Supporting Information

Metal-Free Synthesis of *gem*-Difluorinated Heterocycles from Enaminones and Difluorocarbene Precursors

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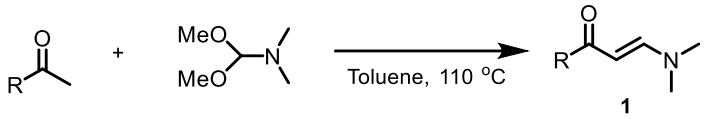
General methods:

Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 400 MHz Bruker or JEOL spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

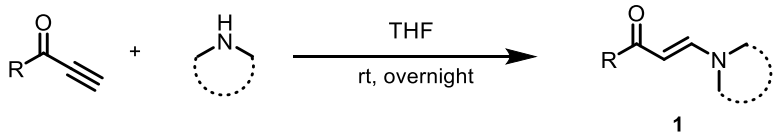
General procedure for synthesis of enaminones and their spectral data:

General procedure A for the synthesis of enaminones[1]:



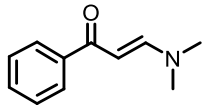
To a stirred solution of ketone (5.0 mmol, 1.0 equiv.) in 5.0 mL of toluene, 1, 1-dimethoxy-*N*, *N*-dimethylmethanamine (7.0 mmol, 1.4 equiv.) was added and stirred at 110 ℃. After completion of the reaction (monitored by TLC), it was quenched with water, extracted with ethyl acetate and dried with anhydrous Na_2SO_4. Then the reaction mixture is concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 1 : 1) to give the desired product **1**.

General procedure B for the synthesis of enaminones[2]:



To a stirred solution of ynones (3.0 mmol, 1.0 equiv.) in 10 mL of THF, amine (7.2 mmol, 2.4 equiv.) was added dropwise and stirred at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture is concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 2 : 1) to give the desired product **1**.

(*E*)-3-(Dimethylamino)-1-phenylprop-2-en-1-one (1a):



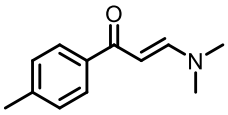
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 90 - 91 ℃. Yield 98% (857.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$)

1. Jiang, Y.; Zhong, V. Y. K.; Emmanuvel, L.; Park, C.-M. Synthesis of 2-aminofurans and 2-unsubstituted furansviacarbenoid-mediated [3 + 2] cycloaddition. *Chem. Commun.* **2012**, *48*, 3133-3135.

2. Šenica, L.; Grošelj, U.; Kasunič, M.; Kočar, D.; Stanovnik, B.; Svete, J. Synthesis of Enaminone-Based Vinylogous Peptides. *Eur. J. Org. Chem.* **2014**, *15*, 3067-3071.

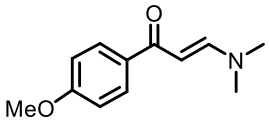
δ 7.91 – 7.89 (m, 2H), 7.79 (d, J = 12.4 Hz, 1H), 7.46 – 7.39 (m, 3H), 5.71 (d, J = 12.4 Hz, 1H), 3.11 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 154.1, 140.4, 130.7, 128.0, 127.3, 92.0, 44.9, 37.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{14}NO$: 176.1075. Found: 176.1075.

(*E*)-3-(Dimethylamino)-1-(p-tolyl)prop-2-en-1-one (1b):



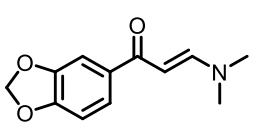
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 87 – 89 ℃. Yield 76% (718.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.77 (m, 3H), 7.22 - 7.20 (m, 2H), 5.72 (d, J = 12.4 Hz, 1H), 3.11 (s, 3H), 2.94 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 139.8, 128.4, 128.2, 126.2, 81.2, 78.9, 46.7, 29.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}O$: 190.1232. Found: 190.1228.

(*E*)-3-(Dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (1c):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 90 - 91 ℃. Yield 82% (840.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.77 (d, J = 12.4 Hz, 1H), 6.90 – 6.87 (m, 2H), 5.69 (d, J = 12.4 Hz, 1H), 3.82 (s, 3H), 3.06 – 2.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 161.9, 153.7, 133.0, 129.4, 113.2, 91.6, 55.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{16}NO_2$: 206.1181. Found: 206.1182.

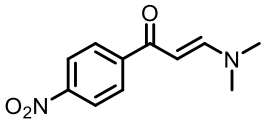
(*E*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(dimethylamino)prop-2-en-1-one (1d):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 127 – 129 ℃. Yield 65% (962.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 12.3 Hz, 1H), 7.45 (dd, J = 8.1, 1.7 Hz, 1H), 7.39 (d, J = 1.6 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 5.96 (s, 2H), 5.60 (d, J = 12.3 Hz, 1H), 3.08 (s, 3H) , 2.90 (s, 3H);

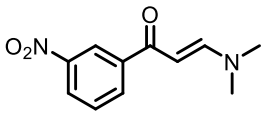
^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 154.2, 150.1, 147.8, 135.2. 122.7, 108.0, 107.7, 101.5, 91.7, 45.2, 37.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{17}O$: 153.1279. Found: 153.1277.

(*E*)-3-(Dimethylamino)-1-(4-nitrophenyl) prop-2-en-1-one (1e):



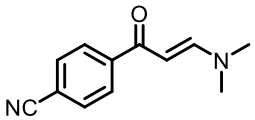
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 148 - 149 ℃. Yield 67% (737.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.23 (m, 2H), 8.01 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 12.4 Hz, 1H), 5.68 (d, J = 12.0 Hz, 1H), 3.21 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 155.2, 149.0, 146.0, 128.3, 123.3, 91.9, 45.3, 37.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O_3$: 221.0926. Found: 221.0932.

(*E*)-3-(Dimethylamino)-1-(3-nitrophenyl) prop-2-en-1-one (1f):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 116 - 117 ℃. Yield: 80% (880.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.32 - 8.29 (m, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 12.2 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 5.72 (d, J = 12.2 Hz, 1H), 3.21 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 155.2, 148.1, 142.0, 138.5, 129.2, 125.3, 122.2, 91.1, 45.3, 37.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O_3$: 221.0926. Found: 221.0922.

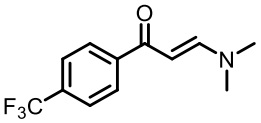
(*E*)-4-(3-(Dimethylamino)acryloyl)benzonitrile (1g):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 117 - 118 ℃. Yield: 82% (820.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 12.2 Hz, 1H), 7.71 – 7.69 (m, 2H), 5.66 (d, J = 12.2, 1H), 3.19 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 156.0, 145.2,

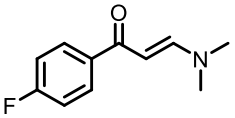
132.9, 128.9, 119.6, 114.9, 92.6, 46.2, 38.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_2O$: 201.1028. Found: 201.1026.

(*E*)-3-(Dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1h):



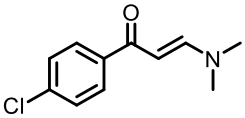
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 107 - 109 ℃. Yield: 76% (923.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8 Hz, 2H), 7.84 (d, J = 12.4 Hz, 1H), 7.66 (d, J = 8 Hz, 2H), 5.68 (d, J = 12.4 Hz, 1H), 3.18 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 154.8, 143.6, 132.4, 132.0, 127.7, 125.08 (q, J = 4.0 Hz), 122.6, 91.9, 45.2, 37.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{12}F_3NO$: 244.0949. Found: 244.0952.

(*E*)-3-(Dimethylamino)-1-(4-fluorophenyl) prop-2-en-1-one (1i):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 83 - 84 ℃. Yield: 88% (849.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.81 (d, J = 12.4 Hz, 1H), 7.10 – 7.05 (m, 2H), 5.67 (d, J = 12.4 Hz, 1H), 3.15 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 164.4 (d, J = 249 Hz), 154.3, 136.6 (d, J = 3.0 Hz), 129.7 (d, J = 9.0 Hz), 114.9 (d, J = 21.0 Hz), 91.6, 45.0, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}FNO$: 194.0981. Found: 194.0984.

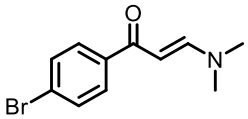
(*E*)-1-(4-Chlorophenyl)-3-(dimethylamino)prop-2-en-1-one (1j):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 88 - 89 ℃. Yield 83% (867.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.80 (d, J = 12.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 5.66 (d, J = 12.4 Hz, 1H), 3.15 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 154.5, 138.8, 136.9,

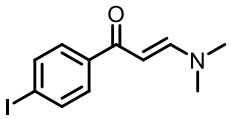
128.9, 128.2, 91.6, 45.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}ClNO$: 210.0686. Found: 210.0690.

(*E*)-1-(4-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (1k):



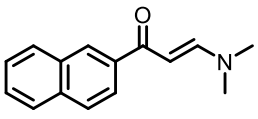
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 82 - 83 ℃. Yield: 84% (1062.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 12.4 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.54 – 7.52 (m, 2H), 5.65 (d, J = 12.0 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 154.5, 139.2, 131.2, 129.1, 125.4, 91.6, 45.0, 37.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}BrNO$: 254.0181. Found: 254.0184.

(*E*)-3-(Dimethylamino)-1-(4-iodophenyl)prop-2-en-1-one (1l):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 121 - 122 ℃. Yield: 65% (978.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 12.4 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.63 – 7.61 (m, 2H), 5.64 (d, J = 12.4 Hz, 1H), 3.12 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 154.4, 139.7, 129.0, 97.7, 91.4, 45.0, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}INO$: 302.0042. Found: 302.0039.

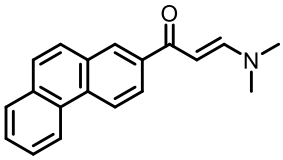
(*E*)-3-(Dimethylamino)-1-(naphthalen-2-yl)prop-2-en-1-one (1m):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 113 - 114 ℃. Yield: 77% (866.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.03 – 8.00 (m, 1H), 7.95 – 7.93 (m, 1H), 7.88 – 7.84 (m, 3H), 7.55 – 7.48 (m, 2H), 7.87 (d, J = 12.4 Hz, 1H), 3.14 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz,

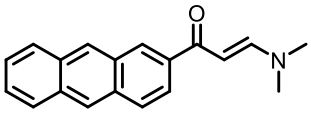
$CDCl_3$) δ 188.4, 154.2, 137.8, 134.6, 132.7, 129.1, 127.7, 127.6, 127.1, 126.1, 124.6, 92.3, 45.0, 37.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{16}NO$: 226.1232. Found: 226.1233.

(*E*)-3-(Dimethylamino)-1-(phenanthren-2-yl)prop-2-en-1-one (1n):



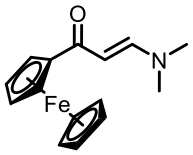
The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 158 - 160 ℃. Yield: 85% (1168.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.65 (m, 2H), 8.43 (d, J = 1.7 Hz, 1H), 8.19 – 8.16 (m, 1H), 7.88 – 7.86 (m, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.66 – 7.57 (m, 2H), 5.87 (d, J = 12.3 Hz, 1H) 3.07 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 154.1, 138.2, 132.4, 131.8, 131.4, 129.7, 128.4, 127.9, 127.3, 127.1, 126.9, 126.5, 125.3, 122.9, 122.4, 92.0, 44.8, 37.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}NO$: 276.1388. Found: 276.1385.

(*E*)-1-(Anthracen-2-yl)-3-(dimethylamino)prop-2-en-1-one (1o):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 182 - 183 ℃. Yield: 87% (1224.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 18.8 Hz, 2H), 8.38 (s, 1H), 8.00 (s, 4H), 7.86 (d, J = 12.2 Hz, 1H), 7.51 – 7.40 (m, 2H), 5.88 (d, J = 12.2 Hz, 1H), 3.08 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 154.2, 137.1, 132.4, 132.3, 131.8, 130.8, 128.4, 128.2, 128.1, 128.0, 128.0, 125.9, 125.4, 124.0, 92.2, 44.9, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}NO$: 276.1388. Found: 276.1385.

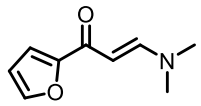
(*E*)-3-(Dimethylamino)-1-ferrocenyl -2-en-1-one (1p):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 65 - 66 ℃. Yield: 34% (481.4 mg); ^{1}H NMR (400 MHz,

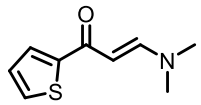
CDCl3) δ 7.71 (d, J = 12.5 Hz, 1H), 5.36 (d, J = 12.5 Hz, 1H), 4.78 (s, 2H), 4.38 (s, 2H), 4.16 (s, 5H), 3.00 (br, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 191.7, 151.6, 93.1, 82.5, 70.9, 69.8, 69.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}FeNO_2$: 284.0738. Found: 284.0739.

(*E*)-3-(Dimethylamino)-1-(furan-2-yl)prop-2-en-1-one (1q):



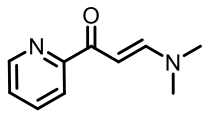
The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 80 - 81 ℃. Yield: 81% (668.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 12.4 Hz, 1H), 7.49 (s, 1H), 7.06 (d, J = 2.8 Hz, 1H), 6.48 (s, 1H), 5.68 (d, J = 12.8 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 154.7, 153.5, 144.1, 113.3, 111.7, 91.4, 44.9, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{12}NO_2$: 166.0868. Found: 166.0869.

(*E*)-3-(Dimethylamino)-1-(thiophen-2-yl)prop-2-en-1-one (1r):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 117 - 118 ℃. Yield: 79% (715.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 12.4 Hz, 1H), 7.62 – 7.61 (m, 1H), 7.47 – 7.45 (m, 1H), 7.08 – 7.06 (m, 1H), 5.62 (d, J = 12.0 Hz, 1H), 3.10 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 153.4, 147.3, 130.0, 128.2, 127.4, 91.5, 44.8, 37.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{12}NOS$: 182.0640. Found: 182.0640.

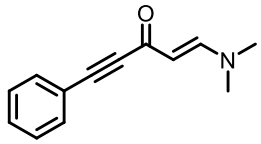
(*E*)-3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (1s):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 124 - 125 ℃. Yield: 71% (625.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 – 8.62 (m, 1H), 8.15 (d, J = 10.4 Hz, 1H), 7.92 (d, J = 12.7 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.38 – 7.34 (m, 1H), 6.45 (d, J = 12.7 Hz, 1H), 3.18 (s, 3H), 3.00 (s, 3H); ^{13}C

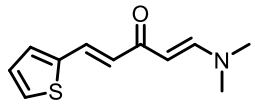
NMR (100 MHz, $CDCl_3$) δ 186.0, 155.5, 154.1, 147.6, 136.1, 124.8, 121.2, 90.4, 44.5, 36.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}N_2O$: 177.1028. Found: 177.1030.

(*E*)-1-(Dimethylamino)-5-phenylpent-1-en-4-yn-3-one (1t):



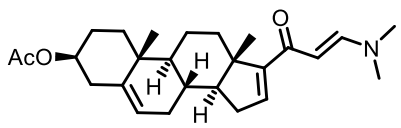
The title compound was prepared according to the general procedure A. The product was obtained as brown solid, Mp. 86 - 87 ℃. Yield: 87% (865.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 12.8 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.39 – 7.33 (m, 3H), 5.31 (d, J = 12.7 Hz, 1H), 3.16 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 132.3, 129.5, 128.4, 121.3, 45.3, 37.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}NO$: 200.1075. Found: 200.1075.

(*1E, 4E*)-1-(Dimethylamino)-5-(thiophen-2-yl) penta-1, 4-dien-3-one (1u):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 109 - 111 ℃. Yield: 52% (538.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.28 (d, J = 4.8 Hz, 1H), 7.20 (d, J = 3.4 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.60 (d, J = 15.5 Hz, 1H), 5.22 (d, J = 12.4 Hz, 1H), 3.11 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 162.5, 153.3, 141.2, 131.1, 129.8, 127.5, 126.9, 44.9, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{14}NOS$: 208.0796. Found: 208.0799.

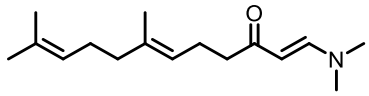
(3*S*, 8*R*, 9*S*, 10*R*, 13*S*, 14*S*)-17-((*E*)-3-(Dimethylamino)acryloyl)-10, 13-dimethyl-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (1v):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 175 - 176 ℃. Yield: 62% (1274.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 12.8 Hz, 1H), 6.48 – 6.36 (m, 1H), 5.44 – 5.34 (m, 2H), 4.66 – 4.55 (m,

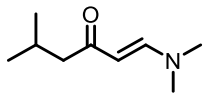
1H), 2.95 (s, 6H), 2.43 – 2.30 (m, 3H), 2.28 – 2.21 (m, 1H), 2.08 – 1.95 (m, 5H), 1.90 – 1.82 (m, 2H), 1.76 – 1.52 (m, 5H), 1.48 – 1.36 (m, 2H), 1.20 – 1.09 (m, 1H), 1.04 (d, *J* = 18.4 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8 , 170.4 , 156.6 , 152.2 , 140.1 , 136.6 , 122.1 , 93.8 , 73.9 , 56.4 , 50.4 , 46.6 , 38.1 , 36.8 , 36.7 , 34.7 , 31.9 , 31.6 , 30.2 , 27.7 , 21.4 , 20.7 , 19.2 , 16.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{26}H_{38}NO_3$: 412.2852. Found: 412.2856.

(1*E*, 6*E*)-1-(Dimethylamino)-6, 11-dimethyldodeca-1, 6, 10-trien-3-one (1w):



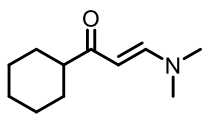
The title compound was prepared according to the general procedure A. The product was obtained as yellow oil. Yield: 72% (899.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 12.8 Hz, 1H), 5.17 – 5.03 (m, 2H), 5.03 (d, *J* = 12.4 Hz, 1H), 3.00 – 2.84 (m, 6H), 2.36 – 2.29 (m, 4H), 2.06 – 2.03 (m, 3H), 1.99 – 1.97 (m, 1H), 1.62 – 1.59 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6 (d, *J* = 9.0 Hz), 152.1, 135.4 (d, *J* = 13.0 Hz), 131.2 (d, *J* = 22.0 Hz), 124.3 (d, *J* = 18.0 Hz), 123.6, 95.7, 41.5, 39.6, 31.8, 26.5 (d, *J* = 12.0 Hz), 25.6 (d, *J* = 3.0 Hz), 24.2, 24.1, 23.3, 17.5 (d, *J* = 1.0 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{28}NO$: 250.2171. Found: 250.2177.

(*E*)-1-(Dimethylamino)-5-methylhex-1-en-3-one (1x):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 80% (620.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.8 Hz, 1H), 3.00 – 2.88 (m, 6H), 2.21 (d, *J* = 6.8 Hz, 2H), 2.17 – 2.07 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 152.2, 96.5, 51.0, 26.2, 22.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{18}NO$: 156.1388. Found: 156.1388.

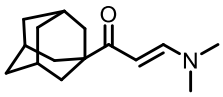
(*E*)-1-Cyclohexyl-3-(dimethylamino) prop-2-en-1-one (1y):



The title compound was prepared according to the general procedure A. The product was obtained as yellow solid, Mp. 41 - 42 ℃. Yield: 14% (127.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$)

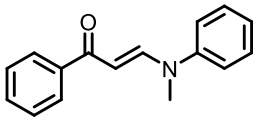
δ 7.55 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 3.05 (s, 3H), 2.83 (s, 3H), 2.30 – 2.24 (m, 1H), 1.80 – 1.76 (m, 4H), 1.68 – 1.65 (m, 1H), 1.44 – 1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 200.8, 151.9, 93.6, 49.6, 44.2, 36.5, 29.3, 25.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{20}NO$: 182.1545. Found: 182.1548.

(*E*)-1-((1r, 3*R*, 5*S*)-Adamantan-1-yl)-3-(dimethylamino) prop-2-en-1-one (1z):



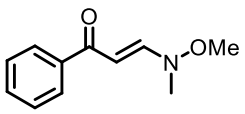
The title compound was prepared according to the general procedure B. The product was obtained as white solid, Mp. 117 - 118 ℃. yield: 34% (397.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 2.87 (s, 6H),1.95 (s, 3H) 1.76 (d, 6H), 1.66 – 1.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 203.1, 153.3, 90.1, 40.0, 39.4, 36.1, 28.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{23}NO$: 234.1858. Found: 234.1858.

(*E*)-3-(Methyl(phenyl)amino)-1-phenylprop-2-en-1-one (1aa):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 110 - 112 ℃. Yield: 70% (830.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.23 (d, *J* = 12.7 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.51 – 7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 7.22 – 7.15 (m, 3H), 6.10 (d, *J* = 12.7 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 189.4, 149.9, 146.4, 140.0, 131.3, 129.5, 128.2, 127.6, 124.9, 120.4, 96.8, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{16}NO$: 238.1232. Found: 238.1234.

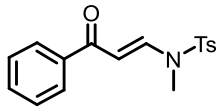
(*E*)-3-(Methoxy(methyl)amino)-1-phenylprop-2-en-1-one (1ab):



The title compound was prepared according to the general procedure B. The product was obtained as brown oil. Yield: 80% (765.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.94 – 7.91 (m, 2H), 7.64 (d, *J* = 12.4 Hz, 1H), 7.48 – 7.40 (m, 3H), 6.13 (d, *J* = 12.4 Hz, 1H), 3.71 (s, 3H),

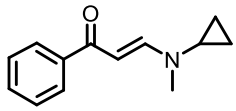
3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 148.9, 139.5, 131.3, 128.1, 127.6, 93.5, 59.7, 39.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{14}NO_2$: 192.1025. Found: 192.1025.

(*E*)-*N*, 4-Dimethyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (1ac):



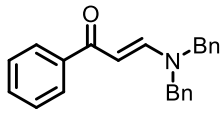
The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 159 - 160 ℃. Yield: 75% (1180.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 13.2 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.73 – 7.71 (m, 2H), 7.56 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 7.35 – 7.33 (m, 2H), 6.14 (d, J = 13.6 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 145.0, 143.7, 138.4, 134.3, 132.4, 130.2, 128.5, 128.0, 127.2, 103.1, 32.4, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{18}NO_3S$: 316.1007. Found: 316.1004.

(*E*)-3-(Cyclopropyl(methyl)amino)-1-phenylprop-2-en-1-one (1ad):



The title compound was prepared according to the general procedure B. The product was obtained as yellow oil. Yield: 80% (805.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.68 (m, 3H), 7.51 – 7.36 (m, 3H), 5.77 (s, 1H), 2.97 (s, 3H), 2.81 (s, 1H), 0.77 (d, J = 12.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 153.5, 140.3, 130.8, 128.0, 127.4, 93.1, 37.7, 36.7, 7.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}NO$: 202.1232. Found: 202.1233.

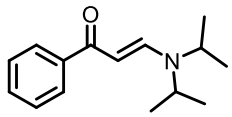
(*E*)-3-(Dibenzylamino)-1-phenylprop-2-en-1-one (1ae):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 111 - 113 ℃. Yield: 80% (1308.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 12.6 Hz, 1H), 7.86 – 7.84 (m, 2H), 7.46 – 7.32 (m, 9H), 7.22 – 7.20 (m, 4H), 6.01 (d, J = 12.6 Hz, 1H), 4.47 (s, 2H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

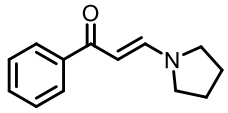
189.2, 154.1, 140.2, 135.6, 135.0, 131.0, 128.9, 128.1, 127.8, 127.5, 127.2, 93.1, 59.3, 50.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{21}NO$: 328.1701. Found: 328.1702.

(E)-3-(Diisopropylamino)-1-phenylprop-2-en-1-one (1af):



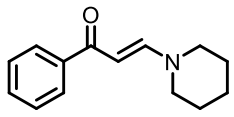
The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 107 - 109 ℃. Yield: 85% (981.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 12.4 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.42 – 7.35 (m, 3H), 5.87 (d, J = 12.4 Hz, 1H), 3.98 (s, 1H), 3.59 (s, 1H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 148.8, 140.8, 130.5, 127.9, 127.3, 91.5, 49.2, 48.0, 23.5, 19.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{22}NO$: 232.1701. Found: 232.1705.

(*E*)-1-Phenyl-3-(pyrrolidin-1-yl)prop-2-en-1-one (1ag):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 121 - 123 ℃. Yield: 87% (875.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 12.4 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.47 – 7.38 (m, 3H), 5.68 (d, J = 12.4 Hz, 1H), 3.55 (d, J = 5.5 Hz, 2H), 3.27 (s, 2H), 2.04 – 1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 149.8, 140.5, 130.6, 128.0, 127.4, 92.9, 52.2, 46.9, 25.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}NO$: 202.1232. Found: 202.1230.

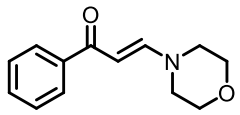
(*E*)-1-Phenyl-3-(piperidin-1-yl)prop-2-en-1-one (1ah):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 93 - 95 ℃. Yield: 85% (914.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.78 (d, J = 12.5 Hz, 1H), 7.46 – 7.38 (m, 3H), 5.82 (d, J = 12.5 Hz, 1H), 3.36 (s, 4H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 153.0, 140.7, 130.7,

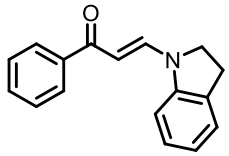
128.0, 127.3, 91.1, 54.8, 23.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}NO$: 216.1388. Found: 216.1390.

(*E*)-3-Morpholino-1-phenylprop-2-en-1-one (1ai):



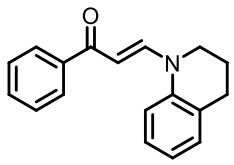
The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 105 - 107 ℃. Yield: 83% (901.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 2H), 7.74 (d, J = 12.6 Hz, 1H), 7.49 – 7.40 (m, 3H), 5.88 (d, J = 12.6 Hz, 1H), 3.76 (t, J = 4.8 Hz, 4H), 3.40 (t, J = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 152.7, 140.1, 131.1, 128.1, 127.5, 92.4, 66.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}NO_2$: 218.1181. Found: 218.1174.

(*E*)-3-(Indolin-1-yl)-1-phenylprop-2-en-1-one (1aj):



The title compound was prepared according to the general procedure B. The product was obtained as yellow solid, Mp. 120 - 122 ℃. Yield: 88% (658.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.35 (m, 1H), 7.96 – 7.92 (m, 2H), 7.48 – 7.41 (m, 3H), 7.22 – 7.15 (m, 2H), 7.10 – 7.05 (m, 1H), 6.98 – 6.94 (m, 1H), 6.04 – 5.98 (m, 1H), 4.00 – 3.79 (m, 2H), 3.33 – 3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 143.8, 141.5, 140.0, 131.6, 131.3, 128.4 (d, J = 2.4 Hz), 128.2, 127.8 (d, J = 1.3 Hz), 125.7, 123.3, 109.2, 48.3, 27.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}NO$: 250.1232. Found: 250.1231.

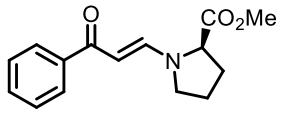
(*E*)-3-(3, 4-Dihydroquinolin-1(2*H*)-yl)-1-phenylprop-2-en-1-one (1ak):



The title compound was prepared according to the general procedure B. The product was obtained as brown oil, Yield: 85% (671.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 12.7 Hz, 1H), 7.96 (d, J = 9.5 Hz, 2H), 7.58 – 7.36 (m, 3H), 7.32 – 7.14 (m, 2H), 7.08 (d, J =

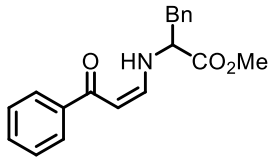
7.3 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.19 (d, *J* = 12.7 Hz, 1H), 3.62 (t, *J* = 6.4 H, 2H), 2.78 – 2.67 (m, 2H), 2.06 – 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 147.1, 140.1 (d, *J* = 4.2 Hz), 131.6, 129.0, 128.9, 128.4, 127.9 (d, *J* = 1.4 Hz), 123.3, 116.7, 97.0, 46.6, 27.5, 22.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{18}NO$: 264.1388. Found: 264.1385.

Methyl (*E*)-(3-oxo-3-phenylprop-1-en-1-yl)-D-prolinate (1al):



The title compound was prepared according to the general procedure B with NMM (1.0 eq) in DCM. The product was obtained as yellow brown oil. Yield: 70% (907.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 3H), 7.47 – 7.38 (m, 3H), 5.79 – 5.65 (m, 1H), 4.32 – 4.29 (m, 1H), 3.74 – 3.32 (m, 5H), 2.17 – 2.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 172.0, 149.3, 140.0, 130.9, 128.0, 127.4, 94.8, 64.0, 52.4, 47.4, 29.6, 23.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}NO_3$: 260.1287. Found: 260.1289.

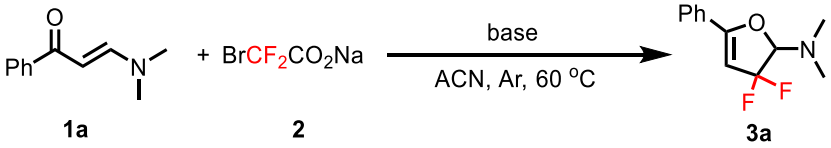
(*Z*)-Methyl 2-((3-oxo-3-phenylprop-1-en-1-yl)amino)-3-phenylpropanoate (1am):



The title compound was prepared according to the general procedure B with NMM (1.0 eq) in DCM. The product was obtained as yellow solid, Mp. 63 - 64 ℃. Yield: 55% (850.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (dd, J_1 = 9.5 Hz, J_2 = 12.0 Hz, 1H), 7.86 – 7.84 (m, 2H), 7.42 – 7.34 (m, 3H), 7.27 – 7.15 (m, 5H), 6.56 (dd, J_1 = 7.7 Hz, J_2 = 12.4 Hz, 1H), 5.64 (d, *J* = 7.6 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.68 (s, 3H), 3.20 (dd, J_1 = 5.0 Hz, J_2 = 13.7 Hz, 1H), 2.99 (dd, J_1 = 8.7 Hz, J_2 = 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 170.7, 152.0, 139.1, 135.5, 130.8, 129.1, 128.4, 128.0, 126.9, 91.1, 62.9, 52.2, 39.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{20}NO_3$: 310.1443. Found: 310.1440.

Optimization of reaction conditions:

Table S-1. Optimization Reaction Conditions by Using $BrCF_2CO_2Na$ (1a)[a]:

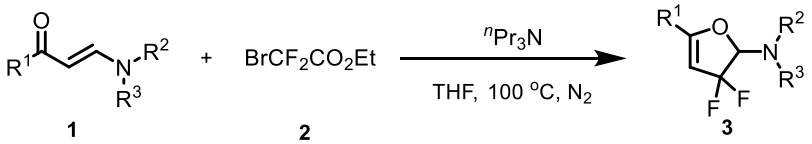


1a **2** **3a**

Entry	Base (eq.)	Solvent	Temperature (℃)	Yield (%)[b]
1	NEt_3 (0.5)	ACN	60	22
2	NEt_3 (1.0)	ACN	60	26
3	NEt_3 (1.5)	ACN	60	32
4	NEt_3 (1.8)	ACN	60	50
5	K_2CO_3 (1.8)	ACN	60	31
6	Cs_2CO_3 (1.8)	ACN	60	59
7	Cs_2CO_3 (1.8)	ACN	60	31
8	Cs_2CO_3 (1.0)	ACN	60	20
9	Cs_2CO_3 (3.0)	ACN	60	64
10	CsF (3.0)	ACN	60	26
11	CsCl (3.0)	ACN	60	23
12	CsBr (3.0)	ACN	60	25
13	CsTFA (3.0)	ACN	60	18
14	Cs_2CO_3 (4.0)	ACN	60	81
15	Cs_2CO_3 (5.0)	ACN	60	71
16	Cs_2CO_3 (3.0)	DMF	60	3
17	Cs_2CO_3 (3.0)	Dioxane	60	12
18	Cs_2CO_3 (3.0)	2-Me-THF	60	72
19	Cs_2CO_3 (3.0)	$PhCF_3$	60	8
20	Cs_2CO_3 (3.0)	THF	60	56
21	Cs_2CO_3 (3.0)	2-Me-THF	70	67
22	Cs_2CO_3 (3.0)	2-Me-THF	80	82
23	Cs_2CO_3 (3.0)	2-Me-THF	100	83
24	Cs_2CO_3 (3.0)	2-Me-THF	120	74
25	Cs_2CO_3 (3.0)	2-Me-THF	90	85
26	Cs_2CO_3 (3.0)	ACN/2-Me-THF (v/v=1/1)	90	93
27	Cs_2CO_3 (3.0)	**ACN/2-Me-THF (v/v=1/1)**	**80**	**97**

[a]Experiments were performed with **1a** (0.20 mmol, 1.0 equiv.), **2** and base in 4.0 mL solvent, and resulting mixture was stirred under Ar protection for 48 hours. [b]Isolated yields.

General procedure for synthesis of 2*H*-furans and their spectral data:

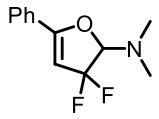


1 **2** **3**

A mixture of enaminone **1** (0.20 mmol, 1.0 equiv.), **2** (0.40 mmol, 2.0 equiv.), $^nPr_3N$ (0.06 mmol, 3.0 equiv.), anhydrous THF (2.0 mL) was sealed in a Schlenk tube under nitrogen protection at 100 ℃ and the mixture was stirred for 48 h or until the **1** was consumed completely. The crude product was filtered through a short pad of Celite, and the filtrate was

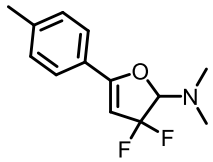
concentrated under vacuum and purified by flash chromatography (eluent: 20% v/v ethyl acetate in petroleum ether) to afford products **3**.

3, 3-Difluoro-*N*, *N*-dimethyl-5-phenyl-2, 3-dihydrofuran-2-amine (3a):



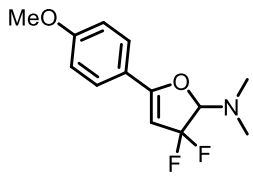
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 96% (43.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.43 – 7.38 (m, 3H), 5.55 (t, J = 2.4 Hz, 1H), 4.19 – 4.12 (m, 1H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, J = 4.0 Hz), 131.2 (dd, J_1 = 270.0 Hz, J_2 = 273.0 Hz), 129.9, 128.6, 128.2, 125.3, 97.4 (d, J = 3.0 Hz), 71.0 (dd, J_1 = 19.0 Hz, J_2 = 35.0 Hz), 41.1 (d, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.18 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.74 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}F_2NO$: 226.1043. Found: 226.1045.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(*p*-tolyl)-2, 3-dihydrofuran-2-amine (3b):



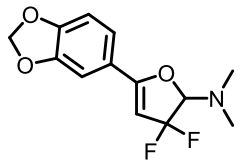
The title compound was prepared according to the general procedure. The product was obtained as brown oil, Yield: 96% (45.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.52 (t, J = 2.2 Hz, 1H), 4.21 – 4.14 (m, 1H), 2.51 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 140.5, 133.8, 131.2, 129.4, 128.4, 125.4, 96.1, 71.1 (dd, J_1 = 18.9 Hz, J_2 =35.1 Hz), 41.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.16 (dd, J_1 = 20.6 Hz, J_2 = 214.5 Hz), -81.81 (dd, J_1 = 9.2 Hz, J_2 = 214.2 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}F_2NO$: 240.1200. Found: 240.1194.

3, 3-Difluoro-5-(4-methoxyphenyl)-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3c):



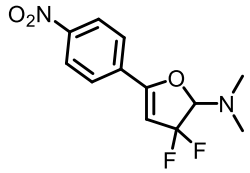
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 45 - 46 ℃. Yield: 96% (49.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 6.92 – 6.89 (m, 2H), 5.39 (t, J = 2.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.83 (s, 3H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.2 (d, J = 4.0 Hz), 131.2 (dd, J_1 = 270.0 Hz, J_2 = 272.0 Hz), 126.9, 120.9, 114.0, 95.1 (d, J = 2.0 Hz), 71.0 (dd, J_1 = 21.0 Hz, J_2 = 34.0 Hz), 41.0 (d, J = 1.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.17 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.87 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}F_2NO_2$: 256.1149. Found: 256.1150.

5-(Benzo[d][1, 3]dioxol-5-yl)-3,3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3d):



The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 95% (51.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.14 (d, J = 8.1 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 6.00 (s, 2H), 5.38 (s, 1H) , 4.15 – 4.09 (m, 1H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.2, 148.0, 134.0, 131.3, 128.6, 122.4, 120.0, 108.5, 105.8, 101.6, 95.9, 71.1 (dd, J_1 = 19.0 Hz, J_2 = 34.4 Hz), 41.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.11 (dd, J_1 = 17.2 Hz, J_2 = 150.7 Hz), -83.84 (d, J = 151.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}F_2NO_3$: 270.0942. Found: 270.0947.

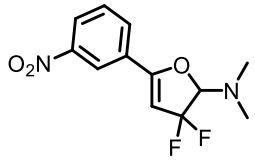
3, 3-Difluoro-*N*, *N*-dimethyl-5-(4-nitrophenyl)-2, 3-dihydrofuran-2-amine (3e):



The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 67 - 68 ℃. Yield: 80% (43.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 5.80 (t, J = 2.4 Hz, 1H), 4.22 – 4.16 (m, 1H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (d, J = 4.0 Hz), 148.3, 133.8, 130.9 (dd, J_1 = 271.0 Hz, J_2 = 274.0 Hz), 126.1, 123.9, 120.0 (d, J = 3.2 Hz), 71.1 (dd, J_1 = 19.0 Hz, J_2 = 35.0 Hz), 41.2 (d, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.44 (d, J =

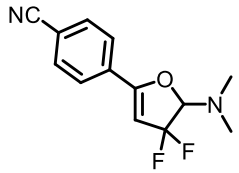
150.4 Hz), -83.27 (d, J = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}F_2N_2O_3$: 271.0894. Found: 271.0890.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(3-nitrophenyl)-2, 3-dihydrofuran-2-amine (3f):



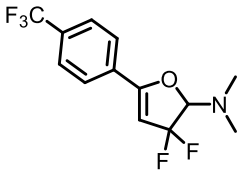
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 96% (51.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 5.77 (t, J = 2.0 Hz, 1H), 4.25 – 4.18 (m, 1H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 (d, J = 4.0 Hz), 148.4, 130.9 (dd, J_1 = 271.0 Hz, J_2 = 274.0 Hz), 130.9, 129.8, 129.8, 124.3, 120.3, 100.3 (d, J = 2.7 Hz), 71.0 (dd, J_1 = 18.9 Hz, J_2 = 34.1 Hz), 41.2 (d, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.38 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.29 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}F_2N_2O_3$: 271.0894. Found: 271.0895.

4-(5-(Dimethylamino)-4, 4-difluoro-4, 5-dihydrofuran-2-yl) benzonitrile (3g):



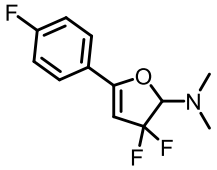
The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 81% (40.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 5.74 (t, J = 2.4 Hz, 1H), 4.22 – 4.16 (m, 1H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (d, J = 3.8 Hz), 132.4, 132.1 (d, J = 0.6 Hz), 130.9 (dd, J_1 = 270.4 Hz, J_2 = 273.7 Hz), 125.8, 118.2, 113.2, 101.2 (d, J = 3.6 Hz), 71.0 (dd, J_1 = 18.9 Hz, J_2 = 34.1 Hz), 41.2 (d, J = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.29 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.22 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}F_2N_2O$: 251.0996. Found: 251.1000.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(4-(trifluoromethyl) phenyl)-2, 3-dihydrofuran-2-amine (3h):



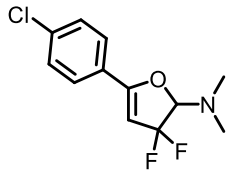
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 55 - 56 ℃. Yield: 98% (57.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 5.69 (t, J = 2.4 Hz, 1H), 4.22 – 4.15 (m, 1H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (d, J = 3.8 Hz), 131.6 (q, J = 32.6 Hz), 131.4, 131.0 (dd, J_1 = 270.6 Hz, J_2 = 273.6 Hz), 125.6, 125.6 (q, J = 3.8 Hz), 123.7 (q, J = 270.9 Hz), 99.9 (d, J = 3.2 Hz), 71.0 (dd, J_1 = 18.8 Hz, J_2 = 34.2 Hz), 41.2 (d, J = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.27 (dd, J_1 = 14.7 Hz, J_2 = 150.4 Hz), -62.80, -83.46 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{13}F_5NO$: 294.0917. Found: 294.0920.

3, 3-Difluoro-5-(4-fluorophenyl)-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3i):



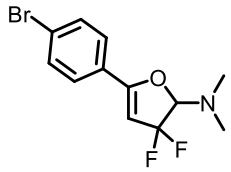
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 98% (47.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.12 – 7.06 (m, 2H), 5.48 (t, J = 2.4 Hz, 1H), 4.18 – 4.11 (m, 1H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, J = 249.2 Hz), 153.4 (d, J = 3.5 Hz), 131.1 (dd, J_1 = 270.4 Hz, J_2 = 272.9 Hz), 127.4 (d, J = 8.3 Hz), 124.5 (d, J = 2.7 Hz), 115.7 (d, J = 21.9 Hz), 97.0, 71.1 (dd, J_1 = 19.0 Hz, J_2 = 34.4 Hz), 41.1 (d, J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.26 (dd, J_1 = 14.7 Hz, J_2 = 150.0 Hz), -83.70 (dd, J_1 = 6.4 Hz, J_2 = 150.0 Hz), -(109.85 – 109.92) (m); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}F_3NO$: 244.0949. Found: 244.0950.

5-(4-Chlorophenyl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3j):



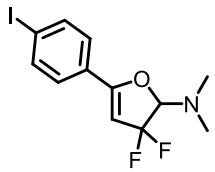
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 98% (50.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.39 – 7.35 (m, 2H), 5.54 (t, J = 2.4 Hz, 1H), 4.18 – 4.12 (m, 1H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (d, J = 3.3 Hz), 135.8, 131.1 (dd, J_1 = 270.4 Hz, J_2 = 273.2 Hz), 128.9, 126.7, 126.6, 98.0 (d, J = 2.5 Hz), 71.0 (dd, J_1 = 18.9 Hz, J_2 = 34.2 Hz), 41.1 (d, J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.27 (dd, J_1 = 15.0 Hz, J_2 = 151.9 Hz), -83.59 (dd, J_1 = 7.5 Hz, J_2 = 150.8 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}ClF_2NO$: 260.0654. Found: 260.0650.

5-(4-Bromophenyl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3k):



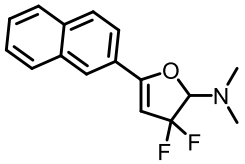
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 99% (60.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.48 – 7.45 (m, 2H), 5.56 (t, J = 2.4 Hz, 1H), 4.17 – 4.11 (m, 1H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (d, J = 3.6 Hz), 131.8, 131.1 (dd, J_1 = 270.2 Hz, J_2 = 273.1 Hz), 127.1, 126.8, 124.1, 98.1 (d, J = 2.4 Hz), 71.0 (dd, J_1 = 18.7 Hz, J_2 = 34.1 Hz), 41.1 (d, J = 1.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.24 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.56 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}BrF_2NO$: 304.0149. Found: 304.0150.

3, 3-Difluoro-5-(4-iodophenyl)-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3l):



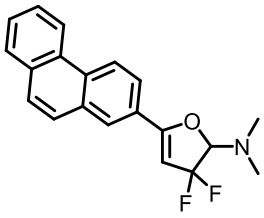
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 97% (53.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.34 – 7.41 (m, 2H), 5.58 (t, J = 2.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 2.48 (d, J = 0.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4 (d, J = 3.7 Hz), 137.7, 131.0 (dd, J_1 = 270.5 Hz, J_2 = 273.1 Hz), 127.6, 126.8, 98.2 (d, J = 2.5 Hz), 96.0, 71.0 (dd, J_1 = 18.7 Hz, J_2 = 34.1 Hz), 41.1 (d, J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.17 (dd, J_1 = 15.0 Hz, J_2 = 149.3 Hz), -83.51 (dd, J_1 = 7.5 Hz, J_2 = 151.2 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}F_2INO$: 352.0010. Found: 352.0010.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(naphthalen-2-yl)-2, 3-dihydrofuran-2-amine (3m):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 46 - 47 ℃. Yield: 95% (52.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.85 – 7.79 (m, 3H), 7.62 – 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 5.64 (t, J = 2.4 Hz, 1H), 4.22 – 4.16 (m, 1H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, J = 3.7 Hz), 133.8, 132.9, 131.2 (dd, J_1 = 269.6 Hz, J_2 = 272.4 Hz), 128.6, 128.3, 127.7, 127.1, 126.7, 125.3, 125.1, 122.3, 98.0 (d, J = 2.8 Hz), 96.0, 71.1 (dd, J_1 = 18.9 Hz, J_2 = 34.2 Hz), 41.1 (d, J = 2.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.13 (dd, J_1 = 6.8 Hz, J_2 = 150.4 Hz), -83.58 (dd, J_1 = 8.3 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{16}F_2NO$: 276.1200. Found: 276.1202.

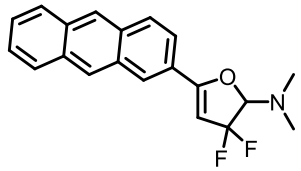
3, 3-Difluoro-*N*, *N*-dimethyl-5-(phenanthren-2-yl)-2, 3-dihydrofuran-2-amine (3n):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 101 - 102 ℃. Yield: 80% (52.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.4 Hz, 2H), 8.10 (s, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.79 – 7.70 (m, 3H),

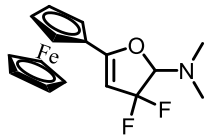
7.66 – 7.58 (m, 2H), 5.68 (s, 1H), 4.24 – 4.18 (m, 1H), 2.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (d, J = 3.5 Hz), 132.4, 131.7, 131.3 (dd, J_1 = 269.7 Hz, J_2 = 272.1 Hz), 131.1, 129.8, 128.6, 127.8, 127.1, 126.9, 126.8, 126.0, 125.5, 123.1, 122.8, 98.0 (d, J = 2.2 Hz), 71.1 (dd, J_1 = 18.8 Hz, J_2 = 34.2 Hz), 41.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.92 (dd, J_1 = 14.7 Hz, J_2 = 150.0 Hz), -83.35 (d, J = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{18}F_2NO$: 326.1356. Found: 326.1355.

5-(Anthracen-2-yl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3o):



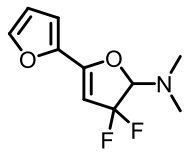
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 140 - 141 ℃. Yield: 74% (48.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.37 (s, 1H), 8.24 (s, 1H), 8.01 – 7.95 (m, 3H), 7.56 (d, J = 8.8 Hz, 1H), 7.51 – 7.47 (m, 2H), 5.69 (t, J = 2.0 Hz, 1H), 4.26 – 4.20 (m, 1H), 2.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, J = 3.4 Hz), 132.4, 132.2, 131.4, 131.3 (dd, J_1 = 269.5 Hz, J_2 = 271.9 Hz), 130.8, 128.7, 128.3, 128.1, 127.6, 126.2, 126.1, 125.8, 125.6, 124.5, 121.7, 98.5 (d, J = 2.0 Hz), 71.1 (dd, J_1 = 19.0 Hz, J_2 = 34.1 Hz), 41.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.02 (dd, J_1 = 15.0 Hz, J_2 = 150.4 Hz), -83.39 (dd, J_1 = 7.1 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{18}F_2NO$: 326.1356. Found: 326.1356.

5-(Ferrocenyl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3p):



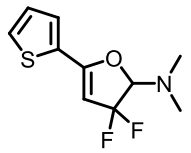
The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 95% (63.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (t, J = 2.4 Hz, 1H), 4.55 (s, 1H), 4.52 (s, 1H), 4.31 (s, 2H), 4.19 (s, 5H), 4.01 – 3.95 (m, 1H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 (d, J = 4.2 Hz), 131.2 (t, J = 270.9 Hz), 94.6, 72.4, 70.9 (dd, J_1 = 18.5 Hz, J_2 = 34.5 Hz), 69.7, 66.6, 66.5, 41.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.19 (dd, J_1 = 14.7 Hz, J_2 = 149.3 Hz), -84.77 (dd, J_1 = 4.5 Hz, J_2 = 151.5 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{18}F_2FeNO$: 334.0706. Found: 334.0705.

4, 4-Difluoro-*N*, *N*-dimethyl-4, 5-dihydro- [2, 2'-bifuran]-5-amine (3q):



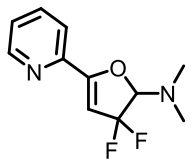
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 94% (40.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 1.2 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H), 6.47 (dd, J_1 = 1.6 Hz, J_2 = 3.2 Hz, 1H), 5.45 (t, J = 2.4 Hz, 1H), 4.18 – 4.12 (m, 1H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (d, J = 4.9 Hz), 144.1, 143.8 (d, J = 1.7 Hz), 131.1 (dd, J_1 = 270.7 Hz, J_2 = 273.0 Hz), 111.4, 110.1, 96.3 (d, J = 3.0 Hz), 70.7 (dd, J_1 = 18.6 Hz, J_2 = 34.1 Hz), 41.1 (d, J = 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.77 (d, J = 150.0 Hz), -83.91 (d, J = 149.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{12}F_2NO_2$: 216.0836. Found: 216.0836.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(thiophen-2-yl)-2, 3-dihydrofuran-2-amine (3r):



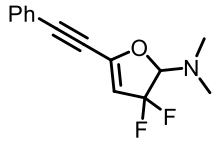
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 87% (40.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J_1 = 0.8 Hz, J_2 = 4.8 Hz, 1H), 7.32 (d, J = 3.6 Hz, 1H), 7.04 (dd, J_1 = 4.0 Hz, J_2 = 4.8 Hz, 1H), 5.37 (t, J = 2.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J = 4.2 Hz), 131.0 (dd, J_1 = 270.9 Hz, J_2 = 273.1 Hz), 130.9, 127.6, 127.2, 126.6, 96.5 (d, J = 2.6 Hz), 71.1 (dd, J_1 = 18.8 Hz, J_2 = 34.3 Hz), 41.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.40 (dd, J_1 = 14.7 Hz, J_2 = 148.9 Hz), -83.72 (dd, J_1 = 6.0 Hz, J_2 = 149.3 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{12}F_2NOS$: 232.0608. Found: 232.0606.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(pyridin-2-yl)-2, 3-dihydrofuran-2-amine (3s):



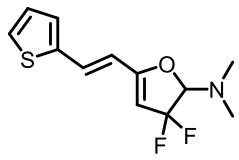
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 97% (45.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.31 – 7.28 (m, 1H), 6.08 (t, J = 2.4 Hz, 1H), 4.22 – 4.16 (m, 1H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (d, J = 3.4 Hz), 149.8, 146.9, 136.8, 131.3 (dd, J_1 = 270.1 Hz, J_2 = 273.8 Hz), 124.2, 120.3, 101.3 (d, J = 2.8 Hz), 71.0 (dd, J_1 = 18.9 Hz, J_2 = 34.3 Hz), 41.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.33 (dd, J_1 = 15.8 Hz, J_2 = 151.5 Hz), -82.88 (dd, J_1 = 7.5 Hz, J_2 = 150.0 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}F_2N_2O$: 227.0996. Found: 227.1000.

3, 3-Difluoro-*N*, *N*-dimethyl-5-(phenylethynyl)-2, 3-dihydrofuran-2-amine (3t):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 84% (42.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.42 – 7.33 (m, 3H), 5.56 (t, J = 2.4 Hz, 1H), 4.13 – 4.06 (m, 1H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (d, J = 5.1 Hz), 131.9, 130.4 (dd, J_1 = 271.0 Hz, J_2 = 273.8 Hz), 129.7, 128.5, 120.8, 109.2 (d, J = 2.6 Hz), 94.1, 77.6, 70.6 (dd, J_1 = 18.5 Hz, J_2 = 33.9 Hz), 41.2 (d, J = 1.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.58 (dd, J_1 = 14.7 Hz, J_2 = 149.3 Hz), -83.71 (dd, J_1 = 6.8 Hz, J_2 = 149.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{14}F_2NO$: 250.1043. Found: 250.1041.

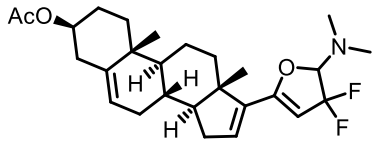
(*E*)-3, 3-Difluoro-*N*, *N*-dimethyl-5-(2-(thiophen-2-yl) vinyl)-2, 3-dihydrofuran-2-amine (3u):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 95% (49.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 2.4 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.00 (dd, J_1 = 4.0 Hz, J_2 = 5.2 Hz, 1H), 6.35 (d, J = 15.6 Hz, 1H), 5.17 (t, J = 2.4 Hz, 1H), 4.10 – 4.04 (m, 1H), 2.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0 (d, J = 3.7 Hz), 141.0, 131.1 (dd, J_1 = 270.2 Hz, J_2 = 272.7 Hz), 128.3, 127.9, 126.5,

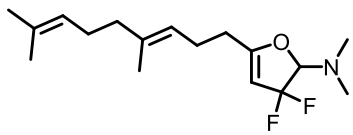
126.2, 114.0, 101.6 (d, J = 2.5 Hz), 70.9 (dd, J_1 = 19.0 Hz, J_2 = 34.2 Hz), 41.1 (d, J = 1.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.33 (dd, J_1 = 14.7 Hz, J_2 = 151.2 Hz), -83.44 (dd, J_1 = 6.0 Hz, J_2 = 149.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}F_2NOS$: 258.0764. Found: 258.0765.

(3*S*, 8*R*, 9*S*, 10*R*, 13*S*, 14*S*)-17-(5-(Dimethylamino)-4, 4-difluoro-4, 5-dihydrofuran-2-yl)-10, 13-dimethyl-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15-dodecahydro-1*H*-cyclopenta[a]phenanthren-3-yl acetate (3v):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 89% (82.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 – 6.13 (m, 1H), 5.40 (d, J = 5.2 Hz, 1H), 5.10 (d, J = 9.6 Hz, 1H), 4.65 – 4.57 (m, 1H), 4.03 (dd, J_1 = 6.8 Hz, J_2 = 14.8 Hz, 1H), 2.44 (s, 6H), 2.37 – 2.32 (m, 2H), 2.30 – 2.22 (m, 1H), 2.07 – 1.95 (m, 7H), 1.90 – 1.83 (m, 2H), 1.74 – 1.46 (m, 8H), 1.10 – 1.03 (m, 4H), 0.96 (d, J = 8.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 151.1 (dd, J_1 = 3.5 Hz, J_2 = 16.0 Hz), 142.5, 142.4, 139.9, 132.9 (d, J = 8.5 Hz), 133.3 – 127.6 (m), 122.1, 98.8 – 96.6 (m), 73.7, 71.1 – 70.6 (m), 56.8, 56.7, 50.2, 50.1, 46.0, 45.8, 41.0, 38.0, 36.8, 36.7, 35.1, 35.0, 31.5, 31.3, 30.1, 30.0, 27.6, 26.8, 21.4, 20.7, 19.2, 16.2, 16.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -(61.28 – 61.79) (m), -(84.30 – 85.12) (m); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{27}H_{38}F_2NO_3$: 462.2820. Found: 462.2820.

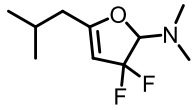
(*E*)-5-(4, 8-Dimethylnona-3, 7-dien-1-yl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3w):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 65% (38.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 – 5.06 (m, 2H), 4.84 (s, 1H), 3.94 – 3.88 (m, 1H), 2.41 (s, 6H), 2.24 (dd, J_1 = 3.4 Hz, J_2 = 5.7 Hz, 4H), 2.09 – 2.02 (m, 3H), 1.99 – 1.96 (m, 1H), 1.69 – 1.60 (m, 9H); ^{13}C NMR (100 MHz,

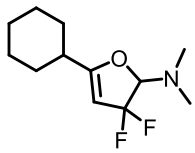
$CDCl_3$) δ 157.8 (d, J = 3.0 Hz), 136.7, 136.6, 131.7, 131.3, 131.2 (dd, J_1 = 270.6 Hz, J_2 = 273.9 Hz), 124.1, 124.0, 123.0, 122.2, 98.1 (t, J = 3.0 Hz), 70.9 – 70.4 (m), 40.9 (d, J = 2.0 Hz), 39.6, 31.9, 28.4, 28.2, 26.6, 26.4, 25.6, 25.6, 24.1, 24.0, 23.3, 17.6, 17.5, 16.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.50 (dd, J_1 = 1.9 Hz, J_2 = 151.3 Hz), -84.41 (dd, J_1 = 25.0 Hz, J_2 = 151.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{28}F_2NO$: 300.2139. Found: 300.2140.

3, 3-Difluoro-5-isobutyl-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3x):



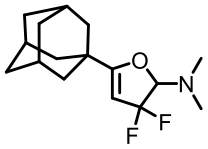
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 75% (31.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 1H), 3.96 – 3.90 (m, 1H), 2.42 (s, 6H), 2.10 (d, J = 6.8 Hz, 2H), 1.99 – 1.88 (m, 1H), 0.95 (dd, J_1 = 4.4 Hz, J_2 = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, J = 2.6 Hz), 131.2 (dd, J_1 = 269.2 Hz, J_2 = 272.0 Hz), 98.9 (d, J = 2.4 Hz), 70.6 (dd, J_1 = 18.5 Hz, J_2 = 34.5 Hz), 41.1, 37.1, 29.7, 25.6, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.32 (dd, J_1 = 15.0 Hz, J_2 = 151.9 Hz), -84.34 (dd, J_1 = 6.0 Hz, J_2 = 151.5 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{18}F_2NO$: 206.1356. Found: 206.1356.

5-Cyclohexyl-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3y):



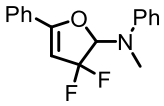
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 70% (32.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 – 4.78 (m, 1H), 3.92 – 3.86 (m, 1H), 2.41 (s, 6H), 2.24 – 2.13 (m, 1H), 1.98 – 1.63 (m, 6H), 1.35 – 1.15 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 2.6 Hz), 131.1 (dd, J_1 = 268.4 Hz, J_2 = 271.1 Hz), 95.7 (d, J = 1.5 Hz), 70.4 (dd, J_1 = 18.6 Hz, J_2 = 34.5 Hz), 41.0, 36.8, 29.6, 25.9, 25.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.67 (dd, J_1 = 15.4 Hz, J_2 = 151.2 Hz), -84.90 (dd, J_1 = 6.8 Hz, J_2 = 151.2 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{20}F_2NO$: 232.1513. Found: 232.1514.

5-((1*r*, 3*R*, 5*S*)-Adamantan-1-yl)-3, 3-difluoro-*N*, *N*-dimethyl-2, 3-dihydrofuran-2-amine (3z):



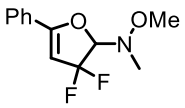
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 60% (33.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (t, J = 2.4 Hz, 1H), 3.90 – 3.84 (m, 1H), 2.40 (s, 6H), 2.06 – 1.98 (m, 4H), 1.83 – 1.67 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (d, J = 2.4 Hz), 131.2 (dd, J_1 = 270.8 Hz, J_2 = 272.6 Hz), 94.4 (d, J = 1.5 Hz), 70.2 (dd, J_1 = 19.0 Hz, J_2 = 34.9 Hz), 40.9, 39.1, 38.2, 36.6, 34.1, 27.9, 27.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.69 (dd, J_1 = 15.1 Hz, J_2 = 150.9 Hz), -85.33 (dd, J_1 = 6.3 Hz, J_2 = 150.9 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{24}F_2NO$: 284.1826. Found: 284.1829.

3, 3-Difluoro-*N*-methyl-*N*, 5-diphenyl-2, 3-dihydrofuran-2-amine (3aa):



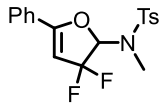
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 78 - 79 ℃. Yield: 93% (53.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.43 – 7.40 (m, 3H), 7.31 – 7.27 (m, 2H), 6.94 – 6.89 (m, 2H), 6.85 – 6.81 (m, 1H), 5.59 (t, J = 2.4 Hz, 1H), 5.33 – 5.27 (m, 1H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, J = 3.2 Hz), 149.2, 130.2 (dd, J_1 = 268.6 Hz, J_2 = 269.3 Hz), 130.2, 129.3, 128.7, 128.0, 125.4, 118.4, 113.6, 97.3 (d, J = 2.9 Hz), 65.9 (dd, J_1 = 21.6 Hz, J_2 = 37.1 Hz), 33.4 (d, J = 2.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.02 (dd, J_1 = 13.4 Hz, J_2 = 149.6 Hz), -81.28 (dd, J_1 = 6.7 Hz, J_2 = 150.0 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}F_2NO$: 288.1200. Found: 288.1200.

***N*-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl)-*N*, *O*-dimethylhydroxylamine (3ab):**



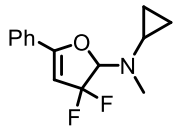
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 55% (26.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.41 – 7.38 (m, 3H), 5.56 (t, J = 2.4 Hz, 1H), 4.25 – 4.19 (m, 1H), 3.56 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 (d, J = 3.3 Hz), 130.1, 129.8 (dd, J_1 = 262.1 Hz, J_2 = 269.6 Hz), 128.5, 128.0, 125.4, 94.7, 73.0 (dd, J_1 = 18.3 Hz, J_2 = 36.0 Hz), 59.8 (d, J = 1.9 Hz), 41.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.48 (d, J = 151.4 Hz), -83.73 (dd, J_1 = 5.3 Hz, J_2 = 152.2 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}F_2NO$: 242.0993. Found: 242.0992.

_N_-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl)-_N_, 4-dimethylbenzenesulfonamide (3ac):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 37% (27.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.43 – 7.38 (m, 3H), 7.35 (d, J = 8.4 Hz, 2H), 5.61 – 5.55 (m, 1H), 5.34 (t, J = 2.8 Hz, 1H), 2.75 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, J = 3.3 Hz), 143.8, 135.6, 130.6, 129.8, 128.9 (t, J = 268.7 Hz), 128.7, 127.3, 127.3, 125.5, 94.7 (d, J = 2.6 Hz), 63.8 (dd, J_1 = 20.2 Hz, J_2 = 41.7 Hz), 30.2 (d, J = 4.4 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.28 (dd, J_1 = 14.3 Hz, J_2 = 151.9 Hz), -81.73 (dd, J_1 = 5.3 Hz, J_2 = 151.9 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{18}F_2NO_3S$: 366.0975. Found: 366.0980.

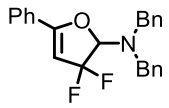
_N_-Cyclopropyl-3, 3-difluoro-_N_-methyl-5-phenyl-2, 3-dihydrofuran-2-amine (3ad):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 67% (33.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.43 – 7.36 (m, 3H), 5.52 – 5.51 (m, 1H), 4.41 – 4.35 (m, 1H), 2.47 (s, 3H), 2.30 – 2.25 (m, 1H), 0.60 – 0.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (d, J = 3.6 Hz), 131.4 (t, J = 270.5 Hz), 129.8, 128.5, 128.3, 125.2, 98.0 (d, J = 2.1 Hz), 69.8 (dd, J_1 = 19.3

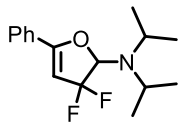
Hz, J_2 = 34.6 Hz), 37.0 (d, J = 4.0 Hz), 35.6 (d, J = 2.5 Hz), 8.3, 7.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.37 (dd, J_1 = 15.1 Hz, J_2 = 150.9 Hz), -82.58 (dd, J_1 = 6.6 Hz, J_2 = 150.8 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}F_2NO$: 252.1200. Found: 252.1200.

***N, N*-Dibenzyl-3, 3-difluoro-5-phenyl-2, 3-dihydrofuran-2-amine (3ae):**



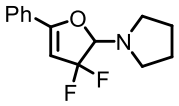
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 99% (74.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.48 (d, J = 7.6 Hz, 4H), 7.45 – 7.40 (m, 7H), 7.35 – 7.32 (m, 2H), 5.58 (t, J = 2.4 Hz, 1H), 4.51 – 4.44 (m, 1H), 4.00 (d, J = 14.0 Hz, 2H), 3.92 (d, J = 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, J = 3.1 Hz), 139.3, 131.6 (t, J = 271.1 Hz), 129.8, 128.7, 128.5, 128.3, 128.2, 127.2, 125.2, 98.3 (d, J = 3.0 Hz), 66.0 (dd, J_1 = 19.2 Hz, J_2 = 34.4 Hz), 54.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.78 (dd, J_1 = 14.9 Hz, J_2 = 150.2 Hz), -80.18 (dd, J_1 = 7.7 Hz, J_2 = 150.3 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{24}H_{22}F_2NO$: 378.1669. Found: 378.1670.

3, 3-Difluoro-*N, N*-diisopropyl-5-phenyl-2, 3-dihydrofuran-2-amine (3af):



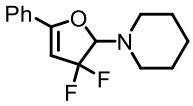
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 94% (49.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.44 – 7.36 (m, 3H), 5.51 (t, J = 2.4 Hz, 1H), 4.49 – 4.42 (m, 1H), 3.17 – 3.08 (m, 2H), 1.11 (d, J = 6.4 Hz, 6H), 1.06 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, J = 3.8 Hz), 130.5 (t, J = 267.2 Hz), 129.5, 128.7 (d, J = 1.0 Hz), 128.5, 125.1, 100.6 (d, J = 4.2 Hz), 62.6 (dd, J_1 = 20.9 Hz, J_2 = 37.0 Hz), 45.7, 22.9, 22.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.59 (dd, J_1 = 16.9 Hz, J_2 = 150.4 Hz), -80.50 (dd, J_1 = 7.5 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{22}F_2NO$: 282.1669. Found: 282.1670.

1-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl) pyrrolidine (3ag):



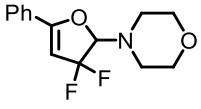
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 99% (49.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.40 – 7.37 (m, 3H), 5.61 (t, J = 2.4 Hz, 1H), 4.27 – 4.21 (m, 1H), 2.89 – 2.84 (m, 2H), 2.80 – 2.75 (m, 2H), 1.87 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (dd, J_1 = 1.4 Hz, J_2 = 3.3 Hz), 130.7 (dd, J_1 = 266.2 Hz, J_2 = 270.3 Hz), 129.8, 128.5, 128.2, 125.3, 97.5 (t, J = 2.2 Hz), 68.5 (dd, J_1 = 19.3 Hz, J_2 = 34.7 Hz), 50.2 (d, J = 2.3 Hz), 24.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.39 (dd, J_1 = 15.8 Hz, J_2 = 150.0 Hz), -82.66 (dd, J_1 = 6.8 Hz, J_2 = 149.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}F_2NO$: 252.1200. Found: 252.1199.

