Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Rhenium-Catalyzed Alkylarylation of Alkenes with $PhI(O_2CR)_2$ via Decarboxylation to Access Indolinones and Dihydroquinolinones

Lei Zhang,[a,b] Yin Wang,[b,c] Yunhui Yang,[b,c] Ping Zhang,[a] and Congyang Wang*[,b,c,d]

[a] National Demonstration Center for Experimental Chemistry Education, Hebei Key Laboratory of Organic Functional Molecules, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China

[b] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[c] University of Chinese Academy of Sciences, Beijing 100049, China

[d] Physical Science Laboratory, Huairou National Comprehensive Science Center, Beijing 101400, China

Email: wangcy@iccas.ac.cn

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1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under a nitrogen atmosphere by using standard Schlenk techniques. Reaction temperatures are recorded on the temperature of the bath oil surrounding the Schlenk tubes. Anhydrous solvents were purified and dried by standard procedures. All commercially available reagents were used as received. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh).

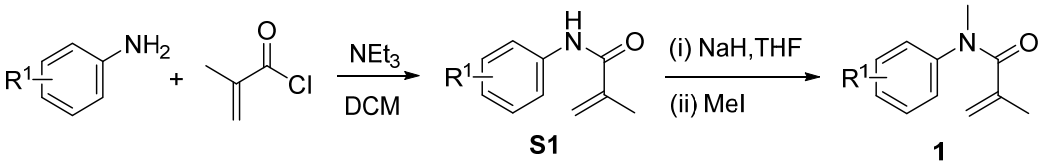
^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on Bruker 300AV, Bruker 400AV and Bruker 500AV spectrometers. All chemical shifts are quoted in parts per million downfield from tetramethylsilane and are referenced to the residue protons of the deuterated solvents ($CDCl_3$: 7.26 ppm ^{1}H and 77.16 ppm ^{13}C). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz). The mass spectra (MS) were recorded on a SHIMADZU QP-2010SE GC-MS spectrometer. The high resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS instrument or a High-Resolution LC-MS spectrometer Thermo Fisher Exactive. Melting points (M.p.) were determined in open capillaries without further correction.

2. Substrate Preparation

2.1 Synthesis of *N*, *N*-disubstituted methacrylmamides

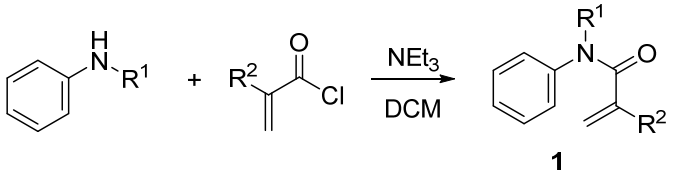
All the substrates **1** were prepared according to the known literature,[1] which are known compounds and their NMR spectral data are in agreement with the literature values.[2]

General procedure A for amides synthesis:



Methacryloyl chloride (1.2 equiv., 6.0 mmol) was added dropwise to a solution of aniline derivative (1.0 equiv, 5.0 mmol) and NEt_3 (1.2 equiv, 6.0 mmol) in DCM (10.0 mL) at 0 °C. The temperature was allowed to rise to ambient temperature, and then the mixture was stirred at the same temperature overnight. Saturated Na_2CO_3 solution was added and the resultant reaction mixture was extracted with DCM. The combined organic phases were washed with 2N HCl, water, brine, and dried over MgSO4. Volatiles were removed in vacuo and the crude mixture purified by column chromatography. THF (10 mL) solution of amide **S1** (5.0 mmol, 1.0 equiv.) was slowly added into the THF (10 mL) suspension of NaH (60% in mineral oil, 0.24 g, 6.0 mmol, 1.2 equiv.) at 0 °C. After stirring for 15 min, CH_3I (7.0 mmol, 1.4 equiv.) was added and the mixture was stirred until completion at RT (monitored by TLC). After distilled water was carefully added, the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over MgSO4. Volatiles were removed in vacuo and the crude mixture purified by column chromatography.

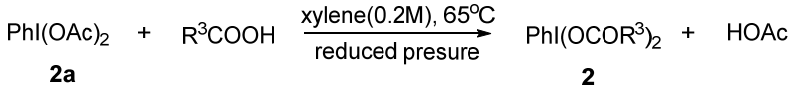
General procedure B for amides synthesis:



The appropriate acid chloride (1.2 equiv., 6.0 mmol) was added dropwise to a solution of aniline derivative (1.0 equiv, 5.0 mmol) and NEt_3 (1.2 equiv, 6.0 mmol) in DCM (10.0 mL) at 0 °C, then the mixture was stirred at r.t. overnight. Saturated Na_2CO_3 solution was added and the resultant reaction mixture was extracted with DCM. The combined organic phases were washed with 2M HCl, brine, water and dried over $MgSO_4$. Volatiles were removed in vacuo and the crude mixture purified by column chromatography.

2.2 Synthesis of hypervalent iodine(III) reagents

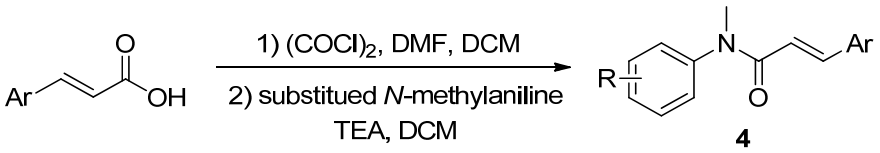
HIR **2a** is commercially available and is used as received. Other HIRs **2** were prepared according to the known literature.[3,4]



In a typical procedure, $PhI(OAc)_2$ (10 mmol, 1.0 eq.) and indicated acid (22 mmol, 2.2 eq.) were dissolved with xylene (50 mL, 0.2 M) in a round-bottom flask, and then the flask was heated to 65 ºC with a rotary evaporator under reduced pressure (about 30-50 Torr.) using a diaphragm pump. When the xylene was removed, product **2** was obtained as a white solid or a viscous oil after wash with petroleum ether (PE), filtered and dried in vacuum, which then could be used directly in the following reaction.

2.3 Synthesis of *N*, *N*-disubstituted cinnamides

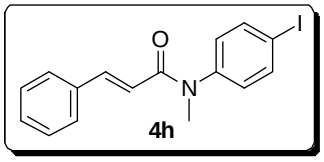
N-methyl-*N*-phenylcinnamamide **4a**, *N*-methyl-*N*-(4-Methylphenyl)cinnamamide **4b**, *N*-(4-Methoxyphenyl)-*N*-methylcinnamamide **4c**, *N*-(4-trifluoromethylphenyl)-*N*-methylcinnamamide **4d**, *N*-(4-Fluorophenyl)-*N*-methylcinnamamide **4e**, *N*-(4-Chlorophenyl)-*N*-methylcinnamamide **4f**, *N*-(4-Bromophenyl)-*N*-methyl cinnamamide **4g** and 3-(4-Chlorophenyl)-*N*-phenyl-*N*-methylacrylamide **4j** were prepared from the corresponding acid chloride and aniline according to the known literatures, and all are known compounds and their NMR spectral data are in agreement with the literature values.[5]



Synthesis of acid chlorides: To a suspension of the indicated acid (1.0 equiv) in DCM (0.3 M) was added a catalytic amount of DMF (0.1 mL / mmol acid). At room temperature, oxalylchloride (1.5 equiv) was added dropwise over a period of 0.5 h, forming a homogenous solution. The resulting solution was kept at room temperature for 3 h. Then, the solvent was removed under reduced pressure and the crude product was directly used in the next step.

Preparation of amides from acid chloride: A solution of acid chloride (1.0 equiv.) in dry DCM (0.50 M) was slowly added dropwise to the solution of the appropriate aniline derivative (1.0 equiv) and Et_3N (2.0 equiv) in DCM (0.25 M). The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion, the mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with NH_4Cl and brine. Dried over Na_2SO_4 and evaporation of the solvent under reduced pressure and purified by flash column chromatography on silica gel (EA/PE) afforded the desired amides.

***N*-(4-iodophenyl)-*N*-methylcinnamamide (4h)**



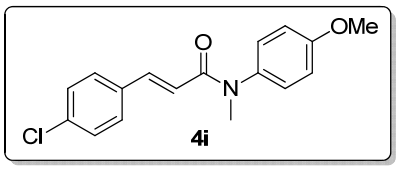
Physical state: white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.35-7.26 (m, 5H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 3.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.06, 143.60, 142.48, 138.92, 135.16, 129.81, 129.30, 128.86, 128.04, 118.43, 92.54, 37.60.

HRMS (ESI-MS): calculated $C_{16}H_{15}ONI$ ($[M + H]^+$): 364.01928, found: 364.01883.

3-(4-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylacrylamide (4i)



Physical state: white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 15.2 Hz, 1H), 7.24 (s, 4H), 7.15-7.12 (m, 2H), 6.96-6.92 (m,

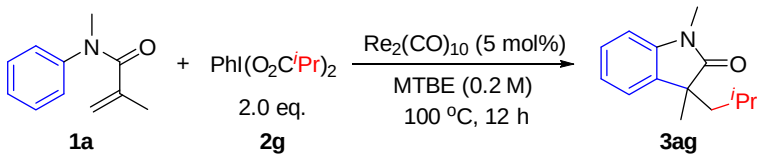
2H), 6.32 (d, J = 15.6 Hz, 1H), 3.85 (s, 3H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 158.95, 140.23, 136.43, 135.33, 133.89, 129.13, 129.01, 128.59, 119.42, 114.92, 55.65, 37.88.

HRMS (ESI-MS): calculated $C_{17}H_{17}O_2NCl$ ($[M + H]^+$): 302.09423, found: 302.09401.

3. Re-Catalyzed Alkylarylation of Alkenes to Access Indolinones

3.1 Screening of Reaction Parameters[a]



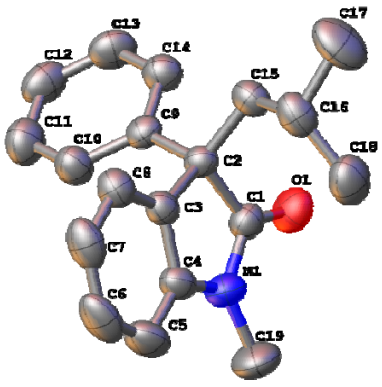
1a **2g** **3ag**

entry	variations of standard conditions	yield of **3ag** (%)[b]
1	none	92 (82)[c]
2	MeCN instead of MTBE	61
3	Toluene instead of MTBE	86
4	THF instead of MTBE	88
5	DMF instead of MTBE	90
6	$ReBr(CO)_5$ instead of $Re_2(CO)_{10}$	66
7	$ReCl(CO)_5$ instead of $Re_2(CO)_{10}$	76
8	without $Re_2(CO)_{10}$	0
9	2.5 instead of 5 mol% of $Re_2(CO)_{10}$	82
10	8 h instead of 12 h	87
11	0.1 M instead of 0.2 M	88
12	0.4 M instead of 0.2 M	83
13	80 °C instead of 100 °C	79
14	1.0 instead of 2.0 eq. of **2g**	71

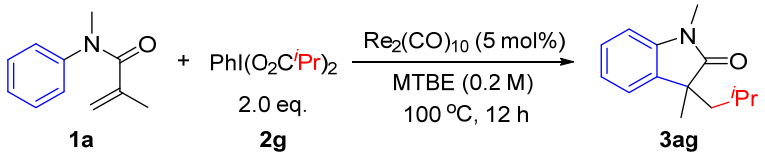
[a] Reaction conditions: **1a** (0.2 mmol), **2g** (0.4 mmol), $Re_2(CO)_{10}$ (5 mol %), MTBE (1.0 mL), 100 °C, 12 h. [b] ^1H NMR yields with 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield on a 0.5 mmol scale.

In addition, indolinone **3og** was unambiguously confirmed by X-ray single-crystal diffraction analysis (**Figure S1**).

Figure S1. X-ray structure of indolinone **3og**



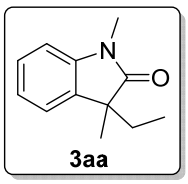
3.2 General Procedure to Access Indolinones



A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. $Re_2(CO)_{10}$ (16.3mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) were added into the reaction vessel under nitrogen atmosphere. Then, the Teflon cap was screwed up and the reaction mixture was stirred in an oil bath (100 °C) for 12 h. After completion of the reaction, the solvent was removed in vacuo. The residue was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ag** as colorless oil.

3.3 Characterization Data for Indolinones

3-ethyl-1,3-dimethylindolin-2-one[6] (3aa)



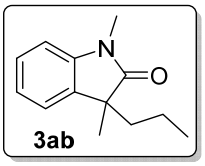
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(OAc)_2$ **2a** (322.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3aa** as colorless oil in 70% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.16 (d, *J* = 6.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.99-1.87 (m, 1H), 1.83-1.71 (m, 1H), 1.35 (s, 3H), 0.59 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.85, 143.58, 134.04, 127.71, 122.60, 122.50, 107.92, 49.04, 31.56, 26.16, 23.41, 8.94.

1,3-dimethyl-3-propyloindolin-2-one[7] (3ab)

According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol),



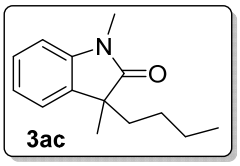
N-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CEt)_2$ **2b** (350.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ab** as colorless oil in 72% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.93-1.83 (m, 1H), 1.75-1.65 (m, 1H), 1.35 (s, 3H), 1.03-0.95 (m, 1H), 0.92-0.82 (m, 1H), 0.77 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.96, 143.44, 134.42, 127.67, 122.58, 122.49, 107.92, 48.61, 40.89, 26.17, 23.84, 17.94, 14.24.

HRMS (ESI-MS): calculated $C_{13}H_{18}ON$ ($[M + H]^+$): 204.13829, found: 204.13827.

3-butyl-1,3-dimethylindolin-2-one[7] (3ac)

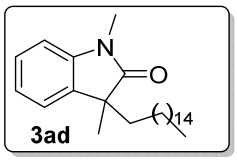


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2C^nPr)_2$ **2c** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ac** as colorless oil in 78% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.25 (m, 1H), 7.19-7.17 (m, 1H), 7.10-7.05 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 1.96-1.86 (m, 1H), 1.79-1.70 (m, 1H), 1.36 (s, 3H), 1.27-1.13 (m, 2H), 1.05-0.83 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.97, 143.43, 134.42, 127.66, 122.55, 122.50, 107.94, 48.51, 38.41, 26.67, 26.18, 23.89, 22.91, 13.91.

3-hexadecyl-1,3-dimethylindolin-2-one[7] (3ad)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CC_{15}H_{31})_2$ **2d** (714.4 mg, 1.0 mmol) and

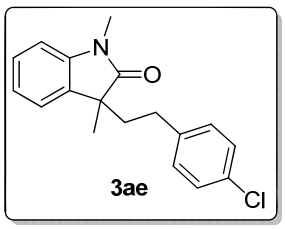
MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ad** as colorless oil in 85% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.23 (m, 1H), 7.16 (d, *J* = 6.6 Hz, 1H), 7.09-7.03 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.93-1.83 (m, 1H), 1.76-1.66 (m, 1H), 1.34 (s, 3H), 1.25-1.14 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.05, 143.46, 134.48, 127.68, 122.58, 122.53, 107.96, 48.59, 38.67, 32.06, 29.88, 29.82, 29.79, 29.73, 29.69, 29.68, 29.49, 29.44, 26.22, 24.58, 23.91, 22.82, 14.25.

HRMS (ESI-MS): calculated $C_{26}H_{43}ONNa$ ($[M + Na]^+$): 408.32369, found: 408.32344.

3-(4-chlorophenethyl)-1,3-dimethylindolin-2-one[8] (3ae)



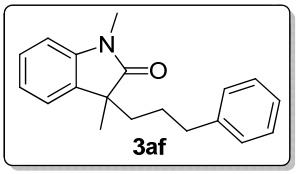
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CR)_2$ (R = 4-Chlorobenzyl) **2e** (543.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ae** as colorless oil in 72% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.26 (m, 1H), 7.22-7.07 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 3H), 2.31-2.19 (m, 2H), 2.14-1.93(m, 2H), 1.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.29, 143.49, 139.86, 133.63, 131.66, 129.76, 128.39, 128.03, 122.75, 122.57, 108.18, 48.40, 40.09, 30.51, 26.24, 24.13.

HRMS (ESI-MS): calculated $C_{18}H_{19}ONCl$ ($[M + H]^+$): 300.11497 found: 300.11478.

1,3-dimethyl-3-(3-phenylpropyl)indolin-2-one[6,7] (3af)

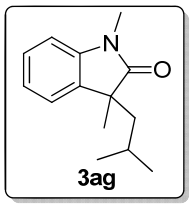


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CR)_2$ (R = 2-Phenylethyl) **2f** (502.5 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3af** as colorless oil in 80% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.18 (m, 3H), 7.14-7.10 (m, 2H), 7.06-7.02 (m, 3H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.18 (s, 3H), 2.57-2.38 (m, 2H), 2.01-1.91 (m, 1H), 1.82-1.72 (m, 1H), 1.39-1.27 (m, 4H), 1.23-1.12 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.72, 143.38, 141.97, 134.08, 128.42, 128.31, 127.74, 125.81, 122.53, 108.00, 48.40, 38.21, 36.04, 26.46, 26.19, 23.96.

3-isobutyl-1,3-dimethyl-indolin-2-one[6,9] (3ag)

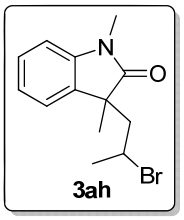


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ag** as colorless oil in 82% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 1.94 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.76 (dd, *J* = 14.0, 5.2 Hz, 1H), 1.32 (s, 3H), 1.28-1.22 (m, 1H), 0.65 (d, *J* = 6.8 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.11, 143.25, 134.26, 127.63, 122.85, 122.38, 108.00, 48.12, 46.80, 26.22, 26.19, 25.58, 24.17, 22.89.

3-(2-bromopropyl)-1,3-dimethylindolin-2-one (3ah)



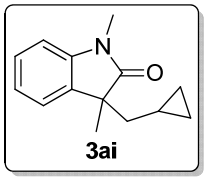
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CR)_2$ (R=1-bromoethyl) **2h** (507.9 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ah** (*dr* = 1.0) as colorless oil in 65% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.05 (m, 3H), 6.89-6.86 (m, 1H), 3.82-3.69 (m, 1H), [3.22 (s), 3.21 (s), 3H], 2.74-2.23 (m, 2H), [1.49 (d, *J* = 6.4 Hz), 1.44 (d, *J* = 6.4 Hz), 3H], 1.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.93, 179.81, 143.76, 143.11, 132.33, 132.27, 128.29, 128.25, 123.17, 122.82, 122.65, 122.41, 108.47, 108.40, 48.28, 48.19, 47.83, 45.99, 45.73, 27.52, 26.58, 26.48, 26.38, 26.11, 25.81.

HRMS (ESI-MS): calculated $C_{13}H_{17}ONBr$ ($[M + H]^+$): 282.04880, found: 282.04870.

3-(cyclopropylmethyl)-1,3-dimethylindolin-2-one (3ai)



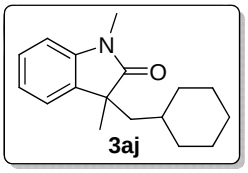
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CR)_2$ (R = Cyclopropyl) **2i** (374.5 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ai** as colorless oil in 63% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.22 (m, 2H), 7.10-7.05 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 1.93 (dd, *J* = 13.5, 5.4 Hz, 1H), 1.61 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.37 (s, 3H), 0.33-0.24 (m, 1H), 0.21-0.16 (m, 2H), 0.10-0.05 (m, 1H), [-0.08]-[-0.15] (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.04, 143.57, 134.55, 127.67, 122.84, 122.33, 107.86, 48.91, 43.35, 26.22, 23.31, 6.58, 3.94, 3.79.

HRMS (ESI-MS): calculated $C_{14}H_{18}ON^+$ ($[M+H^+]$): 216.13829, found: 216.13829.

3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one[6] **(3aj)**

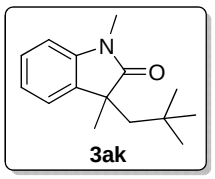


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2CR)_2$ (R = Cyclohexyl) **2j** (687.5 mg, 1.5 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3aj** as colorless oil in 80% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.07-7.04 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 1.93 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.73 (dd, *J* = 14.0, 5.2 Hz, 1H), 1.52-1.45 (m, 3H), 1.36-1.31 (m, 4H), 1.26-1.19 (m, 1H), 1.02-0.73 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.26, 143.19, 134.51, 127.61, 122.80, 122.43, 108.04, 47.96, 45.51, 34.82, 34.55, 33.62, 26.29, 26.24, 26.19 (2C), 26.12.

1,3-dimethyl-3-neopentylindolin-2-one[6,10] **(3ak)**



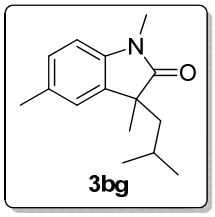
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylmethacrylamide **1a** (87.5 mg, 0.5 mmol), $PhI(O_2C^tBu)_2$ **2k** (609.1 mg, 1.5 mmol) and CH_3CN (2.5 mL) was stirred at 100 °C for 24 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ak** as white solid in 82% isolated yield.

M.p.: 77-79 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.19 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 2.17 (d, *J* = 14.4 Hz, 1H), 1.87 (d, *J* = 14.4 Hz, 1H), 1.31 (s, 3H), 0.62 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.21, 143.05, 134.39, 127.72, 124.04, 122.16, 108.19, 50.98, 47.58, 31.95, 30.99 (3C), 28.46, 26.41.

3-isobutyl-1,3,5-trimethylindolin-2-one (3bg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-(4-methylphenyl)methacrylamide **1b** (94.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3bg** as colorless oil in 85% isolated yield.

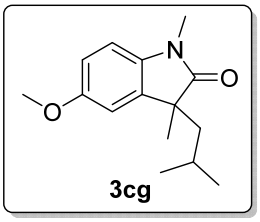
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.18 (s, 3H), 2.34 (s, 3H), 1.91 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.72 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.30 (s, 3H), 1.25-1.21 (m, 1H), 0.62 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.16, 140.95, 134.36, 131.88, 127.88, 123.76, 107.75, 48.21, 46.82, 26.33, 26.30, 25.64, 24.28, 22.82, 21.27.

HRMS (ESI-MS): calculated $C_{15}H_{22}ON$ ($[M + H]^+$): 232.16959, found: 232.16942.

3-isobutyl-5-methoxyl-1,3-dimethylindolin-2-one (3cg)

According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol),



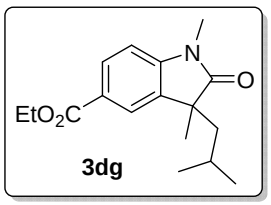
N-(4-methoxyphenyl)-*N*-methylmethacrylamide **1c** (102.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3cg** as colorless oil in 87% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 6.78-6.70 (m, 3H), 3.78 (s, 3H), 3.17 (s, 3H), 1.91 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.71 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.28-1.17 (m, 4H), 0.64-0.59 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.78, 156.04, 136.90, 135.78, 111.51, 110.71, 108.20, 55.87, 48.57, 46.79, 26.33, 25.61, 24.22, 22.82.

HRMS (ESI-MS): calculated $C_{15}H_{22}O_2N$ ($[M + H]^+$): 248.16451, found: 248.16440.

Ethyl 3-isobutyl-1,3-dimethyl-2-oxoindoline-5-carboxylate (3dg)



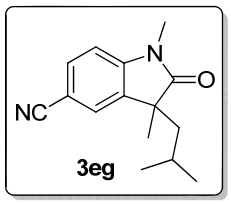
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), ethyl 4-[methyl(2-methyl-1-oxoprop-2-enyl)amino]benzoate **1d** (123.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3dg** as colorless oil in 81% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.2 Hz, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 1.5 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 4.39-4.32 (m, 2H), 3.23 (s, 3H), 1.94 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.80 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 1.27-1.18 (m, 1H), 0.62-0.58 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.45, 166.67, 147.37, 134.23, 130.46, 124.77, 124.13, 107.53, 60.97, 48.03, 46.68, 26.48, 26.17, 25.64, 24.19, 22.79, 14.51.

HRMS (ESI-MS): calculated $C_{17}H_{24}O_3N$ ($[M + H]^+$): 290.17507, found: 290.17493.

3-isobutyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3eg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-cyanophenyl)-*N*,2-dimethyl-2-propenamide **1e** (100.3 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3eg** as white solid in 83% isolated yield.

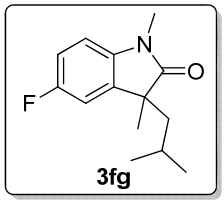
M.p.: 103-105 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 1.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.23 (s, 3H), 1.96 (dd, *J* = 14.1, 7.8 Hz, 1H), 1.76 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.33 (s, 3H), 1.28-1.14 (m, 1H), 0.64-0.60 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.74, 147.20, 135.40, 133.21, 126.25, 119.46, 108.50, 105.59, 48.04, 46.65, 26.53, 26.09, 25.67, 24.19, 22.86.

HRMS (ESI-MS): calculated $C_{15}H_{19}ON_2$ ($[M + H]^+$): 243.14919, found: 243.14933.

5-fluoro-3-isobutyl-1,3-dimethylindolin-2-one (3fg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-flourophenyl)-*N*-methylmethacrylamide **1f** (96.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3fg** as colorless oil in 80% isolated yield.

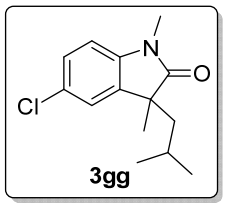
^{1}H NMR (300MHz, $CDCl_3$) δ 6.98-6.89 (m, 2H), 6.76-6.72 (m, 1H), 3.19 (s, 3H), 1.93 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.71 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.30 (s, 3H), 1.27-1.18 (m, 4H), 0.65-0.59 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.77, 159.45 (d, $J_{C\text{-}F}$=238.7 Hz), 139.25, 136.13 (d, $J_{C\text{-}F}$=7.8 Hz), 113.82 (d, $J_{C\text{-}F}$=23.3 Hz), 108.45 (d, $J_{C\text{-}F}$=8.2 Hz), 48.69 (d, $J_{C\text{-}F}$=1.7 Hz), 46.76, 26.43, 26.21, 25.65, 24.18, 22.88.

^{19}F NMR (471 MHz, $CDCl_3$): -121.03

HRMS (ESI-MS): calculated $C_{14}H_{19}ONF$ ($[M + H]^+$): 236.14452, found: 236.14423.

5-chloro-3-isobutyl-1,3-dimethylindolin-2-one (3gg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-chlorophenyl)-*N*-methylmethacrylamide **1g** (105.0 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3gg** as colorless oil in 79% isolated yield.

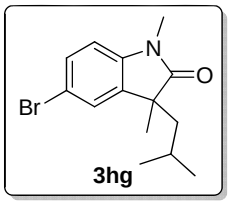
^{1}H NMR (300MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.2 Hz, *J* = 1.9 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.18 (s, 3H), 1.93 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.72 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.30 (s, 3H), 1.27-1.18 (m, 1H), 0.64-0.61 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.61, 141.88, 136.09, 127.87, 127.63, 123.43,

108.98, 48.46, 46.69, 26.41, 26.23, 25.64, 24.23, 22.79.

HRMS (ESI-MS): calculated $C_{14}H_{19}ONCl$ ($[M + H]^+$): 252.11497, found: 252.11481.

5-bromo-3-isobutyl-1,3-dimethylindolin-2-one (3hg)



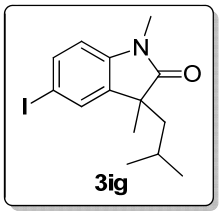
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025mmol), *N*-(4-bromophenyl)-*N*-methylmethacrylamide **1h** (127.1 mg, 0.5mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3hg** as colorless oil in 81% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 3.20 (s, 3H), 1.94 (dd, *J* = 14.1, 7.8 Hz, 1H), 1.74 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.32-1.20 (m, 4H), 0.64 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.50, 142.35, 136.47, 130.53, 126.17, 115.19, 109.52, 48.42, 46.68, 26.38, 26.24, 25.64, 24.24, 22.77.

HRMS (ESI-MS): calculated $C_{14}H_{19}ONBr$ ($[M + H]^+$): 296.06445, found: 296.06441.

5-iodo-3-isobutyl-1,3-dimethylindolin-2-one (3ig)



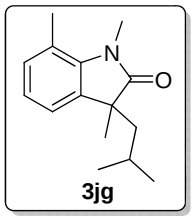
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-iodophenyl)-*N*-methylmethacrylamide **1i** (150.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ig** as colorless oil in 82% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 3.17 (s, 3H), 1.91 (dd, *J* = 14.1, 7.8 Hz, 1H), 1.71 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.31-1.17 (m, 4H), 0.61 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.31, 143.03, 136.81, 136.51, 131.72, 110.14, 85.07, 48.24, 46.66, 26.33, 26.24, 25.62, 24.25, 22.76.

HRMS (ESI-MS): calculated $C_{14}H_{19}ONI$ ($[M + H]^+$): 344.05058, found: 344.05044.

3-isobutyl-1,3,7-trimethylindolin-2-one (3jg)



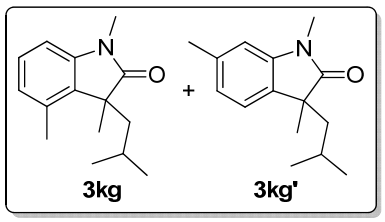
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-(*o*-tolyl)methacrylamide **1j** (94.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3jg** as colorless oil in 80% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.00-6.90 (m, 3H), 3.49 (s, 3H), 2.58 (s, 3H), 1.92 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.72 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.33-1.15 (m, 4H), 0.66 (d, *J* = 6.6 Hz, 3H), 0.60 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.92, 141.08, 134.97, 131.37, 122.33, 120.86, 119.64, 47.47, 47.12, 29.62, 26.68, 25.58, 24.28, 22.96, 19.19.

HRMS (ESI-MS): calculated $C_{15}H_{22}ON$ ($[M + H]^+$): 232.16959, found: 232.16945.

3-isobutyl-1,3,4-trimethylindolin-2-one & 3-isobutyl-1,3,6-trimethylindolin-2-one (3kg & 3kg')



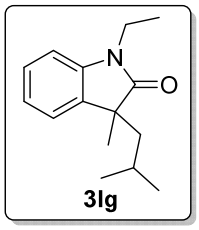
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-(*m*-tolyl)methacrylamide **1k** (94.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded the mix compound (**3kg** & **3kg'**) as colorless oil in 66% isolated yield, mixture was determined by ^{1}H NMR, ratio = 1.2:1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.02 (m, 1H), 6.88-6.81 (m, 1H), 6.68-6.71 (m, 1H), 3.20 (s, 3H), [2.39 (s), 2.35 (s), 3H], 2.03-1.70 (m, 2H), [1.38 (s), 1.30 (s), 3H], 1.23-1.13 (m, 1H), 0.69-0.58 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.55, 181.36, 143.53, 143.40, 137.70, 134.42, 131.35, 130.95, 127.60, 125.00, 122.92, 122.67, 109.05, 105.88, 49.05, 47.97, 46.85, 45.16, 26.41, 26.36, 26.27, 26.08, 25.67, 24.31, 24.08, 24.00, 22.92, 22.37, 21.91, 18.38.

HRMS (ESI-MS): calculated $C_{15}H_{22}ON$ ($[M + H]^+$): 232.16959, found: 232.16949.

1-ethyl-3-isobutyl-3-methylindolin-2-one (3lg)

According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), 

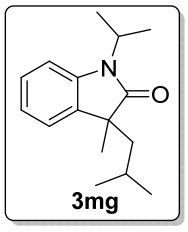
N-ethyl-*N*-phenylmethacrylamide **1l** (94.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3lg** as colorless oil in 69% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 6.9 Hz, 1H), 7.04 (d, *J* = 7.5 Hz,1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.91-3.79 (m, 1H), 3.76-3.64 (m, 1H), 1.95 (dd, *J* = 14.1, 7.8 Hz, 1H), 1.75 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.31 (s, 3H) 1.28-1.23 (m, 4H), 0.67 (d, *J* = 6.6 Hz, 3H), 0.60 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.70, 142.37, 134.58, 127.57, 123.08, 122.16, 108.19, 48.04, 46.74, 34.57, 26.40, 25.65, 24.15, 23.01, 12.57.

HRMS (ESI-MS): calculated $C_{15}H_{22}ON$ ($[M + H]^+$): 232.16959, found: 232.16956.

1-isopropyl-3-isobutyl-3-methylindolin-2-one (3mg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-isopropyl-*N*-phenylmethacrylamide **1m** (101.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3mg** as colorless oil in 72% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.15 (m, 2H), 7.05-7.00 (m, 2H), 4.68 (hept, *J* =

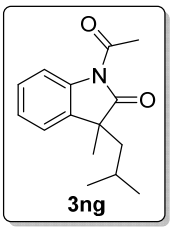
6.9 Hz, 1H), 1.94 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.73 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.48 (d, *J* = 1.8 Hz, 3H), 1.45 (d, *J* = 1.8 Hz, 3H), 1.30-1.20 (m, 4H), 0.67 (d, *J* = 6.9 Hz, 3H), 0.60 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.73, 136.86, 129.85, 122.30, 118.15, 116.79, 104.87, 42.75, 41.83, 38.43, 21.64, 20.62, 19.10, 17.95, 14.46, 14.25.

HRMS (ESI-MS): calculated $C_{16}H_{24}ON$ ($[M + H]^+$): 246.18524, found: 246.18520.

1-acetyl-3-isobutyl-3-methylindolin-2-one (3ng)

According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-acetyl-*N*-phenylmethacrylamide **1n** (101.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3ng** as colorless oil in 45% isolated yield.

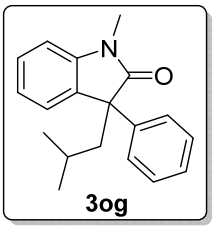


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H), 7.34-7.17 (m, 3H), 2.69 (s, 3H), 1.98 (dd, *J* = 14.1, 8.1 Hz, 1H), 1.81 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.39 (s, 3H), 1.34-1.26 (m, 1H), 0.69-0.63 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.15, 171.25, 139.44, 133.20, 128.16, 125.28, 122.72, 116.76, 48.65, 47.76, 27.45, 26.89, 25.67, 24.17, 22.98.

HRMS (ESI-MS): calculated $C_{15}H_{20}O_2N$ ($[M + H]^+$): 246.14886, found: 246.14887.

3-isobutyl-1-methyl-3-phenyl-indolin-2-one (3og)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*,2-diphenylacrylamide **1o** (118.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and MTBE (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **3og** as colorless solid in 70% isolated yield.

M.p.: 108-110 °C.

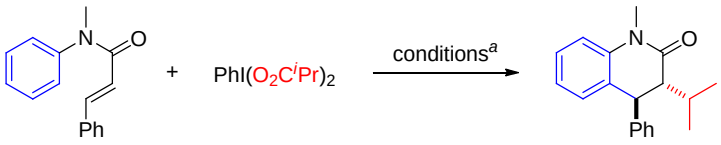
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 3H), 7.28-7.19 (m, 4H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 1.94 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.76 (dd, *J* = 13.6, 5.2 Hz, 1H), 1.39 (hept, *J* = 6.4 Hz, 1H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.16, 144.26, 141.84, 132.11, 128.65, 128.37, 127.37, 126.94, 125.64, 122.60, 108.52, 56.47, 46.85, 26.68, 25.88, 24.57, 23.07.

HRMS (ESI-MS): calculated $C_{19}H_{22}ON$ ($[M + H]^+$): 280.16959, found: 280.16958.

4. Re-Catalyzed Alkylarylation of Alkenes to Access Dihydroquinolinones

4.1 Screening of Reaction Parameters



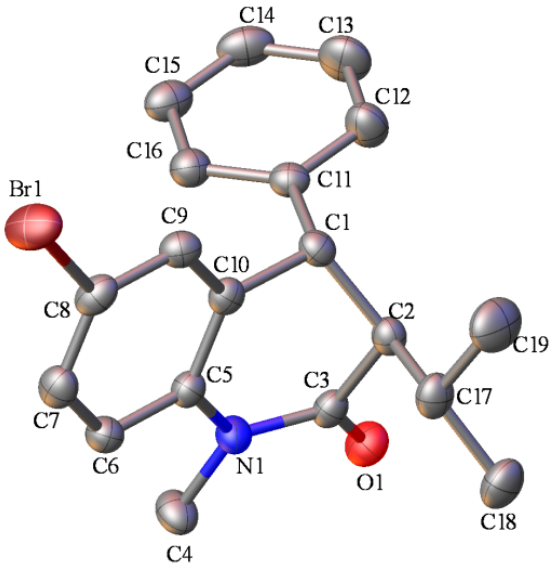
4a **2g** **5ag** (*trans*)

Entry	Catalyst (mol%)	**2g** (eq.)	solvent (M)	additive (0.5 eq.)	T (^{o}C)	t (h)	Yield(%)[b] **5ag**[c]
1	$Re(CO)_5Cl$ (5)	2.0	CH_3CN (0.2)	/	100	12	59
2	$Re(CO)_5Br$ (5)	2.0	CH_3CN (0.2)	/	100	12	60
3	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	100	12	69 (50)[d]
4	$Re_2(CO)_{10}$ (5)	2.0	PhCl (0.2)	/	100	12	61
5	$Re_2(CO)_{10}$ (5)	2.0	THF (0.2)	/	100	12	47
6	$Re_2(CO)_{10}$ (5)	2.0	Dioxane (0.2)	/	100	12	57
7	$Re_2(CO)_{10}$ (5)	2.0	Toluene (0.2)	/	100	12	56
8	$Re_2(CO)_{10}$ (5)	2.0	PhOMe (0.2)	/	100	12	54
9	$Re_2(CO)_{10}$ (5)	2.0	DMF (0.2)	/	100	12	63
10	$Re_2(CO)_{10}$ (5)	2.0	DCE (0.2)	/	100	12	43
11	$Re_2(CO)_{10}$ (5)	2.0	MTBE (0.2)	/	100	12	56
12	$Re_2(CO)_{10}$ (5)	2.0	CCl_4 (0.2)	/	100	12	0
13	$Re_2(CO)_{10}$ (2.5)	2.0	CH_3CN (0.2)	/	100	12	65
14	$Re_2(CO)_{10}$ (10)	2.0	CH_3CN (0.2)	/	100	12	61
15	$Re_2(CO)_{10}$ (5)	1.0	CH_3CN (0.2)	/	100	12	54
16	$Re_2(CO)_{10}$ (5)	3.0	CH_3CN (0.2)	/	100	12	63
17[e]	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.1)	/	100	12	68
18	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.4)	/	100	12	56
19	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	80	12	59
20	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	150	12	57
21	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	$MgBr_2$	100	12	0
22	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	$FeCl_2$	100	12	25
23	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	$ZnCl_2$	100	12	20
24	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	LiCl	100	12	56
25[e]	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	100	8	64
26[e]	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	100	10	65
27	$Re_2(CO)_{10}$ (5)	2.0	CH_3CN (0.2)	/	100	24	62
28[f]	/	2.0	CH_3CN (0.2)	/	100	12	0

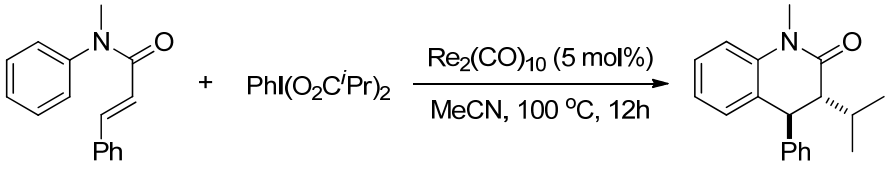
[a] All reactions were carried out on 0.2 mmol scale (**4a**) unless otherwise noted. Small amounts of unisolable byproducts were detected in the reaction. [b] The yields was determined by ^{1}H NMR in the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] The *cis*-isomer was not observed by ^{1}H NMR. [d] Isolated yield of the pure product **5ag** on 1.0 mmol scale. [e] **4a** (0.1 mmol scale). [f] no catalyst.

In order to verify clearly the structure of dihydroquinolinones **5**, the alkylarylation product **5gg** was unambiguously confirmed by X-ray single-crystal diffraction analysis (**Figure S2**).

Figure S2. X-ray structure of Dihydroquinolinone **5gg**



4.2 General Procedure to Access Dihydroquinolinones

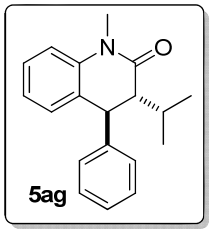


4a **2g** **5ag**

A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-methyl-*N*-phenylcinnamamide **4a** (237.2 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.3 mg, 2.0 mmol) and CH_3CN (5.0 mL) were added into the reaction vessel under nitrogen atmosphere. Then, the Teflon cap was screwed up and the reaction mixture was stirred in an oil bath (100 °C) for 12 h. After completion of the reaction, the solvent was removed in vacuo. The residue was pre-absorbed on silica gel and purified by flash column chromatography affording product **5ag** as colorless oil.

4.3 Characterization Data for Dihydroquinolinones

3-isopropyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9,11,12] (5ag)

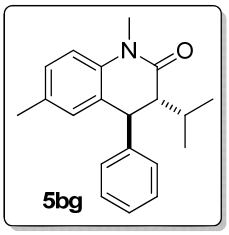


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-methyl-*N*-phenylcinnamamide **4a** (237.2 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.3 mg, 2.0 mmol) and CH_3CN (5.0 mL) stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ag** as colorless oil in 50% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35-7.29 (m, 1H), 7.25-7.12 (m, 4H), 7.07-7.03 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 4.19 (s, 1H), 3.35 (s, 3H), 2.60 (dd, *J* = 9.0, 2.1 Hz, 1H), 1.72-1.64 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.75, 142.26, 140.27, 129.69, 128.83, 128.16, 127.22, 126.87, 126.82, 123.33, 114.91, 56.52, 45.18, 29.59, 28.66, 21.12, 21.06.

3-isopropyl-1,6-dimethyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9,11,12] (5bg)

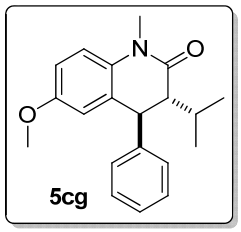


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-Methyl-*N*-(p-tolyl)cinnamamide **4b** (125.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and CH_3CN (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5bg** as colorless oil in 51% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.16-7.09 (m, 2H), 6.98-6.93 (m, 4H), 4.13 (s, 1H), 3.33 (s, 3H), 2.56 (dd, *J* = 9.3 Hz, 1.5 Hz, 1H), 2.29 (s, 3H), 1.73-1.62 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.61, 142.49, 137.93, 132.85, 130.38, 128.83, 128.58, 127.23, 126.78, 126.68, 114.81, 56.76, 45.28, 29.59, 28.68, 21.17, 21.10, 20.72.

3-isopropyl-6-methoxy-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[11] (5cg)



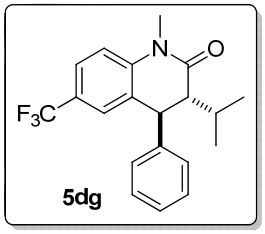
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-(4-Methoxyphenyl)-*N*-methylcinnamamide **4c** (267.1 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.1 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5cg** as colorless oil in 54% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.25-7.12 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 3H), 6.86-6.82 (m, 1H), 6.75 (d, *J* = 2.7 Hz, 1H), 4.13 (s, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 2.57 (dd, *J* = 9.0, 1.8 Hz, 1H), 1.74-1.62 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.30, 155.74, 142.07, 133.94, 128.84, 128.30, 127.22, 126.85, 115.87, 115.58, 112.66, 56.65, 55.59, 45.45, 29.73, 28.62, 21.17, 21.06.

HRMS (ESI-MS): calculated $C_{20}H_{24}O_2N$ ($[M + H]^+$): 310.18016, found: 310.17989.

3-isopropyl-1-methyl-4-phenyl-6-trifluoromethyl-3,4-dihydroquinolin-2(1*H*)-one [9,11] (5dg)



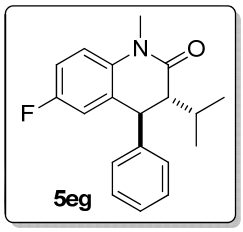
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-(4-trifluoromethylphenyl)-*N*-methyl cinnamamide **4d** (305.2 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.6 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5dg** as colorless oil in 47% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.20-7.13 (m, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.26 (s, 1H), 3.38 (s, 3H), 2.64 (dd, *J* = 9.2, 1.6 Hz, 1H), 1.70-1.61 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.59, 143.11, 141.28, 129.03, 127.32, 127.19, 127.05, 126.53 (q, *J* = 3.6 Hz), 125.55 (q, *J* = 3.6 Hz), 125.26 (q, *J* = 32.7 Hz), 114.87, 56.24, 45.07, 29.68, 28.73, 21.06, 21.01.

^{19}F NMR (471 MHz, $CDCl_3$): -61.84.

6-fluoro-3-isopropyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9] (5eg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-(4-Fluorophenyl)-*N*-methyl cinnamamide **4e** (255.2 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.2 mg, 2.0mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5eg** as colorless oil in 42% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.26-7.15 (m, 3H), 7.02-6.90 (m, 5H), 4.14 (s, 1H), 3.34 (s, 3H), 2.59 (dd, *J* = 9.0, 2.1 Hz, 1H), 1.74-1.60 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

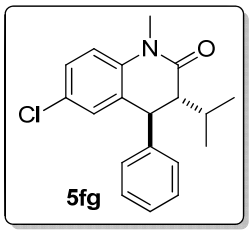
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.31, 158.83 ($J_{C\text{-}F}$ = 241.9 Hz), 141.50, 136.57,

128.95, 127.14, 127.08, 116.54 ($J_{C\text{-}F}$ = 22.7 Hz), 116.06 ($J_{C\text{-}F}$ = 8.0 Hz), 114.47 ($J_{C\text{-}F}$ = 22.3 Hz), 56.17, 45.17, 29.82, 28.71, 21.02.

^{19}F NMR (564 MHz, $CDCl_3$): -120.32.

HRMS (ESI-MS): calculated $C_{19}H_{21}ONF$ ($[M + H]^+$): 298.16017, found: 298.15982.

