Electronic Supplementary Material (ESI) for Dalton Transactions.

A Bezene-bridged Divanadium Complex-Early Transition Metal Catalyst for Alkenes Alkylarylation with $PhI(O_2CR)_2$ *via* Decarboxylation

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1. General Information

All air-sensitive reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. (Nacnac)VCl_2 (**1**) [nacnac$^-$ = $[ArNC(Me)]_2CH$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$],[1] KC_8,[2] (μ-η^6:η^6-C_7H_8)[V(Nacnac)]$_2$ (**2b**),[3] were prepared according to the literature reports. All other commercial available chemicals were used as received unless otherwise noted. 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 spectra were recorded on WIPM-NMR-400, Bruker 300AV or 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). Infrared spectra were recorded in KBr pellets on Thermo Fisher iS50 spectrometer, and elemental analyses were performed using a Vario EL III analyzer. Melting points (M.p.) were measured on an X-6 melting point apparatus and were uncorrected.

2. Substrate Preparation

2.1 Preparation of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$

KC_8 (1.11 g, 8.2 mmol) was added to a C_6H_6 (20 mL) solution of (Nacnac)VCl_2 (**1**; 2.00 g, 3.7 mmol) with stirring at room temperature. After this solution was stirred two days at room temperature, the solvent was removed. The residue was extracted with *n*-hexane (15 mL × 3) and filtered through Celite. The volume of the filtrate was reduced to 15 mL, brown crystals of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ (**2a**) were isolated when this solution was kept at -20 ℃ for three days. Yield: 1.33 g (71%). M.p.: 238-240 ºC (dec.). IR (KBr, cm^{-1}): 2961(m), 2931(m), 2866(m), 1619(m), 1535(m), 1460(m), 1436(m), 1364(m), 1382(m), 1316(m), 1259(s), 1174(m), 1095(s), 1018(s), 797(s). Anal. Calcd for $C_{64}H_{88}N_4V_2$: C, 75.71; H, 8.74, N, 5.52. Found: C, 75.65; H, 8.77, N, 5.55.

Alternatively, we can also obtain the brown crystal of **2a** suitable for single-crystal X-ray diffraction from the benzene solution of **2b**. Catalyst **2a** was unambiguously confirmed by X-ray single-crystal diffraction analysis (**Figure S1**).

Figure S1. X-ray structure of catalyst **2a**

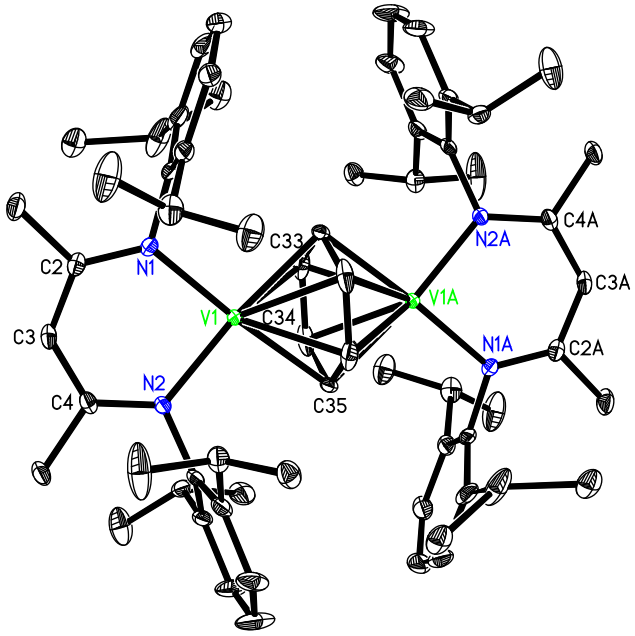


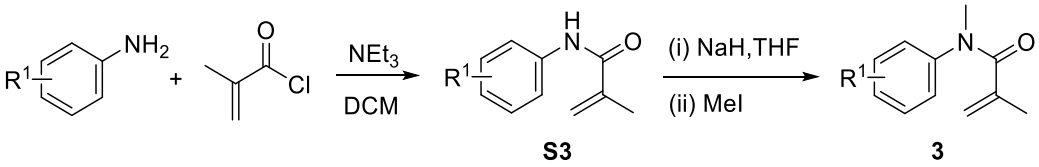
Table S1 Crystal data and experiment parameters for complex **2a**

Compound	**2a**
Formula	$C_{64}H_{88}N_4V_2$
Fw	1015.26
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	14.2394(4)
b (Å)	13.5889(3)
c (Å)	15.0927(4)
α (deg)	90
β (deg)	106.363(3)
γ (deg)	90
V (Å^3)	2802.12(13)
Z	2
ρ_{calc} (g/cm^3)	1.203
μ/mm^{-1}	3.105
radiation	CuKα
size (mm)	0.20 × 0.20 × 0.20
F(000)	1092
2θ range (deg)	3.771 to 71.696
reflns collected	11321
indep. reflns (R_{int})	5383 (0.0291)
data/restr/paras	5383/220/353
abscorr (T_{max}, T_{min})	1.00, 0.93
R	0.044
R_w	0.103
R_{all}	0.049
Gof	1.031
CCDC	2025708

2.2 Preparation of *N*, *N*-disubstituted methacrylmamides

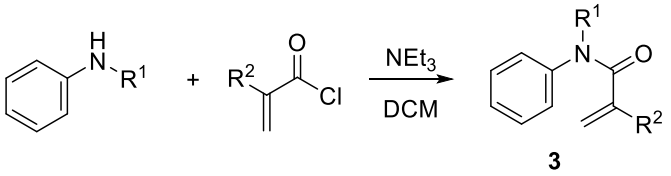
All the substrates **3** were prepared according to the known literature,[4] which are known compounds and their NMR spectral data are in agreement with the literature values.[5]

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 ℃. 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 **S3** (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 ℃. 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 $MgSO_4$. Volatiles were removed in vacuo and the crude mixture purified by column chromatography.

General procedure B for amides synthesis:

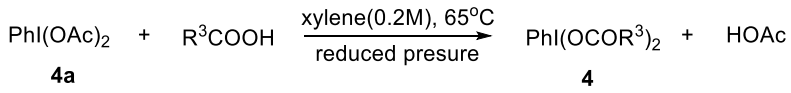


The appropriate acid chloride (1.2 equiv., 6.0 mmol) was added dropwise to a solution of aniline derivative (1.0 equiv, 5.0 mmol) and NEt_3 (1.2 equiv, 6.0 mmol) in

DCM (10.0 mL) at 0 ℃, 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.

2.3 Preparation 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.[6,7]

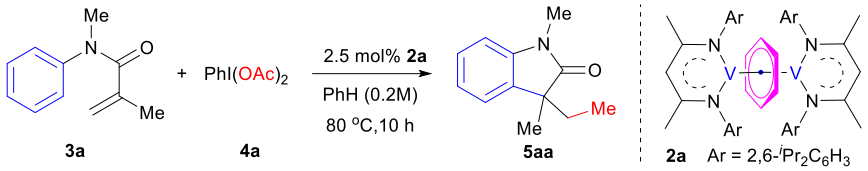


In a typical procedure, $PhI(OAc)_2$ (10 mmol, 1.0 eq.) and indicated acid (22 mmol, 2.2 eq.) were dissolved with xylene (50 mL, 0.2 M) in a round-bottom flask, and then the flask was heated to 65 ℃ with a rotary evaporator under reduced pressure (about 30-50 Torr.) using a diaphragm pump. When the xylene was removed, product **4** 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.

3. V-Catalyzed Alkylarylation of Alkenes to Access Indolinones

3.1 Screening of Reaction Parameters

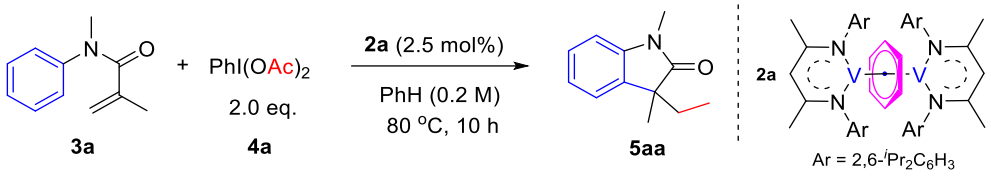
Table S2 Screening of Reaction Parameters[a]



entry	variations of standard conditions	yield of **3ag** (%)[b]
1	**2b** instead of **2a,** and PhMe instead of PhH	58
2	**2b** instead of **2a**	82
2	none	87 (80)[c]
3	**1** instead of **2a**	66
4	5 instead of 2.5 mol% of **2a**	81
5	1.3 instead of 2.5 mol% of **2a**	75
6	Without **2a**	0
7	PhMe instead of PhH	67
8	PhCl instead of PhH	61
9	MeCN instead of PhH	39
10	Et_2O instead of PhH	22
11	THF instead of PhH	27
12	1,4-dioxane instead of PhH	68
13	DME instead of PhH	63
14	MTBE instead of PhH	74
15	6 h instead of 10 h	72
16	12 h instead of 10 h	84
17	0.4 M instead of 0.2 M	71
18	0.1 M instead of 0.2 M	69
19	1.0 instead of 2.0 eq. of **4a**	43
20	3.0 instead of 2.0 eq. of **4a**	87
21	100 °C instead of 80 °C	85
22	50 °C instead of 80 °C	22
23	r.t. instead of 80 °C	0

[a] Reaction conditions: **3a** (0.2 mmol), **4a** (0.4 mmol), **2a** (2.5 mol %), PhH (1.0 mL), 80 °C, 10 h. [b] ^1H NMR yields with 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield on a 0.5 mmol scale.

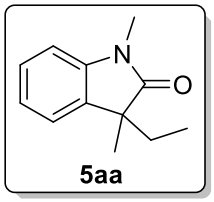
3.2 General Procedure to Access Indolinones



A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(OAc)$_2$ **4a** (378.2 mg, 1.0 mmol) and PhH (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 (80 ℃) for 10 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 **5aa** as colorless oil.

3.3 Characterization Data for Indolinones

3-ethyl-1,3-dimethylindolin-2-one[8] (5aa)

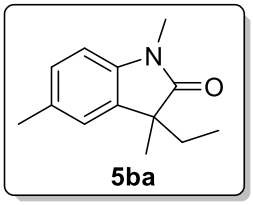


According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(OAc)$_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5aa** as colorless oil in 80% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.23 (m, 1H), 7.16 (d, *J* = 6.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.98-1.86 (m, 1H), 1.82-1.70 (m, 1H), 1.34 (s, 3H), 0.58 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.86, 143.58, 134.04, 127.72, 122.61, 122.51,107.92, 49.04, 31.56, 26.16, 23.41, 8.94.

3-ethyl-1,3,5-trimethylindolin-2-one[8] (5ba)

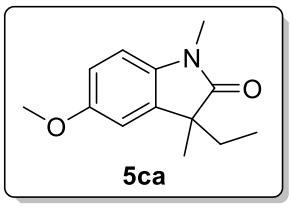


According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-(4-methylphenyl)methacrylamide **3b** (94.5 mg, 0.5 mmol), PhI(OAc)$_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ba** as colorless oil in 71% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.72 (d. *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 1.96-1.87 (m, 1H), 1.79-1.70 (m, 1H), 1.33 (s, 3H), 0.58 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.80, 141.23, 134.11, 131.97, 127.91, 123.49, 107.62, 49.10, 31.57, 26.18, 23.47, 21.26, 8.98.

3-ethyl-5-methoxy-1,3-dimethylindolin-2-one[8] (5ca)



According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-(4-methoxylphenyl)methacrylamide **3c** (102.5 mg, 0.5 mmol), PhI(OAc)$_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ca** as colorless oil in 80% isolated yield.

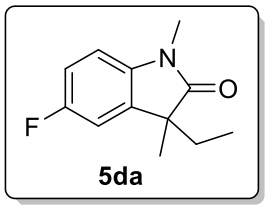
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76-6.69 (m, 3H), 3.77 (s, 3H), 3.15 (s, 3H), 1.94-1.85 (m, 1H), 1.75-1.66 (m, 1H), 1.30 (s, 3H), 0.56 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$), δ 180.39, 156.09, 137.12, 135.43, 111.51, 110.37, 108.05, 55.82, 49.44, 31.55, 26.18, 23.46, 8.92.

3-ethyl-5-fluoro-1,3-dimethylindolin-2-one[8] (5da)

According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-(4-fluorophenyl)-*N*-methylmethacrylamide **3d** (96.5 mg, 0.5

mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5da** as colorless oil in 78% isolated yield.



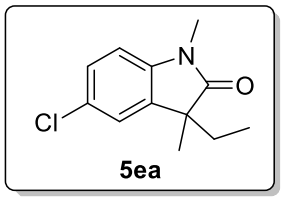
5da

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.89 (m, 2H), 6.76-6.73 (m, 1H), 3.19 (s, 3H), 1.97-1.88 (m, 1H), 1.78-1.69 (m, 1H), 1.33 (s, 3H), 0.58 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.39, 158.27 (d, *J* = 238.8 Hz), 139.47, 135.80 (d, *J* = 7.8 Hz), 113.91(d, *J* = 23.3 Hz), 110.91(d, *J* = 24.3 Hz), 108.33 (d, *J* = 8.0 Hz), 49.55, 31.50, 26.26, 23.32, 8.86.

^{19}F NMR (471 MHz, $CDCl_3$): -121.04.

5-chloro-3-ethyl-1,3-dimethylindolin-2-one[8] (5ea)



5ea

According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-(4-chlorophenyl)-*N*-methylmethacrylamide **3e** (104.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ea** as colorless oil in 76% isolated yield.

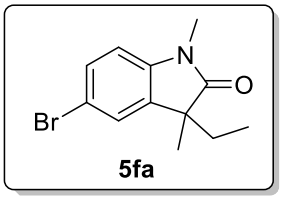
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.14 (d, *J* = 2.0 Hz 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 1.98-1.89 (m, 1H), 1.79-1.70 (m, 1H), 1.34 (s, 3H), 0.59 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.31, 142.20, 135.84, 127.97, 127.68, 123.23, 108.86, 49.40, 31.54, 26.31, 23.37, 8.94.

5-bromo-3-ethyl-1,3-dimethylindolin-2-one[8] (5fa)

According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-(4-bromophenyl)-*N*-methylmethacrylamide **3f** (127 mg, 0.5

mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5fa** as colorless oil in 80% isolated yield.

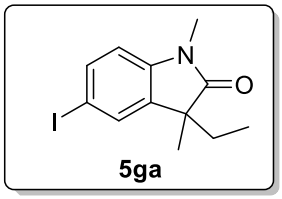


5fa

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 1.96-1.87 (m, 1H), 1.78-1.69 (m, 1H), 1.33 (s, 3H), 0.58 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.13, 142.64, 136.17, 130.56, 125.92, 115.24, 109.37, 49.32, 31.51, 26.25, 23.34, 8.91

3-ethyl-5-iodo-1,3-dimethylindolin-2-one[8] (5ga)



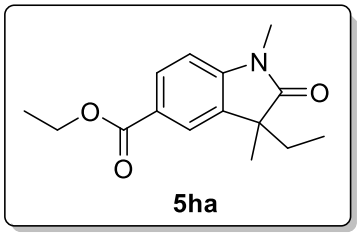
5ga

According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-(4-iodophenyl)-*N*-methylmethacrylamide **3g** (150 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ga** as colorless oil in 82% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 1.96-1.88 (m, 1H), 1.78-1.69 (m, 1H), 1.33 (s, 3H), 0.59 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.00, 143.36, 136.58, 131.51, 110.02, 85.16, 49.19, 31.54, 26.22, 23.37, 8.95.

ethyl 3-ethyl-1,3-dimethyl-2-oxoindoline-5-carboxylate[9] (5ha)



5ha

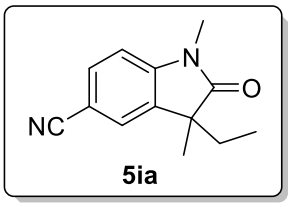
According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), ethyl 4-[methyl(2-methyl-1-oxoprop-2-enyl)amino]benzoate

3h (123.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ha** as light yellow oil in 74% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.36 (q, *J* = 7.4 Hz, 2H), 3.23 (s, 3H), 1.99-1.90 (m, 1H), 1.85-1.76 (m, 1H), 1.39 (t, *J* = 7.2 Hz 3H),1.36 (s, 3H),0.56 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.10, 166.67, 147.69, 133.94, 130.54, 124.84, 123.83, 107.41, 60.98, 48.96, 31.51, 26.36, 23.36, 14.52, 8.92.

3-ethyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile[9] (5ia)



5ia

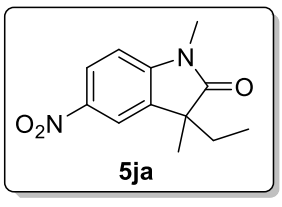
According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-(4-cyanophenyl)-*N*,2-dimethyl-2-propenamide **3i** (100.2 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ia** as white solid in 77% isolated yield.

M.p.: 100-102℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.40 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 1.98-1.89 (m, 1H), 1.82-1.73 (m, 1H), 1.35 (s, 3H), 0.58 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.41, 147.47, 135.08, 133.25, 125.98, 119.42, 108.37, 105.62, 48.91, 31.45, 26.40, 23.16, 8.83.

3-ethyl-1,3-dimethyl-5-nitroindolin-2-one[9] (5ja)



5ja

According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-(4-nitrophenyl)methacrylamide **3j** (110.1mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH

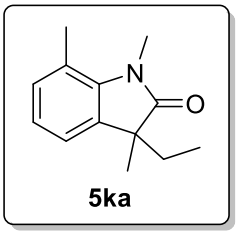
(2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ja** as yellow solid in 73% isolated yield.

M.p.: 101-103℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.06 (s, 1 H), 6.91 (d, *J* = 8.8 Hz, 1 H), 3.28 (s, 3H), 2.04-1.95 (m, 1H), 1.89-1.80 (m, 1H), 1.41 (s, 3H), 0.61 (t, *J* = 7.4 Hz, 3 H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.84, 149.32, 143.61, 134.91, 125.33, 118.59, 107.51, 49.19, 31.52, 26.64, 23.23, 8.90.

3-ethyl-1,3,7-trimethylindolin-2-one[9] (5ka)



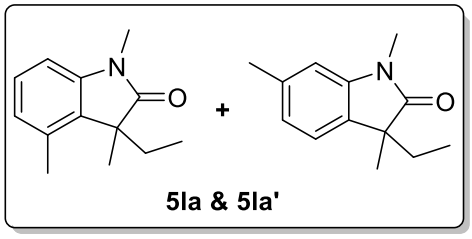
5ka

According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-(2-methylphenyl)methacrylamide **3k** (94.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ka** as colorless oil in 70% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.92 (m, 3H), 3.49 (s, 3H), 2.59 (s, 3H), 1.96-1.87 (m, 1H), 1.77-1.68 (m, 1H), 1.32 (s, 3H), 0.56 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.55, 141.34, 134.68, 131.42, 122.41, 120.51, 119.51, 48.32, 31.86, 29.49, 23.91, 19.17, 8.96.

3-ethyl-1,3,4-trimethylindolin-2-one & 3-ethyl-1,3,6-trimethylindolin-2-one[9] (5la & 5la')



5la & 5la'

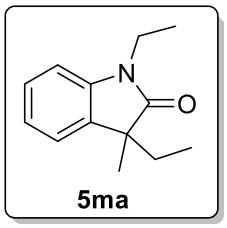
According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$,**2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-(2-methylphenyl)methacrylamide **3l** (94.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was

stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded the mix compound (**5la & 5la'**) as colorless oil in 83% isolated yield, mixture was determined by ^{1}H NMR, ratio = 1.7:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 0.5H), 6.87 (d, *J* = 7.6 Hz, 0.5H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 0.5H), 6.67(s, 1H), 3.20 (s, 3H), 3.19 (s, 1.7H), 2.39 (s, 1.7H), 2.36 (s, 3H), 2.03-1.98 (m, 2H), 1.94-1.85 (m, 0.5H), 1.79-1.69 (m, 0.5H), 1.42 (s, 3H),1.33 (s, 1.7H), 0.59 (t, *J* = 7.4 Hz, 1.7H,), 0.48 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.17, 180.77, 143.85, 143.65, 137.72, 134.22, 131.06, 130.40, 127.57,125.04, 122.94, 122.35, 108.89, 105.70, 50.25, 48.80, 31.53, 29.48, 26.22, 26.11, 23.47, 22.17, 21.85, 18.17, 9.29, 8.94.

1,3-diethyl-3-methylindolin-2-one[10] (5ma)



According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-ethyl-*N*-phenylmethacrylamide **3m** (94.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ma** as colorless oil in 69% isolated yield.

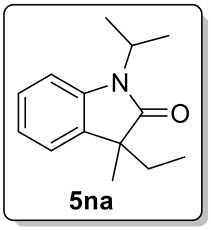
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.10-7.06 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.90-3.82 (m, 1H), 3.78-3.69 (m, 1H), 2.01-1.92 (m, 1H), 1.84-1.75 (m, 1H), 1.37 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.60 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.33, 142.60, 134.21, 127.61, 122.73, 122.23, 108.03, 48.84, 34.51, 31.61, 23.42, 12.83, 8.84.

3-ethyl-1-isopropyl-3-methylindolin-2-one[10] (5na)

According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-isopropyl-*N*-phenylmethacrylamide **3n** (101.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h.

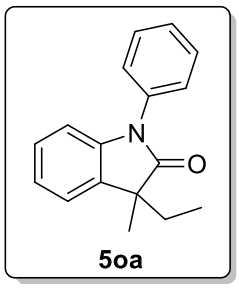
After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5na** as colorless oil in 81% isolated yield



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.06-7.01 (m, 2H), 4.67 (hept, *J* = 6.9 Hz, 1H), 1.97-1.89 (m, 1H), 1.78-1.69 (m, 1H), 1.48 (d, *J* = 3.2 Hz, 3H), 1.46 (d, *J* = 3.2 Hz, 3H), 1.33 (s, 3H), 0.55 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.39, 142.14, 134.42, 127.34, 122.76, 121.89, 109.67, 48.55, 43.49, 31.86, 23.58, 19.63,19.46, 8.78.

3-ethyl-3-methyl-1-phenylindolin-2-one[9] (5oa)

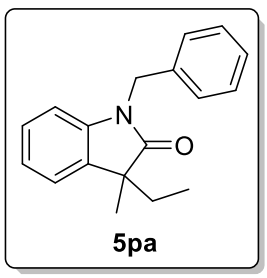


According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*,*N*-diphenylmethacrylamide **3o** (118.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5oa** as colorless oil in 84% isolated yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.0 Hz, 2H), 7.41-7.36 (m, 3H), 7.23-7.16 (m, 2H), 7.11-7.07 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 2.09-2.00 (m, 1H), 1.89-1.81 (m, 1H), 1.47 (s, 3H), 0.71 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.19, 143.47, 134.78, 133.74, 129.60, 127.93, 127.60, 126.63, 122.96, 122.88,109.22, 49.06, 32.13, 23.69, 8.98.

1-benzyl-3-ethyl-3-methylindolin-2-one[10] (5pa)



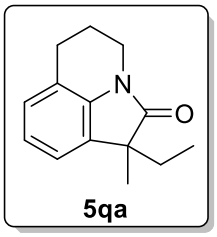
According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-benzyl-*N*-phenylmethacrylamide **3p** (125.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction,

removal of the solvent in vacuo, column chromatography afforded **5pa** as colorless oil in 80% isolated yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4H), 7.26-7.25 (m, 1H), 7.19-7.13 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.99 (d, *J* = 15.6 Hz, 1H,), 4.85 (d, *J* = 15.6 Hz, 1H), 2.06-1.98 (m, 1H), 1.88-1.80 (m, 1H), 1.41 (s, 3H), 0.64 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.93, 142.68, 136.30, 134.00, 128.82 (2C), 127.64,127.61, 127.36 (2C), 122.69, 122.53, 109.04,49.06, 43.74, 31.59, 23.88, 9.17.

1-Ethyl-1-methyl-5,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-2(4*H*)-one[11] (5qa)

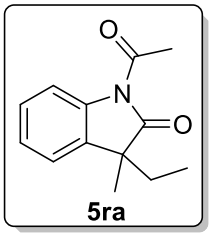


According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), 1,2,3,4-tetrahydro-*N*-methacryloylquinoline **3q** (100.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5qa** as colorless oil in 77% isolated yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.91(m, 3H), 3.70 (t, 2H, *J* = 6.0 Hz), 2.77 (t, *J* = 6.0 Hz, 2H), 2.01-1.96 (m, 2H), 1.93-1.84 (m, 1H), 1.80-1.71 (m, 1H), 1.34 (s, 3H), 0.63 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.65, 139.24, 132.51, 126.45, 121.86, 120.47, 119.89, 50.32, 38.72, 31.25, 24.72, 22.97, 21.39, 8.98.

1-acetyl-3-ethyl-3-methylindolin-2-one[12] (5ra)

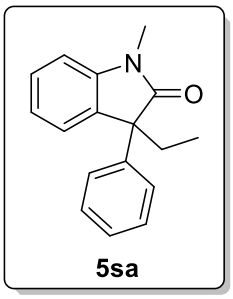


According to the general procedure, a mixture of $(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)[V(Nacnac)]_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-acetyl-*N*-phenylmethacrylamide **3r** (101.6 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ra** as colorless oil in 52% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.33-7.28 (m, 1H), 7.24-7.17 (m, 2H), 2.69 (s, 3H), 2.04-1.95 (m, 1H), 1.85-1.76 (m, 1H), 1.42 (s, 3H), 0.64 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.80, 171.09, 139.73, 132.96, 128.17, 125.34, 122.33, 116.57,49.50, 32.66, 26.79, 24.41, 8.99.

3-ethyl-1-methyl-3-phenylindolin-2-one[13] (5sa)



5sa

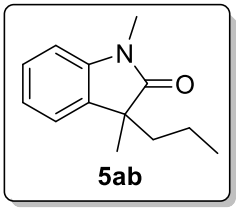
According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*,2-diphenylacrylamide **3s** (118.5 mg, 0.5 mmol), $PhI(OAc)_2$ **4a** (322.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5sa** as white solid in 75% isolated yield.

M.p.:77-79 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (m, 7H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.20 (s, 3H), 2.45- 2.36 (m, 1H), 2.26-2.17 (m, 1H), 0.66 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.72, 144.24, 140.36, 132.19, 128.59, 128.22, 127.31, 127.08, 124.90, 122.68, 108.30, 57.43, 31.00, 26.43, 9.15.

1,3-dimethyl-3-propylindolin-2-one[14] (5ab)



5ab

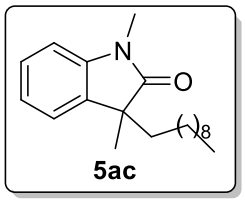
According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), $PhI(O_2CEt)_2$ **4b** (350.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ab** as colorless oil in 76% isolated yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.23 (m, 1H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.06 (t, *J*

= 7.4 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 3.21 (s, 3H), 1.93-1.83 (m, 1H), 1.75-1.65 (m, 1H), 1.35 (s, 3H), 1.06-0.95 (m, 1H), 0.91-0.82 (m, 1H), 0.77 (t, *J* = 6.8 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.

3-decyl-1,3-dimethylindolin-2-one[14] (5ac)



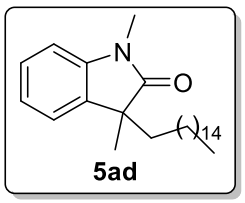
5ac

According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI($O_2CC_9H_{19}$)$_2$ **4c** (546.0 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ac** as colorless oil in 80% isolated yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27-7.24 (m, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.06 (t, *J* = 7.2 Hz ,1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 1.92-1.85 (m, 1H), 1.75-1.68 (m, 1H), 1.34 (s, 3H), 1.29-1.14 (m, 14H), 0.86 (t, *J* = 7.0 Hz, 5H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 180.97, 143.44, 134.44, 127.65, 122.55, 122.49, 107.93, 48.54, 38.65, 31.98, 29.85, 29.64, 29.62, 29.41, 29.36, 26.18, 24.56, 23.89, 22.76, 14.21.

3-hexadecyl-1,3-dimethylindolin-2-one[14] (5ad)



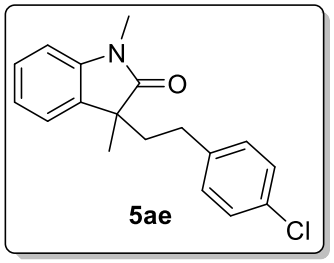
5ad

According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI($O_2CC_{15}H_{31}$)$_2$ **4d** (714.4 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ad** as colorless oil in 75% 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, 134.49, 127.68, 122.59, 122.53, 107.97, 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.

3-(4-chlorophenethyl)-1,3-dimethylindolin-2-one[15a] (5ae)

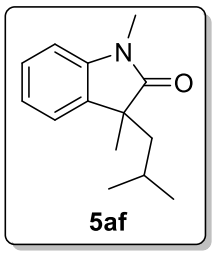


According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(O_2CR)$_2$ (R = 4-Chlorobenzyl) **4e** (543.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ae** as colorless oil in 63% 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 180.30, 143.49, 139.87, 133.64, 131.67, 129.77, 128.39, 128.03, 122.75, 122.58, 108.18, 48.40, 40.09, 30.51, 26.24, 24.13.

3-isobutyl-1,3-dimethylindolin-2-one[10] (5af)



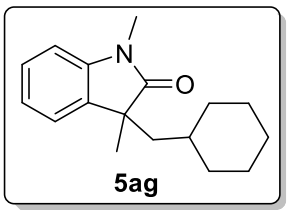
According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(O_2C^iPr)$_2$ **4f** (378.2 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5af** as colorless oil in 77% 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), 1.92 (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 181.12, 143.25, 134.26, 127.63, 122.86, 122.39, 108.00, 48.12, 46.80, 26.22, 26.19, 25.58, 24.17, 22.89.

3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one[10] (5ag)

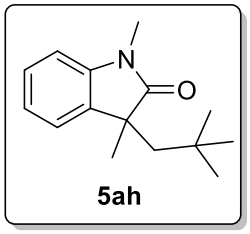


According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(O_2CR)$_2$ (R = Cyclohexyl) **4g** (687.5 mg, 1.5 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ag** 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), 7.07-7.04 (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), 1.22-1.19 (m, 1H), 1.00-0.73 (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, 34.83, 34.56, 33.63, 26.30, 26.24, 26.19 (2C), 26.12.

1,3-dimethyl-3-neopentylindolin-2-one[10,16] (5ah)



According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(O_2C^tBu)$_2$ **4h** (609.1 mg, 1.5 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 24 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ah** as white solid in 73% isolated yield.

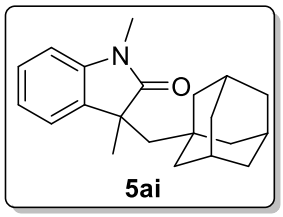
M.p.: 76-78 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 2.16 (d, *J* = 14.4 Hz, 1H), 1.86 (d, *J* = 14.4 Hz, 1H), 1.29

(s, 3H), 0.61 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.14, 142.95, 134.30, 127.64, 123.97, 122.09, 108.13, 50.89, 47.50, 31.88, 30.92(3C), 28.39, 26.35.

3-(-adamantan-1-ylmethyl)-1,3-dimethylindolin-2-one[10] (5ai)



According to the general procedure, a mixture of (μ-η^6:η^6-C_6H_6)[V(Nacnac)]$_2$ **2a** (12.7 mg, 0.0125 mmol), *N*-methyl-*N*-phenylmethacrylamide **3a** (87.5 mg, 0.5 mmol), PhI(O_2CR)$_2$ (R = 1-adamantyl) **4i** (562.1 mg, 1.0 mmol) and PhH (2.5 mL) was stirred at 80 ℃ for 10 h. After completion of the reaction, removal of the solvent in vacuo, column chromatography afforded **5ai** as white solid in 69% isolated yield.

M.p.: 108-110 ℃.

^{1}H NMR (400MHz, $CDCl_3$): 7.28-7.24 (m, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.23 (s, 3H), 1.99 (d, *J* = 14.4 Hz, 1H), 1.73 (d, *J* = 14.4 Hz, 4H),1.50 (d, *J* = 12.0 Hz, 3H), 1.37 (d, *J* = 11.6 Hz, 3H), 1.27 (s, 3H), 1.22-1.14 (m, 6H).

^{13}C NMR (100MHz, $CDCl_3$): 181.22, 142.69, 134.75, 127.56 123.64, 122.07, 108.04, 52.09, 46.69, 43.39 (3C), 36.77 (3C), 33.96, 28.68, 28.62 (3C), 26.34.

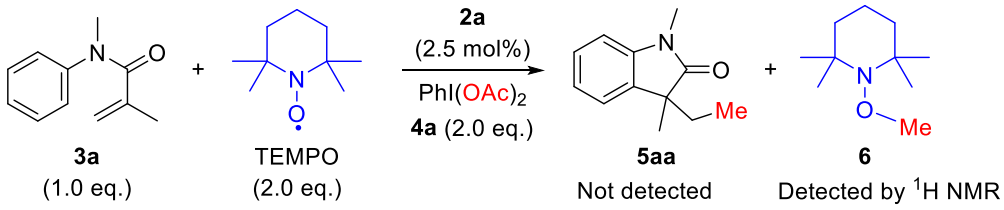
4. Mechanism Studies

4.1 A Radical Trapping Experiment with TEMPO

We further conducted mechanistic experiments to probe insights on this alkylarylation reaction. Firstly, the control experiment was initially carried out with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) under the standard conditions (Scheme S1). As a result, the transformation was completely prohibited. Instead, 1-methoxy-2,2,6,6-tetramethylpiperidine **6**[7,17] as the adduct formed by TEMPO and methyl radical was detected by ^{1}H NMR spectrometer (Figure S2), which implied a radical decarboxylation pathway might operate in this reaction.

