Electronic Supplementary Material (ESI) for ChemComm.

Oxyallyl Cation Promoted Dearomative Semipinacol Rearrangement: Facile Stereodivergent Synthesis of Spiro-indolines with Contiguous Quaternary Centers

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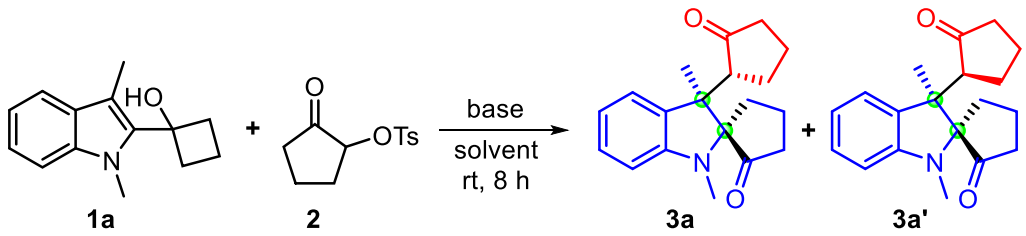
1. General Information

All reactions were performed using oven-dried or flame-dried glassware equipped with a magnetic stir bar under an atmosphere of argon unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification. In addition to commercially available extra dry solvents, all solvents were purified by standard operating method. Toluene, tetrahydrofuran, diethyl ether and benzene were distilled from sodium; Dichloromethane and trichloromethane were distilled from calcium hydride. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid . ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-400 MHz, Varian Mercury-400 or Bruker AM-500 MHz instruments. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), $(CD_3)_2CO$ (2.05 ppm) or tetramethylsilane (0.00 ppm) as internal reference for ^{1}H NMR and the deuterated solvent $CDCl_3$ (77.00 ppm), C_6D_6 (128.06 ppm), $(CD_3)_2CO$ (29.84 ppm) or tetramethylsilane (0.00 ppm) as internal standard for ^{13}C NMR. High-resolution mass spectral analysis (HRMS) data was measured on a Bruker impact II (Q-TOF) mass spectrum by means of the ESI technique. Crystallographic data were obtained from a Bruker D8 VENTURE diffractometer.

2. Screening Conditions

Table S1. Screening Conditions for **3a**[a]



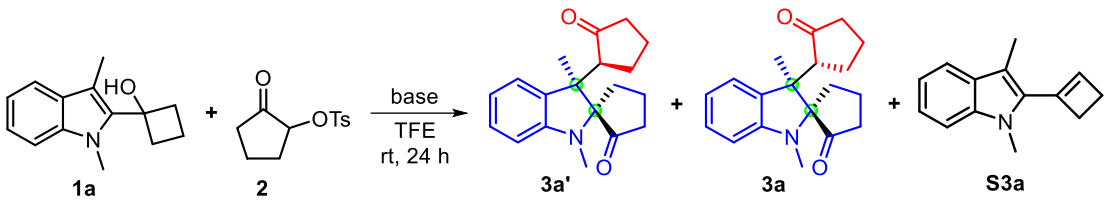
entry	base (3.0 equiv.)	solvent	yield (%)[b]	d.r[c]
1	Li_2CO_3	CH_2Cl_2	<5	-
2	K_3PO_4	CH_2Cl_2	53	6.1:1
3	$KHCO_3$	CH_2Cl_2	<5	-
4	K_2HPO_4	CH_2Cl_2	<5	-
5	DIPEA	CH_2Cl_2	71	6.3:1
6	DIPA	CH_2Cl_2	80	5.9:1
7	Et_3N	Dichloroethane	81	5.5:1
8	Et_3N	CCl_4	71	4.9:1
9	Et_3N	Benzotrifluoride	75	6.1:1
10	Et_3N	EA	59	3.9:1
11	Et_3N	CH_3NO_2	53	5.7:1
12	Et_3N	CH_3OH	<5	-
13	Et_3N	DMF	<5	-
14	Et_3N	DMSO	<5	-

[a]Reaction conditions: Unless otherwise noted, the reaction was conducted with **1a** (0.1 mmol) and **2** (0.15 mmol) at room temperature under Ar. [b]Isolated yield. [c]The ratio was determined by ^{1}H-NMR.

After the screening results in Table 1 and Table S1, we found that the d.r. value of the reaction changes greatly when TFE was used as the solvent, and the reaction results of organic bases and inorganic bases in different solvents were also different. Therefore, we decided to use TFE as the solvent for a new round of condition optimization. Fortunately, we found that when the reaction was performed in presence of 3.0 equiv. of Cs_2CO_3 in TFE, product **3a'** was obtained in 54% yield with 6.8 :1 d.r. value (entry 8, Table S2). In addition, in Scheme 2, when we use TFE as the reaction solvent, By-products by eliminating

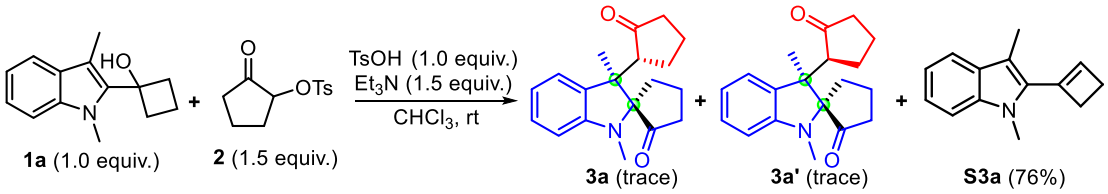
hydroxyl groups are generated during the reaction, which leads to a decrease in the reaction yield. This is why it is necessary to add an equivalent amount of base to neutralize the acid generated in the reaction.

Table S2. Screening Conditions for **3a'**[a]

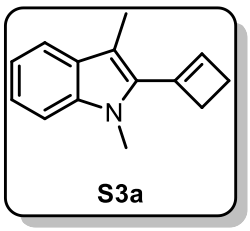


entry	base (3.0 equiv.)	yield (%)[b]	d.r[c]
1	Et_3N	55	1:1.4
2	DIPEA	53	1:1.5
3	DIPA	24	1:1.3
4	Na_2CO_3	45	1:1.5
5	$KHCO_3$	19	1.8:1
6	K_2CO_3	58	3.7:1
7	K_3PO_4	55	2.4:1
8	**Cs_2CO_3**	**54**	**6.8:1**
9	CsOH	36	2.2:1
10	Cs_2TiO_3	50	5.7:1

[a]Reaction conditions: Unless otherwise noted, the reaction was conducted with **1a** (0.1 mmol) and **2** (0.15 mmol) at room temperature under Ar. [b]Isolated yield. [c]The ratio was determined by ^{1}H-NMR.



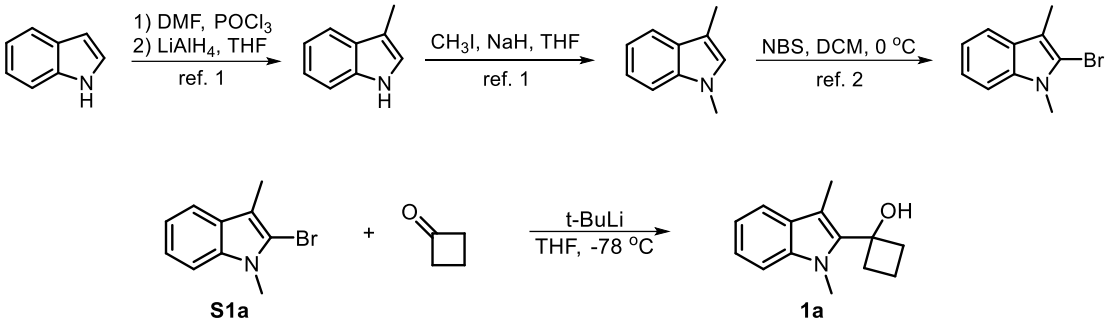
The substrate **1a** (0.1 mmol, 1.0 equiv.) and Et_3N (0.15 mmol, 1.5 equiv.) were dissolved in $CHCl_3$ (2.0 mL) under argon atmosphere. Then, the substrate **2** (0.15 mmol, 1.5 equiv.) and TsOH (0.1 mmol, 1.0 equiv.) were added to the reaction system. After 1 h at room temperature, the substrate **1a** has been completely consumed by TLC monitoring. The reaction produces a main product **S3a** under this reaction condition.



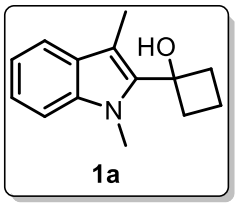
S3a

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.25-7.17 (m, 2H), 7.08 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1H), 6.19 (t, *J* = 1.4 Hz, 1H), 3.79 (s, 3H), 3.17-3.12 (m, 2H), 2.71-2.67 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 138.9, 137.4, 131.1, 129.5, 128.2, 122.1, 118.8, 118.8, 110.4, 108.7, 32.9, 31.2, 29.3, 9.5.

3. Preparation of Substrates 1 and Analytic Data

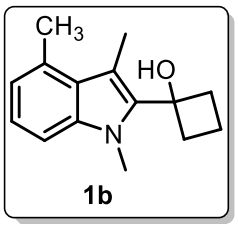


A 100 mL dried round bottom flask equipped with compound **S1a** (2.23 g, 10 mmol, 1.0 equiv.) and a magnetic stirring bar was charged with anhydrous THF (40 mL) under argon atmosphere. Then t-BuLi (1.6 mol/L in hexane) (11.25 mL, 18 mmol, 1.8 equiv.) was added very slowly under argon atmosphere at -78 ℃ and stirred for 30 mins at -78 ℃, then cyclobutanone (1.40 g, 20 mmol, 2.0 equiv.) was added at -78 ℃ under argon atmosphere, and the reaction mixture was stirred for 30 mins at -78 ℃. The reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL) with stirred and the reaction mixture was extracted with EtOAc (3 × 30 mL). The combined organic layer was wash with brine, dried over $MgSO_4$ and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1-10:1) provided the compound **1a** (1.76 g, 82% yield) as a white solid.



1a

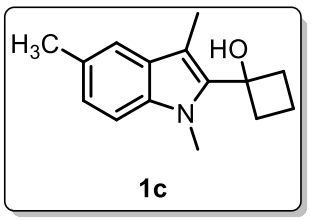
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.24-7.15 (m, 2H), 7.12-7.01 (m, 1H), 3.64 (s, 3H), 2.91-2.77 (m, 2H), 2.50-2.39 (m, 2H), 2.39-2.28 (m, 4H), 2.23 (d, *J* = 5.7 Hz, 1H), 1.96-1.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 138.0, 137.1, 128.2, 122.0, 118.7, 118.6, 108.6, 106.7, 75.2, 36.7, 30.8, 16.9, 9.7. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{14}H_{17}NNaO$, m/z: 238.1202, found: 238.1204.



1b

The compound **1b** (2.31 g, 80% yield) as a white solid was prepared from **S1b** (2.99 g, 12.6 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.19-7.13 (m, 1H), 6.96-6.88 (m, 2H), 3.21 (s, 3H), 2.68 (s, 3H), 2.54-2.46 (m, 2H), 2.35 (s, 3H), 2.34-2.29 (m, 1H), 2.26-2.21 (m, 2H), 1.73-1.64 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 138.4, 138.2, 131.3, 128.1, 127.3, 122.2, 121.4, 108.2, 107.3, 75.4, 37.5, 30.7, 21.2, 17.8, 12.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO$, m/z: 252.1359, found: 252.1362.

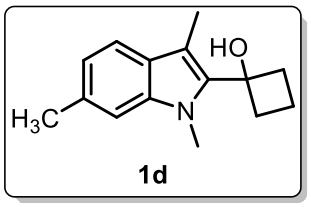


1c

The compound **1c** (1.74 g, 76% yield) as a white solid was prepared from **S1c** (2.37 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.28 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.04-6.97 (m, 1H), 3.60 (s, 3H), 2.89-2.75 (m, 2H), 2.44 (s, 3H), 2.43-2.31 (m, 3H),

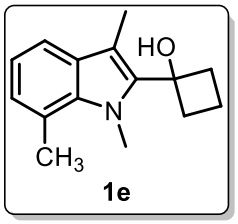
2.28 (s, 3H), 2.16 (s, 1H), 1.95-1.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 138.1, 135.6, 128.4, 127.8, 123.6, 118.3, 108.4, 106.2, 75.3, 36.7, 30.8, 21.4, 16.9, 9.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{19}NNaO$, m/z: 252.1359 , found: 252.1360.



1d

The compound **1d** (2.37 g, 70% yield) as a white solid was prepared from **S1d** (3.51 g, 14.8 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

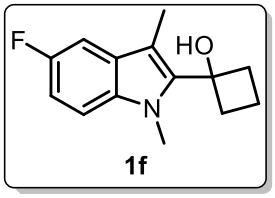
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.43 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.26 (d, *J* = 1.0 Hz, 1H), 3.26 (s, 3H), 2.73-2.66 (m, 2H), 2.55 (s, 3H), 2.49-2.43 (m, 2H), 2.29 (s, 3H), 2.24-2.15 (m, 1H), 1.81 (s, 1H), 1.70-1.63 (m, 1H). **^{13}C NMR** (500 MHz, C_6D_6, ppm): δ 138.0, 137.9, 130.4, 129.8, 128.1, 120.9, 117.7, 116.2, 109.2, 79.7, 37.8, 36.8, 15.7, 15.4, 9.7. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO$, m/z: 252.1359 , found: 252.1360.



1e

The compound **1e** (1.51 g, 66% yield) as a white solid was prepared from **S1e** (2.37 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

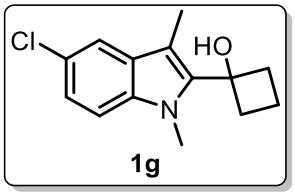
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.33 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.90-2.79 (m, 2H), 2.70 (s, 3H), 2.50-2.40 (m, 2H), 2.40-2.31 (m, 1H), 2.27 (s, 3H), 2.16 (s, 1H), 1.94-1.84 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 138.8, 136.2, 129.1, 125.2, 120.8, 118.9, 116.7, 107.1, 75.3, 37.0, 33.8, 20.4, 16.9, 9.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO$, m/z: 252.1359, found: 252.1359.



1f

The compound **1f** (1.82 g, 78% yield) as a white solid was prepared from **S1f** (2.41 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

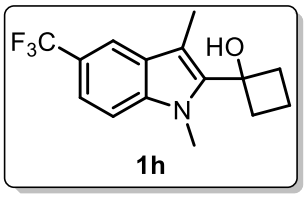
$\mathbf{R_f}$ = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.26 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.99 (td, *J* = 9.0, 2.5 Hz, 1H), 6.74 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.15 (s, 3H), 2.48-2.40 (m, 2H), 2.24-2.17 (m, 1H), 2.13 (ddd, *J* = 11.6, 8.9, 5.1 Hz, 3H), 2.06 (s, 3H), 1.67-1.58 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 158.3 (d, *J* = 233.3 Hz), 140.0, 134.2, 129.3 (d, *J* = 9.2 Hz), 110.3 (d, *J* = 26.0 Hz), 109.7 (d, *J* = 9.5 Hz), 106.8 (d, *J* = 4.8 Hz), 103.9 (d, *J* = 23.0 Hz), 75.0, 36.8, 30.7, 17.2, 9.8. **^{19}F NMR** (471 MHz, C_6D_6, ppm): δ -125.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{14}H_{17}FNO$, m/z: 234.1289, found: 234.1290.



1g

The compound **1g** (1.99 g, 80% yield) as a white solid was prepared from **S1g** (2.57 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

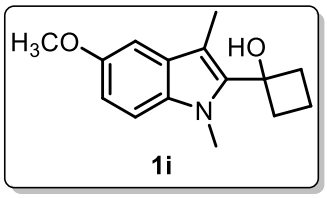
$\mathbf{R_f}$ = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$, ppm): δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.71 (s, 1H), 3.70 (s, 3H), 2.82 (ddd, *J* = 17.2, 8.8, 2.8 Hz, 2H), 2.51-2.44 (m, 2H), 2.43-2.33 (m, 1H), 2.29 (s, 3H), 1.94-1.84 (m, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$, ppm): δ 141.7, 136.4, 130.5, 124.5, 122.0, 118.4, 110.9, 106.4, 74.9, 37.4, 31.4, 17.6, 9.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{14}H_{17}ClNO$, m/z: 250.0993, found: 250.0995.



1h

The compound **1h** (2.12 g, 75% yield) as a white solid was prepared from **S1h** (2.91 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

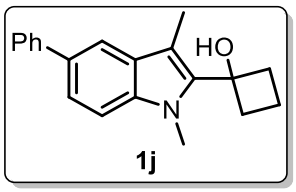
R_f = 0.35 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.83-7.76 (m, 1H), 7.41 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.29-7.22 (m, 1H), 3.70 (s, 3H), 2.92-2.81 (m, 2H), 2.54-2.37 (m, 3H), 2.35 (s, 3H), 2.10 (s, 1H), 2.00-1.88 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 139.1 (d, *J* = 131.8 Hz), 125.5 (q, *J* = 269.5 Hz), 121.1 (q, *J* = 31.7 Hz), 118.7 (d, *J* = 3.5 Hz), 116.5 (q, *J* = 4.3 Hz), 108.9, 107.8, 75.1, 36.7, 31.1, 17.0, 9.6. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -60.0. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{16}F_3NNaO$, m/z: 306.1076, found: 306.1076.



1i

The compound **1i** (2.11 g, 86% yield) as a white solid was prepared from **S1i** (2.53 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

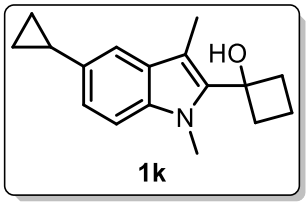
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.13 (d, *J* = 8.7 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.88 (s, 3H), 3.67 (d, *J* = 2.1 Hz, 3H), 2.94-2.83 (m, 2H), 2.54-2.46 (m, 2H), 2.46-2.36 (m, 1H), 2.32 (s, 3H), 2.26 (s, 1H), 1.99-1.89 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 153.6, 138.7, 132.5, 128.4, 112.1, 109.4, 106.3, 100.7, 75.3, 56.0, 36.7, 31.0, 17.0, 9.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO_2$, m/z: 268.1308 , found: 268.1308.



1j

The compound **1j** (2.33 g, 80% yield) as a white solid was prepared from **S1j** (2.99 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

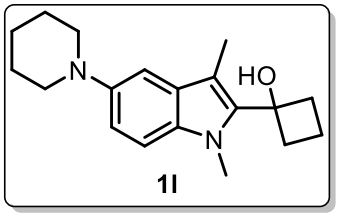
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.71-7.66 (m, 2H), 7.50 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.33 (td, *J* = 8.5, 1.9 Hz, 2H), 3.75 (s, 3H), 2.97-2.87 (m, 2H), 2.57-2.50 (m, 2H), 2.48-2.43 (m, 1H), 2.42 (s, 3H), 2.05 (s, 1H), 2.01-1.92 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 142.7, 138.7, 136.8, 132.4, 128.7, 128.6, 127.3, 126.2, 121.9, 117.3, 109.0, 107.2, 75.3, 36.8, 31.1, 17.0, 9.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{21}NNaO$, m/z: 314.1515, found: 314.1512.



1k

The compound **1k** (2.04 g, 80% yield) as a white solid was prepared from **S1k** (2.63 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

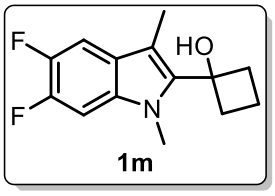
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.44 (d, *J* = 5.0 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.23 (s, 3H), 2.50 (dd, *J* = 17.5, 8.5 Hz, 2H), 2.34-2.27 (m, 1H), 2.27-2.14 (m, 7H), 2.05 (ddd, *J* = 10.5, 8.5, 5.5 Hz, 1H), 1.69-1.61 (m, 1H), 0.89-0.85 (m, 2H), 0.82-0.78 (m, 2H). **^{13}C NMR** (126 MHz, C_6D_6, ppm): δ 138.6, 136.6, 134.1, 129.2 , 121.2, 116.1, 108.9, 106.4, 75.2, 36.9, 30.7, 17.3, 16.3, 10.0, 8.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{17}H_{21}NNaO$, m/z: 278.1515, found: 278.1516.



1l

The compound **1l** (1.64 g, 55% yield) as a white solid was prepared from **S1l** (3.06 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

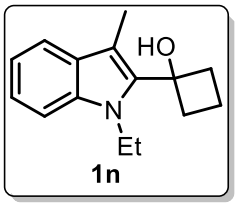
R_f = 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.29 (d, *J* = 2.0 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.30 (s, 3H), 3.14-3.08 (m, 4H), 2.61-2.55 (m, 2H), 2.31-2.22 (m, 6H), 1.72-1.67 (m, 5H), 1.46-1.40 (m, 2H), 0.50 (s, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 147.5, 138.6, 133.8, 129.4, 117.1, 109.4, 107.2, 106.4, 75.2, 54.1, 37.1, 30.8, 27.0, 24.9, 17.3, 10.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{27}N_2O$, m/z: 299.2118, found: 299.2120.



1m

The compound **1m** (1.91 g, 76% yield) as a white solid was prepared from **S1m** (2.59 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

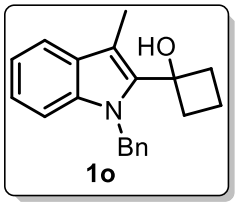
R_f = 0.35 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.17-7.12 (m, 1H), 6.65 (dd, *J* = 10.5, 6.5 Hz, 1H), 3.03 (s, 3H), 2.45-2.38 (m, 2H), 2.24-2.15 (m, 1H), 2.13-2.07 (m, 2H), 1.99 (s, 3H), 1.75 (s, 1H), 1.66-1.58 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 149.54 (d, *J* = 15.8 Hz), 147.58 (dd, *J* = 15.3, 11.4 Hz), 145.66 (d, *J* = 14.9 Hz), 139.73 (d, *J* = 4.0 Hz), 132.70 (d, *J* = 9.8 Hz), 123.99 (d, *J* = 7.2 Hz), 106.83 (dd, *J* = 4.4, 1.5 Hz), 105.60 (d, *J* = 18.6 Hz), 97.07 (d, *J* = 21.7 Hz), 74.79, 36.69, 30.84, 17.15, 9.74. **^{19}F NMR** (471 MHz, C_6D_6, ppm) δ -143.80, -143.85, -148.75, -148.79. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{14}H_{16}F_2NO$, m/z: 252.1194 , found: 252.1195.



1n

The compound **1n** (1.53 g, 67% yield) as a white solid was prepared from **S1n** (2.37 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

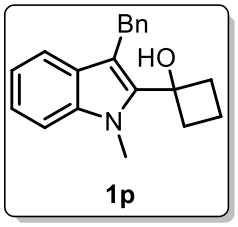
R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$, ppm): δ 7.46 (dt, *J* = 9.5, 1.5 Hz, 1H), 7.28 (dt, *J* = 10.0, 1.0 Hz, 1H), 7.10 (ddd, *J* = 9.5, 7.0, 1.5 Hz, 1H), 6.99 (ddd, *J* = 9.5, 7.0, 1.5 Hz, 1H), 4.56 (s, 1H), 4.22 (q, *J* = 9.0 Hz, 2H), 2.92-2.82 (m, 2H), 2.51-2.42 (m, 2H), 2.41-2.33 (m, 1H), 2.28 (s, 3H), 1.94-1.85 (m, 1H), 1.33 (t, *J* = 9 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$, ppm): δ 139.7, 137.0, 129.9, 122.1, 119.2, 119.1, 109.8, 106.4, 75.3, 39.4, 37.8, 18.0, 15.3, 10.0. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}NNaO$, m/z: 252.1359, found: 252.1359.



1o

The compound **1o** (1.69 g, 58% yield) as a white solid was prepared from **S1o** (2.99 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 20:1-10:1 as eluent.

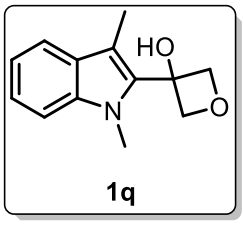
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 7.0, 0.5 Hz, 1H), 7.17-7.12 (m, 2H), 7.01-6.93 (m, 4H), 6.81-6.75 (m, 2H), 5.20 (s, 2H), 2.55-2.47 (m, 2H), 2.28 (s, 3H), 2.24-2.16 (m, 1H), 2.15-2.07 (m, 3H), 1.59-1.51 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 139.2, 138.7, 137.8, 129.4, 128.8, 127.0, 126.0, 122.8, 119.7, 119.2, 110.2, 107.5, 75.2, 47.7, 37.2, 17.6, 10.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{21}NNaO$, m/z: 314.1515, found: 314.1514.



1p

The compound **1p** (1.75 g, 60% yield) as a white solid was prepared from **S1p** (2.99 g, 10 mmol) according to general procedure with petroleum ether/ethyl acetate = 20:1-10:1 as eluent.

R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.33-7.28 (m, 1H), 7.20-7.15 (m, 4H), 7.13-7.08 (m, 3H), 7.04-7.00 (m, 1H), 4.15 (s, 2H), 3.35 (s, 3H), 2.61-2.51 (m, 2H), 2.23-2.15 (m, 3H), 1.79 (s, 1H), 1.61-1.53 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 142.3, 139.4, 138.0, 129.1, 128.7, 128.4, 126.1, 122.5, 119.7, 119.6, 109.9, 109.3, 74.9, 36.8, 30.8, 30.4, 17.3. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{21}NNaO$, m/z: 314.1515, found: 314.1520.

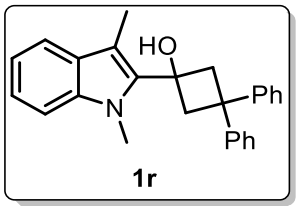


1q

The compound **1q** (1.80 g, 83% yield) as a white solid was prepared from **S1a** (2.23 g, 10 mmol) and oxetan-3-one (1.44 g, 20 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-10:1 as eluent.

R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.51 (d, *J* = 10.0 Hz, 1H), 7.27-7.17 (m, 2H), 7.10 (t, *J* = 9.5 Hz, 1H), 5.27 (d, *J* = 8.5 Hz, 2H), 4.84 (d, *J* = 8.5 Hz, 2H), 3.46 (s, 3H), 3.03 (s, 1H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 137.2, 134.2, 127.9, 122.7, 119.2, 119.0, 108.9, 107.9, 83.2, 73.4, 30.3, 9.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{13}H_{16}NO_2$, m/z:

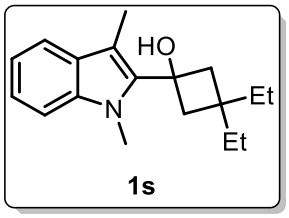
218.1176, found: 218.1175.



1r

The compound **1r** (3.12 g, 85% yield) as a white solid was prepared from **S1a** (2.23 g, 10 mmol) and 3,3-diphenylcyclobutan-1-one (4.44 g, 20 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-5:1 as eluent.

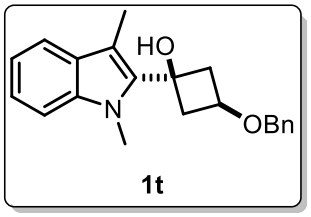
R_f = 0.30 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.44-7.40 (m, 2H), 7.34-7.30 (m, 1H), 7.27-7.23 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.12-7.00 (m, 7H), 6.94-6.90 (m, 1H), 3.40 (dd, *J* = 10.5, 3.0 Hz, 2H), 3.30-3.25 (m, 5H), 2.22 (s, 3H), 1.60 (s, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 151.0, 149.1, 138.3, 137.9, 129.2, 128.7, 128.6, 127.2, 126.1, 125.9, 125.8, 122.4, 119.3, 119.2, 109.2, 107.0, 70.6, 49.9, 46.8, 30.7, 10.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{26}H_{25}NNaO$, m/z: 390.1828, found: 390.1828.



1s

The compound **1s** (2.26 g, 83% yield) as a white solid was prepared from **S1a** (2.23 g, 10 mmol) and 3,3-diethylcyclobutan-1-one (2.52 g, 20 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-5:1 as eluent.

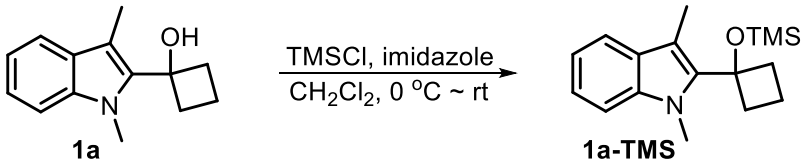
R_f = 0.30 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.52 (d, *J* = 8.0, 1H), 7.25-7.18 (m, 2H), 7.12-7.05 (m, 1H), 3.70 (s, 3H), 2.66-2.58 (m, 2H), 2.36 (s, 3H), 2.35-2.30 (m, 2H), 1.90 (s, 1H), 1.79 (q, *J* = 7.6 Hz, 2H), 1.37 (q, *J* = 7.6 Hz, 2H), 0.84 (t, *J* = 7.6 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 139.3, 137.2, 128.4, 122.0, 118.8, 118.7, 108.7, 106.5, 69.8, 46.2, 36.2, 31.0, 30.9, 29.6, 26.9, 10.2, 8.1, 8.0. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{25}NNaO$, m/z: 294.1828, found: 294.1824.



1t

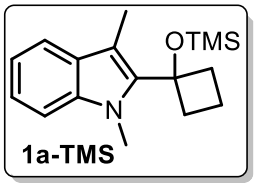
The compound **1t** (2.66 g, 83% yield) as a white solid was prepared from **S1a** (2.23 g, 10 mmol) and 3-(benzyloxy)cyclobutan-1-one (3.52 g, 20 mmol) according to general procedure with petroleum ether/ethyl acetate = 30:1-5:1 as eluent.

R_f = 0.30 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.28-7.22 (m, 3H), 7.22-7.13 (m, 3H), 7.11-7.06 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.18 (s, 2H), 3.59-3.52 (m, 1H), 3.27 (s, 3H), 3.06 (s, 1H), 2.92-2.85 (m, 2H), 2.39-2.31 (m, 2H), 2.26 (s, 3H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 138.8, 138.0, 137.0, 129.1, 128.6, 128.0, 122.4, 119.2, 119.1, 109.1, 107.0, 70.4, 68.8, 67.5, 44.9, 31.1, 10.5. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{21}H_{23}NNaO_2$, m/z: 344.1621, found: 344.1614.



1a **1a-TMS**

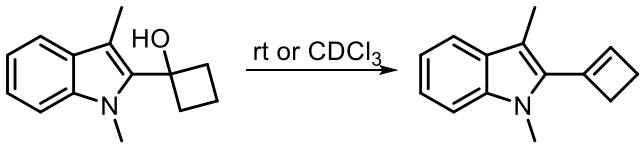
A 15 mL dried round bottom flask equipped with compound **1a** (215 mg, 1 mmol, 1.0 equiv.) and a magnetic stirring bar was charged with anhydrous DCM (5 mL) under argon atmosphere. Imidazole (408 g, 6.0 mmol, 6.0 equiv.) and TMSCl (326 mg , 3.0 mmol, 3.0 equiv.) was added successively under argon atmosphere at 0 ℃. The reaction mixture was stirred for 45 mins with natural warming. Then the reaction was quenched by addition of a saturated solution of $NaHCO_3$ (5 mL) and the reaction mixture was extracted with DCM (3 × 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum, the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 150:1 to 50:1) to give the compound **1a-TMS** (258 mg, 90% yield) as a white solid.



1a-TMS

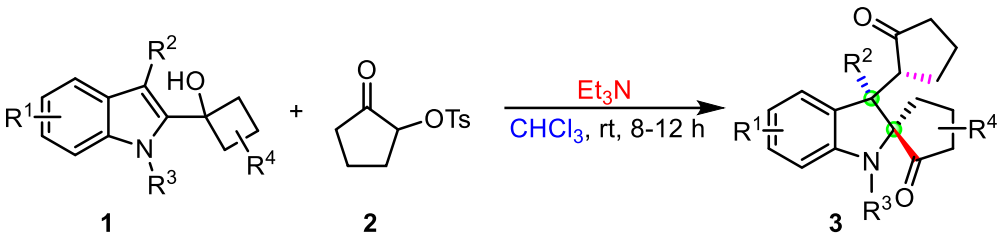
R_f = 0.60 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.29-7.20 (m, 2H), 7.12 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 3.72 (s, 3H), 2.94-2.81 (m, 2H), 2.56-2.48 (m, 2H), 2.46 (s, 3H), 2.24-2.10 (m, 1H), 1.86-1.73 (m, 1H), -0.10 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 137.4, 137.1, 128.5, 121.7, 118.6, 118.5, 108.5, 106.1, 76.2, 38.1, 31.1, 15.8, 10.3, 0.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{17}H_{26}NOSi$, m/z: 288.1778 , found: 288.1779.

Note: Substrate **1** is easily converted to hydroxyl elimination products at room temperature or in Chloroform-d with weak acidity. Therefore, substrate **1** was used immediately after preparation. In example **1a**, as shown below:

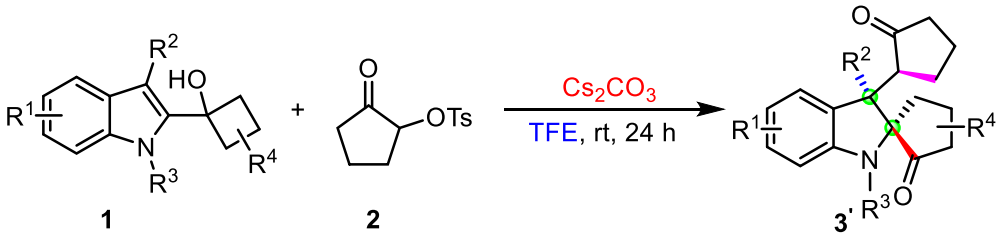


1a **S3a**

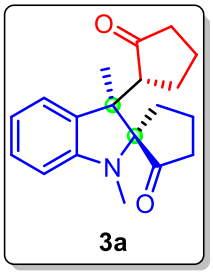
4. General procedure for the Dearomative Oxyallyl Cation Promoted Semipinacol Rearrangement of Indole-type Allylic Alcohols



General procedure A: The substrates **1** (0.1 mmol, 1.0 equiv.) and Et_3N (0.15 mmol, 1.5 equiv.) were dissolved in $CHCl_3$ (2.0 mL) under argon atmosphere. Then, the substrate **2** (0.15 mmol, 1.5 equiv.) was added to the reaction system. After 8-12 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl ether = 10:1~3:1) to afford the desired products **3**.



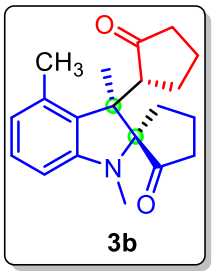
General procedure B: The substrates **1** (0.1 mmol, 1.0 equiv.) and Cs_2CO_3 (0.30 mmol, 3.0 equiv.) were dissolved in TFE (2.0 mL) under argon atmosphere. Then, the substrate **2** (0.15 mmol, 1.5 equiv.) was added to the reaction system. After 24 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl ether = 10:1~3:1) to afford the desired products **3'**.



General procedure A was followed using **1a** (21.5 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired

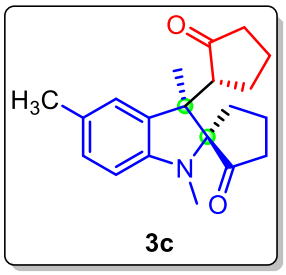
product as a mixture of two diastereoisomers (26.4 mg, 89% yield, 10.8:1 dr). The major isomer **3a** was a white crystal after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **mp**: 101-104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 2.63-2.43 (m, 5H), 2.26-2.20 (m, 1H), 2.18-2.02 (m, 5H), 1.95-1.79 (m, 6H), 1.45-1.31 (m, 1H), 1.28-1.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.8, 219.4, 150.2, 134.3, 128.1, 121.5, 117.5, 105.1, 82.9, 61.2, 52.5, 39.8, 37.7, 29.3, 26.6, 26.1, 19.9, 19.7, 17.2. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{23}NNaO_2$, m/z: 320.1621, found: 320.1622.



General procedure A was followed using **1b** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (23.0 mg, 74% yield, 9.0:1 dr). The major isomer **3b** was a white amorphous solid after further column chromatography.

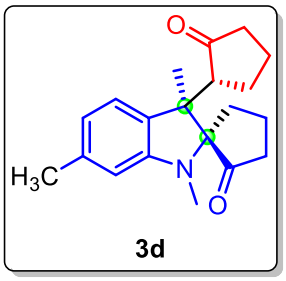
R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.02 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 2.94-2.83 (m, 1H), 2.55-2.45 (m, 1H), 2.27-2.19 (m, 4H), 2.19-2.14 (m, 1H), 2.12 (s, 3H), 2.01-1.93 (m, 5H), 1.86-1.71 (m, 2H), 1.58-1.50 (m, 1H), 1.49-1.40 (m, 1H), 1.38-1.32 (m, 1H), 1.31-1.25 (m, 1H), 1.05-0.93 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 220.1, 218.6, 151.2, 133.1, 130.9, 128.3, 121.8, 103.9, 82.5, 58.5, 54.5, 40.1, 37.9, 29.4, 26.8, 26.4, 21.3, 20.3, 19.9, 17.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1775.



3c

General procedure A was followed using **1c** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (25.8 mg, 83% yield, 7.0:1 dr). The major isomer **3c** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.89 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 2.65-2.55 (m, 1H), 2.54-2.43 (m, 4H), 2.27 (s, 3H), 2.25-2.19 (m, 1H), 2.18-2.10 (m, 2H), 2.10-2.01 (m, 3H), 1.96-1.87 (m, 2H), 1.87-1.79 (m, 4H), 1.44-1.34 (m, 1H), 1.31-1.22 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 221.0, 219.6, 148.2, 134.6, 128.3, 126.9, 122.5, 105.0, 83.1, 61.2, 52.5, 39.8, 37.7, 29.6, 26.2, 20.9, 19.9, 19.7, 17.2. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1780.

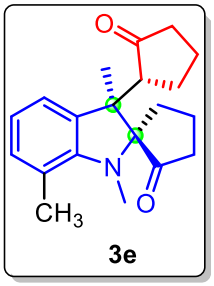


3d

General procedure A was followed using **1d** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (23.3 mg, 75% yield, 7.3:1 dr). The major isomer **3d** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.88 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 0.8 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 3.31 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.01-2.91 (m, 1H), 2.50 (s, 3H), 2.32-2.26 (m, 1H), 2.25 (s, 3H), 2.19-2.10 (m, 2H), 2.05-1.93 (m, 3H), 1.89-1.82 (m, 2H), 1.67-1.59 (m, 2H), 1.54-1.49 (m, 1H), 1.39 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.0,

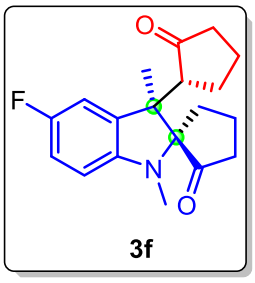
218.6, 148.2, 133.5, 128.2, 126.5, 124.1, 105.6, 84.4, 51.1, 49.9, 39.5, 37.5, 30.2, 28.0, 24.3, 20.9, 19.5, 17.5, 13.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1774.



3e

General procedure A was followed using **1e** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (20.2 mg, 65% yield, 11.7:1 dr). The major isomer **3e** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.86 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 2.84 (s, 3H), 2.64-2.52 (m, 1H), 2.51-2.42 (m, 1H), 2.41 (s, 3H), 2.29-2.21 (m, 1H), 2.21-1.98 (m, 6H), 1.98-1.82 (m, 2H), 1.81 (s, 3H), 1.46-1.35 (m, 1H), 1.28-1.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.8, 219.4, 148.0, 135.5, 131.8, 120.0, 118.3, 117.7, 82.9, 61.3, 51.7, 39.8, 37.6, 33.5, 26.5, 20.1, 20.0, 19.7, 17.3. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1780.

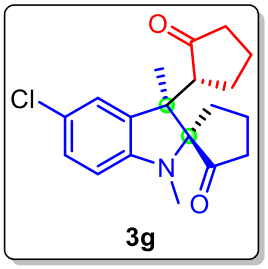


3f

General procedure A was followed using **1f** (23.3 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (26.1 mg, 83% yield, 8.2:1 dr). The major isomer **3f** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.82-6.67 (m, 2H), 6.17 (dd, *J* = 8.4, 4.0 Hz, 1H), 2.62-2.41 (m, 5H), 2.27-2.15 (m, 2H), 2.15-2.01 (m, 4H), 1.97-1.88 (m,

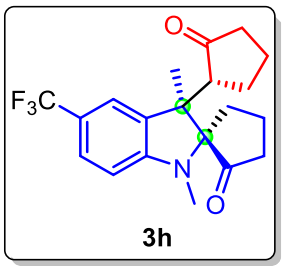
2H), 1.88-1.81 (m, 1H), 1.80 (s, 3H), 1.49-1.36 (m, 1H), 1.36-1.23 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.3, 219.0, 156.7 (d, *J* = 234.4 Hz), 146.4, 136.1 (d, *J* = 7.2 Hz), 113.6 (d, *J* = 22.9 Hz), 109.8 (d, *J* = 24.7 Hz), 105.0 (d, *J* = 8.0 Hz), 83.1, 60.6, 52.2, 39.7, 37.6, 29.8, 26.4, 26.2, 19.9, 19.6, 17.1. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -127.3. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{22}FNNaO_2$, m/z: 338.1527, found: 338.1533



3g

General procedure A was followed using **1g** (24.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (26.1 mg, 79% yield, 12.2:1 dr). The major isomer **3g** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.20 (d, *J* = 8.4 Hz, 1H), 2.60-2.41 (m, 5H), 2.28-2.10 (m, 3H), 2.10-2.01 (m, 3H), 1.96-1.83 (m, 3H), 1.81 (s, 3H), 1.49-1.36 (m, 1H), 1.36-1.23 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.1, 219.0, 148.8, 136.3, 127.8, 122.1, 105.9, 83.0, 60.8, 52.3, 39.6, 37.6, 29.4, 26.7, 26.1, 19.9, 19.6, 17.2. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{22}ClNNaO_2$, m/z: 354.1231, found: 354.1236.

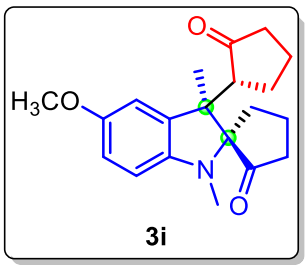


3h

General procedure A was followed using **1h** (28.3 mg, 0.1 mmol) stirred for 12 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired

product as a mixture of two diastereoisomers (24.5 mg, 67% yield, 9.8:1 dr). The major isomer **3h** was a colorless crystal after further column chromatography.

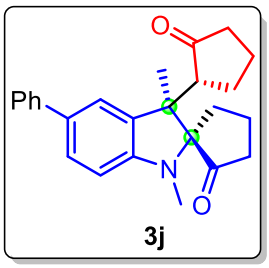
R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **mp**: 107-108 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.34 (ddd, *J* = 8.4, 2.0, 0.8 Hz, 1H), 7.12 (d, *J* = 1.6 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H), 2.55-2.41 (m, 2H), 2.30-2.22 (m, 1H), 2.22-2.00 (m, 5H), 1.98-1.78 (m, 6H), 1.49-1.36 (m, 1H), 1.30-1.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.9, 219.0, 125.1 (q, *J* = 269.0 Hz), 152.6, 134.7, 126.3 (q, *J* = 4.0 Hz), 119.3 (q, *J* = 32.2 Hz), 118.7 (q, *J* = 3.6 Hz), 104.1, 83.0, 60.9, 52.2, 39.6, 37.6, 29.1, 27.4, 26.0, 19.8, 19.6, 17.2. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -60.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{22}F_3NNaO_2$, m/z: 388.1495, found: 388.1497.