6-chloro-3-isopropyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9,11,12] (5fg)

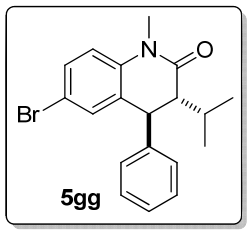


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-(4-Chlorophenyl)-*N*-methyl cinnamamide **4f** (271.5 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.3 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5fg** as colorless oil in 42% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.30-7.14 (m, 5H), 6.99-6.95 (m, 3H), 4.15(d, *J* = 1.2 Hz, 1H), 3.33 (s, 3H), 2.59 (dd, *J* = 9.0, 2.1 Hz, 1H), 1.73-1.61 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.36, 141.51, 138.97, 129.50, 128.98, 128.74, 128.43, 128.06, 127.12, 116.12, 56.22, 45.06, 29.68, 28.76, 21.06, 21.04.

6-bromo-3-isopropyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9] (5gg)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-Bromophenyl)-*N*-methyl cinnamamide **4g** (157.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.0 mg, 1.0 mmol) and CH_3CN (2.5 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5gg** as colorless solid in 45% isolated yield.

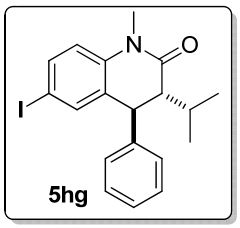
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.26-7.15 (m, 3H), 6.97-6.91 (m, 3H), 4.15 (s, 1H), 3.33 (s, 3H), 2.58 (dd, *J* = 9.3, 2.1 Hz, 1H), 1.73-1.62 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75MHz, $CDCl_3$) δ 170.37, 141.52, 139.49, 132.36, 131.05, 129.12, 129.01,

127.13, 116.53, 115.98, 56.27, 45.04, 29.67, 28.78, 21.09, 21.06.

HRMS (ESI-MS): calculated $C_{19}H_{20}ONBrNa$ ($[M + Na]^+$): 380.06205, found: 380.06158.

6-iodo-3-isopropyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (5hg)



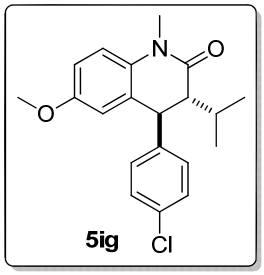
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-(4-Iodophenyl)-*N*-methylcinnamamide **4h** (181.7 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.2 mg, 1.0 mmol) and CH_3CN (2.5 mL) were added into an oven-dried reaction vessel with Teflon screw cap under nitrogen atmosphere. After the reaction was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5hg** as colorless oil in 51% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.27-7.15 (m, 3H), 6.97-6.94 (m, 2H), 6.81 (d, *J* = 8.7 Hz, 1H), 4.12 (d, *J* = 1.2 Hz, 1H), 3.32 (s, 3H), 2.57 (dd, *J* = 9.0, 2.1 Hz, 1H), 1.73-1.61 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.36, 141.54, 140.18, 138.10, 137.06, 129.34, 129.00, 127.12, 116.95, 86.38, 56.34, 44.86, 29.58, 28.74, 21.11.

HRMS (ESI-MS): calculated $C_{19}H_{21}ONI$ ($[M + H]^+$): 406.06623, found: 406.06607.

4-(4-chlorophenyl)-3-isopropyl-6-methoxyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (5ig)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-(4-methoxylphenyl)-*N*-methyl-(4-chloro)-cinnamamide **4i** (301.5 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.2 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ig** as colorless oil in 57% isolated yield.

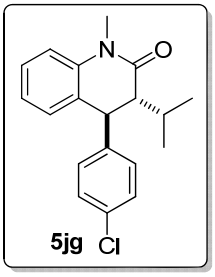
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H),

6.91 (d, *J* = 8.4 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.73 (d, *J* = 2.8 Hz, 1H), 4.09 (s, 1H), 3.78 (s, 3H), 3.32 (s, 3H), 2.51 (dd, *J* = 9.2, 2.0 Hz, 1H), 1.70-1.61 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.97, 155.77, 140.50, 133.75, 132.61, 128.92, 128.62, 127.67, 116.01, 115.54, 112.77, 56.61, 55.58, 44.78, 29.70, 28.45, 21.16, 21.01.

HRMS (ESI-MS): calculated $C_{20}H_{23}O_2NCl$ ($[M + H]^+$): 344.14118, found: 344.14069.

4-(4-chlorophenyl)-3-isopropyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one[9,11] (5jg)

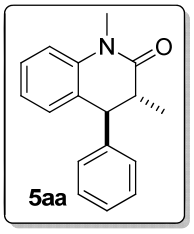


According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-phenyl-*N*-methyl-(4-chloro)-cinnamamide **4j** (271.3 mg, 1.0 mmol), $PhI(O_2C^iPr)_2$ **2g** (756.2 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5jg** as colorless oil in 52% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (td, J = 7.8, 1.2 Hz, 1H), 7.20-7.15(m, 3H), 7.08-7.03 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.15 (s, 1H), 3.34 (s, 3H), 2.55 (dd, *J* = 9.3, 1.8 Hz, 1H), 1.71-1.59 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.42, 140.65, 140.11, 132.59, 129.57, 128.91, 128.60, 128.40, 126.22, 123.44, 115.02, 56.48, 44.50, 29.56, 28.48, 21.11, 21.00.

1,3-dimethyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[12,13] (5aa)



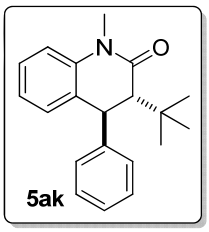
According to the general procedure, a mixture of $Re_2(CO)_{10}$ (32.5 mg, 0.05 mmol), *N*-methyl-*N*-phenylcinnamamide **4a** (237.2 mg, 1.0 mmol), $PhI(OAc)_2$ **1a** (644.2 mg, 2.0 mmol) and CH_3CN (5.0 mL) was stirred at 100 °C for 12 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5aa** (the major isomer was shown, *dr* = 8:1) as colorless oil in 40% isolated yield. The NMR data of

major isomer was shown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.27-7.20 (m, 2H), 7.17-7.11 (m, 2H), 7.07-7.01 (m, 1H), 6.98-6.94 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H), 3.40 (s, 3H), 2.97-2.88 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.31, 141.20, 139.96, 128.92, 128.83, 128.58, 128.36, 127.89, 127.16, 123.01, 114.62, 49.01, 42.16, 29.94, 15.53.

3-(tert-butyl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one[9,11,12] (5ak)



According to the general procedure, a mixture of $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), *N*-methyl-*N*-phenylcinnamamide **4a** (118.5 mg, 0.5 mmol), $PhI(O_2C^tBu)_2$ **2k** (609.1 mg, 1.5 mmol) and CH_3CN (2.5 mL) was stirred at 120 °C for 24 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ak** as colorless oil in 35% isolated yield.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.32-7.10 (m, 5H), 7.05-6.94 (m, 4H), 4.30 (s, 1H), 3.40 (s, 3H), 2.68 (s, 1H), 0.94 (s, 9H).

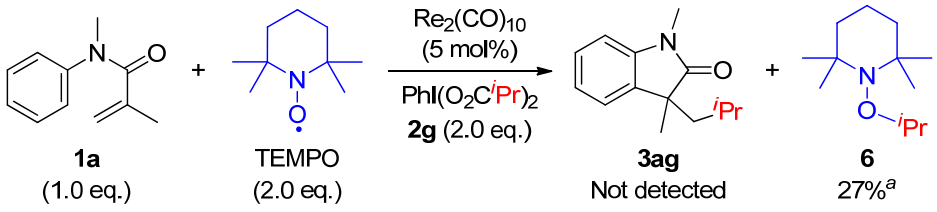
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.59, 143.86, 140.85, 129.21, 128.89, 128.09, 127.61, 127.06, 126.68, 123.52, 114.75, 59.41, 44.01, 34.67, 29.67, 29.01.

5. Mechanism Studies

5.1 A Radical Trapping Experiment with TEMPO

We further conducted mechanistic experiments to probe insights on this alkylarylation reaction. Firstly, upon the addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical scavenger to the reaction of *N*-acrylamide **1a** and HIR **2g**, the transformation was completely prohibited. Instead, 1-isopropoxy-2,2,6,6-tetramethylpiperidine **6** was obtained in 27% isolated yield (Scheme S1), which implied a radical decarboxylation pathway might operate in the reaction.

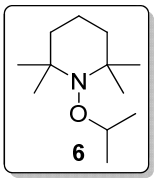
Scheme S1. A radical trapping experiment with TEMPO



[a] Isolated yield.

Experimental Details: A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. $Re_2(CO)_{10}$ (16.3 mg, 0.025 mmol), alkene **1a** (87.5 mg, 0.5 mmol), $PhI(O_2C^iPr)_2$ **2g** (378.0 mg, 1.0 mmol), TEMPO (156.2 mg, 1.0 mmol), and MTBE (2.5 mL) were added into the reaction vessel under nitrogen. Then, the Teflon cap was screwed up and the reaction mixture was stirred in an oil bath (100 ^oC) for 12 h. After completion of the reaction, the solvent was removed in vacuo. The crude reaction mixture was analyzed by ^1H NMR. As a result, the reaction of *N*-acrylamide **1a** and HIR **2g** was completely prohibited. Instead, 1-isopropoxy-2,2,6,6-tetramethyl piperidine **6** was obtained in 27% isolated yield by column chromatography.

1-isopropoxy-2,2,6,6-tetramethylpiperidine[14] 6



^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (hept, *J* = 6.2 Hz, 1H), 1.45-1.12 (m, 6 × CH_3 and 3 × CH_2, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 75.24, 59.66, 40.41, 34.61, 22.53, 20.45, 17.52.

Figure S3. ^{1}H NMR spectrum of **6**

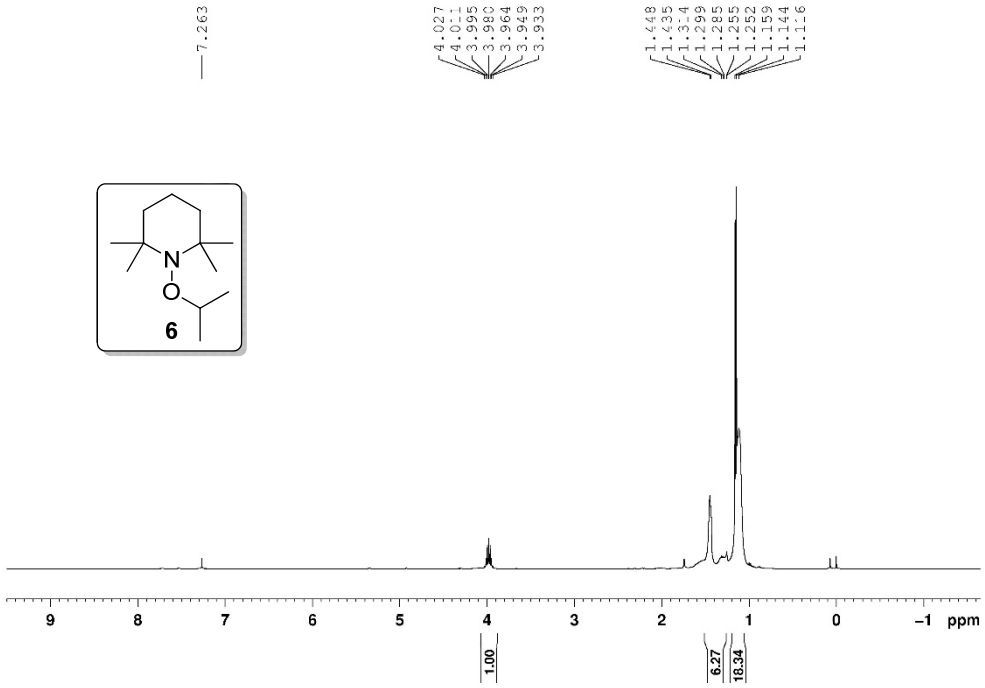
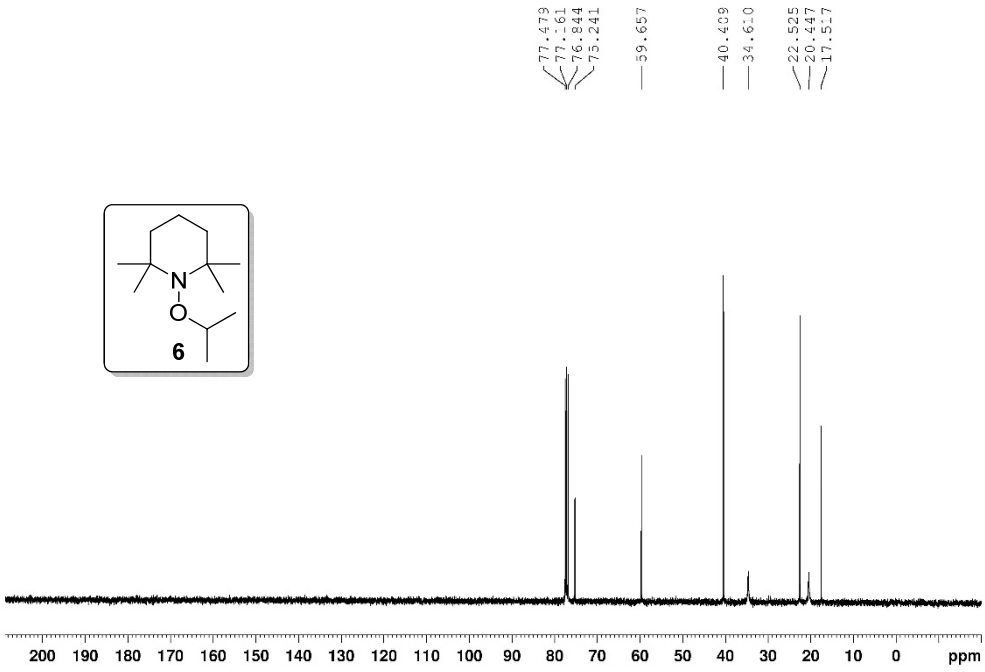


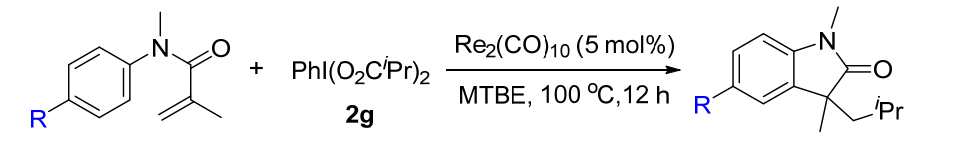
Figure S4. ^{13}C NMR spectrum of **6**



5.2 Competition Experiments of Alkenes

Next, we examined competition experiments between alkenes **1c** and **1d**, bearing an electro-donating methoxy and electro-withdrawing ester group respectively, with HIR **2g** (Scheme S2). It turned out that the yields of the corresponding indolinones **3cg** and **3dg** were 24% and 30%, respectively (Figure S5). This result implied that the intramolecular cyclization process might occur through a radical rather than cationic mechanism.

Scheme S2. Competition experiments of alkenes



1g (1.0 eq.) + **1h**(1.0 eq.) (1.0 eq.)

1c, R = OMe
1d, R = CO_2Et

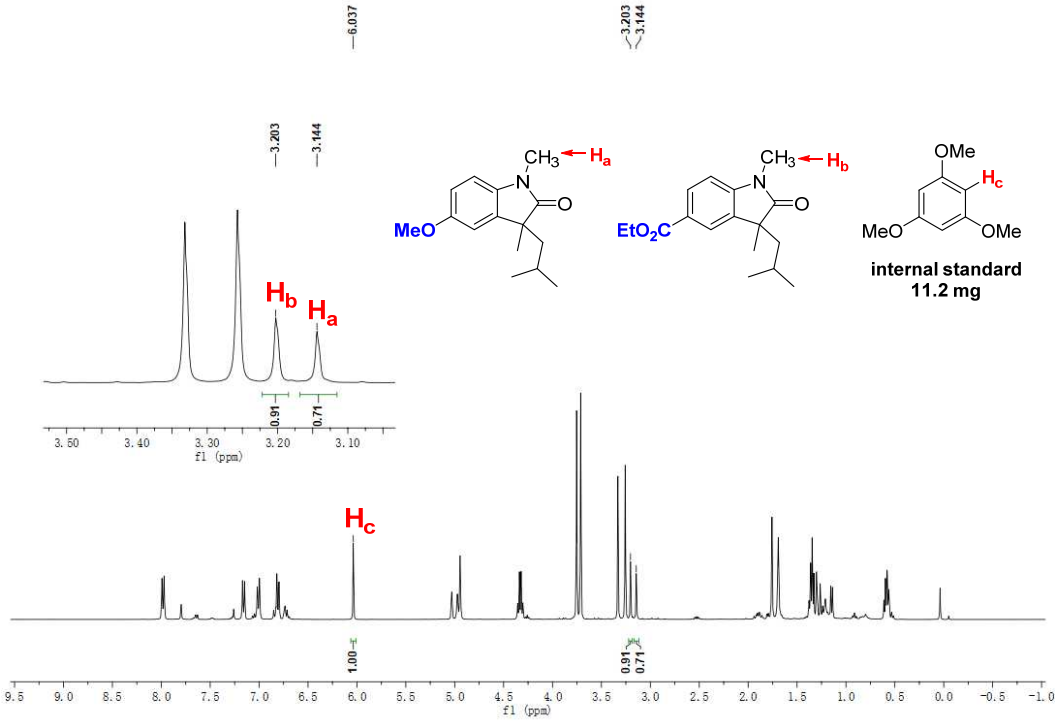
3cg (24%[a]) + **3dg** (30%[a])

3cg, R = OMe
3dg, R = CO_2Et

[a] Determined by ^1H NMR analysis of the crude reaction mixture.

Experimental Details: A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. $Re_2(CO)_{10}$ (6.6 mg, 0.01 mmol), alkenes **1c** (41.1 mg, 0.2 mmol), **1d** (49.4 mg, 0.2 mmol), $PhI(O_2C^iPr)_2$ **2g** (75.6 mg, 0.2 mmol) and 1.0 mL MTBE were added into the reaction vessel under nitrogen. Then, the Teflon cap was screwed up and the reaction mixture was stirred in an oil bath (100 °C) for 12 h. After completion of the reaction, the solvent was removed in vacuo. The crude reaction mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Figure S5. Crude ^{1}H NMR spectrum of the reaction outlined in **Scheme S2**



6. References

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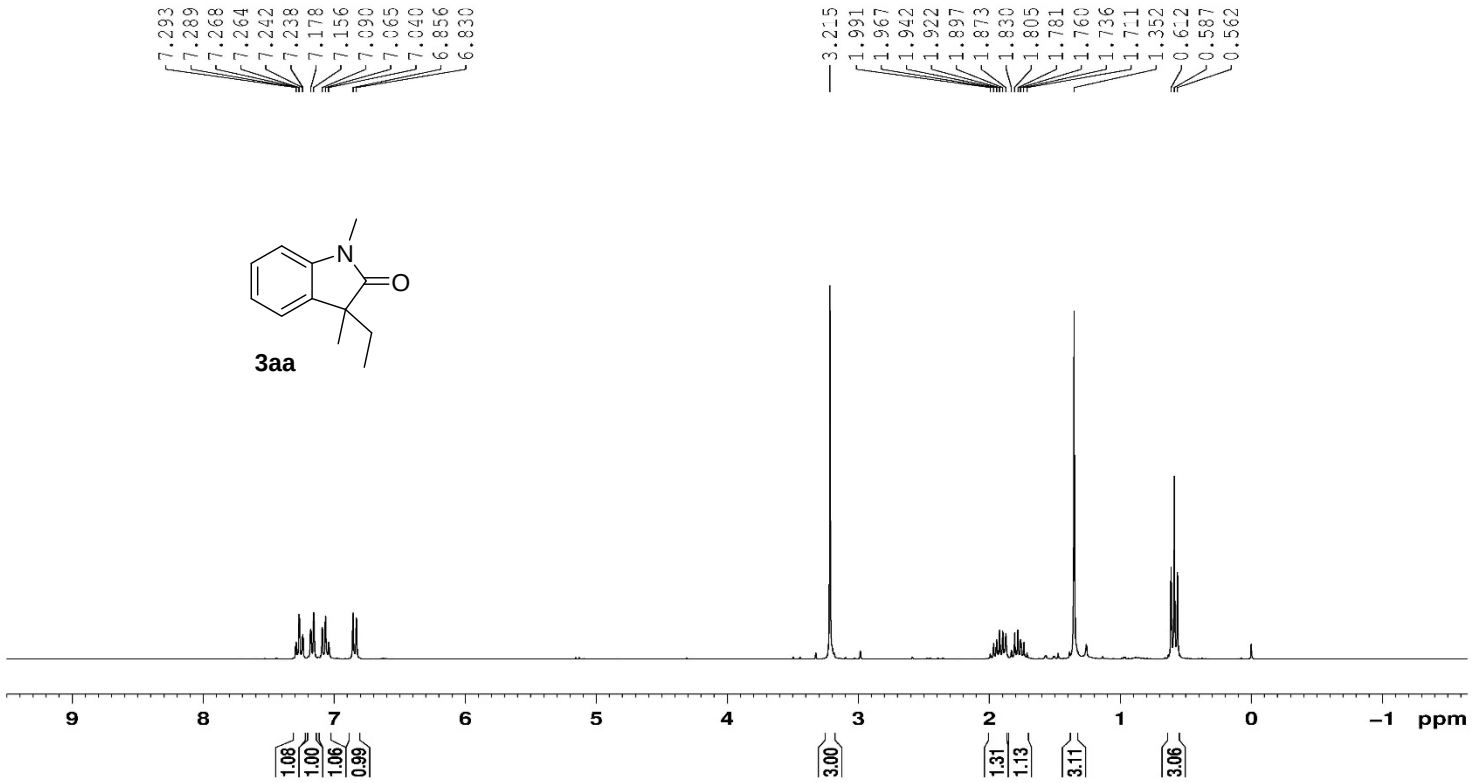
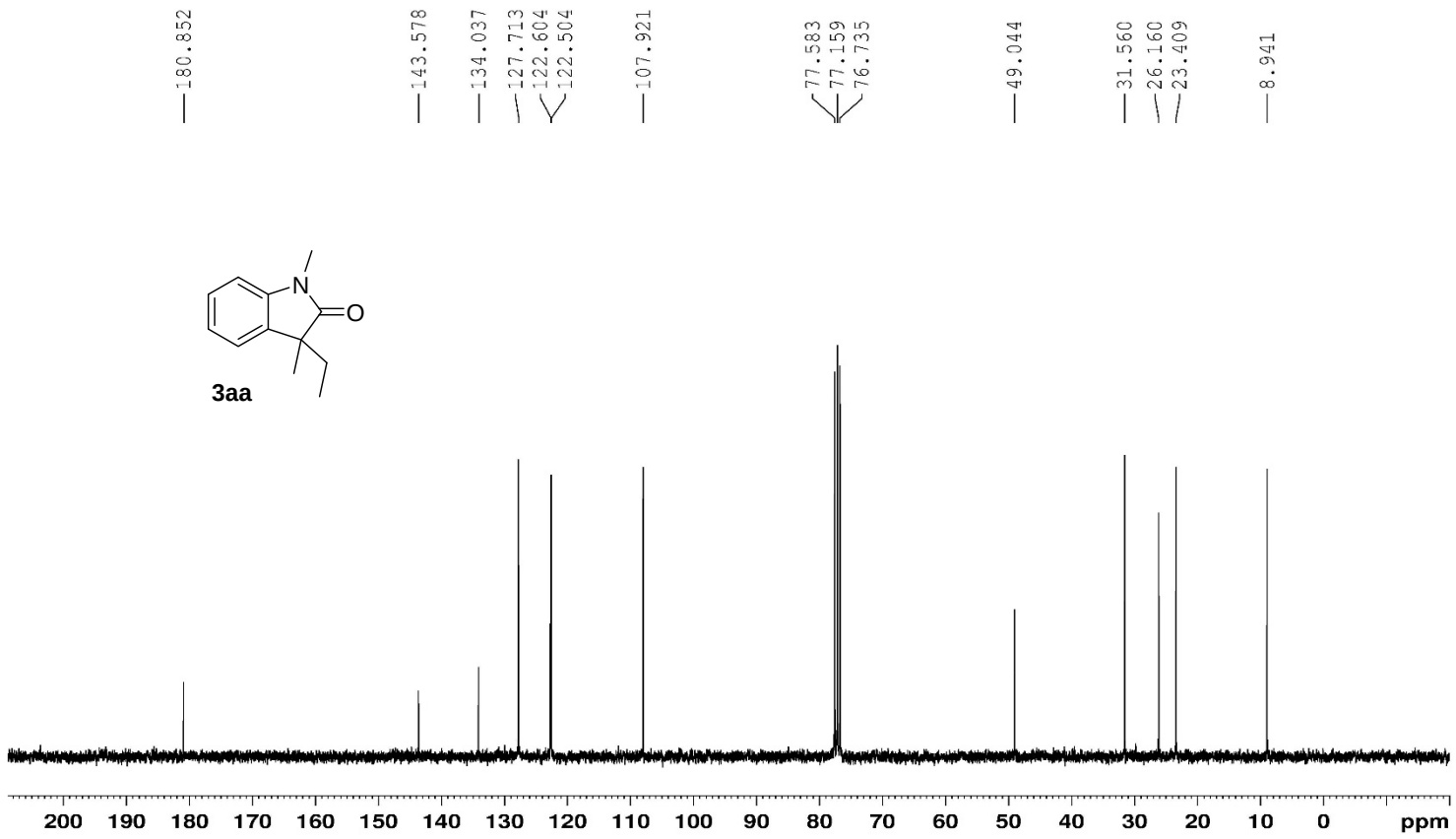
7. Spectra of Products