Notably, because of the Csp^3-H bond in toluene is more susceptible to radicals than aromatic Csp^2-H bonds, we detect some hypothesis products in our reactions (via mass spectrometry). The spectrums are shown in Figures S3-4, suggesting that the hypothesis products were formed as those reported[15] in oxidative benzylarylation of **3a** with toluene (Figures S3) or in the oxidative alkylarylation of **3a** with THF (Figures S4).

Scheme S1. A radical trapping experiment with TEMPO



Experimental Details: A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. **2a** (12.7 mg, 0.0125 mmol), alkene **3a** (87.5 mg, 0.5 mmol), PhI(OAc)$_2$ **4a** (322.0 mg, 1.0 mmol), TEMPO (156.2 mg, 1.0 mmol), and PhH (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 (80 ^{o}C) for 10 h. After completion of the reaction, the solvent was removed in vacuo. The crude reaction mixture was analyzed by ^{1}H NMR. As a result, no indolinone **5aa** was observed. Instead, 1-methoxy-2,2,6,6-tetramethylpiperidine **6**[7,17] as the adduct formed by

TEMPO and methyl radical was detected by ^{1}H NMR spectrometer.

Figure S2. Crude ^{1}H NMR spectrum of the reaction outlined in **Scheme S1**

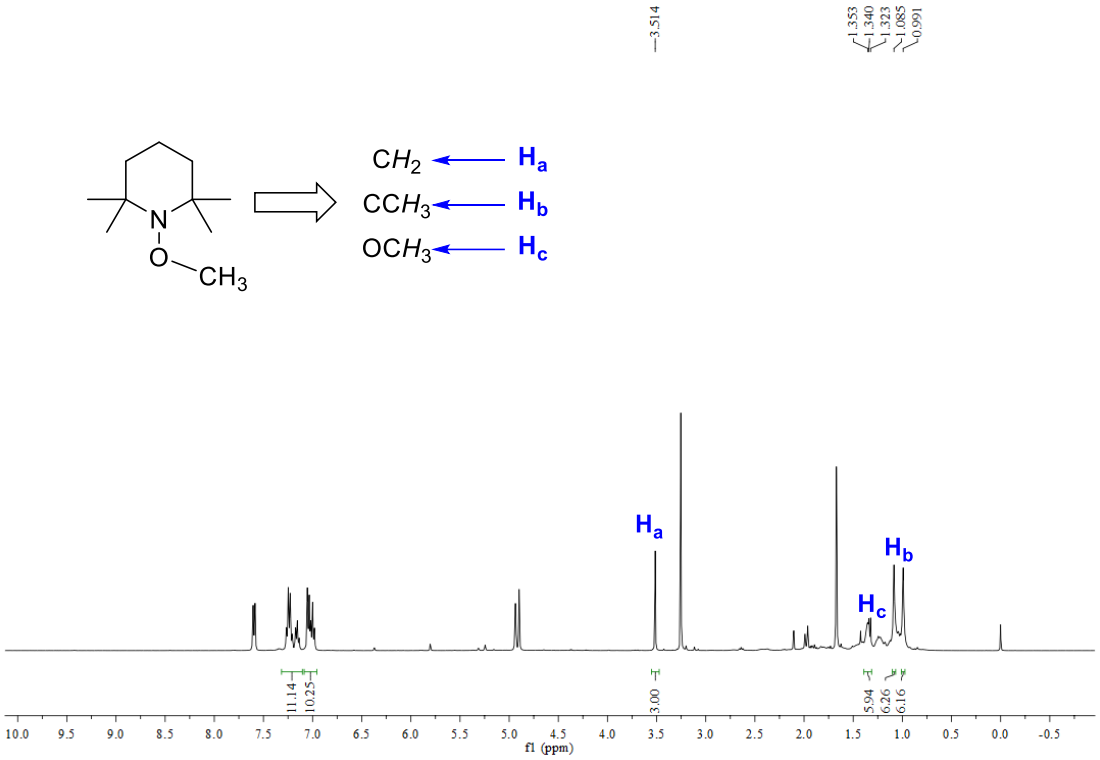


Figure S3. spectrum of the hypothesis product for toluene

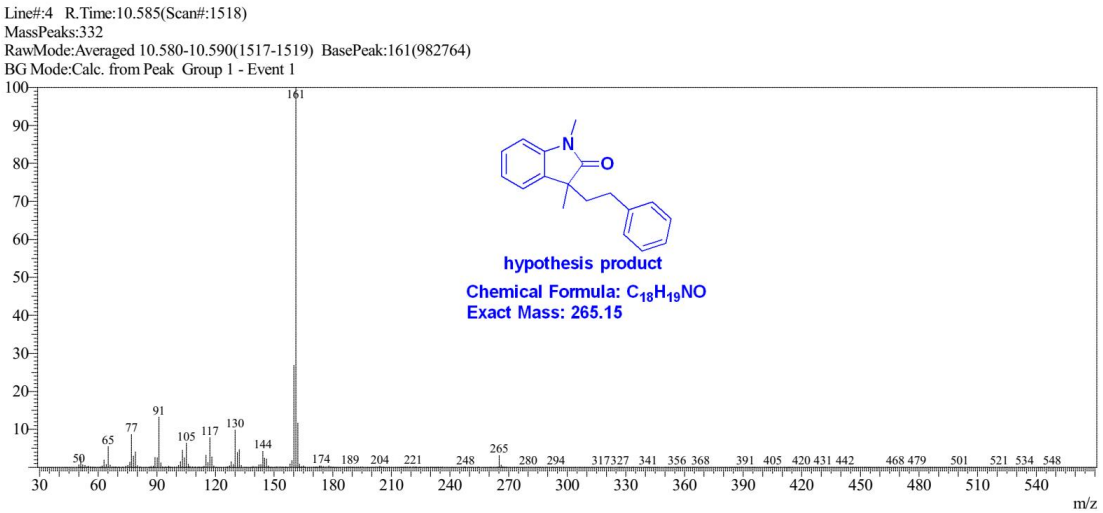
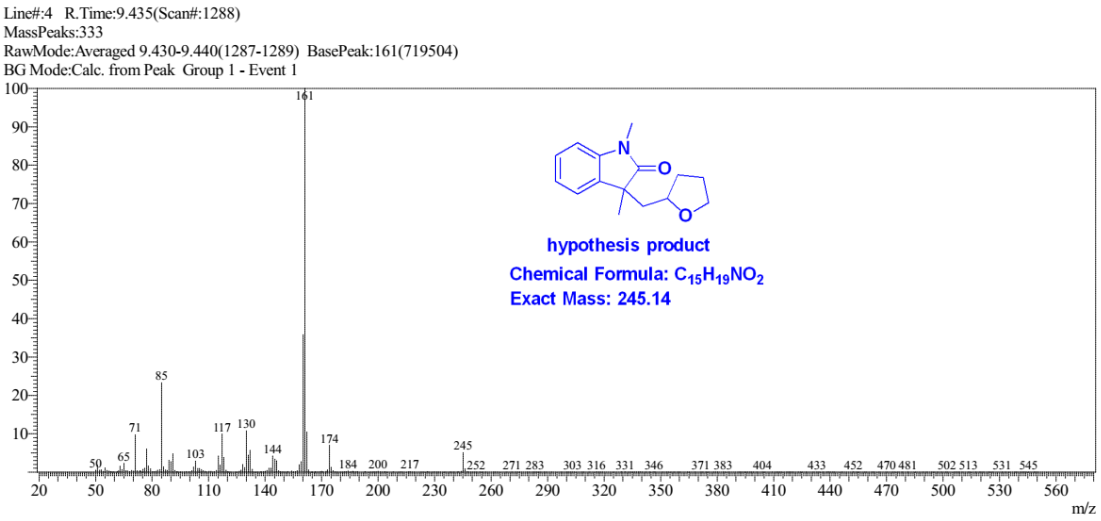


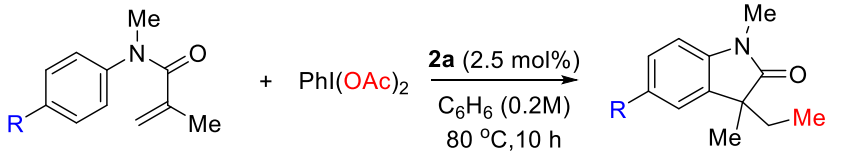
Figure S4. spectrum of the hypothesis product for THF



4.2 Competition Experiments of Alkenes

Next, we examined competition experiments between alkenes **3c** and **3i**, bearing an electro-donating methoxy and electro-withdrawing cyano group respectively, with HIR **4a** (Scheme S2). It turned out that the yields of the corresponding indolinones **5ca** and **5ia** were 17% and 21%, 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



3c, R = OMe, (1.0 eq.)
3i, R = CN, (1.0 eq.)

4a (1.0 eq.)

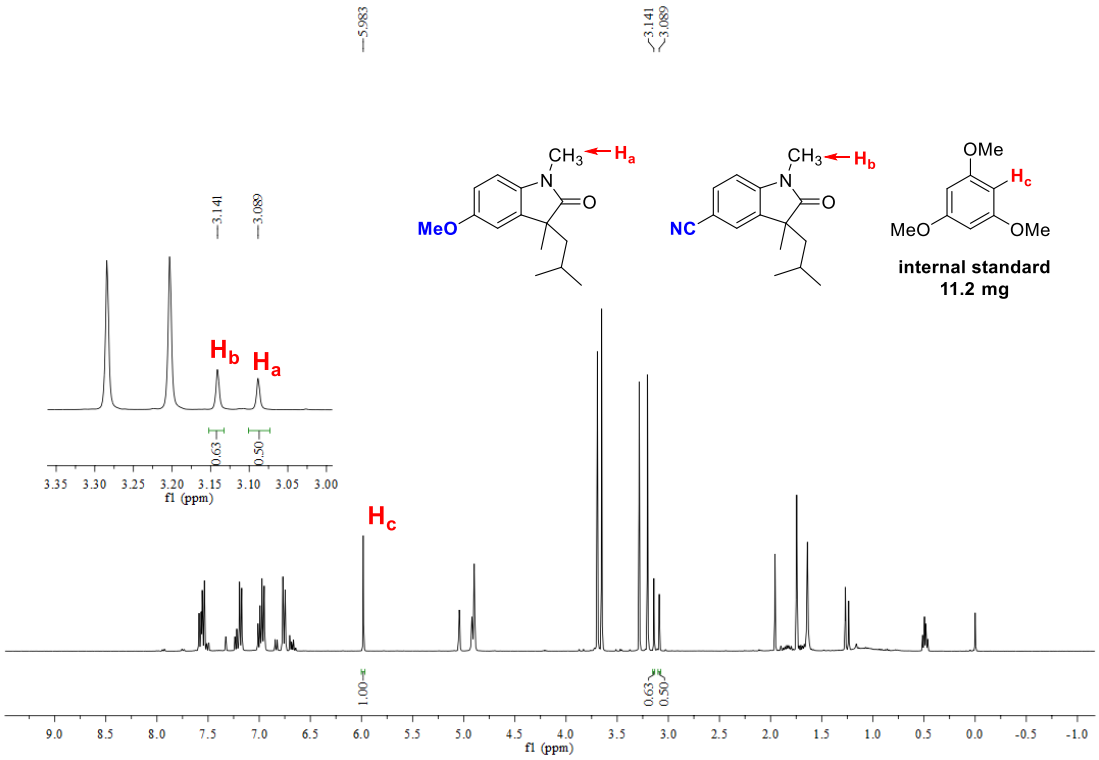
5ca, R = OMe, 17%[b]
5ia, R = CN, 21%[b]

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

Experimental Details: A flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. **2a** (5.1 mg, 0.005 mmol), alkenes **3c** (41.1 mg, 0.2 mmol), **3i** (40.0 mg, 0.2 mmol), $PhI(OAc)_2$ **4a** (64.4 mg, 0.2 mmol) and C_6H_6 (1.0 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 (80 °C) for 10 h. After completion of the

reaction, the solvent was removed in vacuo. The crude reaction mixture was analyzed by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

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



5. References

[1] Budzelaar, P. H. M.; Bart van Oort, A.; Guy Orpen, A. *Eur. J. Inorg. Chem*., **1998**, 1485-1494.

[2] Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814-2819.

[3] Tsai, Y.-C.; Wang, P.-Y.; Lin, K.-M.; Chen, S.-A.; Chen, J.-M. *Chem. Commun*., **2008**, 205-207.

[4] (a) Ackermann, L.; Lygin, A. V.; Hofmann, N. *Org. Lett.* **2011**, *13*, 3278-3281. (b) Mu, X.; Wu, T.; Wang, H.-Y.; Guo, Y.-L.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878-881. (c) Jiang, Y.-Y.; Dou, G.-Y.; Xu, K.; Zeng, C.-C. *Org. Chem. Front*. **2018**, *5*, 2573-2577. (d) Zhang, T.; Chen, B.; Wang, W.; Zhang, Q.; Wang, P.; Wan, W.; Deng, H.; Hao, J.; Jiang, H. *Asian. J. Org. Chem.* **2019**, *8*, 671-674.

[5] (a) Nishio, T.; Koyama, H.; Sasaki, D.; Sakamoto, M. *Helv. Chim. Acta* **2005**, *88*, 996-1003. (b) Fabry, D. C.; Stodulski, M.; Hoerner, S.; Gulder, T. *Chem. Eur. J.* **2012**, *18*, 10834-10838. (c) Lu, K.; Han, X.-W.; Yao, W.- W.; Luan, Y.-X.; Wang, Y.-X.; Chen, H.; Xu, X.-T.; Zhang, K.; Ye, M. *ACS Catal*. **2018**, *8*, 3913-3917. (d) Cao, Y.; Zhao, H.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *Adv. Synth. Catal*. **2016**, *358*, 3610-3615.

[6] Mocci, F.; Uccheddu, G.; Frongia, A.; Cerioni, G. *J. Org. Chem.* **2007**, *72*, 4163-4168.

[7] Y. Wang, L. Zhang, Y.-H.Yang, P. Zhang, Z.-T. Du, C. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 18048-18051.

[8] Xu, Z.-B.; Yan, C.-X..; Liu, Z.-Q. *Org. Lett*. **2014**, 16, 5670-5673.

[9] Dai, Q.; Yu, J.; Jiang, Y.; Guo, S.; Yang, H.; Cheng, J. *Chem. Commun*., **2014**, 50, 3865-3867.

[10] Xie, J.; Xu, P.; Li, H.; Xue, Q.; Jin, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 5672-5674.

[11] Ratushnyy, M.; Kvasovs, N.; Sarkar, S.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2020**, 59, 10316-10320.

[12] Xu, Z.; Jia, R.; Ma, Z.; Cao, S.; Shen, L.; Ji, H. *Synlett* **2019**, *30*, A-E.

[13] Beyer, A.; Buendia, J.; Bolm, C. *Org. Lett*. **2012**, 14, 3948-3951.

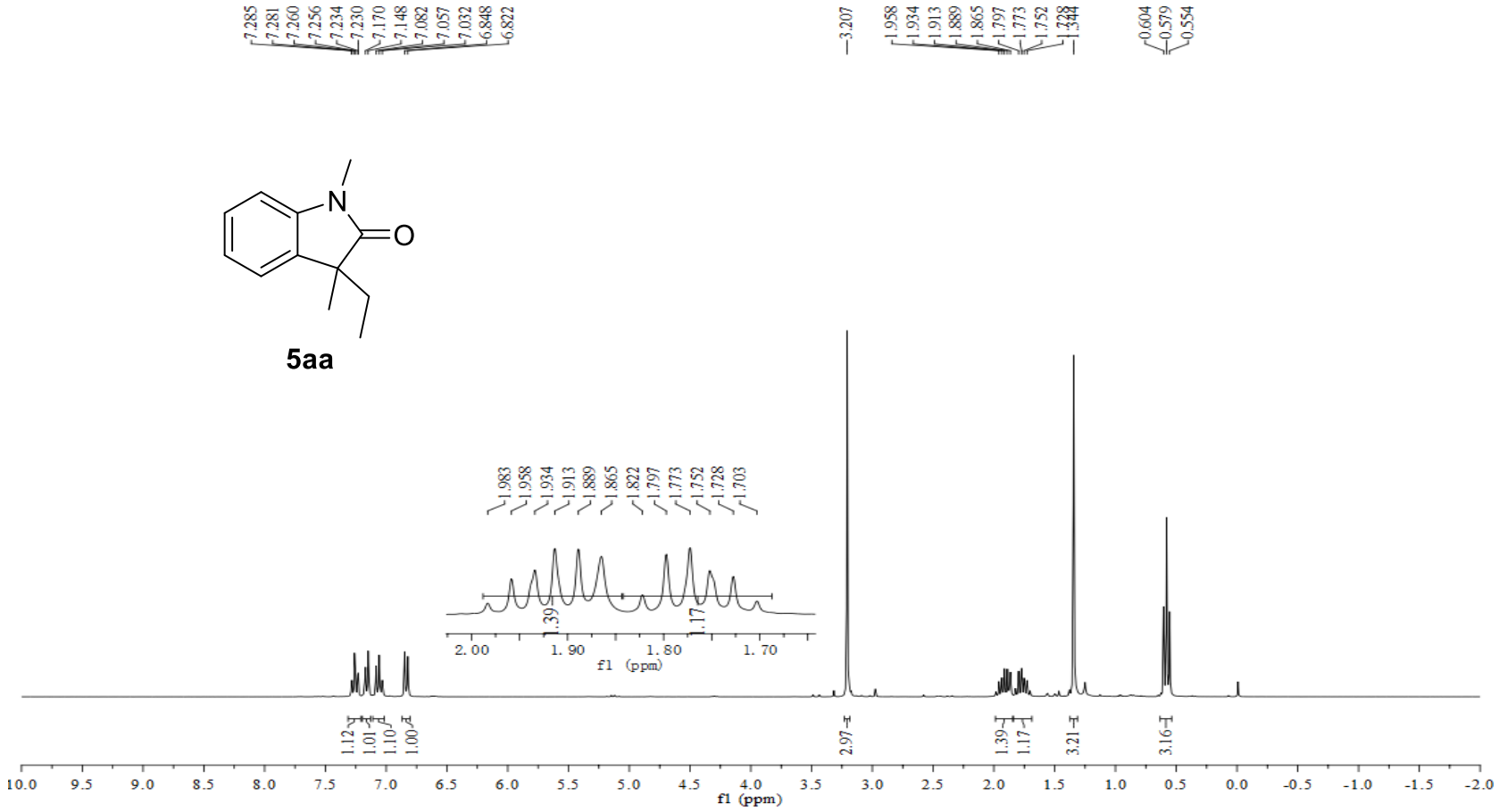
[14] Pan, C.; Fu, Y.; Ni, Q.; Yu, J.-T. *J. Org. Chem.* **2017**, *82*, 5005-5010.

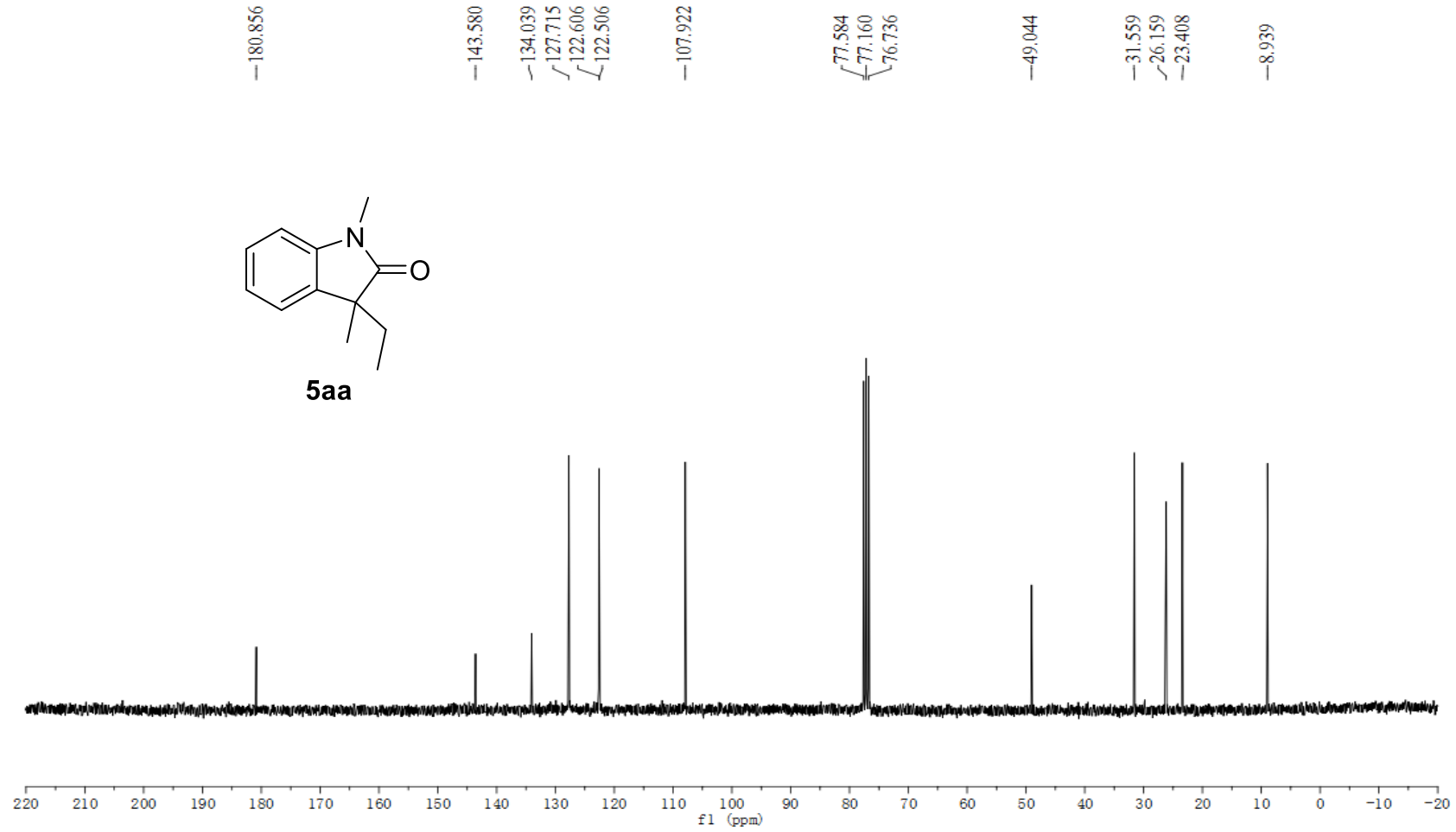
[15] (a) Zhou, S.-L.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Chem. Eur. J.* **2013**, *19*, 12970-12973. (b) Wei, W.-T.; Zhou, M.-B.; Fan, J.-H.; Liu, W.; Song, R.-J.; Liu, Y.; Hu, M.; Xie, P.; Li, J.-H. *Angew. Chem., Int. Ed.*, **2013**, *52*, 3638-3641.

[16] Wu, T.; Zhang, H.; Liu, G. *Tetrahedron*, **2012**, *68*, 5229-5233.

[17] (a) Anderson, J. E.; Casarini, D.; Corrie, J. E. T.; Lunazzi, L. *J. Chem. Soc., Perkin Trans 2*. **1993**, 1299-1304. (b) Hammill, C. L.; Noble, B. B.; Norcott, P. L.; Ciampi, S.; Coote, M. L. *J. Phys. Chem. C* **2019**, *123*, 5273-5281.

