Supporting Information

Copper/B_2pin_2-Catalyzed C-H Difluoroacetylation-Cycloamidation of Anilines Leading to the Formation of 3,3-Difluoro-2-oxindoles

Miaolin Ke [a, b], Qiuling Song [a, *]

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering at Huaqiao University
[b] College of Materials Science at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China

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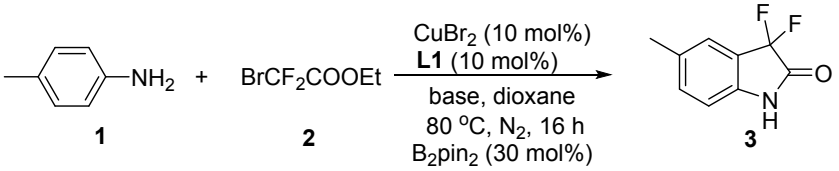
General information: All reactions were accomplished in Schlenk tubes under an atmosphere of N_2. Column chromatography was performed over silica gel (200-300 mesh). ^1H NMR spectra were recorded on a 500 M spectrometer and chemical shifts (in ppm) were referred to $CDCl_3$ (δ = 7.26 ppm),d_6-DMSO (δ = 2.5 ppm) (as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.0 ppm), d_6-DMSO (δ = 40.0 ppm). ^{19}F NMR spectrometers were operated on the same NMR spectrometer with $CDCl_3$ or d_6-DMSO The following abbreviations were used to illuminate the diversities: δ = chemical shifts, J = coupling constant, s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet. HRMS (EI) were measured with a quadrupole and TOF mass spectrometers. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer. All reagents and solvents were obtained from commercial suppliers, and used without further purification. Reactions were monitored by thin-layer chromatography (TLC). The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

General procedure for the synthesis of 3,3-difluoro-2-oxindole derivatives

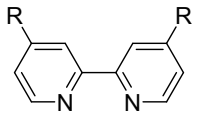
Anilines (0.3 mmol), B_2pin_2 (30 mol%), $Cu(OAc)_2.H_2O$ (10 mol%), **L1** (10 mol%), NaOAc (0.6 mmol) were added to a 25 mL Schlenk tube under air atmosphere. Then the mixture was evacuated and backfilled with N_2 (3 times). Ethyl bromodifluoroacetate (0.36 mmol, 58 μL) and DCE (2 mL) were added subsequently. The Schlenk tube was screw-capped. And the mixture was stirred in 100 ^oC for 16 h. The crude production was diluted with ethyl ethylate and directly concentrated in vacuo, and purified by flash column chromatograph to give the pure products.

Optimization of the reaction conditions (Table S1-S5)

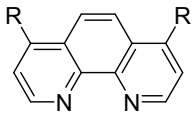
Table S1 Base effect on the reaction



1 **2** **3**



R=t-Bu, **L1**
R=Me, **L2**
R=OMe, **L3**
R=H, **L4**

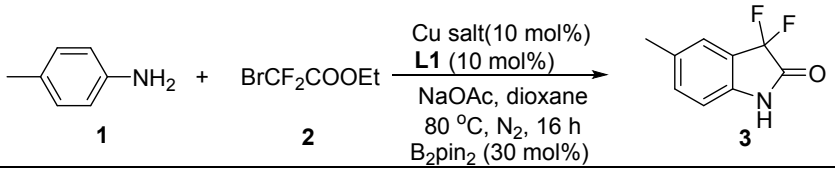


R=H, **L5**
R=Me, **L6**

entry	catalyst	ligand	base	solvent	yield (%)
1	$CuBr_2$	**L1**	$NaHCO_3$	dioxane	40
2	$CuBr_2$	**L1**	Na_2CO_3	dioxane	38
3	$CuBr_2$	**L1**	NaOAc	dioxane	54
4	$CuBr_2$	**L1**	K_2CO_3	dioxane	34
5	$CuBr_2$	**L1**	K_3PO_4	dioxane	trace
6	$CuBr_2$	**L1**	Cs_2CO_3	dioxane	trace
7	$CuBr_2$	**L1**	NaOH	dioxane	trace

Reaction condition:,**1** (0.2 mmol), **2** (0.24 mmol), B_2pin_2 (30 mol%), $CuBr_2$ (10 mol%), **L1** (10 mol%), base (2 equiv), dioxane , 80 ^oC, 16 h, N_2. All yields were isolated.

Table S2 Catalyst effect on the reaction

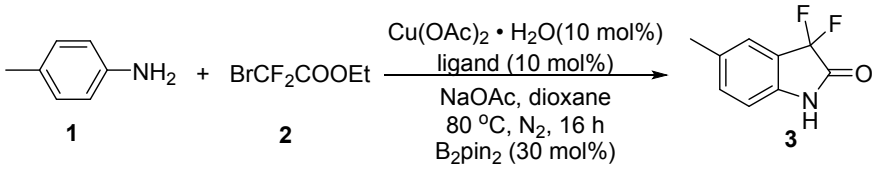


1 **2** **3**

entry	catalyst	ligand	base	solvent	yield (%)
1	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	dioxane	55
2	$Cu(aca)_2$	**L1**	NaOAc	dioxane	35
3	CuBr	**L1**	NaOAc	dioxane	41
4	CuSCN	**L1**	NaOAc	dioxane	36
5	$Cu(OTf)_2$	**L1**	NaOAc	dioxane	31
6	$Cu(TFA)_2$	**L1**	NaOAc	dioxane	38

Reaction condition:,**1** (0.2 mmol), **2** (0.24 mmol), B_2pin_2 (30 mol%), Cu salt (10 mol%), **L1** (10 mol%), NaOAc (2 equiv), dioxane , 80 ^oC, 16 h, N_2. All yields were isolated.

Table S3 Ligand effect on the reaction

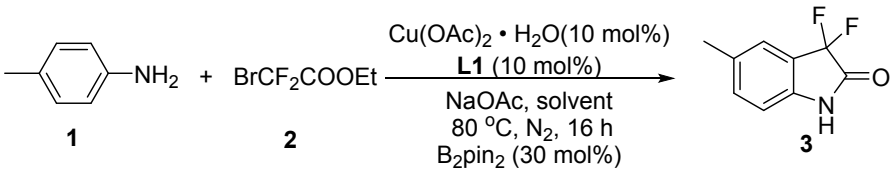


1 **2** **3**

entry	catalyst	ligand	base	solvent	yield (%)
1	$Cu(OAc)_2 \cdot H_2O$	**L2**	NaOAc	dioxane	54
2	$Cu(OAc)_2 \cdot H_2O$	**L3**	NaOAc	dioxane	46
3	$Cu(OAc)_2 \cdot H_2O$	**L4**	NaOAc	dioxane	28
4	$Cu(OAc)_2 \cdot H_2O$	**L5**	NaOAc	dioxane	36
5	$Cu(OAc)_2 \cdot H_2O$	**L6**	NaOAc	dioxane	39

Reaction condition:,**1** (0.2 mmol), **2** (0.24 mmol), B_2pin_2 (30 mol%), $Cu(OAc)_2 \cdot H_2O$ (10 mol%), ligand (10 mol%), NaOAc (2 equiv), dioxane , 80 ^oC, 16 h, N_2. All yields were isolated.

Table S4 Solvent effect on the reaction

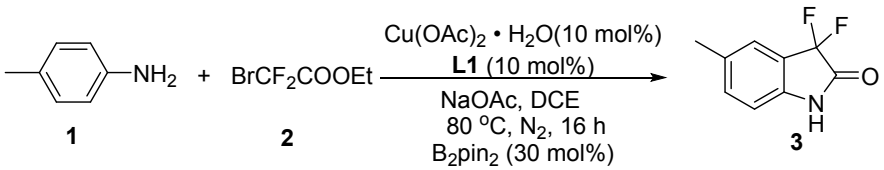


1 **2** **3**

entry	catalyst	ligand	base	solvent	yield (%)
1	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	THF	tracce
2	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	toluene	40
3	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	CH_3CN	50
4	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DMSO	trace
5	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	MeOH	trace
6	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	61
7	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DMF	trace
8	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	$CHCl_3$	trace
9	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	HFIP	NR
10	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	acetone	trace

Reaction condition:,**1** (0.2 mmol), **2** (0.24 mmol), B_2pin_2 (30 mol%), $Cu(OAc)_2 \cdot H_2O$ (10 mol%), **L1**(10 mol%), NaOAc (2 equiv), solvent (1 mL) , 80 ^oC, 16 h, N_2. All yields were isolated.

Table S5 Other factor effect on the reaction

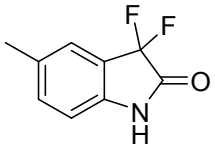


1 **2** **3**

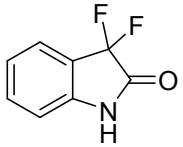
entry	catalyst	ligand	base	solvent	yield (%)
1[a]	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	67
2[b]	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	71
3	-	**L1**	NaOAc	DCE	0
4	$Cu(OAc)_2 \cdot H_2O$	**-**	NaOAc	DCE	0
5	$Cu(OAc)_2 \cdot H_2O$	**L1**	-	DCE	0
6[c]	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	0
7[d]	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	trace
8[e]	$Cu(OAc)_2 \cdot H_2O$	**L1**	NaOAc	DCE	trace

Reaction condition:,**1** (0.2 mmol), **2** (0.24 mmol), B_2pin_2 (30 mol%), $Cu(OAc)_2 \cdot H_2O$ (10 mol%), **L1**(10 mol%), NaOAc (2 equiv), DCE(1 mL) , 80 °C, 16 h, N_2. [a] at 90 °C. [b] at 100 °C. [c] abscence of B_2pin_2. [d] under oxygen atmosphere, [e] under air atmosphere. All yields were isolated.

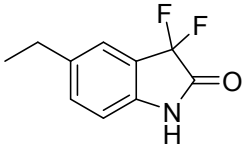
Characterization Data



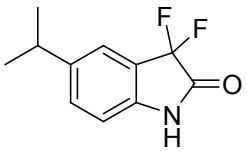
3,3-Difluoro-5-methyl-2-oxindole (**3**).[1] The procedure was operated in general method. The reaction gave 26 mg of 3,3-difluoro-5-methyl-2-oxindole in 71 % isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.38 (s, 1H), 7.27 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7 (t, J = 30.4 Hz), 138.6 (t, J = 7.4 Hz), 134.0, 133.9, 125.4, 120.2 (t, J = 22.8 Hz), 111.7, 111.3 (t, J = 250.2 Hz), 20.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ -111.7.



3,3-Difluoro-2-oxindole (**4**).[2] The procedure was operated in general method. The reaction gave 40 mg of 3,3-difluoro-2-oxindole in 78 % isolated yield as a brown solid (PE/EA=5:1).^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.54 (d, J = 7.3 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5 (t, J = 30.3 Hz), 141.1 (t, J = 7.4 Hz), 133.7, 125.0, 124.0, 120.2 (t, J = 23.1 Hz), 111.9, 111.0 (t, J = 250.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.0.

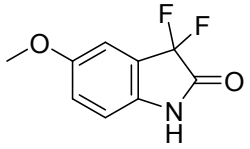


3,3-Difluoro-5-ethyl-2-oxindole (**5**). The procedure was operated in general method. The reaction gave 38 mg of 3,3-difluoro-5-ethyl-2-oxindole in 64 % isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO): δ 11.09 (s, 1H), 7.49 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 2.59 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, DMSO): δ 166.3 (t, J = 29.5 Hz), 140.7 (t, J = 7.9 Hz), 139.7, 133.8, 124.60, 119.73 (t, J = 22.6 Hz), 112.1, 111.9 (t, J = 248.5 Hz), 28.0, 16.2. ^{9}F NMR (470 MHz, DMSO): δ -110.6. HRMS calcd. for $C_{10}H_9F_2NO$: 197.0652; Found: 197.0657.

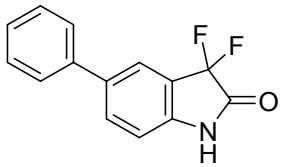


3,3-Difluoro-5-isopropyl-2-oxindole (**6**). The procedure was operated in general

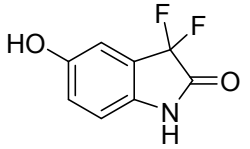
method. The reaction gave 38 mg of 3,3-difluoro-5-isopropyl-2-oxindole in 64 % isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.09 (s, 1H), 7.52 (d, J = 1.3 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 2.88 (dq, J = 13.8, 6.9 Hz, 1H), 1.18 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, DMSO): δ 166.4 (t, J = 29.5 Hz), 144.4, 140.8 (t, J = 7.9 Hz), 132.5, 123.2, 119.7 (t, J = 22.6 Hz), 112.2, 112.0 (t, J = 248.6 Hz), 33.5, 24.3. ^{19}F NMR (470 MHz, DMSO): δ -110.6. HRMS calcd. for $C_{11}H_{11}F_2NO$: 211.0809; Found: 211.0817.



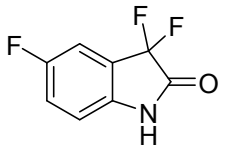
3,3-Difluoro-5-methoxy-2-oxindole (**7**). The procedure was operated in general method. The reaction gave 43 mg of 3,3-difluoro-5-methoxy-2-oxindole in 72 % isolated yield as a brown solid (PE/EA=3:1). ^{1}H NMR (500 MHz, DMSO) δ 11.00 (s, 1H), 7.29 (d, J = 2.1 Hz, 1H), 7.07 (dd, J = 8.6, 2.5 Hz, 1H), 6.91 (d, J = 8.6 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 166.3 (t, J = 29.3 Hz), 156.3, 135.9 (t, J = 7.9 Hz), 120.5 (t, J = 22.4 Hz), 120.1, 113.2, 112.0 (t, J = 249.3 Hz), 111.3, 56.3. ^{19}F NMR (470 MHz, DMSO): δ -110.7. HRMS calcd. for $C_9H_7F_2NO_2$: 199.0445; Found: 199.0444.



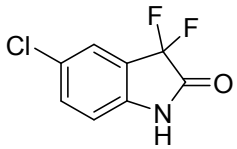
3,3-Difluoro-5-phenyl-2-oxindole (**8**). The procedure was operated in general method. The reaction gave 47 mg of 3,3-difluoro-5-phenyl-2-oxindole in 64 % isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.17 (s, 1H), 7.79 (d, J = 1.3 Hz, 1H), 7.67 (dd, J = 8.2, 1.1 Hz, 1H), 7.35 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, DMSO): δ 166.4 (t, J = 29.7 Hz), 149.0, 140.6 (t, J = 7.8 Hz), 137.0 (s), 131.3, 127.4, 126.5, 122.2, 120.3 (t, J = 22.6 Hz), 114.7, 112.6, 112.0 (t, J = 249.0 Hz). ^{19}F NMR (470 MHz, DMSO): δ -110.5. HRMS calcd. for $C_{14}H_9F_2NO$: 245.0652; Found: 245.0658.



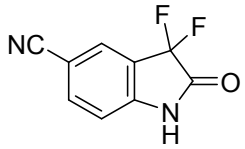
3,3-Difluoro-5-hydroxy-2-oxindole (**9**). The procedure was operated in general method. The reaction gave 39 mg of 3,3-difluoro-5-hydroxy-2-oxindole 70% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 10.89 (s, 1H), 9.63 (s, 1H), 6.99 (d, J = 1.6 Hz, 1H), 6.90 (dd, J = 8.4, 2.3 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 166.2 (t, J = 29.3 Hz), 154.2, 134.3 (t, J = 7.8 Hz), 120.7, 120.4 (t, J = 22.4 Hz), 113.2, 112.3, 112.0 (t, J = 248.9 Hz). ^{19}F NMR (470 MHz, DMSO): δ -110.6. HRMS calcd. for $C_8H_5F_2NO_2$: 185.0288; Found: 185.0289.



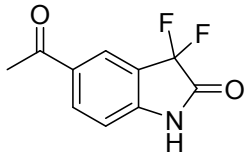
3,3,5-Trifluoro-2-oxindole (**10**). The procedure was operated in general method. The reaction gave 47 mg of 3,3,5-trifluoro-2-oxindole in 82% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.23 (s, 1H), 7.70 – 7.63 (m, 1H), 7.38 (ddd, *J* = 9.6, 2.5, 1.3 Hz, 1H), 7.00 (dd, *J* = 8.6, 4.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): *δ* 166.3 (t, *J* = 29.0 Hz), 158.8 (d, *J* = 240.4 Hz), 139.3 (td, *J* = 7.7, 2.0 Hz), 121.4 (d, *J* = 23.7 Hz), 120.8 (td, *J* = 22.9, 8.5 Hz), 113.8 (d, *J* = 7.9 Hz), 113.4 (d, *J* = 25.9 Hz), 113.36, 111.4(d, *J* = 249.9 Hz). HRMS calcd. for $C_8H_4F_3NO$: 187.0245; Found: 187.0252.



5-Chloro-3,3-difluoro-2-oxindole (**11**).[1] The procedure was operated in general method. The reaction gave 42 mg of 5-chloro-3,3-difluoro-2-oxindole in 69% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) *δ* 11.35 (s, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.62 – 7.49 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO)： *δ* 165.9 (t, *J* = 29.3 Hz), 141.9 (t, *J* = 7.7 Hz)， 134.5, 127.8, 125.6, 121.2 (t, *J* = 22.9 Hz), 114.0, 111.1 (t, *J* = 250.0 Hz). ^{19}F NMR (470 MHz, DMSO): *δ* -111.1.

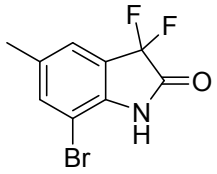


3,3-Difluoro-2-oxindole-5-carbonitrile (**12**).[1] The procedure was operated in general method. The reaction gave 28 mg of 3,3-difluoro-2-oxindole-5-carbonitrile in 48% isolated yield as a brown solid (PE/EA=3:1). ^{1}H NMR (500 MHz, DMSO) δ 11.71 (s, 1H), 8.27 (d, *J* = 1.3 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): *δ* 166.1 (t, J = 29.2 Hz), 147.2 (t, J = 7.3 Hz), 139.6, 129.6, 120.6 (t, J = 23.2 Hz), 118.7, 113.4, 110.5 (t, J = 250.3 Hz), 106.2. ^{19}F NMR (470 MHz, DMSO): *δ* -111.5.

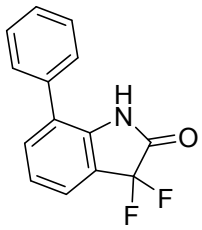


5-Acetyl-3,3-difluoro-2-oxindole (**13**).[1] The procedure was operated in general method. The reaction gave 38 mg of 5-acetyl-3,3-difluoro-2-oxindole in 60% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.60 (s, 1H),

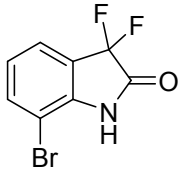
8.21 (d, J = 1.3 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 196.5, 166.6 (t, J = 29.5 Hz), 147.2 (t, J = 7.4 Hz), 135.4, 132.8, 125.6, 119.8 (t, J = 23.1 Hz), 112.4, 111.1 (t, J = 249.4 Hz), 27.1. ^{19}F NMR (470 MHz, DMSO): δ -111.2.



7-Bromo-3,3-difluoro-5-methy-2-oxindole (**14**).[1] The procedure was operated in general method. The reaction gave 29 mg of 7-bromo-3,3-difluoro-5-methyl-2-oxindole in 38% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.40 (s, 1H), 7.30 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8 (t, J = 30.4 Hz), 137.9 (t, J = 7.2 Hz), 136.3, 135.6 (t, J = 1.6 Hz), 124.5, 121.5 (t, J = 23.5 Hz), 111.2 (t, J = 252.1 Hz), 104.2, 20.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ -110.3.

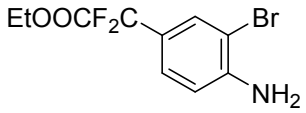


3,3-Difluoro-7-phenyl-2-oxindole (**15**). The procedure was operated in general method. The reaction gave 38 mg of 3,3-difluoro-7-phenyl-2-oxindole in 51% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.56 – 7.49 (m, 3H), 7.48 – 7.42 (m, 2H), 7.40 (dd, J = 8.1, 1.2 Hz, 2H), 7.24 (d, J = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2 (d, J = 30.3 Hz), 138.23 (t, J = 7.1 Hz), 135.7, 133.9, 129.6, 128.6, 127.9, 125.9, 124.3, 124.0, 120.7 (t, J = 23.2 Hz), 110.7 (t, J = 250.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -111.0. HRMS calcd. for $C_{14}H_9F_2NO$: 245.0652; Found: 245.0658.

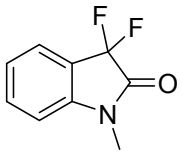


7-Bromo-3,3-difluoro-2-oxindole (**16**). The procedure was operated in general method. The reaction gave 28 mg of 7-bromo-3,3-difluoro-2-oxindole in 38% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.56 (s, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.68 (dd, J = 7.4, 1.0 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 166.3 (t, J = 29.2 Hz), 142.6 (t, J = 7.5 Hz), 137.5, 125.6, 124.5, 121.4 (t, J = 23.2 Hz), 111.6 (t, J = 249.4 Hz), 104.6. ^{19}F NMR (470 MHz,

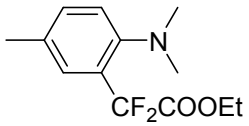
DMSO): δ -110.0. HRMS calcd. for $C_8H_4BrF_2NO$: 246.9444; Found: 246.9450.



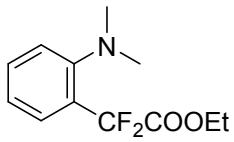
Ethyl 2-(4-amino-3-bromophenyl)-2,2-difluoroacetate (**17**). The procedure was operated in general method. The reaction gave 20 mg of ethyl 2-(4-amino-3-bromophenyl)-2,2-difluoroacetate in 23% isolated yield as a yellow liquid (PE/EA=5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 1.9 Hz, 1H), 7.32 (dd, J = 8.4, 2.0 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 4.37 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2 (t, J = 36.2 Hz), 146.4, 129.9, 125.8, 123.0 (t, J = 26.8 Hz), 114.9, 112.8 (t, J = 252.3 Hz), 108.3, 63.1, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ -102.33. HRMS calcd. for $C_{10}H_{10}BrF_2NO_2$: 292.9863; Found:292.9868.



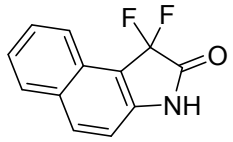
3,3-Difluoro-1-methyl-2-oxindole (**18**). The procedure was operated in general method. The reaction gave 32 mg of 3,3-difluoro-1-methyl-2-oxindole in 58% isolated yield as a brown solid (PE/EA=20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 3.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3 (t, J = 30.2 Hz), 143.9 (t, J = 7.1 Hz), 133.6, 124.6, 123.9 (t, J = 1.7 Hz), 120.1 (t, J = 23.1 Hz), 110.8 (t, J = 249.5 Hz), 109.4, 26.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3. HRMS calcd. for $C_9H_7F_2NO$: 183.0496; Found: 183.0494.



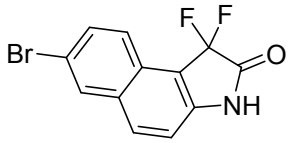
Ethyl 2-(2-(dimethylamino)-5-methylphenyl)-2,2-difluoroacetate (**19**). The procedure was operated in general method. The reaction gave 41 mg of ethyl 2-(2-(dimethylamino)-5-methylphenyl)-2,2-difluoroacetate in 54% isolated yield as a yellow liquid (PE/EA=20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 1.4 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1H), 4.30 (p, J = 7.1 Hz, 2H), 2.54 (s, 6H), 2.37 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (t, J = 33.1 Hz), 149.7 (t, J = 5.1 Hz), 135.2, 132.5, 130.7 (t, J = 23.6 Hz), 126.4 (t, J = 6.4 Hz), 122.3, 112.5 (t, J = 246.1 Hz), 62.1, 45.4, 21.0, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ -98.3. HRMS calcd. for $C_{13}H_{17}F_2NO_2$: 257.1227; Found: 257.1231.



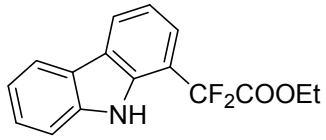
Ethyl 2-(2-(dimethylamino)phenyl)-2,2-difluoroacetate (**20**). The procedure was operated in general method. The reaction gave 32 mg of ethyl 2-(2-(dimethylamino)-5-methylphenyl)-2,2-difluoroacetate in 44% isolated yield as a yellow liquid (PE/EA=20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 6H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 164.1 (t, *J* = 33.1 Hz), 152.4 (t, *J* = 5.0 Hz), 131.8, 131.1 (t, *J* = 23.9 Hz), 126.2 (t, *J* = 6.6 Hz), 125.4, 122.5, 112.5 (t, *J* = 246.2 Hz), 62.1, 45.4, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -98.3. HRMS calcd. for $C_{12}H_{15}F_2NO_2$: 243.1071; Found: 243.1078.



1,1-Difluoro-1,3-dihydro-2H-benzo[e]indol-2-one (**21**). The procedure was operated in general method. The reaction gave 49 mg of 1,1-difluoro-1,3-dihydro-2H-benzo[e]indol-2-one in 75% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.33 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.27 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO) δ 167.4 (t, *J* = 29.4 Hz), 143.5 (t, *J* = 8.8 Hz), 136.2, 130.4, 130.2, 130.0, 128.8, 125.6, 121.8, 113.4 (t, *J* = 248.4 Hz), 113.2, 111.0 (t, *J* = 21.7 Hz). ^{19}F NMR (470 MHz, DMSO): δ -111.3. HRMS calcd. for $C_{12}H_7F_2NO$: 219.0496; Found: 219.0491.

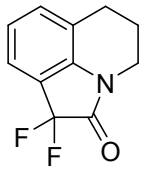


7-Bromo-1,1-difluoro-1,3-dihydro-2H-benzo[e]indol-2-one (**22**). The procedure was operated in general method. The reaction gave 54 mg of 7-bromo-1,1-difluoro-1,3-dihydro-2H-benzo[e]indol-2-one in 61% isolated yield as a brown solid (PE/EA=5:1). ^{1}H NMR (500 MHz, DMSO) δ 11.41 (s, 1H), 8.30 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.76 (s, 2H), 7.32 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 167.0 (t, *J* = 29.3 Hz), 143.9 (t, *J* = 8.7 Hz), 135.3, 132.7, 131.9, 131.4, 127.2, 123.7, 118.0, 114.3. 112.9 (t, *J* = 227.3 Hz). 111.0 (t, *J* = 21.3 Hz). ^{19}F NMR (470 MHz, DMSO): *δ* -111.30. HRMS calcd. for $C_{12}H_6BrF_2NO$: 296.9601; Found: 296.9608.

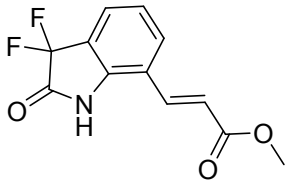


Ethyl 2-(9H-carbazol-1-yl)-2,2-difluoroacetate (**23**). The procedure was operated in general method. The reaction gave 34 mg of ethyl 2-(9H-carbazol-1-yl)-2,2-difluoroacetate in 40% isolated yield as a white solid (PE/EA=50:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.69

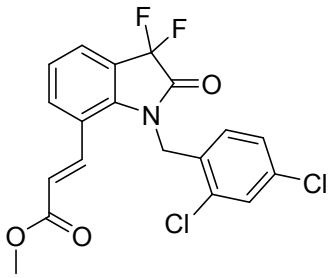
(d, J = 7.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.32 (dd, J = 16.1, 8.1 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4 (t, J = 35.6 Hz), 139.5, 135.8 (t, J = 3.2 Hz), 126.6, 124.7, 123.2, 122.7 (t, J = 7.2 Hz), 122.2, 120.3, 119.9, 118.8, 114.4 (t, J = 26.6 Hz), 114.1 (t, J = 252.2 Hz), 111.0, 63.5, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ -104.33. HRMS calcd. for $C_{16}H_{13}F_2NO_2$: 289.0914; Found: 289.0924.



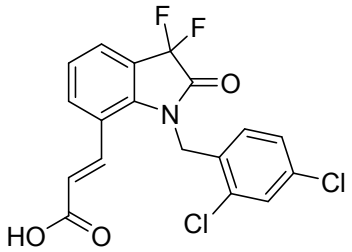
1,1-Difluoro-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**24**). The procedure was operated in general method. The reaction gave 30 mg of 1,1-difluoro-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one in 48% isolated yield as a white solid (PE/EA=40:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.4 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 3.73 – 3.69 (m, 2H), 2.78 (t, J = 6.1 Hz, 2H), 2.03 (dt, J = 12.0, 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (t, J = 30.9 Hz), 139.6 (t, J = 7.4 Hz), 132.3, 123.3, 122.3, 121.6, 118.6 (t, J = 23.5 Hz), 112.0 (t, J = 252.3 Hz), 38.7, 24.1, 20.4. ^{19}F NMR (471 MHz, $CDCl_3$): δ -112.2. HRMS calcd. for $C_{11}H_9F_2NO$: 209.0652; Found: 209.0647.



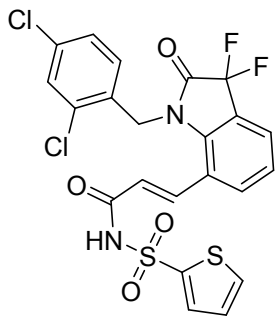
Methyl (E)-3-(3,3-difluoro-2-oxoindolin-7-yl)acrylate (**25**). The compound **17** (0.1 mol%), $Pd(OAc)_2$ (10 mol%)，(o-toxyl)$_3$P (20 mol%), toluene were added to a 25 mL sealing tube in air. Then the mixture was stirred in pre-heated to 60 ^{o}C for 24 h. The crude product was concentrated in vacuo and purified by flash column chromatograph to give the pure products (**27**, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.98 (d, J = 15.8 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 7.4 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 6.51 (d, J = 15.8 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 166.5 (t, J = 30.2 Hz), 140.8 (t, J = 7.0 Hz), 137.3, 130.6, 126.5, 124.0, 121.4 (t, J = 23.3 Hz), 120.3, 118.6, 110.2 (t, J = 250.1 Hz), 52.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ -111.9. HRMS calcd. for $C_{12}H_9F_2NO_3$: 253.0550; Found: 253.0552.