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122.604
122.504
107.921
77.583
77.159
76.735
49.044
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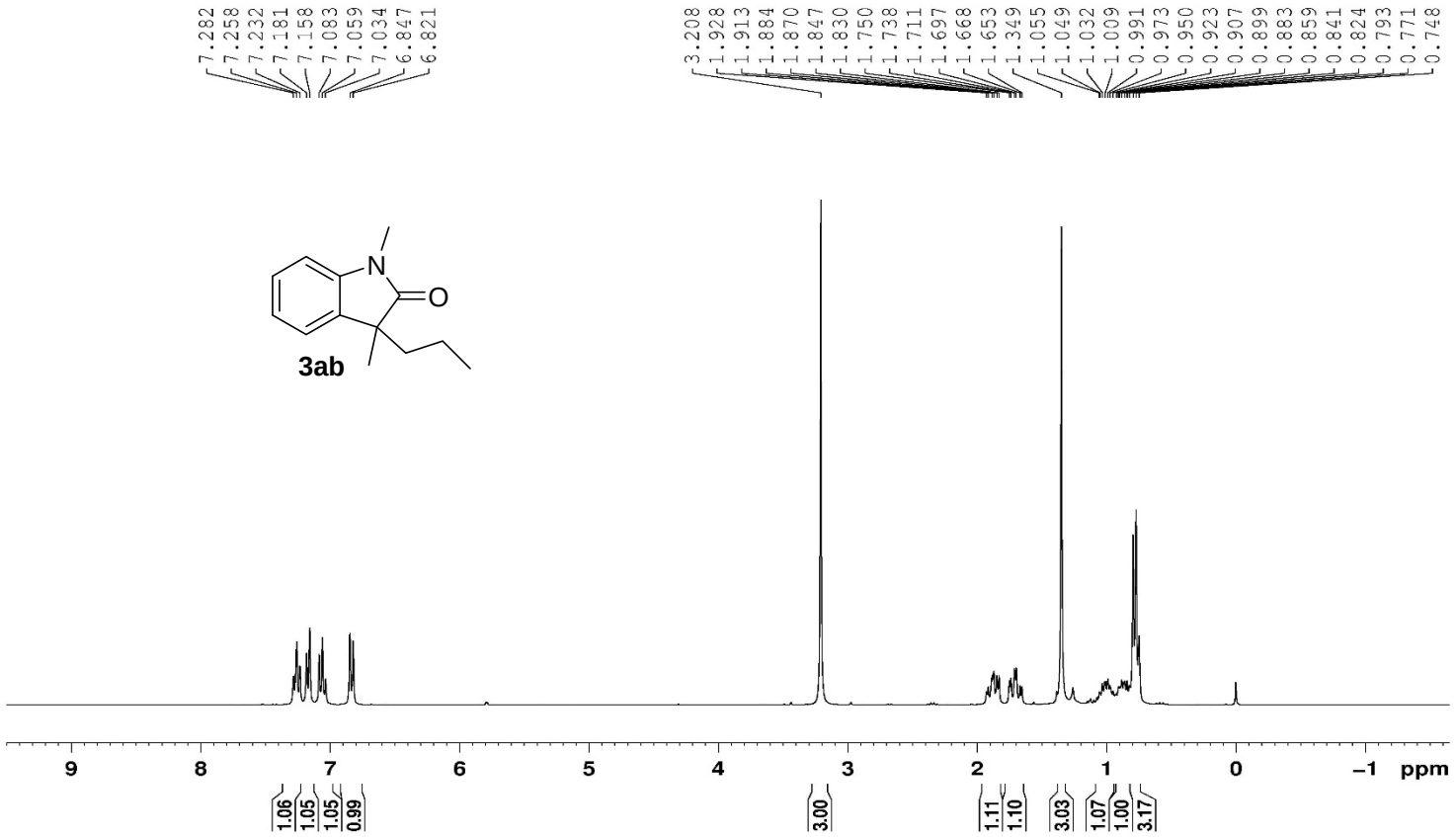
26.160
23.409
8.941
N
O
3aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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N
O
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9
8
7
6
5
4
3
2
1
0
−1
ppm
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1.10
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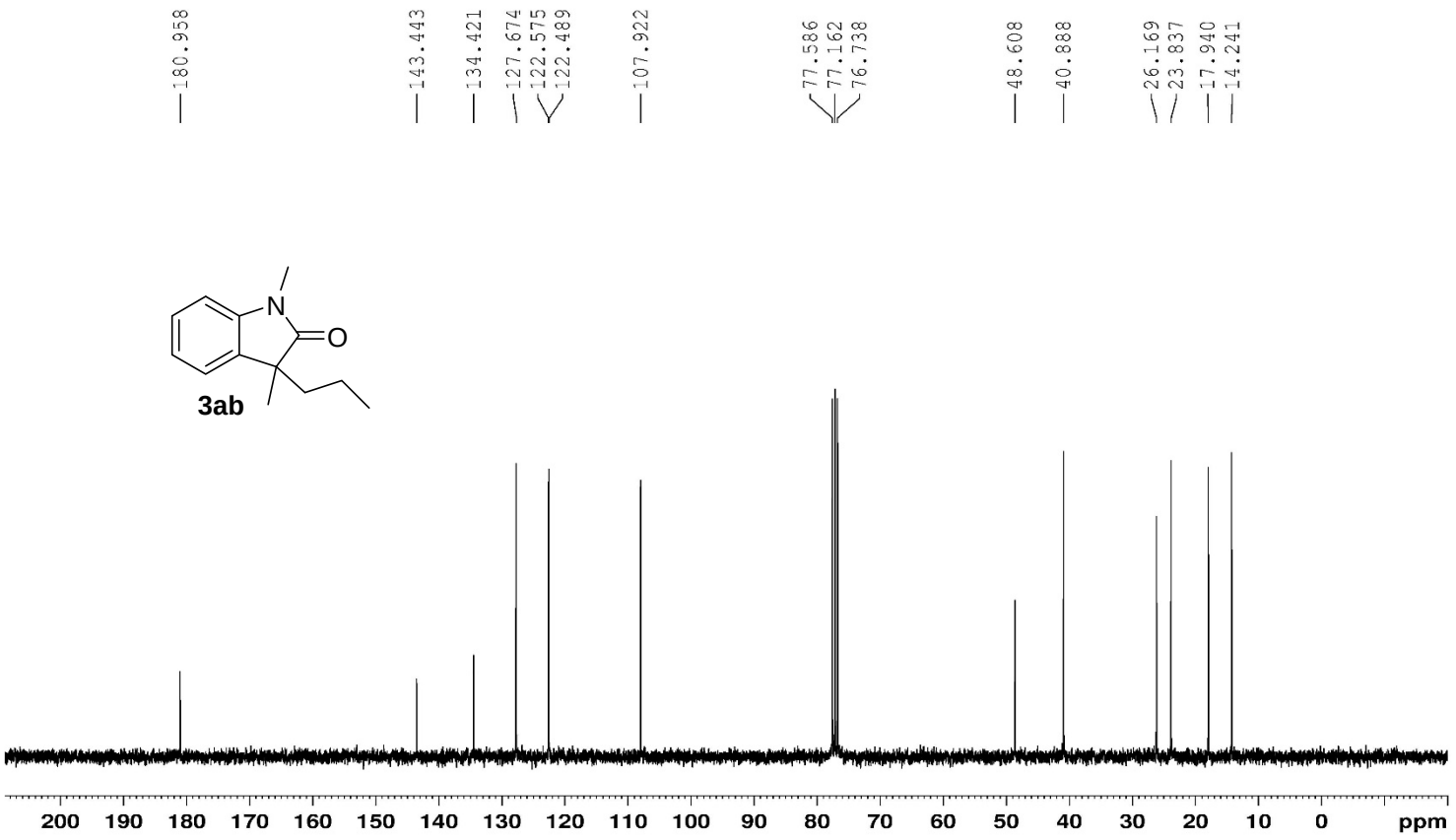
3.17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76.738
48.608
40.888
26.169
23.837
17.940
14.241
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O
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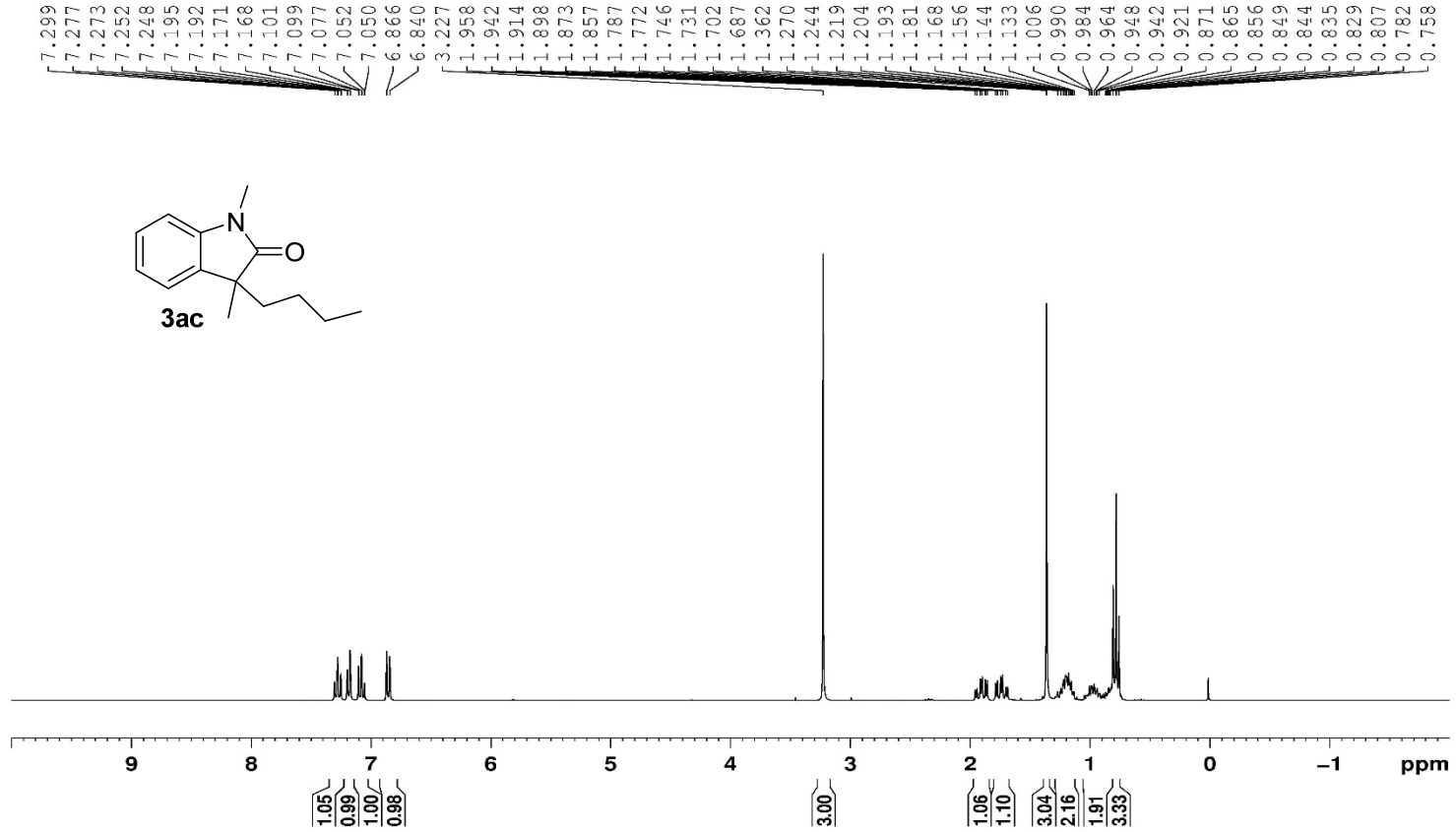
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.050
6.866
6.840
3.227
1.958
1.942
1.914
1.898
1.873
1.857
1.787
1.772
1.746
1.731
1.702
1.687
1.362
1.270
1.244
1.219
1.204
1.193
1.181
1.168
1.156
1.144
1.133
1.006
0.990
0.984
0.964
0.948
0.942
0.921
0.871
0.865
0.856
0.849
0.844
0.835
0.829
0.807
0.782
0.758
N
O
3ac
9
8
7
6
5
4
3
2
1
0
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1.00
0.98
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1.06
1.10
3.04
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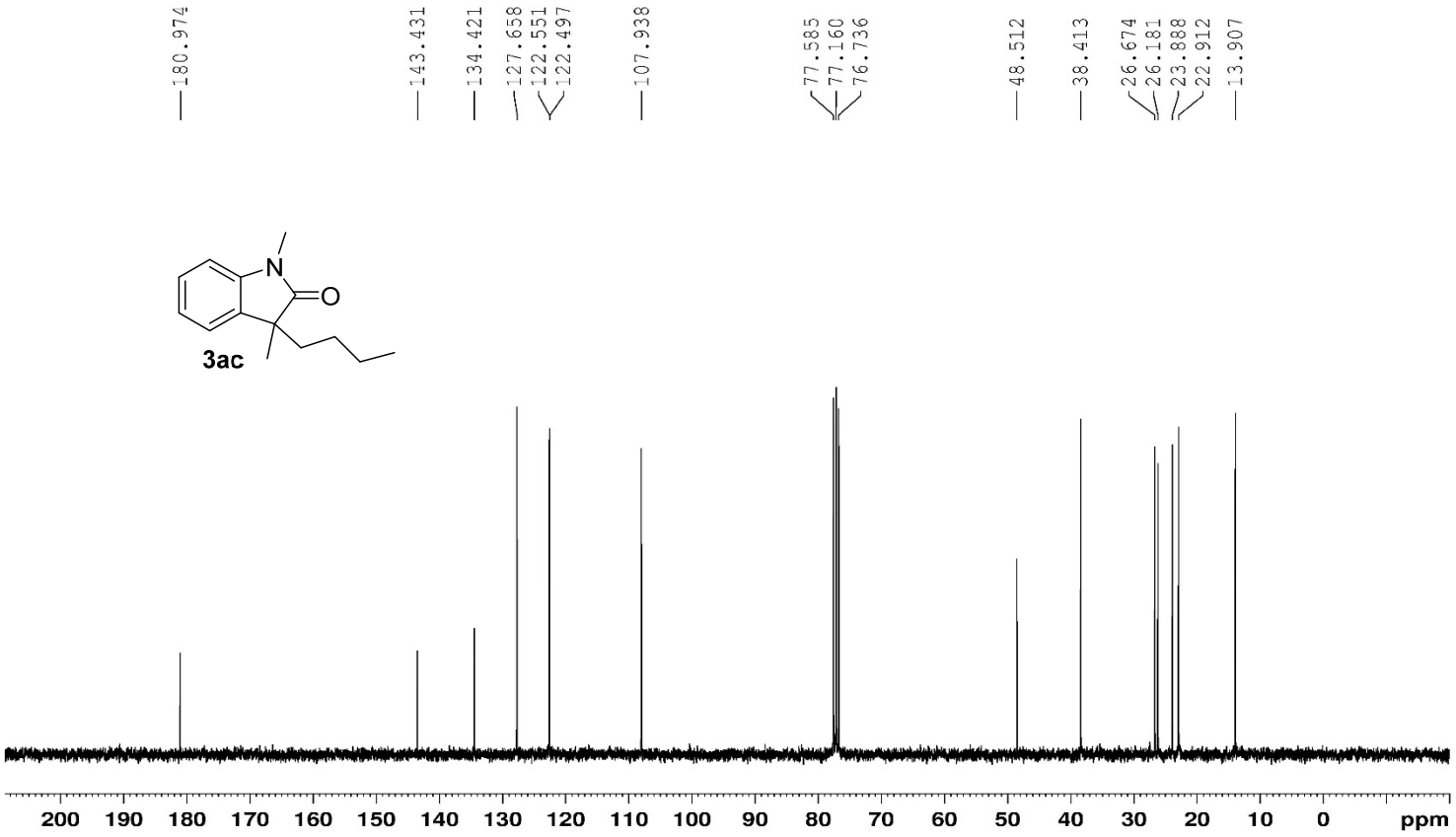
1.91
3.33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38.413
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23.888
22.912
13.907
N
O
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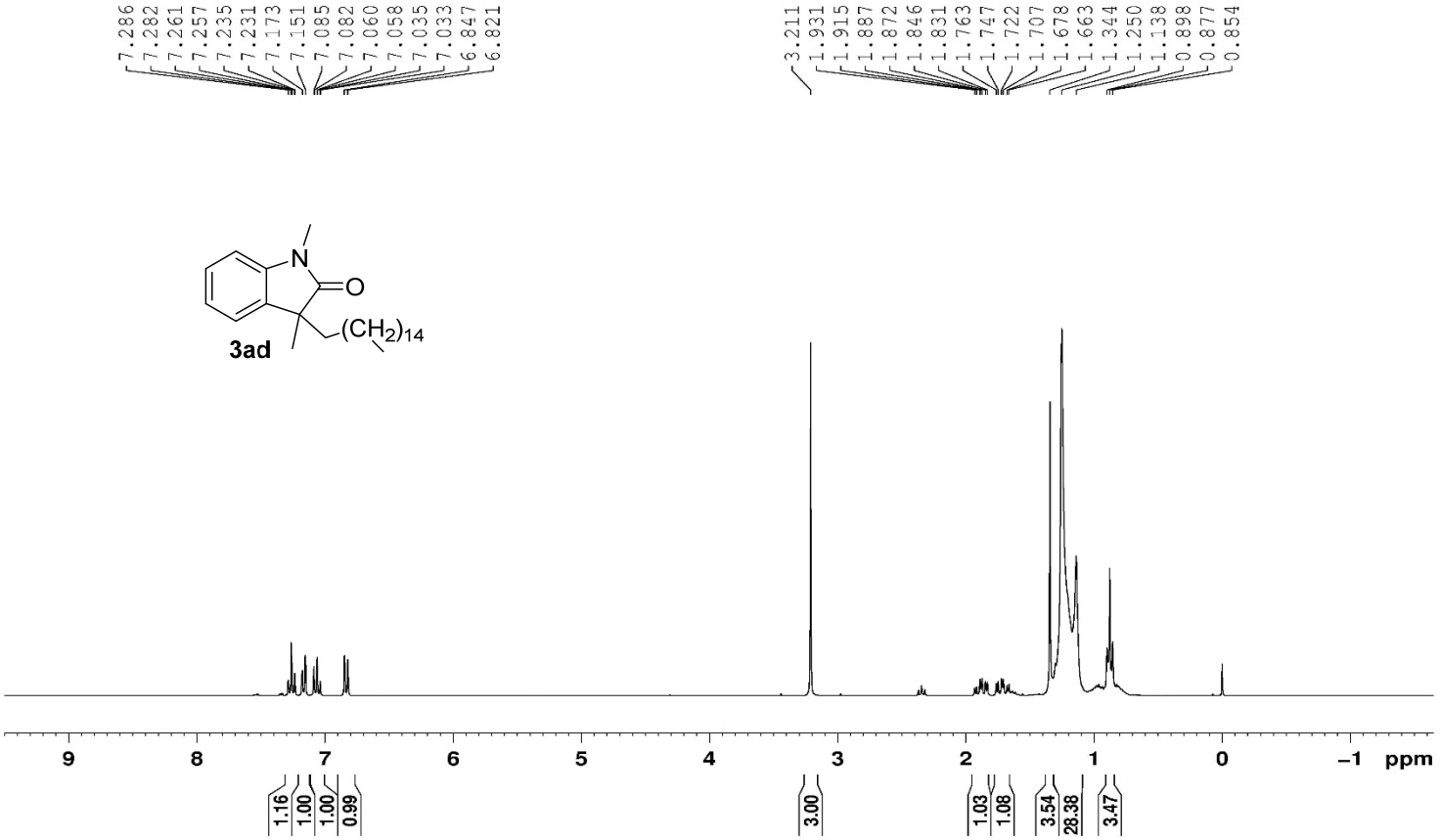
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.261
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7.173
7.151
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7.060
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7.035
7.033
6.847
6.821
3.211
1.931
1.915
1.887
1.872
1.846
1.831
1.763
1.747
1.722
1.707
1.678
1.663
1.344
1.250
1.138
0.898
0.877
0.854
N
O
(CH2)14
3ad
9
8
7
6
5
4
3
2
1
0
−1
ppm
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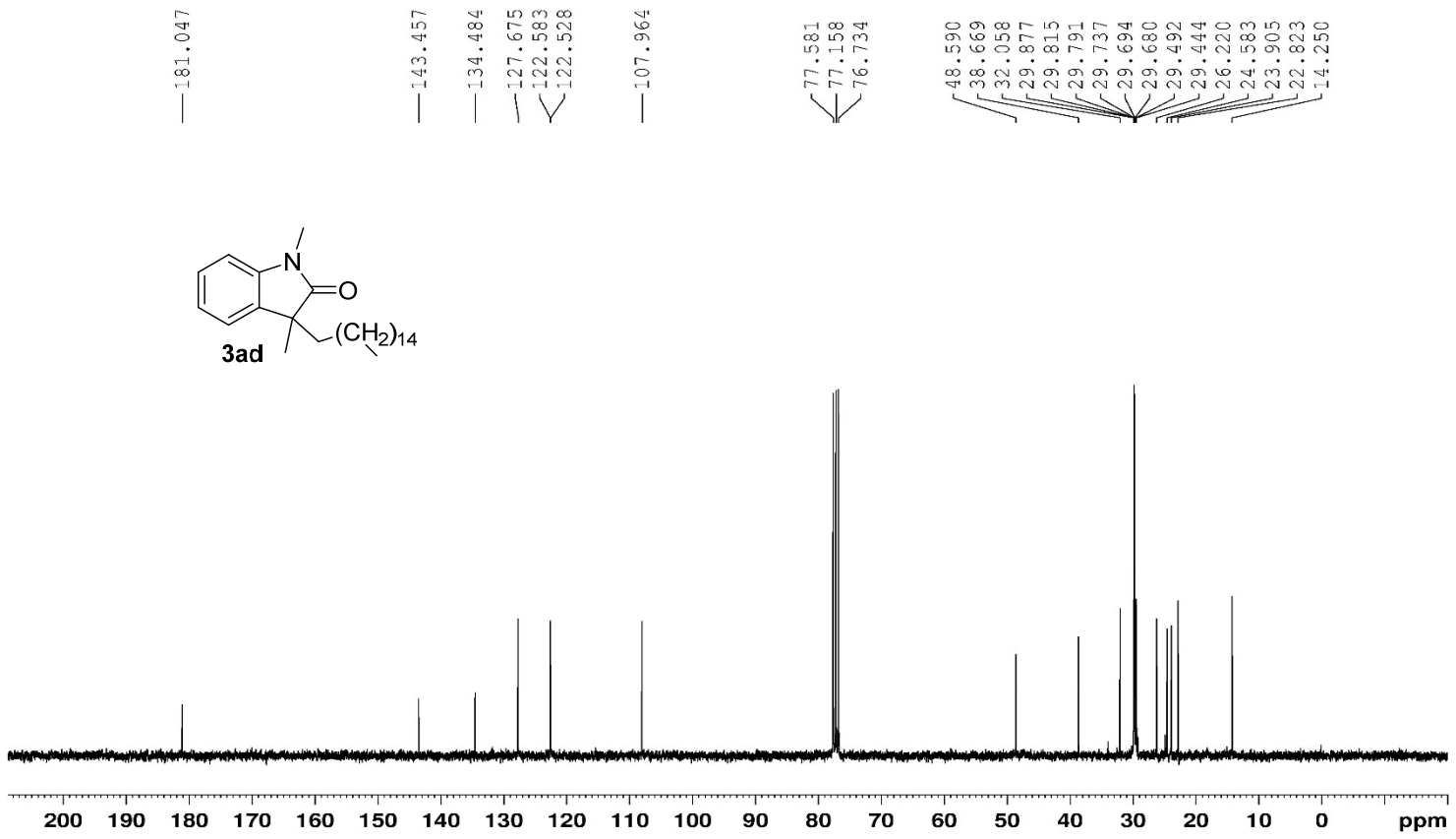
1.00
1.00
0.99
3.00
1.03
1.08
3.54
28.38
3.47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32.058
29.877
29.815
29.791
29.737
29.694
29.680
29.492
29.444
26.220
24.583
23.905
22.823
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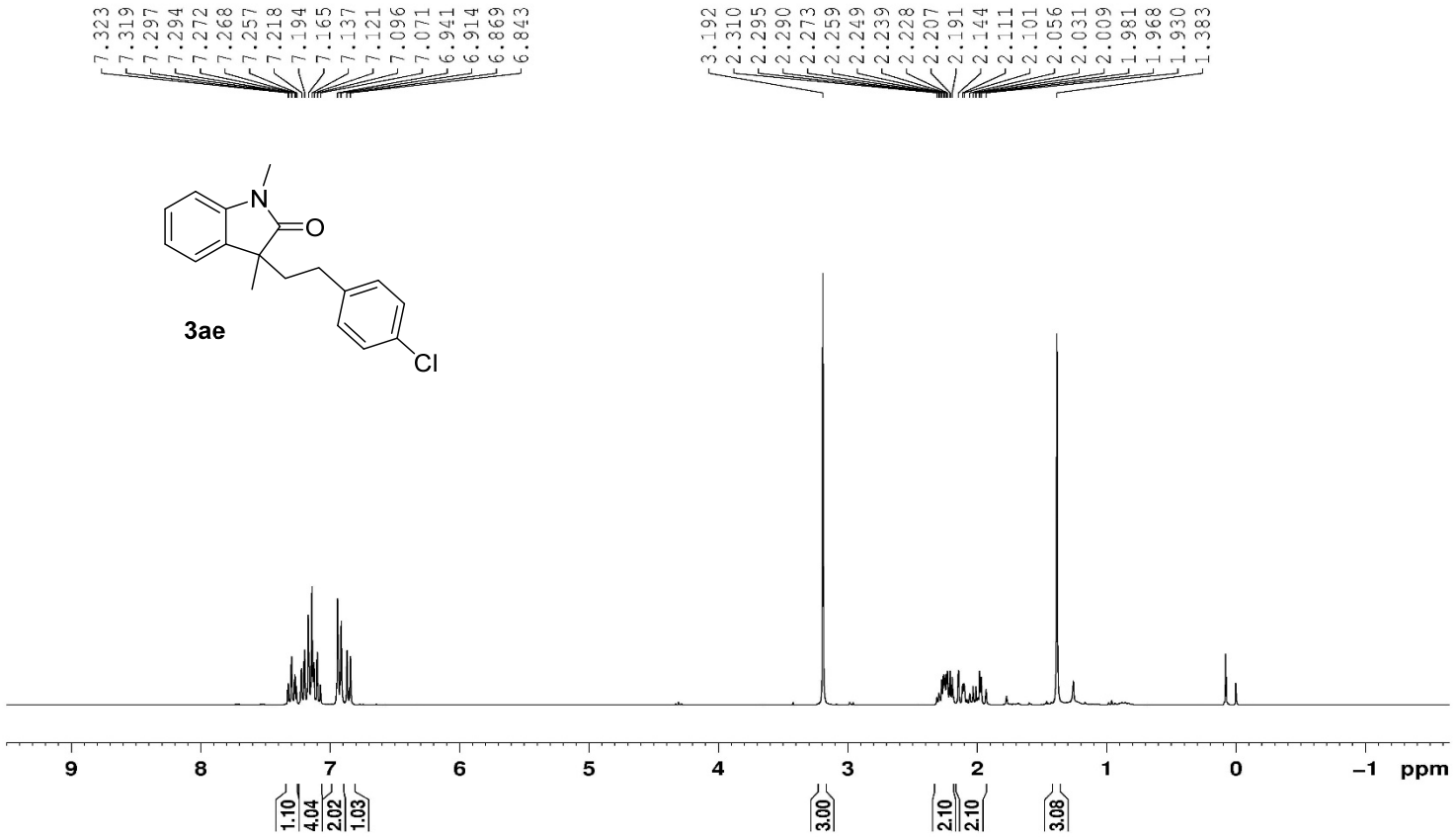
N
O
(CH2)14
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.294
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7.218
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7.165
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7.121
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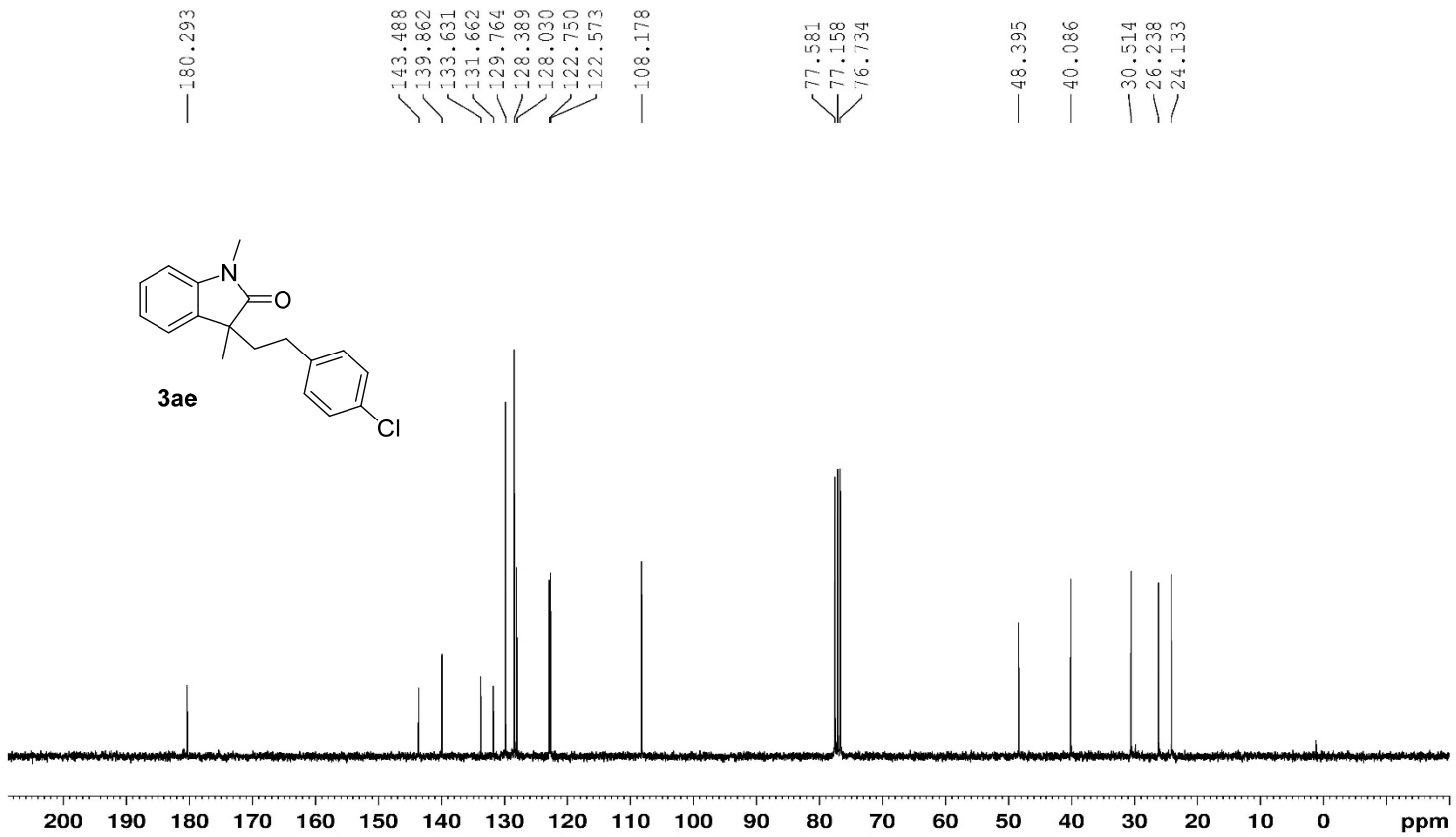
7.071
6.941
6.914
6.869
6.843
3.192
2.310
2.295
2.290
2.273
2.259
2.249
2.239
2.228
2.207
2.191
2.144
2.111
2.101
2.056
2.031
2.009
1.981
1.968
1.930
1.383
N
O
Cl
3ae
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.10
4.04
2.02
1.03
3.00
2.10
2.10
3.08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139.862
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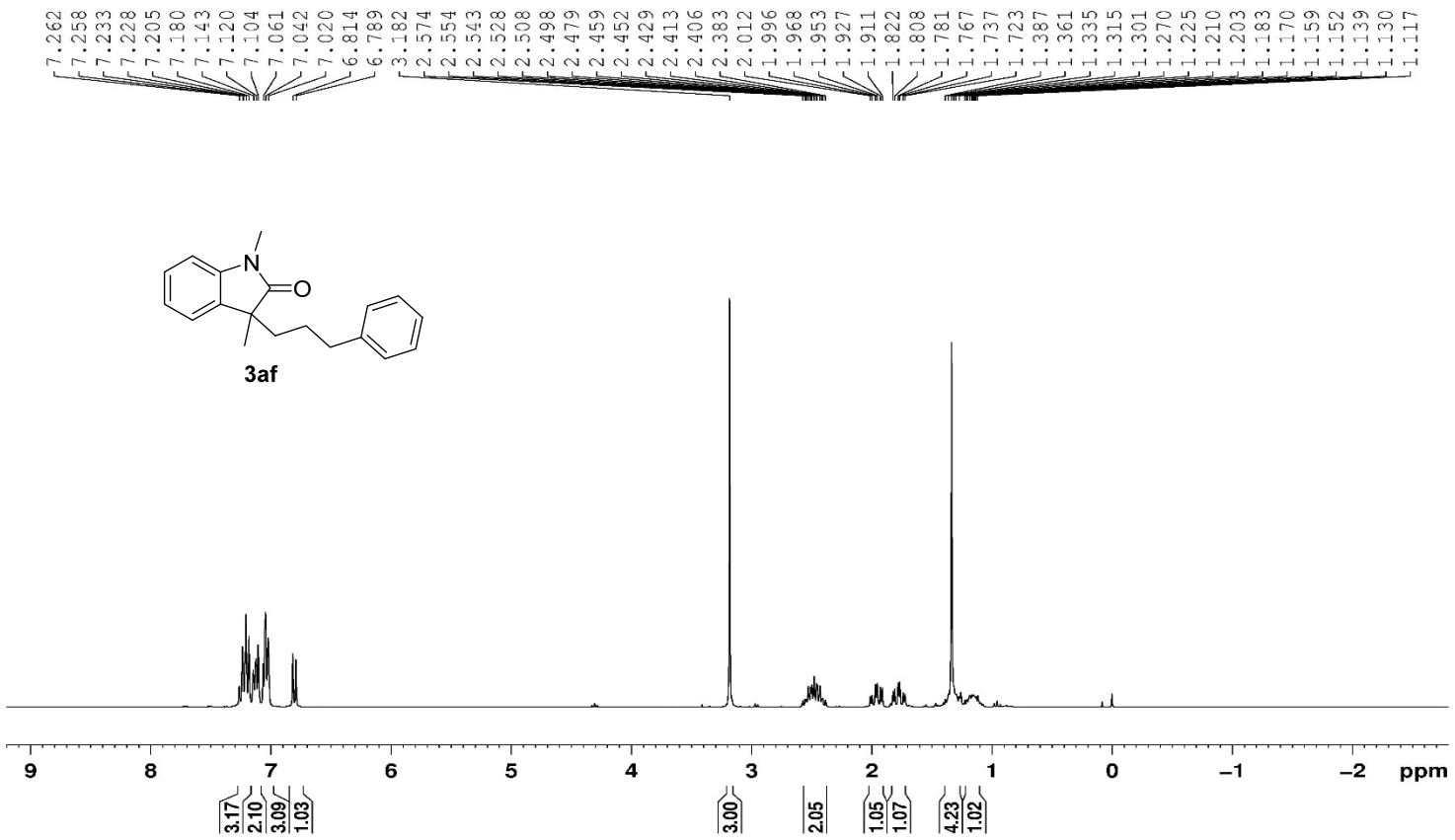
128.030
122.750
122.573
108.178
77.581
77.158
76.734
48.395
40.086
30.514
26.238
24.133
N
O
Cl
3ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.258
7.233
7.228
7.205
7.180
7.143
7.120
7.104
7.061
7.042
7.020
6.814
6.789
3.182
2.574
2.554
2.543
2.528
2.508
2.498
2.479
2.459
2.452
2.429
2.413
2.406
2.383
2.012
1.996
1.968
1.953
1.927
1.911
1.822
1.808
1.781
1.767
1.737
1.723
1.387
1.361
1.335
1.315
1.301
1.270
1.225
1.210
1.203
1.183
1.170
1.159
1.152
1.139
1.130
1.117
N
O
3af
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm
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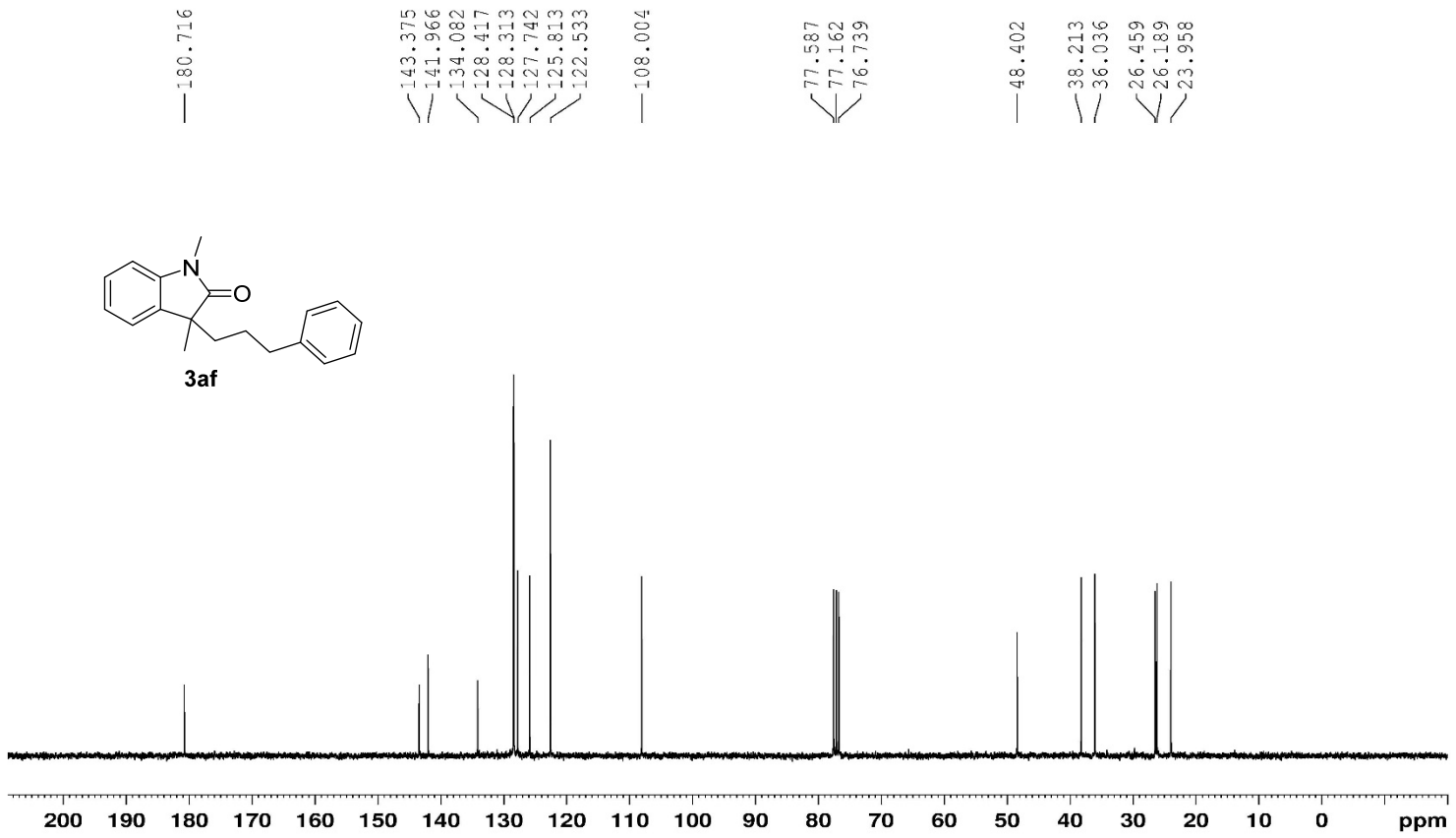
2.10
3.09
1.03
3.00
2.05
1.05
1.07
4.23
1.02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76.739
48.402
38.213
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26.459
26.189
23.958
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O
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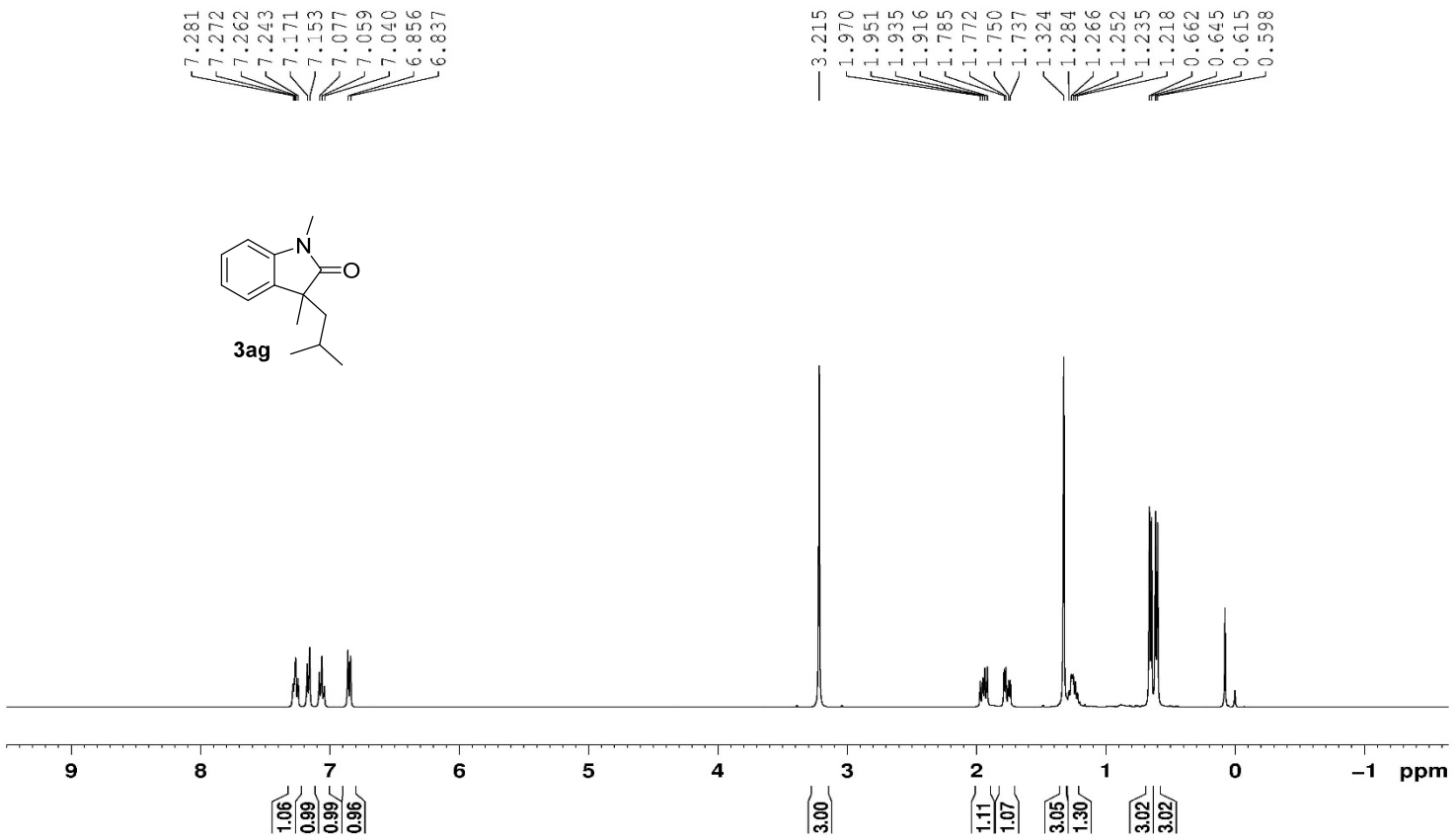
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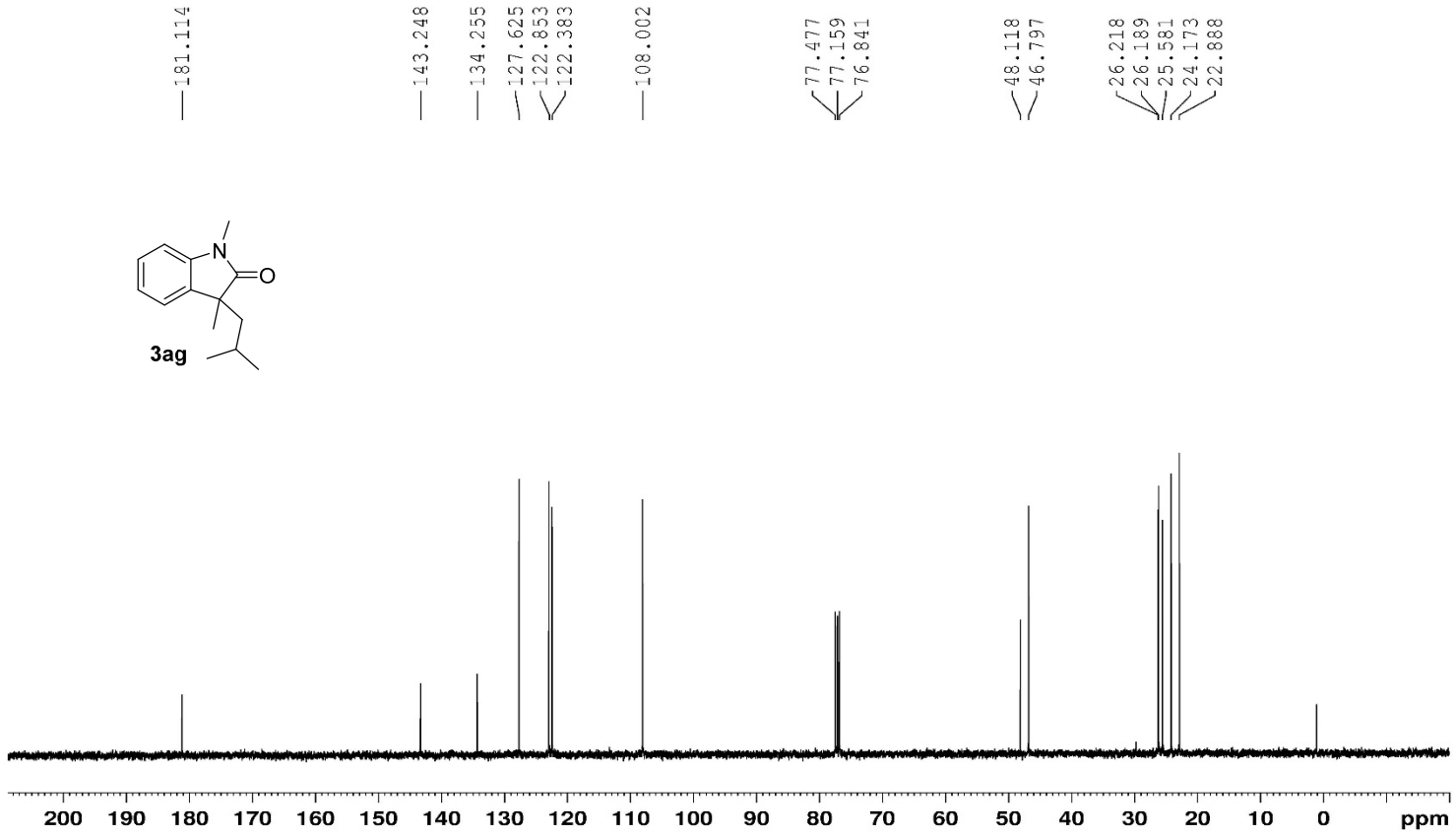
7.272
7.262
7.243
7.171
7.153
7.077
7.059
7.040
6.856
6.837
3.215
1.970
1.951
1.935
1.916
1.785
1.772
1.750
1.737
1.324
1.284
1.266
1.252
1.235
1.218
0.662
0.645
0.615
0.598
N
O
3ag
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.06
0.99
0.99
0.96
3.00
1.11
1.07
3.05
1.30
3.02
3.02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77.477
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76.841
48.118
46.797
26.218
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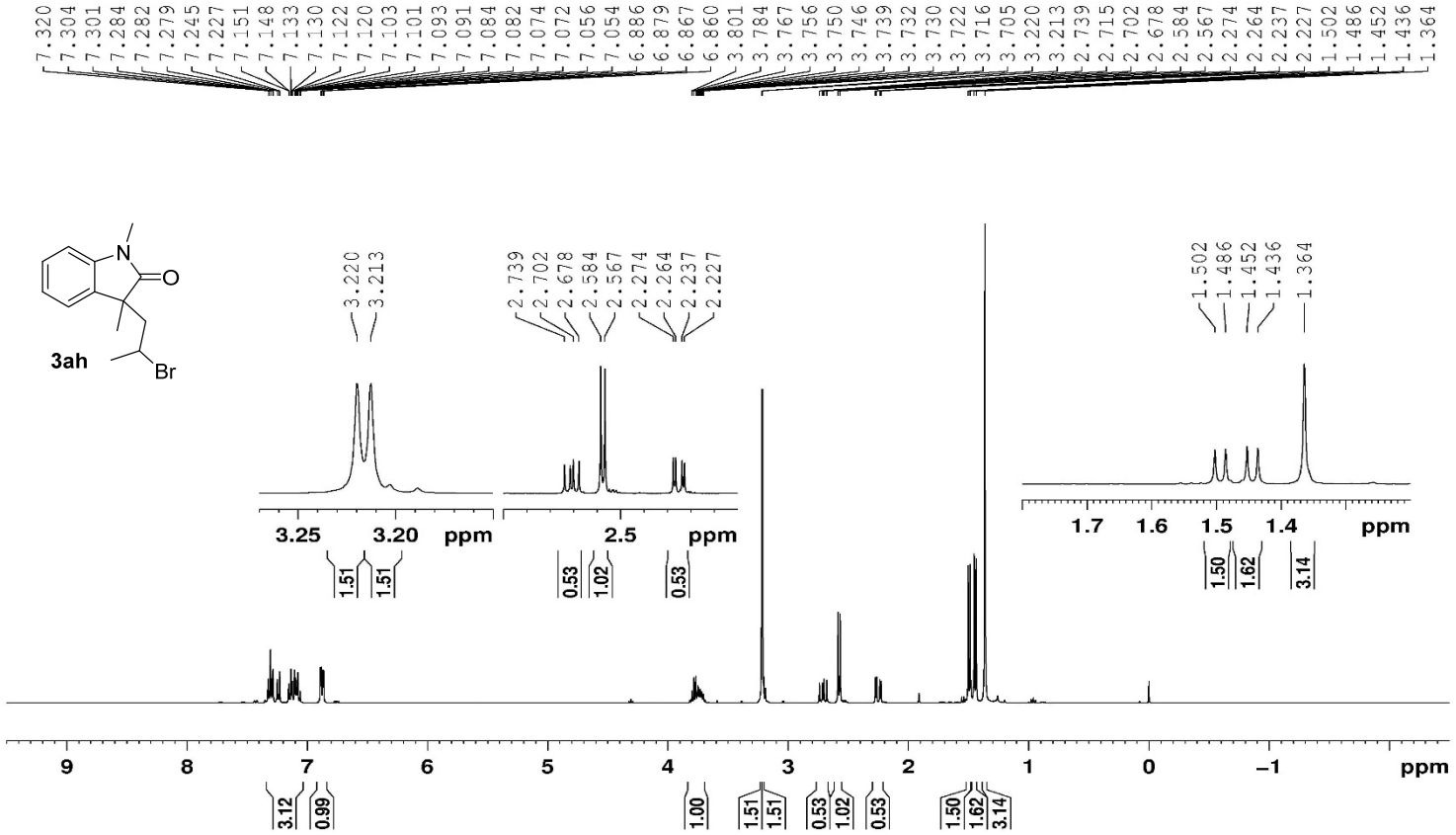
25.581
24.173
22.888
N
O
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.282
7.279
7.245
7.227
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7.133
7.130
7.122
7.120
7.103
7.101
7.093
7.091
7.084
7.082
7.074
7.072
7.056
7.054
6.886
6.879
6.867
6.860
3.801
3.784
3.767
3.756
3.750
3.746
3.739
3.732
3.730
3.722
3.716
3.705
3.220
3.213
2.739
2.715
2.702
2.678
2.584
2.567
2.274
2.264
2.237
2.227
1.502
1.486
1.452
1.436
1.364
3ah
Br
O
N
3.25
3.20
ppm
2.5
ppm
1.7
1.6
1.5
1.4
ppm
1.51
1.51
0.53
1.02
0.53
1.50
1.62
3.14
9
8
7
6
5
4
3
2
1
0
−1
ppm
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1.00
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1.51
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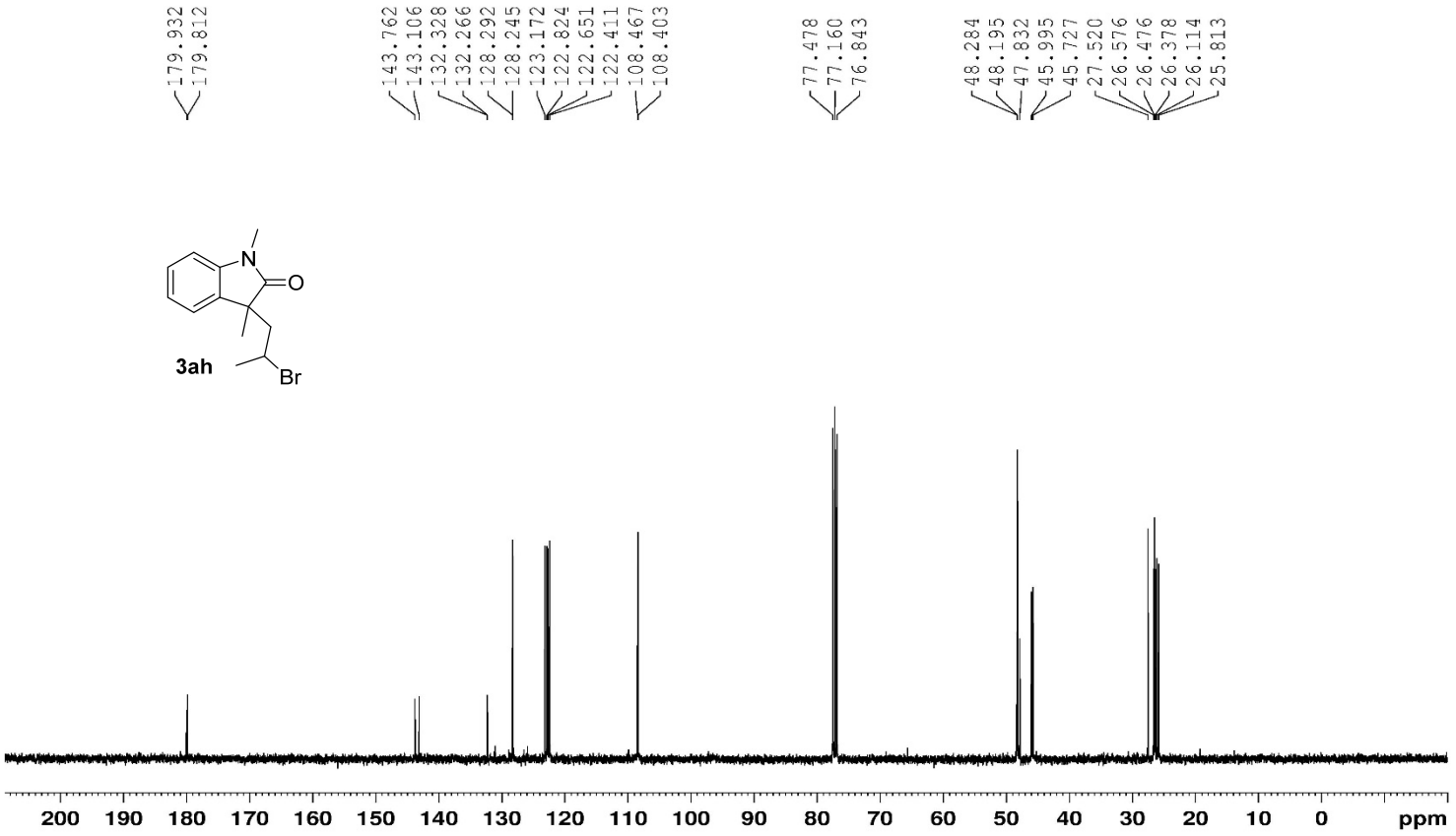
1.50
1.62
3.14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128.245
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122.824
122.651
122.411
108.467
108.403
77.478
77.160
76.843
48.284
48.195
47.832
45.995
45.727
27.520
26.576
26.476
26.378
26.114
25.813
N
O
Br
3ah
200
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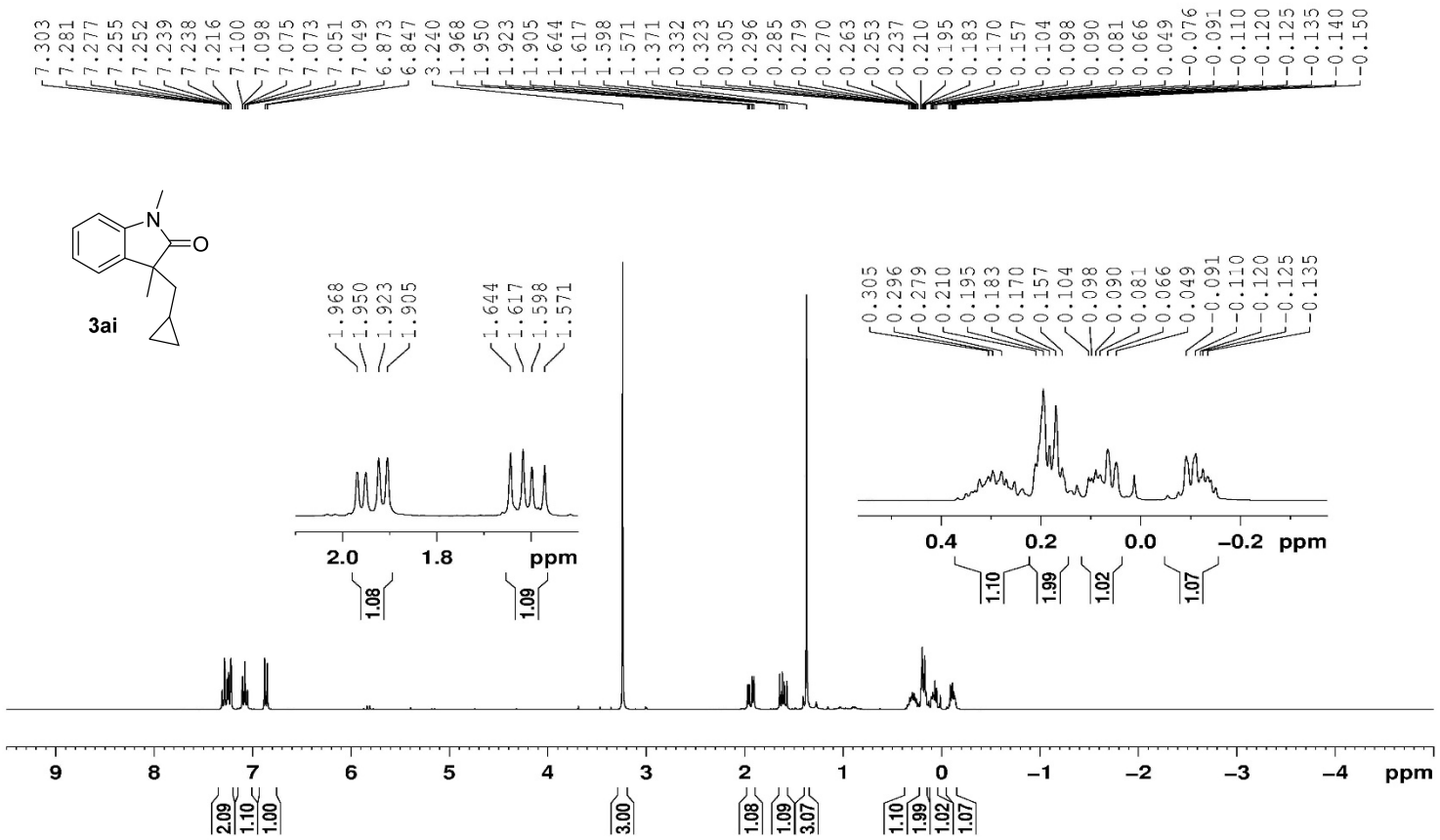
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.239
7.238
7.216
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7.098
7.075
7.073
7.051
7.049
6.873
6.847
3.240
1.968
1.950
1.923
1.905
1.644
1.617
1.598
1.571
1.371
0.332
0.323
0.305
0.296
0.285
0.279
0.270
0.263
0.253
0.237
0.210
0.195
0.183
0.170
0.157
0.104
0.098
0.090
0.081
0.066
0.049
−0.076
−0.091
−0.110
−0.120
−0.125
−0.135
−0.140
−0.150
N
O
3ai
2.0
1.8
ppm
1.08
1.09
0.4
0.2
0.0
−0.2
ppm
1.10
1.99
1.02
1.07
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
ppm
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1.10
1.00
3.00
1.08
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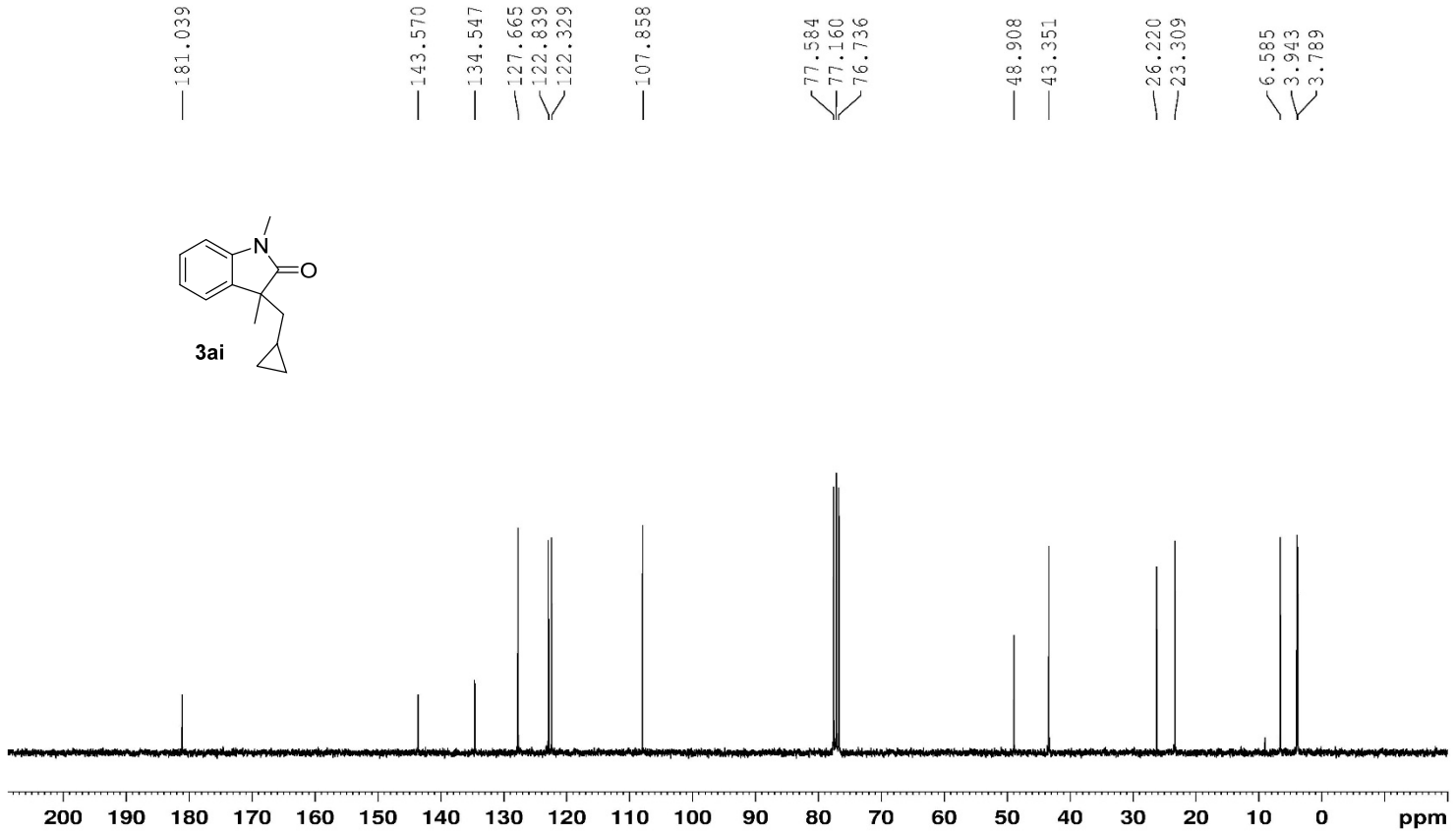
3.07
1.10
1.99
1.02
1.07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76.736
48.908
43.351
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3.943
3.789
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O
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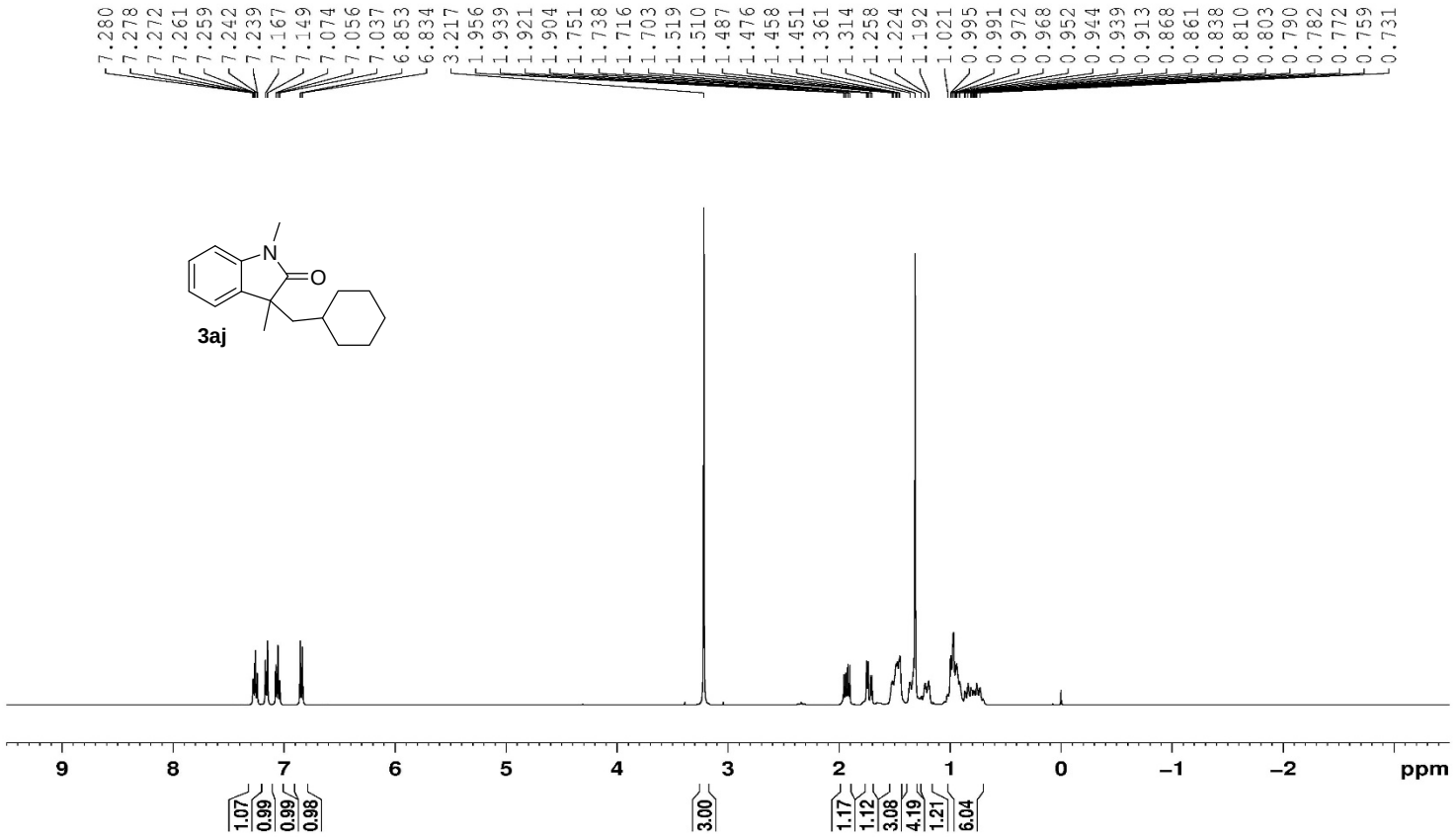
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7.074
7.056
7.037
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6.834
3.217
1.956
1.939
1.921
1.904
1.751
1.738
1.716
1.703
1.519
1.510
1.487
1.476
1.458
1.451
1.361
1.314
1.258
1.224
1.192
1.021
0.995
0.991
0.972
0.968
0.952
0.944
0.939
0.913
0.868
0.861
0.838
0.810
0.803
0.790
0.782
0.772
0.759
0.731
N
O
3aj
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm
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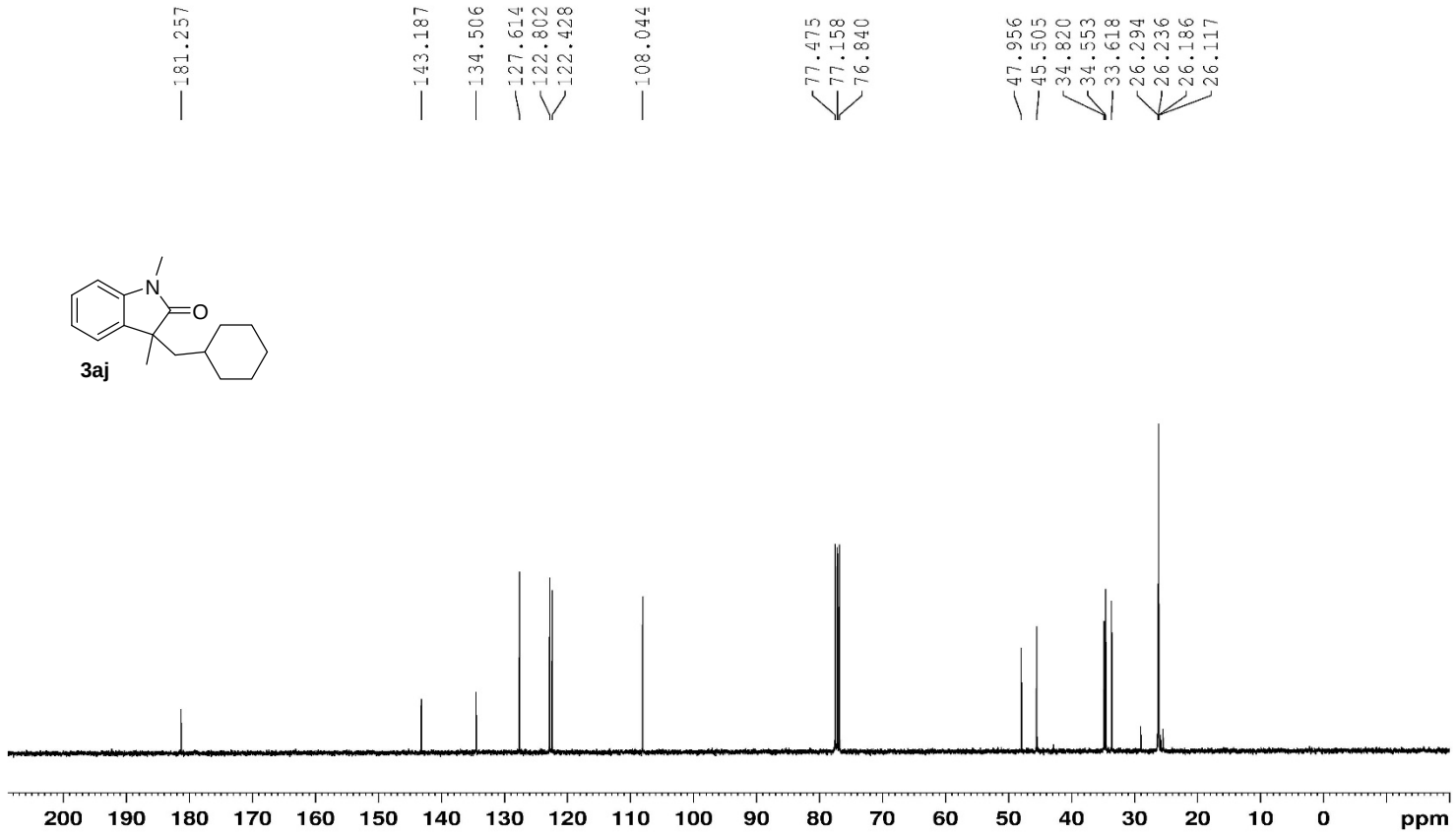
1.12
3.08
4.19
1.21
6.04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34.820
34.553
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26.186
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N
O
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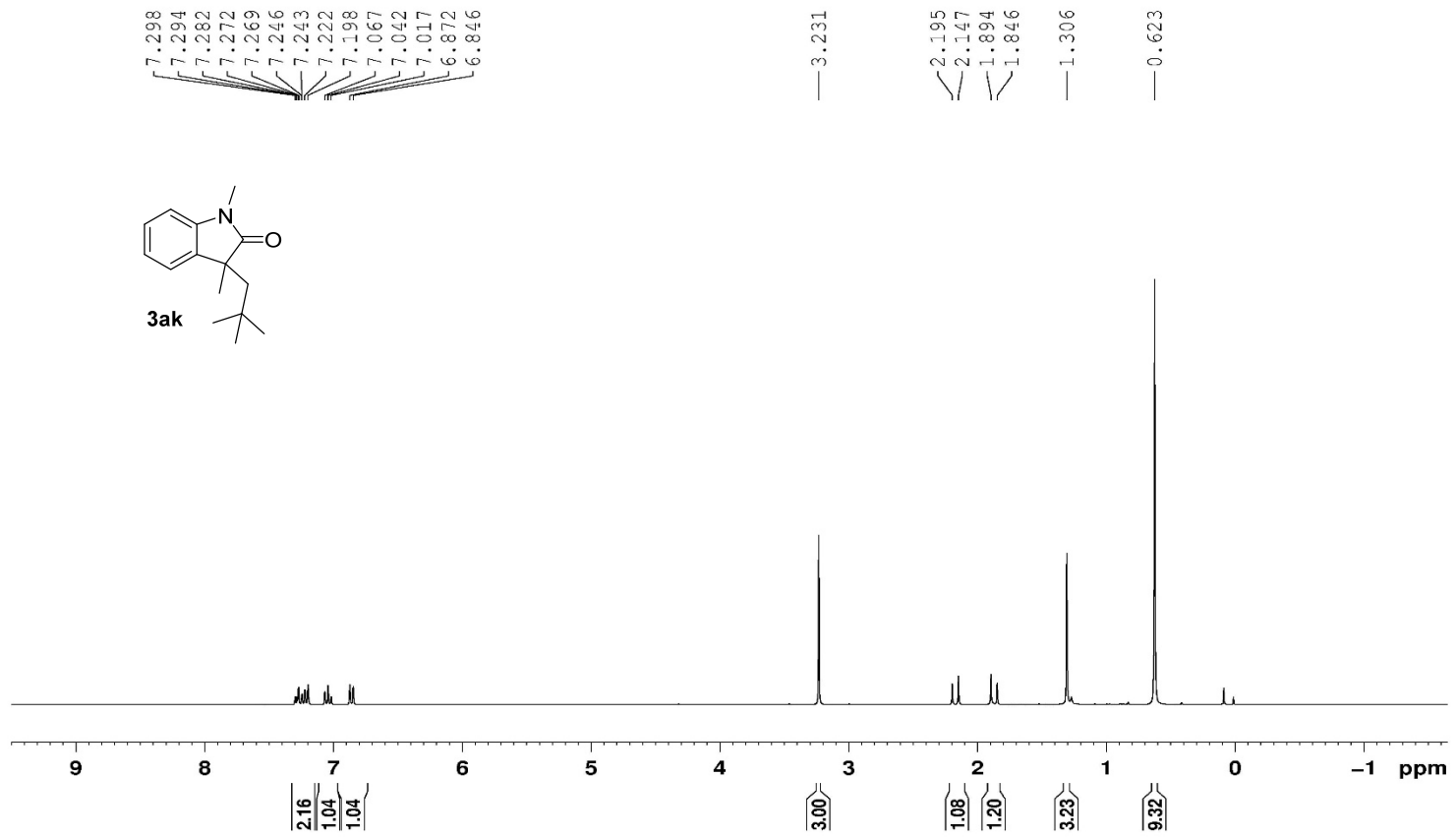
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7.246
7.243
7.222
7.198
7.067
7.042
7.017
6.872
6.846
3.231
2.195
2.147
1.894
1.846
1.306
0.623
N
O
3ak
9
8
7
6
5
4
3
2
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0
−1
ppm
2.16
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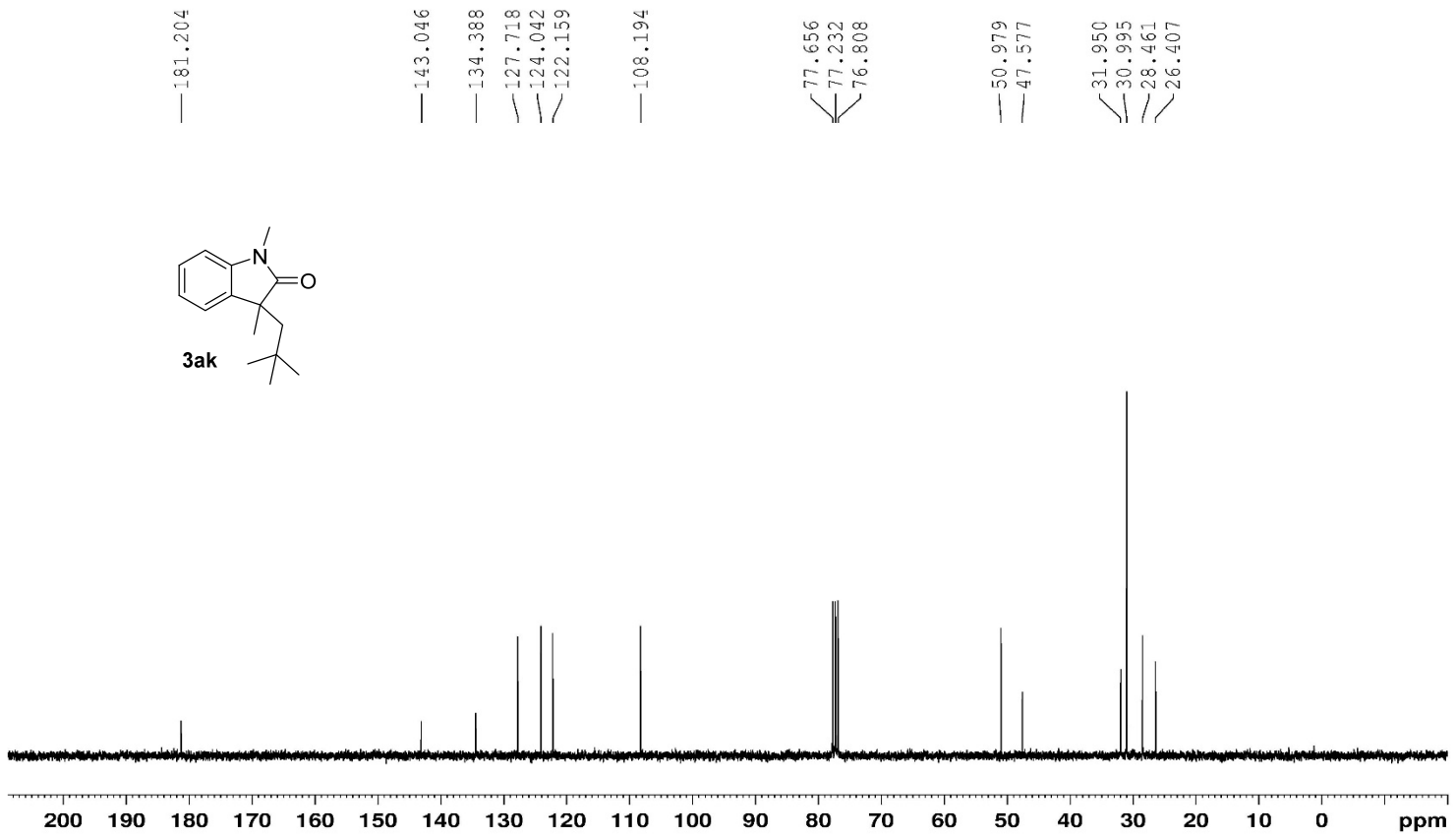
1.04
3.00
1.08
1.20
3.23
9.32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76.808
50.979
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30.995
28.461
26.407
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O
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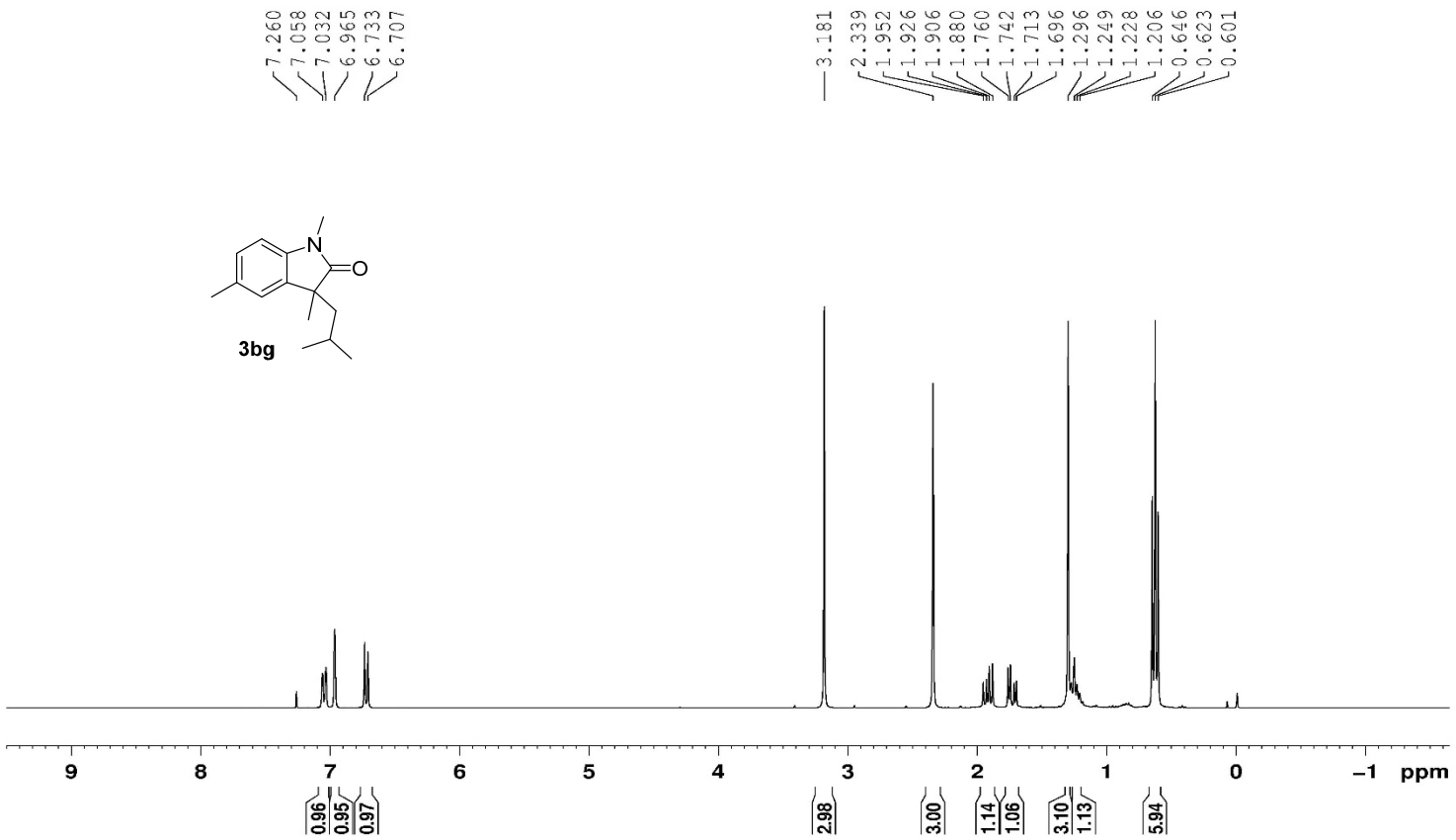
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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1.880
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1.742
1.713
1.696
1.296
1.249
1.228
1.206
0.646
0.623
0.601
N
O
3bg
9
8
7
6
5
4
3
2
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0
−1
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0.95
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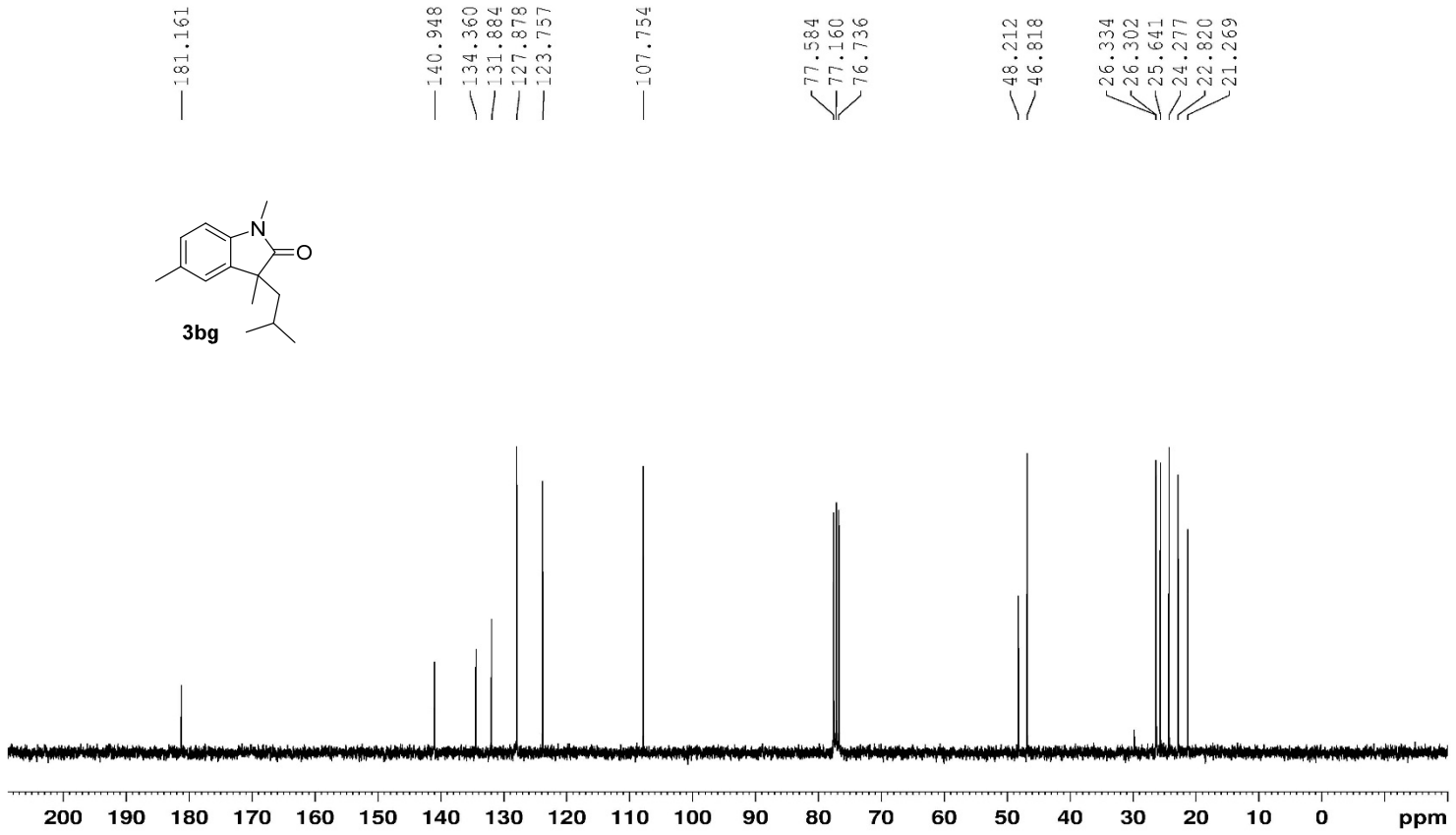
5.94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26.334
26.302
25.641
24.277
22.820
21.269
N
O
3bg
200
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180
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140
130
120
110
100
90
80
70
60
50
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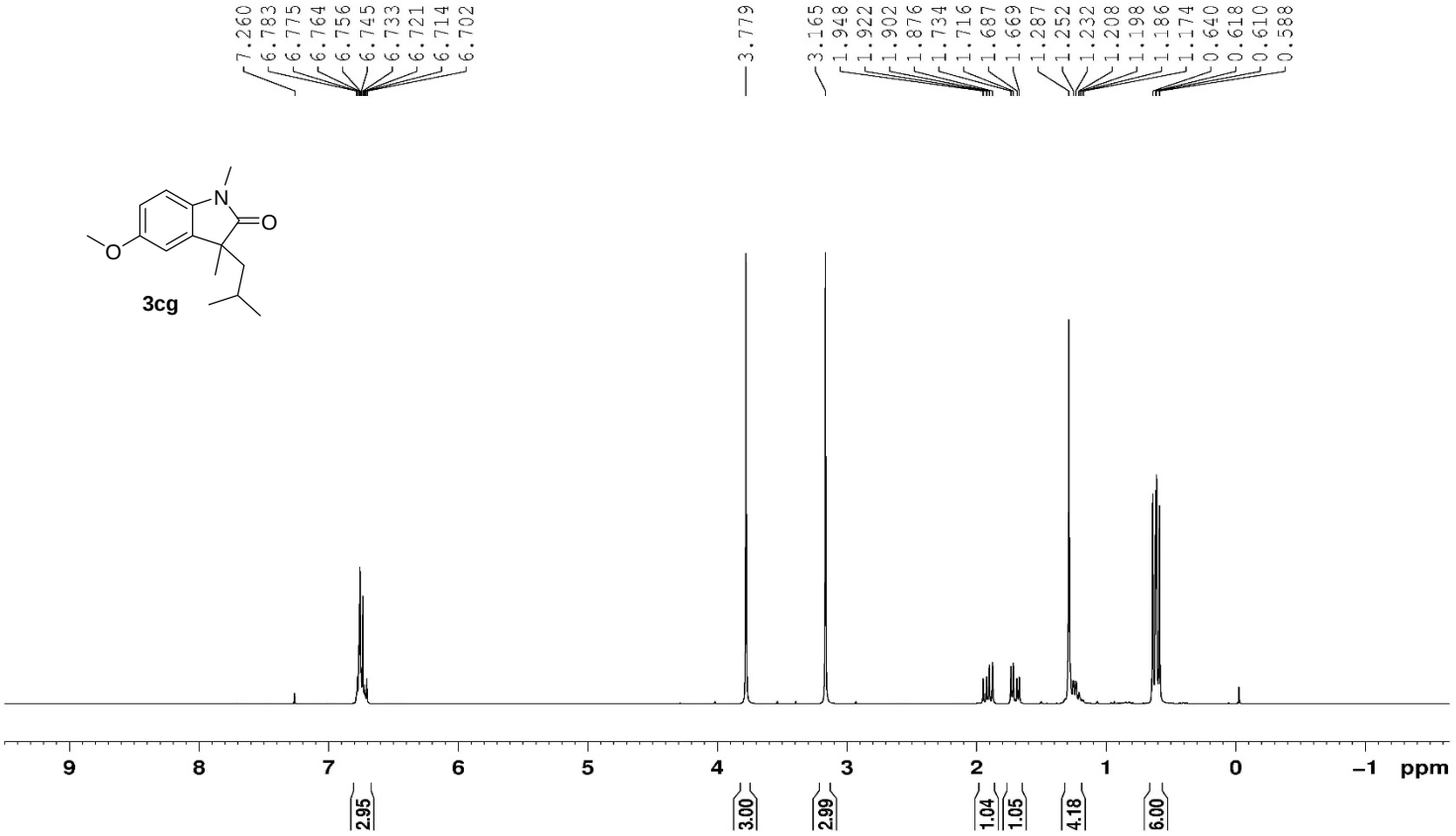
ppm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6.702
3.779
3.165
1.948
1.922
1.902
1.876
1.734
1.716
1.687
1.669
1.287
1.252
1.232
1.208
1.198
1.186
1.174
0.640
0.618
0.610
0.588
N
O
O
3cg
9
8
7
6
5
4
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2
1
0
−1
ppm
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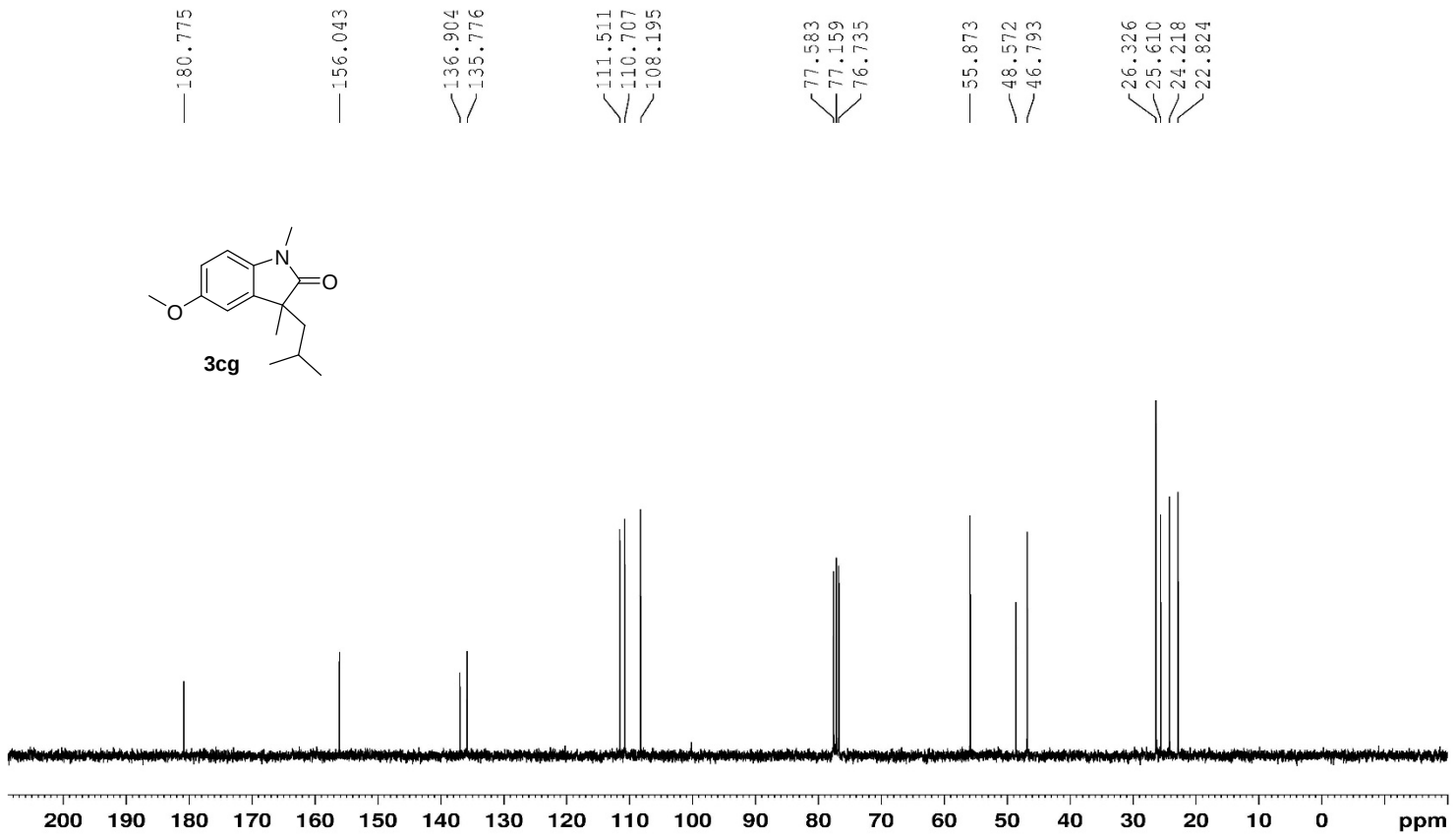
6.00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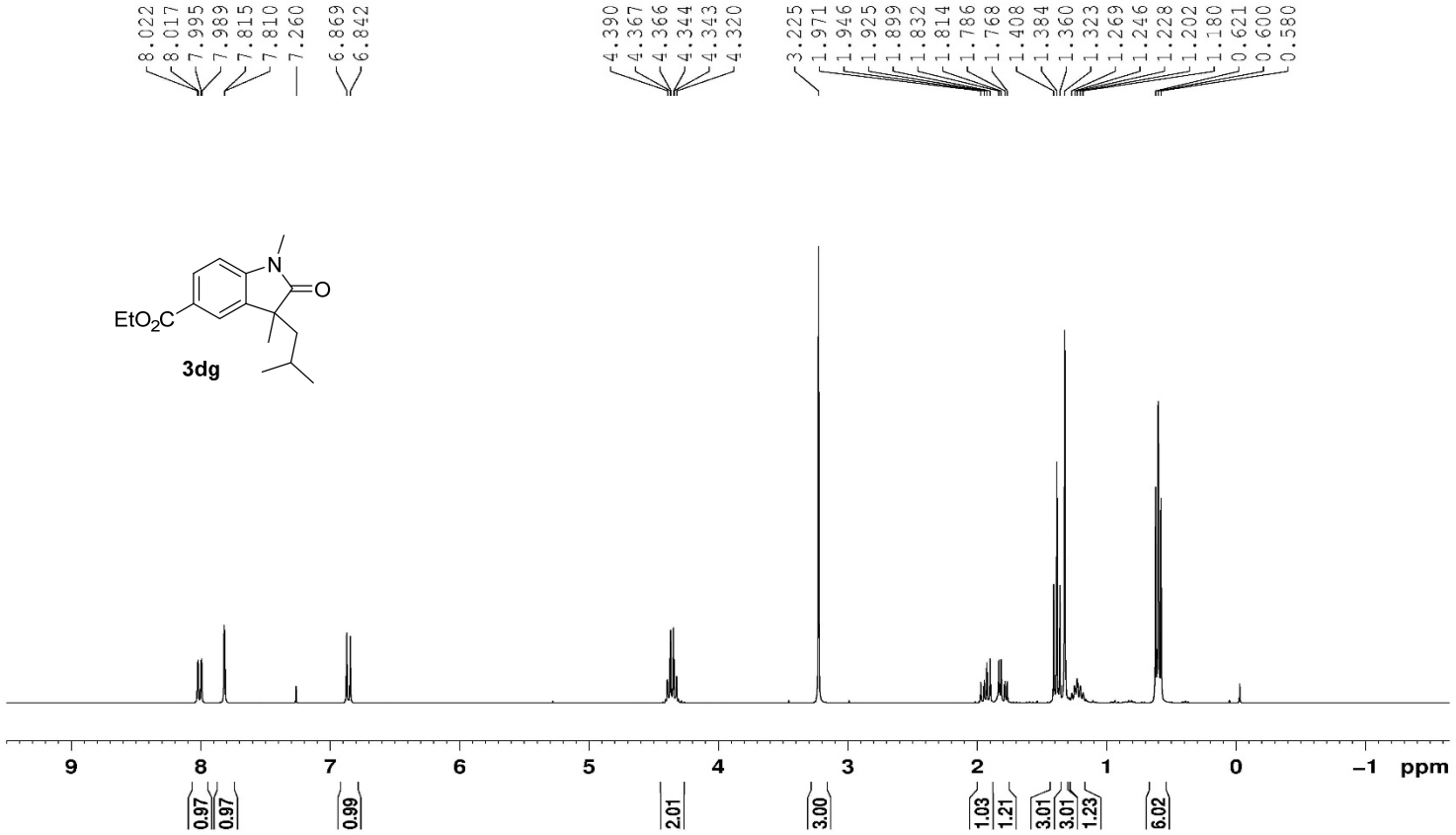
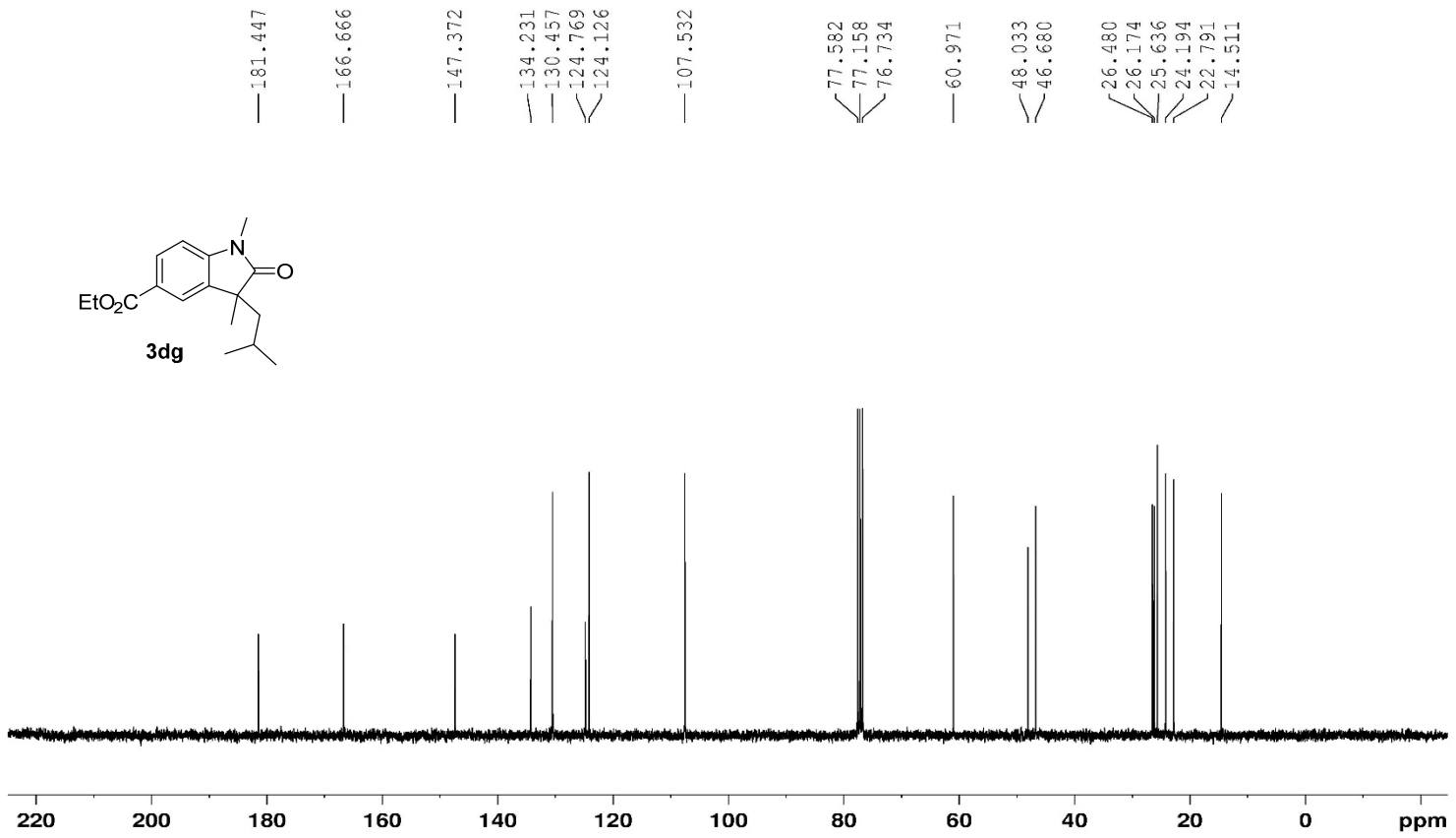
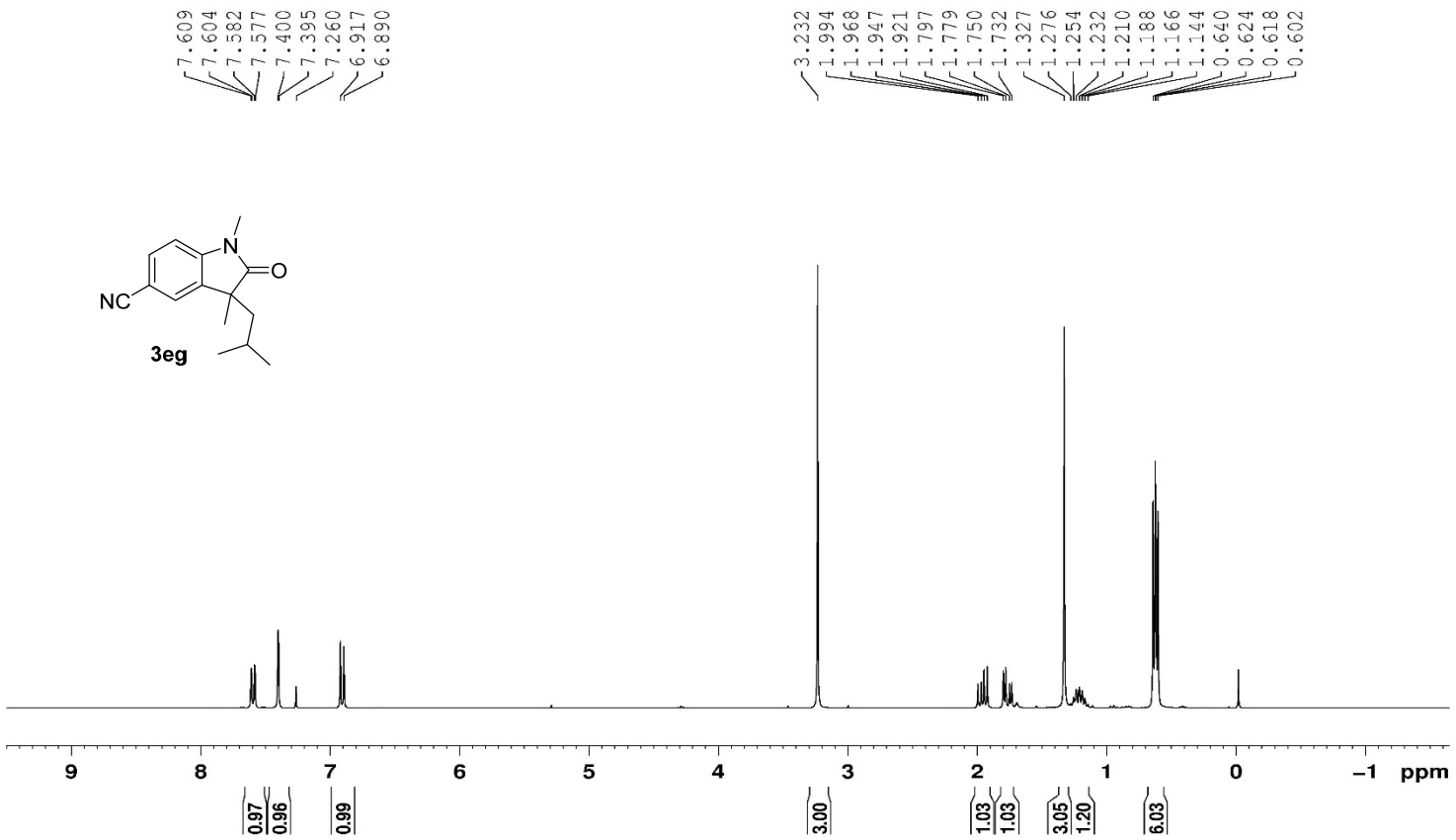
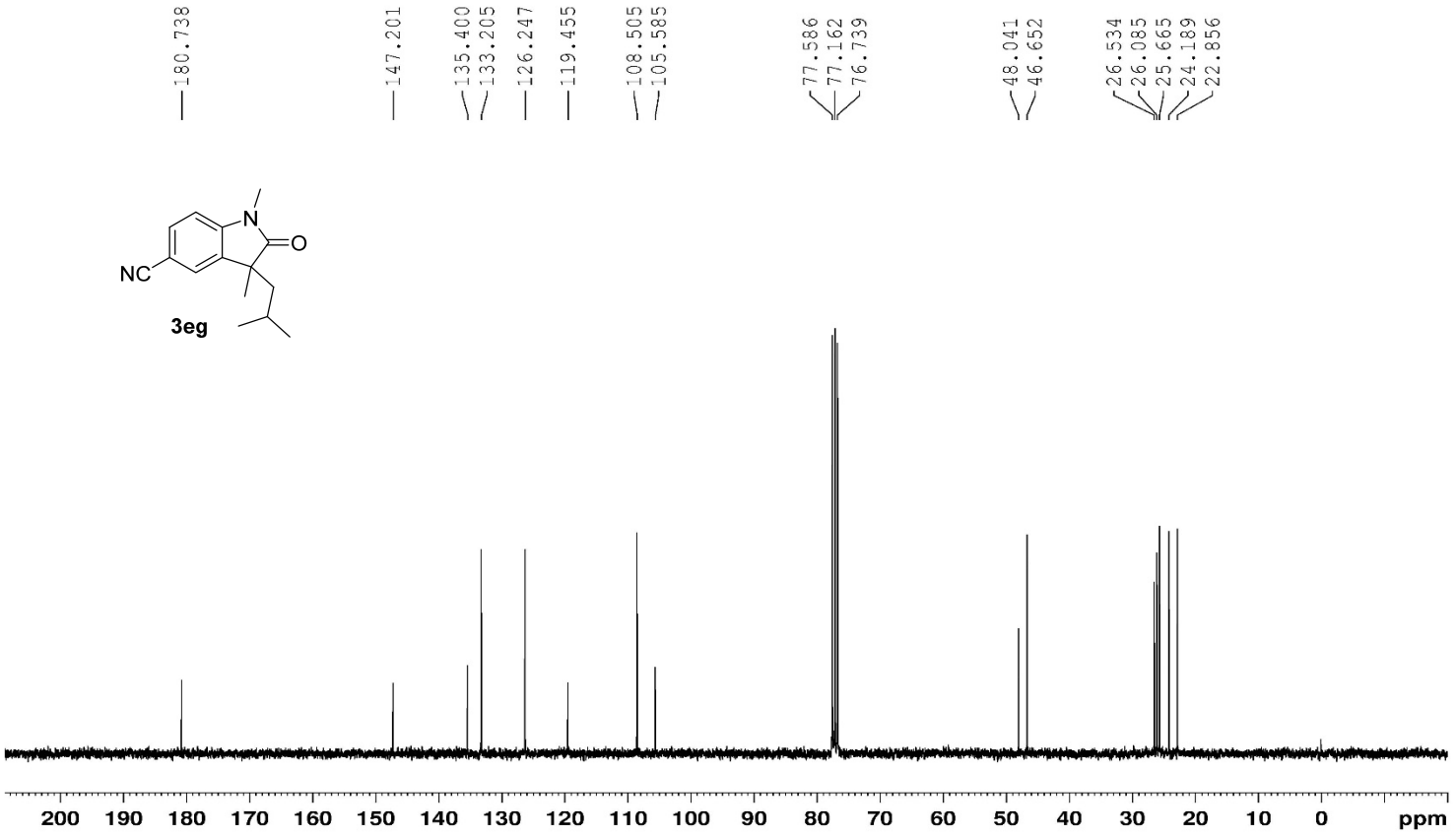
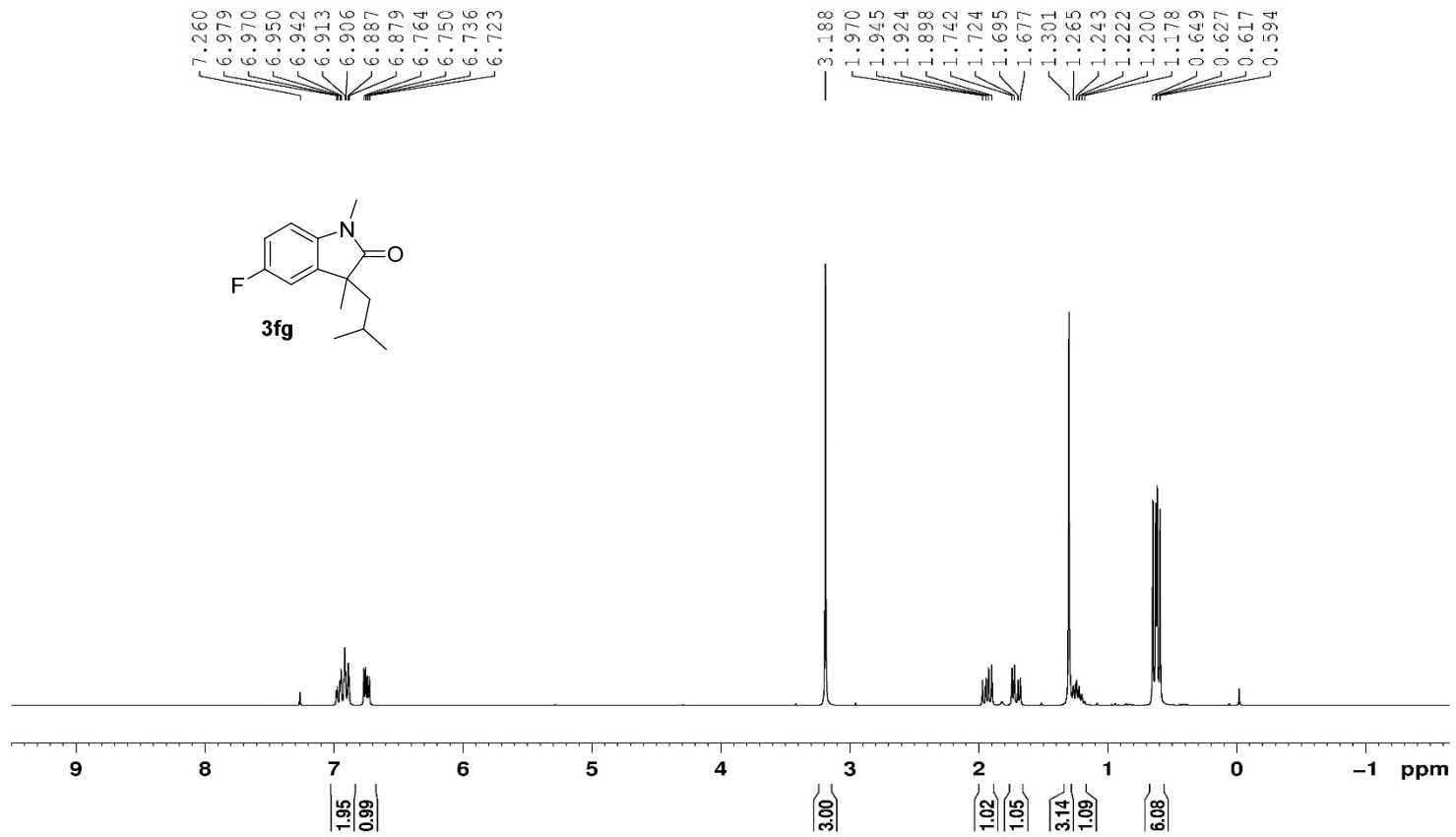
108.195
77.583
77.159
76.735
55.873
48.572
46.793
26.326
25.610
24.218
22.824
N
O
O
3cg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