1-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl) piperidine (3ah):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 98% (51.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.41 – 7.35 (m, 3H), 5.57 (t, J = 2.4 Hz, 1H), 4.17 – 4.11 (m, 1H), 2.82 – 2.77 (m, 2H), 2.70 – 2.65 (m, 2H), 1.64 – 1.52 (m, 4H), 1.49 – 1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (d, J = 3.5 Hz), 131.1 (dd, J_1 = 268.9 Hz, J_2 = 272.5 Hz), 129.8, 128.5, 128.3, 125.2, 97.3 (d, J = 1.9 Hz), 71.6 (dd, J_1 = 18.8 Hz, J_2 = 34.7 Hz), 50.2, 26.4, 24.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.95 (dd, J_1 = 15.5 Hz, J_2 = 150.1 Hz), -82.96 (dd, J_1 = 4.1 Hz, J_2 = 149.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}F_2NO$: 266.1356. Found: 266.1359.

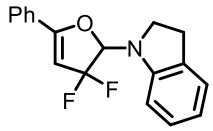
4-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl) morpholine (3ai):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 96% (29.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.41 – 7.38 (m, 3H), 5.57 (t, J = 2.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.71 (t, J = 4.8 Hz, 4H), 2.87 – 2.82 (m, 2H), 2.76 – 2.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7 (d, J

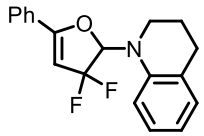
= 3.6 Hz), 130.7 (dd, J_1 = 268.8 Hz, J_2 = 272.0 Hz), 130.0, 128.5, 128.0 (d, J = 0.8 Hz), 125.3, 96.1 (dd, J_1 = 0.7 Hz, J_2 = 2.9 Hz), 71.0 (dd, J_1 = 18.6 Hz, J_2 = 35.1 Hz), 67.2, 49.5 (d, J = 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.57 (dd, J_1 = 15.4 Hz, J_2 = 150.4 Hz), -83.28 (dd, J_1 = 6.0 Hz, J_2 = 150.4 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}F_2NO_2$: 268.1149. Found: 268.1149.

1-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl) indoline (3aj):



The title compound was prepared according to the general procedure. The product was obtained as brown solid, Mp. 98 - 101 ℃. Yield: 82% (49.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.43 – 7.42 (m, 3H), 7.13 – 7.08 (m, 2H), 6.75 – 6.71 (m, 1H), 6.65 – 6.62 (m, 1H), 5.64 (s, 1H) , 5.14 – 5.08 (m, 1H), 3.58 – 3.45 (m, 2H), 3.00 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 149.1, 129.2, 129.1 (dd, J_1 = 270.9 Hz, J_2 = 272.6 Hz), 128.7, 127.7, 127.0 (d, J = 0.7 Hz), 126.4, 124.4, 123.8, 117.5, 105.6, 95.3, 62.1 (dd, J_1 = 20.4 Hz, J_2 = 37.5 Hz), 48.0, 27.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (dd, J_1 = 13.5 Hz, J_2 = 149.2 Hz), -81.93 (dd, J_1 = 9.0 Hz, J_2 = 149.2 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{16}F_2NO$: 300.1200. Found: 300.1198

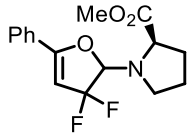
1-(3, 3-Difluoro-5-phenyl-2, 3-dihydrofuran-2-yl)-1, 2, 3, 4-tetrahydroquinoline (3ak):



The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 78% (48.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.46 – 7.42 (m, 3H), 7.16 – 7.12 (m, 1H), 7.05 – 7.03 (m, 1H), 6.83 – 6.81 (m, 1H), 6.75 – 6.71 (m, 1H), 5.61 (t, J = 2.2 Hz, 1H), 5.38 – 5.33 (m, 1H), 3.44 – 3.38 (m, 1H), 3.23 – 3.18 (m, 1H), 2.88 – 2.73 (m, 2H), 1.97 – 1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 143.7, 129.2 (dd, J_1 = 270.9 Hz, J_2 = 272.6 Hz), 129.1, 128.4, 127.7, 127.0 (d, J = 1.0 Hz), 126.2, 124.4, 122.8, 116.5, 95.9, 63.7 (dd, J_1 = 21.8 Hz, J_2 = 37.1 Hz), 43.1, 27.1, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.69 (dd, J_1 = 12.7 Hz, J_2 = 149.6 Hz), -81.13 (dd, J_1 = 5.2 Hz,

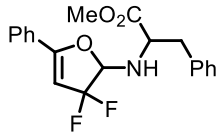
J_2 = 149.5 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_2NO$: 314.1356 Found: 314.1351.

Methyl (3, 3-difluoro-5-phenyl-2, 3-dihydrofuran-2-yl)-D-prolinate (3al):



The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 90% (55.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.40 – 7.26 (m, 3H), 5.69 (t, J = 2.4 Hz, 1H), 4.59 – 4.53 (m, 1H), 3.84 (dd, J_1 = 8.6, J_2 = 5.0 Hz, 1H), 3.74 (s, 3H), 3.19 – 3.14 (m, 1H), 2.87 – 2.83 (m, 1H), 2.21 – 2.13 (m, 1H), 2.05 – 2.00 (m, 1H), 1.88 – 1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 154.0, 133.7, 131.0, 130.0, 128.7, 128.3, 125.4, 98.8, 66.30 (dd, J_1 = 19.0 Hz, J_2 = 34.8 Hz), 62.3, 52.2, 48.2, 30.3, 24.2; ^{19}F NMR (376 MHz, CDCl3) δ -61.19 (dd, J_1 = 14.2 Hz, J_2 = 150.5 Hz), -82.51 (d, J = 159.1 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{18}F_2NO_3$: 310.1255. Found: 310.1252.

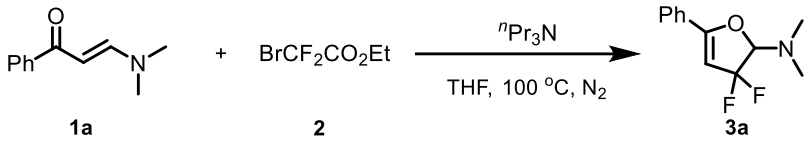
Methyl (3, 3-difluoro-5-phenyl-2, 3-dihydrofuran-2-yl) phenylalaninate (3am):



The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 28% (20.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.38 – 7.37 (m, 3H), 7.32 – 7.29 (m, 2H), 7.26 (s, 1H), 7.24 – 7.19 (m, 2H), 5.43 – 5.32 (m, 1H), 4.25 – 4.10 (m, 1H), 3.82 – 3.71 (m, 1H), 3.71 – 3.60 (m, 3H), 3.07 – 3.01 (m, 1H), 2.96 – 2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 154.6, 137.0, 130.1, 129.5, 128.7, 128.6, 128.1, 127.0, 125.4, 98.7, 64.2 (dd, J_1 = 21.8 Hz, J_2 = 35.6 Hz), 60.7, 60.1, 52.1, 40.2; ^{19}F NMR (376 MHz, CDCl3) δ -67.65 (dd, J_1 = 13.9 Hz, J_2 = 149.3 Hz), -83.95 (dd, J_1 = 8.3 Hz, J_2 = 149.3 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{20}F_2NO_3$: 360.1411. Found: 360.1407.

General procedures for synthetic applications and their spectral data:

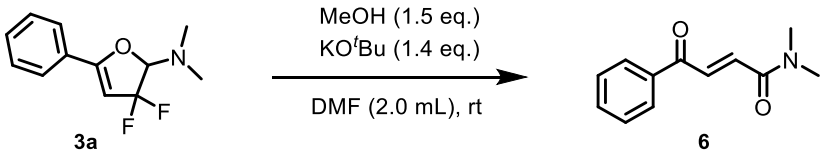
Gram scale synthesis for the preparation of 3, 3-difluoro-*N*, *N*-dimethyl-5-phenyl-2, 3-dihydrofuran-2-amine (3a):



1a 2 3a

A mixture of enaminone **1a** (10.0 mmol, 1.0 equiv.), **2** (20.0 mmol, 2.0 equiv.), $^{n}Pr_3N$ (30.0 mmol, 3.0 equiv.), anhydrous THF (100.0 mL) was sealed in a Schlenk tube under nitrogen protection at 100 ^{o}C and the mixture was stirred for 48 h or until the **1a** was consumed completely. The crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum and purified by flash chromatography (eluent: 20% v/v ethyl acetate in petroleum ether) to afford product **3a** as yellow oil in 85% yield (1.91 g).

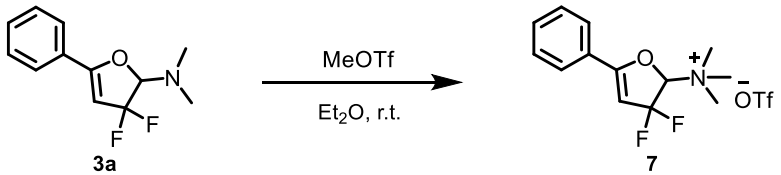
(*E*)-*N*, *N*-Dimethyl-4-oxo-4-phenylbut-2-enamide (6):



3a 6

A Schlenk tube was charged with MeOH (0.3 mmol), KO^{t}Bu (1 M in THF) (0.28 mmol) and DMF (3 mL) under argon atmosphere. The reaction mixture was stirred at 25 ℃ for 10 minutes and then 2*H*-furan **3a** (0.2 mmol, 45.1 mg) was added. The mixture was stirred at 25 ℃ for 3 h. The product was obtained as pale-yellow solid, Mp. 68 - 70 ℃. Yield: 77% (31.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.95 (d, J = 15.0 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.53 – 7.47 (m, 3H), 3.18 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 165.3, 137.2, 134.1, 133.8, 132.6, 129.0, 37.7, 36.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_2$: 204.1024. Found: 204.1026.

3, 3-Difluoro-*N*, *N*, *N*-trimethyl-5-phenyl-2, 3-dihydrofuran-2-aminium trifluoromethanesulfonate (7):

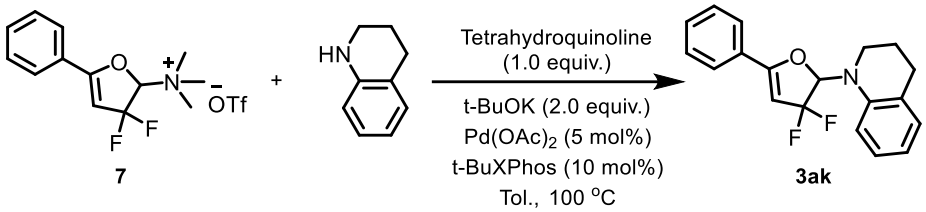


3a 7

To a stirred solution of 2*H*-furan **3a** (1.0 mmol) in Et_2O (3.0 ml), the Methyl trifluoromethanesulfonate (1.1 mmol) was added. The reaction mixture was stirred at room

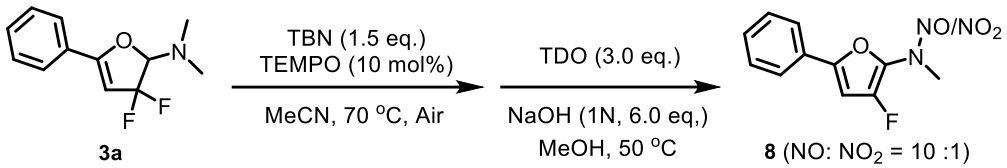
temperature until complete conversion monitored by TLC (30 min) (MeOH/DCM = 1/9, R_f = 0.25), and then the crude product was filtered. The crude product wash with ether to give corresponding pure Quaternary ammonium salt. The product was obtained as brown solid, Mp. 57 - 59 ℃. Yield: 90% (350.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.51 – 7.46 (m, 1H), 7.46 – 7.40 (m, 2H), 6.14 (t, J = 2.5 Hz, 1H), 5.29 – 5.24 (m, 1H), 3.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, J = 2.9 Hz), 132.0, 128.9, 126.3, 125.6, 120.2 (q, J = 316.9 Hz), 89.9, 77.6 (dd, J_1 = 17.2 Hz, J_2 =44.8 Hz), 52.0, 50.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.55 (dd, J_1 = 12.7 Hz, J_2 = 161.8 Hz), -78.58 , -82.56 (d, J = 161.6 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}F_5NO_4S$: 390.0798. Found: 390.0802.

5-((Benzoyloxy)methyl)-3, 3-difluoro-*N*, *N*, *N*-trimethyl-2, 3-dihydrofuran-2-aminium trifluoromethanesulfonate (3ak):



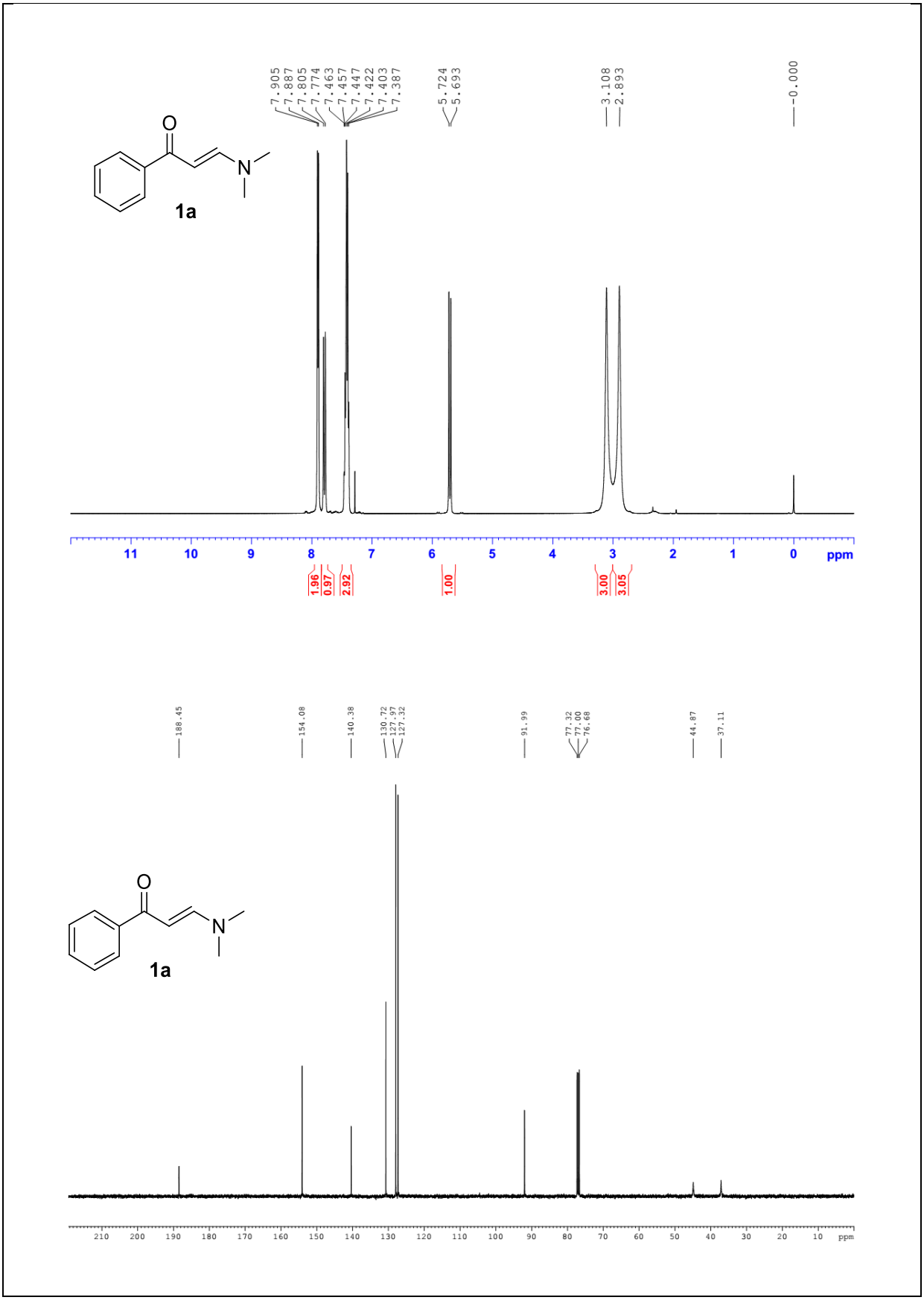
To a stirred solution of quaternary ammonium salt **7** (0.1 mmol, 38.9 mg) in PhMe (2.0 ml), the tetrahydroquinoline (0.1 mmol, 13.4 mg) and potassium *tert*-butoxide (0.2 mmol, 22.5 mg) was added slowly. The mixture was stirred at room temperature for about 0.5 h. Then $Pd(OAc)_2$ (0.005 mmol, 1.2 mg) and *t*-BuXPhos (0.01 mmol, 4.3 mg) were added to the test tube. The reaction mixture was stirred at 100 ℃ for 24 h (EA/PE = 1/4, R_f = 0.8). The product was obtained as brown oil. Yield: 75% (23.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.47 – 7.39 (m, 3H), 7.20 – 7.11 (m, 1H), 7.04 – 7.02 (m, 1H), 6.86 – 6.78 (m, 1H), 6.75 – 6.70 (m, 1H), 5.64 – 5.56 (m, 1H), 5.40 – 5.30 (m, 1H), 3.43 – 3.37 (m, 1H), 3.22 – 3.17 (m, 1H), 2.88 – 2.72 (m, 2H), 1.97 – 1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (d, J = 3.4 Hz), 144.7, 132.9, 130.1, 129.3, 128.6, 128.0 (d, J = 1.0 Hz), 127.2, 125.4, 123.8, 117.5, 111.1 (d, J = 1.8 Hz), 96.9 (d, J = 3.3 Hz), 64.7 (dd, J_1 = 21.8 Hz, J_2 = 37.1 Hz), 44.0 (d, J = 2.4 Hz), 28.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.69 (dd, J_1 = 12.7 Hz, J_2 = 149.6 Hz), -81.13 (dd, J_1 = 5.2 Hz, J_2 = 149.5 Hz); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_2NO$: 314.1356 Found: 314.1351.

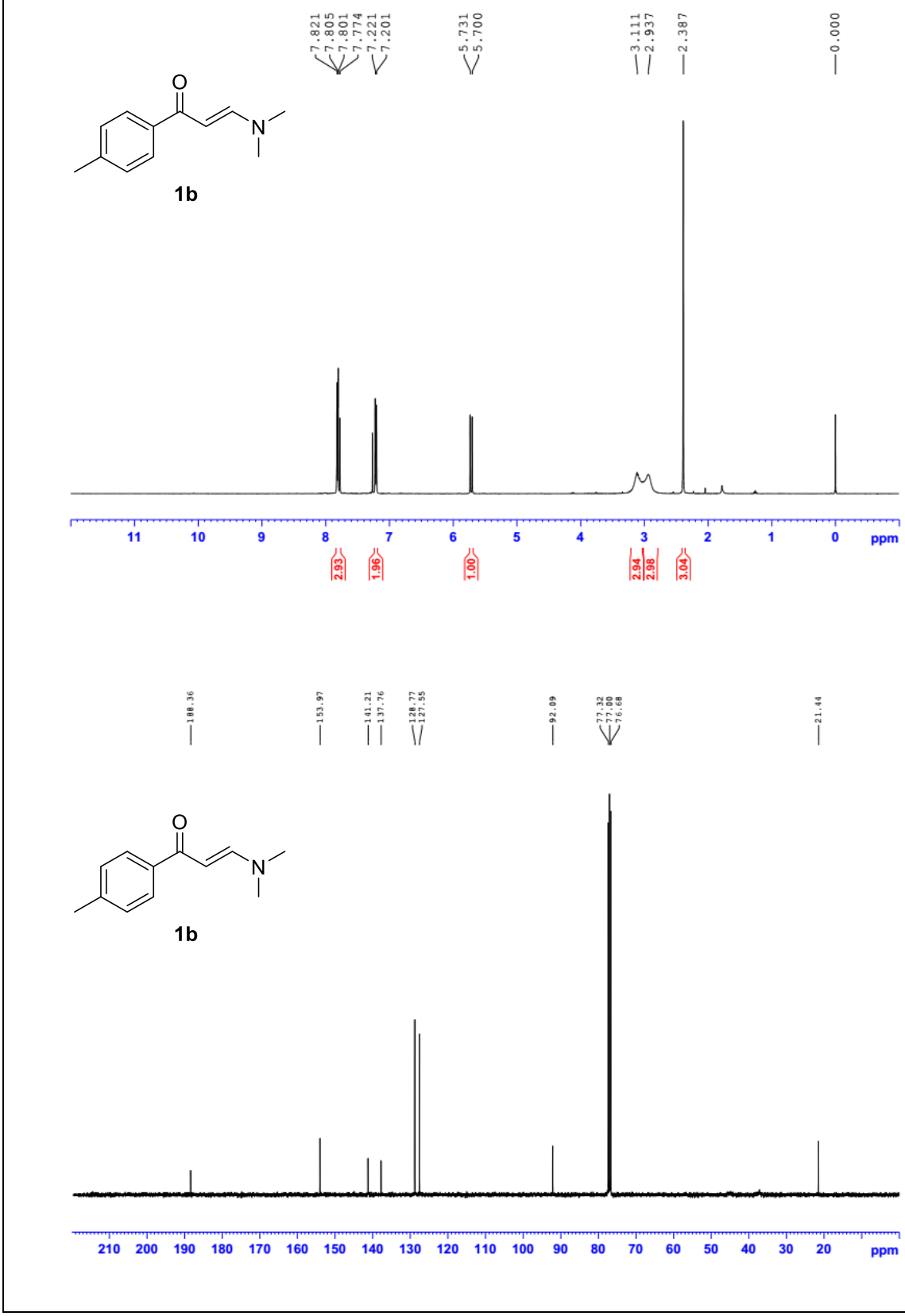
***N*-(3-Fluoro-5-phenylfuran-2-yl)-*N*-methylnitrousa mide + *N*-(3-Fluoro-5-phenylfuran-2-yl)-*N*-methylnitramide (8):**



A tube was charged with 2*H*-furan **3a** (0.4 mmol), *t*-butyl nitrite (TBN) (0.6 mmol), 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO) (0.04 mmol), CH_3CN (5 mL) was added subsequently and the reaction mixture was stirred at 70 ℃ until the starting material was fully consumed (24 h), The organic phase was spin-dried and dissolved in methanol, and thiourea dioxide (TDO) (1.2 mmol) and NaOH (1 N, 2.4 mmol) were added separately, the reaction mixture was stirred at 50 ℃ for 3 h. (EA/PE = 1/4, R_f = 0.8). The product was obtained as brown oil, Yield: 71% (62.5mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.56 – 7.52 (m, 0.18H), 7.44 – 7.39 (m, 2H), 7.39 – 7.36 (m, 0.18H), 7.35 – 7.30 (m, 1H), 7.30 – 7.27 (m, 0.09H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 0.09H), 4.09 (d, *J* = 0.8 Hz, 0.27 H), 3.39 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.3, 143.8, 129.0, 128.9, 128.4, 126.8, 123.5, 105.2 (d, *J* = 5.2 Hz), 102.6, 101.2 (d, *J* = 1.5 Hz) 32.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.86, -118.64; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{10}FN_2O_2$: 221.0726. Found: 221.0729. Calcd for $C_{11}H_{10}FN_2O_3$: 237.0675. Found: 237.0677.

NMR Spectra of enamines:

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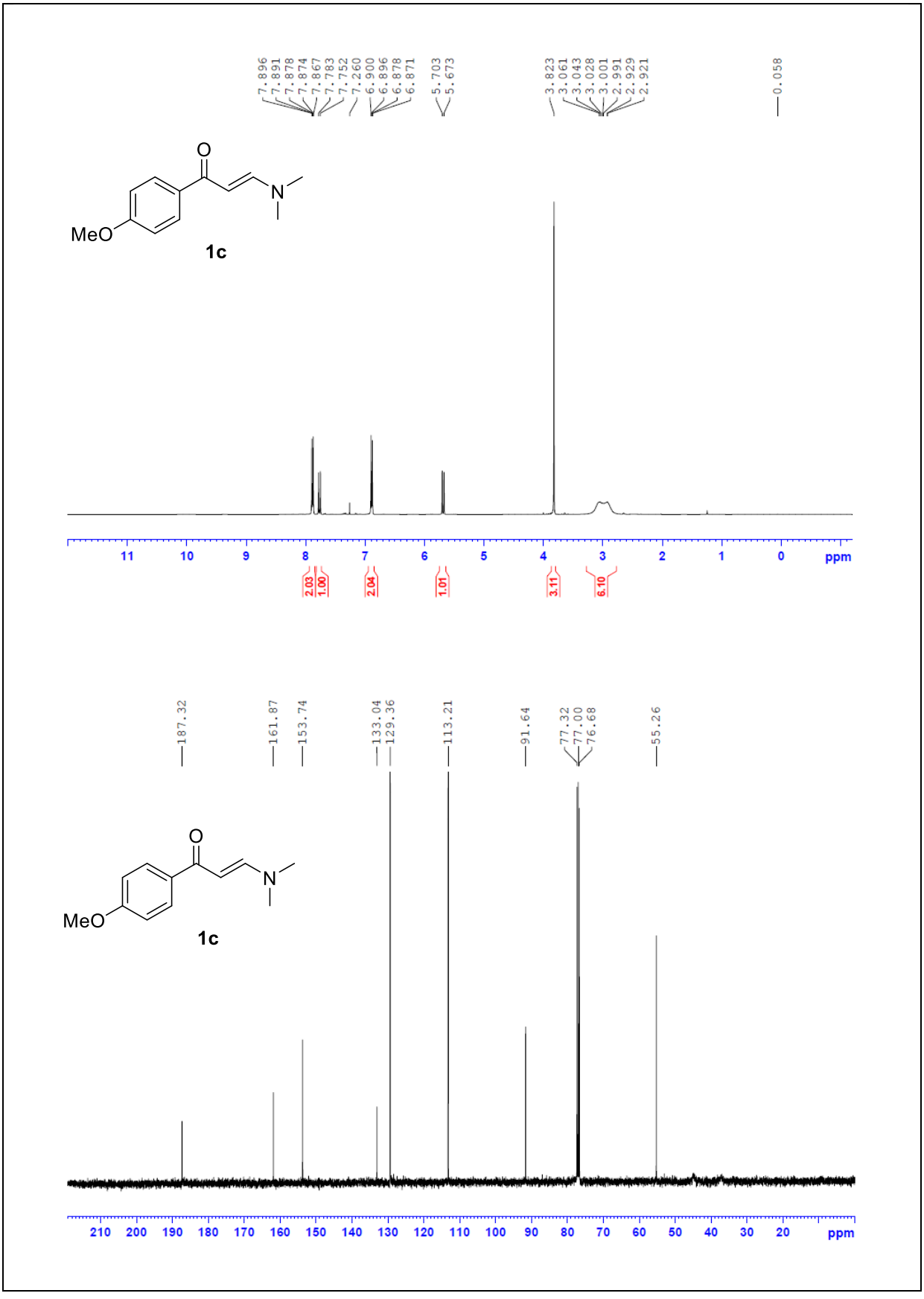
7.801
7.774
7.221
7.201
5.731
5.700
3.111
2.937
2.387
0.000
O
N
1b
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.93
1.96
1.00
2.94
2.98
3.04
188.36
153.97
141.21
137.76
128.77
127.55
92.09
77.32
77.00
76.68
21.44
O
N
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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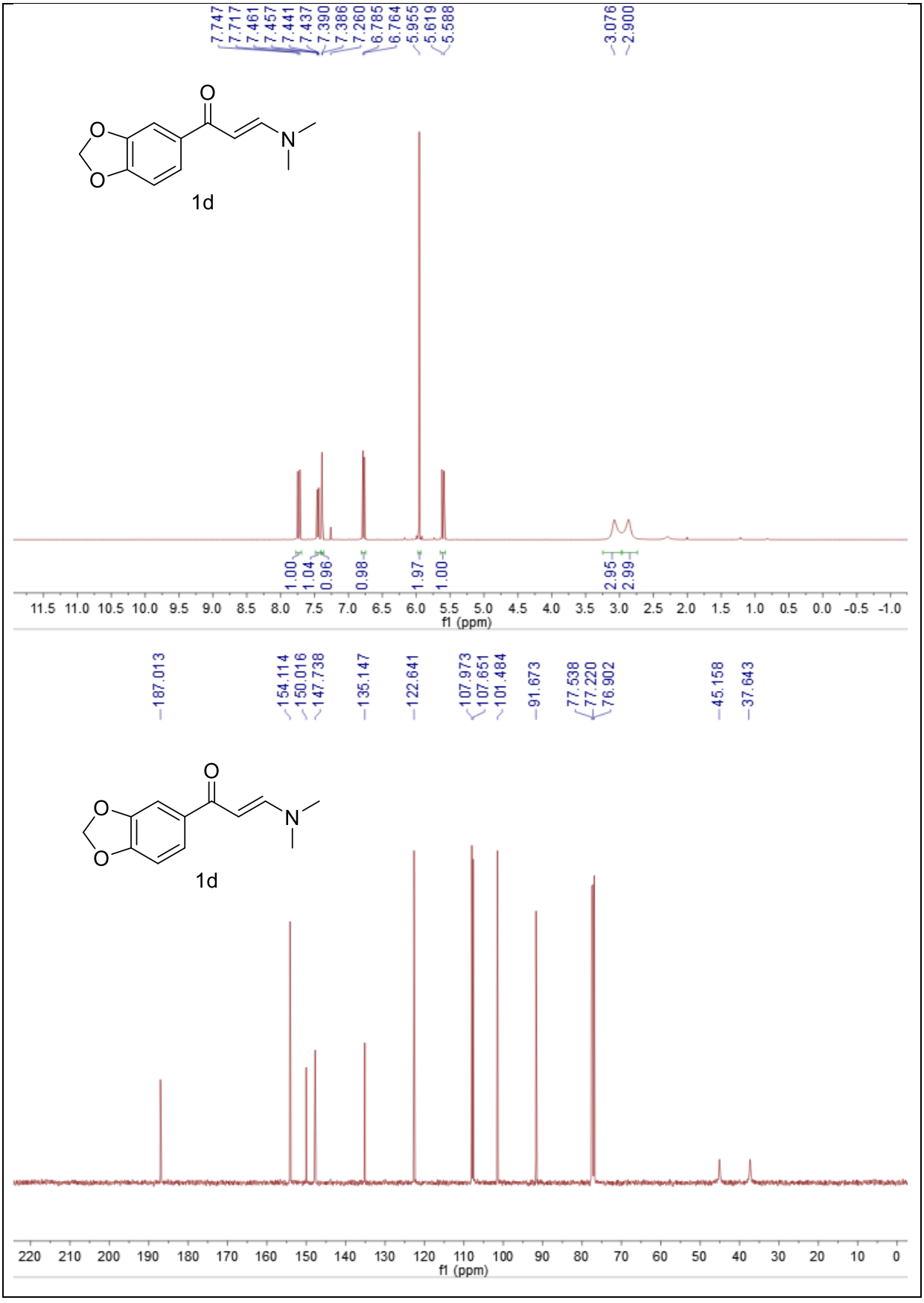
7.891
7.878
7.874
7.867
7.783
7.752
7.260
6.900
6.896
6.878
6.871
5.703
5.673
3.823
3.061
3.043
3.028
3.001
2.991
2.929
2.921
0.058
O
N
MeO
1c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.00
2.04
1.01
3.11
6.10
187.32
161.87
153.74
133.04
129.36
113.21
91.64
77.32
77.00
76.68
55.26
O
N
MeO
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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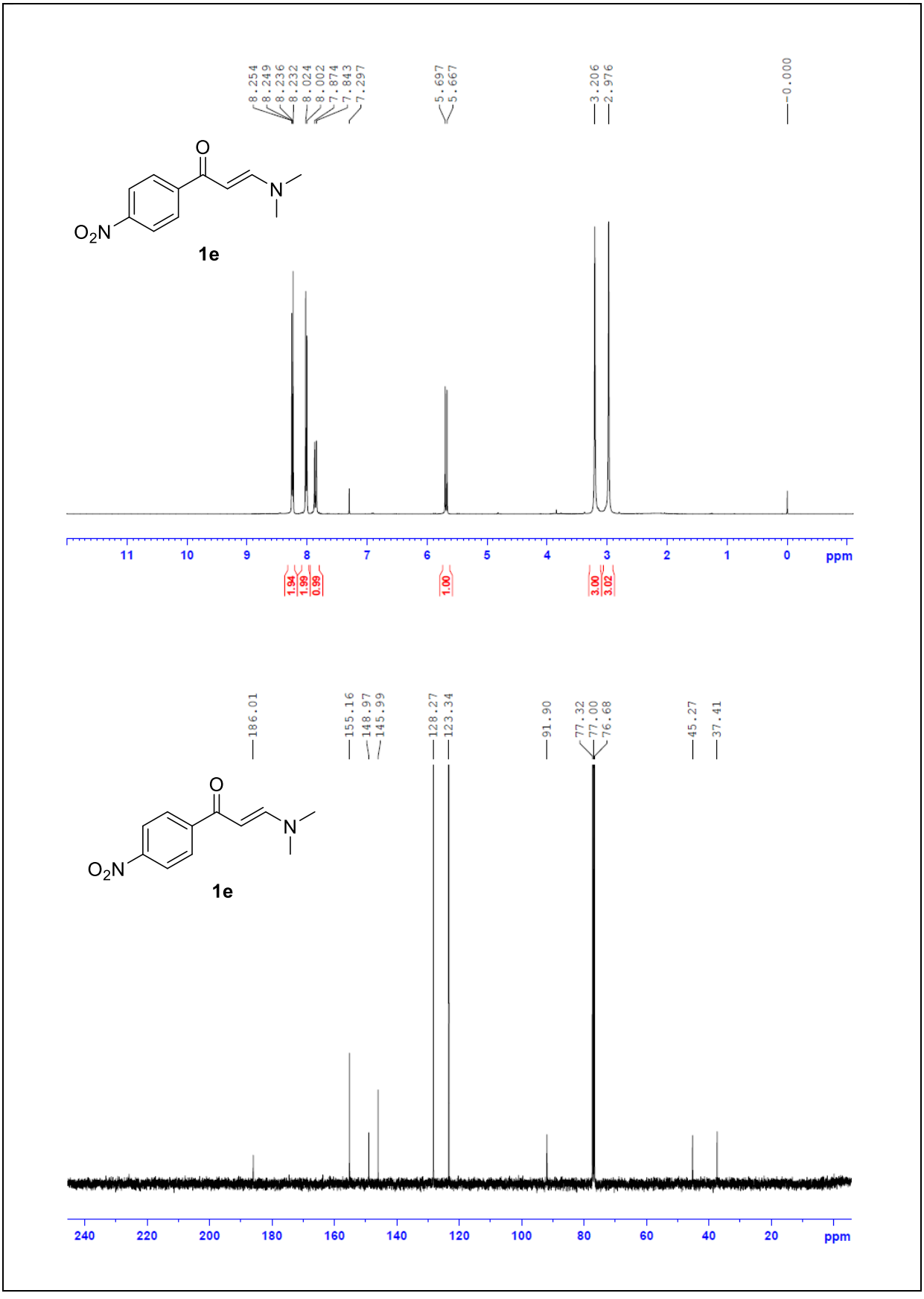
7.461
7.457
7.441
7.437
7.390
7.386
7.260
6.785
6.764
5.955
5.619
5.588
3.076
2.900
O
O
O
N
1d
1.00
1.04
0.96
0.98
1.97
1.00
2.95
2.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
187.013
154.114
150.016
147.738
135.147
122.641
107.973
107.651
101.484
91.673
77.538
77.220
76.902
45.158
37.643
O
O
O
N
1d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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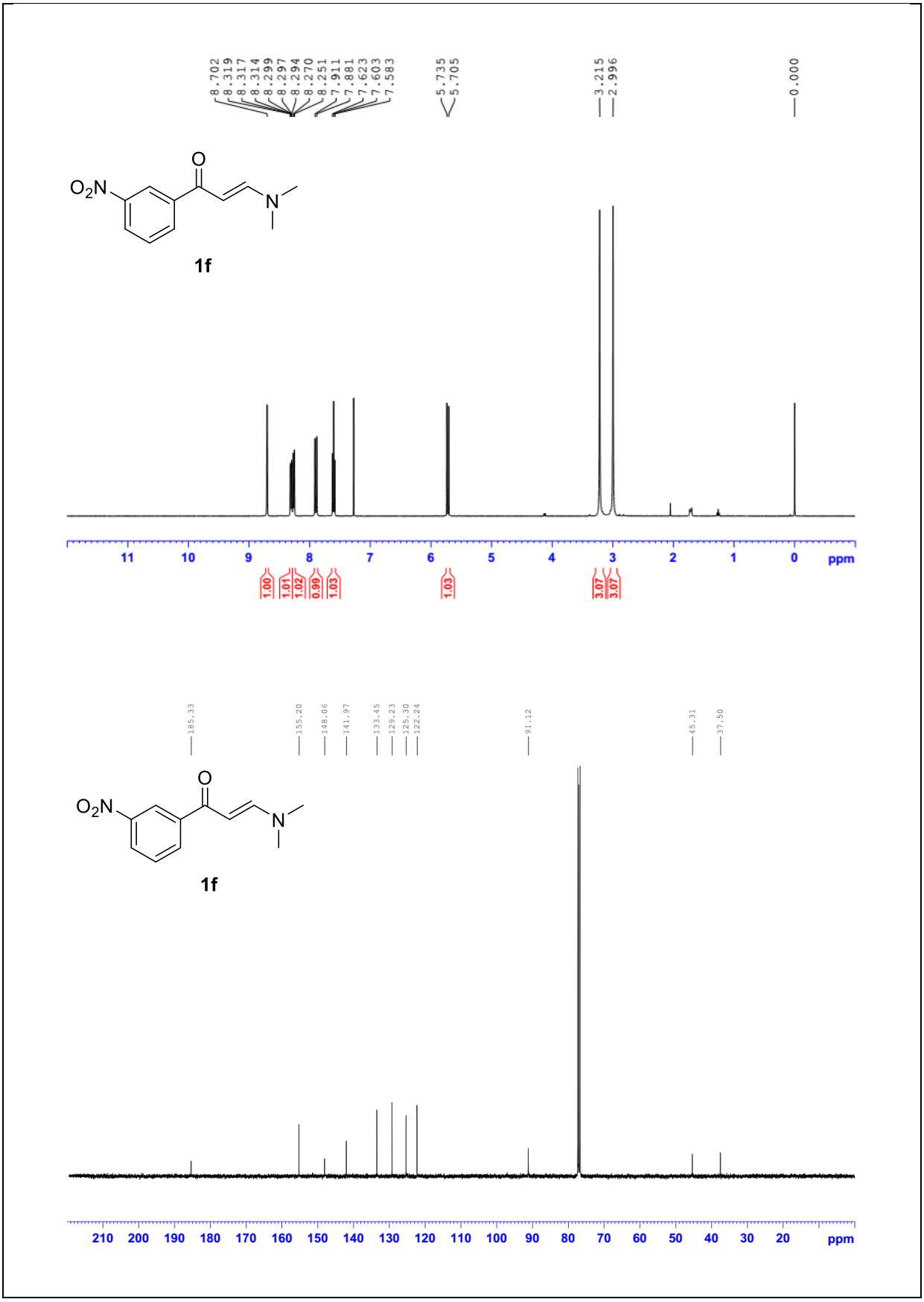
8.249
8.236
8.232
8.024
8.002
7.874
7.843
7.297
5.697
5.667
3.206
2.976
0.000
O
N
O2N
1e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.99
0.99
1.00
3.00
3.02
186.01
155.16
148.97
145.99
128.27
123.34
91.90
77.32
77.00
76.68
45.27
37.41
O
N
O2N
1e
240
220
200
180
160
140
120
100
80
60
40
20
ppm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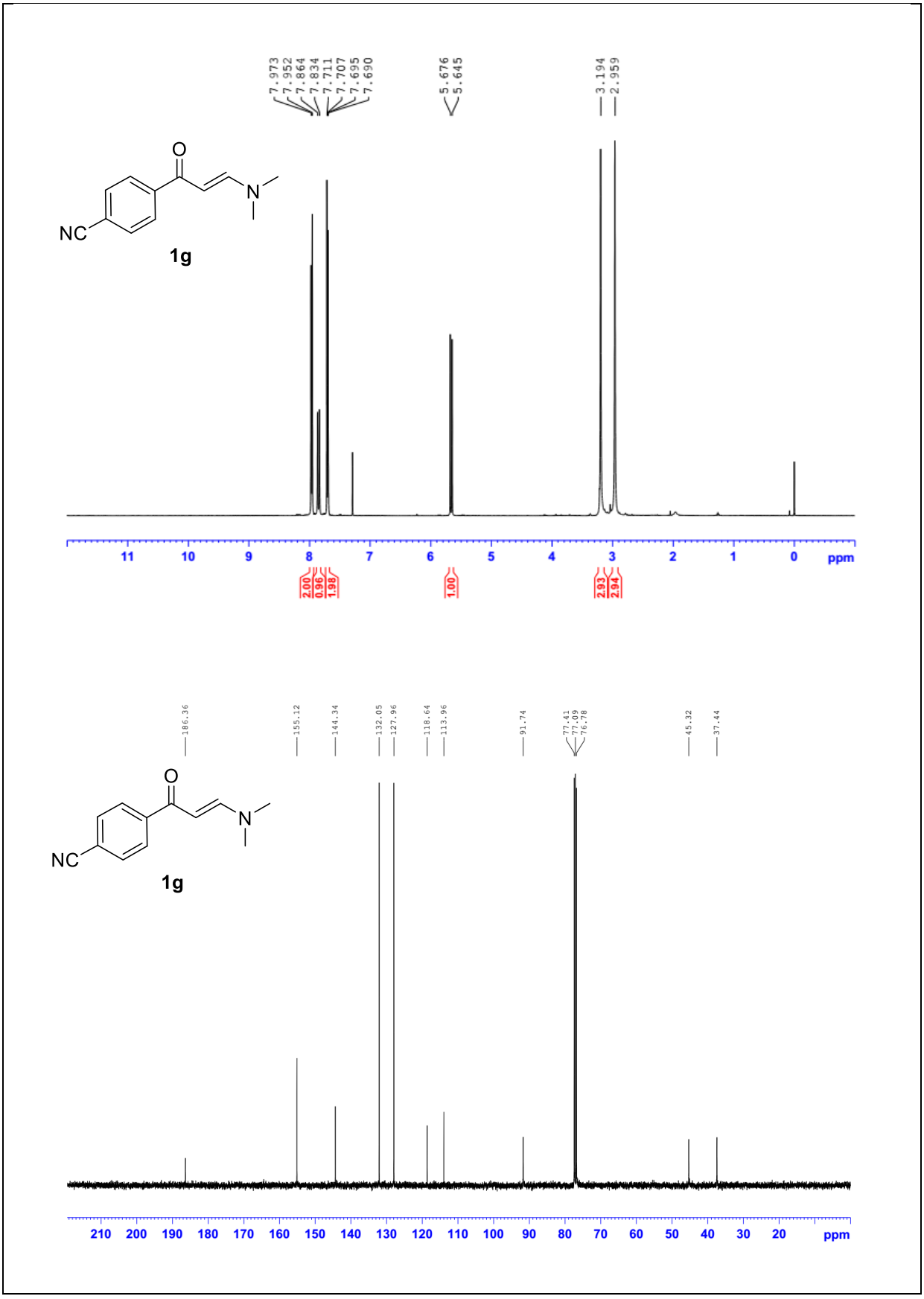
8.317
8.314
8.299
8.297
8.294
8.270
8.251
7.911
7.881
7.623
7.603
7.583
5.735
5.705
3.215
2.996
0.000
O
O2N
N
1f
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.01 1.02 0.99 1.03 1.03 3.07 3.07
185.33
155.20
148.06
141.97
133.45
129.23
125.30
122.24
91.12
45.31
37.50
O
O2N
N
1f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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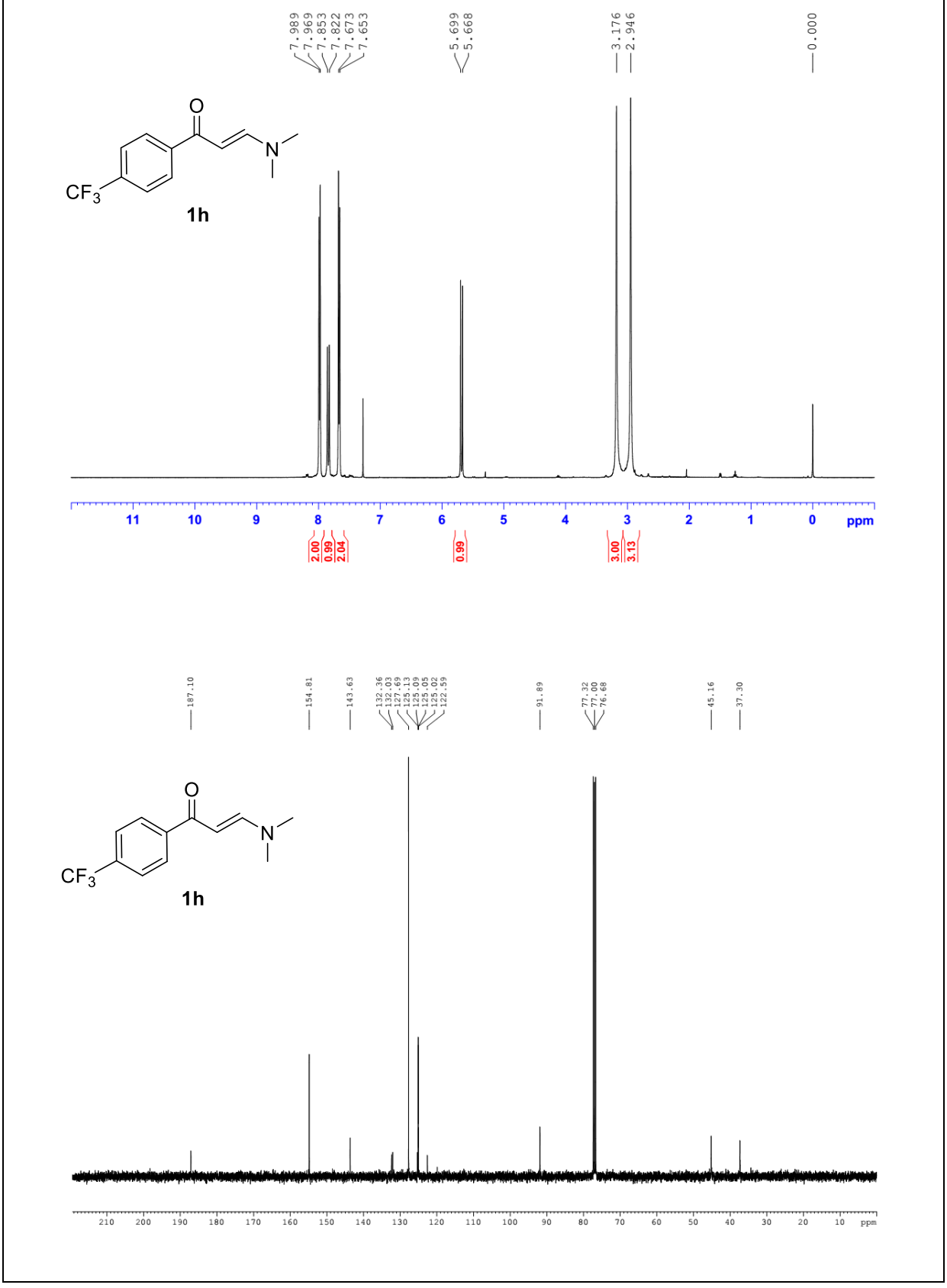
7.952
7.864
7.834
7.711
7.707
7.695
7.690
5.676
5.645
3.194
2.959
O
N
NC
1g
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
0.96
1.98
1.00
2.93
2.94
186.36
155.12
144.34
132.05
127.96
118.64
113.96
91.74
77.41
77.09
76.78
45.32
37.44
O
N
NC
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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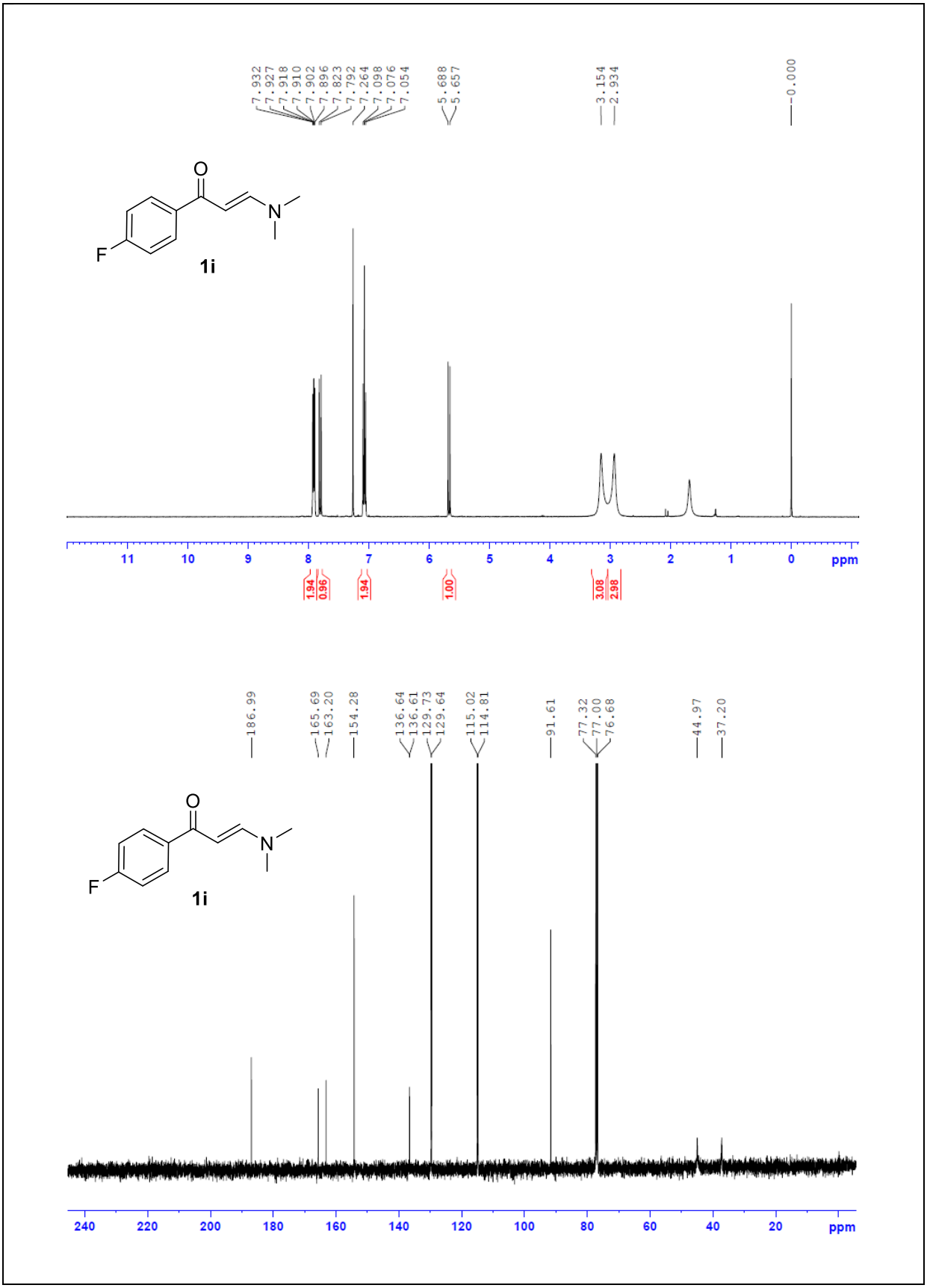
7.969
7.853
7.822
7.673
7.653
5.699
5.668
3.176
2.946
0.000
O
N
CF3
1h
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00 0.99 2.04 0.99 3.00 3.13
187.10
154.81
143.63
132.36
132.03
127.69
125.13
125.09
125.05
125.02
122.59
91.89
77.32
77.00
76.68
45.16
37.30
O
N
CF3
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.918
7.910
7.902
7.896
7.823
7.792
7.264
7.098
7.076
7.054
5.688
5.657
3.154
2.934
0.000
O
N
F
1i
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
0.96
1.94
1.00
3.08
2.98
186.99
165.69
163.20
154.28
136.64
136.61
129.73
129.64
115.02
114.81
91.61
77.32
77.00
76.68
44.97
37.20
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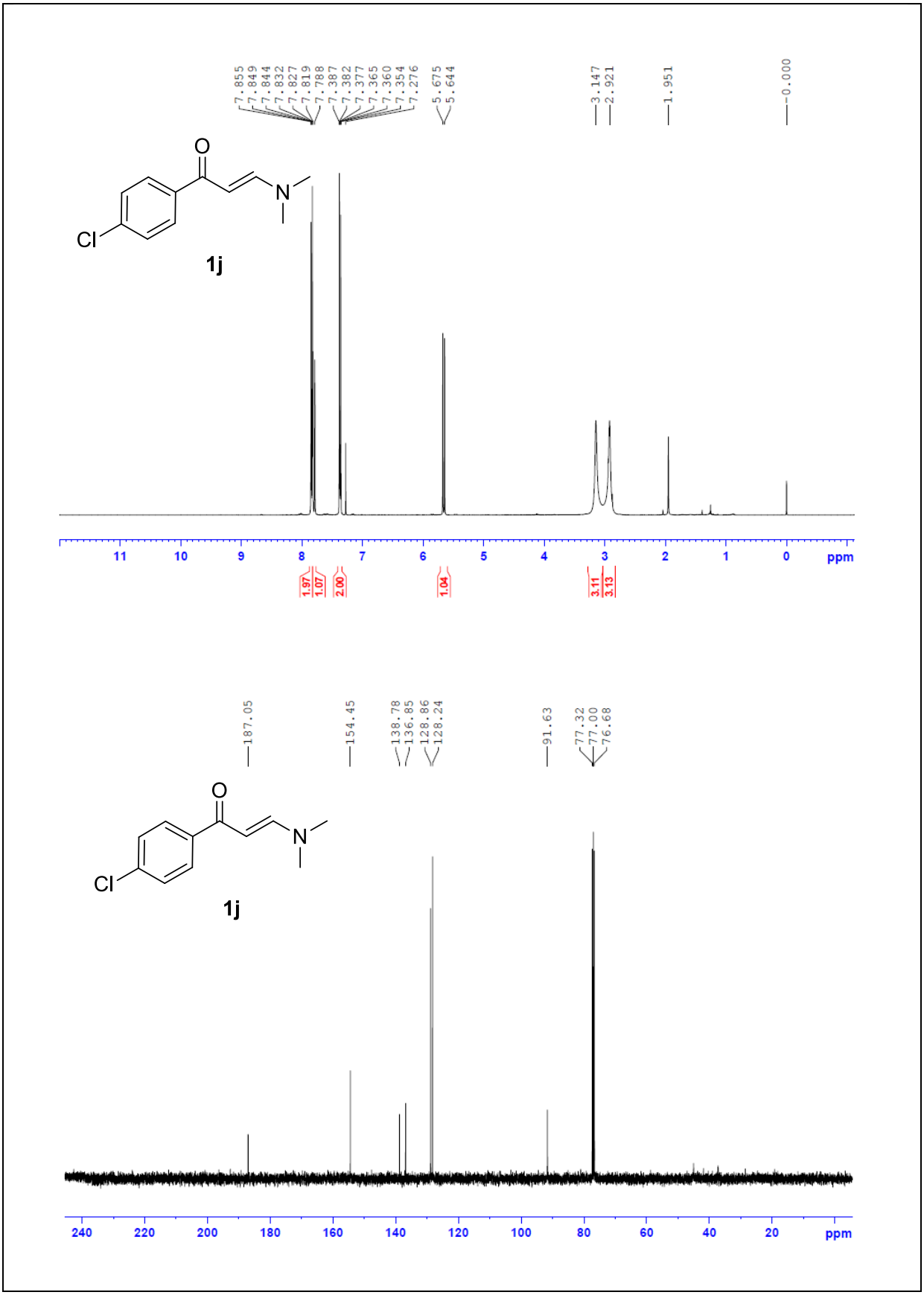
N
F
1i
240
220
200
180
160
140
120
100
80
60
40
20
ppm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7.832
7.827
7.819
7.788
7.387
7.382
7.377
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7.360
7.354
7.276
5.675
5.644
3.147
2.921
1.951
0.000
O
N
Cl
1j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
1.07
2.00
1.04
3.11
3.13
187.05
154.45
138.78
136.85
128.86
128.24
91.63
77.32
77.00
76.68
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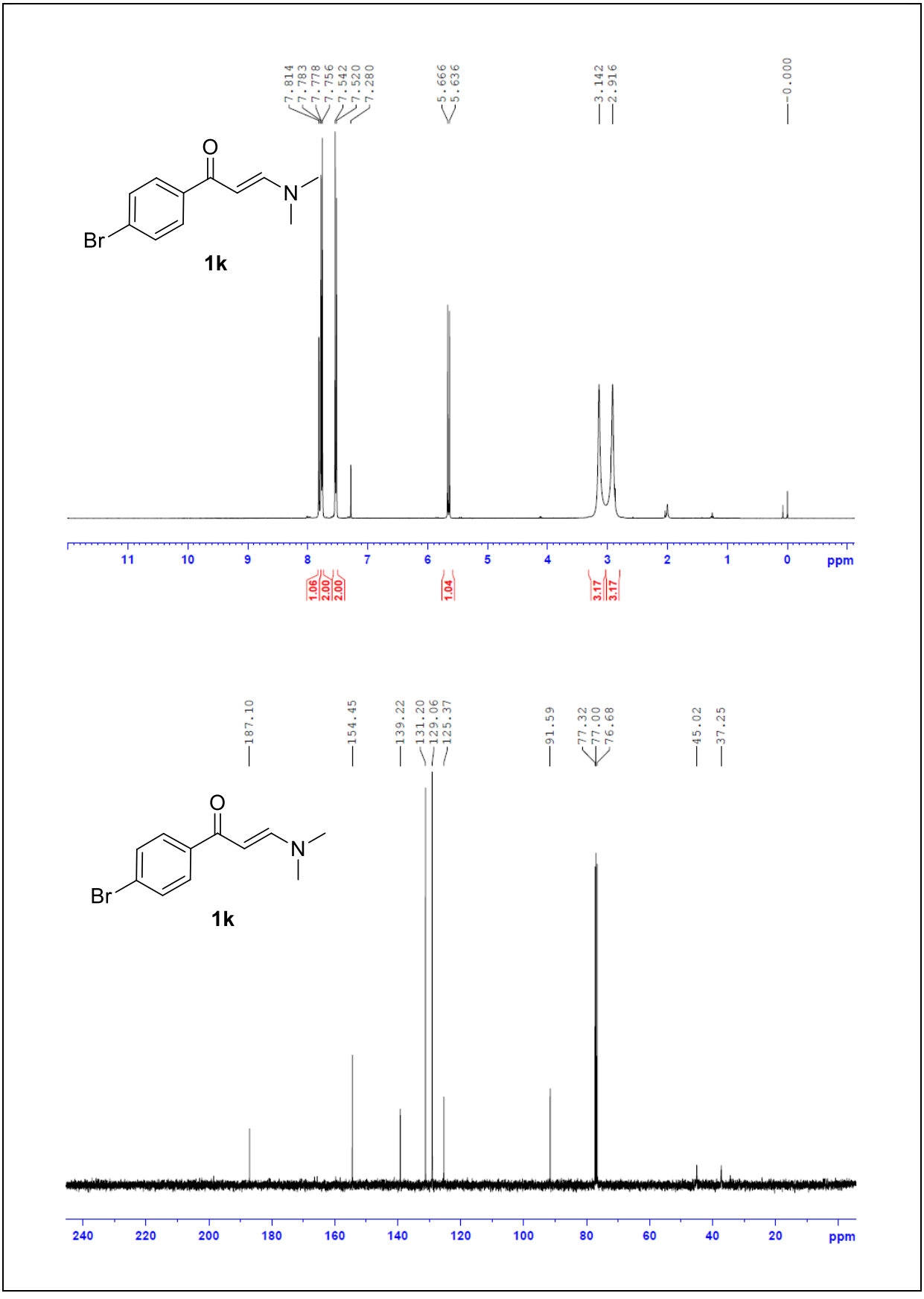
N
Cl
1j
240
220
200
180
160
140
120
100
80
60
40
20
ppm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7.542
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5.666
5.636
3.142
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O
N
Br
1k
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
2.00
2.00
1.04
3.17
3.17
187.10
154.45
139.22
131.20
129.06
125.37
91.59
77.32
77.00
76.68
45.02
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Br
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60
40
20
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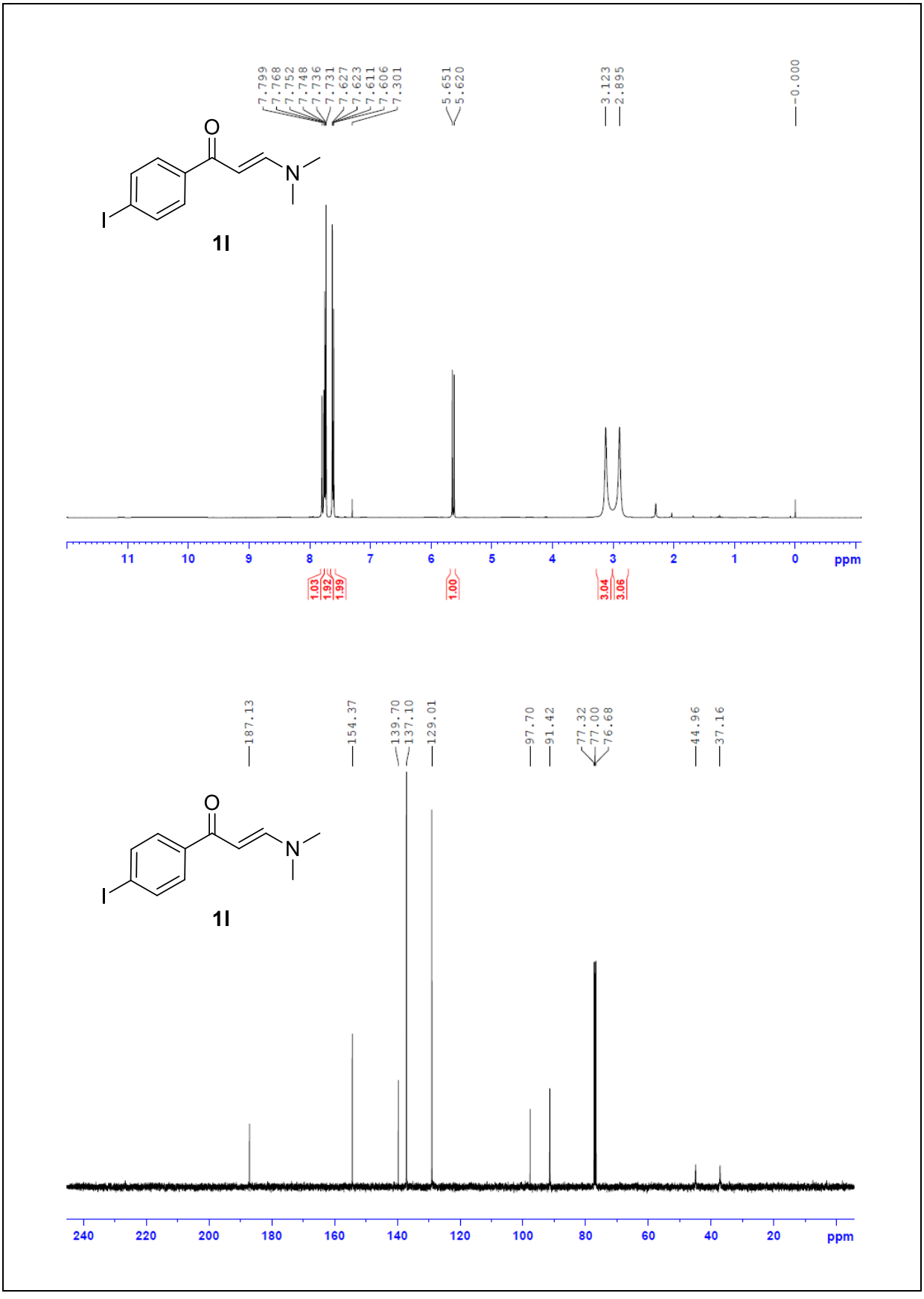
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7.752
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7.606
7.301
5.651
5.620
3.123
2.895
-0.000
O
N
I
1l
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.92
1.99
1.00
3.04
3.06
187.13
154.37
139.70
137.10
129.01
97.70
91.42
77.32
77.00
76.68
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1l
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20
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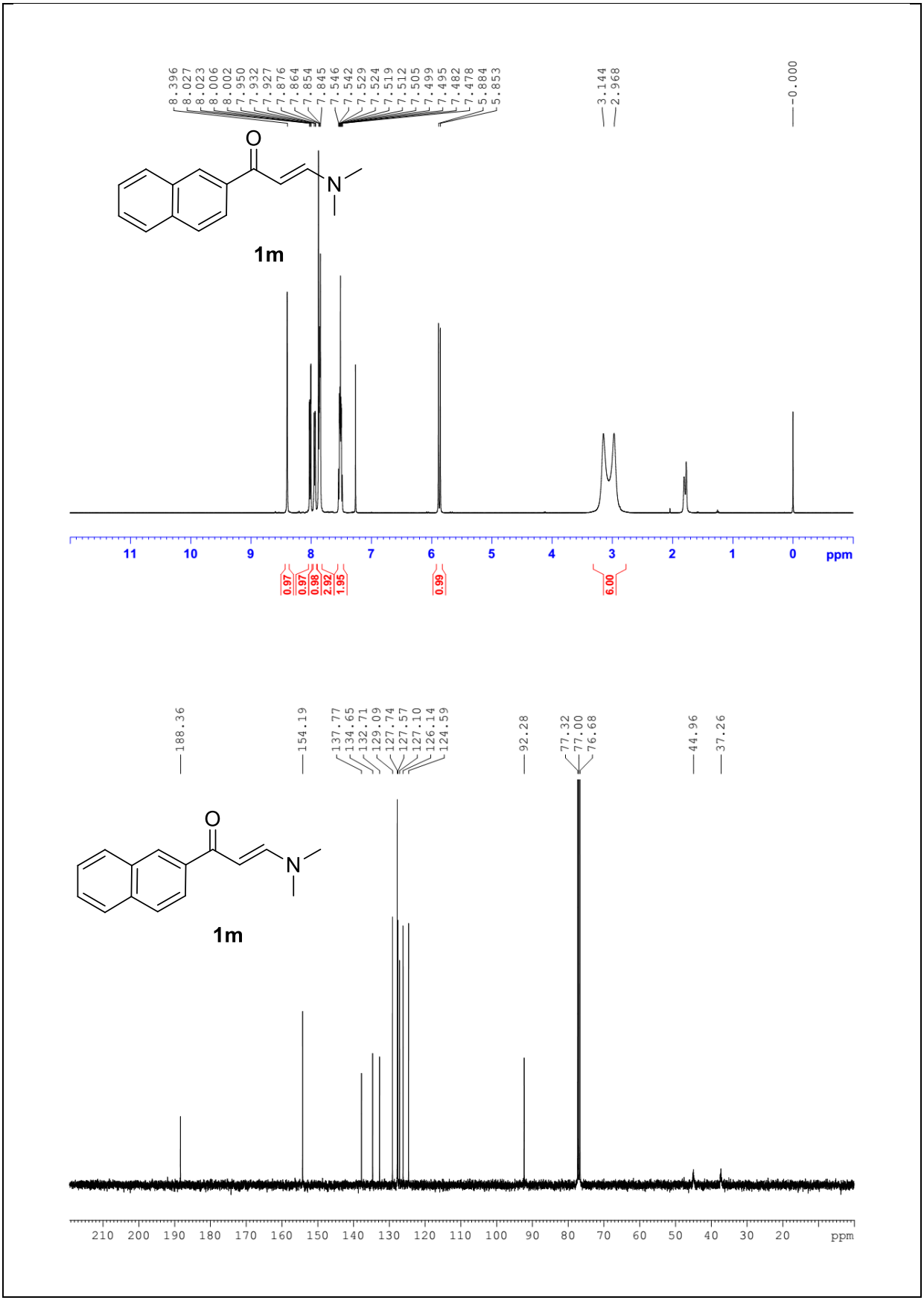
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7.546
7.542
7.529
7.524
7.519
7.512
7.505
7.499
7.495
7.482
7.478
5.884
5.853
3.144
2.968
0.000
O
N
1m
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.97 0.97 0.98 2.92 1.95 0.99 6.00
188.36
154.19
137.77
134.65
132.71
129.09
127.74
127.57
127.10
126.14
124.59
92.28
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77.00
76.68
44.96
37.26
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N
1m
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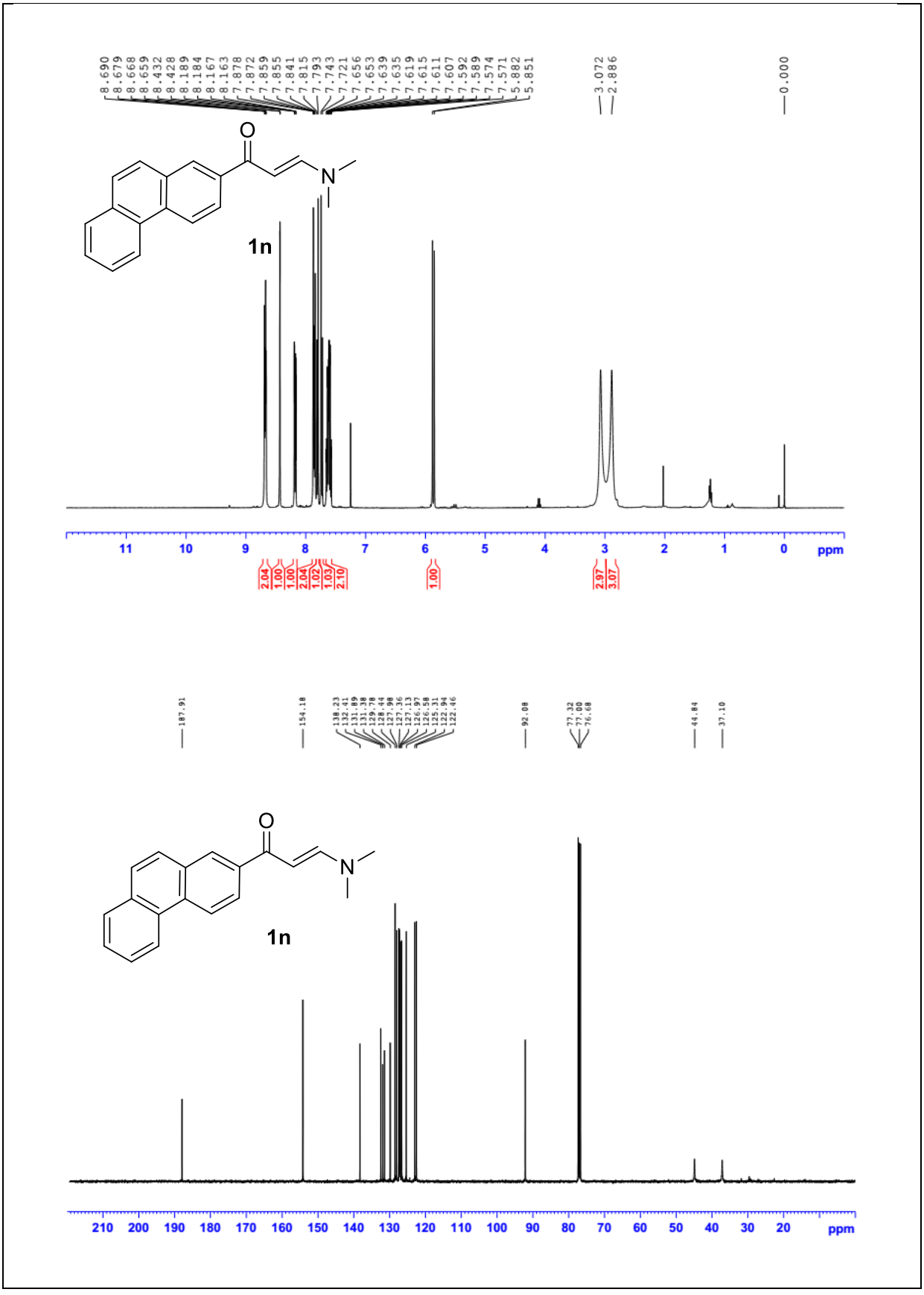
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7.859
7.855
7.841
7.815
7.793
7.743
7.721
7.656
7.653
7.639
7.635
7.619
7.615
7.611
7.607
7.592
7.589
7.574
7.571
5.882
5.851
3.072
2.886
0.000
O
N
1n
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.04
1.00
1.00
2.04
1.02
1.03
2.10
1.00
2.97
3.07
187.91
154.18
138.23
132.41
131.89
131.38
129.78
129.44
127.94
127.36
127.13
126.97
126.58
125.31
122.94
122.46
92.08
77.32
77.00
76.68
44.84
37.10
O
N
1n
210
200
190
180
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160
150
140
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100
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80
70
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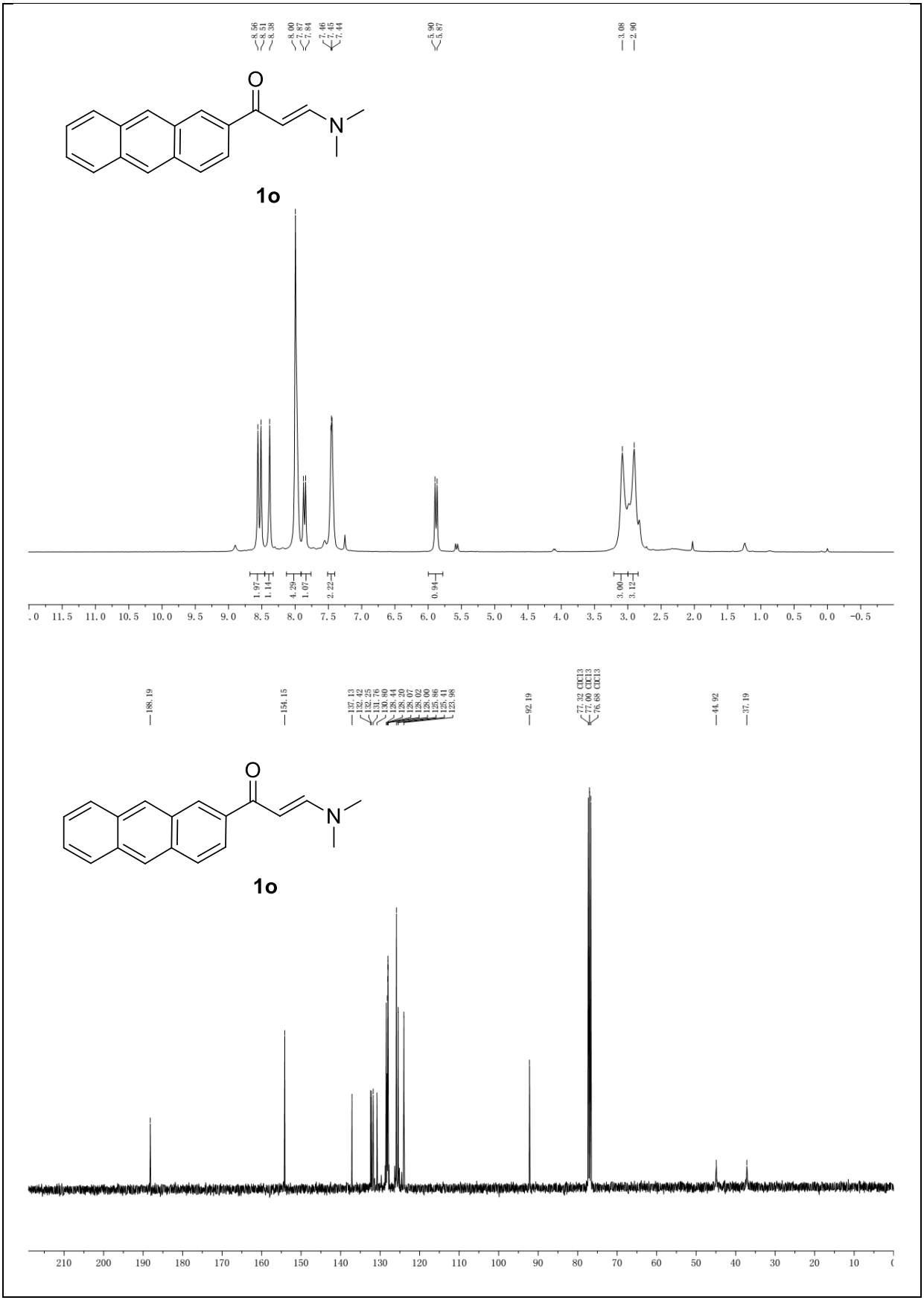
50
40
30
20
ppm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8.38
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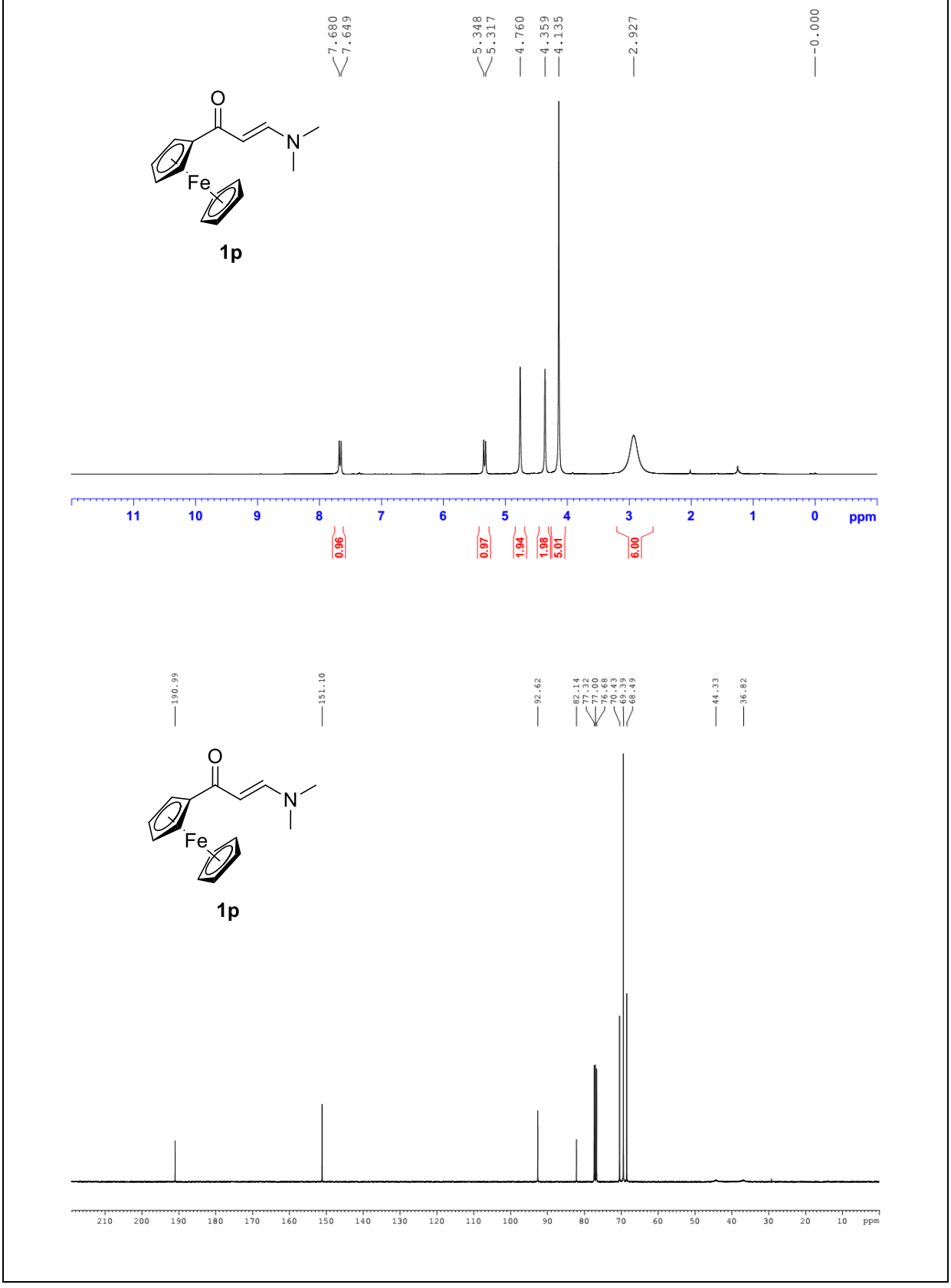
7.84
7.46
7.45
7.44
5.90
5.87
3.08
2.90
O
N
1o
1.97
1.14
4.29
1.07
2.22
0.94
3.00
3.12
188.19
154.15
137.13
132.82
132.25
131.76
130.80
128.44
128.30
128.07
128.02
126.00
125.86
125.41
123.98
92.19
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
44.92
37.19
O
N
1o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2.927
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O
N
Fe
1p
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.97
1.94
1.98
5.01
6.00
190.99
151.10
92.62
82.14
77.32
77.00
76.68
70.43
69.39
68.49
44.33
36.82
O
N
Fe
1p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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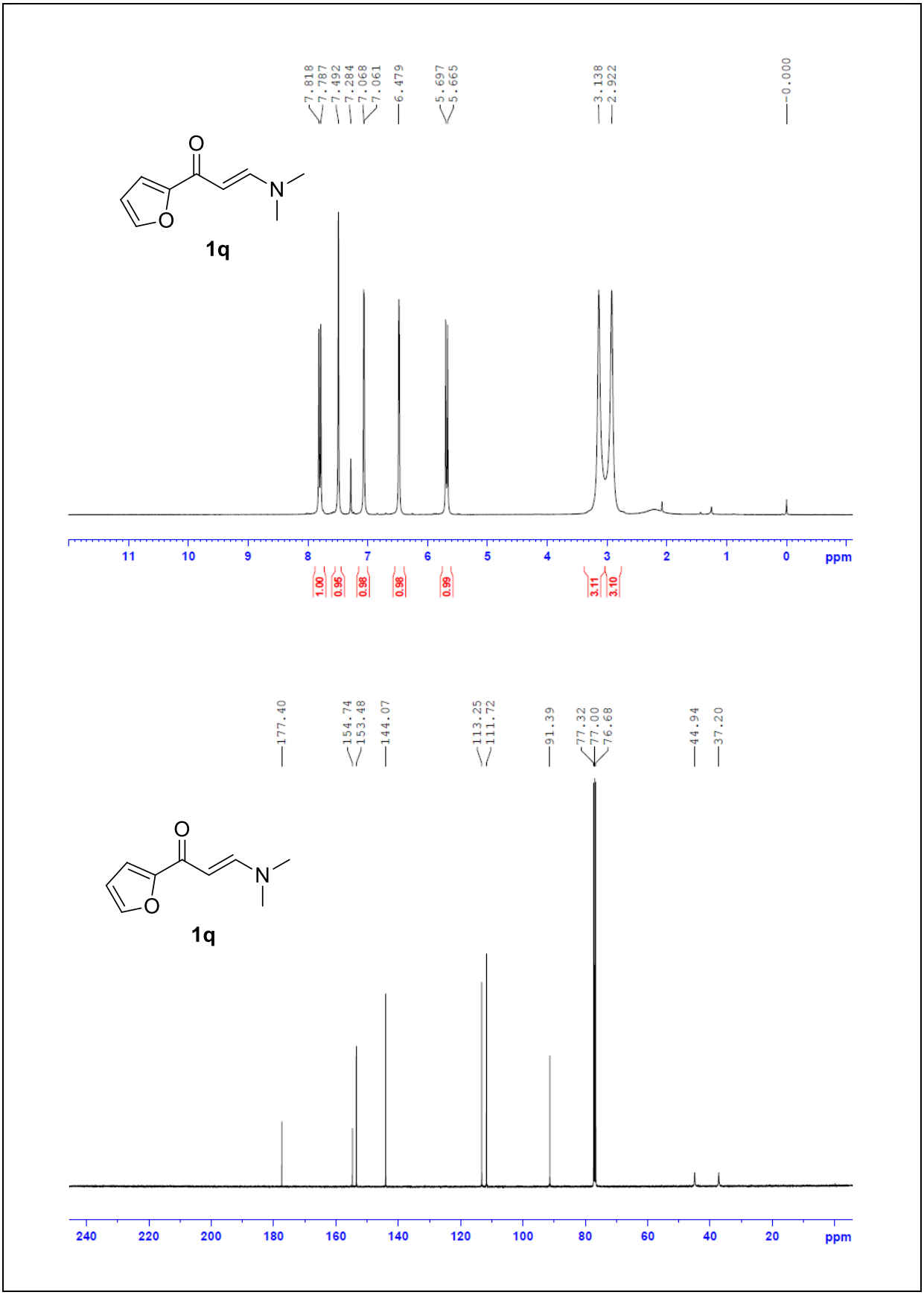
40
30
20
10
ppm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7.787
7.492
7.284
7.068
7.061
6.479
5.697
5.665
3.138
2.922
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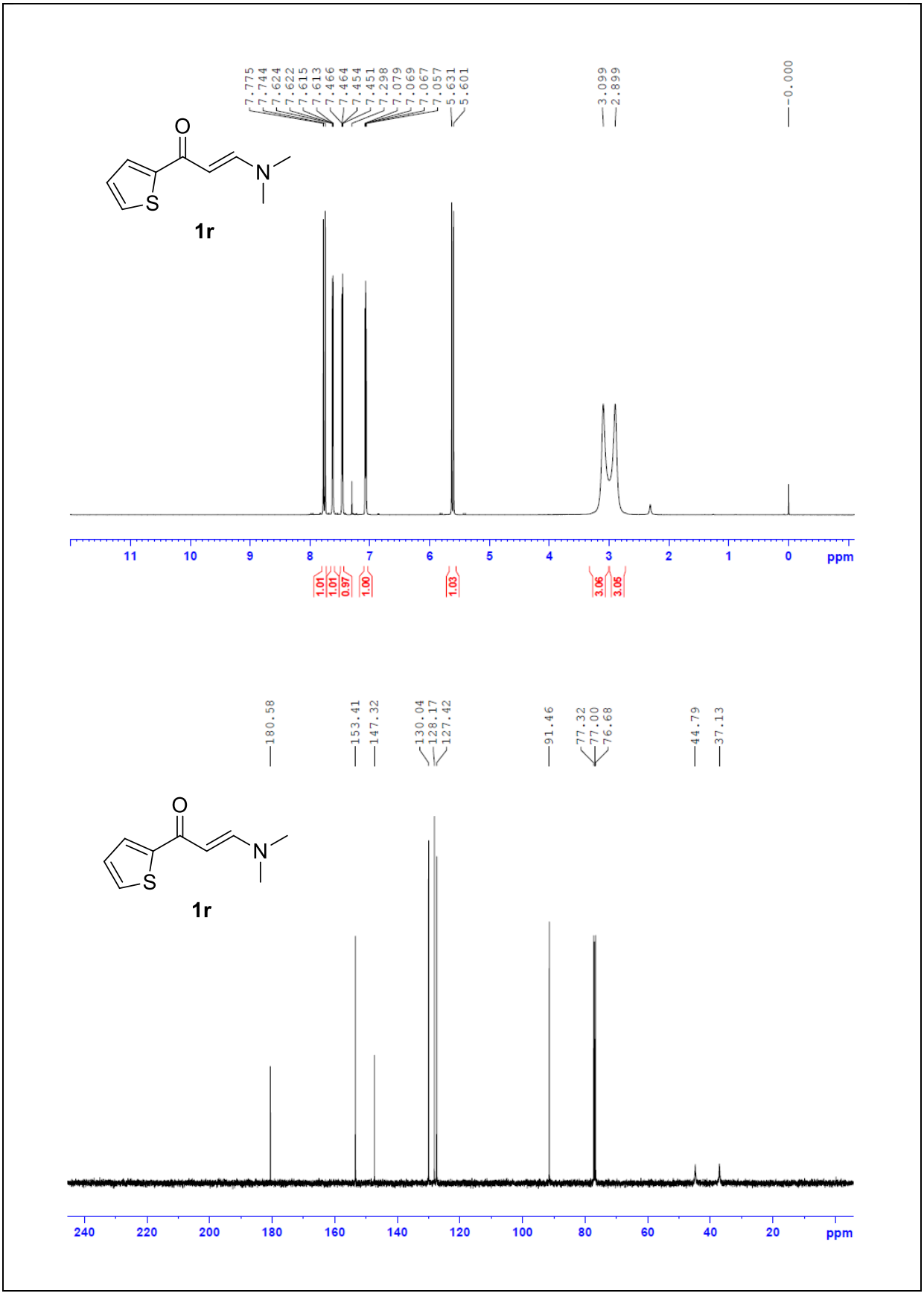
1q
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.95
0.98
0.98
0.99
3.11
3.10
177.40
154.74
153.48
144.07
113.25
111.72
91.39
77.32
77.00
76.68
44.94
37.20
1q
240
220
200
180
160
140
120
100
80
60
40
20
ppm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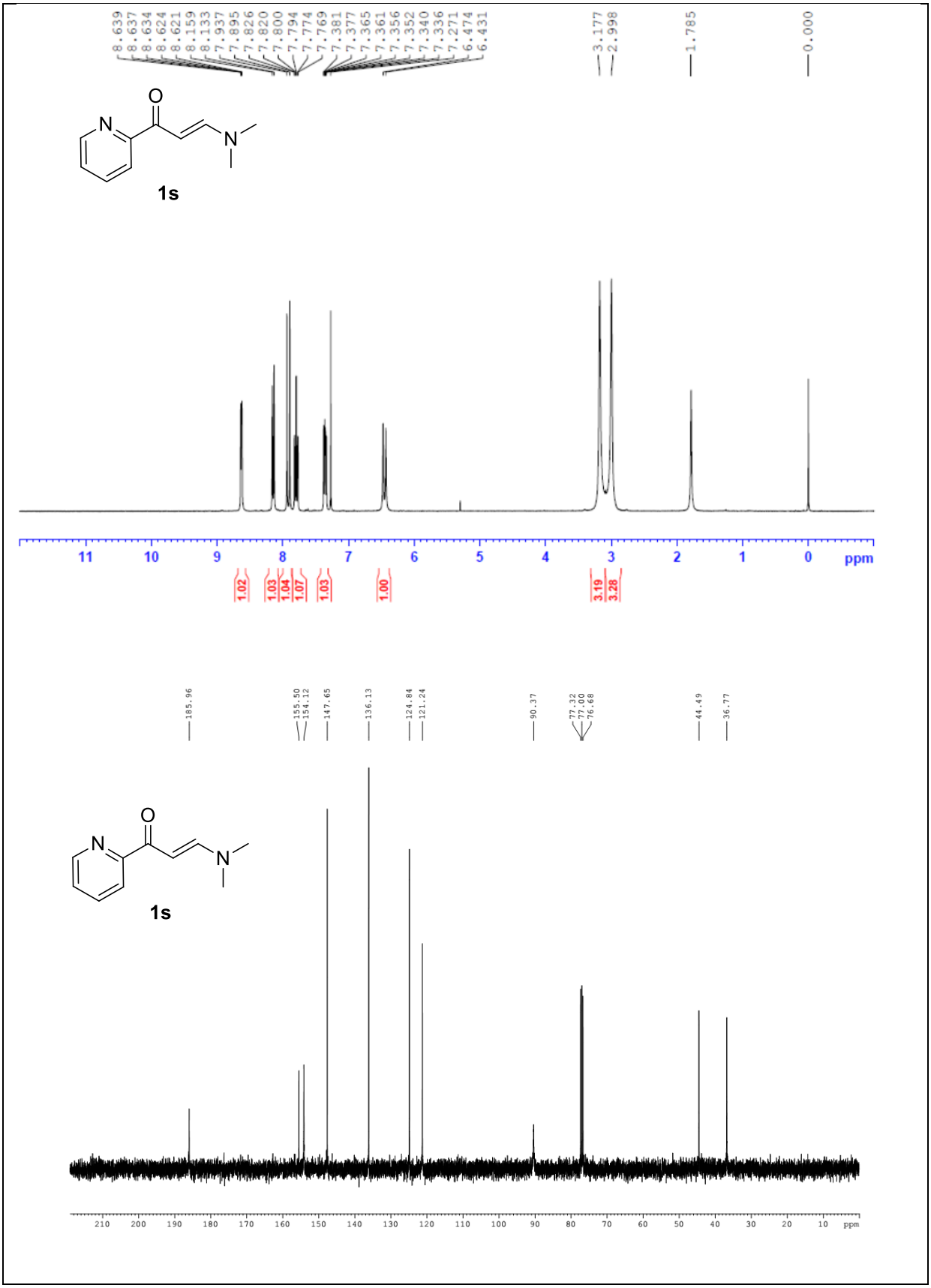
7.624
7.622
7.615
7.613
7.466
7.464
7.454
7.451
7.298
7.079
7.069
7.067
7.057
5.631
5.601
3.099
2.899
0.000
O
N
S
1r
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.01
0.97
1.00
1.03
3.06
3.05
180.58
153.41
147.32
130.04
128.17
127.42
91.46
77.32
77.00
76.68
44.79
37.13
O
N
S
1r
240
220
200
180
160
140
120
100
80
60
40
20
ppm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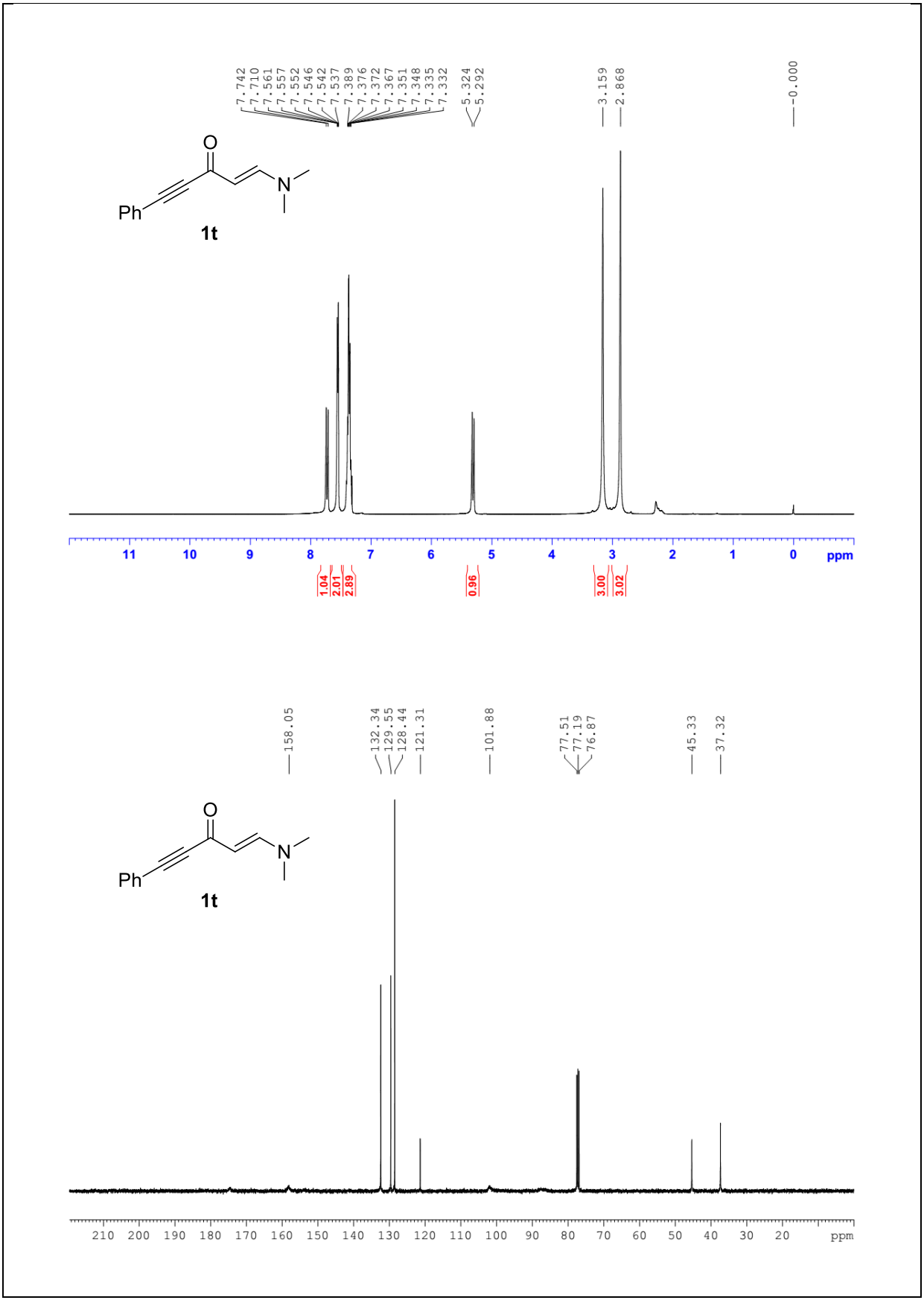
8.637
8.634
8.624
8.621
8.159
8.133
7.937
7.895
7.826
7.820
7.800
7.794
7.774
7.769
7.381
7.377
7.365
7.361
7.356
7.352
7.340
7.336
7.271
6.474
6.431
3.177
2.998
1.785
0.000
O
N
N
1s
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.03
1.04
1.07
1.03
1.00
3.19
3.28
185.96
155.50
154.12
147.65
136.13
124.84
121.24
90.37
77.32
77.00
76.68
44.49
36.77
O
N
N
1s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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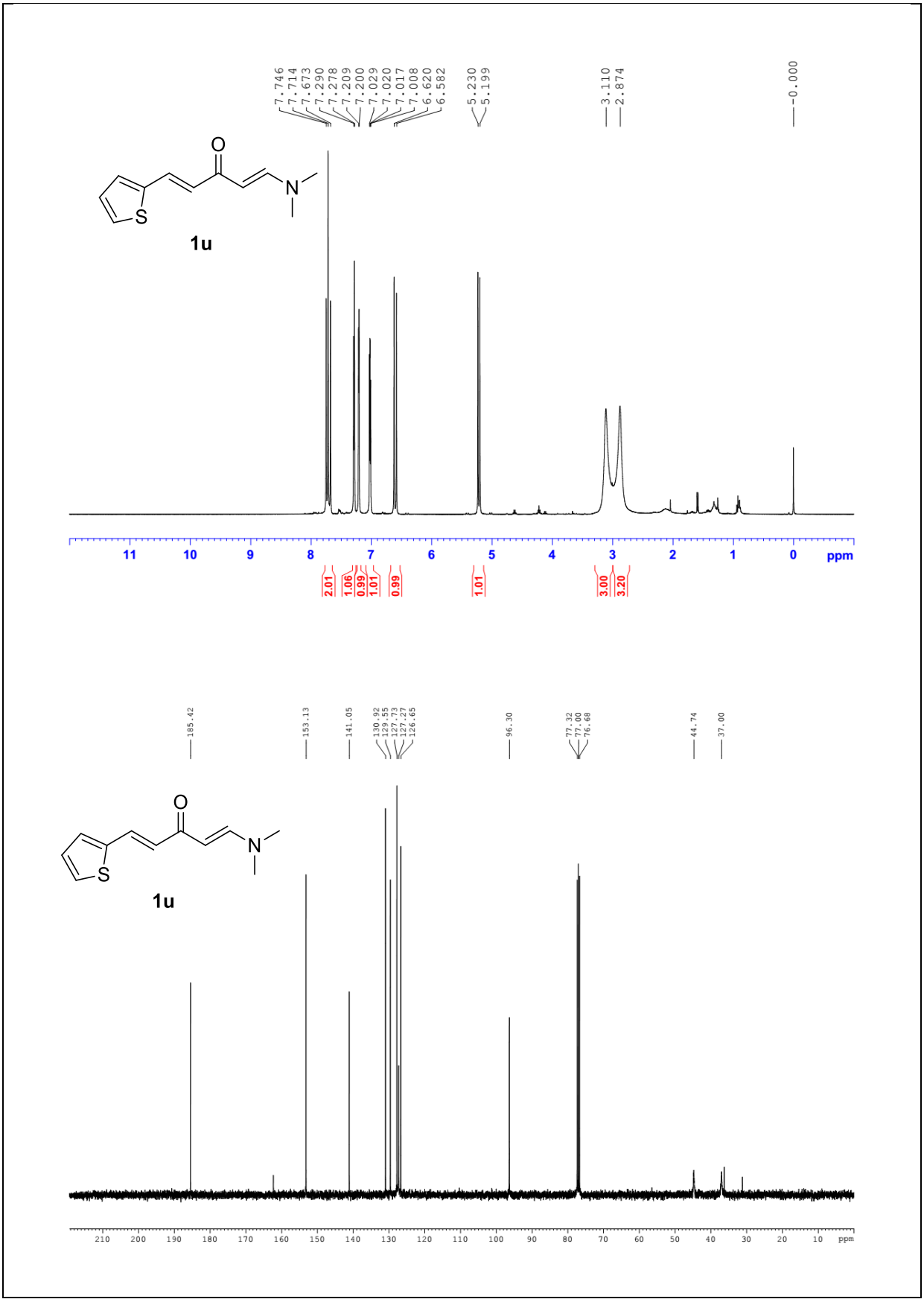
7.542
7.537
7.389
7.376
7.372
7.367
7.351
7.348
7.335
7.332
5.324
5.292
3.159
2.868
0.000
O
N
Ph
1t
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
2.01
2.89
0.96
3.00
3.02
158.05
132.34
129.55
128.44
121.31
101.88
77.51
77.19
76.87
45.33
37.32
O
N
Ph
1t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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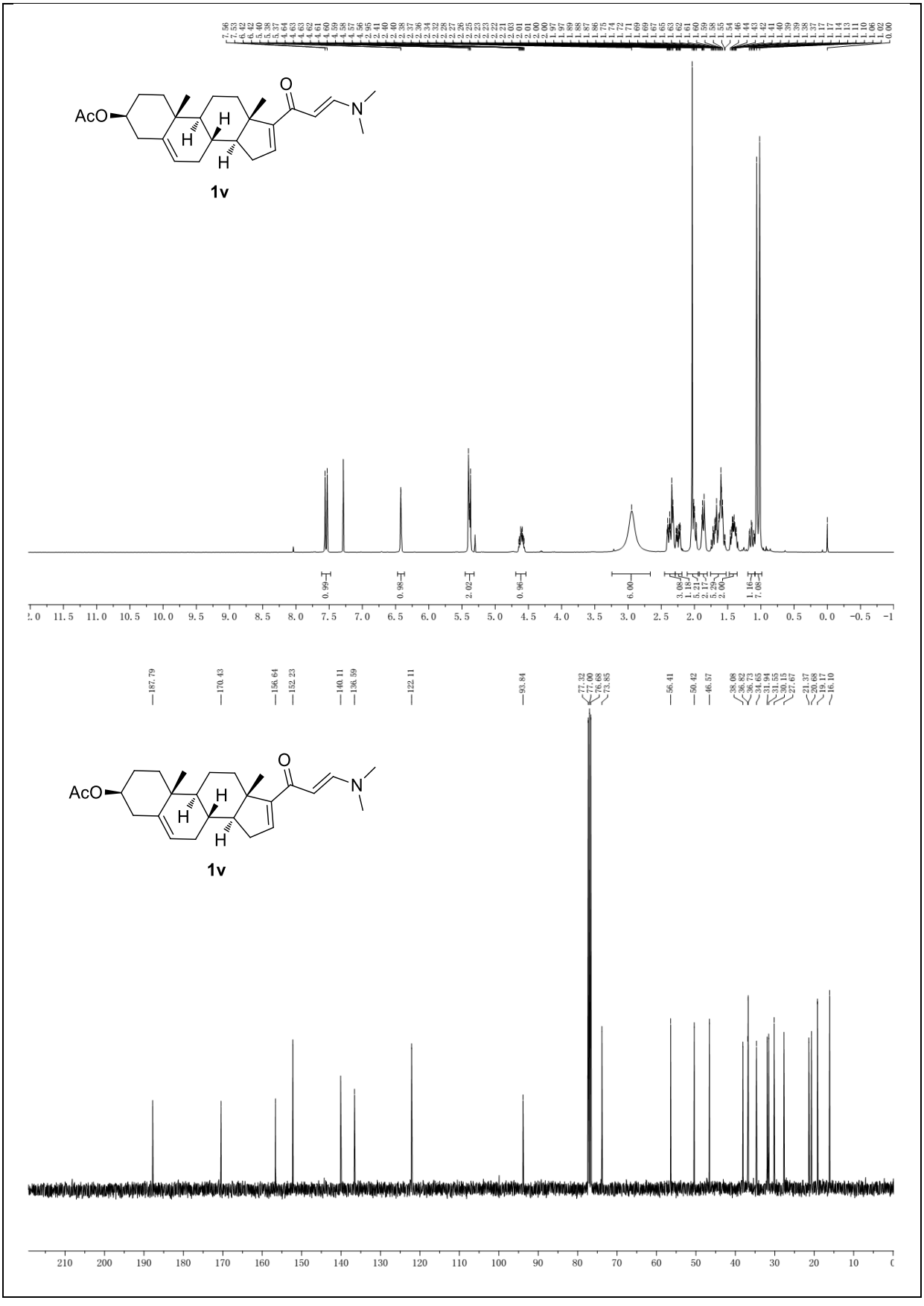
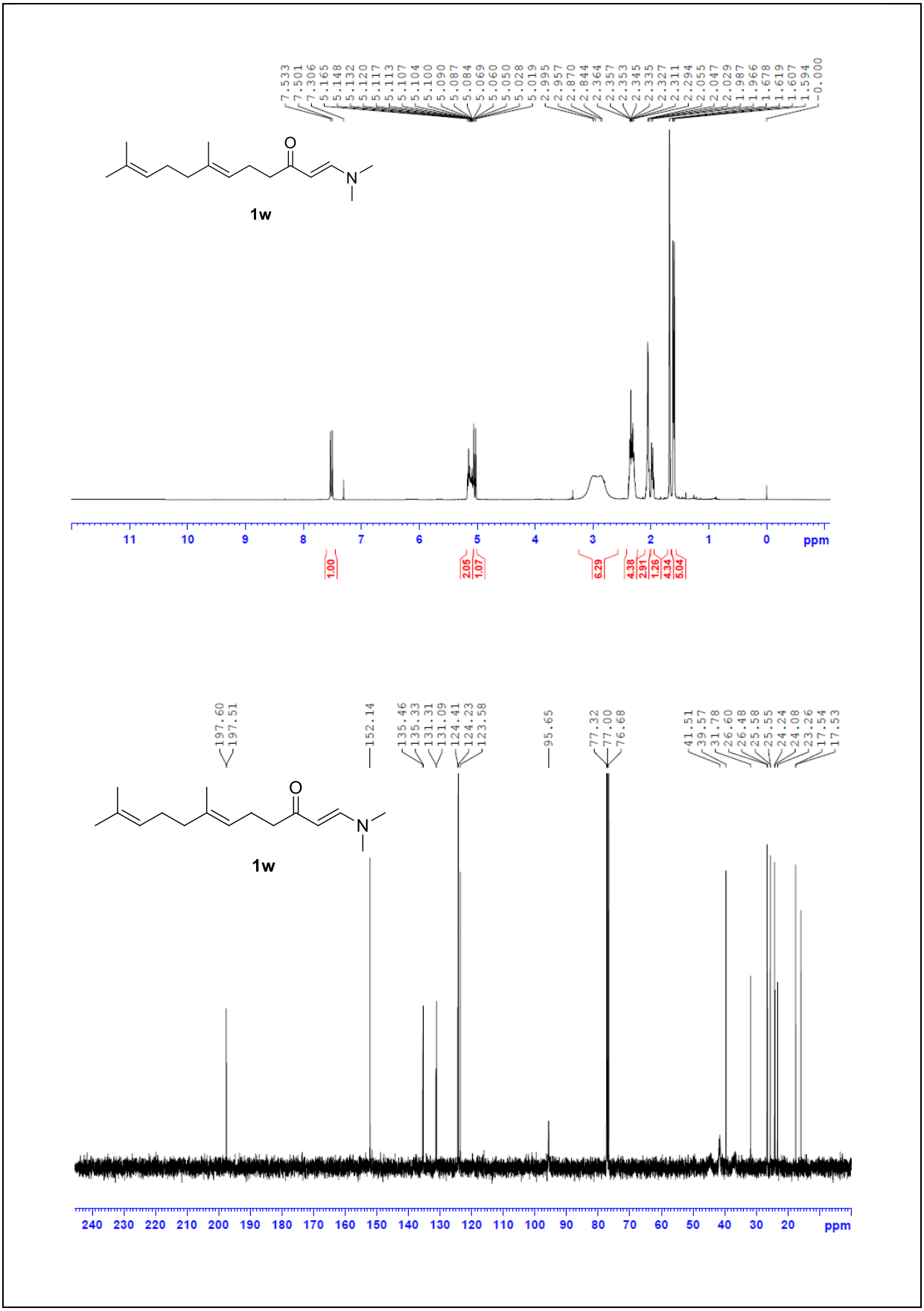
7.673
7.290
7.278
7.209
7.200
7.029
7.020
7.017
7.008
6.620
6.582
5.230
5.199
3.110
2.874
0.000
O
N
S
1u
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.01
1.06
0.99
1.01
0.99
1.01
3.00
3.20
185.42
153.13
141.05
130.92
129.55
127.73
127.27
126.65
96.30
77.32
77.00
76.68
44.74
37.00
O
N
S
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