3i

General procedure A was followed using **1i** (24.5 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (28.1 mg, 86% yield, 4.9:1 dr). The major isomer **3i** was a white amorphous solid after further column chromatography.

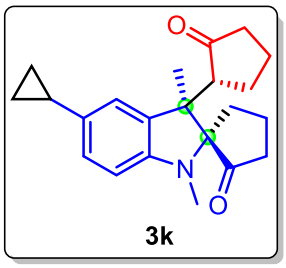
R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.67-6.59 (m, 2H), 6.21 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 2.65-2.53 (m, 1H), 2.52-2.42 (m, 4H), 2.24-2.02 (m, 6H), 1.97-1.83 (m, 3H), 1.81 (s, 3H), 1.46-1.34 (m, 1H), 1.33-1.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 220.7, 219.3, 152.9, 144.7, 136.1, 111.6, 110.0, 105.1, 83.1, 60.9, 56.0, 52.4, 39.7, 37.6, 29.9, 26.3, 26.1, 19.9, 19.7, 17.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_3$, m/z: 350.1727, found: 350.1724.



3j

General procedure A was followed using **1j** (29.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (29.8 mg, 80% yield, 11.2:1 dr). The major isomer **3j** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 7.55 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.42-7.35 (m, 3H), 7.28-7.23 (m, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 2.64-2.45 (m, 5H), 2.34-2.27 (m, 1H), 2.24-2.04 (m, 5H), 1.98-1.90 (m, 5H), 1.88-1.79 (m, 1H), 1.45-1.28 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 220.7, 219.5, 149.8, 141.5, 135.1, 130.9, 128.6, 127.0, 126.2, 126.0, 120.5, 105.3, 83.1, 61.3, 52.5, 39.8, 37.7, 29.4, 26.8, 26.2, 19.9, 19.8, 17.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{28}NO_2$, m/z: 374.2115, found: 374.2115.

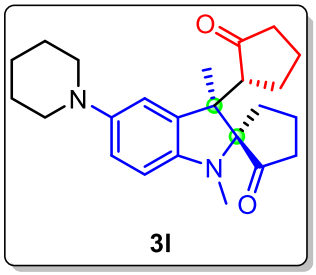


3k

General procedure A was followed using **1k** (25.5 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (29.0 mg, 86% yield, 6.9:1 dr). The major isomer **3k** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 2.84 (qd, *J* = 13.0, 7.0 Hz, 1H), 2.52-2.43 (m, 1H), 2.23 (s, 3H), 2.21-2.12 (m, 1H), 1.94 (dd, *J* = 17.5, 8.5 Hz, 1H), 1.87-1.79 (m, 6H), 1.78-1.69 (m, 2H), 1.55-1.47 (m, 1H), 1.46-1.37 (m, 1H), 1.35-1.29 (m, 1H), 1.29-1.22 (m, 1H), 1.01-0.89 (m, 1H), 0.80-0.74 (m, 2H), 0.67-0.62 (m, 2H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 219.5, 218.1, 149.1, 135.2, 133.2, 125.9, 120.2, 105.4, 83.2, 61.2, 52.7, 39.8, 37.7, 29.5, 26.5, 20.1, 20.0, 17.5, 15.8, 8.6, 8.5.

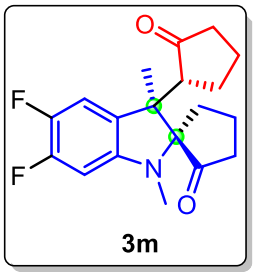
HRMS (ESI) calcd for $[M+Na]^+$ $C_{22}H_{27}NNaO_2$, m/z: 360.1934, found: 360.1932.



3l

General procedure A was followed using **1l** (29.8 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1:1) to afford the desired product as a mixture of two diastereoisomers (20.1 mg, 53% yield, 6.5:1 dr). The major isomer **3l** was a yellow amorphous solid after further column chromatography.

R_f = 0.34 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 6.80-6.65 (m, 2H), 6.21 (d, *J* = 8.5 Hz, 1H), 3.05-2.89 (m, 4H), 2.58 (qd, *J* = 12.5, 6.0 Hz, 1H), 2.53-2.43 (m, 4H), 2.22-2.16 (m, 1H), 2.16-2.12 (m, 1H), 2.12-2.09 (m, 1H), 2.09-2.00 (m, 3H), 1.95-1.87 (m, 2H), 1.86-1.79 (m, 4H), 1.76-1.69 (m, 4H), 1.57-1.49 (m, 2H), 1.40-1.31 (m, 1H), 1.31-1.23 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 221.1, 219.7, 145.8, 145.1, 135.5, 116.5, 114.5, 105.0, 83.1, 61.1, 53.3, 52.6, 39.8, 37.6, 29.8, 26.4, 26.3, 26.2, 24.1, 19.9, 19.7, 17.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{33}N_2O_2$, m/z: 381.2537, found: 381.2545.

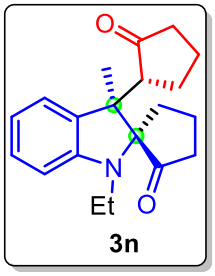


3m

General procedure A was followed using **1m** (25.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (25.6 mg, 77% yield, 8.0:1 dr). The major isomer **3m** was a yellow amorphous solid after further column chromatography.

R_f = 0.40 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 6.81 (t, *J* = 9.0 Hz, 1H), 6.06 (dd, *J* = 11.0, 6.5 Hz, 1H), 2.54-2.43 (m, 5H), 2.26-2.15 (m, 2H), 2.14-2.01 (m, 4H), 1.98-1.82 (m, 3H), 1.76 (s, 3H), 1.48-1.37 (m, 1H), 1.36-1.27 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 219.8, 218.9, 151.3 (d, *J* = 13.8 Hz), 149.4 (d, *J* = 13.6 Hz), 146.5 (d, *J* = 9.3 Hz), 144.3 (d, *J* = 13.5 Hz), 142.4

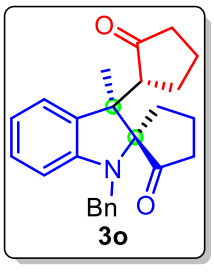
(d, J = 13.6 Hz), 129.7, 111.2 (d, J = 19.9 Hz), 94.5 (d, J = 22.6 Hz), 82.9, 60.6, 51.8, 39.6, 37.6, 29.7, 26.7, 26.2, 19.9, 19.6, 17.1. **^{19}F NMR** (471 MHz, $CDCl_3$, ppm): δ -139.4, -139.4, -152.6, -152.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{21}F_2NNaO_2$, m/z: 356.1433, found: 356.1434.



3n

General procedure A was followed using **1n** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (21.8 mg, 70% yield, 3.3:1 dr). The major isomer **3n** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 7.07 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.0 Hz, 1H), 6.67 (t, J = 7.5 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 3.05-2.94 (m, 1H), 2.80-2.64 (m, 2H), 2.52-2.42 (m, 1H), 2.31 (dd, J = 14.0, 6.5 Hz, 1H), 2.20-2.08 (m, 3H), 2.08-2.00 (m, 2H), 1.96-1.71 (m, 6H), 1.45-1.31 (m, 1H), 1.31-1.16 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 221.2, 219.6, 149.3, 134.3, 128.0, 121.6, 116.9, 104.7, 83.4, 61.6, 52.5, 39.8, 39.6, 37.6, 28.8, 26.0, 20.0, 19.6, 17.2, 13.7. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1782.

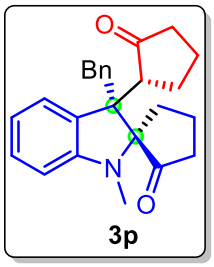


3o

General procedure A was followed using **1o** (29.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (25.0 mg, 67% yield, 9.2:1 dr). The major isomer **3o** was a white amorphous solid after further column chromatography.

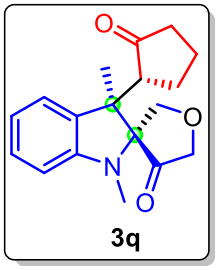
R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.48 (d, J = 7.6 Hz,

2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 7.6 Hz, 1H), 4.05 (d, *J* = 15.2 Hz, 1H), 3.96(d, *J* = 15.2 Hz, 1H), 2.89-2.75 (m, 1H), 2.56-2.37 (m, 2H), 2.29-2.05 (m, 5H), 2.02-1.87 (m, 6H), 1.51-1.39 (m, 1H), 1.38-1.29 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 221.0, 219.4, 149.9, 138.6, 134.8, 128.4, 127.8, 127.4, 127.0, 121.6, 118.2, 107.3, 83.6, 61.4, 52.6, 50.7, 39.8, 37.9, 28.7, 26.4, 20.4, 20.0, 17.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{28}NO_2$, m/z: 374.2115, found: 374.2110.



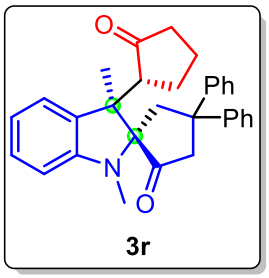
General procedure A was followed using **1p** (29.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (21.6 mg, 58% yield, 7.0:1 dr). The major isomer **3p** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.29-7.22 (m, 3H), 7.20-7.14 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 6.8 Hz, 1H), 3.97 (d, *J* = 12.8 Hz, 1H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.67-2.61 (m, 1H), 2.60 (s, 3H), 2.48-2.38 (m, 2H), 2.38-2.30 (m, 1H), 2.28-2.14 (m, 2H), 2.12-1.96 (m, 3H), 1.94-1.82 (m, 2H), 1.60-1.46 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.2, 217.6, 151.0, 137.5, 132.0, 131.9, 128.2, 127.8, 126.7, 125.0, 117.0, 106.0, 81.7, 56.5, 54.5, 40.2, 38.5, 38.3, 29.9, 28.9, 26.4, 19.9, 17.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{25}H_{27}NNaO_2$, m/z: 396.1934, found: 396.1934.



General procedure A was followed using **1q** (21.7 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (23.3 mg, 78% yield, 13.0:1 dr). The major isomer **3q** was a white amorphous solid after further column chromatography.

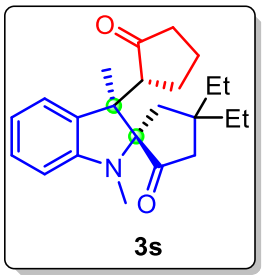
R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 7.07 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 4.27-4.20 (m, 1H), 3.98 (d, *J* = 10.5 Hz, 1H), 3.48-3.41 (m, 2H), 2.55-2.43 (m, 1H), 2.25 (s, 3H), 2.05-1.90 (m, 2H), 1.88 (s, 3H), 1.87-1.82 (m, 1H), 1.50-1.41 (m, 1H), 1.25-1.18 (m, 1H), 0.99-0.89 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 217.7, 216.3, 150.3, 134.9, 128.5, 128.1, 122.3, 118.8, 105.7, 80.2, 72.4, 68.1, 60.9, 52.1, 39.5, 29.5, 26.5, 20.0, 19.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{21}NNaO_3$, m/z: 322.1414, found: 322.1407.



3r

General procedure A was followed using **1r** (36.7 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 2:1) to afford the desired product as a mixture of two diastereoisomers (22.4 mg, 50% yield, 8.2:1 dr). The major isomer **3r** was a white amorphous solid after further column chromatography.

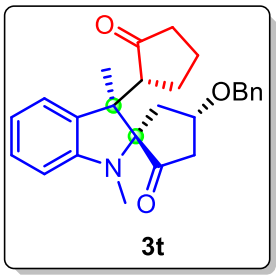
R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.31-7.27 (m, 4H), 7.25-7.22 (m, 4H), 7.21-7.15 (m, 1H), 7.15-7.10 (m, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.69 (td, *J* = 7.6, 1.2 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 3.64 (d, *J* = 15.2 Hz, 1H), 3.48 (dd, *J* = 16.0, 2.4 Hz, 1H), 3.24 (d, *J* = 16.4 Hz, 1H), 2.70-2.54 (m, 2H), 2.20-2.08 (m, 3H), 1.86 (s, 3H), 1.85 (s, 3H), 1.83-1.79 (m, 1H), 1.42-1.32 (m, 1H), 1.26-1.18 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.2, 215.9, 150.1, 148.7, 147.6, 135.0, 128.6, 128.6, 128.2, 127.1, 126.5, 126.4, 126.3, 121.3, 117.9, 105.7, 82.9, 62.6, 53.0, 51.7, 47.0, 41.4, 39.5, 28.9, 26.33, 22.5, 20.0. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{31}H_{31}NNaO_2$, m/z: 472.2247, found: 472.2246.



3s

General procedure A was followed using **1s** (27.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 2:1) to afford the desired product as a mixture of two diastereoisomers (19.8 mg, 56% yield, 6.4:1 dr). The major isomer **3s** was an light yellow amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.68 (td, *J* = 7.2, 1.2 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 2.67 (qd, *J* = 12.4, 6.4 Hz, 1H), 2.60-2.52 (m, 4H), 2.25 (d, *J* = 15.6 Hz, 1H), 2.16-2.12 (m, 2H), 2.12-2.04 (m, 2H), 1.90 (s, 3H), 1.87-1.76 (m, 1H), 1.69-1.61 (m, 1H), 1.59-1.52 (m, 2H), 1.39-1.29 (m, 2H), 1.29-1.20 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.0, 217.7, 150.3, 135.0, 128.1, 121.3, 117.8, 105.4, 84.1, 62.2, 52.4, 51.4, 39.7, 36.8, 35.7, 31.0, 30.8, 29.1, 26.4, 21.8, 20.1, 8.5, 7.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{23}H_{31}NNaO_2$, m/z: 376.2247, found: 376.2245.



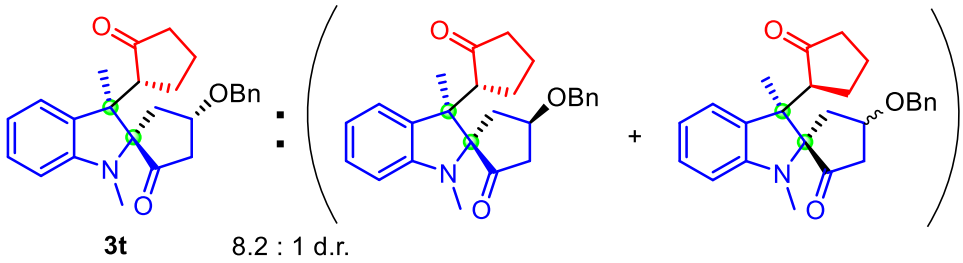
3t

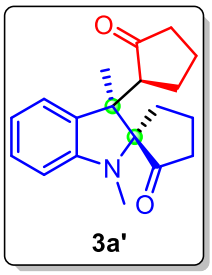
General procedure A was followed using **1t** (32.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 2:1) to afford the desired product as a mixture of two diastereoisomers (26.6 mg, 66% yield, 8.2:1 dr). The major isomer **3t** was a white amorphous solid after further column chromatography.

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.39-7.24 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 4.55 (s, 2H), 4.32-4.21 (m, 1H), 2.71-2.58 (m, 3H), 2.54 (s, 3H), 2.47-2.31 (m, 3H), 2.31-2.19 (m, 1H), 2.18-

2.04 (m, 1H), 1.95-1.84 (m, 1H), 1.69 (s, 3H), 1.55-1.44 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 218.6, 216.1, 149.2, 137.8, 136.0, 128.5, 127.9, 127.8, 127.6, 122.6, 118.5, 105.8, 83.2, 72.3, 71.0, 59.9, 51.3, 47.0, 39.3, 35.6, 30.0, 26.9, 21.7, 20.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{30}NO_3$, m/z: 404.2220, found: 404.2214.

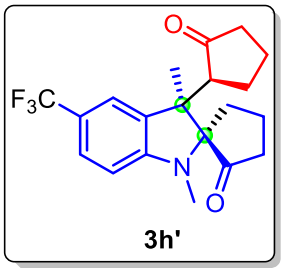
Note: based on our previous experimental results[2,3], we speculated that the relative configuration of **3t** was as follows:





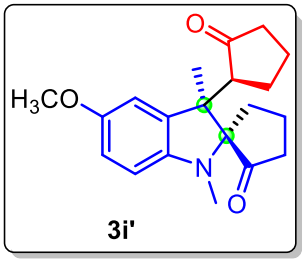
General procedure B was followed using **1a** (21.5 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (16.0 mg, 54% yield, 6.8:1 dr). The major isomer **3a'** was a colorless syrupy liquid after further column chromatography.

R_f = 0.37 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.06 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 1H), 3.36-3.25 (m, 1H), 3.02-2.89 (m, 1H), 2.52 (s, 3H), 2.32-2.06 (m, 3H), 2.05-1.89 (m, 3H), 1.89-1.79 (m, 2H), 1.66-1.54 (m, 2H), 1.53-1.46 (m, 1H), 1.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.8, 218.3, 150.1, 133.1, 127.9, 123.1, 117.1, 105.6, 84.1, 51.0, 49.9, 39.3, 37.4, 29.8, 27.8, 24.6, 19.4, 17.4, 13.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{23}NNaO_2$, m/z: 320.1621, found: 320.1622.



General procedure B was followed using **1h** (28.3 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (17.2 mg, 47% yield, 5.0:1 dr). The major isomer **3h'** was a colorless crystal after further column chromatography.

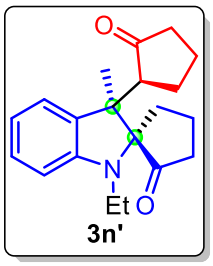
R_f = 0.32 (petroleum ether/ethyl acetate = 5:1). **mp**: 118-120 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.35-7.30 (m, 1H), 7.06 (d, *J* = 1.6 Hz, 1H), 6.31 (d, *J* = 8.4 Hz, 1H), 3.77 (q, *J* = 8.4 Hz, 1H), 3.34-3.24 (m, 1H), 3.02-2.92 (m, 1H), 2.57 (s, 3H), 2.34-2.20 (m, 2H), 2.19-2.08 (m, 1H), 2.06-1.94 (m, 3H), 1.93-1.79 (m, 2H), 1.65-1.60 (m, 1H), 1.56-1.48 (m, 1H), 1.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.6, 217.5, 152.6, 133.5, 126.2 (q, *J* = 4.0 Hz), 125.1 (q, *J* = 269.0 Hz), 120.2 (q, *J* = 3.6 Hz), 118.9 (q, *J* = 32.3 Hz), 104.6, 84.1, 50.8, 49.9, 39.4, 37.5, 29.6, 27.7, 25.6, 19.5, 17.6, 13.9. **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -62.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{22}F_3NNaO_2$, m/z: 388.1495, found: 388.1497.



General procedure B was followed using **1i** (24.5 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (17.7 mg, 54% yield, 6.7:1 dr). The major isomer **3i'** was a colorless syrupy liquid after further column chromatography.

R_f = 0.37 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, C_6D_6, ppm): δ 6.66-6.61 (m, 2H), 6.13 (d, *J* = 9.0 Hz, 1H), 3.56 (dd, *J* = 13.0, 8.5 Hz, 1H), 3.48 (s, 3H), 3.07-2.98 (m, 1H), 2.30 (s, 3H), 1.91-1.86 (m, 1H), 1.83-1.77 (m, 2H), 1.50-1.42 (m, 3H), 1.33-1.25 (m, 2H), 1.22 (s, 3H), 1.20-1.14 (m,

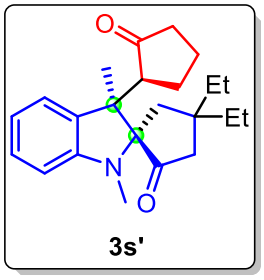
2H), 0.94-0.88 (m, 1H). **^{13}C NMR** (125 MHz, C_6D_6, ppm): δ 218.3, 215.8, 153.3, 145.3, 135.8, 128.1, 112.6, 111.7, 105.5, 84.4, 55.7, 51.1, 50.0, 39.2, 37.5, 30.3, 28.1, 24.5, 19.6, 17.8, 14.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_3$, m/z: 350.1727, found: 350.1724.



3n'

General procedure B was followed using **1n** (22.9 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 3:1) to afford the desired product as a mixture of two diastereoisomers (18.0 mg, 58% yield, 3.4:1 dr). The major isomer **3n'** was a colorless syrupy liquid after further column chromatography.

R_f = 0.37 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): 7.06 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 7.5 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 3.40-3.31 (m, 1H), 3.00-2.88 (m, 2H), 2.72-2.62 (m, 1H), 2.33-2.23 (m, 2H), 2.18-2.08 (m, 1H), 2.03-1.92 (m, 3H), 1.89-1.82 (m, 1H), 1.78-1.69 (m, 1H), 1.67-1.61 (m, 2H), 1.57-1.48 (m, 1H), 1.39 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 220.1, 218.5, 149.4, 133.1, 127.9, 123.4, 116.5, 104.9, 84.7, 51.2, 49.9, 40.0, 39.5, 37.5, 28.0, 27.1, 19.5, 17.5, 14.0, 13.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{20}H_{25}NNaO_2$, m/z: 334.1777, found: 334.1782.



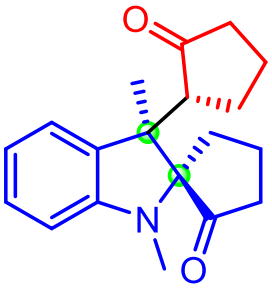
3s'

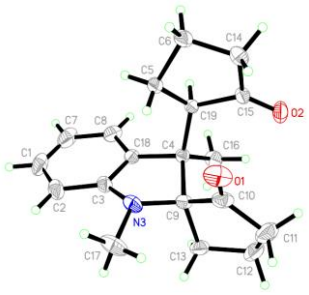
General procedure B was followed using **1s** (27.1 mg, 0.1 mmol) stirred for 8 h at rt. The crude mixture was purified by silica gel flash chromatography (petroleum ether/ethyl ether = 2:1) to afford the desired product as a mixture of two diastereoisomers (22.6 mg, 64% yield, 5.2:1 dr). The major isomer **3s'** was a light yellow syrupy liquid after further column chromatography.

R_f = 0.37 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm): δ 7.07 (td, *J* = 7.5, 1.5 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 3.32 (dd, *J* = 13.0, 8.0 Hz, 1H), 2.98 (d, *J* = 17.0 Hz, 1H), 2.55 (s, 3H), 2.34-2.22 (m, 2H), 2.10 (d, *J* = 16.0 Hz, 1H), 2.03-1.92 (m, 1H), 1.87-1.79 (m, 1H), 1.65-1.59 (m, 2H), 1.56-1.48 (m, 3H), 1.43 (s, 3H), 1.39-1.25 (m, 3H), 0.83 (t, *J* = 7.5 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm): δ 219.5, 215.3, 150.3, 134.0, 128.0, 123.0, 117.6, 106.4, 86.1, 51.6, 51.1, 50.3, 39.5, 36.2, 33.5, 31.3, 30.6, 29.9, 28.9, 19.7, 15.0, 8.6, 7.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{23}H_{31}NNaO_2$, m/z: 376.2247, found: 376.2245.

5. X-Ray Analysis of Compound 3a, 3h and 3h'

X-ray diffraction data of compound **3a**



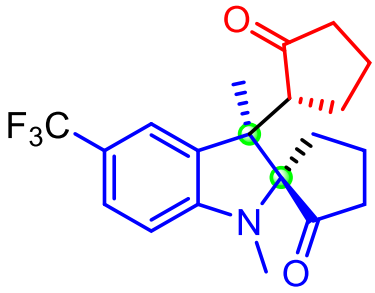


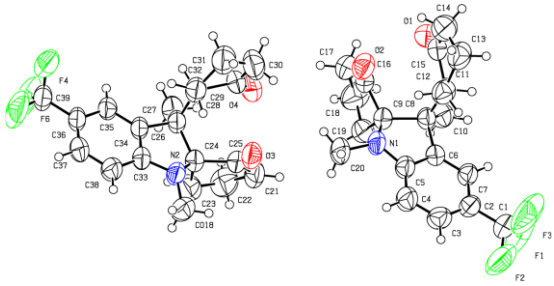
3a **CCDC 1992544**

Crystal data and structure refinement for 3a

Identification code	**3a**
Empirical formula	$C_{19}H_{23}NO_2$
Formula weight	297.38
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.2267(7) A alpha = 90 deg. b = 21.6420(17) A beta = 112.336(2) deg. c = 8.7088(7) A gamma = 90 deg.
Volume	1608.5(2) A^3
Z, Calculated density	4, 1.228 Mg/m^3
Absorption coefficient	0.623 mm^-1
F(000)	640
Crystal size	0.200 x 0.200 x 0.200 mm
Theta range for data collection	5.182 to 68.269 deg.
Limiting indices	-11<=h<=11, -26<=k<=26, -10<=l<=10
Reflections collected / unique	24900 / 2913 [R(int) = 0.0256]
Completeness to theta = 67.679	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2913 / 2 / 205
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1450
R indices (all data)	R1 = 0.0535, wR2 = 0.1478
Extinction coefficient	n/a
Largest diff. peak and hole	0.219 and -0.200 e.A^-3

X-ray diffraction data of compound **3h**



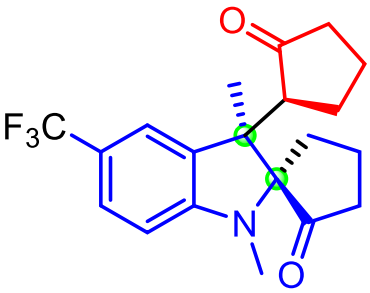


3h **CCDC: 2050194**

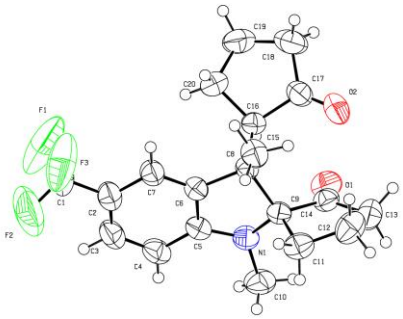
Crystal data and structure refinement for 3h

Identification code	**3h**
Empirical formula	$C_{40}H_{43}F_6N_2O_4$
Formula weight	729.76
Temperature	297(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.2944(6) A alpha = 68.586(2) deg. b = 12.0674(7) A beta = 89.702(3) deg. c = 15.9401(8) A gamma = 78.260(3) deg.
Volume	1799.73(18) A^3
Z, Calculated density	2, 1.347 Mg/m^3
Absorption coefficient	0.908 mm^-1
F(000)	766
Crystal size	0.200 x 0.100 x 0.100 mm
Theta range for data collection	2.986 to 68.324 deg.
Limiting indices	-11<=h<=12, -14<=k<=14, -19<=l<=19
Reflections collected / unique	19333 / 6484 [R(int) = 0.0676]
Completeness to theta = 67.679	98.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6484 / 0 / 473
Goodness-of-fit on F^2	1.634
Final R indices [I>2sigma(I)]	R1 = 0.0924, wR2 = 0.2598
R indices (all data)	R1 = 0.1297, wR2 = 0.2891
Extinction coefficient	n/a
Largest diff. peak and hole	0.592 and -0.363 e.A^-3

X-ray diffraction data of compound **3h'**



3h'



CCDC 2050195

Crystal data and structure refinement for 3h'

Identification code	**3h'**
Empirical formula	$C_{20}H_{22}F_3NO_2$
Formula weight	365.38
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.432 A alpha = 90 deg. b = 10.4321(5) A beta = 90 deg. c = 32.8983(16) A gamma = 90 deg.
Volume	3580.2(2) A^3
Z, Calculated density	8, 1.356 Mg/m^3
Absorption coefficient	0.913 mm^-1
F(000)	1536
Crystal size	0.180 x 0.160 x 0.150 mm
Theta range for data collection	2.686 to 68.348 deg.
Limiting indices	-12<=h<=11, -12<=k<=12, -39<=l<=39
Reflections collected / unique	26856 / 3276 [R(int) = 0.0460]
Completeness to theta = 67.679	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3276 / 0 / 237
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1961
R indices (all data)	R1 = 0.0753, wR2 = 0.2081
Extinction coefficient	n/a
Largest diff. peak and hole	0.875 and -0.416 e.A^-3

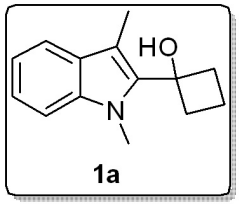
6. References

1 (a) Cheng, H.-G.; Lu, L.-Q.; Wang, T.; Yang, Q.-Q.; Liu, X.-P.; Li, Y.; Deng, Q.-H.; Chen, J.-R.; Xiao, W.-J., Highly Enantioselective Friedel–Crafts Alkylation/N-Hemiacetalization Cascade Reaction with Indoles. *Angew. Chem. Int. Ed.* **2013,** *52*, 3250-3254. (b) Chen, W.; Xia, Y.; Lin, L.; Yuan, X.; Guo, S.; Liu, X.; Feng, X., Asymmetric Synthesis of Furo[3,4-b]indoles by Catalytic [3+2] Cycloaddition of Indoles with Epoxides. *Chem. Eur. J.* **2015,** *21*, 15104-15107.

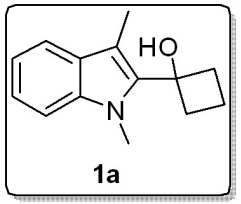
2 Wang, S.-H.; Si, R.-Q.; Zhuang, Q.-B.; Guo, X.; Ke, T.; Zhang, X.-M.; Zhang, F.-M.; Tu, Y.-Q., Collective Total Synthesis of Aspidofractinine Alkaloids through the Development of a Bischler–Napieralski/Semipinacol Rearrangement Reaction. *Angew. Chem. Int. Ed.* **2020,** *59*, 21954-21958.

3 Peng, J.-B.; Qi, Y.; Ma, A.-J.; Tu, Y.-Q.; Zhang, F.-M.; Wang, S.-H.; Zhang, S.-Y., Cascade Oxidative Dearomatization/Semipinacol Rearrangement: An Approach to 2-Spirocyclo-3-oxindole Derivatives. *Chem. Asian J.* **2013,** *8*, 883-887.

7. Copies of NMR Spectra


HO
N
1a

7.512
7.492
7.211
7.198
7.190
7.186
7.086
7.079
7.074
7.066
7.059
7.054
7.046
3.637
2.874
2.852
2.844
2.830
2.822
2.801
2.466
2.458
2.450
2.445
2.437
2.421
2.413
2.407
2.377
2.354
2.330
2.315
2.236
1.909
1.901
1.874
0.000 TMS
1.00
2.03
1.01
3.04
2.06
2.20
4.05
1.05
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

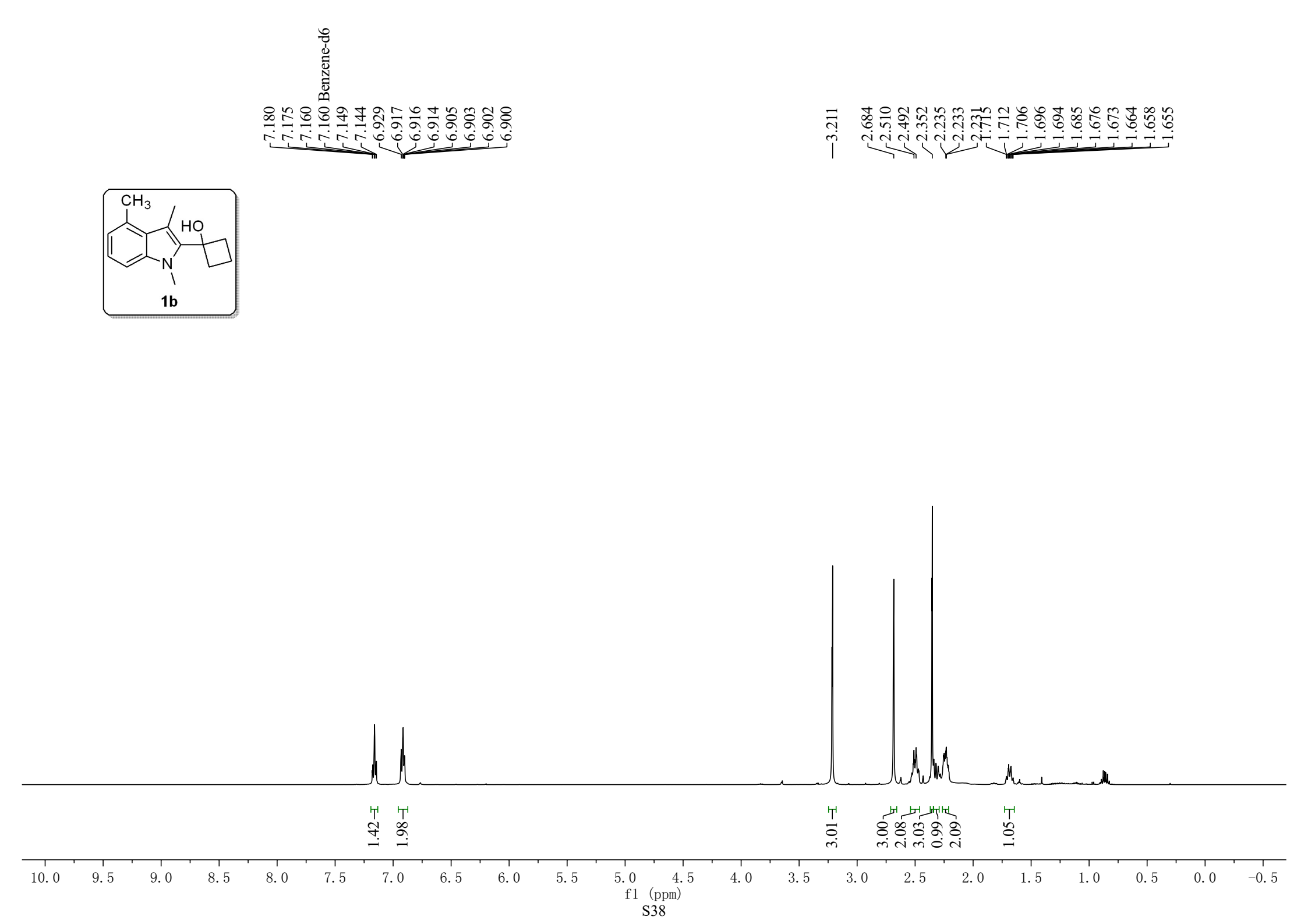


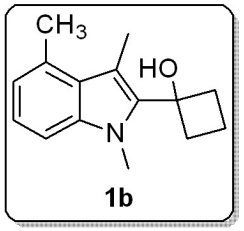
1a

137.98
137.12
128.23
121.98
118.70
118.64
108.65
106.74
77.00 Chloroform-d
75.23
36.70
30.83
16.90
9.68

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

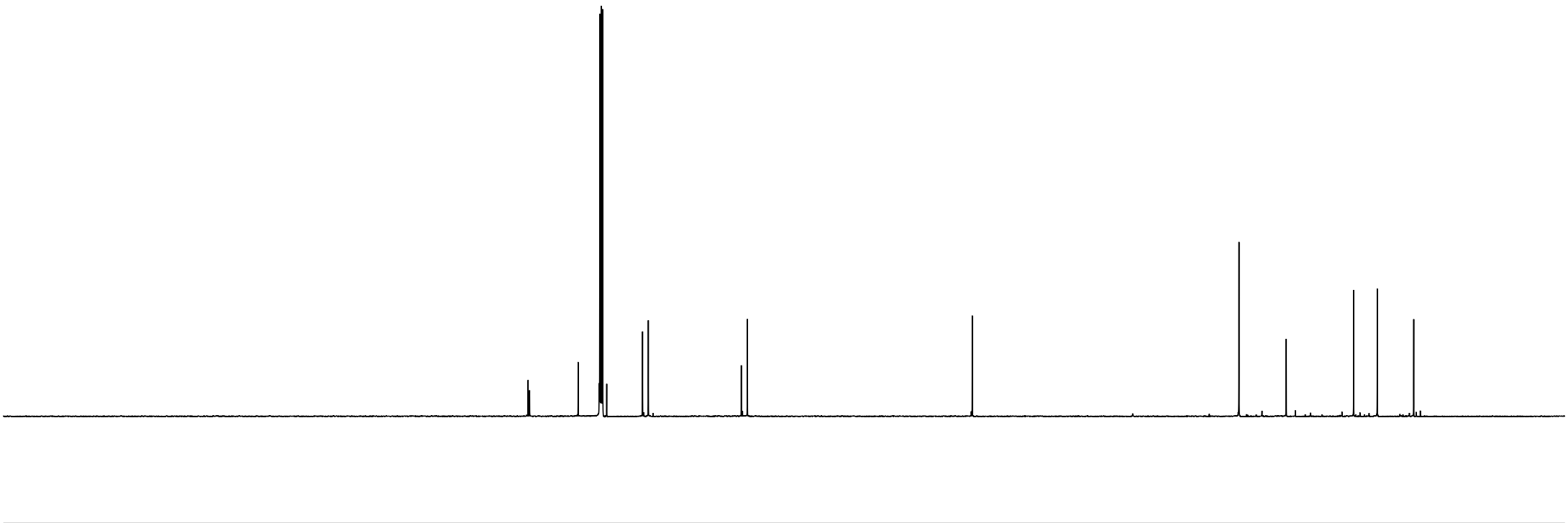
f1 (ppm)


7.180
7.175
7.160
7.160 Benzene-d6
7.149
7.144
6.929
6.917
6.916
6.914
6.905
6.903
6.902
6.900
3.211
2.684
2.510
2.492
2.352
2.235
2.233
2.231
1.715
1.712
1.706
1.696
1.694
1.685
1.676
1.673
1.664
1.658
1.655
CH3
HO
N
1b
1.42
1.98
3.01
3.00
2.08
3.03
0.99
2.09
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



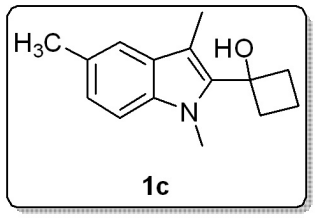
1b

138.443
138.238
131.336
128.060 Benzene-d6
127.276
122.186
121.366
108.161
107.298
75.347
37.448
30.739
21.160
17.801
12.623

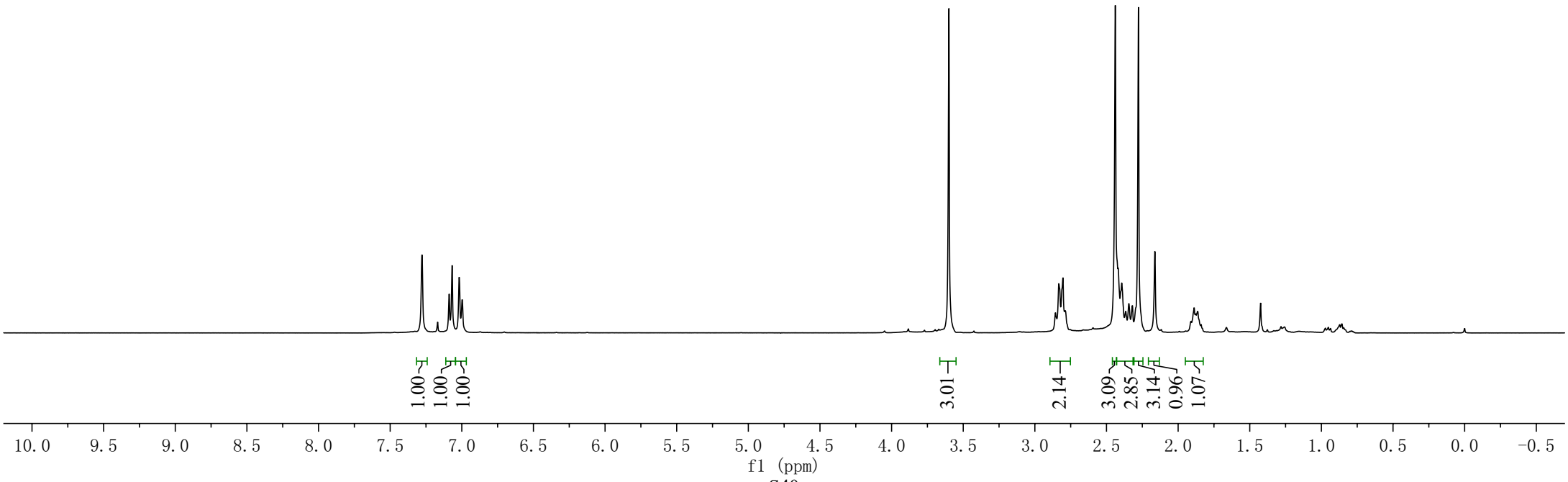


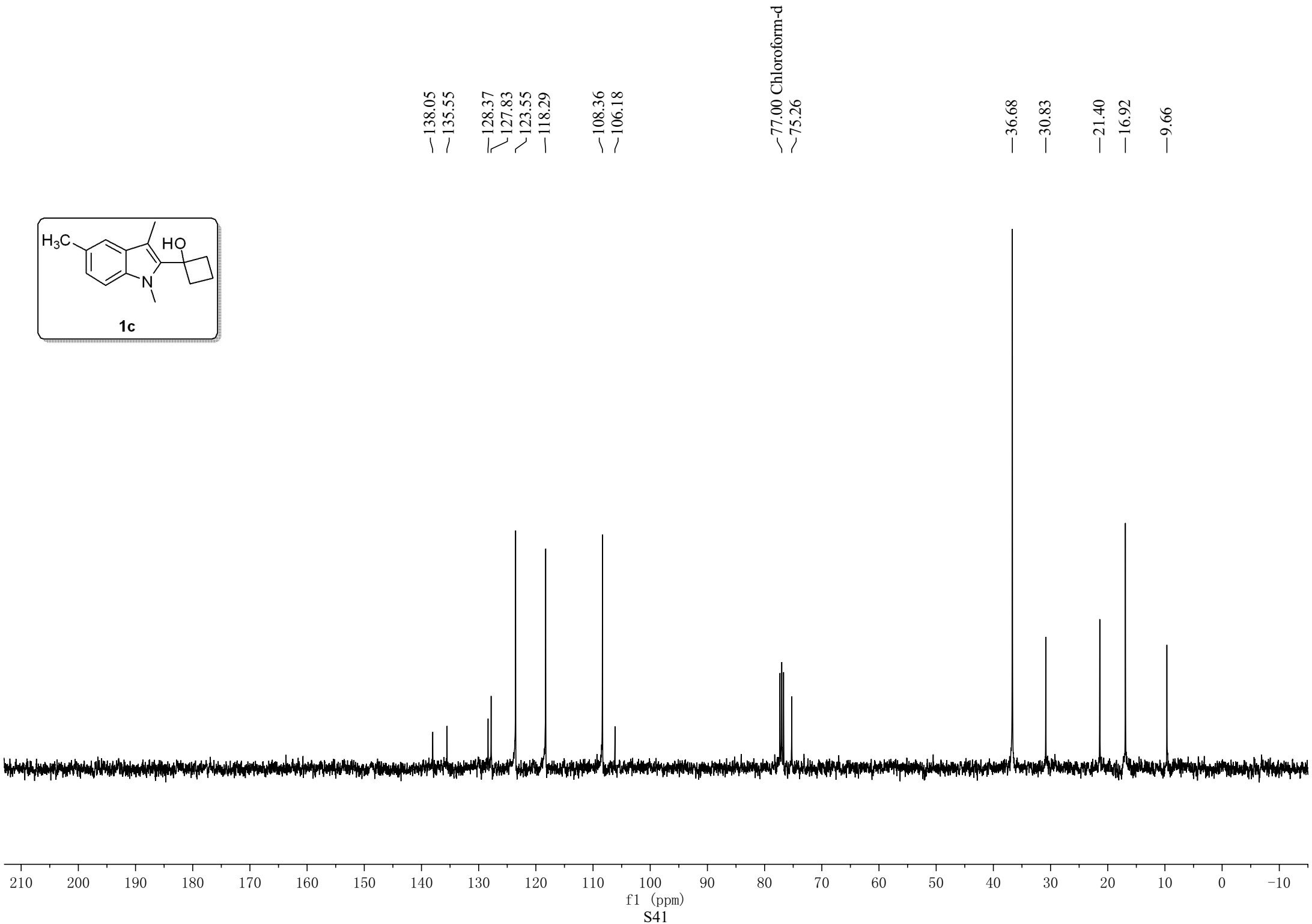
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