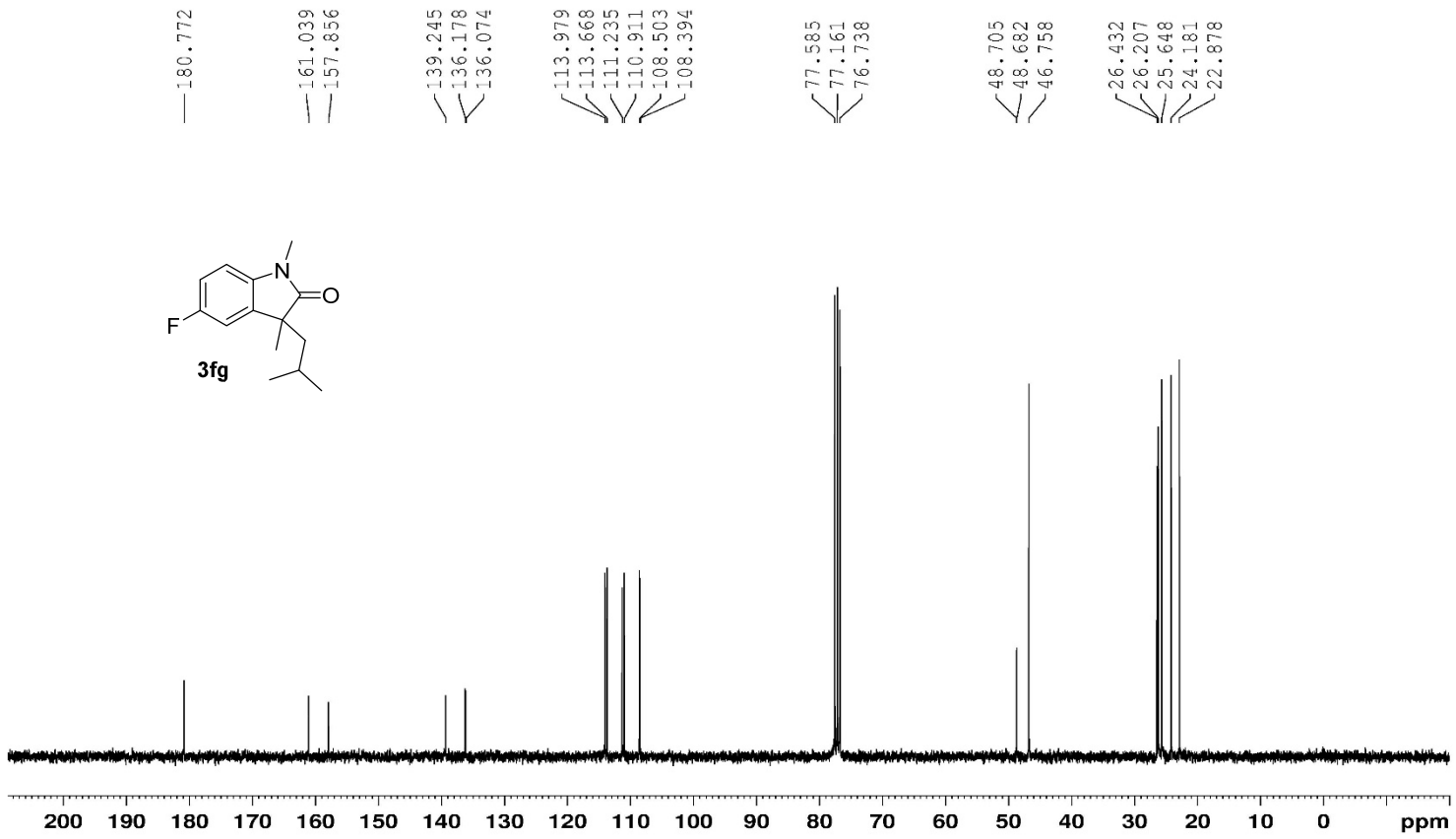

8.022
8.017
7.995
7.989
7.815
7.810
7.260
6.869
6.842
4.390
4.367
4.366
4.344
4.343
4.320
3.225
1.971
1.946
1.925
1.899
1.832
1.814
1.786
1.768
1.408
1.384
1.360
1.323
1.269
1.246
1.228
1.202
1.180
0.621
0.600
0.580
N
O
EtO2C
3dg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.97
0.97
0.99
2.01
3.00
1.03
1.21
3.01
3.01
1.23
6.02