AcO
O
N
H
H
H
1v
0.99
0.98
2.02
0.96
6.00
3.08
1.18
5.21
2.17
2.29
2.00
1.16
7.08
AcO
O
N
H
H
H
1v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5.132
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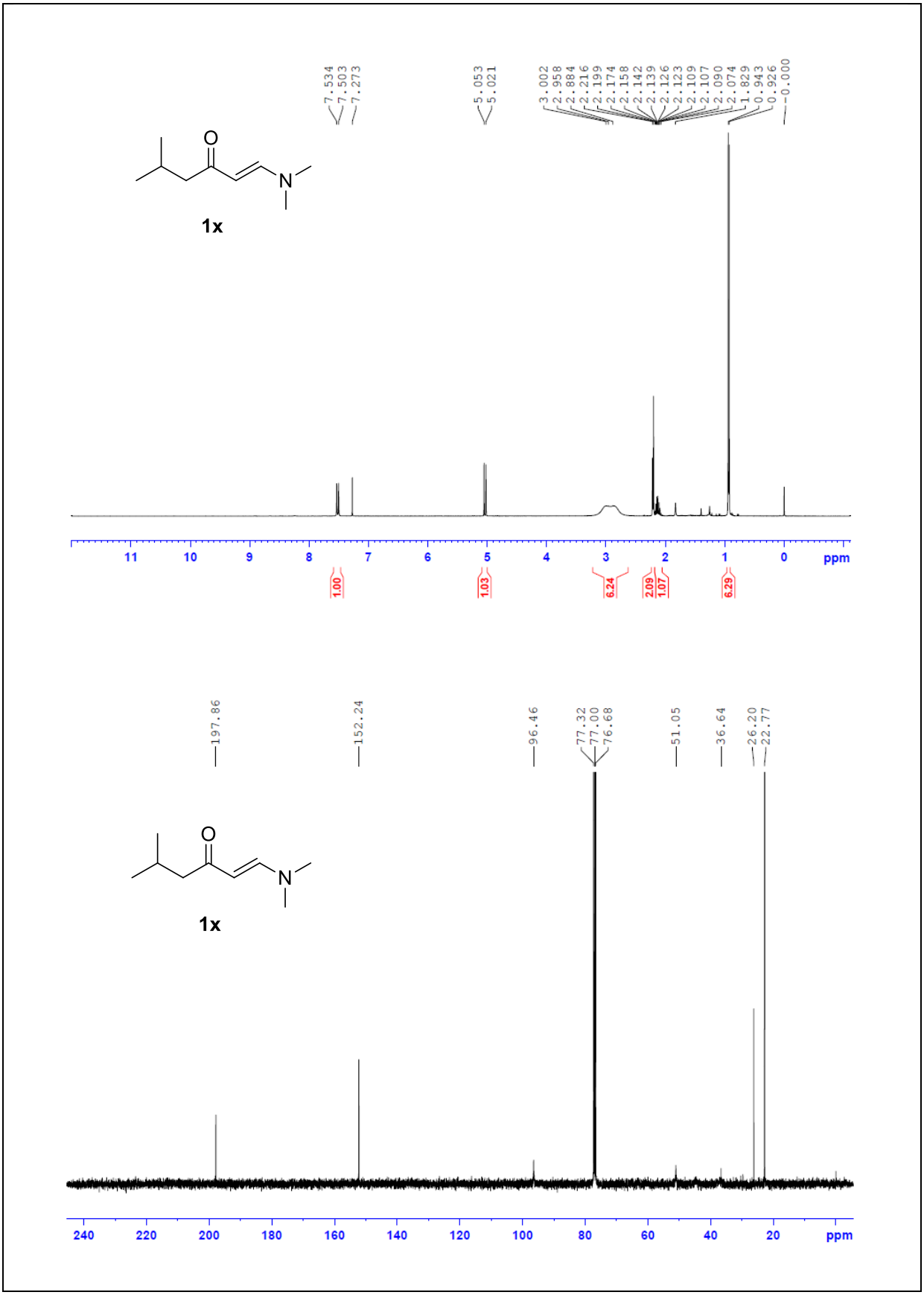
5.117
5.113
5.107
5.104
5.100
5.090
5.087
5.084
5.069
5.060
5.050
5.028
5.019
2.995
2.957
2.870
2.844
2.364
2.357
2.353
2.345
2.335
2.327
2.311
2.294
2.055
2.047
2.029
1.987
1.966
1.678
1.619
1.607
1.594
0.000
O
N
1w
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.05
1.07
6.29
4.38
2.91
1.26
4.34
5.04
197.60
197.51
152.14
135.46
135.33
131.31
131.09
124.41
124.23
123.58
95.65
77.32
77.00
76.68
41.51
39.57
31.78
26.60
26.48
25.58
25.55
24.24
24.08
23.26
17.54
17.53
O
N
1w
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.273
5.053
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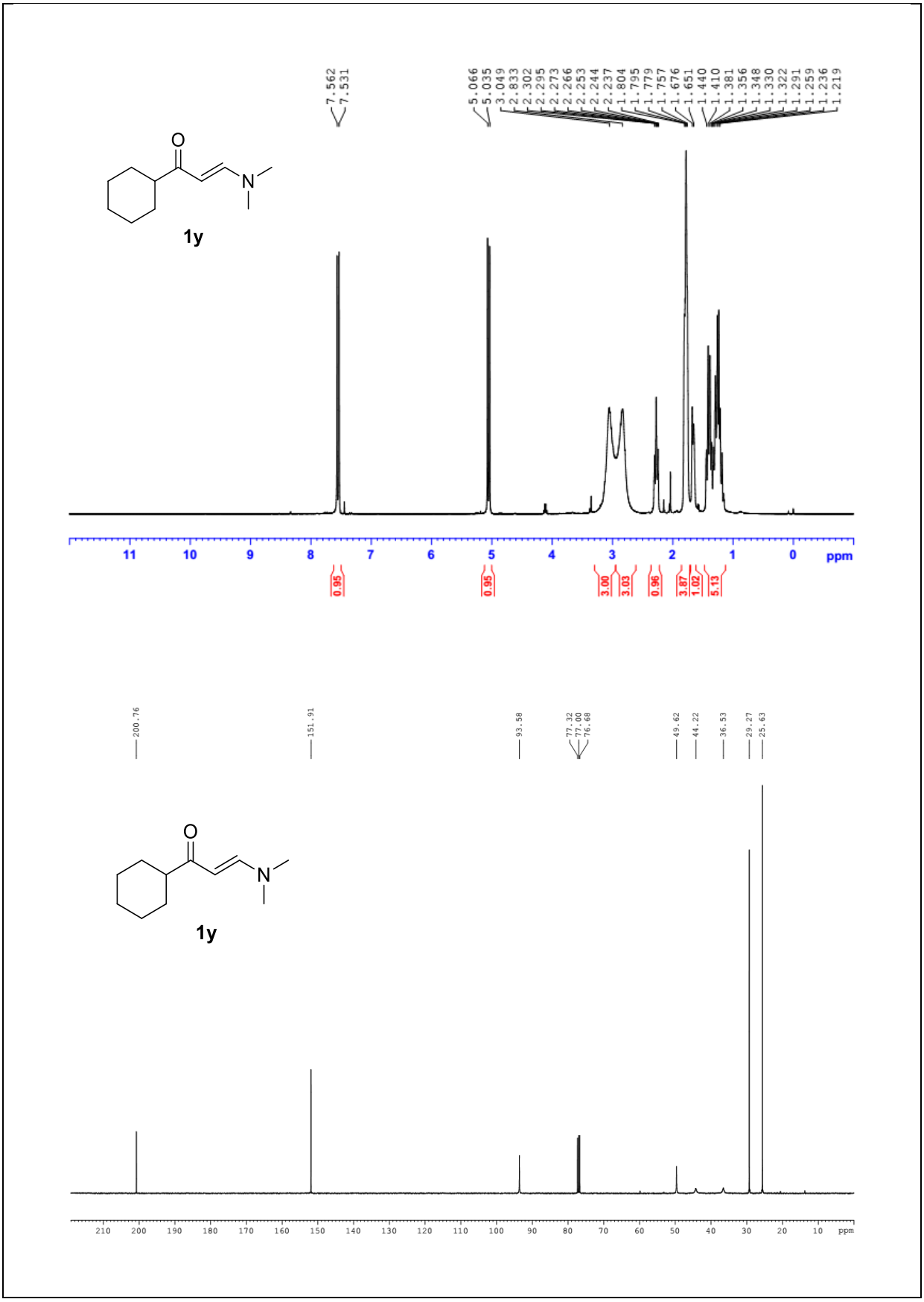
2.884
2.216
2.199
2.174
2.158
2.142
2.139
2.126
2.123
2.109
2.107
2.090
2.074
1.829
0.943
0.926
0.000
1x
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
6.24
2.09
1.07
6.29
197.86
152.24
96.46
77.32
77.00
76.68
51.05
36.64
26.20
22.77
1x
240
220
200
180
160
140
120
100
80
60
40
20
ppm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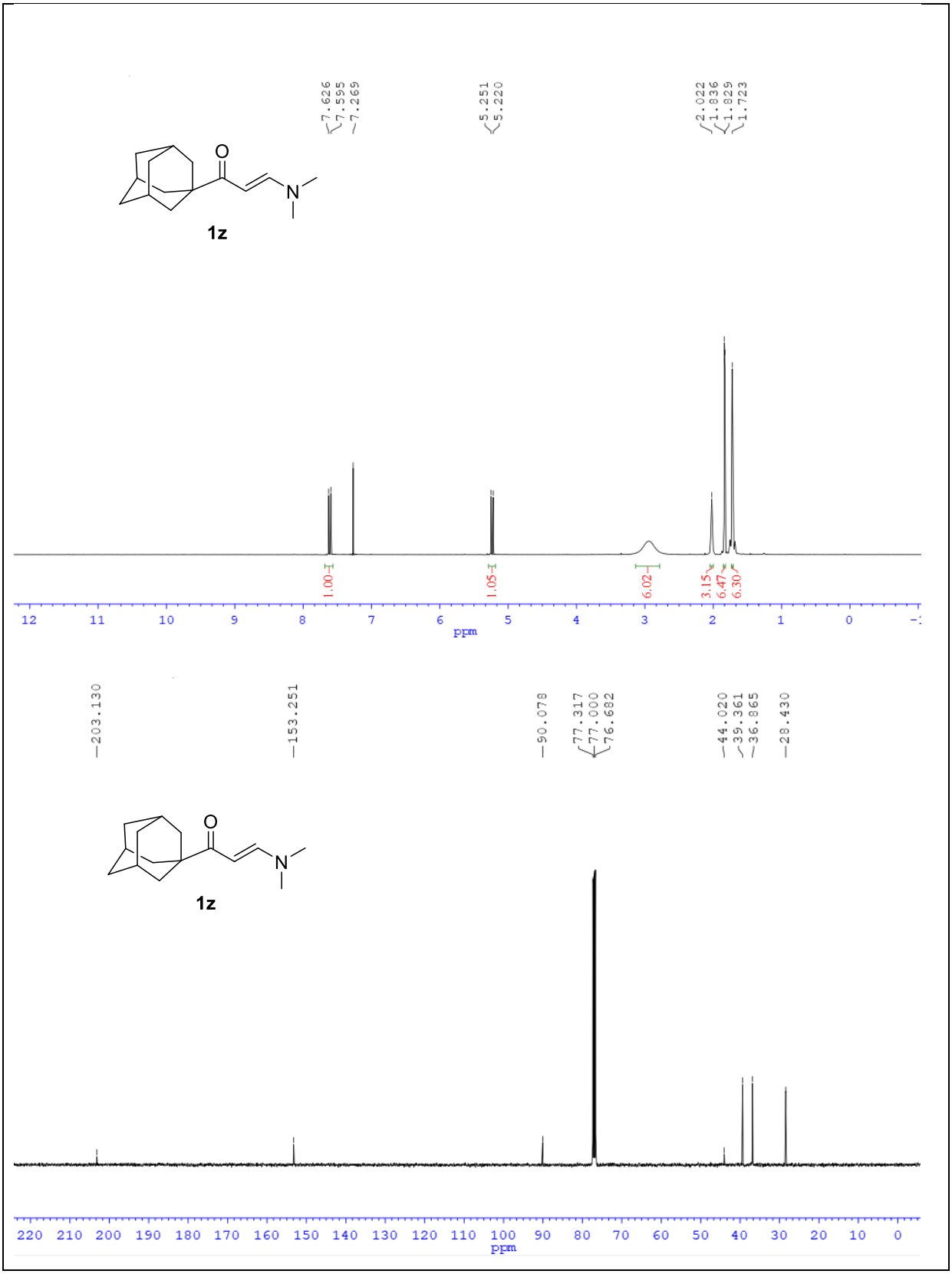
7.531
5.066
5.035
3.049
2.833
2.302
2.295
2.273
2.266
2.253
2.244
2.237
1.804
1.795
1.779
1.757
1.676
1.651
1.440
1.410
1.381
1.356
1.348
1.330
1.322
1.291
1.259
1.236
1.219
O
N
1y
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.95
0.95
3.00
3.03
0.96
3.87
1.02
5.13
200.76
151.91
93.58
77.32
77.00
76.68
49.62
44.22
36.53
29.27
25.63
O
N
1y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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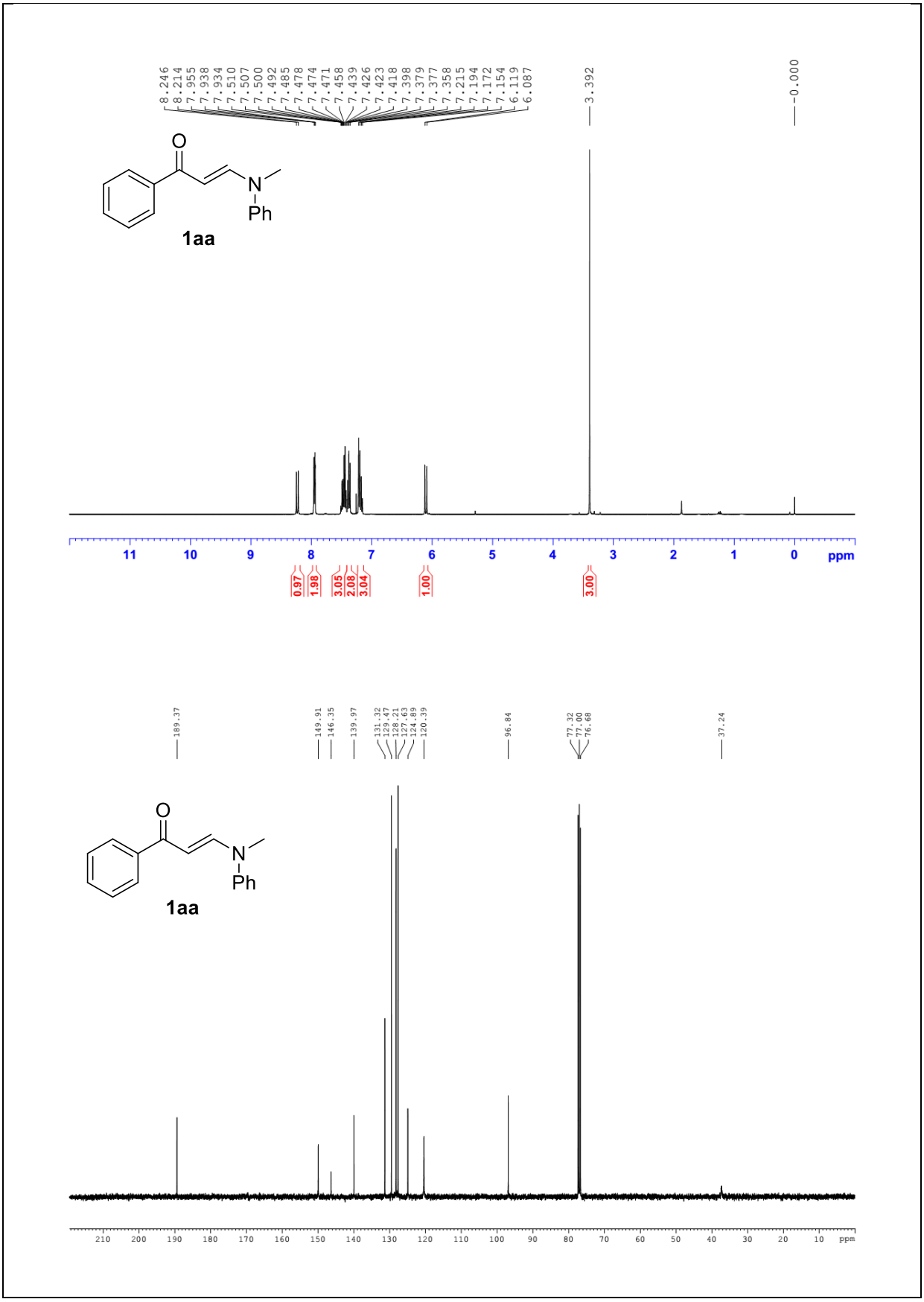
1.829
1.723
O
N
1z
1.00
1.05
6.02
3.15
6.47
6.30
12 11 10 9 8 7 6 5 4 3 2 1 0
ppm
203.130
153.251
90.078
77.317
77.000
76.682
44.020
39.361
36.865
28.430
O
N
1z
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.938
7.934
7.510
7.507
7.500
7.492
7.485
7.478
7.474
7.471
7.458
7.439
7.426
7.423
7.418
7.398
7.379
7.377
7.358
7.215
7.194
7.172
7.154
6.119
6.087
3.392
0.000
O
N
Ph
1aa
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.97
1.98
3.05
2.08
3.04
1.00
3.00
189.37
149.91
146.35
139.97
131.32
129.47
128.21
127.63
124.89
120.39
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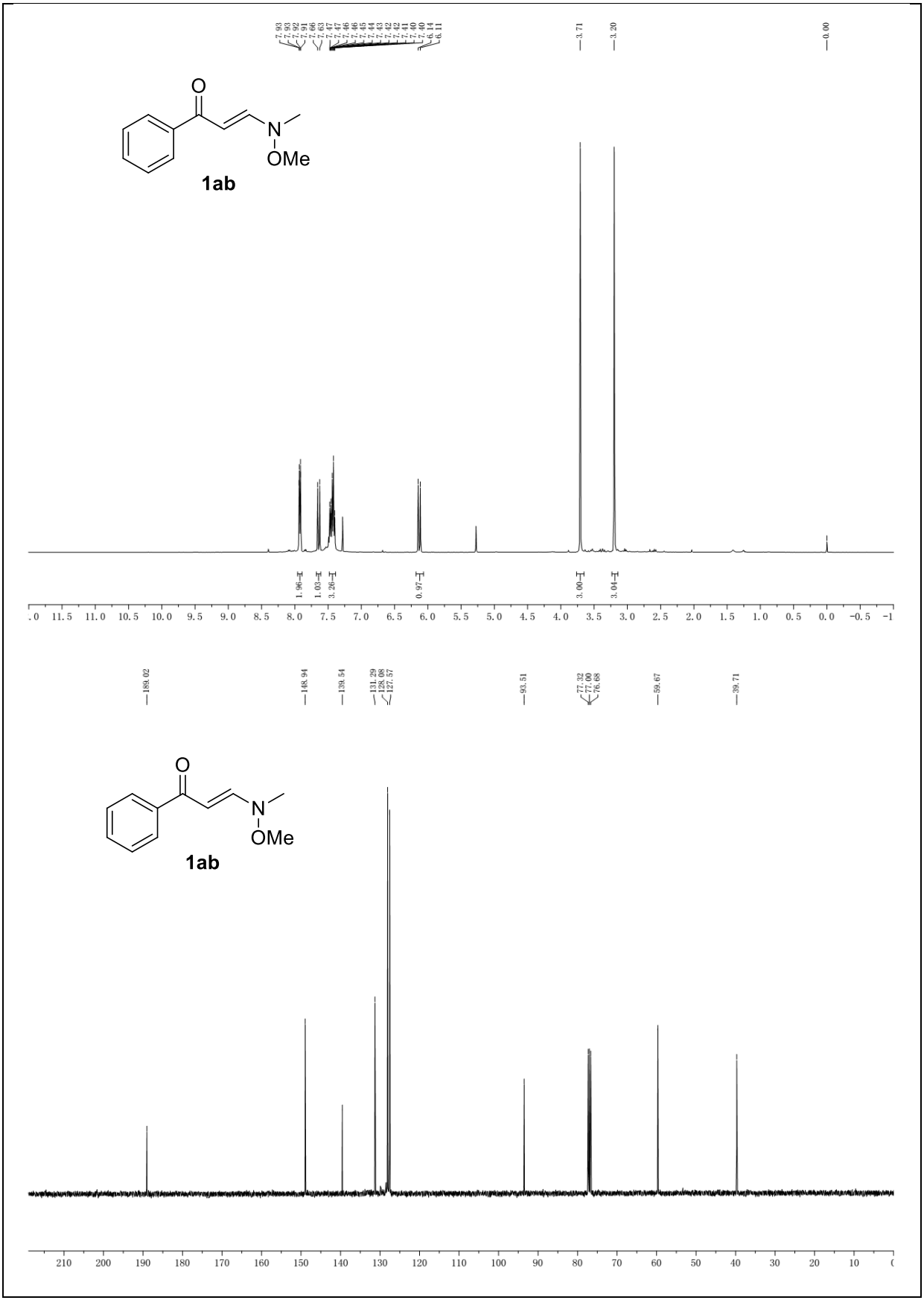
77.00
76.68
37.24
O
N
Ph
1aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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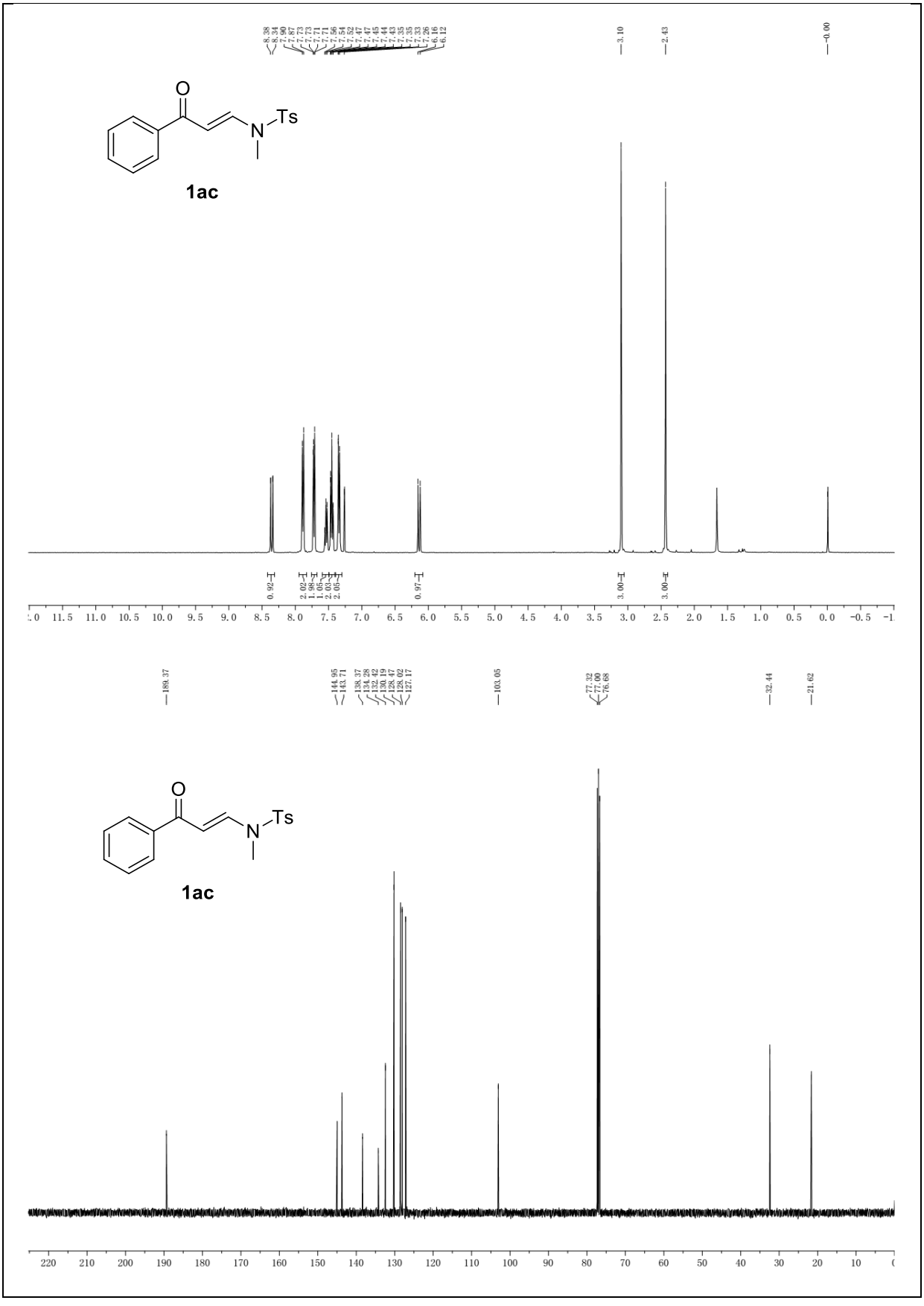
1ab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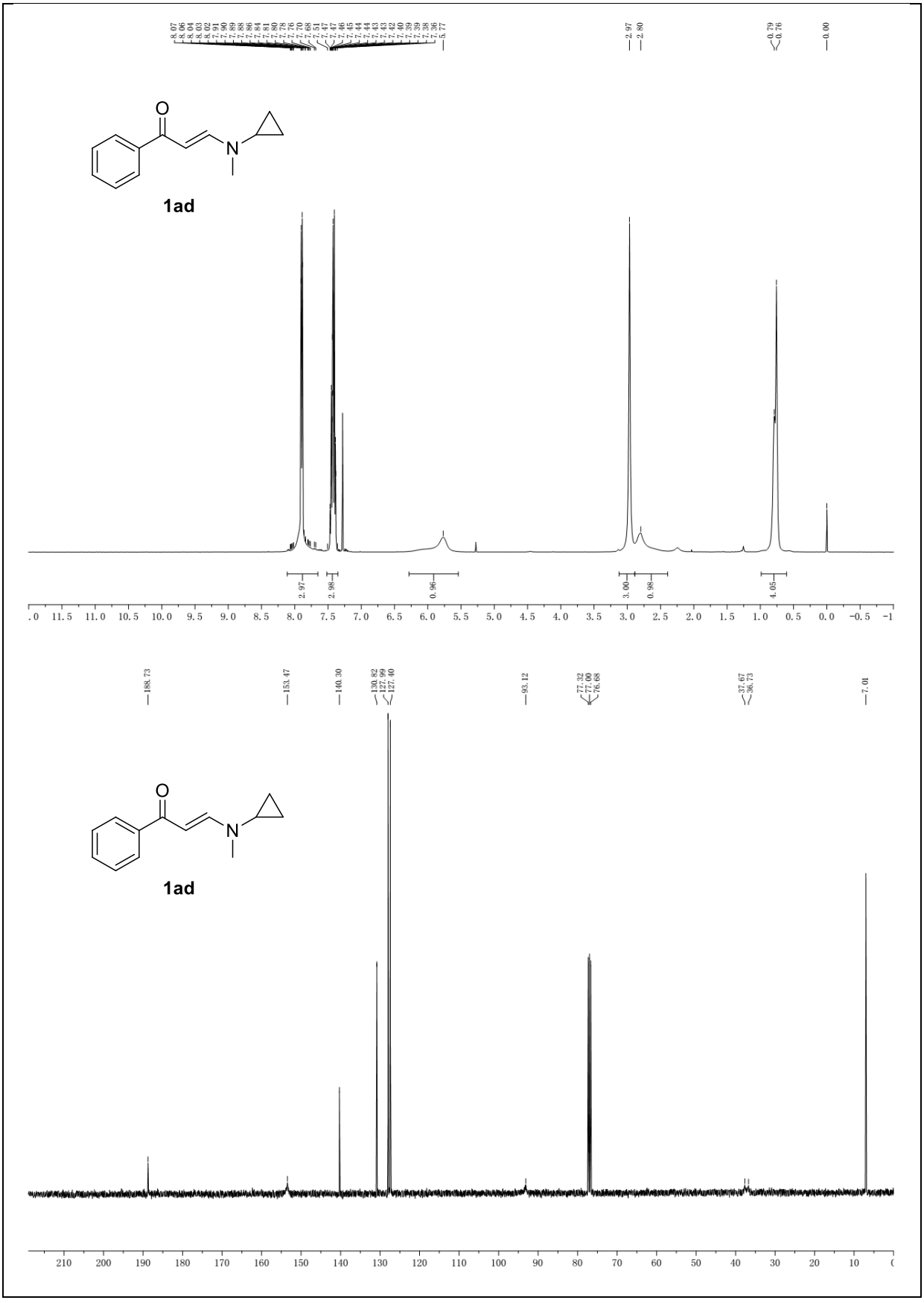
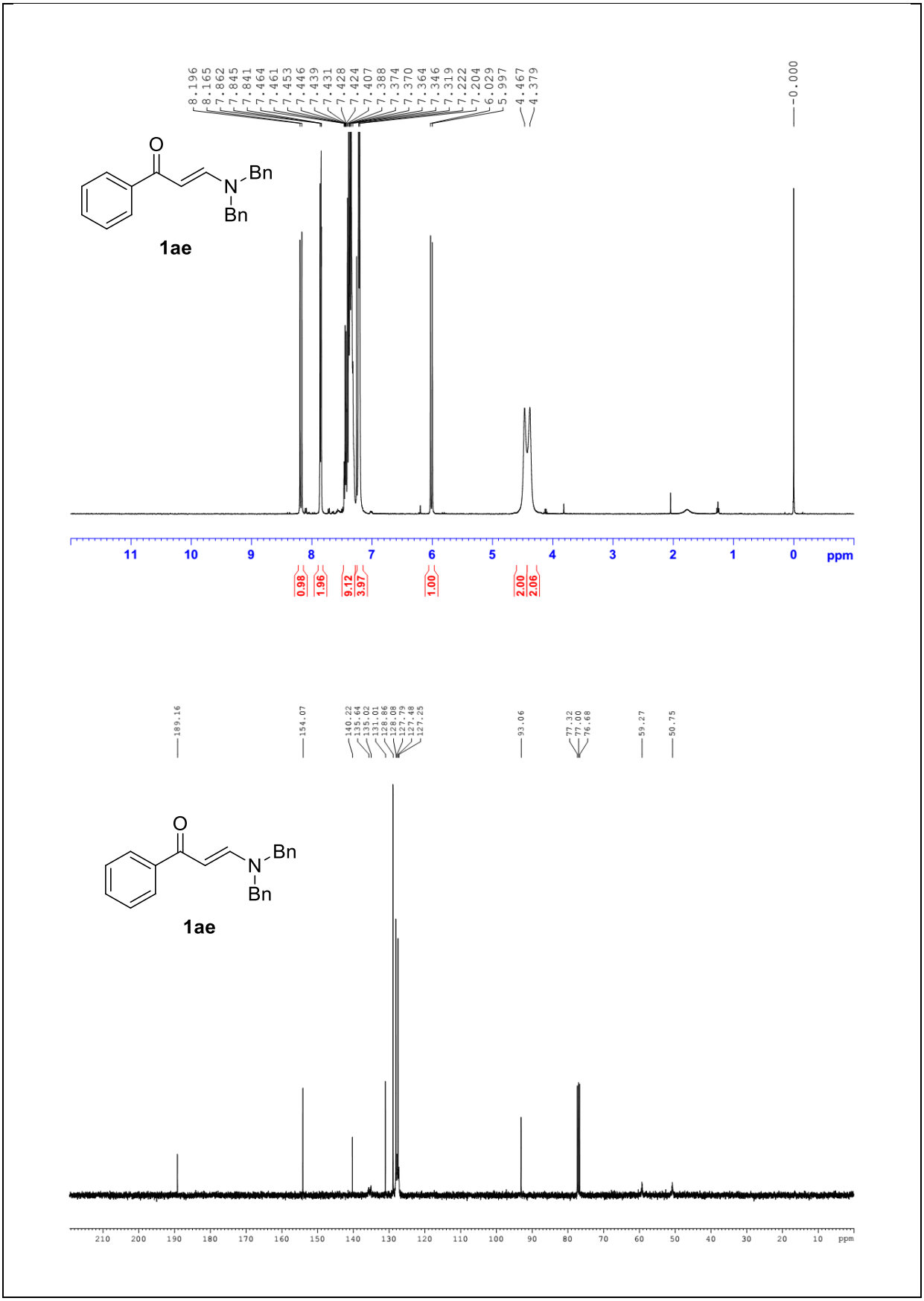