Methyl (*E*)-3-(1-(2,4-dichlorobenzyl)-3,3-difluoro-2-oxoindolin-7-yl)acrylate (**26**).[3] The compound **27** (0.1 mmol), K_2CO_3 (2 equiv), DMF (1 mL) were added to the 25 mL sealing tube in air. Then the mixture was stirred in 50 °C for 6 h. The crude product was concentrated in vacuo and purified by flash column chromatograph to give the pure products (**26**, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 15.6 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.12 (d, *J* = 15.6 Hz, 1H), 5.11 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2 (t, *J* = 30.0 Hz), 165.5, 140.4 (t, *J* = 6.7 Hz), 138.1, 134.5, 133.3, 133.2, 130.6, 129.9, 127.7, 126.8, 125.9, 124.8, 123.4, 121.5 (t, *J* = 23.0 Hz), 120.4, 109.7 (t, *J* = 248.3 Hz), 51.8, 44.0. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -111.01.

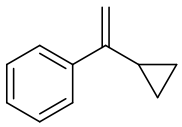


(E)-3-(1-(2,4-dichlorobenzyl)-3,3-difluoro-2-oxoindolin-7-yl)acrylic acid (**27**).[3]The compound **26** (0.1 mmol), NaOH (2 equiv), MeOH (0.5 ml), H_2O (0.5 mL) were added to the 25 mL sealing tube in air. Then the mixture was stirred in room temperature for 12 h. The crude product was concentrated in vacuo and purified by flash column chromatograph to give the pure products (**27**, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.7 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.24 (dd, *J* = 30.9, 7.8 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.17 (d, *J* = 15.5 Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 166.2 (t, *J* = 29.9 Hz), 140.6 (t, *J* = 6.5 Hz), 140.4, 134.6, 133.4, 133.3, 130.4, 130.1, 127.7, 126.8, 126.4, 124.8, 122.6, 121.6 (t, *J* = 23.2 Hz), 120.0, 109.7 (t, *J* = 248.5 Hz), 44.0. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -111.1.

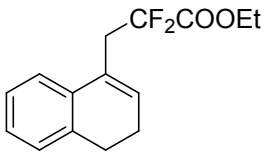


(E)-3-(1-(2,4-Dichlorobenzyl)-3,3-difluoro-2-oxoindolin-7-yl)-N-(thiophen-2-

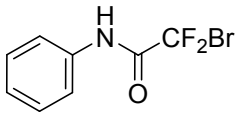
ylsulfonyl)acrylamide (**A**).[3] The compound **27** (0.1 mmol), DECl (2.4 equiv, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride), DMAP (2.5 equiv), DCM (2 mL) were added to the 25 mL sealing tube in air. Then the mixture was stirred in room temperature for 24 h. The crude product was concentrated in vacuo and purified by flash column chromatograph to give the pure products (**A**, 62% yield). ^{1}H NMR (500 MHz, DMSO) δ 12.36 (s, 1H), 8.11 (d, *J* = 4.2 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 2.8 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.14 (d, *J* = 15.3 Hz, 1H), 5.03 (s, 2H). ^{13}C NMR (125 MHz, DMSO) δ 166.0 (t, *J* = 29.8 Hz), 162.5, 141.0 (t, *J* = 6.9 Hz), 140.0, 138.3, 135.3, 134.7, 134.3, 133.5, 133.1, 131.4, 129.8, 128.3, 128.1, 128.0, 126.5, 125.4, 124.4, 121.0, 120.8 (t, *J* = 24.8 Hz), 110.5 (t, *J* = 247.0 Hz), 44.1. ^{19}F NMR (471 MHz, DMSO): *δ* -109.9.



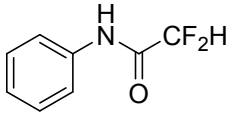
(1-Cyclopropylvinyl)benzene (**28**).[4] Methyltriphenylphosphonium bromide (3 equiv), *tert*-BuOK (3 equiv) were suspended in dry THF (0.2 M) and cooled to 0 °C for 30 min. Cyclopropyl(phenyl)methanone (1 equiv) was added and the reaction was gradually heated to room temperature for 12h. The reaction was quenched with H_2O and extracted with EtOAc. The combinedorganic layers were washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the pure alkene. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 5.15 (d, *J* = 169.8 Hz, 2H), 1.75 – 1.66 (m, 1H), 0.88 (q, *J* = 4.7 Hz, 2H), 0.64 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 141.6, 128.1, 127.4, 126.1, 109.0, 15.6, 6.7.



Ethyl 3-(3,4-dihydronaphthalen-1-yl)-2,2-difluoropropanoate (**29**).[5]The procedure was operated in general method. The reaction gave 14 mg of ethyl 3-(3,4-dihydronaphthalen-1-yl)-2,2-difluoropropanoate in 26% isolated yield as a colorless liquid (PE/EA=50:1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 1H), 7.21 (td, *J* = 7.4, 1.8 Hz, 1H), 7.17-7.12 (m, 2H), 6.09 (t, *J* = 4.6 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 15.9 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.28 (td, *J* = 8.0, 4.8 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 164.1 (t, *J* = 32.6 Hz), 136.3, 133.7, 131.6, 127.6, 127.31 (t, *J* = 4.4 Hz), 127.1, 126.3, 122.8, 115.5 (t, *J* = 252.3 Hz), 62.7, 37.3 (t, *J* = 24.2 Hz), 28.0, 23.2, 13.7. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -103.3.



2-Bromo-2,2-difluoro-N-phenylacetamide (**30**).[6] Aniline (1 mmol), $BrCF_2COOEt$ (1.2 mmol) were added into 25 mL Schlenck. Then the mixture was evacuated and backfilled with N_2 (3 times) and stirred at room temperature for 5h. The crude production was diluted with ethyl ethylate and directly concentrated in vacuo, and purified by flash column chromatograph to give the pure products (PE/EA=10:1, yield: 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$): *δ* 157.5 (t, *J* = 27.5 Hz), 135.3, 129.4, 126.24, 114.00, 111.5 (t, *J* = 315.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -60.6.

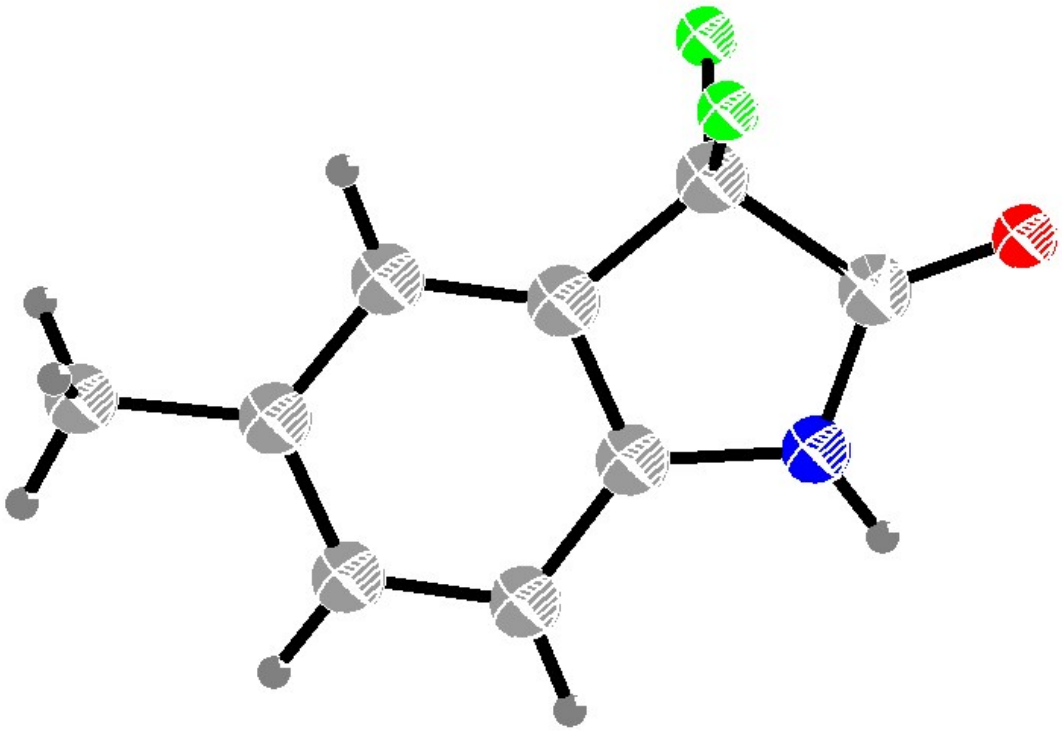


2,2-difluoro-N-phenylacetamide (**31**).[7] The procedure was operated in general method. The reaction gave 12 mg of 2,2-difluoro-N-phenylacetamide in 23% isolated yield as a white solid (PE/EA=10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.02 (t, *J* = 54.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3 (t, *J* = 24.4 Hz), 135.6, 129.3, 125.8, 120.3, 108.5 (t, *J* = 254.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -125.5.

Reference
1. Y. Ohtsuk and T. Yamakawa, *Tetrahedron*. **2011**, *67*, 2323.
2. S. S. Nigudkar, K. Stine and A. V. Demchenko, *J. Am. Chem. Soc*. **2014**, *136*, 921.
3. N. Zhou, A. Polozov, M. O. Connell, J. Burgeson, P. Yu, W. Zeller, J. Zhang, E. Onua, J. Ramirez, G. Palsdottir, G. Halldorsdottir, T. Andresson, A. Kiselyov, M. Gurney and J. Singh, *Bioorg. Med. Chem. Lett*. **2010**, *20*, 2658.
4. T. W. Liwosz and S. R. Chemler, *Chem. Eur. J.* **2013**, *19*, 12771–1277.
5. F. Zhang, Q.-Q. Min and X. Zhang, Synthesis, 2015, 2912-2923
6. H. Morimoto, R. Fujiwara, Y. Shimuzu, K. Morisaki and T. Ohshima, *Org. Lett*. **2014**, *16*, 2018
7. C. Jones, P. K. Baruah, A. L. Thompson, S. Scheiner and M. Smith, *J. Am. Chem. Soc*. **2012**, *134*, 12064.

Crystal data

Crystallographic data for compound **3** (CCDC- 1507706) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Displacement ellipsoids are drawn at 30% probability level

Bond precision: C-C = 0.0032 A Wavelength=0.71073

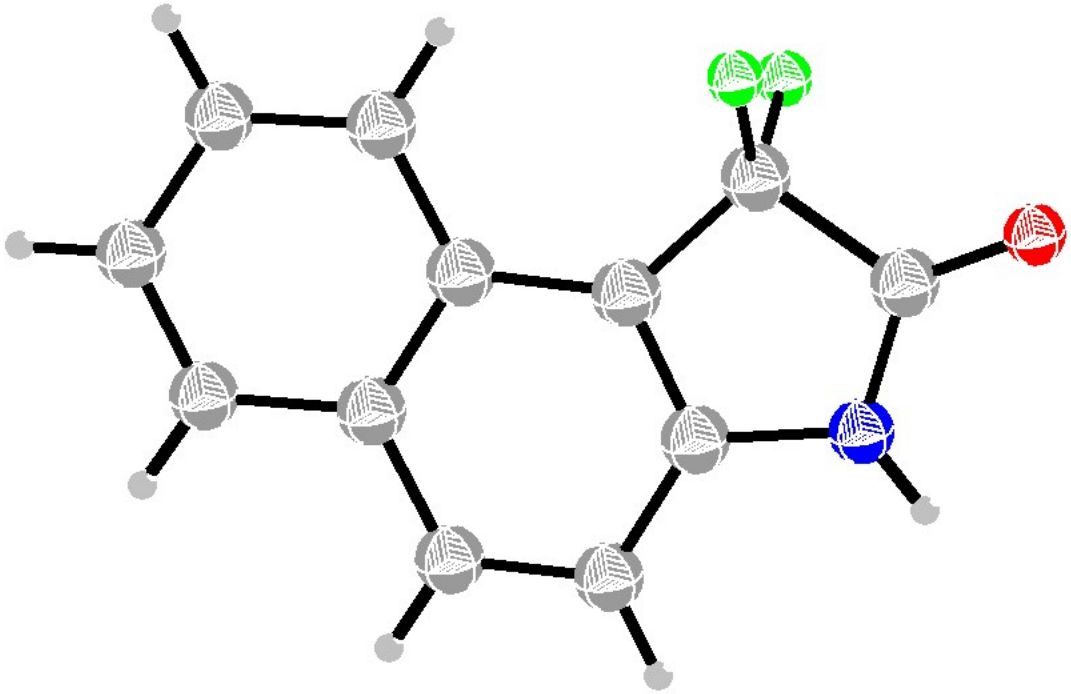
Cell: a=8.4538(8) b=9.4567(7) c=10.8021(8)
alpha=89.874(6) beta=74.590(8) gamma=81.932(7)

Temperature: 293 K

	Calculated	Reported
Volume	823.73(12)	823.73(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C9 H7 F2 N O	?
Sum formula	C9 H7 F2 N O	C9 H7 F2 N O
Mr	183.16	183.16
Dx,g cm-3	1.477	1.477
Z	4	4
Mu (mm-1)	0.128	0.128
F000	376.0	376.0
F000'	376.26	
h,k,lmax	11,12,14	11,12,14
Nref	4417	3757
Tmin,Tmax	0.940,0.962	0.966,1.000
Tmin'	0.938	

Correction method= # Reported T Limits: Tmin=0.966 Tmax=1.000
AbsCorr = ?
Data completeness= 0.851 Theta(max)= 29.091
R(reflections)= 0.0517(2384) wR2(reflections)= 0.1388(3757)
S = 1.033 Npar= 237

Crystallographic data for compound 2**1** (CCDC- 1507707) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Displacement ellipsoids are drawn at 30% probability level

Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell: a=10.9946(10) b=7.5522(7) c=11.4653(10)
alpha=90 beta=97.431(9) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	944.01(15)	944.01(15)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C12 H7 F2 N O	?
Sum formula	C12 H7 F2 N O	C12 H7 F2 N O
Mr	219.19	219.19
Dx,g cm-3	1.542	1.542
Z	4	4
Mu (mm-1)	0.126	0.126
F000	448.0	448.0
F000'	448.29	
h,k,lmax	15,10,15	14,10,14
Nref	2566	2259
Tmin,Tmax	0.941,0.963	0.907,1.000
Tmin'	0.939	

Correction method= # Reported T Limits: Tmin=0.907 Tmax=1.000

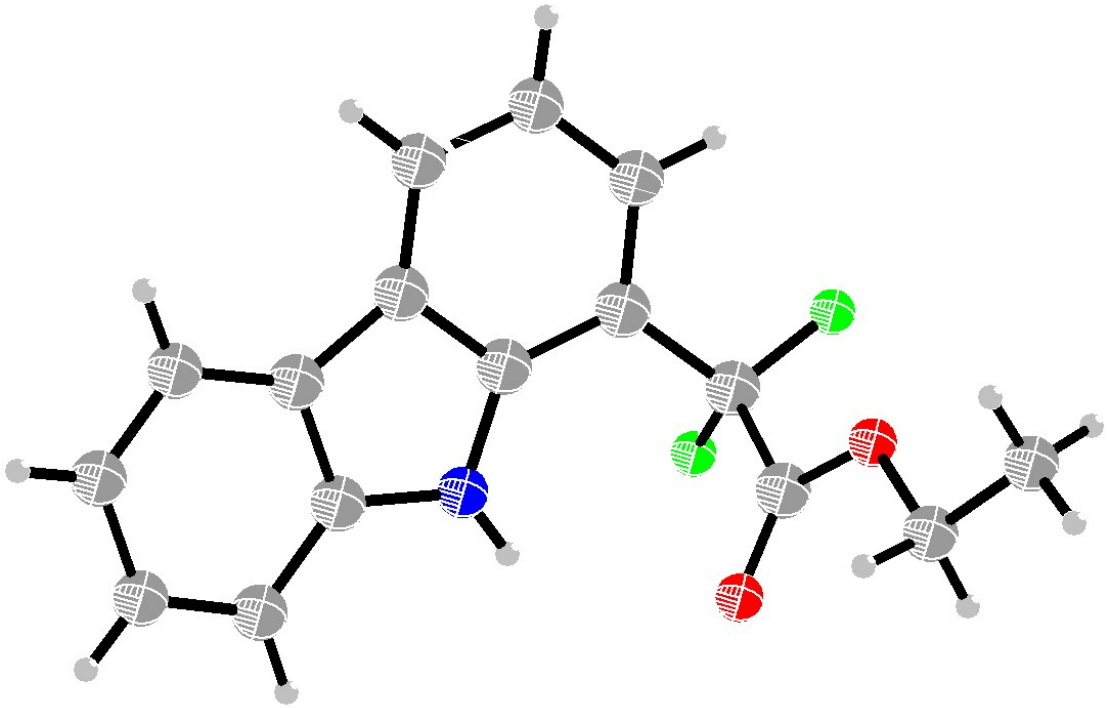
AbsCorr = ?

Data completeness= 0.880 Theta(max)= 29.250

R(reflections)= 0.0449(1605) wR2(reflections)= 0.1224(2259)

S = 1.061 Npar= 145

Crystallographic data for compound **23** (CCDC- 1507666) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Displacement ellipsoids are drawn at 30% probability level

Bond precision: C-C = 0.0024 A Wavelength=0.71073

Cell: a=12.1928(12) b=8.0344(6) c=14.1806(13)
alpha=90 beta=103.454(9) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1351.0(2)	1351.0(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H13 F2 N O2	?
Sum formula	C16 H13 F2 N O2	C16 H13 F2 N O2
Mr	289.27	289.27
Dx,g cm-3	1.422	1.422
Z	4	4
Mu (mm-1)	0.112	0.112
F000	600.0	600.0
F000'	600.37	
h,k,lmax	16,11,19	16,10,19
Nref	3678	3086

Tmin,Tmax	0.948,0.967	0.856,1.000
Tmin'	0.946	

Correction method= # Reported T Limits: Tmin=0.856 Tmax=1.000
AbsCorr = MULTI-SCAN
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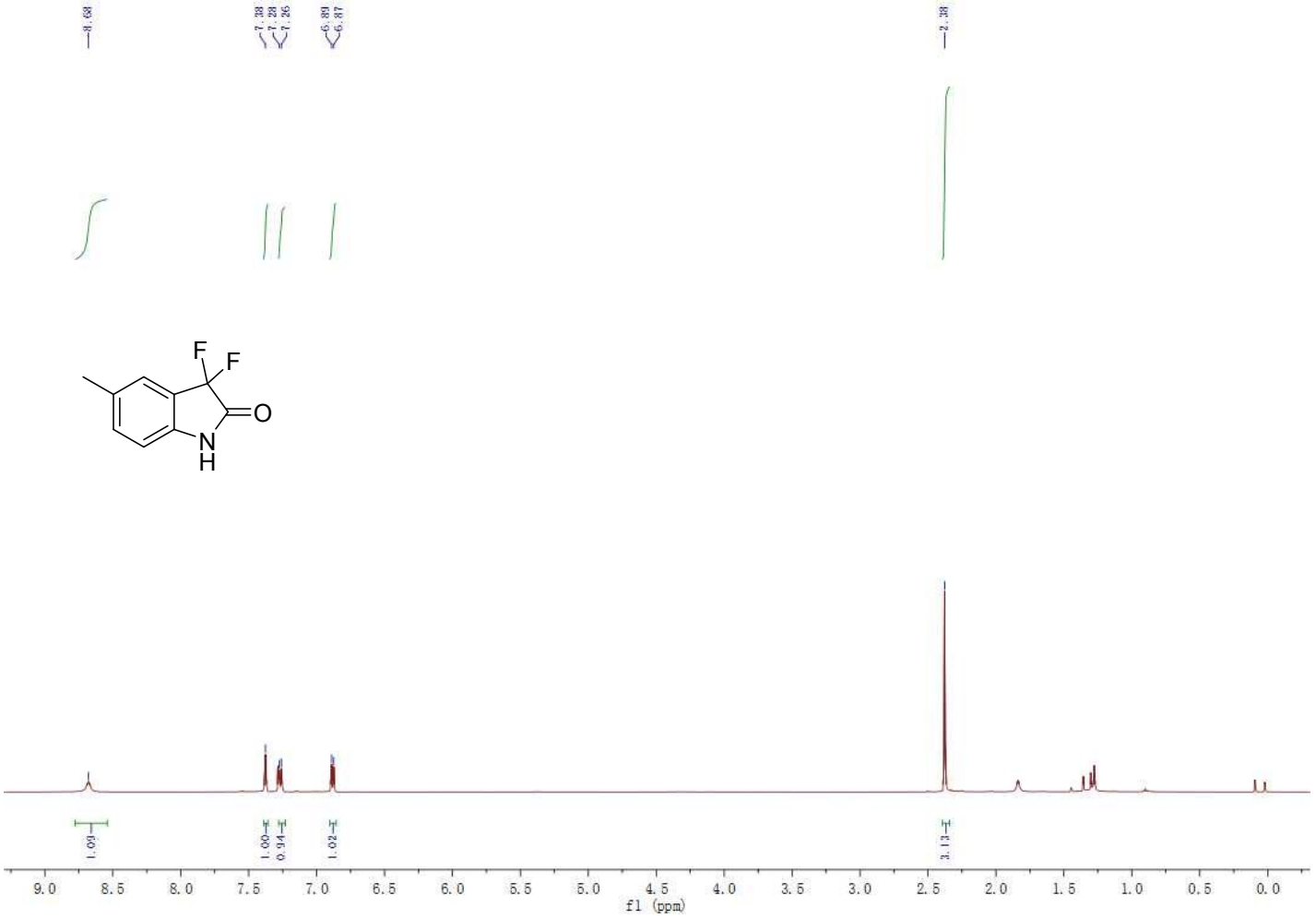
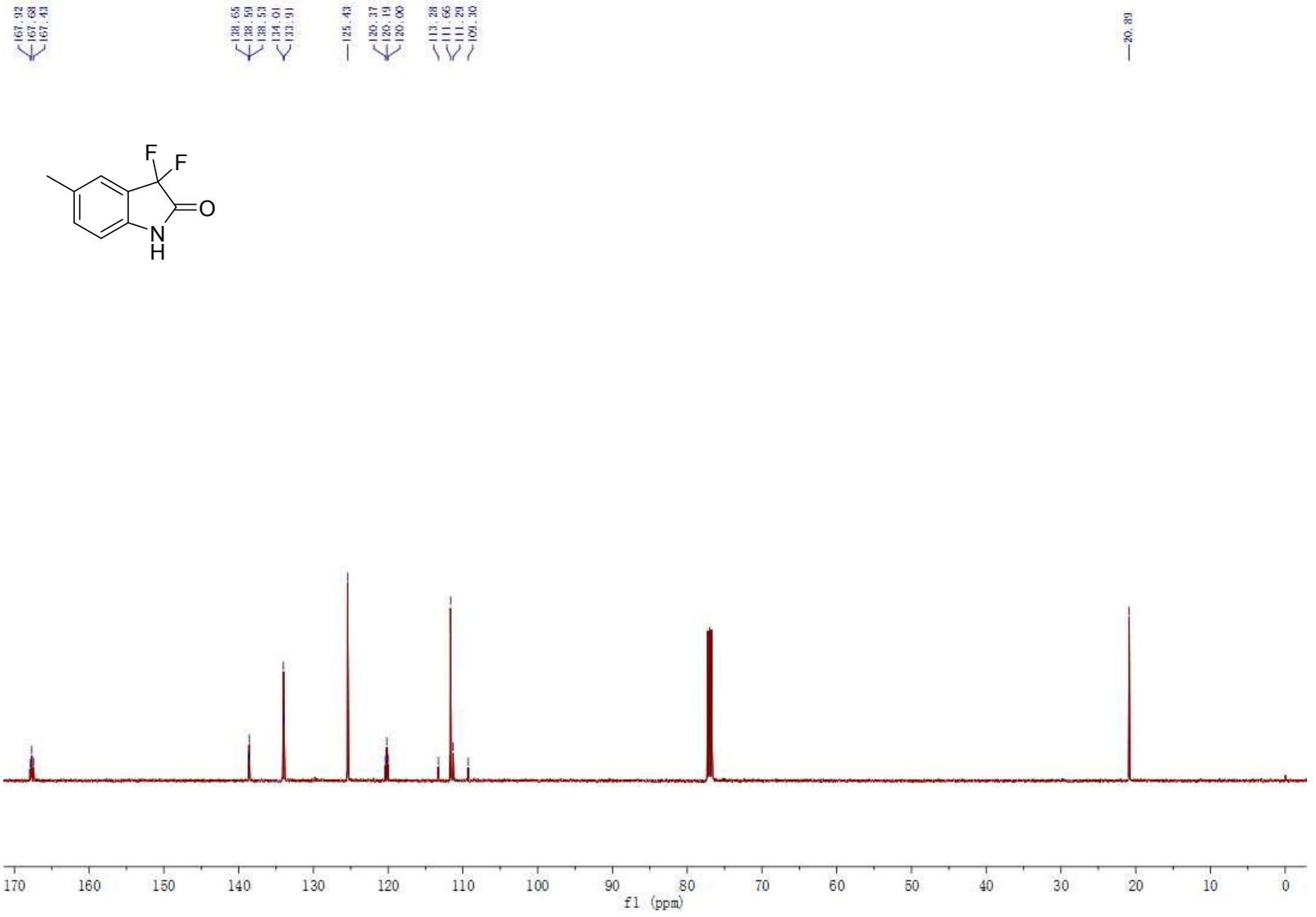
S = 1.005 Npar= 191

NMR Spectroscopic Data

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109.30
20.89
F
F
O
N
H
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130
120
110
100
90
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50
40
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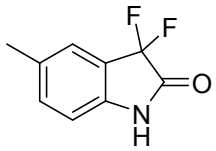
f1 (ppm)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N
H