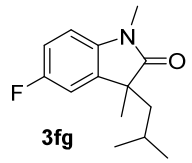

181.447
166.666
147.372
134.231
130.457
124.769
124.126
107.532
77.582
77.158
76.734
60.971
48.033
46.680
26.480
26.174
25.636
24.194
22.791
14.511
N
O
EtO2C
3dg
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.609
7.604
7.582
7.577
7.400
7.395
7.260
6.917
6.890
3.232
1.994
1.968
1.947
1.921
1.797
1.779
1.750
1.732
1.327
1.276
1.254
1.232
1.210
1.188
1.166
1.144
0.640
0.624
0.618
0.602
N
O
NC
3eg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.97
0.96
0.99
3.00
1.03
1.03
3.05
1.20
6.03


180.738
147.201
135.400
133.205
126.247
119.455
108.505
105.585
77.586
77.162
76.739
48.041
46.652
26.534
26.085
25.665
24.189
22.856
N
O
NC
3eg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

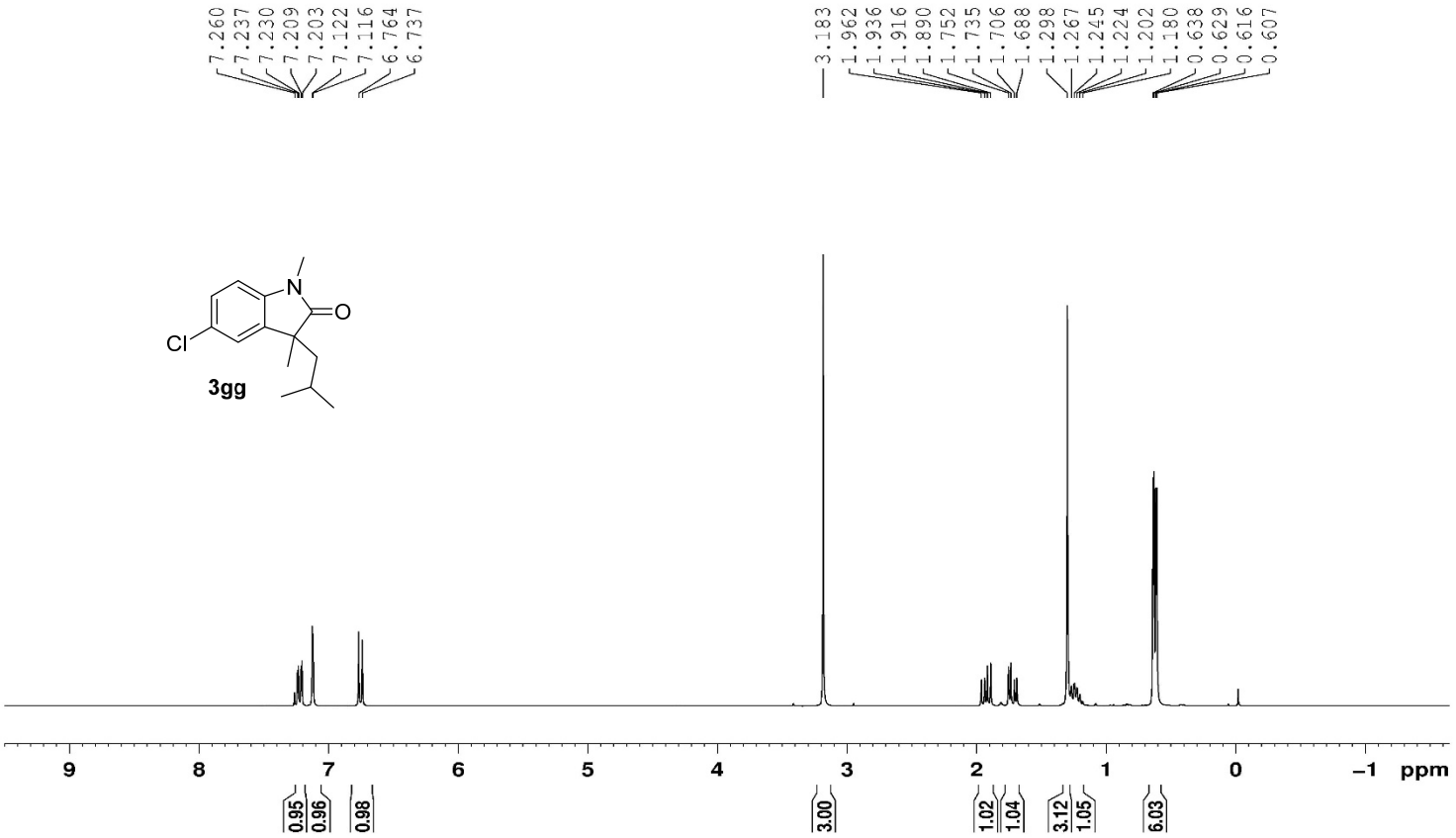

7.260
6.979
6.970
6.950
6.942
6.913
6.906
6.887
6.879
6.764
6.750
6.736
6.723
3.188
1.970
1.945
1.924
1.898
1.742
1.724
1.695
1.677
1.301
1.265
1.243
1.222
1.200
1.178
0.649
0.627
0.617
0.594
N
O
F
3fg
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.95
0.99
3.00
1.02
1.05
3.14
1.09
6.08

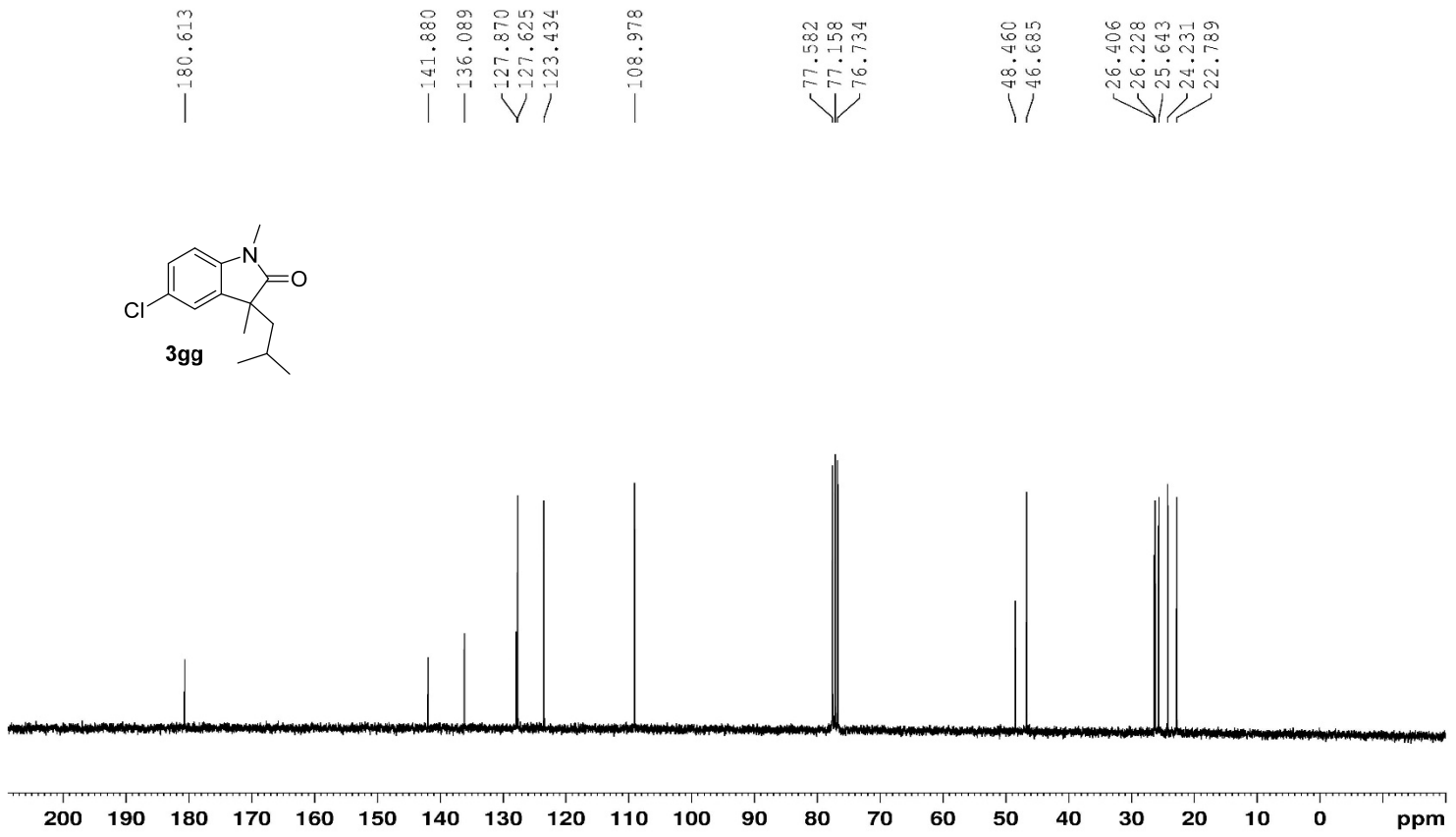

180.772
161.039
157.856
139.245
136.178
136.074
113.979
113.668
111.235
110.911
108.503
108.394
77.585
77.161
76.738
48.705
48.682
46.758
26.432
26.207
25.648
24.181
22.878
N
O
F
3fg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

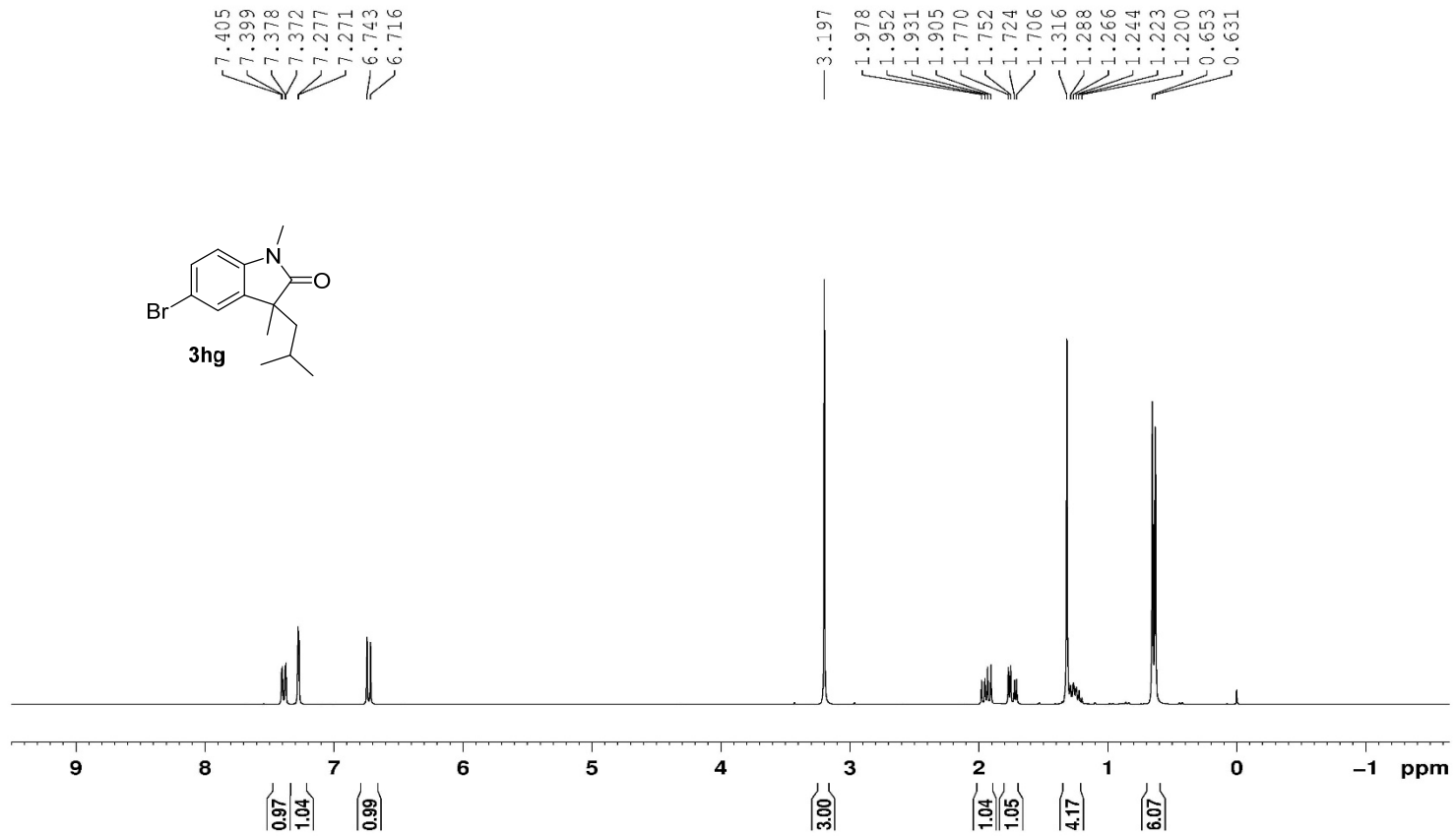

N
O
F

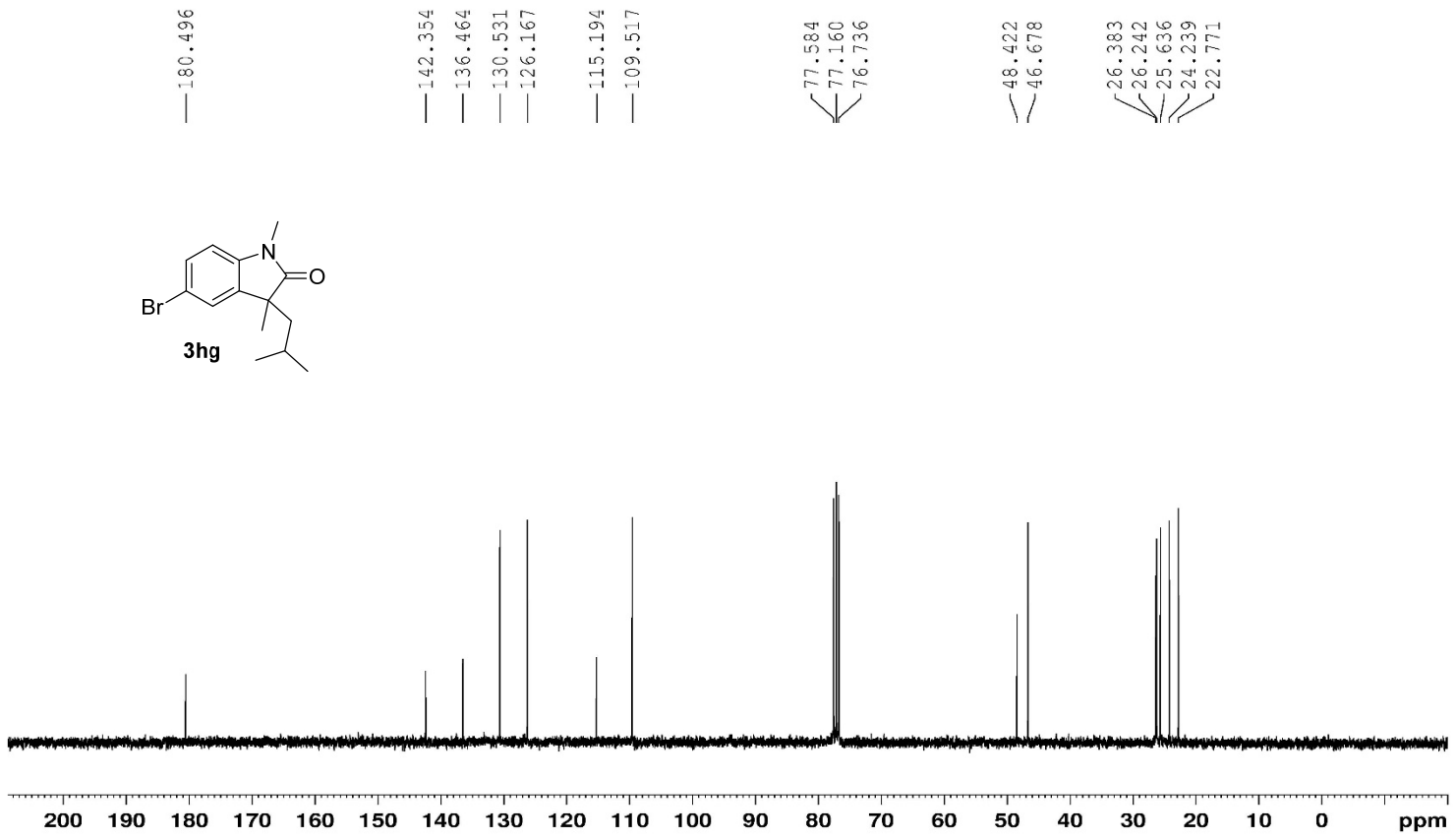
3fg

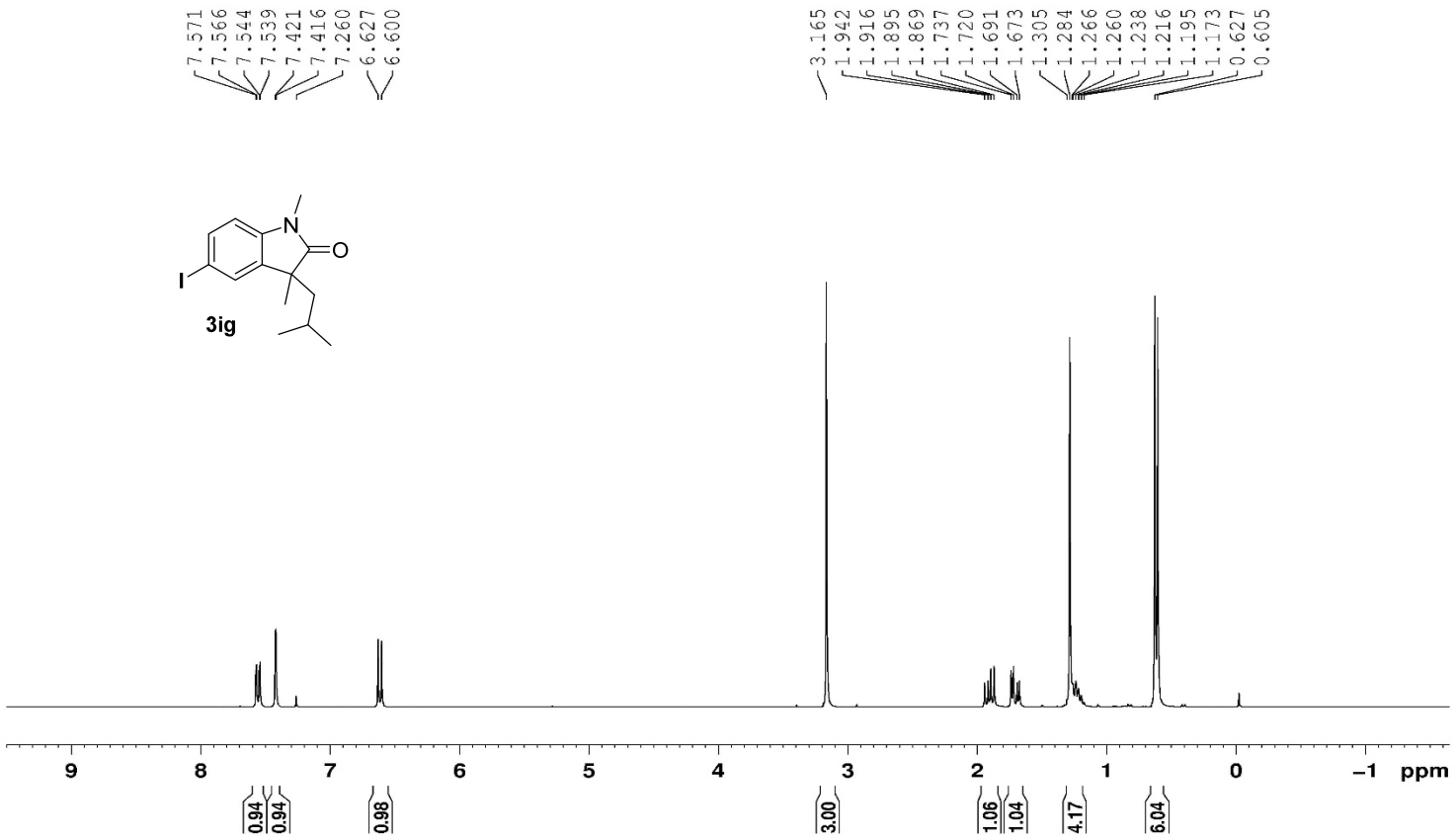
-121.033
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
f1 (ppm)

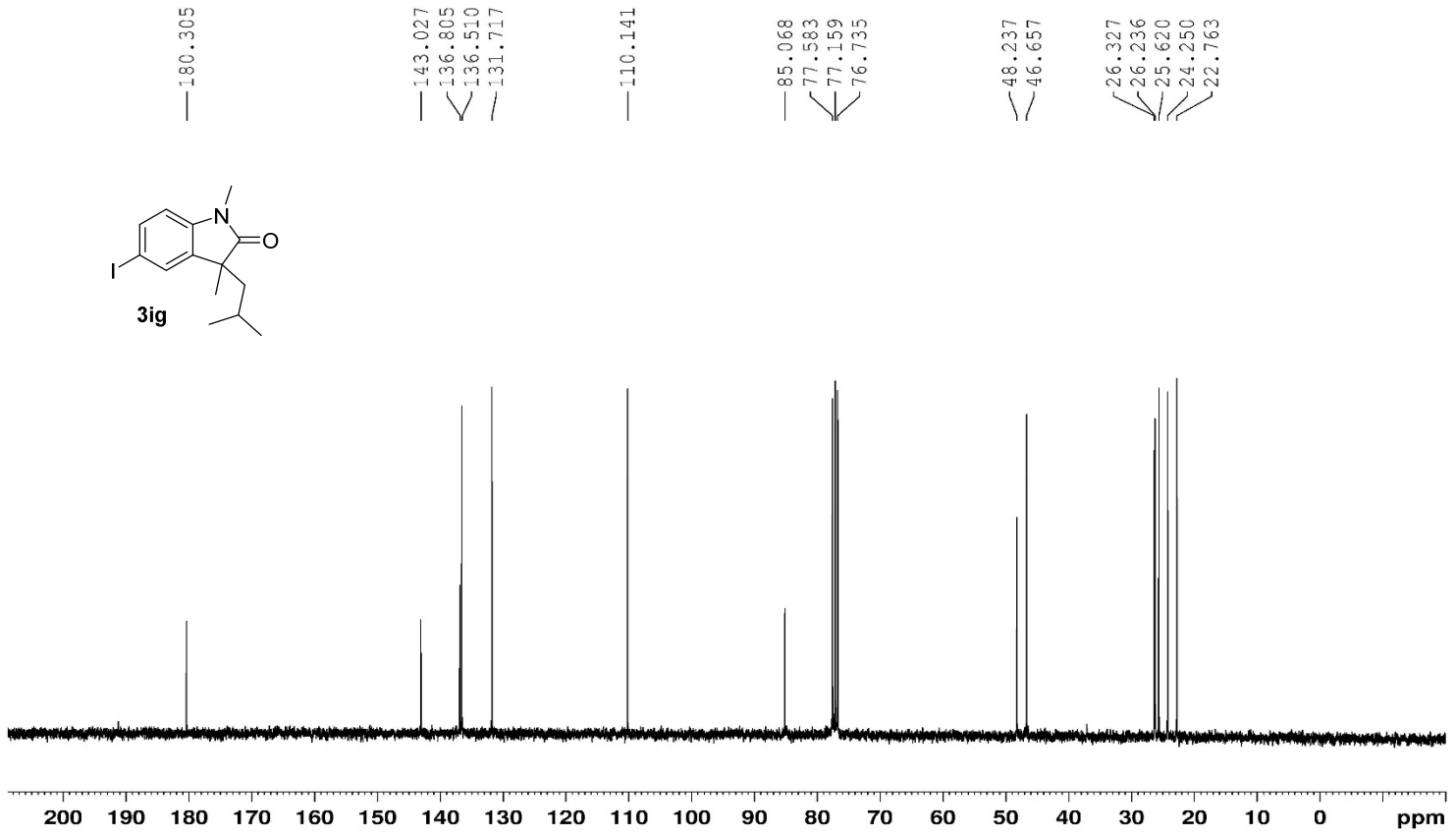

7.260
7.237
7.230
7.209
7.203
7.122
7.116
6.764
6.737
3.183
1.962
1.936
1.916
1.890
1.752
1.735
1.706
1.688
1.298
1.267
1.245
1.224
1.202
1.180
0.638
0.629
0.616
0.607
N
O
Cl
3gg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.95
0.96
0.98
3.00
1.02
1.04
3.12
1.05
6.03

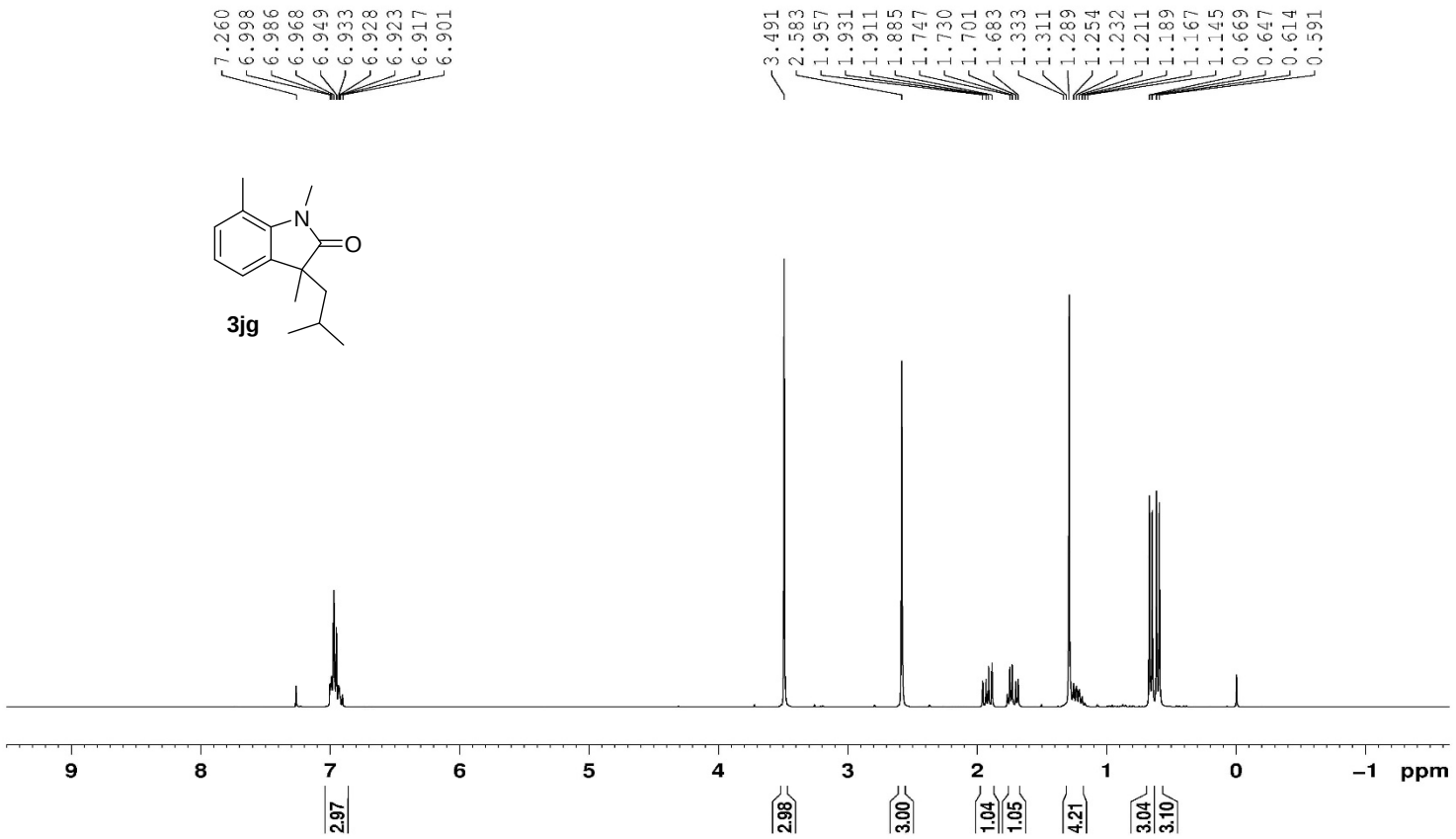

180.613
141.880
136.089
127.870
127.625
123.434
108.978
77.582
77.158
76.734
48.460
46.685
26.406
26.228
25.643
24.231
22.789
N
O
Cl
3gg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

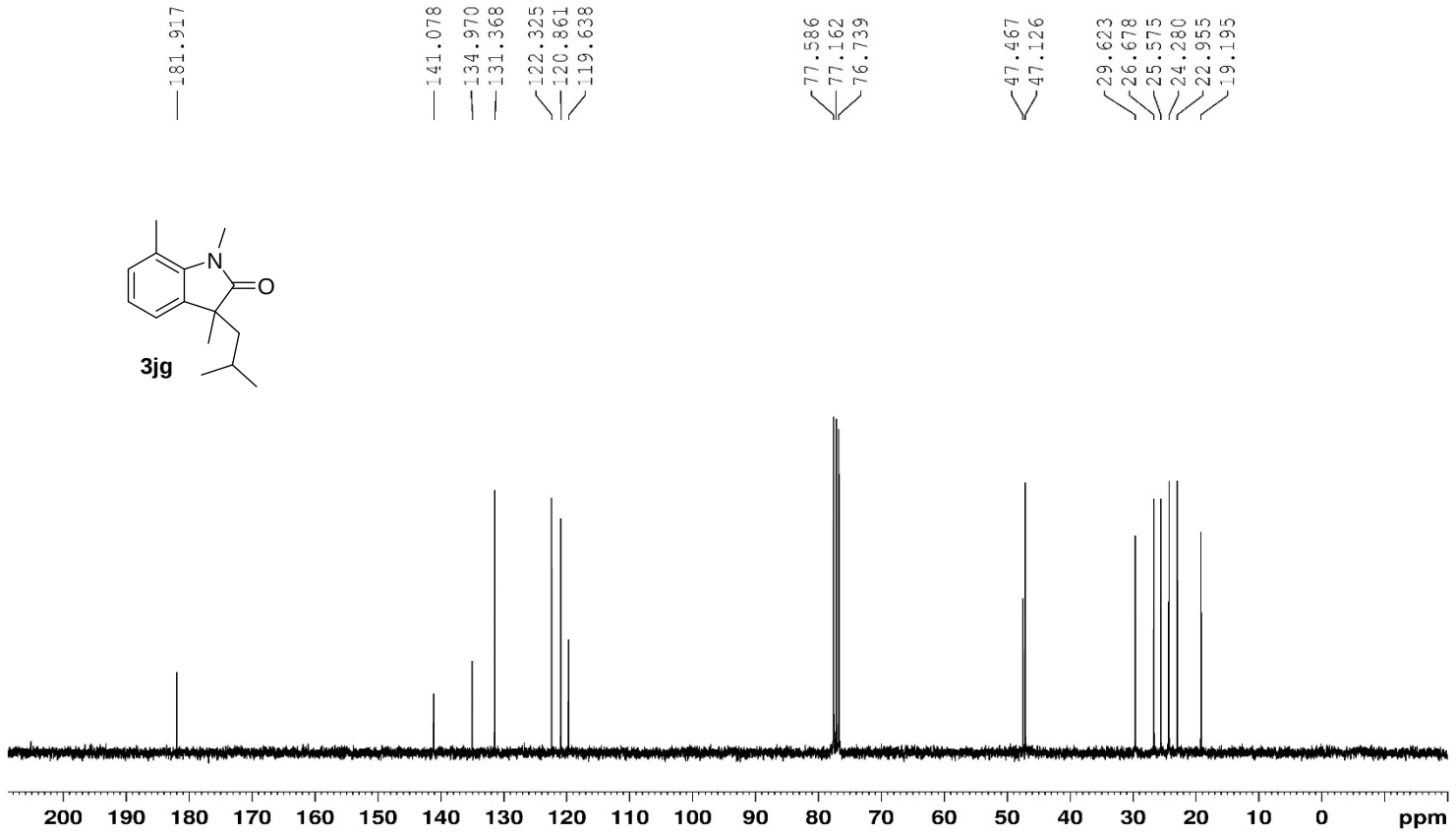

7.405
7.399
7.378
7.372
7.277
7.271
6.743
6.716
3.197
1.978
1.952
1.931
1.905
1.770
1.752
1.724
1.706
1.316
1.288
1.266
1.244
1.223
1.200
0.653
0.631
N
O
Br
3hg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.97
1.04
0.99
3.00
1.04
1.05
4.17
6.07

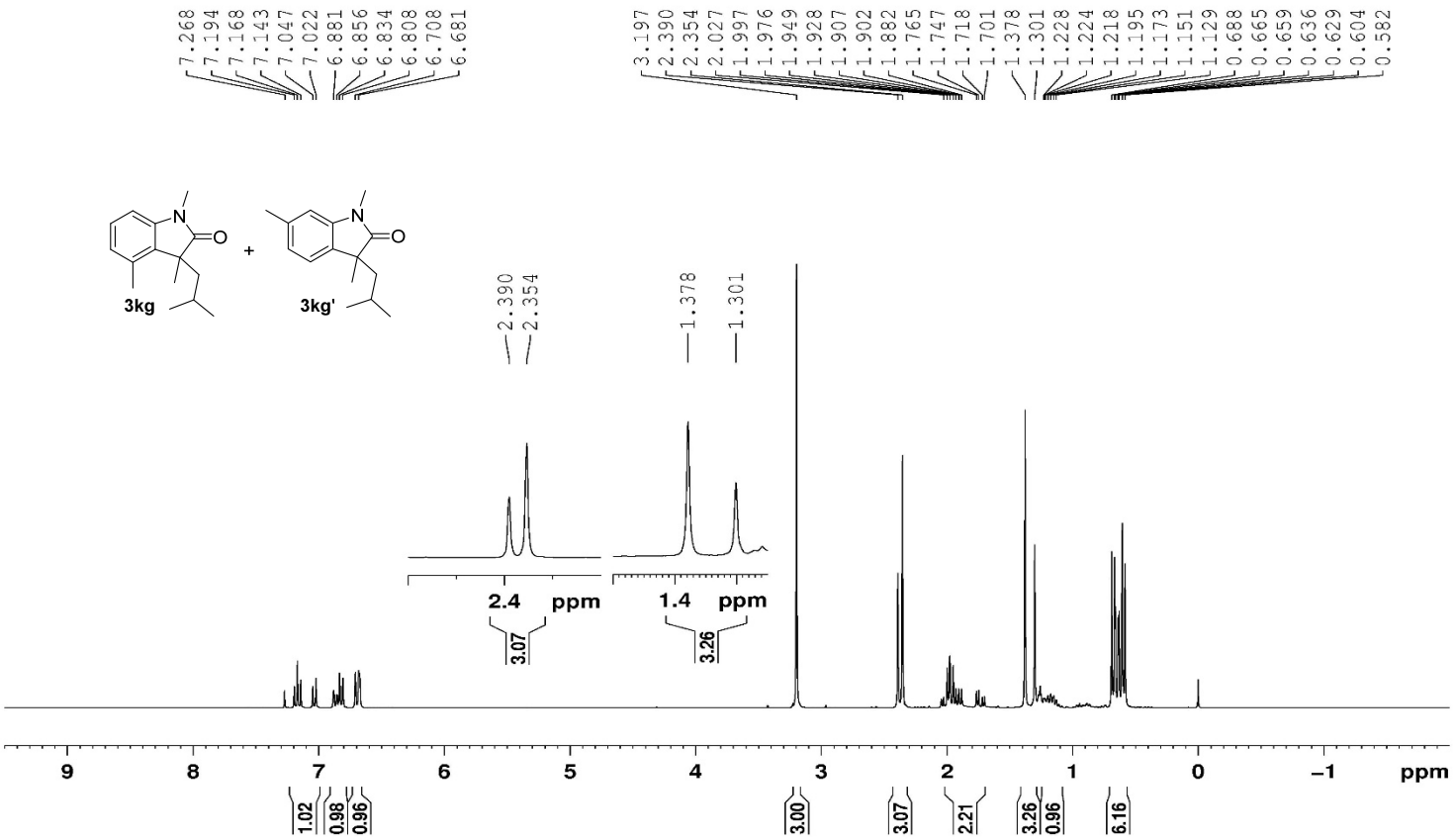

180.496
142.354
136.464
130.531
126.167
115.194
109.517
77.584
77.160
76.736
48.422
46.678
26.383
26.242
25.636
24.239
22.771
N
O
Br
3hg
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

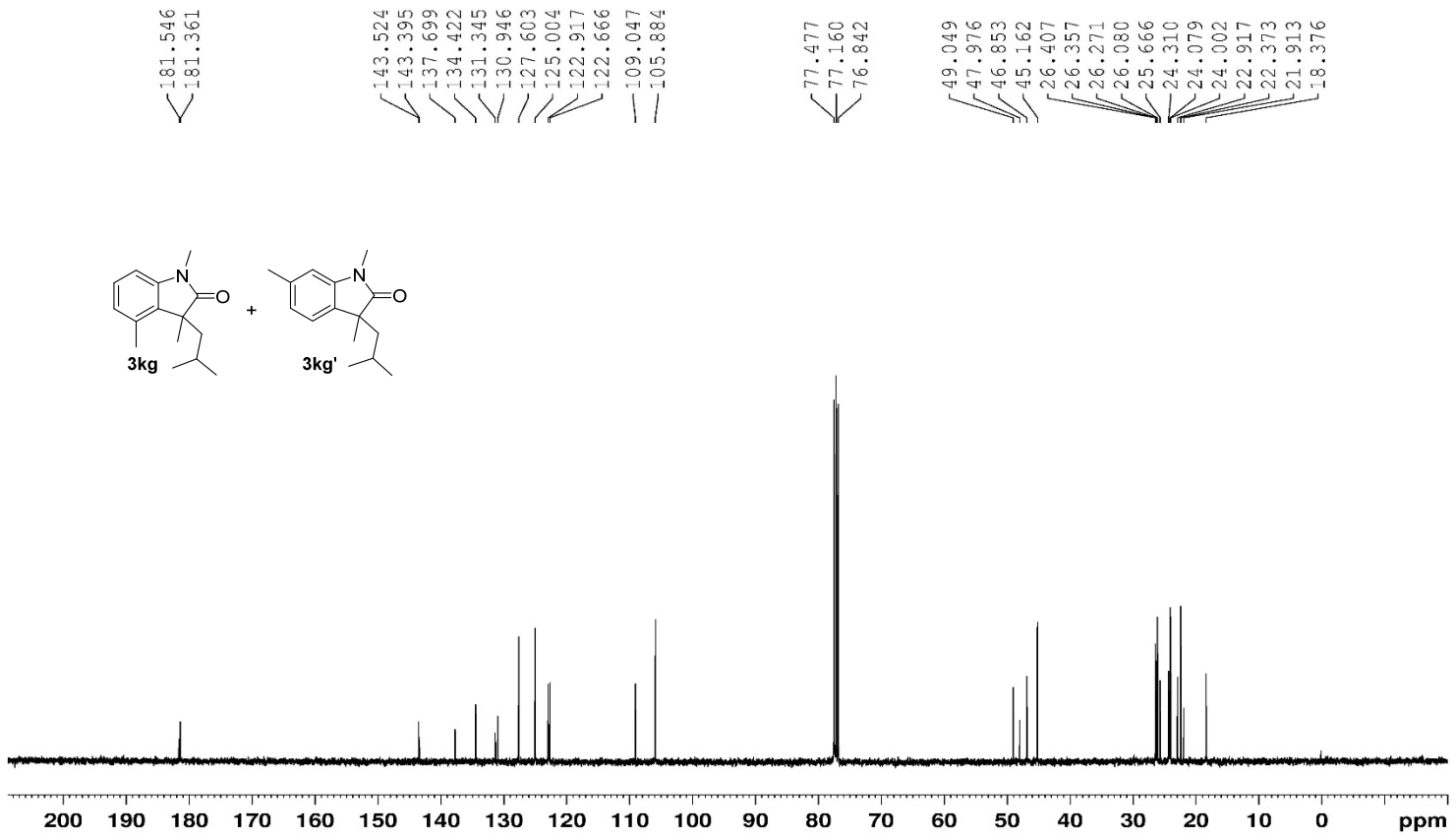

7.571
7.566
7.544
7.539
7.421
7.416
7.260
6.627
6.600
3.165
1.942
1.916
1.895
1.869
1.737
1.720
1.691
1.673
1.305
1.284
1.266
1.260
1.238
1.216
1.195
1.173
0.627
0.605
N
O
I
3ig
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.94
0.94
0.98
3.00
1.06
1.04
4.17
6.04