1ad
1ad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7.453
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7.439
7.431
7.428
7.424
7.407
7.388
7.374
7.370
7.364
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7.319
7.222
7.204
6.029
5.997
4.467
4.379
0.000
O
N
Bn
Bn
1ae
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.96
9.12
3.97
1.00
2.00
2.06
189.16
154.07
140.22
135.64
135.02
131.01
128.86
128.08
127.79
127.48
127.25
93.06
77.32
77.00
76.68
59.27
50.75
O
N
Bn
Bn
1ae
210
200
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130
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90
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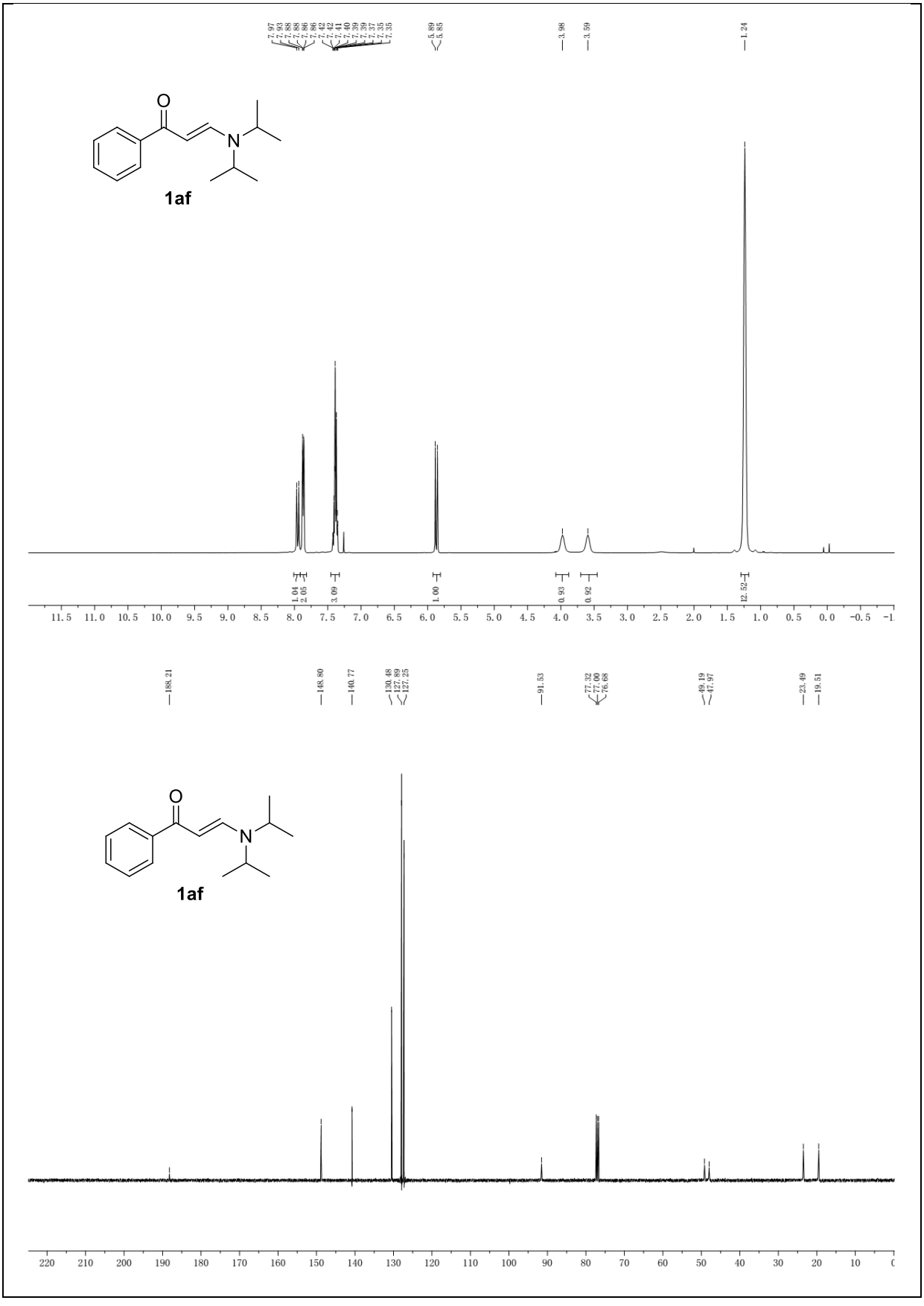
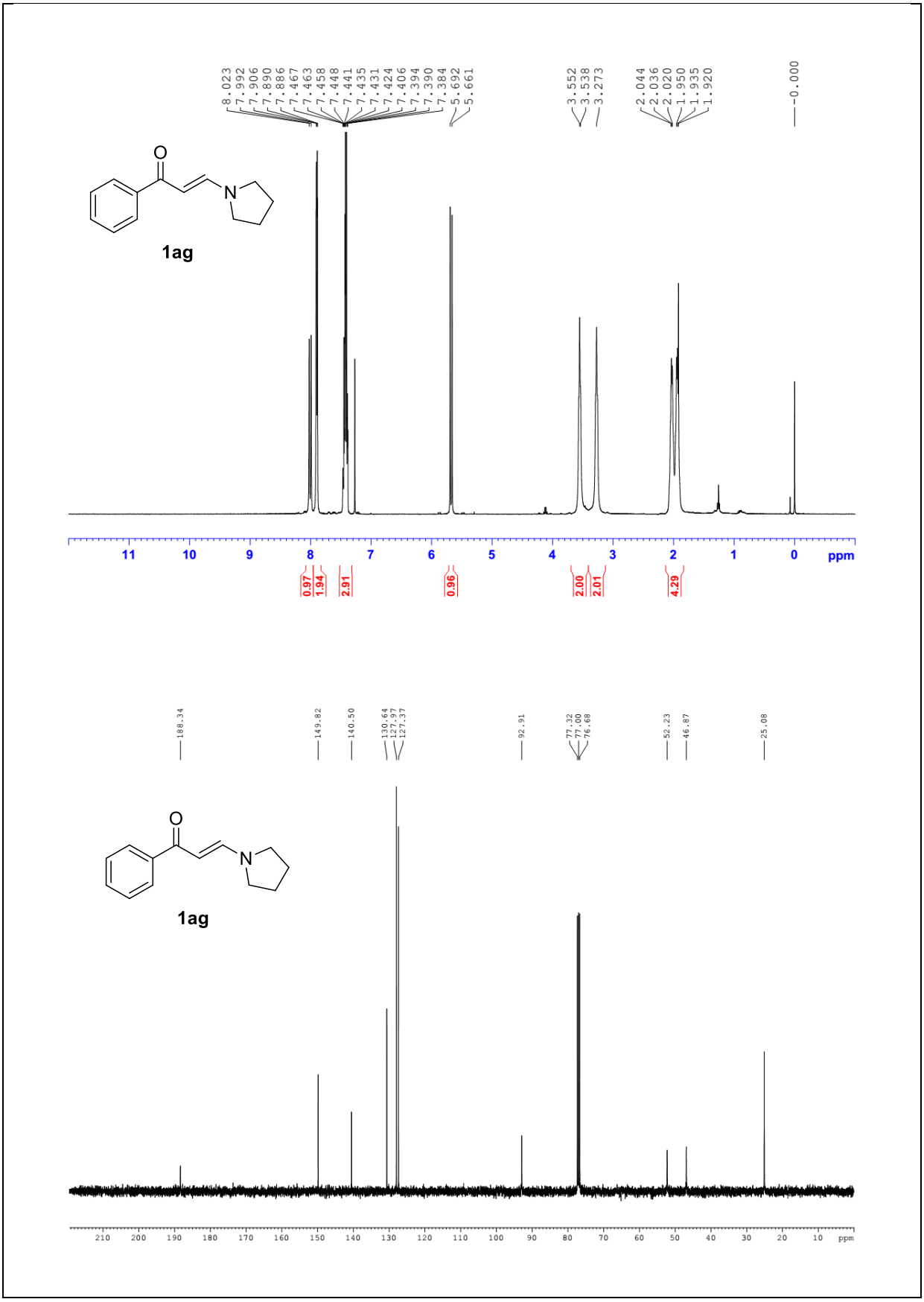
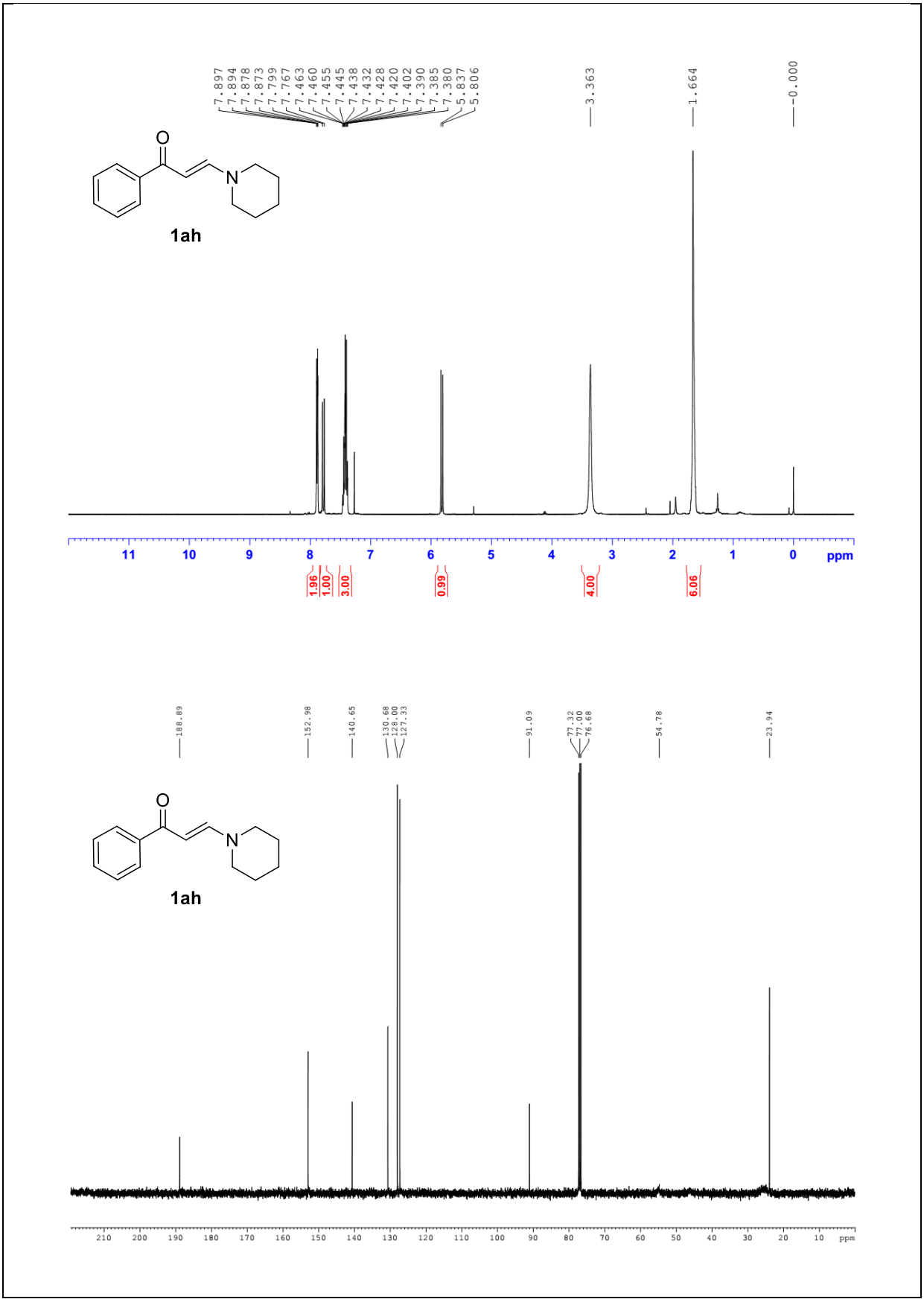
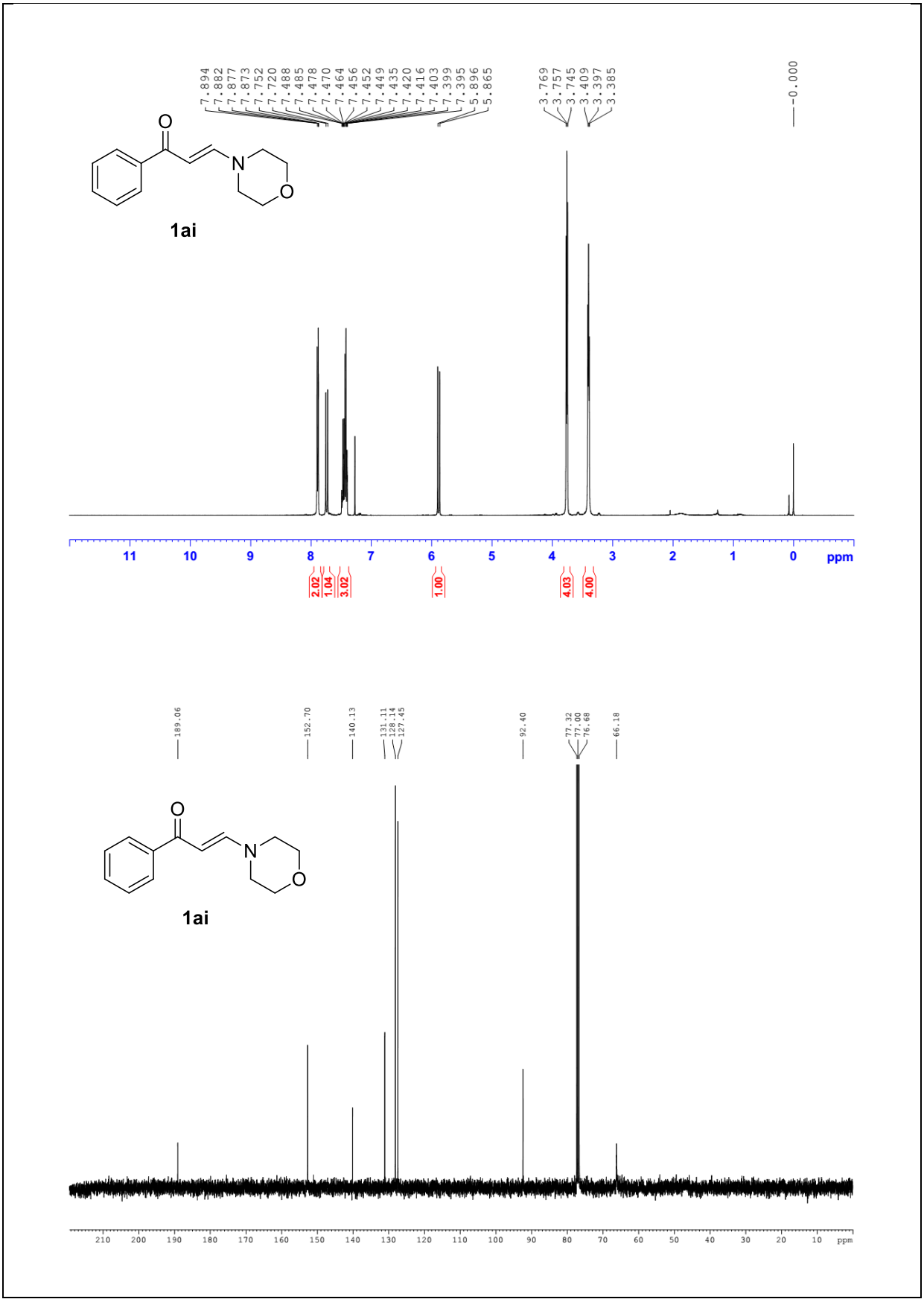
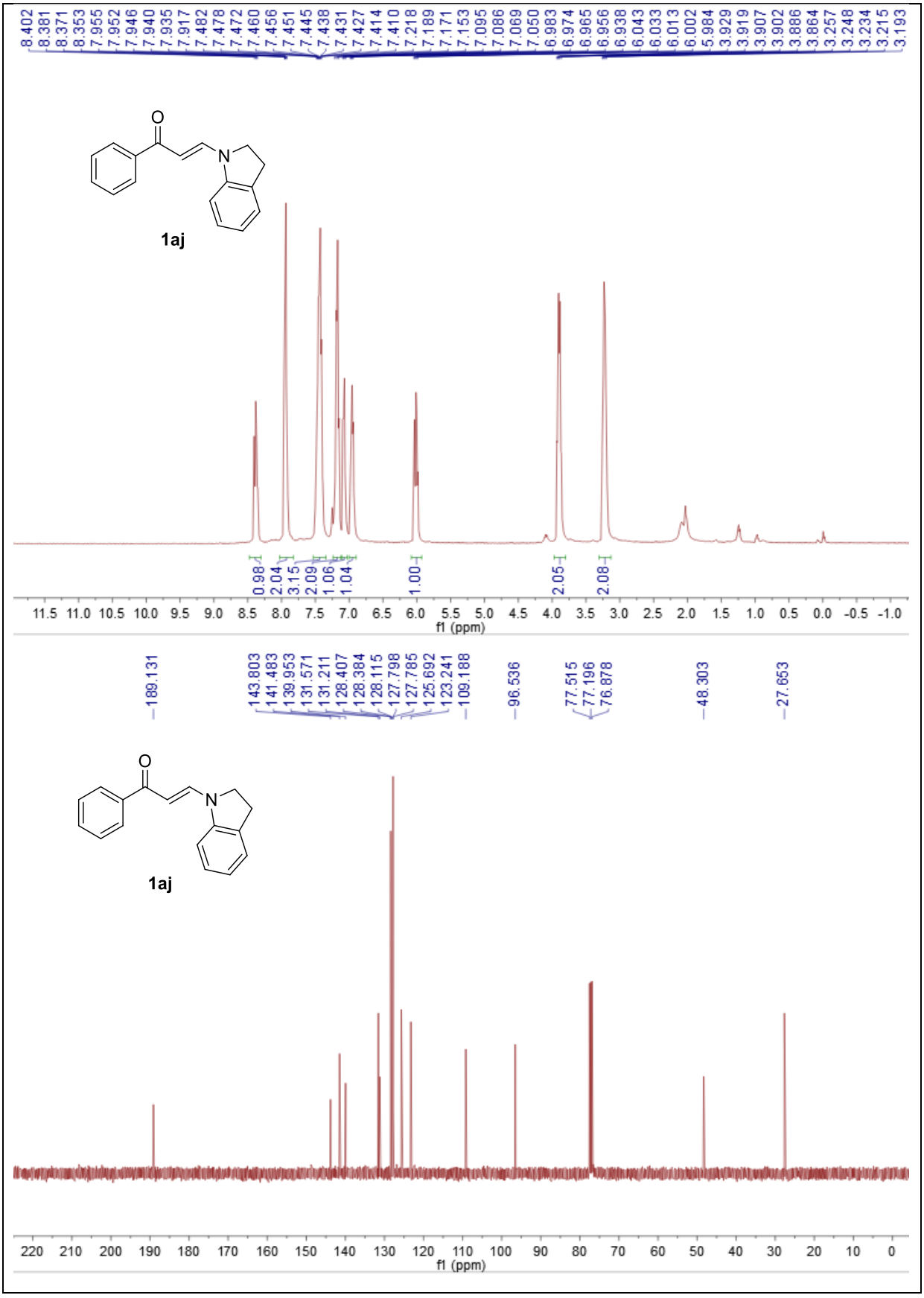
70
60
50
40
30
20
10
ppm

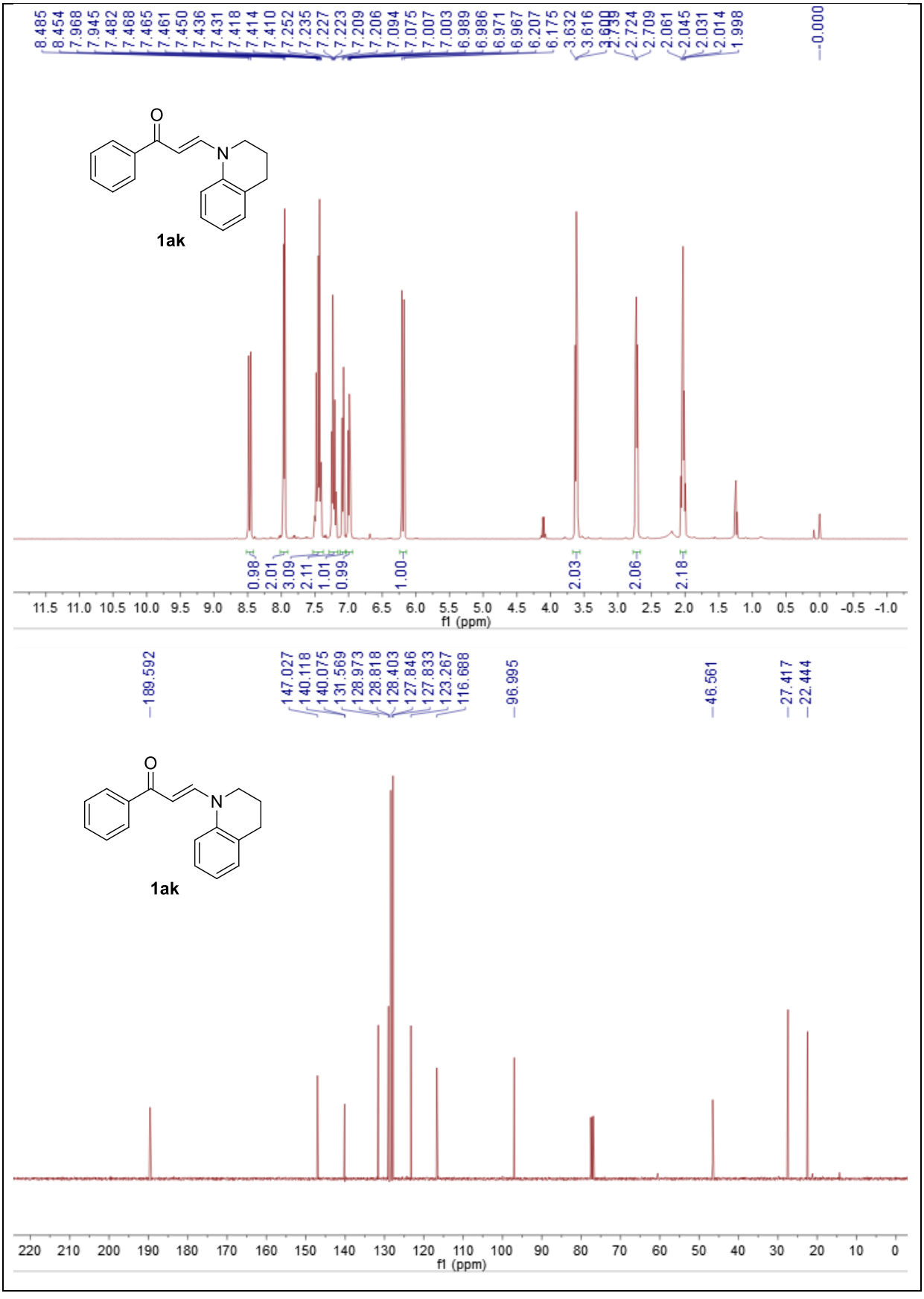

1af
1af

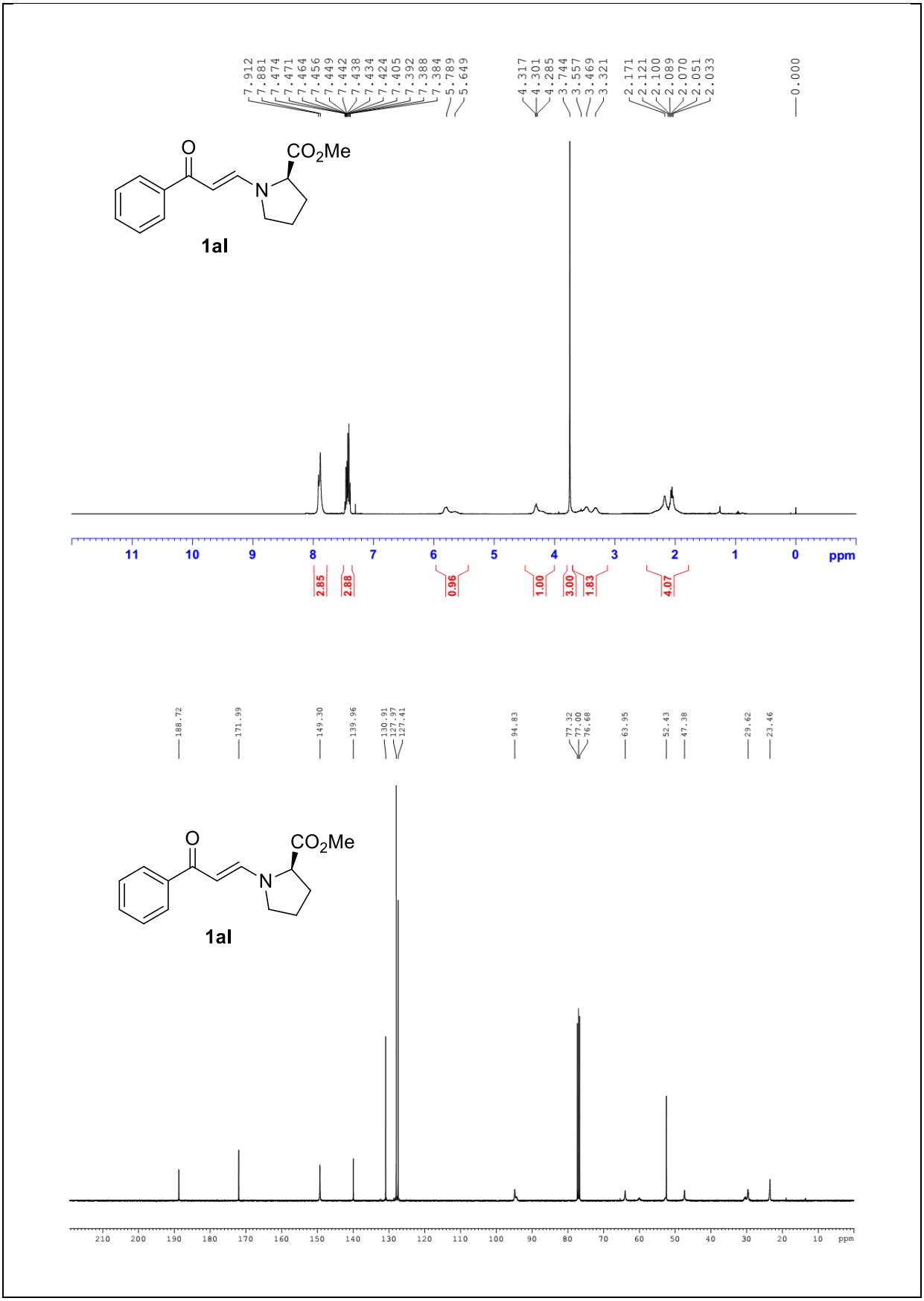

8.023
7.992
7.906
7.890
7.886
7.467
7.463
7.458
7.448
7.441
7.435
7.431
7.424
7.406
7.394
7.390
7.384
5.692
5.661
3.552
3.538
3.273
2.044
2.036
2.020
1.950
1.935
1.920
0.000
O
N
1ag
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.97
1.94
2.91
0.96
2.00
2.01
4.29
188.34
149.82
140.50
130.64
127.97
127.37
92.91
77.32
77.00
76.68
52.23
46.87
25.08
O
N
1ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

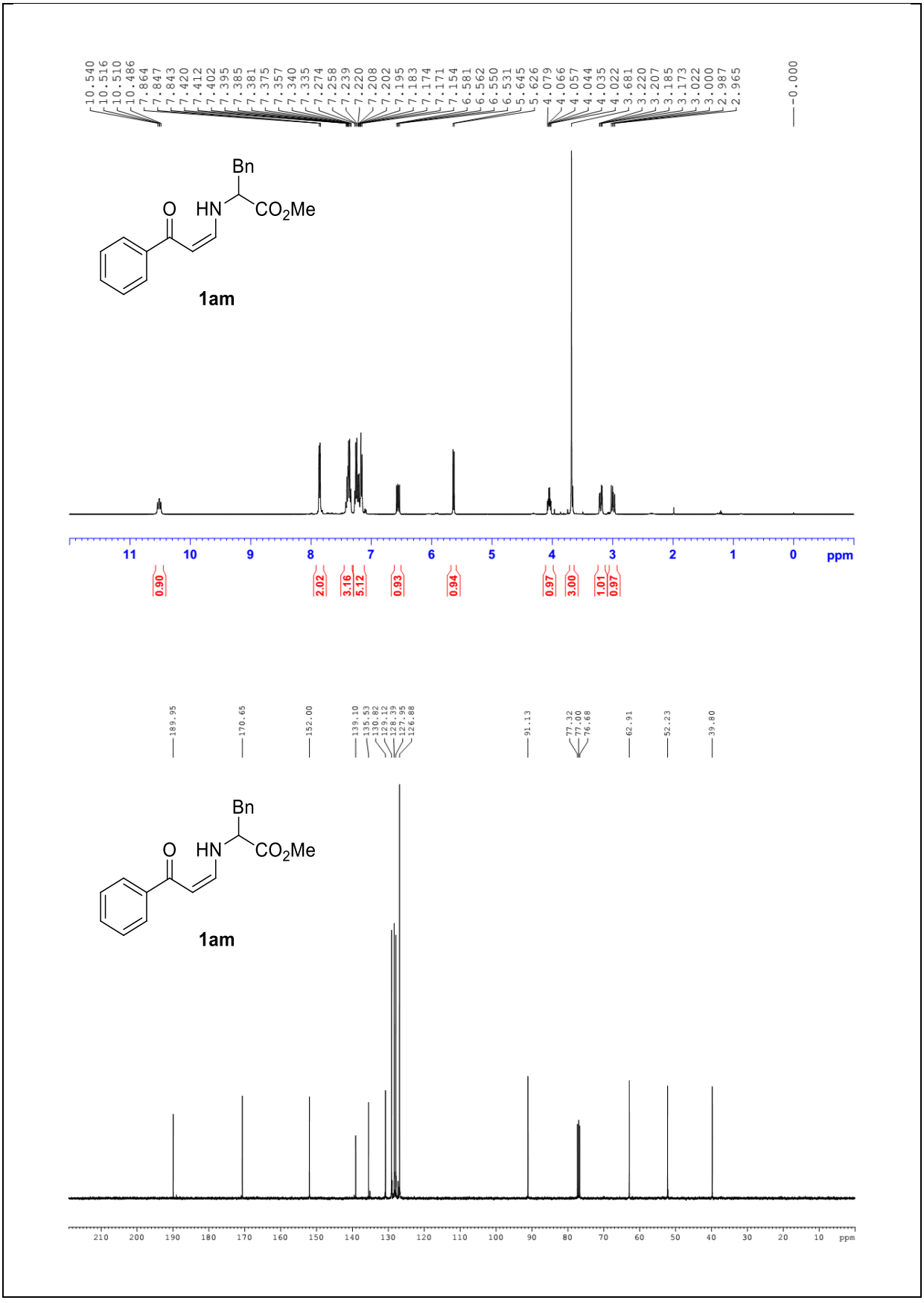

7.897
7.894
7.878
7.873
7.799
7.767
7.463
7.460
7.455
7.445
7.438
7.432
7.428
7.420
7.402
7.390
7.385
7.380
5.837
5.806
3.363
1.664
0.000
O
N
1ah
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.96
1.00
3.00
0.99
4.00
6.06
188.89
152.98
140.65
130.68
128.00
127.33
91.09
77.32
77.00
76.68
54.78
23.94
O
N
1ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.894
7.882
7.877
7.873
7.752
7.720
7.488
7.485
7.478
7.470
7.464
7.456
7.452
7.449
7.435
7.420
7.416
7.403
7.399
7.395
5.896
5.865
3.769
3.757
3.745
3.409
3.397
3.385
-0.000
O
N
O
1ai
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
1.04
3.02
1.00
4.03
4.00
189.06
152.70
140.13
131.11
128.14
127.45
92.40
77.32
77.00
76.68
66.18
O
N
O
1ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

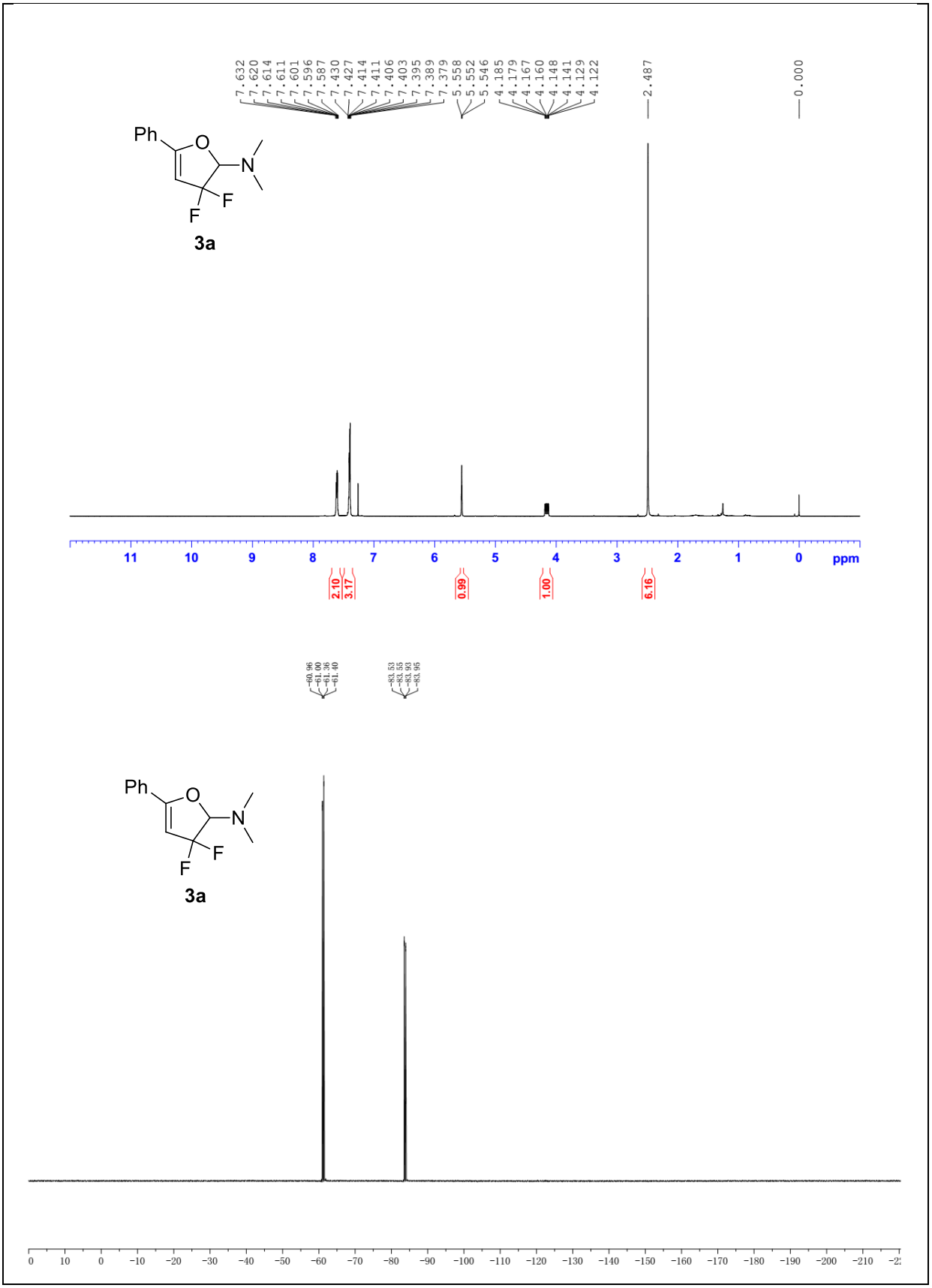

8.402
8.381
8.371
8.353
7.955
7.952
7.946
7.940
7.935
7.917
7.482
7.478
7.472
7.460
7.456
7.451
7.445
7.438
7.431
7.427
7.414
7.410
7.218
7.189
7.171
7.153
7.095
7.086
7.069
7.050
6.983
6.974
6.965
6.956
6.938
6.043
6.033
6.013
6.002
5.984
3.929
3.919
3.907
3.902
3.886
3.864
3.257
3.248
3.234
3.215
3.193
O
N
1aj
0.98
2.04
3.15
2.09
1.06
1.04
1.00
2.05
2.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
189.131
143.803
141.483
139.953
131.571
131.211
128.407
128.384
128.115
127.798
127.785
125.692
123.241
109.188
96.536
77.515
77.196
76.878
48.303
27.653
O
N
1aj
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

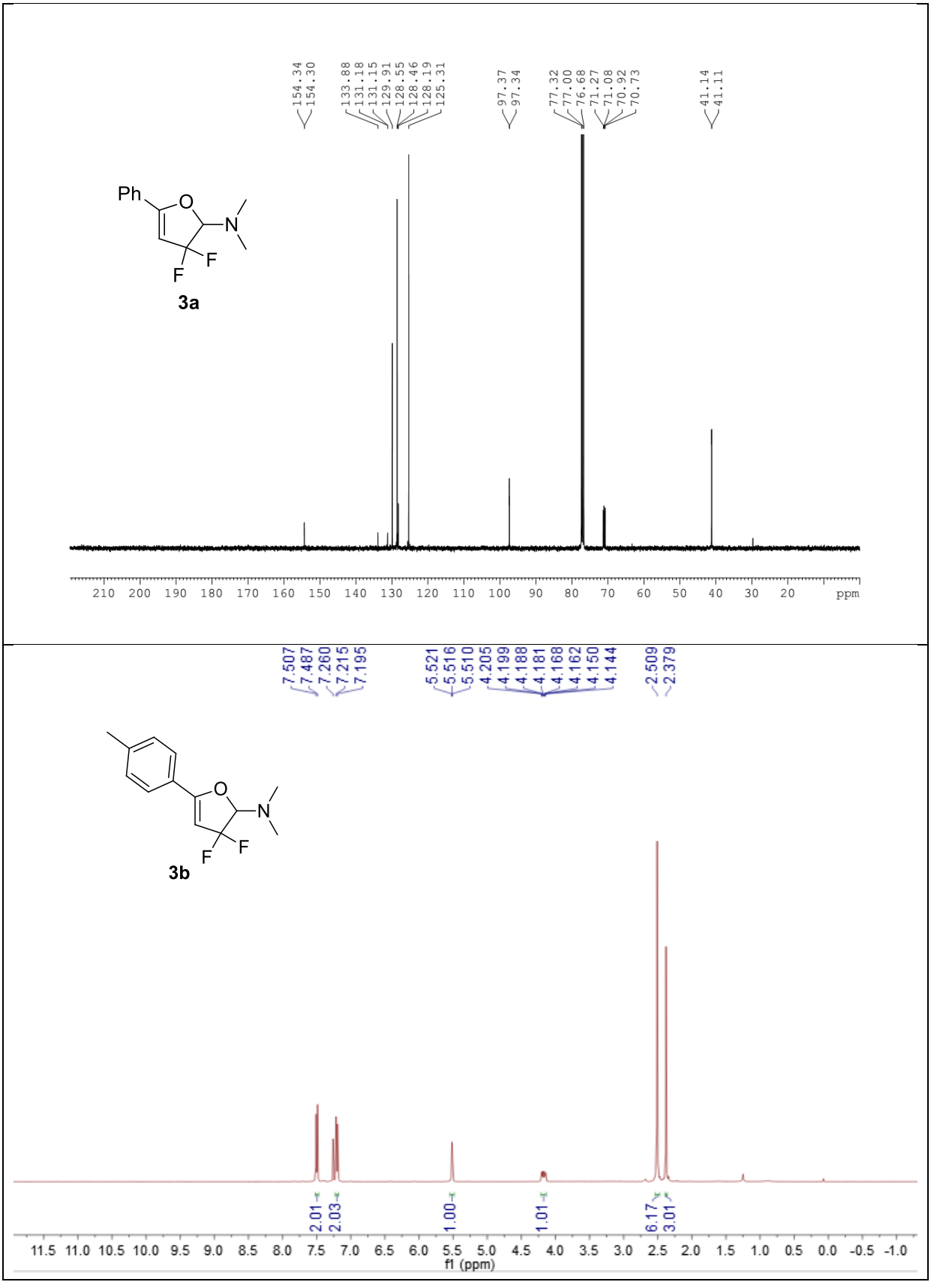

8.485
8.454
7.968
7.945
7.482
7.468
7.465
7.461
7.450
7.436
7.431
7.418
7.414
7.410
7.252
7.235
7.227
7.223
7.209
7.206
7.094
7.075
7.007
7.003
6.989
6.986
6.971
6.967
6.207
6.175
3.632
3.616
2.724
2.709
2.061
2.045
2.031
2.014
1.998
0.000
O
N
1ak
0.98
2.01
3.09
2.11
1.01
0.99
1.00
2.03
2.06
2.18
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
189.592
147.027
140.118
140.075
131.569
128.973
128.818
128.403
127.846
127.833
123.267
116.688
96.995
46.561
27.417
22.444
O
N
1ak
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

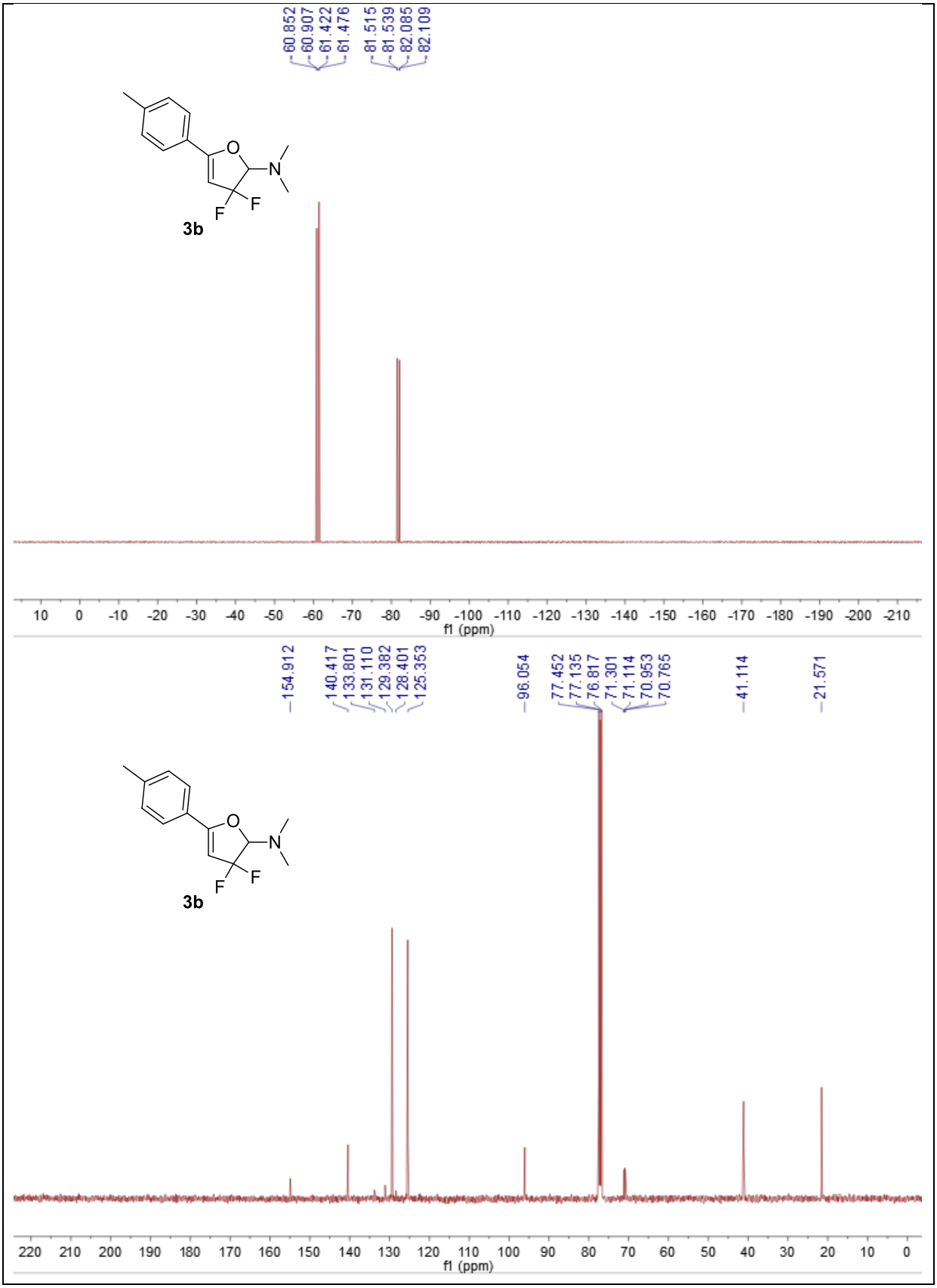

7.912
7.881
7.474
7.471
7.464
7.456
7.449
7.442
7.438
7.434
7.424
7.405
7.392
7.388
7.384
5.789
5.649
4.317
4.301
4.285
3.744
3.557
3.469
3.321
2.171
2.121
2.100
2.089
2.070
2.051
2.033
0.000
O
CO2Me
N
1al
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.85
2.88
0.96
1.00
3.00
1.83
4.07
188.72
171.99
149.30
139.96
130.91
127.97
127.41
94.83
77.32
77.00
76.68
63.95
52.43
47.38
29.62
23.46
O
CO2Me
N
1al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

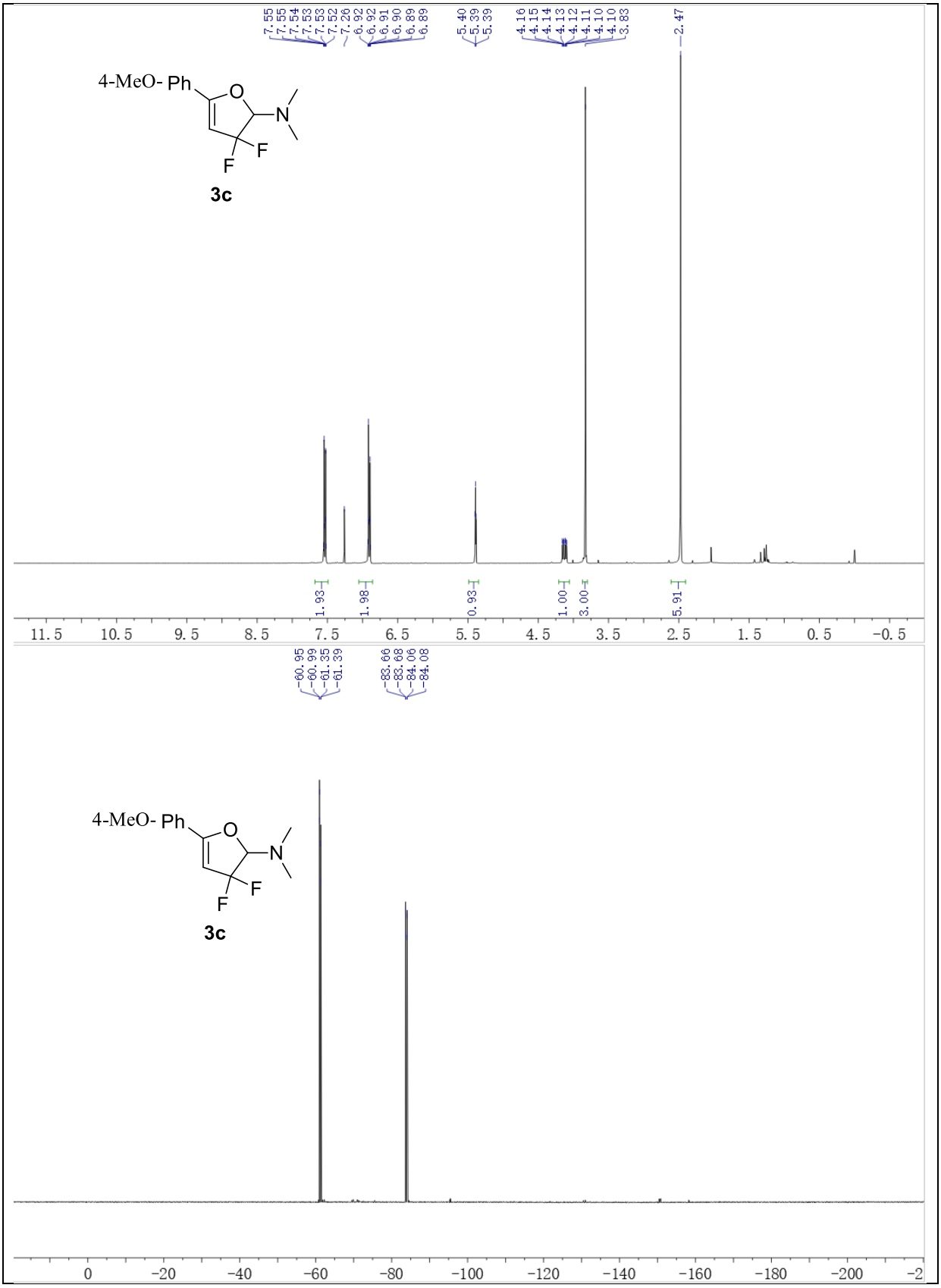

10.540
10.516
10.510
10.486
7.864
7.847
7.843
7.420
7.412
7.402
7.395
7.385
7.381
7.375
7.357
7.340
7.335
7.274
7.258
7.239
7.220
7.208
7.202
7.195
7.183
7.174
7.171
7.154
6.581
6.562
6.550
6.531
5.645
5.626
4.079
4.066
4.057
4.044
4.035
4.022
3.681
3.220
3.207
3.185
3.173
3.022
3.000
2.987
2.965
-0.000
Bn
O
HN
CO2Me
1am
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
2.02
3.16
5.12
0.93
0.94
0.97
3.00
1.01
0.97
189.95
170.65
152.00
139.10
135.53
130.82
129.12
128.39
127.85
126.88
91.13
77.32
77.00
76.68
62.91
52.23
39.80
Bn
O
HN
CO2Me
1am
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

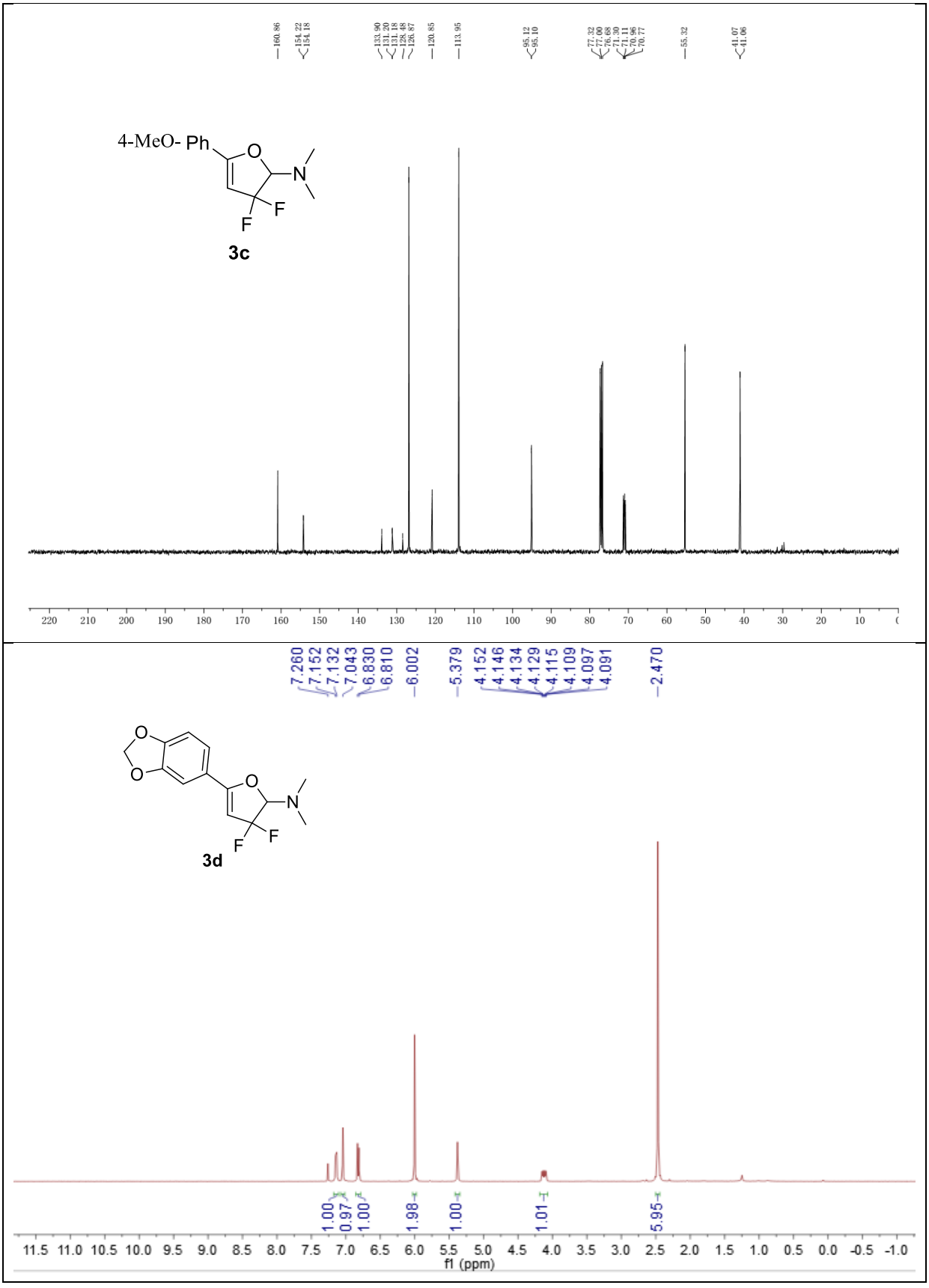
NMR Spectra of *gem*-difluorinated 2*H*-furans:

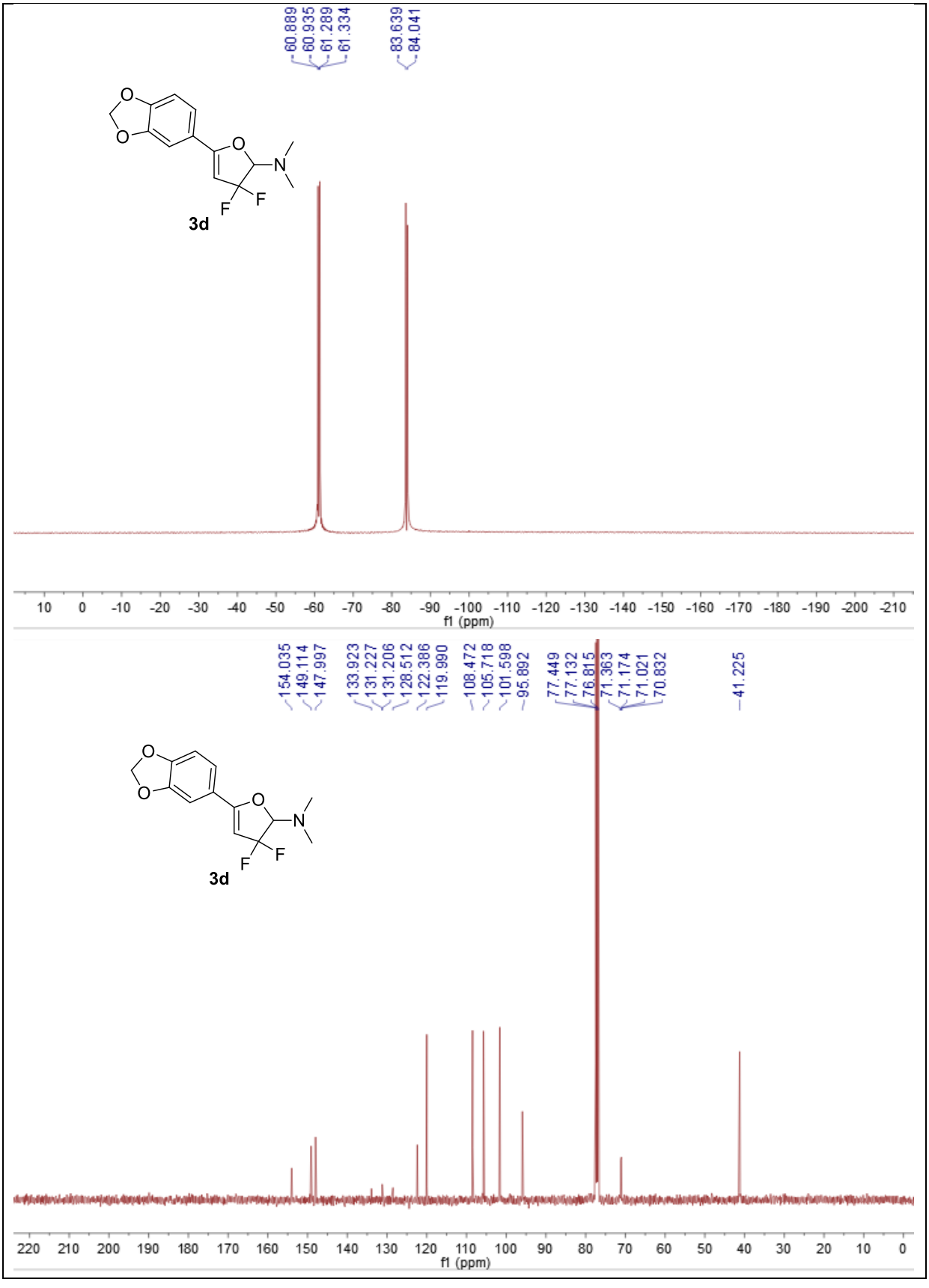


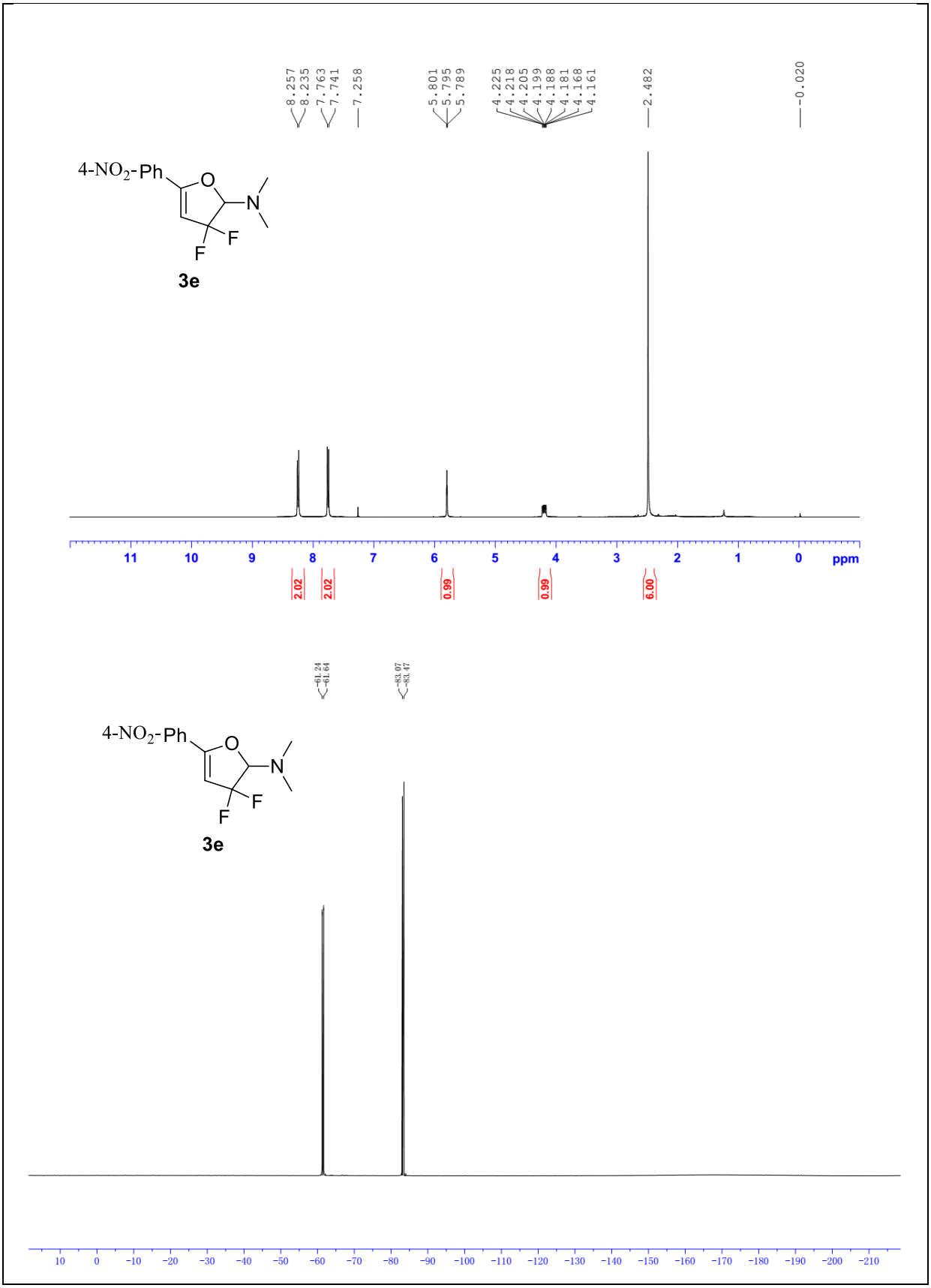

154.34
154.30
133.88
131.18
131.15
129.91
128.55
128.46
128.19
125.31
97.37
97.34
77.32
77.00
76.68
71.27
71.08
70.92
70.73
41.14
41.11
Ph
O
N
F
F
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
7.507
7.487
7.260
7.215
7.195
5.521
5.516
5.510
4.205
4.199
4.188
4.181
4.168
4.162
4.150
4.144
2.509
2.379
O
N
F
F
3b
2.01
2.03
1.00
1.01
6.17
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

