Electronic Supplementary Information

A synthetically useful catalytic system for aliphatic C−H oxidation with a nonheme cobalt complex and *m*-CPBA

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Table of Contents

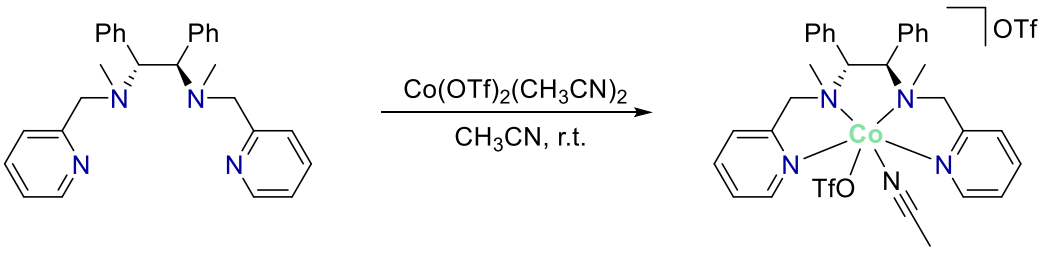
Experimental Section

Materials. All chemicals were purchased from Energy Chemical, Bidepharm, Aldrich, and TCI with the maximum purity available, and used as received unless otherwise indicated. Solvents were dried according to published procedures and distilled under argon prior to use.[S1] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash column chromatography was performed on silica gel (particle size 200−300 mesh) and eluted with petroleum ether/ethyl acetate. $Co(CF_3SO_3)_2 \cdot 2CH_3CN$ was synthesized by reacting cobalt powder with trifluoromethanesulfonic acid (CF_3SO_3H) under an inert atmosphere in H_2O, and then recrystallized with CH_3CN/Et_2O.[S2] Ligands MPP,[S3] 6-Me_2-MPP,[S3] BPMCN,[S4] BQPN,[S3] and BQCN[S5] were prepared according to the reported procedures. Substrates **7a-8a**,[S6] **10a-11a,**[S7] **12a-14a,**[S7] **15a,**[S8] **16a,**[S7] **17a,**[S9] **18a-19a,**[S10] **21a-23a,**[S8] and **26a-28a**[S11] were prepared using published protocols and were found to match reported physical properties. Substrates **6a**, **9a**, and **20a, 24a, 25a, 30a, 31a,** and **32a** are commercially available.

Instrumentation. NMR spectra were recorded on Bruker AVQ-400 (400 MHz for ^1H; 101 MHz for ^{13}C) or AVANCE III HD-600 (600 MHz for ^1H; 151 MHz for ^{13}C). The chemical shifts (δ) are given in parts per million relative to Chloroform-d (7.26 ppm for ^1H) or TMS (0 ppm for ^1H) and Chloroform-d (77.0 ppm for ^{13}C). Coupling constants are reported in Hertz (Hz). Abbreviations for splitting patterns are as follows: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; sext, sextet; hept, heptet; m, multiplet; br., broad. Where coincident coupling constants have been observed, the apparent (app.) multiplicity of the proton resonance has been reported. High-resolution mass spectral (HRMS) data were obtained with Thermo LTQ−FTICR (ESI) mass spectrometers. X-band EPR spectra were taken at 5.0 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Elemental analysis was performed on a Thermo Finnigan Italia SpA (Flash EA 1,112) CHN analyzer. For X-ray structural analysis, crystallographic data collections were carried out on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo $K\alpha$ (λ = 0.71073 Å) incident beam. Melting points were recorded using a

X-5 Micro melting point instrument, Beijing Tech Instrument Co., LTD. GC-MS spectra were recorded on a GCMS-QP2010 SE.

Synthesis and Characterization of Nonheme Cobalt(II) Complexes

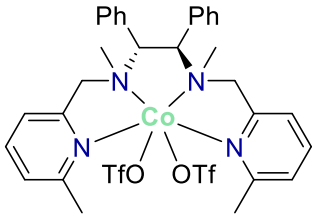


(*R*,*R*)-MPP

[Co(MPP)(OTf)(CH$_3$CN)](OTf) (**1**)

[Co(*R*,*R*-MPP)(OTf)(CH$_3$CN)](OTf) (**1**): Under nitrogen atmosphere, a solution of Co(CF$_3$SO$_3$)$_2$(CH$_3$CN)$_2$ (1.2 mmol, 527 mg) in anhydrous CH$_3$CN (2.0 mL) was added dropwise to a vigorously stirred solution of tetradentate N4 ligand (*R*,*R*)-MPP (1.0 mmol, 422 mg) in CH$_3$CN (1.5 mL) at room temperature. After stirring for 12 hours, anhydrous diethyl ether freshly taken from solvent delivery system was added to the resulting solution to precipitate out the complex. The resultant solid was washed thoroughly with ether, dried under vacuum, and recrystalized with CH$_3$CN/ether to yield the desired complex as a pink solid (755 mg, 0.92 mmol, 92% yield). **HRMS** (ESI+, Figure S1 in the Electronic Supplementary Information): *m*/*z* 240.5896 [Co^{II}(*R*,*R*-MPP)]$^{2+}$, and 630.1317 [Co^{II}(*R*,*R*-MPP)(CF$_3$SO$_3$)]$^+$. **Anal. Calcd.** for C$_{32}$H$_{33}$N$_5$O$_6$S$_2$F$_6$Co: C, 46.83; H, 4.05; N, 8.53. Found: C, 46.95; H, 4.08; N, 8.71.

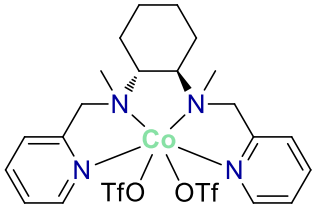
Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of anhydrous diethyl ether into an acetonitrile solution of [Co(MPP)(OTf)(CH$_3$CN)](OTf) (**1**).



[Co(6-Me$_2$-MPP)(OTf)$_2$ (**2**)

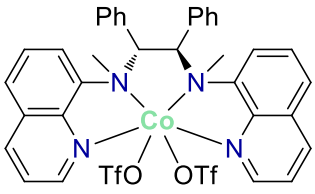
[Co(*R*,*R*-6-Me$_2$-MPP)(OTf)$_2$] (**2**): Following the general procedure for the preparation of complex **1** using (*R*,*R*)-6-Me$_2$-MPP ligand, provided the title complex as a pink solid (711 mg, 0.88 mmol, 88% yield). **HRMS** (ESI+, Figure S2 in the Electronic Supplementary Information): *m*/*z* 254.6051 [Co^{II}(*R*,*R*-6-Me$_2$-MPP)]$^{2+}$, and 658.1630 [Co^{II}(*R*,*R*-6-Me$_2$-MPP)(CF$_3$SO$_3$)]$^+$. **Anal. Calcd.** for C$_{32}$H$_{34}$N$_4$O$_6$S$_2$F$_6$Co: C,

47.59; H, 4.24; N, 6.94. Found: C, 47.45; H, 4.38; N, 6.79.



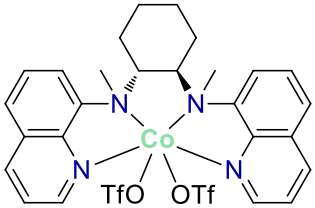
[Co(BPMCN)(OTf)$_2$] (**3**)

[Co(*R*,*R*-BPMCN)(OTf)$_2$] (**3**): Following the general procedure for the preparation of complex **1** using (*R*,*R*)-BPMCN ligand, provided the title complex as a pink solid (545 mg, 0.80 mmol, 80% yield). **HRMS** (ESI+, Figure S3 in the Electronic Supplementary Information): *m*/*z* 191.5814 [Co^{II}(*R*,*R*-BPMCN)]$^{2+}$, and 532.1161 [Co^{II}(*R*,*R*-BPMCN)(CF_3SO_3)]$^+$. **Anal. Calcd.** for $C_{22}H_{28}N_4O_6S_2F_6Co$: C, 38.77; H, 4.14; N, 8.22. Found: C, 38.55; H, 4.30; N, 8.02.



[Co(BQPN)(OTf)$_2$] (**4**)

[Co(*R*,*R*-BQPN)(OTf)$_2$] (**4**): Following the general procedure for the preparation of complex **1** using (*R*,*R*)-BQPN ligand, provided the title complex as a pink solid (664 mg, 0.78 mmol, 78% yield). **HRMS** (ESI+, Figure S4 in the Electronic Supplementary Information): *m*/*z* 276.5896 [Co^{II}(*R*,*R*-BQPN)]$^{2+}$, and 702.1319 [Co^{II}(*R*,*R*-BQPN)(CF_3SO_3)]$^+$. **Anal. Calcd.** for $C_{36}H_{30}N_4O_6S_2F_6Co$: C, 50.77; H, 3.55; N, 6.58. Found: C, 50.56; H, 3.68; N, 6.53.



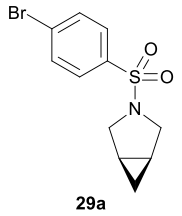
[Co(BQCN)(OTf)$_2$] (**5**)

[Co(*R*,*R*-BQCN)(OTf)$_2$] (**5**): Following the general procedure for the preparation of

complex **C1** using (*R*,*R*)-BQCN ligand, provided the title complex as a pink solid (678 mg, 0.90 mmol, 90% yield). **HRMS** (ESI+, Figure S5 in the Electronic Supplementary Information): *m*/*z* 227.5815 $[Co^{II}(R,R\text{-BQCN})]^{2+}$, and 604.1162 $[Co^{II}(R,R\text{-BQCN})(CF_3SO_3)]^{+}$. **Anal. Calcd.** for $C_{28}H_{28}N_4O_6S_2F_6Co$: C, 44.63; H, 3.75; N, 7.43. Found: C, 44.58; H, 3.78; N, 7.35.

Synthesis and Characterization of Substrates

3-((4-Bromophenyl)sulfonyl)-3-azabicyclo[3.1.0]hexane (29a)



29a

Et_3N (11 mmol, 1.1 equiv) was added to a round bottom flask containing (1*R*,5*S*)-3-azabicyclo[3.1.0]hexane (10 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (30 mL) at room temperature. Then, the solution was cooled down to 0 ºC, and 4-bromobenzene-1-sulfonyl chloride (12 mmol, 1.2 equiv) was added dropwise. After that the reaction mixture was warmed to room temperature and stirred for additional 16 h. The mixture was then washed with 1.0 M aqueous HCl solution, and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and filtered. The solution was then concentrated under reduced pressure and purified by flash chromatography on silica gel to afford **29a** as a white solid (2.6 g, 8.6 mmol, 86%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.60 (m, 4H), 3.51 (d, *J* = 9.2 Hz, 2H), 3.06 (d, *J* = 9.0 Hz, 2H), 1.47 – 1.39 (m, 2H), 0.63-0.54 (m, 1H), 0.38-0.30 (m, 1H).

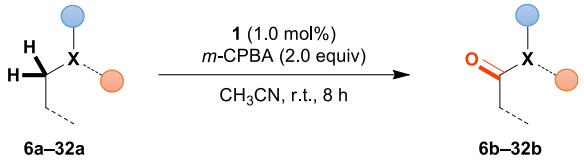
^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.8, 132.4, 129.1, 127.7, 50.0, 15.7, 7.8.

HRMS (ESI+): *m*/*z* calculated for $C_{11}H_{13}BrNO_2S$ $[M+H]^+$: 301.9850, found 301.9842.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 40:1)

m.p.: 148.1 – 149.4 ºC

General Procedure for Catalytic C(sp^3)−H Oxidation

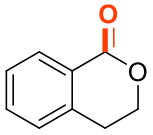


6a–32a 6b–32b

[Co(*R*,*R*-MPP)(OTf)(CH_3CN)](OTf) (**1**) (4.1 mg, 5.0 × 10^{-3} mmol) and substrate (0.50 mmol) were added to a Schlenk tube in CH_3CN (2.0 mL). Then *m*-CPBA (138 mg, 1.0 mmol, 2.0 equiv) was added in one batch under aerobic conditions. The final concentrations of reagents were 2.5 mM cobalt catalyst, 0.50 M *m*-CPBA and 0.25 M substrate. After stirring the reaction mixture for 8 h at room temperature, the resulting solution was concentrated to a minimum amount of solvent. The residue was dissolved in DCM (~15 mL) and washed sequentially with sat. aq. Na_2SO_3 and sat. aq. $NaHCO_3$ solution. The aqueous layer was extracted with DCM (3 × 10 mL) and the combined organic layer was dried over Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

Characterization of the Oxidation Products

Isochroman-1-one (6b)



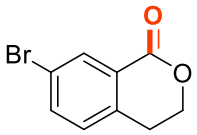
6b

Following the general procedure for C(sp^3)–H oxidation using isochroman **6a** (67 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 30:1) provided the title compound as a white solid (64 mg, 0.44 mmol, 87%). Spectral data are consistent with those reported in the literature.[S12]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16-8.04 (m, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.29 – 7.23 (m, 1H), 4.58-4.48 (m, 2H), 3.06 (t, *J* = 6.0 Hz, 2H).

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 20:1).

7-Bromoisochroman-1-one (7b)



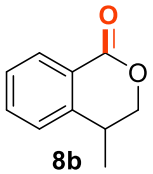
7b

Following the general procedure for C(sp^3)–H oxidation using 7-bromoisochroman **7a** (107 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 30:1) provided the title compound as a white solid (87.4 mg, 0.38 mmol, 77%). Spectral data are consistent with those reported in the literature.[S12]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 4.53 (t, *J* = 6.0 Hz, 2H), 3.02 (t, *J* = 6.0 Hz, 2H).

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 20:1).

4-Methylisochroman-1-one (8b)



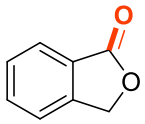
8b

Following the general procedure for C(sp^3)–H oxidation using 4-methylisochroman **8a** (74.1 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 30:1) provided the title compound as a white solid (74.6 mg, 0.46 mmol, 92%). Spectral data are consistent with those reported in the literature.[S12]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 4.52 (dd, *J* = 10.9, 4.1 Hz, 1H), 4.24 (dd, *J* = 10.9, 6.6 Hz, 1H), 3.23 – 3.10 (m, 1H), 1.37 (d, *J* = 7.1 Hz, 3H).

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 20:1).

Isobenzofuran-1(3H)-one (9b)



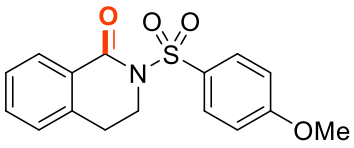
9b

Following the general procedure for C(sp^3)–H oxidation using 1,3-dihydroisobenzofuran **9a** (60.1 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 25:1) provided the title compound as a white solid (57.0 mg, 0.43 mmol, 85%). Spectral data are consistent with those reported in the literature.[S12]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.69 (td, *J* = 7.5, 1.0 Hz, 1H), 7.58 – 7.47 (m, 2H), 5.33 (s, 2H).

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 20:1).

2-((4-Methoxyphenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (10b)



10b

Following the general procedure for C(sp^3)–H oxidation using 2-((4-methoxyphenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **10a** (152 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 12:1) provided the title compound as a white solid (103 mg, 0.33 mmol, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 8.01 – 7.96 (m, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.02 – 6.95 (m, 2H), 4.26 – 4.18 (m, 2H), 3.86 (s, 3H), 3.12 (t, *J* = 6.2 Hz, 2H).

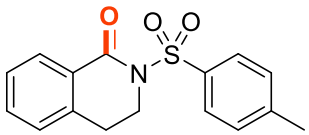
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 163.6, 139.4, 133.6, 131.0, 130.6, 129.2, 128.4, 127.54, 127.47, 114.1, 55.8, 44.8, 29.1.

HRMS (ESI+): *m/z* calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$: 318.0800, found 318.0795.

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 10:1).

m.p.: 121.4 – 122.6 °C.

2-Tosyl-3,4-dihydroisoquinolin-1(2H)-one (11b)



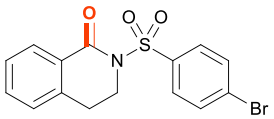
11b

Following the general procedure for C(sp^3)–H oxidation using 2-tosyl-1,2,3,4-tetrahydroisoquinoline **11a** (144 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 18:1) provided the title compound as a white solid (125 mg, 0.42 mmol, 83%).[S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03-7.93 (m, 3H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35-7.28 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.24 (t, *J* = 6.2 Hz, 2H), 3.13 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H).

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 10:1).

2-((4-Bromophenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (12b)



12b

Following the general procedure for C(sp^3)−H oxidation using 2-((4-bromophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **12a** (176 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (159 mg, 0.44 mmol, 87%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 3H), 7.70 – 7.63 (m, 2H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 4.29 – 4.19 (t, *J* = 6.2 Hz, 2H), 3.14 (t, *J* = 6.2 Hz, 2H).

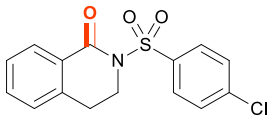
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 139.3, 138.1, 133.9, 132.2, 130.3, 129.3, 129.1, 128.0, 127.7, 127.6, 44.9, 29.0.

HRMS (ESI+): *m*/*z* calculated for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$: 365.9800, found 365.9792.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 10:1).

m.p.: 164.2 – 165.5 °C.

2-((4-Chlorophenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (13b)



13b

Following the general procedure for C(sp^3)−H oxidation using 2-((4-chlorophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **13a** (154 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (127 mg, 0.39 mmol, 79%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 8.00 – 7.94 (m, 1H), 7.54 – 7.45 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 4.23 (t, *J* = 6.2 Hz, 2H), 3.14 (t, *J* = 6.2 Hz, 2H).

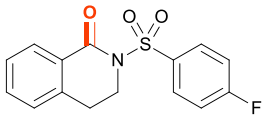
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 140.5, 139.3, 137.6, 133.8, 130.2, 129.3, 129.2, 128.0, 127.7, 127.6, 44.9, 29.0.

HRMS (ESI+): *m/z* calculated for $C_{15}H_{13}ClNO_3S$ $[M+H]^+$: 322.0305, found 322.0308.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 10:1).

m.p.: 135.6 – 136.9 °C.

2-((4-Fluorophenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (14b)



14b

Following the general procedure for C(sp^3)–H oxidation using 2-((4-fluorophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **14a** (146 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (130 mg, 0.42 mmol, 85%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19-8.09 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.16 (m, 3H), 4.23 (t, *J* = 6.2 Hz, 2H), 3.14 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 164.6, 163.6, 139.4, 135.1 (d, *J* = 4.0 Hz), 133.8, 131.7 (d, *J* = 10.1 Hz), 129.3, 128.1, 127.6 (d, *J* = 10.1 Hz), 116.2 (d, *J* = 25.2 Hz), 44.9, 29.0.

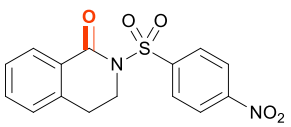
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.23.

HRMS (ESI+): *m/z* calculated for $C_{15}H_{13}FNO_3S$ $[M+H]^+$: 306.0600, found 306.0593.

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 10:1).

m.p.: 117.1 – 118.3 °C.

2-((4-Nitrophenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (15b)



15b

Following the general procedure for C(sp^3)−H oxidation using 2-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **15a** (159 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 6:1) provided the title compound as a white solid (106 mg, 0.32 mmol, 64%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.35 (m, 2H), 8.32 – 8.24 (m, 2H), 7.99 – 7.90 (m, 1H), 7.51 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 4.27 (t, *J* = 6.2 Hz, 2H), 3.18 (t, *J* = 6.2 Hz, 2H).

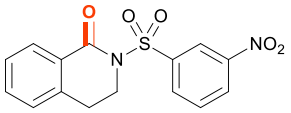
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 150.7, 144.7, 139.3, 134.2, 130.2, 129.4, 127.8, 127.7, 127.7, 124.1, 45.1, 29.0.

HRMS (ESI+): *m*/*z* calculated for $C_{15}H_{13}N_2O_5S$ $[M+H]^+$: 333.0545, found 333.0555.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 5:1).

m.p.: 193.8 – 195.0 °C.

2-((3-Nitrophenyl)sulfonyl)-3,4-dihydroisoquinolin-1(2H)-one (16b)



16b

Following the general procedure for C(sp^3)−H oxidation using 2-((3-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **16a** (159 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 7:1) provided the title compound as a white solid (115 mg, 0.34 mmol, 69%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (t, *J* = 1.9 Hz, 1H), 8.53-8.42 (m, 2H), 7.99 – 7.93 (m, 1H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 4.29 (t, *J* = 6.2 Hz, 2H), 3.18 (t, *J* = 6.2 Hz, 2H).

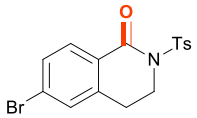
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 148.2, 141.2, 139.4, 134.9, 134.2, 130.2, 129.4, 128.3, 127.8, 127.71, 127.69, 123.8, 45.1, 29.0.

HRMS (ESI+): *m*/*z* calculated for $C_{15}H_{13}N_2O_5S$ $[M+H]^+$: 333.0545, found 333.0552.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 5:1).

m.p.: 162.2 – 163.0 °C.

6-Bromo-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (17b)



17b

Following the general procedure for C(sp^3)–H oxidation using 6-bromo-2-tosyl-1,2,3,4-tetrahydroisoquinoline **17a** (183 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 10:1) provided the title compound as a white solid (167 mg, 0.44 mmol, 88%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.41-7.37 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.26 – 4.15 (m, 2H), 3.10 (t, *J* = 6.2 Hz, 2H), 2.43 (s, 3H).

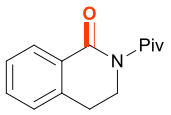
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.9, 145.1, 141.1, 136.05, 131.0, 130.9, 130.53, 129.6, 128.74, 128.70, 127.3, 44.7, 28.8, 21.8.

HRMS (ESI+): *m*/*z* calculated for $C_{16}H_{15}BrNO_3S$ $[M+H]^+$: 379.9956, found 379.9948.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 5:1).

m.p.: 173.2 – 174.2 °C.

2-Pivaloyl-3,4-dihydroisoquinolin-1(2H)-one (18b)



18b

Following the general procedure for C(sp^3)–H oxidation using 1-(3,4-dihydroisoquinolin-2(1H)-yl)-2,2-dimethylpropan-1-one **18a** (109 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 20:1) provided the title compound as a white solid (95 mg, 0.41 mmol, 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.43 – 7.35 (m, 1H), 7.31 – 7.24 (m, 1H), 3.94 – 3.70 (m, 2H), 3.06 (t, *J* = 12 Hz, 2H), 1.40 (s, 9H).

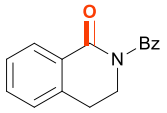
^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.3, 165.9, 140.1, 133.3, 129.3, 128.7, 127.6, 127.4, 46.0, 43.8, 28.8, 28.0.

HRMS (ESI+): *m*/*z* calculated for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found 232.1346.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 5:1).

m.p.: 168.2 – 169.0 °C.

2-Benzoyl-3,4-dihydroisoquinolin-1(2H)-one (19b)



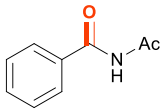
19b

Following the general procedure for C(sp^3)–H oxidation using *N*-benzoyl-1,2,3,4-tetrahydroisoquinoline **19a** (119 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 20:1) provided the title compound as a white solid (106 mg, 0.42 mmol, 84%). Spectral data are consistent with those reported in the literature.[S12]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.56 –7.49 (m, 1H), 7.48 – 7.37 (m, 4H), 4.0 (t, *J* = 6.1 Hz, 2H), 3.2 (d, *J* = 6.2 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 174.0, 165.1, 141.0, 136.3, 133.7, 131.4, 128.6, 128.13, 128.08, 128.04, 127.7, 127.1, 44.2, 27.6.

***N*-acetylbenzamide (20b)**



20b

Following the general procedure for C(sp^3)–H oxidation using *N*-benzylacetamide **20a** (74.6 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (75.1 mg, 0.46 mmol, 92%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 2.62 (s, 3H).

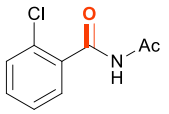
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 165.9, 133.3, 132.8, 129.1, 127.9, 25.7.

HRMS (ESI+): *m*/*z* calculated for $C_9H_{10}NO_2$ $[M+H]^+$: 164.0712, found 164.0705.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 10:1).

m.p.: 142.9 – 144.2 °C.

***N*-acetyl-2-chlorobenzamide (21b)**



21b

Following the general procedure for C(sp^3)–H oxidation using *N*-(2-chlorobenzyl)acetamide **21a** (91.8 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (86.0 mg, 0.44 mmol, 87%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 2H), 7.42 – 7.36 (m, 1H), 2.58 (s, 3H).

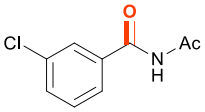
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.3, 165.4, 133.8, 132.8, 131.0, 130.8, 130.2, 127.5, 25.7.

HRMS (ESI+): *m*/*z* calculated for $C_9H_9ClNO_2$ $[M+H]^+$: 198.0322, found 198.0315.

***R*$_f$**: 0.30 (Petroleum ether:EtOAc 10:1).

m.p.: 104 – 106 °C.

***N*-acetyl-3-chlorobenzamide (22b)**



22b

Following the general procedure for C(sp^3)–H oxidation using N-(3-chlorobenzyl)acetamide **22a** (91.8 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (93.0 mg, 0.47 mmol, 94%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.10 (s, 1H), 7.90 (s, 1H), 7.76 (d, *J* = 7.8 Hz,

1H), 7.60 – 7.55 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 2.61 (s, 3H).

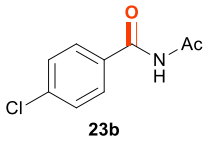
^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.9, 164.8, 135.4, 134.5, 133.4, 130.4, 128.4, 125.9, 25.8.

HRMS (ESI+): *m*/*z* calculated for $C_9H_9ClNO_2$ $[M+H]^+$: 198.0322, found 198.0318.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 10:1).

m.p.: 105 – 106 °C

***N*-acetyl-4-chlorobenzamide (23b)**



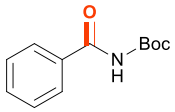
23b

Following the general procedure for C(sp^3)−H oxidation using *N*-(4-chlorobenzyl)acetamide **23a** (91.8 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (85.0 mg, 0.43 mmol, 86%). Spectral data are consistent with those reported in the literature.[S14]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.85 – 7.79 (m, 2H), 7.51 – 7.46 (m, 2H), 2.61 (s, 3H).

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 10:1).

***tert*-Butyl benzoylcarbamate (24b)**



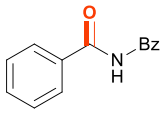
24b

Following the general procedure for C(sp^3)−H oxidation using *N*-*tert*-butoxycarbonylbenzylamine **24a** (104 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 10:1) provided the title compound as a white solid (80 mg, 0.325 mmol, 65%). Spectral data are consistent with those reported in the literature.[S15]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.83 – 7.81(m, 2H), 7.60 – 7.55 (m, 1H), 7.51 – 7.43 (m, 2H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.4, 149.9, 133.5, 132.9, 128.9, 127.7, 83.0, 28.1.

_N_-Benzoyl-benzamide (25b)



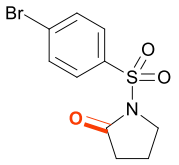
25b

Following the general procedure for C(sp^3)–H oxidation using *N*-benzylbenzamide **25a** (106 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 10:1) provided the title compound as a white solid (80 mg, 0.355 mmol, 71%). Spectral data are consistent with those reported in the literature.[S16]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 7.93 – 7.76(m, 4 H), 7.64 – 7.56 (m, 2H), 7.54 – 7.44 (m, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 166.6, 133.5, 133.2, 129.0, 128.1.

1-((4-Bromophenyl)sulfonyl)pyrrolidin-2-one (26b)



26b

Following the general procedure for C(sp^3)–H oxidation using 1-((4-bromophenyl)sulfonyl)pyrrolidine **26a** (145 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (112 mg, 0.37 mmol, 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.73 – 7.64 (m, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 2.45 (t, *J* = 8.1 Hz, 2H), 2.14-2.02 (m, 2H).

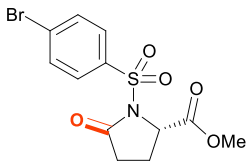
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 137.1, 132.5, 129.7, 129.5, 47.4, 32.3, 18.4.

HRMS (ESI+): *m/z* calculated for $C_{10}H_{11}BrNO_3S$ $[M+H]^+$: 303.9643, found 303.9638.

***R*$_f$**: 0.20 (Petroleum ether:EtOAc 10:1).

m.p.: 168.1 – 169.1 °C.

Methyl (*S*)-1-((4-bromophenyl)sulfonyl)-5-oxopyrrolidine-2-carboxylate (27b)



27b

Following the general procedure for C(sp^3)–H oxidation using (*S*)-methyl 1-((4-bromophenyl)sulfonyl)pyrrolidine-2-carboxylate **27a** (174 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 6:1) provided the title compound as a white solid (112 mg, 0.31 mmol, 62%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.72 – 7.65 (m, 2H), 4.95 – 4.87 (m, 1H), 3.80 (s, 3H), 2.63 – 2.38 (m, 3H), 2.18 – 2.07 (m, 1H).

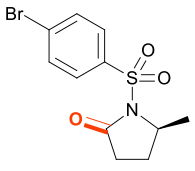
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 171.2, 136.8, 132.1, 130.8, 129.8, 59.4, 53.1, 30.5, 23.5.

HRMS (ESI+): *m/z* calculated for $C_{12}H_{13}BrNO_5S$ $[M+H]^+$: 361.9698, found 361.9690.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 3:1).

m.p.: 151.7 – 153.5 °C.

(*S*)-1-((4-Bromophenyl)sulfonyl)-5-methylpyrrolidin-2-one (28b)



28b

Following the general procedure for C(sp^3)–H oxidation using (*S*)-1-((4-bromophenyl)sulfonyl)-2-methylpyrrolidine **28a** (152 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 8:1) provided

the title compound as a white solid (89.1 mg, 0.28 mmol, 56%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 4.56-4.49 (m, 1H), 2.61-2.52 (m, 1H), 2.37 (ddd, *J* = 17.5, 9.3, 2.5 Hz, 1H), 2.33 – 2.23 (m, 1H), 1.77 – 1.70 (m, 1H), 1.46 (d, *J* = 6.4 Hz, 3H).

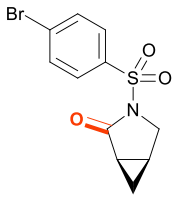
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 138.1, 132.3, 129.9, 129.3, 56.6, 30.6, 26.7, 21.6.