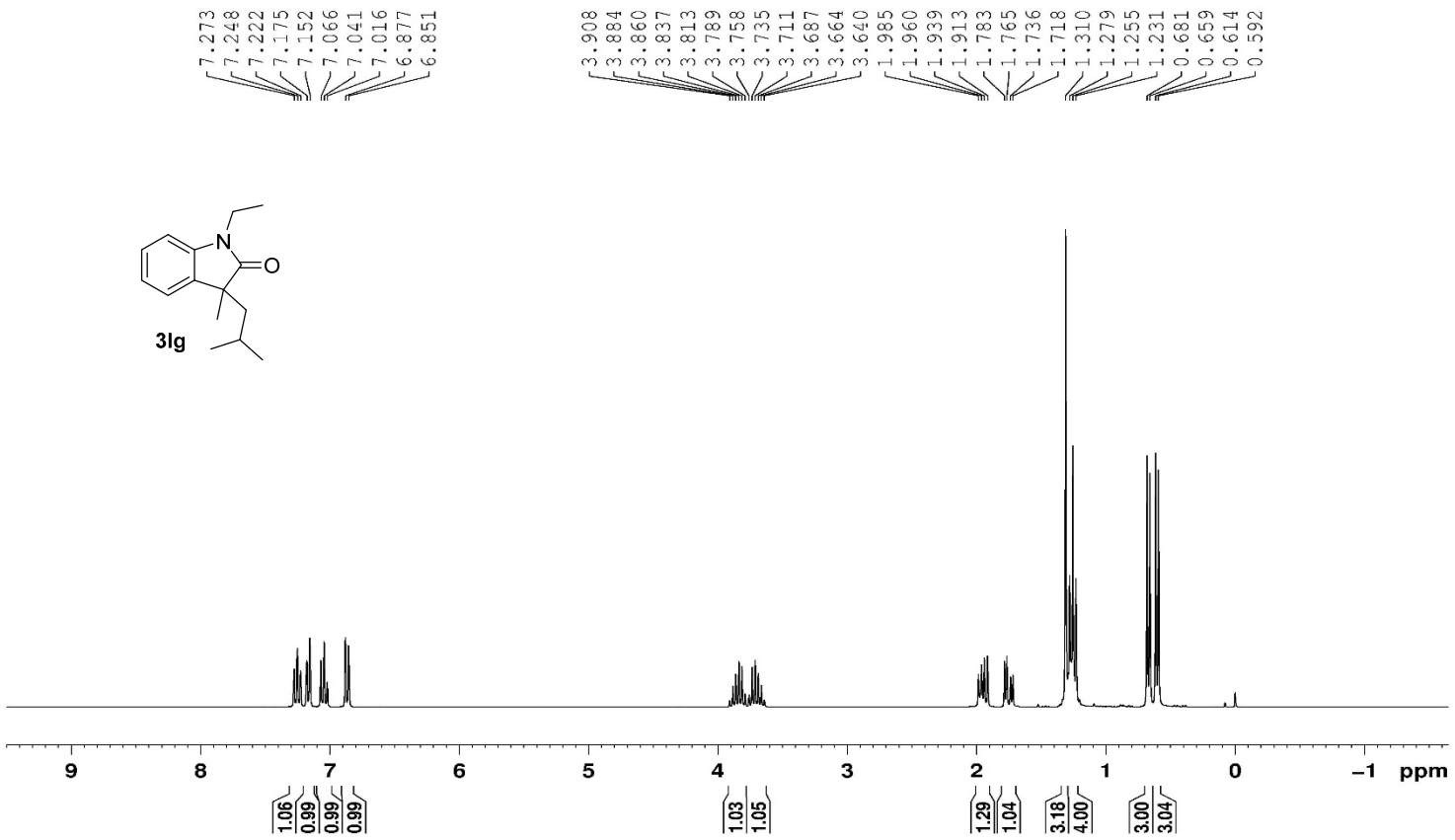

180.305
143.027
136.805
136.510
131.717
110.141
85.068
77.583
77.159
76.735
48.237
46.657
26.327
26.236
25.620
24.250
22.763
N
O
I
3ig
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

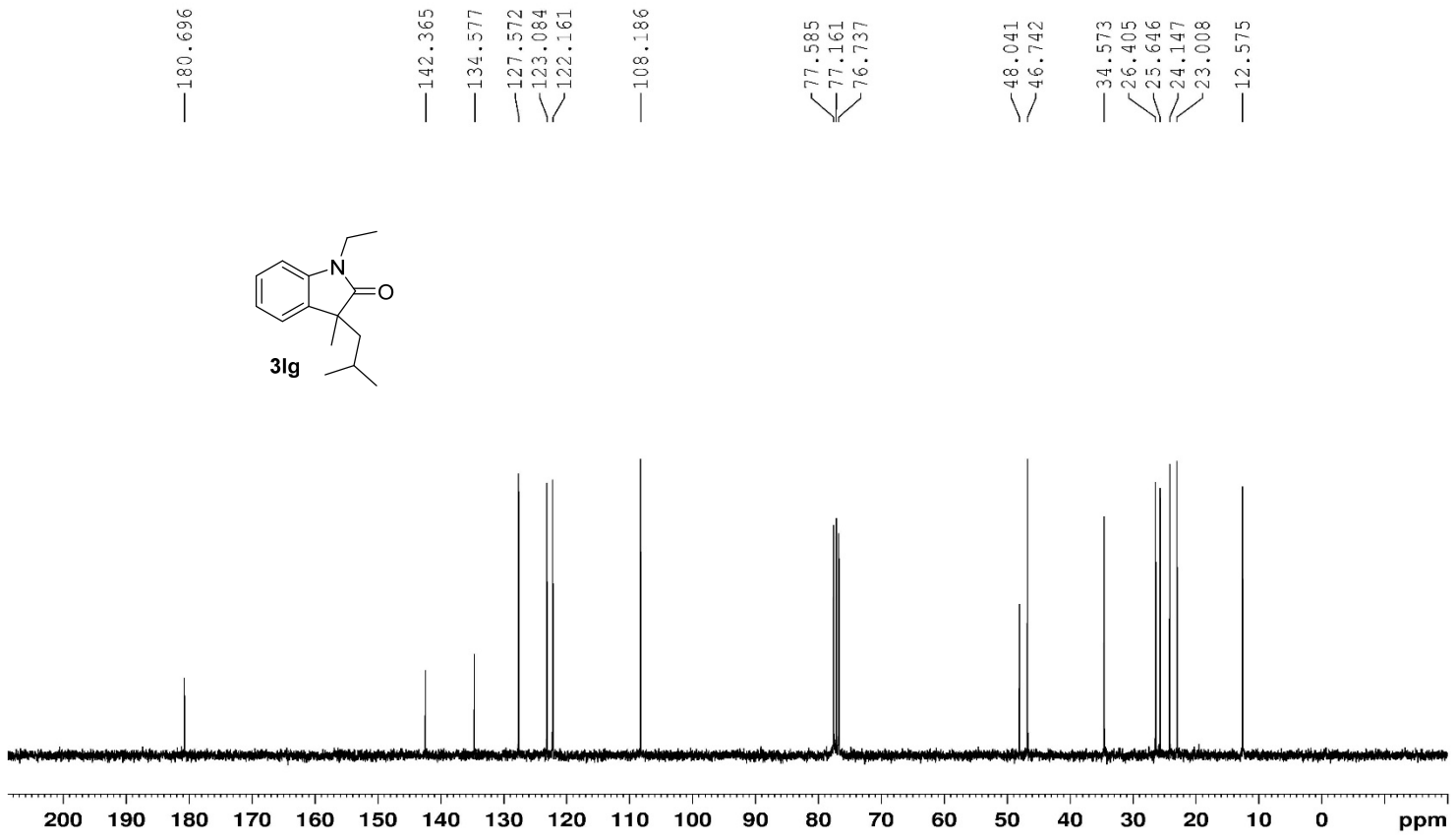

7.260
6.998
6.986
6.968
6.949
6.933
6.928
6.923
6.917
6.901
3.491
2.583
1.957
1.931
1.911
1.885
1.747
1.730
1.701
1.683
1.333
1.311
1.289
1.254
1.232
1.211
1.189
1.167
1.145
0.669
0.647
0.614
0.591
N
O
3jg
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.97
2.98
3.00
1.04
1.05
4.21
3.04
3.10

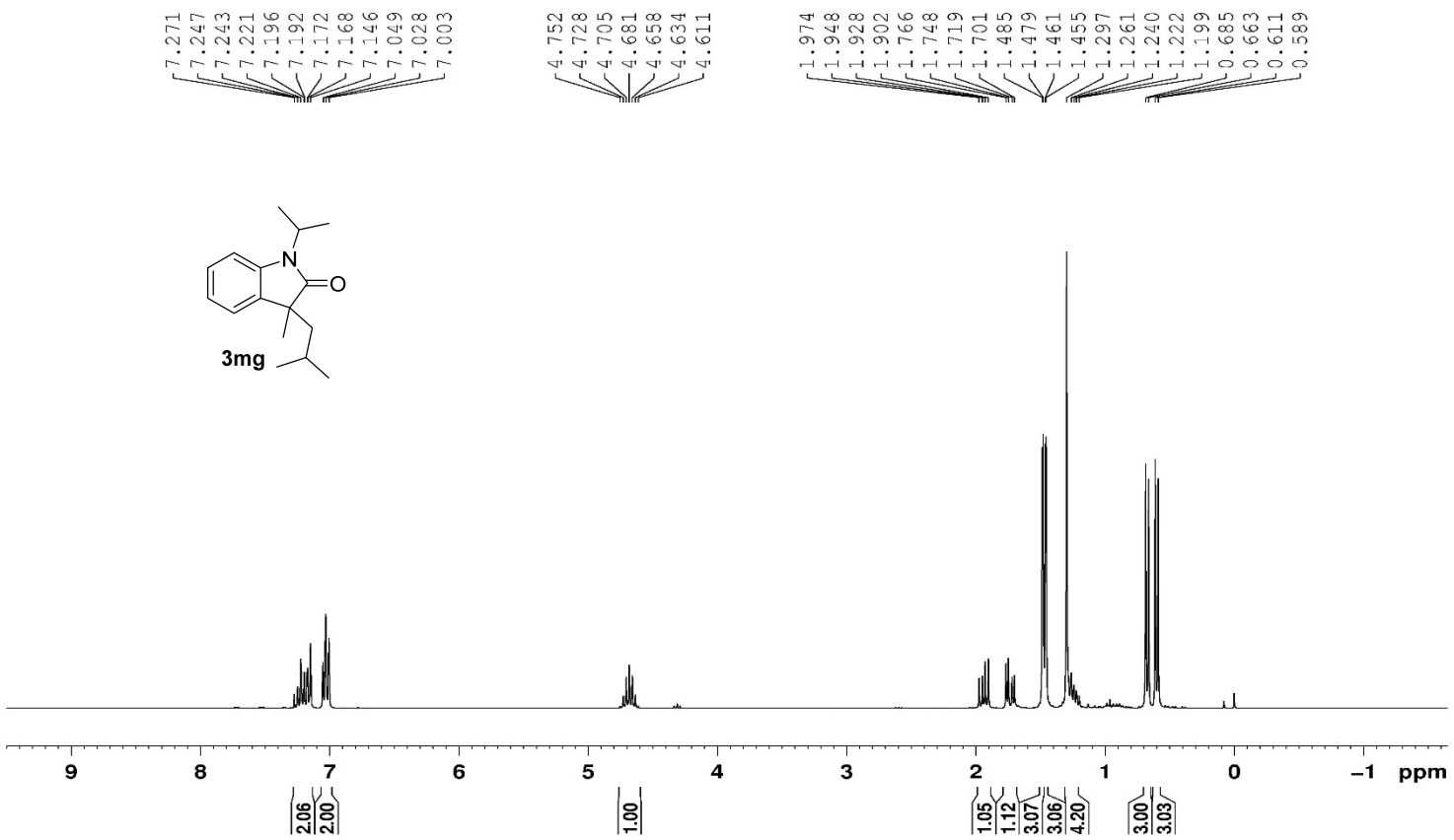

181.917
141.078
134.970
131.368
122.325
120.861
119.638
77.586
77.162
76.739
47.467
47.126
29.623
26.678
25.575
24.280
22.955
19.195
N
O
3jg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

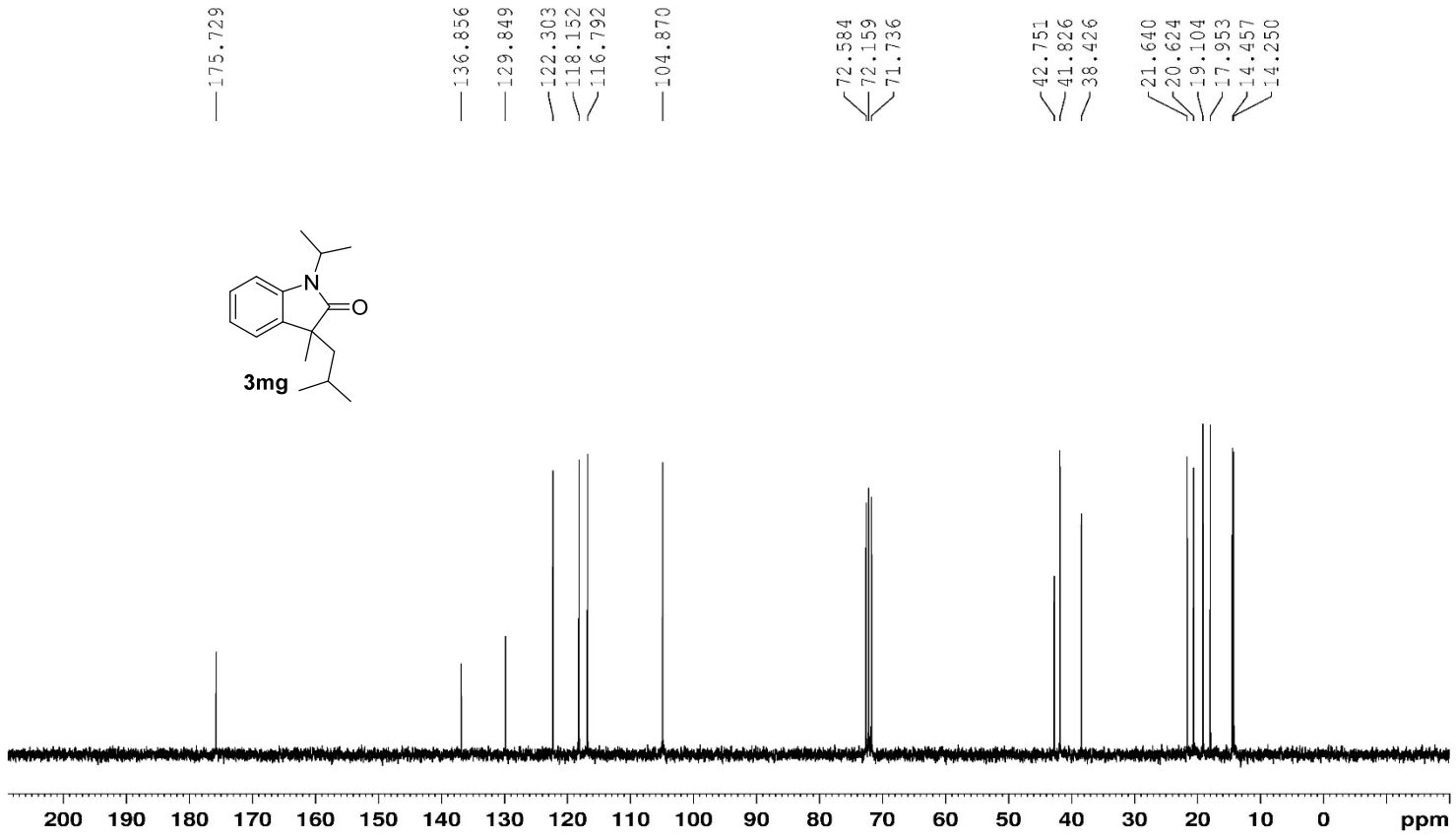

7.268
7.194
7.168
7.143
7.047
7.022
6.881
6.856
6.834
6.808
6.708
6.681
3.197
2.390
2.354
2.027
1.997
1.976
1.949
1.928
1.907
1.902
1.882
1.765
1.747
1.718
1.701
1.378
1.301
1.228
1.224
1.218
1.195
1.173
1.151
1.129
0.688
0.665
0.659
0.636
0.629
0.604
0.582
3kg
3kg'
2.390
2.354
1.378
1.301
2.4 ppm
1.4 ppm
3.07
3.26
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.02
0.98
0.96
3.00
3.07
2.21
3.26
0.96
6.16

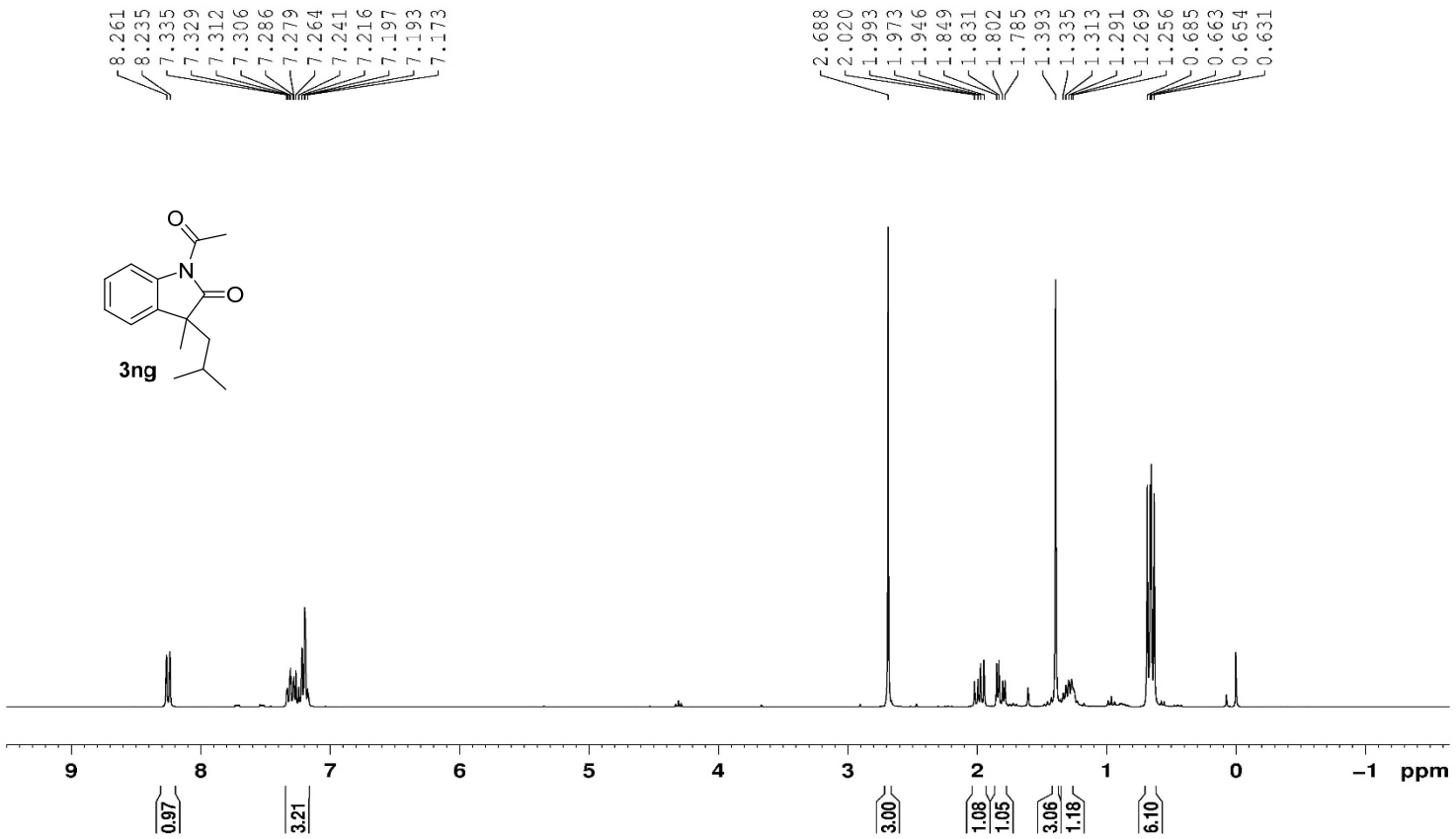

181.546
181.361
143.524
143.395
137.699
134.422
131.345
130.946
127.603
125.004
122.917
122.666
109.047
105.884
77.477
77.160
76.842
49.049
47.976
46.853
45.162
26.407
26.357
26.271
26.080
25.666
24.310
24.079
24.002
22.917
22.373
21.913
18.376
3kg
+
3kg'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

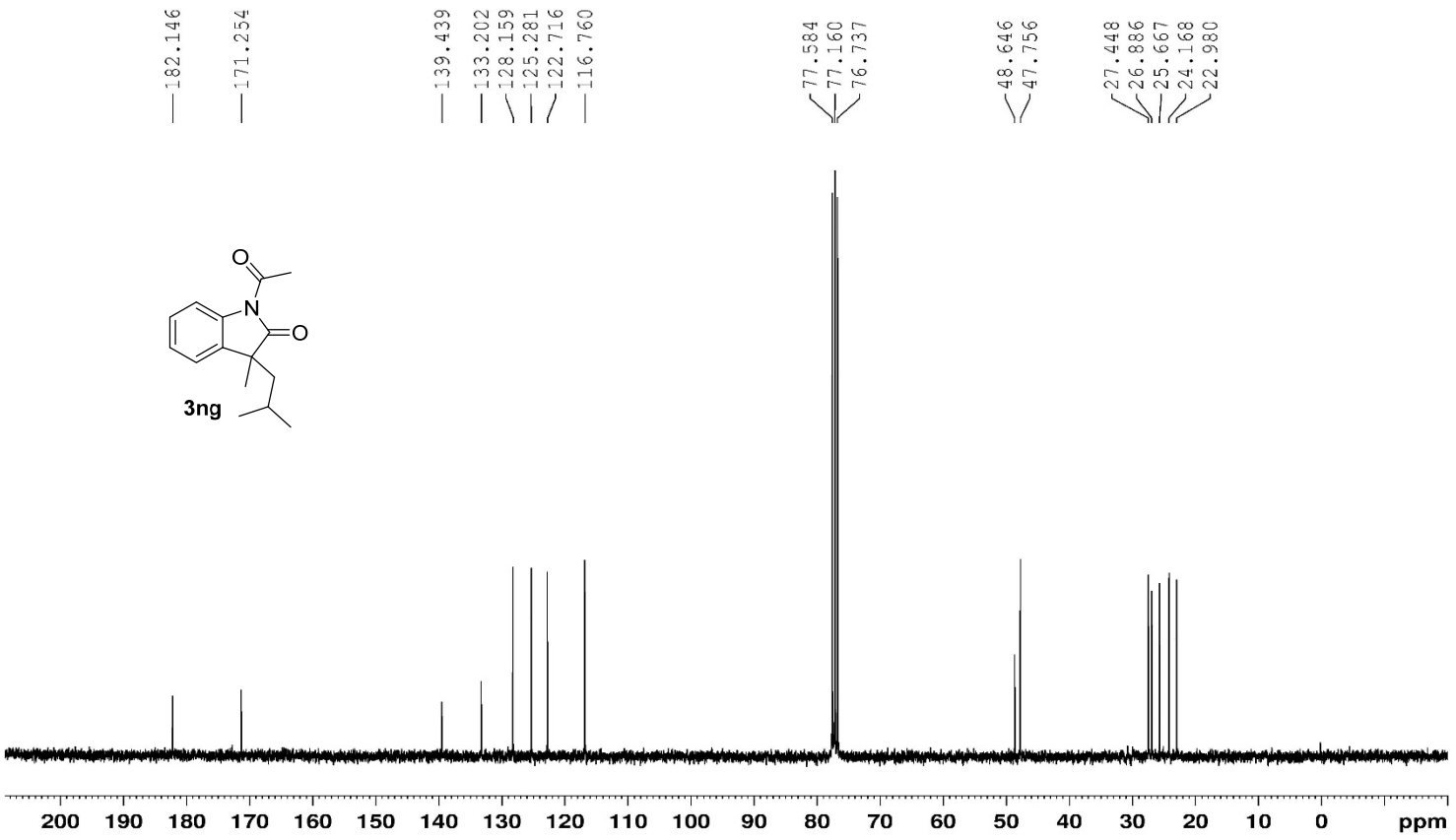

7.273
7.248
7.222
7.175
7.152
7.066
7.041
7.016
6.877
6.851
3.908
3.884
3.860
3.837
3.813
3.789
3.758
3.735
3.711
3.687
3.664
3.640
1.985
1.960
1.939
1.913
1.783
1.765
1.736
1.718
1.310
1.279
1.255
1.231
0.681
0.659
0.614
0.592
N
O
3lg
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.06
0.99
0.99
0.99
1.03
1.05
1.29
1.04
3.18
4.00
3.00
3.04

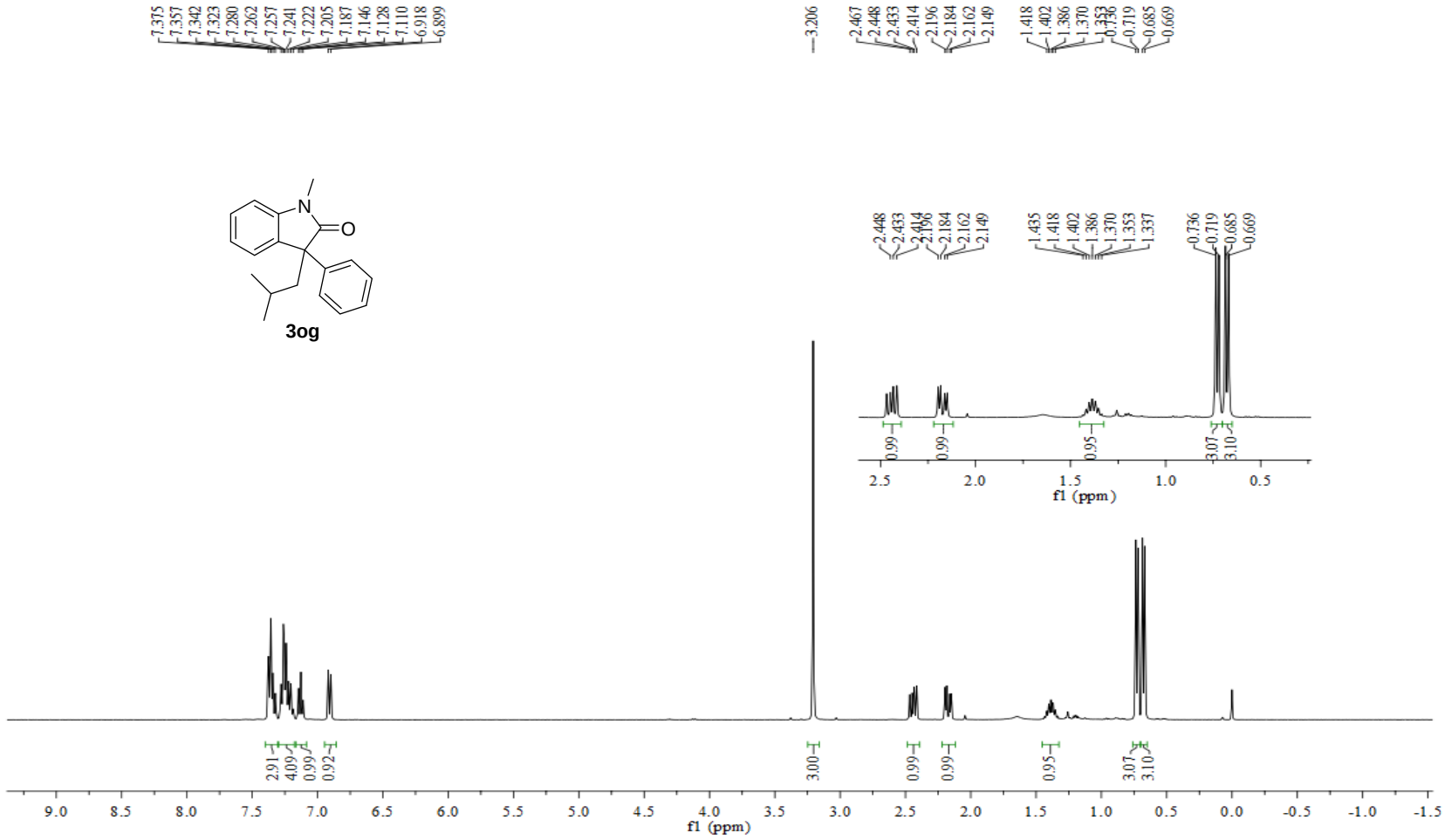

180.696
142.365
134.577
127.572
123.084
122.161
108.186
77.585
77.161
76.737
48.041
46.742
34.573
26.405
25.646
24.147
23.008
12.575
N
O
3lg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

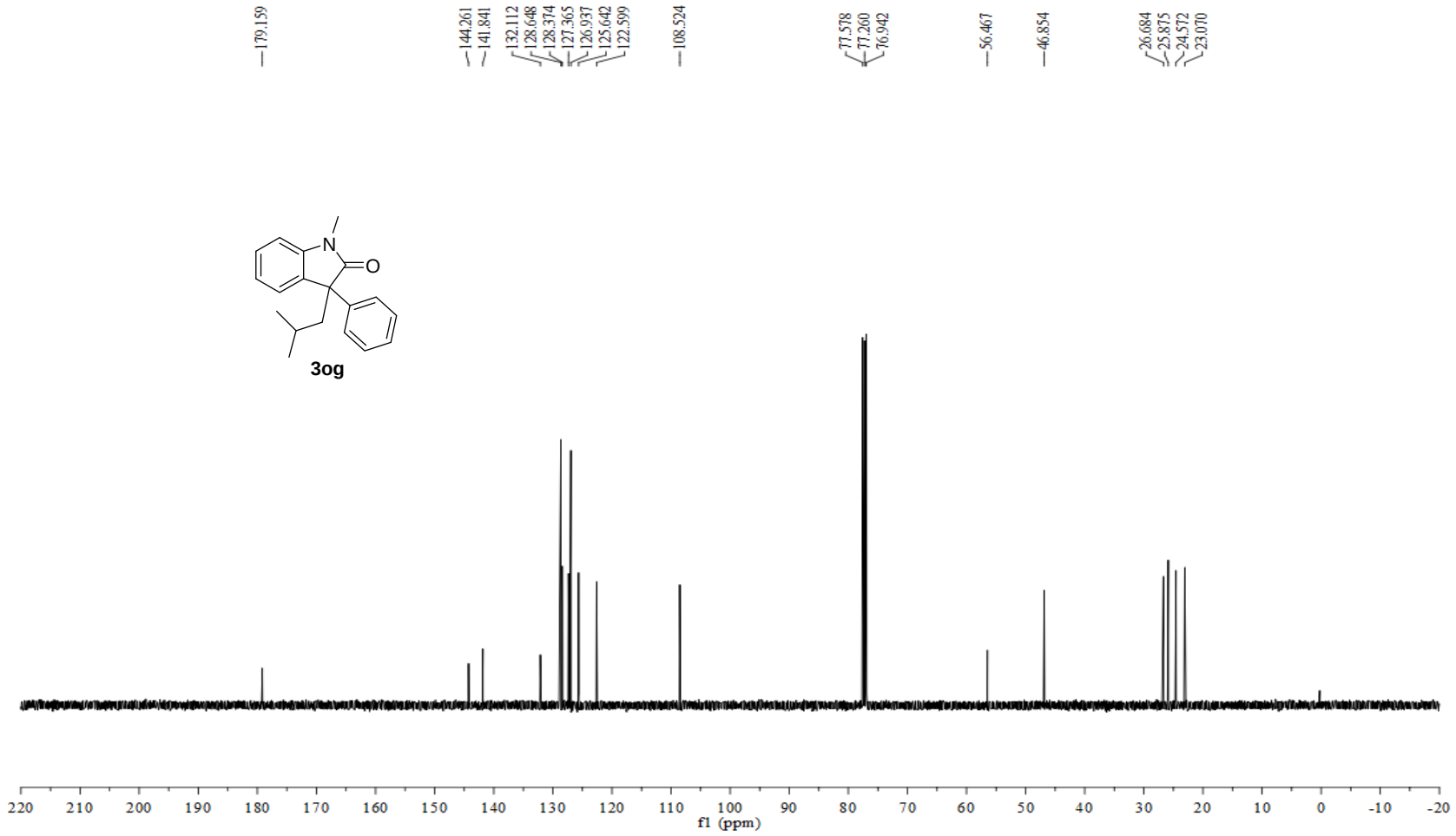

7.271
7.247
7.243
7.221
7.196
7.192
7.172
7.168
7.146
7.049
7.028
7.003
4.752
4.728
4.705
4.681
4.658
4.634
4.611
1.974
1.948
1.928
1.902
1.766
1.748
1.719
1.701
1.485
1.479
1.461
1.455
1.297
1.261
1.240
1.222
1.199
0.685
0.663
0.611
0.589
N
O
3mg
9
8
7
6
5
4
3
2
1
0
–1
ppm
2.06
2.00
1.00
1.05
1.12
3.07
3.06
4.20
3.00
3.03

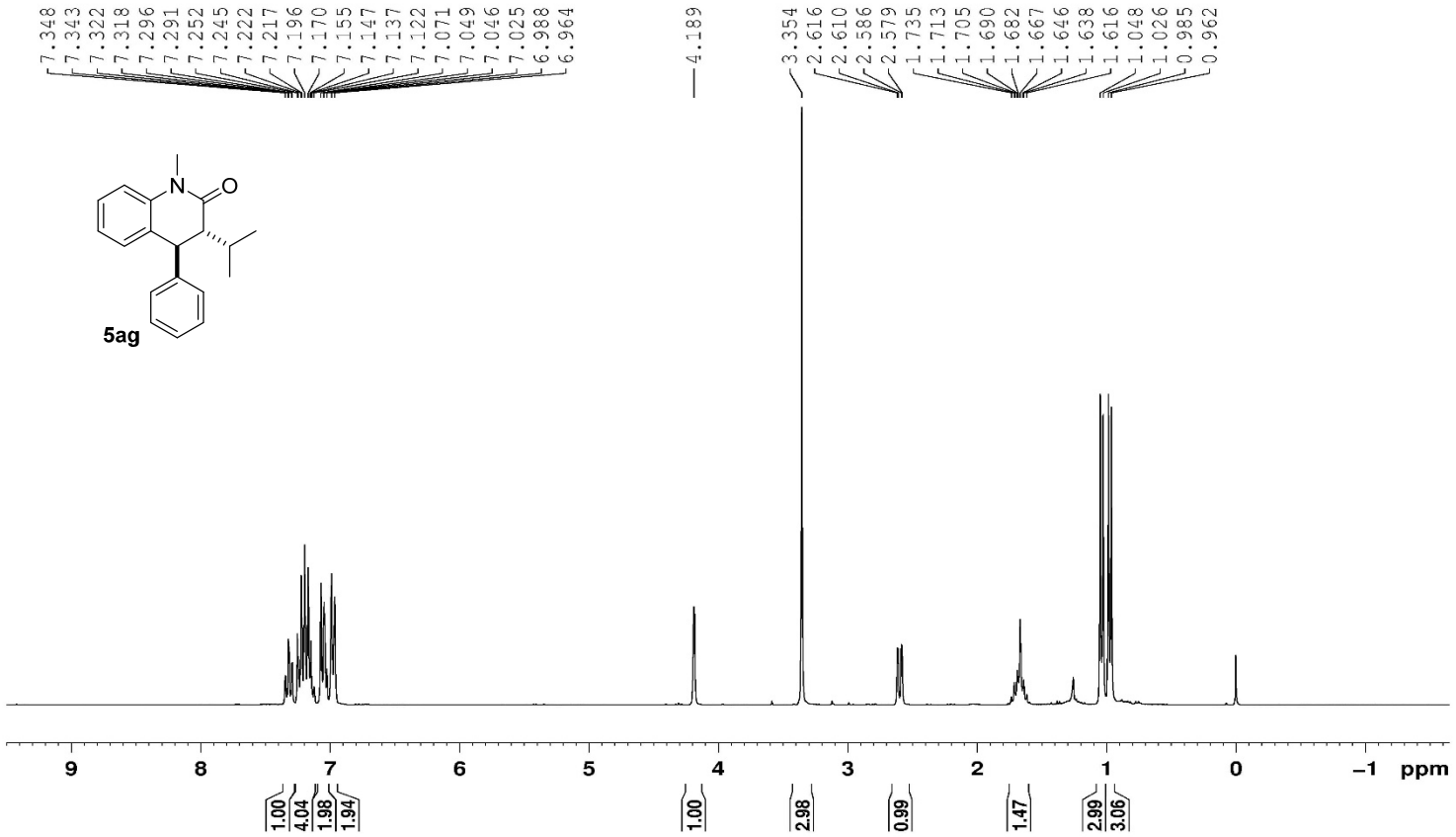

175.729
136.856
129.849
122.303
118.152
116.792
104.870
72.584
72.159
71.736
42.751
41.826
38.426
21.640
20.624
19.104
17.953
14.457
14.250
N
O
3mg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

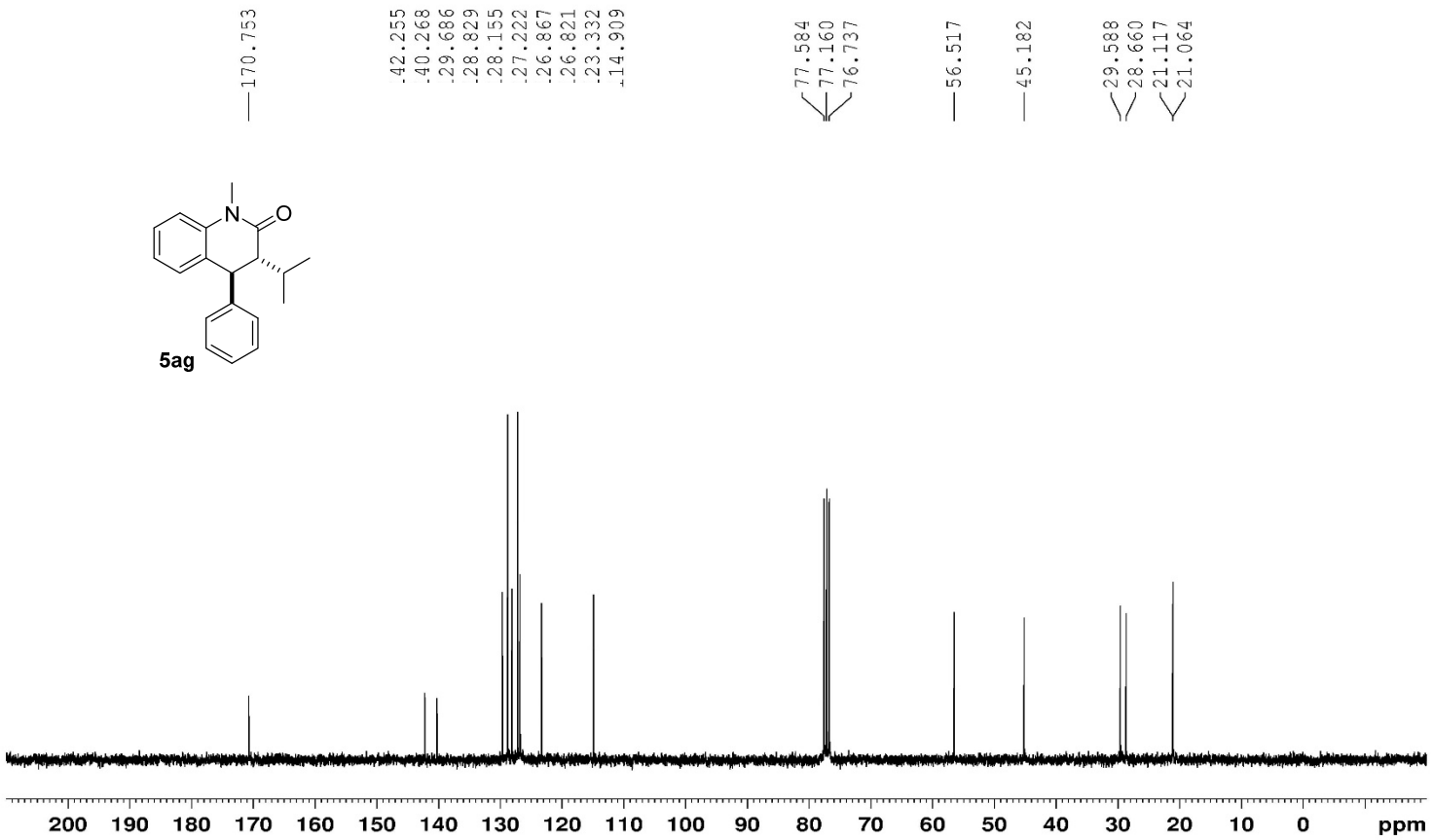

8.261
8.235
7.335
7.329
7.312
7.306
7.286
7.279
7.264
7.241
7.216
7.197
7.193
7.173
2.688
2.020
1.993
1.973
1.946
1.849
1.831
1.802
1.785
1.393
1.335
1.313
1.291
1.269
1.256
0.685
0.663
0.654
0.631
O
N
O
3ng
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.97
3.21
3.00
1.08
1.05
3.06
1.18
6.10

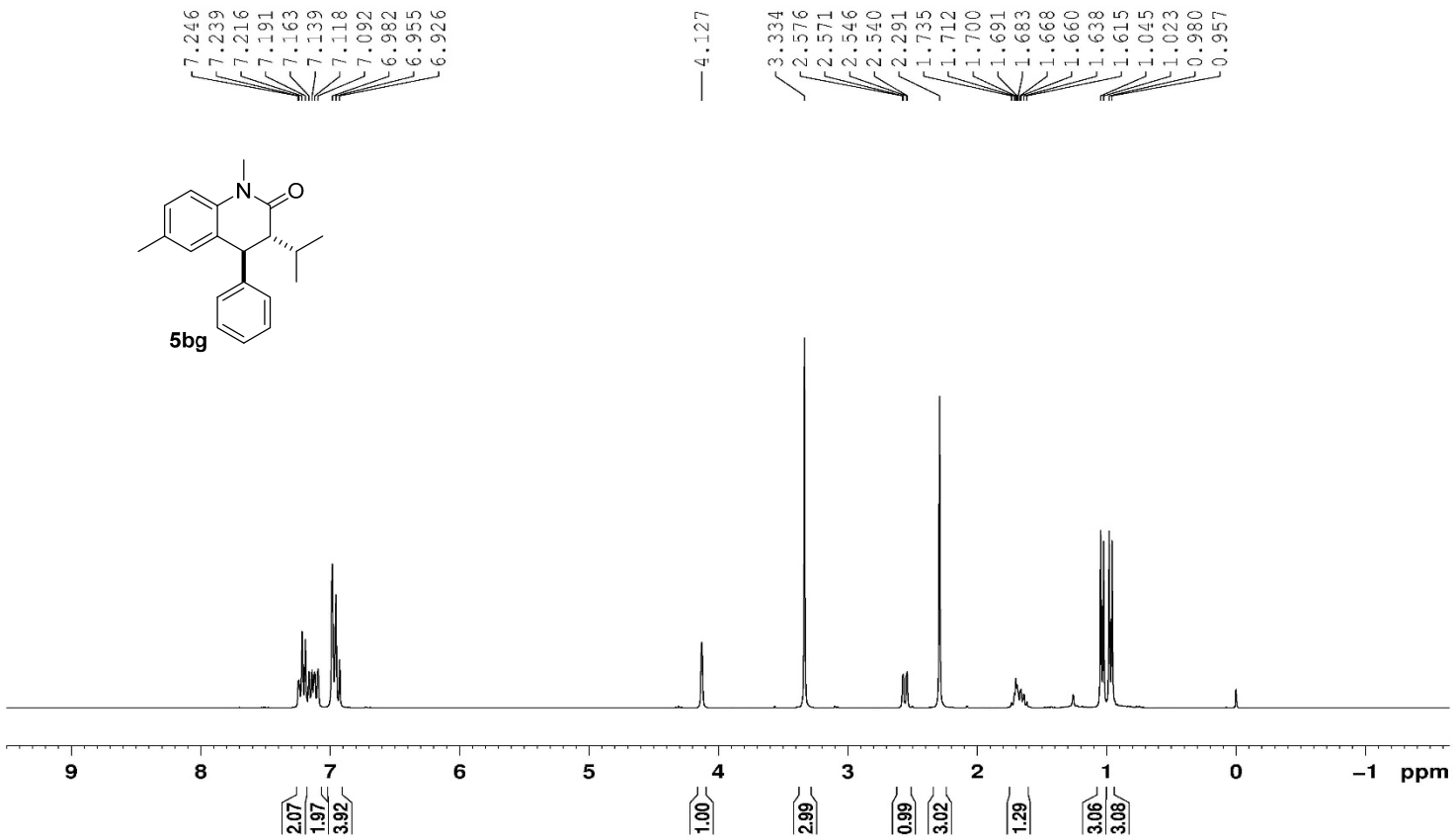

182.146
171.254
139.439
133.202
128.159
125.281
122.716
116.760
77.584
77.160
76.737
48.646
47.756
27.448
26.886
25.667
24.168
22.980
O
N
O
3ng
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

