Electronic Supplementary Information

Rhodium(III)-Catalyzed Chemodivergent Annulations between *N*-Methoxybenzamides and Sulfoxonium Ylides via C-H Activation

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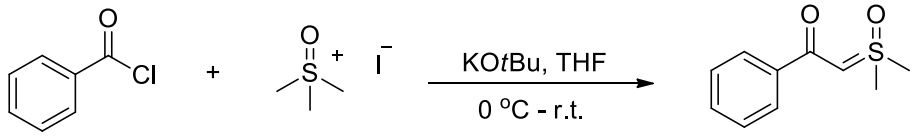
Table of Contents

I. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glove box in absolute ethanol. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. HRMS data were obtained via ESI mode with TOF mass analyzer. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or dichloromethane (DCM)/ petroleum ether (PE).

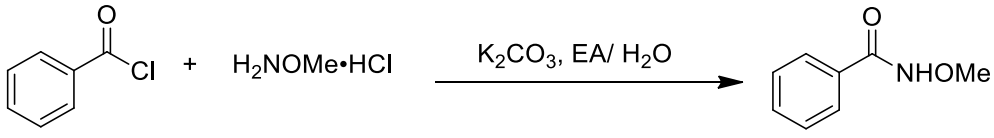
II. Synthesis of Substrates

(a) General Procedure for Preparation of Sulfoxonium Ylides



Sulfoxonium ylides were prepared according to reported procedures.[1] To a stirred solution of potassium *tert*-butoxide (3.0 g, 27.2 mmol) in THF (30 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture is refluxed for 2 h. Then reaction mixture was cooled to 0 °C, followed by addition of acyl chlorides (7 mmol) in THF (5 mL). The reaction was allowed to room temperature and stirred for 3 h. Next, the solvent was evaporated and water (15 mL) and ethyl acetate (20 mL) were added to the resulting slurry. The layers were separated and the aqueous layer was washed with ethyl acetate (2 x 30 mL) and the organic layers were combined. The organic solution was dried over anhydrous sodium sulfate (Na_2SO_4), filtered over a sintered funnel, and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using EtOAc/MeOH (95:5) to afford the corresponding sulfoxonium ylide.

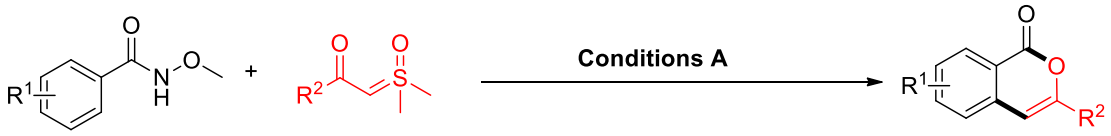
(b) General Procedure for Preparation of *N*-methoxybenzamides



N-Methoxybenzamides were prepared according to reported procedures.[2] In a reaction flask, a mixture of $MeONH_2 \cdot HCl$ (1.5 equiv) and K_2CO_3 (2 equiv) in a 2:1 mixture of EtOAc:H_2O (0.3 M) was stirred at 0 °C, followed by dropwise addition of the benzoyl chloride. The reaction was stirred at room temperature overnight. Afterwards, the reaction was quenched with aqueous $NaHCO_3$ solution and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc/Pentane.

III. Rhodium(III)-Catalyzed Coupling of *N*-methoxybenzamides with Sulfoxonium Ylides

(a) Synthesis of Isocoumarins

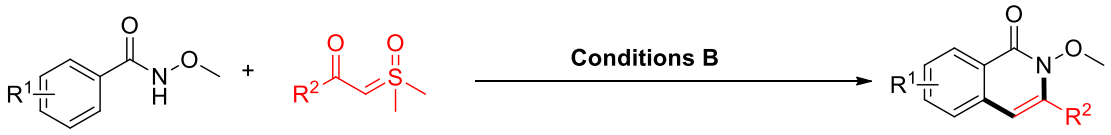


1 **2** **3**

Conditions A: **1** (0.2 mmol), **2** (0.4 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), CsOAc (30 mol %), PivOH (0.4 mmol), DCE (4 mL), 100 °C, 18 h.

A pressure tube was charged with $[RhCp^*Cl_2]_2$ (4.9 mg, 4 mol %), CsOAc (11.6 mg, 30 mol %), HOPiv (40.8 mg, 0.4 mmol), *N*-methoxybenzamides (0.2 mmol), sulfoxonium ylides (0.4 mmol), and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 18 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA or PE/DCM to afford the product.

(b) Synthesis of Isoquinolones

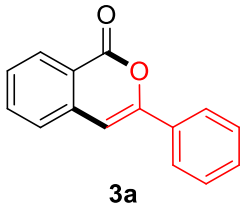


1 **2** **4**

Conditions B: **1** (0.2 mmol), **2** (0.4 mmol), $RhCp^*(MeCN)_3(SbF_6)_2$ (5 mol %), $Zn(OTf)_2$ (50 mol %), DCE (4 mL), 100 °C, 15 h.

A pressure tube was charged with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8.3 mg, 5 mol %), $Zn(OTf)_2$ (36.4 mg, 50 mol %), *N*-methoxybenzamides (0.2 mmol), sulfoxonium ylides (0.4 mmol) and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 15 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product.

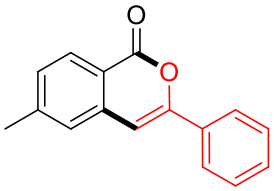
IV. Characterization Data



3a

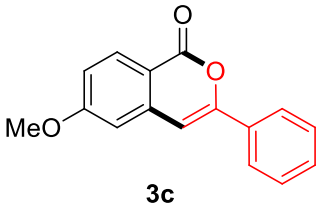
3-phenyl-1*H*-isochromen-1-one[3]

White solid, 40.0 mg, yield: 90% (purified by silica gel chromatography using PE/EA 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.2 Hz, 1H), 7.87 (dd, J = 8.0, 1.4 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.50 – 7.40 (m, 5H), 6.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.5, 137.4, 134.8, 131.9, 129.9, 129.6, 128.8, 128.1, 125.9, 125.2, 120.5, 101.8.



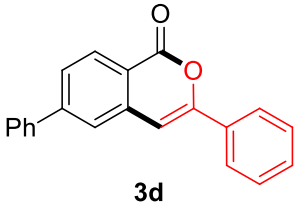
3b 6-methyl-3-phenyl-1*H*-isochromen-1-one[3]

White solid, 37.3 mg, yield: 79% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 7.86 – 7.83 (m, 2H), 7.46 – 7.38 (m, 3H), 7.29 – 7.25 (m, 2H), 6.86 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.5, 145.9, 137.5, 132.0, 129.8, 129.5, 128.7, 125.9, 125.1, 118.0, 101.7, 21.9.



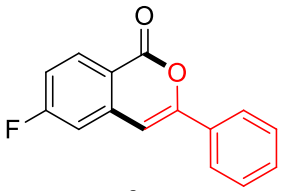
3c 6-methoxy-3-phenyl-1*H*-isochromen-1-one[3]

White solid, 47.9 mg, yield: 95% (purified by silica gel chromatography using PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.45 – 7.39 (m, 3H), 6.98 (dd, J = 8.8, 2.4 Hz, 1H), 6.84 – 6.83 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 162.0, 154.0, 139.7, 131.9, 131.7, 129.9, 128.7, 125.2, 116.5, 113.6, 107.8, 101.8, 55.6.



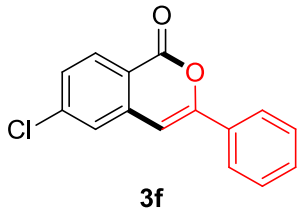
3d 3,6-diphenyl-1*H*-isochromen-1-one[3]

White solid, 49.1 mg, yield: 82% (purified by silica gel chromatography using PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.2 Hz, 1H), 7.89 (dd, J = 8.0, 1.4 Hz, 2H), 7.71 – 7.65 (m, 4H), 7.52 – 7.41 (m, 6H), 6.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 153.9, 147.6, 139.4, 137.9, 131.9, 130.2, 130.0, 129.0, 128.8, 128.7, 127.4, 127.1, 125.2, 124.1, 119.2, 101.9.



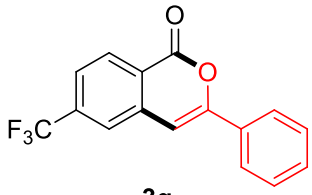
3e 6-fluoro-3-phenyl-1*H*-isochromen-1-one[3]

Whtie solid, 43.1 mg, yield: 90% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 8.7, 5.6 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.48 – 7.32 (m, 3H), 7.19 – 7.11 (m, 2H), 6.89 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 (d, $J_{C\text{-}F}$ = 256.5 Hz), 161.3, 154.8, 140.2 (d, $J_{C\text{-}F}$ = 10.8 Hz), 132.9 (d, $J_{C\text{-}F}$ = 10.4 Hz), 131.5, 130.3, 128.8, 125.4, 116.9 (d, $J_{C\text{-}F}$ = 2.1 Hz), 116.4 (d, $J_{C\text{-}F}$ = 23.4 Hz), 111.5 (d, $J_{C\text{-}F}$ = 22.6 Hz), 101.1 (d, $J_{C\text{-}F}$ = 2.9 Hz).



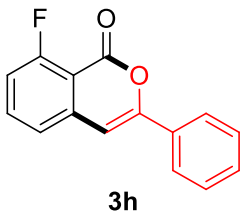
3f 6-chloro-3-phenyl-1*H*-isochromen-1-one[3]

White solid, 47.6 mg, yield: 93% (purified by silica gel chromatography using PE/DCM 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 1H), 7.87 – 7.85 (m, 2H), 7.47 – 7.42 (m, 5H), 6.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.9, 141.5, 138.9, 131.5, 131.3, 130.4, 128.9, 128.6, 125.4, 125.4, 118.8, 100.7.



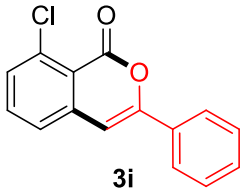
3g 3-phenyl-6-(trifluoromethyl)-1*H*-isochromen-1-one[3]

White solid, 47.6 mg, yield: 82% (purified by silica gel chromatography using PE/DCM 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.3 Hz, 1H), 7.87 – 7.84 (M, 2H), 7.75 (s, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.49 – 7.42 (m, 3H), 6.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 155.0, 137.8, 136.3 (q, $J_{C\text{-}F}$ = 32.9 Hz), 131.3, 130.6, 130.5, 128.9, 125.4, 124.2 (q, $J_{C\text{-}F}$ = 3.4 Hz), 123.2 (q, $J_{C\text{-}F}$ = 273.3 Hz), 123.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 122.7, 101.0.



3h 8-fluoro-3-phenyl-1*H*-isochromen-1-one

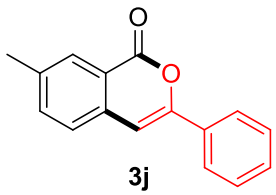
White solid, 43.5 mg, yield: 91% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.67 – 7.62 (m, 1H), 7.46 – 7.43 (m, 3H), 7.26 (d, J = 7.7 Hz, 1H), 7.11 (dd, J = 10.2, 8.6 Hz, 1H), 6.90 (d, J = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 266.7 Hz), 157.7 (d, $J_{C\text{-}F}$ = 5.4 Hz), 154.4, 140.0, 136.1 (d, $J_{C\text{-}F}$ = 10.2 Hz), 131.3, 130.3, 128.8, 125.3, 121.8 (d, $J_{C\text{-}F}$ = 4.3 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.3 Hz), 109.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 101.0 (d, $J_{C\text{-}F}$ = 3.1 Hz). HRMS (ESI): calculated for $C_{15}H_{10}FO_2^+$ 241.0657, found 241.0659.



3i 8-chloro-3-phenyl-1*H*-isochromen-1-one

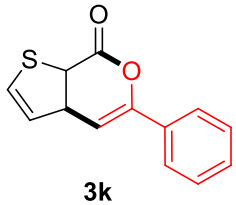
White solid, 50.7 mg, yield: 99% (purified by silica gel chromatography using PE/DCM 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (dd, J = 7.4, 1.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.36 (d, J = 7.7 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 154.1, 140.5,

137.1, 134.5, 131.3, 130.8, 130.3, 128.8, 125.2, 124.9, 117.4, 101.4. HRMS (ESI): calculated for $C_{15}H_{10}ClO_2^+$ 257.0357, found 257.0364.



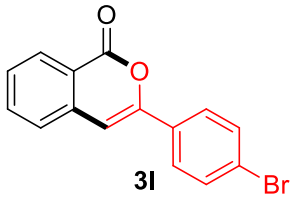
3j 7-methyl-3-phenyl-1*H*-isochromen-1-one[3]

White solid, 42.5 mg, yield: 90% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.85 – 7.83 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.45 – 7.36 (m, 4H), 6.89 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 152.7, 138.4, 136.1, 134.9, 132.0, 129.6, 129.2, 128.7, 125.8, 125.0, 120.3, 101.7, 21.3.



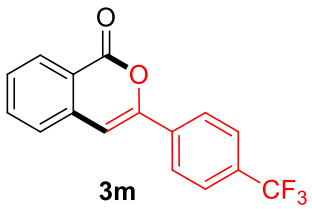
3k (3aS)-5-phenyl-3a*H*-thieno[2,3-c]pyran-7(7a*H*)-one

White solid, 32.1 mg, yield: 70% (purified by silica gel chromatography using PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 3H), 7.48 – 7.42 (m, 3H), 7.23 (d, J = 5.1 Hz, 1H), 7.11 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.4, 147.5, 136.8, 131.8, 130.1, 128.9, 125.3, 124.7, 122.9, 99.0. HRMS (ESI): calculated for $C_{13}H_9O_2S^+$ 229.0318, found 229.0317.



3l 3-(4-bromophenyl)-1*H*-isochromen-1-one[4]

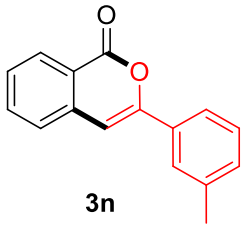
White solid, 53.6 mg, yield: 89% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.9 Hz, 1H), 7.71 – 7.67 (m, 3H), 7.53 (d, J = 8.6 Hz, 2H), 7.49 – 7.44 (m, 2H), 6.89 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 152.5, 137.2, 135.0, 132.0, 130.8, 129.7, 128.4, 126.6, 126.1, 124.3, 120.5, 102.1.



3m 3-(4-(trifluoromethyl)phenyl)-1*H*-isochromen-1-one[5]

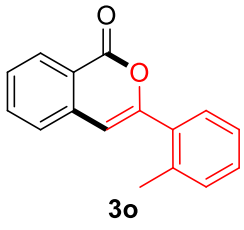
White solid, 52.2 mg, yield: 90% (purified by silica gel chromatography using PE/DCM 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.77 – 7.70 (m, 3H), 7.56

– 7.52 (m, 2H), 7.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 152.0, 136.9, 135.3, 135.1, 131.6 (q, $J_{C\text{-}F}$ = 33.0 Hz), 129.8, 128.9, 126.3, 125.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.5, 123.8 (q, $J_{C\text{-}F}$ = 272.5 Hz), 120.9, 103.4.



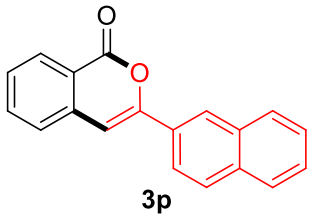
3n 3-(*m*-tolyl)-1*H*-isochromen-1-one[3]

White solid, 42.1 mg, yield: 85% (purified by silica gel chromatography using PE/EA 20:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.1 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.50 – 7.47 (m, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 6.93 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 153.8, 138.6, 137.6, 134.8, 131.8, 130.8, 129.6, 128.7, 128.0, 125.9, 125.8, 122.4, 120.5, 101.7, 21.4.



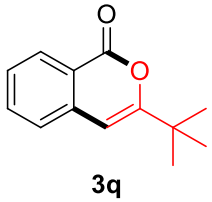
3o 3-(*o*-tolyl)-1*H*-isochromen-1-one[3]

Colorless oil, 40.2 mg, yield: 85% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 1H), 7.72 (td, J = 7.8, 1.3 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.36 – 7.32 (m, 1H), 7.28 – 7.24 (m, 2H), 6.60 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 155.5, 137.4, 136.7, 134.8, 132.7, 131.0, 129.7, 129.5, 129.1, 128.2, 125.9, 125.8, 120.3, 105.9, 20.7.



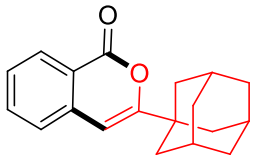
3p 3-(naphthalen-2-yl)-1*H*-isochromen-1-one[3]

Yellow solid, 49.3 mg, yield: 90% (purified by silica gel chromatography using PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.27 (d, J = 7.9 Hz, 1H), 7.89 – 7.78 (m, 4H), 7.69 – 7.65 (m, 1H), 7.50 – 7.43 (m, 4H), 6.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 153.3, 137.4, 134.8, 133.7, 133.0, 129.5, 128.8, 128.7, 128.5, 128.1, 127.6, 127.1, 126.7, 125.9, 125.1, 121.8, 120.4, 102.1.



3q 3-(*tert*-butyl)-1*H*-isochromen-1-one[3]

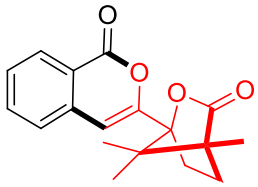
Colorless oil, 32.5 mg, yield: 80% (purified by silica gel chromatography using PE/EA 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 6.30 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.0, 137.6, 134.6, 129.3, 127.5, 125.4, 120.1, 99.6, 35.6, 27.9.



3r

3-((3r,5r,7r)-adamantan-1-yl)-1*H*-isochromen-1-one

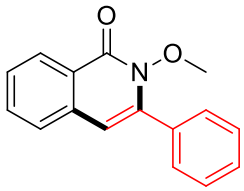
White solid, 51.6 mg, yield: 92% (purified by silica gel chromatography using PE/EA 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.9 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.9 Hz, 1H), 6.20 (s, 1H), 2.08 (apparent s, 3H), 1.95-1.94 (m, 6H), 1.79-1.71 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.1, 137.8, 134.5, 129.3, 127.4, 125.4, 120.2, 99.6, 39.6, 37.2, 36.5, 28.0. HRMS (ESI): calculated for $C_{19}H_{21}O_2^+$ 281.1536, found 281.1541.



3s

3-(4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-1*H*-isochromen-1-one

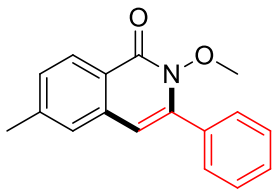
White solid, 23.9 mg, yield: 40% (purified by silica gel chromatography using PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 1H), 7.74 (td, J = 7.7, 1.2 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.46 (d, J = 7.8 Hz, 1H), 6.76 (s, 1H), 2.75 – 2.68 (m, 1H), 2.04 – 1.94 (m, 2H), 1.82 – 1.75 (m, 1H), 1.17 – 1.16 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 161.5, 151.4, 136.5, 135.1, 129.7, 128.7, 126.1, 120.5, 104.1, 90.7, 55.1, 54.0, 30.7, 29.0, 17.1, 16.7, 9.9. HRMS (ESI): calculated for $C_{19}H_{21}O_2^+$ 299.1278, found 299.1279.



4a

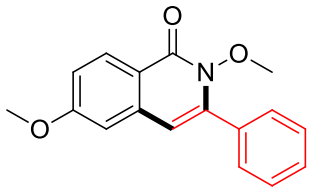
2-methoxy-3-phenylisoquinolin-1(2*H*)-one[6]

White solid, yield: 95% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.1 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.55 – 7.50 (m, 2H), 7.48 – 7.46 (m, 3H), 6.48 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 142.1, 135.8, 132.5, 132.5, 129.3, 129.2, 128.2, 127.8, 126.6, 126.3, 126.2, 106.7, 63.4.



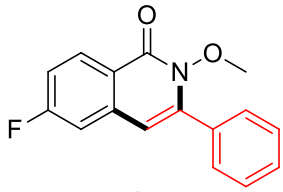
4b 2-methoxy-6-methyl-3-phenylisoquinolin-1(2*H*)-one

White solid, yield: 97% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.6 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.47 – 7.46 (m, 3H), 7.33 – 7.32 (m, 2H), 6.41 (s, 1H), 3.69 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 143.0, 142.1, 135.9, 132.7, 129.2, 129.1, 128.3, 128.1, 127.7, 125.9, 124.0, 106.5, 63.3, 21.7. HRMS (ESI): calculated for $C_{17}H_{16}NO_2^+$ 266.1176, found 266.1179.



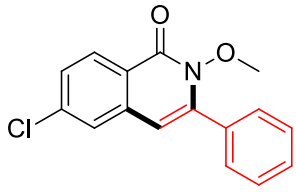
4c 2,6-dimethoxy-3-phenylisoquinolin-1(2*H*)-one[6]

White solid, 49.0 mg, yield: 87% (purified by silica gel chromatography using PE/EA/Et_3N 40:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.9 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.48 – 7.45 (m, 3H), 7.06 (dd, J = 8.9, 2.5 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.39 (s, 1H), 3.90 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 158.4, 142.6, 137.8, 132.6, 129.8, 129.2, 129.2, 128.2, 120.1, 116.2, 106.9, 106.3, 63.4, 55.5.



4d 6-fluoro-2-methoxy-3-phenylisoquinolin-1(2*H*)-one[6]

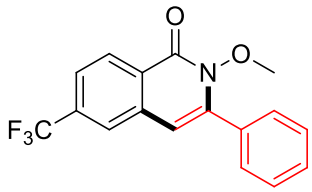
White solid, yield: 97% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ8.47 (dd, J = 8.9, 5.7 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.49 – 7.46 (m, 3H), 7.22 – 7.14 (m, 2H), 6.41 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, $J_{C\text{-}F}$ = 253.0 Hz), 158.2, 143.5, 138.0 (d, $J_{C\text{-}F}$ = 10.5 Hz), 132.2, 131.1 (d, $J_{C\text{-}F}$ = 10.1 Hz), 129.5, 129.3, 128.3, 122.9 (d, $J_{C\text{-}F}$ = 1.5 Hz), 115.5 (d, $J_{C\text{-}F}$ = 23.6 Hz), 111.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 105.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 63.6.



4e 6-chloro-2-methoxy-3-phenylisoquinolin-1(2*H*)-one[6]

White solid, yield: 96% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.6 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.51 (d, J = 1.7 Hz, 1H), 7.48

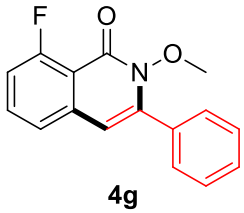
– 7.46 (m, 3H), 7.42 (dd, J = 8.6, 1.9 Hz, 1H), 6.38 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 143.5, 138.9, 136.9, 132.1, 129.6, 129.5, 129.2, 128.3, 127.1, 125.4, 124.6, 105.5, 63.5.



4f

2-methoxy-3-phenyl-6-(trifluoromethyl)isoquinolin-1(2*H*)-one

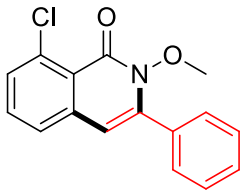
White solid, yield: 88% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.68 (dd, J = 8.5, 1.2 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.50 – 7.47 (m, 3H), 6.53 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 143.8, 135.7, 134.2 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.0, 129.6, 129.2, 129.0, 128.3, 123.6 (q, $J_{C\text{-}F}$ = 273.0 Hz), 123.6 (q, $J_{C\text{-}F}$ = 4.1 Hz), 122.5 (q, $J_{C\text{-}F}$ = 3.3 Hz), 106.2, 63.6 (one signal missing due to overlap). HRMS (ESI): calculated for $C_{17}H_{13}F_3NO_2^+$ 320.0893, found 320.0894.



4g

8-fluoro-2-methoxy-3-phenylisoquinolin-1(2*H*)-one

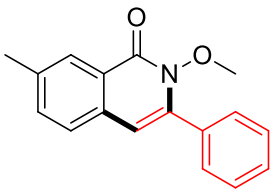
White solid, 30.2 mg, yield: 56% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.617.59 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.45 (m, 3H), 7.28 (d, J = 7.9 Hz, 1H), 7.09 (dd, J = 11.3, 8.2 Hz, 1H), 6.41 (d, J = 1.5 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 264.3 Hz), 155.9 (d, J = 4.9 Hz), 143.3 (d, J = 1.2 Hz), 138.4, 133.3 (d, J = 9.9 Hz), 132.1, 129.4, 129.1, 128.2, 122.1 (d, J = 4.6 Hz), 115.2 (d, J = 5.9 Hz), 113.3 (d, J = 21.4 Hz), 105.7 (d, J = 2.5 Hz), 63.3. HRMS (ESI): calculated for $C_{16}H_{13}FNO_2^+$ 270.0925, found 270.0926.



4h

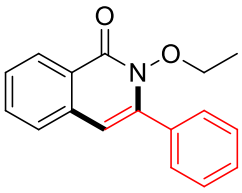
8-chloro-2-methoxy-3-phenylisoquinolin-1(2*H*)-one

White solid, 40.5 mg, yield: 71% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.48 – 7.45 (m, 5H), 7.39 (dd, J = 6.6, 2.6 Hz, 1H), 6.39 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 143.1, 138.7, 135.5, 132.1, 132.1, 129.7, 129.4, 129.1, 128.2, 125.5, 122.5, 105.8, 63.3. HRMS (ESI): calculated for $C_{16}H_{13}ClNO_2^+$ 286.0629, found 286.0631.



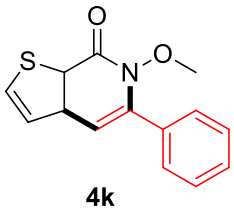
4i 2-methoxy-7-methyl-3-phenylisoquinolin-1(2*H*)-one[7]

White solid, 41.3 mg, yield: 78% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.63 – 7.61 (m, 2H), 7.49 – 7.42 (m, 5H), 6.45 (s, 1H), 3.68 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 141.1, 136.8, 134.0, 133.4, 132.7, 129.3, 129.0, 128.1, 127.3, 126.2, 126.2, 106.7, 63.3, 21.4.



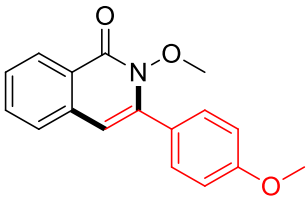
4j 2-ethoxy-3-phenylisoquinolin-1(2*H*)-one

White solid, 40.1 mg, yield: 90% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.1 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.54 (d, J = 7.9 Hz, 1H), 7.51 – 7.45 (m, 4H), 6.48 (s, 1H), 3.95 (d, J = 7.0 Hz, 2H), 1.03 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 142.6, 135.8, 132.8, 132.4, 129.4, 129.1, 128.0, 127.8, 126.6, 126.3, 126.2, 106.5, 71.8, 13.0. HRMS (ESI): calculated for $C_{17}H_{16}NO_2^+$ 266.1176, found 266.1175.



4k (3aS)-6-methoxy-5-phenyl-6,7a-dihydrothieno[2,3-c]pyridin-7(3a*H*)-one

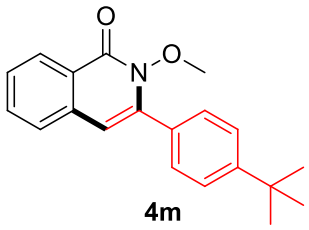
White solid, 36.0 mg, yield: 89% (purified by silica gel chromatography using PE/EA/Et_3N 60:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 5.1 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.49 – 7.45 (m, 3H), 7.22 (d, J = 5.2 Hz, 1H), 6.61 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 143.7, 143.5, 133.9, 132.6, 129.9, 129.3, 129.3, 128.2, 124.3, 103.3, 63.8. HRMS (ESI): calculated for $C_{14}H_{12}NO_2S^+$ 258.0583, found 258.0584.



4l 2-methoxy-3-(4-methoxyphenyl)isoquinolin-1(2*H*)-one[6]

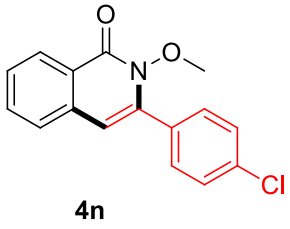
White solid, 41.3 mg, yield: 73% (purified by silica gel chromatography using PE/EA/Et_3N 40:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.1 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.59 – 7.55 (m, 2H), 7.51 (d, J = 7.9 Hz, 1H), 7.49 – 7.45 (m, 1H), 6.99 – 6.97 (m, 2H), 6.44 (s, 1H), 3.87 (s, 3H), 3.69

(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.8, 141.9, 135.9, 132.4, 130.7, 127.7, 126.4, 126.1, 124.8, 113.6, 106.2, 63.2, 55.3.



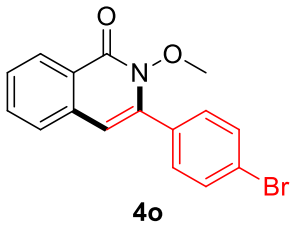
4m 3-(4-(*tert*-butyl)phenyl)-2-methoxyisoquinolin-1(2*H*)-one

White solid, 51.5 mg, yield: 84% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.1 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.49 – 7.46 (m, 3H), 6.47 (s, 1H), 3.71 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 152.4, 142.1, 135.8, 132.4, 129.6, 128.9, 127.7, 126.4, 126.2, 126.1, 125.1, 106.5, 63.4, 34.7, 31.2. HRMS (ESI): calculated for $C_{20}H_{22}NO_2^+$ 308.1645, found 308.1643.



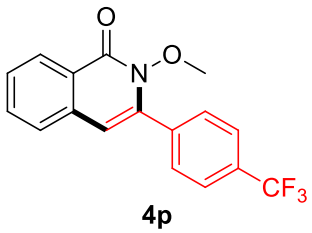
4n 3-(4-chlorophenyl)-2-methoxyisoquinolin-1(2*H*)-one[6]

White solid, 37.0 mg, yield: 65% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.1 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.59 – 7.57 (m, 2H), 7.55 – 7.49 (m, 2H), 7.46 – 7.44 (m, 2H), 6.47 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158. 6, 140.9, 135.5, 135.4, 132.6, 130.9, 130.6, 128.5, 127.8, 126.9, 126.4, 126.3, 106.8, 63.4.



4o 3-(4-bromophenyl)-2-methoxyisoquinolin-1(2*H*)-one[6]

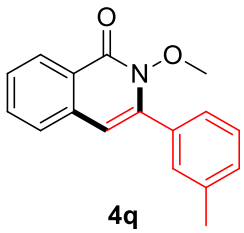
White solid, yield: 75% (purified by silica gel chromatography using PE/EA/Et_3N 80:6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.54 – 7.50 (m, 4H), 6.46 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 140.9, 135.5, 132.6, 131.5, 131.4, 130.8, 127.8, 126.9, 126.4, 126.3, 123.7, 106.8, 63.5.



4p 2-methoxy-3-(4-(trifluoromethyl)phenyl)isoquinolin-1(2*H*)-one

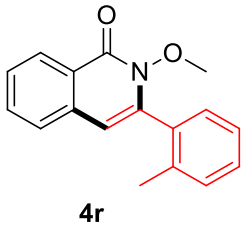
White solid, yield: 75% (purified by silica gel chromatography using PE/EA/Et_3N 40:3:0.5). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.1 Hz, 1H), 7.78 – 7.72 (m, 4H), 7.70 – 7.66 (m, 1H), 7.56 – 7.50 (m, 2H), 6.50 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 140.5, 136.0, 135.4, 132.7, 131.2 (q, J_{C-F} = 32.8 Hz), 129.6, 127.8, 127.2, 126.6, 126.4, 125.2 (q, J_{C-F} = 3.7 Hz), 123.8 (q, J_{C-F} = 273.3 Hz) 107.4, 63.5. HRMS (ESI): calculated for $C_{17}H_{13}F_3NO_2^+$ 320.0893, found 320.0890.



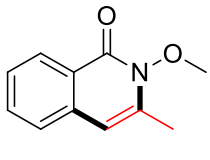
4q 2-methoxy-3-(*m*-tolyl)isoquinolin-1(2*H*)-one

White solid, yield: 88% (purified by silica gel chromatography using PE/EA/Et_3N 40:3:0.5). ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.1 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.42 (m, 2H), 7.35 (t, J = 7.9 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 6.46 (s, 1H), 3.71 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 142.3, 137.9, 135.8, 132.5, 132.4, 129.9, 129.9, 128.0, 127.7, 126.5, 126.4, 126.2, 126.2, 106.6, 63.4, 21.4. HRMS (ESI): calculated for $C_{17}H_{16}NO_2^+$ 266.1176, found 266.1178.



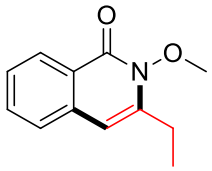
4r 2-methoxy-3-(*o*-tolyl)isoquinolin-1(2*H*)-one

White solid, yield: 65% (purified by silica gel chromatography using PE/EA/Et_3N 40:3:0.5). ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.54 – 7.49 (m, 2H), 7.41 – 7.37 (m, 2H), 7.31 – 7.26 (m, 2H), 6.38 (s, 1H), 3.70 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 142.2, 138.1, 135.8, 132.6, 132.4, 129.9, 129.5, 129.4, 127.8, 126.6, 126.5, 126.1, 125.4, 106.2, 63.7, 19.9. HRMS (ESI): calculated for $C_{17}H_{16}NO_2^+$ 266.1176, found 266.1177.



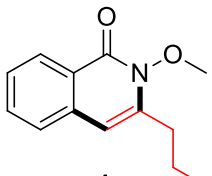
4s 2-methoxy-3-methylisoquinolin-1(2*H*)-one[6]

White solid, 34.1 mg, yield: 90% (purified by silica gel chromatography using PE/EA/Et_3N 60:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.9 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.43 – 7.39 (m, 2H), 6.26 (s, 1H), 4.08 (s, 3H), 2.44 (d, J = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 139.1, 135.9, 132.2, 127.5, 125.8, 125.7, 125.2, 104.2, 63.5, 17.1.



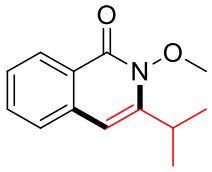
4t 3-ethyl-2-methoxyisoquinolin-1(2*H*)-one

White solid, 36.0 mg, yield: 89% (purified by silica gel chromatography using PE/EA/Et_3N 60:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.1, 1H), 7.60 – 7.56 (m, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 6.24 (s, 1H), 4.07 (s, 3H), 2.76 (q, J = 7.4 Hz, 2H), 1.32 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 144.4, 136.0, 132.2, 127.4, 125.8, 125.7, 125.5, 102.4, 63.7, 23.5, 12.3. HRMS (ESI): calculated for $C_{12}H_{14}NO_2^+$ 204.1019, found 204.1027.



4u 2-methoxy-3-propylisoquinolin-1(2*H*)-one

White solid, 29.6 mg, yield: 68% (purified by silica gel chromatography using PE/EA/Et_3N 60:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.1 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.44 – 7.37 (m, 2H), 6.24 (s, 1H), 4.07 (s, 3H), 2.71 – 2.64 (t, J = 7.3 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 142.8, 135.9, 132.2, 127.4, 125.8, 125.7, 125.4, 103.5, 63.7, 32.52, 21.4, 13.7. HRMS (ESI): calculated for $C_{13}H_{16}NO_2^+$ 218.1176, found 266.1183.

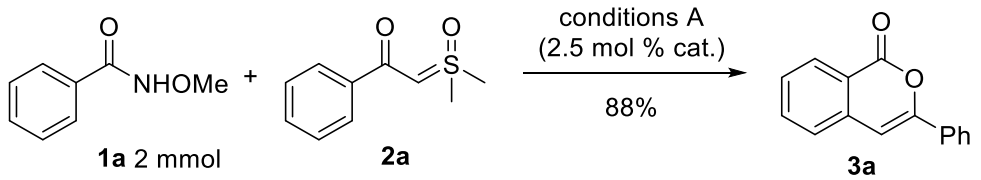


4v 3-isopropyl-2-methoxyisoquinolin-1(2*H*)-one

White solid, 37.5 mg, yield: 86% (purified by silica gel chromatography using PE/EA/Et_3N 60:6:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.1 Hz, 1H), 7.63 - 7.59 (m, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.44 - 7.40 (m, 1H), 6.30 (s, 1H), 4.09 (s, 3H), 3.21 (hept, J = 6.8 Hz, 1H), 1.35 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.8, 136.0, 132.1, 127.4, 125.8, 125.7, 125.6, 100.7, 63.9, 28.3, 22.1. HRMS (ESI): calculated for $C_{13}H_{16}NO_2^+$ 218.1176, found 266.1189.

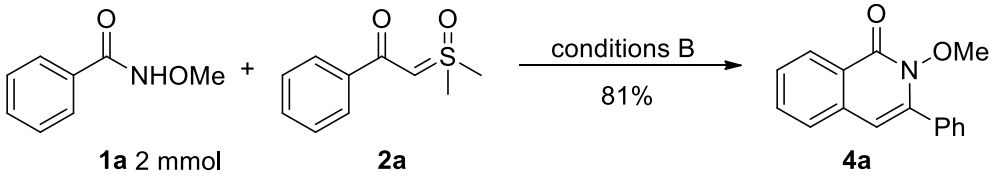
V. Larger-Scale Preparation and Transformations

(a) Larger-Scale Preparation of **3a**



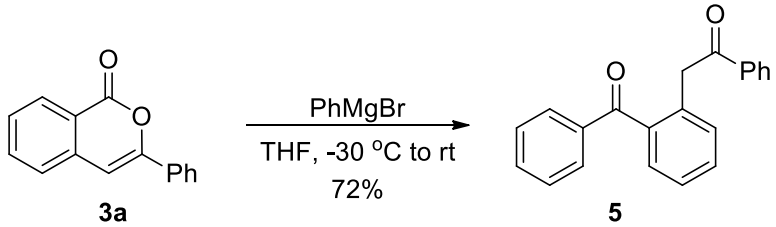
A pressure tube was charged with $[RhCp^*Cl_2]_2$ (31 mg, 2.5 mol %), CsOAc (115 mg, 30 mol %), HOPiv (408 mg, 0.4 mmol), *N*-methoxybenzamides (**1a**, 2 mmol), sulfoxonium ylides (**2a**, 4 mmol) and DCE (40 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 24 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford product as a white solid (391 mg, yield: 88%).

