Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An Organocatalyst Bound α-Aminoalkyl Radical Intermediate for Controlled Aerobic Oxidation of Iminium Ion

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Table of Contents

Experimental Procedures

General Information

The oxidation reactions were carried out with anhydrous solvents in flame-dried glass wares under anhydrous oxygen or air atmosphere. All other reactions were carried out under anhydrous and argon atmosphere. THF was dried over sodium before use. All other solvents were purchased anhydrous and stored under argon over 4 Å molecular sieves. Analytical thin-layer chromatography was performed on glass plates pre-coated with silica gel (Silica Gel 60 F_{254}; Merck). Plates were visualized using UV light (λ=254 nm) and then stained with either aqueous basic potassium permanganate ($KMnO_4$) or p-anisaldehyde and developed upon heating in Hitachi heat gun. Flash chromatography was performed using silica gel (Merck and Spectrochem, 230-400 mesh), eluting with solvents as indicated. Flash column was performed using Sebo aquarium air pump (SB-548A).

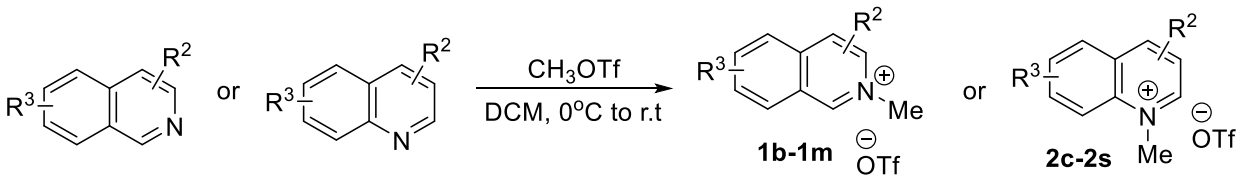
^{1}H and ^{13}C spectras were acquired in deuterated solvents at room temperature on Bruker: Ultrashield 400 MHz, Ultrashield 500 MHz spectrometer. Chemical shifts (δ) are reported for ^{1}HNMR in ppm from TMS as internal standard and ^{13}C from the residual solvent peak. ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). Melting points were checked in Buchi Melting Point B-540 instrument and reported in ºC. FT-IR were analyzed in Bruker ALPHA instrument and reported as cm^{-1}. High resolution (HRMS) mass spectral analyses were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Chiral HPLC separations were achieved using an Agilent 1260 Infinity series normal phase HPLC unit and HP Chemstation software with Chiralpak® IA columns (250 × 4.6 mm). All eluent systems were isocratic.

Materials

Commercially available reagents were purchased and used as obtained. Substituted analogs of quinoline, isoquinoline and chiral phoshite catalysts were synthesized following literature procedures: 3-bromoquinoline,[1] 3-bromoisoquinoline,[2] 5-nitroisoquinoline,[3] 3-phenylisoquinoline,[4] 6-methylisoquinoline,[5] 5,8-dibromoquinoline,[6] 5-nitroquinoline and 8-nitroquinoline,[7] 4-(phenylethynyl)isoquinoline,[8] 5,8-dibromoisoquinoline,[9] N,N-dimethylquinolin-3-amine,[10] 8-methoxyquinoline,[11] 4-chloroquinoline and 4-methoxyquinoline,[12] 3-phenylquinoline,[13] and 8-(allyloxy)quinolone.[14] The literature reported spectral data were compared favorably with our ^{1}H NMR spectra of these compounds.

Preparation of Starting Materials:

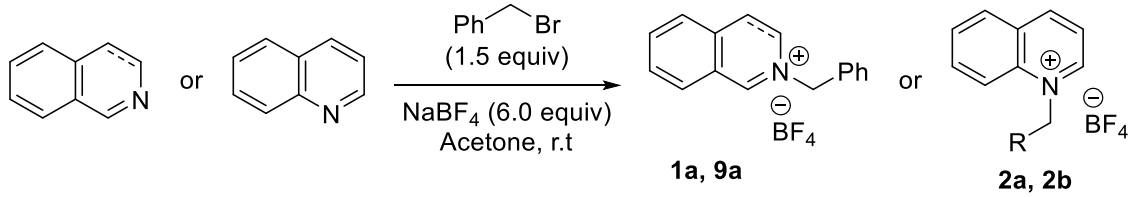
General Procedure for the Synthesis of Salts of Isoquinoline and Quinoline derivatives with trifluoromethanesulfonate as counter anion



To a flame dried 50 ml round-bottom flask under argon atmosphere, isoquinoline or quinoline derivatives (2.0 mmol, 1.0 equiv) was taken followed by dry DCM (10 ml). The solution was cooled to 0 °C, and methyl trifluoromethanesulfonate (3.0 mmol, 1.5 equiv) was added dropwise via syringe. The reaction mixture was

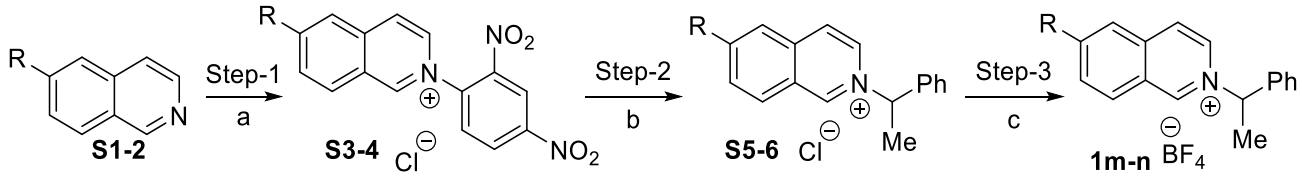
slowly warmed to room temperature with TLC monitoring. Upon consumption of starting material, DCM was removed under reduced pressure, and the residue was washed with diethyl ether (3-5 times) to remove low polar impurities to obtain pure salt. In few cases, the ether wash was not sufficient, and the salts were purified by flash column chromatography using 5-10% methanol in DCM as the eluting solvent.

General Procedure for the Synthesis of Salts of Isoquinoline and Quinoline derivatives with tertafluoroborate as counter anion



To a flame dried 50 ml round-bottom flask under argon atmosphere, isoquinoline or quinoline derivatives (5.0 mmol, 1.0 equiv) was dissolved in dry acetone (30 ml) at r.t. To this solution, benzyl bromide (10.0 mmol, 2.0 equiv) was added followed by sodium tetrafluroborate (30.0 mmol, 6.0 equiv) and stirred at r.t. The TLC analysis shows two polar spots with major low polar one. The reaction stopped after no further change in relative intensities for those polar spots, and the precipitate was removed by filtration. The solvent was removed under reduced pressure, and the residual solid was purified via silica column chromatography by 5:95 MeOH/DCM as eluent to obtain tetrafluoroborate salt as the major product (lower polar) as well as some bromo salt (higher polar spot).

Preparation of 2-(1-phenylethyl)isoquinolin-2-ium trifluoromethanesulfonate (1m):



R = H, Me

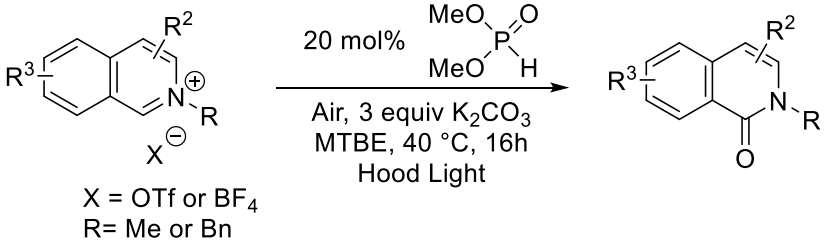
Condition: a)2,4-dinitrobenzene, Acetone, 80 ^{o}C. b) (±)-1-phenylethylamine/(S)-(-)-1-phenylethylamine, diethylamine, rt, 48 h. c) silver tetrafluoroborate, DCM, 0 ^{o}C to r.t.

S3-4 and both racemic and **S5** and **S6** were prepared according to literature procedure, and the analytical data were matched.[15,16]

Step-3:

DCM (10 ml) was added to a dry 50 ml round bottom flask containing isoquinolinium salt (**S5-6**, 1.5 mmol) under argon and stirred at room temperature for 10-15 min until the salt dissolved. Then the mixture was cooled to 0 ^{o}C, and silver tetrafluoroborate (439 mg, 2.25 mmol, 1.5 equiv) was added followed by slow warming to r.t. The anion exchange was monitored by TLC with the tetrafluoroborate as lower polar spot. Once the complete exchange judged by TLC, the silver chloride was filtered off and the solvent was removed under reduced pressure. The residual solid was purified by small silica pad filtration to obtain pure salt **1m-n**. Both racemic as well as chiral salt prepared by the above procedure.

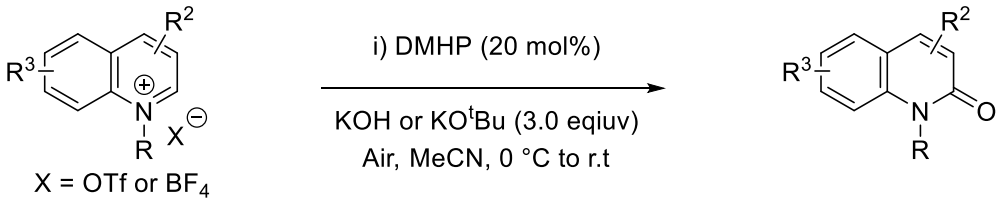
General optimized reaction procedure for aerobic oxidation of isoquinolinium salts



MTBE (2 ml) was added to a 10 ml reaction tube containing isoquinolinium salt (0.3 mmol) under air, followed by dimethyl hydrogen phosphite (5.5 microliter, 0.06 mmol, 20 mol %) and 3 equiv K_2CO_3 (0.9 mmol). The reaction tube was closed via an open top cap with septa and heated to 40 °C for 16 h. The reaction was monitored by TLC for the consumption of isoquinilonium salt. Upon completion, saturated sodium chloride solution (5 ml) was added to quench the reaction, and the organic layer was extracted with ethyl acetate (3 times). The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to obtain the crude which was filtered through a 6-inch silica column to get the desired product in pure form.

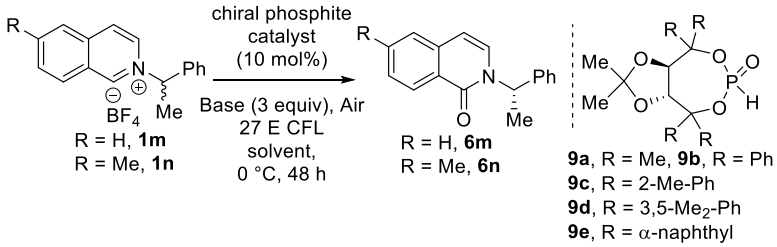
Cyclic N-aryl iminium salts (**3b-c**) were synthesized following literature procedure.[18]

General optimized reaction procedure for aerobic oxidation of quinolinium salts



MeCN (2 ml) was added to a dry 10 ml reaction tube containing quinolinium salt (0.3 mmol) under air and stirred at room temperature for 10-15 min until the salt dissolved. The reaction tube was closed via an open top cap with septa and cooled to 0 °C under air balloon. To the above mixture dimethyl hydrogen phosphite (20 mol %) was added followed by appropriate base (3 equiv) and stirred for 2h. Then the reaction tube was slowly brought to room temperature with TLC monitoring for the consumption of starting quinolinium salt. Upon completion, saturated sodium chloride solution (5 ml) was added to quench the reaction, and the organic layer was extracted with ethyl acetate (3 times). The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to obtain the crude which was filtered through a 6-inch silica column to get the desired product in pure form.

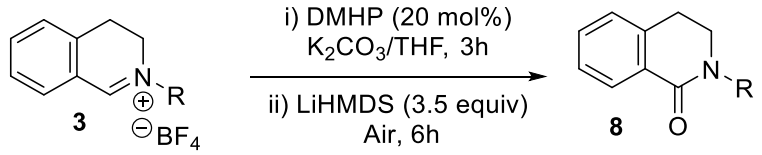
General optimized reaction procedure for kinetic resolution of isoquinolinium salts



DCE (2 ml) was added to a dry 10 ml reaction tube containing isoquinolinium salt (0.2 mmol, 1.0 equiv.) and stirred at room temperature for 5-10 min until the salt dissolved. Then the mixture was cooled to 0 °C. To the above mixture chiral phosphite (10 mol %) was added followed by DABCO (3.0 equiv.). The above reaction

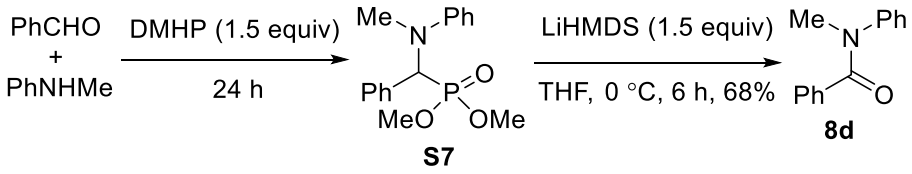
mixture was exposed to household light (Philips CFL, 27 W). The reaction was monitored by TLC and stopped at near 50 % conversion, and directly load in silica column to isolate the desired product, catalyst, and unreacted starting salt.

Aerobic auto-oxidation of Aromatic Iminium Salt to Lactum:



THF (3 ml) was added to a dry 25 ml round bottom flask containing salt **3** (0.3 mmol) and stirred at room temperature for 10-15 min until the salt dissolved. The reaction mixture was cooled to 0 °C with an air baloon, and dimethyl phosphite (20 mol%.) was added followed by K_2CO_3 (0.15 mmol, 2.5 equiv. to catalyst) and stirred at the same temperature for 1h.[17] Then LiHMDS (1M solution in THF, 1.05 mmol, 3.5 equiv.) solution was added to it dropwise over a period of 4h via gastight syringe. The reaction was monitored by TLC for the consumption of isoquinilonium salt. Upon completion, saturated sodium chloride solution (5 ml) was added to quench the reaction, and the organic layer was extracted with ethyl acetate (3 times). The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to obtain the crude which was filtered through a 6-inch silica column to get the desired product in pure form.[18]

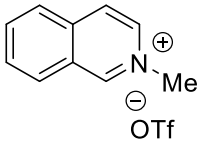
Oxidative coupling of aldehyde an amine to Amide



Benzaldehyde (1.0 mmol), N-methyl aniline (1.2 mmol, 1.2 equiv), and dimethylphosphite (1.5 mmol, 1.5 equiv) was taken together and stirred at room temperature (35 °C) with 100 mg 4 Å molecular sieves. Upon complete consumption of aldehyde, the reaction mixture was dissolved in DCM and dried with sodium sulfate, filtered and solvent was removed. 6 ml THF was added to the crude and cooled to 0 °C under air baloon. Then LiHMDS (1.5 mmol, 1.5 equiv) was added to it dropwise over 10 minutes and stirred at that temperature for 6h. The reaction was monitored by TLC for the consumption of isoquinilonium salt. Upon completion, saturated sodium chloride solution (5 ml) was added to quench the reaction, and the organic layer was extracted with ethyl acetate (3 times). The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to obtain the crude which was filtered through a 6-inch silica column to get the desired product in pure form. R_f (Ethyl acetate/Pet. ether = 30:70) = 0.5, yield 60 %.[19]

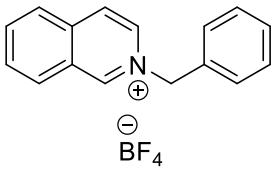
I. Compounds characterization data

2-Methylisoquinolin-2-ium trifluoromethanesulfonate (1a)



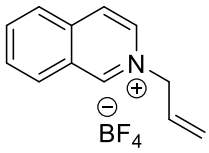
Obtained as a white color solid (628.8 mg, 80 % yield). R_f (MeOH/DCM = 05:95) = 0.4; **MP =** 90.7 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.50 (s, 3 H), 8.07 (t, *J* = 7.63 Hz, 1 H), 8.26 (t, *J* = 7.32 Hz, 1 H), 8.33 (d, *J* = 8.39, 1 H), 8.48 (d, *J* = 7.93 Hz, 1 H), 8.57 (d, *J* = 6.71 Hz, 1 H), 8.71 (d, *J* = 6.71 Hz, 1 H), 10.00 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 47.9, 125.4, 127.0, 127.2, 130.1, 131.1, 135.8, 136.6, 136.7, 150.6. **FTIR (cm^{-1}):** 3057, 2291, 2185, 2017, 1929, 1648, 1614, 1460, 1387, 1152, 1025. **HRMS:** Calculated for $C_{10}H_{10}N$ $[M]^+$: 144.0813, found: 144.0808 .

2-benzylisoquinolin-2-ium tetrafluoroborate (1b)



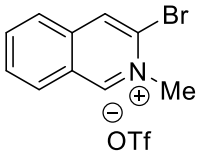
Obtained as a light yellow solid (4.6 g, 65 % yield). R_f (MeOH/DCM = 05:95) = 0.5; **MP =** 147.2 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 5.98 (s, 2 H) 7.43 - 7.49 (m, 3 H), 7.58 - 7.60 (m, 2 H), 8.08 - 8.12 (m, 1 H), 8.28 - 8.30 (m, 1 H), 8.35 - 8.37 (m, 1 H), 8.54 (d, *J* = 7.93 Hz, 1 H), 8.61 (d, *J* = 7.32 Hz, 1 H), 8.83 (d, *J* = 7.32 Hz, 1 H), 10.28 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 63.4, 126.4, 127.4, 128.8, 129.2, 129.3, 129.3, 130.6, 131.4, 134.3, 134.8, 137.1, 137.2, 150.2. **FTIR (cm^{-1}):** 3096, 3057, 2317, 1641, 1610, 1287, 1198, 1154, 1040. **HRMS:** Calculated for $C_{16}H_{14}N$ $[M]^+$: 220.1126 found: 220.1121.

2-allylisoquinolin-2-ium tetrafluoroborate (1c)



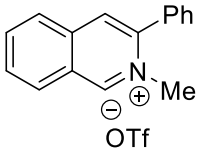
Obtained as a brown color solid (1.028 gm, 80 % yield). R_f (MeOH/DCM; 05:95) = 0.4; **MP =** 99-101 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 5.40 (d, *J* = 6.10 Hz, 2H), 5.46-5.59 (m, 2H), 6.16-6.37 (m, 1H), 8.10 (t, *J* = 16.04 Hz, 1H), 8.29 (t, *J* = 14.88 Hz, 1H), 8.37 (d, *J* = 8.39 Hz, 1H), 8.54 (d, *J* = 8.01 Hz, 1H), 8.62 (d, *J* = 6.87 Hz, 1H), 8.73 (d, *J* = 8.05, 1H), 10.04 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 62.5, 122.1, 126.0, 127.3, 130.5, 131.2, 131.5, 134.8, 137.0, 137.1, 150.1. **FTIR (cm^{-1}):** 3022, 2928, 1590, 1216, 767. **HRMS:** Calculated for $C_{12}H_{12}N$ $[M]^+$: 170.0970, found: 170.0977.

3-Bromo-2-methylisoquinolin-2-ium trifluoromethanesulfonate (1d)



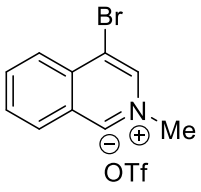
Obtained as a white solid (667.8 mg, 90 % yield). R_f (MeOH/DCM = 05:95) = 0.4; **MP =** 139.4 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 4.45 (s, 3 H), 8.17 (t, *J* = 7.02 Hz, 1 H), 8.31 - 8.47 (m, 2 H), 8.55 (d, *J* = 8.54 Hz, 1 H), 9.24 (s, 1 H), 10.07 (s, 1 H). **^{13}C NMR (DMSO-d_6, 100 MHz)** δ 47.9, 121.0, 125.9, 127.2, 131.4, 132.1, 135.5, 137.2, 138.5, 150.8. **FTIR (cm^{-1}):** 3125, 3036, 2286, 1856, 1703, 1636, 1559, 1462, 1341, 1274, 1149, 1028. **HRMS:** Calculated for $C_{10}H_9NBr$ $[M]^+$: 221.9918, found: 221.9913.

2-Methy-3-phenyllisoquinolin-2-ium trifluoromethanesulfonate (1e)



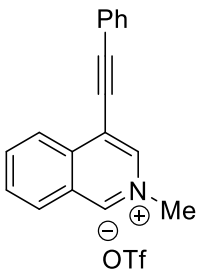
Obtained as a brown solid (686 mg, 93 % yield). R_f (MeOH/DCM = 05:95) = 0.4; **MP =** 141.8 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.50 (s, 3 H), 7.63 - 7.68 (m, 5 H), 8.07 - 8.11 (m, 2 H), 8.21 - 8.25 (m, 1 H), 8.56 (d, *J* = 8.01 Hz, 1 H), 8.78 (s, 1 H), 10.01 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 47.8, 125.0, 127.4, 129.2, 129.6, 130.0, 130.9, 131.0, 133.0, 134.9, 135.2, 137.21, 137.5, 149.7. **FTIR (cm^{-1}):** 3045, 2667, 2291, 1878, 1643, 1457, 1269, 1158, 1028. **HRMS:** Calculated for$C_{16}H_{14}N$ $[M]^+$: 220.1126, found: 220.1121.

4-Bromo-2-methylisoquinolin-2-ium trifluoromethanesulfonate (1f)



Obtained as a white solid (705 mg, 95 % yield). R_f (MeOH/DCM = 05:95) = 0.4; **MP =** 136.3 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.45 (s, 3 H), 8.18 - 8.25 (m, 1 H), 8.38 - 8.43 (m, 2 H), 8.55 (d, *J* = 8.39 Hz, 1 H), 9.24 (s, 1 H), 10.07 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 47.9, 120.9, 125.9, 127.2, 131.3, 132.0, 135.4, 137.2, 138.5, 150.8. **FTIR (cm^{-1}):** 3125, 2724, 2021, 1633, 1574, 1263, 1225, 1028. **HRMS:** Calculated for $C_{10}H_9NBr$ $[M]^+$: 221.9918, found: 221.9916.

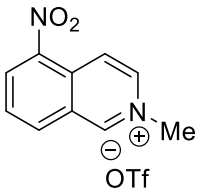
2-Methyl-4-(phenylethynyl)isoquinolin-2-ium trifluoromethanesulfonate (1g)



Obtained as a brown solid (626.8 mg, 96 % yield). R_f(MeOH/DCM = 05:95) = 0.4; **MP =** 211.3 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 4.48 (s, 3 H), 7.56 - 7.58 (m, 3 H), 7.83 (t, *J* = 7.93, 2 H),

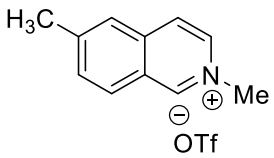
8.16 (t, *J* = 15.26 Hz, 1 H), 8.38 (t, *J* = 7.63 Hz, 1 H), 8.55 - 8.63 (m, 2 H), 9.13 (s, 1 H), 10.01 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 100 MHz)** δ 48.1, 81.1, 100.1, 119.3, 120.5, 125.2, 126.8, 129.1, 130.5, 131.1, 131.8, 132.0, 135.7, 137.9, 138.7, 150.4. **FTIR (cm^{-1}):** 3091, 2290, 2220, 1633, 1571, 1455, 1344, 1271, 1153, 1062, 1027. **HRMS:** Calculated for $C_{16}H_{14}N$ $[M]^+$: 244.1126, found: 244.1121.

2-Methyl-5-nitroisoquinolin-2-ium trifluoromethanesulfonate (1h)



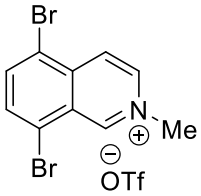
Obtained as a yellow solid (522 mg, 77 % yield). ***R$_f$*** (MeOH/DCM = 05:95) = 0.4; **MP =** 62.7 °C. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 4.54 (s, 3 H), 8.25 (t, *J* = 8.01 Hz, 1 H), 8.84 (d, *J* = 8.01 Hz, 1 H), 8.88 (d, *J* = 6.87 Hz, 1 H), 8.94 (d, *J* = 7.25 Hz, 1 H), 9.03 (d, *J* = 7.63 Hz, 1 H), 10.21 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 125 MHz)** δ 48.2, 121.3, 128.0, 129.0, 130.6, 134.2, 137.3, 138.6, 144.2, 151.9. **FTIR (cm^{-1}):** 3128, 3073, 2284, 1652, 1617, 1569, 1458, 1226, 1026. **HRMS:** Calculated for $C_{10}H_9N_2O_2$ $[M]^+$: 189.0664, found: 189.0659.

2,6-Dimethylisoquinolin-2-ium trifluoromethanesulfonate (1i)



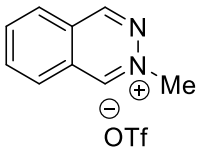
Obtained as a brown solid (595 mg, 97 % yield). ***R$_f$*** (MeOH/DCM = 05:95) = 0.4; **MP =** 118.2 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 2.66 (s, 3 H), 4.44 (s, 3 H), 7.92 (d, *J* = 8.39 Hz, 1 H), 8.12 (s, 1 H), 8.37 (d, *J* = 8.39 Hz, 1 H), 8.42 (d, *J* = 6.48 Hz, 1 H), 8.64 (d, *J*=6.49 Hz, 1 H), 9.88 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 100 MHz)** δ 22.2, 47.6, 124.5, 125.4, 126.0, 129.9, 133.3, 135.9, 136.9, 148.3, 149.9. **FTIR (cm^{-1}):** 3057, 2723, 2289, 1646, 1616, 1575, 1456, 1265, 1156, 1030. **HRMS:** Calculated for $C_{11}H_{12}N$ $[M]^+$: 158.0970, found: 158.0964.

5,8-dibromo-2-methylisoquinolin-2-ium trifluoromethanesulfonate (1j)



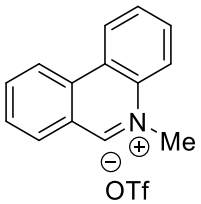
Obtained as a light brown solid (1.15 gm, 85 % yield). ***R$_f$*** (MeOH/DCM = 05:95) = 0.4; **MP =** 159.5 °C. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 4.61 (s, 3 H), 8.30 (d, *J* = 8.01 Hz, 1 H), 8.48 (d, *J* = 8.01 Hz, 1 H), 8.66 (d, *J* = 6.87 Hz, 1 H), 8.90 (d, *J* = 7.63, 1 H), 10.03 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 125 MHz)** δ 48.3, 120.7, 123.4, 125.0, 127.6, 135.8, 137.4, 138.8, 140.4, 150.8. **FTIR (cm^{-1}):** 3071, 3036, 2298, 1932, 1647, 1582, 1547, 1458, 1265, 1220, 1155, 1031. **HRMS:** Calculated for $C_{10}H_8NBr^{81}Br$ $[M]^+$: 301.9003, found: 301.8993.

2-Methylphthalazin-2-ium trifluoromethanesulfonate (1k)



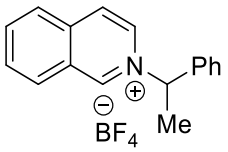
Obtained as a light brown solid (529 mg, 90 % yield). ***R$_f$*** (MeOH/DCM = 05:95) = 0.4; **MP =** 113.5 °C. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 4.61 (s, 3 H), 8.43 (t, *J* = 15.26 Hz, 1 H), 8.52 (t, *J* = 7.44 Hz, 1 H), 8.58 - 8.63 (m, 2 H), 10.06 (s, 1 H), 10.58 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 125 MHz)** δ 50.8, 127.2, 127.6, 128.3, 130.1, 136.2, 138.9, 151.7, 154.5. **FTIR (cm^{-1}):** 3022, 2291, 1715, 1592, 1263, 1226, 1163, 1027. **HRMS:** Calculated for $C_9H_9N_2$ $[M]^+$: 145.0766, found: 145.0760.

5-Methylphenanthridin-5-ium trifluoromethanesulfonate (1l)



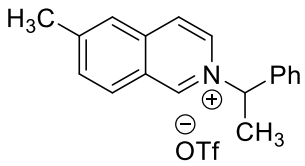
Obtained as a white solid (583 mg, 85 % yield). ***R$_f$*** (MeOH/DCM = 05:95) = 0.4; **MP =** 142.4 °C. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 4.68 (s, 3 H), 8.10 - 8.18 (m, 3 H), 8.40 (t, *J* = 7.82 Hz, 1 H), 8.55 (dd, *J* = 8.01, 3.81 Hz, 2 H), 9.12 (d, *J* = 8.01 Hz, 1 H), 9.16 (d, *J* = 8.39 Hz, 1 H), 10.28 (s, 1 H). **^{13}C NMR (DMSO-d$_6$, 125 MHz)** δ 45.8, 120.0, 123.2, 123.5, 124.6, 125.4, 130.3, 131.9, 132.6, 134.1, 134.2, 137.8, 156.0. **FTIR (cm^{-1}):** 3139, 30732289, 1659, 1627, 1525, 1158, 1027. **HRMS:** Calculated for $C_{14}H_{12}N$ $[M]^+$: 194.0970, found: 194.0964.

2-(1-phenylethyl)isoquinolin-2-ium trifluoromethanesulfonate (1m)



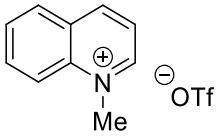
Obtained as white solid (321 mg, 67 % yield). R_f (MeOH/DCM = 05:95) = 0.6; **MP =** 157.3 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 2.17 (d, *J* = 7.25 Hz, 3 H), 6.33 - 6.37 (m, 1 H), 7.44 - 7.50 (m, 3 H), 7.60 - 7.62 (m, 2 H), 8.12 (t, *J* = 7.63 Hz, 1 H), 8.28 - 8.31 (m, 1 H), 8.36 (d, *J* = 8.39 Hz, 1 H), 8.59 (t, *J* = 8.01 Hz, 2 H), 8.84 - 8.85 (m, 1 H), 10.33 (s, 1 H). **^{13}C NMR (DMSO-d_6, 125 MHz)** δ 19.8, 69.5, 126.4, 127.3, 127.4, 129.2, 129.3, 129.3, 130.8, 131.3, 133.4, 137.2, 138.2, 148.8. **FTIR (cm^{-1}):** 3126, 3066, 2160, 1640, 1608, 1156, 1043. **HRMS:** Calculated for $C_{17}H_{16}N$ $[M]^+$: 234.1283, found: 234.1282.

6-methyl-2-(1-phenylethyl)isoquinolin-2-ium trifluoromethanesulfonate (1n)



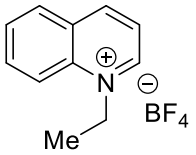
Obtained as yellow color sticky liquid (90 mg, 75% yield). R_f(MeOH/DCM = 10:90) = 0.65; **^{1}H NMR (400 MHz, DMSO-d_6)** δ 2.13 (d, J = 7.32 Hz, 3 H), 2.66 (s, 3 H), 6.30 (q, J = 6.71 Hz, 1 H), 7.33 - 7.51 (m, 3 H), 7.57 (d, J = 7.32 Hz, 2 H), 7.95 (d, J = 8.55 Hz, 1 H), 8.12 (s, 1 H), 8.38 - 8.52 (m, 2 H), 8.78 (d, J =7 .32 Hz, 1 H), 10.25 (s, 1 H).**^{13}C NMR (100 MHz, DMSO-d_6)** δ 20.3, 22.7, 69.5, 125.9, 126.2, 126.5, 127.7, 129.7, 129.7, 131.0, 133.9, 134.0, 137.9, 138.8, 148.6, 149.4. **FTIR** (**cm^{-1}**): 3022, 2972, 2861, 2402, 2255, 1595, 1421, 1117, 911. **HRMS**: Calculated for $C_{18}H_{18}N$ $[M]^+$: 248.1434, found: 248.1436.

1-methylquinolin-1-ium trifluoromethanesulfonate (2a)



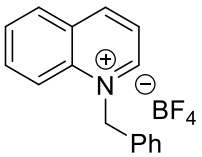
Obtained as a white solid (486 mg, 83 % yield). R_f (Methanol/DCM = 10:90) = 0.45; **MP** = 118.4 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 4.66 (s, 3 H), 8.00 - 8.14 (m, 1 H), 8.14 - 8.26 (m, 1 H), 8.31 (t, *J* = 7.93 Hz, 1 H), 8.54 (d, *J* = 9.16 Hz, 1 H), 8.51 (d, *J* = 8.55 Hz, 1 H), 9.31 (d, *J* = 8.55 Hz, 1 H), 9.55 (d, *J* = 5.49 Hz, 1 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 45.9, 119.6, 122.5, 129.6, 130.4, 130.8, 135.9, 138.8, 147.5, 150.6. **FTIR** (**cm^{-1}**): 2984, 1528, 1268, 1224, 1129, 1023, 837, 778, 630. **HRMS:** Calculated for $C_{10}H_{10}N$ $[M]^+$: 144.0813, found: 144.0808.

1-ethylquinolin-1-ium tetrafluoroborate (2b)



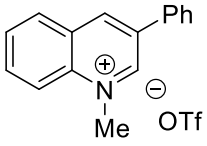
Obtained as a yellow Solid (1134 mg, 60 % yield). R_f (Methanol/DCM = 10:90) = 0.5; **MP =** 142.6 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 1.65 (t, *J* = 7.25 Hz, 3 H), 5.16 (q, *J* = 6.99 Hz, 2 H), 8.09 (t, *J* = 7.63 Hz, 1 H), 8.24 (dd, *J* = 8.20, 5.91 Hz, 1 H), 8.32 (t, *J* = 7.63 Hz, 1 H), 8.54 (d, *J* = 8.01 Hz, 1 H), 8.68 (d, *J* = 8.77 Hz, 1 H), 9.35 (d, *J* = 8.39 Hz, 1 H), 9.66 (d, *J* = 5.34 Hz, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 15.2, 52.9, 118.8, 122.3, 129.6, 129.8, 130.7, 135.6, 137.1, 147.1, 149.3. **FTIR** (**cm^{-1}**): 2914, 2845, 1592, 1524, 1434, 1358, 803, 766, 731. **HRMS:** Calculated for $C_{11}H_{12}N$ $[M]^+$: 158.0970, found: 158.0964.

1-benzylquinolin-1-ium tetrafluoroborate (2c)



Obtained as a white powder (2443 mg, 80 % yield). R_f (Methanol/DCM = 05:95) = 0.4; **MP** = 163 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 6.45 (s, 2 H), 7.29 - 7.49 (m, 5 H), 7.97 - 8.11 (m, 1 H), 8.23 (t, *J* = 7.93 Hz, 1 H), 8.33 (dd, *J* = 7.93, 6.10 Hz, 1 H), 8.47 - 8.62 (m, 2 H), 9.43 (d, *J* = 8.55 Hz, 1 H), 9.86 (d, *J* = 5.49 Hz, 1 H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 59.8, 119.3, 122.5, 127.3, 128.8, 129.1, 129.9, 130.0, 130.9, 133.9, 135.7, 137.5, 148.2, 150.4. **FTIR** (**cm^{-1}**): 3004, 1585, 1528, 1360, 1232, 1150, 1043, 811, 767, 717, 645. **HRMS:** Calculated for $C_{16}H_{14}N$ $[M]^+$: 220.1126 found: 220.1121.

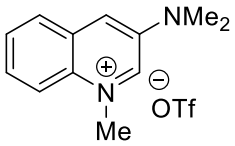
1-methyl-3-phenylquinolin-1-ium trifluoromethanesulfonate (2d)



Obtained as a White Solid (199 mg, 54 % yield). R_f (Methanol/DCM = 10:90) = 0.2; **MP** = 181.6 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.72 (s, 3 H), 7.56 - 7.64 (m, 1 H), 7.64 - 7.71 (m, 2 H), 8.03 (d, *J* = 7.25 Hz, 2 H), 8.09 (t, *J* = 7.63 Hz, 1 H), 8.18 - 8.35 (m, 1 H), 8.53 (d, *J* = 8.77 Hz,

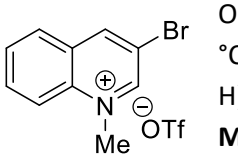
1 H), 8.49 (d, *J* = 8.01 Hz, 1 H), 9.62 (s, 1 H), 9.91 - 10.02 (m, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 45.9, 119.4, 127.9, 129.7, 130.0, 130.3, 130.7, 131.0, 133.9, 134.0, 135.6, 137.7, 143.4, 149.8. **FTIR** (**cm^{-1}**): 2985, 2885, 1538, 1387, 1246, 1142, 1029, 764, 694, 638. **HRMS:** Calculated for $C_{16}H_{14}N$ [M] $^{+}$: 220.1126, found: 220.1121.

3-(dimethylamino)-1-methylquinolin-1-ium trifluoromethanesulfonate (2e)



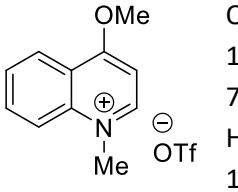
Obtained as a yellow Solid (376 mg, 56 % yield). ***R$_f$*** (Methanol/DCM = 10:90) = 0.3; **MP** =134 °C **^{1}H NMR (500 MHz, DMSO-d_6)** δ 3.17 (s, 6 H), 4.62 (s, 3 H), 7.75 - 7.90 (m, 2 H), 8.08 - 8.17 (m, 1 H), 8.17 - 8.31 (m, 2 H), 9.20 (d, *J* = 2.67 Hz, 1 H)**. ^{13}C NMR (125 MHz, DMSO-d_6)** δ 29.0, 45.4, 118.4, 121.1, 127.9, 129.5, 129.6, 130.2, 131.2, 139.0, 143.7. **FTIR** (**cm^{-1}**): 3058, 1619, 1538, 1390, 1267, 1137, 1020, 879, 765, 629. **HRMS:** Calculated for $C_{12}H_{15}N_2$ [M] $^{+}$: 187.1235, found: 187.1230.

3-bromo-1-methylquinolin-1-ium trifluoromethanesulfonate (2f)



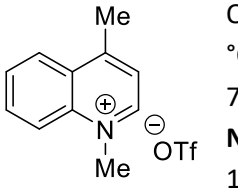
Obtained as a yellow solid (1428 mg, 65 % yield). ***R$_f$*** (Methanol/DCM = 10:90) = 0.5; **MP** = 177 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 4.62 (s, 3 H), 8.09 (t, *J* = 7.32 Hz, 1 H), 8.31 (t, *J* = 7.93 Hz, 1 H), 8.39 (d, *J* = 8.55 Hz, 1 H), 8.50 (d, *J* = 8.55 Hz, 1 H), 9.63 (s, 1 H), 9.89 (s, 1 H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 45.7, 114.9, 119.7, 130.0, 131.3, 136.1, 137.7, 148.6, 151.8. **FTIR** (**cm^{-1}**): 3043, 1524, 1250, 1151, 1023, 896, 776, 757, 624. **HRMS:** Calculated for $C_{10}H_9BrN$ [M] $^{+}$: 221.9918, found: 221.9913.

4-methoxy-1-methylquinolin-1-ium trifluoromethanesulfonate (2g)



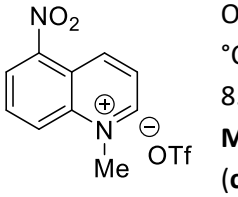
Obtained as a pale yellow solid (338 mg, 52 % yield). ***R$_f$*** (Methanol/DCM = 10:90) = 0.2; **MP** = 133.5 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.34 (s, 3 H), 4.43 (s, 3 H), 7.65 (d, *J* = 6.87 Hz, 1 H), 7.98 (t, *J* = 7.63 Hz, 1 H), 8.24 (t, *J* = 8.01 Hz, 1 H), 8.37 (d, *J* = 8.77 Hz, 1 H), 8.47 (d, *J* = 8.01 Hz, 1 H), 9.32 (d, *J* = 7.25 Hz, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 44.1, 59.4, 102.8, 119.5, 121.2, 124.1, 129.4, 135.5, 139.6, 152.0, 168.8. **FTIR** (**cm^{-1}**): 2967, 1580, 1538, 1400, 1258, 1224, 1132, 1015, 947, 859, 769, 630. **HRMS:** Calculated for $C_{11}H_{12}NO$ [M] $^{+}$: 174.0919, found: 174.0912.

1,4-dimethylquinolin-1-ium trifluoromethanesulfonate (2h)



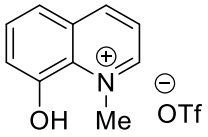
Obtained as a white solid (497 mg, 80 % yield). ***R$_f$*** (Methanol/DCM = 10:90) = 0.2; **MP** = 114.6 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 3.01 (s, 3 H), 4.58 (s, 3 H), 8.00 - 8.11 (m, 2 H), 8.27 (t, *J* = 7.63 Hz, 1 H), 8.49 (d, *J* = 8.77 Hz, 1 H), 8.54 (d, *J* = 8.39 Hz, 1 H), 9.33 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 19.6, 45.0, 119.5, 122.5, 126.8, 128.5, 129.7, 134.9, 137.7, 149.0, 158.2. **FTIR** (**cm^{-1}**): 2985, 1589, 1524, 1396, 1243, 1137, 1023, 840, 765, 637. **HRMS:** Calculated for $C_{11}H_{12}N$ [M] $^{+}$: 158.0970, found: 158.0964.

1-methyl-5-nitroquinolin-1-ium trifluoromethanesulfonate (2i)



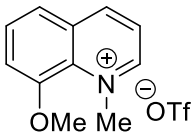
Obtained as a yellow solid (486 mg, 72 % yield). ***R$_f$*** /Methanol/DCM = 10:90) = 0.2; **MP** = 158.7 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.80 (s, 3 H), 8.34 - 8.57 (m, 2 H), 8.82 (d, *J* = 7.63 Hz, 1 H), 8.99 (d, *J* = 9.16 Hz, 1 H), 9.59 (d, *J* = 9.16 Hz, 1 H), 9.73 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 47.2, 122.2, 124.9, 125.9, 127.5, 134.3, 139.0, 142.8, 146.7, 152.2. **FTIR** (**cm^{-1}**): 3087, 1606, 1535, 1351, 1239, 1145, 1021, 896, 809, 737, 637. **HRMS:** Calculated for $C_{10}H_9N_2O_2$ [M] $^{+}$: 189.0664, found: 189.0659.

8-hydroxy-1-methylquinolin-1-ium trifluoromethanesulfonate (2j)



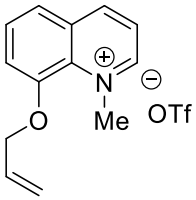
Obtained as a light greenish powder (595 mg, 96 % yield). R_f (Methanol/DCM = 10:90) = 0.15; **MP** = 128.8 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.83 (s, 3 H), 7.41 - 7.64 (m, 1 H), 7.66 - 7.89 (m, 2 H), 8.01 (dd, *J* = 8.39, 5.72 Hz, 1 H), 9.10 (d, *J* = 8.39 Hz, 1 H), 9.25 (d, *J* = 5.72 Hz, 1 H), 11.74 (s, 1 H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 51.8, 120.0, 121.0, 122.1, 122.8, 131.0, 132.4, 147.4, 150.4, 151.7. **FTIR** (**cm^{-1}**): 2984, 1587, 1548, 1376, 1237, 1146, 1027, 835, 757, 636. **HRMS:** Calculated for $C_{10}H_{10}NO$ [M] $^+$: 160.0762, found: 160.0757.

8-methoxy-1-methylquinolin-1-ium trifluoromethanesulfonate (2k)



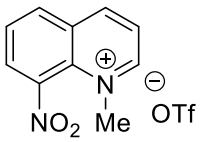
Obtained as a light yellow solid (313 mg, 48 % yield). R_f **(**Methanol/DCM = 10:90) = 0.5; **MP** = 119.8 °C**. ^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.08 (s, 3 H), 4.80 (s, 3 H), 7.68 - 7.86 (m, 1 H), 7.87 - 8.03 (m, 2 H), 8.10 (dd, *J* = 8.39, 5.72 Hz, 1 H), 9.18 (d, *J* = 8.01 Hz, 1 H), 9.31 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 52.4, 57.8, 116.8, 122.5, 122.6, 130.8, 132.1, 147.5, 151.8, 152.2. **FTIR** (**cm^{-1}**): 3071, 1580, 1535, 1406, 1321, 1253, 1226, 1134, 1031, 951, 861, 770, 636. **HRMS:** Calculated for $C_{11}H_{12}NO$ [M] $^+$: 174.0919, found: 174.0912.

8-(allyloxy)-1-methylquinolin-1-ium trifluoromethanesulfonate (2l)



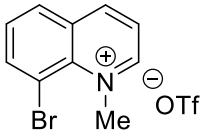
Obtained as a White powder (500 mg, 71 % yield). R_f (Methanol/DCM = 10:90) = 0.6; **MP** = 108 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.83 (s, 3 H), 4.92 (d, *J* = 5.34 Hz, 2 H), 5.40 (d, *J* = 10.68 Hz, 1 H), 5.47 - 5.61 (m, 1 H), 6.11 - 6.30 (m, 1 H), 7.78 (d, *J* = 7.63 Hz, 1 H), 7.92 (t, *J* = 8.01 Hz, 1 H), 7.98 (d, *J* = 8.01 Hz, 1 H), 8.09 (dd, *J* = 8.20, 5.91 Hz, 1 H), 9.18 (d, *J* = 8.39 Hz, 1 H), 9.32 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 52.5, 71.6, 118.1, 119.6, 122.60, 122.8, 130.8, 131.0, 132.2, 132.9, 147.6, 150.5, 152.4. **FTIR** (**cm^{-1}**): 3073, 2984, 1603, 1529, 1383, 1244, 1149, 1023, 918, 880, 749, 626. **HRMS:** Calculated for $C_{13}H_{14}NO$ [M] $^+$: 200.1075, found: 200.1070.

1-methyl-8-nitroquinolin-1-ium trifluoromethanesulfonate (2m)



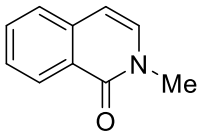
Obtained as a yellow solid (466 mg, 69 % yield). R_f (Methanol/DCM = 10:90) = 0.2; **MP** = 113.6 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.42 (s, 3 H), 8.20 (t, *J* = 7.82 Hz, 1 H), 8.39 (dd, *J* = 8.20, 5.91 Hz, 1 H), 8.82 (d, *J* = 7.63 Hz, 1 H), 8.79 (d, *J* = 8.01 Hz, 1 H), 9.48 (d, *J* = 8.39 Hz, 1 H), 9.65 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 47.6, 124.4, 129.9, 130.3, 131.4, 132.9, 136.1, 142.1, 148.8, 155.3. **FTIR** (**cm^{-1}**): 2968, 1598, 1529, 1456, 1358, 1251, 1151, 1029, 967, 835, 756, 623. **HRMS:** Calculated for $C_{10}H_9N_2O_2$ [M] $^+$: 189.0664, found: 189.0659.

8-bromo-1-methylquinolin-1-ium trifluoromethanesulfonate (2n)



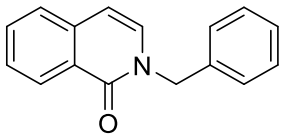
The titled compound was prepared (1 mmol scale) by following the general procedure **A**, Obtained as a White solid (175 mg, 47 % yield). R_f (Methanol/DCM = 10:90) = 0.15; **MP** = 140.9 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 4.99 (s, 3 H), 7.87 (br. s, 1 H), 8.08 - 8.28 (m, 1 H), 8.48 (d, *J* = 7.25 Hz, 1 H), 8.53 - 8.72 (m, 1 H), 9.33 (d, *J* = 8.39 Hz, 1 H), 9.51 (d, *J* = 5.72 Hz, 1 H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 52.2, 111.2, 123.0, 130.8, 132.0, 132.9, 137.5, 143.6, 149.5, 154.6. **FTIR** (**cm^{-1}**): 2972, 1543, 1243, 1226, 1135, 1029, 845, 757, 629. **HRMS:** Calculated for $C_{10}H_9BrN$ [M] $^+$: 221.9918, found: 221.9913.

2-methylisoquinolin-1(2H)-one (6a)



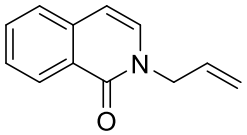
This compound is previously known in literature.[21] Obtained as a light yellow solid (40 mg, 84 % yield).

2-benzylnaphthalen-1(2H)-one (6b)



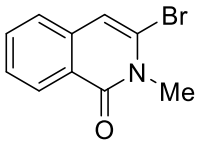
This compound is previously known in literature.[22] Obtained as sticky yellow oil (56 mg, 79% yield). R_f(Ethylacetate/Pet. ether = 20:80) = 0.45

2-allylisoquinolin-1(2H)-one (5



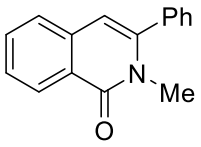
Colorless liquid (43 mg, 79 % yield). R_f(Ethyl acetate/Pet. Ether; 20:80); = 0.25.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.65 (d, *J* = 6.10 Hz, 2H), 5.08-5.33 (m, 2H), 5.98 (qd, *J* = 11.09, 5.80 Hz, 1H), 6.51 (d, *J* = 7.32 Hz, 1H), 7.05 (d, *J* = 7.32 Hz, 1H), 7.40-7.56 (m, 2H) 7.63 (t, *J* = 7.32 Hz, 1H), 8.44 (d, *J* = 7.93 Hz, 1H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 50.6, 106.2, 117.9, 125.8, 126.2, 126.8, 127.9, 131.1, 132.1, 132.8, 137.0, 161.9. **FTIR(cm^{-1}):** 3062, 2972, 1625, 1445, 1228, 682. **HRMS:** Calculated for $C_{12}H_{12}NO[M+H]^+$: 186.0878; found: 186.0925.

3-bromo-2-methylisoquinolin-1(2H)-one (6d)



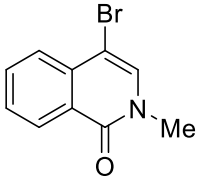
Obtained as a white solid (49 mg, 69 % yield). R_f(Ethyl acetate/Pet. ether = 50:50) = 0.6; **MP** = 123.3 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.60 (s, 3 H), 7.36 (s, 1 H), 7.55 (t, *J* = 7.63 Hz, 1 H), 7.73 (t, *J* = 15.77 Hz, 1 H), 7.80 (t, *J* = 8.26 Hz, 1 H), 8.44 (d, *J* = 8.01 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 36.9, 99.5, 125.8, 126.3, 127.8, 128.1, 132.8, 132.9, 135.5, 161.7. **FTIR (cm^{-1}):** 2924, 2858, 1650, 1625, 1377, 1313, 1097. **HRMS:** Calculated for $C_{16}H_{14}NO$ $[M+H]^+$: 237.9868, found: 237.9862.

2-methyl-3-phenylisoquinolin-1(2H)-one (6e)



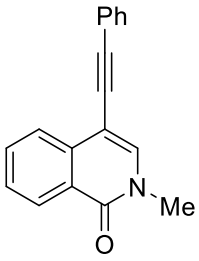
Obtained as a white solid (57 mg, 81 % yield).R_f(Ethyl acetate/Pet. ether = 50:50) = 0.6; **MP** = 178.9 °C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.67 (s, 3 H), 7.06 (s, 1 H), 7.40 - 7.45 (m, 3 H), 7.46 - 7.52 (m, 2 H), 7.52 - 7.58 (m, 2 H), 7.58 - 7.63 (m, 1 H), 8.54 (d, *J* = 8.01 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 37.0, 119.5, 124.6, 125.9, 126.9, 127.7, 128.0, 128.6, 129.9, 131.5, 132.0, 136.3, 136.4, 162.2. **FTIR (cm^{-1}):** 2927, 2859, 1621, 1425, 1035.**HRMS:** Calculatedfor $C_{16}H_{14}NO$ $[M+H]^+$: 236.1075, found: 236.1070.

4-bromo-2-methylisoquinolin-1(2H)-one (6f)



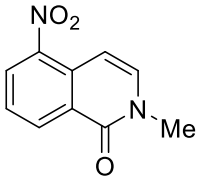
Obtained as a yellow solid (58 mg, 82 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.5; **MP** = 127.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.60 (s, 3 H), 7.37 (s, 1 H), 7.55 (t, *J* = 7.63 Hz, 1 H), 7.74 (d, *J* = 15.77 Hz, 1 H), 7.80 (d, *J* = 8.26 1 H), 8.44 (dd, *J* = 8.01 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 36.9, 99.5, 125.8, 126.3, 127.8, 128.1, 132.8, 132.9, 135.5, 161.7. **FTIR (cm^{-1}):** 2924, 2858, 1650, 1625, 1377, 1313, 1097. **HRMS:** Calculated for $C_{10}H_9NOBr$ $[M+H]^+$:237.9868, found: 237.9862.

2-methyl-4-(phenylethynyl)isoquinolin-1(2H)-one (6g)



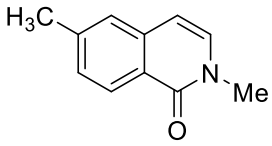
Obtained as light yellow solid (57 mg, 60 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.6; **MP** = 120.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.64 (s, 3 H), 7.37 - 7.39 (m, 3 H), 7.53 (s, 1 H), 7.55 - 7.57 (m, 3 H), 7.77 (t, *J* = 7.63 Hz, 1 H), 8.01 (d, *J* = 7.93 Hz, 1 H), 8.46 (d, *J* = 7.93 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 37.2, 83.5, 92.9, 101.1, 123.1, 124.9, 125.4, 127.5, 127.8, 128.3, 128.4, 131.4, 132.5, 136.1, 136.6, 161.8. **FTIR (cm^{-1}):** 3065, 2926, 2858, 2249, 2214, 1652, 1615, 1488, 1444, 1316, 1247, 1179. **HRMS:** Calculated for $C_{18}H_{14}NO$ $[M+H]^+$: 260.1075, found: 260.1070.

2-methyl-5-nitroisoquinolin-1(2H)-one (6h)



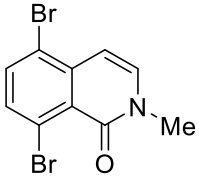
Obtained as yellow solid (44 mg, 72 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.5; **MP** = 112.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.65 (s, 3 H), 7.29 (d, *J* = 2.29 Hz, 2 H), 7.57 (t, *J* = 8.01 Hz, 1 H), 8.41 (dd, *J* = 7.78, 1.37 Hz, 1 H), 8.76 (dd, *J* = 8.24 Hz, 1.45 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 37.2, 100.5, 125.7, 127.9, 129.3, 130.9, 134.2, 136.1, 144.5, 161.0. **FTIR (cm^{-1}):** 2925, 2860, 1655, 1477, 1336. **HRMS:** Calculated for $C_{10}H_9N_2O_3$ $[M+H]^+$:205.0613, found:205.0608.

2,6-dimethylisoquinolin-1(2H)-one (6i)



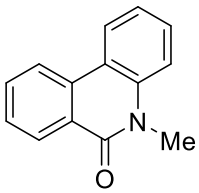
Obtained as a white solid (45 mg, 86 % yield).R_f(Ethyl acetate/Pet. ether = 50:50) = 0.5; **MP** = 85.6 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 2.47 (s, 3 H), 3.59 (s, 3 H), 6.42 (d, J = 7.25 Hz, 1 H), 7.04 (d, J = 7.25 Hz, 1 H), 7.29 (d, *J* = 7.65 Hz, 2 H), 8.31 (d, *J* = 8.77 Hz, 2 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 21.8, 36.9, 105.8, 123.9, 125.6, 127.6, 128.5, 132.5, 137.3, 142.5, 162.6. **FTIR (cm^{-1}):** 2926, 2826, 1645, 1712, 1606, 1466, 1382, 1351, 1300. **HRMS:** Calculated for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0919, found:174.0913.

5,8-dibromo-2-methylisoquinolin-1(2H)-one (6j)



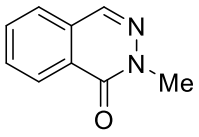
Obtained as white color solid (45 mg, 47 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.5; **MP** = 120.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.57 (s, 3 H), 6.81 (d, *J* = 7.63 Hz, 1 H), 7.20 (d, *J* = 7.63 Hz, 1 H), 7.57 (d, *J* = 8.39 Hz, 1 H), 7.62 (d, *J* = 8.39 Hz, 1 H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 37.8, 104.3, 120.0, 122.3, 124.3, 134.0, 134.3, 135.7, 138.8, 160.2. **FTIR (cm^{-1}):** 2926, 2880, 1653, 1582, 1476, 1374, 1335, 1104. **HRMS:** Calculated for $C_{10}H_8ONBr^{81}Br$ $[M+H]^+$: 317. 8952, found: 371.8947.

5-methylphenanthridin-6(5H)-one (6l)



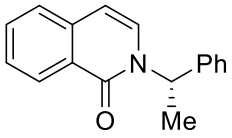
This compound is previously known in literature.[23] Obtained as a white color solid (53 mg, 85 % yield).

2-methylphthalazin-1(2H)-one (6k)



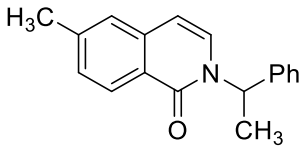
This compound is previously known in literature.[24] Obtained as yellow color solid (40 mg, 83 % yield).

(S)-2-(1-phenylethyl)isoquinolin-1(2H)-one (6m)



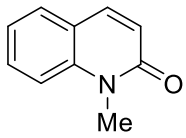
Obtained as a white color solid[25] (41 mg, 82 % yield, 98 % ee) starting with chiral **1m** (<98% ee). For kinetic resolution (16 mg, 32% yield, 70% ee). From recovered salt (19 mg, 76% yield, 33% ee). The HPLC analysis was done using Isopropanol:n-Hexane (30:70) in chiralpak® IA columns (250 × 4.6 mm).

6-methyl-2-(1-phenylethyl)isoquinolin-1(2H)-one



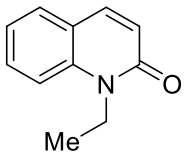
Obtained as a colorless sticky liquid (15 mg, 29 % yield at 40% conversion; 42 mg, 80% for racemic reaction with DMHP). The HPLC analysis was done using Isopropanol:n-Hexane (3:97) in chiralpak® IA columns (250 × 4.6 mm). R_f (Ethyl acetate/Pet. ether = 20:80) = 0.55; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.75 (d, J = 6.87 Hz, 3 H) 2.47 (s, 3 H) 6.38 (d, J = 7.63 Hz, 1 H) 6.56 (q, J = 6.99 Hz, 1 H) 6.88 (d, J=7.63 Hz, 1 H) 7.26 (s, 1 H) 7.27 - 7.33 (m, 2 H) 7.33 - 7.36 (m, 4 H) 8.37 (d, J = 8.01 Hz, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 18.8, 21.8, 51.9, 106.4, 123.9, 125.6, 127.4, 127.7, 128.1, 128.18, 128.5, 128.7, 136.8, 140.8, 142.8, 162.0. **FTIR** (**cm^{-1}**): 3156, 2978, 2927, 2865, 2255, 1803, 1642, 1600, 1382, 1171, 908. **HRMS**: Calculated for $C_{18}H_{17}ON$ [M+Na] $^+$: 286.1202, found: 286.1202.

1-methylquinolin-2(1H)-one (7a)



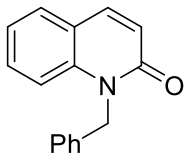
The titled compound was prepared by following the general procedure D and previously known in literature.[26] Obtained as a pale yellow solid (42 mg, 90% yield). R_f (Ethyl acetate/Pet. ether = 40:60) = 0.2.

1-ethylquinolin-2(1H)-one (7b)



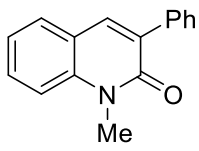
The titled compound was prepared by following the general procedure D. Obtained as a pale yellow viscous oil (41 mg, 78 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.35; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.37 (t, *J* = 7.06 Hz, 3 H), 4.37 (q, *J* = 7.12 Hz, 2 H), 6.70 (d, *J* = 9.54 Hz, 1 H), 7.22 (t, *J* = 7.44 Hz, 1 H), 7.39 (d, *J* = 9.16 Hz, 1 H), 7.54 - 7.60 (m, 2 H), 7.67 (d, *J* = 9.54 Hz, 1 H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 12.8, 37.3, 114.0, 121.0, 121.8, 121.9, 129.0, 130.6, 139.0, 161.9. **FTIR** (**cm^{-1}**): 2984, 2879, 1638, 1573, 1453, 1161, 833, 752, 619. HRMS: Calculated for $C_{11}H_{12}NO$ [M+H] $^+$: 174.0919, found: 174.0913.

1-benzylquinolin-2(1H)-one (7c)



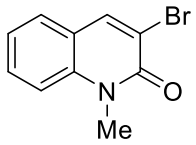
The titled compound was prepared by following the general optimized procedure with KOH as base and previously known in literature.[21] Obtained as a white solid (59 mg, 83 % yield). R_f (Ethyl acetate/Pet. ether = 20:80) = 0.4.

1-methyl-3-phenylquinolin-2(1H)-one (7d)



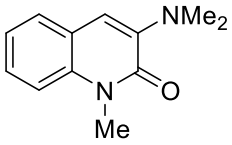
The titled compound was prepared by following the general procedure with KO^{t}Bu as base and previously known in literature.[27] Obtained as a white solid (56 mg, 79 % yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.3.

3-bromo-1-methylquinolin-2(1H)-one (7e)



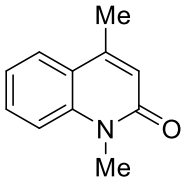
The titled compound was prepared by following the general optimized procedure with KOH as base and previously known in literature.[28] Obtained as a white solid (7 mg, 10% yield). R_f (Ethyl acetate/Pet. ether = 20:80) = 0.25.

3-(dimethylamino)-1-methylquinolin-2(1H)-one (7f)



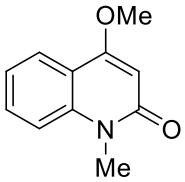
The titled compound was prepared (0.1 mmol scale) by following the general procedure with KO^{t}Bu as base at 50 °C. Obtained as a white solid (34 mg, 56% yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.1; MP = 174 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 2.95 (s, 6 H), 3.76 (s, 3 H), 6.88 (br. s., 1 H), 7.14 - 7.23 (m, 1 H), 7.30 (d, *J* = 8.39 Hz, 1 H), 7.34 - 7.42 (m, 1 H), 7.47 (d, *J* = 7.63 Hz, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 29.7, 30.0, 42.0, 113.6, 117.0, 121.1, 121.6, 122.2, 126.8, 135.9, 139.6, 159.7. **FTIR (cm^{-1})**: 2926, 2854, 1655, 1264, 732, 703. **HRMS:** Calculated for $C_{12}H_{15}N_2O$ $[M+H]^+$: 203.1184, found: 203.1179.

1,4-dimethylquinolin-2(1H)-one (7h)



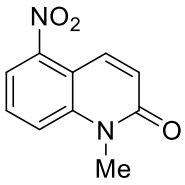
The titled compound was prepared by following the general procedure with 150 mol% DMP catalyst and previously known in literature.[29] Obtained as a white solid (47 mg, 92% yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.15.

4-methoxy-1-methylquinolin-2(1H)-one (7g)



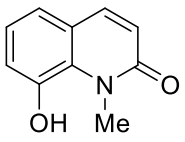
The titled compound was prepared by following the general procedure with KO^{t}Bu as base and previously known in literature.[30] Obtained as orange solid (50 mg, 89% yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.5.

1-methyl-5-nitroquinolin-2(1H)-one (7i)



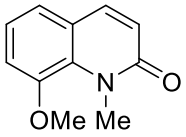
The titled compound was prepared by following the general procedure with KOH as base. Obtained as a light yellow solid (56 mg, 91% yield). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.2; **MP** = 134.9 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.79 (s, 3 H), 6.91 (d, *J* = 9.92 Hz, 1 H), 7.67 (d, *J* = 7.63 Hz, 2 H), 7.83 (dd, *J* = 7.25, 1.53 Hz, 1 H), 8.29 (d, *J* = 9.92 Hz, 1 H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 30.2, 113.7, 118.4, 119.0, 125.1, 129.8, 132.7, 141.3, 147.7, 160.9. **FTIR (cm^{-1})**: 2972, 2883, 1655, 1518, 1351, 1287, 955, 844, 728, 618. **HRMS:** Calculated for $C_{10}H_9N_2O_3$ $[M+H]^+$: 205.0613, found: 205.0607.

8-hydroxy-1-methylquinolin-2(1H)-one (7j)



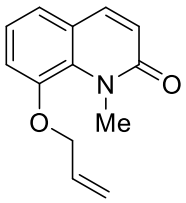
The titled compound was prepared by following the general procedure with KOH as base. Obtained as a white solid (45 mg, 85 %). R_f (Ethyl acetate/Pet. ether = 50:50) = 0.1; **MP** = 274.5 °C. (**^{1}H NMR (500 MHz, DMSO-d_6 + $CDCl_3$)** δ 3.88 (s, 3 H), 6.54 (d, *J* = 9.54 Hz, 1 H), 6.98 - 7.09 (m, 2 H), 7.09 - 7.15 (m, 1 H), 7.76 (d, *J* = 9.16 Hz, 1 H), 10.05 (s, 1 H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 34.6, 118.1, 120.4, 121.3, 123.2, 123.2, 129.8, 140.0, 146.3, 162.7. **FTIR (cm^{-1})**: 3450, 3066, 1641, 1284, 1049, 990, 826, 757. **HRMS:** Calculated for $C_{10}H_{10}NO_2$ $[M+H]^+$: 160.0762, found: 160.0757.

8-methoxy-1-methylquinolin-2(1H)-one (7k)



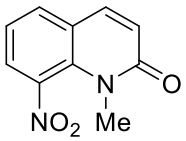
The titled compound was prepared (0.1 mmol scale) by following the general procedure with KO^{t}Bu as base. Obtained as a white solid (43 mg, 76 % yield). ***R*$_f$** (Ethyl acetate/Pet. ether = 50:50) = 0.5; MP = 139.8 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 3.90 (s, 3 H), 3.97 (s, 3 H), 6.69 (d, *J* = 9.16 Hz, 1 H), 7.06 (dd, *J* = 6.87, 2.29 Hz, 1 H), 7.09 - 7.21 (m, 2 H), 7.59 (d, *J* = 9.16 Hz, 1 H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 35.2, 56.6, 113.8, 121.6, 121.9, 122.7, 122.9, 131.4, 139.2, 148.6, 163.7. **FTIR** (**cm^{-1}**): 2974, 1660, 1457, 1267, 1078, 835, 727. **HRMS:** Calculated for $C_{11}H_{12}NO_2$ [M+H] $^+$: 190.0864, found: 190.0861.

8-(allyloxy)-1-methylquinolin-2(1H)-one (7l)



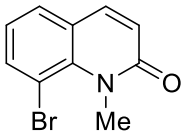
The titled compound was prepared by following the general procedure with KO^{t}Bu as base. Obtained as a light yellow liquid (29 mg, 45% yield). ***R*$_f$** (Ethyl acetate/Pet. ether = 50:50) = 0.3; MP = 118 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 3.99 (s, 3 H), 4.61 (d, *J* = 5.34 Hz, 2 H), 5.34 (d, *J* = 10.68 Hz, 1 H), 5.40 - 5.48 (m, 1 H), 6.04 - 6.16 (m, 1 H), 6.70 (d, *J* = 9.54 Hz, 1 H), 7.04 - 7.10 (m, 1 H), 7.10 - 7.19 (m, 2 H), 7.60 (d, *J* = 9.54 Hz, 1 H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 35.4, 71.2, 115.5, 118.4, 121.8, 121.9, 122.7, 123.0, 131.6, 132.6, 139.2, 147.5, 163.7. **FTIR** (**cm^{-1}**): 2936, 1638, 1586, 1456, 1269, 1121, 835, 747. **HRMS:** Calculated for $C_{13}H_{14}NO_2$ [M+H] $^+$: 216.1025, found: 216.1018.

1-methyl-8-nitroquinolin-2(1H)-one (7m)



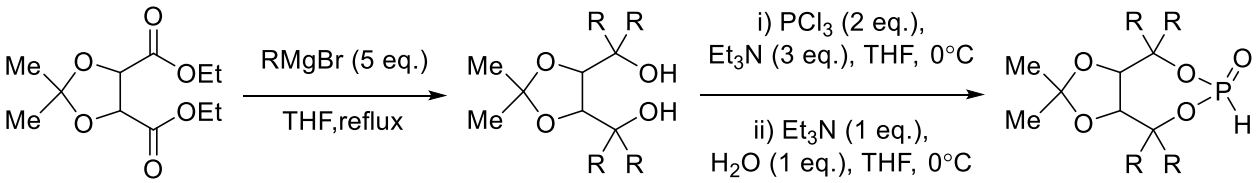
The titled compound was prepared by following the general procedure with KOH as base. Obtained as a light brown solid (46 mg, 75 % yield). ***R*$_f$** (Ethyl acetate/Pet. ether = 50:50) = 0.2; **MP** = 114.9 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 3.48 (s, 3 H), 6.82 (d, *J* = 9.54 Hz, 1 H), 7.16 - 7.38 (m, 1 H), 7.65 - 7.79 (m, 2 H), 7.80 - 7.91 (m, 1 H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 34.3, 121.6, 123.2, 123.4, 127.0, 132.6, 133.7, 138.6, 139.8, 162.6. **FTIR** (**cm^{-1}**): 2971, 2880, 1653, 1590, 1529, 1453, 1351, 1287, 1122, 1064, 961, 843, 728, 618. **HRMS:** Calculated for $C_{10}H_9N_2O_3$ [M+H] $^+$: 205.0613, found: 205.0606.

8-bromo-1-methylquinolin-2(1H)-one (7n)



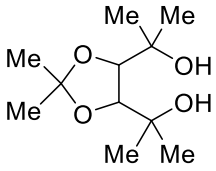
The titled compound was prepared (0.18 mmol scale) by following the general procedure with KOH as base. Obtained as a light yellow solid (62 mg, 87 % yield). ***R*$_f$** (Ethyl acetate/Pet. ether = 100:0) = 0.6; **MP** = 127.3 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 3.99 (s, 3 H), 6.72 (d, *J* = 9.54 Hz, 1 H), 6.98 - 7.12 (m, 1 H), 7.39 - 7.53 (m, 1 H), 7.60 (d, *J* = 9.16 Hz, 1 H), 7.73 - 7.87 (m, 1 H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 37.6, 108.1, 122.2, 123.5, 124.1, 128.5, 137.8, 139.1, 139.8, 164.0. **FTIR** (**cm^{-1}**): 3411, 2933, 1637, 1575, 1437, 1277, 1120, 1023, 835, 751, 618. **HRMS:** Calculated for $C_{10}H_9BrNO$ [M+H] $^+$: 237.9868, found: 237.9862.

Preparation of chiral phosphites: TADOLs and phosphites were prepared following literature procedures.[34]



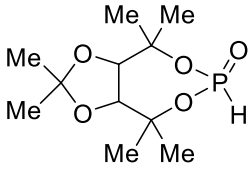
Preparation of (4*R,* 5*R*)-2, 2-dimethyl-tetramethyl-TADDOL: Prepared following literature procedure with 4R,5R)-diethyl-2,2-dimethyl-1,3-dioxolane-4,5- dicarboxylate (900 mg, 3.3 mmol) to obtain 4*R,* 5*R*)-2, 2-dimethyl-tetramethyl-TADDOL as white solid (600 mg, 76 %).

(4*R,* 5*R*)-2, 2-dimethyl-tetramethyl-TADDOL (S8)



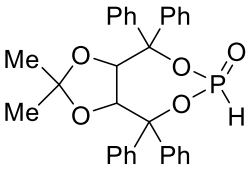
***R**_f* (Ethyl acetate/Pet. ether = 30:70) = 0.3; MP =130.1 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.28 (s, 6 H), 1.32 (s, 6 H), 1.38 (s, 6 H), 1.65 (br. s, 2 H), 3.76 (s, 2 H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 23.9, 27.4, 29.1, 70.6, 82.7, 107.7. **FTIR** (**cm^{-1}**): 3456, 1412, 1304, 1026, 945, 703. **HRMS:** Calculated for $C_{11}H_{22}O_4Na$ $[M]^+$: 241.1416, found: 241.1410.

(1*R*, 7*R*)-9, 9-dimethyl-4-hydrido-4-oxo-2, 2, 6, 6-tetramethyl-3, 5, 8, 10 tetraoxa-4-phosphabicyclo[5.3.0]decane (13a)



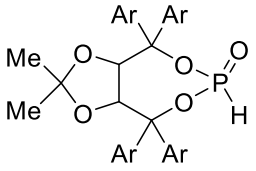
The titled compound was prepared by following the literature procedure, using 600 mg (2.75 mmol) of (4*R,* 5*R*)-2, 2-dimethyl-tetramethyl-TADDOL in 10 ml THF, which afforded 712 mg (98%) of the product as white crystals. ***R**_f* (Ethyl acetate/Pet. ether = 50:50) = 0.6. MP = 91.3 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.40 - 1.43 (m, 9 H), 1.47 (s, 3 H), 1.62 (s, 3 H), 1.65 (s, 3 H), 3.98 (d, *J* = 9.54 Hz, 1 H), 4.47 (d, *J* = 8.17 Hz, 1 H), 6.73 (d, $J_{H\text{-}P}$ = 732 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 22.0, 22.0, 22.0, 27.0, 27.0, 29.0, 29.0, 29.7, 29.7, 80.4, 80.4, 81.7, 82.0, 82.12, 82.2, 110.4. **^{31}P NMR (200 MHz, $CDCl_3$)**: δ 1.15. **FTIR** (**cm^{-1}**): 2979, 1597, 1445, 1371, 1243, 1164, 1076, 929, 847, 745. **HRMS:** Calculated for $C_{22}H_{42}O_{10}NaP_2$ $[M]^+$: 551.2151, found: 551.2145.

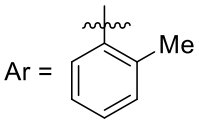
(1*R*, 7*R*)-9, 9-dimethyl-4-hydrido-4-oxo-2, 2, 6, 6-tetraphenyl-3, 5, 8, 10 tetraoxa-4-phosphabicyclo[5.3.0]decane (13b)



The titled compound was prepared by following the literature procedure, using 1166 mg (2.5 mmol) of (4R, 5R)-2, 2-dimethyl-tetraphenyl-TADDOL in 10 ml THF, which afforded 1100 mg (78%) of the product as white crystals. ***R**_f* (Ethyl acetate/Pet. ether = 20:80) = 0.2. The spectral values were matched favorably with literature values.[34]

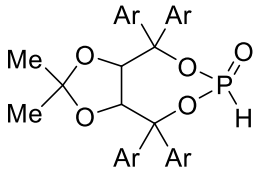
(1*R*, 7*R*)-9, 9-dimethyl-4-hydrido-4-oxo-2,2,6,6-tetra(2-methylphenyl)-3,5,8,10-tetraoxa- 4-phosphabicyclo[5.3.0]decane (13c)

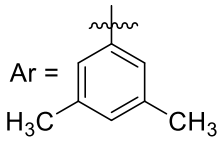




The titled compound was prepared by following the literature procedure, using 600 mg (1.15 mmol) of (4R, 5R)-2, 2-dimethyl-tetra(2-methylphenyl)- TADDOL in 10 ml THF, which afforded 490 mg (78%) of the product as white crystals. ***R**_f* (Ethyl acetate/Pet. ether = 30:70) = 0.6. The spectral values were matched favorably with the literature values.[34]

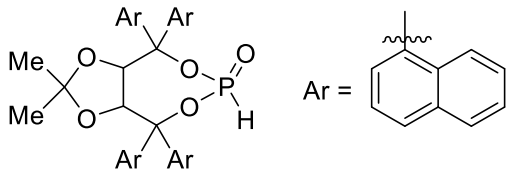
(1*R*, 7*R*)-9, 9-dimethyl-4-hydrido-4-oxo-2, 2, 6, 6-tetra(3,5-dimethylphenyl)-3, 5, 8, 10 tetraoxa-4-phosphabicyclo[5.3.0]decane(13d)





The titled compound was prepared by following the literature procedure, using 727 mg (1.26 mmol) of (4*R,* 5*R*)-2, 2-dimethyl-tetra(3,5-dimethylphenyl)-TADDOL in 10 ml THF, which afforded 446 mg (57%) of the product as white crystals. ***R**_f* (Ethyl acetate/Pet. ether = 20:80) = 0.5. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.51 (s, 3 H), 0.97 (s, 3 H), 2.26 - 2.32 (m, 24 H), 5.09 - 5.15 (m, 2 H), 6.29 (s, 0.5 H), 6.88 (s, 2 H), 6.88 – 7.12 (m, 12 H), 7.71 (s, 0.5 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 21.4, 21.5, 21.6, 21.6, 26.1, 27.1, 80.4, 88.0, 88.1, 88.4, 88.5, 113.7, 124.4, 124.6, 125.5, 125.9, 126.5, 128.9, 129.5, 129.6, 130.1, 130.2, 136.6, 137.0, 137.4, 138.1, 138.9, 138.9, 139.2, 139.2, 143.1, 143.7. **^{31}P NMR (500 MHz, $CDCl_3$)** δ -5.08.

(1*R*, 7*R*)-9, 9-dimethyl-4-hydrido-4-oxo-2, 2, 6, 6-tetranapthyl-3, 5, 8, 10 tetraoxa-4-phosphabicyclo[5.3.0]decane(13e)



The titled compound was prepared by following the literature procedure, using 666 mg (1 mmol) of (4*R,* 5*R*)-2, 2-dimethyl-tetranapthyl-TADDOL in 10 ml THF, which afforded 423 mg (70%) of the product as white crystals. R_f (Ethyl acetate/Pet. ether = 20:80) = 0.2.

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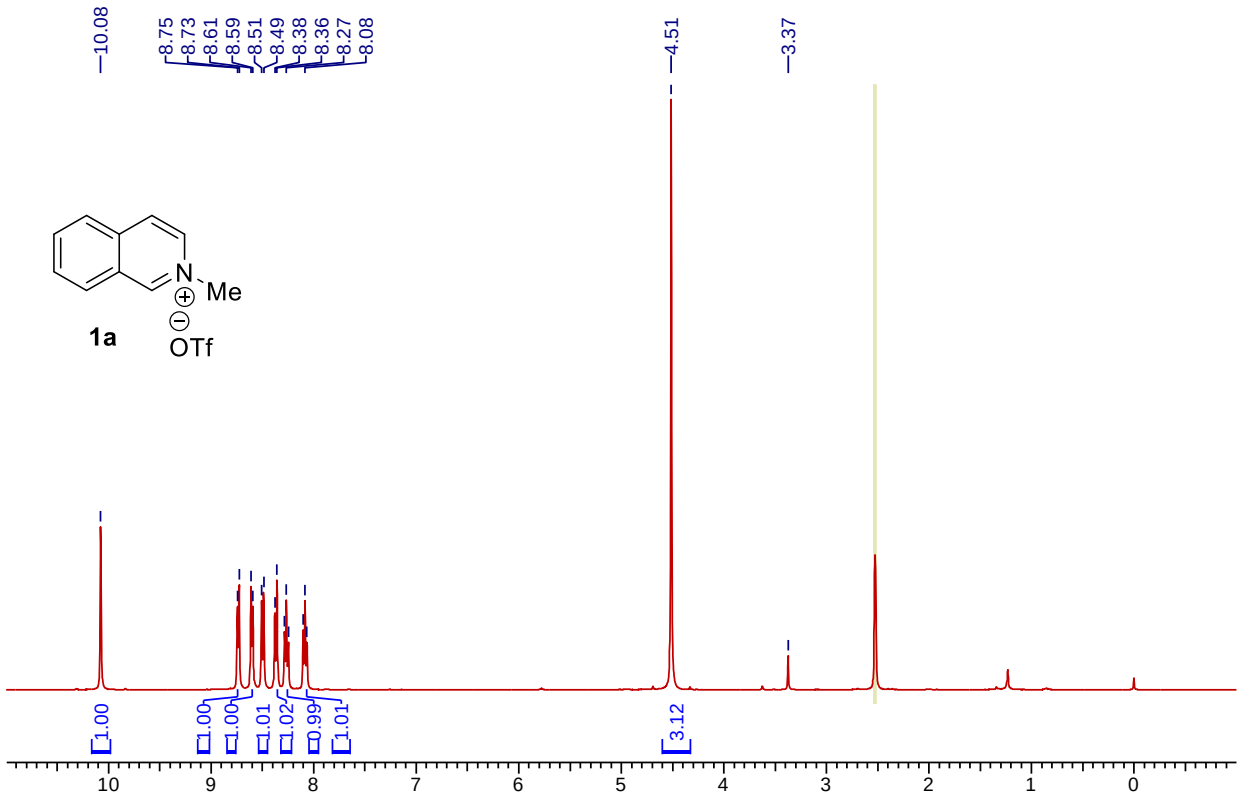
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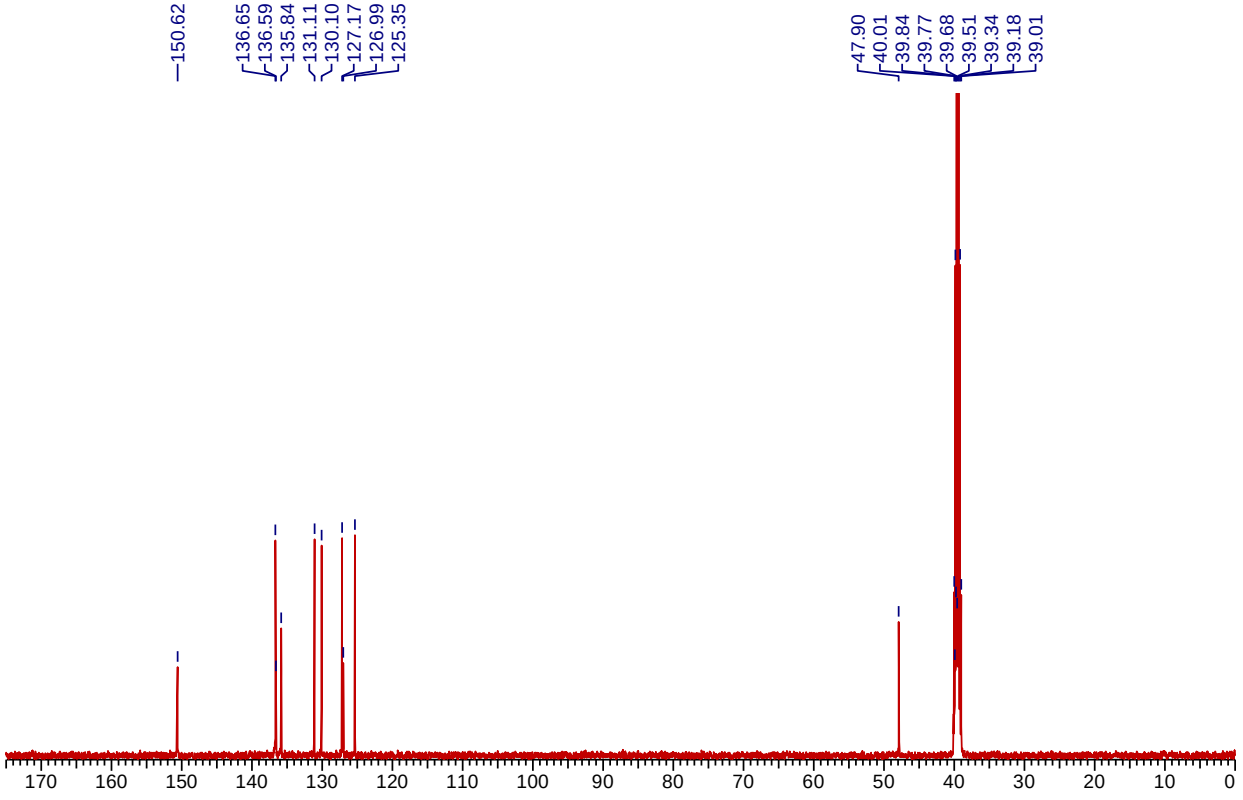
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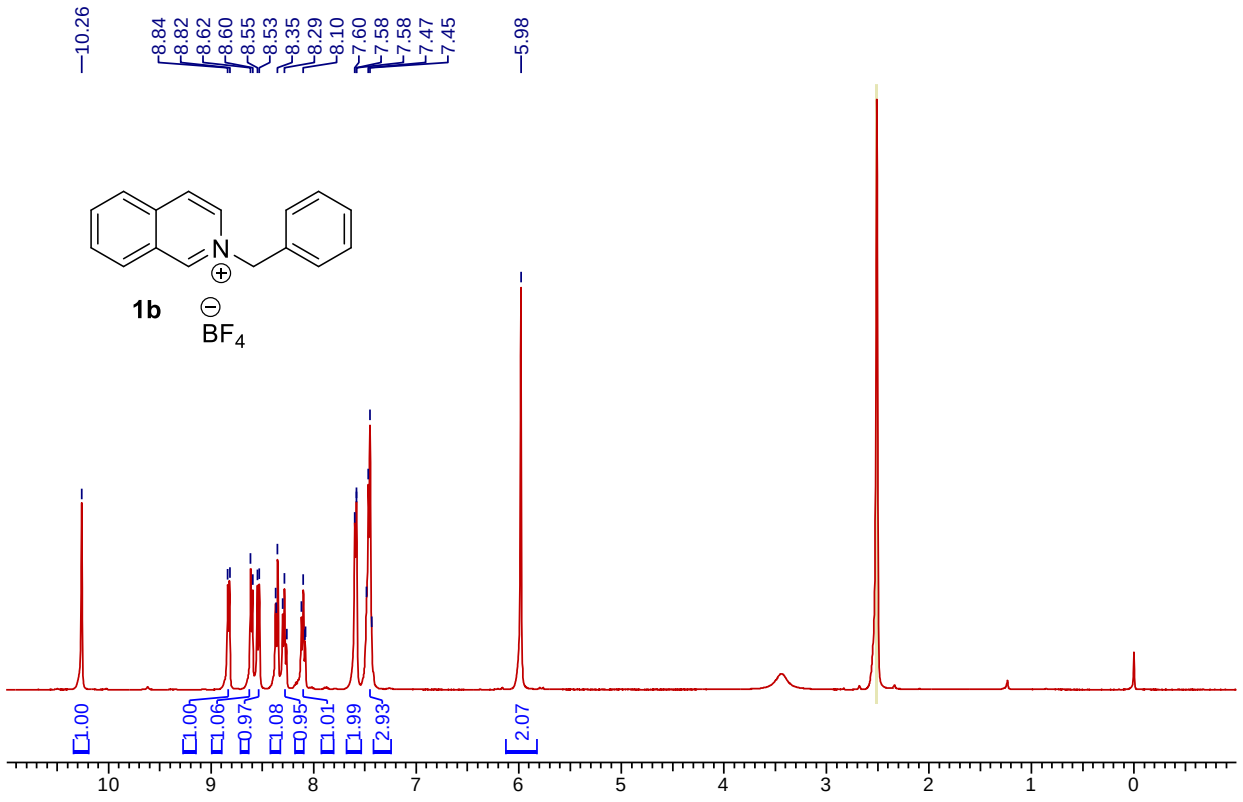
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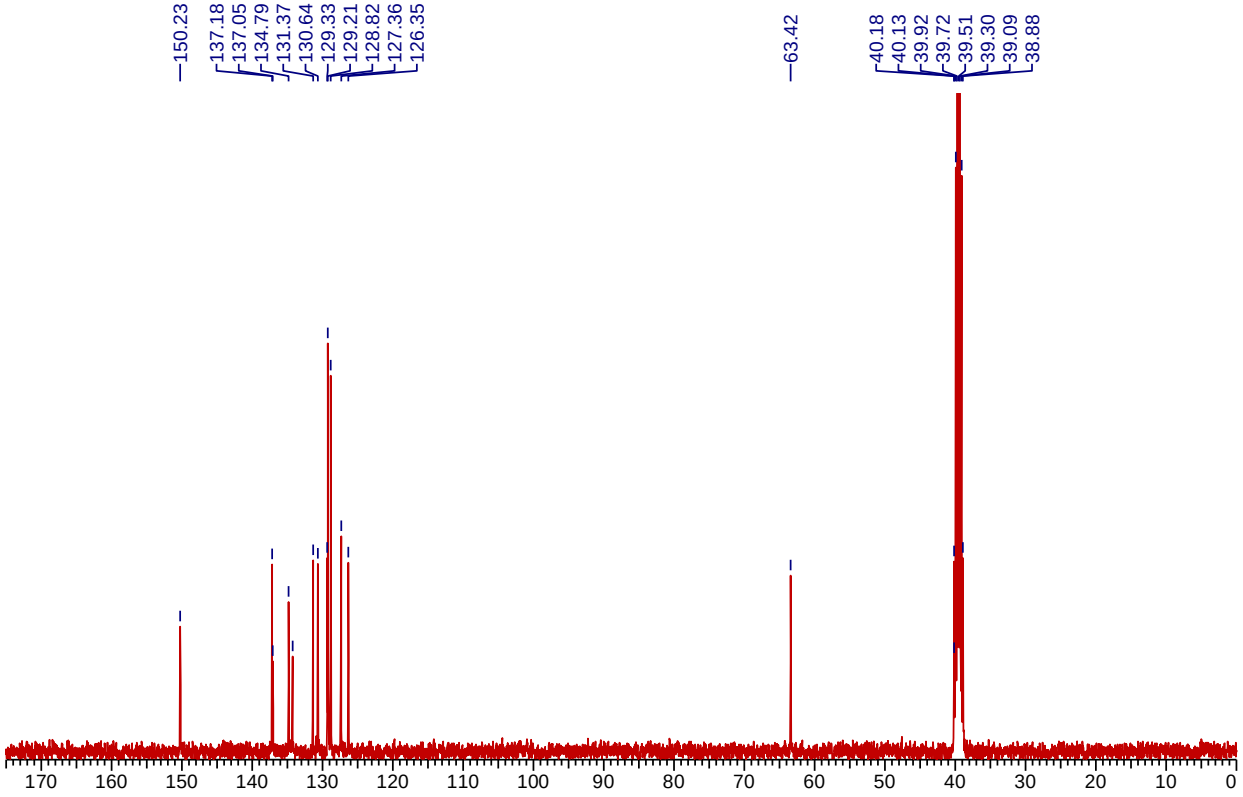
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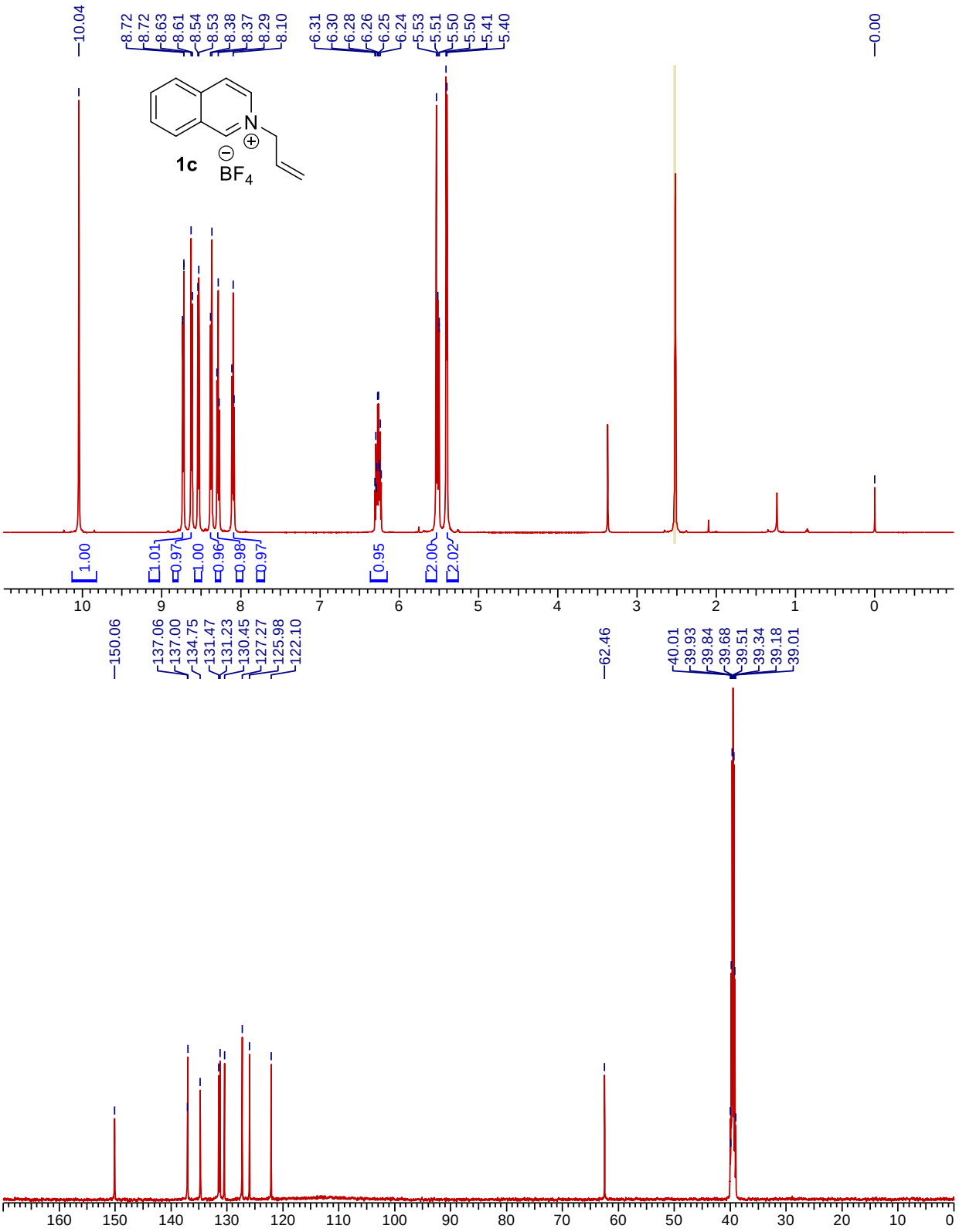
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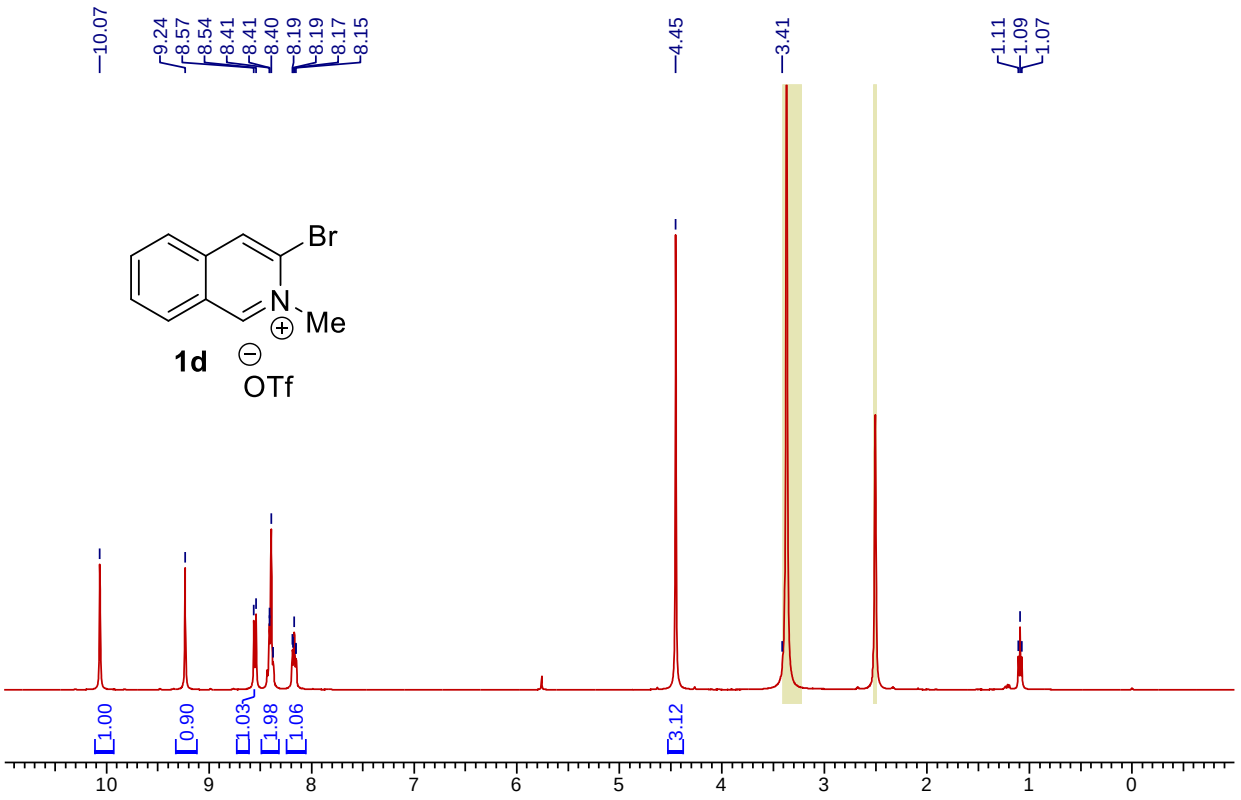
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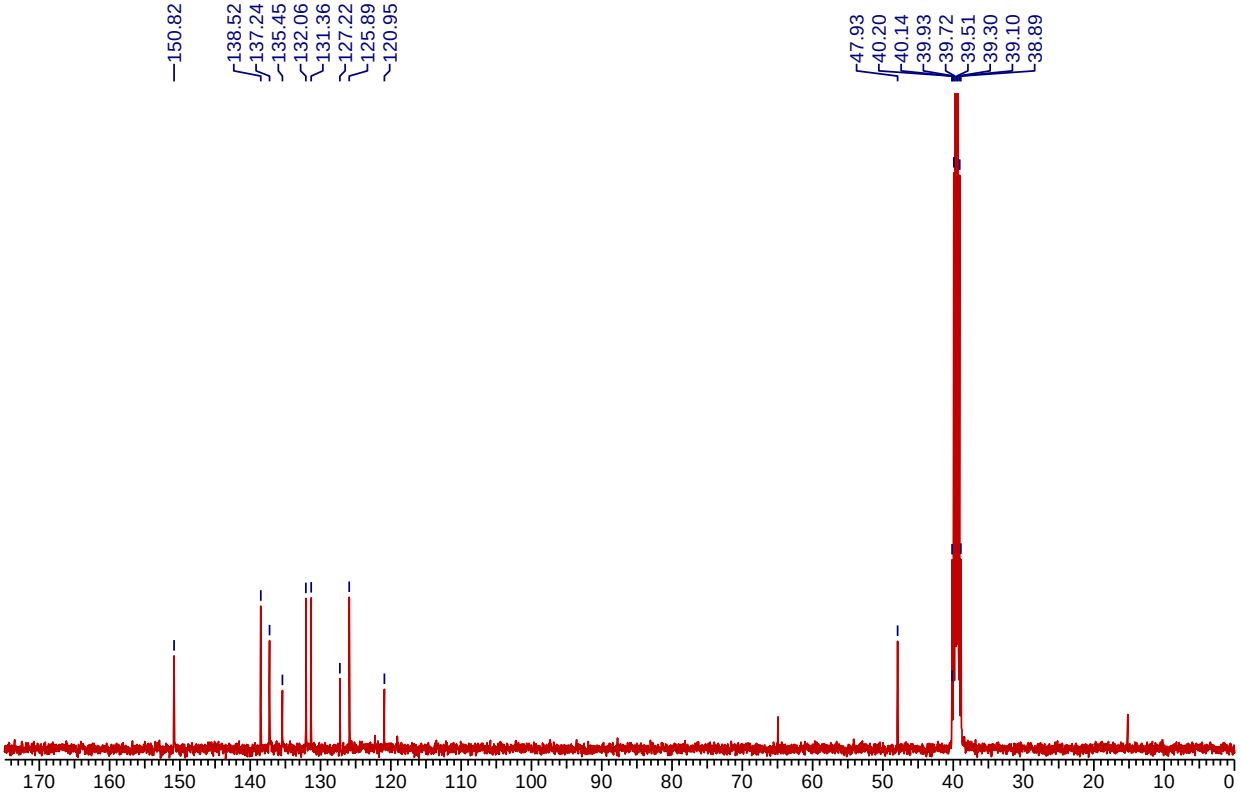
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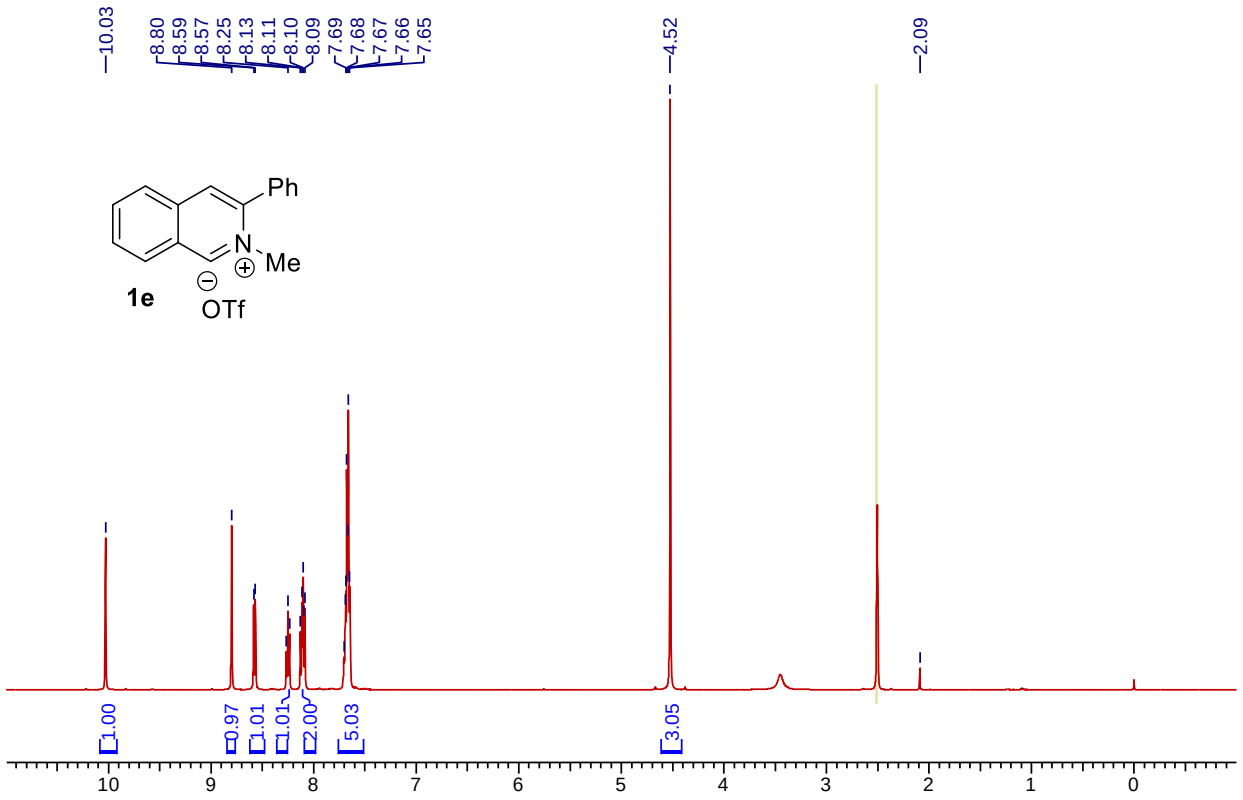
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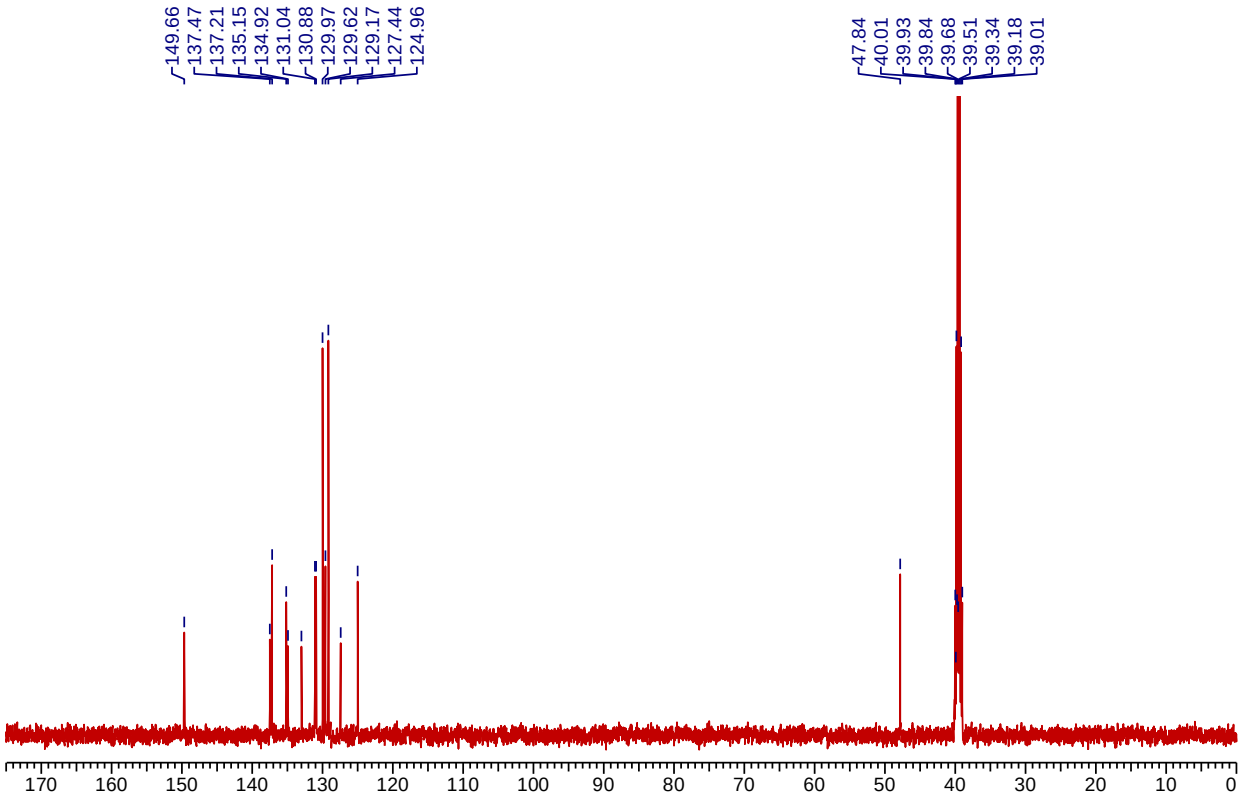
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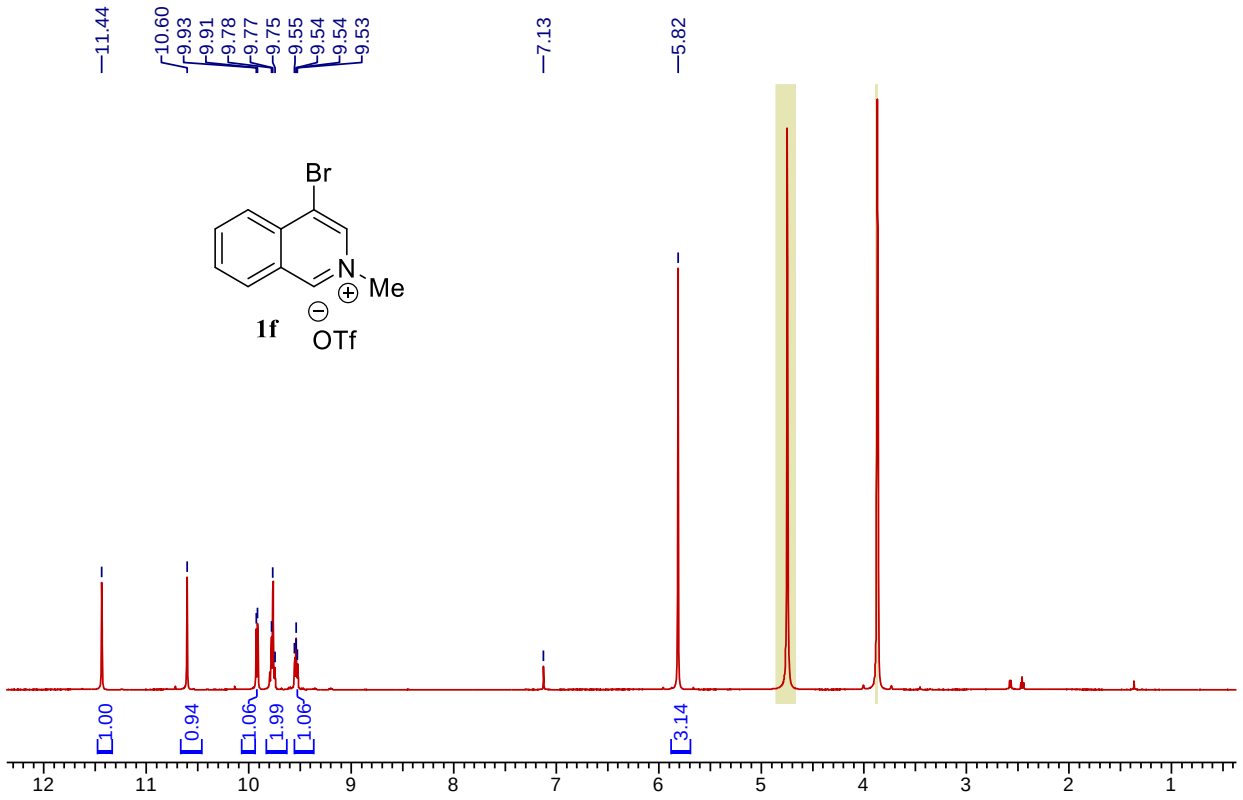
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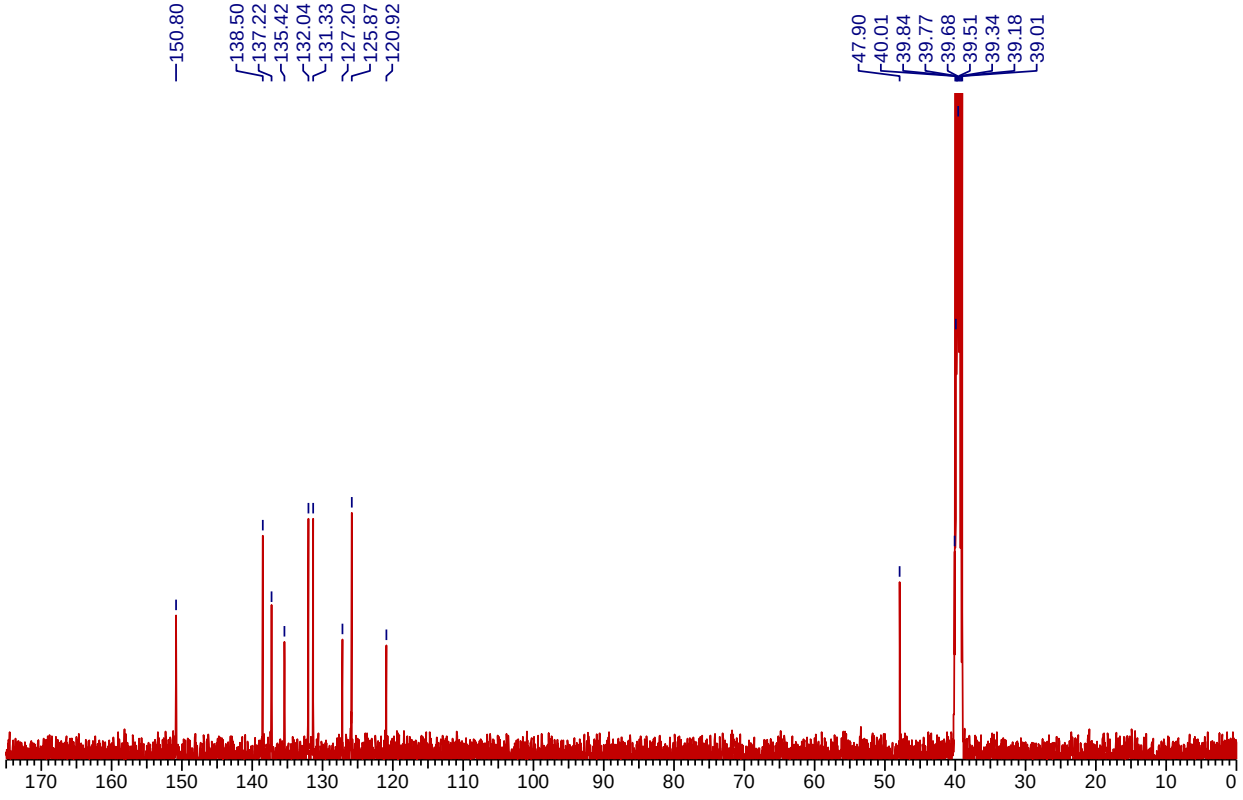
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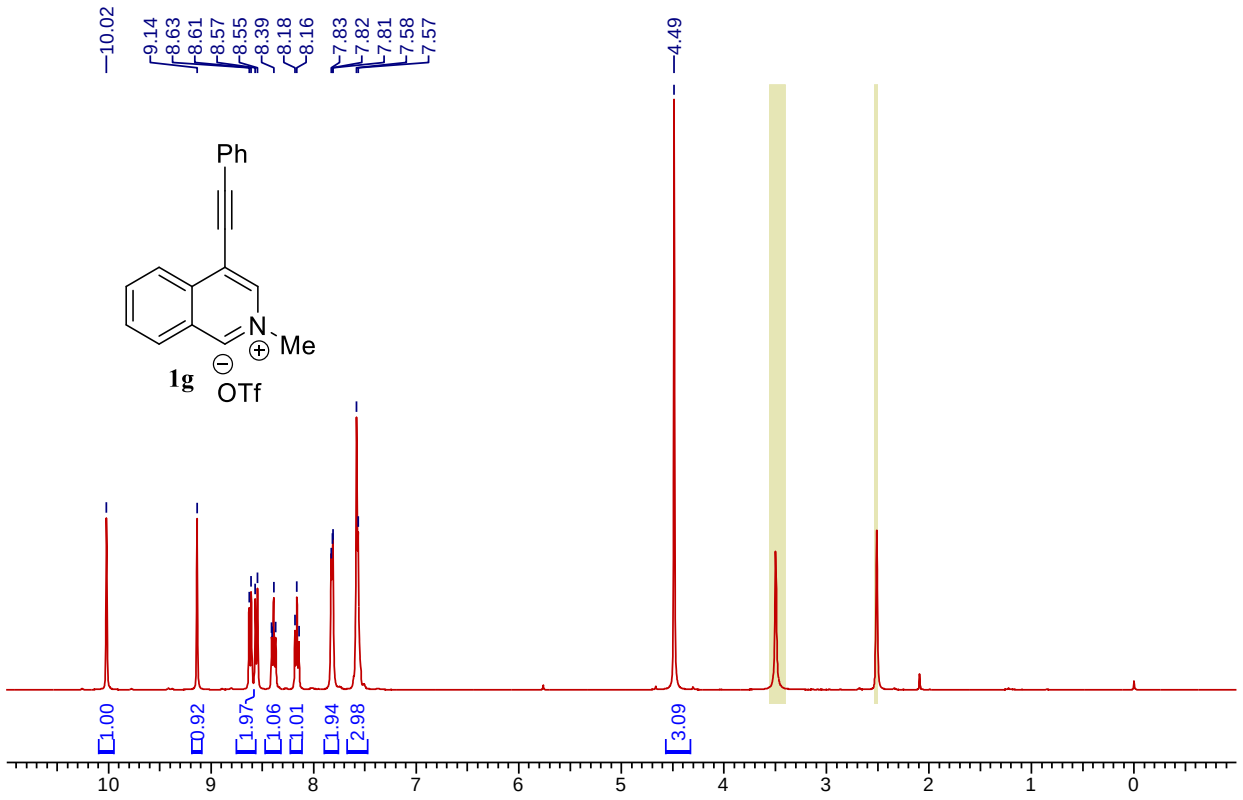
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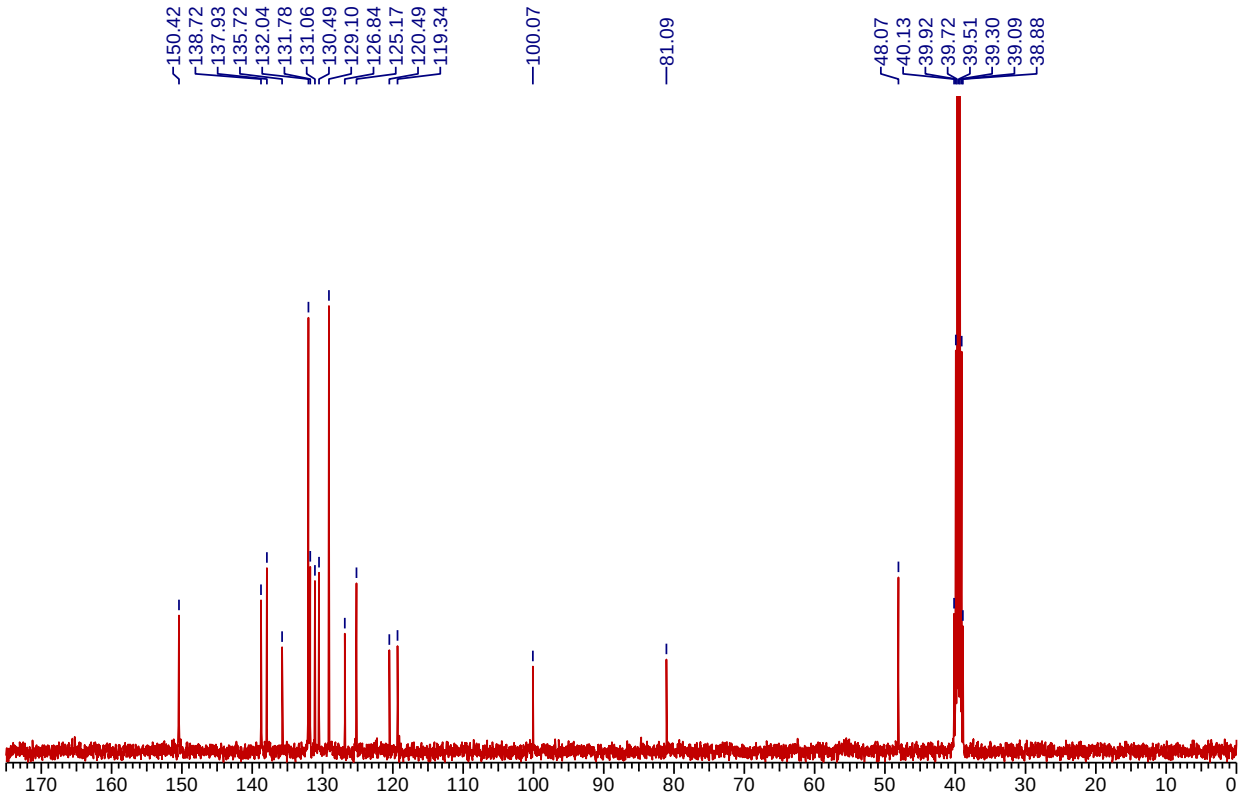
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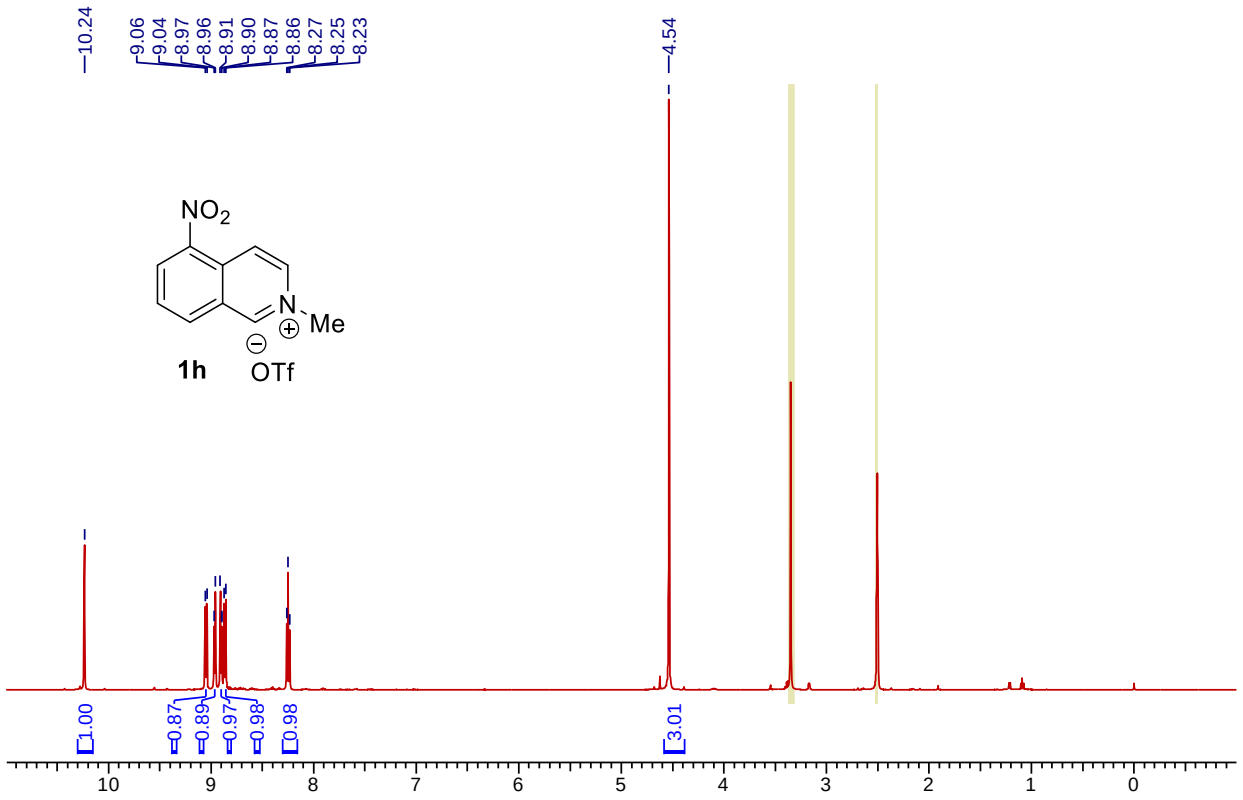
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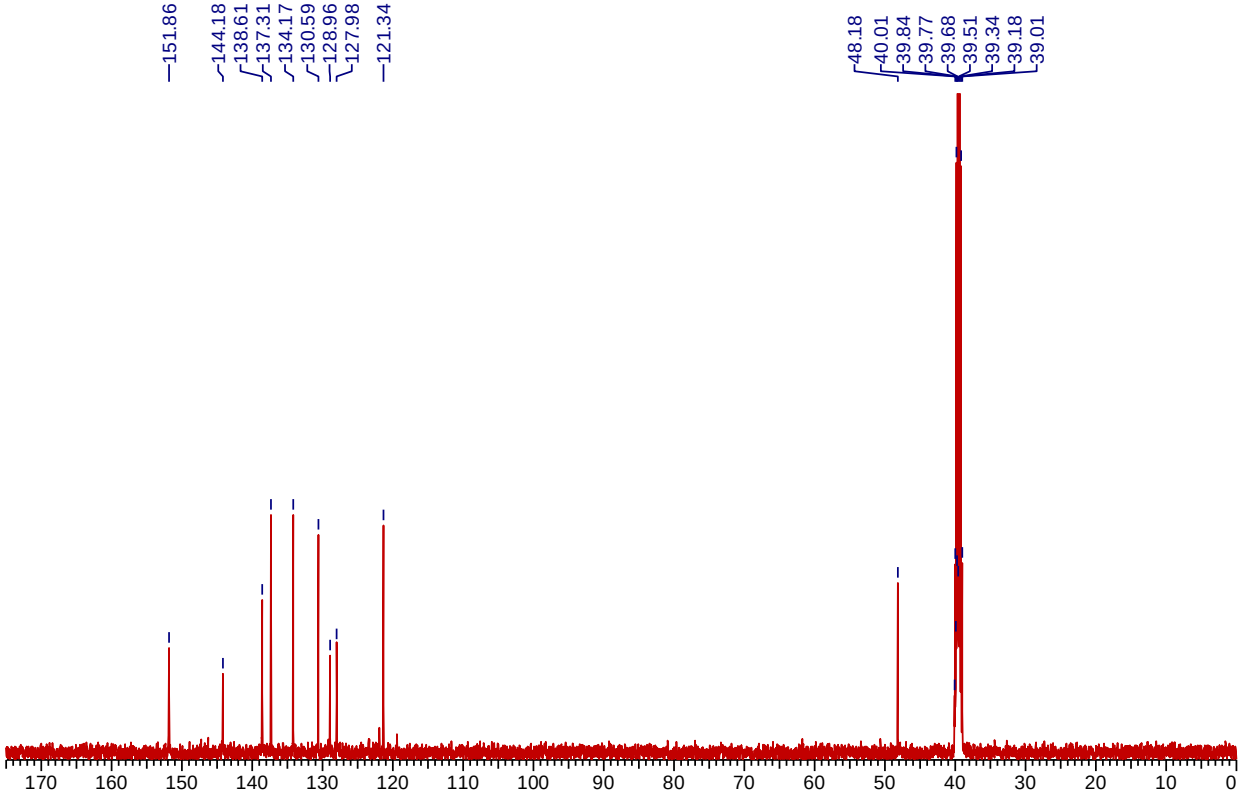
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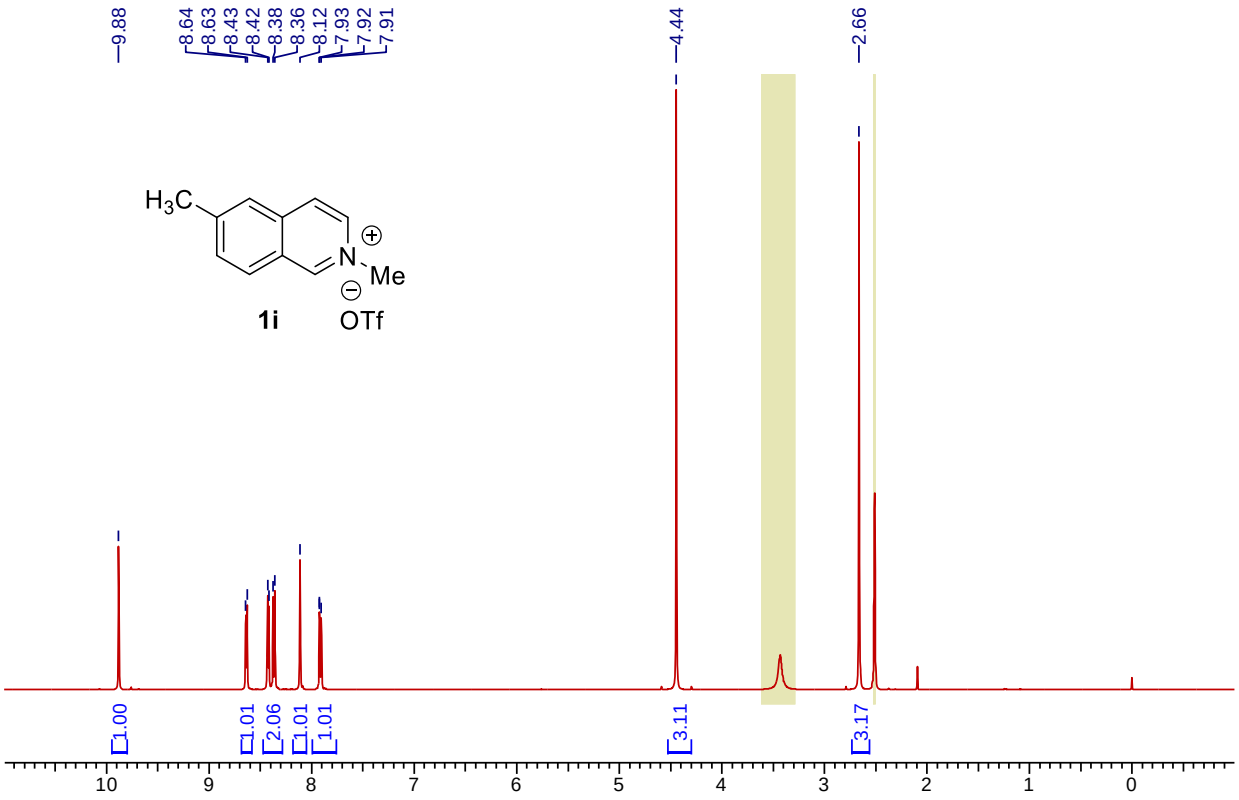
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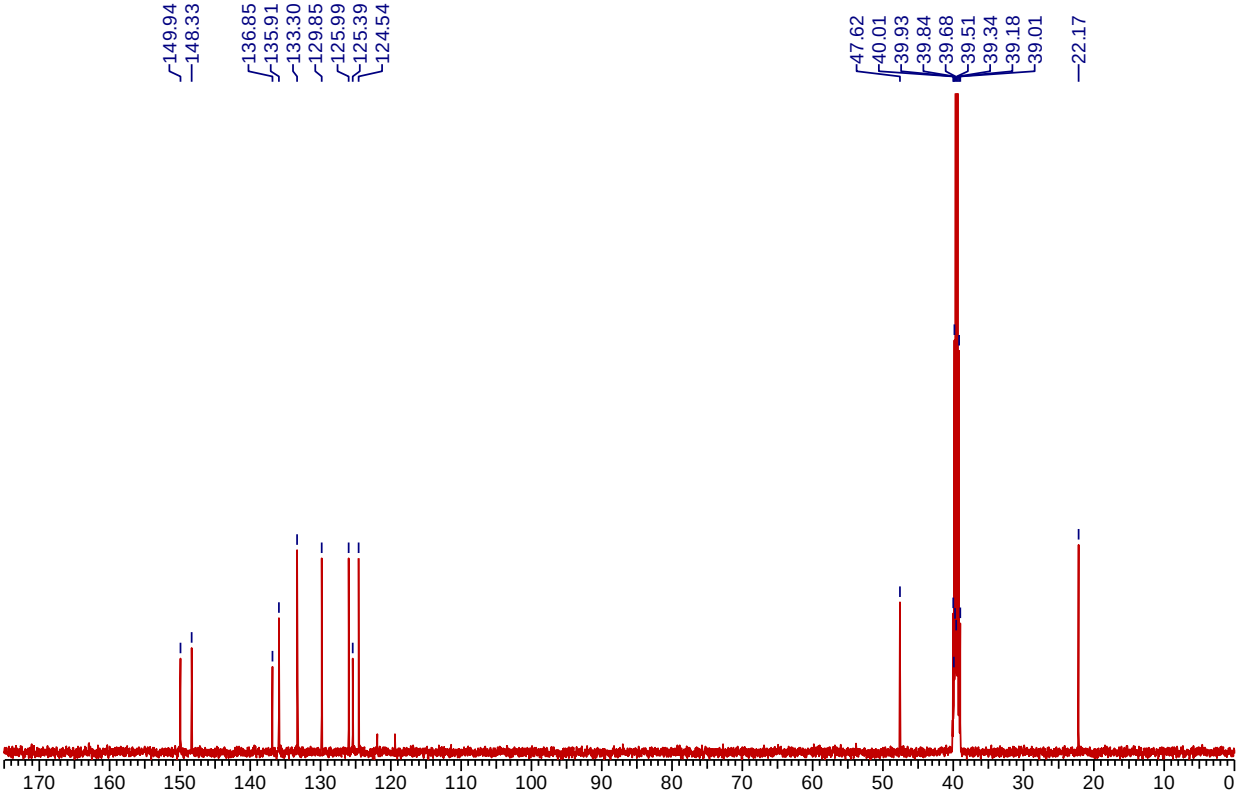
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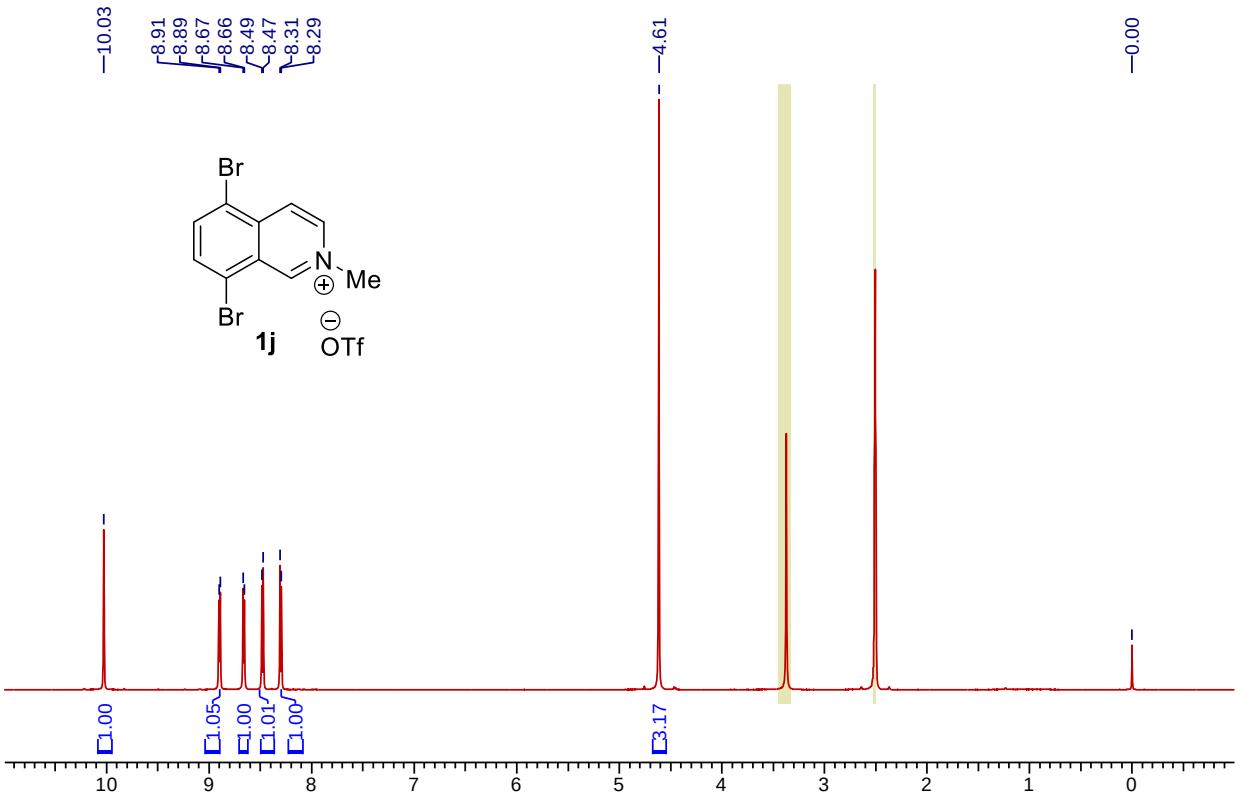
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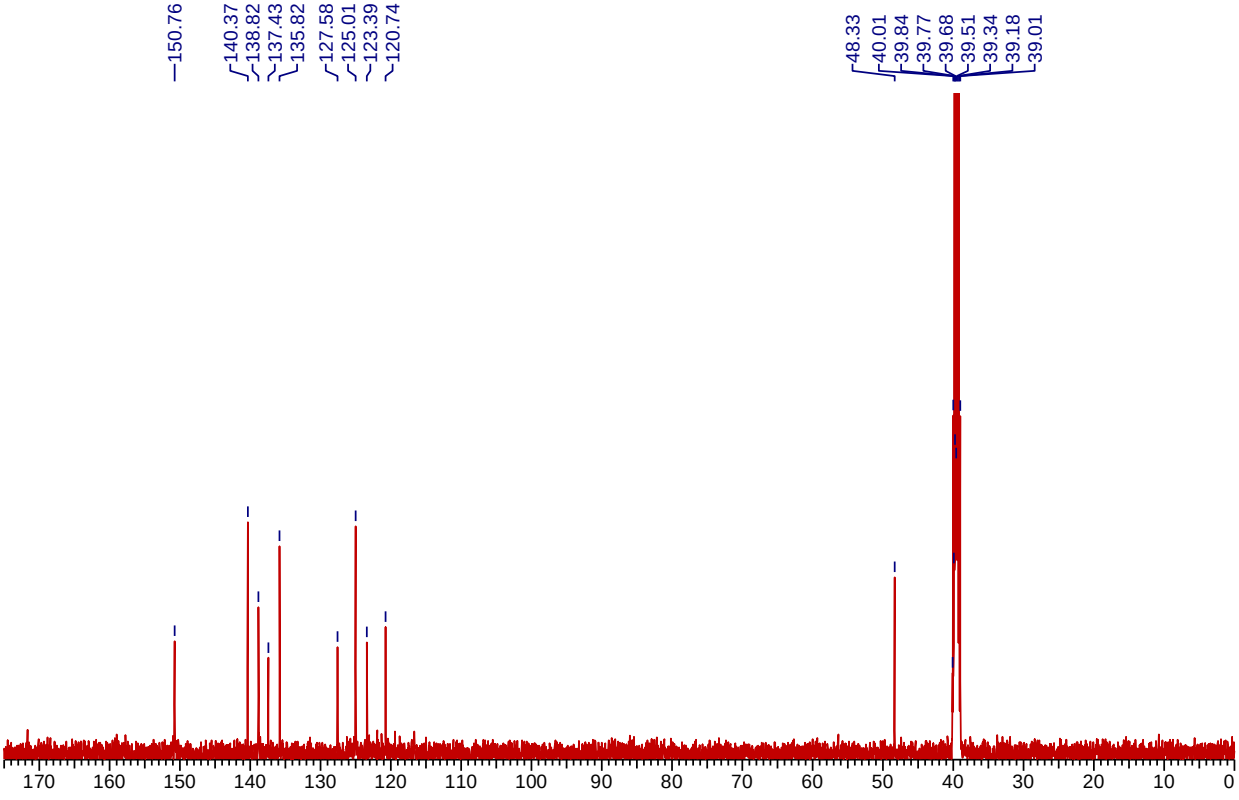
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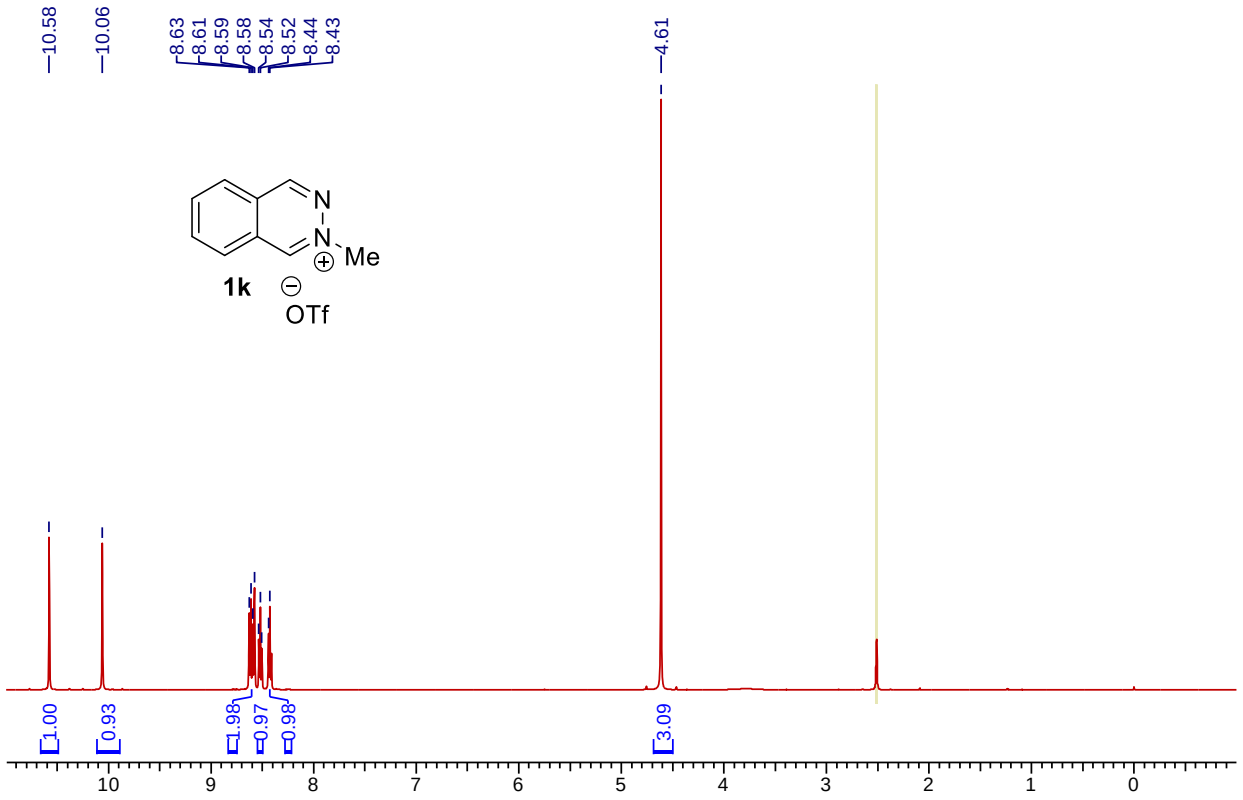
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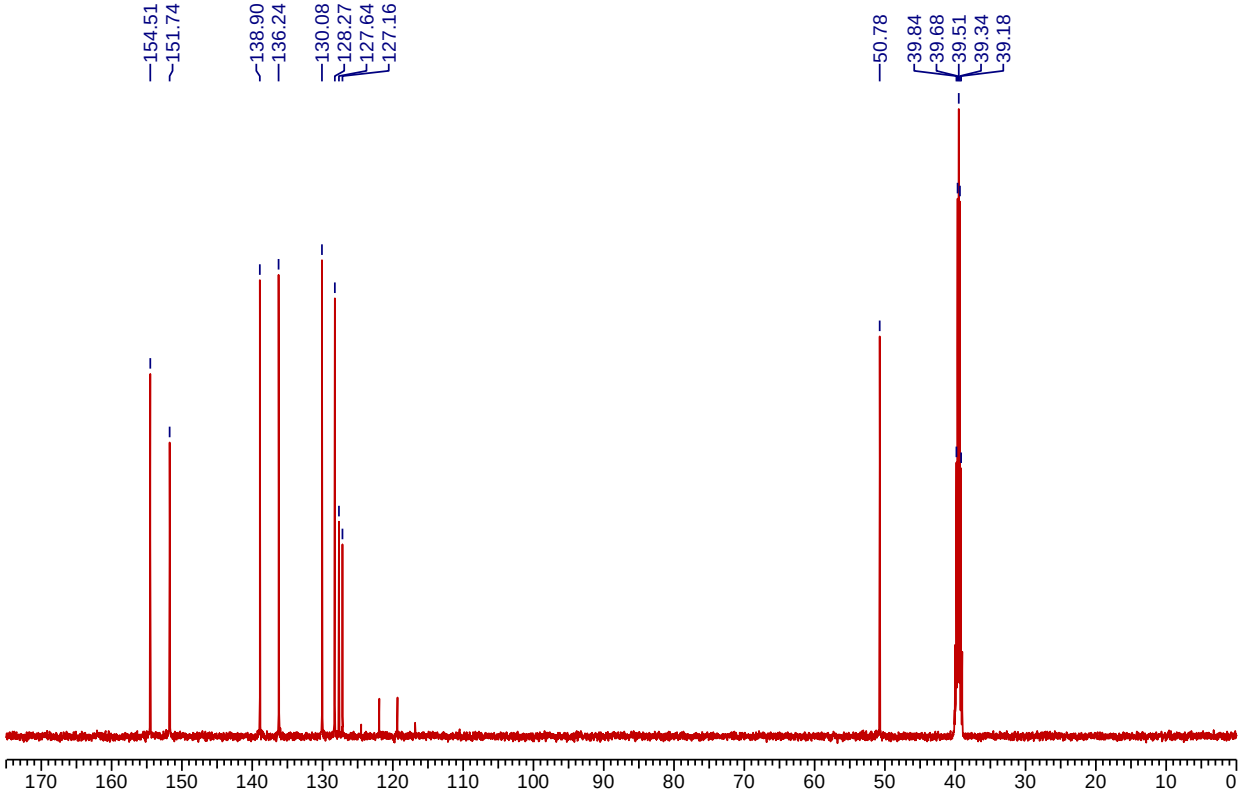
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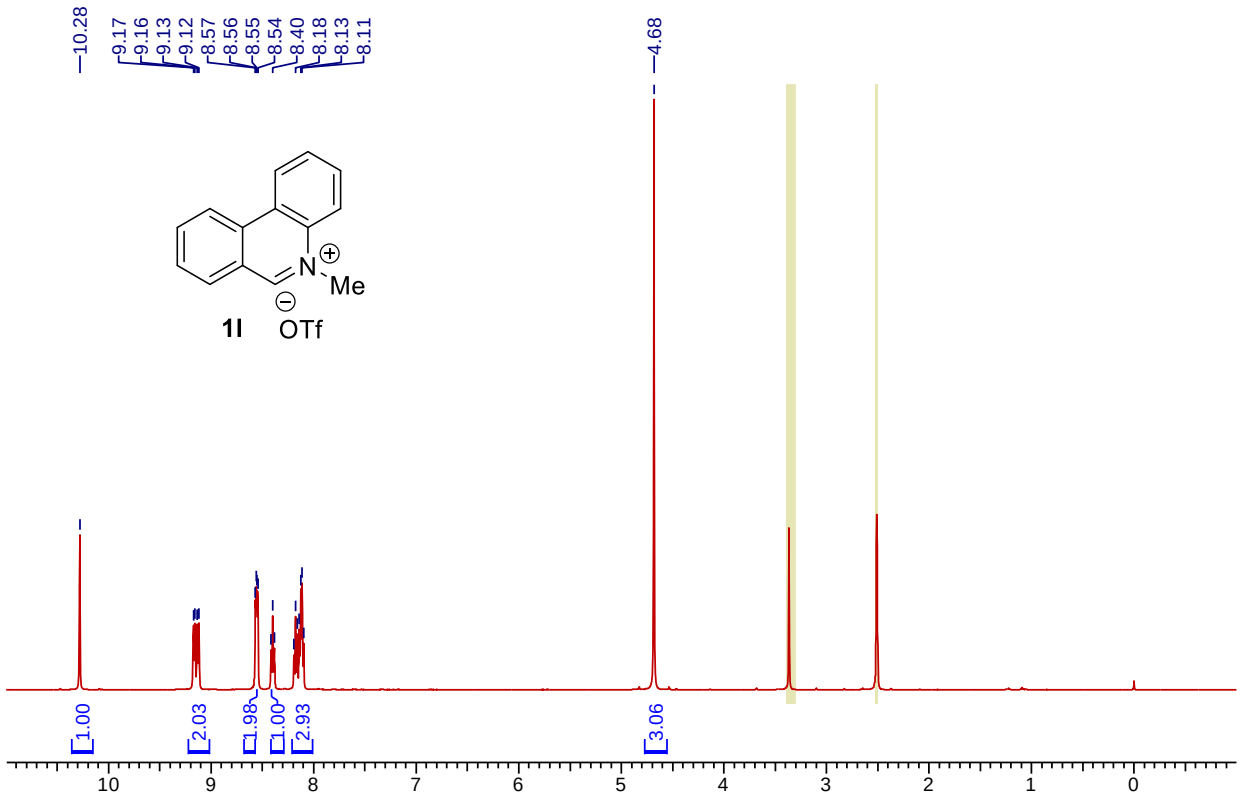
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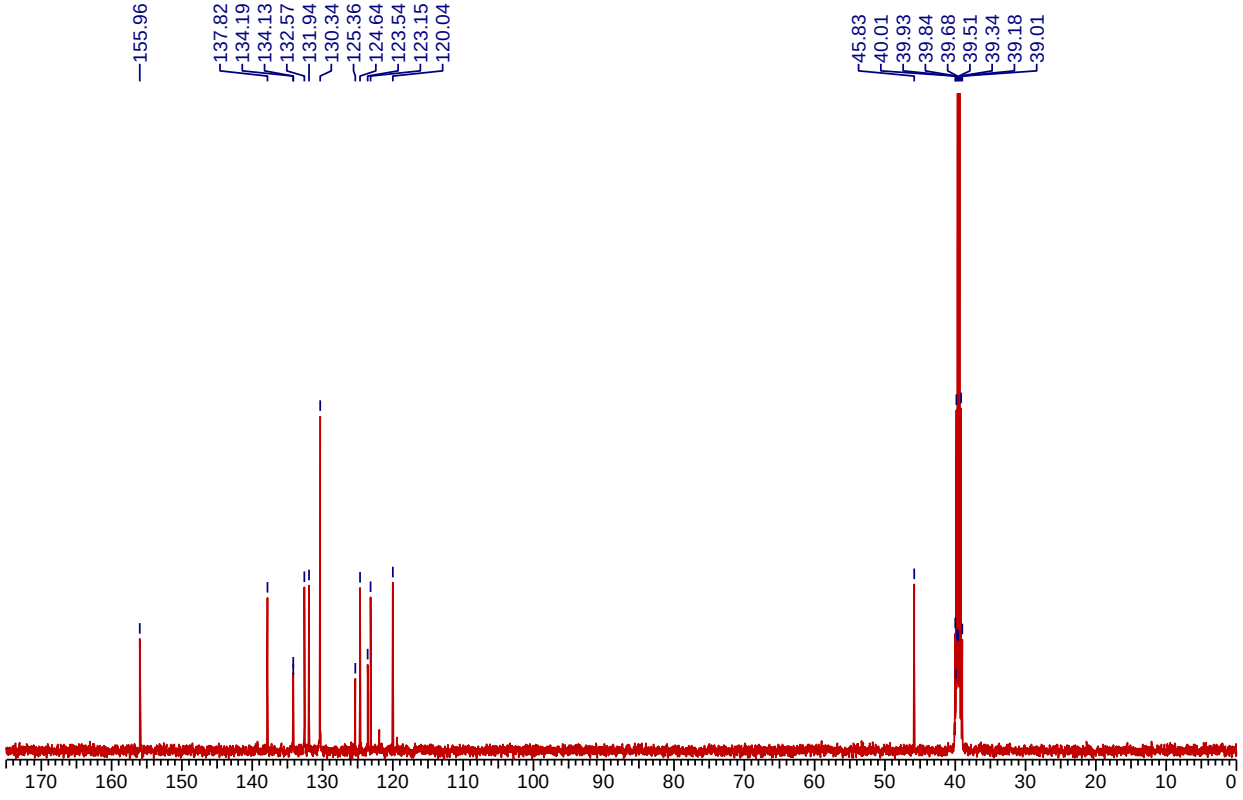
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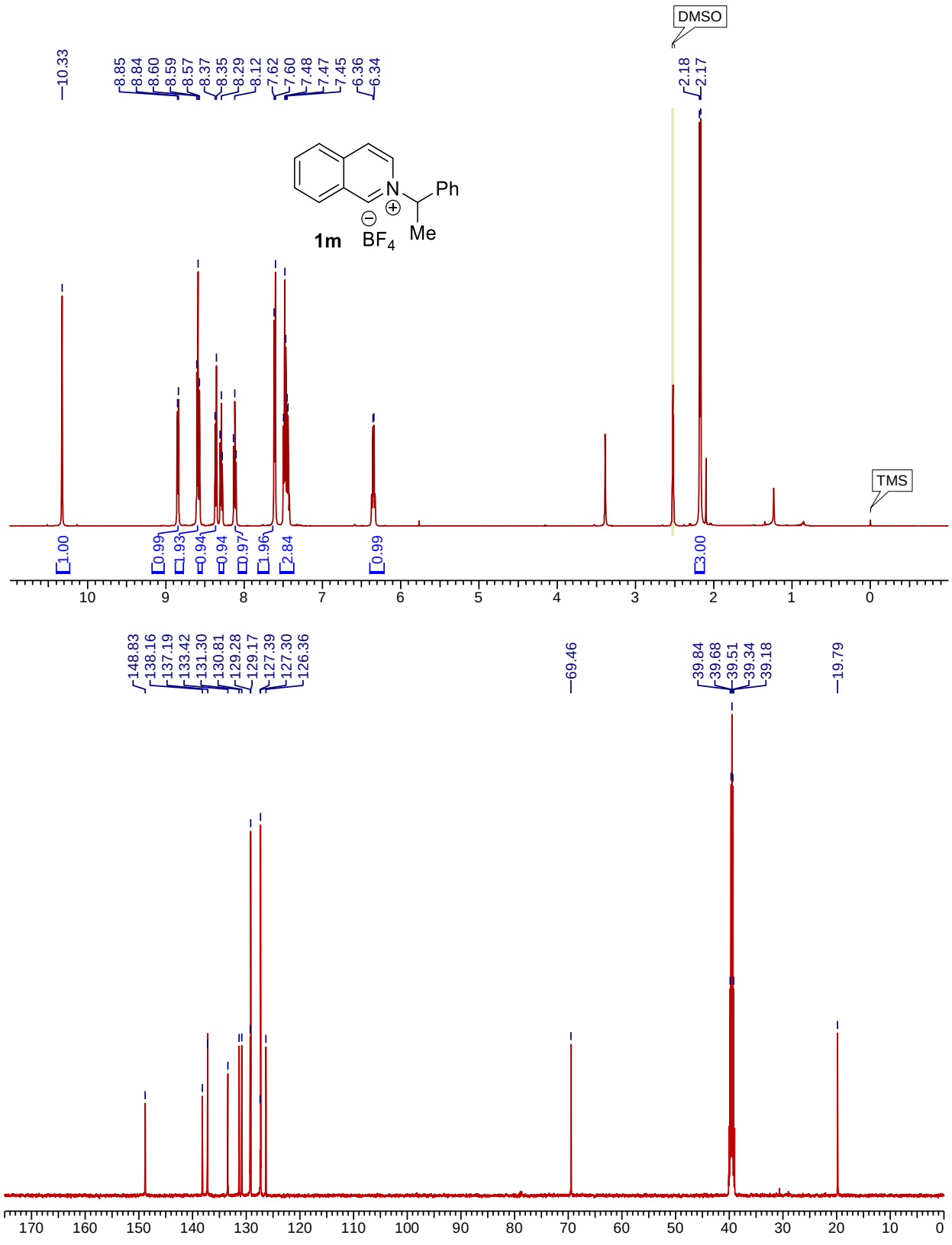
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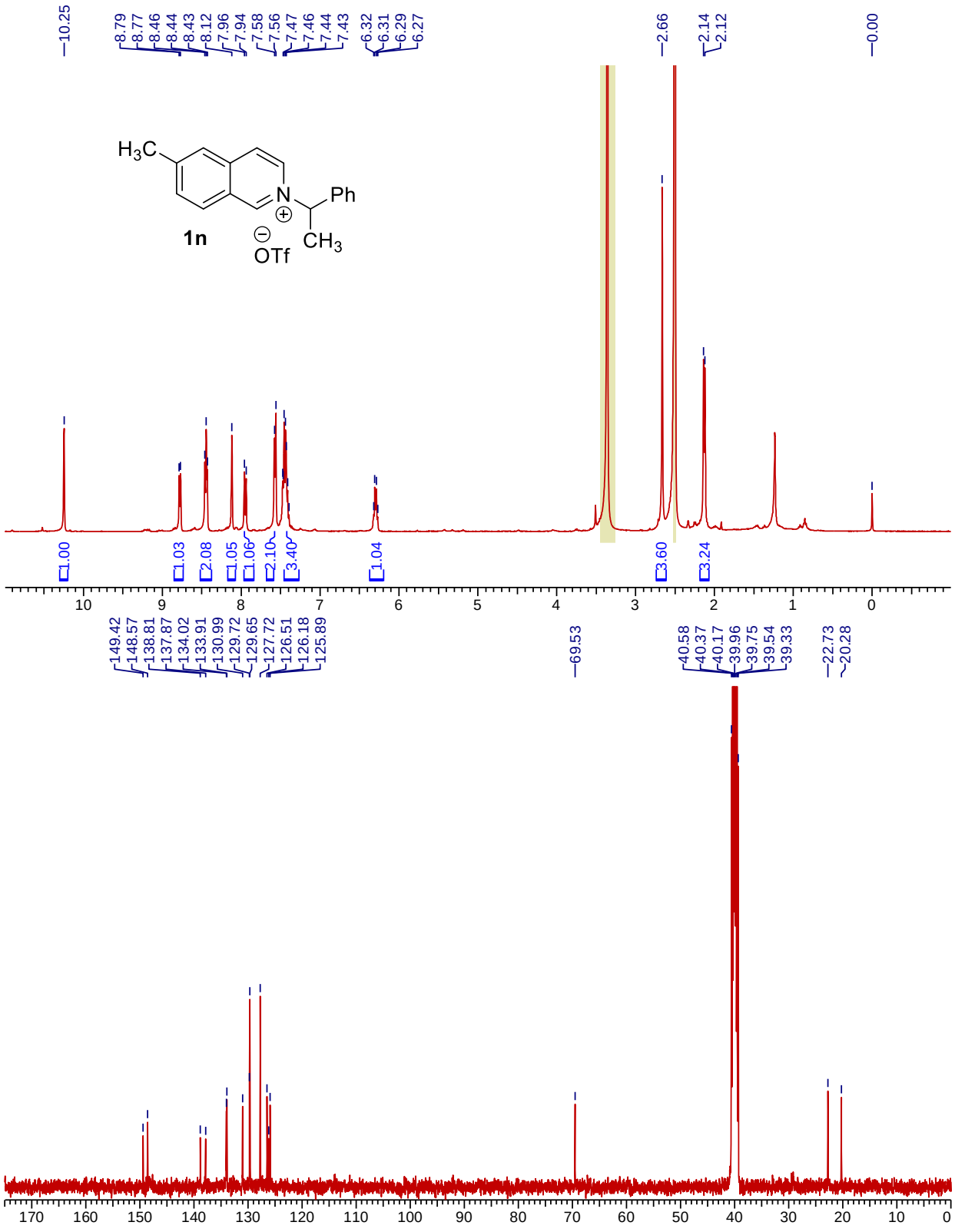
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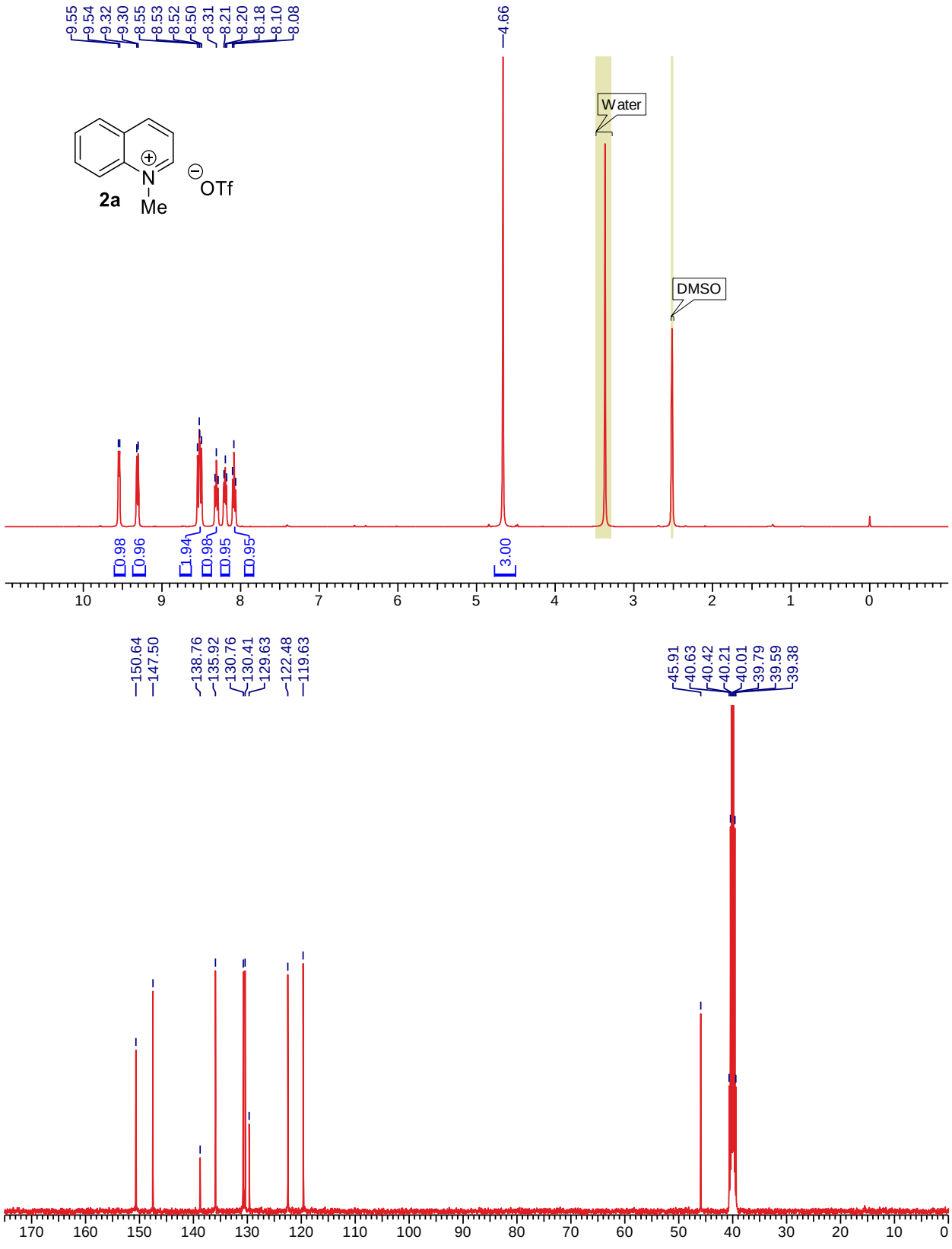
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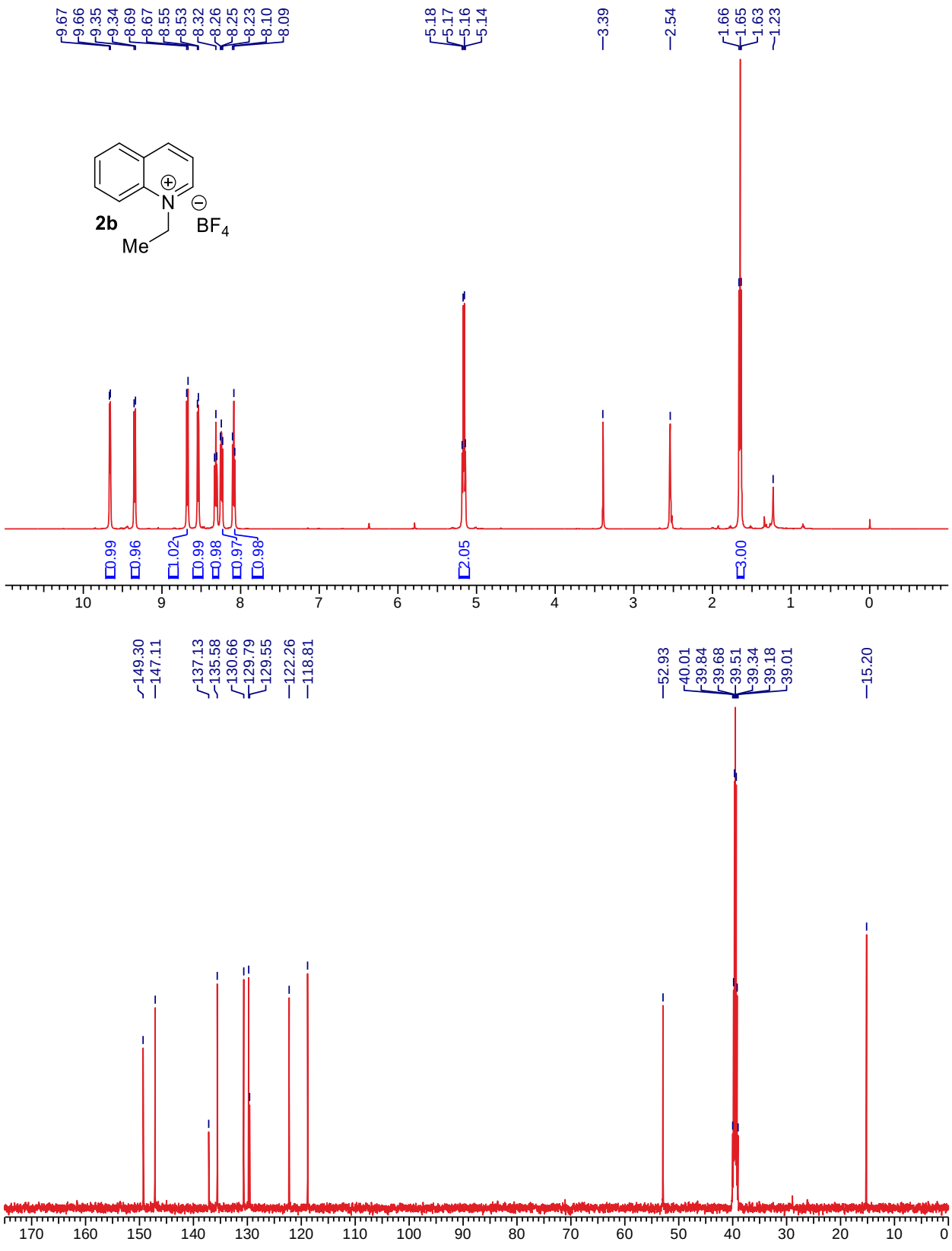
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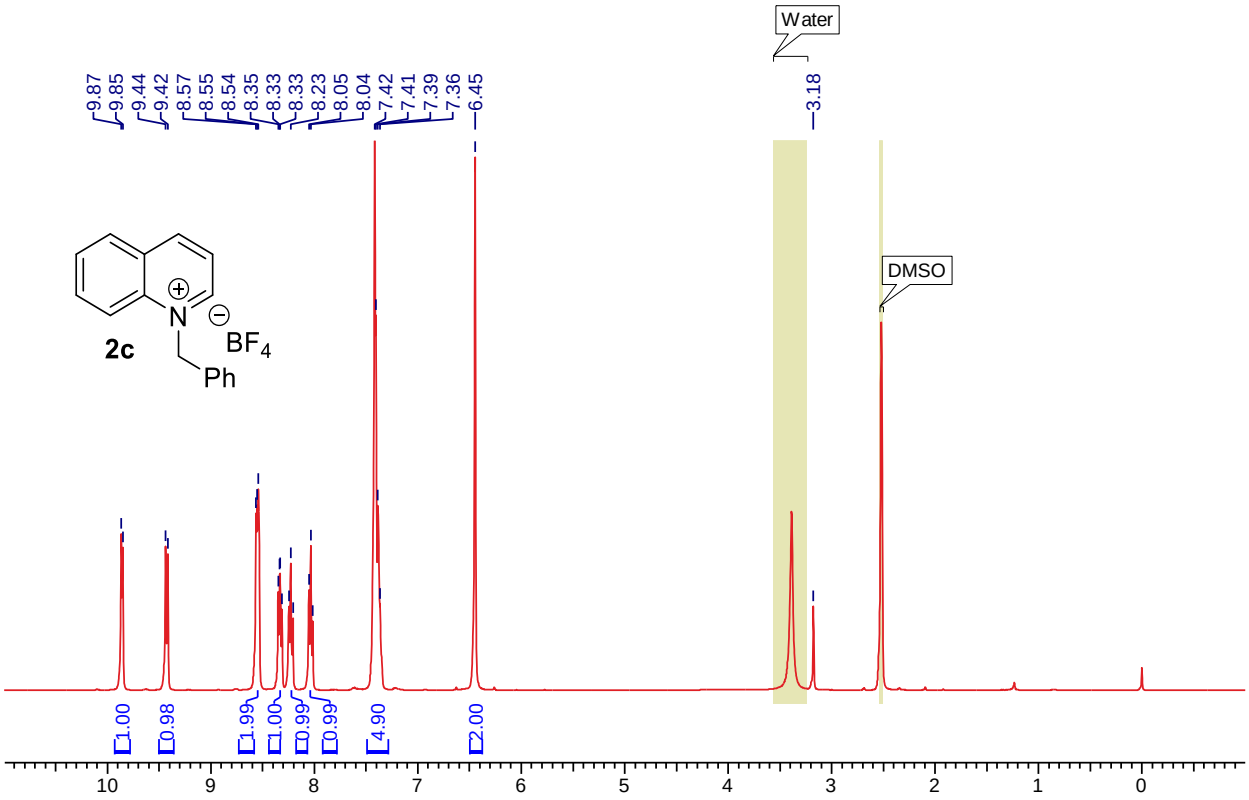
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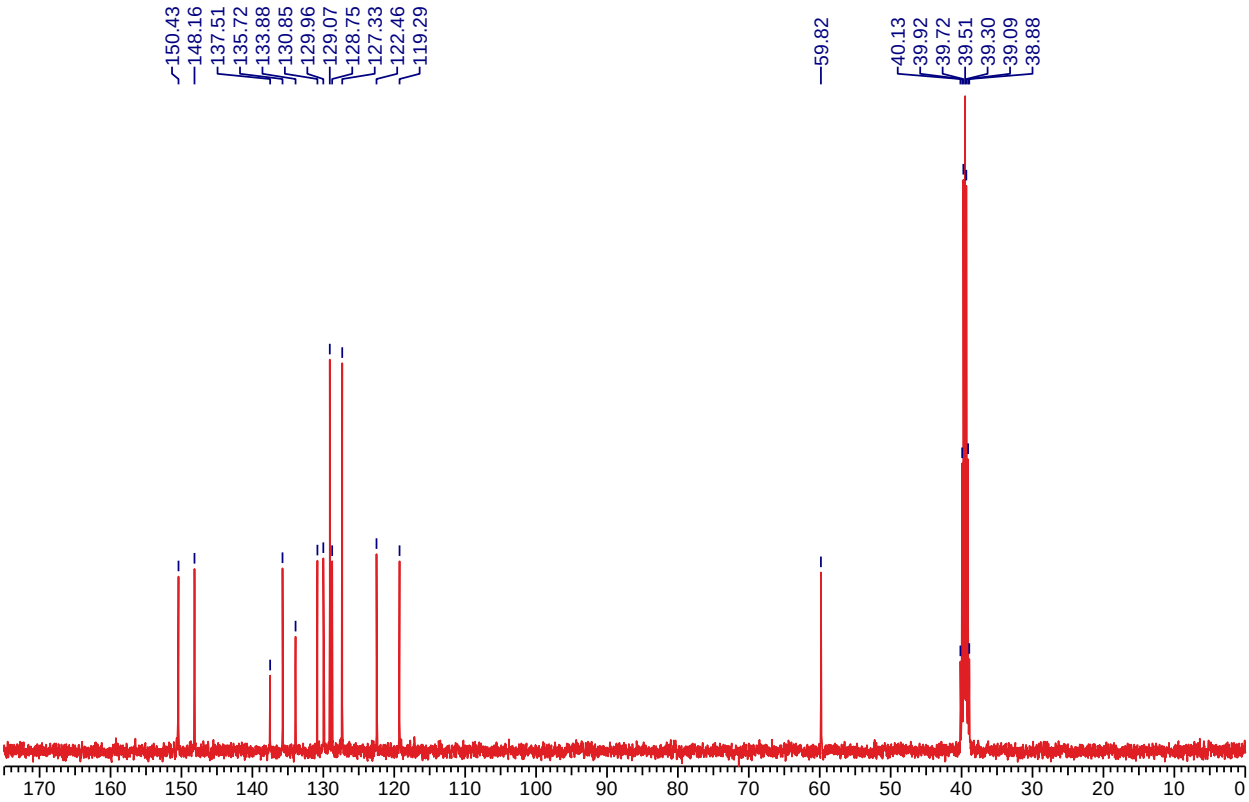
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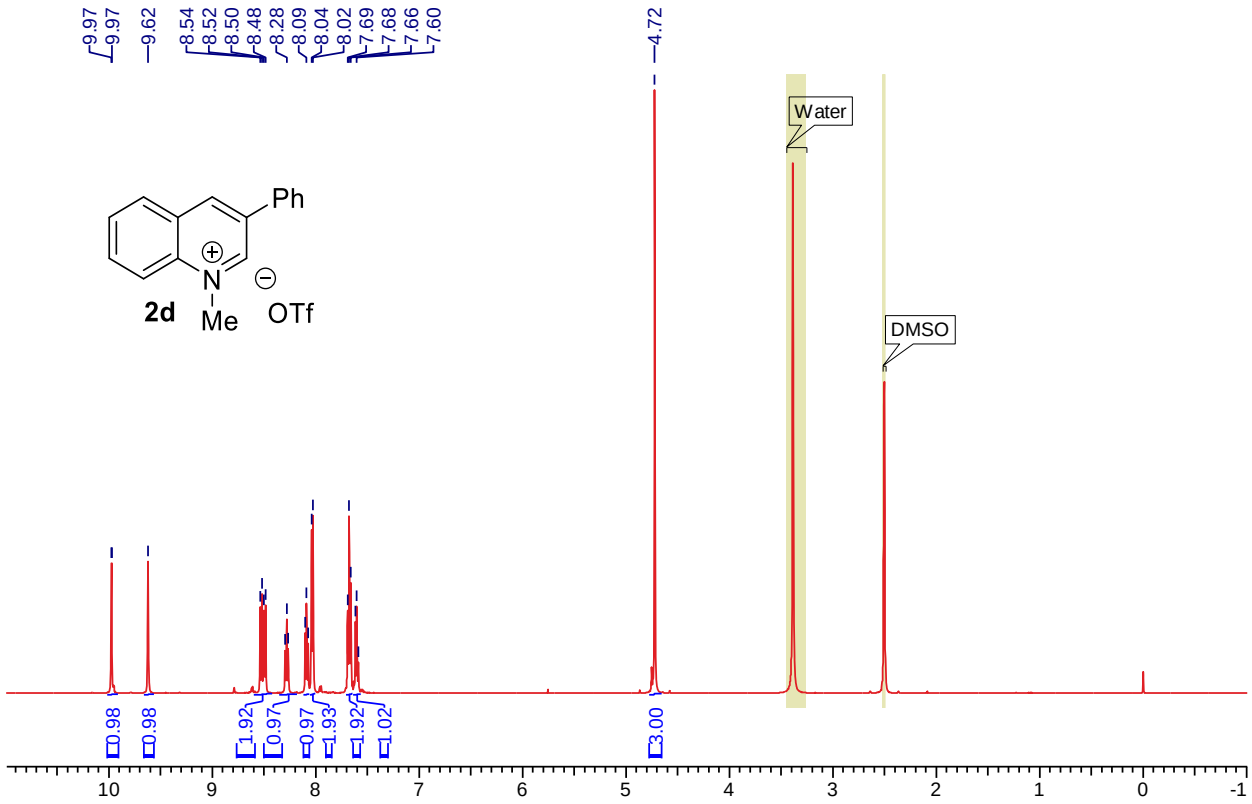
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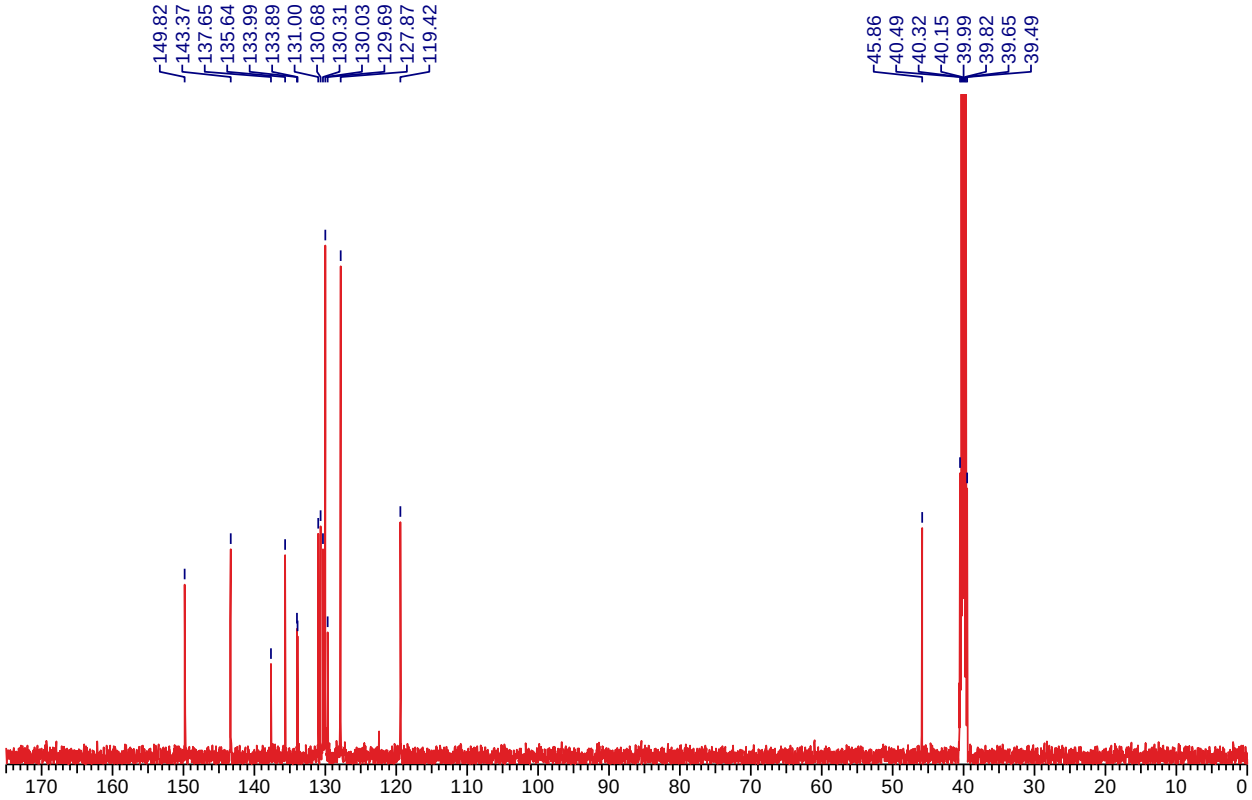
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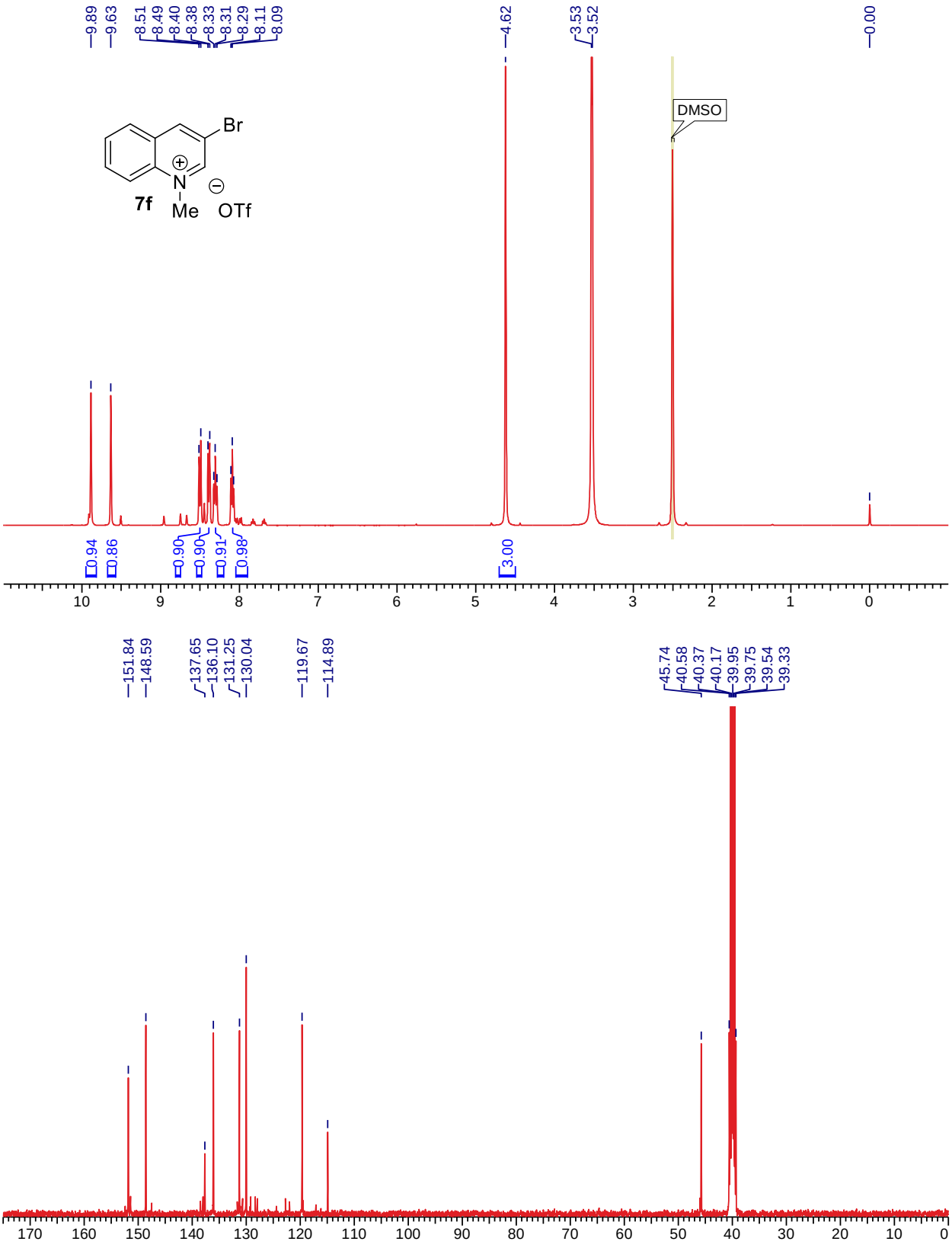
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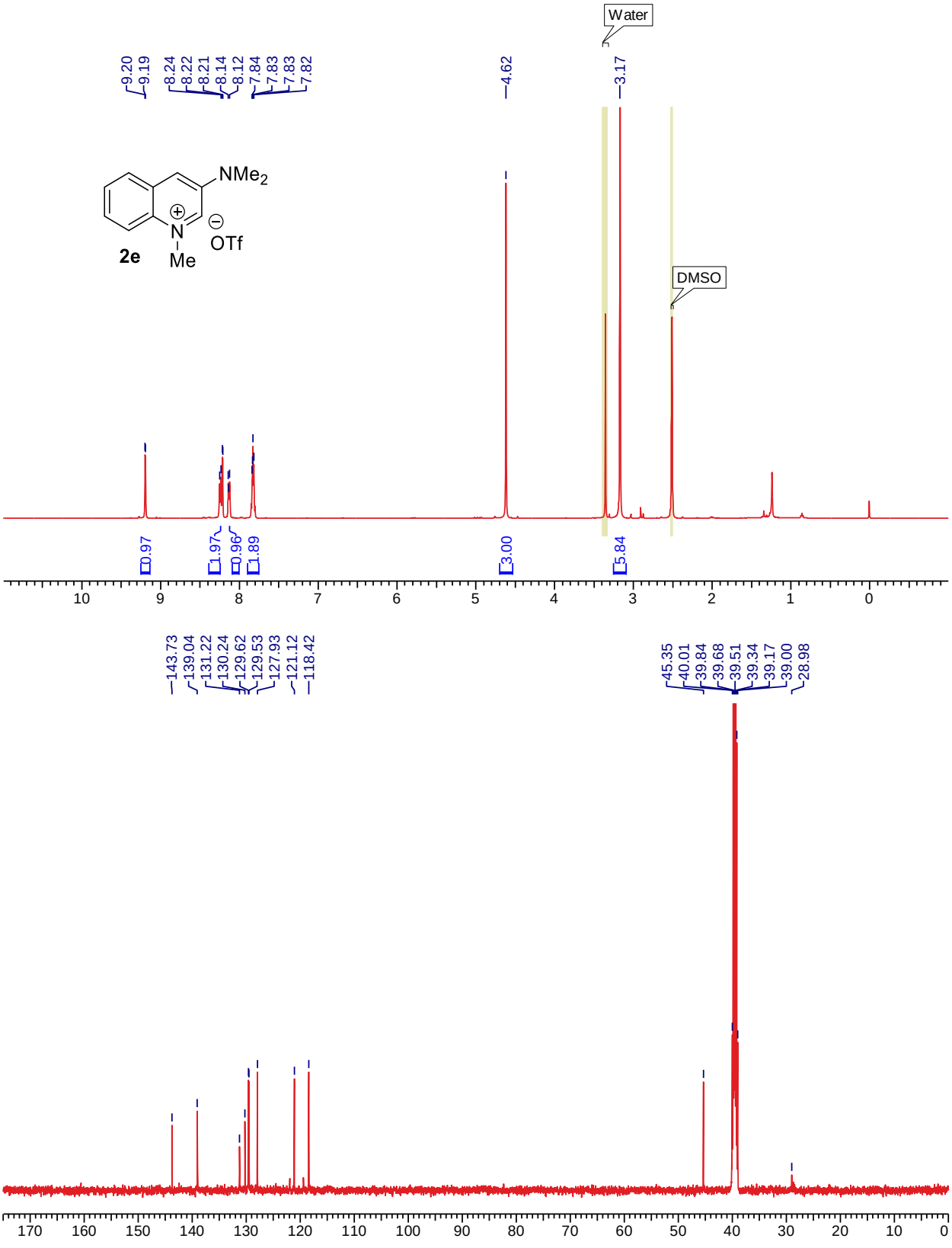
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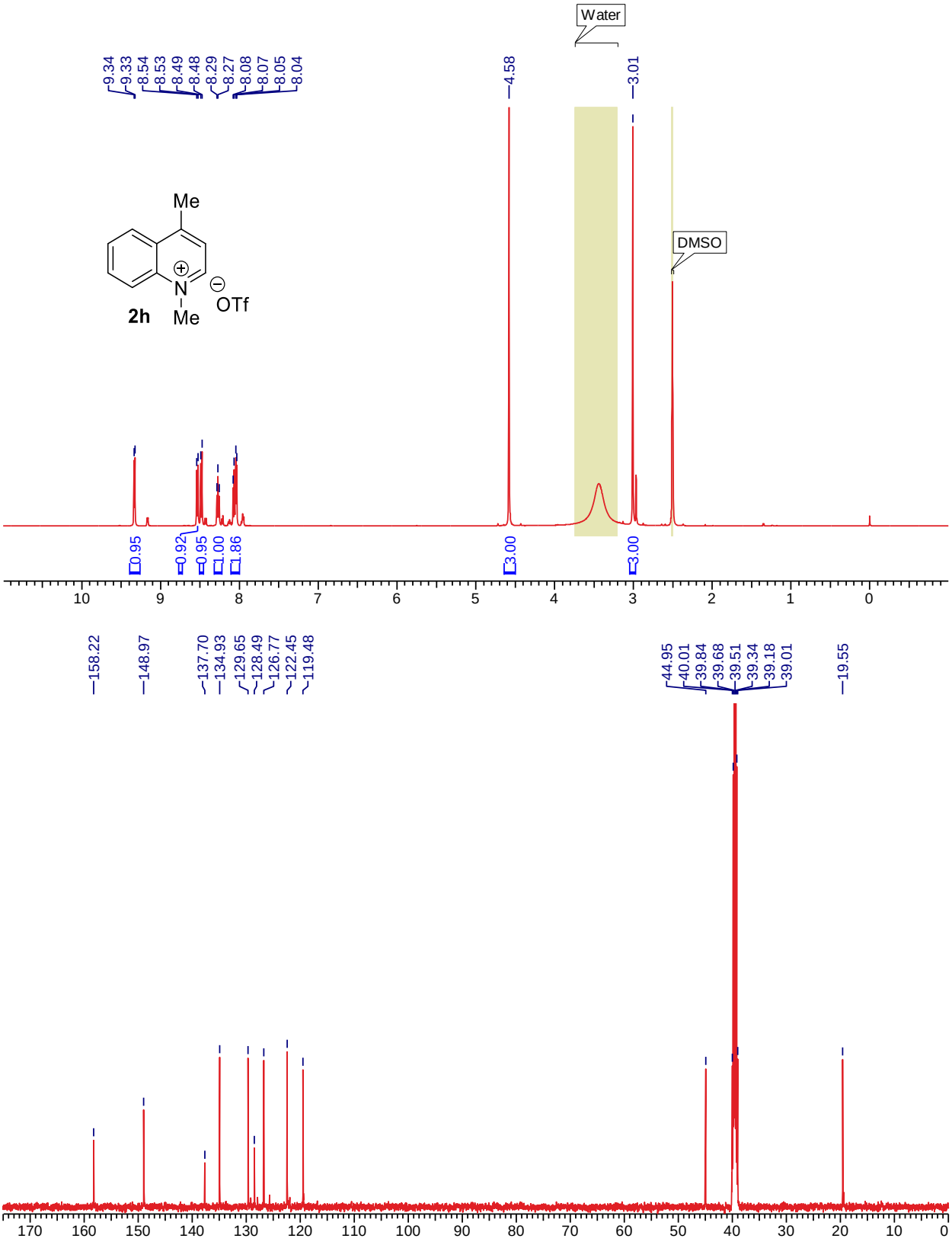
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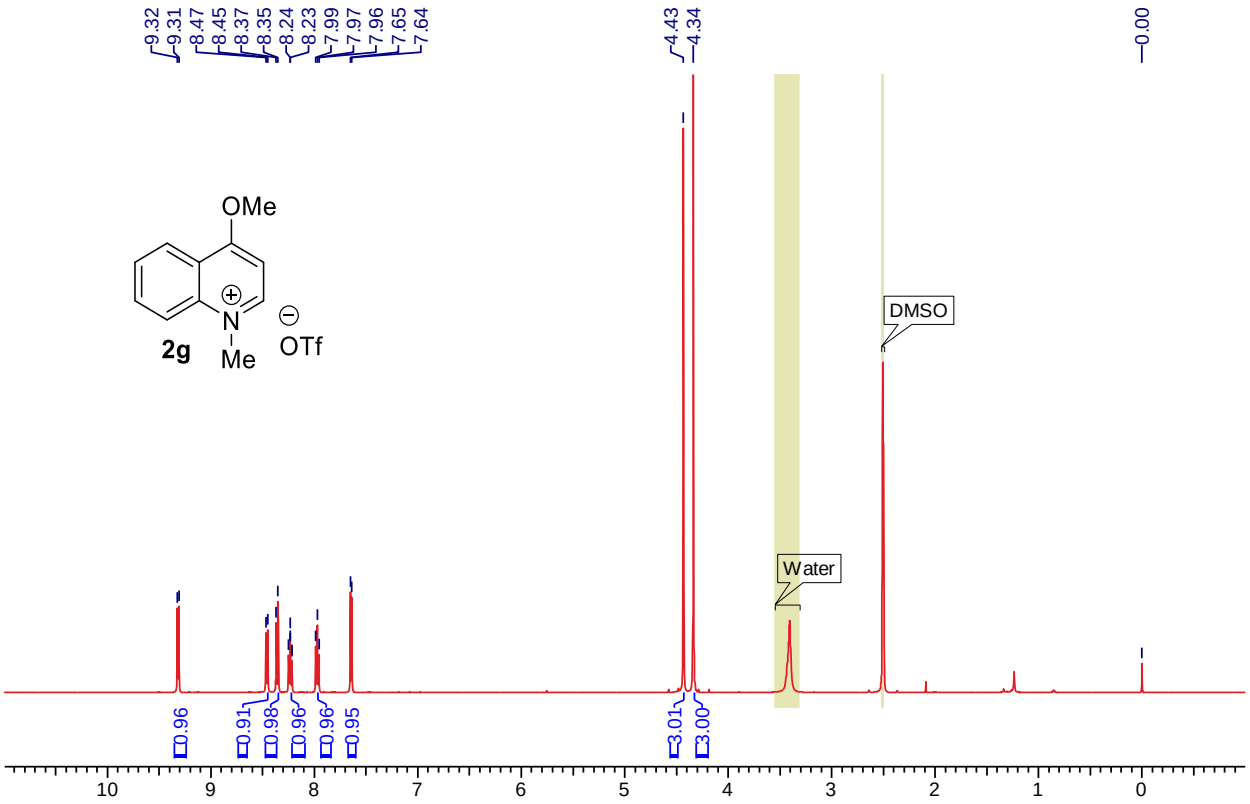
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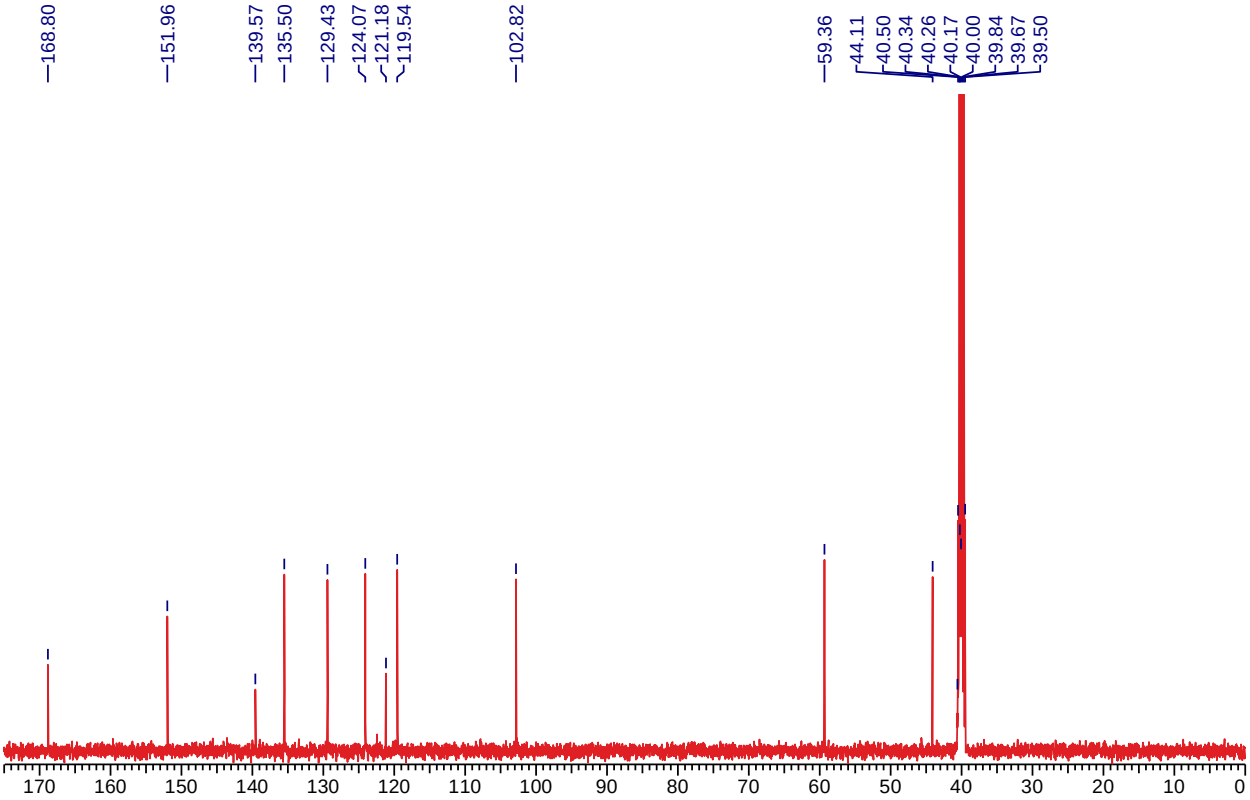
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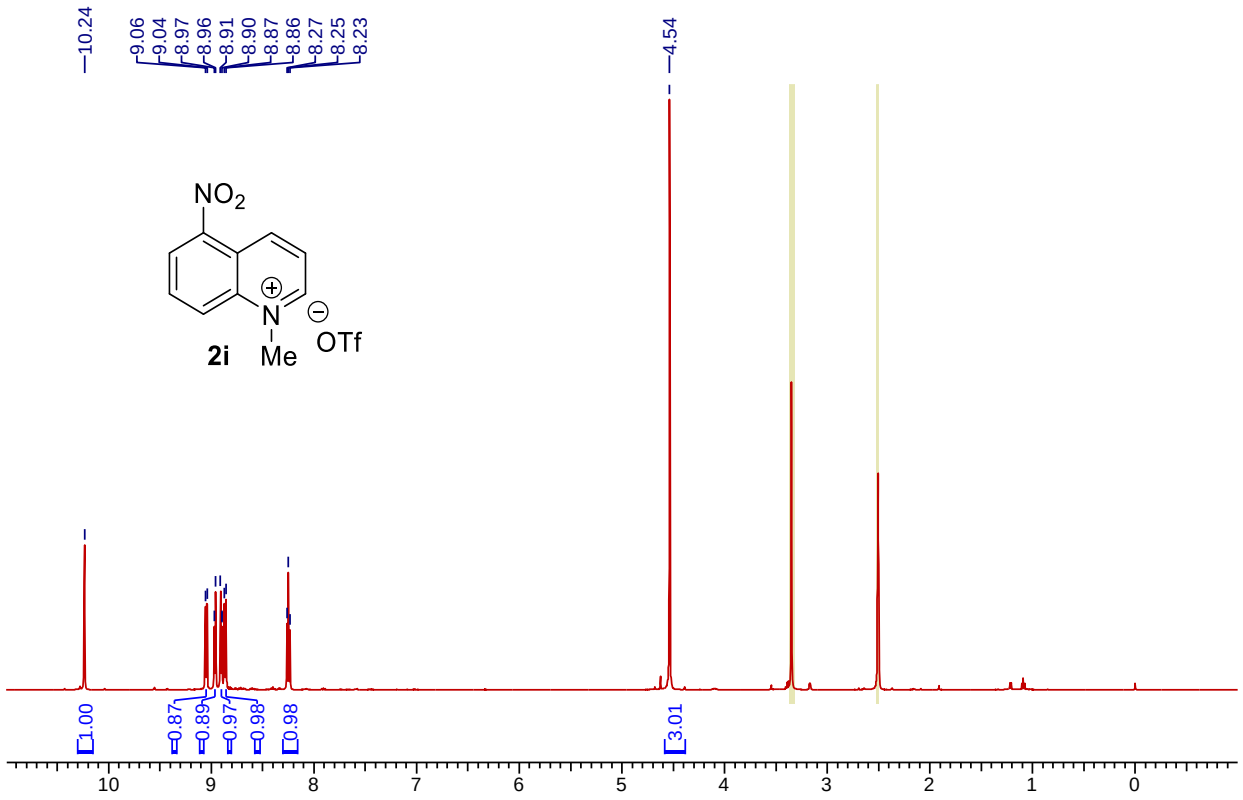
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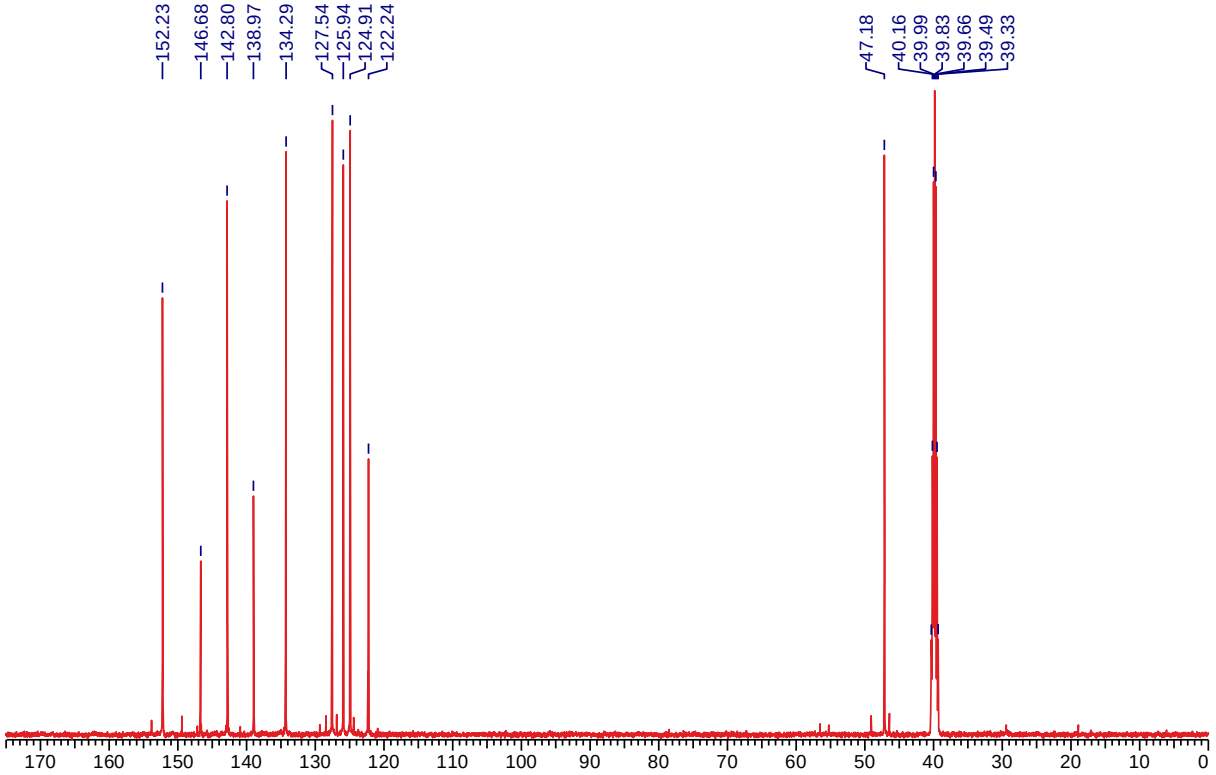
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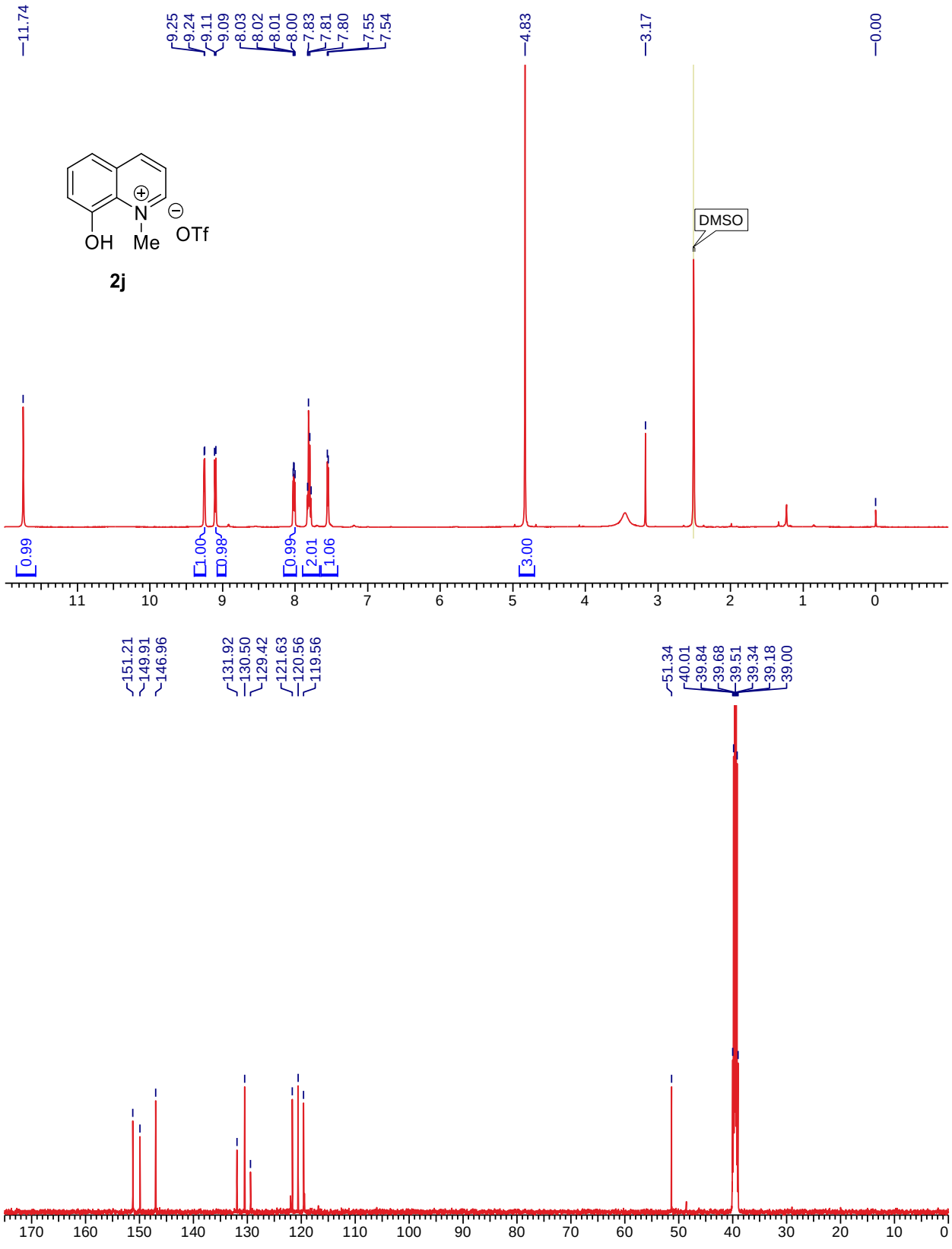
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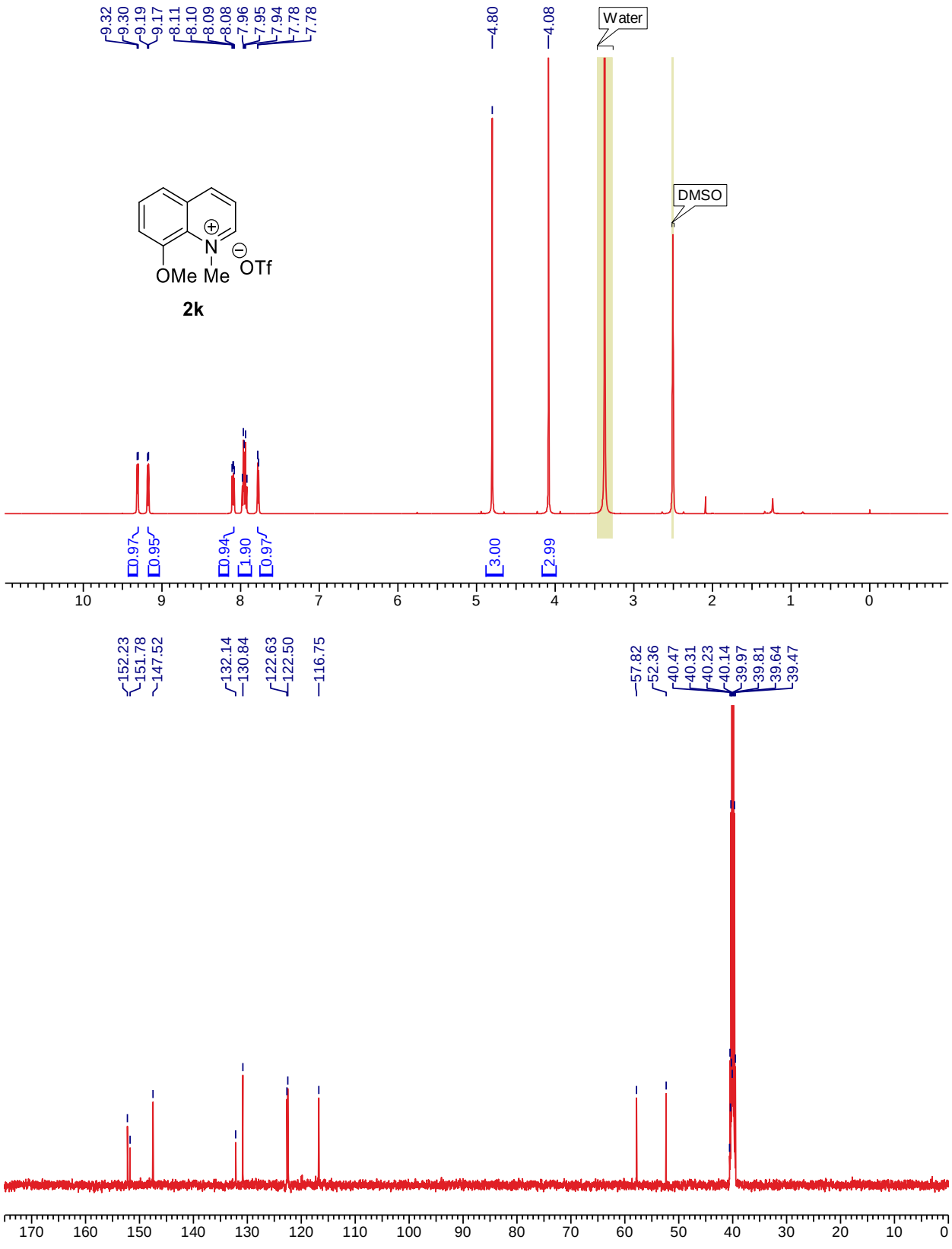
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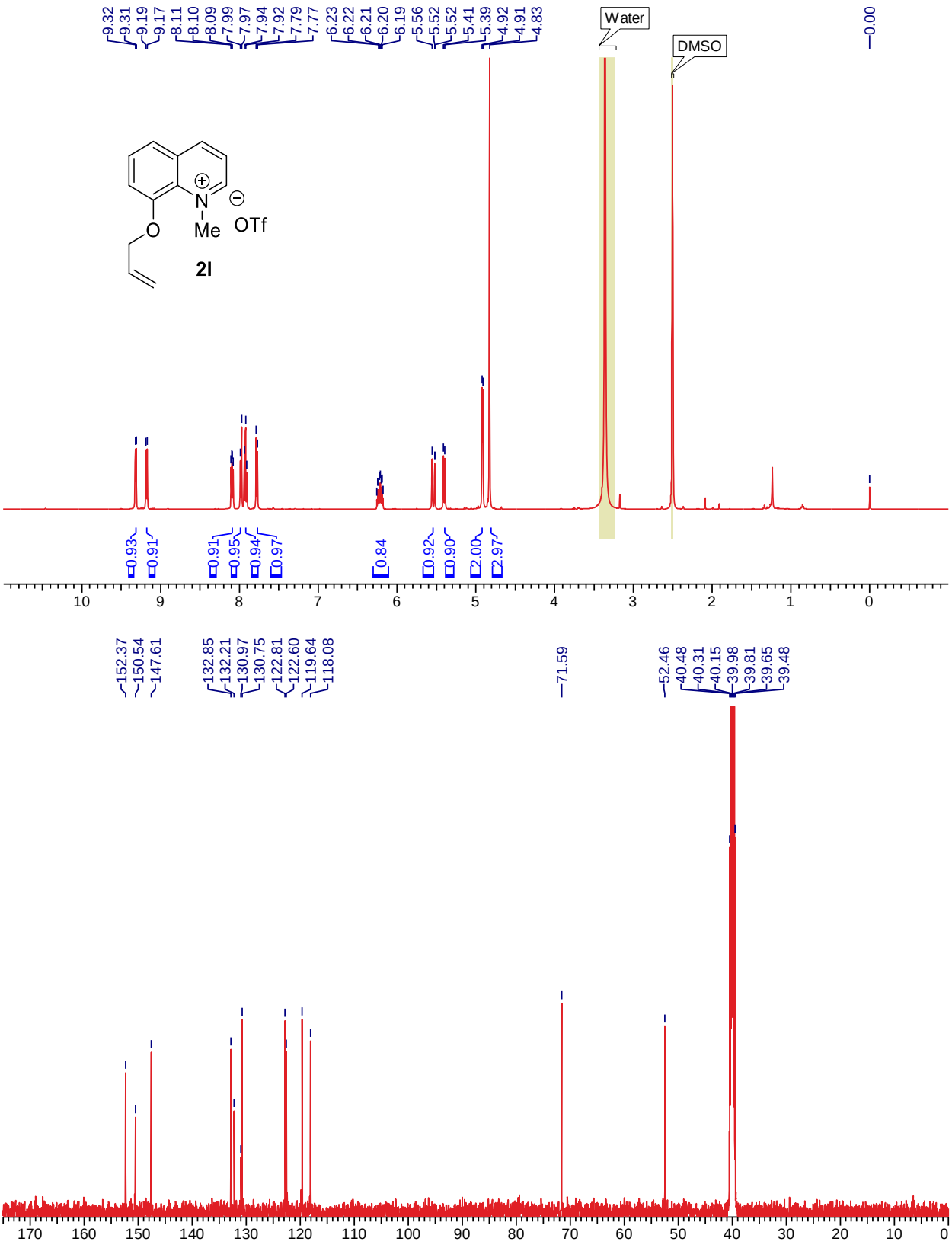
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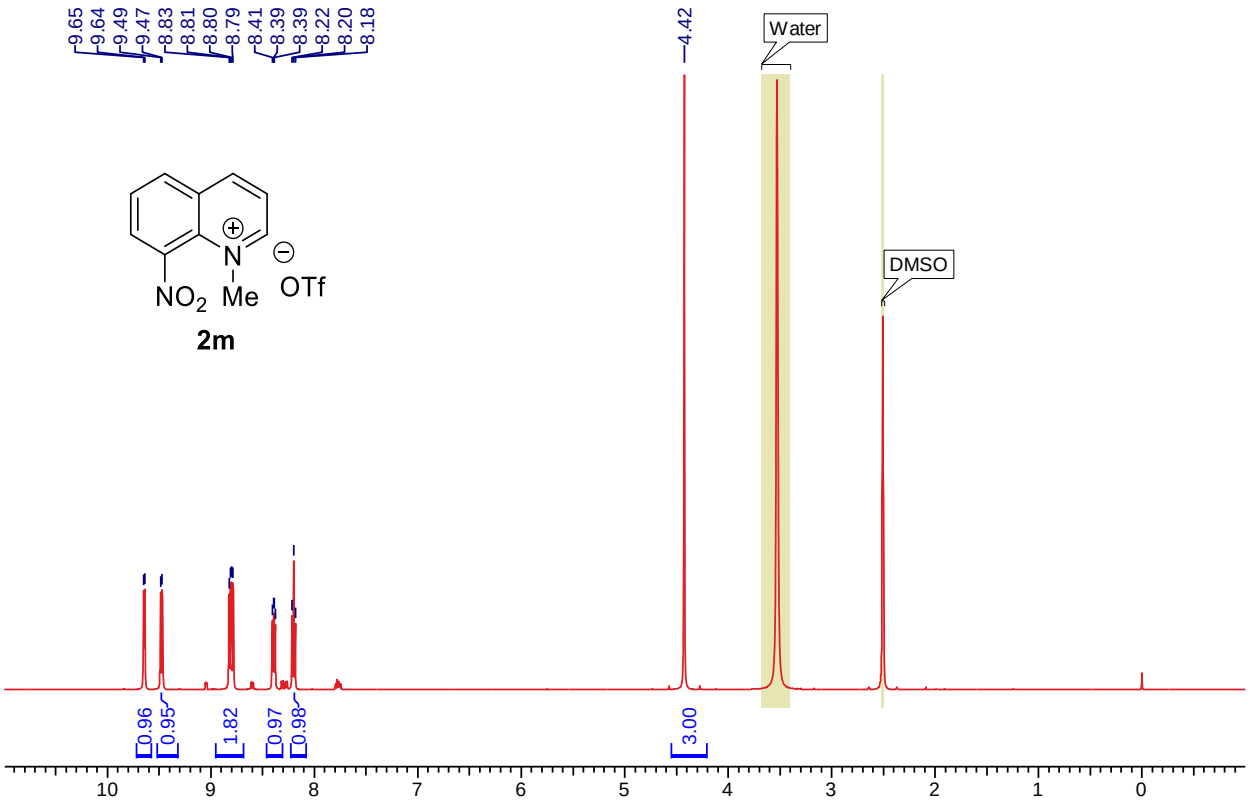
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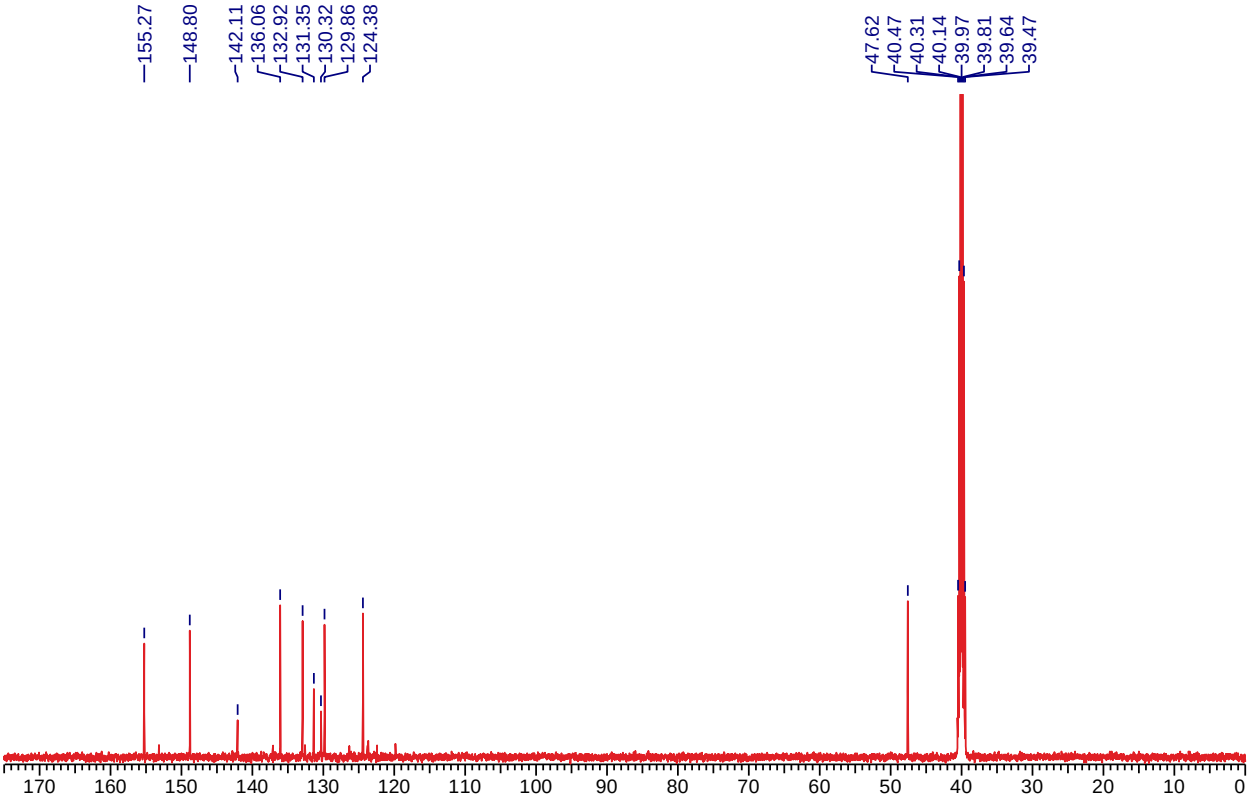
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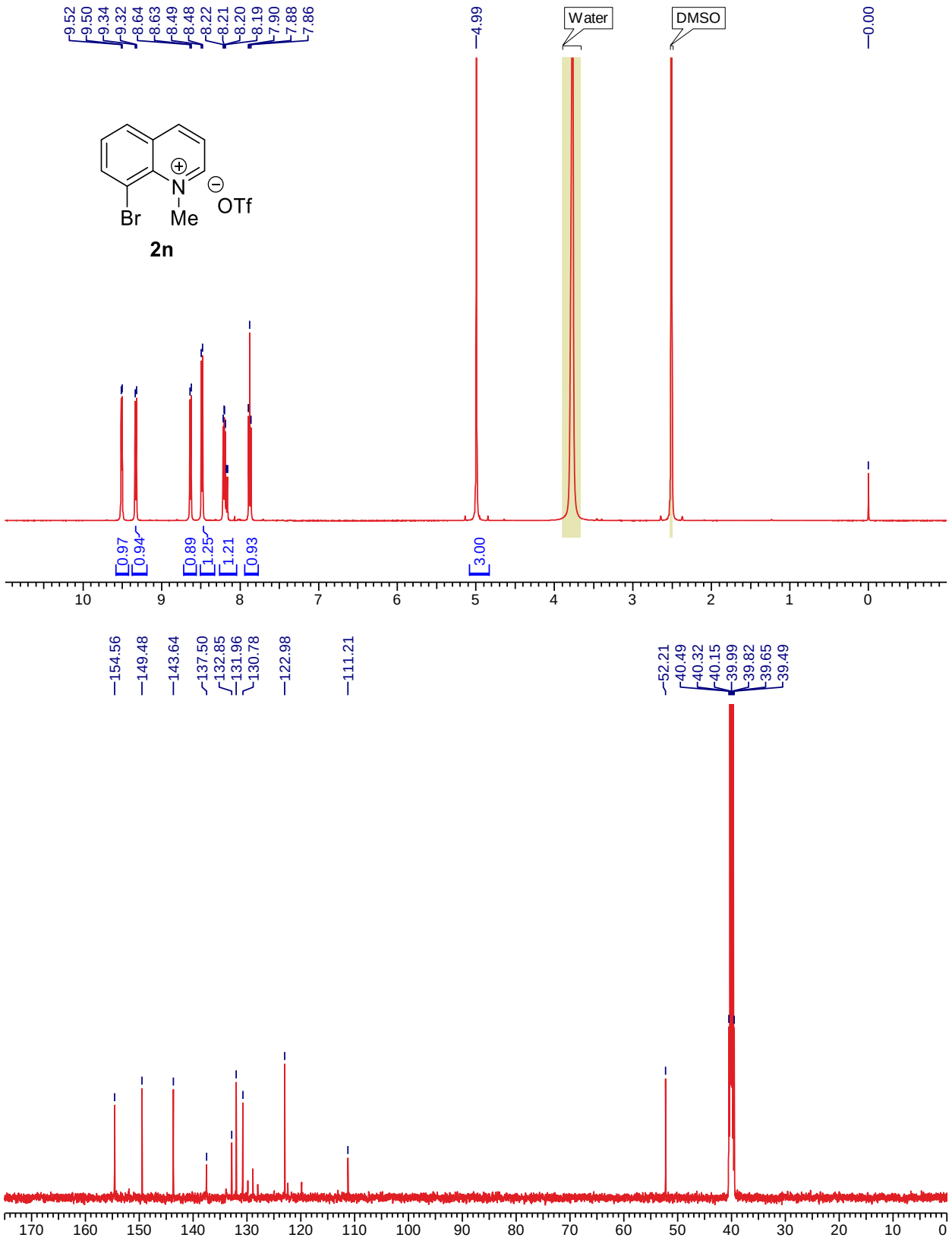
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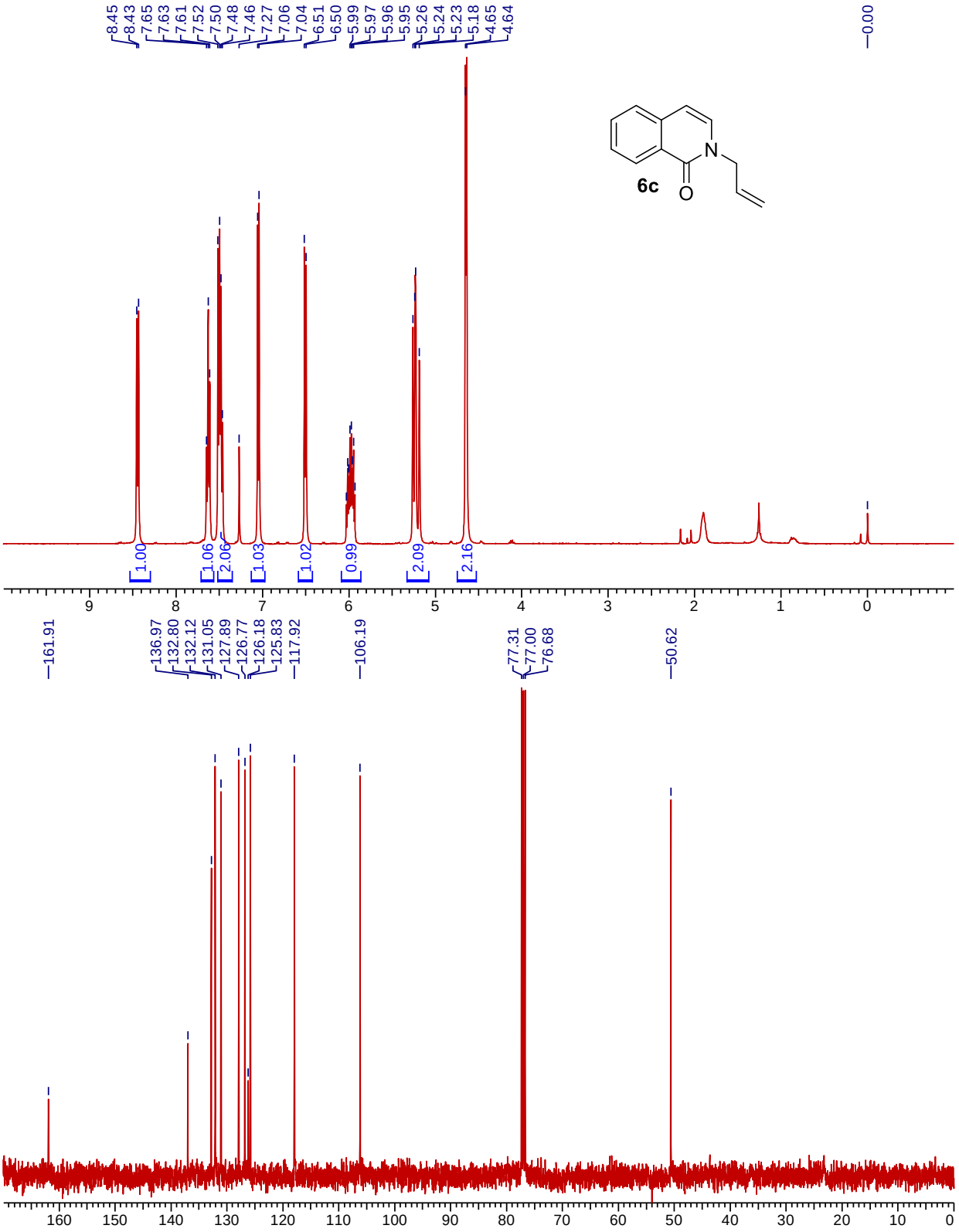
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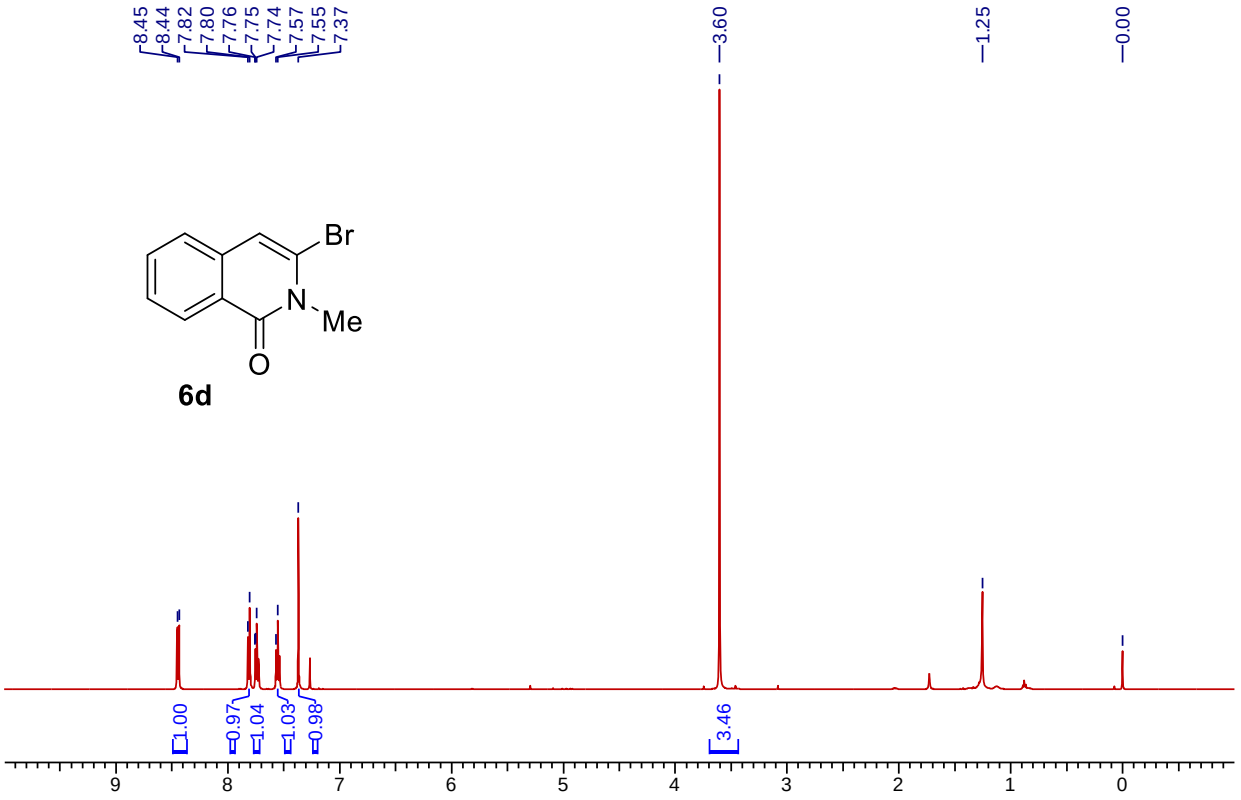
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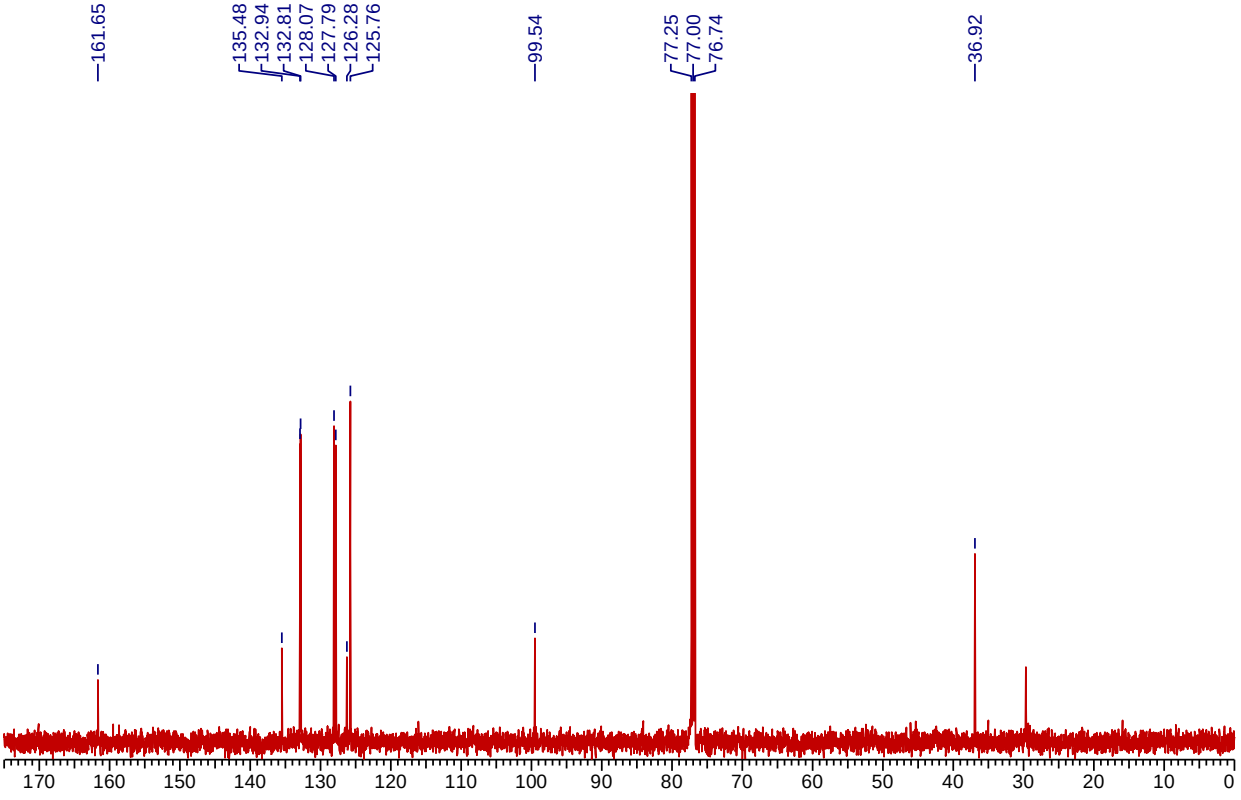
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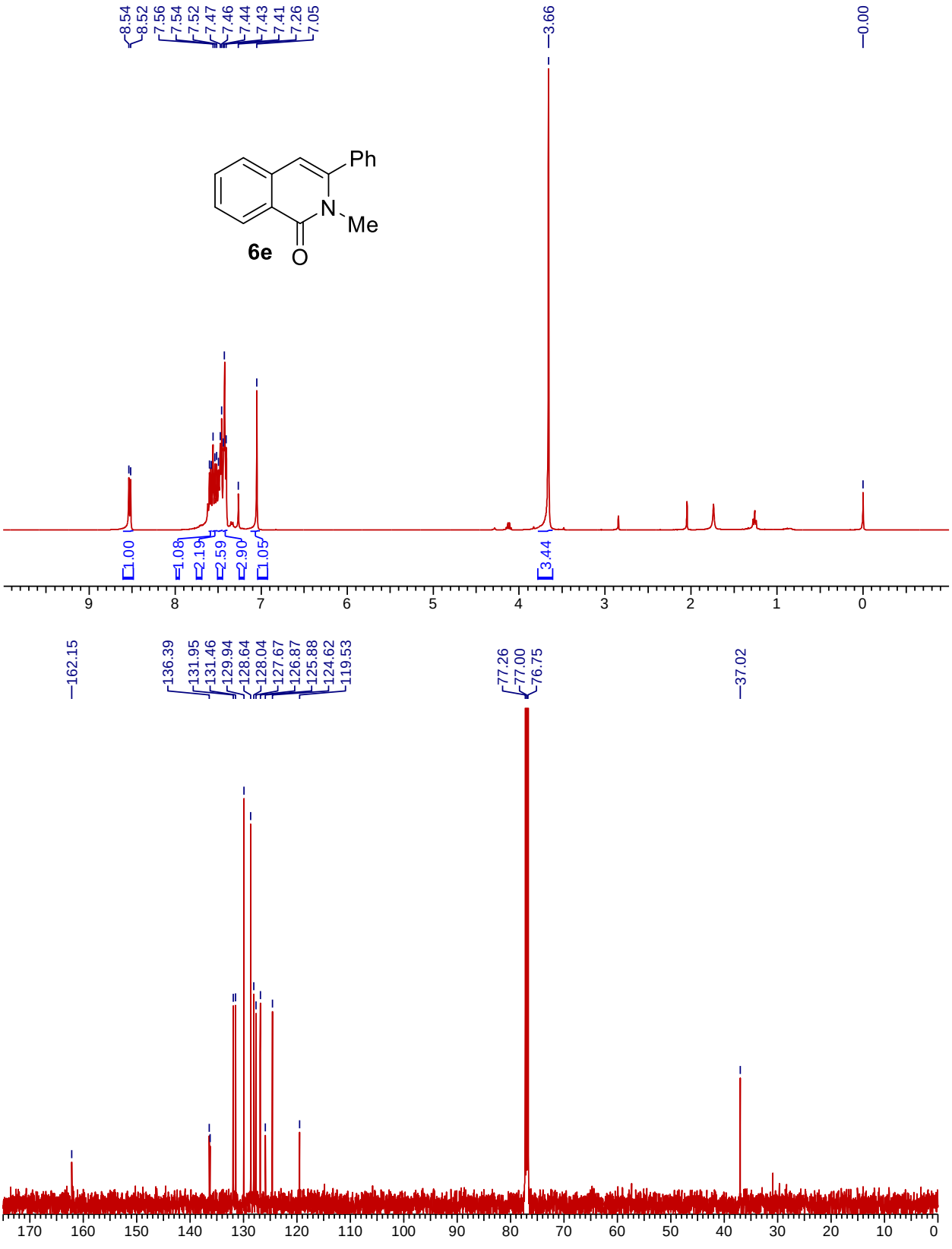
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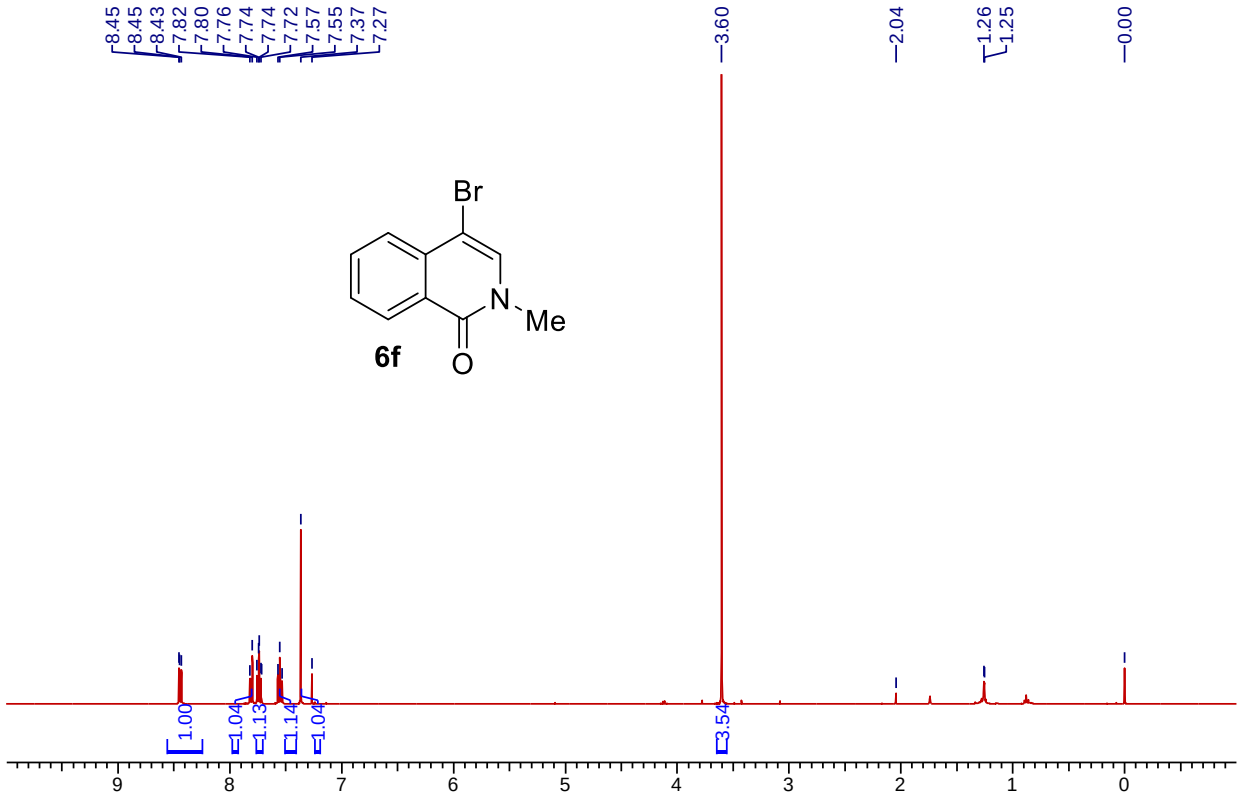
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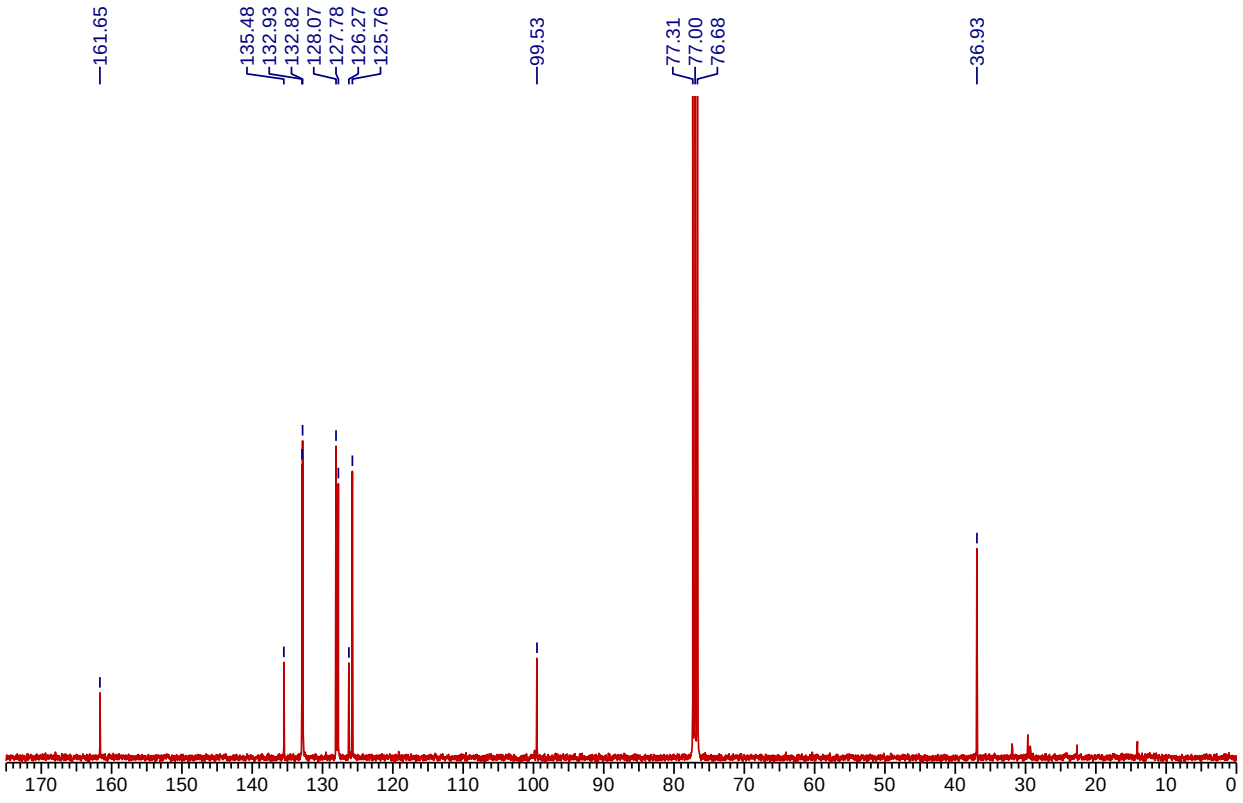
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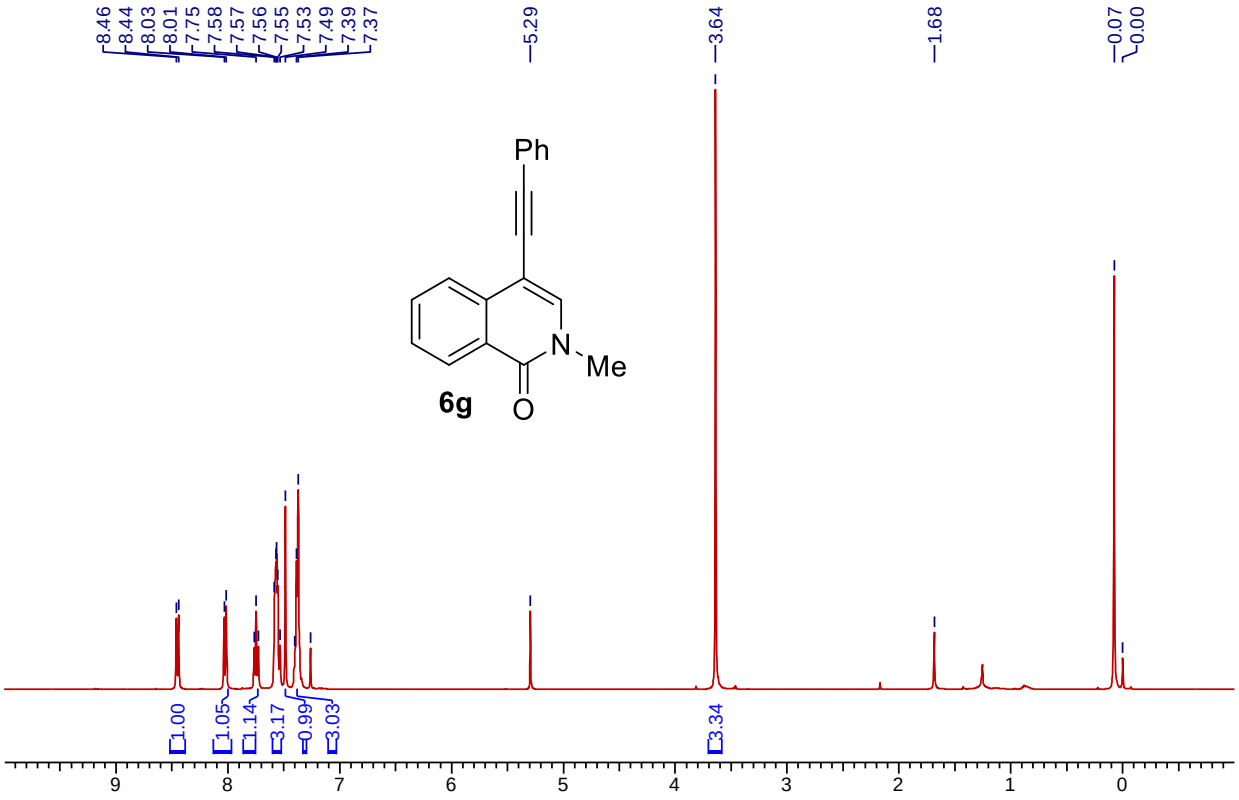
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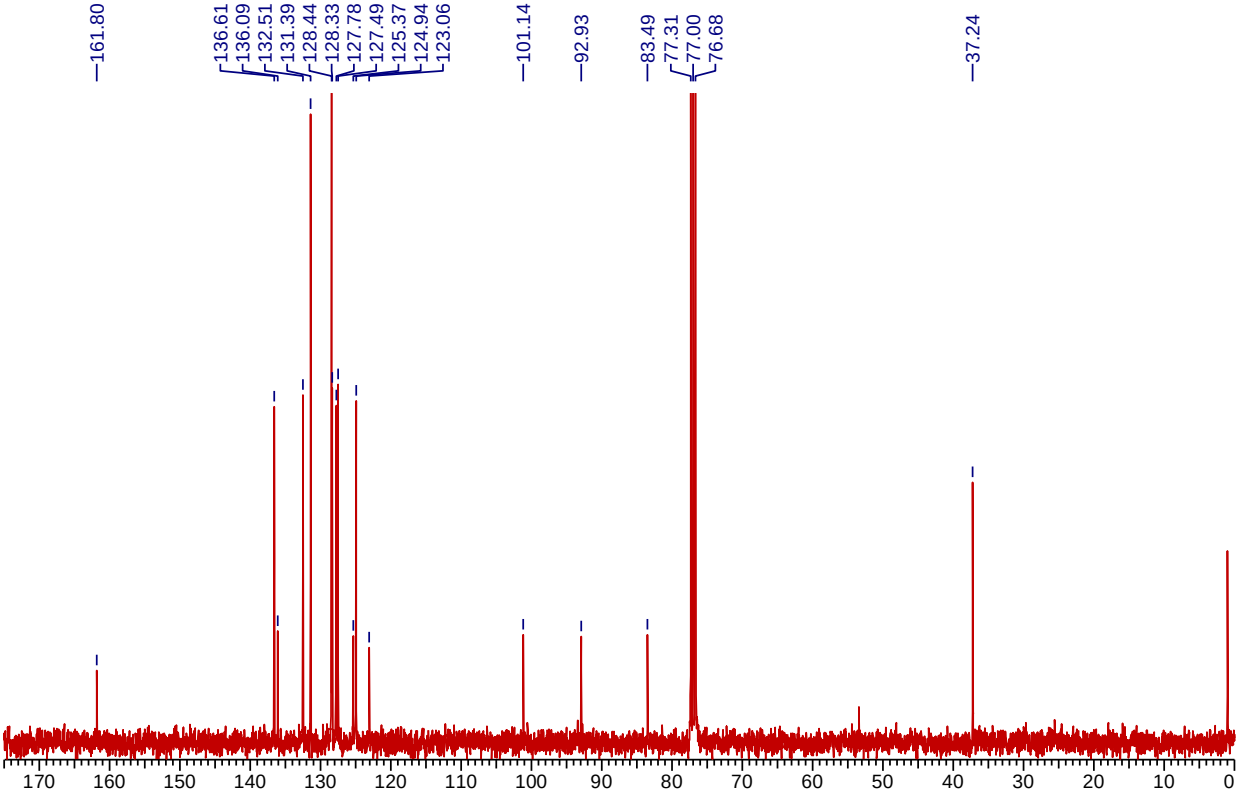
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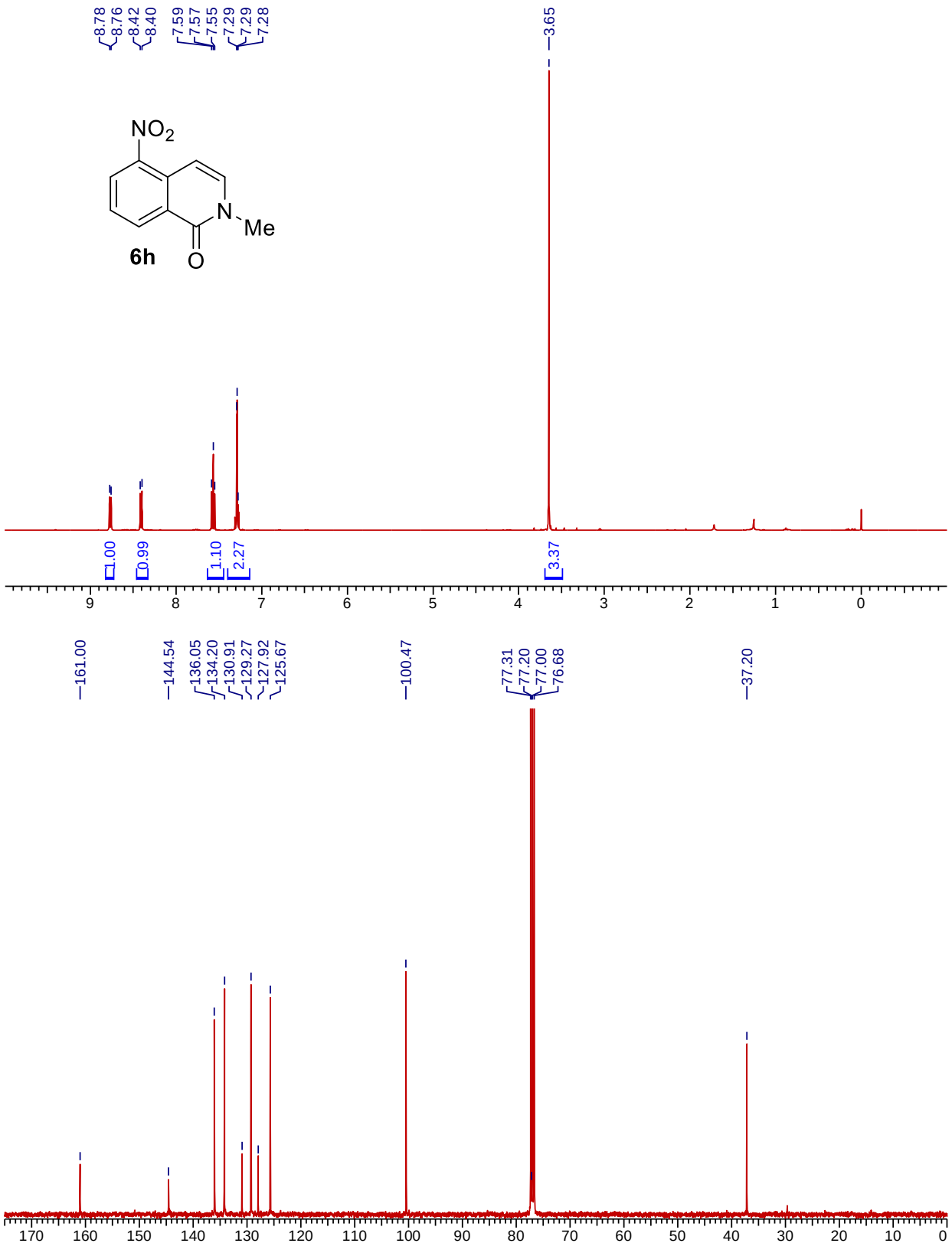
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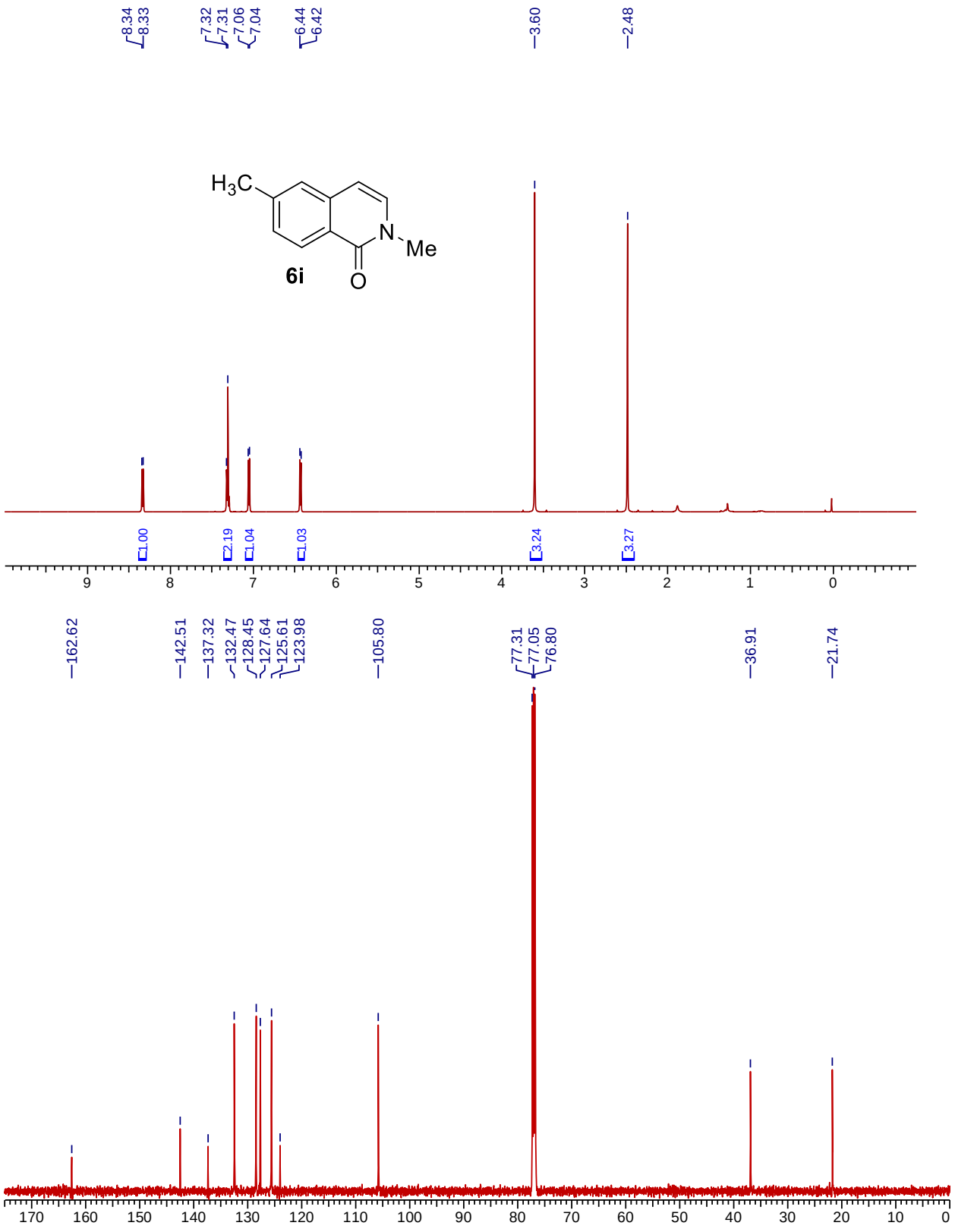
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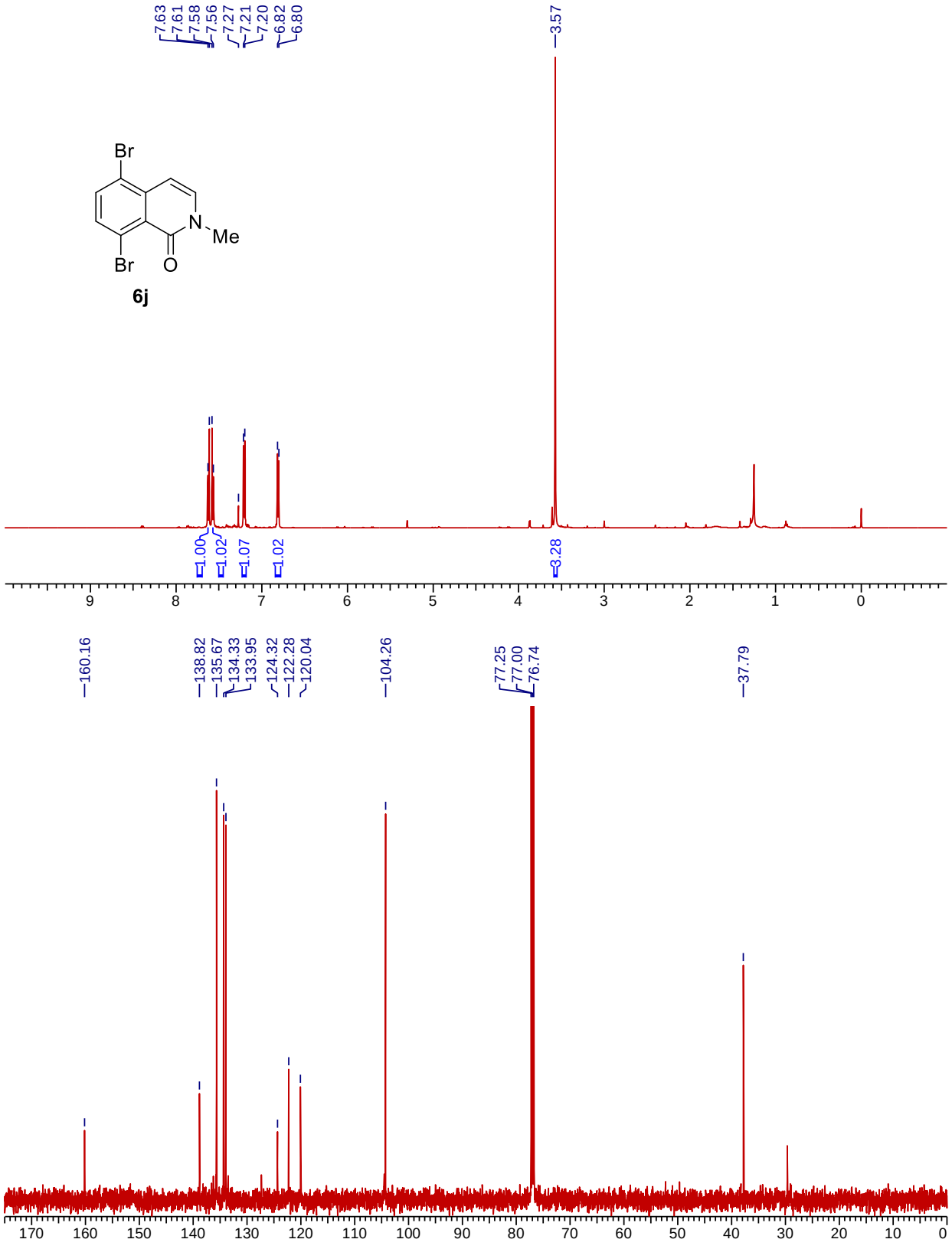
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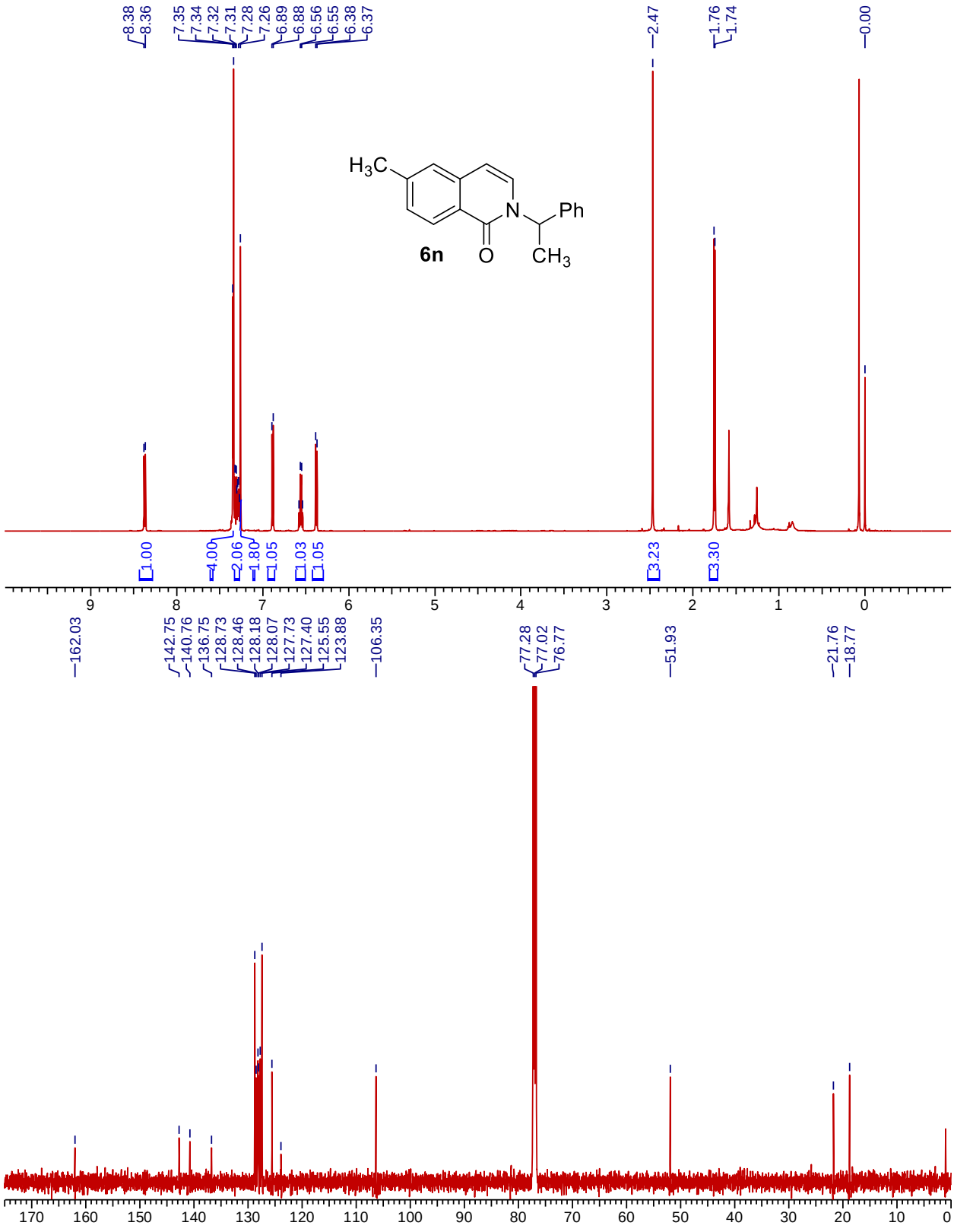
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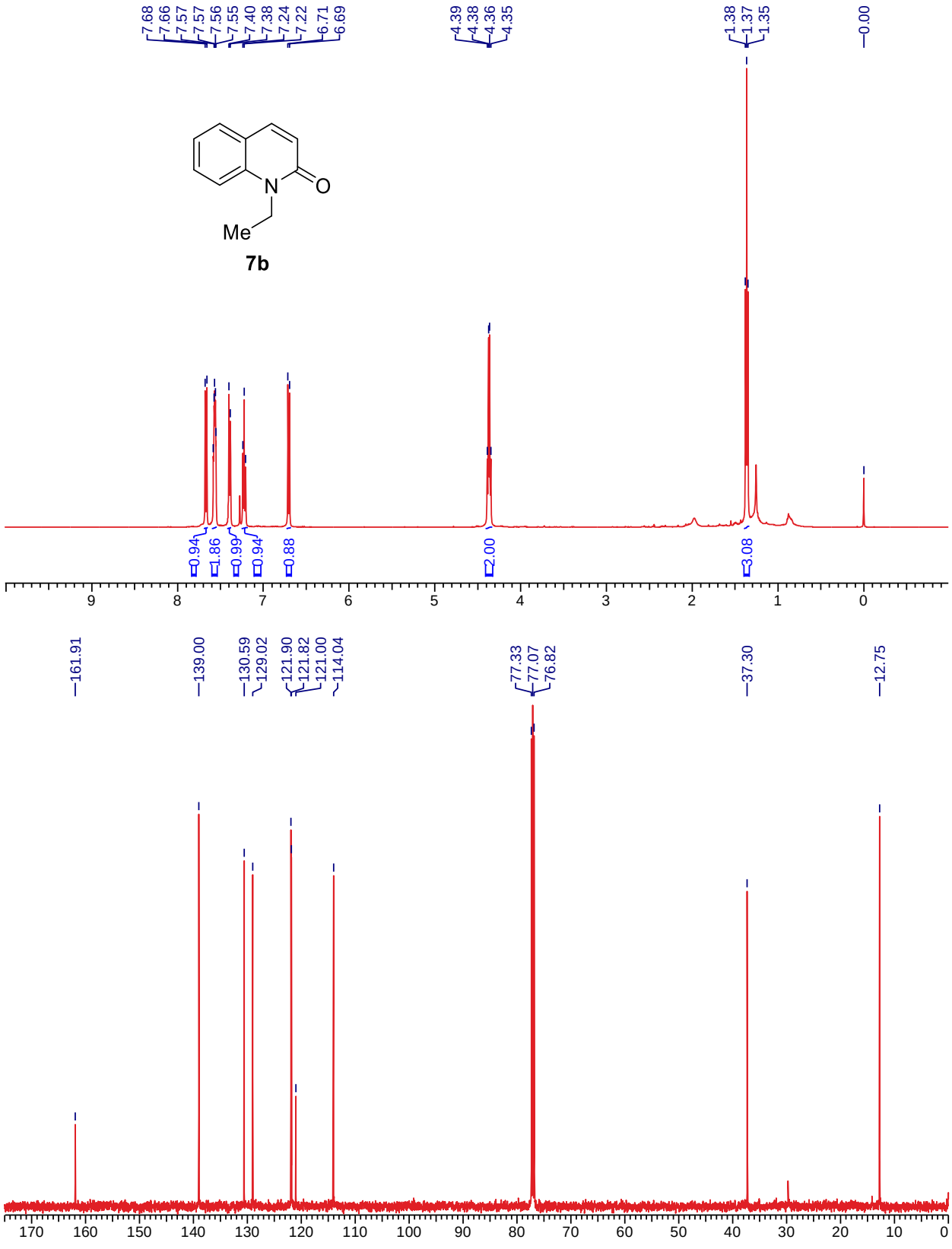
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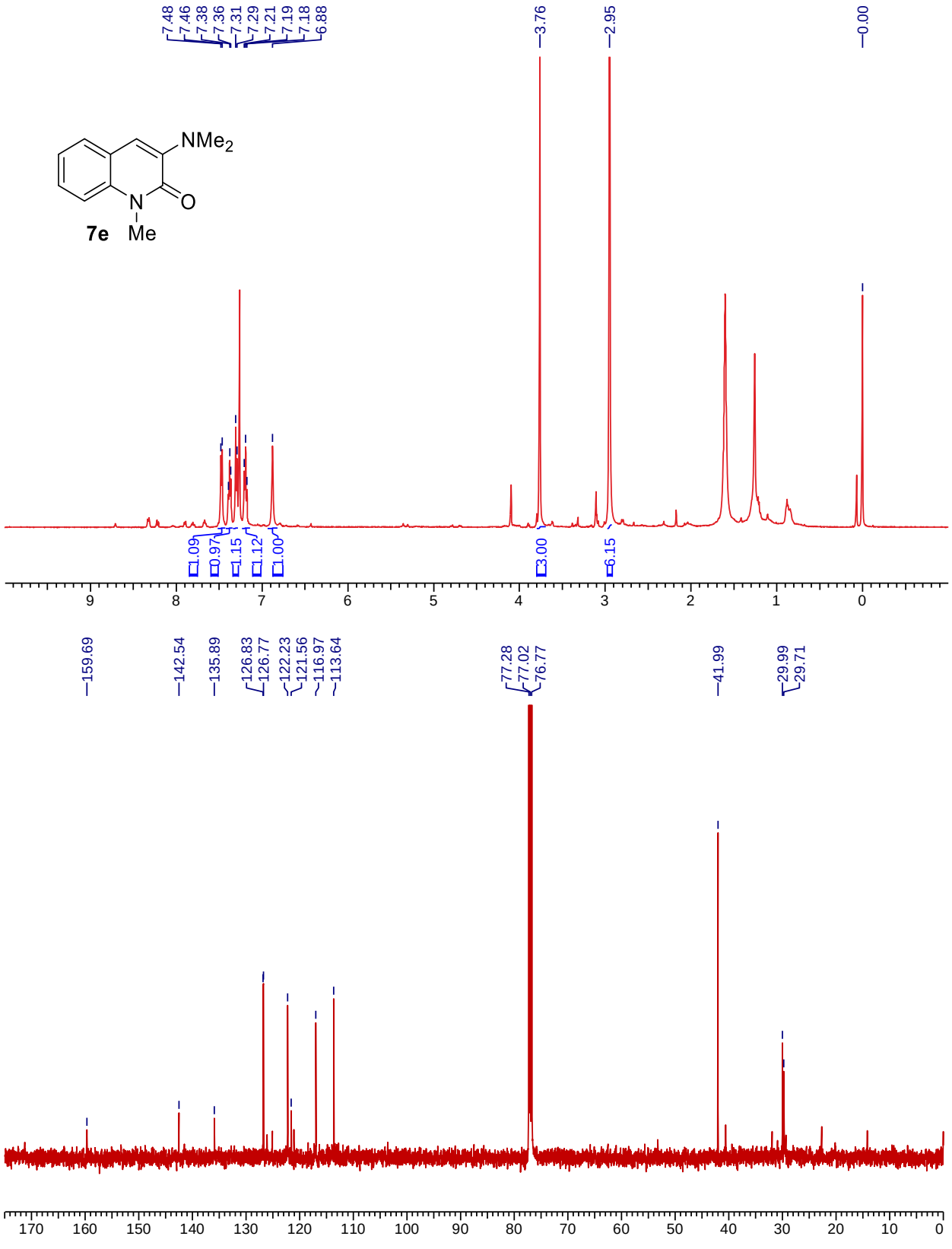
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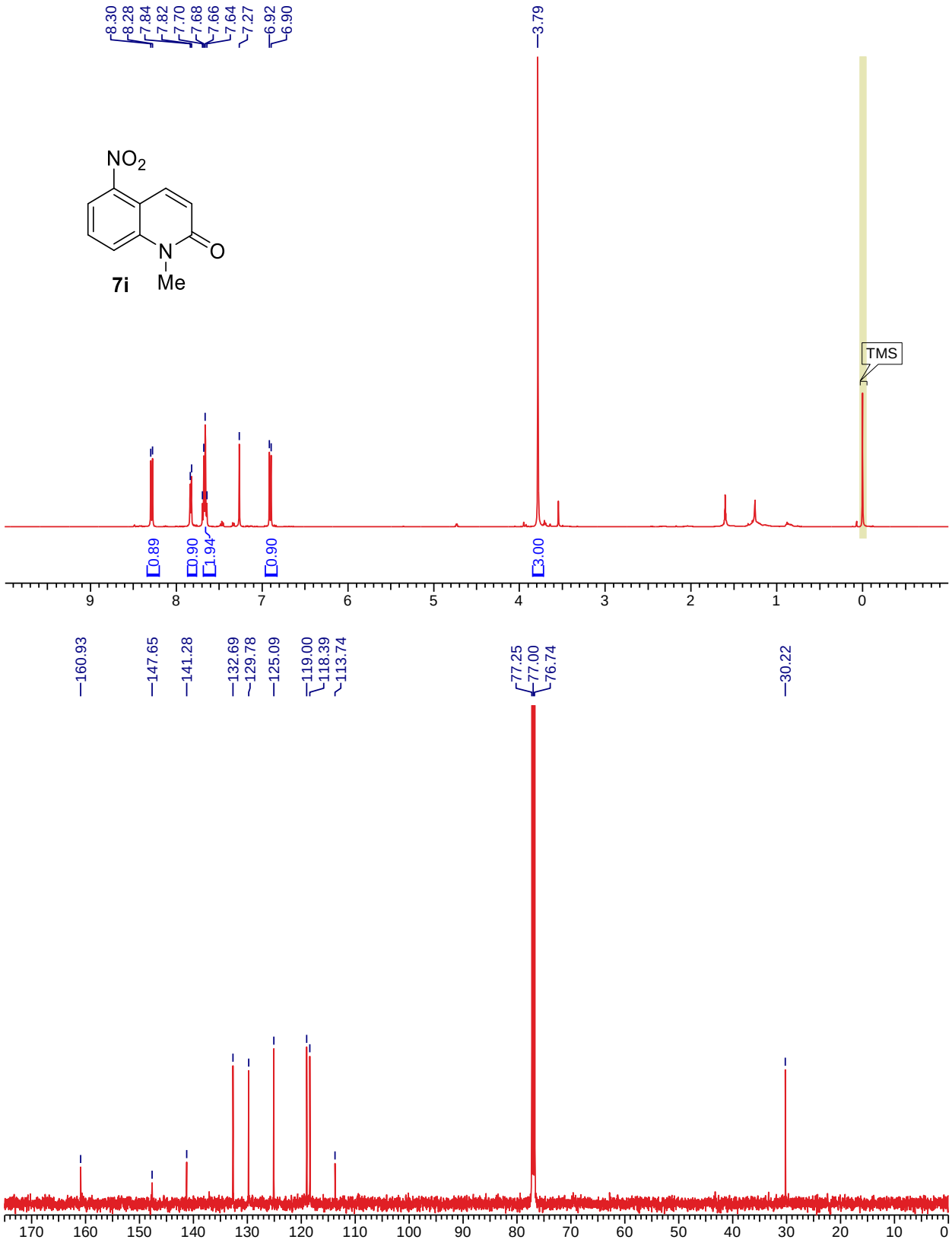
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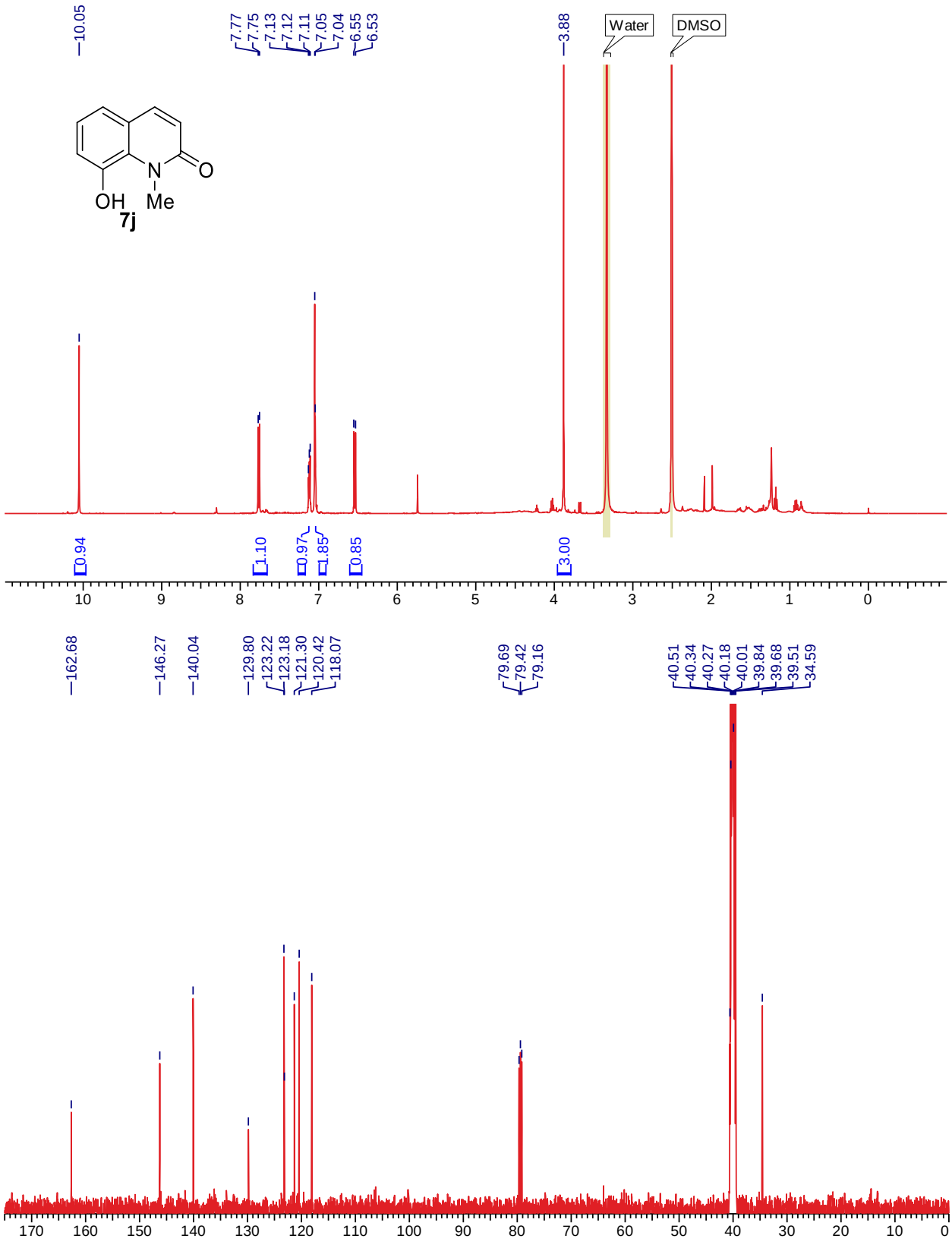
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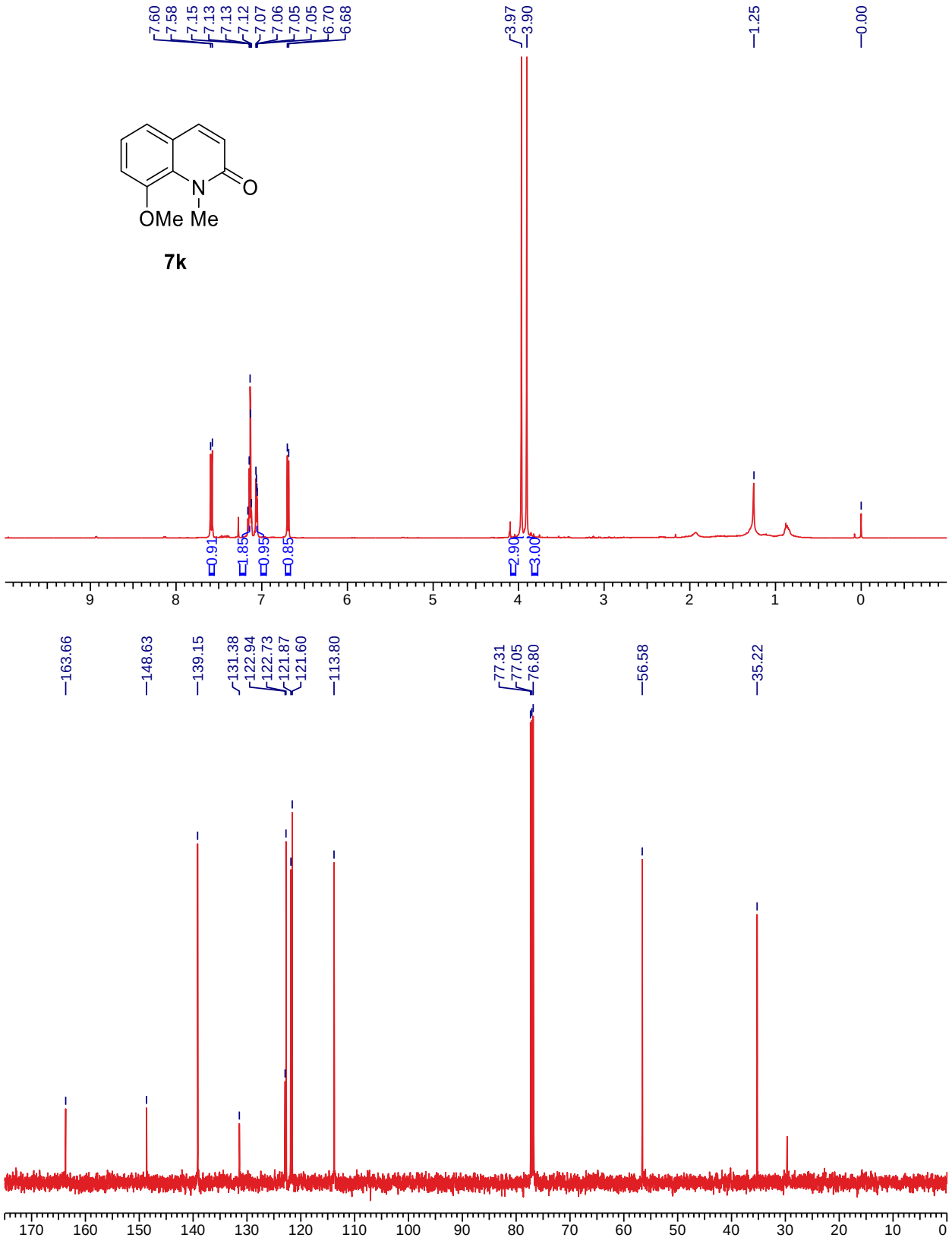
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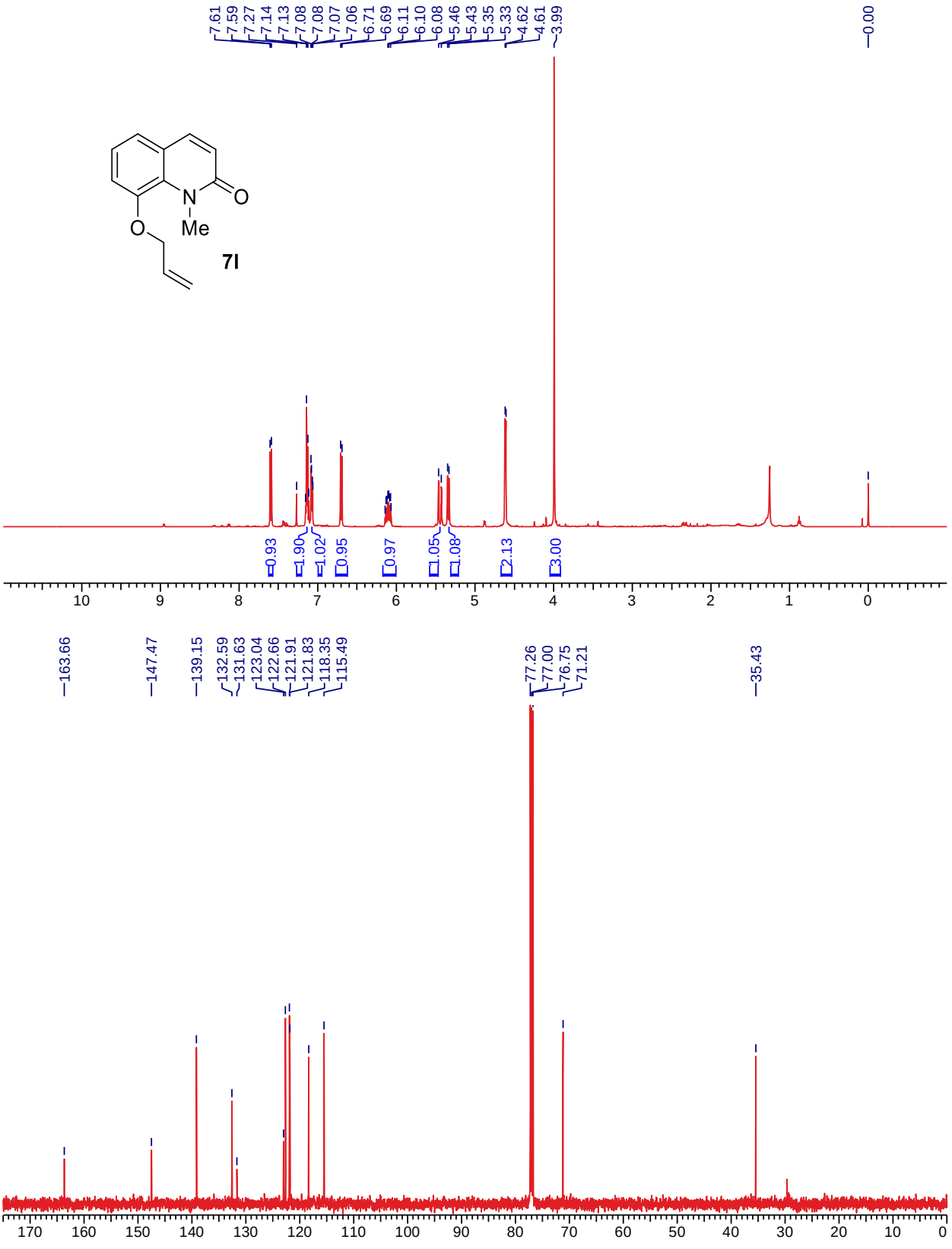
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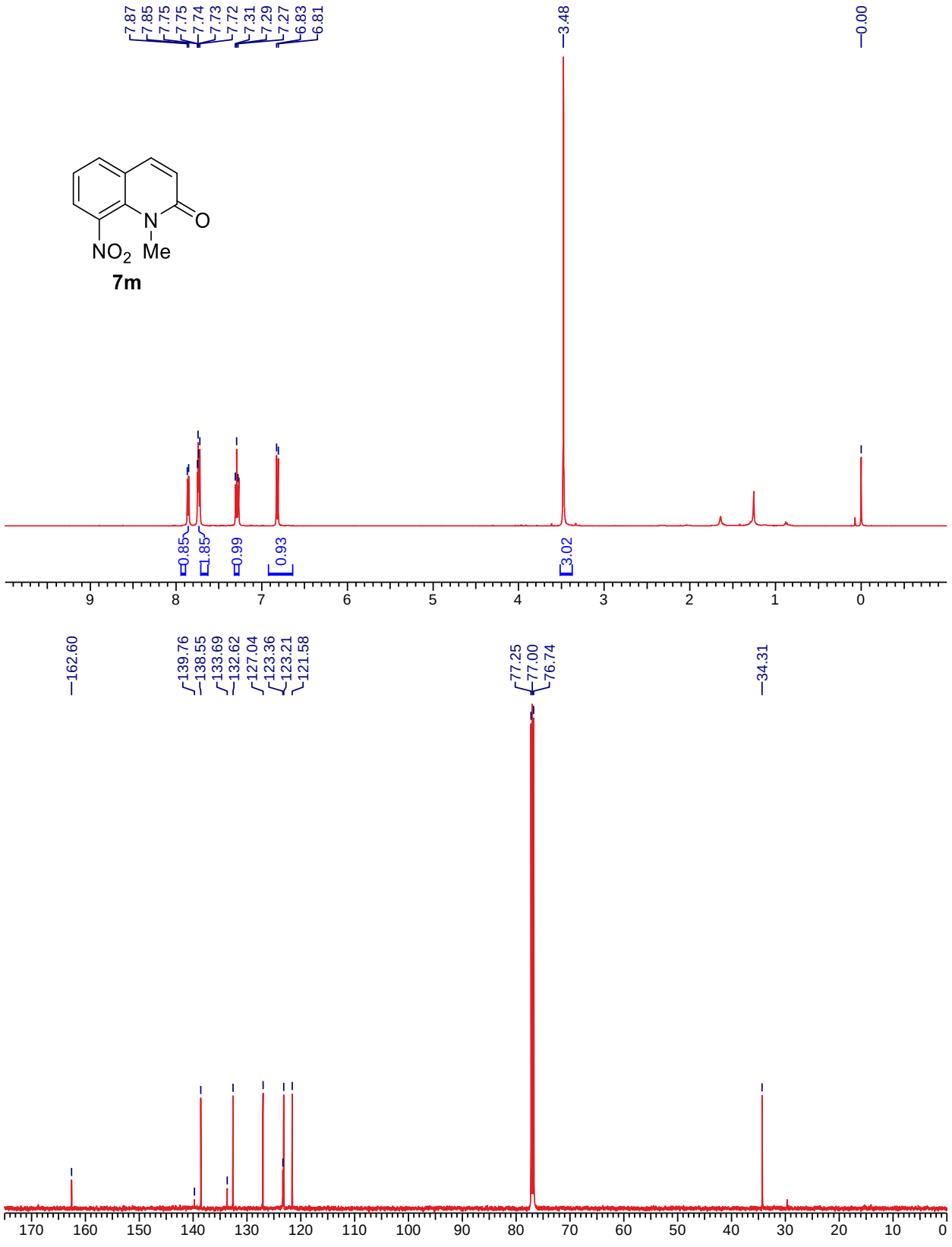
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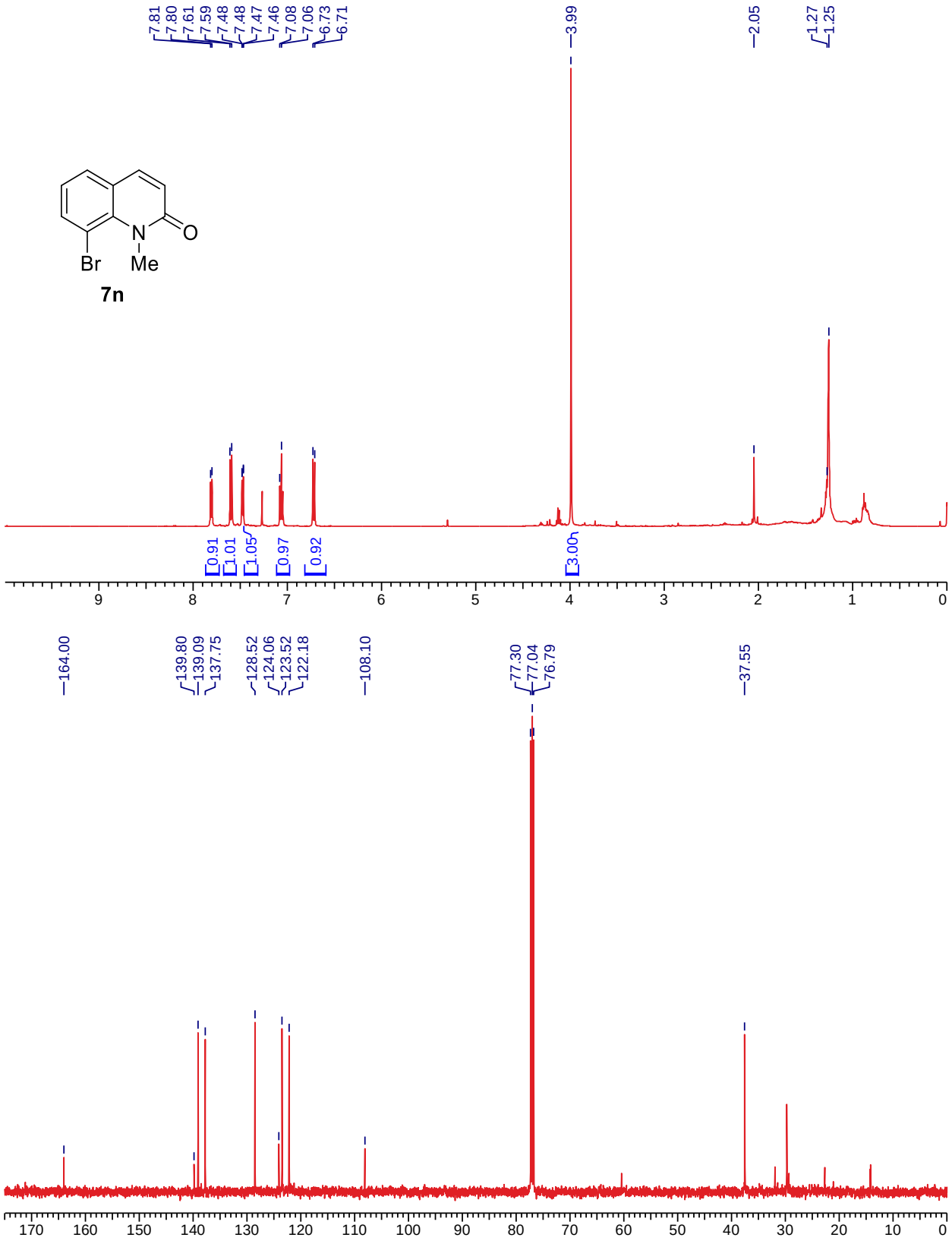
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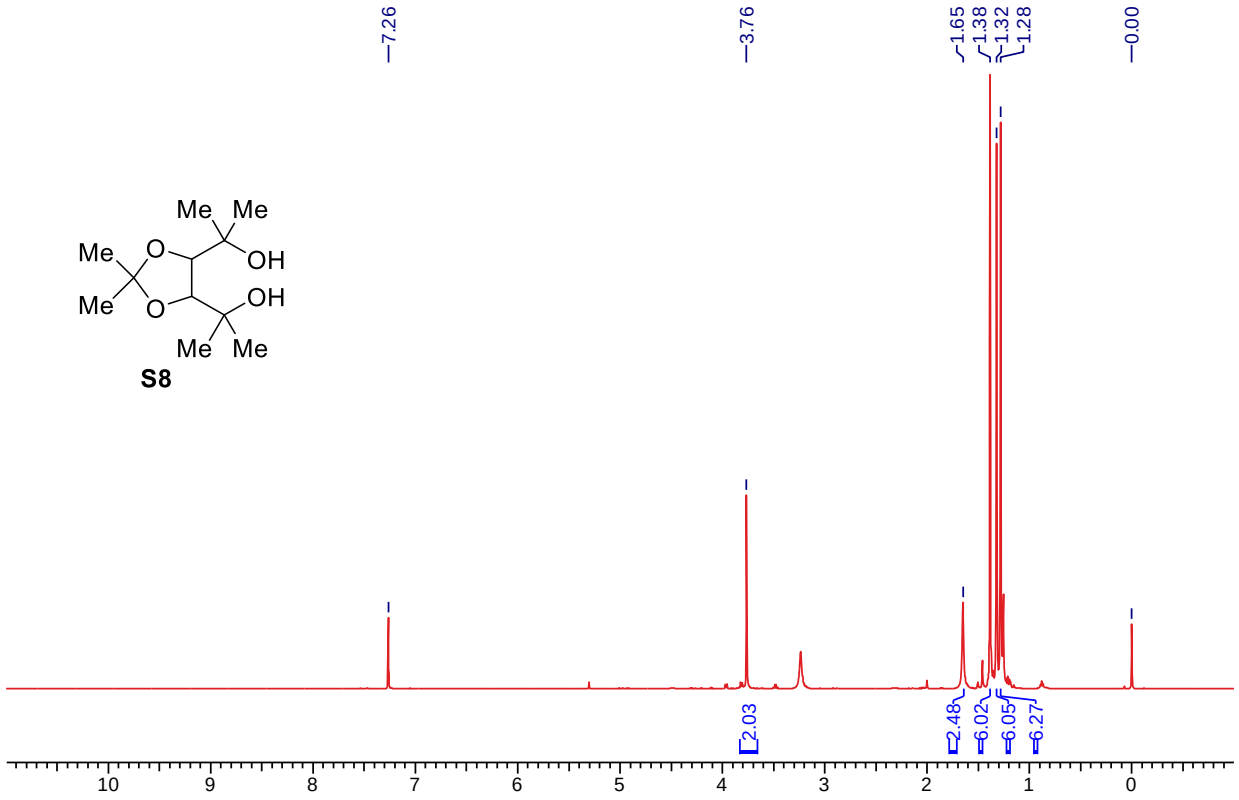
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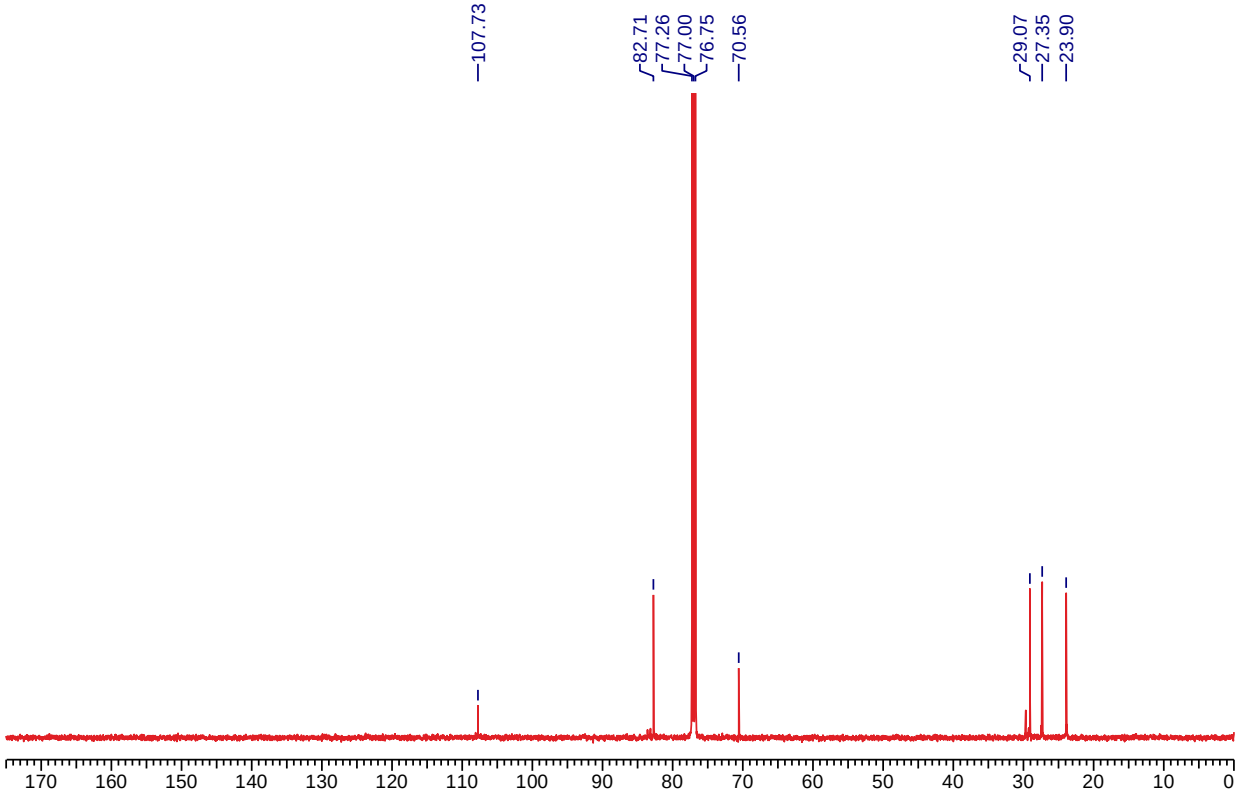
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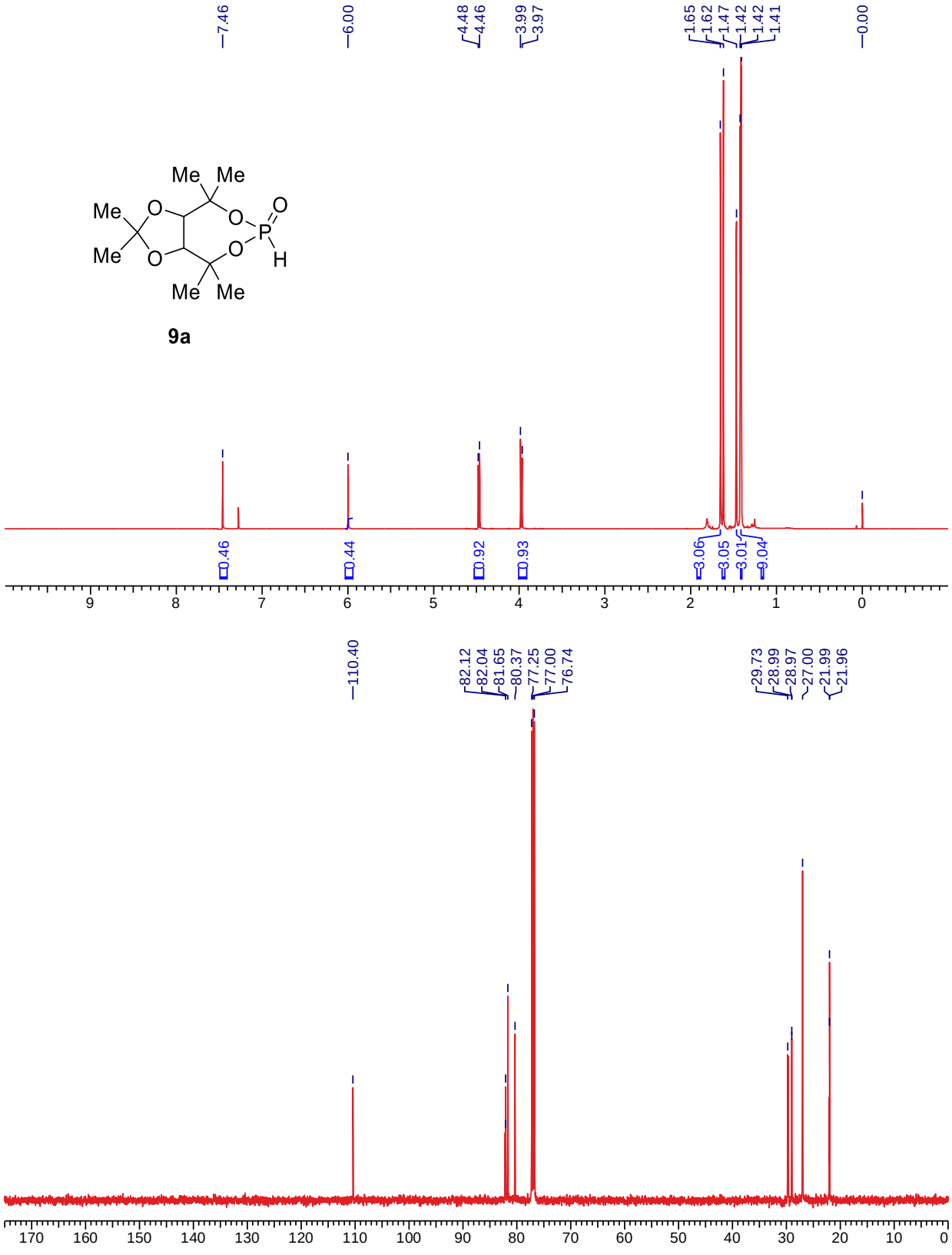
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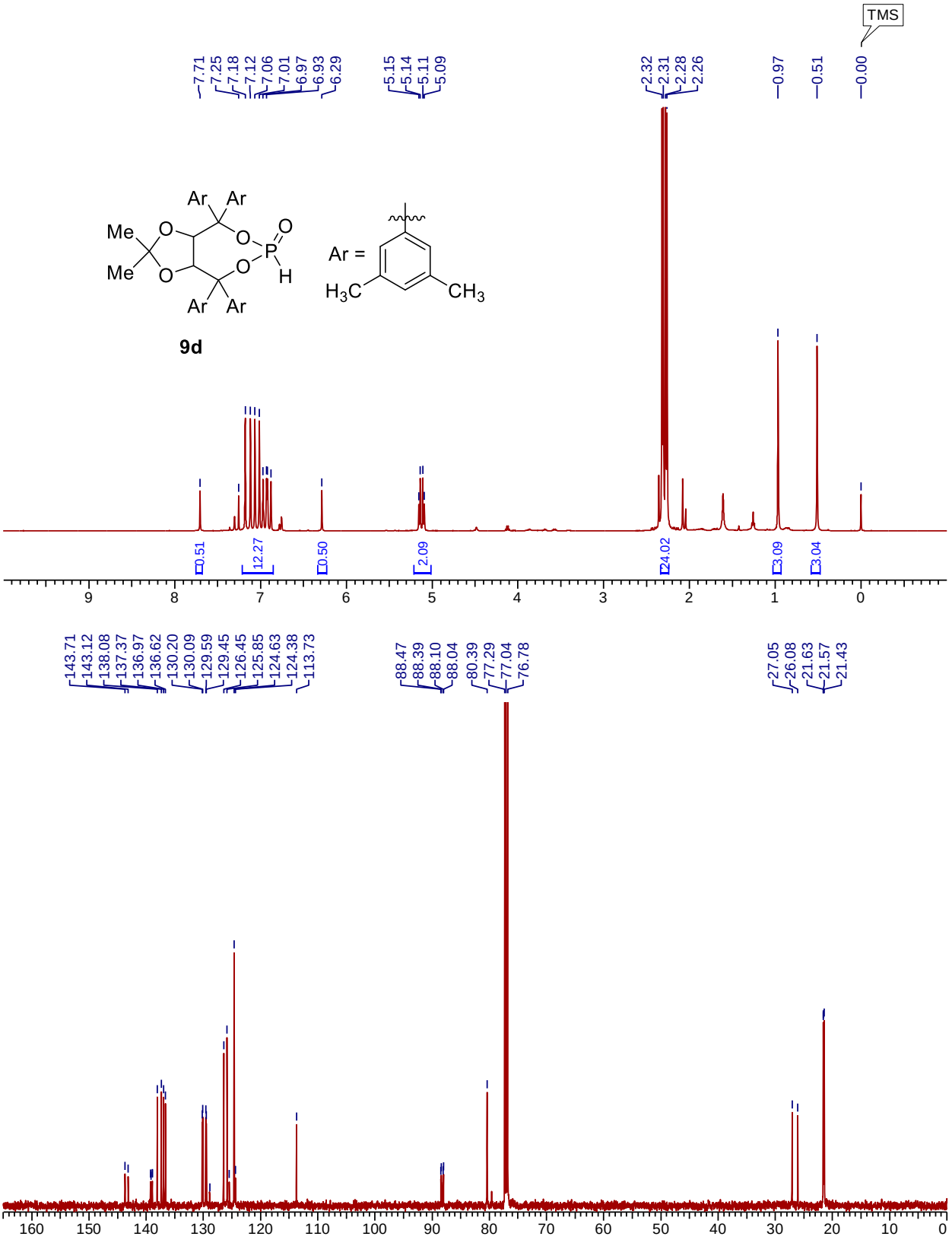
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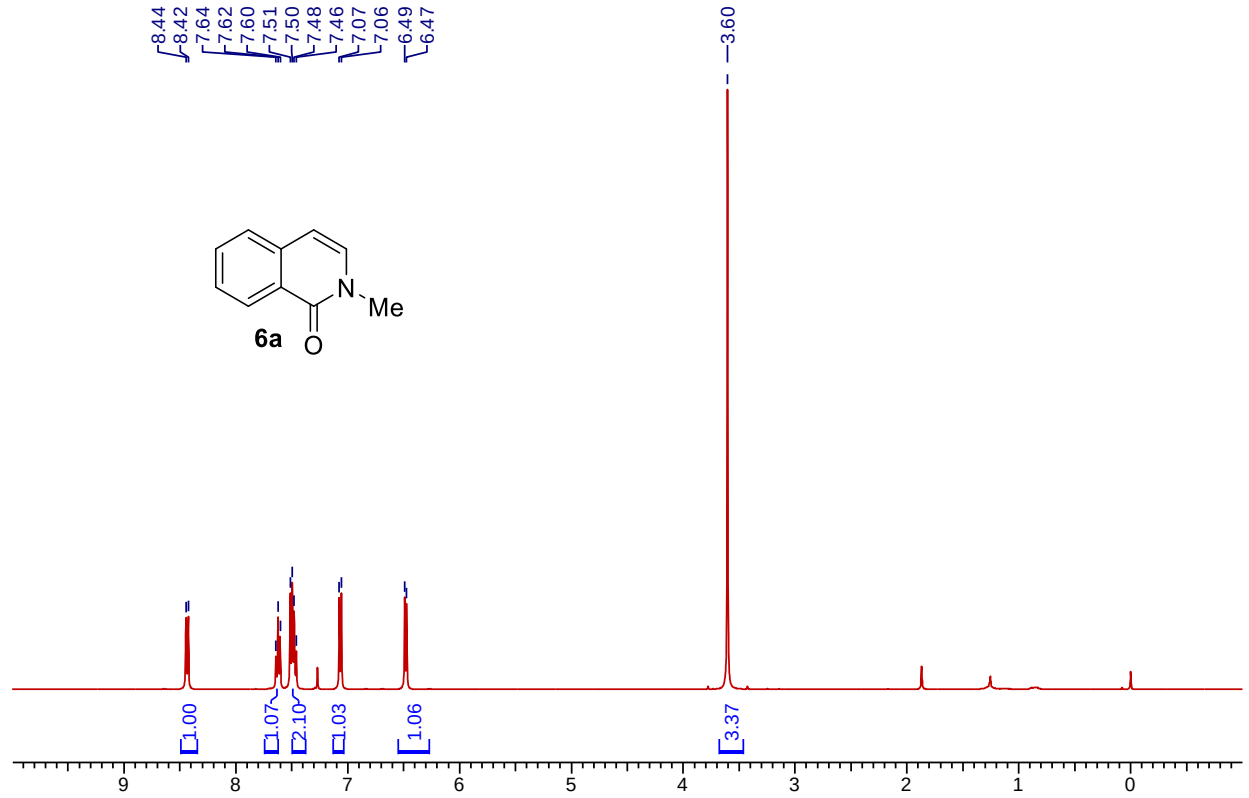
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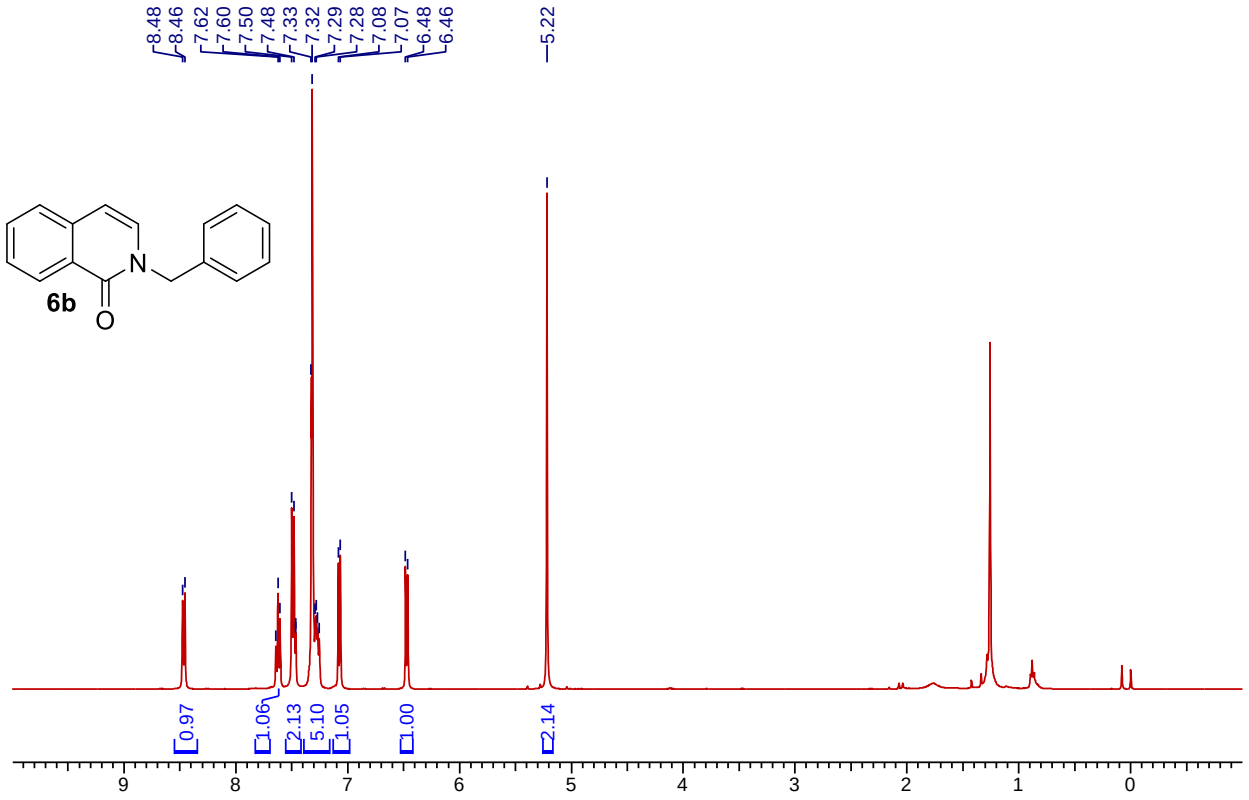
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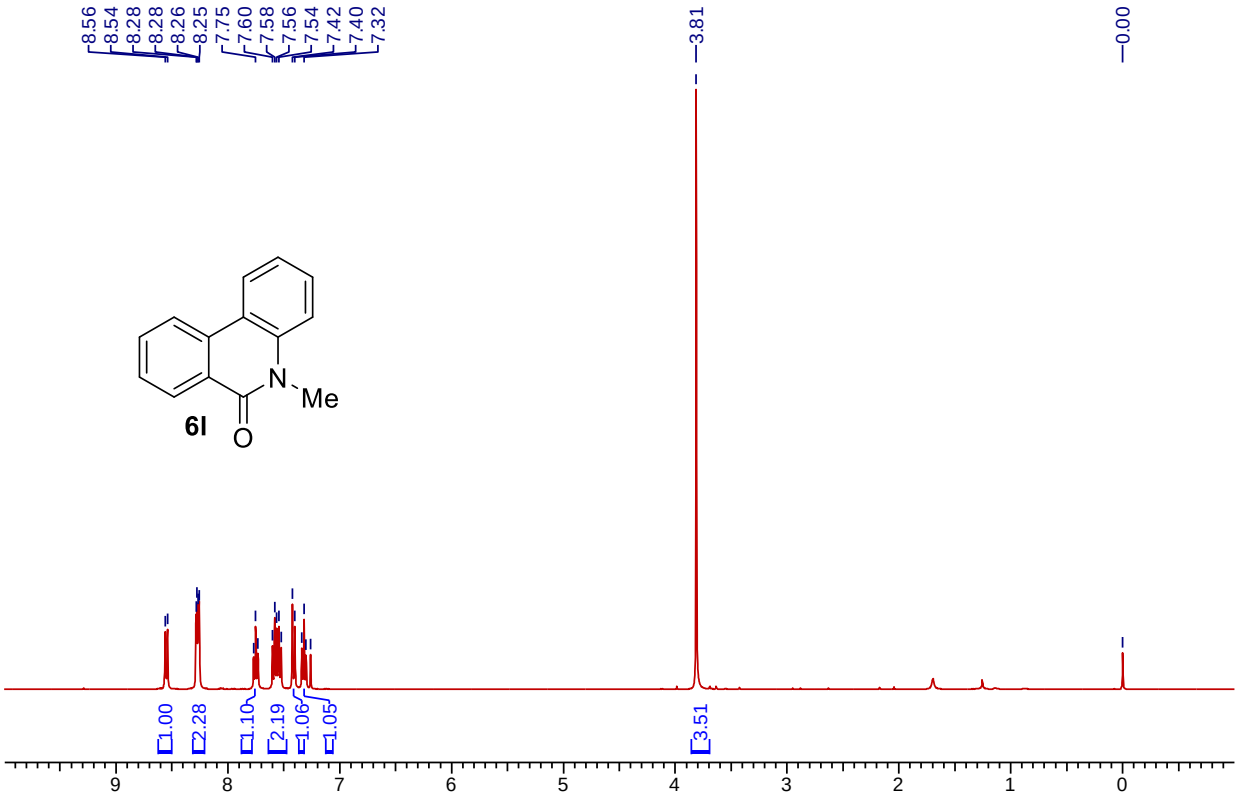
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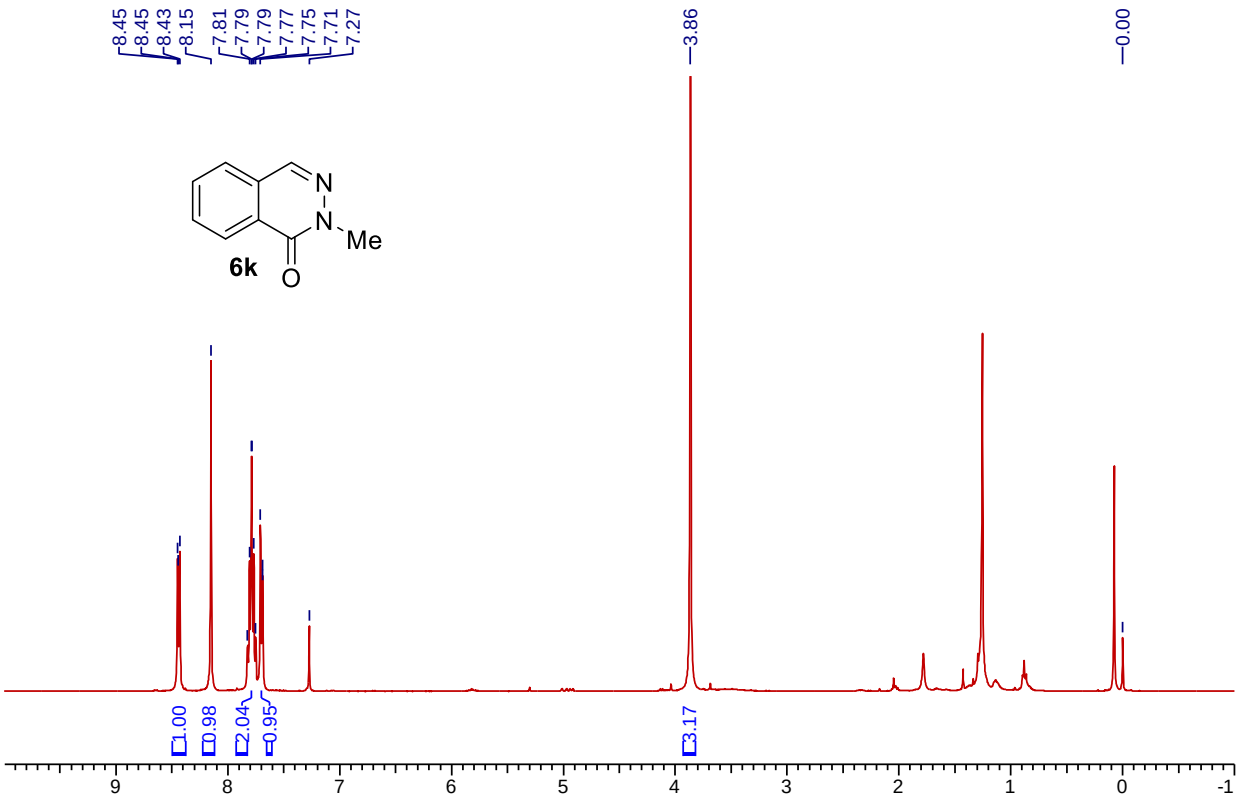
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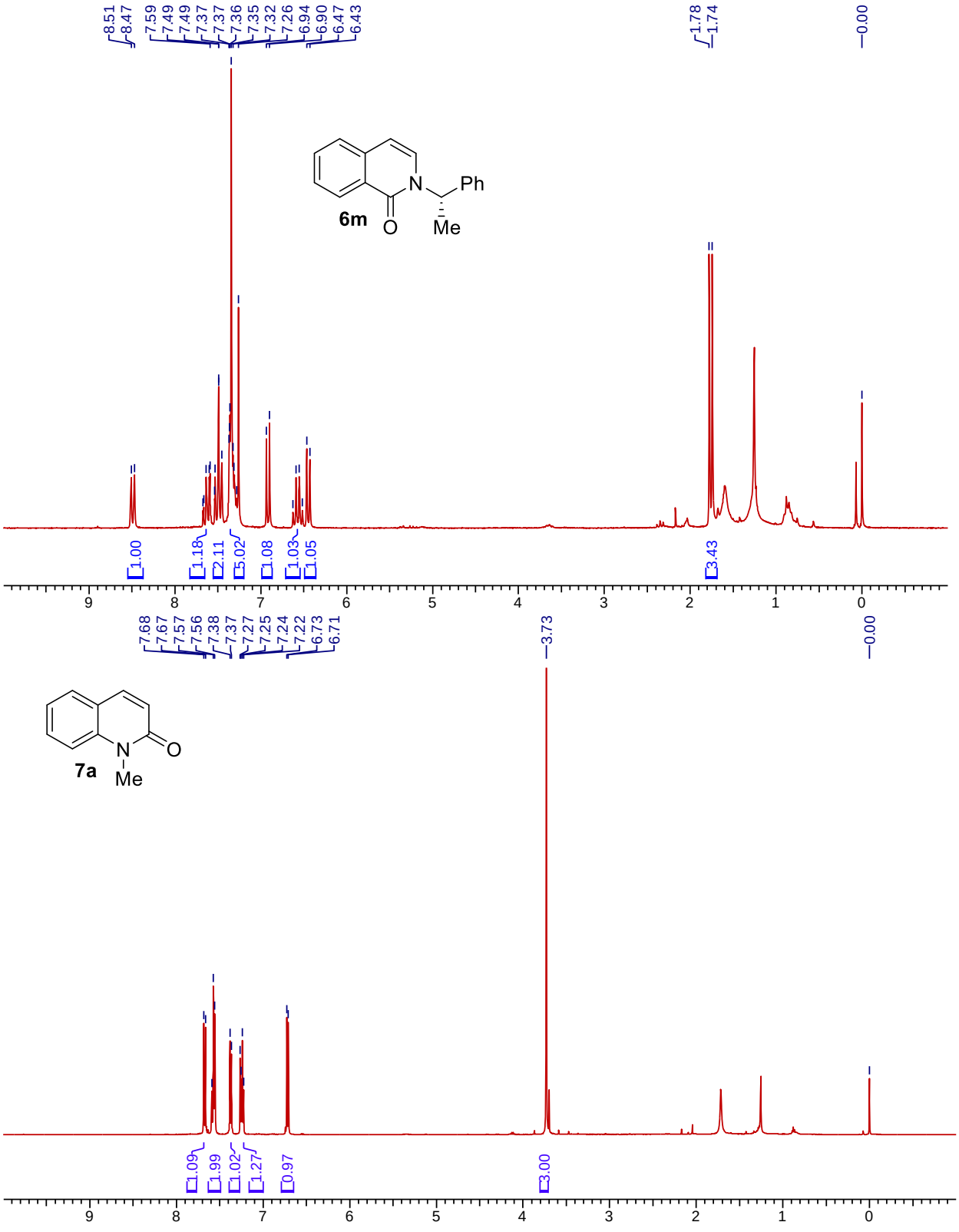
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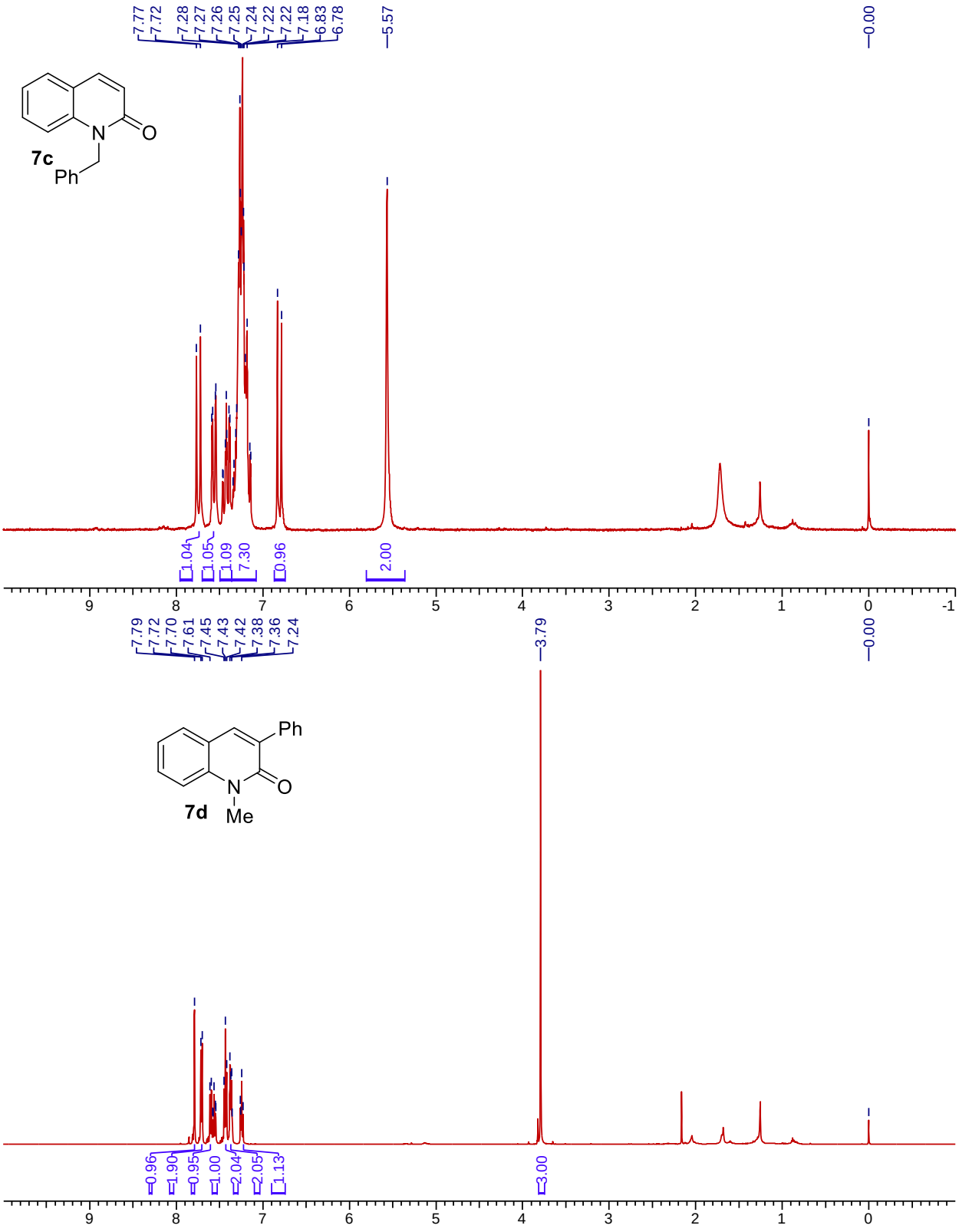
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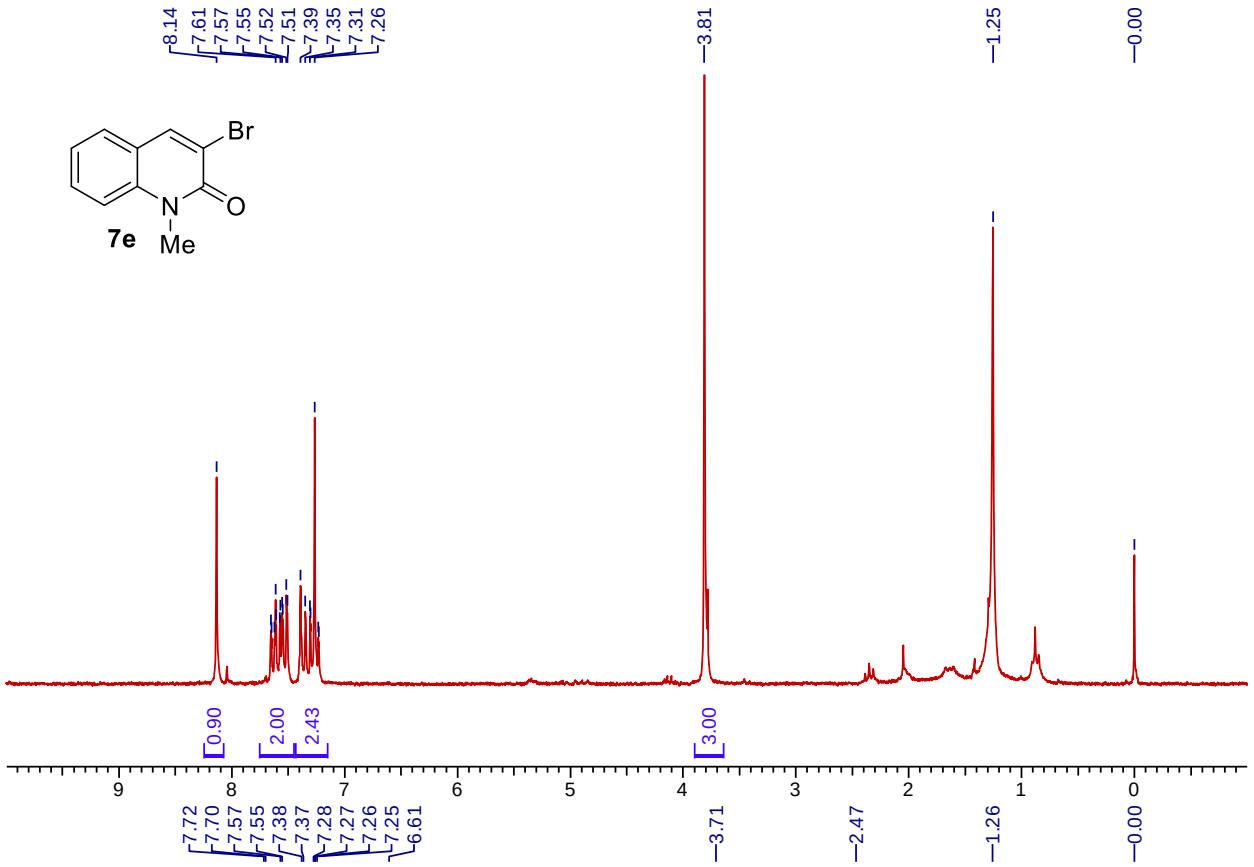
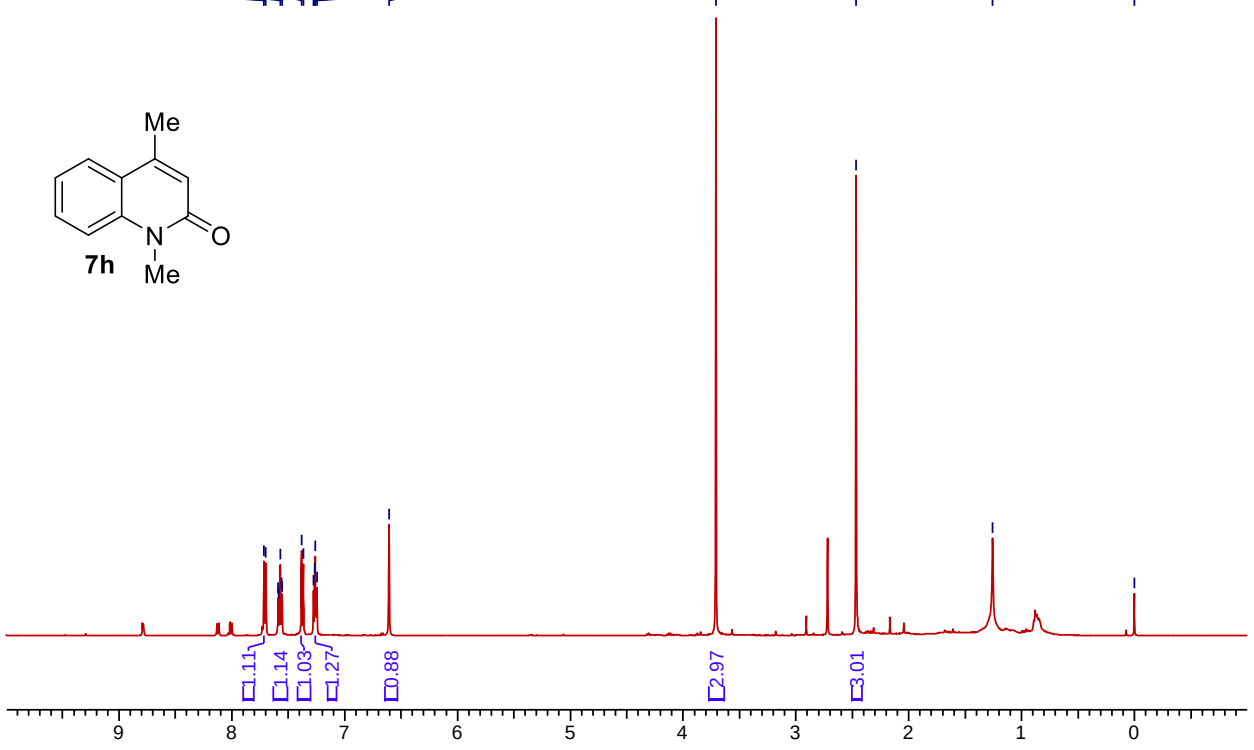
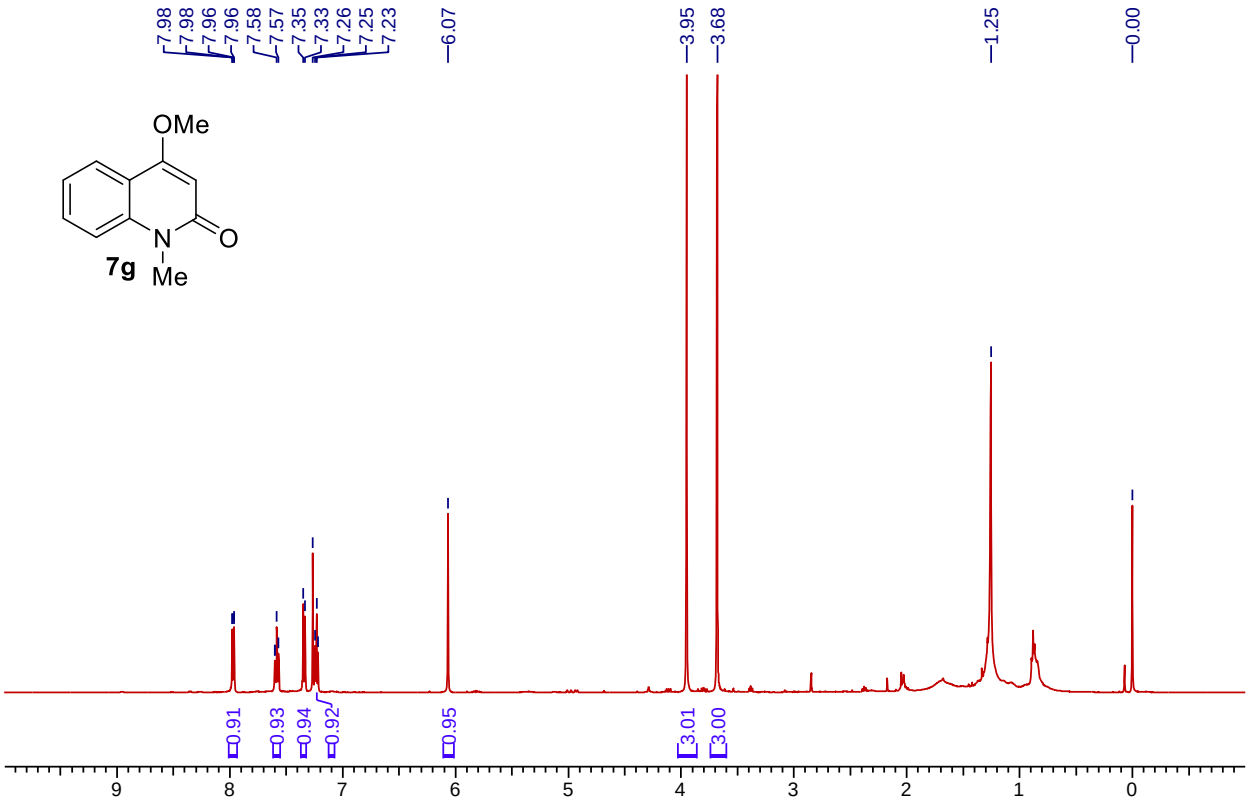
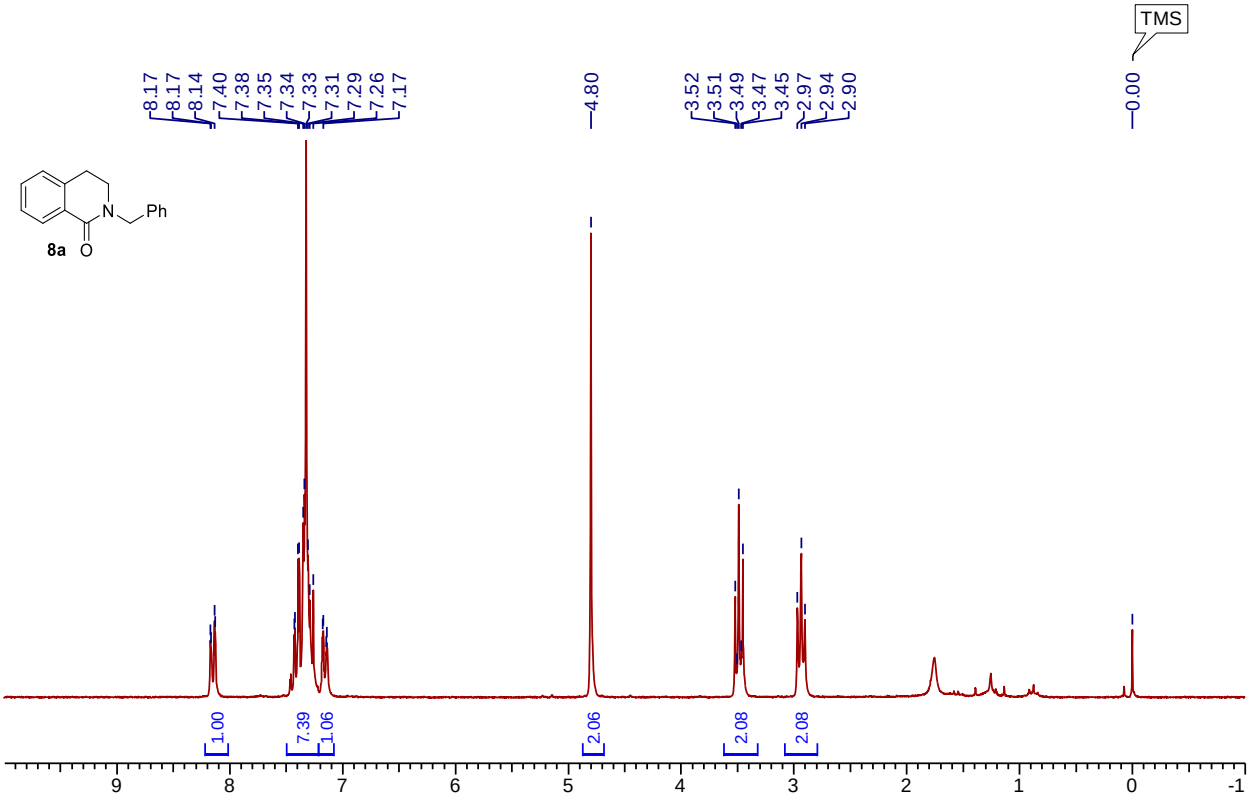
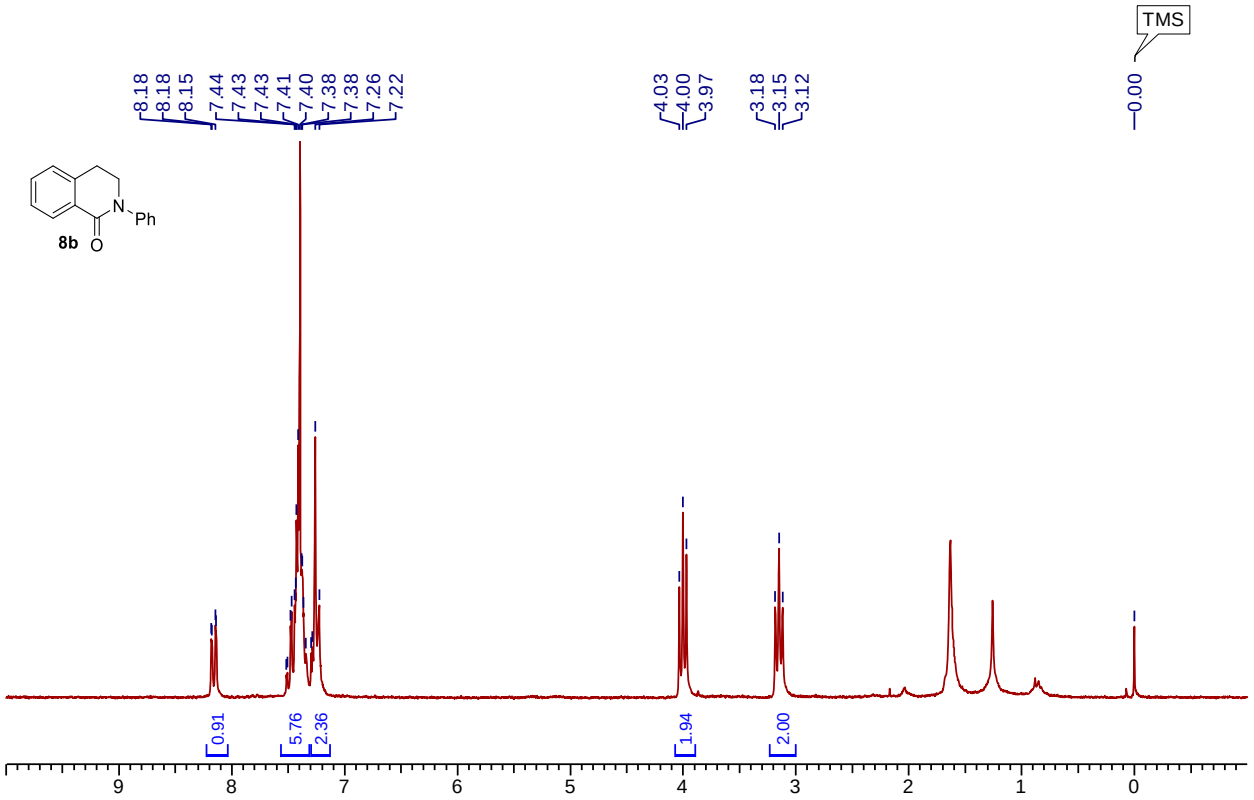
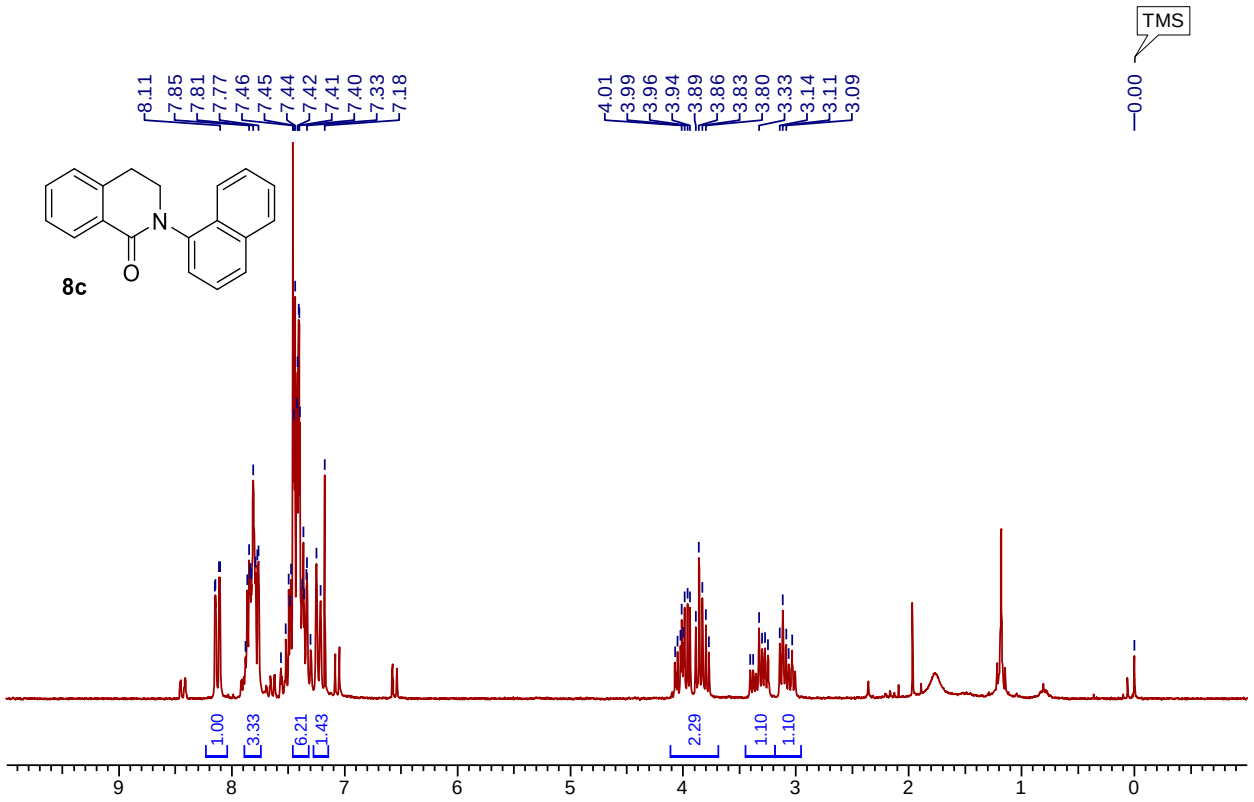

8.14
7.61
7.57
7.55
7.52
7.51
7.39
7.35
7.31
7.26
3.81
1.25
0.00
Br
N
O
Me
7e
0.90
2.00
2.43
3.00

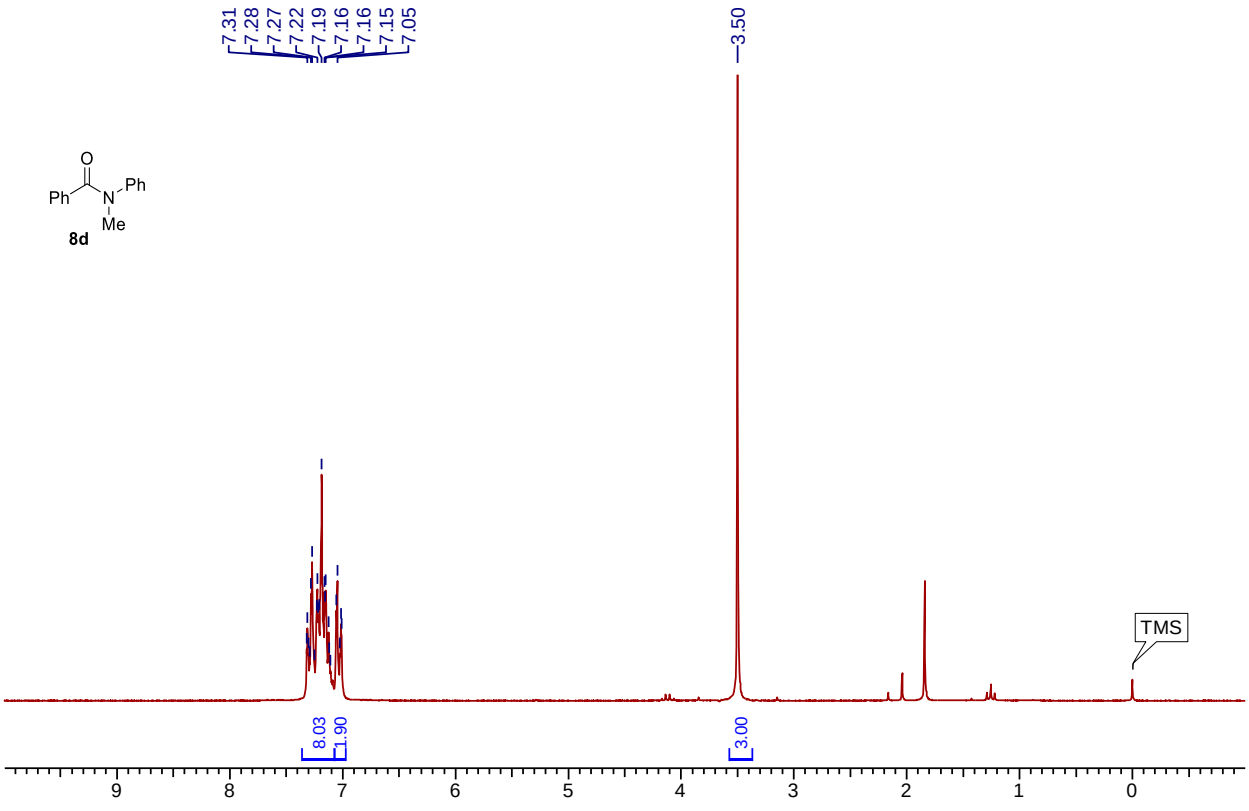

7.72
7.70
7.57
7.55
7.38
7.37
7.28
7.27
7.26
7.25
6.61
3.71
2.47
1.26
0.00
Me
N
O
Me
7h
1.11
1.14
1.03
1.27
0.88
2.97
3.01

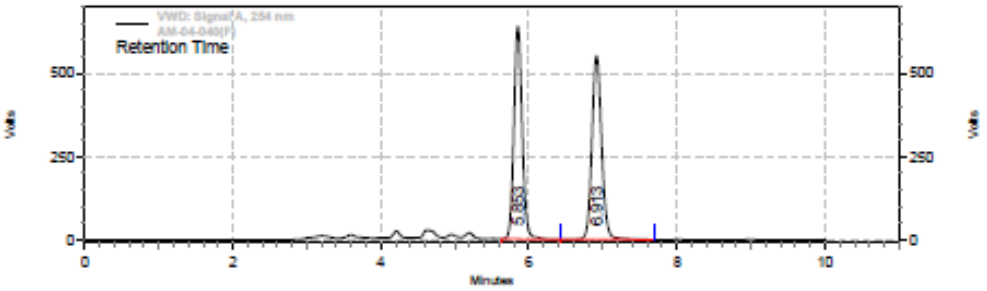

7.98
7.98
7.96
7.96
7.58
7.57
7.35
7.33
7.26
7.25
7.23
6.07
3.95
3.68
1.25
0.00
OMe
N
O
Me
7g
0.91
0.93
0.94
0.92
0.95
3.01
3.00
9
8
7
6
5
4
3
2
1
0


TMS
8.17
8.17
8.14
7.40
7.38
7.35
7.34
7.33
7.31
7.29
7.26
7.17
4.80
3.52
3.51
3.49
3.47
3.45
2.97
2.94
2.90
0.00
N
Ph
O
8a
1.00
7.39
1.06
2.06
2.08
2.08
9
8
7
6
5
4
3
2
1
0
-1


TMS
8.18
8.18
8.15
7.44
7.43
7.43
7.41
7.40
7.38
7.38
7.26
7.22
4.03
4.00
3.97
3.18
3.15
3.12
0.00
N
Ph
O
8b
0.91
5.76
2.36
1.94
2.00
9
8
7
6
5
4
3
2
1
0


TMS
8.11
7.85
7.81
7.77
7.46
7.45
7.44
7.42
7.41
7.40
7.33
7.18
4.01
3.99
3.96
3.94
3.89
3.86
3.83
3.80
3.33
3.14
3.11
3.09
0.00
N
O
8c
1.00
3.33
6.21
1.43
2.29
1.10
1.10
9
8
7
6
5
4
3
2
1
0


7.31
7.28
7.27
7.22
7.19
7.16
7.16
7.15
7.05
3.50
O
Ph
N
Ph
Me
8d
TMS
8.03
1.90
3.00
9
8
7
6
5
4
3
2
1
0

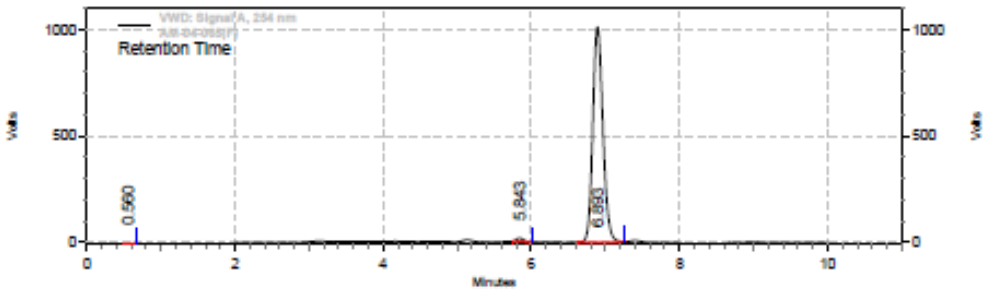


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
5.853	83231234	49.59
6.913	84615440	50.41
Totals		
	167846674	100.00

Column : Chiralpak IA
Eluent System : 70 : 30 (HEXANE:IPA)
Flow rate: 1.0 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml

HPLC traces for racemic **6m**

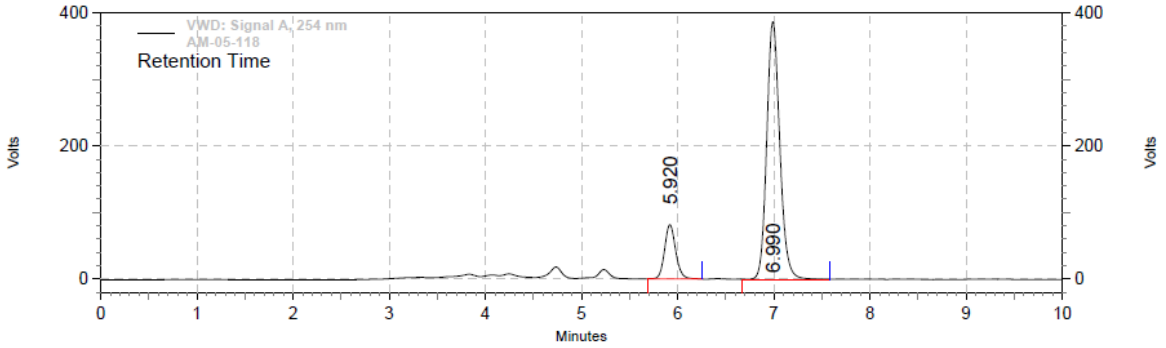


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
0.560	580	0.00
5.843	1694047	1.04
6.893	160698086	98.96
Totals		
	162392713	100.00

Column : Chiralpak IA
Eluent System : 70 : 30 (HEXANE:IPA)
Flow rate: 1.0 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml

HPLC traces for oxidation product from chiral (S) **1m**

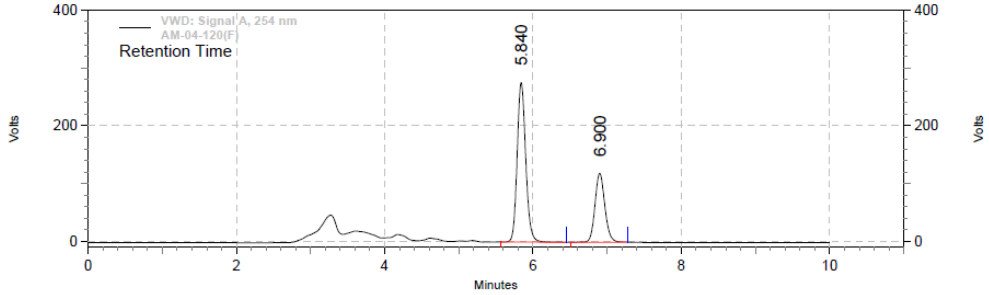


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
5.920	10961721	15.20
6.990	61144272	84.80
Totals		
	72105993	100.00

Column : CHIRALPAK-IA
Eluent System : 70 : 30 (n-HEXANE:IPA)
Flow rate: 1.0 ml/min
Injection vol..: 10 ul
Wavelength: 254 nm
Sample Conc.: 1.0 mg/ ml

HPLC traces for kinetic oxidation with **9e** catalyst and racemic **1m**

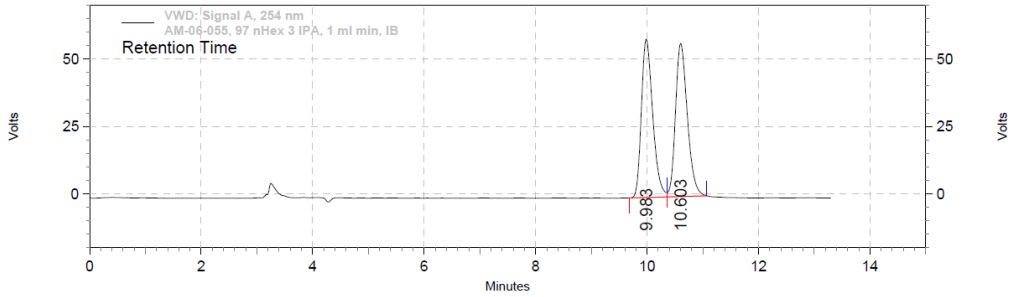


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
5.840	37157225	66.85
6.900	18426185	33.15
Totals		
	55583410	100.00

Column : Chiralpak IA
Eluent System : 70 : 30 (HEXANE:IPA)
Flow rate: 1.0 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml

HPLC traces of oxidized product from the recovered salt (**1m**) of kinetic resolution

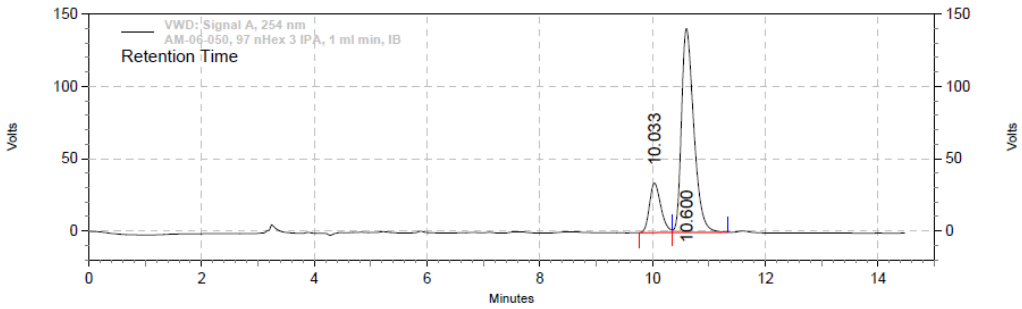


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
9.983	13896016	49.68
10.603	14075266	50.32
Totals	27971282	100.00

Column : CHIRALPAK IB
Eluent System : 97:03 (nHex:IPA)
Flow rate: 1 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml

HPLC traces for racemic **6n**



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
10.033	8036460	18.27
10.600	35951317	81.73
Totals	43987777	100.00

Column : CHIRALPAK IB
Eluent System : 97:03 (nHex:IPA)
Flow rate: 1 ml/min
Injection vol..: 10ul
Wavelength: 254 nm
Sample Conc.: 1 mg/ ml

HPLC traces for kinetic oxidation with **9e** catalyst and racemic **1n** to enantioenriched **6n.**