HRMS (ESI+): *m*/*z* calculated for $C_{11}H_{13}BrNO_3S$ $[M+H]^+$: 317.9800, found 317.9792.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 5:1).

m.p.: 142.9 – 144.2 °C.

(1*R*,5*S*)-3-((4-bromophenyl)sulfonyl)-3-azabicyclo[3.1.0]hexan-2-one (29b)



29b

Following the general procedure for C(sp^3)−H oxidation using (1*R*,5*S*)-3-((4-bromophenyl)sulfonyl)-3-azabicyclo[3.1.0]hexane **29a** (151 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 8:1) provided the title compound as a white solid (109 mg, 0.34 mmol, 69%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2H), 7.72 – 7.63 (m, 2H), 3.99 – 3.92 (m, 1H), 3.83 (dd, *J* = 10.1, 5.6 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.94-1.87 (m, 1H), 1.29 – 1.19 (m, 1H), 0.87 – 0.77 (m, 1H).

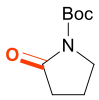
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 137.0, 132.5, 129.6, 129.4, 48.8, 20.9, 12.9, 12.4.

HRMS (ESI+): *m*/*z* calculated for $C_{11}H_{11}BrNO_3S$ $[M+H]^+$: 315.9643, found 315.9639.

***R*$_f$**: 0.33 (Petroleum ether:EtOAc 5:1).

m.p.: 165.4 – 166.5 °C.

***tert*-Butyl 2-oxopyrrolidine-1-carboxylate (30b)**



30b

Following the general procedure for C(sp^3)–H oxidation using *N*-Boc-pyrrolidine **30a** (86 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 15:1) provided the title compound as a white solid (74 mg, 0.40 mmol, 80%). Spectral data are consistent with those reported in the literature.[S17]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.71 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 8.1 Hz, 2H), 2.01 – 1.91 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 150.3, 82.8, 46.6, 33.0, 28.1, 17.5.

***N*-Benzoyl-2-pyrrolidinon (31b)**

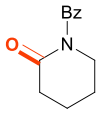
31b

Following the general procedure for C(sp^3)–H oxidation using *N*-benzoylpyrrolidine **31a** (88 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 10:1) provided the title compound as a white solid (81 mg, 0.43 mmol, 86%). Spectral data are consistent with those reported in the literature.[S18]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 3.96 (t, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.07 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.6, 170.8, 134.4, 132.0, 129.0, 127.9, 46.6, 33.4, 17.8.

***N*-Benzoyl-6-piperidone (32b)**



32b

Following the general procedure for C(sp3)–H oxidation using *N*-benzoylpiperidine

32a (94 mg, 0.50 mmol) and purified by silica gel column chromatography (Petroleum ether:EtOAc 10:1) provided the title compound as a white solid (80 mg, 0.395 mmol, 79%). Spectral data are consistent with those reported in the literature.[S19]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.31 (m, 2H), 3.80 (t, *J* = 5.7 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.02 – 1.88 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.8, 173.6, 136.2, 131.6, 128.20, 127.96, 46.2, 34.7, 22.9, 21.5.

Scalable Oxidation Experiment

[Co(MPP)(OTf)(CH_3CN)](OTf) (**1**) (65.6 mg, 8.0 × 10^{-2} mmol) and (1*R*,5*S*)-3-((4-bromophenyl)sulfonyl)-3-azabicyclo[3.1.0]hexane (**29a**, 2.42 g, 8.0 mmol) were added to a 25 mL Schlenk tube in CH_3CN (15 mL). Then *m*-CPBA (2.76 g, 16 mmol, 2.0 equiv) was added in one batch under aerobic conditions. The final concentrations of reagents were 5.3 mM cobalt catalyst, 1.1 M *m*-CPBA and 0.53 M substrate. After stirring the reaction mixture for 5 h, the resulting solution was concentrated to a minimum amount of solvent. The residue was dissolved in DCM (~20 mL) and washed sequentially with sat. aq. Na_2SO_3 and sat. aq. $NaHCO_3$. The aqueous layer was extracted with DCM (3 × 20 mL) and the combined organic layer was dried over Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

Stoichiometric Oxidation of Adamantane

[Co(MPP)(OTf)(CH_3CN)](OTf) (**1**) (5.0×10^{-4} mmol, 1.0 equiv) and adamantane (68 mg, 0.50 mmol, 1000 equiv) were added to a Schlenk tube in CH_3CN. Then *m*-CPBA (0.01 mmol, 20 equiv) was added in one batch under aerobic conditions. The final concentrations of reagents were 0.25 mM cobalt catalyst, 5.0 mM *m*-CPBA and 250 mM substrate. After stirring the reaction mixture for 8 h at room temperature, an internal standard (decane) was added. The reaction solution was filtered through a basic alumina plug and analyzed by GC. Products were identified by comparing with authentic samples, and product yields were determined by comparison with the internal standard integration. The $3^o/2^o$ ratio is derived from the amount of 1-adamantanol divided by the amounts of 2-adamantanol and 2-adamantanone and multiplied by 3 to correct for the higher number of secondary C–H bonds.

Determination of Kinetic Isotope Effect

[Co(MPP)(OTf)(CH_3CN)](OTf) (**1**) (0.60 mL, 1.0×10^{-3} mmol, 1.37 mg/mL in CH_3CN) and a mixture of cyclohexane and cyclohexane-d_{12} (total: 1.0 mmol) with various molar ratios (1/1, 1/2, 1/3, 1/4, 1/5 and 1/6) were added to a Schlenk tube in CH_3CN (1.4 mL). Then *m*-CPBA (2.0×10^{-2} mmol) was added in one batch under aerobic conditions. After stirring the reaction mixture for 8 h at room temperature, decane was added as an internal standard. The resulting solution was then filtered through a pad of silica gel washing with ethyl acetate, and yields of cyclohexanol and cyclohexanol-d_{12} were determined by GC and GC-MS. All the reactions were run three times, and the data reported was the average of three runs.

References

(S1) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*. 6th edn, Pergamon Press, Oxford, U.K. 2009.

(S2) Hagen, K. S. Iron(II) Triflate Salts as Convenient Substitutes for Perchlorate Salts: Crystal Structures of $[Fe(H_2O)_6](CF_3SO_3)_2$ and $Fe(MeCN)_4(CF_3SO_3)_2$. *Inorg. Chem*. **2000**, *39*, 5867–5869.

(S3) Chen, J.; Zhang, J.; Sun, Y.; Xu, Y.; Wang, B. Mononuclear Non-Heme Manganese-Catalyzed Enantioselective *cis*-Dihydroxylation of Alkenes Modeling Rieske Dioxygenases. *J. Am. Chem. Soc*. **2023**, *145*, 27626–27638.

(S4) Chen, J.; Song, W.; Yao J.; Wang, B. Hydrogen Bonding-Assisted and Nonheme Manganese-Catalyzed Remote Hydroxylation of C–H Bonds in Nitrogen-Containing Molecules. *J. Am. Chem. Soc.* **2023**, *145*, 5456–5466.

(S5) England, J.; Britovsek, G.; Rabadia N. Ligand Topology Variations and the Importance of Ligand Field Strength in Non-Heme Iron Catalyzed Oxidations of Alkanes. *Inorg. Chem.* **2007**, *46*, 3752–3767.

(S6) Xia, Q.; Wang, Q.; Yan, C. Merging Photoredox with Brønsted Acid Catalysis: The Cross-Dehydrogenative C−O Coupling for sp^3 C–H Bond Peroxidation. *Chem. Eur. J.* **2017**, *23*, 10871–10877.

(S7) J. Pagliero R.; Mercado R.; McCracken V. Rapid and Facile Synthesis of N-benzenesulfonyl Derivatives of Heterocycles and their Antimicrobial Properties. *Lett. Drug. Des. Discov.* **2011**, *8*, 778–791.

(S8) Chang, Z.; Huang, J.; Wang, S.; Chen, G.; Zhao, H.; Wang, R.; Zhao, D. Copper Catalyzed Late-Stage C(sp^3)–H Functionalization of Nitrogen Heterocycles. *Nat. Commun*. **2021**, *12*, No. 4342.

(S9) Shi, Z.; Zhao, Q.; Yin, D. Synthesis of Tetrahydroisoquinolines Through $TiCl_4$-Mediated Cyclization and Et_3SiH Reduction. *Chin. Chem. Lett*. **2020**, *31*, 729–732.

(S10) Huang J; Sun, F; Liu, W. Manganese-Catalyzed Deoxygenation of Secondary and Tertiary Amides Under Mild Conditions. *J. Catal.* **2023**, *423*, 19–25.

(S11) Ji, Y.; Li, J.; Li, C.; Qu, S.; Zhang, B. Manganese-Catalyzed N–F Bond Activation for Hydroamination and Carboamination of Alkenes. *Org. Let*. **2020**, *23*, 207–212.

(S12) Geng, P.; Tang, Y.; Pan, G.; Wang, W.; Hu, J.; Cai, Y. AgC_3N_4-Based Heterogeneous Photocatalyst for Visible Light Mediated Aerobic Benzylic C–H Oxygenations. *Green Chem.* **2019**, *21*, 6116–6122.

(S13) Morimoto, T.; Fujioka, M.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. Rh(I)-Catalyzed CO Gas-Free Carbonylative Cyclization of Organic Halides with Tethered Nucleophiles using Aldehydes as a Substitute for Carbon Monoxide. *J. Organomet. Chem.* **2007**, *692*, 625–634.

(S14) Hu, Y.; Zhou, L.; Lu, W. Transition-Metal and Halogen-Free Oxidation of Benzylic sp^3 C–H Bonds to Carbonyl Groups using Potassium Persulfate. *Synthesis*. **2017**, *49*, 4007–4016.

(S15) Kanbayashi, N.; Takenaka, K.; Okamura, T.; Onitsuka, K. Asymmetric Auto-Tandem Catalysis with a Planar-Chiral Ruthenium Complex: Sequential Allylic Amidation and Atom-Transfer Radical Cyclization. *Angew. Chem., Int. Ed.* **2013**, *52*, 4897–4901.

(S16) Digwal, C. S.; Yadav, U.; Sri Ramya, P. V.; Sana, S.; Swain, B.; Kamal, A. Vanadium-Catalyzed Oxidative C(CO)–C(CO) Bond Cleavage for C–N Bond Formation: One-Pot Domino Transformation of 1,2-Diketones and Amidines into Imides and Amides. *J. Org. Chem.* **2017**, *82*, 7332–7345.

(S17) Laudadio, G.; Govaerts, S.; Wang, Y.; Ravelli, D.; Koolman, H. F.; Fagnoni, M.; Djuric, S. W.; Noël, T. Selective C(sp^3)−H Aerobic Oxidation Enabled by Decatungstate Photocatalysis in Flow. *Angew. Chem., Int. Ed.* **2018**, *57*, 4078–4082.

(S18) Zhang, J.; Hong, S. H. Direct *N*-Acylation of Lactams, Oxazolidinones, and Imidazolidinones with Aldehydes by Shvo's Catalyst. *Org. Lett.* **2012**, *14*, 4646–4649.

(S19) Gigant, N.; Chausset-Boissarie, L.; Belhomme, M.-C.; Poisson, T.; Pannecoucke, X.; Gillaizeau, I. Copper-Catalyzed Direct Arylation of Cyclic Enamides Using Diaryliodonium Salts. *Org. Lett.* **2013**, *15*, 278–281.

Table S1. Crystallographic Data and Structure Refinement for [Co(MPP)(OTf)(CH3CN)](OTf) (**1**)

Identification code	(CCDC 2346530)	
Empirical formula	$C_{32}H_{33}CoF_6N_5O_6S_2$	
Formula weight	820.68	
Temperature (K)	293	
Wavelength (Å)	0.71073	
Crystal system	Orthorhombic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.7317(2) Å	α = 90°
	b = 20.2300(5) Å	β = 90°
	c = 21.9275(5) Å	γ = 90°
Volume (Å)	3873.32(16)	
Z	4	
Calculated density (g cm^{-3})	1.407	
Absorption coefficient (mm^{-1})	0.626	
F(000)	1684	
Crystal size (mm^3)	0.600 × 0.600 × 0.400	
θ range for data collection (°)	3.1 to 26.4°	
Miller index ranges	$-10 \leq h \leq 10$, $-25 \leq k \leq 25$, $-27 \leq l \leq 27$	
Reflections collected	51369	
Independent reflections	7891 [R_{int} = 0.044]	
Completeness to theta = 25.242°	99.5%	
Max. and min. transmission	0.8589 and 1.0000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6781 / 25 / 484	
Goodness-of-fit on F^2	1.052	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0643, wR2 = 0.1088	
R indices (all data)	R1 = 0.0522, wR2 = 0.1022	
Largest diff. peak and hole (e $Å^{-3}$)	0.608 and –0.599	

Table S2. Selected Bond Distances (Å) and Angles (º) for 1 (CCDC 2346530)

Identification code	**1**, CCDC 2346530
Bond Distances (Å)	
Co1-N1	2.181(4)
Co1-N2	2.156(4)
Co1-N3	2.129(5)
Co1-N4	2.114(4)
Co1-N5	2.126(5)
Co1-O1	2.109(4)
Bond Angles (°)	
N1-Co1-N2	83.55(15)
N1-Co1-N3	77.87(18)
N1-Co1-N4	96.92(17)
N1-Co1-N5	169.6(2)
N1-Co1-O1	94.78(16)
N2-Co1-N3	102.55(18)
N2-Co1-N4	78.73(17)
N2-Co1-N5	92.82(18)
N2-Co1-O1	167.79(17)
N3-Co1-N4	174.38(19)
N3-Co1-N5	93.4(2)
N3-Co1-O1	88.85(18)
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N4-Co1-O1	89.50(17)
N5-Co1-O1	90.80(18)

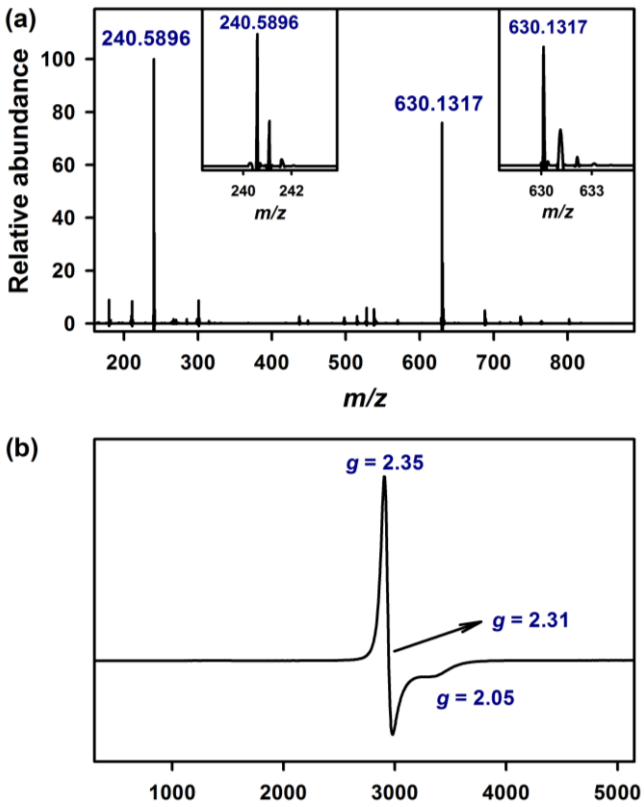


Figure S1. (a) ESI-MS spectrum of [Co(*R*,*R*-MPP)(CH_3CN)(OTf)](OTf) (**1**) in CH_3CN. HRMS peaks at *m*/*z* = 240.5896 and 630.1317 correspond to $[Co^{II}(R,R\text{-MPP})]^{2+}$ (calculated *m*/*z* of 240.5901) and $[Co^{II}(R,R\text{-MPP})(CF_3SO_3)]^{+}$ (calculated *m*/*z* of 630.1323), respectively. Insets show the observed isotope distribution patterns for $[Co^{II}(R,R\text{-MPP})]^{2+}$ at *m*/*z* = 240.5896 (left panel) and $[Co^{II}(R,R\text{-MPP})(CF_3SO_3)]^{+}$ at *m*/*z* = 630.1317 (right panel). (b) X-band EPR spectrum of **(1)** (*g* values = 2.35, 2.31, 2.05) recorded in CH_3CN at 5 K.

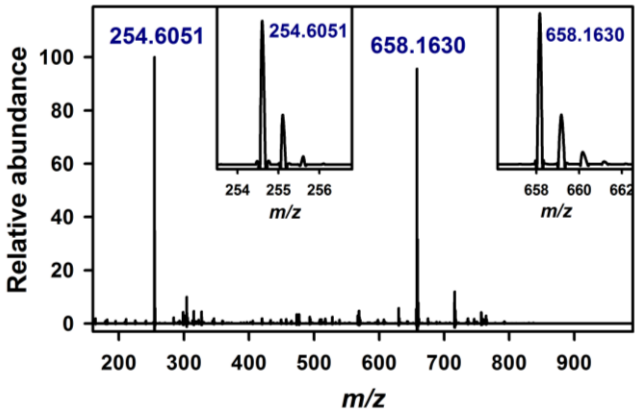


Figure S2. (a) ESI-MS spectrum of [Co(*R*,*R*-6-Me$_2$-MPP)(OTf)$_2$] (**2**) in CH_3CN. HRMS peaks at *m*/*z* = 254.6051 and 658.1630 correspond to $[Co^{II}(R,R\text{-6-Me}_2\text{-MPP})]^{2+}$ (calculated *m*/*z* of 254.6057) and $[Co^{II}(R,R\text{-6-Me}_2\text{-MPP})(CF_3SO_3)]^{+}$ (calculated *m*/*z* of 658.1636), respectively. Insets show the observed isotope distribution patterns for $[Co^{II}(R,R\text{-6-Me}_2\text{-MPP})]^{2+}$ at *m*/*z* = 254.6051 (left panel) and $[Co^{II}(R,R\text{-6-Me}_2\text{-MPP})(CF_3SO_3)]^{+}$ at *m*/*z* = 658.1630 (right panel).

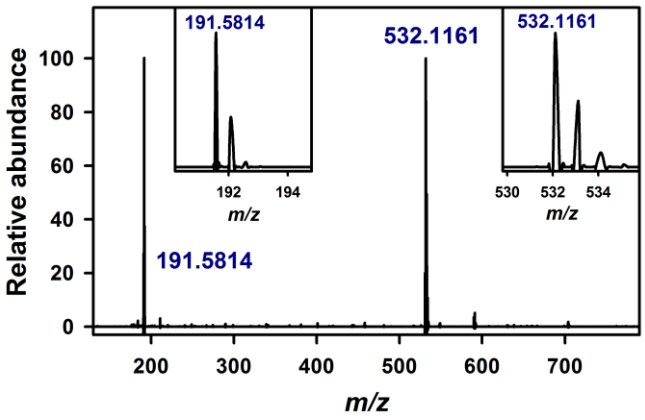


Figure S3. (a) ESI-MS spectrum of [Co(*R*,*R*-BPMCN)$(OTf)_2$] (**3**) in CH_3CN. HRMS peaks at *m*/*z* = 191.5814 and 532.1161 correspond to $[Co^{II}(R,R\text{-BPMCN})]^{2+}$ (calculated *m*/*z* of 191.5823) and $[Co^{II}(R,R\text{-BPMCN})(CF_3SO_3)]^{+}$ (calculated *m*/*z* of 532.1166), respectively. Insets show the observed isotope distribution patterns for $[Co^{II}(R,R\text{-BPMCN})]^{2+}$ at *m*/*z* = 191.5814 (left panel) and $[Co^{II}(R,R\text{-BPMCN})(CF_3SO_3)]^{+}$ at *m*/*z* = 532.1161 (right panel).

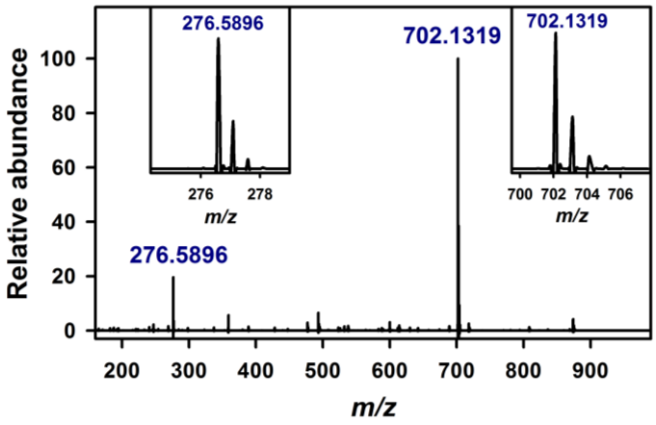


Figure S4. (a) ESI-MS spectrum of [Co(*R*,*R*-BQPN)(OTf)$_2$] (**4**) in CH_3CN. HRMS peaks at *m*/*z* = 276.5896 and 702.1319 correspond to $[Co^{II}(R,R\text{-BQPN})]^{2+}$ (calculated *m*/*z* of 276.5901) and $[Co^{II}(R,R\text{-BQPN})(CF_3SO_3)]^{+}$ (calculated *m*/*z* of 702.1323), respectively. Insets show the observed isotope distribution patterns for $[Co^{II}(R,R\text{-BQPN})]^{2+}$ at *m*/*z* = 276.5896 (left panel) and $[Co^{II}(R,R\text{-BQPN})(CF_3SO_3)]^{+}$ at *m*/*z* = 702.1319 (right panel).

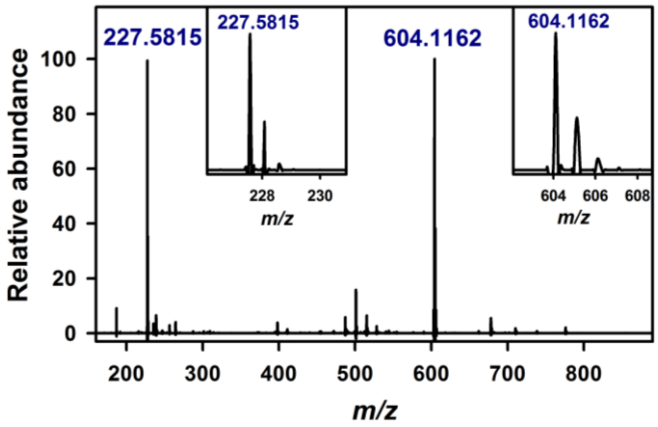
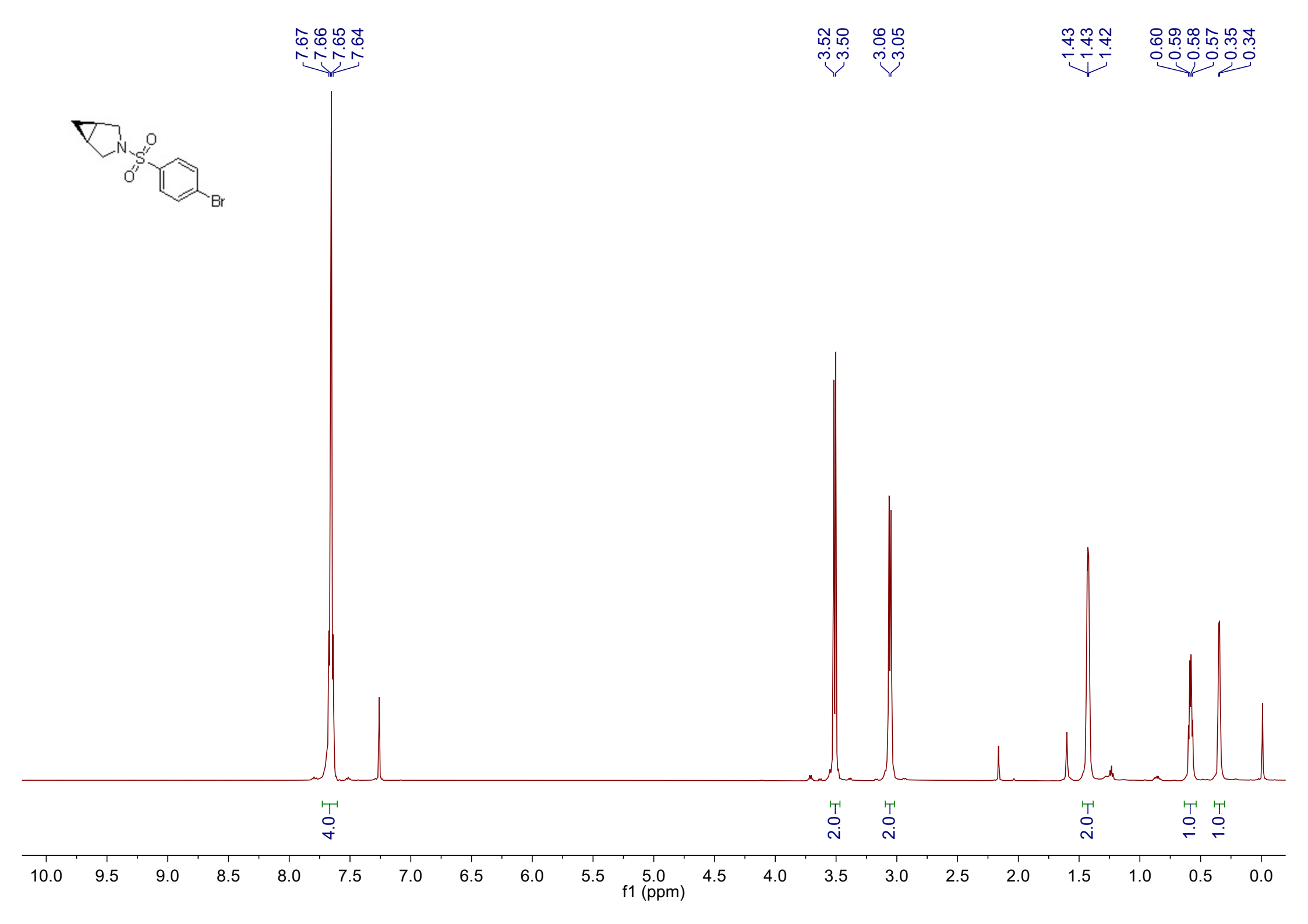


Figure S5. (a) ESI-MS spectrum of [Co(*R*,*R*-BQCN)(OTf)$_2$] (**5**) in CH_3CN. HRMS peaks at *m*/*z* = 227.5815 and 604.1162 correspond to $[Co^{II}(R,R\text{-BQCN})]^{2+}$ (calculated *m*/*z* of 227.5823) and $[Co^{II}(R,R\text{-BQCN})(CF_3SO_3)]^{+}$ (calculated *m*/*z* of 604.1166), respectively. Insets show the observed isotope distribution patterns for $[Co^{II}(R,R\text{-BQCN})]^{2+}$ at *m*/*z* = 227.5815 (left panel) and $[Co^{II}(R,R\text{-BQCN})(CF_3SO_3)]^{+}$ at *m*/*z* = 604.1162 (right panel).