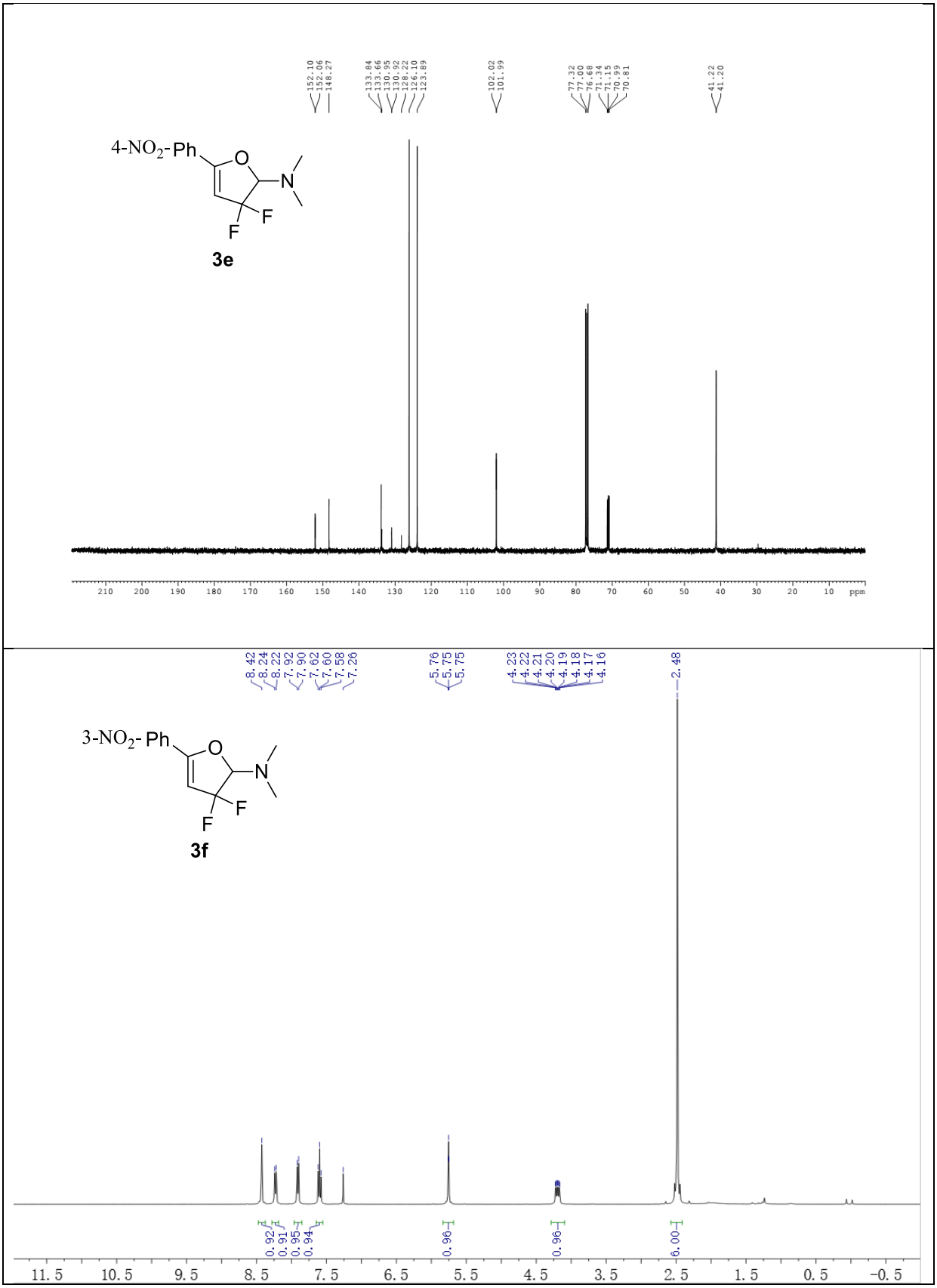

60.852
60.907
61.422
61.476
81.515
81.539
82.085
82.109
3b
f1 (ppm)
154.912
140.417
133.801
131.110
129.382
128.401
125.353
96.054
77.452
77.135
76.817
71.301
71.114
70.953
70.765
41.114
21.571
3b
f1 (ppm)

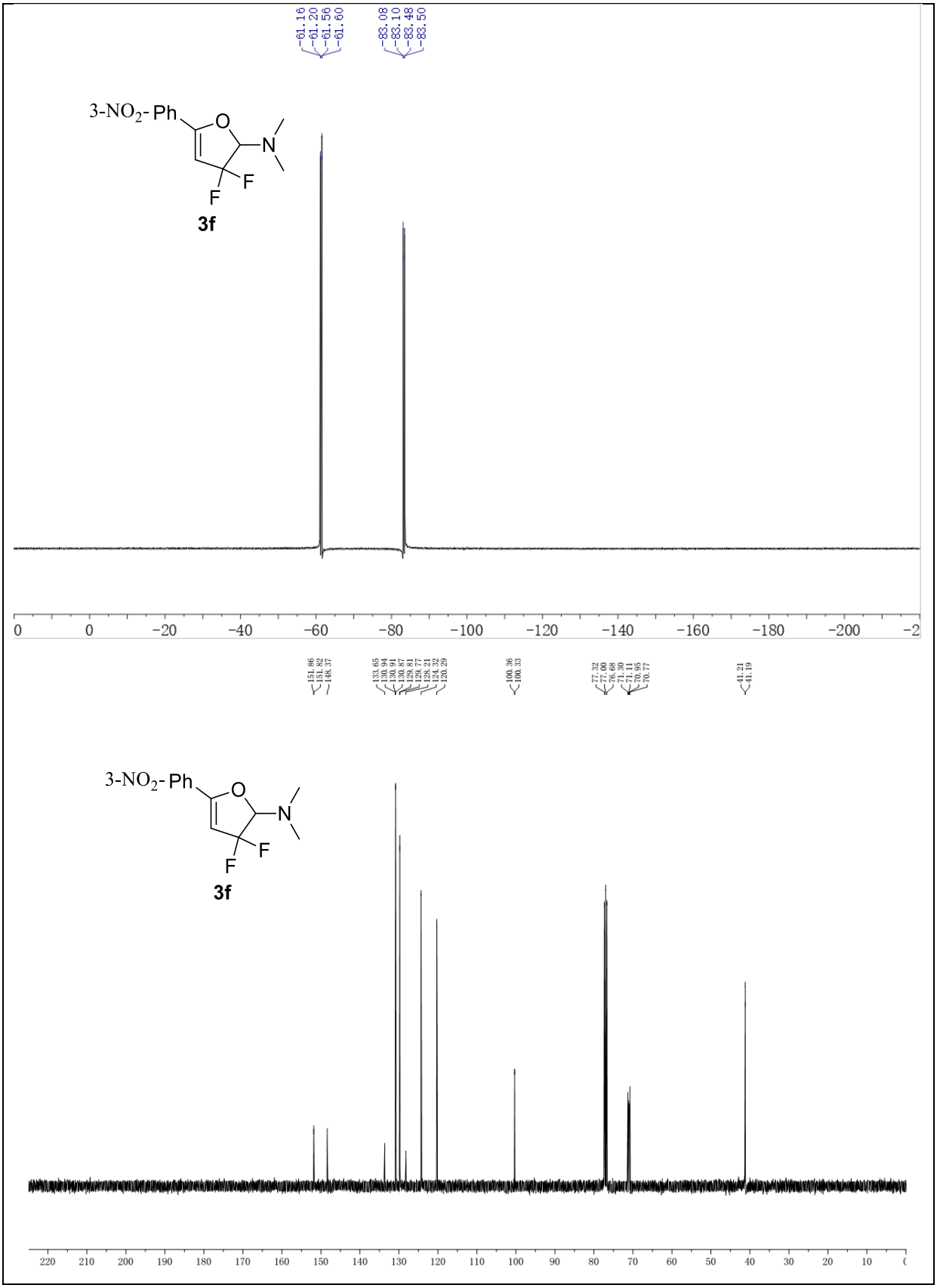

4-MeO- Ph
O
N
F
F
3c
7.55
7.55
7.54
7.53
7.53
7.52
7.26
6.92
6.92
6.91
6.90
6.89
6.89
5.40
5.39
5.39
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.10
3.83
2.47
1.93
1.98
0.93
1.00
3.00
5.91
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-60.95
-60.99
-61.35
-61.39
-83.66
-83.68
-84.06
-84.08
4-MeO- Ph
O
N
F
F
3c
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

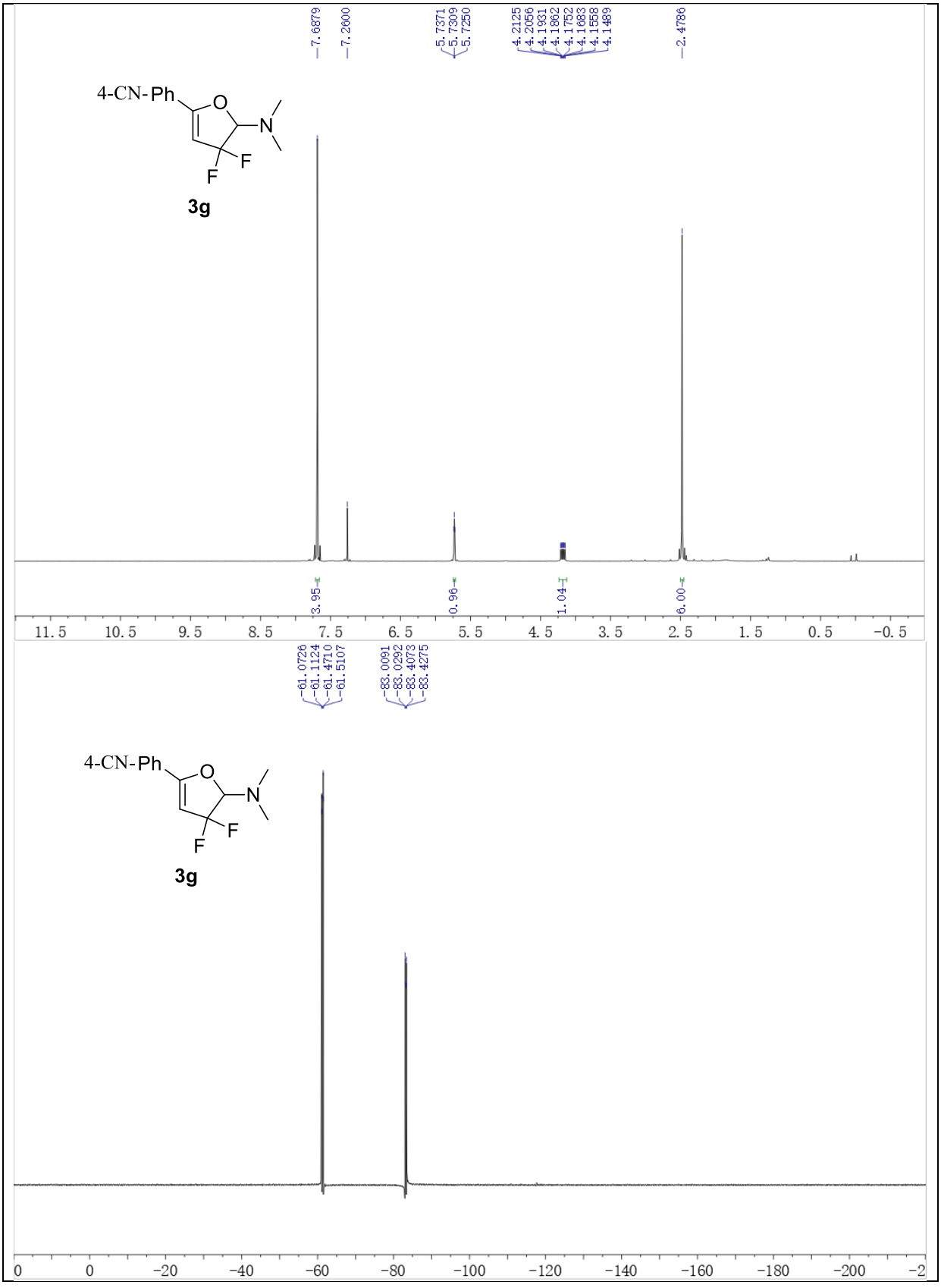

160.86
154.22
154.18
133.90
131.20
131.18
126.46
126.87
120.85
113.95
95.12
95.10
77.32
77.00
76.68
71.30
71.11
70.96
70.77
55.32
41.07
41.06
4-MeO- Ph
O
N
F
F
3c
7.260
7.152
7.132
7.043
6.830
6.810
6.002
5.379
4.152
4.146
4.134
4.129
4.115
4.109
4.097
4.091
2.470
O
O
O
N
F
F
3d
1.00
0.97
1.00
1.98
1.00
1.01
5.95
f1 (ppm)

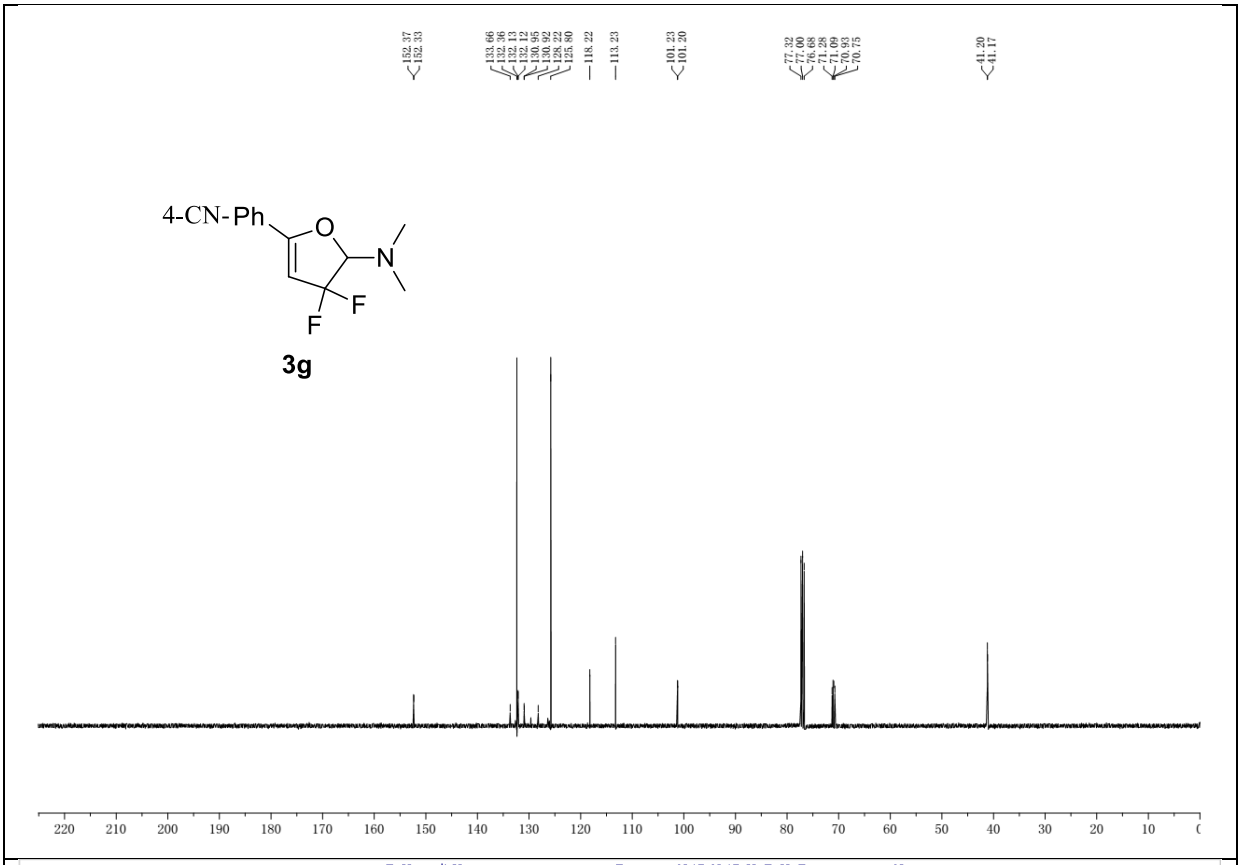

60.889
60.935
61.289
61.334
83.639
84.041
3d
f1 (ppm)
154.035
149.114
147.997
133.923
131.227
131.206
128.512
122.386
119.990
108.472
105.718
101.598
95.892
77.449
77.132
76.815
71.363
71.174
71.021
70.832
41.225
3d
f1 (ppm)

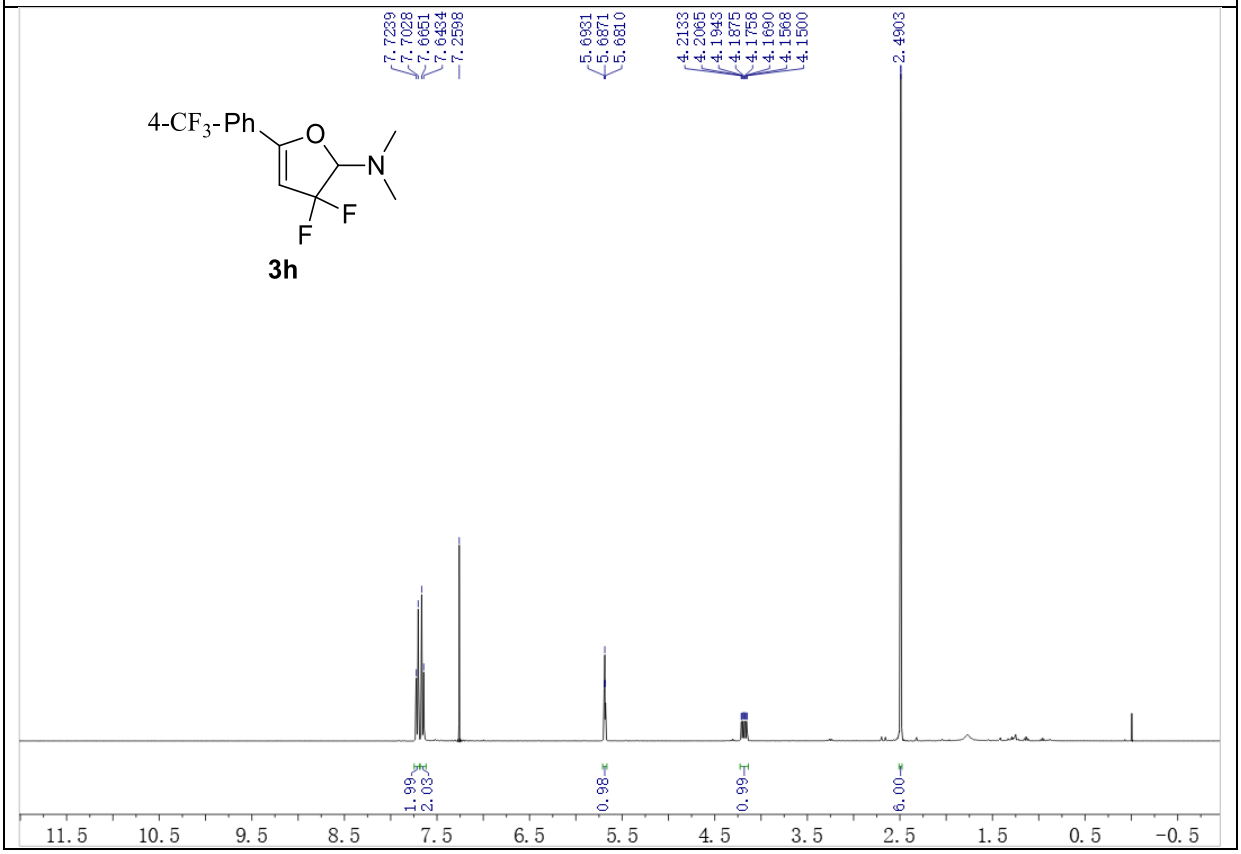

8.257
8.235
7.763
7.741
7.258
5.801
5.795
5.789
4.225
4.218
4.205
4.199
4.188
4.181
4.168
4.161
2.482
-0.020
4-NO2-Ph
O
N
F
F
3e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.02
0.99
0.99
6.00
-61.24
-61.64
-83.07
-83.47
4-NO2-Ph
O
N
F
F
3e
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

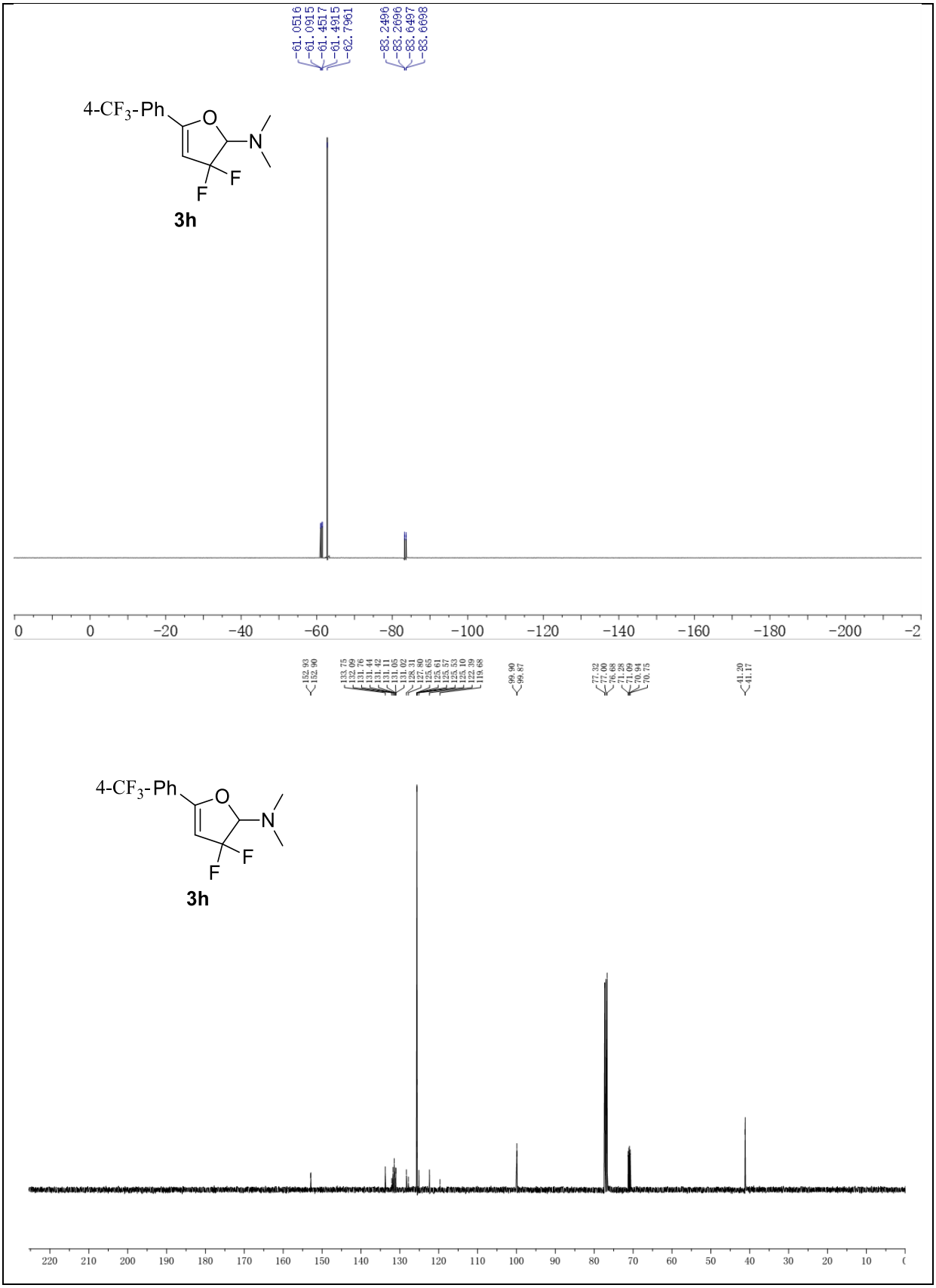

152.10
152.06
148.27
133.84
133.66
130.95
130.92
128.22
126.10
123.89
102.02
101.99
77.32
77.00
76.68
71.34
71.15
70.99
70.81
41.22
41.20
4-NO2-Ph
O
N
F
F
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
8.42
8.24
8.22
7.92
7.90
7.62
7.60
7.58
7.26
5.76
5.75
5.75
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
2.48
3-NO2-Ph
O
N
F
F
3f
0.92
0.91
0.95
0.94
0.96
0.96
6.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5


-61.16
-61.20
-61.56
-61.60
-83.08
-83.10
-83.48
-83.50
3-NO2-Ph
O
N
F
F
3f
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
151.86
151.82
148.37
133.65
130.94
130.91
130.87
129.91
129.77
128.21
124.32
120.29
100.36
100.33
77.32
77.00
76.68
71.30
71.11
70.95
70.77
41.21
41.19
3-NO2-Ph
O
N
F
F
3f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.6879
7.2600
5.7371
5.7309
5.7250
4.2125
4.2056
4.1931
4.1862
4.1752
4.1683
4.1558
4.1489
2.4786
4-CN-Ph
O
N
F
F
3g
3.95
0.96
1.04
6.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-61.0726
-61.1124
-61.4710
-61.5107
-83.0091
-83.0292
-83.4073
-83.4275
4-CN-Ph
O
N
F
F
3g
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2