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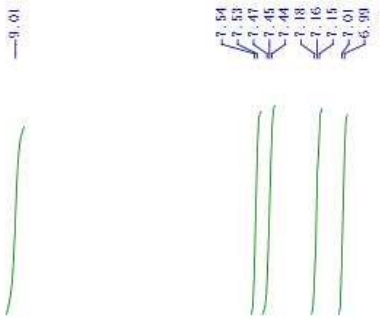
f1 (ppm)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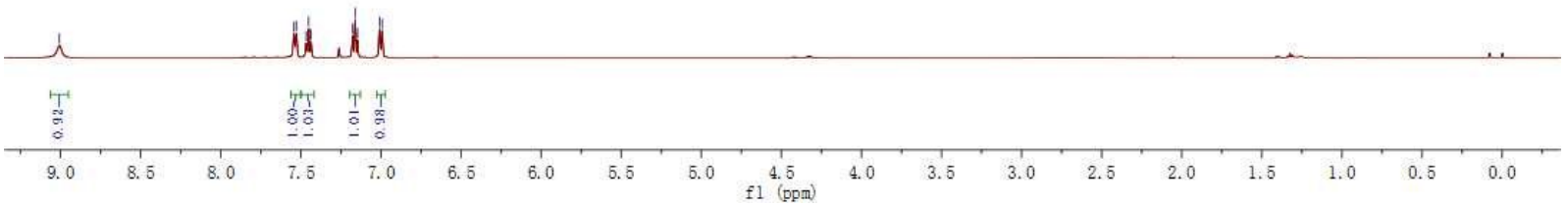
F
O
N
H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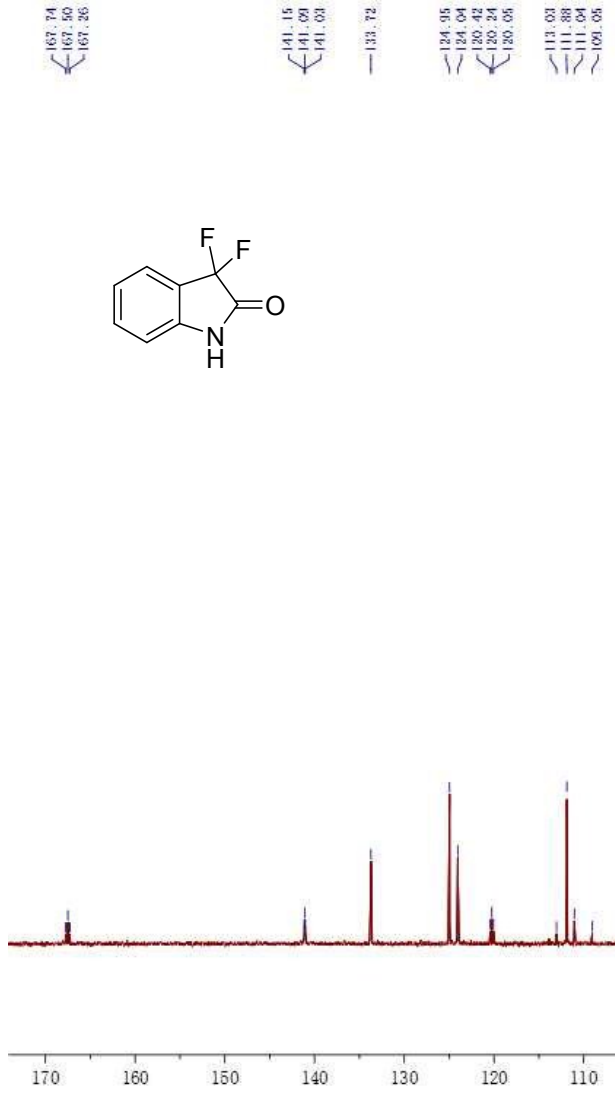
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F
O
N
H
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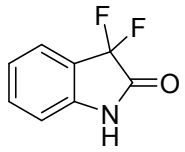
f1 (ppm)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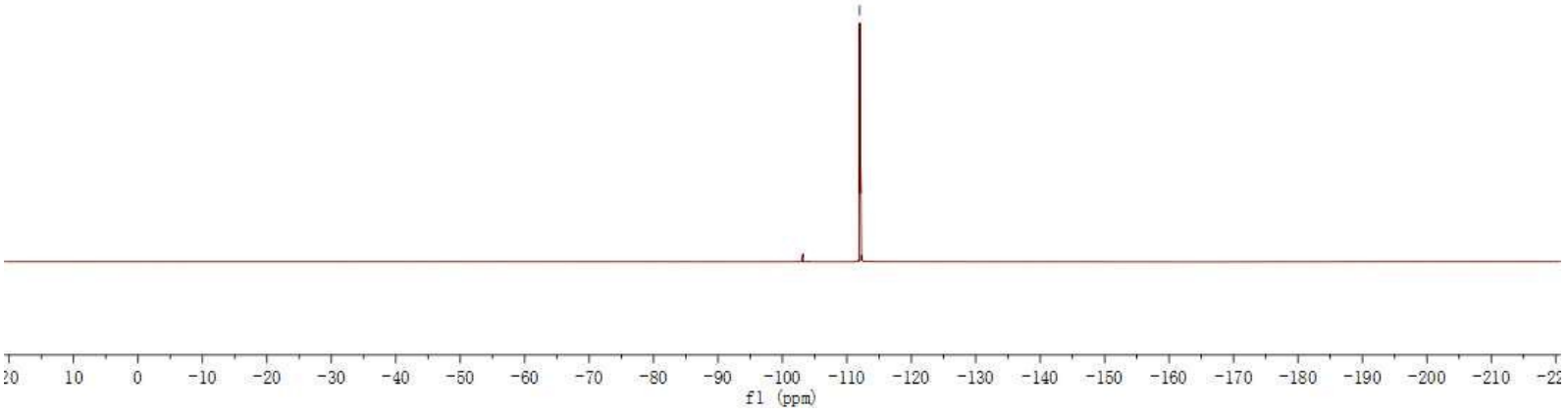
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-170
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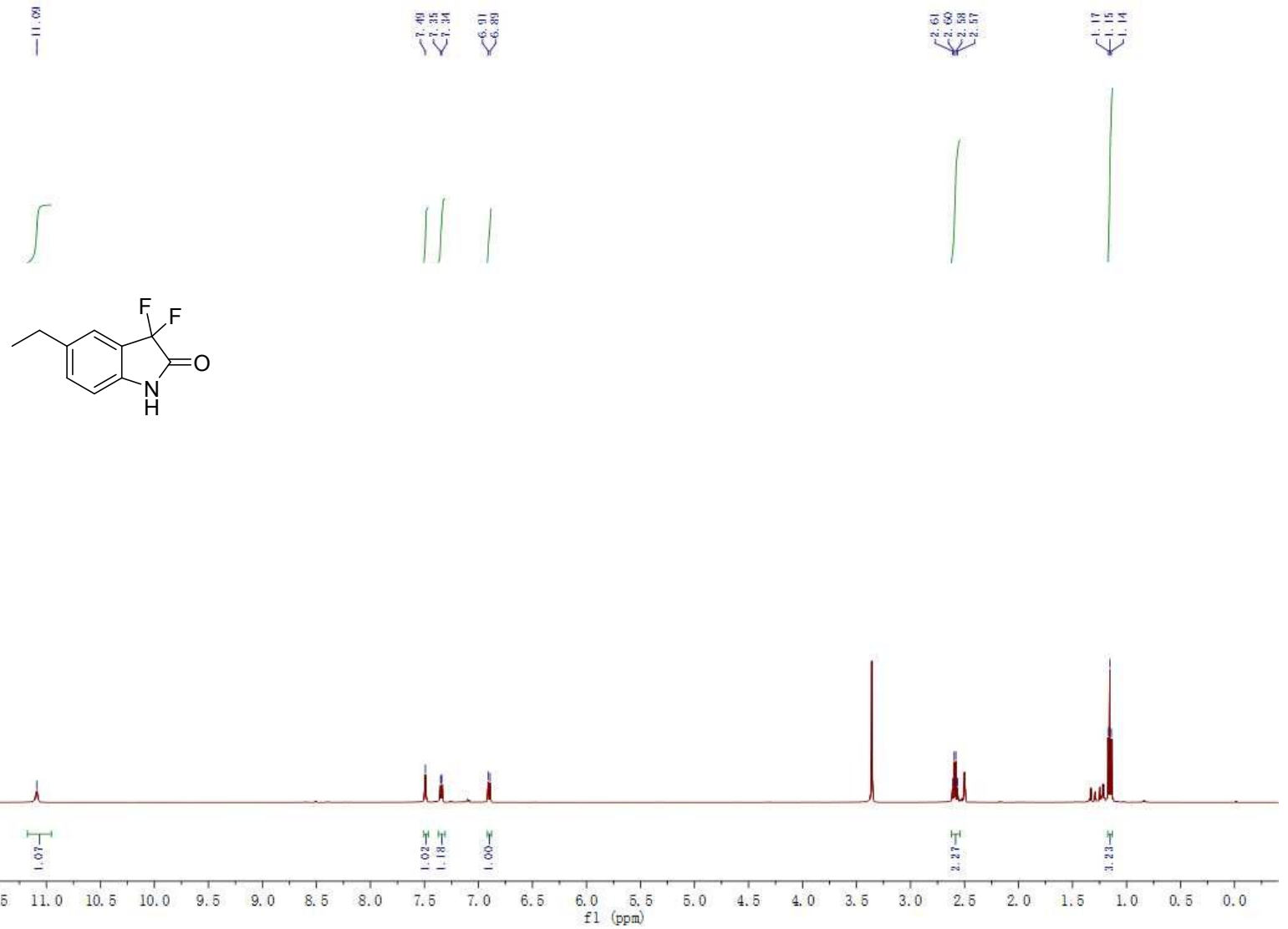
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1.02
1.18
1.00
2.27
3.23
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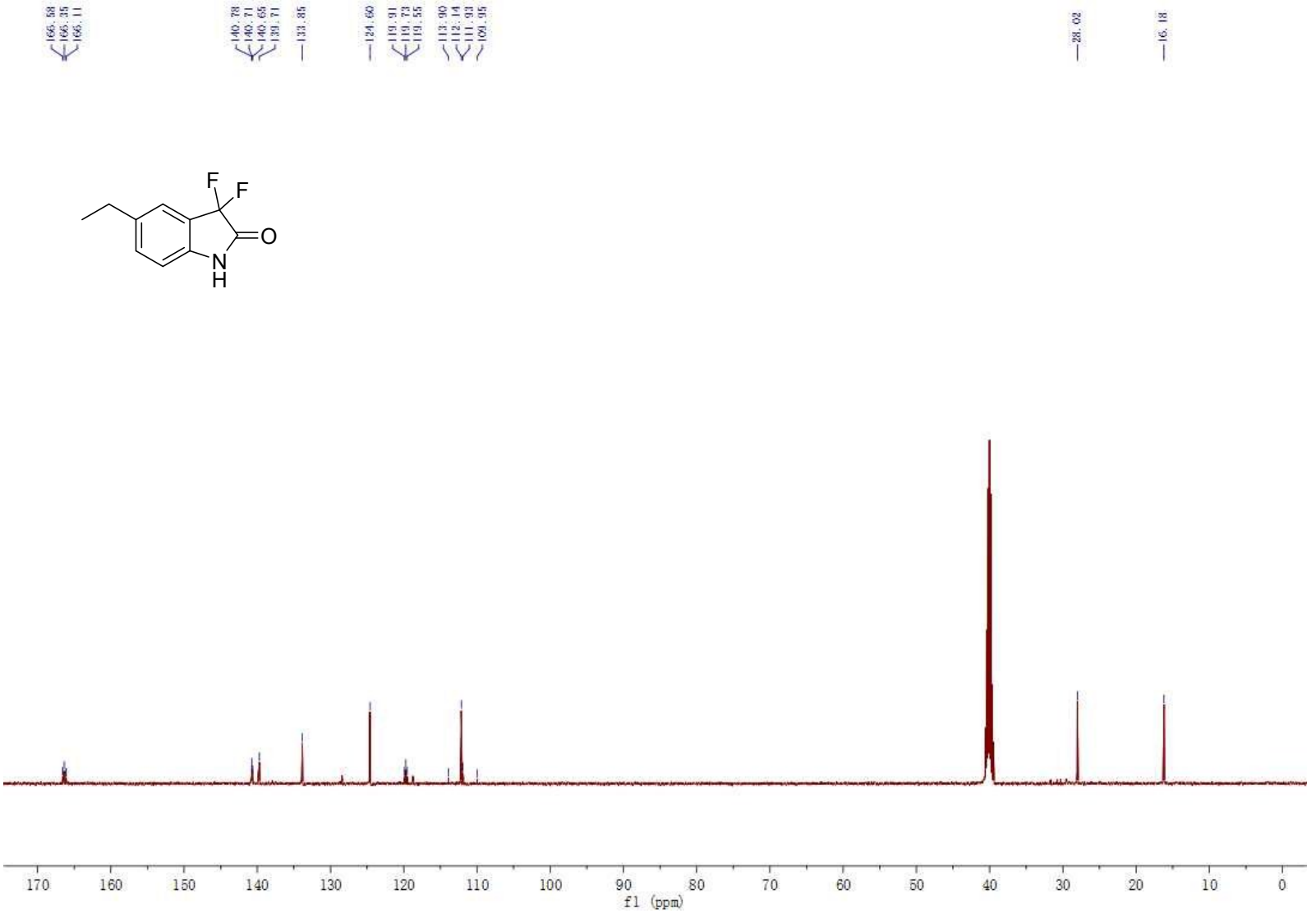
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H
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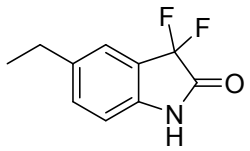
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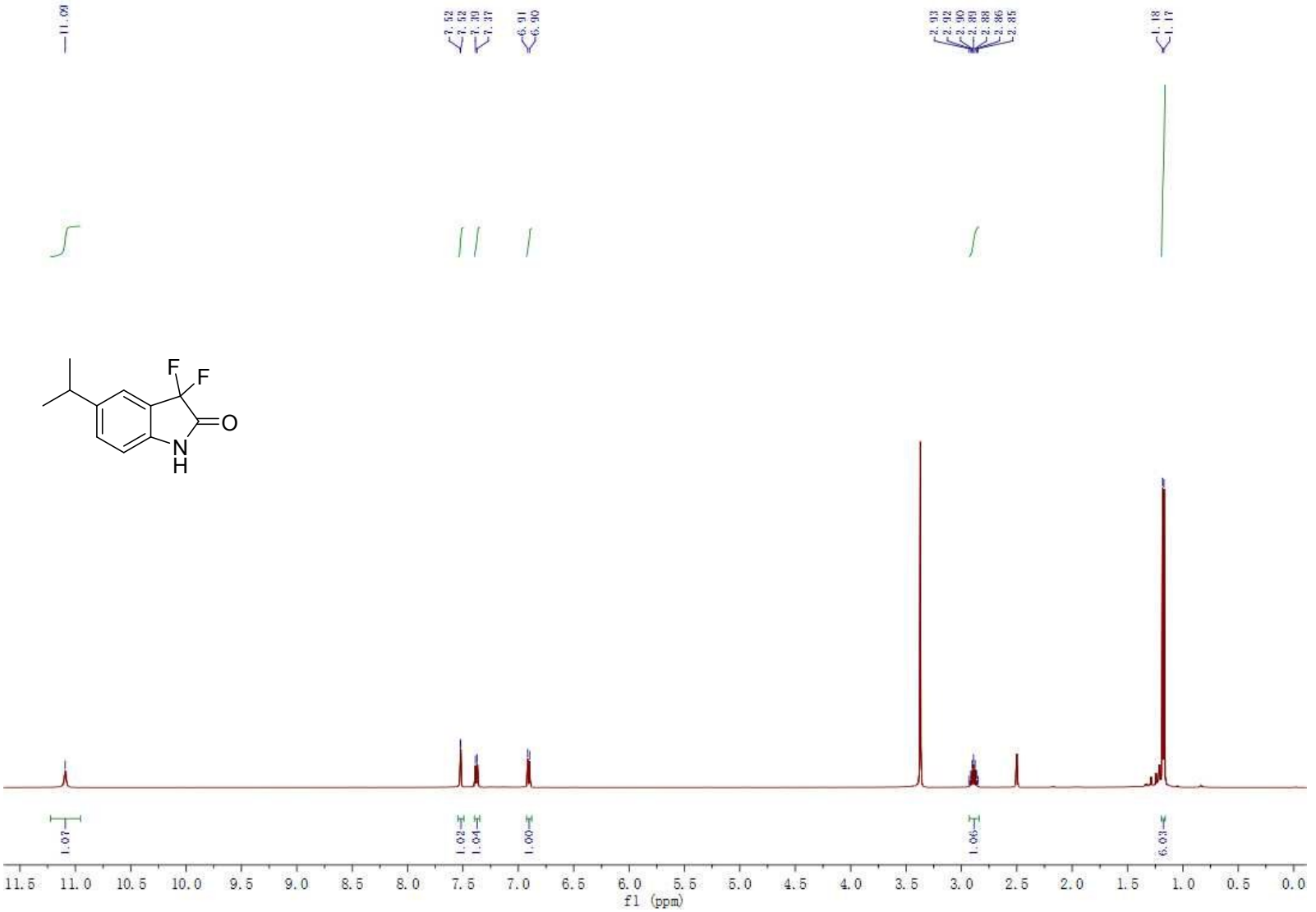
f1 (ppm)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1.17
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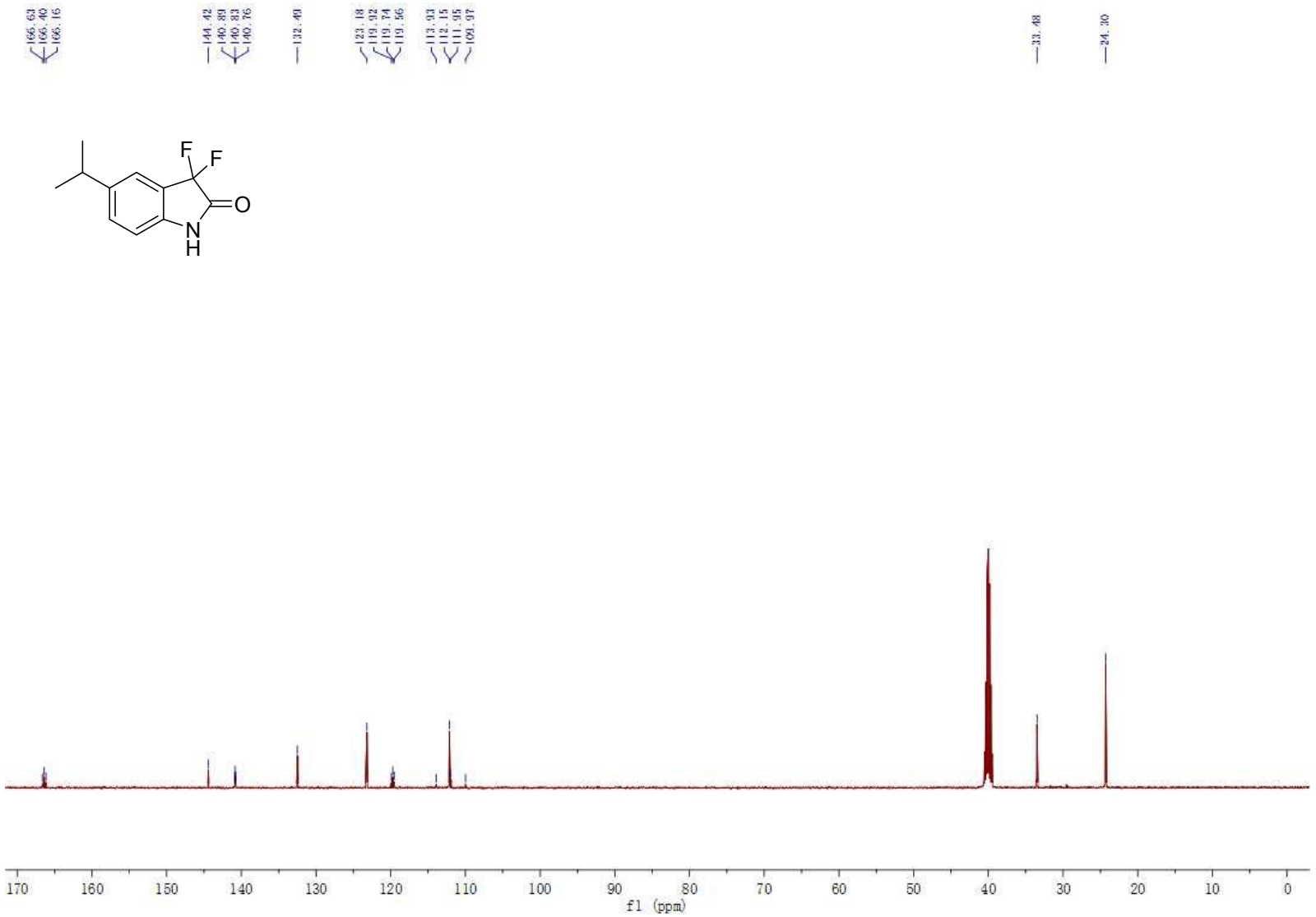
F
O
N
H
1.07
1.02
1.04
1.00
1.06
6.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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N
H
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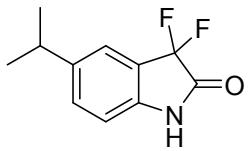
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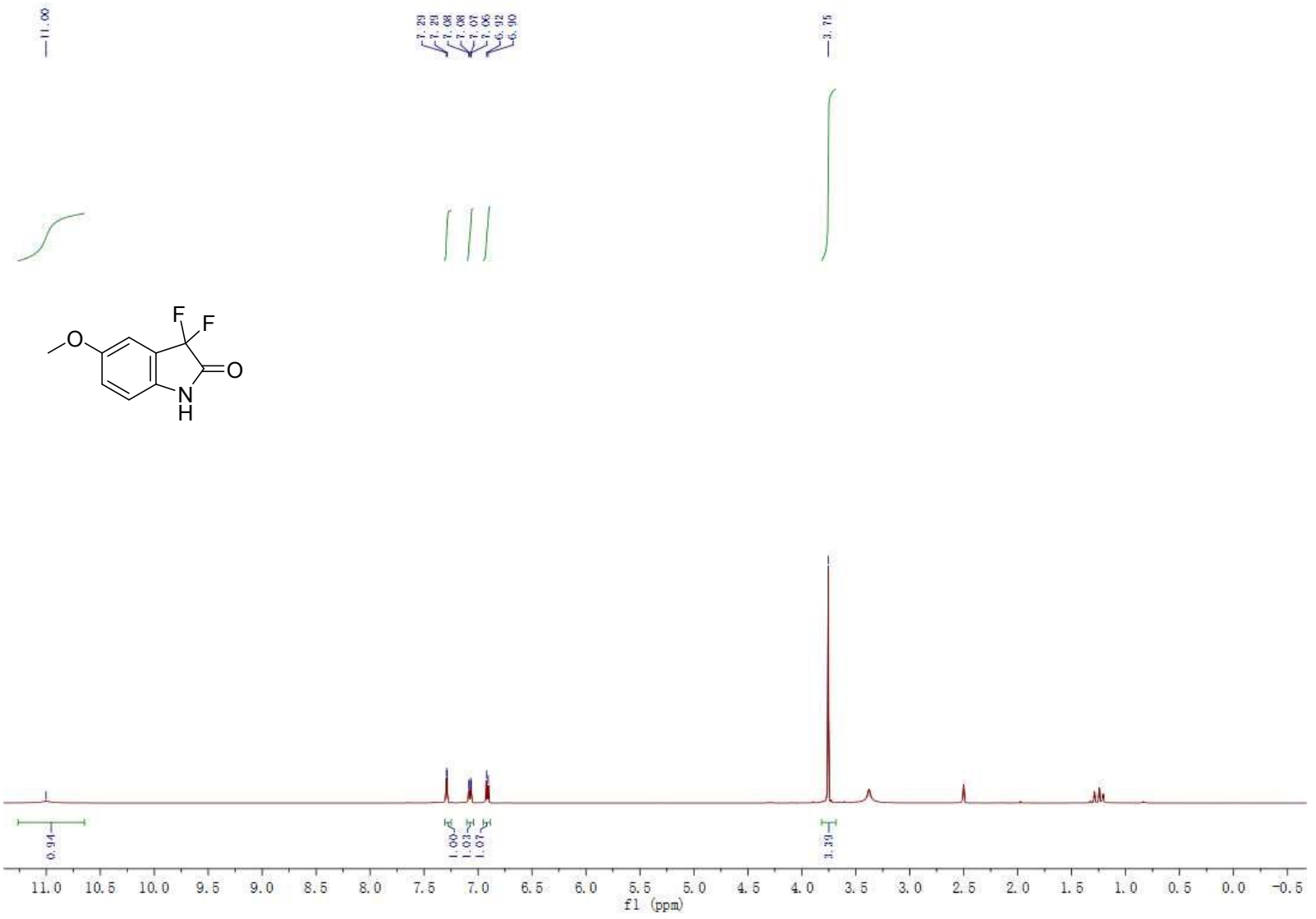
f1 (ppm)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H
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1.03
1.07
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10.0
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8.0
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7.0
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6.0
5.5
5.0
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3.0
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0.5
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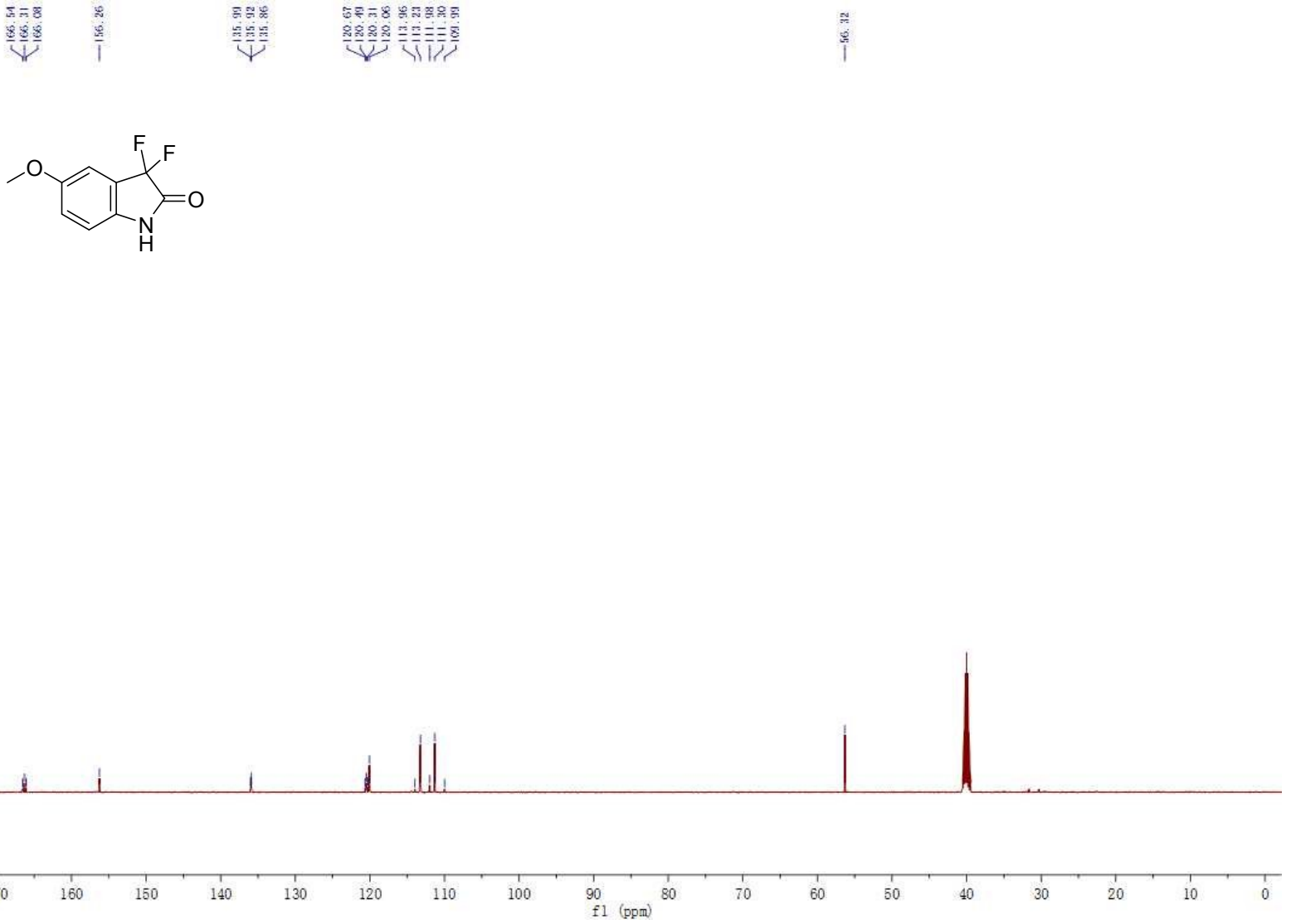
f1 (ppm)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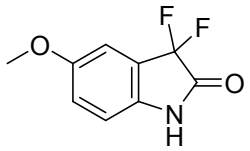
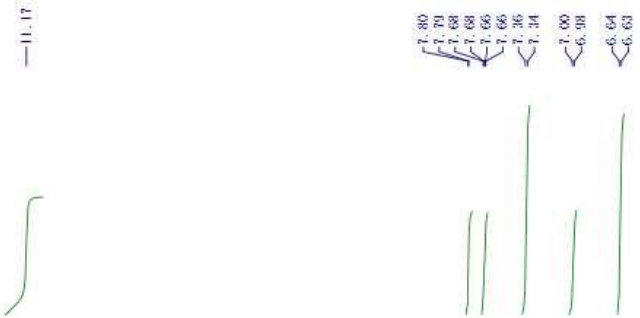
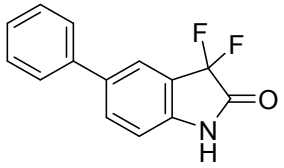
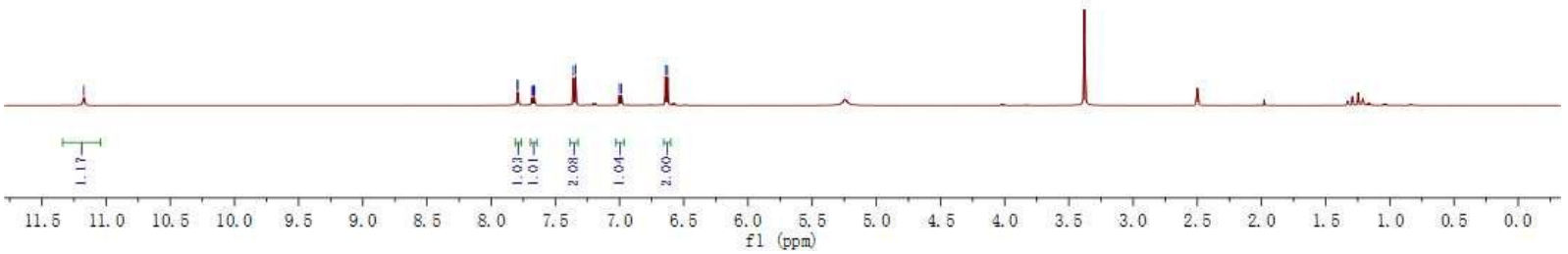
F
O
O
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

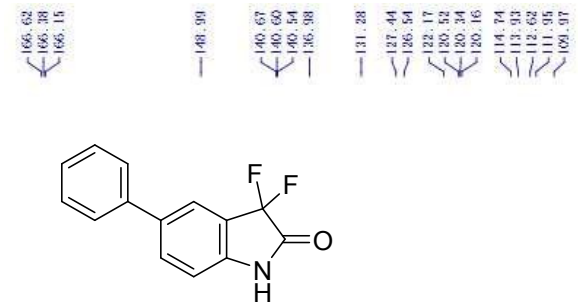

F
F
O
O
N
H

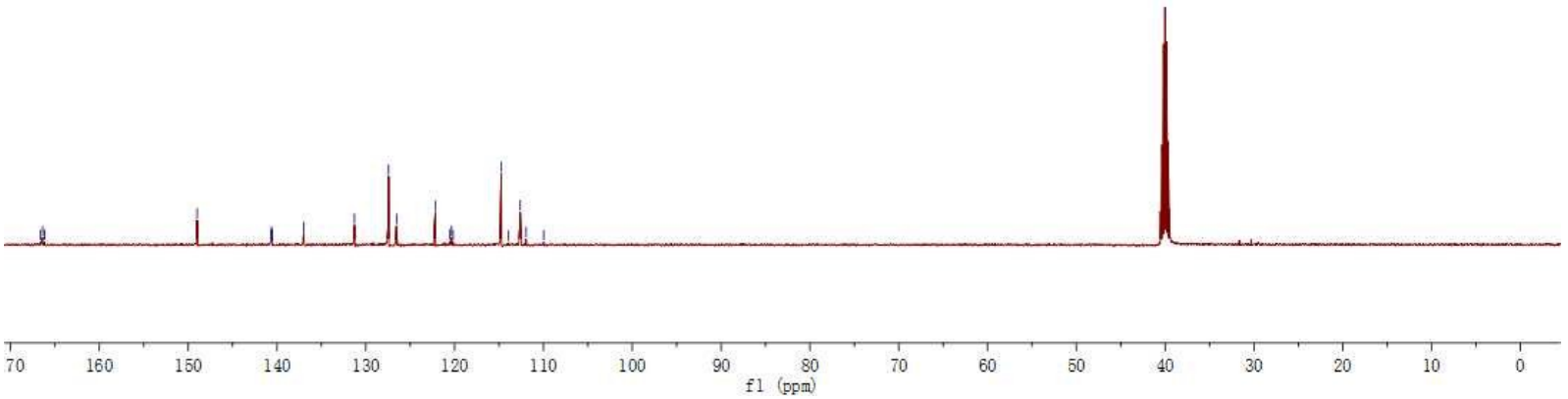
-110.68
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