Additional Data: ^{1}H and ^{13}C NMR spectra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0.57
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0.34
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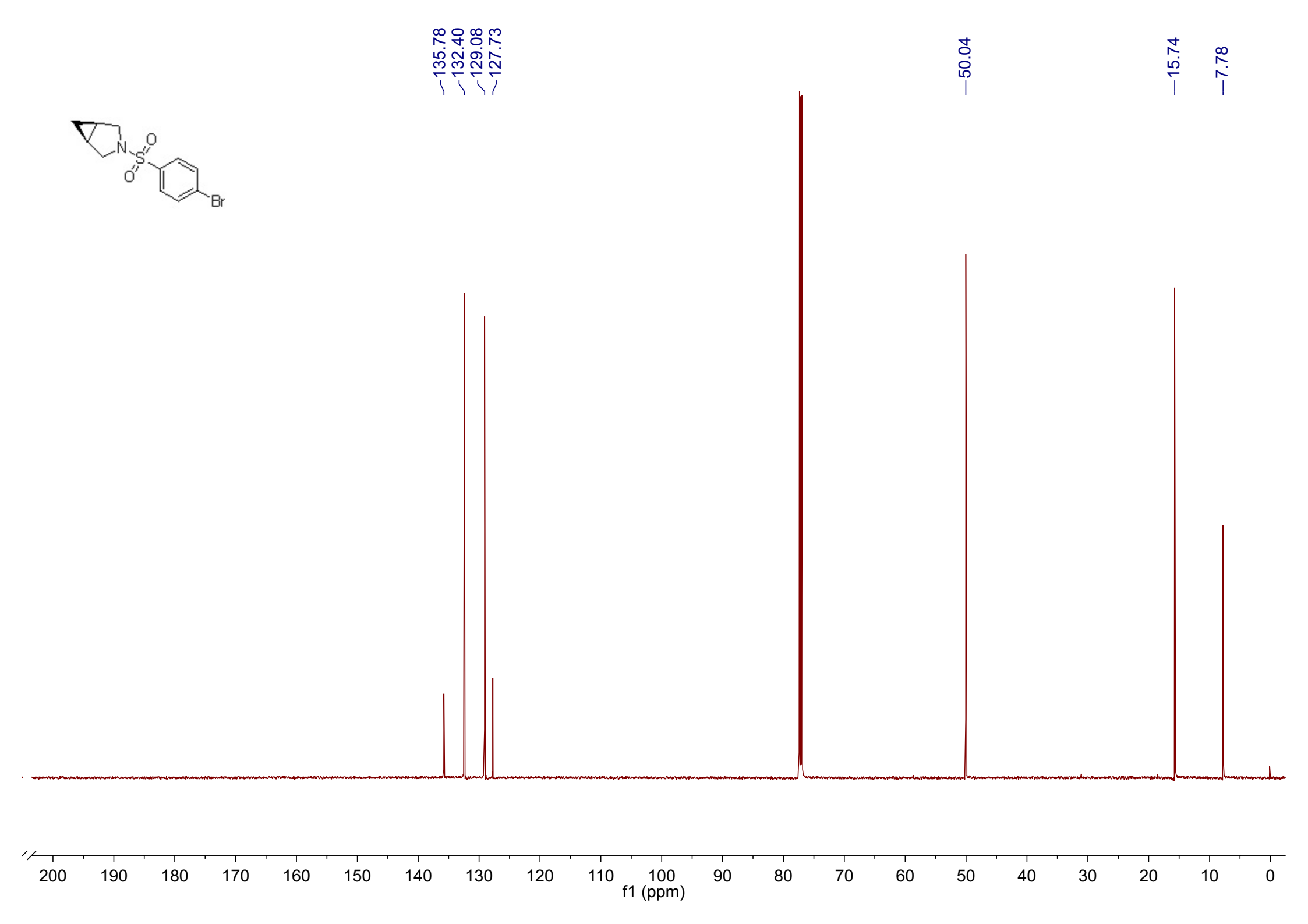
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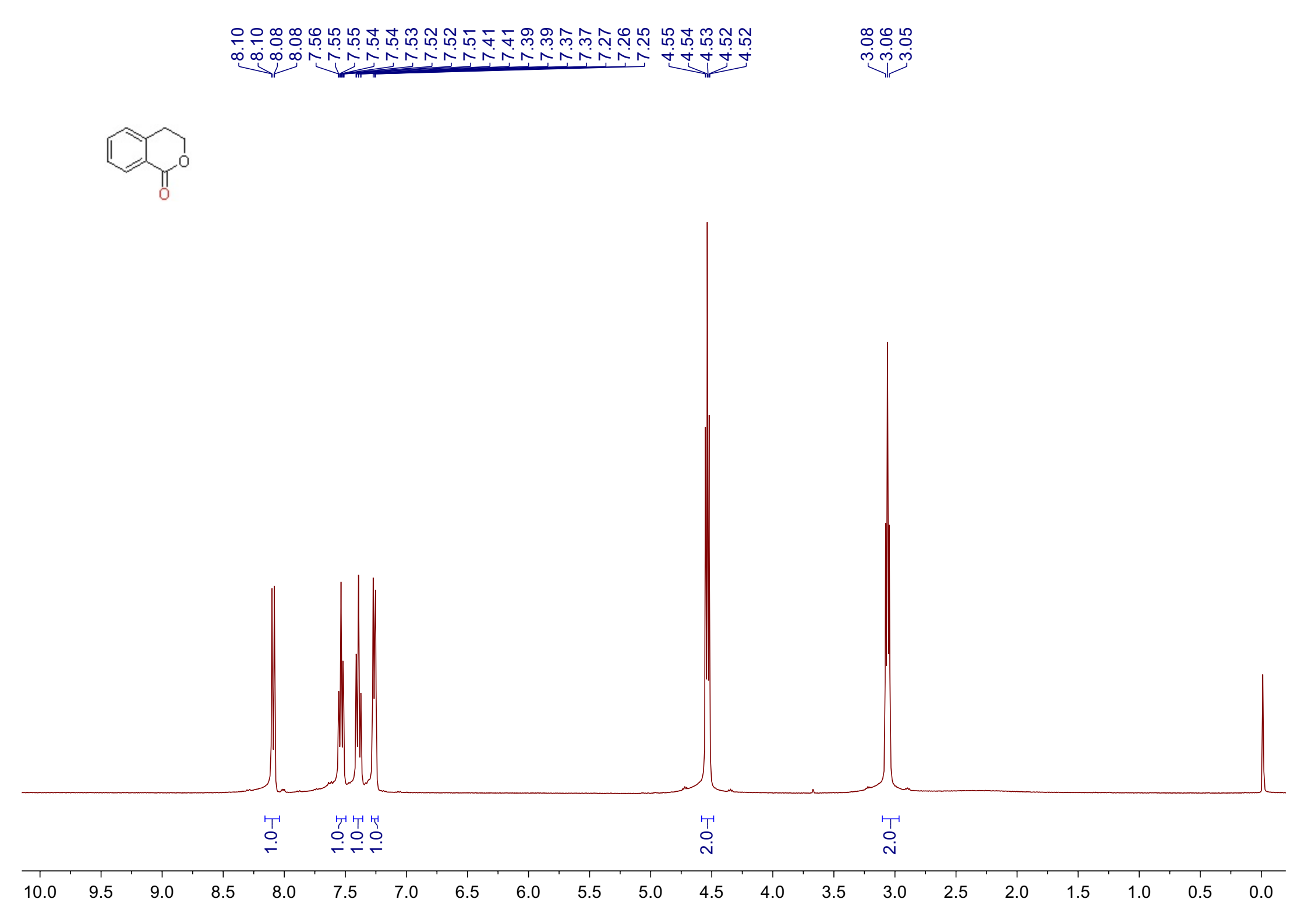
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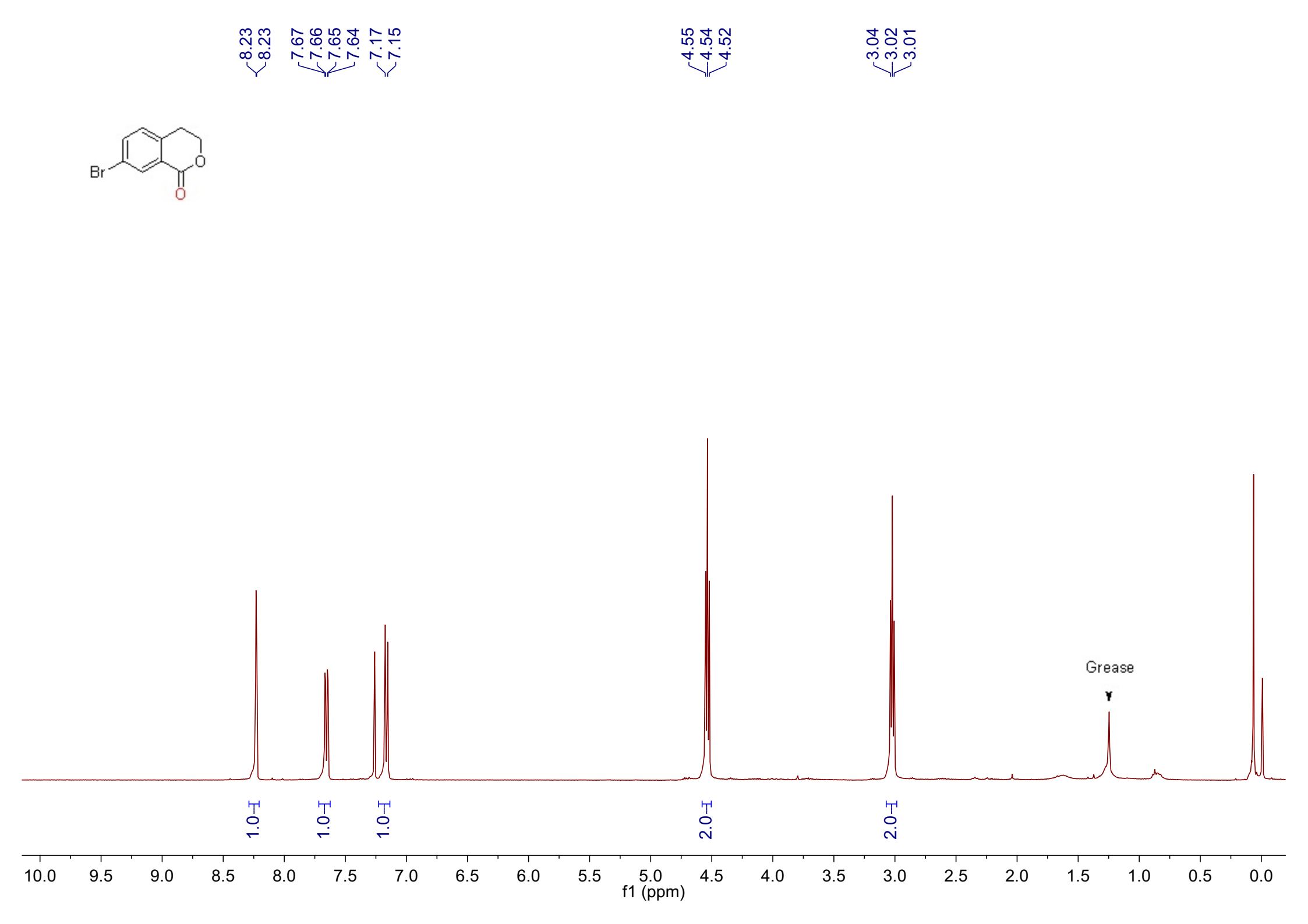
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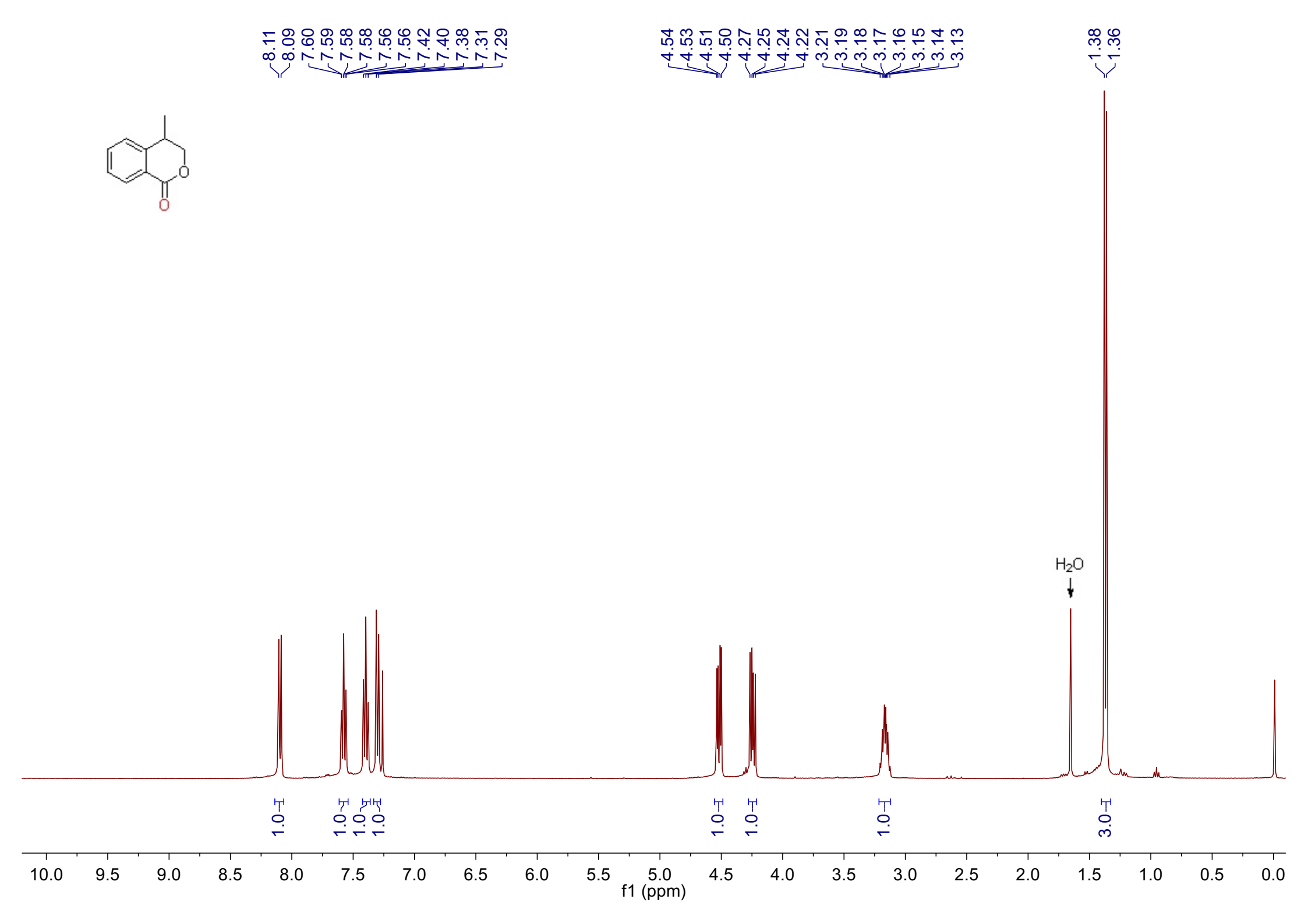
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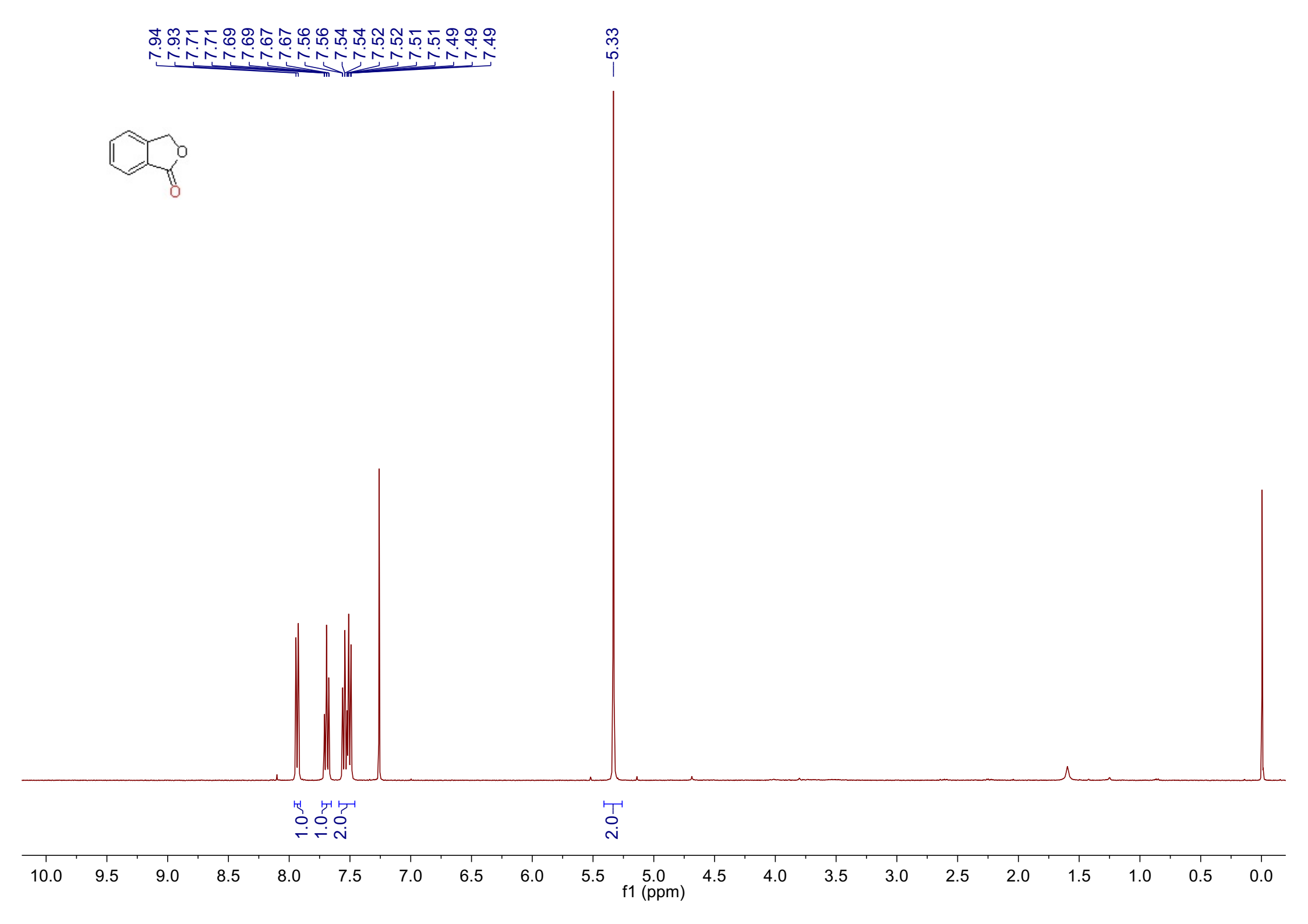
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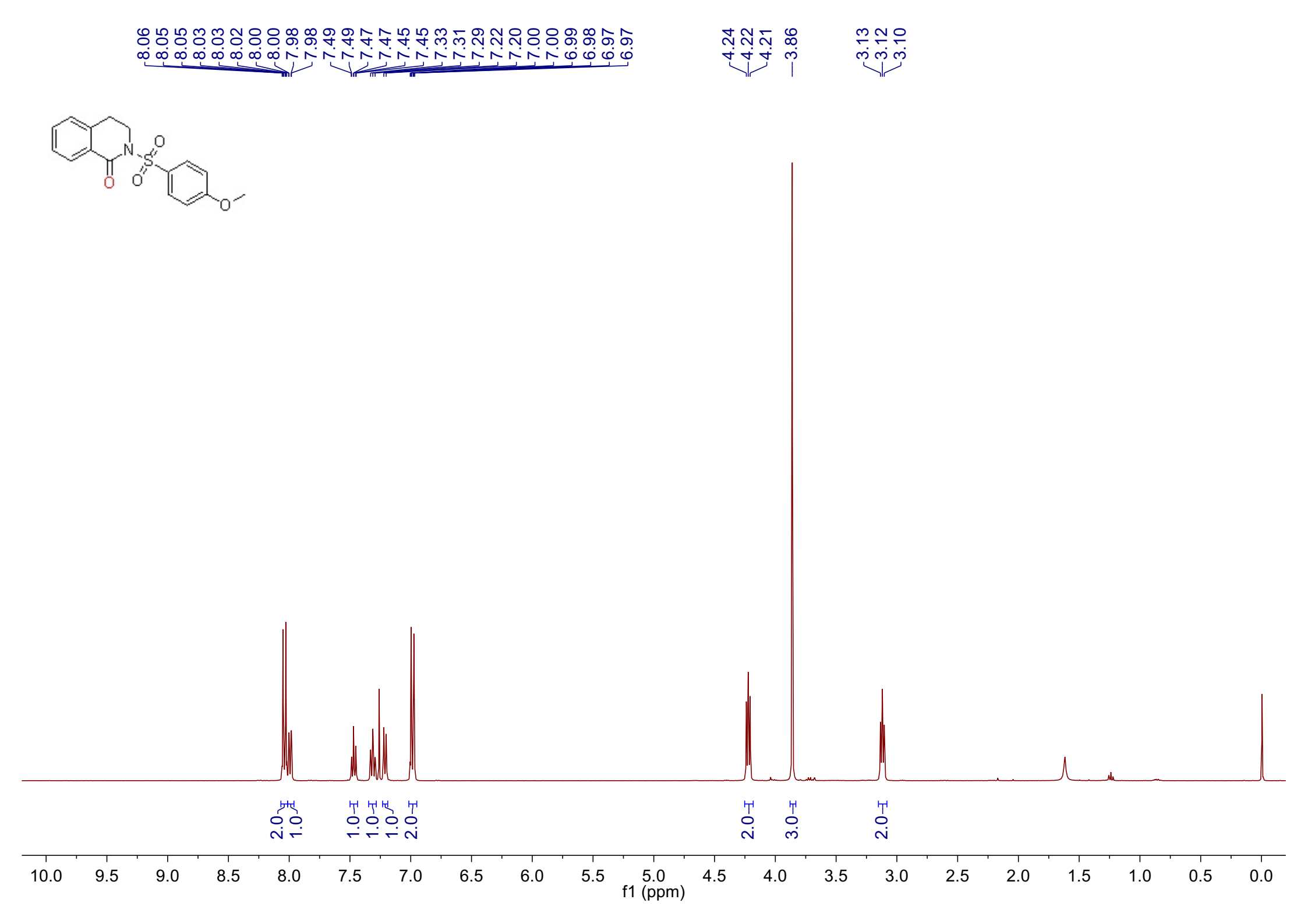
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7.00
6.99
6.98
6.97
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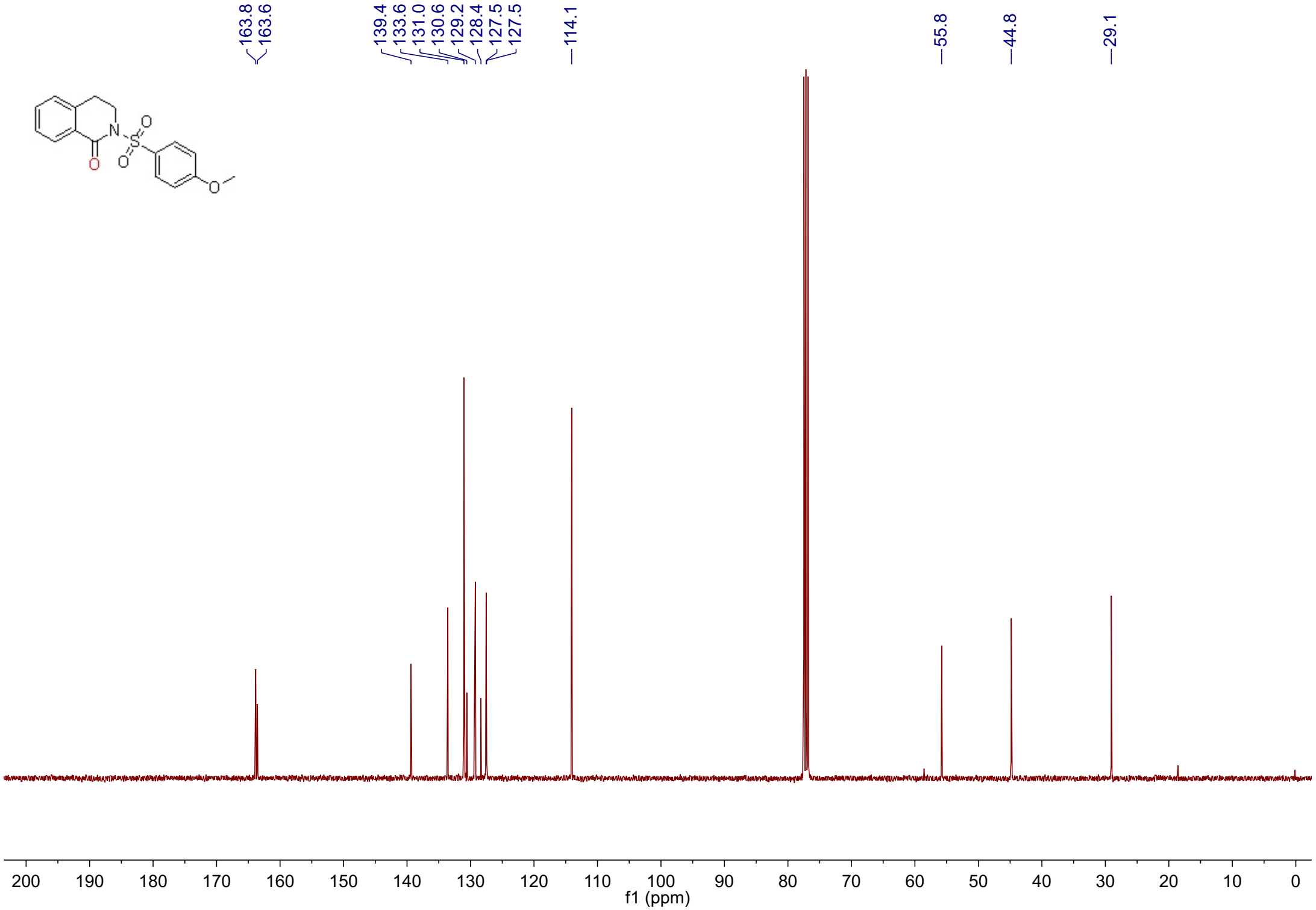
f1 (ppm)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128.4
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127.5
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44.8
29.1
O
N
S
O
O
O
200
190
180
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130
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110
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90
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50
40
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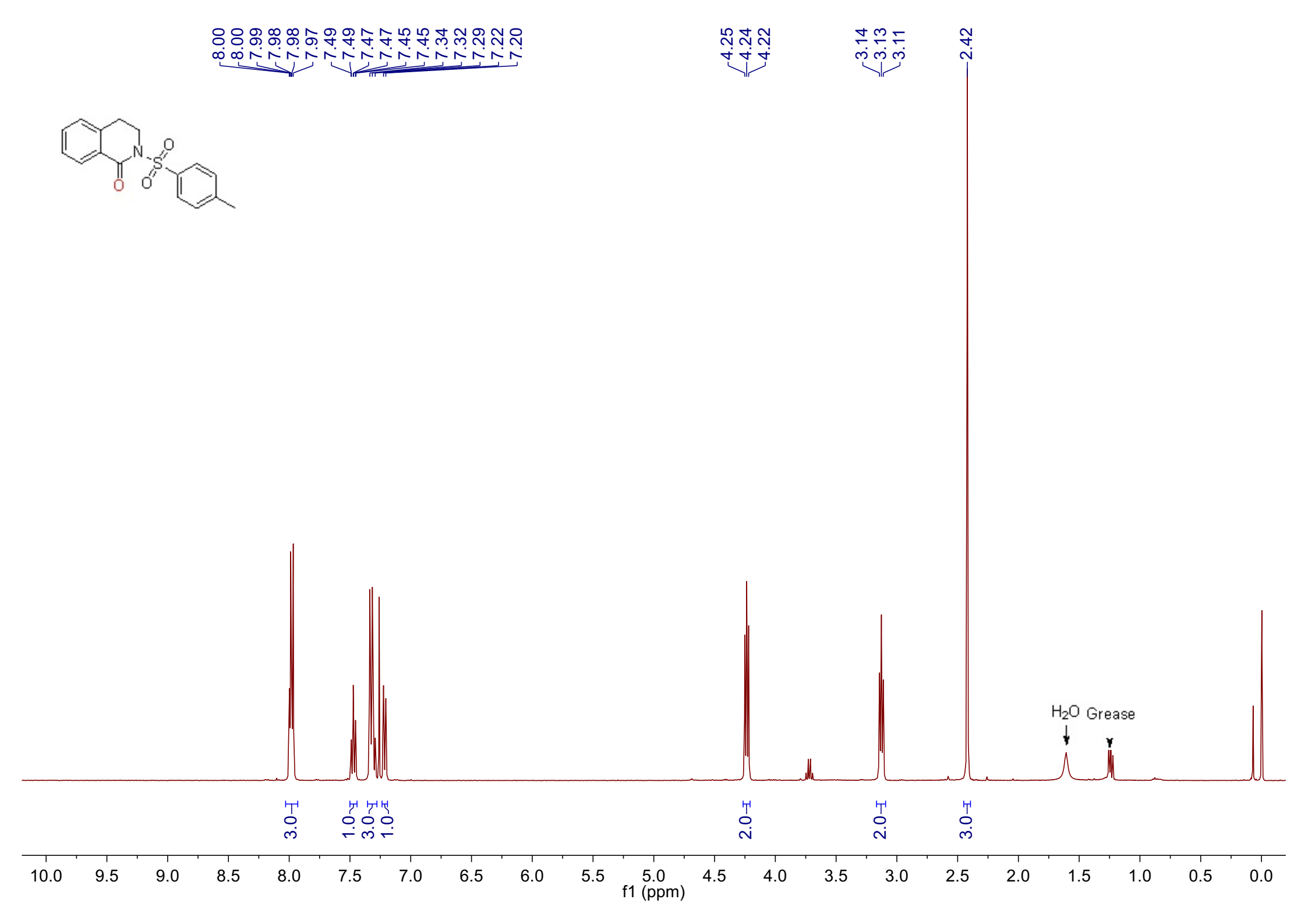
f1 (ppm)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7.47
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7.34
7.32
7.29
7.22
7.20
4.25
4.24
4.22
3.14
3.13
3.11
2.42
H2O
Grease
3.0
1.0
3.0
1.0
2.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
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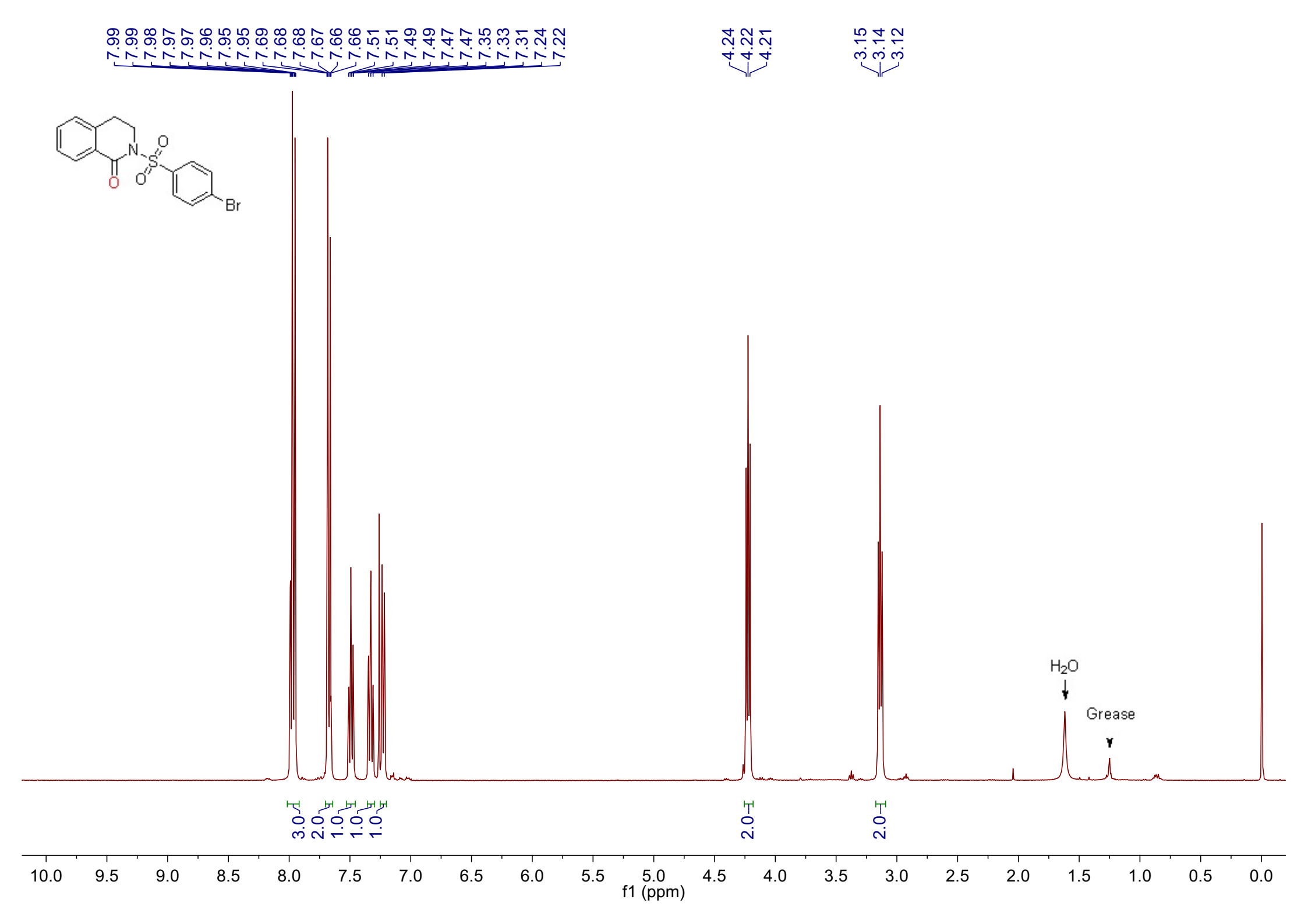
0.0
f1 (ppm)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7.51
7.49
7.49
7.47
7.47
7.35
7.33
7.31
7.24
7.22
4.24
4.22
4.21
3.15
3.14
3.12
O
N
S
O
O
Br
H2O
Grease
3.0
2.0
1.0
1.0
1.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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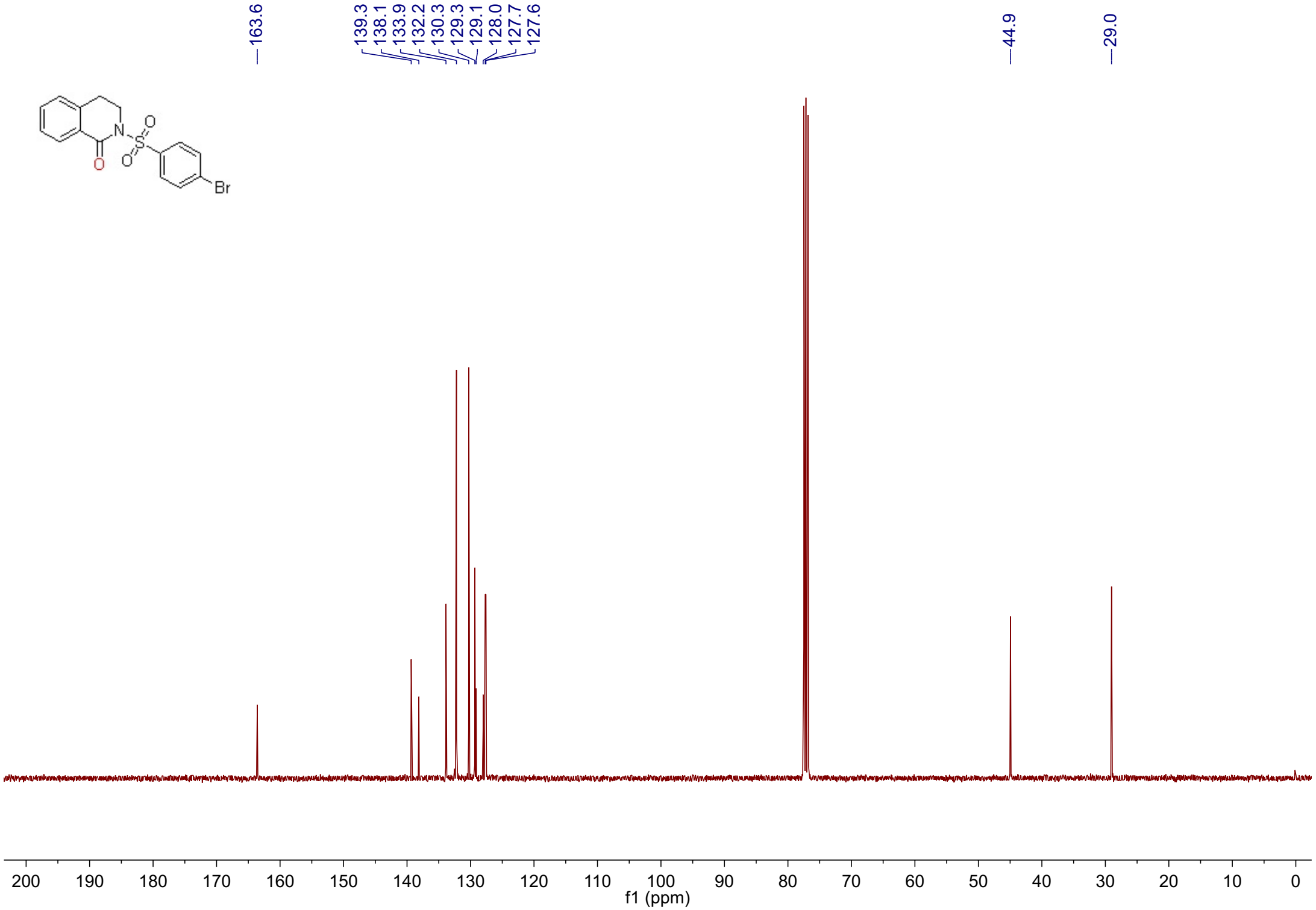
0.0
f1 (ppm)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139.3
138.1
133.9