6. Spectra of Products

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76.736
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31.559
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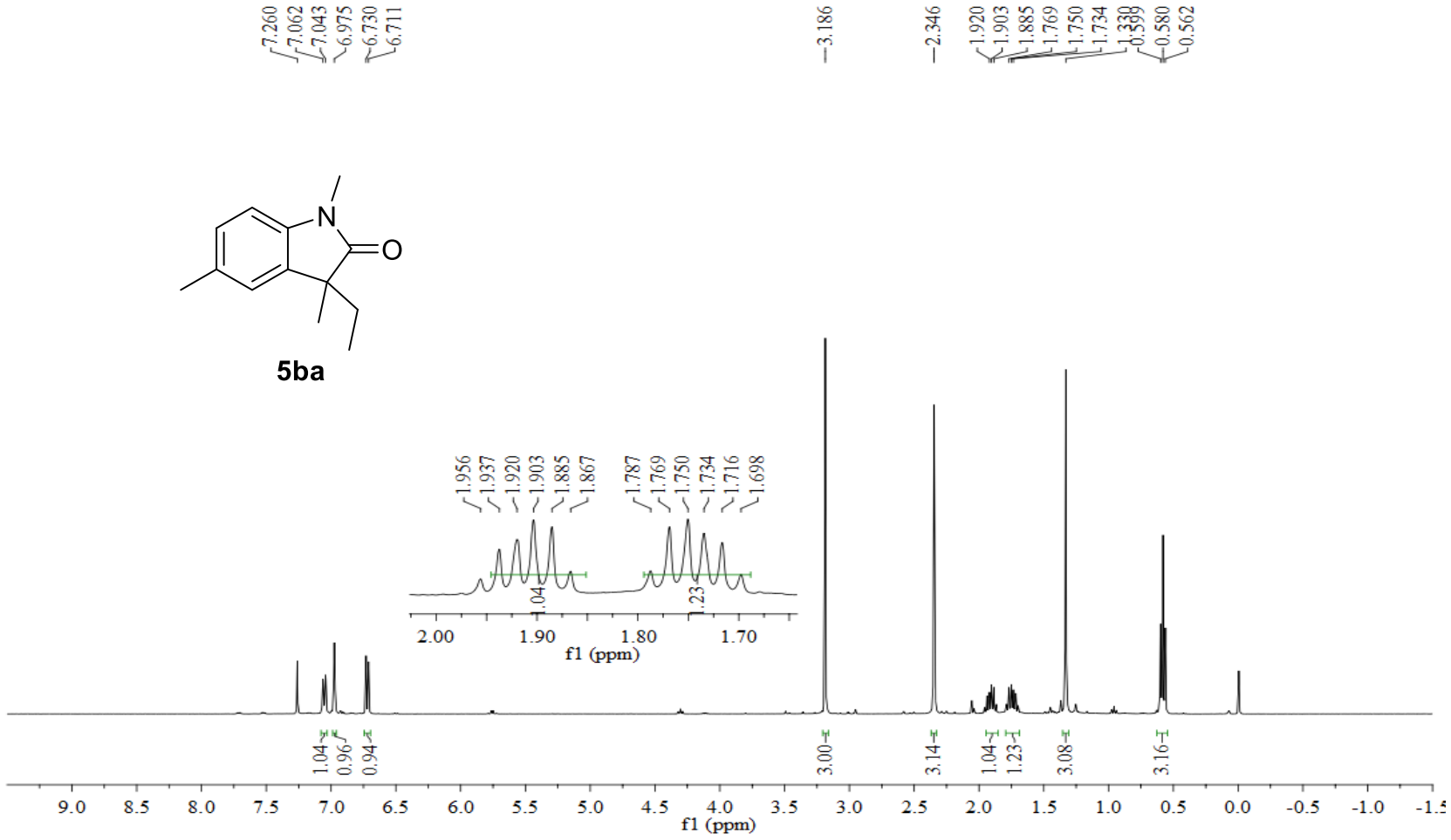
N
O
5aa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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N
O
5ba
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1.903
1.885
1.867
1.787
1.769
1.750
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1.698
1.04
1.23
2.00
1.90
1.80
1.70
f1 (ppm)
1.04
0.96
0.94
3.00
3.14
1.04
1.23
3.08
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
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0.0
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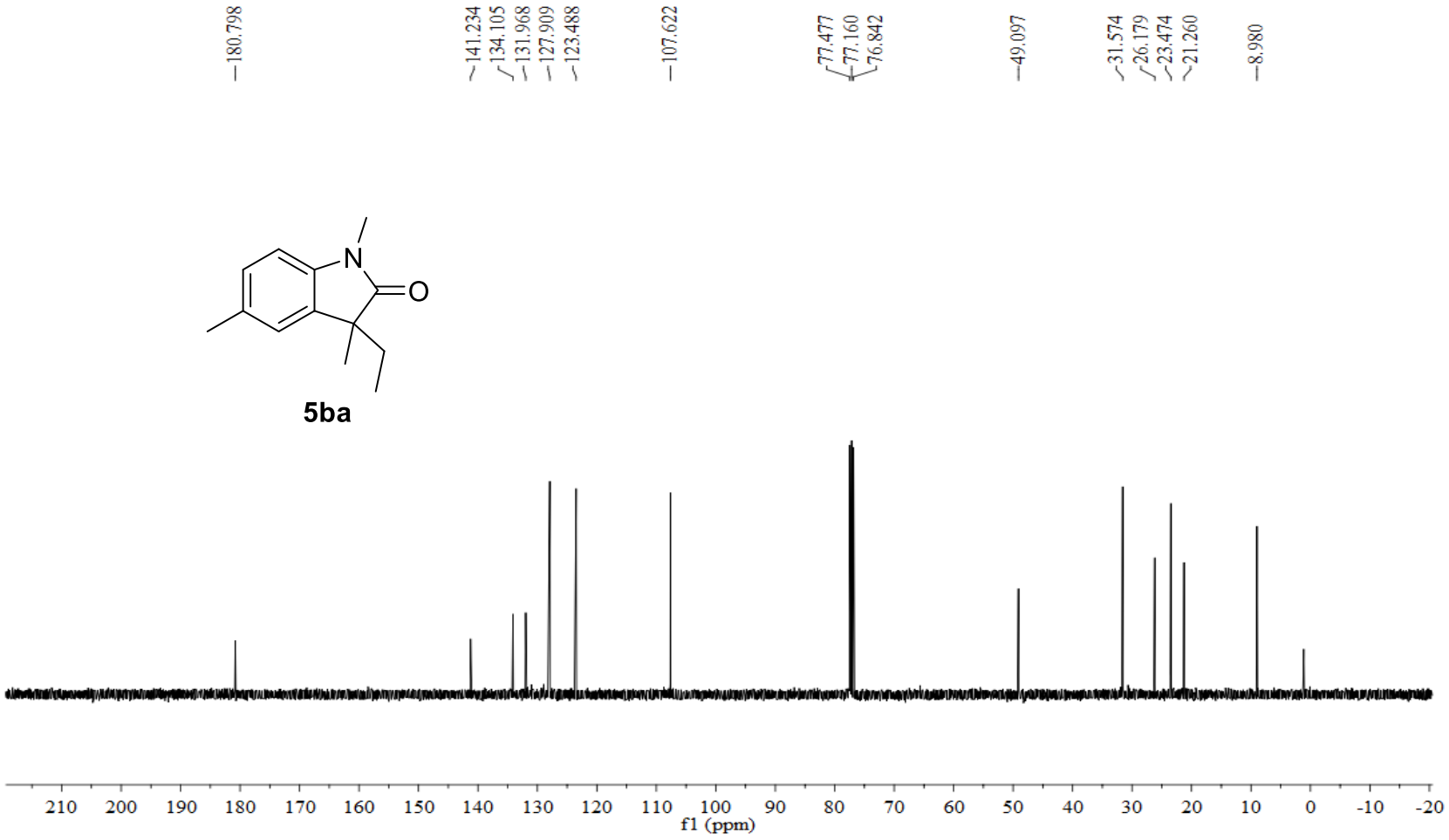
f1 (ppm)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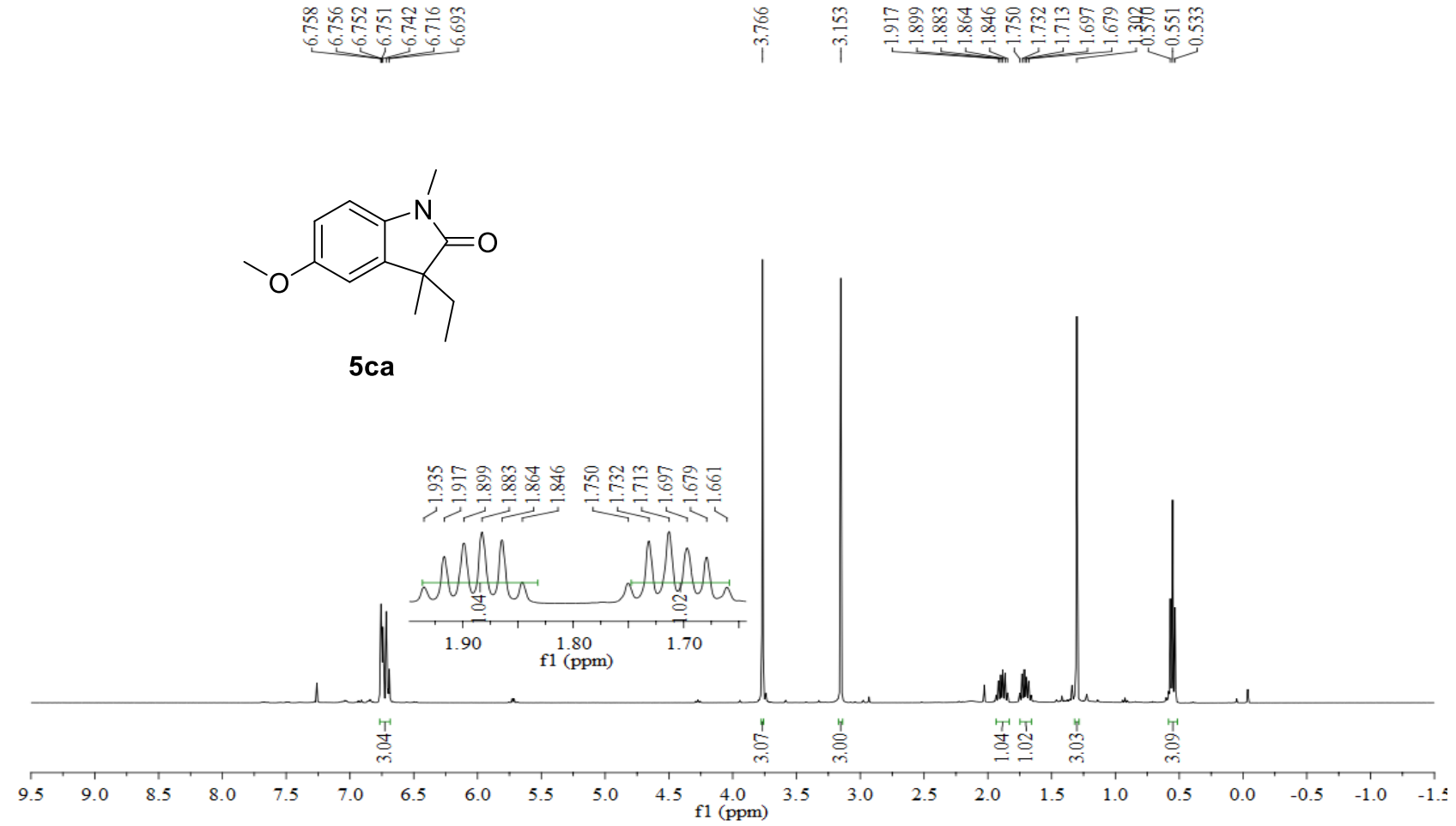
f1 (ppm)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O
5ca
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1.899
1.883
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1.750
1.732
1.713
1.697
1.679
1.661
1.04
1.02
1.90
1.80
1.70
f1 (ppm)
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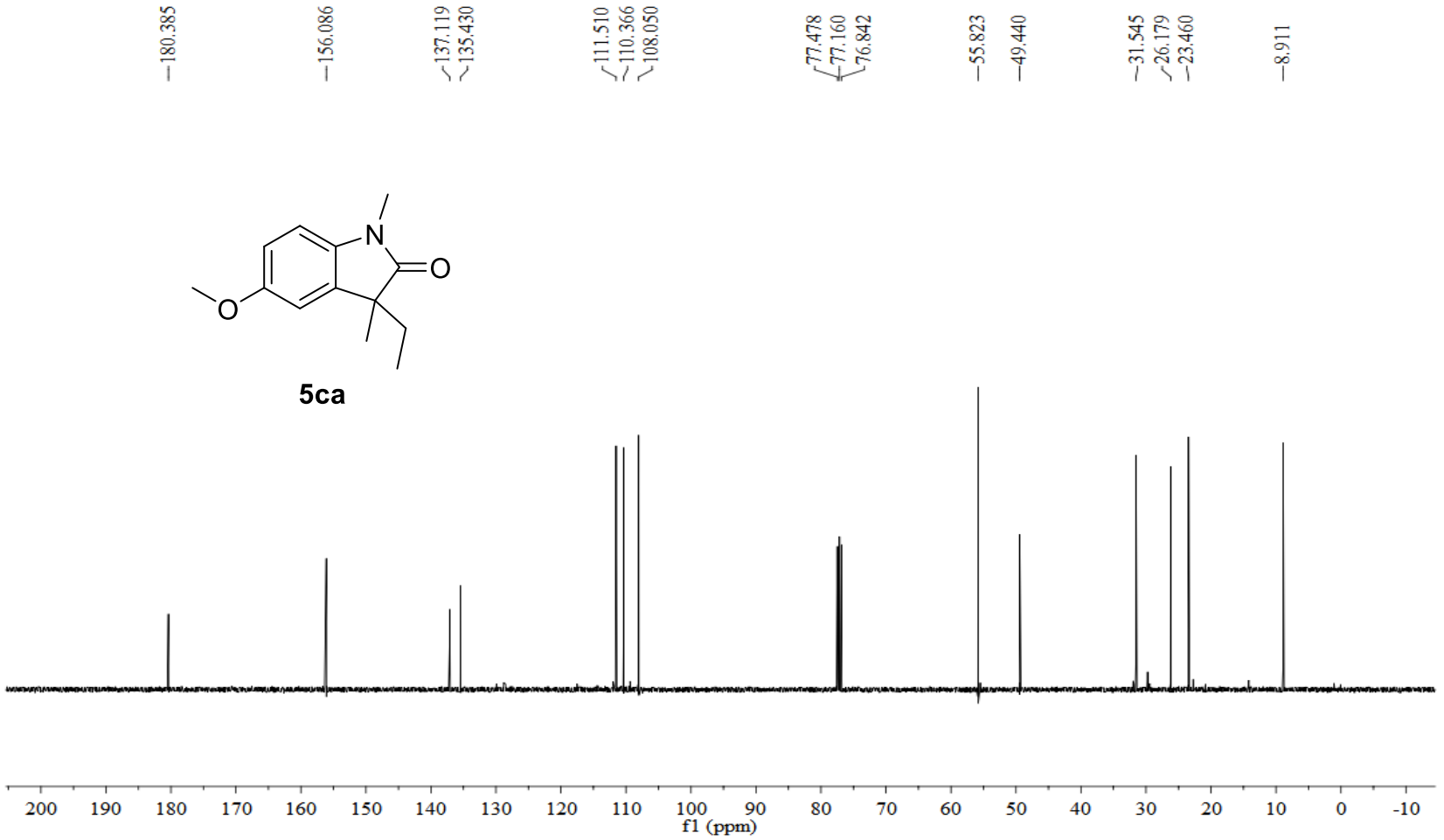
3.07
3.00
1.04
1.02
3.03
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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31.545
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O
O
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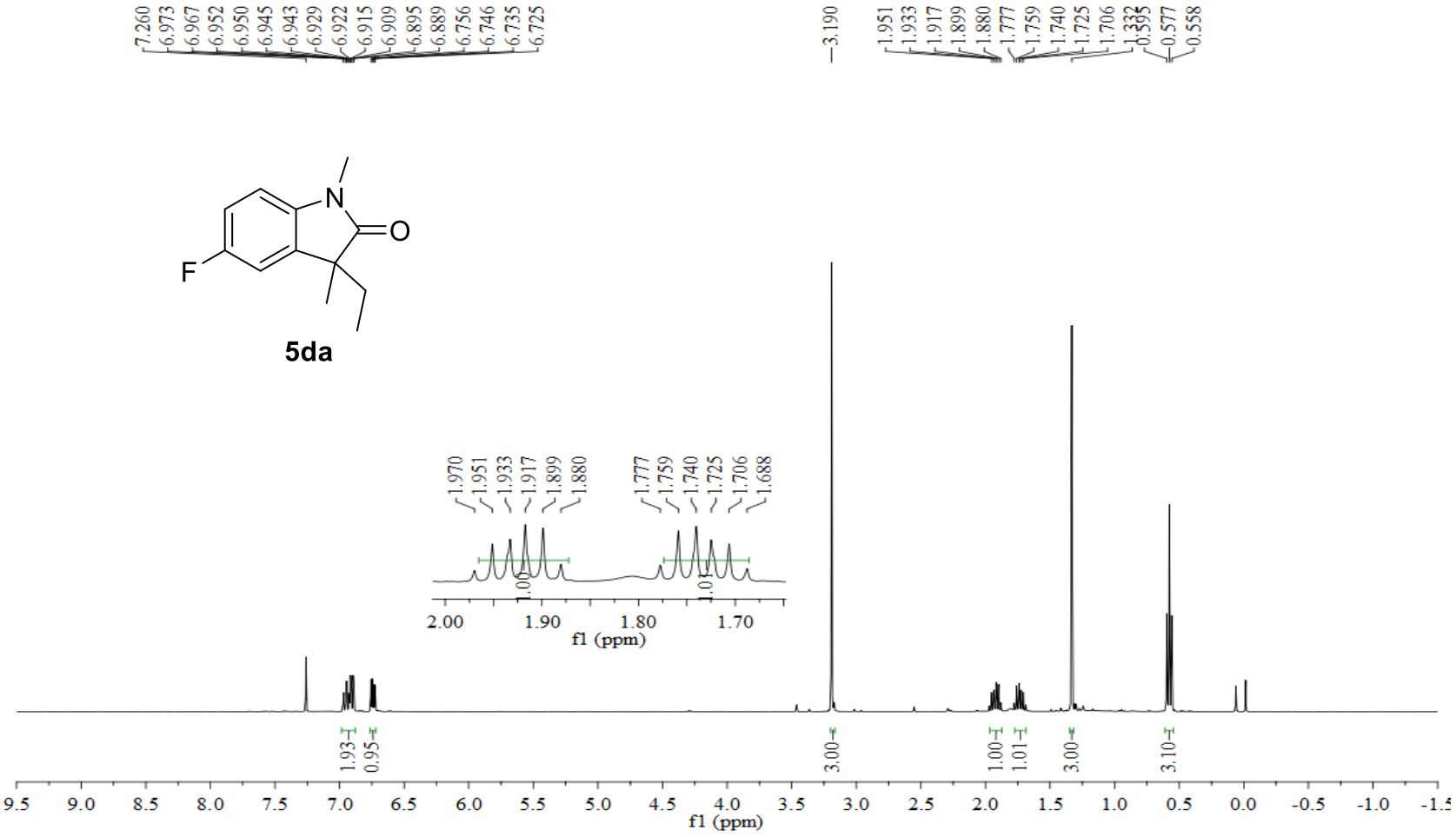
f1 (ppm)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O
F
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1.933
1.917
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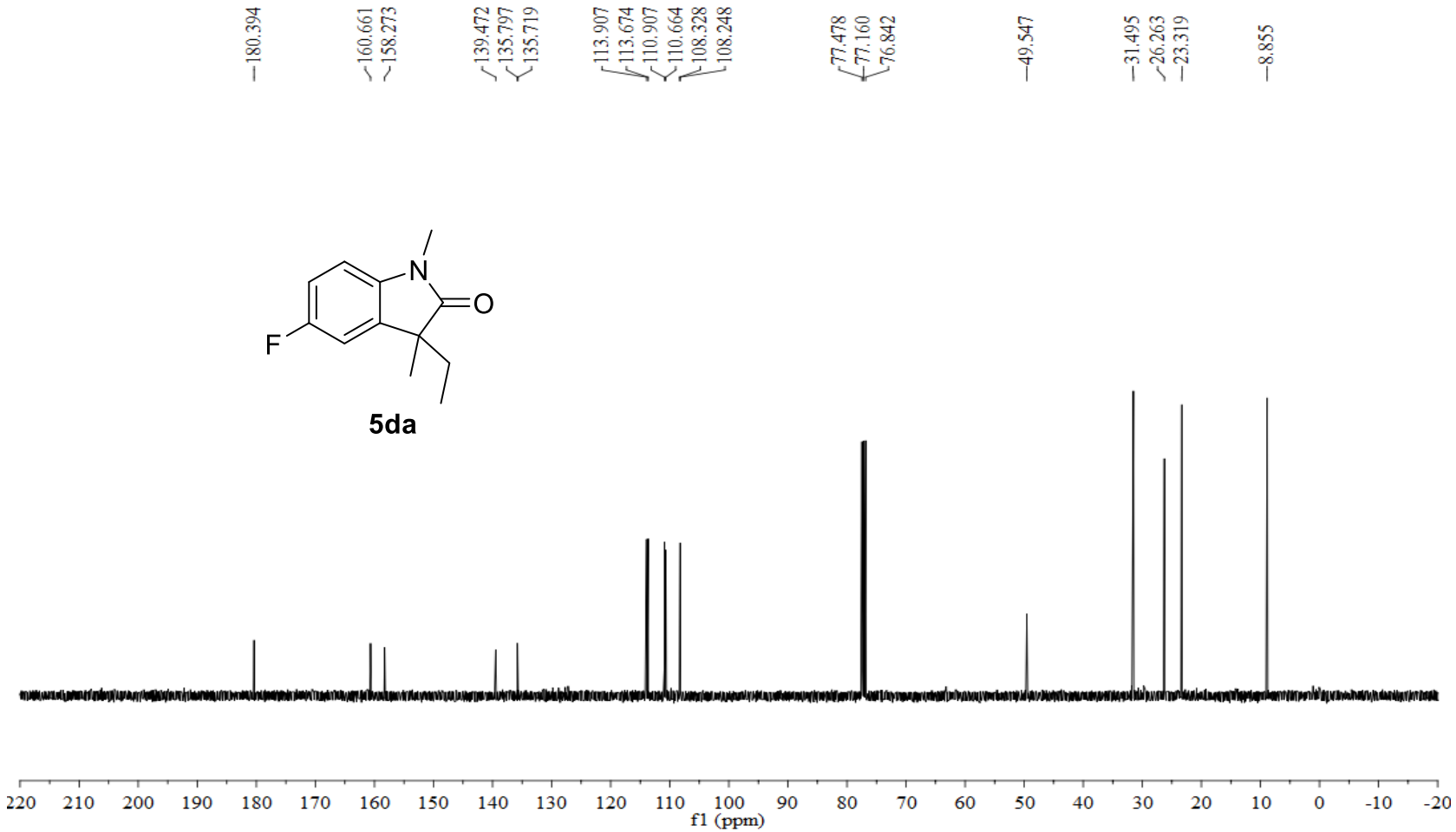
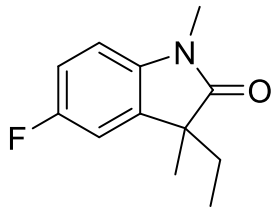
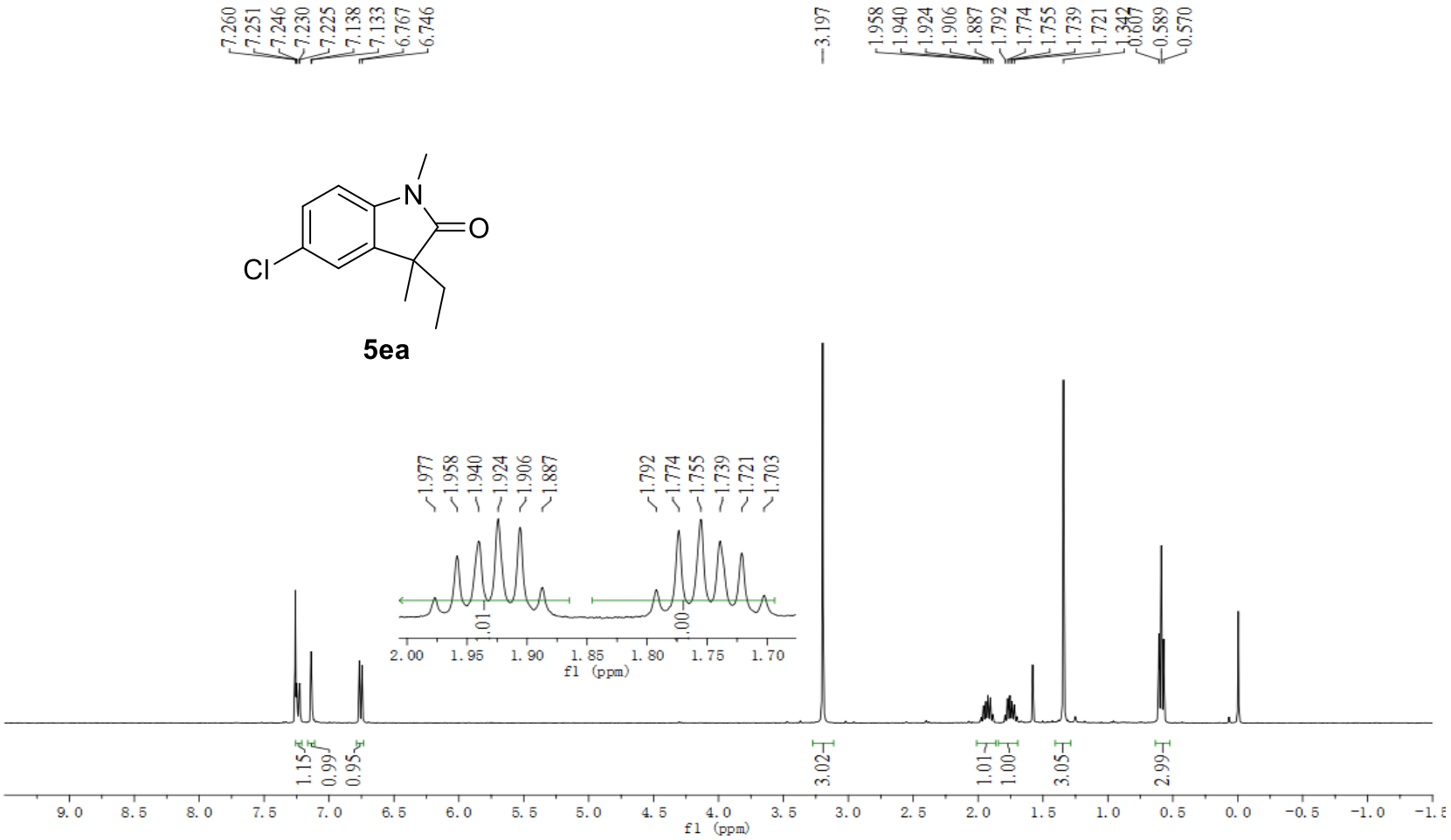
1.688
1.00
1.01
2.00
1.90
1.80
1.70
f1 (ppm)
1.93
0.95
3.00
1.00
1.01
3.00
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

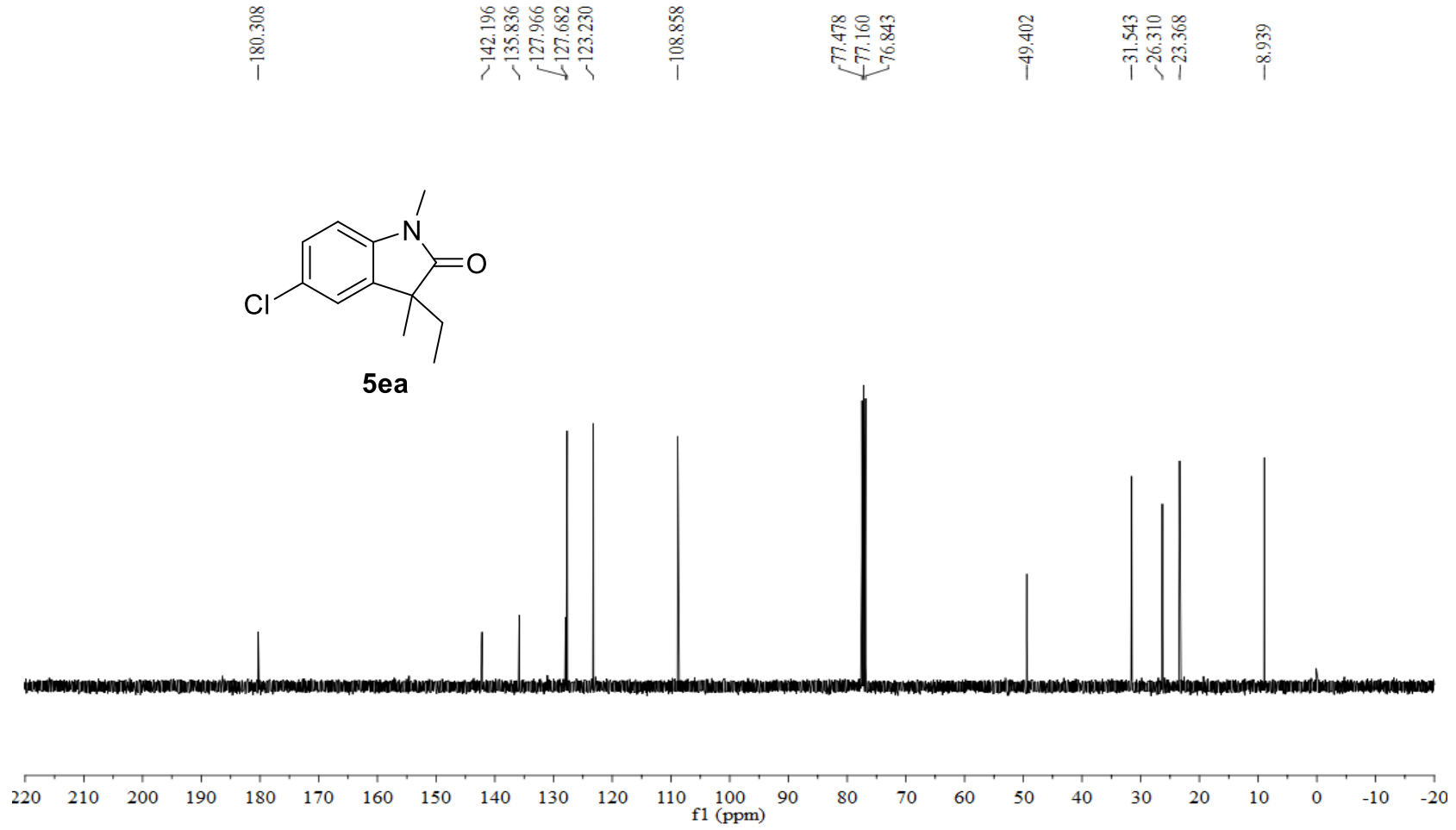

180.394
160.661
158.273
139.472
135.797
135.719
113.907
113.674
110.907
110.664
108.328
108.248
77.478
77.160
76.842
49.547
31.495
26.263
23.319
8.855
N
O
F
5da
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

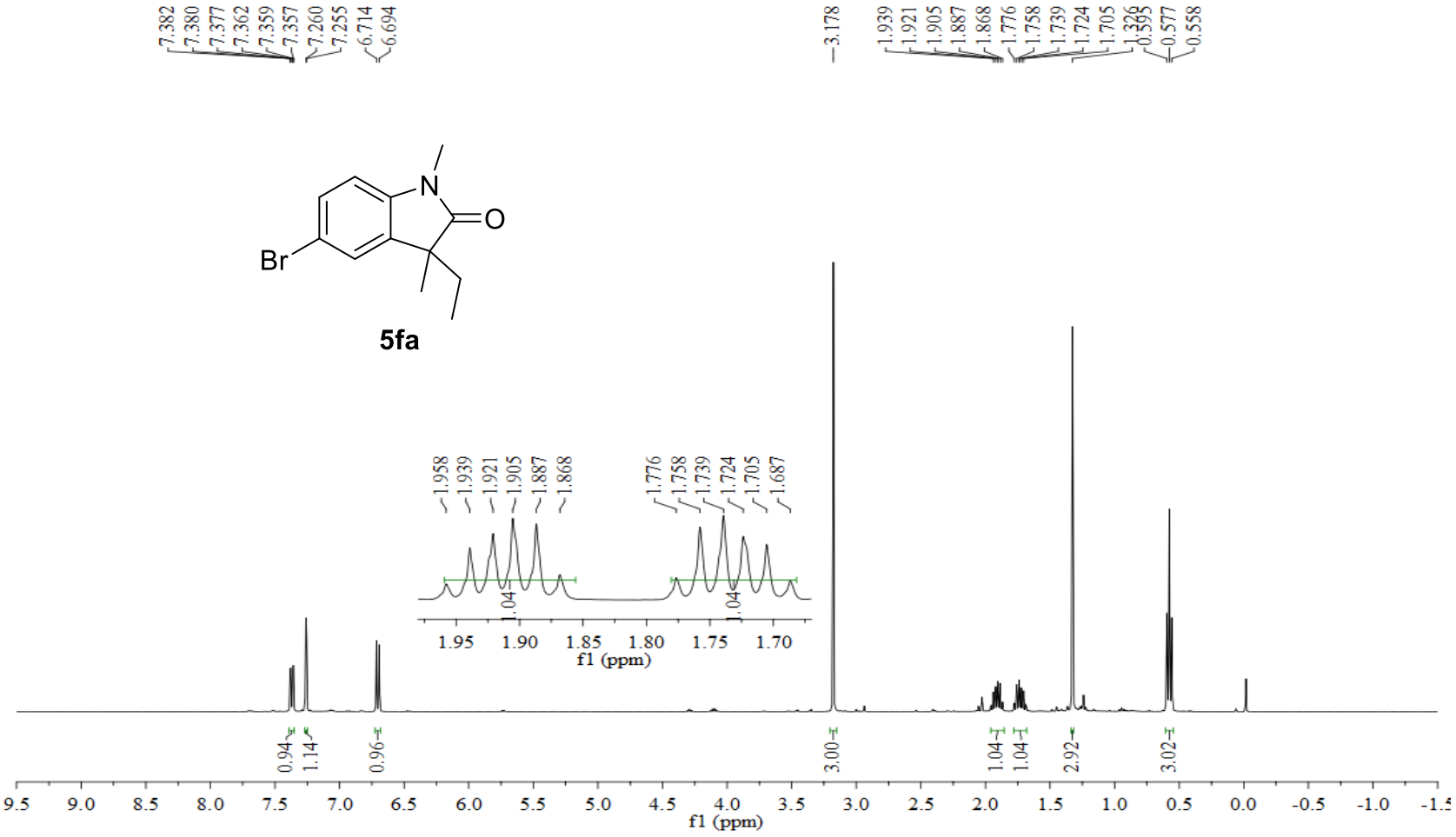

N
O
F

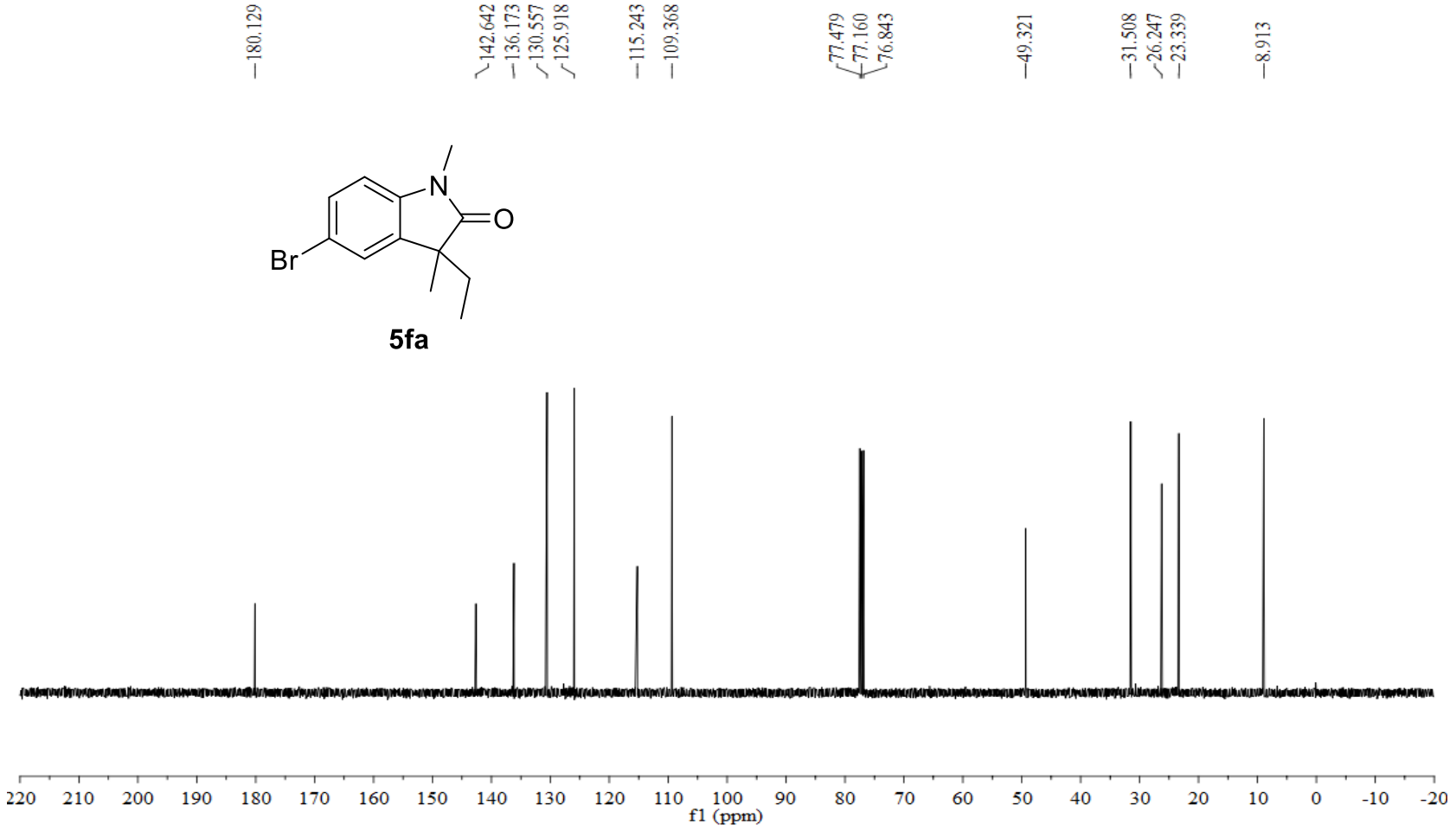
5da

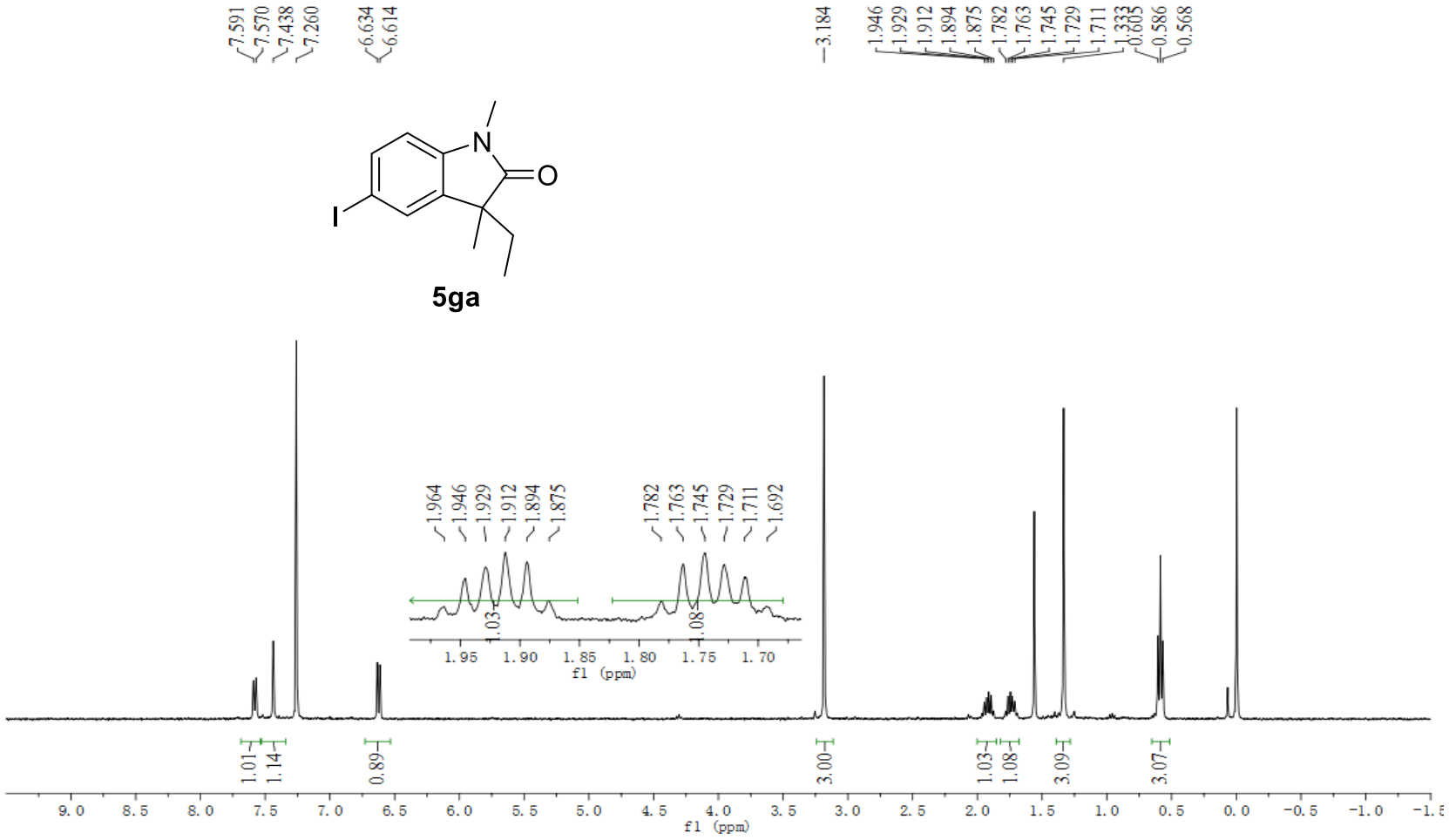
-121.035
90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