(b) Larger-Scale Preparation of **4a**

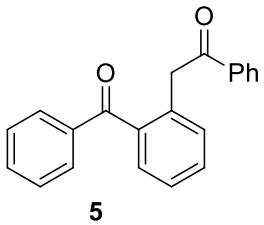


A pressure tube was charged with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (83 mg, 5 mol %), $Zn(OTf)_2$ (364 mg, 50 mol %), *N*-methoxybenzamides (**1a**, 2 mmol), sulfoxonium ylides (**2a**, 4 mmol) and DCE (40 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 24 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product as a white solid (410 mg, yield: 81%).

(c) Transformations of **3a**

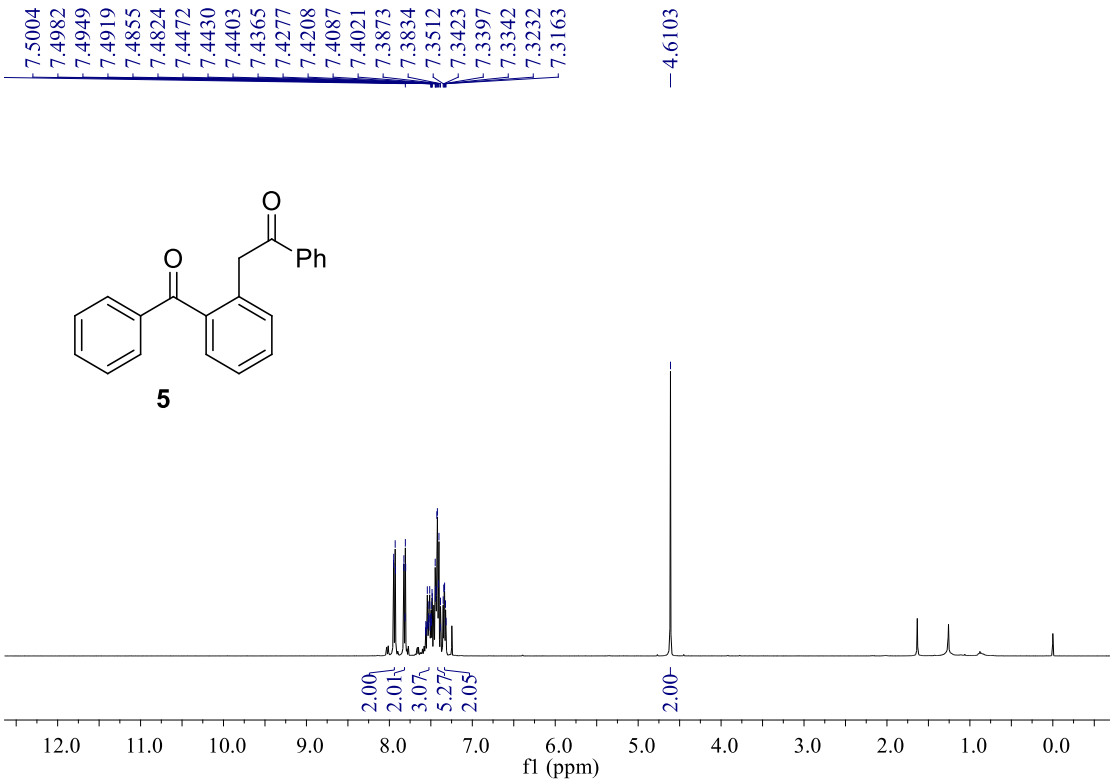


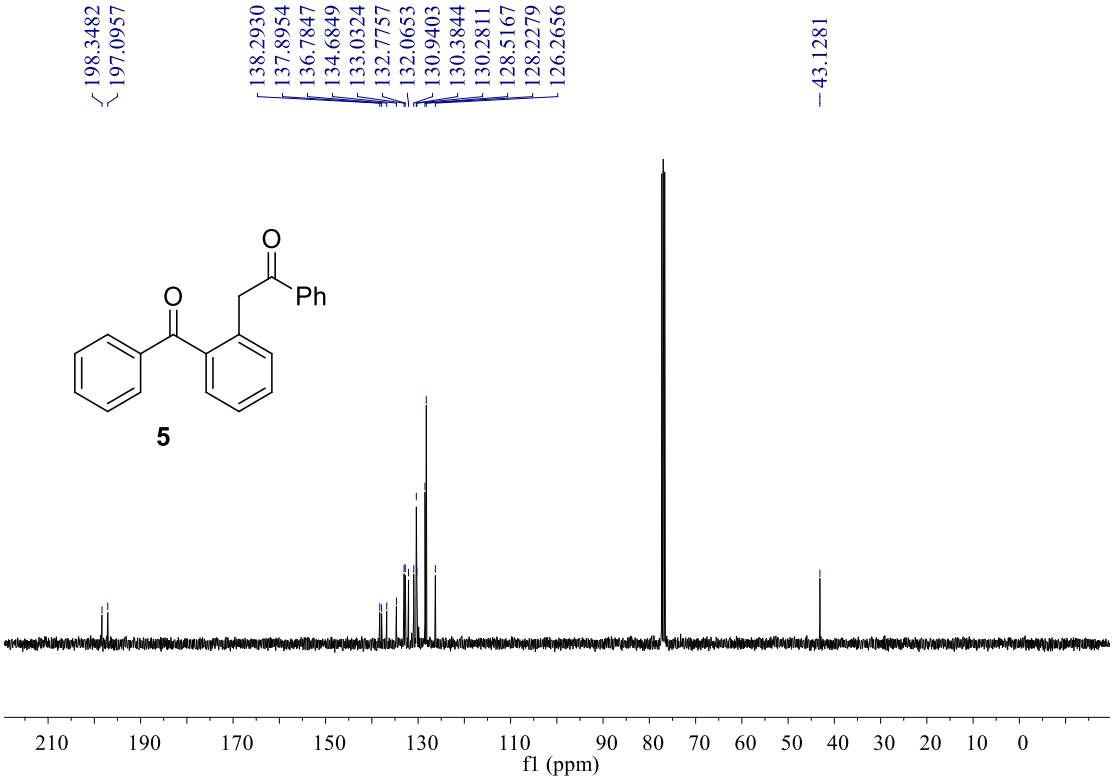
To a solution of **3a** (111.1 mg, 0.5 mmol) in THF (2 mL) was added phenyl Grignard reagent (0.7 mL, 1 mol/L in THF) at -30 °C, and the reaction was stirred at room temperature overnight. The reaction was then quenched with aqueous NH_4Cl, extracted between water and DCM. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash chromatography to give the products as a yellow liquid (108 mg, yield: 72%).[8]



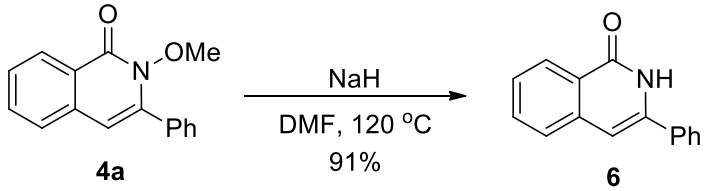
2-(2-benzoylphenyl)-1-phenylethanone[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.84 – 7.80 (m, 2H), 7.56 – 7.48 (m, 3H), 7.44 – 7.38 (m, 5H), 7.36 – 7.31 (m, 2H), 4.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 197.1, 138.3, 137.9, 136.8, 134.7, 133.0, 132.8, 132.1, 130.9, 130.4, 130.3, 128.5, 128.2, 126.3, 43.1.


7.5004
7.4982
7.4949
7.4919
7.4855
7.4824
7.4472
7.4430
7.4403
7.4365
7.4277
7.4208
7.4087
7.4021
7.3873
7.3834
7.3512
7.3423
7.3397
7.3342
7.3232
7.3163
4.6103
O
O
Ph
5
2.00
2.01
3.07
5.27
2.05
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

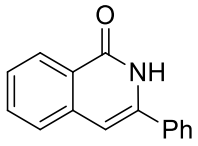

198.3482
197.0957
138.2930
137.8954
136.7847
134.6849
133.0324
132.7757
132.0653
130.9403
130.3844
130.2811
128.5167
128.2279
126.2656
43.1281
O
O
Ph
5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(d) Transformations of **4a**



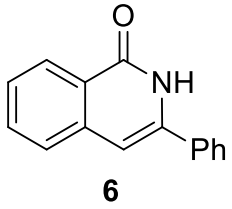
4a **6**

NaH (0.6 mmol, 60% in mineral oil) was added into a stirred solution of *N*-methoxyl isoquinolone **4a** (0.2 mmol) in DMF (1 mL), and the resulting mixture was heated at 120 °C for 1 h. After the reaction was completed, the reaction mixture was allowed to cool down to room temperature, and H_2O (8 mL) was added, followed by extraction with DCM (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography to give the products as a white solid (40.2 mg, yield: 91%).[6,9]

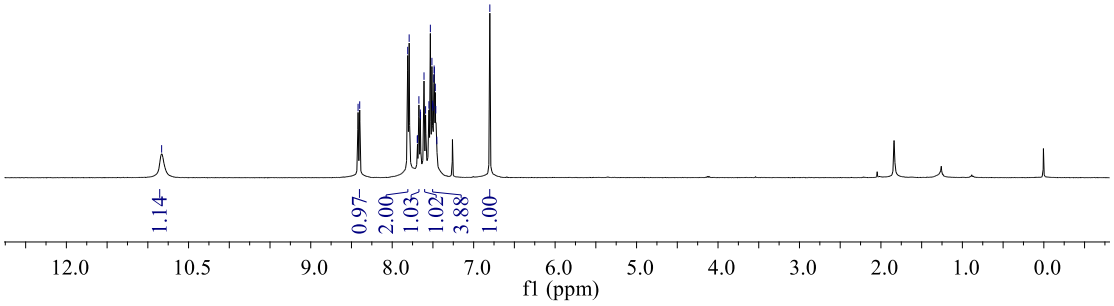


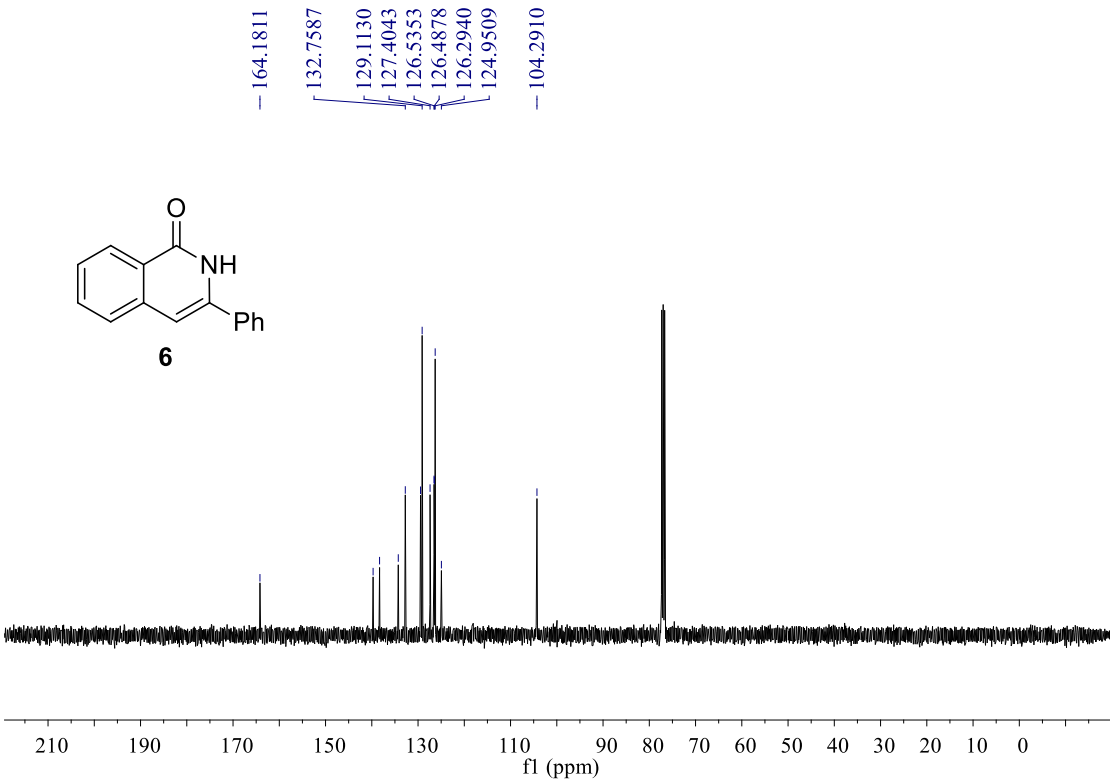
6 3-phenylisoquinolin-1(2*H*)-one[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (brs, 1H), 8.41 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.3 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.55 – 7.45 (m, 4H), 6.80 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 139.7, 138.3, 134.3, 132.8, 129.5, 129.1, 127.4, 126.5, 126.5, 126.3, 125.0, 104.3.



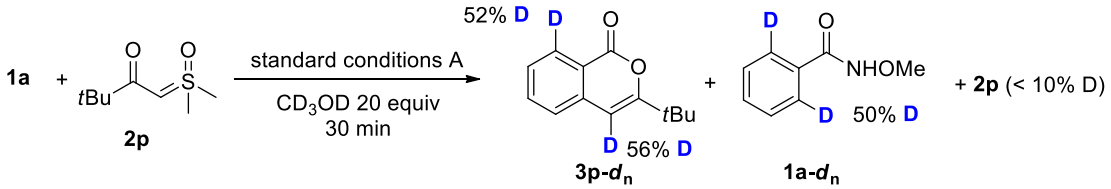
6



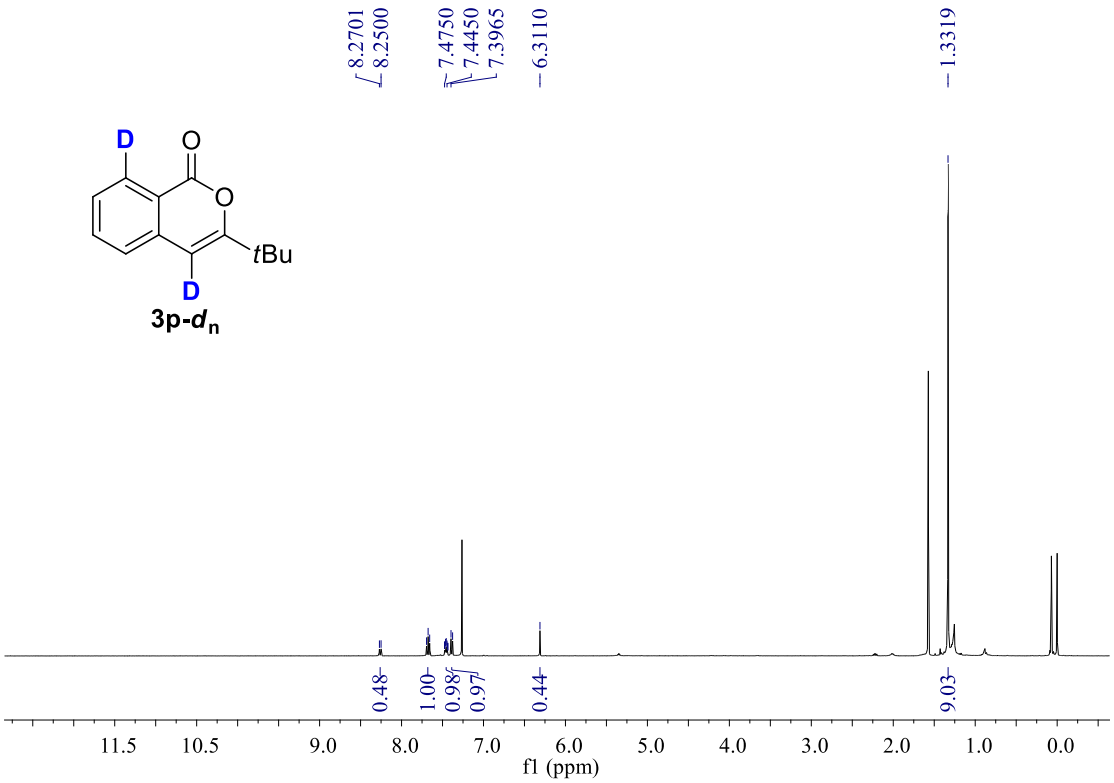


VI. Mechanism Study

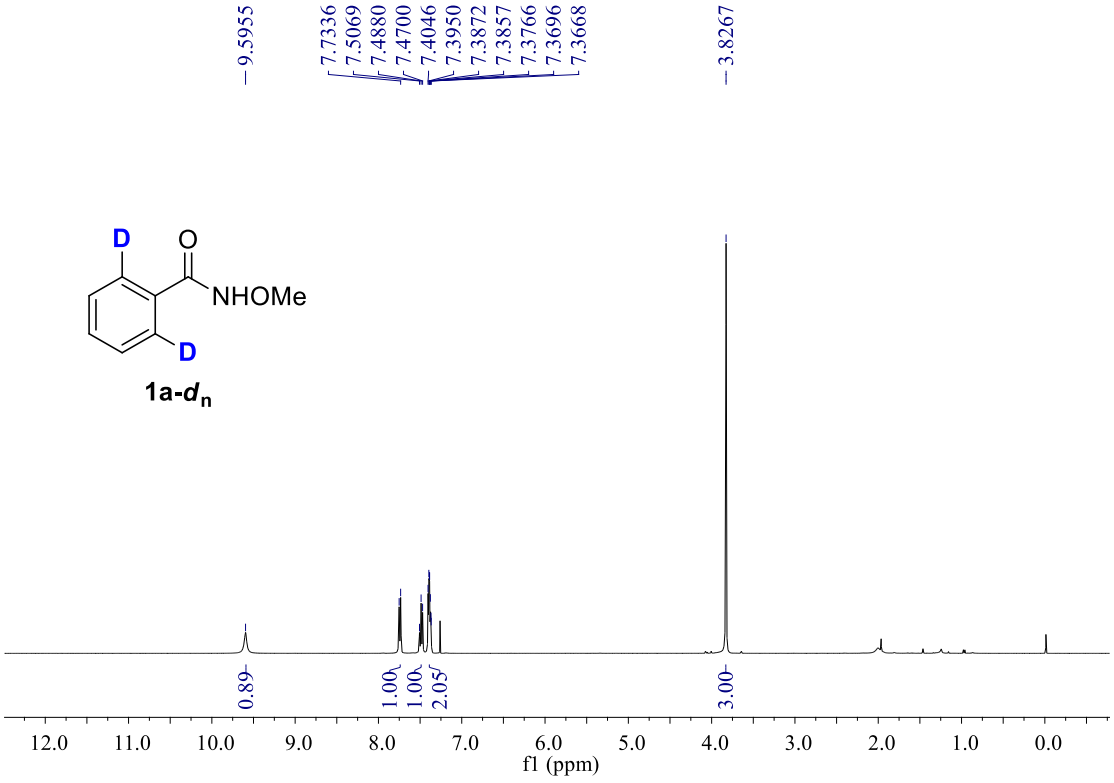
(a) Deuterium Labeling Experiments



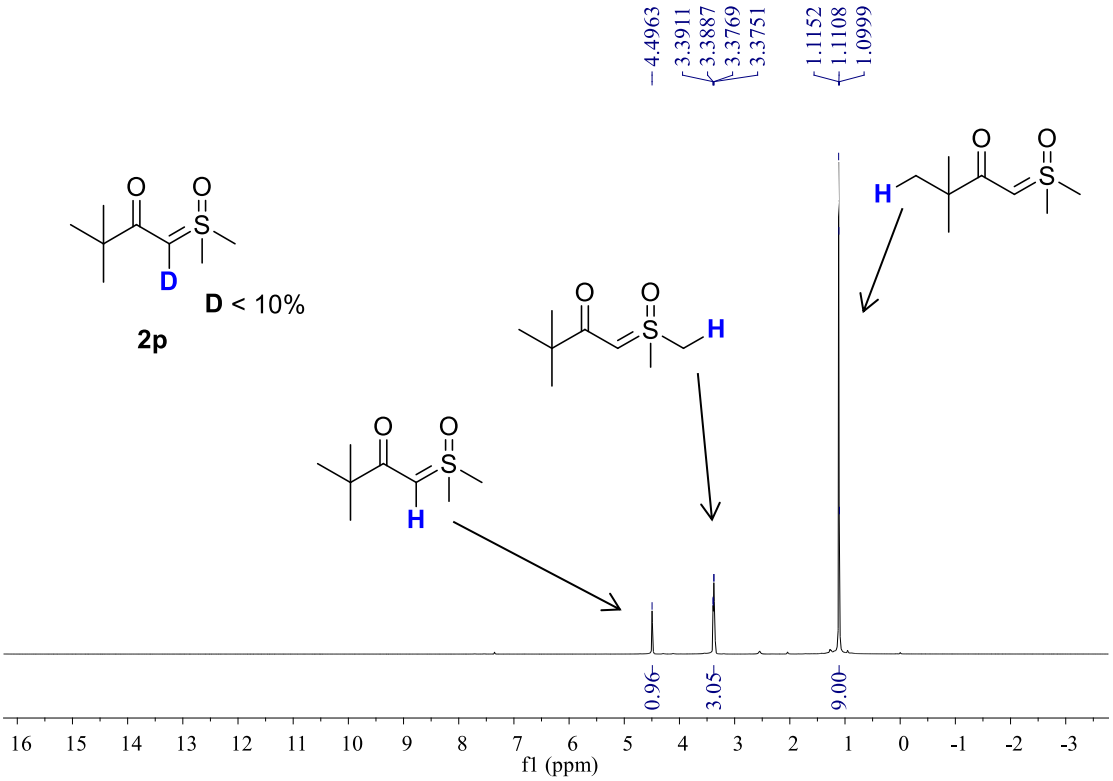
A pressure tube was charged with $[RhCp^*Cl_2]_2$ (4.9 mg, 4 mol %), CsOAc (11.6 mg, 30 mol %), HOPiv (40.8 mg, 0.4 mmol), *N*-methoxybenzamide (**1a**, 0.2 mmol), sulfoxonium ylide (**2p**, 0.4 mmol), CD_3OD (144 mg, 4 mmol) and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 30 min. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the deuterated product (**3p-*d*$_n$**) and the recovered substrates *N*-methoxybenzamides (**1a-*d*$_n$**) and **2p**.

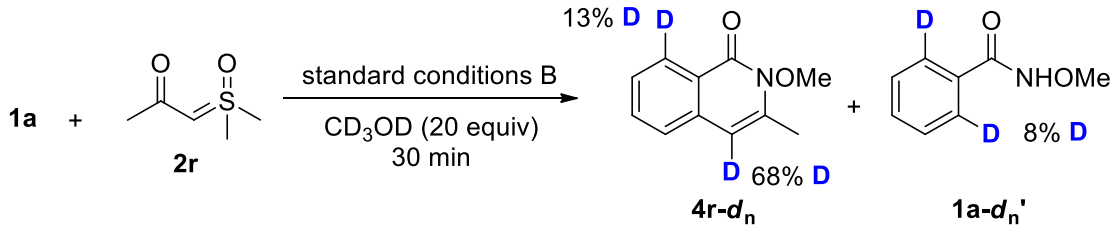

8.2701
8.2500
7.4750
7.4450
7.3965
6.3110
1.3319
D
O
O
tBu
D
0.48
1.00
0.98
0.97
0.44
9.03
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

3p-d_n

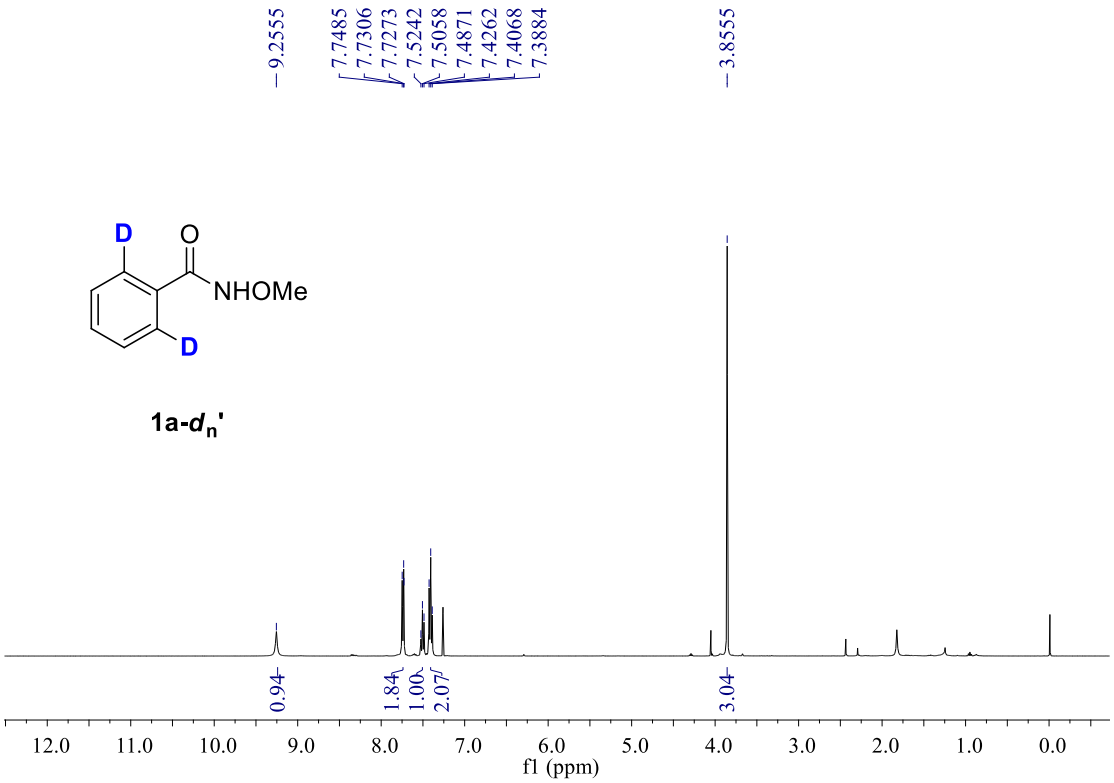

9.5955
7.7336
7.5069
7.4880
7.4700
7.4046
7.3950
7.3872
7.3857
7.3766
7.3696
7.3668
3.8267
D
O
NHOMe
D
0.89
1.00
1.00
2.05
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

1a-d_n

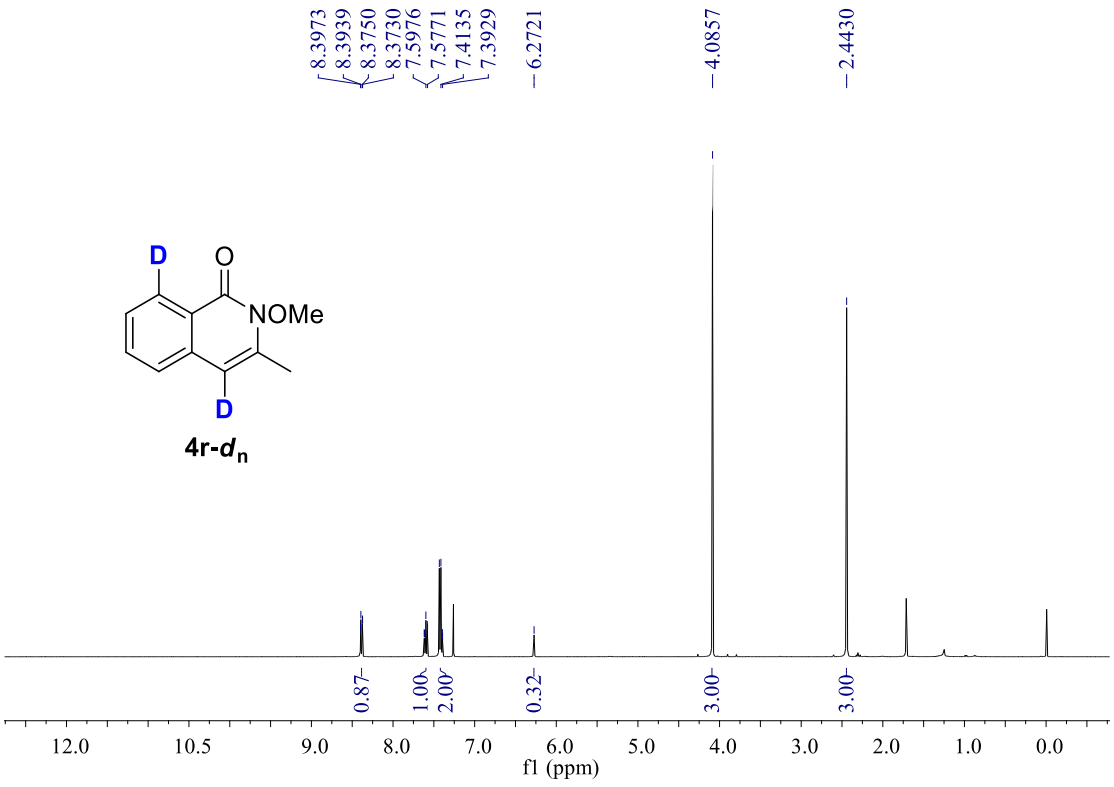




A pressure tube was charged with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8.3 mg, 5 mol %), $Zn(OTf)_2$ (36.4 mg, 50 mol %), *N*-methoxybenzamide (**1a**, 0.2 mmol), sulfoxonium ylide (**2r**, 0.4 mmol), CD_3OD (144 mg, 4 mmol), and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 30 min. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the deuterated product (**4r-*d*$_n$**) and the recovered *N*-methoxybenzamide with H/D exchange (**1a-*d*$_n$'**).

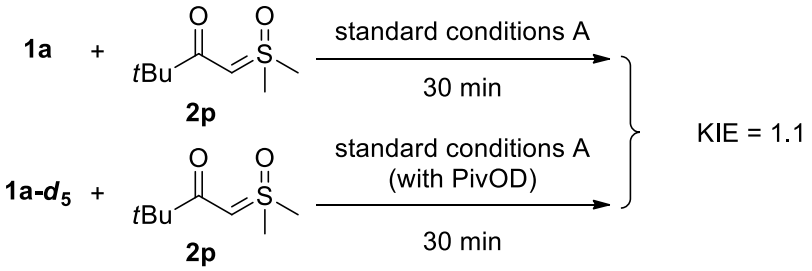

9.2555
7.7485
7.7306
7.7273
7.5242
7.5058
7.4871
7.4262
7.4068
7.3884
3.8555
D
O
NHOMe
D
0.94
1.84
1.00
2.07
3.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

1a-d_n'

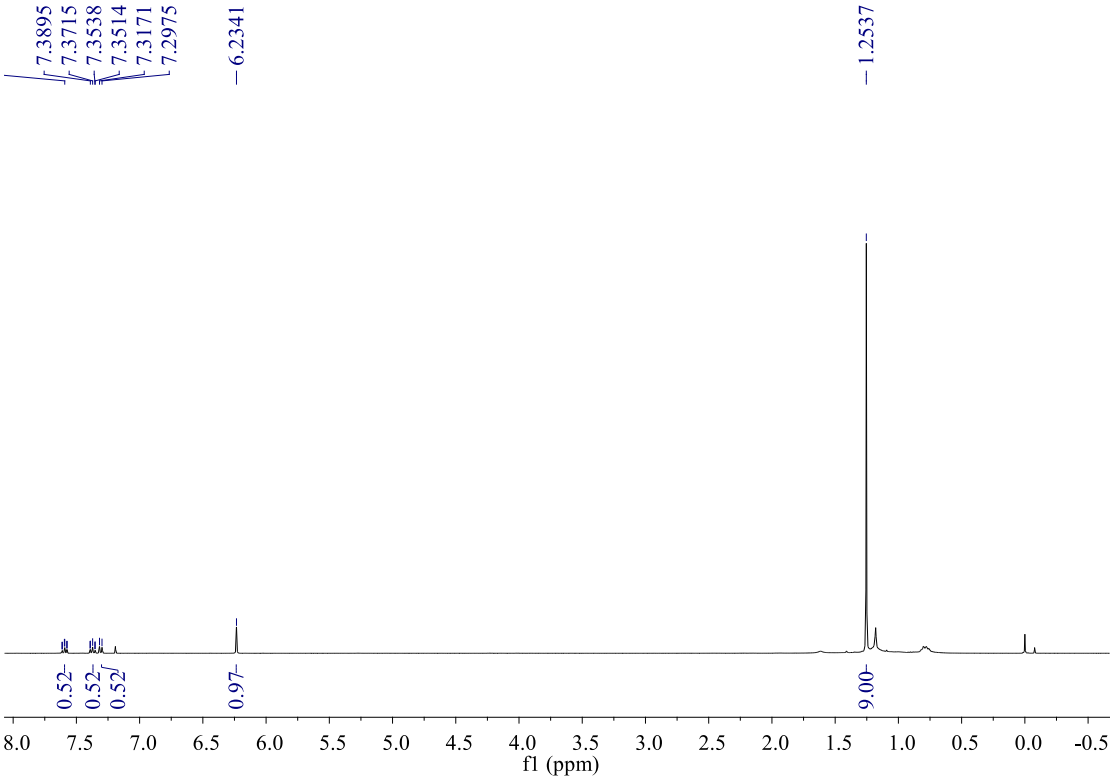

8.3973
8.3939
8.3750
8.3730
7.5976
7.5771
7.4135
7.3929
6.2721
4.0857
2.4430
D
O
NOMe
D
0.87
1.00
2.00
0.32
3.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

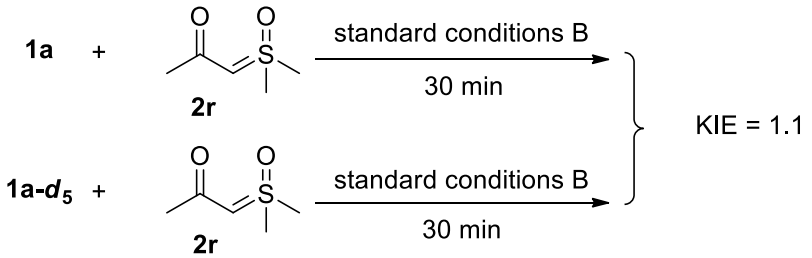
4r-d_n

(b) Kinetic Isotope Effect Experiments



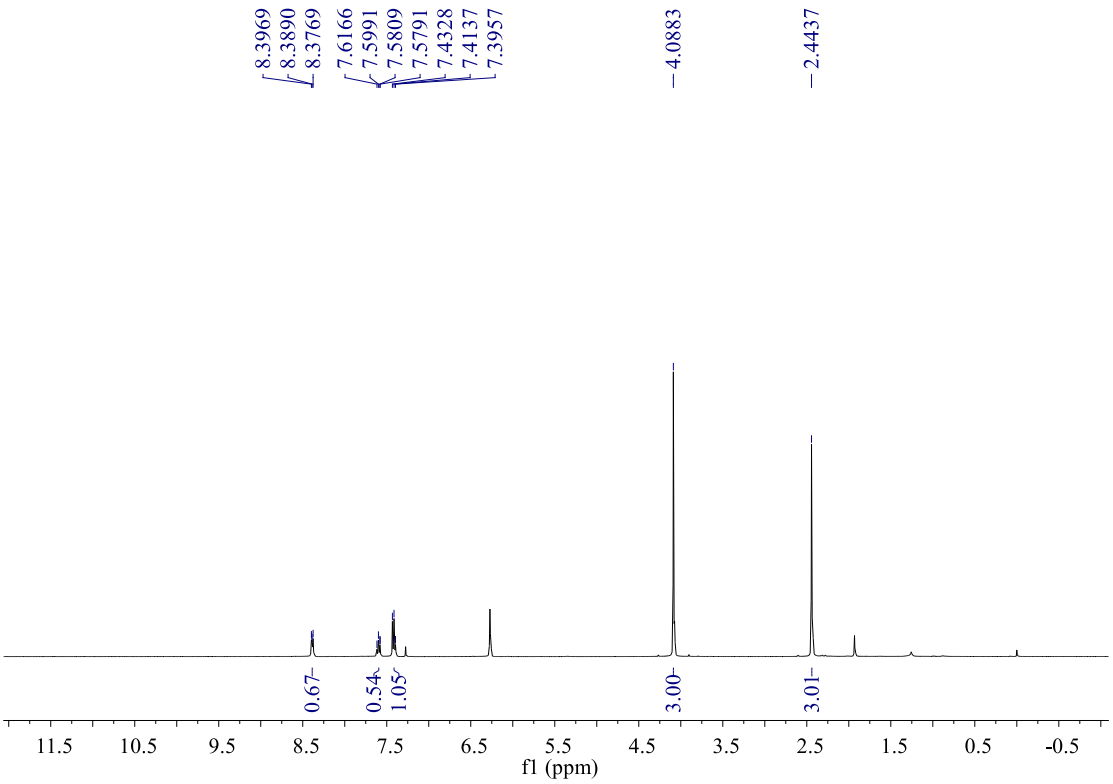
Two pressure tubes were charged with $[RhCp^*Cl_2]_2$ (4.9 mg, 4 mol %), CsOAc (11.6 mg, 30 mol %), HOPiv or DOPiv (0.4 mmol), *N*-methoxybenzamide (**1a** or **1a-*d*$_5$**, 0.4 mmol), sulfoxonium ylide (**2p** , 0.2 mmol) and DCE (4 mL). The reaction mixture was stirred side by side under N_2 condition at 100 °C for 30 min. After that, the reaction was cooled to 0 °C rapidly and was quenched with pentane. The two mixtures were combined and the solvent was removed under vacuum. The residue was purified by silica gel chromatography using PE/EA to afford a mixture of **3p** and **3p-*d*$_4$**. The KIE value was determined to be k_H/k_D = 1.1 on the basis of ^{1}H NMR analysis.



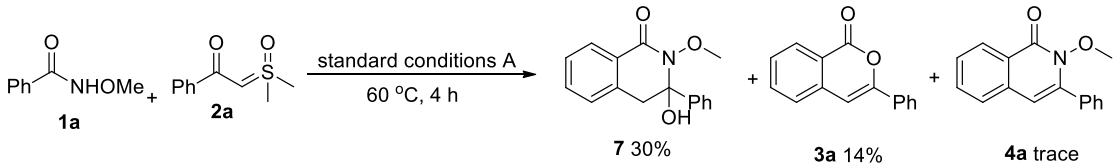


Two pressure tubes were charged with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8.3 mg, 5 mol %), $Zn(OTf)_2$ (36.4 mg, 50 mol %), *N*-methoxybenzamide (**1a** or **1a-*d*$_5$**, 0.2 mmol), sulfoxonium ylide (**2r** , 0.4 mmol), and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 100 °C for 30 min. After that, the

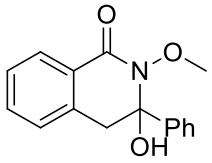
reaction was cooled to 0 °C rapidly and was quenched with pentane. The two mixtures were combined, and the solvent was removed under vacuum. The residue was purified by silica gel chromatography using PE/EA to afford a mixture of **4r** and **4r-*d*$_4$**. The KIE value was determined to be k_H/k_D = 1.1 on the basis of ^{1}H NMR analysis.