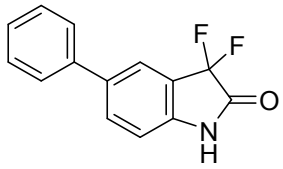

11.17
7.80
7.79
7.68
7.68
7.66
7.66
7.36
7.34
7.00
6.98
6.64
6.63


F
F
O
N
H

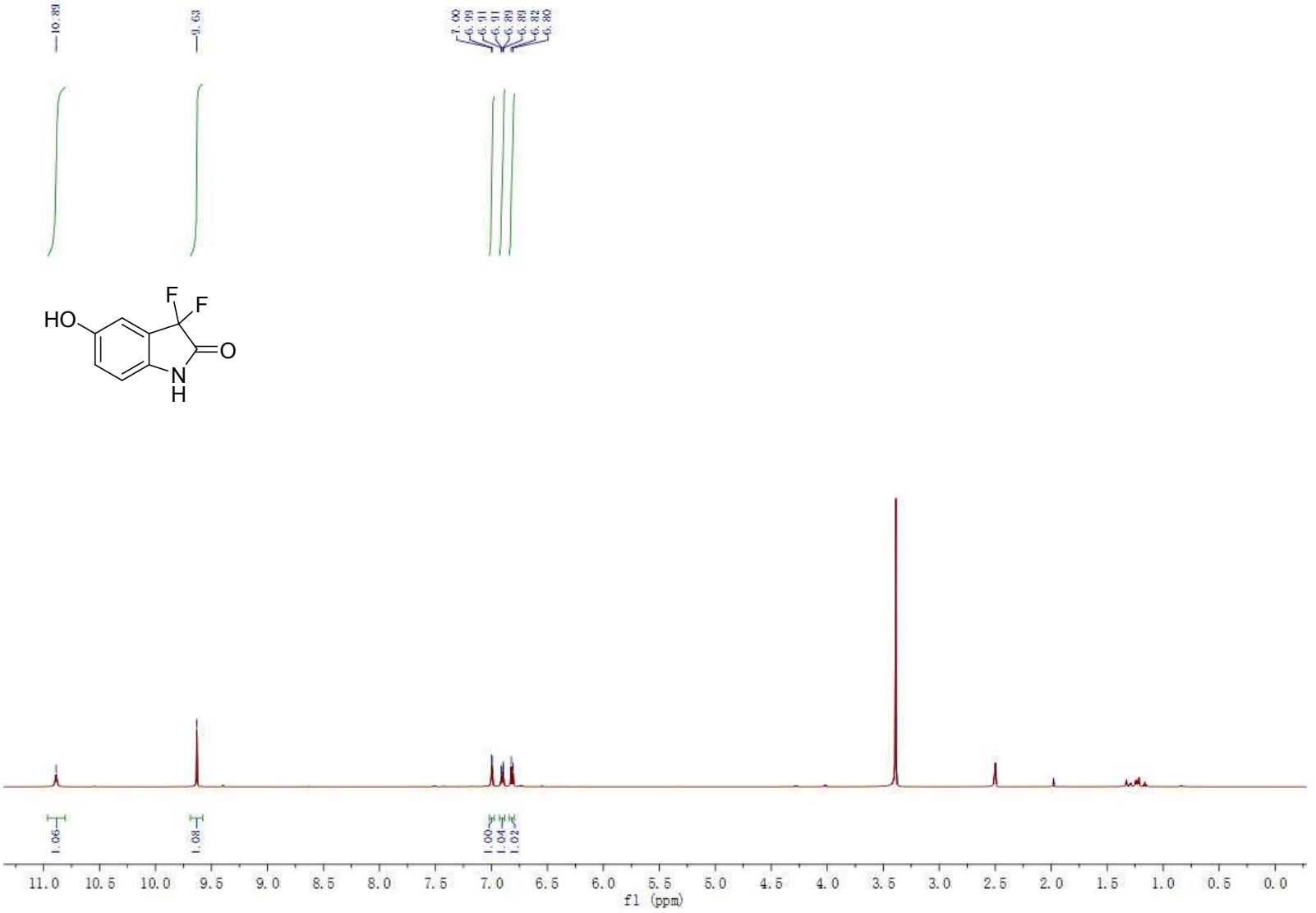

1.17
1.03
1.01
2.08
1.04
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

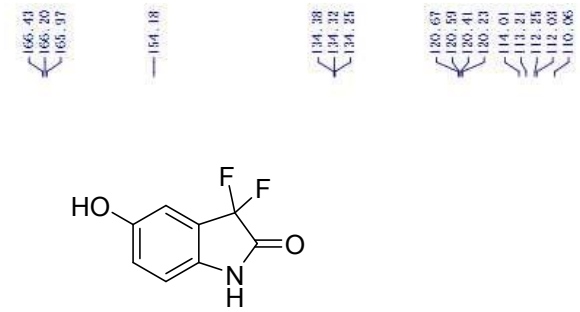

166.62
166.38
166.15
148.99
140.67
140.60
140.54
136.98
131.28
127.44
126.54
122.17
120.52
120.34
120.16
114.74
113.93
112.62
111.95
109.97
F
F
O
N
H

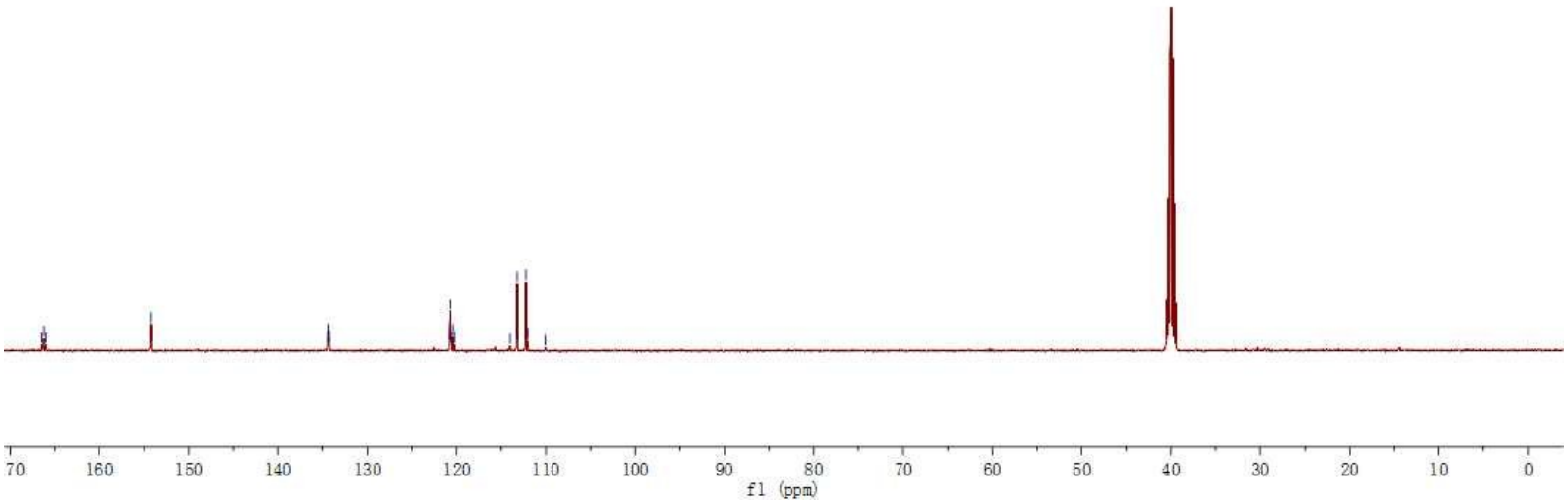

70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

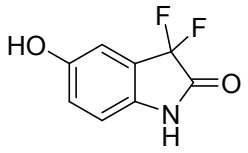

F
F
O
N
H

-110.64
20
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)

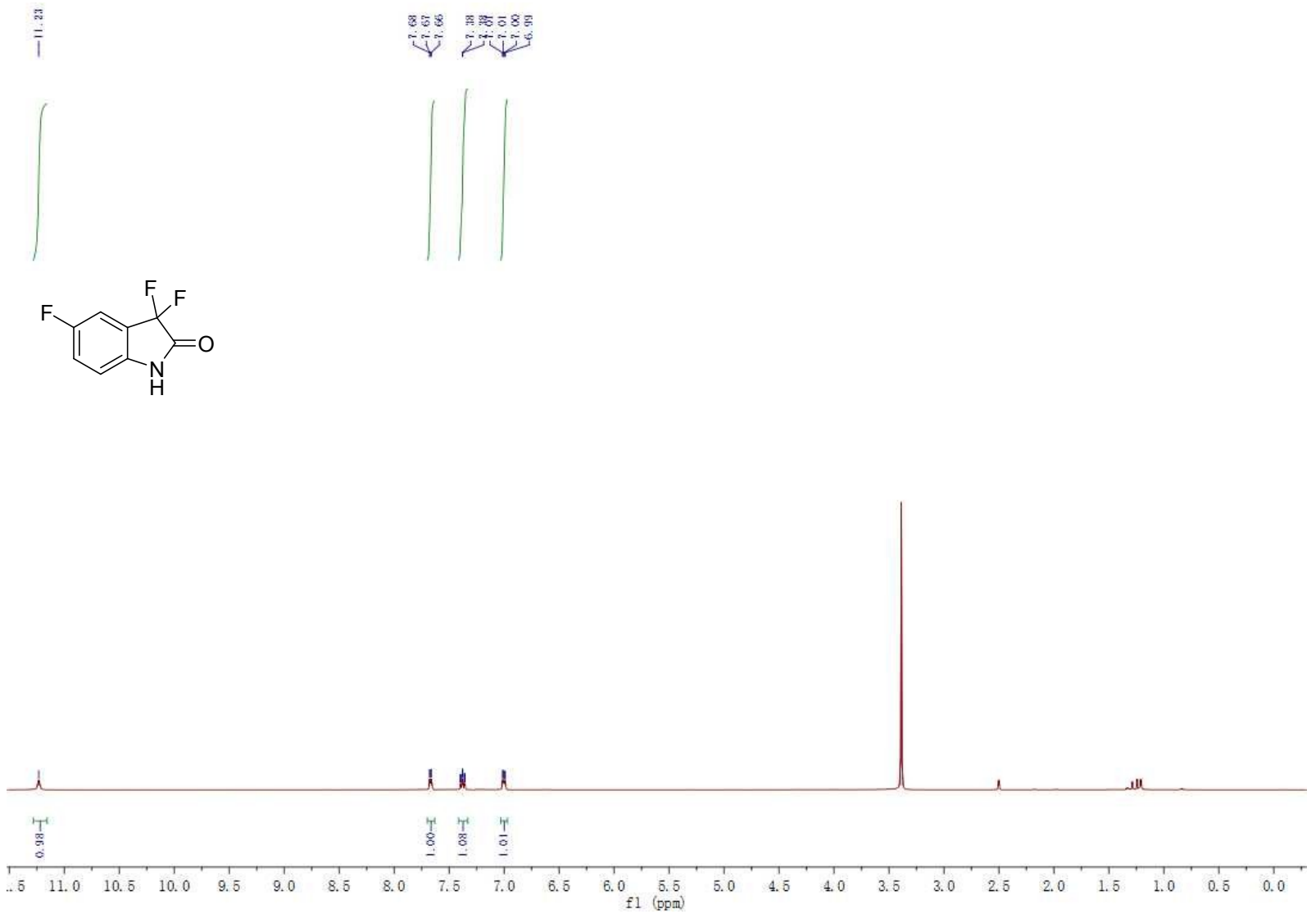

10.89
9.63
7.00
6.99
6.91
6.91
6.89
6.89
6.82
6.80
HO
F
F
O
N
H
1.06
1.08
1.00
1.04
1.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.43
166.20
165.97
154.18
134.38
134.32
134.25
120.67
120.59
120.41
120.23
114.01
113.21
112.25
112.03
110.06
HO
F
F
O
N
H

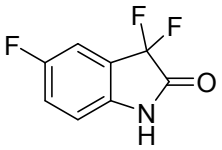

70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

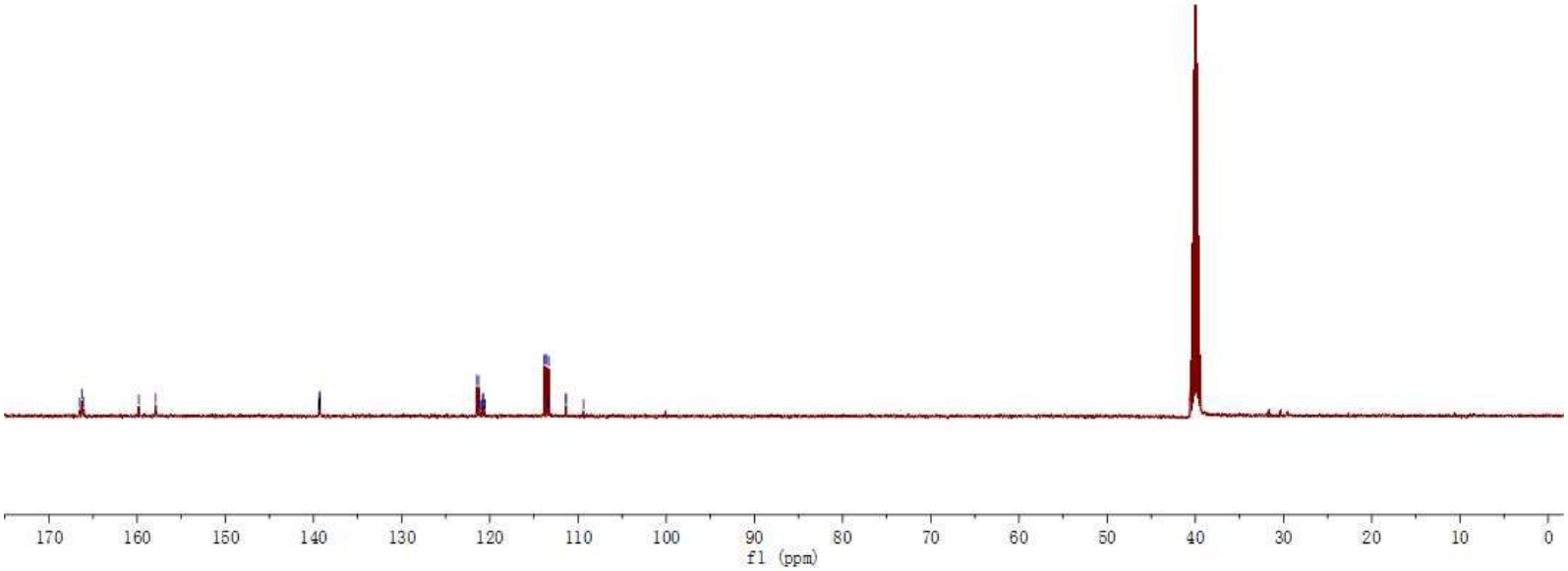

HO
F
F
O
N
H

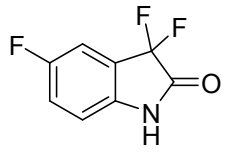
-110.62
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


11.23
7.68
7.67
7.66
7.38
7.38
7.01
7.00
6.99
F
F
F
O
N
H
0.98
1.00
1.03
1.01
f1 (ppm)

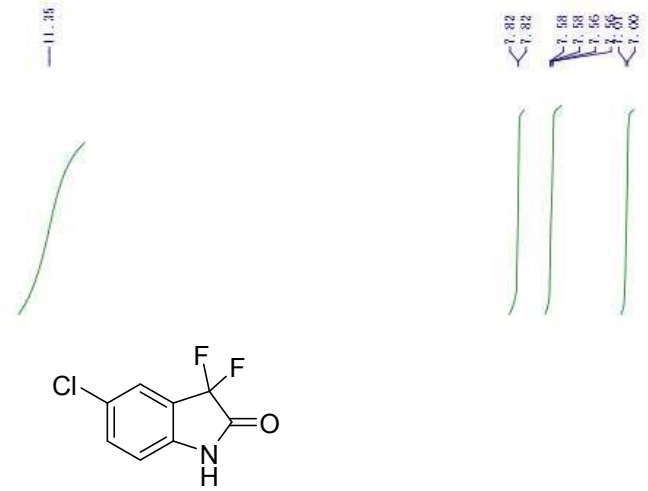

166.60
166.27
166.04
159.81
157.89
139.37
139.35
139.31
139.29
139.25
139.23
121.47
121.28
120.99
120.92
120.81
120.74
120.62
120.55
113.83
113.77
113.51
113.37
113.36
113.31
111.38
111.37
109.38

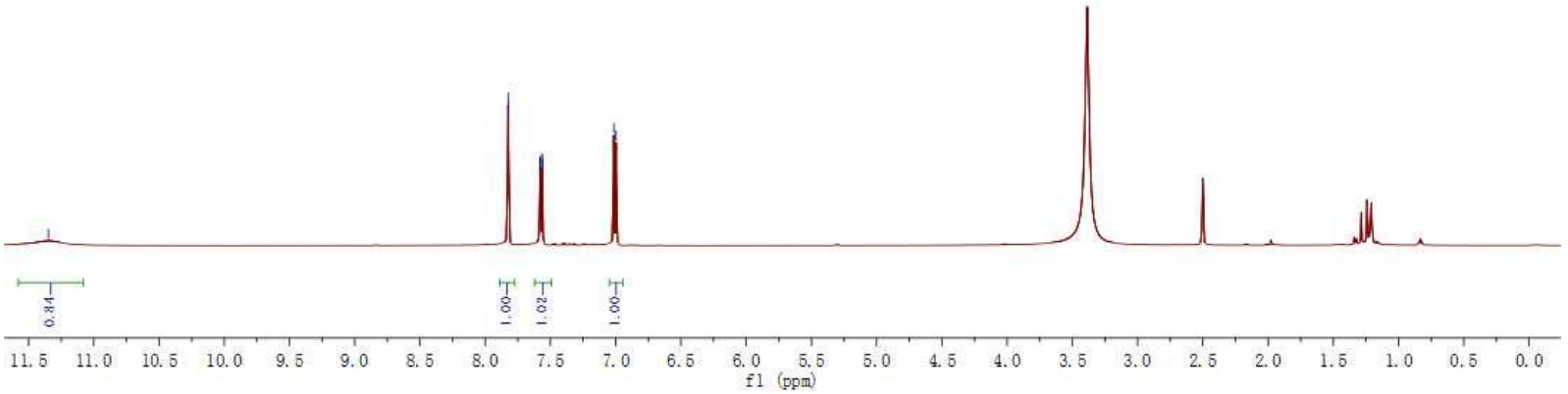

F
F
F
O
N
H

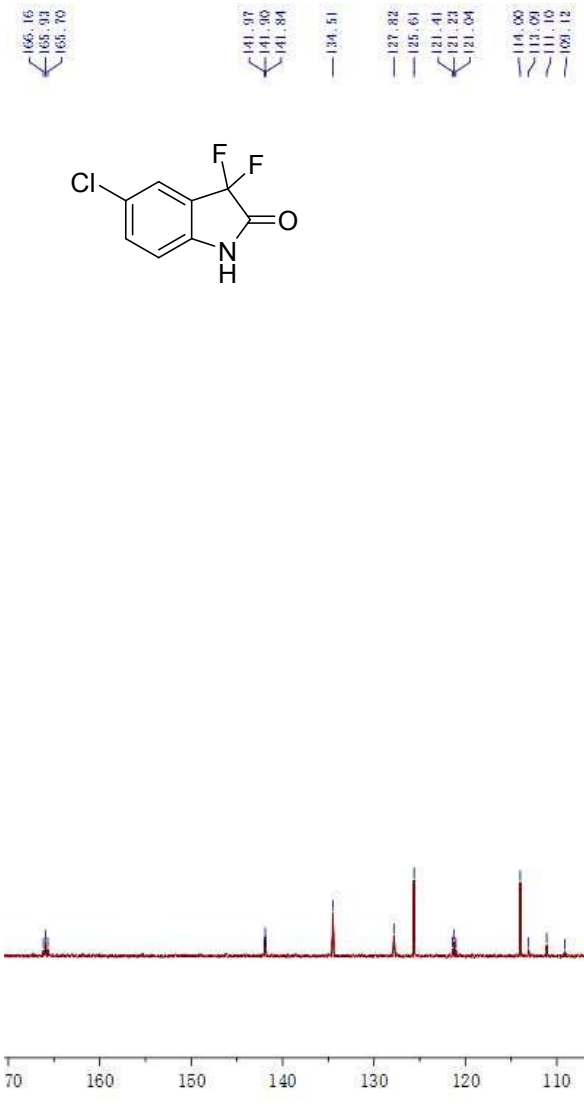

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

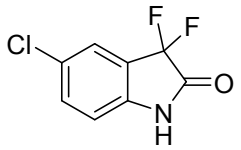

F
F
F
O
N
H

-111.14
-119.08
20
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)

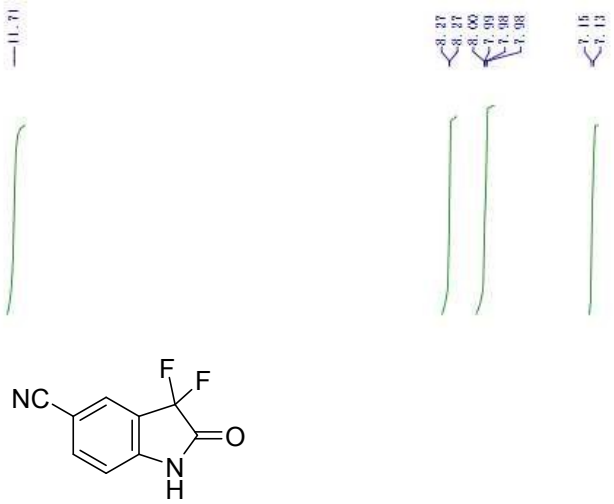

11.35
7.82
7.32
7.58
7.58
7.56
7.55
7.55
7.00
F
F
Cl
O
N
H

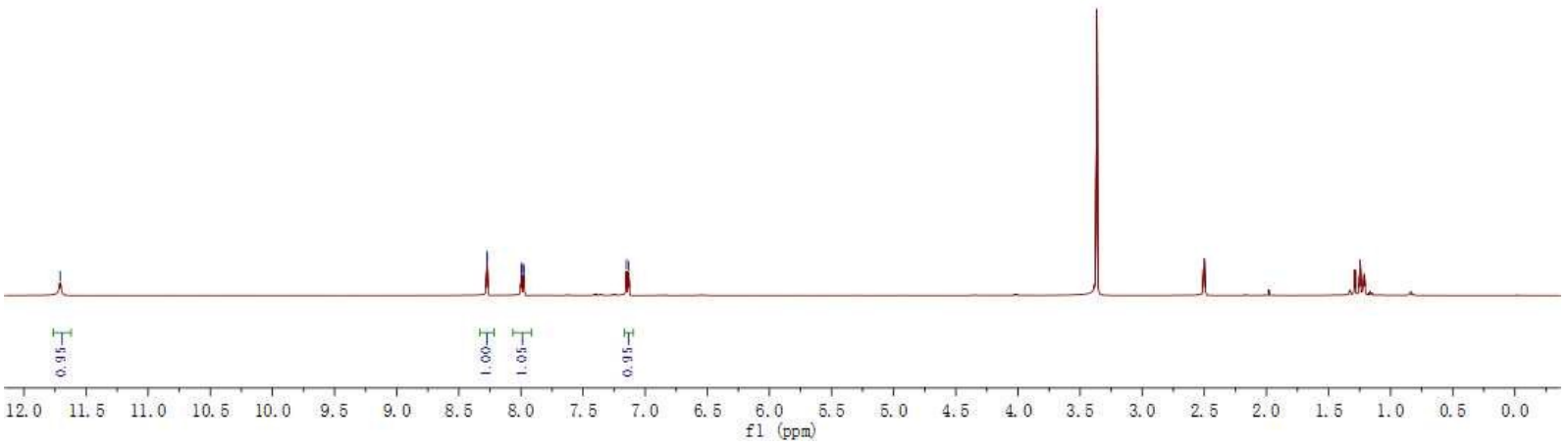

0.84
1.00
1.02
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.16
165.93
165.70
141.97
141.90
141.84
134.51
127.82
125.61
121.41
121.23
121.04
114.00
113.69
111.10
109.12
F
F
Cl
O
N
H
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

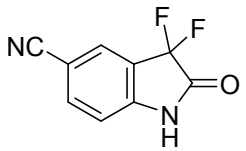

F
F
Cl
O
N
H

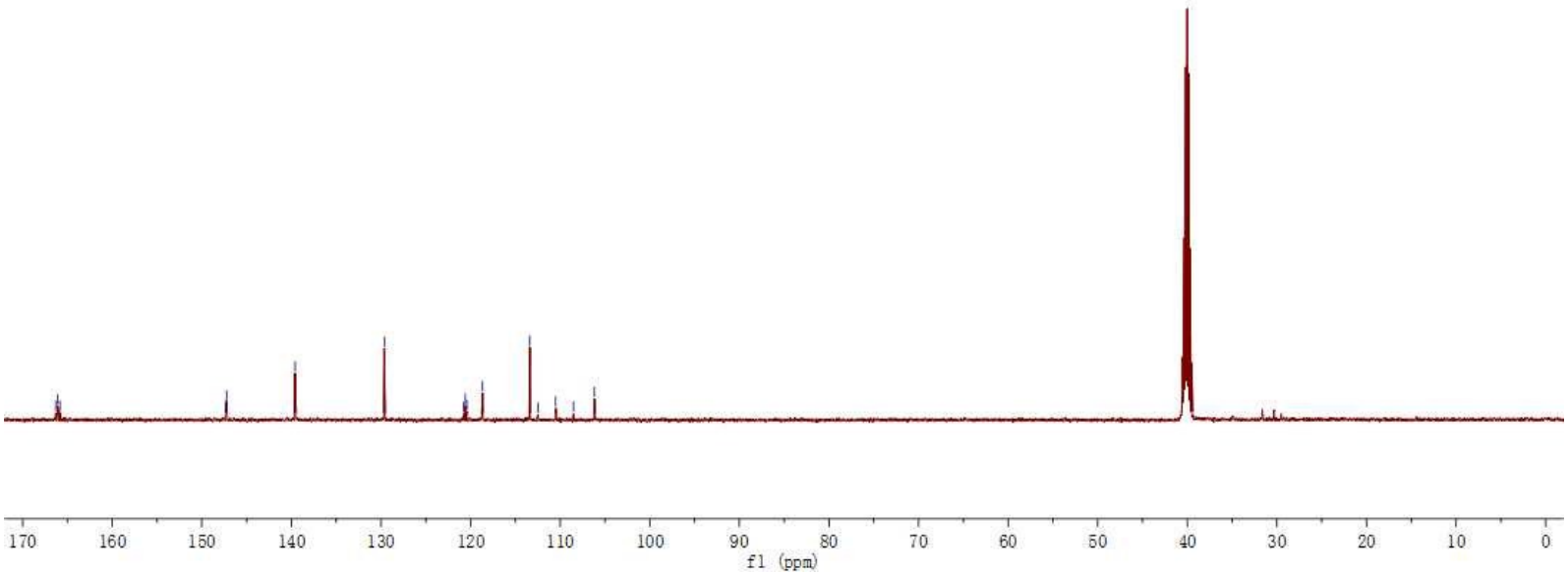
-111.10
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

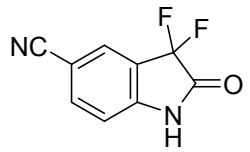

11.71
8.27
8.27
8.00
7.99
7.98
7.98
7.15
7.13
F
F
NC
O
N
H


0.95
1.00
1.05
0.95
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

166.30
166.07
165.84
147.30
147.24
147.18
139.59
129.63
120.77
120.58
120.46
118.67
113.38
112.30
110.51
108.52
106.18






F
F
NC
O
N
H

-111.51
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
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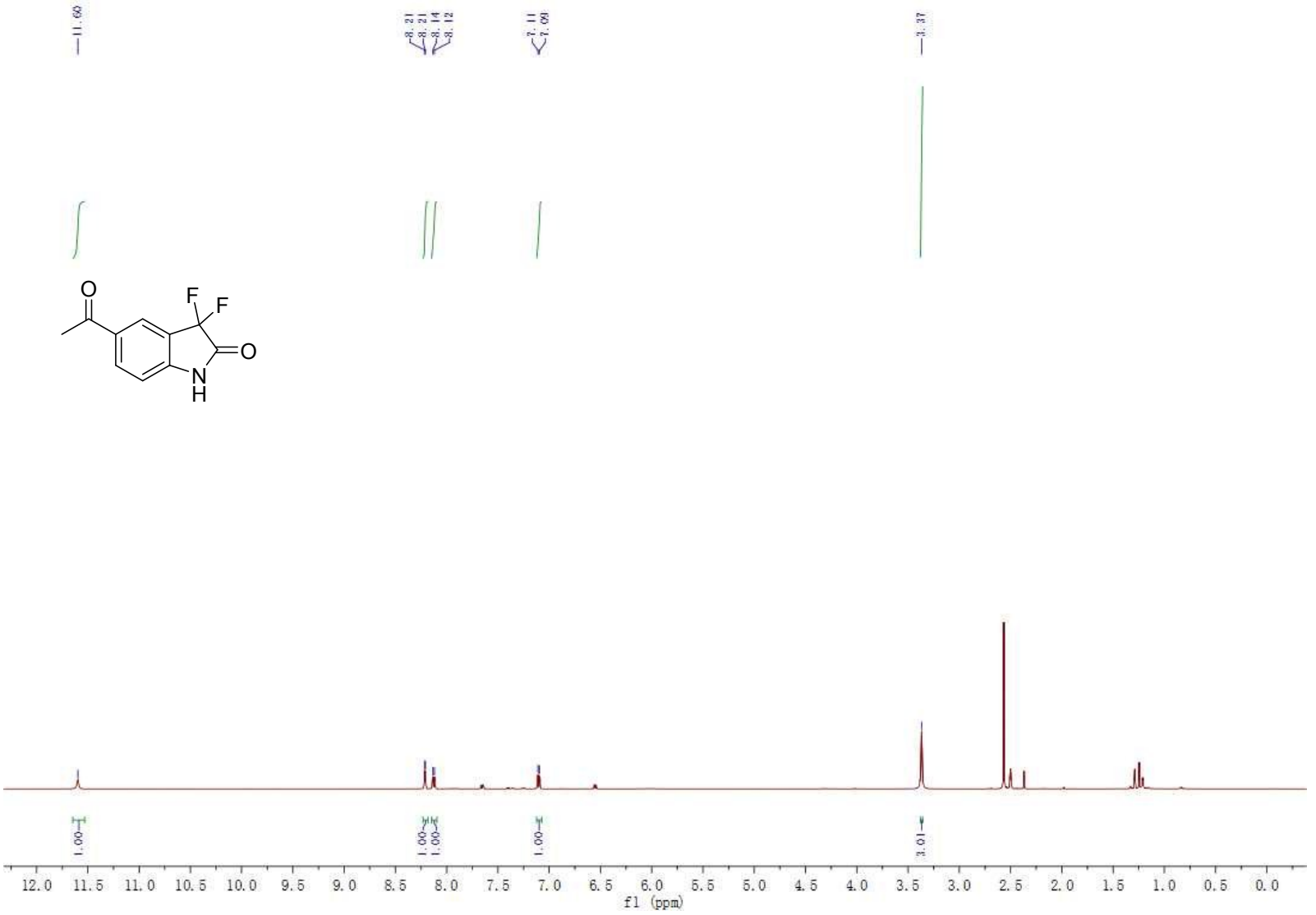
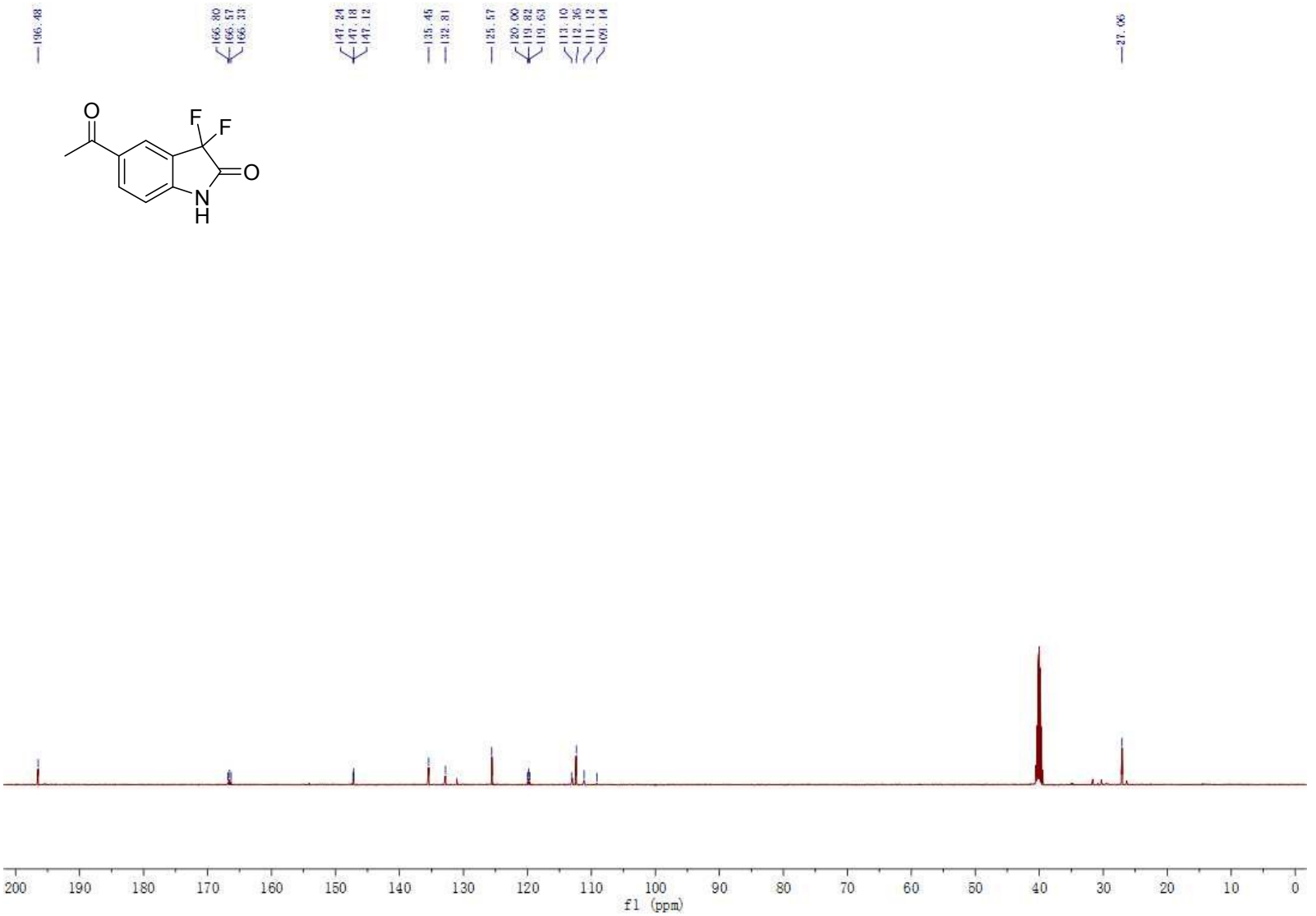
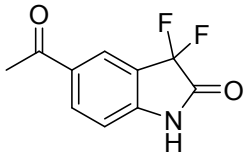
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


11.69
8.21
8.21
8.14
8.12
7.11
7.09
3.37
O
F
F
O
N
H
1.00
1.00
1.00
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.48
166.80
166.57
166.33
147.24
147.18
147.12
135.45
132.81
125.57
120.00
119.82
119.63
113.10
112.36
111.12
109.14
27.06
O
F
F
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
F
F
O
N
H

-111.18
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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-120
-130
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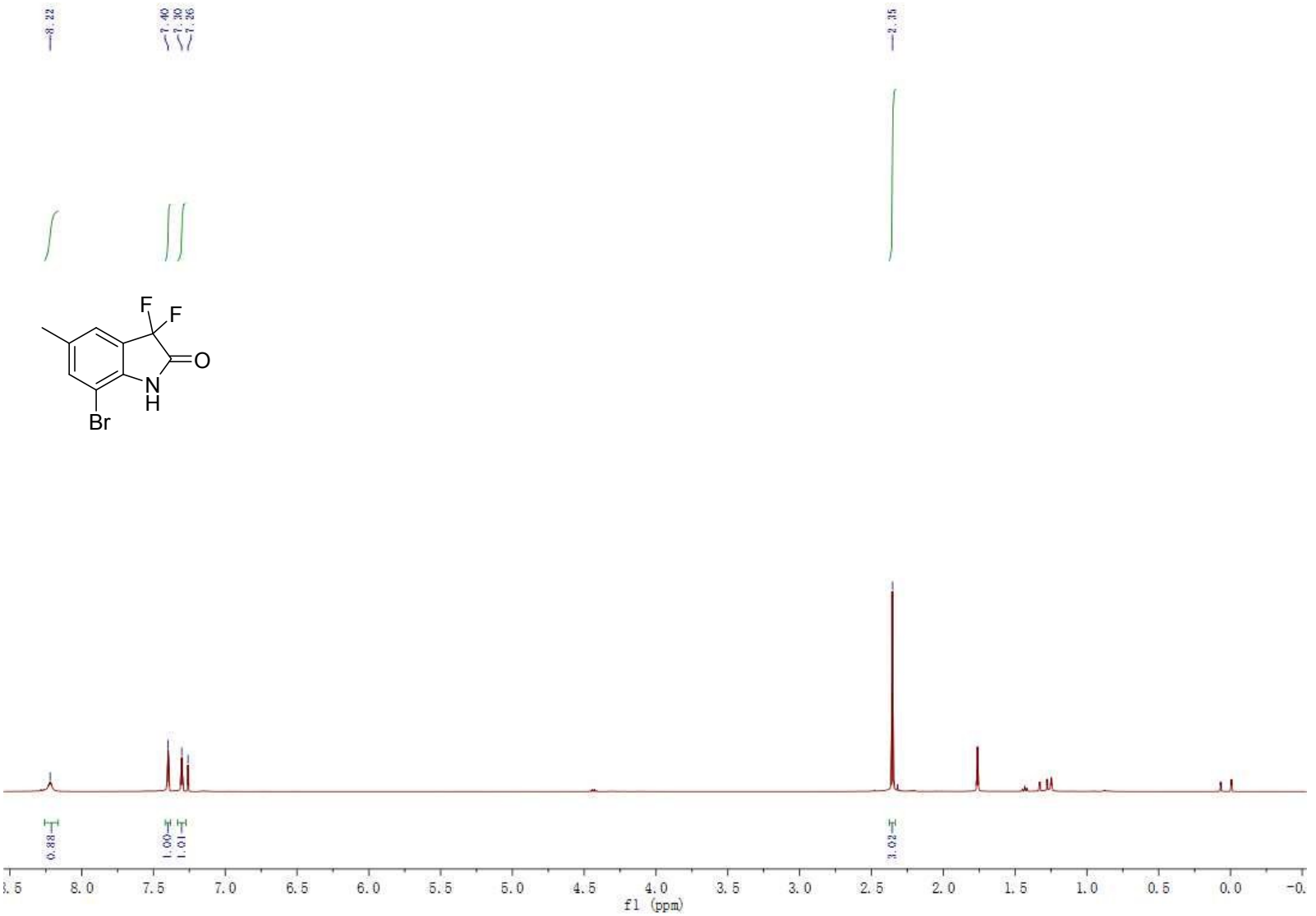
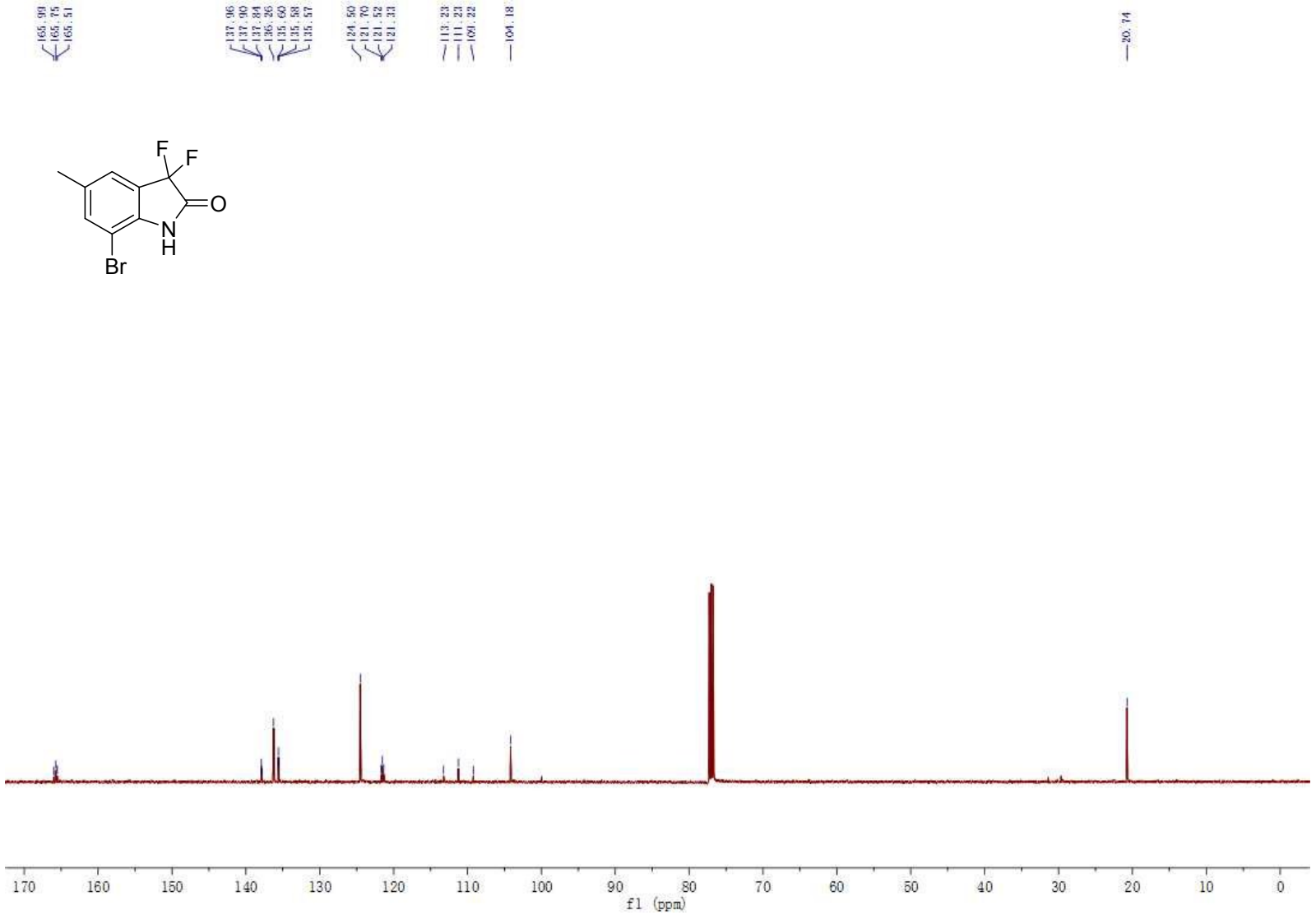
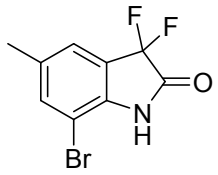
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.22
7.40
7.30
7.26
2.35
F
F
O
N
H
Br
0.88
1.00
1.01
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.99
165.75
165.51
137.96
137.90
137.84
136.26
135.60
135.58
135.57
124.59
121.70
121.52
121.33
113.23
111.23
109.22
104.18
20.74
F
F
O
N
H
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
N
H
Br

-110.28
20
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)


7.69
7.55
7.53
7.53
7.52
7.50
7.50
7.48
7.47
7.46
7.45
7.45
7.44
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7.43
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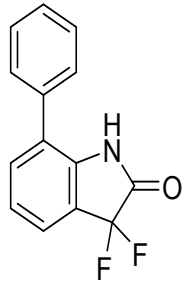
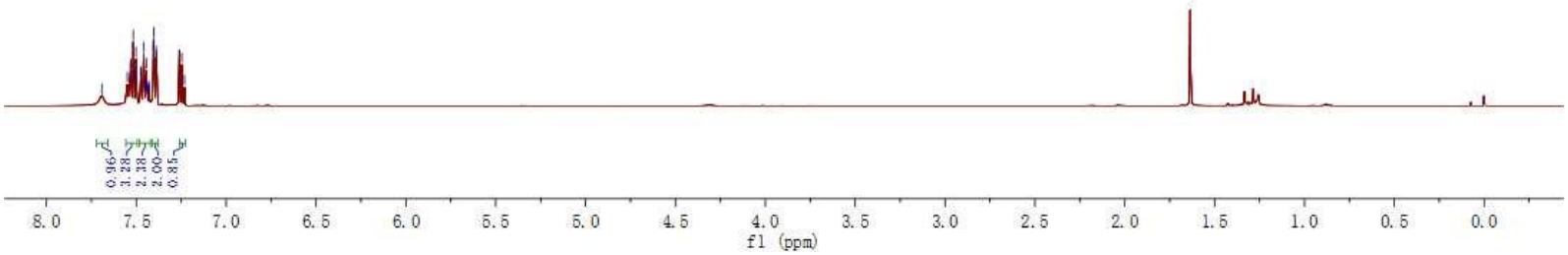
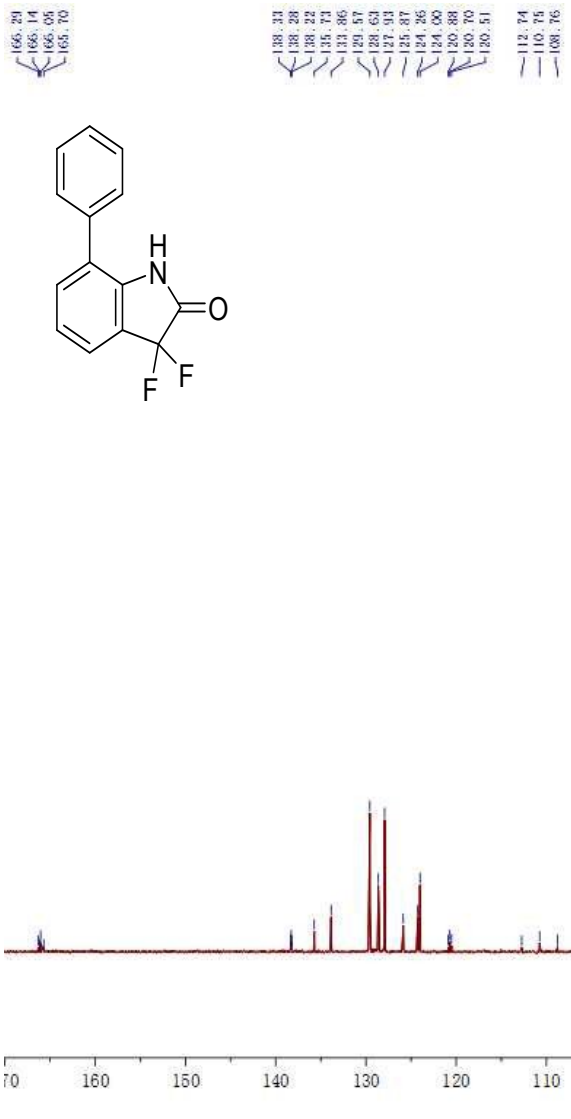
7.41
7.40
7.39
7.39
7.25
7.23


H
N
O
F
F


0.96
3.28
2.38
2.00
0.85
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.29
166.14
166.05
165.70
138.33
138.28
138.22
135.73
133.86
129.57
128.63
127.93
125.87
124.26
124.00
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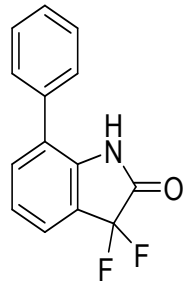
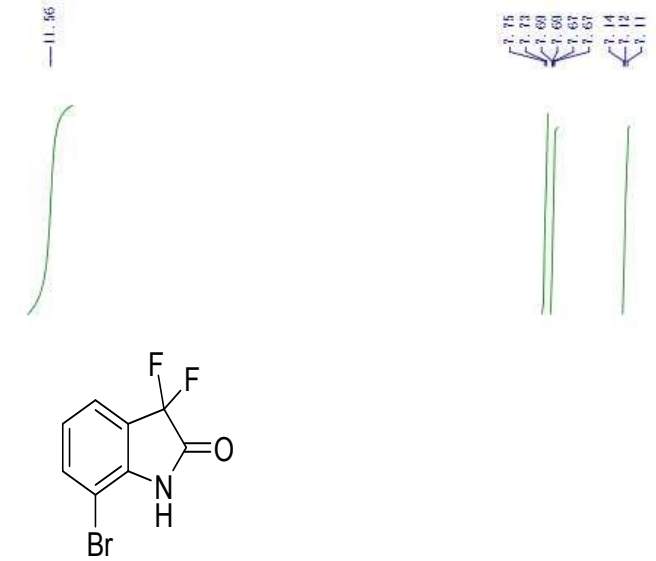
120.70
120.51
112.74
110.75
108.76
H
N
O
F
F
f1 (ppm)


H
N
O
F
F

-110.96
20
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)


11.56
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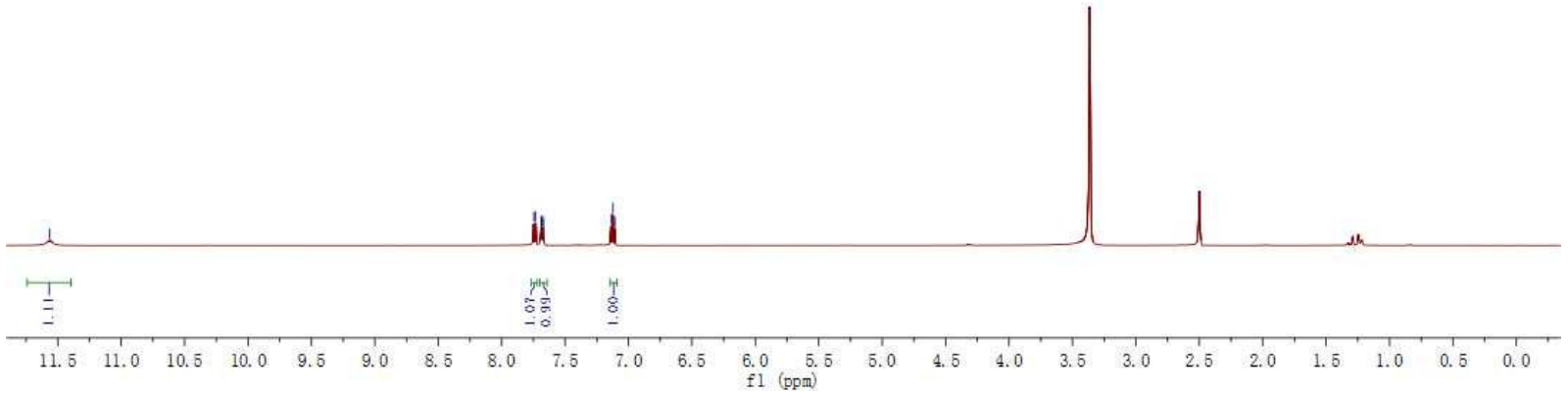
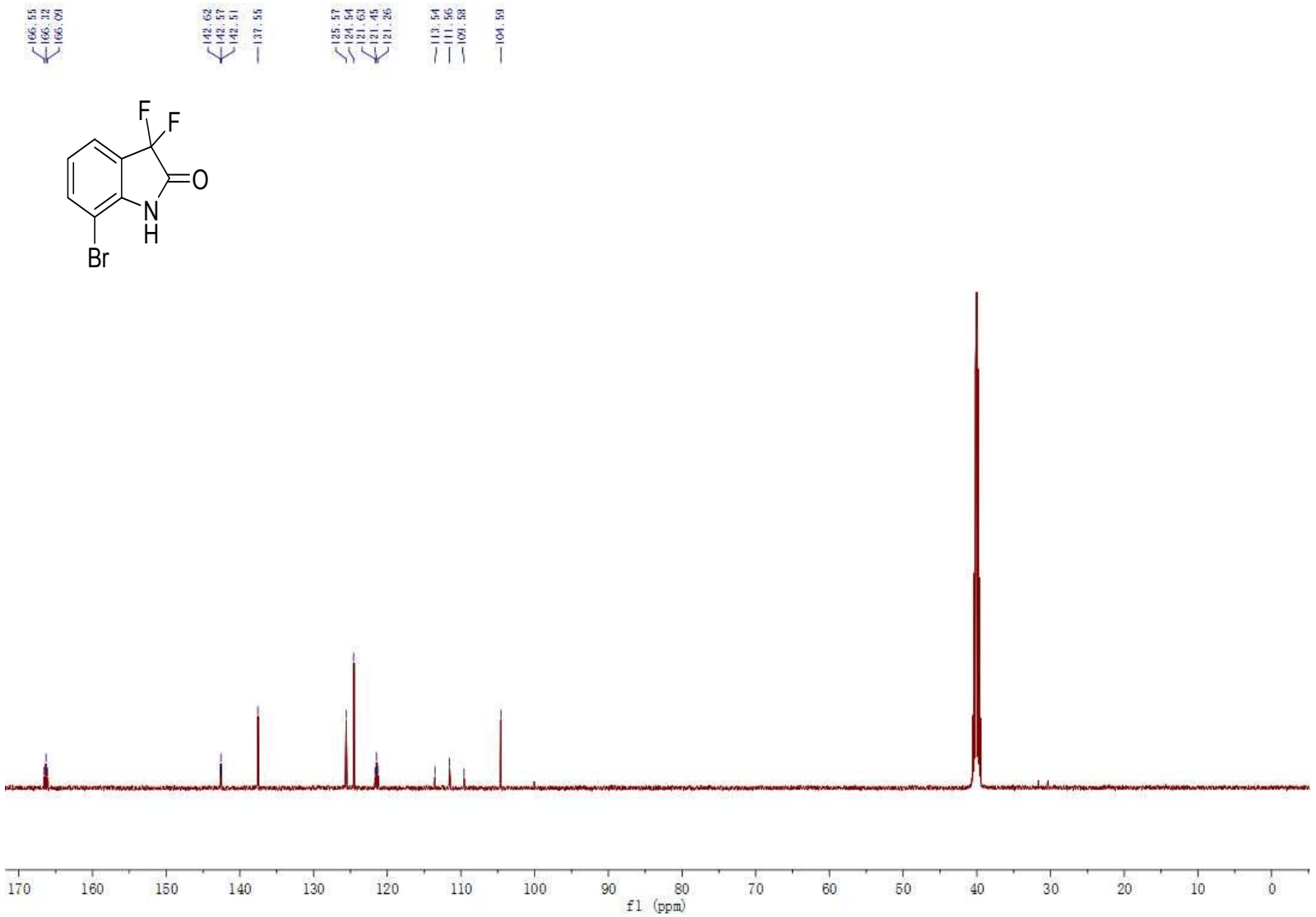
7.67
7.67
7.14
7.12
7.11
F
F
O
N
H
Br


1.11
1.07
0.93
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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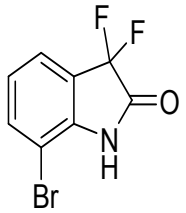
166.32
166.09
142.62
142.57
142.51
137.55
125.57
124.54
121.63
121.45
121.26
113.54
111.56
109.58
104.59
F
F
O
N
H
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
N
H
Br

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-10
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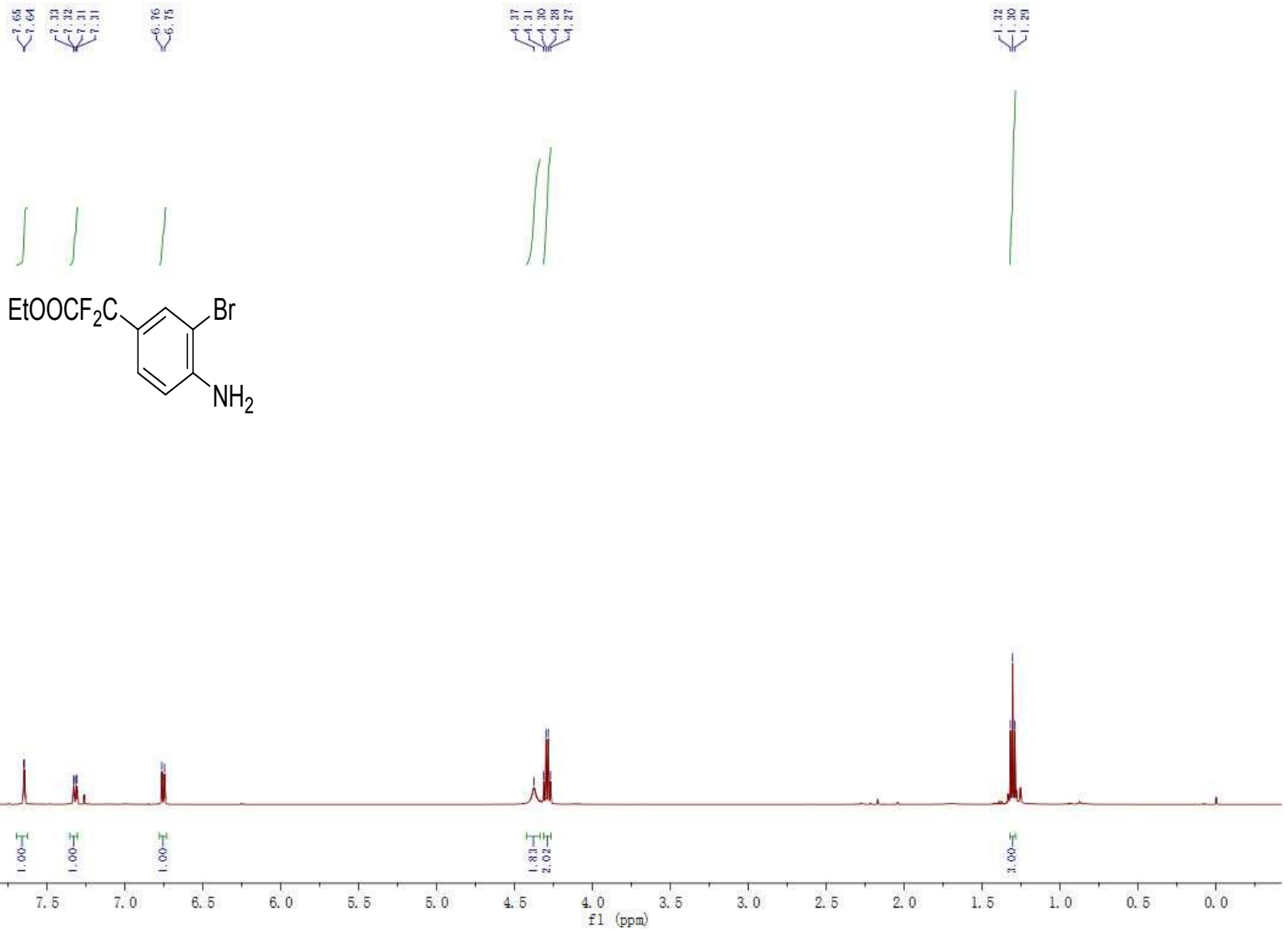
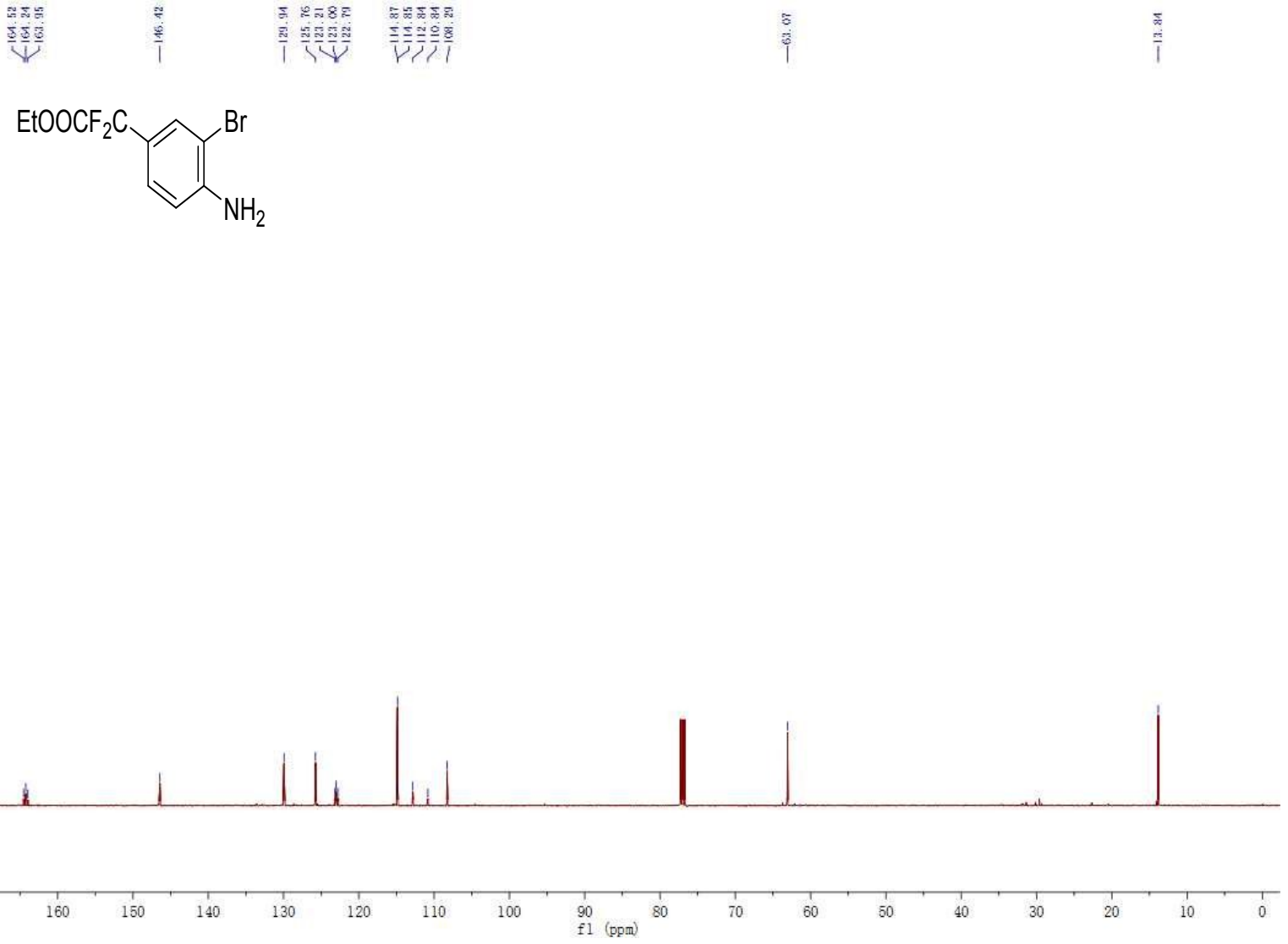
-170
-180
-190
-200
-210
f1 (ppm)


7.65
7.64
7.33
7.32
7.31
7.31
6.76
6.75
1.37
1.31
1.30
1.28
1.27
1.32
1.30
1.29
EtOOCF2C
Br
NH2
1.00
1.00
1.00
1.83
2.02
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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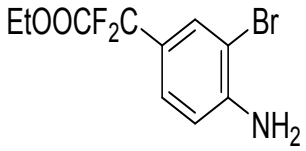
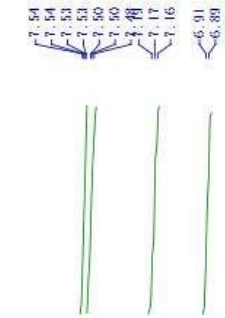
164.24
163.95
146.42
129.94
125.76
123.21
123.00
122.79
114.87
114.85
112.84
110.84
108.29
63.67
13.84
EtOOCF2C
Br
NH2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


EtOOCF2C
Br
NH2

-102.33
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)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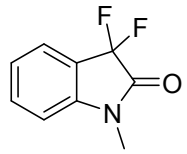
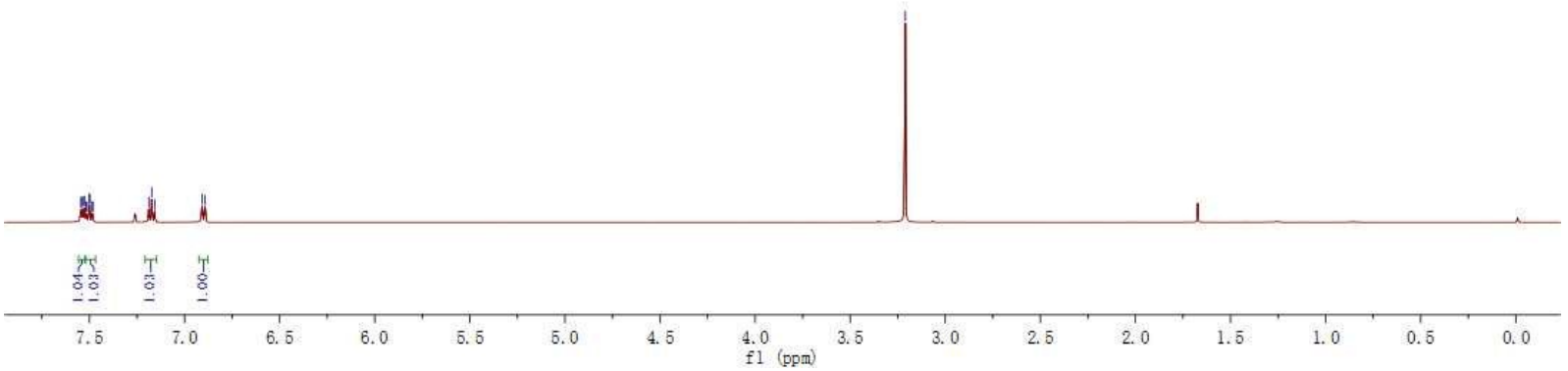
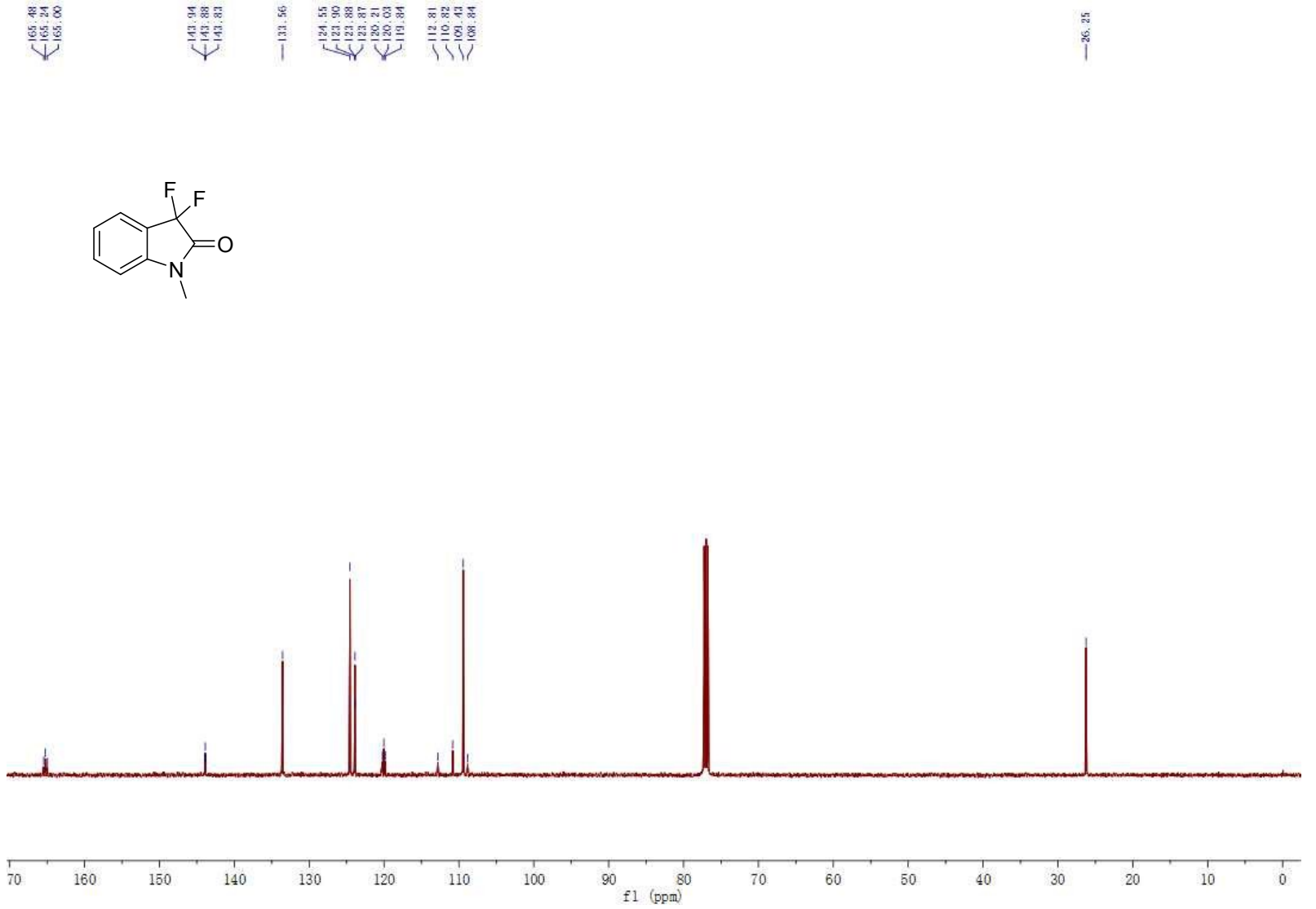
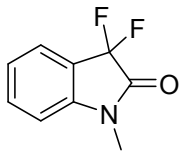
7.54
7.53
7.53
7.50
7.50
7.17
7.16
6.91
6.89

3.21


F
F
O
N


1.04
1.03
1.03
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.48
165.24
165.00
143.94
143.88
143.83
133.56
124.55
123.90
123.88
123.87
120.21
120.03
119.84
112.81
110.82
109.43
108.84
26.25
F
F
O
N
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
N

-112.37
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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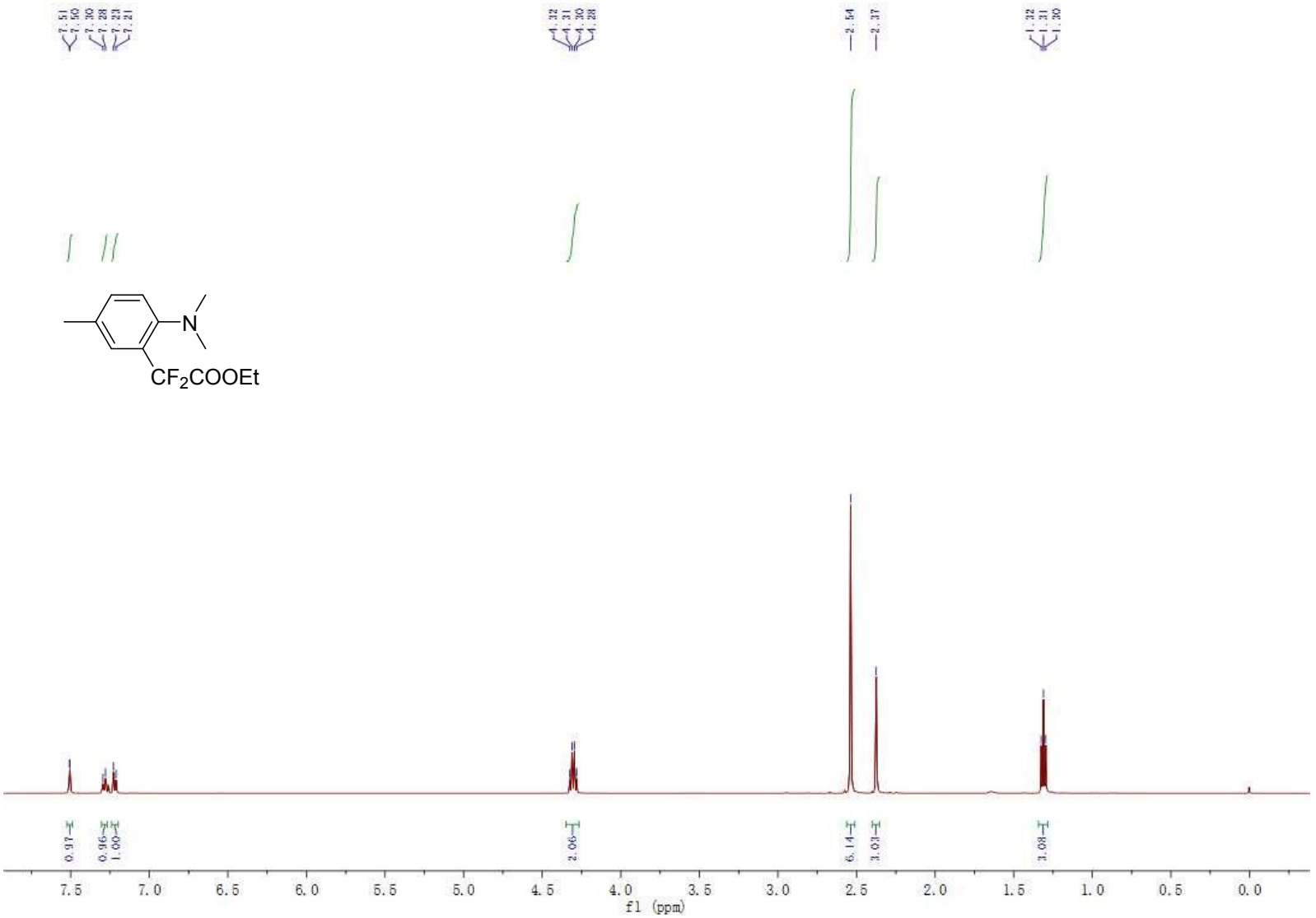
-170
-180
-190
-200
-210
f1 (ppm)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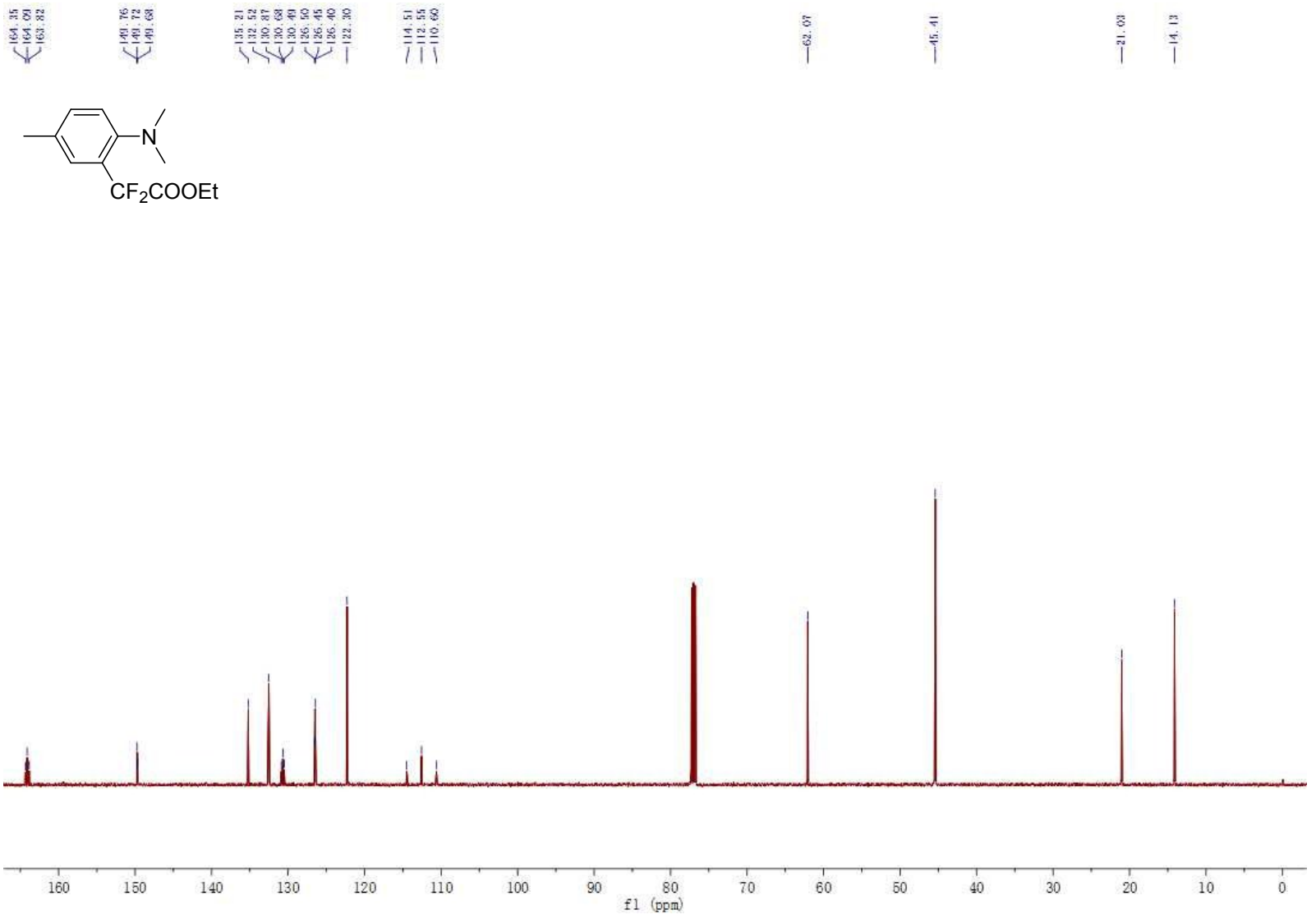
7.50
7.30
7.28
7.23
7.21
1.32
1.31
1.30
1.28
2.54
2.37
1.32
1.31
1.30
N
CF2COOEt
0.97
0.96
1.00
2.06
6.14
3.03
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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164.09
163.82
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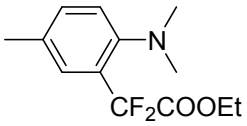
150.72
150.68
135.21
132.52
130.87
130.68
130.49
126.50
126.45
126.40
122.30
114.51
112.55
110.60
62.07
45.41
21.03
14.13
N
CF2COOEt
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
CF2COOEt

-98.33
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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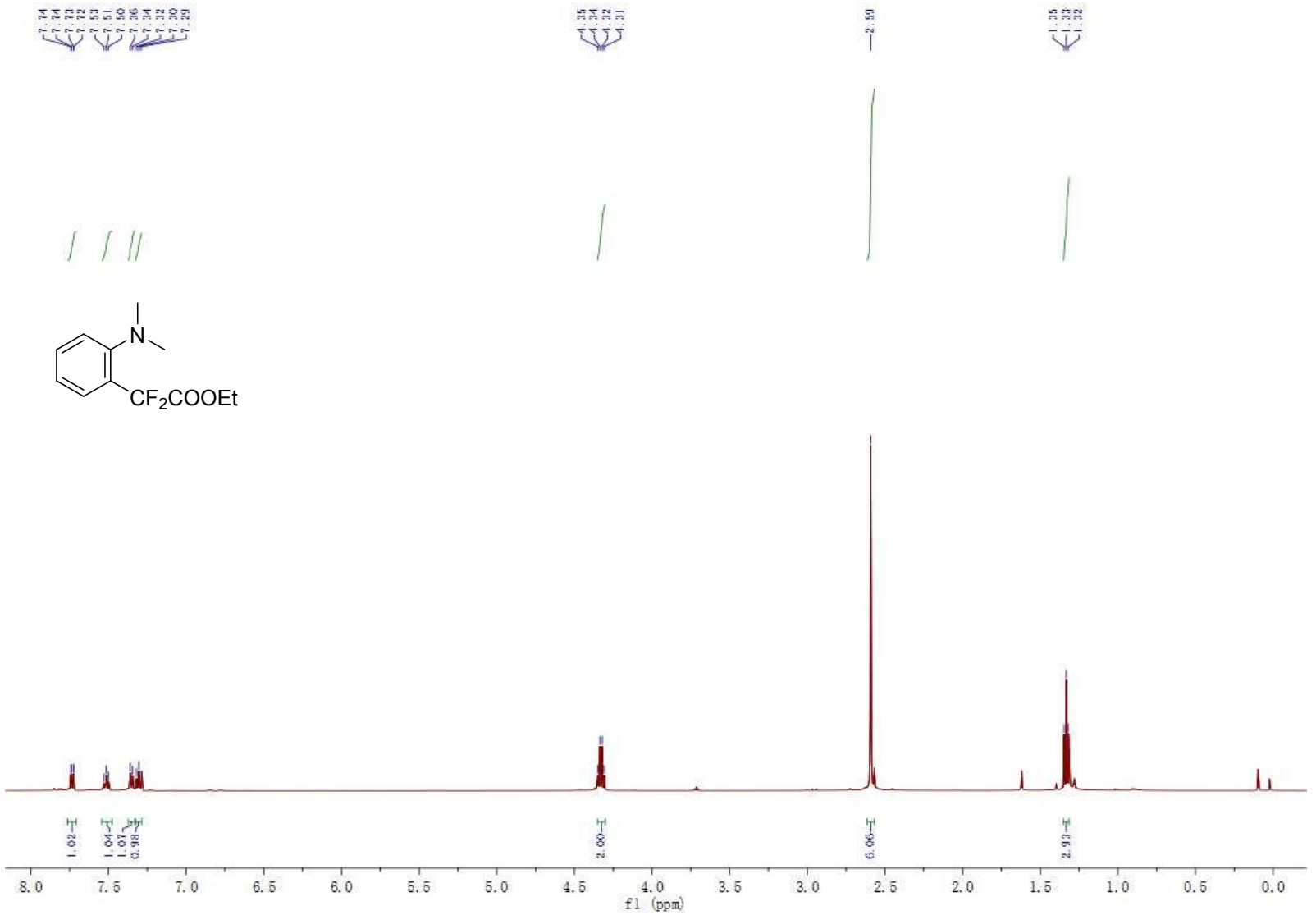
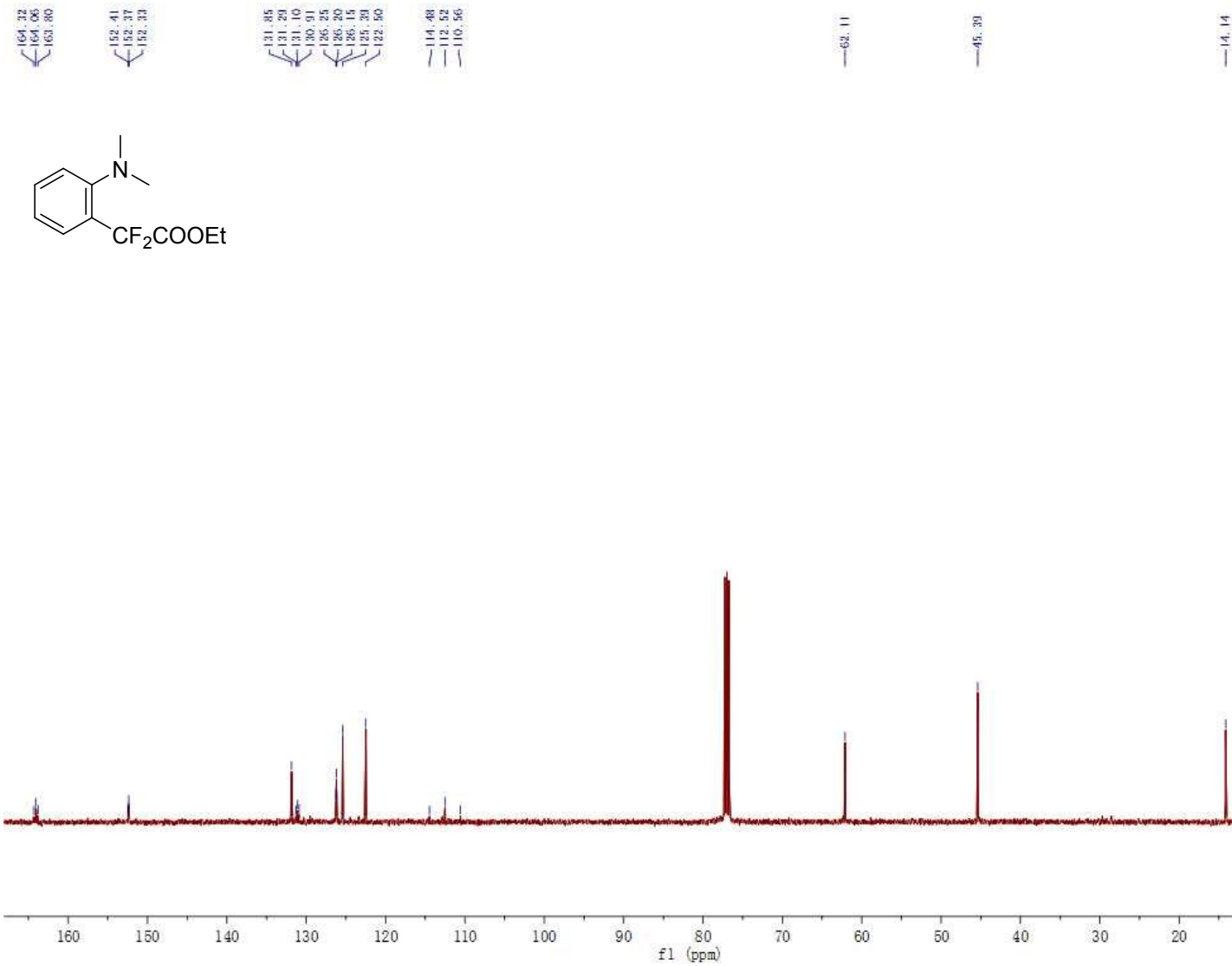
-170
-180
-190
-200
-210
f1 (ppm)


7.74
7.74
7.73
7.72
7.53
7.51
7.50
7.36
7.34
7.32
7.30
7.29
1.35
1.34
1.32
1.31
2.59
1.35
1.33
1.32
N
CF2COOEt
1.02
1.04
1.07
0.98
2.00
6.06
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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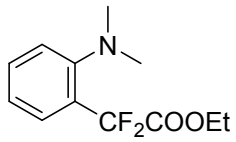
164.06
163.80
152.41
152.37
152.33
131.85
131.29
131.10
130.91
126.25
126.20
126.15
125.39
122.50
114.48
112.52
110.56
62.11
45.39
14.14
N
CF2COOEt
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
CF2COOEt

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-10
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-70
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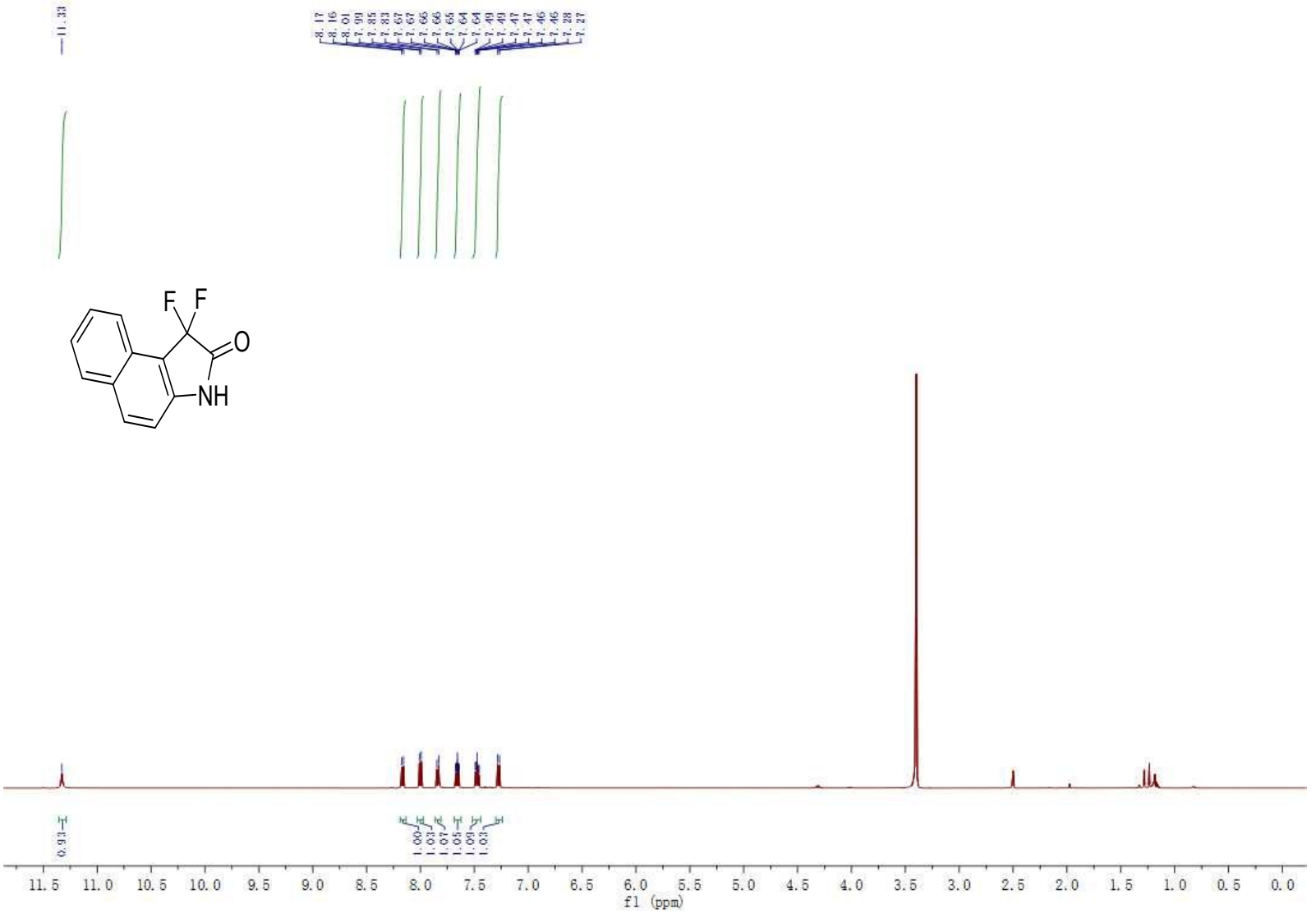
-160
-170
-180
-190
-200
-210
f1 (ppm)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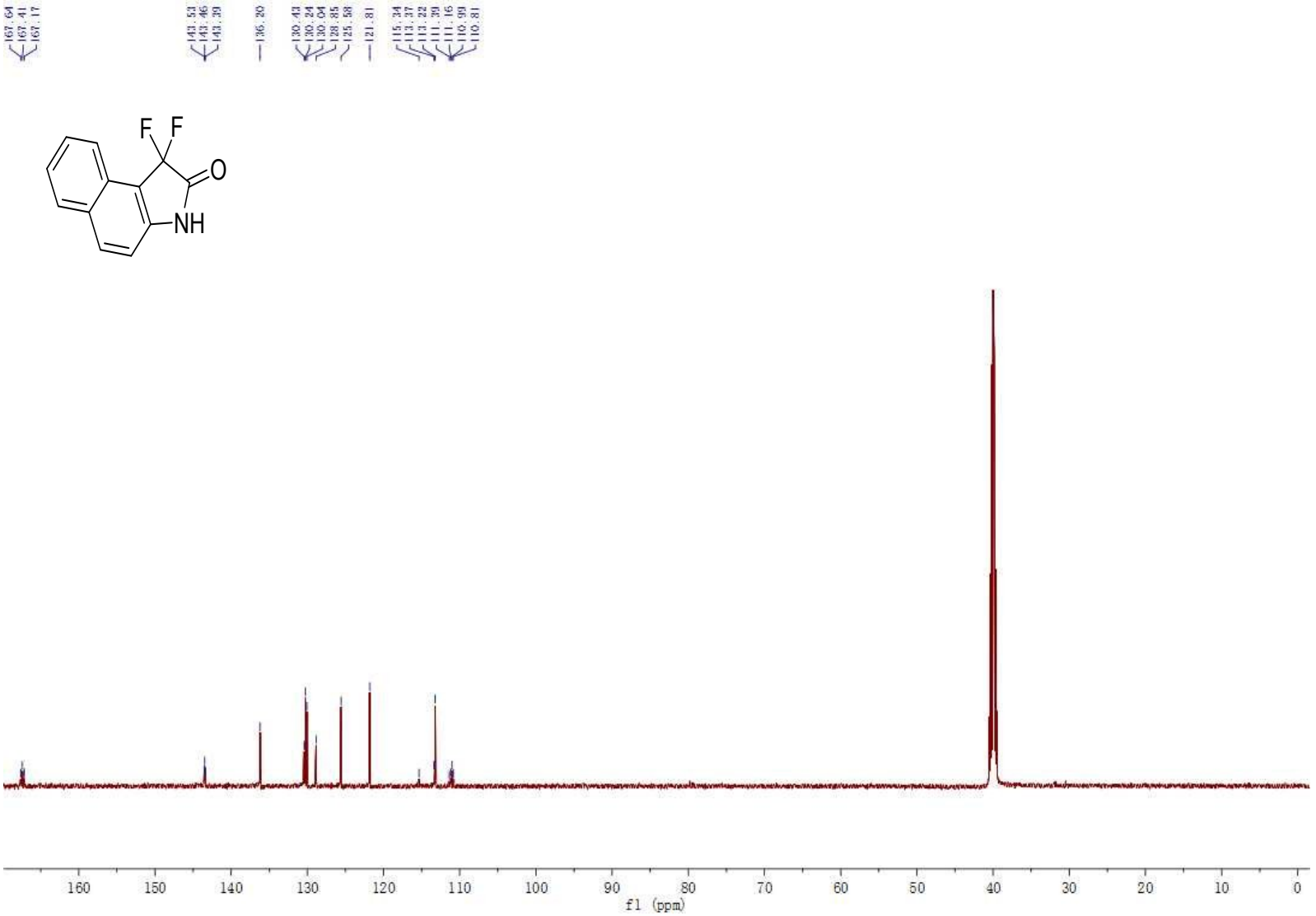
8.01
7.99
7.85
7.83
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.49
7.49
7.47
7.47
7.46
7.46
7.28
7.27
F
F
O
NH
0.93
1.00
1.03
1.07
1.05
1.09
1.03
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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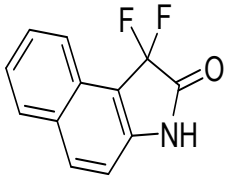
167.41
167.17
143.53
143.46
143.39
136.20
130.43
130.24
130.04
128.85
125.58
121.81
115.34
113.37
113.22
111.39
111.16
110.99
110.81
F
F
O
NH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
NH

-111.35
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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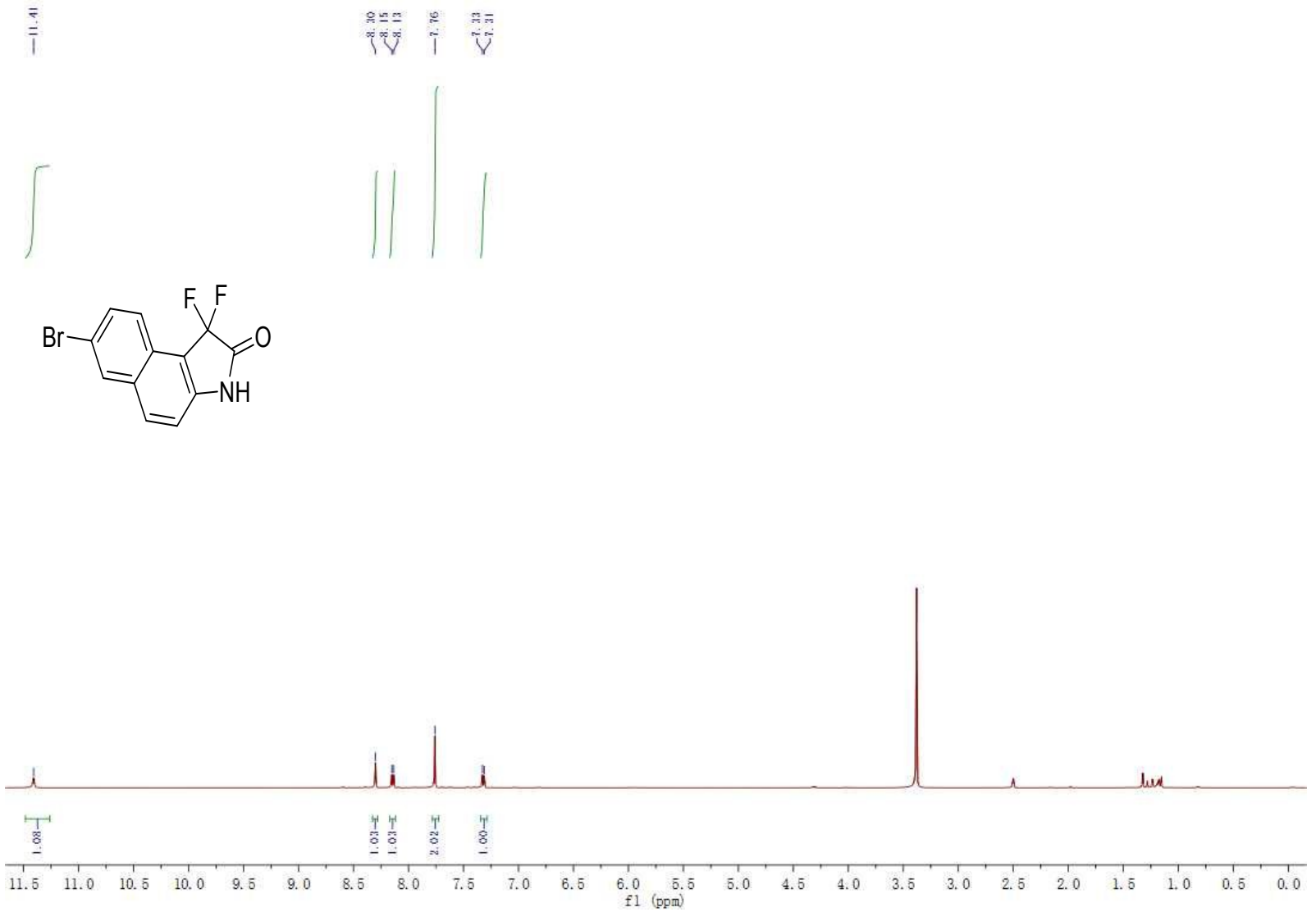
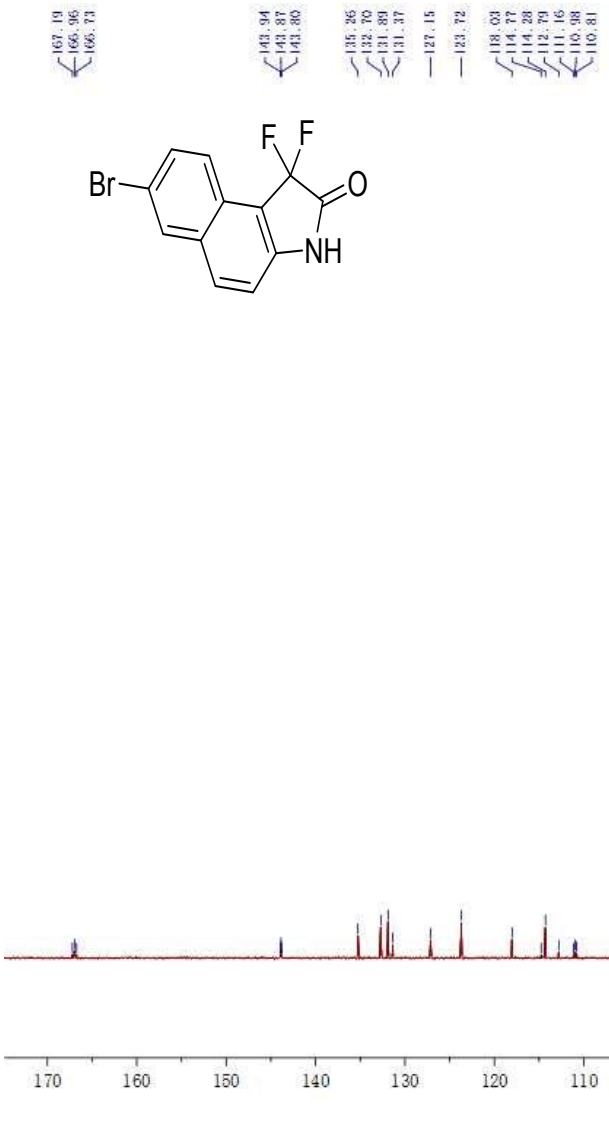
-170
-180
-190
-200
-210
f1 (ppm)


11.41
8.30
8.15
8.13
7.76
7.33
7.31
F
F
Br
O
NH
1.08
1.03
1.03
2.02
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.19
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166.73
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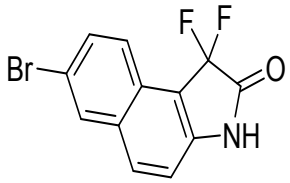
143.87
143.80
135.26
132.70
131.89
131.37
127.15
123.72
118.03
114.77
114.28
112.79
111.16
110.98
110.81
F
F
O
Br
NH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
Br
O
NH

-111.30
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10
0
-10
-20
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-50
-60
-70
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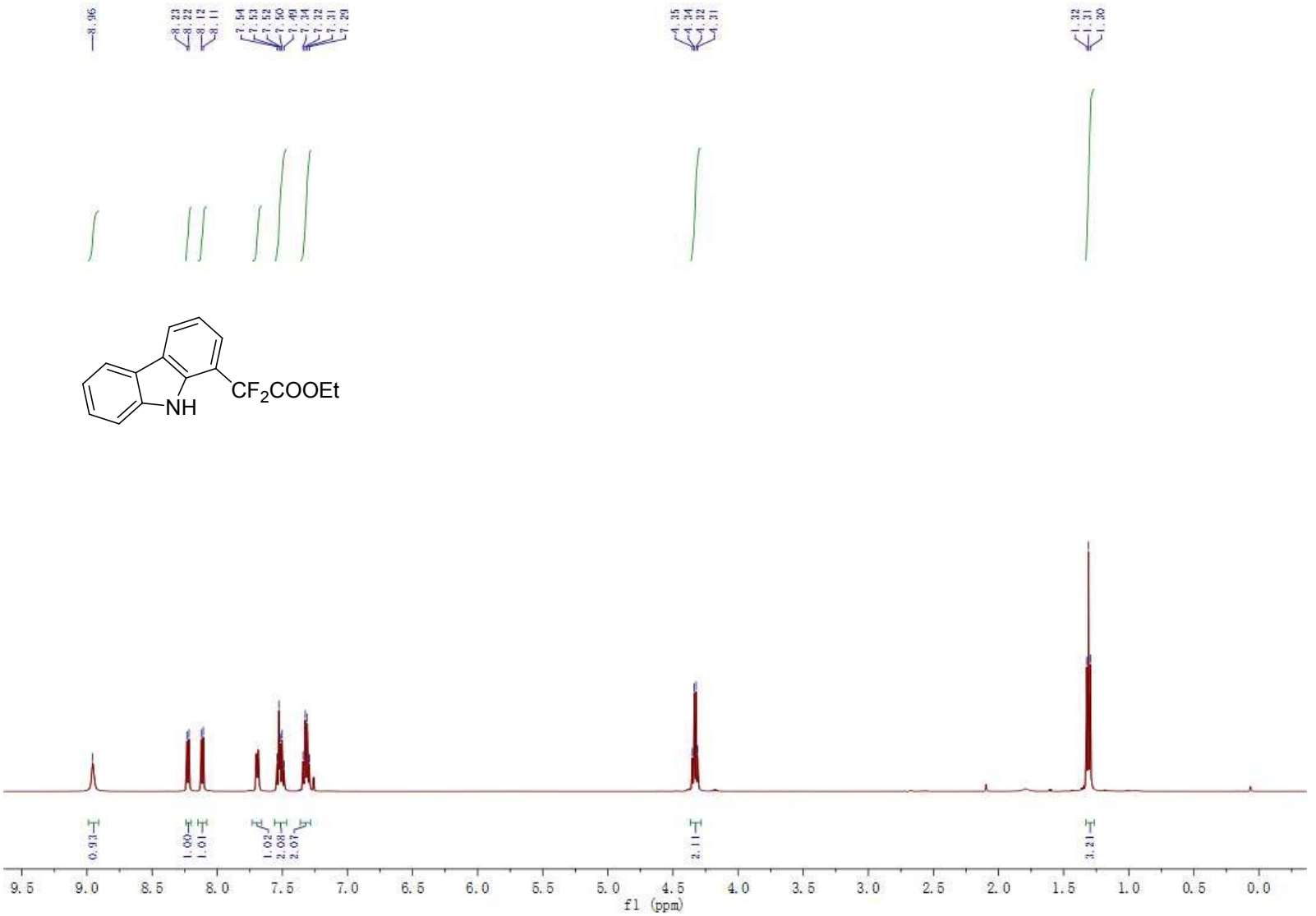
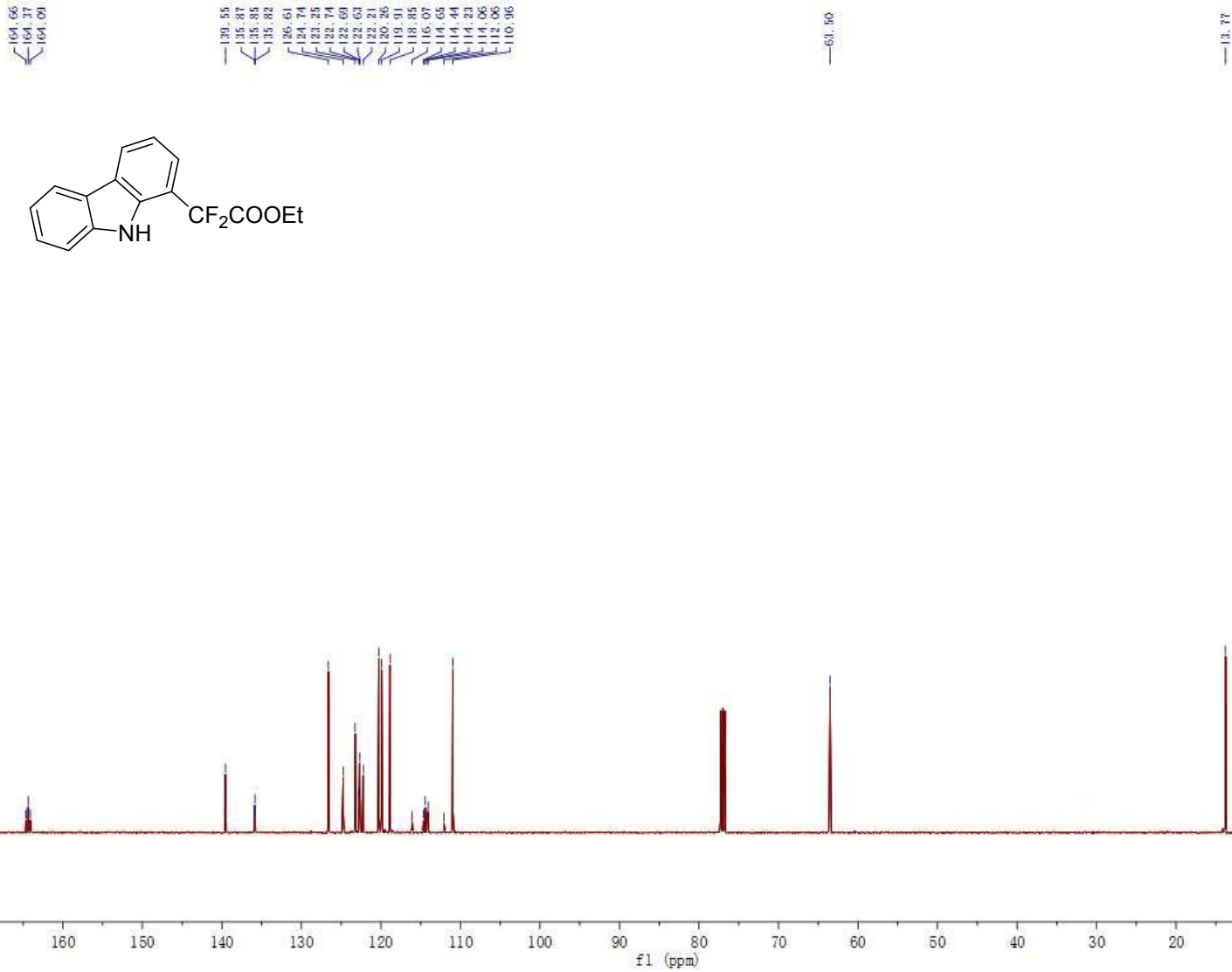
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.96
8.23
8.22
8.12
8.11
7.54
7.53
7.52
7.50
7.49
7.34
7.32
7.31
7.29
4.35
4.34
4.32
4.31
1.32
1.31
1.30
NH
CF2COOEt
0.93
1.00
1.01
1.02
2.08
2.07
2.11
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.66
164.37
164.09
139.55
135.87
135.85
135.82
126.61
124.74
123.25
122.74
122.69
122.63
122.21
120.26
119.91
118.85
116.07
114.65
114.44
114.23
114.06
112.06
110.96
63.50
13.77
NH
CF2COOEt
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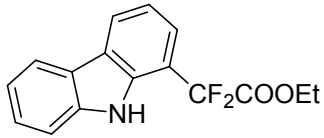
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
CF2COOEt

-104.33
20
10
0
-10
-20
-30
-40
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-60
-70
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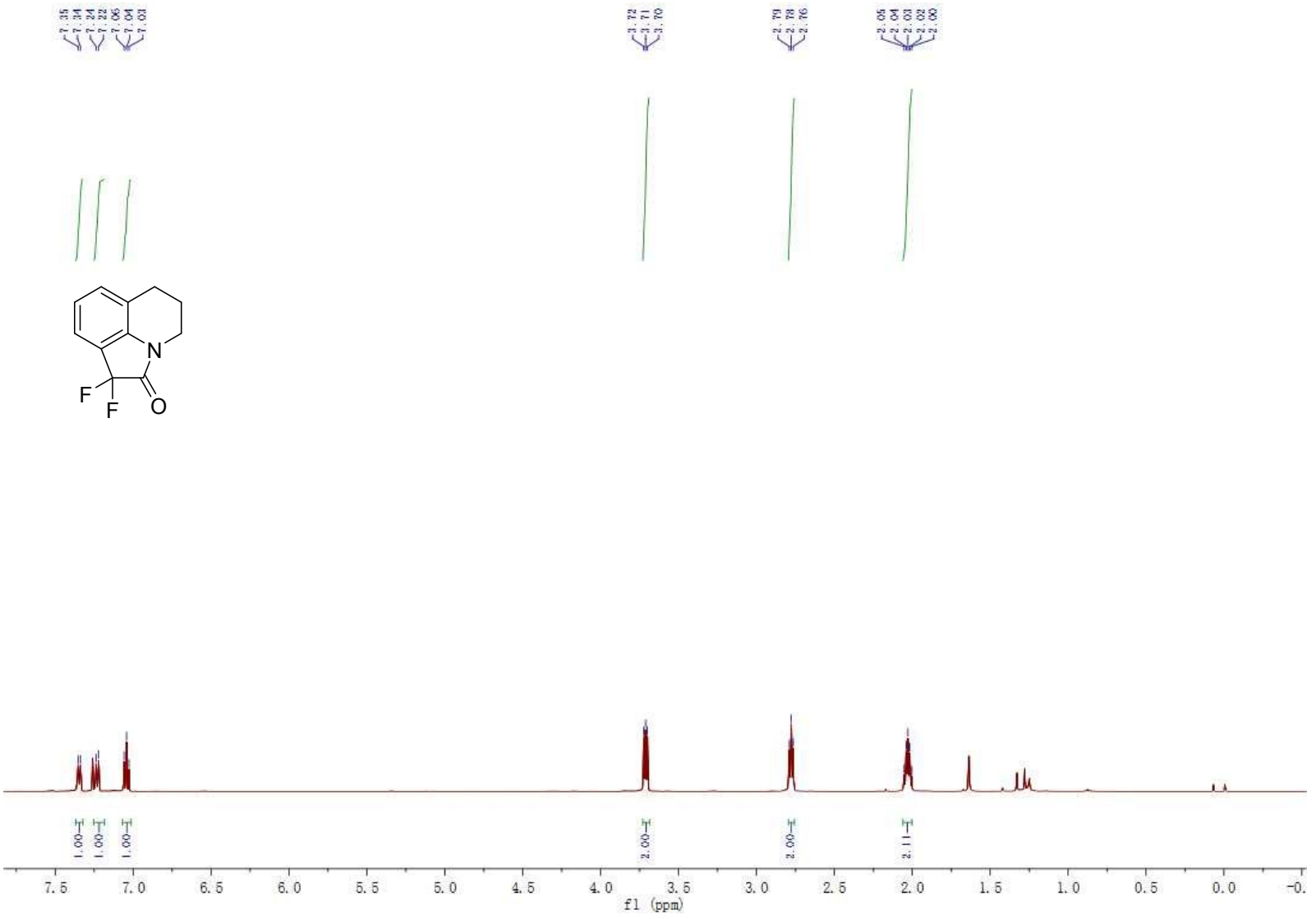
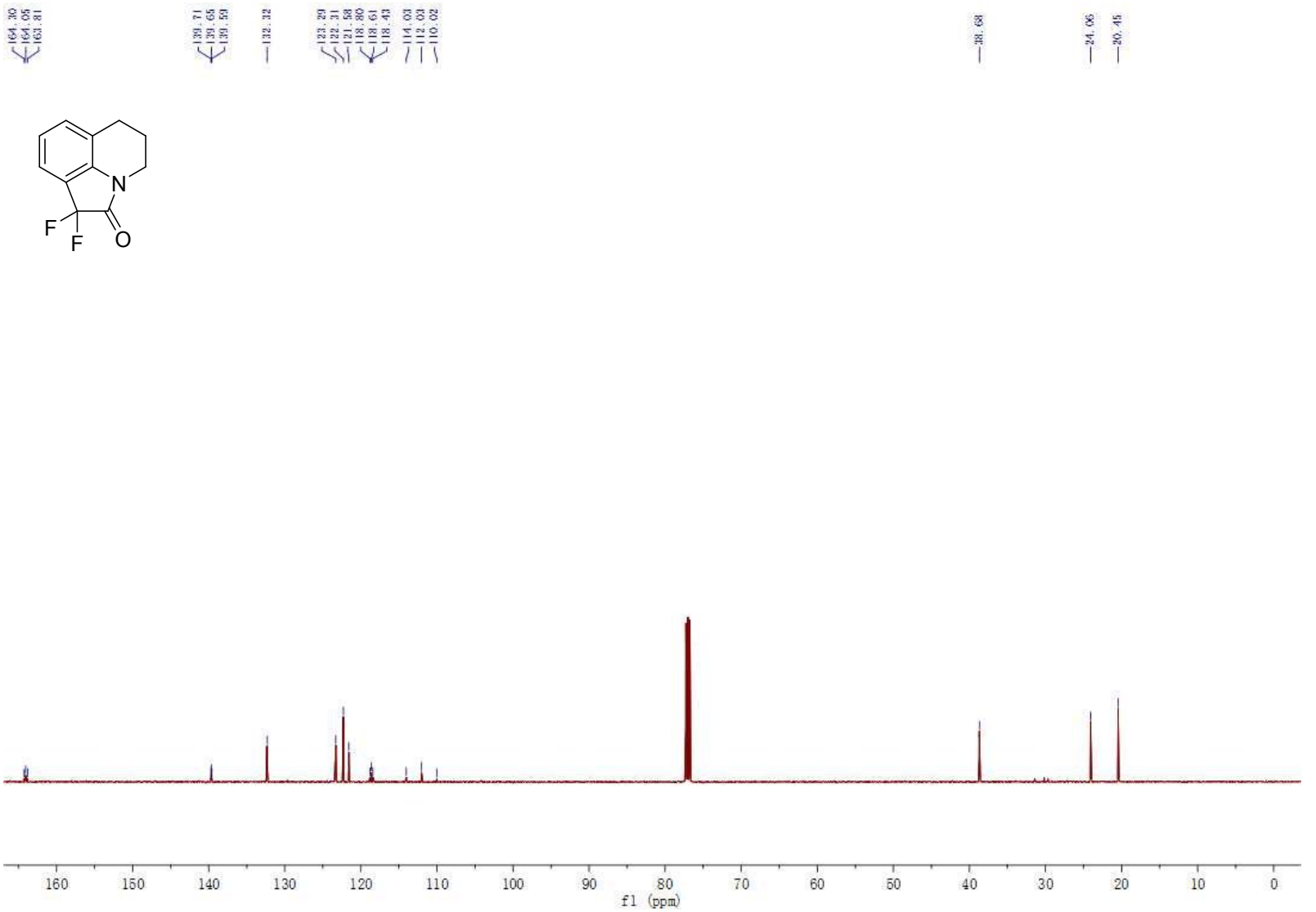
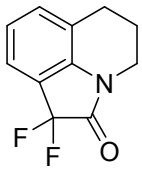
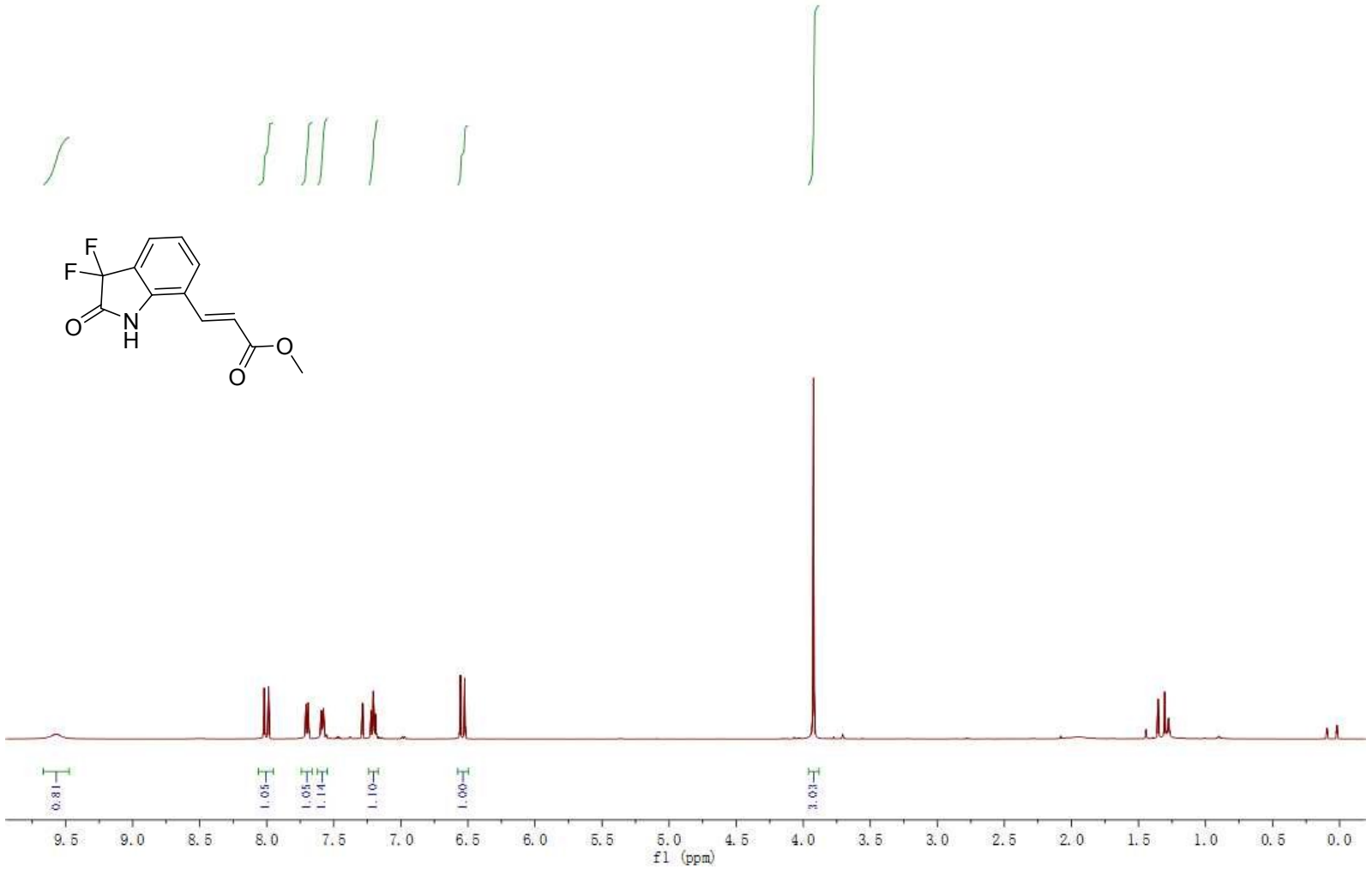
-170
-180
-190
-200
-210
f1 (ppm)