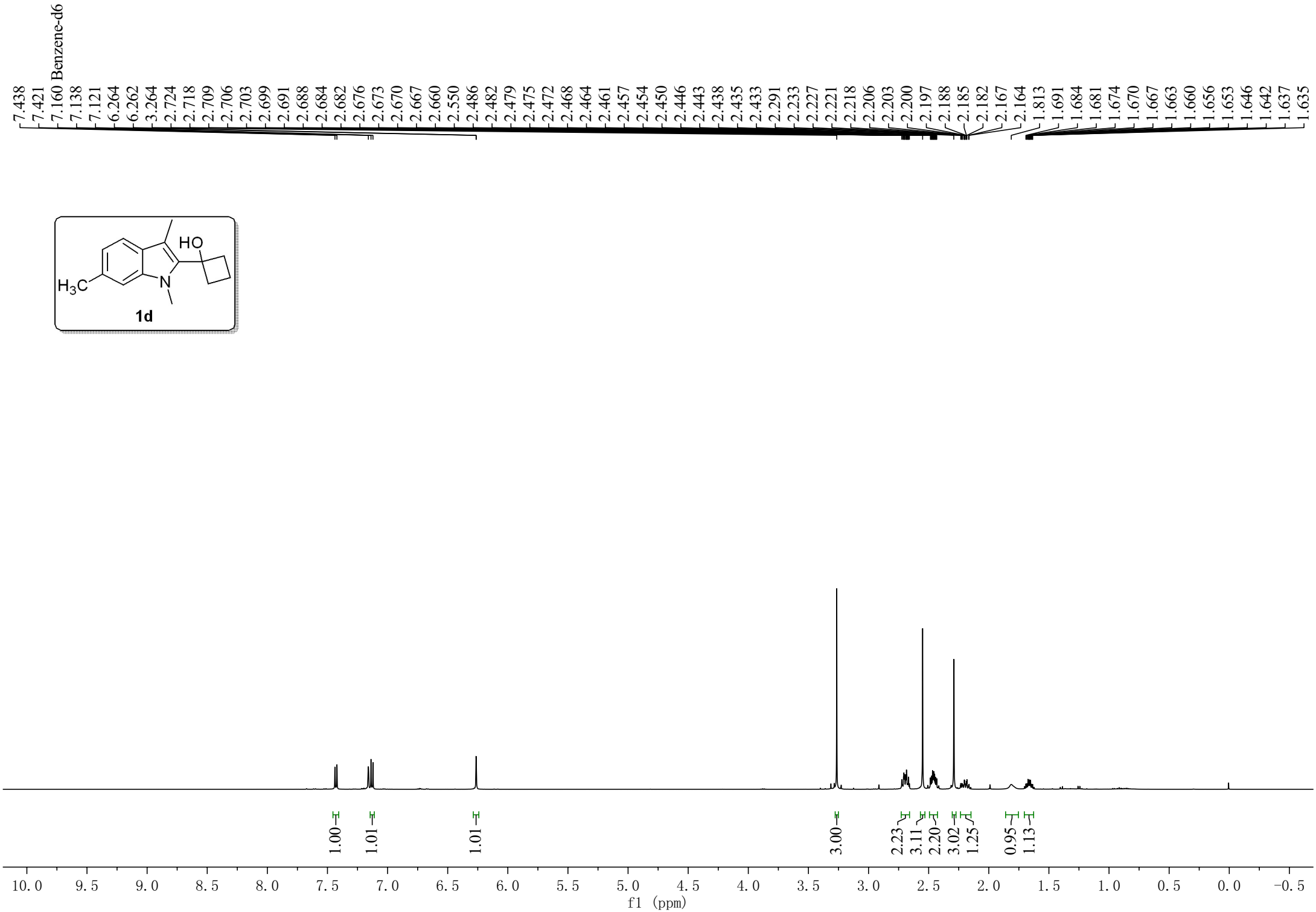
f1 (ppm)

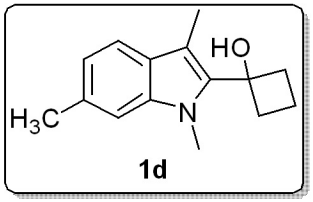

H3C
HO
N

1c


7.278
7.088
7.068
7.019
7.015
6.997
3.600
2.857
2.833
2.826
2.811
2.804
2.439
2.418
2.401
2.393
2.388
2.365
2.344
2.319
2.297
2.281
2.277
2.163
1.895
1.888
1.879
1.862
0.000 TMS
1.00
1.00
1.00
3.01
2.14
3.09
2.85
3.14
0.96
1.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


138.05
135.55
128.37
127.83
123.55
118.29
108.36
106.18
77.00 Chloroform-d
75.26
36.68
30.83
21.40
16.92
9.66
H3C
HO
N
1c
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)

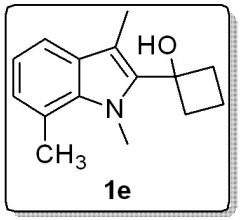

Benzene-d6
7.438
7.421
7.160
7.138
7.121
6.264
6.262
3.264
2.724
2.718
2.709
2.706
2.703
2.699
2.691
2.688
2.684
2.682
2.676
2.673
2.670
2.667
2.660
2.550
2.486
2.482
2.479
2.475
2.472
2.468
2.464
2.461
2.457
2.454
2.450
2.446
2.443
2.438
2.435
2.433
2.291
2.233
2.227
2.221
2.218
2.206
2.203
2.200
2.197
2.188
2.185
2.182
2.167
2.164
1.813
1.691
1.684
1.681
1.674
1.670
1.667
1.663
1.660
1.656
1.653
1.646
1.642
1.637
1.635
HO
H3C
N
1d
1.00
1.01
1.01
3.00
2.23
3.11
2.20
3.02
1.25
0.95
1.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



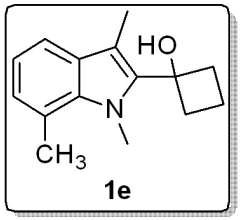
137.96
137.91
130.38
129.77
128.06 Benzene-d6
120.89
117.65
116.15
109.16
79.67
37.77
36.81
15.66
15.38
9.73

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)


HO
N
CH3
1e

7.339
7.320
6.948
6.930
6.911
6.883
6.865
3.875
2.877
2.856
2.848
2.833
2.825
2.811
2.804
2.704
2.479
2.471
2.462
2.457
2.449
2.443
2.433
2.425
2.418
2.362
2.337
2.271
2.162
1.902
1.875
0.000 TMS
1.03
1.01
1.00
3.00
2.17
3.16
2.31
1.24
3.02
1.02
1.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

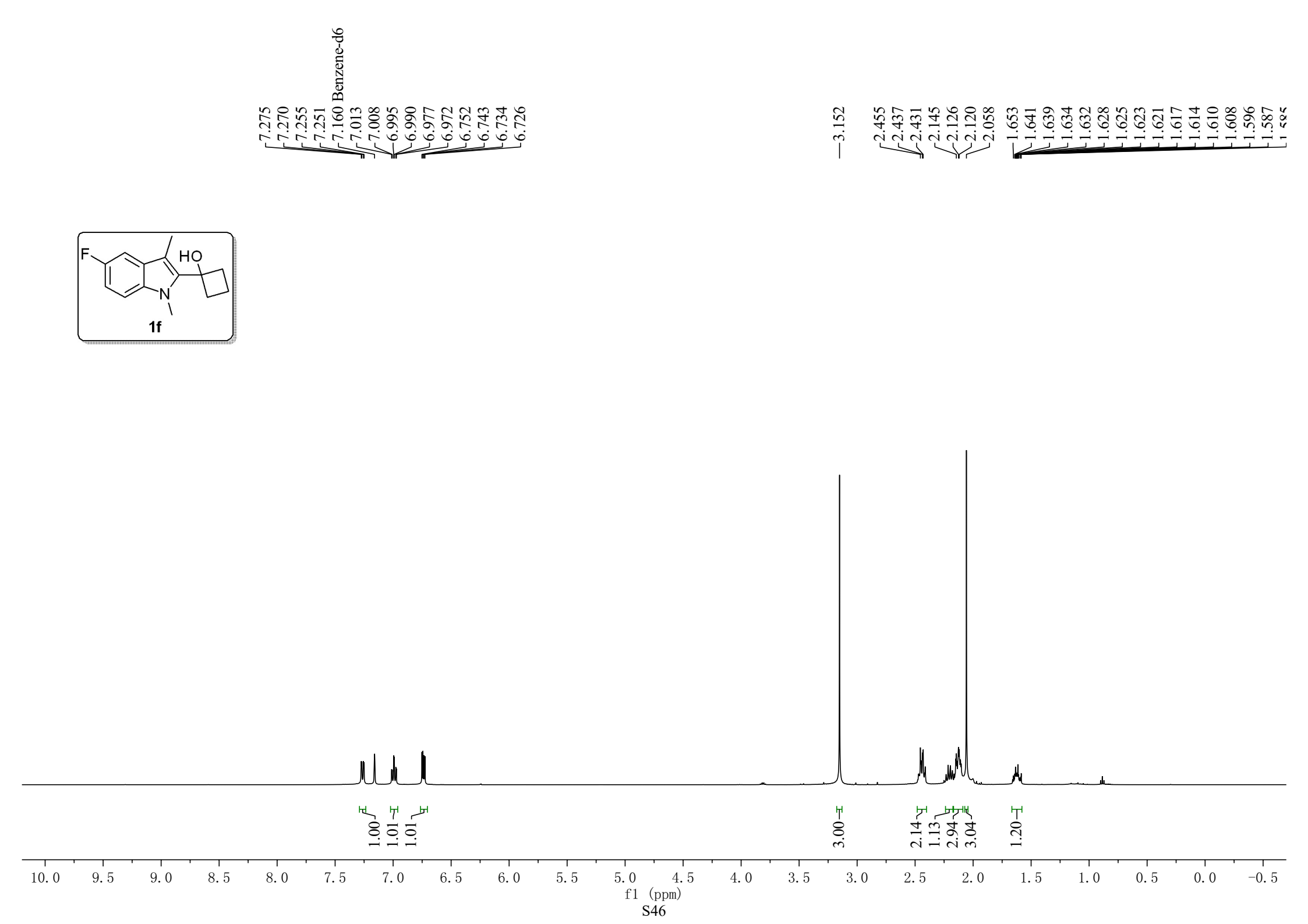


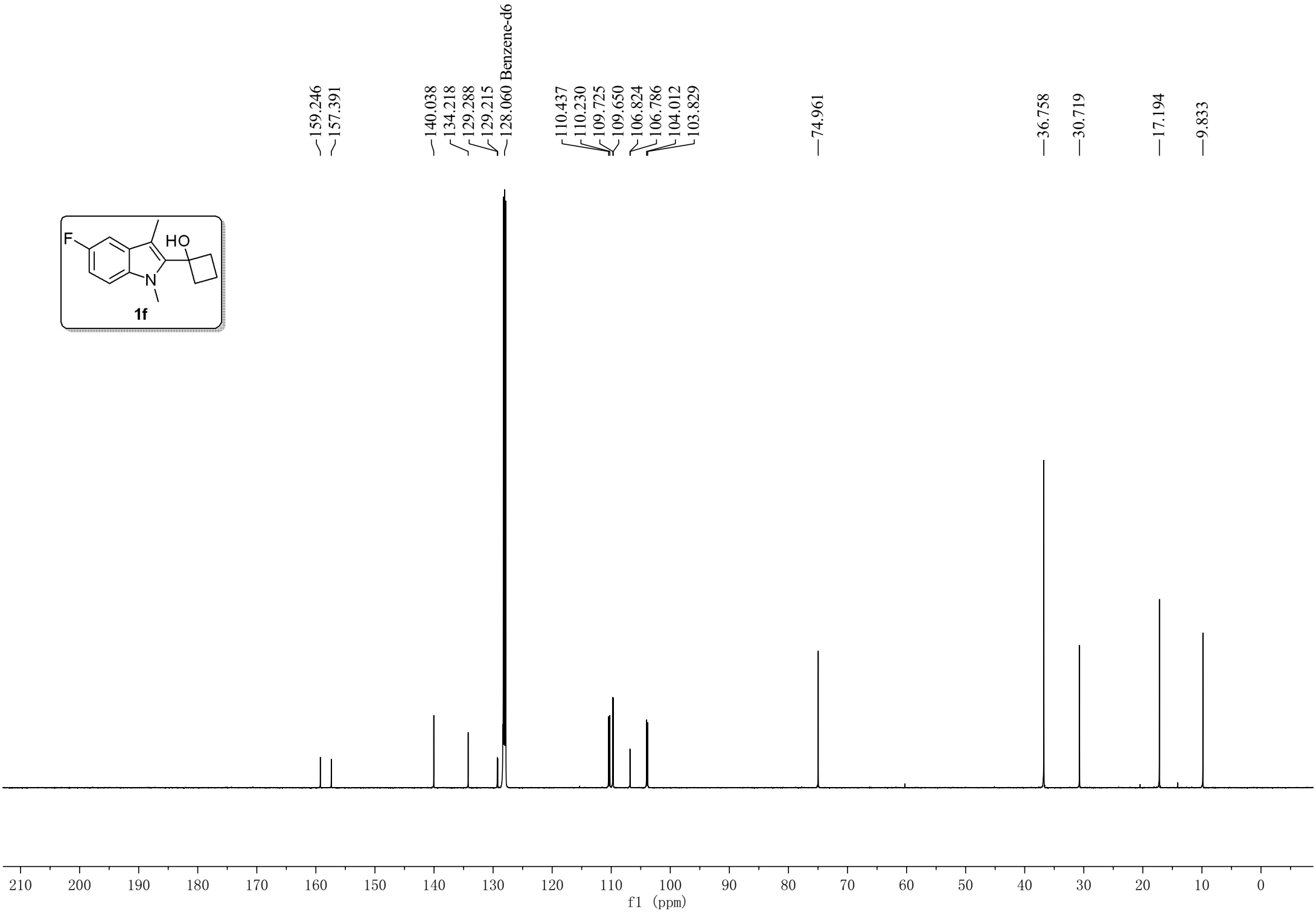
1e

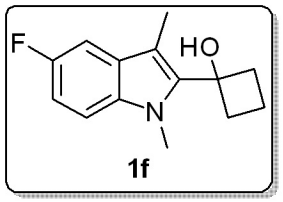
138.75
136.19
129.08
125.20
120.78
118.85
116.67
107.14
77.00 Chloroform-d
75.26
36.95
33.79
20.42
16.92
9.81

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)


7.275
7.270
7.255
7.251
7.160 Benzene-d6
7.013
7.008
6.995
6.990
6.977
6.972
6.752
6.743
6.734
6.726
3.152
2.455
2.437
2.431
2.145
2.126
2.120
2.058
1.653
1.641
1.639
1.634
1.632
1.628
1.625
1.623
1.621
1.617
1.614
1.610
1.608
1.596
1.587
F
HO
N
1f
1.00
1.01
1.01
3.00
2.14
1.13
2.94
3.04
1.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.246
157.391
140.038
134.218
129.288
129.215
128.060
Benzene-d6
110.437
110.230
109.725
109.650
106.824
106.786
104.012
103.829
74.961
36.758
30.719
17.194
9.833
F
HO
N
1f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
HO
N
1f

-125.448
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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-140
-150
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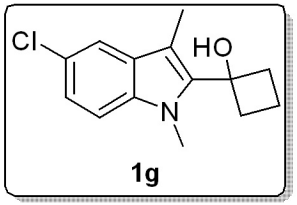
-170
-180
-190
-200
-210
f1 (ppm)


Cl
HO
N
1g

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7.476
7.270
7.249
7.116
7.111
7.094
7.089
4.707
3.705
2.860
2.837
2.829
2.815
2.807
2.793
2.786
2.505
2.498
2.488
2.484
2.476
2.470
2.463
2.460
2.453
2.446
2.403
2.399
2.381
2.378
2.355
2.335
2.287
1.903
1.882
1.00
1.06
1.01
1.01
3.12
2.18
2.21
1.14
3.14
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7.5
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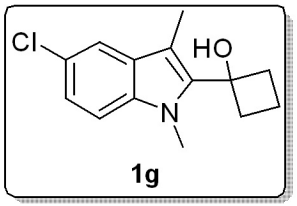
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

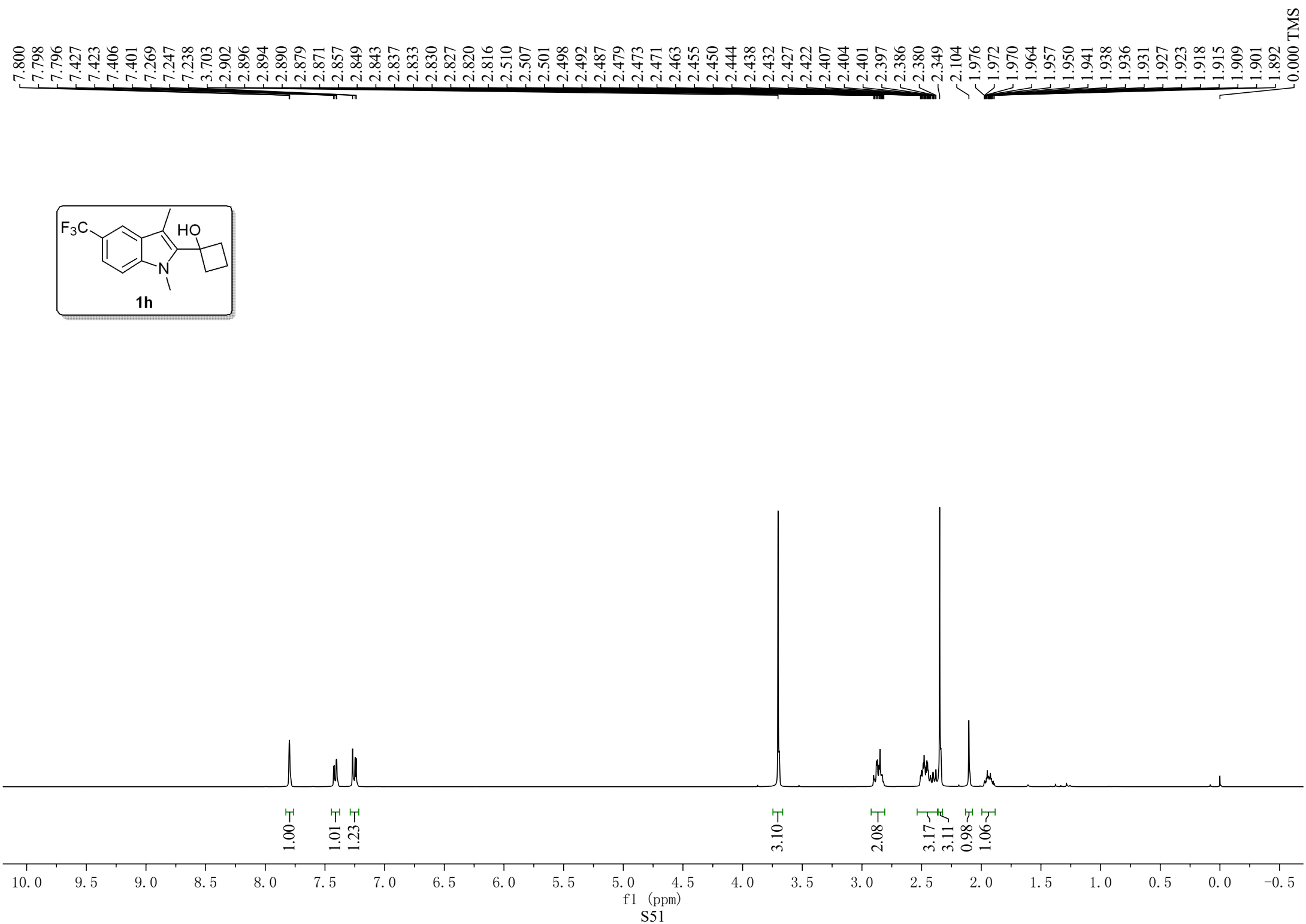


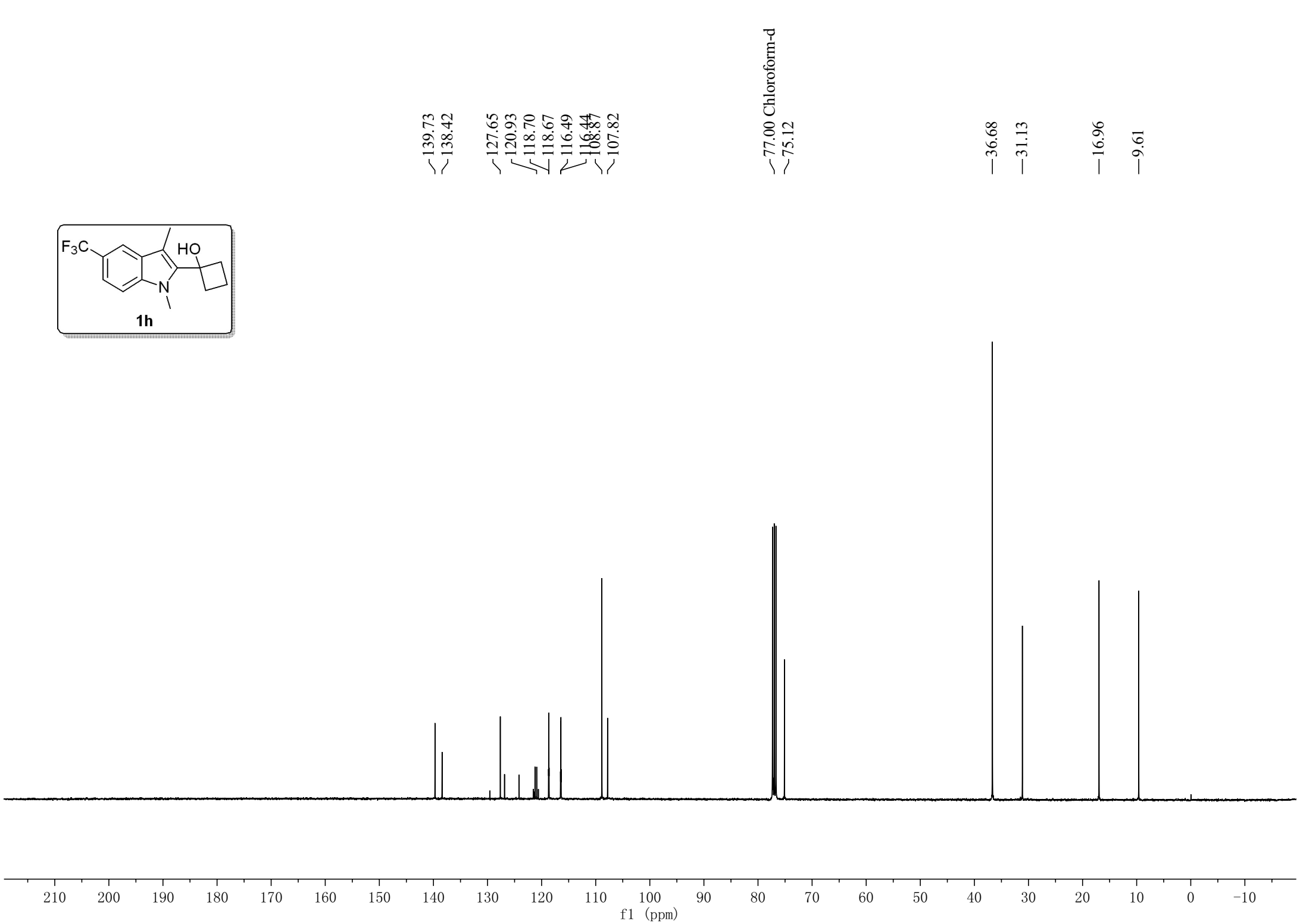
1g

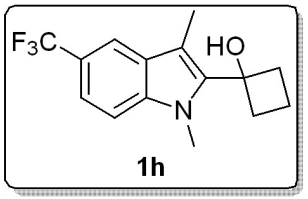
141.645
136.363
130.502
124.452
122.000
118.378
110.847
106.403
74.882
37.399
31.358
29.840 Acetone-d6
17.634
9.769

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

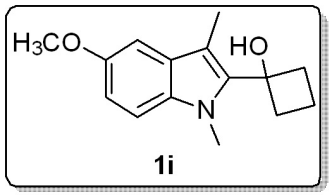
f1 (ppm)


7.800
7.798
7.796
7.427
7.423
7.406
7.401
7.269
7.247
7.238
3.703
2.902
2.896
2.894
2.890
2.879
2.871
2.857
2.849
2.843
2.837
2.833
2.830
2.827
2.820
2.816
2.510
2.507
2.501
2.498
2.492
2.487
2.479
2.473
2.471
2.463
2.455
2.450
2.444
2.438
2.432
2.427
2.422
2.407
2.404
2.401
2.397
2.386
2.380
2.349
2.104
1.976
1.972
1.970
1.964
1.957
1.950
1.941
1.938
1.936
1.931
1.927
1.923
1.918
1.915
1.909
1.901
1.892
0.000 TMS
F3C
HO
N
1h
1.00
1.01
1.23
3.10
2.08
3.17
3.11
0.98
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


139.73
138.42
127.65
120.93
118.70
118.67
116.49
116.44
108.87
107.82
77.00 Chloroform-d
75.12
36.68
31.13
16.96
9.61
F3C
HO
N
1h
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)

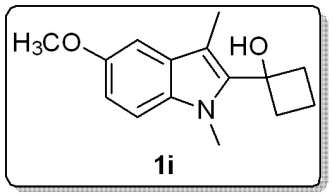

F3C
HO
N
1h

-60.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


H3CO
HO
N

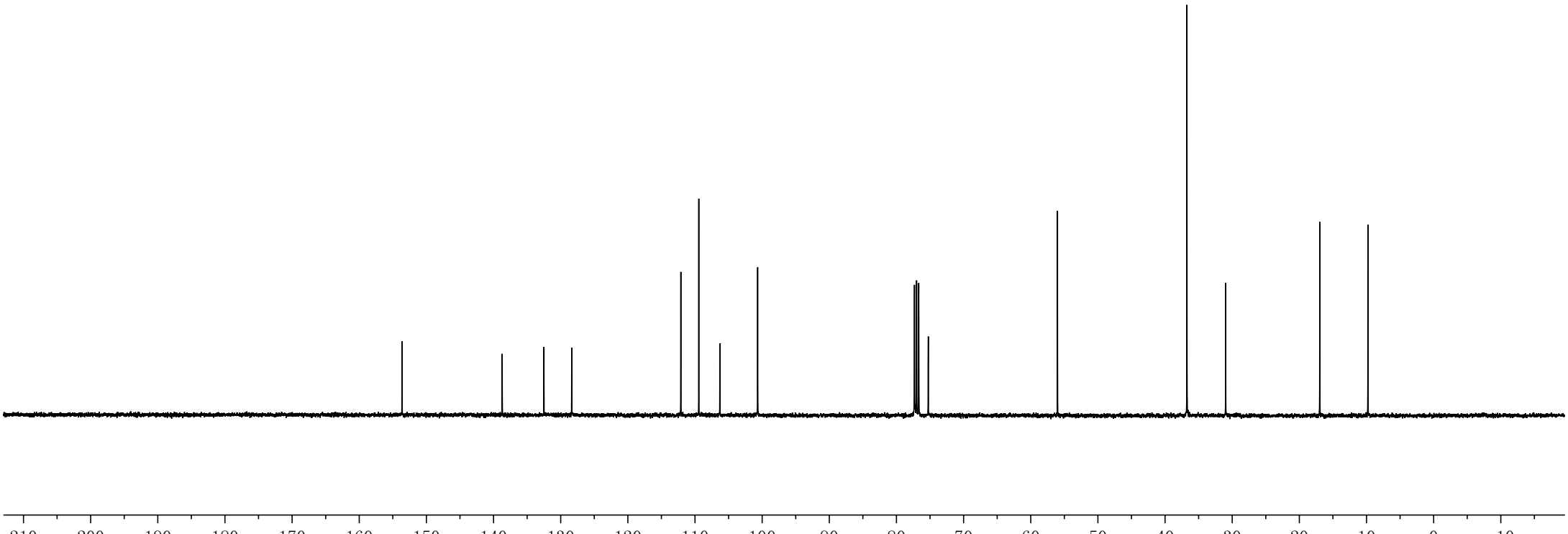
1i

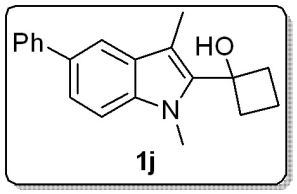
7.260 Chloroform-d
7.143
7.121
6.979
6.973
6.900
6.894
6.878
6.872
3.875
3.673
3.667
2.922
2.899
2.892
2.877
2.869
2.522
2.514
2.501
2.491
2.476
2.468
2.462
2.452
2.433
2.428
2.412
2.410
2.407
2.385
2.364
2.324
1.960
1.952
1.944
1.930
1.00
0.98
0.98
3.08
3.07
2.07
2.05
1.10
3.04
0.92
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

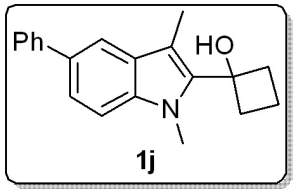


1i

153.64
138.73
132.51
128.37
112.12
109.44
106.31
100.68
77.00 Chloroform-d
75.26
56.02
36.75
30.98
16.96
9.79

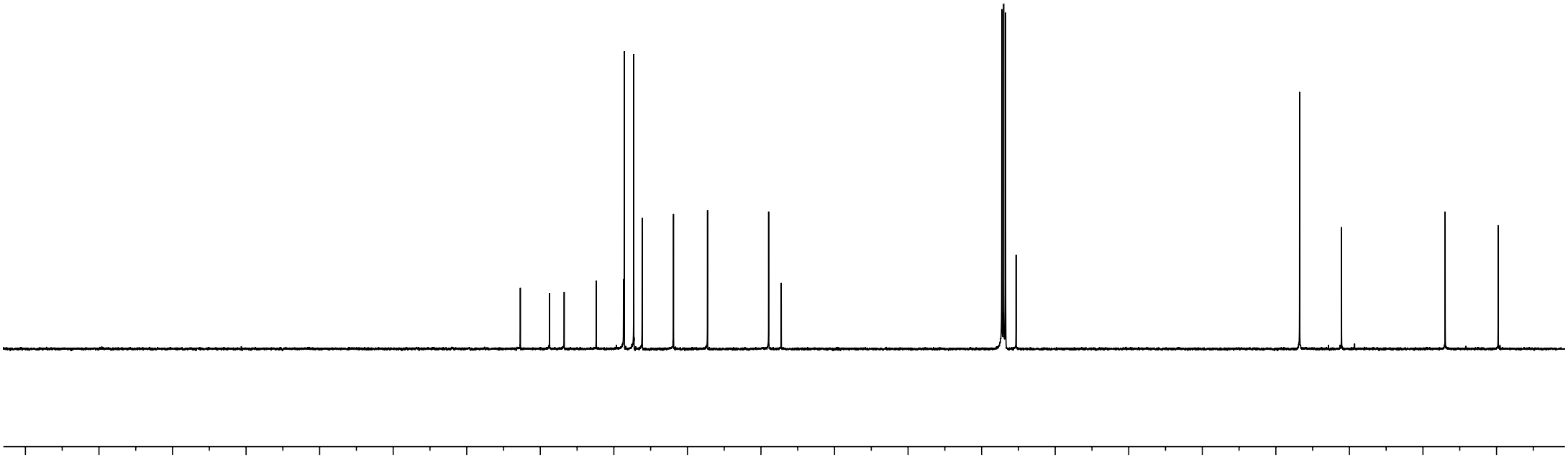


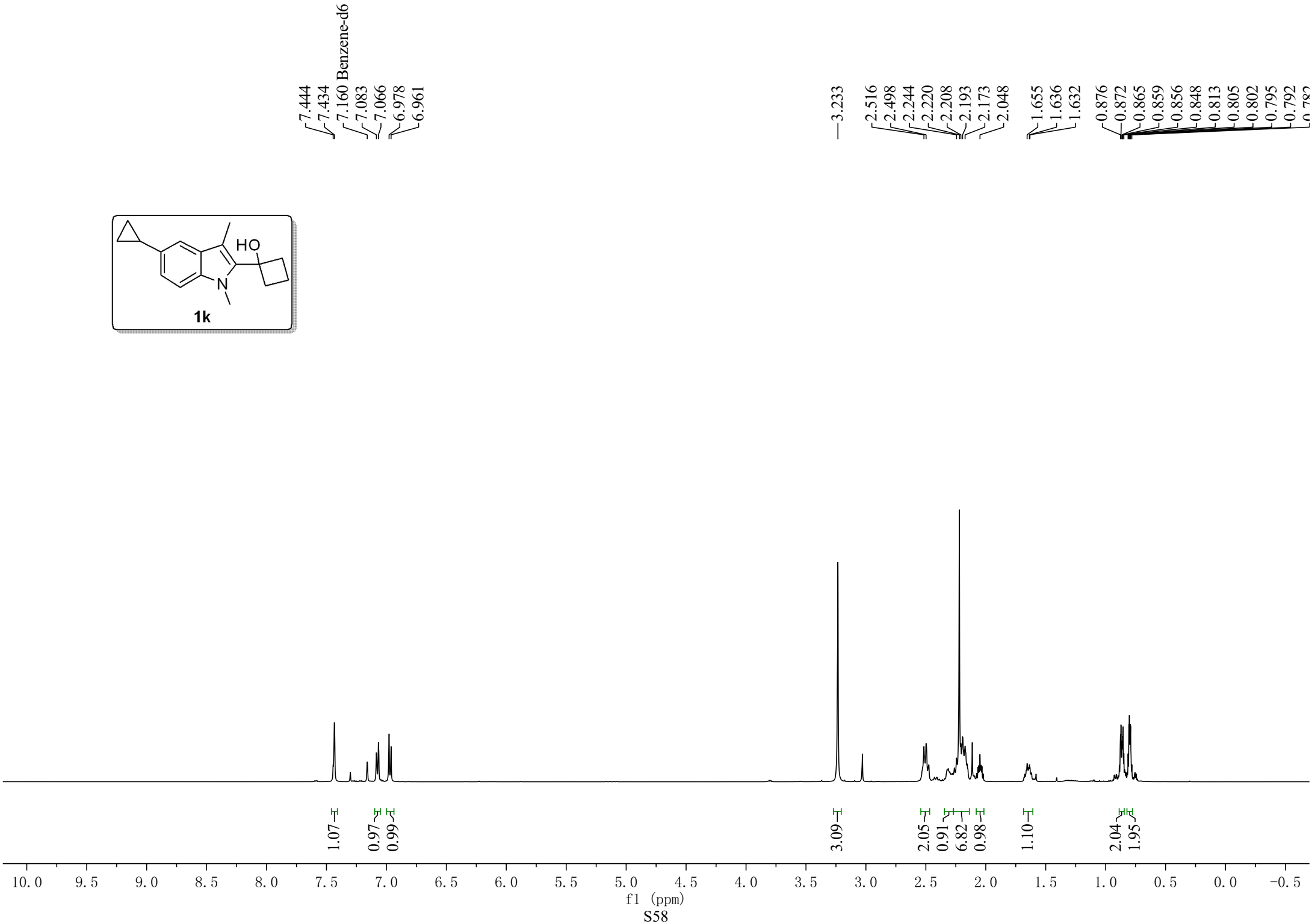

Ph
HO
N
1j

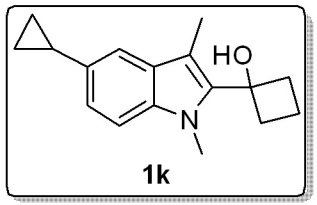


1j

142.71
138.74
136.75
132.39
128.69
128.59
127.30
126.15
121.89
117.27
108.96
107.24
77.00 Chloroform-d
75.32
36.77
31.07
16.98
9.78




7.444
7.434
7.160 Benzene-d6
7.083
7.066
6.978
6.961
3.233
2.516
2.498
2.244
2.220
2.208
2.193
2.173
2.048
1.655
1.636
1.632
0.876
0.872
0.865
0.859
0.856
0.848
0.813
0.805
0.802
0.795
0.792
HO
N
1k
1.07
0.97
0.99
3.09
2.05
0.91
6.82
0.98
1.10
2.04
1.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

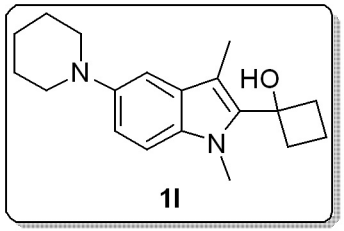


1k

138.567
136.563
134.113
129.207
128.060 Benzene-d6
121.213
116.125
108.875
106.360
75.153
36.908
30.674
17.281
16.266
9.995
8.922

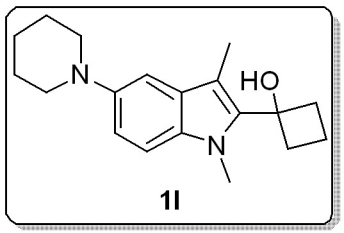
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


N
HO
N

1l

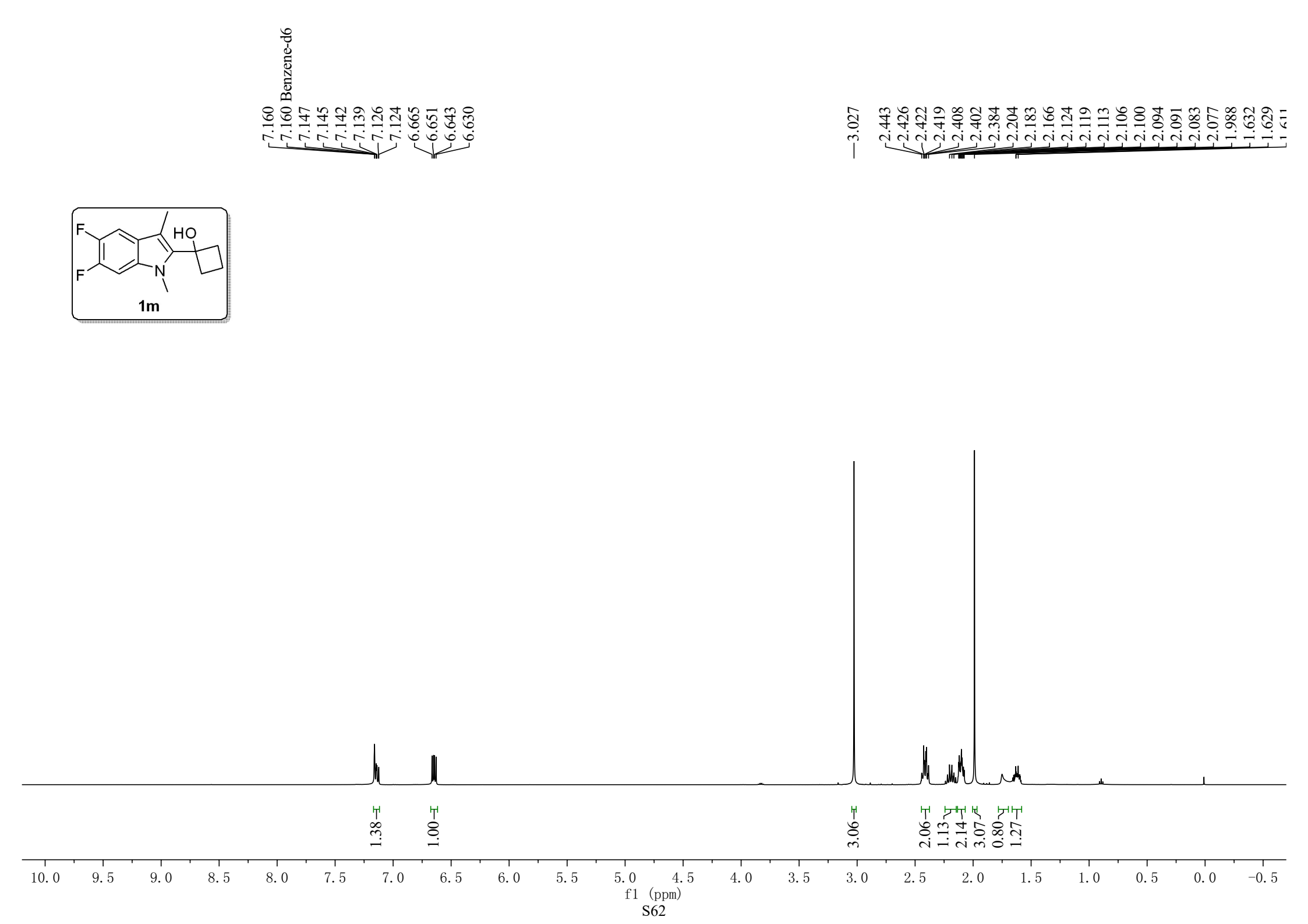
7.296
7.292
7.160 Benzene-d6
7.150
7.146
7.025
7.008
3.304
3.119
3.108
3.097
2.600
2.582
2.294
2.287
2.270
1.707
1.702
1.696
1.691
1.685
1.673
1.440
1.429
0.502
1.00
0.97
0.99
3.01
4.13
2.01
6.11
5.05
2.26
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

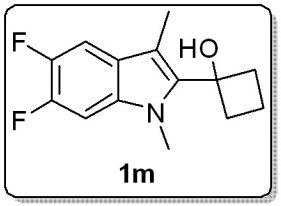


1l

147.497
138.603
133.757
129.404
128.060 Benzene-d6
117.134
109.348
107.165
106.434
75.190
54.124
37.088
30.777
27.013
24.895
17.333
10.174