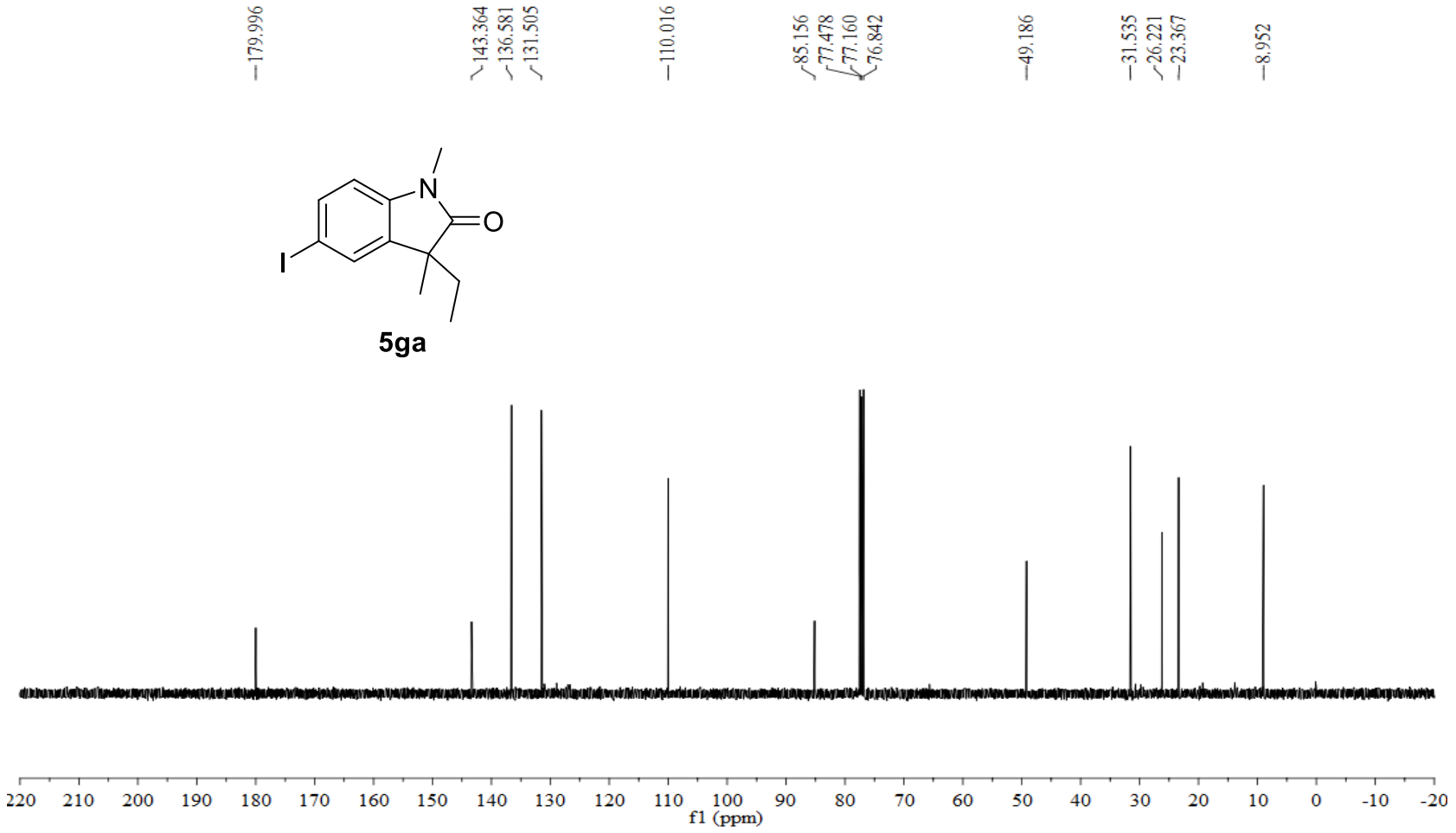

7.260
7.251
7.246
7.230
7.225
7.138
7.133
6.767
6.746
3.197
1.958
1.940
1.924
1.906
1.887
1.792
1.774
1.755
1.739
1.721
0.589
0.570
Cl
N
O
5ea
1.977
1.958
1.940
1.924
1.906
1.887
1.792
1.774
1.755
1.739
1.721
1.703
f1 (ppm)
f1 (ppm)

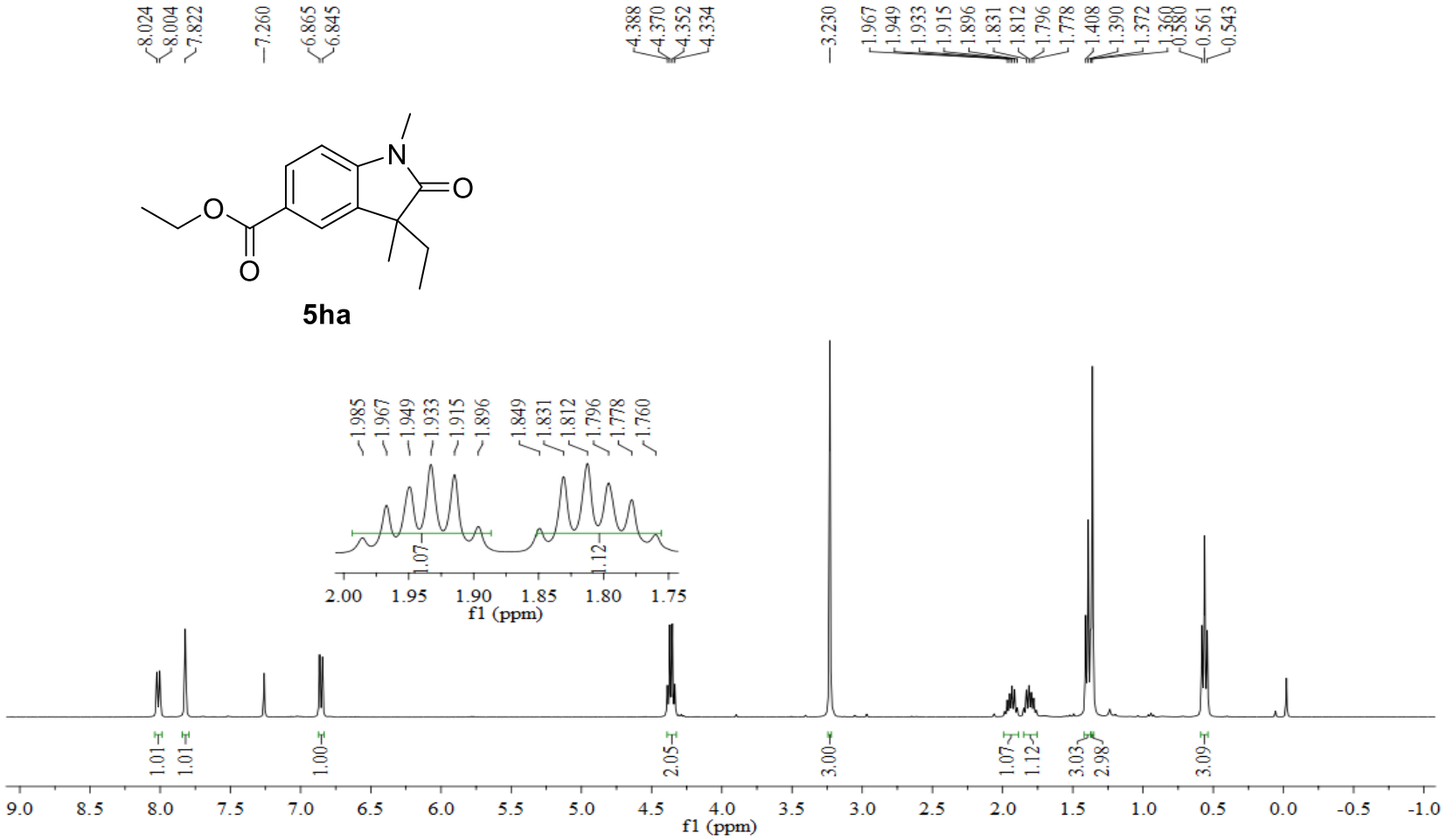

180.308
142.196
135.836
127.966
127.682
123.230
108.858
77.478
77.160
76.843
49.402
31.543
26.310
23.368
8.939
N
O
Cl
5ea
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

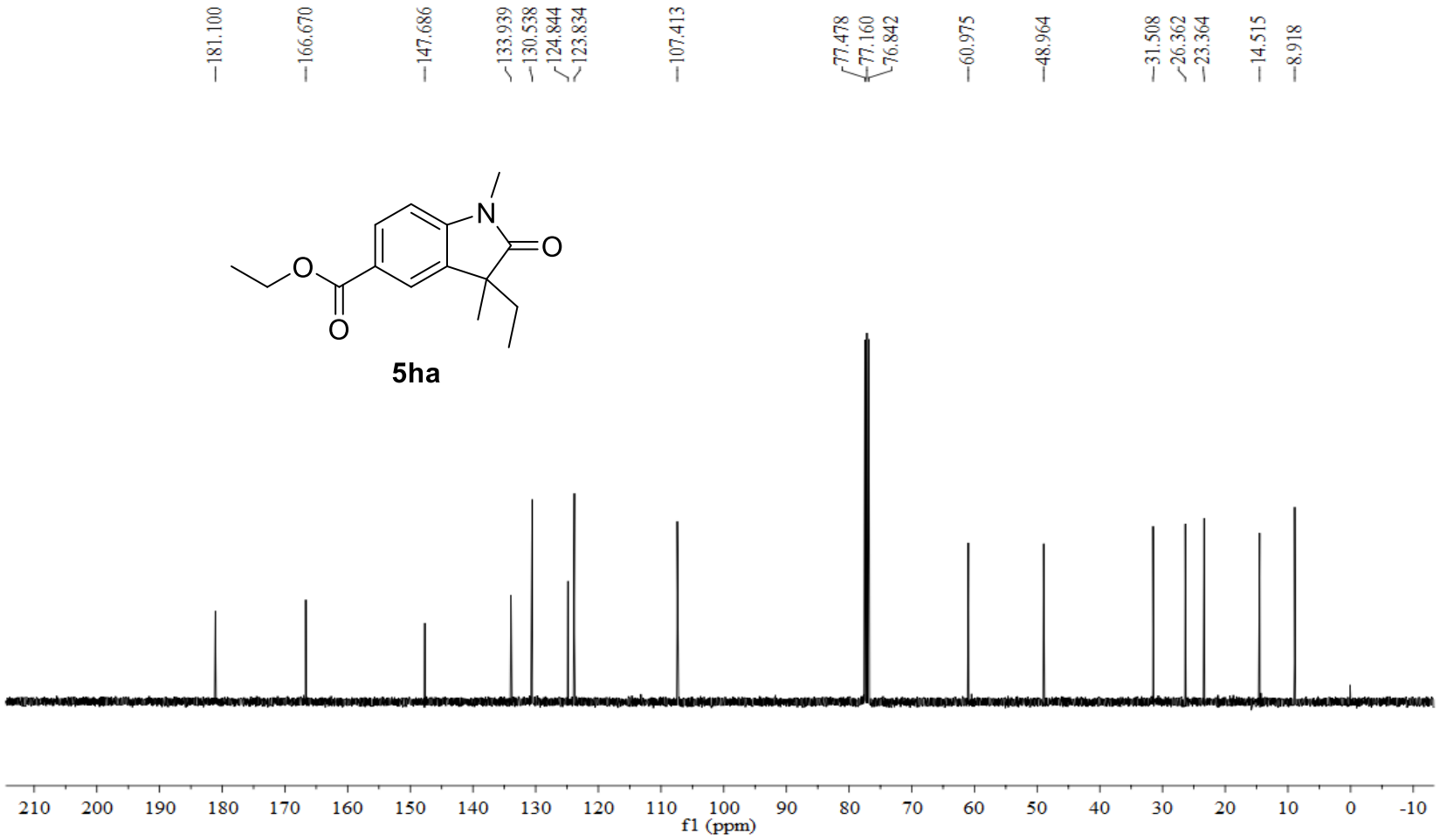

7.382
7.380
7.377
7.362
7.359
7.357
7.260
7.255
6.714
6.694
3.178
1.939
1.921
1.905
1.887
1.868
1.776
1.758
1.739
1.724
1.705
1.326
0.595
0.577
0.558
Br
N
O
5fa
1.958
1.939
1.921
1.905
1.887
1.868
1.776
1.758
1.739
1.724
1.705
1.687
1.04
1.04
1.95 1.90 1.85 1.80 1.75 1.70
f1 (ppm)
0.94
1.14
0.96
3.00
1.04
1.04
2.92
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

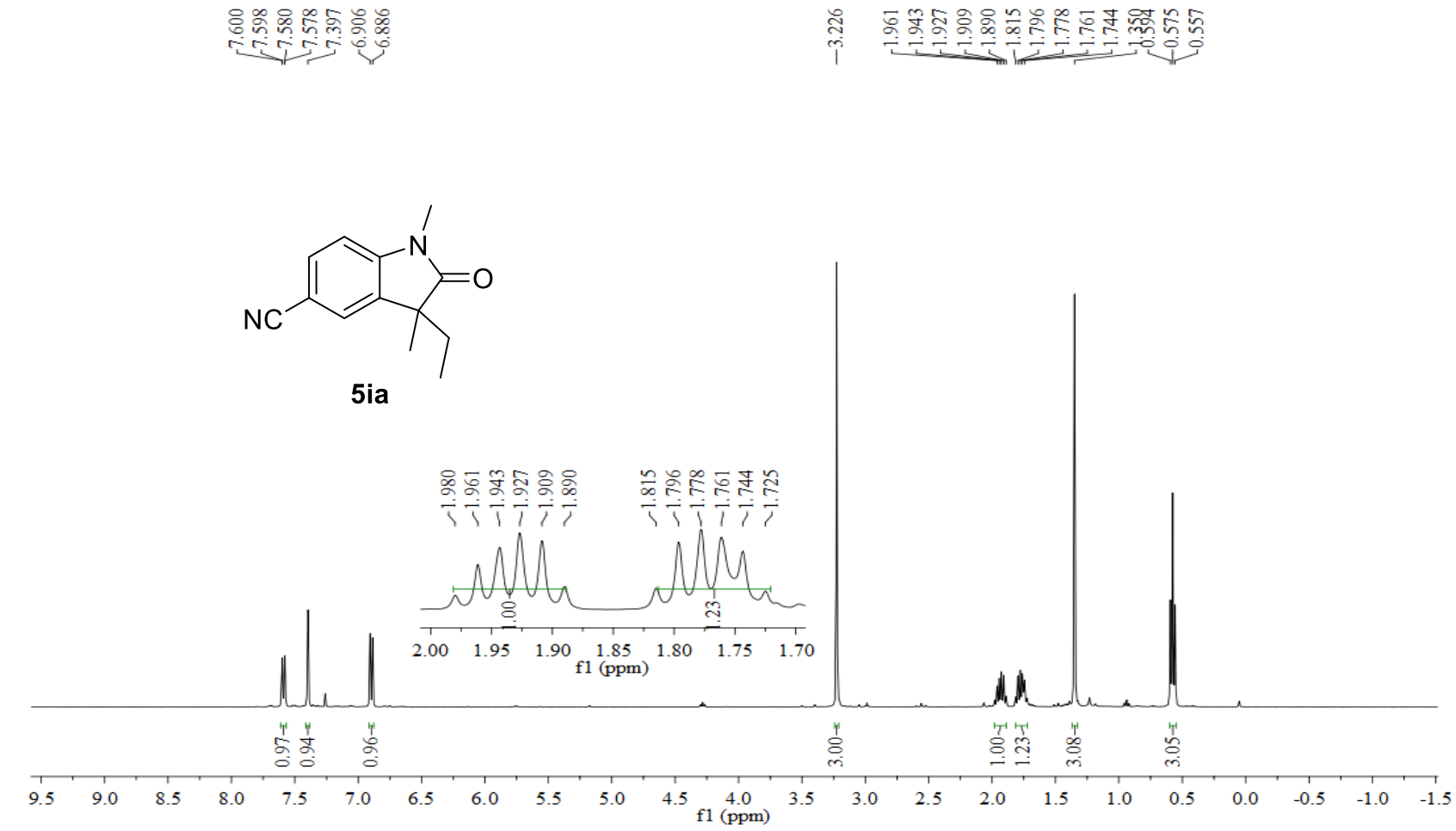

180.129
142.642
136.173
130.557
125.918
115.243
109.368
77.479
77.160
76.843
49.321
31.508
26.247
23.339
8.913
N
O
Br
5fa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

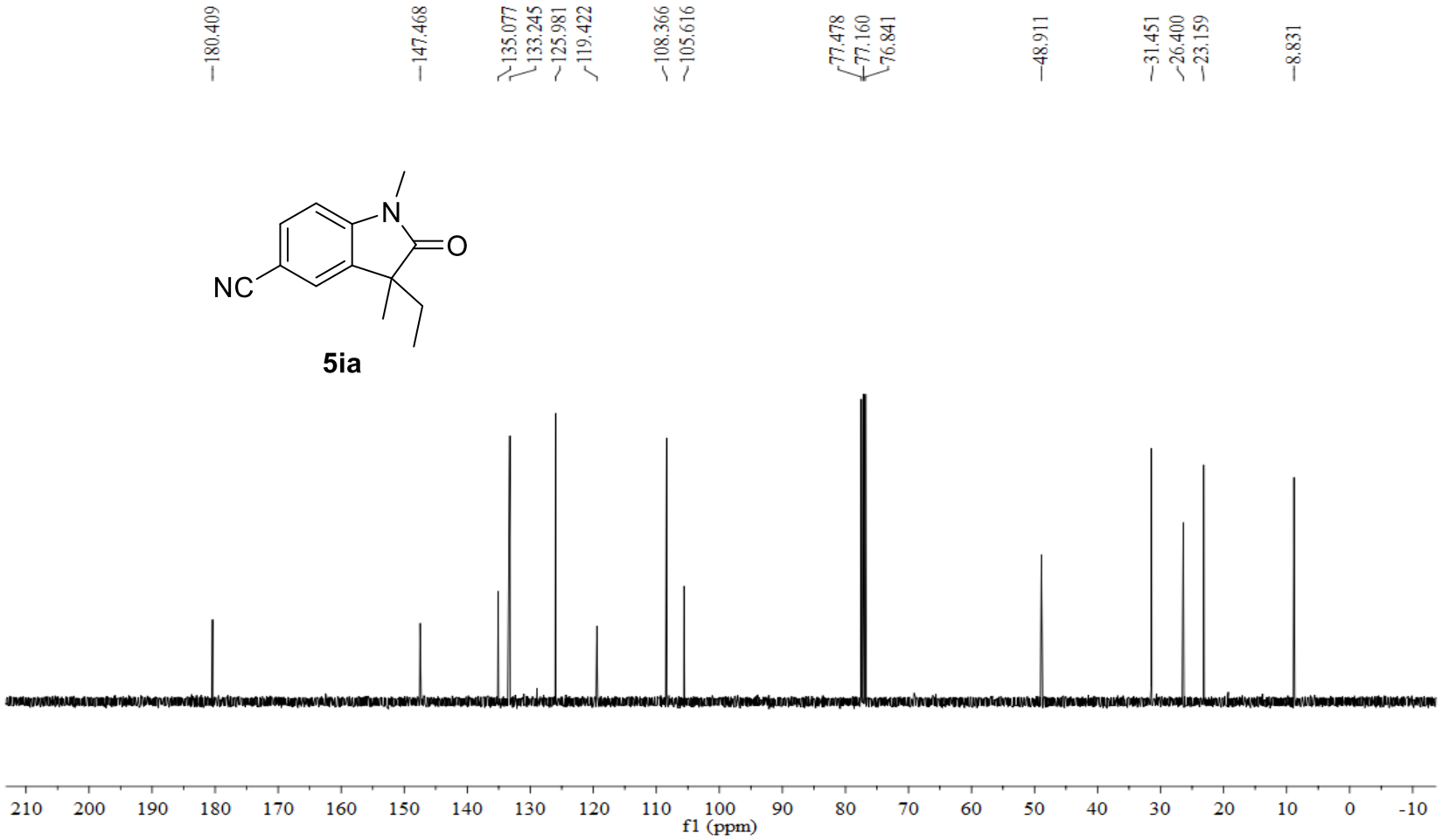

7.591
7.570
7.438
7.260
6.634
6.614
3.184
1.946
1.929
1.912
1.894
1.875
1.782
1.763
1.745
1.729
1.711
1.333
0.605
0.586
0.568
N
O
I
5ga
1.964
1.946
1.929
1.912
1.894
1.875
1.782
1.763
1.745
1.729
1.711
1.692
1.03
1.08
1.95
1.90
1.85
1.80
1.75
1.70
f1 (ppm)
1.01
1.14
0.89
3.00
1.03
1.08
3.09
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

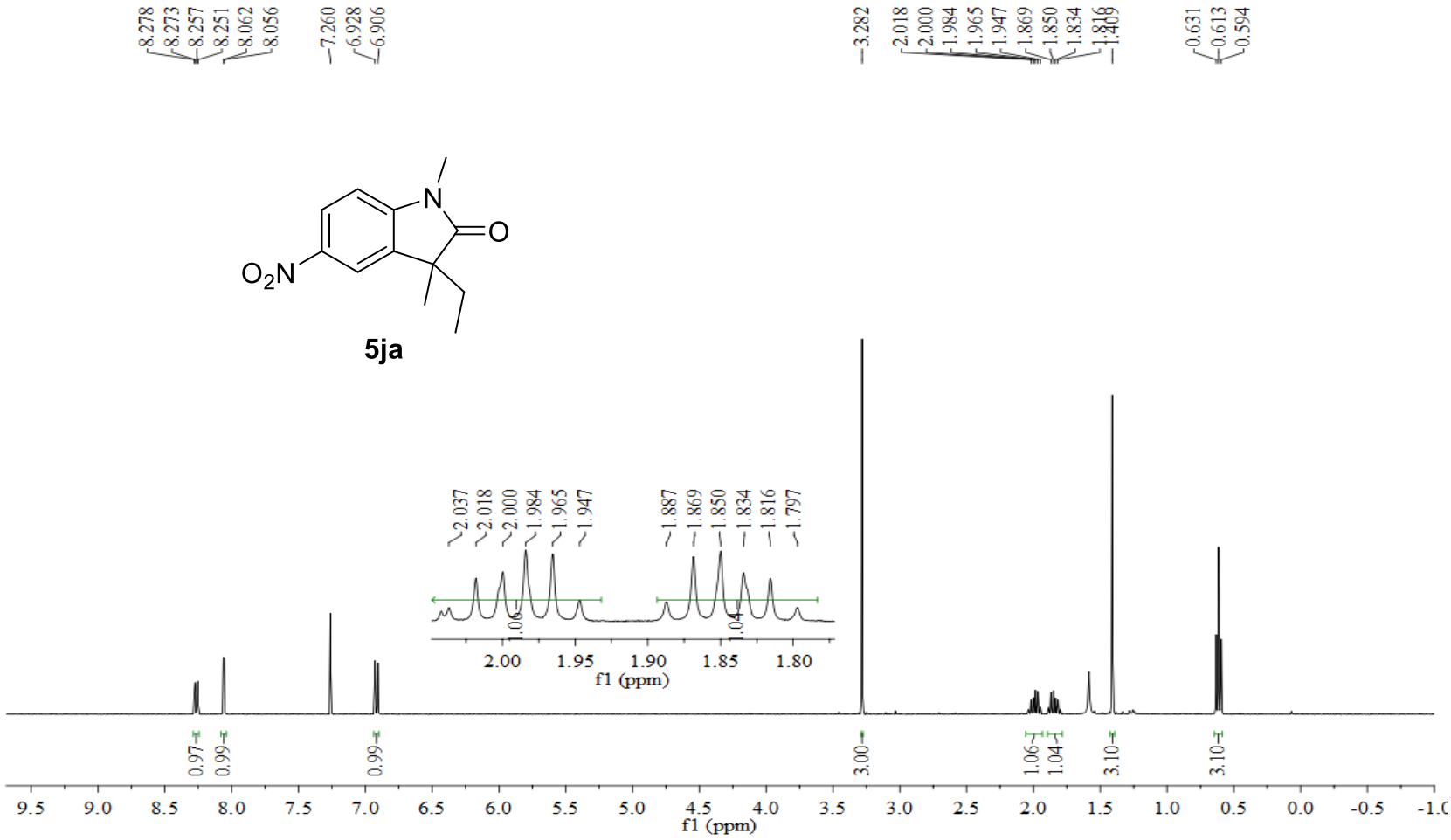

179.996
143.364
136.581
131.505
110.016
85.156
77.478
77.160
76.842
49.186
31.535
26.221
23.367
8.952
N
O
I
5ga
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

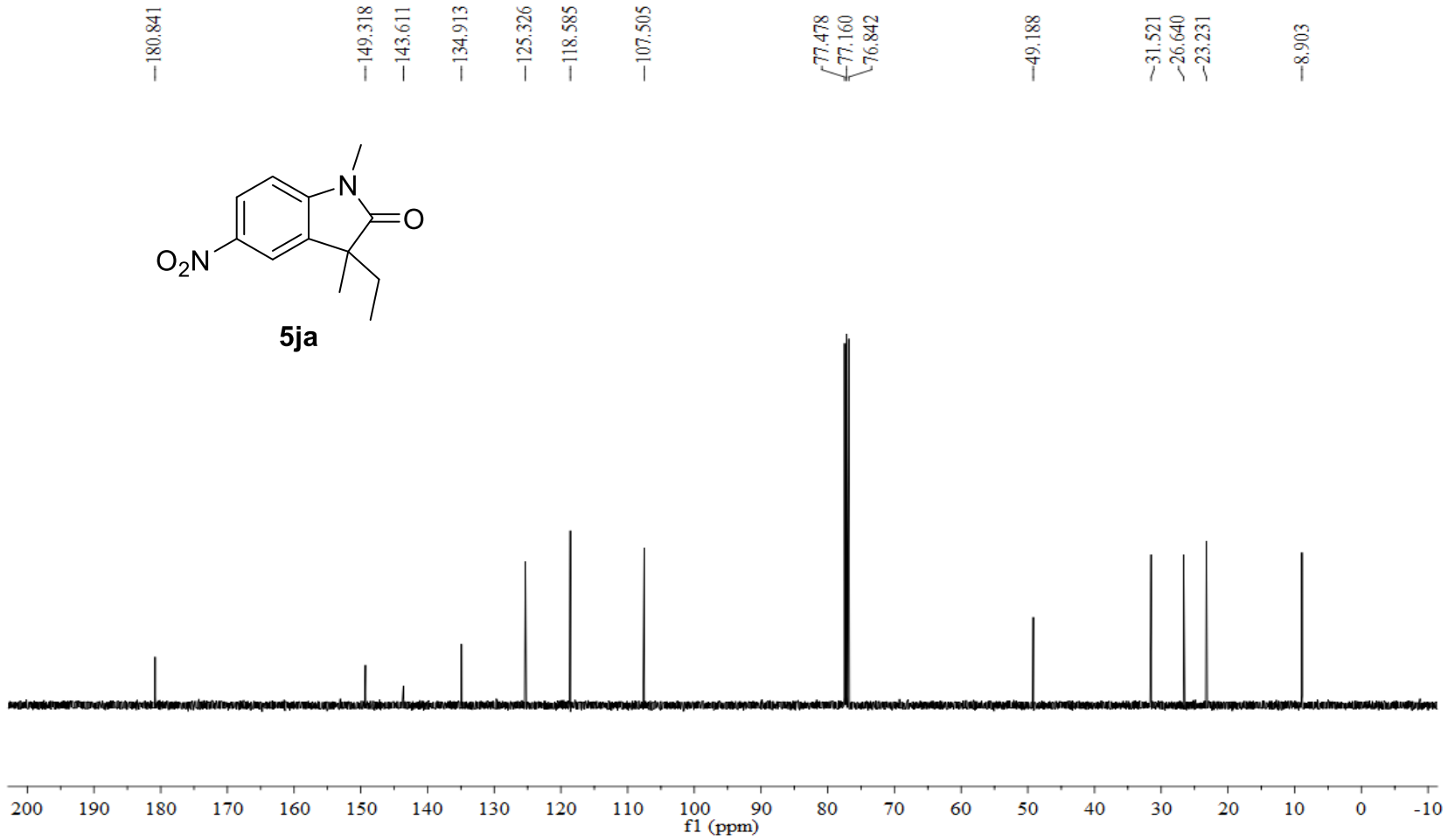

8.024
8.004
7.822
7.260
6.865
6.845
4.388
4.370
4.352
4.334
3.230
1.967
1.949
1.933
1.915
1.896
1.831
1.812
1.796
1.778
1.408
1.390
1.372
1.360
0.580
0.561
0.543
N
O
O
O
5ha
1.985
1.967
1.949
1.933
1.915
1.896
1.849
1.831
1.812
1.796
1.778
1.760
1.07
1.12
2.00 1.95 1.90 1.85 1.80 1.75
f1 (ppm)
1.01
1.01
1.00
2.05
3.00
1.07
1.12
3.03
2.98
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

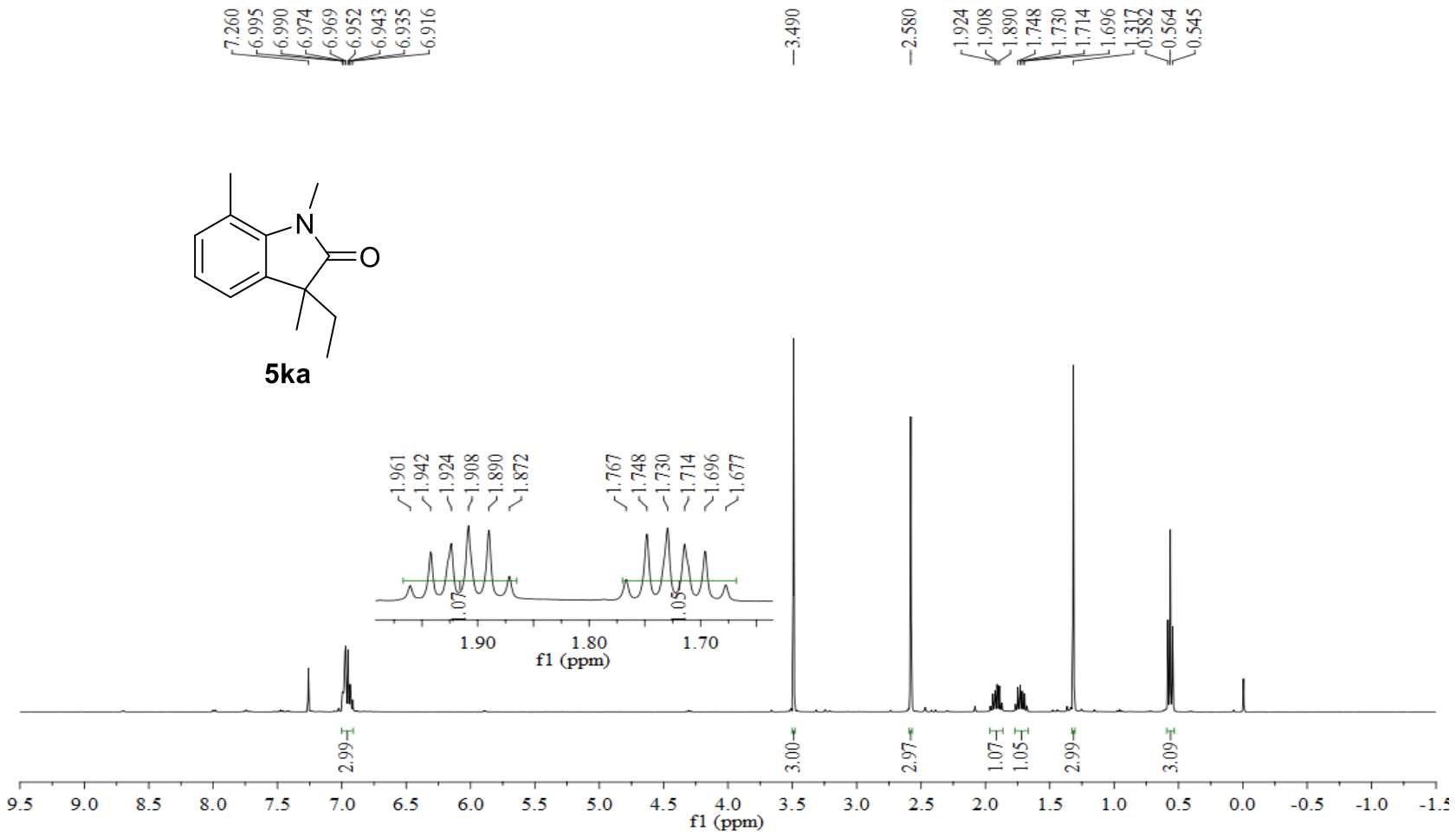

181.100
166.670
147.686
133.939
130.538
124.844
123.834
107.413
77.478
77.160
76.842
60.975
48.964
31.508
26.362
23.364
14.515
8.918
N
O
O
O
5ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

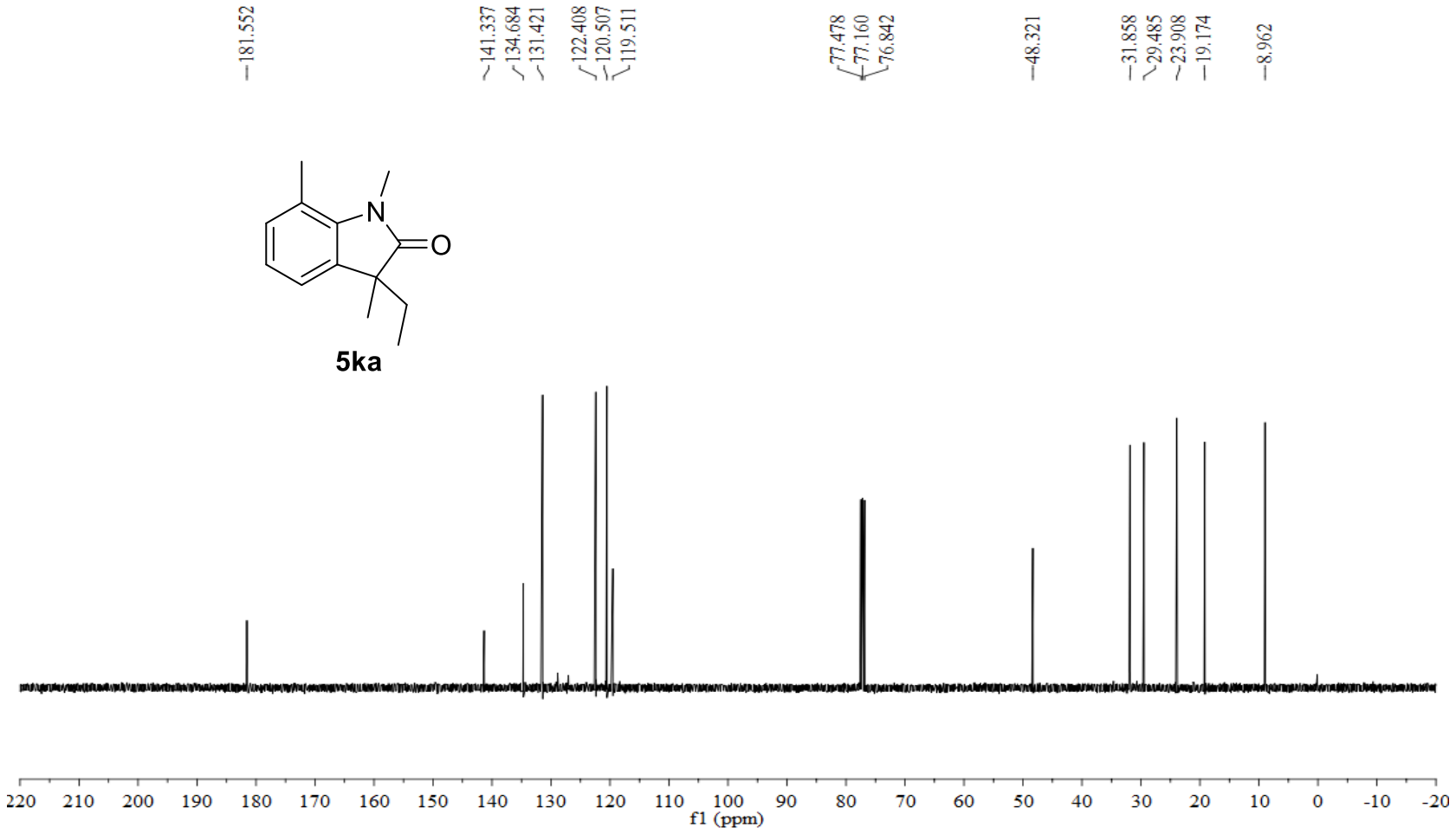

7.600
7.598
7.580
7.578
7.397
6.906
6.886
3.226
1.961
1.943
1.927
1.909
1.890
1.815
1.796
1.778
1.761
1.744
1.350
1.334
0.575
0.557
N
O
NC
5ia
1.980
1.961
1.943
1.927
1.909
1.890
1.815
1.796
1.778
1.761
1.744
1.725
1.00
1.23
2.00 1.95 1.90 1.85 1.80 1.75 1.70
f1 (ppm)
0.97
0.94
0.96
3.00
1.00
1.23
3.08
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