4-CN-Ph
O
N
F
F
3g


4-CF3-Ph
O
N
F
F
3h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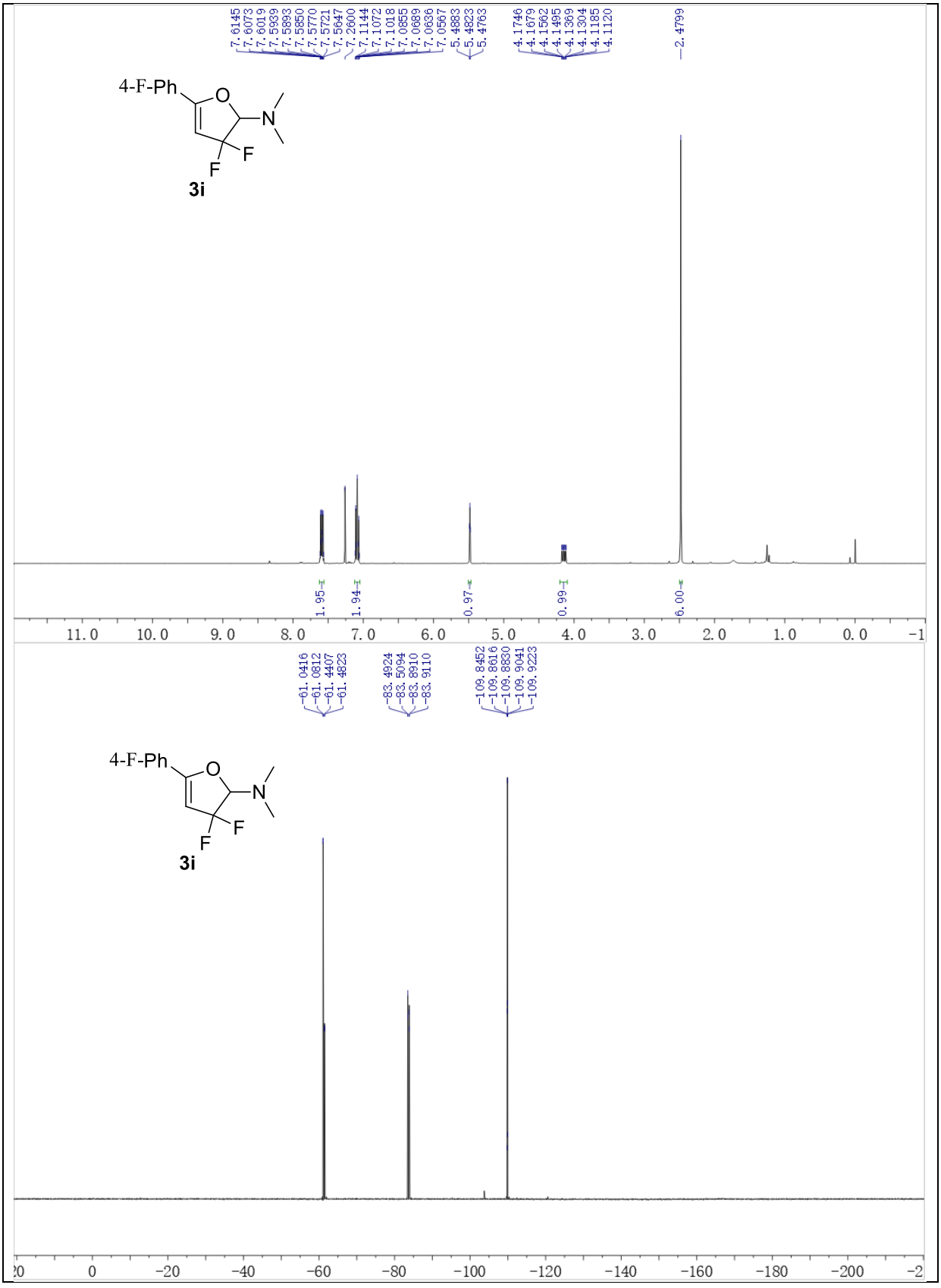
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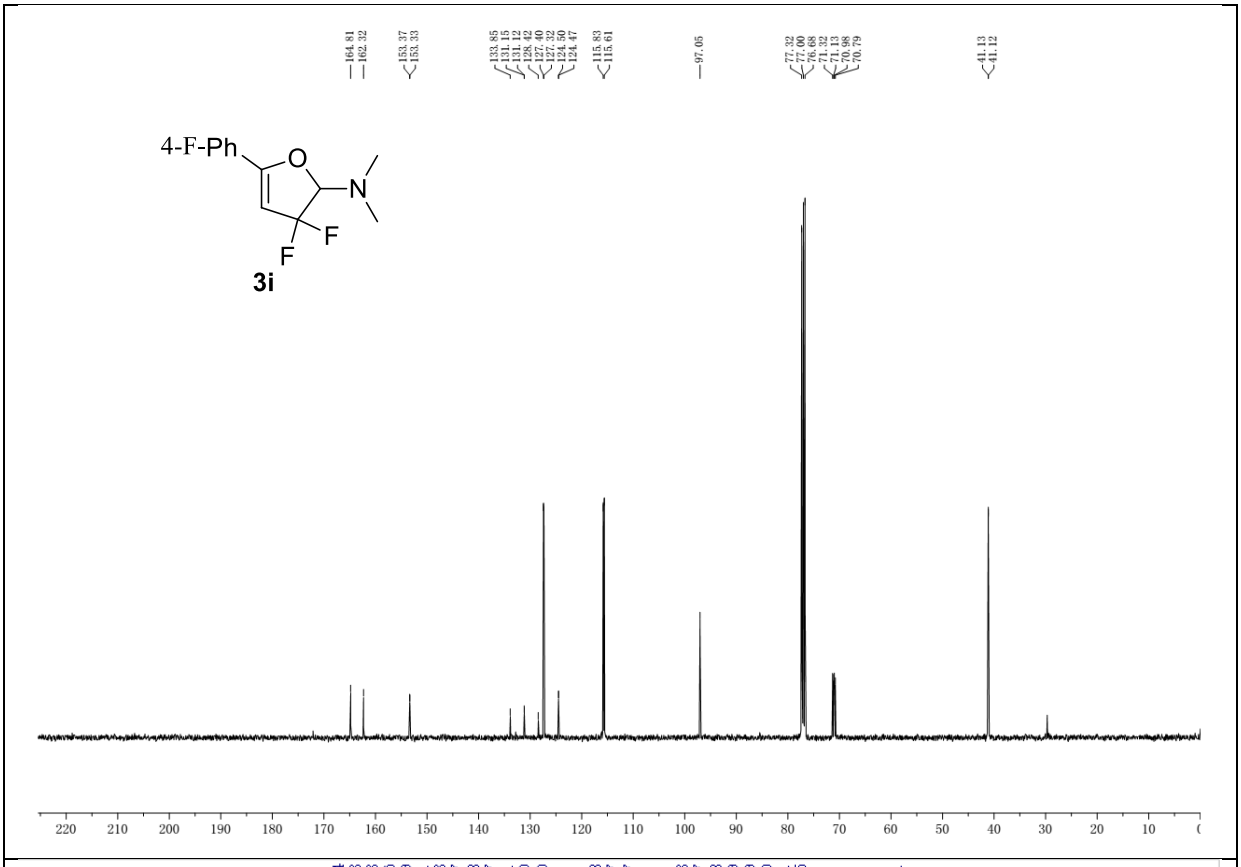
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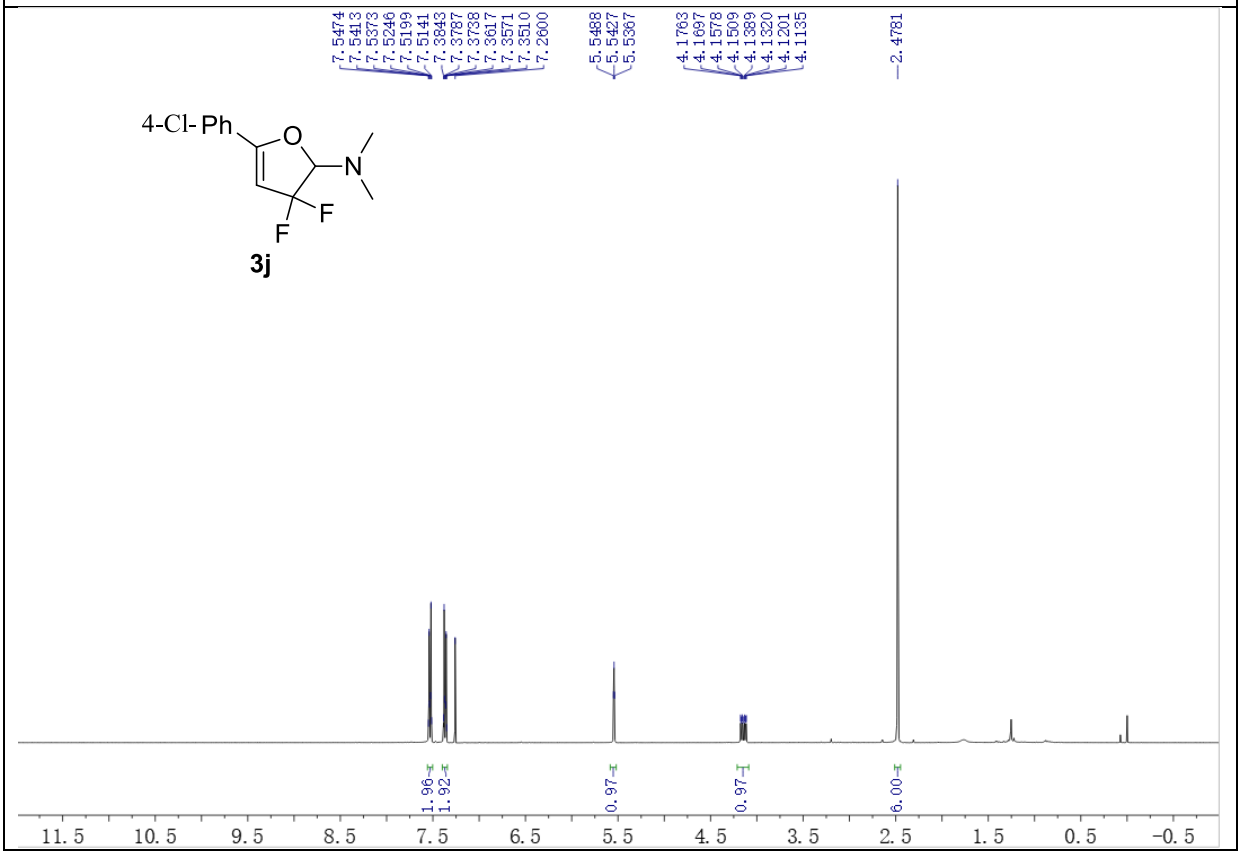
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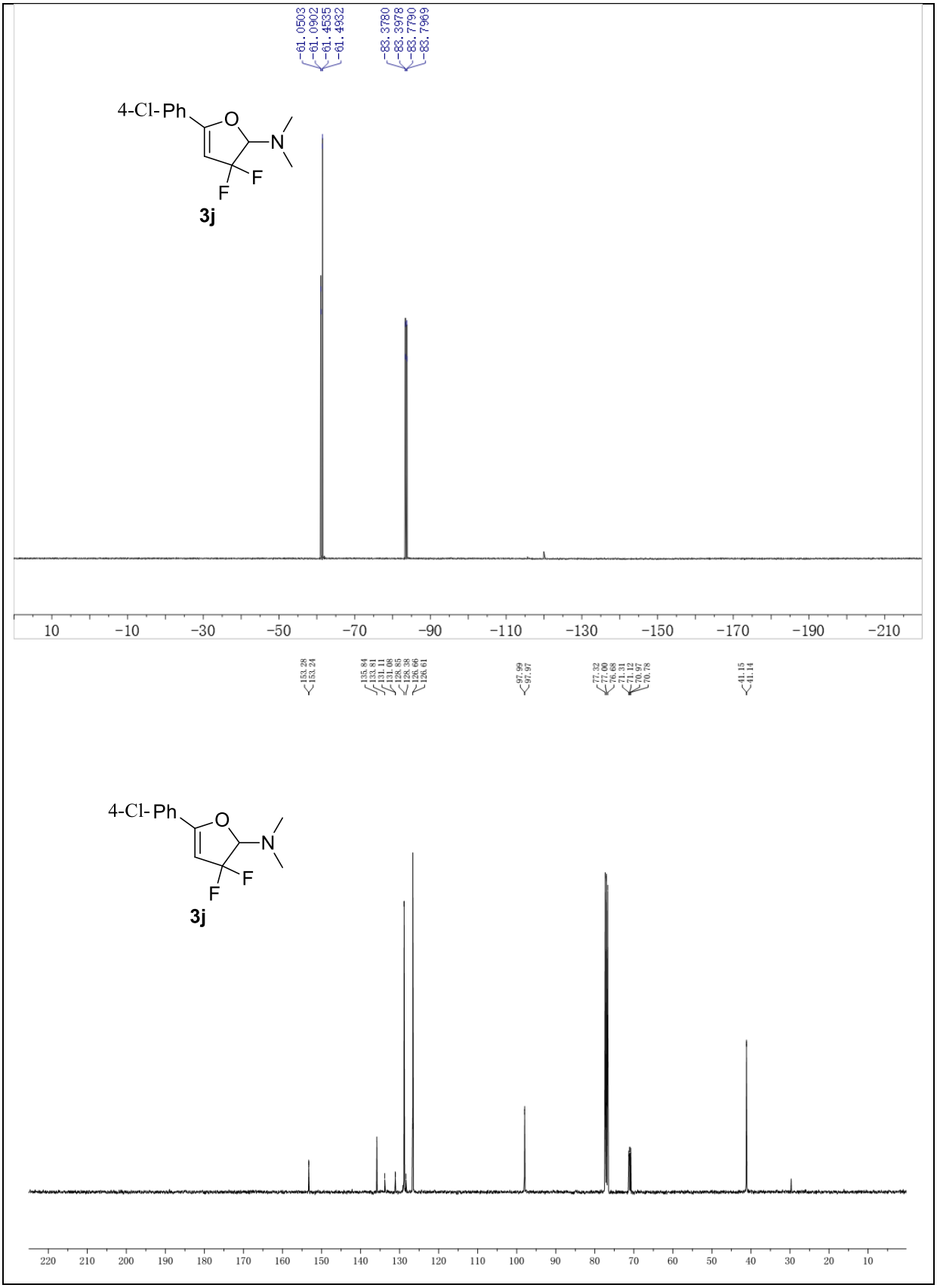
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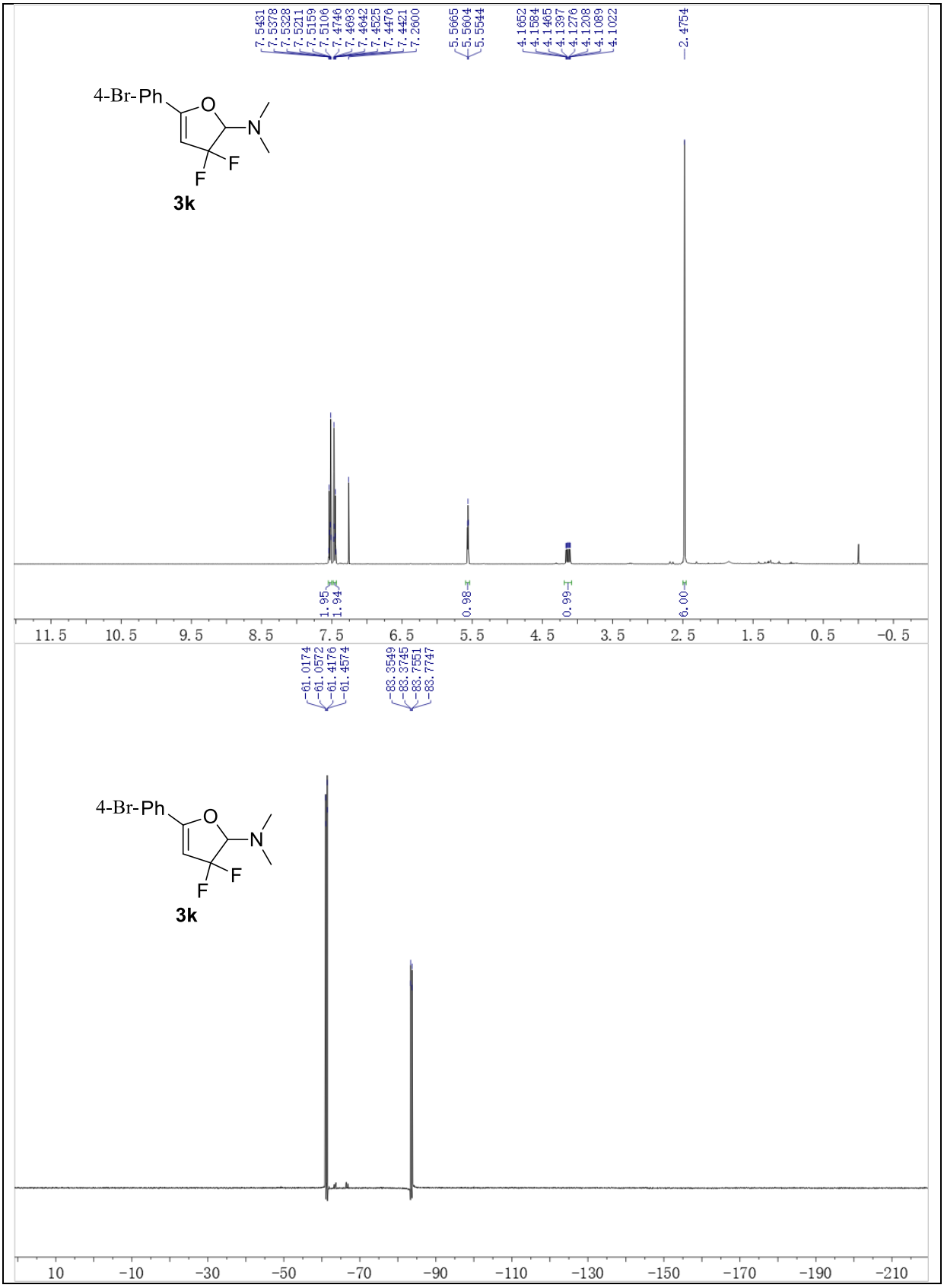
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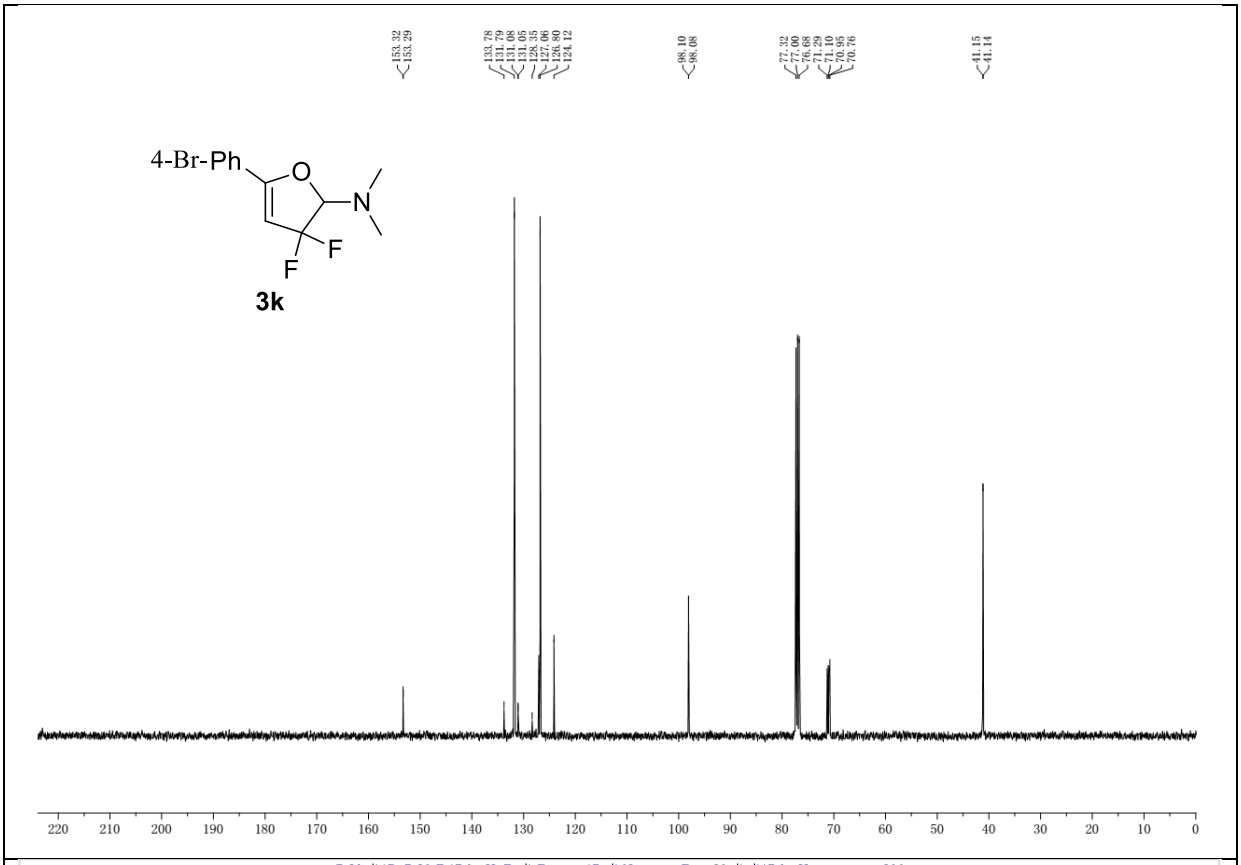
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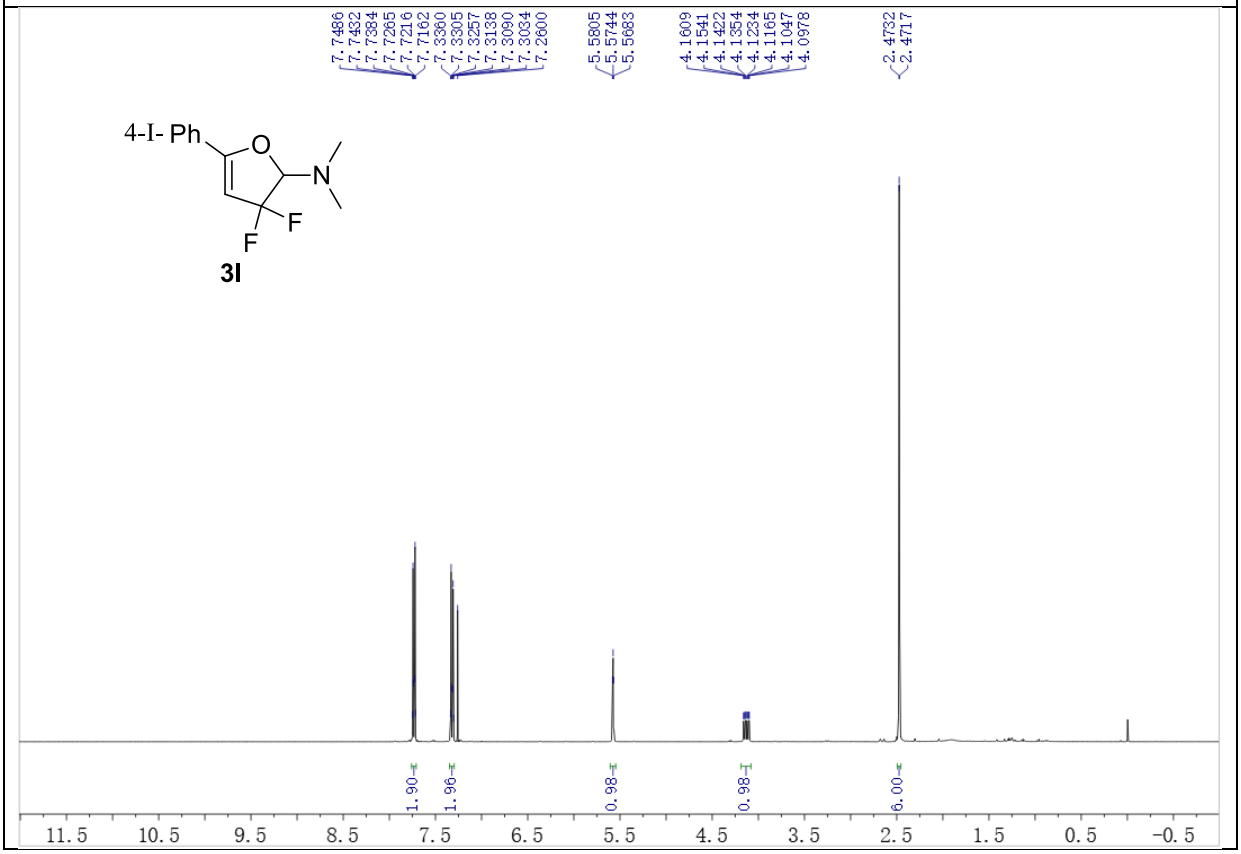
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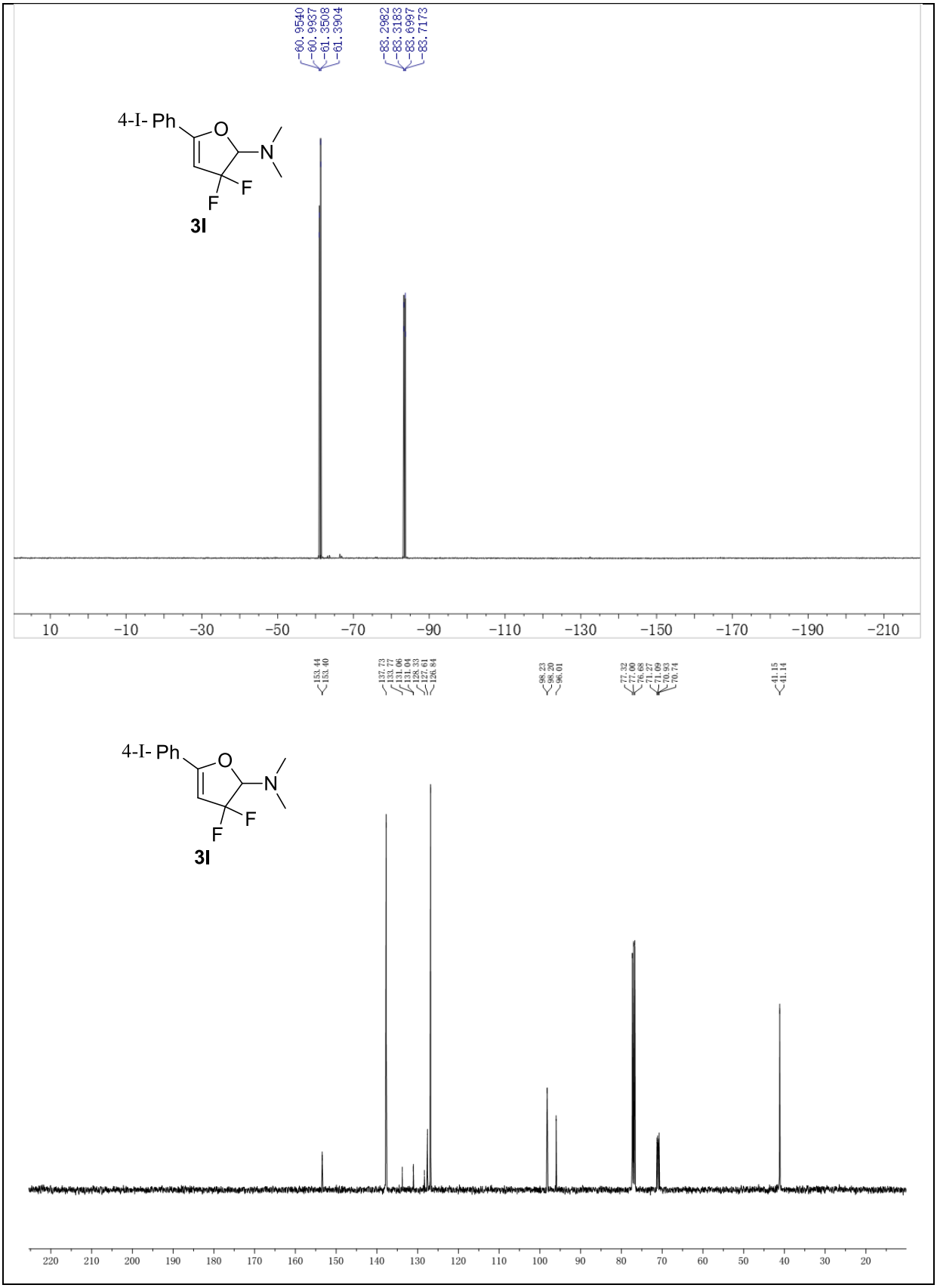
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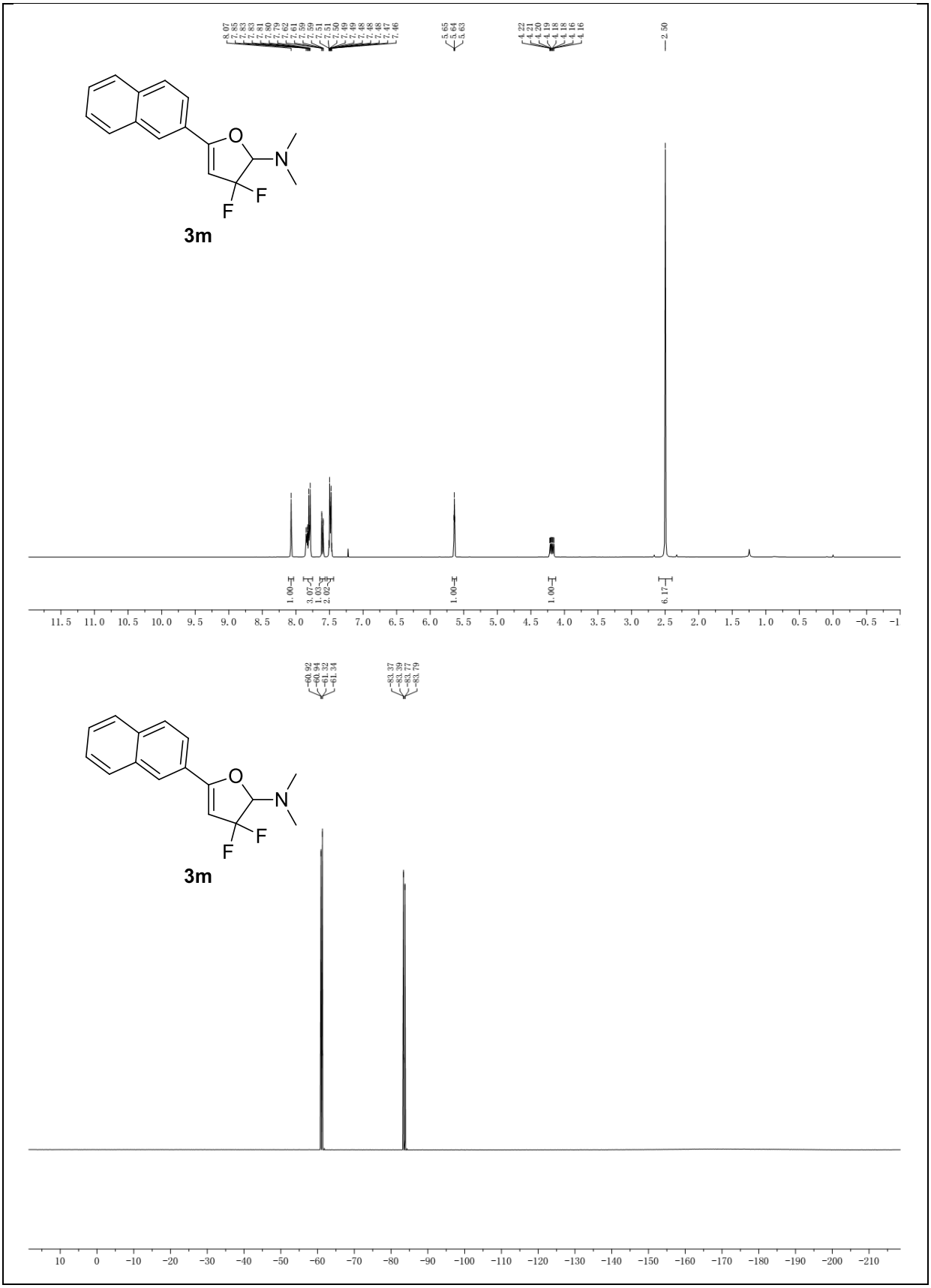
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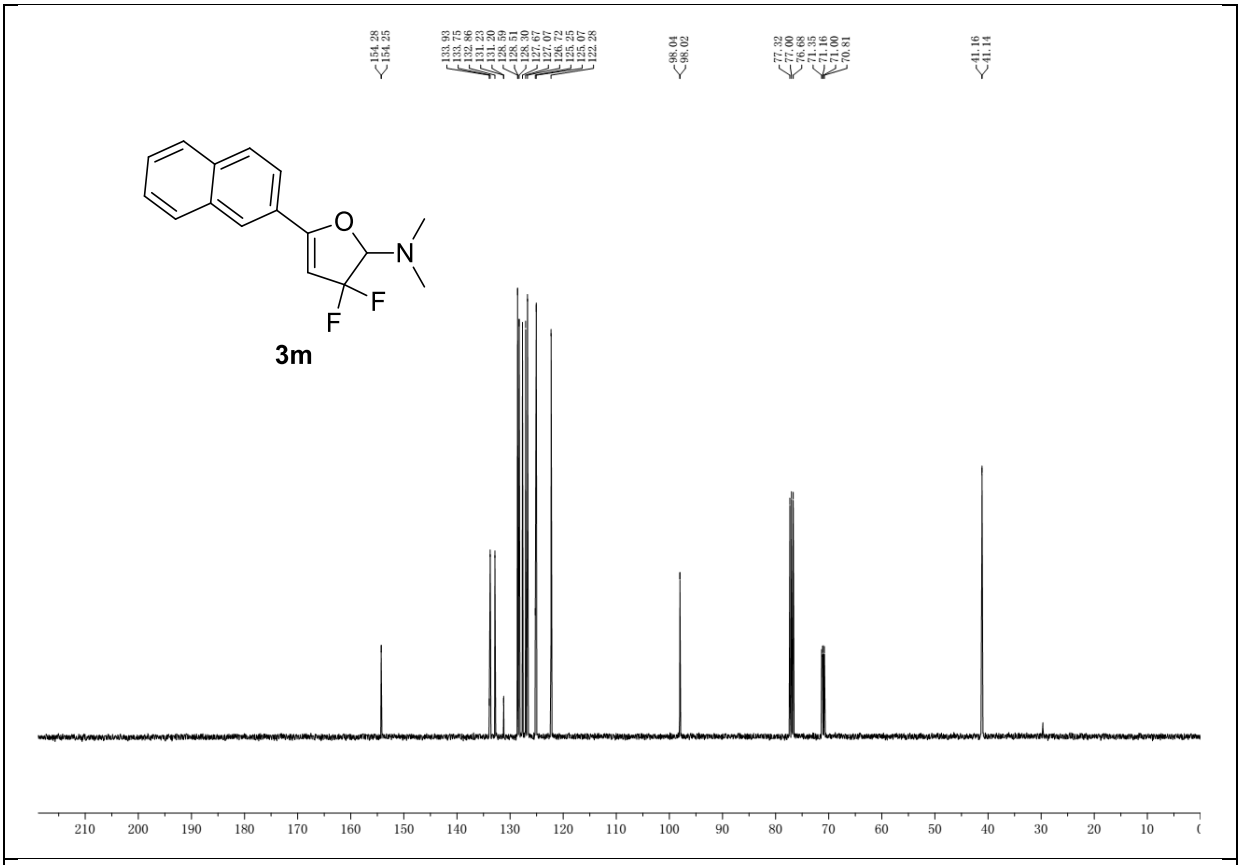
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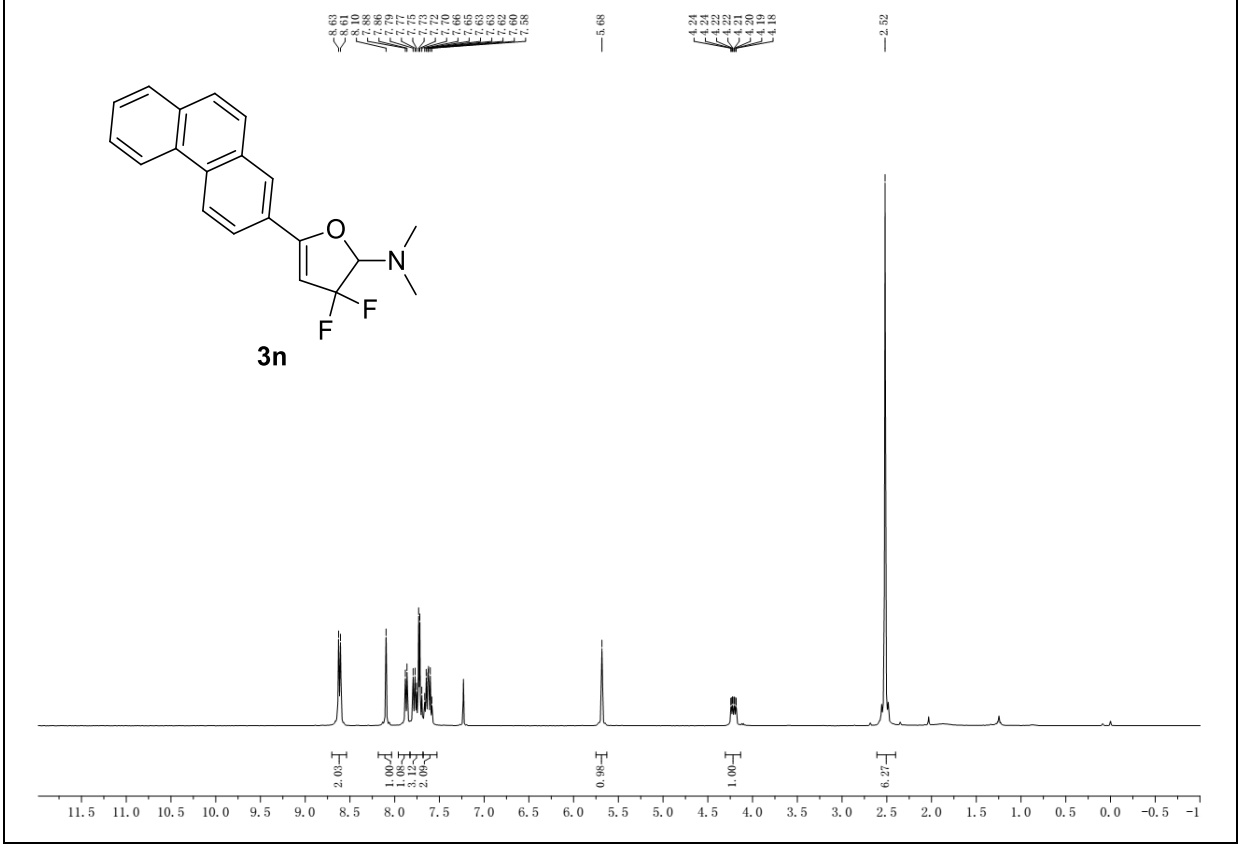
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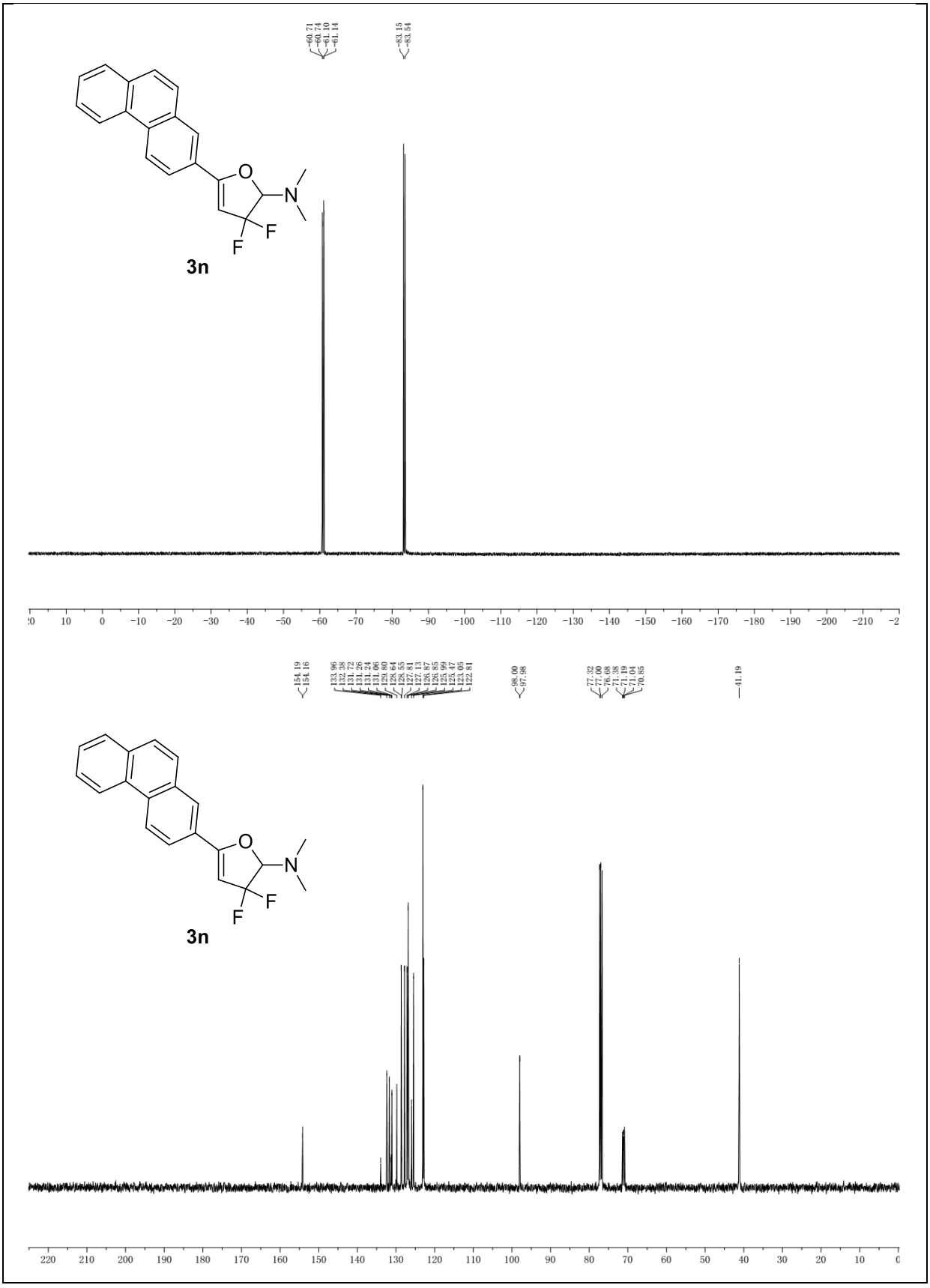
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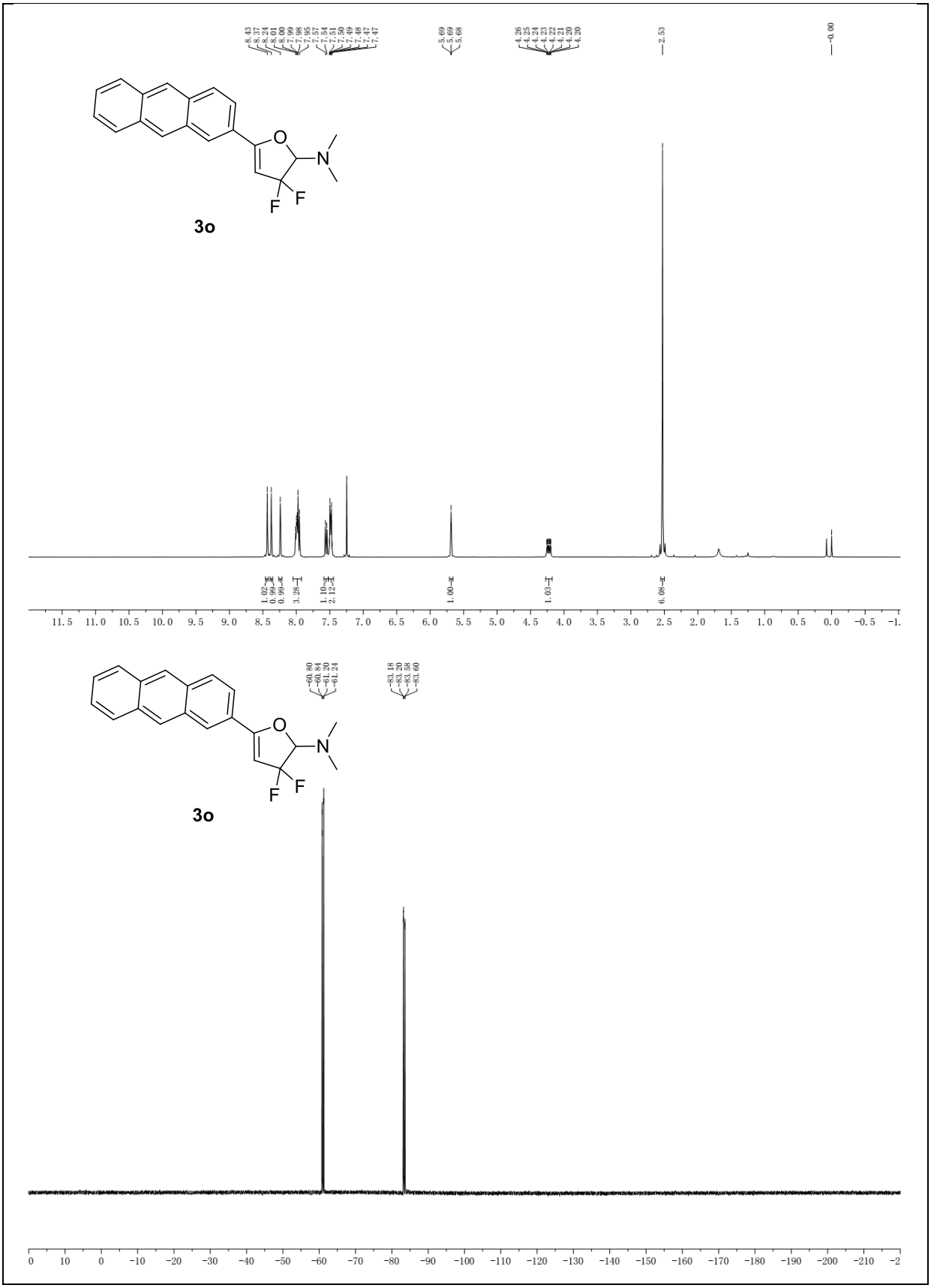
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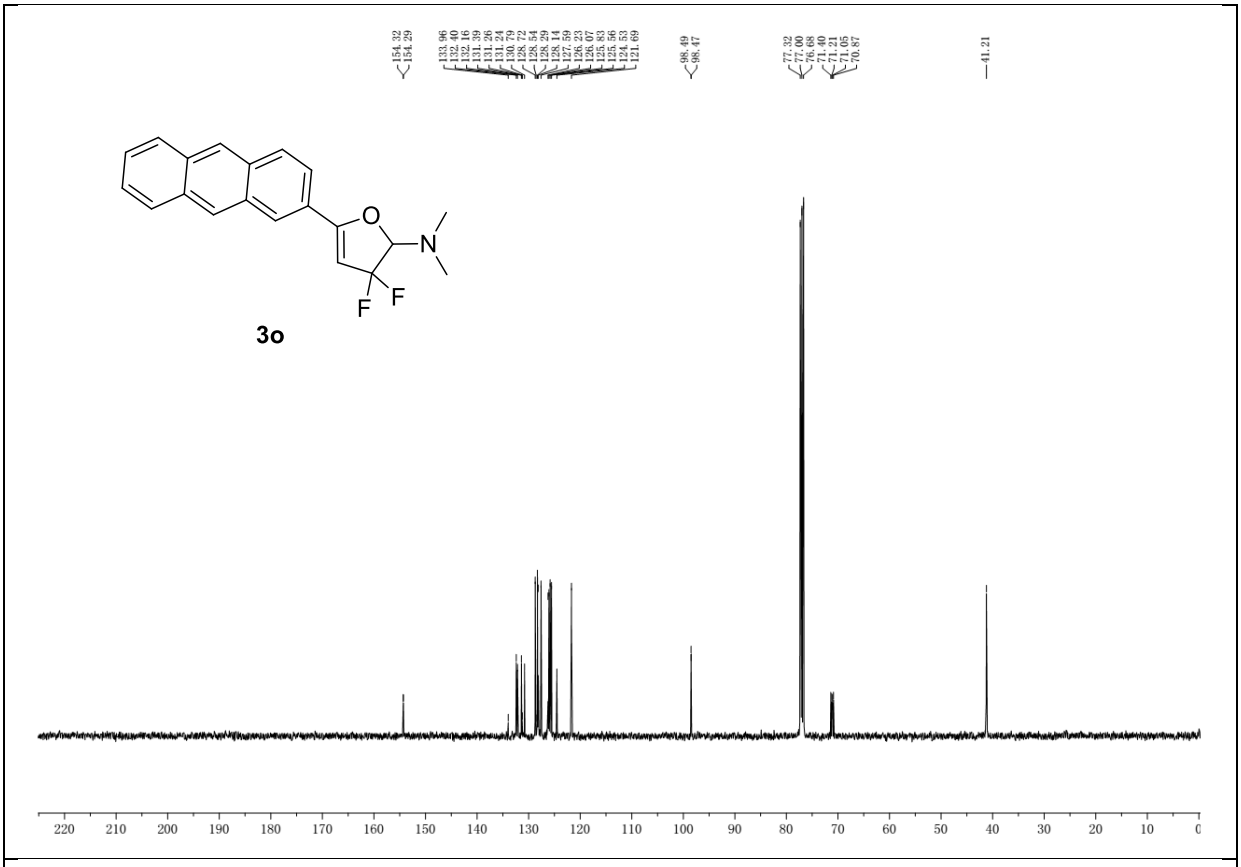
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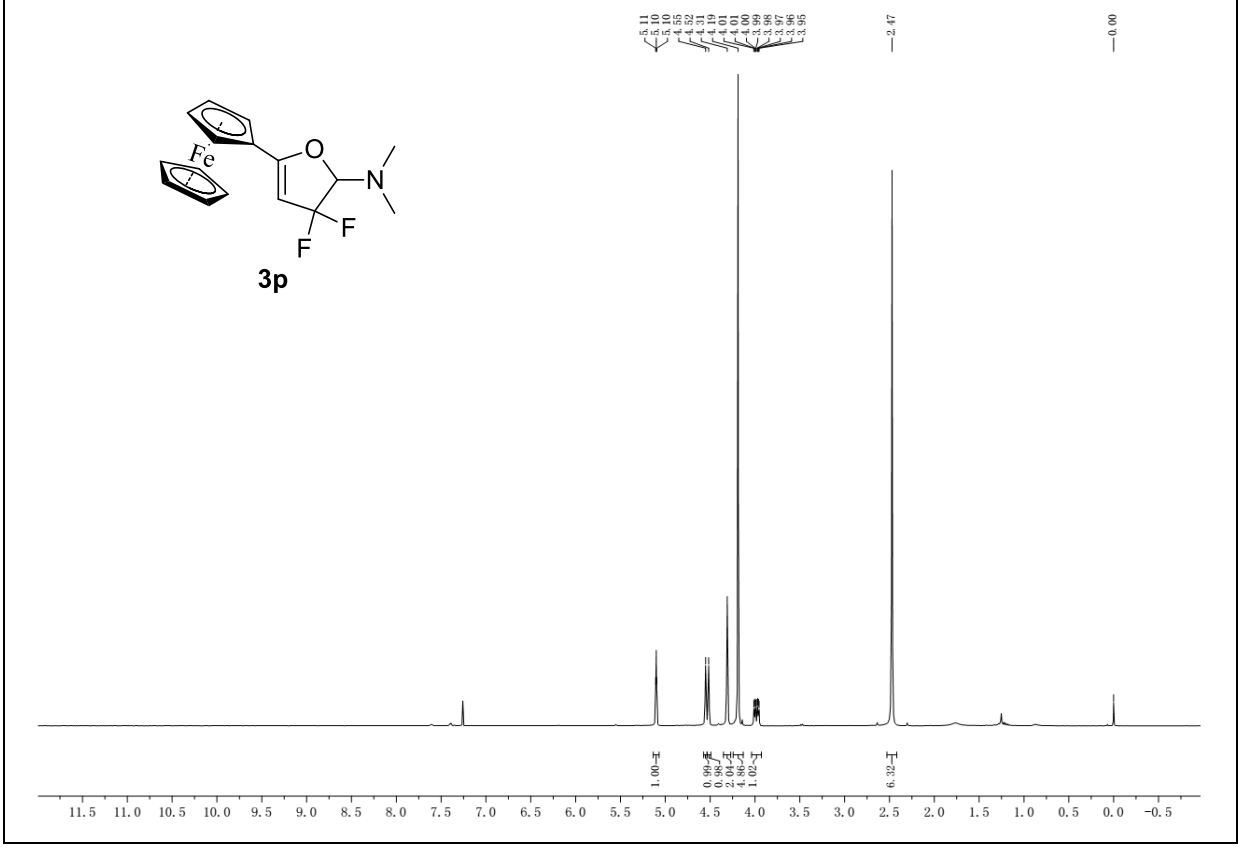
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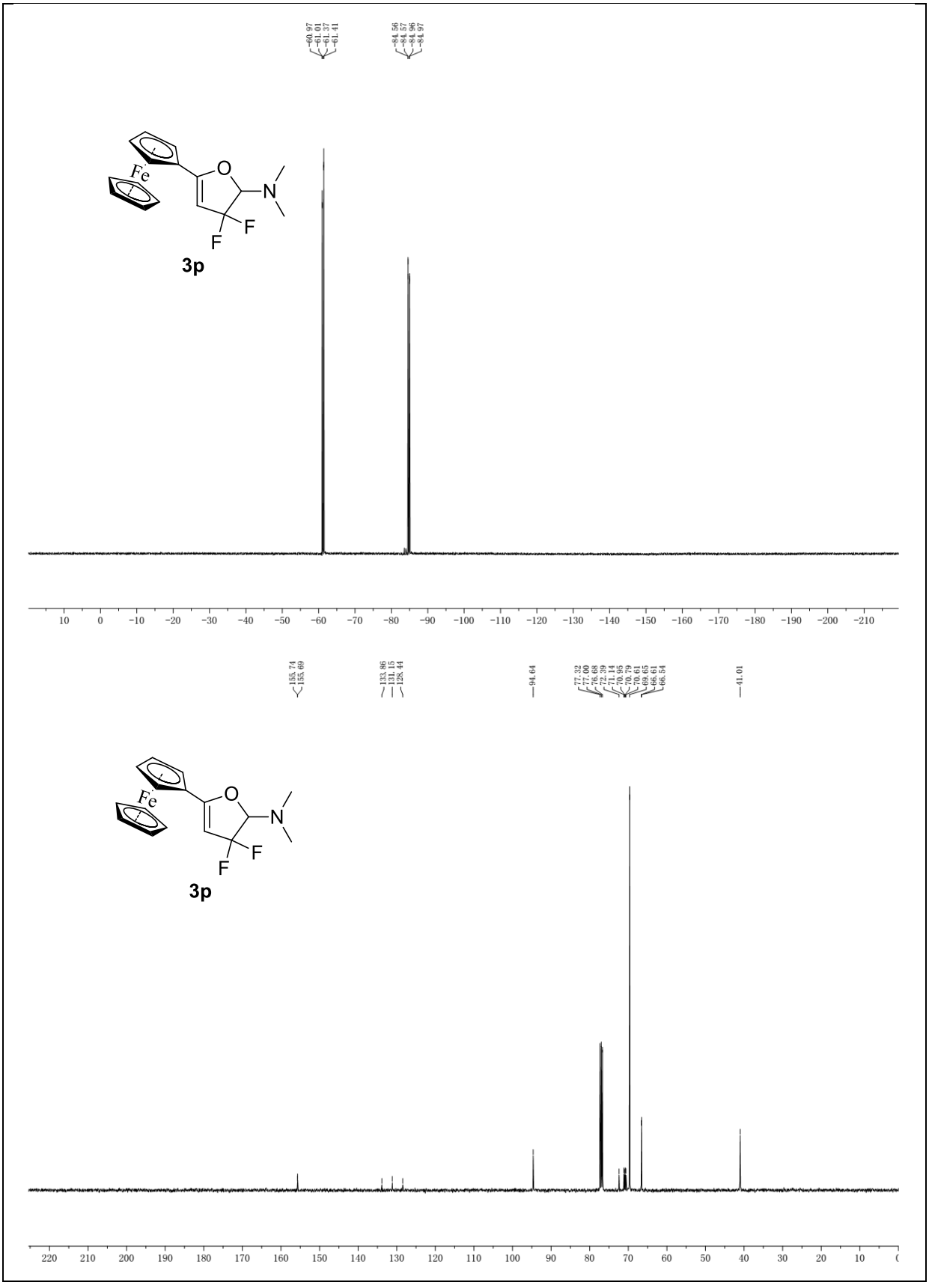
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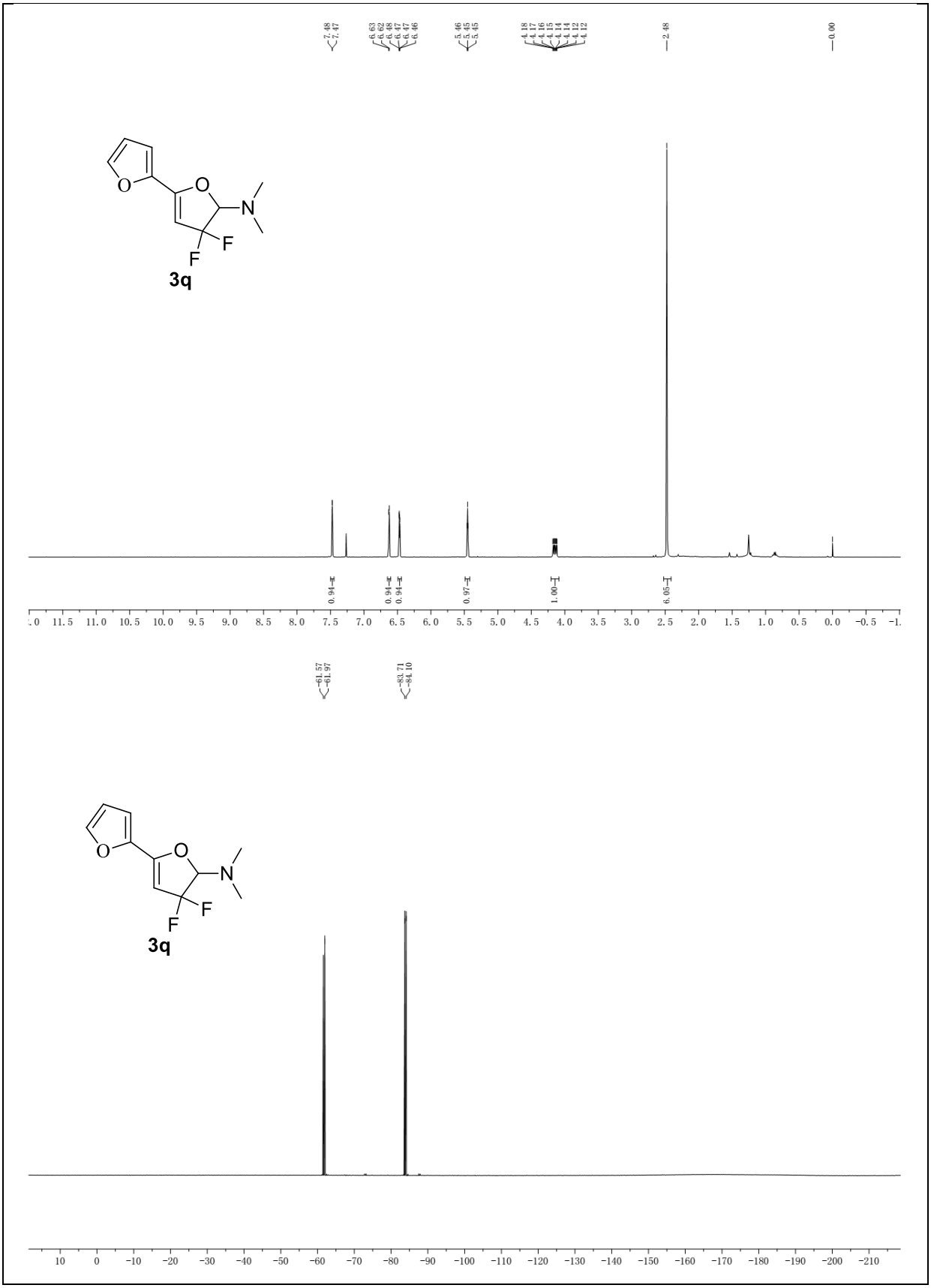
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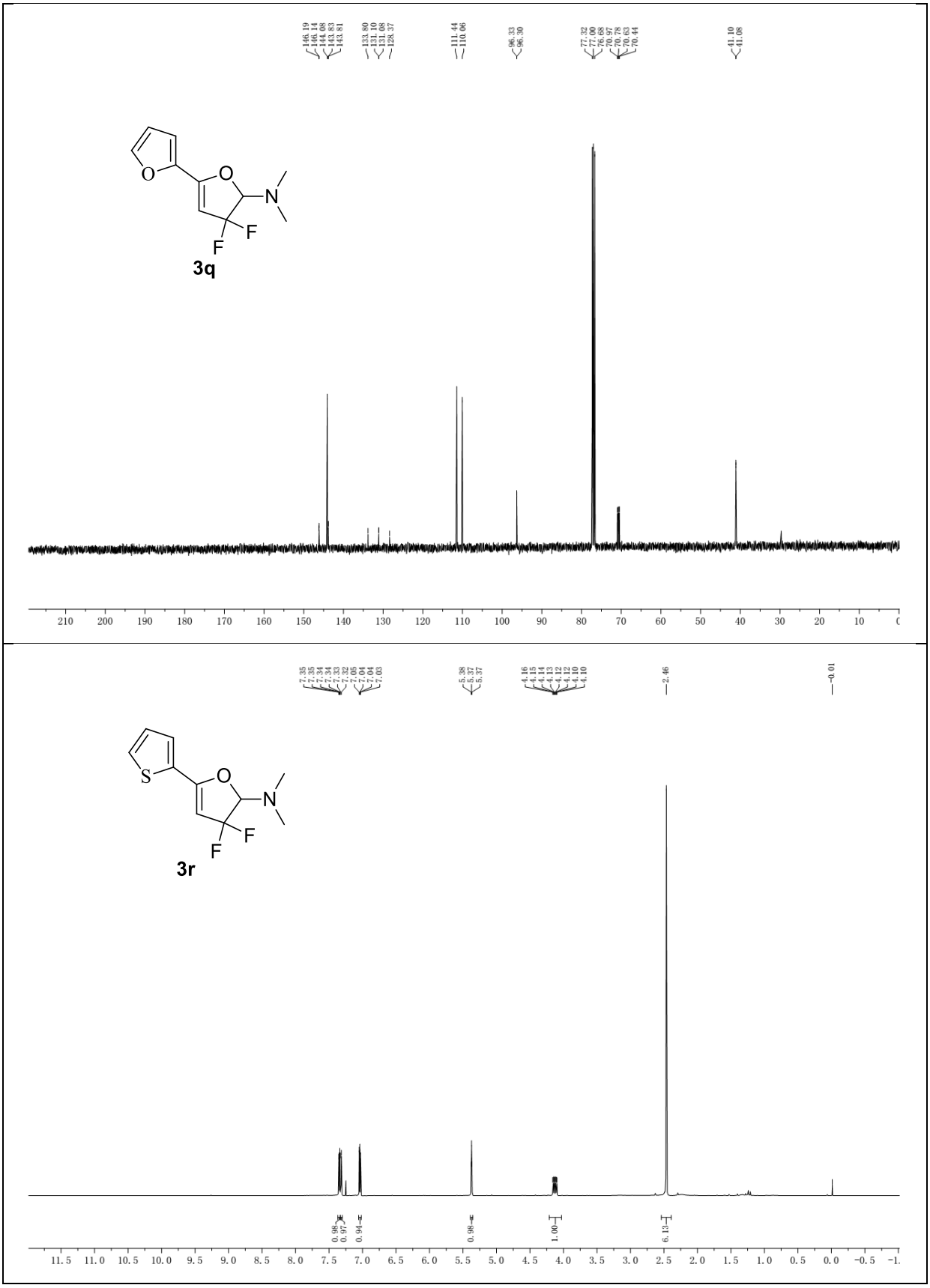
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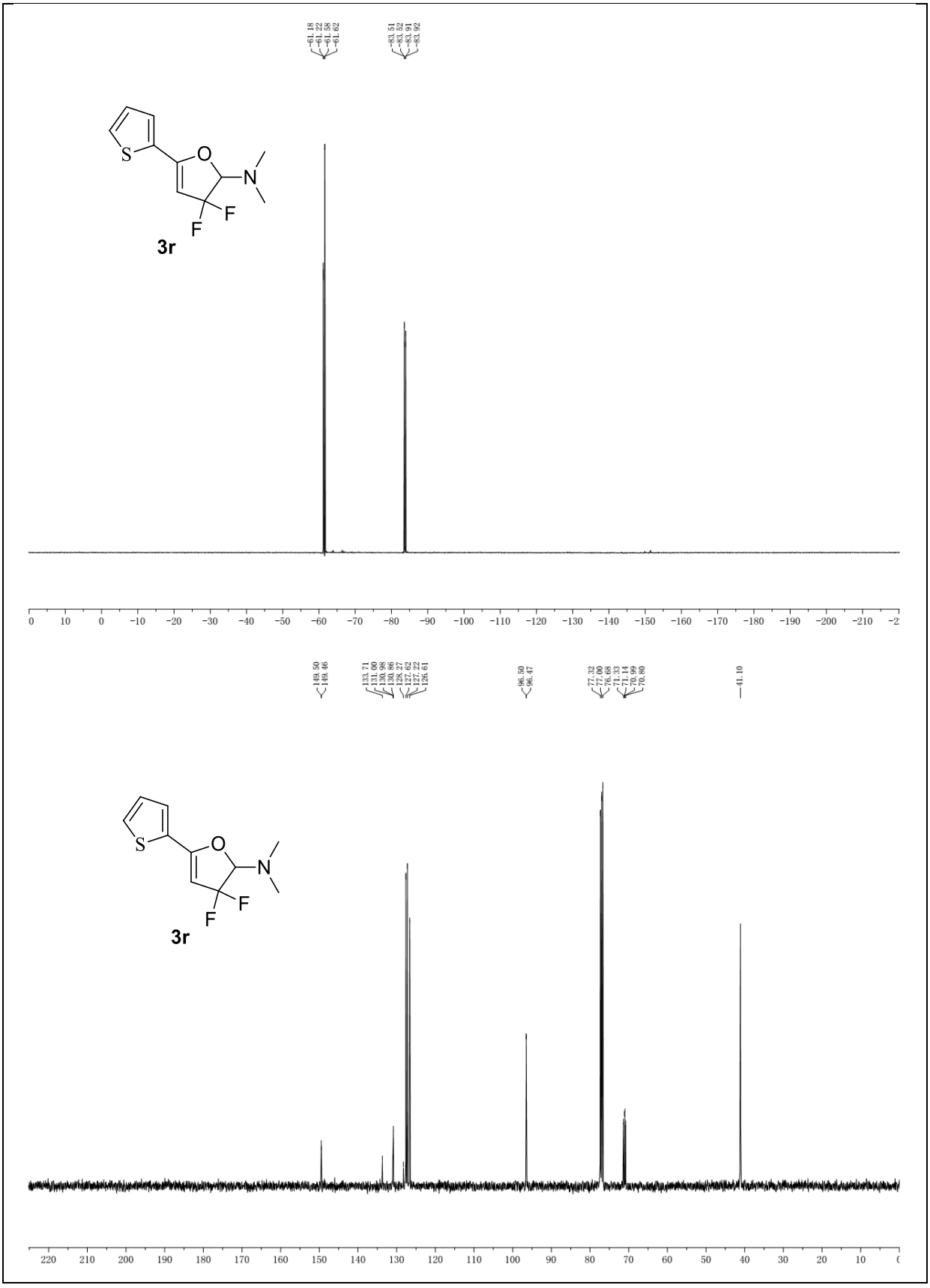
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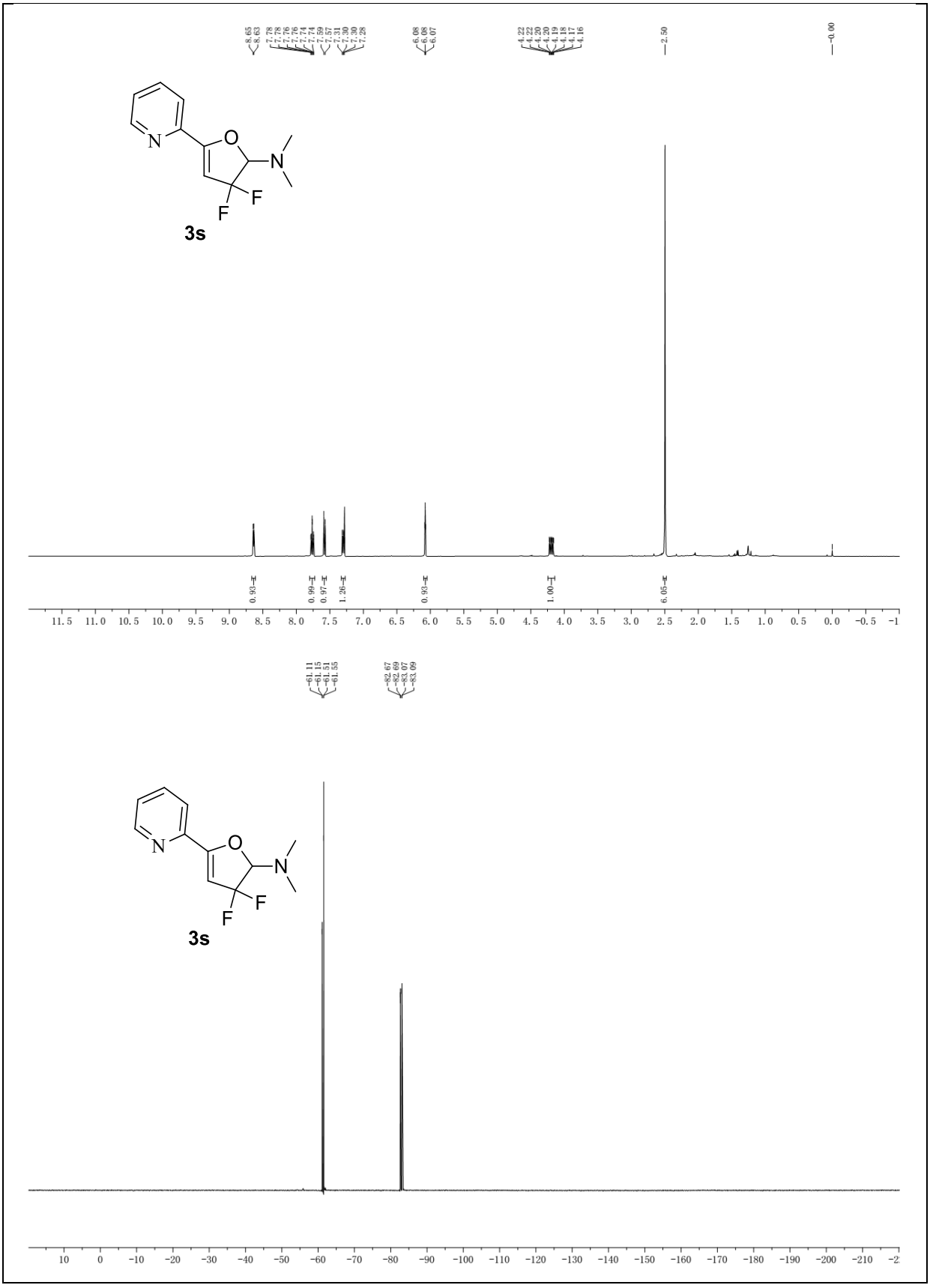
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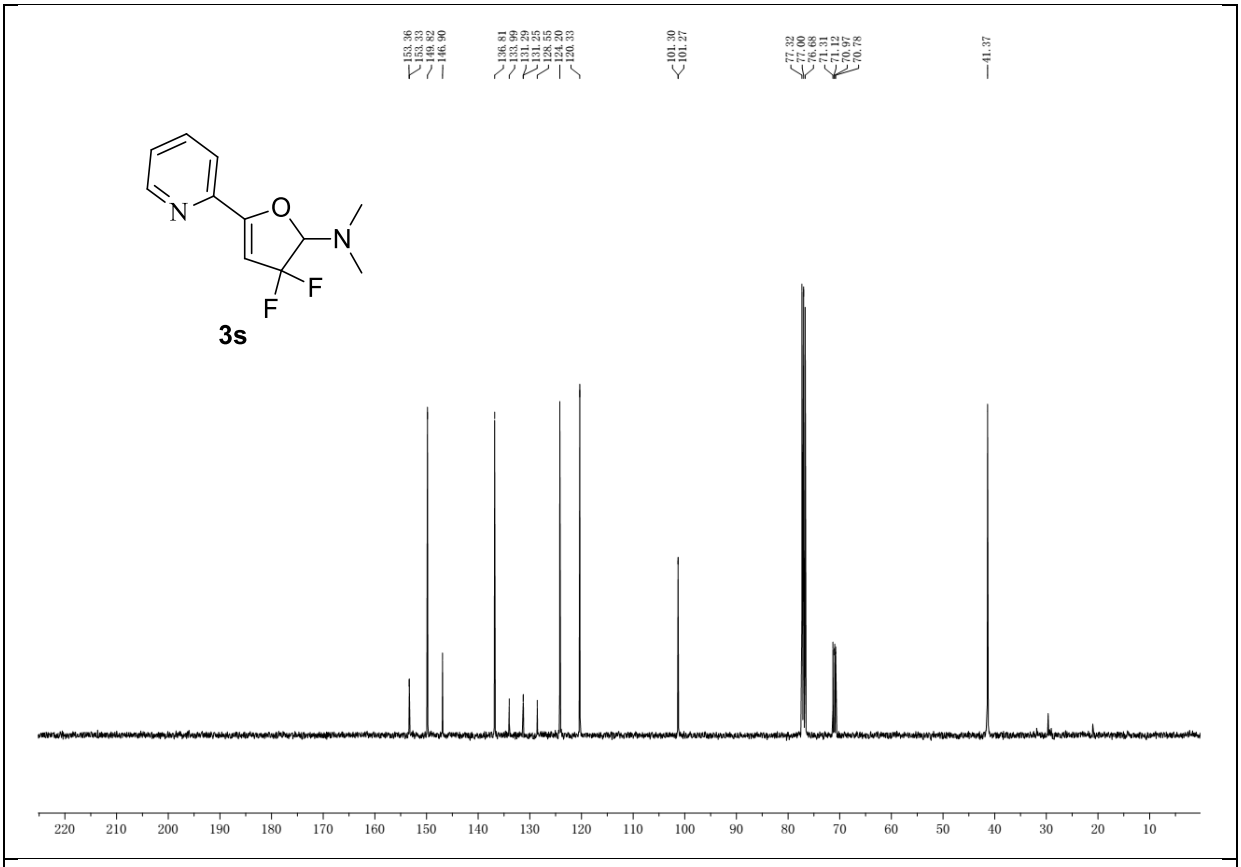
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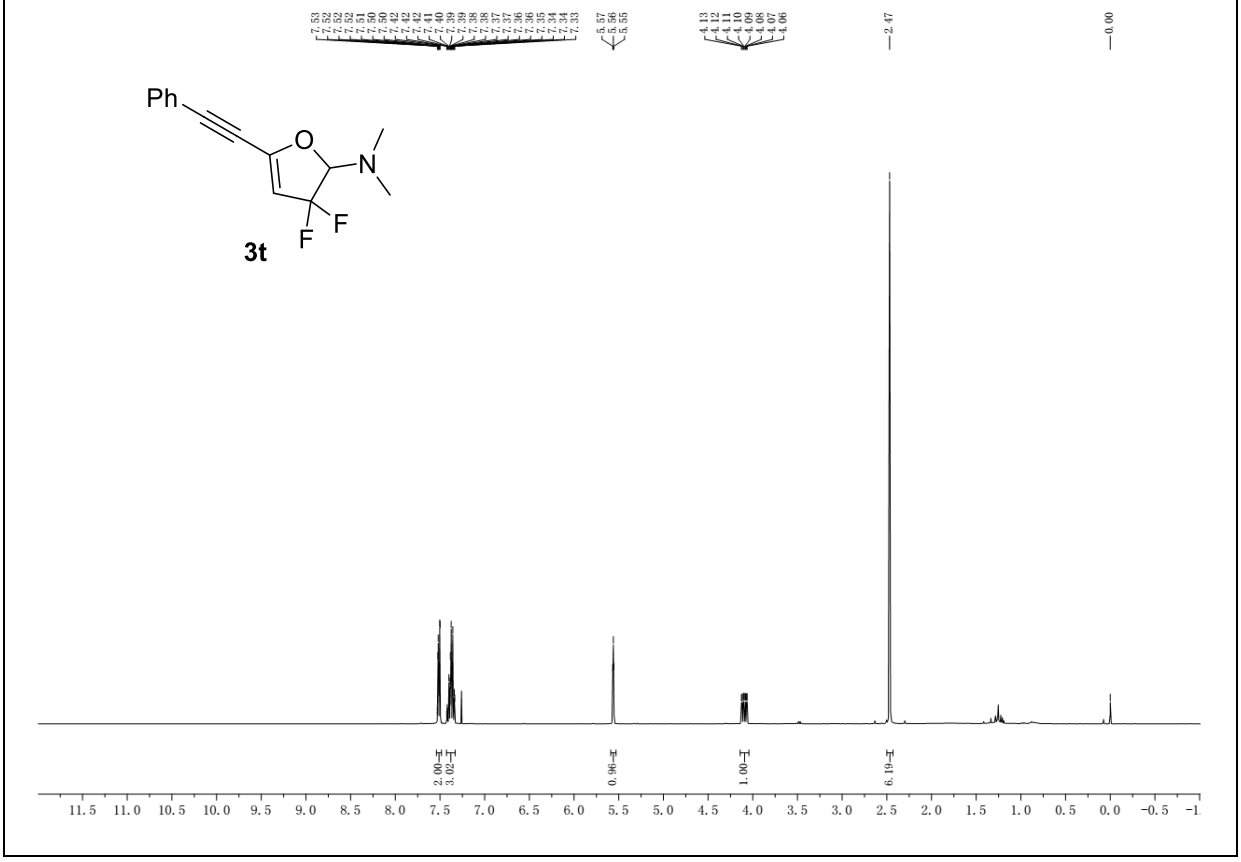
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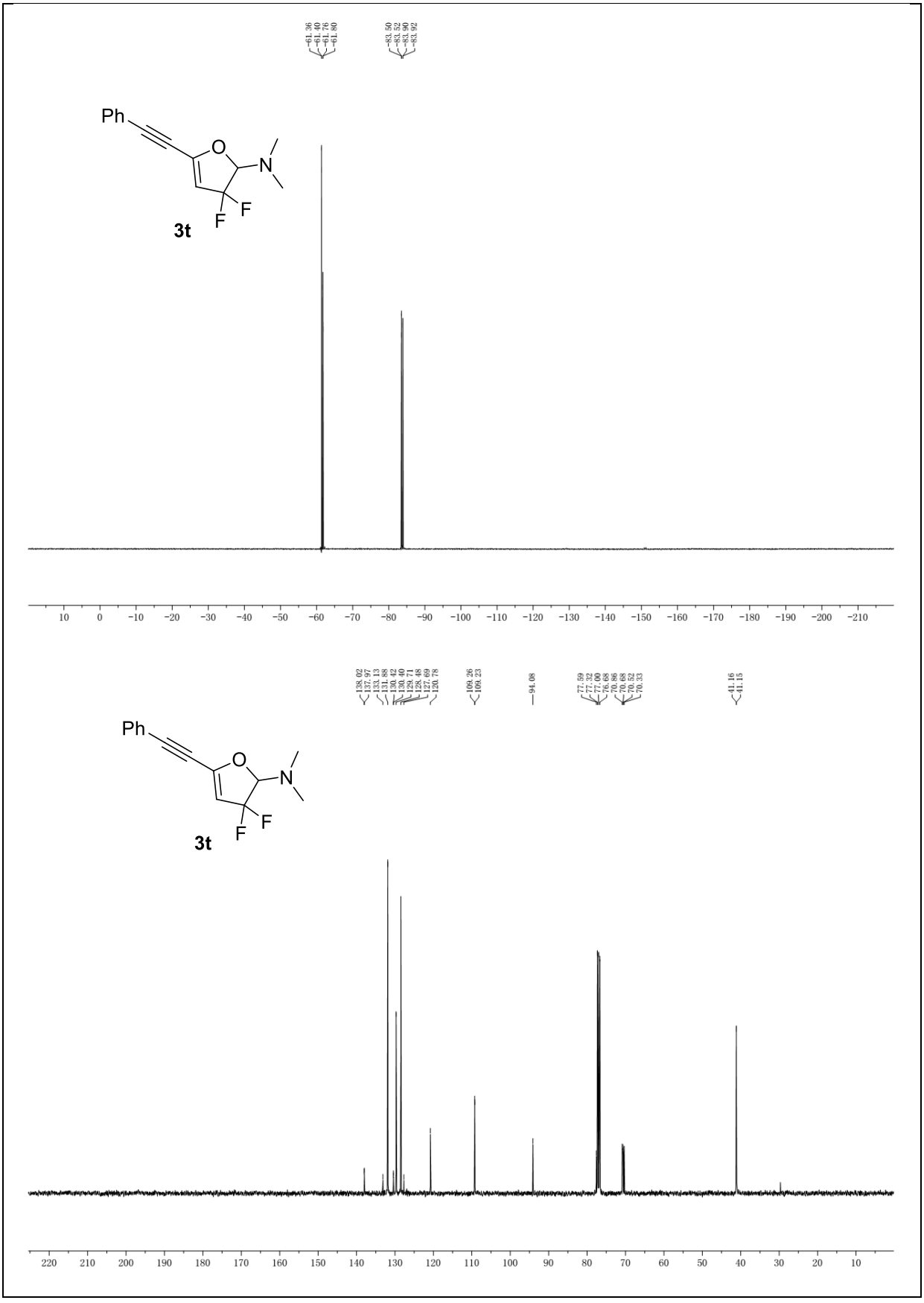
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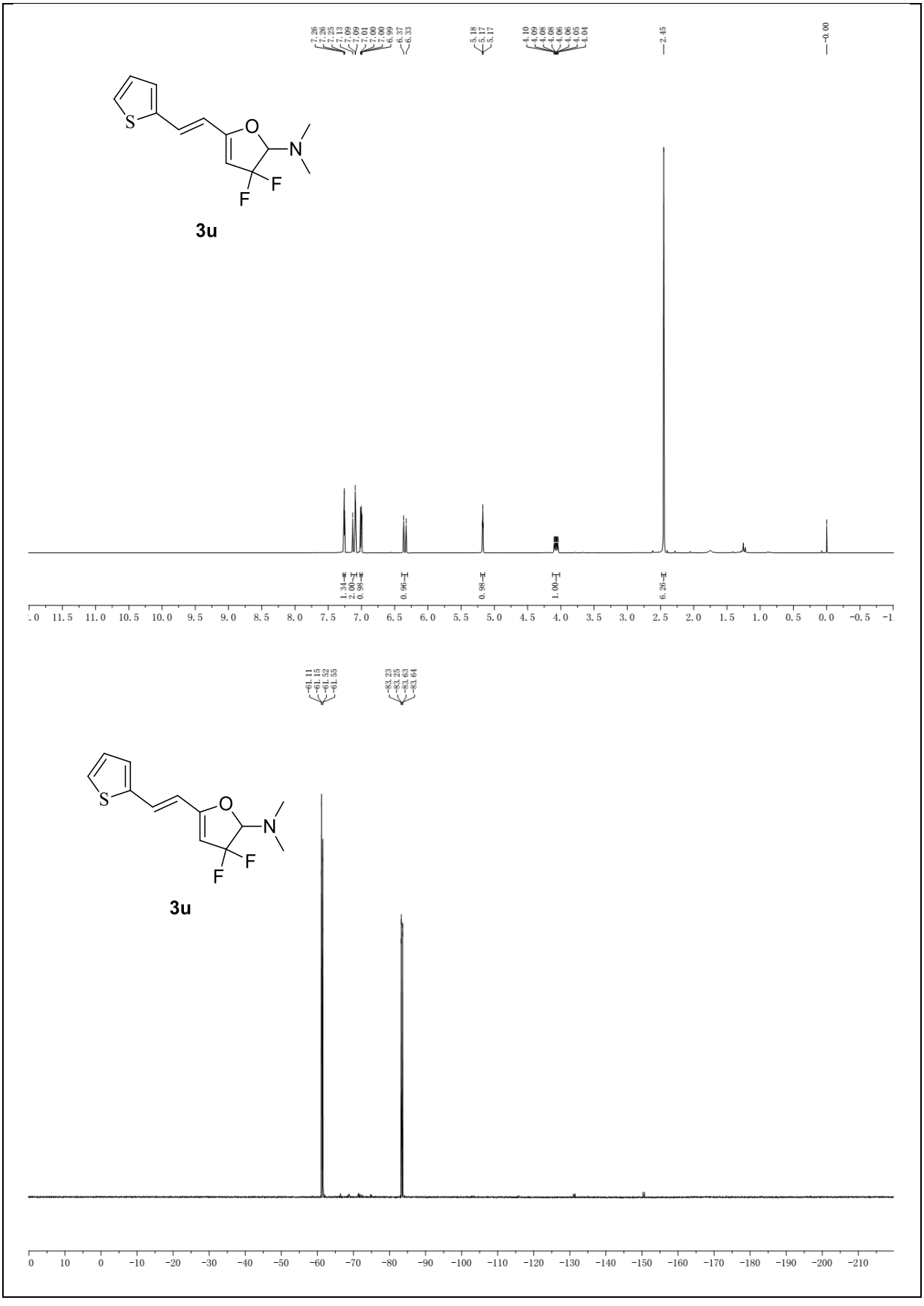
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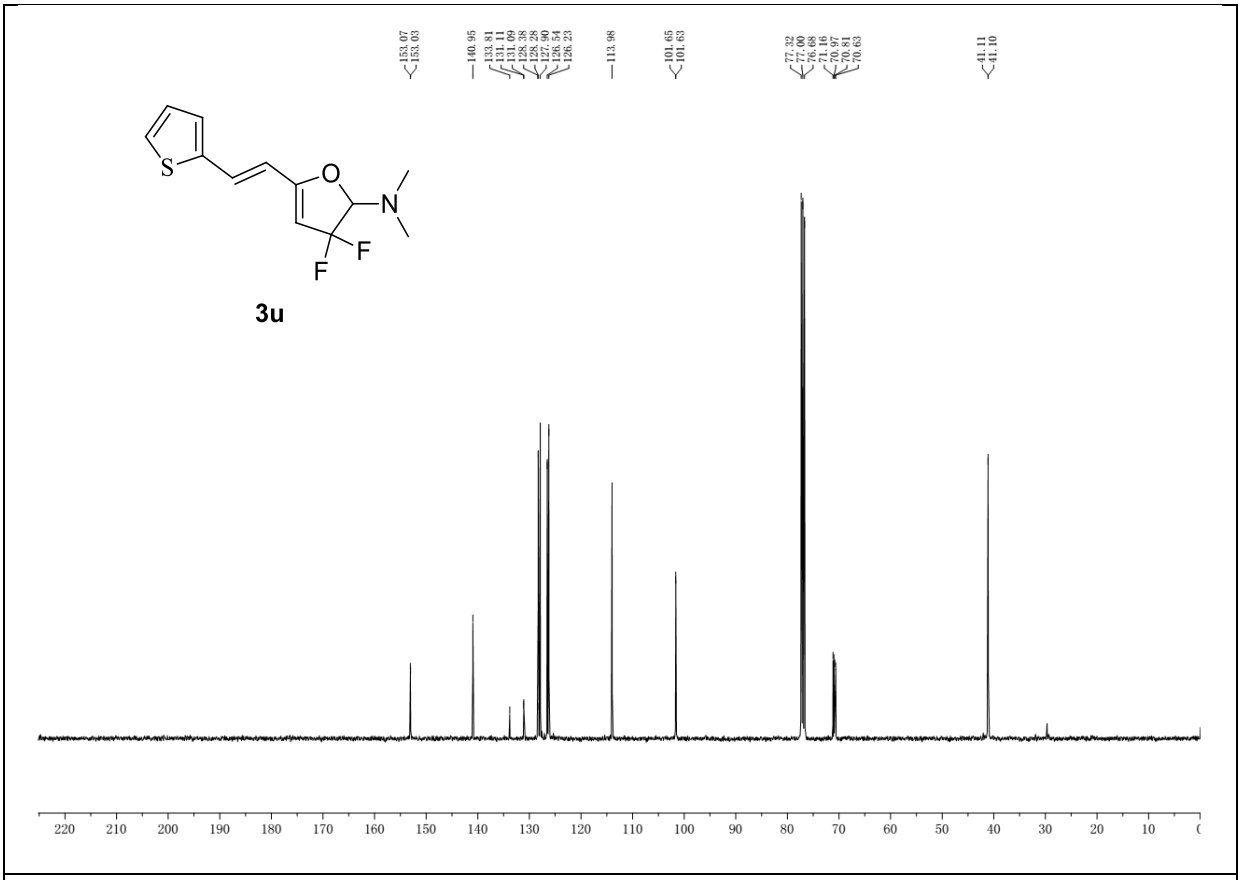
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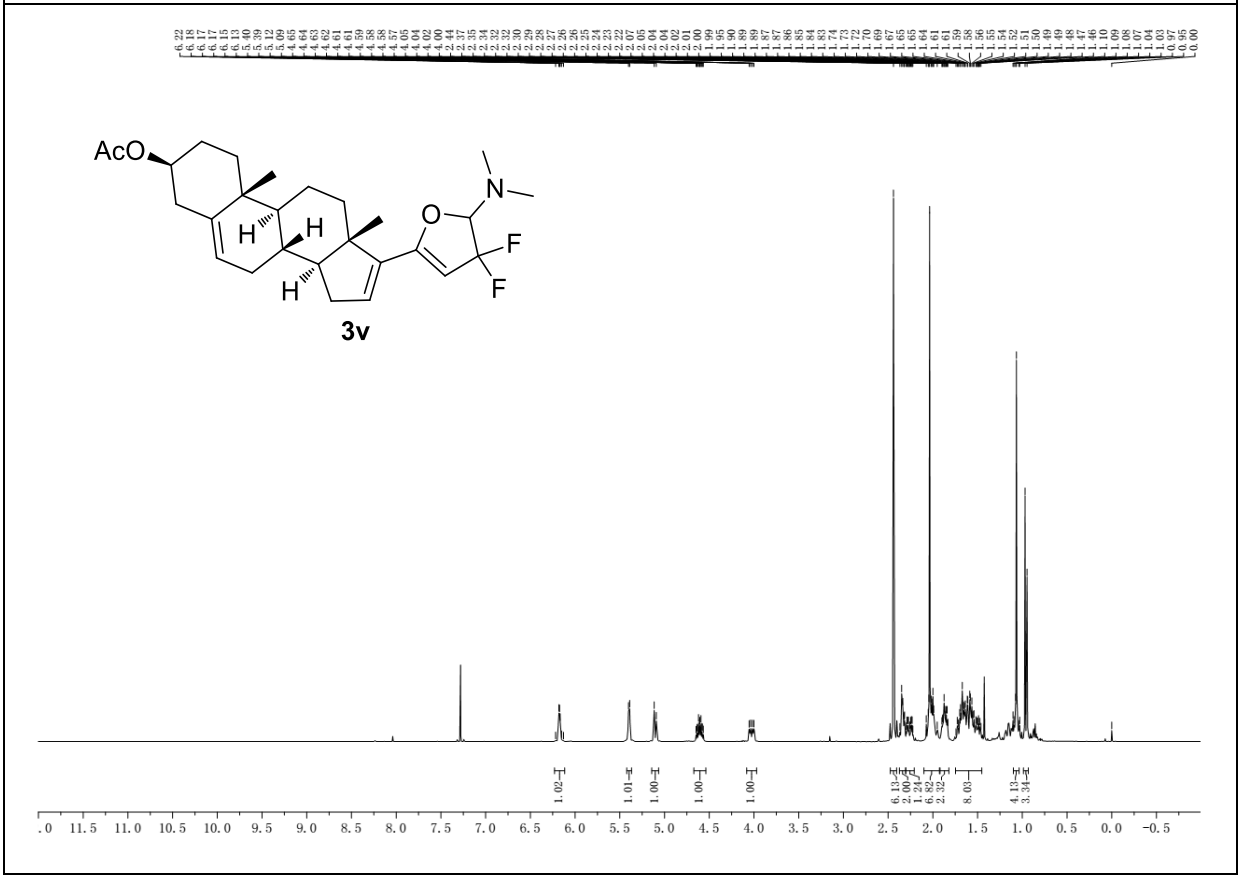
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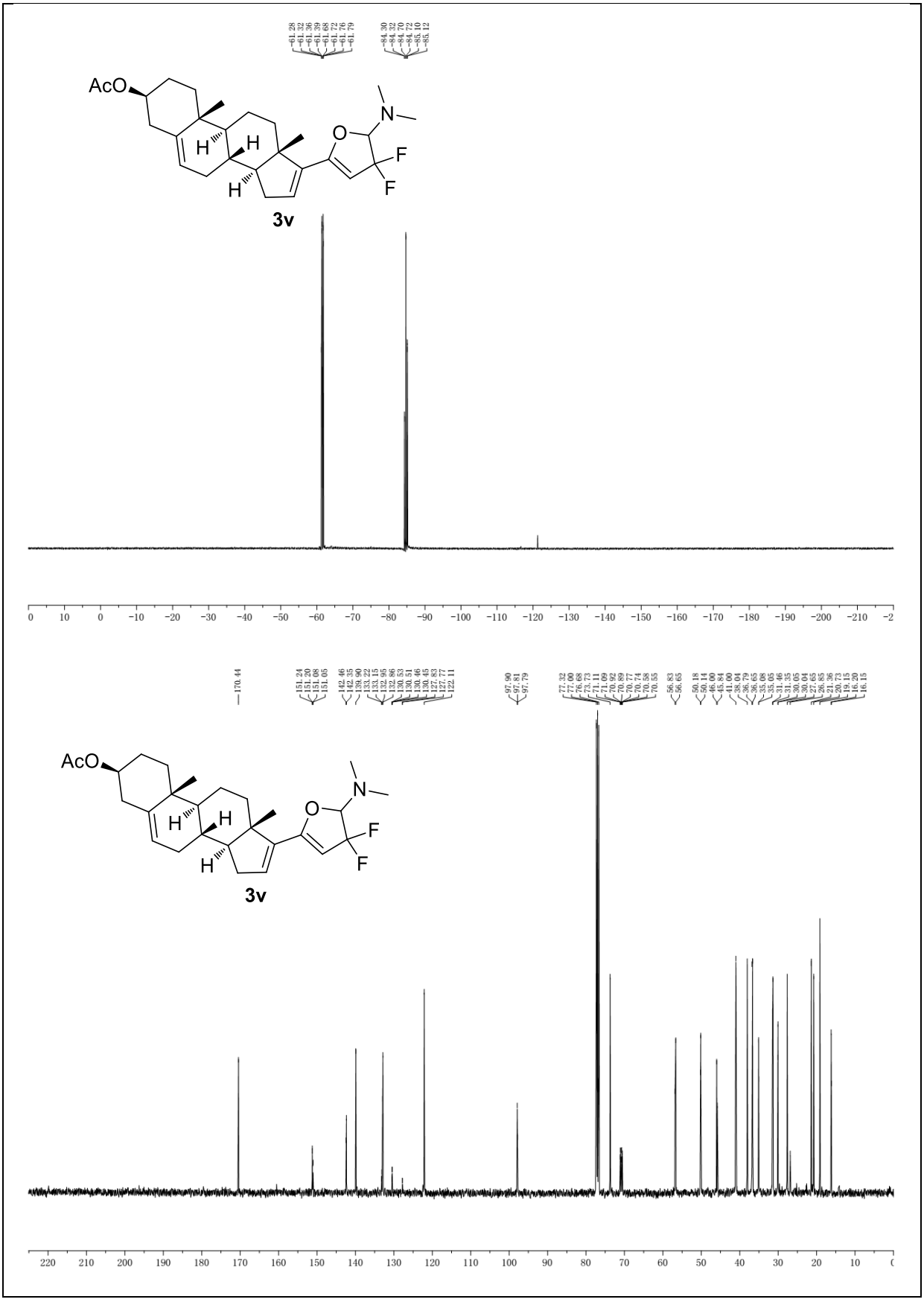
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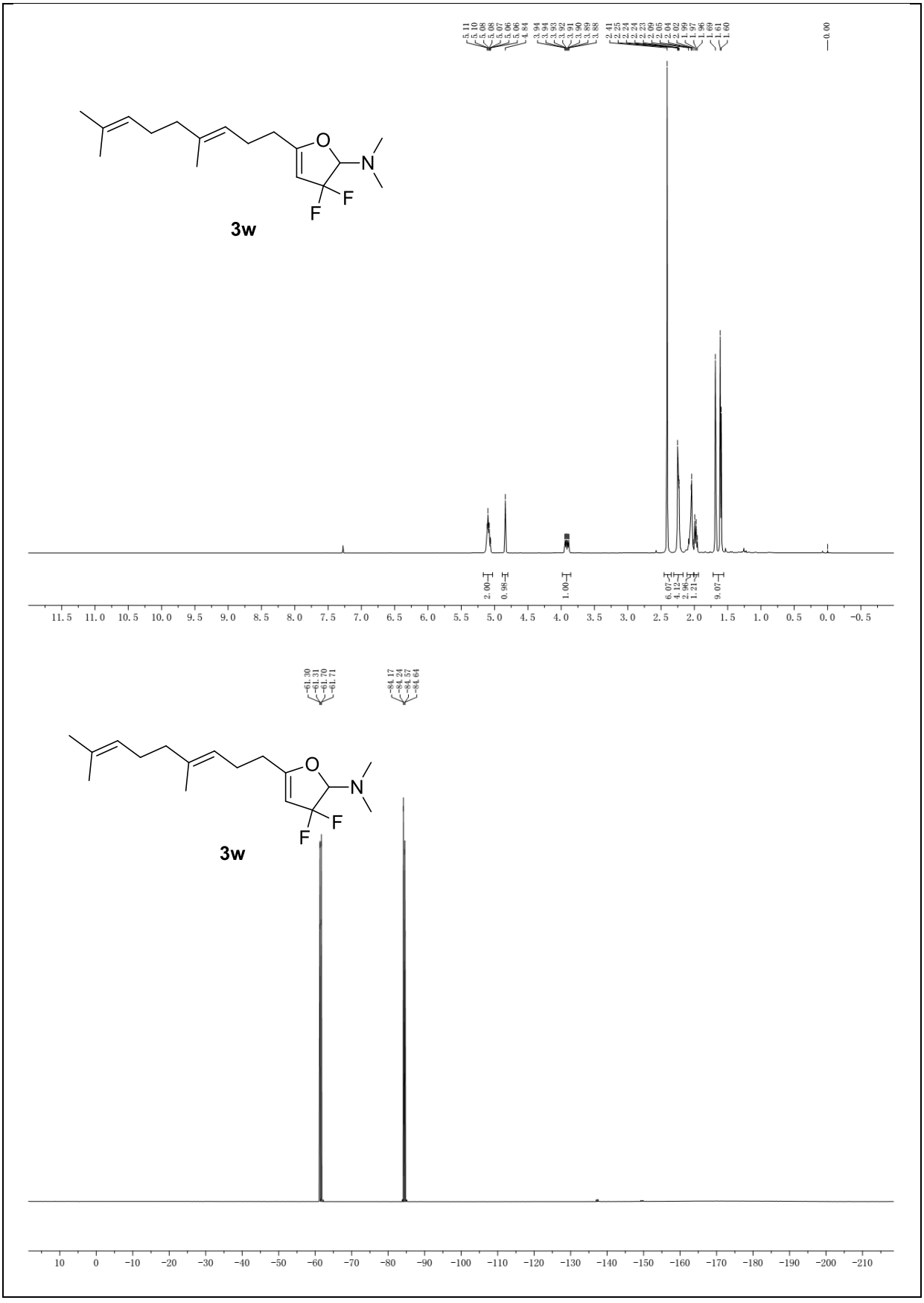
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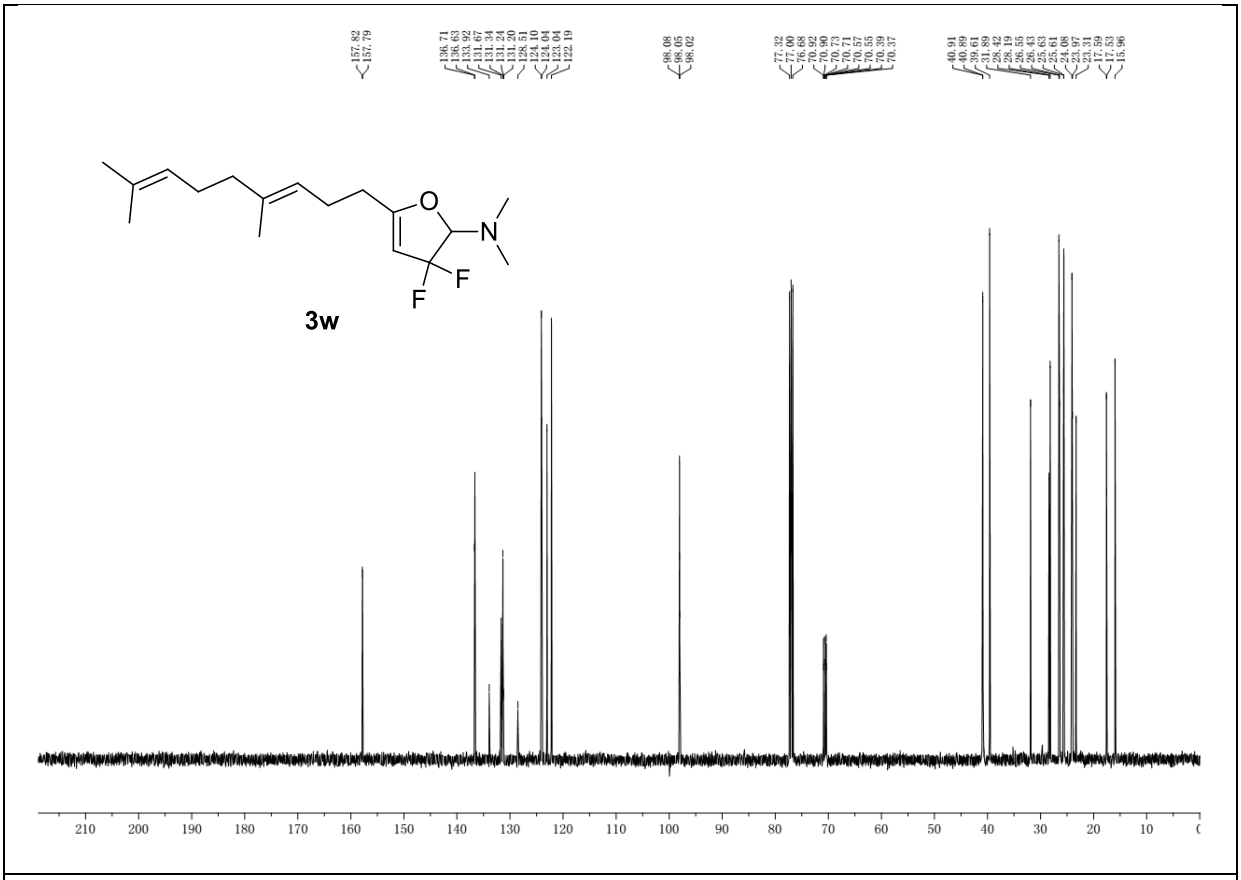
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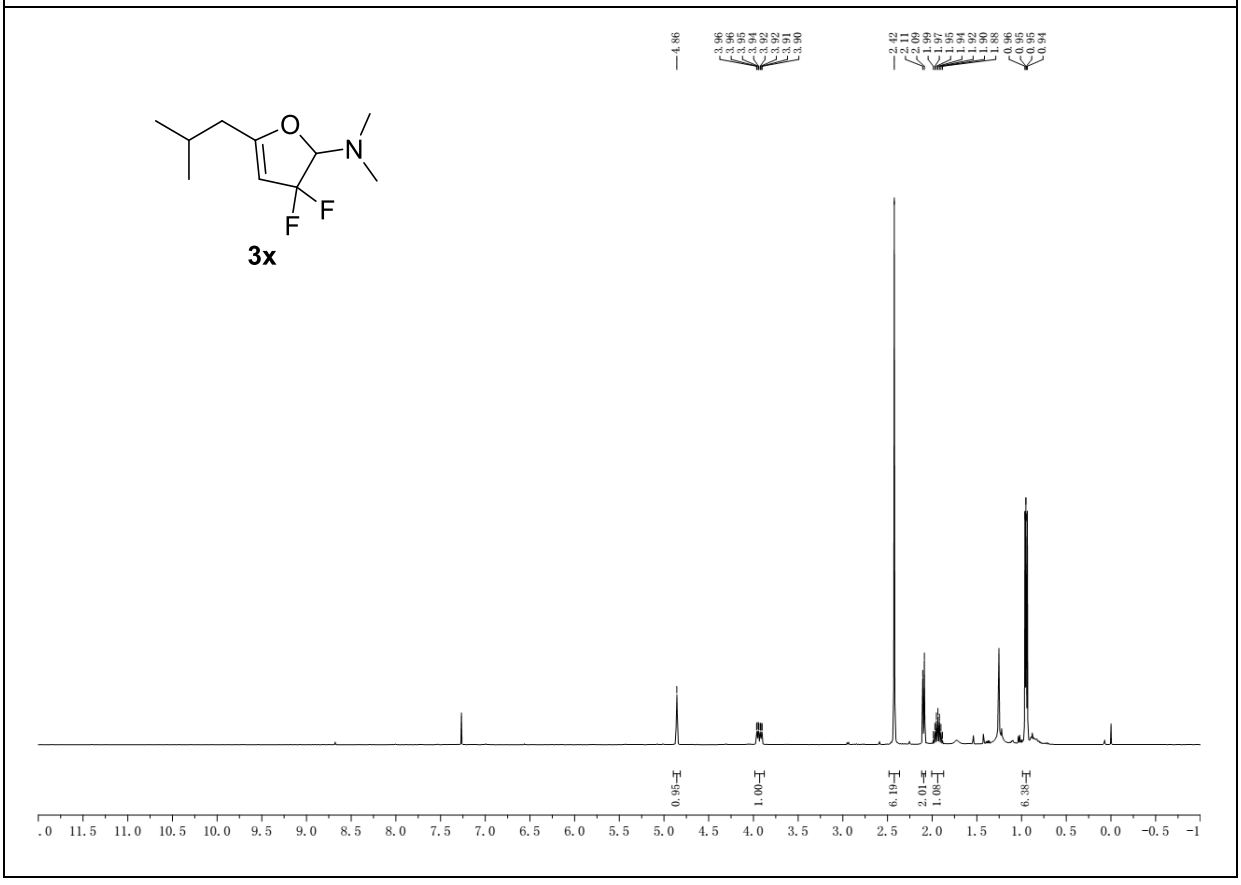