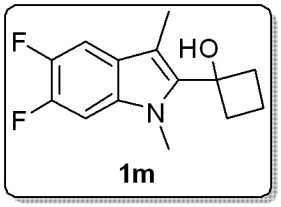
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.160
7.160 Benzene-d6
7.147
7.145
7.142
7.139
7.126
7.124
6.665
6.651
6.643
6.630
3.027
2.443
2.426
2.422
2.419
2.408
2.402
2.384
2.204
2.183
2.166
2.124
2.119
2.113
2.106
2.100
2.094
2.091
2.083
2.077
1.988
1.632
1.629
F
F
HO
N
1m
1.38
1.00
3.06
2.06
1.13
2.14
3.07
0.80
1.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

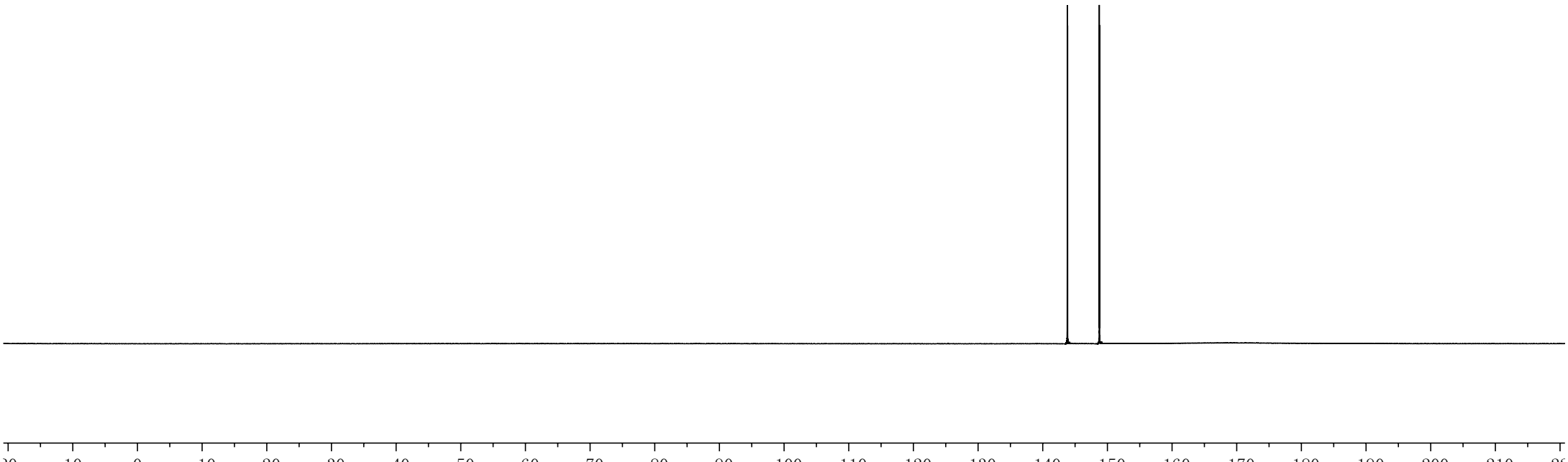


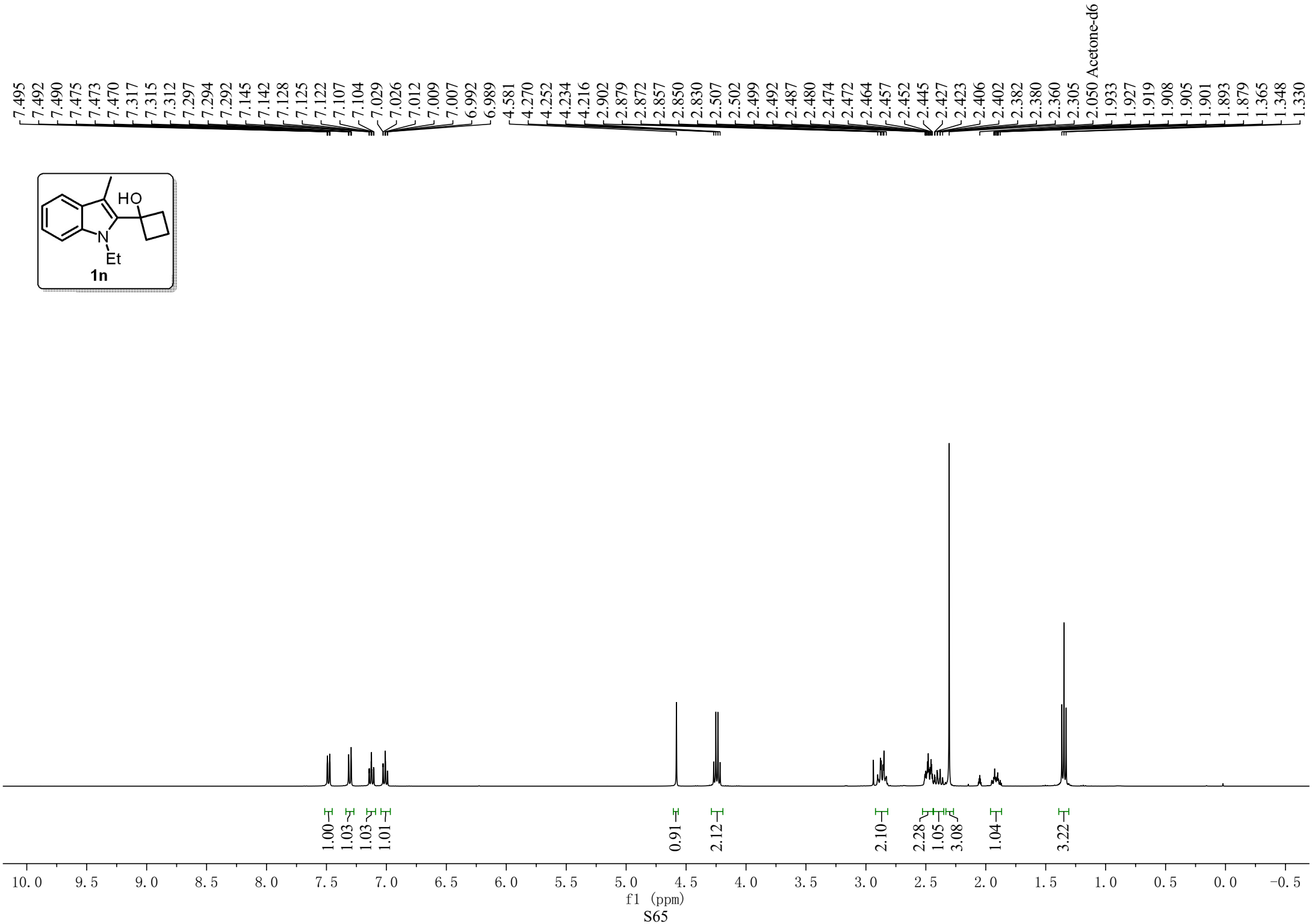
149.599
149.473
147.691
147.597
147.566
147.479
145.717
145.598
139.742
139.710
132.740
132.662
128.060 Benzene-d6
124.017
123.960
106.846
106.823
105.675
105.527
97.157
96.985
74.790
36.692
30.836
17.146
9.742

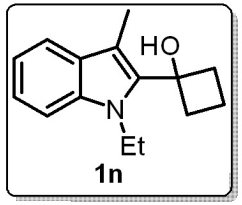
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



-143.800
-143.845
-148.748
-148.792




7.495
7.492
7.490
7.475
7.473
7.470
7.317
7.315
7.312
7.297
7.294
7.292
7.145
7.142
7.128
7.125
7.122
7.107
7.104
7.029
7.026
7.012
7.009
7.007
6.992
6.989
4.581
4.270
4.252
4.234
4.216
2.902
2.879
2.872
2.857
2.850
2.830
2.507
2.502
2.499
2.492
2.487
2.480
2.474
2.472
2.464
2.457
2.452
2.445
2.427
2.423
2.406
2.402
2.382
2.380
2.360
2.305
Acetone-d6
2.050
1.933
1.927
1.919
1.908
1.905
1.901
1.893
1.879
1.365
1.348
1.330
HO
N
Et
1n
1.00
1.03
1.03
1.01
0.91
2.12
2.10
2.28
1.05
3.08
1.04
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

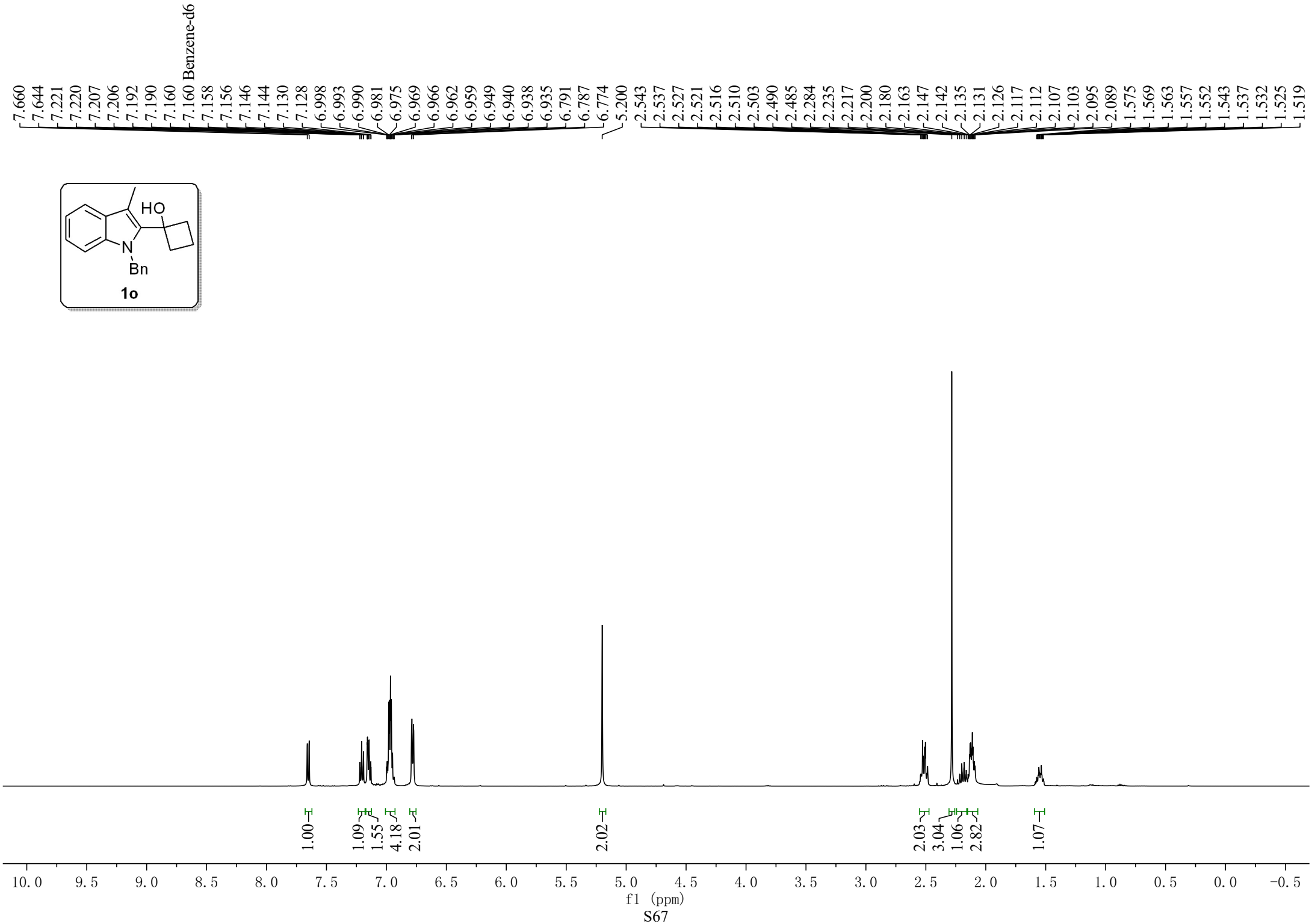


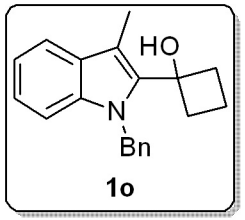
1n

139.66
136.98
129.89
122.11
119.18
119.12
109.84
106.42
75.28
39.38
37.80
29.84 Acetone-d6
18.02
15.34
9.98

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

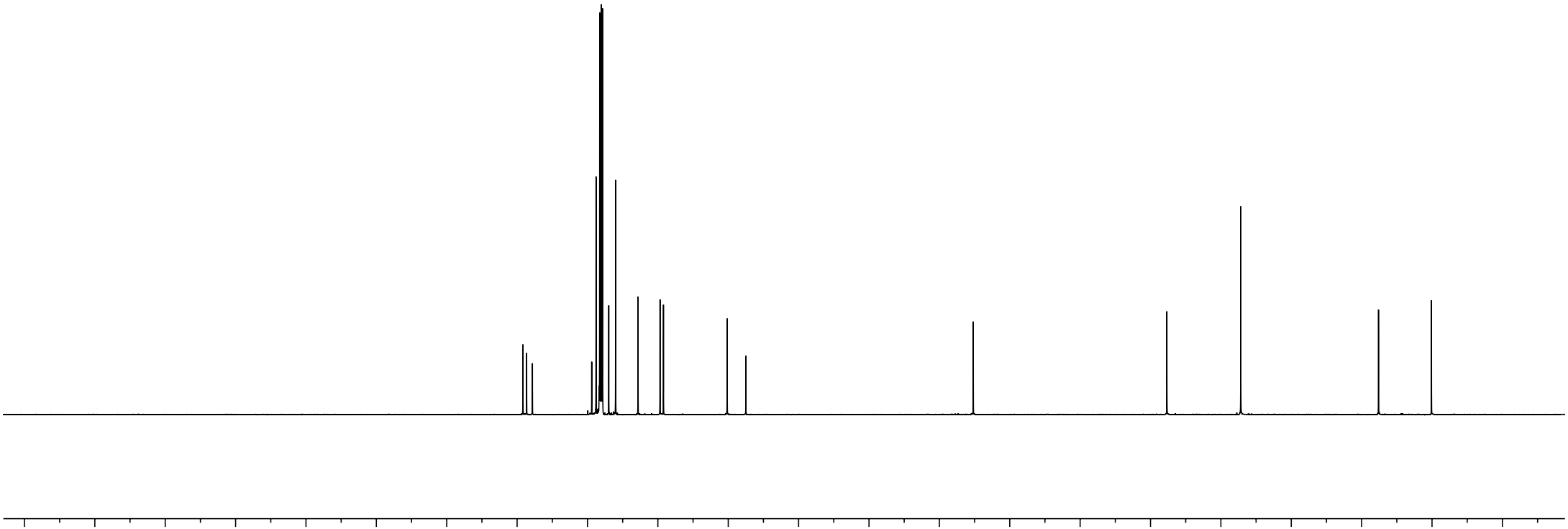
f1 (ppm)


Benzene-d6
7.660
7.644
7.221
7.220
7.207
7.206
7.192
7.190
7.160
7.160
7.158
7.156
7.146
7.144
7.130
7.128
6.998
6.993
6.990
6.981
6.975
6.969
6.966
6.962
6.959
6.949
6.940
6.938
6.935
6.791
6.787
6.774
5.200
2.543
2.537
2.527
2.521
2.516
2.510
2.503
2.490
2.485
2.284
2.235
2.217
2.200
2.180
2.163
2.147
2.142
2.135
2.131
2.126
2.117
2.112
2.107
2.103
2.095
2.089
1.575
1.569
1.563
1.557
1.552
1.543
1.537
1.532
1.525
1.519
HO
N
Bn
1o
1.00
1.09
1.55
4.18
2.01
2.02
2.03
3.04
1.06
2.82
1.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



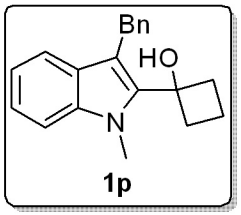
1o

139.168
138.645
137.823
128.781
128.060
Benzene-d6
125.999
122.814
119.690
110.153
107.496
75.186
47.675
37.175
17.601
10.083

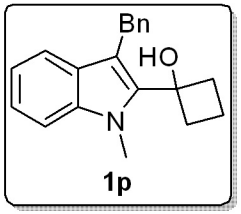


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

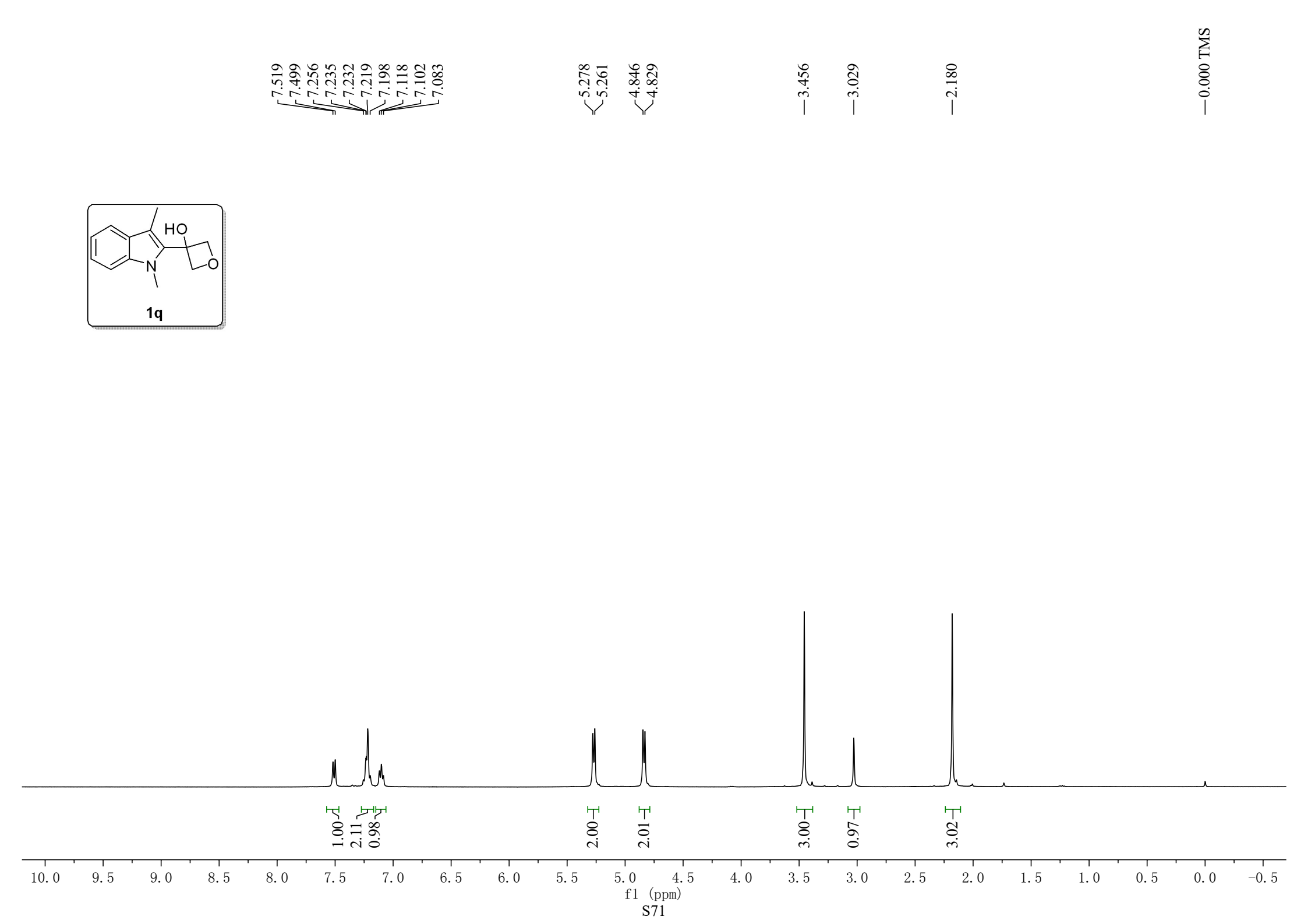

Bn
HO
N
1p

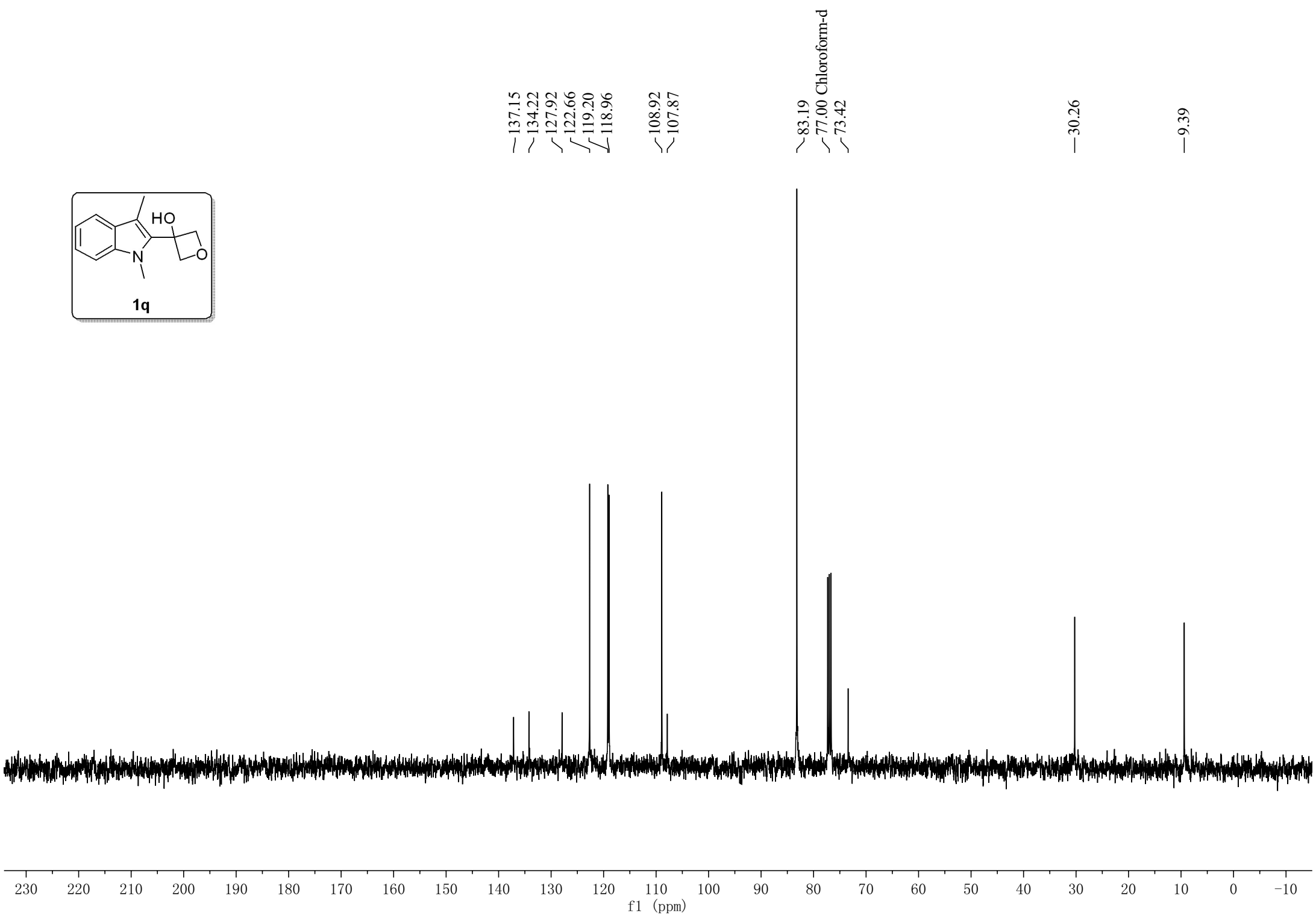
7.567
7.551
7.316
7.314
7.300
7.286
7.284
7.199
7.197
7.183
7.175
7.169
7.168
7.160
7.160 Benzene-d6
7.128
7.114
7.100
7.084
7.035
7.021
7.006
4.150
3.346
2.572
2.565
2.554
2.548
2.212
2.203
2.193
2.182
1.793
1.599
1.595
1.588
1.580
1.570
1.563
1.551
1.543
1.537
1.532
1.00
1.09
3.88
3.27
1.13
2.02
3.12
2.17
3.20
0.83
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

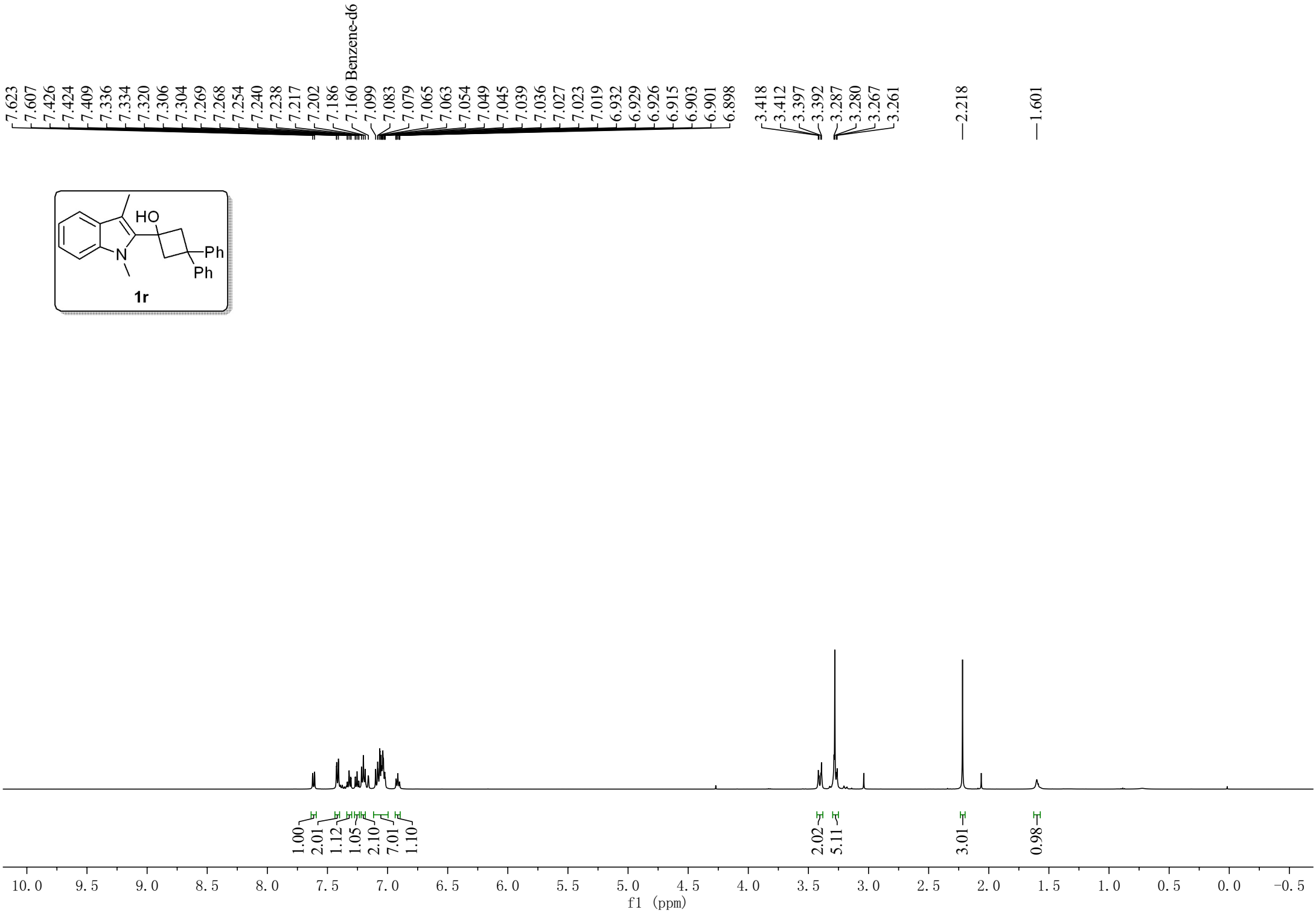


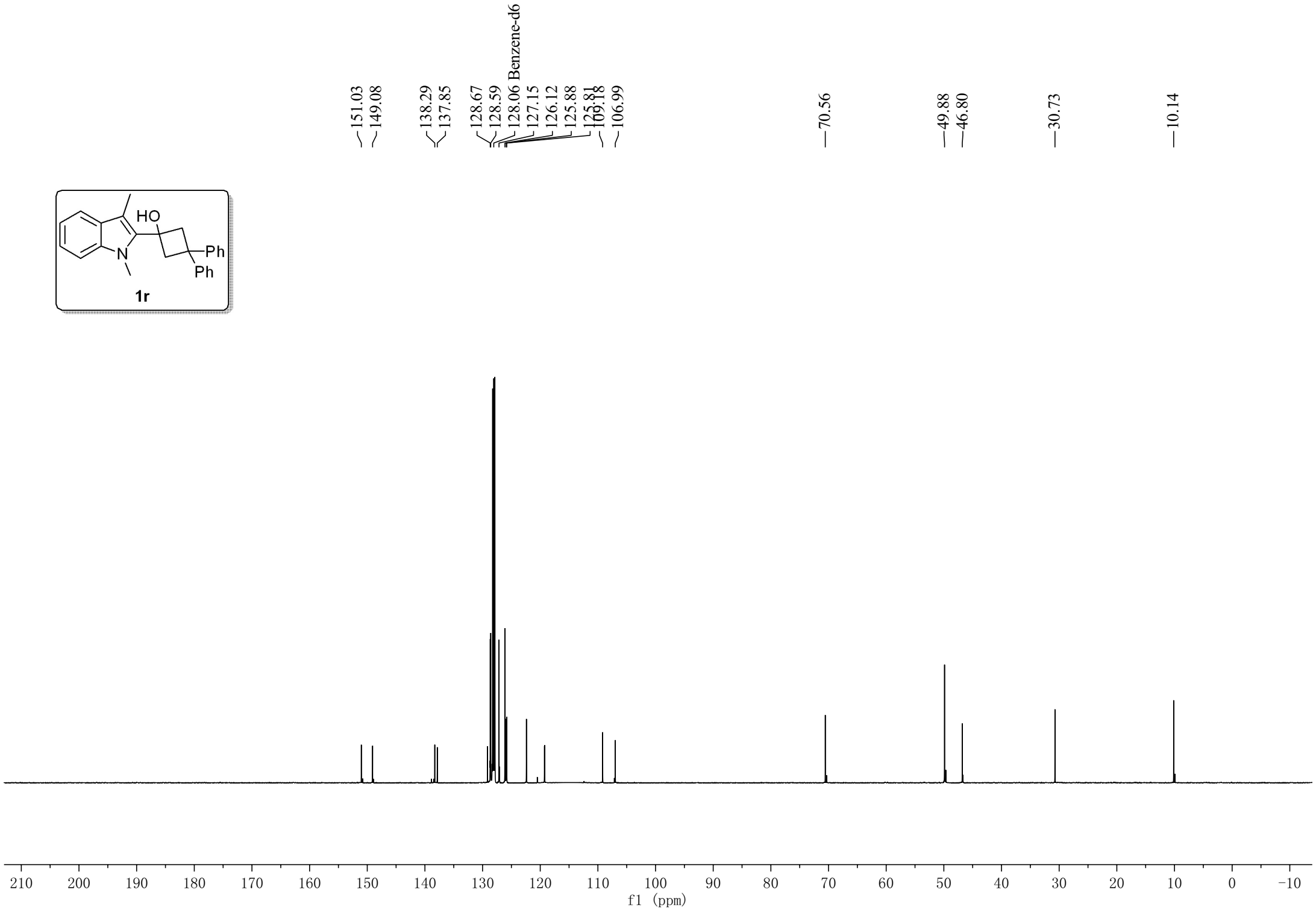
142.342
139.431
137.956
128.723
128.370
128.060 Benzene-d6
126.143
122.517
119.554
109.884
109.248
74.900
36.830
30.802
30.440
17.269

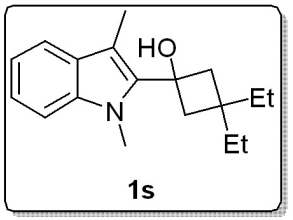
f1 (ppm)

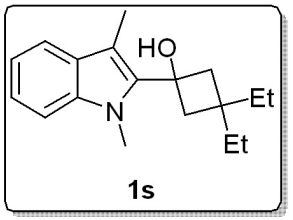

7.519
7.499
7.256
7.235
7.232
7.219
7.198
7.118
7.102
7.083
5.278
5.261
4.846
4.829
3.456
3.029
2.180
0.000 TMS
HO
N
O
1q
1.00
2.11
0.98
2.00
2.01
3.00
0.97
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.15
134.22
127.92
122.66
119.20
118.96
108.92
107.87
83.19
77.00 Chloroform-d
73.42
30.26
9.39
HO
N
O
1q
230
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)


7.623
7.607
7.426
7.424
7.409
7.336
7.334
7.320
7.306
7.304
7.269
7.268
7.254
7.240
7.238
7.217
7.202
7.186
7.160 Benzene-d6
7.099
7.083
7.079
7.065
7.063
7.054
7.049
7.045
7.039
7.036
7.027
7.023
7.019
6.932
6.929
6.926
6.915
6.903
6.901
6.898
3.418
3.412
3.397
3.392
3.287
3.280
3.267
3.261
2.218
1.601
HO
N
Ph
Ph
1r
1.00
2.01
1.12
1.05
2.10
7.01
1.10
2.02
5.11
3.01
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

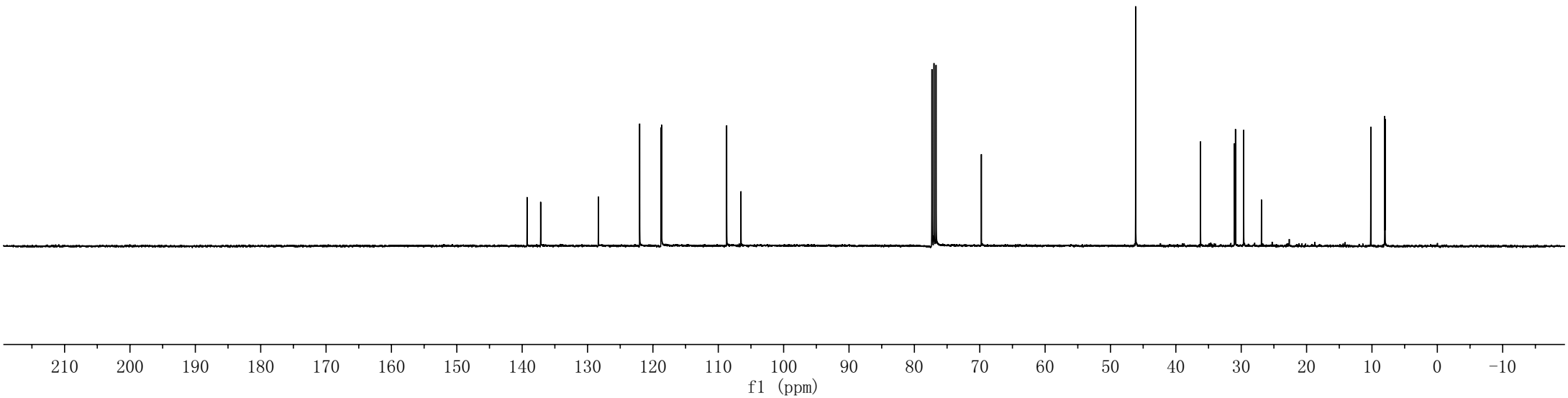

151.03
149.08
138.29
137.85
128.67
128.59
128.06 Benzene-d6
127.15
126.12
125.88
125.81
109.18
106.99
70.56
49.88
46.80
30.73
10.14
HO
N
Ph
Ph
1r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

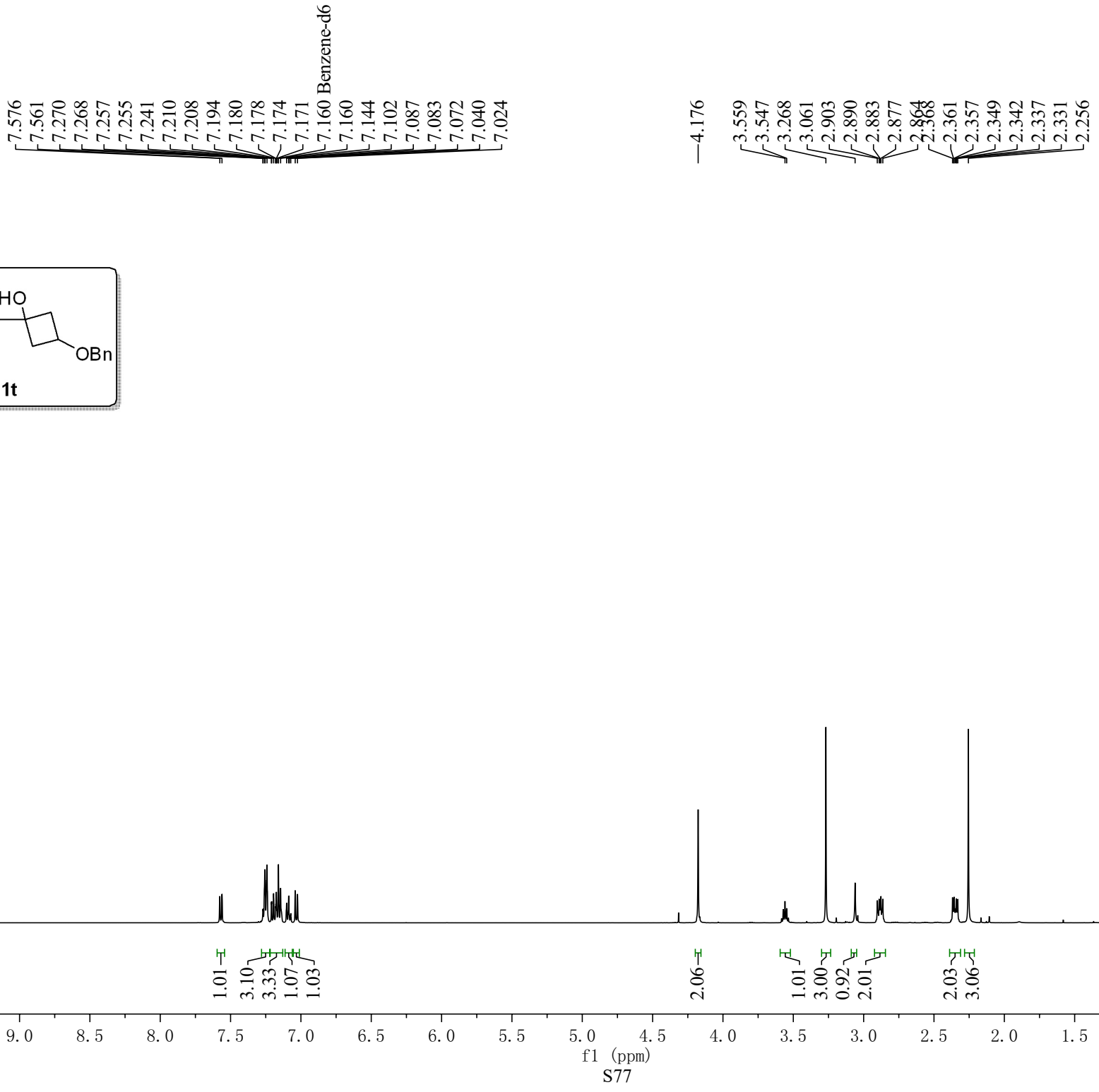

HO
N
Et
Et
1s

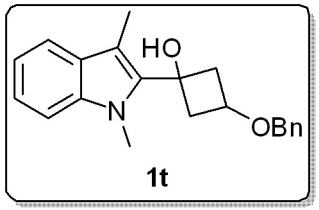


1s

139.25
137.17
128.35
122.03
118.76
118.67
108.72
106.52
77.00 Chloroform-d
69.75
46.15
36.23
31.03
30.88
29.63
26.90
10.18
8.05
7.99




7.576
7.561
7.270
7.268
7.257
7.255
7.241
7.210
7.208
7.194
7.180
7.178
7.174
7.171
7.160 Benzene-d6
7.160
7.144
7.102
7.087
7.083
7.072
7.040
7.024
4.176
3.559
3.547
3.268
3.061
2.903
2.890
2.883
2.877
2.864
2.361
2.357
2.349
2.342
2.337
2.331
2.256
HO
N
OBn
1t
1.01
3.10
3.33
1.07
1.03
2.06
1.01
3.00
0.92
2.01
2.03
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

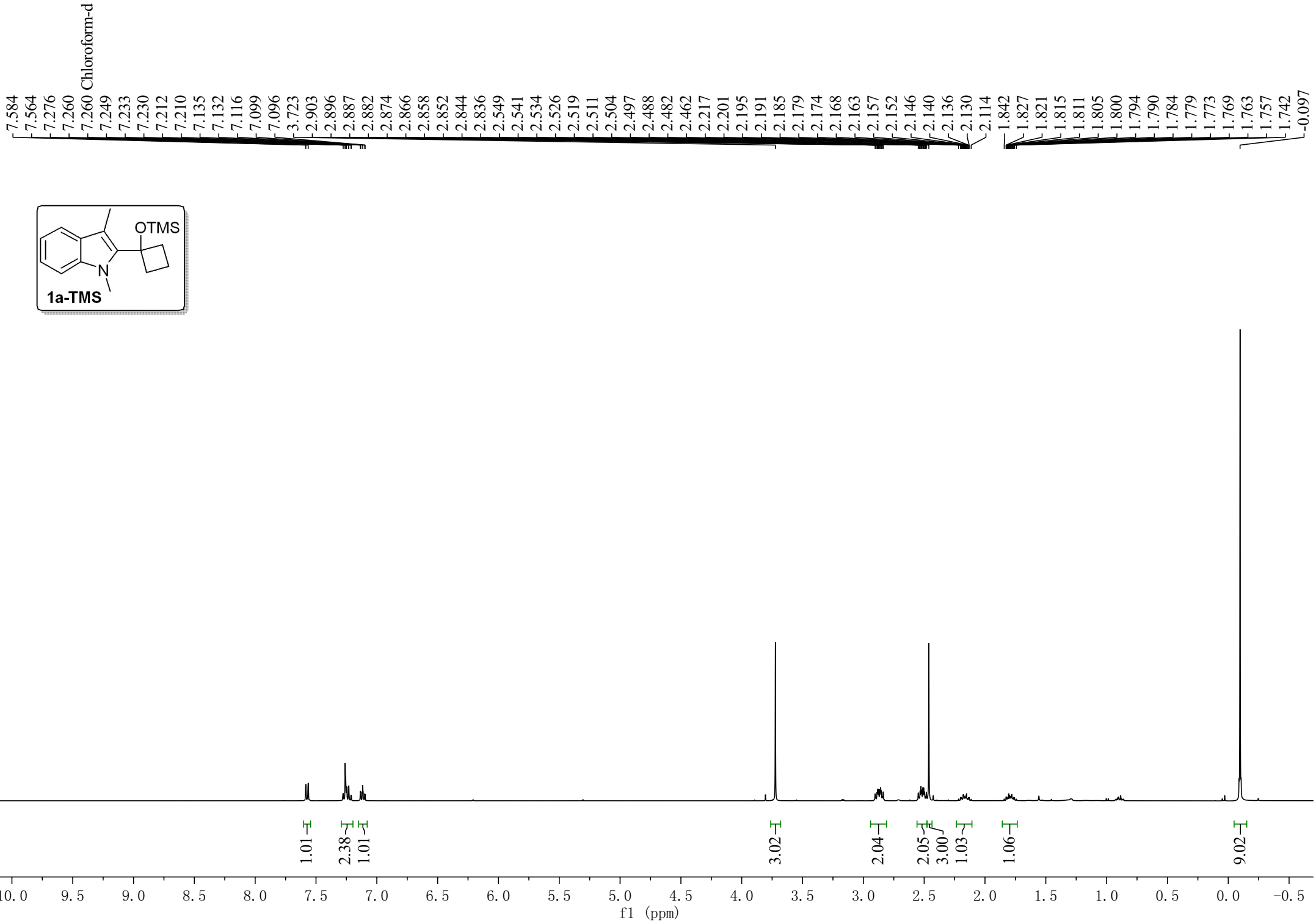


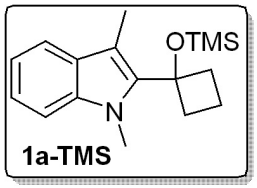
1t

138.761
137.954
136.999
128.635
128.060 Benzene-d6
128.001
122.418
119.237
119.138
109.136
106.977
70.383
68.807
67.523
44.885
31.129
10.471

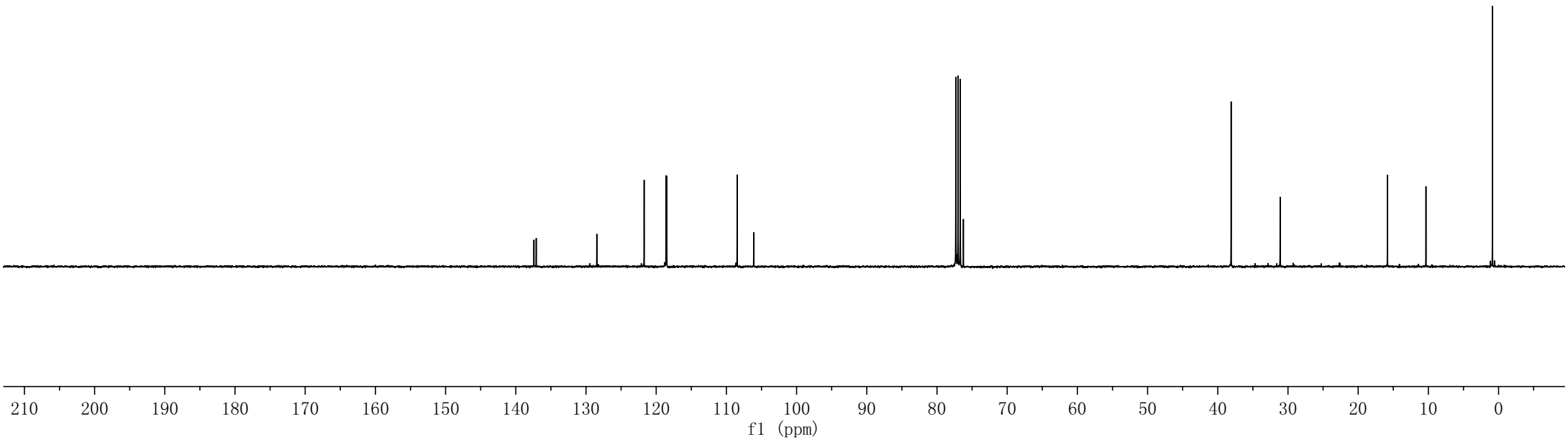
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

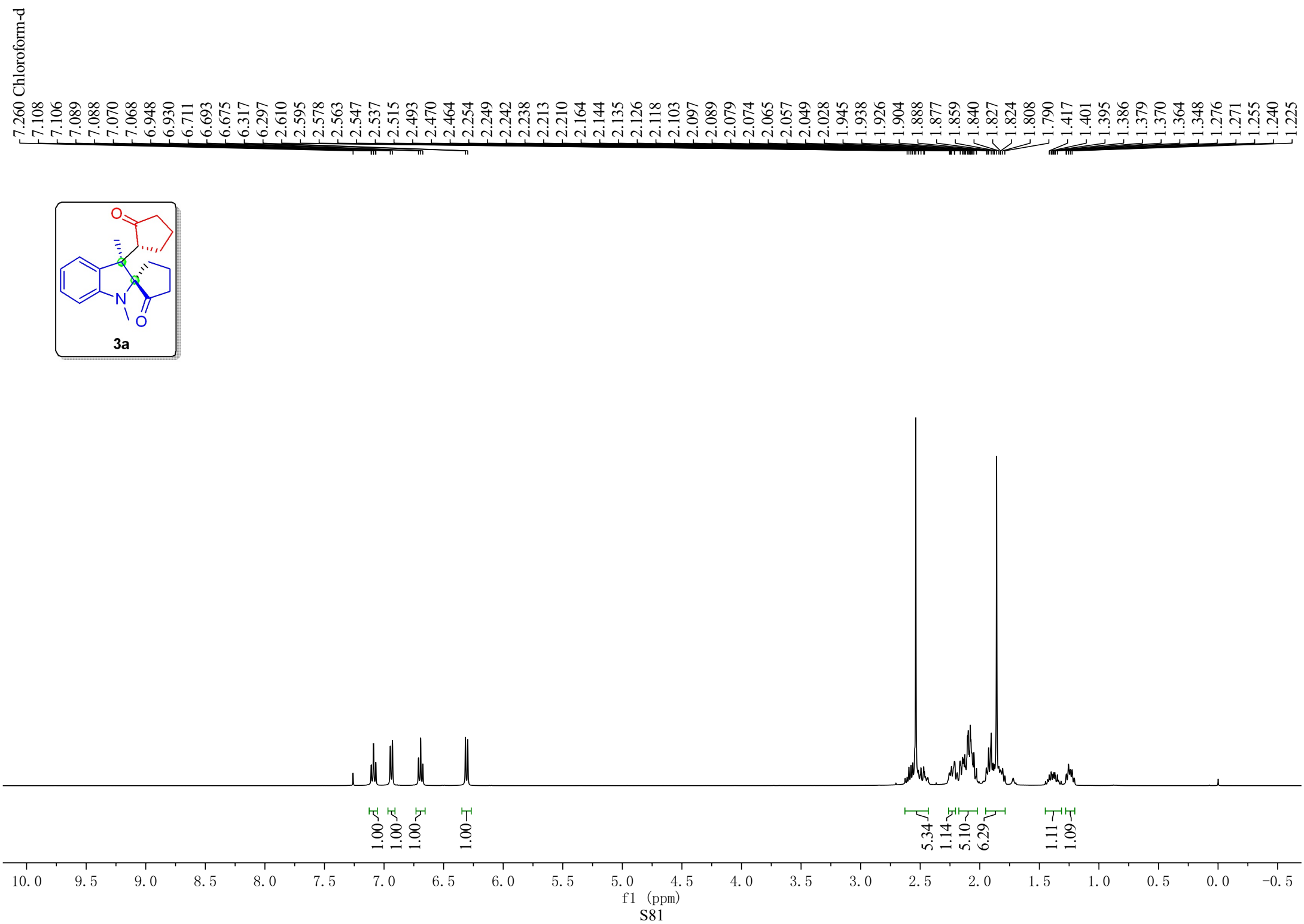
f1 (ppm)

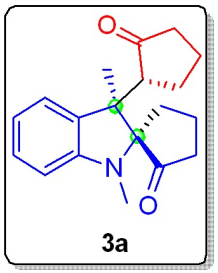

Chloroform-d
7.584
7.564
7.276
7.260
7.260
7.249
7.233
7.230
7.212
7.210
7.135
7.132
7.116
7.099
7.096
3.723
2.903
2.896
2.887
2.882
2.874
2.866
2.858
2.852
2.844
2.836
2.549
2.541
2.534
2.526
2.519
2.511
2.504
2.497
2.488
2.482
2.462
2.217
2.201
2.195
2.191
2.185
2.179
2.174
2.168
2.163
2.157
2.152
2.146
2.140
2.136
2.130
2.114
1.842
1.827
1.821
1.815
1.811
1.805
1.800
1.794
1.790
1.784
1.779
1.773
1.769
1.763
1.757
1.742
-0.097
OTMS
N
1a-TMS
1.01
2.38
1.01
3.02
2.04
2.05
3.00
1.03
1.06
9.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



137.41
137.09
128.46
121.72
118.60
118.49
108.47
106.11
77.00 Chloroform-d
76.24
38.10
31.12
15.83
10.34
0.87

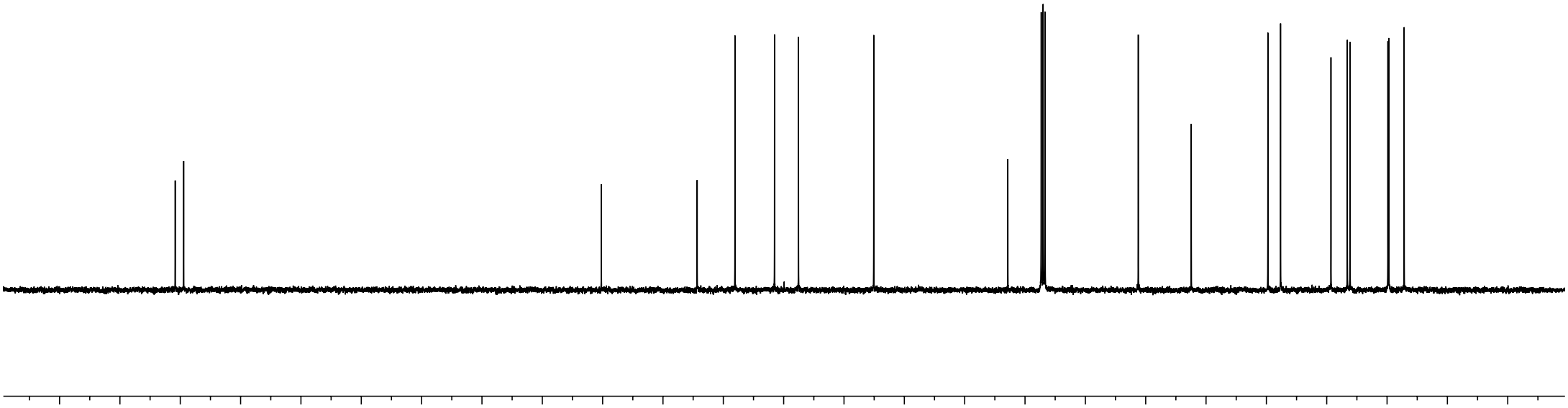


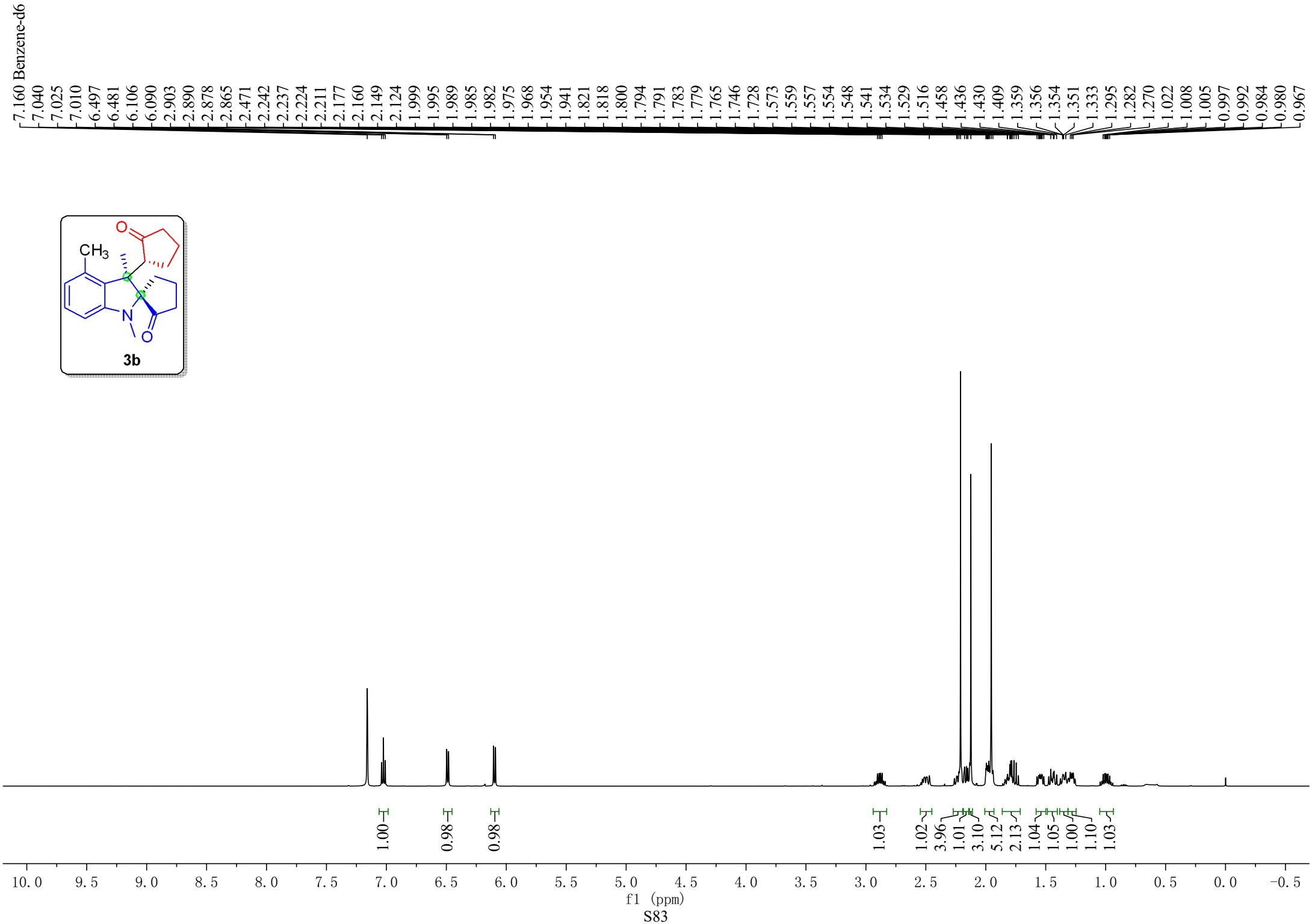

Chloroform-d
7.260
7.108
7.106
7.089
7.088
7.070
7.068
6.948
6.930
6.711
6.693
6.675
6.317
6.297
2.610
2.595
2.578
2.563
2.547
2.537
2.515
2.493
2.470
2.464
2.254
2.249
2.242
2.238
2.213
2.210
2.164
2.144
2.135
2.126
2.118
2.103
2.097
2.089
2.079
2.074
2.065
2.057
2.049
2.028
1.945
1.938
1.926
1.904
1.888
1.877
1.859
1.840
1.827
1.824
1.808
1.790
1.417
1.401
1.395
1.386
1.379
1.370
1.364
1.348
1.276
1.271
1.255
1.240
1.225
O
N
O
3a
1.00
1.00
1.00
1.00
5.34
1.14
5.10
6.29
1.11
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

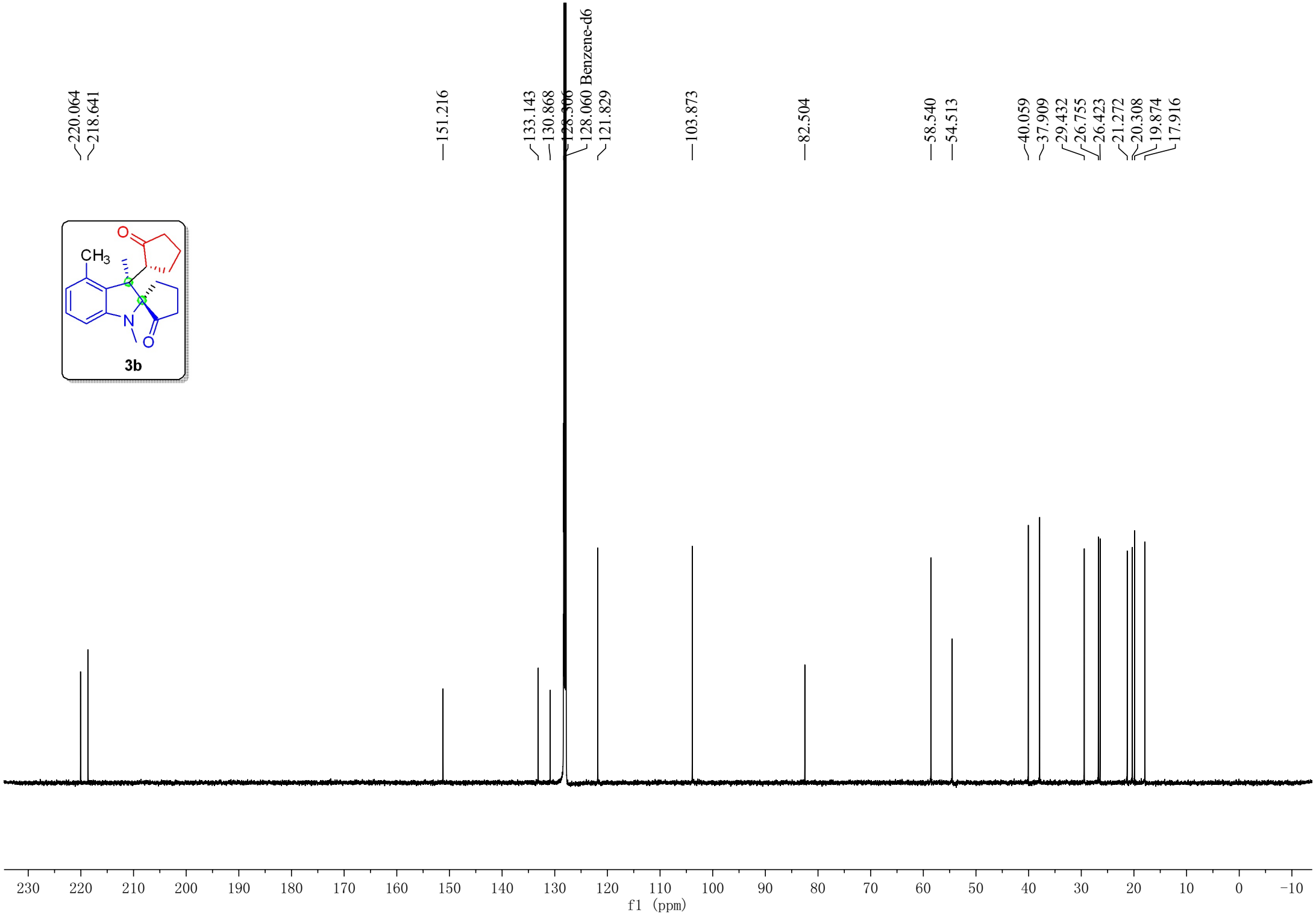


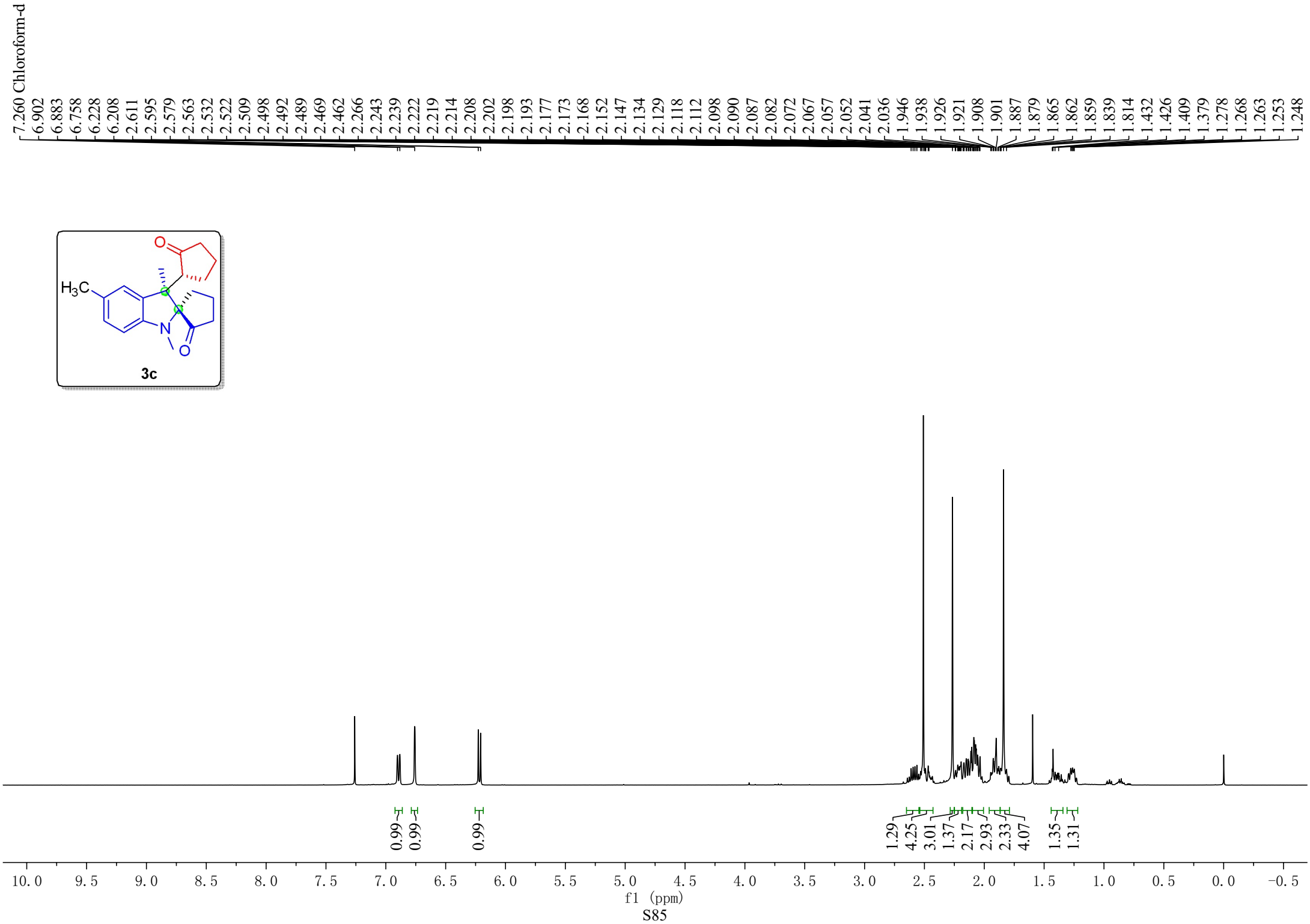
3a

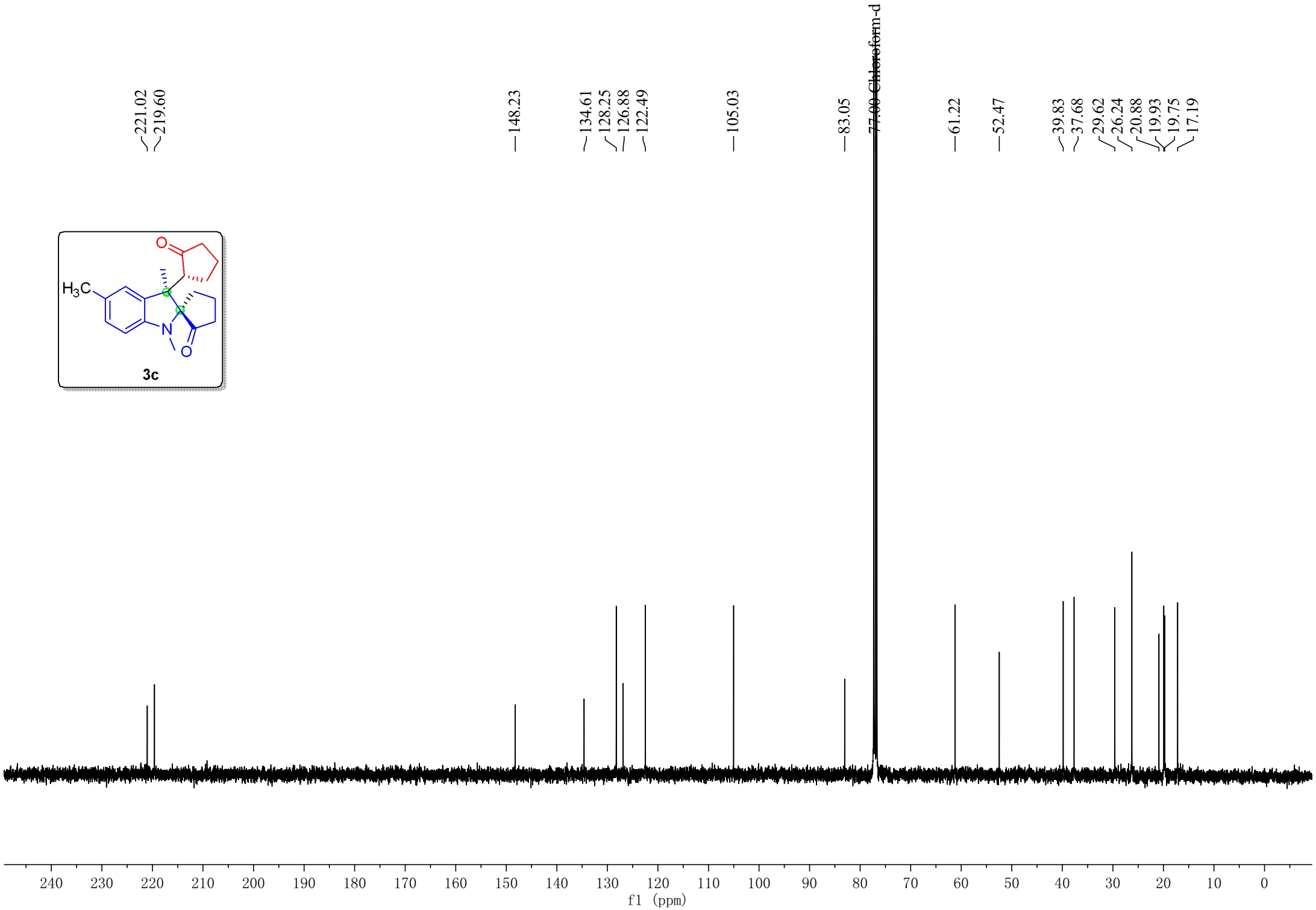
220.84
219.43
150.21
134.33
128.07
121.52
117.54
105.07
82.85
77.00 Chloroform-d
61.23
52.44
39.75
37.65
29.30
26.59
26.14
19.86
19.70
17.16

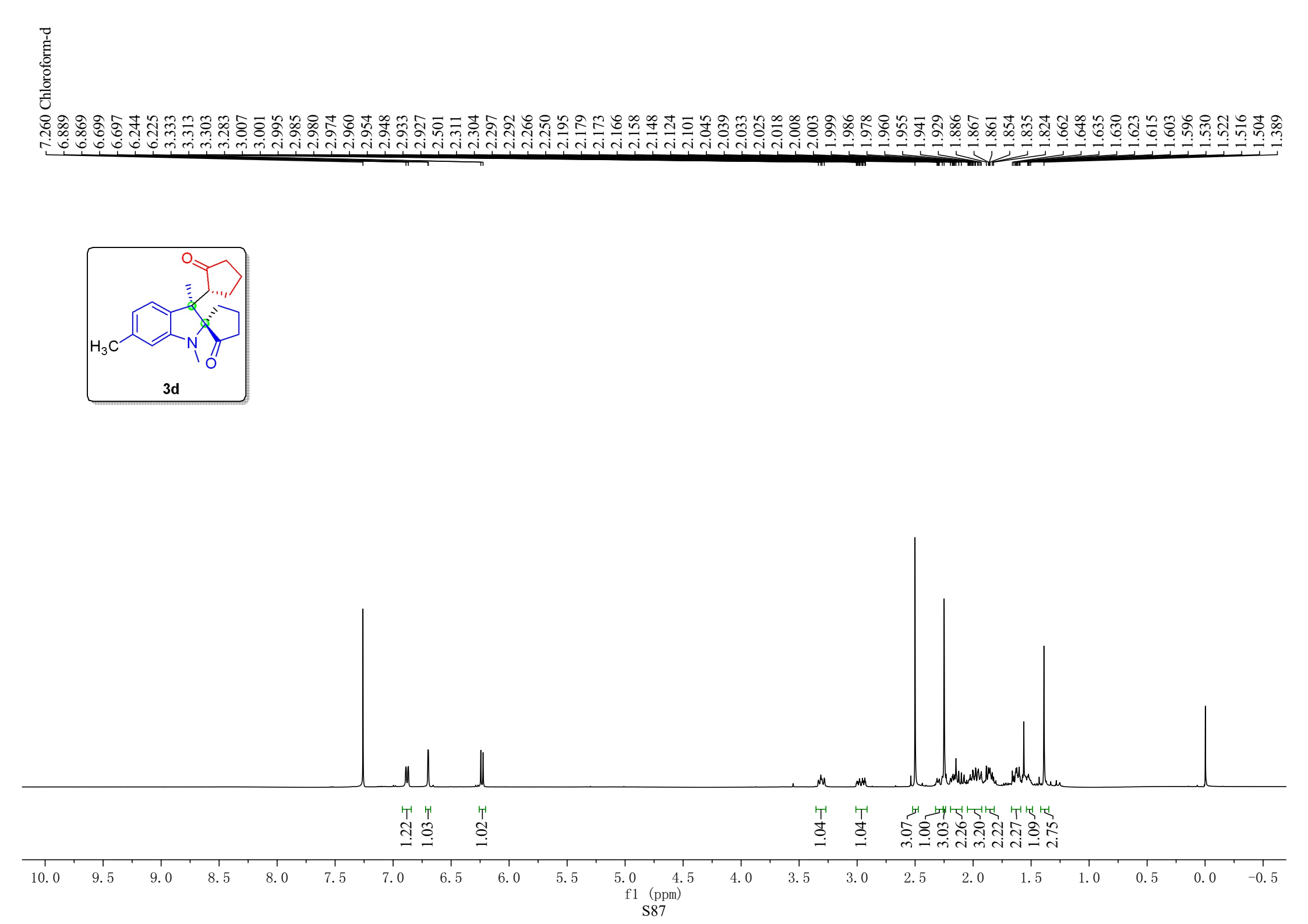


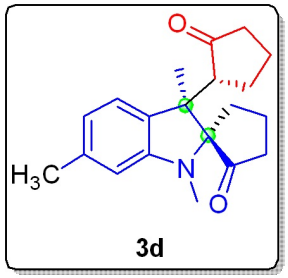

Benzene-d6
7.160
7.040
7.025
7.010
6.497
6.481
6.106
6.090
2.903
2.890
2.878
2.865
2.471
2.242
2.237
2.224
2.211
2.177
2.160
2.149
2.124
1.999
1.995
1.989
1.985
1.982
1.975
1.968
1.954
1.941
1.821
1.818
1.800
1.794
1.791
1.783
1.779
1.765
1.746
1.728
1.573
1.559
1.557
1.554
1.548
1.541
1.534
1.529
1.516
1.458
1.436
1.430
1.409
1.359
1.356
1.354
1.351
1.333
1.295
1.282
1.270
1.022
1.008
1.005
0.997
0.992
0.984
0.980
0.967
CH3
O
N
O
3b
1.00
0.98
0.98
1.03
1.02
3.96
1.01
3.10
5.12
2.13
1.04
1.05
1.00
1.10
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.064
218.641
151.216
133.143
130.868
128.306
128.060 Benzene-d6
121.829
103.873
82.504
58.540
54.513
40.059
37.909
29.432
26.755
26.423
21.272
20.308
19.874
17.916
CH3
O
N
O
3b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.260 Chloroform-d
6.902
6.883
6.758
6.228
6.208
2.611
2.595
2.579
2.563
2.532
2.522
2.509
2.498
2.492
2.489
2.469
2.462
2.266
2.243
2.239
2.222
2.219
2.214
2.208
2.202
2.198
2.193
2.177
2.173
2.168
2.152
2.147
2.134
2.129
2.118
2.112
2.098
2.090
2.087
2.082
2.072
2.067
2.057
2.052
2.041
2.036
1.946
1.938
1.926
1.921
1.908
1.901
1.887
1.879
1.865
1.862
1.859
1.839
1.814
1.432
1.426
1.409
1.379
1.278
1.268
1.263
1.253
1.248
H3C
O
N
O
3c
0.99
0.99
0.99
1.29
4.25
3.01
1.37
2.17
2.93
2.33
4.07
1.35
1.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


221.02
219.60
148.23
134.61
128.25
126.88
122.49
105.03
83.05
77.00 Chloroform-d
61.22
52.47
39.83
37.68
29.62
26.24
20.88
19.93
19.75
17.19
H3C
O
N
O
3c
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260 Chloroform-d
6.889
6.869
6.699
6.697
6.244
6.225
3.333
3.313
3.303
3.283
3.007
3.001
2.995
2.985
2.980
2.974
2.960
2.954
2.948
2.933
2.927
2.501
2.311
2.304
2.297
2.292
2.266
2.250
2.195
2.179
2.173
2.166
2.158
2.148
2.124
2.101
2.045
2.039
2.033
2.025
2.018
2.008
2.003
1.999
1.986
1.978
1.960
1.955
1.941
1.929
1.886
1.867
1.861
1.854
1.835
1.824
1.662
1.648
1.635
1.630
1.623
1.615
1.603
1.596
1.530
1.522
1.516
1.504
1.389
O
H3C
N
O
3d
1.22
1.03
1.02
1.04
1.04
3.07
1.00
3.03
2.26
3.20
2.22
2.27
1.09
2.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

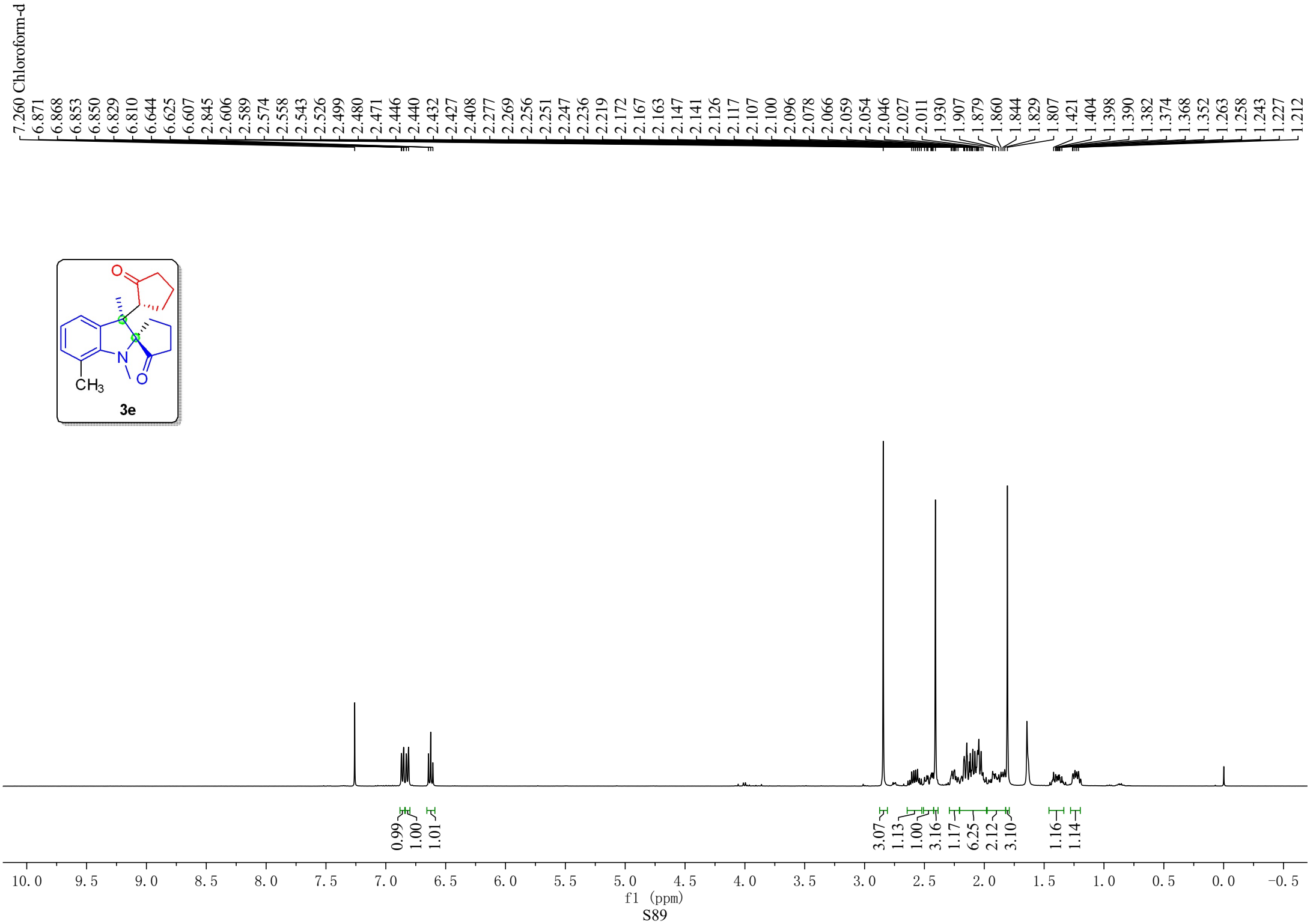


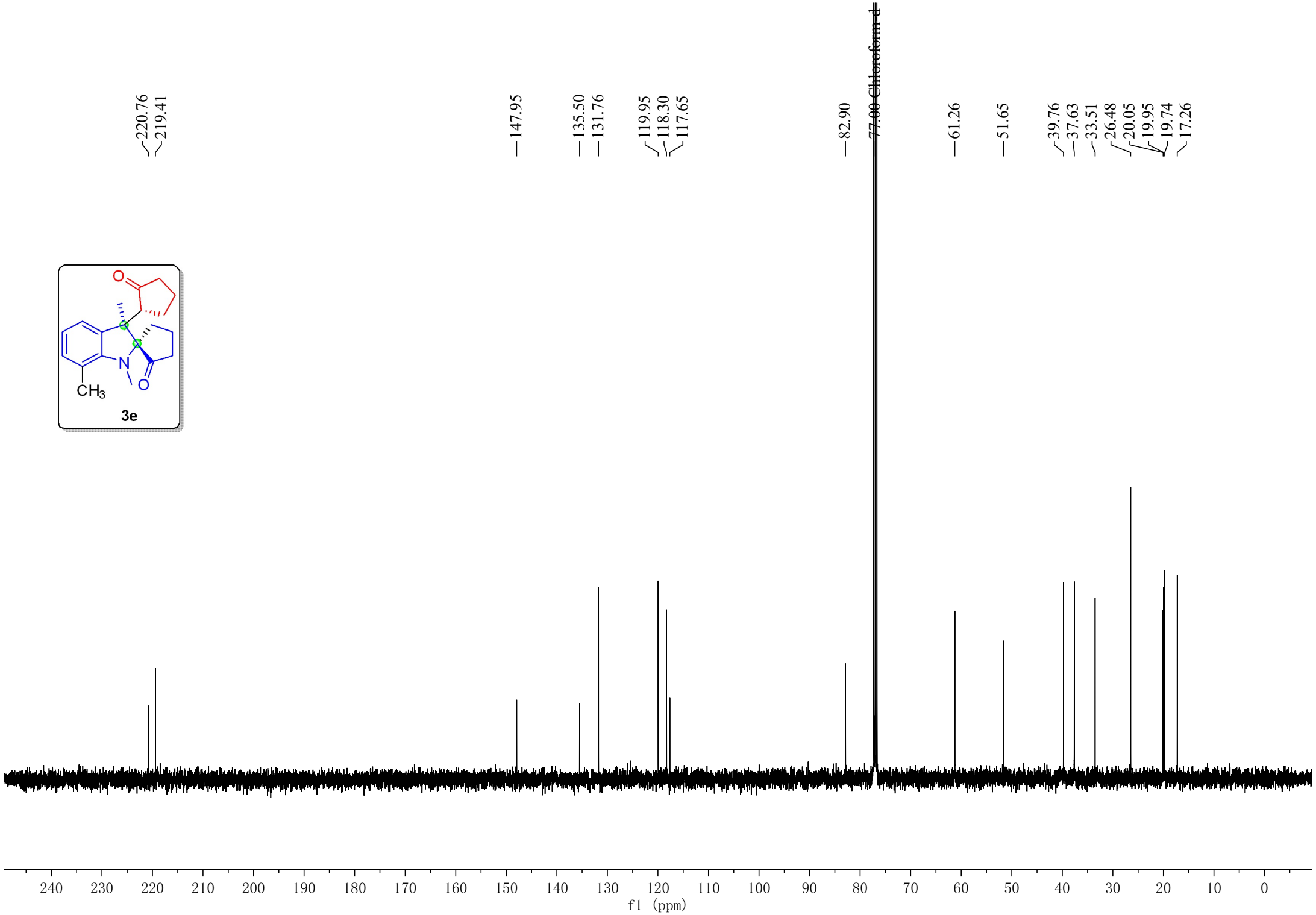
3d

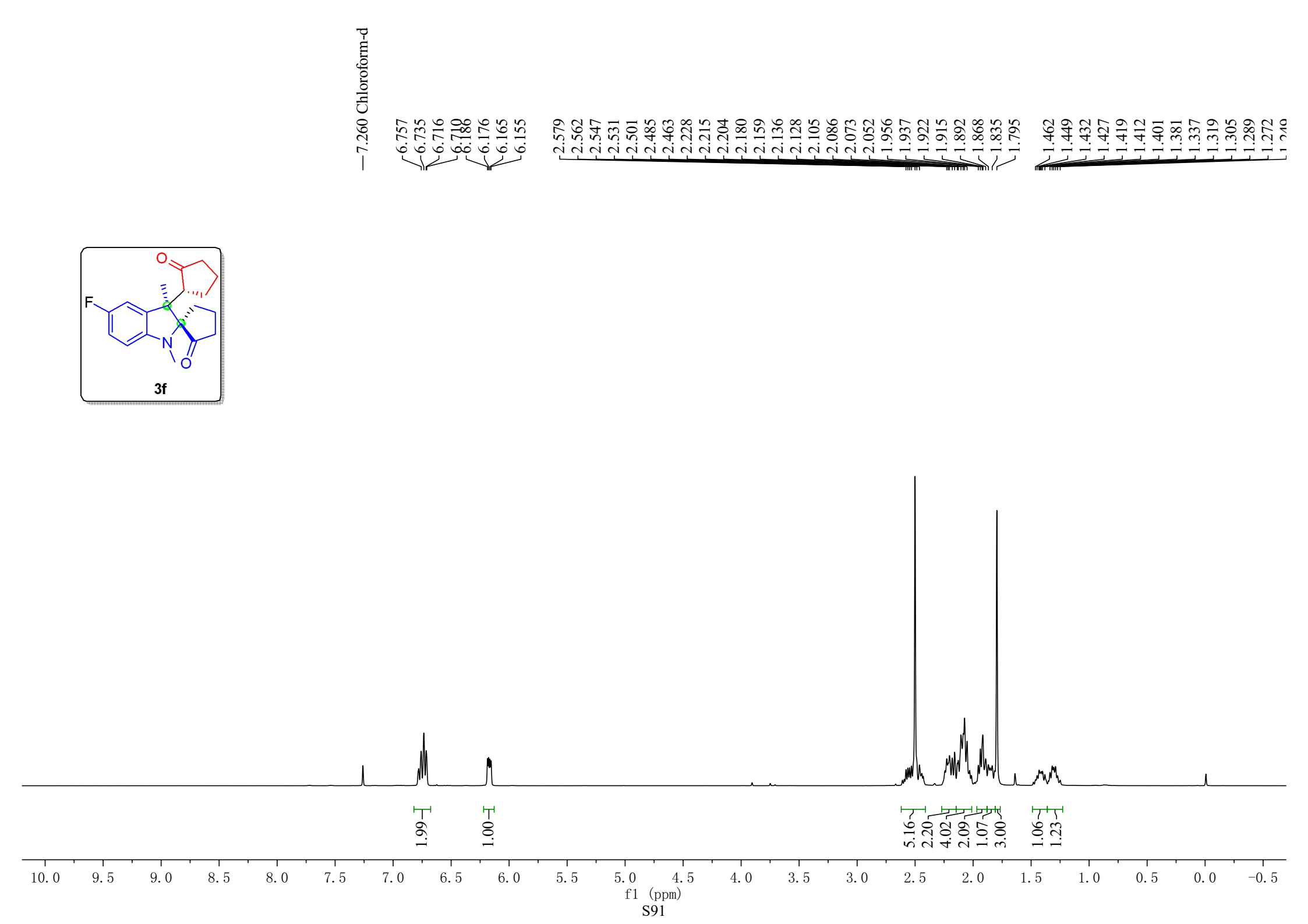
219.95
218.59
148.19
133.47
128.19
126.50
124.14
105.62
84.36
77.00 Chloroform-d
51.12
49.91
39.47
37.53
30.17
28.00
24.29
20.92
19.54
17.51
13.88

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


Chloroform-d
7.260
6.871
6.868
6.853
6.850
6.829
6.810
6.644
6.625
6.607
2.845
2.606
2.589
2.574
2.558
2.543
2.526
2.499
2.480
2.471
2.446
2.440
2.432
2.427
2.408
2.277
2.269
2.256
2.251
2.247
2.236
2.219
2.172
2.167
2.163
2.147
2.141
2.126
2.117
2.107
2.100
2.096
2.078
2.066
2.059
2.054
2.046
2.027
2.011
1.930
1.907
1.879
1.860
1.844
1.829
1.807
1.421
1.404
1.398
1.390
1.382
1.374
1.368
1.352
1.263
1.258
1.243
1.227
1.212
O
N
O
CH3
3e
0.99
1.00
1.01
3.07
1.13
1.00
3.16
1.17
6.25
2.12
3.10
1.16
1.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


220.76
219.41
147.95
135.50
131.76
119.95
118.30
117.65
82.90
77.00 Chloroform-d
61.26
51.65
39.76
37.63
33.51
26.48
20.05
19.95
19.74
17.26
O
N
CH3
O
3e
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260 Chloroform-d
6.757
6.735
6.716
6.710
6.186
6.176
6.165
6.155
2.579
2.562
2.547
2.531
2.501
2.485
2.463
2.228
2.215
2.204
2.180
2.159
2.136
2.128
2.105
2.086
2.073
2.052
1.956
1.937
1.922
1.915
1.892
1.868
1.835
1.795
1.462
1.449
1.432
1.427
1.419
1.412
1.401
1.381
1.337
1.319
1.305
1.289
1.272
F
O
N
O
3f
1.99
1.00
5.16
2.20
4.02
2.09
1.07
3.00
1.06
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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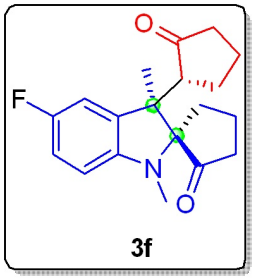
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

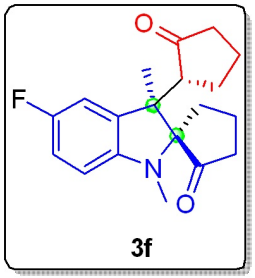


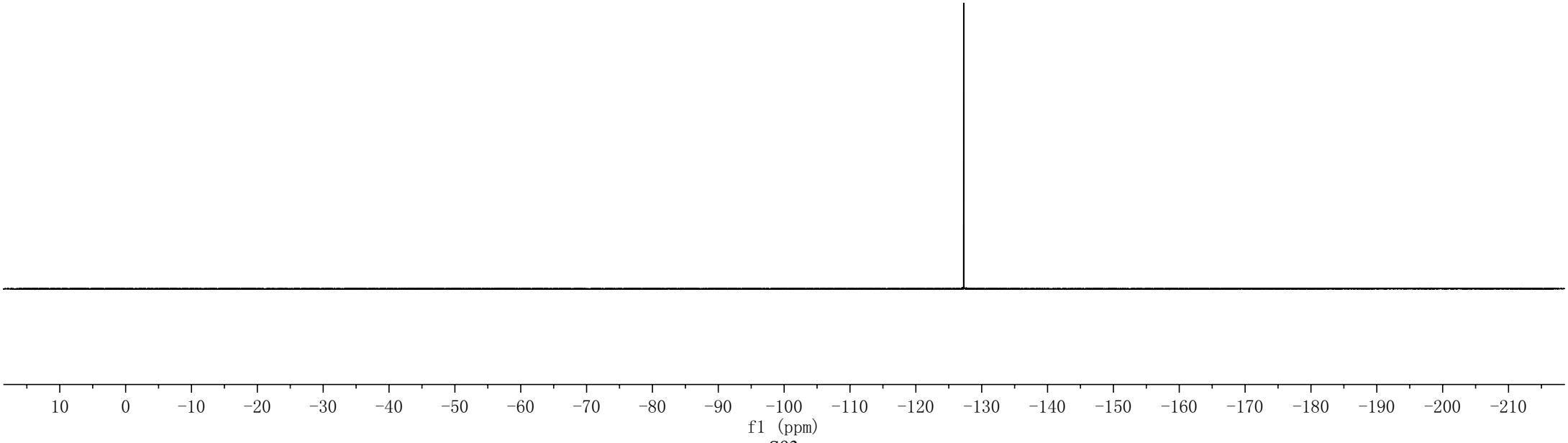
3f

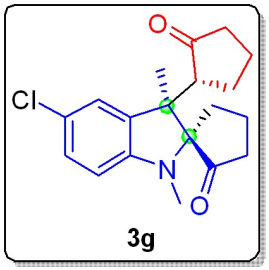
220.31
219.05
157.86
155.53
146.41
136.12
136.05
113.72
113.49
109.88
109.64
105.07
104.99
83.10
77.00 Chloroform-d
60.65
52.18
39.68
37.61
29.80
26.41
26.20
19.92
19.60
17.15

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

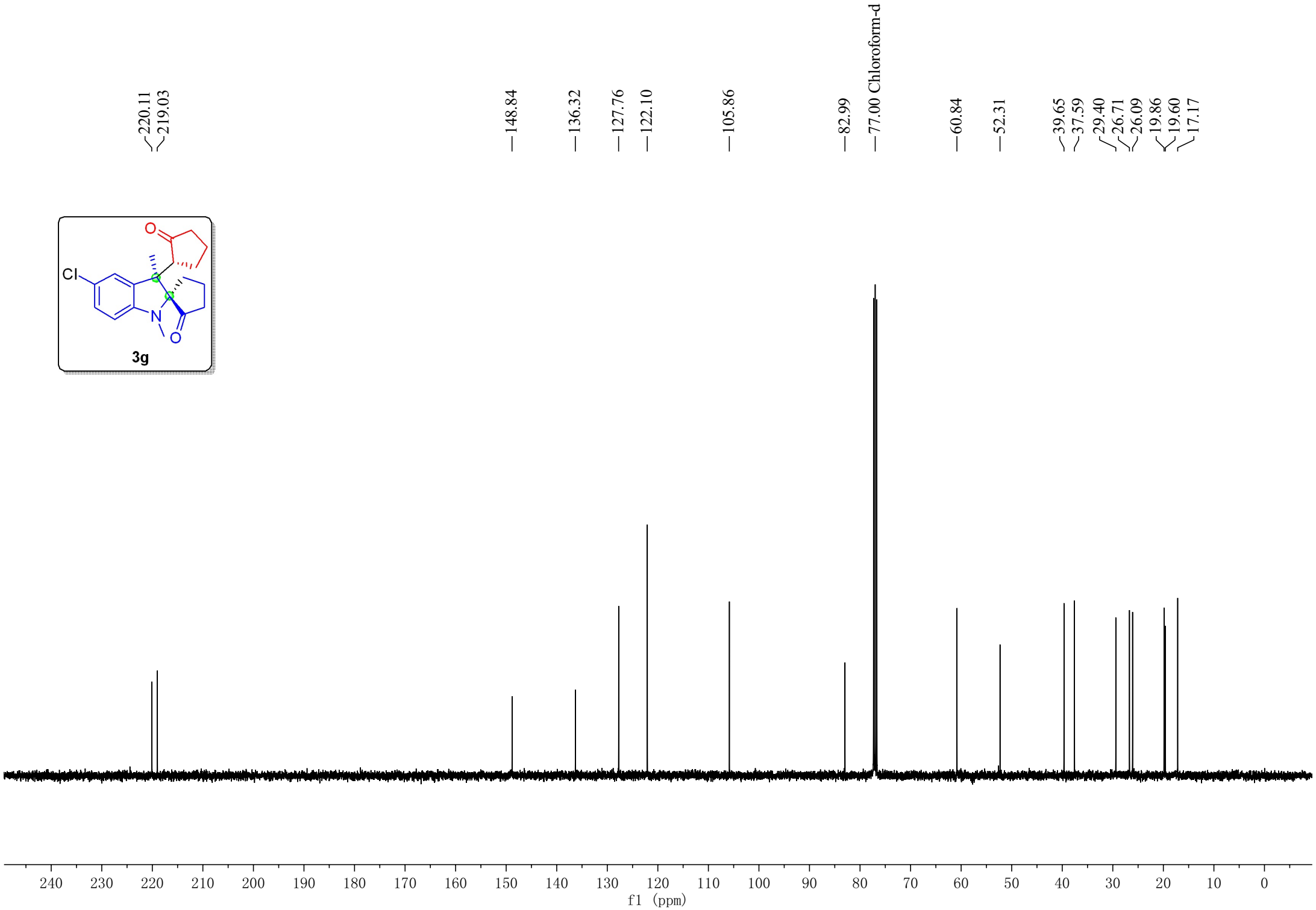
f1 (ppm)

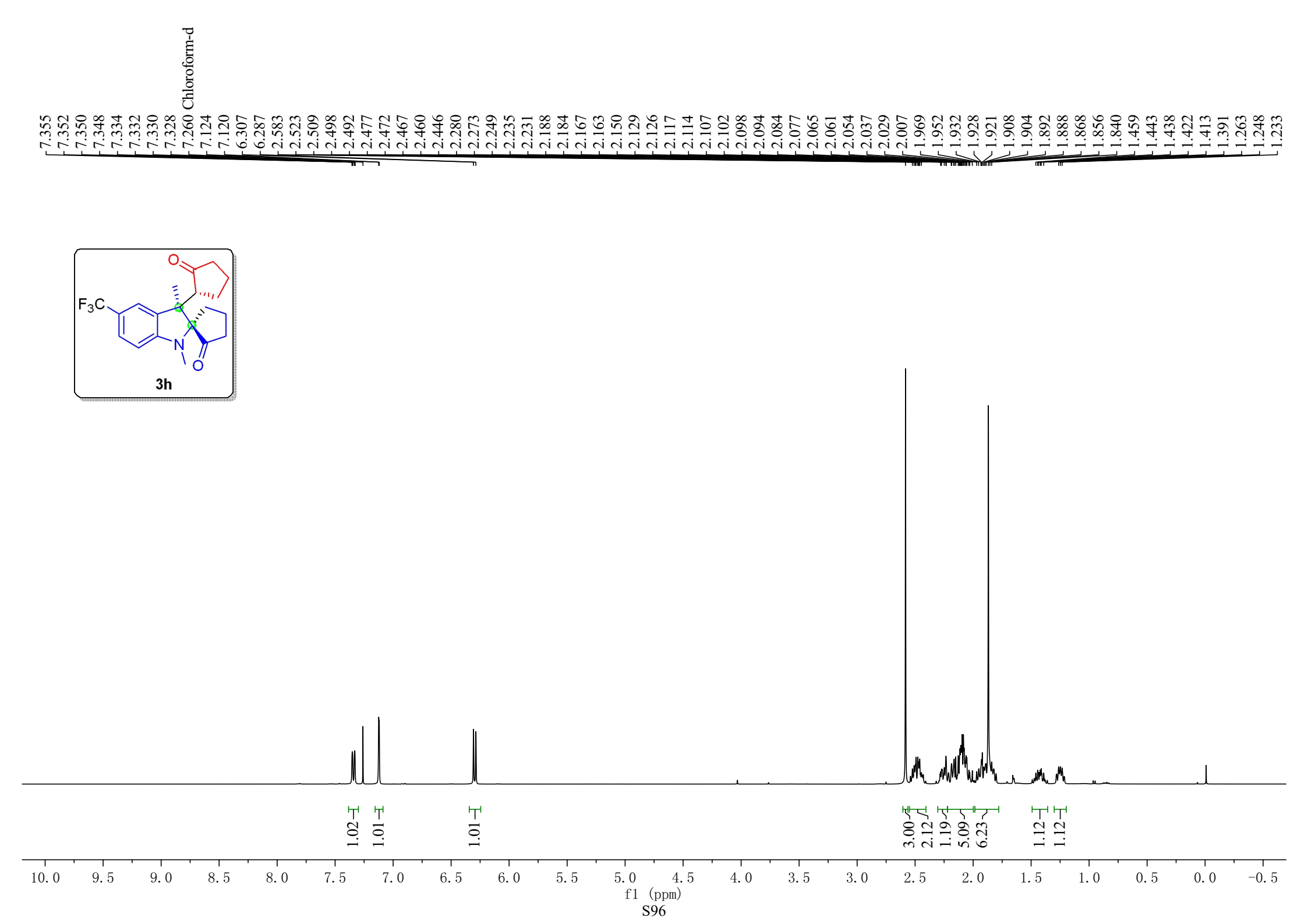

O
F
N
O
3f

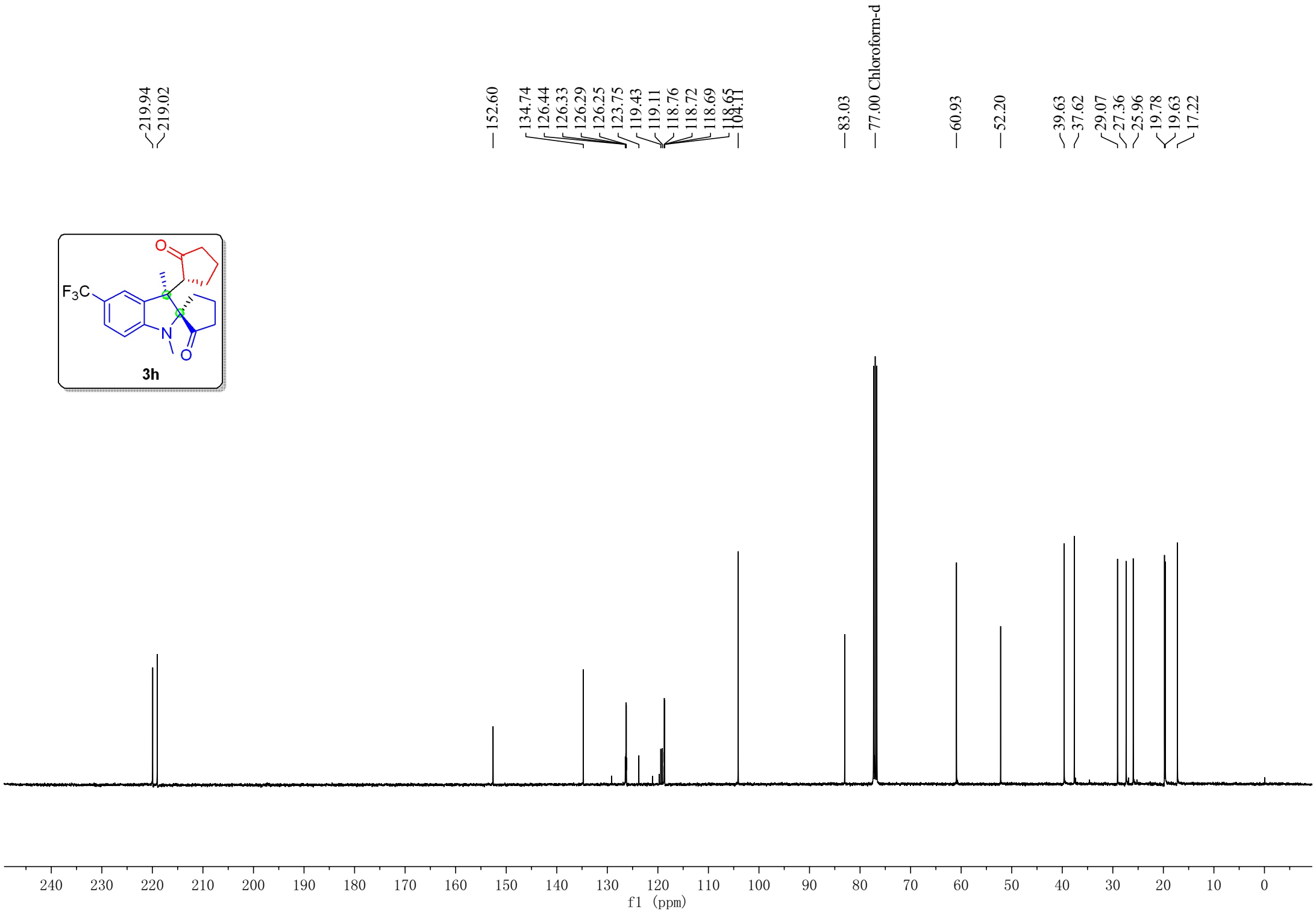

-127.26
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

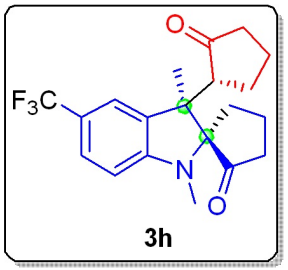

Cl
O
N
O
3g

7.260 Chloroform-d
7.032
7.027
7.011
7.006
6.895
6.889
6.208
6.187
2.554
2.537
2.511
2.477
2.457
2.438
2.244
2.226
2.199
2.175
2.154
2.131
2.110
2.089
2.084
2.064
2.050
2.044
2.032
2.014
1.929
1.911
1.890
1.877
1.860
1.843
1.812
1.444
1.429
1.424
1.414
1.407
1.397
1.377
1.343
1.338
1.322
1.308
1.292
1.275
1.00
1.00
1.02
5.25
3.08
3.27
2.99
3.07
1.16
1.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.11
219.03
148.84
136.32
127.76
122.10
105.86
82.99
77.00 Chloroform-d
60.84
52.31
39.65
37.59
29.40
26.71
26.09
19.86
19.60
17.17
Cl
O
N
O
3g
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.355
7.352
7.350
7.348
7.334
7.332
7.330
7.328
7.260 Chloroform-d
7.124
7.120
6.307
6.287
2.583
2.523
2.509
2.498
2.492
2.477
2.472
2.467
2.460
2.446
2.280
2.273
2.249
2.235
2.231
2.188
2.184
2.167
2.163
2.150
2.129
2.126
2.117
2.114
2.107
2.102
2.098
2.094
2.084
2.077
2.065
2.061
2.054
2.037
2.029
2.007
1.969
1.952
1.932
1.928
1.921
1.908
1.904
1.892
1.888
1.868
1.856
1.840
1.459
1.443
1.438
1.422
1.413
1.391
1.263
1.248
1.233
F3C
O
N
O
3h
1.02
1.01
1.01
3.00
2.12
1.19
5.09
6.23
1.12
1.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


219.94
219.02
152.60
134.74
126.44
126.33
126.29
126.25
123.75
119.43
119.11
118.76
118.72
118.69
118.65
104.11
83.03
77.00 Chloroform-d
60.93
52.20
39.63
37.62
29.07
27.36
25.96
19.78
19.63
17.22
F3C
O
N
O
3h
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

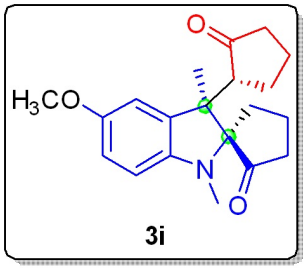


3h

-60.35

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)



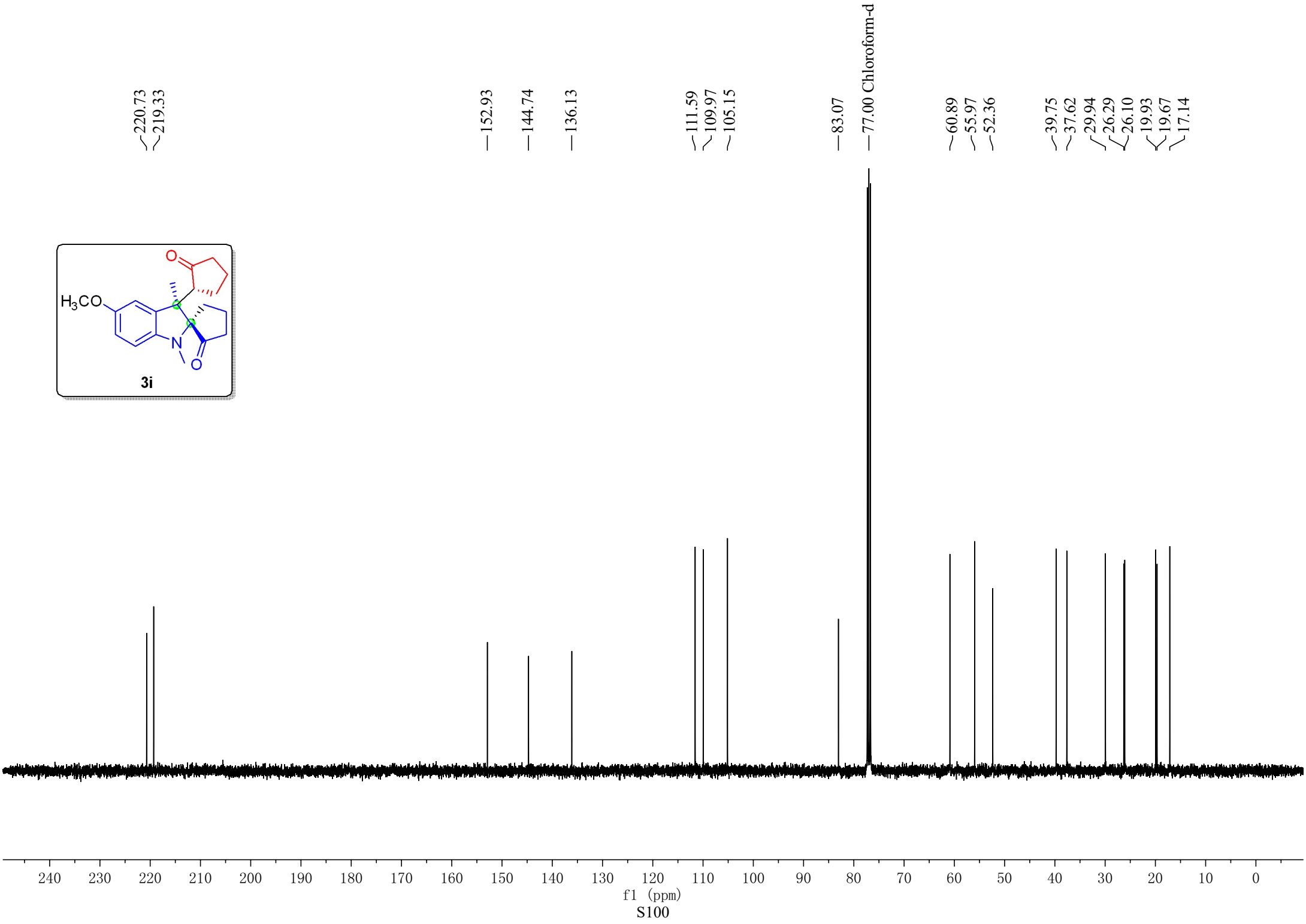
3i

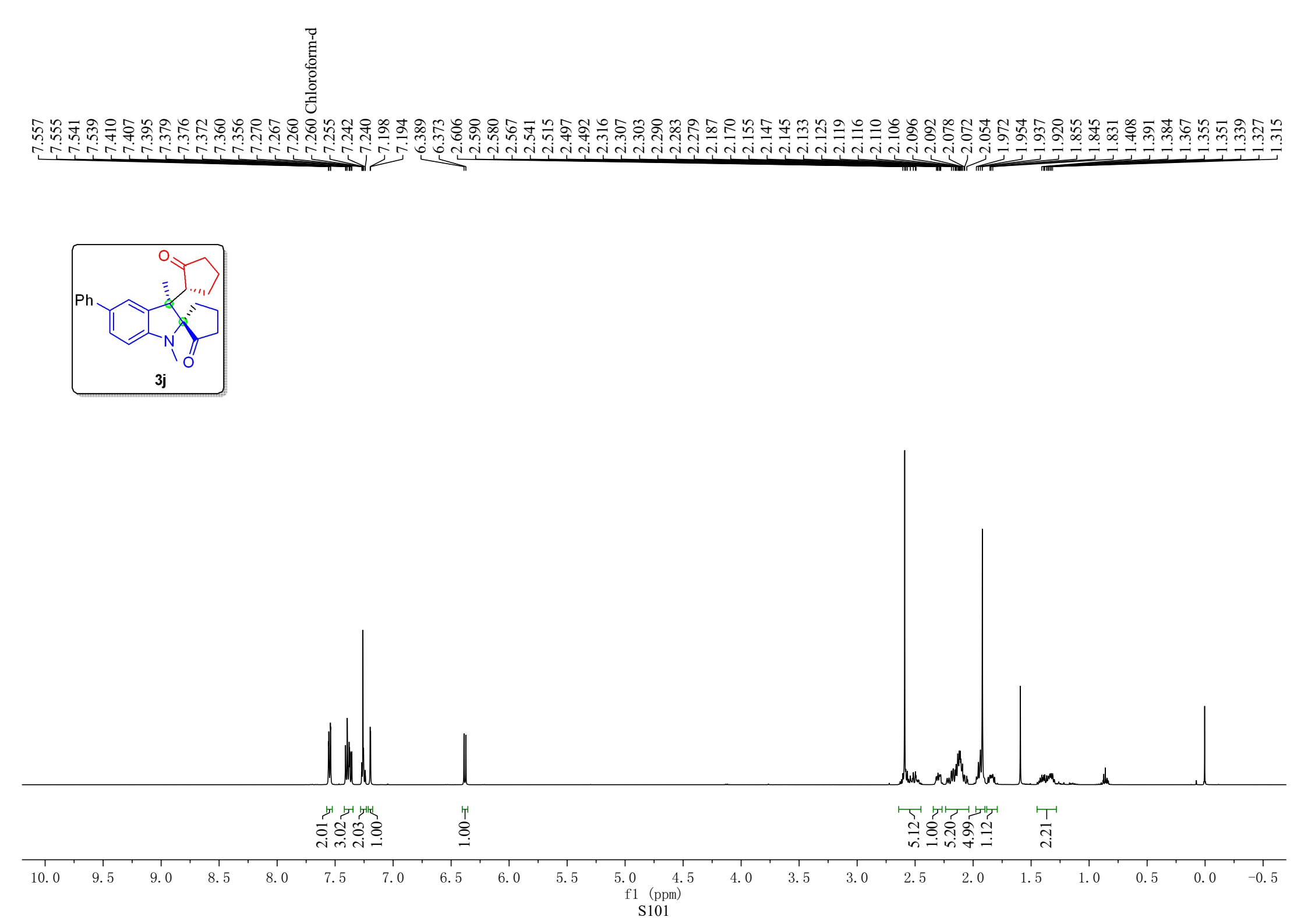
7.260 Chloroform-d
6.644
6.638
6.622
6.218
6.197
3.748
2.487
2.191
2.165
2.145
2.128
2.107
2.100
2.079
2.067
2.063
1.906
1.811
1.435
1.422
1.405
1.400
1.390
1.384
1.374
1.353
1.324
1.305
1.291
1.276
1.257

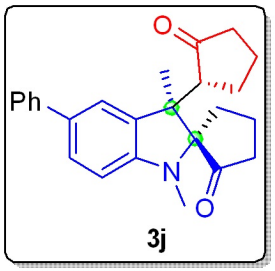
2.00
1.00
3.02
1.09
4.03
6.11
2.93
3.00
1.02
1.17

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

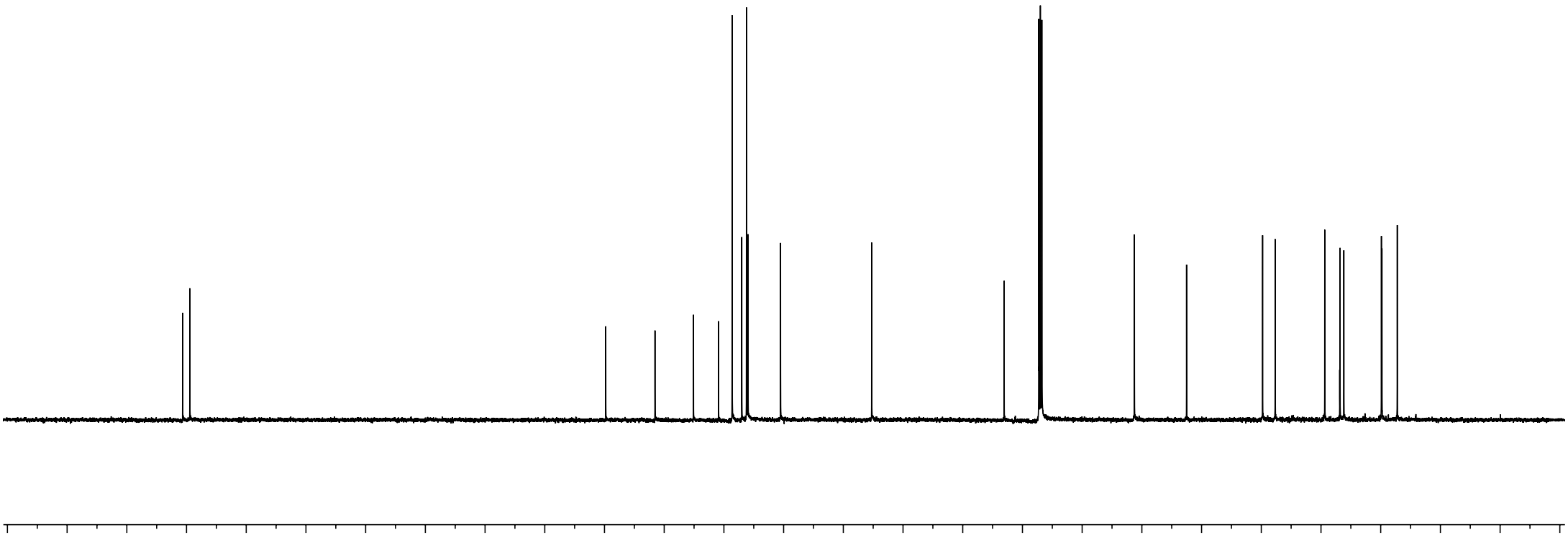
f1 (ppm)

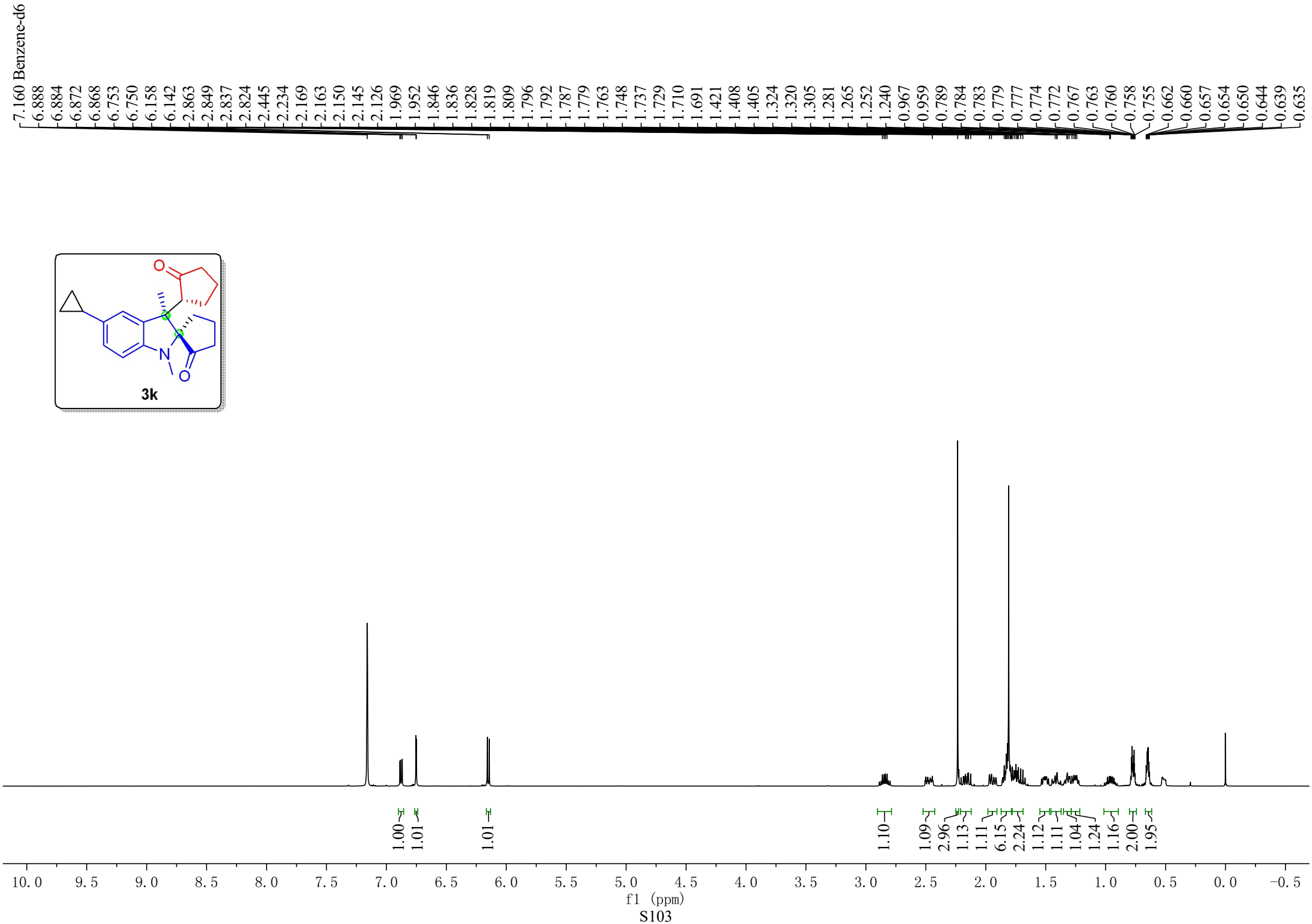

220.73
219.33
152.93
144.74
136.13
111.59
109.97
105.15
83.07
77.00 Chloroform-d
60.89
55.97
52.36
39.75
37.62
29.94
26.29
26.10
19.93
19.67
17.14
H3CO
O
N
O
3i
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

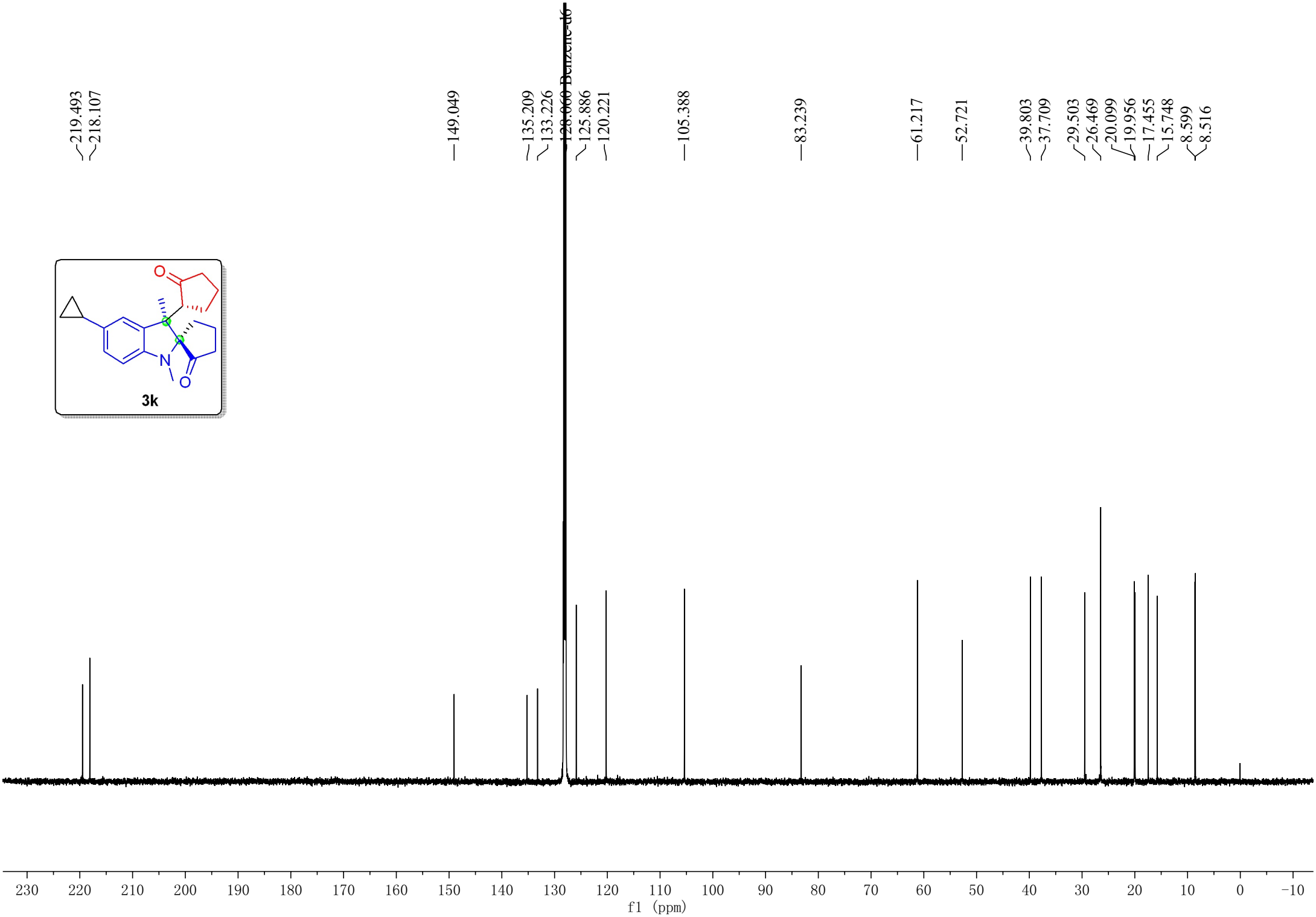

Chloroform-d
7.557
7.555
7.541
7.539
7.410
7.407
7.395
7.379
7.376
7.372
7.360
7.356
7.270
7.267
7.260
7.260
7.255
7.242
7.240
7.198
7.194
6.389
6.373
2.606
2.590
2.580
2.567
2.541
2.515
2.497
2.492
2.316
2.307
2.303
2.290
2.283
2.279
2.187
2.170
2.155
2.147
2.145
2.133
2.125
2.119
2.116
2.110
2.106
2.096
2.092
2.078
2.072
2.054
1.972
1.954
1.937
1.920
1.855
1.845
1.831
1.408
1.391
1.384
1.367
1.355
1.351
1.339
1.327
1.315
Ph
O
N
O
3j
2.01
3.02
2.03
1.00
1.00
5.12
1.00
5.20
4.99
1.12
2.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

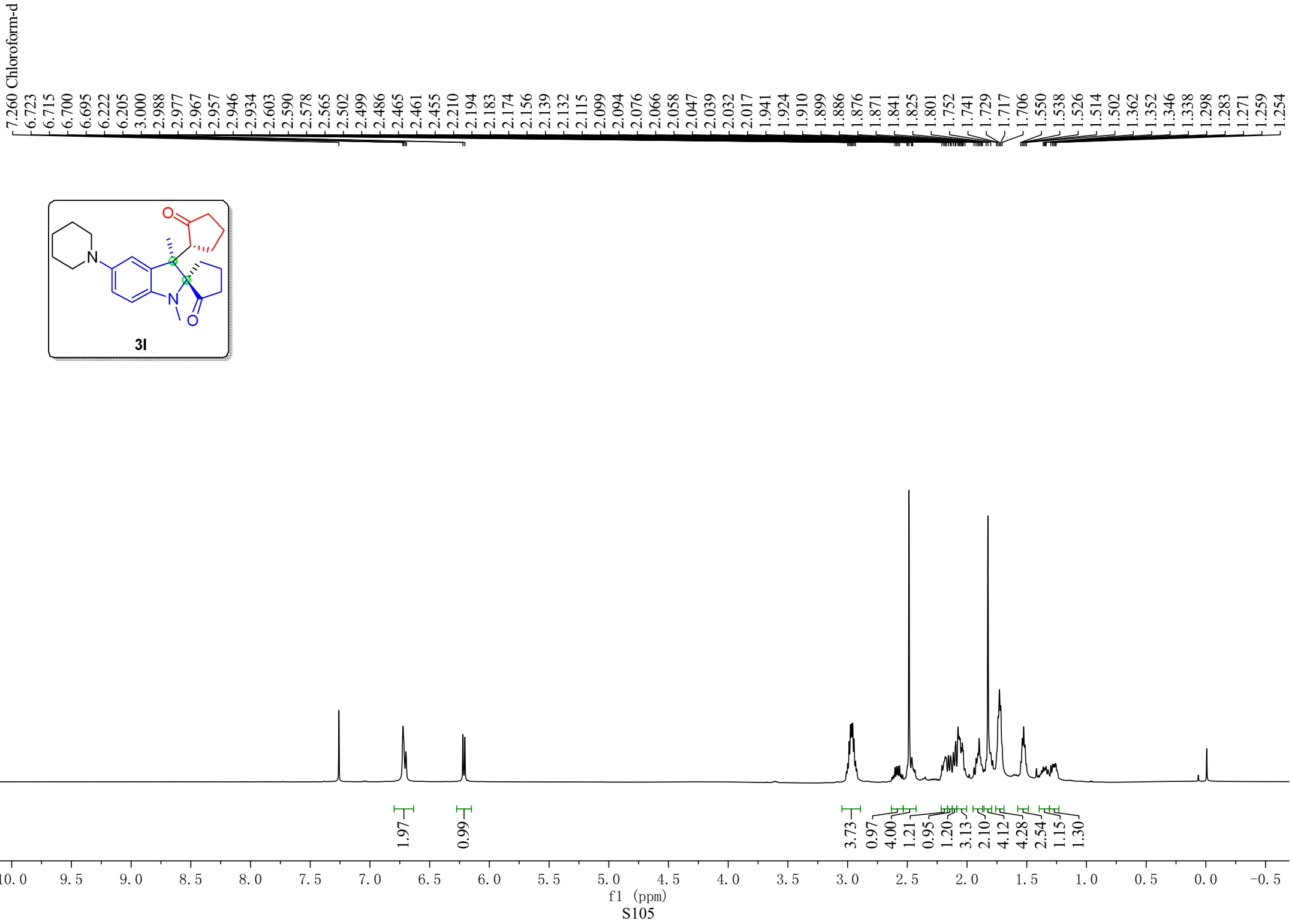


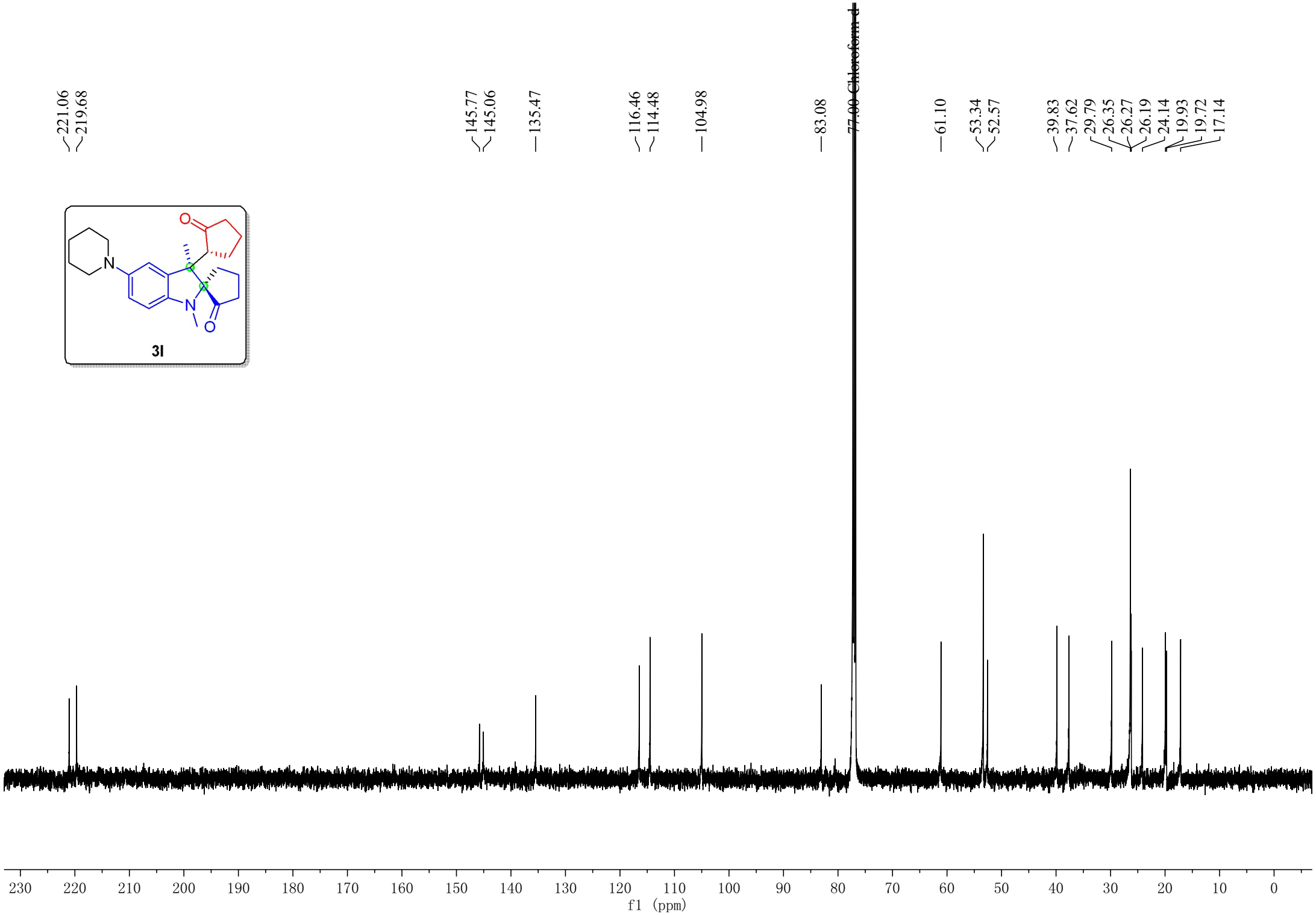
220.65
219.45
149.79
141.54
135.10
130.90
128.62
127.01
126.22
125.96
120.51
105.25
83.06
77.00 Chloroform-d
61.25
52.51
39.78
37.67
29.37
26.81
26.17
19.88
19.79
17.23

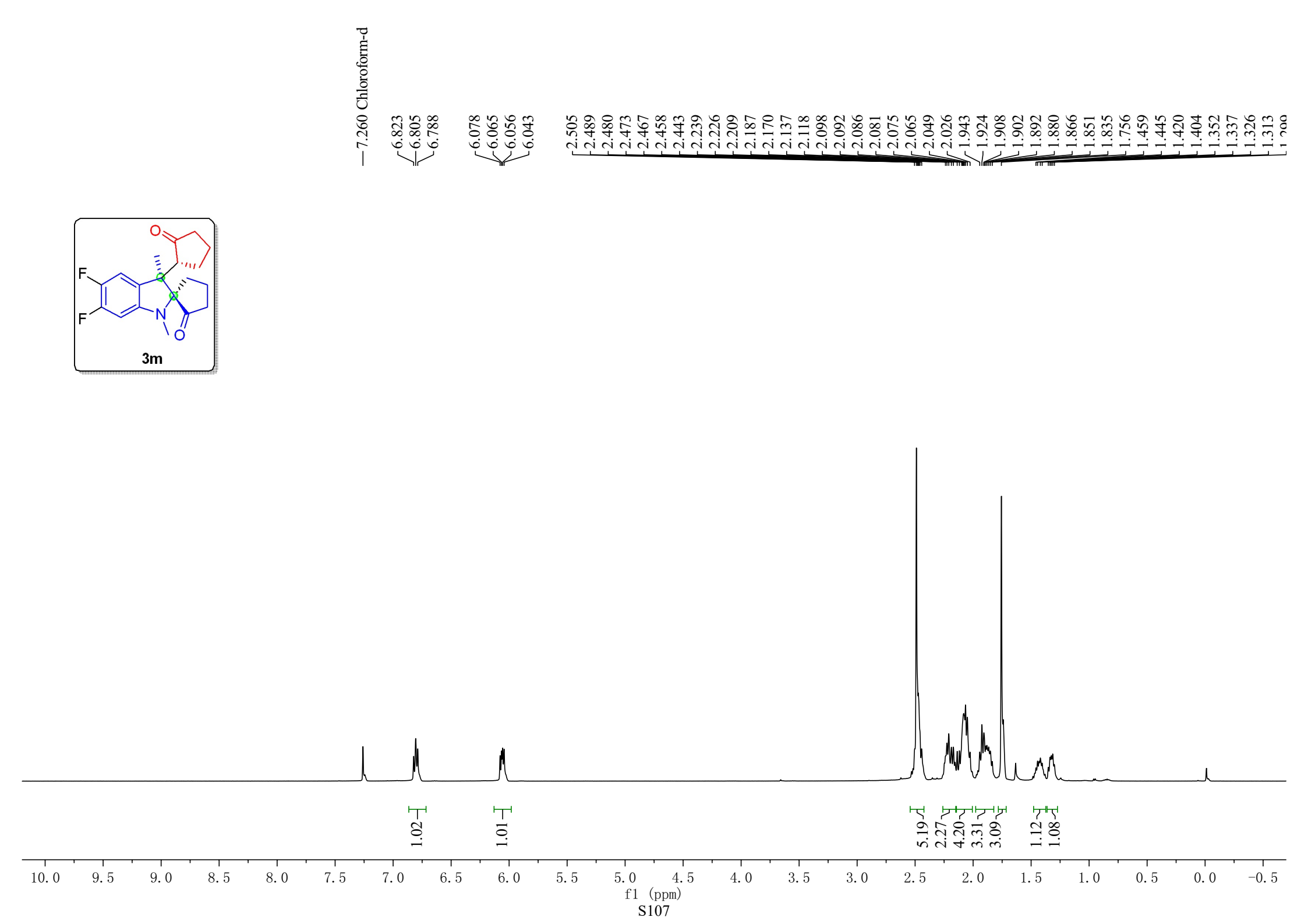


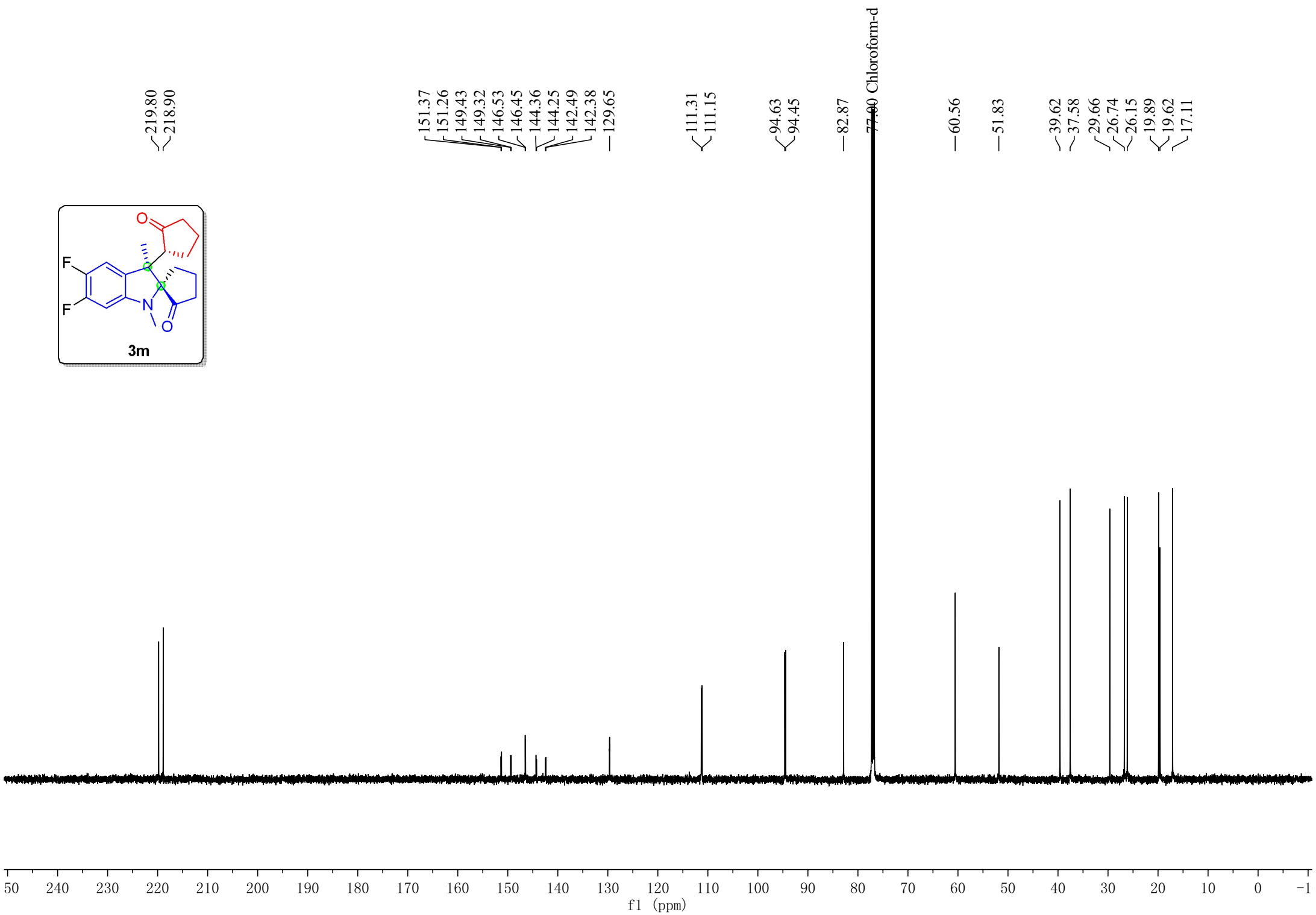

7.160 Benzene-d6
6.888
6.884
6.872
6.868
6.753
6.750
6.158
6.142
2.863
2.849
2.837
2.824
2.445
2.234
2.169
2.163
2.150
2.145
2.126
1.969
1.952
1.846
1.836
1.828
1.819
1.809
1.796
1.792
1.787
1.779
1.763
1.748
1.737
1.729
1.710
1.691
1.421
1.408
1.405
1.324
1.320
1.305
1.281
1.265
1.252
1.240
0.967
0.959
0.789
0.784
0.783
0.779
0.777
0.774
0.772
0.767
0.763
0.760
0.758
0.755
0.662
0.660
0.657
0.654
0.650
0.644
0.639
0.635
O
N
O
3k
1.00
1.01
1.01
1.10
1.09
2.96
1.13
1.11
6.15
2.24
1.12
1.11
1.04
1.24
1.16
2.00
1.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

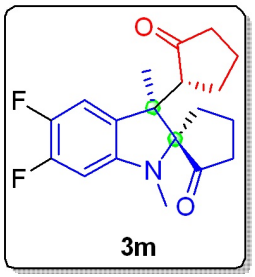

219.493
218.107
149.049
135.209
133.226
128.060 Benzene-d6
125.886
120.221
105.388
83.239
61.217
52.721
39.803
37.709
29.503
26.469
20.099
19.956
17.455
15.748
8.599
8.516
O
N
O
3k
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.260 Chloroform-d
6.723
6.715
6.700
6.695
6.222
6.205
3.000
2.988
2.977
2.967
2.957
2.946
2.934
2.603
2.590
2.578
2.565
2.502
2.499
2.486
2.465
2.461
2.455
2.210
2.194
2.183
2.174
2.156
2.139
2.132
2.115
2.099
2.094
2.076
2.066
2.058
2.047
2.039
2.032
2.017
1.941
1.924
1.910
1.899
1.886
1.876
1.871
1.841
1.825
1.801
1.752
1.741
1.729
1.717
1.706
1.550
1.538
1.526
1.514
1.502
1.362
1.352
1.346
1.338
1.298
1.283
1.271
1.259
1.254
O
N
N
O
3l
1.97
0.99
3.73
0.97
4.00
1.21
0.95
1.20
3.13
2.10
4.12
4.28
2.54
1.15
1.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


221.06
219.68
145.77
145.06
135.47
116.46
114.48
104.98
83.08
77.00 Chloroform-d
61.10
53.34
52.57
39.83
37.62
29.79
26.35
26.27
26.19
24.14
19.93
19.72
17.14
3l
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260 Chloroform-d
6.823
6.805
6.788
6.078
6.065
6.056
6.043
2.505
2.489
2.480
2.473
2.467
2.458
2.443
2.239
2.226
2.209
2.187
2.170
2.137
2.118
2.098
2.092
2.086
2.081
2.075
2.065
2.049
2.026
1.943
1.924
1.908
1.902
1.892
1.880
1.866
1.851
1.835
1.756
1.459
1.445
1.420
1.404
1.352
1.337
1.326
1.313
F
F
N
O
O
3m
1.02
1.01
5.19
2.27
4.20
3.31
3.09
1.12
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


219.80
218.90
151.37
151.26
149.43
149.32
146.53
146.45
144.36
144.25
142.49
142.38
129.65
111.31
111.15
94.63
94.45
82.87
77.00 Chloroform-d
60.56
51.83
39.62
37.58
29.66
26.74
26.15
19.89
19.62
17.11
F
F
N
O
O
3m
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

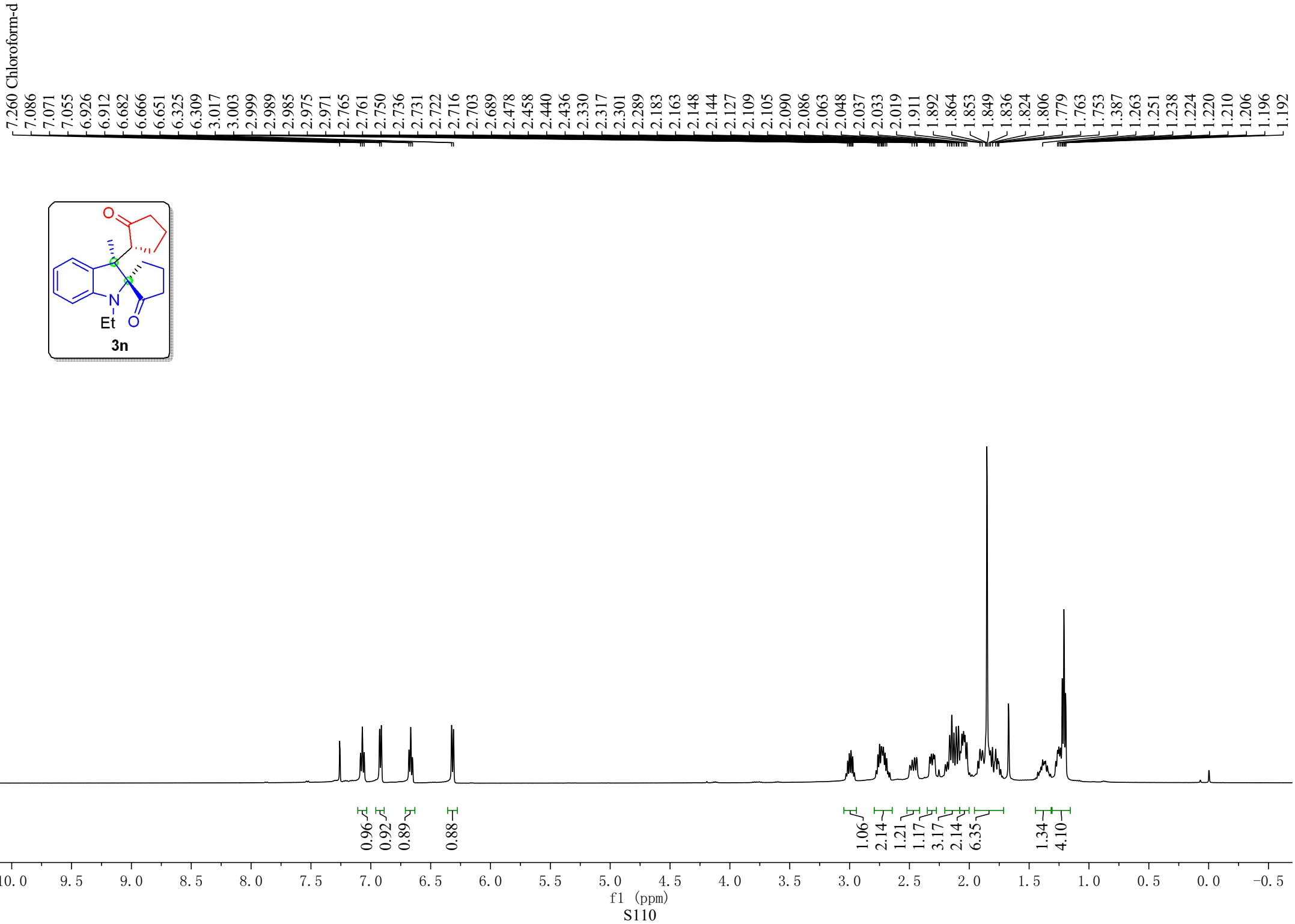


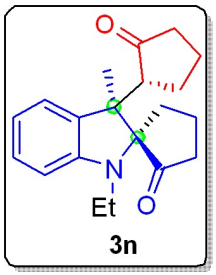
3m

-139.35
-139.39
-152.55
-152.59

20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −22

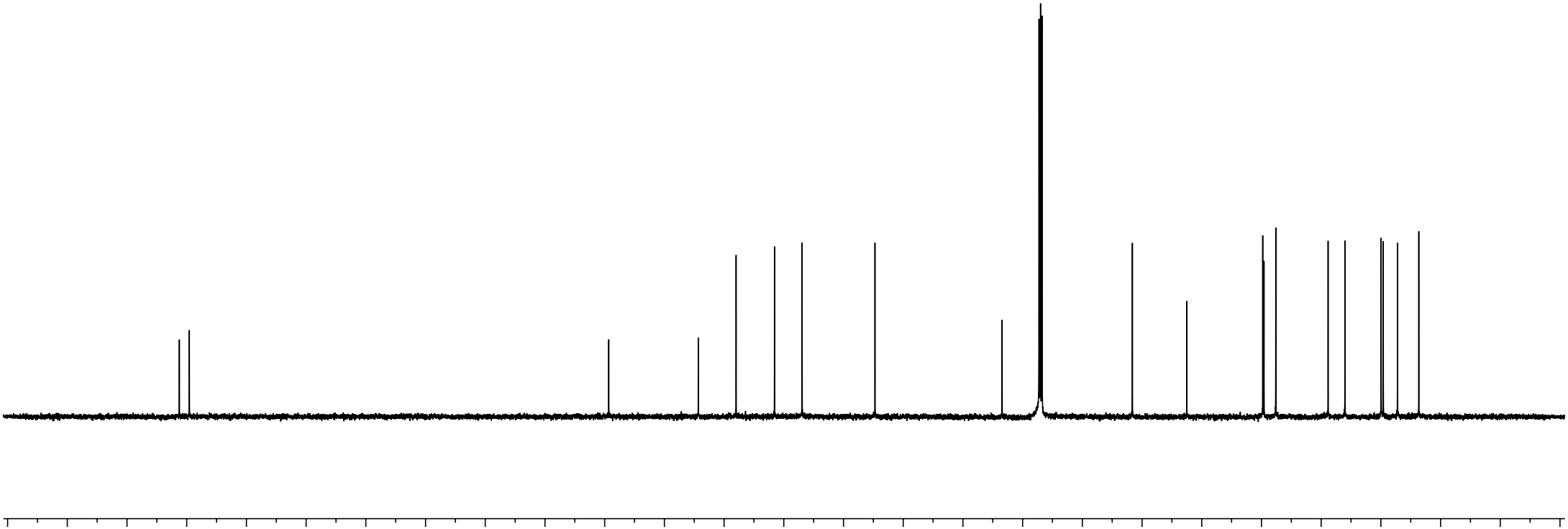
f1 (ppm)

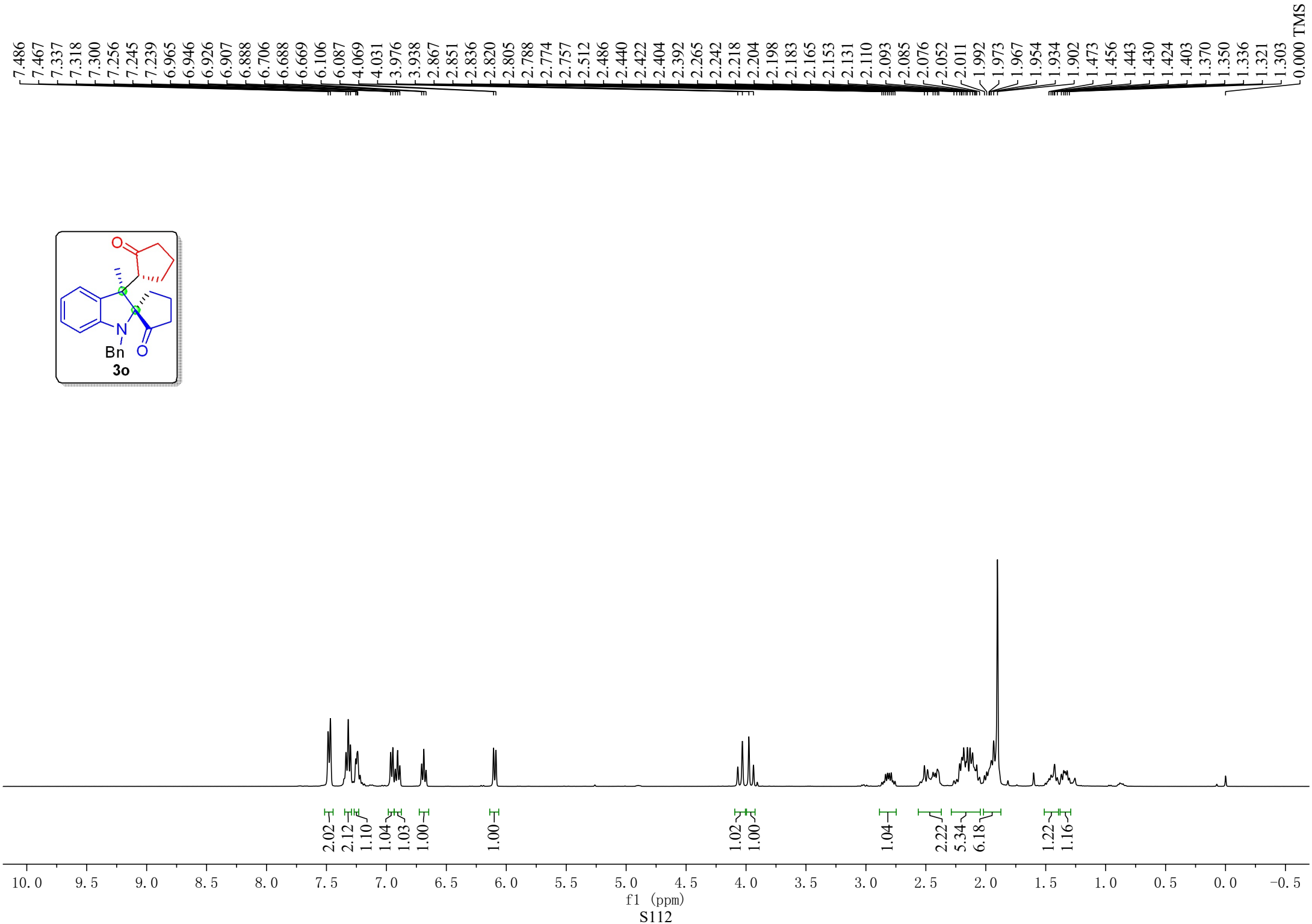

Chloroform-d
7.260
7.086
7.071
7.055
6.926
6.912
6.682
6.666
6.651
6.325
6.309
3.017
3.003
2.999
2.989
2.985
2.975
2.971
2.765
2.761
2.750
2.736
2.731
2.722
2.716
2.703
2.689
2.478
2.458
2.440
2.436
2.330
2.317
2.301
2.289
2.183
2.163
2.148
2.144
2.127
2.109
2.105
2.090
2.086
2.063
2.048
2.037
2.033
2.019
1.911
1.892
1.864
1.853
1.849
1.836
1.824
1.806
1.779
1.763
1.753
1.387
1.263
1.251
1.238
1.224
1.220
1.210
1.206
1.196
1.192
O
N
Et
O
3n
0.96
0.92
0.89
0.88
1.06
2.14
1.21
1.17
3.17
2.14
6.35
1.34
4.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3n

221.23
219.56
149.32
134.32
127.99
121.56
116.93
104.73
83.43
77.00 Chloroform-d
61.62
52.51
39.79
39.57
37.60
28.83
26.01
19.96
19.60
17.21
13.65

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7.337
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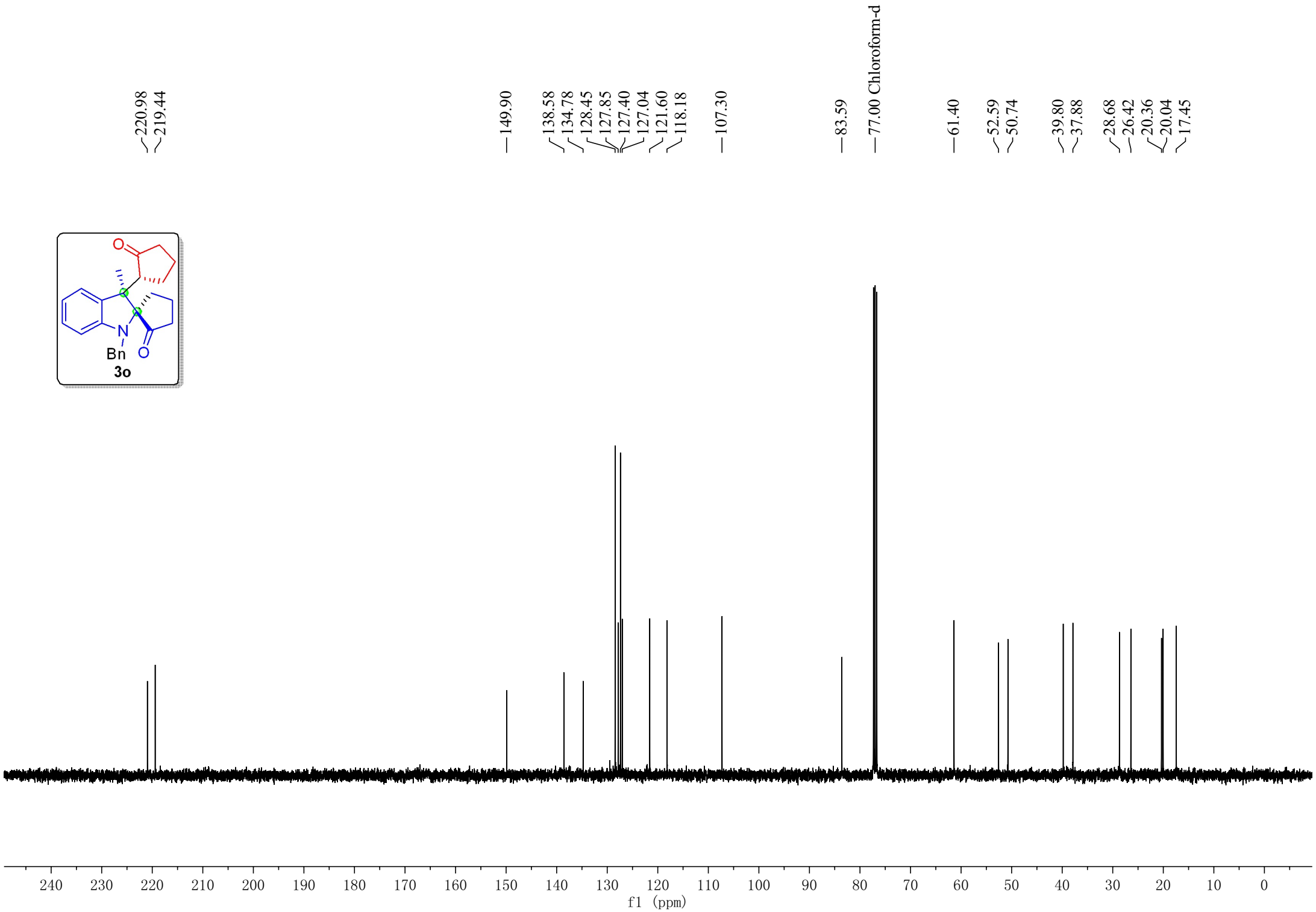
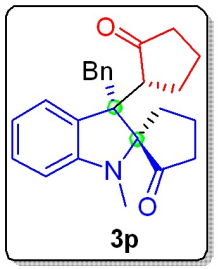
7.256
7.245
7.239
6.965
6.946
6.926
6.907
6.888
6.706
6.688
6.669
6.106
6.087
4.069
4.031
3.976
3.938
2.867
2.851
2.836
2.820
2.805
2.788
2.774
2.757
2.512
2.486
2.440
2.422
2.404
2.392
2.265
2.242
2.218
2.204
2.198
2.183
2.165
2.153
2.131
2.110
2.093
2.085
2.076
2.052
2.011
1.992
1.973
1.967
1.954
1.934
1.902
1.473
1.456
1.443
1.430
1.424
1.403
1.370
1.350
1.336
1.321
1.303
0.000 TMS
O
N
Bn
O
O
3o
2.02
2.12
1.10
1.04
1.03
1.00
1.00
1.02
1.00
1.04
2.22
5.34
6.18
1.22
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


220.98
219.44
149.90
138.58
134.78
128.45
127.85
127.40
127.04
121.60
118.18
107.30
83.59
77.00 Chloroform-d
61.40
52.59
50.74
39.80
37.88
28.68
26.42
20.36
20.04
17.45
O
N
Bn
O
3o
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

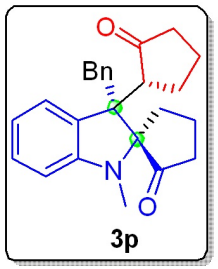


7.260 Chloroform-d
7.260
7.249
7.181
7.174
7.167
7.158
7.077
7.059
7.042
6.459
6.440
6.422
6.388
6.368
6.158
6.141
3.986
3.954
3.027
2.995
2.632
2.616
2.613
2.604
2.601
2.425
2.411
2.402
2.389
2.280
2.244
2.223
2.200
2.090
2.076
2.060
2.028
1.913
1.901
1.891
1.882
1.870

3.98 2.21 1.18 1.06 1.06 1.01 0.91 0.99 1.08 3.03 2.21 0.99 2.22 3.31 2.28 2.02

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

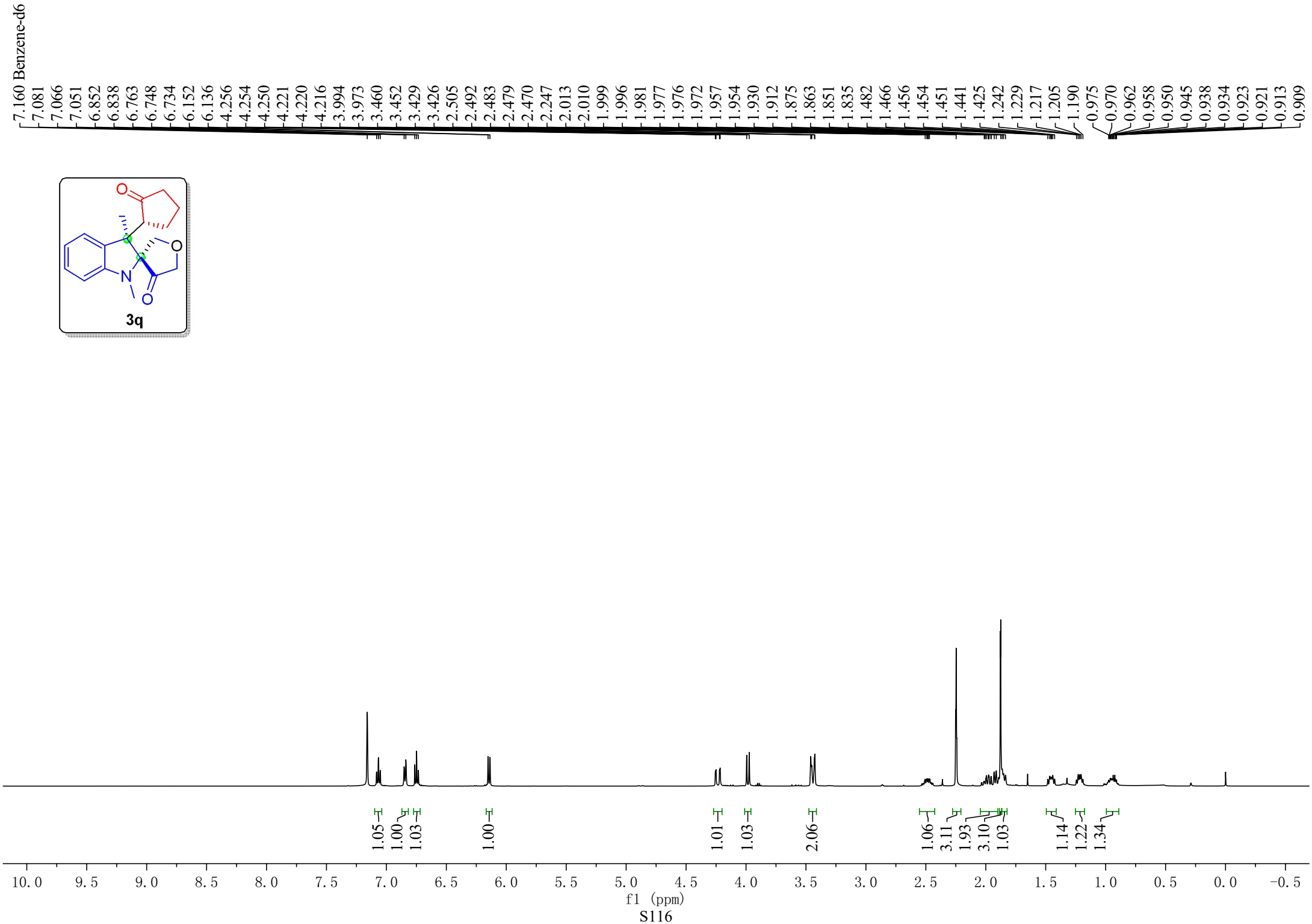
f1 (ppm)

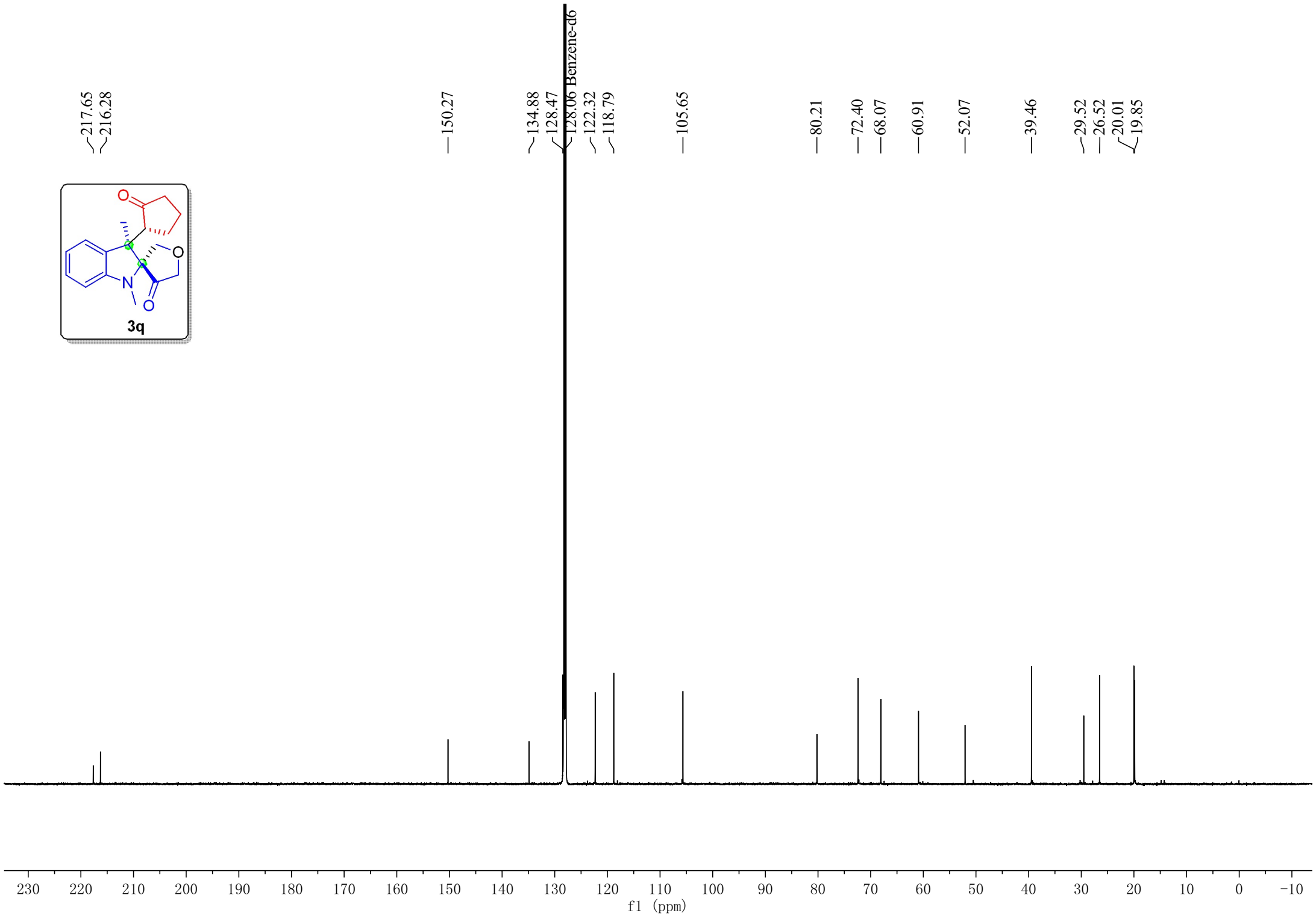


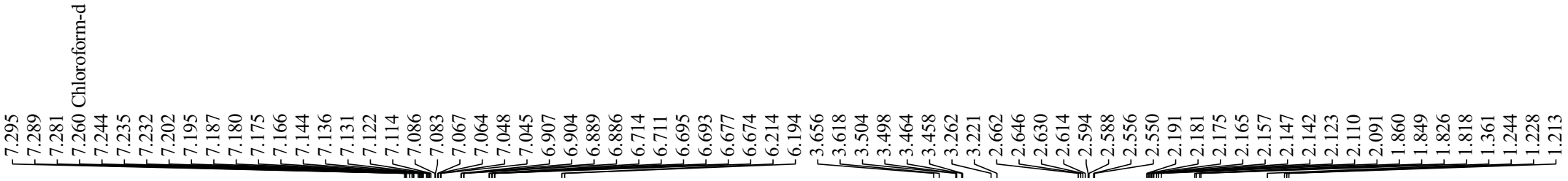
219.24
217.56
151.03
137.47
131.99
131.89
128.18
127.81
126.66
124.95
117.01
106.00
77.00 Chloroform-d
56.51
54.49
40.21
38.49
38.34
29.85
28.92
26.39
19.85
17.61

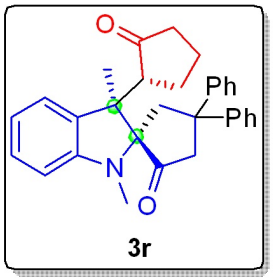
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

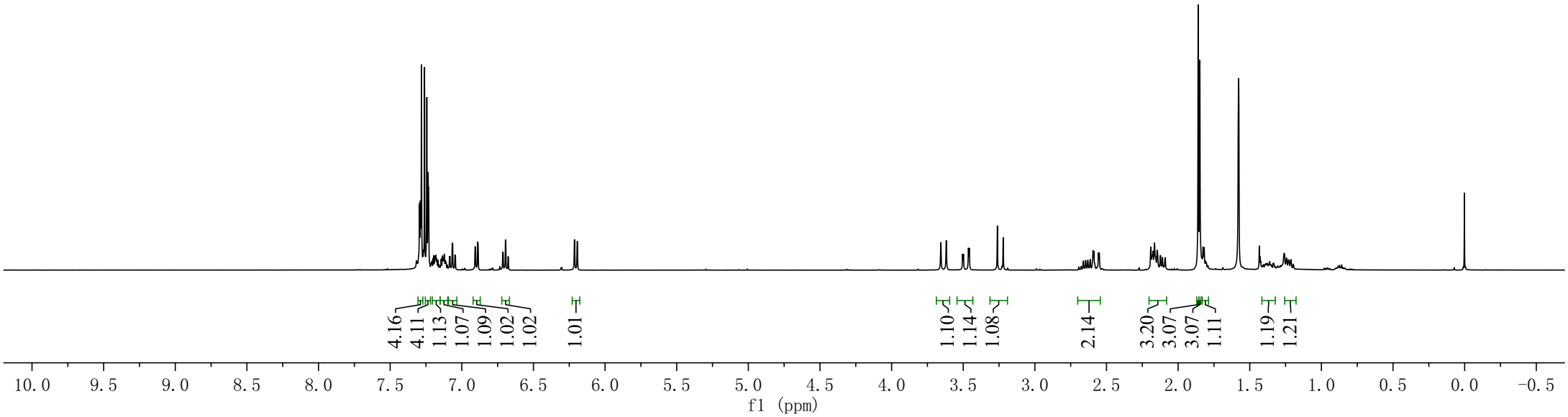

7.160 Benzene-d6
7.081
7.066
7.051
6.852
6.838
6.763
6.748
6.734
6.152
6.136
4.256
4.254
4.250
4.221
4.220
4.216
3.994
3.973
3.460
3.452
3.429
3.426
2.505
2.492
2.483
2.479
2.470
2.247
2.013
2.010
1.999
1.996
1.981
1.977
1.976
1.972
1.957
1.954
1.930
1.912
1.875
1.863
1.851
1.835
1.482
1.466
1.456
1.454
1.451
1.441
1.425
1.242
1.229
1.217
1.205
1.190
0.975
0.970
0.962
0.958
0.950
0.945
0.938
0.934
0.923
0.921
0.913
0.909
O
O
N
O
3q
1.05
1.00
1.03
1.00
1.01
1.03
2.06
1.06
3.11
1.93
3.10
1.03
1.14
1.22
1.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

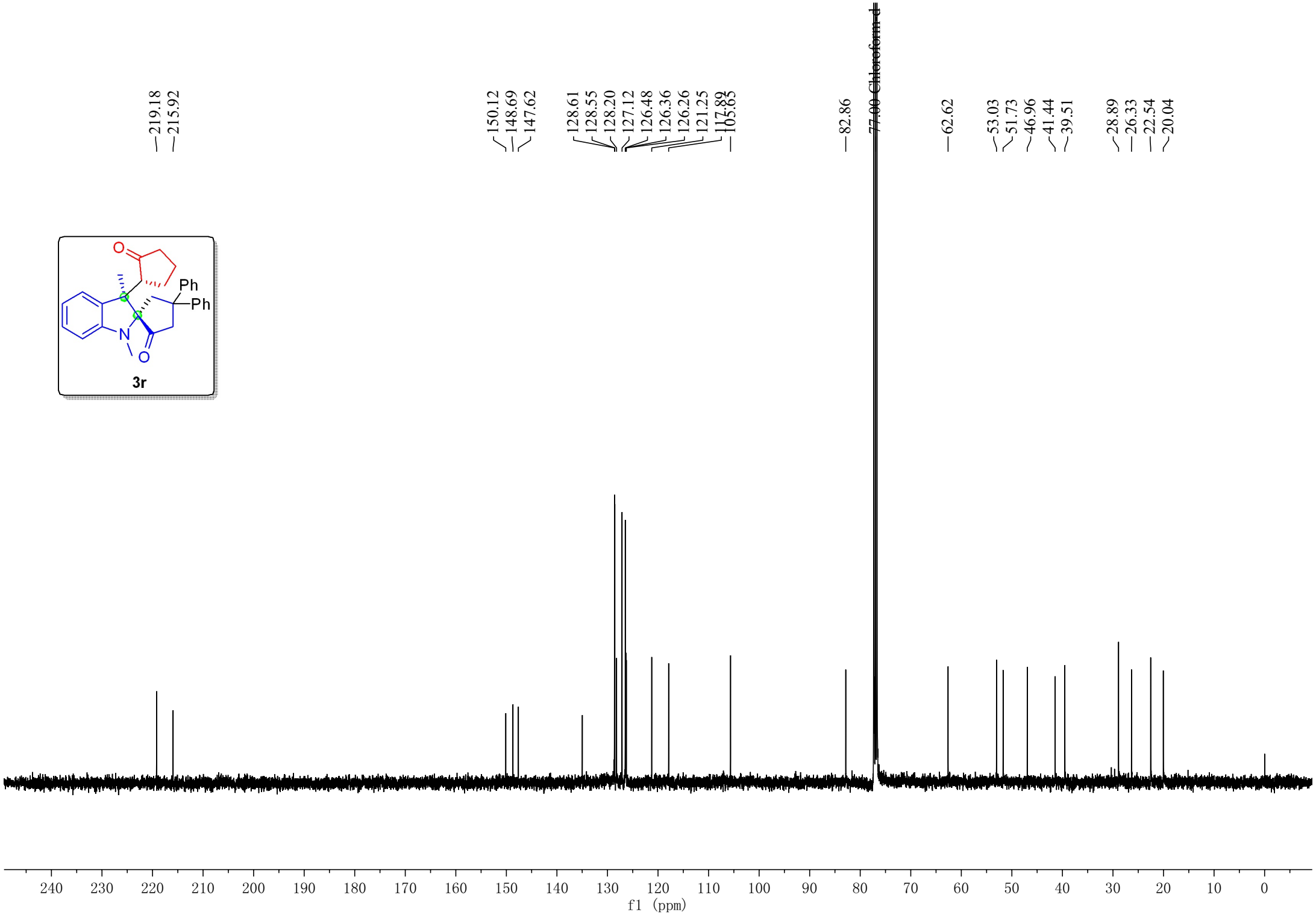

217.65
216.28
150.27
134.88
128.47
128.06 Benzene-d6
122.32
118.79
105.65
80.21
72.40
68.07
60.91
52.07
39.46
29.52
26.52
20.01
19.85
3q
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

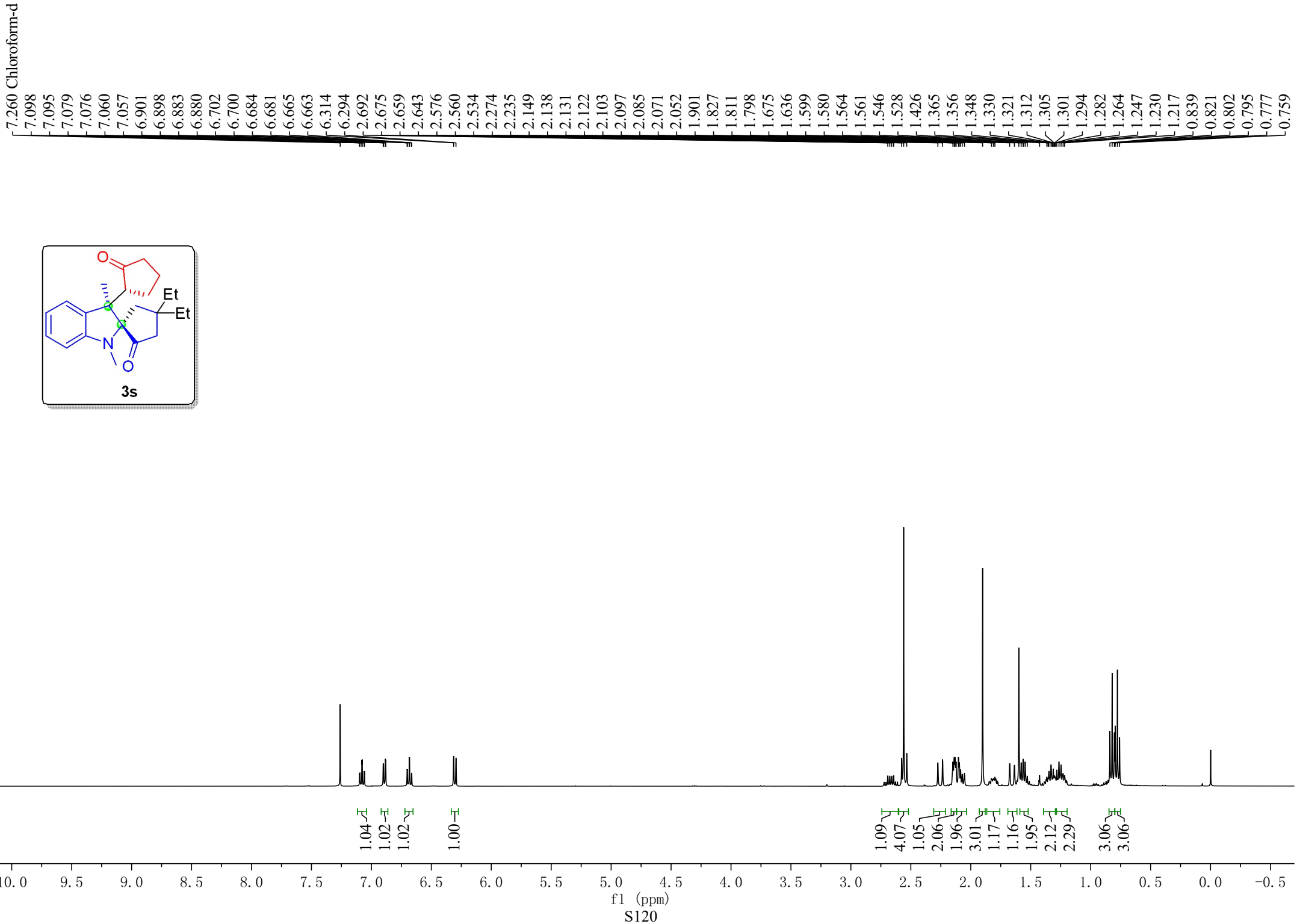

Chloroform-d
7.295
7.289
7.281
7.260
7.244
7.235
7.232
7.202
7.195
7.187
7.180
7.175
7.166
7.144
7.136
7.131
7.122
7.114
7.086
7.083
7.067
7.064
7.048
7.045
6.907
6.904
6.889
6.886
6.714
6.711
6.695
6.693
6.677
6.674
6.214
6.194
3.656
3.618
3.504
3.498
3.464
3.458
3.262
3.221
2.662
2.646
2.630
2.614
2.594
2.588
2.556
2.550
2.191
2.181
2.175
2.165
2.157
2.147
2.142
2.123
2.110
2.091
1.860
1.849
1.826
1.818
1.361
1.244
1.228
1.213

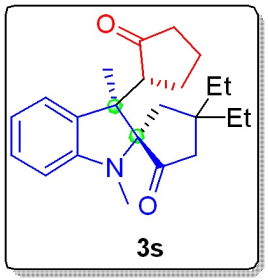

O
Ph
Ph
N
O

3r


4.16
4.11
1.13
1.07
1.09
1.02
1.02
1.01
1.10
1.14
1.08
2.14
3.20
3.07
3.07
1.11
1.19
1.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


219.18
215.92
150.12
148.69
147.62
128.61
128.55
128.20
127.12
126.48
126.36
126.26
121.25
117.89
105.85
82.86
77.00 Chloroform-d
62.62
53.03
51.73
46.96
41.44
39.51
28.89
26.33
22.54
20.04
O
Ph
Ph
N
O
3r
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Chloroform-d
7.260
7.098
7.095
7.079
7.076
7.060
7.057
6.901
6.898
6.883
6.880
6.702
6.700
6.684
6.681
6.665
6.663
6.314
6.294
2.692
2.675
2.659
2.643
2.576
2.560
2.534
2.274
2.235
2.149
2.138
2.131
2.122
2.103
2.097
2.085
2.071
2.052
1.901
1.827
1.811
1.798
1.675
1.636
1.599
1.580
1.564
1.561
1.546
1.528
1.426
1.365
1.356
1.348
1.330
1.321
1.312
1.305
1.301
1.294
1.282
1.264
1.247
1.230
1.217
0.839
0.821
0.802
0.795
0.777
0.759
O
Et
Et
N
O
3s
1.04
1.02
1.02
1.00
1.09
4.07
1.05
2.06
1.96
3.01
1.17
1.16
1.95
2.12
2.29
3.06
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

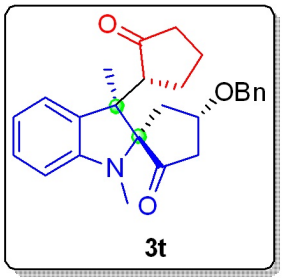


3s

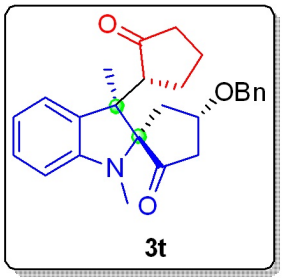
218.97
217.73
150.25
134.97
128.10
121.32
117.75
105.38
84.11
77.00 Chloroform-d
62.21
52.42
51.42
39.68
36.79
35.74
30.96
30.83
29.11
26.38
21.79
20.11
8.51
7.78

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


O
OBn
N
O
3t

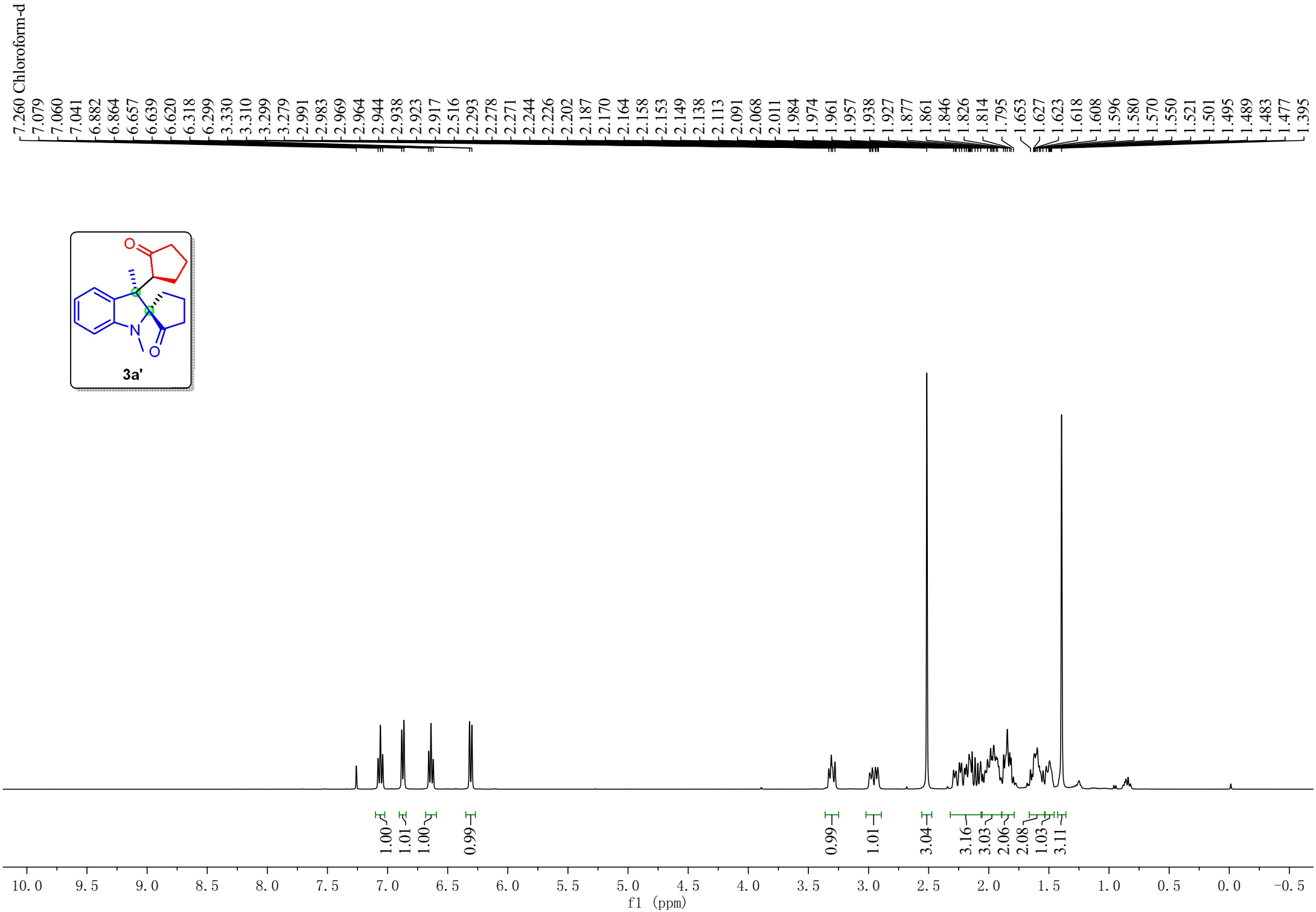
218.63
216.13
149.24
137.78
136.04
128.47
127.89
127.78
127.63
122.58
118.54
105.79
83.20
77.00 Chloroform-d
72.33
70.99
59.91
51.25
46.97
39.32
35.60
30.04
26.91
21.70
20.18

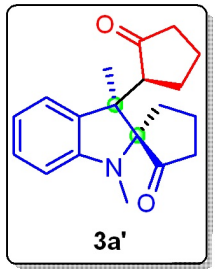


3t

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)


Chloroform-d
7.260
7.079
7.060
7.041
6.882
6.864
6.657
6.639
6.620
6.318
6.299
3.330
3.310
3.299
3.279
2.991
2.983
2.969
2.964
2.944
2.938
2.923
2.917
2.516
2.293
2.278
2.271
2.244
2.226
2.202
2.187
2.170
2.164
2.158
2.153
2.149
2.138
2.113
2.091
2.068
2.011
1.984
1.974
1.961
1.957
1.938
1.927
1.877
1.861
1.846
1.826
1.814
1.795
1.653
1.627
1.623
1.618
1.608
1.596
1.580
1.570
1.550
1.521
1.501
1.495
1.489
1.483
1.477
1.395
O
N
O
3a'
1.00
1.01
1.00
0.99
0.99
1.01
3.04
3.16
3.03
2.06
2.08
1.03
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)



219.77
218.28
150.14
133.09
127.94
123.15
117.15
105.58
84.06
77.00 Chloroform-d
50.97
49.89
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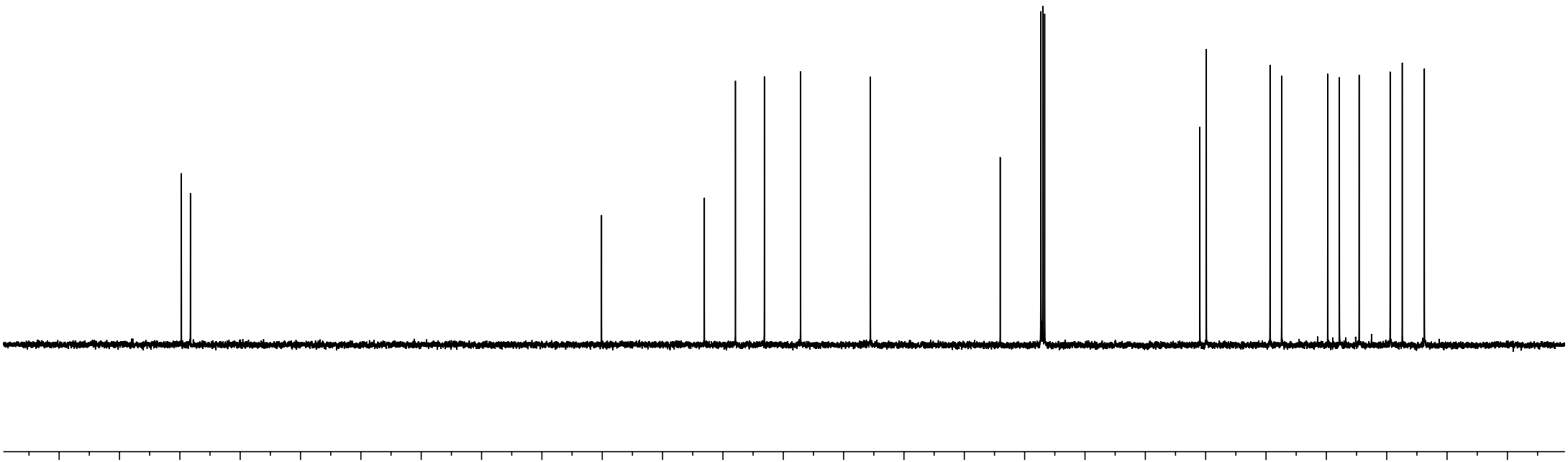
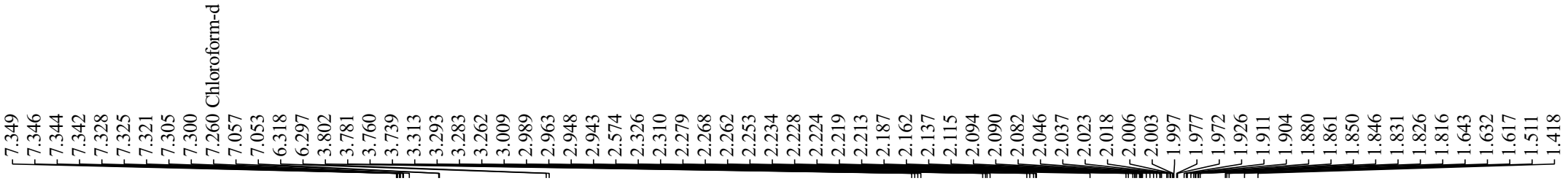
29.78
27.85
24.57
19.43
17.43
13.76




7.349
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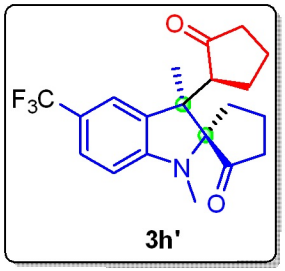
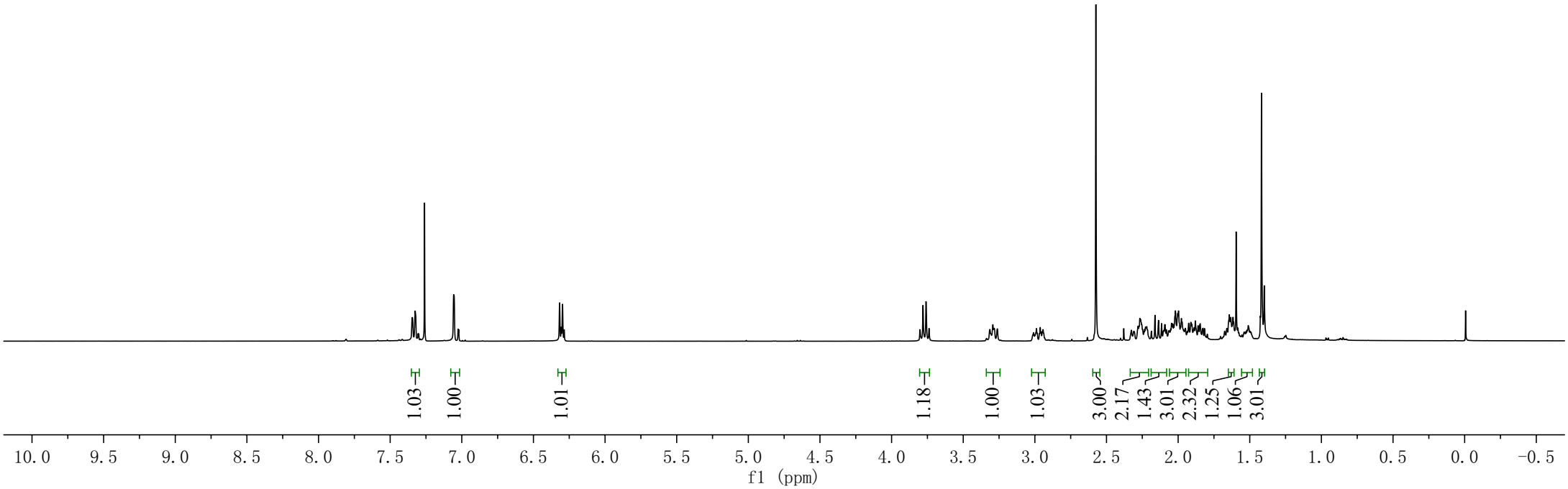
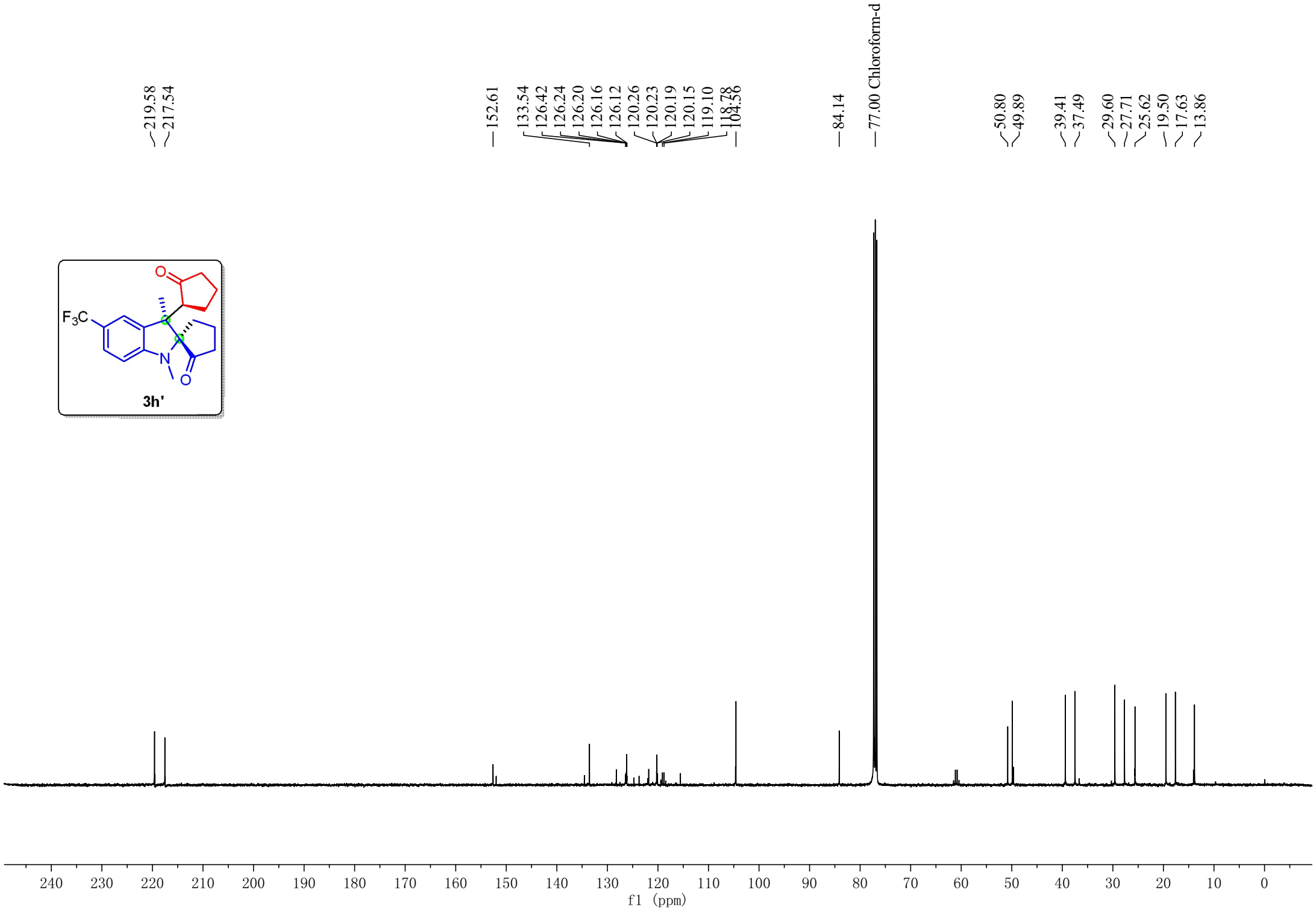
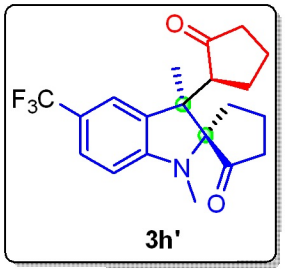
7.344
7.342
7.328
7.325
7.321
7.305
7.300
7.260 Chloroform-d
7.057
7.053
6.318
6.297
3.802
3.781
3.760
3.739
3.313
3.293
3.283
3.262
3.009
2.989
2.963
2.948
2.943
2.574
2.326
2.310
2.279
2.268
2.262
2.253
2.234
2.228
2.224
2.219
2.213
2.187
2.162
2.137
2.115
2.094
2.090
2.082
2.046
2.037
2.023
2.018
2.006
2.003
1.997
1.977
1.972
1.926
1.911
1.904
1.880
1.861
1.850
1.846
1.831
1.826
1.816
1.643
1.632
1.617
1.511
1.418


F3C
O
N
O

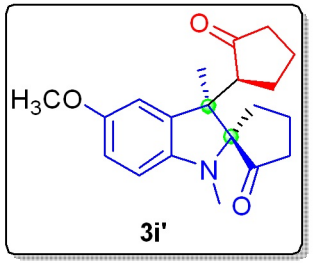
3h'


1.03
1.00
1.01
1.18
1.00
1.03
3.00
2.17
1.43
3.01
2.32
1.25
1.06
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

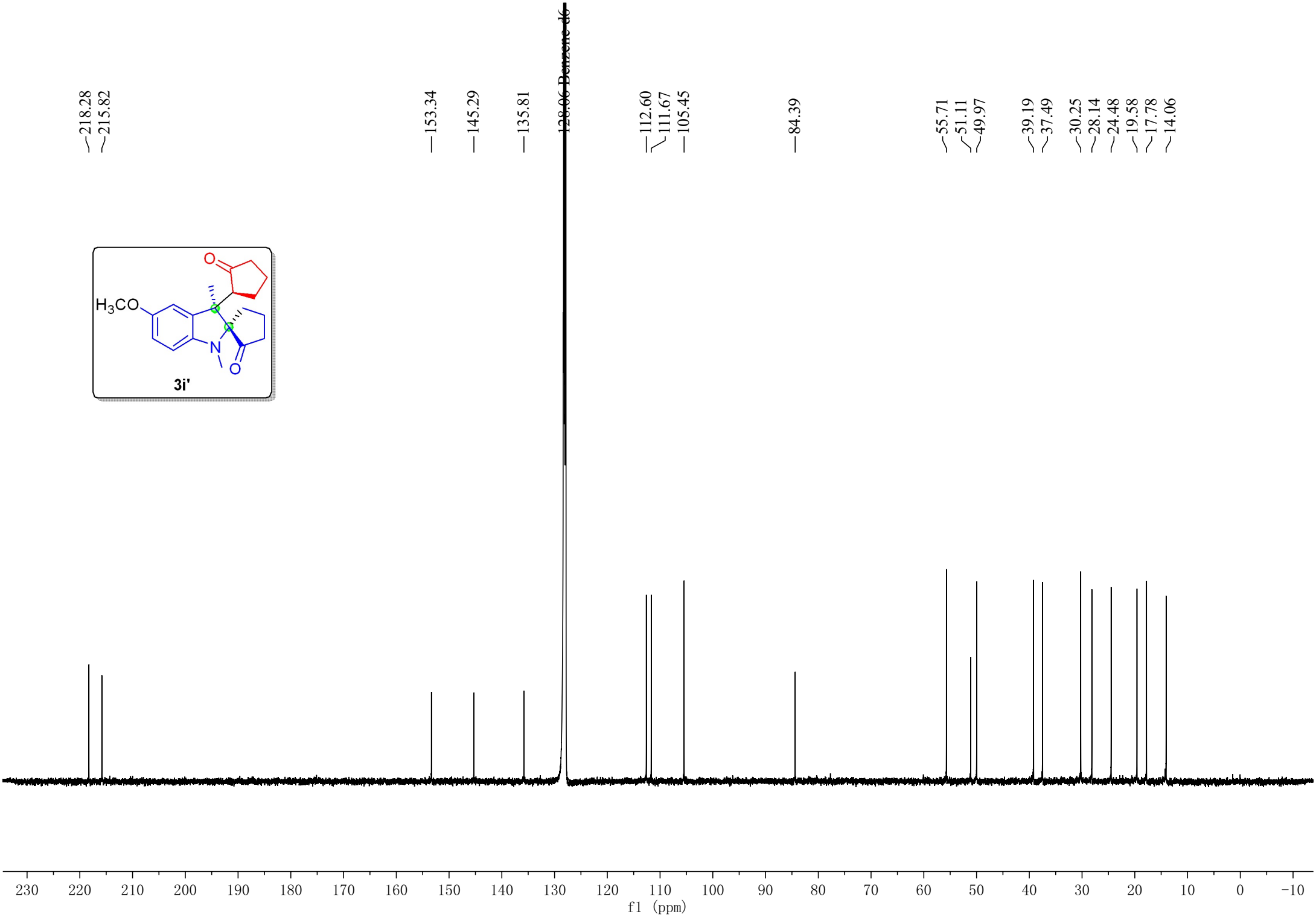

219.58
217.54
152.61
133.54
126.42
126.24
126.20
126.16
126.12
120.26
120.23
120.19
120.15
119.10
118.78
104.56
84.14
77.00 Chloroform-d
50.80
49.89
39.41
37.49
29.60
27.71
25.62
19.50
17.63
13.86
F3C
O
N
O
3h'
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

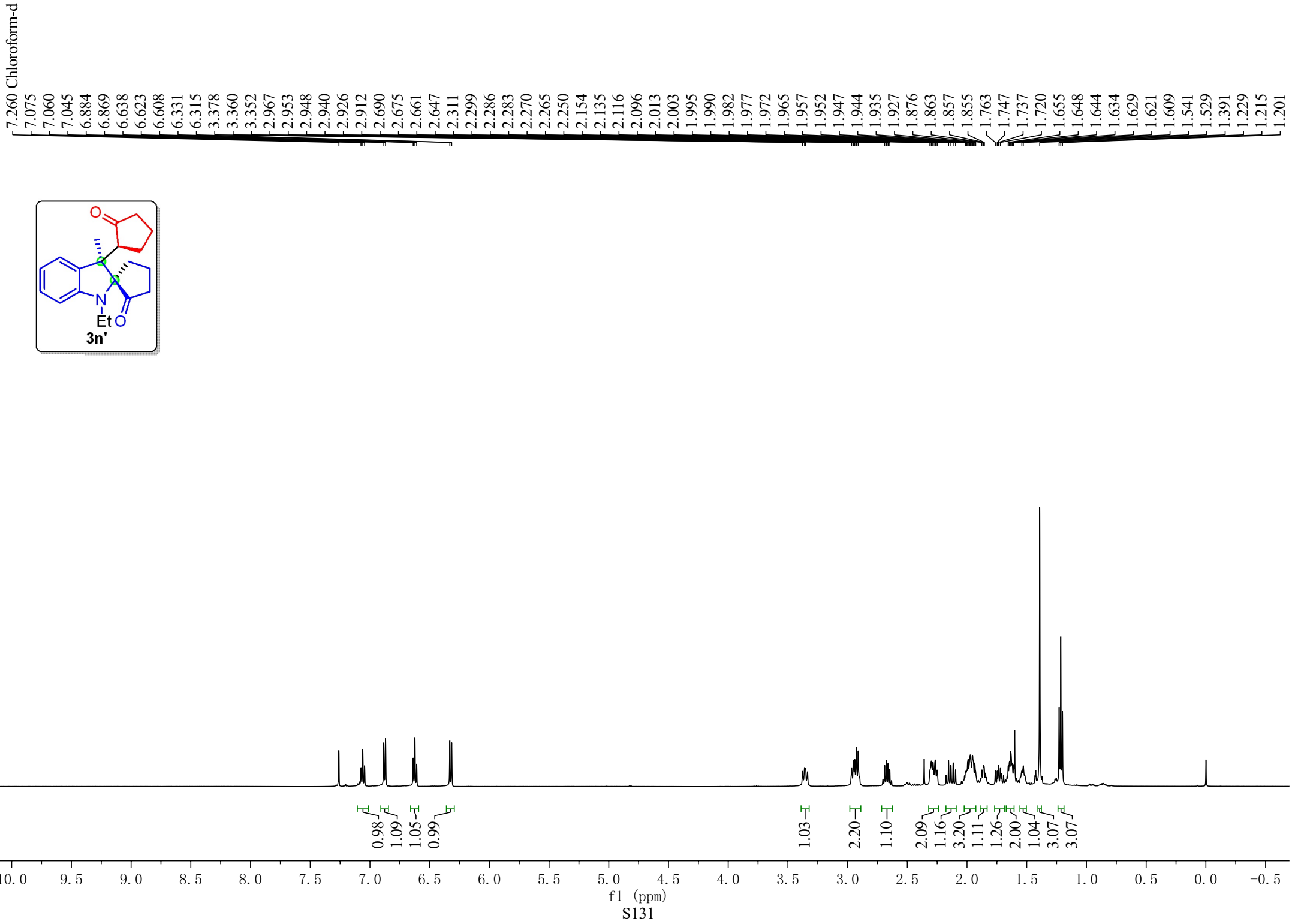

O
F3C
N
O
3h'

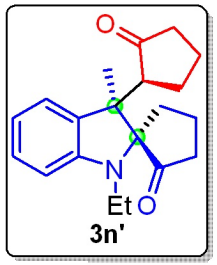
-62.645
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
H3CO
N
O
3i'

7.160 Benzene-d6
6.642
6.628
6.624
6.138
6.120
3.578
3.561
3.552
3.535
3.476
3.058
3.040
3.035
3.020
3.001
2.303
1.861
1.824
1.817
1.803
1.796
1.486
1.480
1.470
1.462
1.449
1.443
1.219
1.200
1.189
1.182
1.177
1.173
2.00
1.00
1.12
3.02
1.07
3.07
1.38
2.09
3.12
2.09
3.08
2.13
1.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


218.28
215.82
153.34
145.29
135.81
128.06 Benzene-d6
112.60
111.67
105.45
84.39
55.71
51.11
49.97
39.19
37.49
30.25
28.14
24.48
19.58
17.78
14.06
H3CO
O
N
O
3i'
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

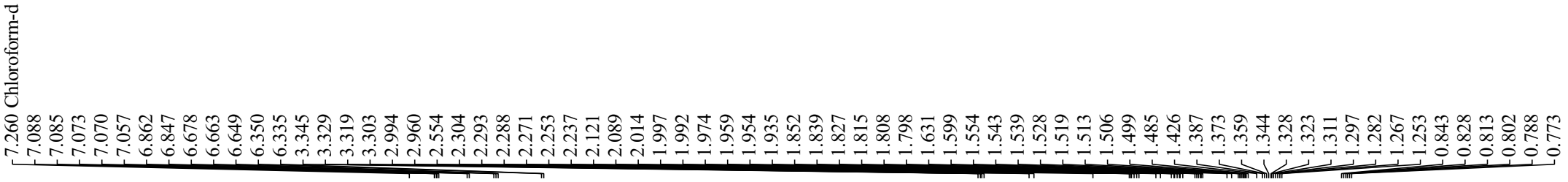

Chloroform-d
7.260
7.075
7.060
7.045
6.884
6.869
6.638
6.623
6.608
6.331
6.315
3.378
3.360
3.352
2.967
2.953
2.948
2.940
2.926
2.912
2.690
2.675
2.661
2.647
2.311
2.299
2.286
2.283
2.270
2.265
2.250
2.154
2.135
2.116
2.096
2.013
2.003
1.995
1.990
1.982
1.977
1.972
1.965
1.957
1.952
1.947
1.944
1.935
1.927
1.876
1.863
1.857
1.855
1.763
1.747
1.737
1.720
1.655
1.648
1.644
1.634
1.629
1.621
1.609
1.541
1.529
1.391
1.229
1.215
1.201
O
N
Et
O
3n'
0.98
1.09
1.05
0.99
1.03
2.20
1.10
2.09
1.16
3.20
1.11
1.26
2.00
1.04
3.07
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

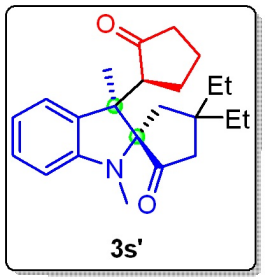


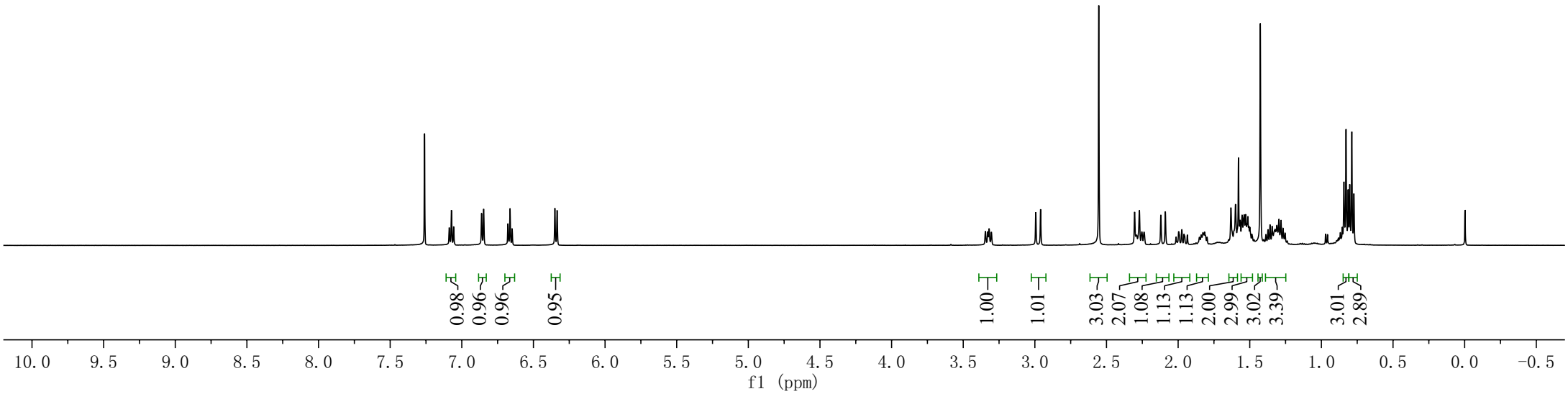
220.06
218.45
149.42
133.14
127.91
123.37
116.46
104.89
84.74
77.00 Chloroform-d
51.21
49.90
39.95
39.48
37.46
28.00
27.09
19.47
17.54
14.02
13.75

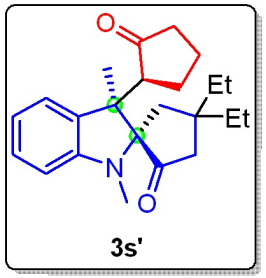
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)


Chloroform-d
7.260
7.088
7.085
7.073
7.070
7.057
6.862
6.847
6.678
6.663
6.649
6.350
6.335
3.345
3.329
3.319
3.303
2.994
2.960
2.554
2.304
2.293
2.288
2.271
2.253
2.237
2.121
2.089
2.014
1.997
1.992
1.974
1.959
1.954
1.935
1.852
1.839
1.827
1.815
1.808
1.798
1.631
1.599
1.554
1.543
1.539
1.528
1.519
1.513
1.506
1.499
1.485
1.426
1.387
1.373
1.359
1.344
1.328
1.323
1.311
1.297
1.282
1.267
1.253
0.843
0.828
0.813
0.802
0.788
0.773


O
Et
Et
N
O
3s'


0.98
0.96
0.96
0.95
1.00
1.01
3.03
2.07
1.08
1.13
1.13
2.00
2.99
3.02
3.39
3.01
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3s'

219.51
215.33
150.28
133.98
127.96
123.01
117.61
106.37
86.08
77.00 Chloroform-d
51.59
51.11
50.32
39.46
36.22
33.47
30.55
29.90
28.91
19.67
15.03
8.56
7.88

50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)