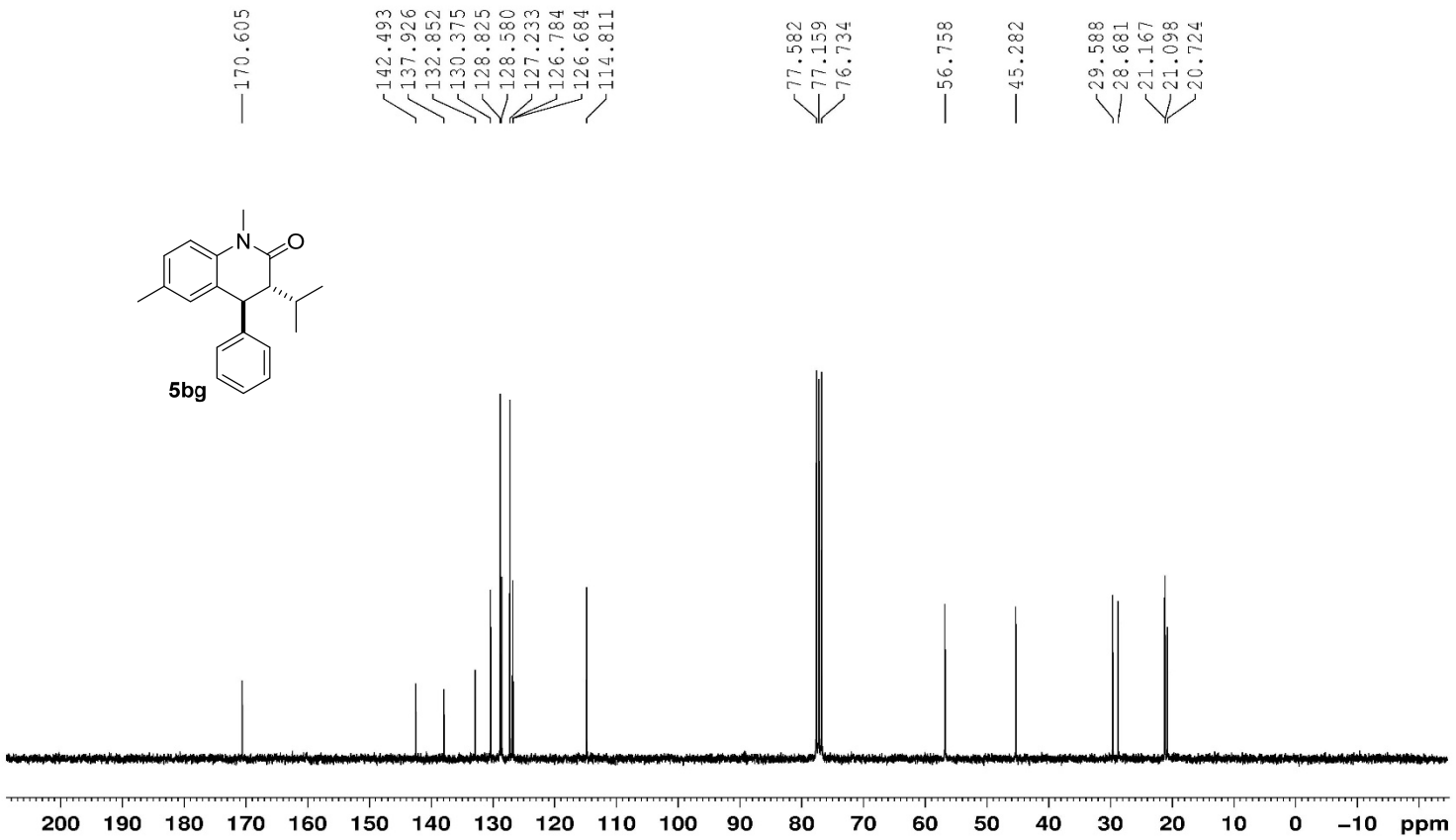

7.375
7.357
7.342
7.323
7.280
7.262
7.257
7.241
7.222
7.205
7.187
7.146
7.128
7.110
6.918
6.899
3.206
2.467
2.448
2.433
2.414
2.196
2.184
2.162
2.149
1.418
1.402
1.386
1.370
0.736
0.719
0.685
0.669
N
O
3og
f1 (ppm)
2.91
4.09
0.99
0.92
3.00
0.99
0.99
0.95
3.07
3.10

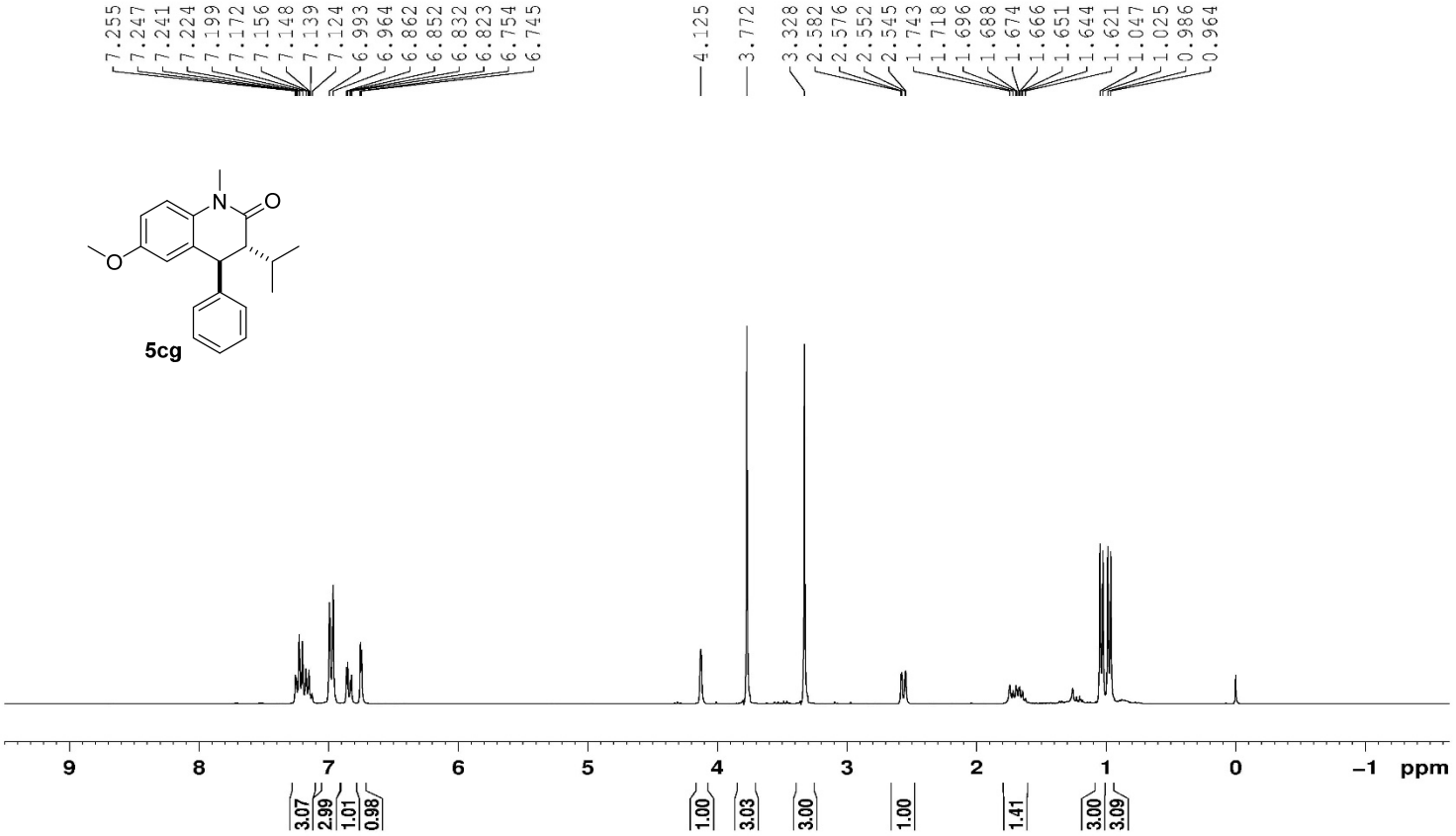

179.159
144.261
141.841
132.112
128.648
128.374
127.365
126.937
125.642
122.599
108.524
77.578
77.260
76.942
56.467
46.854
26.684
25.875
24.572
23.070
N
O
3og
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

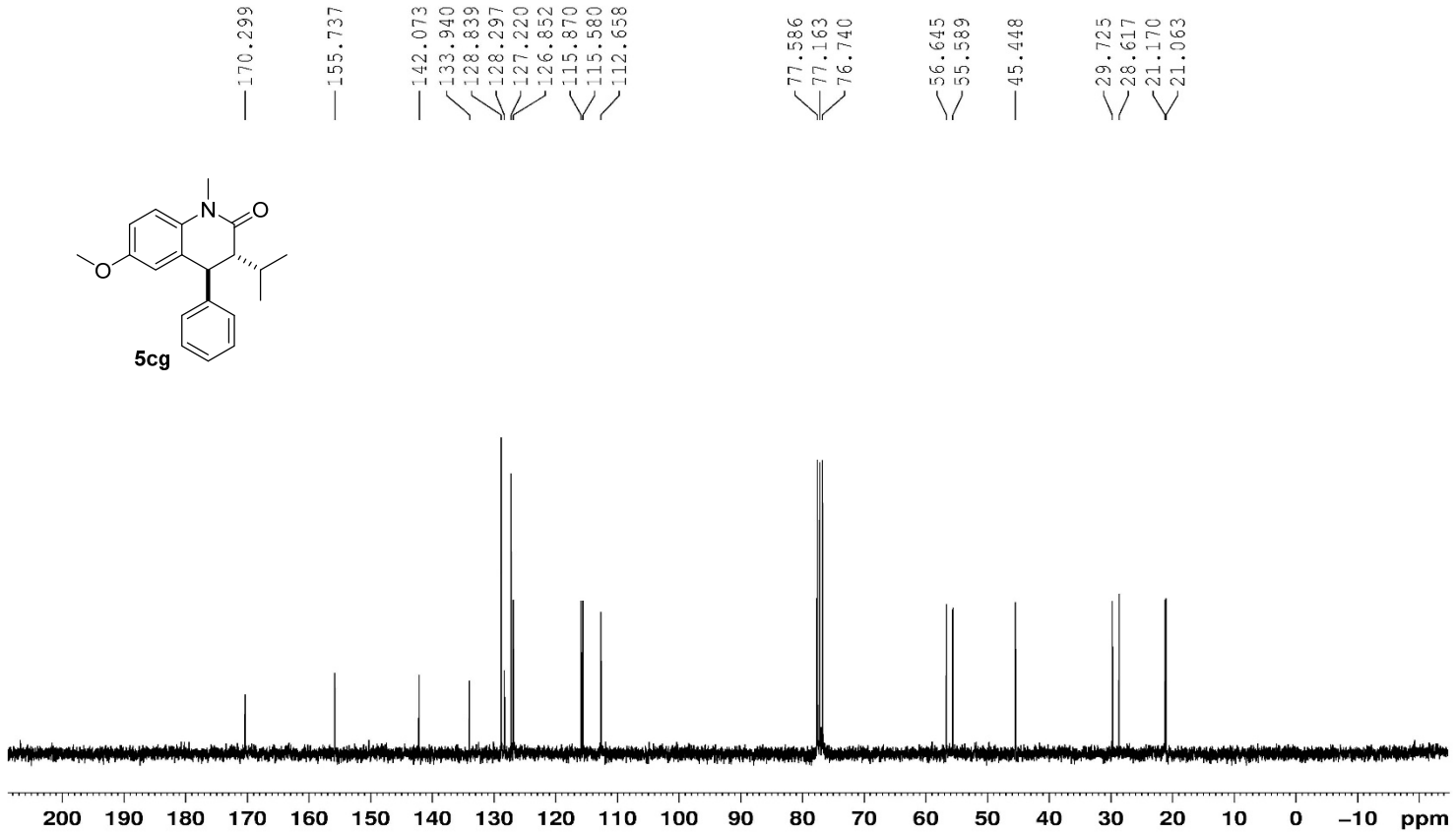

7.348
7.343
7.322
7.318
7.296
7.291
7.252
7.245
7.222
7.217
7.196
7.170
7.155
7.147
7.137
7.122
7.071
7.049
7.046
7.025
6.988
6.964
4.189
3.354
2.616
2.610
2.586
2.579
1.735
1.713
1.705
1.690
1.682
1.667
1.646
1.638
1.616
1.048
1.026
0.985
0.962
N
O
5ag
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
4.04
1.98
1.94
1.00
2.98
0.99
1.47
2.99
3.06

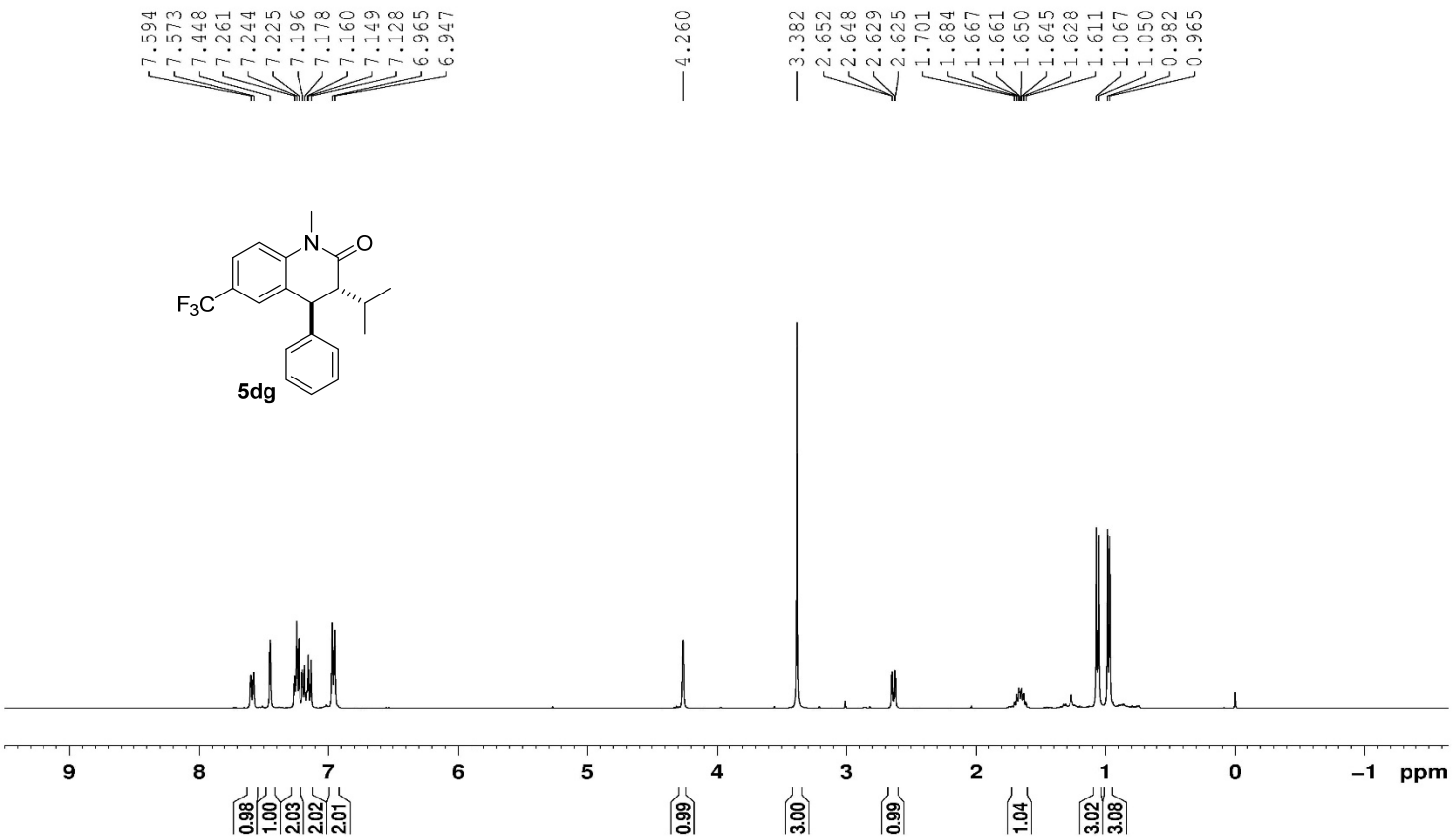

170.753
42.255
40.268
29.686
28.829
28.155
27.222
26.867
26.821
23.332
14.909
77.584
77.160
76.737
56.517
45.182
29.588
28.660
21.117
21.064
N
O
5ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

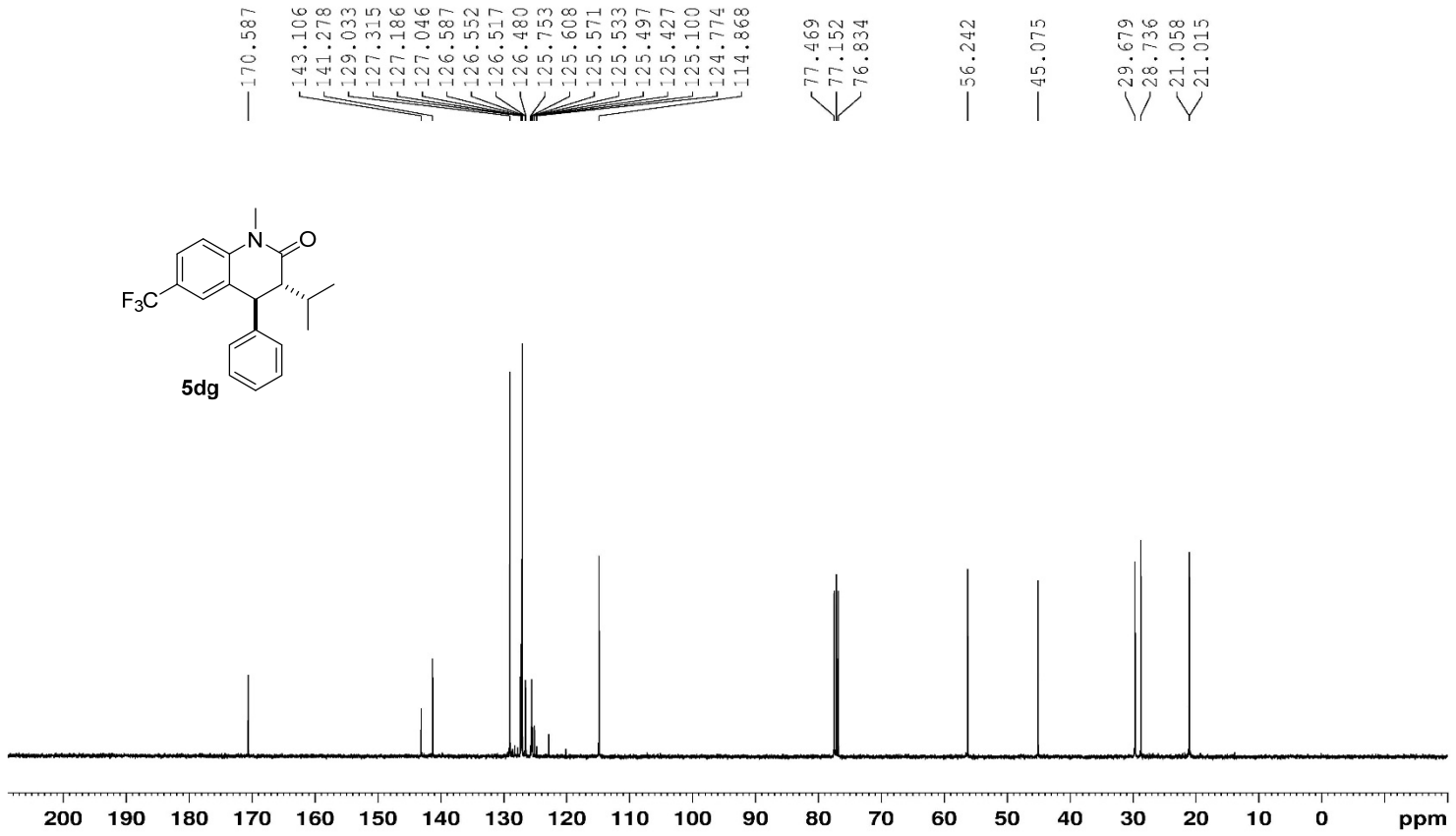

7.246
7.239
7.216
7.191
7.163
7.139
7.118
7.092
6.982
6.955
6.926
4.127
3.334
2.576
2.571
2.546
2.540
2.291
1.735
1.712
1.700
1.691
1.683
1.668
1.660
1.638
1.615
1.045
1.023
0.980
0.957
N
O
5bg
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.07
1.97
3.92
1.00
2.99
0.99
3.02
1.29
3.06
3.08

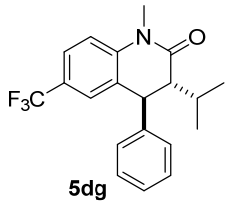

170.605
142.493
137.926
132.852
130.375
128.825
128.580
127.233
126.784
126.684
114.811
77.582
77.159
76.734
56.758
45.282
29.588
28.681
21.167
21.098
20.724
N
O
5bg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm


7.255
7.247
7.241
7.224
7.199
7.172
7.156
7.148
7.139
7.124
6.993
6.964
6.862
6.852
6.832
6.823
6.754
6.745
4.125
3.772
3.328
2.582
2.576
2.552
2.545
1.743
1.718
1.696
1.688
1.674
1.666
1.651
1.644
1.621
1.047
1.025
0.986
0.964
N
O
O
5cg
9
8
7
6
5
4
3
2
1
0
−1
ppm
3.07
2.99
1.01
0.98
1.00
3.03
3.00
1.00
1.41
3.00
3.09


170.299
155.737
142.073
133.940
128.839
128.297
127.220
126.852
115.870
115.580
112.658
77.586
77.163
76.740
56.645
55.589
45.448
29.725
28.617
21.170
21.063
N
O
O
5cg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

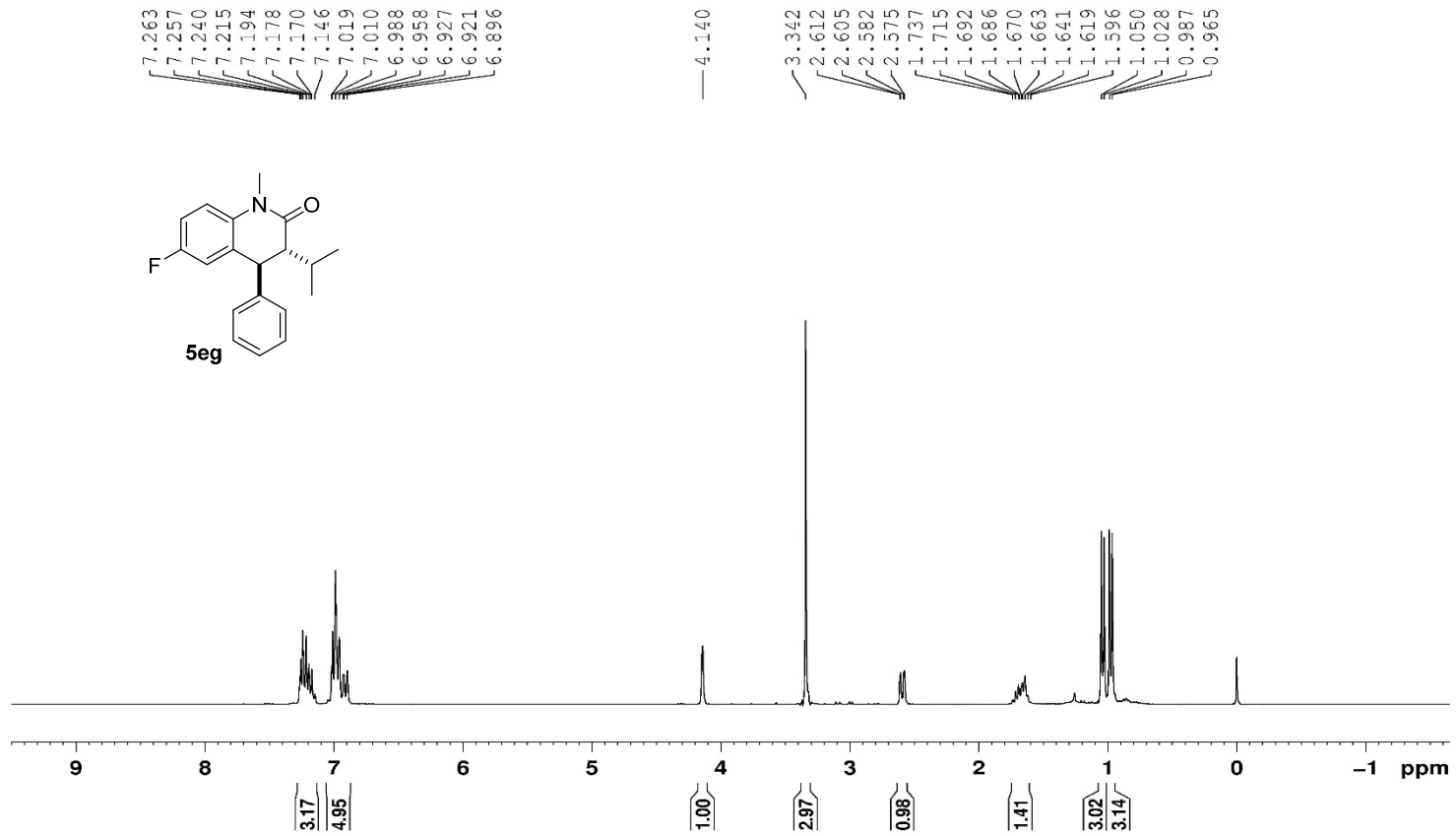

7.594
7.573
7.448
7.261
7.244
7.225
7.196
7.178
7.160
7.149
7.128
6.965
6.947
4.260
3.382
2.652
2.648
2.629
2.625
1.701
1.684
1.667
1.661
1.650
1.645
1.628
1.611
1.067
1.050
0.982
0.965
N
O
F3C
5dg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.98
1.00
2.03
2.02
2.01
0.99
3.00
0.99
1.04
3.02
3.08

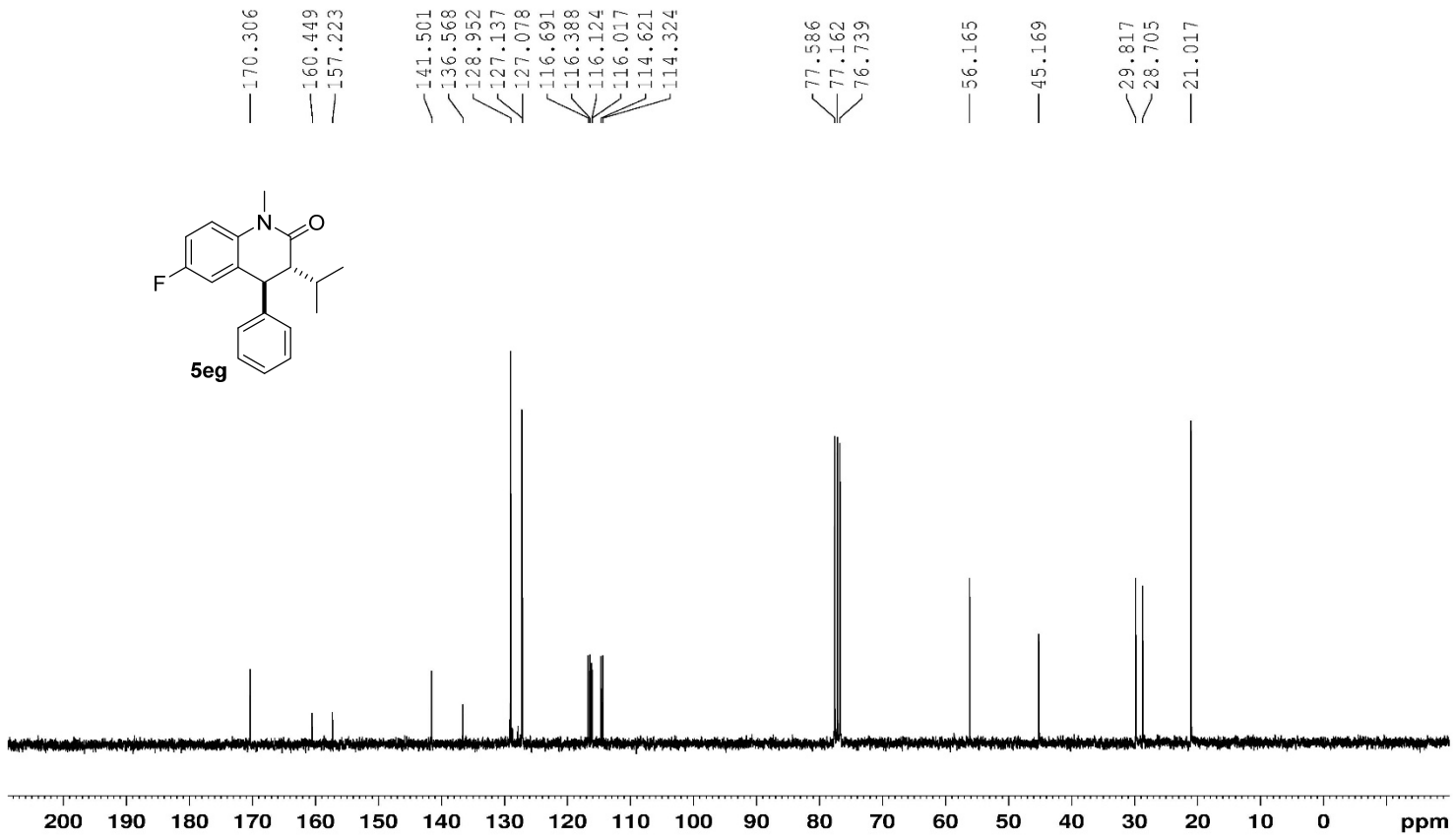

170.587
143.106
141.278
129.033
127.315
127.186
127.046
126.587
126.552
126.517
126.480
125.753
125.608
125.571
125.533
125.497
125.427
125.100
124.774
114.868
77.469
77.152
76.834
56.242
45.075
29.679
28.736
21.058
21.015
N
O
F3C
5dg
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

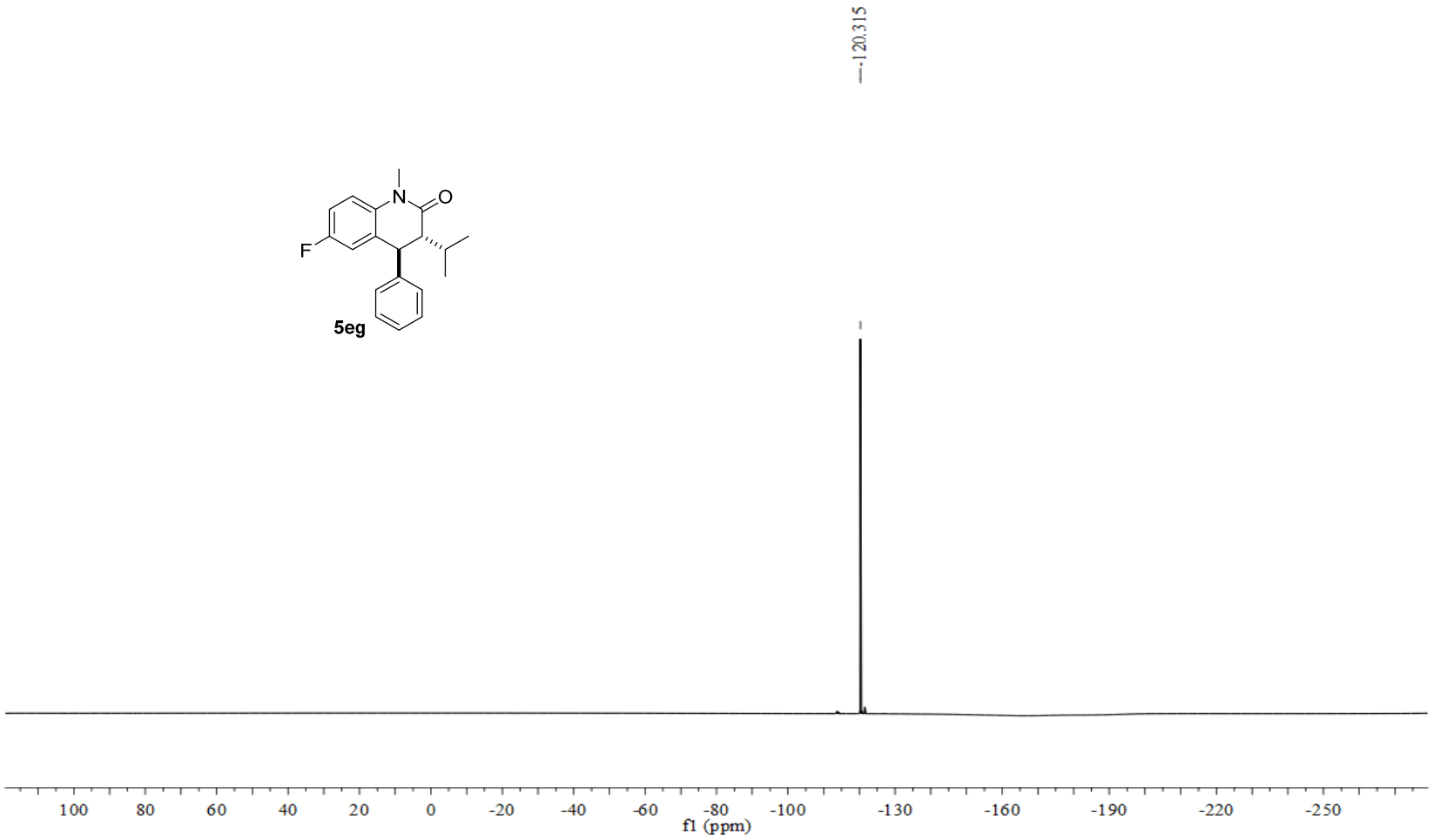

N
O
F3C

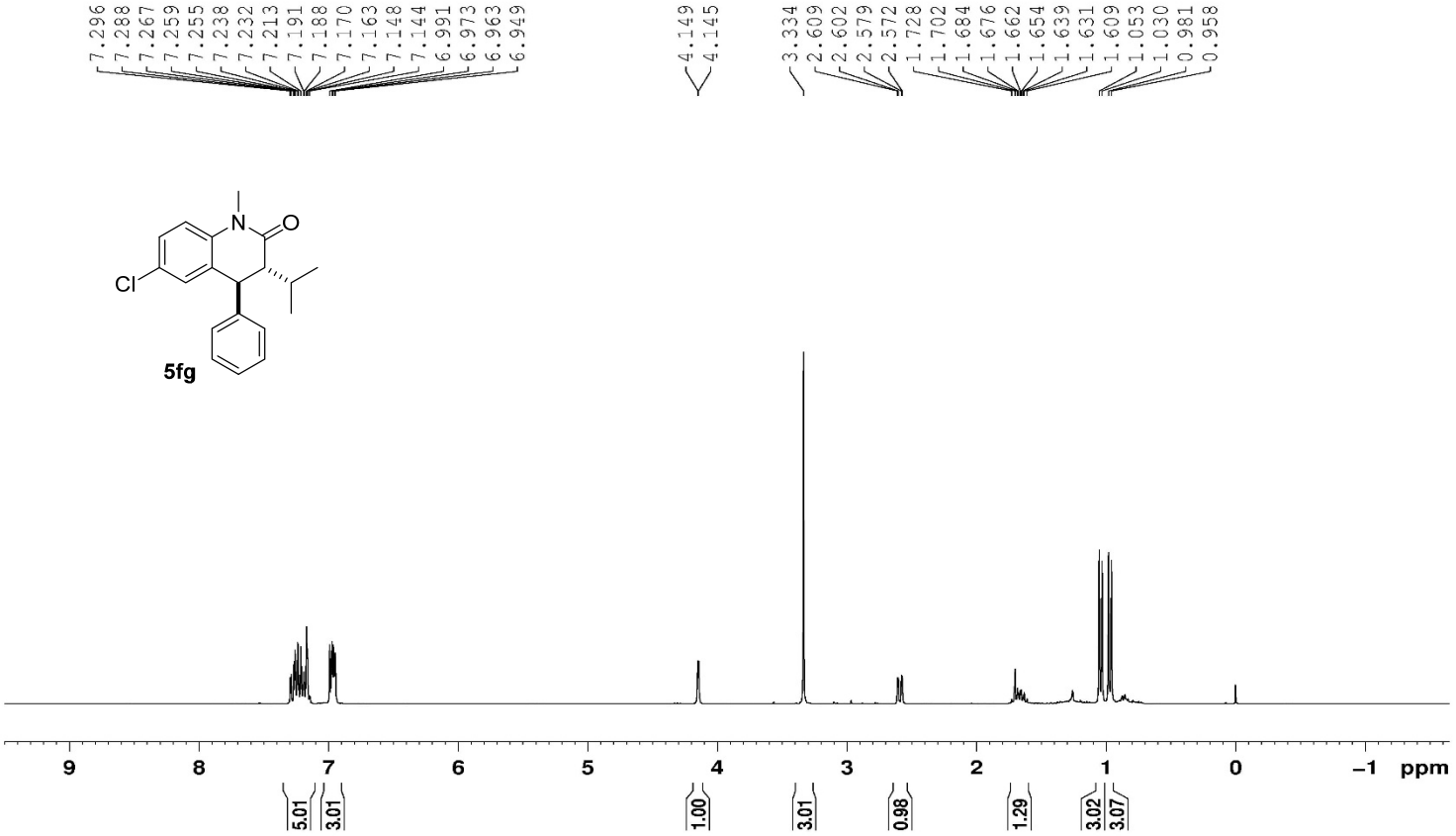
5dg

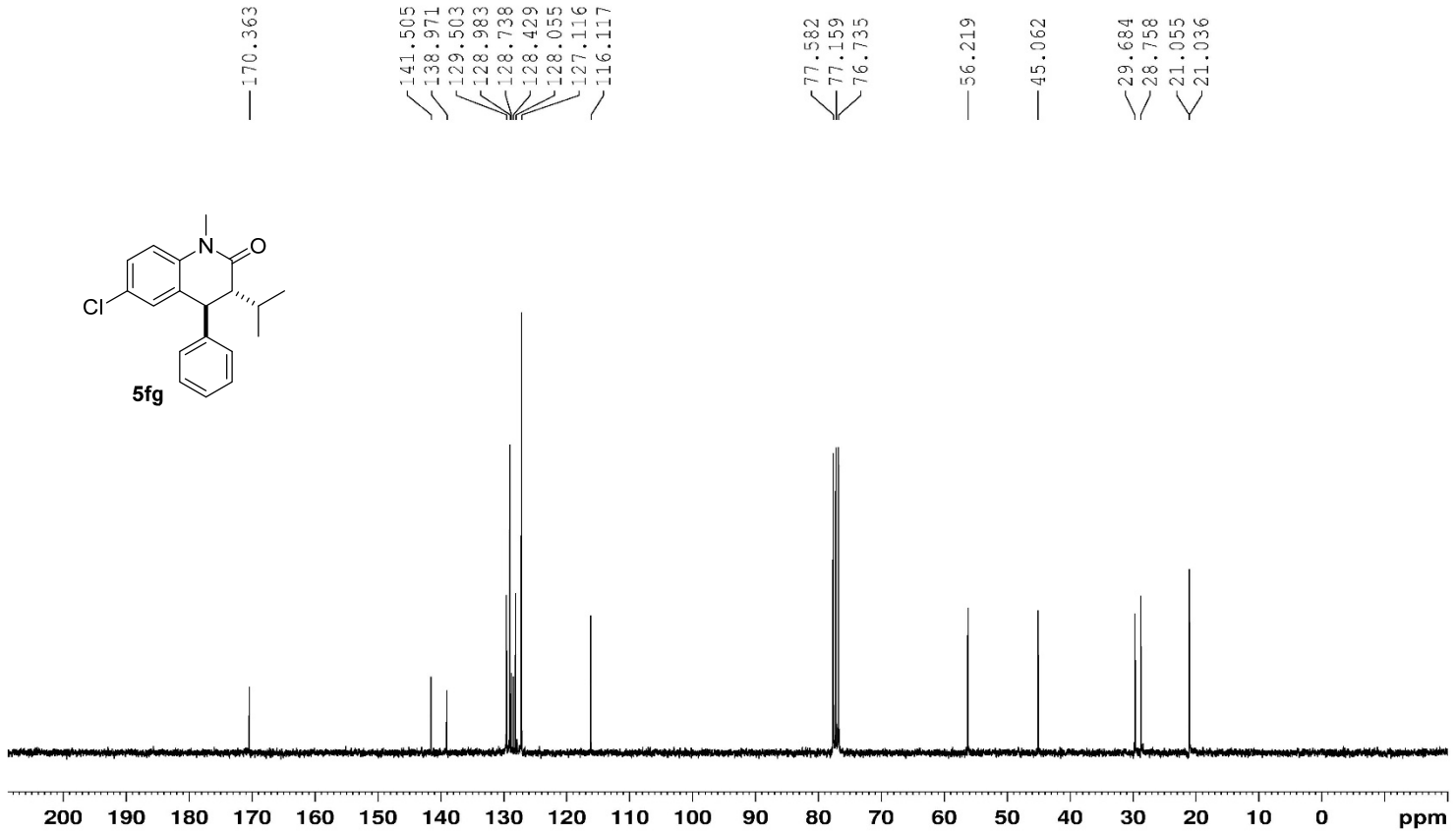
-61.839
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
f1 (ppm)

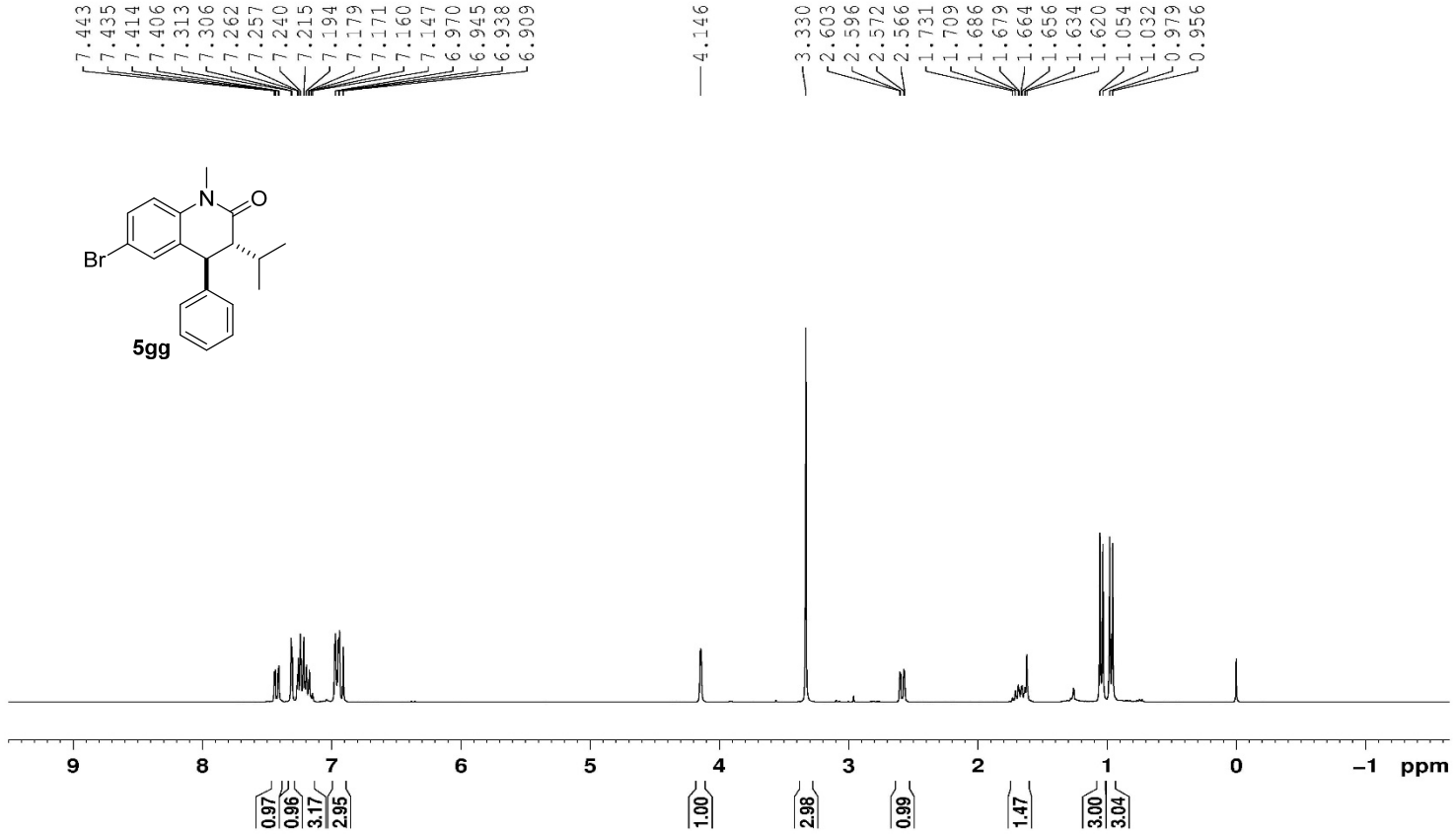

7.263
7.257
7.240
7.215
7.194
7.178
7.170
7.146
7.019
7.010
6.988
6.958
6.927
6.921
6.896
4.140
3.342
2.612
2.605
2.582
2.575
1.737
1.715
1.692
1.686
1.670
1.663
1.641
1.619
1.596
1.050
1.028
0.987
0.965
N
O
F
5eg
9
8
7
6
5
4
3
2
1
0
−1
ppm
3.17
4.95
1.00
2.97
0.98
1.41
3.02
3.14