132.2
130.3
129.3
129.1
128.0
127.7
127.6
44.9
29.0
O
N
S
O
O
Br
200
190
180
170
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130
120
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100
90
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50
40
30
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10
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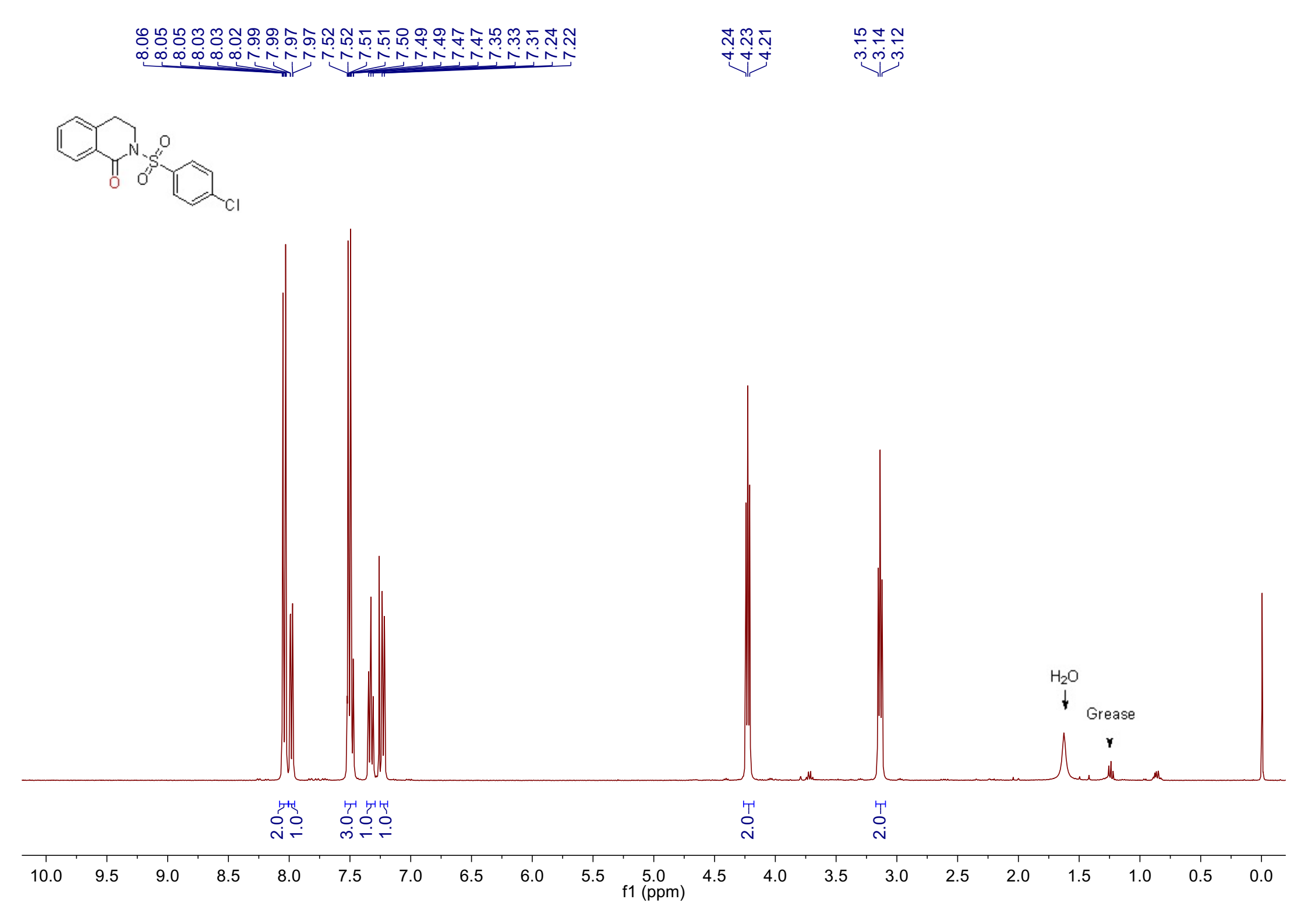
f1 (ppm)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8.05
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8.02
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7.99
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7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.35
7.33
7.31
7.24
7.22
4.24
4.23
4.21
3.15
3.14
3.12
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N
O
O
O
Cl
H2O
Grease
2.0
1.0
3.0
1.0
1.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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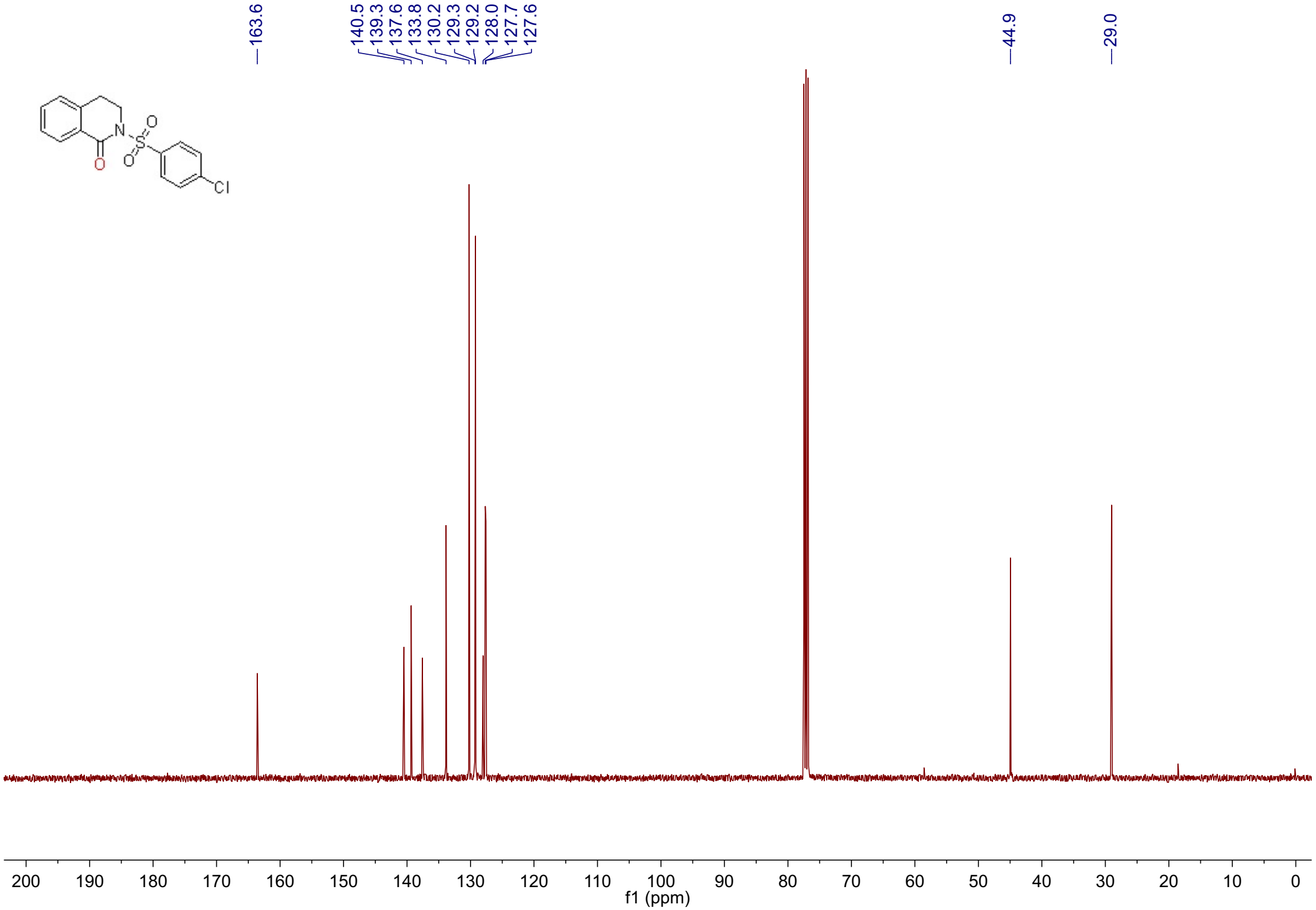
0.0
f1 (ppm)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140.5
139.3
137.6
133.8
130.2
129.3
129.2
128.0
127.7
127.6
44.9
29.0
O
N
S
O
O
Cl
200
190
180
170
160
150
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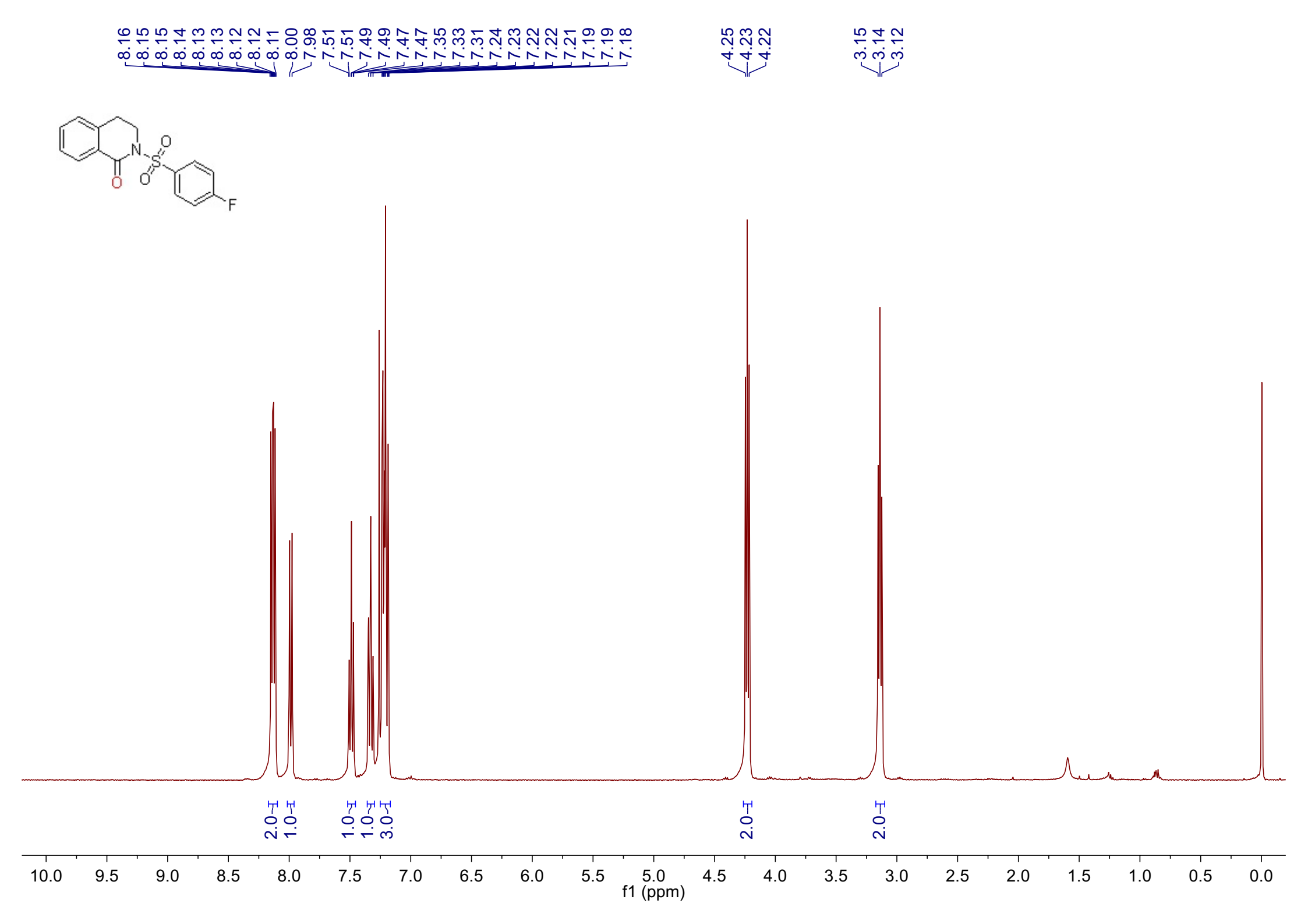
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.15
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8.13
8.12
8.12
8.11
8.00
7.98
7.51
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7.49
7.49
7.47
7.47
7.35
7.33
7.31
7.24
7.23
7.22
7.22
7.21
7.19
7.19
7.18
4.25
4.23
4.22
3.15
3.14
3.12
O
N
S
O
O
O
F
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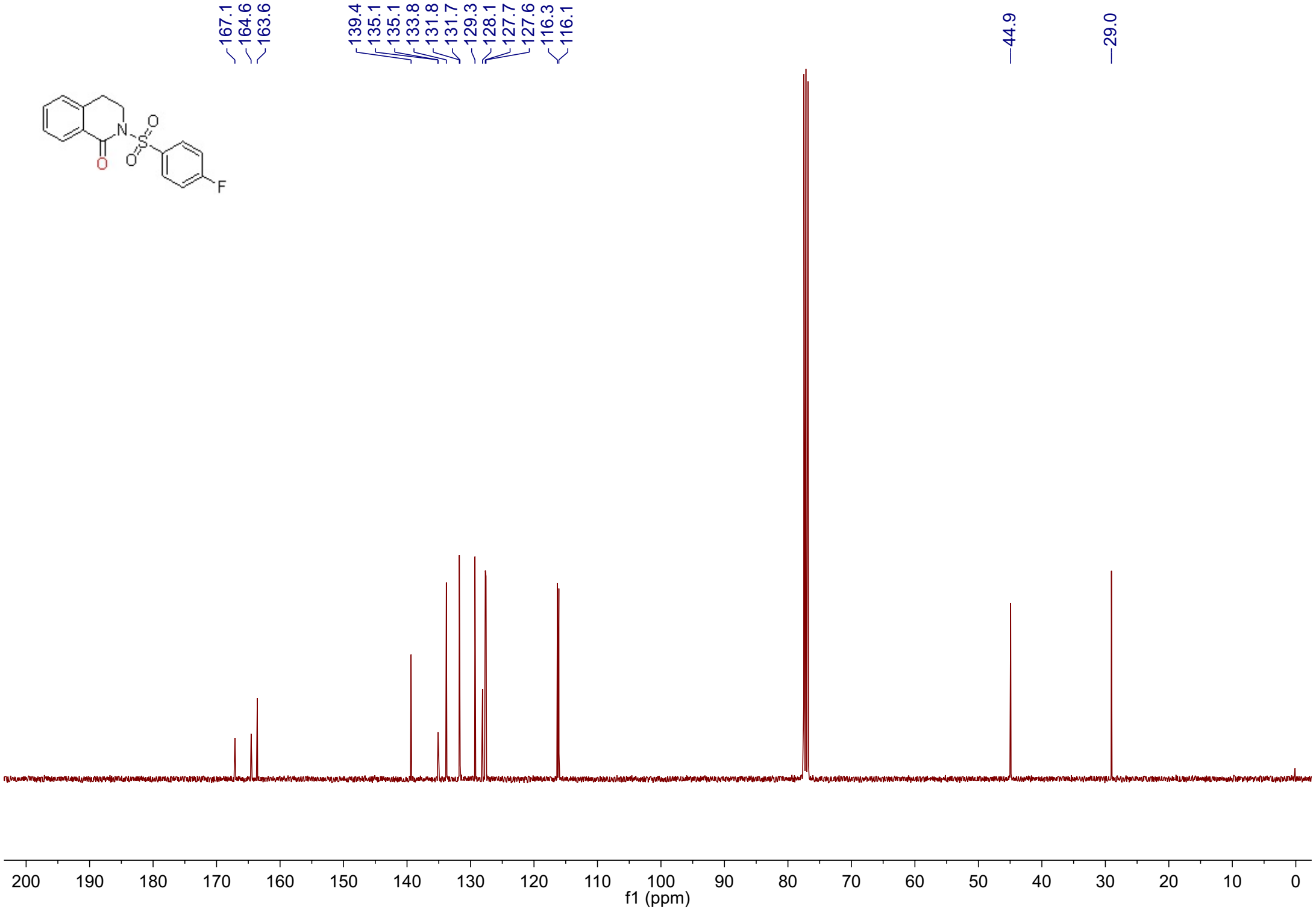
1.0
1.0
1.0
3.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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163.6
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135.1
135.1
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131.8
131.7
129.3
128.1
127.7
127.6
116.3
116.1
44.9
29.0
O
N
S
O
O
F
200
190
180
170
160
150
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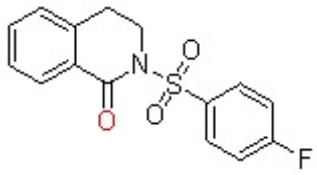
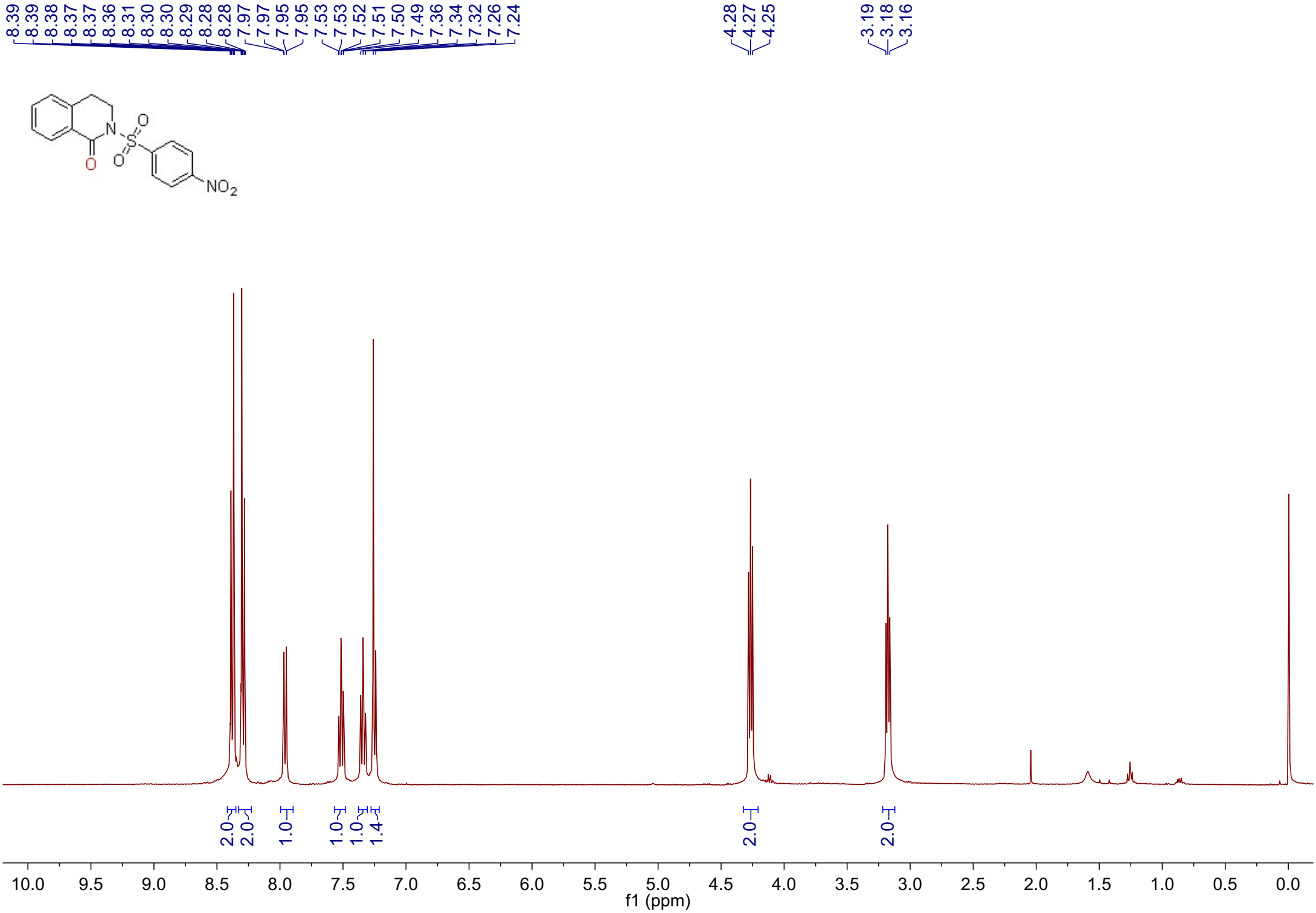
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



-103.23

-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240

f1 (ppm)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8.28
8.28
7.97
7.97
7.95
7.95
7.53
7.53
7.52
7.51
7.50
7.49
7.36
7.34
7.32
7.26
7.24
4.28
4.27
4.25
3.19
3.18
3.16
O
N
S
O
O
O
NO2
2.0
2.0
1.0
1.0
1.0
1.4
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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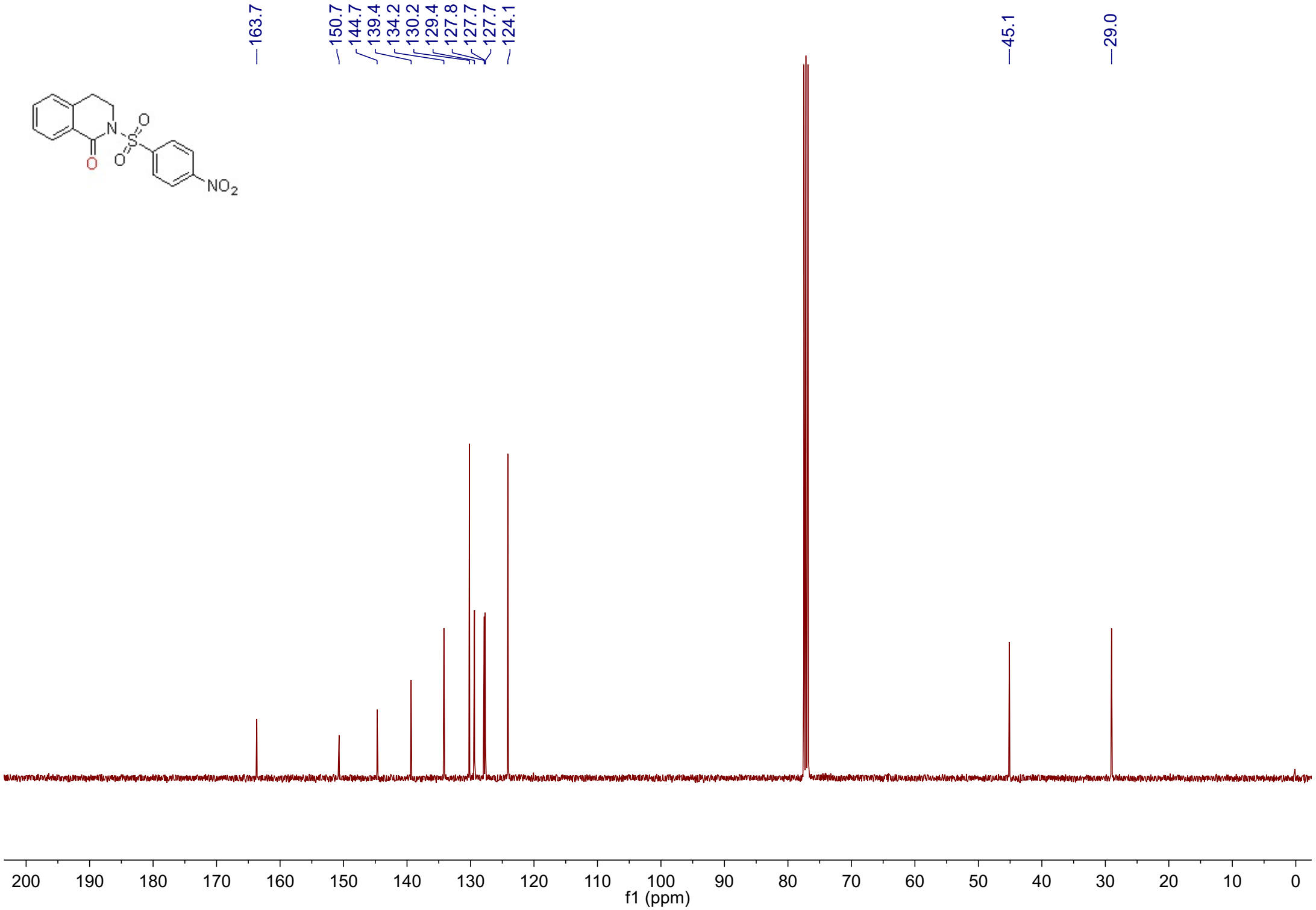
0.0
f1 (ppm)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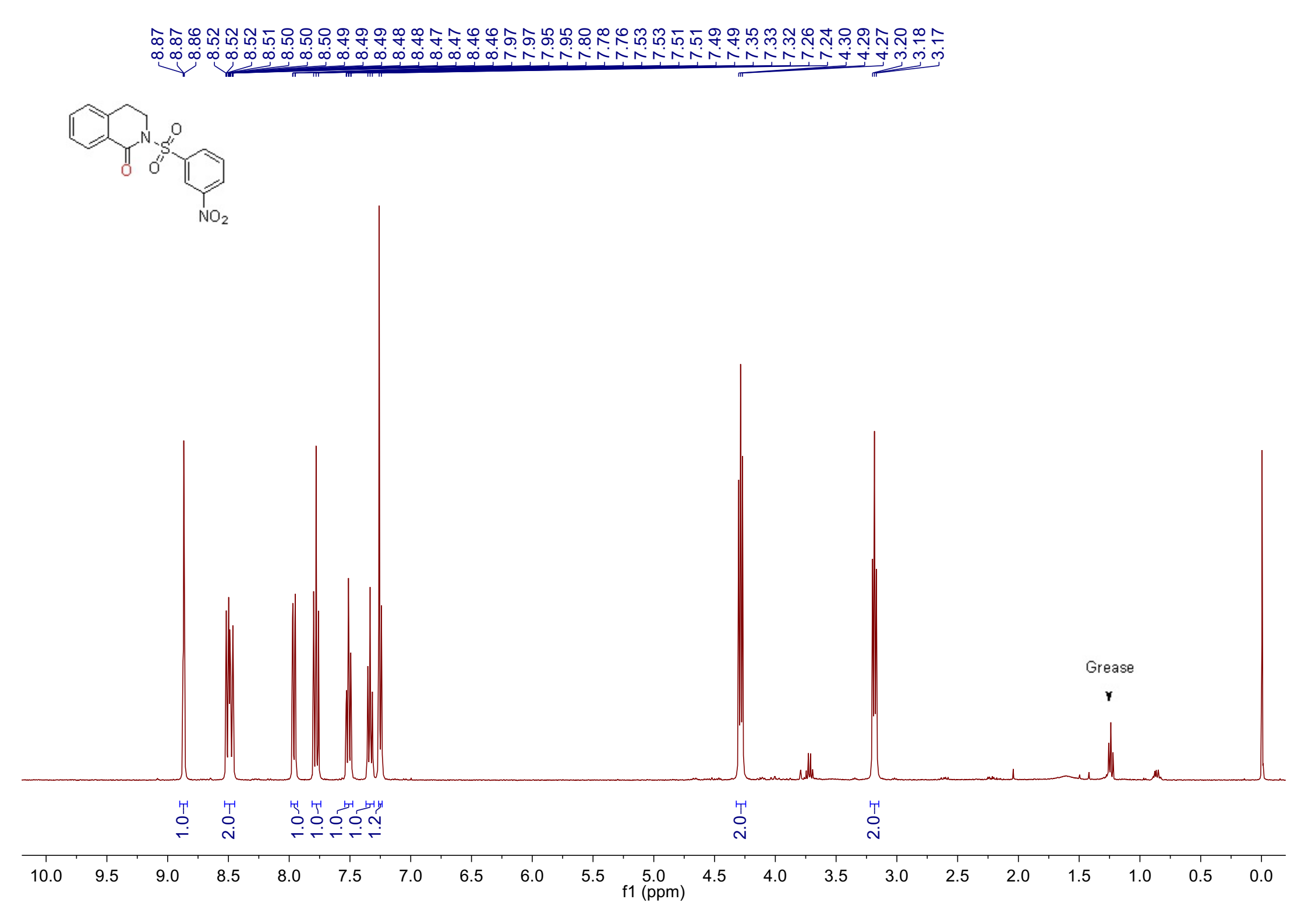
130.2
129.4
127.8
127.7
127.7
124.1
45.1
29.0
O
N
S
O
O
O
NO2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.49
8.48
8.48
8.47
8.47
8.46
8.46
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7.97
7.95
7.95
7.80
7.78
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7.53
7.51
7.51
7.49
7.49
7.35
7.33
7.32
7.26
7.24
4.30
4.29
4.27
3.20
3.18
3.17
O
N
S
O
O
O
NO2
Grease
1.0
2.0
1.0
1.0
1.0
1.0
1.2
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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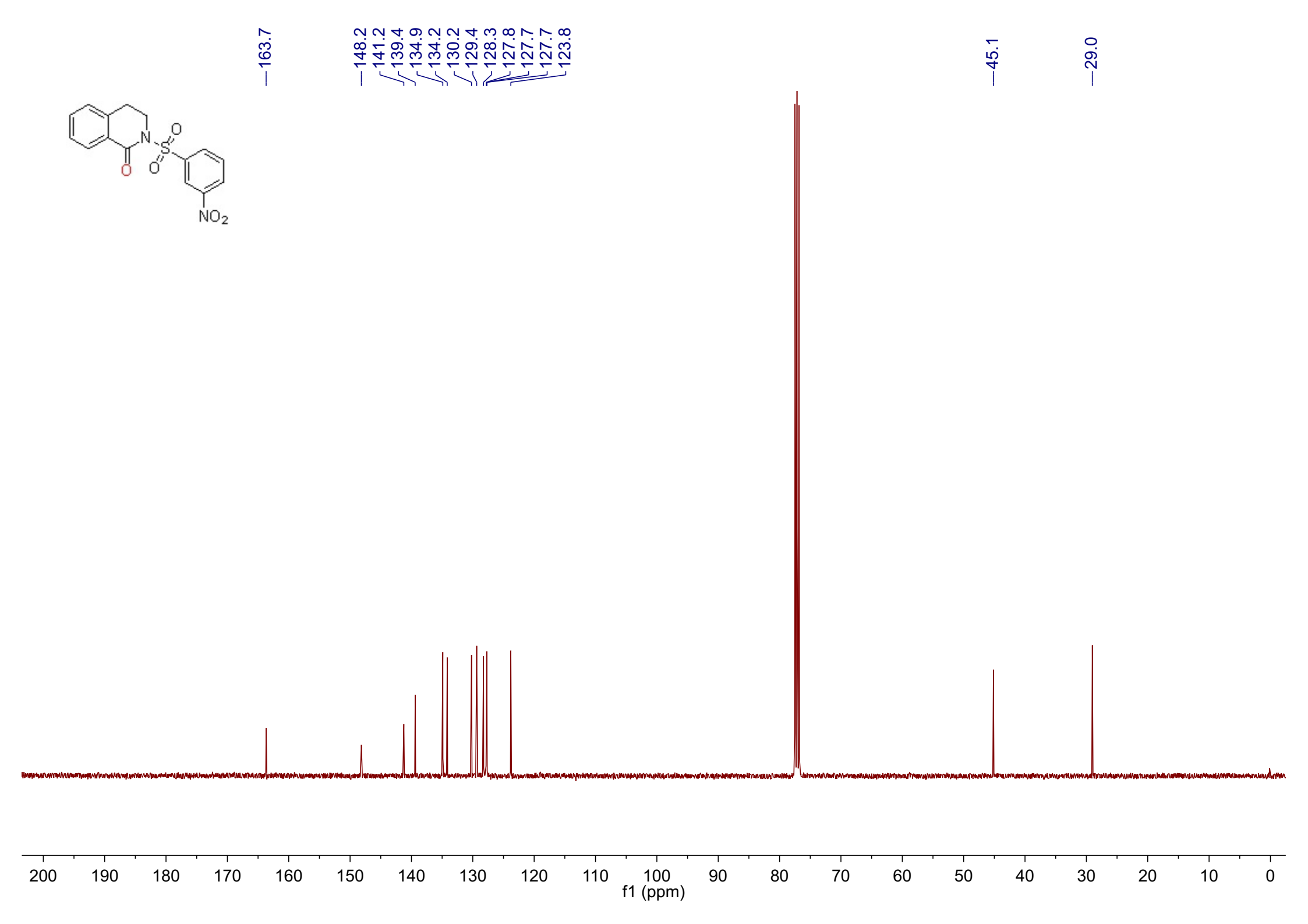
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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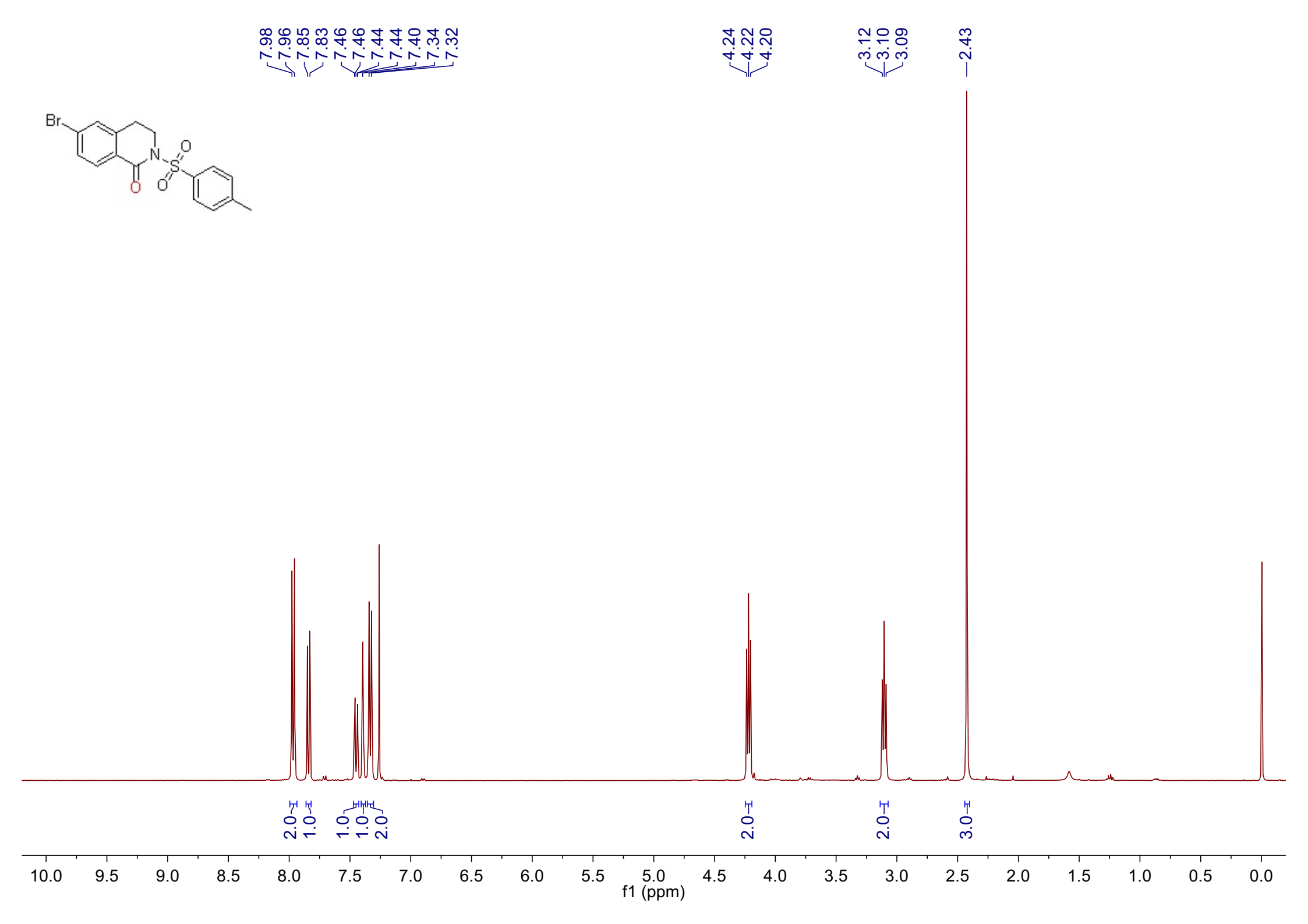
148.2
141.2
139.4
134.9
134.2
130.2
129.4
128.3
127.8
127.7
127.7
123.8
45.1
29.0
O
N
S
O
O
O
NO2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.44
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7.34
7.32
4.24
4.22
4.20
3.12
3.10
3.09
2.43
Br
N
S
O
O
O
2.0
1.0
1.0
1.0
2.0
2.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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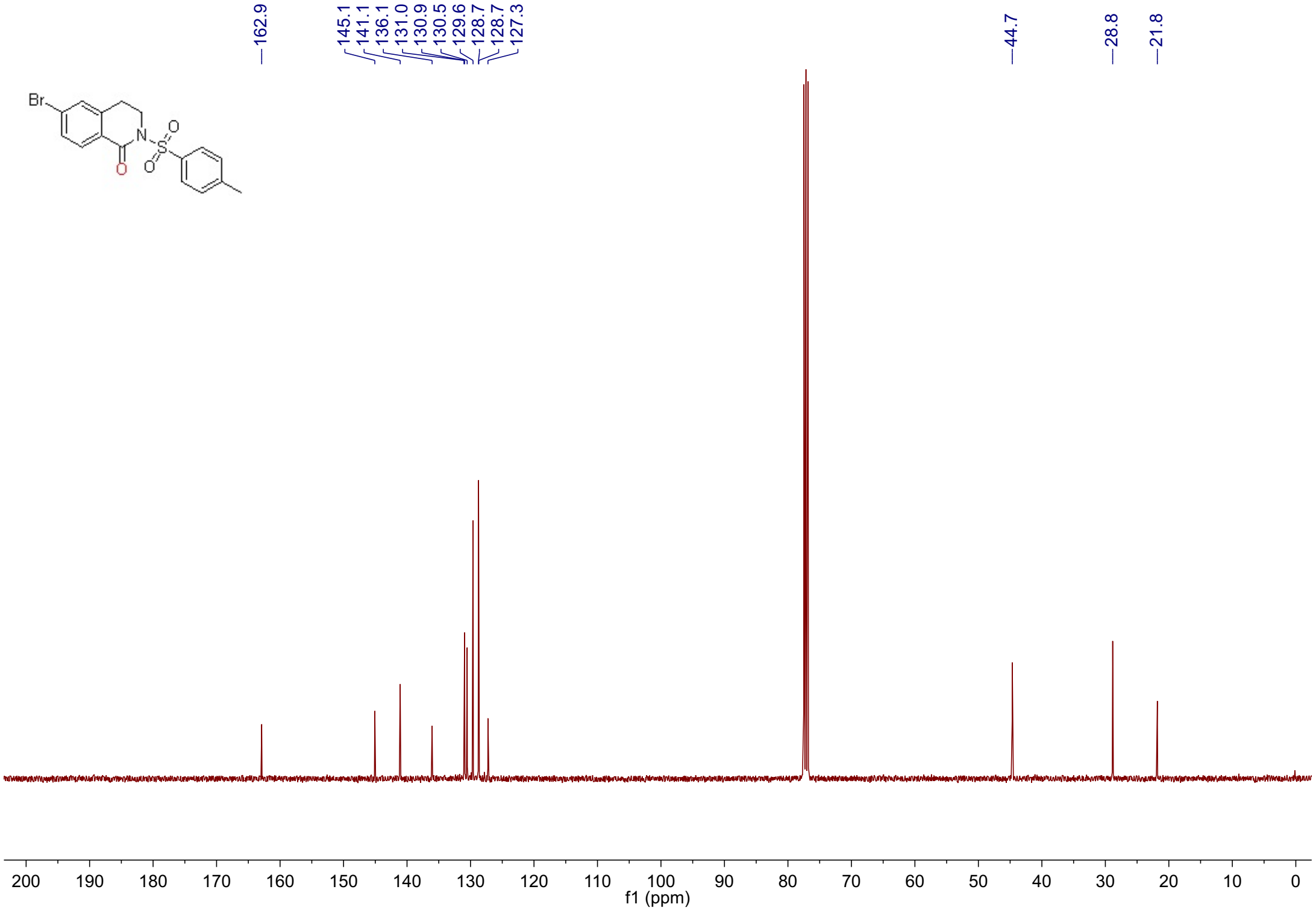
0.0
f1 (ppm)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136.1
131.0
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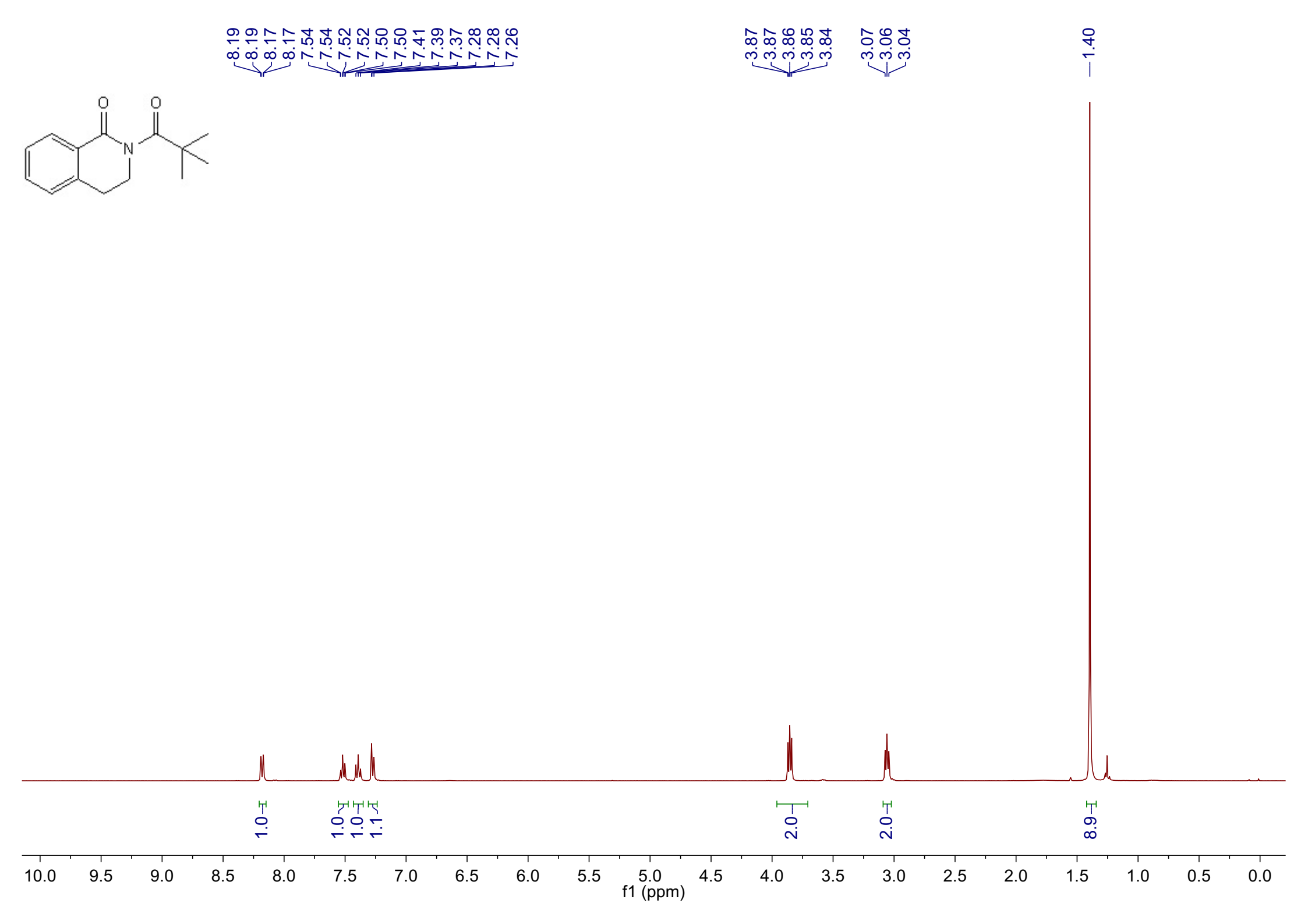
130.5
129.6
128.7
128.7
127.3
44.7
28.8
21.8
Br
N
S
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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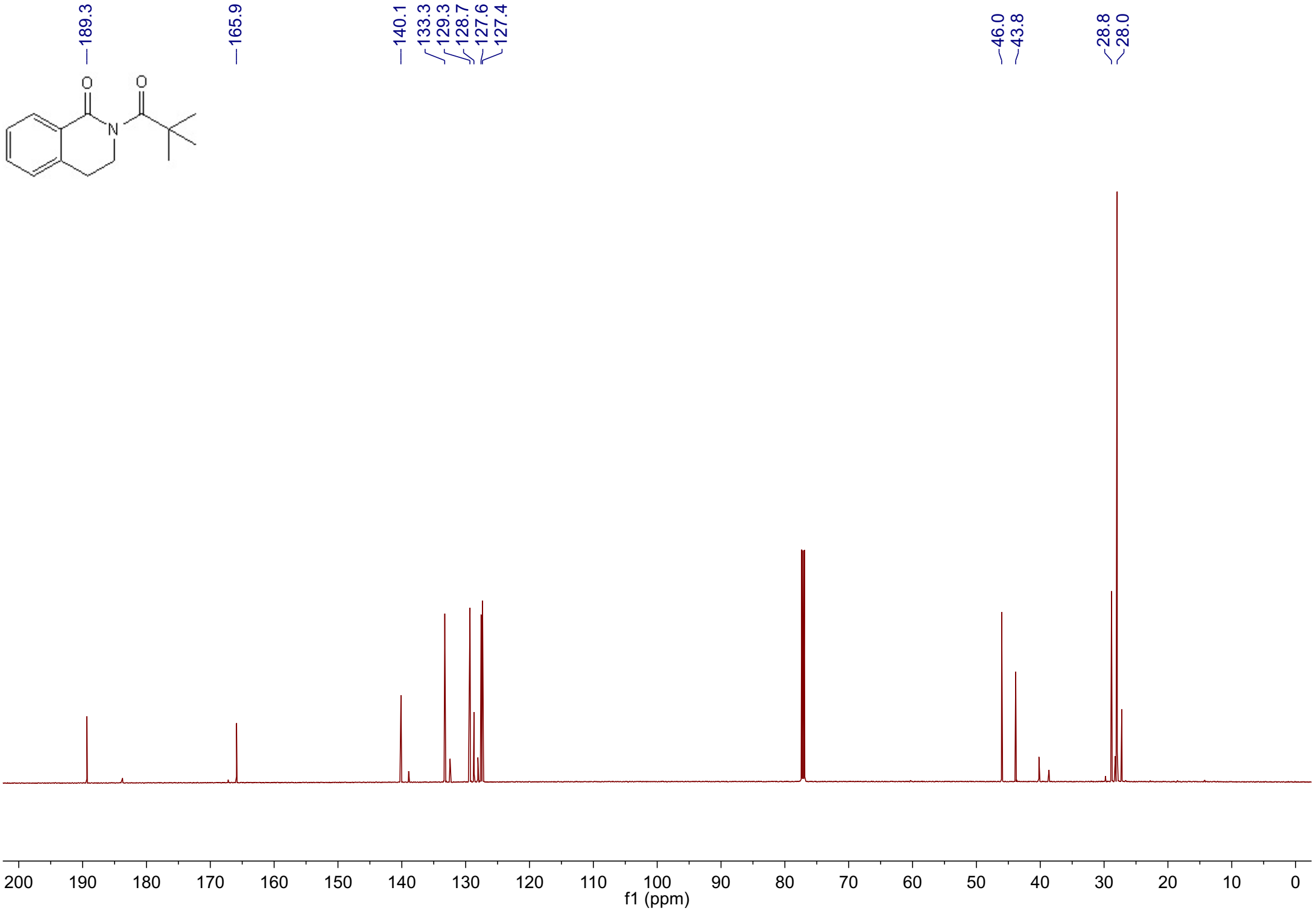
7.52
7.52
7.50
7.50
7.41
7.39
7.37
7.28
7.28
7.26
3.87
3.87
3.86
3.85
3.84
3.07
3.06
3.04
1.40
O
O
N
1.0
1.0
1.0
1.1
2.0
2.0
8.9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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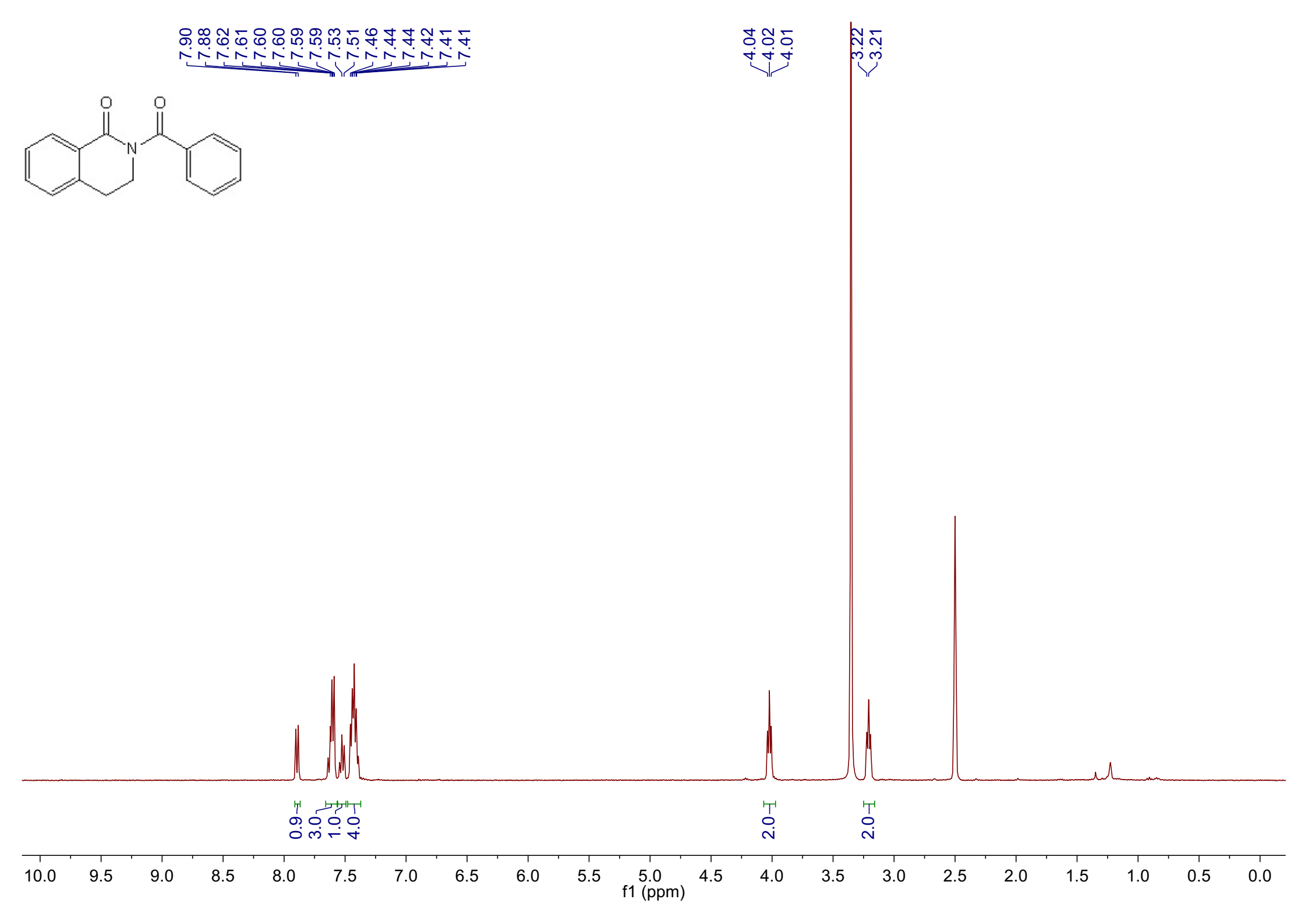
129.3
128.7
127.6
127.4
46.0
43.8
28.8
28.0
O
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.62
7.61
7.60
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7.59
7.53
7.51
7.46
7.44
7.44
7.42
7.41
7.41
4.04
4.02
4.01
3.22
3.21
O
O
N
0.9
3.0
1.0
4.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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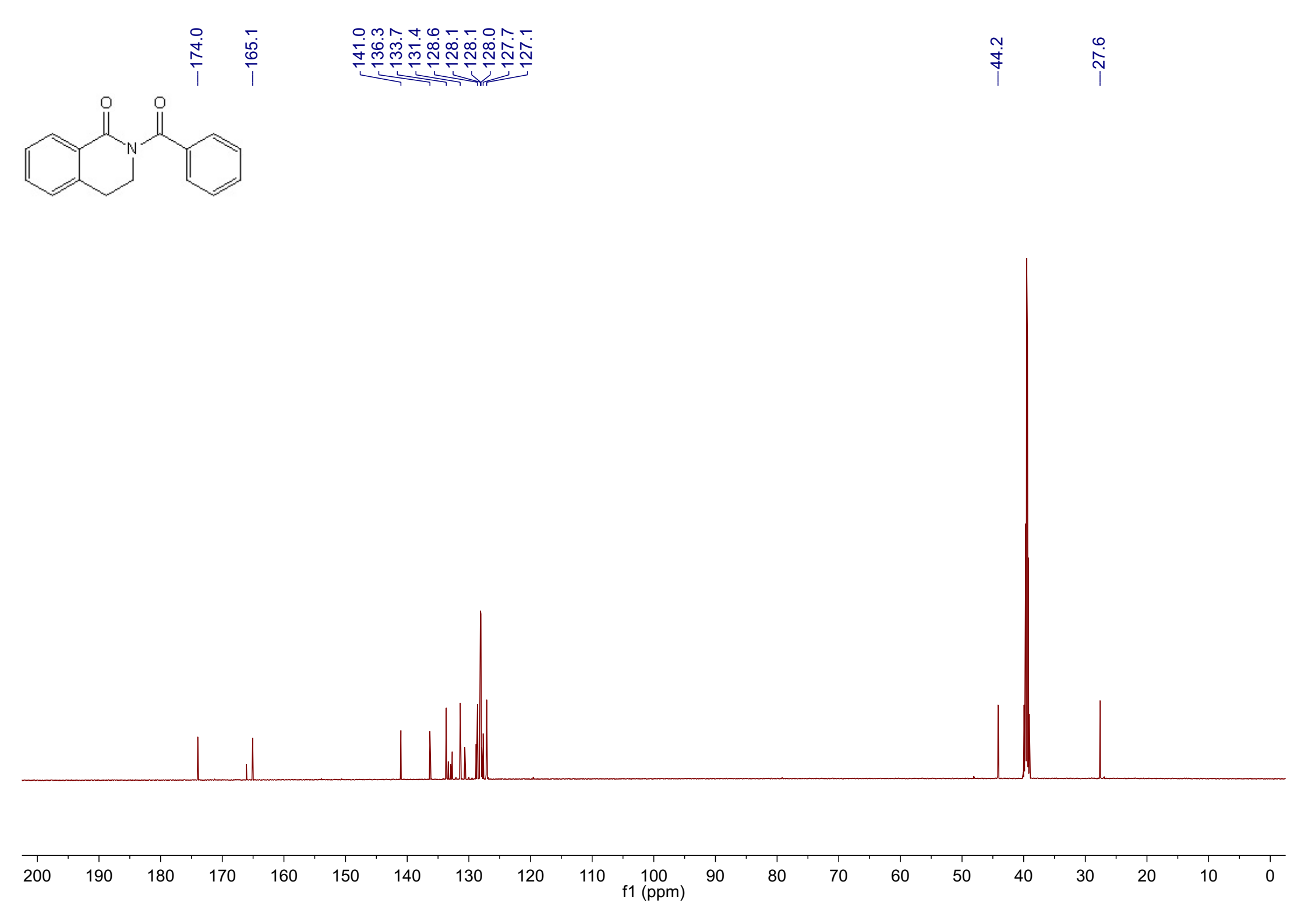
0.0
f1 (ppm)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141.0
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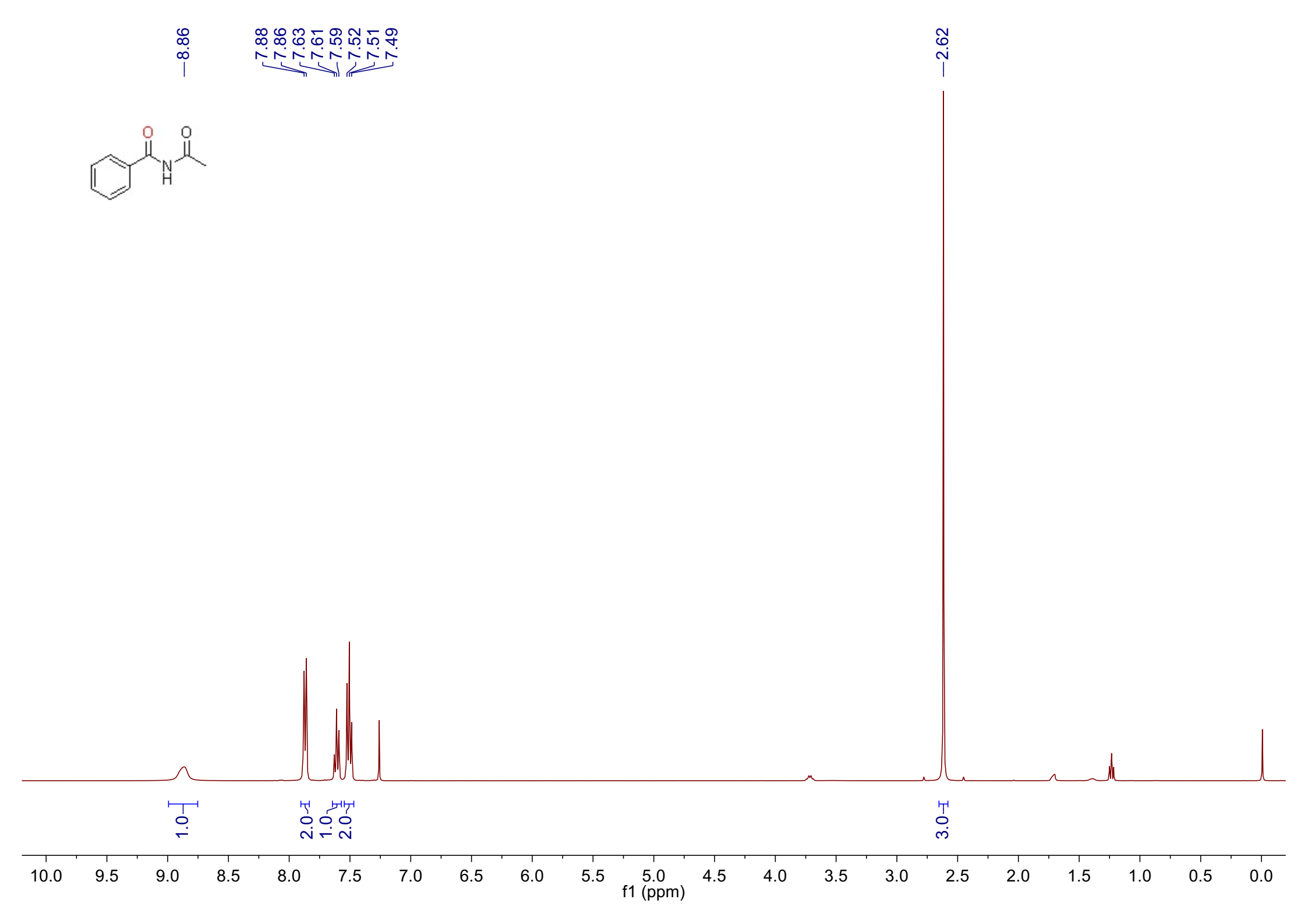
131.4
128.6
128.1
128.1
128.0
127.7
127.1
44.2
27.6
O
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.86
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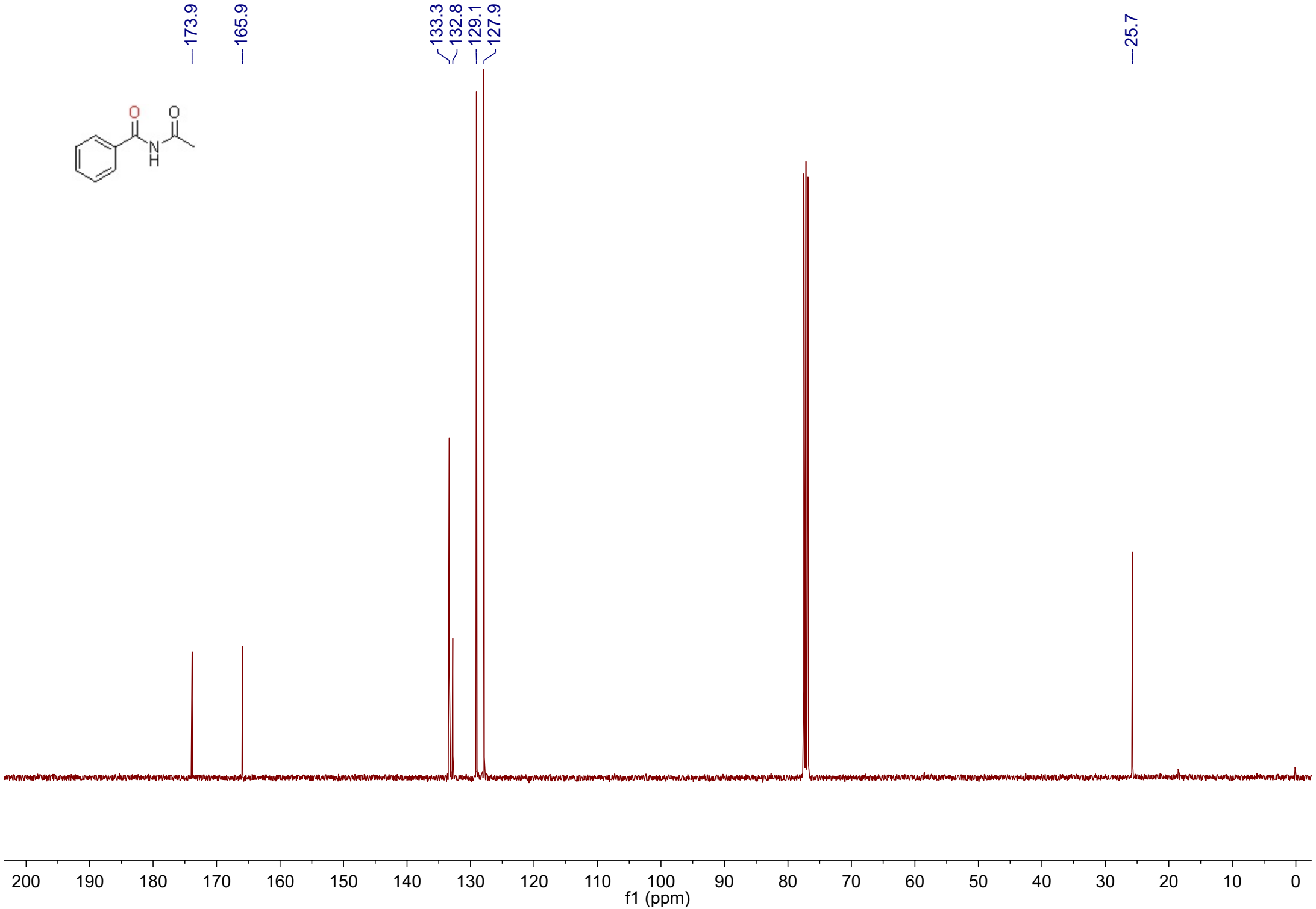
7.59
7.52
7.51
7.49
2.62
O
O
N
H
1.0
2.0
1.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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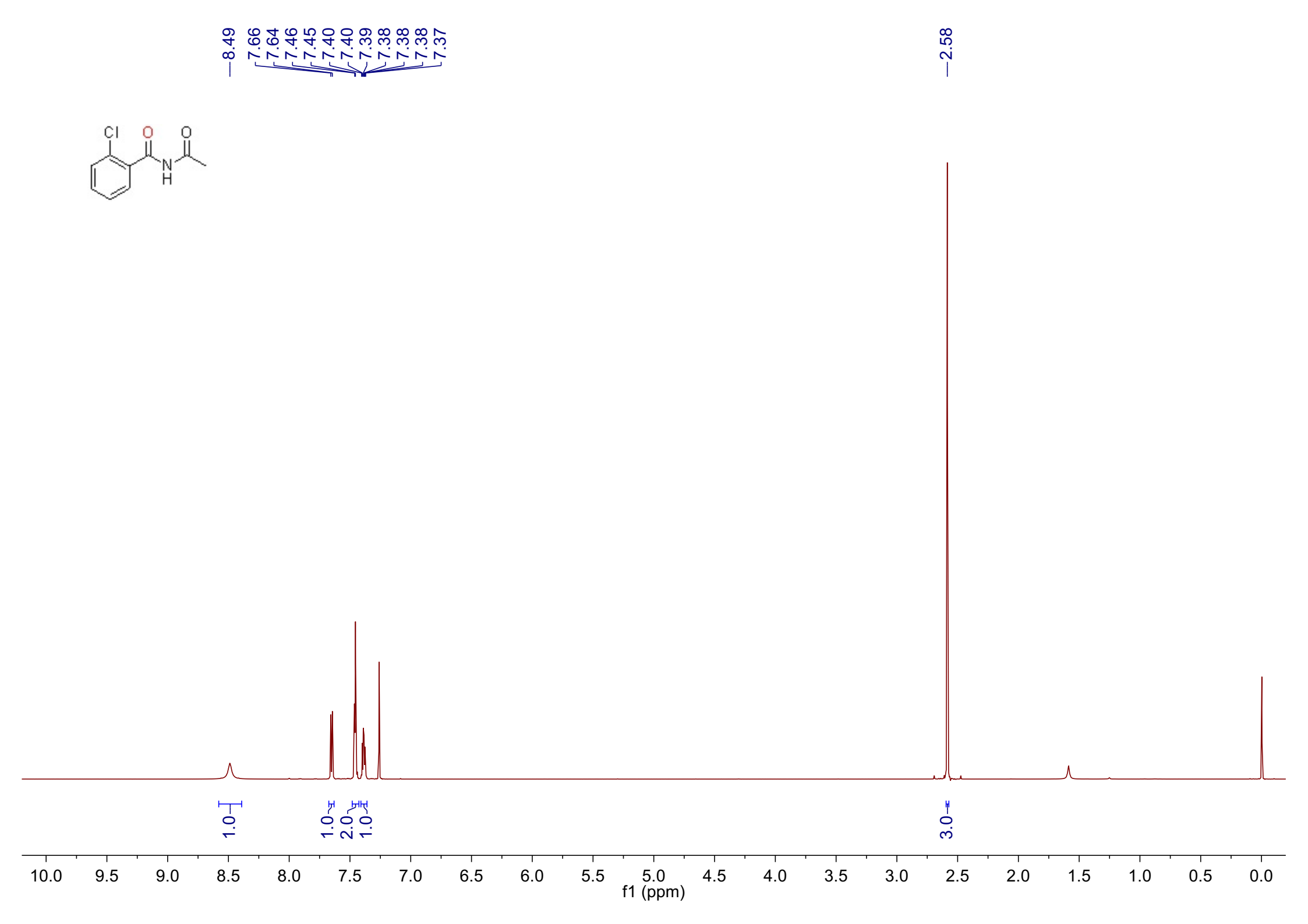
165.9
133.3
132.8
129.1
127.9
25.7
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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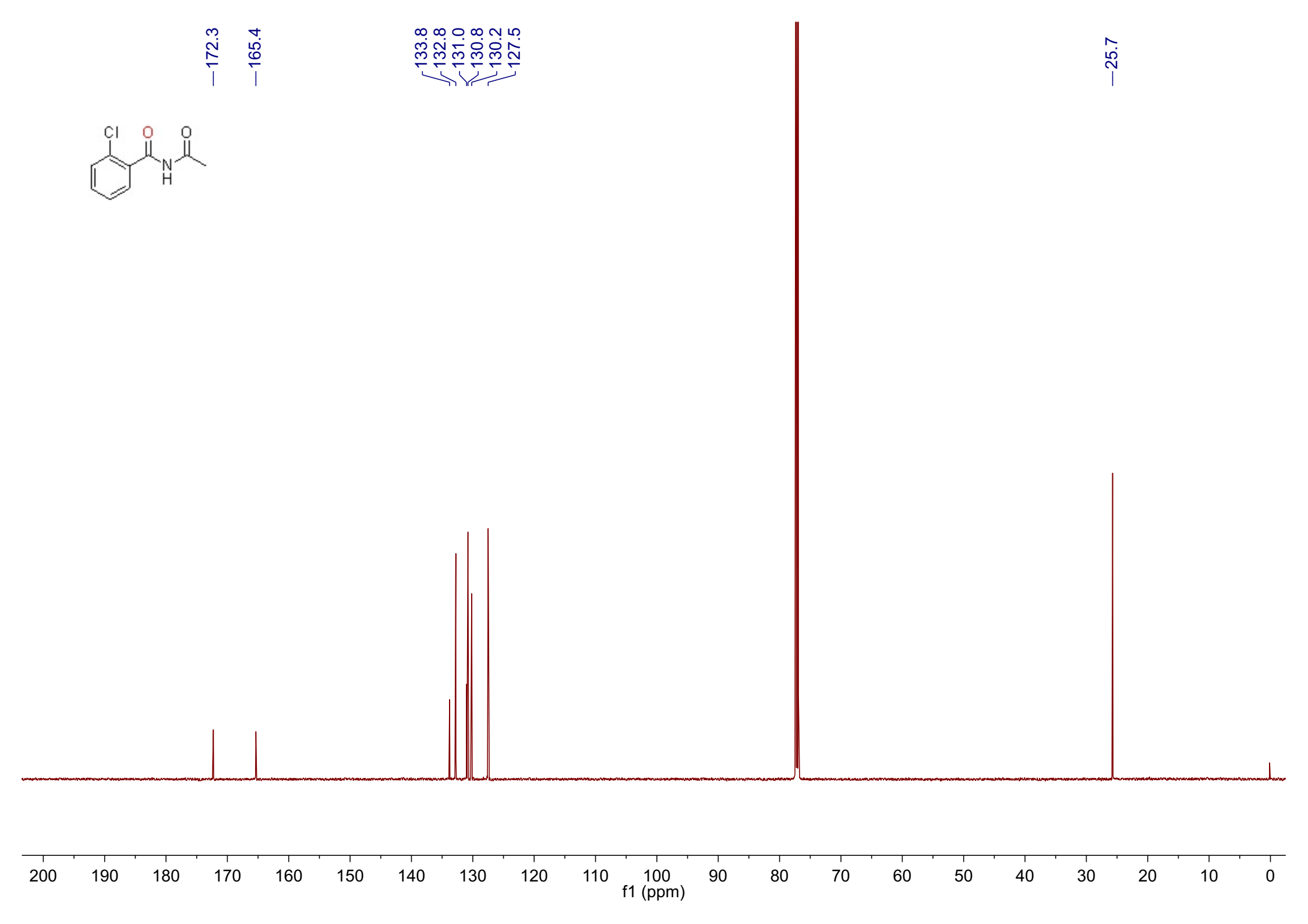
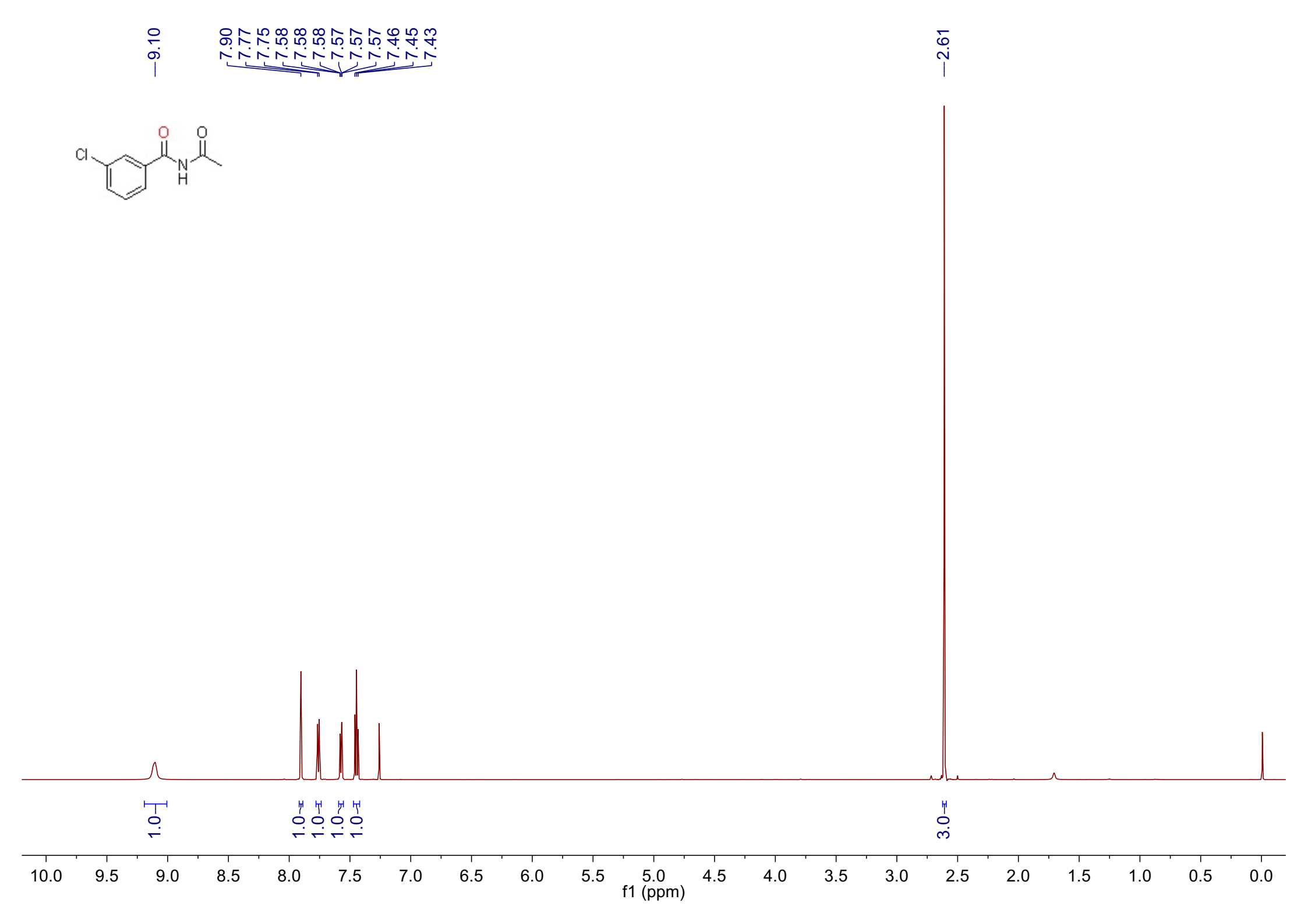
7.39
7.38
7.38
7.38
7.37
2.58
Cl
O
O
N
H
1.0
1.0
2.0
1.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.3
165.4
133.8
132.8
131.0
130.8
130.2
127.5
25.7
Cl
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.75
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7.58
7.58
7.57
7.57
7.57
7.46
7.45
7.43
2.61
Cl
O
N
H
O
1.0
1.0
1.0
1.0
1.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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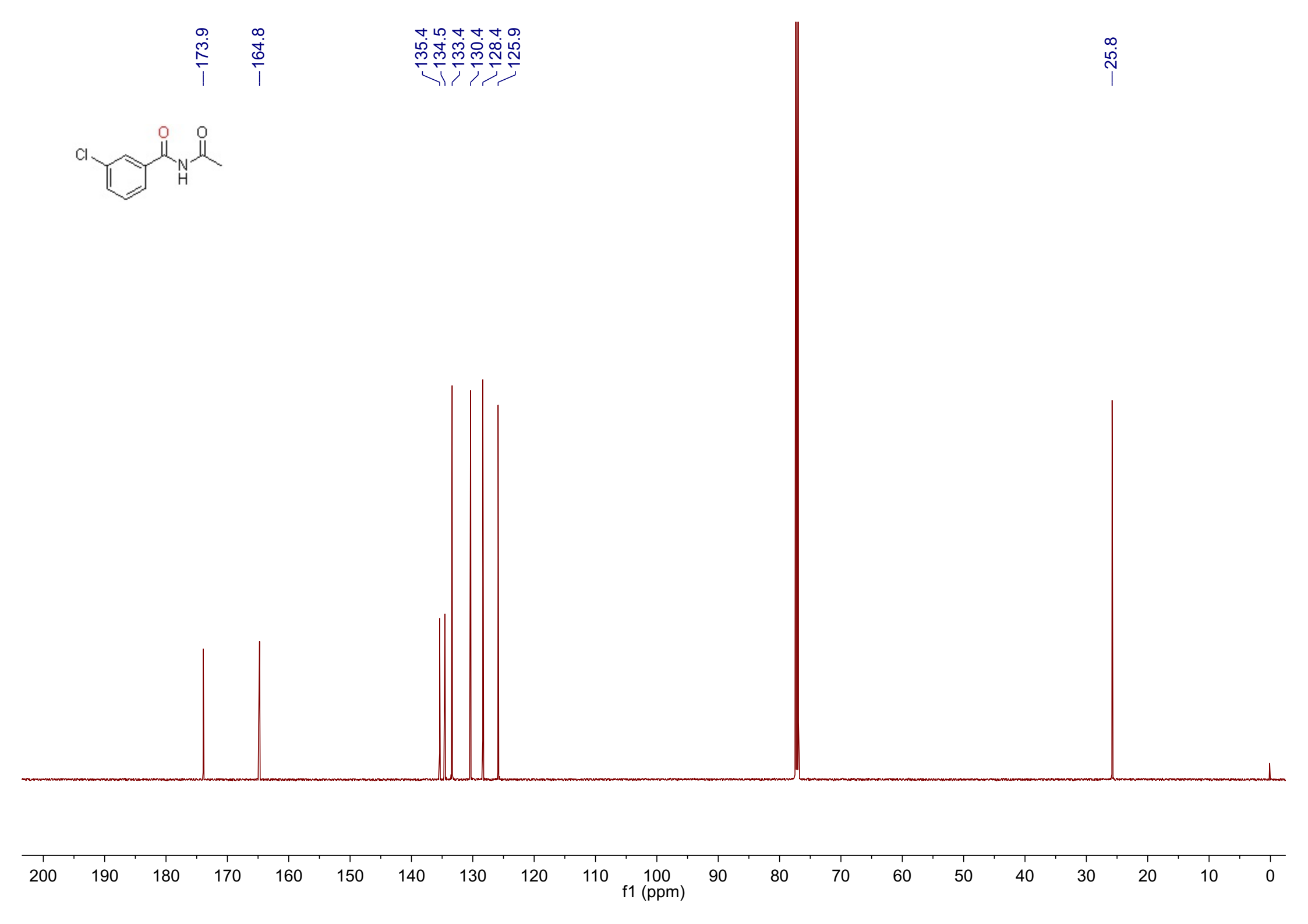
1.5
1.0
0.5
0.0
f1 (ppm)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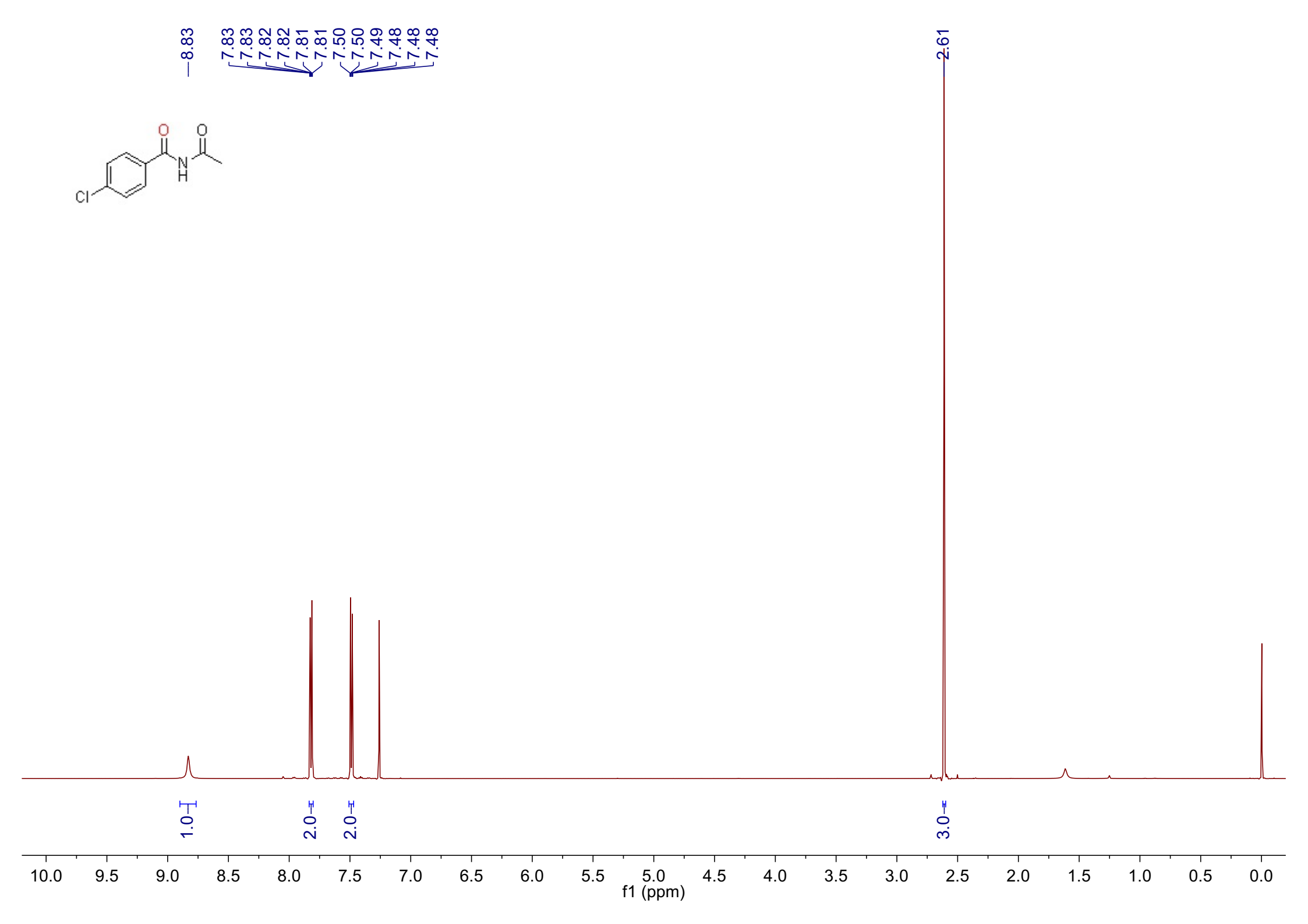
164.8
135.4
134.5
133.4
130.4
128.4
125.9
25.8
Cl
O
N
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.83
7.83
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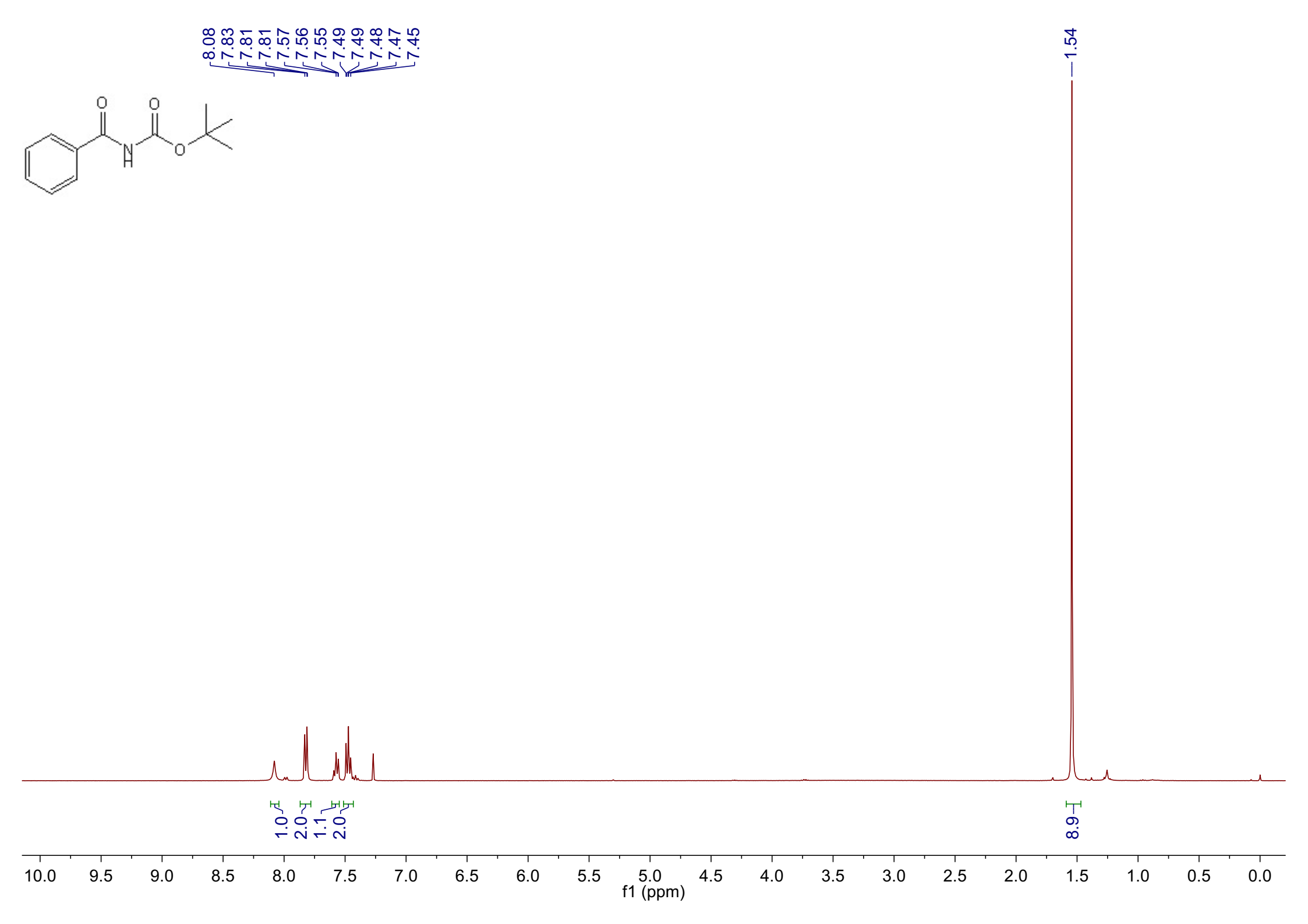
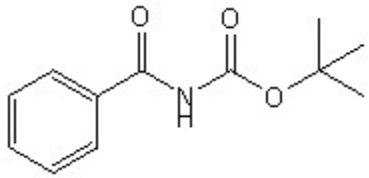
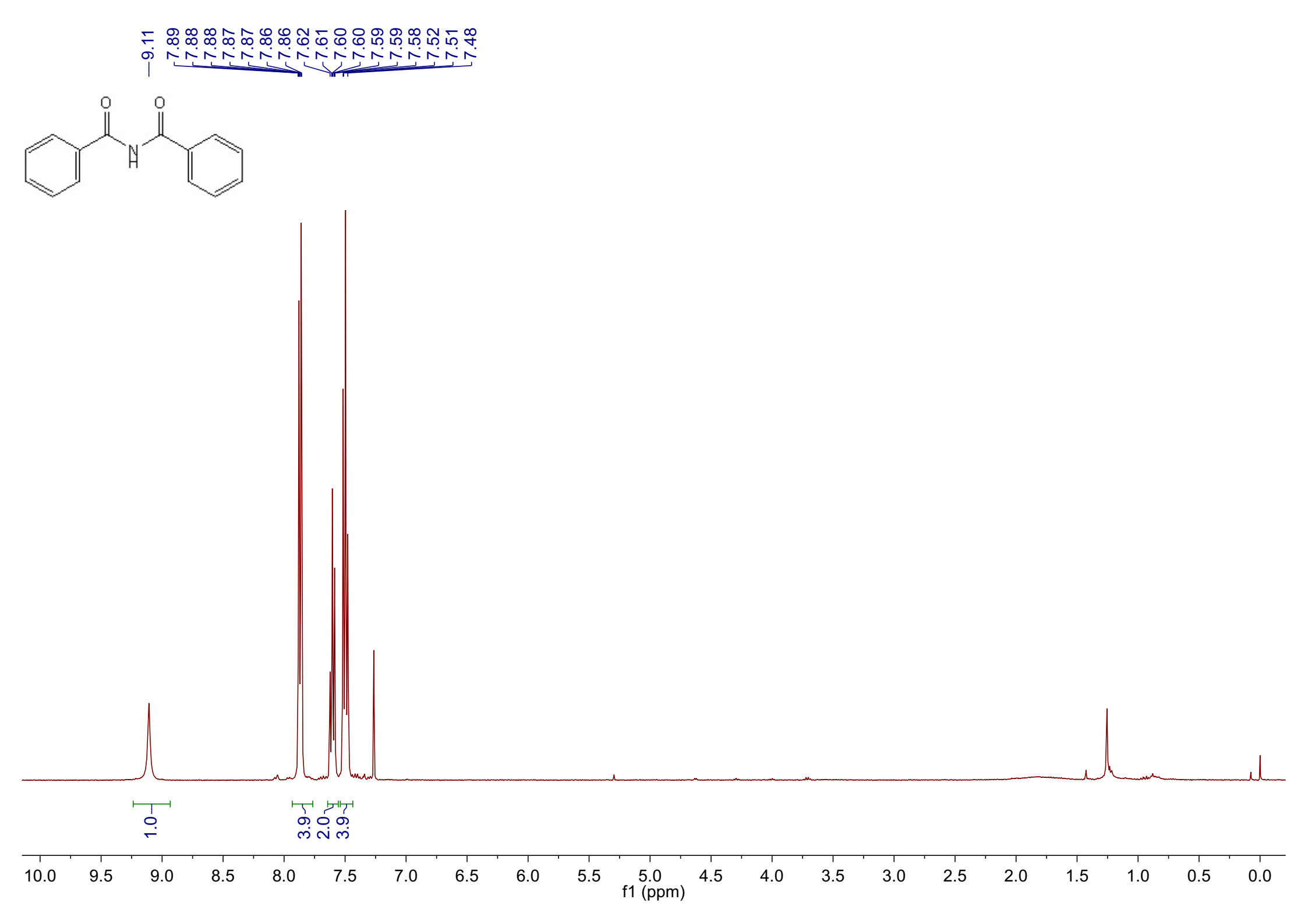
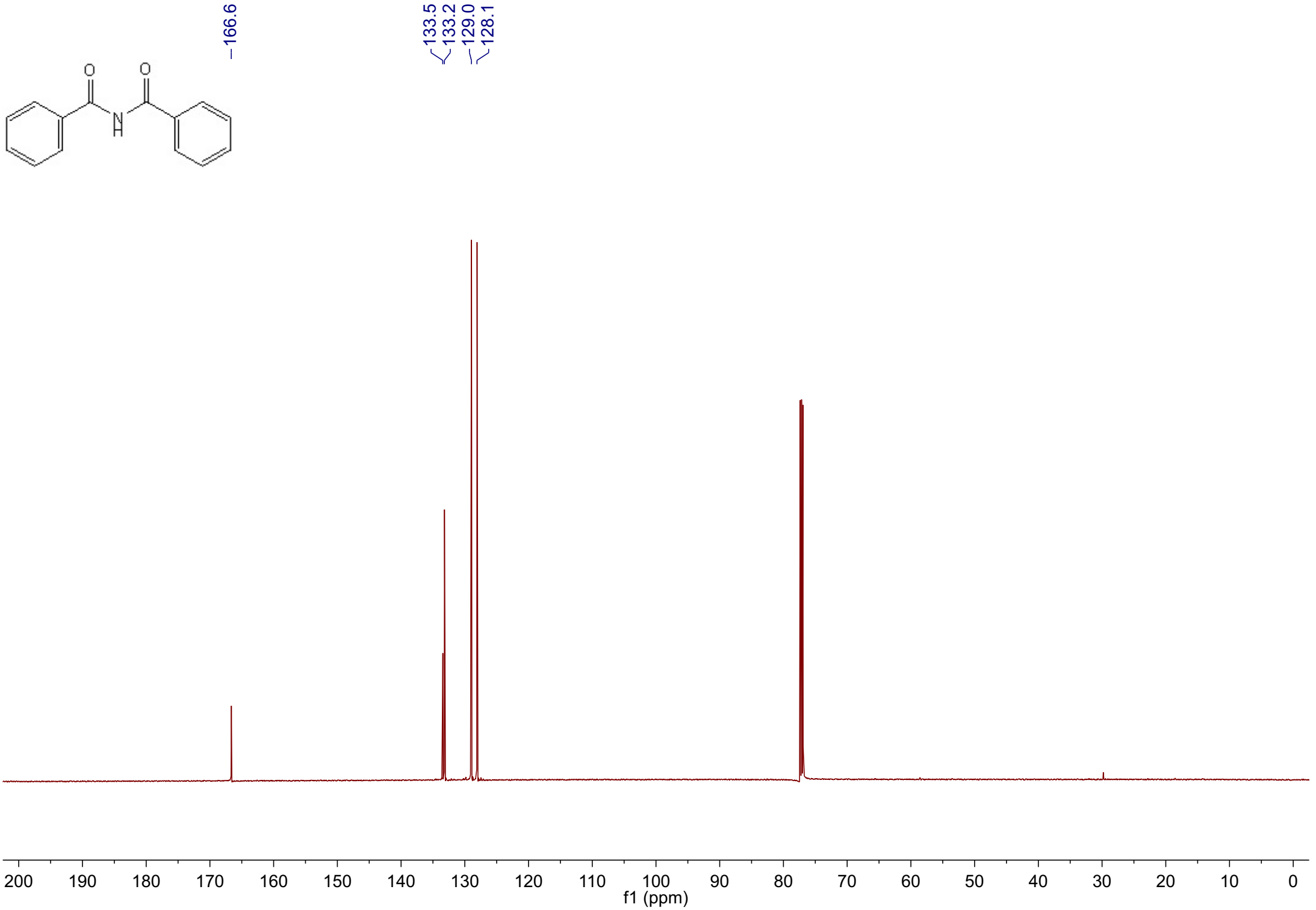
7.82
7.81
7.81
7.50
7.50
7.49
7.48
7.48
7.48
2.61
O
O
N
H
Cl
1.0
2.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

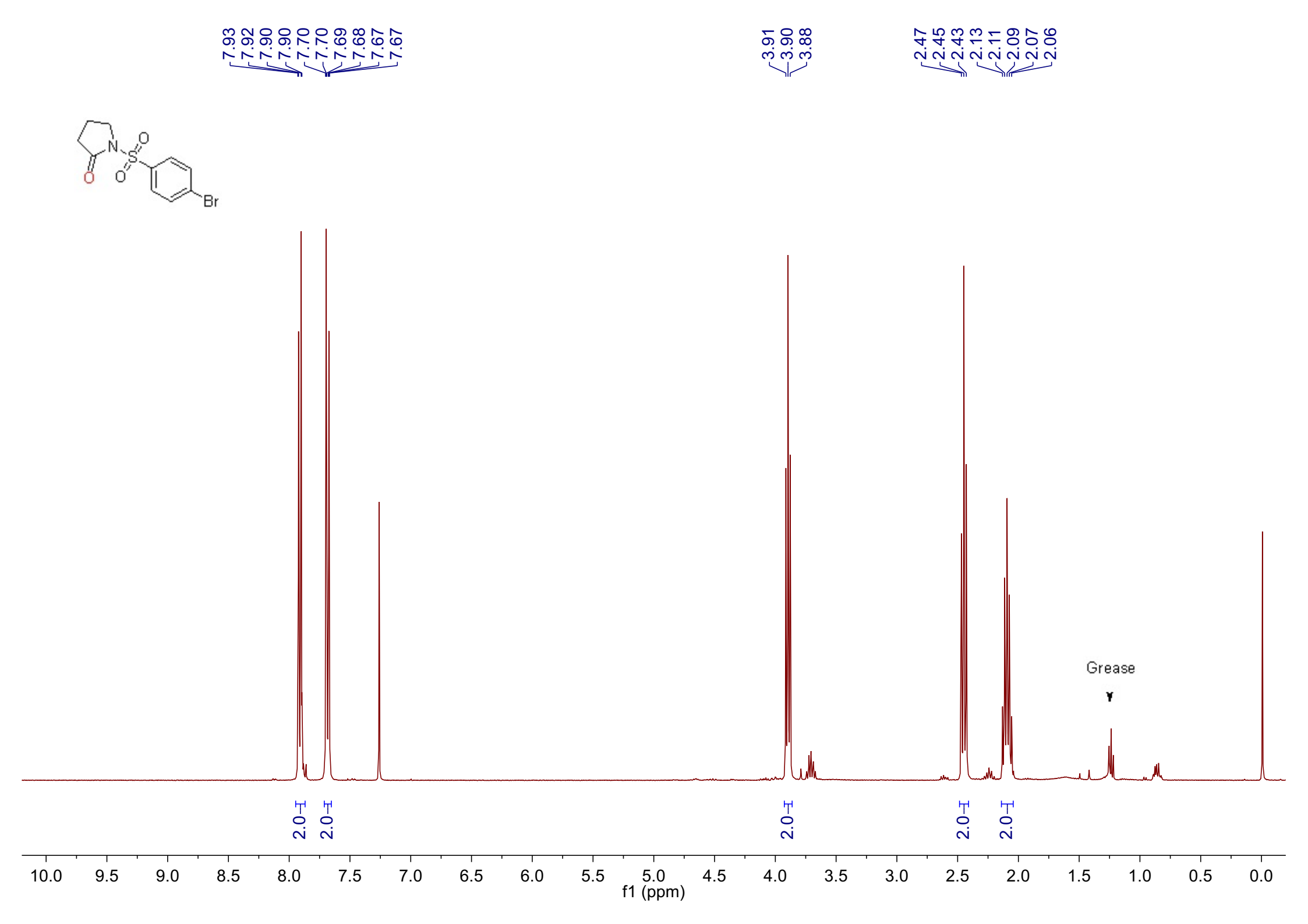

8.08
7.83
7.81
7.81
7.57
7.56
7.55
7.49
7.49
7.48
7.47
7.45
1.54
O
O
N
H
O
1.0
2.0
1.1
2.0
8.9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
N
H
O

165.4
149.9
133.5
132.9
128.9
127.7
83.0
28.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.11
7.89
7.88
7.88
7.87
7.87
7.86
7.86
7.62
7.61
7.60
7.60
7.59
7.59
7.58
7.52
7.51
7.48
O
O
N
H
1.0
3.9
2.0
3.9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.6
133.5
133.2
129.0
128.1
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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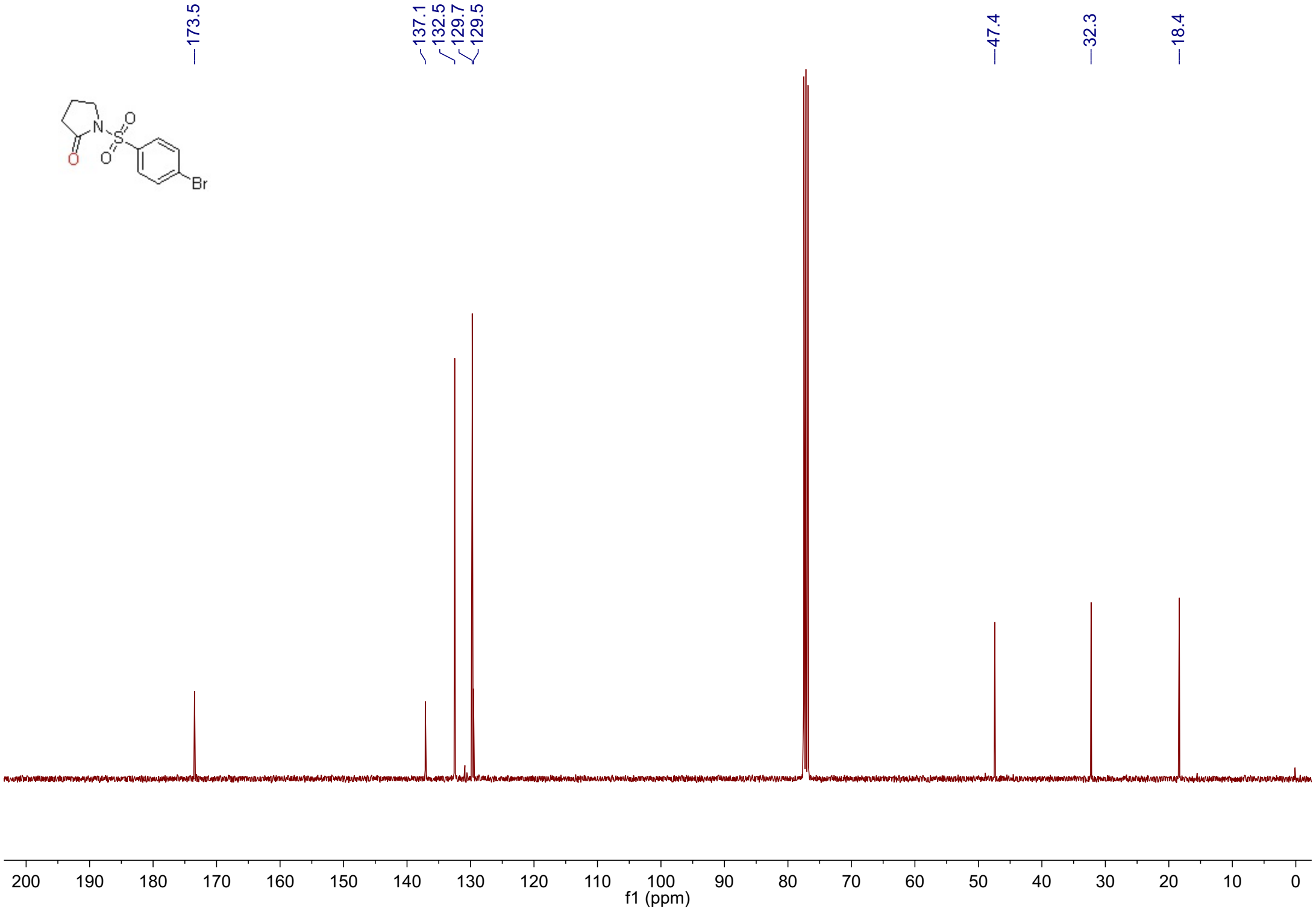
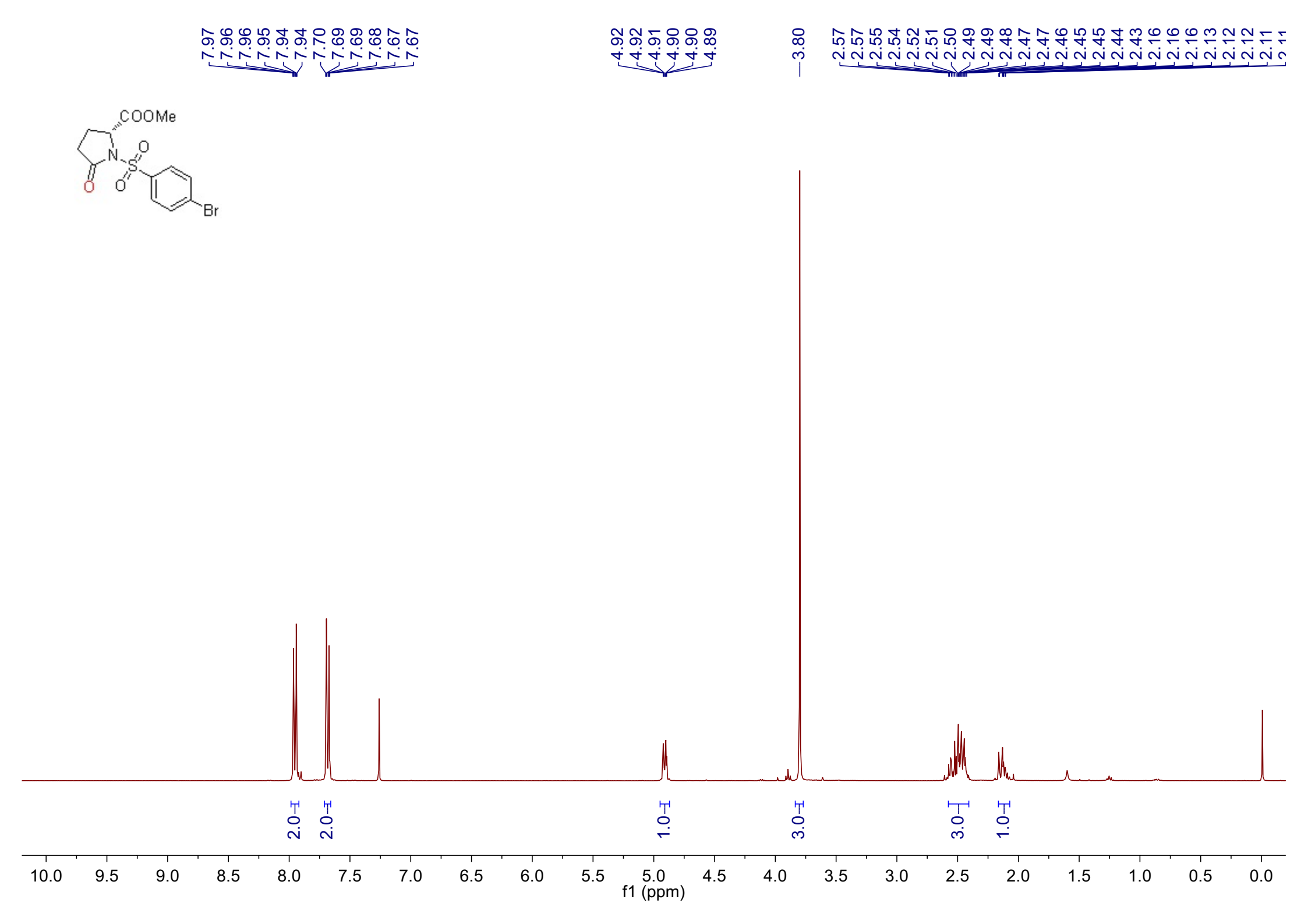
7.92
7.90
7.90
7.70
7.70
7.69
7.68
7.67
7.67
3.91
3.90
3.88
2.47
2.45
2.43
2.13
2.11
2.09
2.07
2.06
O
N
S
O
O
Br
Grease
2.0
2.0
2.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.5
137.1
132.5
129.7
129.5
47.4
32.3
18.4
O
N
S
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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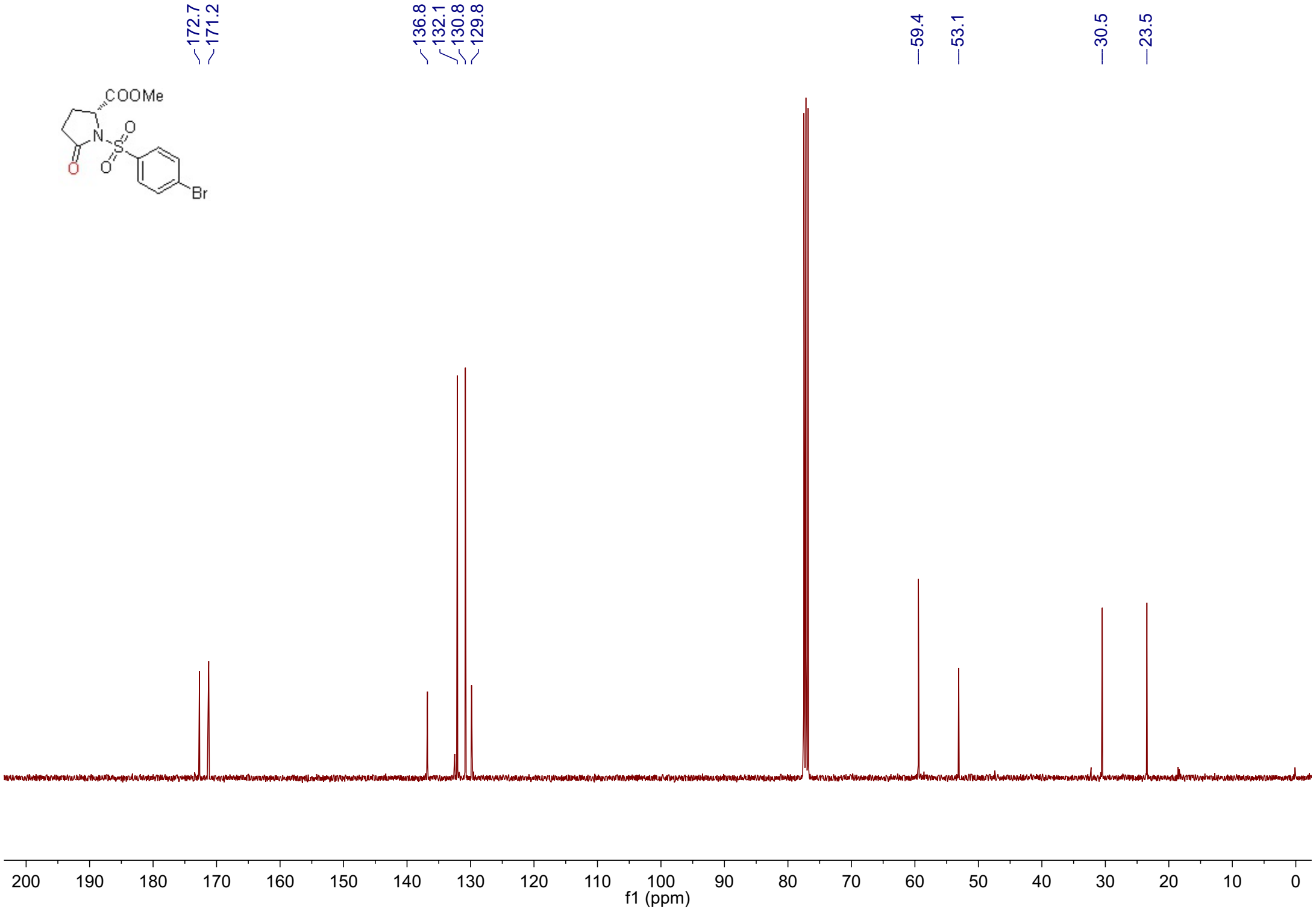
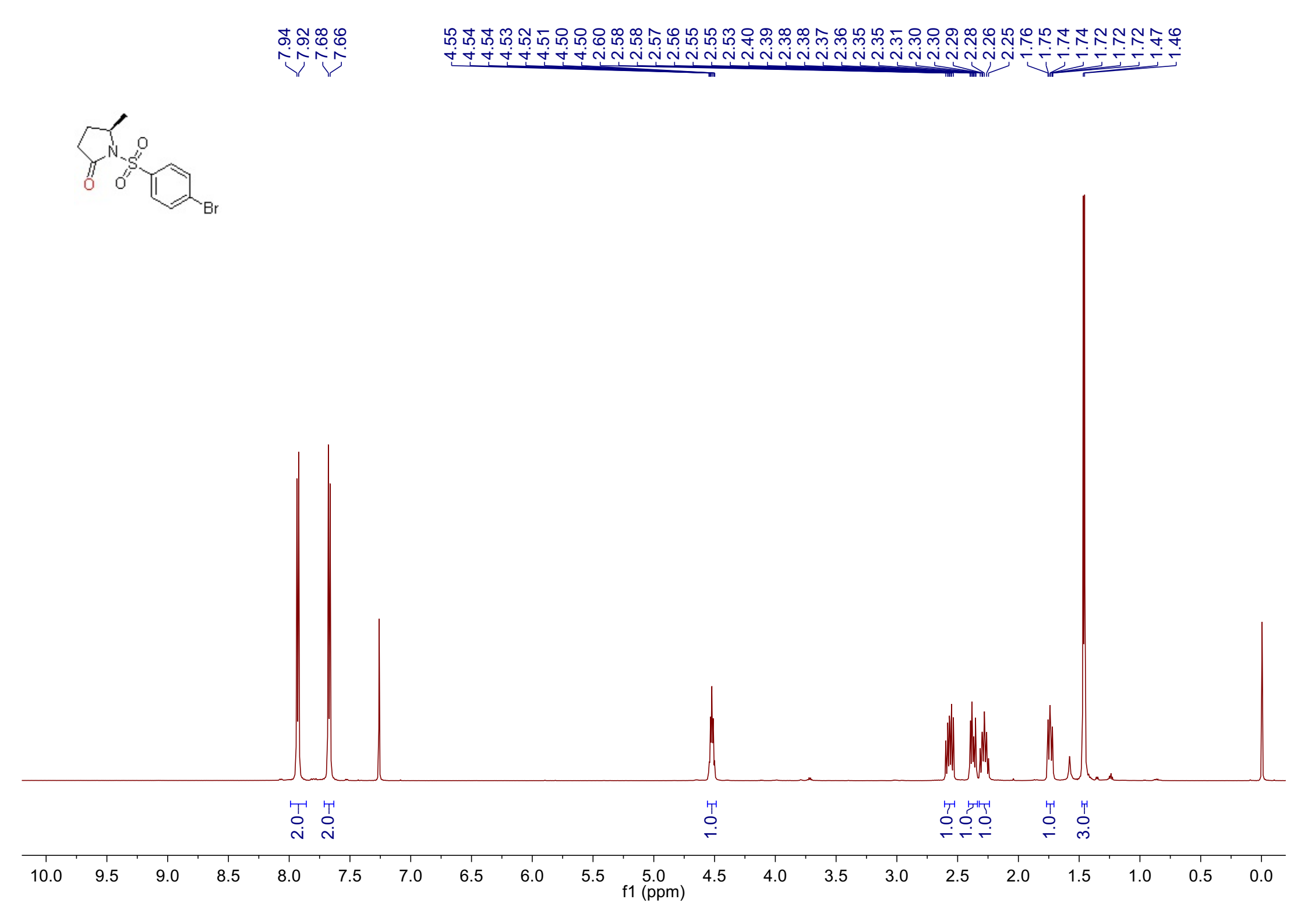
7.96
7.96
7.95
7.94
7.94
7.70
7.69
7.69
7.68
7.67
7.67
4.92
4.92
4.91
4.90
4.90
4.89
3.80
2.57
2.57
2.55
2.54
2.52
2.51
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.16
2.16
2.16
2.13
2.12
2.12
2.11
COOMe
N
S
O
O
O
Br
2.0
2.0
1.0
3.0
3.0
1.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.7
171.2
136.8
132.1
130.8
129.8
59.4
53.1
30.5
23.5
COOMe
N
O
O
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.94
7.92
7.68
7.66
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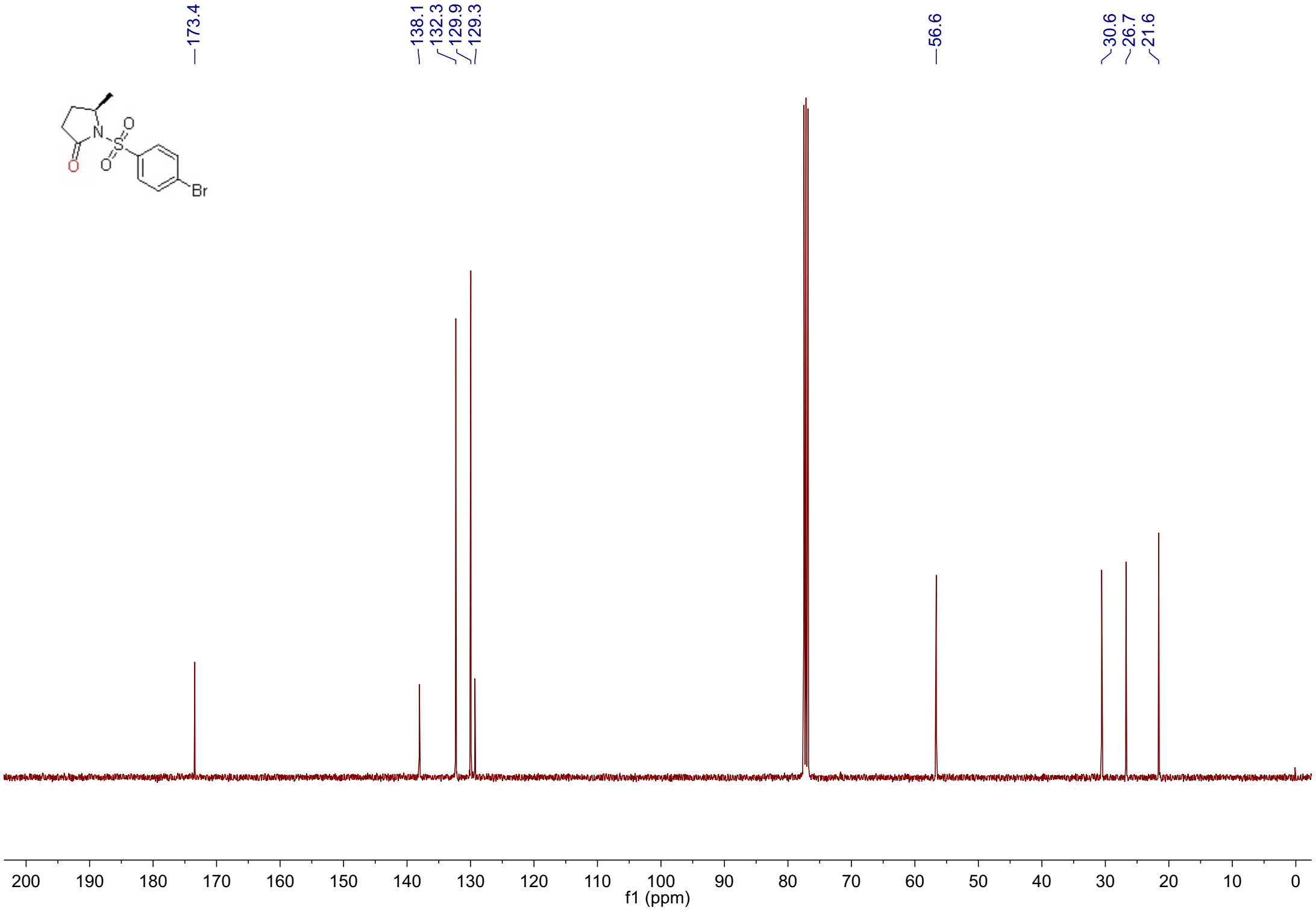
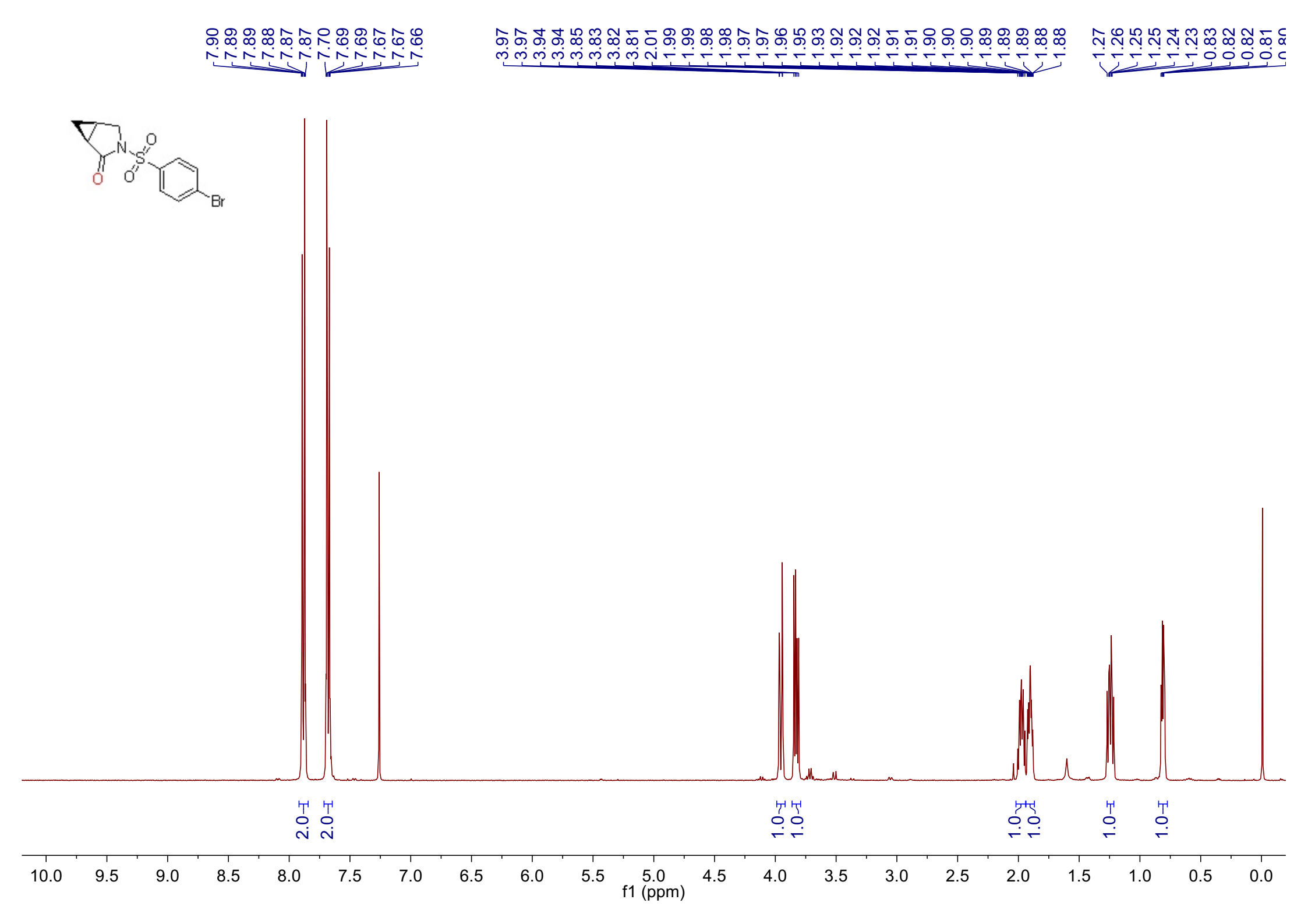
4.54
4.54
4.53
4.52
4.51
4.50
4.50
2.60
2.58
2.58
2.57
2.56
2.55
2.55
2.53
2.40
2.39
2.38
2.38
2.37
2.36
2.35
2.35
2.31
2.30
2.30
2.29
2.28
2.26
2.25
1.76
1.75
1.74
1.74
1.72
1.72
1.72
1.47
1.46
O
N
S
O
O
Br
2.0
2.0
1.0
1.0
1.0
1.0
1.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.4
138.1
132.3
129.9
129.3
56.6
30.6
26.7
21.6
O
N
S
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.69
7.67
7.67
7.66
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3.97
3.94
3.94
3.85
3.83
3.82
3.81
2.01
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1.98
1.98
1.97
1.97
1.96
1.95
1.93
1.92
1.92
1.92
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1.91
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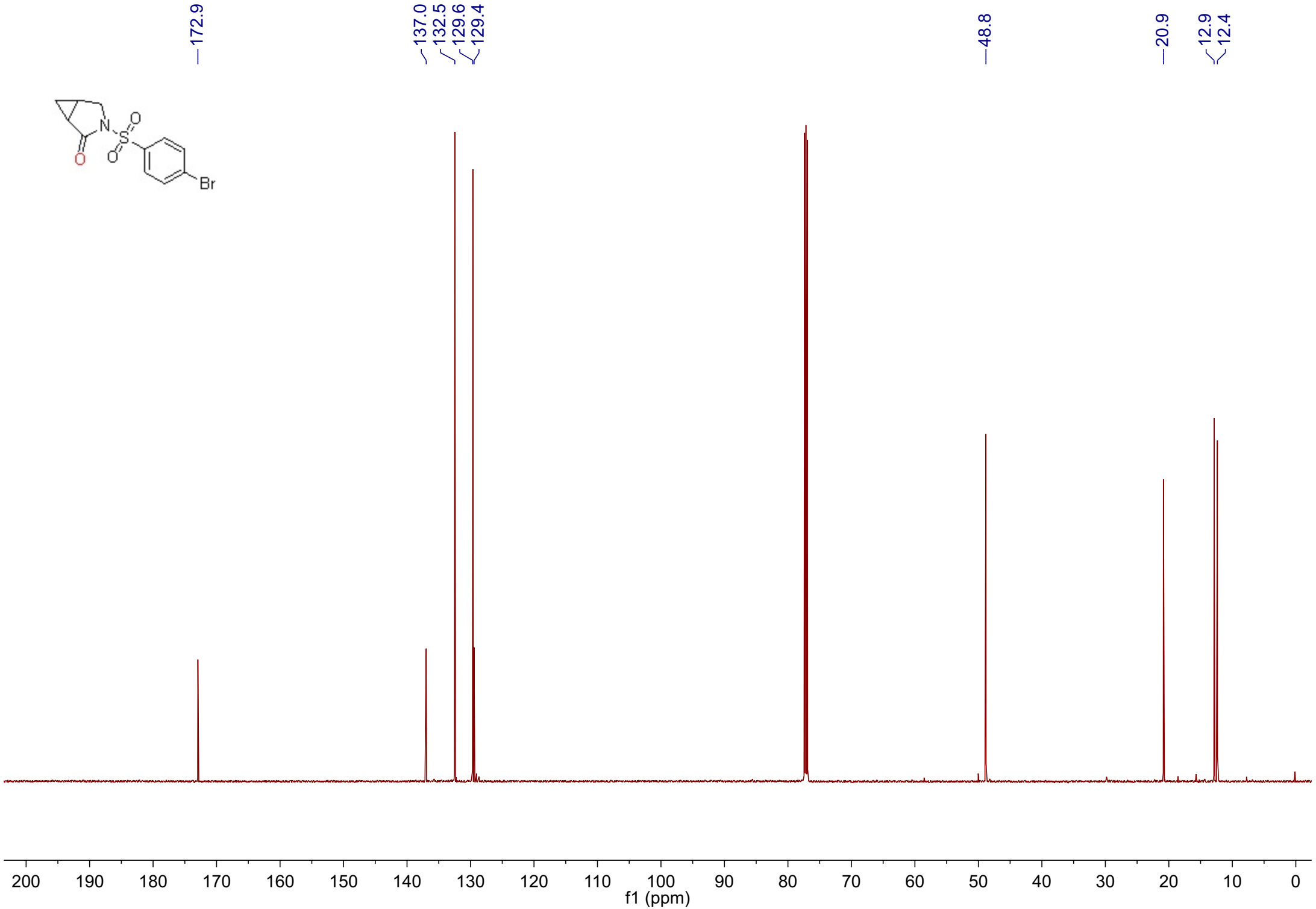
1.90
1.90
1.89
1.89
1.89
1.88
1.88
1.27
1.26
1.25
1.25
1.24
1.23
0.83
0.82
0.82
0.81
O
N
O
S
O
O
Br
2.0
2.0
1.0
1.0
1.0
1.0
1.0
1.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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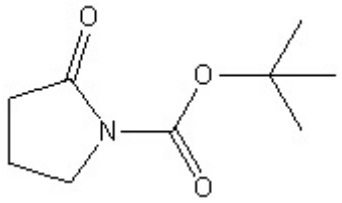
137.0
132.5
129.6
129.4
48.8
20.9
12.9
12.4
N
S
O
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N
O
O