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1.08
6.38
.0
11.5
11.0
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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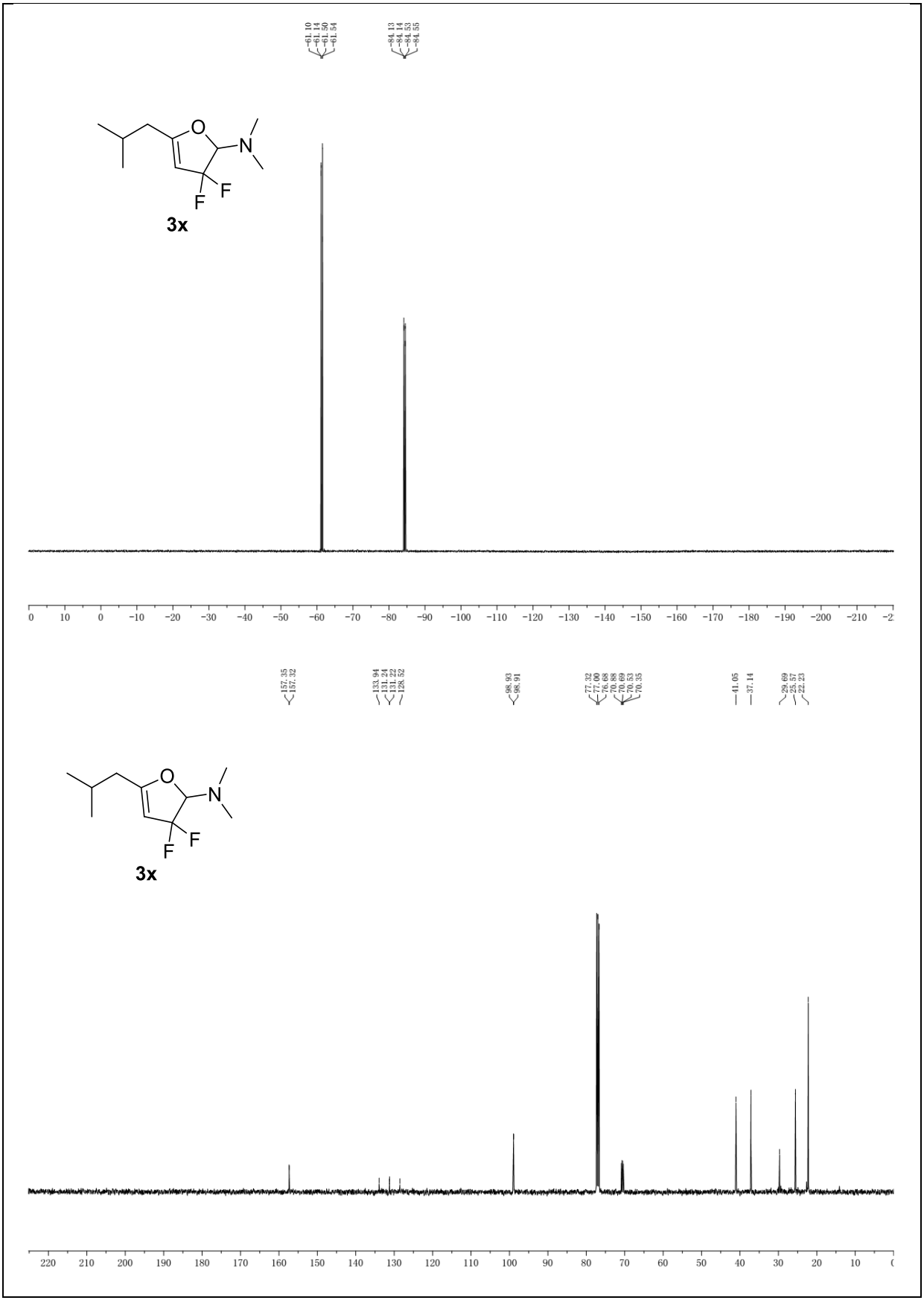
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77.00
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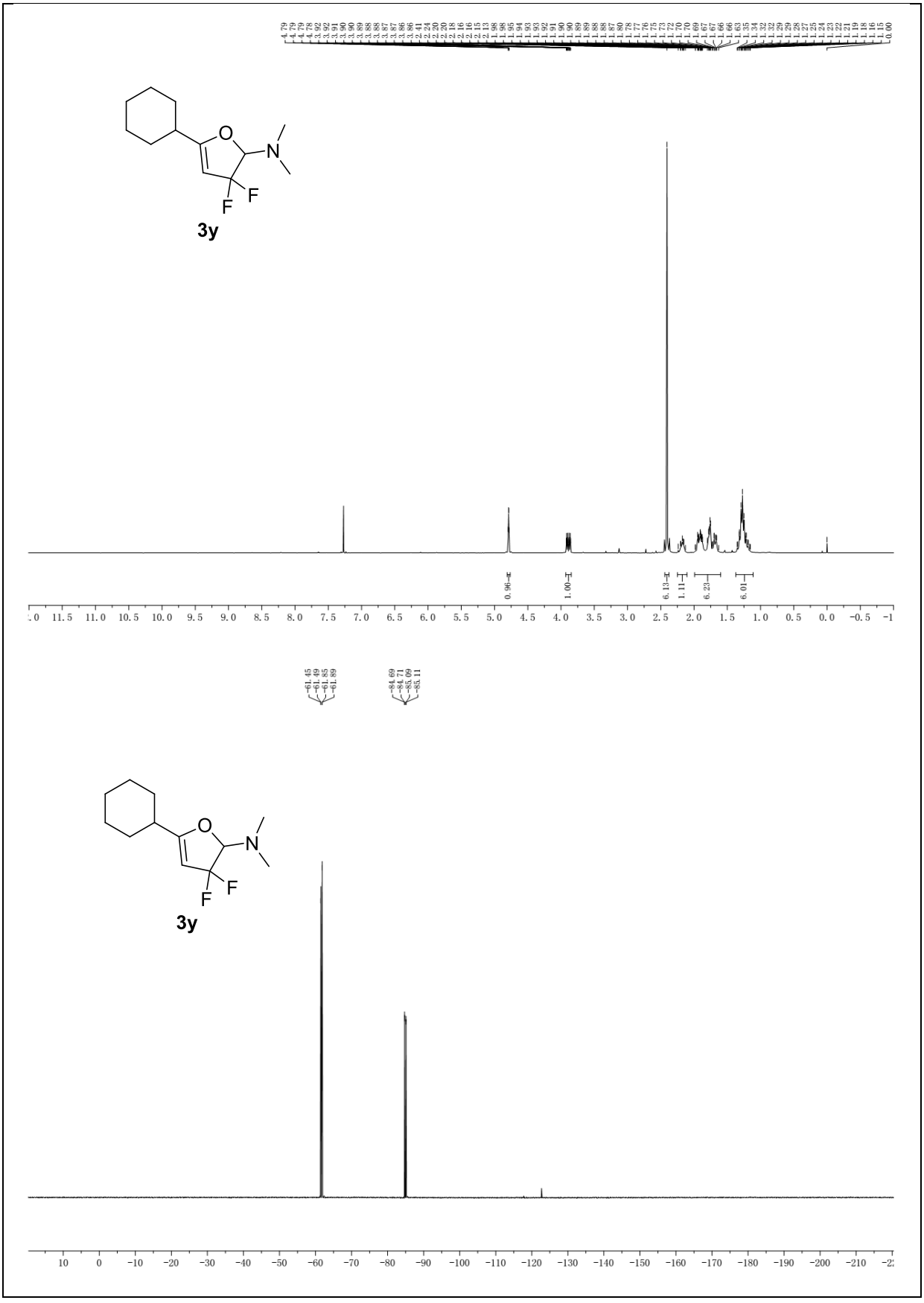
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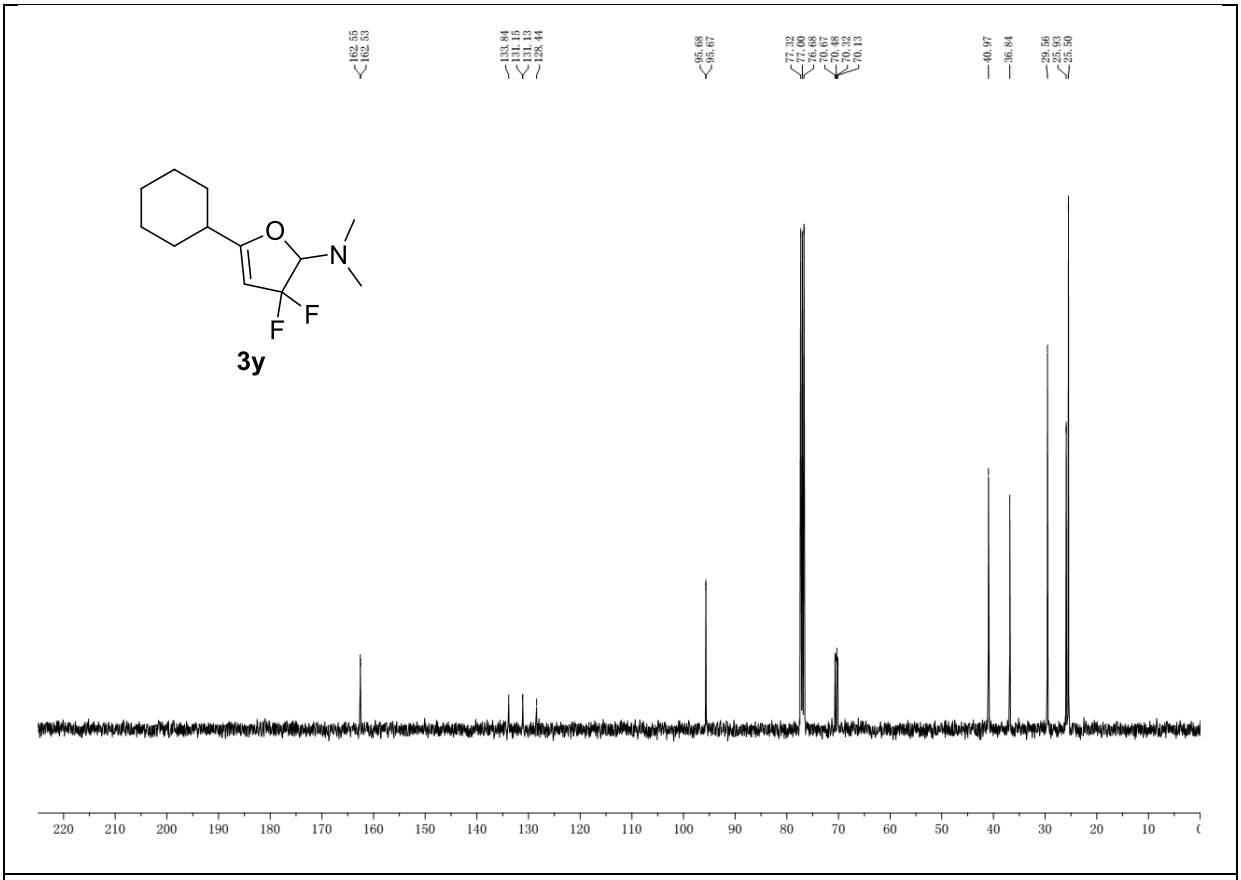
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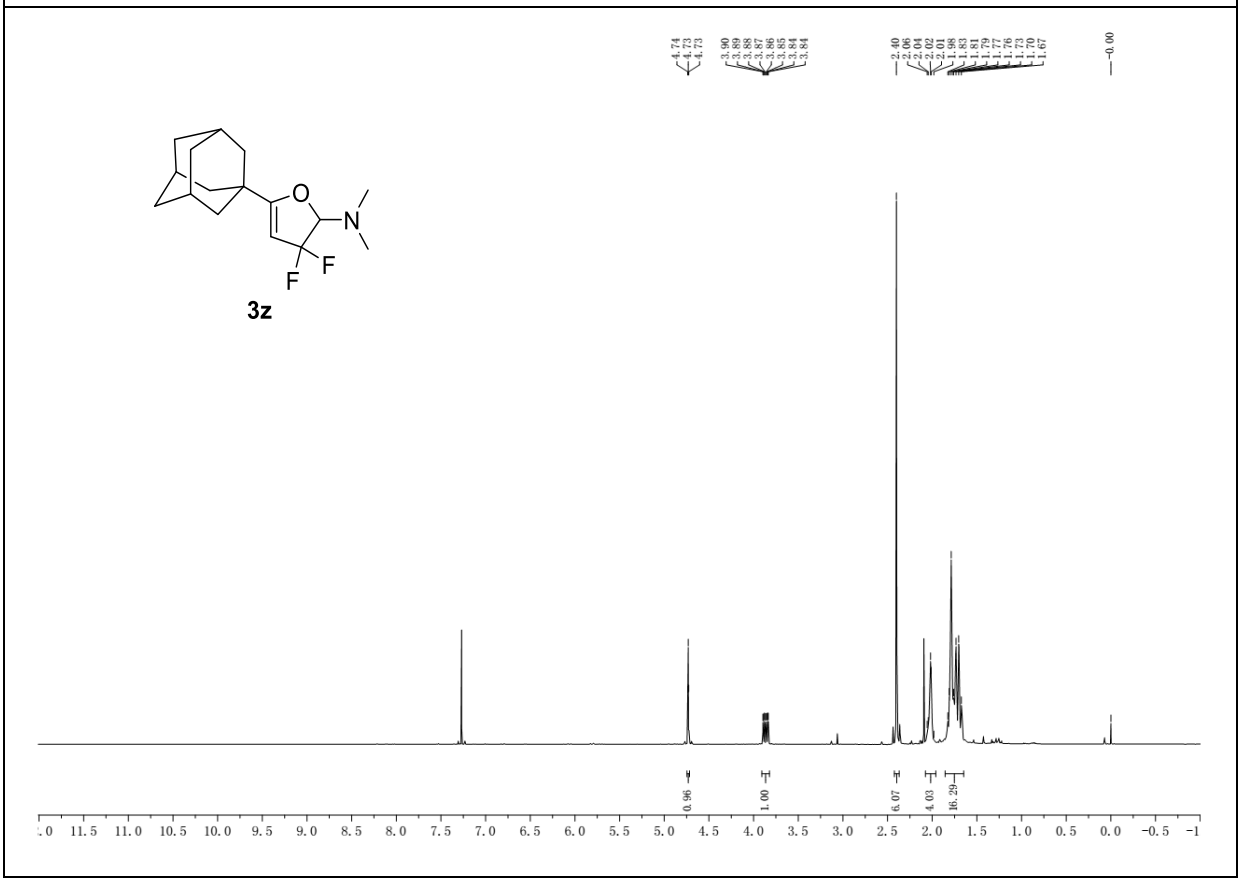
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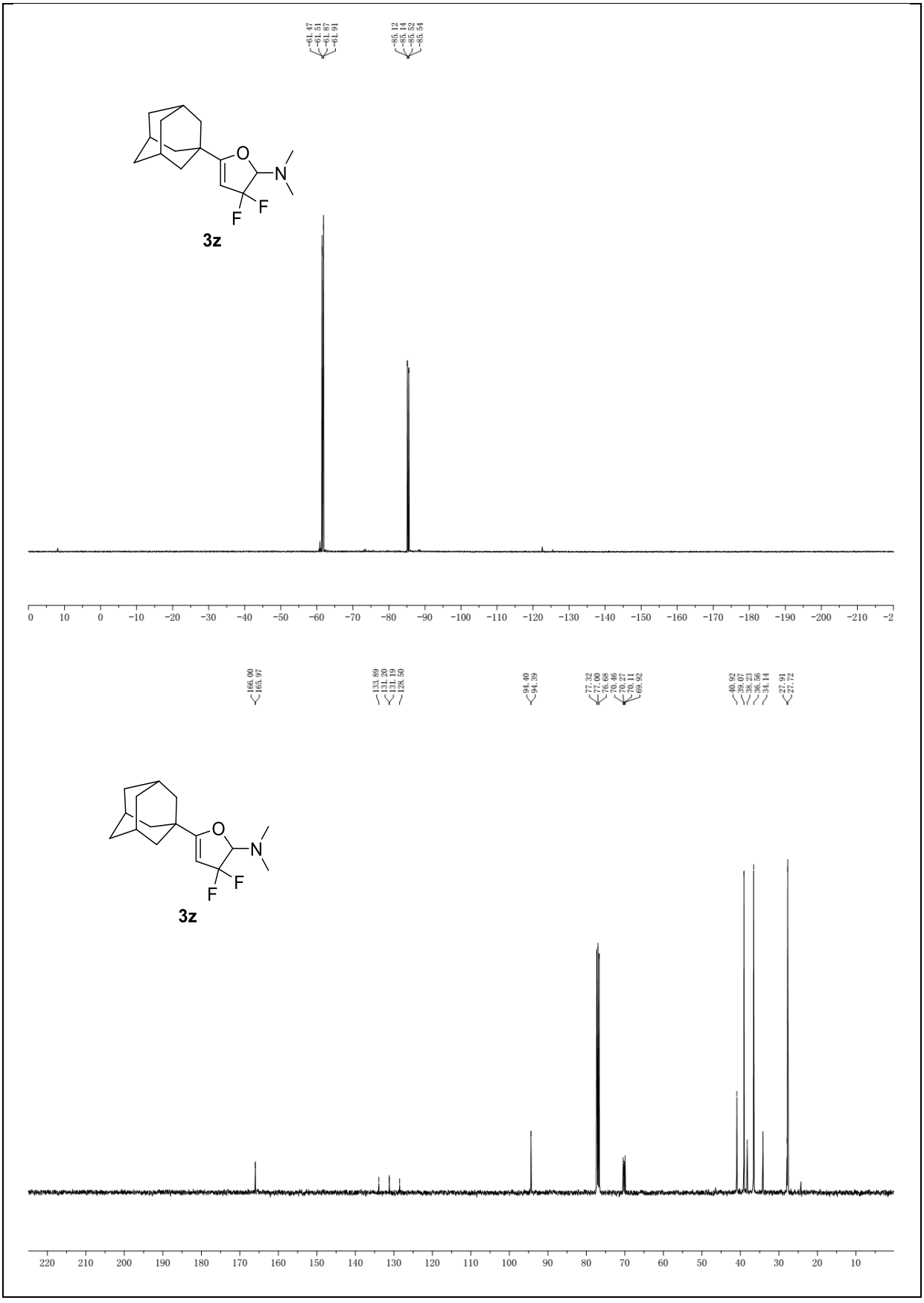
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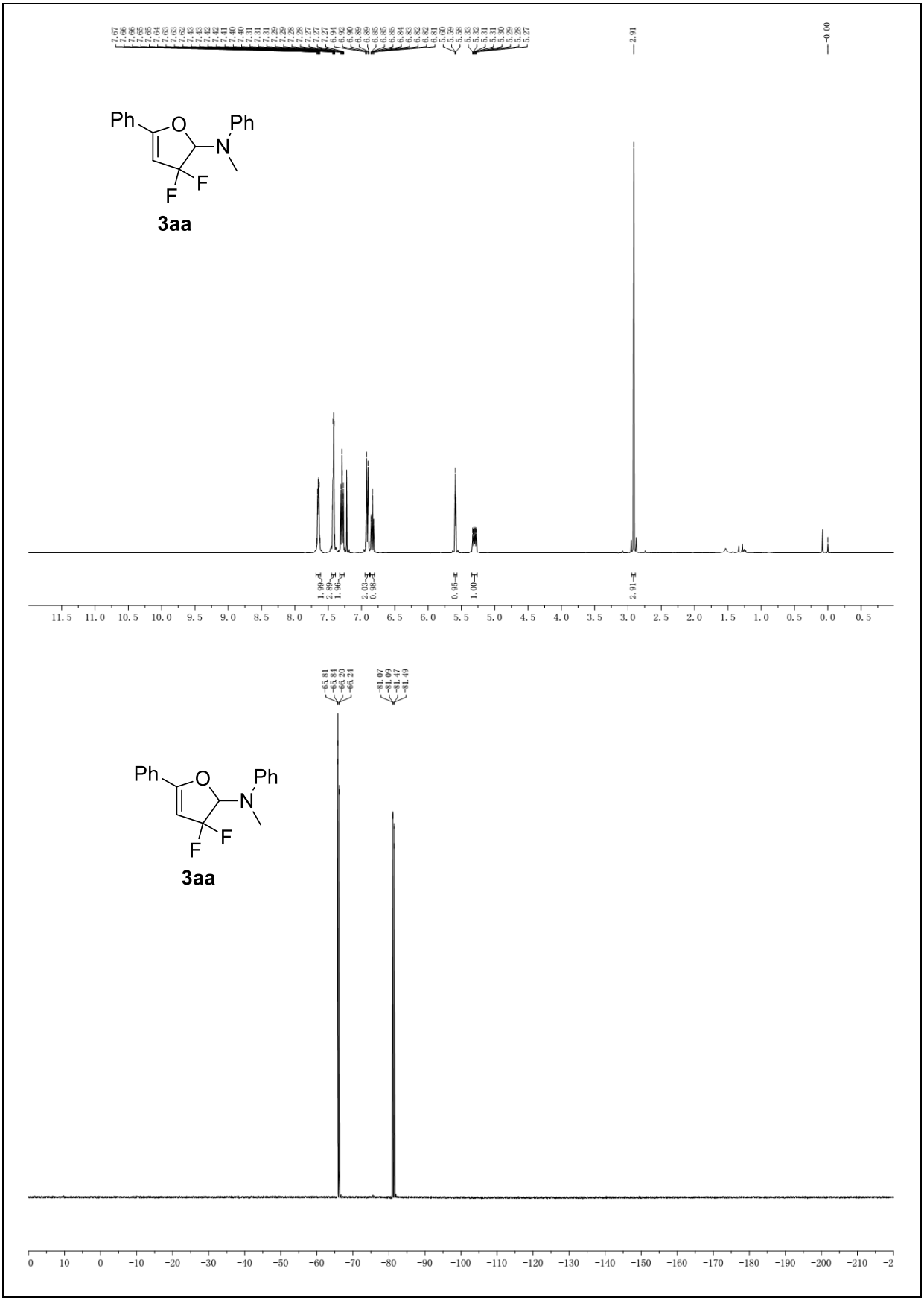
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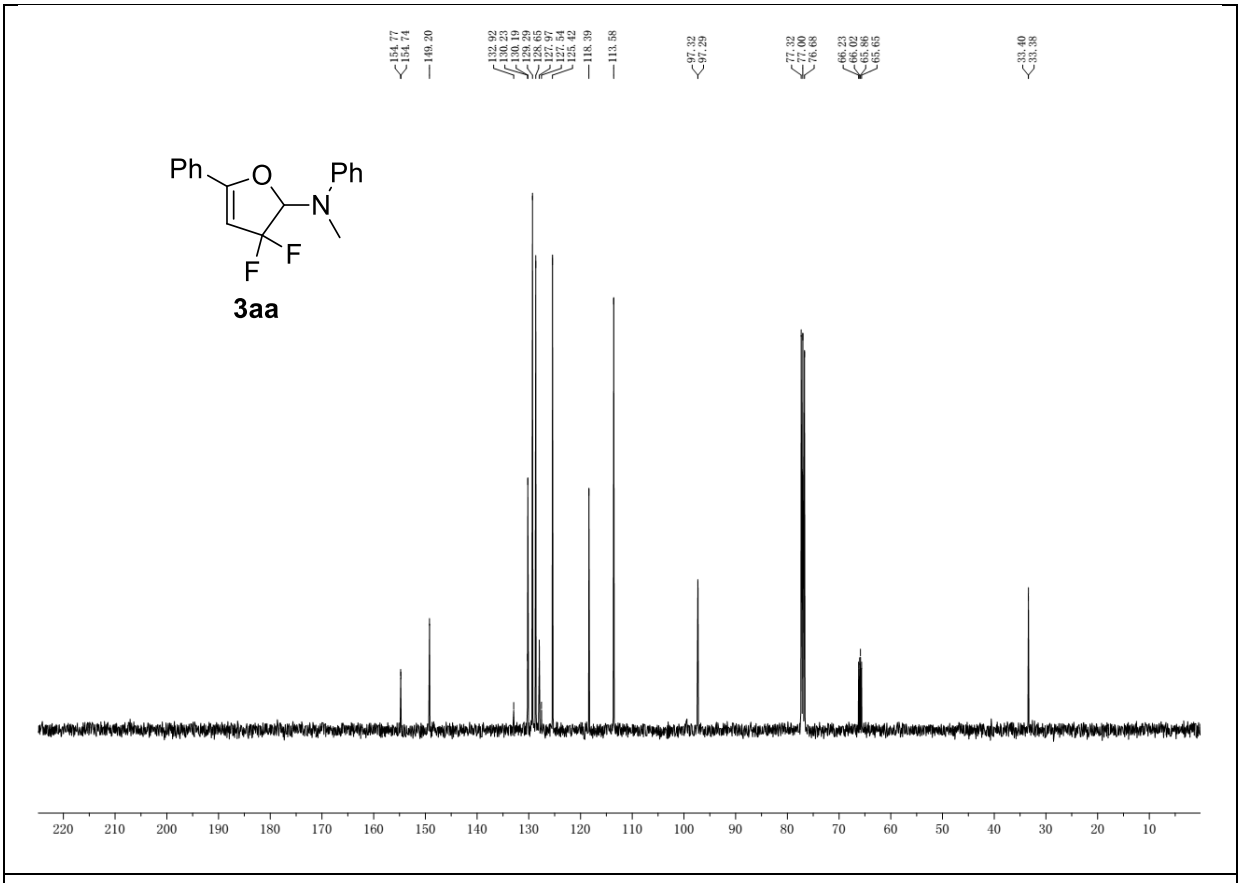
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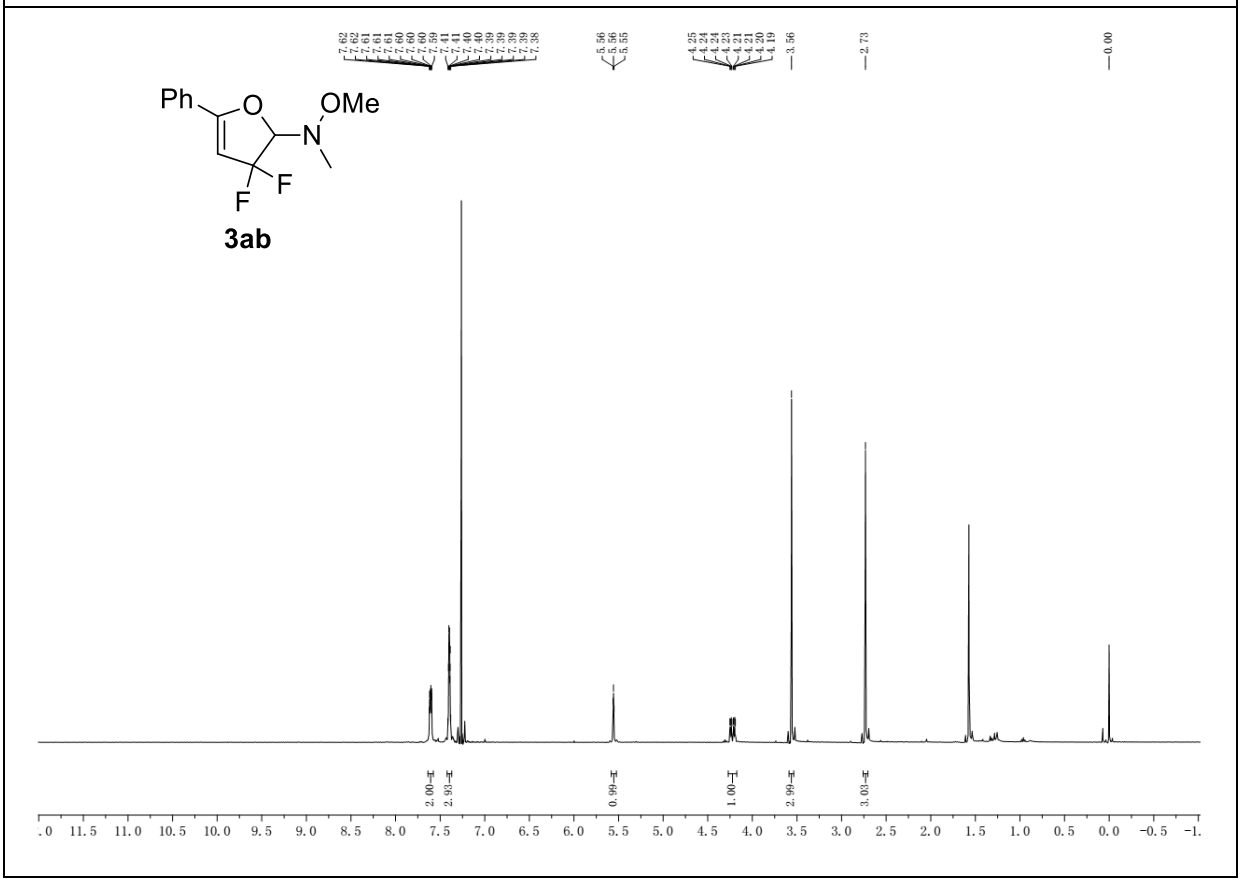
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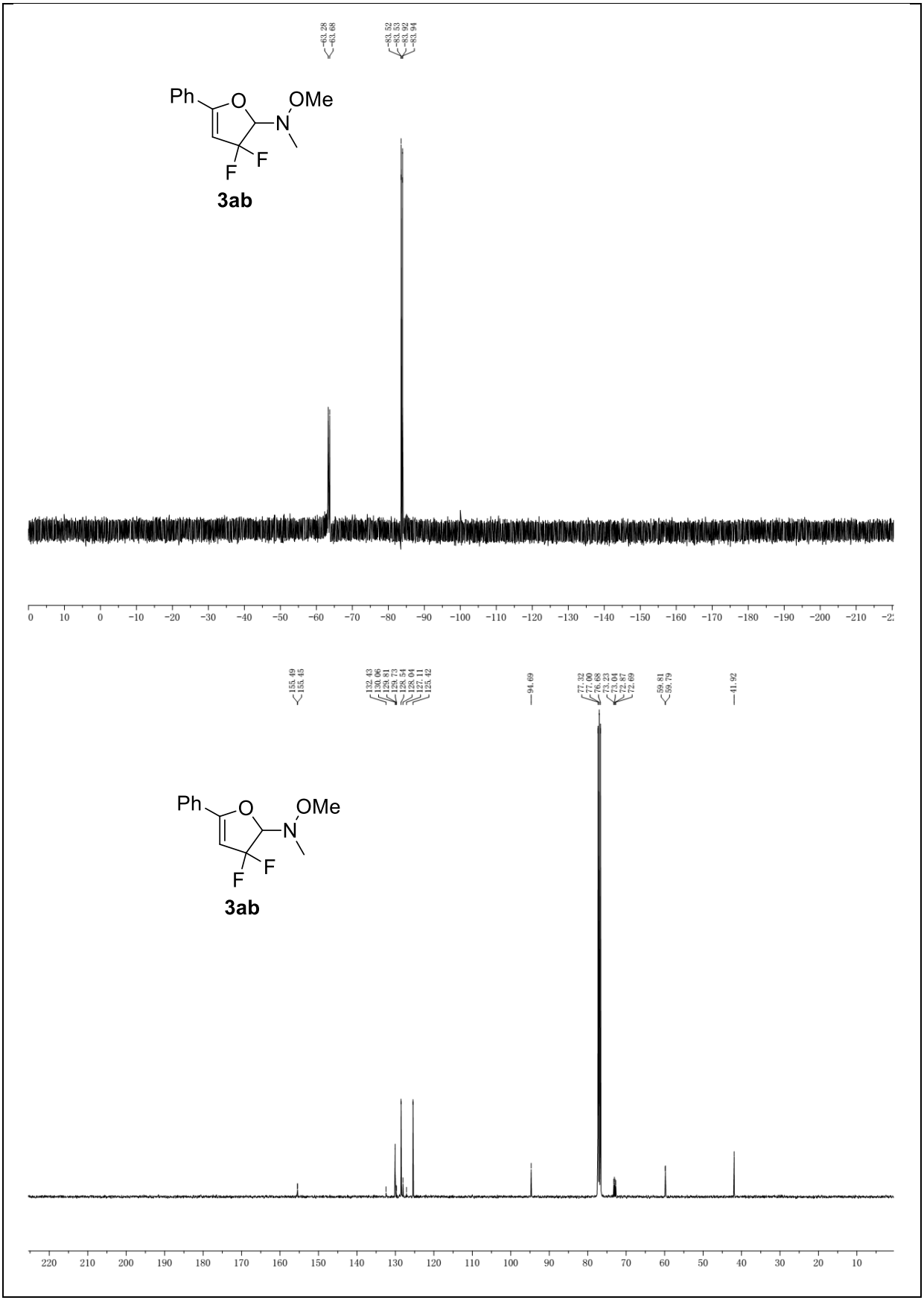
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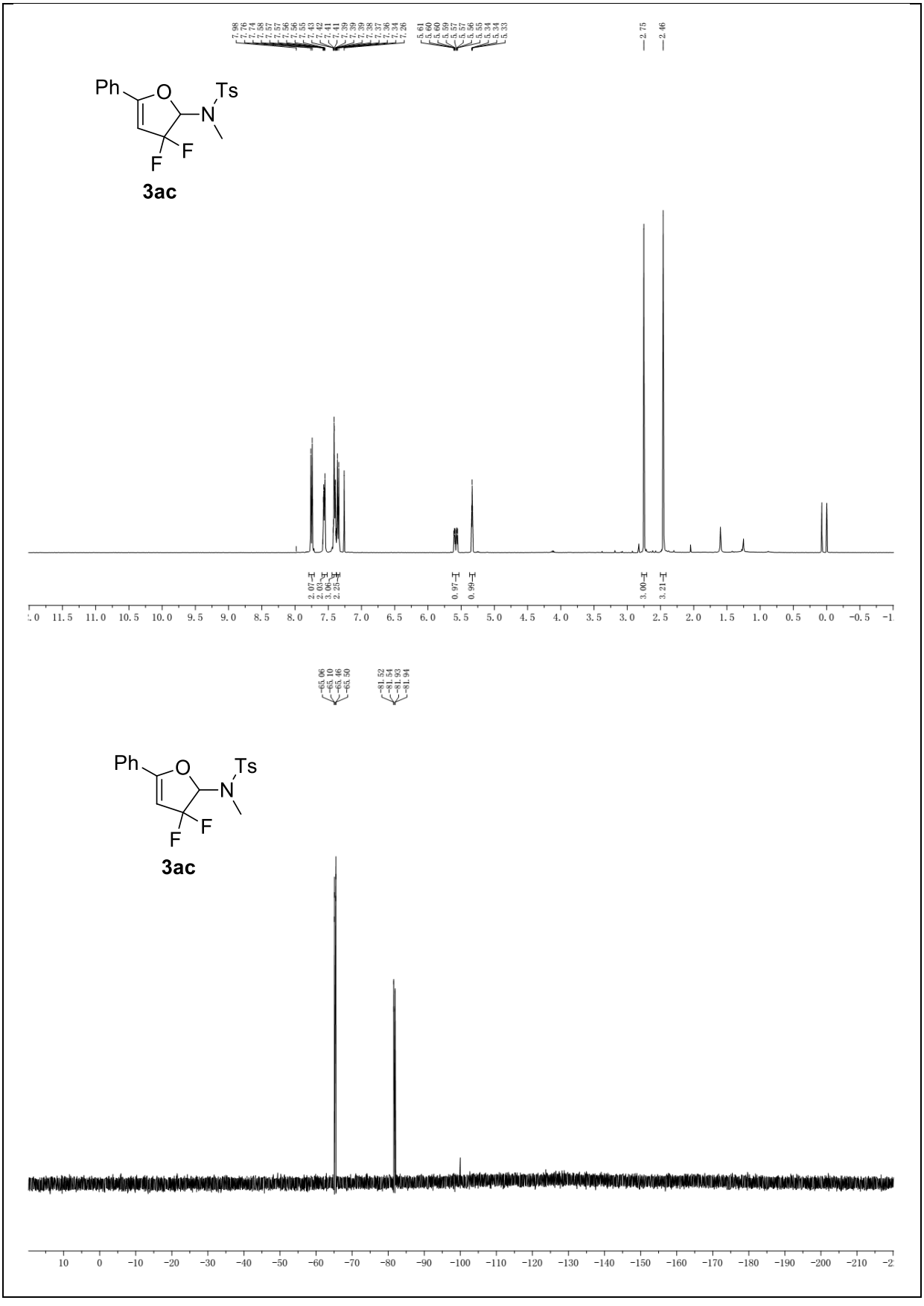
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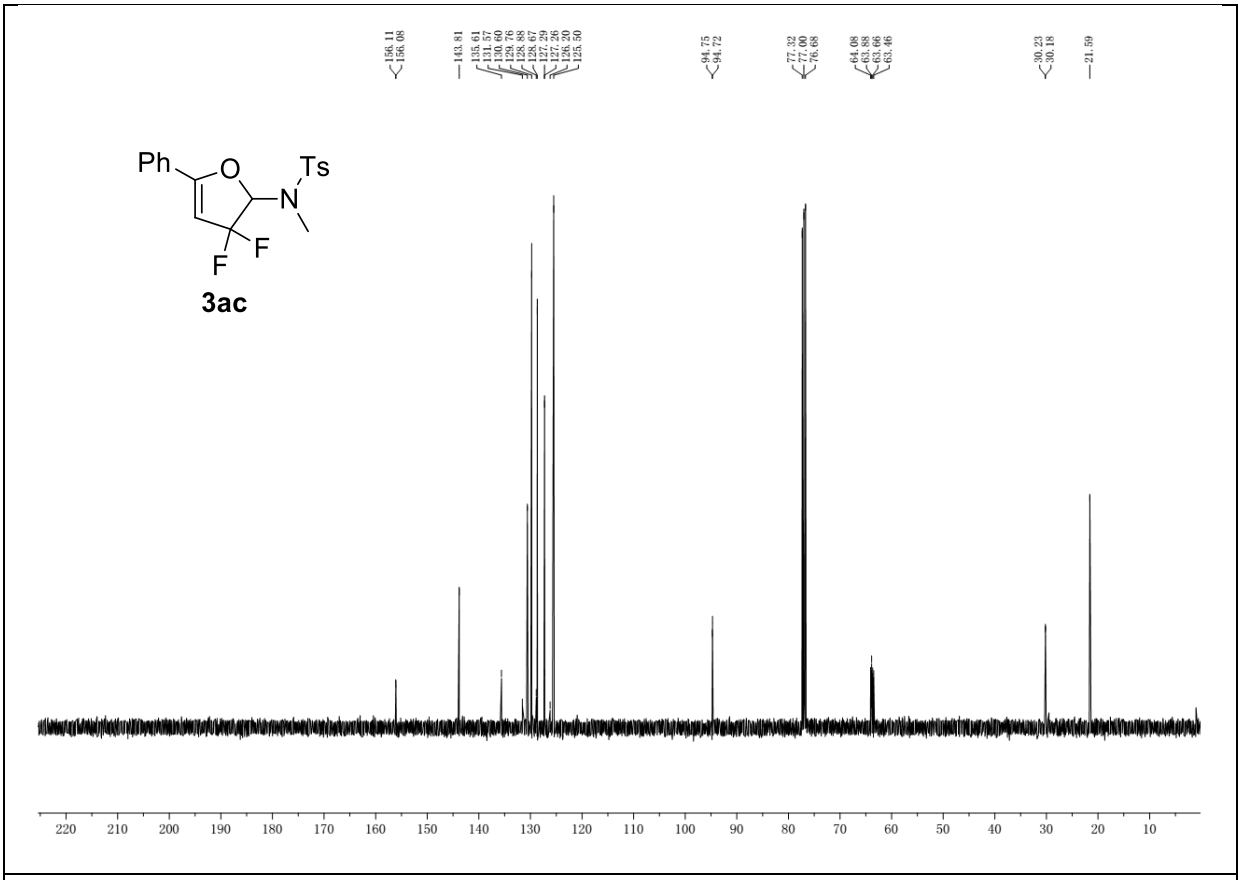
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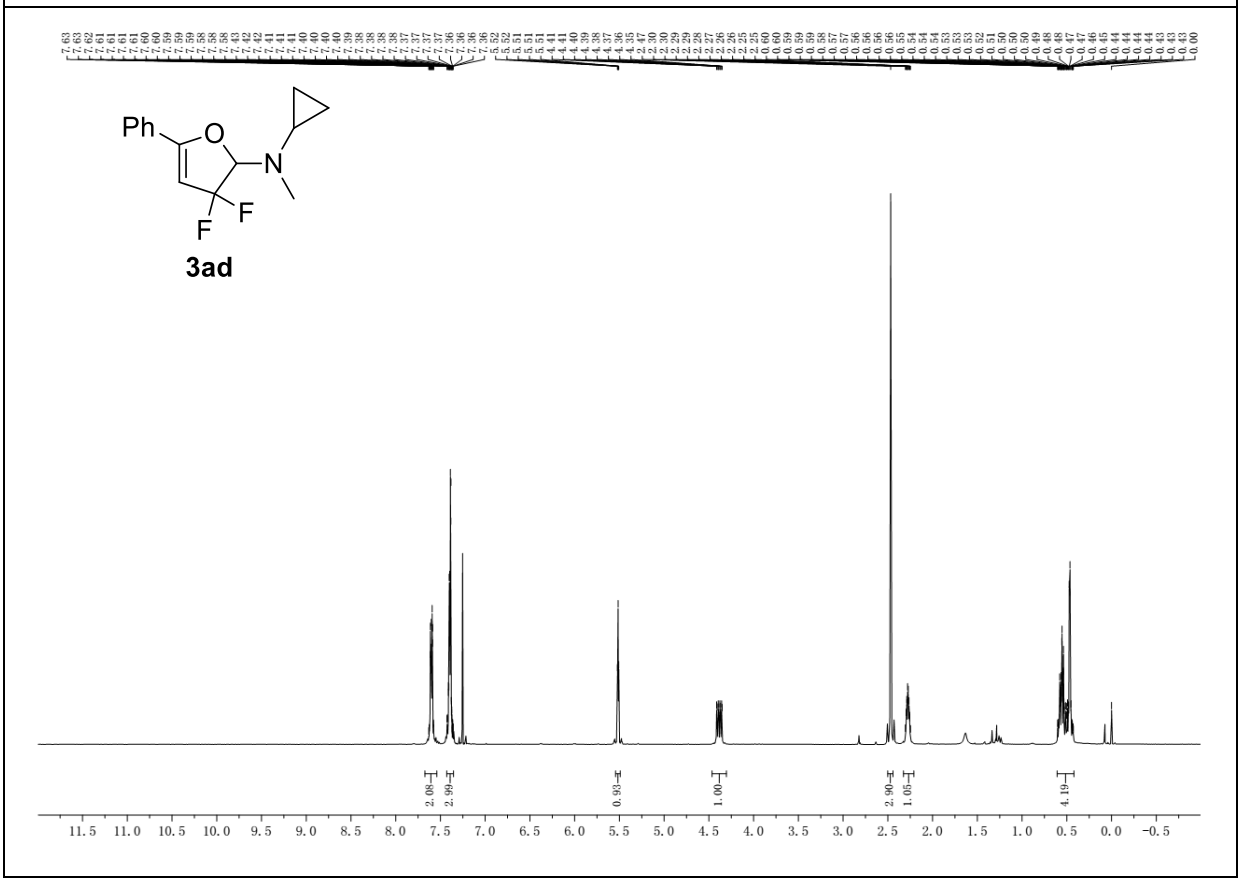
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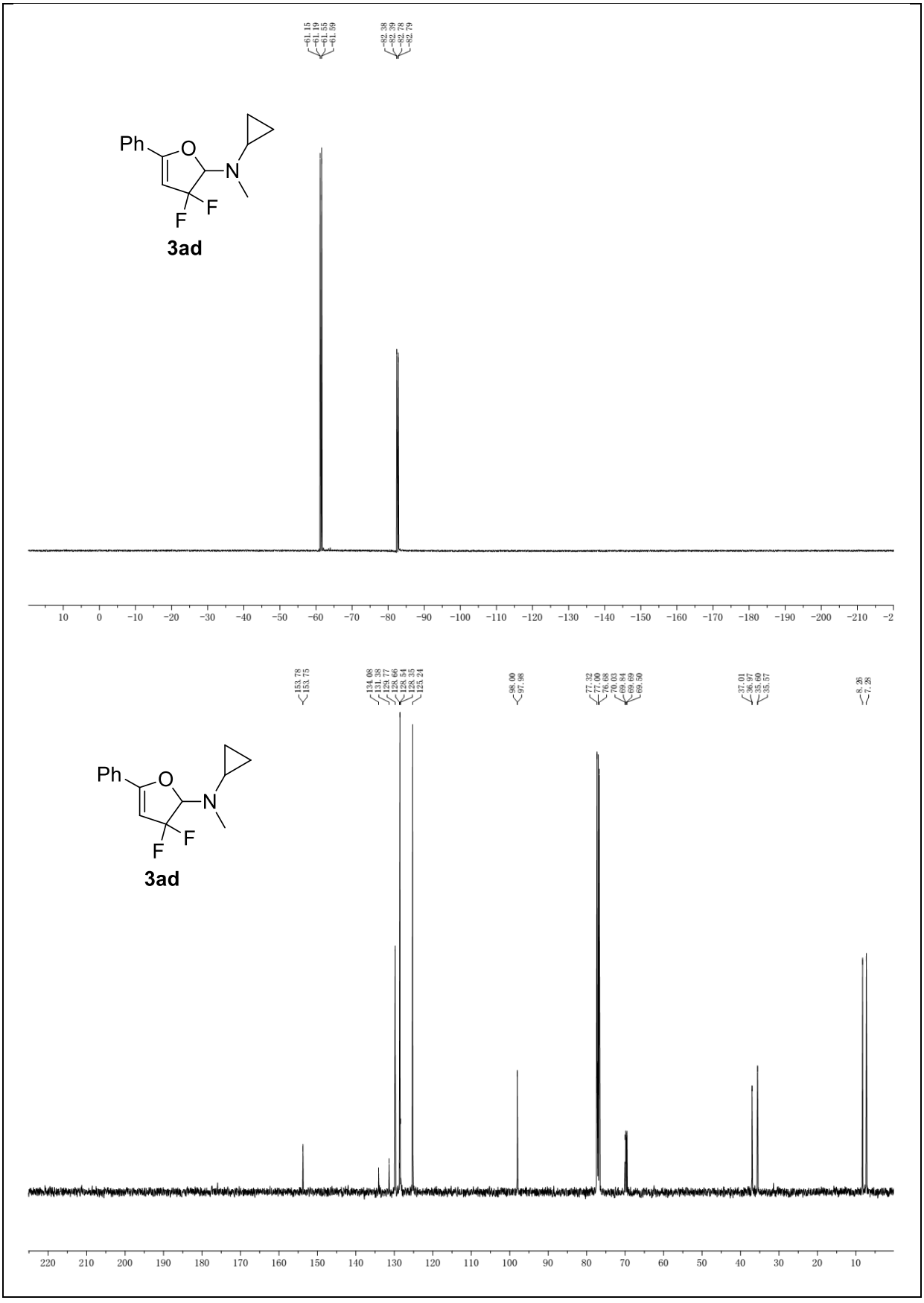
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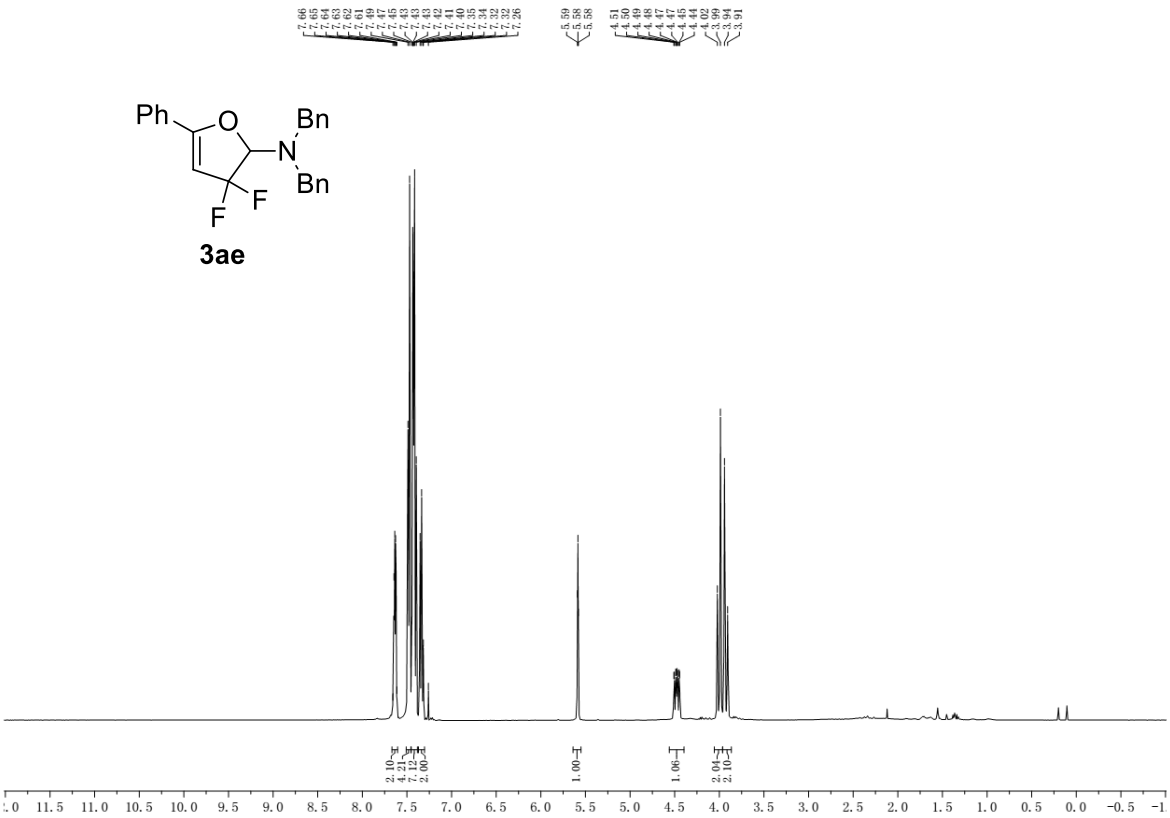
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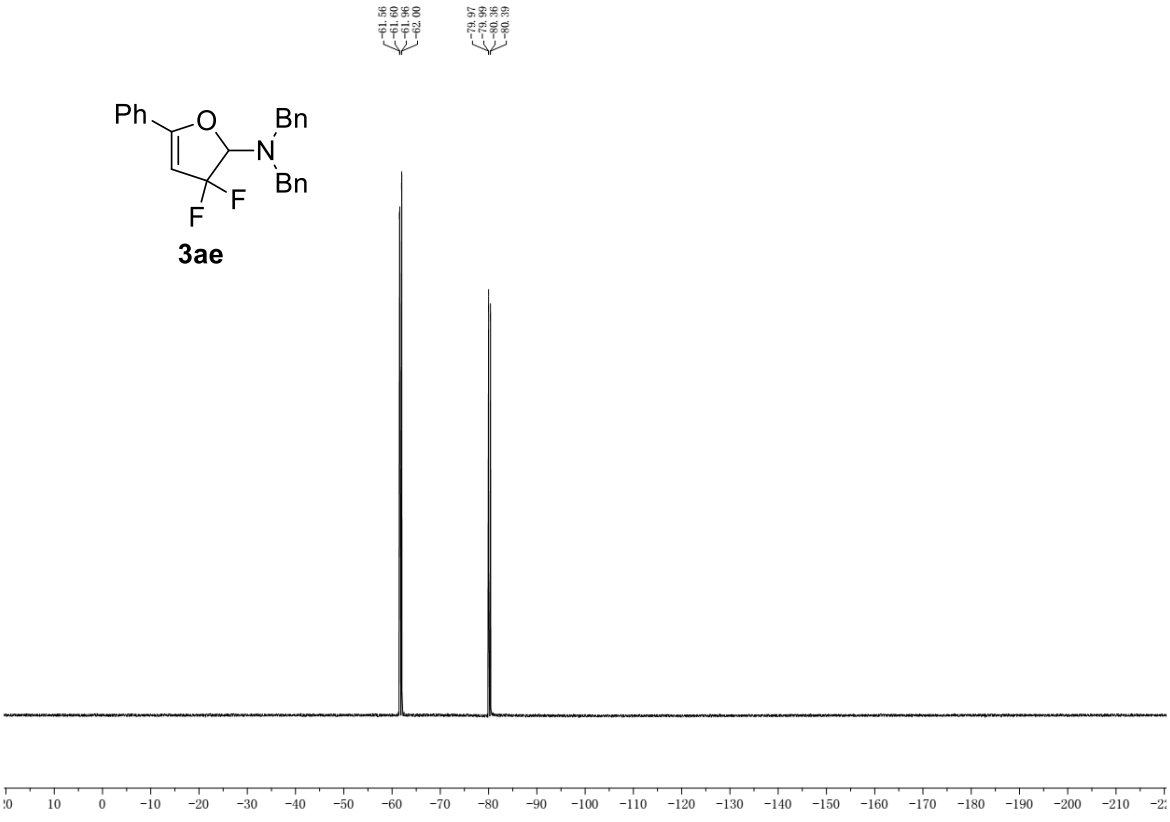
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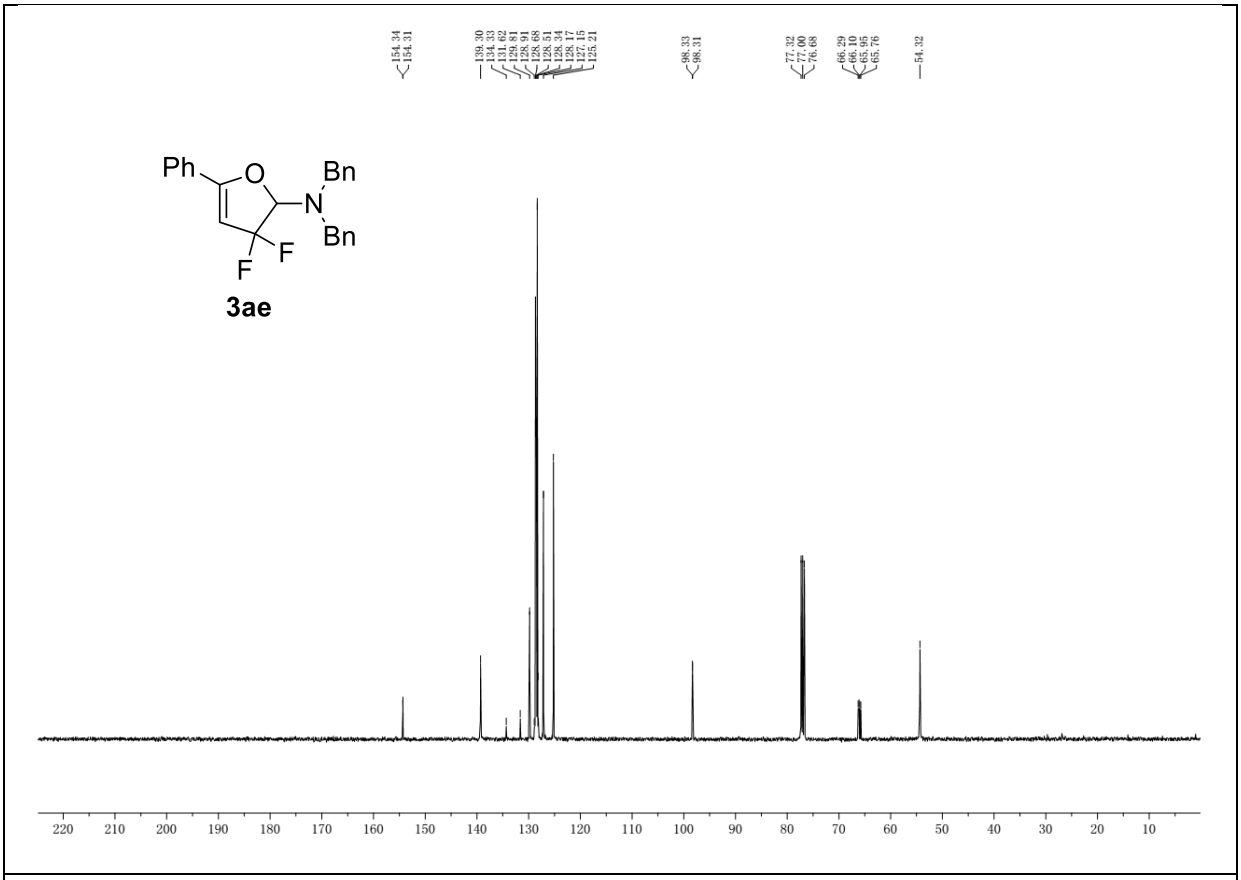
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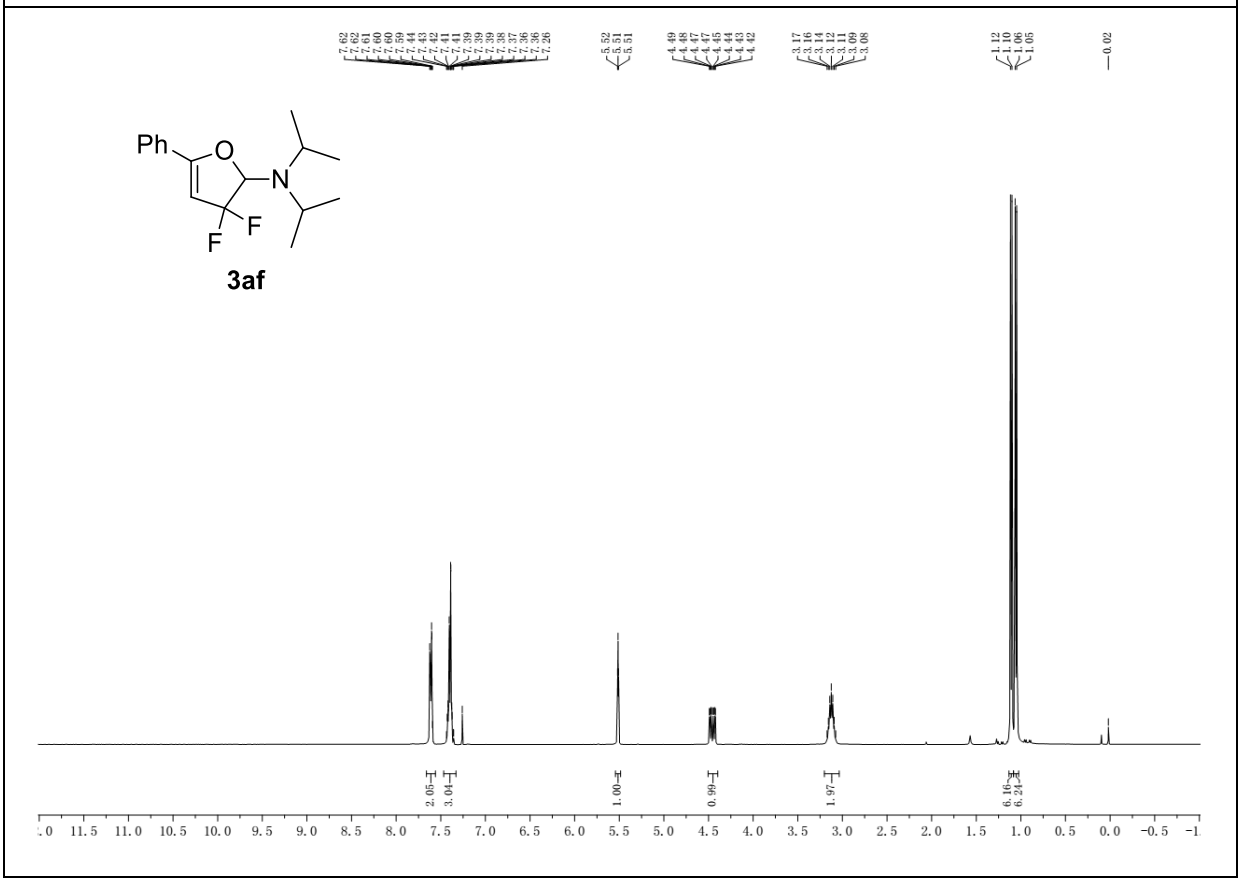
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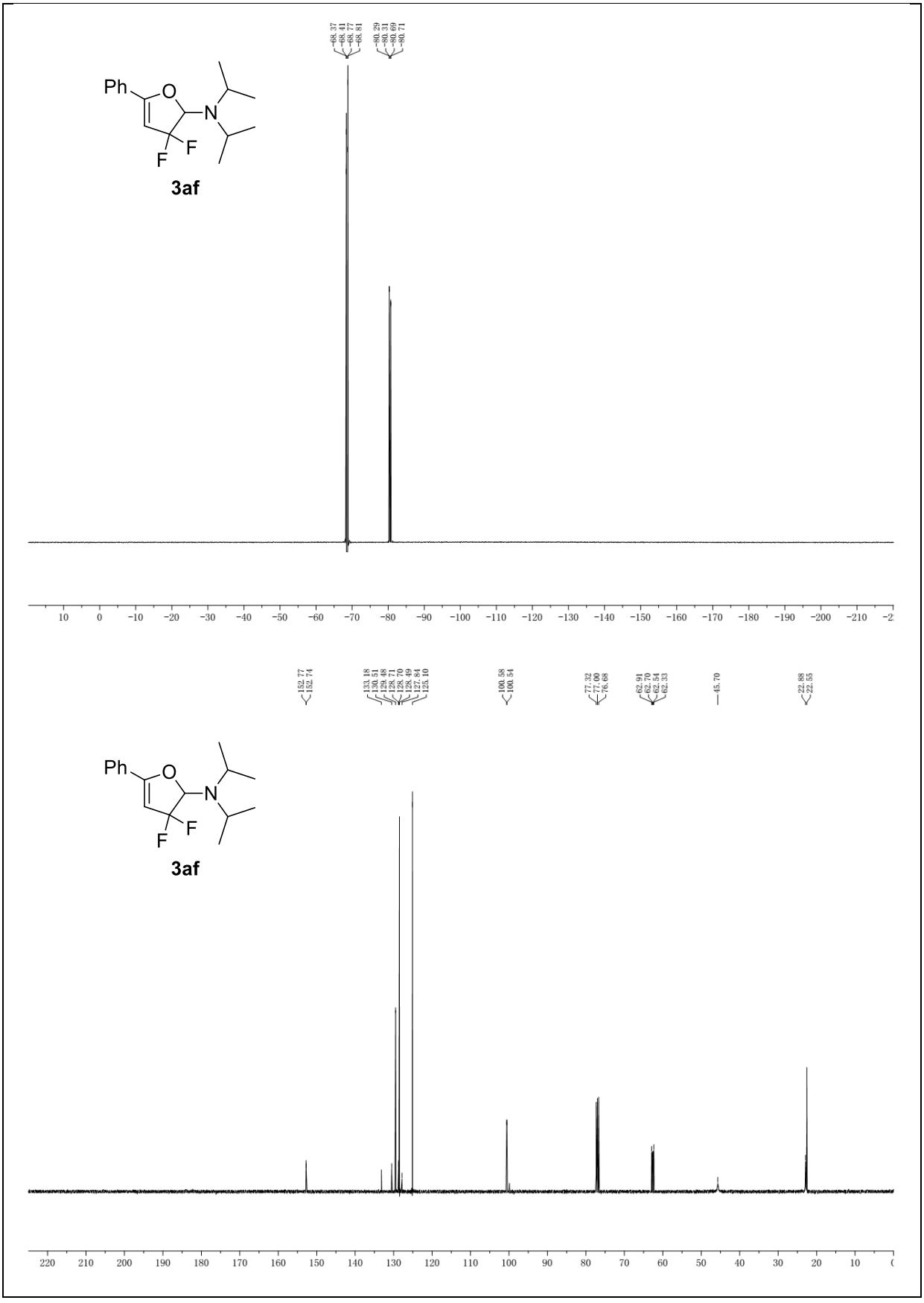
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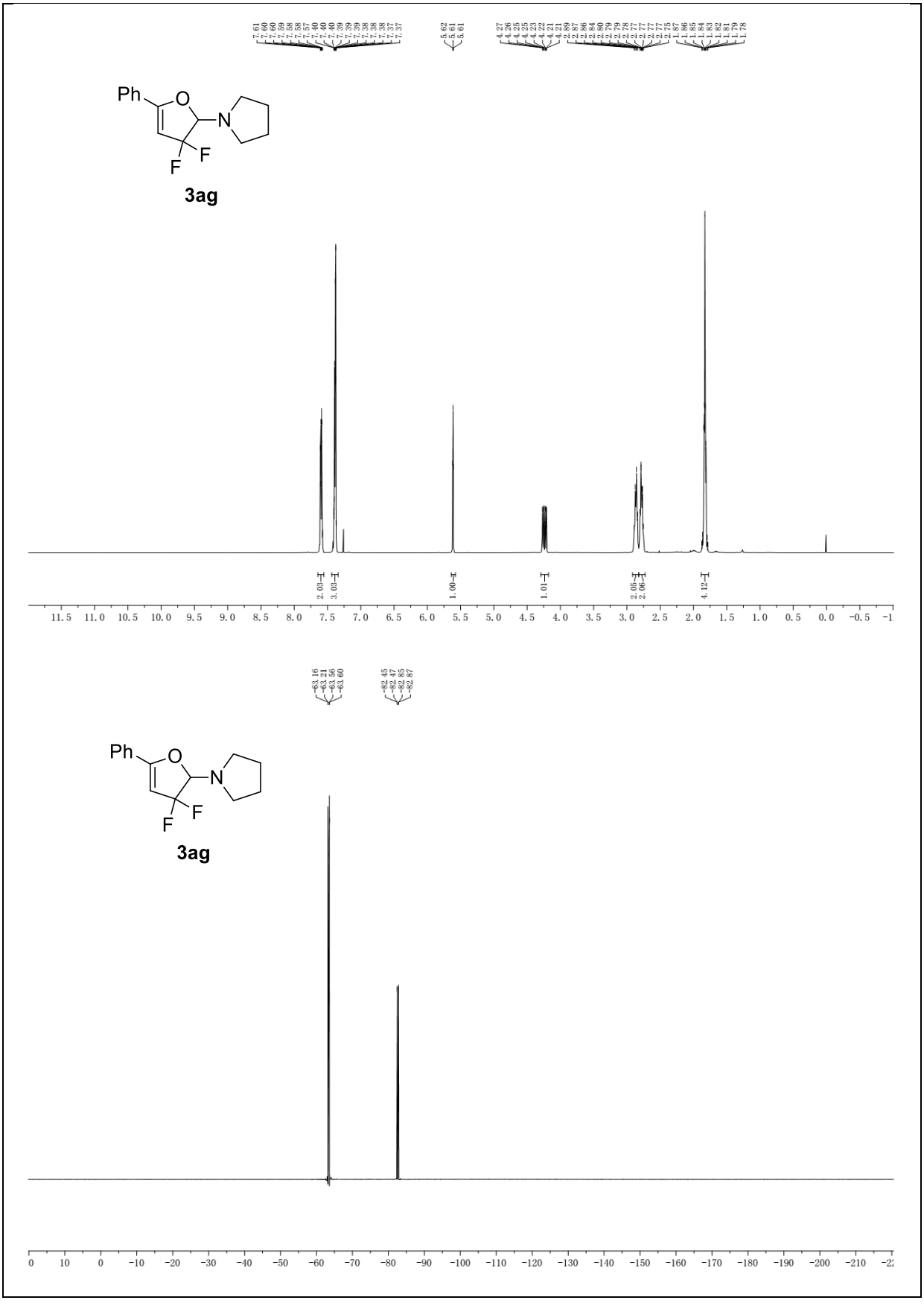
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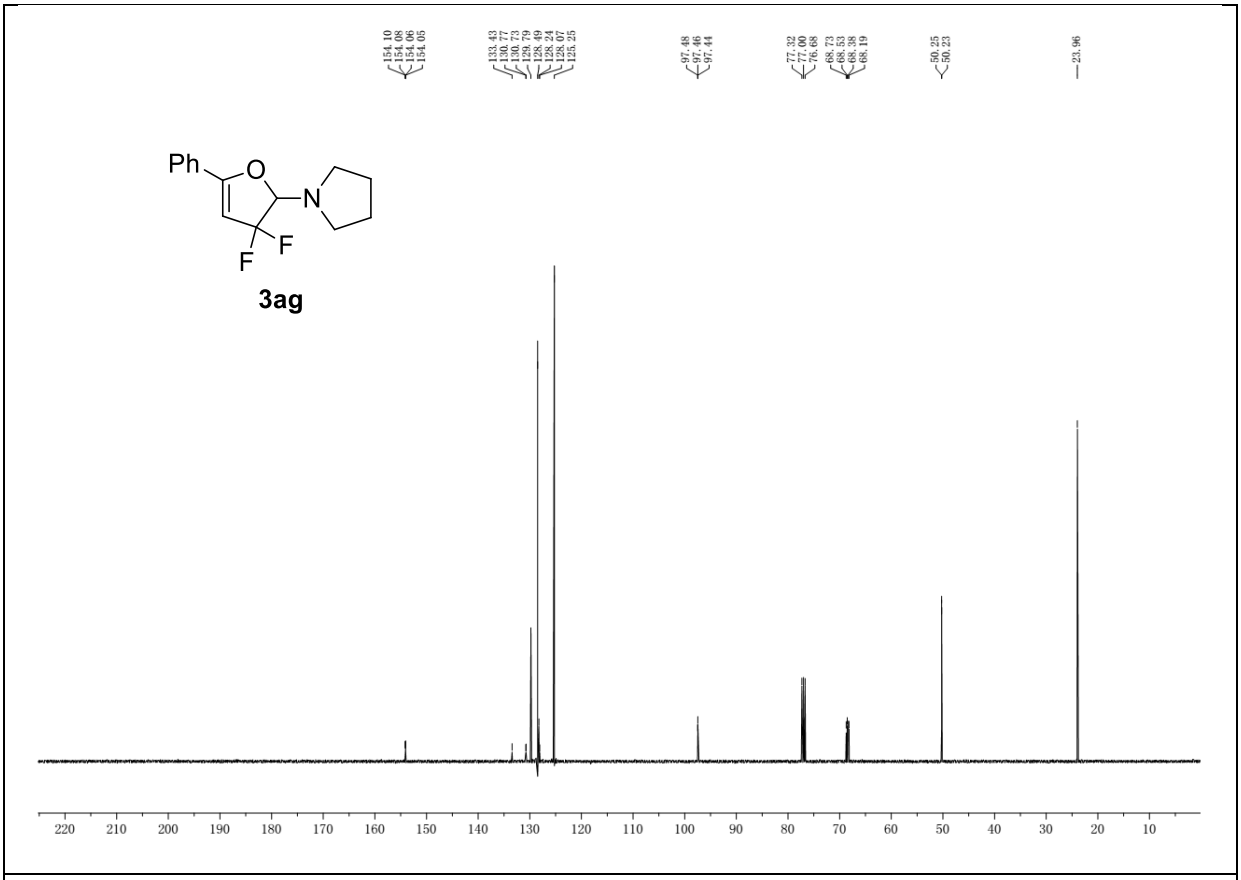
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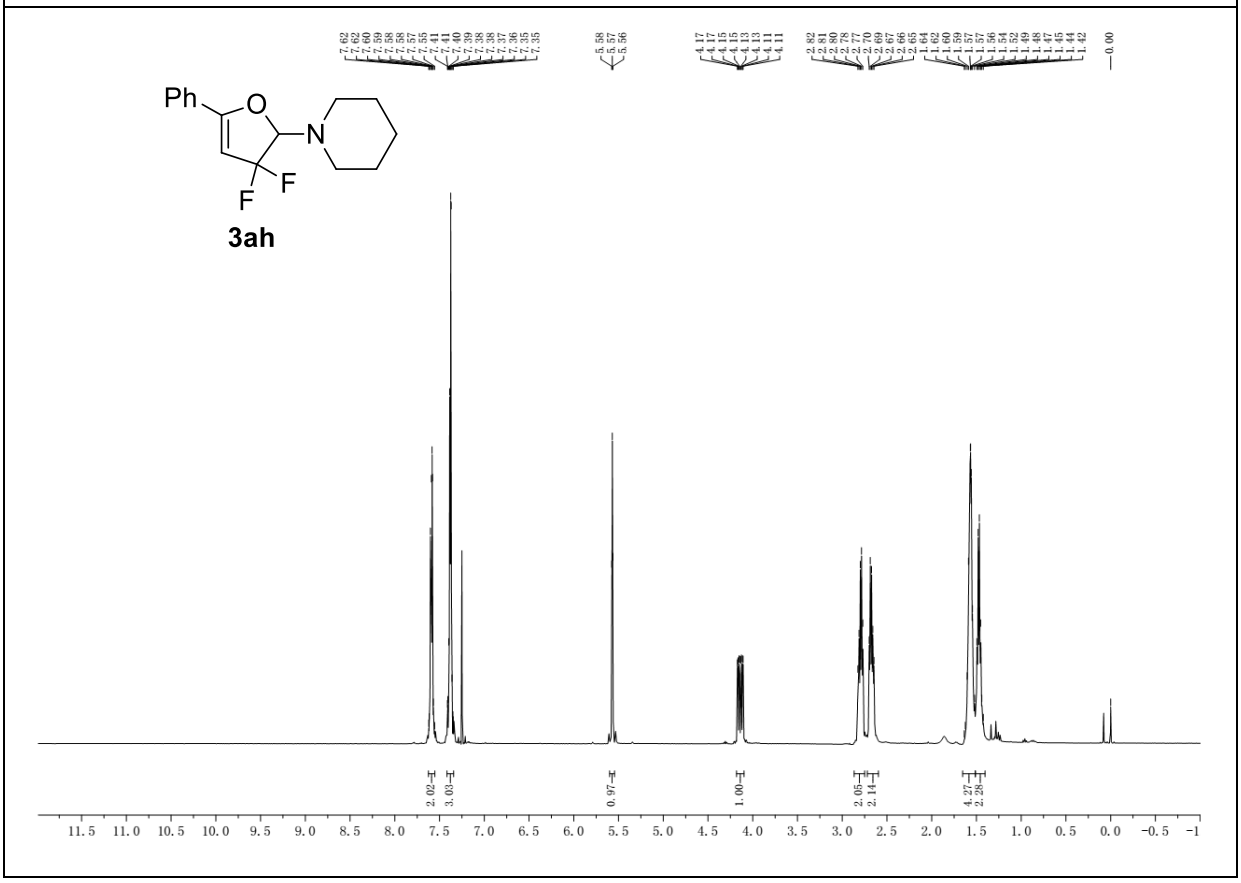
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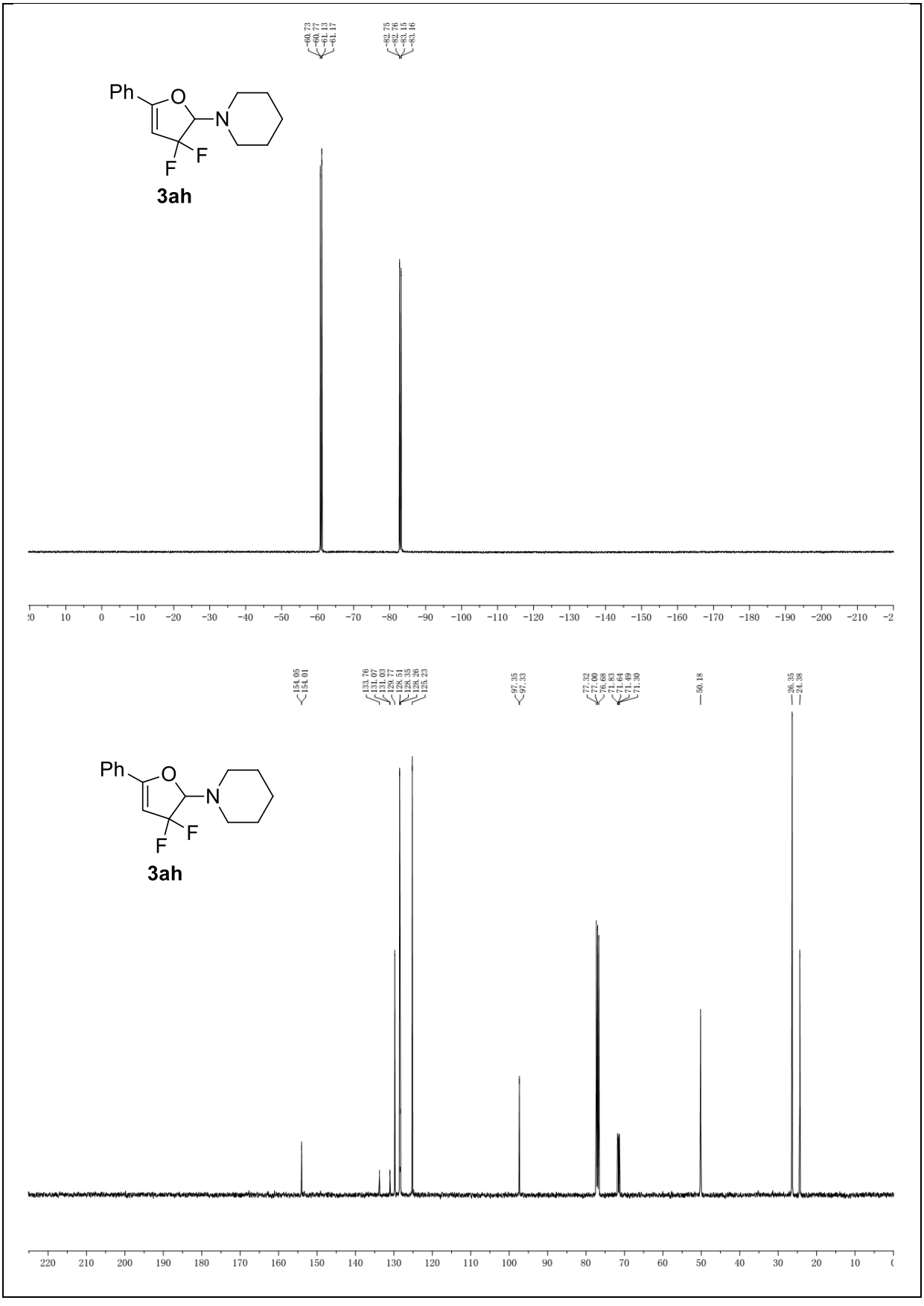
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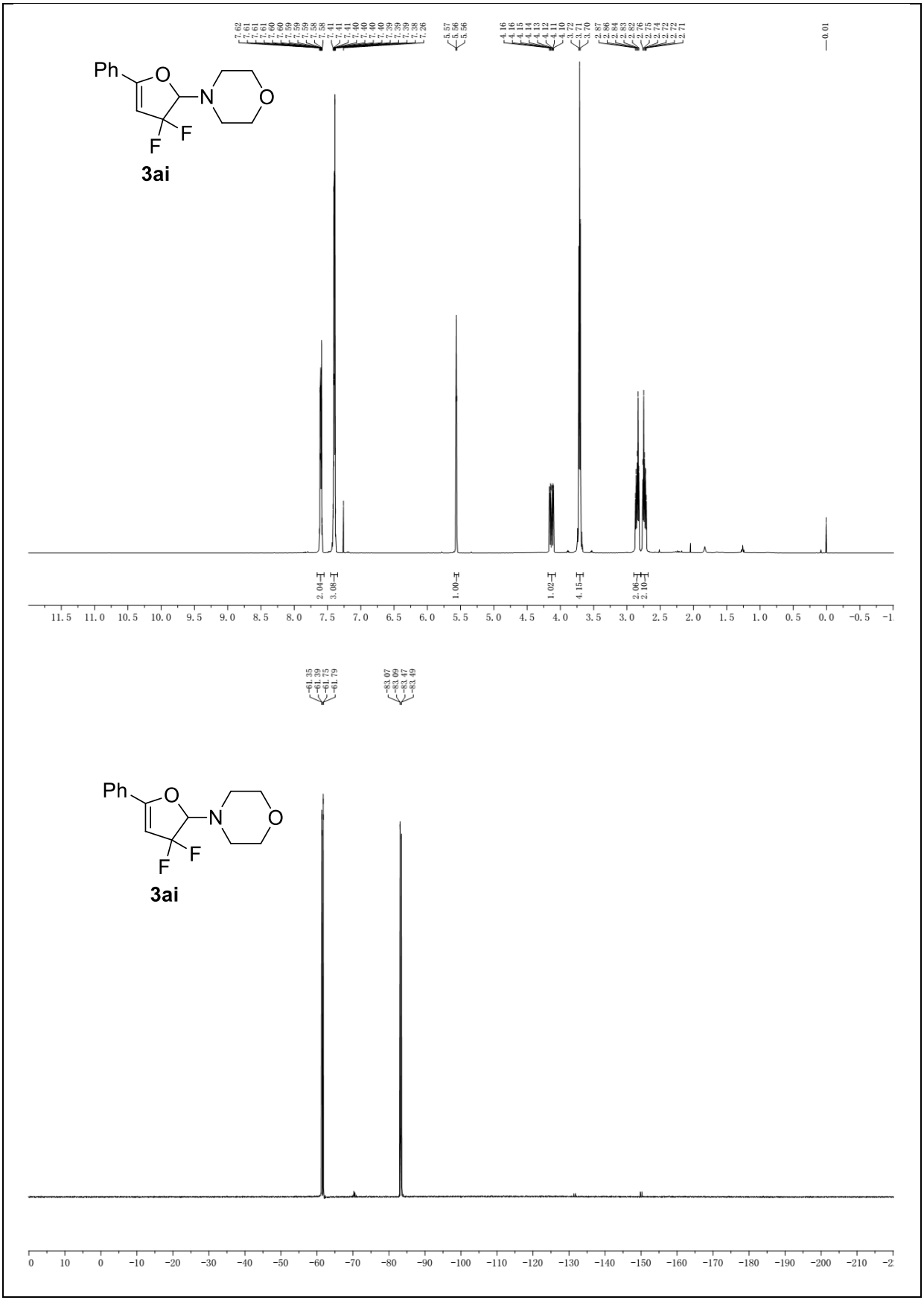
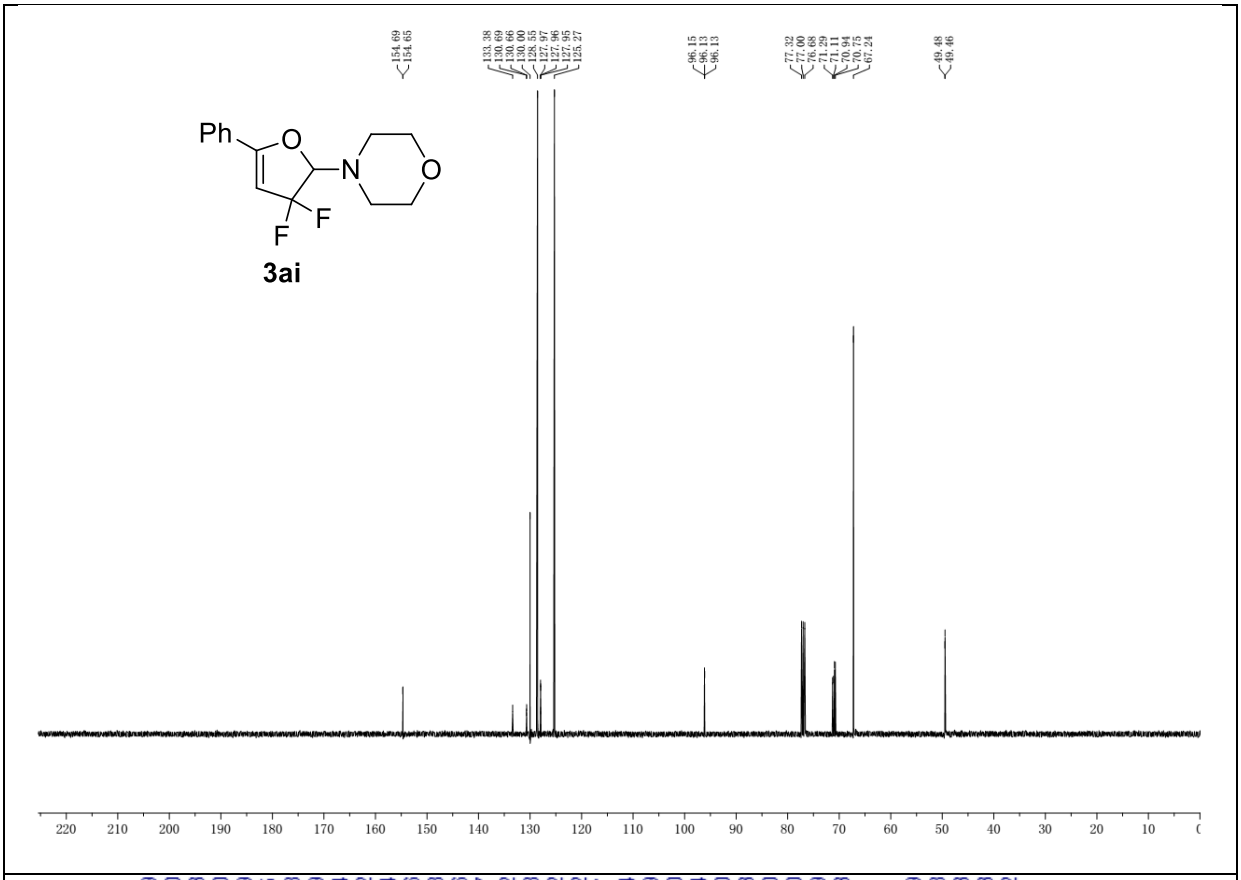
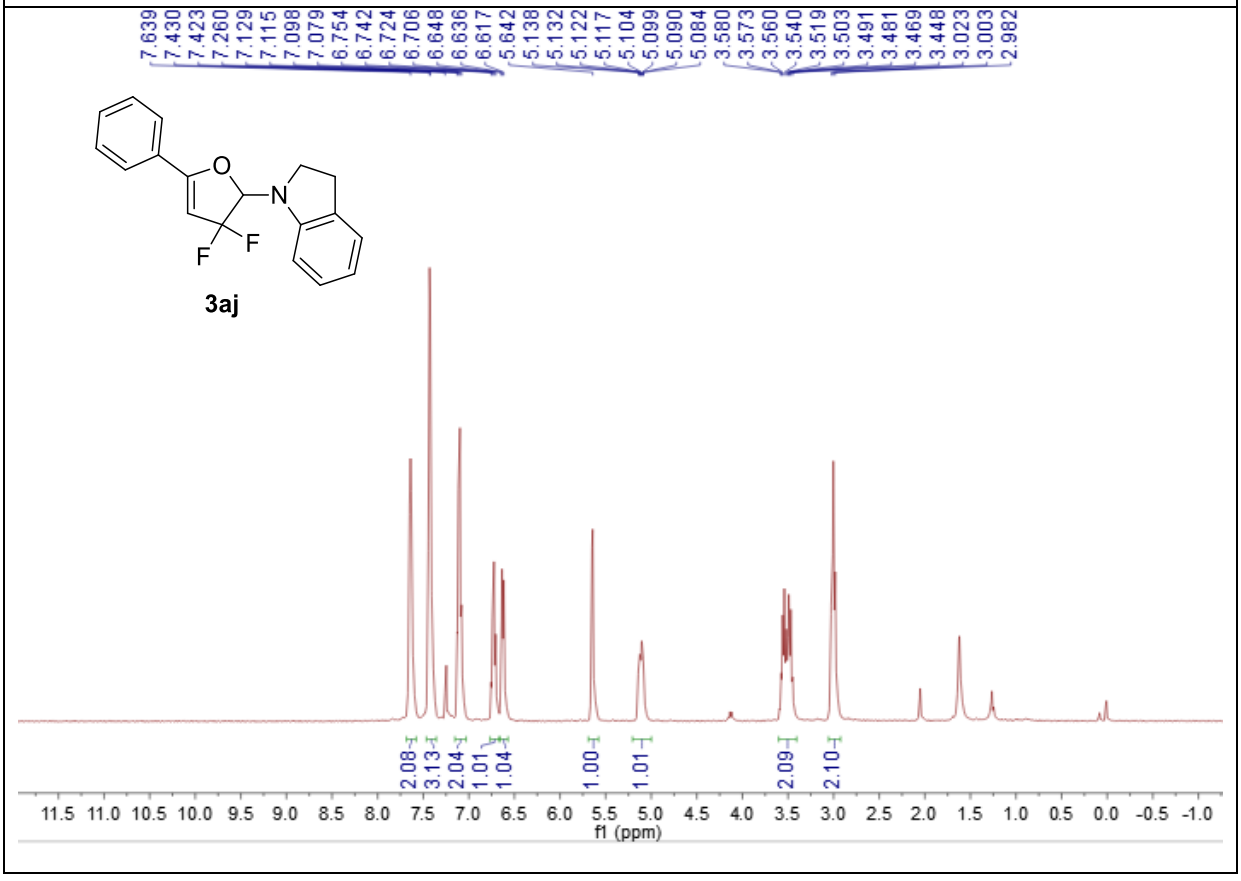
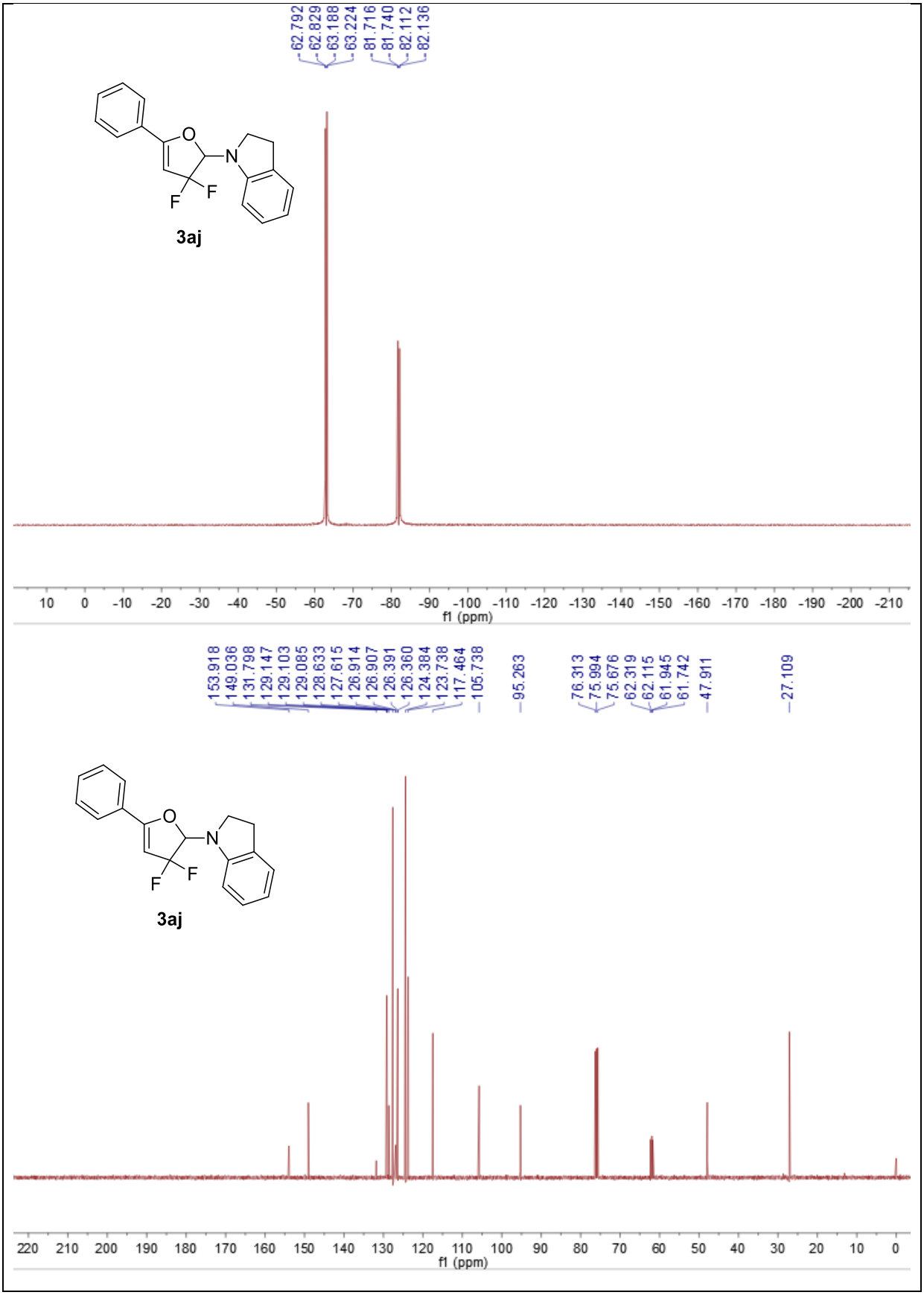
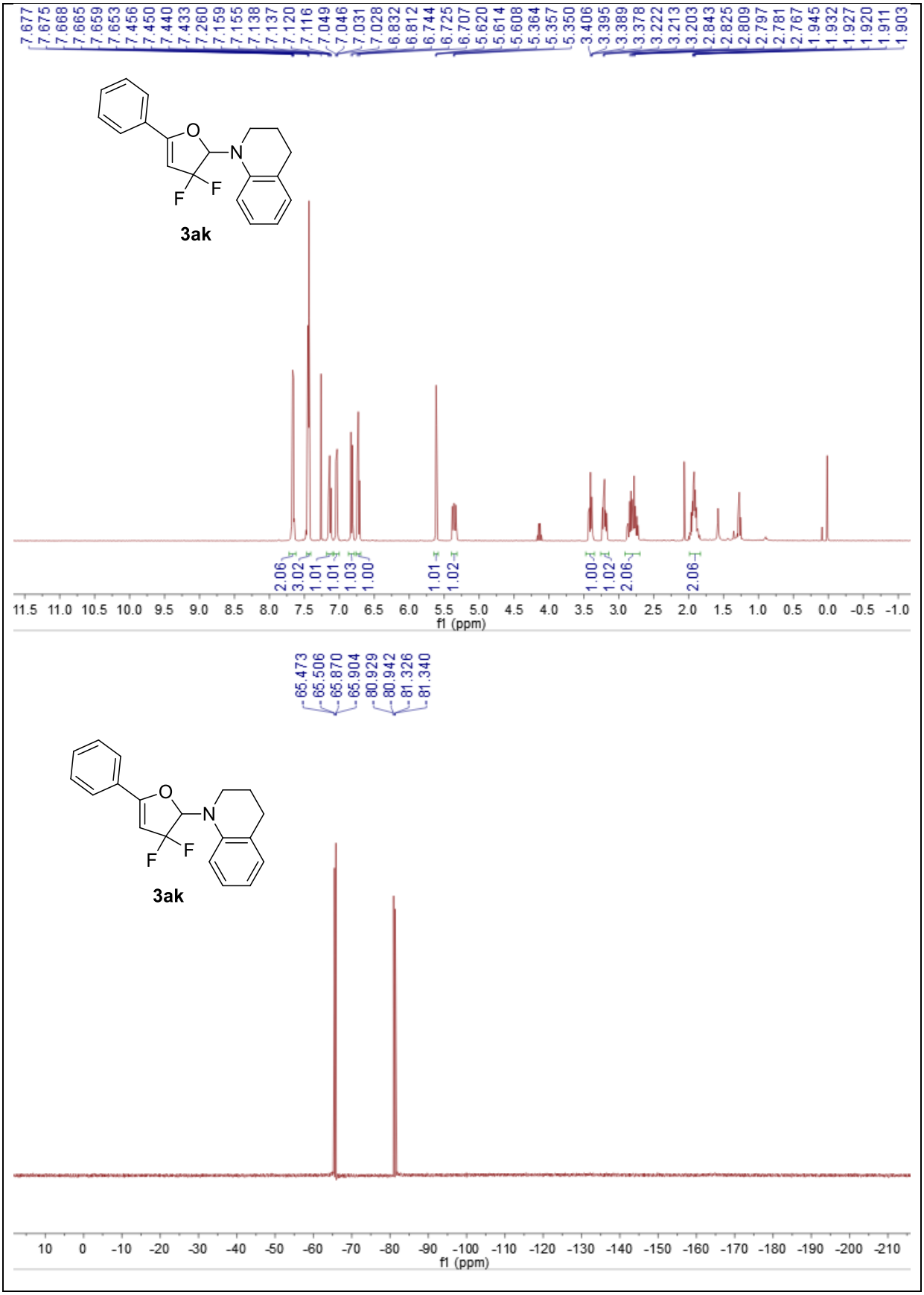
F
3ah
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
154.05
154.01
133.76
131.07
131.03
129.77
128.51
128.35
128.26
125.23
97.35
97.33
77.32
77.00
76.68
71.83
71.64
71.49
71.30
50.18
26.35
24.38
Ph
O
N
F
F
3ah
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

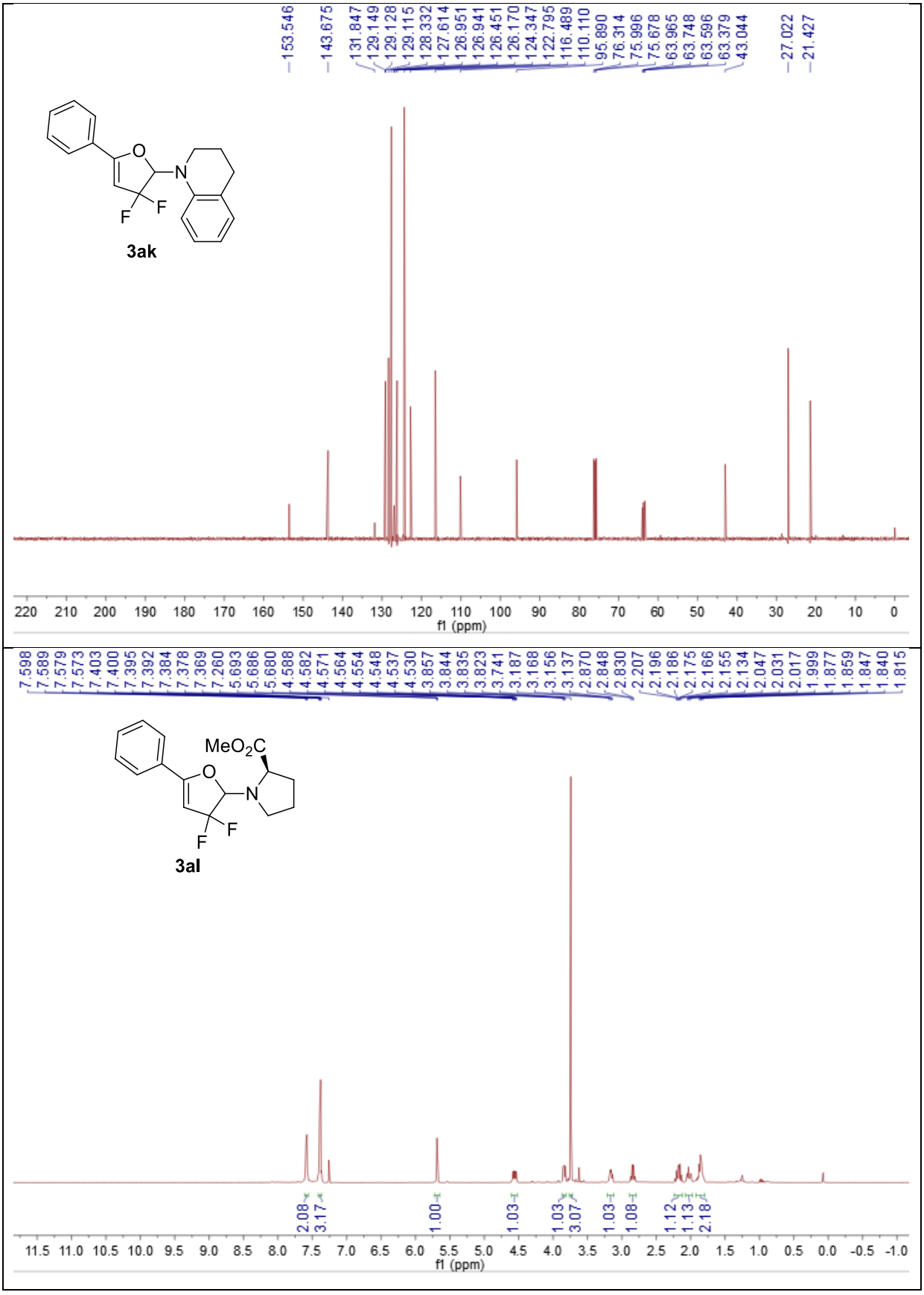

Ph
O
N
O
F
F
3ai
7.62
7.61
7.61
7.61
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.41
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.26
5.57
5.96
5.96
4.16
4.16
4.15
4.14
4.13
4.12
4.11
4.10
3.72
3.71
3.70
2.87
2.86
2.84
2.83
2.82
2.76
2.75
2.74
2.72
2.72
2.71
0.01
2.04
3.08
1.00
1.02
4.15
2.06
2.10
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
−61.35
−61.39
−61.75
−61.79
−83.07
−83.09
−83.47
−83.49
Ph
O
N
O
F
F
3ai
0 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

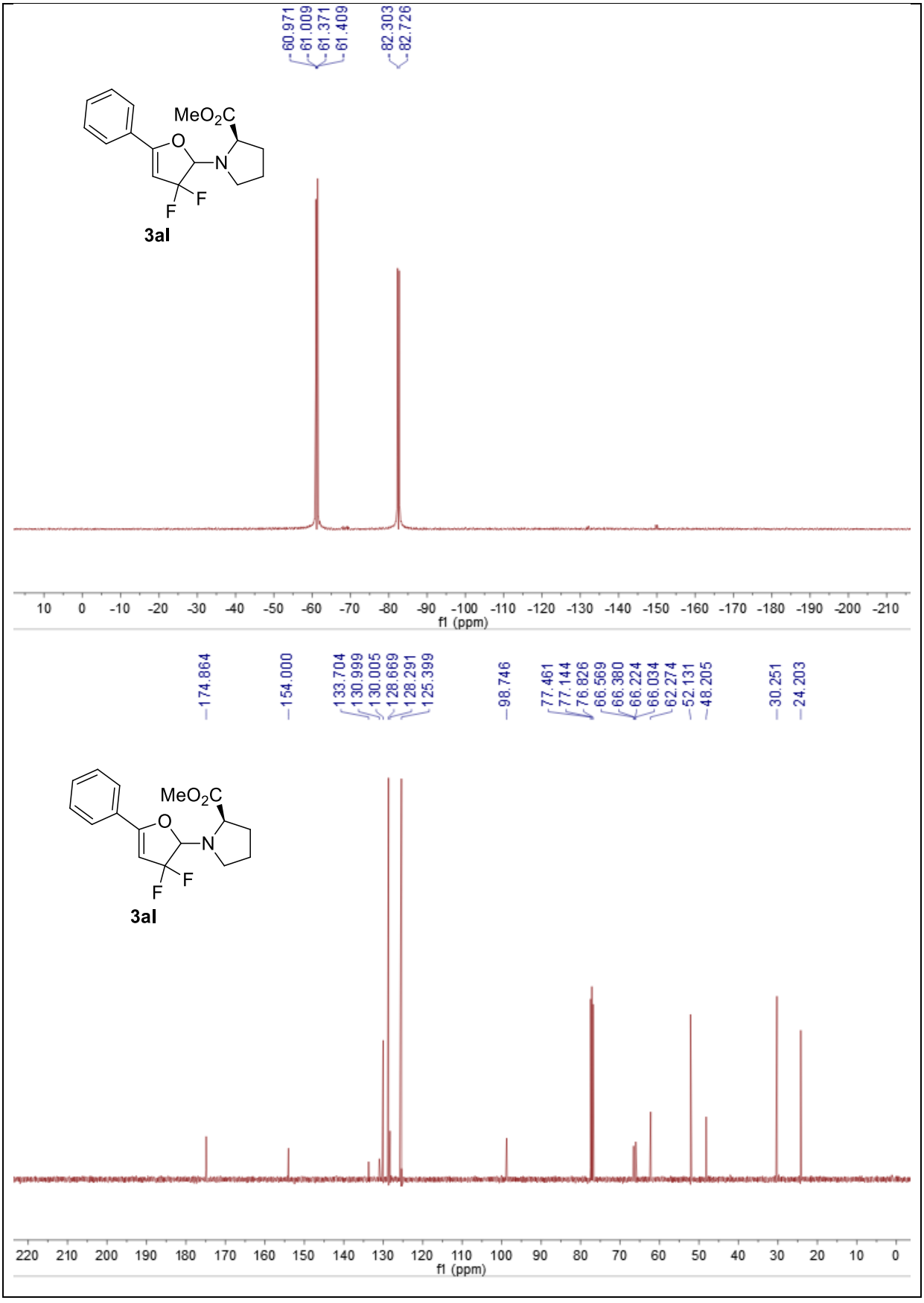

Ph
O
N
O
F
F
3ai

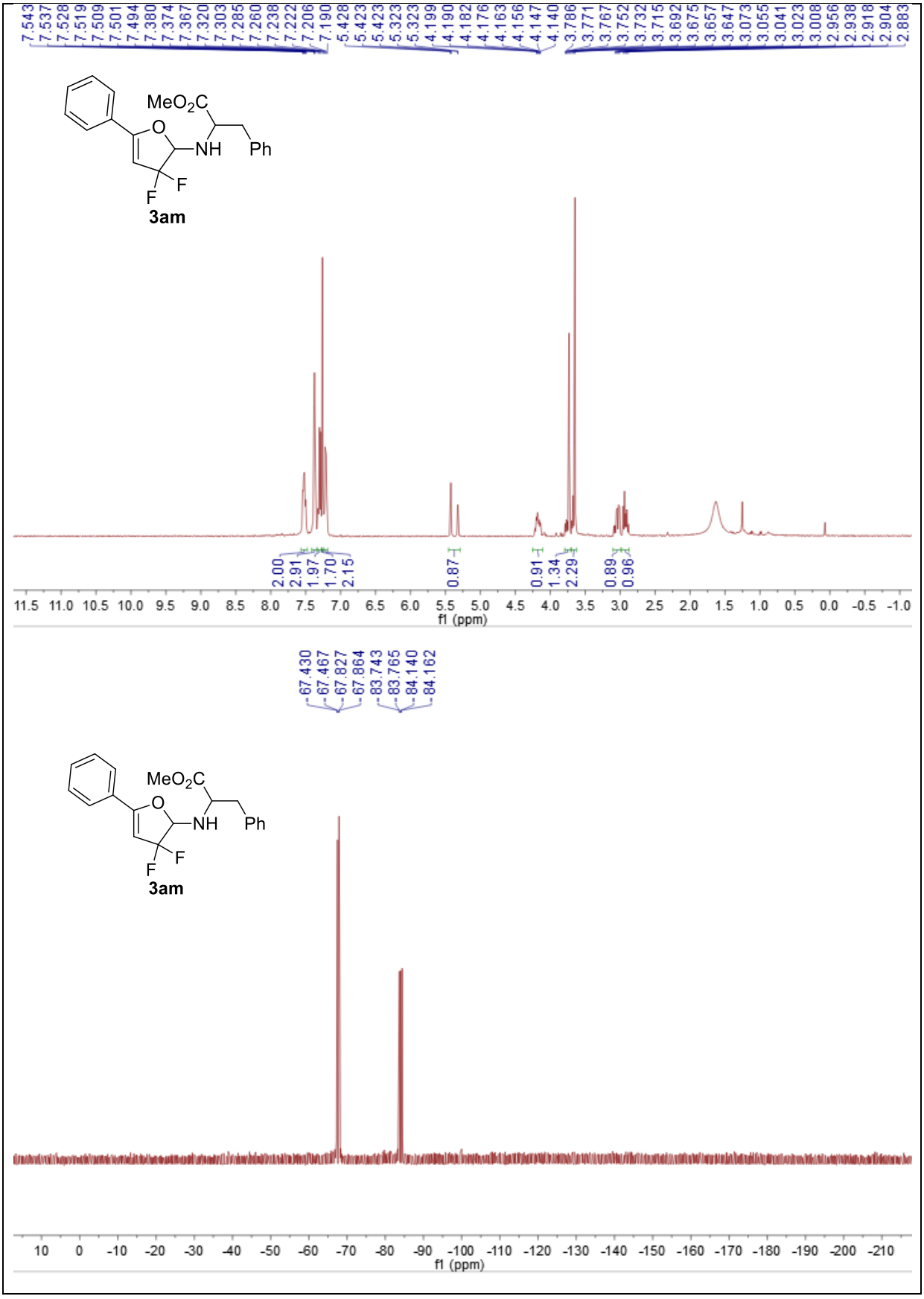

O
N
F
F
3aj
fl (ppm)

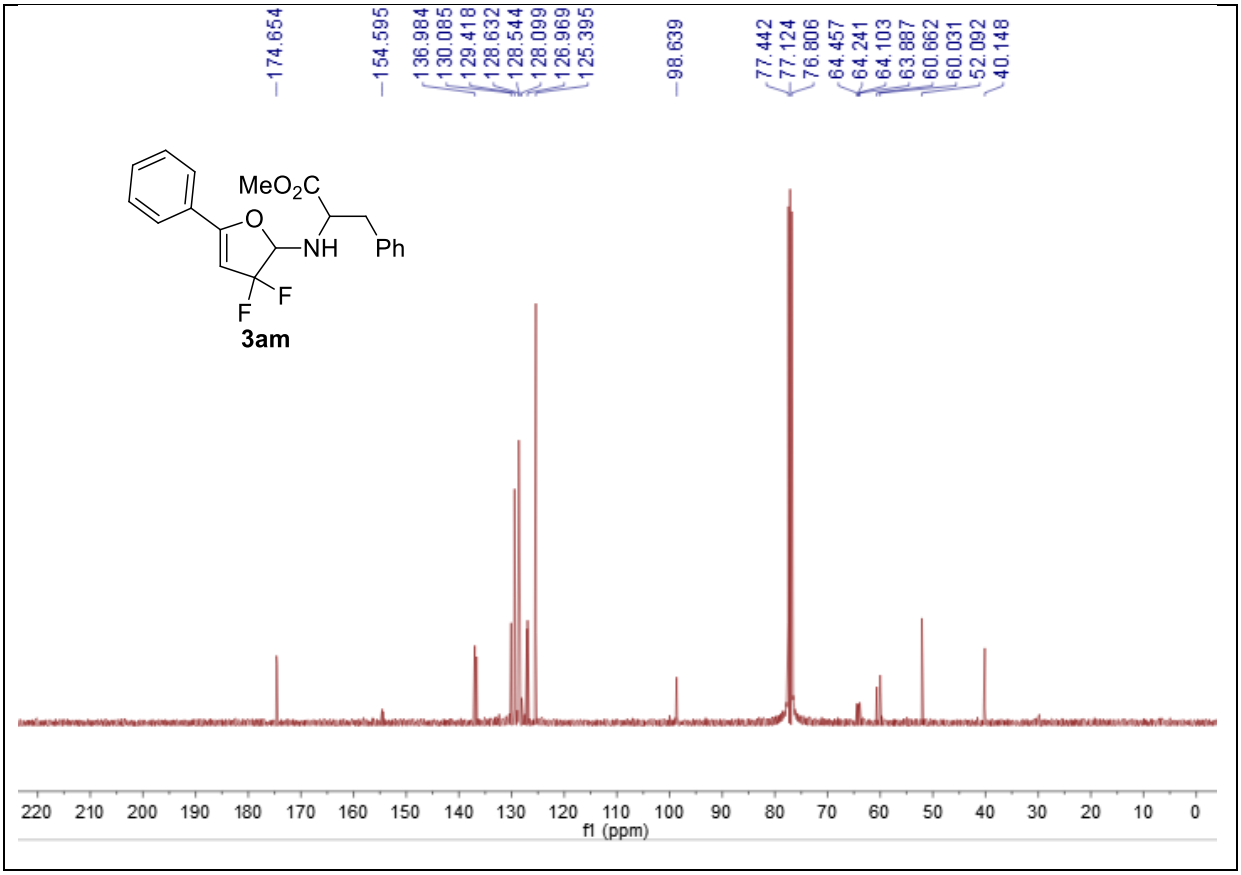

62.792
62.829
63.188
63.224
81.716
81.740
82.112
82.136
O
N
F
F
3aj
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
153.918
149.036
131.798
129.147
129.103
129.085
128.633
127.615
126.914
126.907
126.391
126.360
124.384
123.738
117.464
105.738
95.263
76.313
75.994
75.676
62.319
62.115
61.945
61.742
47.911
27.109
O
N
F
F
3aj
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.677
7.675
7.668
7.665
7.659
7.653
7.456
7.450
7.440
7.433
7.260
7.159
7.155
7.138
7.137
7.120
7.116
7.049
7.046
7.031
7.028
6.832
6.812
6.744
6.725
6.707
5.620
5.614
5.608
5.364
5.357
5.350
3.406
3.395
3.389
3.378
3.222
3.213
3.203
2.843
2.825
2.809
2.797
2.781
2.767
1.945
1.932
1.927
1.920
1.911
1.903
O
N
F
F
3ak
2.06
3.02
1.01
1.01
1.03
1.00
1.01
1.02
1.00
1.02
2.06
2.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
65.473
65.506
65.870
65.904
80.929
80.942
81.326
81.340
O
N
F
F
3ak
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

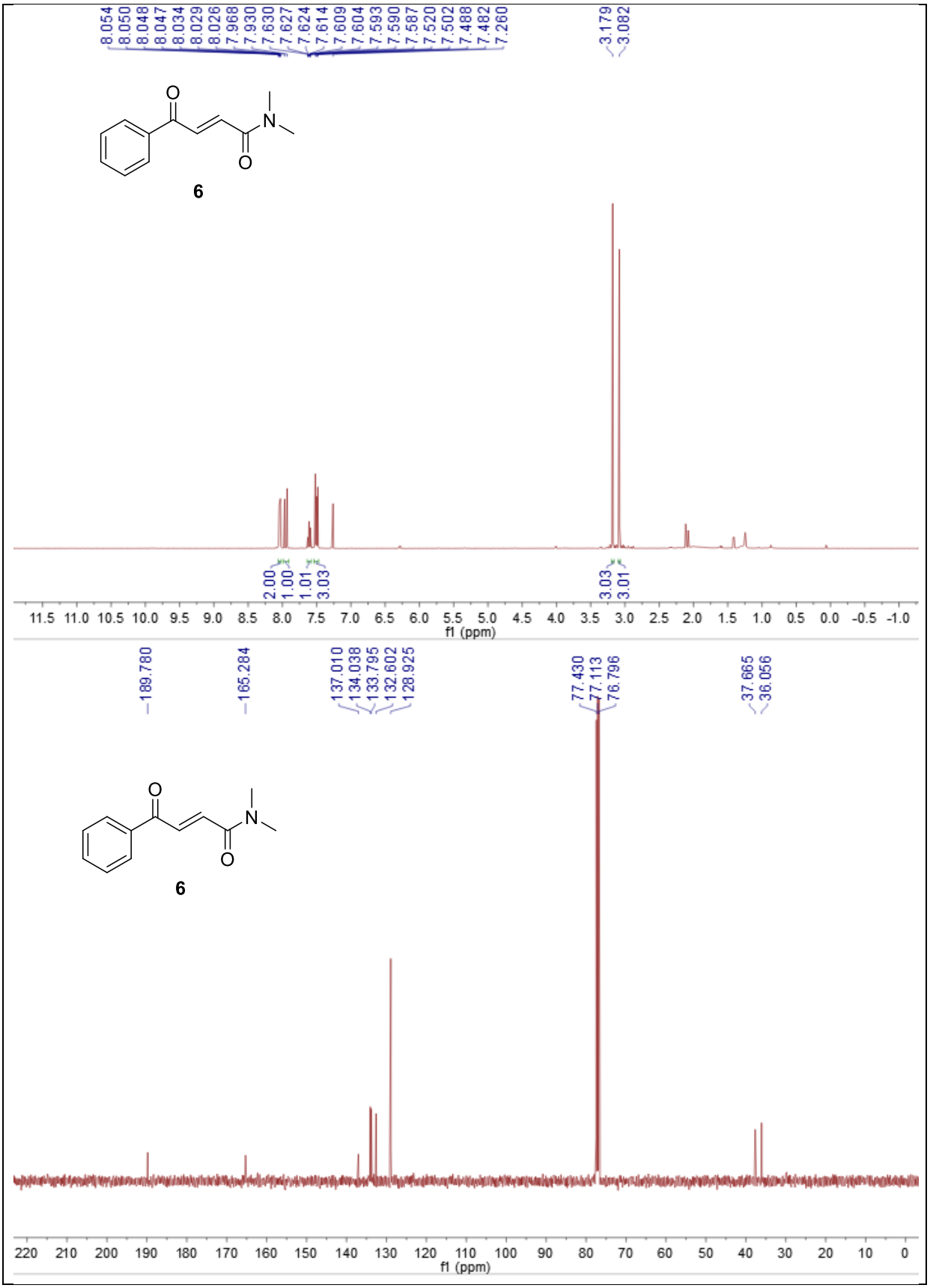

153.546
143.675
131.847
129.149
129.128
129.115
128.332
127.614
126.951
126.941
126.451
126.170
124.347
122.795
116.489
110.110
95.890
76.314
75.996
75.678
63.965
63.748
63.596
63.379
43.044
27.022
21.427
O
N
F
F
3ak
f1 (ppm)
7.598
7.589
7.579
7.573
7.403
7.400
7.395
7.392
7.384
7.378
7.369
7.260
5.693
5.686
5.680
4.588
4.582
4.571
4.564
4.554
4.548
4.537
4.530
3.857
3.844
3.835
3.823
3.741
3.187
3.168
3.156
3.137
2.870
2.848
2.830
2.207
2.196
2.186
2.175
2.166
2.155
2.134
2.047
2.031
2.017
1.999
1.877
1.859
1.847
1.840
1.815
MeO2C
O
N
F
F
3al
2.08
3.17
1.00
1.03
1.03
3.07
1.03
1.08
1.12
1.13
2.18
f1 (ppm)

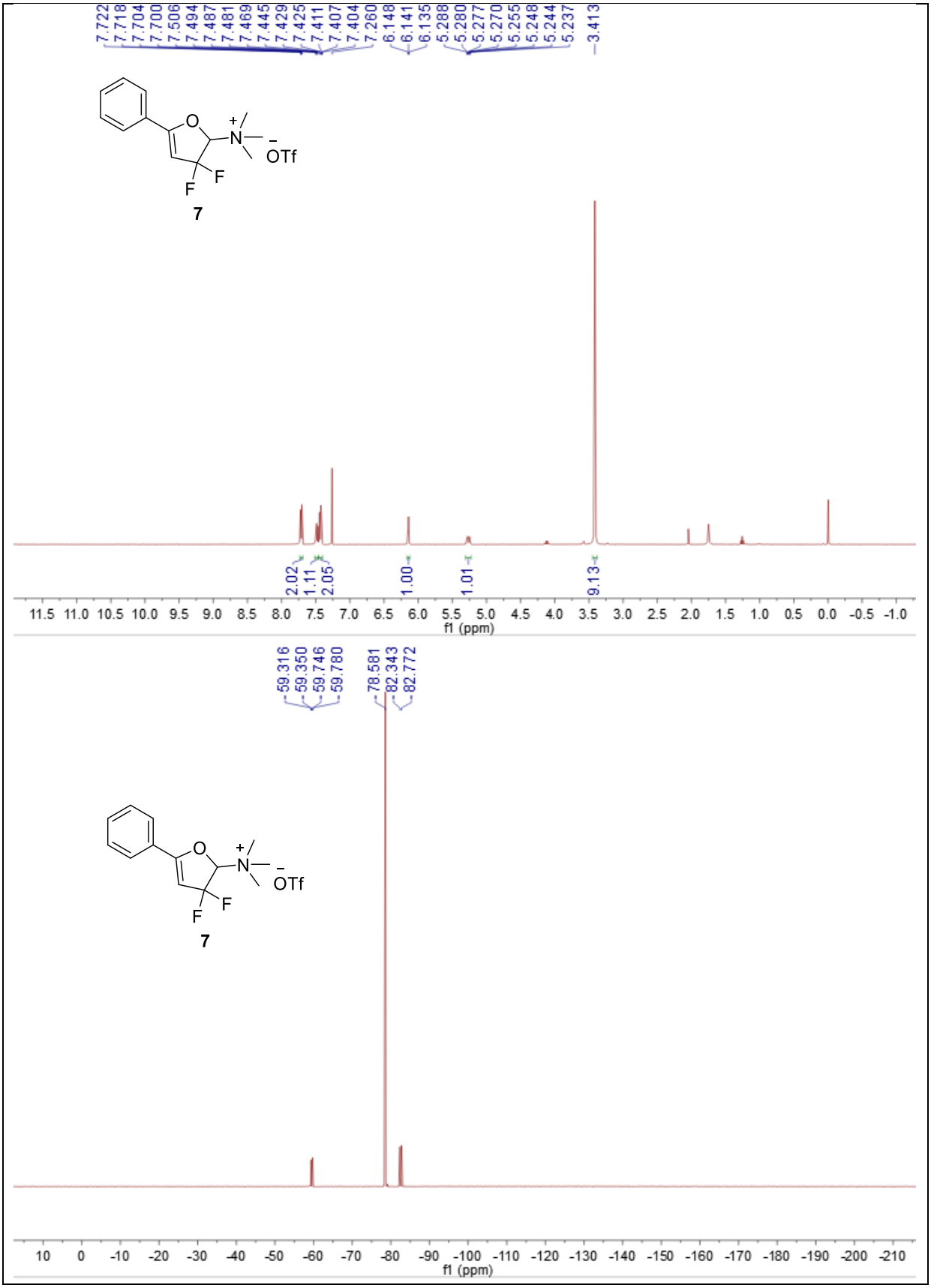

60.971
61.009
61.371
61.409
82.303
82.726
MeO2C
O
N
F
F
3al
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
174.864
154.000
133.704
130.999
130.005
128.669
128.291
125.399
98.746
77.461
77.144
76.826
66.569
66.380
66.224
66.034
62.274
52.131
48.205
30.251
24.203
MeO2C
O
N
F
F
3al
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

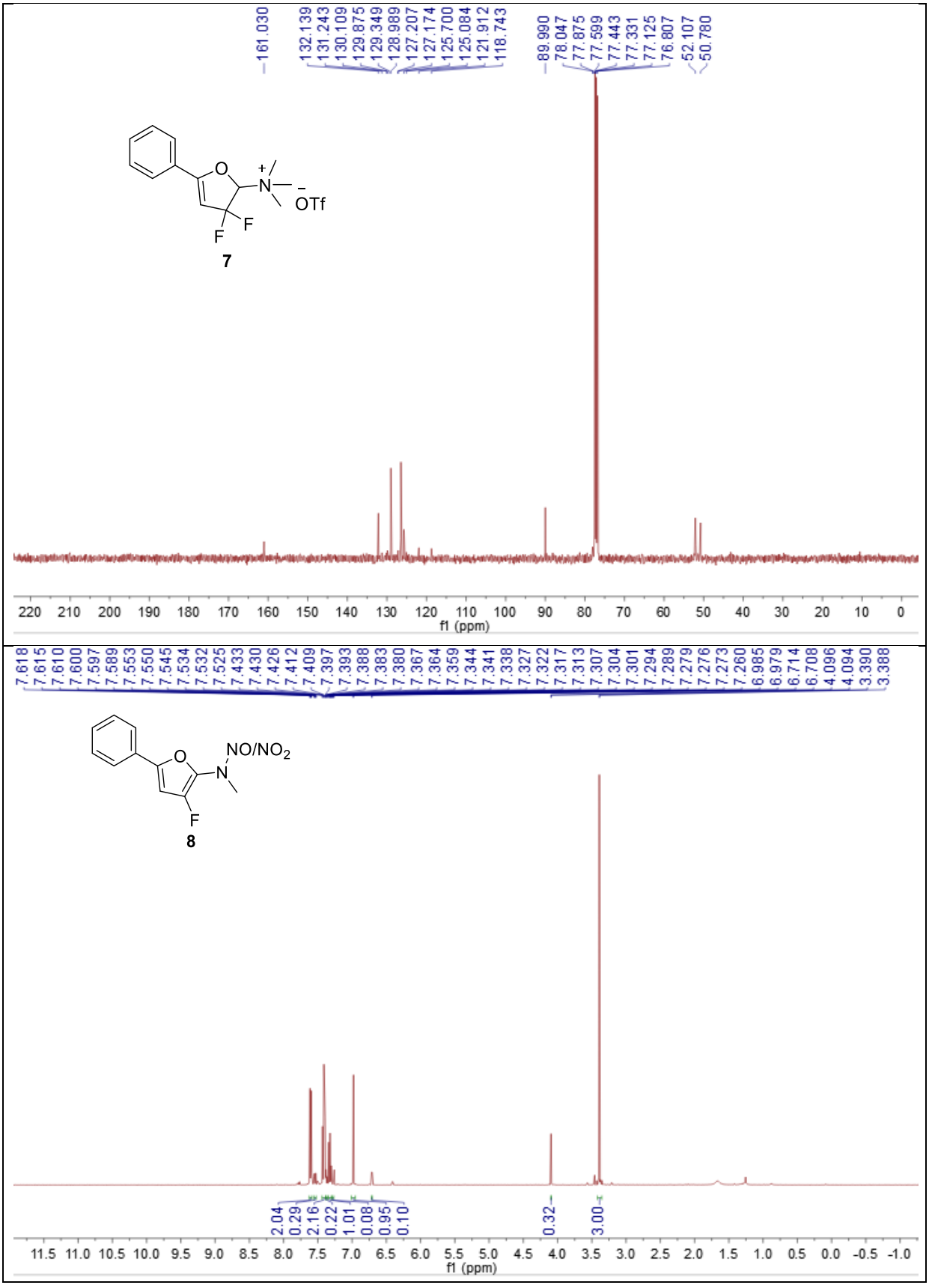

7.543 7.537 7.528 7.519 7.509 7.501 7.494 7.380 7.374 7.367 7.320 7.303 7.285 7.260 7.238 7.222 7.206 7.190 5.428 5.423 5.423 5.323 5.323 4.199 4.190 4.182 4.176 4.163 4.156 4.147 4.140 3.786 3.771 3.767 3.752 3.732 3.715 3.692 3.675 3.657 3.647 3.073 3.055 3.041 3.023 3.008 2.956 2.938 2.918 2.904 2.883
MeO2C
O
NH
Ph
F
F
3am
2.00 2.91 1.97 1.70 2.15 0.87 0.91 1.34 2.29 0.89 0.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
67.430 67.467 67.827 67.864 83.743 83.765 84.140 84.162
MeO2C
O
NH
Ph
F
F
3am
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

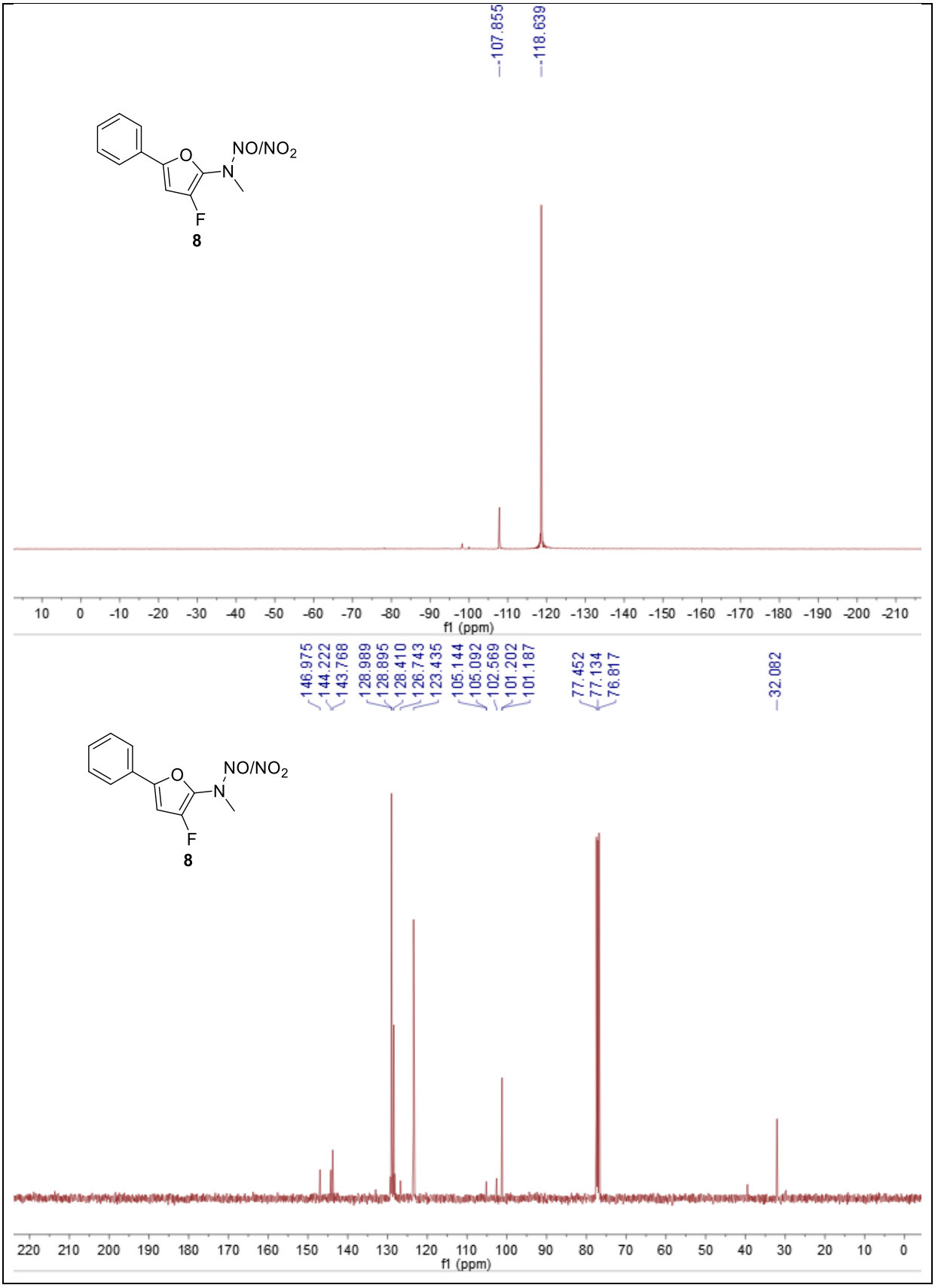

174.654
154.595
136.984
130.085
129.418
128.632
128.544
128.099
126.969
125.395
98.639
77.442
77.124
76.806
64.457
64.241
64.103
63.887
60.662
60.031
52.092
40.148
MeO2C
O
NH
Ph
F
F
3am
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

NMR Spectra for applications of *gem*-difluorinated 2*H*-furans:




7.722
7.718
7.704
7.700
7.506
7.494
7.487
7.481
7.469
7.445
7.429
7.425
7.411
7.407
7.404
7.260
6.148
6.141
6.135
5.288
5.280
5.277
5.270
5.255
5.248
5.244
5.237
3.413
O
N
OTf
F
F
7
2.02
1.11
2.05
1.00
1.01
9.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
59.316
59.350
59.746
59.780
78.581
82.343
82.772
O
N
OTf
F
F
7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


161.030
132.139
131.243
130.109
129.875
129.349
128.989
127.207
127.174
125.700
125.084
121.912
118.743
89.990
78.047
77.875
77.599
77.443
77.331
77.125
76.807
52.107
50.780
O
N
OTf
F
F
7
f1 (ppm)
7.618
7.615
7.610
7.600
7.597
7.589
7.553
7.550
7.545
7.534
7.532
7.525
7.433
7.430
7.426
7.412
7.409
7.397
7.393
7.388
7.383
7.380
7.367
7.364
7.359
7.344
7.341
7.338
7.327
7.322
7.317
7.313
7.307
7.304
7.301
7.294
7.289
7.279
7.276
7.273
7.260
6.985
6.979
6.714
6.708
4.096
4.094
3.390
3.388
O
NO/NO2
N
F
8
2.04
0.29
2.16
0.22
1.01
0.08
0.95
0.10
0.32
3.00
f1 (ppm)


-107.855
-118.639
NO/NO2
O
N
F
8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
146.975
144.222
143.768
128.989
128.895
128.410
126.743
123.435
105.144
105.092
102.569
101.202
101.187
77.452
77.134
76.817
32.082
NO/NO2
O
N
F
8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)