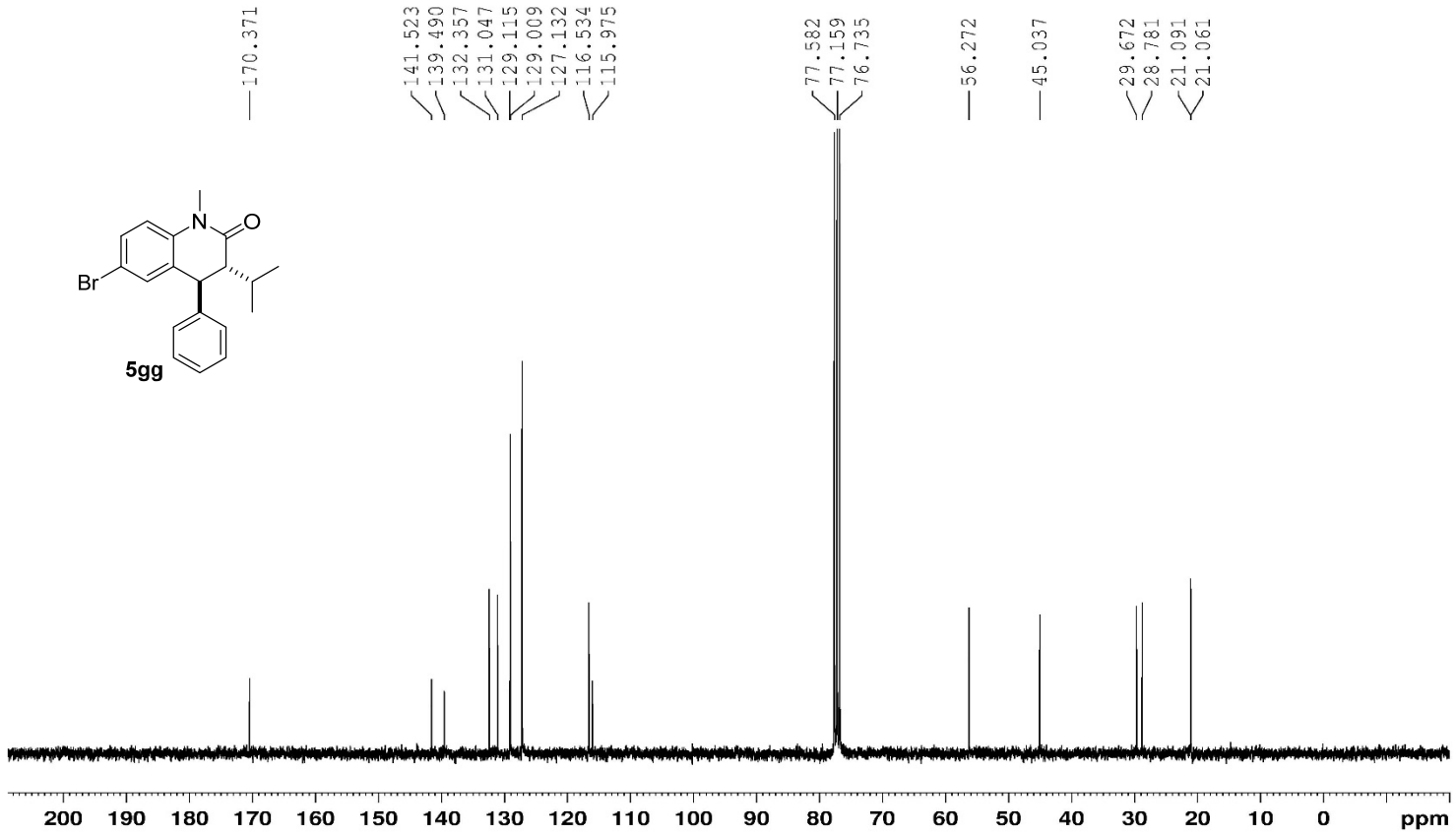

170.306
160.449
157.223
141.501
136.568
128.952
127.137
127.078
116.691
116.388
116.124
116.017
114.621
114.324
77.586
77.162
76.739
56.165
45.169
29.817
28.705
21.017
N
O
F
5eg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

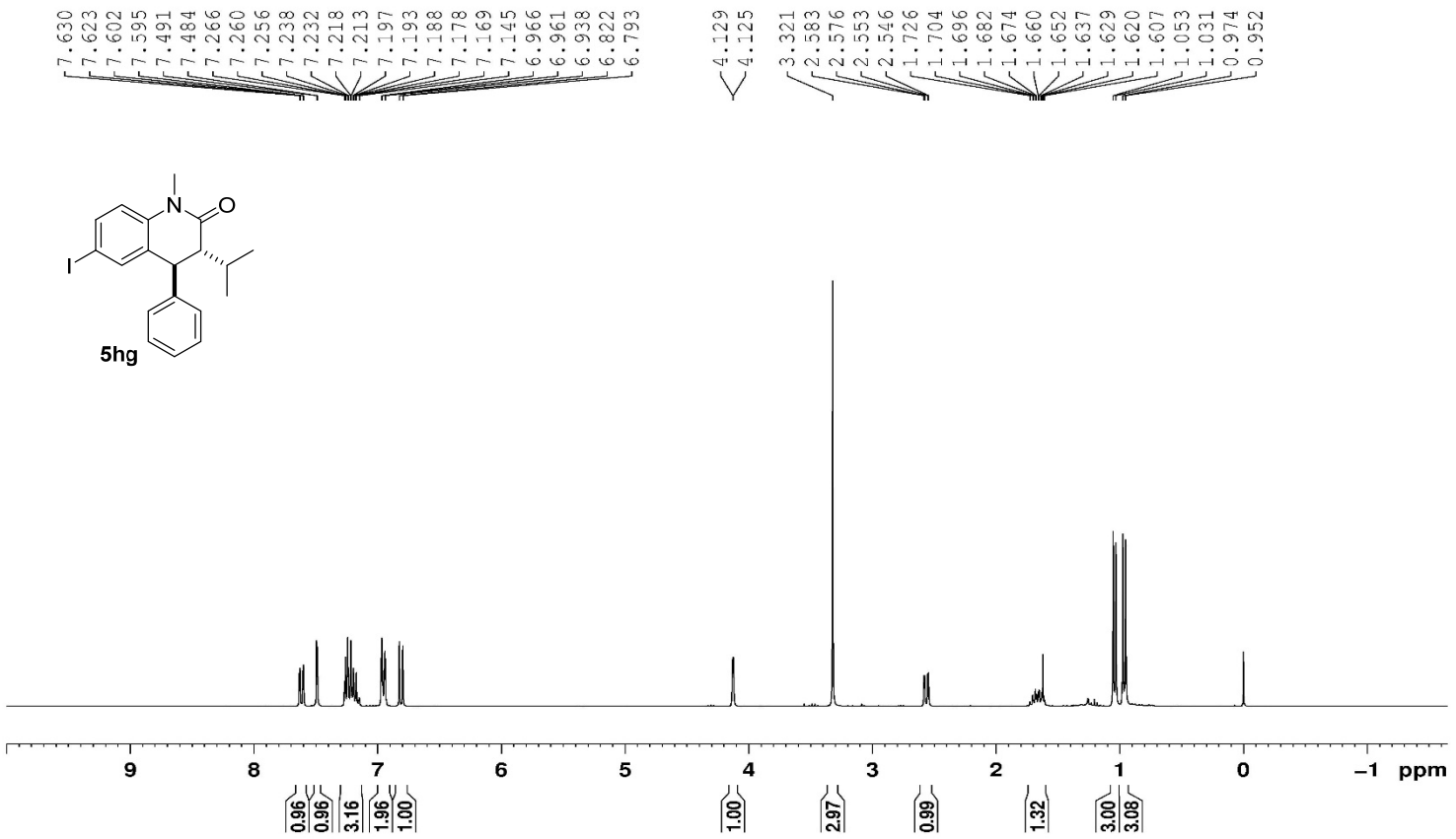

-120.315
N
O
F
5eg
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
f1 (ppm)

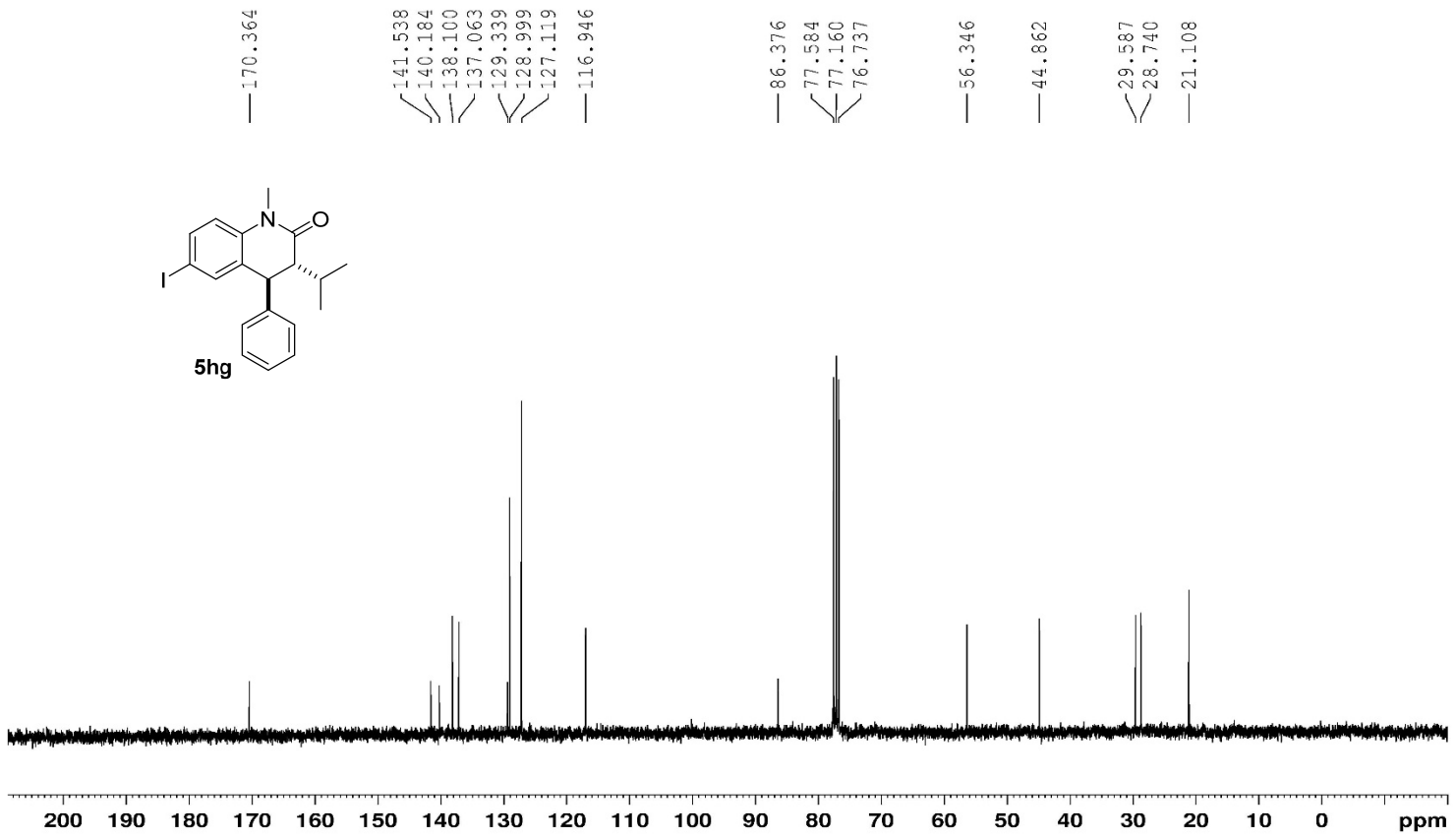

7.296
7.288
7.267
7.259
7.255
7.238
7.232
7.213
7.191
7.188
7.170
7.163
7.148
7.144
6.991
6.973
6.963
6.949
4.149
4.145
3.334
2.609
2.602
2.579
2.572
1.728
1.702
1.684
1.676
1.662
1.654
1.639
1.631
1.609
1.053
1.030
0.981
0.958
N
O
Cl
5fg
9
8
7
6
5
4
3
2
1
0
−1
ppm
5.01
3.01
1.00
3.01
0.98
1.29
3.02
3.07

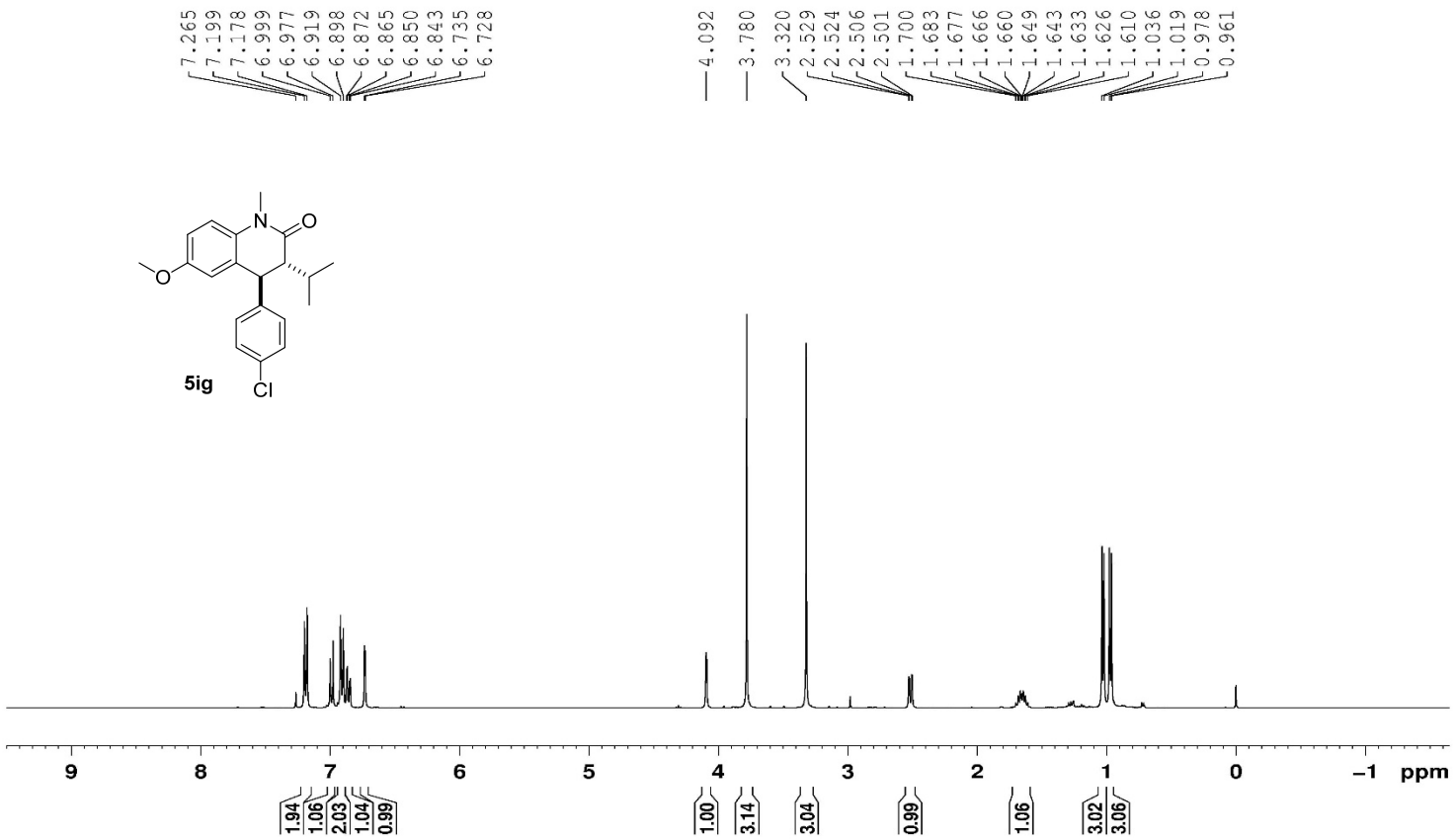

170.363
141.505
138.971
129.503
128.983
128.738
128.429
128.055
127.116
116.117
77.582
77.159
76.735
56.219
45.062
29.684
28.758
21.055
21.036
N
O
Cl
5fg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

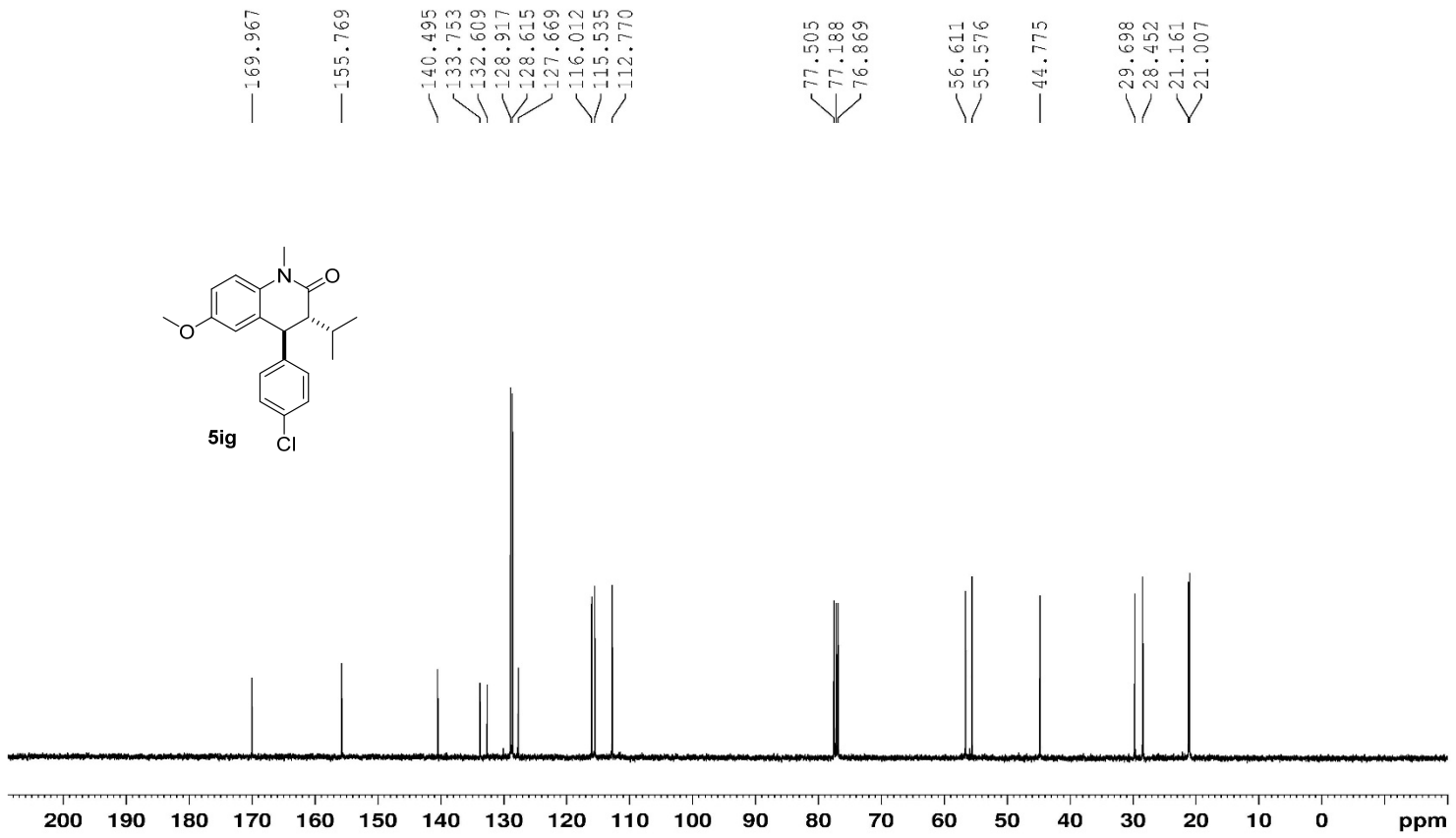

7.443
7.435
7.414
7.406
7.313
7.306
7.262
7.257
7.240
7.215
7.194
7.179
7.171
7.160
7.147
6.970
6.945
6.938
6.909
4.146
3.330
2.603
2.596
2.572
2.566
1.731
1.709
1.686
1.679
1.664
1.656
1.634
1.620
1.054
1.032
0.979
0.956
N
O
Br
5gg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.97
0.96
3.17
2.95
1.00
2.98
0.99
1.47
3.00
3.04

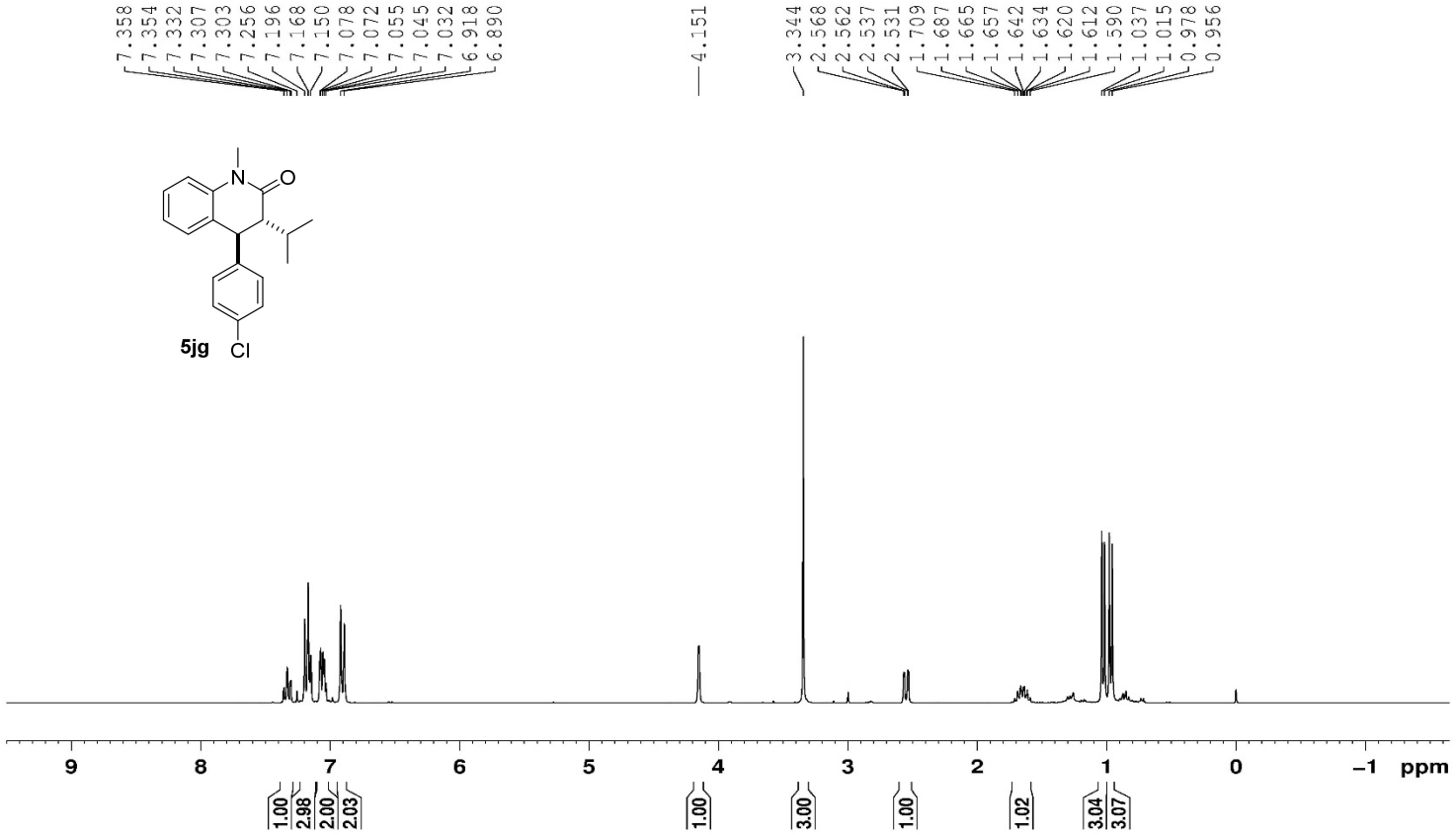

170.371
141.523
139.490
132.357
131.047
129.115
129.009
127.132
116.534
115.975
77.582
77.159
76.735
56.272
45.037
29.672
28.781
21.091
21.061
N
O
Br
5gg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

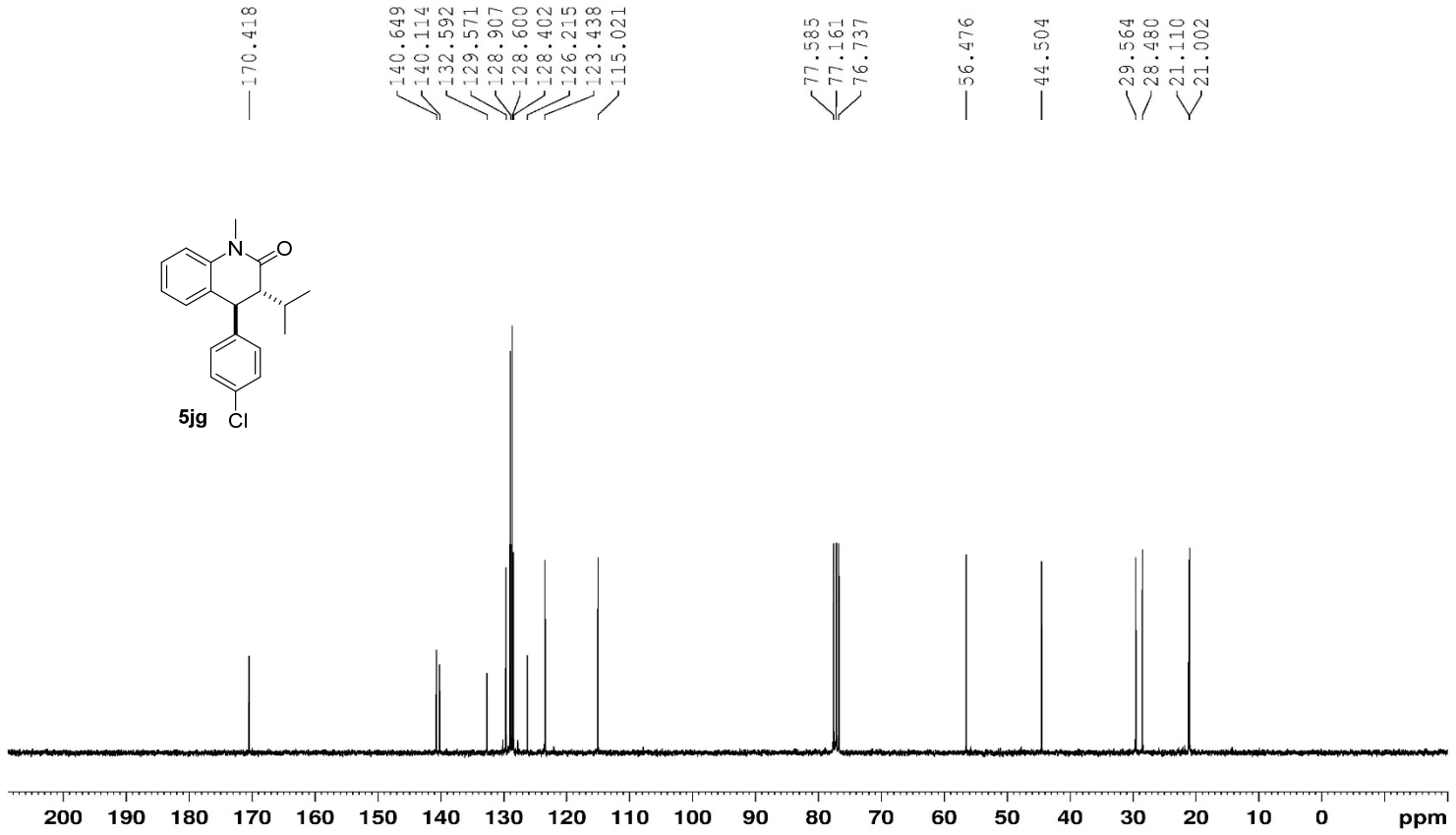

7.630
7.623
7.602
7.595
7.491
7.484
7.266
7.260
7.256
7.238
7.232
7.218
7.213
7.197
7.193
7.188
7.178
7.169
7.145
6.966
6.961
6.938
6.822
6.793
4.129
4.125
3.321
2.583
2.576
2.553
2.546
1.726
1.704
1.696
1.682
1.674
1.660
1.652
1.637
1.629
1.620
1.607
1.053
1.031
0.974
0.952
N
O
I
5hg
9
8
7
6
5
4
3
2
1
0
−1
ppm
0.96
0.96
3.16
1.96
1.00
1.00
2.97
0.99
1.32
3.00
3.08

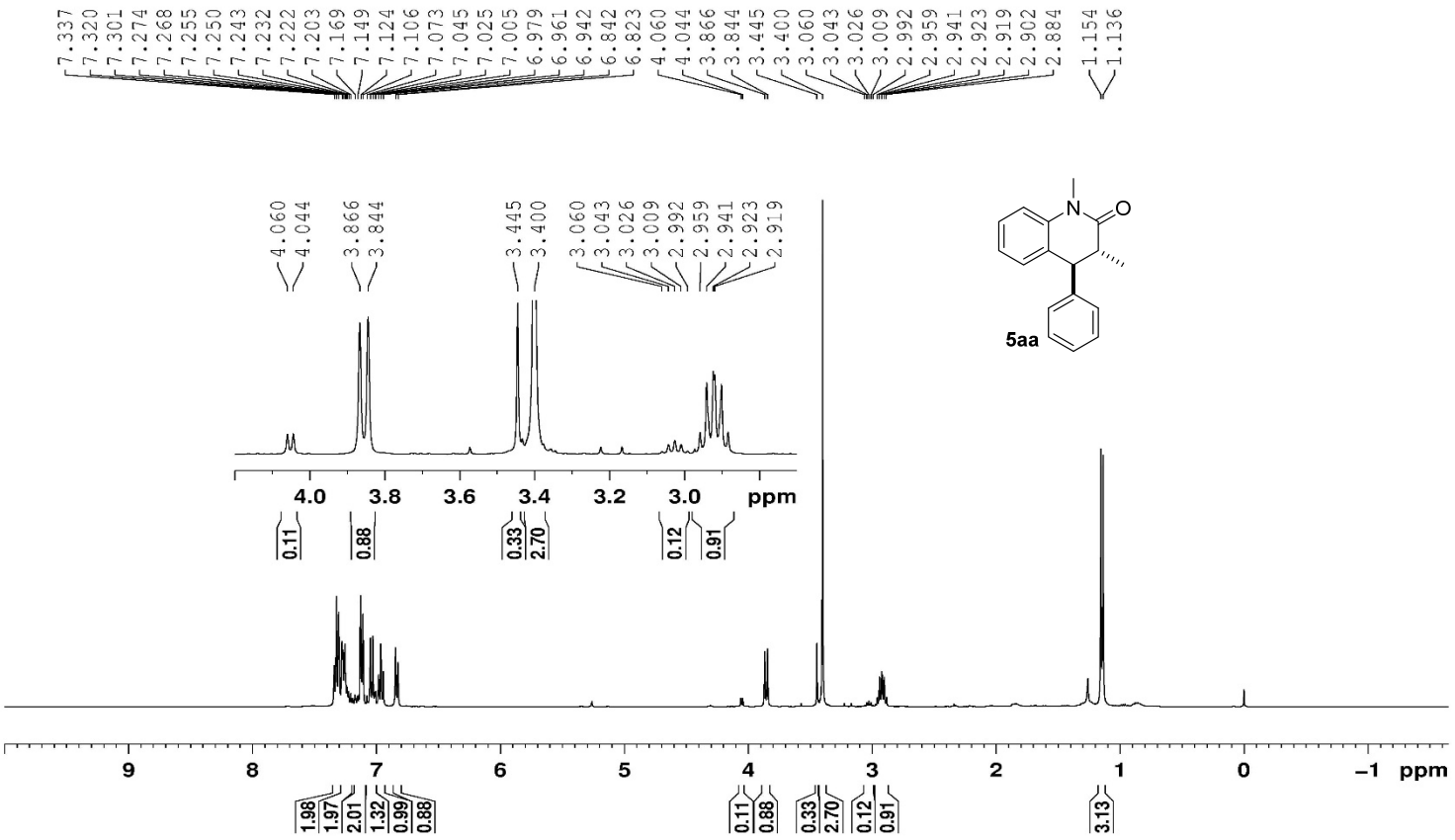

170.364
141.538
140.184
138.100
137.063
129.339
128.999
127.119
116.946
86.376
77.584
77.160
76.737
56.346
44.862
29.587
28.740
21.108
N
O
I
5hg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

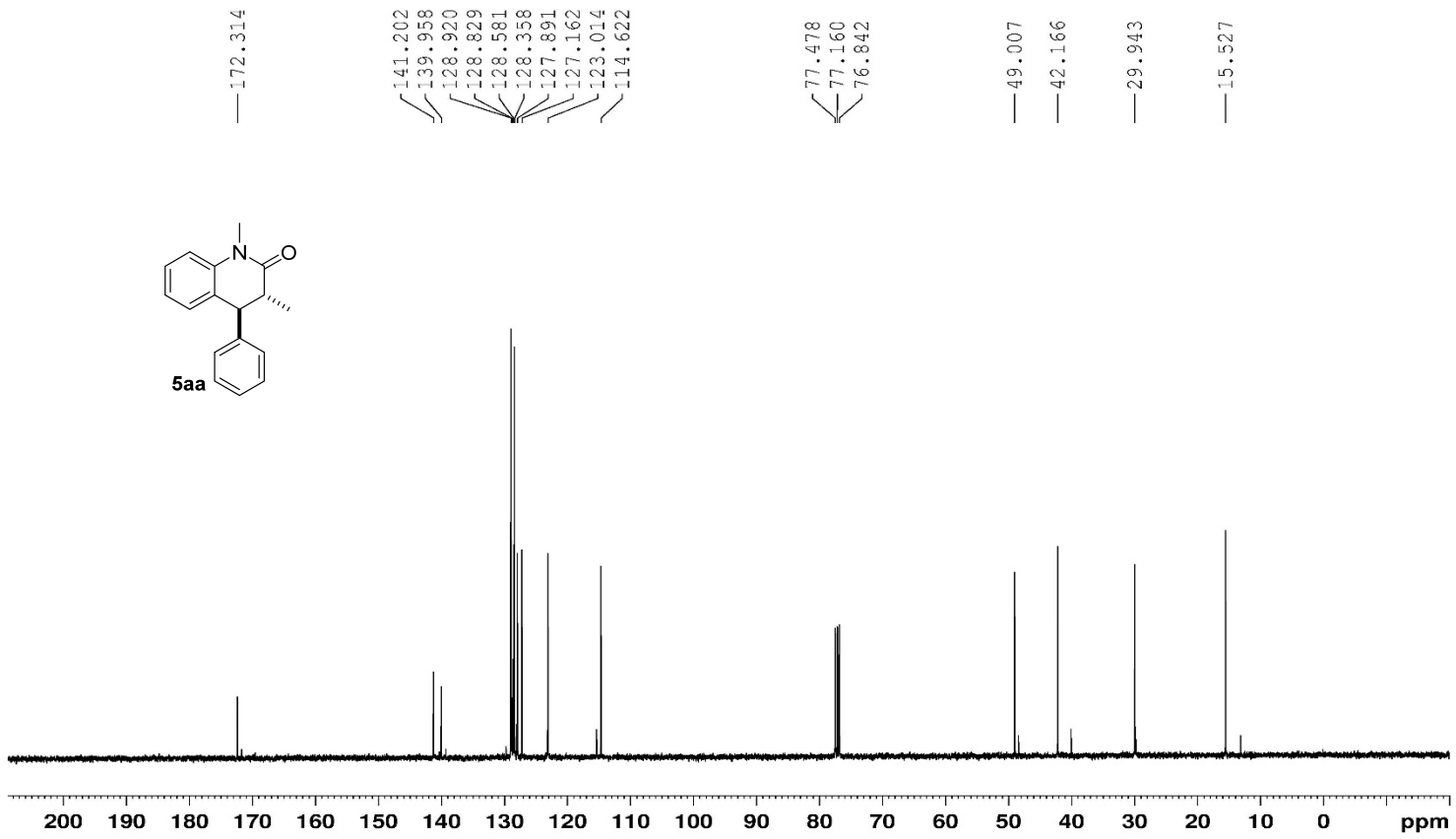

7.265
7.199
7.178
6.999
6.977
6.919
6.898
6.872
6.865
6.850
6.843
6.735
6.728
4.092
3.780
3.320
2.529
2.524
2.506
2.501
1.700
1.683
1.677
1.666
1.660
1.649
1.643
1.633
1.626
1.610
1.036
1.019
0.978
0.961
N
O
O
Cl
5ig
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.94
1.06
2.03
1.04
0.99
1.00
3.14
3.04
0.99
1.06
3.02
3.06

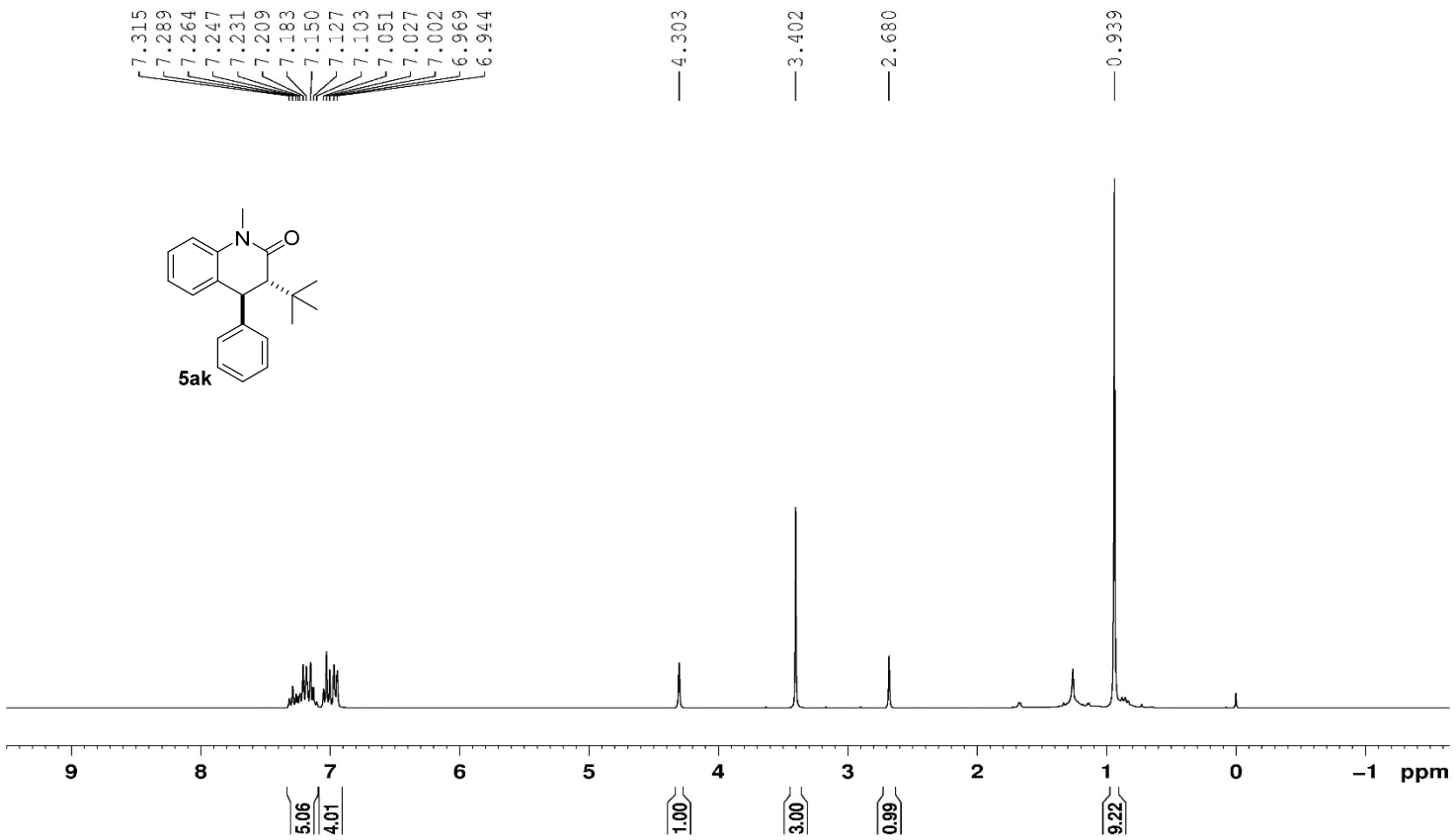

169.967
155.769
140.495
133.753
132.609
128.917
128.615
127.669
116.012
115.535
112.770
77.505
77.188
76.869
56.611
55.576
44.775
29.698
28.452
21.161
21.007
N
O
O
Cl
5ig
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

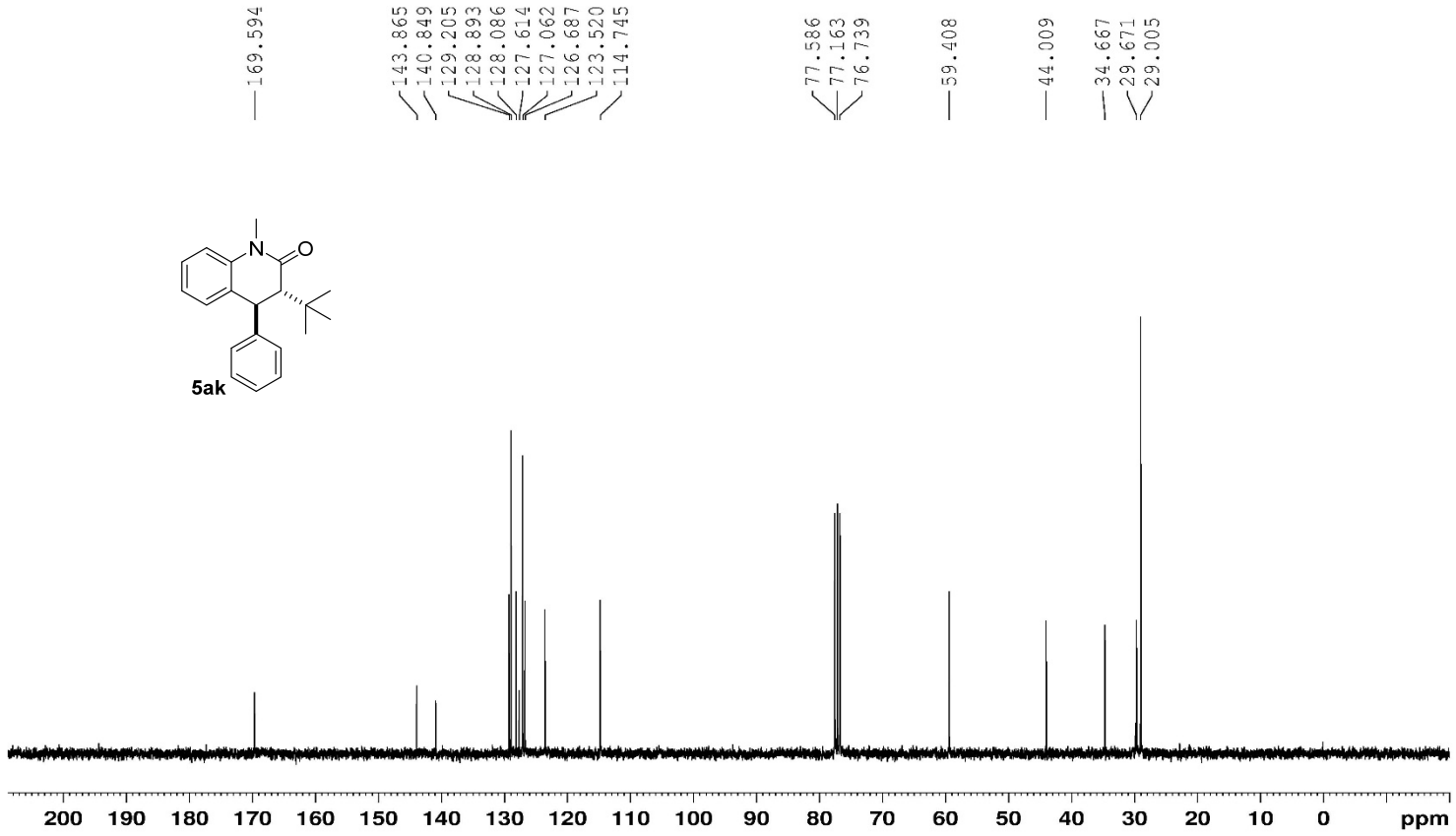

7.358
7.354
7.332
7.307
7.303
7.256
7.196
7.168
7.150
7.078
7.072
7.055
7.045
7.032
6.918
6.890
4.151
3.344
2.568
2.562
2.537
2.531
1.709
1.687
1.665
1.657
1.642
1.634
1.620
1.612
1.590
1.037
1.015
0.978
0.956
N
O
Cl
5jg
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
2.98
2.00
2.03
1.00
3.00
1.00
1.02
3.04
3.07


170.418
140.649
140.114
132.592
129.571
128.907
128.600
128.402
126.215
123.438
115.021
77.585
77.161
76.737
56.476
44.504
29.564
28.480
21.110
21.002
N
O
Cl
5jg
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.337
7.320
7.301
7.274
7.268
7.255
7.250
7.243
7.232
7.222
7.203
7.169
7.149
7.124
7.106
7.073
7.045
7.025
7.005
6.979
6.961
6.942
6.842
6.823
4.060
4.044
3.866
3.844
3.445
3.400
3.060
3.043
3.026
3.009
2.992
2.959
2.941
2.923
2.919
2.902
2.884
1.154
1.136
5aa
ppm
0.11
0.88
0.33
2.70
0.12
0.91
1.98
1.97
2.01
1.32
0.99
0.88
3.13


172.314
141.202
139.958
128.920
128.829
128.581
128.358
127.891
127.162
123.014
114.622
77.478
77.160
76.842
49.007
42.166
29.943
15.527
N
O
5aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.315
7.289
7.264
7.247
7.231
7.209
7.183
7.150
7.127
7.103
7.051
7.027
7.002
6.969
6.944
4.303
3.402
2.680
0.939
N
O
5ak
9
8
7
6
5
4
3
2
1
0
−1
ppm
5.06
4.01
1.00
3.00
0.99
9.22


169.594
143.865
140.849
129.205
128.893
128.086
127.614
127.062
126.687
123.520
114.745
77.586
77.163
76.739
59.408
44.009
34.667
29.671
29.005
N
O
5ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm