
7.994
7.721
7.718
7.706
7.701
7.697
7.657
7.646
7.642
7.639
7.627
7.623
7.620
7.617
7.601
7.586
7.583
7.514
7.511
7.495
7.487
7.481
7.476
7.464
7.459
7.150
7.147
7.130
7.128
7.112
7.109
O
Ph
NH
O
Cl
1d
0.91
0.97
2.00
1.94
3.06
4.02
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

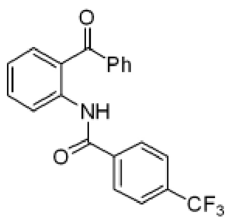

200.400
164.632
140.952
138.641
138.294
134.687
134.099
132.920
132.423
129.748
129.012
128.798
128.306
122.925
122.289
121.295
77.318
77.000
76.683
O
Ph
NH
O
Cl
1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.109
8.888
8.866
8.181
8.161
7.774
7.753
7.722
7.703
7.660
7.642
7.628
7.602
7.584
7.513
7.495
7.476
7.260
7.169
7.150
7.131
O
Ph
NH
O
CF3
1e
0.93
0.98
2.00
1.97
2.01
3.03
1.99
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

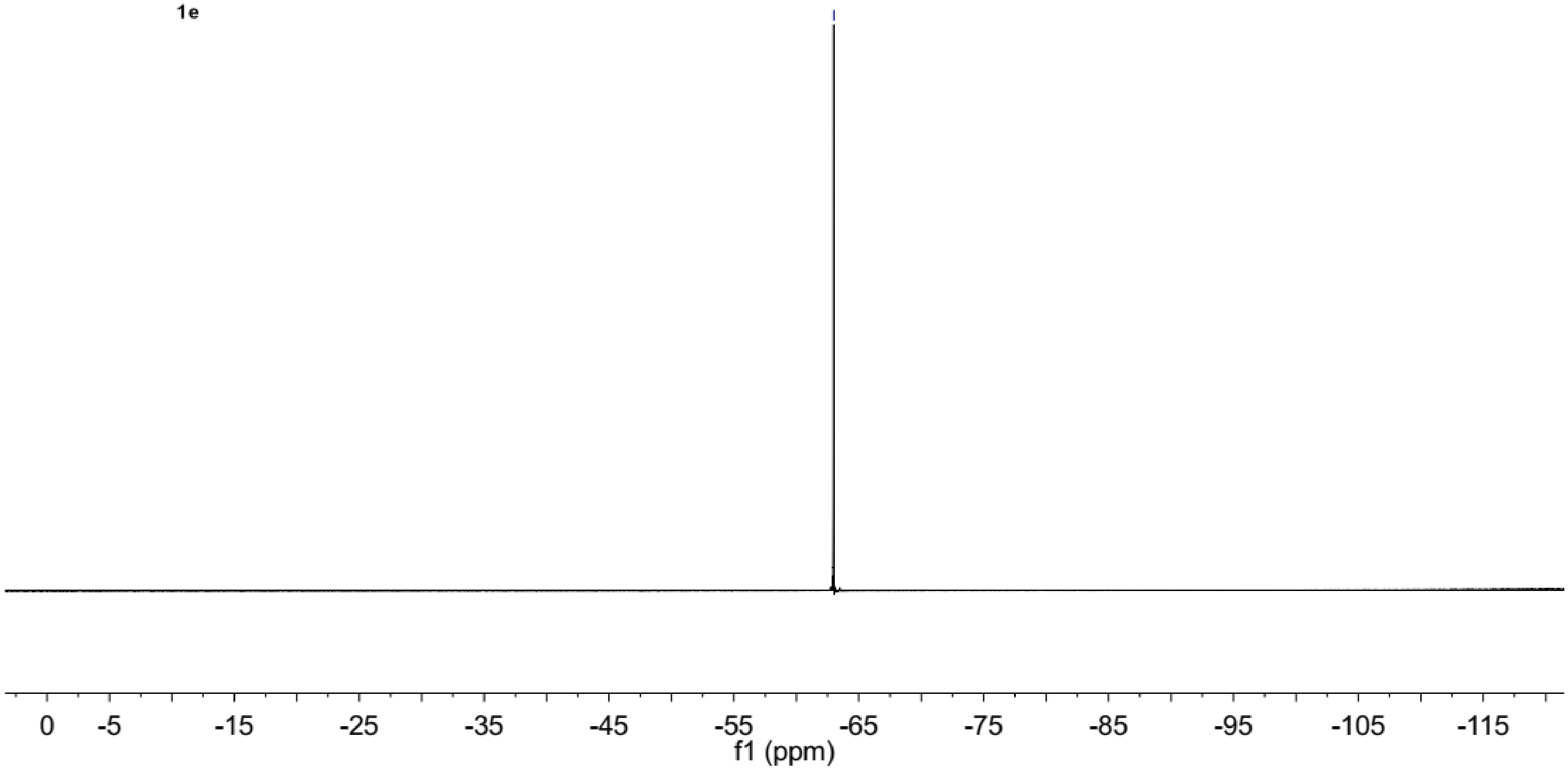


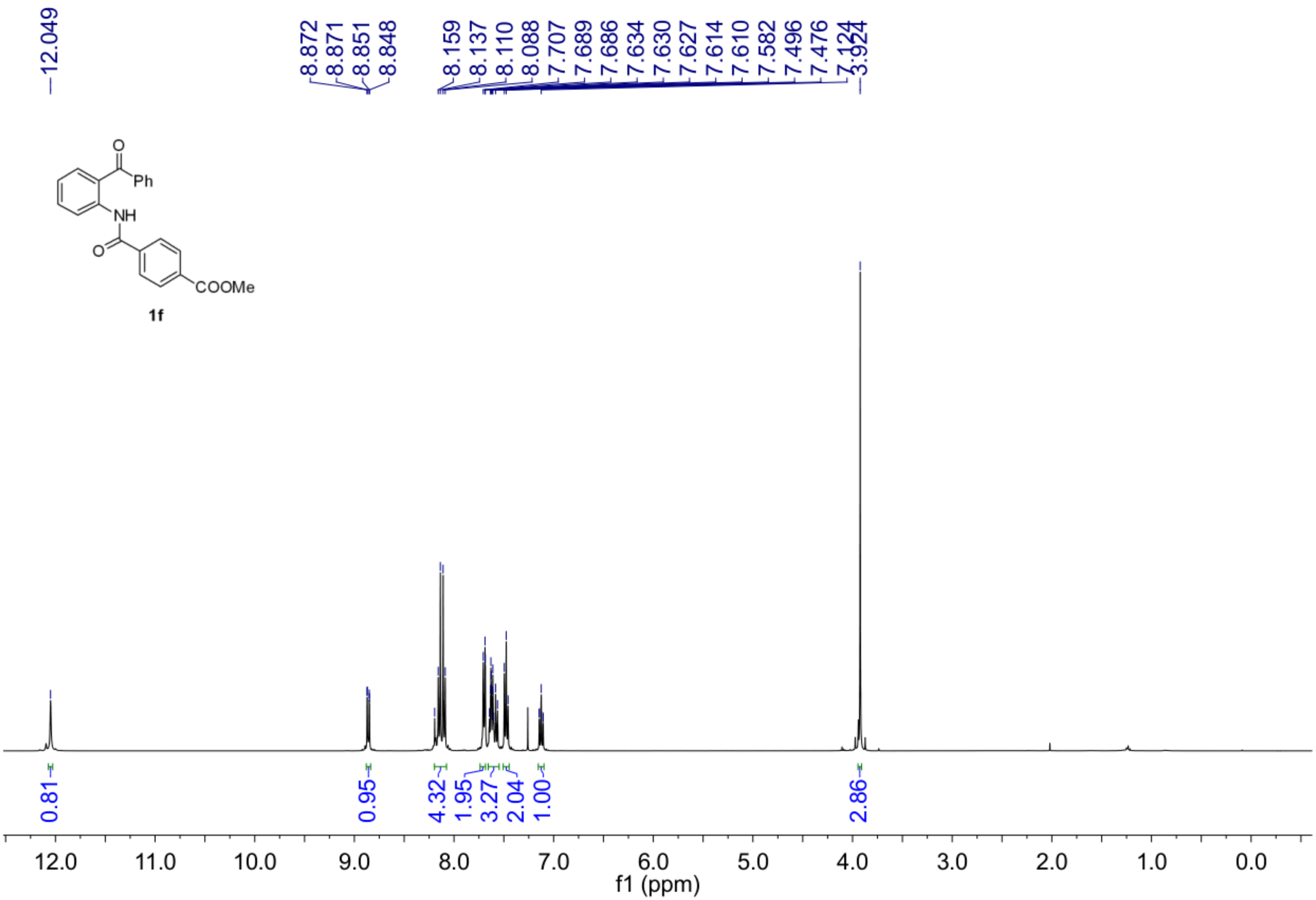
200.378
164.304
140.743
138.545
137.833
134.689
134.106
133.669
132.473
129.765
128.306
127.812
125.834
125.799
125.762
125.725
123.008
122.536
121.321
77.318
77.000
76.682
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1e



1e

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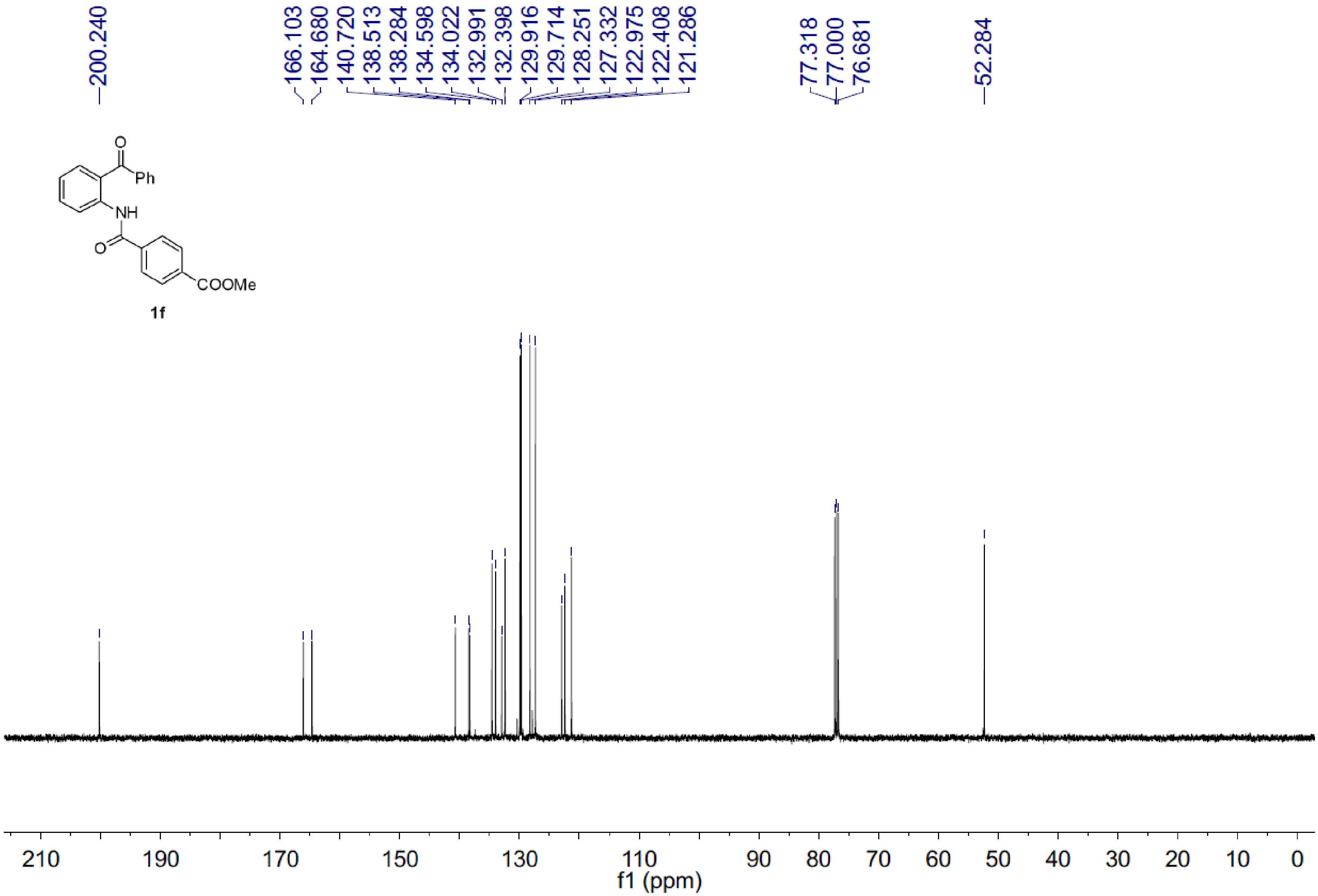
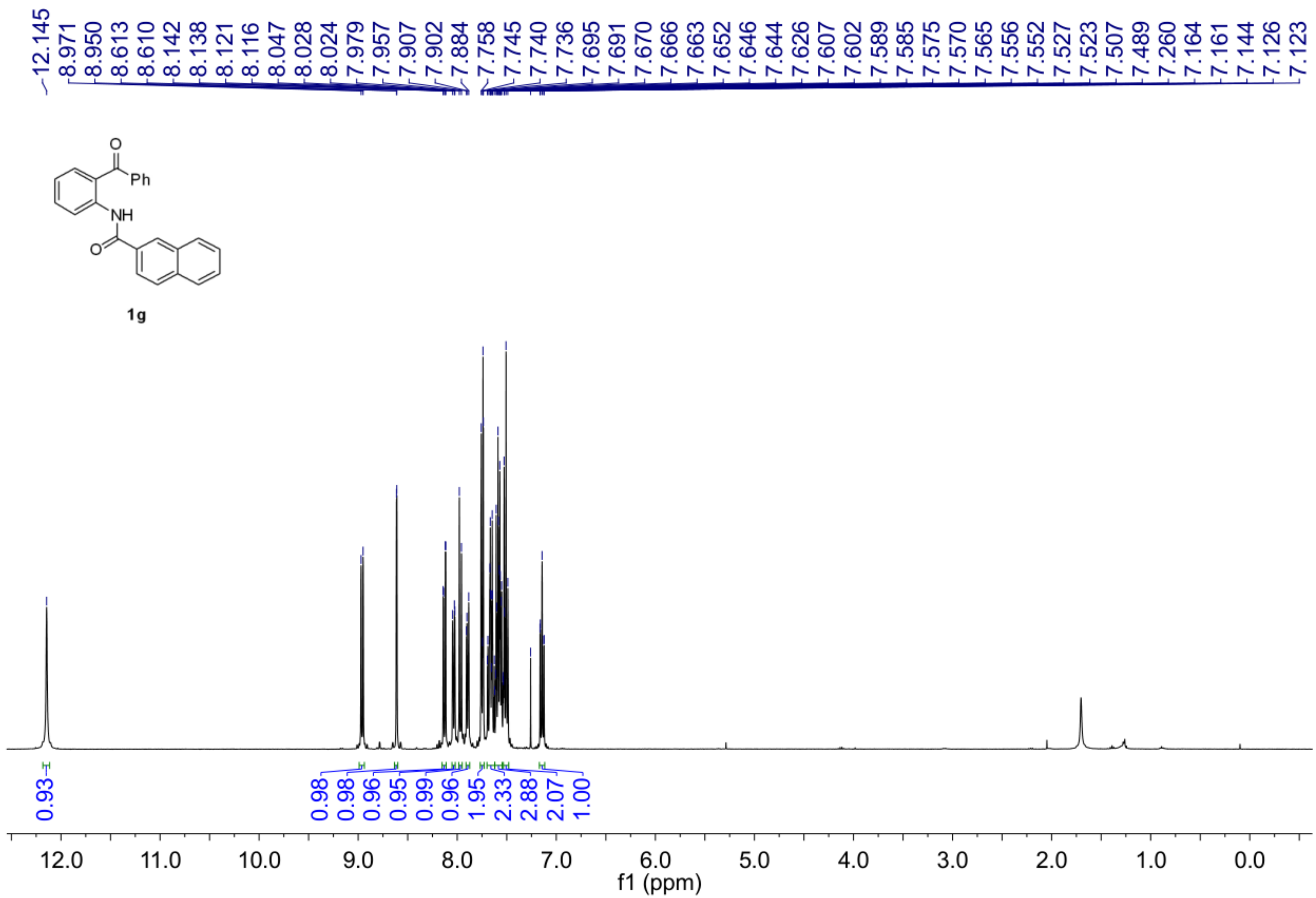
8.871
8.851
8.848
8.159
8.137
8.110
8.088
7.707
7.689
7.686
7.634
7.630
7.627
7.614
7.610
7.582
7.496
7.476
7.124
3.924
O
Ph
NH
O
COOMe
1f
0.81
0.95
4.32
1.95
3.27
2.04
1.00
2.86
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


200.240
166.103
164.680
140.720
138.513
138.284
134.598
134.022
132.991
132.398
129.916
129.714
128.251
127.332
122.975
122.408
121.286
77.318
77.000
76.681
52.284
O
Ph
NH
O
COOMe
1f
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1g
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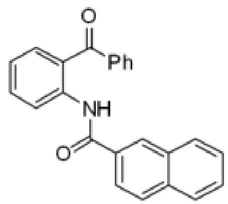
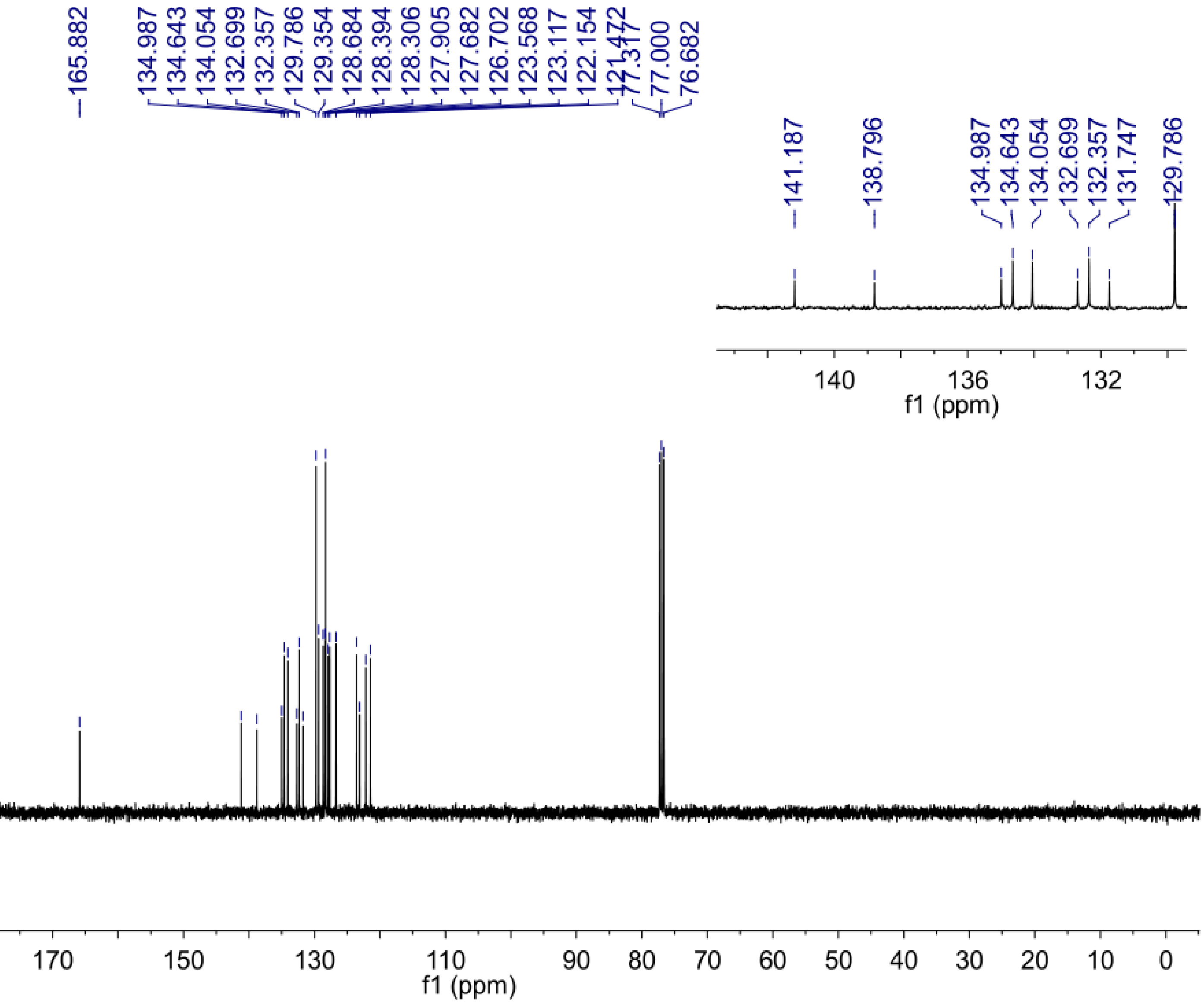
8.971
8.950
8.613
8.610
8.142
8.138
8.121
8.116
8.047
8.028
8.024
7.979
7.957
7.907
7.902
7.884
7.758
7.745
7.740
7.736
7.695
7.691
7.670
7.666
7.663
7.652
7.646
7.644
7.626
7.607
7.602
7.589
7.585
7.575
7.570
7.565
7.556
7.552
7.527
7.523
7.507
7.489
7.260
7.164
7.161
7.144
7.126
7.123
0.93
0.98
0.98
0.96
0.95
0.99
0.96
1.95
2.33
2.88
2.07
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


O
Ph
NH
O

1g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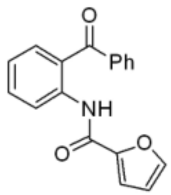
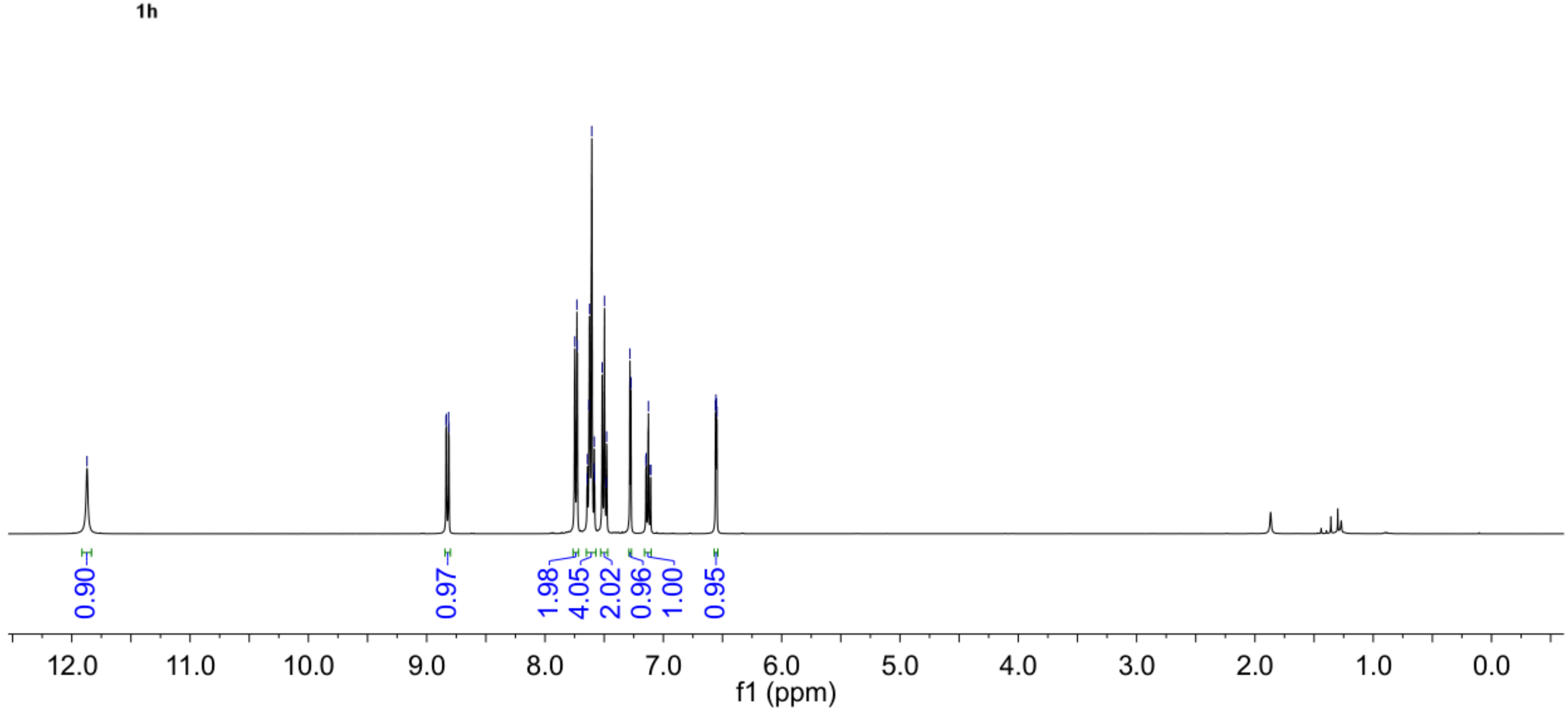
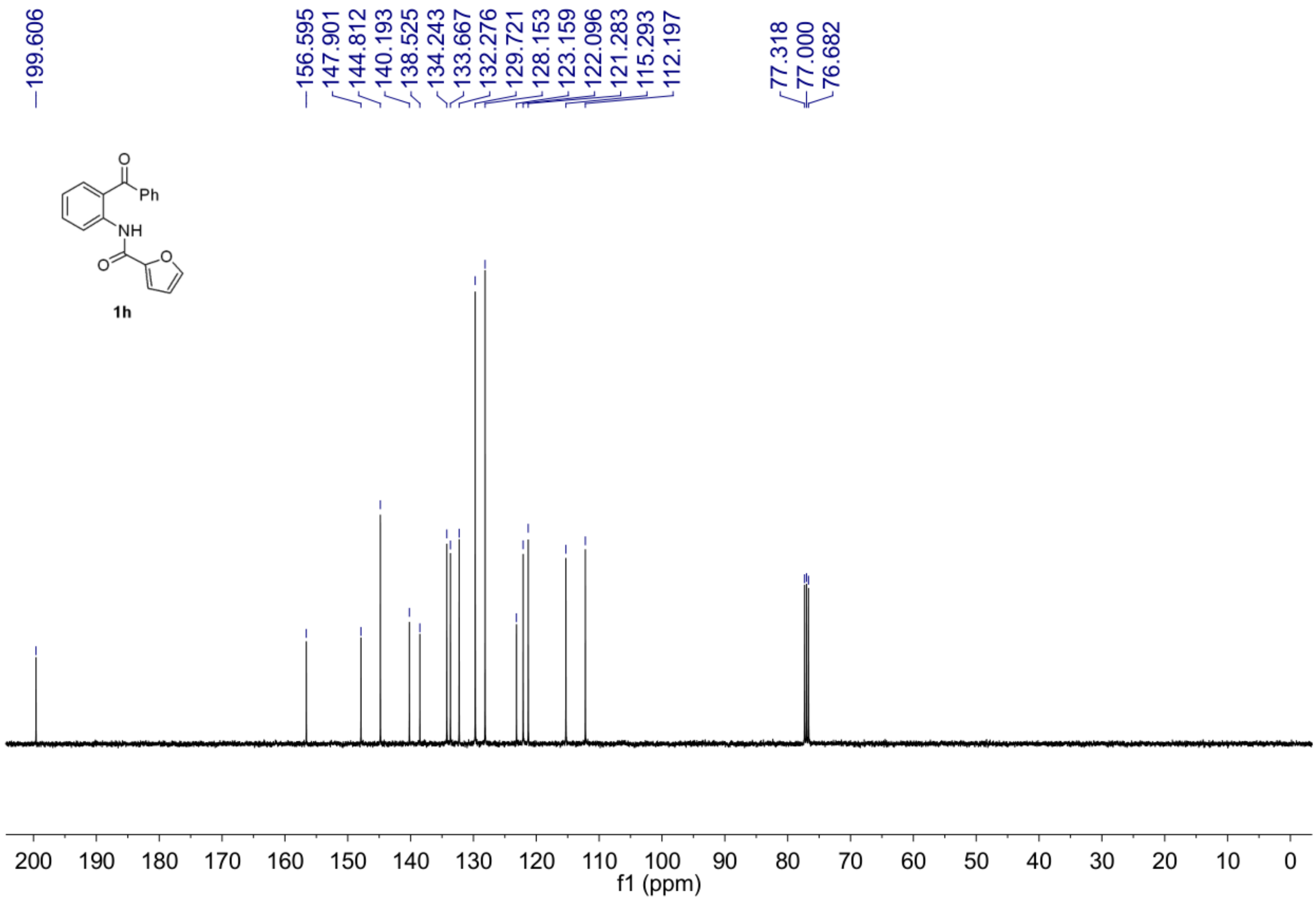
134.643
134.054
132.699
132.357
129.786
129.354
128.684
128.394
128.306
127.905
127.682
126.702
123.568
123.117
122.154
121.472
77.317
77.000
76.682
141.187
138.796
134.987
134.643
134.054
132.699
132.357
131.747
129.786
140
136
132
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

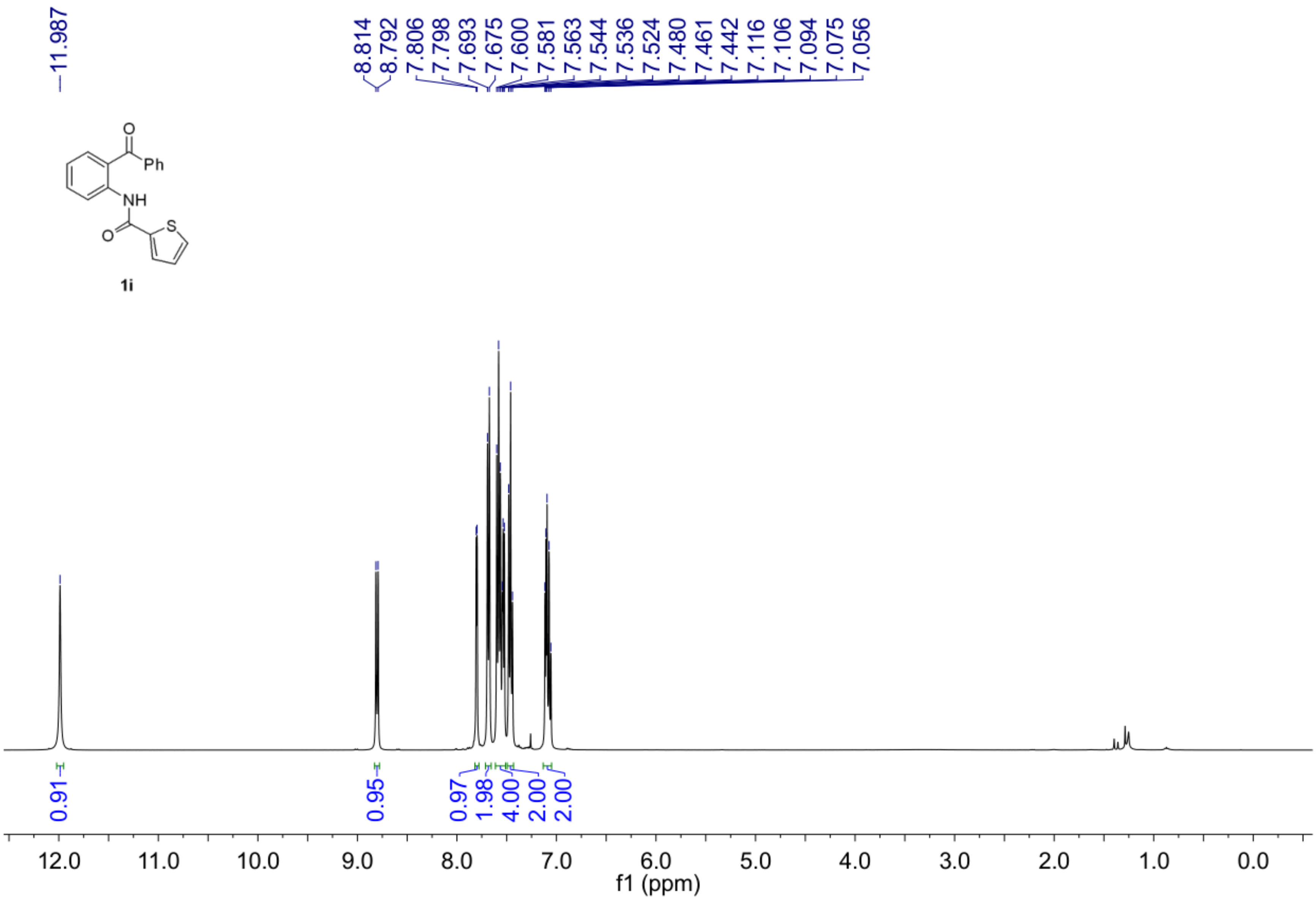


1h



11.871
8.837
8.835
8.815
8.812
7.748
7.731
7.625
7.605
7.497
6.560
6.556
6.551
6.547
0.90
0.97
1.98
4.05
2.02
0.96
1.00
0.95
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.606
156.595
147.901
144.812
140.193
138.525
134.243
133.667
132.276
129.721
128.153
123.159
122.096
121.283
115.293
112.197
77.318
77.000
76.682
O
Ph
NH
O
O
1h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.792
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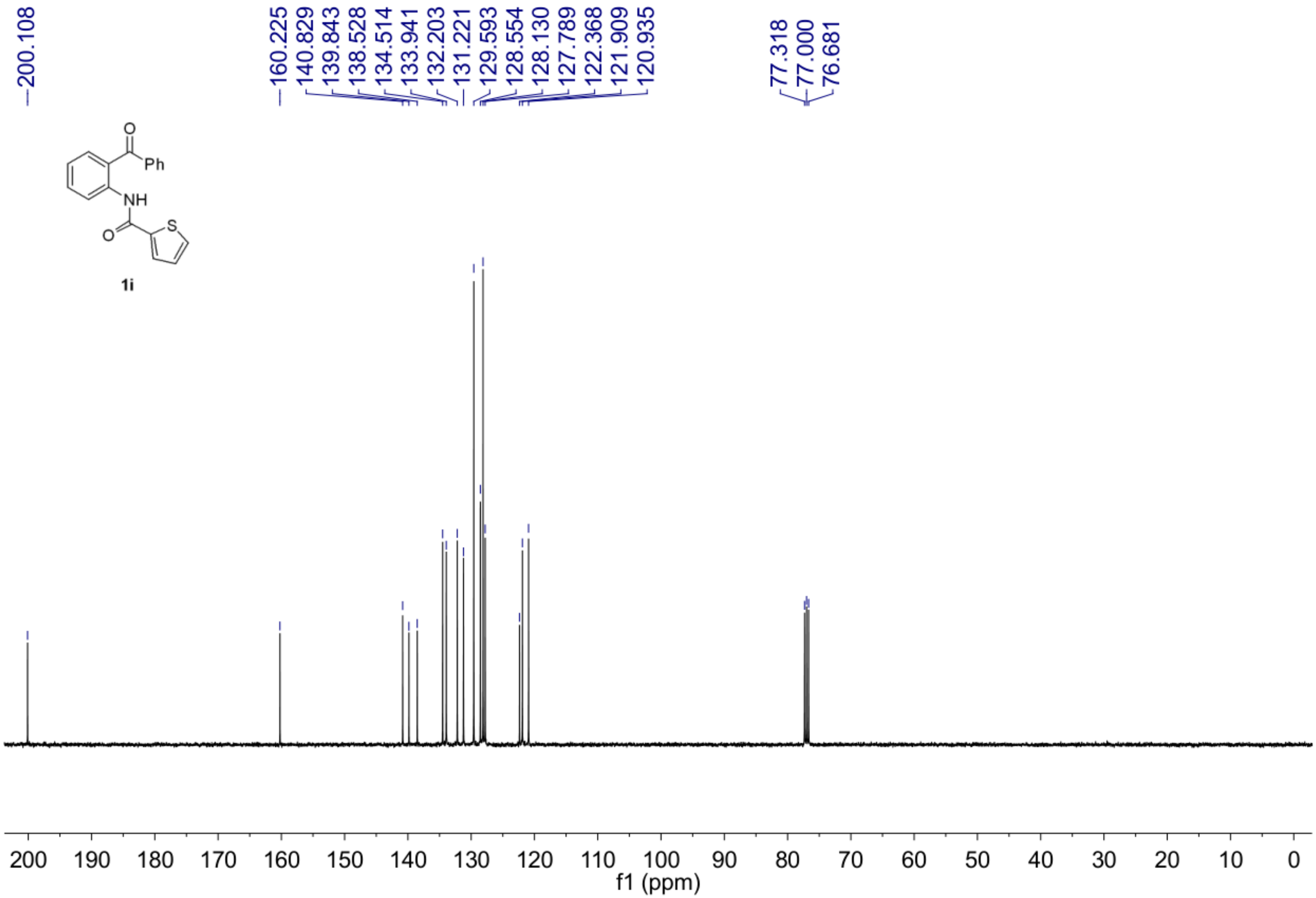
7.693
7.675
7.600
7.581
7.563
7.544
7.536
7.524
7.480
7.461
7.442
7.116
7.106
7.094
7.075
7.056
O
Ph
NH
O
S
1i
0.91
0.95
0.97
1.98
4.00
2.00
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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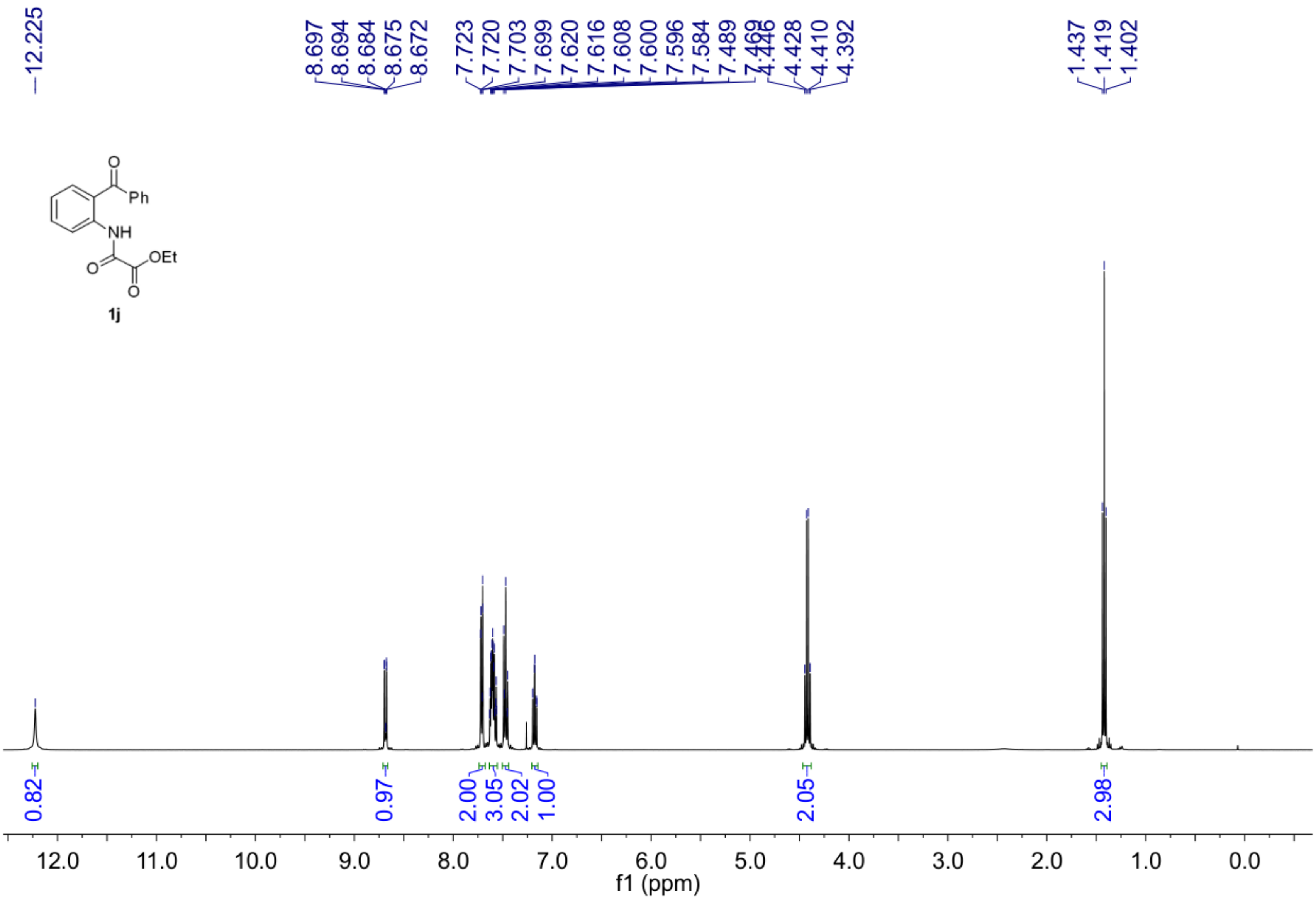
138.528
134.514
133.941
132.203
131.221
129.593
128.554
128.130
127.789
122.368
121.909
120.935
77.318
77.000
76.681
O
Ph
NH
S
O
1i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.675
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7.720
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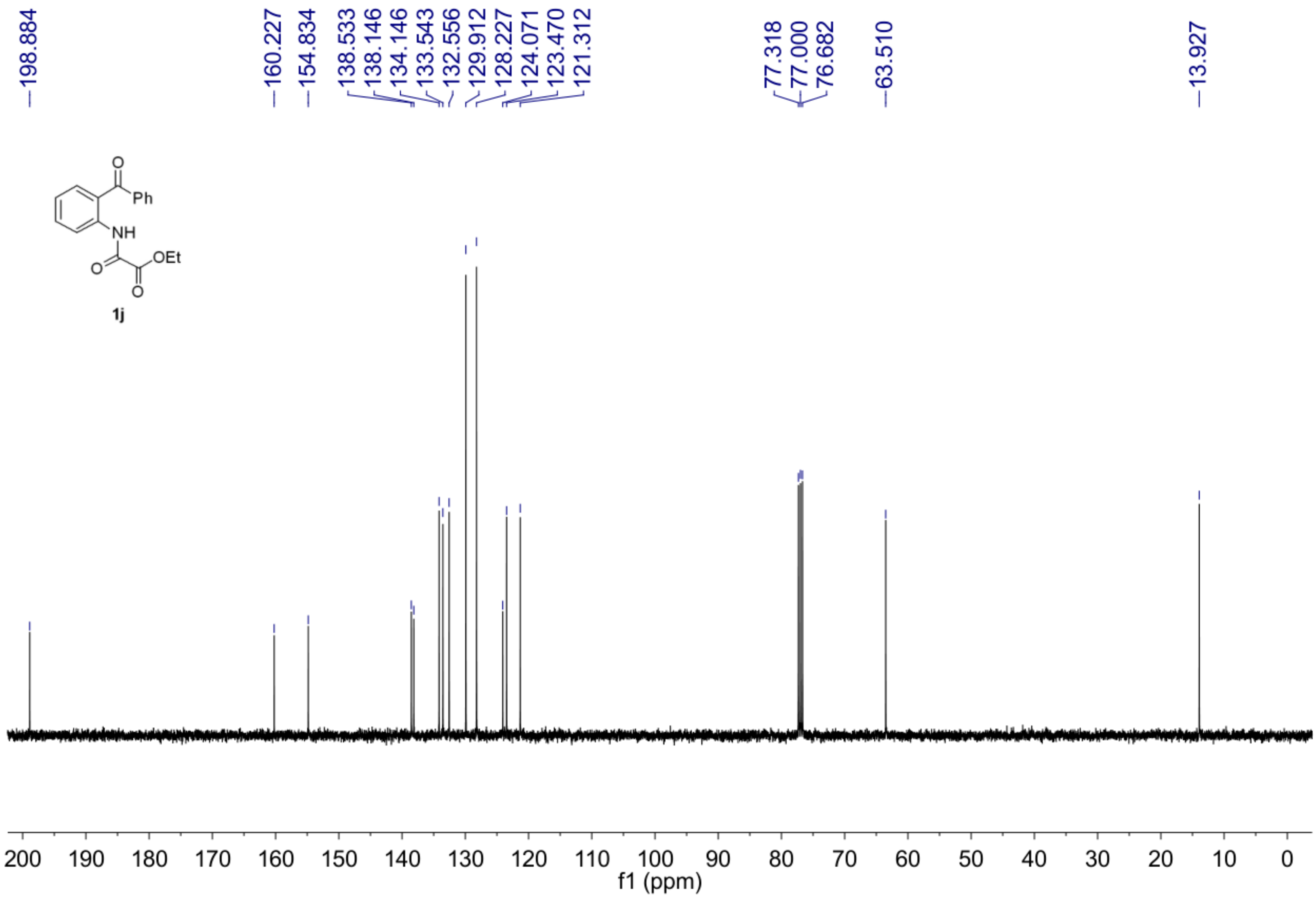
7.699
7.620
7.616
7.608
7.600
7.596
7.584
7.489
4.446
4.428
4.410
4.392
1.437
1.419
1.402
O
Ph
NH
O
OEt
O
0.82
0.97
2.00
3.05
2.02
1.00
2.05
2.98
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

1j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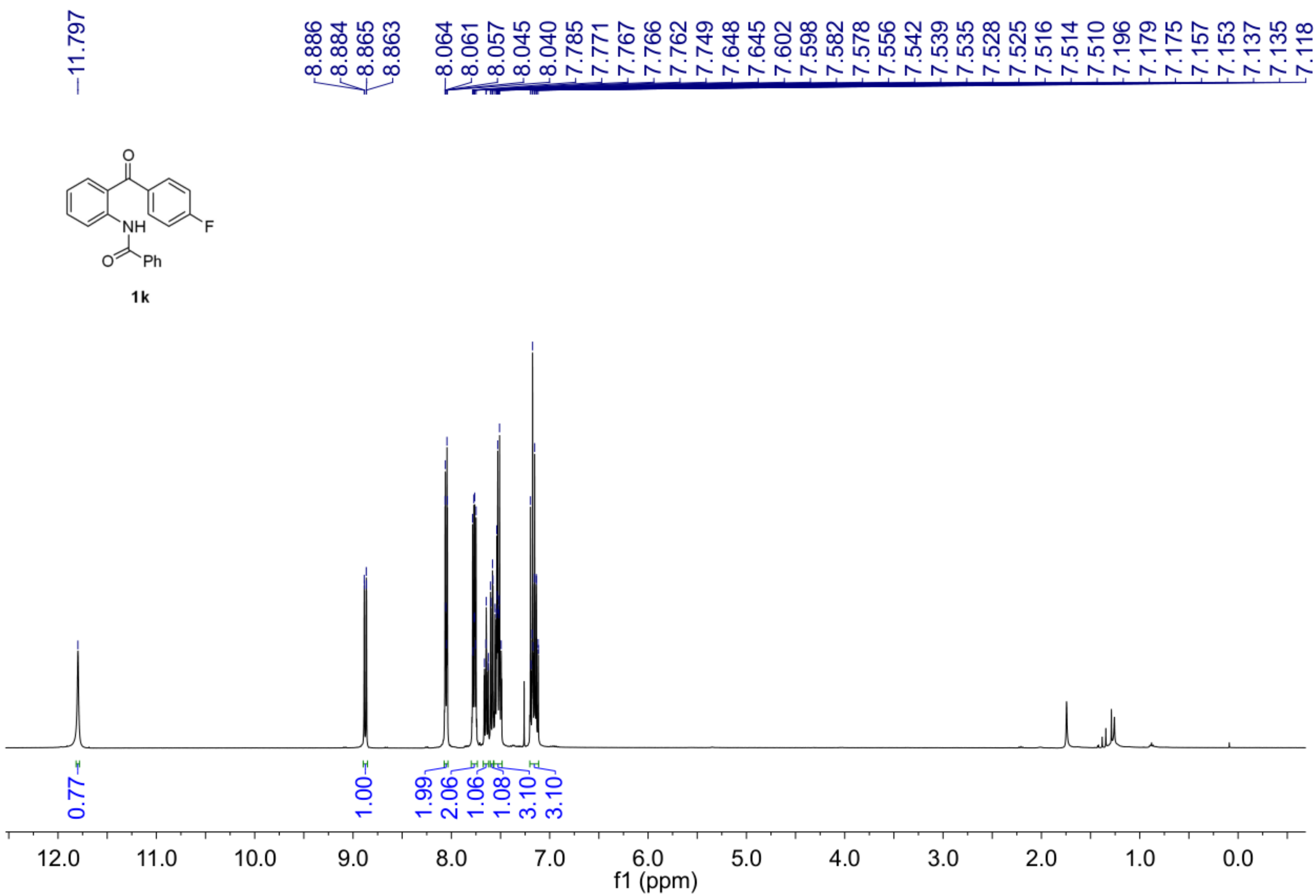
138.146
134.146
133.543
132.556
129.912
128.227
124.071
123.470
121.312
77.318
77.000
76.682
63.510
13.927
O
Ph
NH
OEt
O
O
1j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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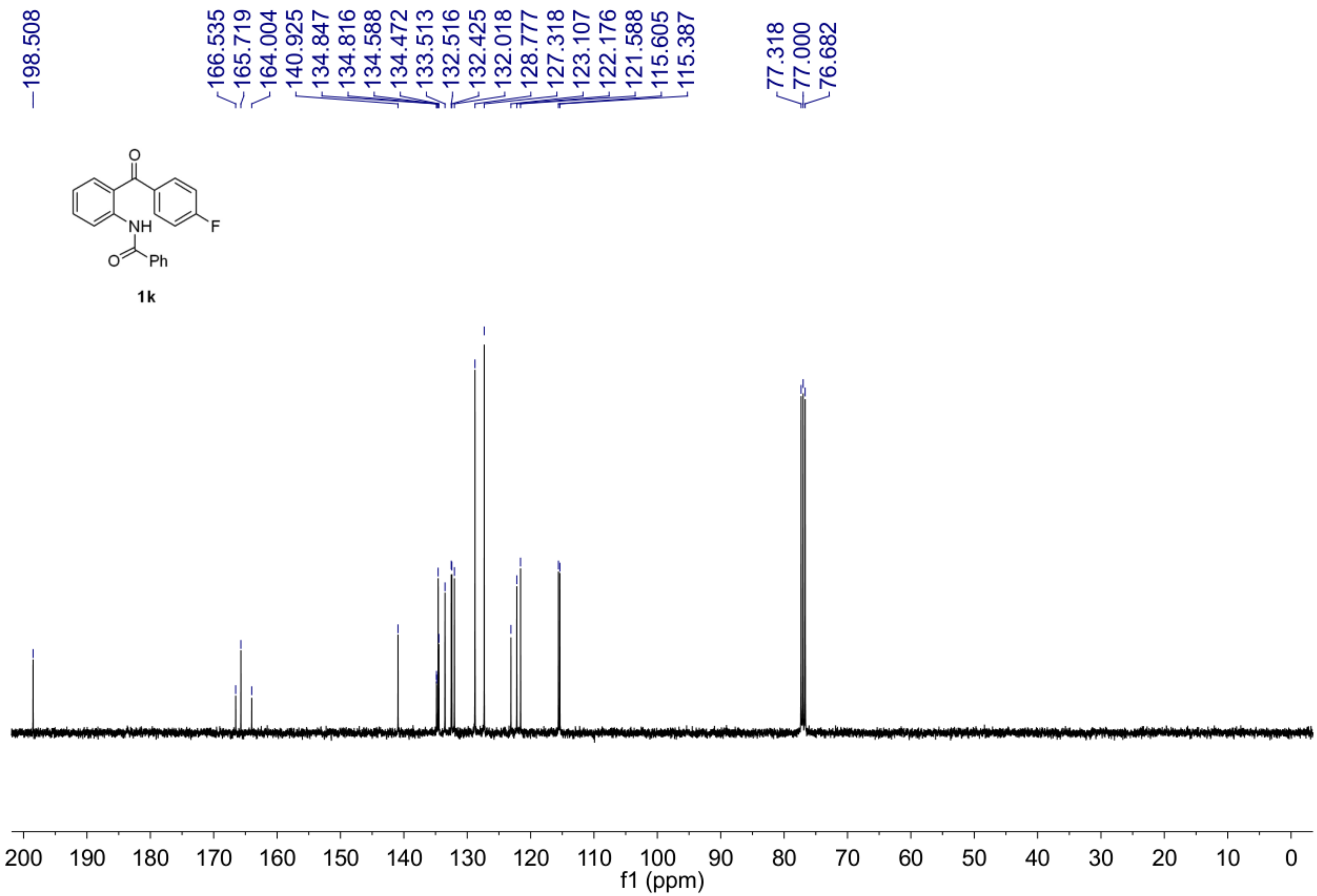
8.064
8.061
8.057
8.045
8.040
7.785
7.771
7.767
7.766
7.762
7.749
7.648
7.645
7.602
7.598
7.582
7.578
7.556
7.542
7.539
7.535
7.528
7.525
7.516
7.514
7.510
7.196
7.179
7.175
7.157
7.153
7.137
7.135
7.118
O
NH
F
O
Ph
1k
0.77
1.00
1.99
2.06
1.06
1.08
3.10
3.10
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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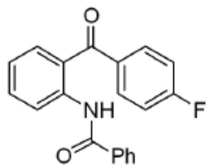
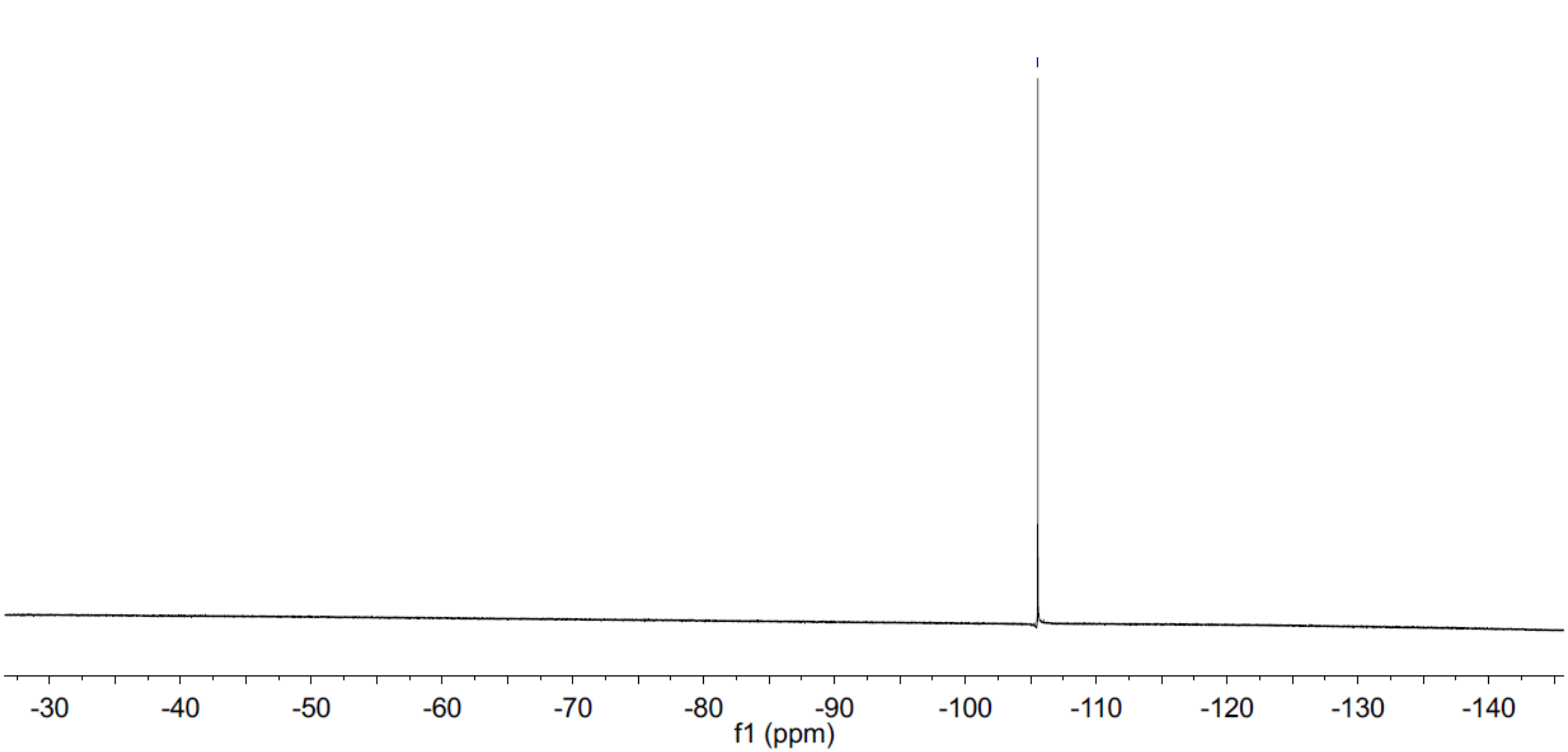
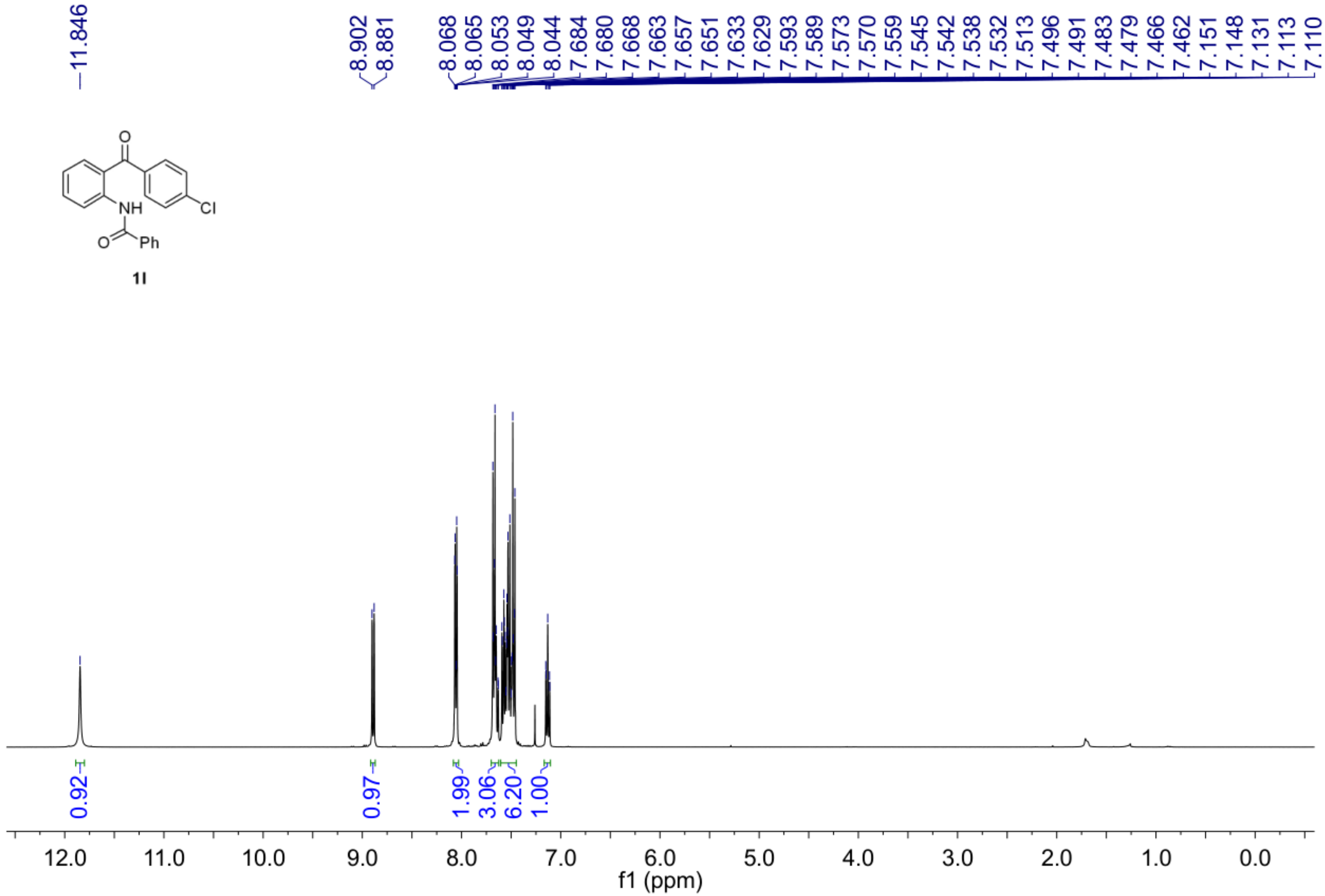
164.004
140.925
134.847
134.816
134.588
134.472
133.513
132.516
132.425
132.018
128.777
127.318
123.107
122.176
121.588
115.605
115.387
77.318
77.000
76.682
O
NH
F
O
Ph
1k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1k

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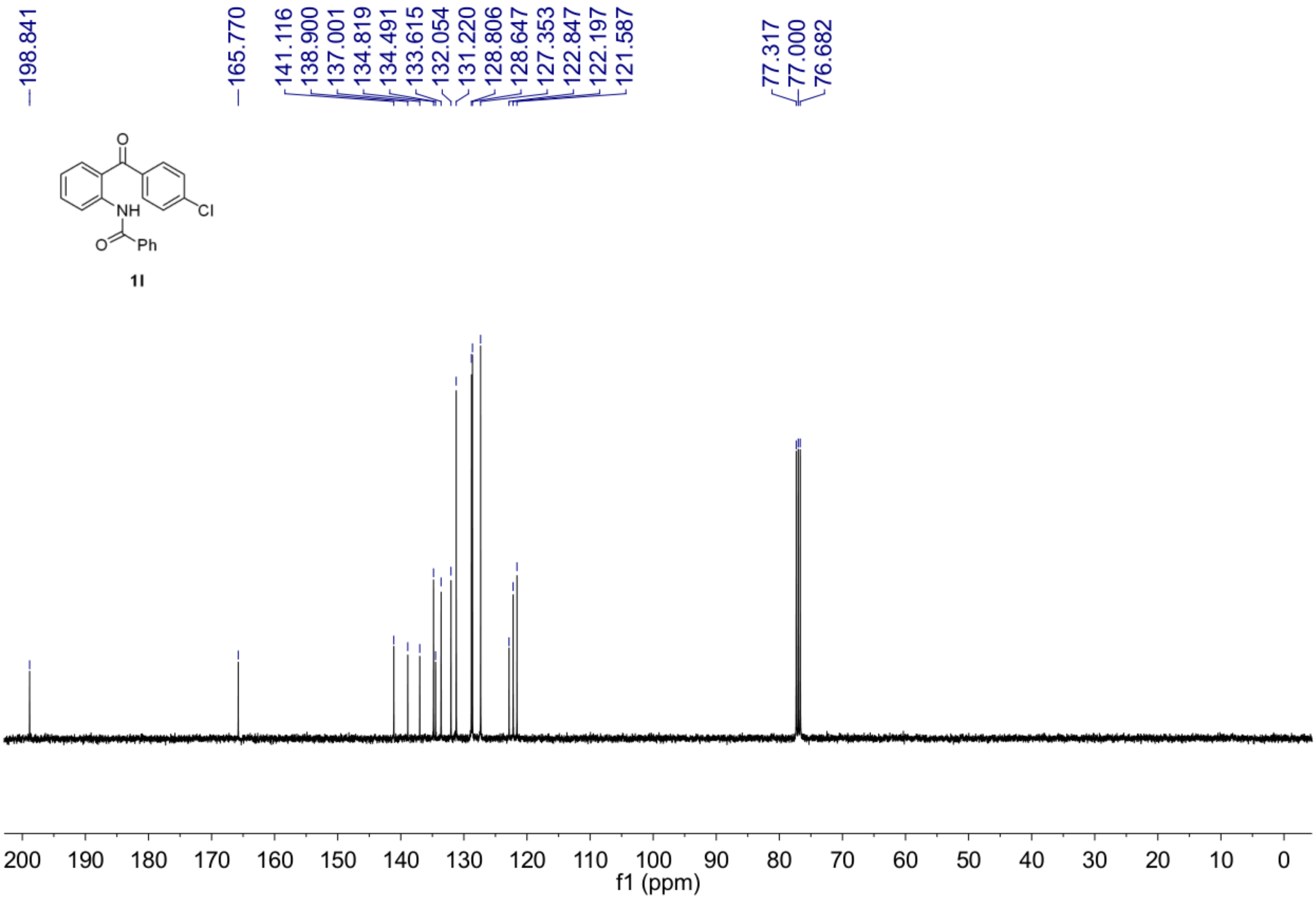
8.065
8.053
8.049
8.044
7.684
7.680
7.668
7.663
7.657
7.651
7.633
7.629
7.593
7.589
7.573
7.570
7.559
7.545
7.542
7.538
7.532
7.513
7.496
7.491
7.483
7.479
7.466
7.462
7.151
7.148
7.131
7.113
7.110
O
NH
Cl
O
Ph
1l
0.92
0.97
1.99
3.06
6.20
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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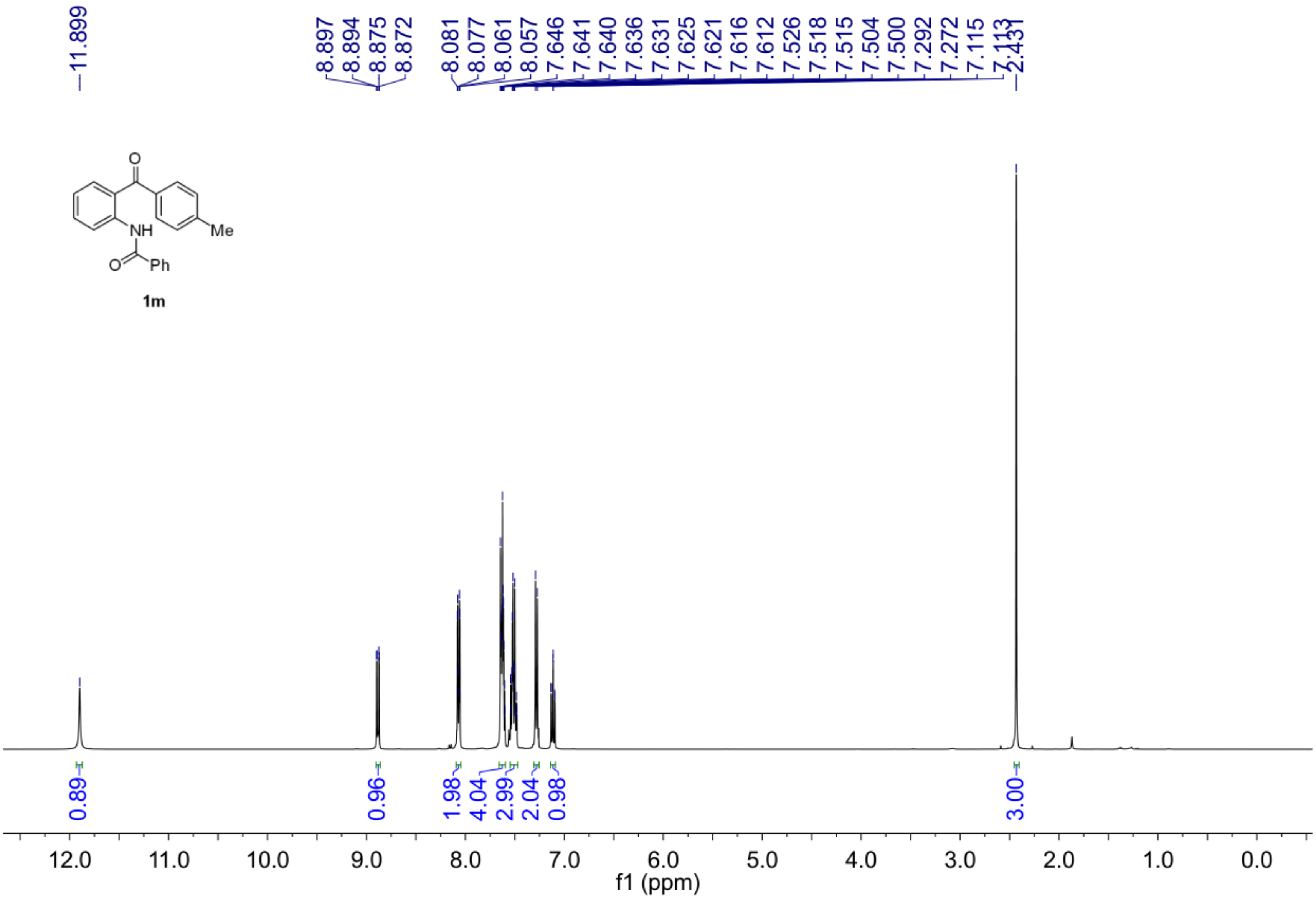
165.770
141.116
138.900
137.001
134.819
134.491
133.615
132.054
131.220
128.806
128.647
127.353
122.847
122.197
121.587
77.317
77.000
76.682
O
NH
Cl
O
Ph
1l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.899
8.897
8.894
8.875
8.872
8.081
8.077
8.061
8.057
7.646
7.641
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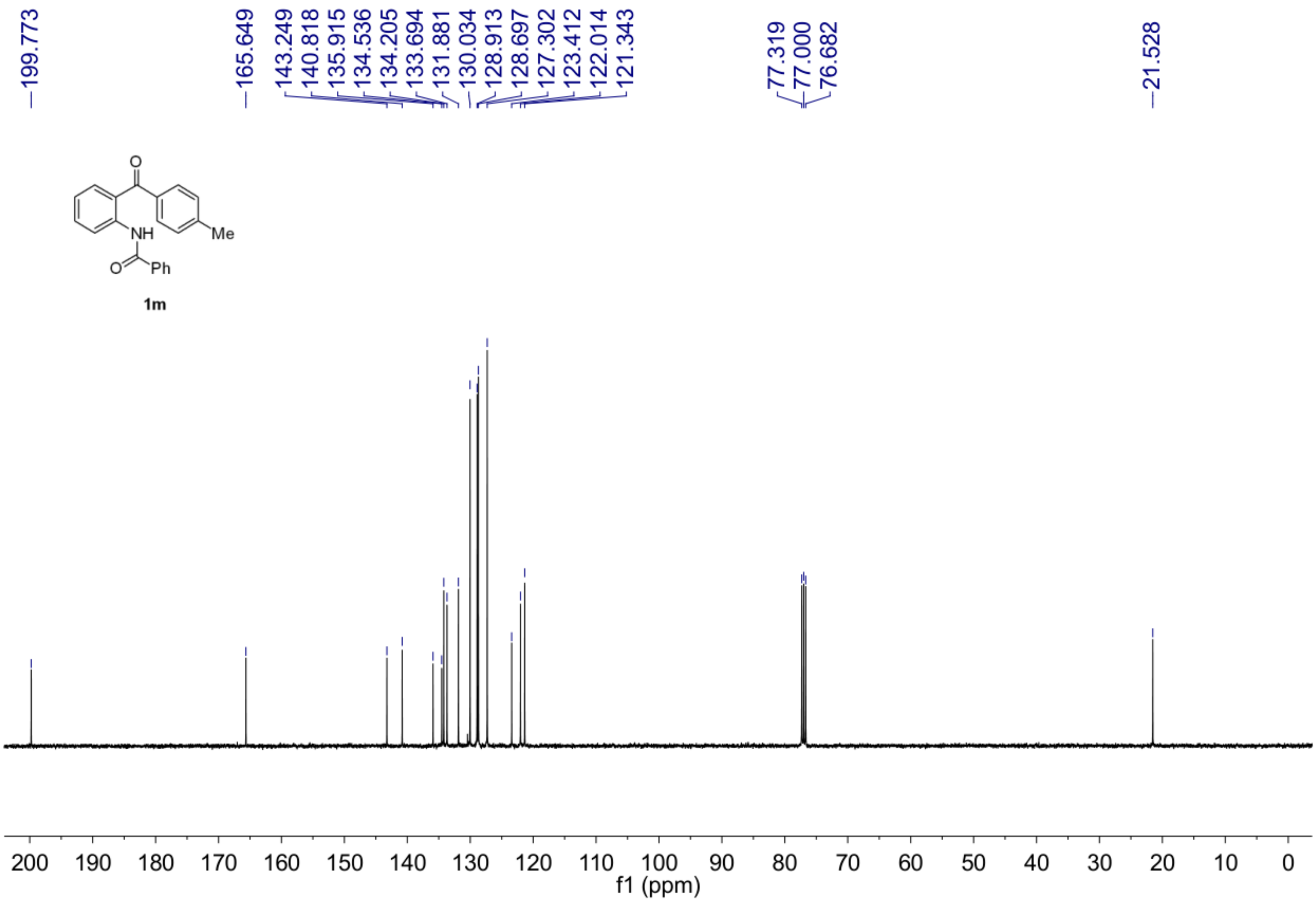
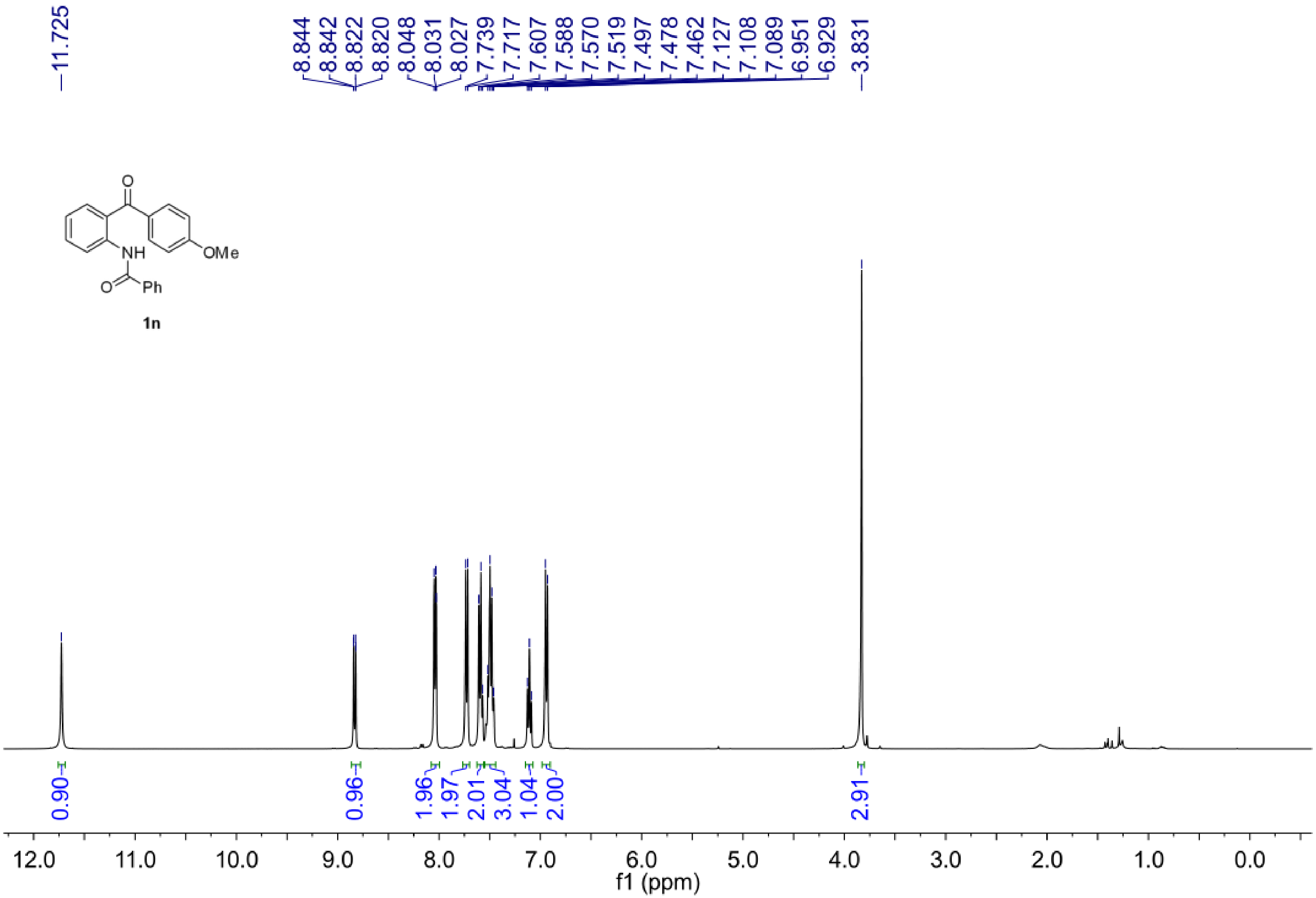
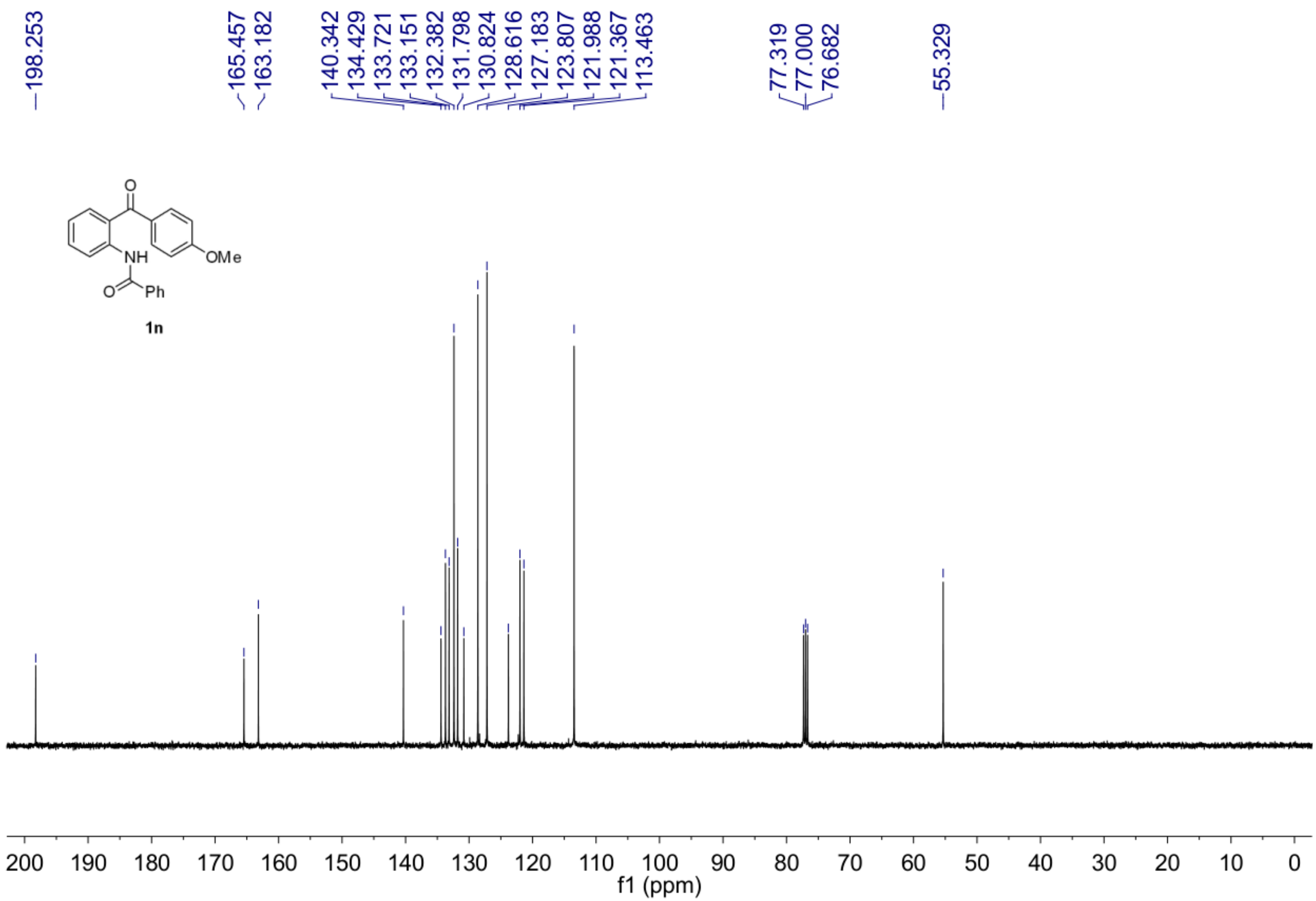
7.636
7.631
7.625
7.621
7.616
7.612
7.526
7.518
7.515
7.504
7.500
7.292
7.272
7.115
7.113
2.431
O
NH
Me
O
Ph
1m
0.89
0.96
1.98
4.04
2.99
2.04
0.98
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.773
165.649
143.249
140.818
135.915
134.536
134.205
133.694
131.881
130.034
128.913
128.697
127.302
123.412
122.014
121.343
77.319
77.000
76.682
21.528
O
NH
Me
O
Ph
1m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



11.725
8.844
8.842
8.822
8.820
8.048
8.031
8.027
7.739
7.717
7.607
7.588
7.570
7.519
7.497
7.478
7.462
7.127
7.108
7.089
6.951
6.929
3.831
O
NH
OMe
O
Ph
1n
0.90
0.96
1.96
1.97
2.01
3.04
1.04
2.00
2.91
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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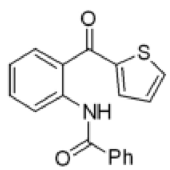
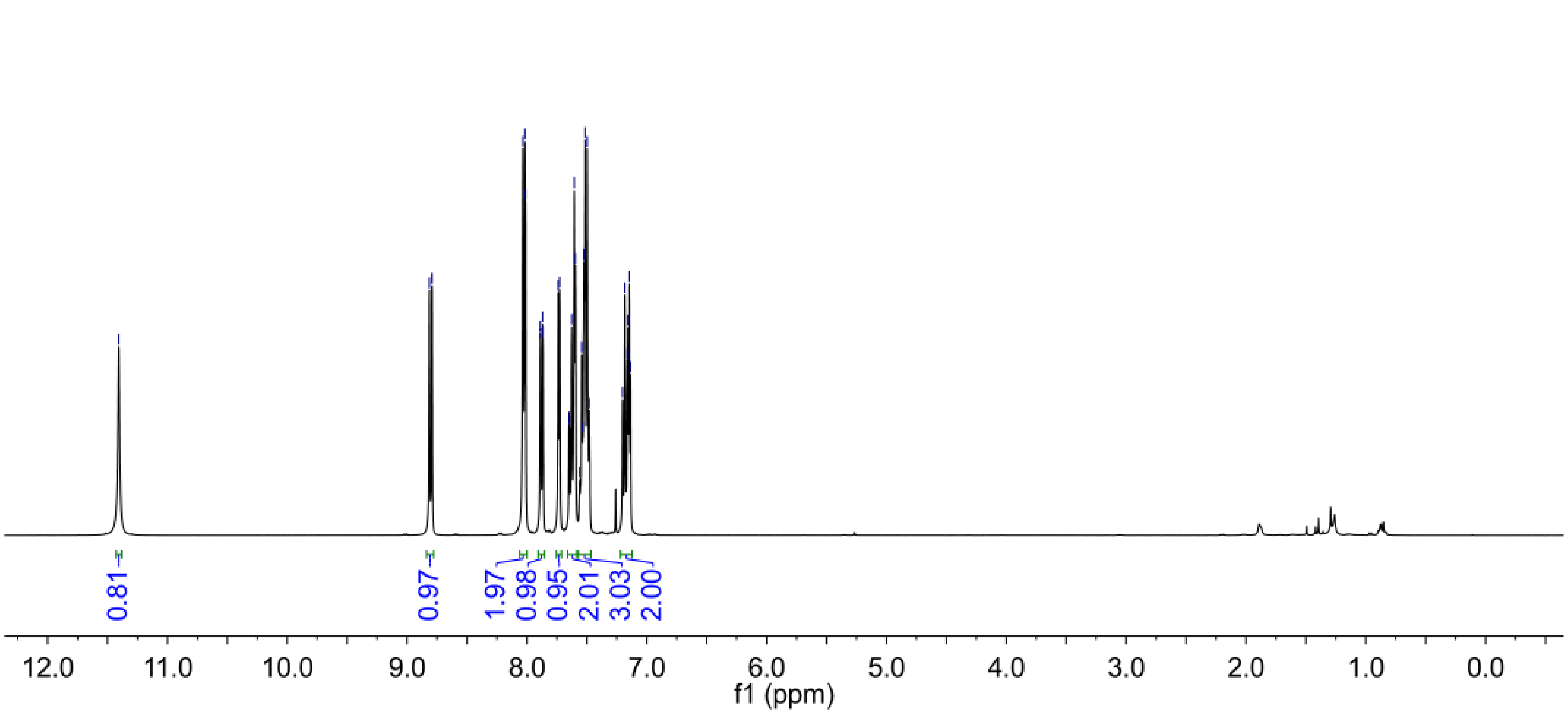
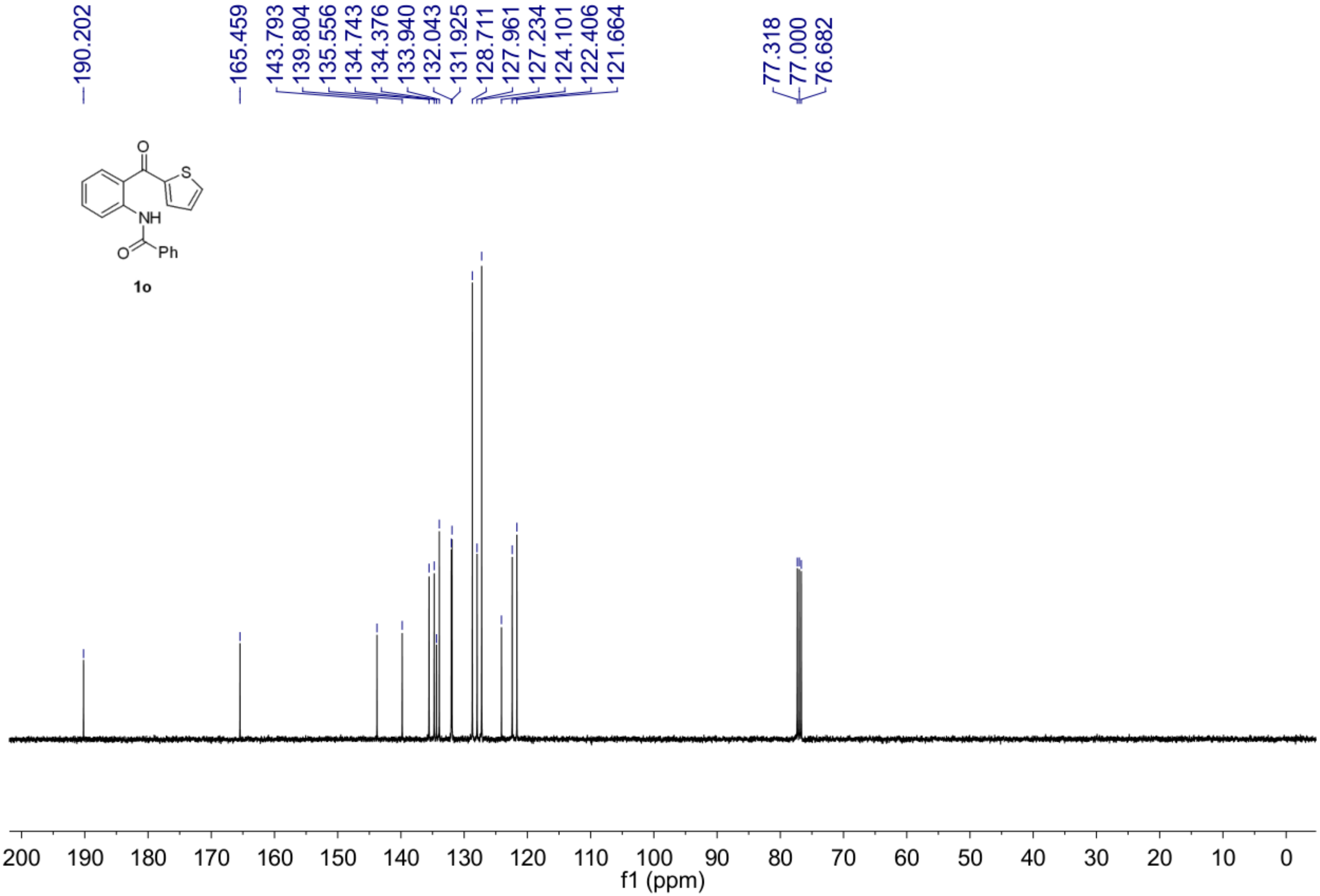
165.457
163.182
140.342
134.429
133.721
133.151
132.382
131.798
130.824
128.616
127.183
123.807
121.988
121.367
113.463
77.319
77.000
76.682
55.329
O
NH
OMe
O
Ph
1n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1o



11.407
8.814
8.793
8.033
8.016
8.013
7.888
7.886
7.869
7.866
7.740
7.727
7.648
7.646
7.627
7.605
7.595
7.561
7.542
7.535
7.525
7.516
7.497
7.480
7.476
7.203
7.183
7.162
7.158
7.148
7.136
0.81
0.97
1.97
0.98
0.95
2.01
3.03
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



1o

190.202
165.459
143.793
139.804
135.556
134.743
134.376
133.940
132.043
131.925
128.711
127.961
127.234
124.101
122.406
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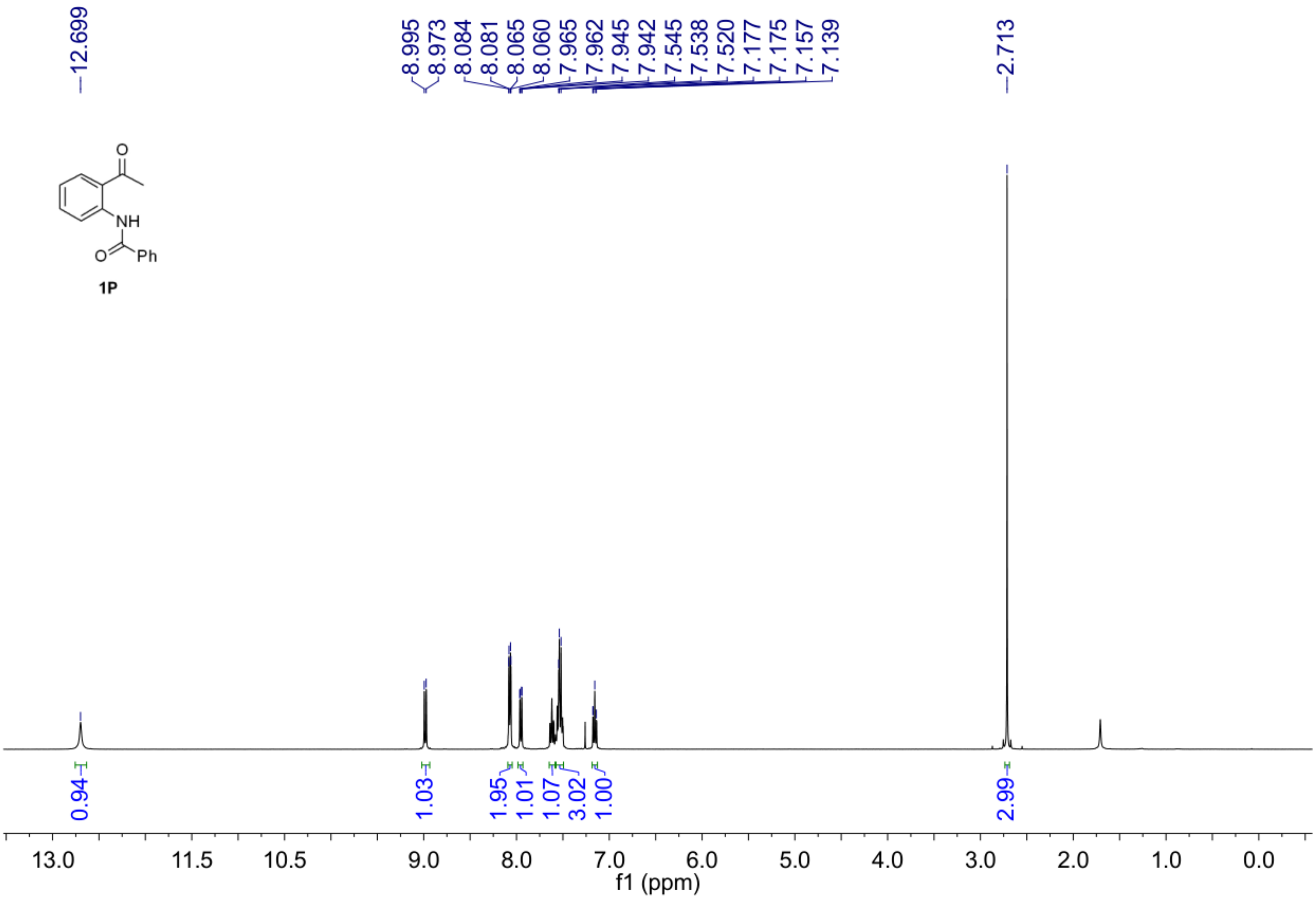
77.318
77.000
76.682
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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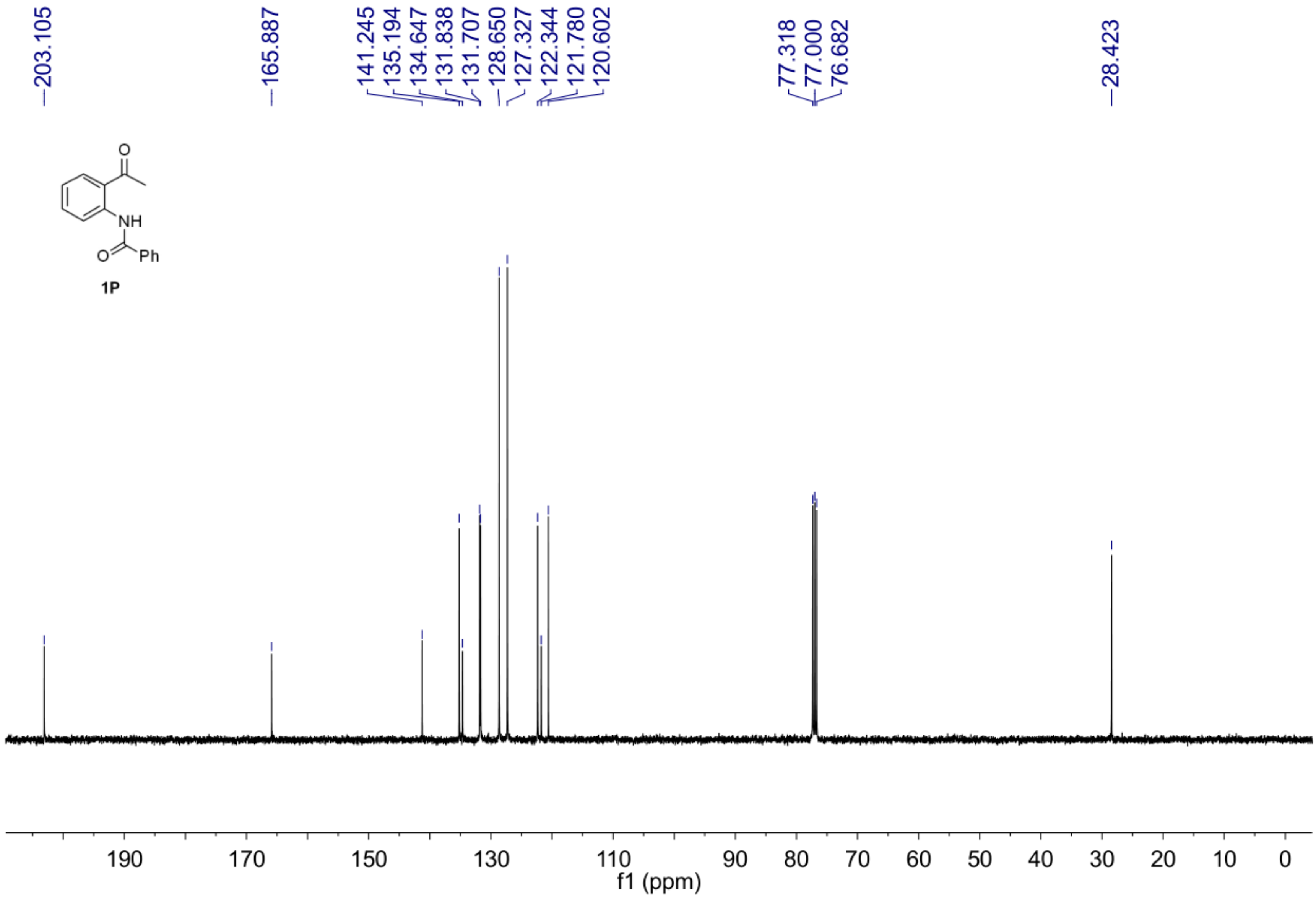
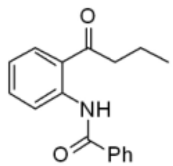
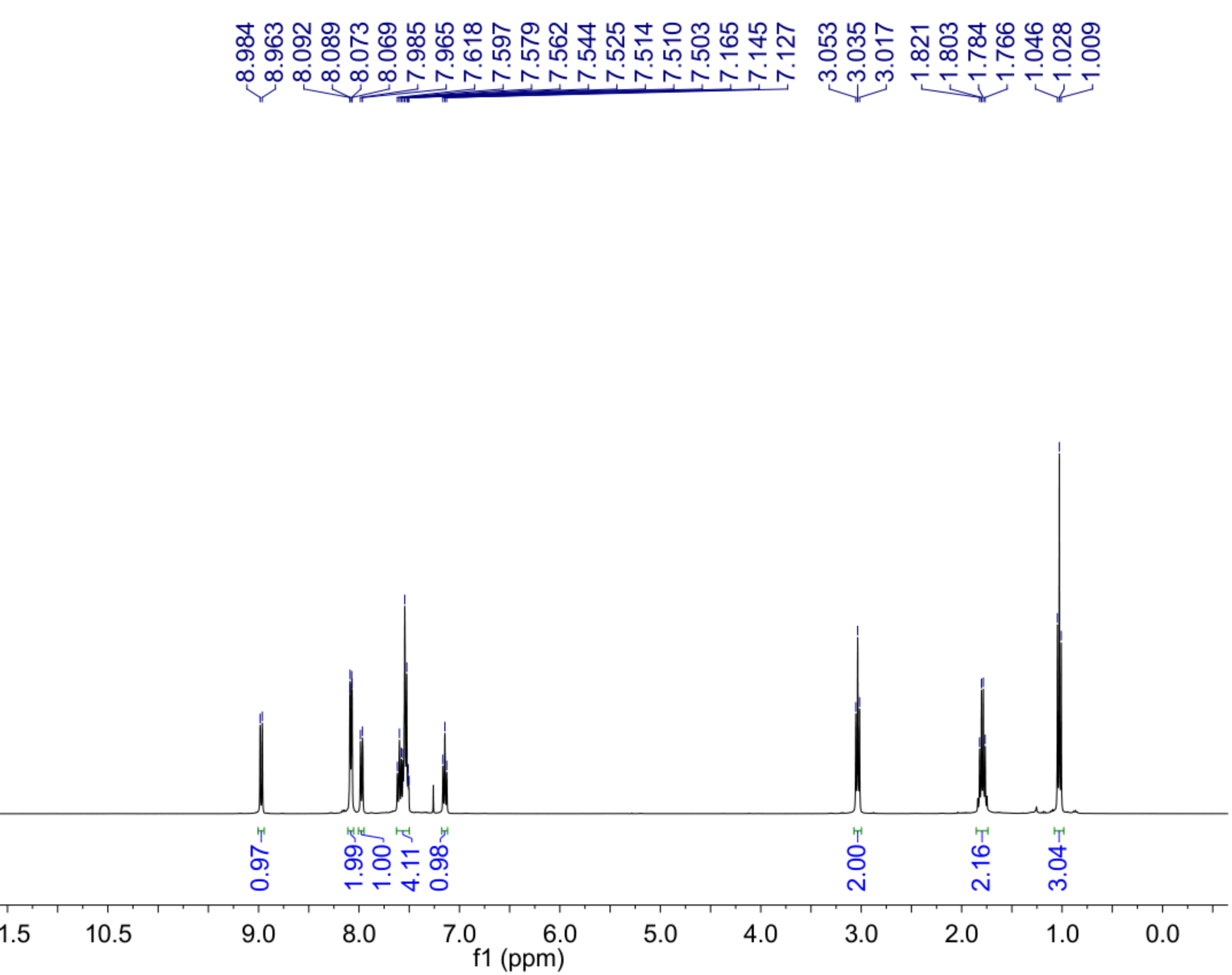
8.995
8.973
8.084
8.081
8.065
8.060
7.965
7.962
7.945
7.942
7.545
7.538
7.520
7.177
7.175
7.157
7.139
2.713
O
NH
O
Ph
1P
0.94
1.03
1.95
1.01
1.07
3.02
1.00
2.99
13.0
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

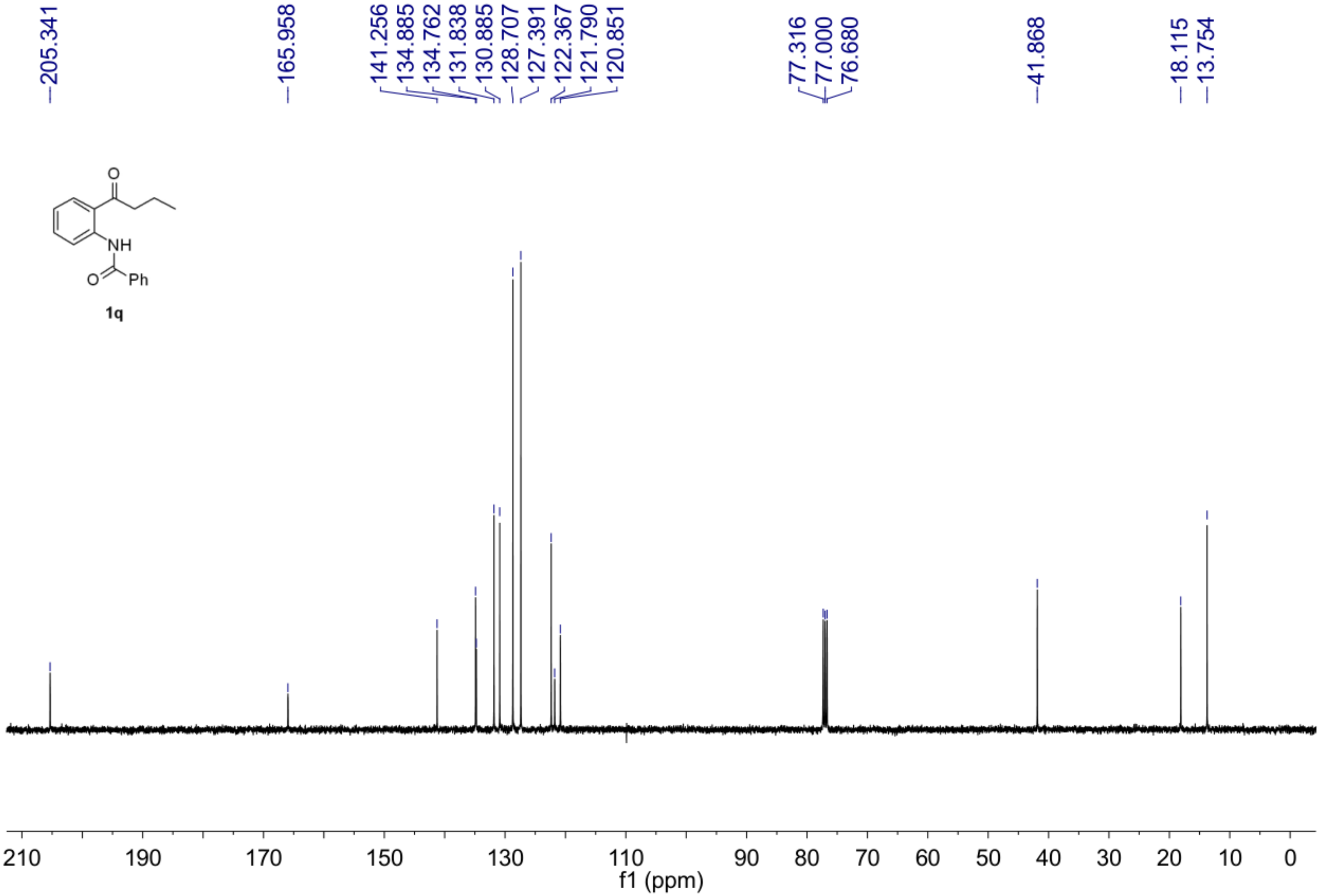


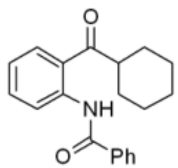
203.105
165.887
141.245
135.194
134.647
131.838
131.707
128.650
127.327
122.344
121.780
120.602
77.318
77.000
76.682
28.423
O
NH
O
Ph
1P
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



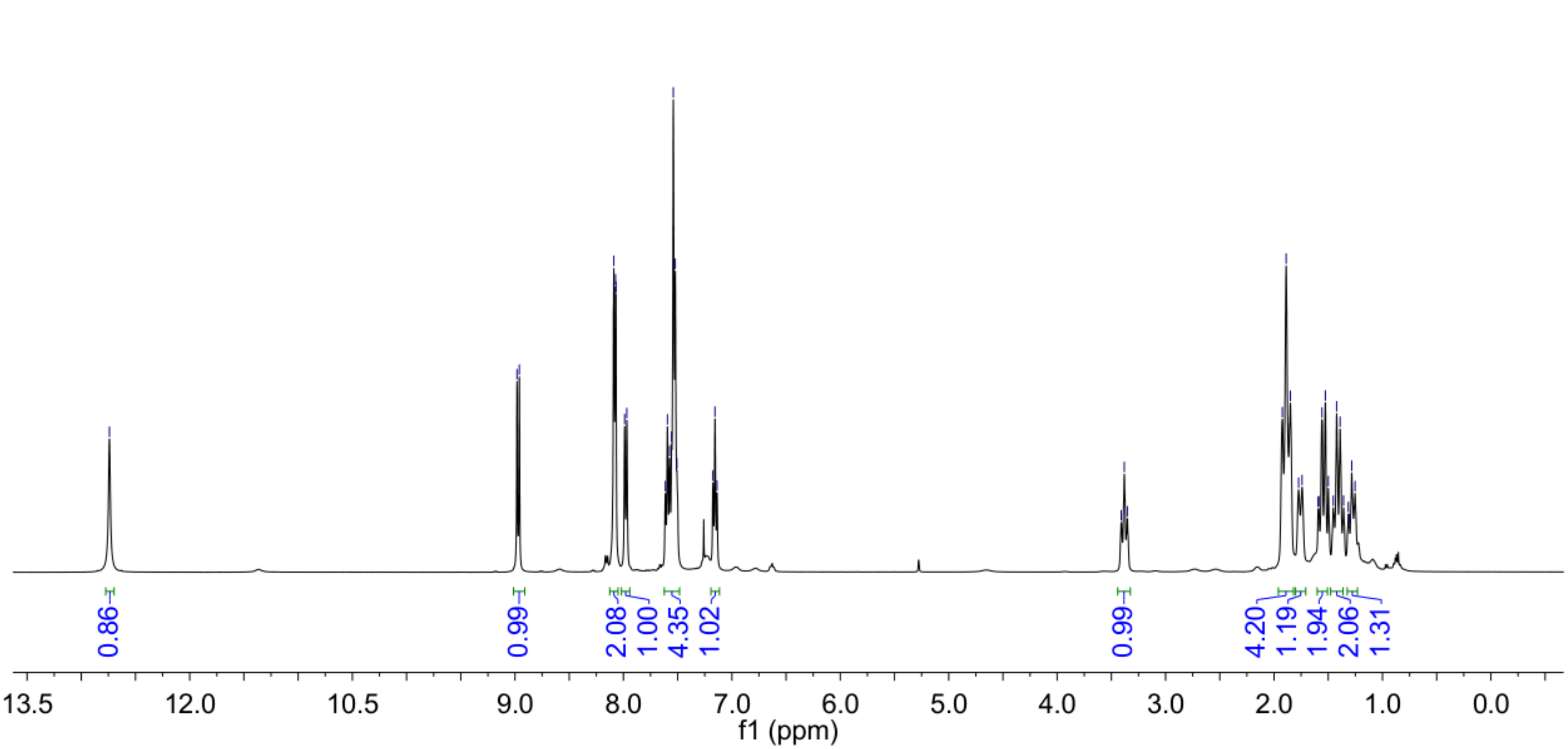
1q

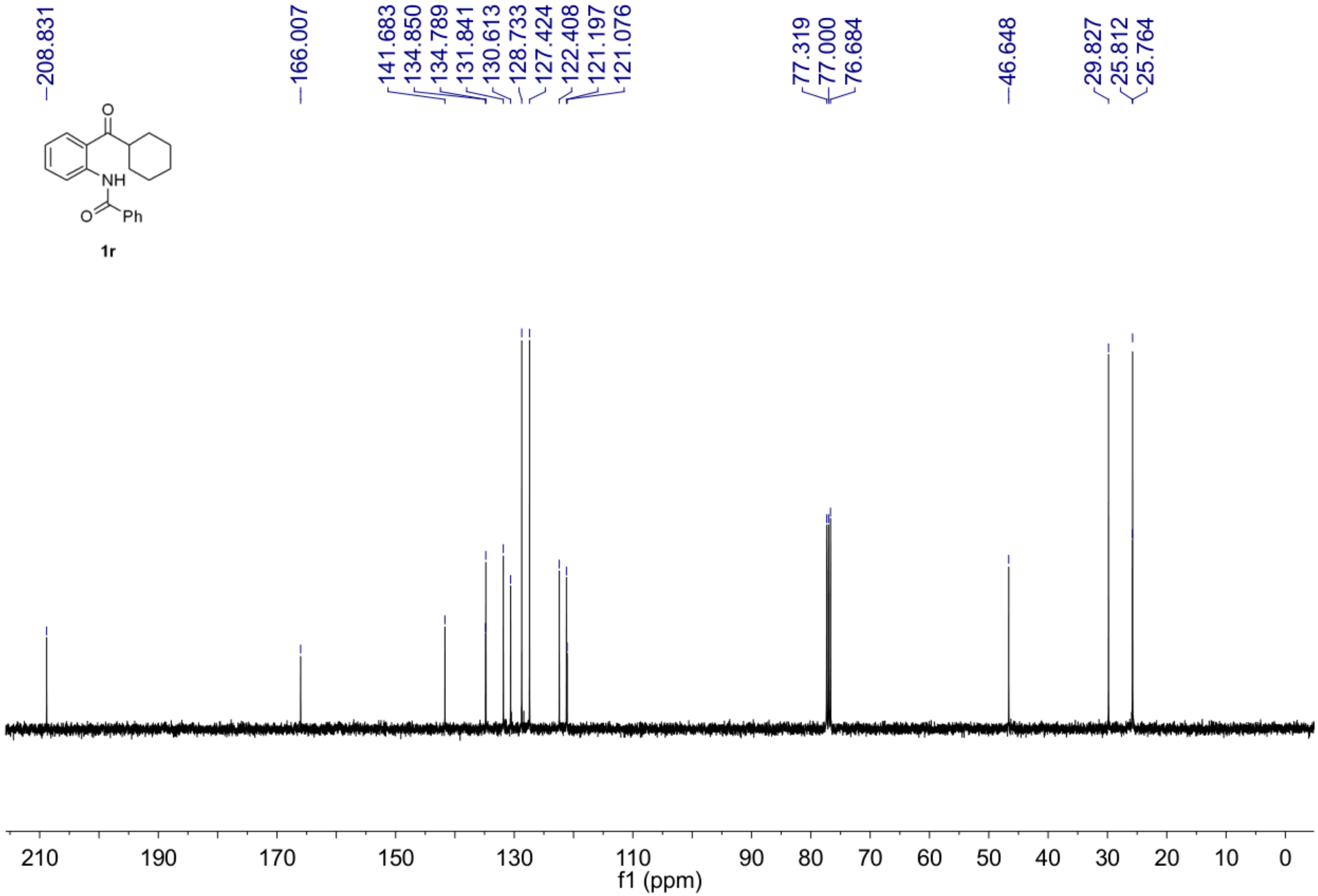

12.736
8.984
8.963
8.092
8.089
8.073
8.069
7.985
7.965
7.618
7.597
7.579
7.562
7.544
7.525
7.514
7.510
7.503
7.165
7.145
7.127
3.053
3.035
3.017
1.821
1.803
1.784
1.766
1.046
1.028
1.009
0.89
0.97
1.99
1.00
4.11
0.98
2.00
2.16
3.04
13.0
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


205.341
165.958
141.256
134.885
134.762
131.838
130.885
128.707
127.391
122.367
121.790
120.851
77.316
77.000
76.680
41.868
18.115
13.754
O
NH
O
Ph
1q
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

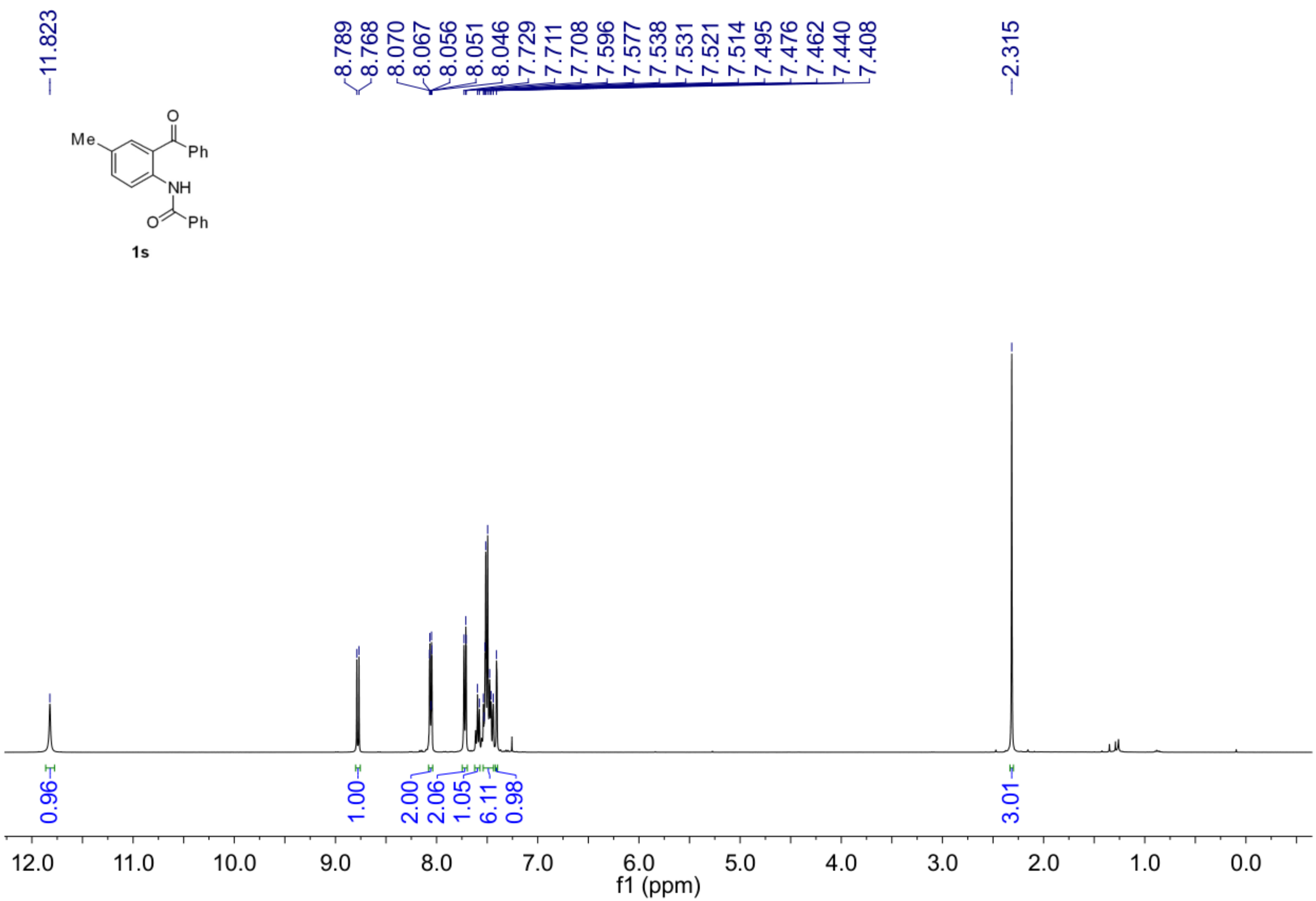

O
NH
O
Ph

1r


12.740
8.981
8.960
8.089
8.073
8.069
7.989
7.969
7.614
7.594
7.575
7.556
7.540
7.522
7.508
7.175
7.156
7.137
3.409
3.381
3.353
1.924
1.888
1.850
1.773
1.742
1.559
1.527
1.500
1.423
1.391
1.284
1.253
0.86
0.99
2.08
1.00
4.35
1.02
0.99
4.20
1.19
1.94
2.06
1.31
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

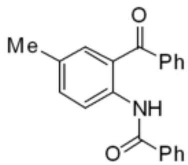


208.831
166.007
141.683
134.850
134.789
131.841
130.613
128.733
127.424
122.408
121.197
121.076
77.319
77.000
76.684
46.648
29.827
25.812
25.764
O
NH
O
Ph
1r
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

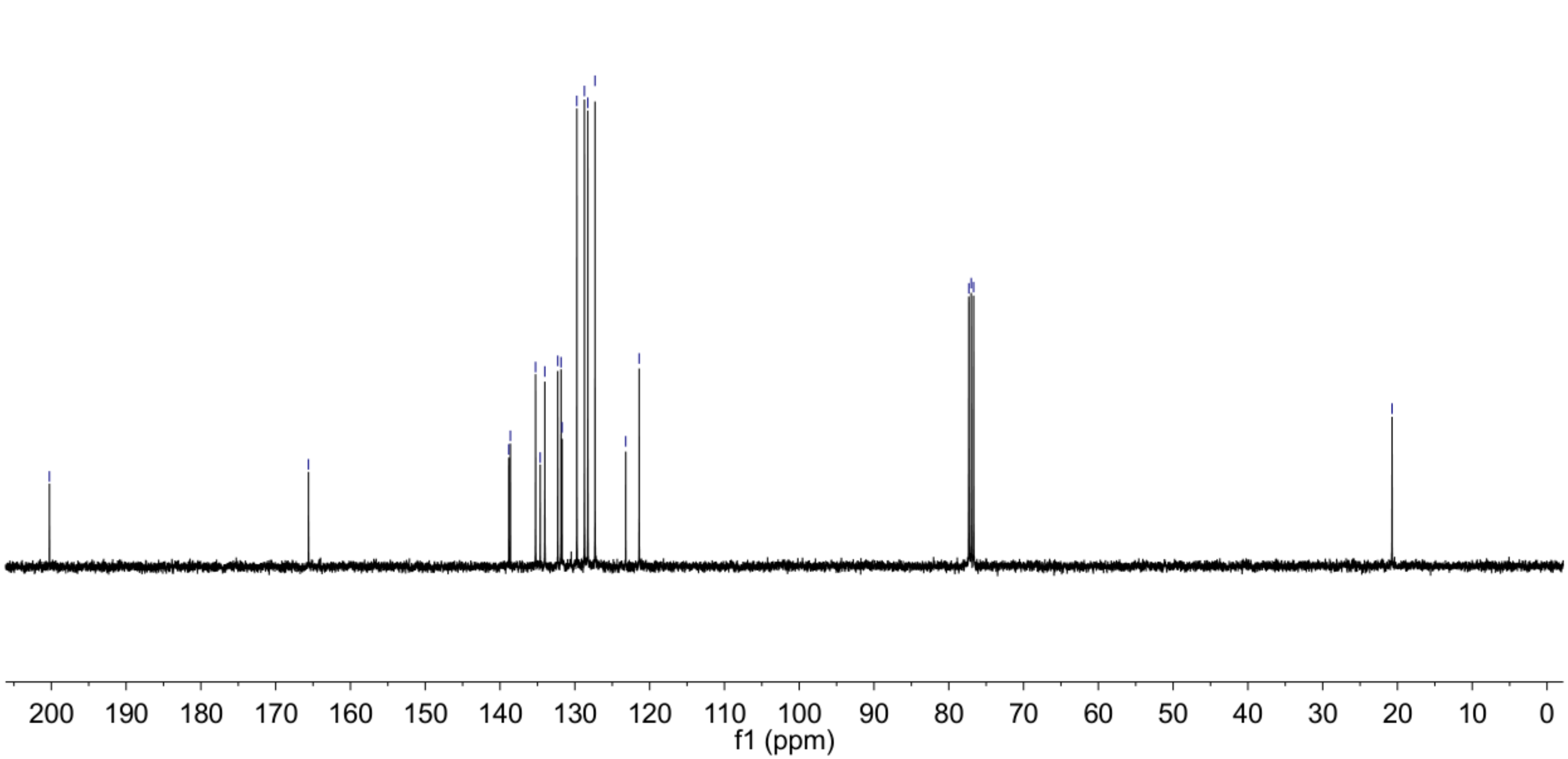


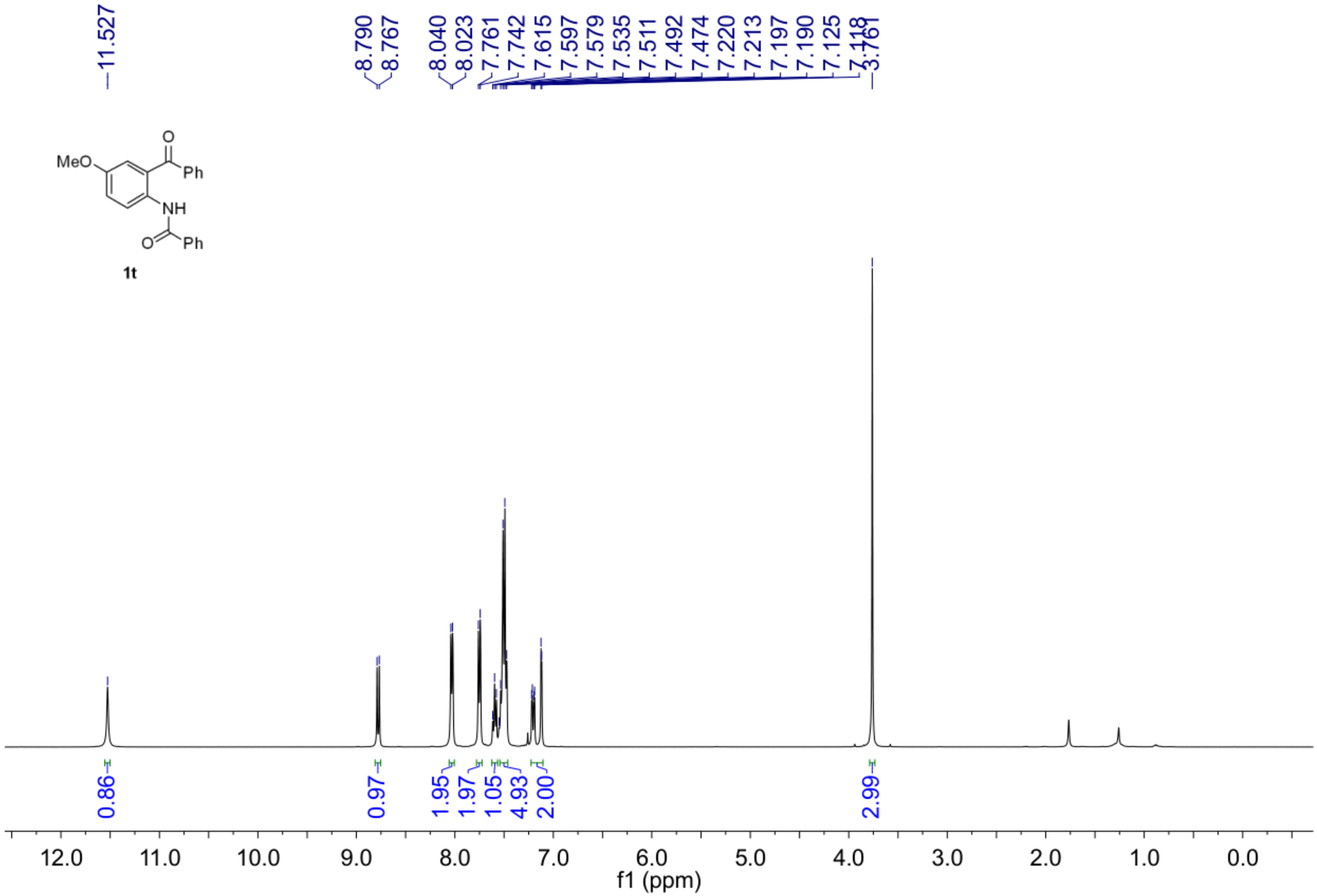
11.823
8.789
8.768
8.070
8.067
8.056
8.051
8.046
7.729
7.711
7.708
7.596
7.577
7.538
7.531
7.521
7.514
7.495
7.476
7.462
7.440
7.408
2.315
Me
O
Ph
NH
O
Ph
0.96
1.00
2.00
2.06
1.05
6.11
0.98
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

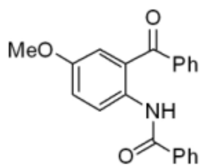
1s


Me
O
Ph
NH
O
Ph

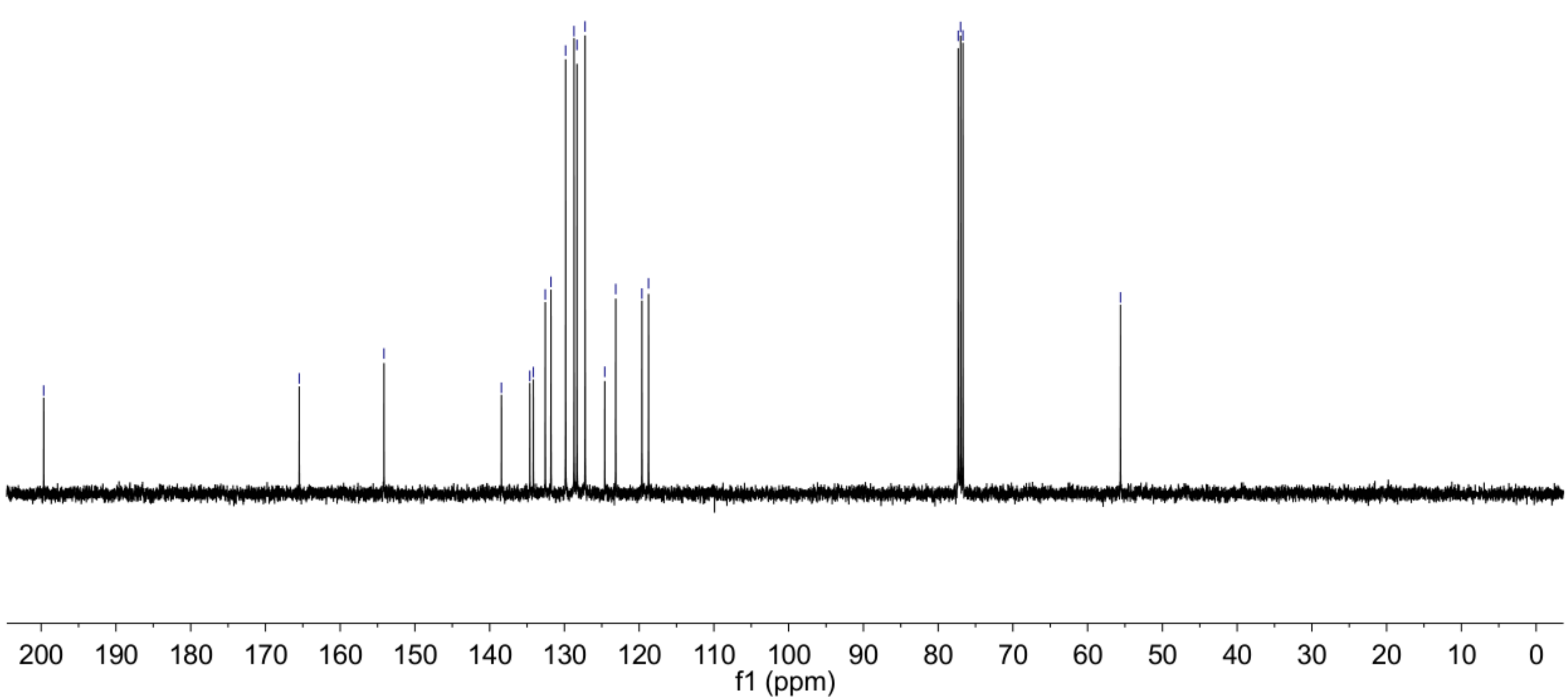
1s


200.257
165.616
138.830
138.624
135.252
134.629
134.015
132.287
131.847
131.710
129.733
128.715
128.263
127.300
123.194
121.397
77.318
77.000
76.683
20.723
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.527
8.790
8.767
8.040
8.023
7.761
7.742
7.615
7.597
7.579
7.535
7.511
7.492
7.474
7.220
7.213
7.197
7.190
7.125
7.118
3.761
MeO
O
Ph
NH
O
Ph
1t
0.86
0.97
1.95
1.97
1.05
4.93
2.00
2.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


MeO
O
Ph
NH
O
Ph

1t


199.660
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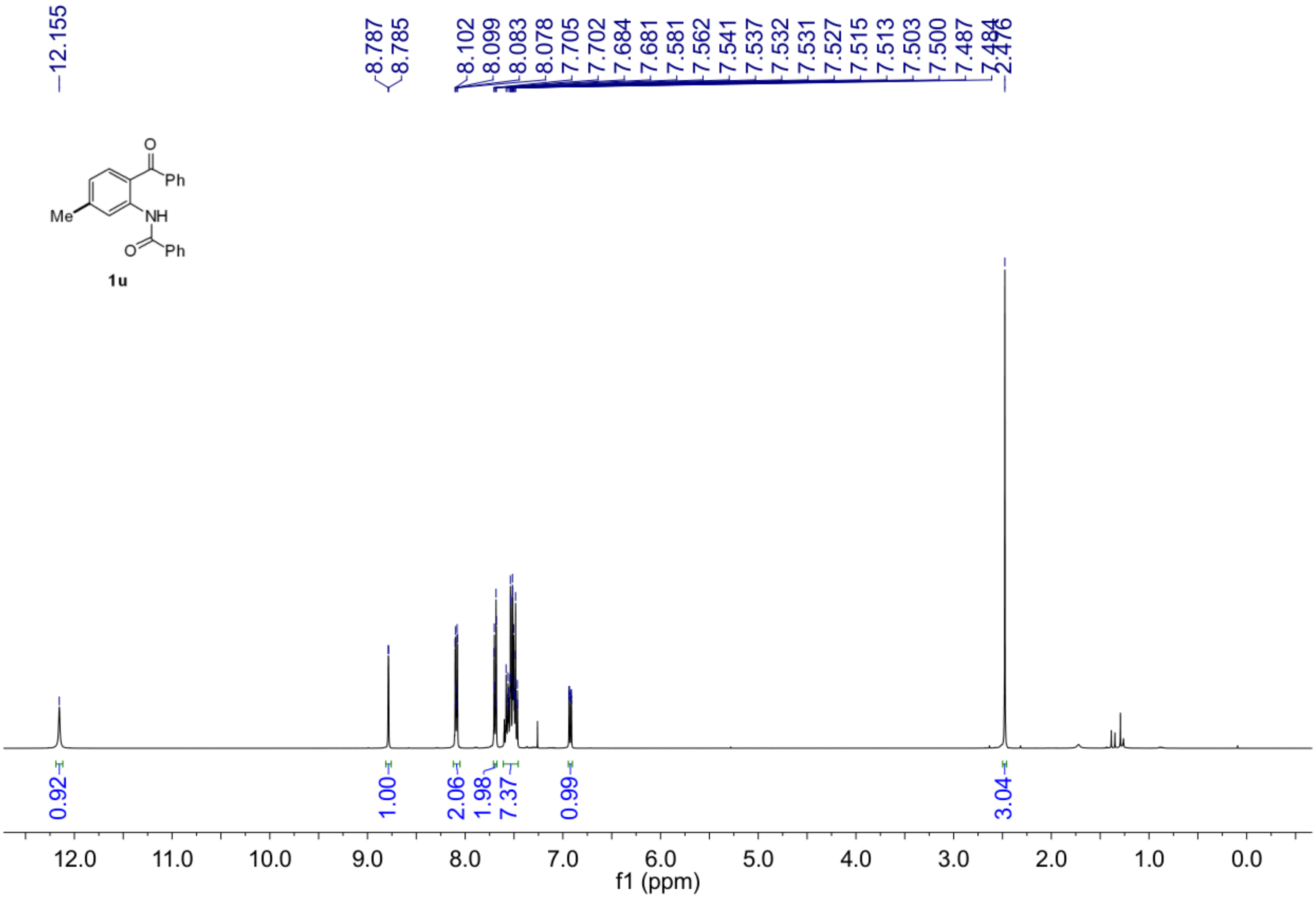
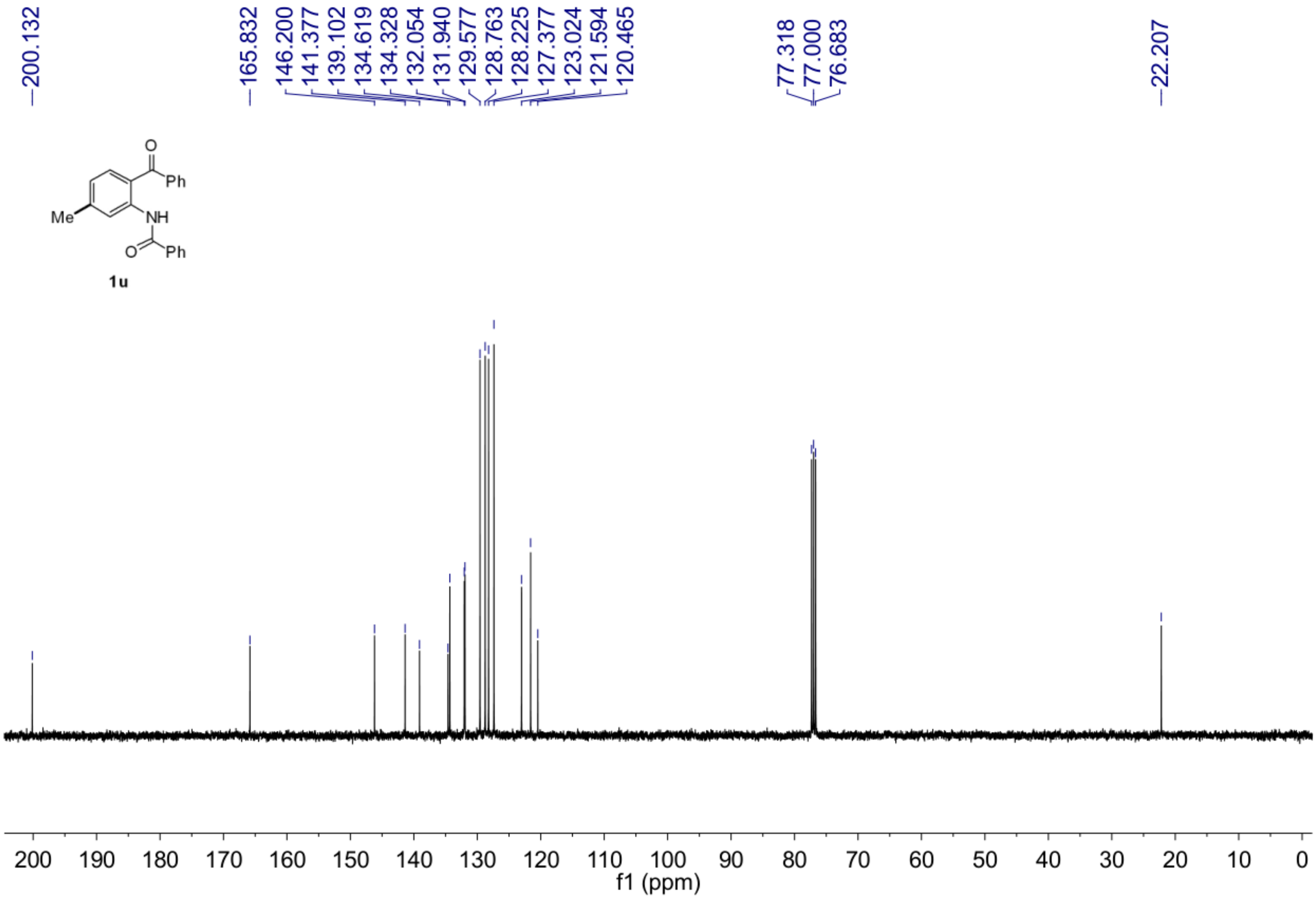
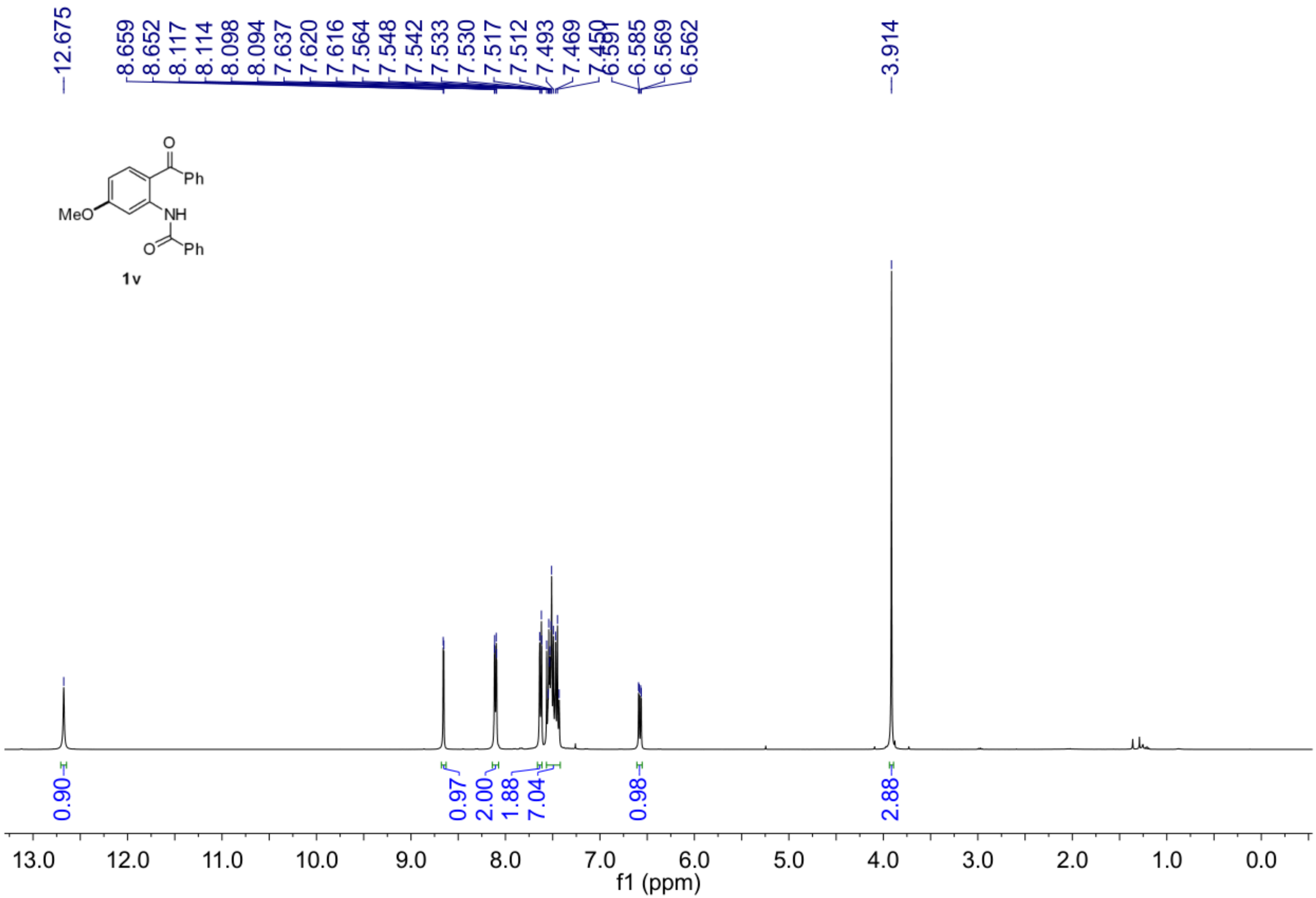
154.142
138.428
134.629
134.160
132.563
131.801
129.835
128.716
128.328
127.232
124.606
123.139
119.631
118.750
77.318
77.000
76.682
55.610
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Ph
Me
NH
O
Ph
1u
12.155
8.787
8.785
8.102
8.099
8.083
8.078
7.705
7.702
7.684
7.681
7.581
7.562
7.541
7.537
7.532
7.531
7.527
7.515
7.513
7.503
7.500
7.487
7.484
2.476
0.92
1.00
2.06
1.98
7.37
0.99
3.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



200.132
165.832
146.200
141.377
139.102
134.619
134.328
132.054
131.940
129.577
128.763
128.225
127.377
123.024
121.594
120.465
77.318
77.000
76.683
22.207
O
Ph
Me
NH
O
Ph
1u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



12.675
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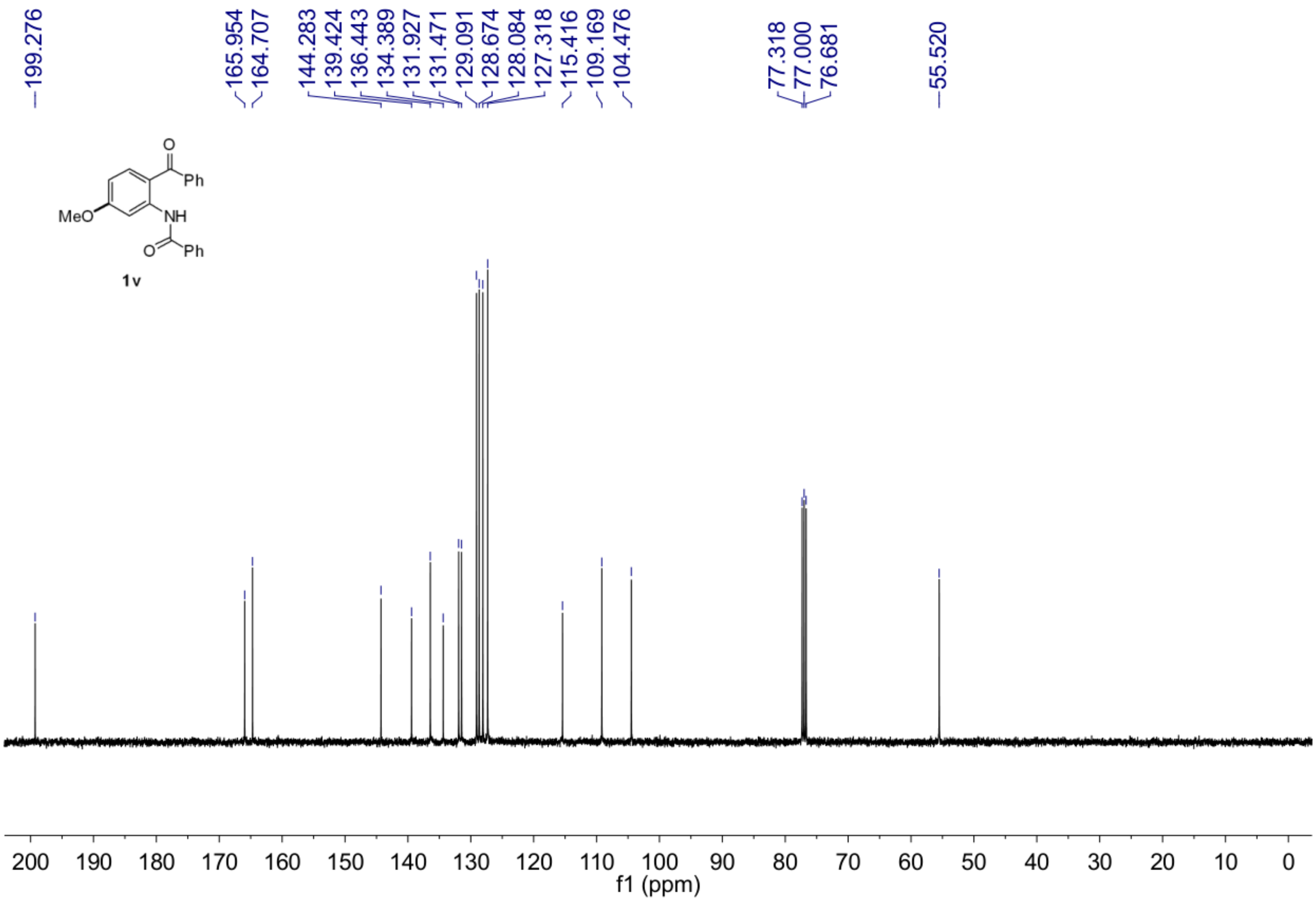
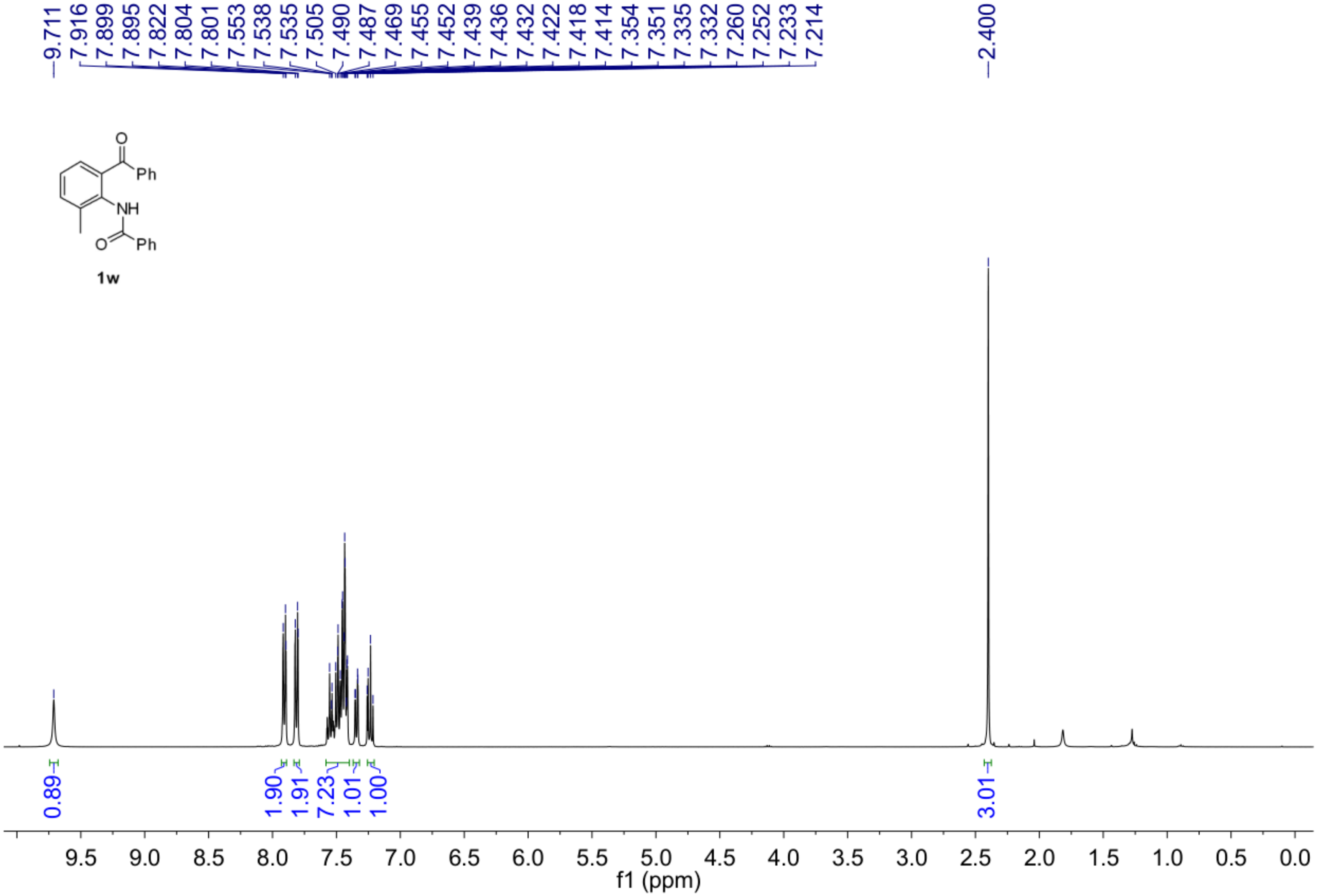
8.117
8.114
8.098
8.094
7.637
7.620
7.616
7.564
7.548
7.542
7.533
7.530
7.517
7.512
7.493
7.469
7.450
6.591
6.585
6.569
6.562
3.914
O
Ph
MeO
NH
O
Ph
1v
0.90
0.97
2.00
1.88
7.04
0.98
2.88
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



199.276
165.954
164.707
144.283
139.424
136.443
134.389
131.927
131.471
129.091
128.674
128.084
127.318
115.416
109.169
104.476
77.318
77.000
76.681
55.520
O
Ph
MeO
NH
O
Ph
1v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.822
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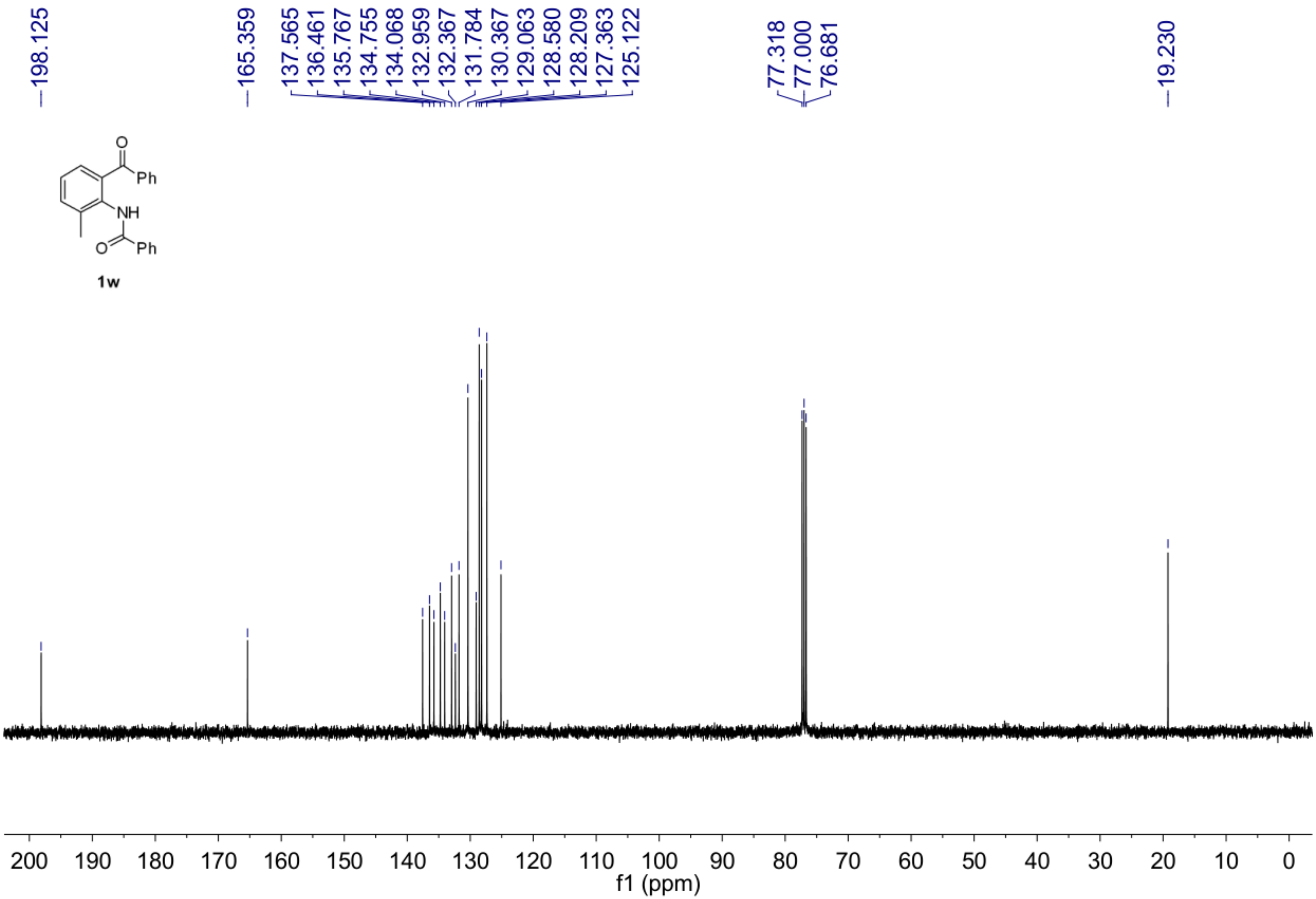
7.801
7.553
7.538
7.535
7.505
7.490
7.487
7.469
7.455
7.452
7.439
7.436
7.432
7.422
7.418
7.414
7.354
7.351
7.335
7.332
7.260
7.252
7.233
7.214
2.400
O
Ph
NH
O
Ph
1w
0.89
1.90
1.91
7.23
1.01
1.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.068
132.959
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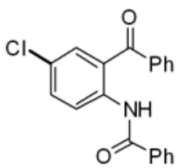
131.784
130.367
129.063
128.580
128.209
127.363
125.122
77.318
77.000
76.681
19.230
O
Ph
NH
O
Ph
1w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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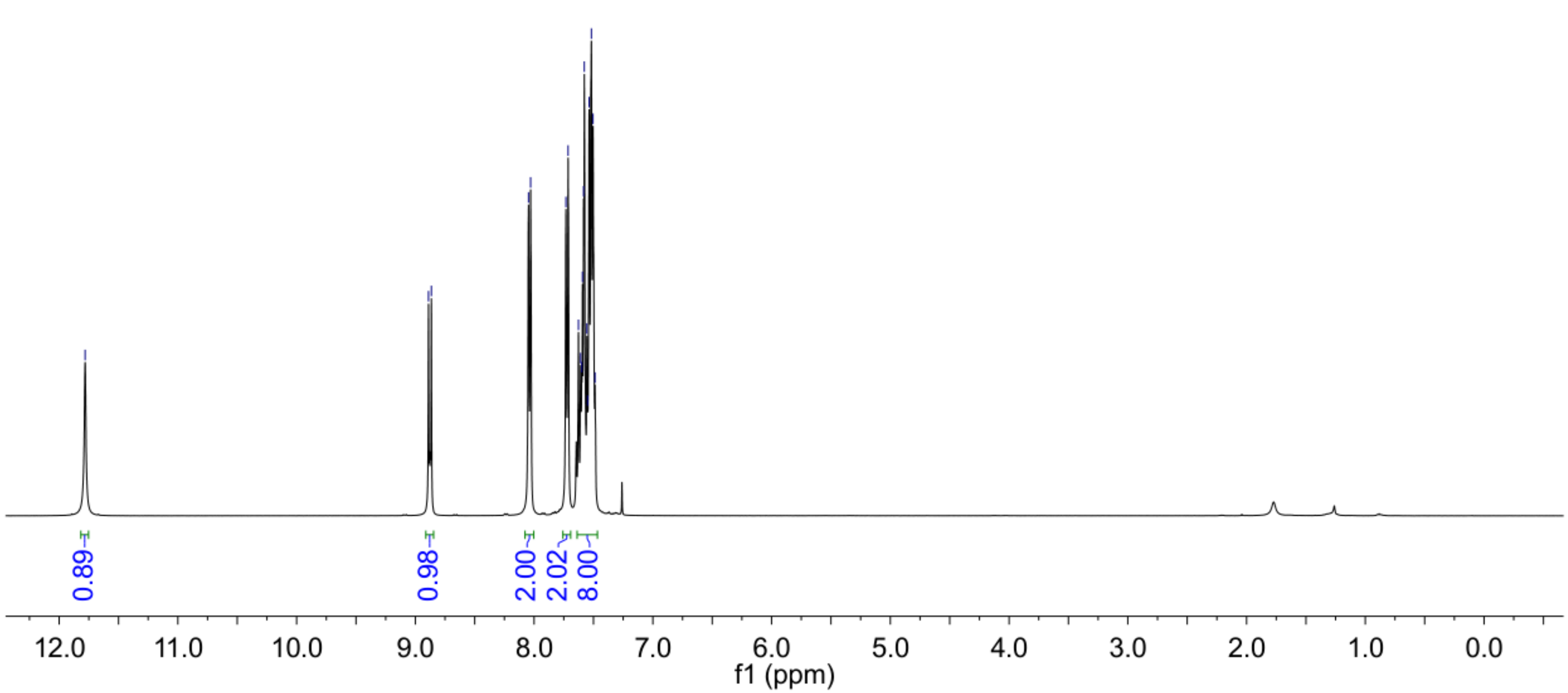
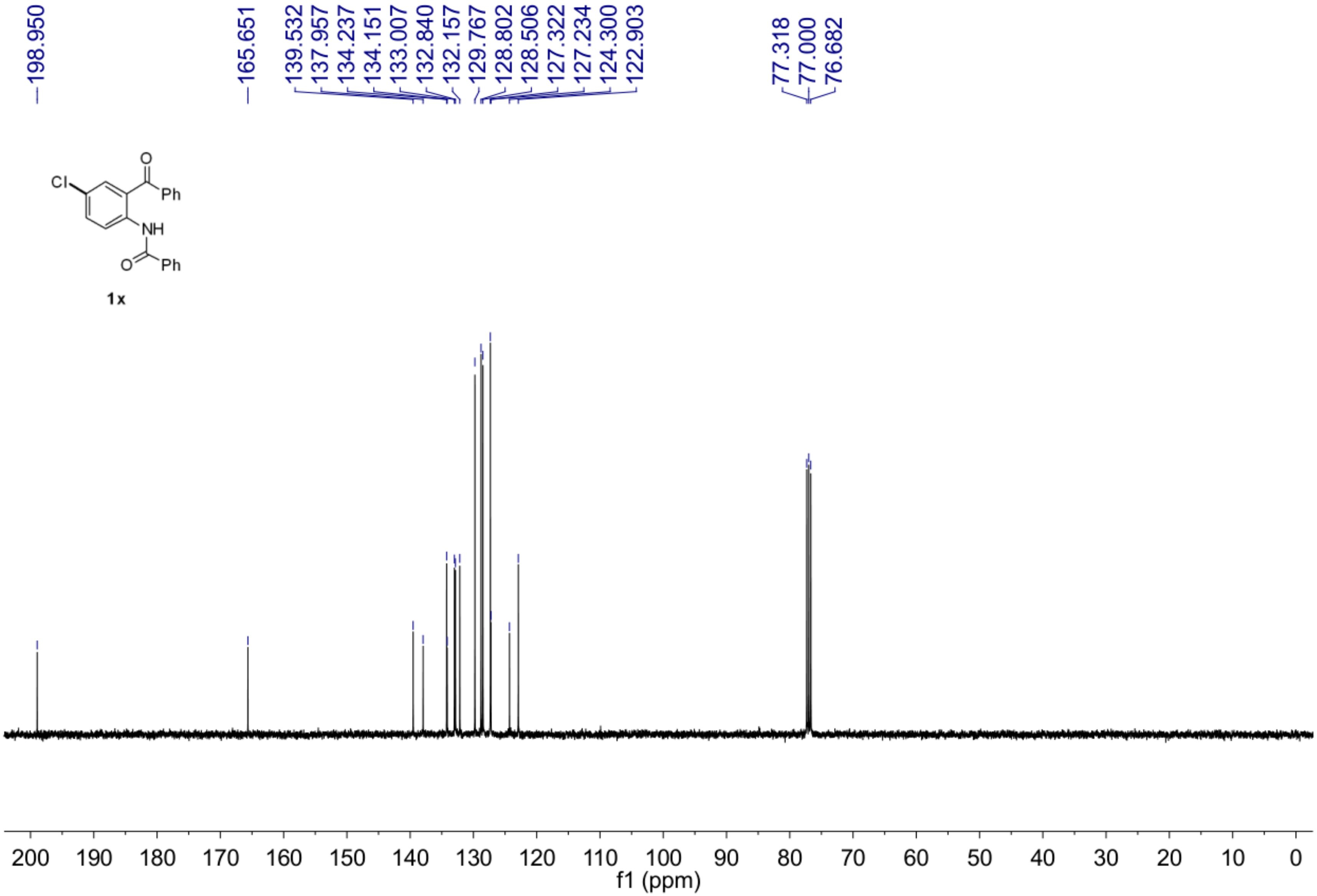

11.781
8.889
8.865
8.047
8.030
7.732
7.714
7.627
7.608
7.599
7.593
7.583
7.577
7.556
7.549
7.537
7.518
7.504
7.487
0.89
0.98
2.00
2.02
8.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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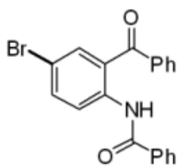
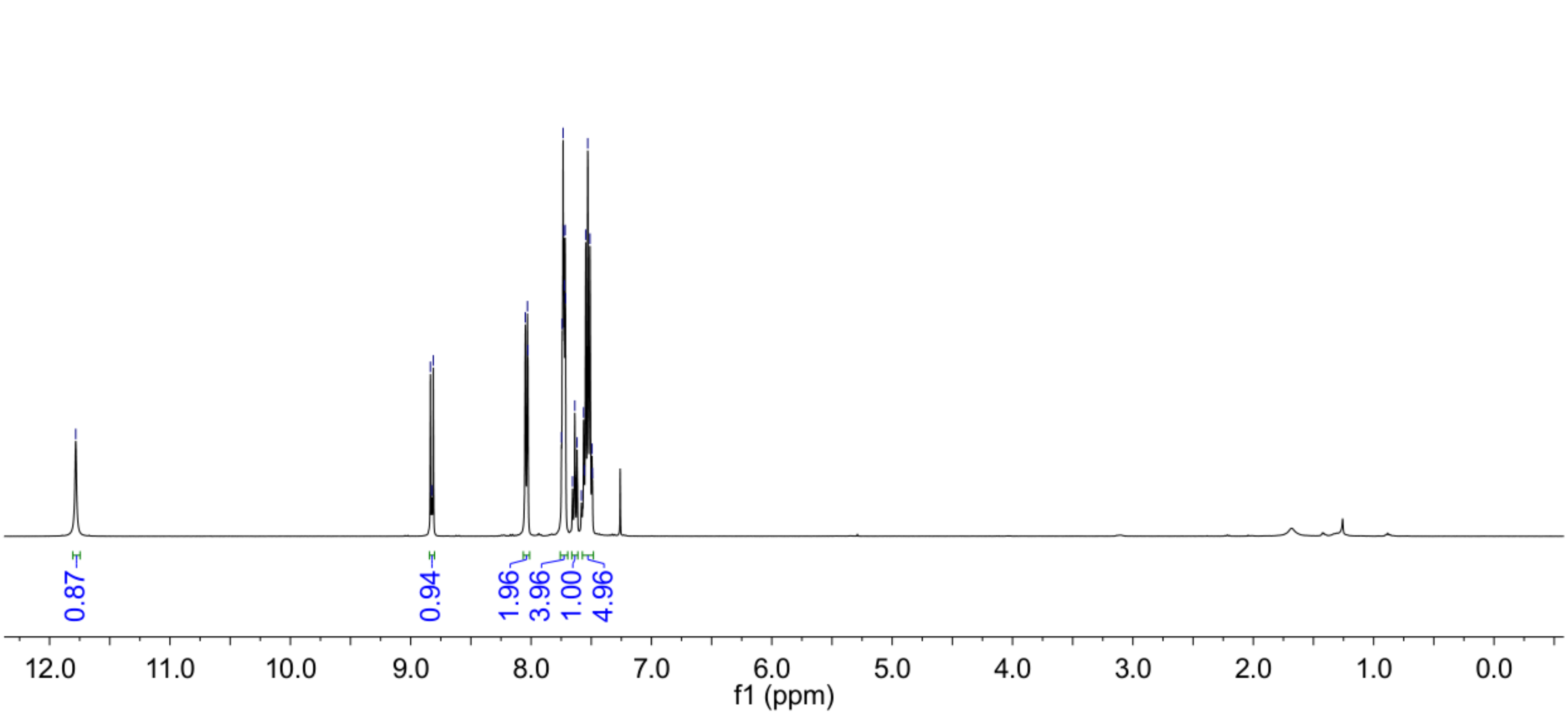
133.007
132.840
132.157
129.767
128.802
128.506
127.322
127.234
124.300
122.903
77.318
77.000
76.682
Cl
O
Ph
NH
O
Ph
1x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

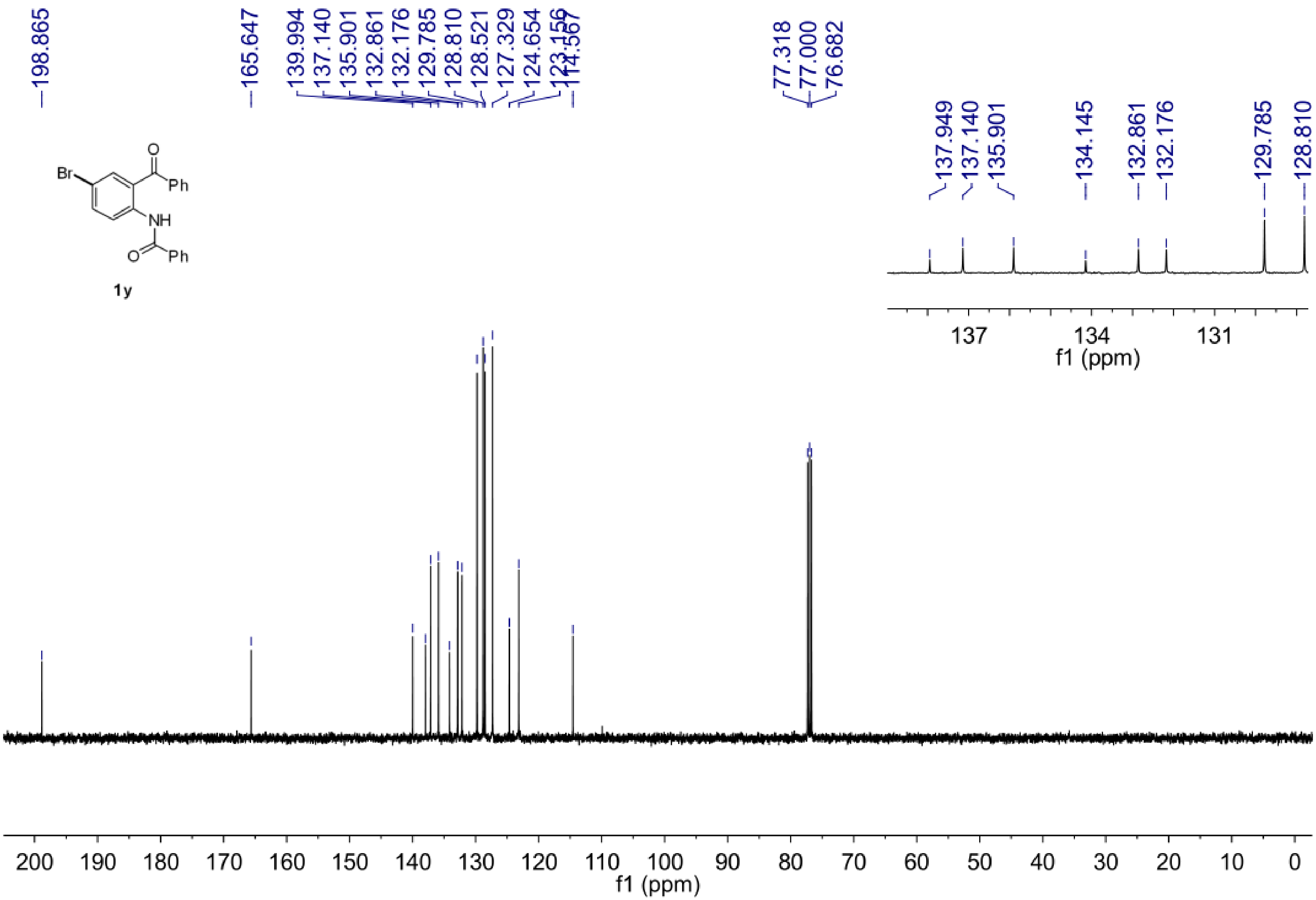


Br
O
Ph
NH
O
Ph

1y



11.783
8.836
8.826
8.812
8.048
8.030
8.027
7.747
7.741
7.734
7.728
7.724
7.717
7.714
7.655
7.637
7.618
7.582
7.563
7.557
7.546
7.529
7.511
7.494
7.490
0.87
0.94
1.96
3.96
1.00
4.96
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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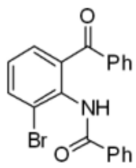
165.647
139.994
137.140
135.901
132.861
132.176
129.785
128.810
128.521
127.329
124.654
123.156
114.567
77.318
77.000
76.682
137.949
137.140
135.901
134.145
132.861
132.176
129.785
128.810
137
134
131
f1 (ppm)
Br
O
Ph
NH
O
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1y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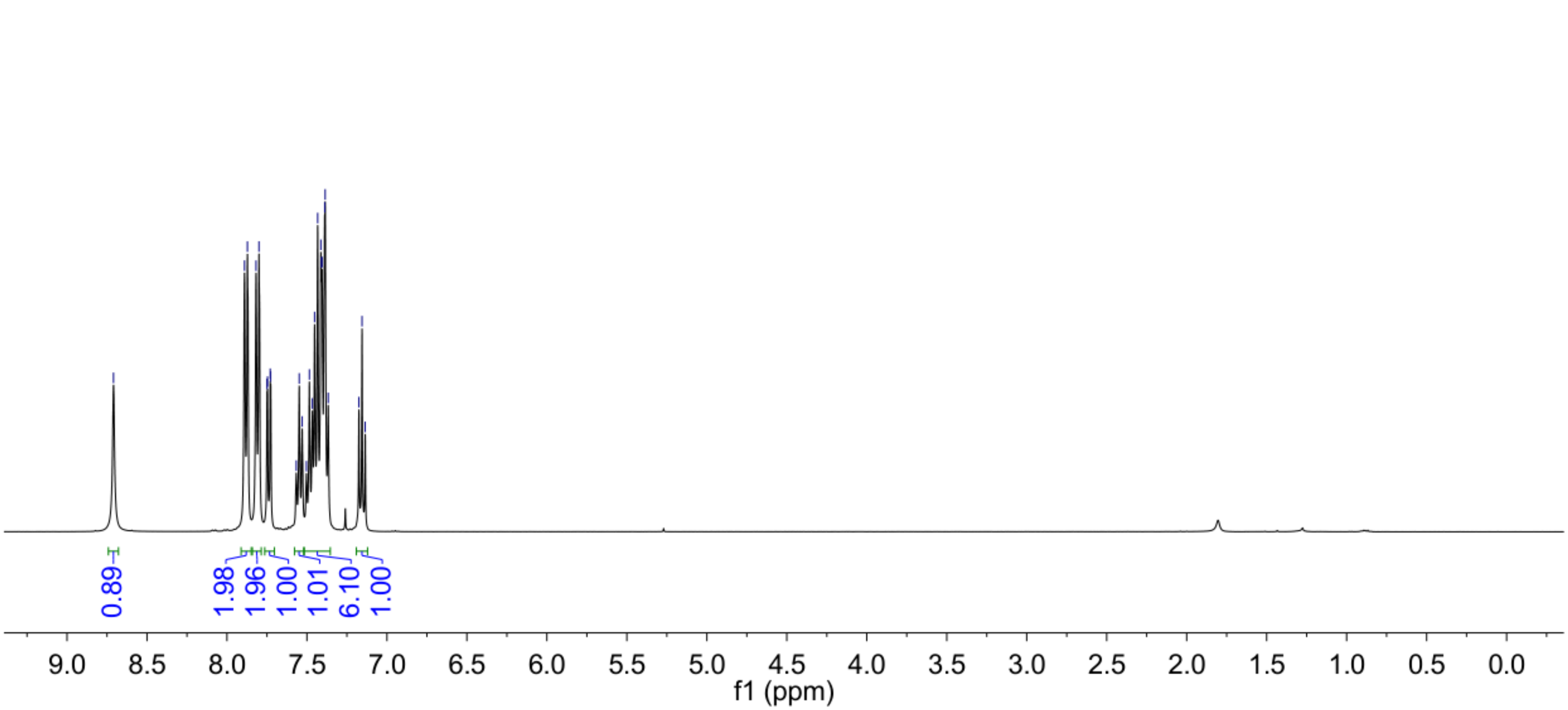
Ph
NH
Br
O
Ph

1z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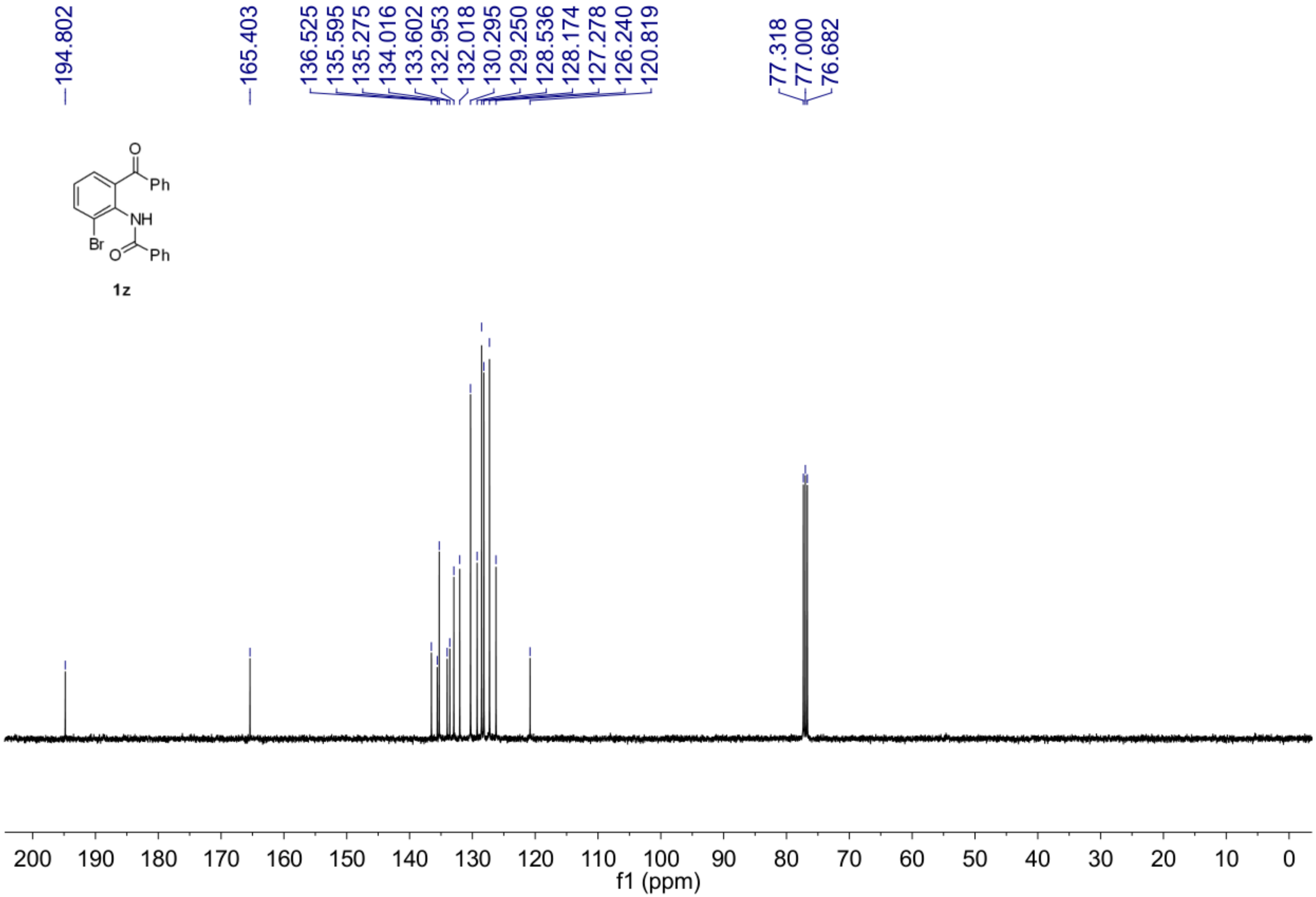
7.872
7.818
7.800
7.749
7.747
7.729
7.727
7.567
7.548
7.530
7.503
7.485
7.466
7.452
7.433
7.413
7.410
7.406
7.389
7.386
7.367
7.175
7.156
7.136
0.89
1.98
1.96
1.00
1.01
6.10
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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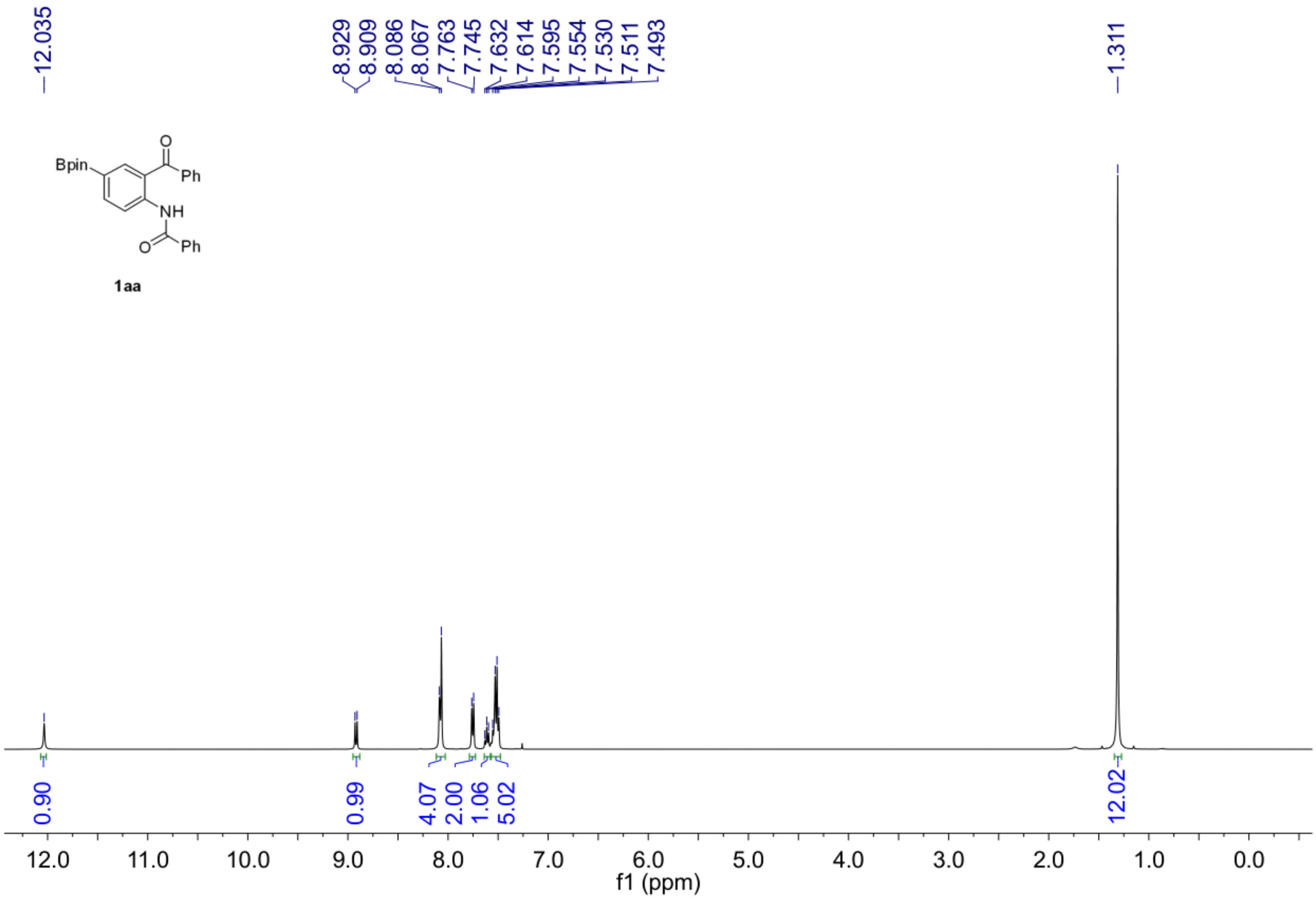
133.602
132.953
132.018
130.295
129.250
128.536
128.174
127.278
126.240
120.819
77.318
77.000
76.682
O
Ph
NH
Br
O
Ph
1z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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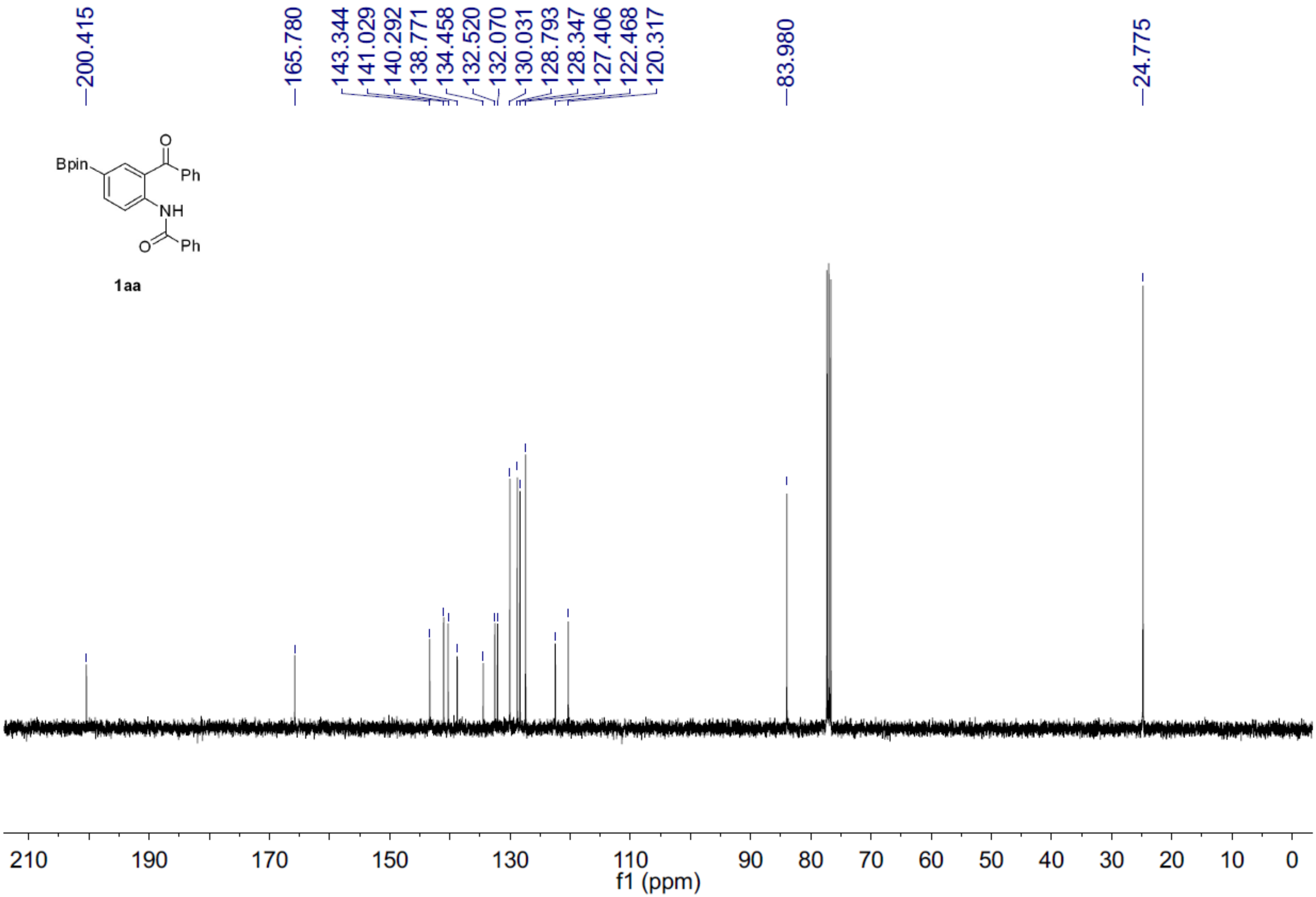
8.929
8.909
8.086
8.067
7.763
7.745
7.632
7.614
7.595
7.554
7.530
7.511
7.493
1.311
Bpin
O
Ph
NH
O
Ph
1aa
0.90
0.99
4.07
2.00
1.06
5.02
12.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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165.780
143.344
141.029
140.292
138.771
134.458
132.520
132.070
130.031
128.793
128.347
127.406
122.468
120.317
83.980
24.775
Bpin
O
Ph
NH
O
Ph
210
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170
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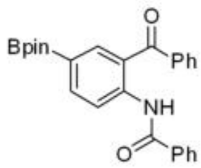
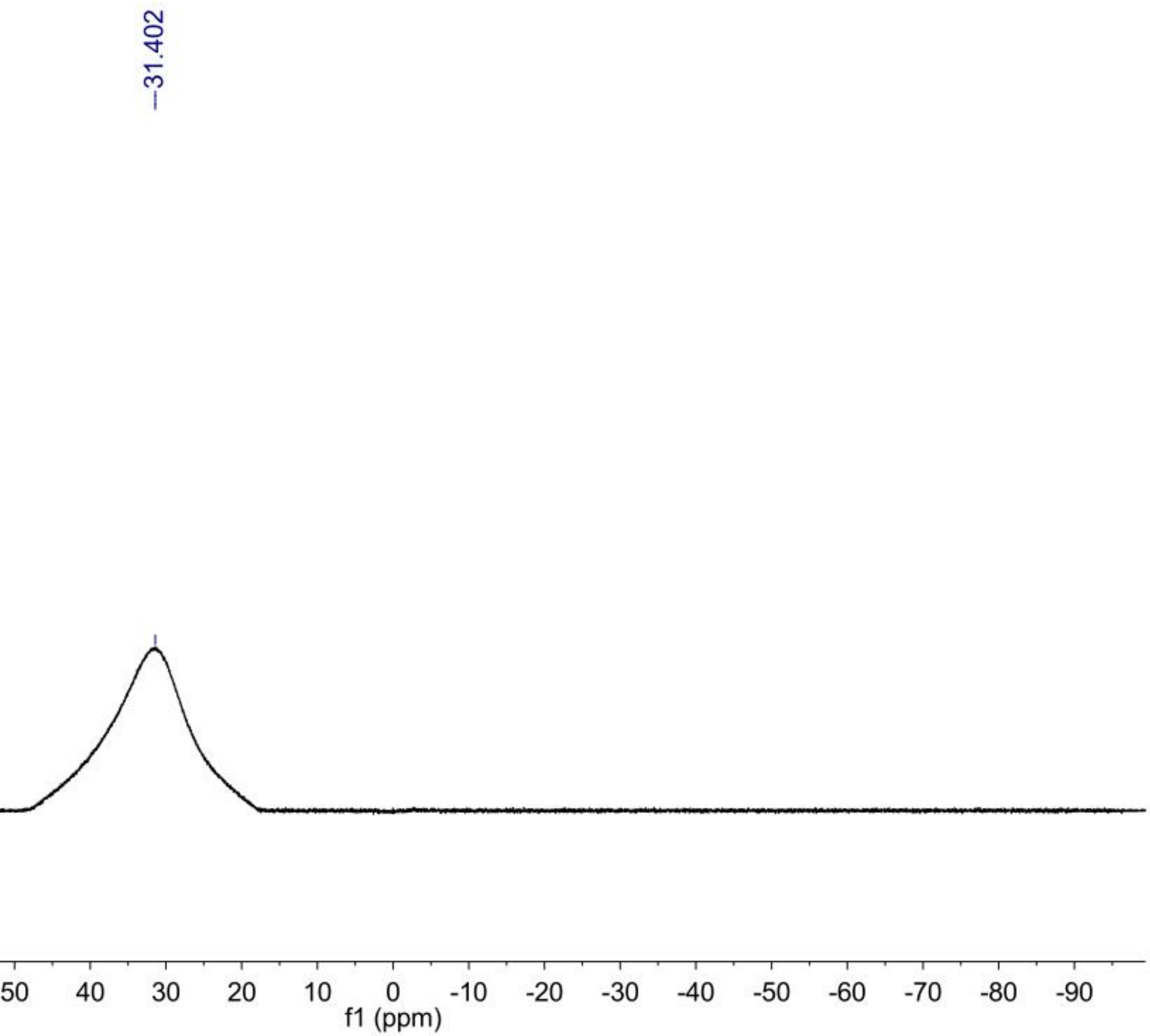
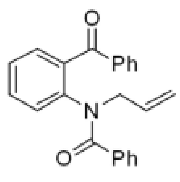
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1aa

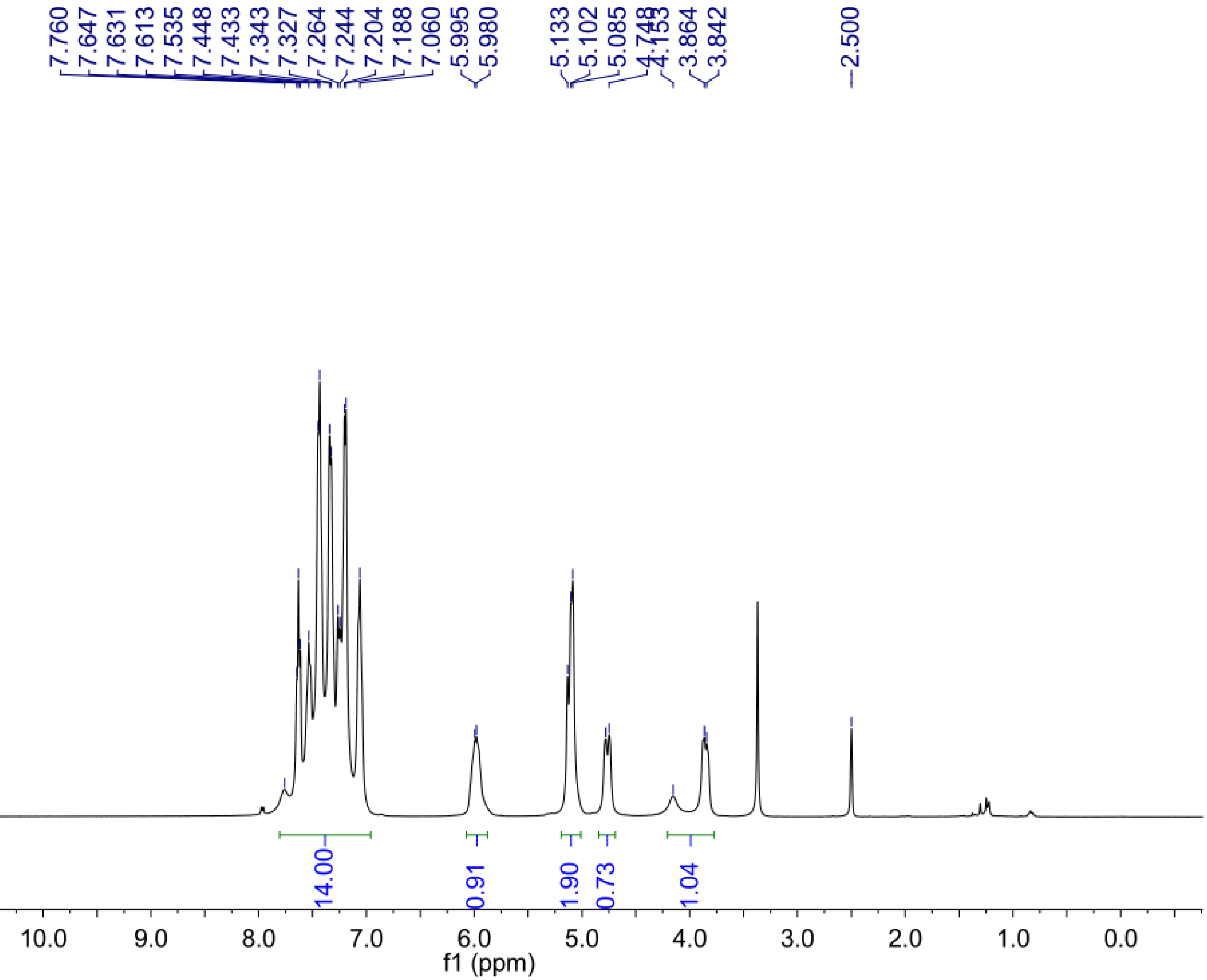

Bpin
O
Ph
NH
O
Ph

1aa


31.402
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


O
Ph
N
O
Ph

1ab
DMSO-D$_6$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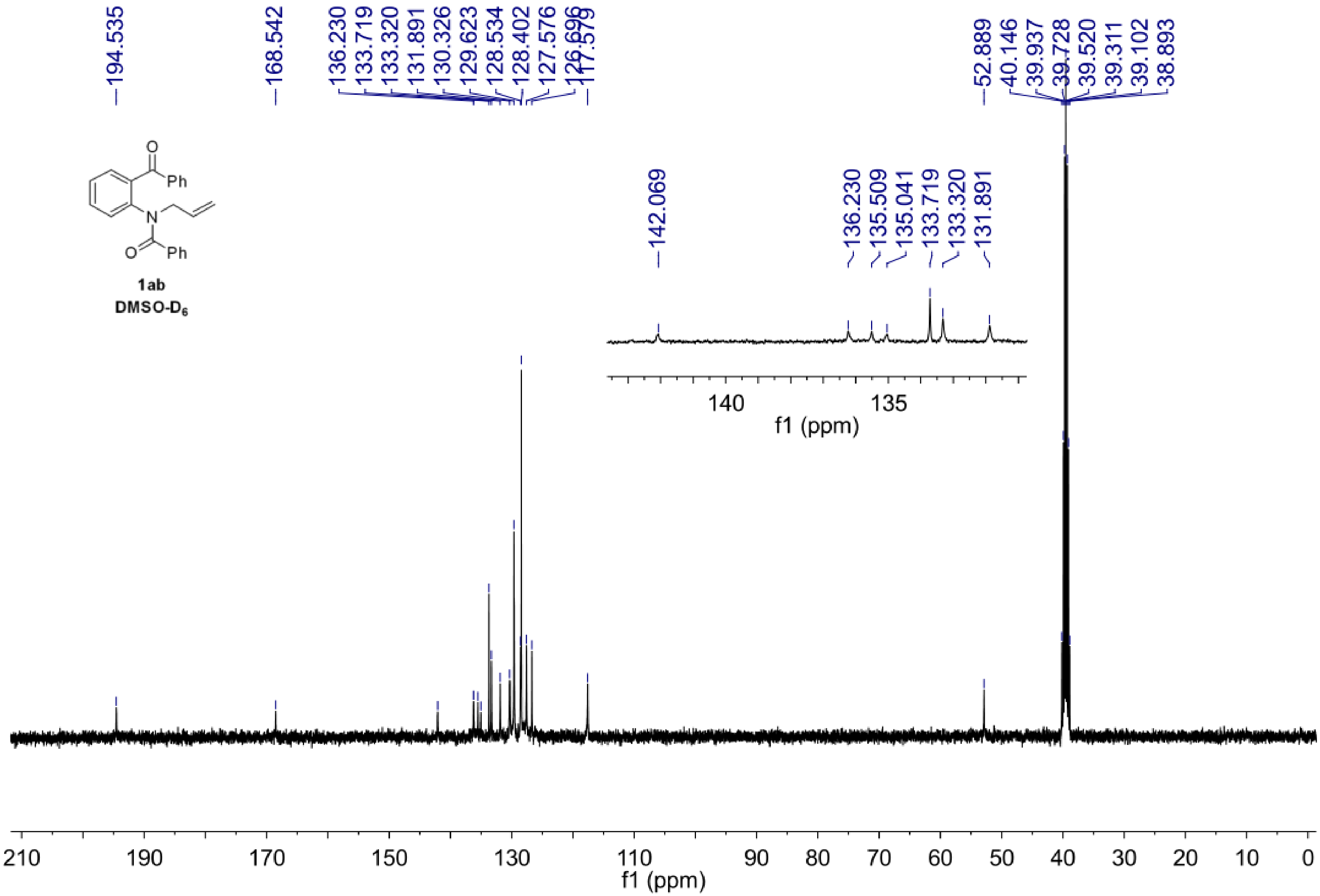
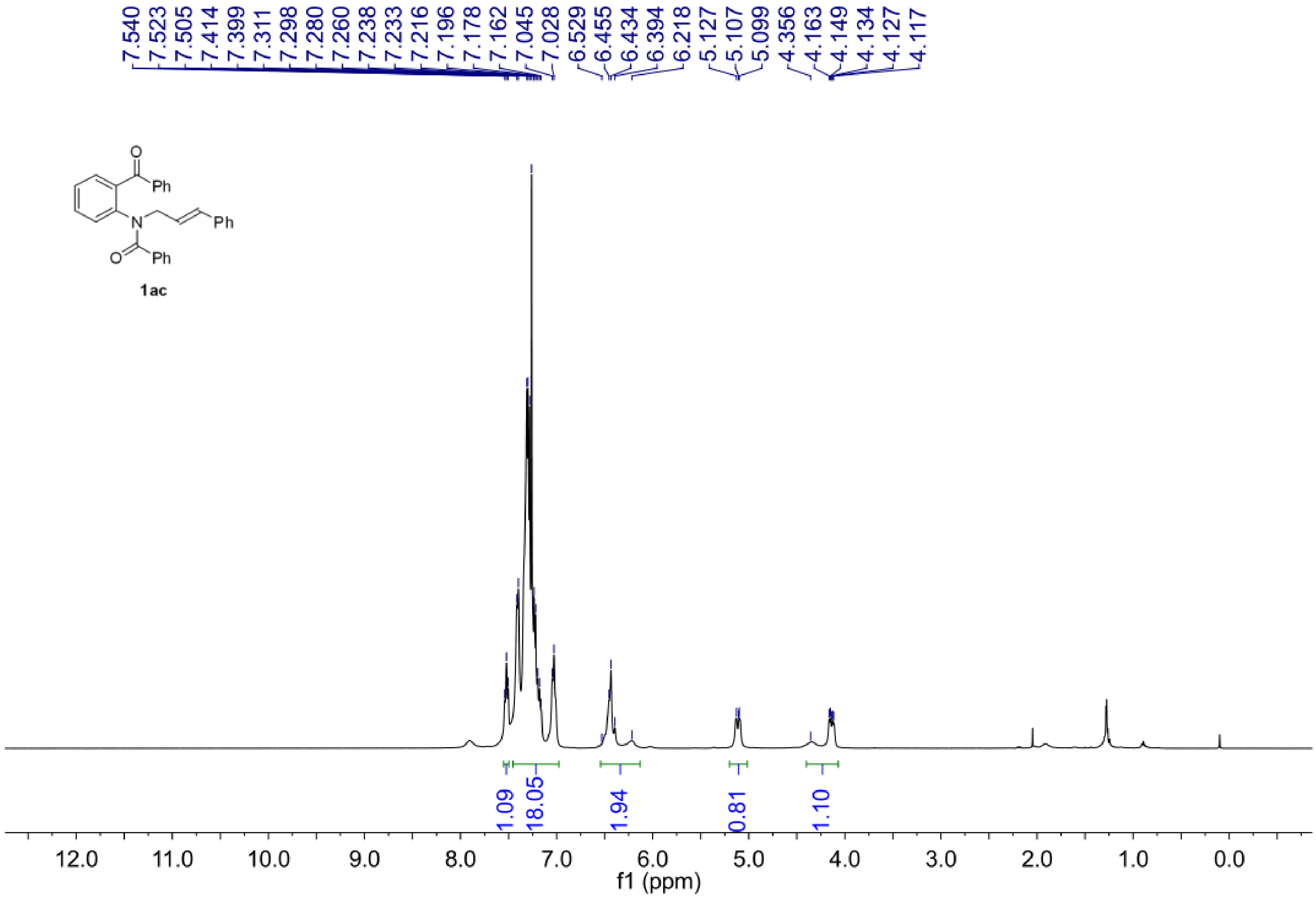
7.631
7.613
7.535
7.448
7.433
7.343
7.327
7.264
7.244
7.204
7.188
7.060
5.995
5.980
5.133
5.102
5.085
4.748
4.153
3.864
3.842
2.500
14.00
0.91
1.90
0.73
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


194.535
168.542
136.230
133.719
133.320
131.891
130.326
129.623
128.534
128.402
127.576
126.696
117.579
52.889
40.146
39.937
39.728
39.520
39.311
39.102
38.893
O
Ph
N
O
Ph
1ab
DMSO-D$_6$
142.069
136.230
135.509
135.041
133.719
133.320
131.891
140
135
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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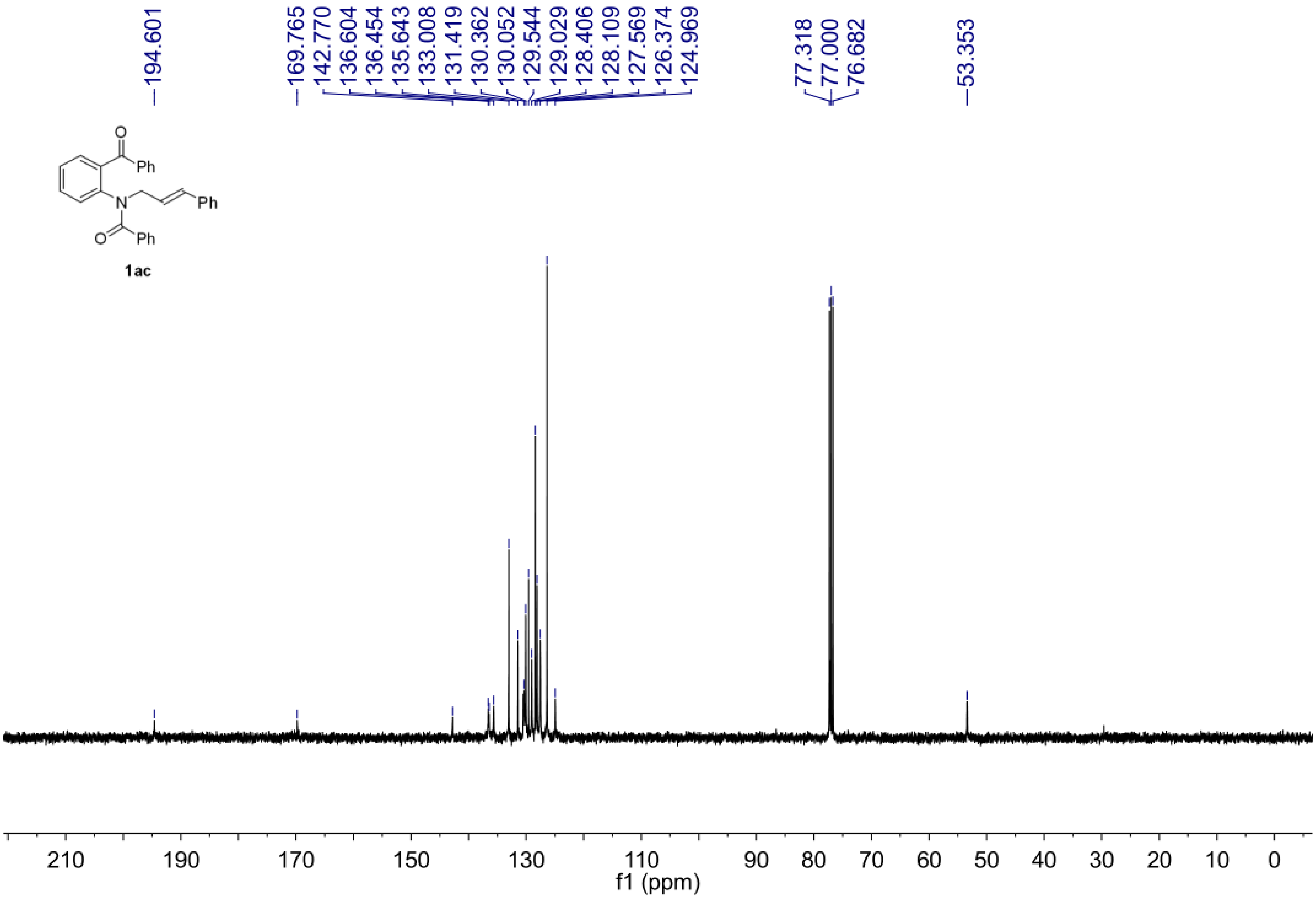
7.523
7.505
7.414
7.399
7.311
7.298
7.280
7.260
7.238
7.233
7.216
7.196
7.178
7.162
7.045
7.028
6.529
6.455
6.434
6.394
6.218
5.127
5.107
5.099
4.356
4.163
4.149
4.134
4.127
4.117
O
Ph
N
Ph
O
Ph
1ac
1.09
18.05
1.94
0.81
1.10
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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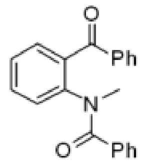
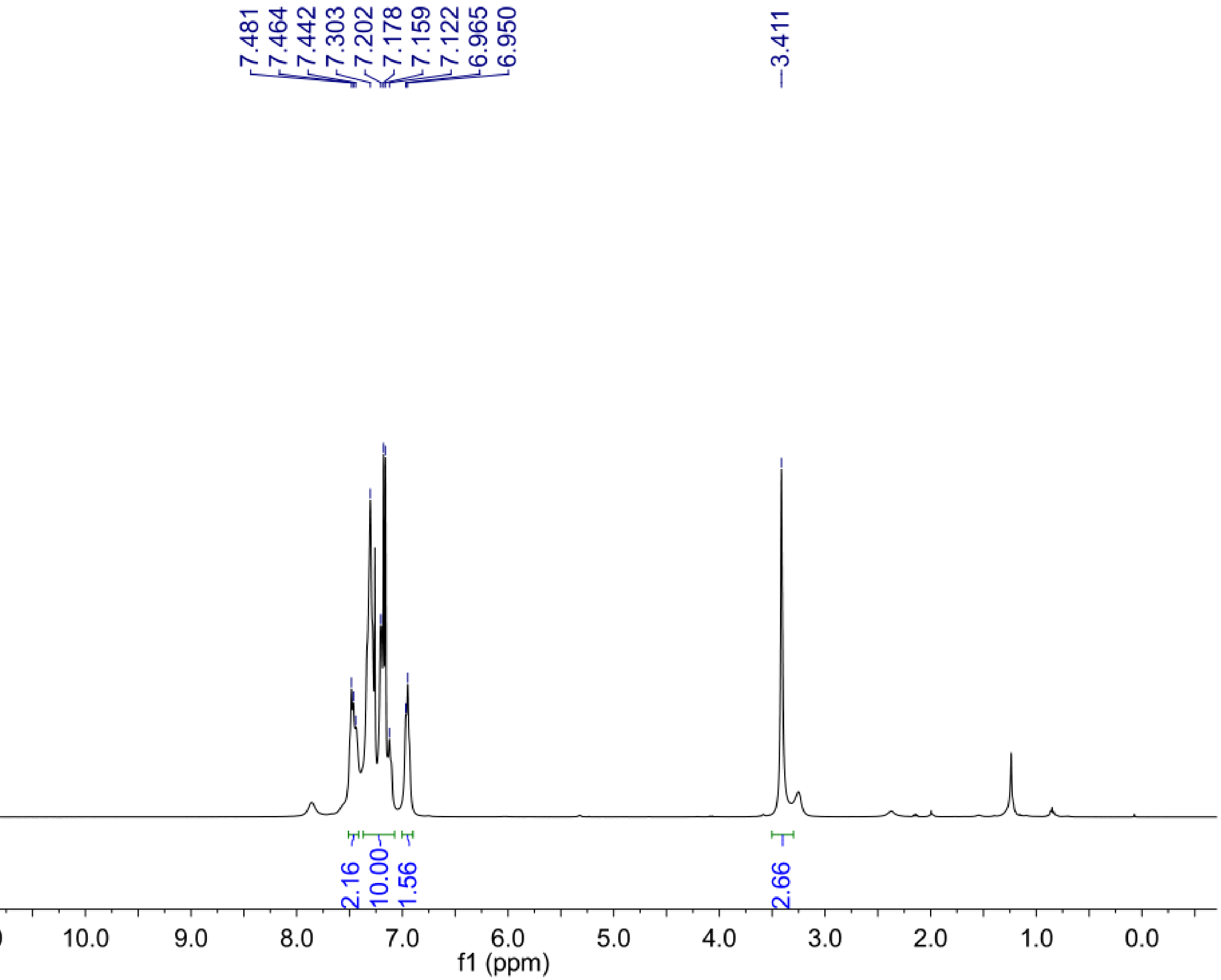
169.765
142.770
136.604
136.454
135.643
133.008
131.419
130.362
130.052
129.544
129.029
128.406
128.109
127.569
126.374
124.969
77.318
77.000
76.682
53.353
O
Ph
N
Ph
O
Ph
1ac
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Ph
N
O
Ph

1ad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7.464
7.442
7.303
7.202
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7.159
7.122
6.965
6.950
3.411
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10.00
1.56
2.66
12.0
11.0
10.0
9.0
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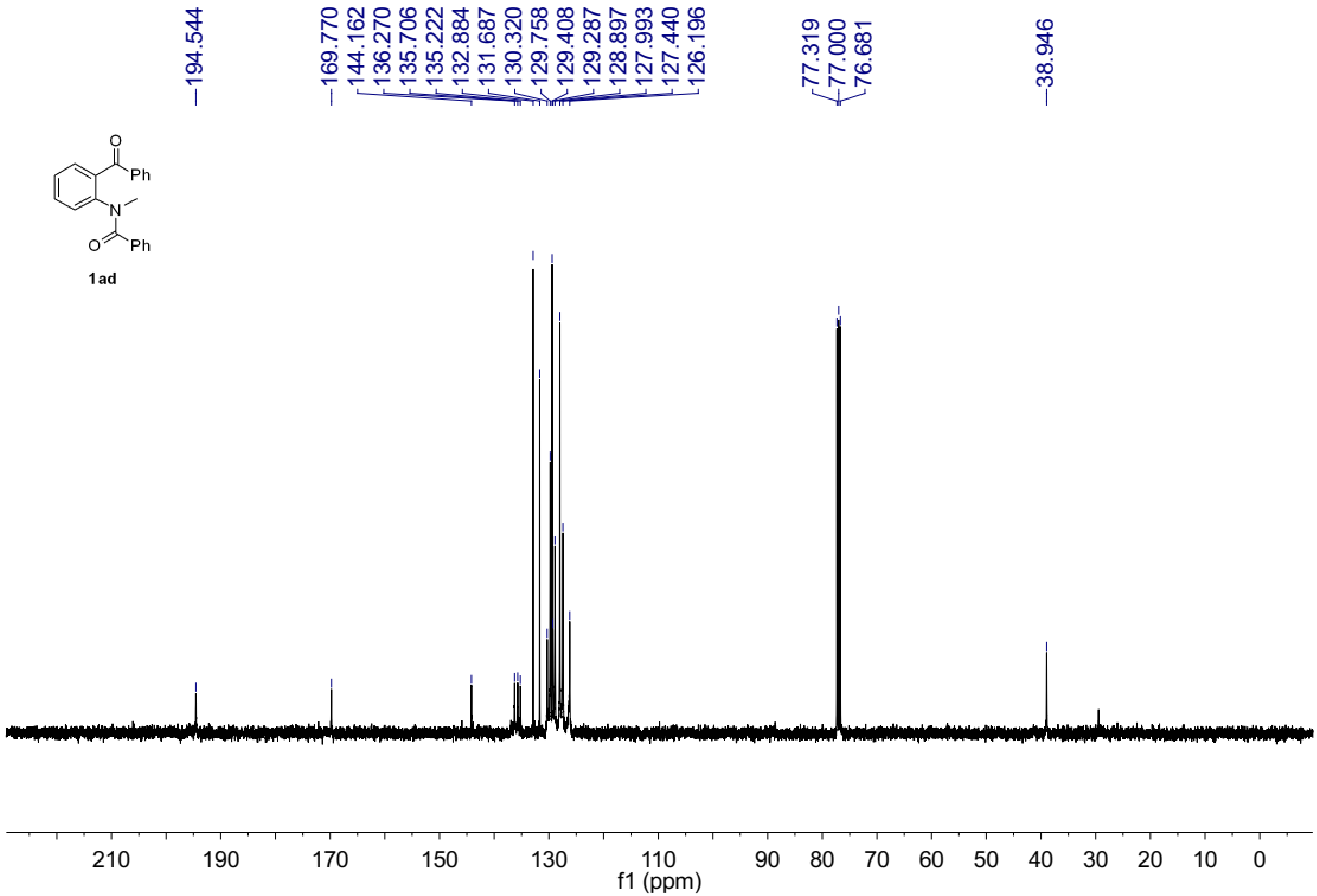
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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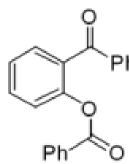
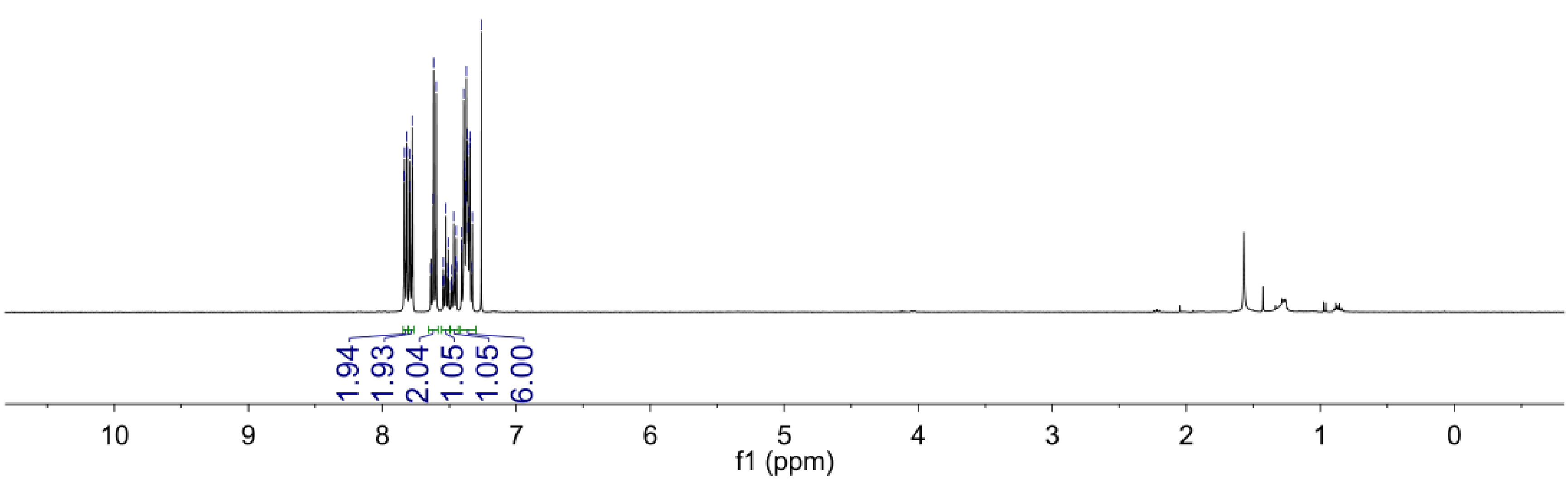
144.162
136.270
135.706
135.222
132.884
131.687
130.320
129.758
129.408
129.287
128.897
127.993
127.440
126.196
77.319
77.000
76.681
38.946
O
Ph
N
O
Ph
1ad
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
Ph
O
O

1ae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7.772
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7.620
7.616
7.597
7.548
7.544
7.541
7.526
7.510
7.507
7.504
7.488
7.485
7.482
7.467
7.461
7.451
7.448
7.445
7.410
7.407
7.391
7.388
7.384
7.381
7.375
7.372
7.367
7.363
7.360
7.354
7.348
7.346
7.332
7.328
7.260
1.94
1.93
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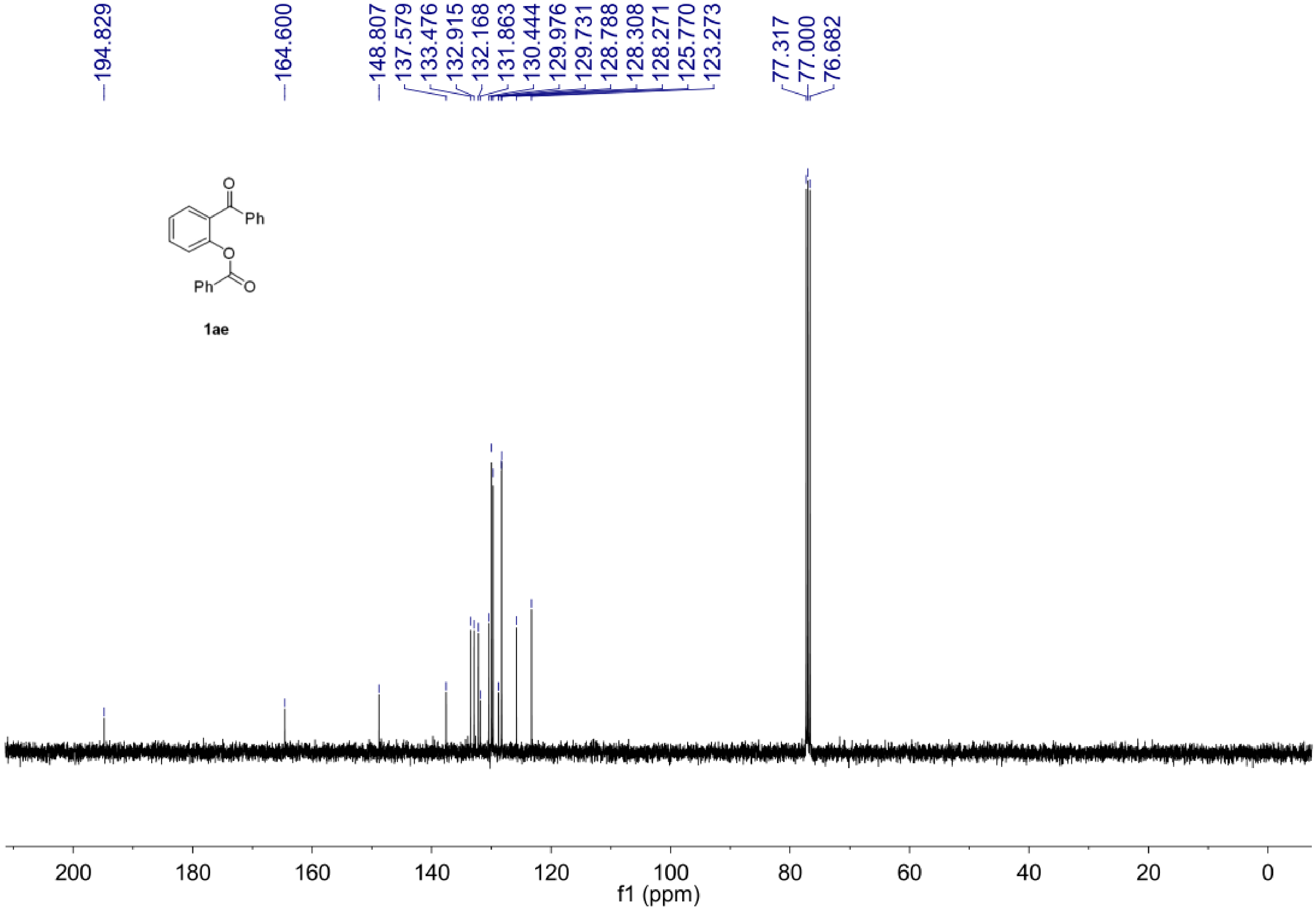
1.05
1.05
6.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



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164.600
148.807
137.579
133.476
132.915
132.168
131.863
130.444
129.976
129.731
128.788
128.308
128.271
125.770
123.273
77.317
77.000
76.682
O
Ph
O
Ph
O
1ae
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180
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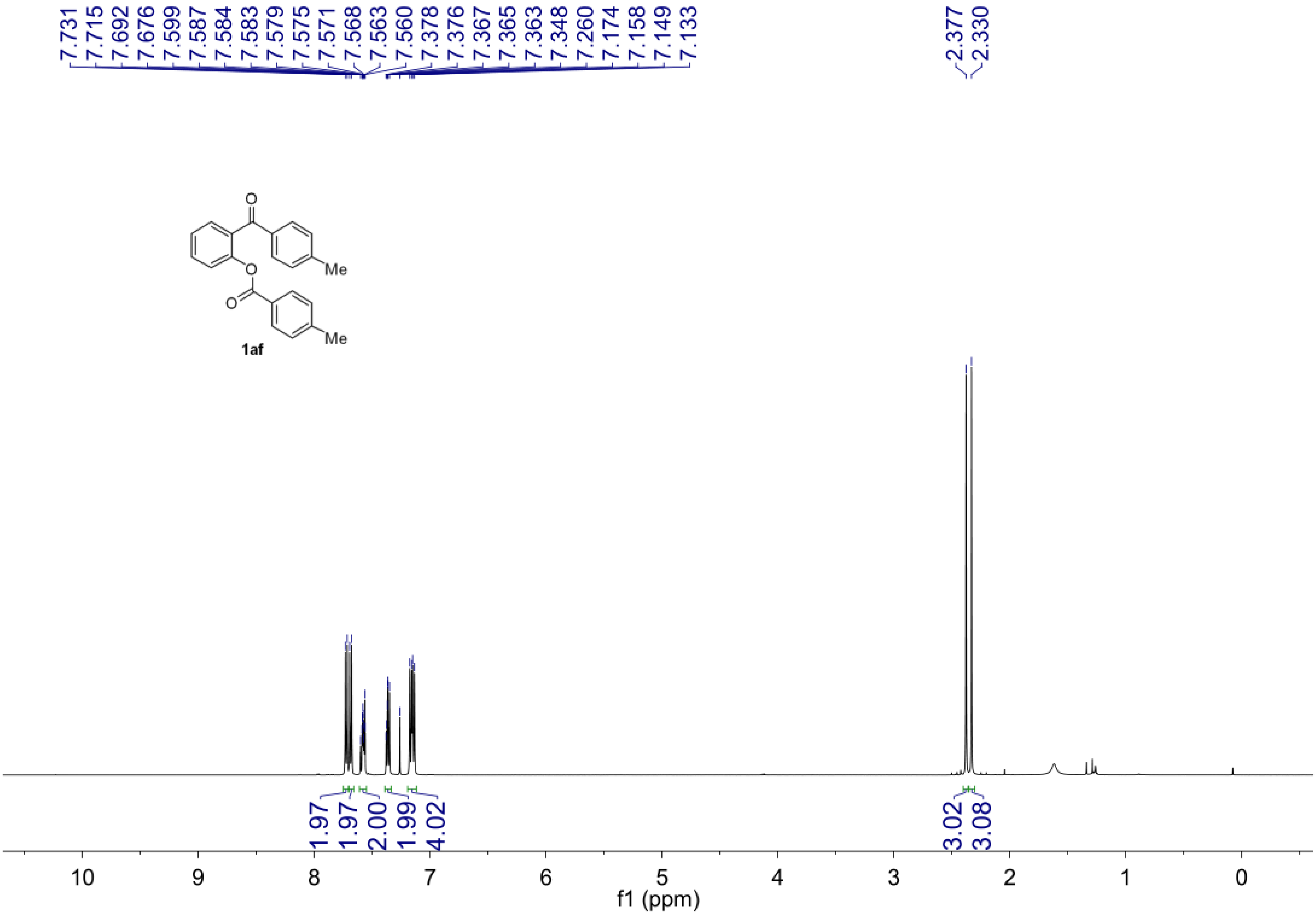
140
120
100
80
60
40
20
0
f1 (ppm)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7.583
7.579
7.575
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7.568
7.563
7.560
7.378
7.376
7.367
7.365
7.363
7.348
7.260
7.174
7.158
7.149
7.133
2.377
2.330
O
O
O
Me
Me
1af
1.97
1.97
2.00
1.99
4.02
3.02
3.08
10
9
8
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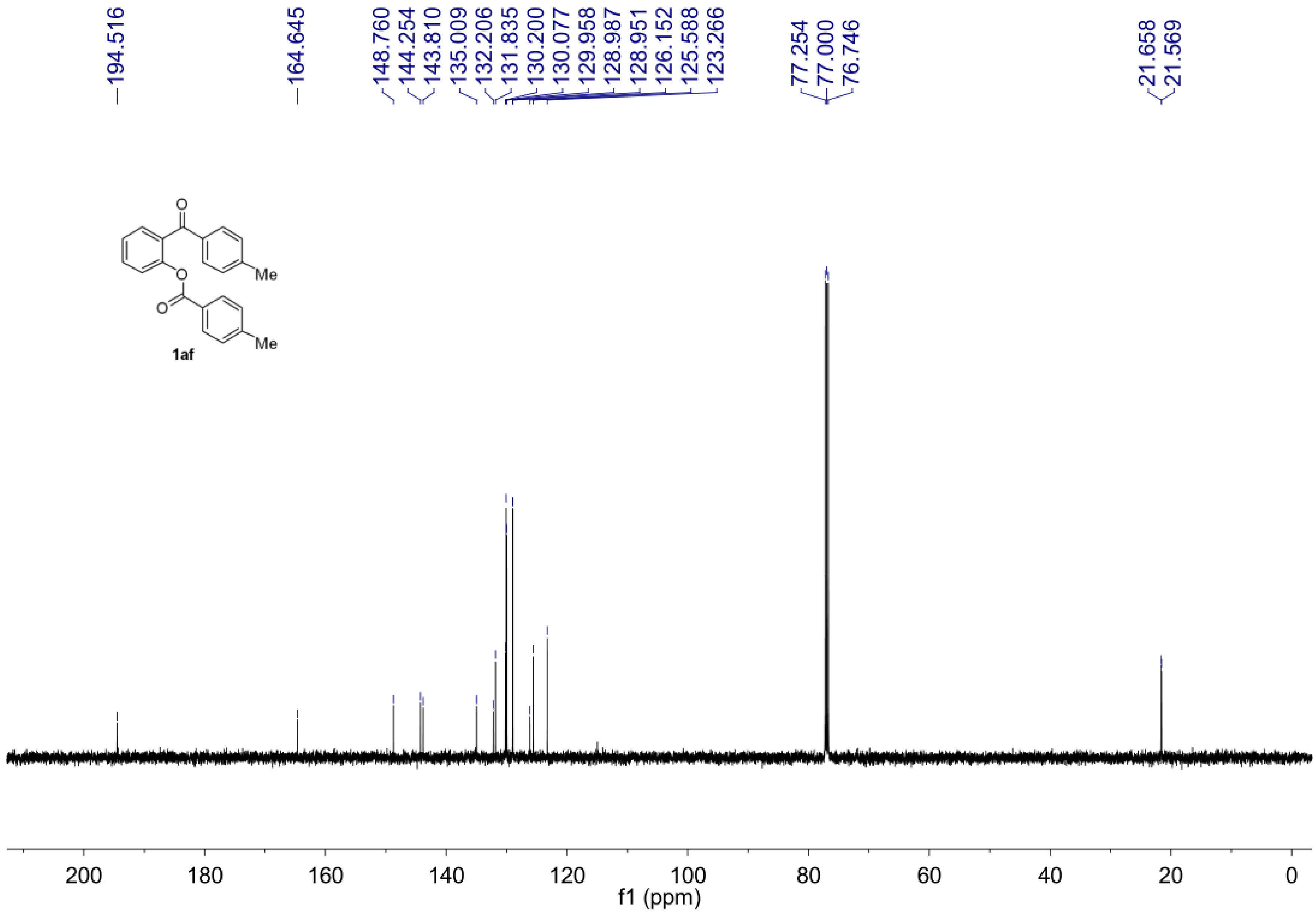
6
5
4
3
2
1
0
f1 (ppm)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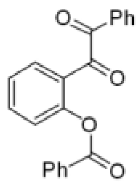
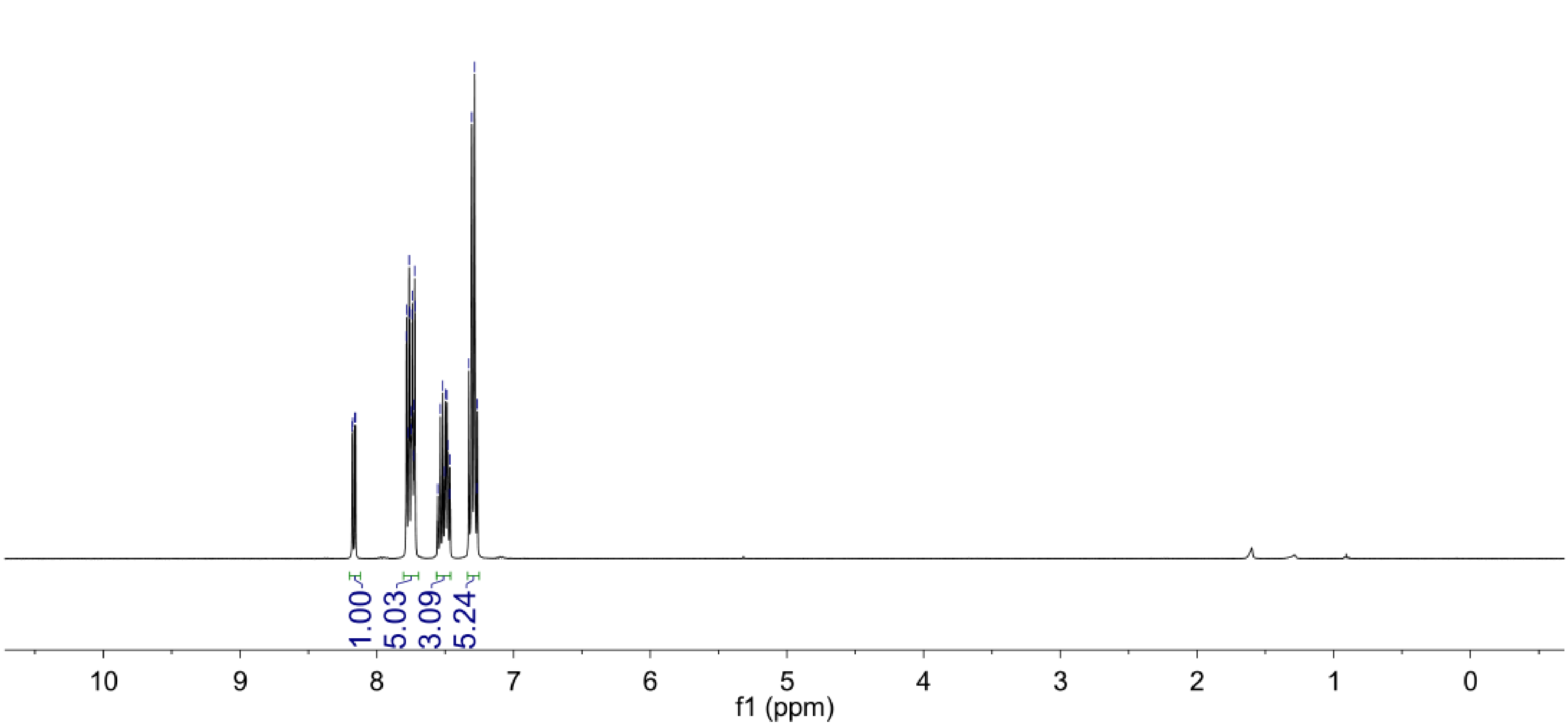
130.077
129.958
128.987
128.951
126.152
125.588
123.266
77.254
77.000
76.746
21.658
21.569
O
O
O
Me
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1af


O
Ph
O
O
Ph
O

1ag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8.156
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7.764
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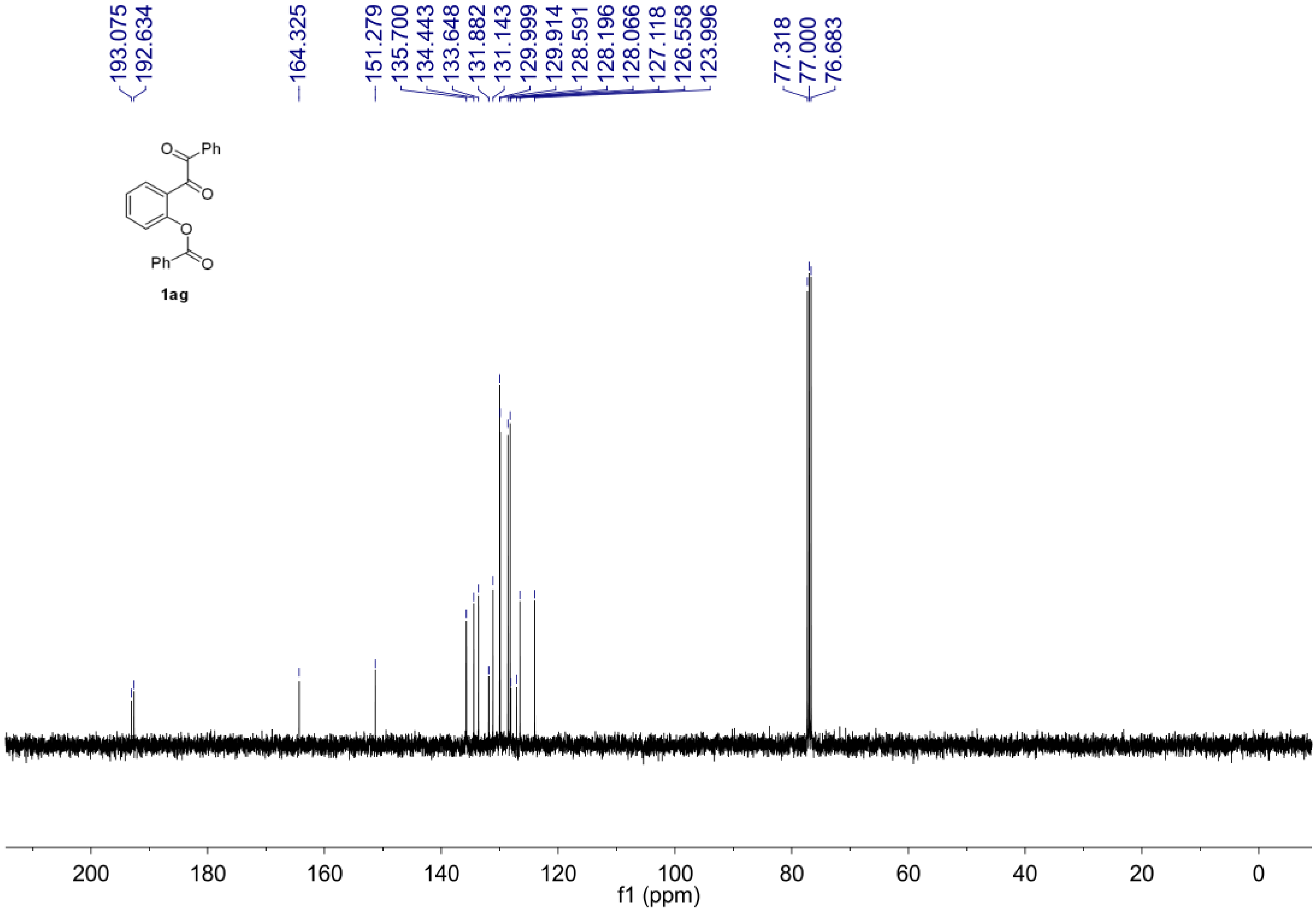
7.749
7.747
7.742
7.739
7.731
7.726
7.721
7.718
7.554
7.535
7.516
7.503
7.497
7.484
7.480
7.469
7.466
7.326
7.304
7.284
7.269
7.265
1.00
5.03
3.09
5.24
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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129.999
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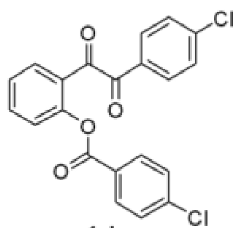
128.591
128.196
128.066
127.118
126.558
123.996
77.318
77.000
76.683
O
Ph
O
O
Ph
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1ag



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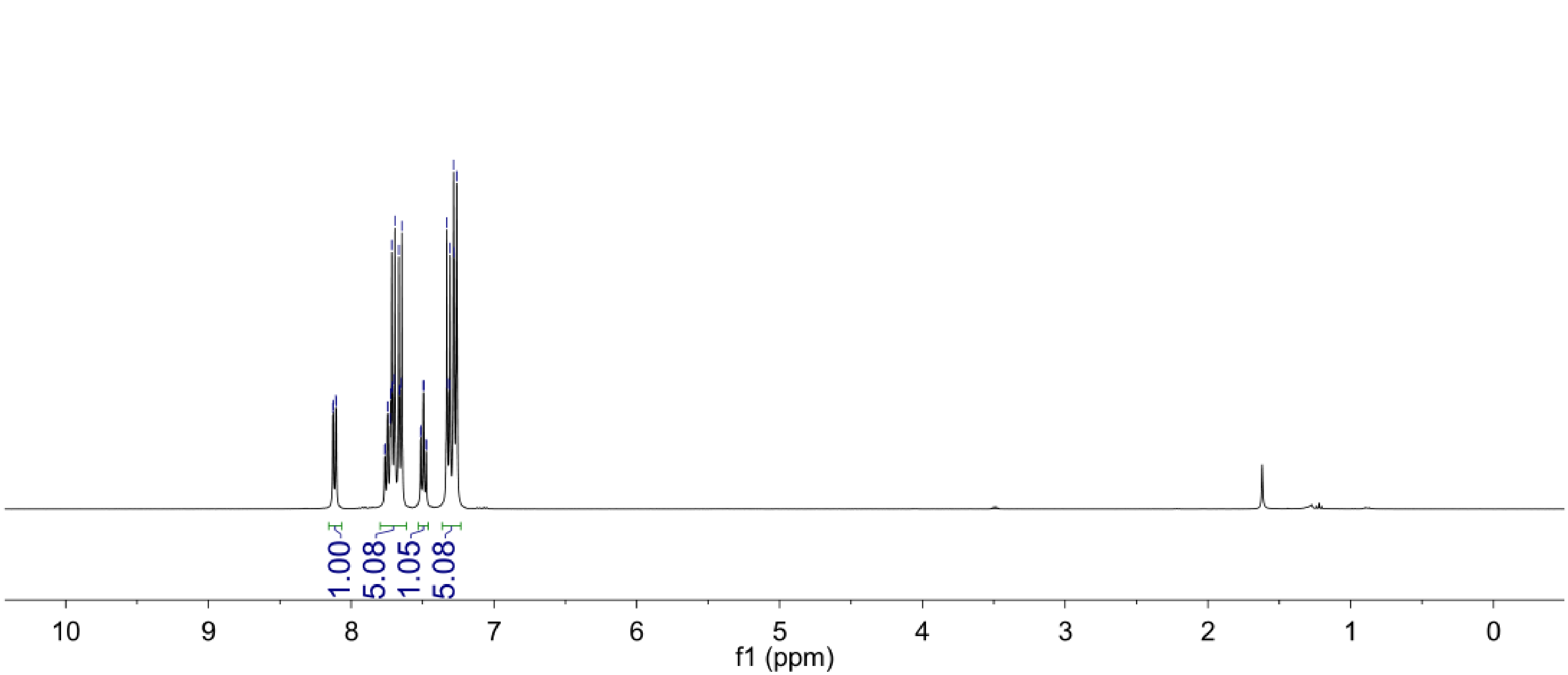
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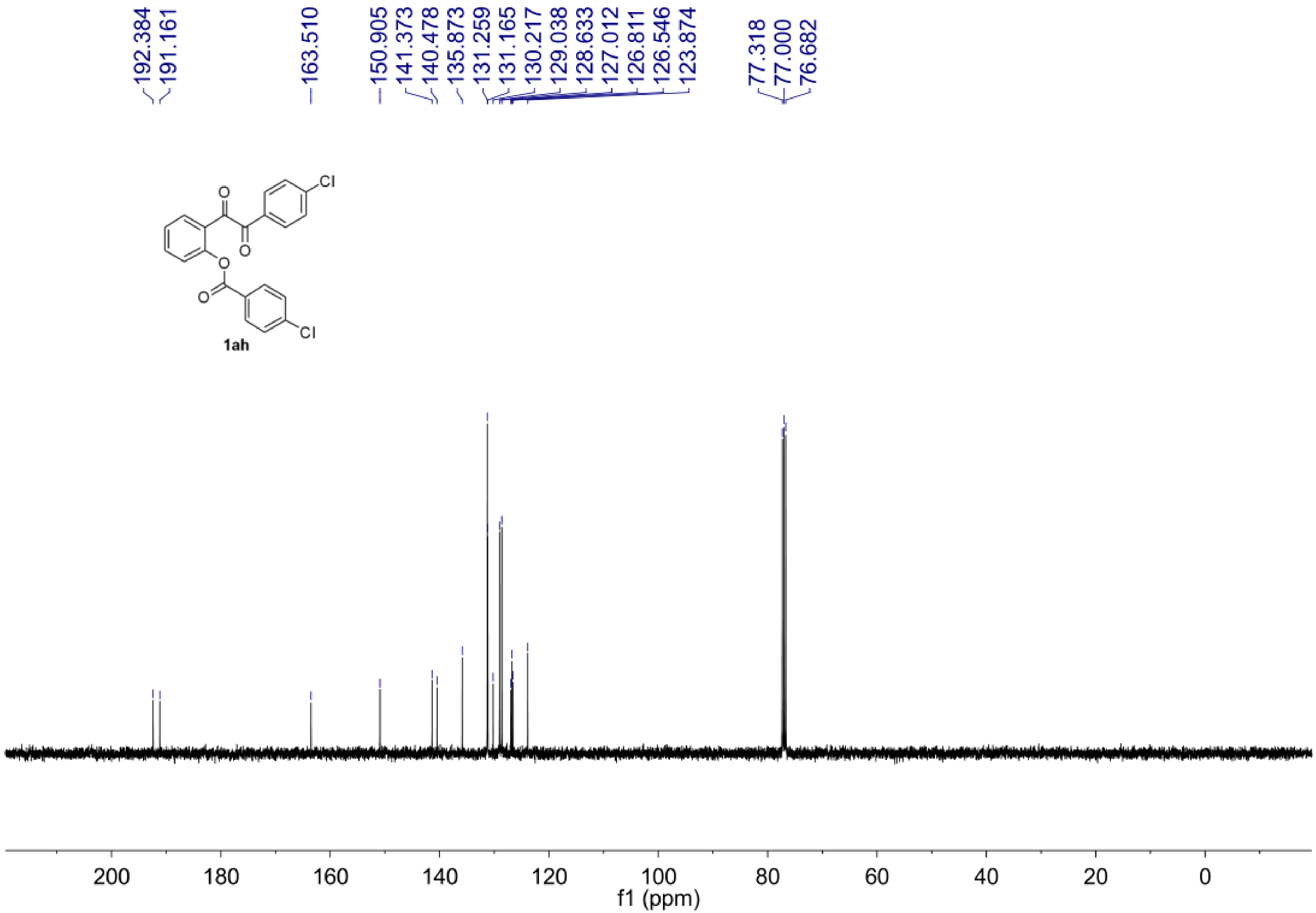
1.05
5.08
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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140.478
135.873
131.259
131.165
130.217
129.038
128.633
127.012
126.811
126.546
123.874
77.318
77.000
76.682
Cl
O
O
O
O
Cl
1ah
200
180
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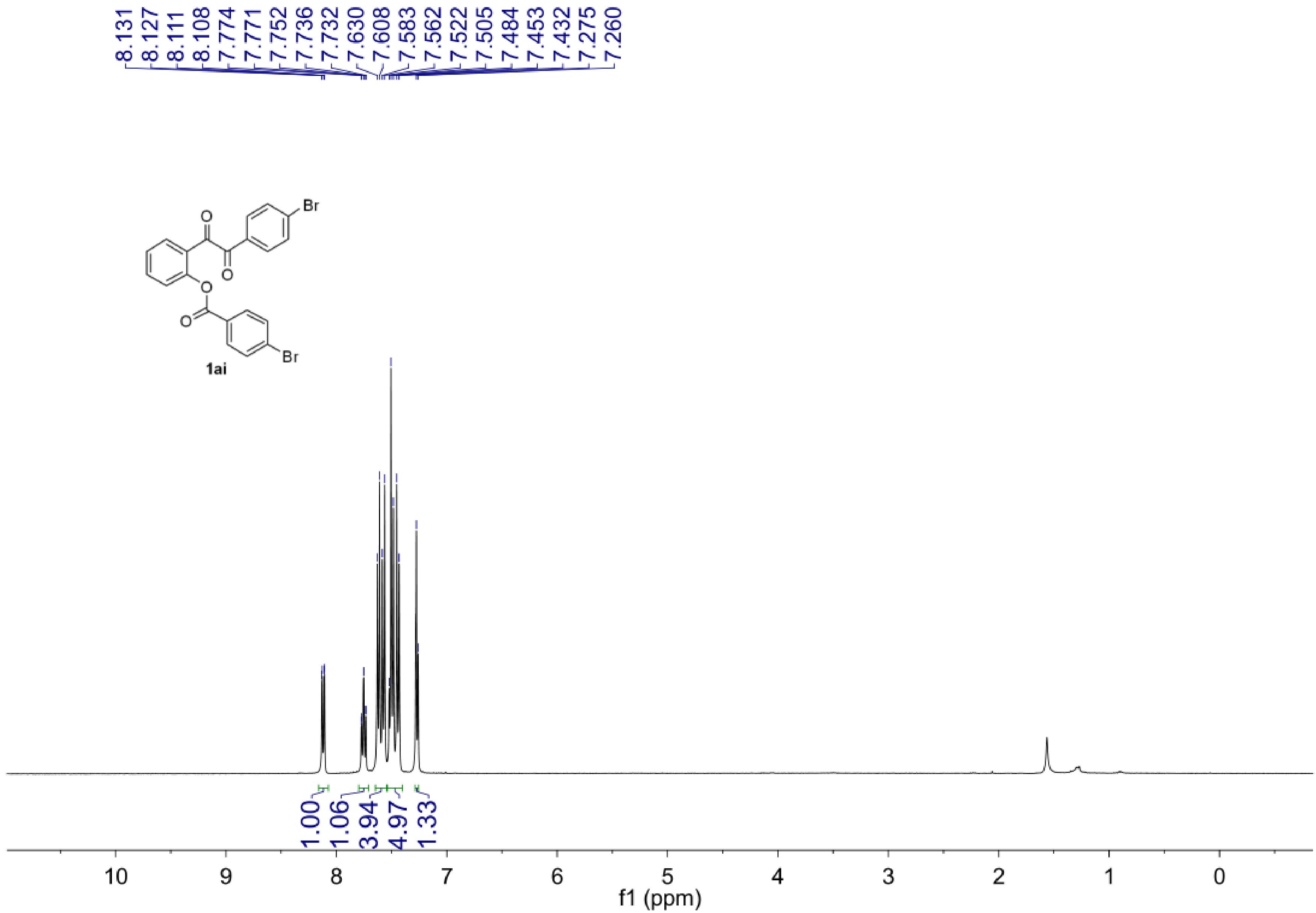
140
120
100
80
60
40
20
0
f1 (ppm)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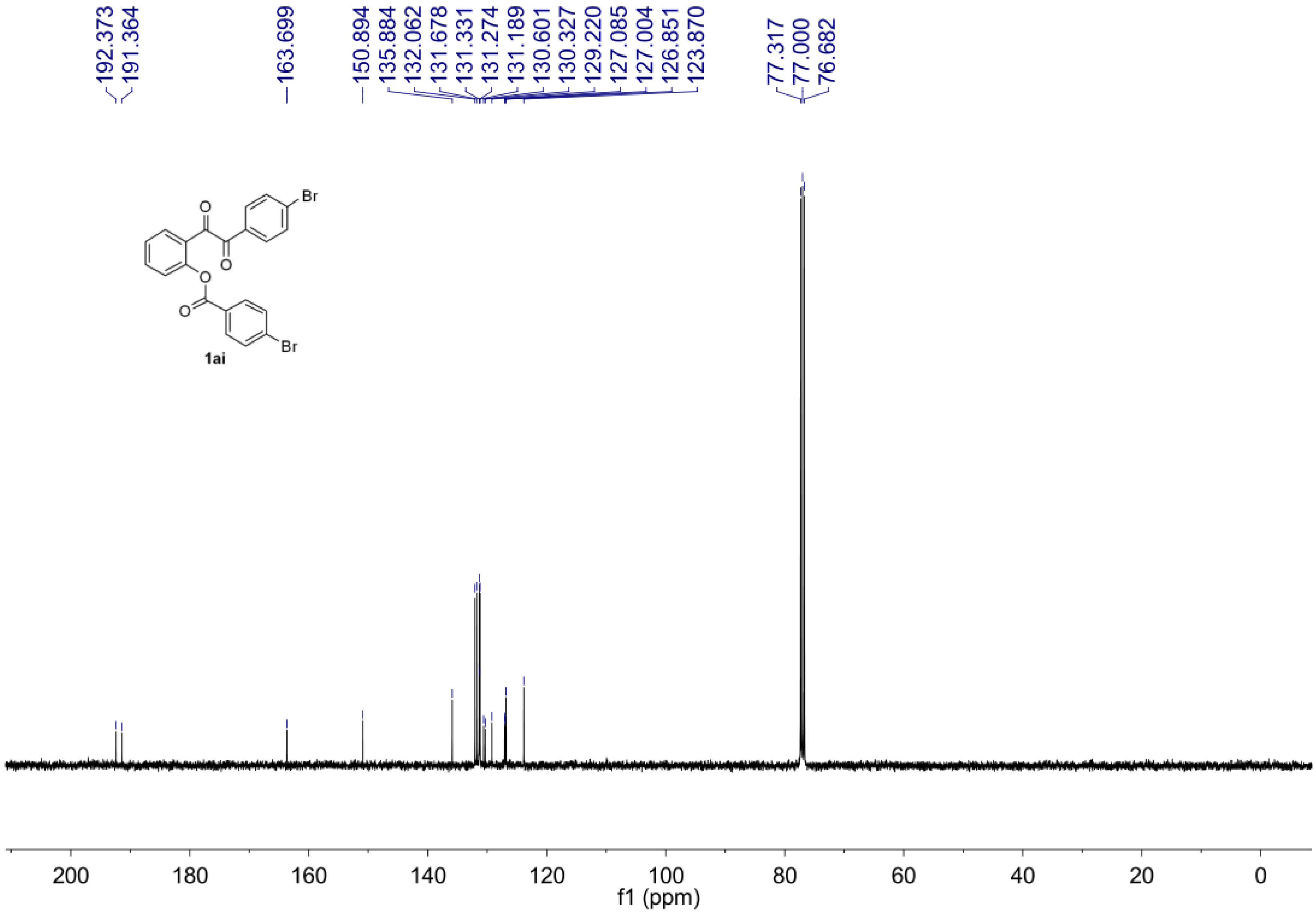
7.630
7.608
7.583
7.562
7.522
7.505
7.484
7.453
7.432
7.275
7.260
Br
O
O
O
O
Br
1ai
1.00
1.06
3.94
4.97
1.33
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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131.189
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130.327
129.220
127.085
127.004
126.851
123.870
77.317
77.000
76.682
Br
O
O
O
O
Br
1ai
200
180
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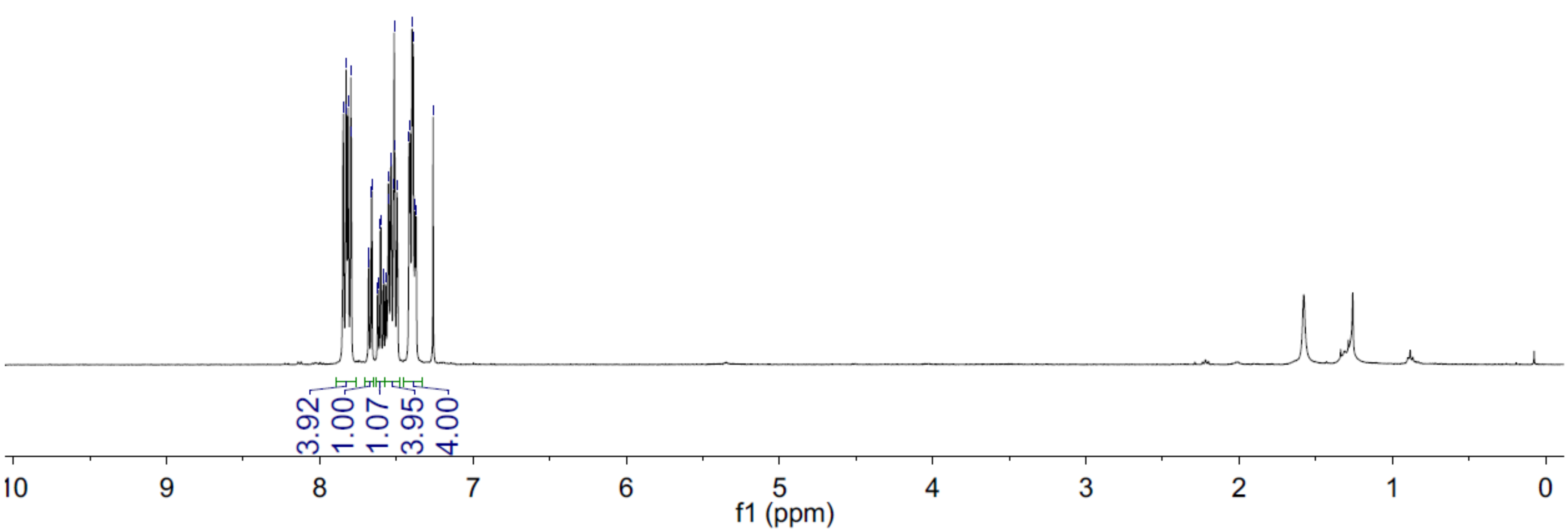
140
120
100
80
60
40
20
0
f1 (ppm)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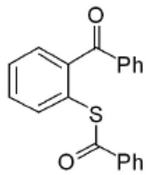
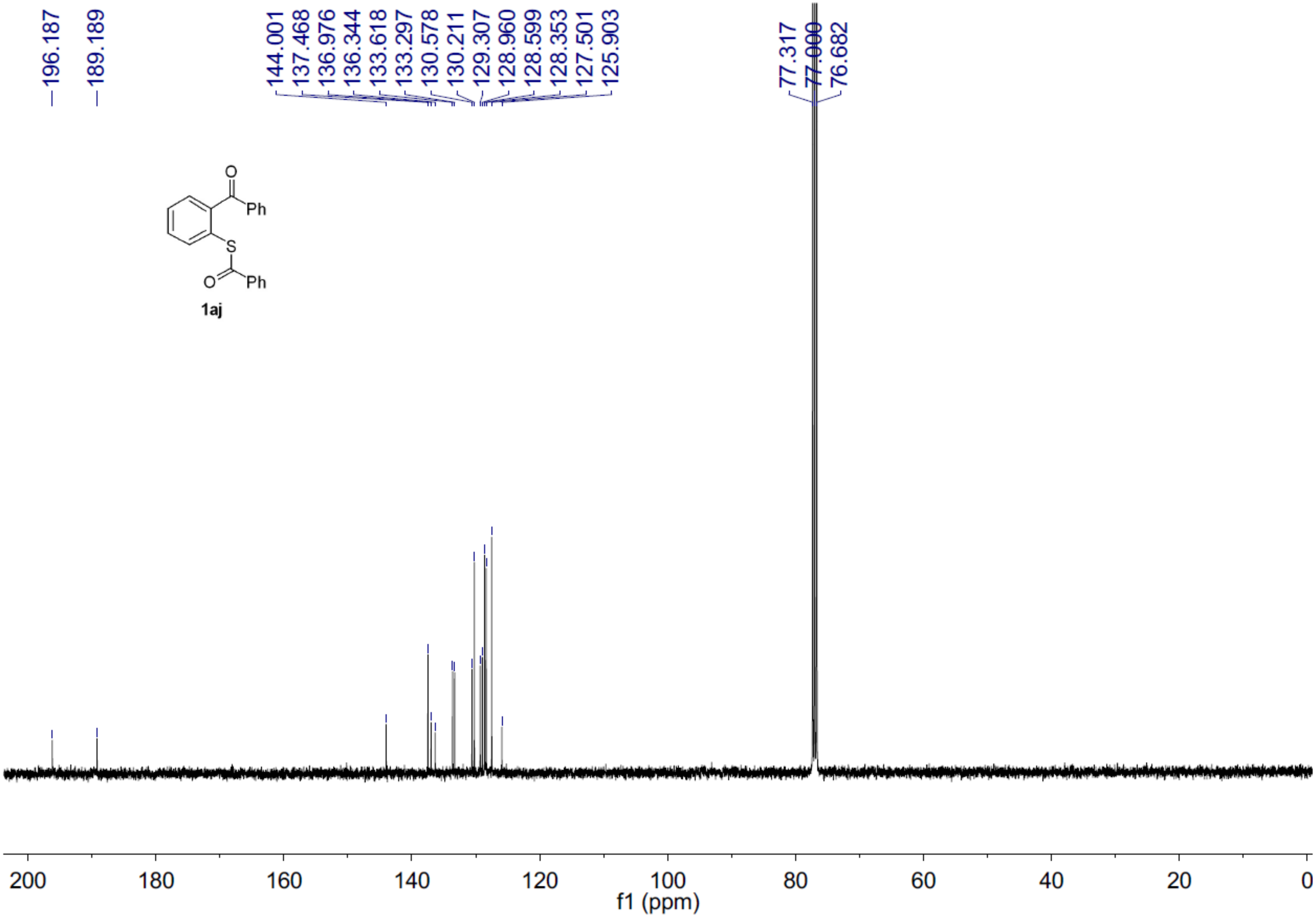
7.619
7.605
7.601
7.586
7.582
7.571
7.552
7.549
7.537
7.534
7.519
7.514
7.510
7.495
7.417
7.410
7.397
7.390
7.379
7.371
7.260
3.92
1.00
1.07
3.95
4.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


O
Ph
S
O
Ph

1aj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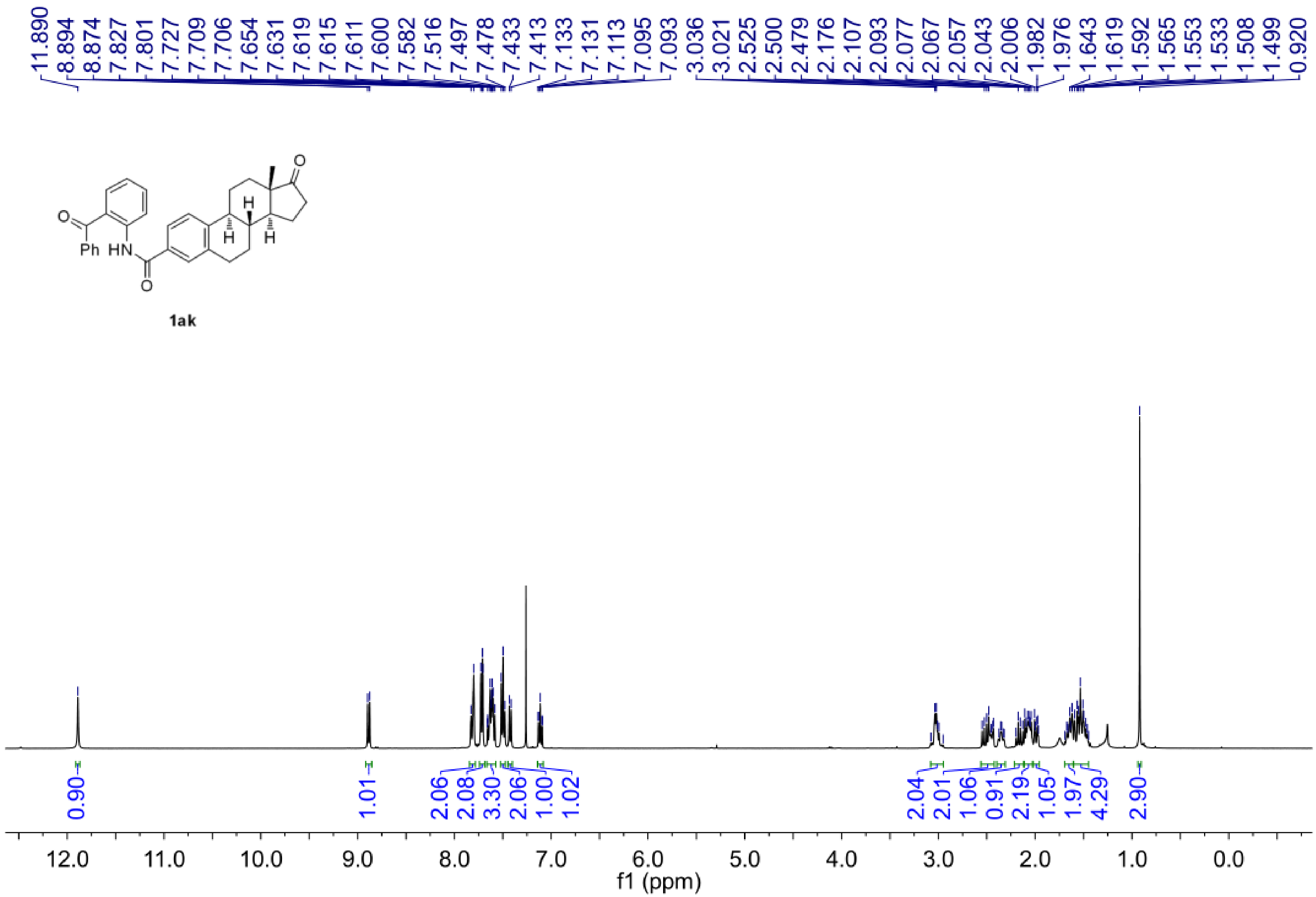
128.599
128.353
127.501
125.903
77.317
77.000
76.682
O
Ph
S
O
Ph
1aj
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.631
7.619
7.615
7.611
7.600
7.582
7.516
7.497
7.478
7.433
7.413
7.133
7.131
7.113
7.095
7.093
3.036
3.021
2.525
2.500
2.479
2.176
2.107
2.093
2.077
2.067
2.057
2.043
2.006
1.982
1.976
1.643
1.619
1.592
1.565
1.553
1.533
1.508
1.499
0.920
O
Ph
HN
O
H
H
H
O
1ak
0.90
1.01
2.06
2.08
3.30
2.06
1.00
1.02
2.04
2.01
1.06
0.91
2.19
1.05
1.97
4.29
2.90
12.0
11.0
10.0
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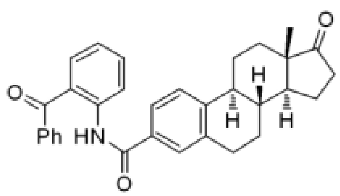
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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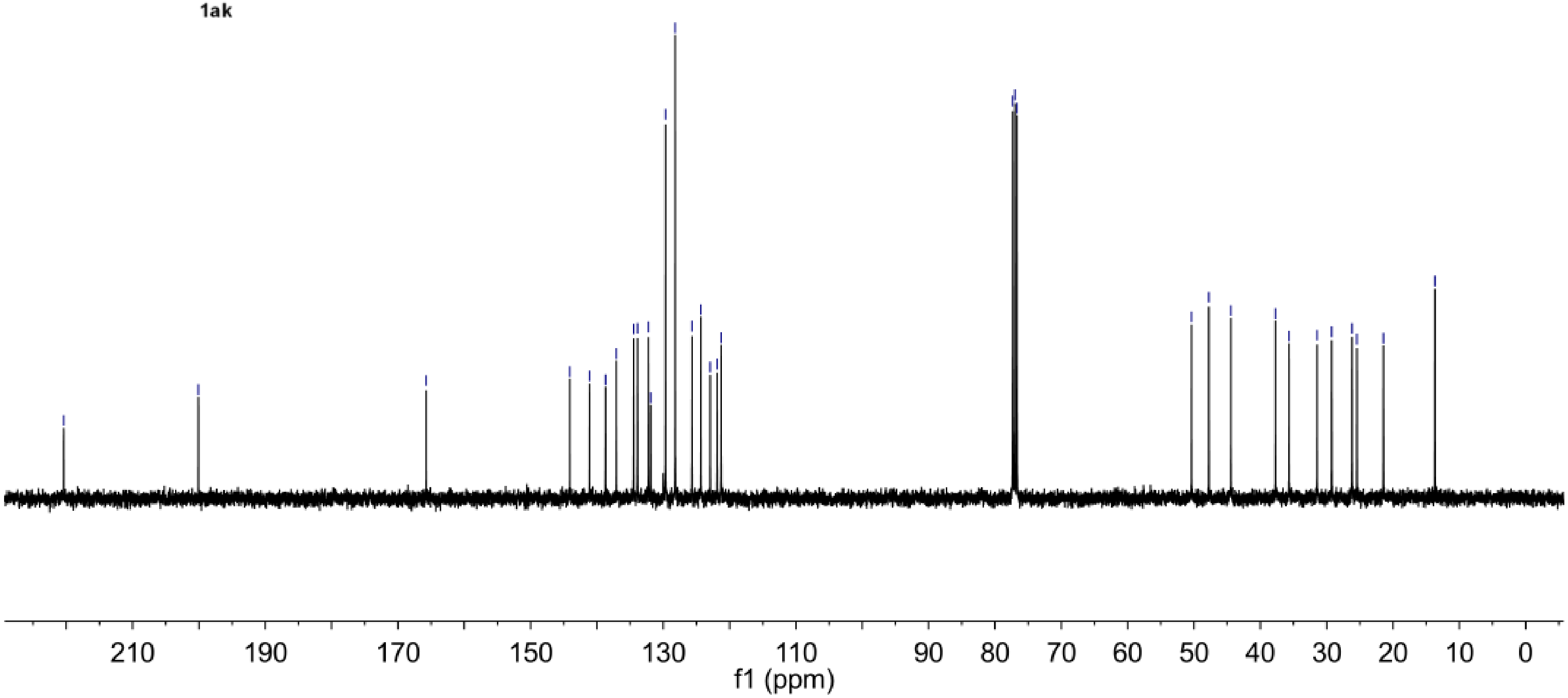

220.394
200.075
165.757
144.097
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138.712
137.075
134.485
133.901
132.235
131.906
129.670
128.198
125.680
124.326
122.918
121.904
121.264
77.318
77.000
76.682
50.386
47.756
44.443
37.720
35.679
31.426
29.247
26.161
25.451
21.453
13.696
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170
150
130
110
90
80
70
60
50
40
30
20
10
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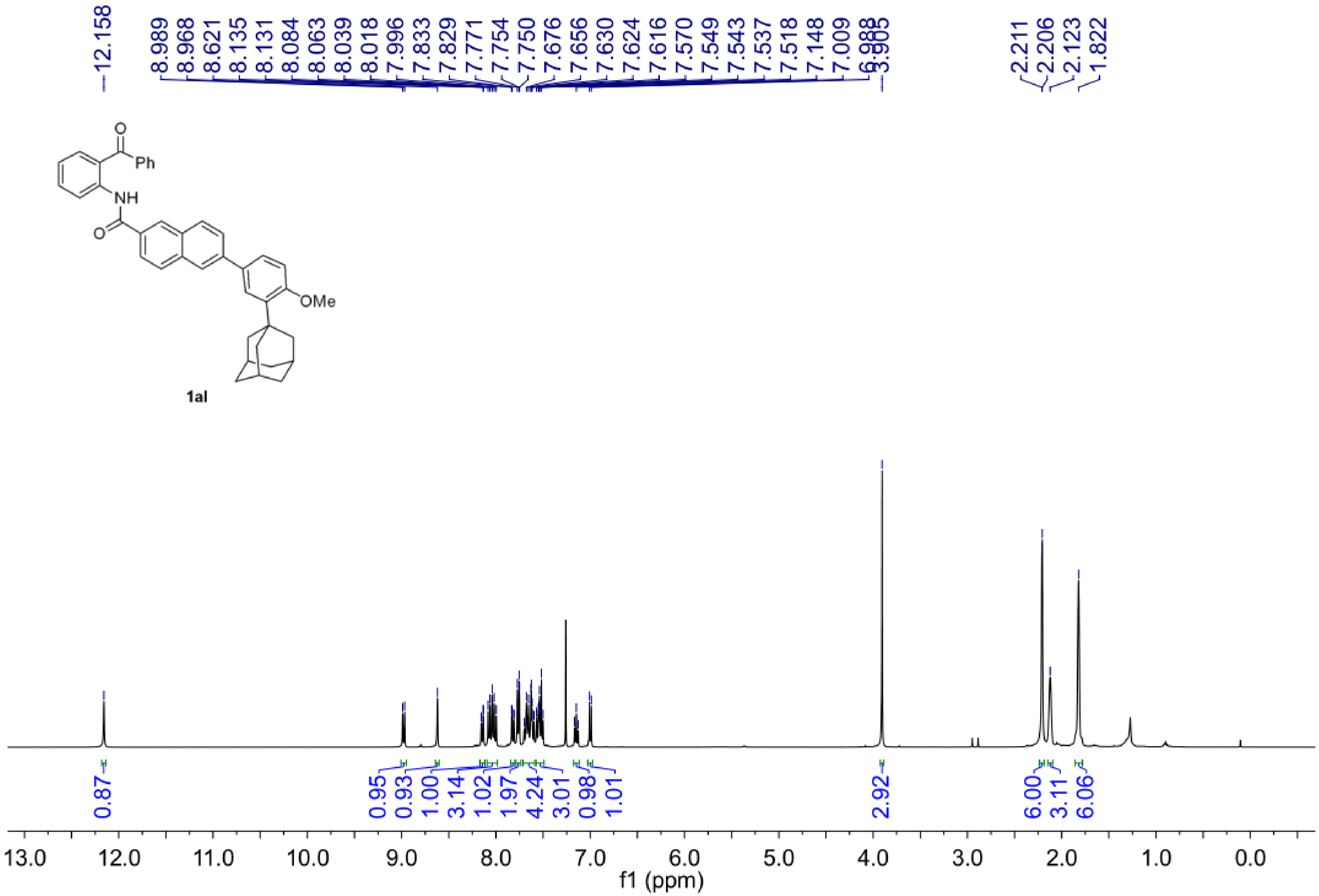
f1 (ppm)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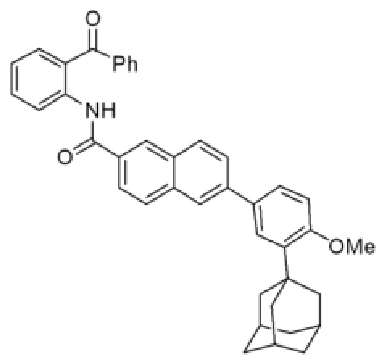
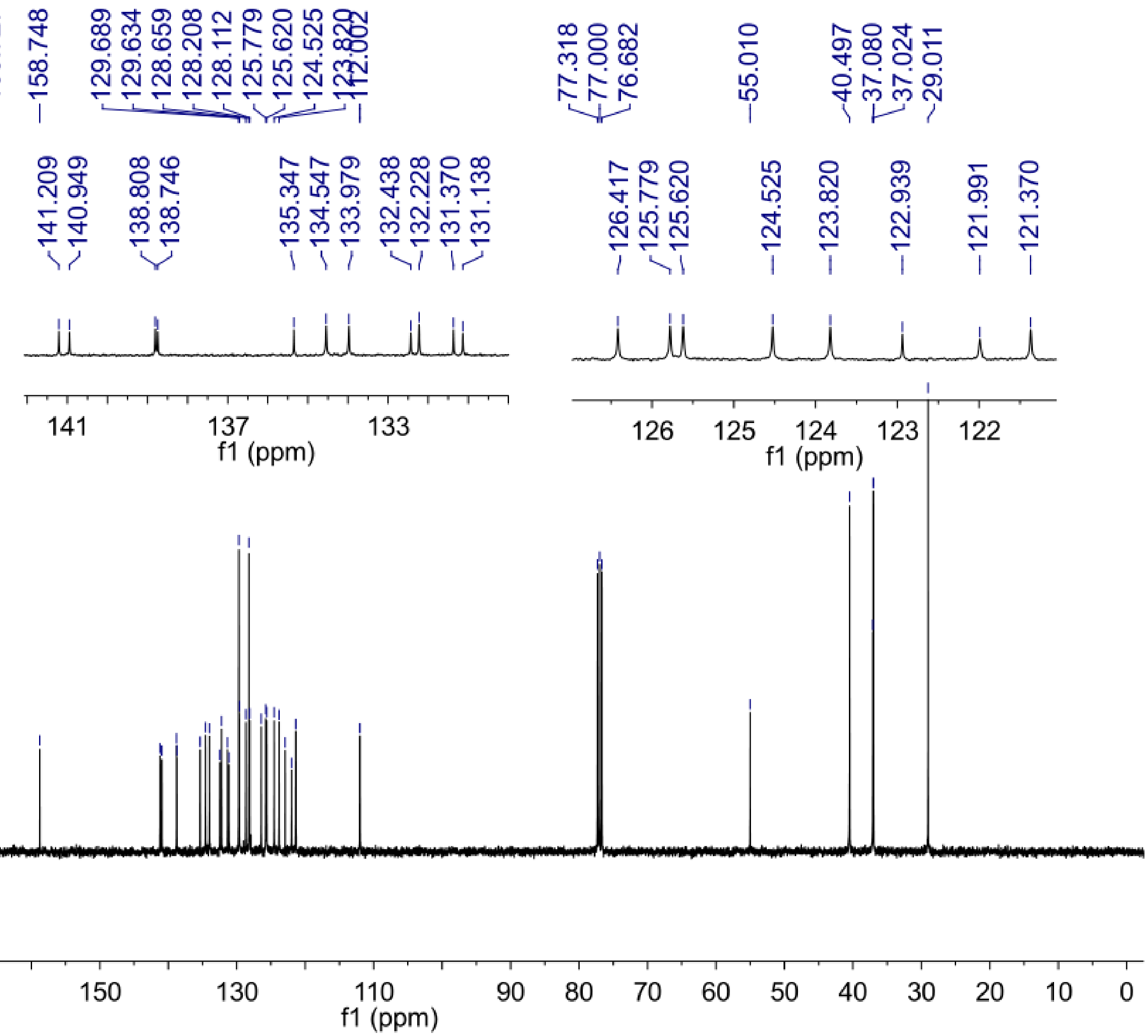
8.063
8.039
8.018
7.996
7.833
7.829
7.771
7.754
7.750
7.676
7.656
7.630
7.624
7.616
7.570
7.549
7.543
7.537
7.518
7.148
7.009
6.988
3.905
2.211
2.206
2.123
1.822
Ph
NH
OMe
1al
0.87
0.95
0.93
1.00
3.14
1.02
1.97
4.24
3.01
0.98
1.01
2.92
6.00
3.11
6.06
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



1al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158.748
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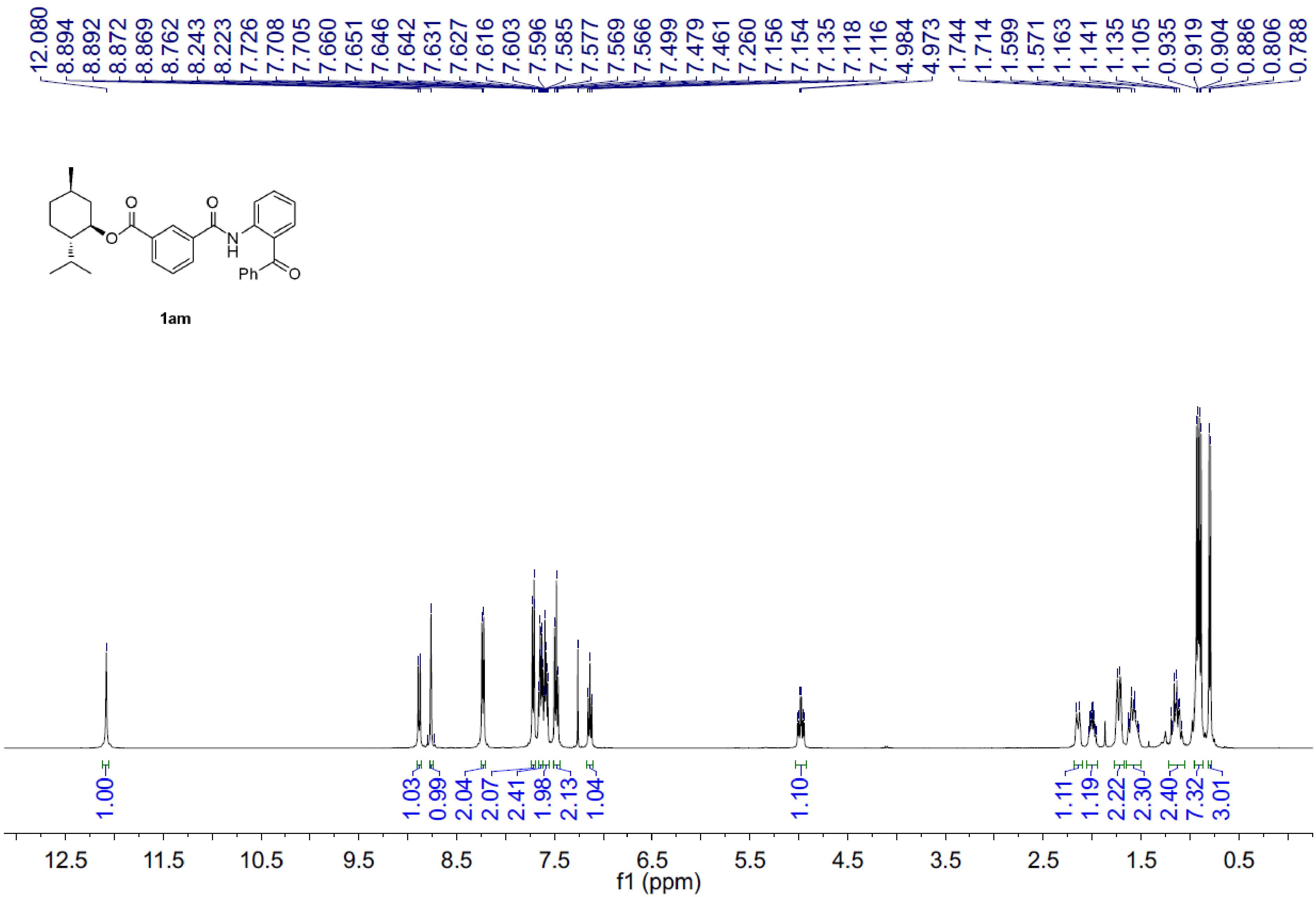
129.634
128.659
128.208
128.112
125.779
125.620
124.525
123.820
112.002
77.318
77.000
76.682
55.010
40.497
37.080
37.024
29.011
141.209
140.949
138.808
138.746
135.347
134.547
133.979
132.438
132.228
131.370
131.138
126.417
125.779
125.620
124.525
123.820
122.939
121.991
121.370
f1 (ppm)
f1 (ppm)
f1 (ppm)



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8.892
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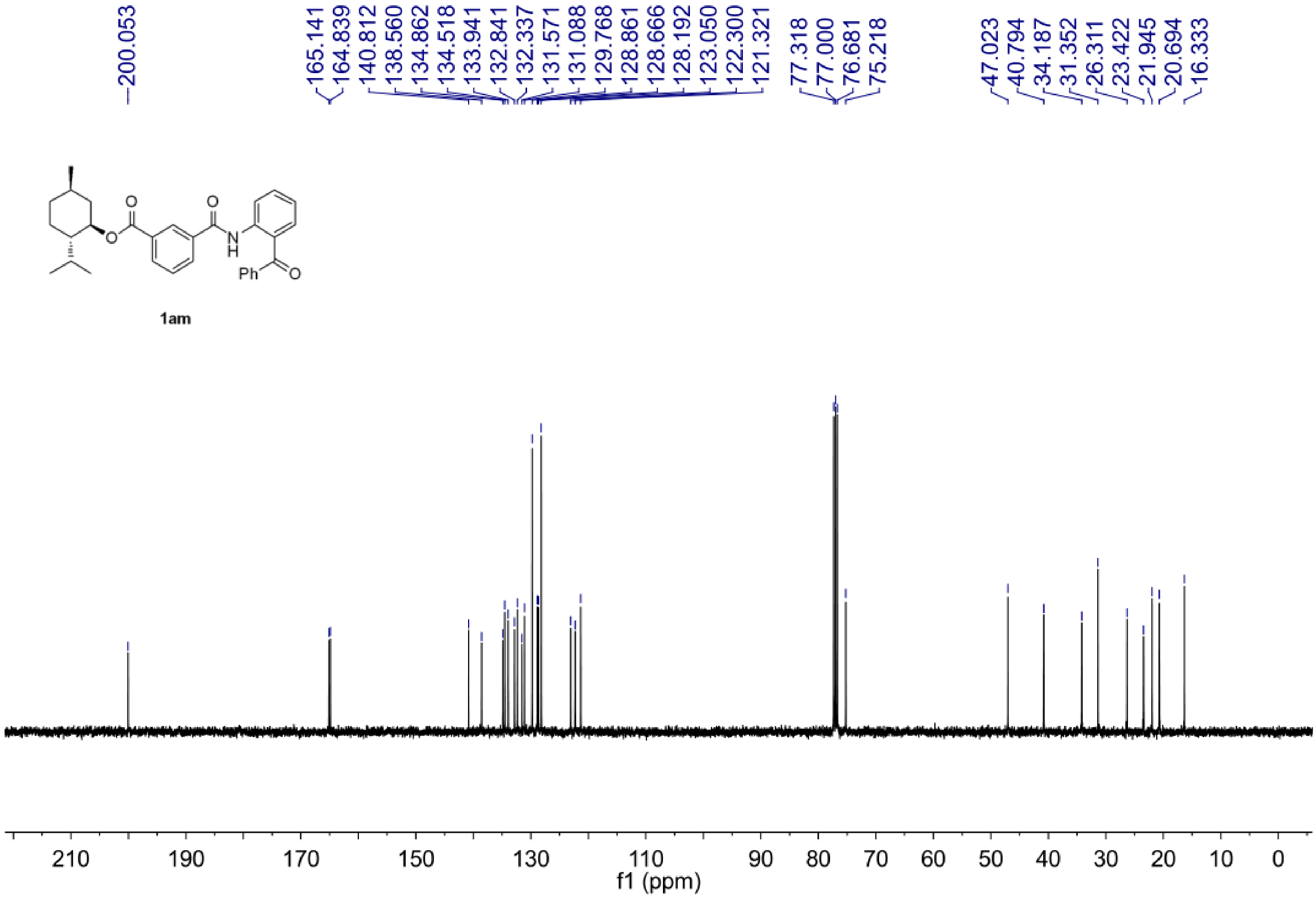
8.869
8.762
8.243
8.223
7.726
7.708
7.705
7.660
7.651
7.646
7.642
7.631
7.627
7.616
7.603
7.596
7.585
7.577
7.569
7.566
7.499
7.479
7.461
7.260
7.156
7.154
7.135
7.118
7.116
4.984
4.973
1.744
1.714
1.599
1.571
1.163
1.141
1.135
1.105
0.935
0.919
0.904
0.886
0.806
0.788
1.00
1.03
0.99
2.04
2.07
2.41
1.98
2.13
1.04
1.10
1.11
1.19
2.22
2.30
2.40
7.32
3.01
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

1am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164.839
140.812
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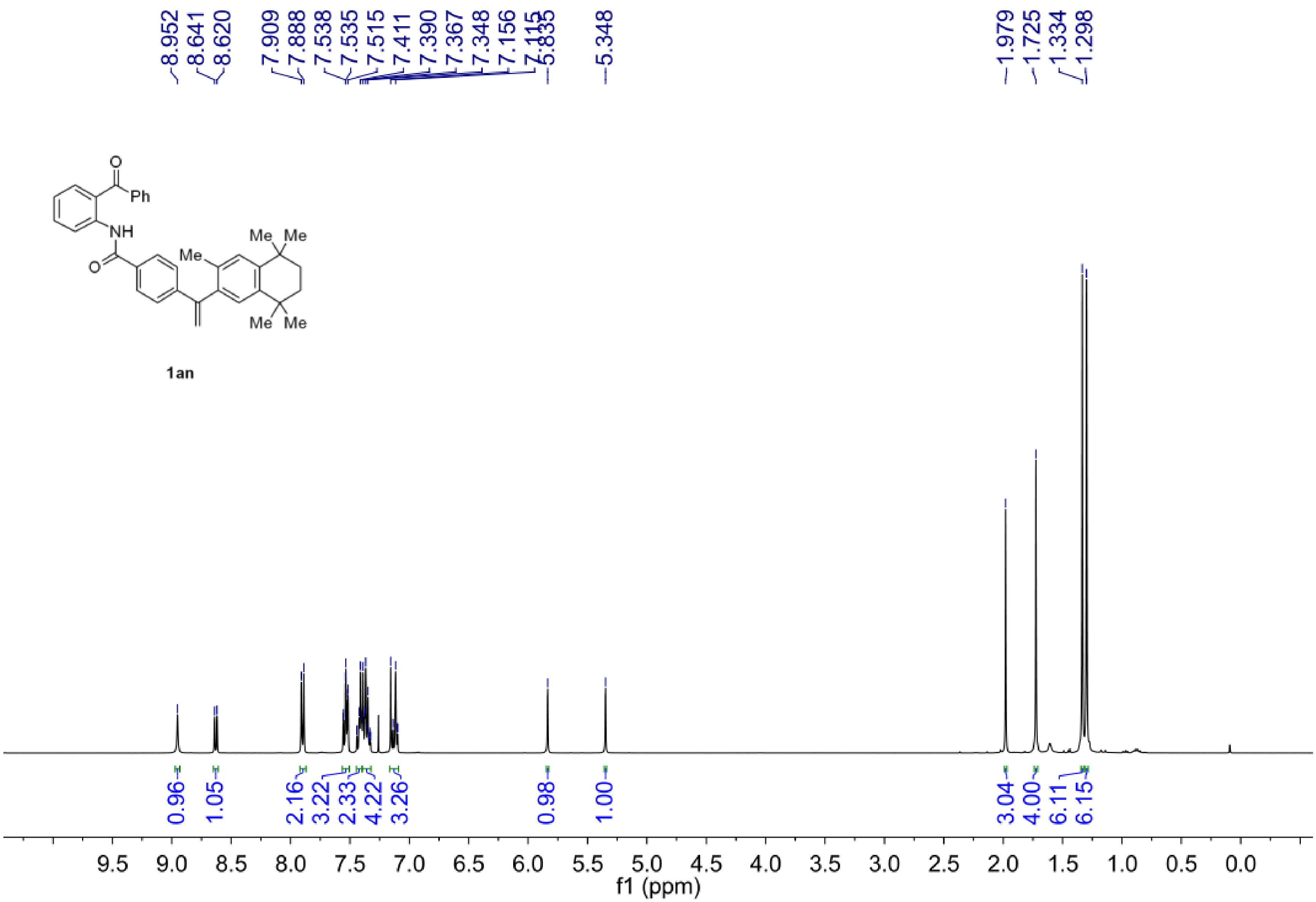
134.518
133.941
132.841
132.337
131.571
131.088
129.768
128.861
128.666
128.192
123.050
122.300
121.321
77.318
77.000
76.681
75.218
47.023
40.794
34.187
31.352
26.311
23.422
21.945
20.694
16.333
O
O
O
N
H
Ph
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1am


O
Ph
NH
O
Me
Me
Me
Me
Me
1an
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8.641
8.620
7.909
7.888
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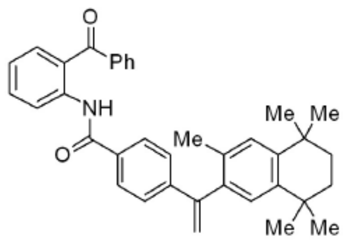
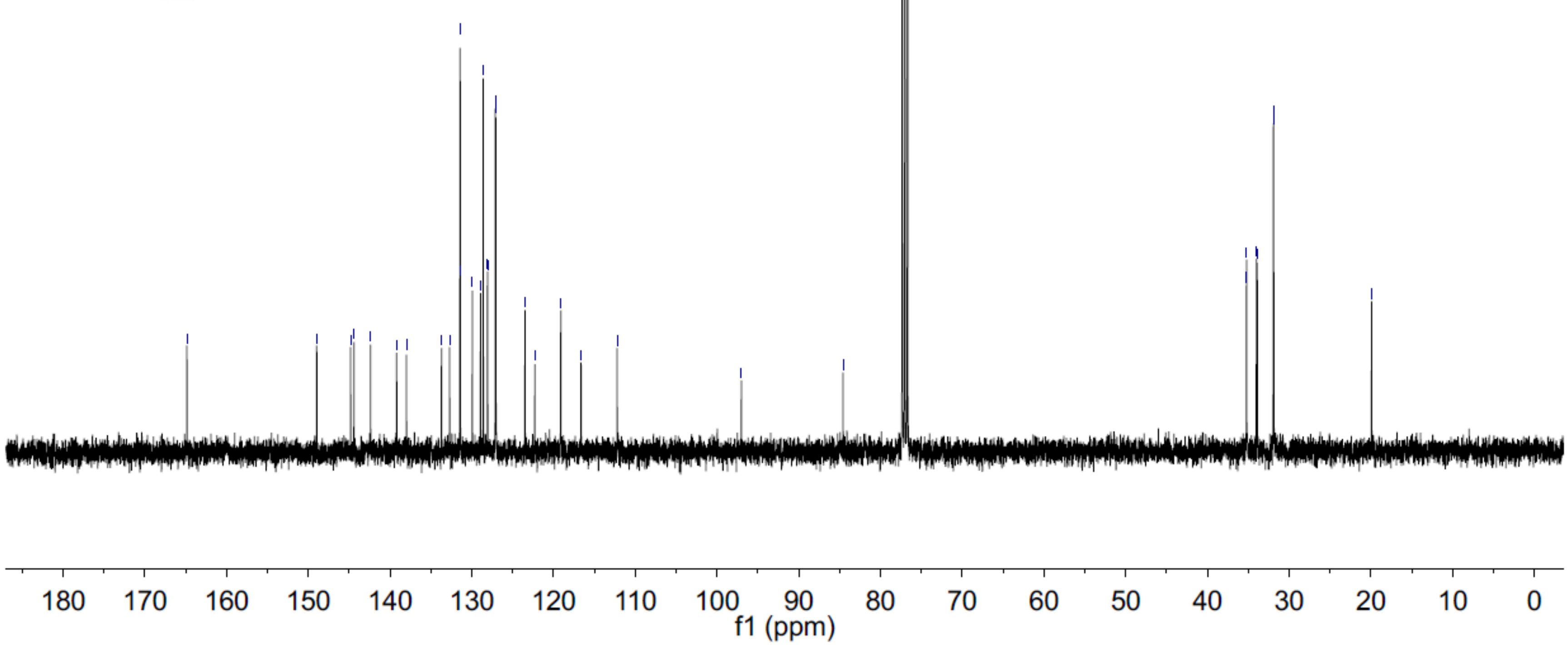
7.535
7.515
7.411
7.390
7.367
7.348
7.156
7.135
5.835
5.348
1.979
1.725
1.334
1.298
0.96
1.05
2.16
3.22
2.33
4.22
3.26
0.98
1.00
3.04
4.00
6.11
6.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

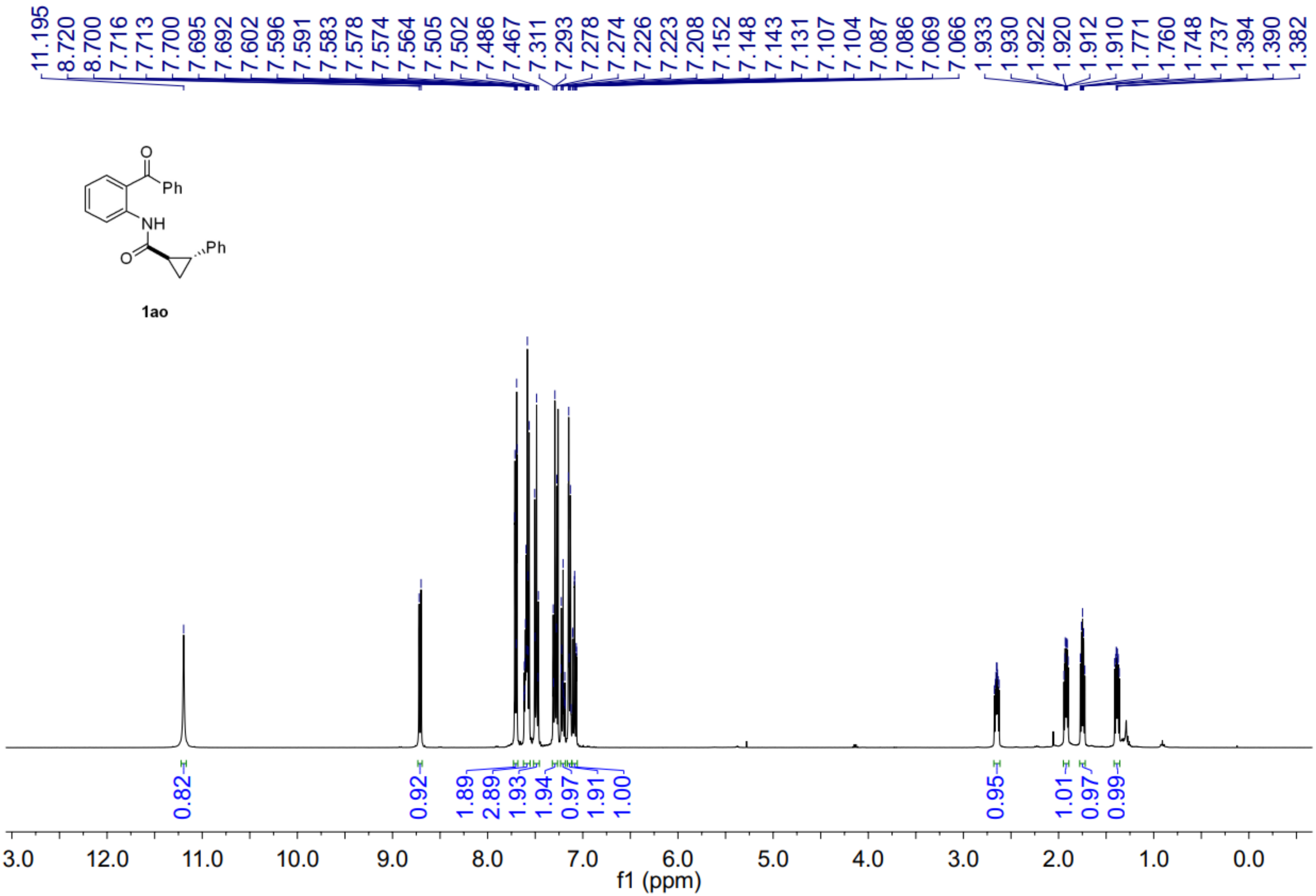


O
Ph
NH
O
Me
Me
Me
Me
Me

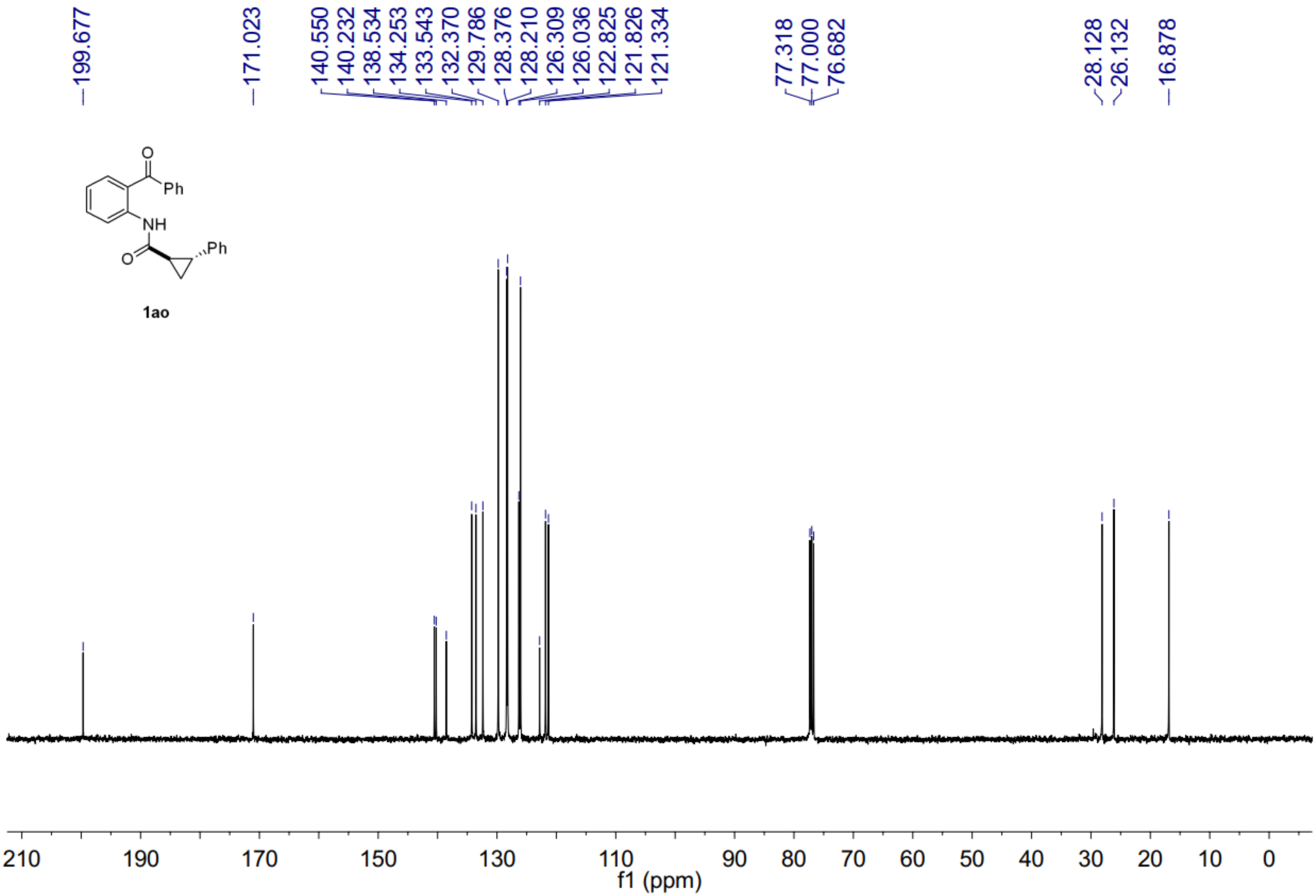
1an



164.831
148.954
144.805
144.398
142.367
133.692
131.449
131.406
129.918
128.915
128.585
128.064
128.044
127.102
127.043
123.478
119.097
97.008
84.564
77.318
77.000
76.682
35.216
35.199
34.000
33.893
31.929
31.884
19.907
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1ao
11.195
8.720
8.700
7.716
7.713
7.700
7.695
7.692
7.602
7.596
7.591
7.583
7.578
7.574
7.564
7.505
7.502
7.486
7.467
7.311
7.293
7.278
7.274
7.226
7.223
7.208
7.152
7.148
7.143
7.131
7.107
7.104
7.087
7.086
7.069
7.066
1.933
1.930
1.922
1.920
1.912
1.910
1.771
1.760
1.748
1.737
1.394
1.390
1.382
0.82
0.92
1.89
2.89
1.93
1.94
0.97
1.91
1.00
0.95
1.01
0.97
0.99
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



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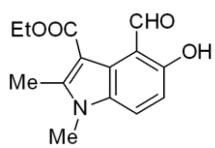
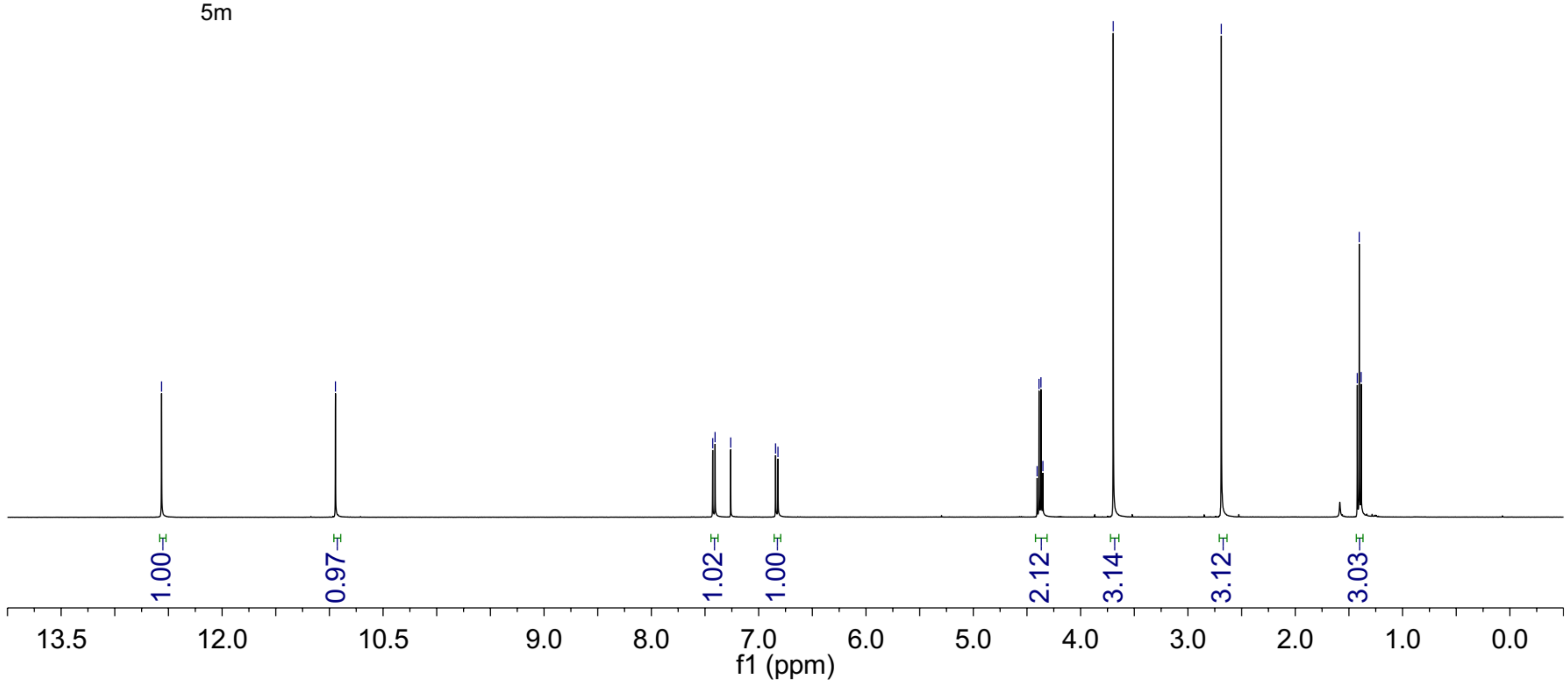
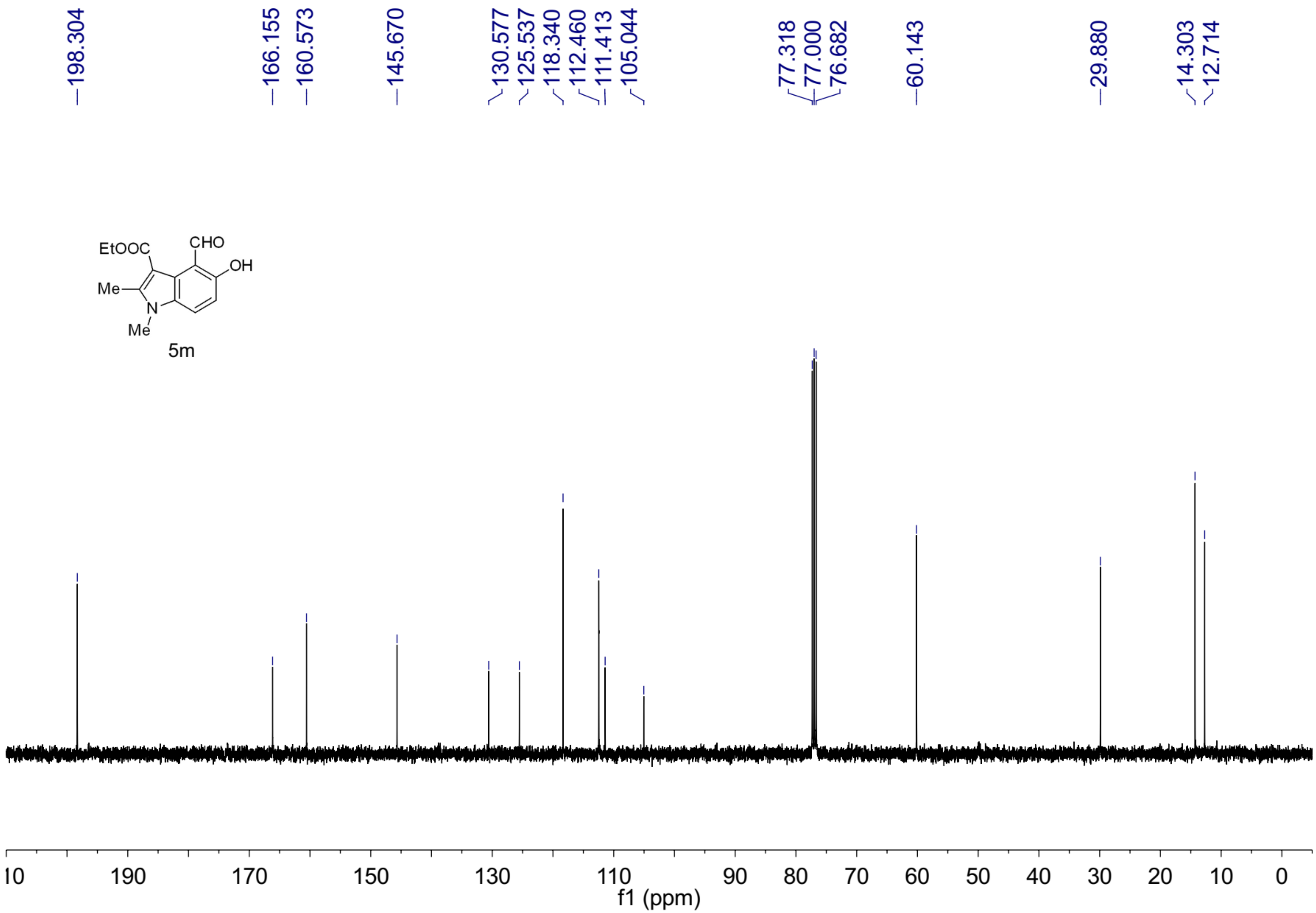
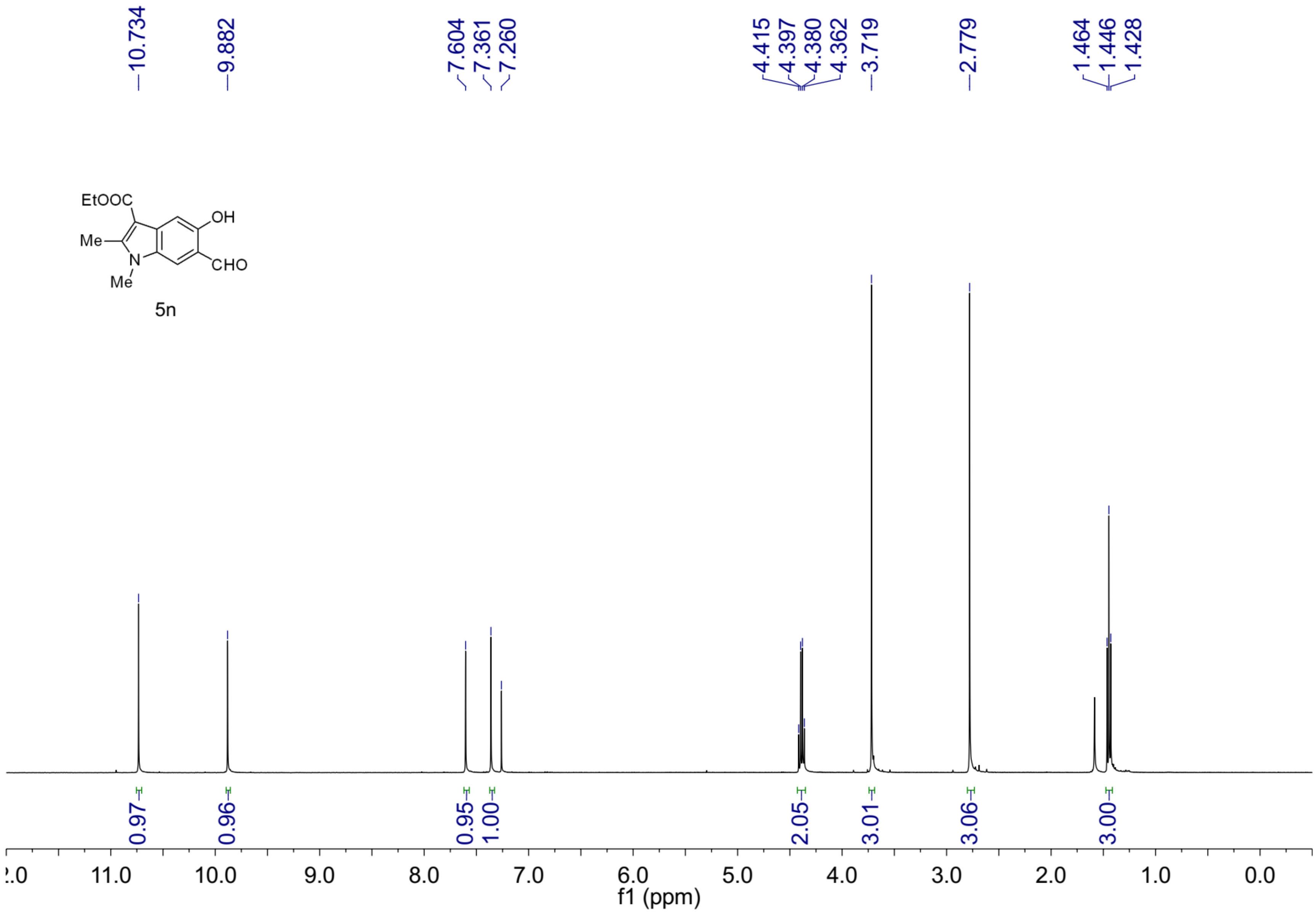
140.550
140.232
138.534
134.253
133.543
132.370
129.786
128.376
128.210
126.309
126.036
122.825
121.826
121.334
77.318
77.000
76.682
28.128
26.132
16.878
O
Ph
NH
O
Ph
1ao
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


EtOOC
CHO
OH
Me
N
Me
5m


12.564
10.944
7.429
7.406
7.260
6.843
6.820
4.405
4.388
4.370
4.352
3.696
2.689
1.422
1.404
1.386
1.00
0.97
1.02
1.00
2.12
3.14
3.12
3.03
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


198.304
166.155
160.573
145.670
130.577
125.537
118.340
112.460
111.413
105.044
77.318
77.000
76.682
60.143
29.880
14.303
12.714
EtOOC
CHO
OH
Me
N
Me
5m
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.734
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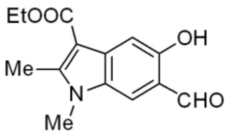
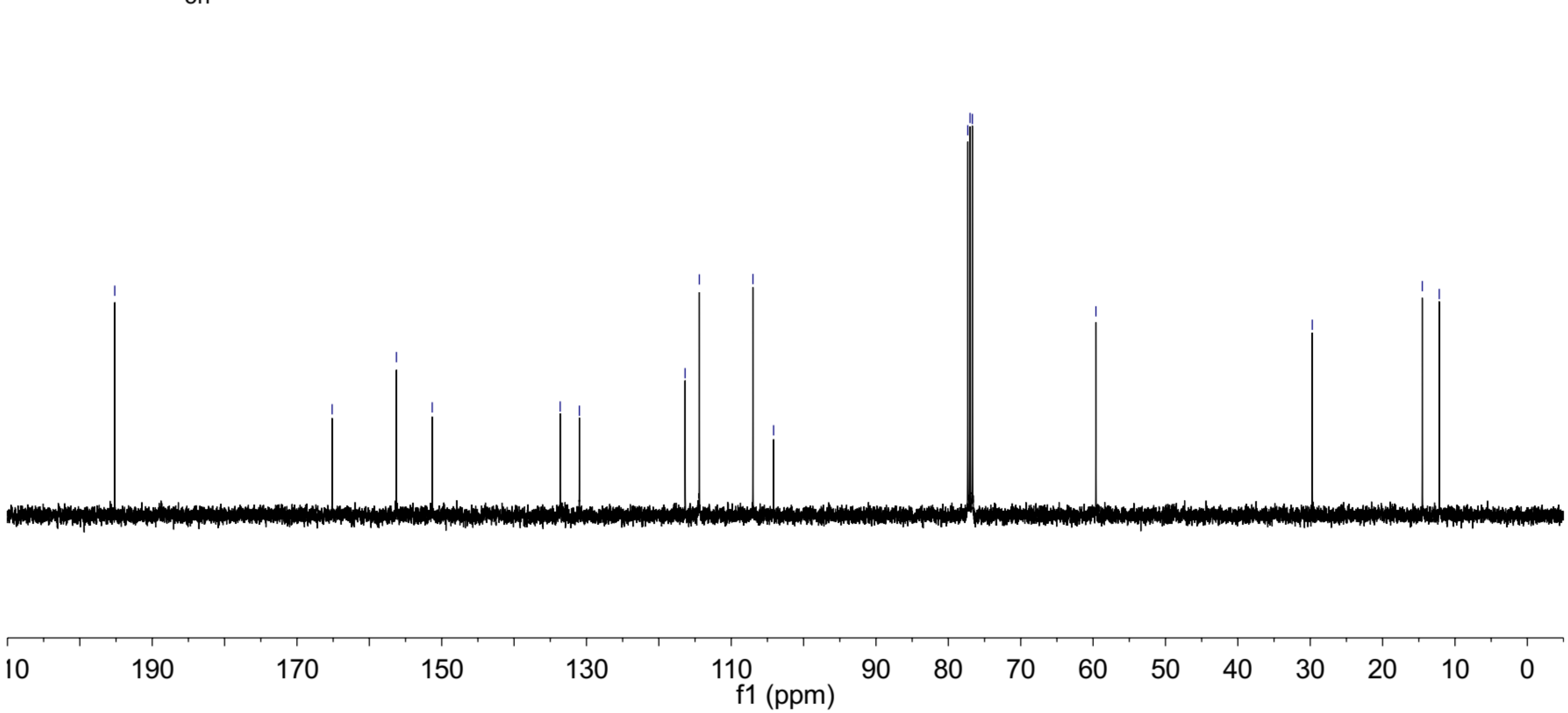
7.604
7.361
7.260
4.415
4.397
4.380
4.362
3.719
2.779
1.464
1.446
1.428
EtOOC
OH
Me
N
Me
CHO
5n
0.97
0.96
0.95
1.00
2.05
3.01
3.06
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


EtOOC
OH
Me
N
Me
CHO

5n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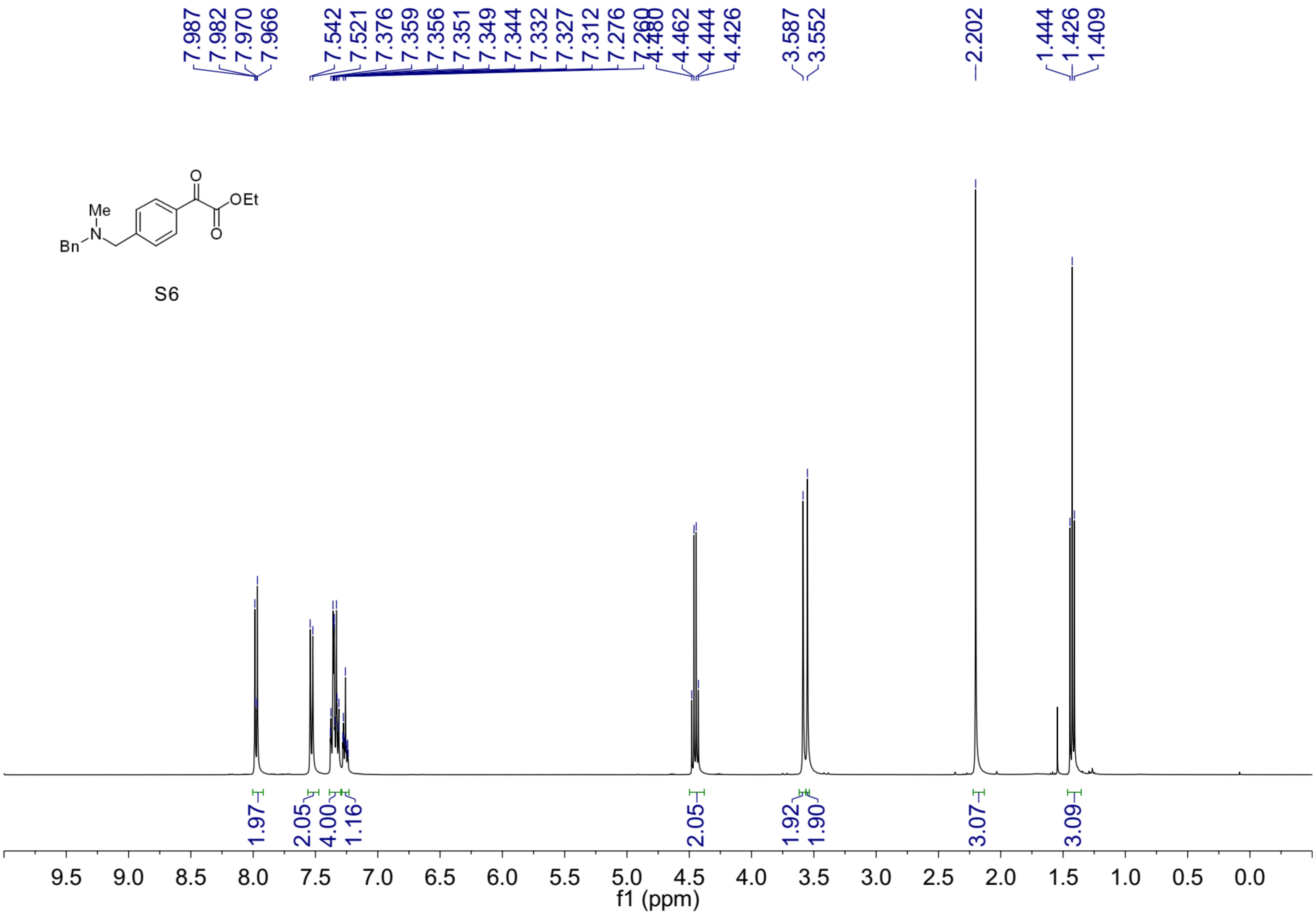
165.141
156.257
151.314
133.634
130.980
116.372
114.405
107.000
104.146
77.318
77.000
76.682
59.611
29.716
14.515
12.173
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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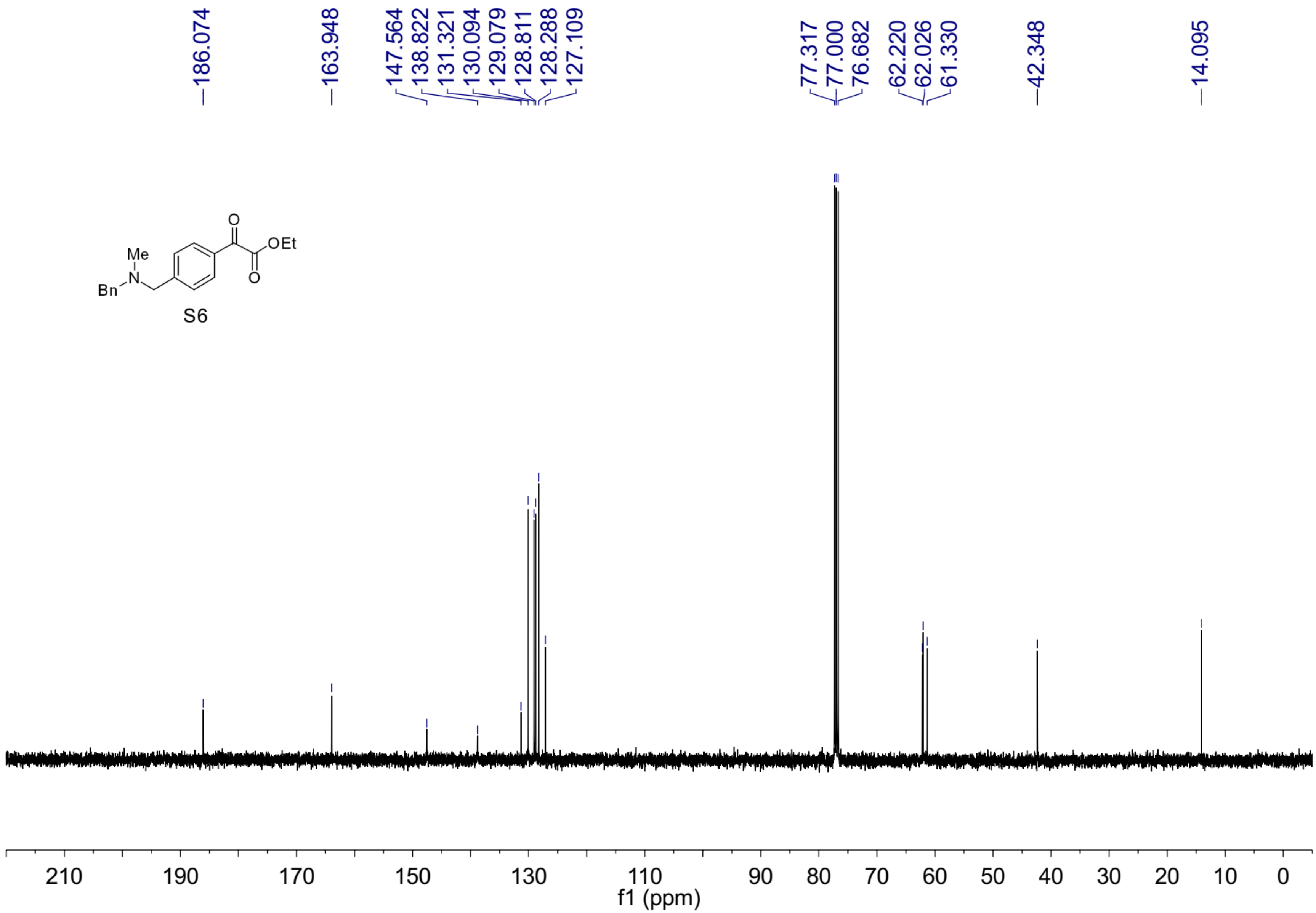
7.376
7.359
7.356
7.351
7.349
7.344
7.332
7.327
7.312
7.276
7.260
4.480
4.462
4.444
4.426
3.587
3.552
2.202
1.444
1.426
1.409
O
OEt
O
Me
N
Bn
S6
1.97
2.05
4.00
1.16
2.05
1.92
1.90
3.07
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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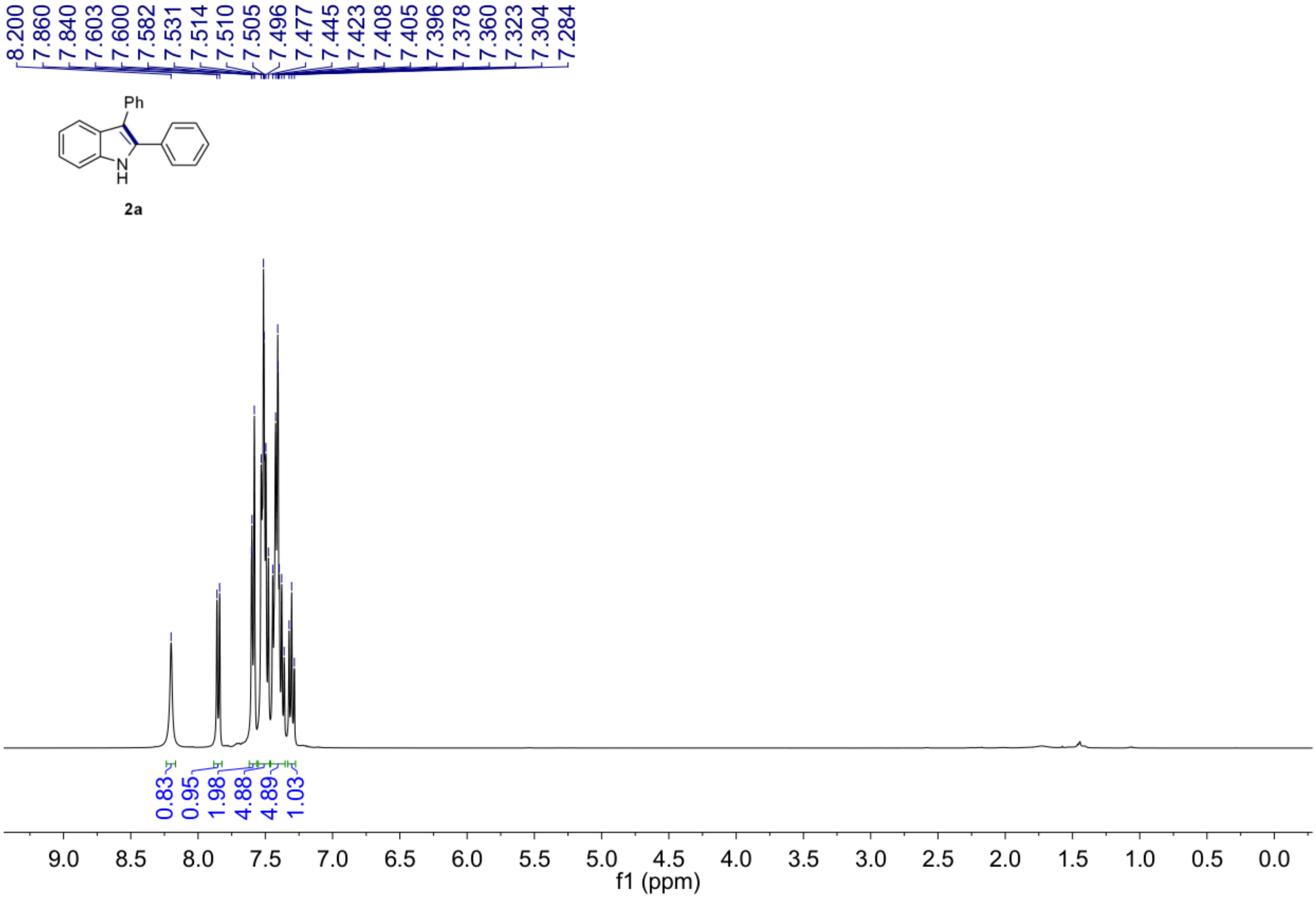
163.948
147.564
138.822
131.321
130.094
129.079
128.811
128.288
127.109
77.317
77.000
76.682
62.220
62.026
61.330
42.348
14.095
Me
N
Bn
O
OEt
O
S6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.600
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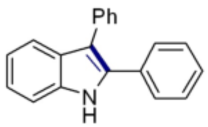
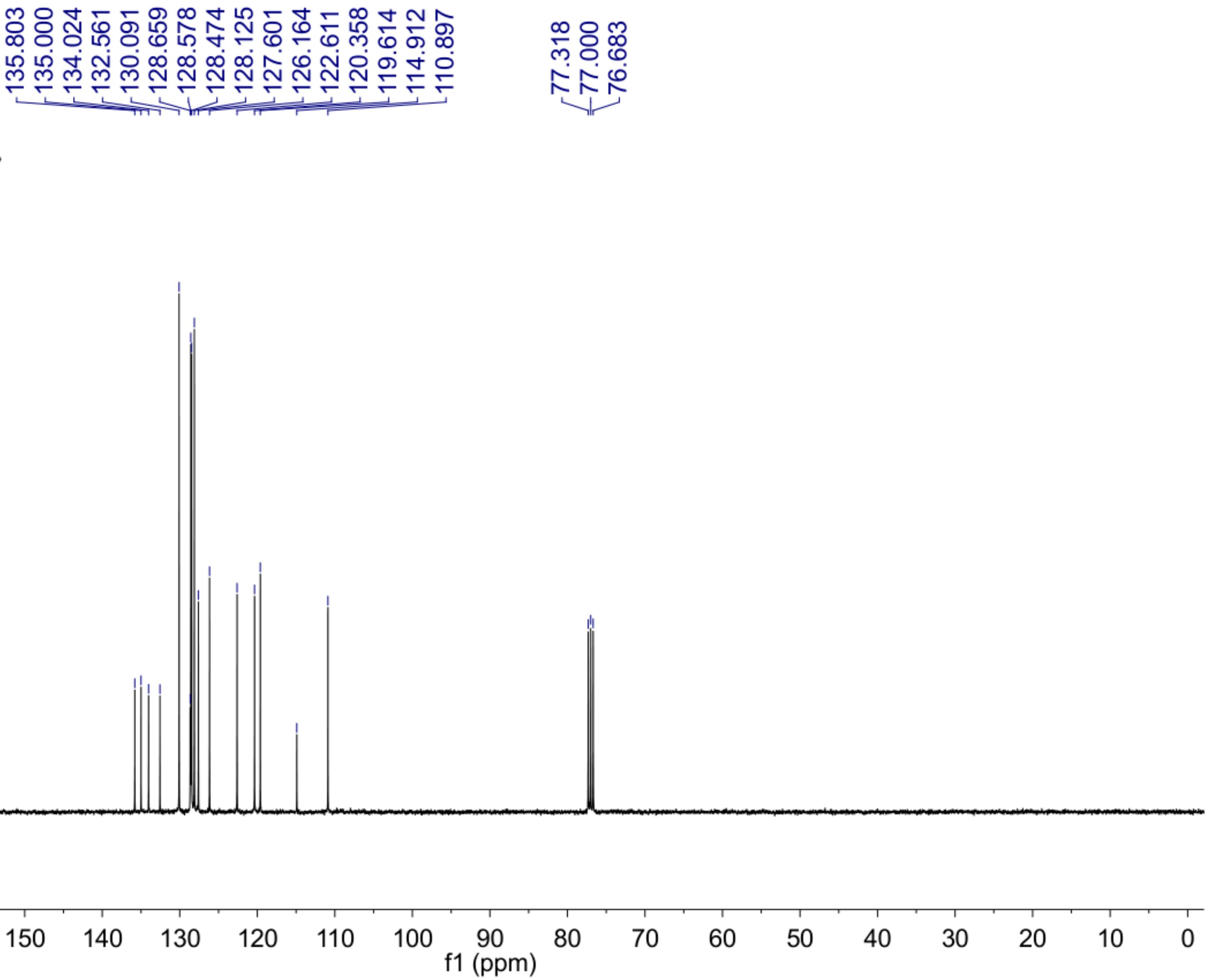
7.531
7.514
7.510
7.505
7.496
7.477
7.445
7.423
7.408
7.405
7.396
7.378
7.360
7.323
7.304
7.284
Ph
N
H
2a
0.83
0.95
1.98
4.88
4.89
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
N
H

2a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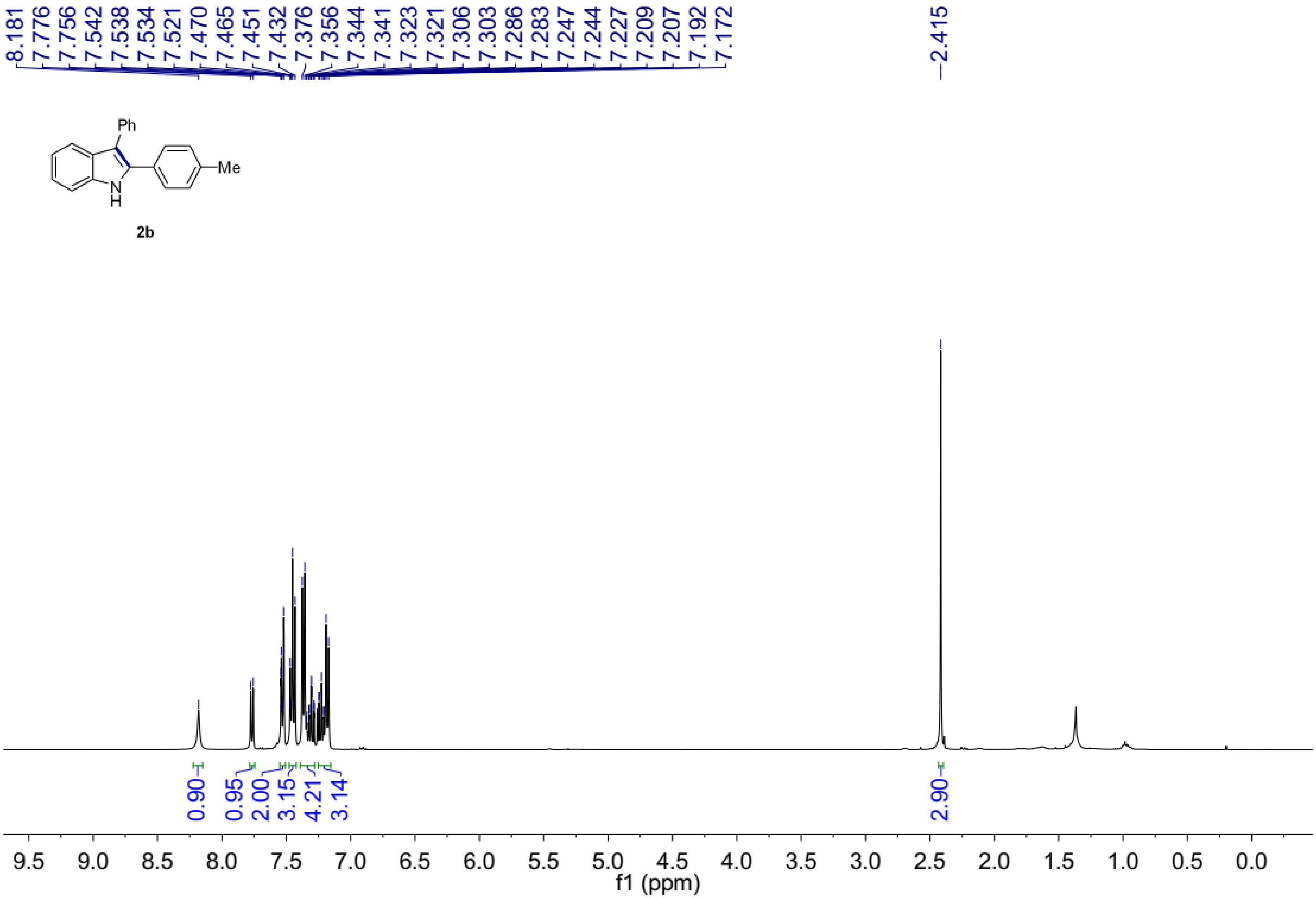
132.561
130.091
128.659
128.578
128.474
128.125
127.601
126.164
122.611
120.358
119.614
114.912
110.897
77.318
77.000
76.683
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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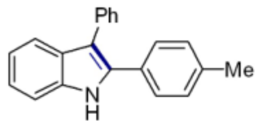
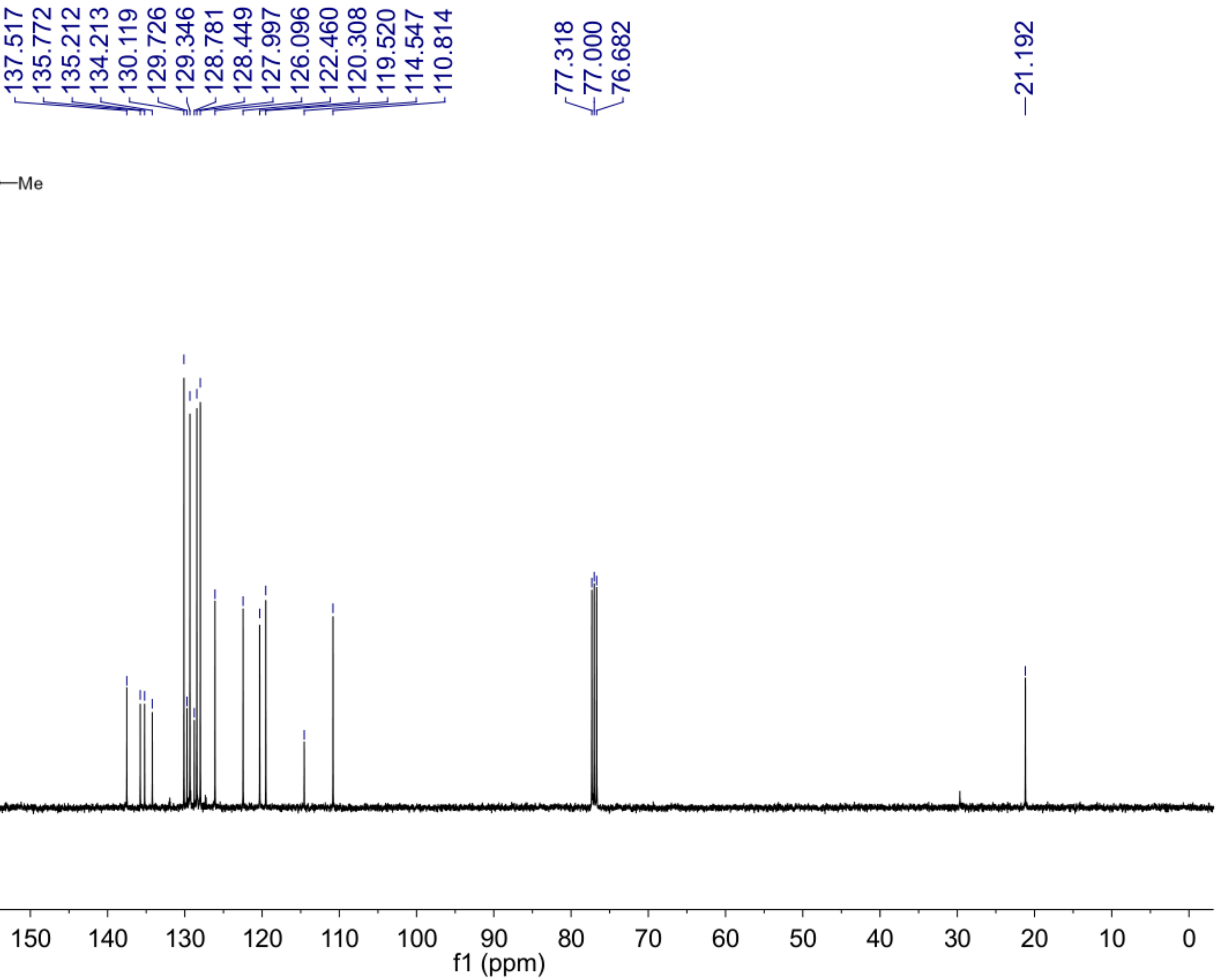
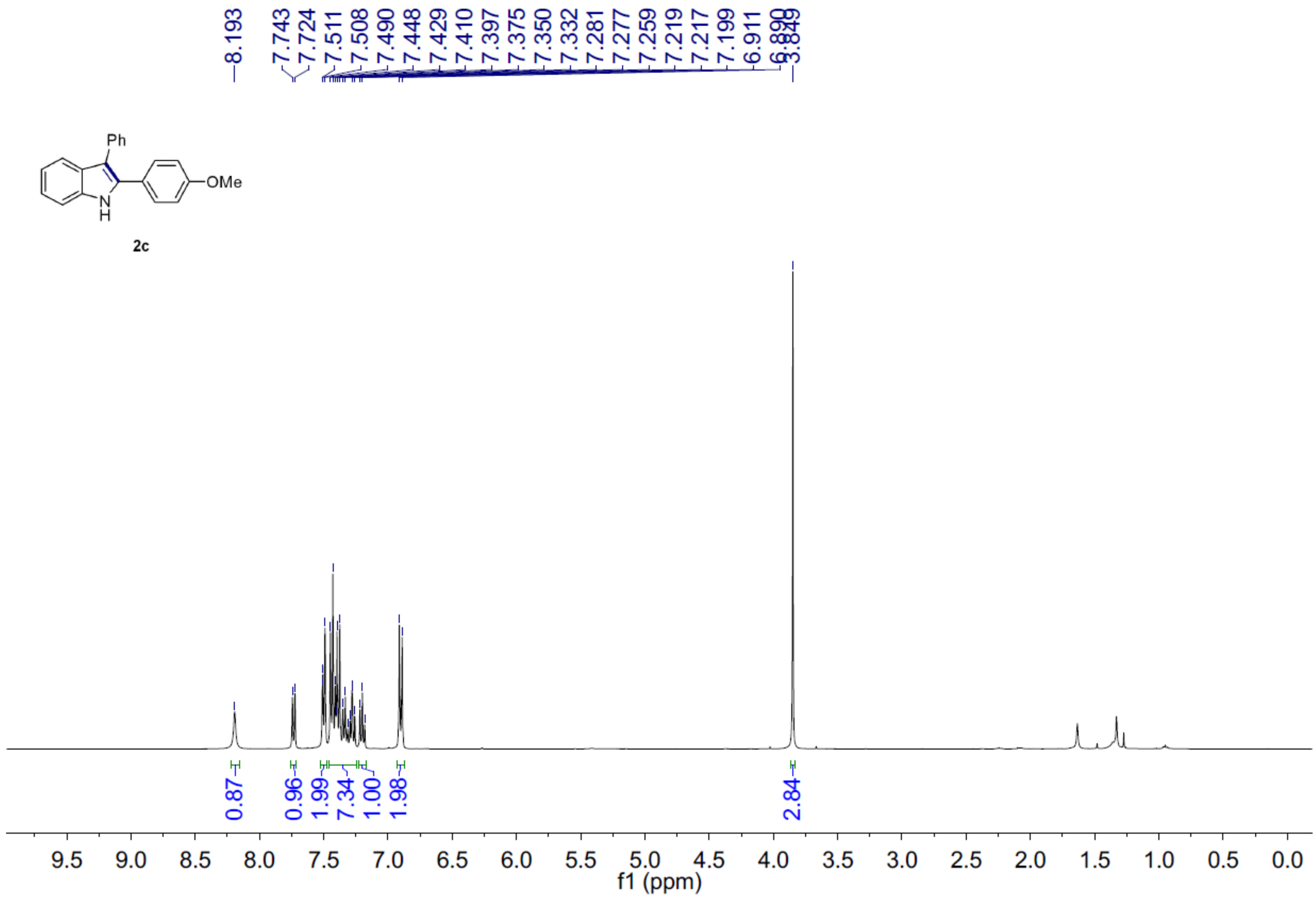
7.534
7.521
7.470
7.465
7.451
7.432
7.376
7.356
7.344
7.341
7.323
7.321
7.306
7.303
7.286
7.283
7.247
7.244
7.227
7.209
7.207
7.192
7.172
2.415
Ph
Me
N
H
2b
0.90
0.95
2.00
3.15
4.21
3.14
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



2b



137.517
135.772
135.212
134.213
130.119
129.726
129.346
128.781
128.449
127.997
126.096
122.460
120.308
119.520
114.547
110.814
77.318
77.000
76.682
21.192
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.193
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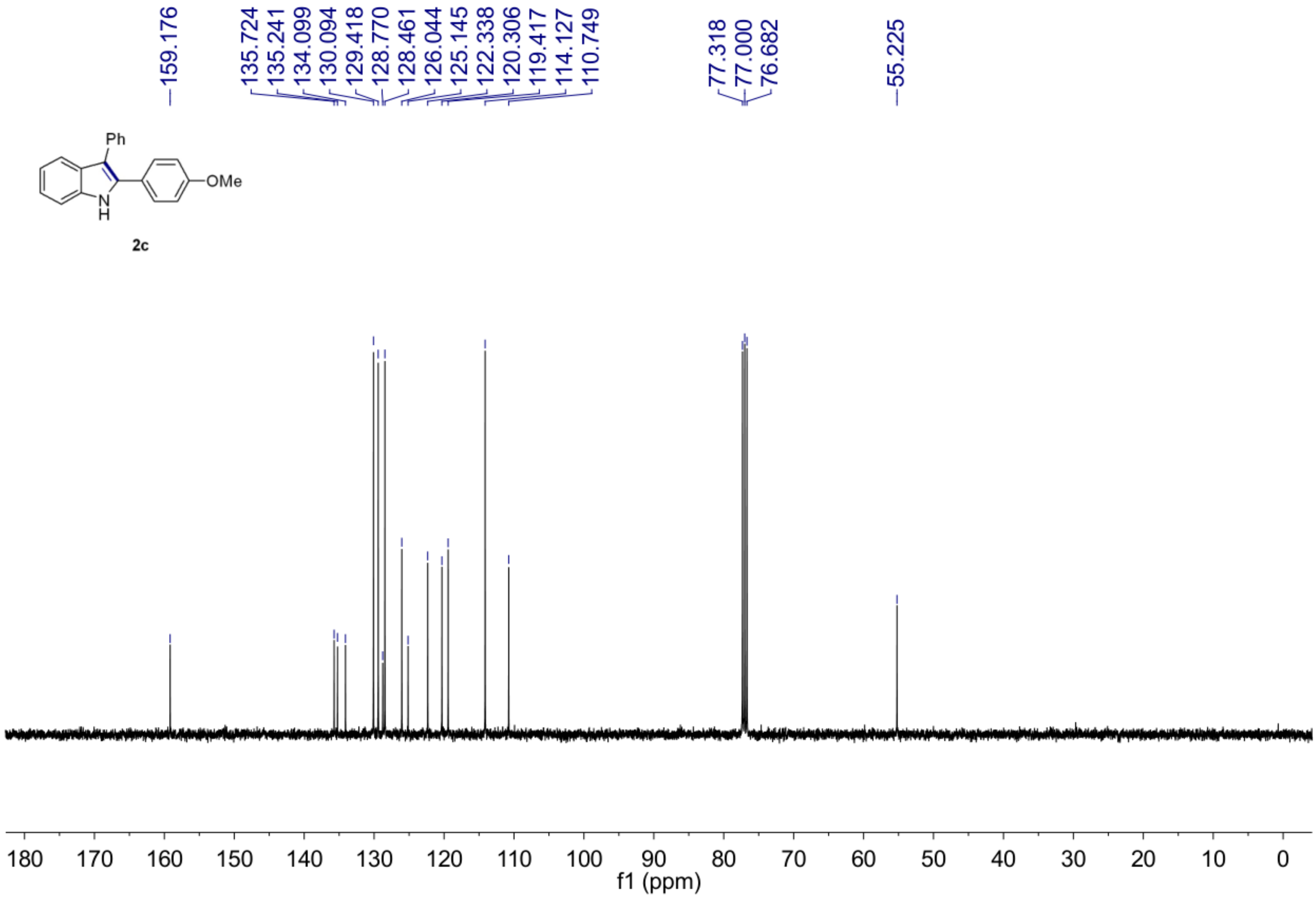
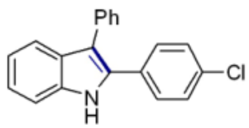
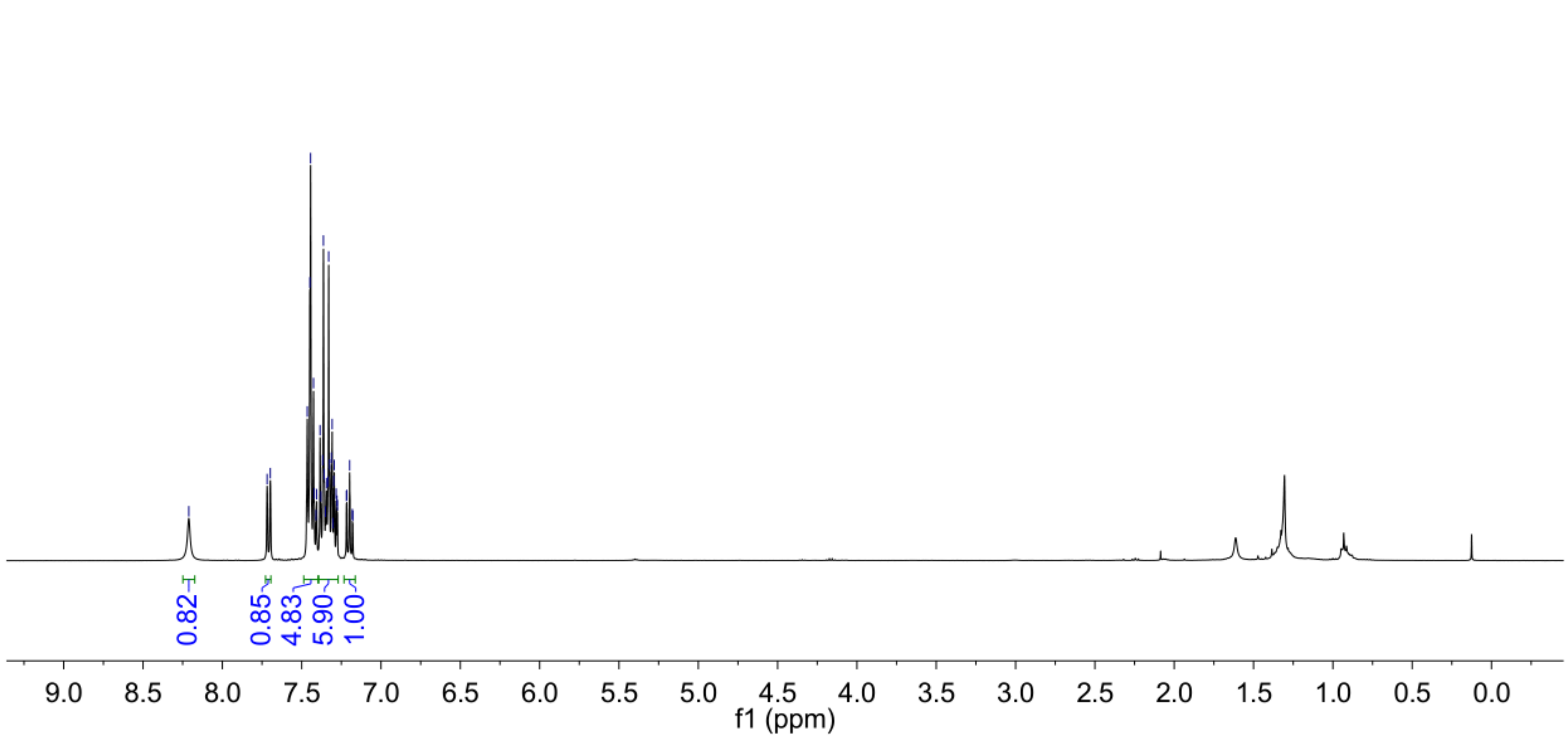
7.724
7.511
7.508
7.490
7.448
7.429
7.410
7.397
7.375
7.350
7.332
7.281
7.277
7.259
7.219
7.217
7.199
6.911
6.890
3.849
Ph
OMe
N
H
2c
0.87
0.96
1.99
7.34
1.00
1.98
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



159.176
135.724
135.241
134.099
130.094
129.418
128.770
128.461
126.044
125.145
122.338
120.306
119.417
114.127
110.749
77.318
77.000
76.682
55.225
Ph
OMe
N
H
2c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
N
H
Cl

2d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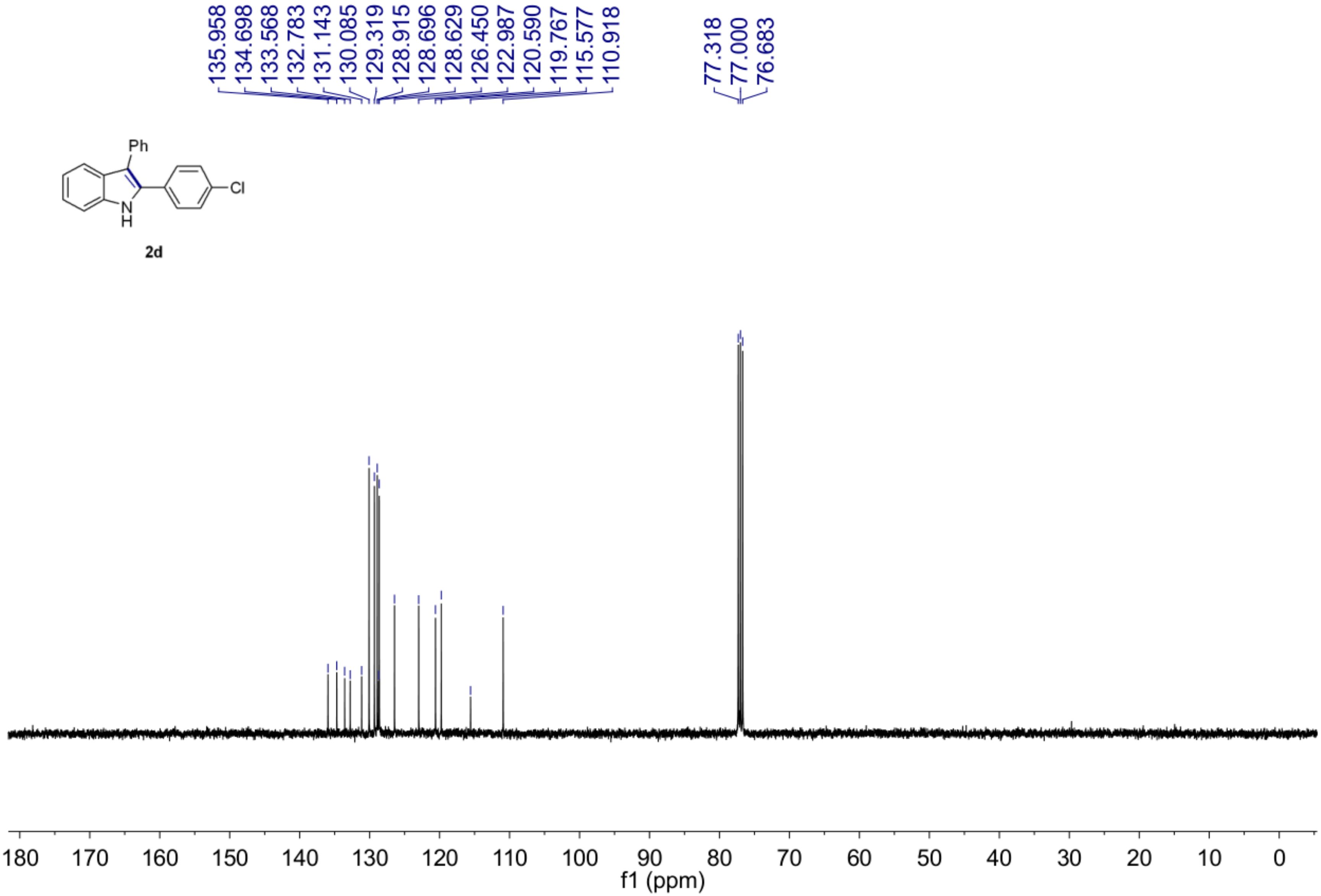
7.718
7.698
7.465
7.448
7.444
7.425
7.421
7.410
7.406
7.384
7.379
7.368
7.363
7.358
7.350
7.344
7.335
7.330
7.324
7.313
7.308
7.302
7.297
7.295
7.283
7.277
7.275
7.218
7.216
7.198
7.180
7.178
0.82
0.85
4.83
5.90
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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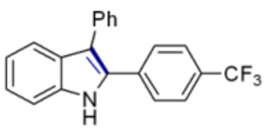
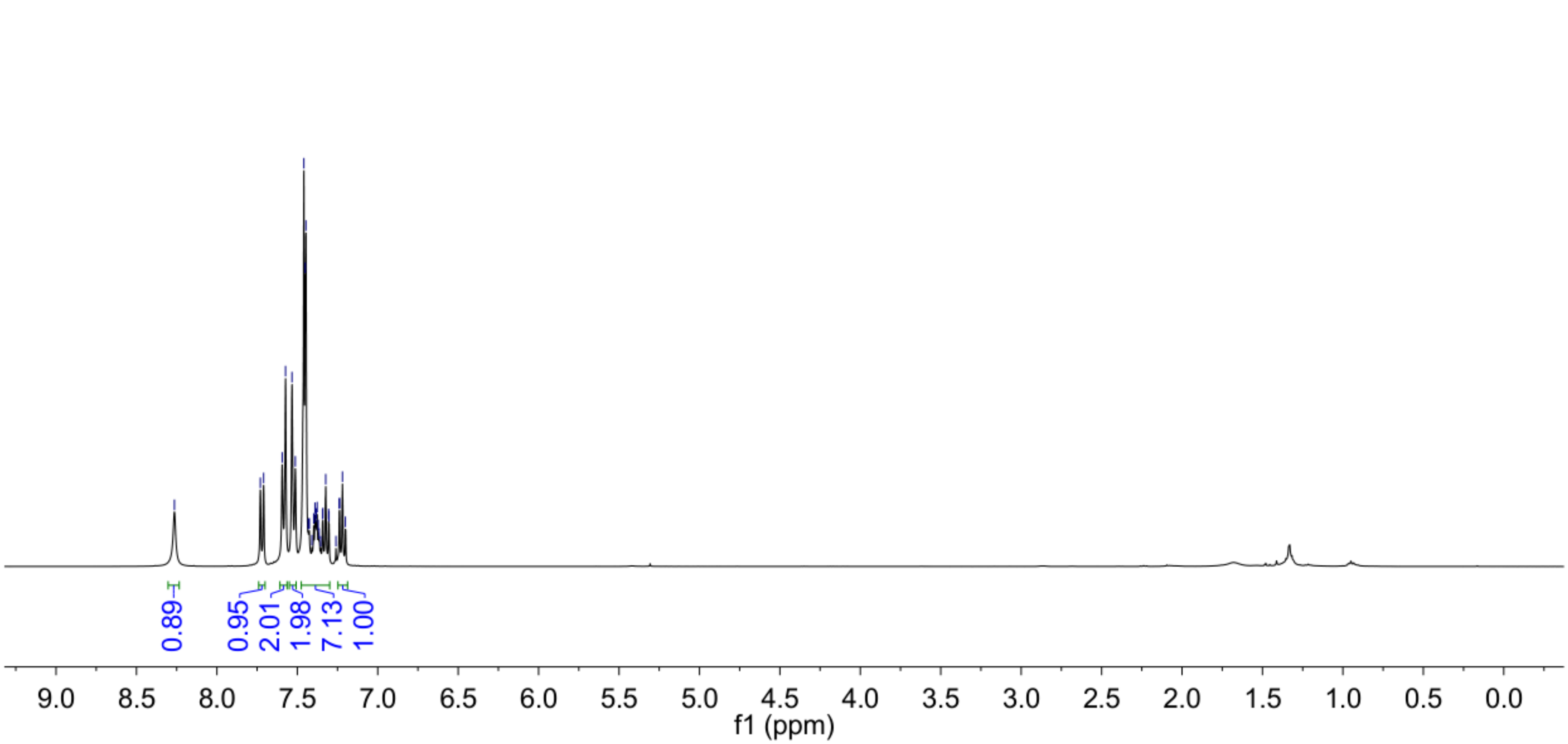
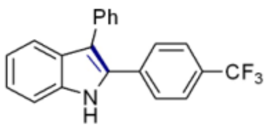
134.698
133.568
132.783
131.143
130.085
129.319
128.915
128.696
128.629
126.450
122.987
120.590
119.767
115.577
110.918
77.318
77.000
76.683
Ph
N
H
Cl
2d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

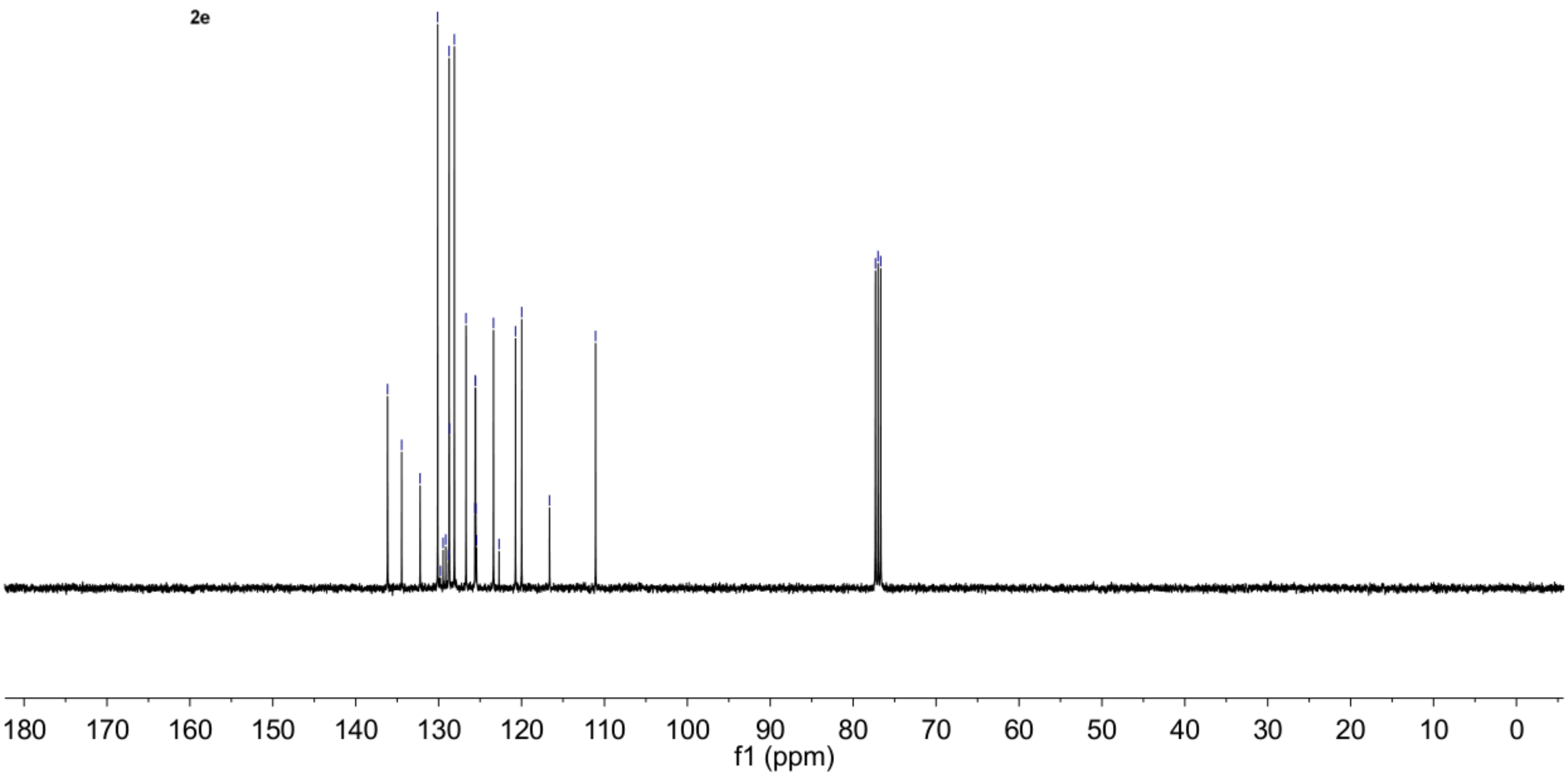

Ph
CF3
N
H

2e


8.264
7.730
7.710
7.594
7.573
7.533
7.512
7.459
7.451
7.446
7.432
7.428
7.426
7.409
7.398
7.390
7.386
7.382
7.376
7.370
7.364
7.355
7.343
7.341
7.323
7.305
7.303
7.260
7.239
7.237
7.219
7.201
0.89
0.95
2.01
1.98
7.13
1.00
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)


Ph
CF3
N
H

2e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134.459
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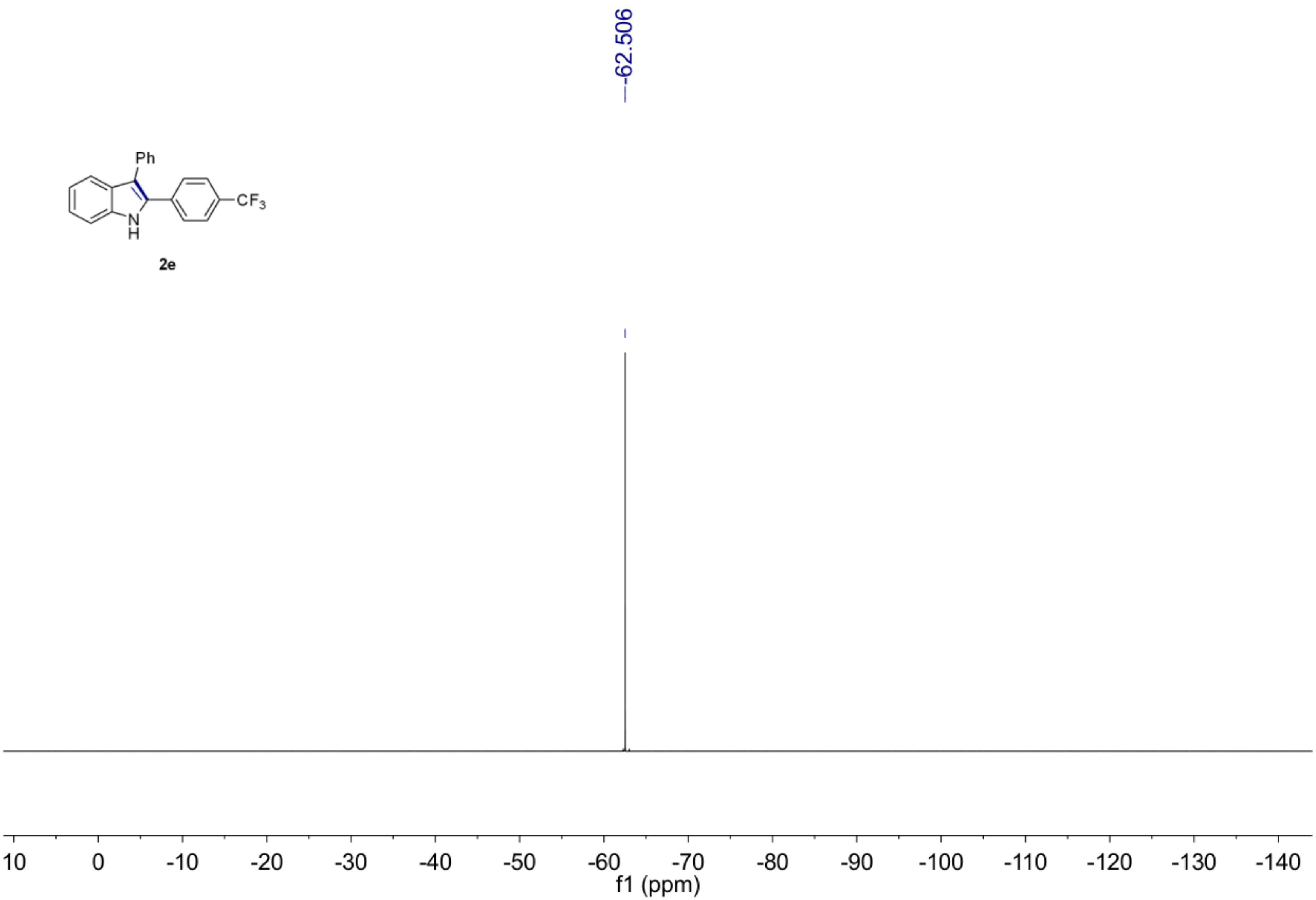
130.118
129.784
129.460
129.135
128.810
128.737
128.709
128.103
126.696
125.625
125.588
125.550
125.513
125.418
123.388
122.715
120.730
119.983
116.627
111.071
77.317
77.000
76.682
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
CF3
N
H
2e
-62.506
10
0
-10
-20
-30
-40
-50
-60
-70
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-90
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-110
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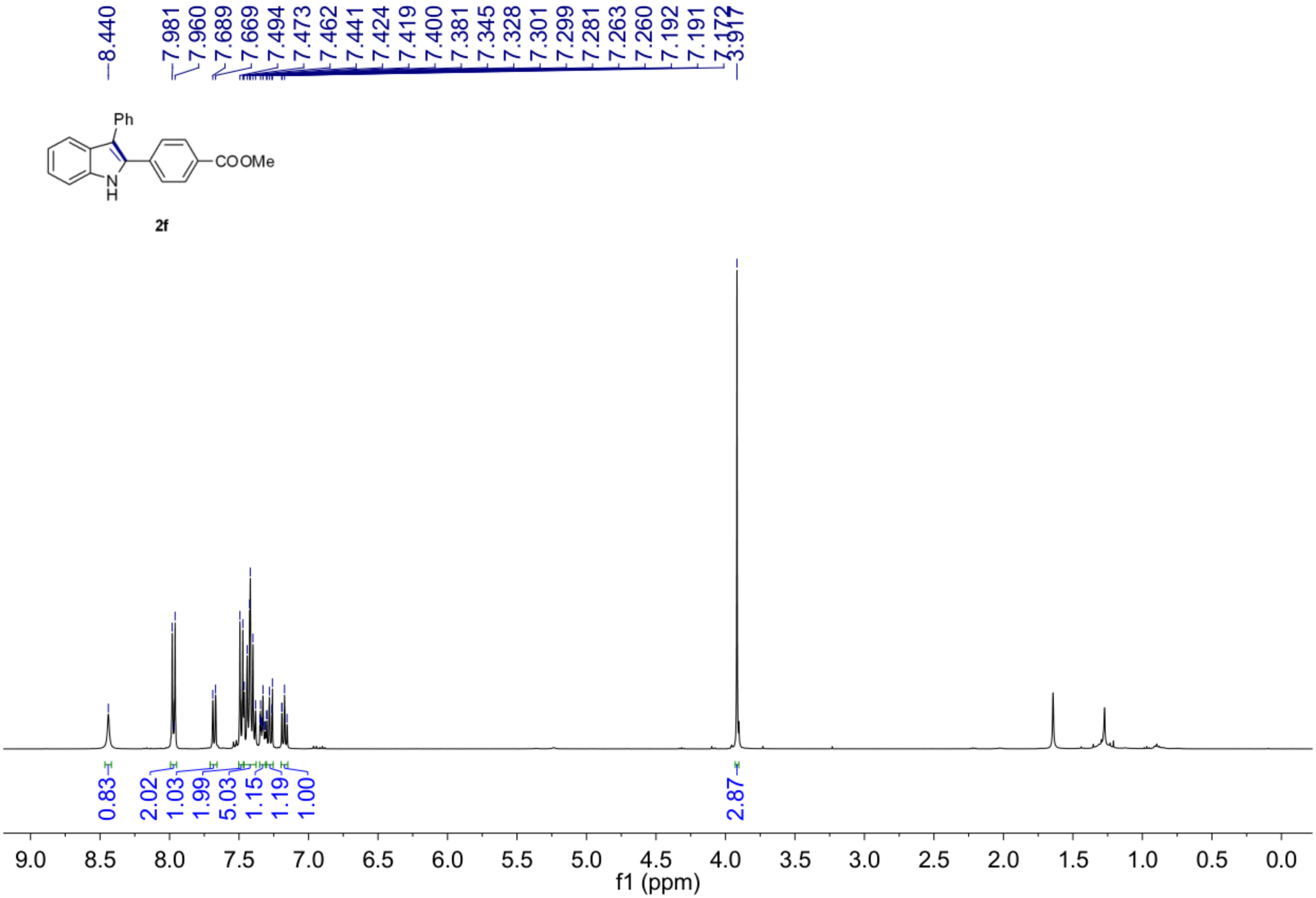
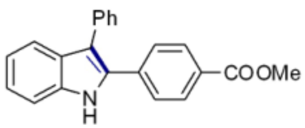
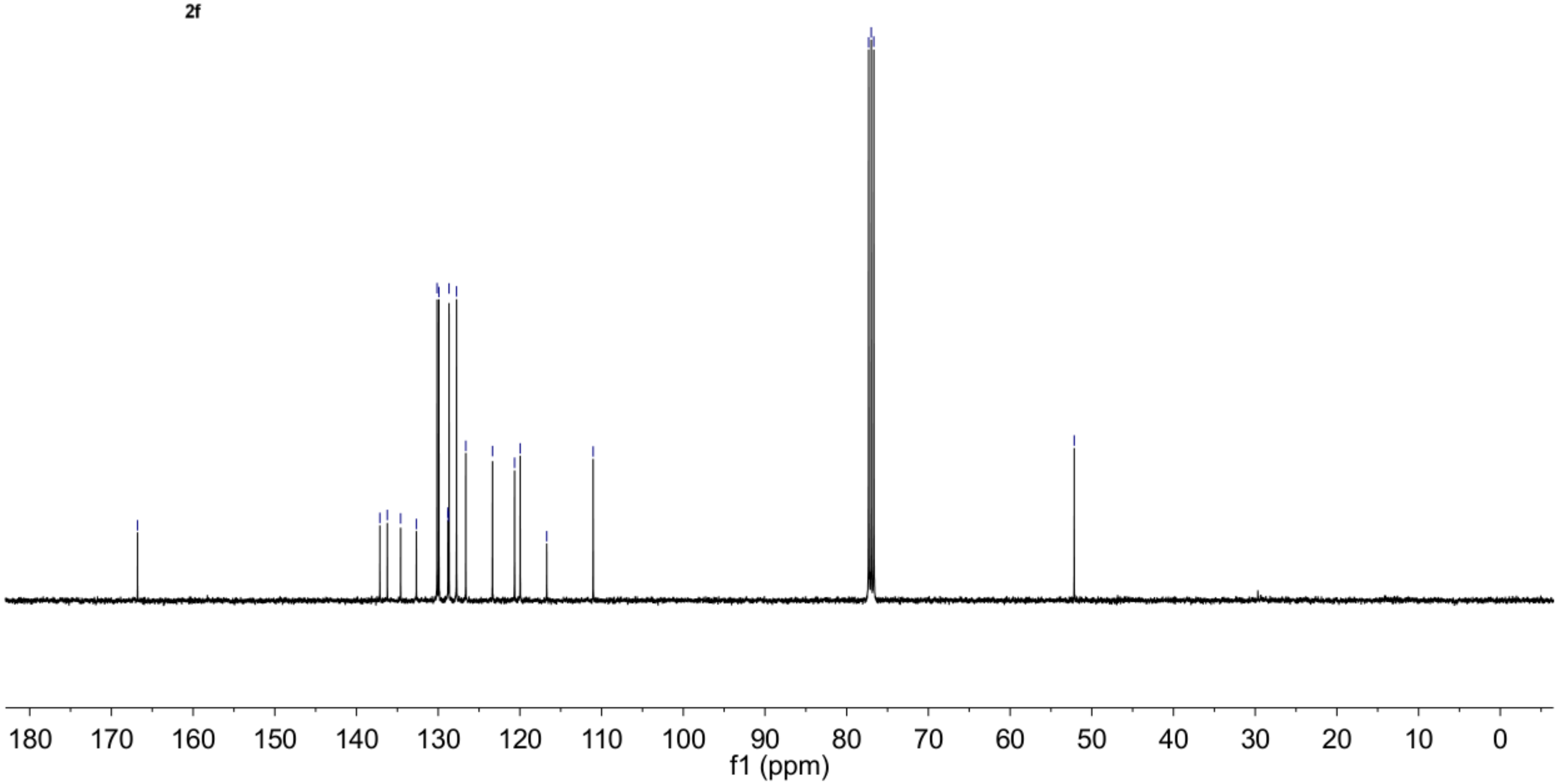
-130
-140
f1 (ppm)

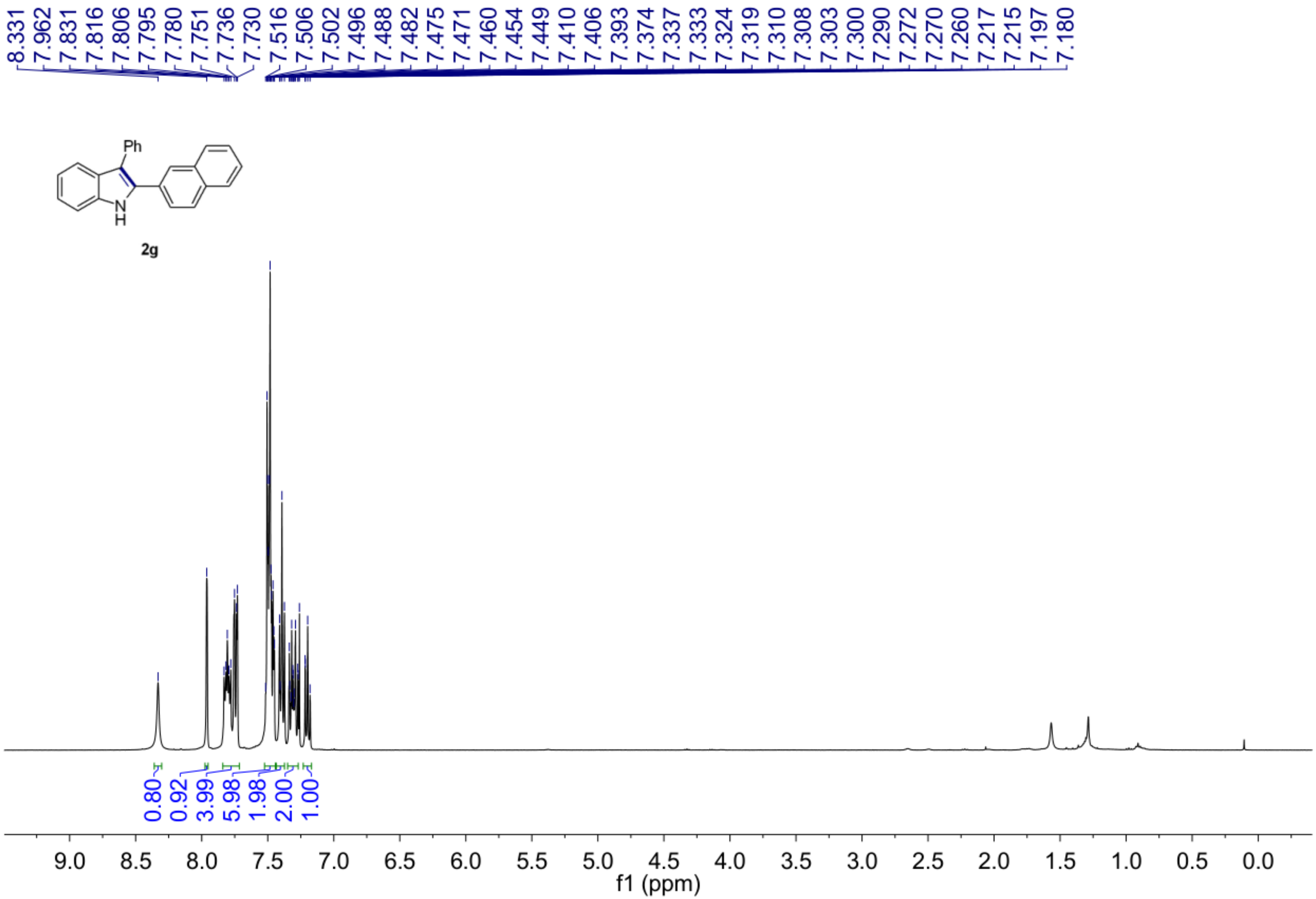

8.440
7.981
7.960
7.689
7.669
7.494
7.473
7.462
7.441
7.424
7.419
7.400
7.381
7.345
7.328
7.301
7.299
7.281
7.263
7.260
7.192
7.191
7.172
3.917
Ph
COOMe
N
H
2f
0.83
2.02
1.03
1.99
5.03
1.15
1.19
1.00
2.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2f

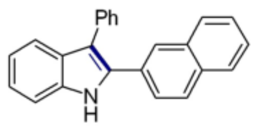


166.804
137.143
136.226
134.602
132.672
130.137
129.915
128.813
128.743
128.674
127.760
126.623
123.353
120.652
119.964
116.718
111.036
77.317
77.000
76.682
52.157
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

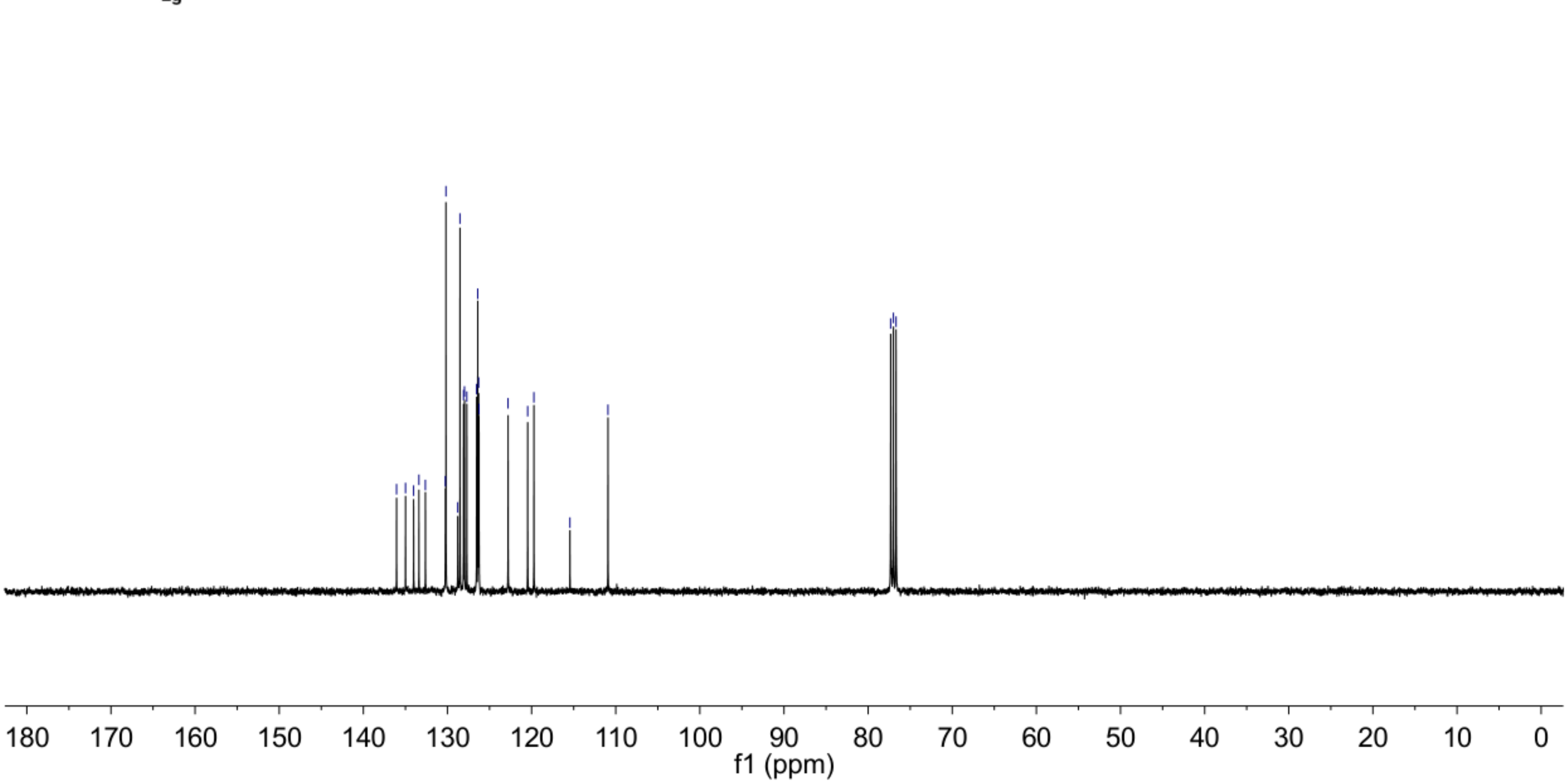


8.331
7.962
7.831
7.816
7.806
7.795
7.780
7.751
7.736
7.730
7.516
7.506
7.502
7.496
7.488
7.482
7.475
7.471
7.460
7.454
7.449
7.410
7.406
7.393
7.374
7.337
7.333
7.324
7.319
7.310
7.308
7.303
7.300
7.290
7.272
7.270
7.260
7.217
7.215
7.197
7.180
Ph
N
H
0.80
0.92
3.99
5.98
1.98
2.00
1.00
9.0
8.5
8.0
7.5
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)

2g


Ph
N
H

2g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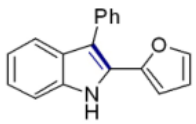
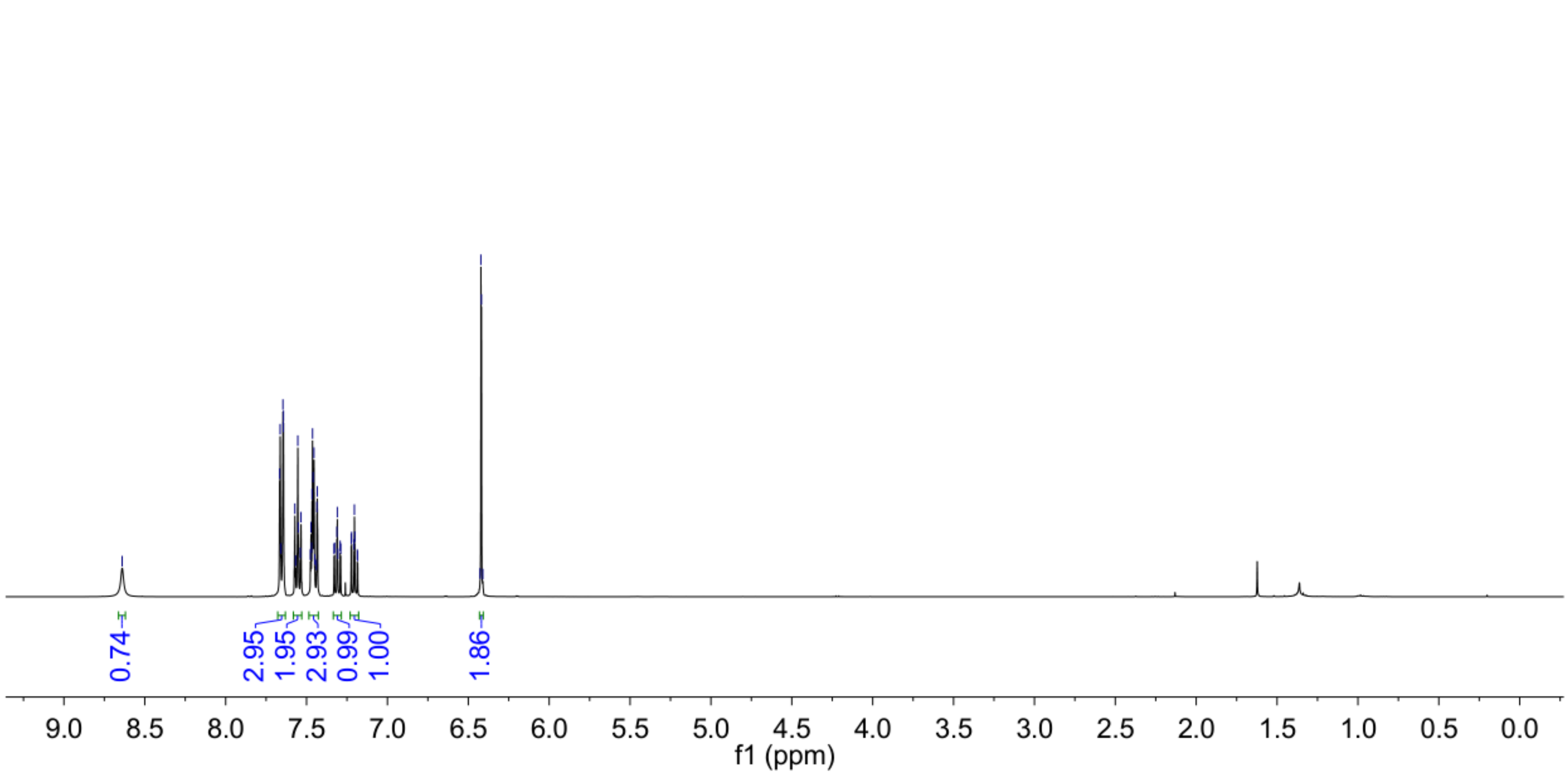
134.026
133.395
132.624
130.254
130.184
128.784
128.518
128.095
127.975
127.702
126.547
126.401
126.294
126.255
122.797
120.467
119.725
115.450
110.924
77.318
77.000
76.682
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
N
H

2h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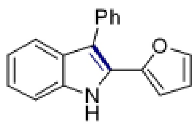
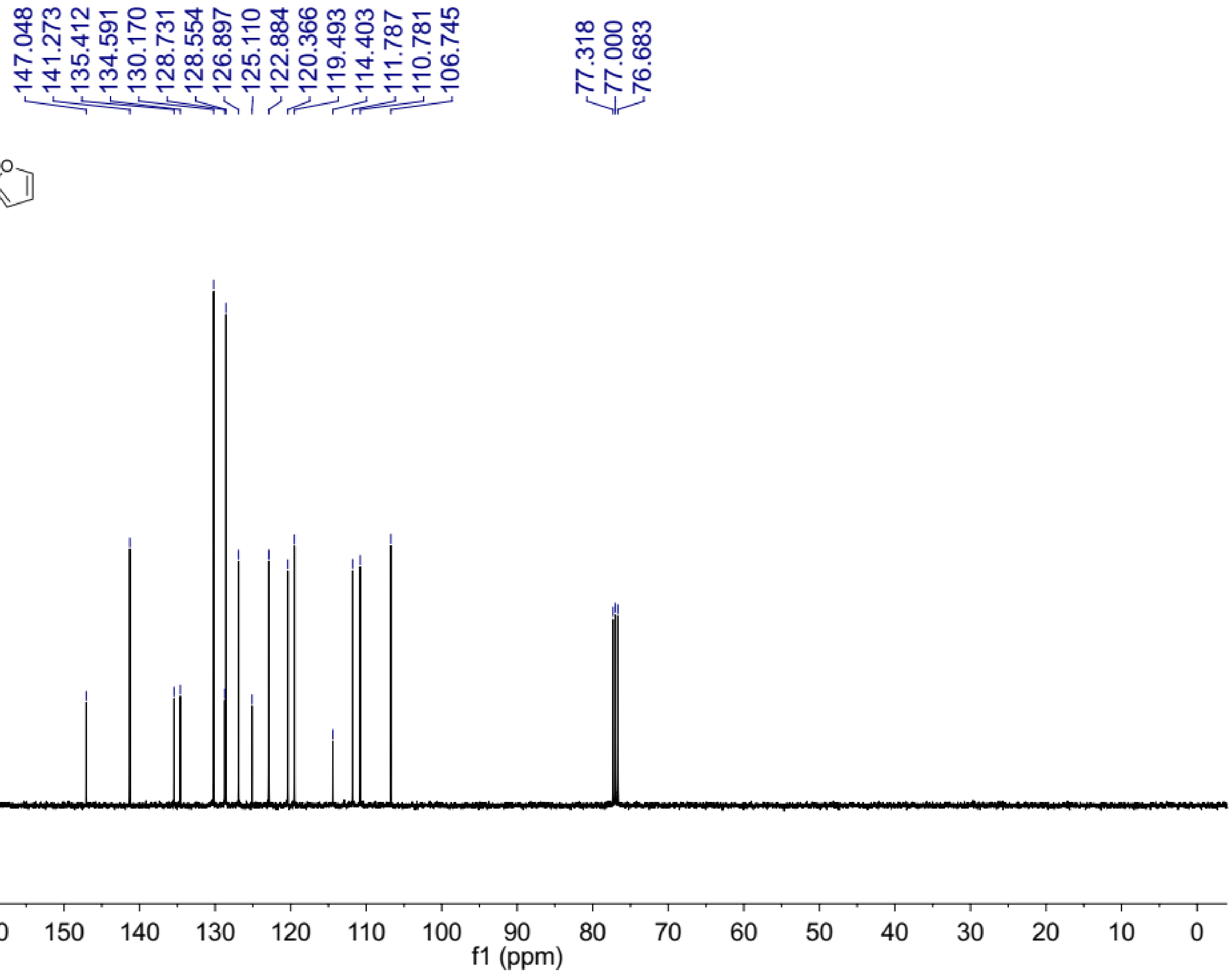
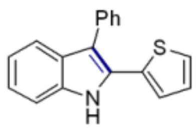
7.667
7.663
7.646
7.644
7.643
7.554
7.463
7.454
6.428
6.422
6.419
6.410
0.74
2.95
1.95
2.93
0.99
1.00
1.86
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

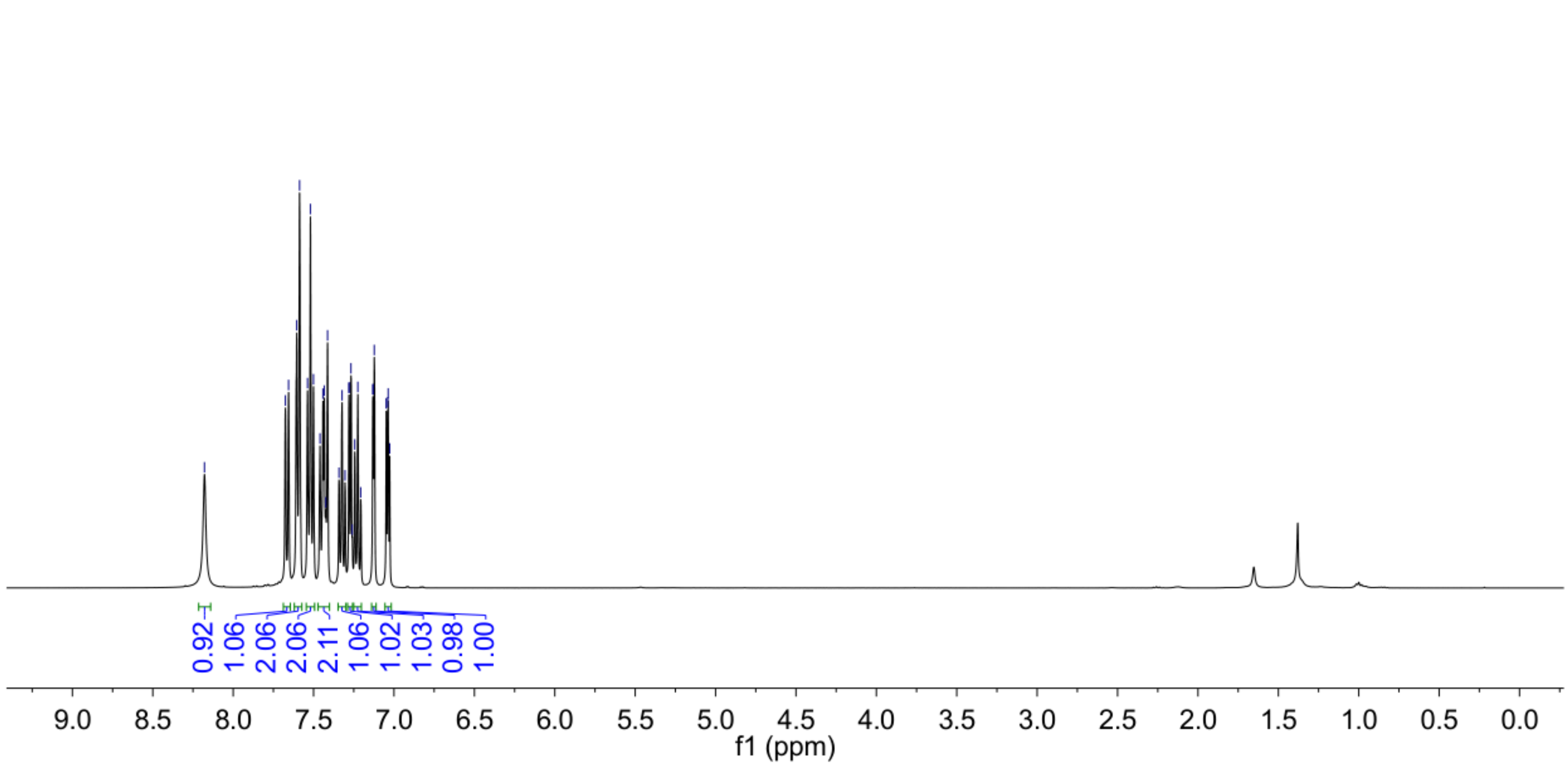


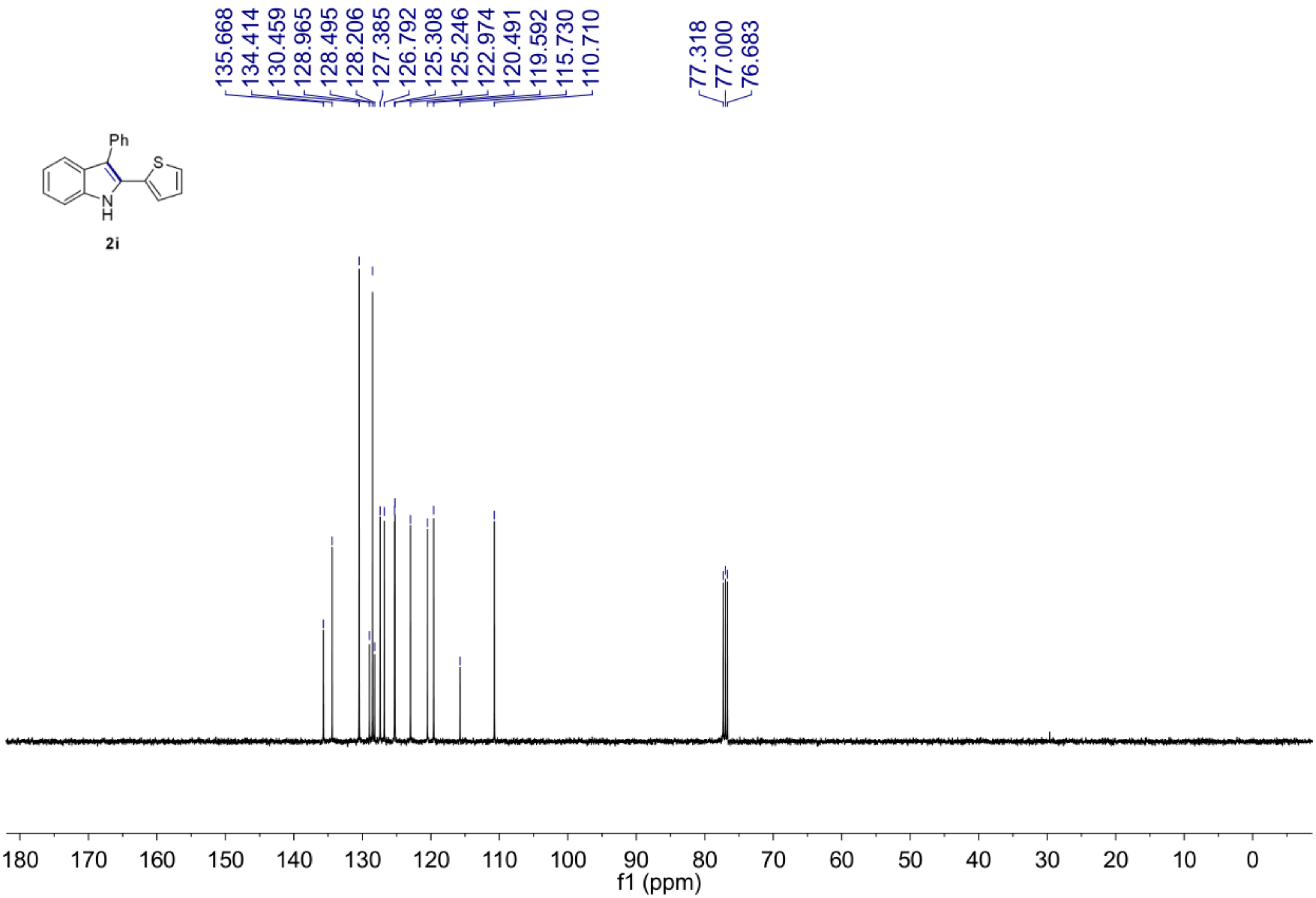
2h


147.048
141.273
135.412
134.591
130.170
128.731
128.554
126.897
125.110
122.884
120.366
119.493
114.403
111.787
110.781
106.745
77.318
77.000
76.683
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
S
N
H

2i


8.179
7.676
7.656
7.605
7.587
7.538
7.520
7.501
7.460
7.442
7.434
7.424
7.413
7.342
7.323
7.305
7.280
7.279
7.268
7.260
7.244
7.225
7.207
7.131
7.130
7.123
7.048
7.039
7.036
7.027
0.92
1.06
2.06
2.06
2.11
1.06
1.02
1.03
0.98
1.00
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)


135.668
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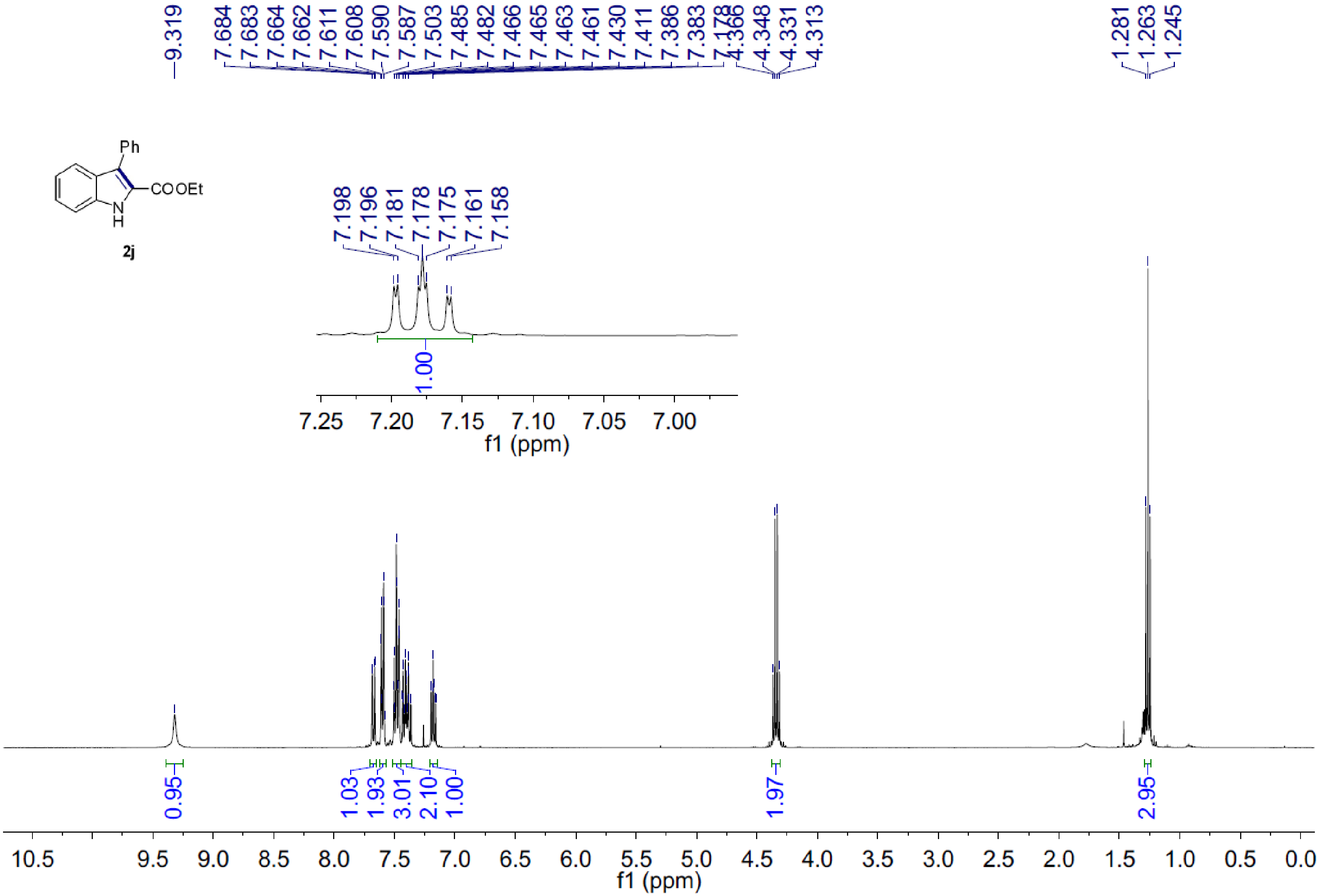
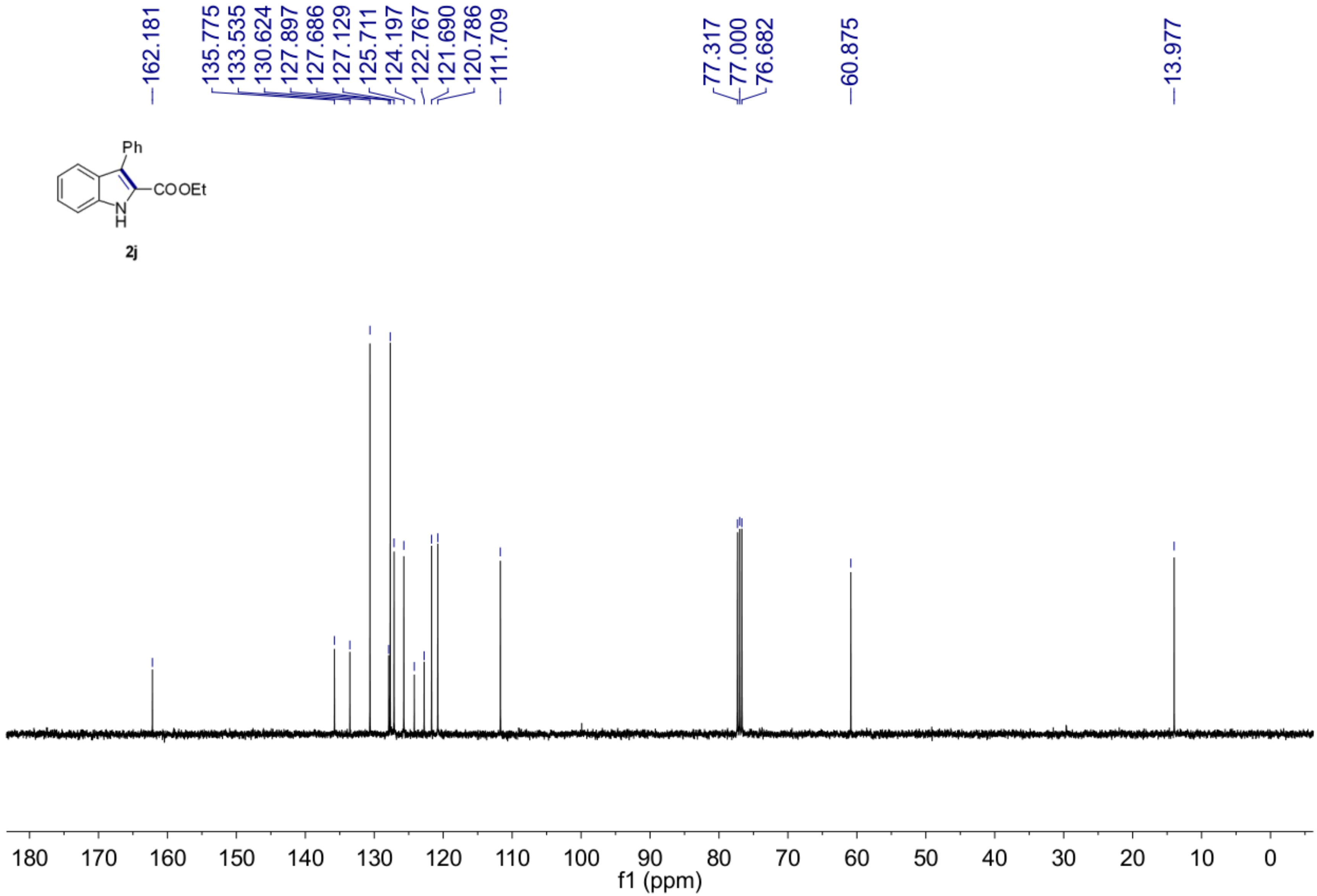
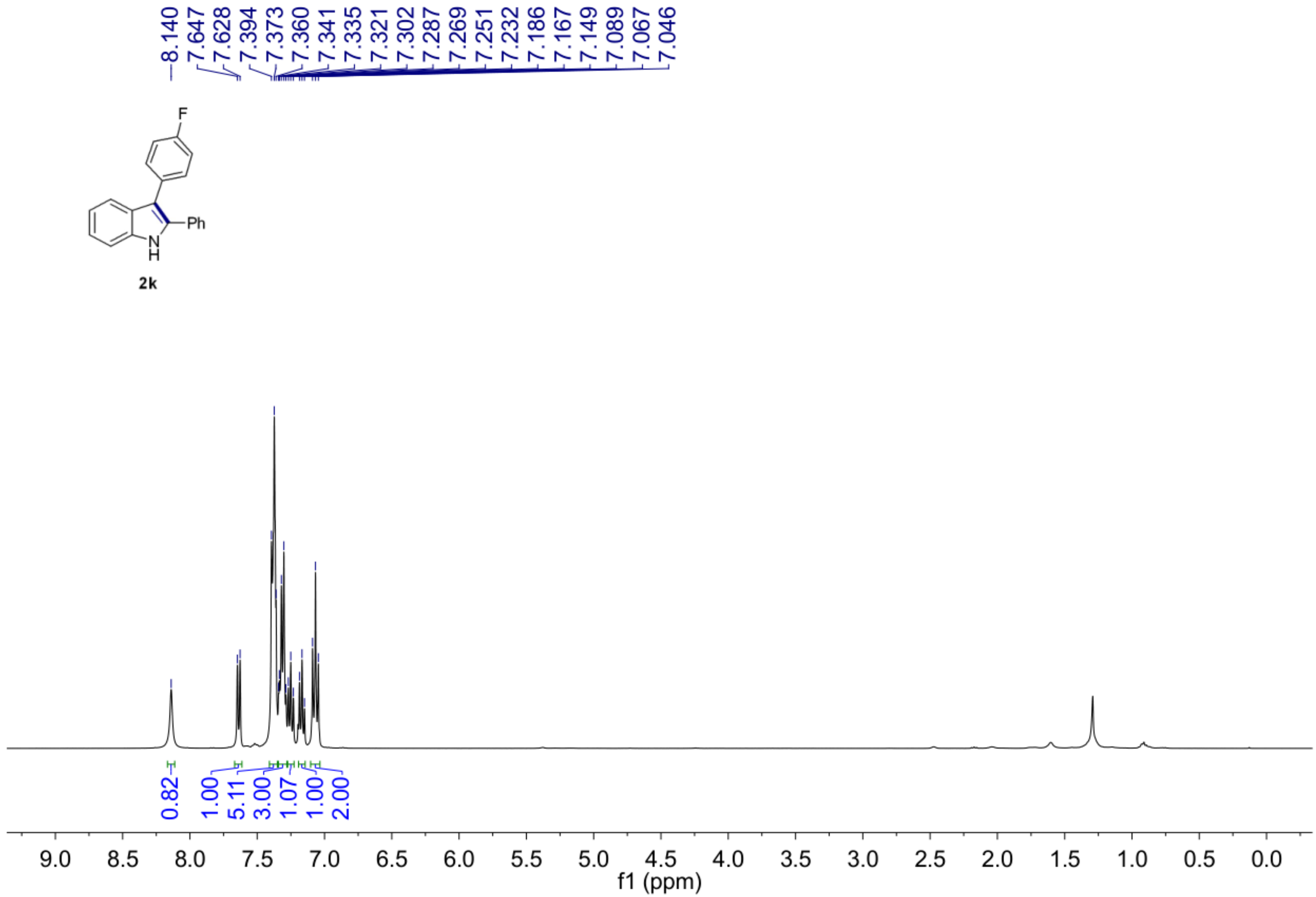
128.495
128.206
127.385
126.792
125.308
125.246
122.974
120.491
119.592
115.730
110.710
77.318
77.000
76.683
Ph
S
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

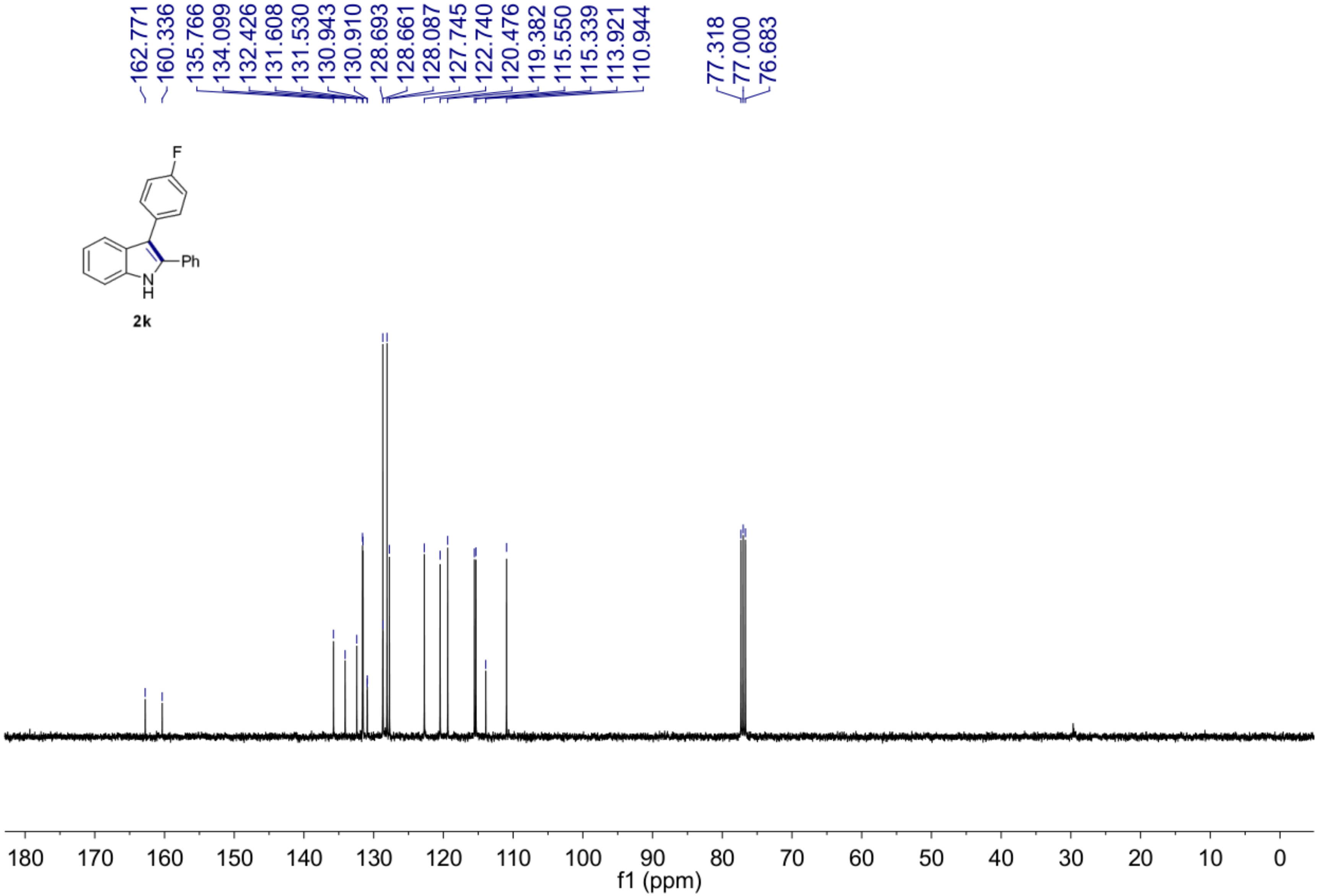
2i


9.319
7.684 7.683 7.664 7.662 7.611 7.608 7.590 7.587 7.503 7.485 7.482 7.466 7.465 7.463 7.461 7.430 7.411 7.386 7.383 7.178
4.366 4.348 4.331 4.313
1.281 1.263 1.245
Ph
COOEt
N
H
2j
7.198 7.196 7.181 7.178 7.175 7.161 7.158
1.00
7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
0.95 1.03 1.93 3.01 2.10 1.00 1.97 2.95
10.5 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)

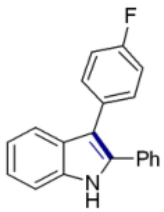

162.181
135.775
133.535
130.624
127.897
127.686
127.129
125.711
124.197
122.767
121.690
120.786
111.709
77.317
77.000
76.682
60.875
13.977
Ph
COOEt
N
H
2j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



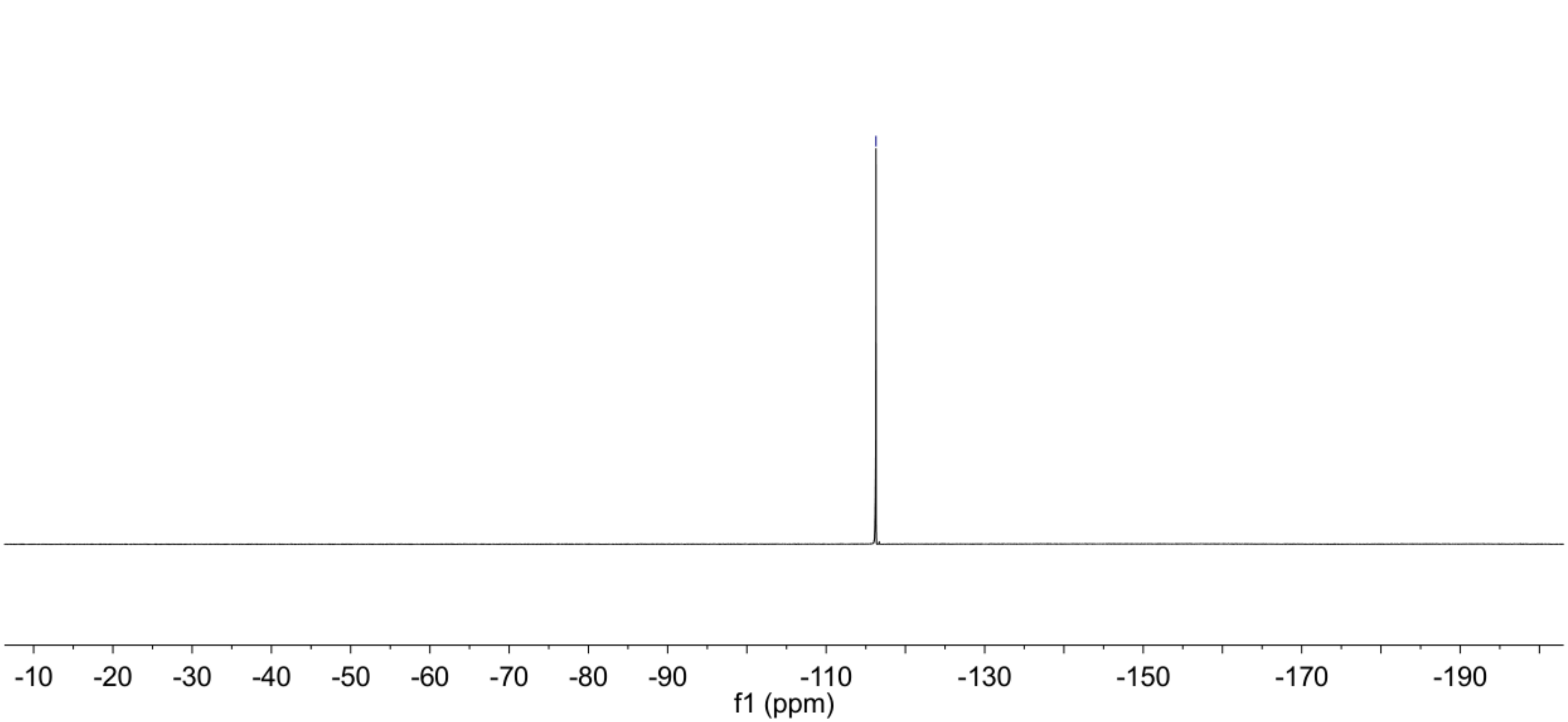
8.140
7.647
7.628
7.394
7.373
7.360
7.341
7.335
7.321
7.302
7.287
7.269
7.251
7.232
7.186
7.167
7.149
7.089
7.067
7.046
F
Ph
N
H
2k
0.82
1.00
5.11
3.00
1.07
1.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

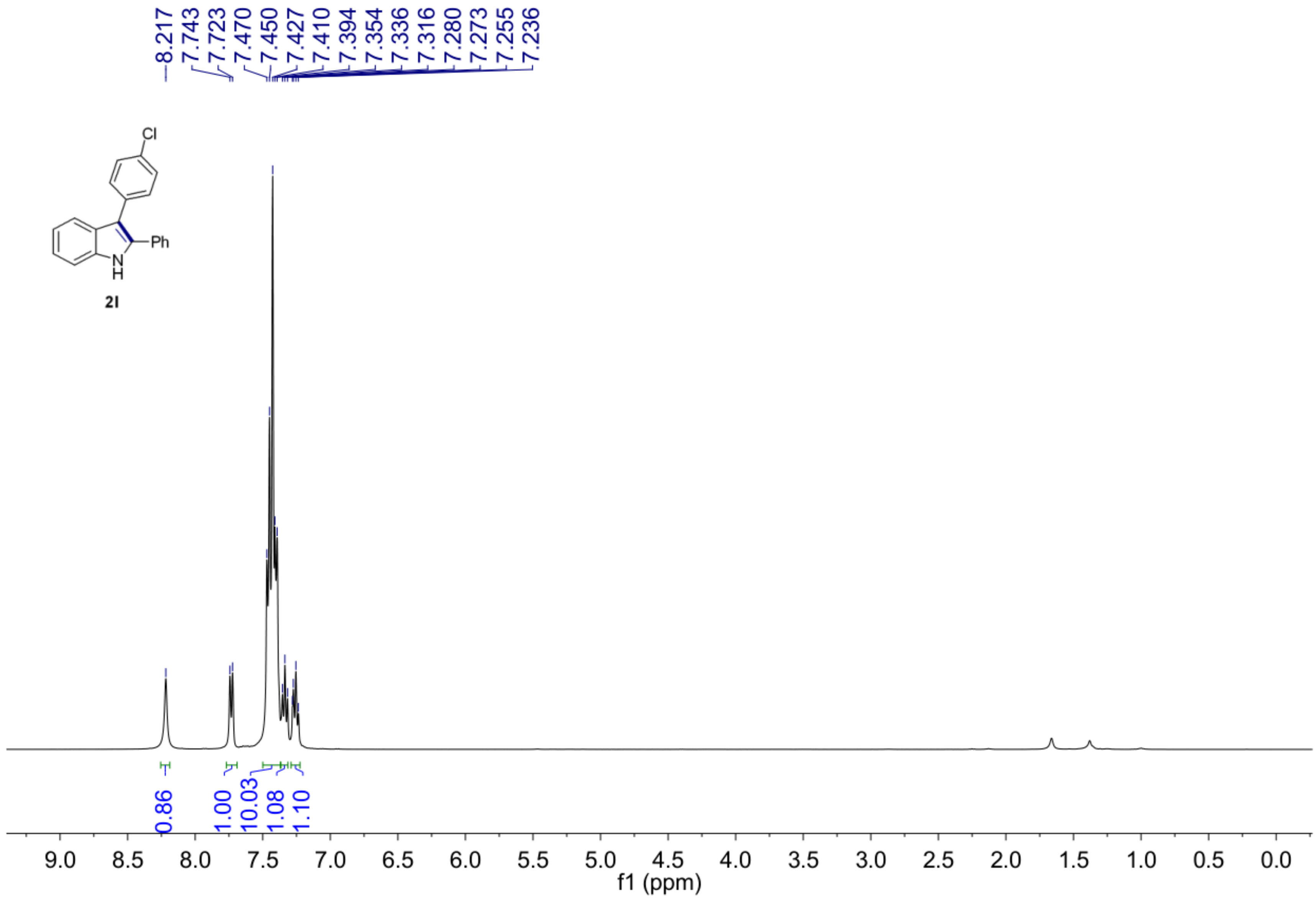


162.771
160.336
135.766
134.099
132.426
131.608
131.530
130.943
130.910
128.693
128.661
128.087
127.745
122.740
120.476
119.382
115.550
115.339
113.921
110.944
77.318
77.000
76.683
F
Ph
N
H
2k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2k