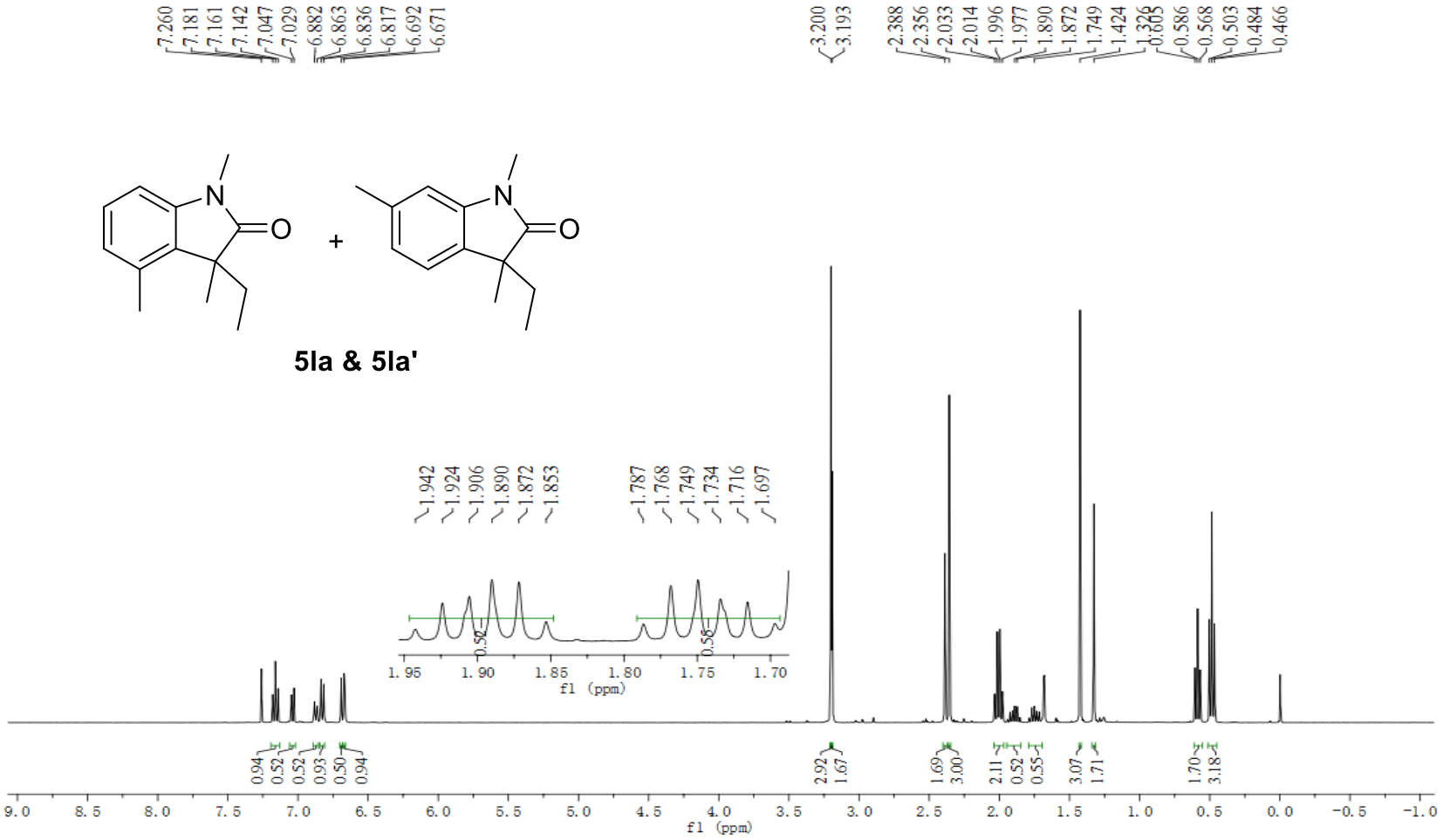

180.409
147.468
135.077
133.245
125.981
119.422
108.366
105.616
77.478
77.160
76.841
48.911
31.451
26.400
23.159
8.831
N
O
NC
5ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

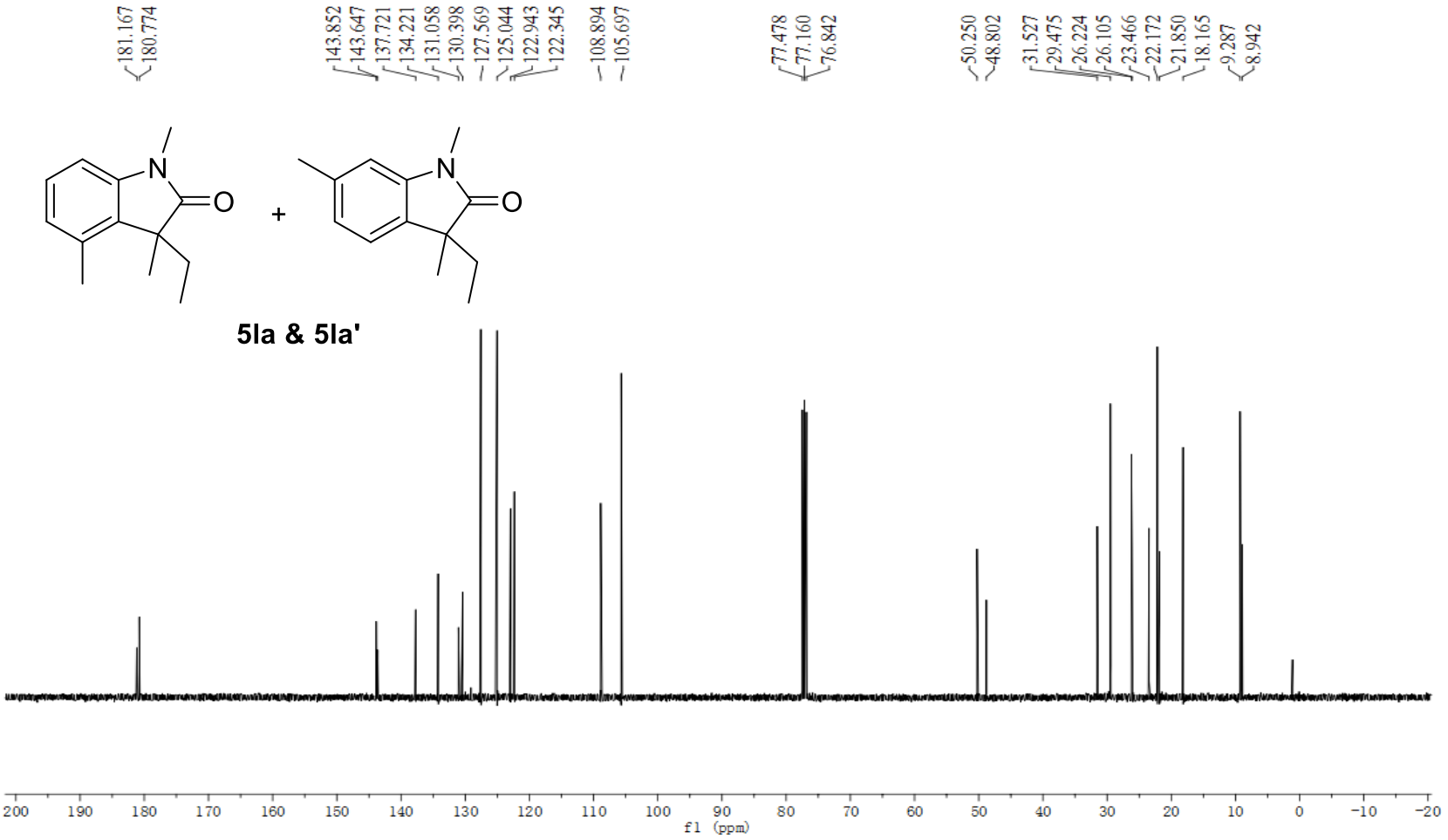

8.278
8.273
8.257
8.251
8.062
8.056
7.260
6.928
6.906
3.282
2.018
2.000
1.984
1.965
1.947
1.869
1.850
1.834
1.816
1.409
0.631
0.613
0.594
N
O
O2N
5ja
2.037
2.018
2.000
1.984
1.965
1.947
1.887
1.869
1.850
1.834
1.816
1.797
1.06
1.04
2.00
1.95
1.90
1.85
1.80
f1 (ppm)
0.97
0.99
0.99
3.00
1.06
1.04
3.10
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

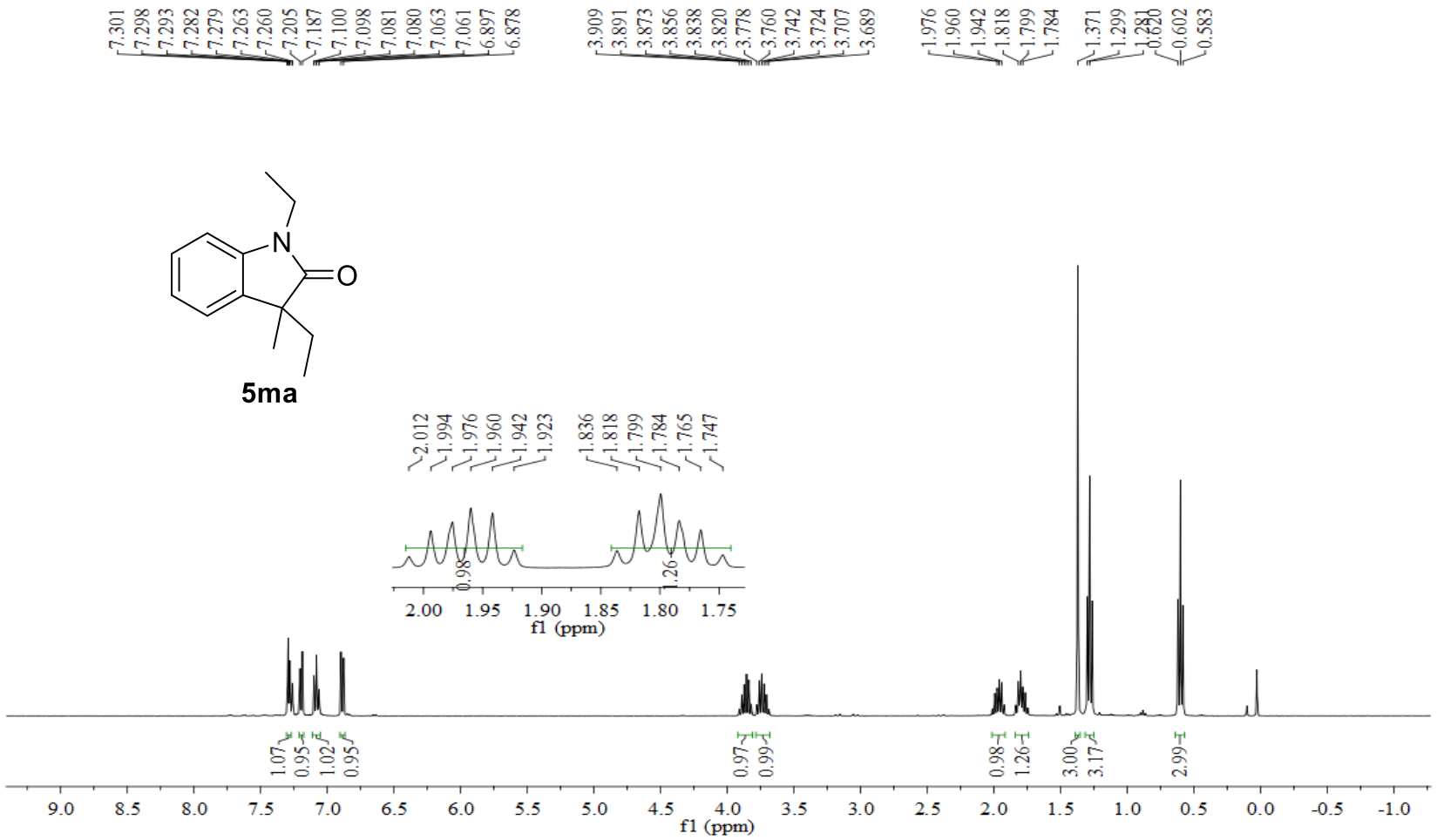

180.841
149.318
143.611
134.913
125.326
118.585
107.505
77.478
77.160
76.842
49.188
31.521
26.640
23.231
8.903
N
O
O2N
5ja
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

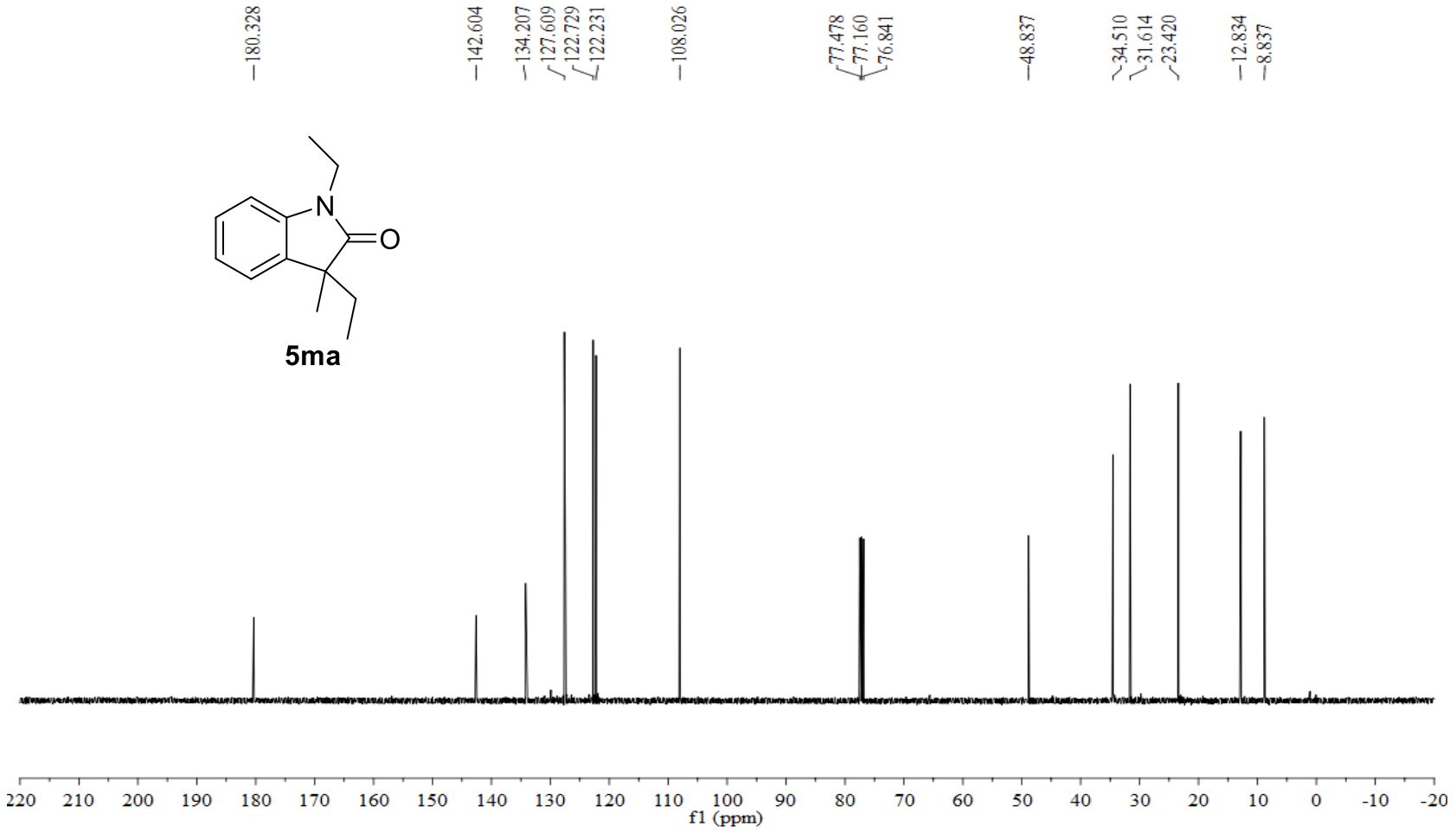

7.260
6.995
6.990
6.974
6.969
6.952
6.943
6.935
6.916
3.490
2.580
1.924
1.908
1.890
1.748
1.730
1.714
1.696
1.317
0.582
0.564
0.545
N
O
5ka
1.961
1.942
1.924
1.908
1.890
1.872
1.767
1.748
1.730
1.714
1.696
1.677
1.07
1.05
1.90
1.80
1.70
f1 (ppm)
2.99
3.00
2.97
1.07
1.05
2.99
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

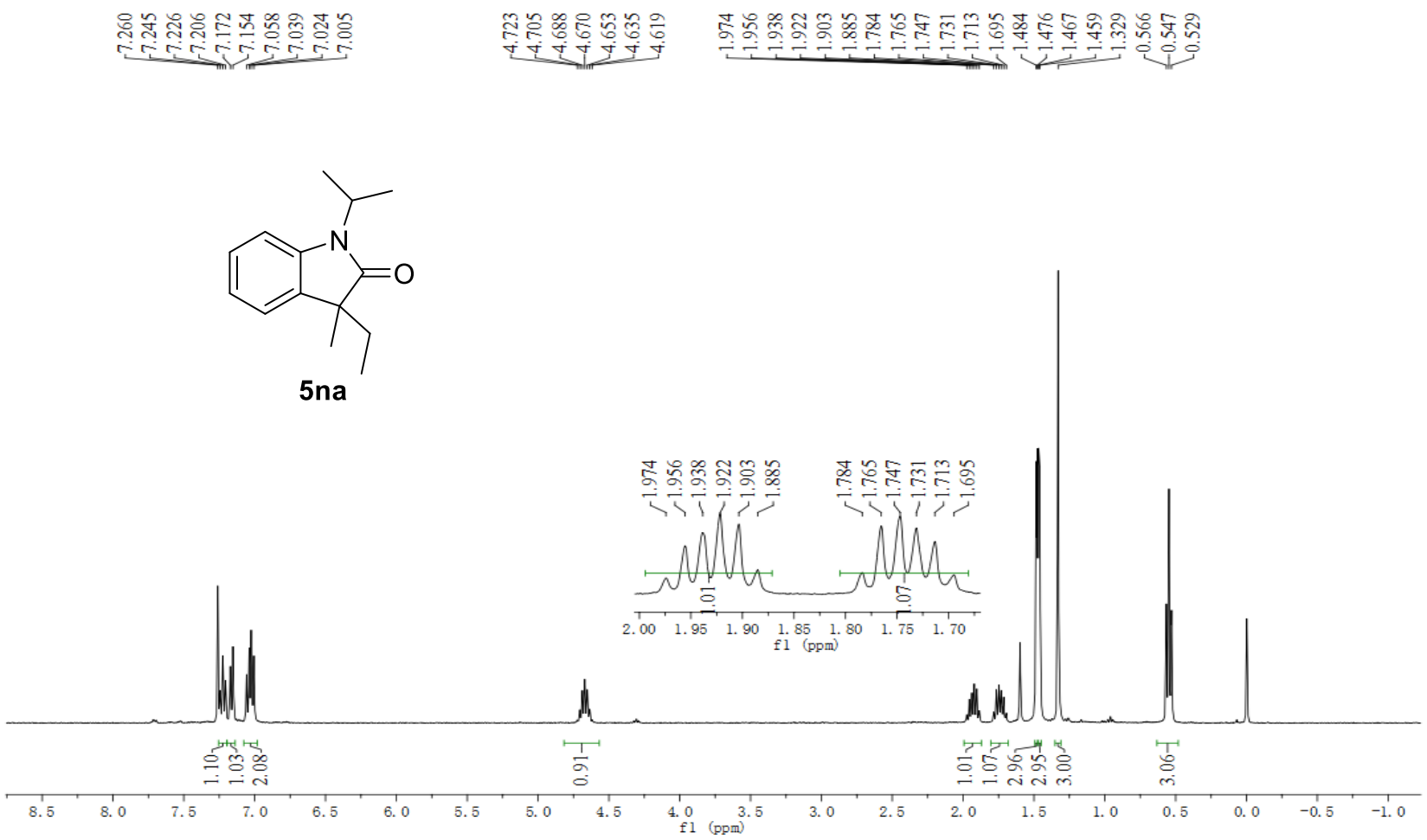

181.552
141.337
134.684
131.421
122.408
120.507
119.511
77.478
77.160
76.842
48.321
31.858
29.485
23.908
19.174
8.962
N
O
5ka
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

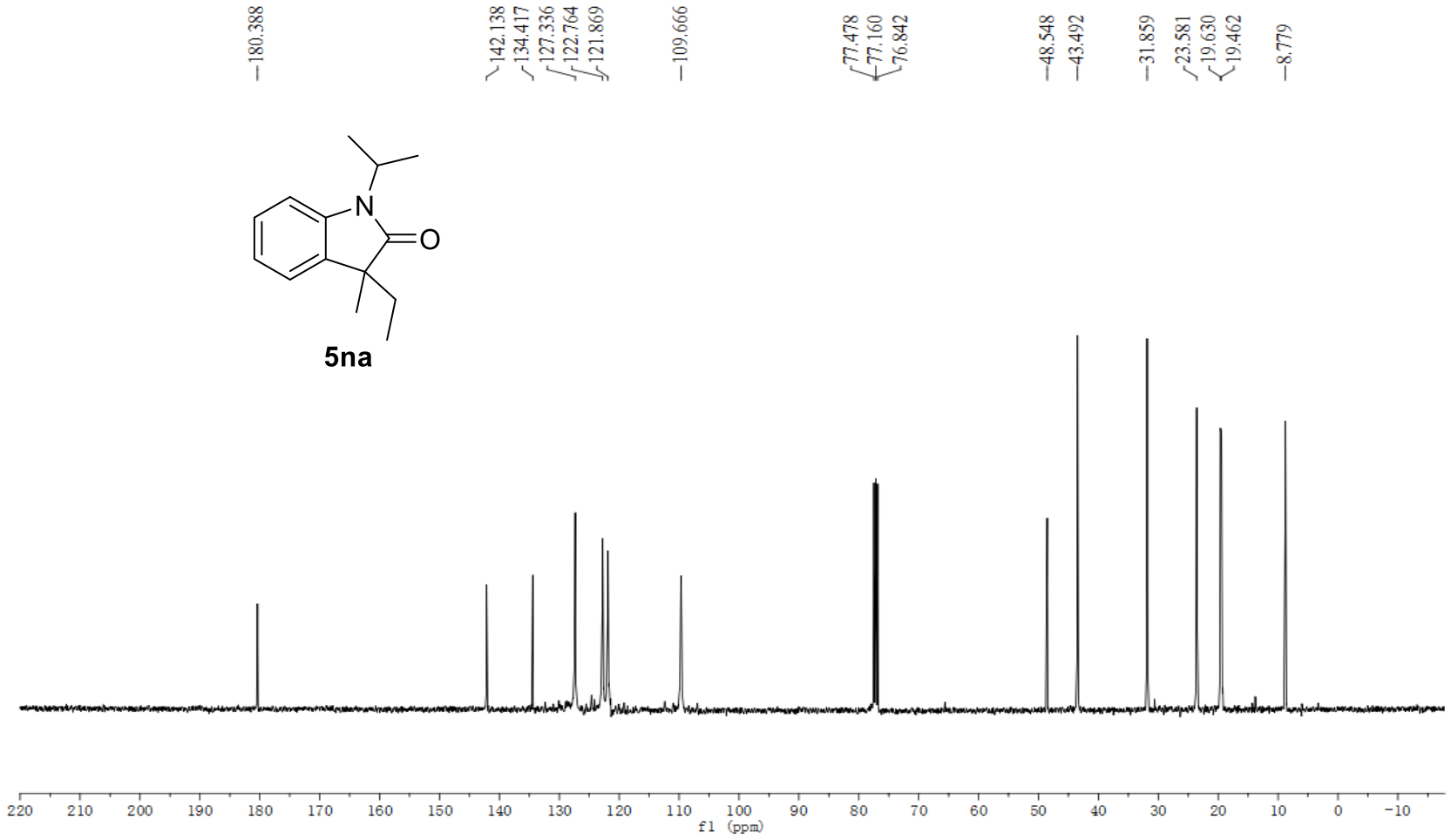

7.260
7.181
7.161
7.142
7.047
7.029
6.882
6.863
6.836
6.817
6.692
6.671
3.200
3.193
2.388
2.356
2.033
2.014
1.996
1.977
1.890
1.872
1.749
1.424
1.326
0.605
0.586
0.568
0.503
0.484
0.466
N
O
+
N
O
5la & 5la'
1.942
1.924
1.906
1.890
1.872
1.853
1.787
1.768
1.749
1.734
1.716
1.697
0.58
0.58
1.95
1.90
1.85
1.80
1.75
1.70
f1 (ppm)
0.94
0.52
0.52
0.93
0.50
0.94
2.92
1.67
1.69
3.00
2.11
0.52
0.55
3.07
1.71
1.70
3.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


181.167
180.774
143.852
143.647
137.721
134.221
131.058
130.398
127.569
125.044
122.943
122.345
108.894
105.697
77.478
77.160
76.842
50.250
48.802
31.527
29.475
26.224
26.105
23.466
22.172
21.850
18.165
9.287
8.942
N
O
+
N
O
5la & 5la'
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)


7.301
7.298
7.293
7.282
7.279
7.263
7.260
7.205
7.187
7.100
7.098
7.081
7.080
7.063
7.061
6.897
6.878
3.909
3.891
3.873
3.856
3.838
3.820
3.778
3.760
3.742
3.724
3.707
3.689
1.976
1.960
1.942
1.818
1.799
1.784
1.371
1.299
1.281
0.620
0.602
0.583
N
O
5ma
2.012
1.994
1.976
1.960
1.942
1.923
1.836
1.818
1.799
1.784
1.765
1.747
0.98
1.26
2.00 1.95 1.90 1.85 1.80 1.75
f1 (ppm)
1.07
0.95
1.02
0.95
0.97
0.99
0.98
1.26
3.00
3.17
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


180.328
142.604
134.207
127.609
122.729
122.231
108.026
77.478
77.160
76.841
48.837
34.510
31.614
23.420
12.834
8.837
N
O
5ma
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)


7.260
7.245
7.226
7.206
7.172
7.154
7.058
7.039
7.024
7.005
4.723
4.705
4.688
4.670
4.653
4.635
4.619
1.974
1.956
1.938
1.922
1.903
1.885
1.784
1.765
1.747
1.731
1.713
1.695
1.484
1.476
1.467
1.459
1.329
0.566
0.547
0.529
N
O
5na
1.01
1.07
2.00 1.95 1.90 1.85 1.80 1.75 1.70
f1 (ppm)
1.10
1.03
2.08
0.91
1.01
1.07
2.96
2.95
3.00
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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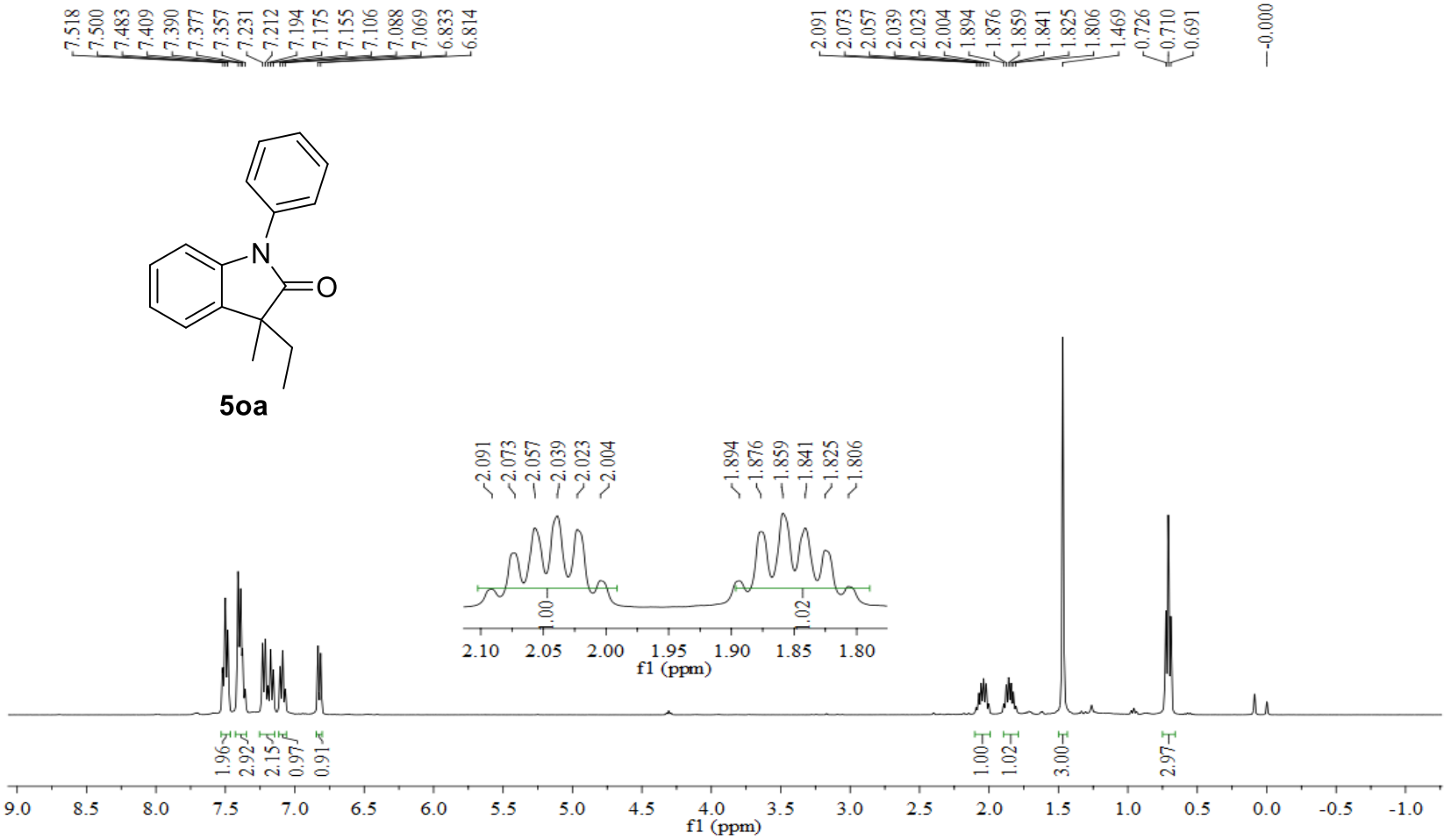
142.138
134.417
127.336
122.764
121.869
109.666
77.478
77.160
76.842
48.548
43.492
31.859
23.581
19.630
19.462
8.779
N
O
5na
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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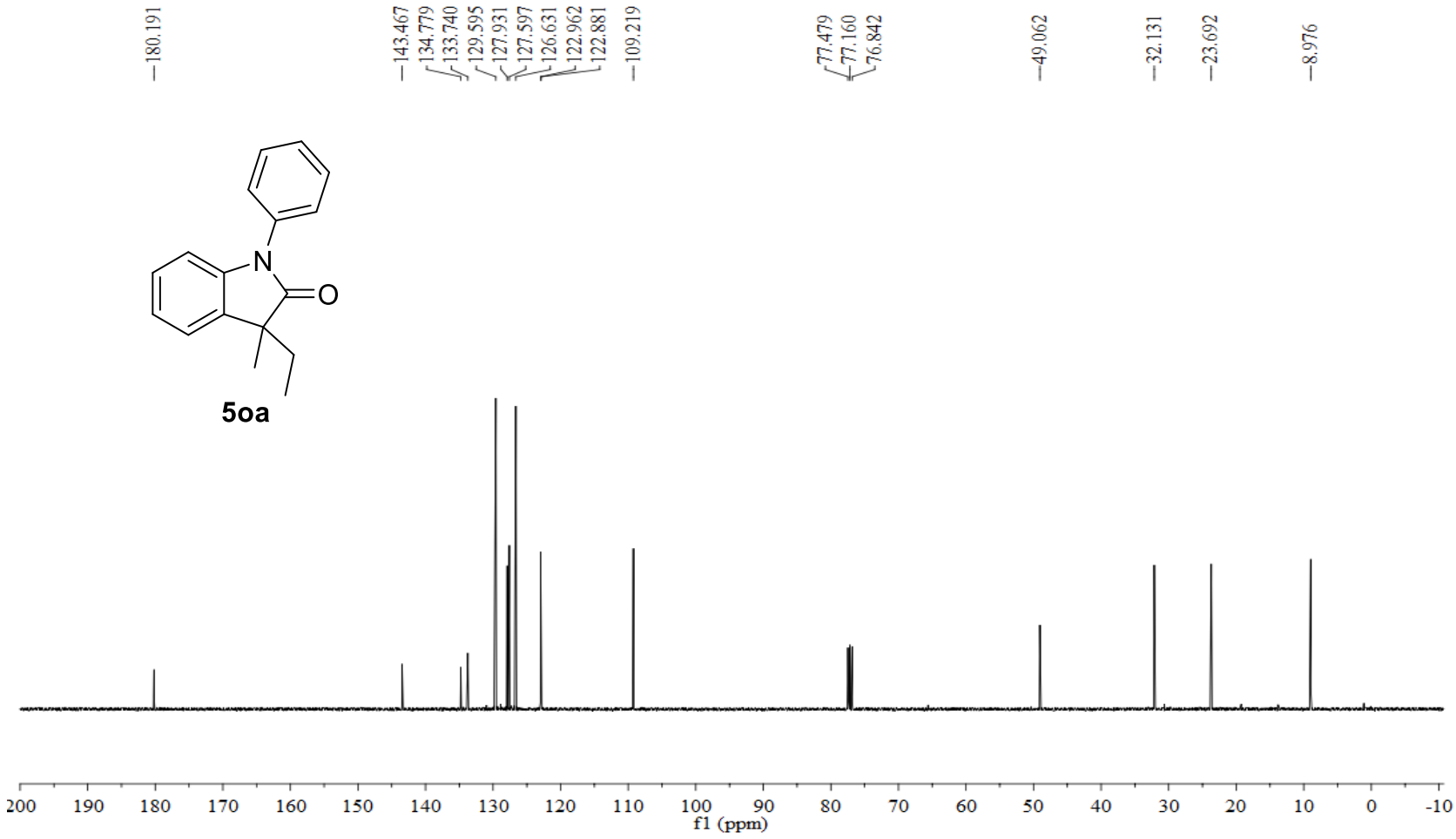
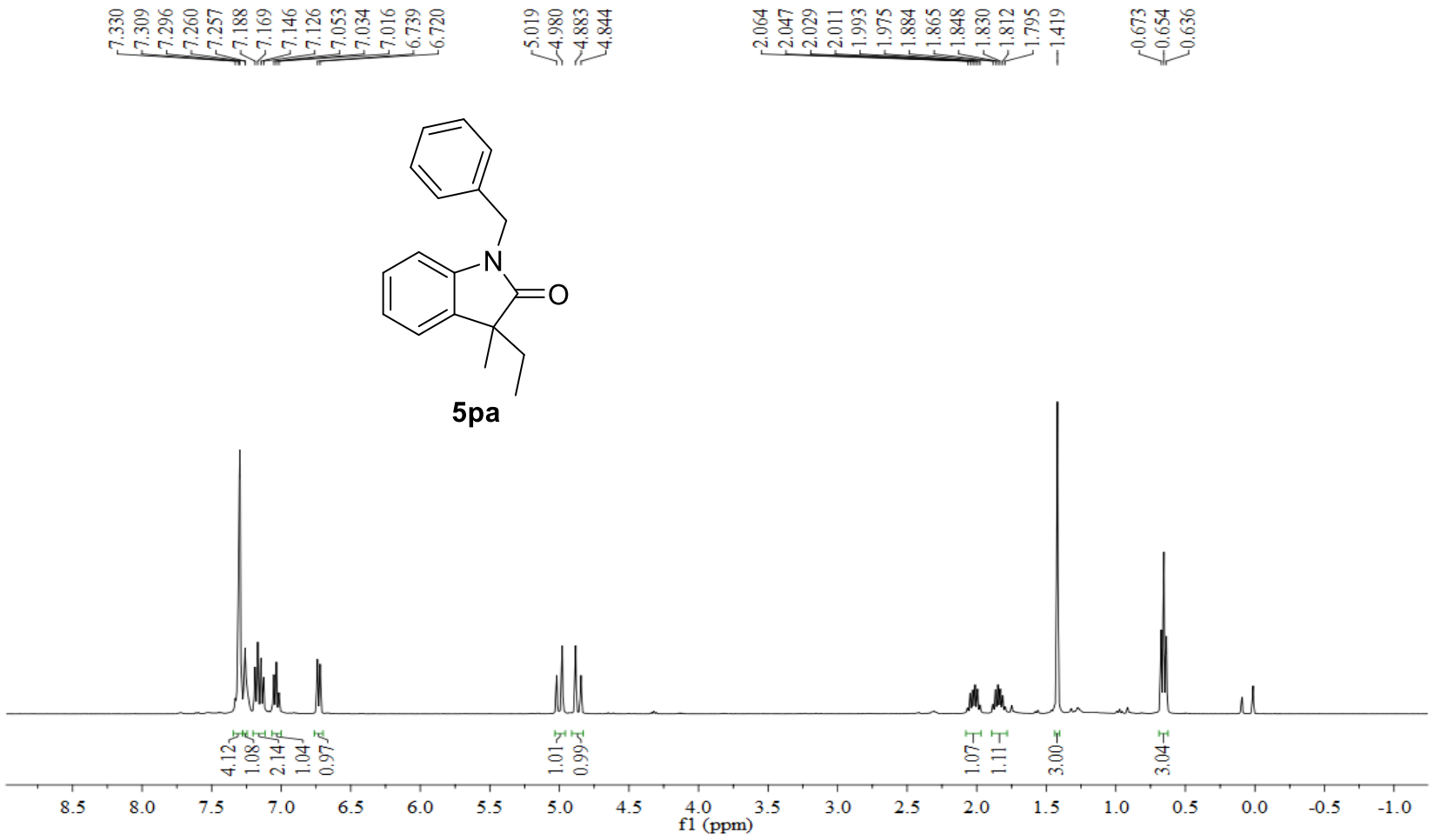
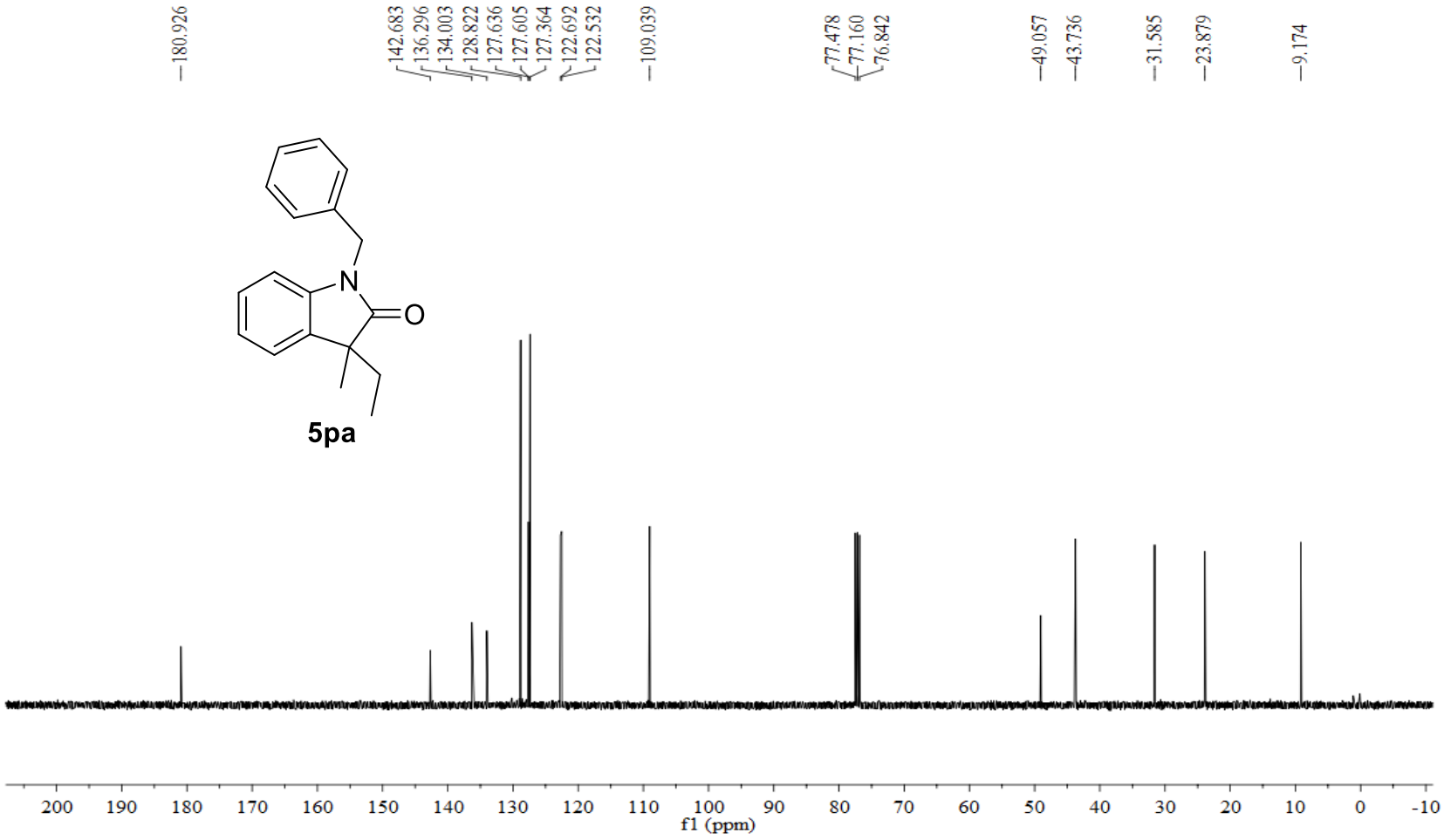
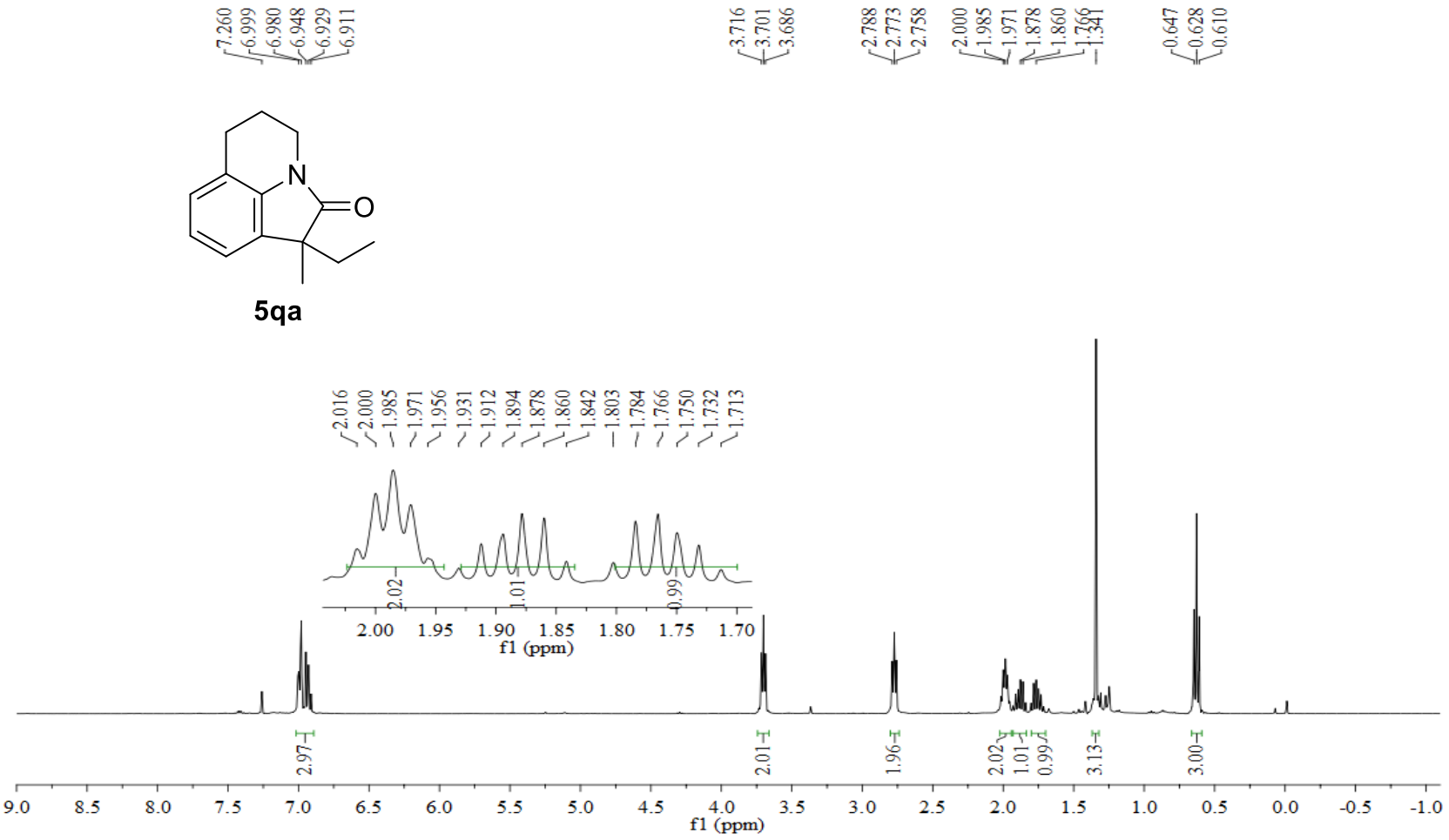
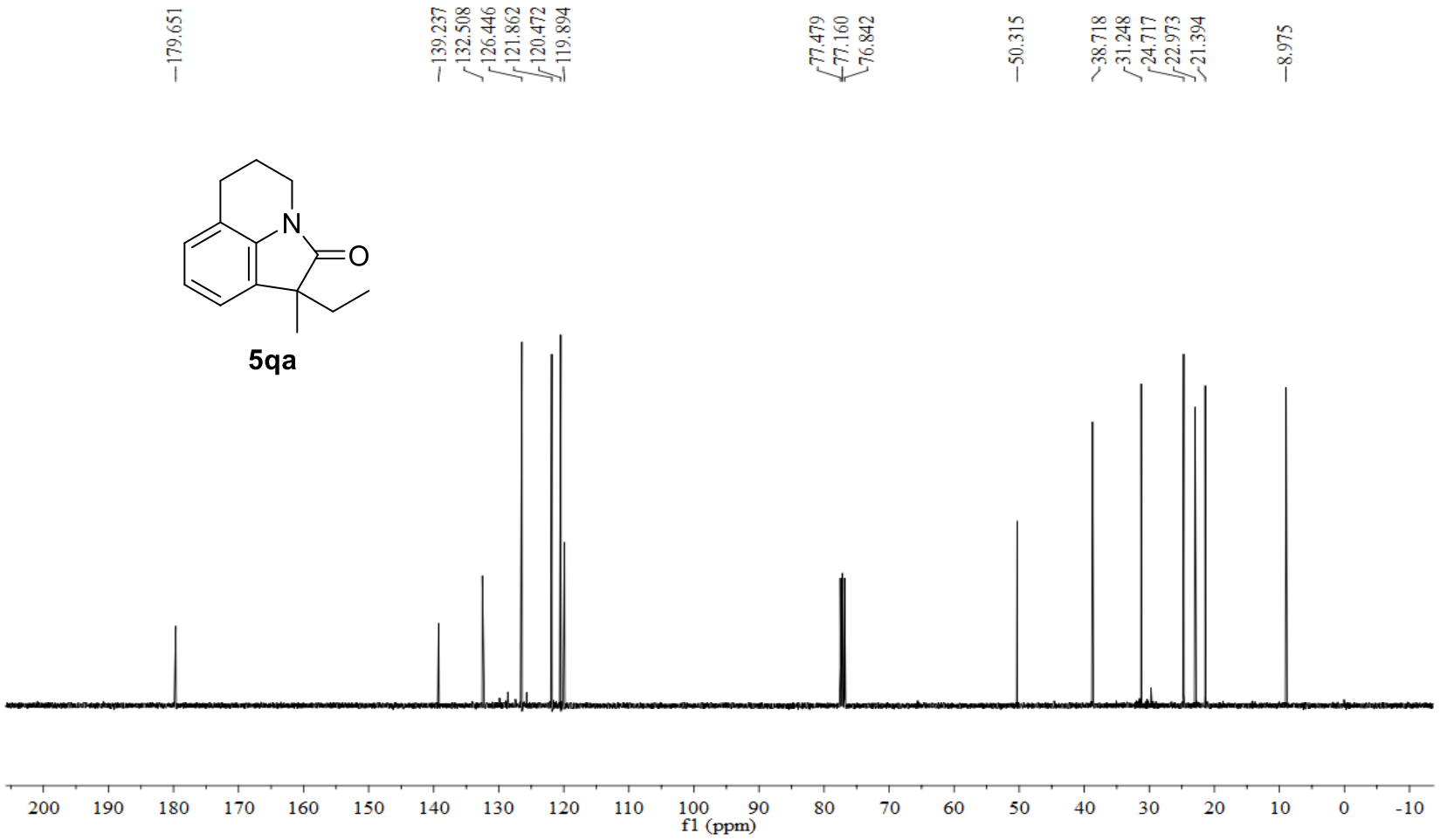
7.500
7.483
7.409
7.390
7.377
7.357
7.231
7.212
7.194
7.175
7.155
7.106
7.088
7.069
6.833
6.814
2.091
2.073
2.057
2.039
2.023
2.004
1.894
1.876
1.859
1.841
1.825
1.806
1.469
0.726
0.710
0.691
-0.000
N
O
5oa
1.00
1.02
2.10 2.05 2.00 1.95 1.90 1.85 1.80
f1 (ppm)
1.96
2.92
2.15
0.97
0.91
1.00
1.02
3.00
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

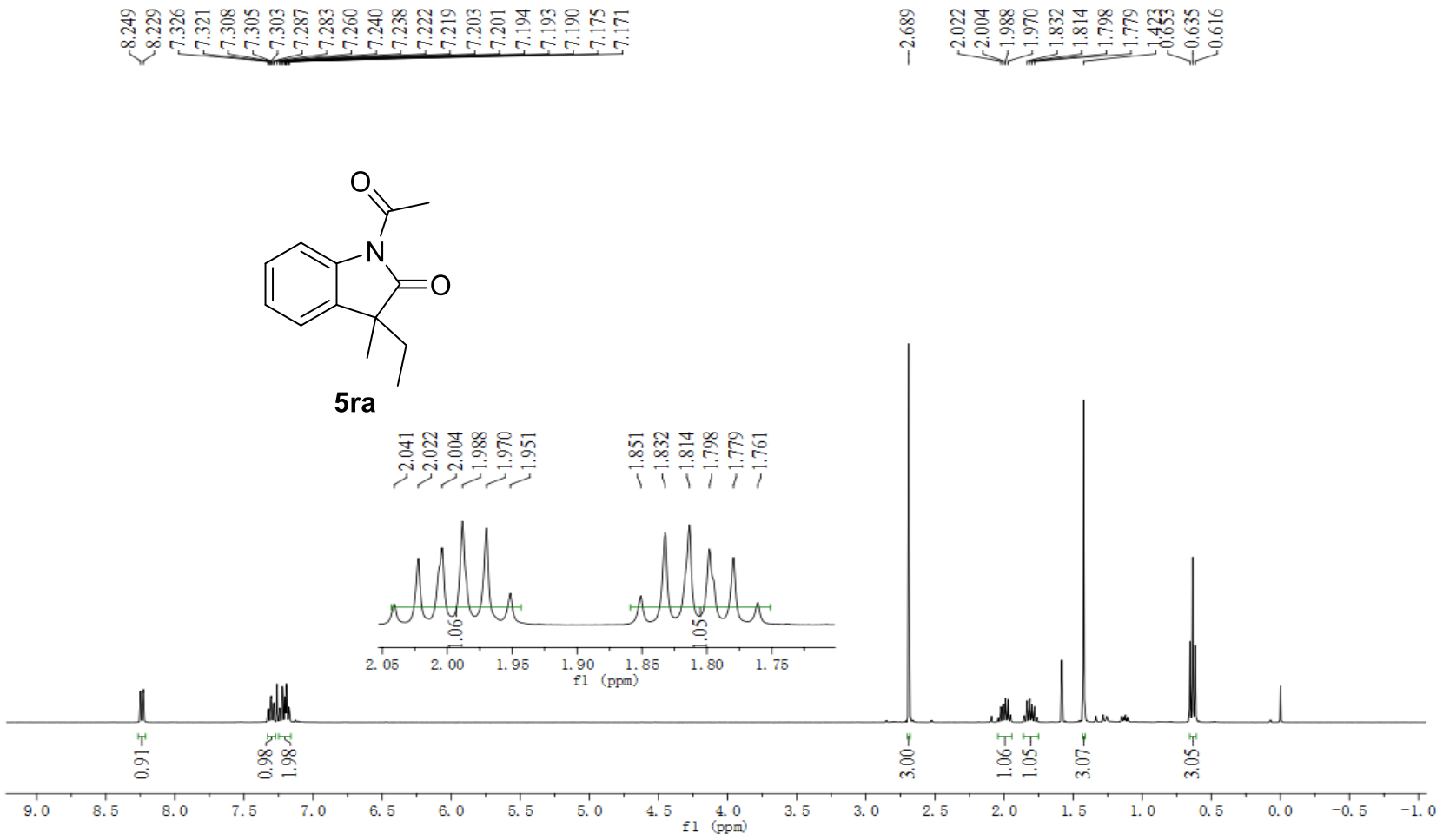

180.191
143.467
134.779
133.740
129.595
127.931
127.597
126.631
122.962
122.881
109.219
77.479
77.160
76.842
49.062
32.131
23.692
8.976
N
O
5oa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

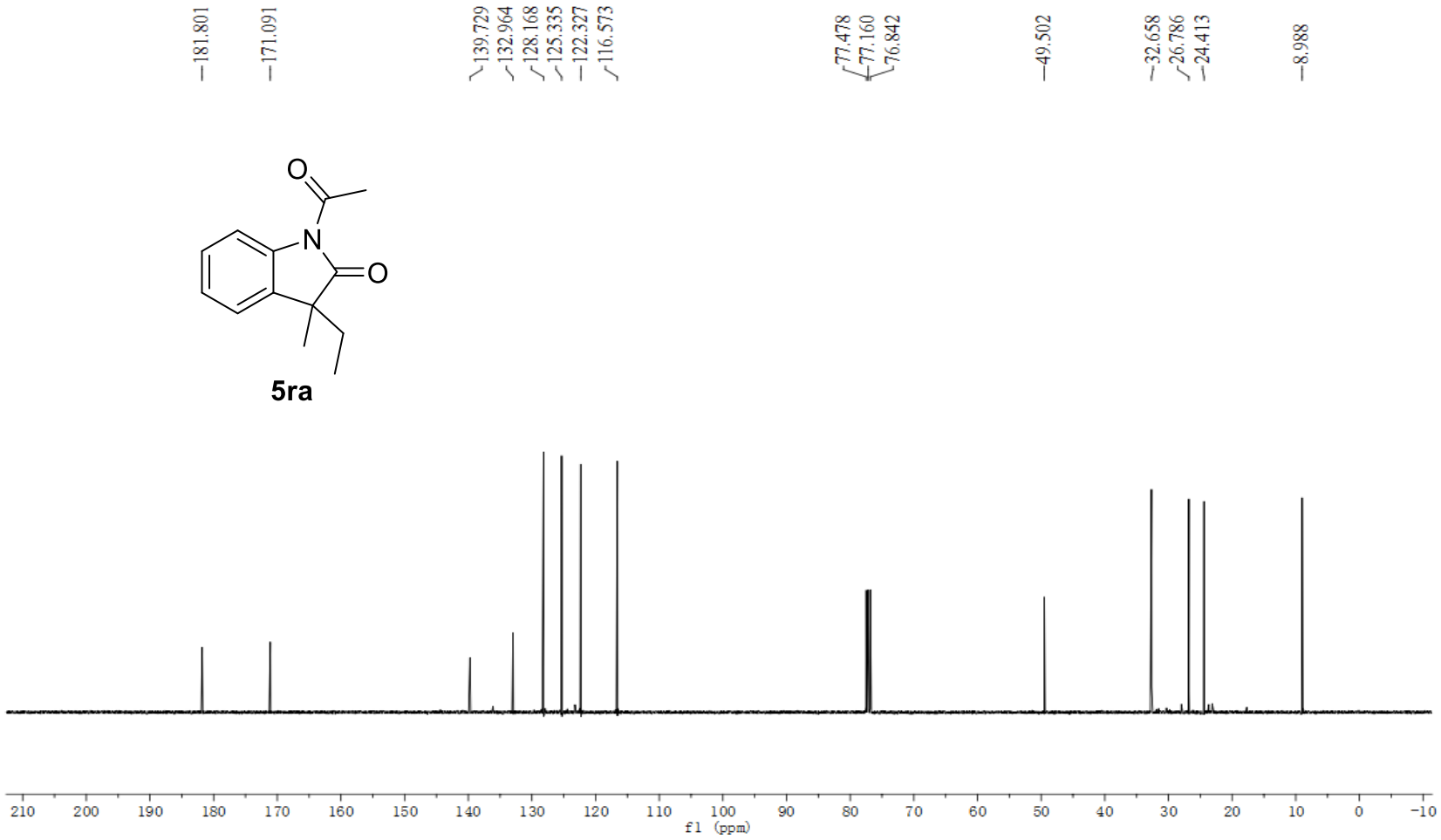

7.330
7.309
7.296
7.260
7.257
7.188
7.169
7.146
7.126
7.053
7.034
7.016
6.739
6.720
5.019
4.980
4.883
4.844
2.064
2.047
2.029
2.011
1.993
1.975
1.884
1.865
1.848
1.830
1.812
1.795
1.419
0.673
0.654
0.636
N
O
5pa
4.12
1.08
2.14
1.04
0.97
1.01
0.99
1.07
1.11
3.00
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

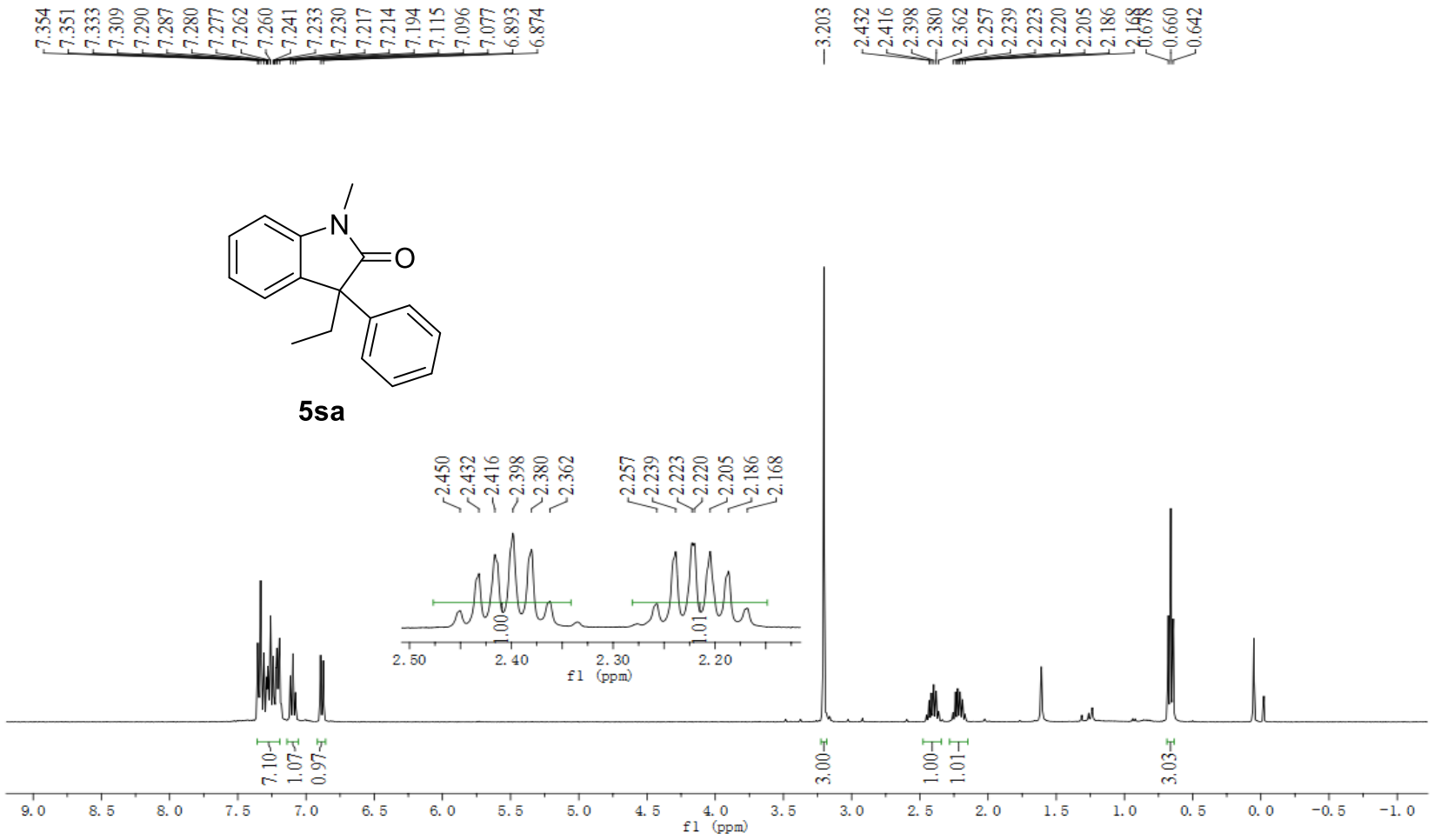

180.926
142.683
136.296
134.003
128.822
127.636
127.605
127.364
122.692
122.532
109.039
77.478
77.160
76.842
49.057
43.736
31.585
23.879
9.174
N
O
5pa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

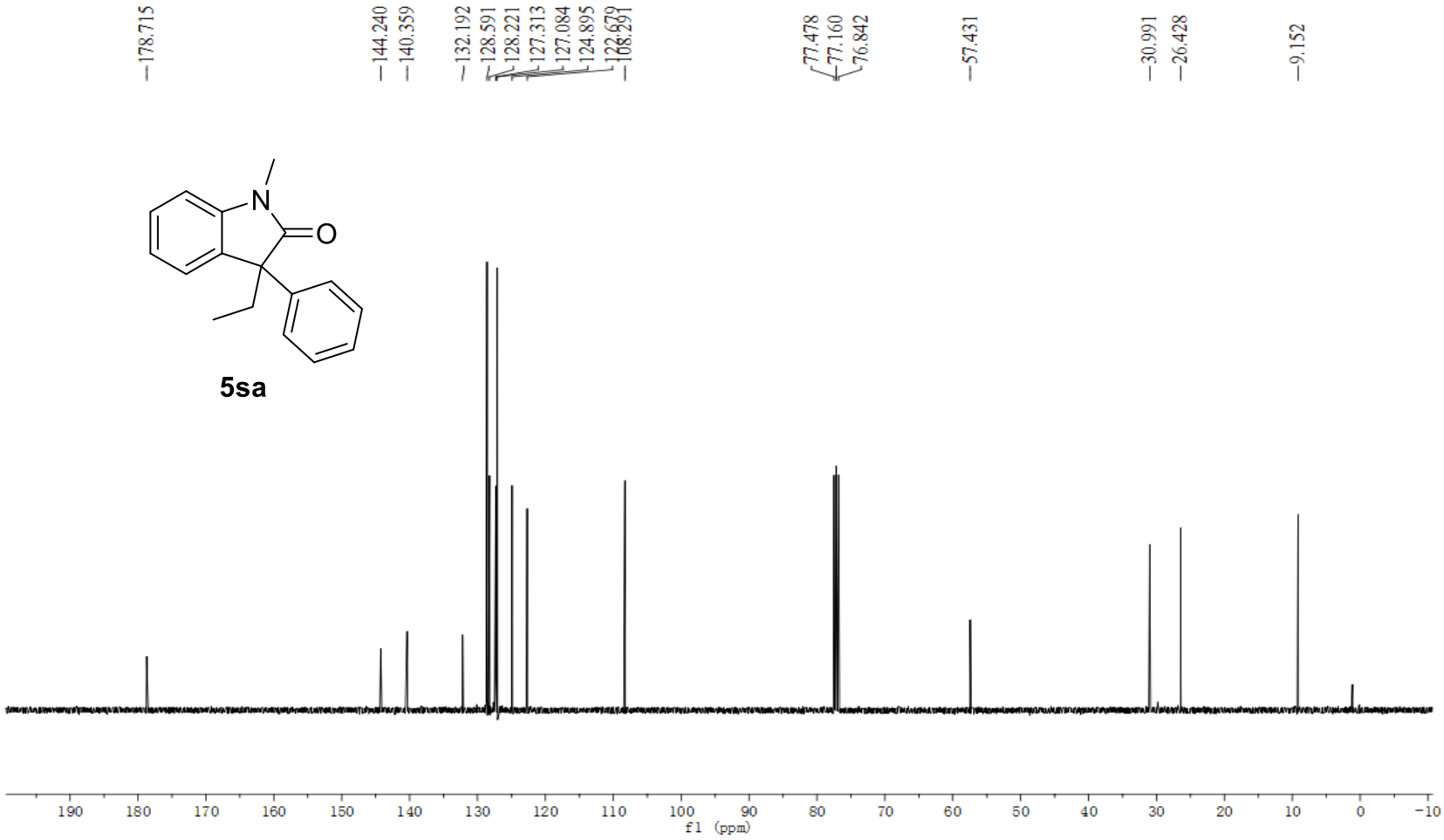

7.260
6.999
6.980
6.948
6.929
6.911
3.716
3.701
3.686
2.788
2.773
2.758
2.000
1.985
1.971
1.878
1.860
1.766
1.341
0.647
0.628
0.610
N
O
5qa
2.016
2.000
1.985
1.971
1.956
1.931
1.912
1.894
1.878
1.860
1.842
1.803
1.784
1.766
1.750
1.732
1.713
2.02
1.01
0.99
2.00 1.95 1.90 1.85 1.80 1.75 1.70
f1 (ppm)
2.97
2.01
1.96
2.02
1.01
0.99
3.13
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

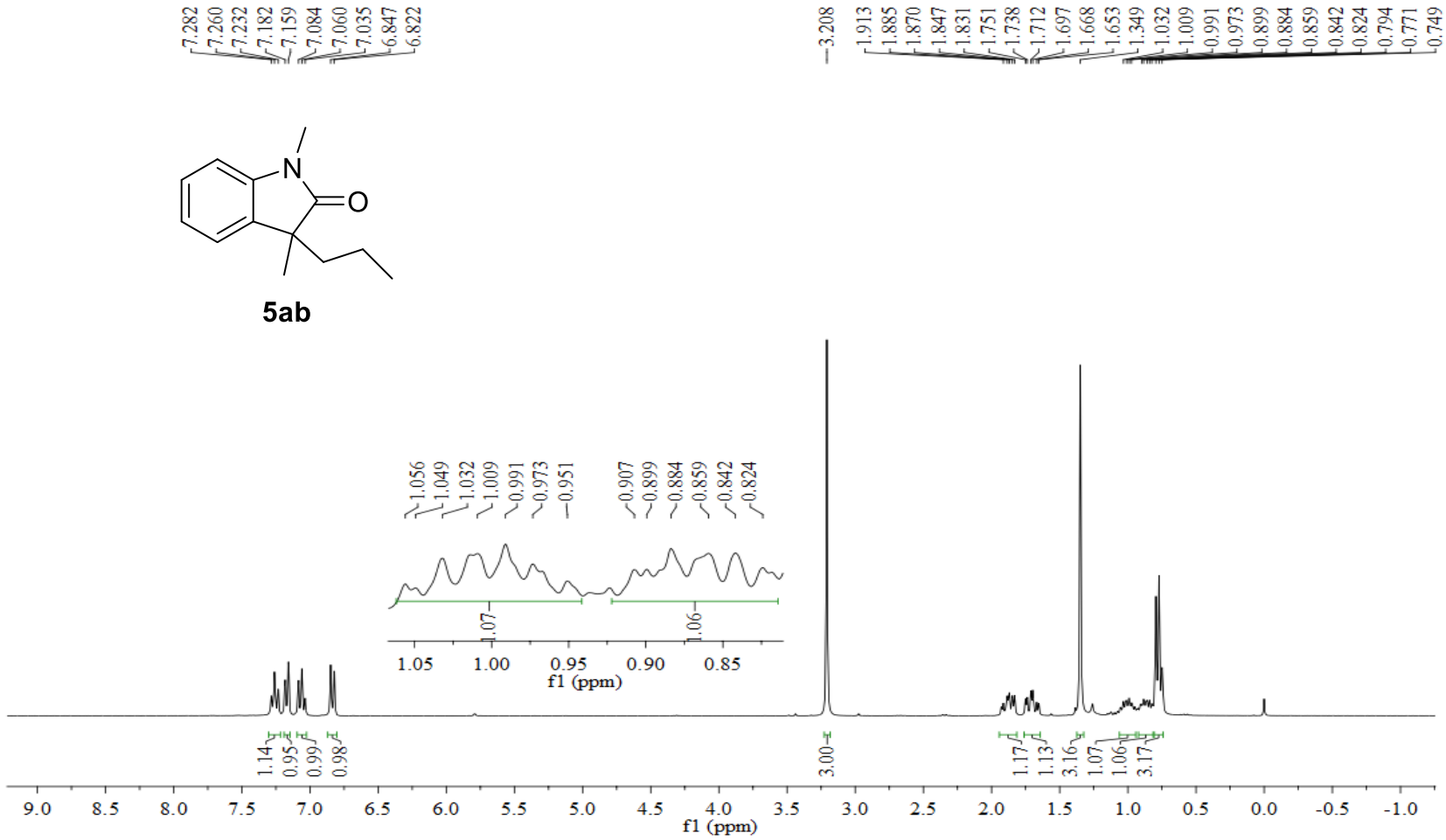

179.651
139.237
132.508
126.446
121.862
120.472
119.894
77.479
77.160
76.842
50.315
38.718
31.248
24.717
22.973
21.394
8.975
N
O
5qa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

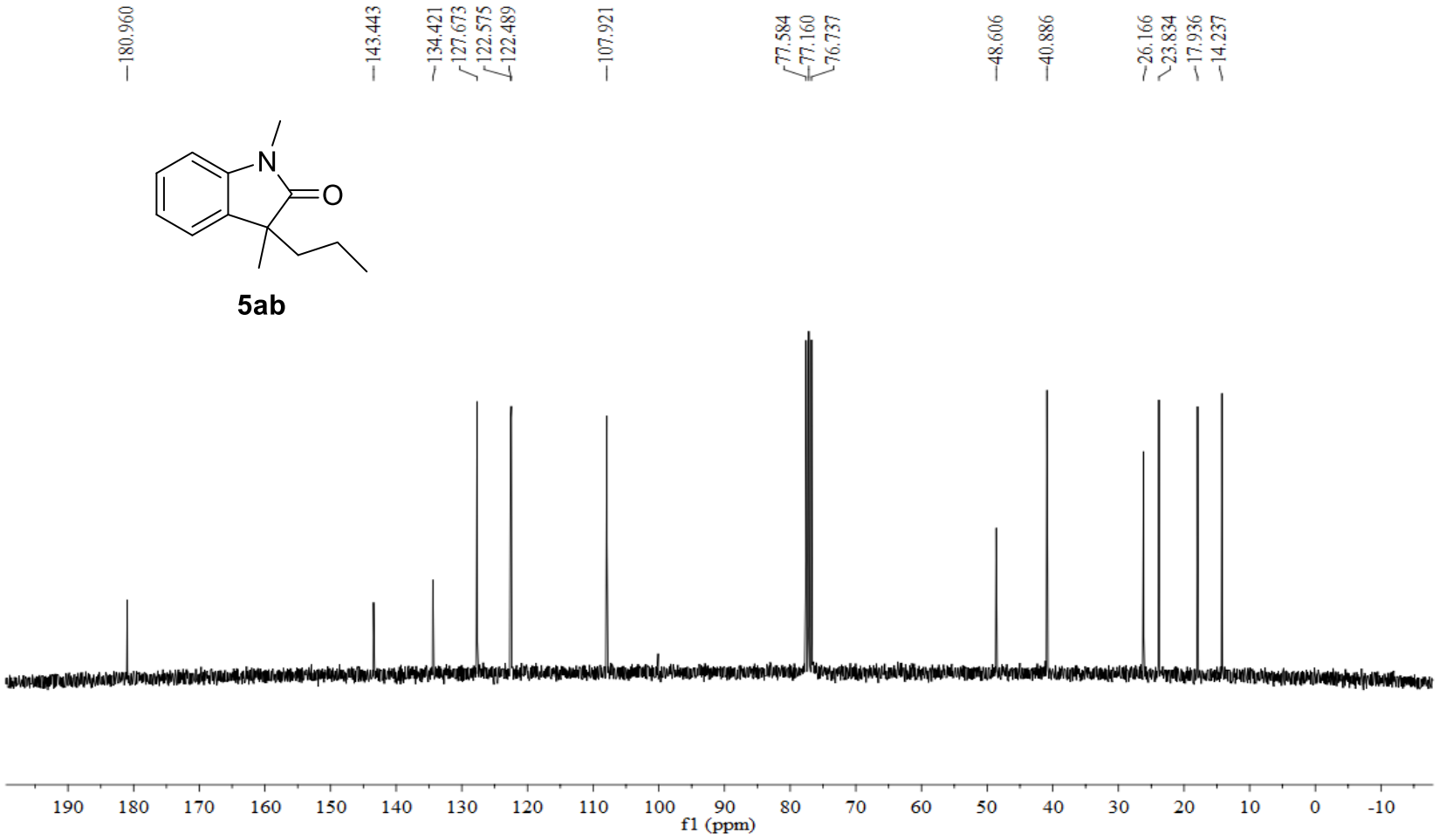

8.249
8.229
7.326
7.321
7.308
7.305
7.303
7.287
7.283
7.260
7.240
7.238
7.222
7.219
7.203
7.201
7.194
7.193
7.190
7.175
7.171
2.689
2.022
2.004
1.988
1.970
1.832
1.814
1.798
1.779
1.423
0.653
0.635
0.616
O
N
O
5ra
2.041
2.022
2.004
1.988
1.970
1.951
1.851
1.832
1.814
1.798
1.779
1.761
1.06
1.05
2.05 2.00 1.95 1.90 1.85 1.80 1.75
f1 (ppm)
0.91
0.98
1.98
3.00
1.06
1.05
3.07
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

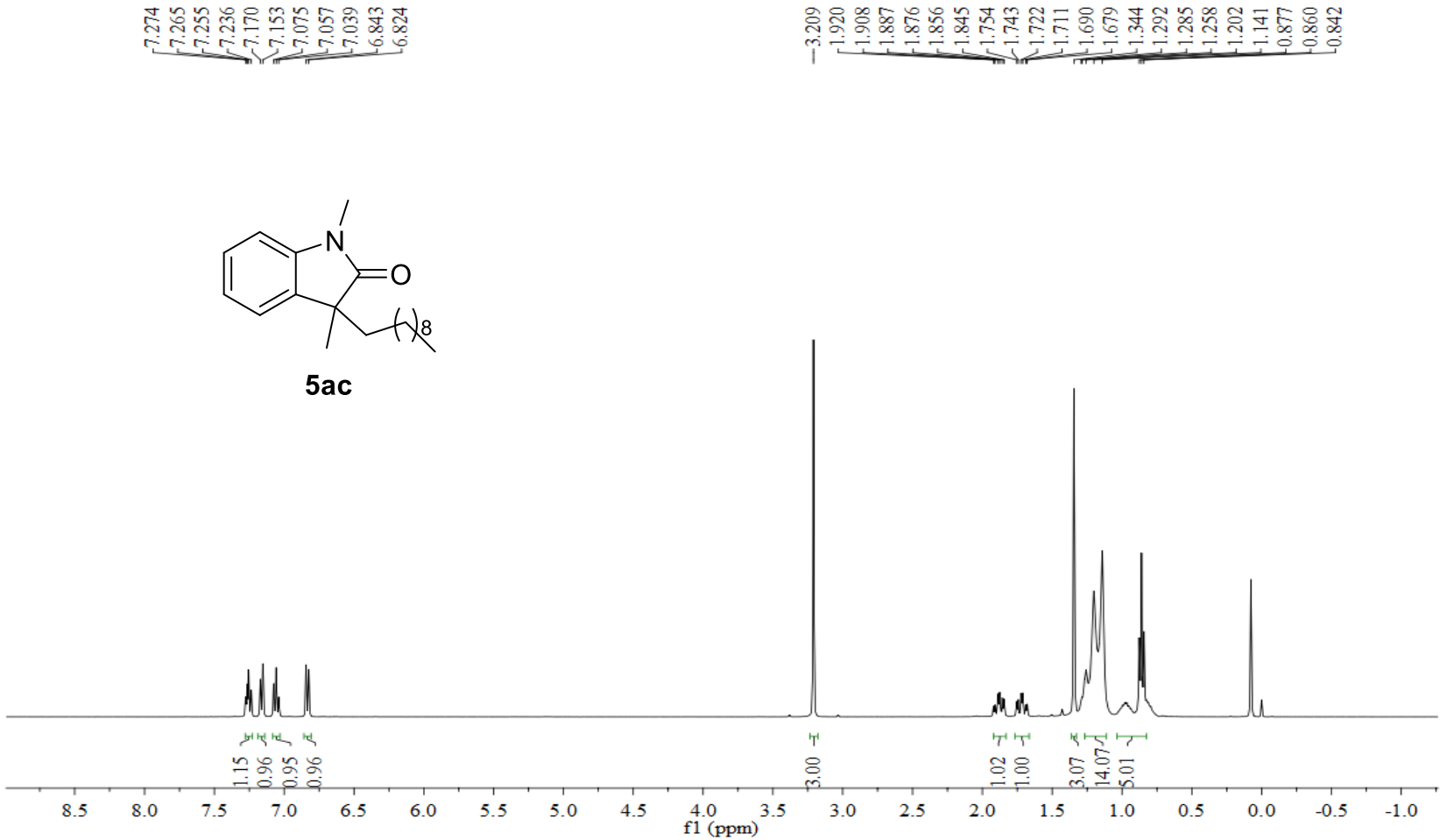

181.801
171.091
139.729
132.964
128.168
125.335
122.327
116.573
77.478
77.160
76.842
49.502
32.658
26.786
24.413
8.988
O
N
O
5ra
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

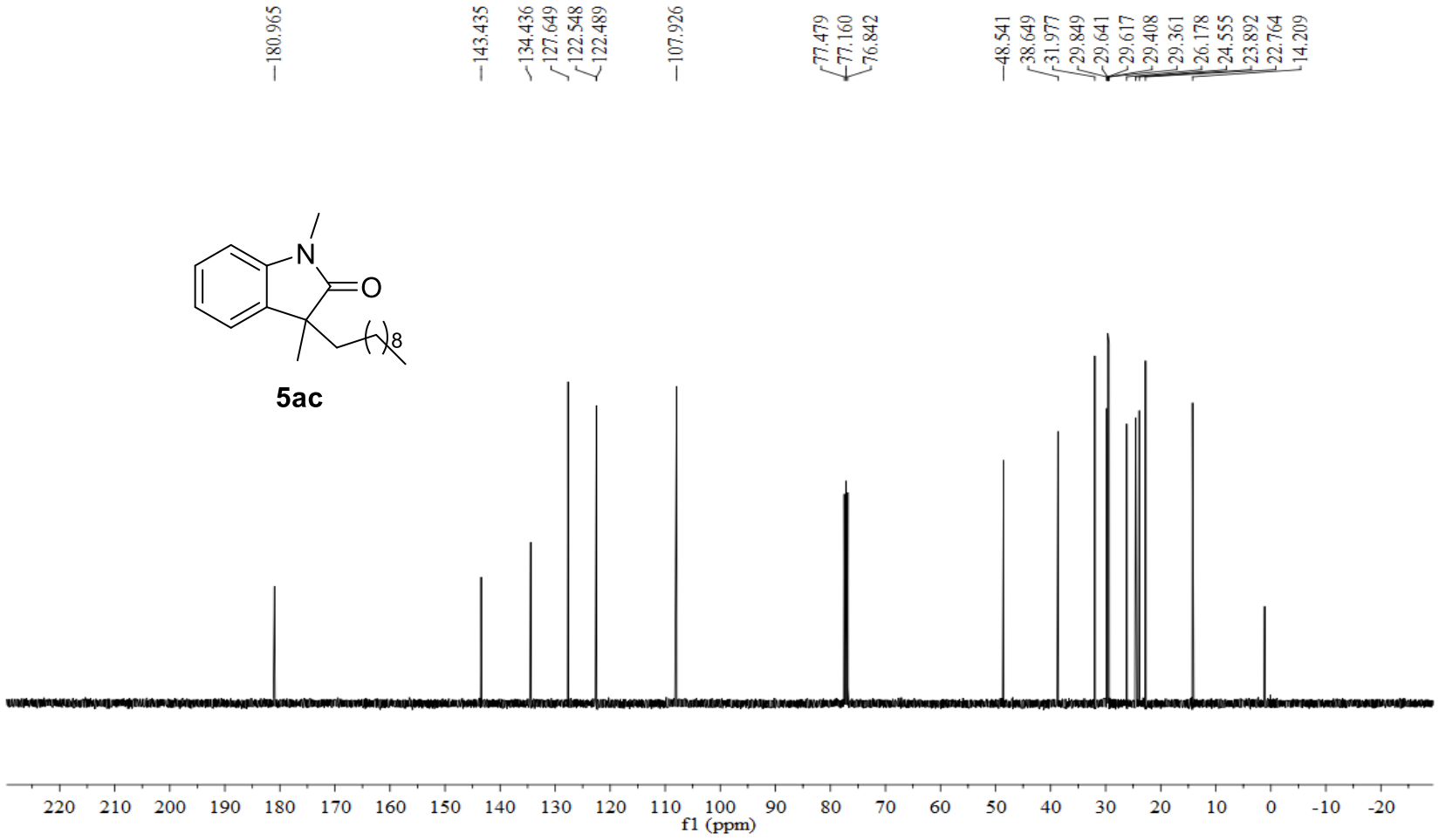

7.354
7.351
7.333
7.309
7.290
7.287
7.280
7.277
7.262
7.260
7.241
7.233
7.230
7.217
7.214
7.194
7.115
7.096
7.077
6.893
6.874
3.203
2.432
2.416
2.398
2.380
2.362
2.257
2.239
2.223
2.220
2.205
2.186
2.168
0.660
0.642
N
O
5sa
2.450
2.432
2.416
2.398
2.380
2.362
2.257
2.239
2.223
2.220
2.205
2.186
2.168
1.00
1.01
2.50
2.40
2.30
2.20
f1 (ppm)
7.10
1.07
0.97
3.00
1.00
1.01
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


178.715
144.240
140.359
132.192
128.591
128.221
127.313
127.084
124.895
122.679
108.291
77.478
77.160
76.842
57.431
30.991
26.428
9.152
N
O
5sa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.282
7.260
7.232
7.182
7.159
7.084
7.060
7.035
6.847
6.822
3.208
1.913
1.885
1.870
1.847
1.831
1.751
1.738
1.712
1.697
1.668
1.653
1.349
1.032
1.009
0.991
0.973
0.899
0.884
0.859
0.842
0.824
0.794
0.771
0.749
N
O
5ab
1.056
1.049
1.032
1.009
0.991
0.973
0.951
0.907
0.899
0.884
0.859
0.842
0.824
1.07
1.06
1.05
1.00
0.95
0.90
0.85
f1 (ppm)
1.14
0.95
0.99
0.98
3.00
1.17
1.13
3.16
1.07
1.06
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


180.960
143.443
134.421
127.673
122.575
122.489
107.921
77.584
77.160
76.737
48.606
40.886
26.166
23.834
17.936
14.237
N
O
5ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.274
7.265
7.255
7.236
7.170
7.153
7.075
7.057
7.039
6.843
6.824
3.209
1.920
1.908
1.887
1.876
1.856
1.845
1.754
1.743
1.722
1.711
1.690
1.679
1.344
1.292
1.285
1.258
1.202
1.141
0.877
0.860
0.842
N
O
8
5ac
1.15
0.96
0.95
0.96
3.00
1.02
1.00
3.07
14.07
5.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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134.436
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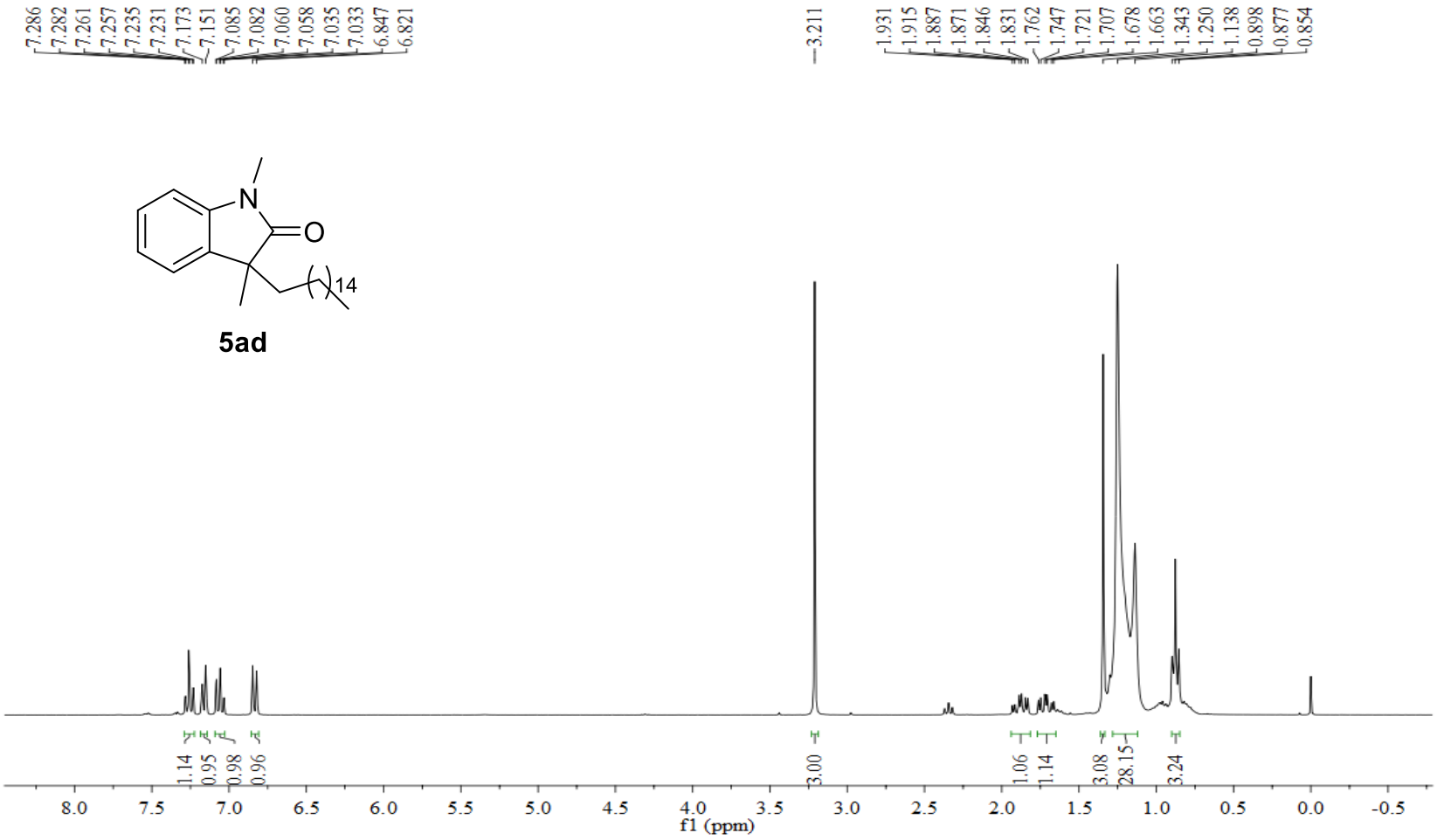
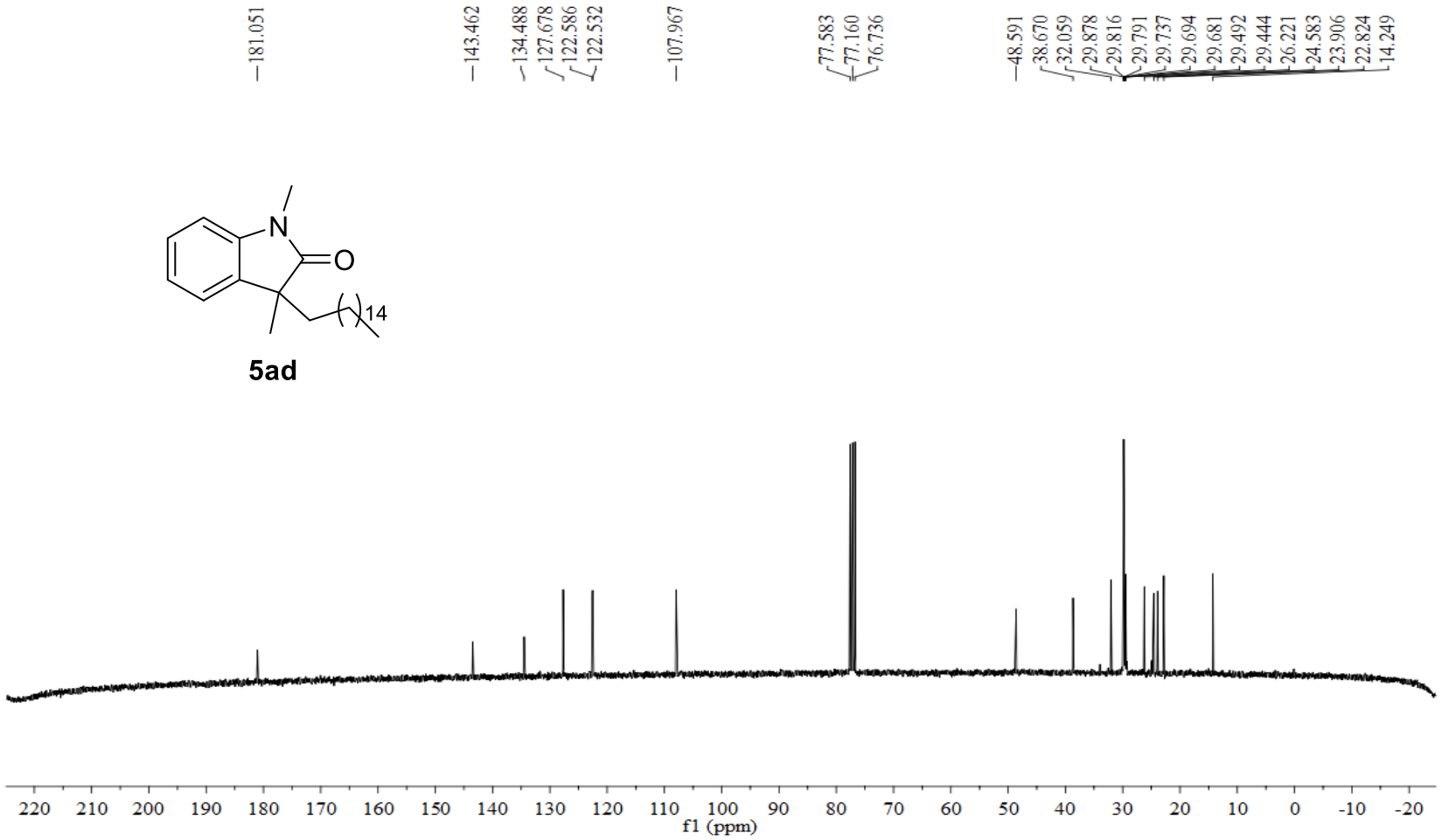
122.548
122.489
107.926
77.479
77.160
76.842
48.541
38.649
31.977
29.849
29.641
29.617
29.408
29.361
26.178
24.555
23.892
22.764
14.209
N
O
8
5ac
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.286
7.282
7.261
7.257
7.235
7.231
7.173
7.151
7.085
7.082
7.060
7.058
7.035
7.033
6.847
6.821
3.211
1.931
1.915
1.887
1.871
1.846
1.831
1.762
1.747
1.721
1.707
1.678
1.663
1.343
1.250
1.138
0.898
0.877
0.854
N
O
14
5ad
1.14
0.95
0.98
0.96
3.00
1.06
1.14
3.08
28.15
3.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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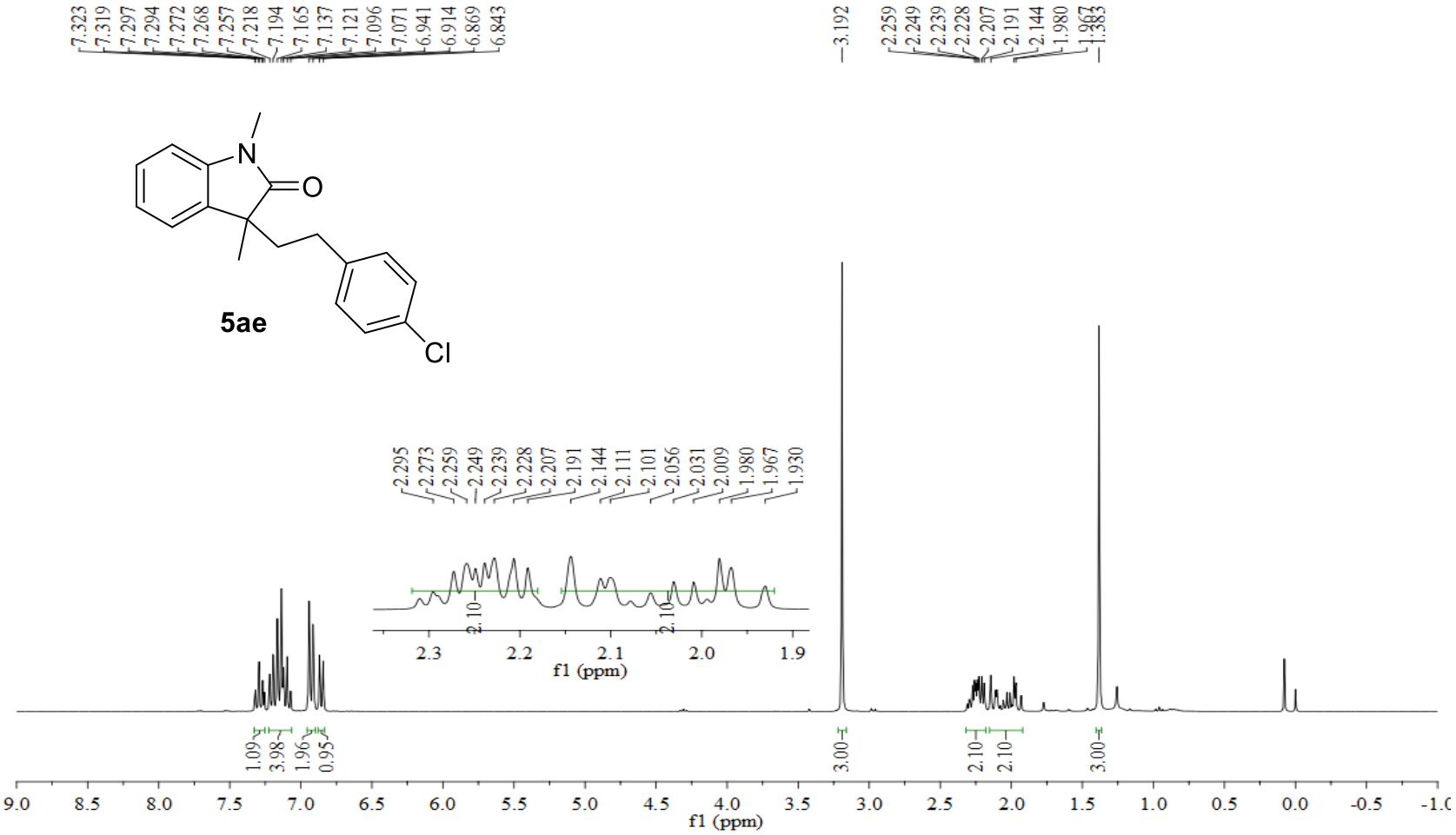
143.462
134.488
127.678
122.586
122.532
107.967
77.583
77.160
76.736
48.591
38.670
32.059
29.878
29.816
29.791
29.737
29.694
29.681
29.492
29.444
26.221
24.583
23.906
22.824
14.249
N
O
14
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

5ad


7.323
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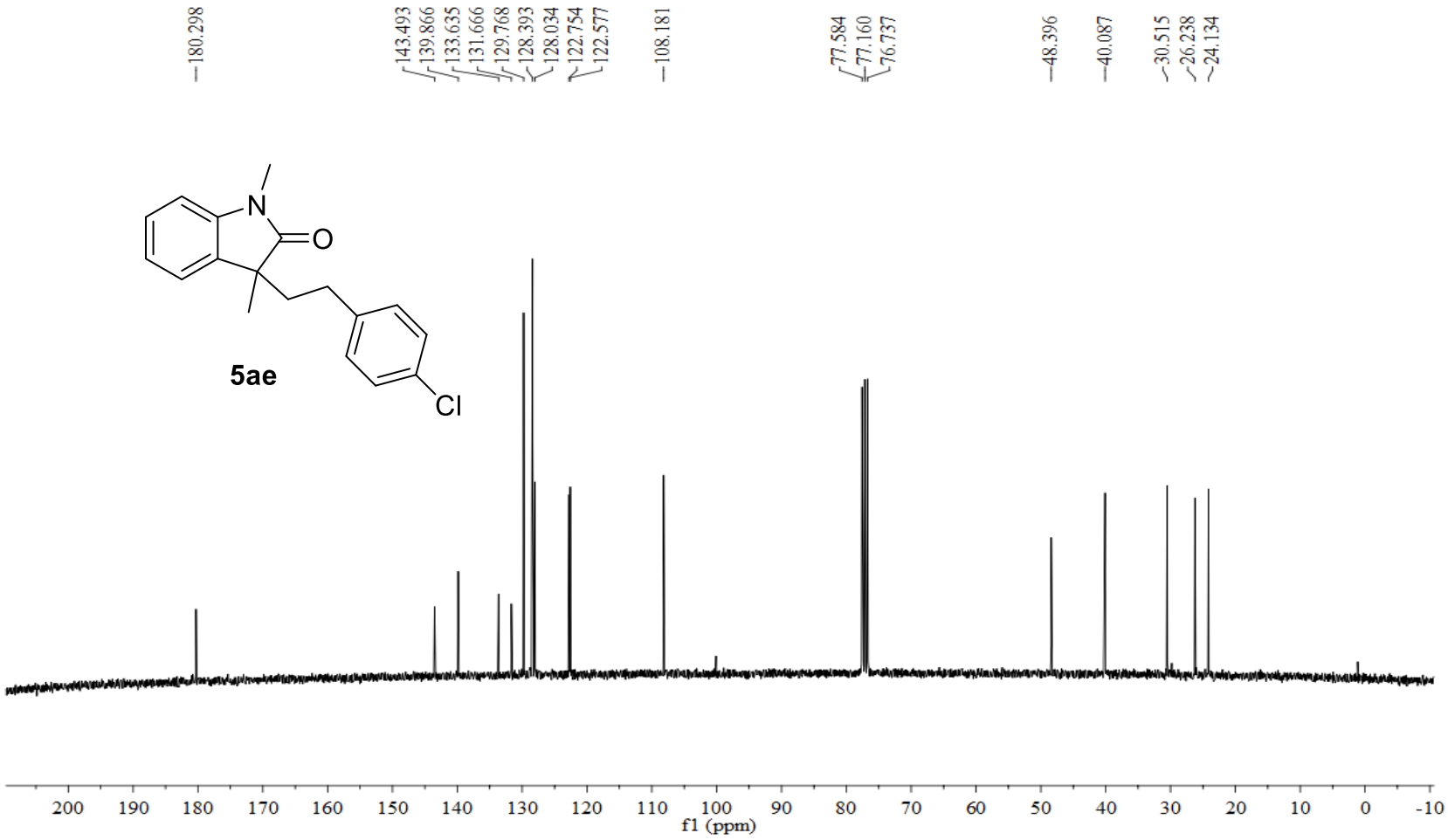
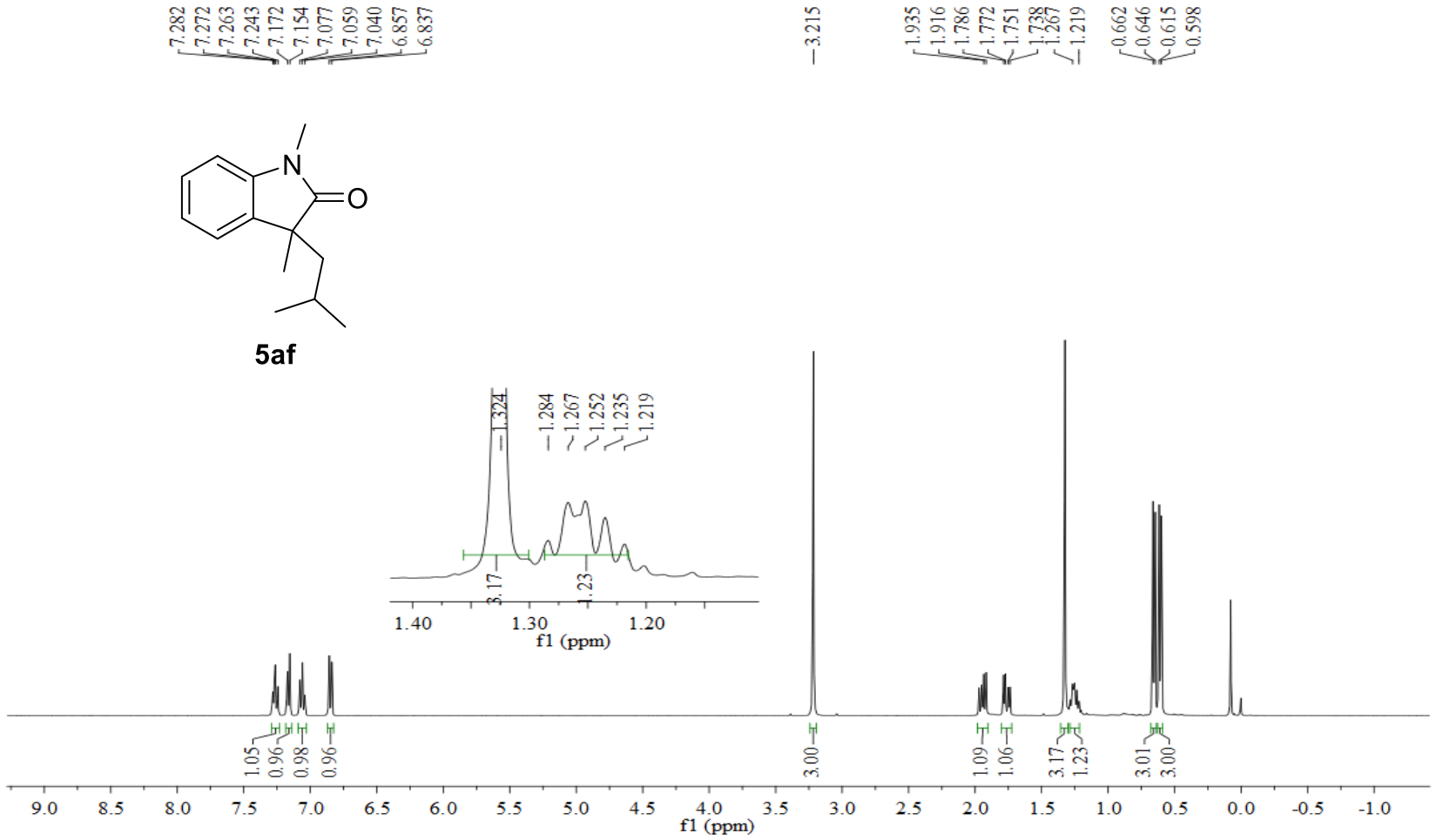
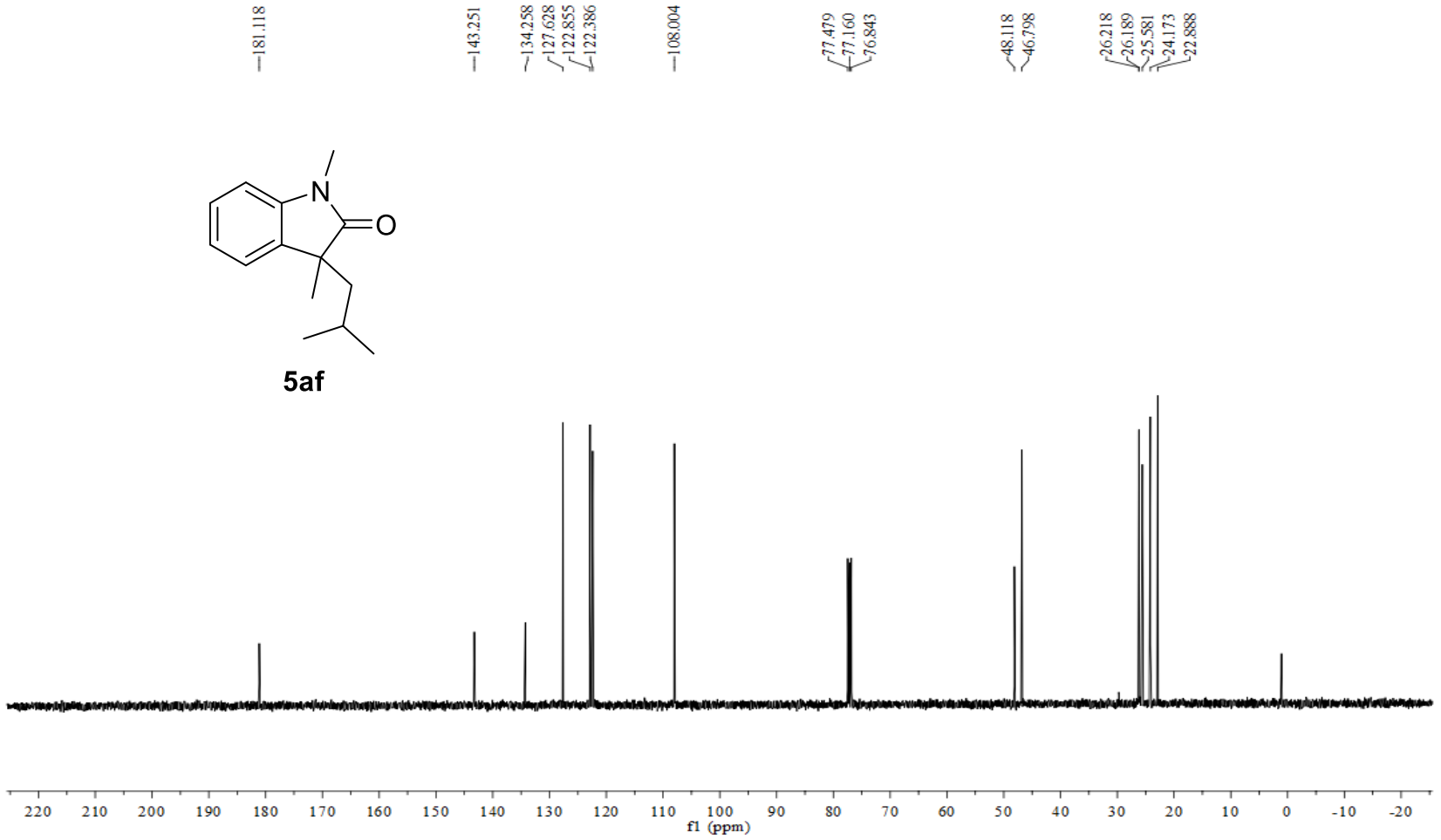
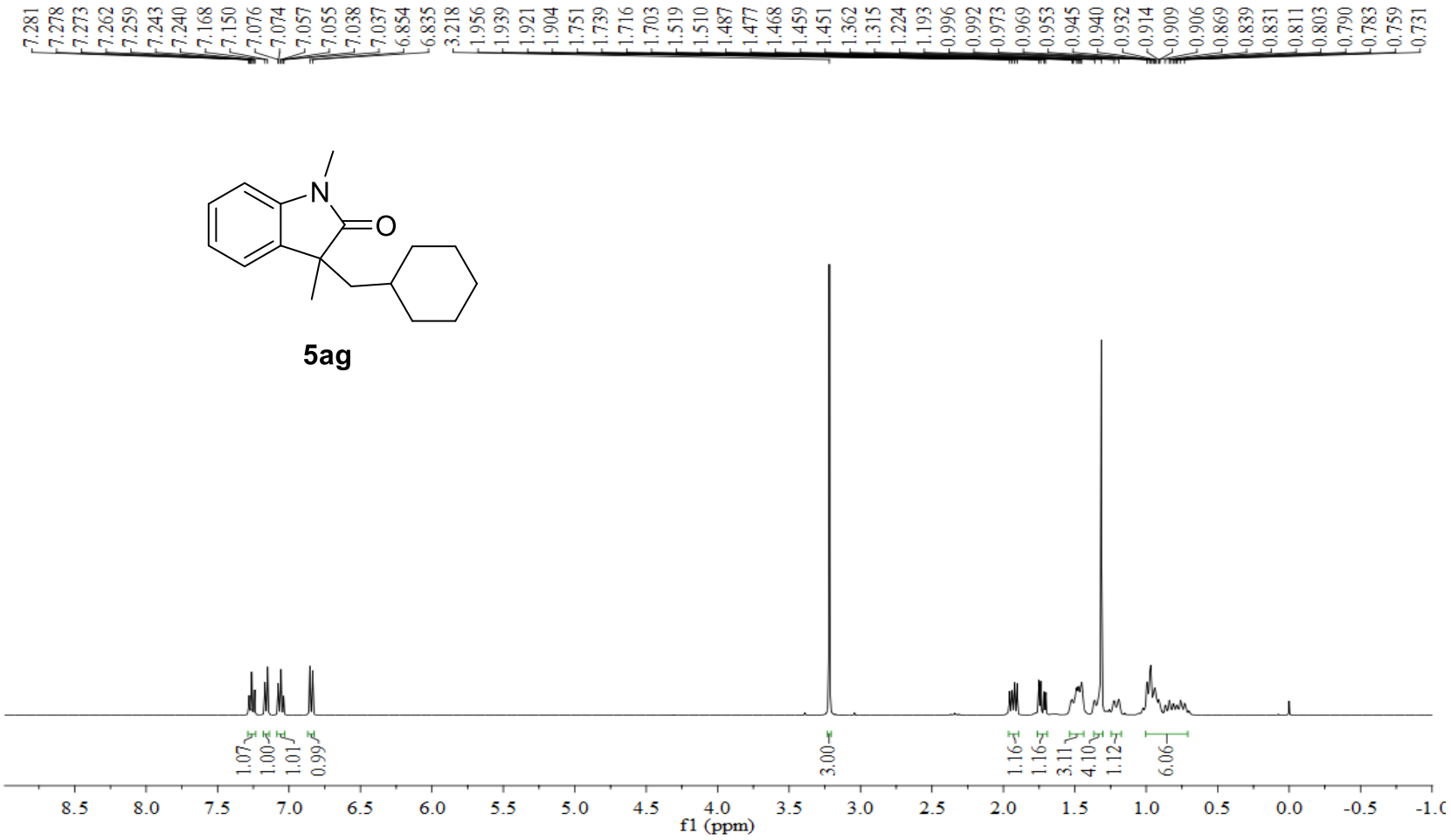
7.294
7.272
7.268
7.257
7.218
7.194
7.165
7.137
7.121
7.096
7.071
6.941
6.914
6.869
6.843
3.192
2.259
2.249
2.239
2.228
2.207
2.191
2.144
1.980
1.967
1.383
N
O
Cl
5ae
2.295
2.273
2.259
2.249
2.239
2.228
2.207
2.191
2.144
2.111
2.101
2.056
2.031
2.009
1.980
1.967
1.930
2.10
2.10
2.3
2.2
2.1
2.0
1.9
f1 (ppm)
1.09
3.98
1.96
0.95
3.00
2.10
2.10
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

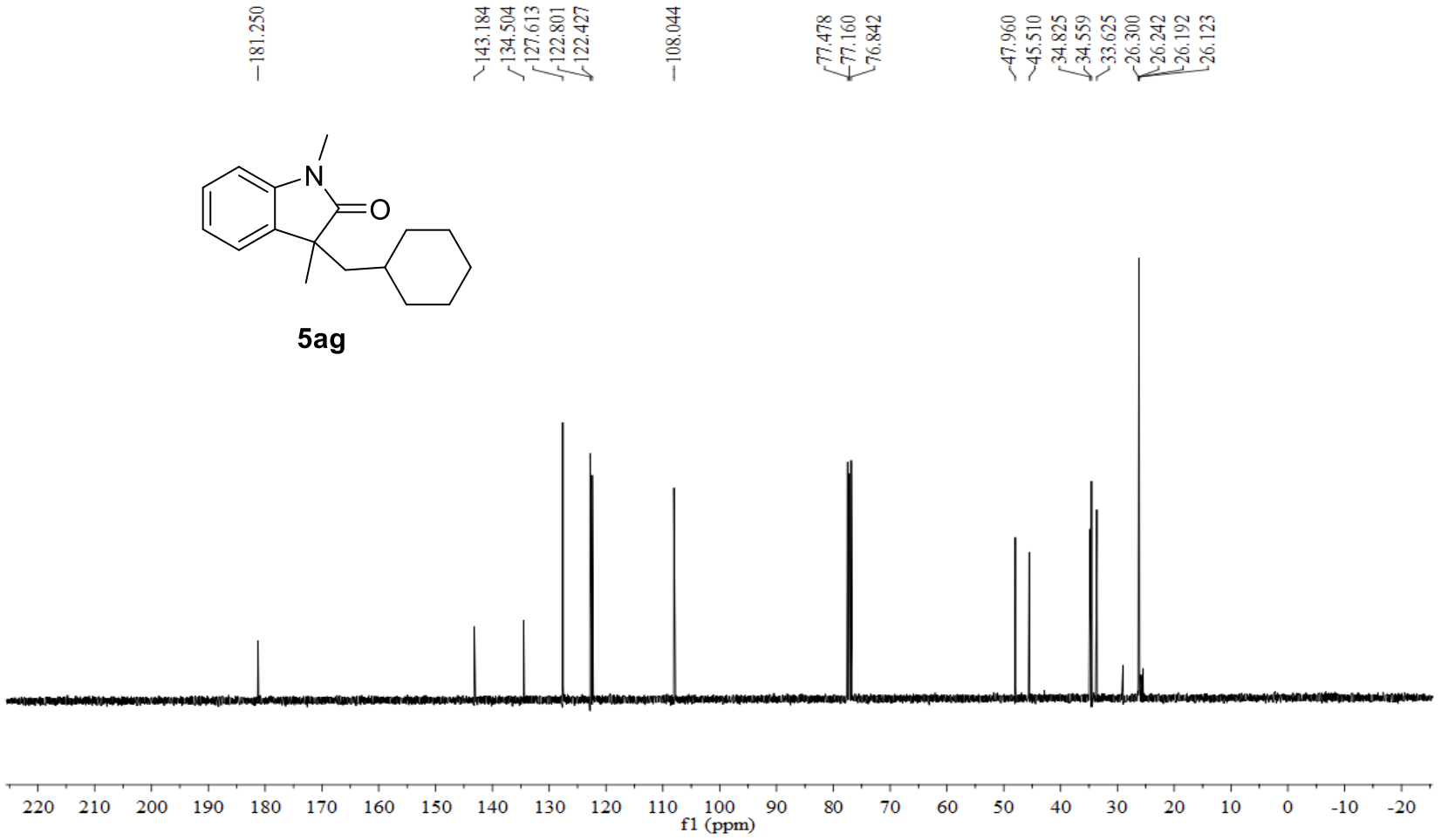

180.298
143.493
139.866
133.635
131.666
129.768
128.393
128.034
122.754
122.577
108.181
77.584
77.160
76.737
48.396
40.087
30.515
26.238
24.134
N
O
Cl
5ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.282
7.272
7.263
7.243
7.172
7.154
7.077
7.059
7.040
6.857
6.837
3.215
1.935
1.916
1.786
1.772
1.751
1.738
1.267
1.219
0.662
0.646
0.615
0.598
N
O
5af
1.324
1.284
1.267
1.252
1.235
1.219
3.17
1.23
1.40
1.30
1.20
f1 (ppm)
1.05
0.96
0.98
0.96
3.00
1.09
1.06
3.17
1.23
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

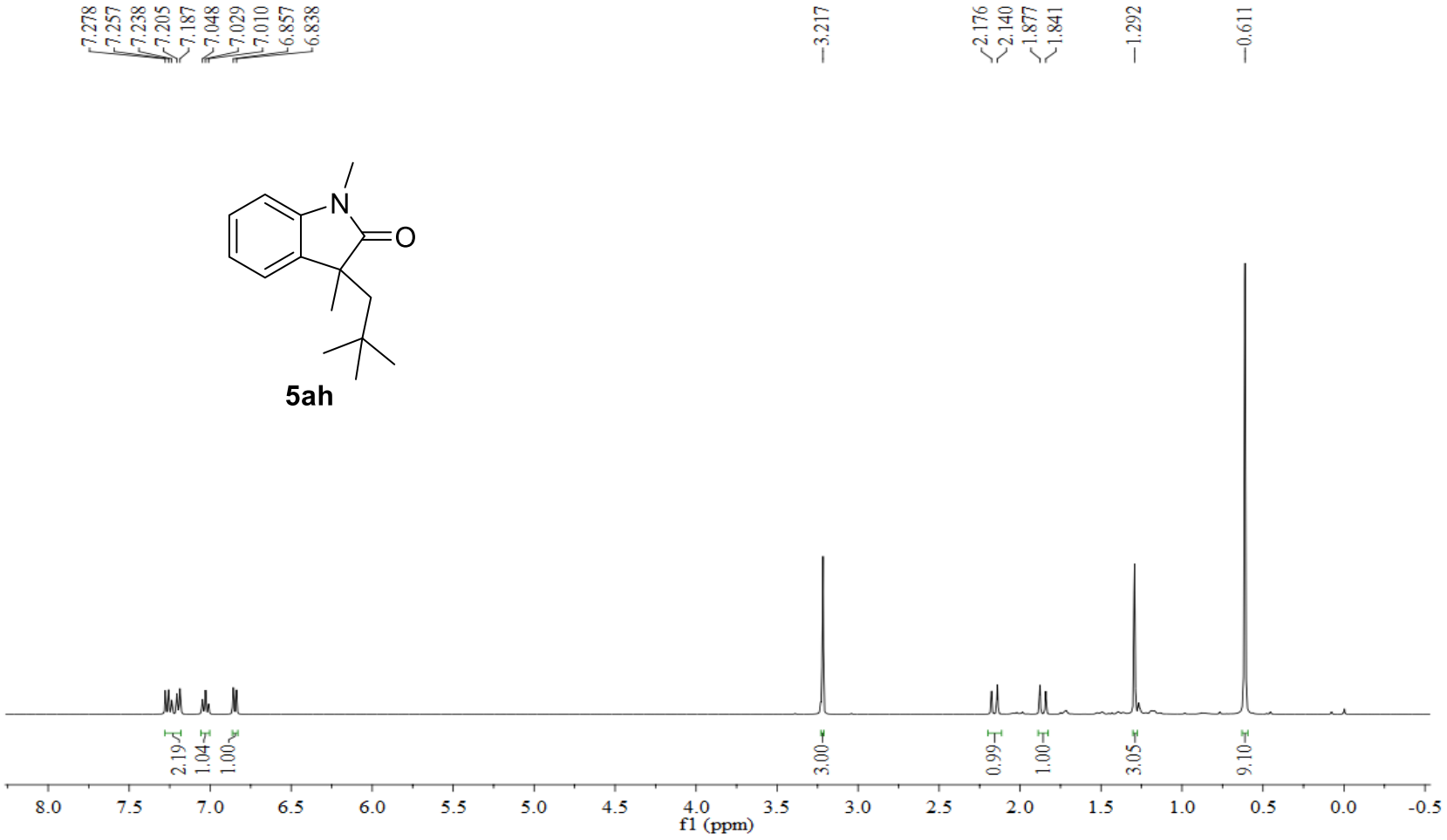

181.118
143.251
134.258
127.628
122.855
122.386
108.004
77.479
77.160
76.843
48.118
46.798
26.218
26.189
25.581
24.173
22.888
N
O
5af
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

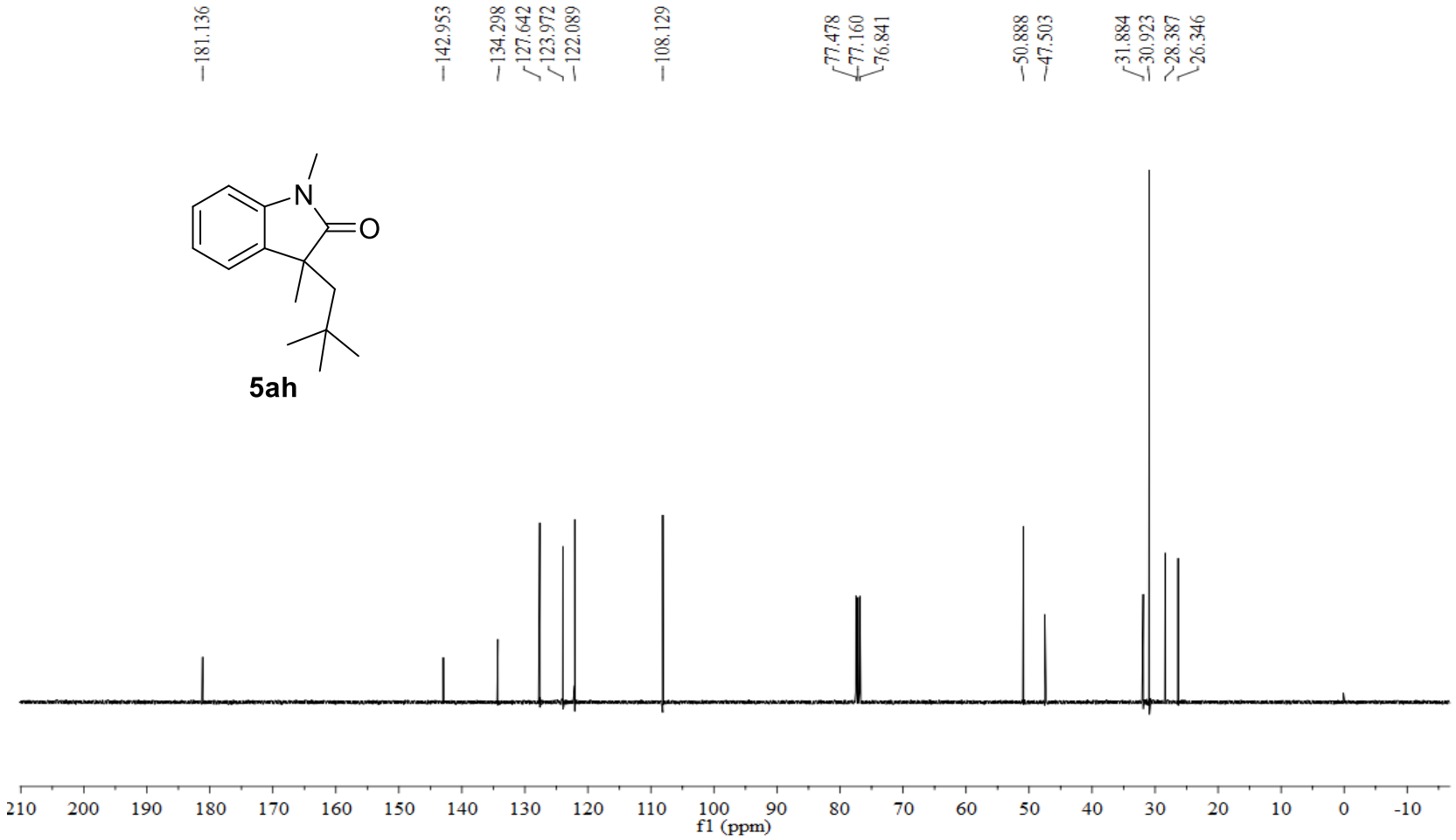

7.281
7.278
7.273
7.262
7.259
7.243
7.240
7.168
7.150
7.076
7.074
7.057
7.055
7.038
7.037
6.854
6.835
3.218
1.956
1.939
1.921
1.904
1.751
1.739
1.716
1.703
1.519
1.510
1.487
1.477
1.468
1.459
1.451
1.362
1.315
1.224
1.193
0.996
0.992
0.973
0.969
0.953
0.945
0.940
0.932
0.914
0.909
0.906
0.869
0.839
0.831
0.811
0.803
0.790
0.783
0.759
0.731
N
O
1.07
1.00
1.01
0.99
3.00
1.16
1.16
3.11
4.10
1.12
6.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

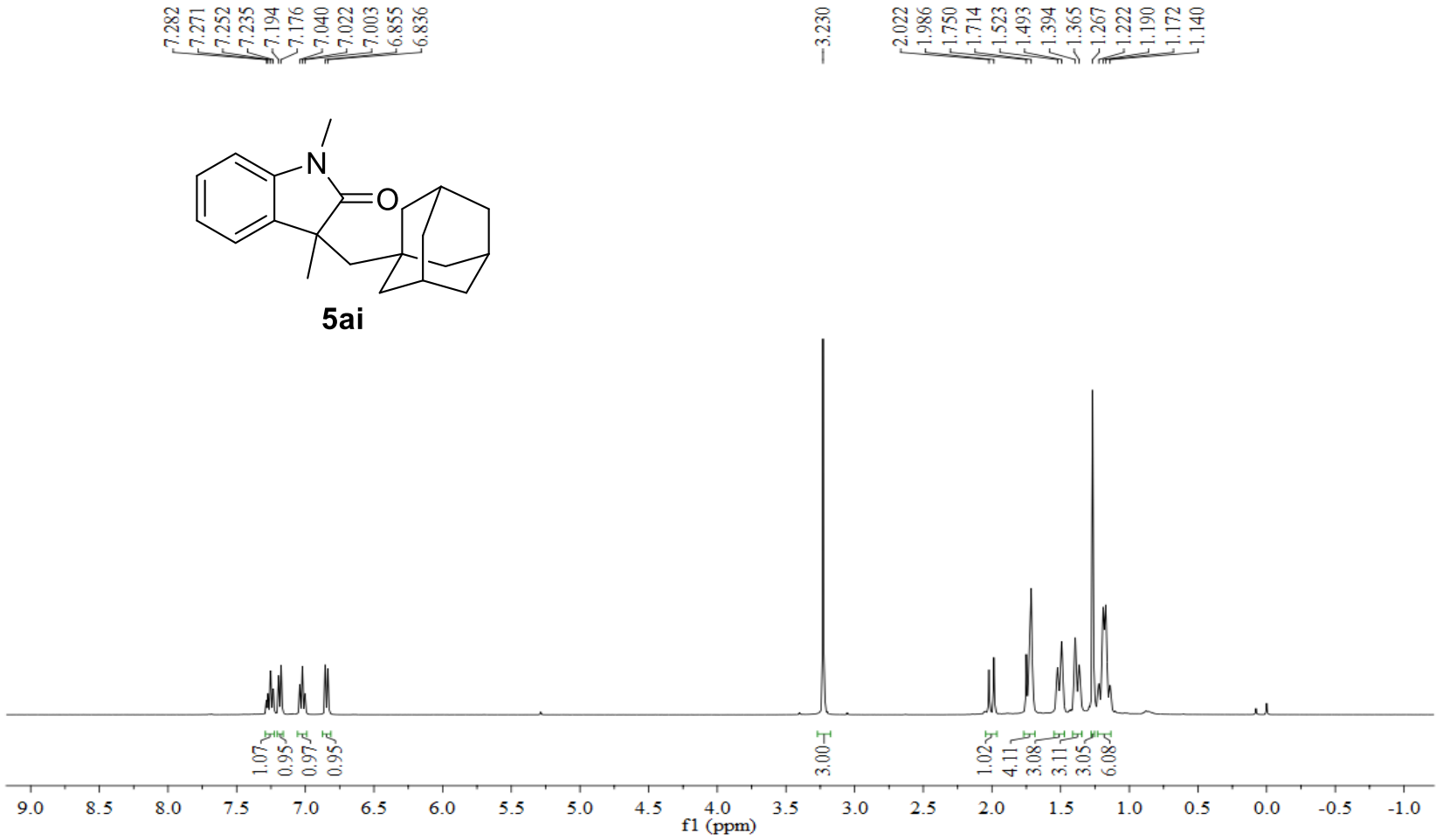
5ag

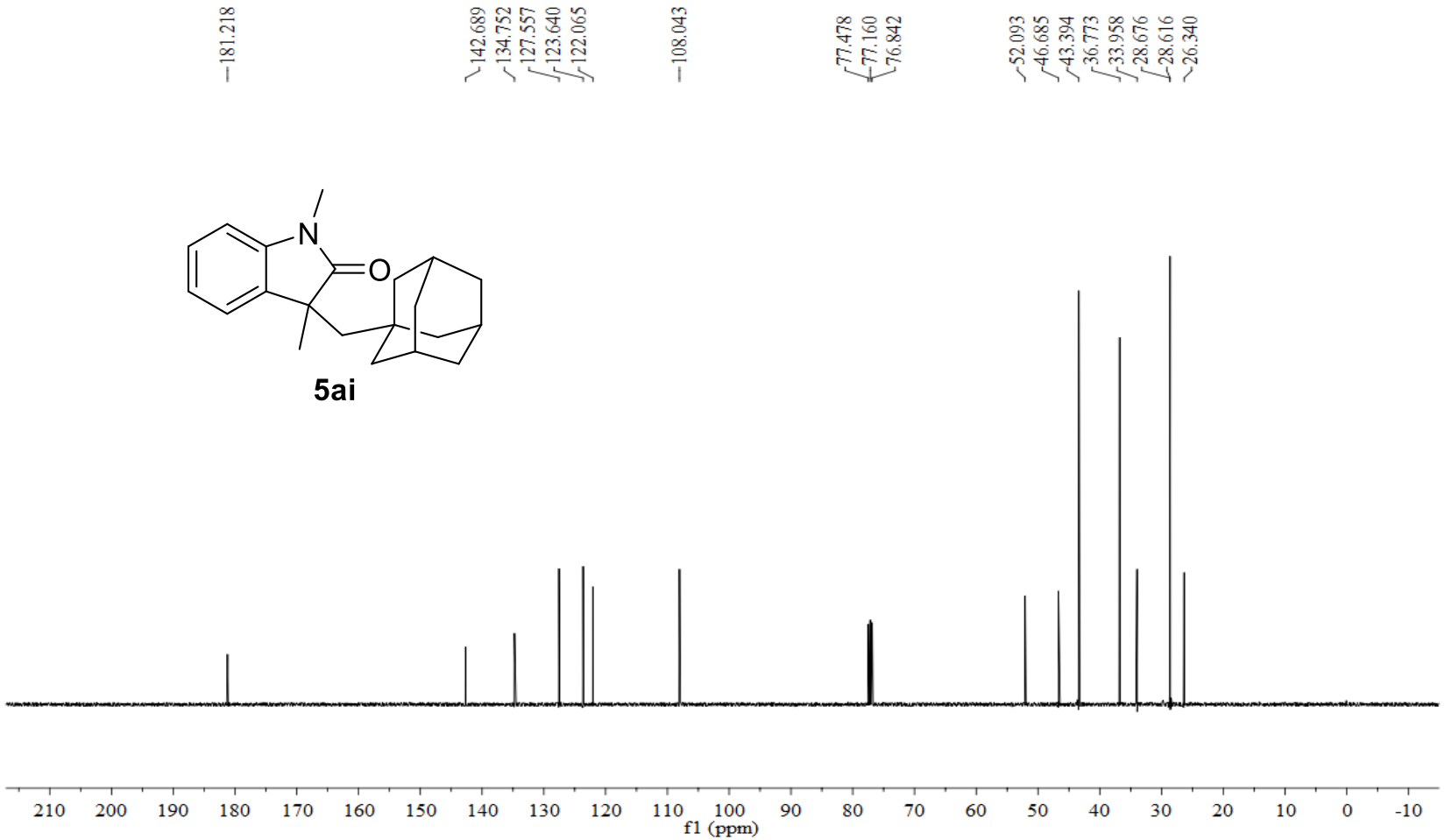

181.250
143.184
134.504
127.613
122.801
122.427
108.044
77.478
77.160
76.842
47.960
45.510
34.825
34.559
33.625
26.300
26.242
26.192
26.123
N
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

5ag


7.278
7.257
7.238
7.205
7.187
7.048
7.029
7.010
6.857
6.838
3.217
2.176
2.140
1.877
1.841
1.292
0.611
N
O
5ah
2.19
1.04
1.00
3.00
0.99
1.00
3.05
9.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


181.136
142.953
134.298
127.642
123.972
122.089
108.129
77.478
77.160
76.841
50.888
47.503
31.884
30.923
28.387
26.346
N
O
5ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.282
7.271
7.252
7.235
7.194
7.176
7.040
7.022
7.003
6.855
6.836
3.230
2.022
1.986
1.750
1.714
1.523
1.493
1.394
1.365
1.267
1.222
1.190
1.172
1.140
N
O
5ai
1.07
0.95
0.97
0.95
3.00
1.02
4.11
3.08
3.11
3.05
6.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


181.218
142.689
134.752
127.557
123.640
122.065
108.043
77.478
77.160
76.842
52.093
46.685
43.394
36.773
33.958
28.676
28.616
26.340
N
O
5ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)