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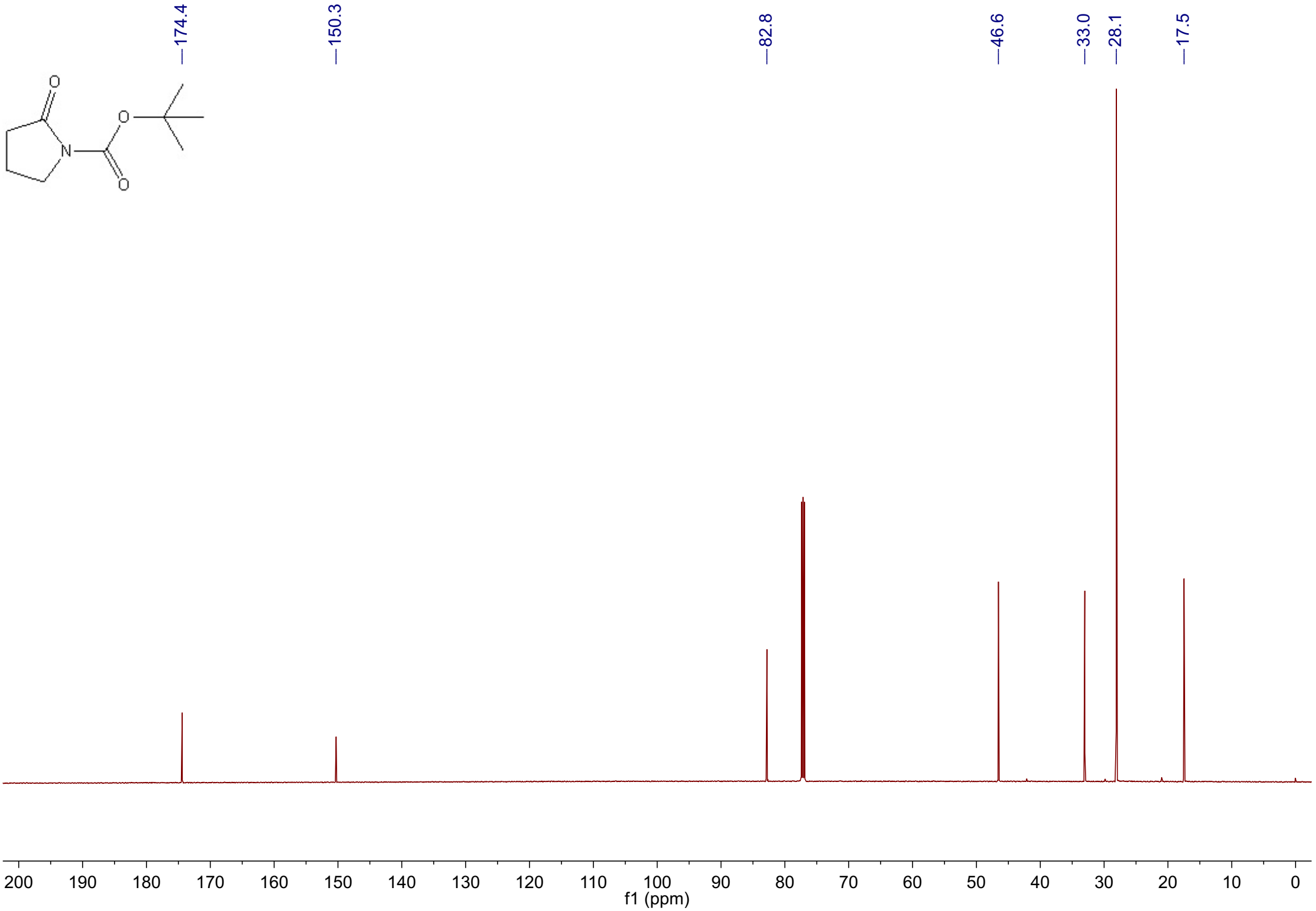
3.71
3.69
2.49
2.47
2.45
2.00
1.98
1.98
1.96
1.94
1.94
1.92
1.48
2.0
2.0
2.0
8.9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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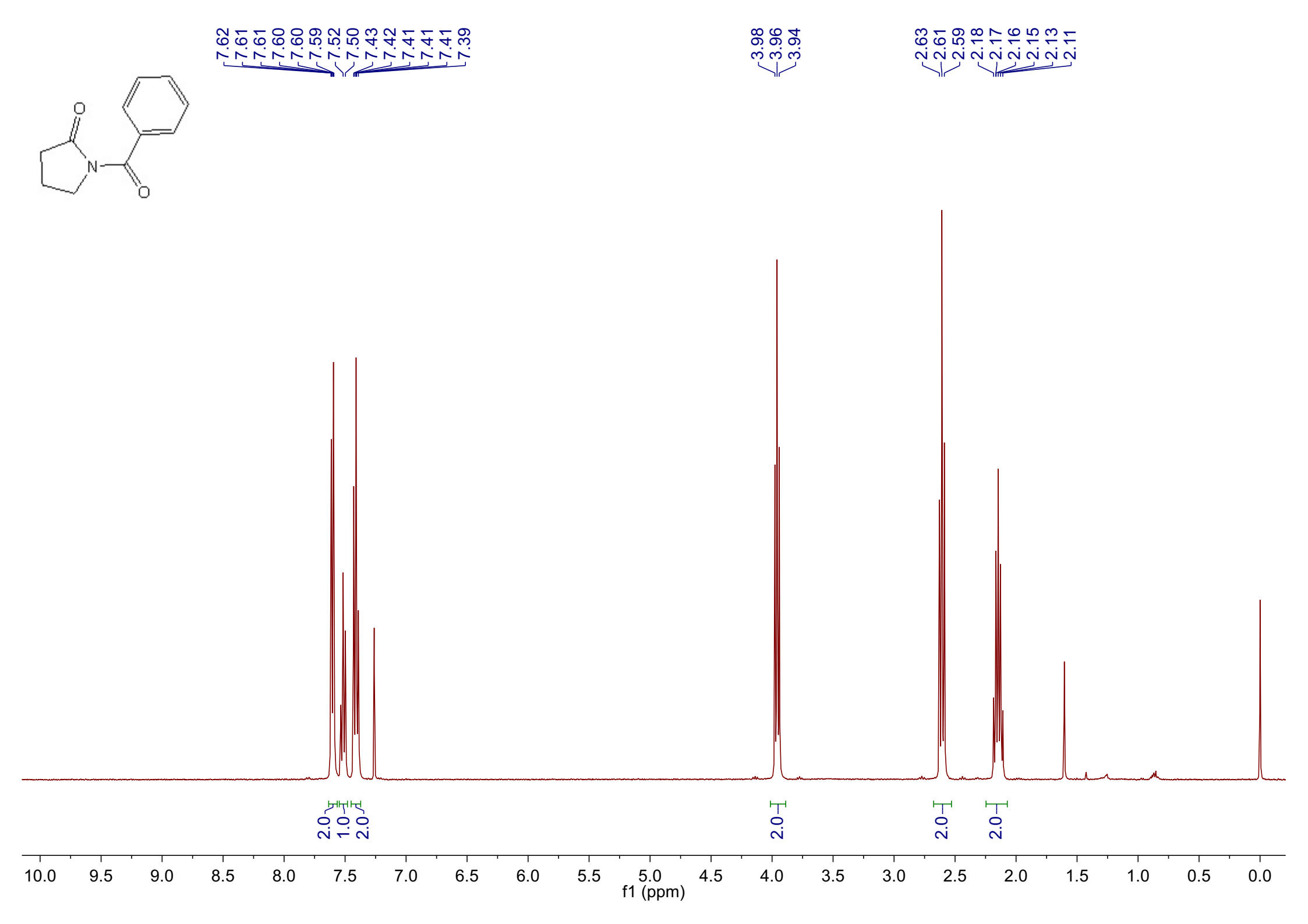
150.3
82.8
46.6
33.0
28.1
17.5
O
O
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.59
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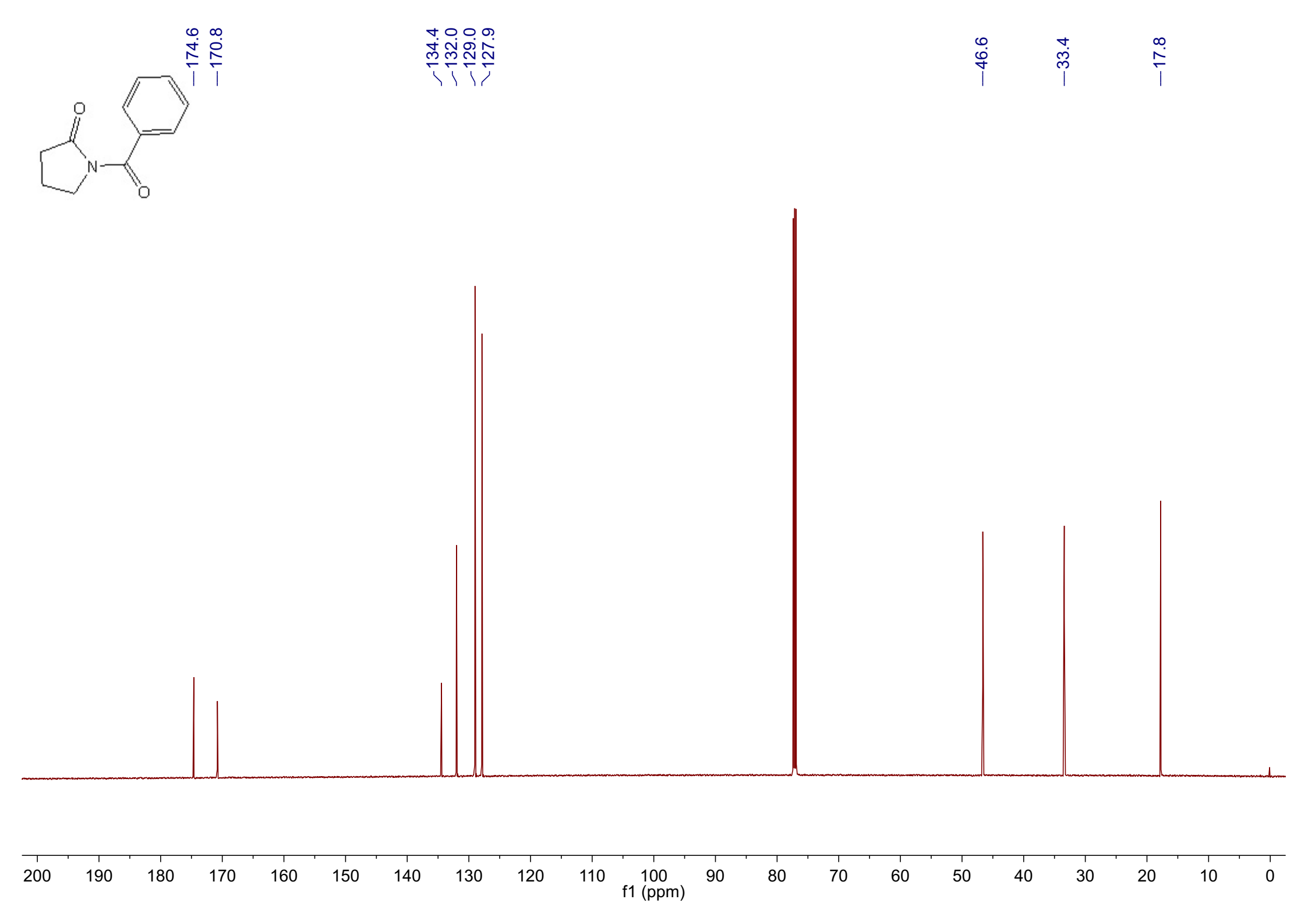
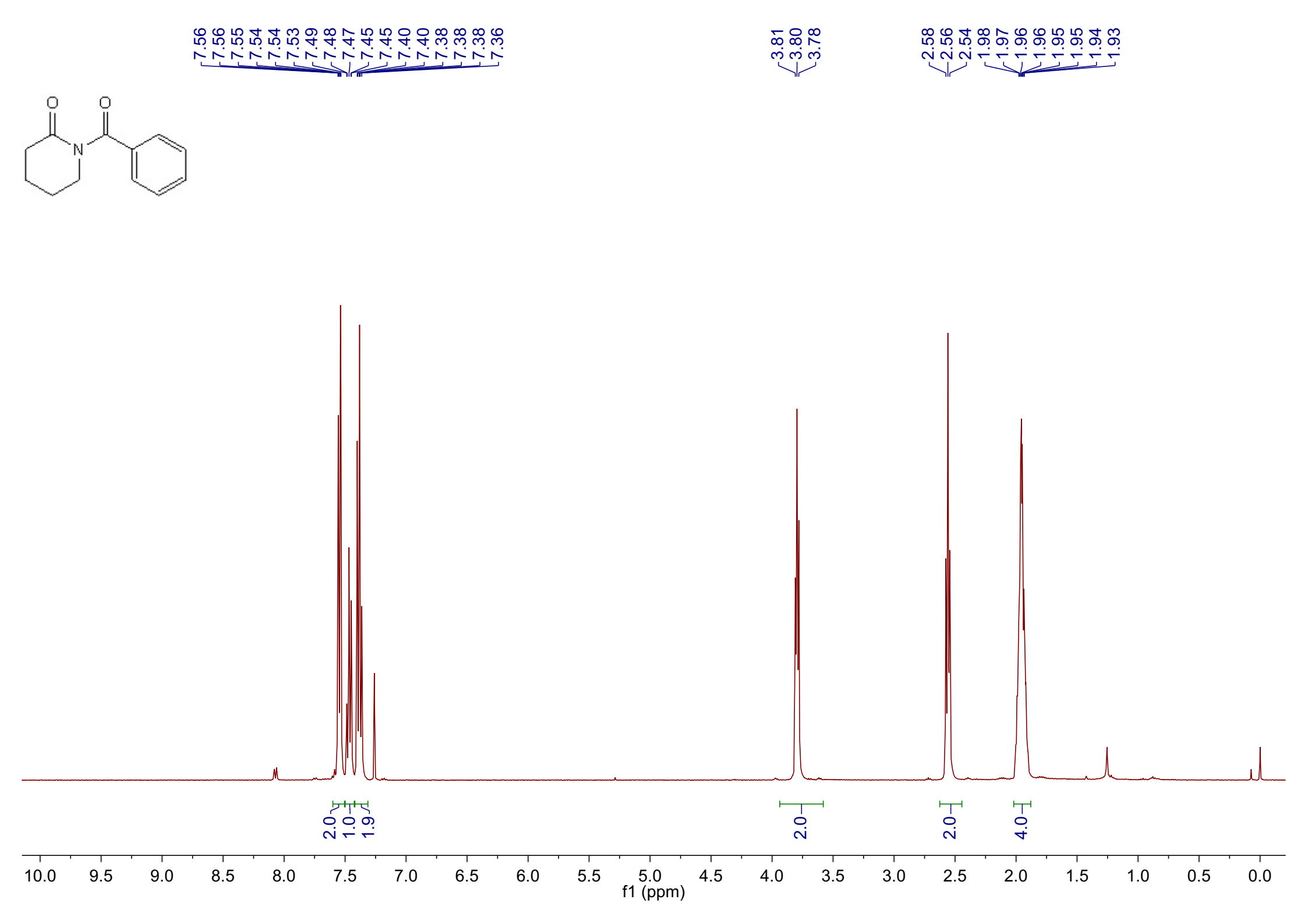
7.50
7.43
7.42
7.41
7.41
7.41
7.39
3.98
3.96
3.94
2.63
2.61
2.59
2.18
2.17
2.16
2.15
2.13
2.11
O
N
O
2.0
1.0
2.0
2.0
2.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.6
170.8
134.4
132.0
129.0
127.9
46.6
33.4
17.8
O
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.56
7.55
7.54
7.54
7.53
7.49
7.48
7.47
7.45
7.45
7.40
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7.38
7.38
7.38
7.36
3.81
3.80
3.78
2.58
2.56
2.54
1.98
1.97
1.96
1.96
1.95
1.95
1.94
1.93
O
O
N
2.0
1.0
1.9
2.0
2.0
4.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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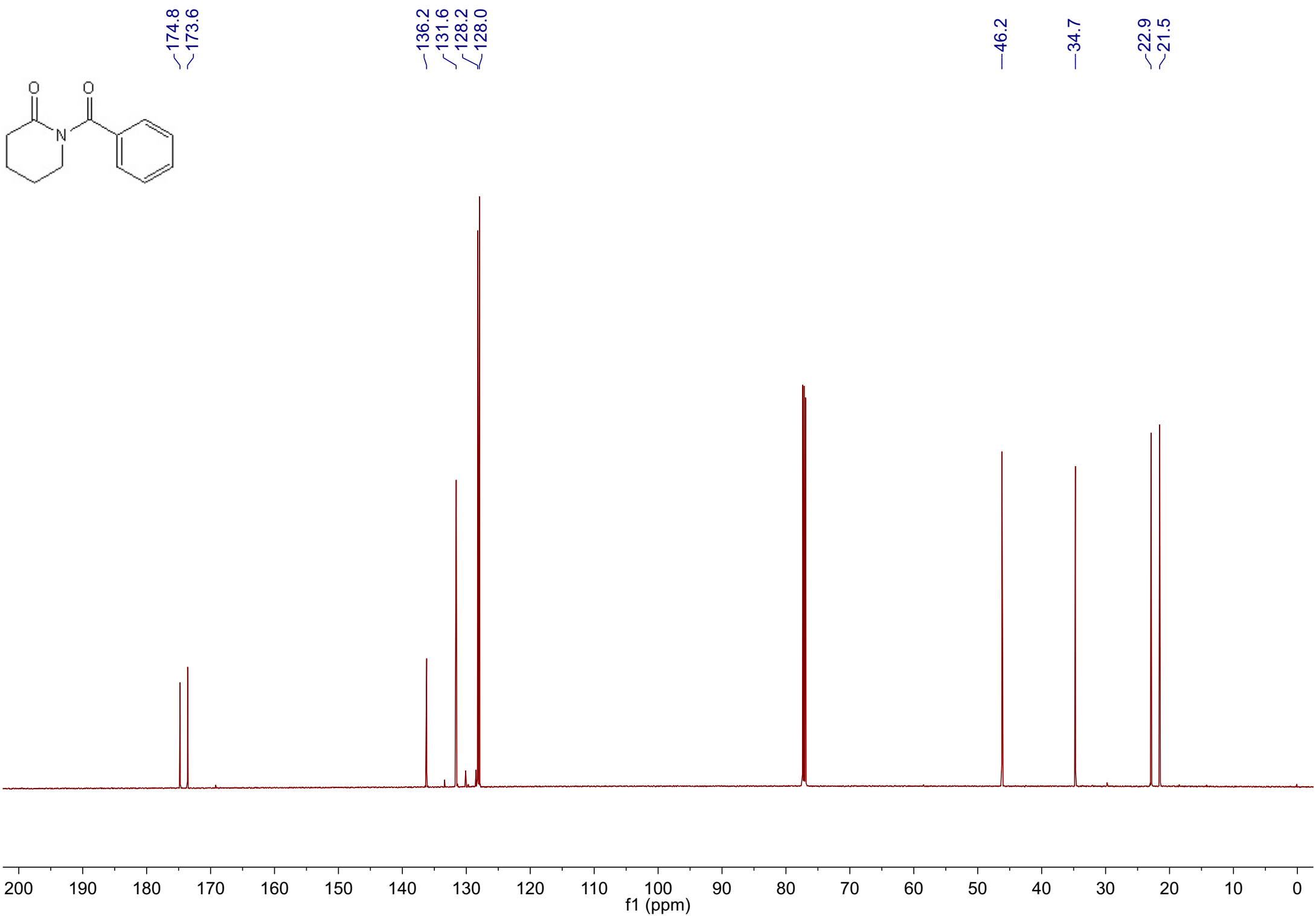
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.8
173.6
136.2
131.6
128.2
128.0
46.2
34.7
22.9
21.5
O
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)