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7.450
7.427
7.410
7.394
7.354
7.336
7.316
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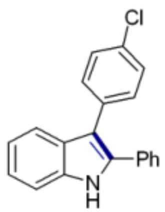
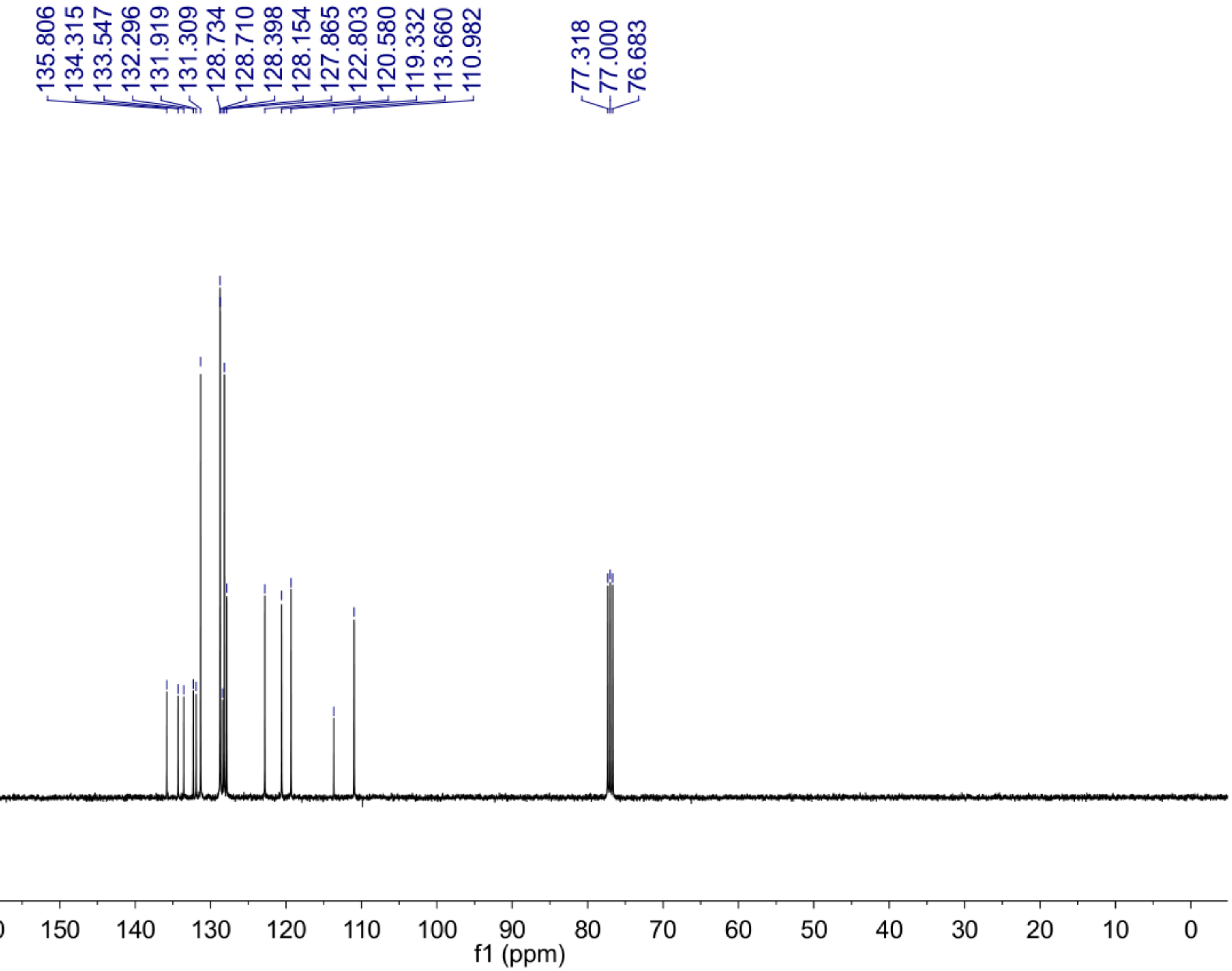
7.273
7.255
7.236
Cl
Ph
N
H
2l
0.86
1.00
10.03
1.08
1.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



Cl
Ph
N
H

2l



135.806
134.315
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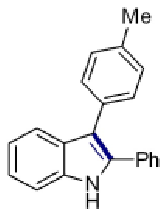
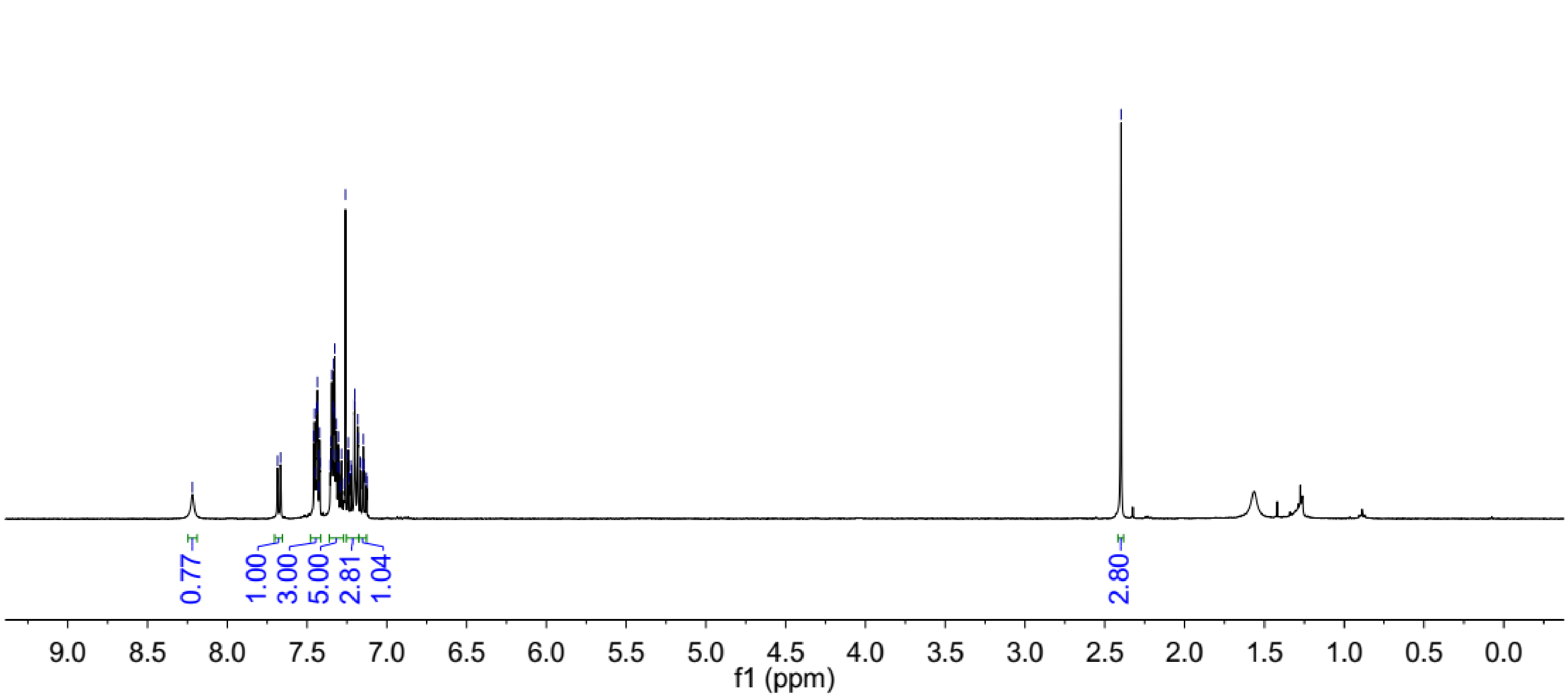
132.296
131.919
131.309
128.734
128.710
128.398
128.154
127.865
122.803
120.580
119.332
113.660
110.982
77.318
77.000
76.683
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



2m



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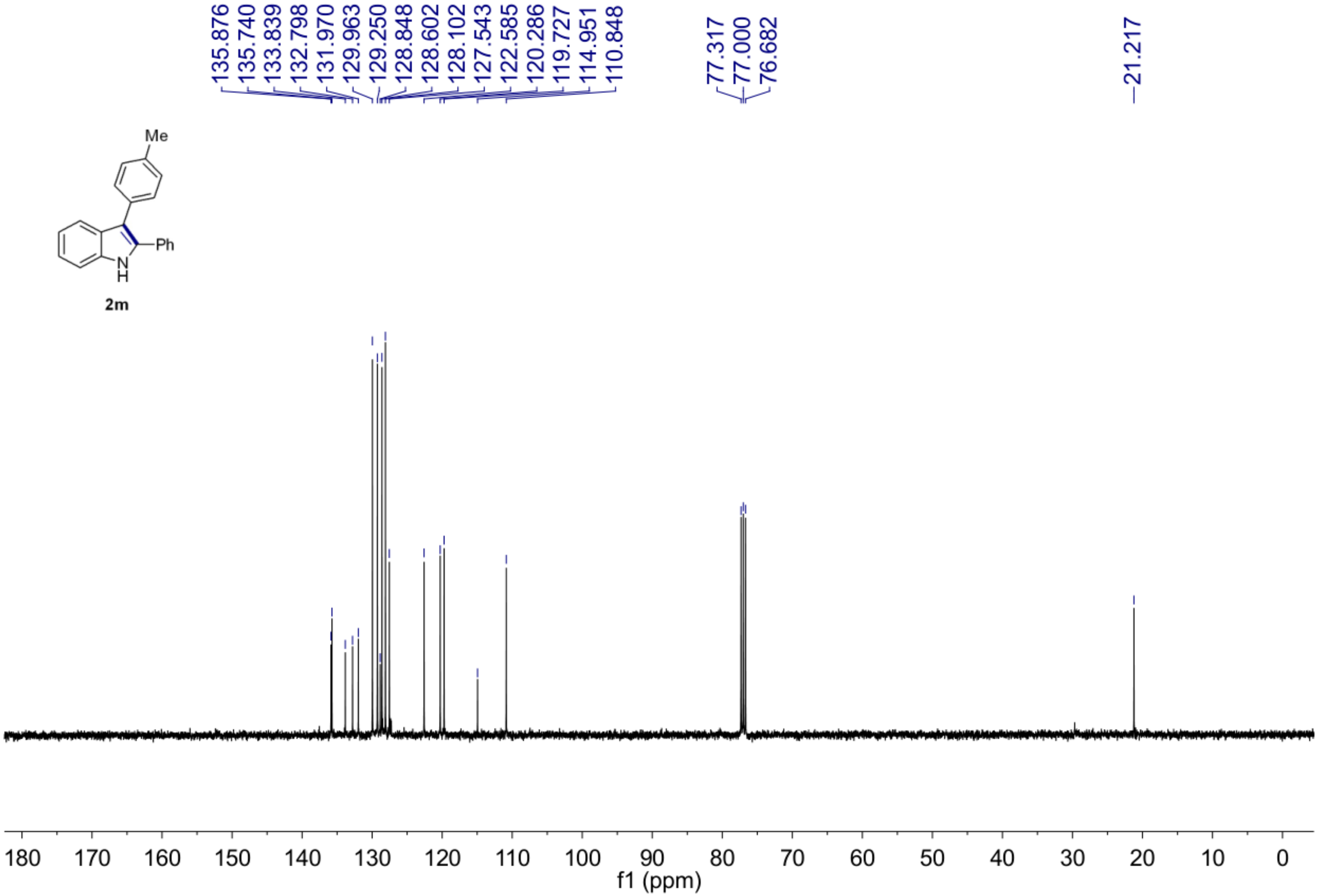
7.457
7.453
7.440
7.436
7.433
7.423
7.421
7.350
7.346
7.342
7.335
7.333
7.330
7.326
7.319
7.315
7.302
7.285
7.260
7.244
7.242
7.203
7.202
7.182
7.181
7.146
2.400
0.77
1.00
3.00
5.00
2.81
1.04
2.80
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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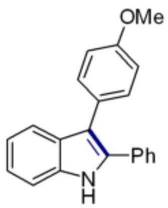
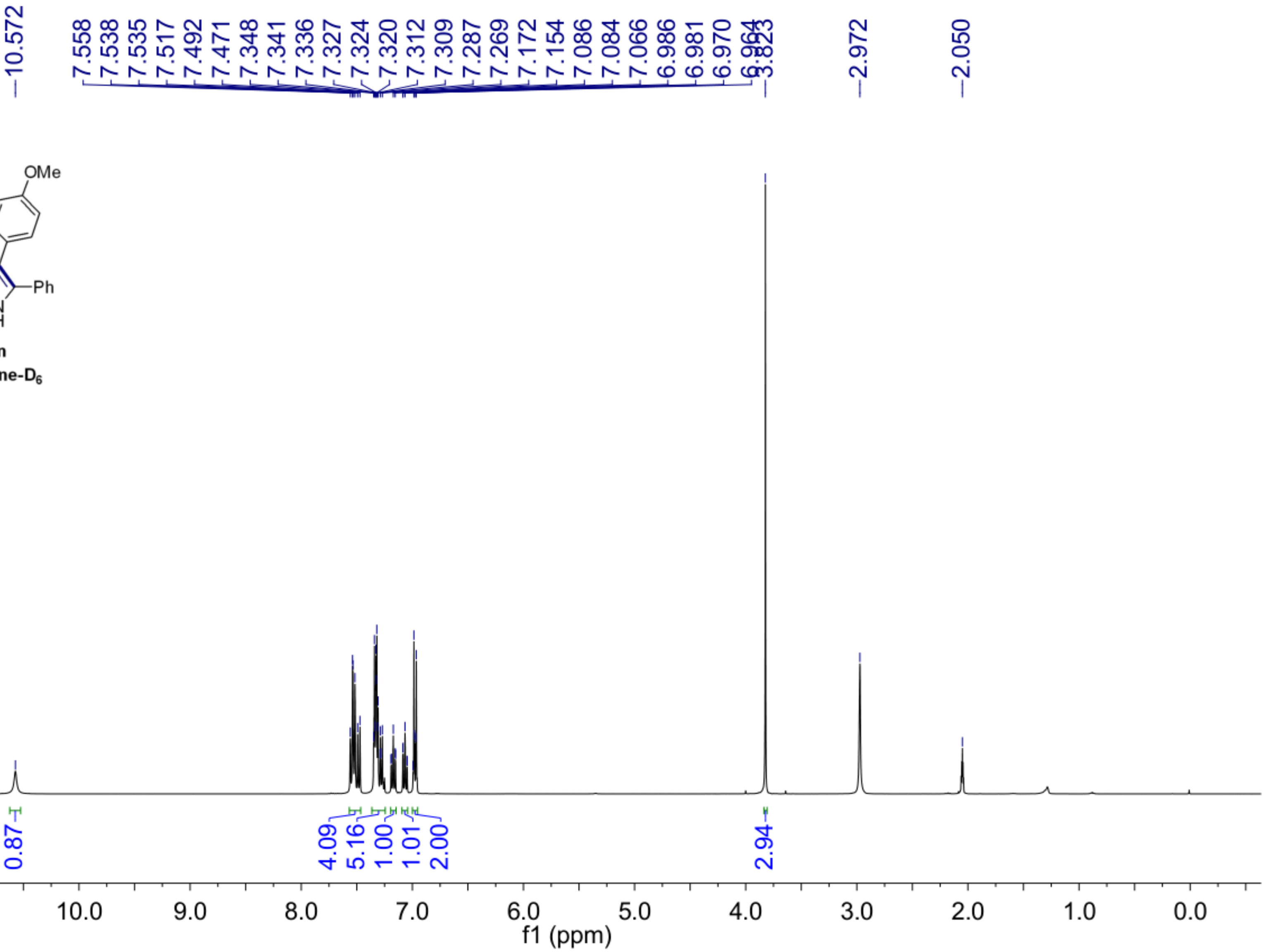
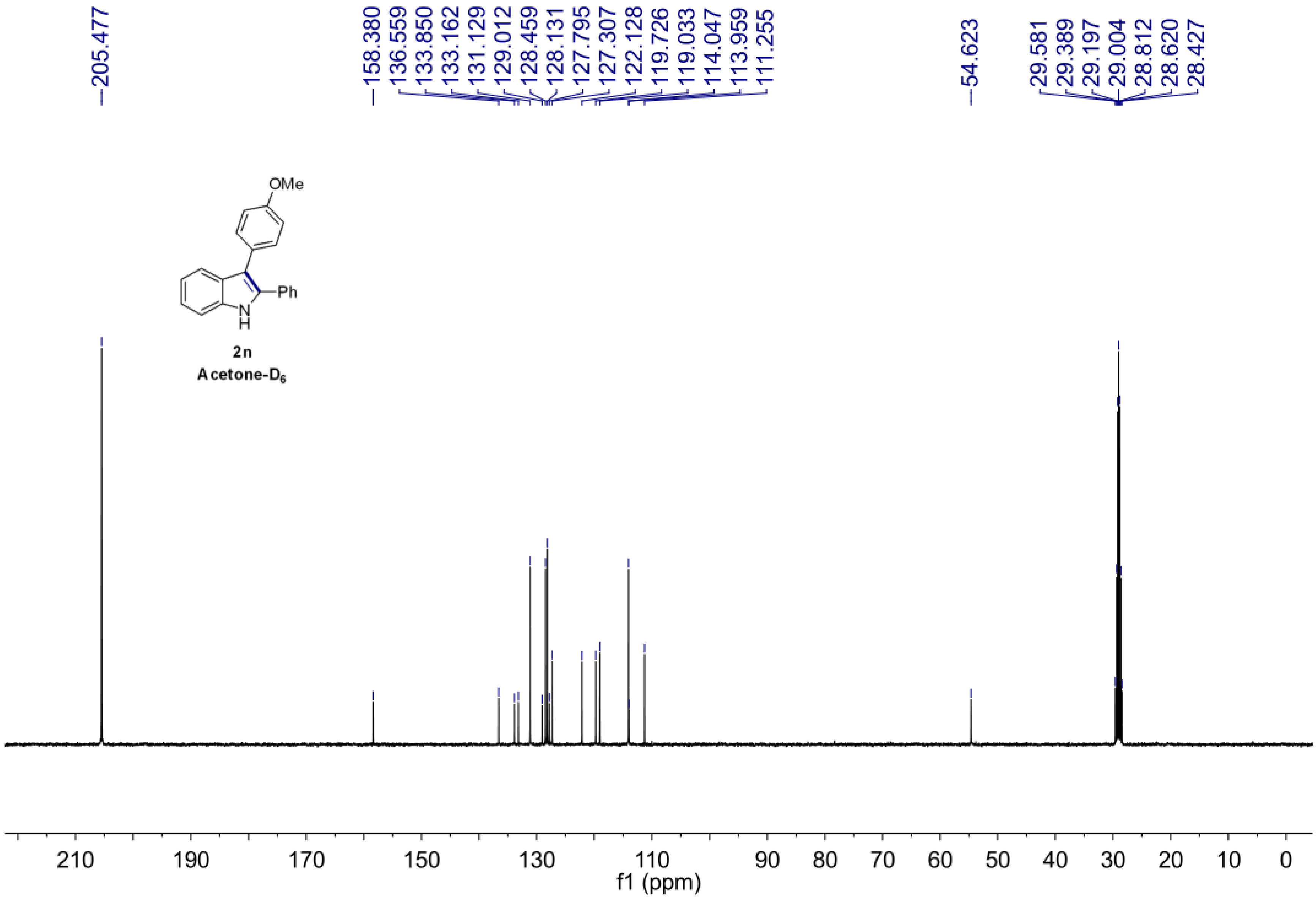
131.970
129.963
129.250
128.848
128.602
128.102
127.543
122.585
120.286
119.727
114.951
110.848
77.317
77.000
76.682
21.217
Me
Ph
N
H
2m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

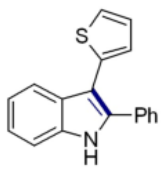


2n
Acetone-D$_6$



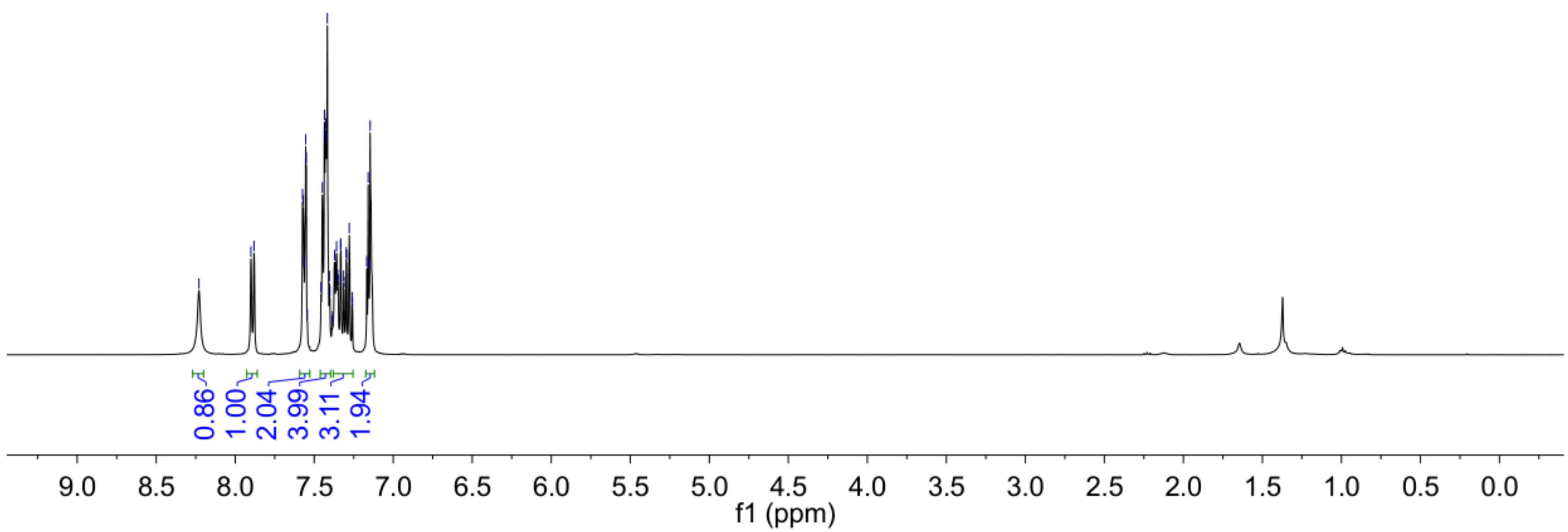


205.477
158.380
136.559
133.850
133.162
131.129
129.012
128.459
128.131
127.795
127.307
122.128
119.726
119.033
114.047
113.959
111.255
54.623
29.581
29.389
29.197
29.004
28.812
28.620
28.427
OMe
Ph
N
H
2n
Acetone-D$_6$
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

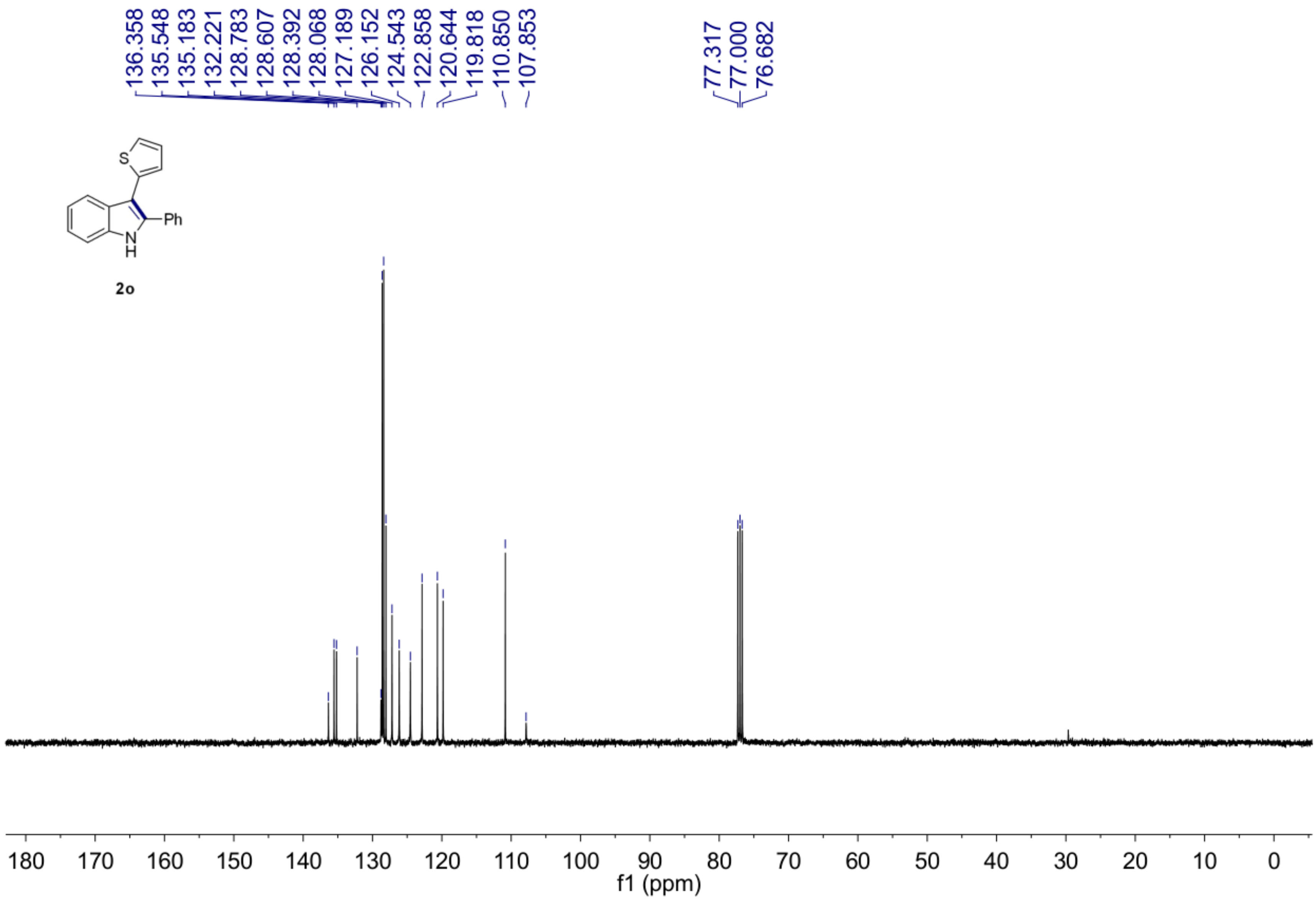


S
Ph
N
H

2o



8.230
7.900
7.881
7.574
7.569
7.565
7.554
7.550
7.544
7.457
7.449
7.435
7.430
7.427
7.422
7.417
7.404
7.401
7.388
7.384
7.371
7.359
7.351
7.349
7.333
7.331
7.314
7.311
7.298
7.295
7.278
7.260
7.258
7.167
7.159
7.155
7.146
0.86
1.00
2.04
3.99
3.11
1.94
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)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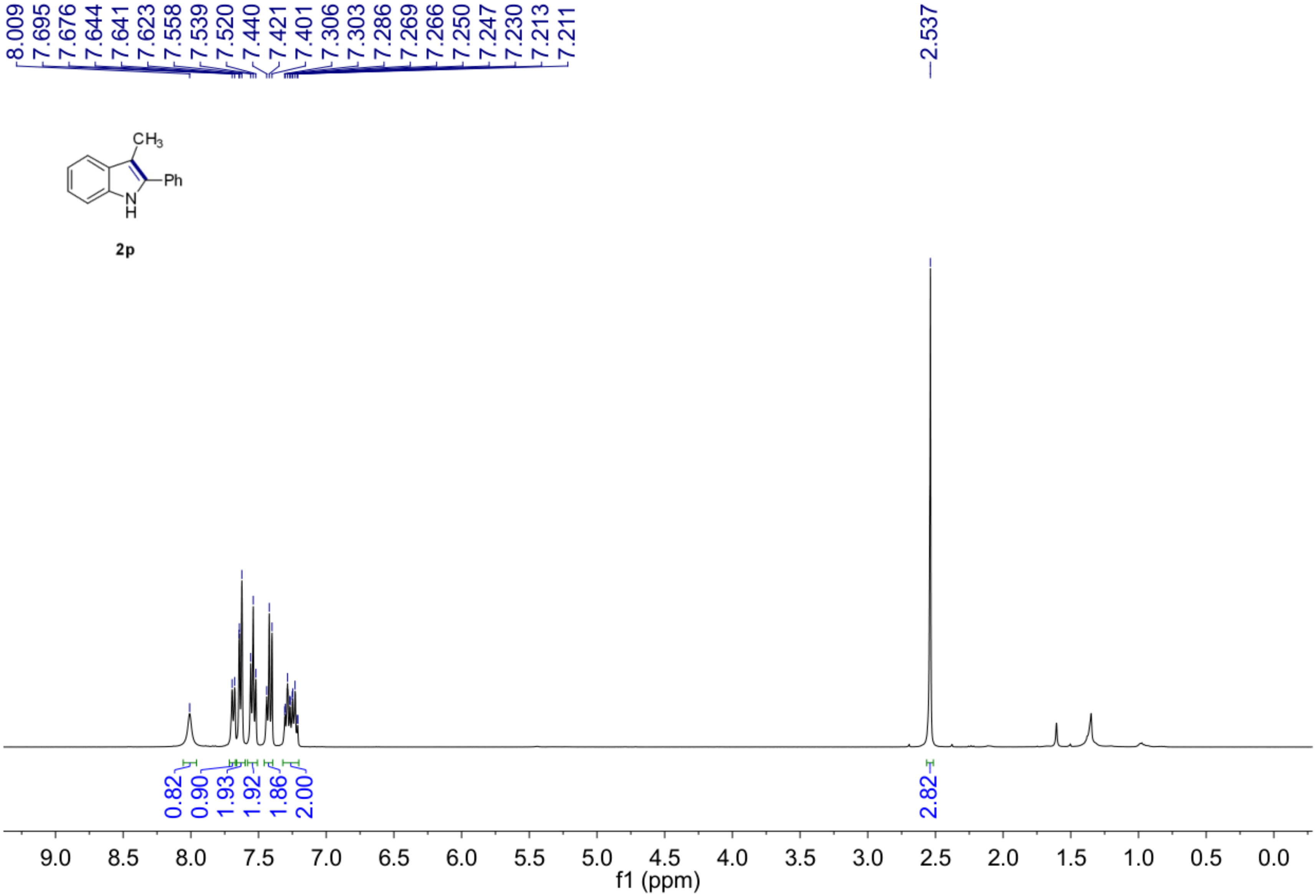
128.392
128.068
127.189
126.152
124.543
122.858
120.644
119.818
110.850
107.853
77.317
77.000
76.682
S
Ph
N
H
2o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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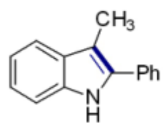
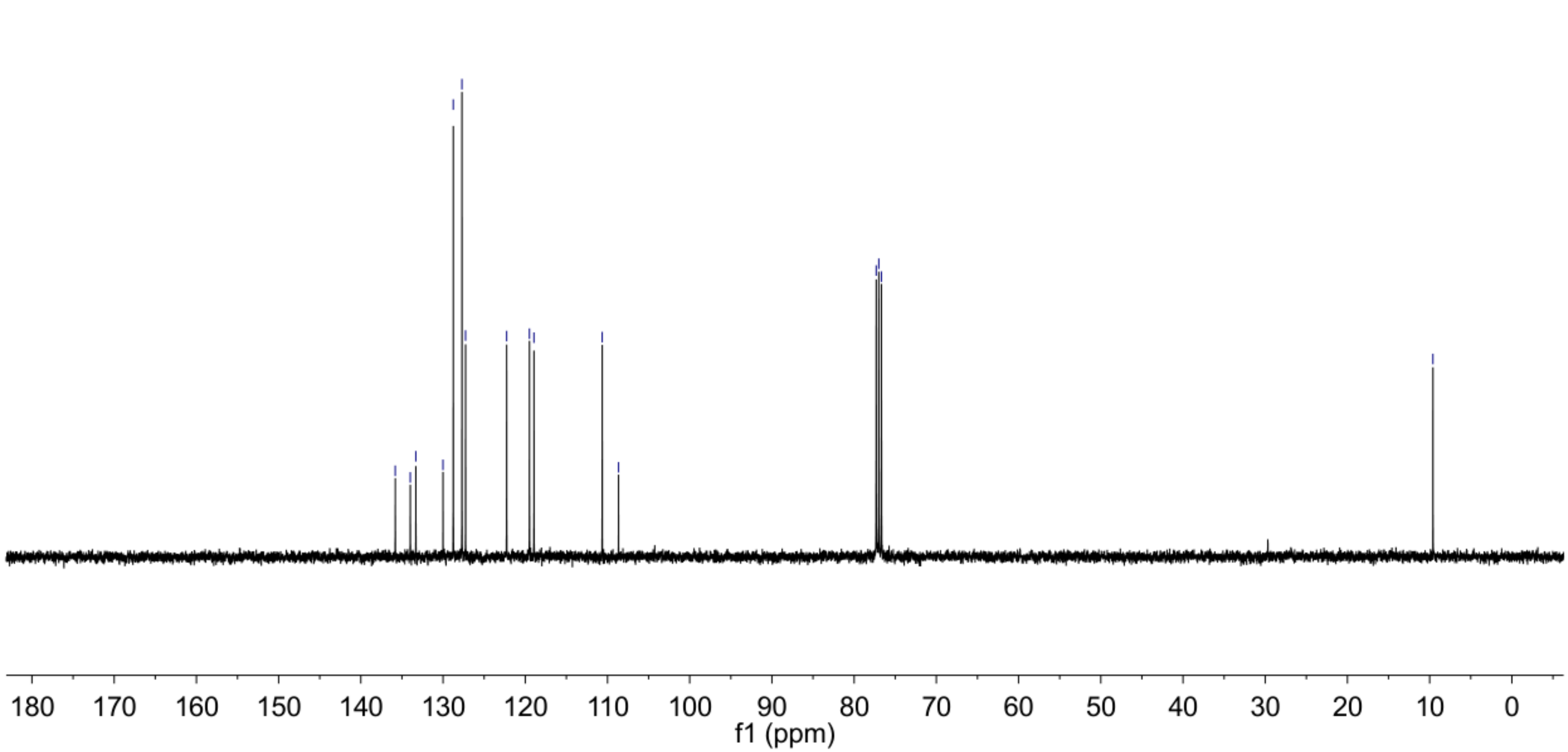
7.695
7.676
7.644
7.641
7.623
7.558
7.539
7.520
7.440
7.421
7.401
7.306
7.303
7.286
7.269
7.266
7.250
7.247
7.230
7.213
7.211
2.537
CH3
Ph
N
H
0.82
0.90
1.93
1.92
1.86
2.00
2.82
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2p


CH3
Ph
N
H

2p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127.701
127.264
122.271
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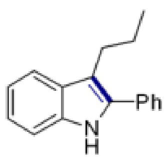
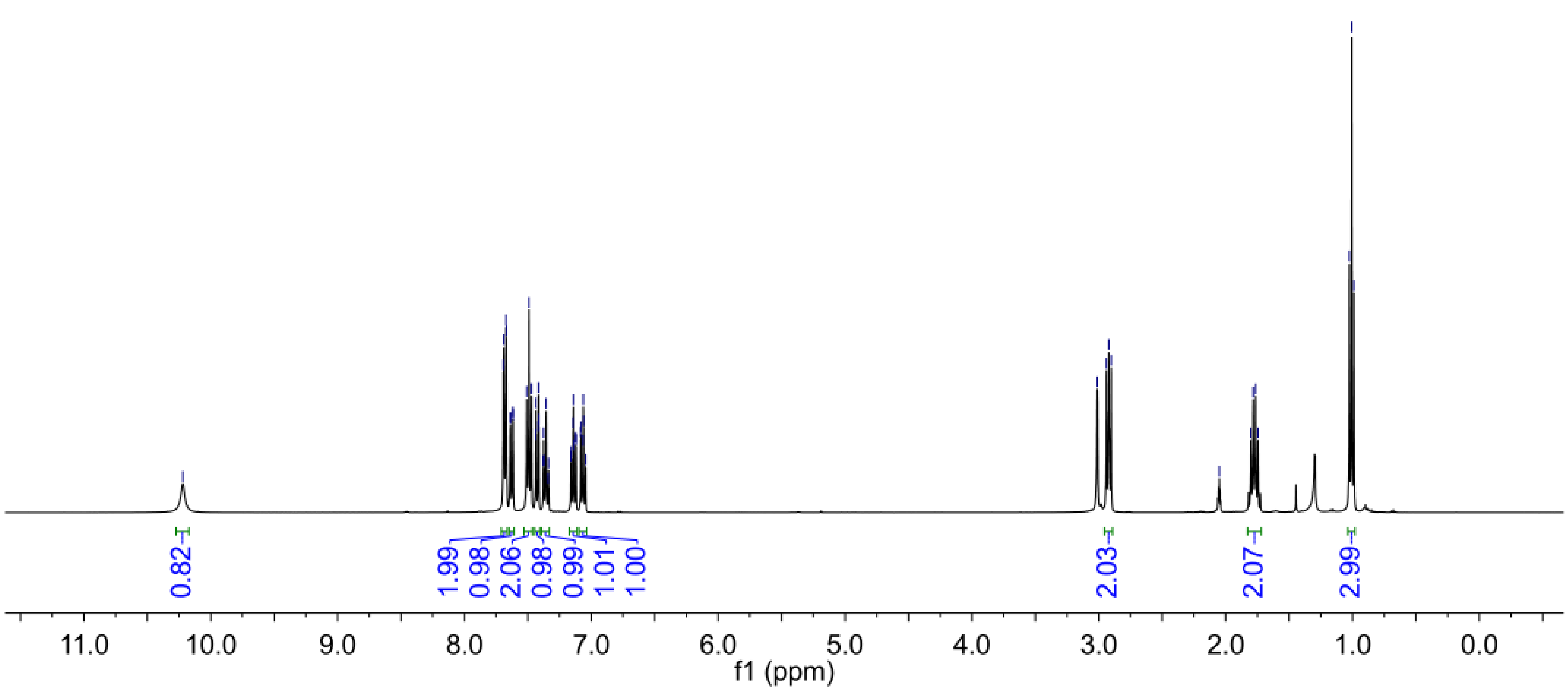
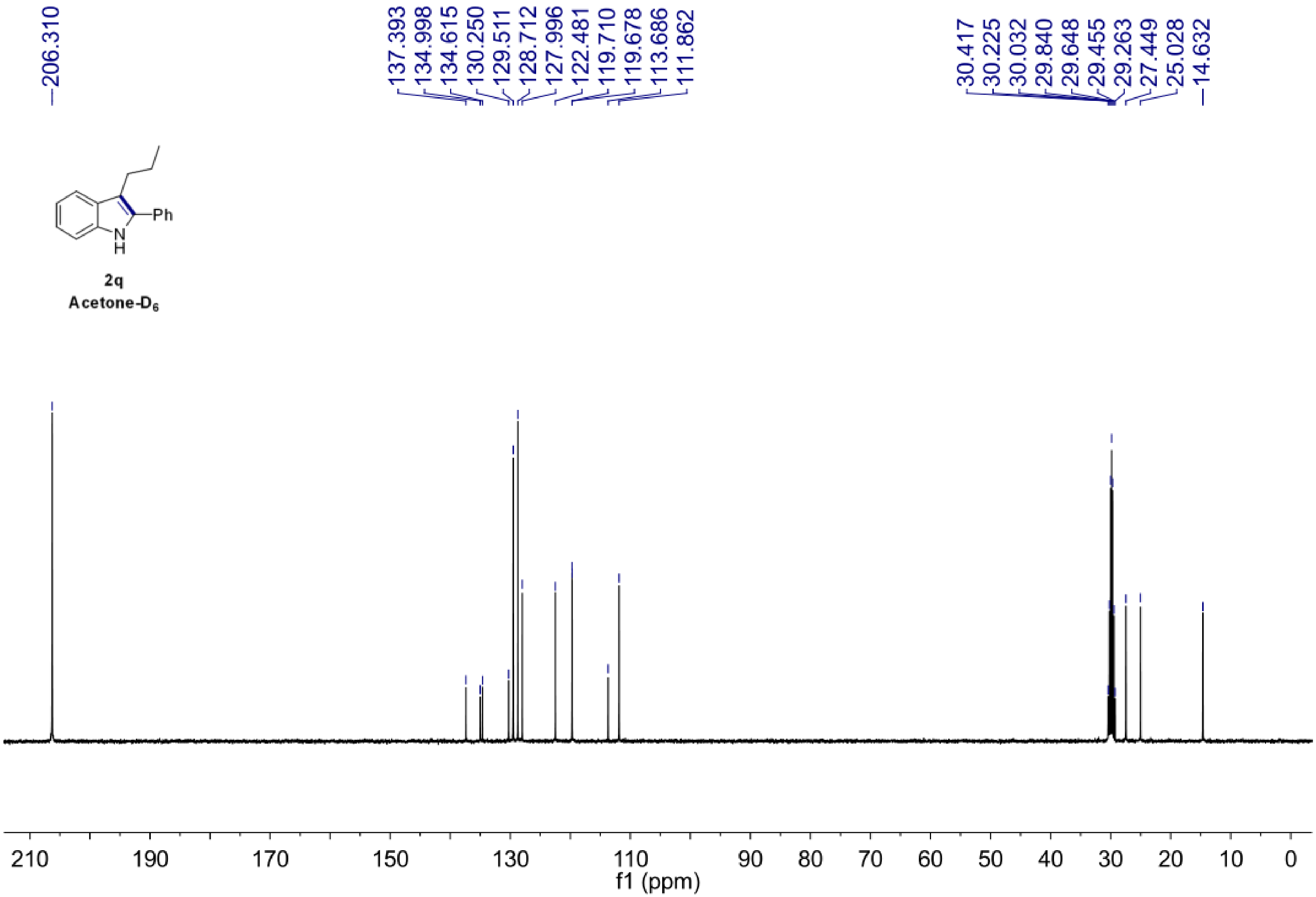
118.944
110.646
108.658
77.318
77.000
76.683
9.603
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2q
Acetone-D_6

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134.998
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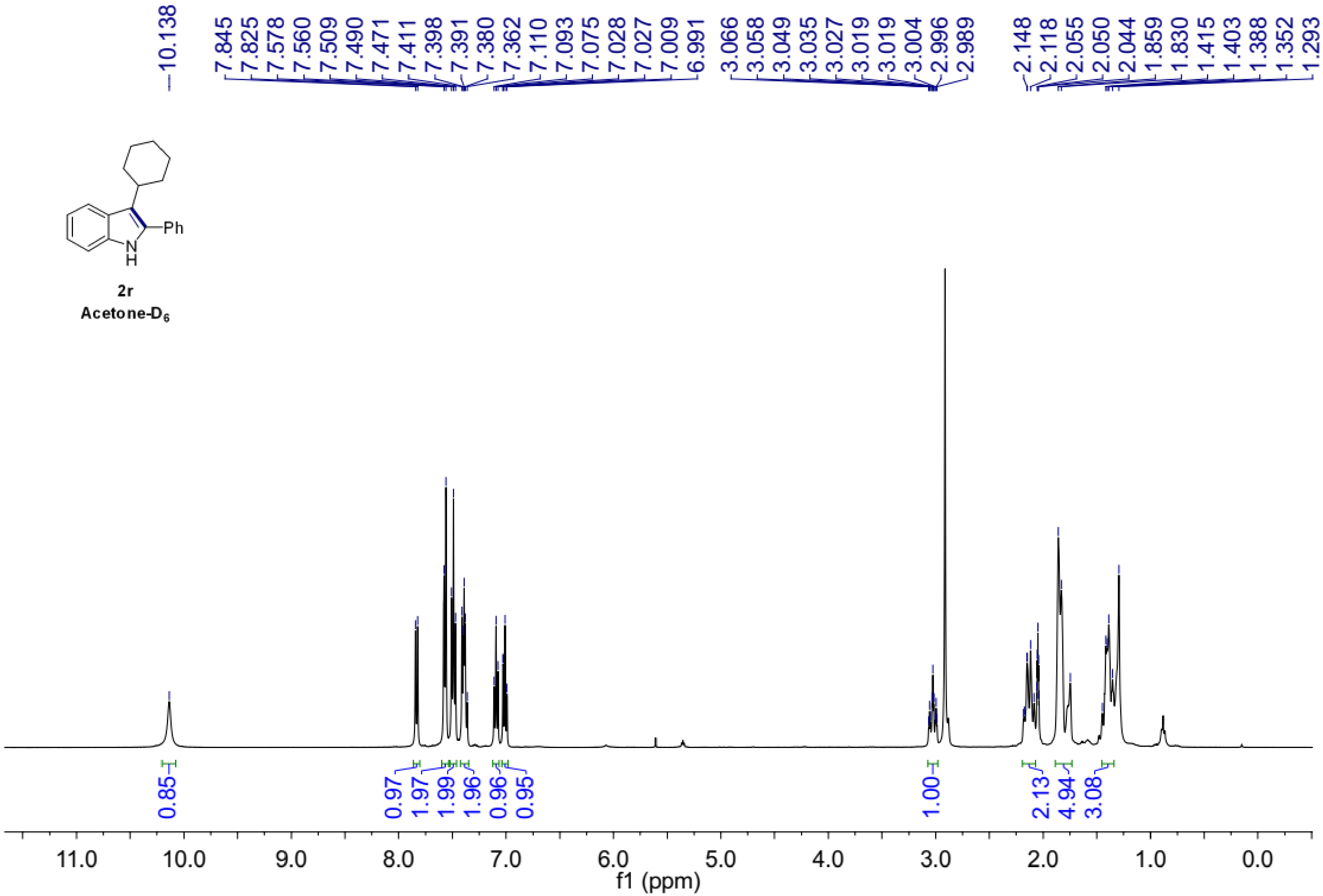
130.250
129.511
128.712
127.996
122.481
119.710
119.678
113.686
111.862
30.417
30.225
30.032
29.840
29.648
29.455
29.263
27.449
25.028
14.632
Ph
N
H
2q
Acetone-D6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.138
7.845
7.825
7.578
7.560
7.509
7.490
7.471
7.411
7.398
7.391
7.380
7.362
7.110
7.093
7.075
7.028
7.027
7.009
6.991
3.066
3.058
3.049
3.035
3.027
3.019
3.019
3.004
2.996
2.989
2.148
2.118
2.055
2.050
2.044
1.859
1.830
1.415
1.403
1.388
1.352
1.293
Ph
N
H
2r
Acetone-D6
0.85
0.97
1.97
1.99
1.96
0.96
0.95
1.00
2.13
4.94
3.08
11.0
10.0
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7.0
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5.0
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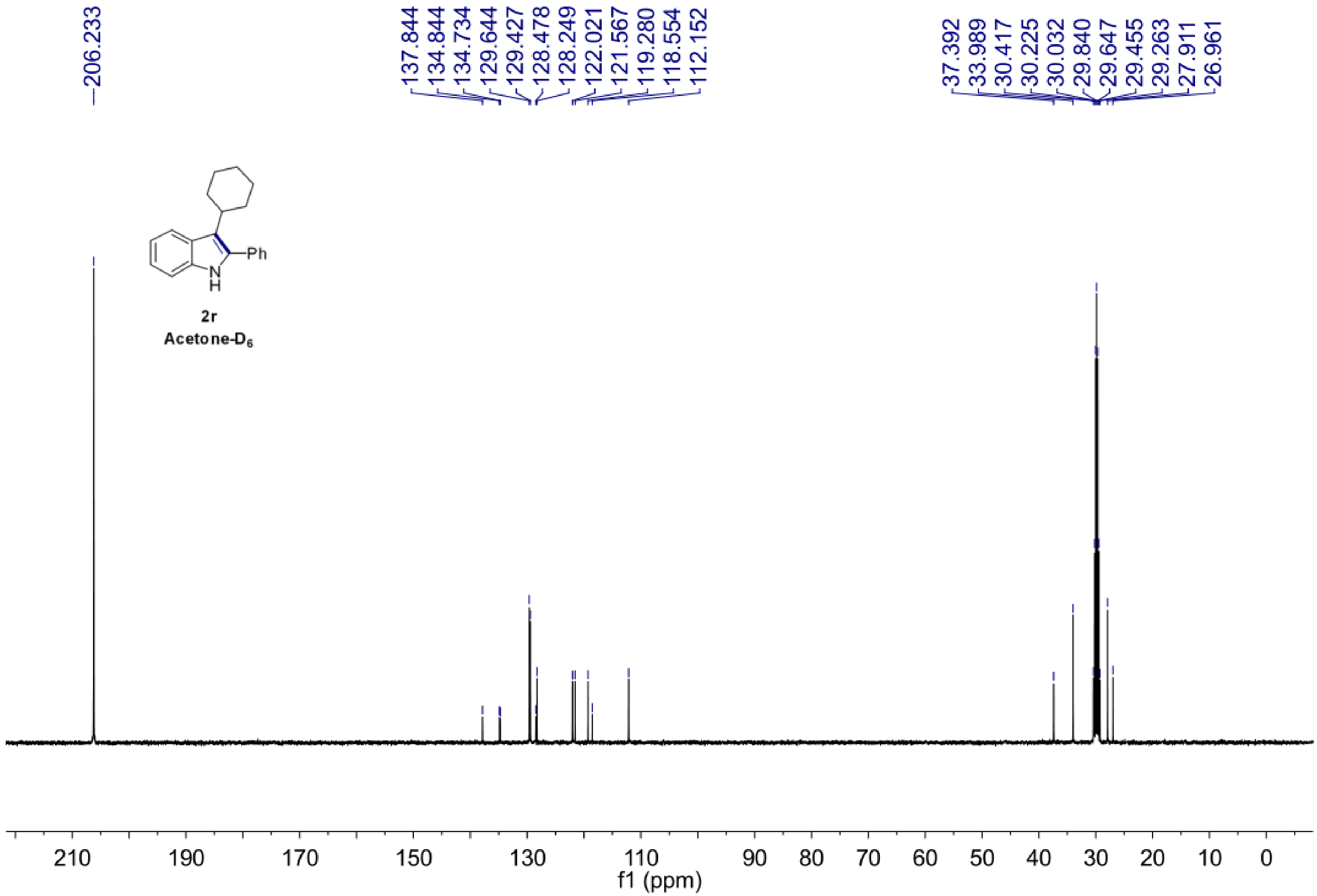
3.0
2.0
1.0
0.0
f1 (ppm)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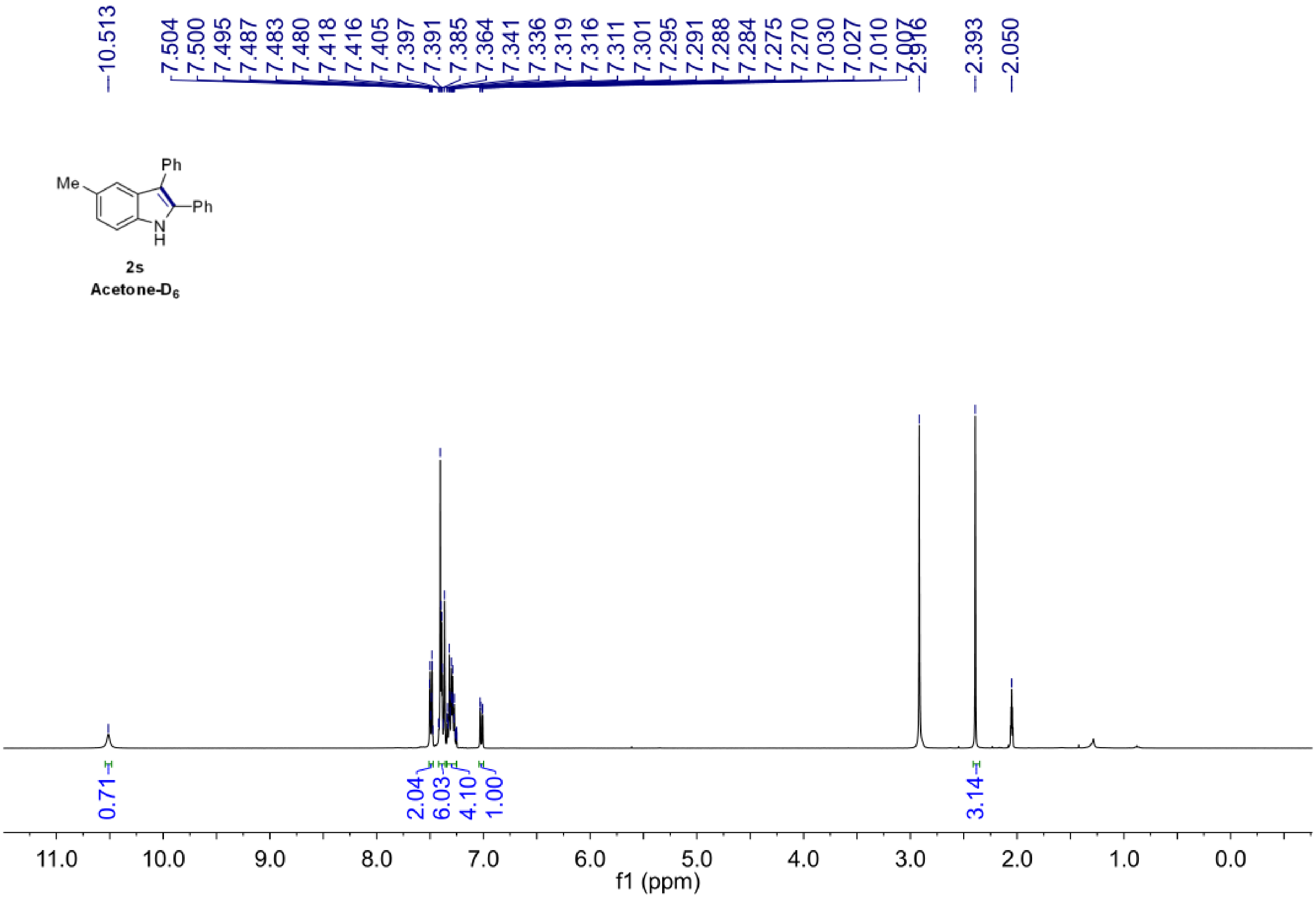
134.844
134.734
129.644
129.427
128.478
128.249
122.021
121.567
119.280
118.554
112.152
37.392
33.989
30.417
30.225
30.032
29.840
29.647
29.455
29.263
27.911
26.961
Ph
N
H
2r
Acetone-D6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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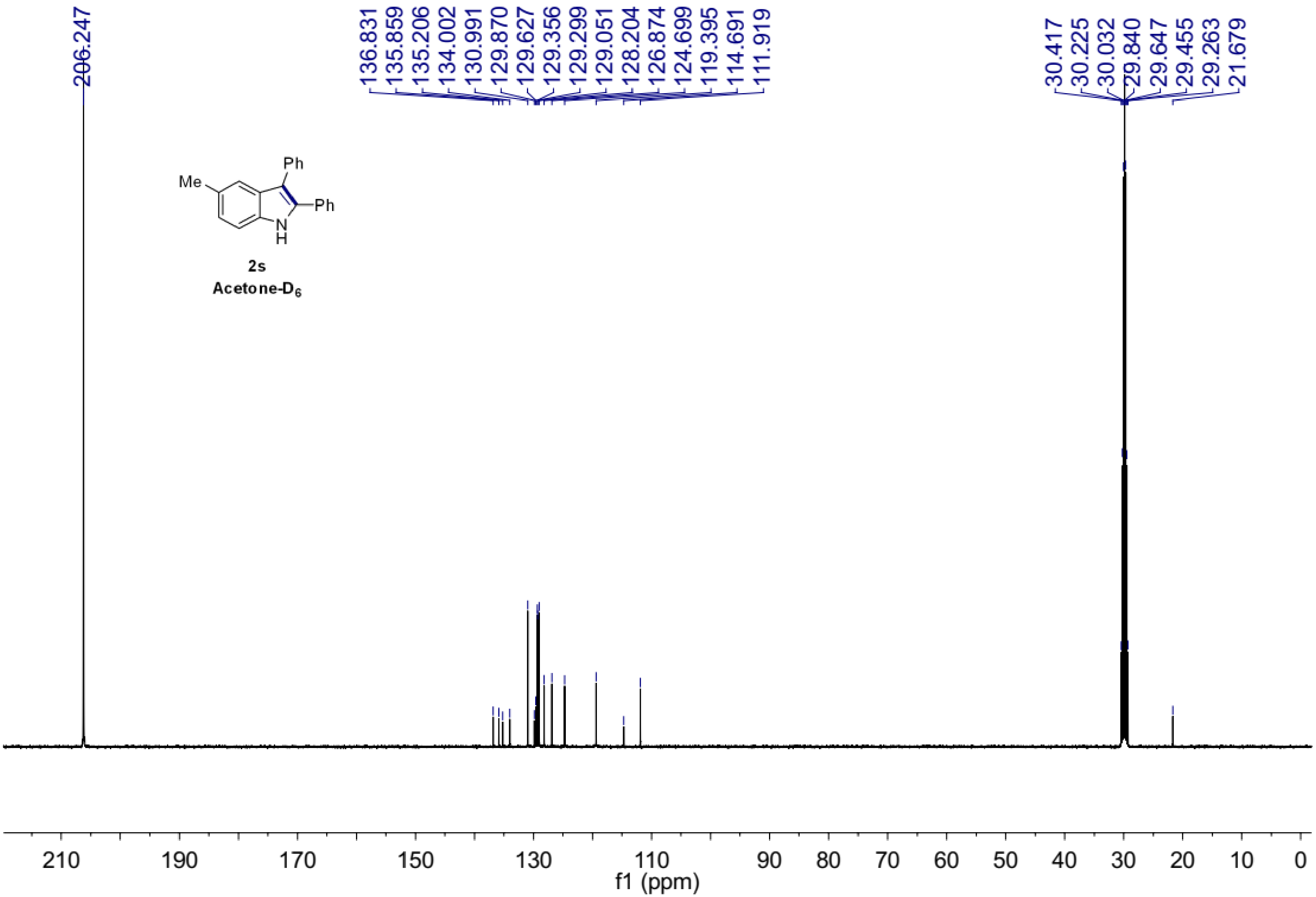
7.504
7.500
7.495
7.487
7.483
7.480
7.418
7.416
7.405
7.397
7.391
7.385
7.364
7.341
7.336
7.319
7.316
7.311
7.301
7.295
7.291
7.288
7.284
7.275
7.270
7.030
7.027
7.010
7.007
2.916
2.393
2.050
Ph
Me
Ph
N
H
2s
Acetone-D6
0.71
2.04
6.03
4.10
1.00
3.14
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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135.859
135.206
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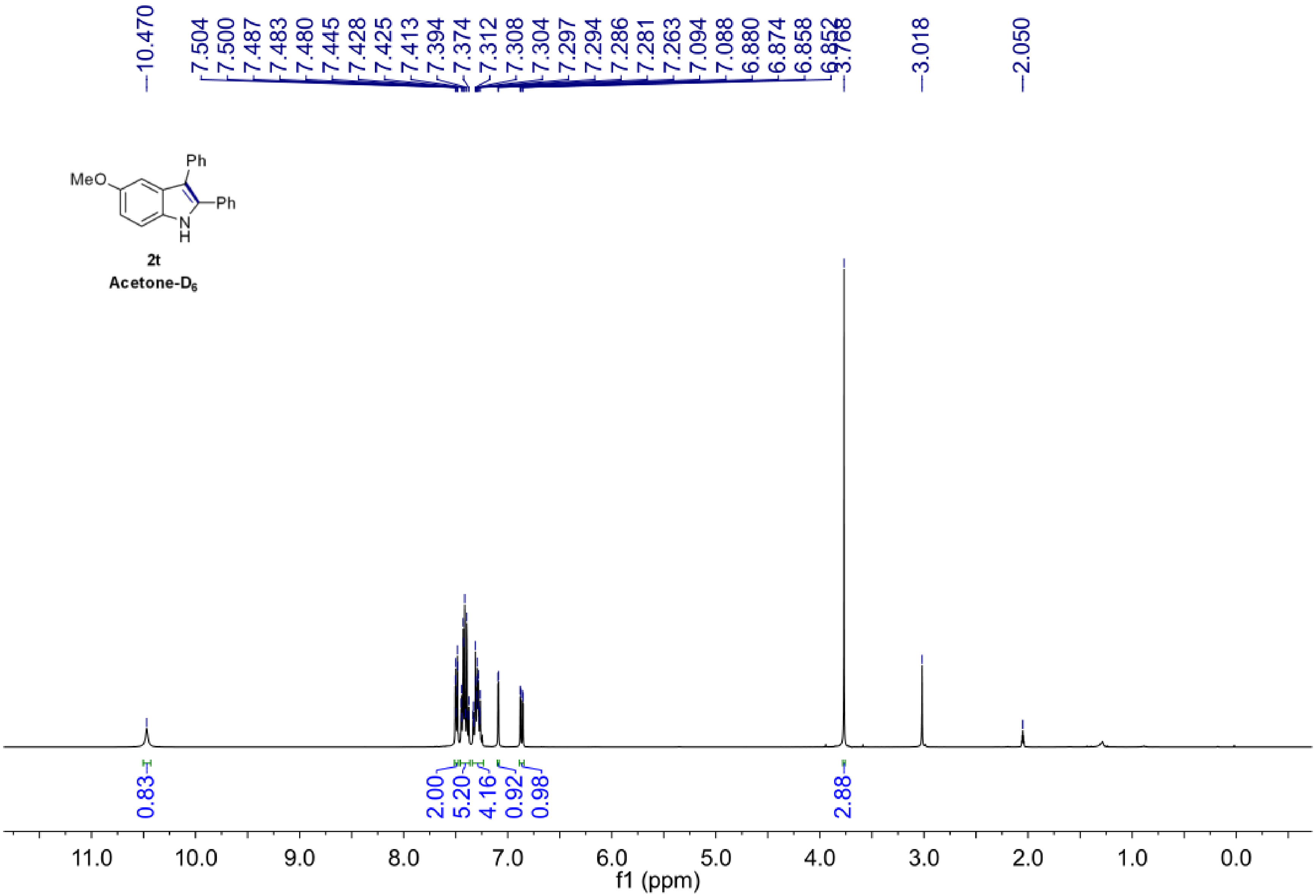
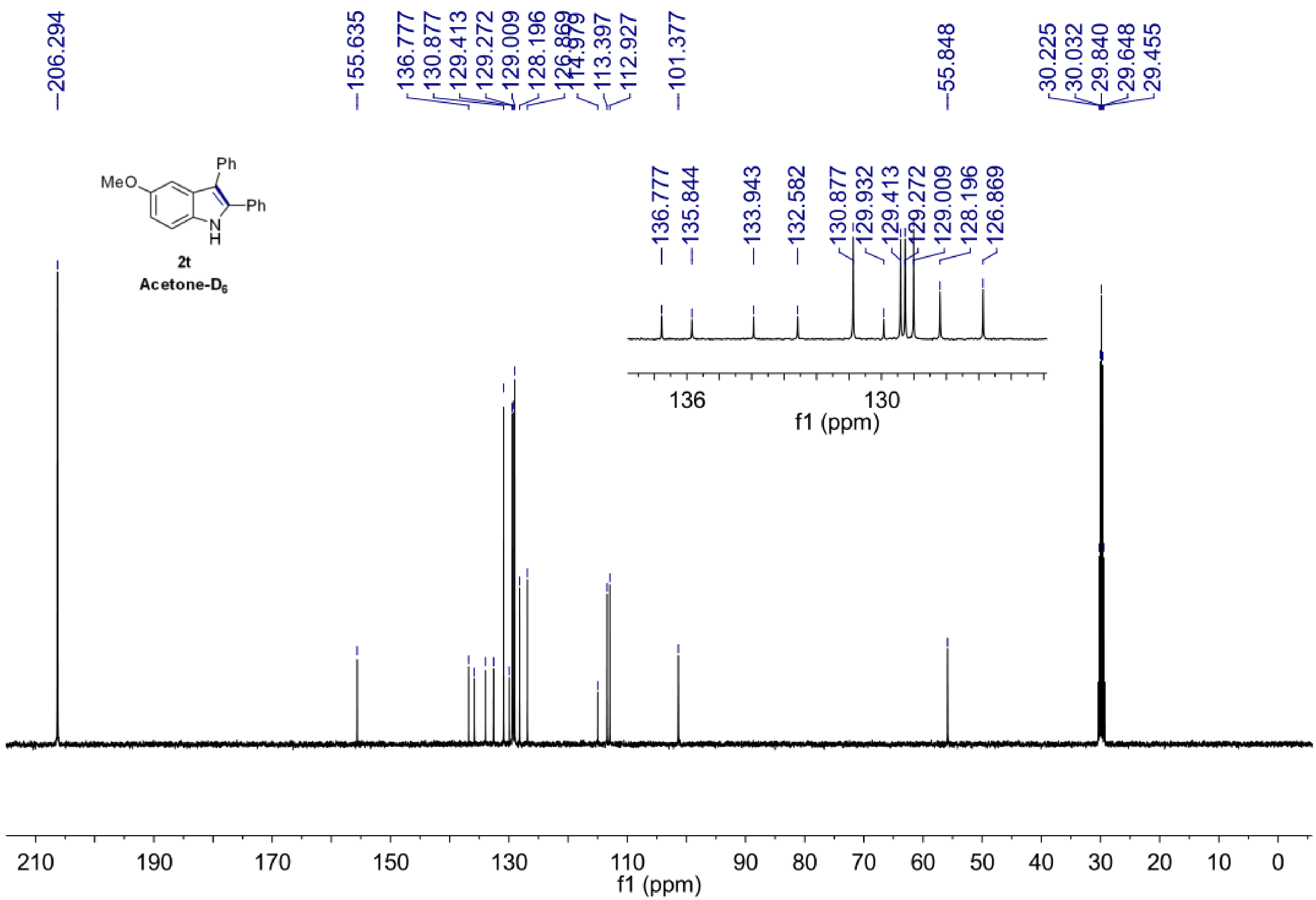
130.991
129.870
129.627
129.356
129.299
129.051
128.204
126.874
124.699
119.395
114.691
111.919
30.417
30.225
30.032
29.840
29.647
29.455
29.263
21.679
Me
Ph
Ph
N
H
2s
Acetone-D6
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
MeO
Ph
N
H
2t
Acetone-D6
f1 (ppm)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129.272
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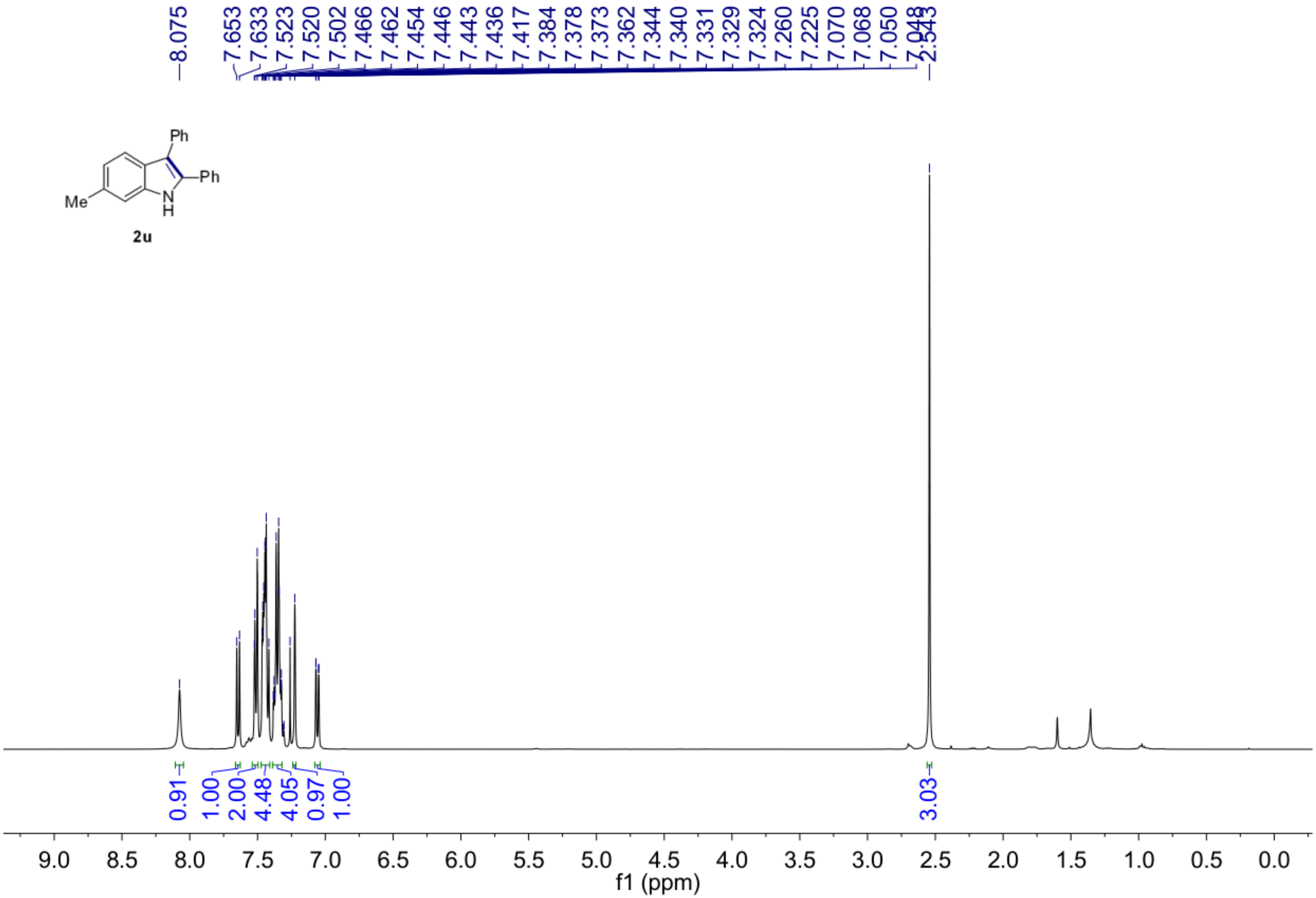
128.196
126.869
114.979
113.397
112.927
101.377
55.848
30.225
30.032
29.840
29.648
29.455
MeO
Ph
Ph
N
H
2t
Acetone-D6
136.777
135.844
133.943
132.582
130.877
129.932
129.413
129.272
129.009
128.196
126.869
136
130
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.443
7.436
7.417
7.384
7.378
7.373
7.362
7.344
7.340
7.331
7.329
7.324
7.260
7.225
7.070
7.068
7.050
7.048
2.543
Ph
Ph
Me
N
H
0.91
1.00
2.00
4.48
4.05
0.97
1.00
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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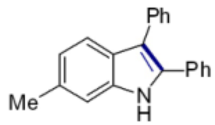
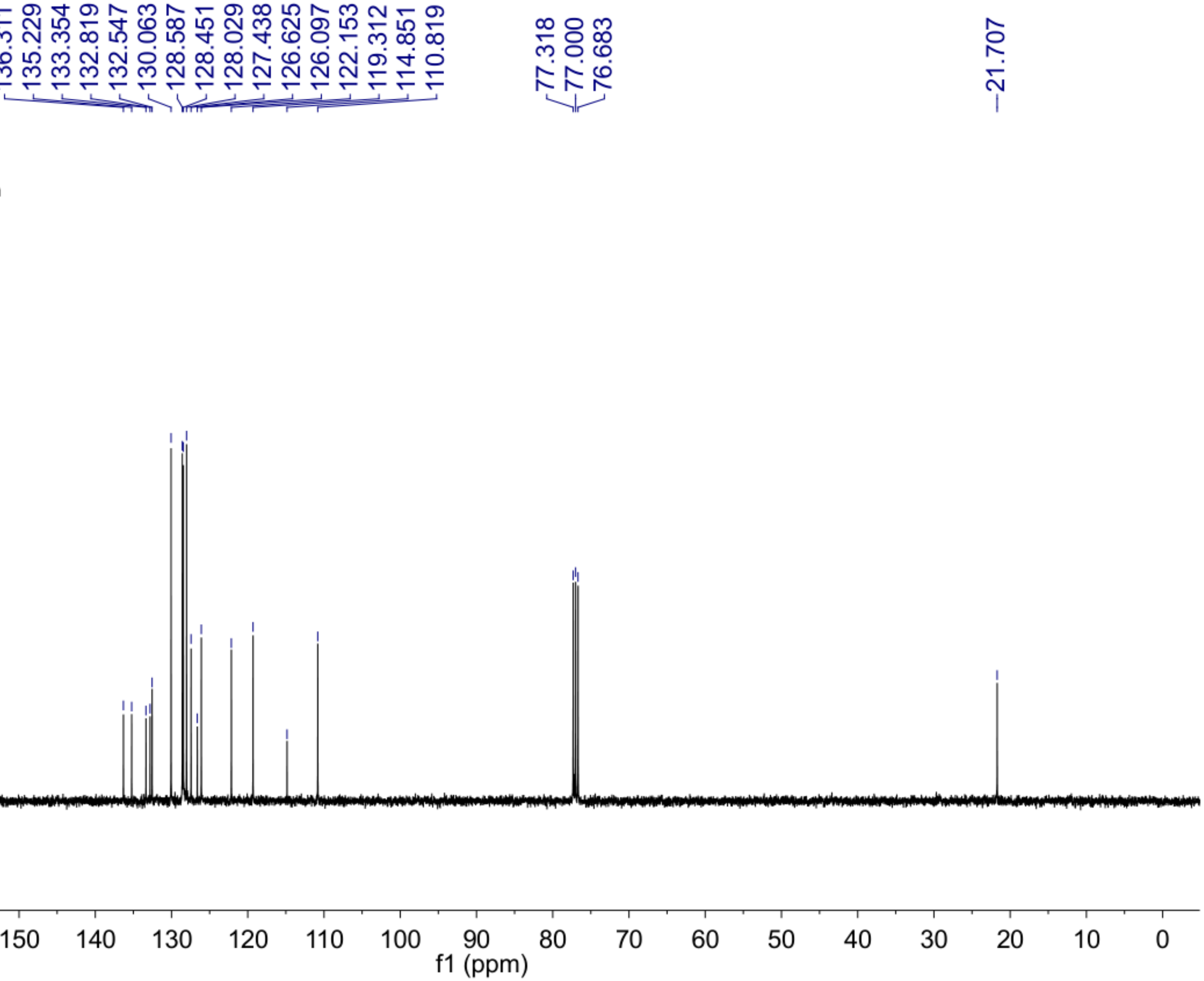
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2u


Ph
Ph
Me
N
H

2u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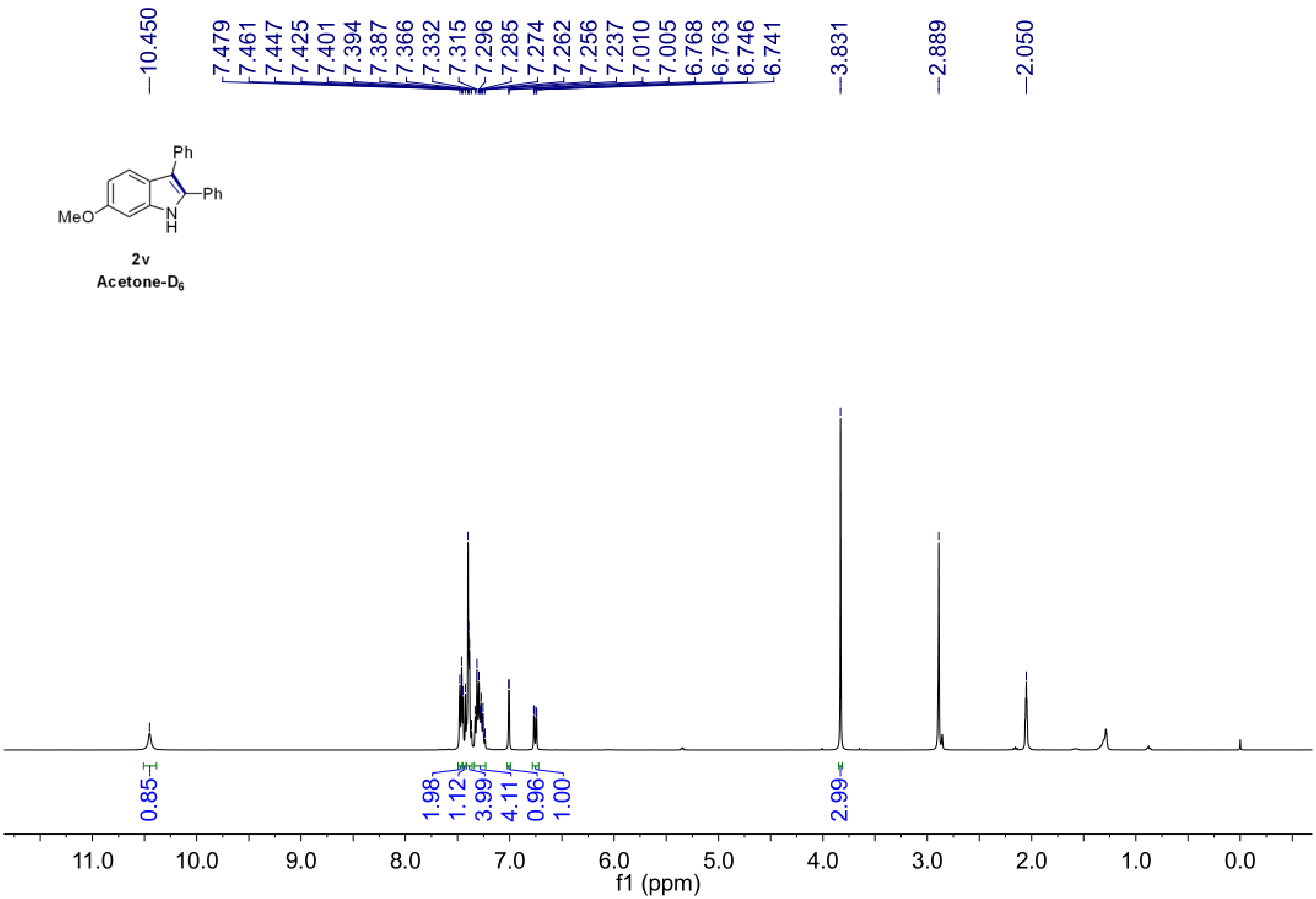
128.451
128.029
127.438
126.625
126.097
122.153
119.312
114.851
110.819
77.318
77.000
76.683
21.707
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.425
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7.387
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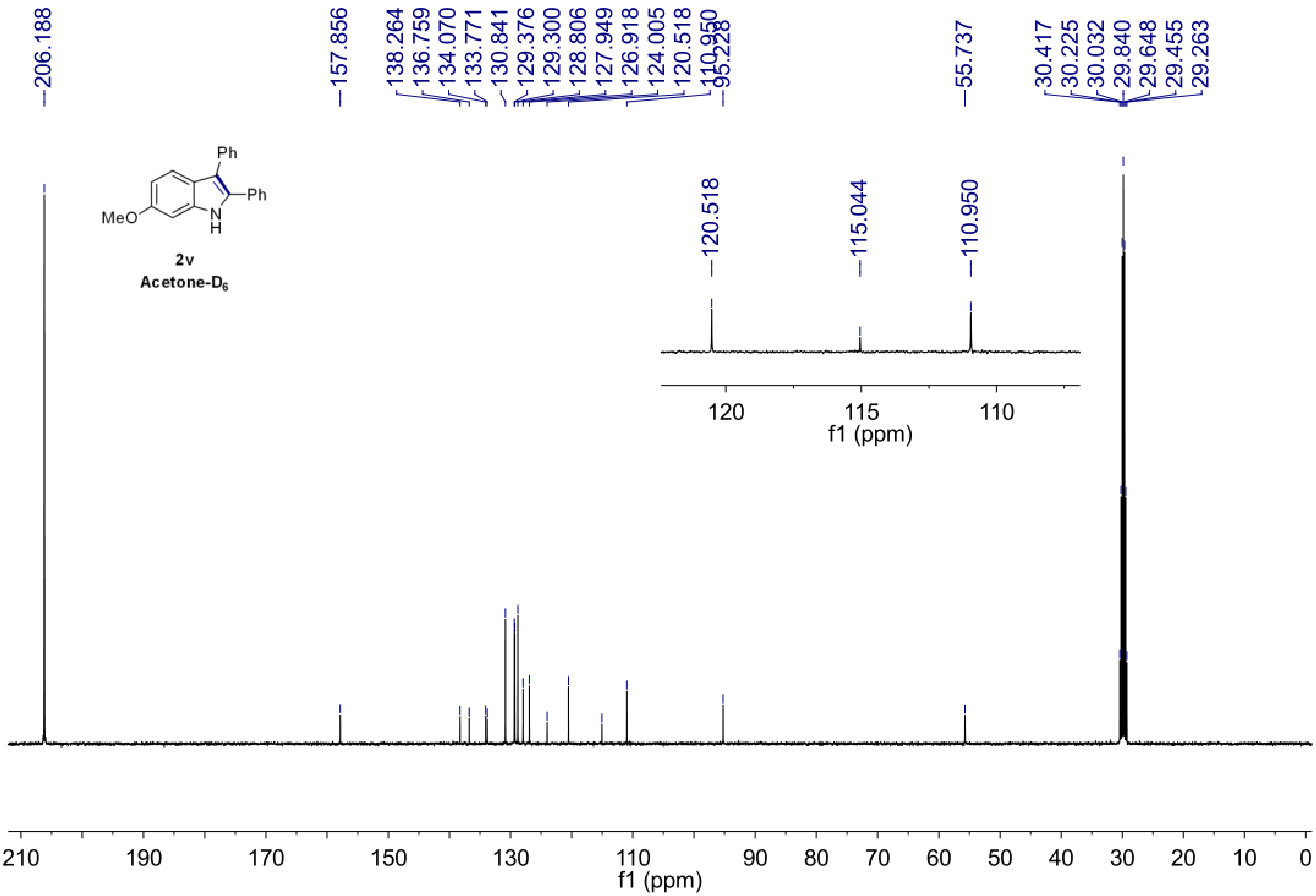
7.332
7.315
7.296
7.285
7.274
7.262
7.256
7.237
7.010
7.005
6.768
6.763
6.746
6.741
3.831
2.889
2.050
Ph
Ph
MeO
N
H
2v
Acetone-D6
0.85
1.98
1.12
3.99
4.11
0.96
1.00
2.99
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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130.841
129.376
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128.806
127.949
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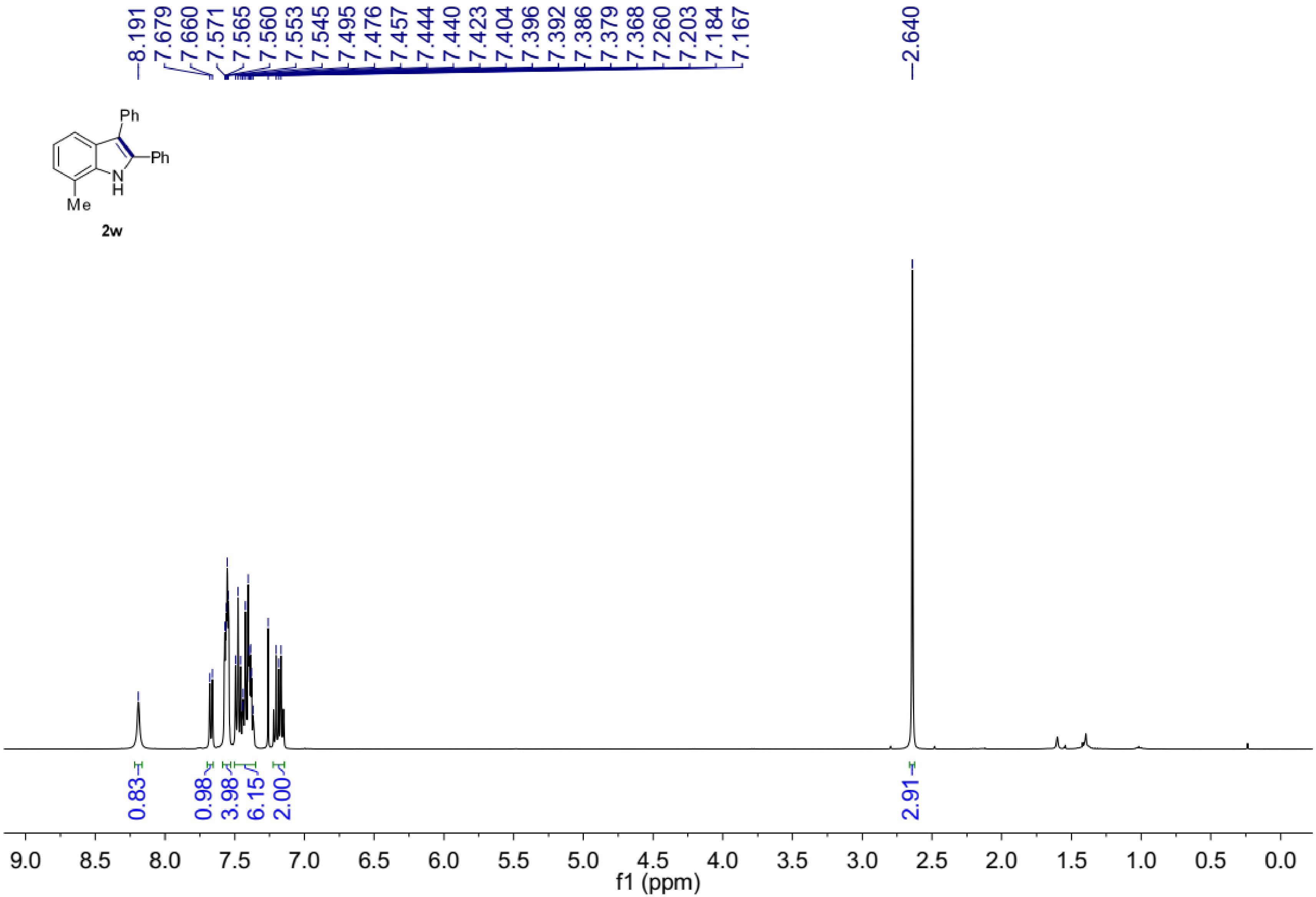
124.005
120.518
110.950
95.228
55.737
30.417
30.225
30.032
29.840
29.648
29.455
29.263
Ph
Ph
MeO
N
H
2v
Acetone-D6
120.518
115.044
110.950
120
115
110
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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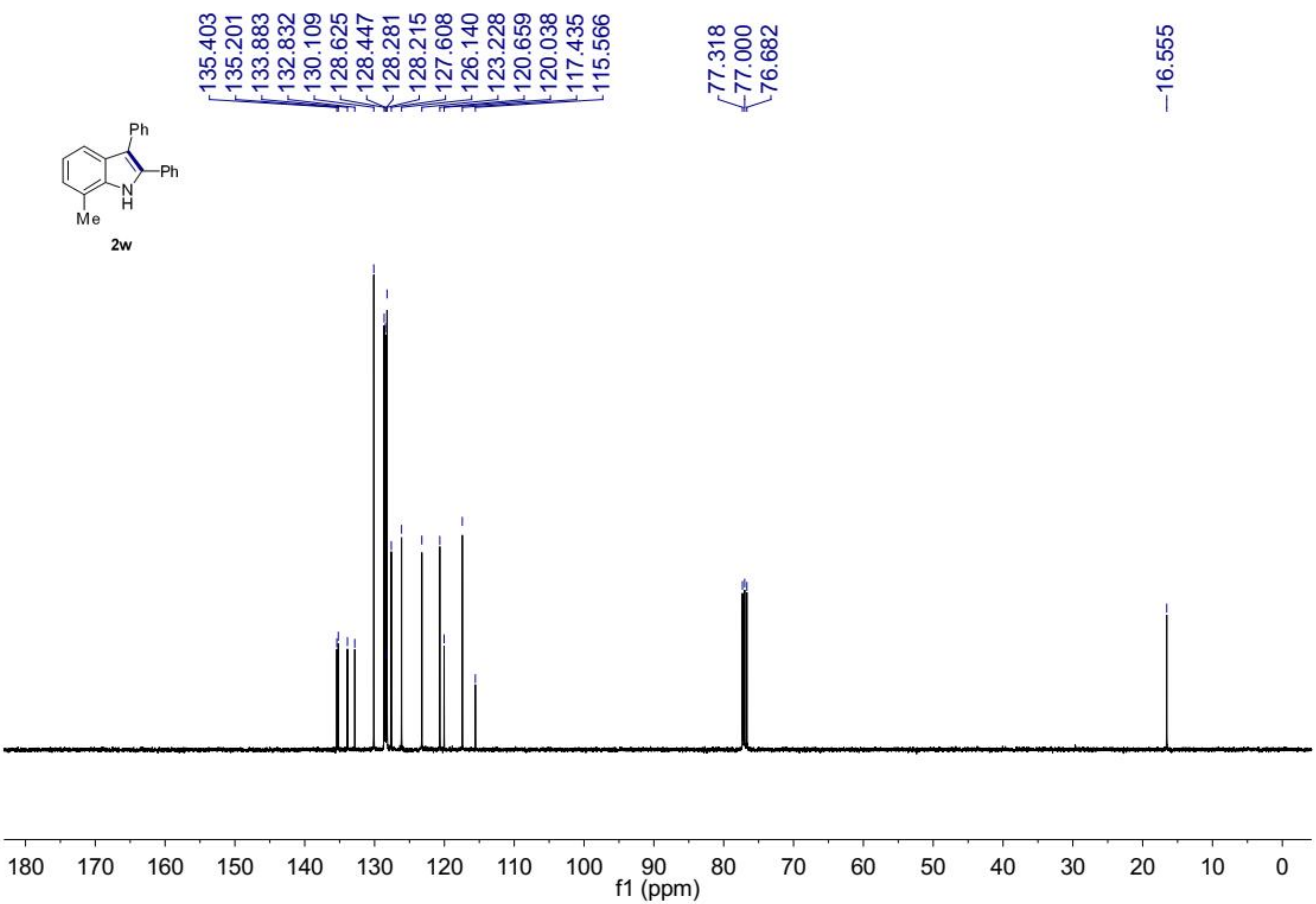
7.444
7.440
7.423
7.404
7.396
7.392
7.386
7.379
7.368
7.260
7.203
7.184
7.167
2.640
Ph
Ph
N
H
Me
2w
0.83
0.98
3.98
6.15
2.00
2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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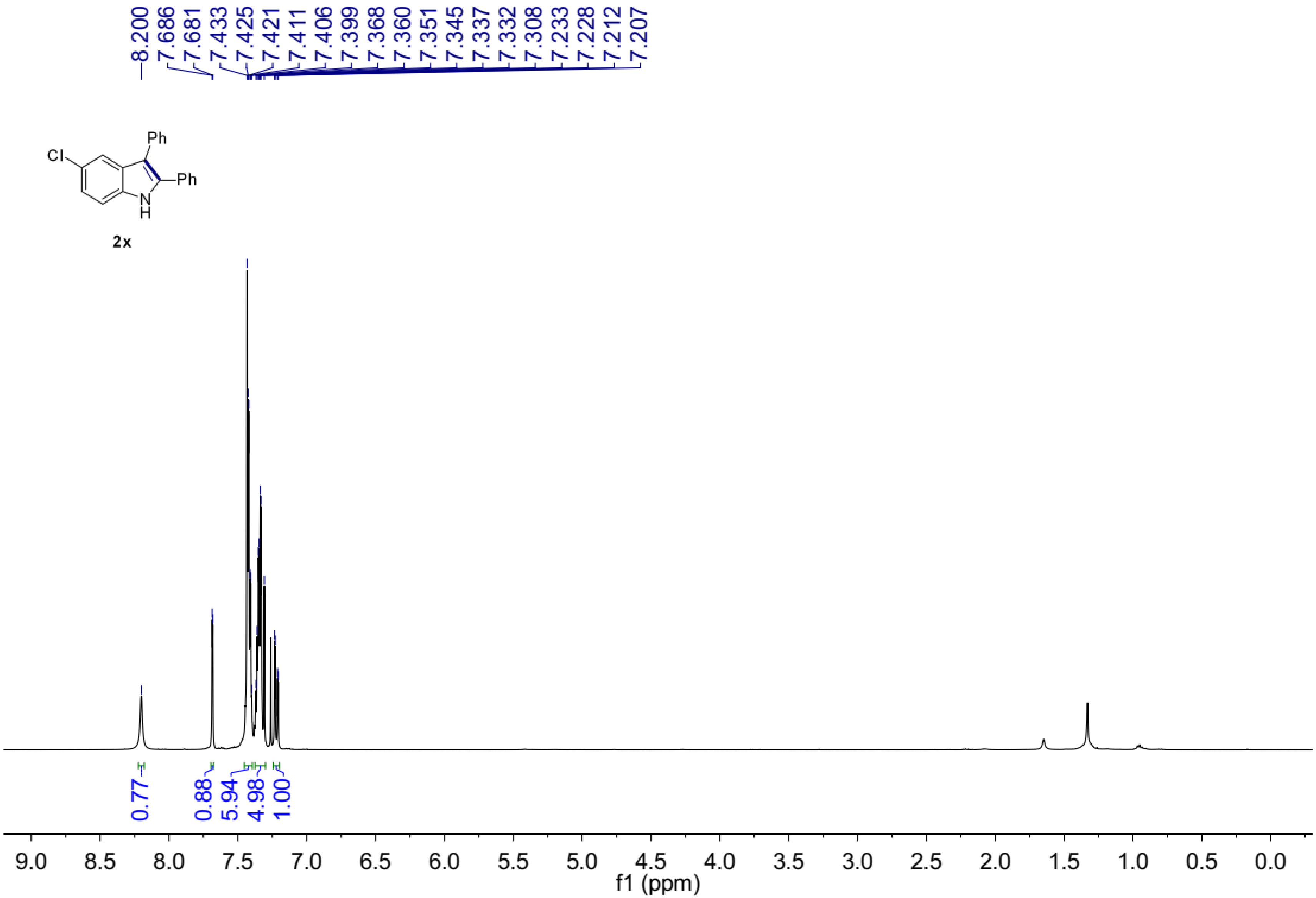
133.883
132.832
130.109
128.625
128.447
128.281
128.215
127.608
126.140
123.228
120.659
120.038
117.435
115.566
77.318
77.000
76.682
16.555
Ph
Ph
N
H
Me
2w
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.368
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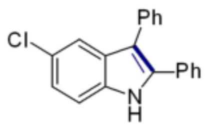
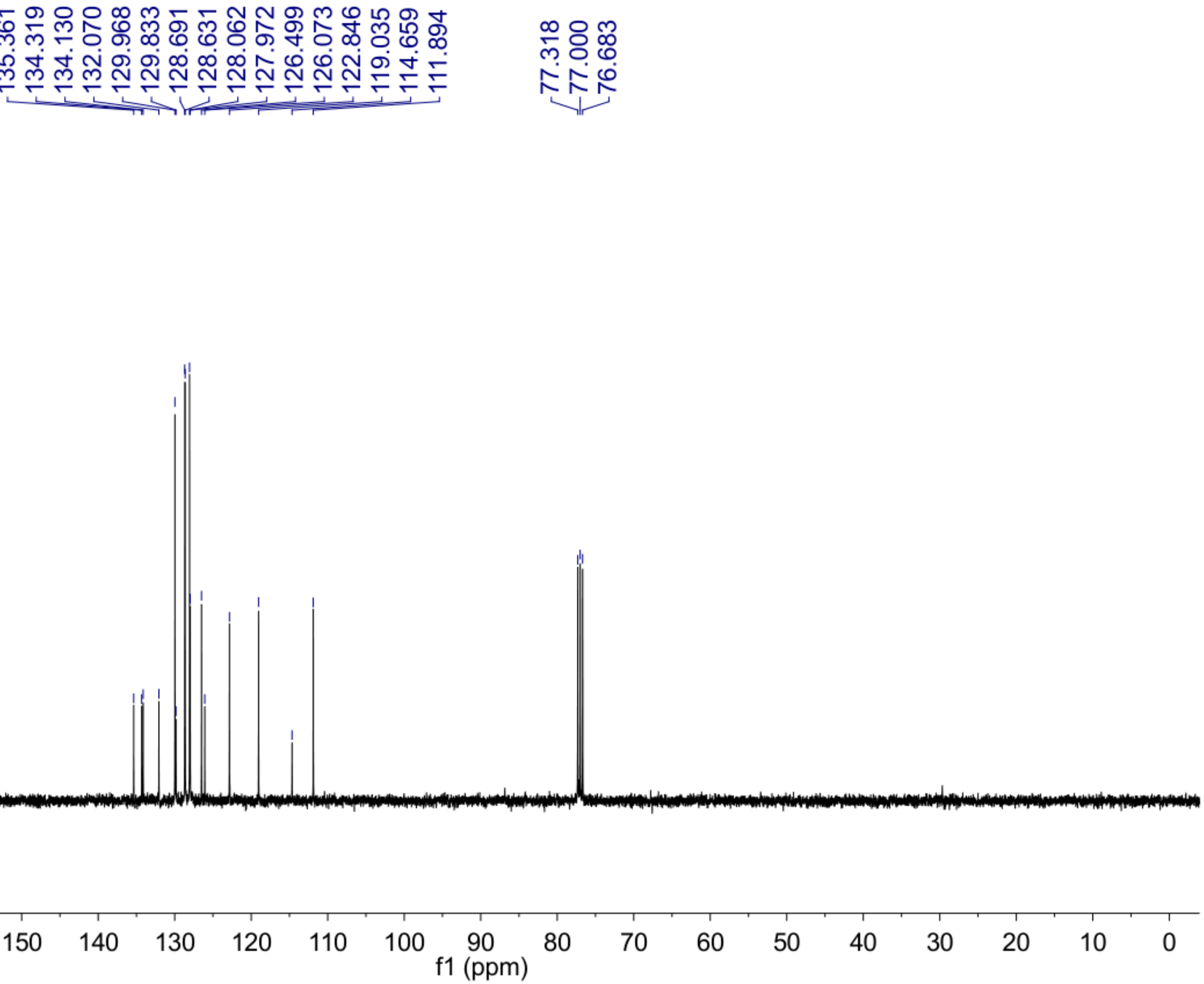
7.345
7.337
7.332
7.308
7.233
7.228
7.212
7.207
Cl
Ph
Ph
N
H
2x
0.77
0.88
5.94
4.98
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
Ph
Ph
N
H

2x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128.631
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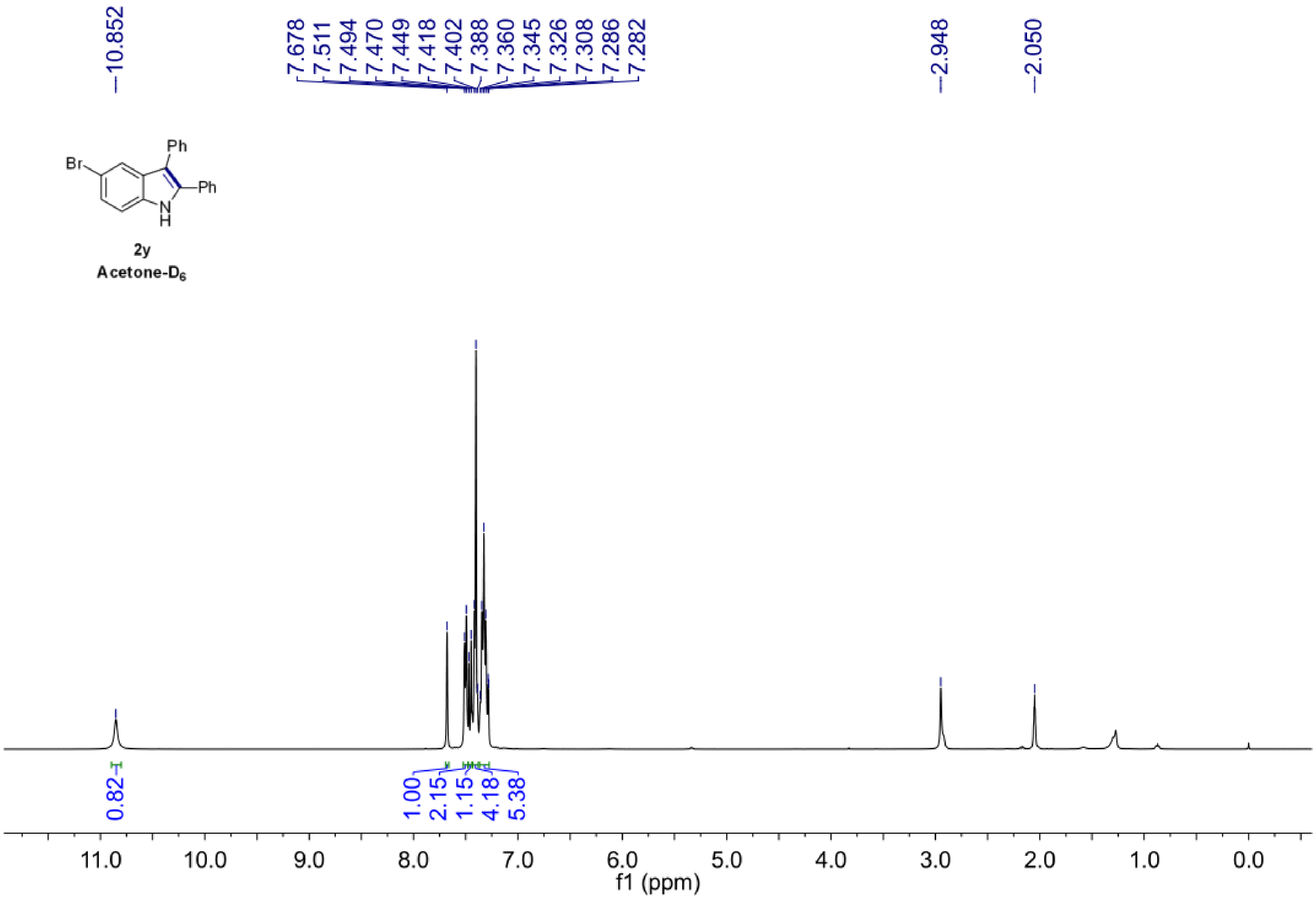
127.972
126.499
126.073
122.846
119.035
114.659
111.894
77.318
77.000
76.683
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.470
7.449
7.418
7.402
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7.360
7.345
7.326
7.308
7.286
7.282
2.948
2.050
Br
Ph
Ph
N
H
2y
Acetone-D6
0.82
1.00
2.15
1.15
4.18
5.38
11.0
10.0
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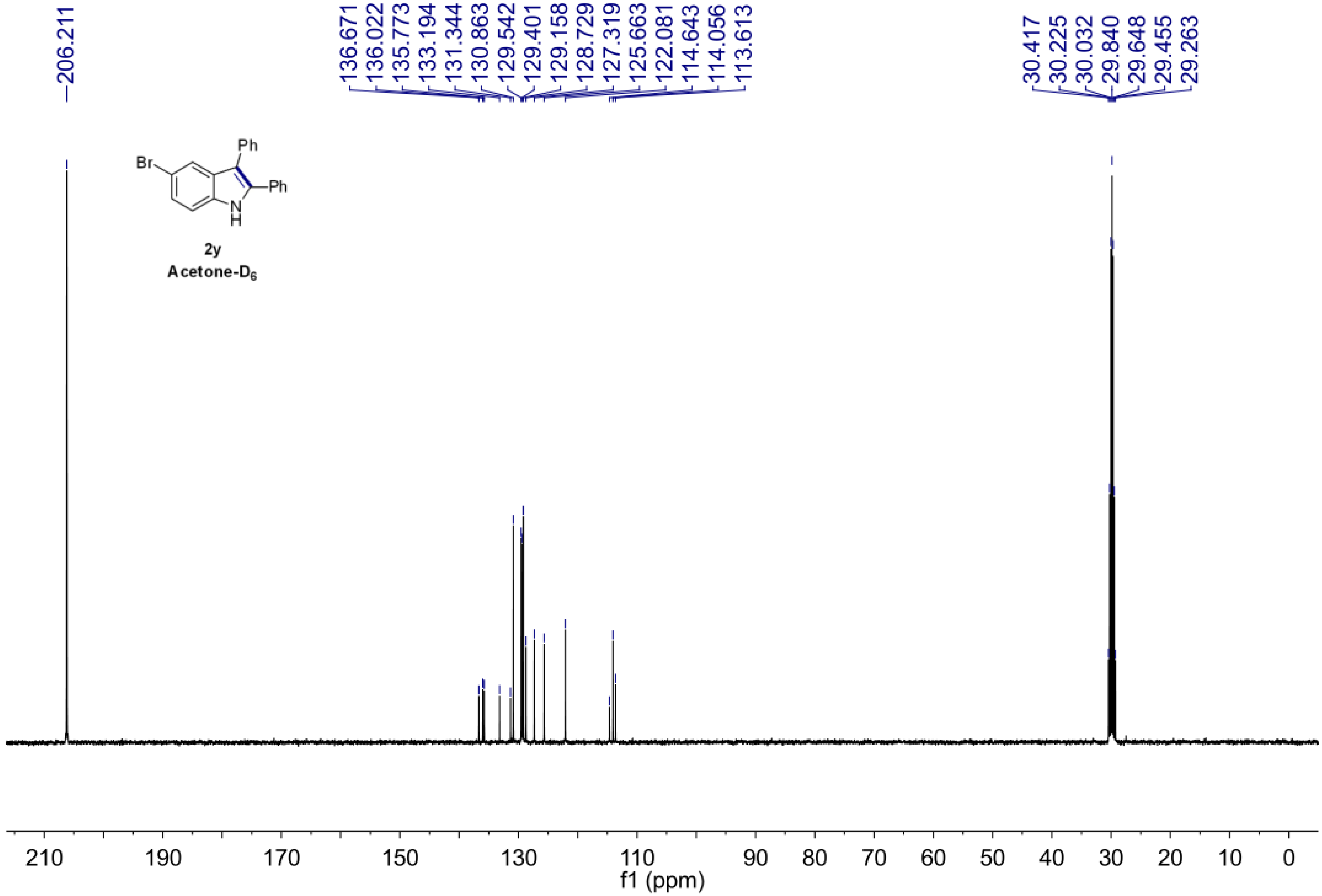
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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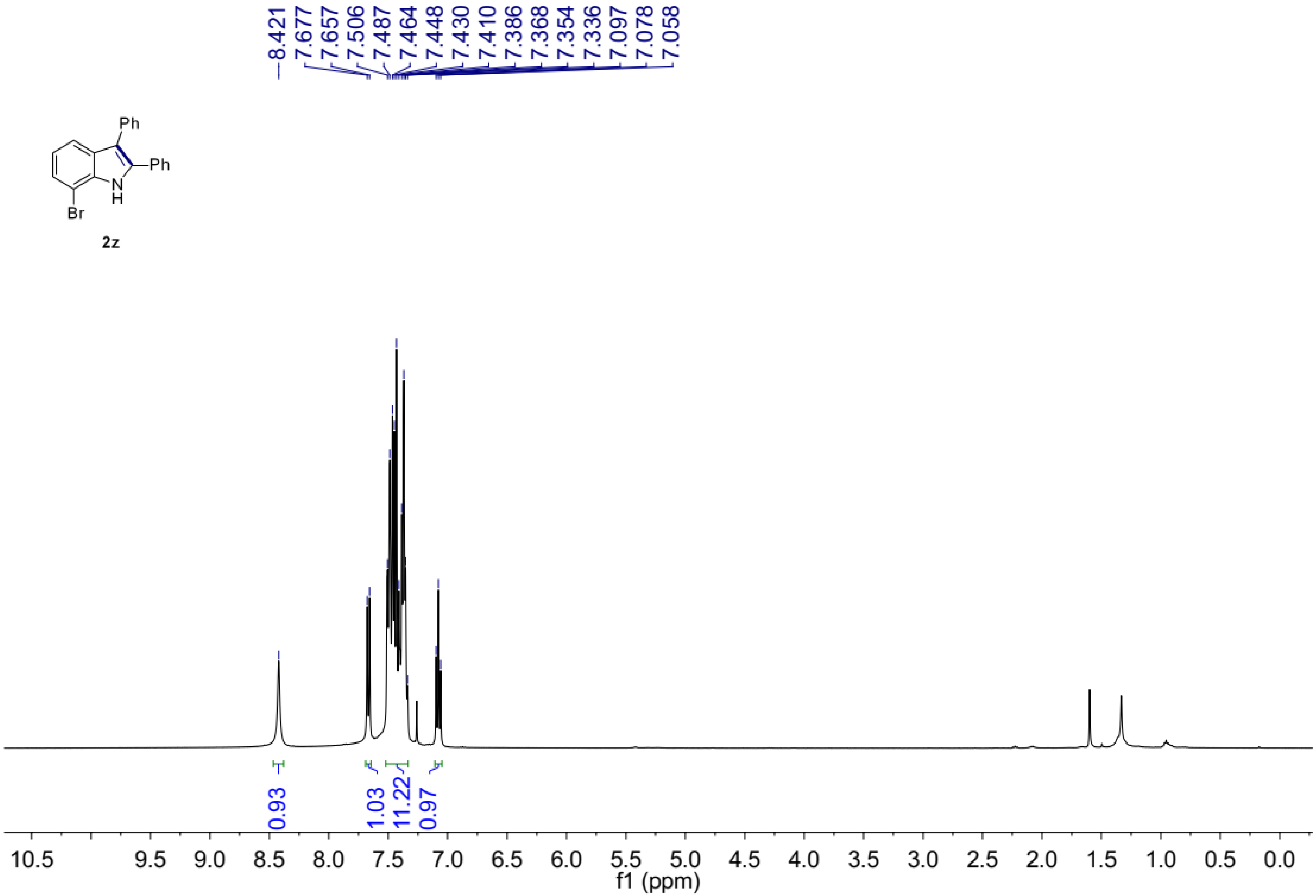
129.542
129.401
129.158
128.729
127.319
125.663
122.081
114.643
114.056
113.613
30.417
30.225
30.032
29.840
29.648
29.455
29.263
Br
Ph
Ph
N
H
2y
Acetone-D6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Ph
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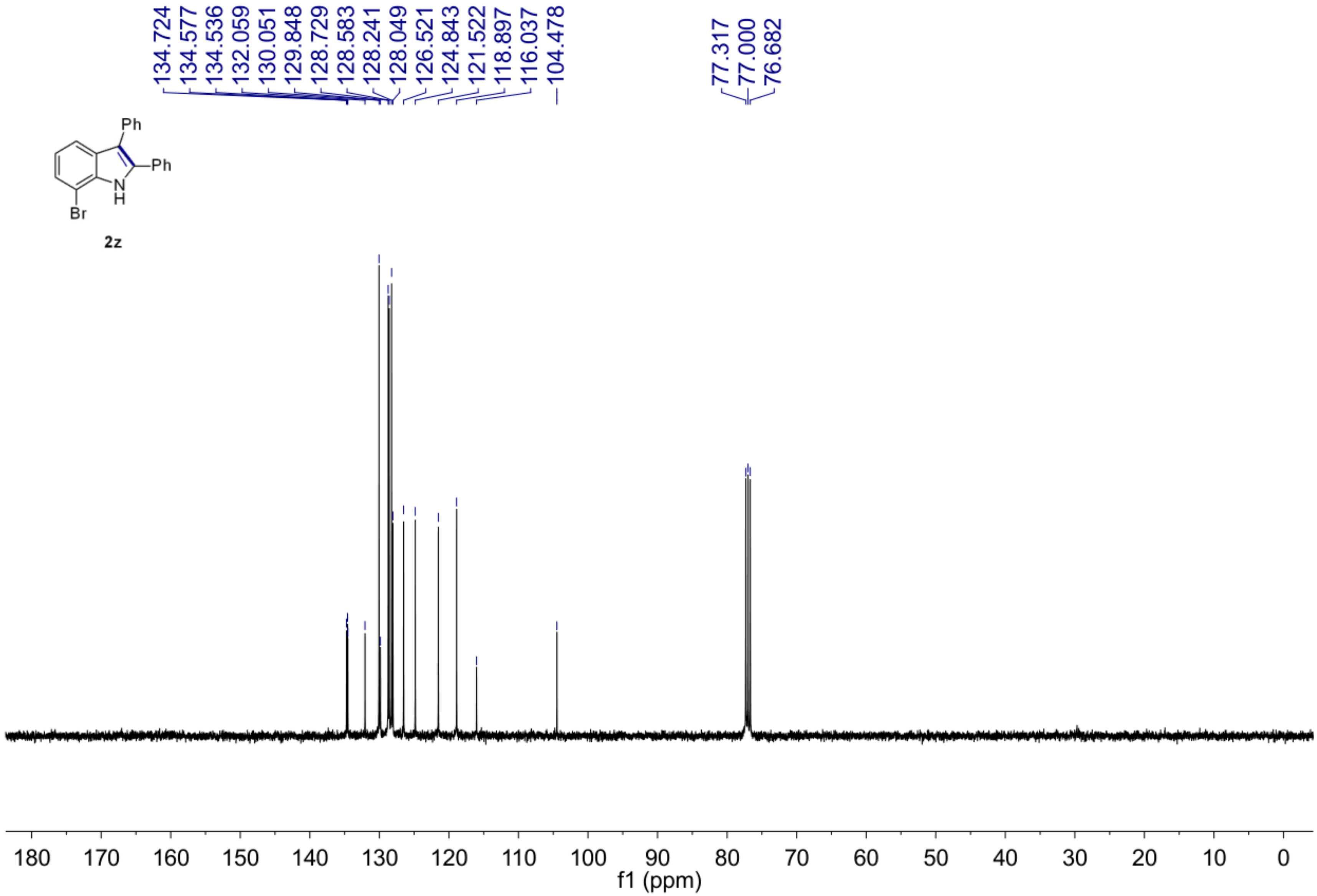
H
Br
8.421
7.677
7.657
7.506
7.487
7.464
7.448
7.430
7.410
7.386
7.368
7.354
7.336
7.097
7.078
7.058
0.93
1.03
11.22
0.97
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2z



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128.729
128.583
128.241
128.049
126.521
124.843
121.522
118.897
116.037
104.478
77.317
77.000
76.682
Ph
Ph
N
H
Br
2z
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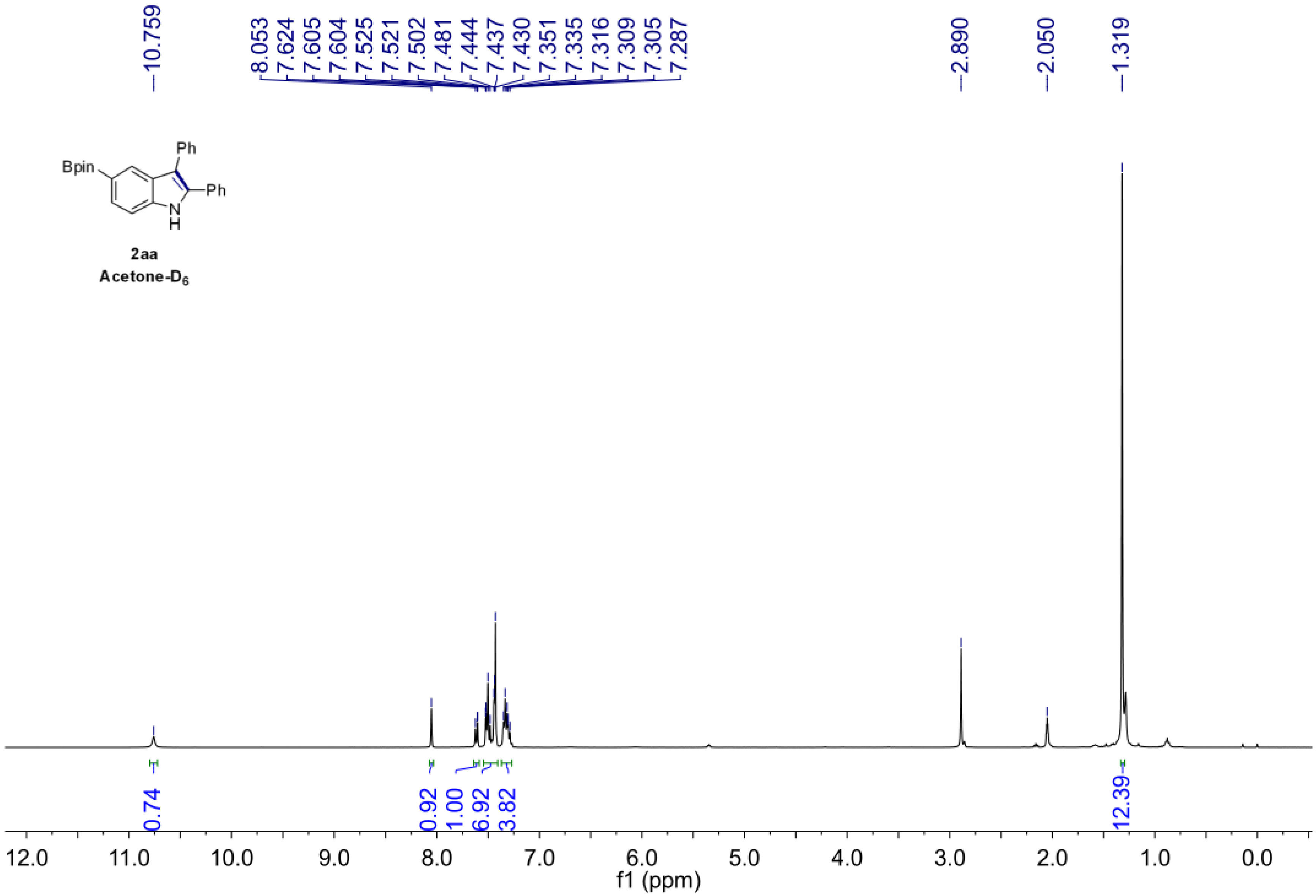
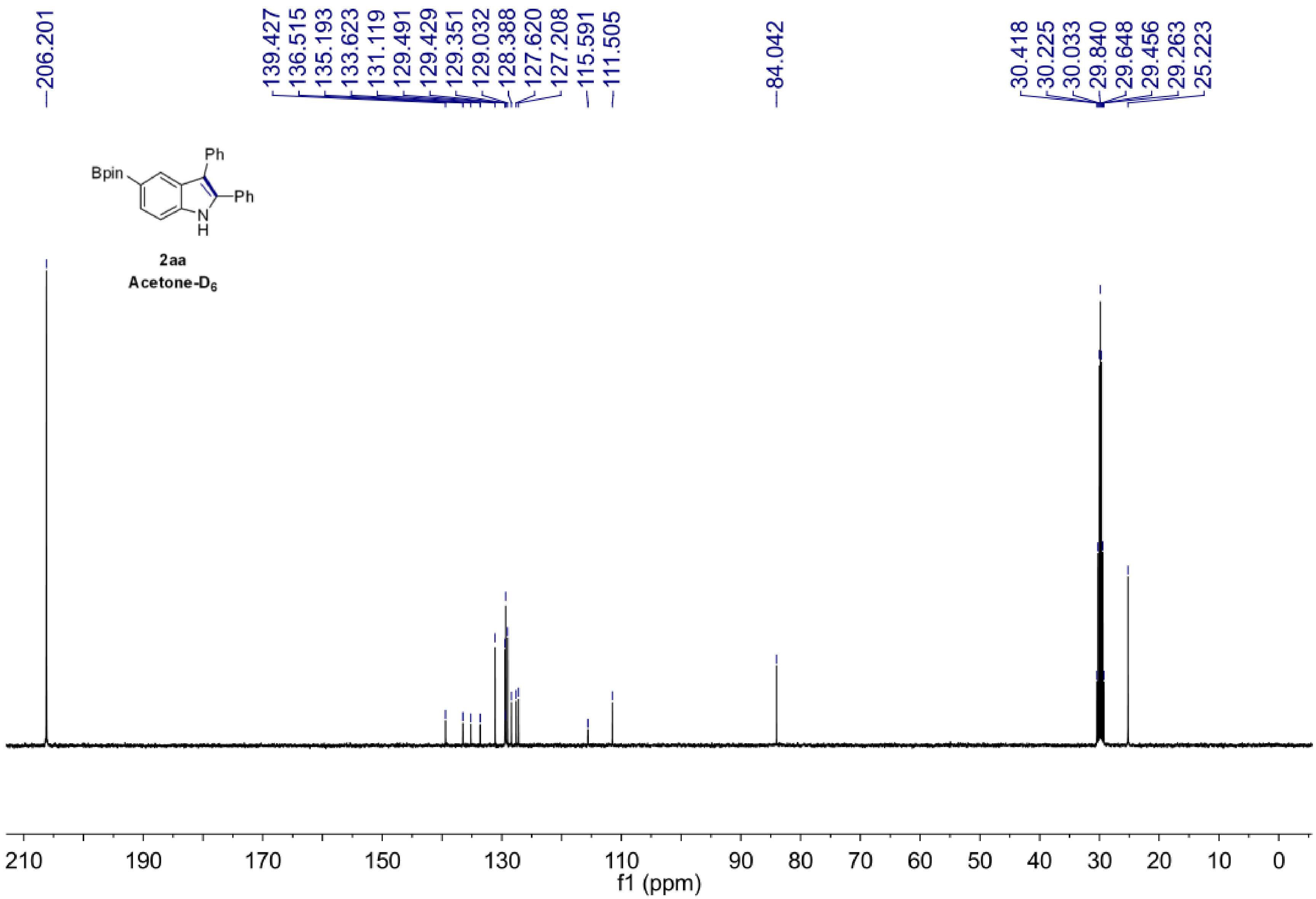
f1 (ppm)



2aa
Acetone-D$_6$



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139.427
136.515
135.193
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131.119
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129.429
129.351
129.032
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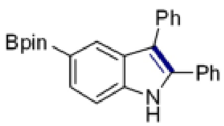
127.620
127.208
115.591
111.505
84.042
30.418
30.225
30.033
29.840
29.648
29.456
29.263
25.223
Bpin
Ph
Ph
N
H
2aa
Acetone-D6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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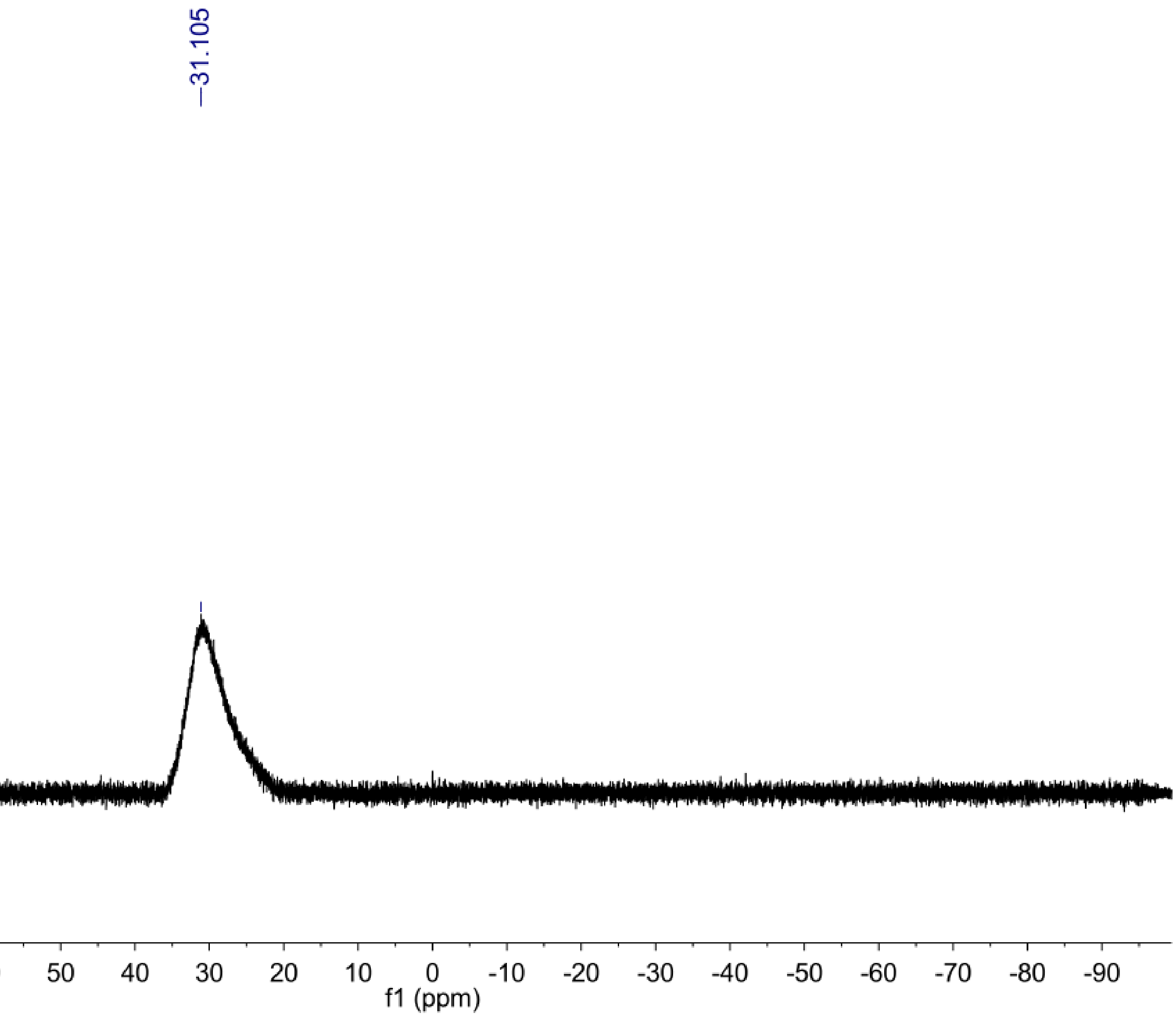

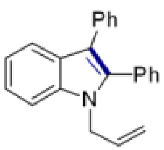

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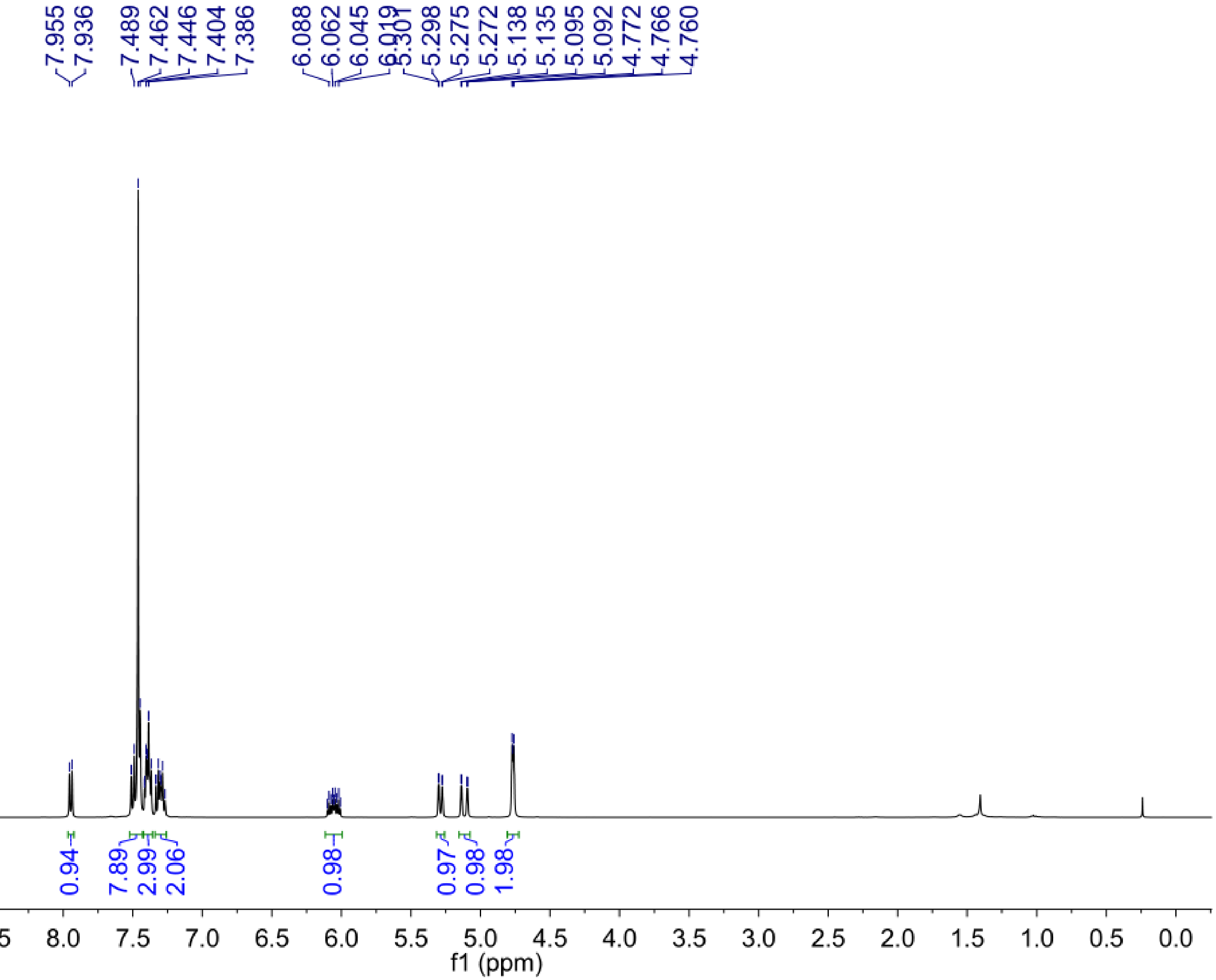
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7.489
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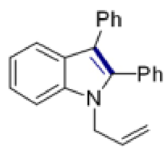
7.446
7.404
7.386
6.088
6.062
6.045
6.019
5.301
5.298
5.275
5.272
5.138
5.135
5.095
5.092
4.772
4.766
4.760
0.94
7.89
2.99
2.06
0.98
0.97
0.98
1.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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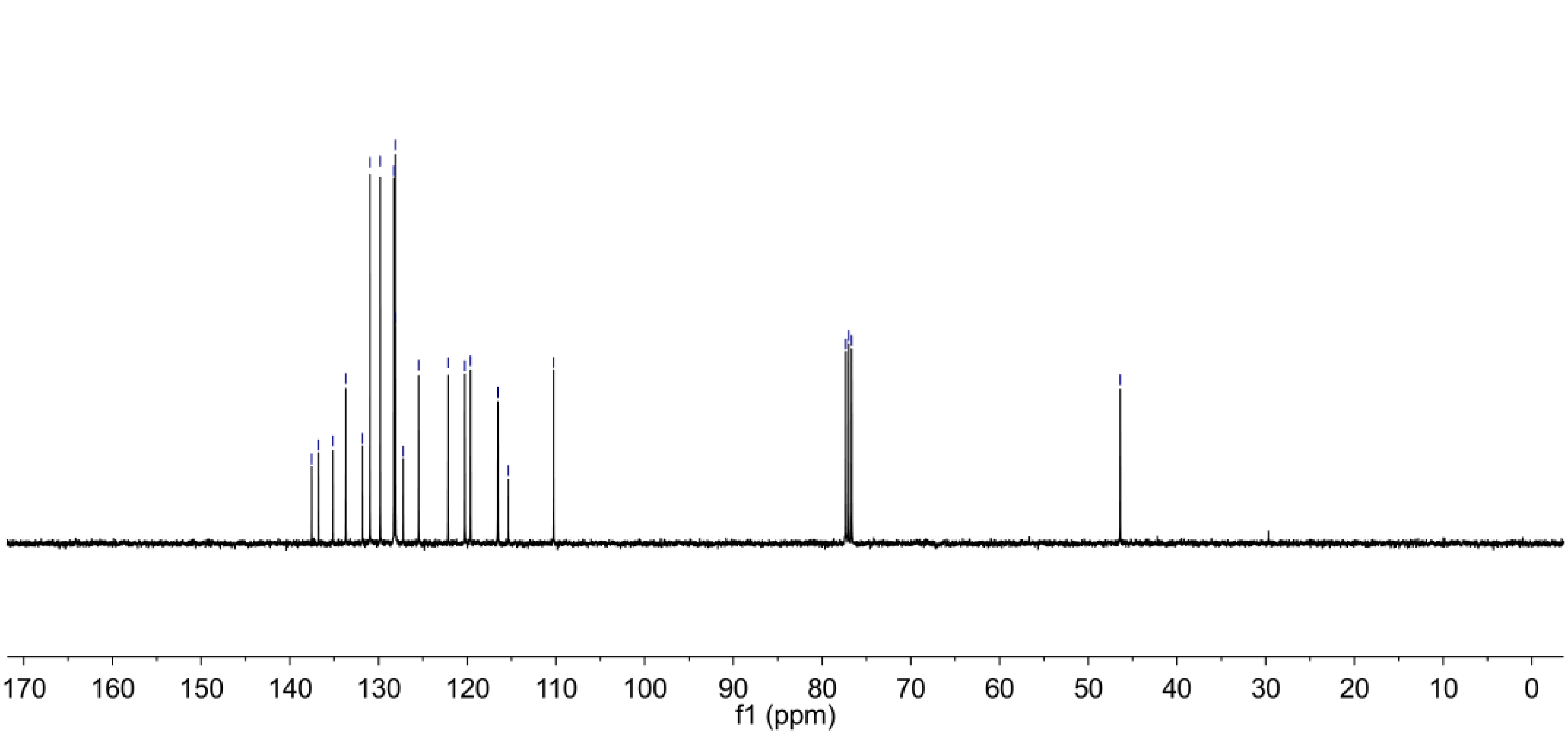
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136.771
135.128
133.689
131.838
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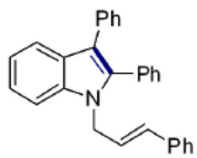
129.831
128.291
128.117
128.096
127.219
125.490
122.168
120.281
119.646
116.547
115.380
110.274
77.318
77.000
76.682
46.398
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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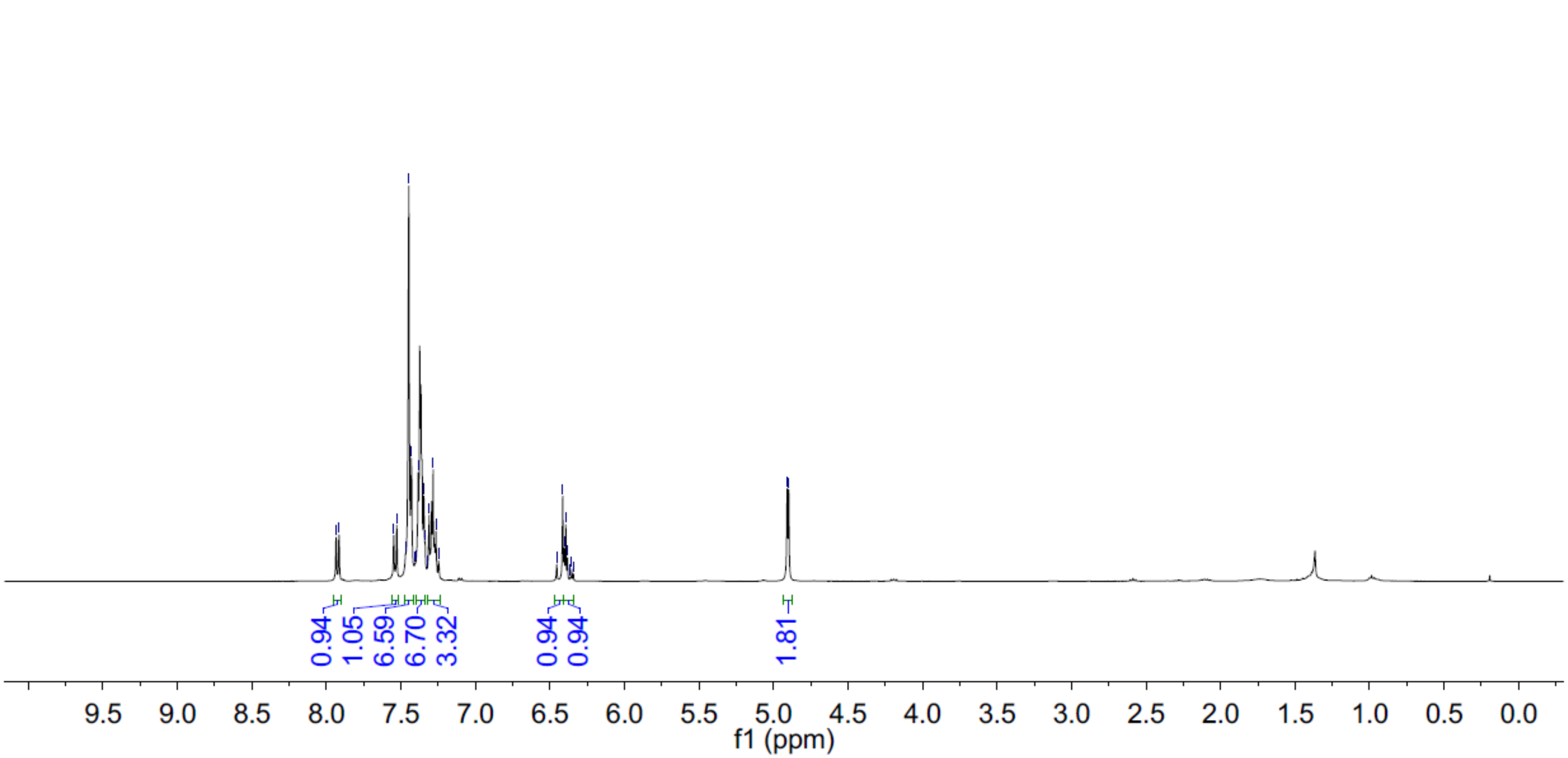
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7.915
7.548
7.528
7.469
7.447
7.430
7.401
7.384
7.347
7.339
7.310
7.284
7.265
7.246
6.454
6.414
6.404
6.394
6.382
6.364
6.354
6.342
4.908
4.898
0.94
1.05
6.59
6.70
3.32
0.94
0.94
1.81
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.5
1.0
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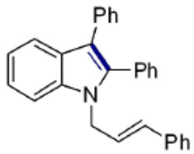
0.0
f1 (ppm)



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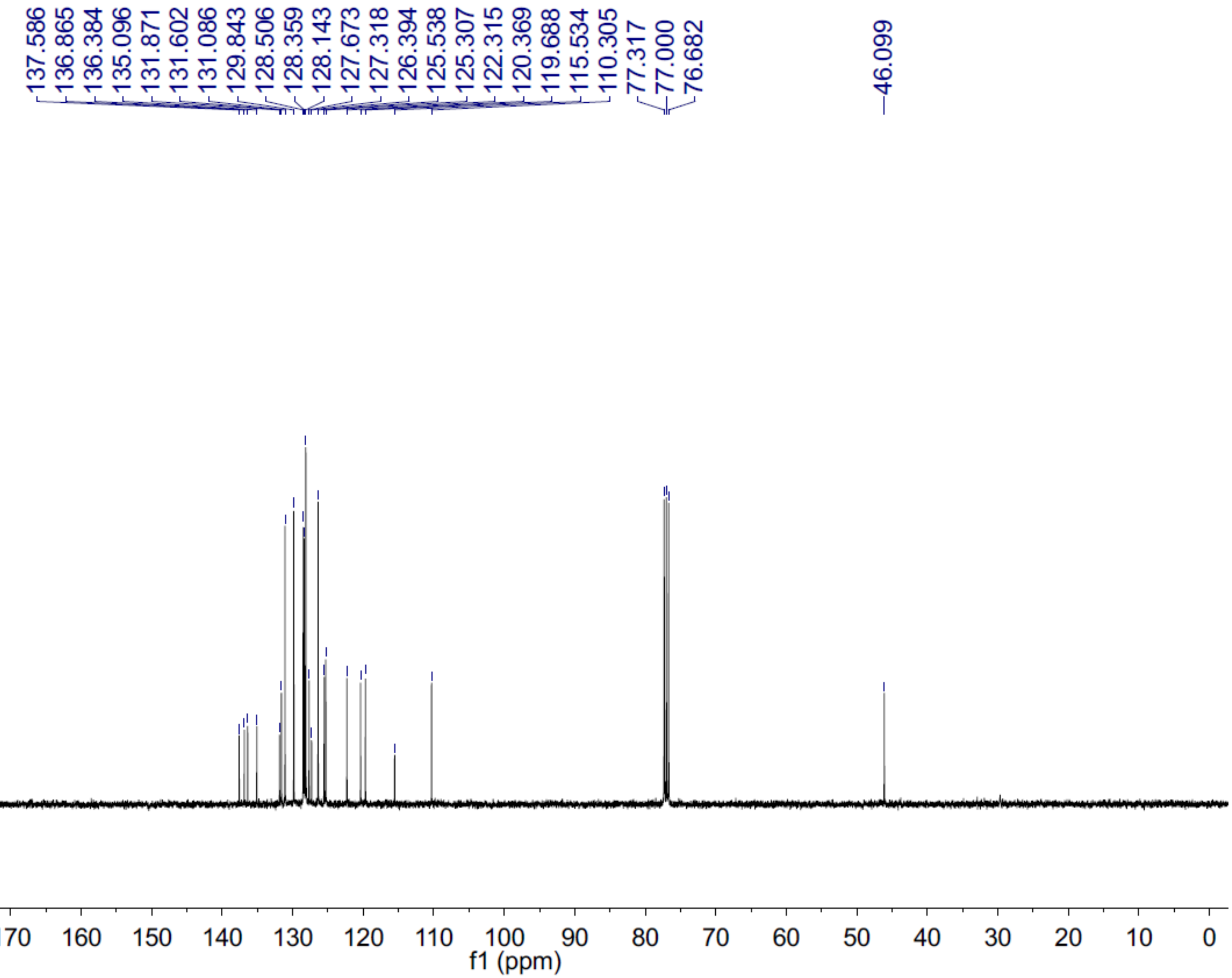

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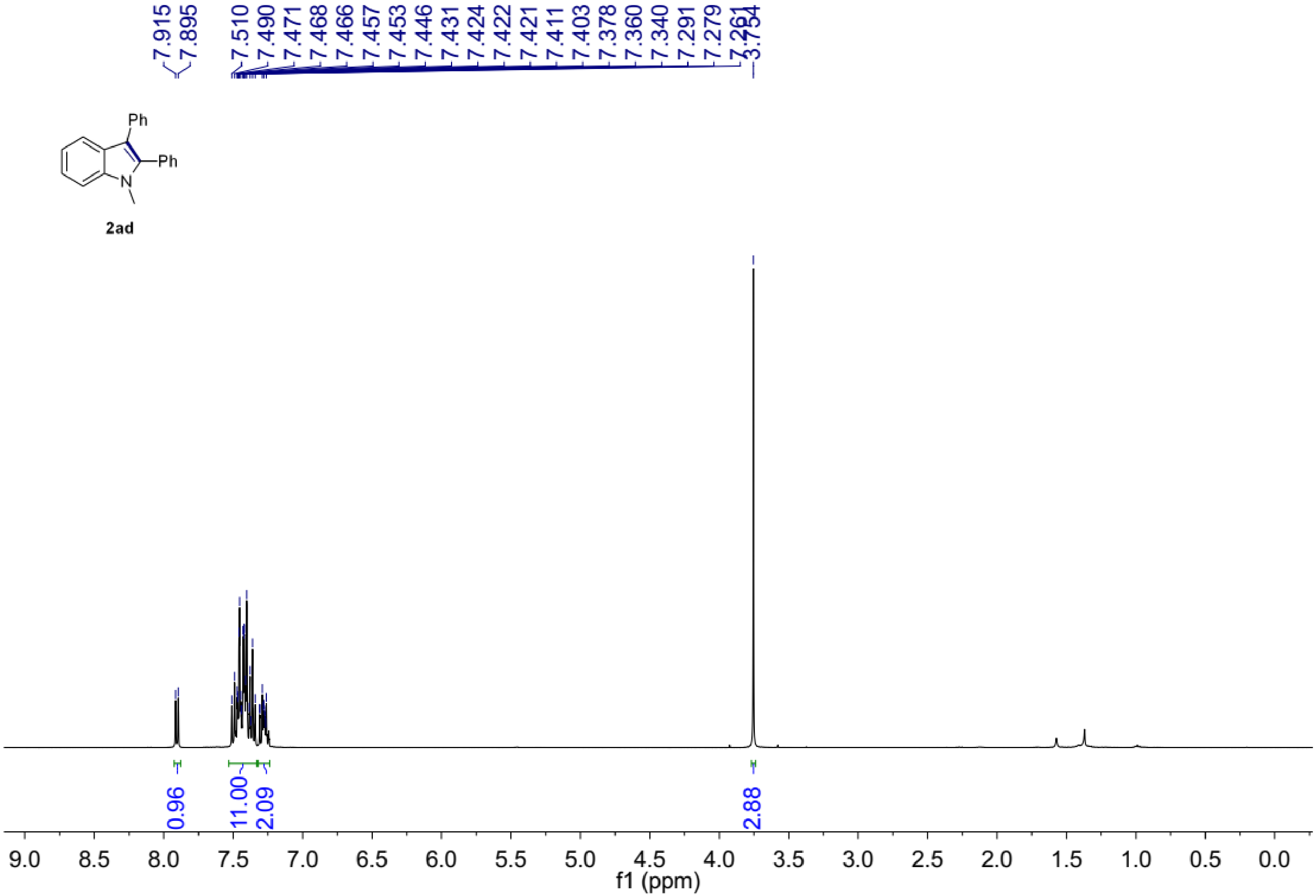
136.865
136.384
135.096
131.871
131.602
131.086
129.843
128.506
128.359
128.143
127.673
127.318
126.394
125.538
125.307
122.315
120.369
119.688
115.534
110.305
77.317
77.000
76.682
46.099
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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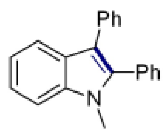
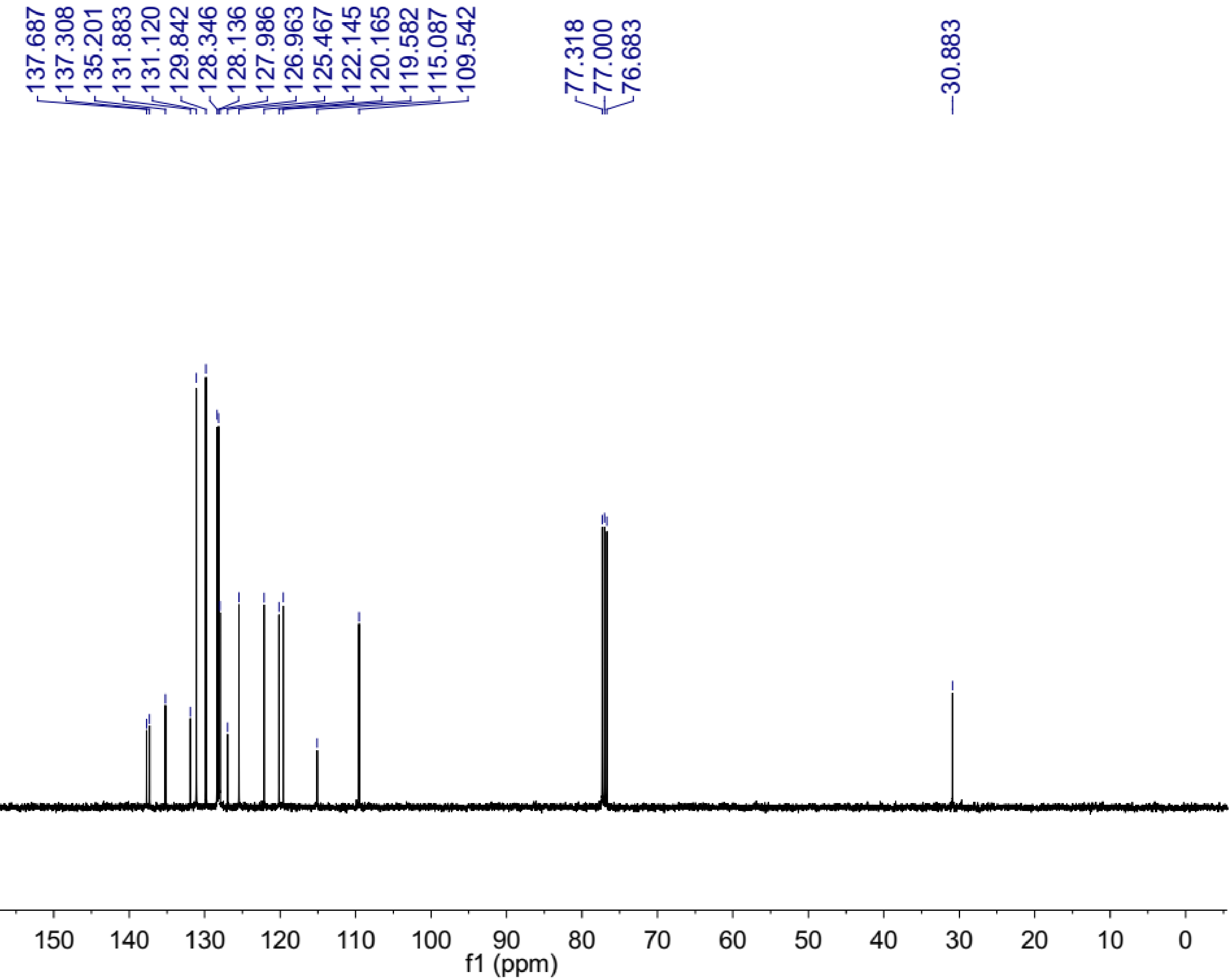
7.895
7.510
7.490
7.471
7.468
7.466
7.457
7.453
7.446
7.431
7.424
7.422
7.421
7.411
7.403
7.378
7.360
7.340
7.291
7.279
7.261
3.754
Ph
Ph
N
2ad
0.96
11.00
2.09
2.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
Ph
N

2ad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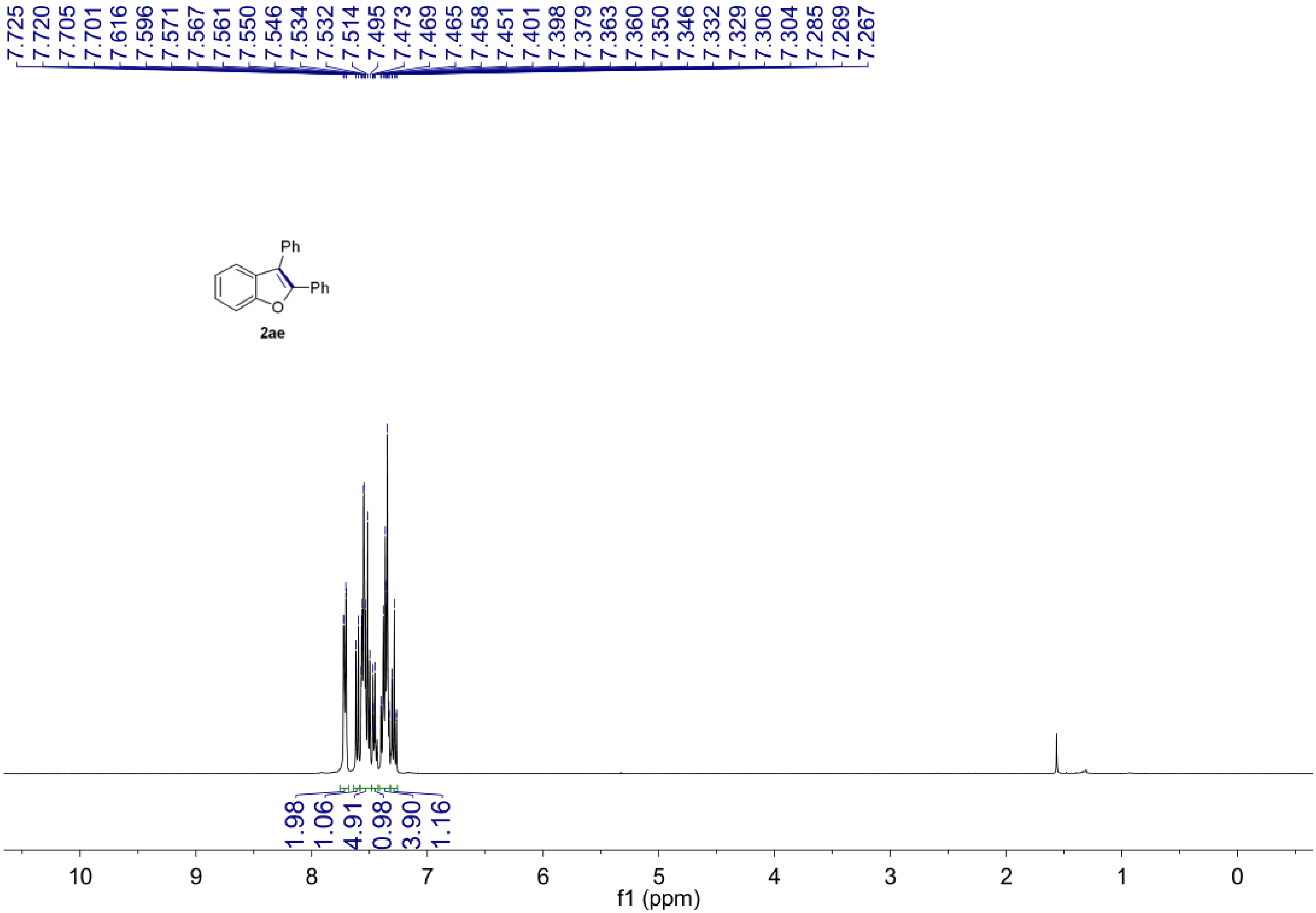
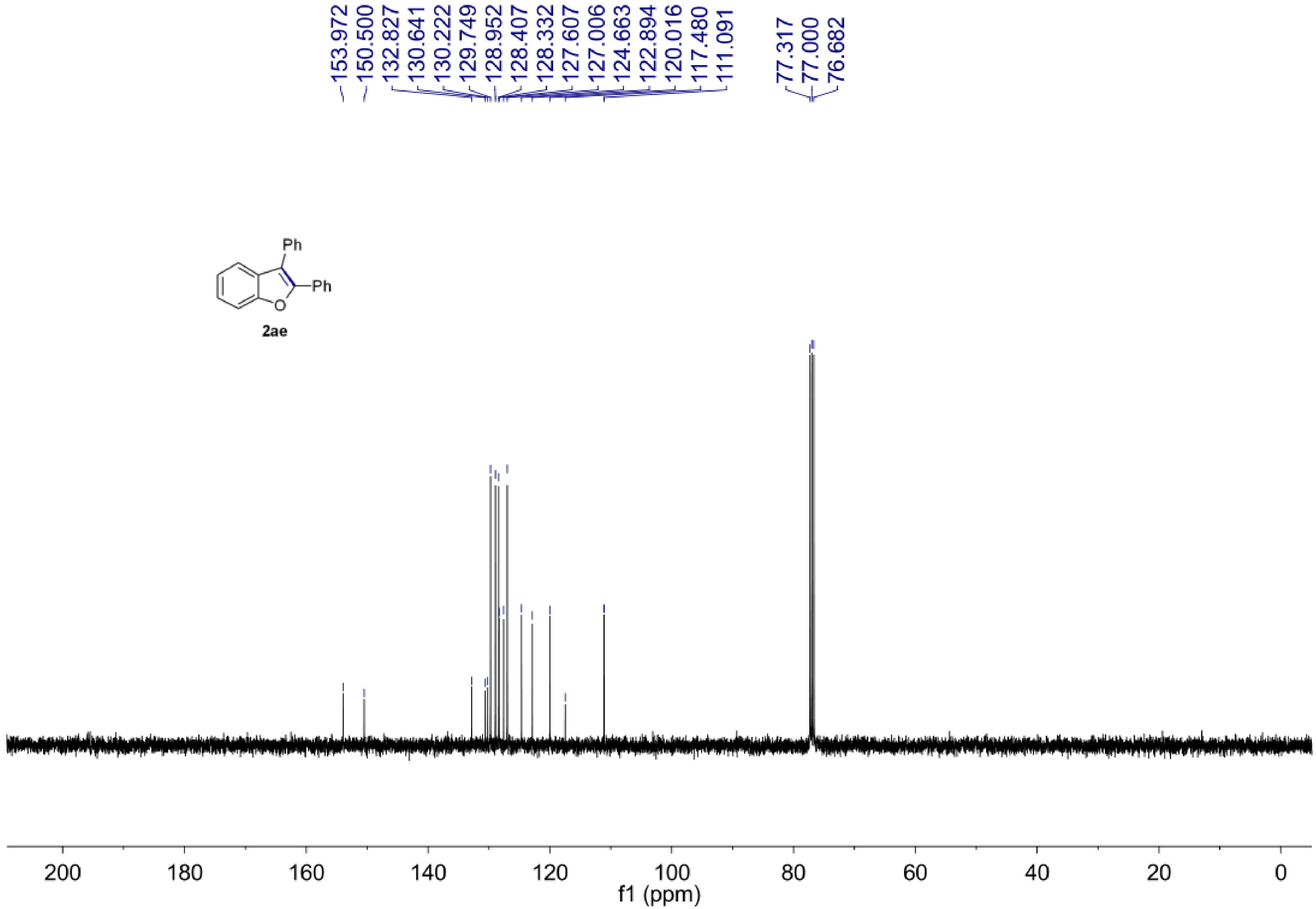
137.308
135.201
131.883
131.120
129.842
128.346
128.136
127.986
126.963
125.467
122.145
120.165
119.582
115.087
109.542
77.318
77.000
76.683
30.883
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7.725 7.720 7.705 7.701 7.616 7.596 7.571 7.567 7.561 7.550 7.546 7.534 7.532 7.514 7.495 7.473 7.469 7.465 7.458 7.451 7.401 7.398 7.379 7.363 7.360 7.350 7.346 7.332 7.329 7.306 7.304 7.285 7.269 7.267
Ph
Ph
O
2ae
1.98 1.06 4.91 0.98 3.90 1.16
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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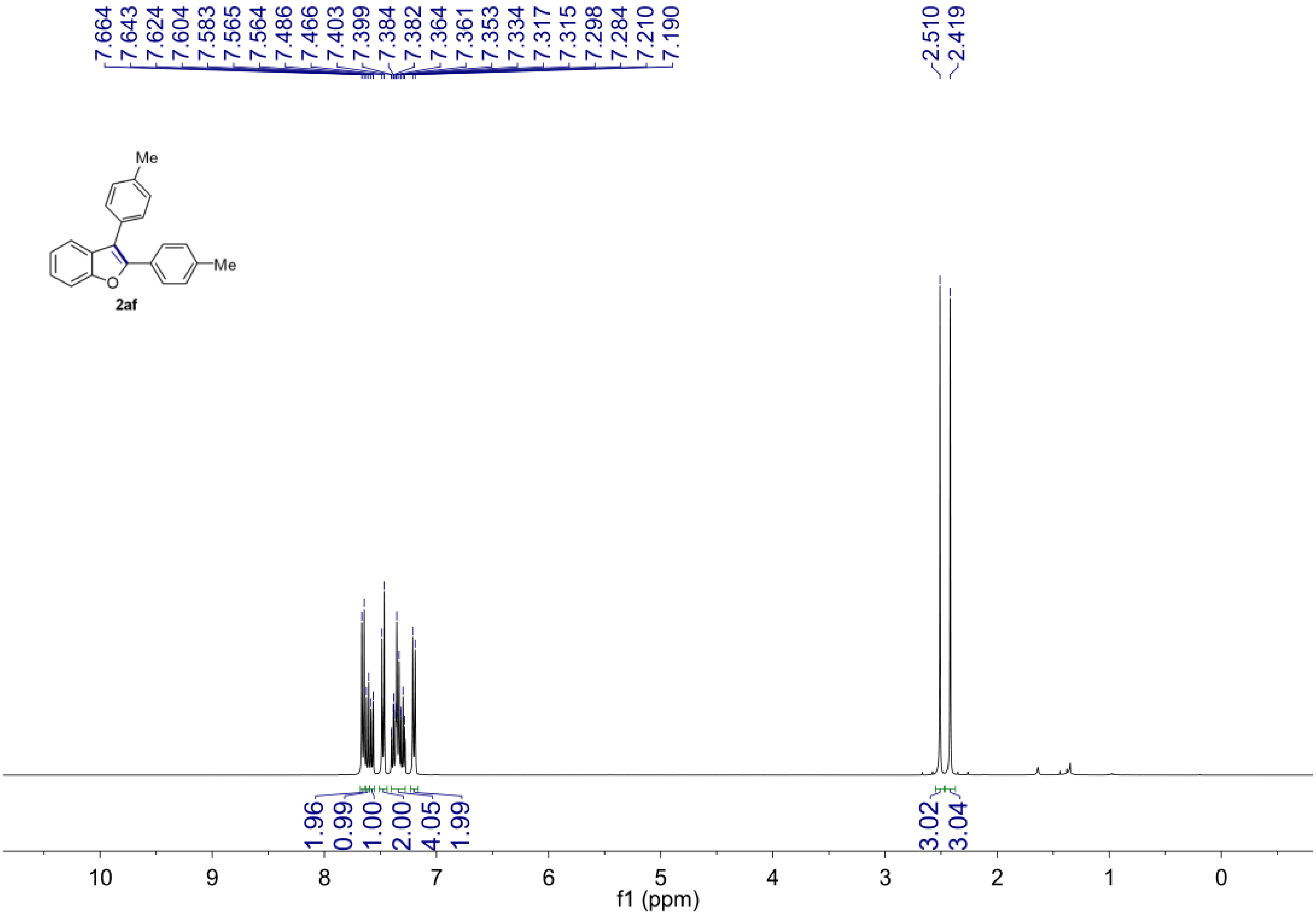
150.500
132.827
130.641
130.222
129.749
128.952
128.407
128.332
127.607
127.006
124.663
122.894
120.016
117.480
111.091
77.317
77.000
76.682
Ph
Ph
O
2ae
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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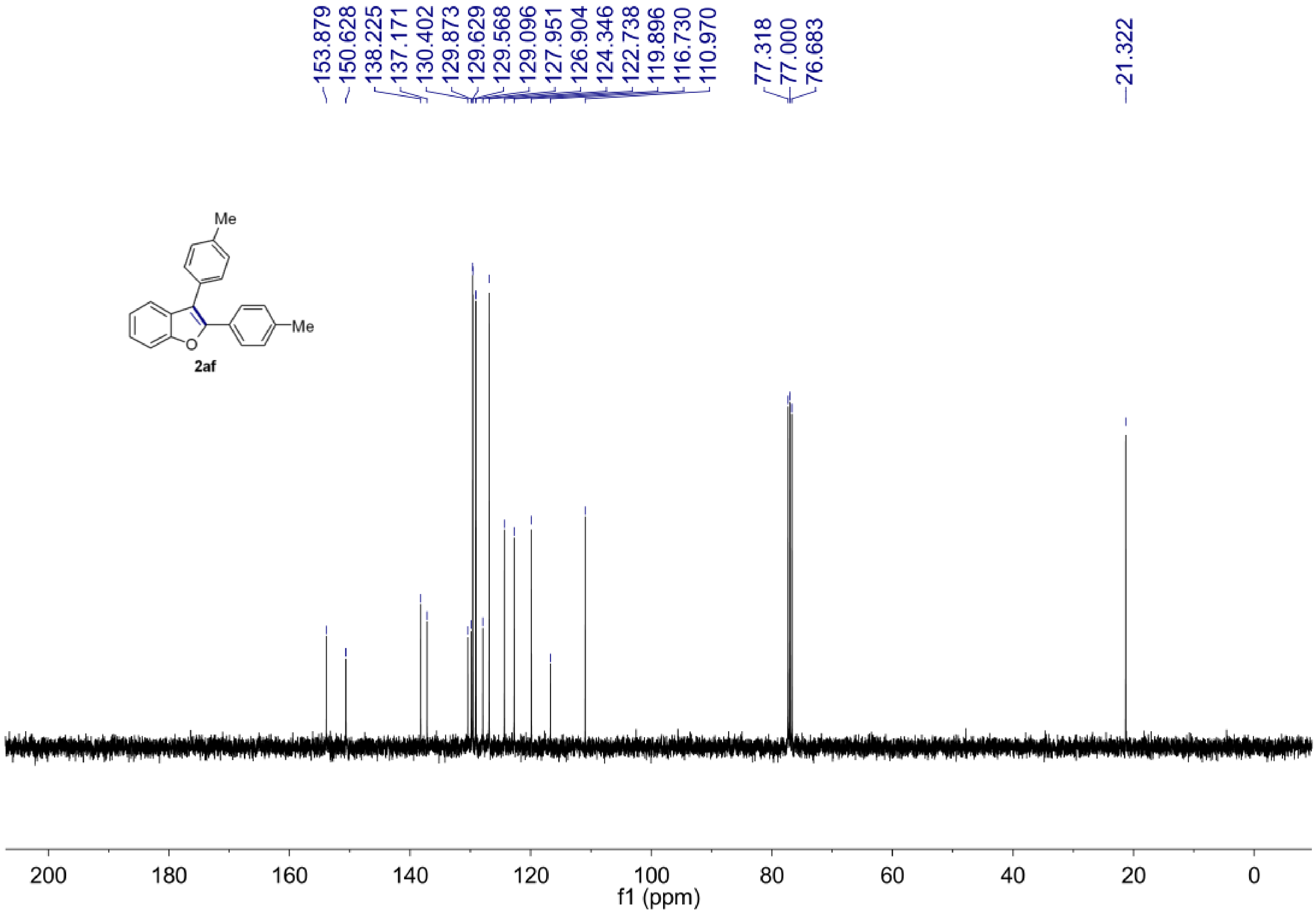
7.583
7.565
7.564
7.486
7.466
7.403
7.399
7.384
7.382
7.364
7.361
7.353
7.334
7.317
7.315
7.298
7.284
7.210
7.190
2.510
2.419
Me
Me
2af
1.96
0.99
1.00
2.00
4.05
1.99
3.02
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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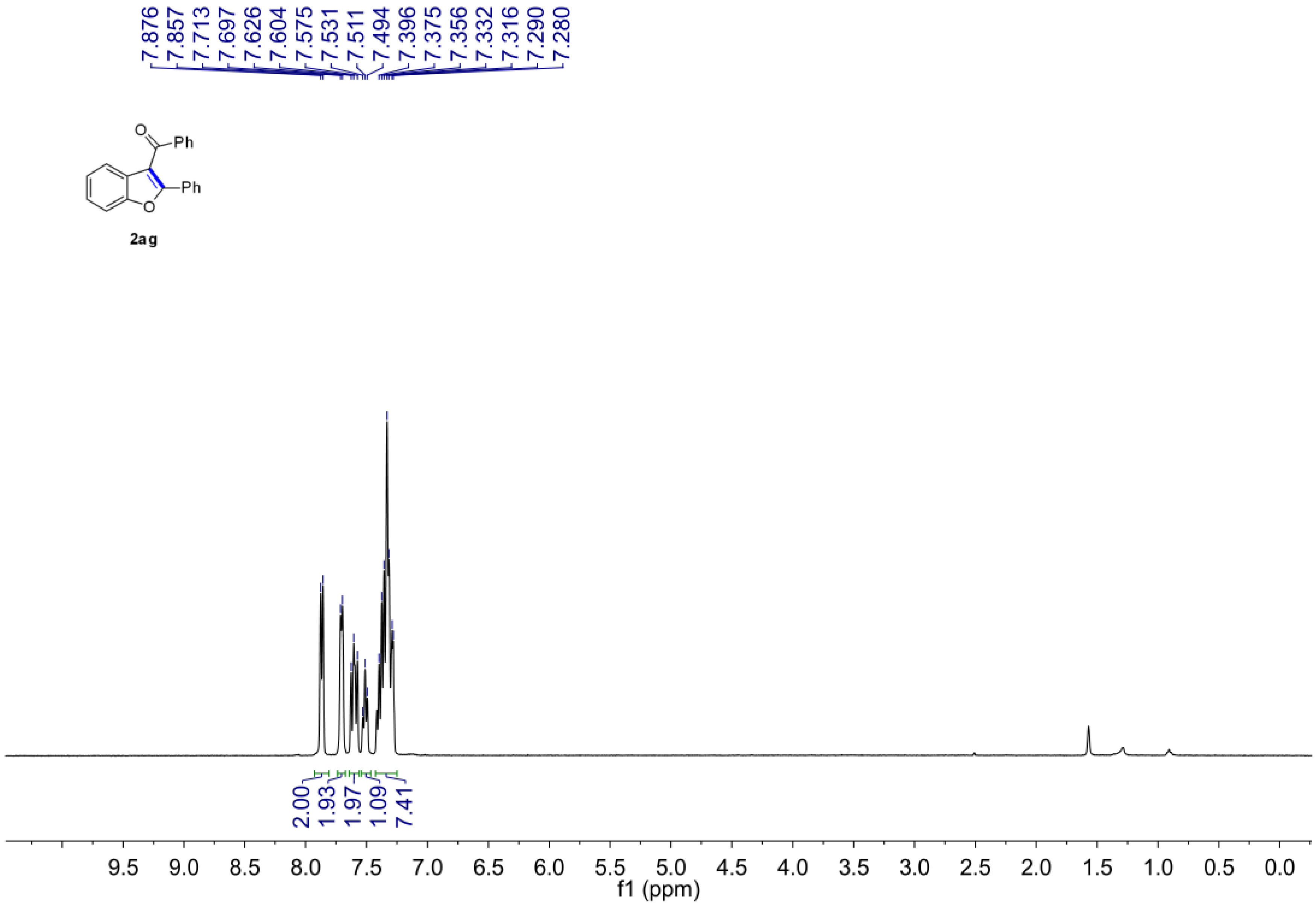
138.225
137.171
130.402
129.873
129.629
129.568
129.096
127.951
126.904
124.346
122.738
119.896
116.730
110.970
77.318
77.000
76.683
21.322
Me
Me
O
2af
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



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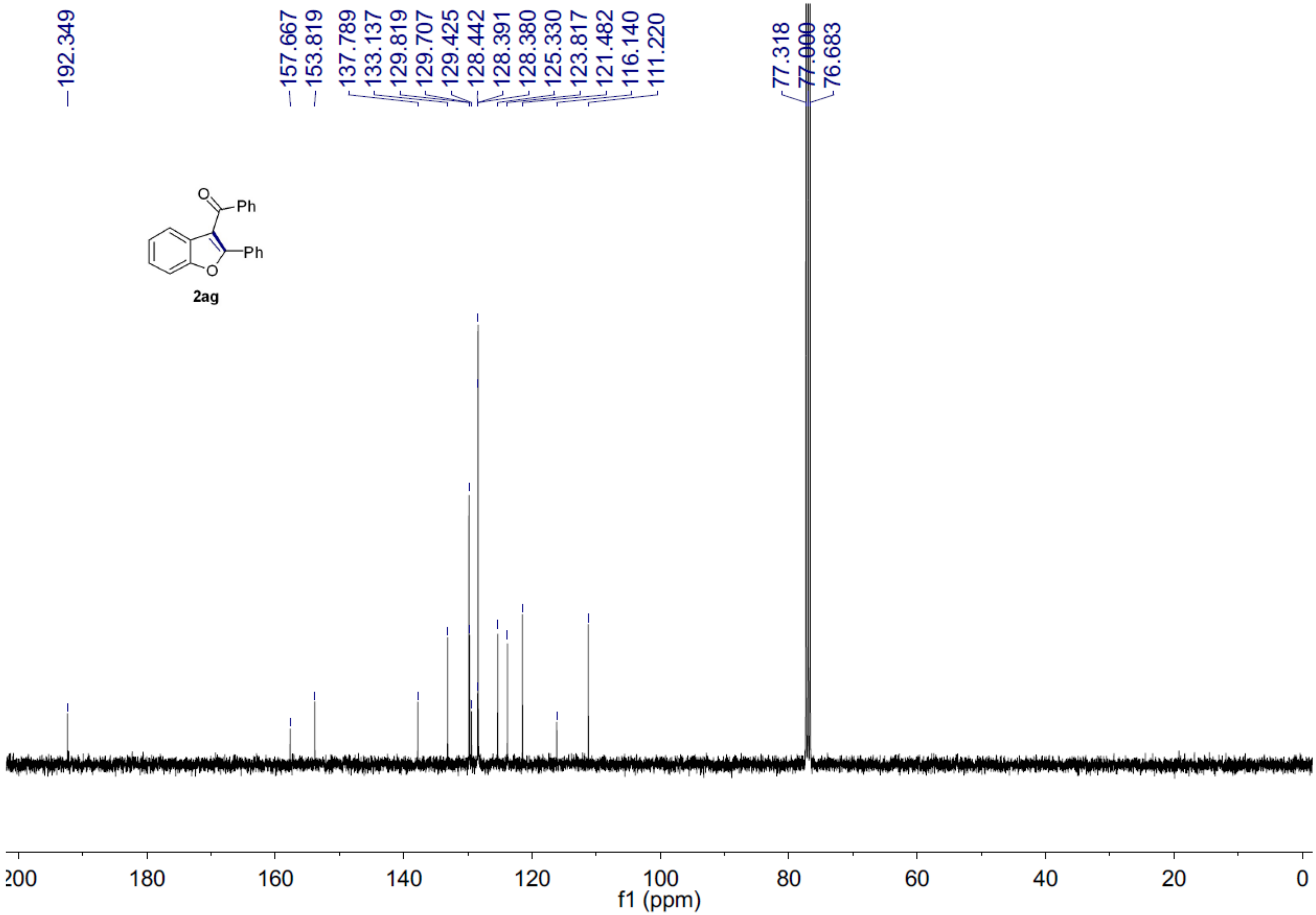
7.857
7.713
7.697
7.626
7.604
7.575
7.531
7.511
7.494
7.396
7.375
7.356
7.332
7.316
7.290
7.280
O
Ph
Ph
O
2ag
2.00
1.93
1.97
1.09
7.41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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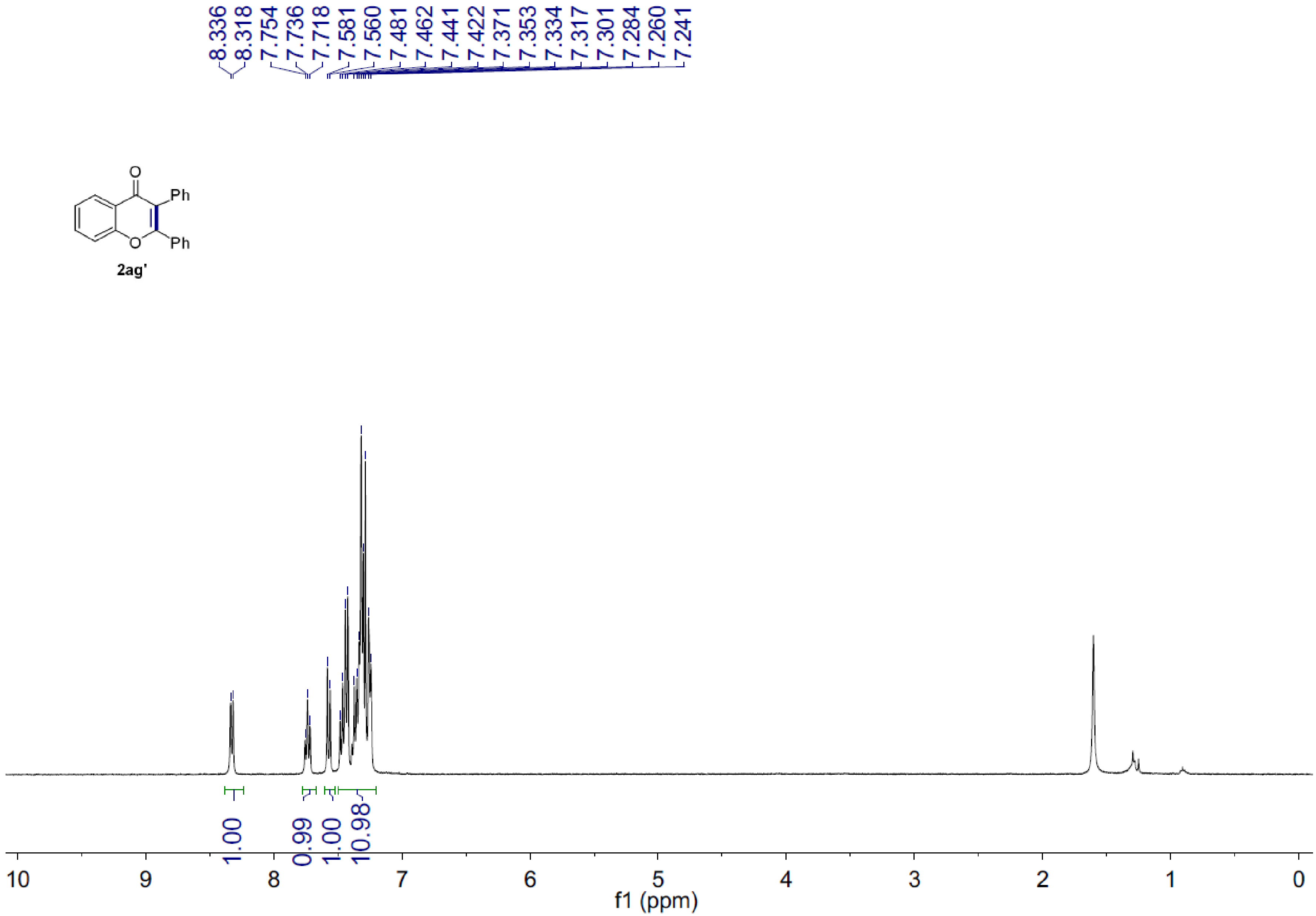
133.137
129.819
129.707
129.425
128.442
128.391
128.380
125.330
123.817
121.482
116.140
111.220
77.318
77.000
76.683
O
Ph
Ph
O
2ag
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



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8.318
7.754
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7.718
7.581
7.560
7.481
7.462
7.441
7.422
7.371
7.353
7.334
7.317
7.301
7.284
7.260
7.241
O
Ph
O
Ph
2ag'
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1.00
10.98
10
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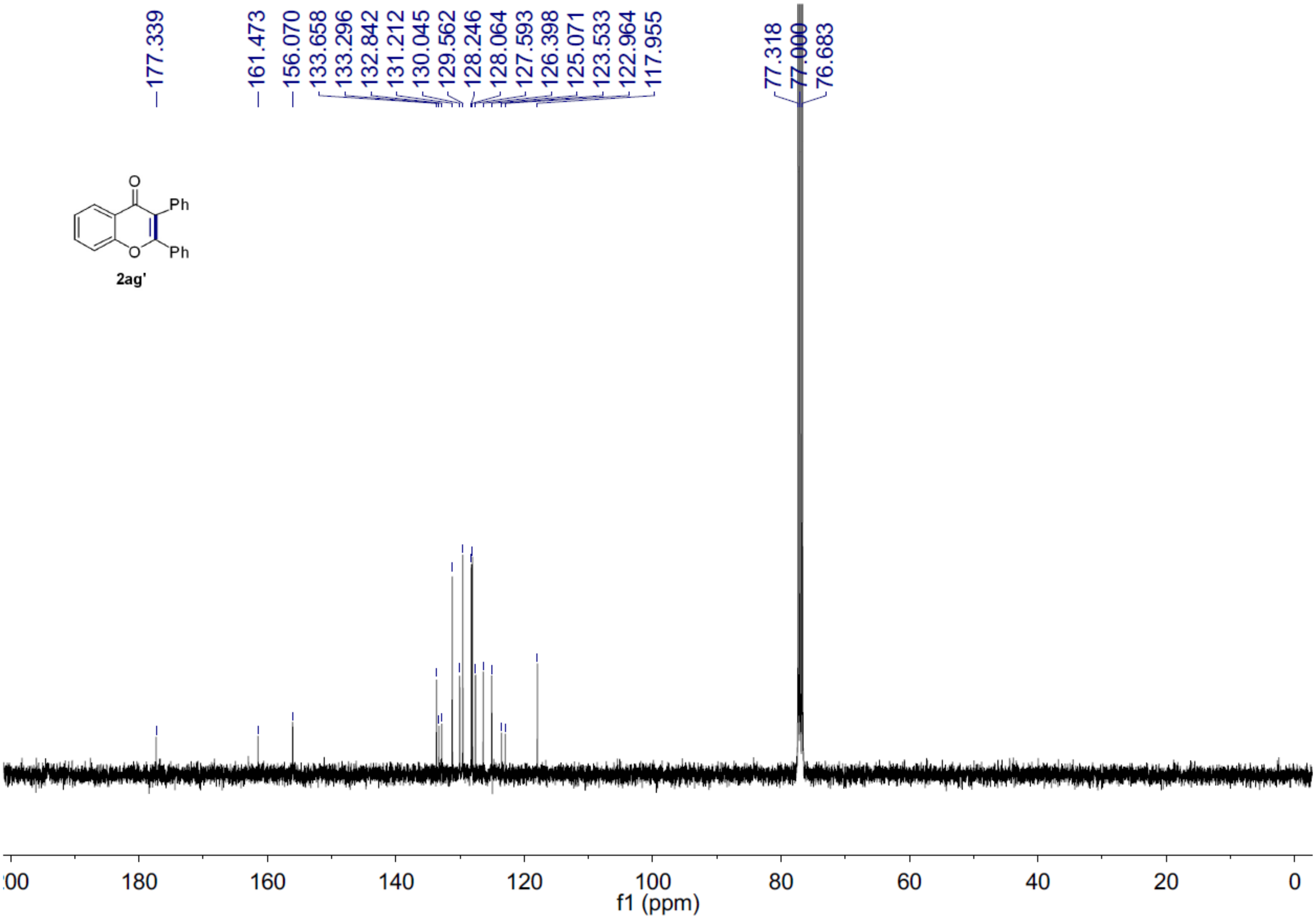
8
7
6
5
4
3
2
1
0
f1 (ppm)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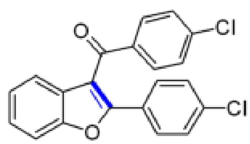
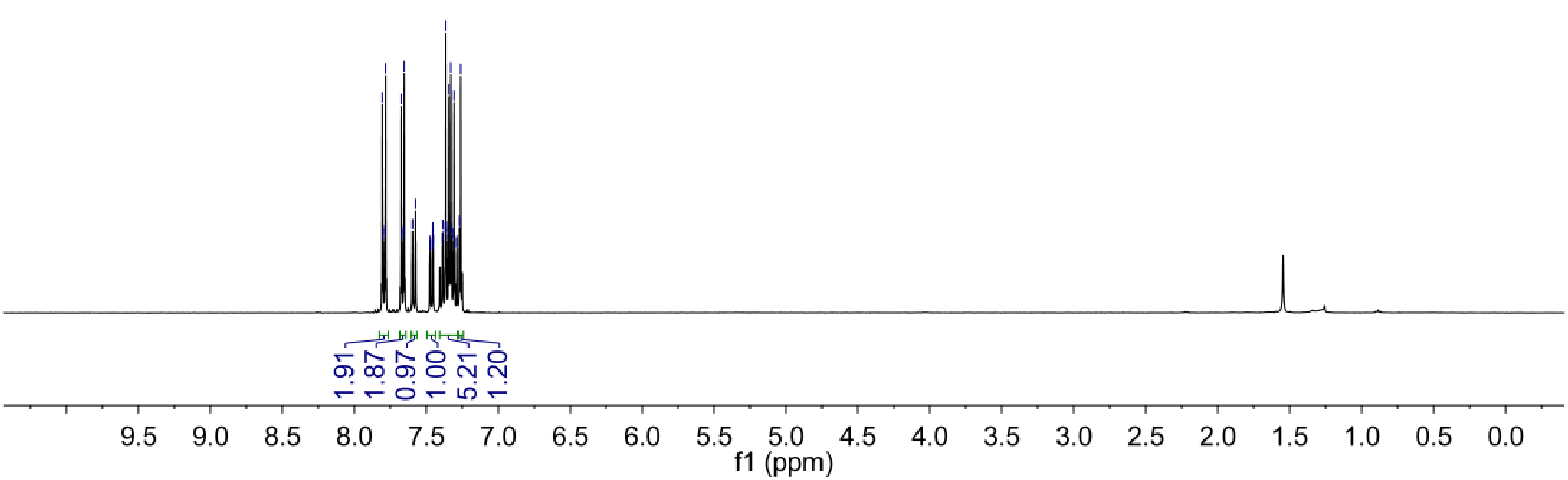
133.296
132.842
131.212
130.045
129.562
128.246
128.064
127.593
126.398
125.071
123.533
122.964
117.955
77.318
77.000
76.683
O
Ph
Ph
O
2ag'
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



O
Cl
Cl
O

2ah



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7.800
7.789
7.784
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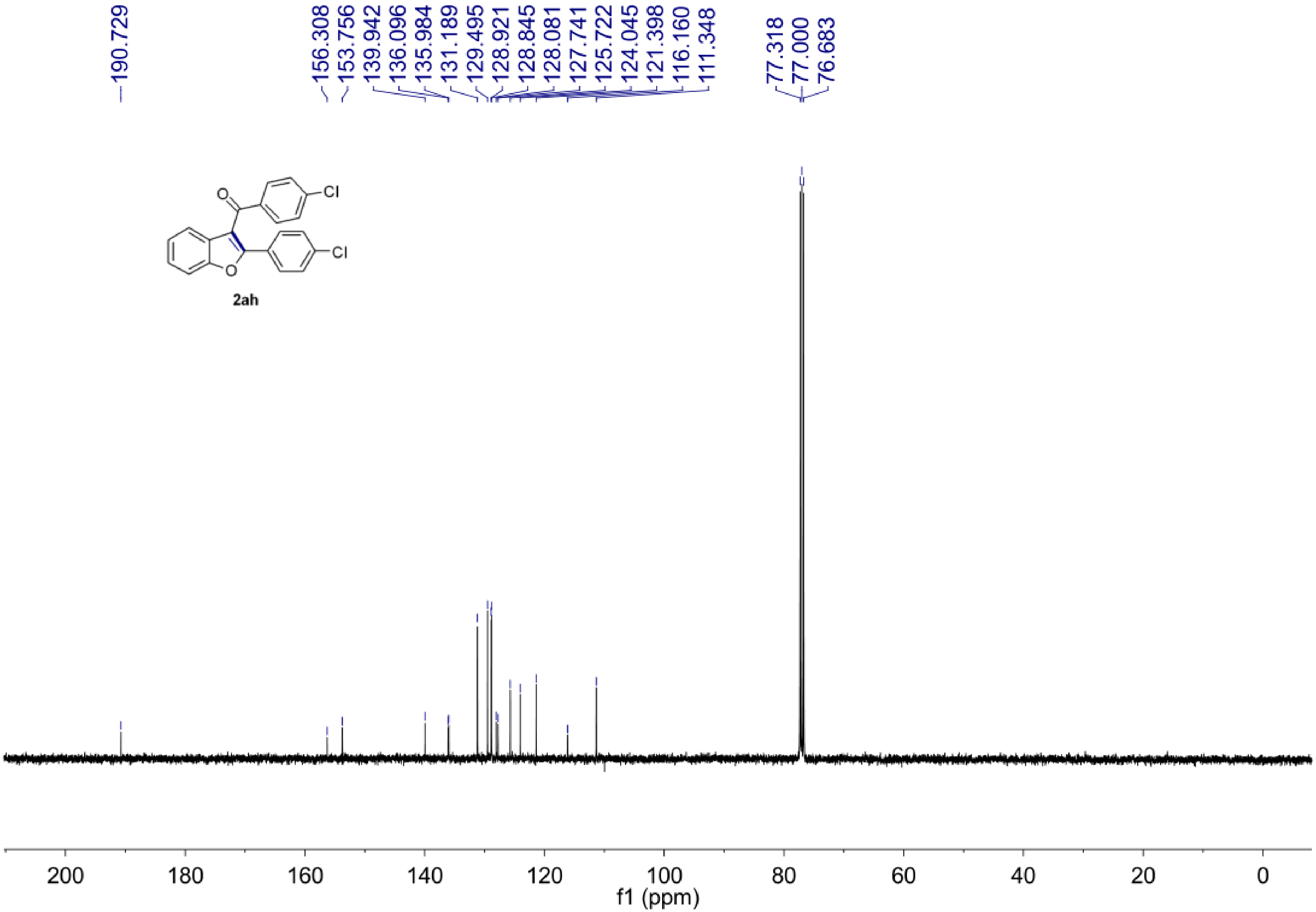
7.658
7.653
7.596
7.575
7.475
7.473
7.456
7.455
7.453
7.452
7.388
7.385
7.367
7.364
7.359
7.347
7.342
7.329
7.324
7.312
7.307
7.289
7.287
7.269
7.260
1.91
1.87
0.97
1.00
5.21
1.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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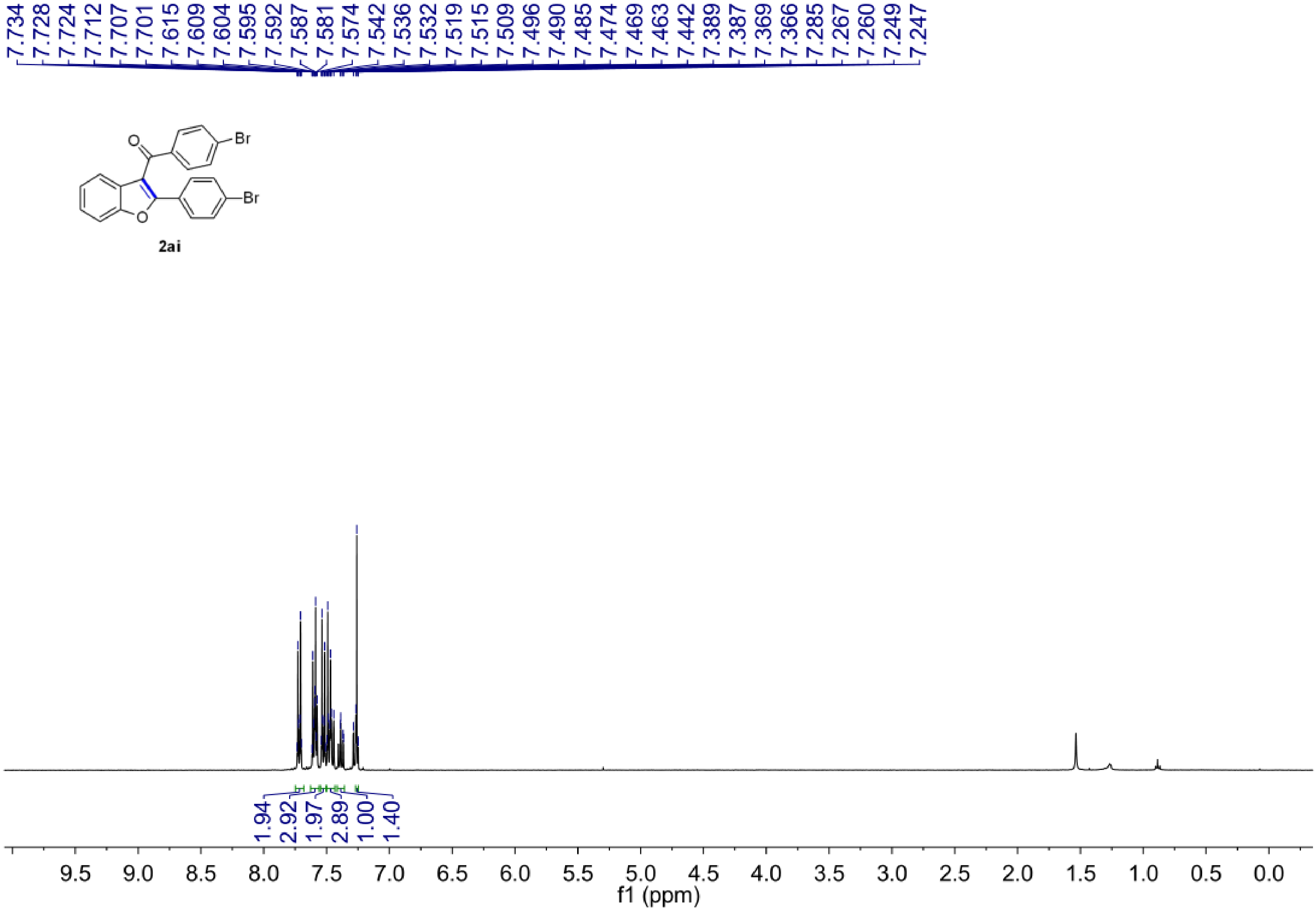
128.081
127.741
125.722
124.045
121.398
116.160
111.348
77.318
77.000
76.683
O
Cl
Cl
O
2ah
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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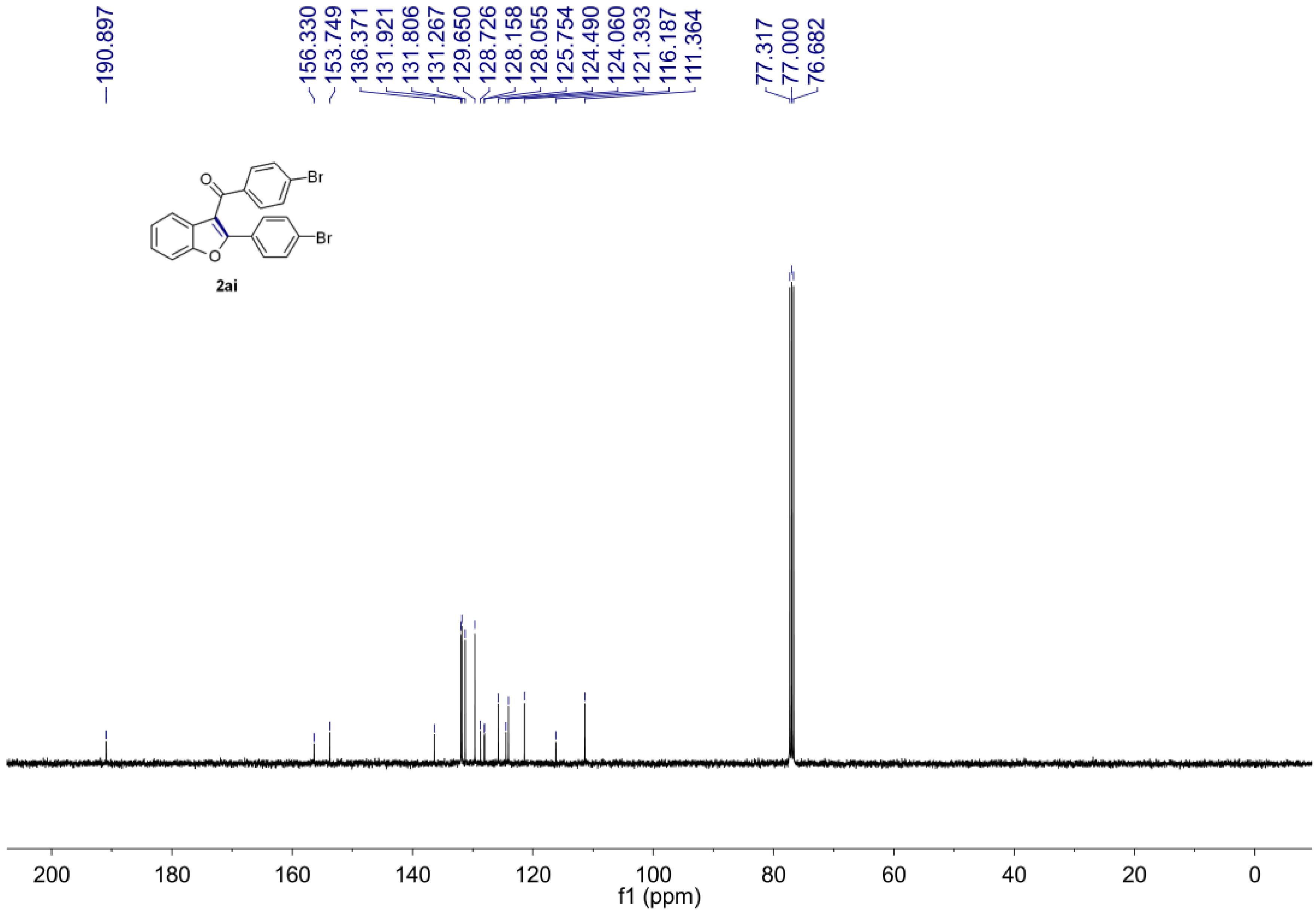
O
Br
Br
O
2ai
1.94 2.92 1.97 2.89 1.00 1.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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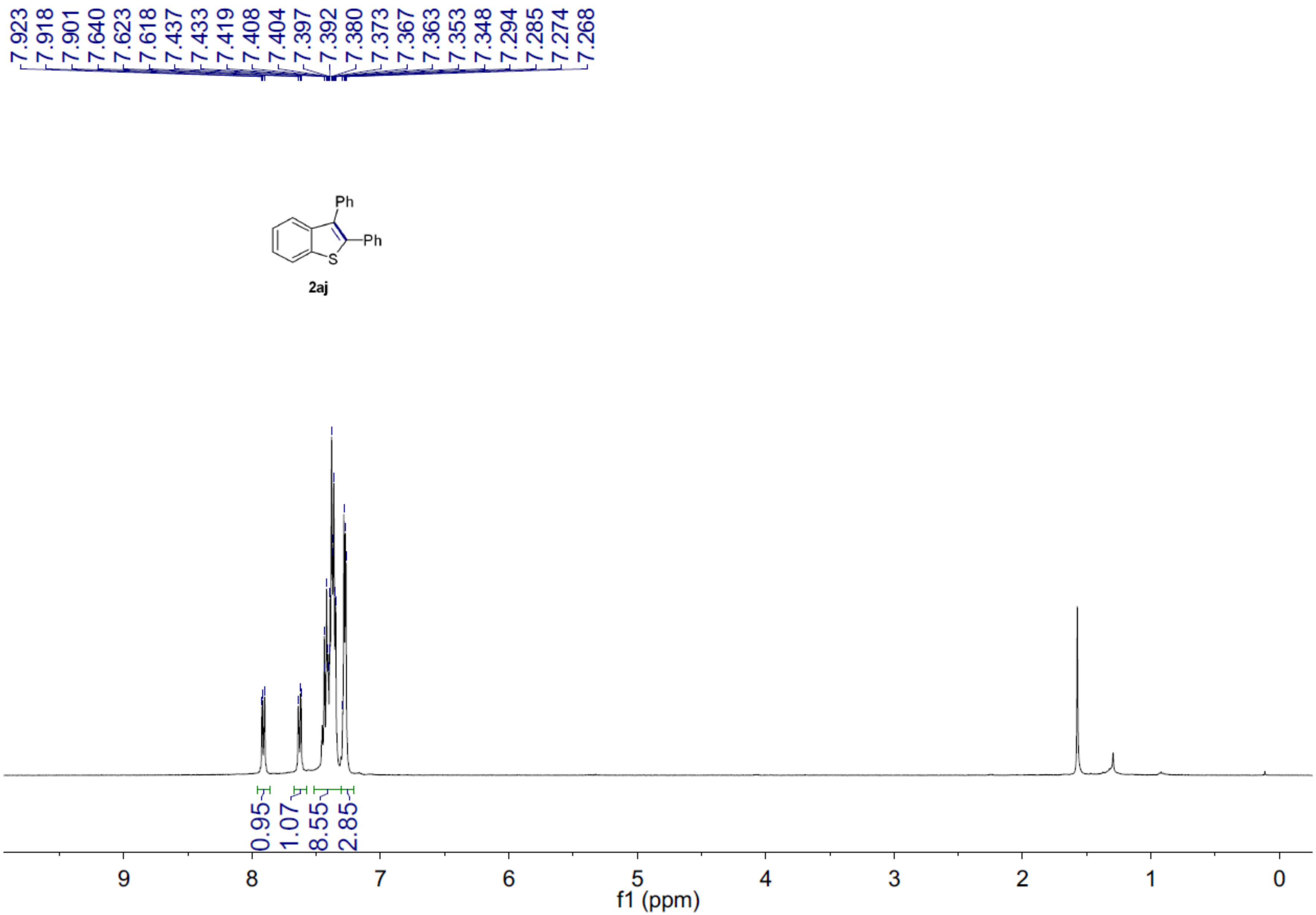
136.371
131.921
131.806
131.267
129.650
128.726
128.158
128.055
125.754
124.490
124.060
121.393
116.187
111.364
77.317
77.000
76.682
O
Br
Br
O
2ai
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Ph
Ph
S
2aj
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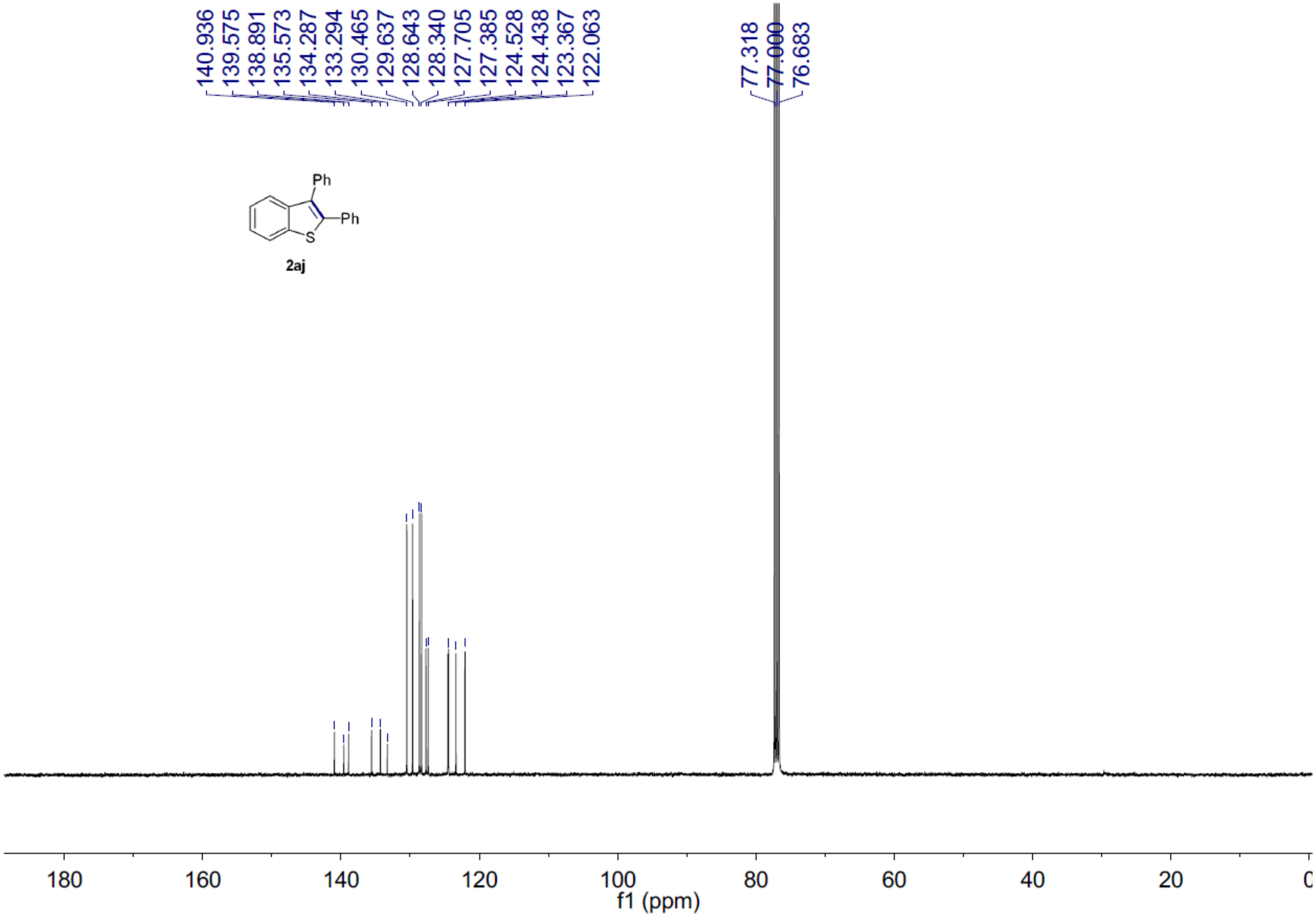
2.85
9 8 7 6 5 4 3 2 1 0
f1 (ppm)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129.637
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128.340
127.705
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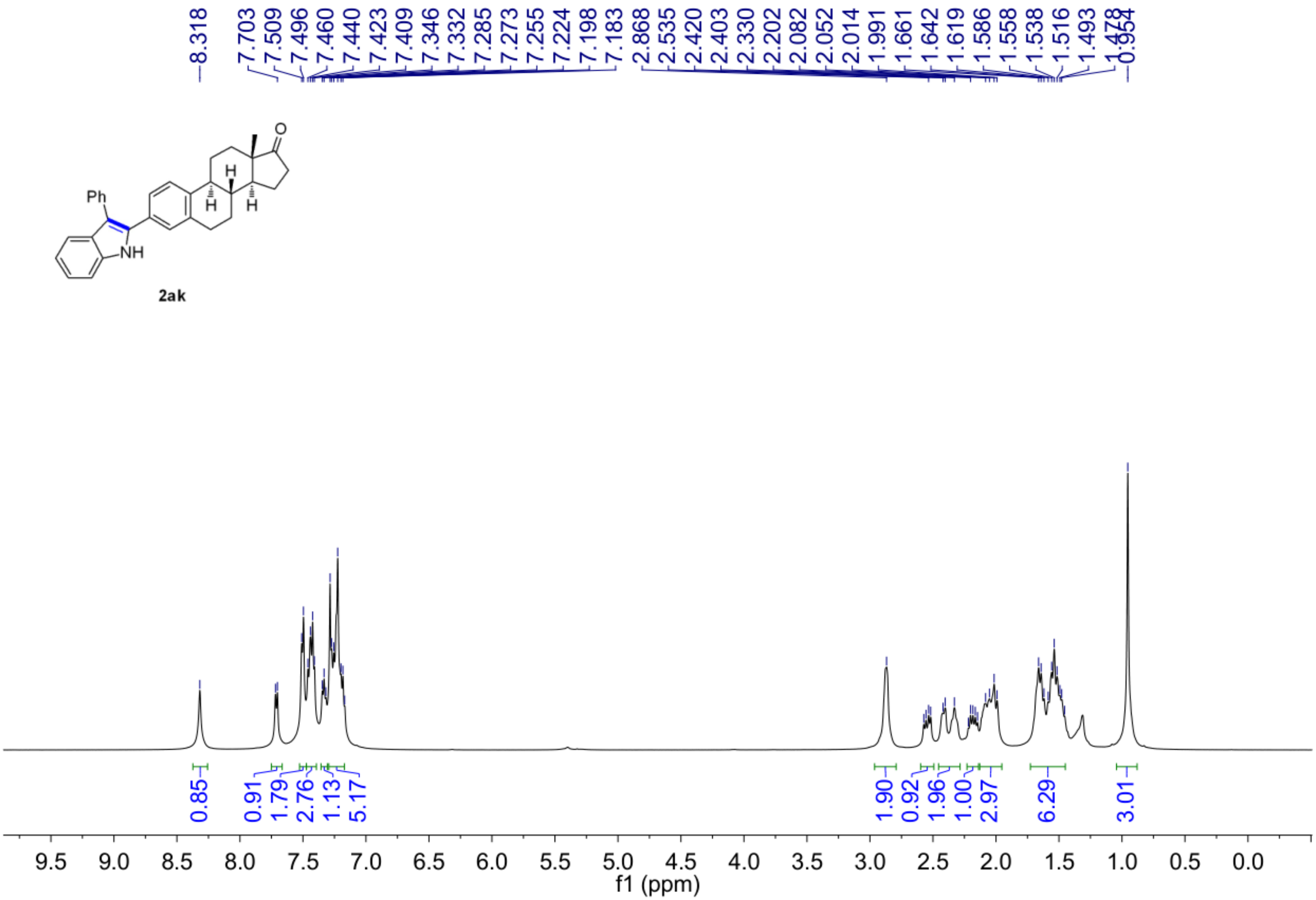
124.528
124.438
123.367
122.063
77.318
77.000
76.683
Ph
Ph
S
2aj
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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H
H
O
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7.460
7.440
7.423
7.409
7.346
7.332
7.285
7.273
7.255
7.224
7.198
7.183
2.868
2.535
2.420
2.403
2.330
2.202
2.082
2.052
2.014
1.991
1.661
1.642
1.619
1.586
1.558
1.538
1.516
1.493
1.478
0.954
0.85
0.91
1.79
2.76
1.13
5.17
1.90
0.92
1.96
1.00
2.97
6.29
3.01
9.5
9.0
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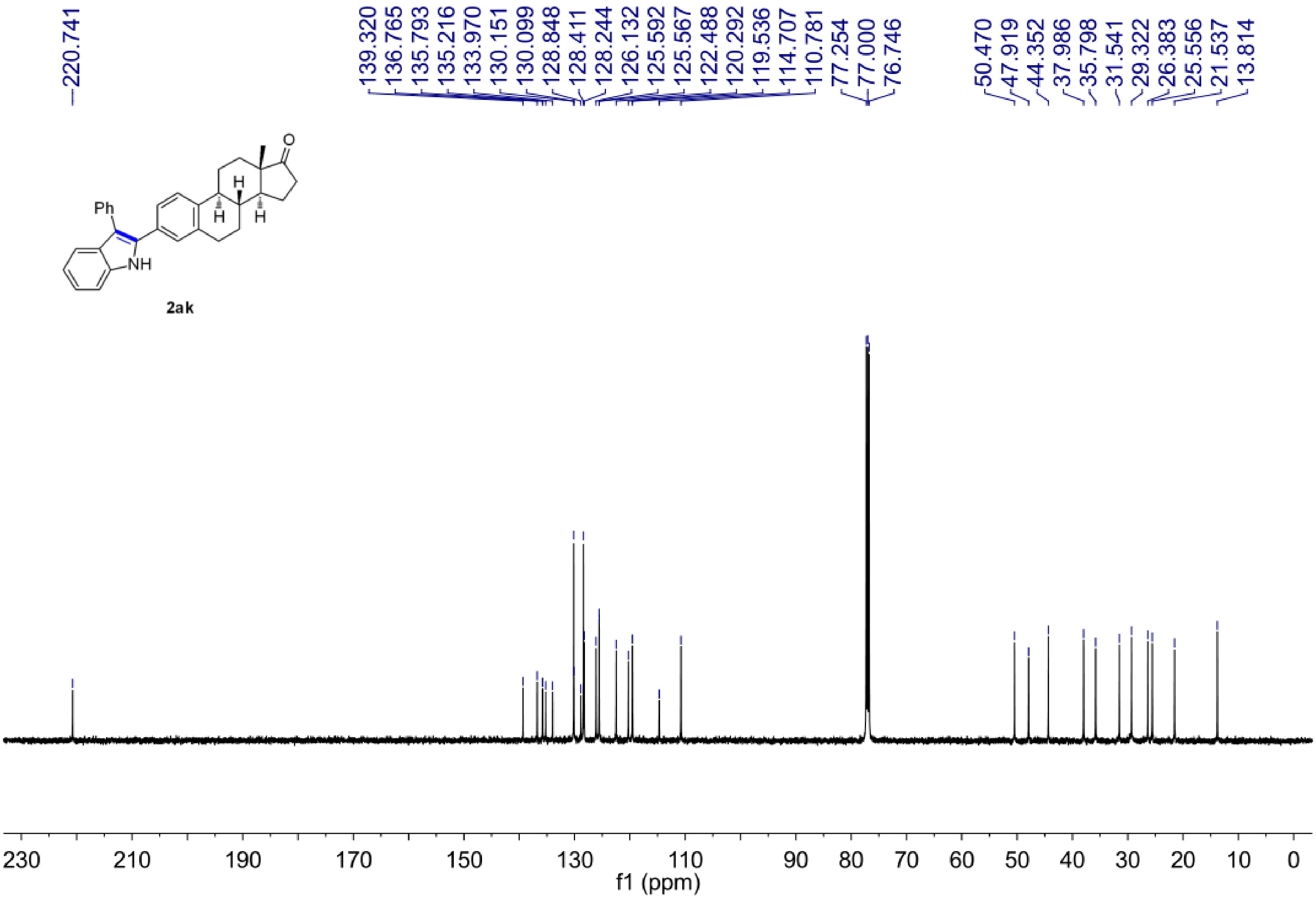
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2ak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130.099
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128.411
128.244
126.132
125.592
125.567
122.488
120.292
119.536
114.707
110.781
77.254
77.000
76.746
50.470
47.919
44.352
37.986
35.798
31.541
29.322
26.383
25.556
21.537
13.814
Ph
NH
H
H
H
O
2ak
230
210
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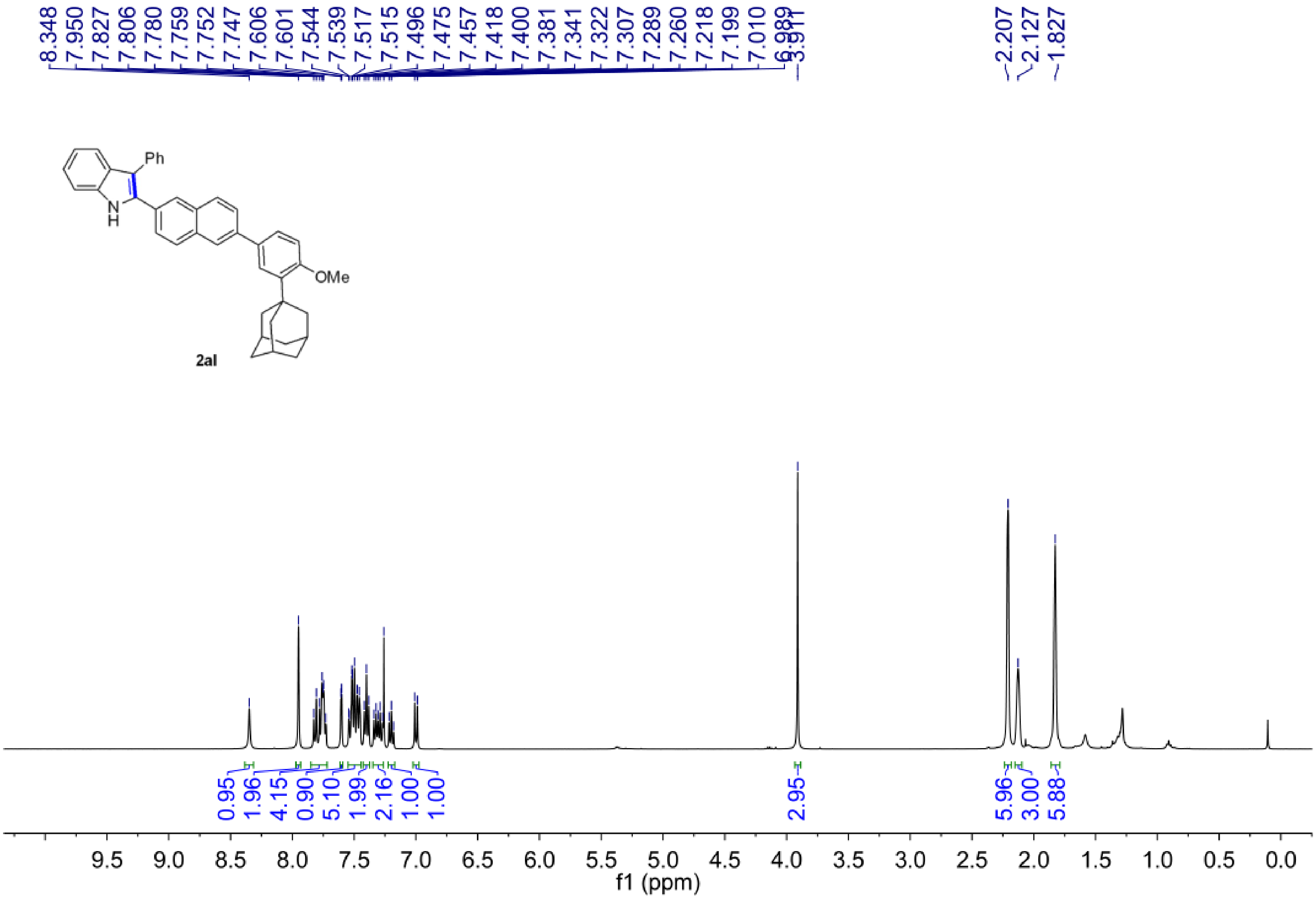
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.759
7.752
7.747
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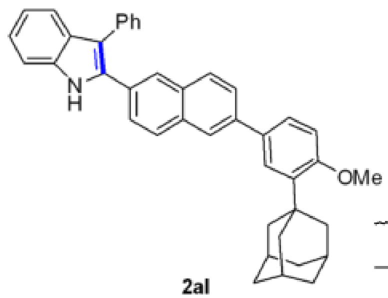
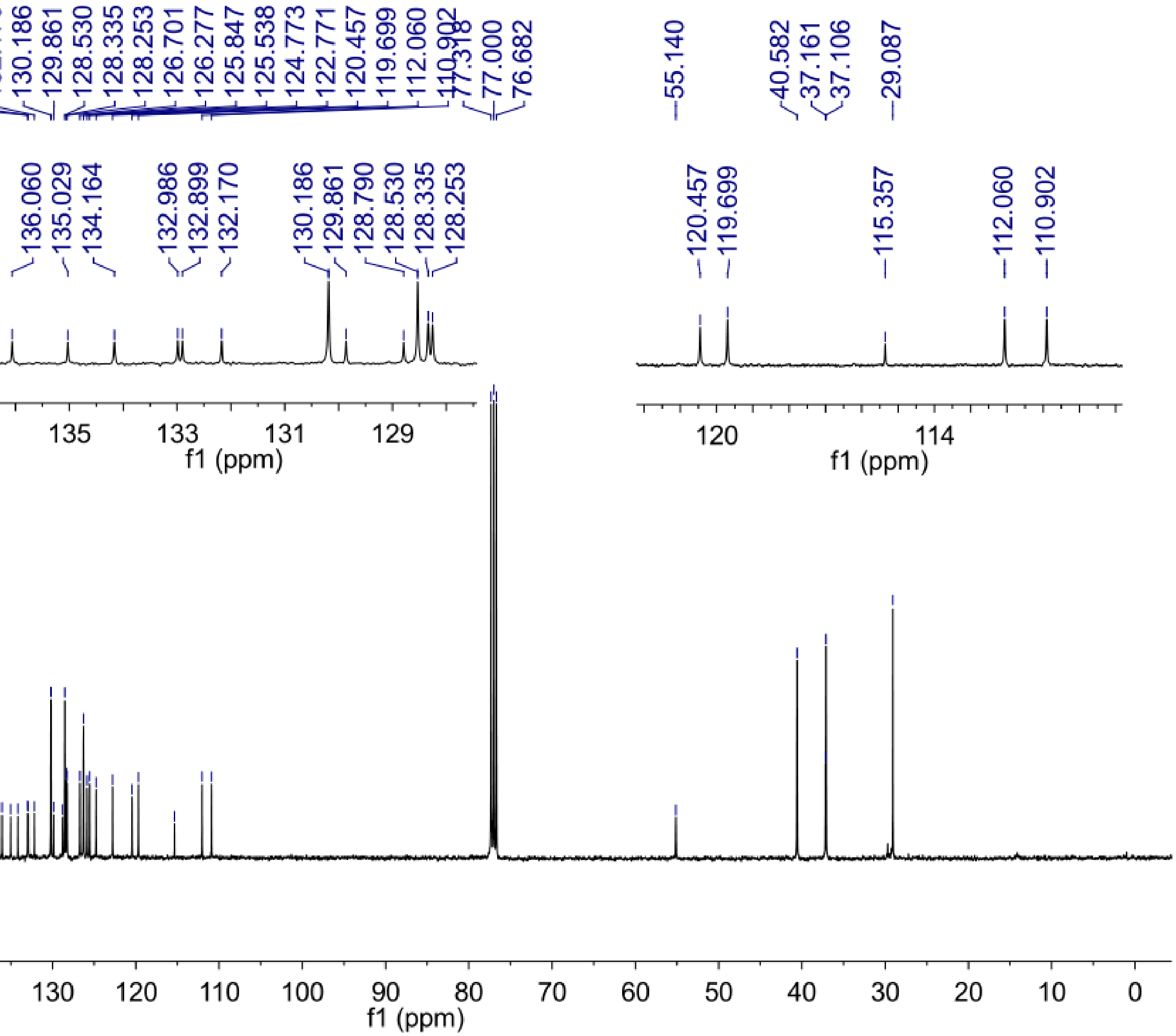
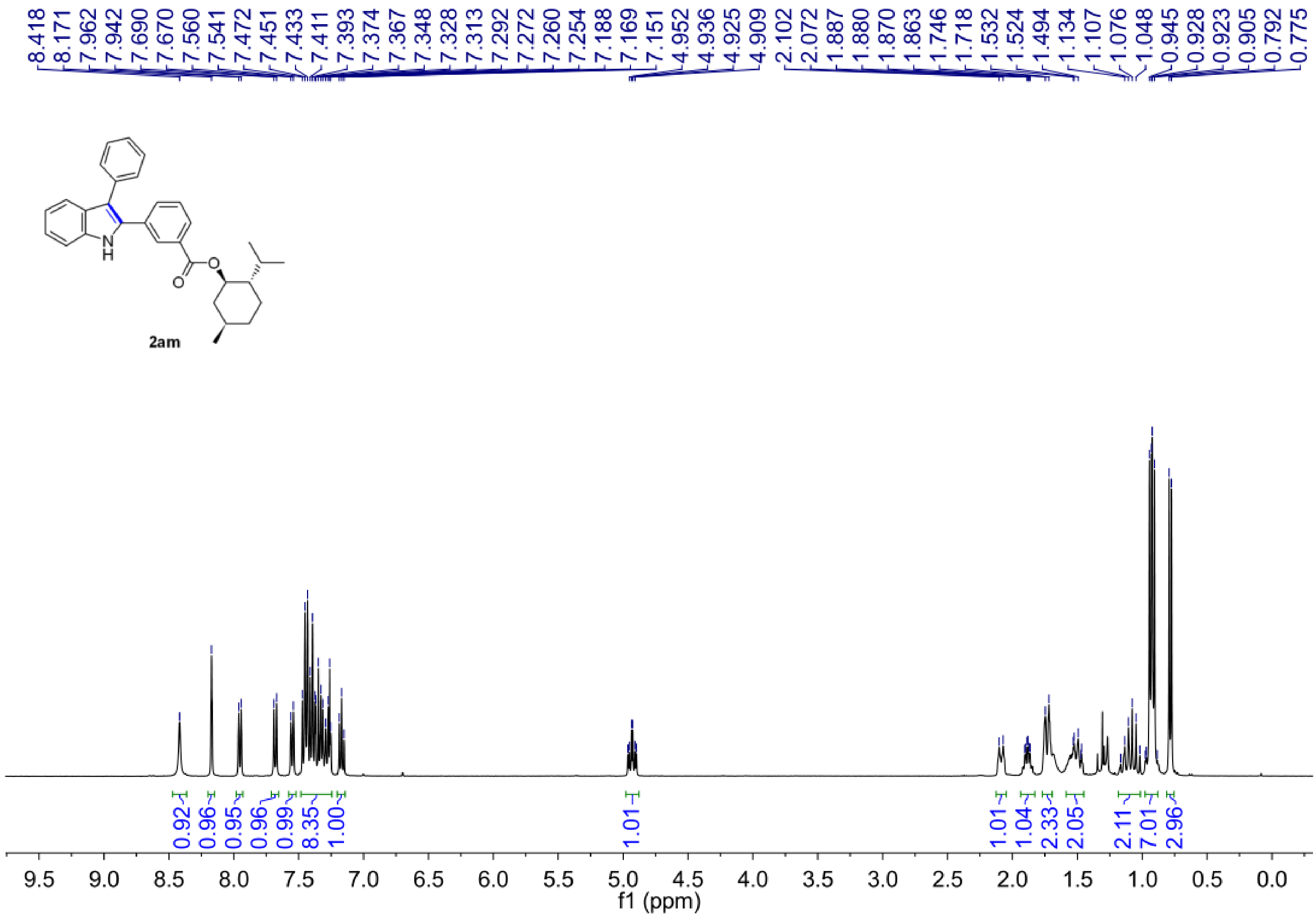
7.601
7.544
7.539
7.517
7.515
7.496
7.475
7.457
7.418
7.400
7.381
7.341
7.322
7.307
7.289
7.260
7.218
7.199
7.010
6.989
3.911
2.207
2.127
1.827
Ph
N
H
OMe
2al
0.95
1.96
4.15
0.90
5.10
1.99
2.16
1.00
1.00
2.95
5.96
3.00
5.88
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

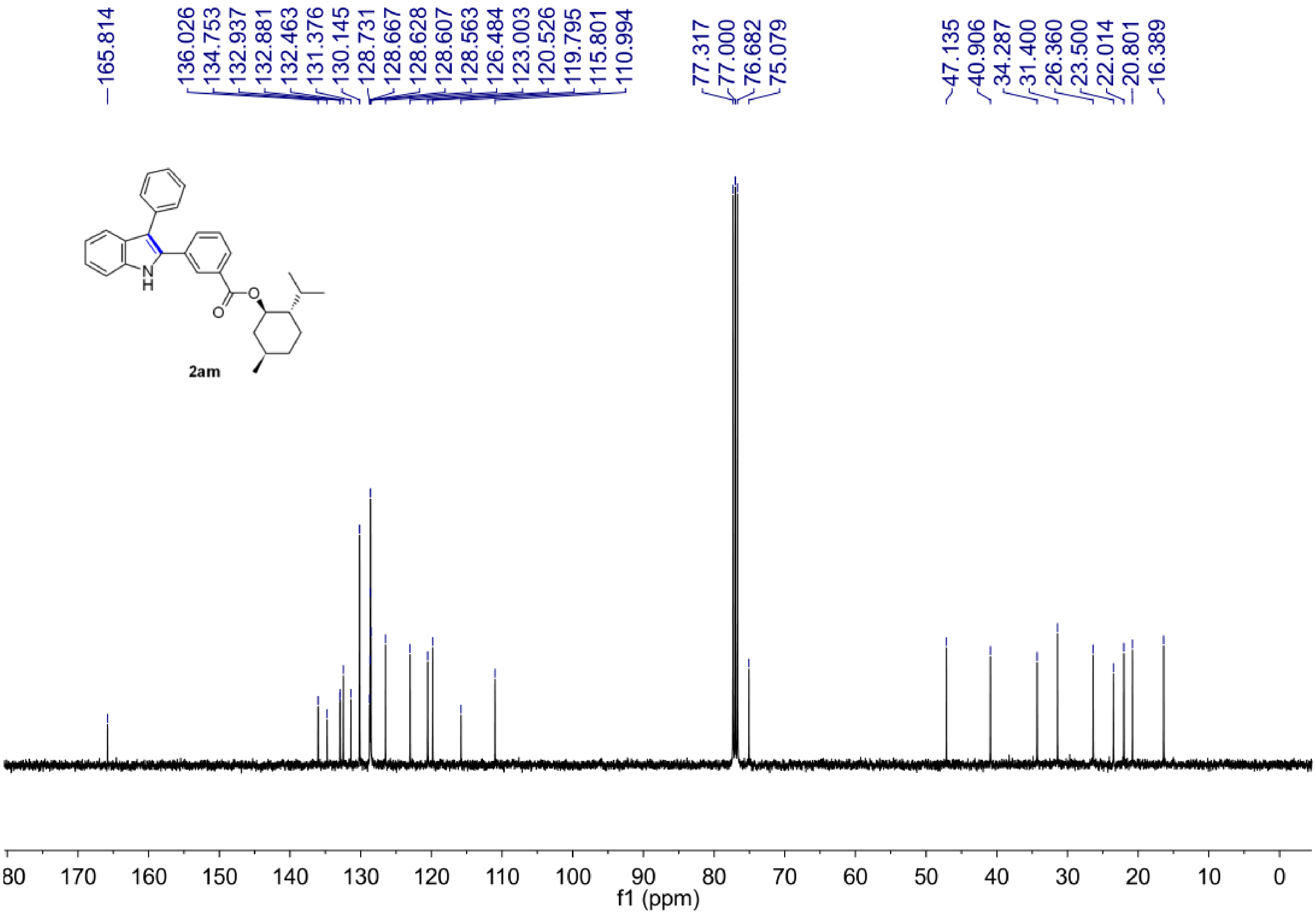


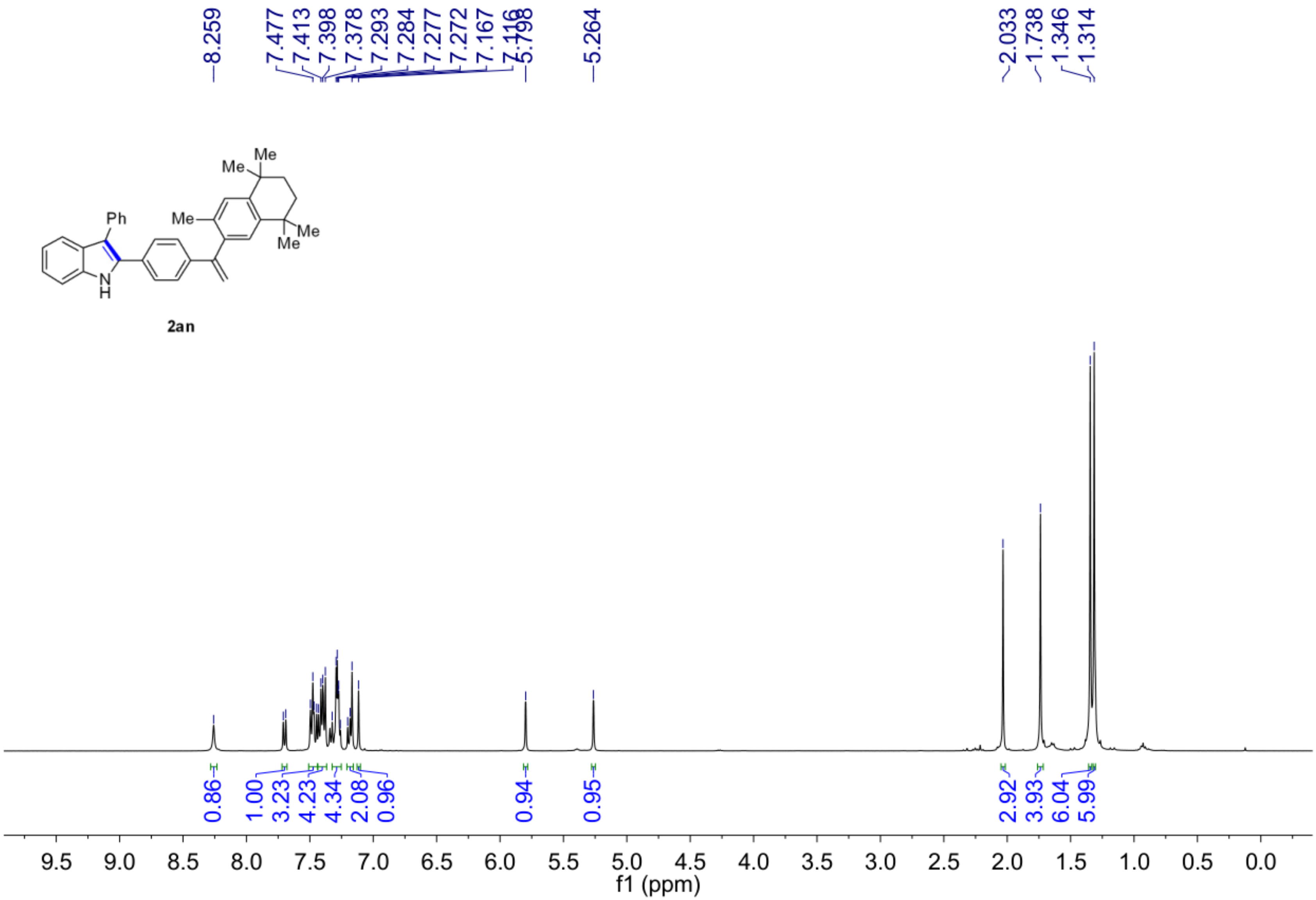
2al



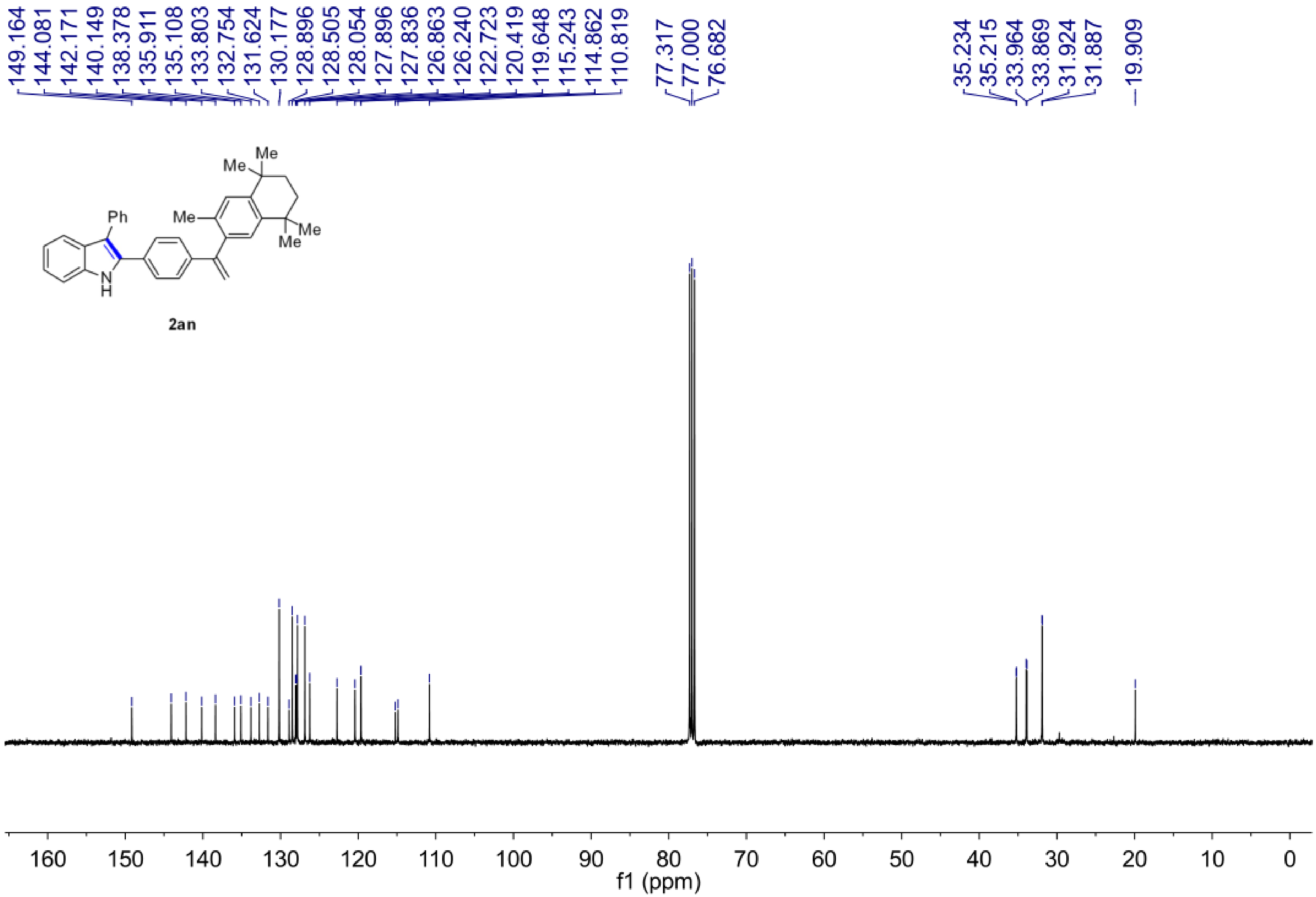
158.624
139.437
138.880
132.986
132.899
132.170
130.186
129.861
128.530
128.335
128.253
126.701
126.277
125.847
125.538
124.773
122.771
120.457
119.699
112.060
110.902
77.318
77.000
76.682
55.140
40.582
37.161
37.106
29.087
136.060
135.029
134.164
132.986
132.899
132.170
130.186
129.861
128.790
128.530
128.335
128.253
135
133
131
129
f1 (ppm)
120.457
119.699
115.357
112.060
110.902
120
114
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

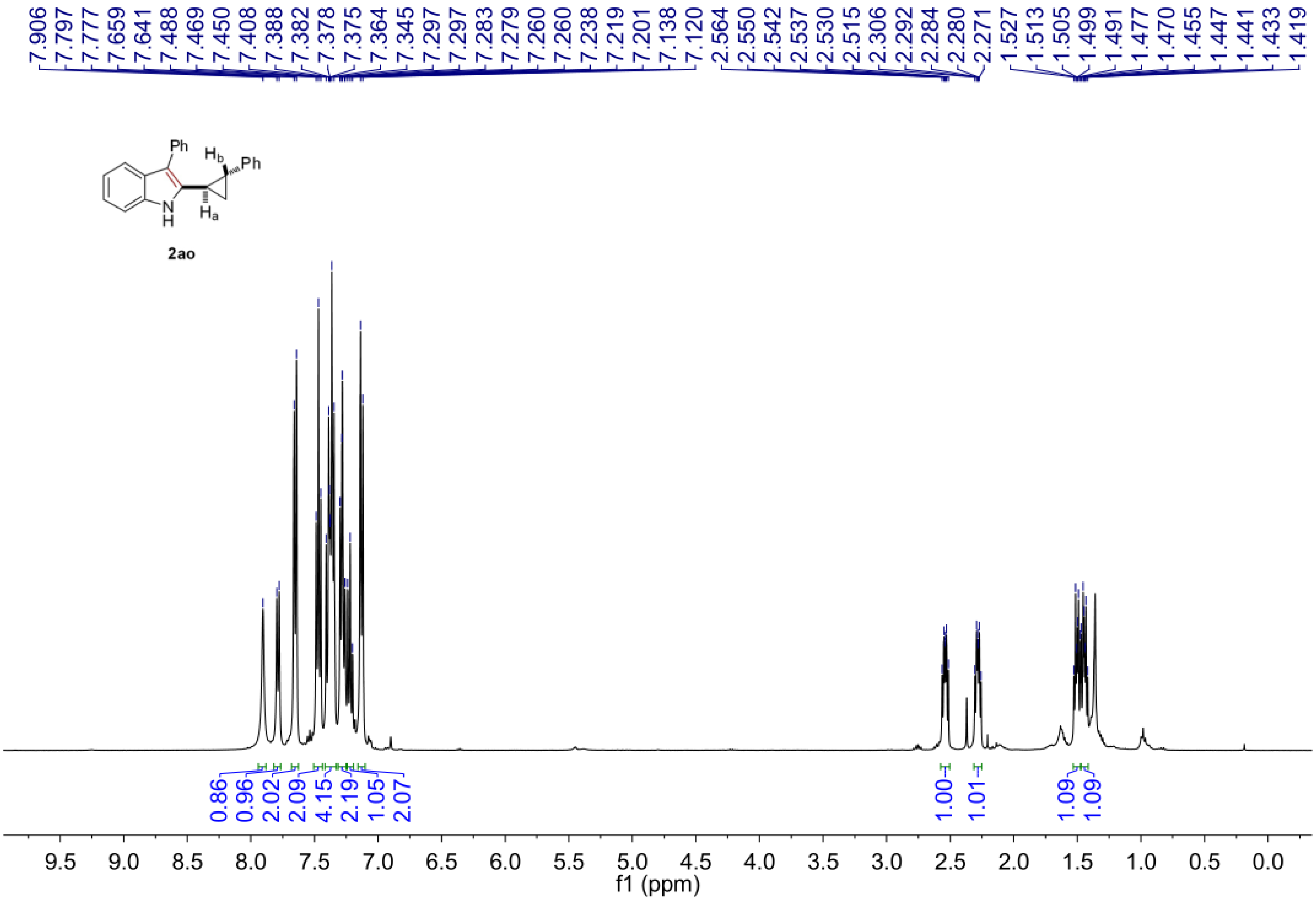

8.418 8.171 7.962 7.942 7.690 7.670 7.560 7.541 7.472 7.451 7.433 7.411 7.393 7.374 7.367 7.348 7.328 7.313 7.292 7.272 7.260 7.254 7.188 7.169 7.151 4.952 4.936 4.925 4.909 2.102 2.072 1.887 1.880 1.870 1.863 1.746 1.718 1.532 1.524 1.494 1.134 1.107 1.076 1.048 0.945 0.928 0.923 0.905 0.792 0.775
2am
0.92 0.96 0.95 0.96 0.99 8.35 1.00 1.01 1.01 1.04 2.33 2.05 2.11 7.01 2.96
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)

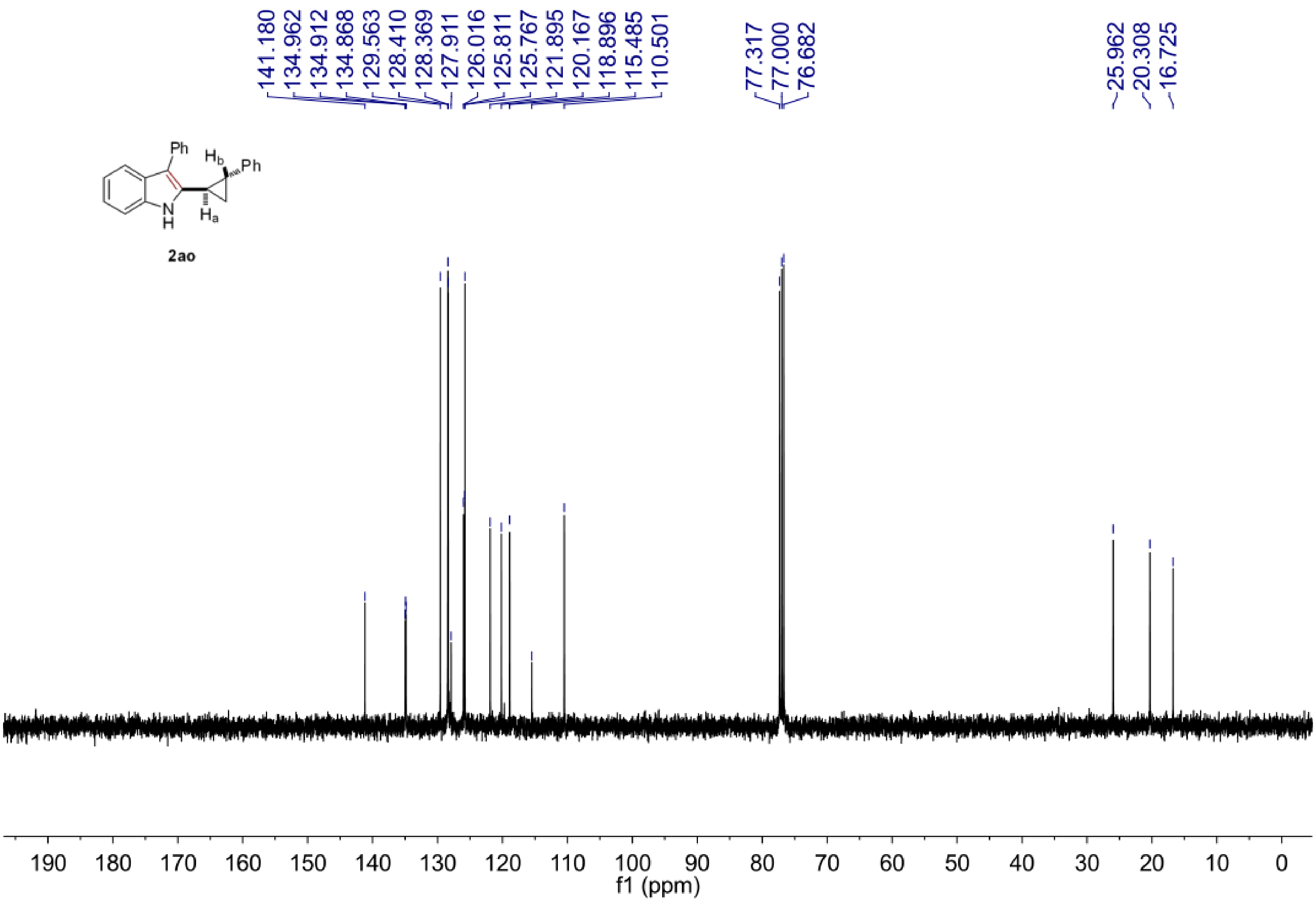

165.814
136.026
134.753
132.937
132.881
132.463
131.376
130.145
128.731
128.667
128.628
128.607
128.563
126.484
123.003
120.526
119.795
115.801
110.994
77.317
77.000
76.682
75.079
47.135
40.906
34.287
31.400
26.360
23.500
22.014
20.801
16.389
2am
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



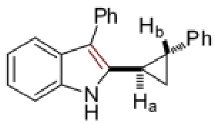
8.259
7.477
7.413
7.398
7.378
7.293
7.284
7.277
7.272
7.167
7.116
5.798
5.264
2.033
1.738
1.346
1.314
Ph
Me
N
H
2an
0.86
1.00
3.23
4.23
4.34
2.08
0.96
0.94
0.95
2.92
3.93
6.04
5.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.164
144.081
142.171
140.149
138.378
135.911
135.108
133.803
132.754
131.624
130.177
128.896
128.505
128.054
127.896
127.836
126.863
126.240
122.723
120.419
119.648
115.243
114.862
110.819
77.317
77.000
76.682
35.234
35.215
33.964
33.869
31.924
31.887
19.909
Ph
N
H
Me
Me
Me
Me
Me
2an
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

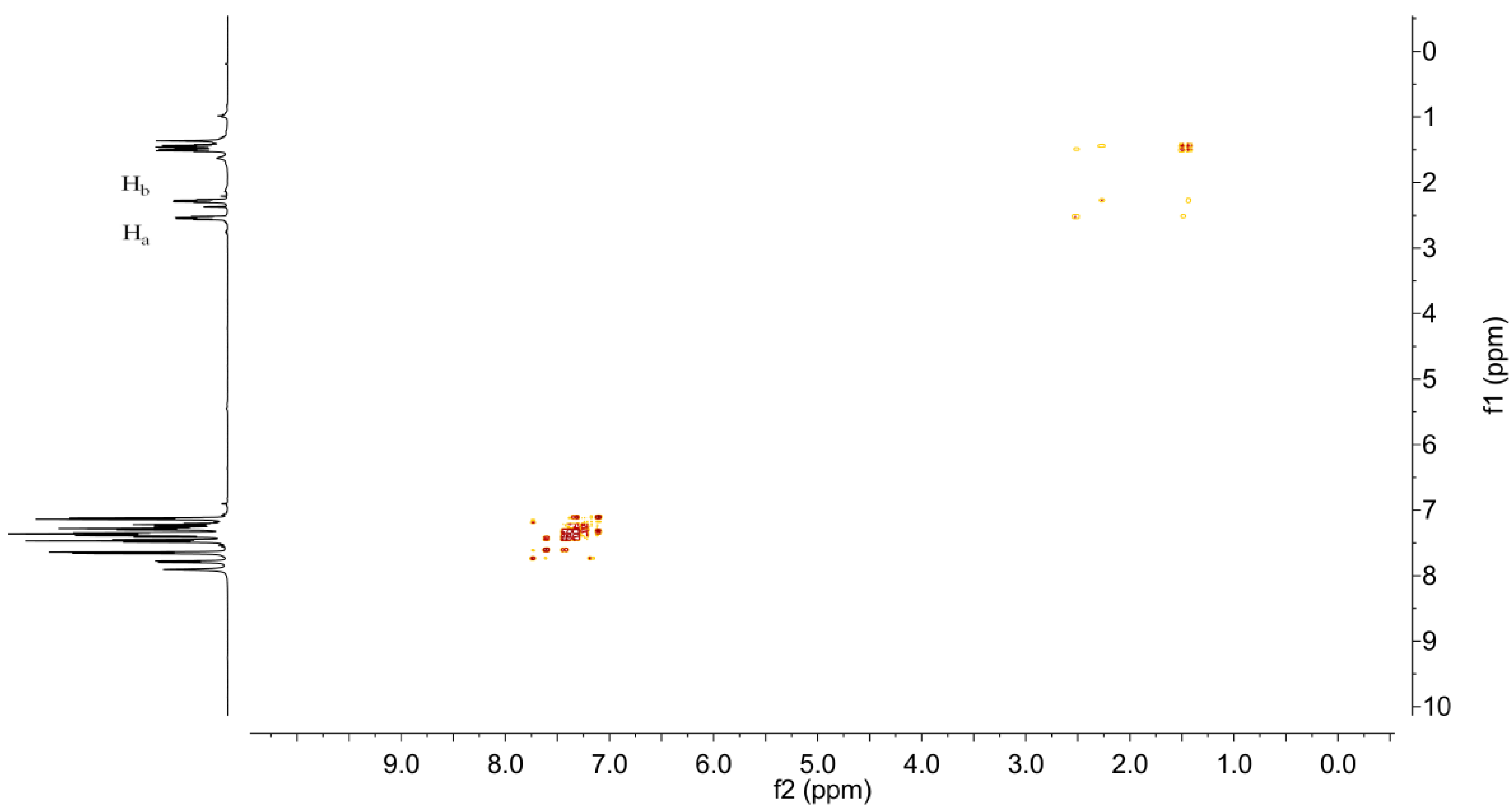

7.906 7.797 7.777 7.659 7.641 7.488 7.469 7.450 7.408 7.388 7.382 7.378 7.375 7.364 7.345 7.297 7.297 7.283 7.279 7.260 7.260 7.238 7.219 7.201 7.138 7.120
2.564 2.550 2.542 2.537 2.530 2.515 2.306 2.292 2.284 2.280 2.271
1.527 1.513 1.505 1.499 1.491 1.477 1.470 1.455 1.447 1.441 1.433 1.419
Ph
Hb
Ph
N
H
Ha
2ao
0.86 0.96 2.02 2.09 4.15 2.19 1.05 2.07
1.00 1.01
1.09 1.09
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)


141.180
134.962
134.912
134.868
129.563
128.410
128.369
127.911
126.016
125.811
125.767
121.895
120.167
118.896
115.485
110.501
77.317
77.000
76.682
25.962
20.308
16.725
Ph
H
b
Ph
N
H
H
a
2ao
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

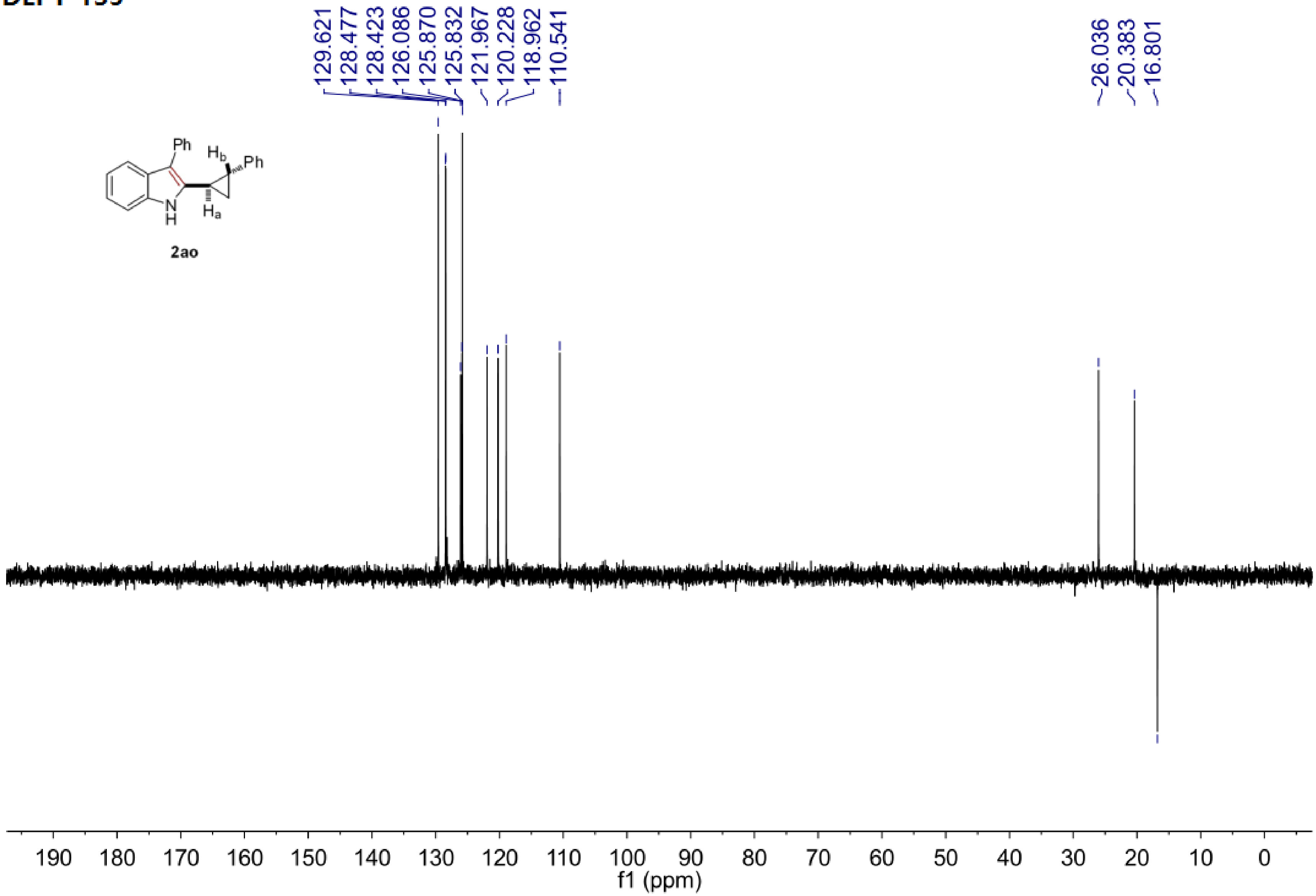
COSY



2ao

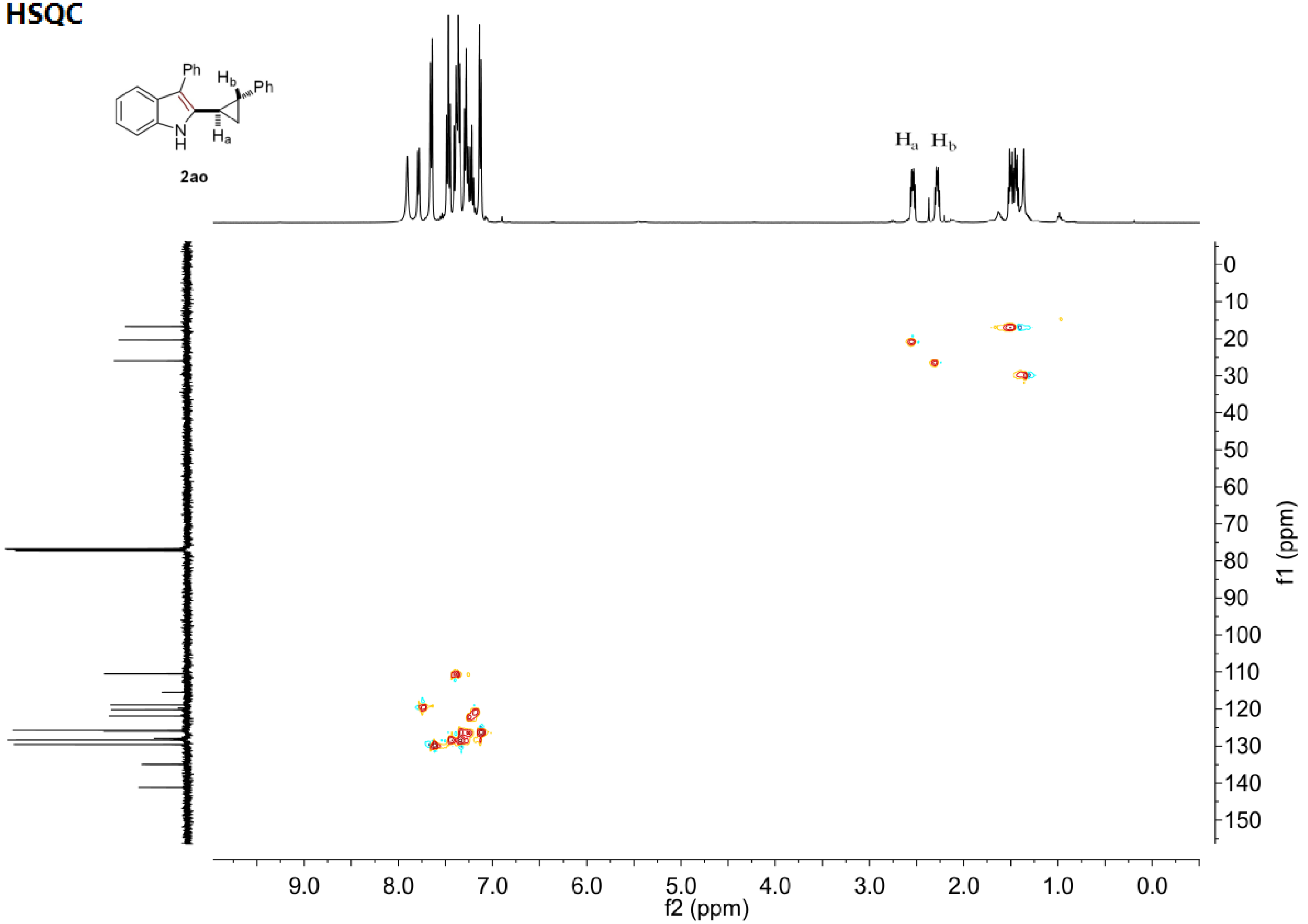

Ha
Hb
Hb
Ha
0
1
2
3
4
5
6
7
8
9
10
f1 (ppm)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)

DEPT-135

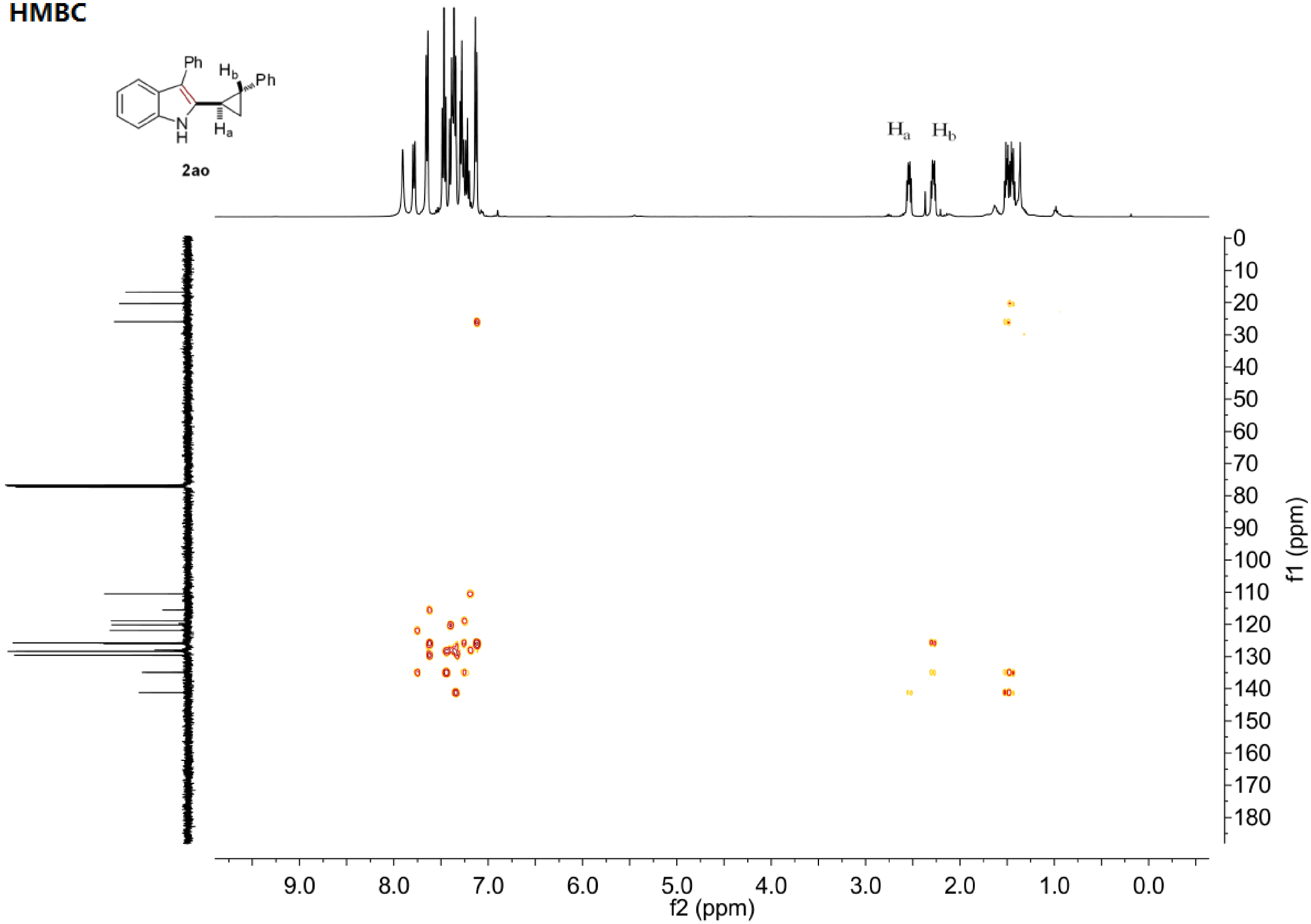


Ph
Hb
Ph
N
H
Ha
2ao
129.621
128.477
128.423
126.086
125.870
125.832
121.967
120.228
118.962
110.541
26.036
20.383
16.801
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

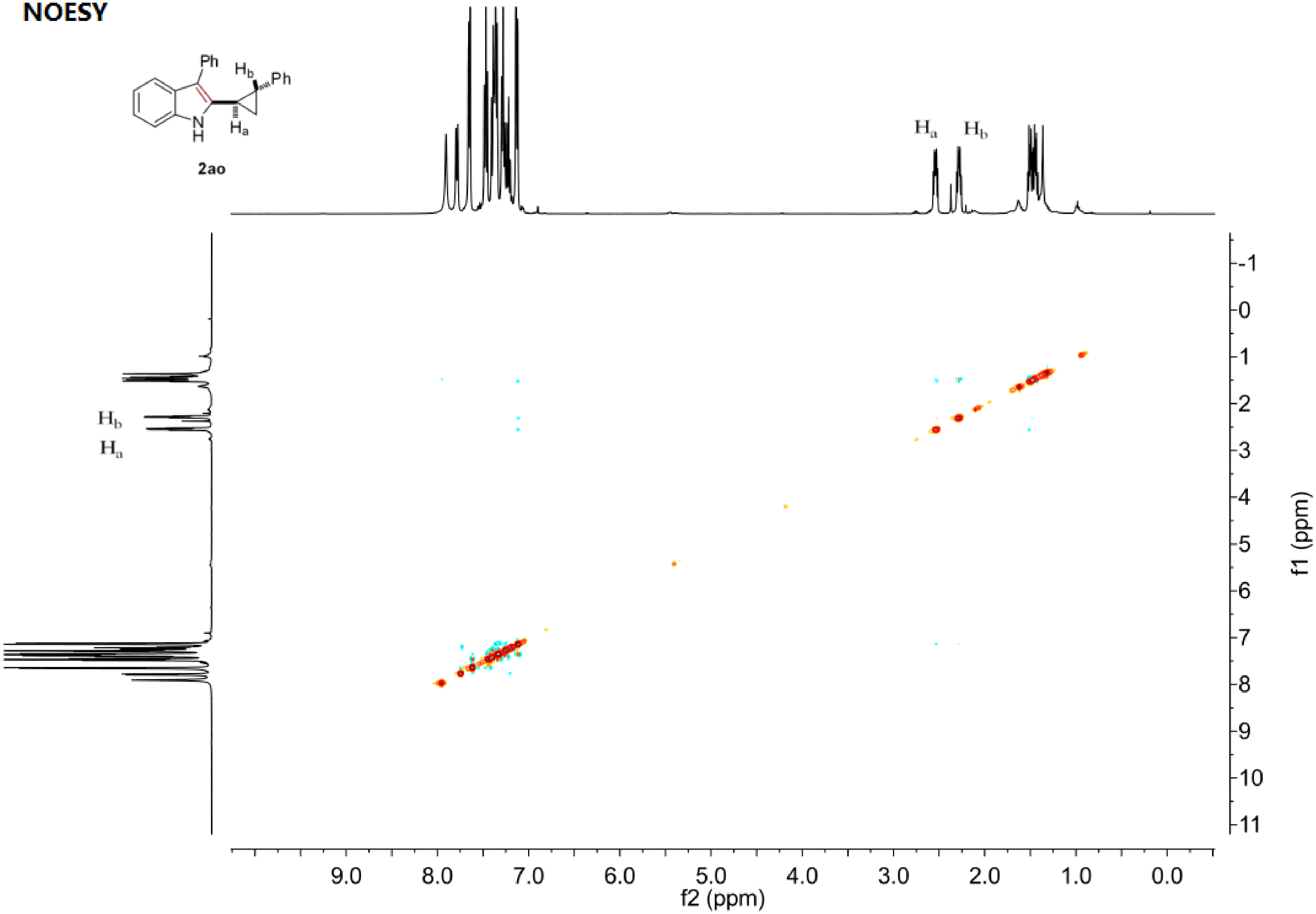
HSQC


Ph
Hb
Ph
N
H
Ha
2ao
Ha Hb
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)

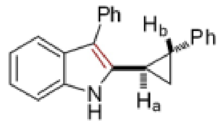
HMBC



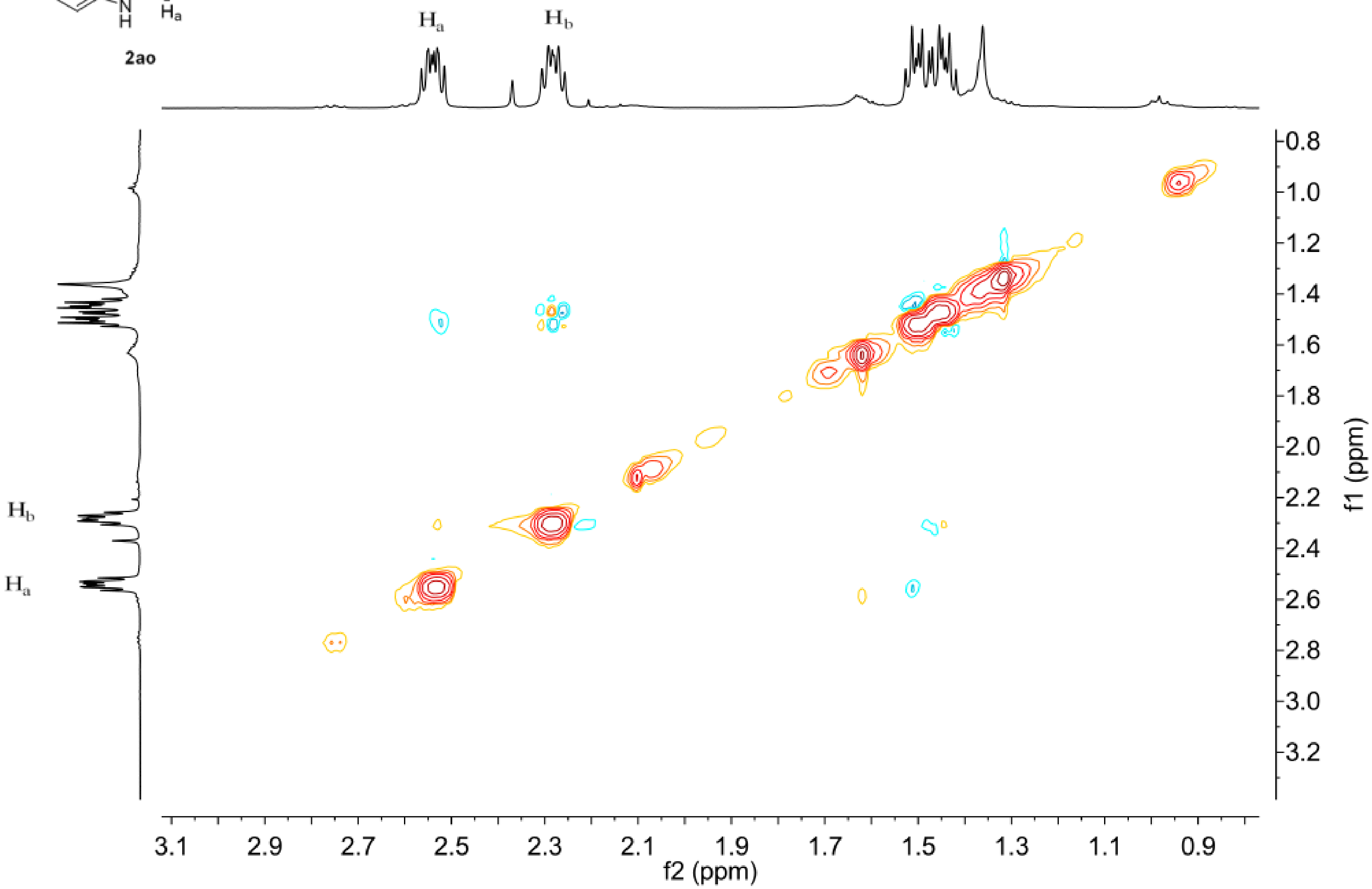
NOESY


Ph
Hb
Ph
N
H
Ha
2ao
Ha
Hb
Hb
Ha
-1
0
1
2
3
4
5
6
7
8
9
10
11
f1 (ppm)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)

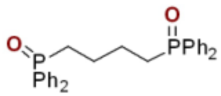
NOESY



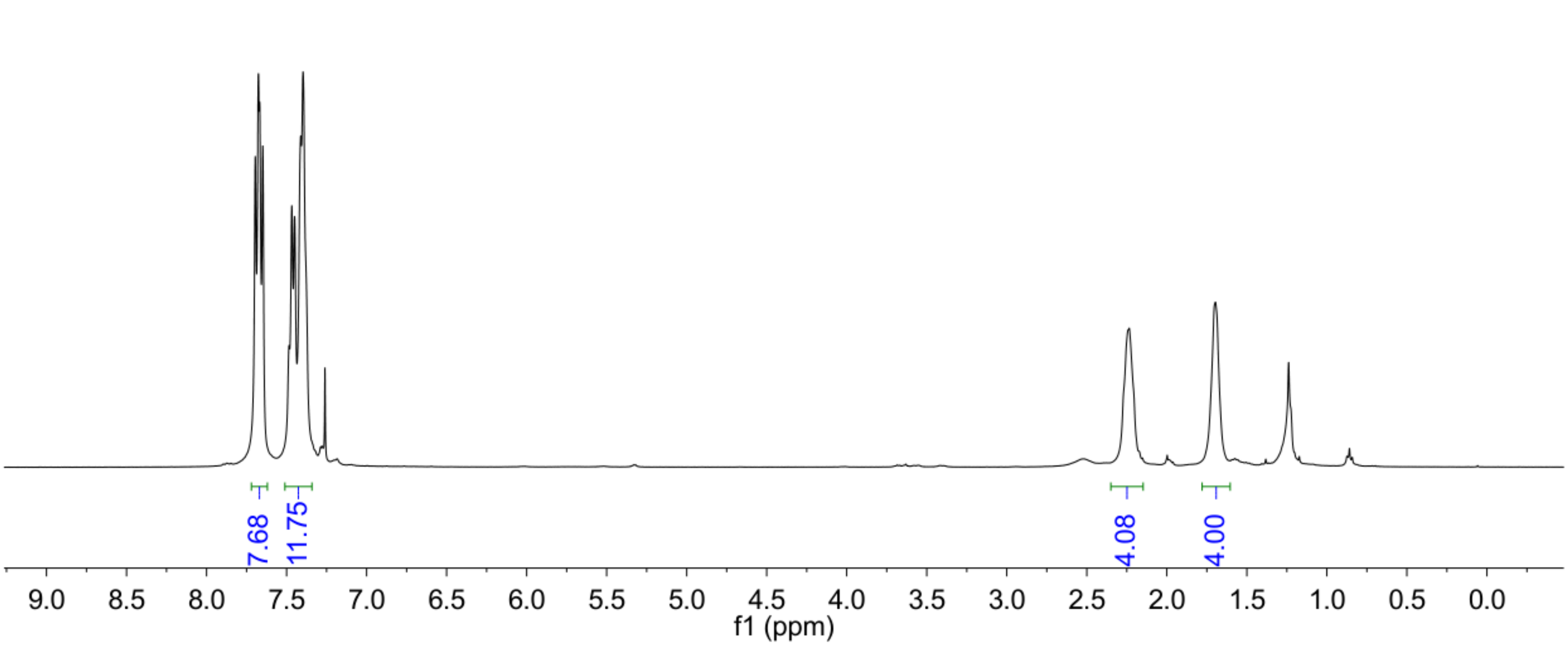
2ao



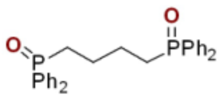
Ha
Hb
Hb
Ha
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
f1 (ppm)
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
f2 (ppm)



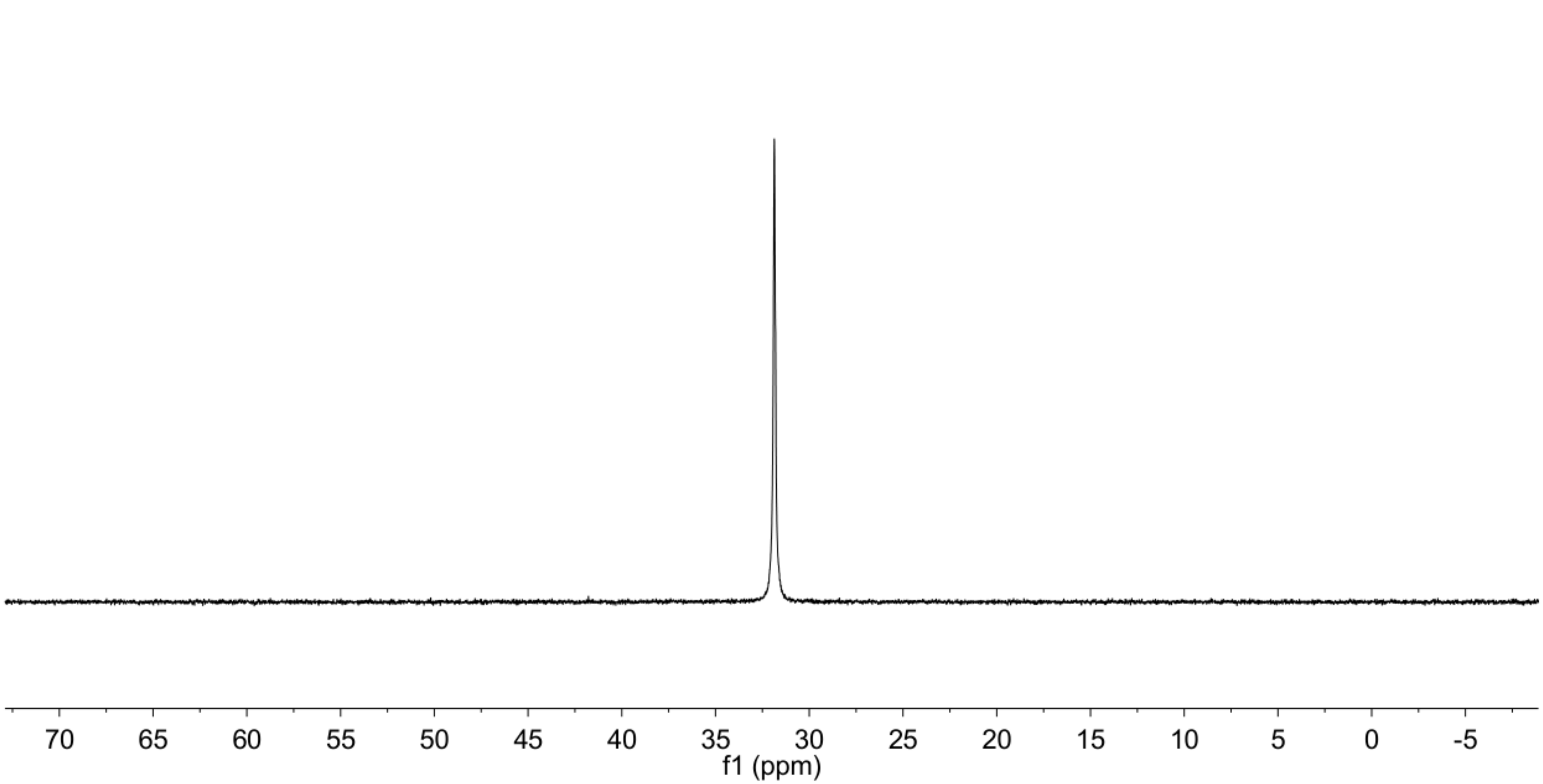
P2

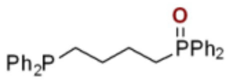


7.696
7.676
7.668
7.649
7.484
7.467
7.450
7.411
7.397
2.235
1.696
7.68
11.75
4.08
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



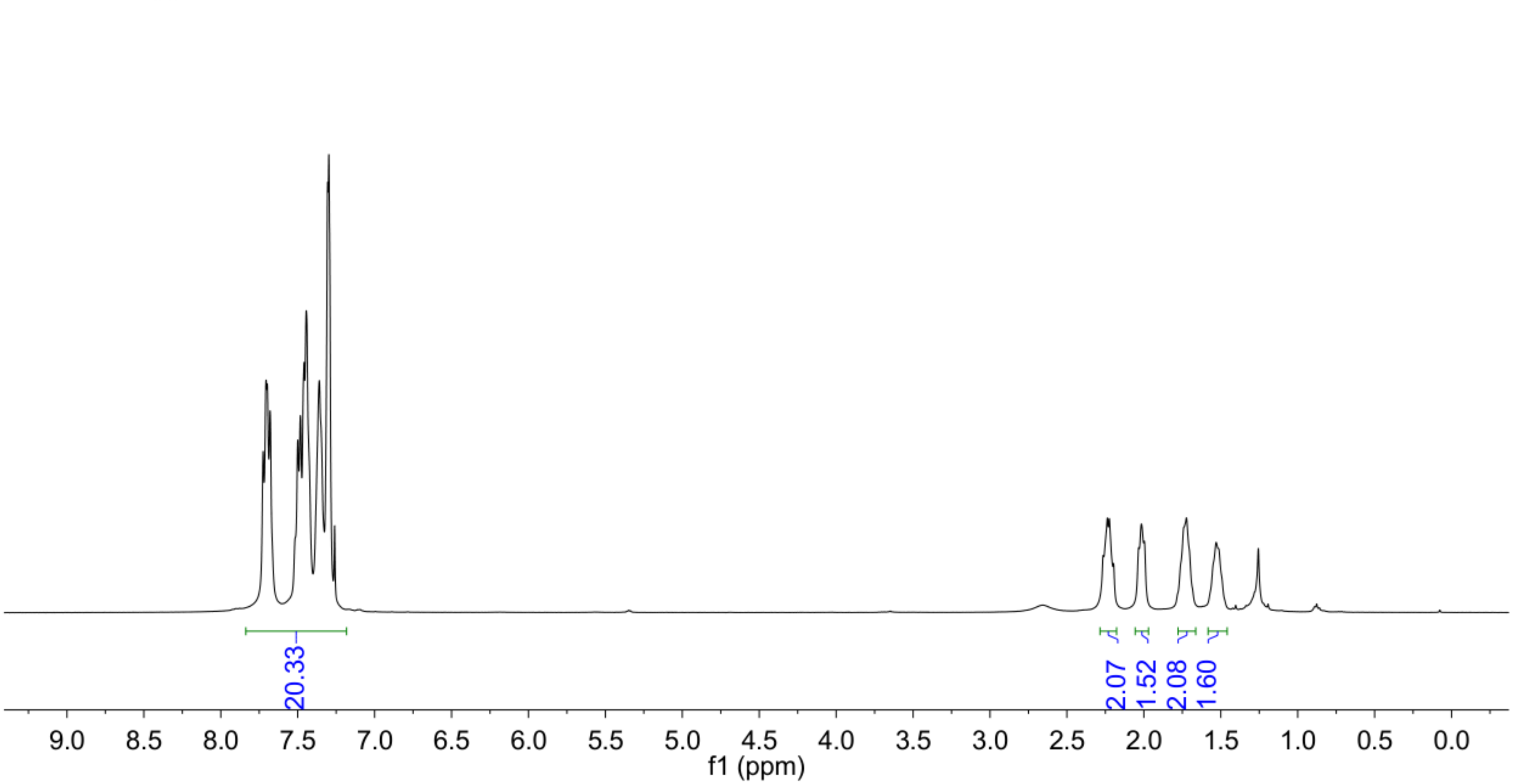
P2



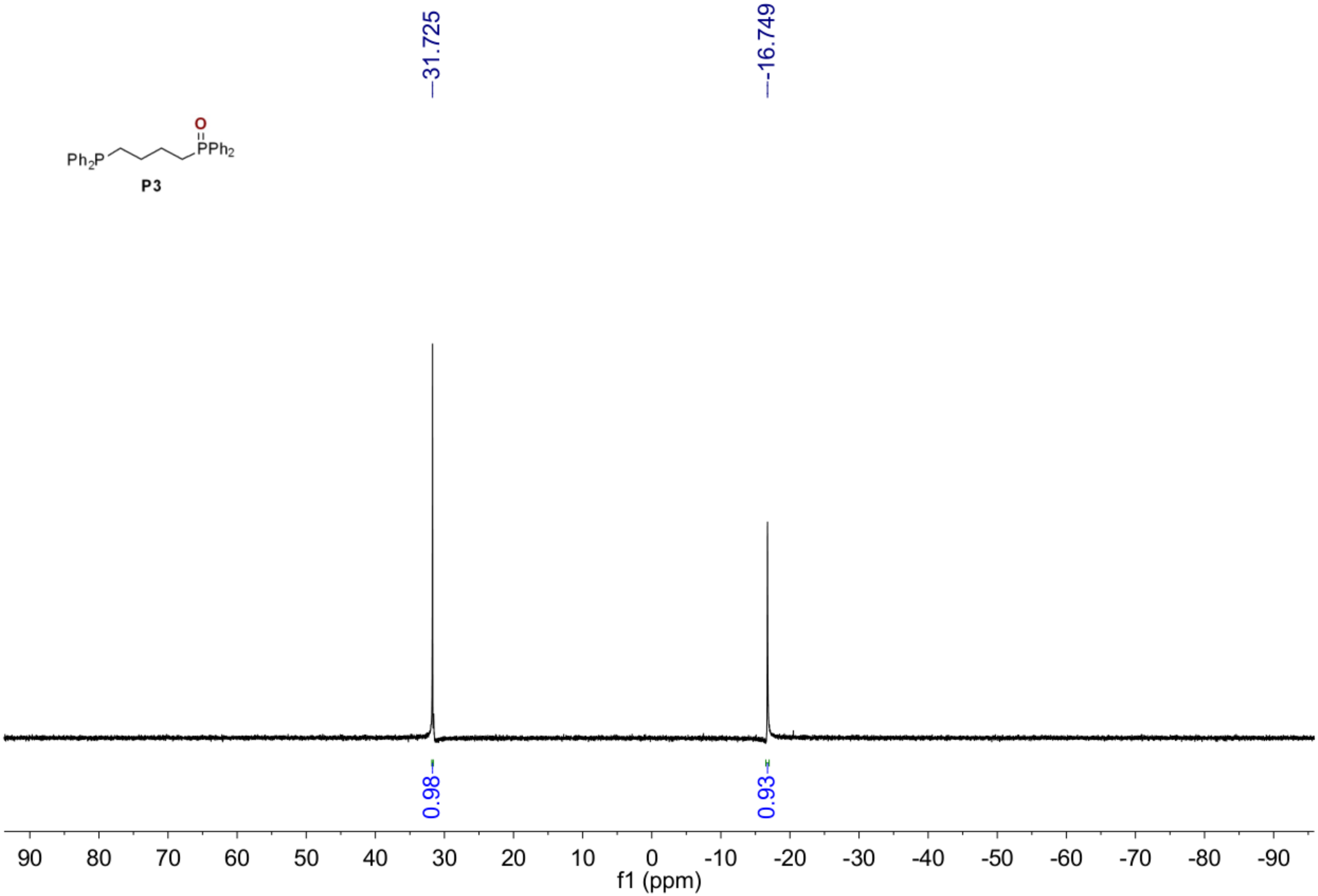


O
Ph2P
PPh2

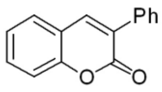
P3



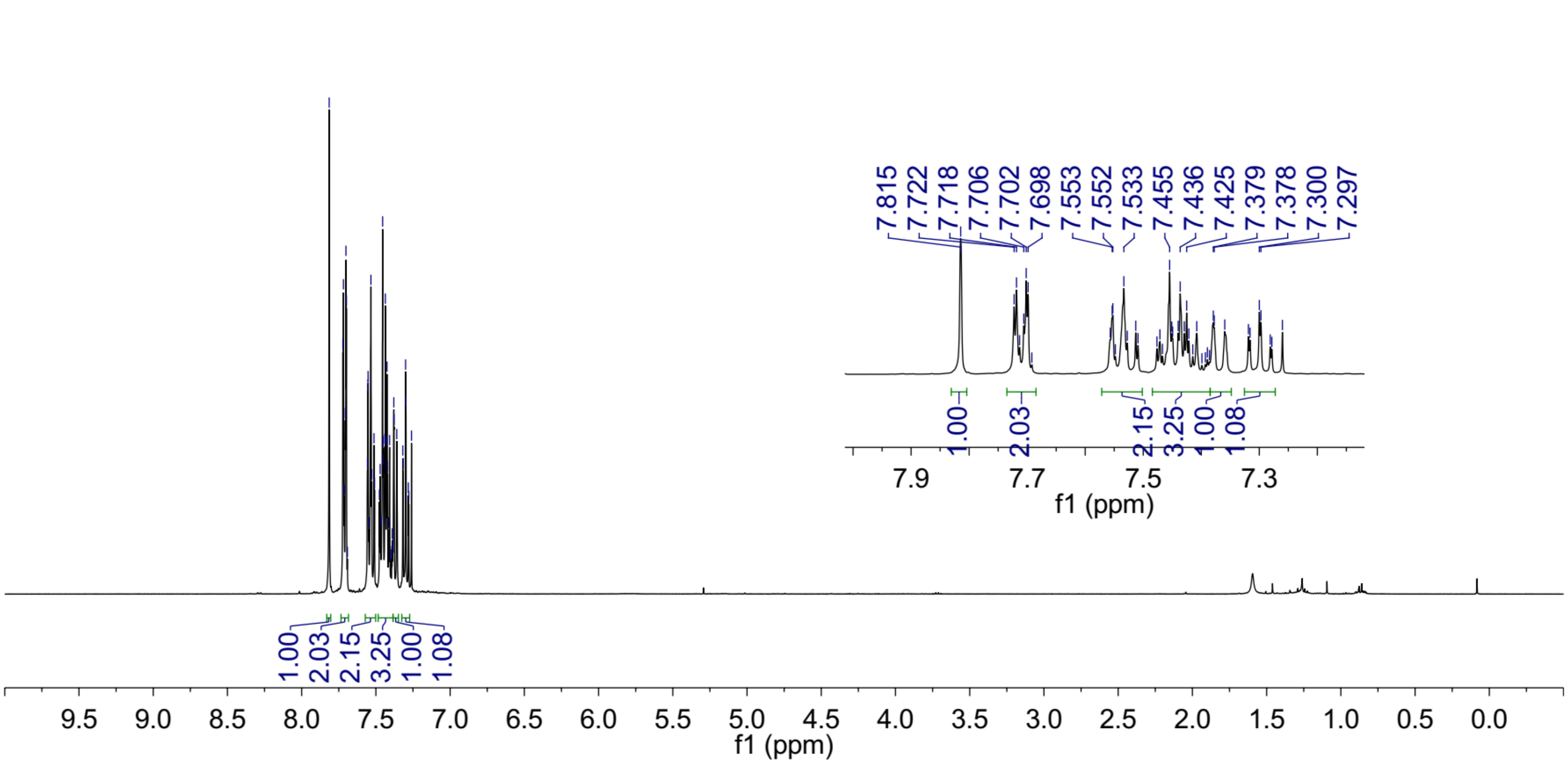
7.725
7.706
7.698
7.679
7.499
7.483
7.459
7.444
7.360
7.305
7.298
2.264
2.237
2.225
2.197
2.033
2.016
1.997
1.724
1.530
20.33
2.07
1.52
2.08
1.60
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

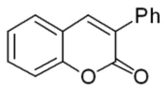


Ph2P
PPh2
O
P3
31.725
-16.749
0.98
0.93
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

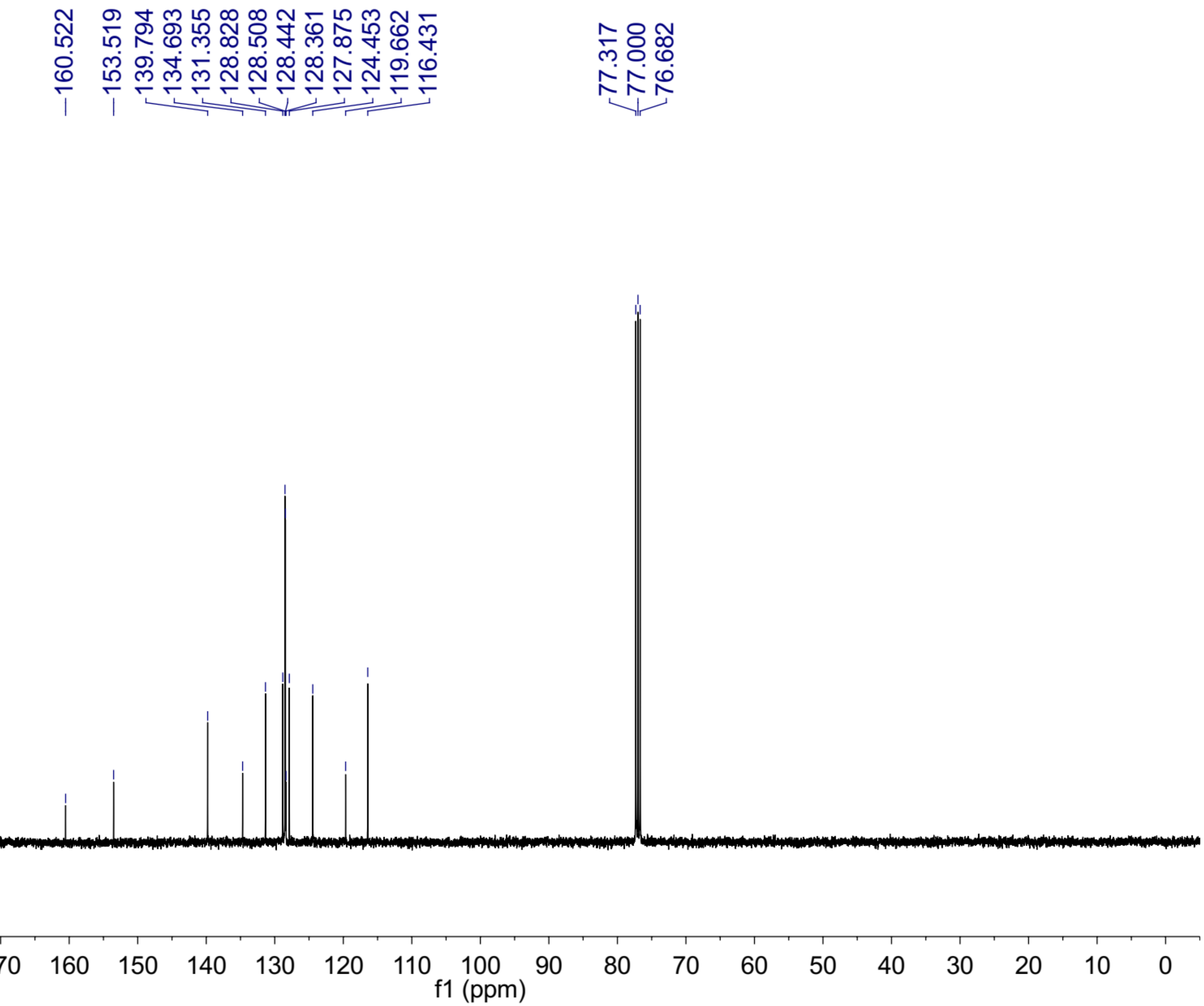

Ph
O
O

7a

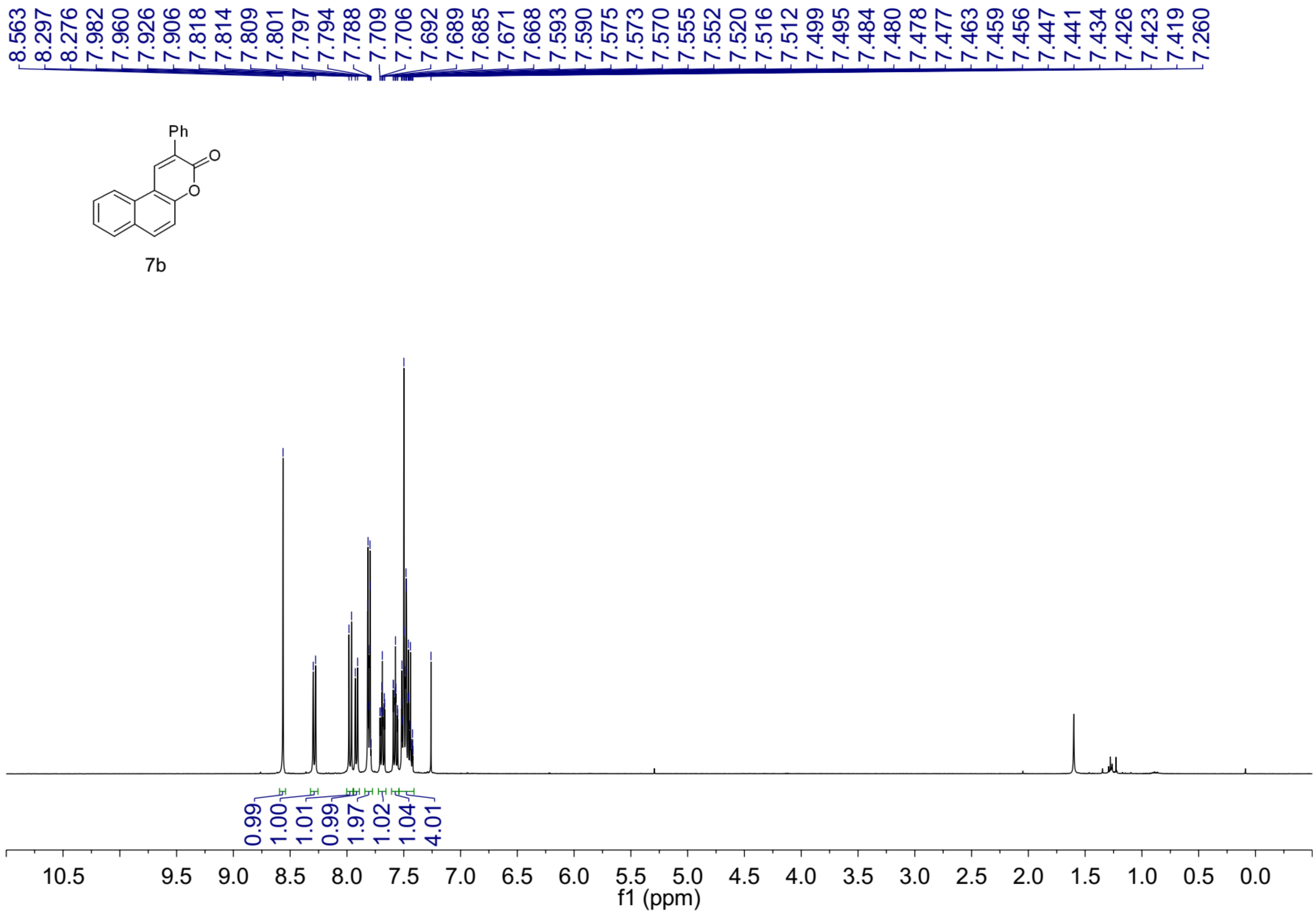

7.815 7.722 7.718 7.713 7.706 7.702 7.698 7.692 7.557 7.553 7.552 7.548 7.533 7.527 7.513 7.509 7.476 7.471 7.467 7.455 7.451 7.449 7.440 7.436 7.429 7.425 7.421 7.415 7.408 7.399 7.393 7.389 7.386 7.379 7.378 7.360 7.319 7.316 7.300 7.297 7.281 7.278 7.260
7.815 7.722 7.718 7.706 7.702 7.698 7.553 7.552 7.533 7.455 7.436 7.425 7.379 7.378 7.300 7.297
1.00 2.03 2.15 3.25 1.00 1.08
7.9 7.7 7.5 7.3
f1 (ppm)
1.00 2.03 2.15 3.25 1.00 1.08
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)

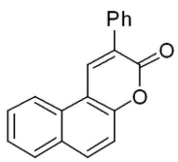


7a

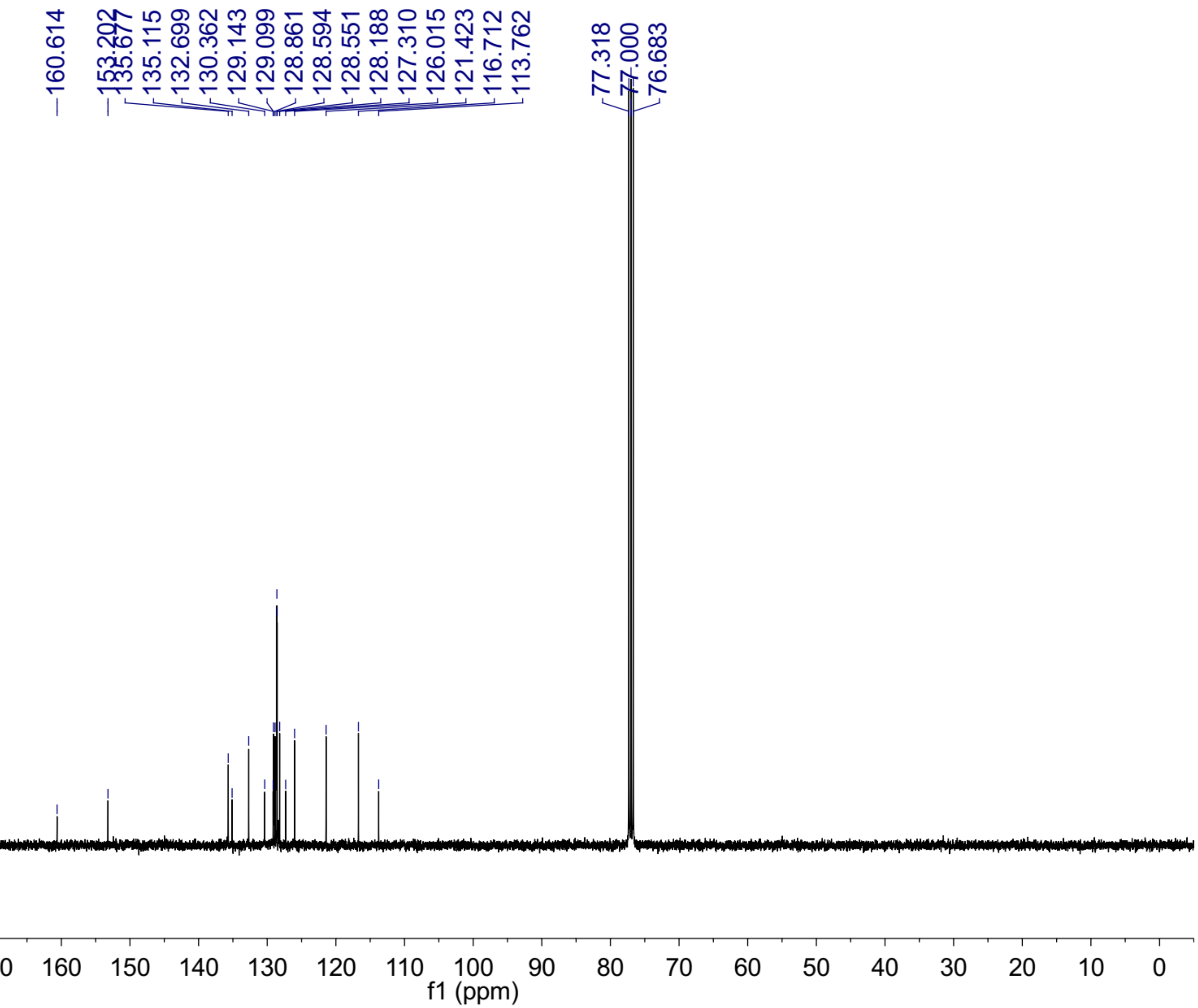


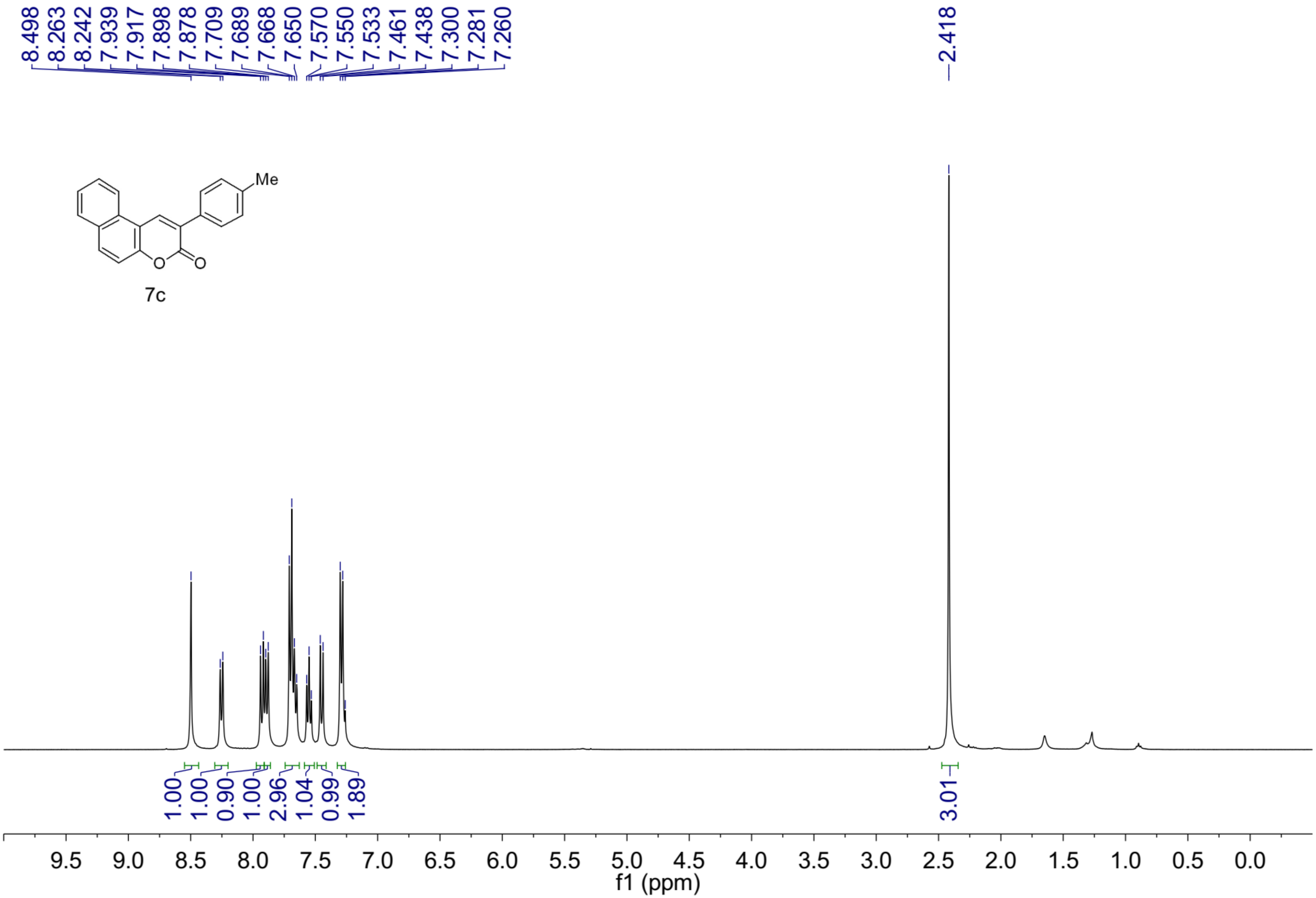
160.522
153.519
139.794
134.693
131.355
128.828
128.508
128.442
128.361
127.875
124.453
119.662
116.431
77.317
77.000
76.682
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

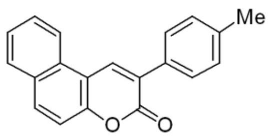

8.563
8.297
8.276
7.982
7.960
7.926
7.906
7.818
7.814
7.809
7.801
7.797
7.794
7.788
7.709
7.706
7.692
7.689
7.685
7.671
7.668
7.593
7.590
7.575
7.573
7.570
7.555
7.552
7.520
7.516
7.512
7.499
7.495
7.484
7.480
7.478
7.477
7.463
7.459
7.456
7.447
7.441
7.434
7.426
7.423
7.419
7.260
Ph
O
O
7b
0.99
1.00
1.01
0.99
1.97
1.02
1.04
4.01
10.5
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)


Ph
O
O

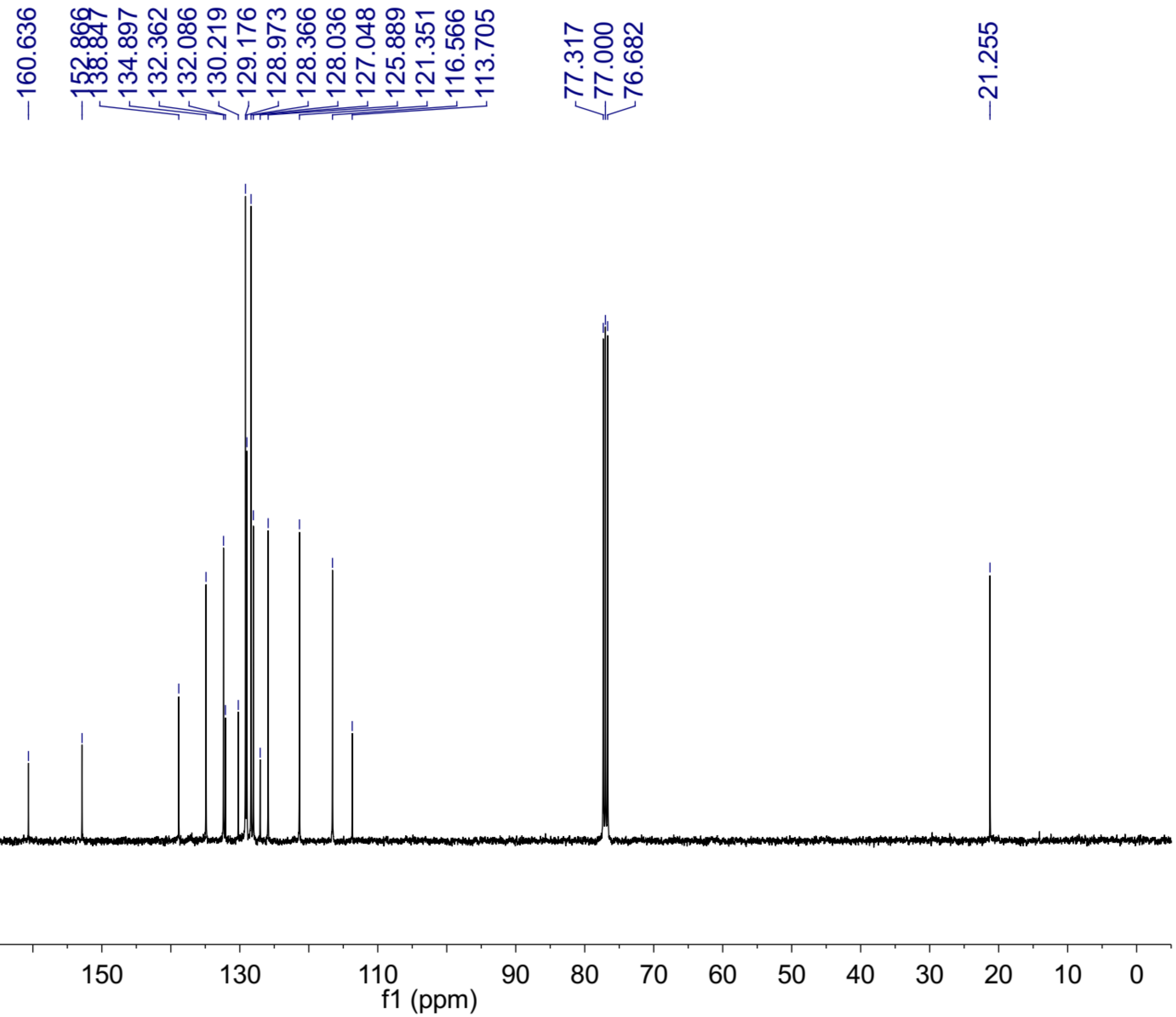
7b

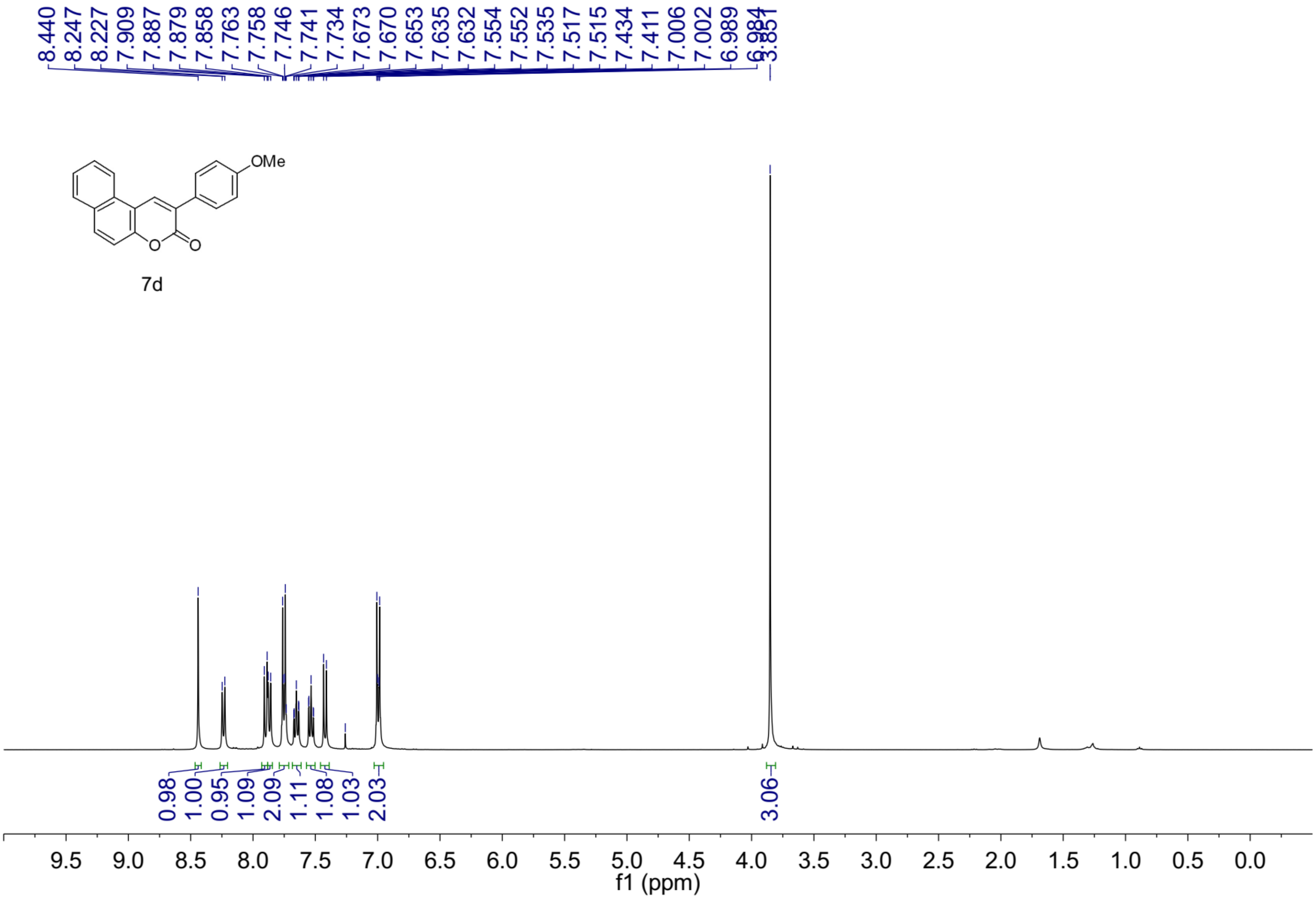

160.614
153.202
135.677
135.115
132.699
130.362
129.143
129.099
128.861
128.594
128.551
128.188
127.310
126.015
121.423
116.712
113.762
77.318
77.000
76.683
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
O
7c
8.498
8.263
8.242
7.939
7.917
7.898
7.878
7.709
7.689
7.668
7.650
7.570
7.550
7.533
7.461
7.438
7.300
7.281
7.260
2.418
1.00
1.00
0.90
1.00
2.96
1.04
0.99
1.89
3.01
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)


Me

7c


160.636
152.866
138.847
134.897
132.362
132.086
130.219
129.176
128.973
128.366
128.036
127.048
125.889
121.351
116.566
113.705
77.317
77.000
76.682
21.255
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
O
O