(c) Synthesis of intermediate **7**



A pressure tube was charged with $[RhCp^*Cl_2]_2$ (4.9 mg, 4 mol %), CsOAc (11.6 mg, 30 mol %), HOPiv (40.8 mg, 0.4 mmol), *N*-methoxybenzamide (**1a**, 0.2 mmol), sulfoxonium ylide (**2a**, 0.4 mmol) and DCE (4 mL). The reaction mixture was stirred under N_2 condition at 60 °C for 4h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the intermediate **7** and the product **3a**.

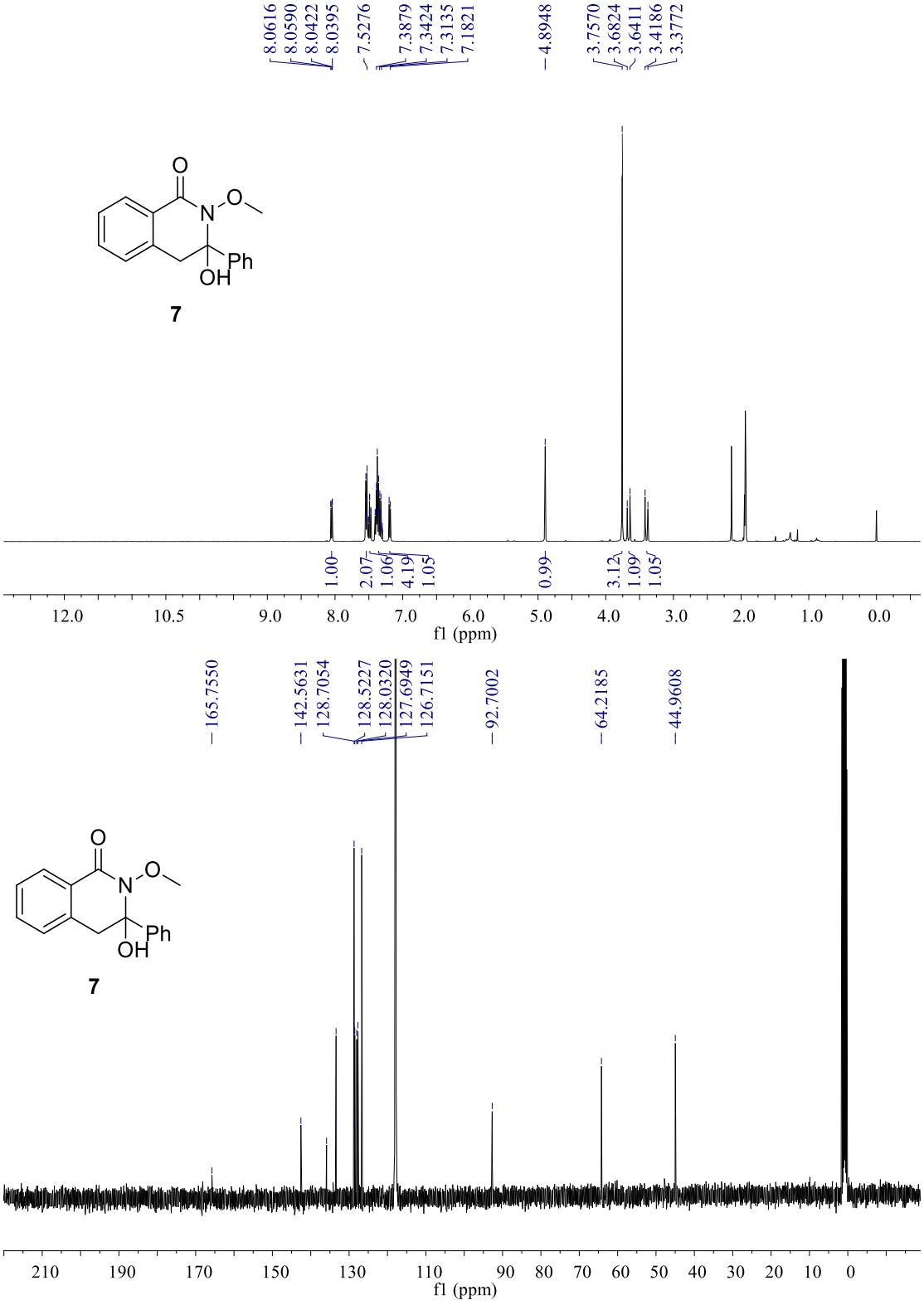


7

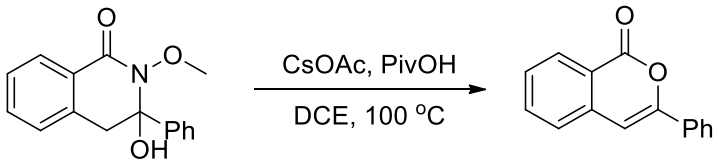
3-hydroxy-2-methoxy-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one

^{1}H NMR (400 MHz, CD_3CN) δ 8.05 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.89 (brs, 1H), 3.76 (s, 3H), 3.66 (d, *J* =

16.5 Hz, 1H), 3.40 (d, J = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 165.8, 142.6, 135.9, 133.4, 128.8, 128.7, 128.7, 128.5, 128.0, 127.7, 126.7, 92.7, 64.2, 45.0. HRMS (ESI): calculated for $C_{16}H_{16}NO_3^+$ 270.1125, found 270.1123.

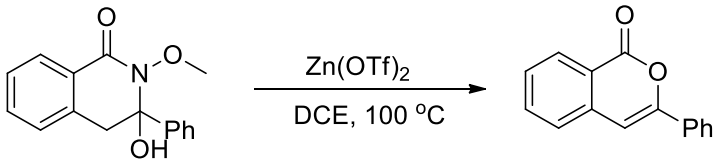


(d) Transformation of **7** to **3a** or **4a**



7 **3a**

The solution of 7 with CsOAc 30 mol % and PivOH 2 equiv in DCE was stirred at 100 °C for 1 h, full conversion was ovserved.



7 **4a**

The solution of 7 with $Zn(OTf)_2$ 50 mol % in DCE was stirred at 100 °C for 1 h, full conversion was ovserved.

VII. Reference

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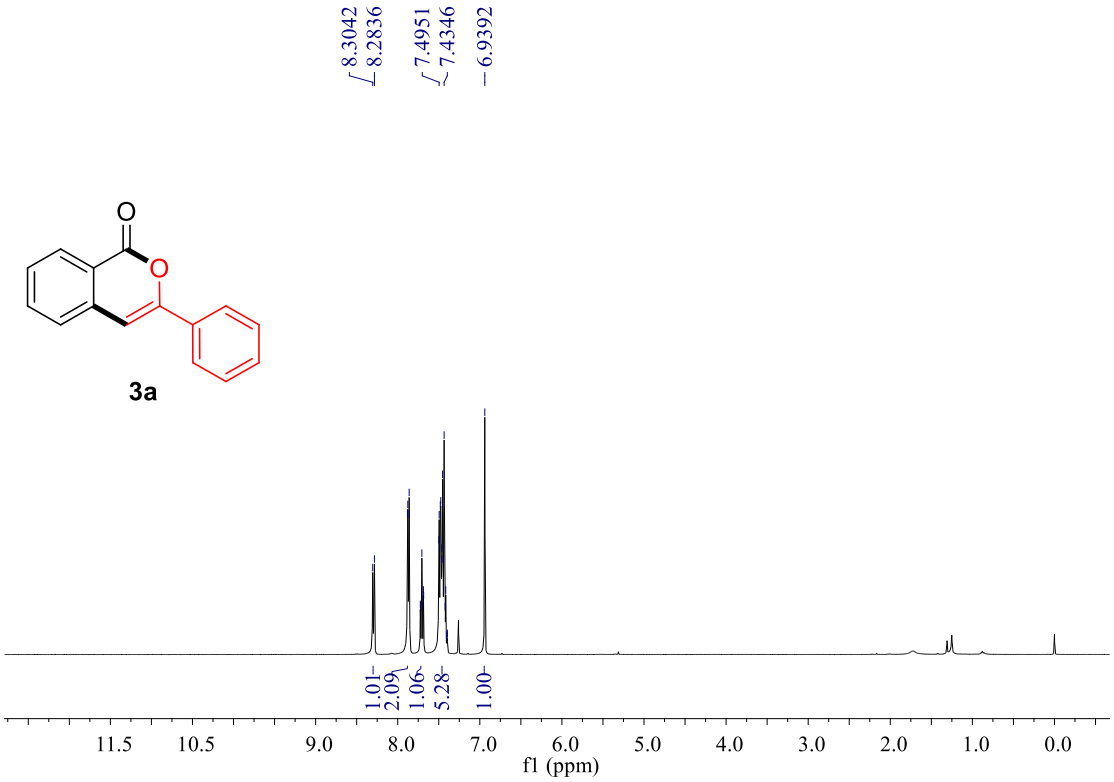
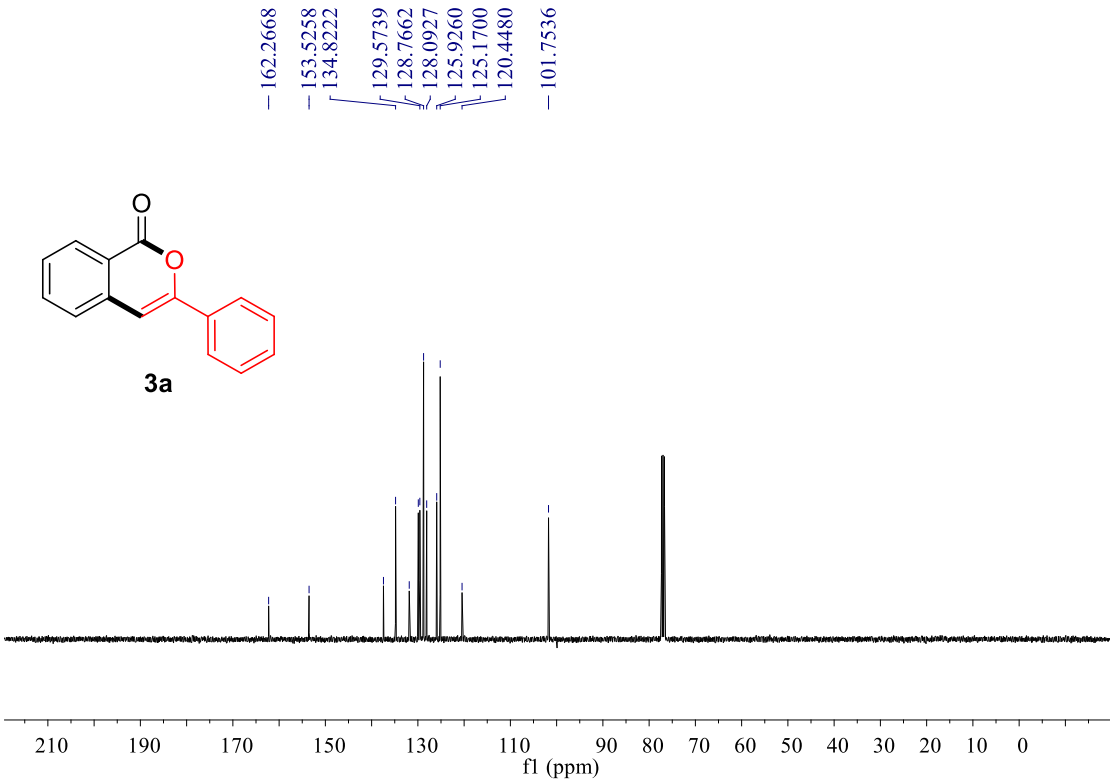
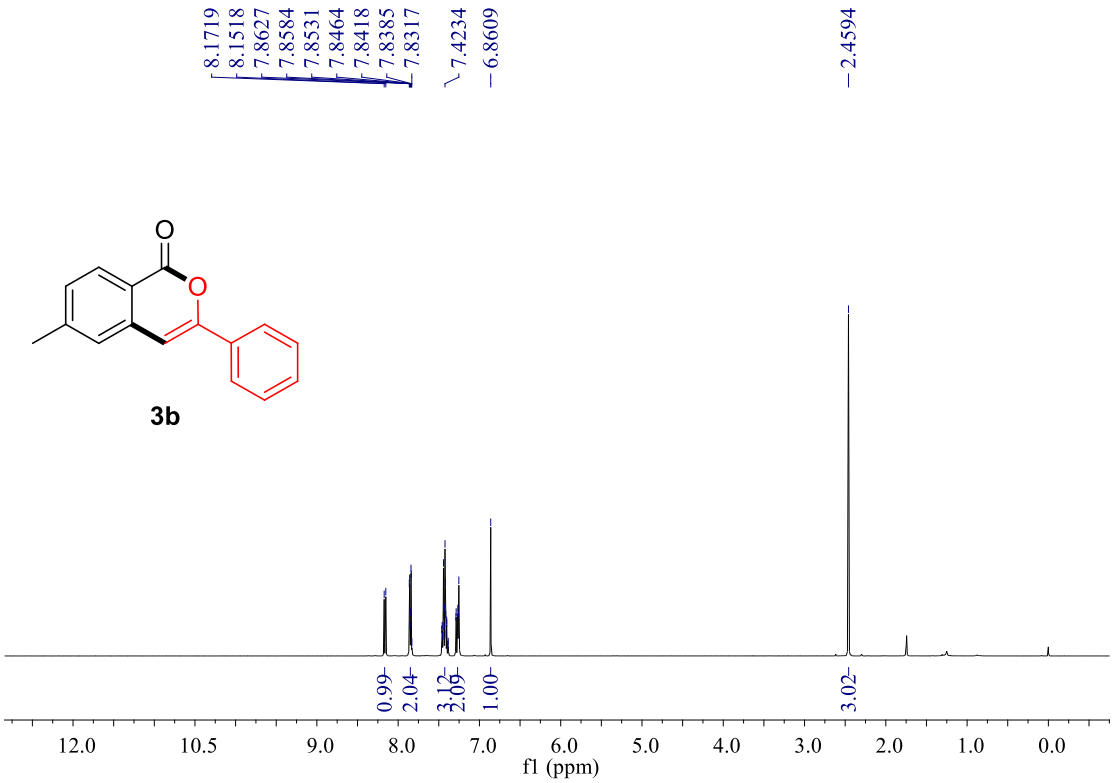
(8) S. Perveen, Z. Zhao, G. Zhang, J. Liu, M. Anwar and X. Fang, *Org. Lett.* 2017, **19**, 2470.

(9) H. Zhong, D. Yang, S. Wang and J. Huang, *Chem. Commun.* 2012, **48**, 3236.

VIII. NMR Spectra of Products



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7.8418
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7.8317
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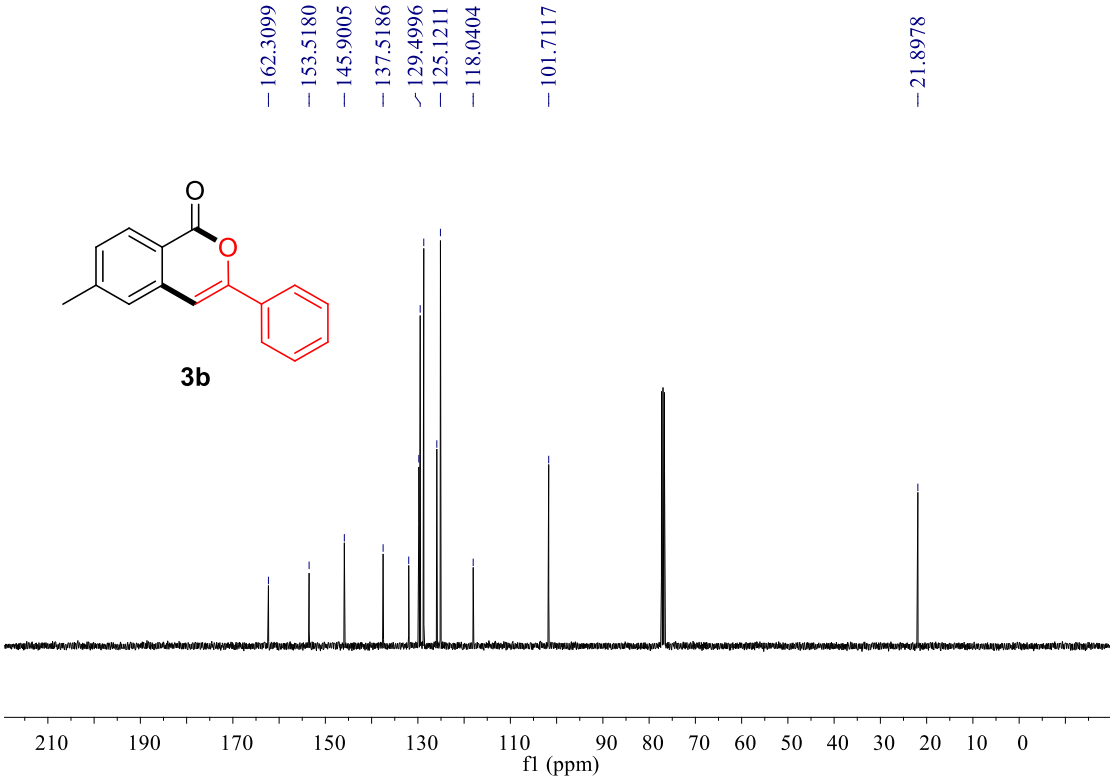
6.8609
2.4594
O
O
3b
0.99
2.04
3.12
2.09
1.00
3.02
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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3b
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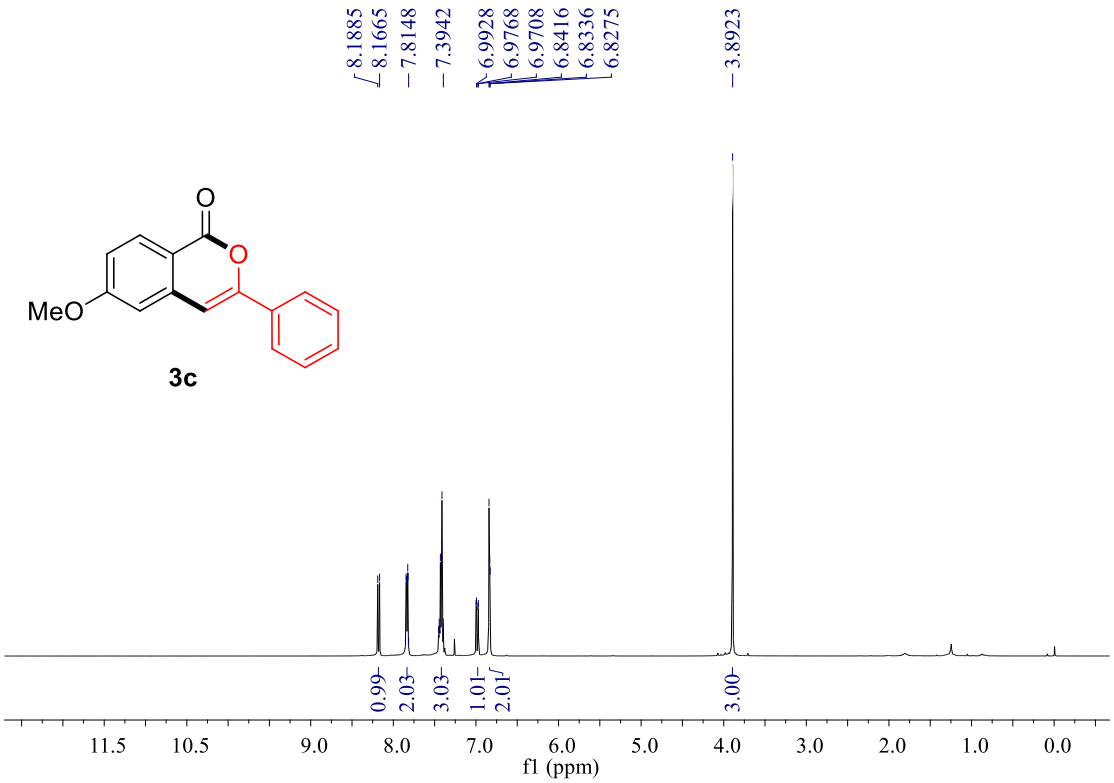
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3942
6.9928
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6.9708
6.8416
6.8336
6.8275
3.8923
O
O
MeO
3c
0.99
2.03
3.03
1.01
2.01
3.00
11.5
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7.0
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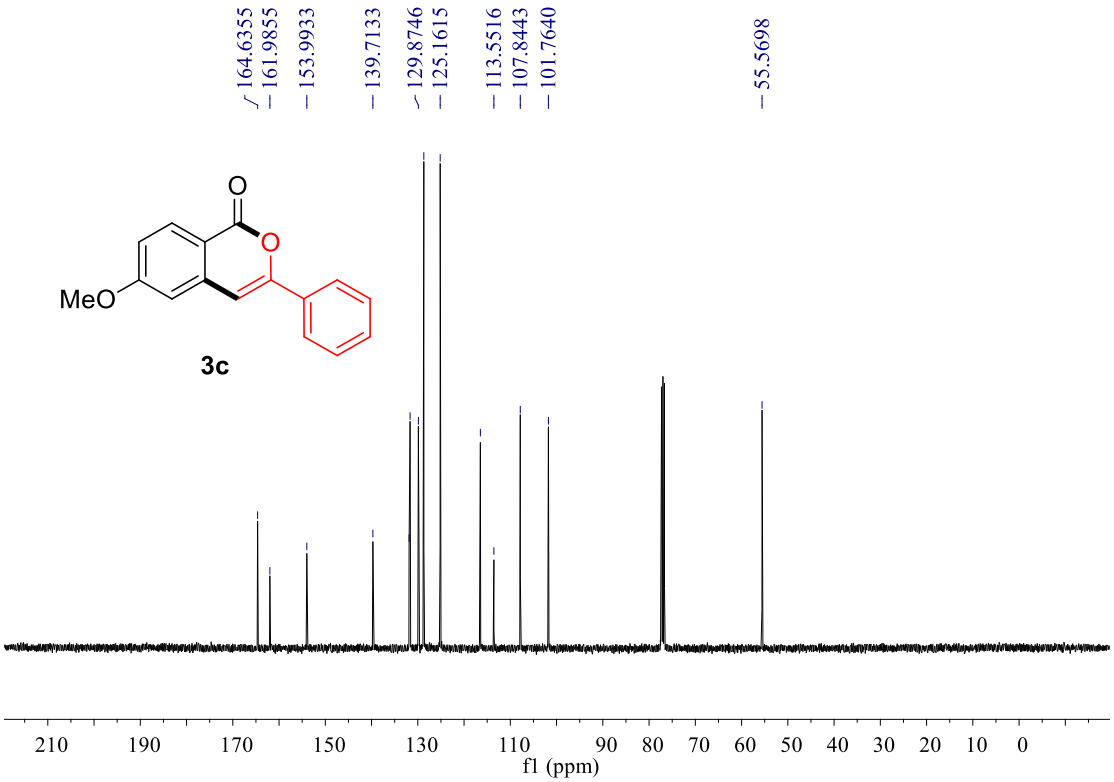
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55.5698
O
O
MeO
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150
130
110
90
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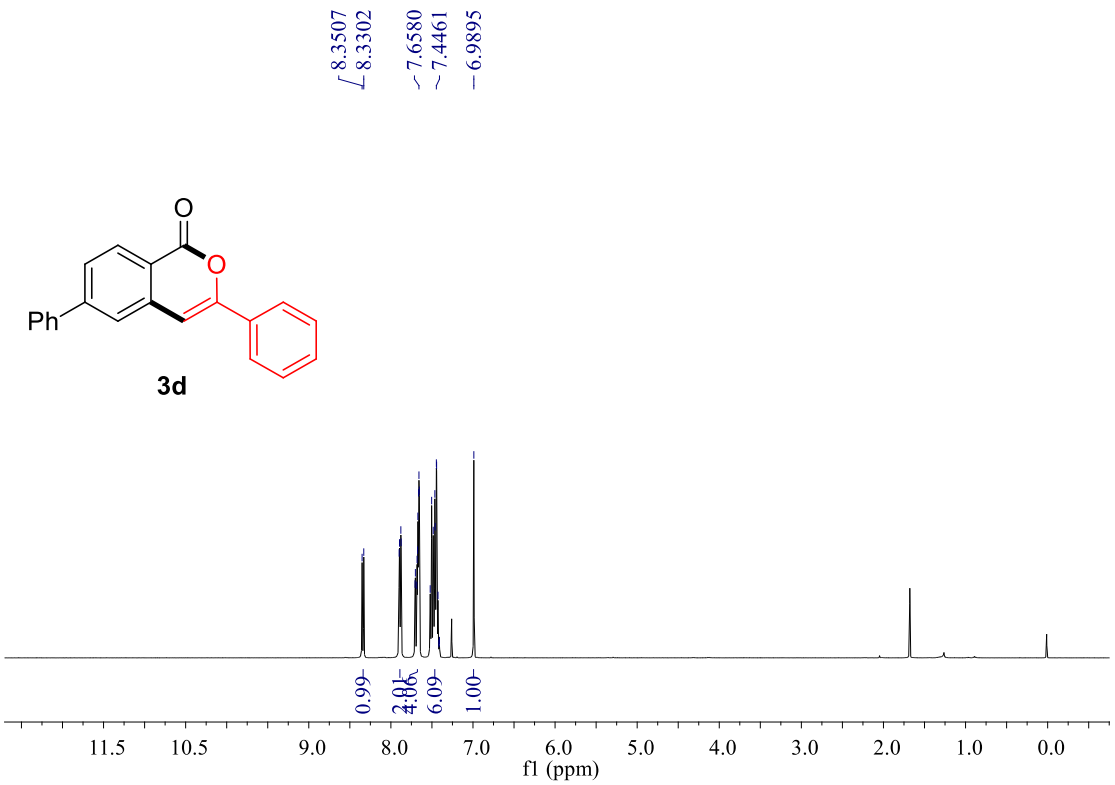
70
60
50
40
30
20
10
0
f1 (ppm)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O
Ph
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6.09
1.00
11.5
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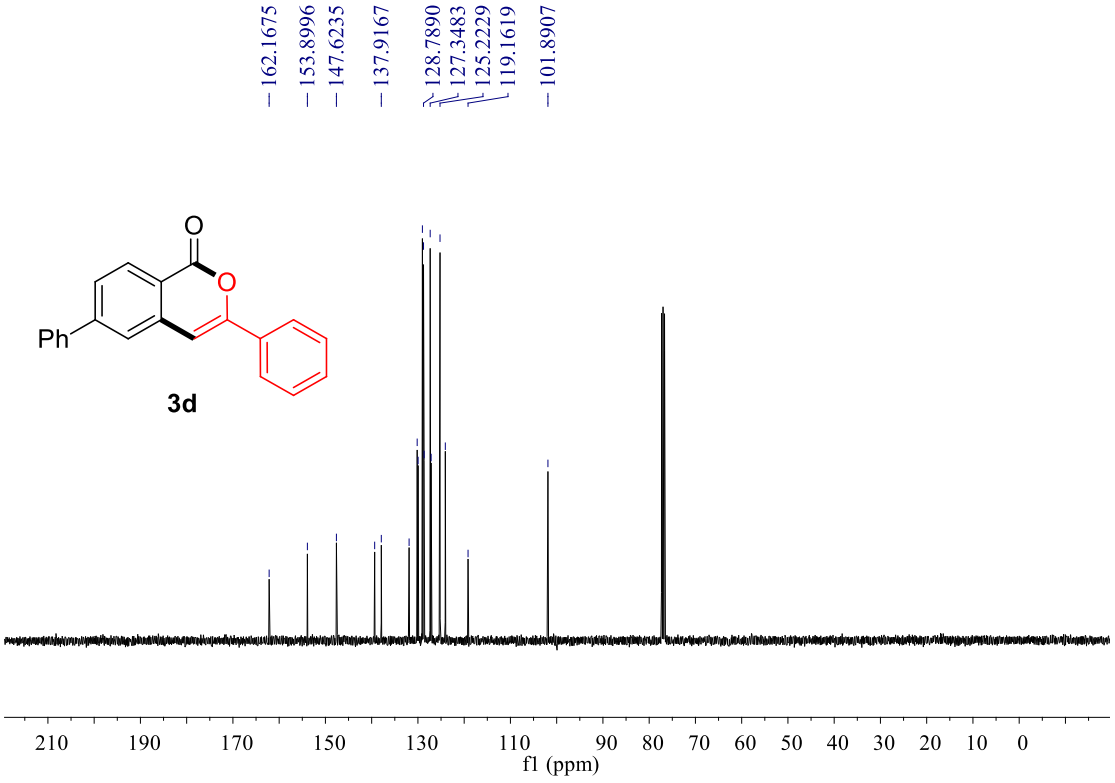
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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O
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170
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30
20
10
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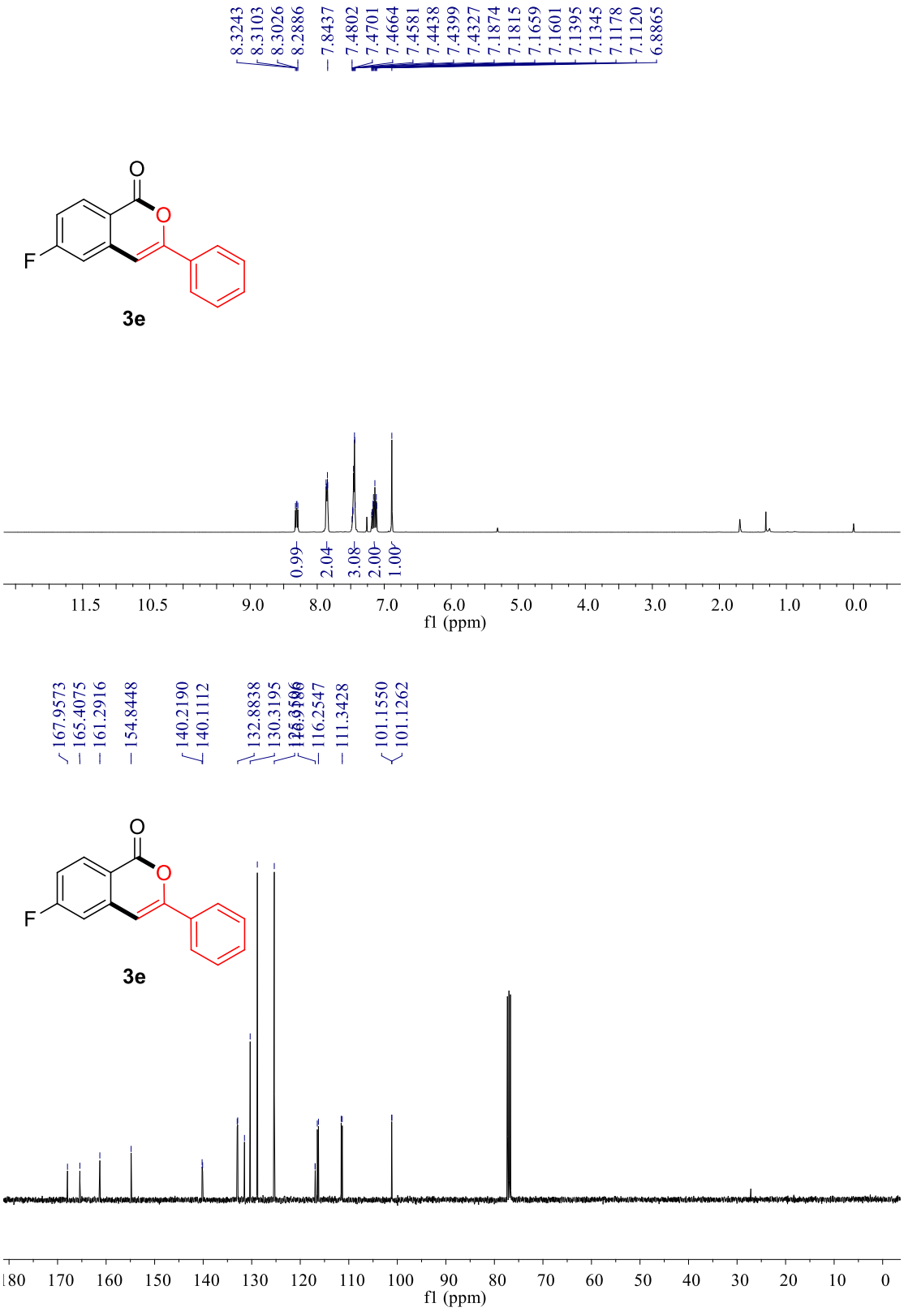
f1 (ppm)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7.4581
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7.4399
7.4327
7.1874
7.1815
7.1659
7.1601
7.1395
7.1345
7.1178
7.1120
6.8865
O
O
F
3e
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2.04
3.08
2.00
1.00
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
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154.8448
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140.1112
132.8838
130.3195
116.2547
111.3428
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O
O
F
3e
180
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130
120
110
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90
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40
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10
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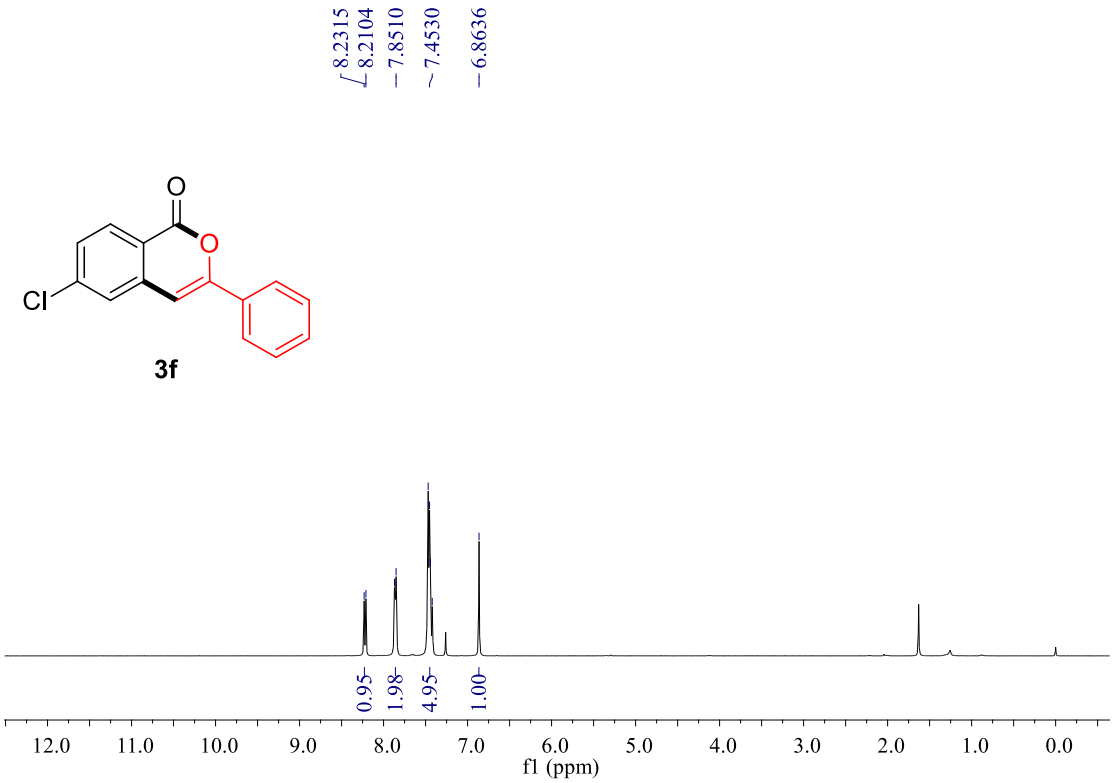
f1 (ppm)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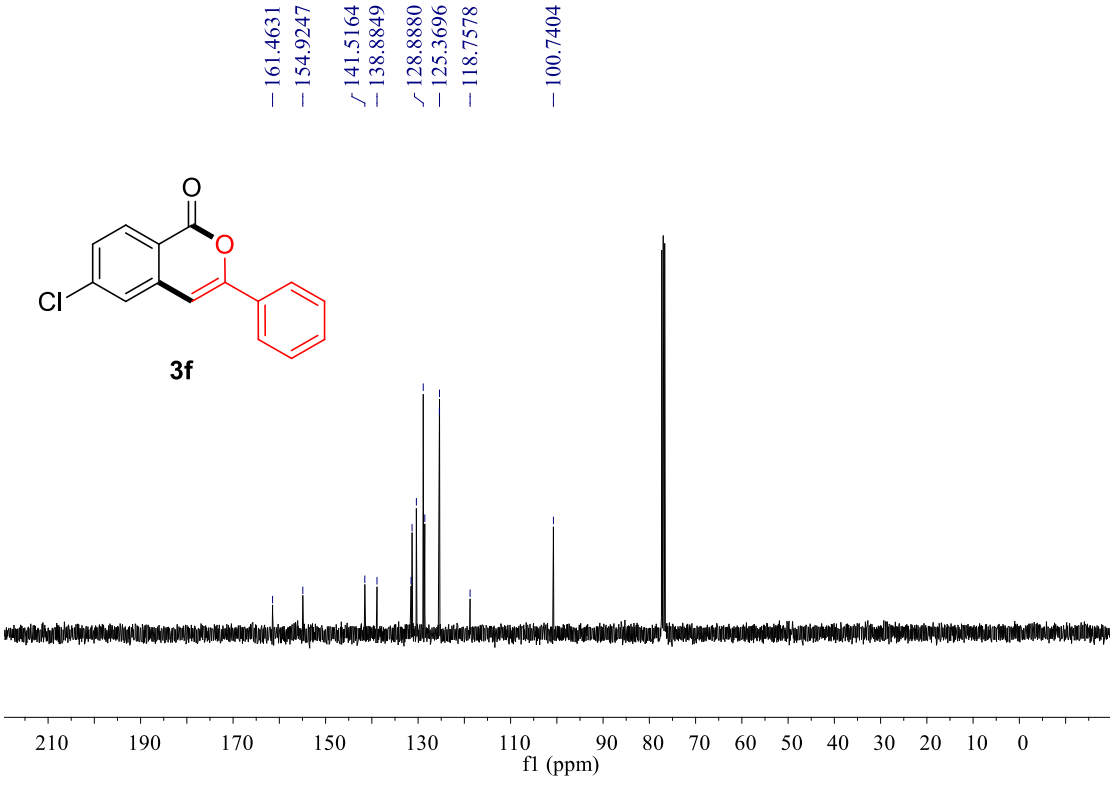
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O
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90
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50
40
30
20
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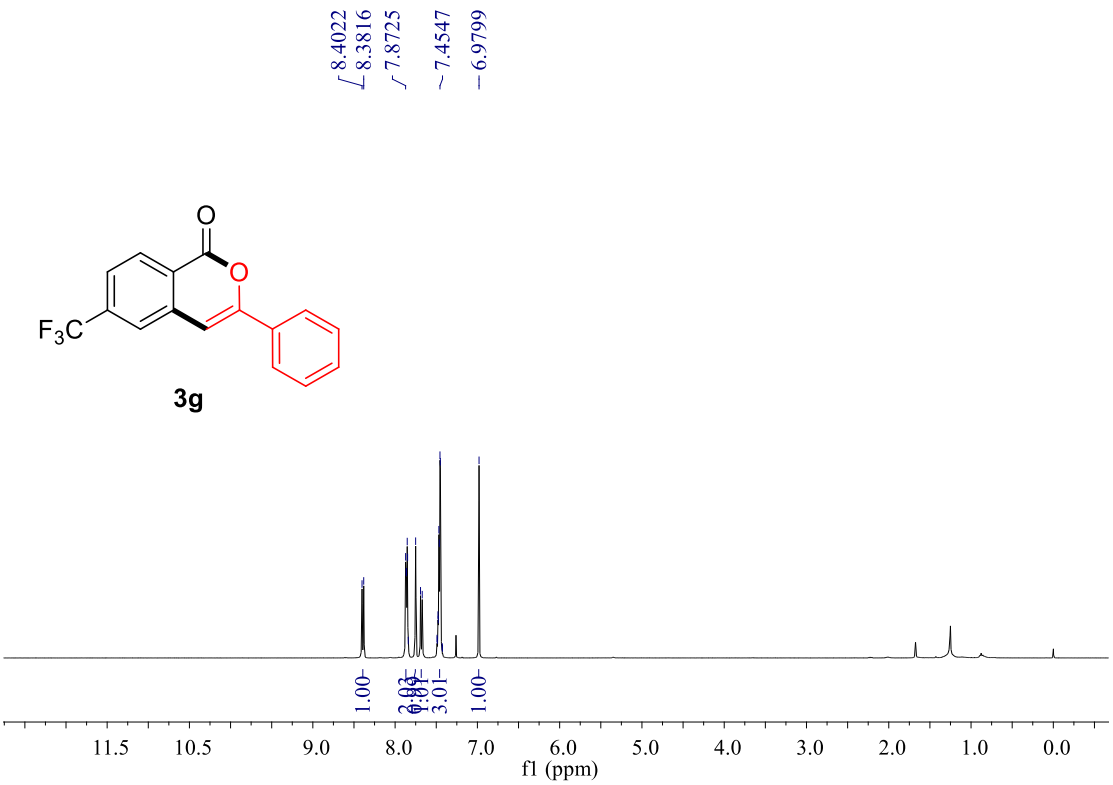
f1 (ppm)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O
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1.01
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1.00
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3.0
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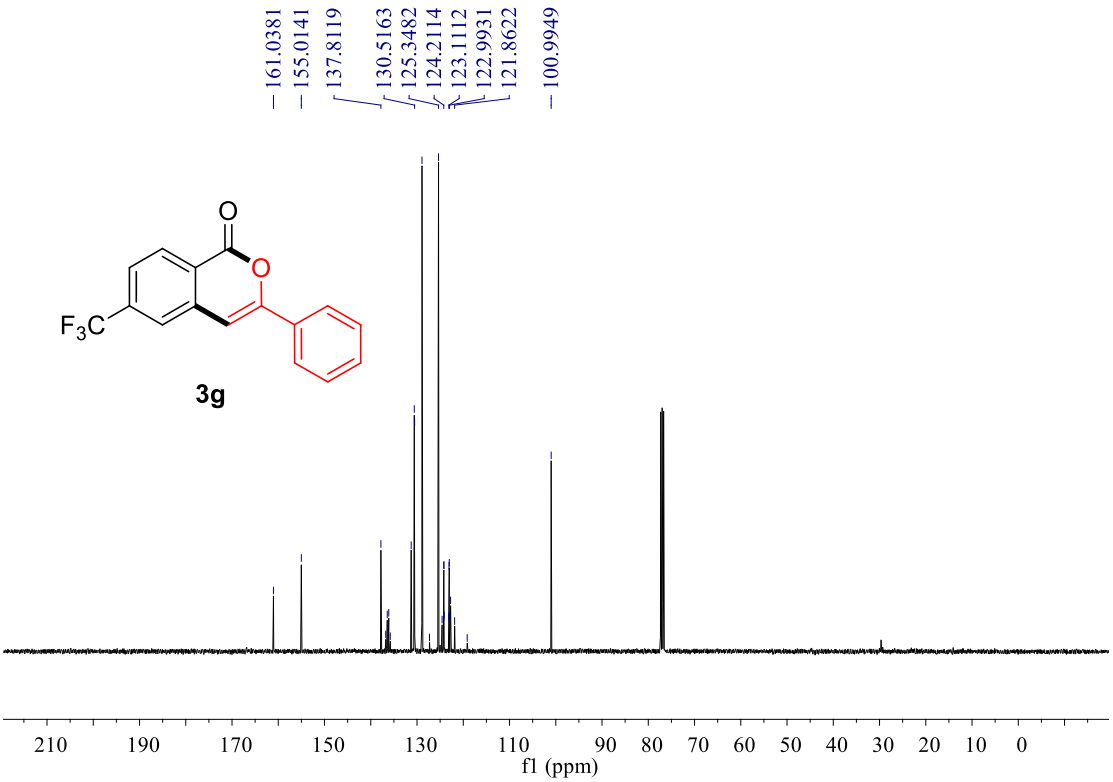
f1 (ppm)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O
F3C
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50
40
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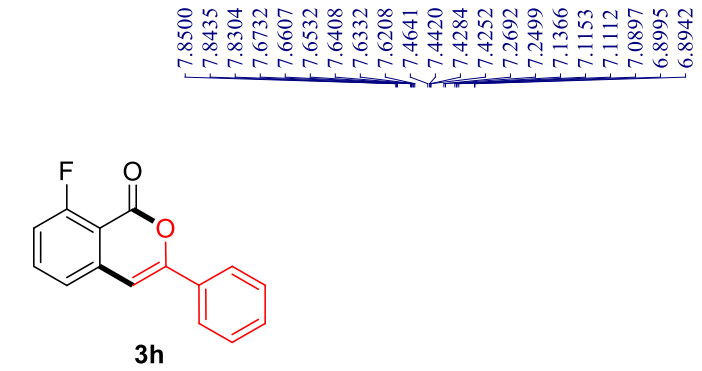
20
10
0
f1 (ppm)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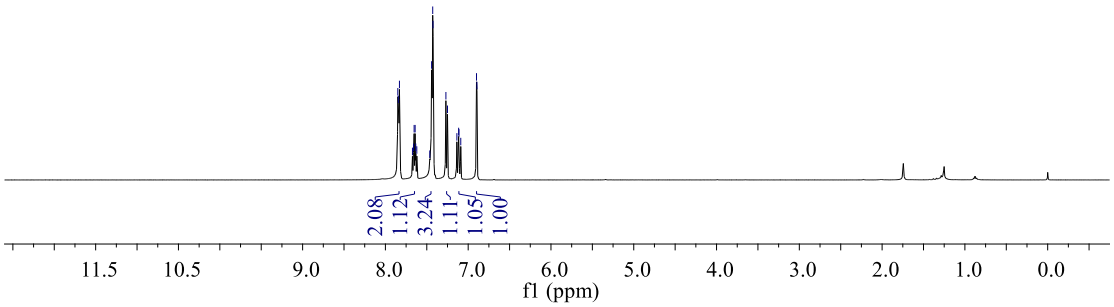
F
O
O
3h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1.00
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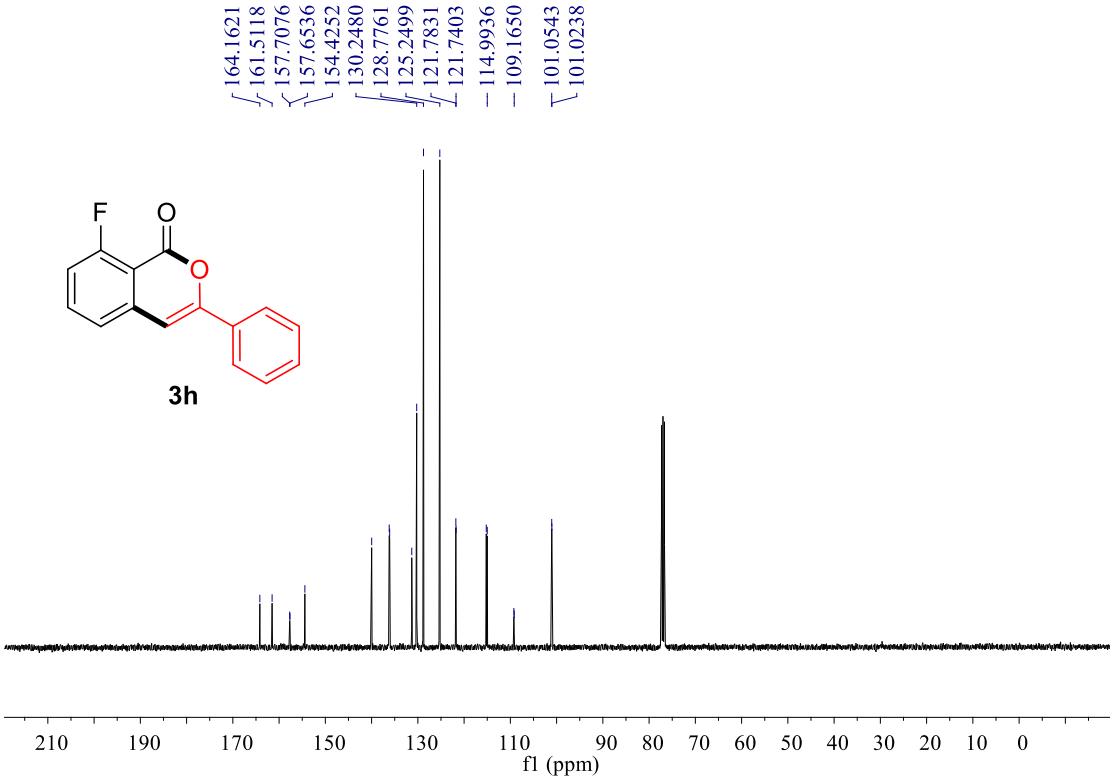
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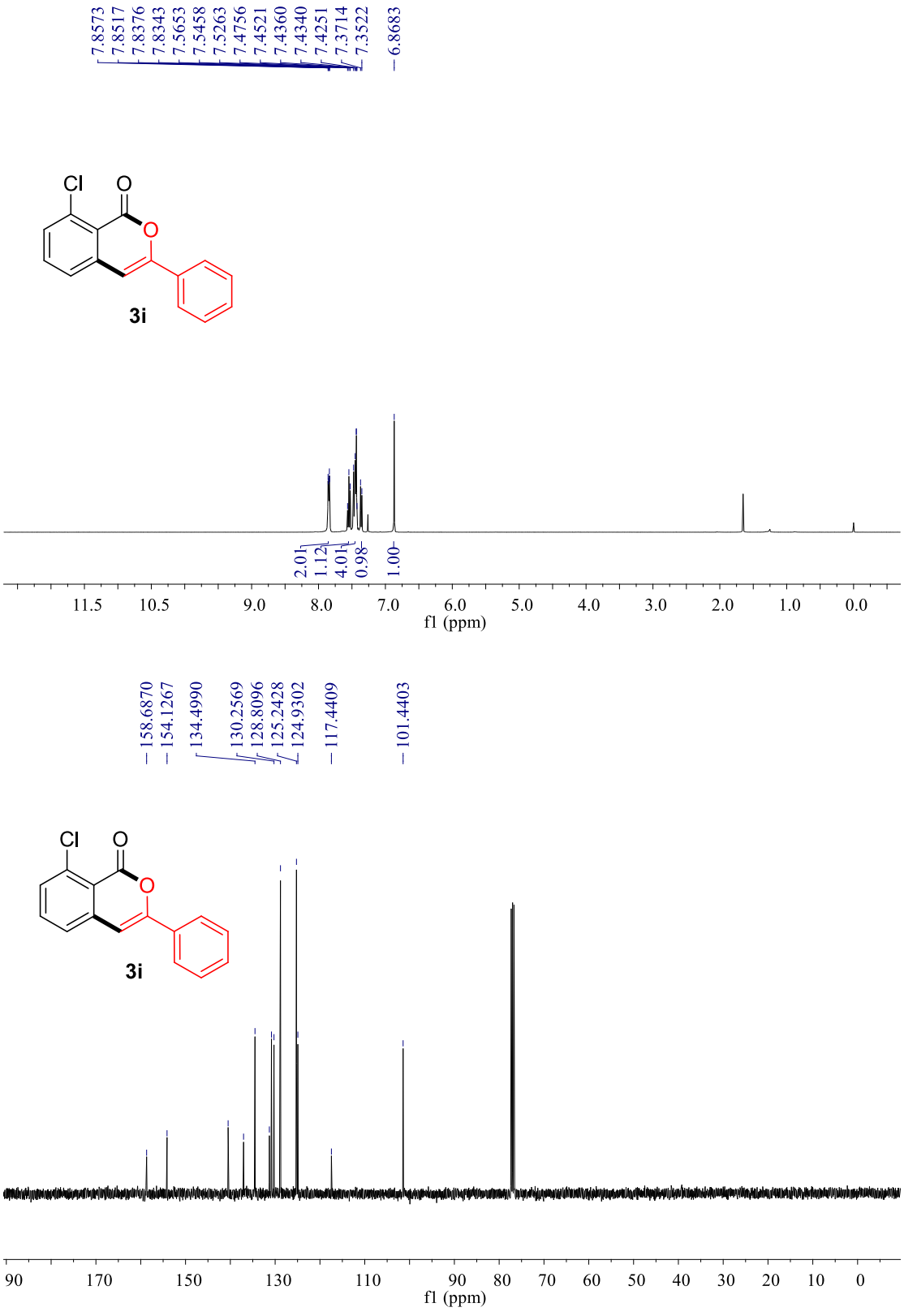
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7.4251
7.3714
7.3522
6.8683
Cl
O
O
3i
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1.12
4.01
0.98
1.00
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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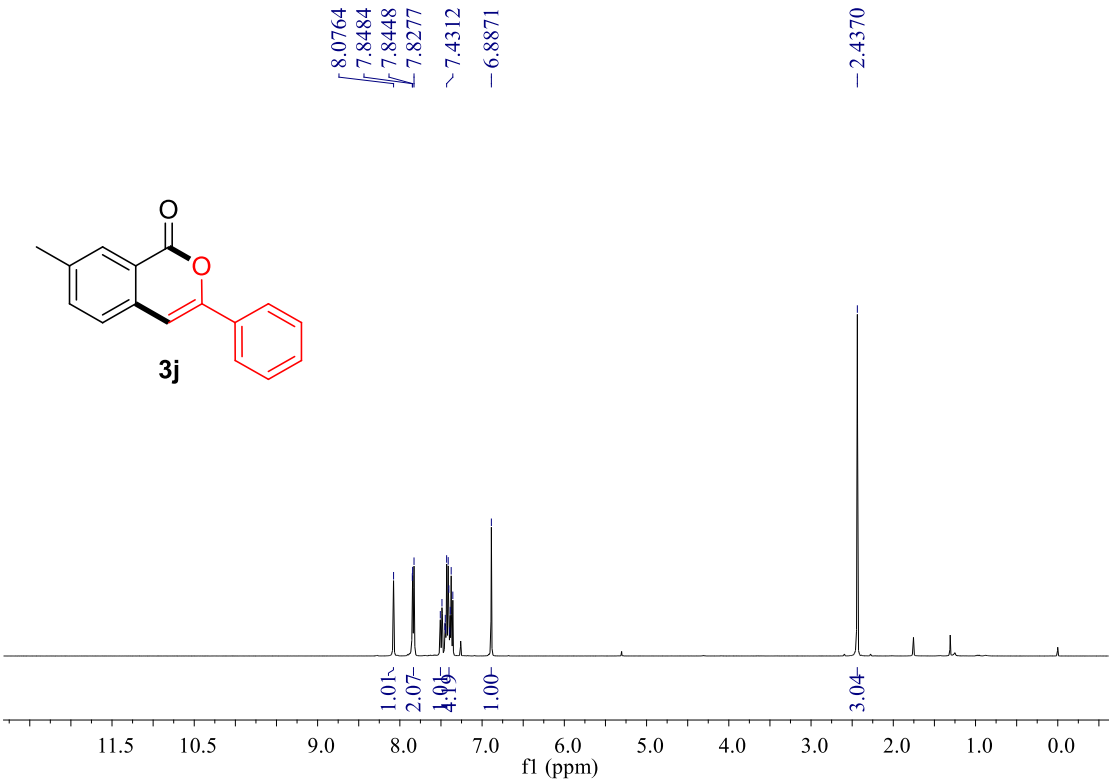
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11.5
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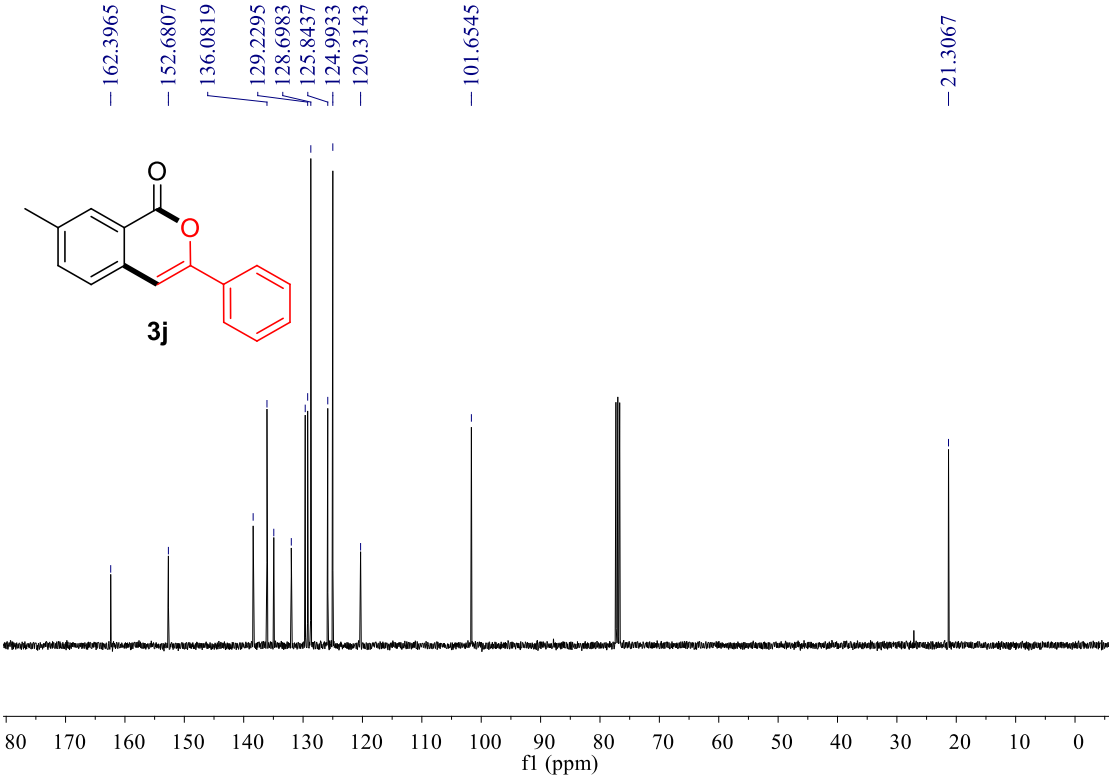
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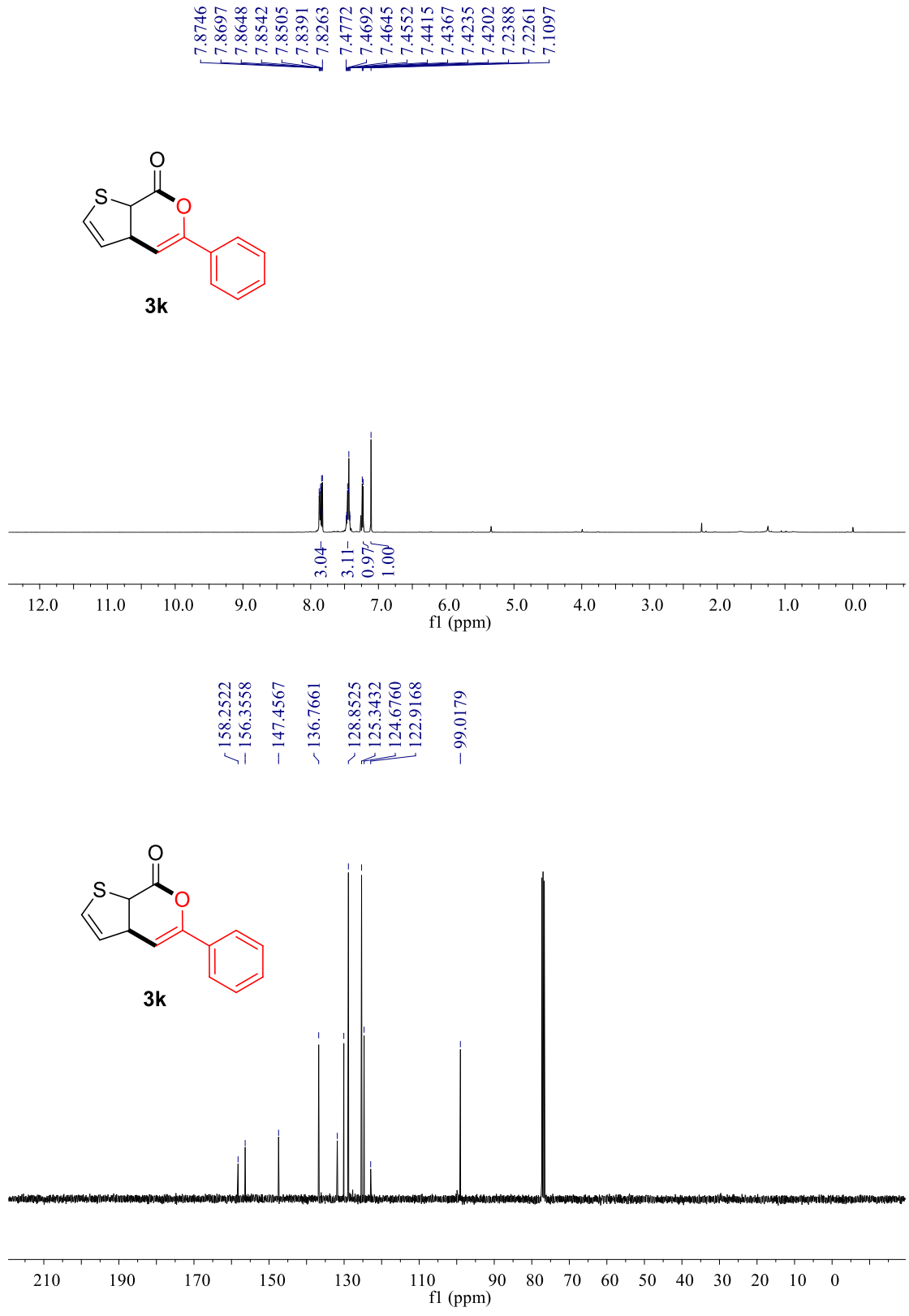
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7.4202
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S
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3k
3.04
3.11
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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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122.9168
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S
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50
40
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0
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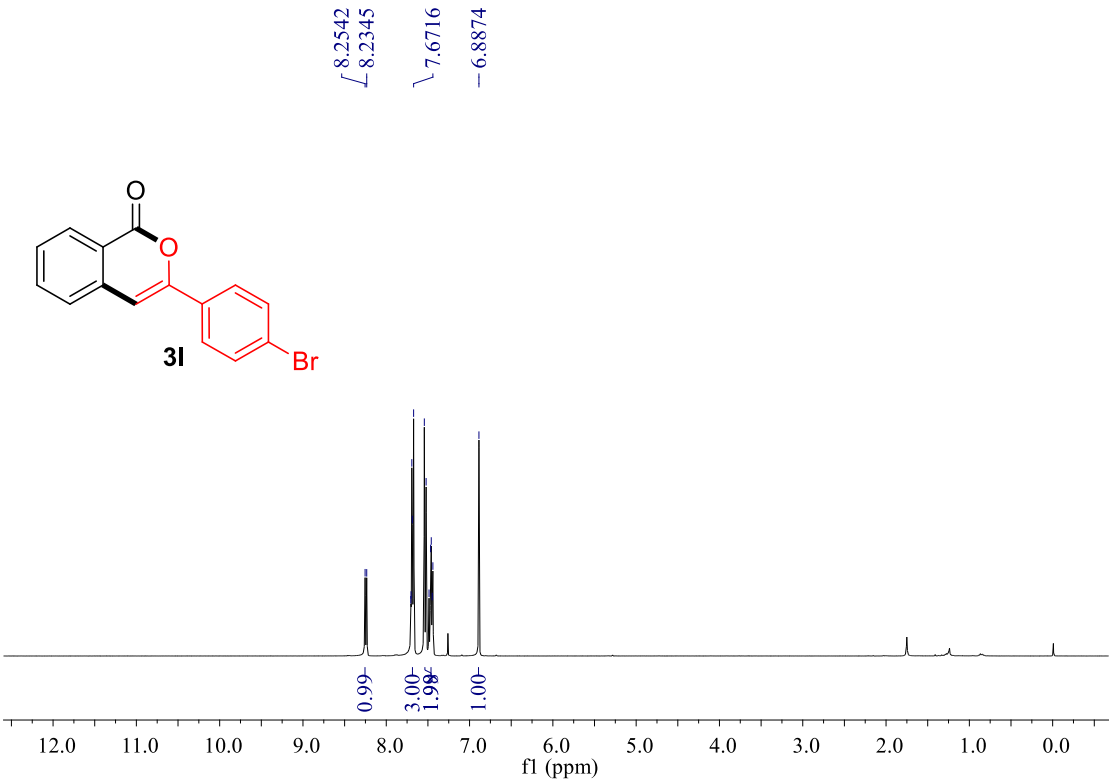
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10.0
9.0
8.0
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4.0
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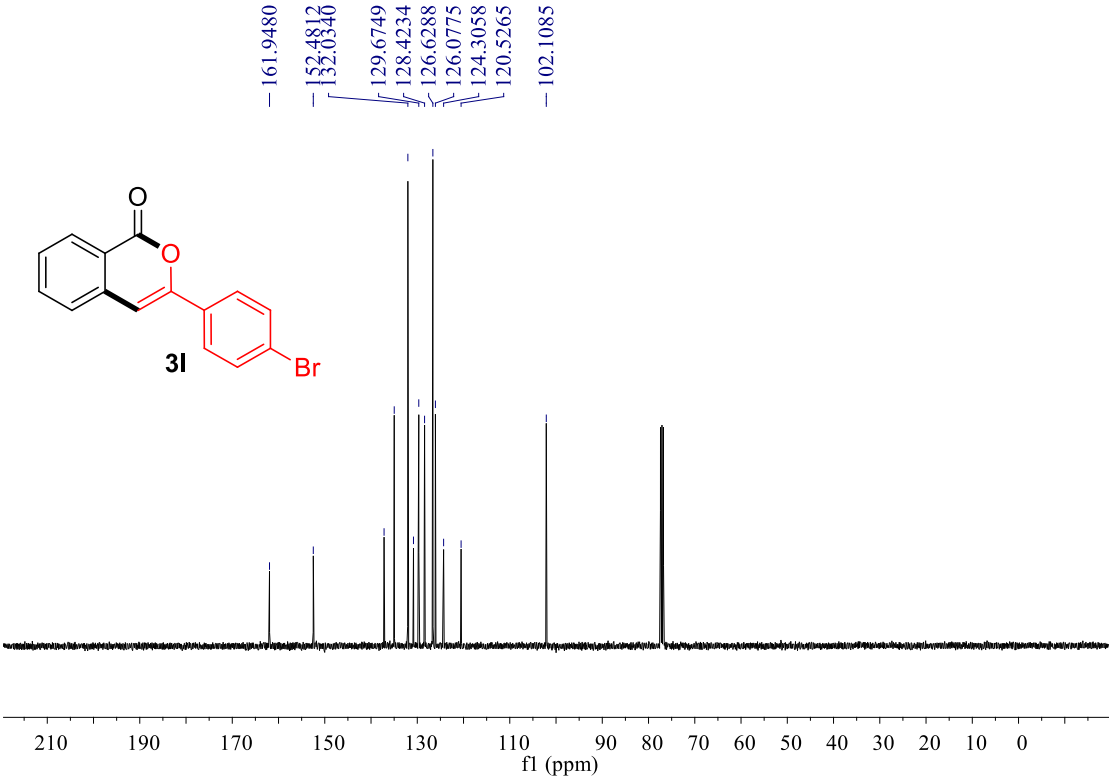
f1 (ppm)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132.0340
129.6749
128.4234
126.6288
126.0775
124.3058
120.5265
102.1085
O
O
Br
3l
210
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170
150
130
110
90
80
70
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50
40
30
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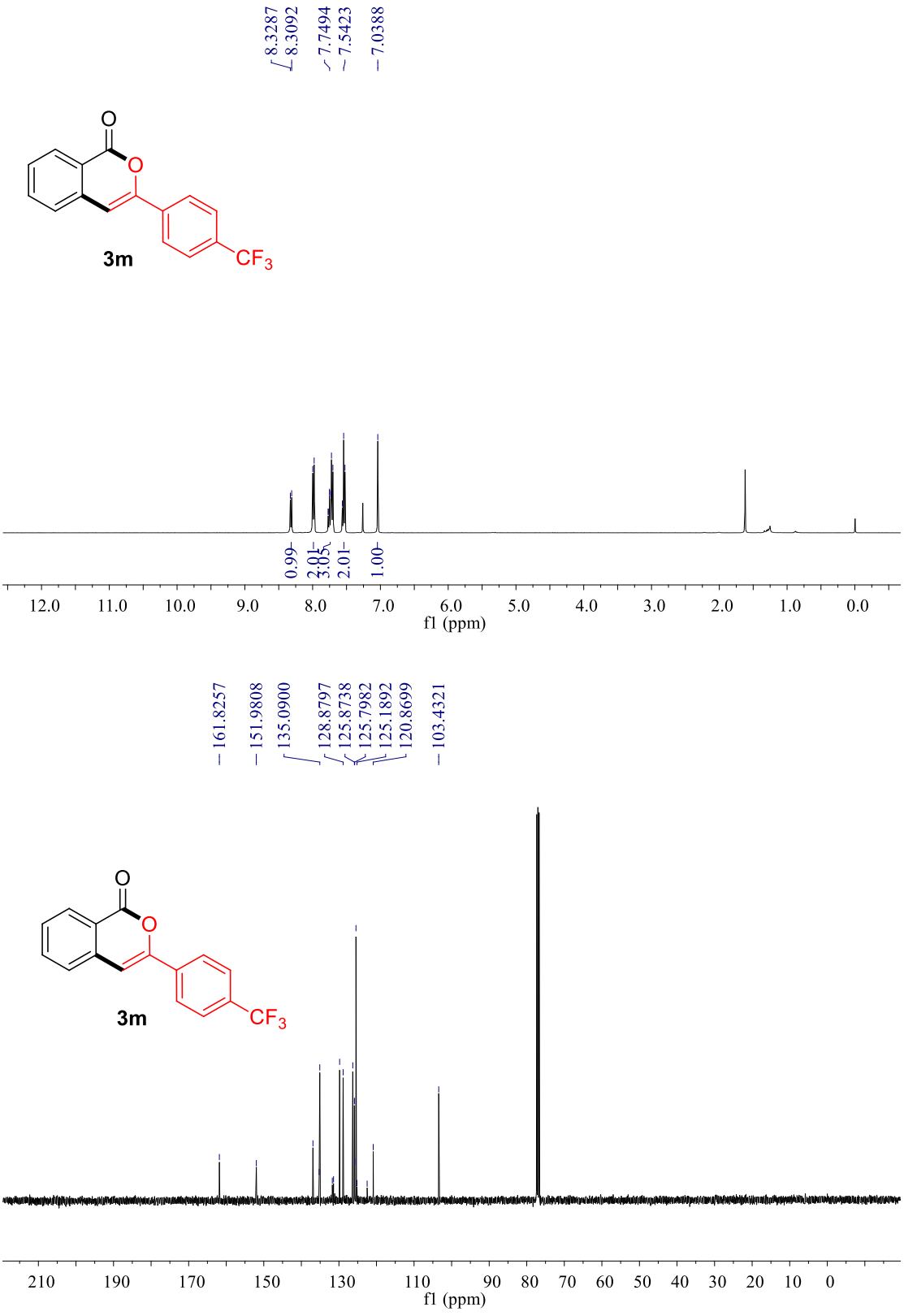
f1 (ppm)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7.7494
7.5423
7.0388
O
O
CF3
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2.01
3.05
2.01
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
161.8257
151.9808
135.0900
128.8797
125.8738
125.7982
125.1892
120.8699
103.4321
O
O
CF3
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170
150
130
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90
80
70
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50
40
30
20
10
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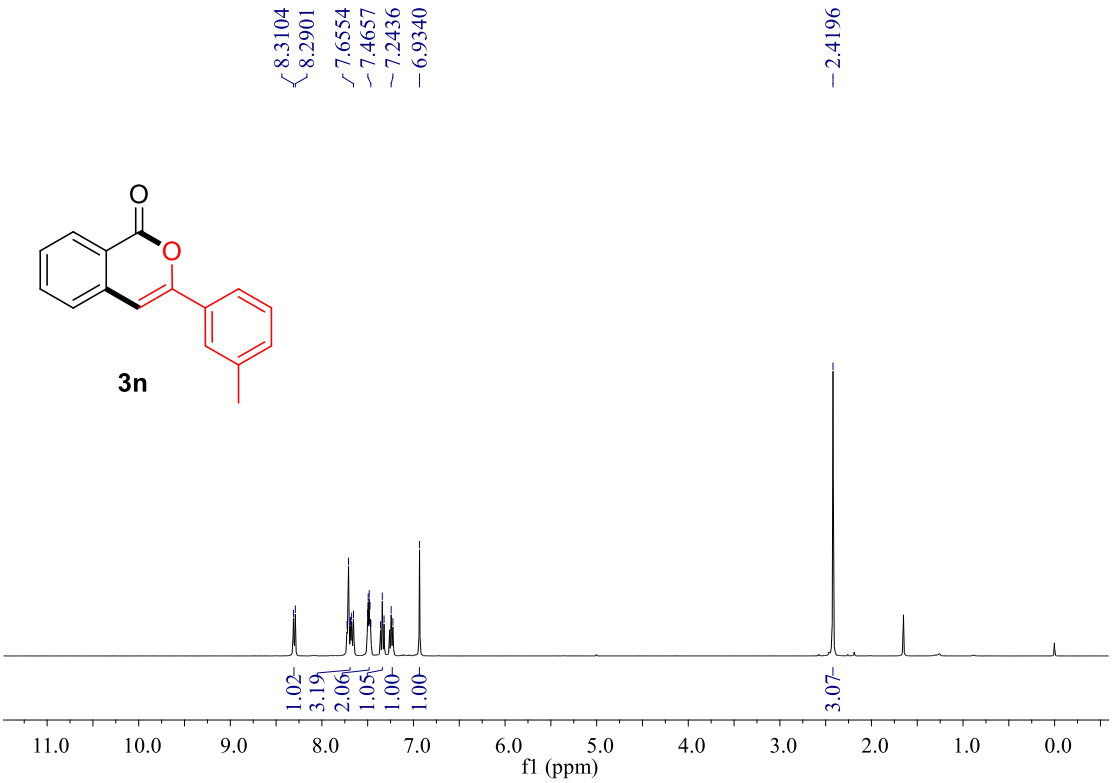
f1 (ppm)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7.2436
6.9340
2.4196
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1.02
3.19
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1.05
1.00
1.00
3.07
11.0
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5.0
4.0
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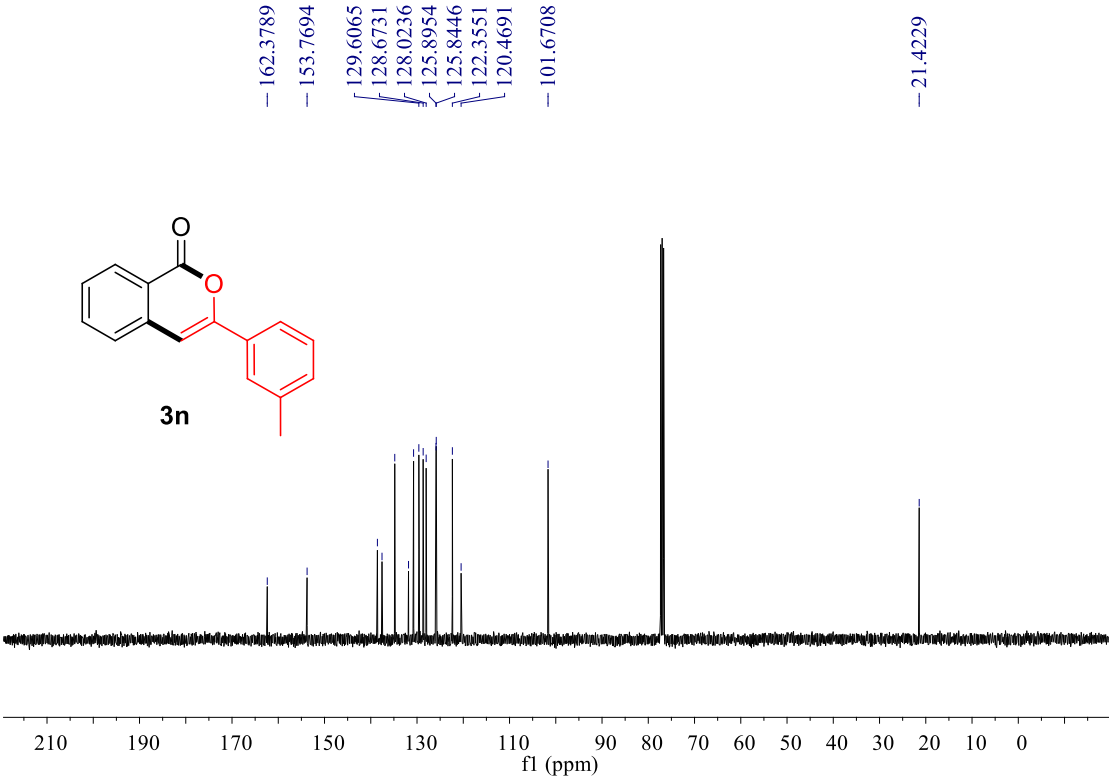
0.0
f1 (ppm)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101.6708
21.4229
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90
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70
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50
40
30
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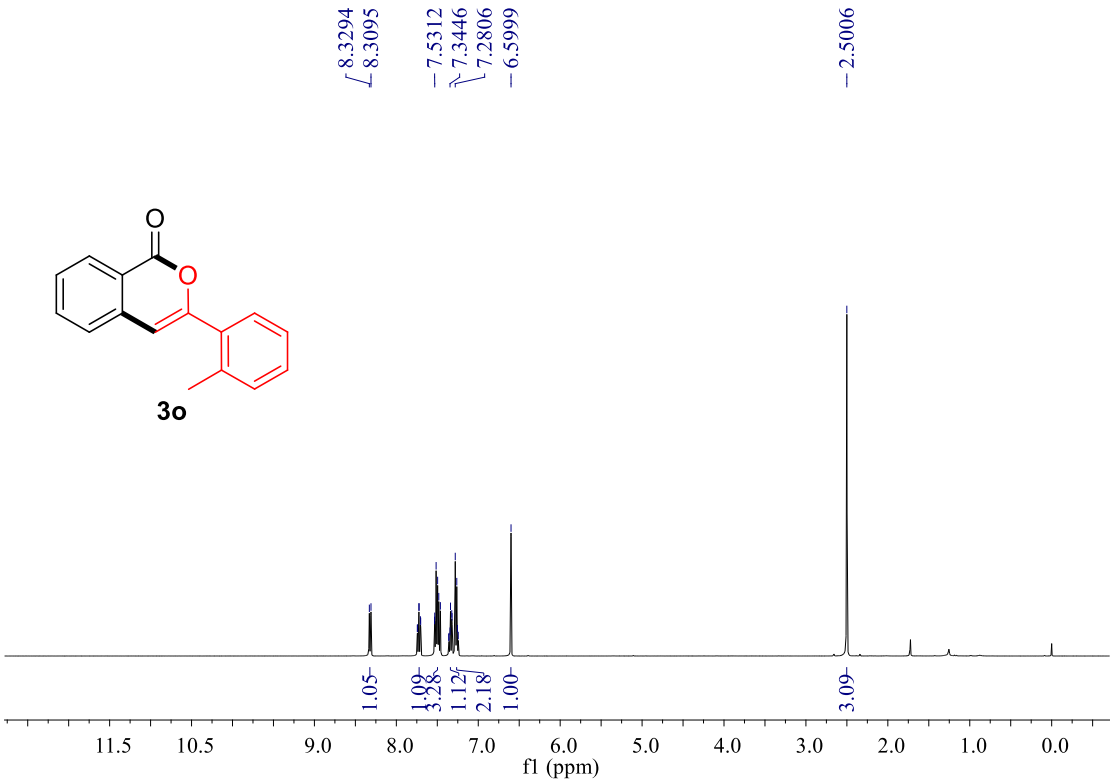
10
0
f1 (ppm)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7.5312
7.3446
7.2806
6.5999
2.5006
3o
1.05
1.09
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1.12
2.18
1.00
3.09
11.5
10.5
9.0
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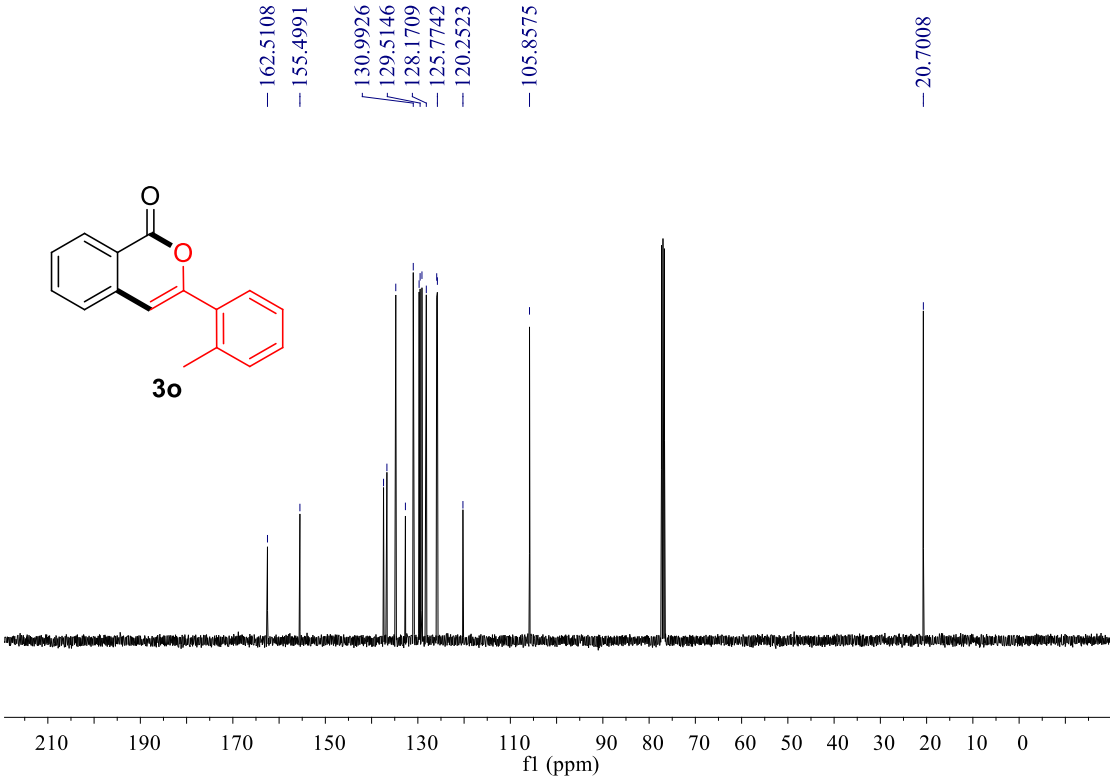
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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155.4991
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129.5146
128.1709
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120.2523
105.8575
20.7008
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150
130
110
90
80
70
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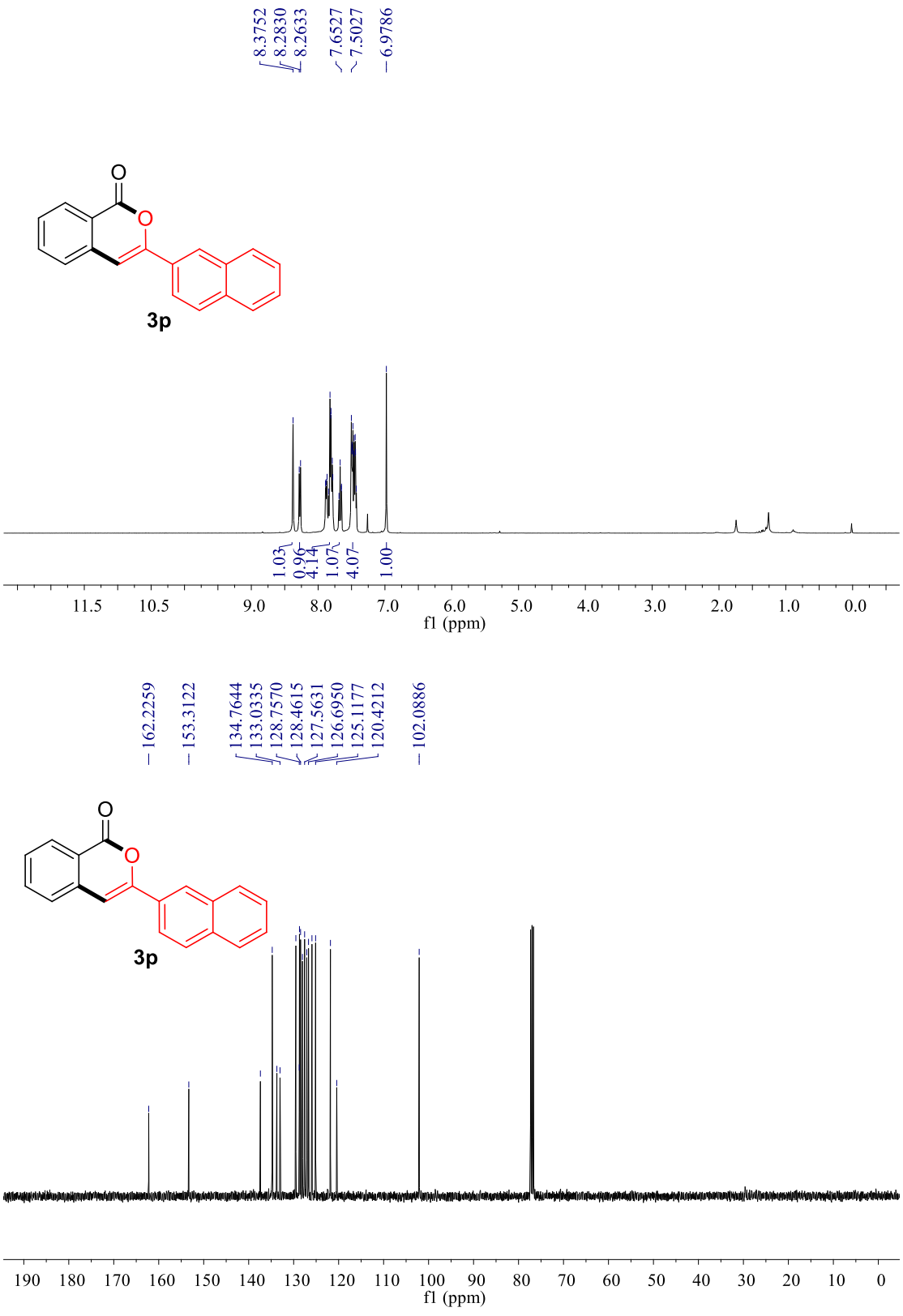
50
40
30
20
10
0
f1 (ppm)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8.2830
8.2633
7.6527
7.5027
6.9786
3p
1.03
0.96
4.14
1.07
4.07
1.00
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
162.2259
153.3122
134.7644
133.0335
128.7570
128.4615
127.5631
126.6950
125.1177
120.4212
102.0886
3p
190
180
170
160
150
140
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120
110
100
90
80
70
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50
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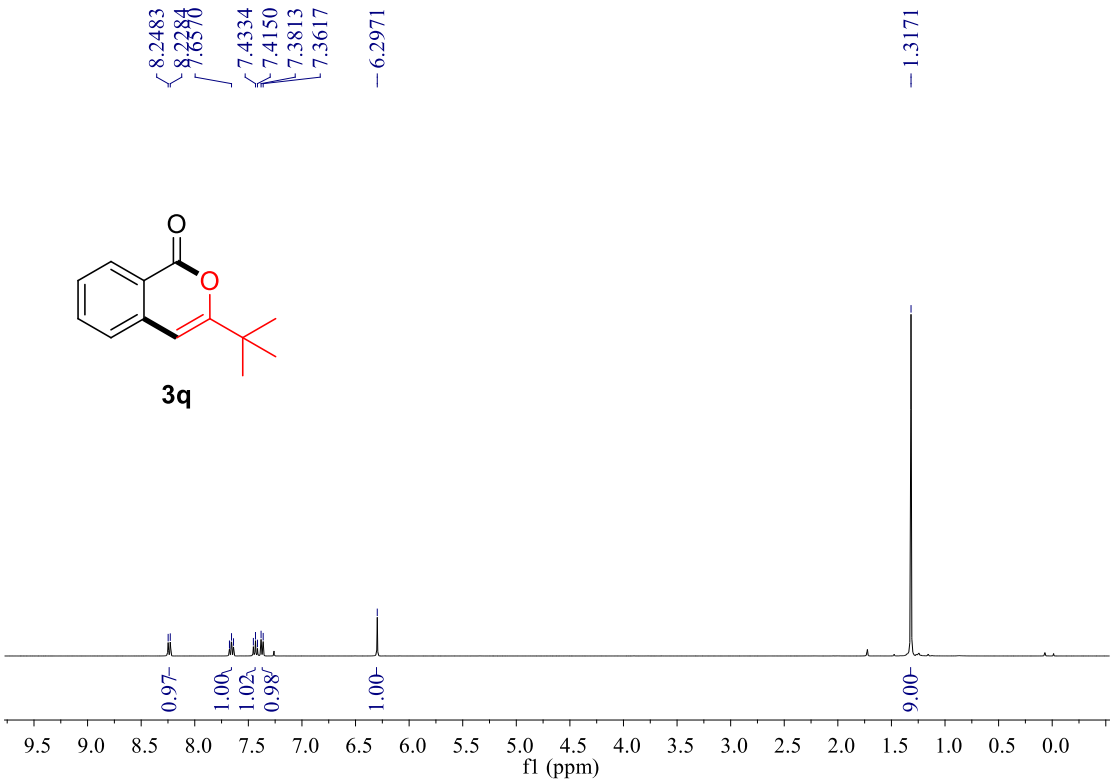
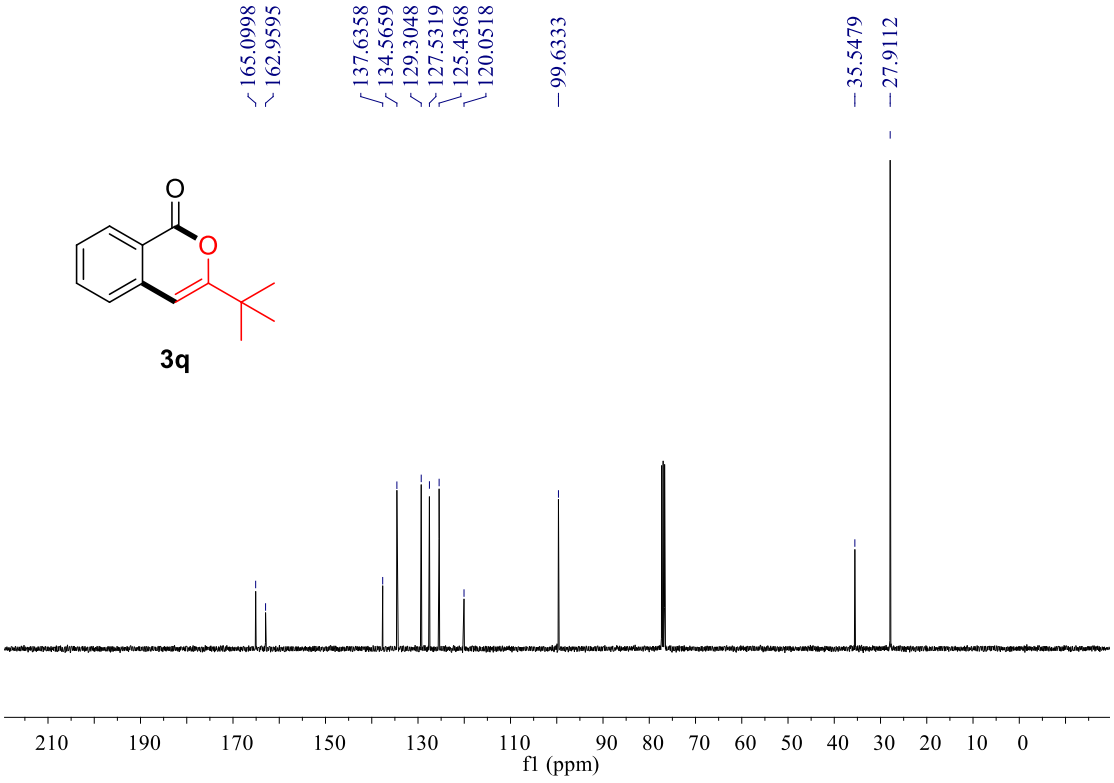
30
20
10
0
f1 (ppm)


8.2483
8.2284
7.6570
7.4334
7.4150
7.3813
7.3617
6.2971
1.3171
O
O
3q
0.97
1.00
1.02
0.98
1.00
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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162.9595
137.6358
134.5659
129.3048
127.5319
125.4368
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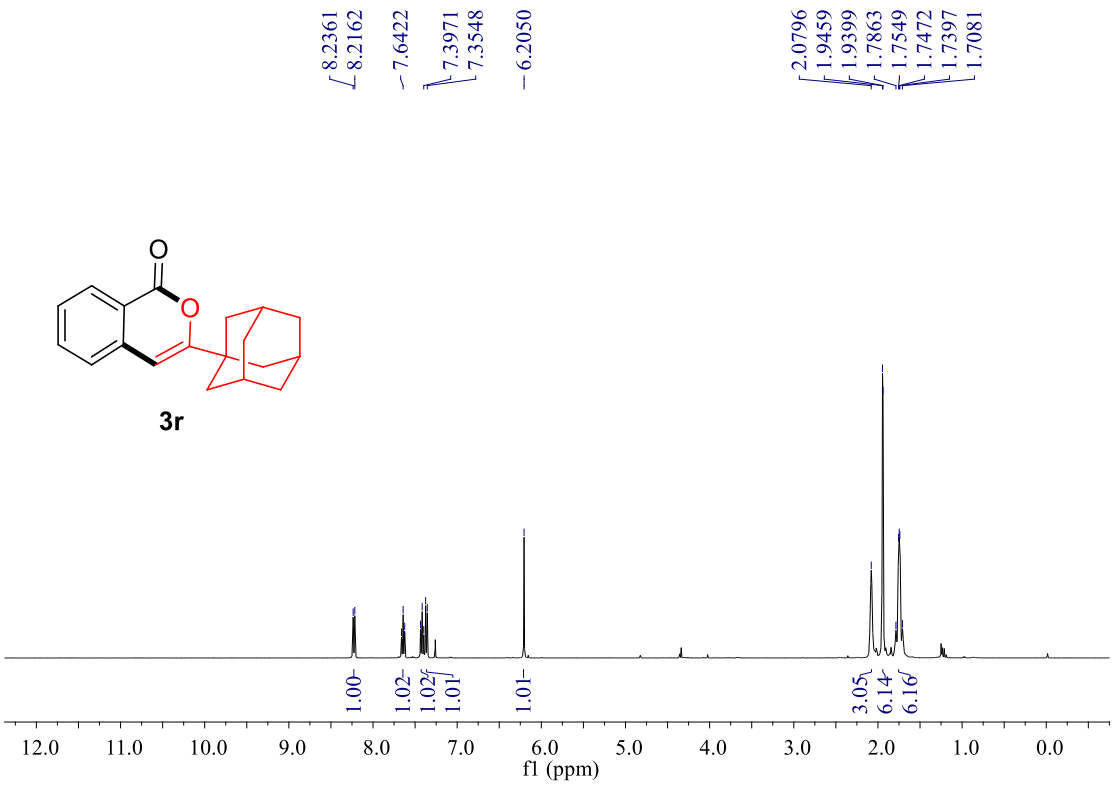
27.9112
O
O
3q
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.2162
7.6422
7.3971
7.3548
6.2050
2.0796
1.9459
1.9399
1.7863
1.7549
1.7472
1.7397
1.7081
O
O
3r
1.00
1.02
1.02
1.01
1.01
3.05
6.14
6.16
12.0
11.0
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9.0
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7.0
6.0
5.0
4.0
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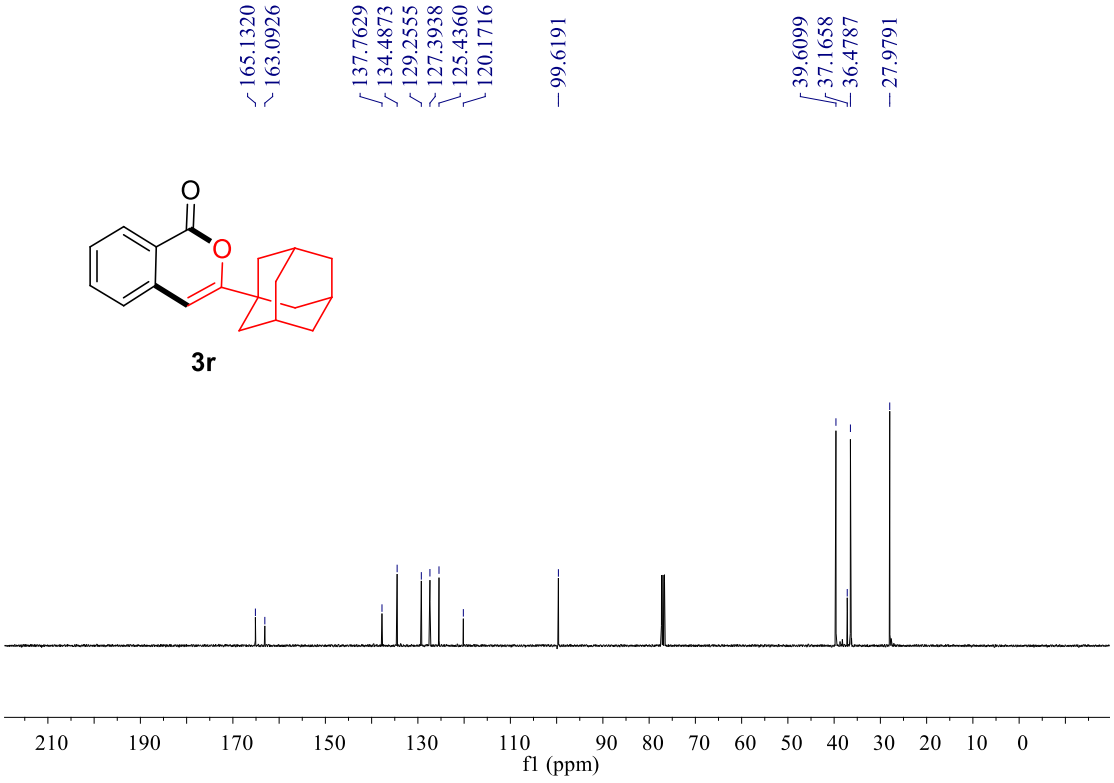
2.0
1.0
0.0
f1 (ppm)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163.0926
137.7629
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127.3938
125.4360
120.1716
99.6191
39.6099
37.1658
36.4787
27.9791
O
O
3r
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170
150
130
110
90
80
70
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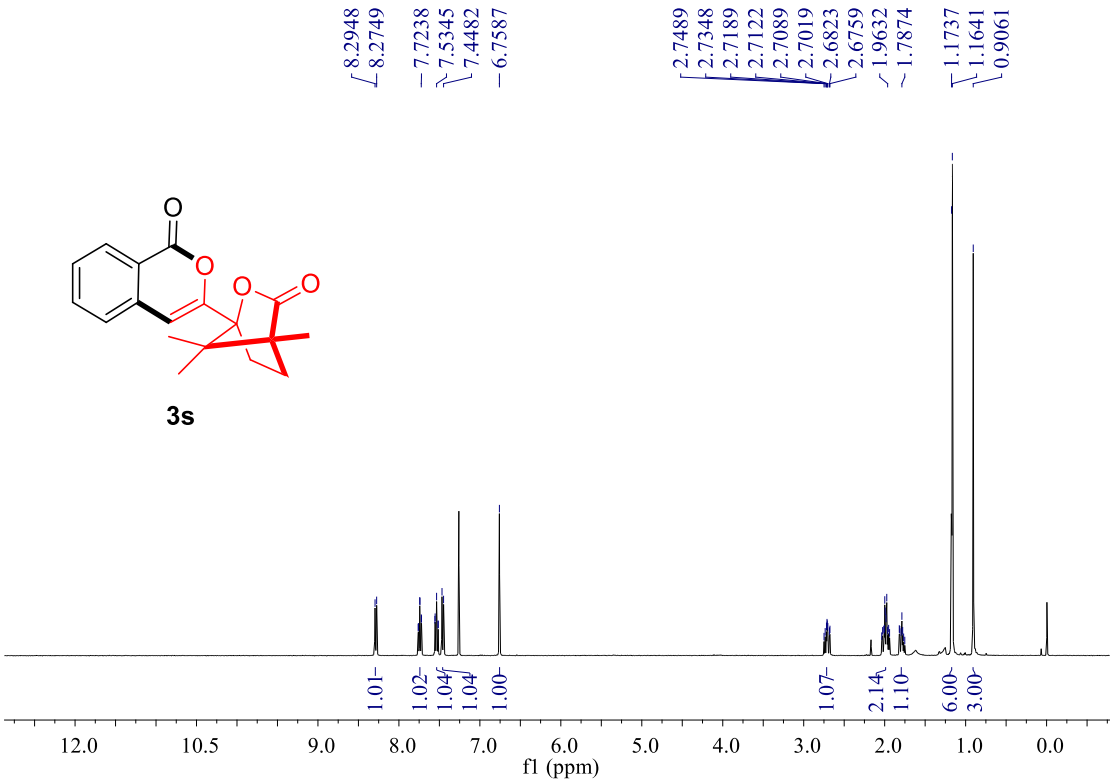
50
40
30
20
10
0
f1 (ppm)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7.4482
6.7587
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2.7348
2.7189
2.7122
2.7089
2.7019
2.6823
2.6759
1.9632
1.7874
1.1737
1.1641
0.9061
1.01
1.02
1.04
1.04
1.00
1.07
2.14
1.10
6.00
3.00
12.0
10.5
9.0
8.0
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6.0
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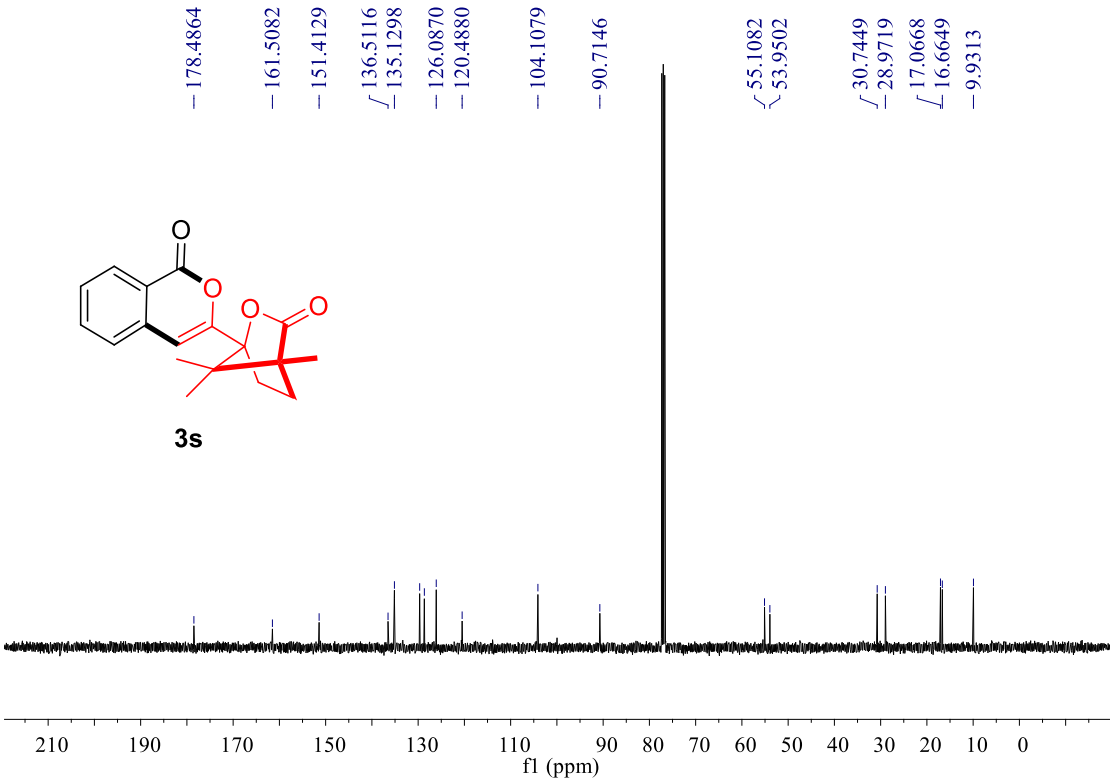
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

3s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151.4129
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126.0870
120.4880
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90.7146
55.1082
53.9502
30.7449
28.9719
17.0668
16.6649
9.9313
210
190
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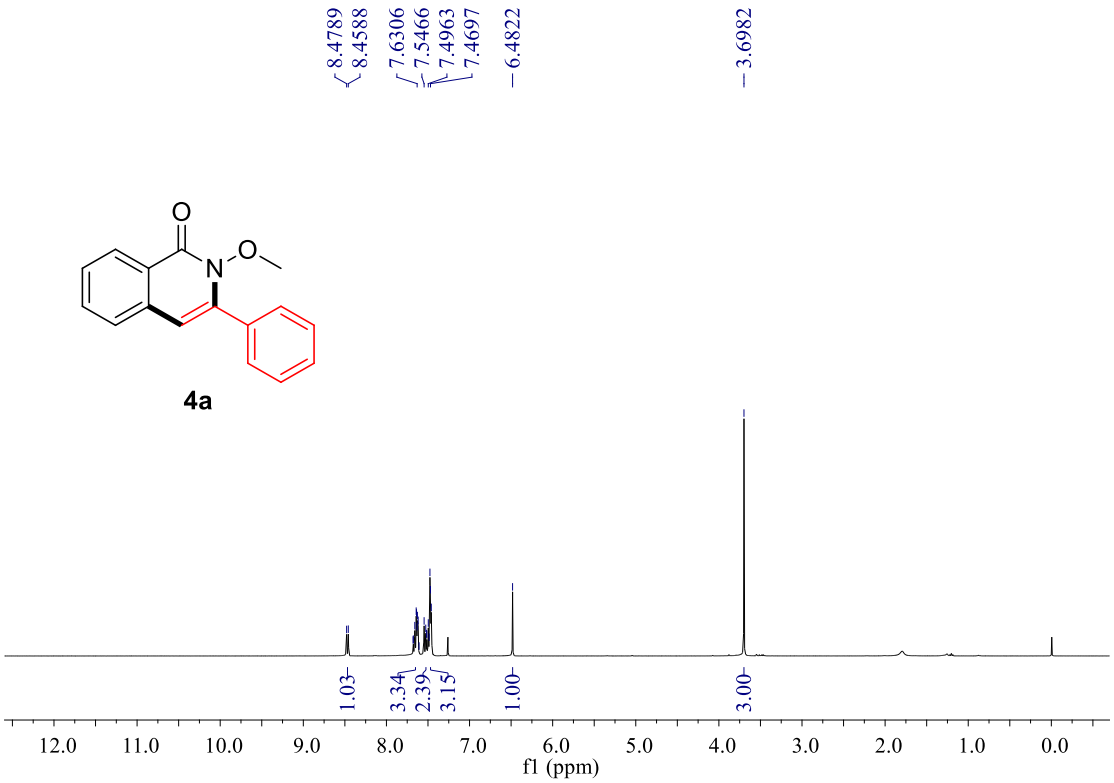
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3s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7.6306
7.5466
7.4963
7.4697
6.4822
3.6982
O
N
O
4a
1.03
3.34
2.39
3.15
1.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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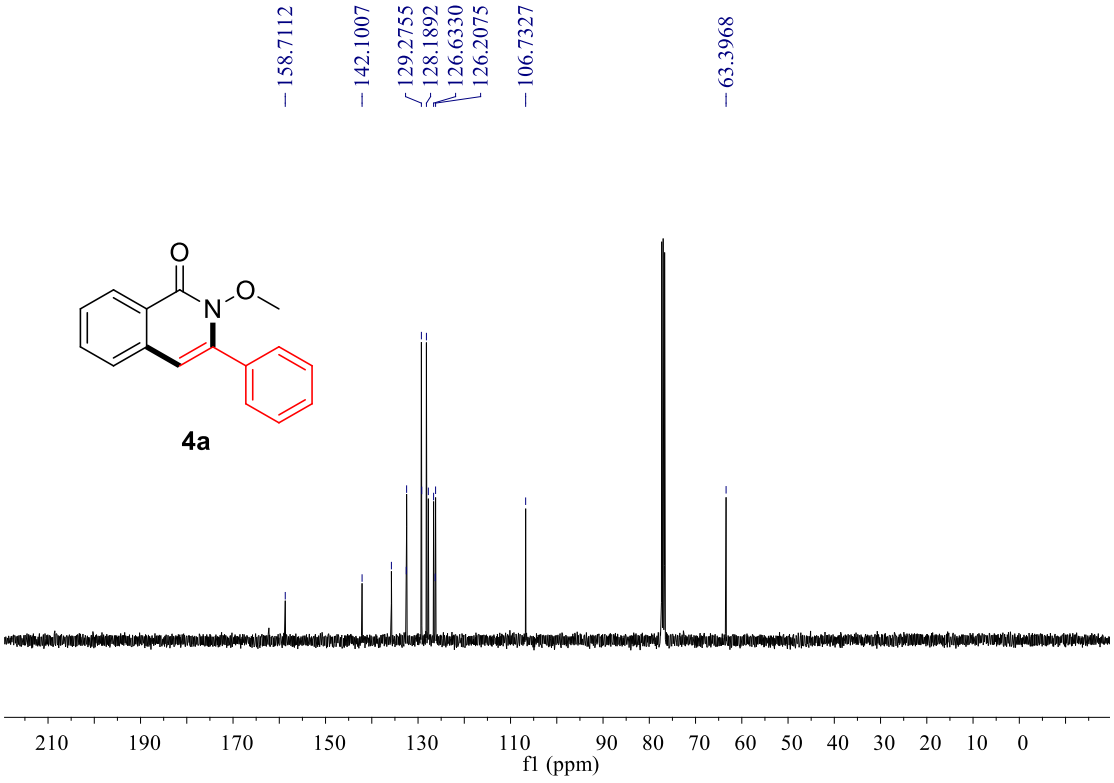
0.0
f1 (ppm)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129.2755
128.1892
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126.2075
106.7327
63.3968
O
N
O
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210
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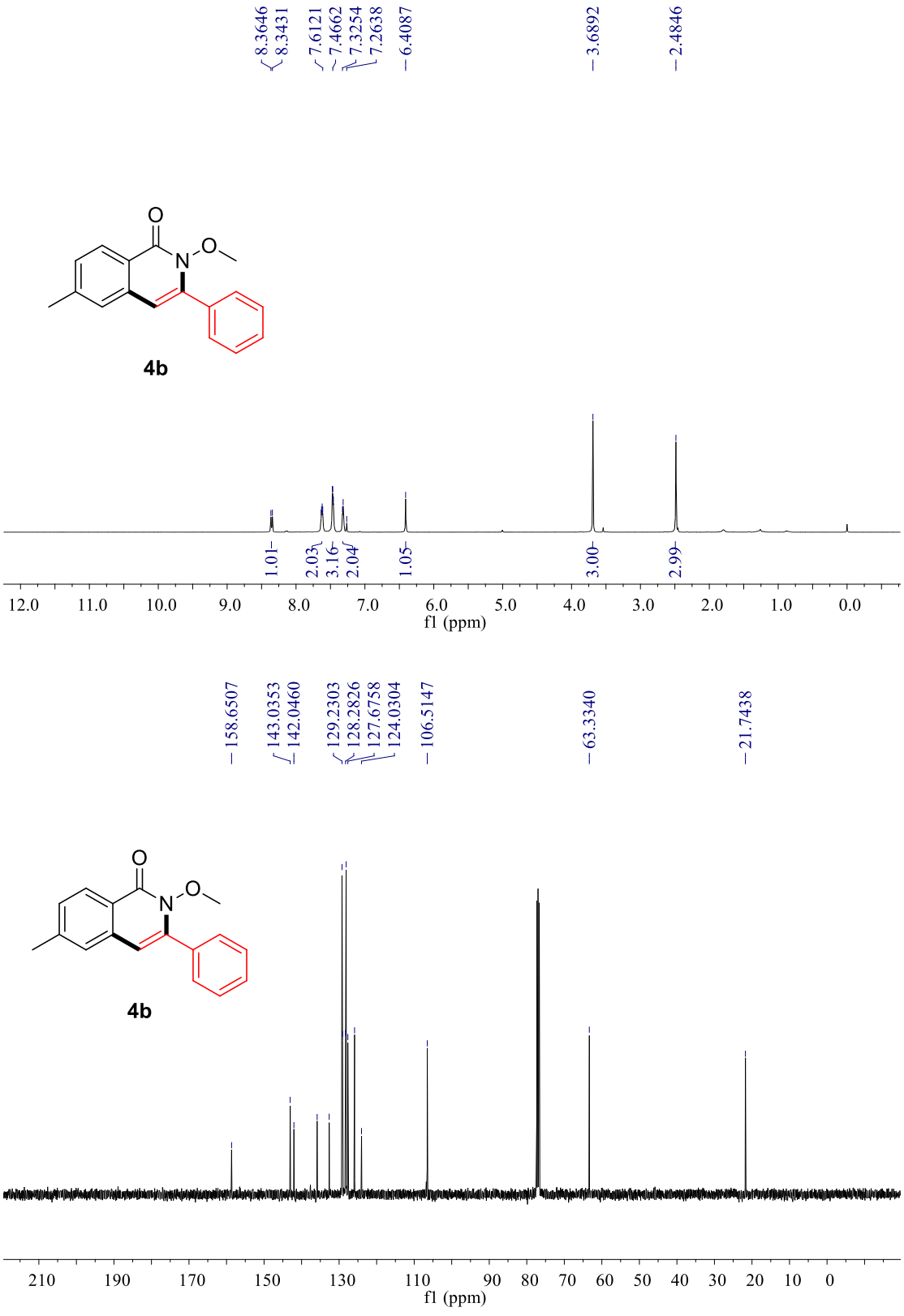
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4662
7.3254
7.2638
6.4087
3.6892
2.4846
4b
1.01
2.03
3.16
2.04
1.05
3.00
2.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
158.6507
143.0353
142.0460
129.2303
128.2826
127.6758
124.0304
106.5147
63.3340
21.7438
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70
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50
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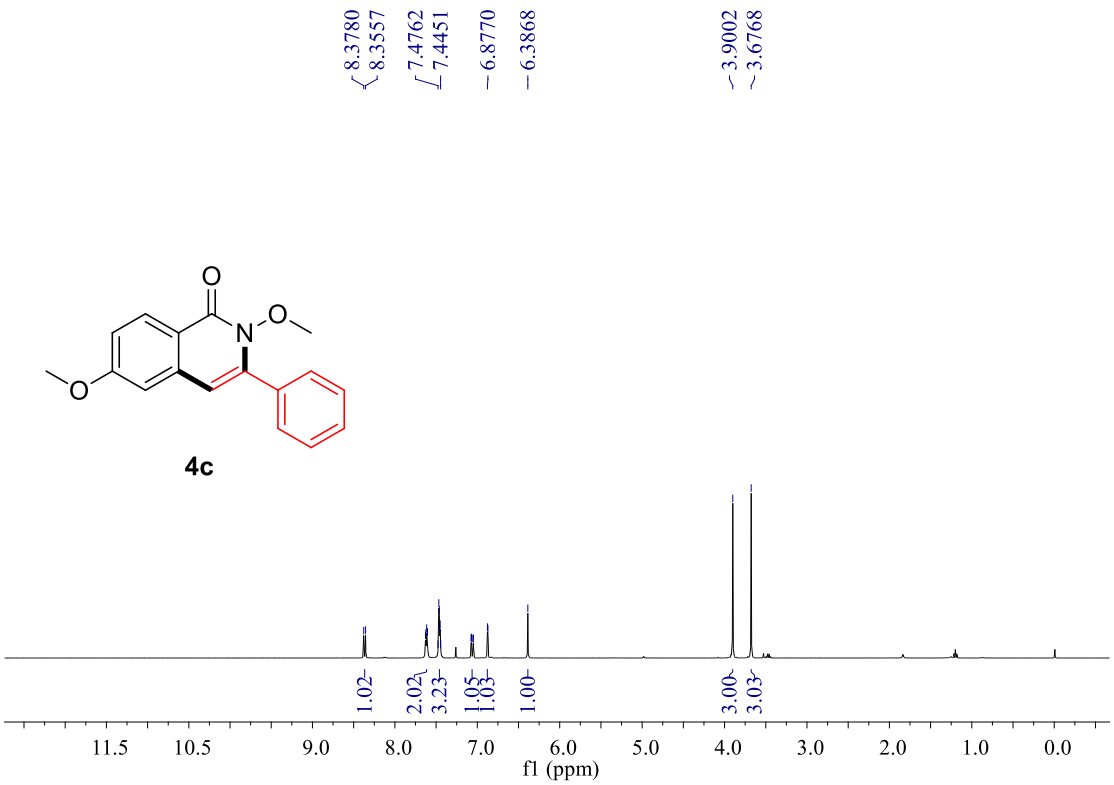
f1 (ppm)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3.9002
3.6768
4c
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2.02
3.23
1.05
1.03
1.00
3.00
3.03
11.5
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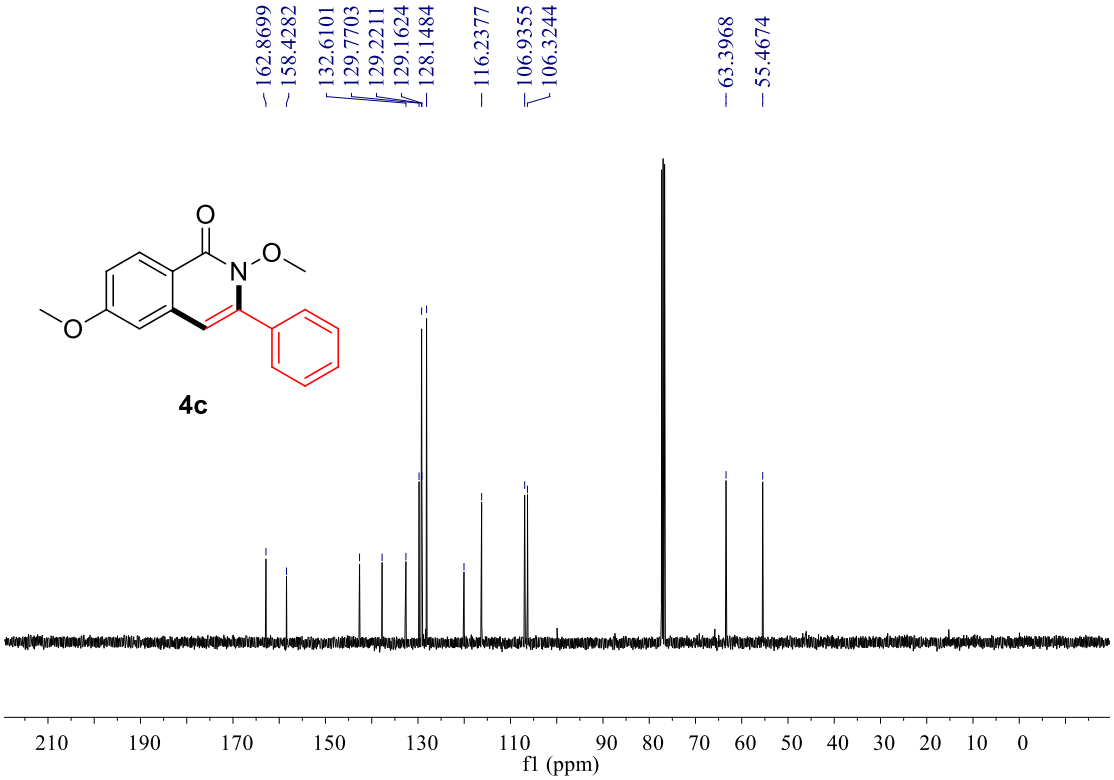
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.7703
129.2211
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128.1484
116.2377
106.9355
106.3244
63.3968
55.4674
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90
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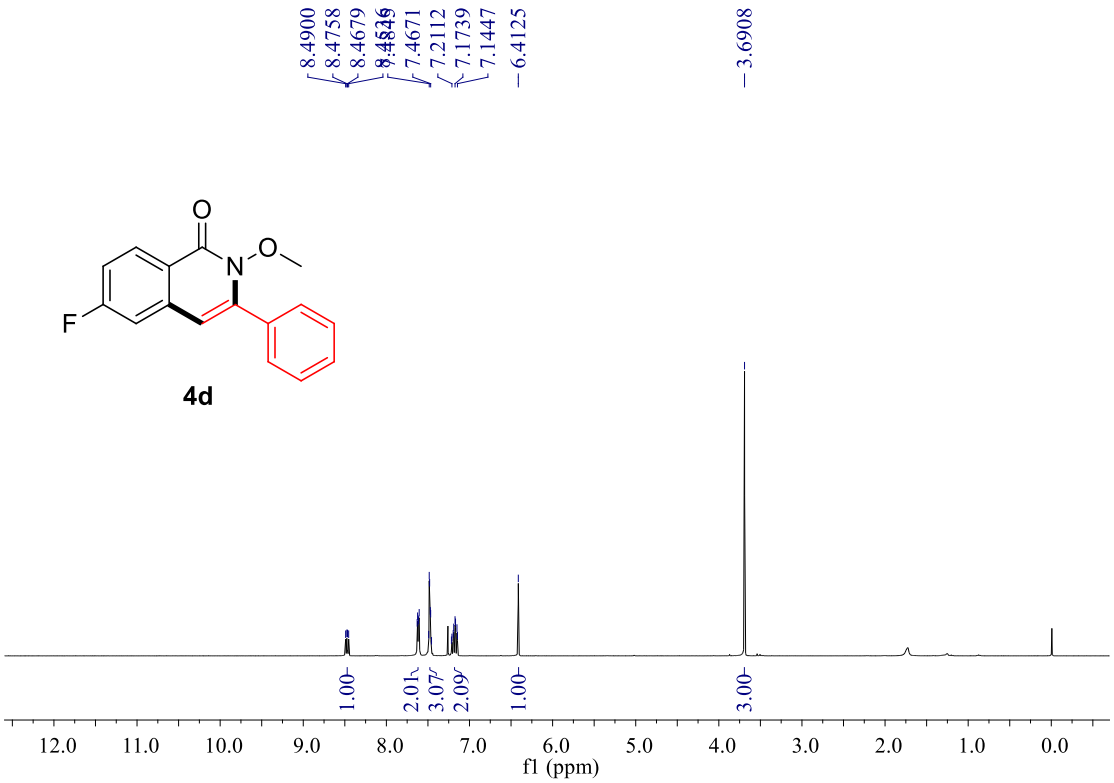
50
40
30
20
10
0
f1 (ppm)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8.4679
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7.2112
7.1739
7.1447
6.4125
3.6908
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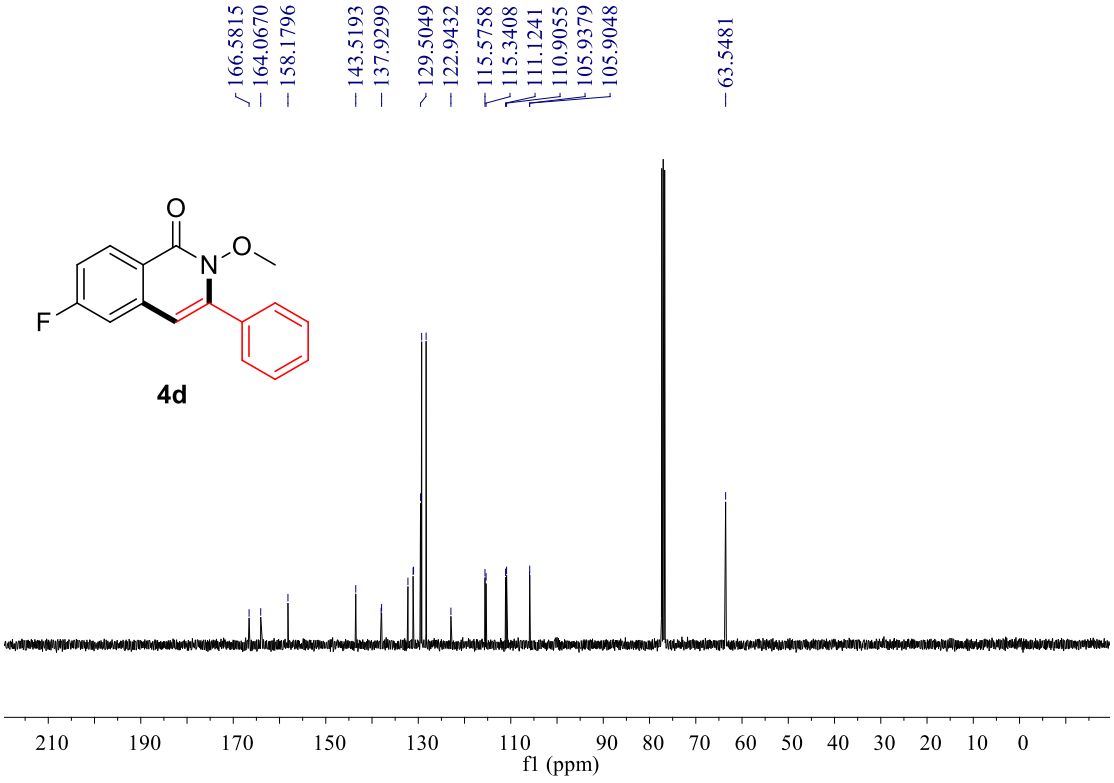
N
O
F
4d
1.00
2.01
3.07
2.09
1.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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137.9299
129.5049
122.9432
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115.3408
111.1241
110.9055
105.9379
105.9048
63.5481
O
N
O
F
4d
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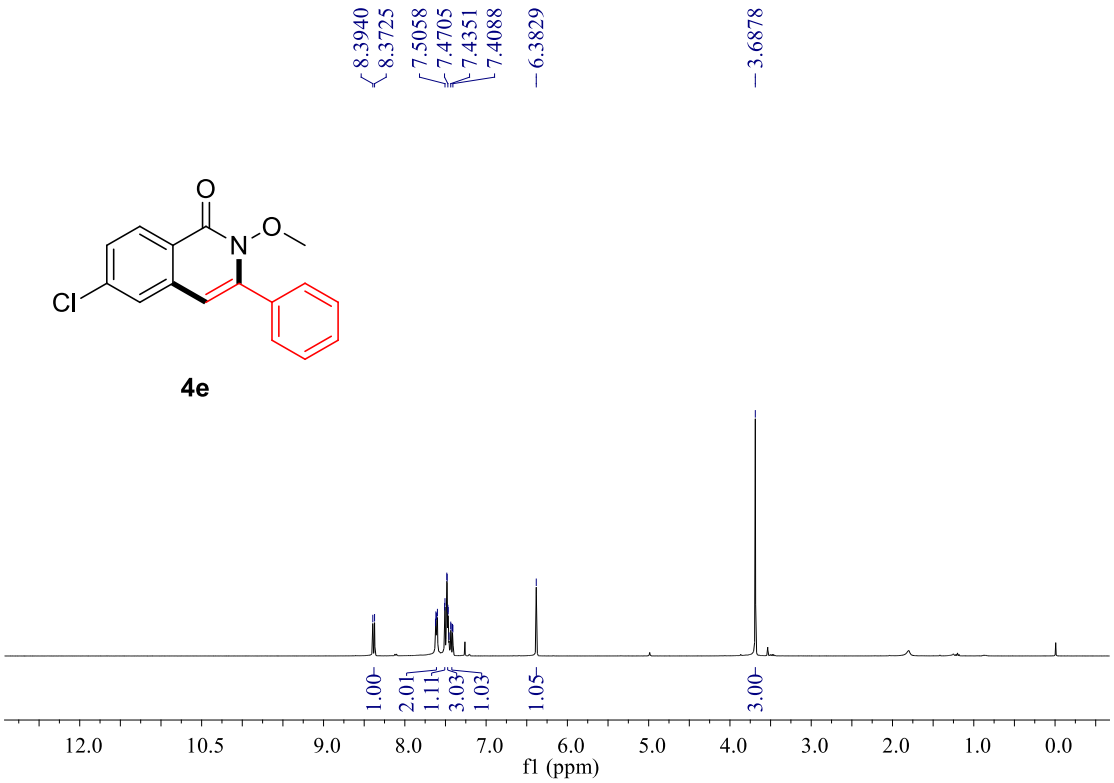
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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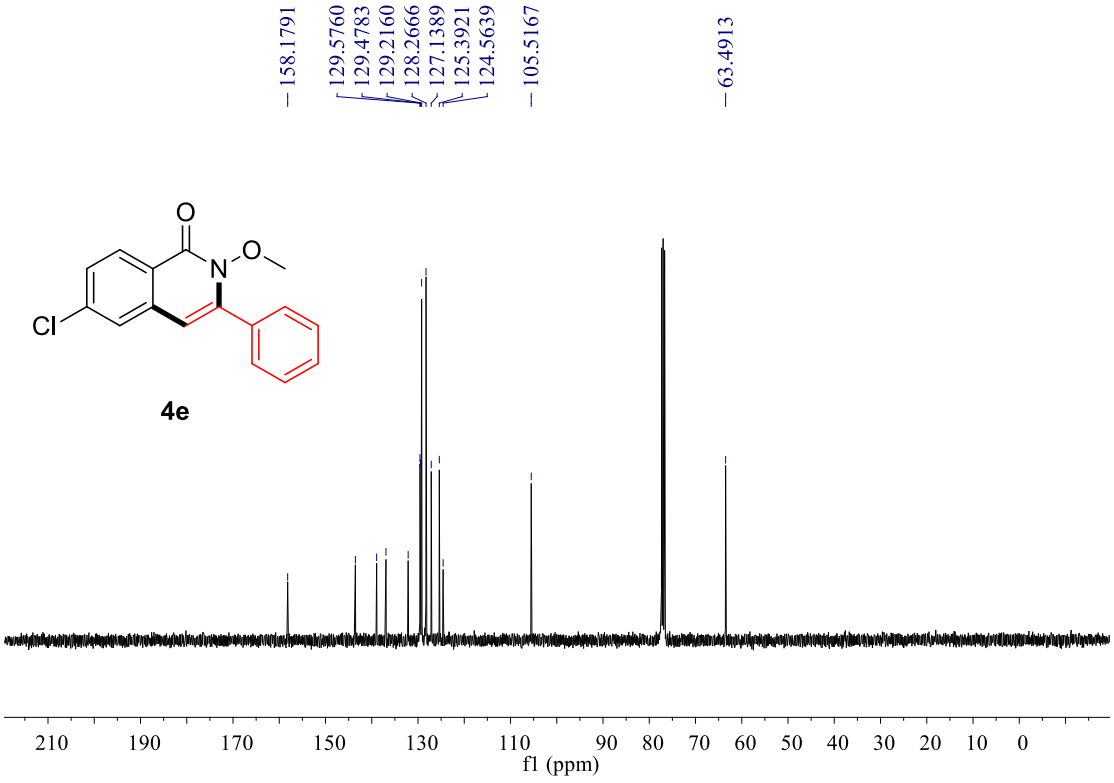
7.5058
7.4705
7.4351
7.4088
6.3829
3.6878
O
N
O
Cl
4e
1.00
2.01
1.11
3.03
1.03
1.05
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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O
N
O
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170
150
130
110
90
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70
60
50
40
30
20
10
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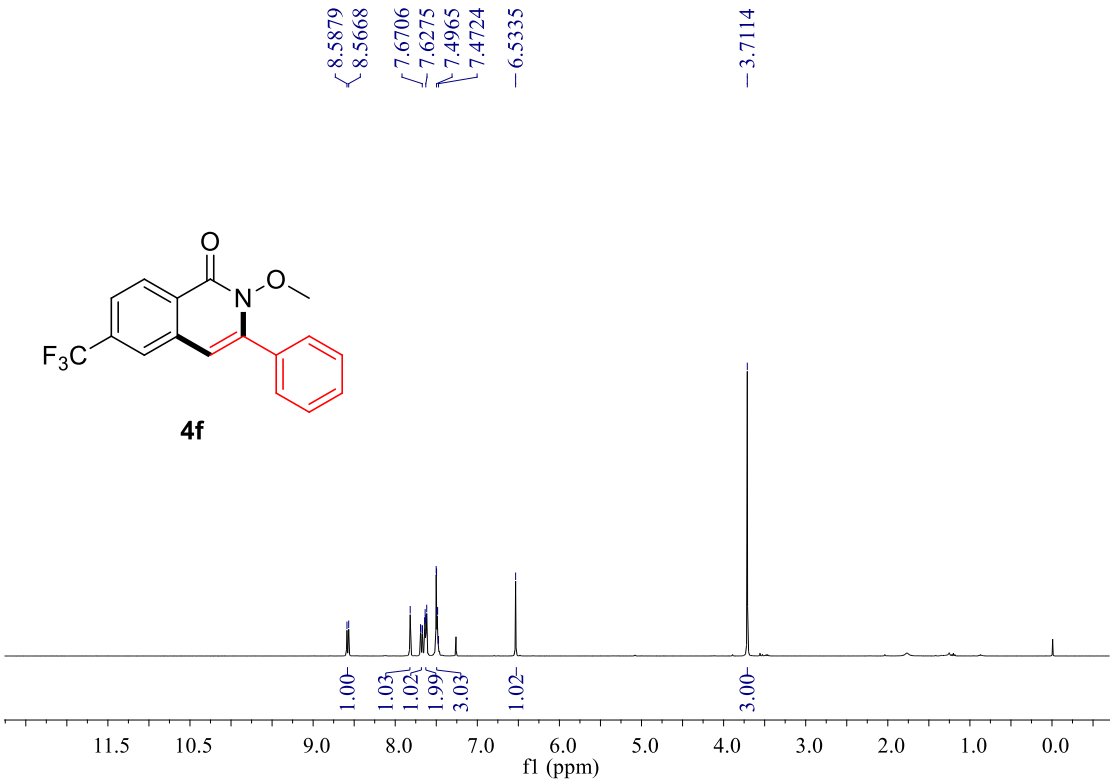
f1 (ppm)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O
F3C
4f
1.00
1.03
1.02
1.99
3.03
1.02
3.00
11.5
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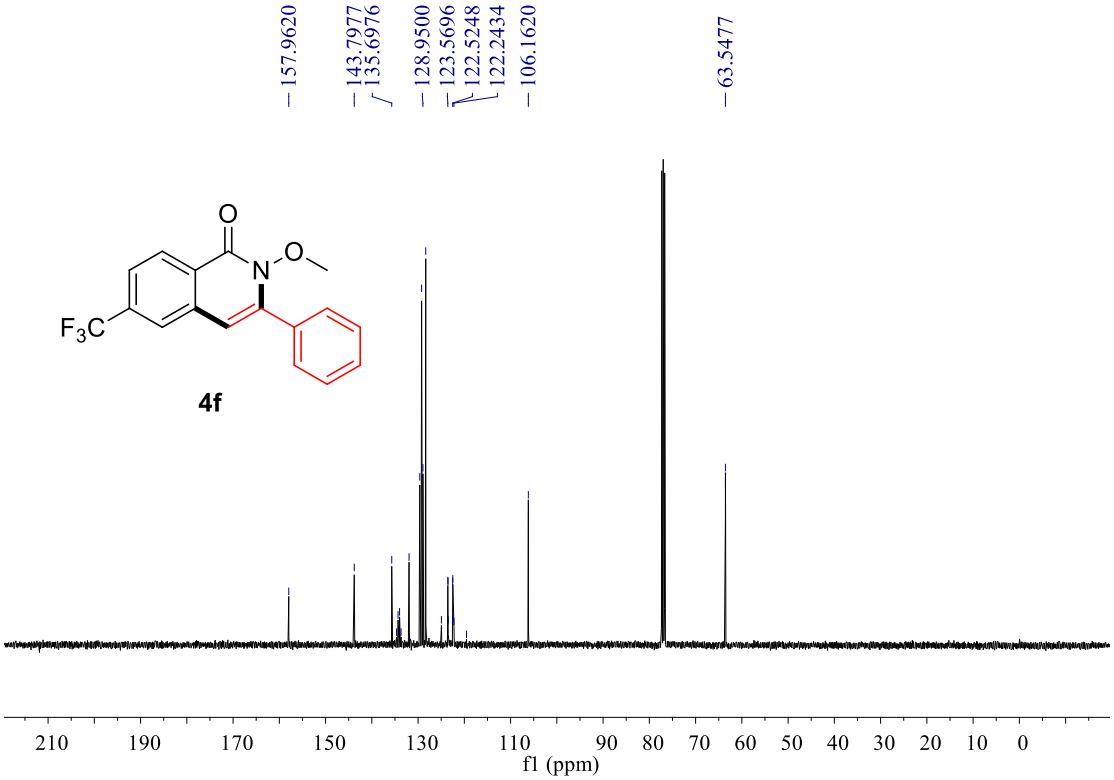
0.0
f1 (ppm)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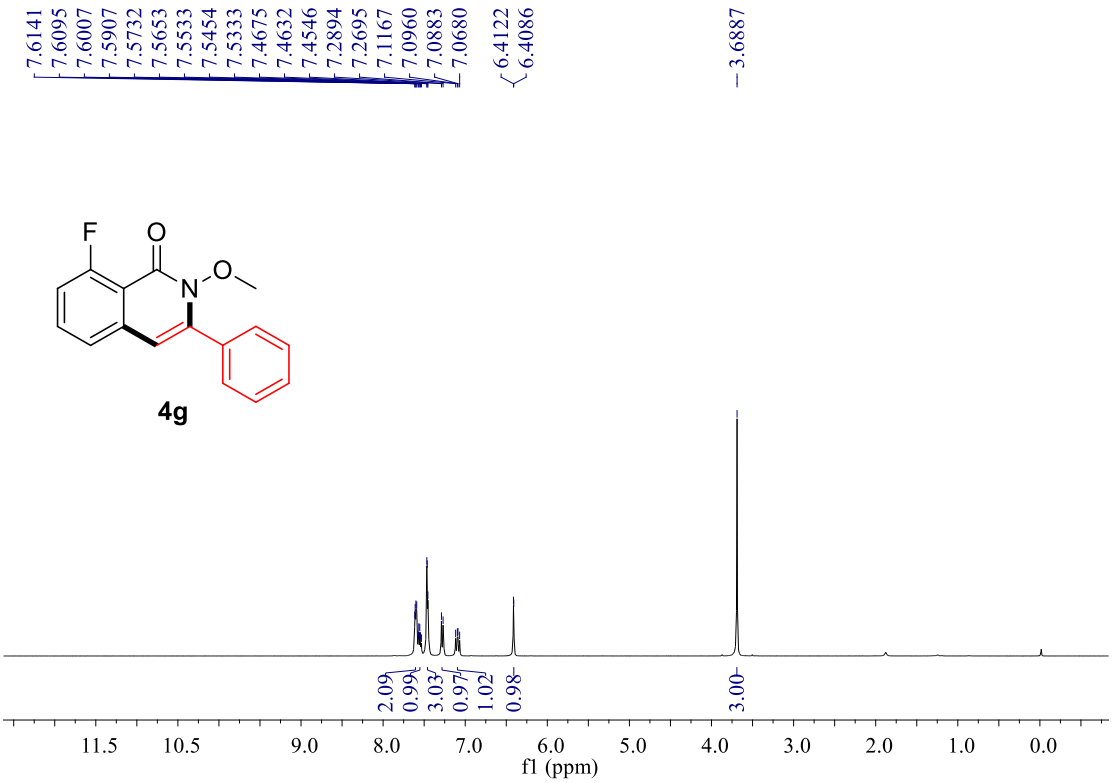
63.5477
O
N
O
F3C
4f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4546
7.2894
7.2695
7.1167
7.0960
7.0883
7.0680
6.4122
6.4086
3.6887
F
O
N
O
4g
2.09
0.99
3.03
0.97
1.02
0.98
3.00
11.5
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7.0
6.0
5.0
4.0
3.0
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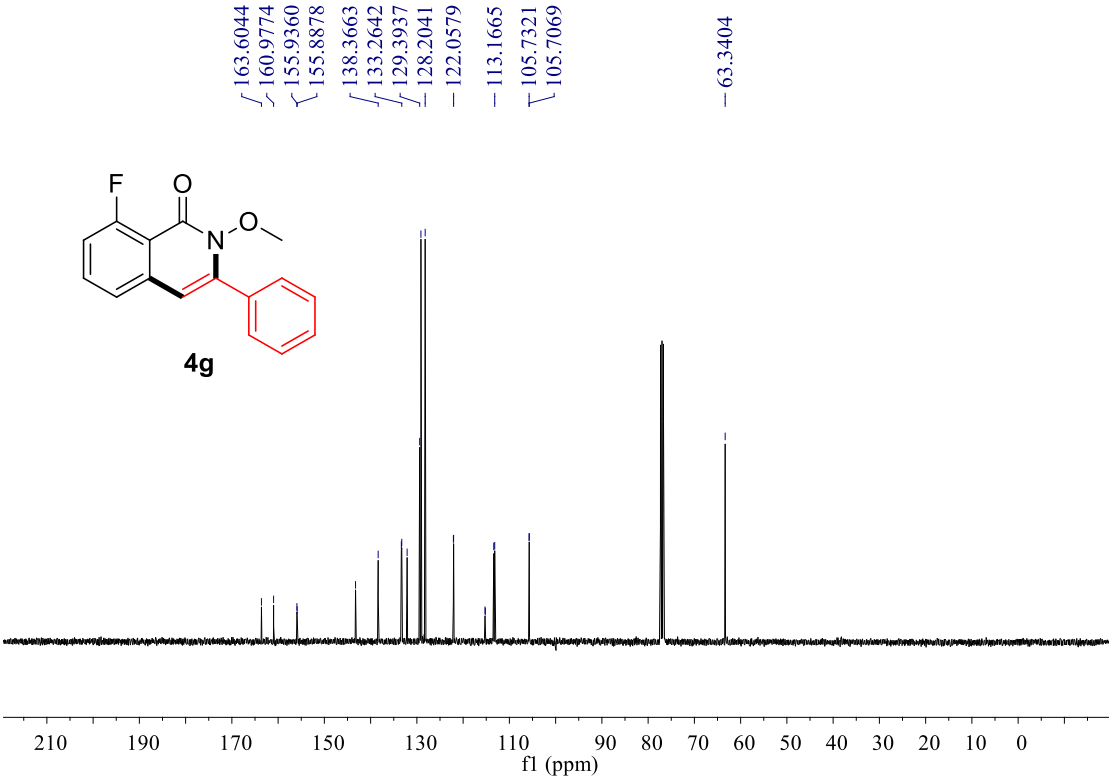
1.0
0.0
f1 (ppm)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129.3937
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105.7069
63.3404
F
O
N
O
4g
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170
150
130
110
90
80
70
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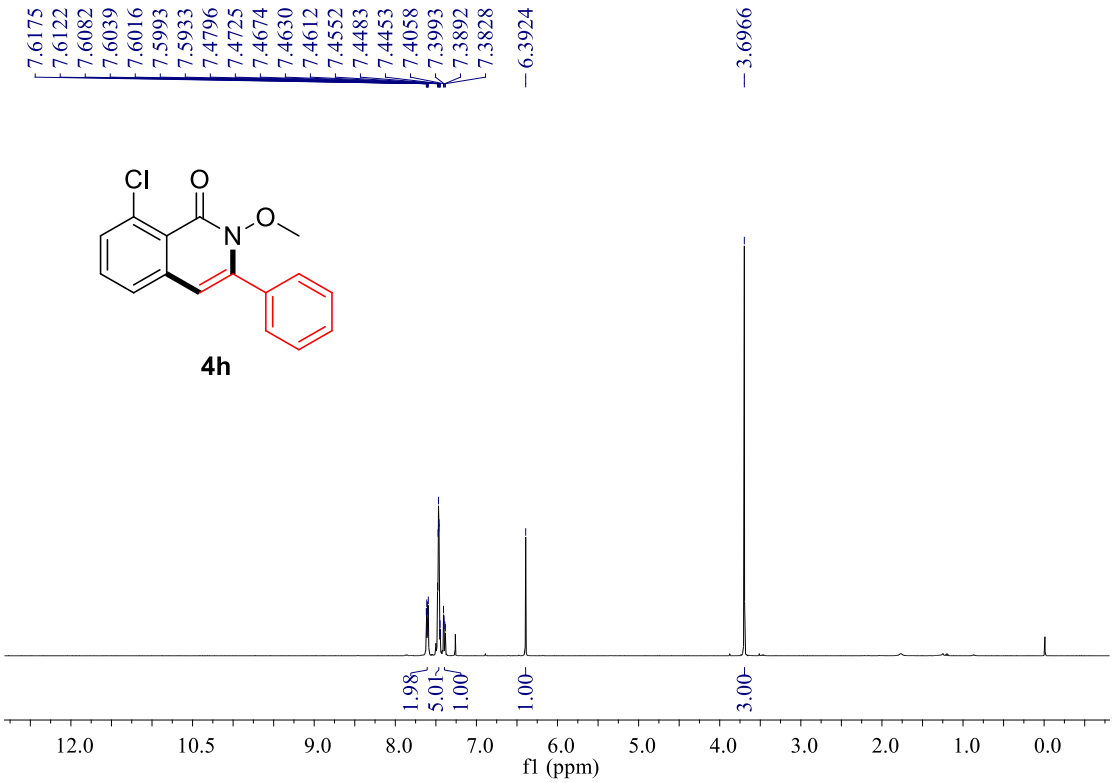
50
40
30
20
10
0
f1 (ppm)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7.3993
7.3892
7.3828
6.3924
3.6966
Cl
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N
O
4h
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1.00
1.00
3.00
12.0
10.5
9.0
8.0
7.0
6.0
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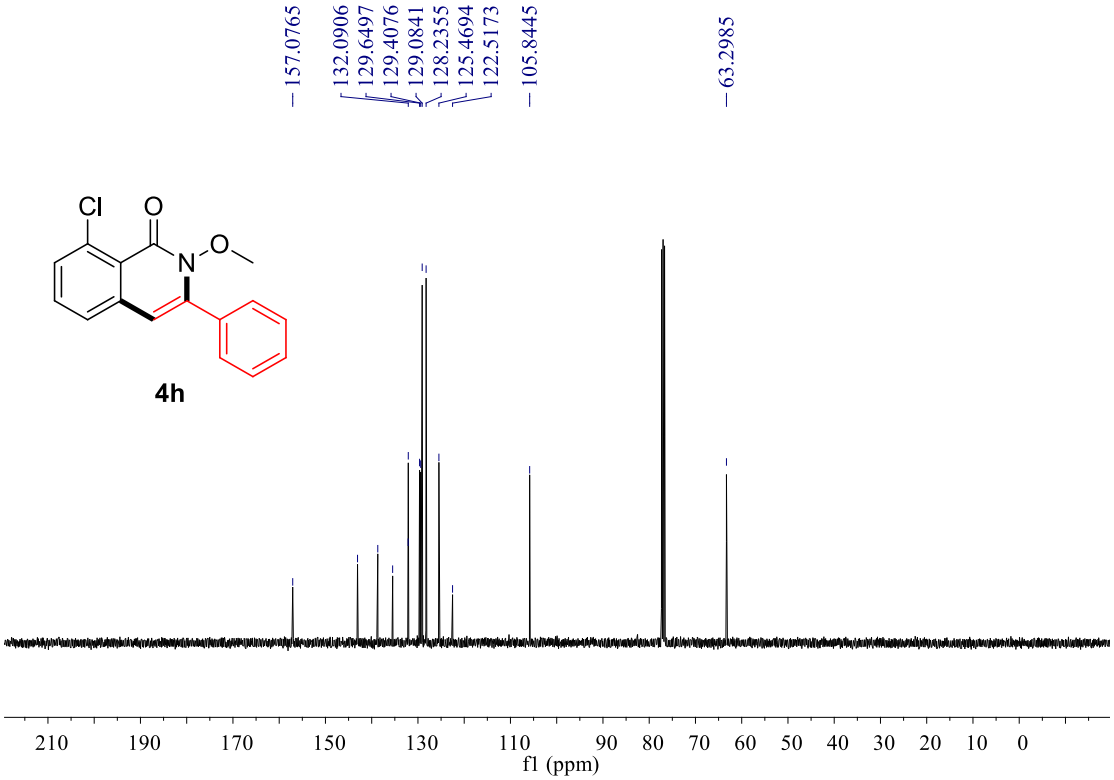
f1 (ppm)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129.4076
129.0841
128.2355
125.4694
122.5173
105.8445
63.2985
Cl
O
N
O
4h
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170
150
130
110
90
80
70
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50
40
30
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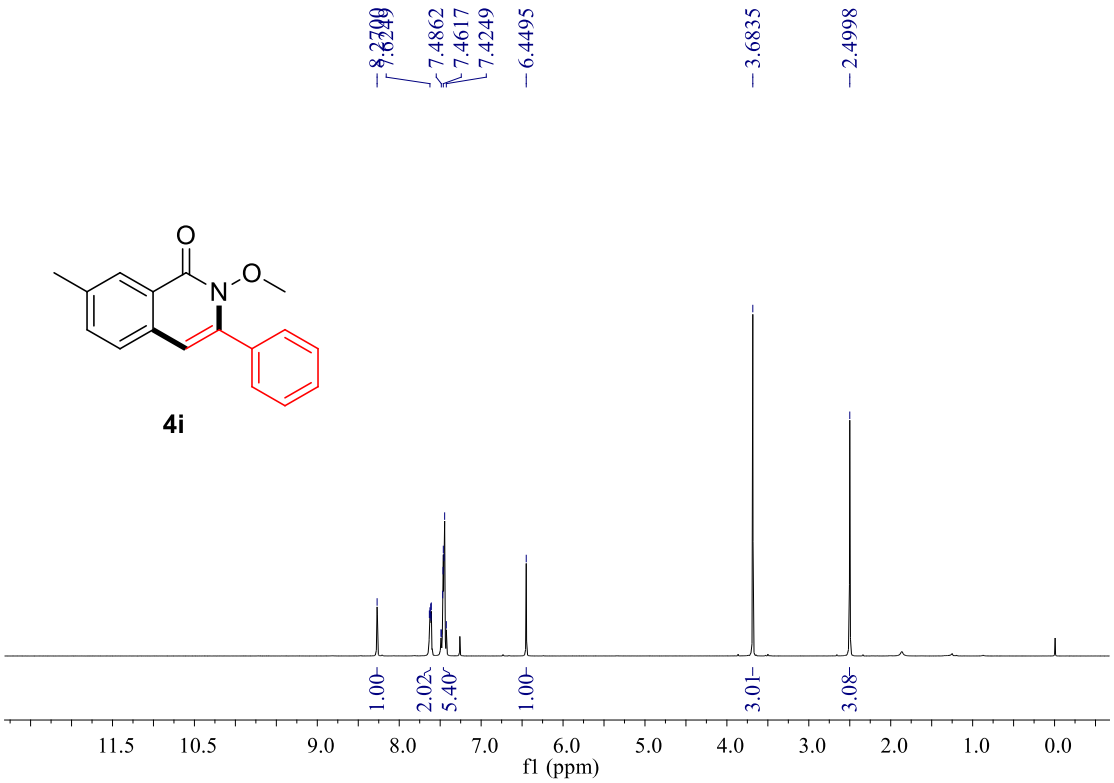
f1 (ppm)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7.4249
6.4495
3.6835
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O
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O
4i
1.00
2.02
5.40
1.00
3.01
3.08
11.5
10.5
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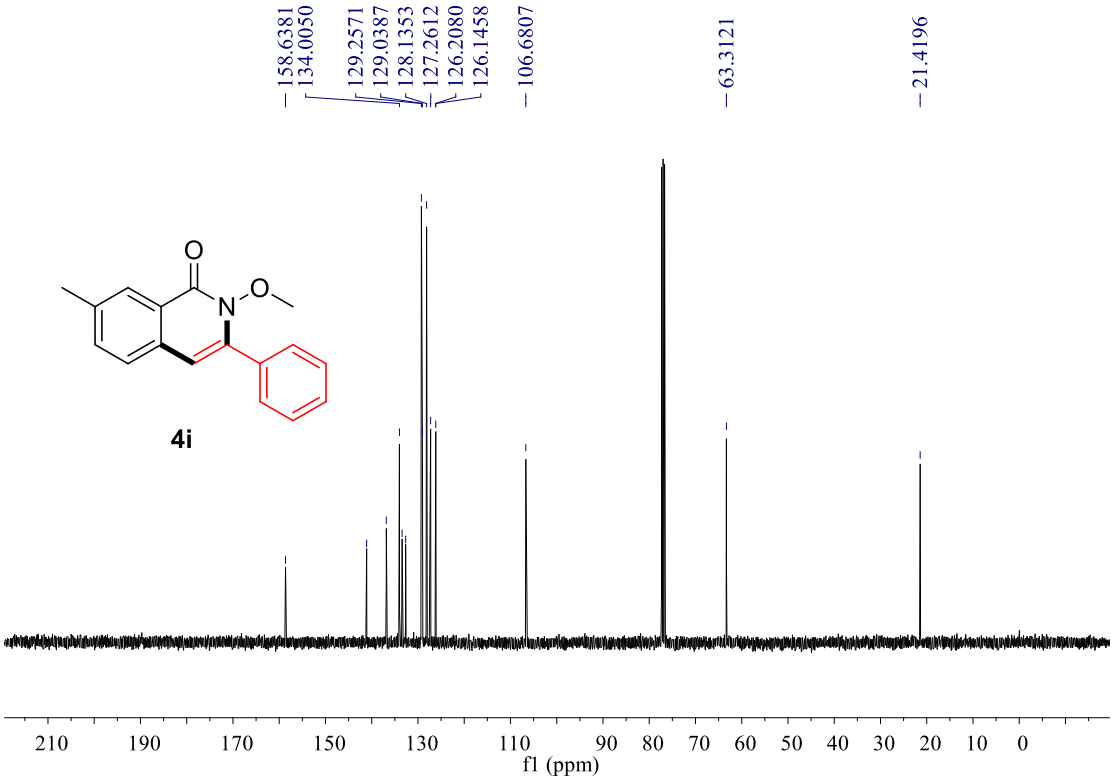
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.2571
129.0387
128.1353
127.2612
126.2080
126.1458
106.6807
63.3121
21.4196
O
N
O
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170
150
130
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90
80
70
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50
40
30
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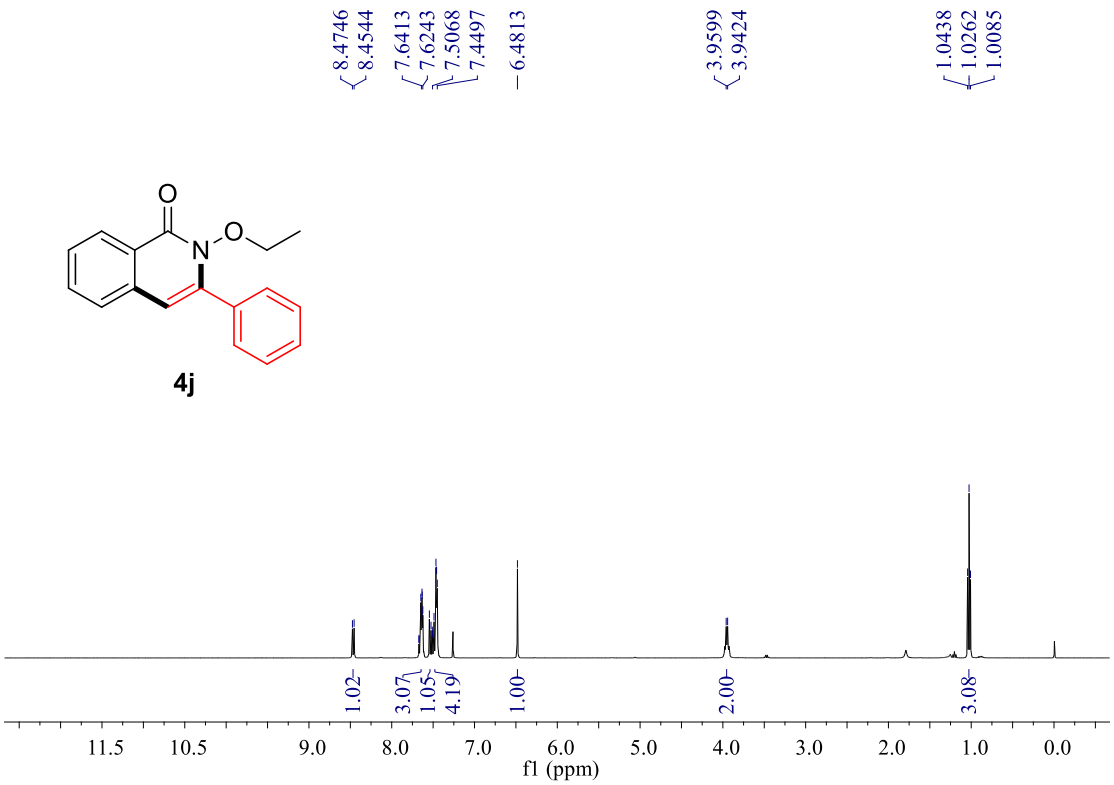
10
0
f1 (ppm)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7.5068
7.4497
6.4813
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3.9424
1.0438
1.0262
1.0085
O
N
O
4j
1.02
3.07
1.05
4.19
1.00
2.00
3.08
11.5
10.5
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7.0
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5.0
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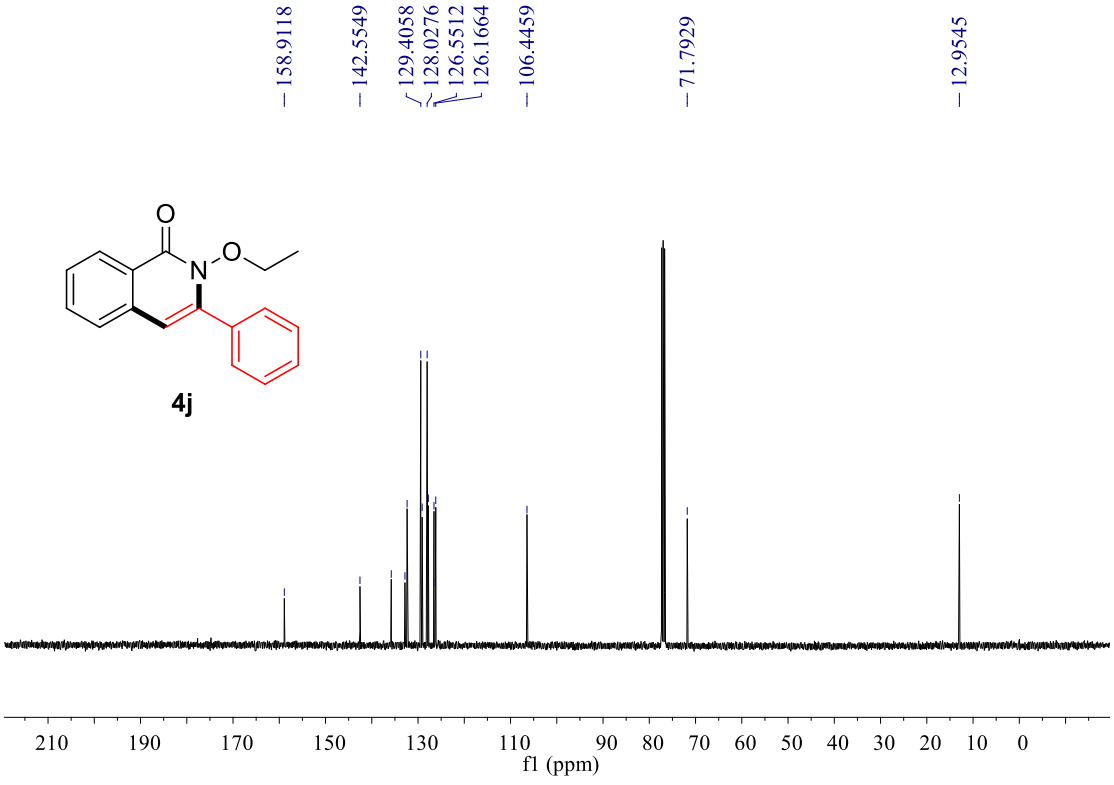
2.0
1.0
0.0
f1 (ppm)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106.4459
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12.9545
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N
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170
150
130
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90
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50
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30
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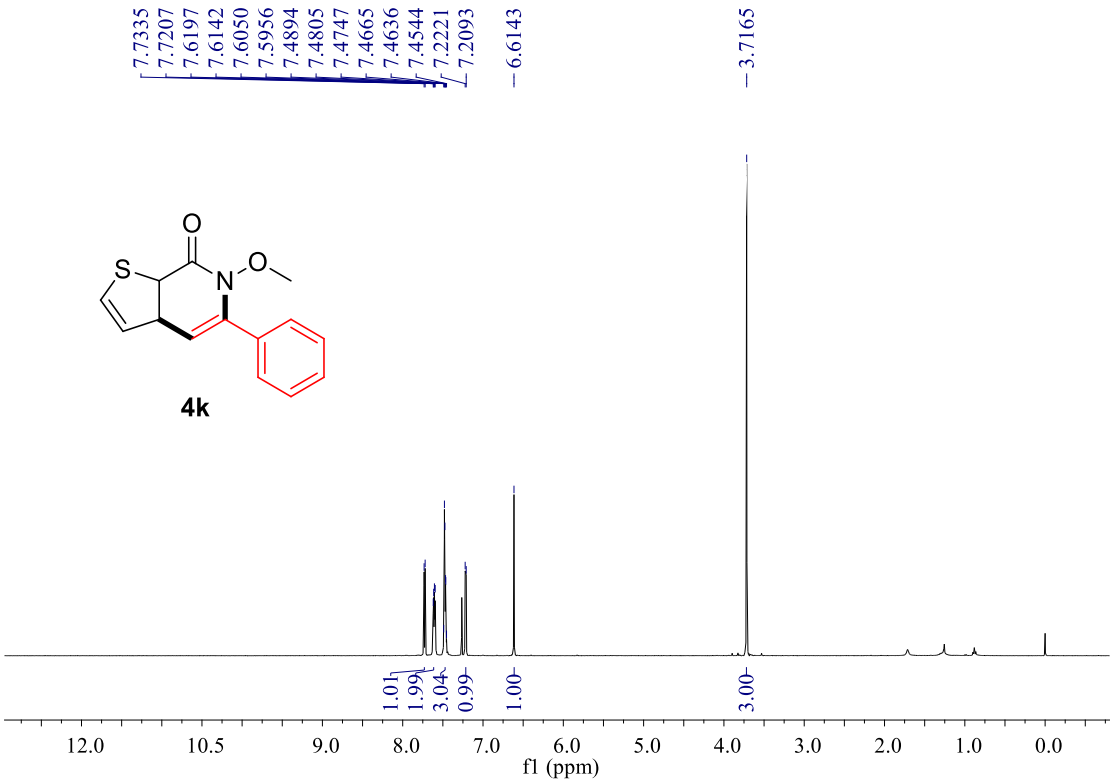
f1 (ppm)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7.7207
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7.4894
7.4805
7.4747
7.4665
7.4636
7.4544
7.2221
7.2093
6.6143
3.7165
O
S
N
O
4k
1.01
1.99
3.04
0.99
1.00
3.00
12.0
10.5
9.0
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7.0
6.0
5.0
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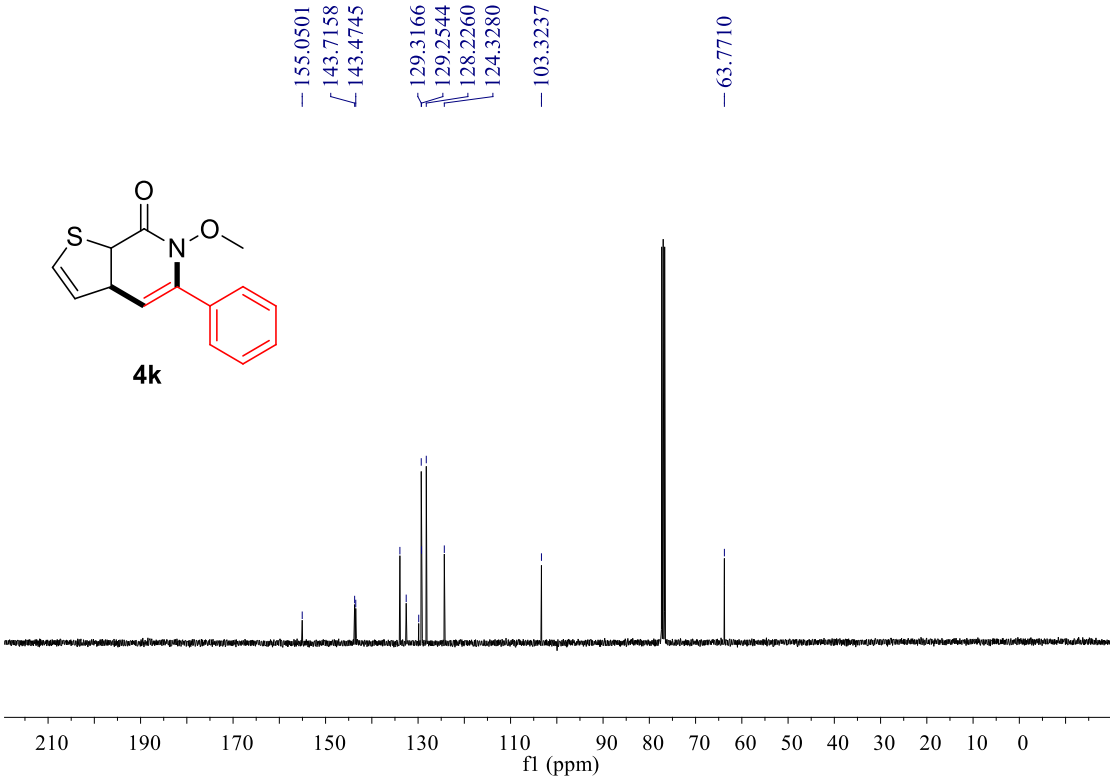
0.0
f1 (ppm)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143.4745
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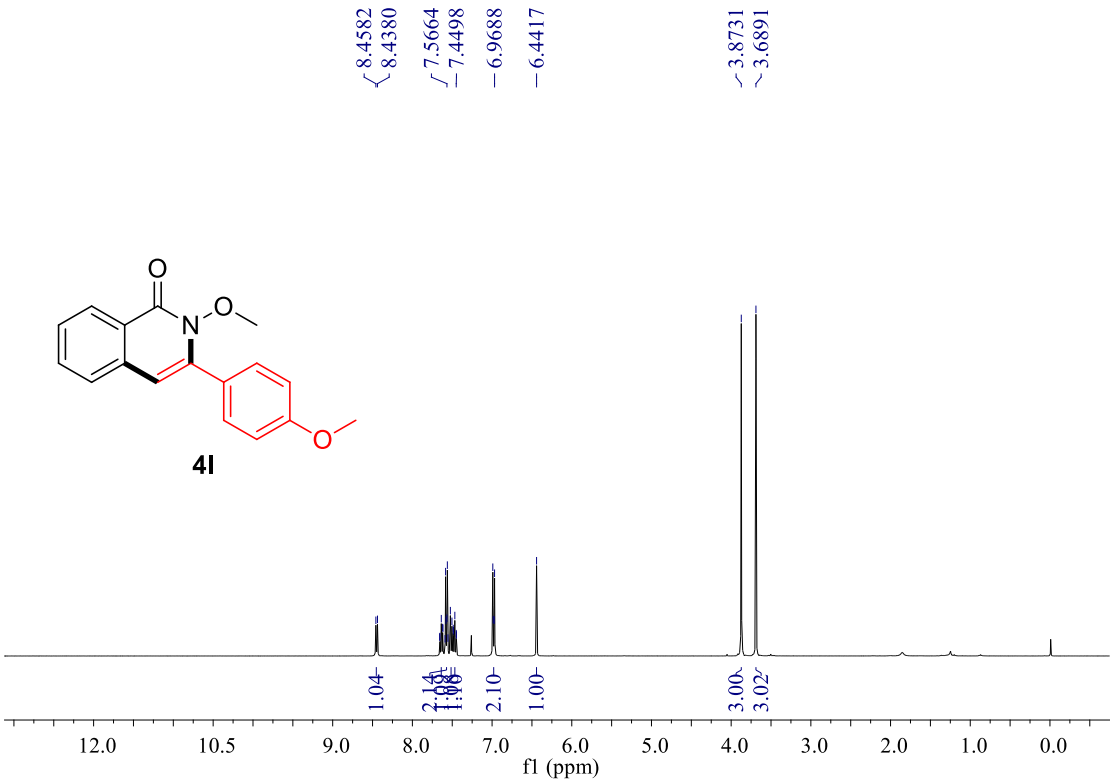
129.2544
128.2260
124.3280
103.3237
63.7710
O
S
N
O
4k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.4582
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7.5664
7.4498
6.9688
6.4417
3.8731
3.6891
4l
1.04
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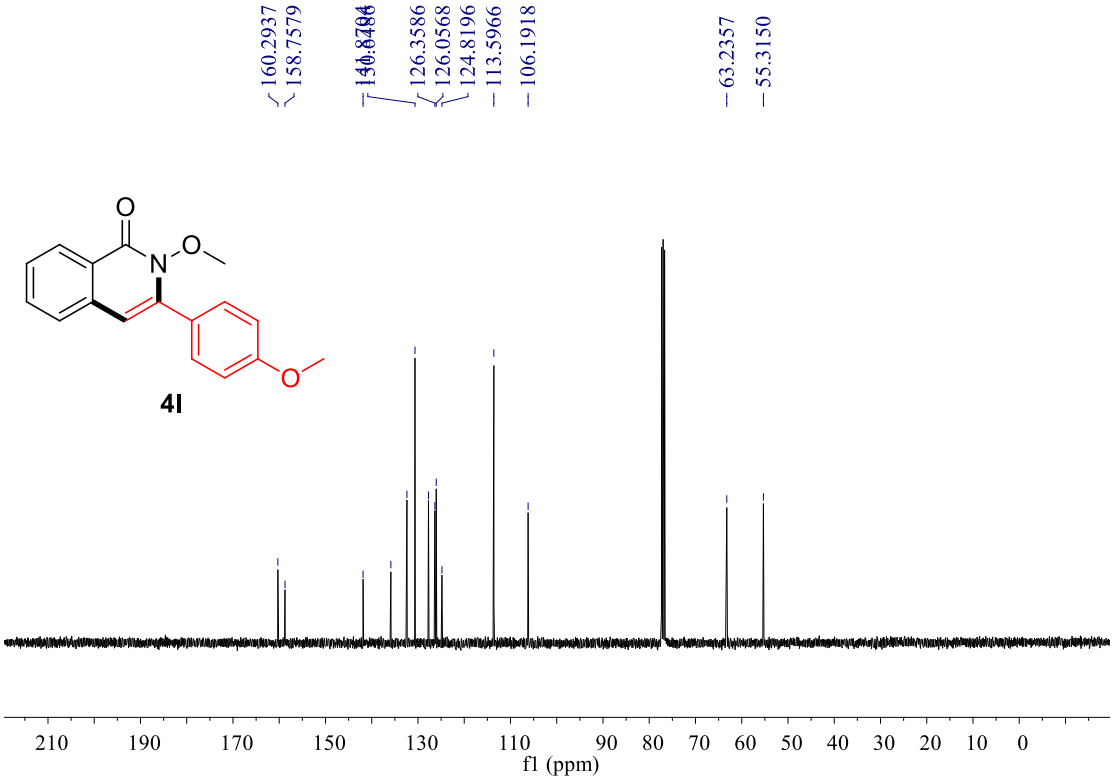
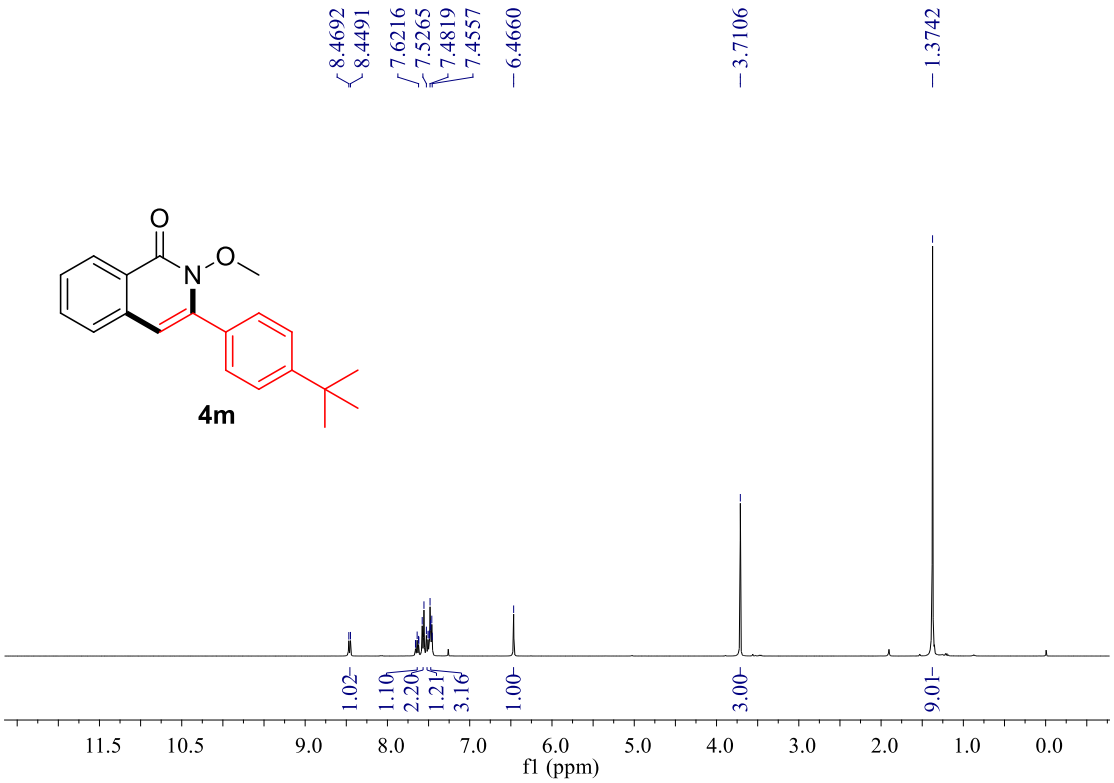
1.08
2.10
1.00
3.00
3.02
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


160.2937
158.7579
126.3586
126.0568
124.8196
113.5966
106.1918
63.2357
55.3150
4l
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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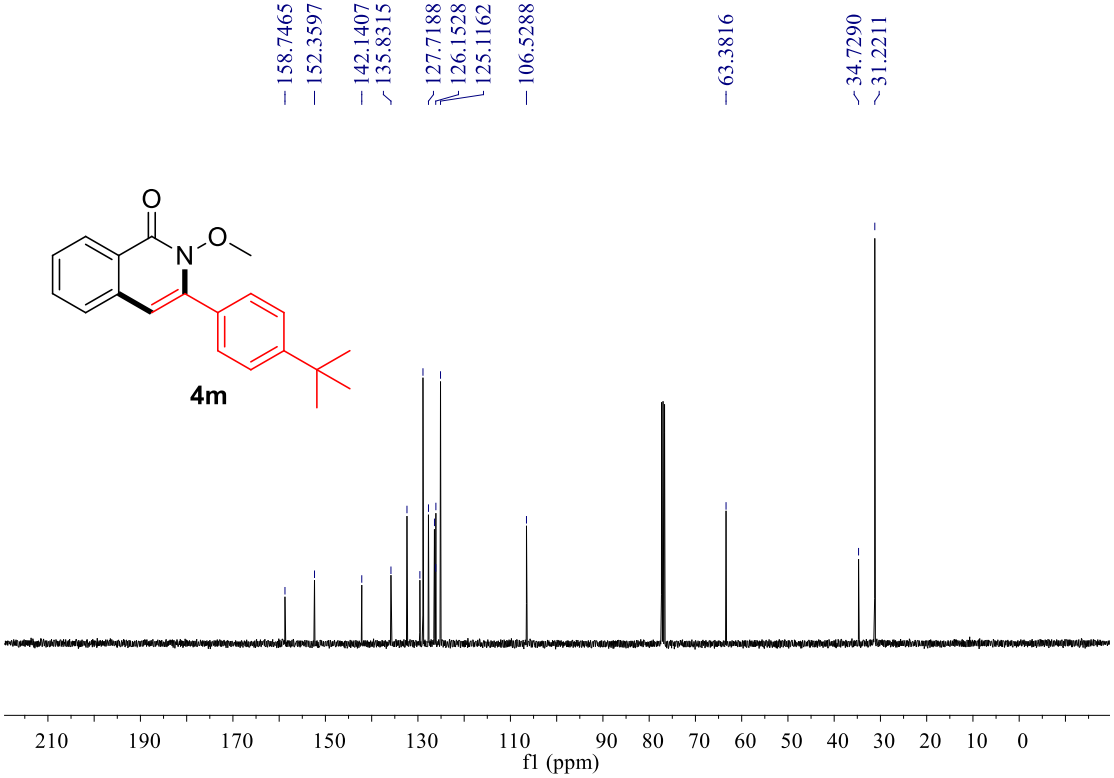
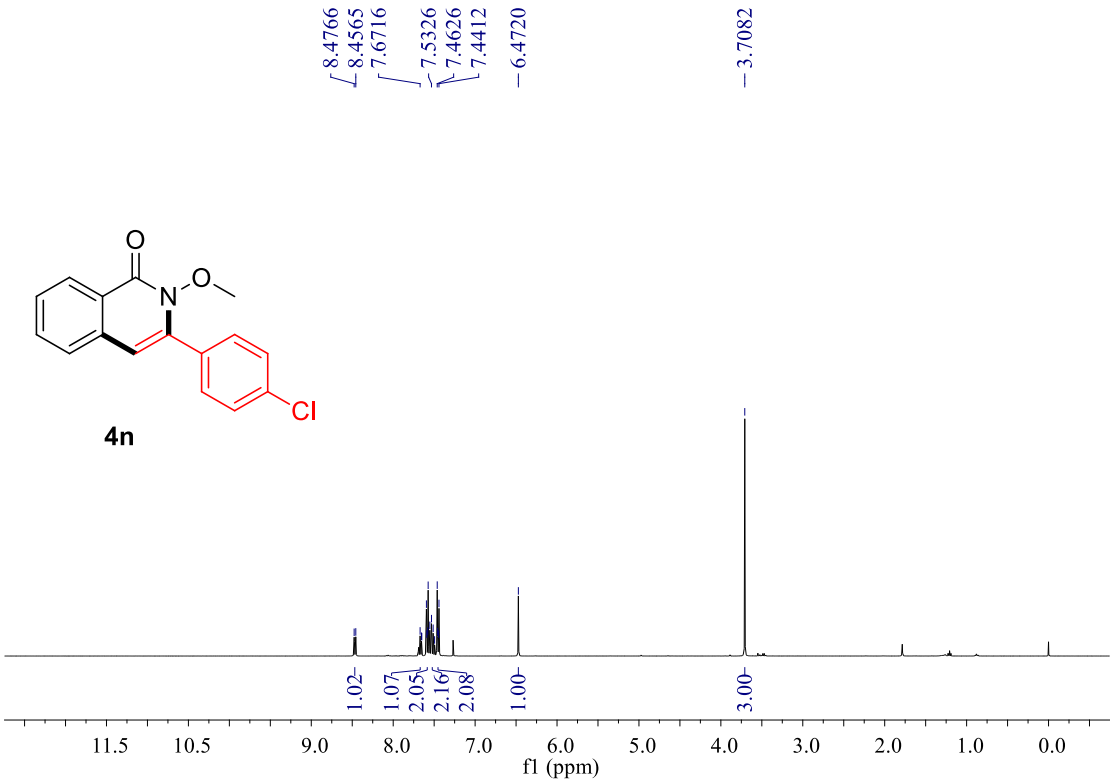
8.4491
7.6216
7.5265
7.4819
7.4557
6.4660
3.7106
1.3742
4m
1.02
1.10
2.20
1.21
3.16
1.00
3.00
9.01
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


158.7465
152.3597
142.1407
135.8315
127.7188
126.1528
125.1162
106.5288
63.3816
34.7290
31.2211
4m
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.6716
7.5326
7.4626
7.4412
6.4720
3.7082
O
N
O
Cl
4n
1.02
1.07
2.05
2.16
2.08
1.00
3.00
11.5
10.5
9.0
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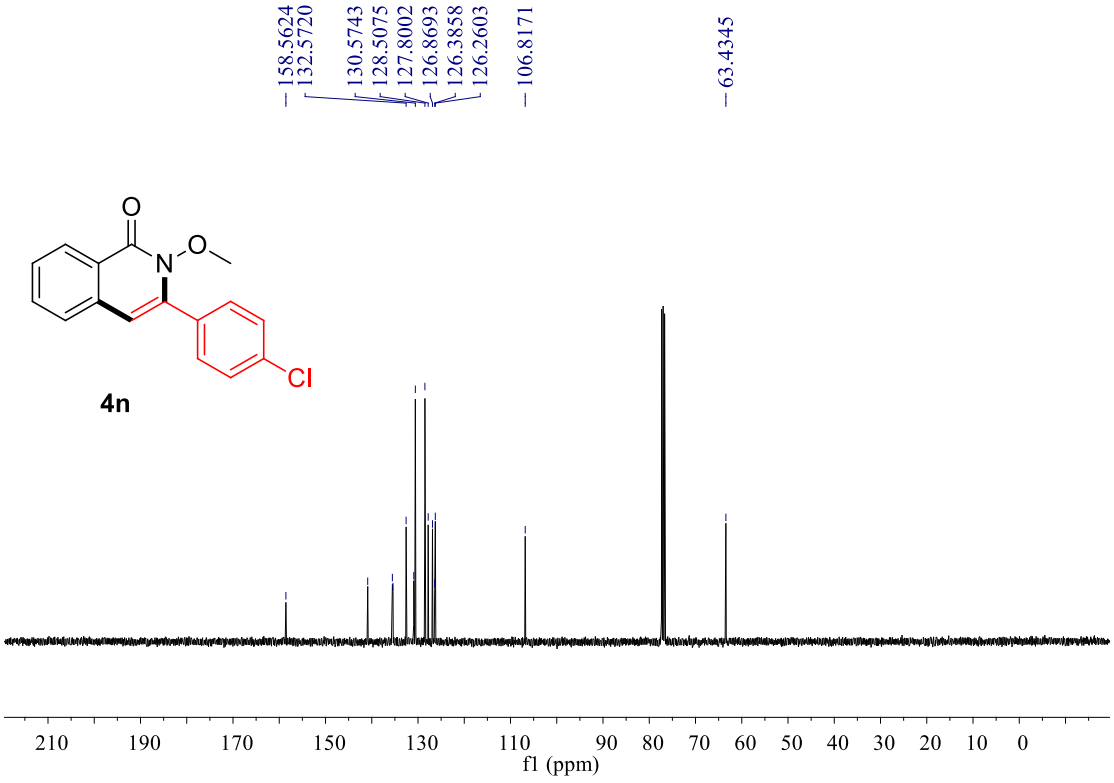
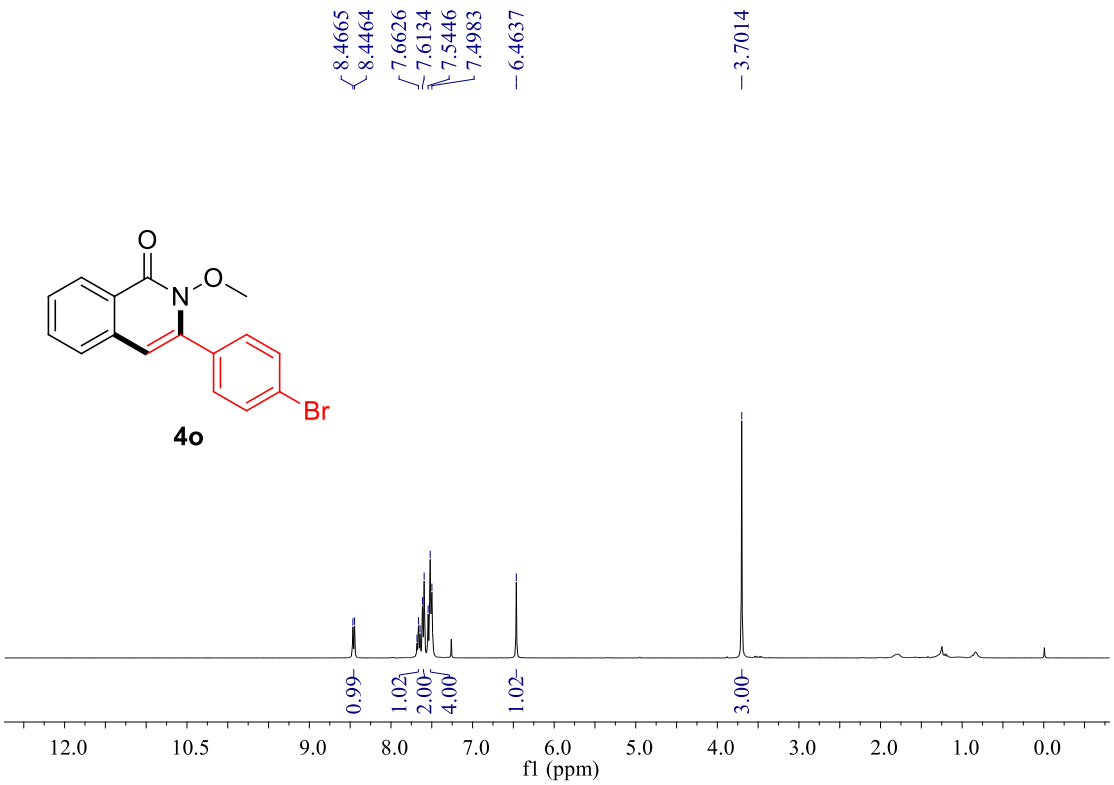
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


158.5624
132.5720
130.5743
128.5075
127.8002
126.8693
126.3858
126.2603
106.8171
63.4345
O
N
O
Cl
4n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.6626
7.6134
7.5446
7.4983
6.4637
3.7014
O
N
O
Br
4o
0.99
1.02
2.00
4.00
1.02
3.00
12.0
10.5
9.0
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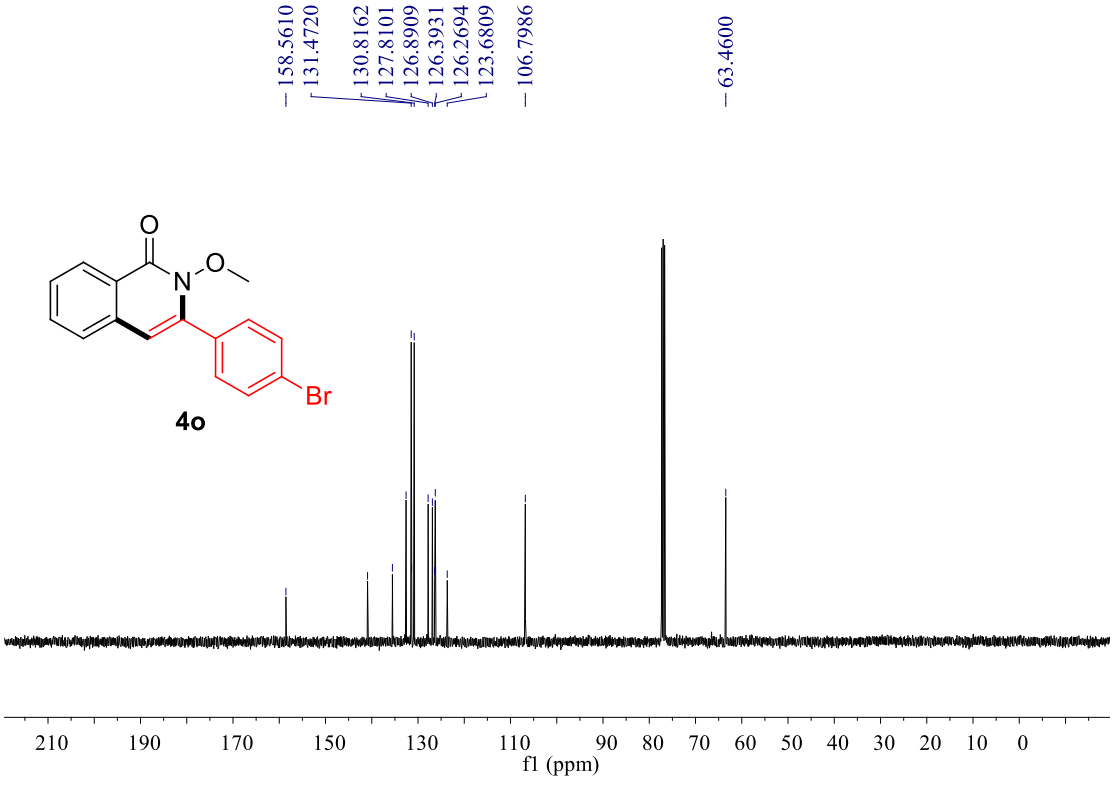
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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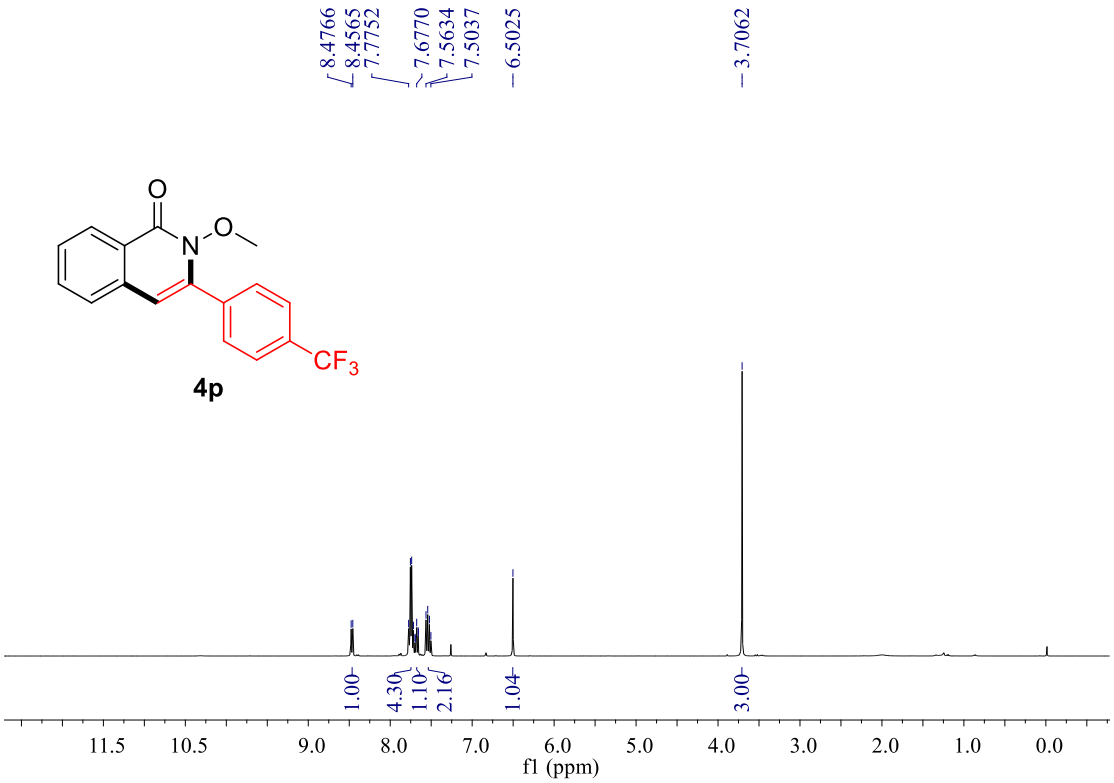
130.8162
127.8101
126.8909
126.3931
126.2694
123.6809
106.7986
63.4600
O
N
O
Br
4o
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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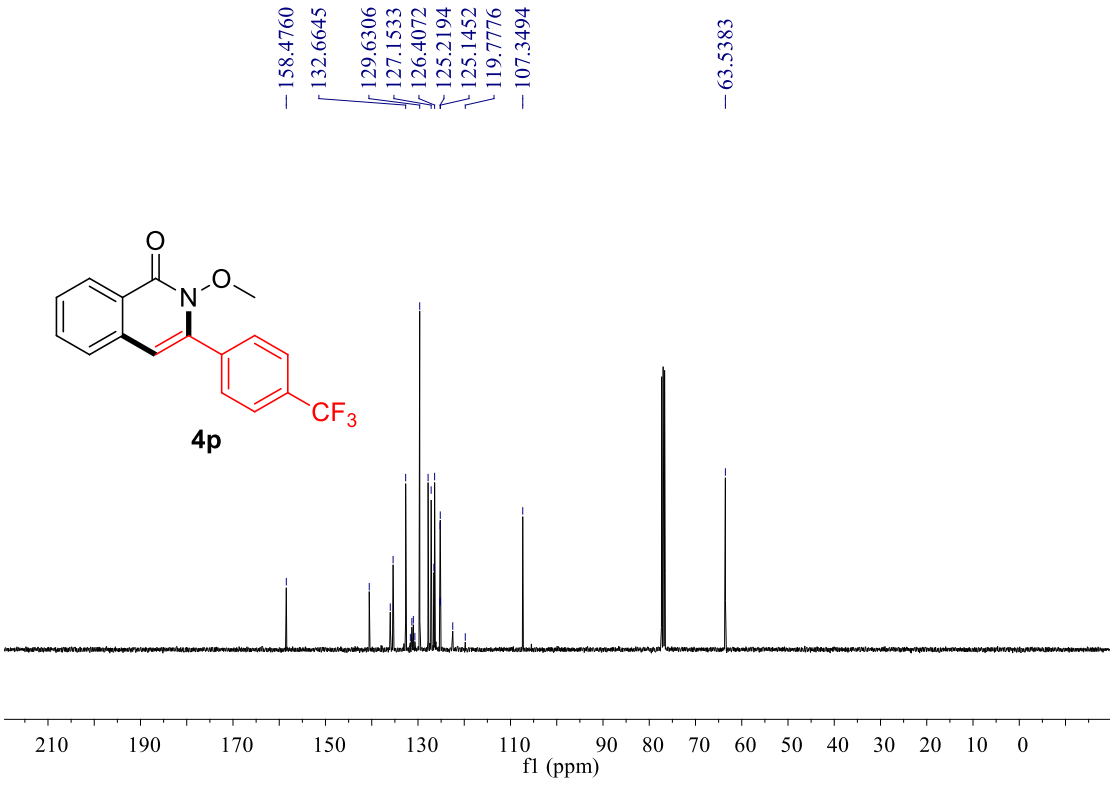
7.7752
7.6770
7.5634
7.5037
6.5025
3.7062
O
N
O
CF3
4p
1.00
4.30
1.10
2.16
1.04
3.00
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.6306
127.1533
126.4072
125.2194
125.1452
119.7776
107.3494
63.5383
O
N
O
CF3
4p
210
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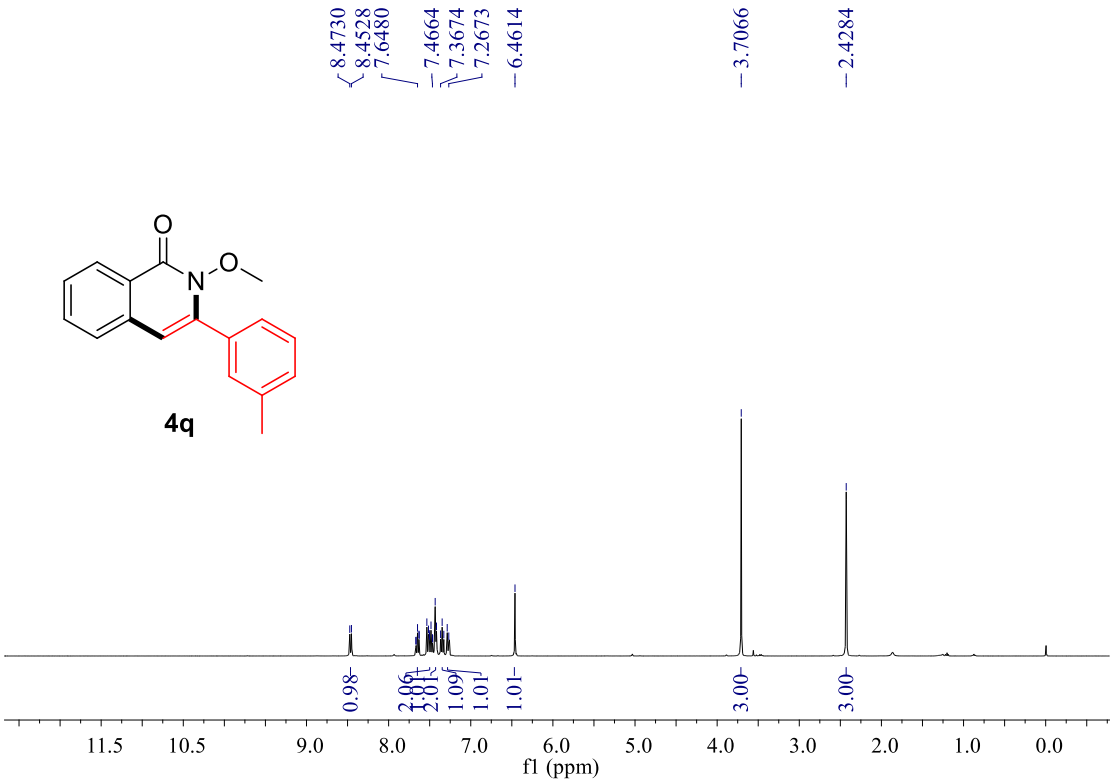
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4664
7.3674
7.2673
6.4614
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2.4284
O
N
O
4q
0.98
2.06
2.01
1.09
1.01
1.01
3.00
3.00
11.5
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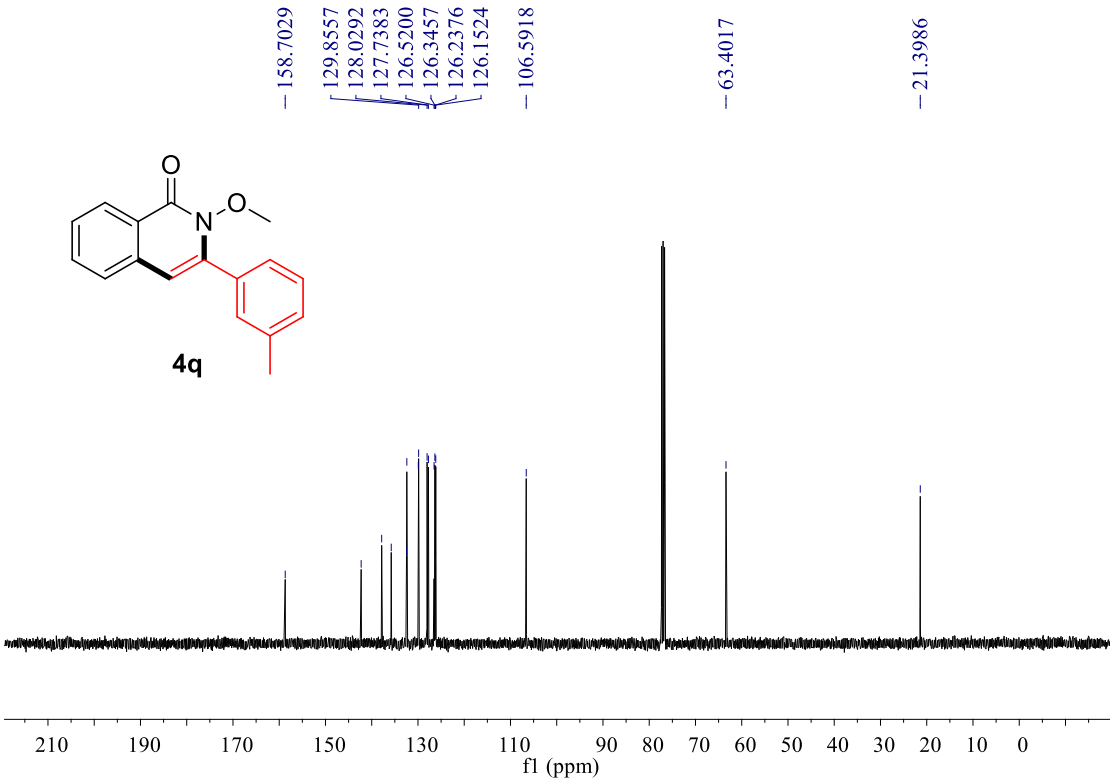
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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126.5200
126.3457
126.2376
126.1524
106.5918
63.4017
21.3986
O
N
O
4q
210
190
170
150
130
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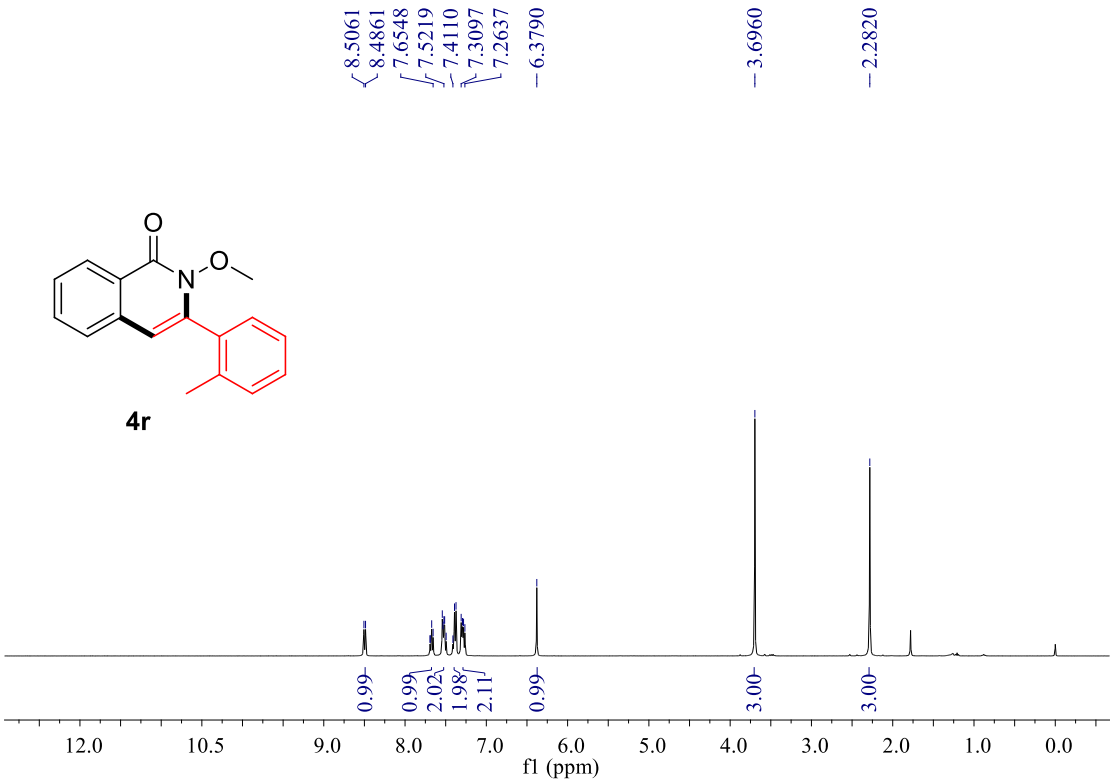
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.6548
7.5219
7.4110
7.3097
7.2637
6.3790
3.6960
2.2820
O
N
O
4r
0.99
0.99
2.02
1.98
2.11
0.99
3.00
3.00
12.0
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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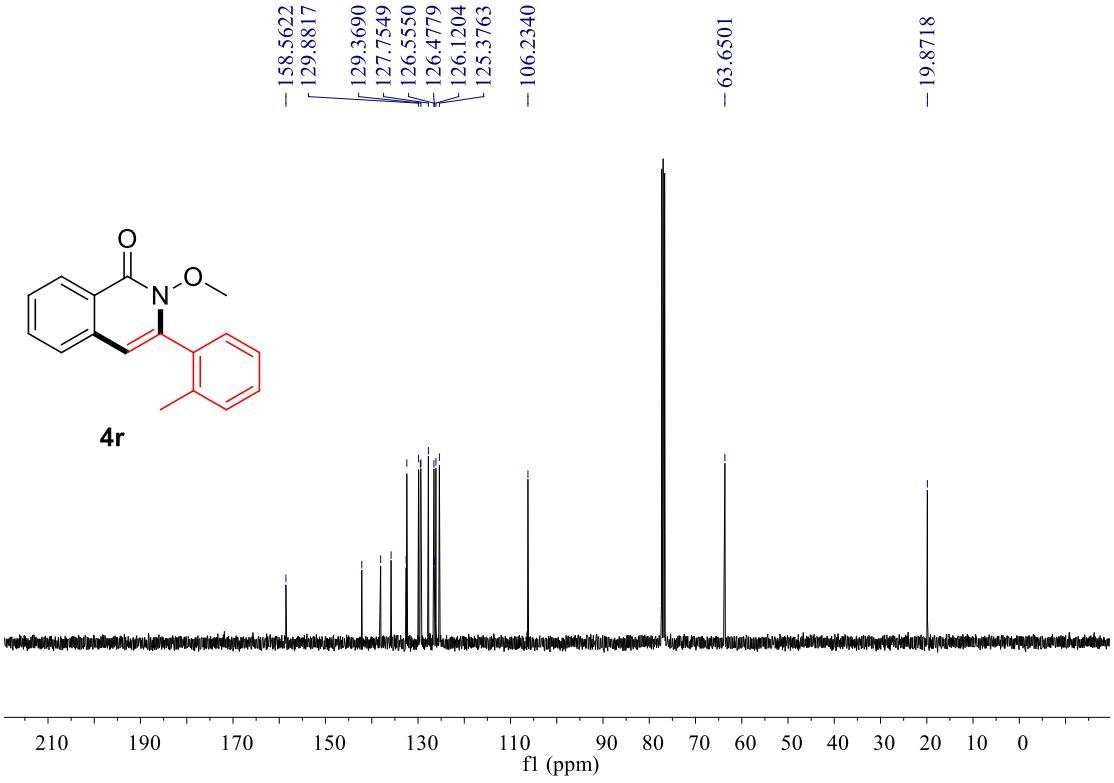
0.0
f1 (ppm)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126.1204
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63.6501
19.8718
O
N
O
4r
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170
150
130
110
90
80
70
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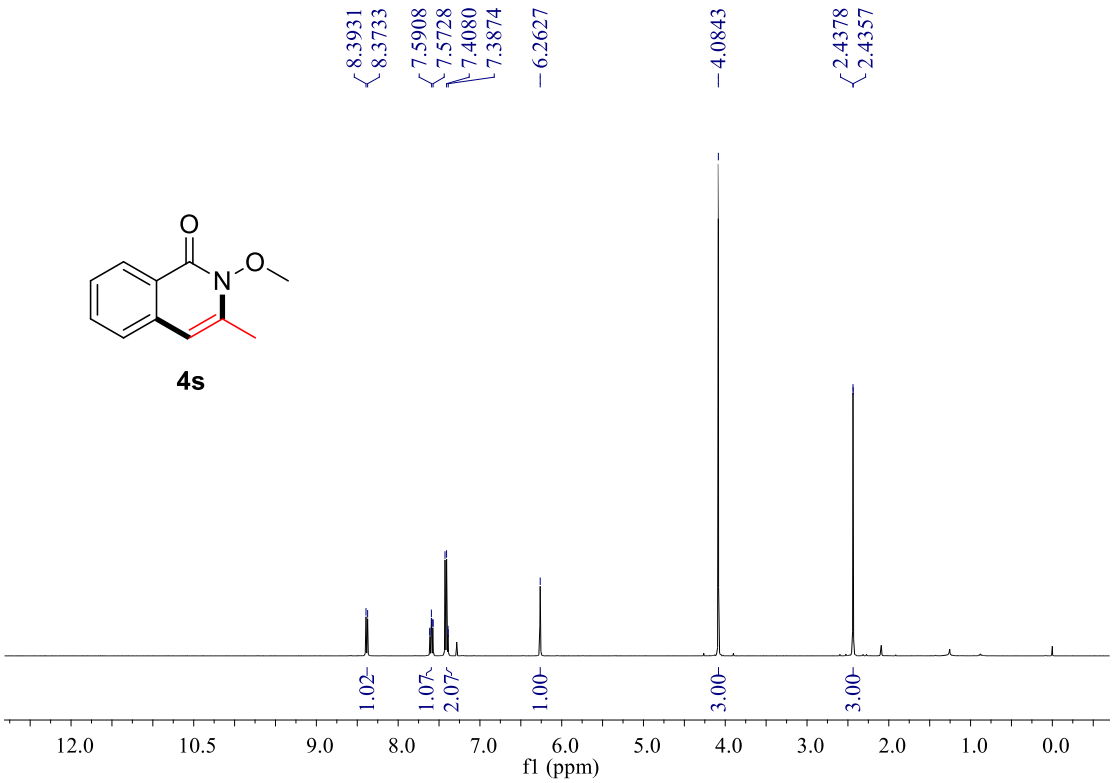
50
40
30
20
10
0
f1 (ppm)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1.07
2.07
1.00
3.00
3.00
12.0
10.5
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8.0
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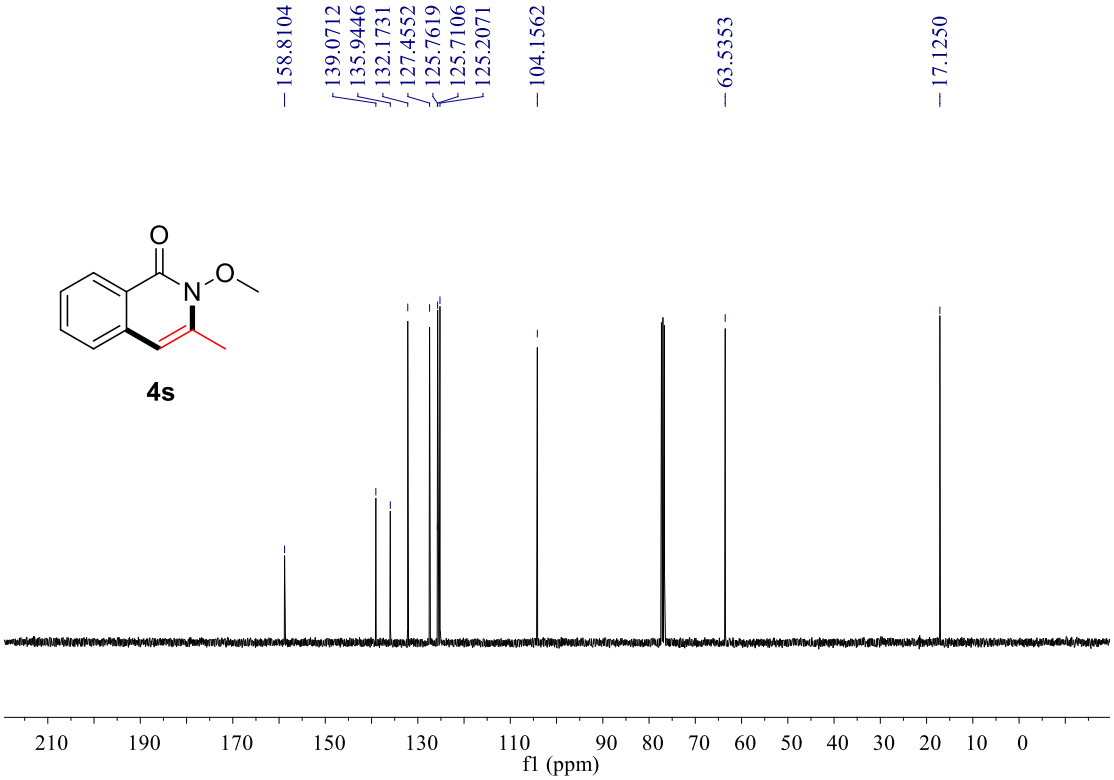
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

4s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125.7106
125.2071
104.1562
63.5353
17.1250
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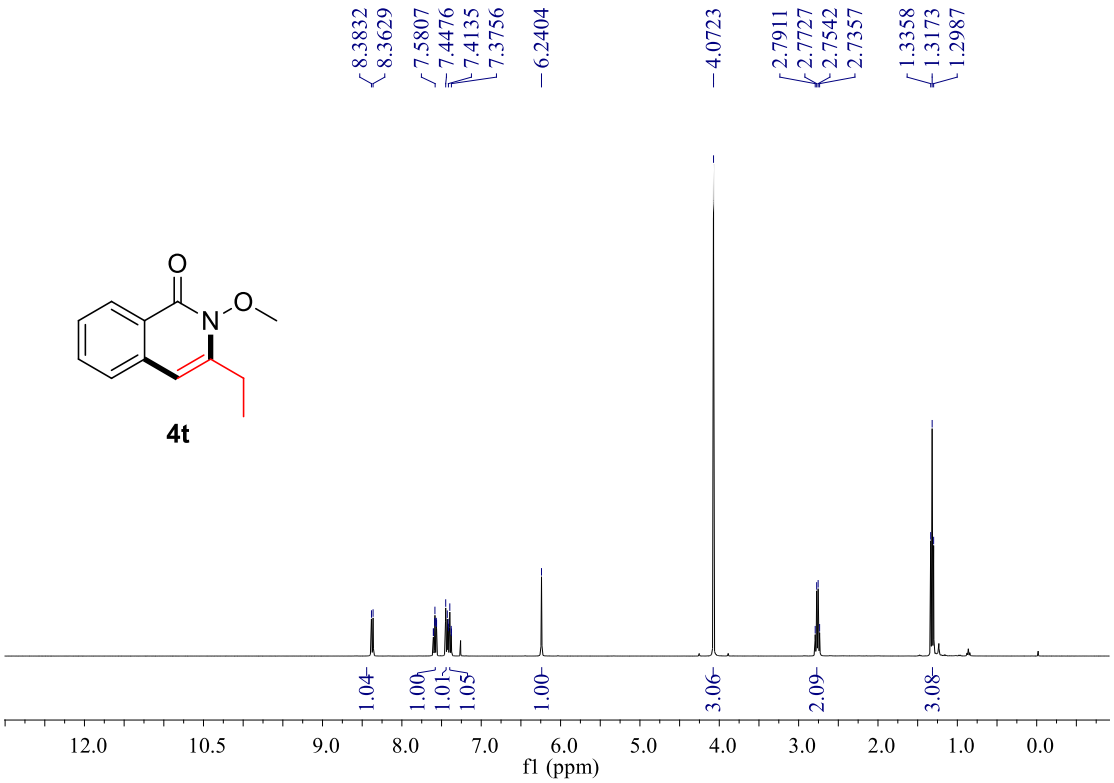
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4s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2.7357
1.3358
1.3173
1.2987
1.04
1.00
1.01
1.05
1.00
3.06
2.09
3.08
12.0
10.5
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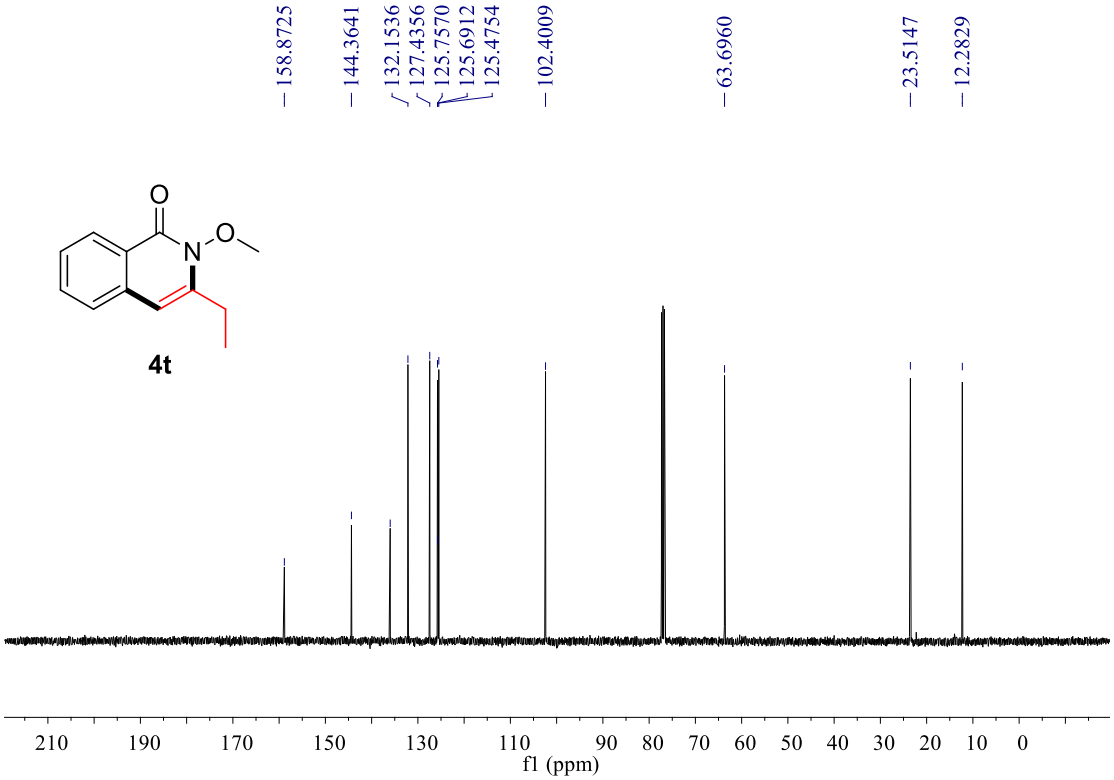
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

4t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125.4754
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63.6960
23.5147
12.2829
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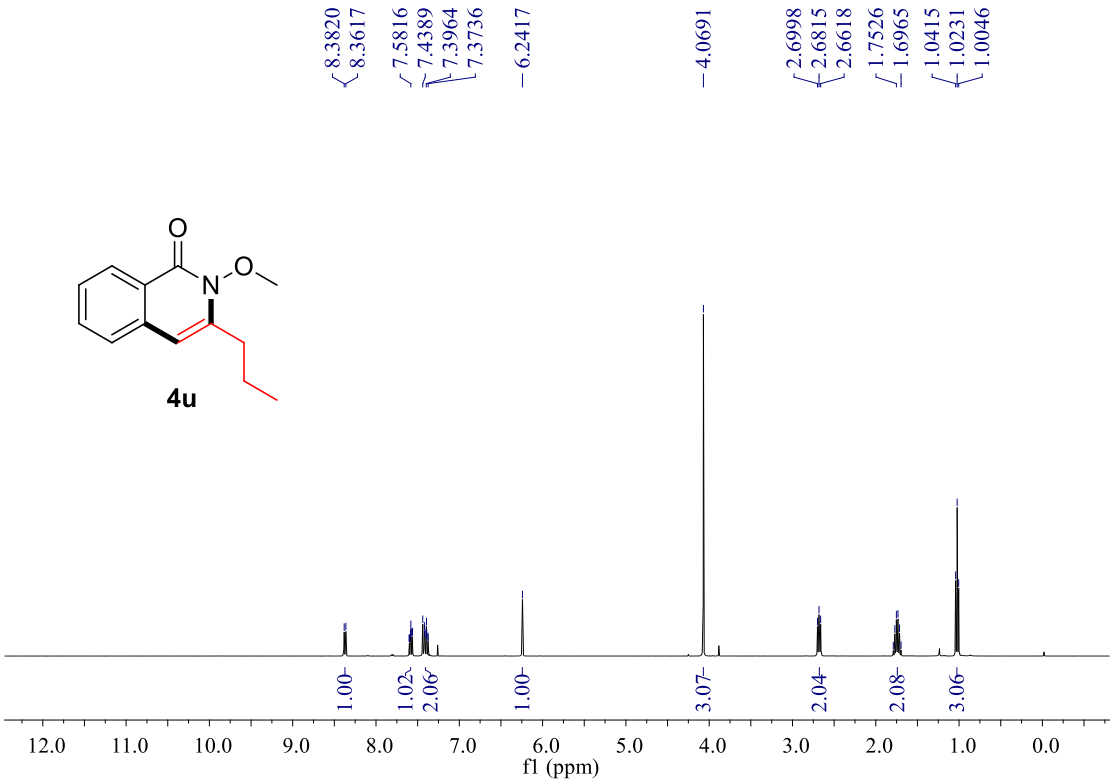
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4t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6.2417
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2.6618
1.7526
1.6965
1.0415
1.0231
1.0046
O
N
O
4u
1.00
1.02
2.06
1.00
3.07
2.04
2.08
3.06
12.0
11.0
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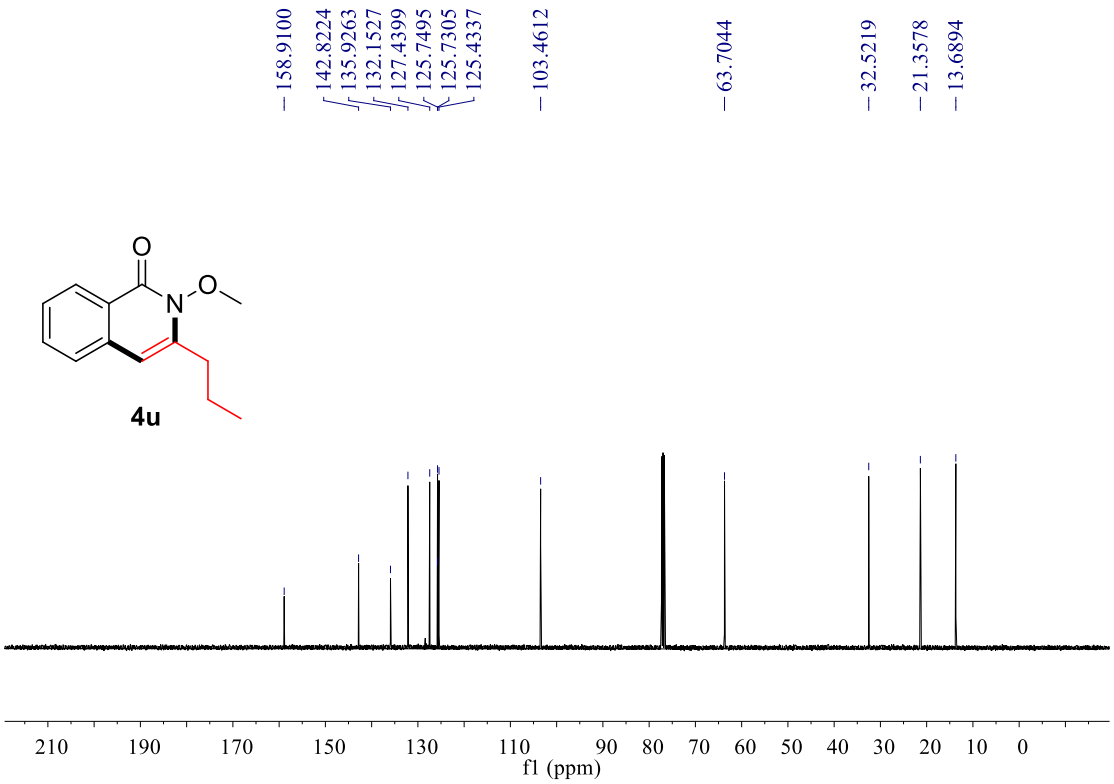
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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103.4612
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21.3578
13.6894
O
N
O
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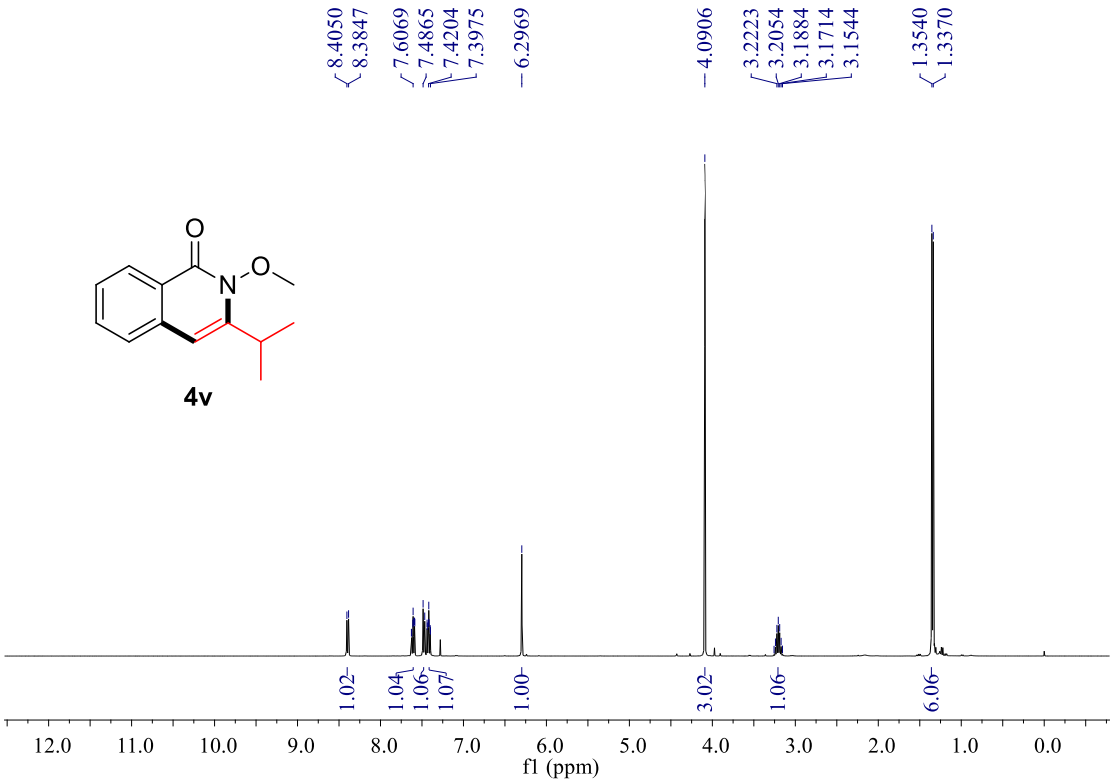
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.2969
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3.1884
3.1714
3.1544
1.3540
1.3370
O
N
O
4v
1.02
1.04
1.06
1.07
1.00
3.02
1.06
6.06
12.0
11.0
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6.0
5.0
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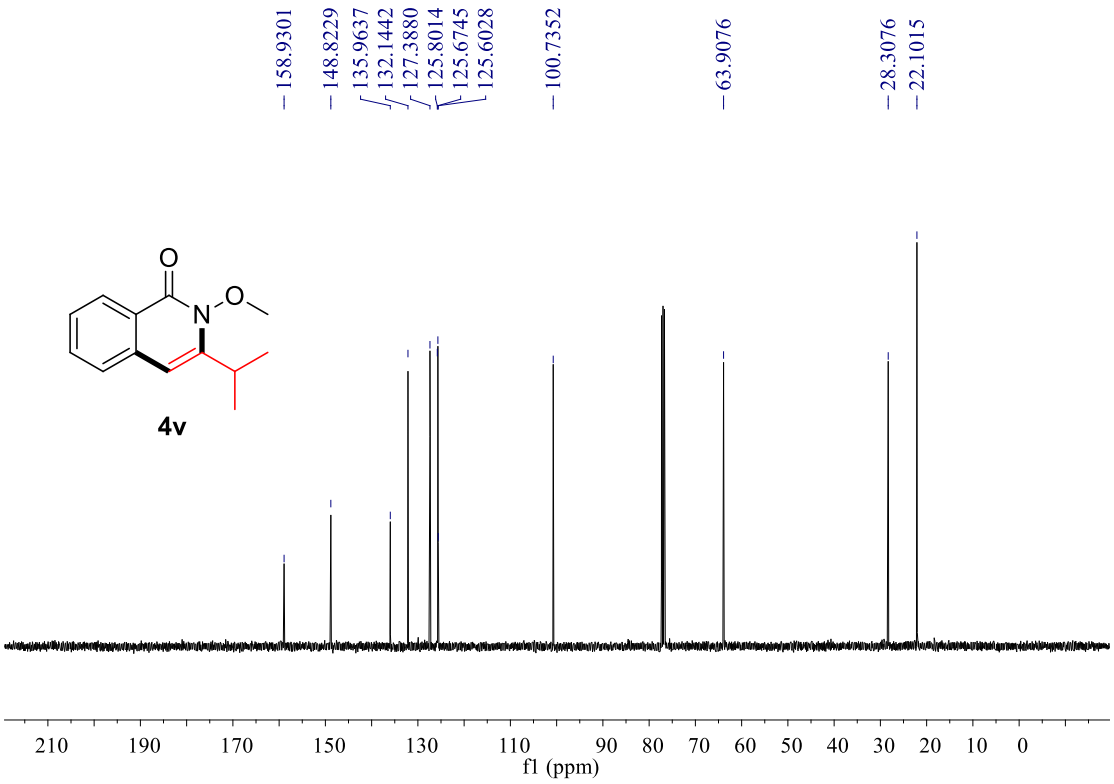
2.0
1.0
0.0
f1 (ppm)


158.9301
148.8229
135.9637
132.1442
127.3880
125.8014
125.6745
125.6028
100.7352
63.9076
28.3076
22.1015
O
N
O
4v
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)