7d

8.440
8.247
8.227
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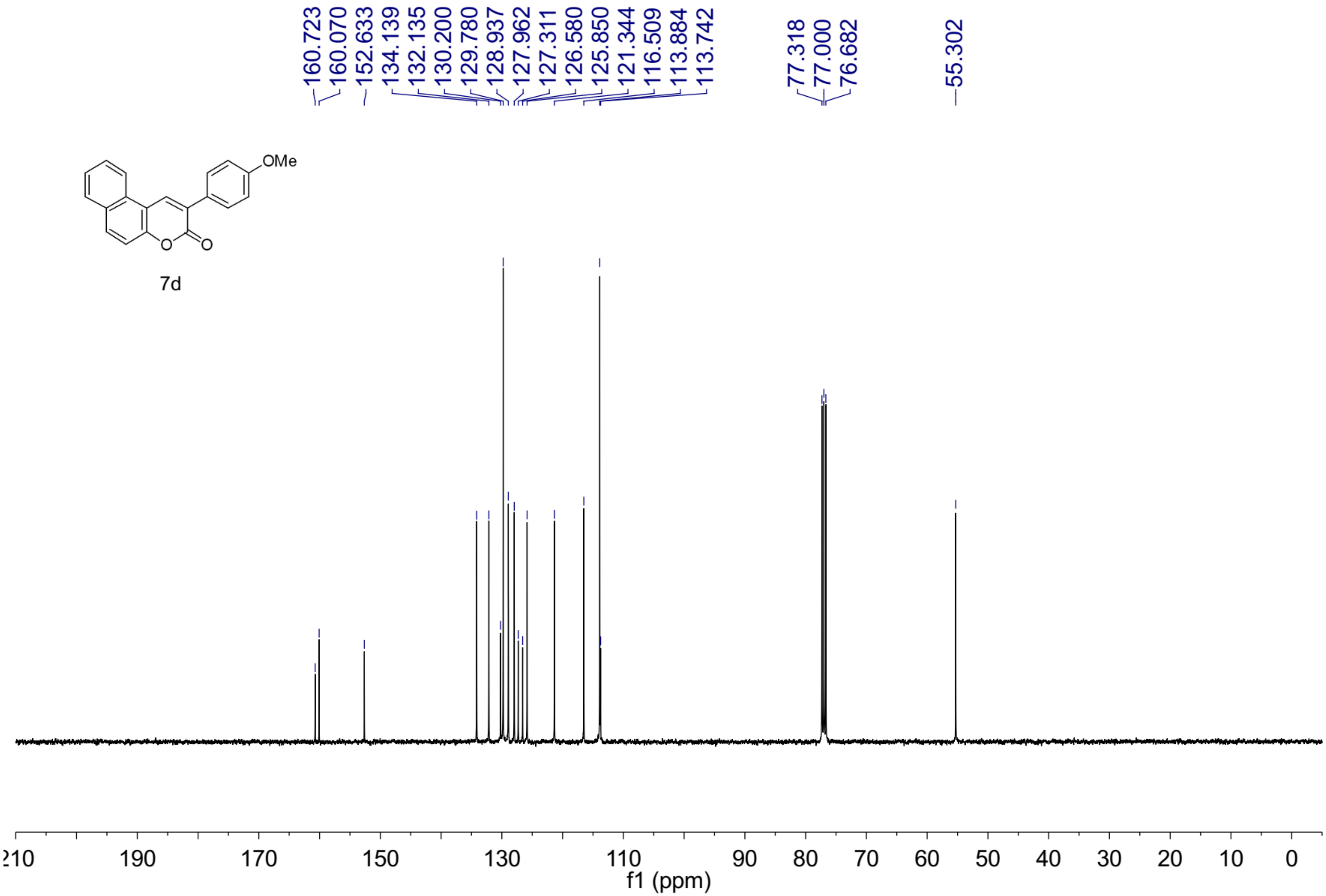
7.887
7.879
7.858
7.763
7.758
7.746
7.741
7.734
7.673
7.670
7.653
7.635
7.632
7.554
7.552
7.535
7.517
7.515
7.434
7.411
7.006
7.002
6.989
6.984
3.851
0.98
1.00
0.95
1.09
2.09
1.11
1.08
1.03
2.03
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.633
134.139
132.135
130.200
129.780
128.937
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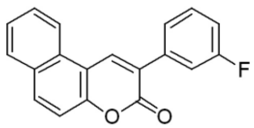
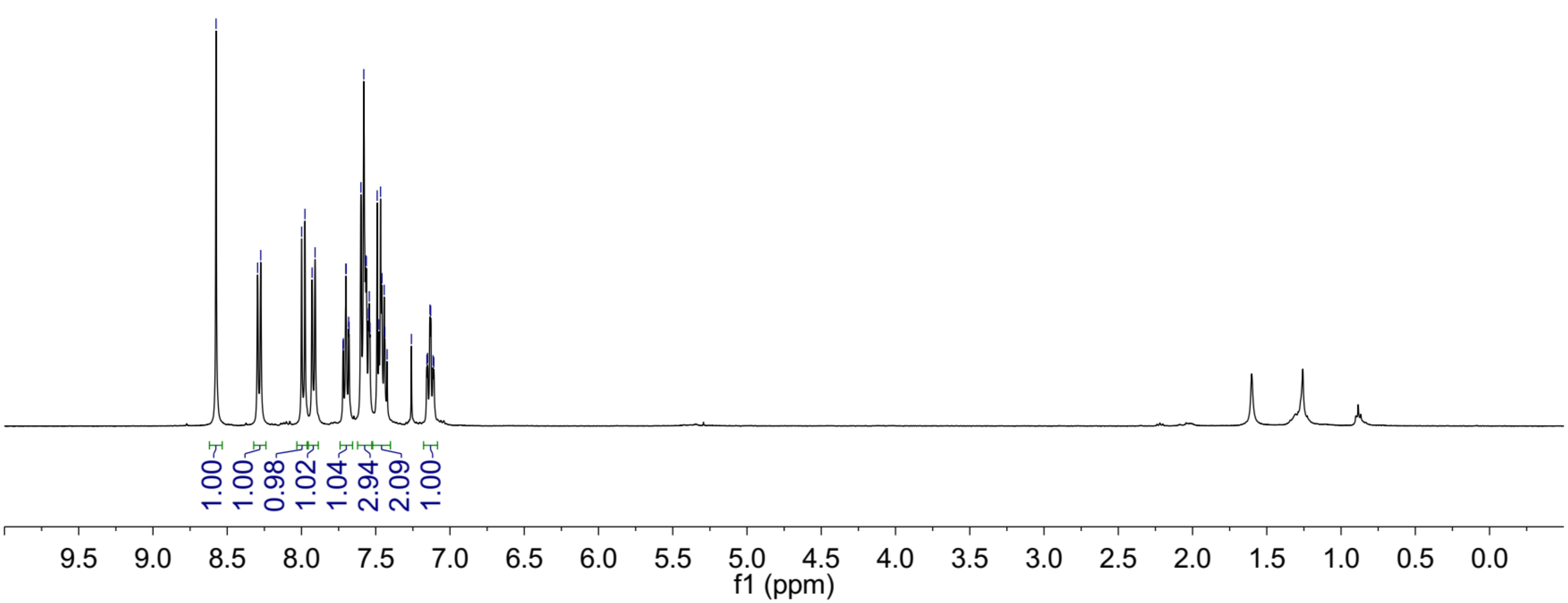
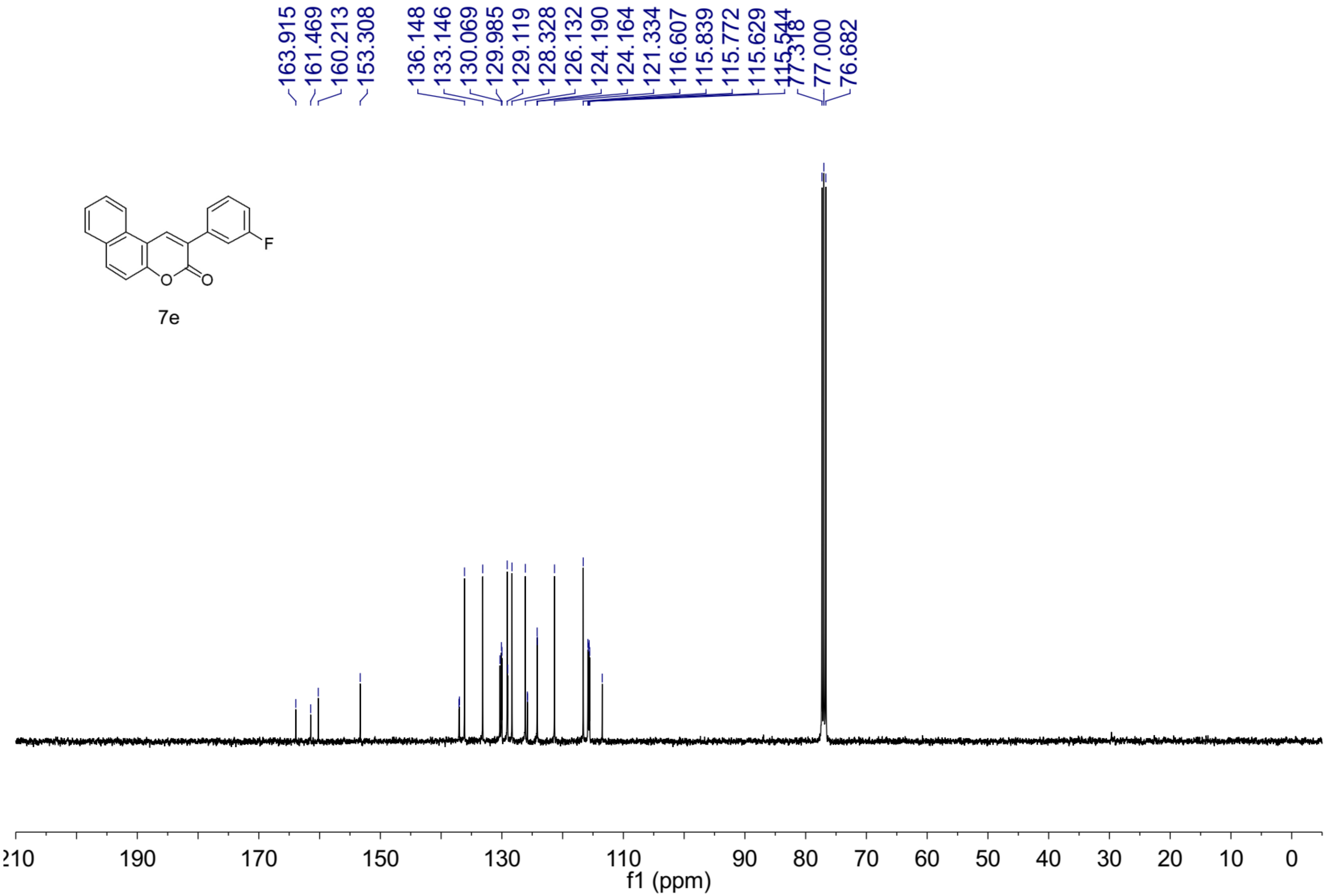
127.311
126.580
125.850
121.344
116.509
113.884
113.742
77.318
77.000
76.682
55.302
OMe
O
O
7d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7e



8.575
8.295
8.274
7.999
7.977
7.929
7.909
7.721
7.718
7.700
7.700
7.682
7.680
7.600
7.580
7.568
7.563
7.549
7.544
7.539
7.490
7.478
7.468
7.458
7.443
7.439
7.423
7.260
7.156
7.151
7.135
7.130
7.114
7.109
1.00
1.00
0.98
1.02
1.04
2.94
2.09
1.00
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)


F
O
O
7e
163.915
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160.213
153.308
136.148
133.146
130.069
129.985
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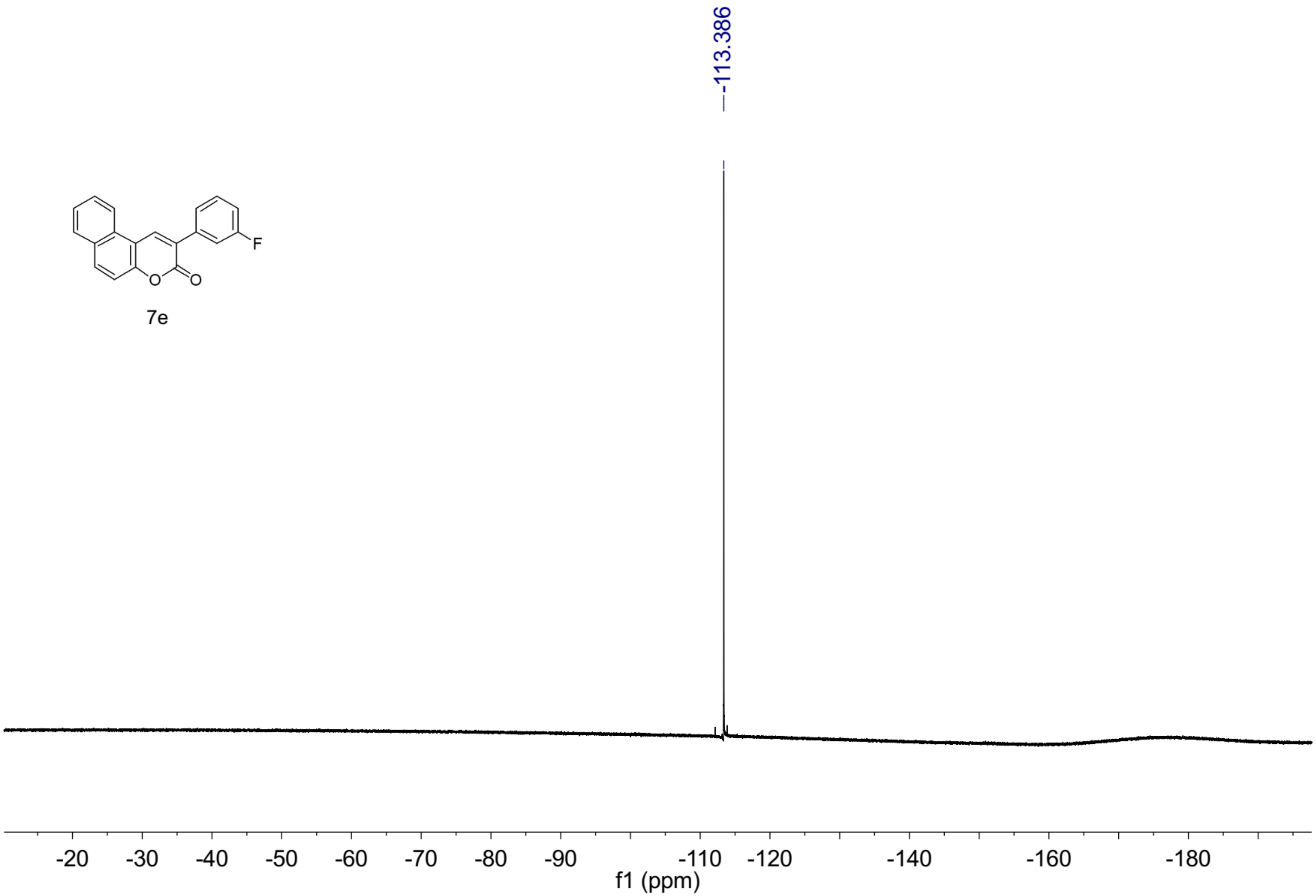
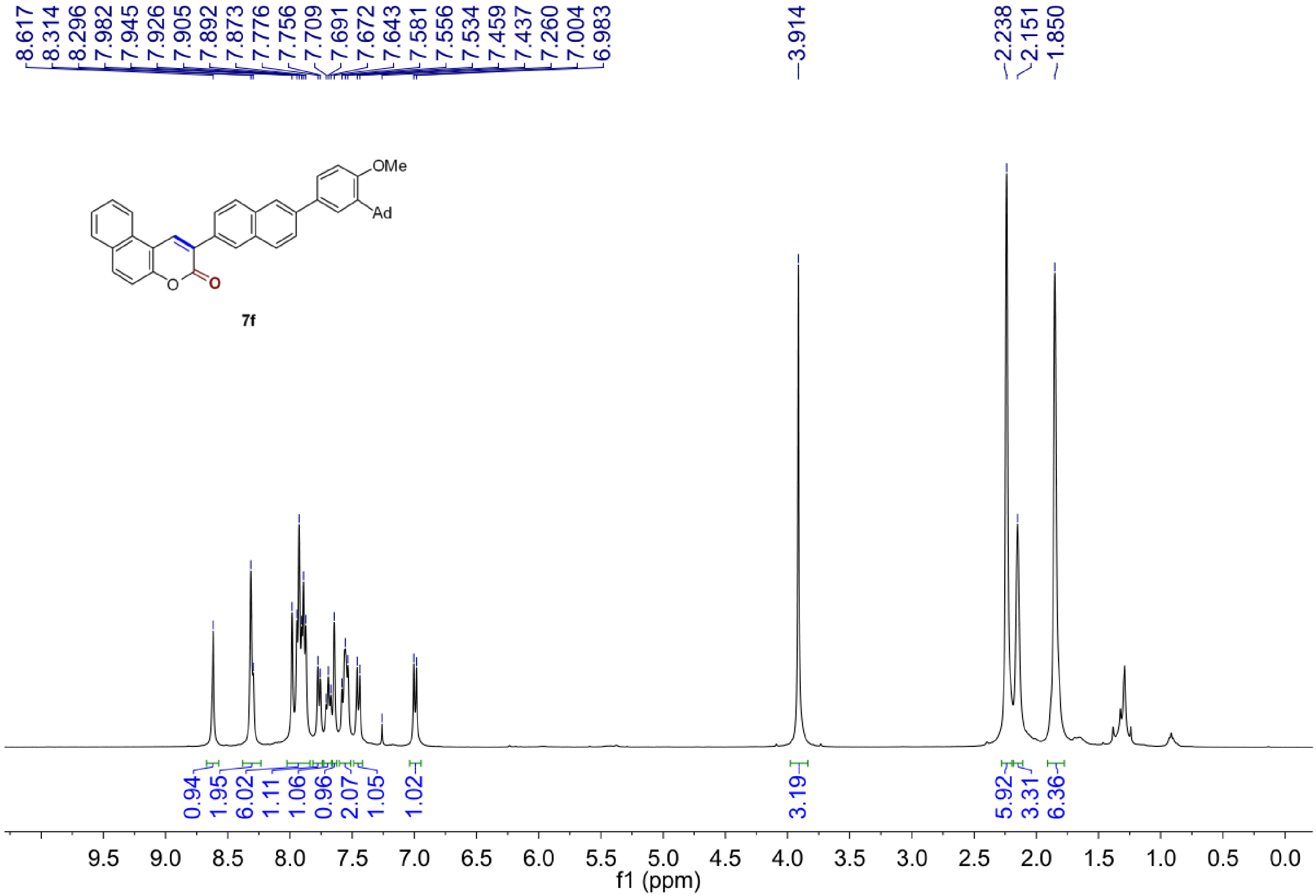
128.328
126.132
124.190
124.164
121.334
116.607
115.839
115.772
115.629
115.544
77.318
77.000
76.682
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7e
-113.386
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
-180
f1 (ppm)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8.296
7.982
7.945
7.926
7.905
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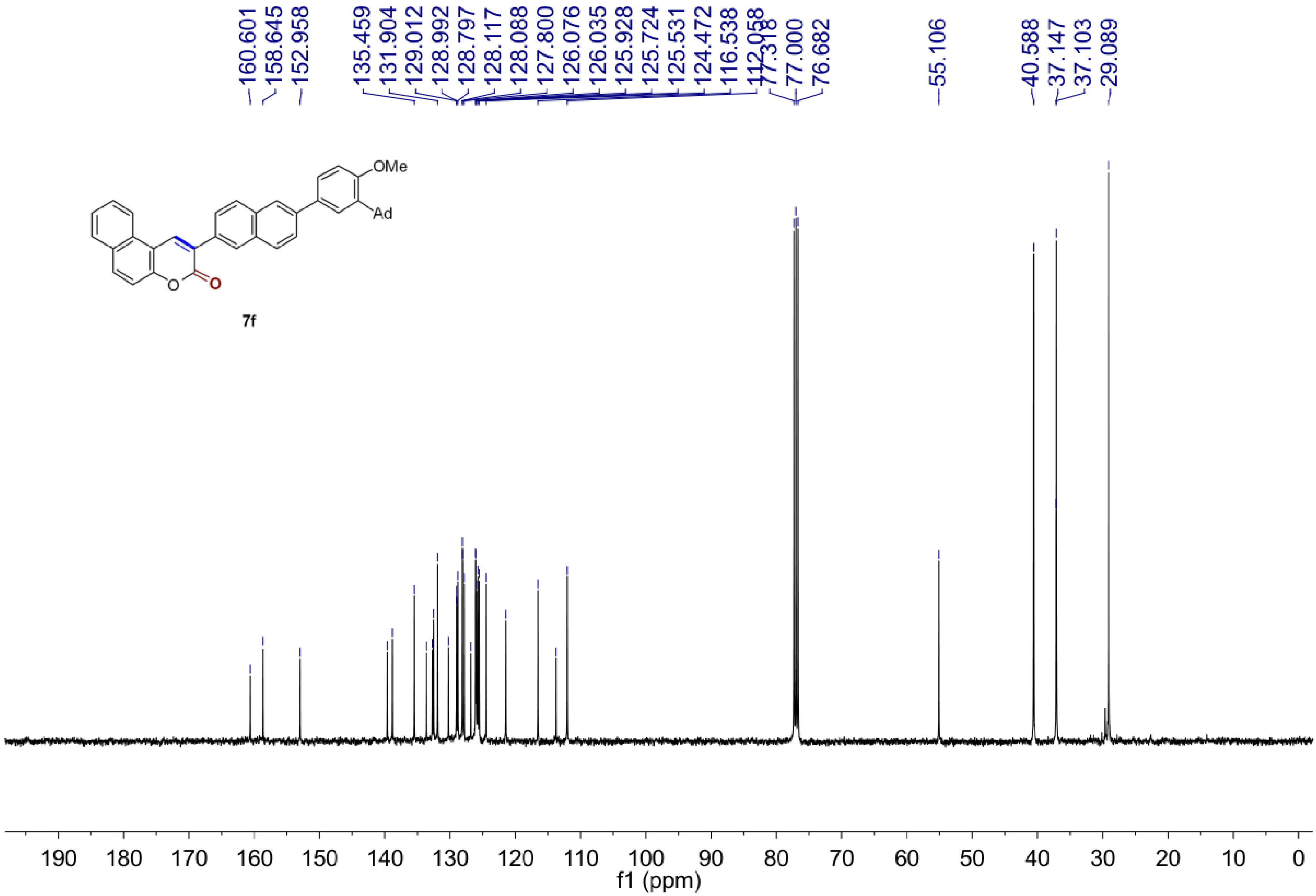
7.873
7.776
7.756
7.709
7.691
7.672
7.643
7.581
7.556
7.534
7.459
7.437
7.260
7.004
6.983
3.914
2.238
2.151
1.850
OMe
Ad
O
O
7f
0.94
1.95
6.02
1.11
1.06
0.96
2.07
1.05
1.02
3.19
5.92
3.31
6.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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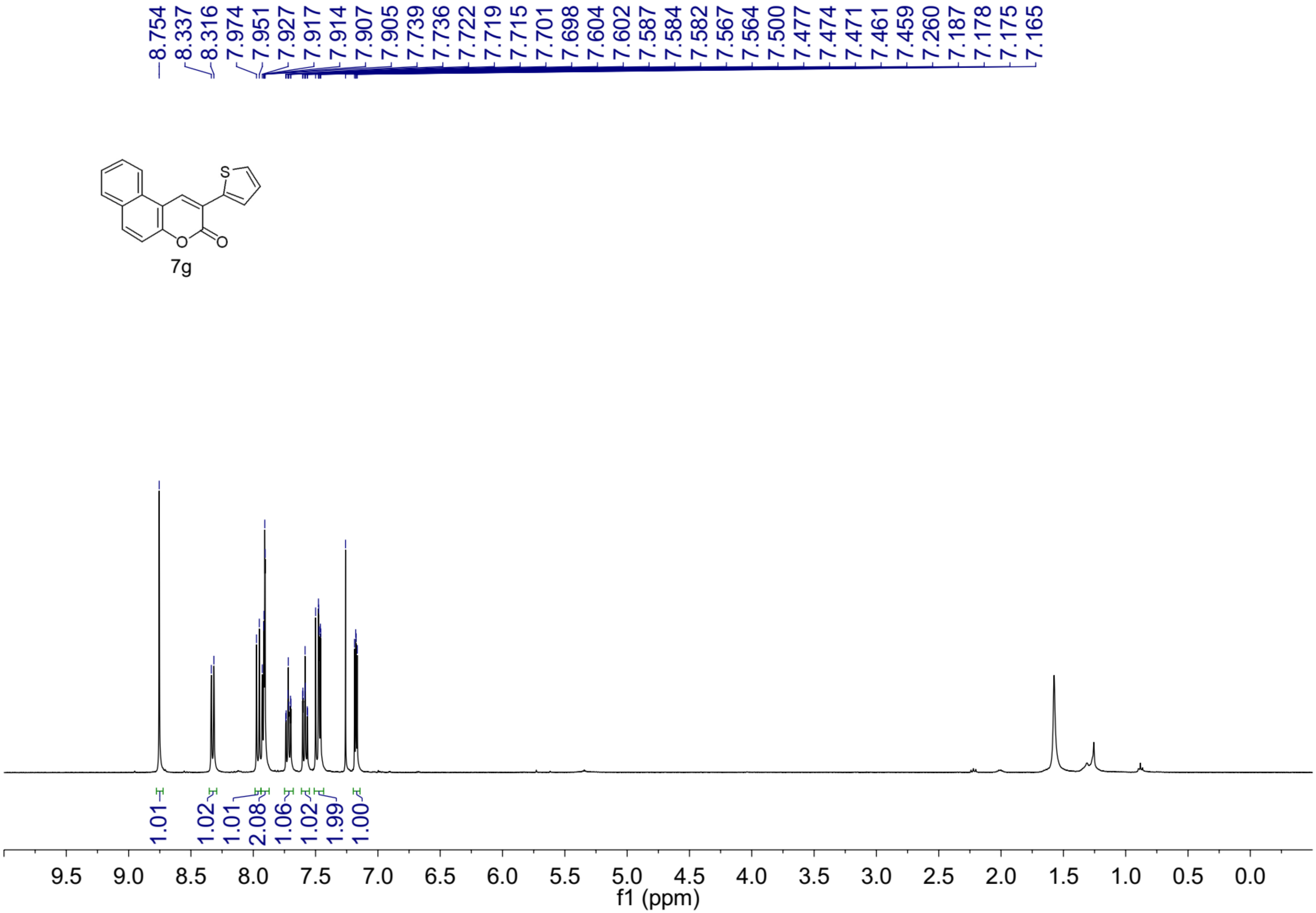
158.645
152.958
135.459
131.904
129.012
128.992
128.797
128.117
128.088
127.800
126.076
126.035
125.928
125.724
125.531
124.472
116.538
112.058
77.318
77.000
76.682
55.106
40.588
37.147
37.103
29.089
OMe
Ad
O
O
7f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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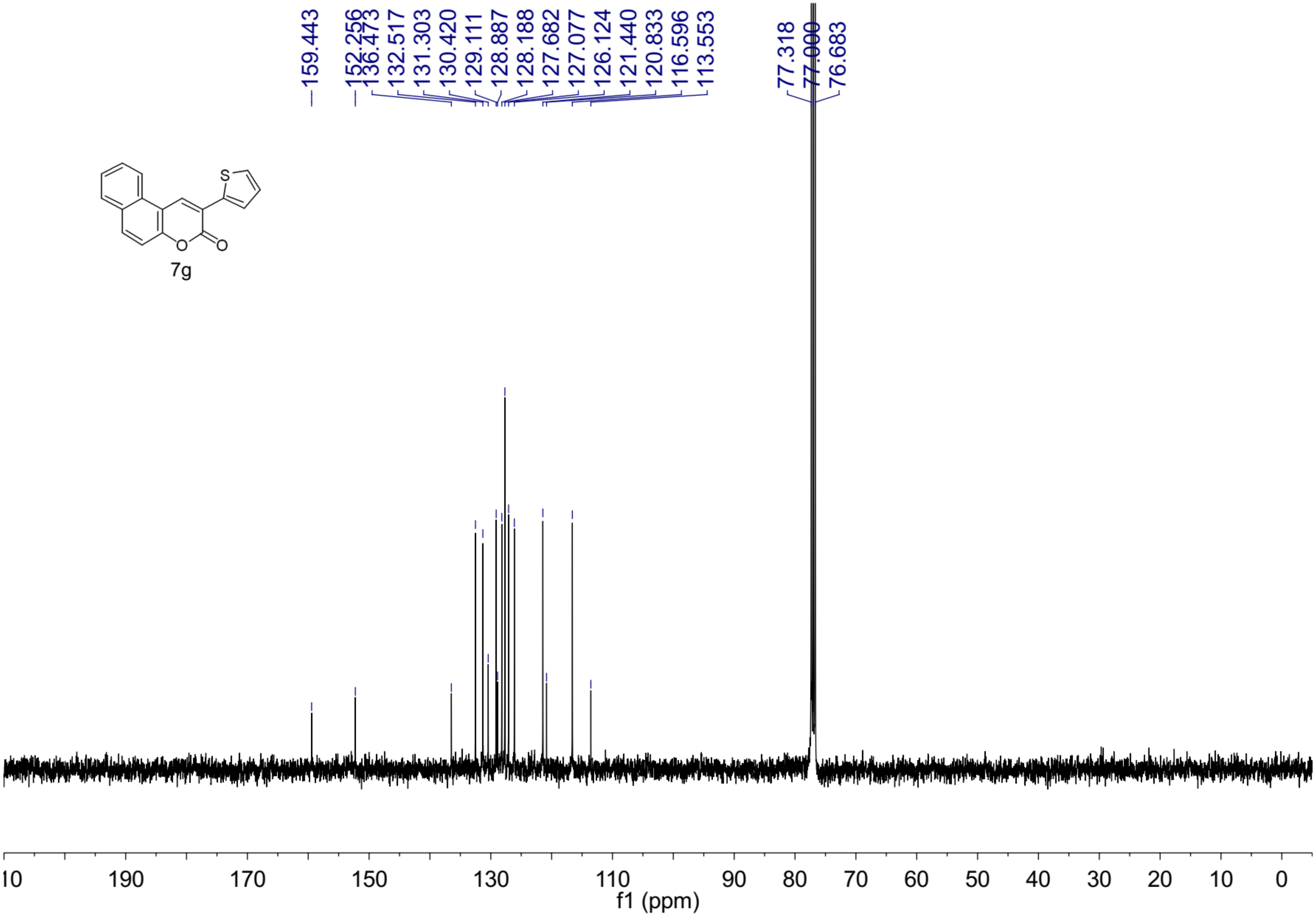
8.337
8.316
7.974
7.951
7.927
7.917
7.914
7.907
7.905
7.739
7.736
7.722
7.719
7.715
7.701
7.698
7.604
7.602
7.587
7.584
7.582
7.567
7.564
7.500
7.477
7.474
7.471
7.461
7.459
7.260
7.187
7.178
7.175
7.165
7g
1.01
1.02
1.01
2.08
1.06
1.02
1.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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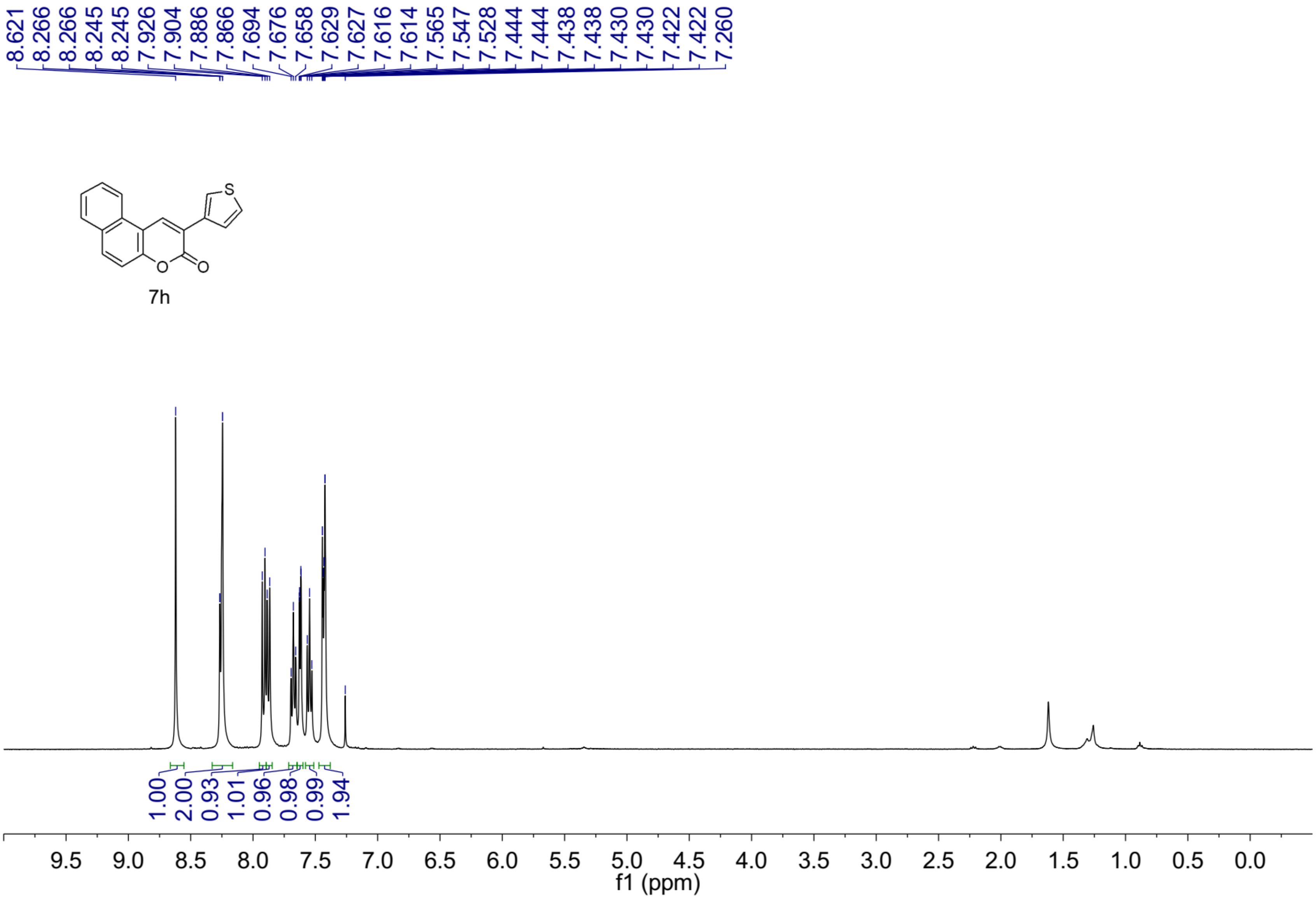
152.256
136.473
132.517
131.303
130.420
129.111
128.887
128.188
127.682
127.077
126.124
121.440
120.833
116.596
113.553
77.318
77.000
76.683
S
O
O
7g
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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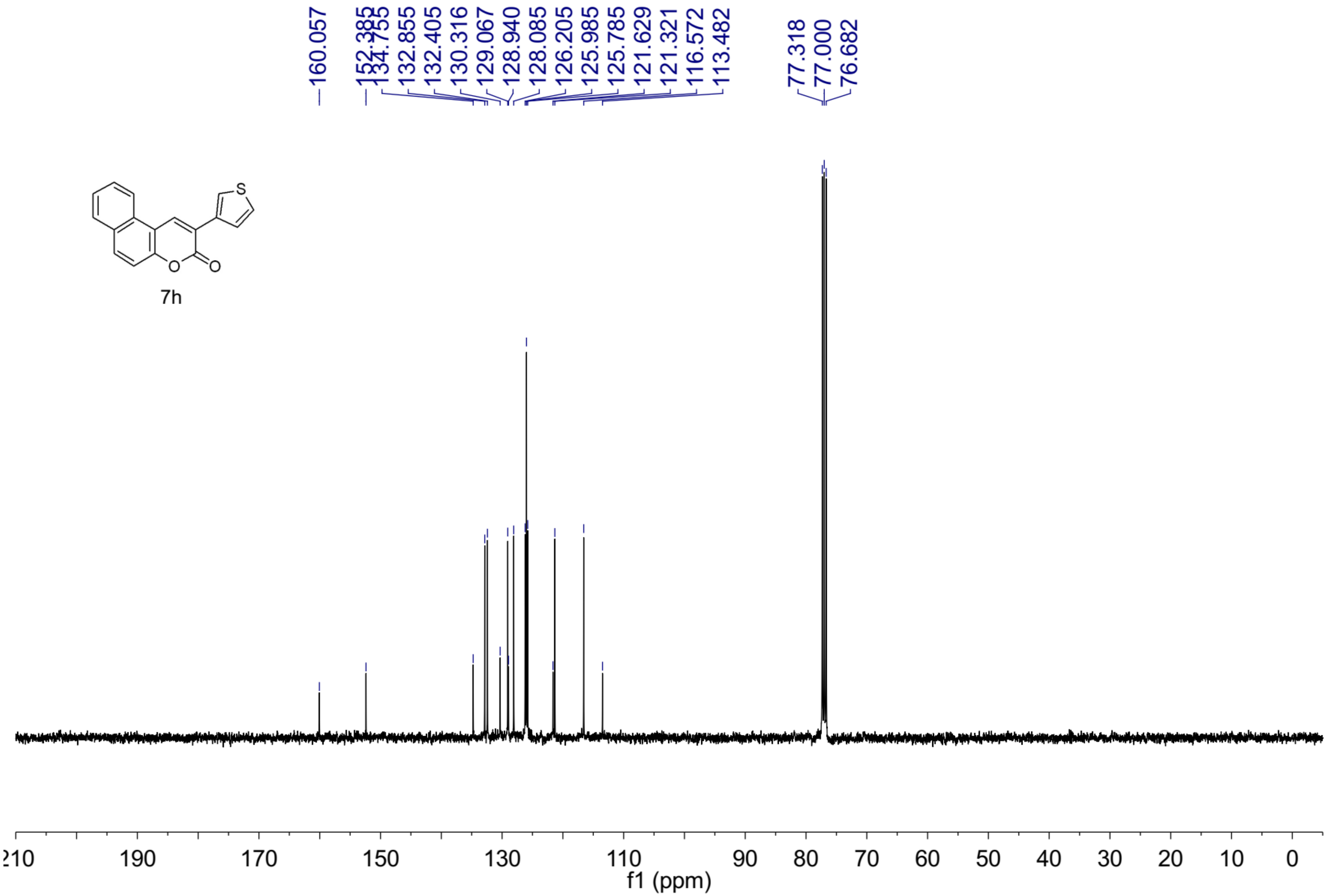
8.266
8.266
8.245
8.245
7.926
7.904
7.886
7.866
7.694
7.676
7.658
7.629
7.627
7.616
7.614
7.565
7.547
7.528
7.444
7.444
7.438
7.438
7.430
7.430
7.422
7.422
7.260
S
O
O
7h
1.00
2.00
0.93
1.01
0.96
0.98
0.99
1.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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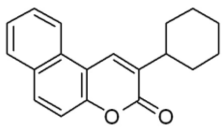
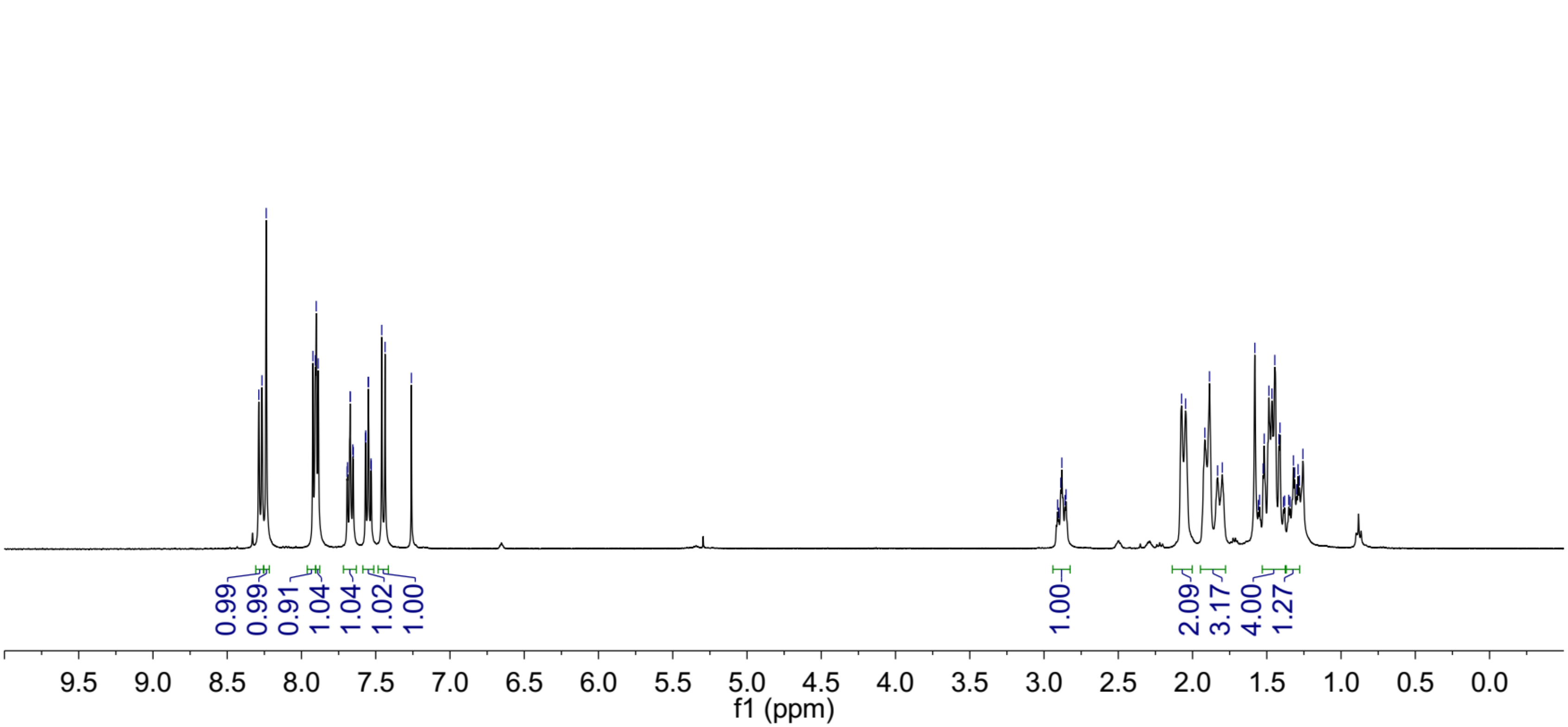
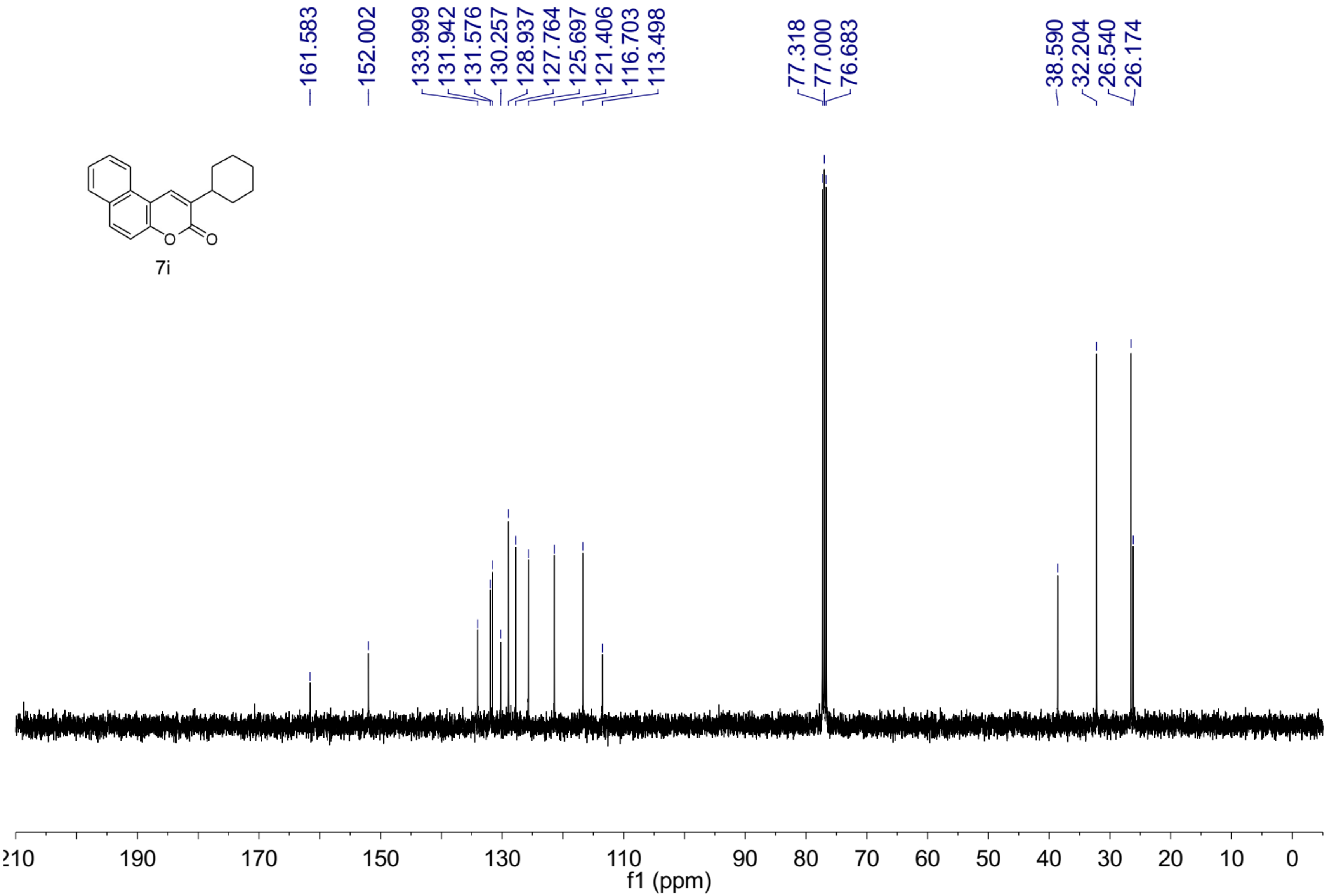
134.755
132.855
132.405
130.316
129.067
128.940
128.085
126.205
125.985
125.785
121.629
121.321
116.572
113.482
77.318
77.000
76.682
S
O
O
7h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7i


8.287 8.266 8.238 7.923 7.906 7.901 7.888 7.693 7.690 7.672 7.672 7.654 7.652 7.569 7.568 7.550 7.550 7.532 7.530 7.460 7.437 7.260
2.887 2.880 2.859 2.852 2.074 2.046 1.917 1.886 1.831 1.800 1.581 1.549 1.524 1.517 1.486 1.466 1.446 1.418 1.411 1.380 1.352 1.321 1.312 1.299 1.289 1.281 1.257
0.99 0.99 0.91 1.04 1.04 1.02 1.00
1.00
2.09 3.17 4.00 1.27
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)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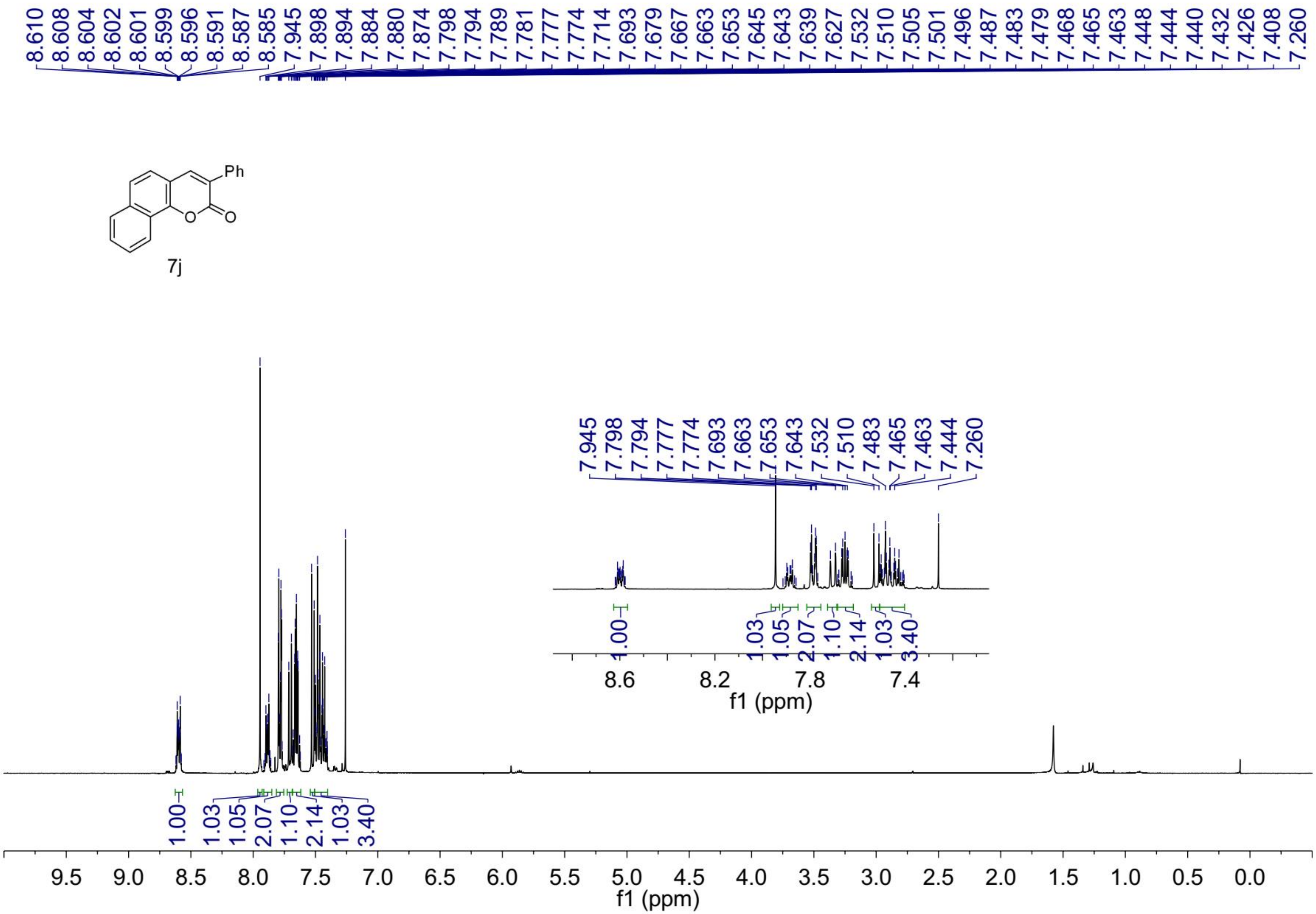
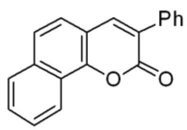
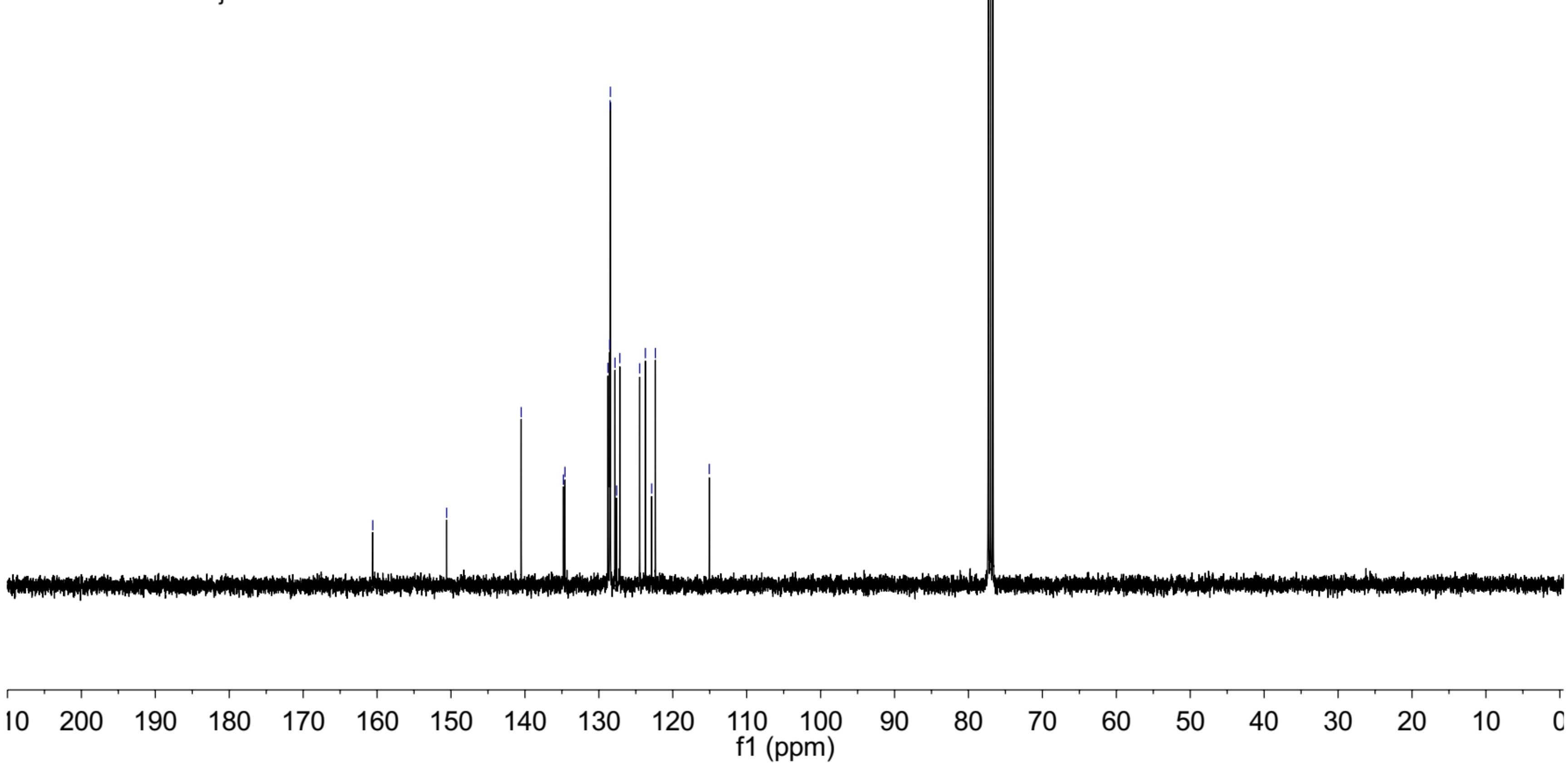
133.999
131.942
131.576
130.257
128.937
127.764
125.697
121.406
116.703
113.498
77.318
77.000
76.683
38.590
32.204
26.540
26.174
7i
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.610 8.608 8.604 8.602 8.601 8.599 8.596 8.591 8.587 8.585 7.945 7.898 7.894 7.884 7.880 7.874 7.798 7.794 7.789 7.781 7.777 7.774 7.714 7.693 7.679 7.667 7.663 7.653 7.645 7.643 7.639 7.627 7.532 7.510 7.505 7.501 7.496 7.487 7.483 7.479 7.468 7.465 7.463 7.448 7.444 7.440 7.432 7.426 7.408 7.260
Ph
O
O
7j
7.945 7.798 7.794 7.777 7.774 7.693 7.663 7.653 7.643 7.532 7.510 7.483 7.465 7.463 7.444 7.260
1.00 1.03 1.05 2.07 1.10 2.14 1.03 3.40
8.6 8.2 7.8 7.4
f1 (ppm)
1.00 1.03 1.05 2.07 1.10 2.14 1.03 3.40
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)


Ph
O
O

7j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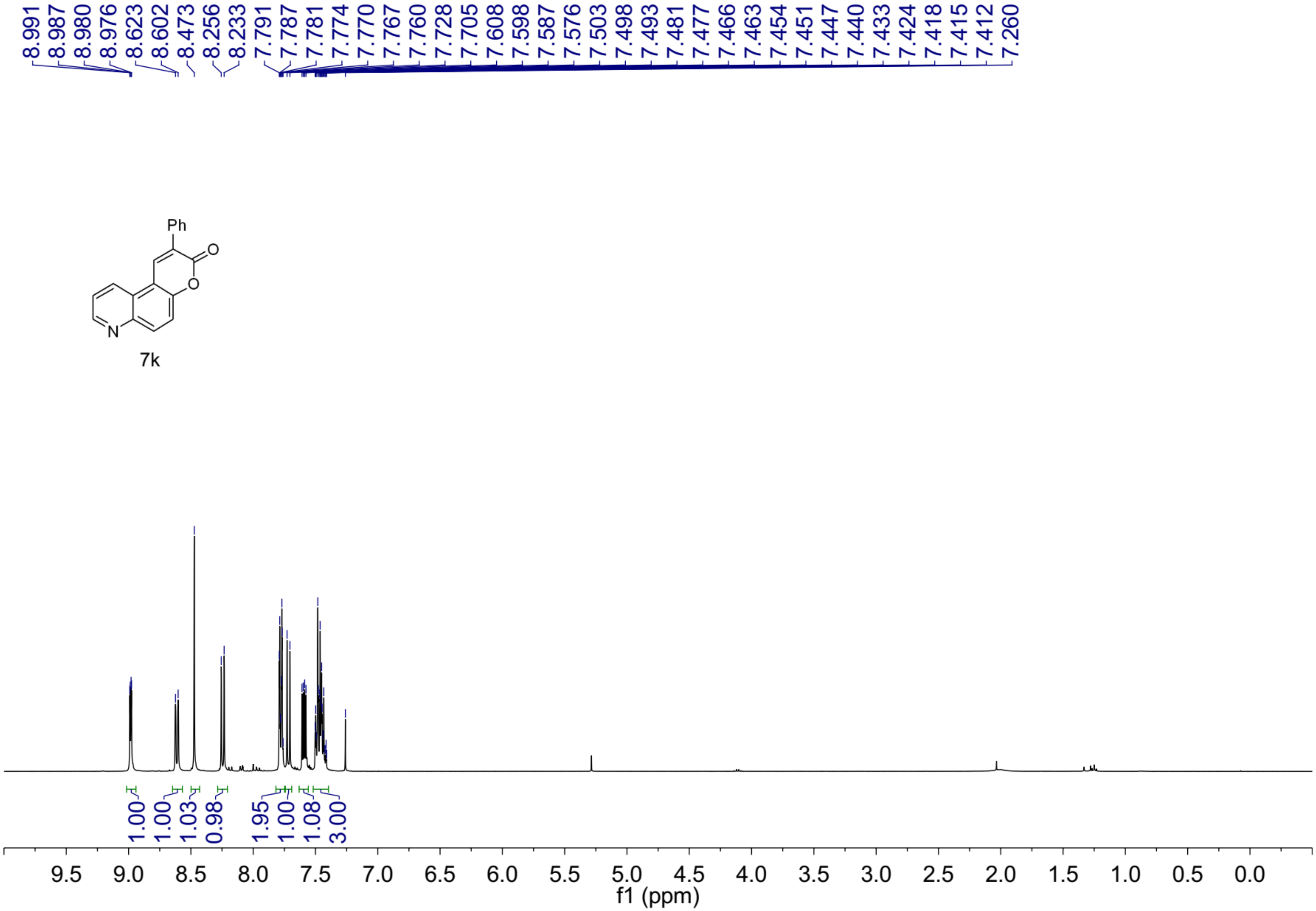
128.486
128.437
127.811
127.592
127.167
124.476
123.707
122.852
122.346
115.067
77.317
77.000
76.682
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.473
8.256
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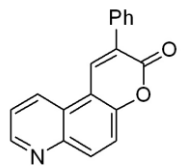
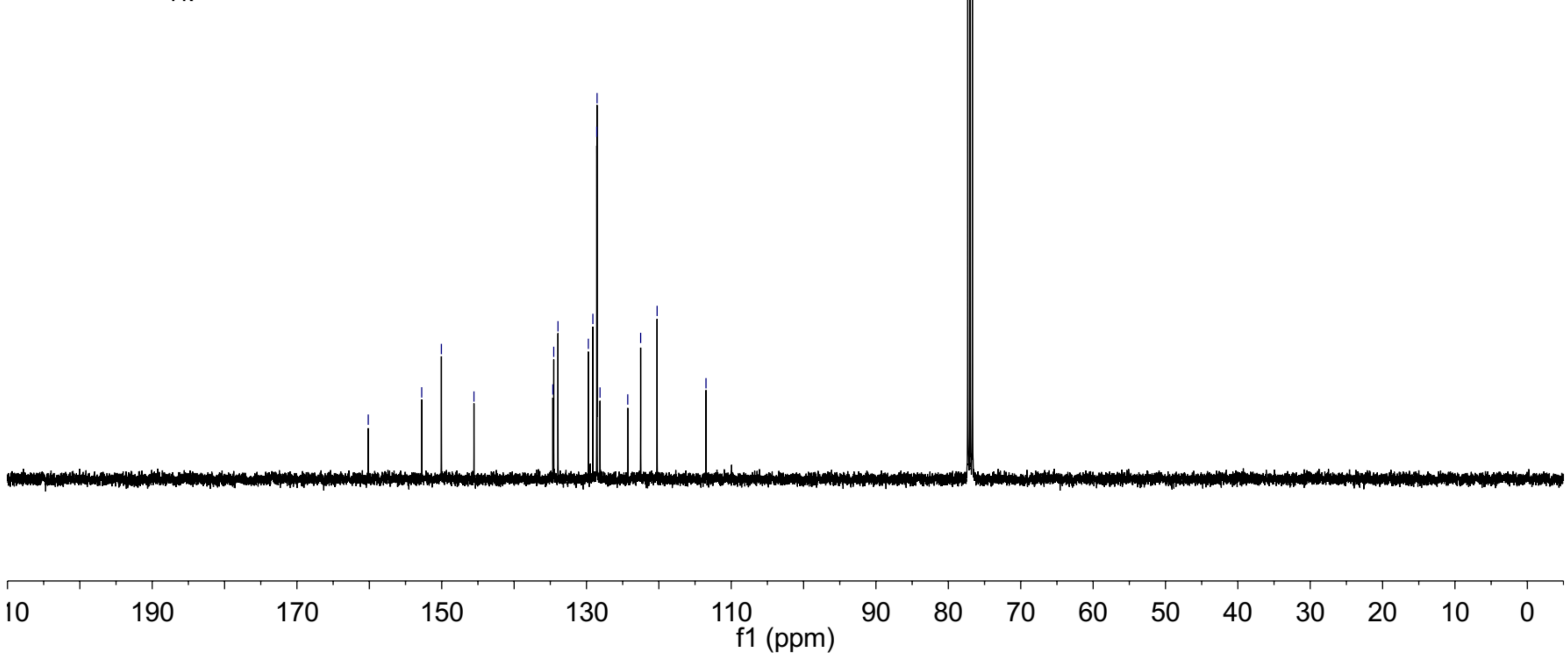
7.787
7.781
7.774
7.770
7.767
7.760
7.728
7.705
7.608
7.598
7.587
7.576
7.503
7.498
7.493
7.481
7.477
7.466
7.463
7.454
7.451
7.447
7.440
7.433
7.424
7.418
7.415
7.412
7.260
Ph
O
O
N
7k
1.00
1.00
1.03
0.98
1.95
1.00
1.08
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
O
O
N

7k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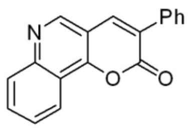
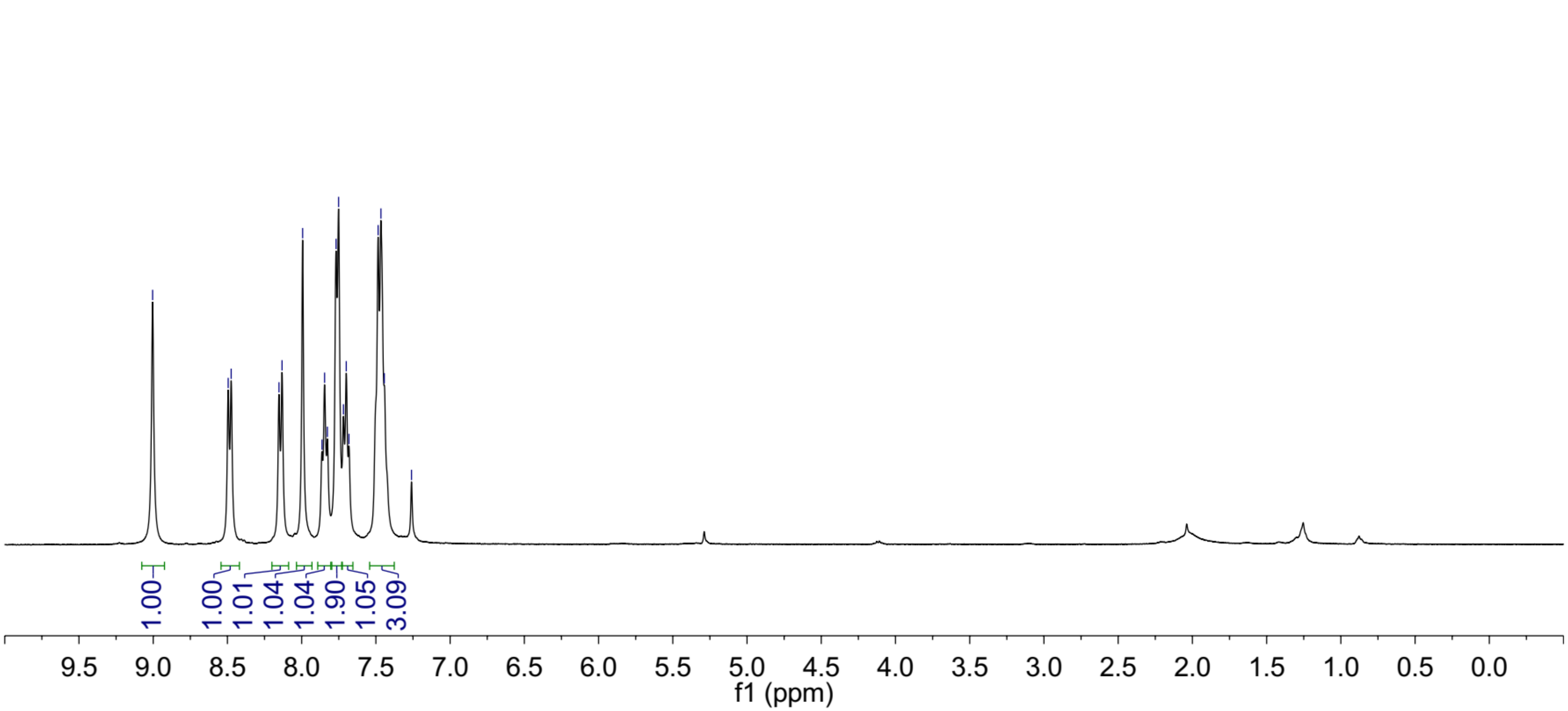
134.518
133.942
129.739
129.121
128.578
128.532
128.132
124.300
122.511
120.246
113.486
77.317
77.000
76.682
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7l



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8.153
8.132
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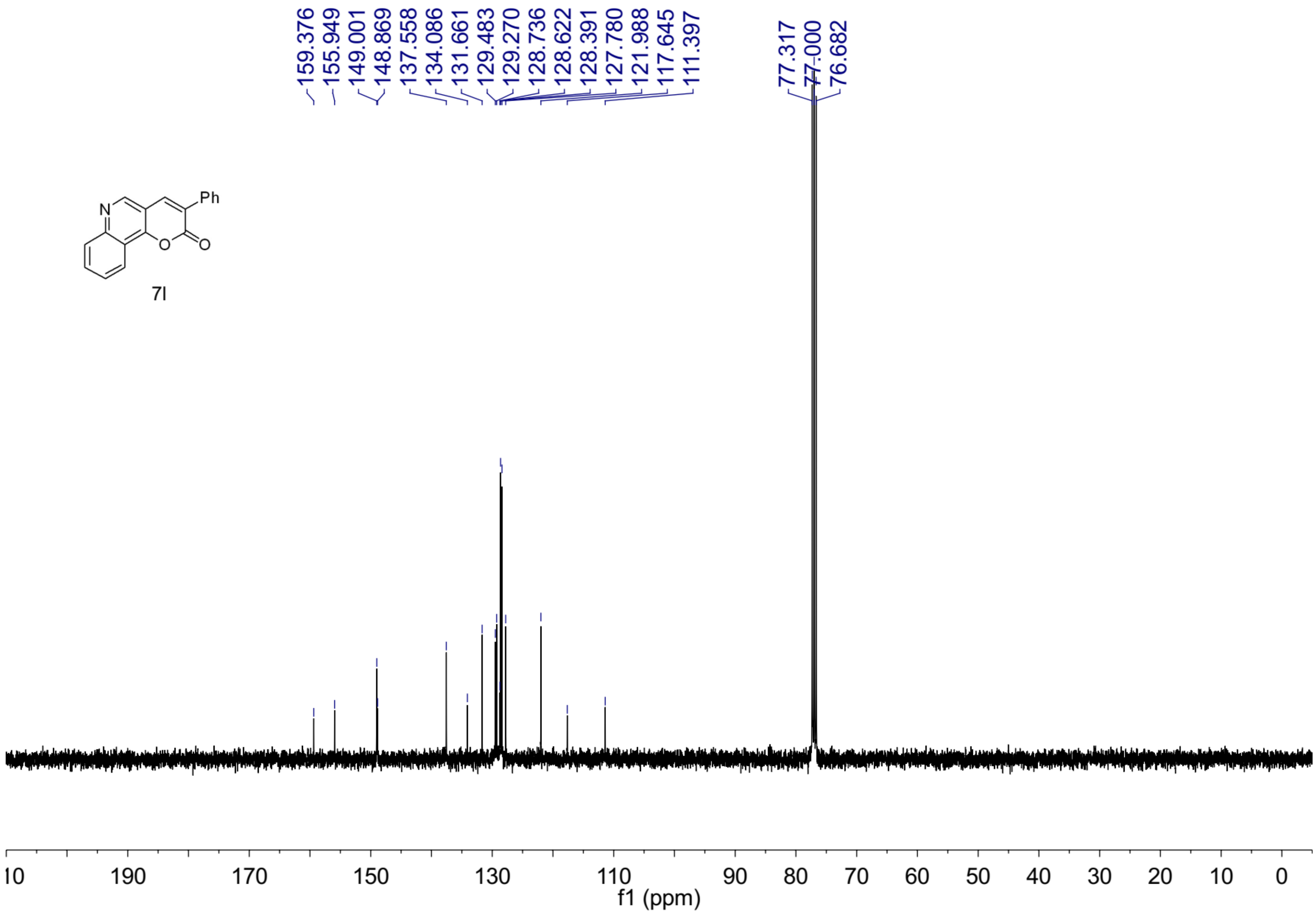
7.863
7.846
7.827
7.768
7.751
7.718
7.700
7.682
7.485
7.466
7.443
7.260
1.00
1.00
1.01
1.04
1.04
1.90
1.05
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.483
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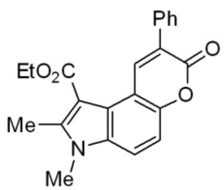
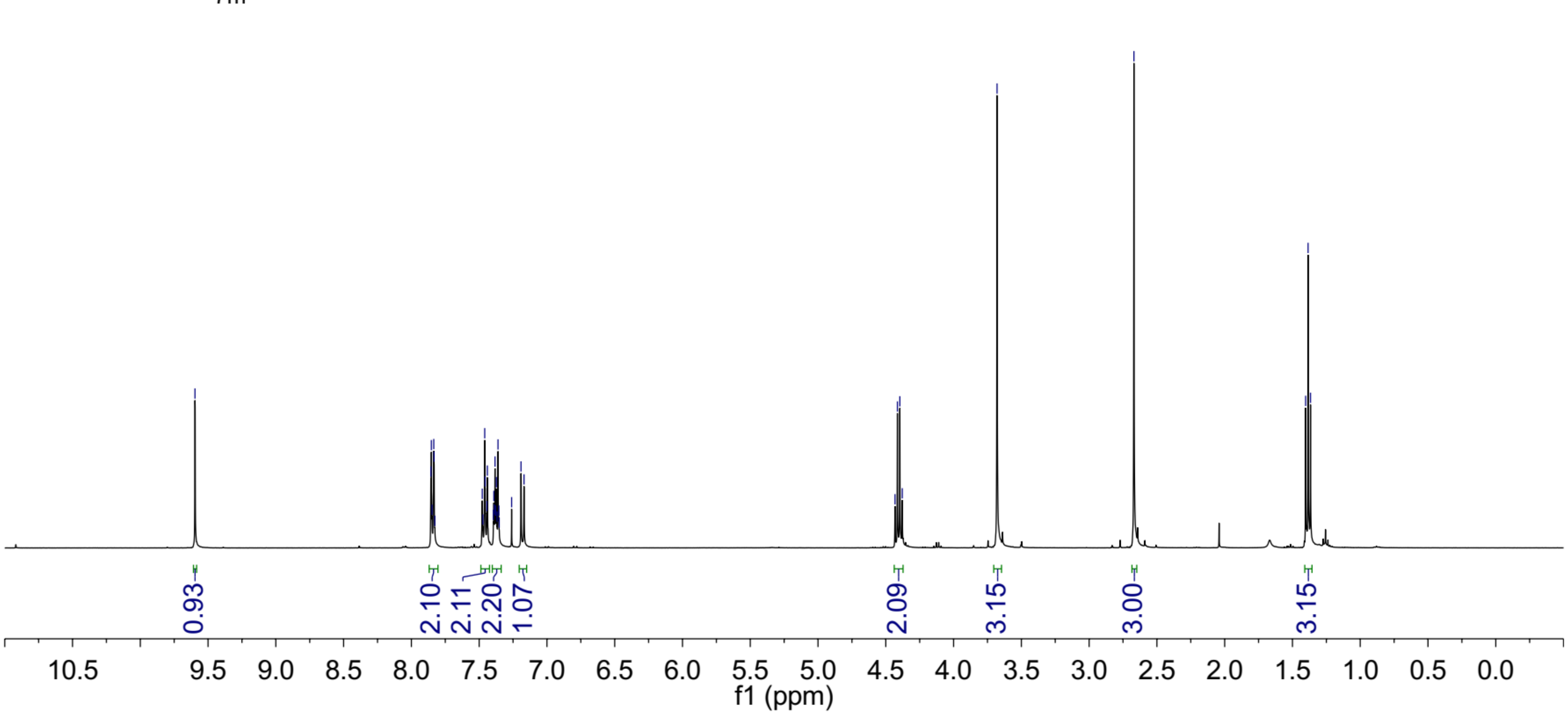
128.736
128.622
128.391
127.780
121.988
117.645
111.397
77.317
77.000
76.682
Ph
N
O
O
7l
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Ph
O
EtO2C
Me
N
Me
O

7m



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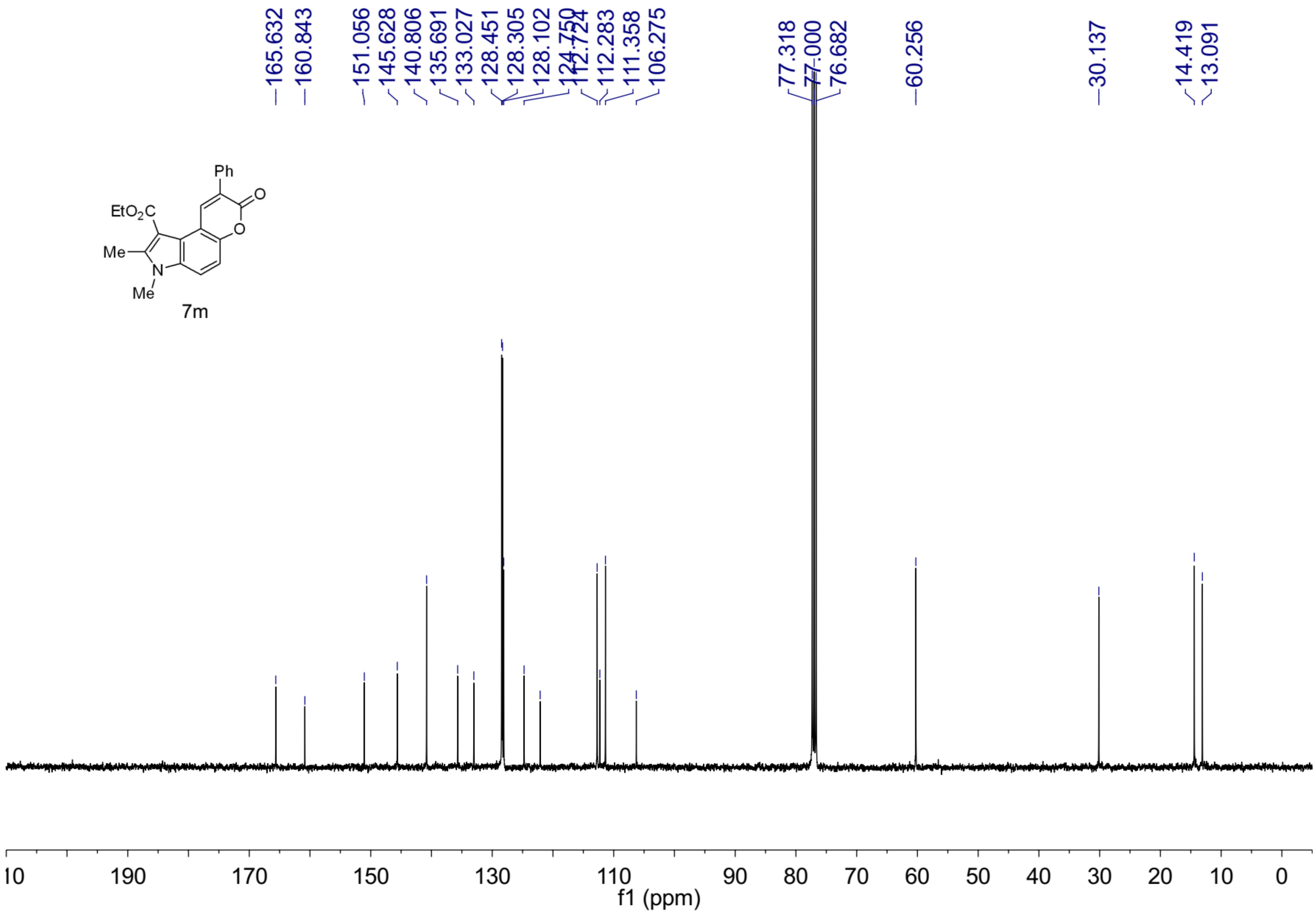
7.848
7.835
7.832
7.477
7.459
7.456
7.443
7.440
7.392
7.388
7.383
7.379
7.373
7.361
7.355
7.260
7.191
7.169
4.432
4.414
4.396
4.379
3.679
2.670
1.403
1.385
1.367
0.93
2.10
2.11
2.20
1.07
2.09
3.15
3.00
3.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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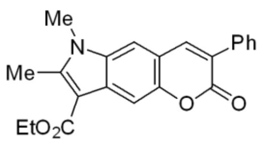
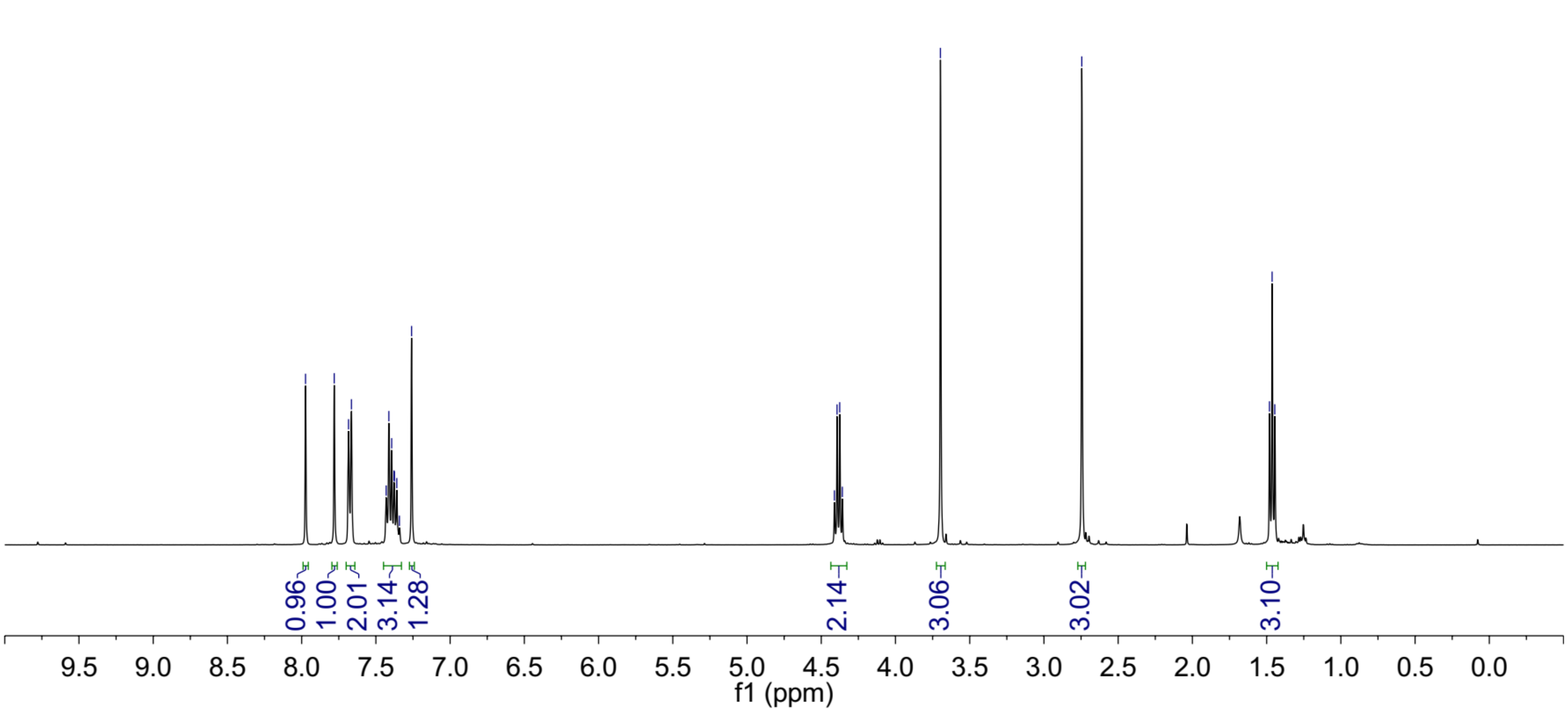
151.056
145.628
140.806
135.691
133.027
128.451
128.305
128.102
124.750
122.724
112.283
111.358
106.275
77.318
77.000
76.682
60.256
30.137
14.419
13.091
Ph
O
EtO2C
Me
N
Me
7m
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
N
Me
Ph
O
O
EtO2C

7n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7.684
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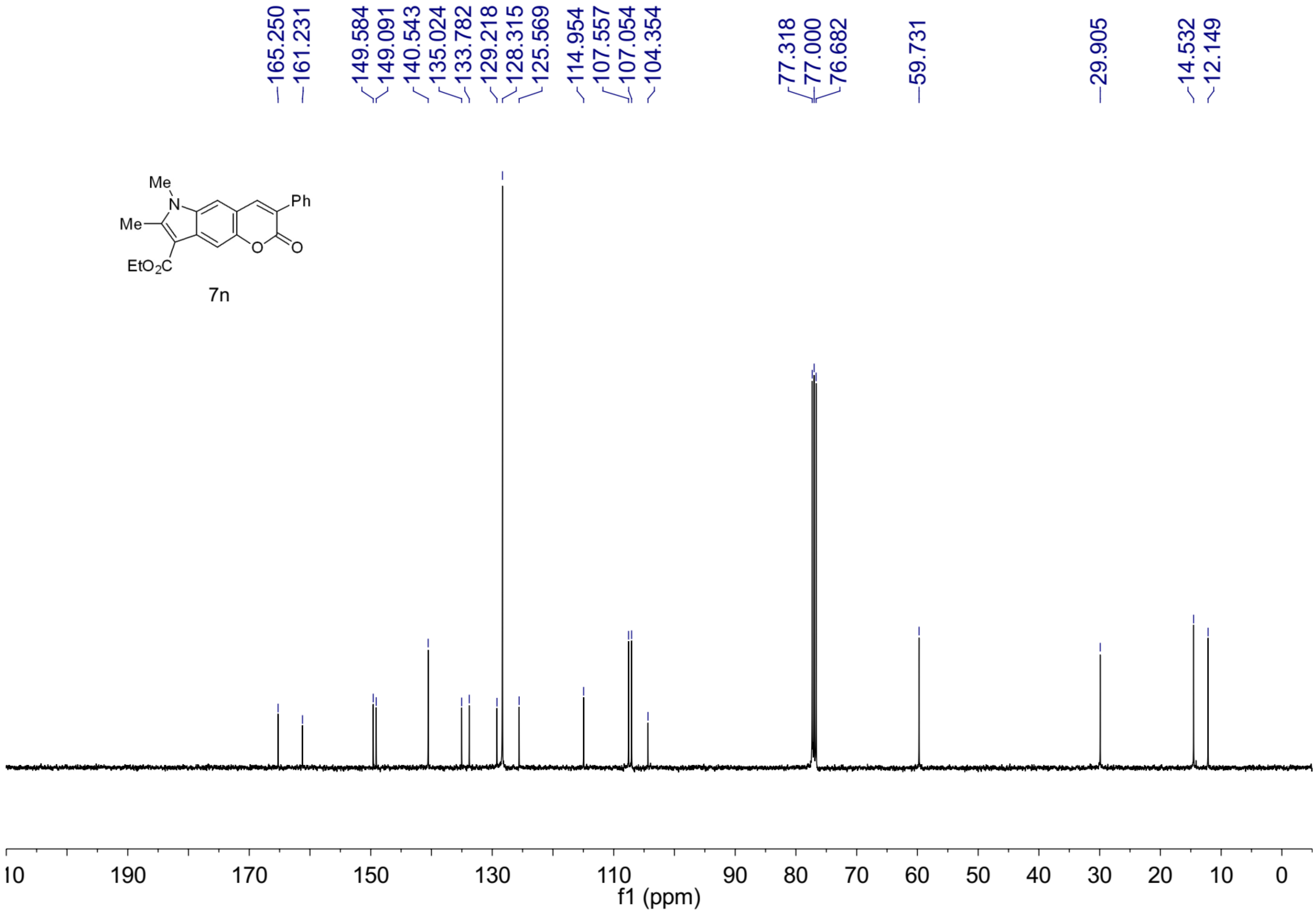
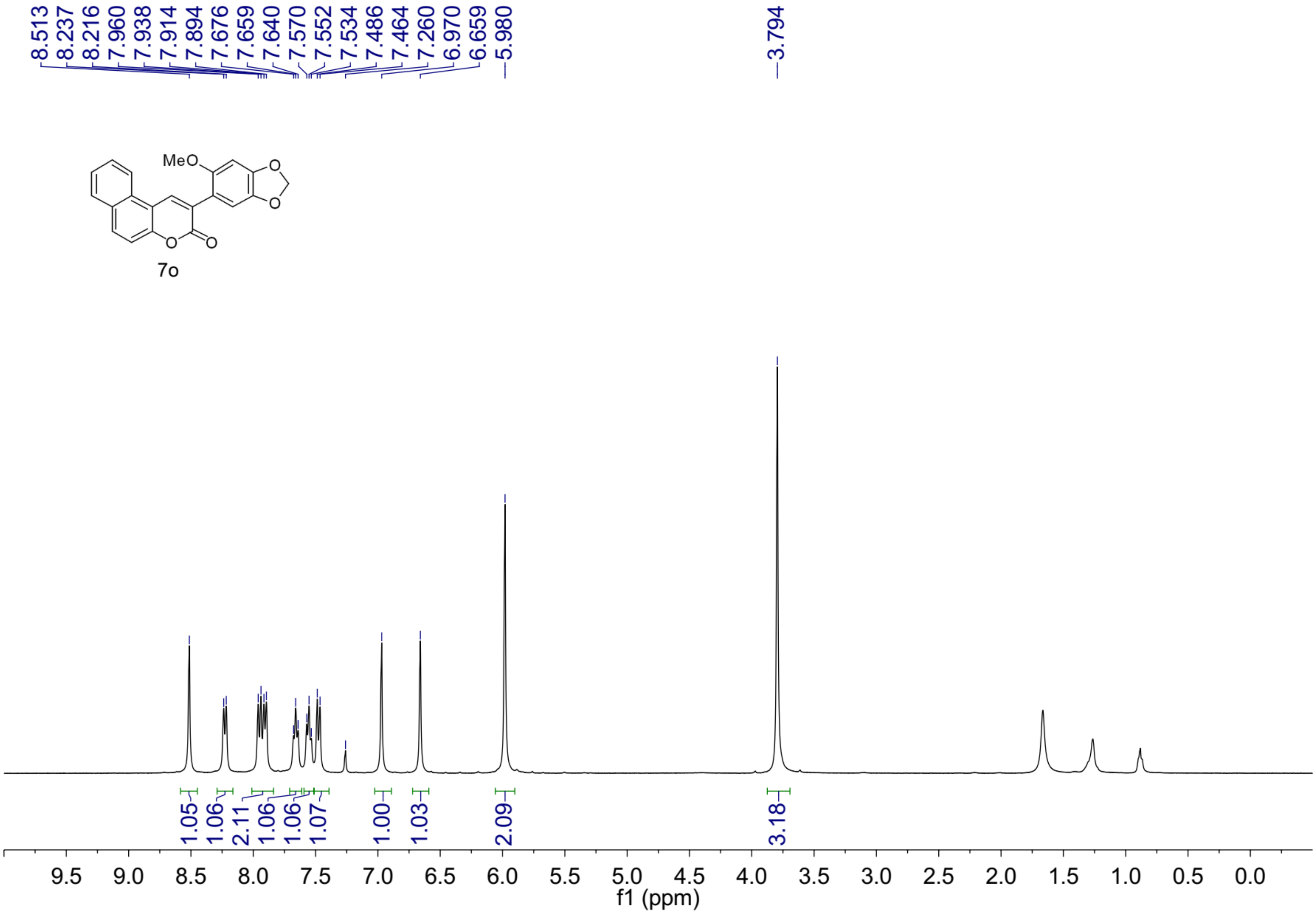
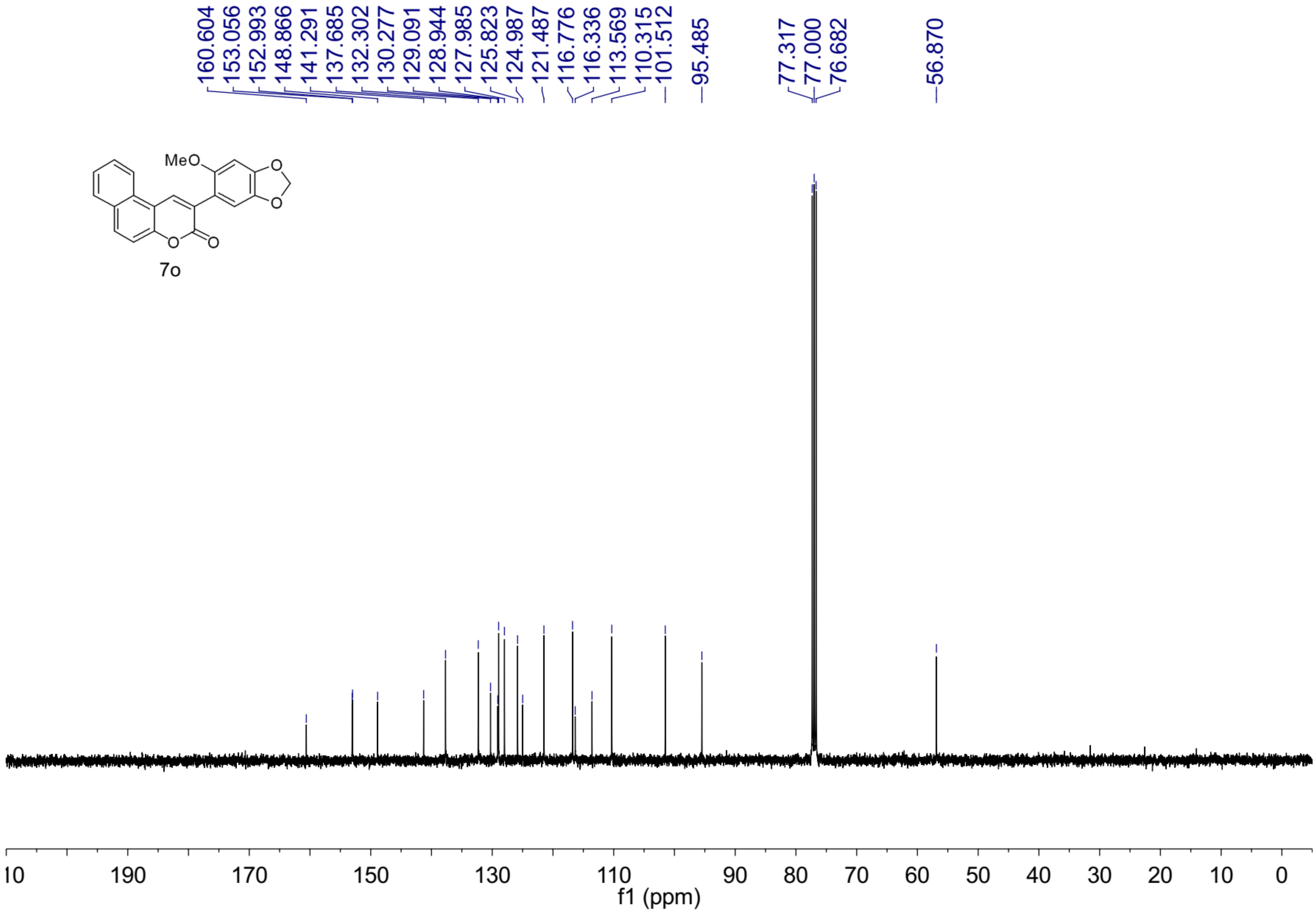
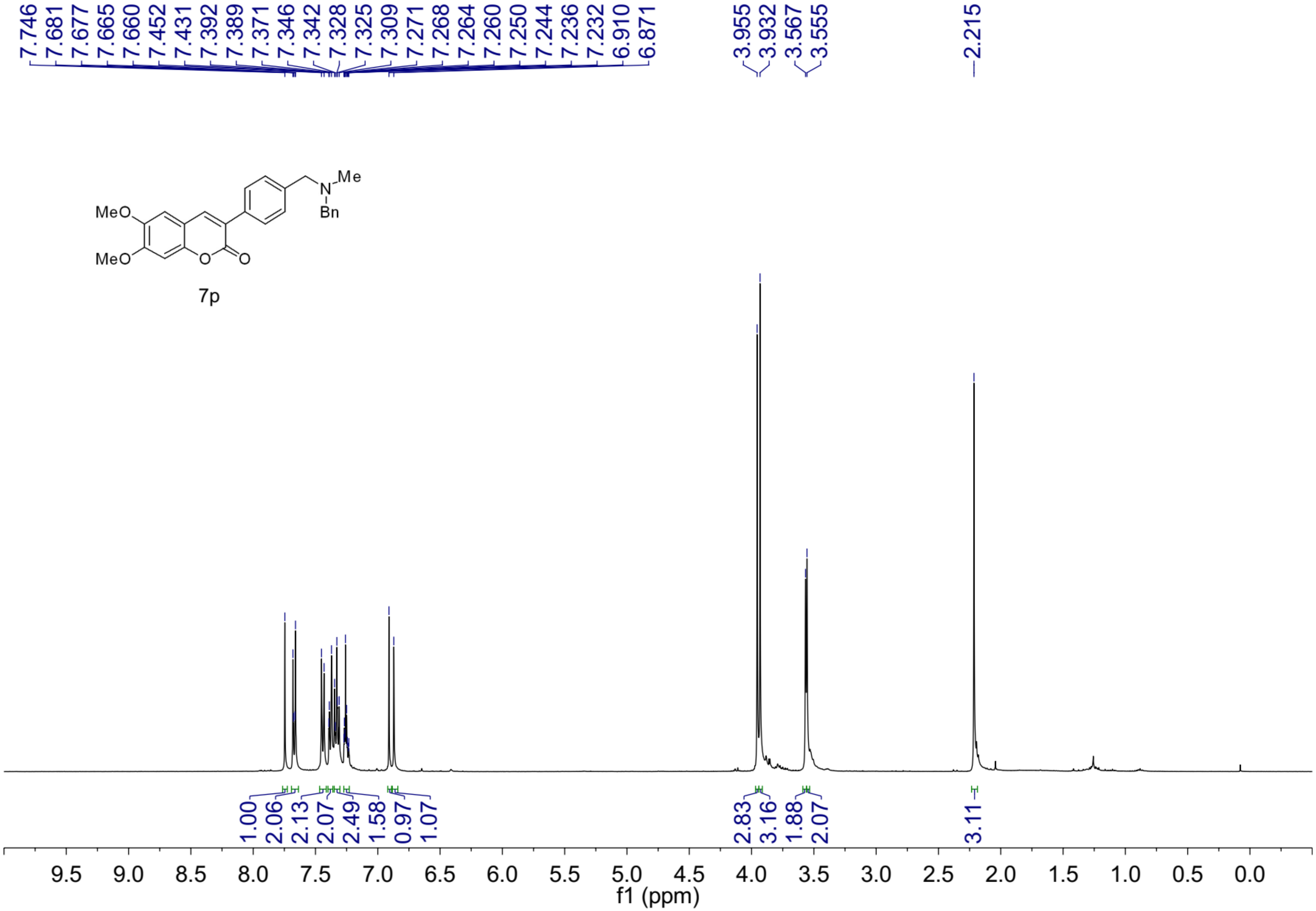
7.413
7.394
7.377
7.375
7.359
7.342
7.260
4.411
4.394
4.376
4.358
3.697
2.745
1.481
1.463
1.445
0.96
1.00
2.01
3.14
1.28
2.14
3.06
3.02
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

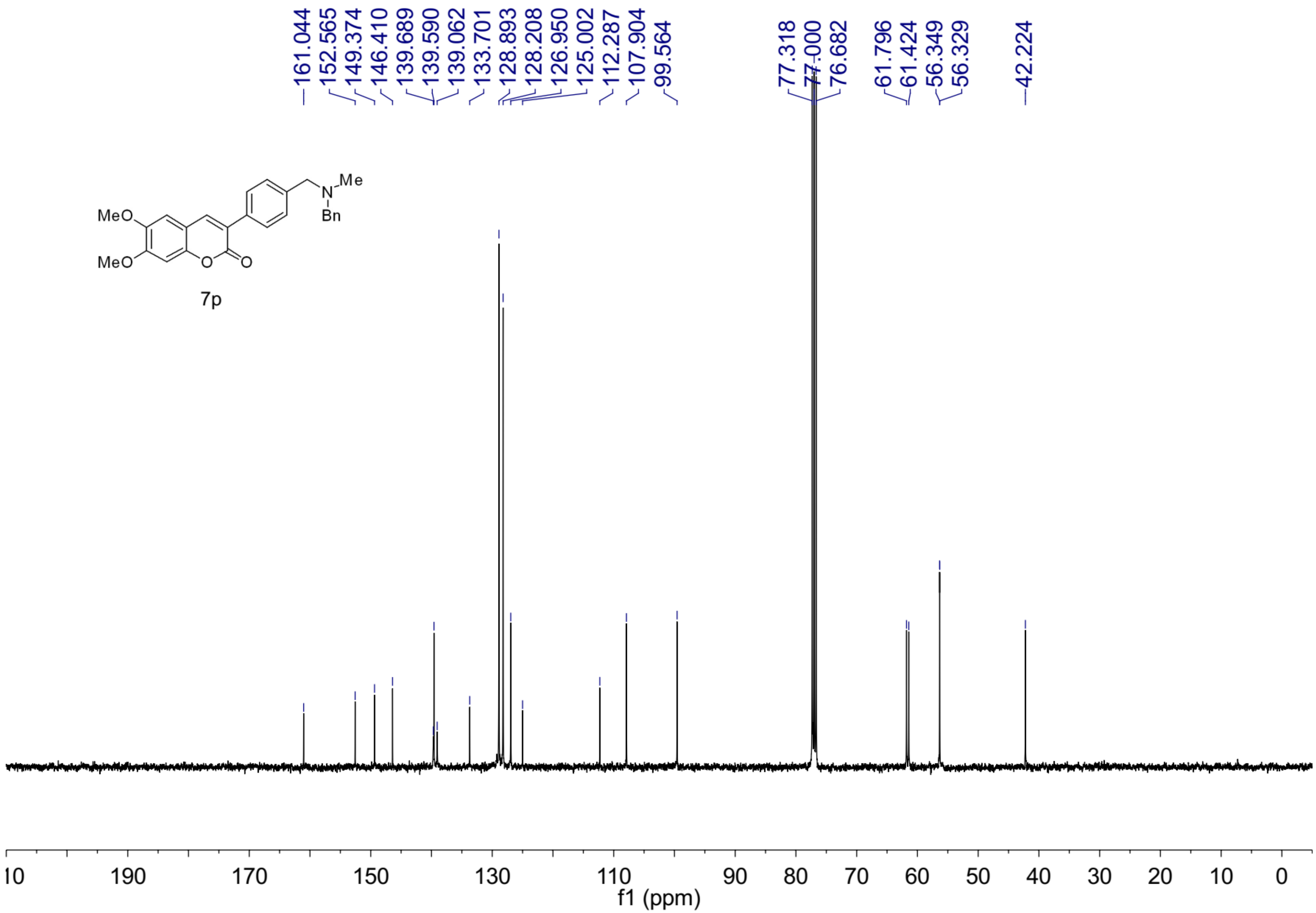

165.250
161.231
149.584
149.091
140.543
135.024
133.782
129.218
128.315
125.569
114.954
107.557
107.054
104.354
77.318
77.000
76.682
59.731
29.905
14.532
12.149
Me
N
Me
Ph
O
O
EtO2C
7n
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

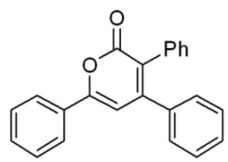

8.513
8.237
8.216
7.960
7.938
7.914
7.894
7.676
7.659
7.640
7.570
7.552
7.534
7.486
7.464
7.260
6.970
6.659
5.980
3.794
MeO
O
O
O
O
7o
1.05
1.06
2.11
1.06
1.06
1.07
1.00
1.03
2.09
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.604
153.056
152.993
148.866
141.291
137.685
132.302
130.277
129.091
128.944
127.985
125.823
124.987
121.487
116.776
116.336
113.569
110.315
101.512
95.485
77.317
77.000
76.682
56.870
MeO
O
O
O
O
7o
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

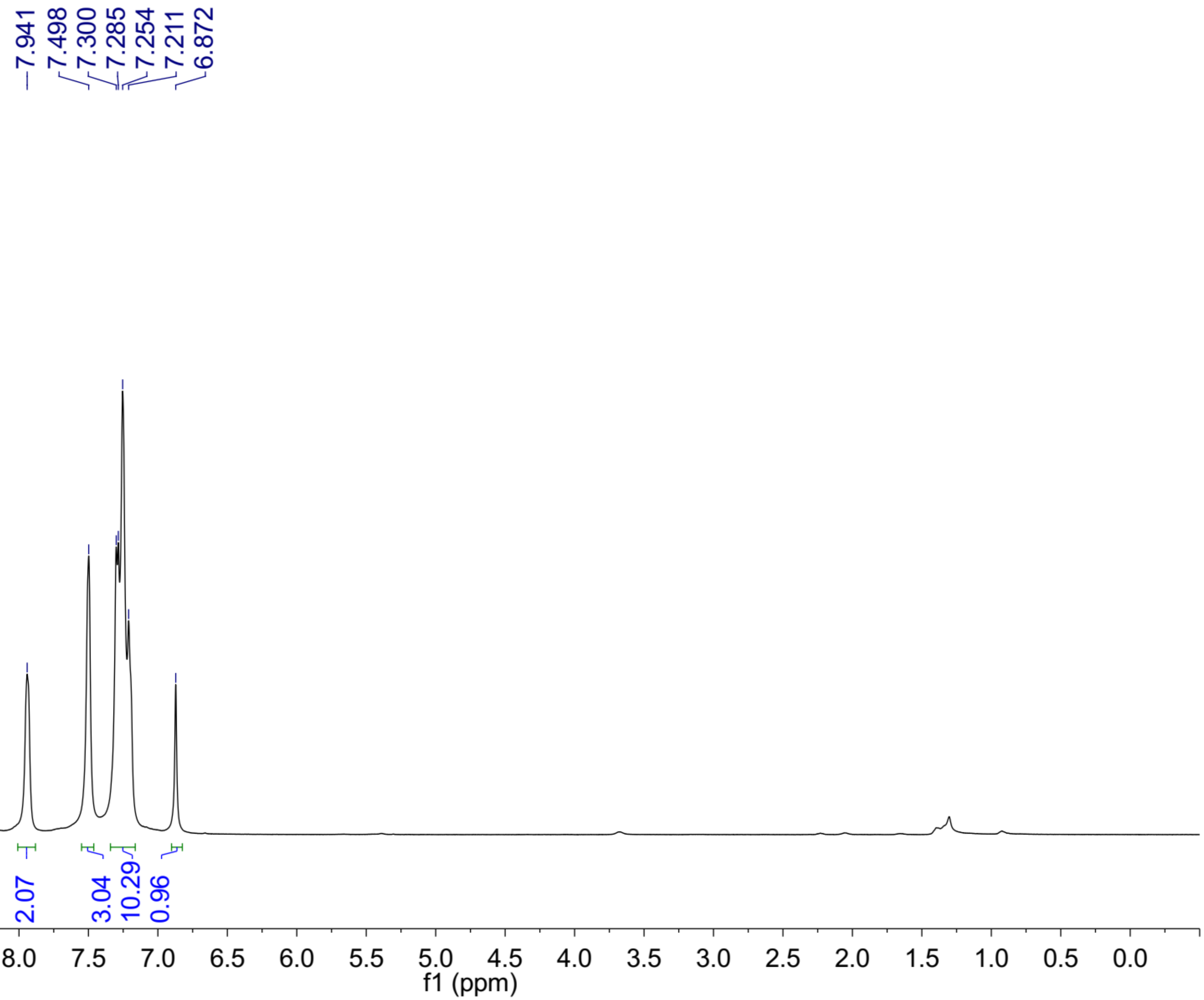

7.746
7.681
7.677
7.665
7.660
7.452
7.431
7.392
7.389
7.371
7.346
7.342
7.328
7.325
7.309
7.271
7.268
7.264
7.260
7.250
7.244
7.236
7.232
6.910
6.871
3.955
3.932
3.567
3.555
2.215
1.00
2.06
2.13
2.07
2.49
1.58
0.97
1.07
2.83
3.16
1.88
2.07
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
Me
N
Bn
MeO
MeO
O
O

7p

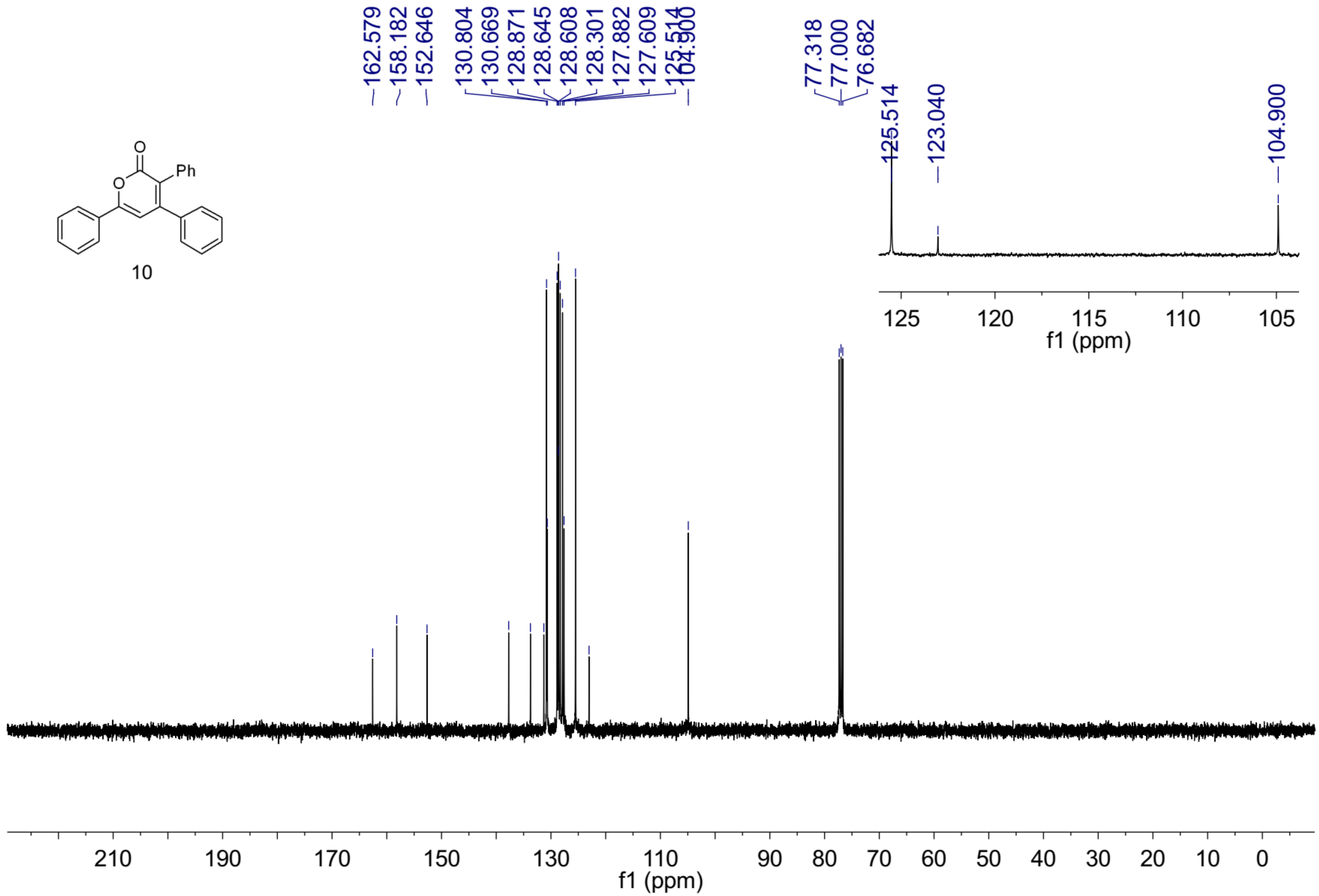

161.044
152.565
149.374
146.410
139.689
139.590
139.062
133.701
128.893
128.208
126.950
125.002
112.287
107.904
99.564
77.318
77.000
76.682
61.796
61.424
56.349
56.329
42.224
MeO
MeO
O
O
N
Me
Bn
7p
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



10



7.941
7.498
7.300
7.285
7.254
7.211
6.872
2.07
3.04
10.29
0.96
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)


162.579
158.182
152.646
130.804
130.669
128.871
128.645
128.608
128.301
127.882
127.609
125.514
104.900
77.318
77.000
76.682
125.514
123.040
104.900
125
120
115
110
105
f1 (ppm)
O
O
Ph
10
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)