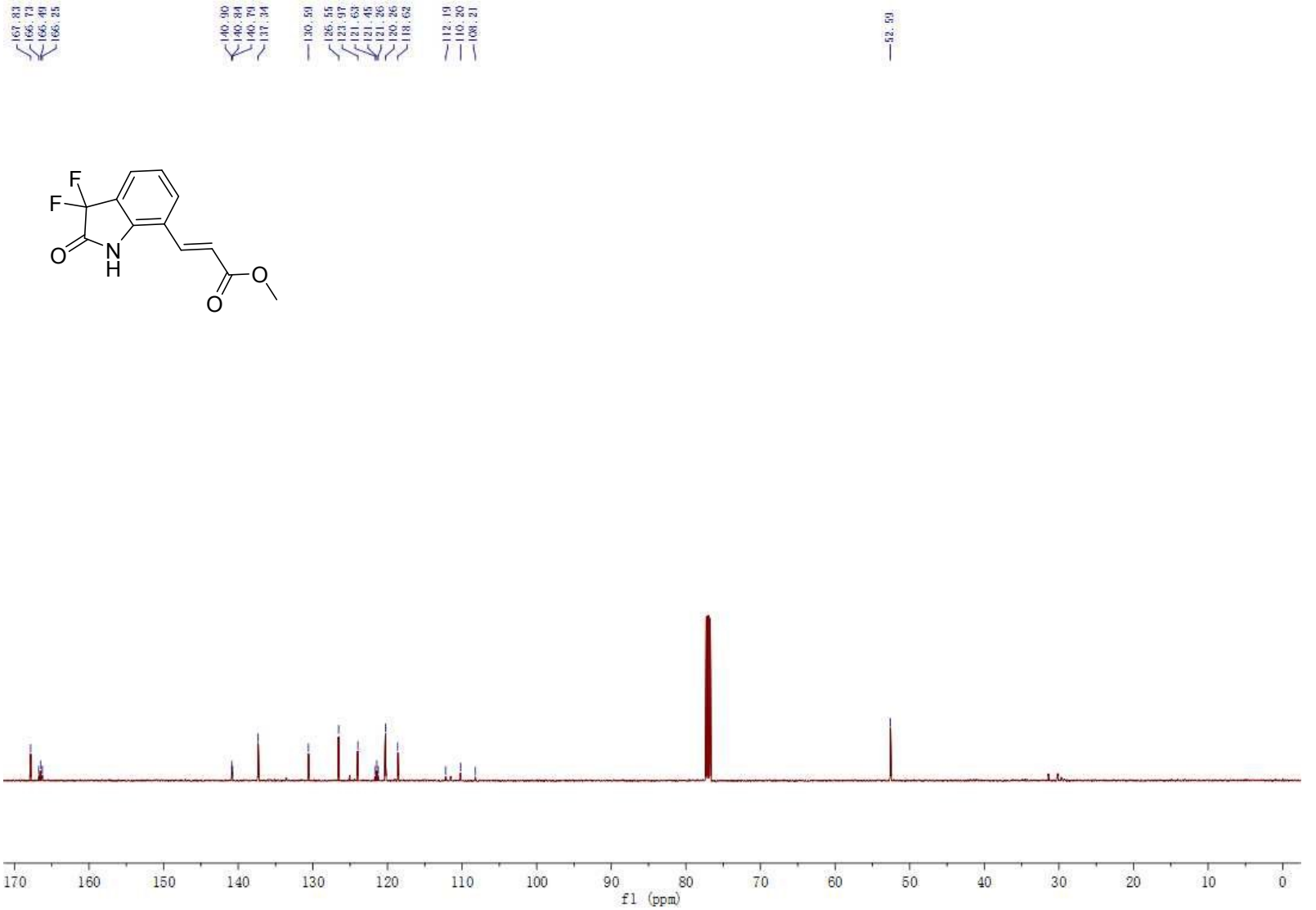

7.35
7.34
7.24
7.22
7.06
7.04
7.03
3.72
3.71
3.70
2.79
2.78
2.76
2.05
2.04
2.03
2.02
2.00
N
F
F
O
1.00
1.00
1.00
2.00
2.00
2.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

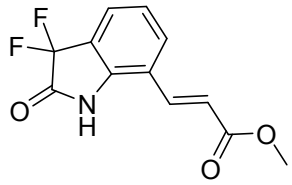

164.30
164.05
163.81
139.71
139.65
139.59
132.32
123.29
122.31
121.58
118.80
118.61
118.43
114.03
112.03
110.02
38.68
24.06
20.45
F
F
O
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
F
F
O

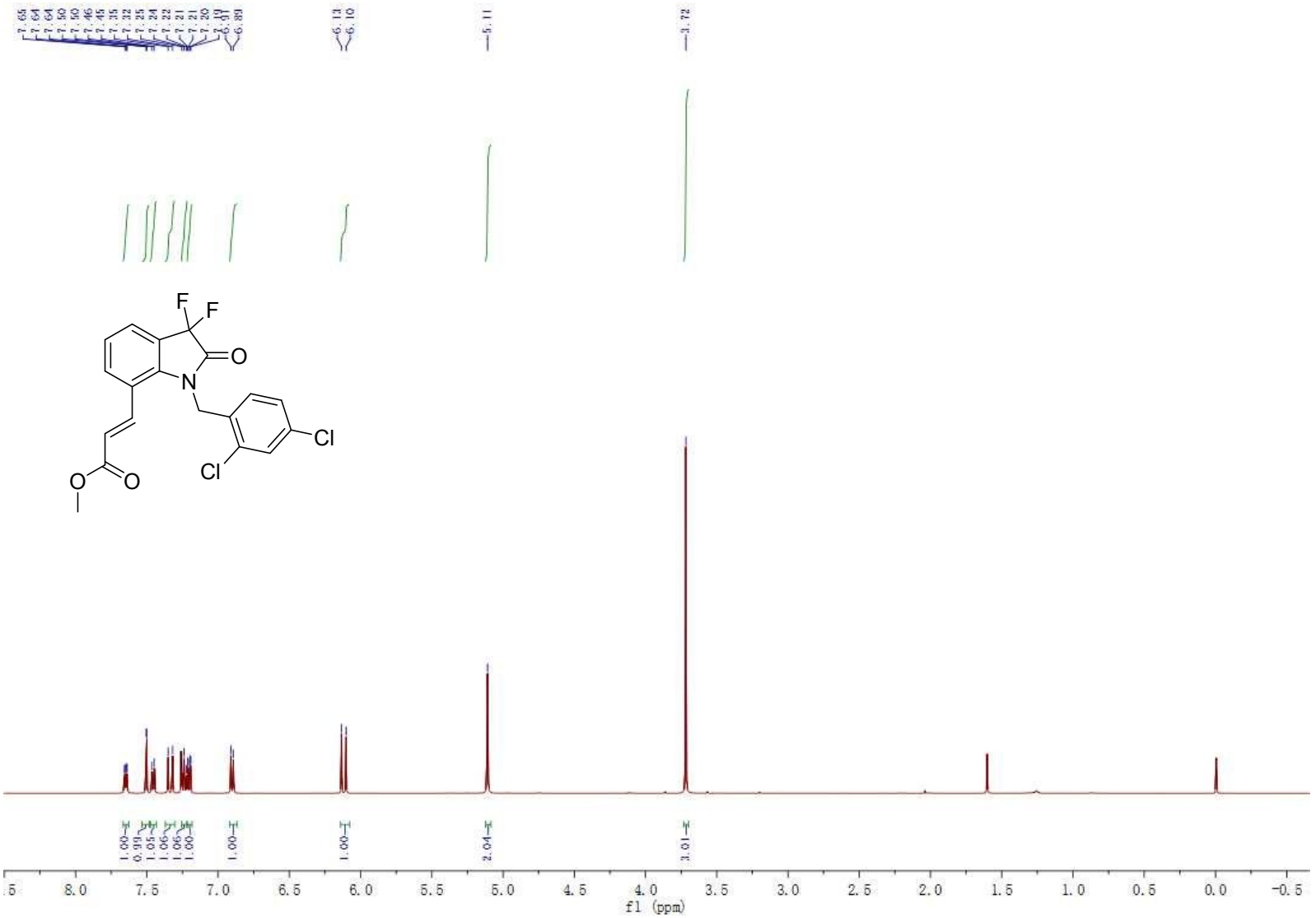
-112.18
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

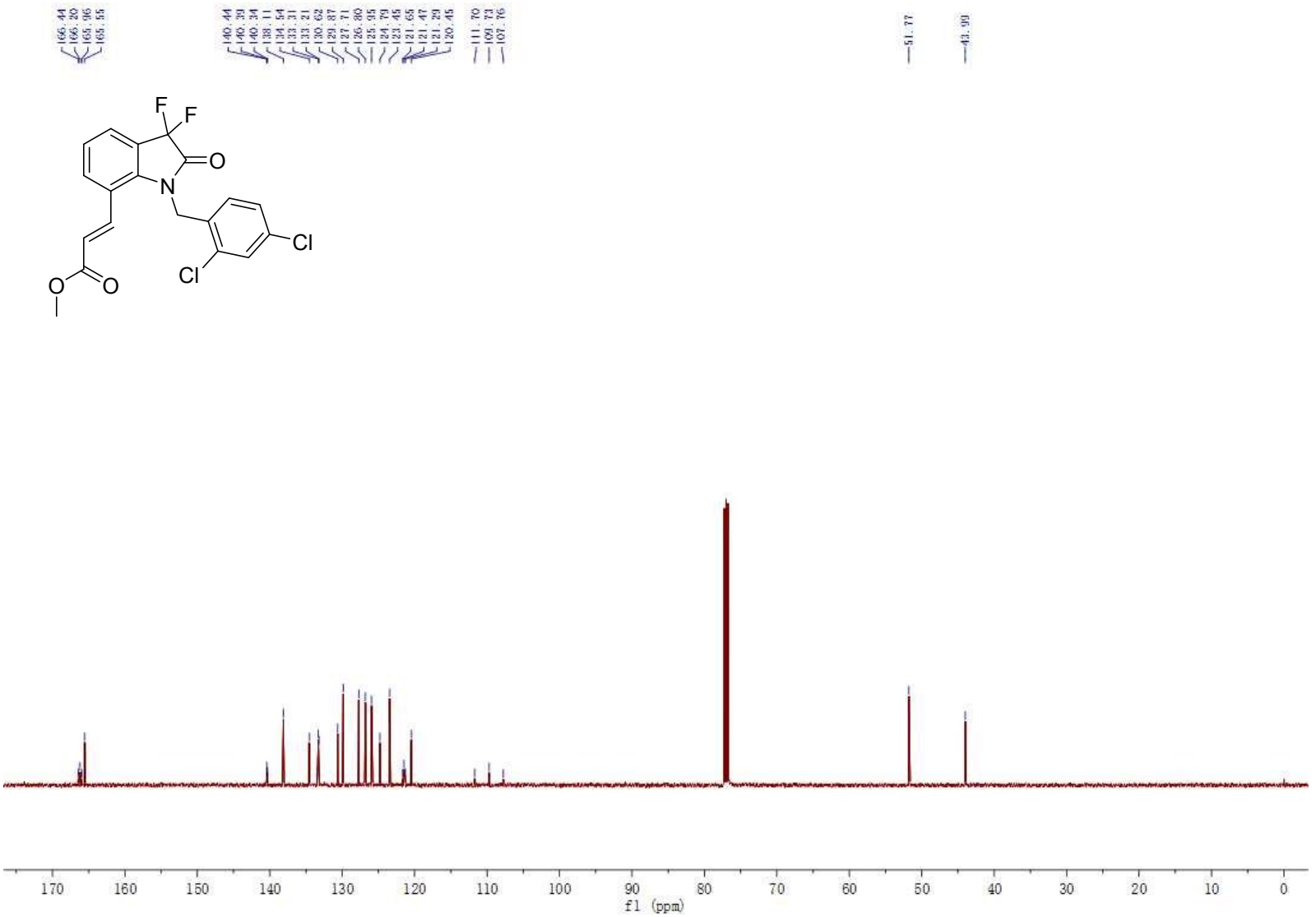

F
F
O
N
H
O
O
0.81
1.05
1.05
1.14
1.10
1.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

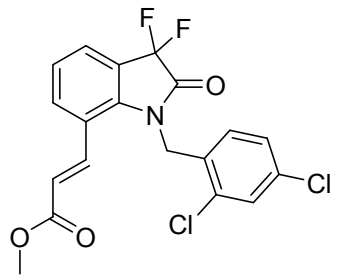

167.83
166.73
166.49
166.25
140.90
140.84
140.79
137.34
130.59
126.55
123.97
121.63
121.45
121.26
120.26
118.62
112.19
110.20
108.21
52.59
F
F
O
N
H
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
N
H
O
O

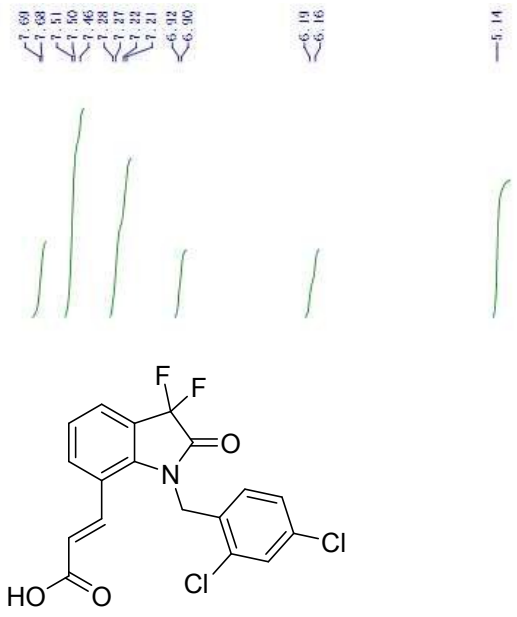
-111.89
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

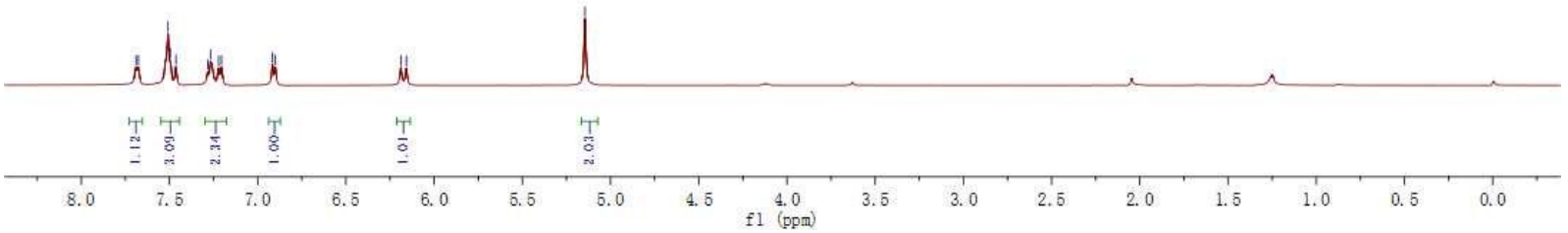

7.65
7.64
7.64
7.59
7.59
7.46
7.46
7.35
7.32
7.25
7.24
7.22
7.21
7.21
7.20
6.13
6.10
6.09
6.09
6.89
5.11
3.72
F
F
O
N
Cl
Cl
O
O
1.00
0.99
1.05
1.06
1.06
1.00
1.00
1.00
2.04
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

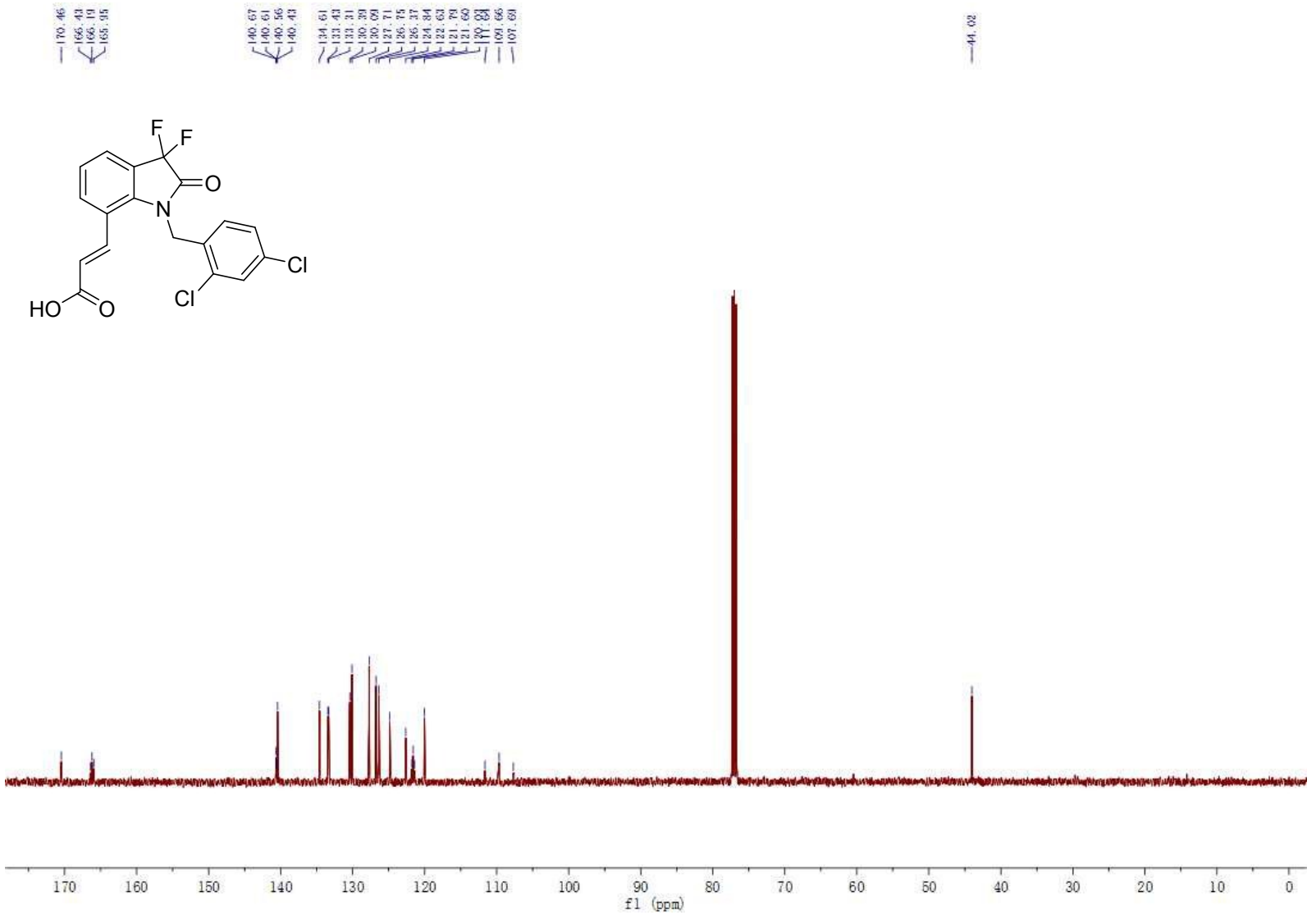

166.44
166.20
165.96
165.55
140.44
140.39
140.34
138.11
134.54
133.31
133.21
130.62
129.87
127.71
126.80
125.95
124.79
123.45
121.65
121.47
121.29
120.45
111.70
109.73
107.76
51.77
43.99
F
F
O
N
Cl
Cl
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

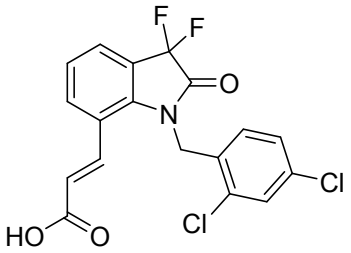

F
F
O
N
Cl
Cl
O
O

-111.05
20
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)

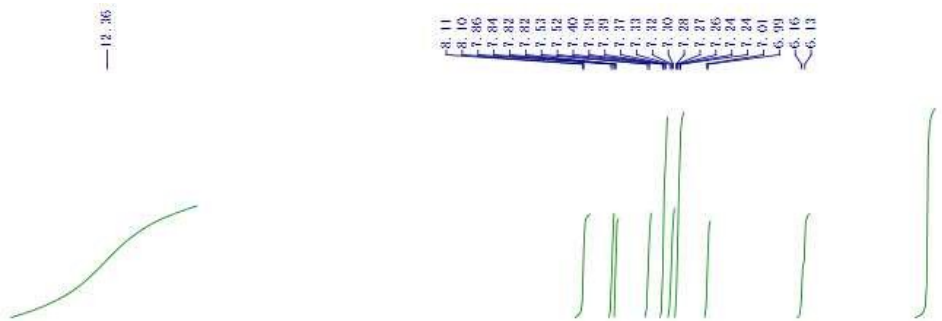

F
F
O
N
Cl
Cl
HO
O

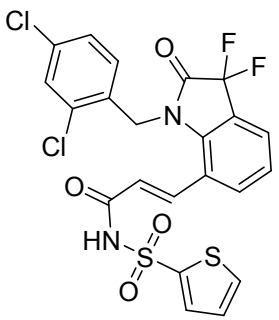

1.12
3.09
2.34
1.00
1.01
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

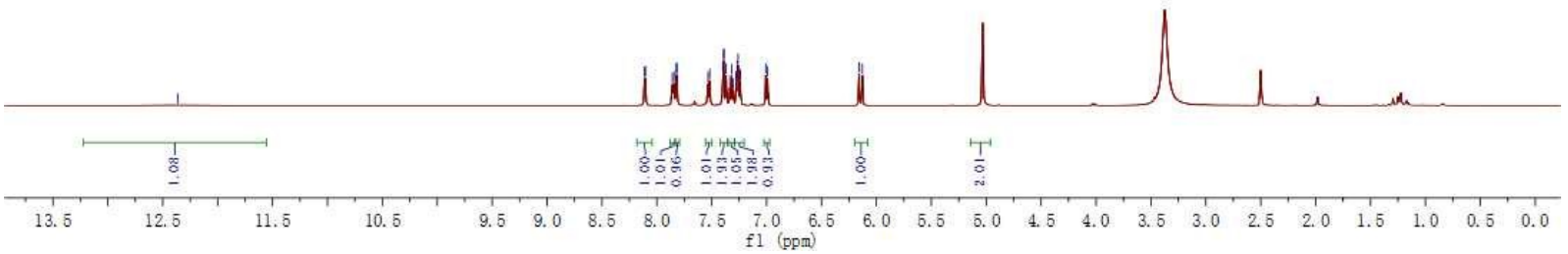

170.46
166.43
166.19
165.95
140.67
140.61
140.56
140.43
134.61
133.43
133.31
130.39
130.09
127.71
126.75
126.37
124.84
122.63
121.79
121.60
120.03
117.83
109.66
107.69
41.02
F
F
O
N
Cl
Cl
HO
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

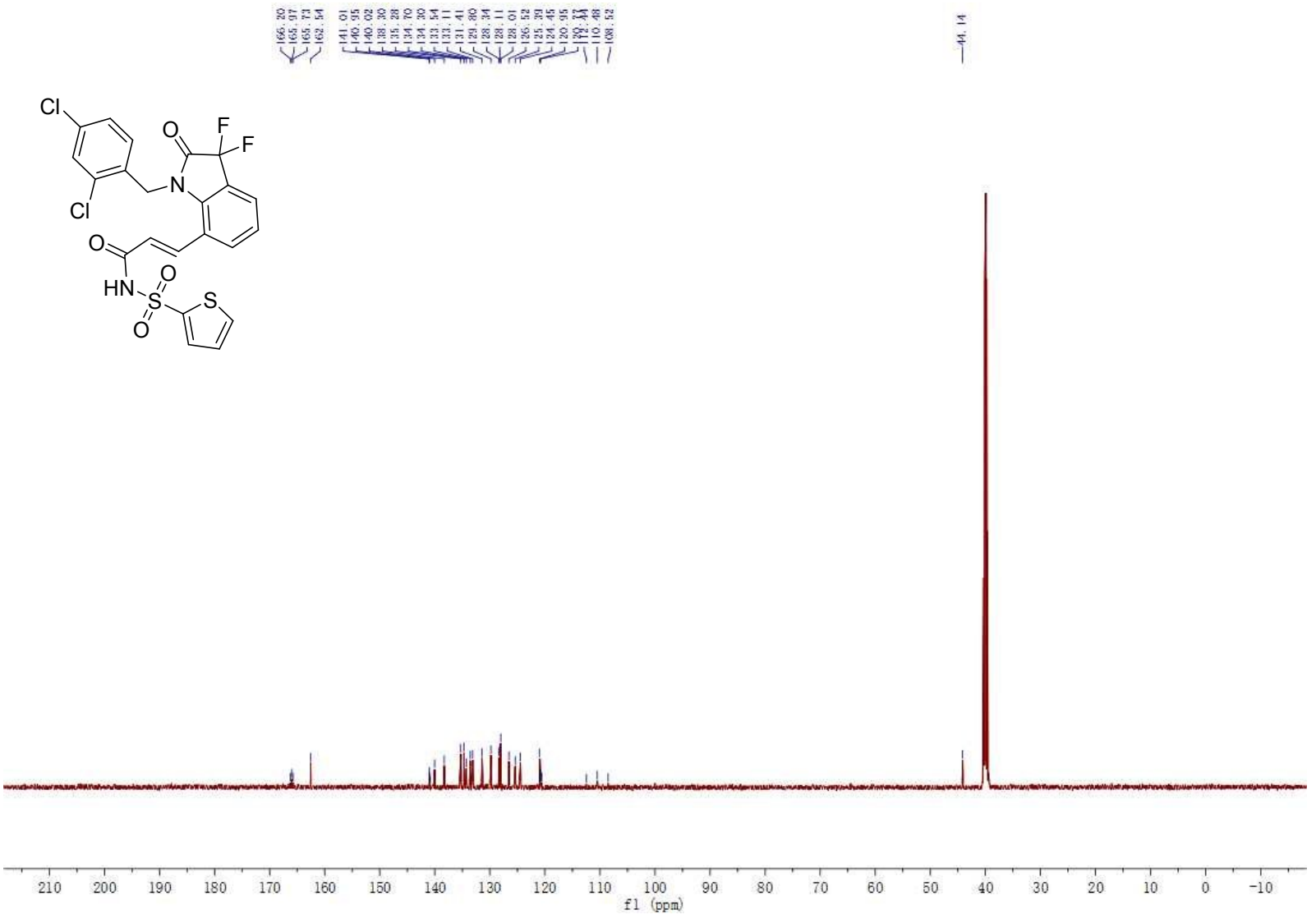

F
F
O
N
Cl
Cl
HO
O

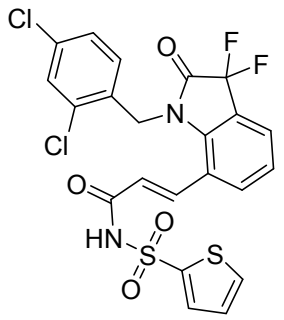
-111.008
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


12.36
8.11
8.10
7.36
7.34
7.32
7.32
7.53
7.52
7.40
7.39
7.39
7.37
7.33
7.32
7.30
7.28
7.27
7.26
7.24
7.01
6.99
6.16
6.13

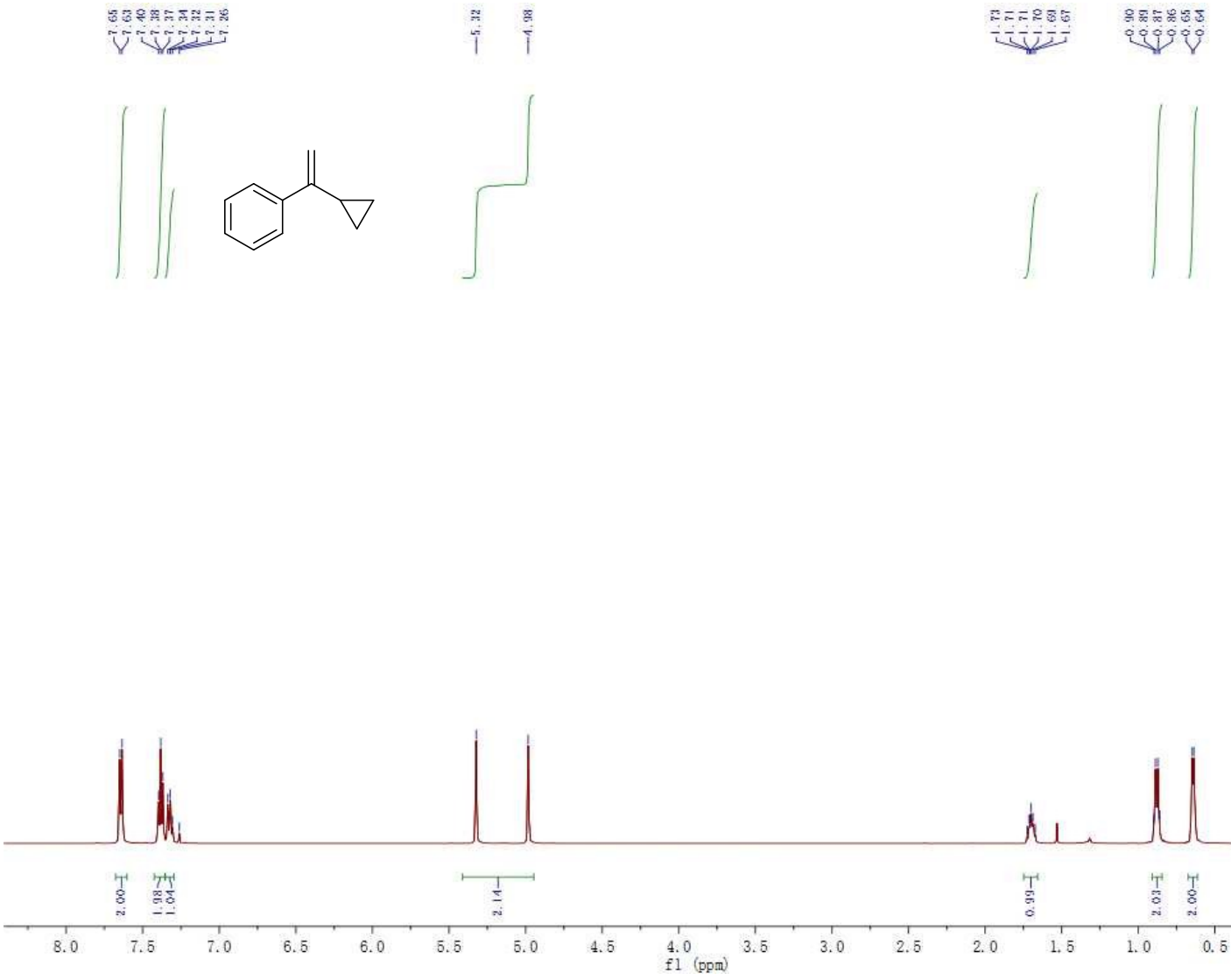

Cl
Cl
O
F
F
N
O
HN
O
S
O
S

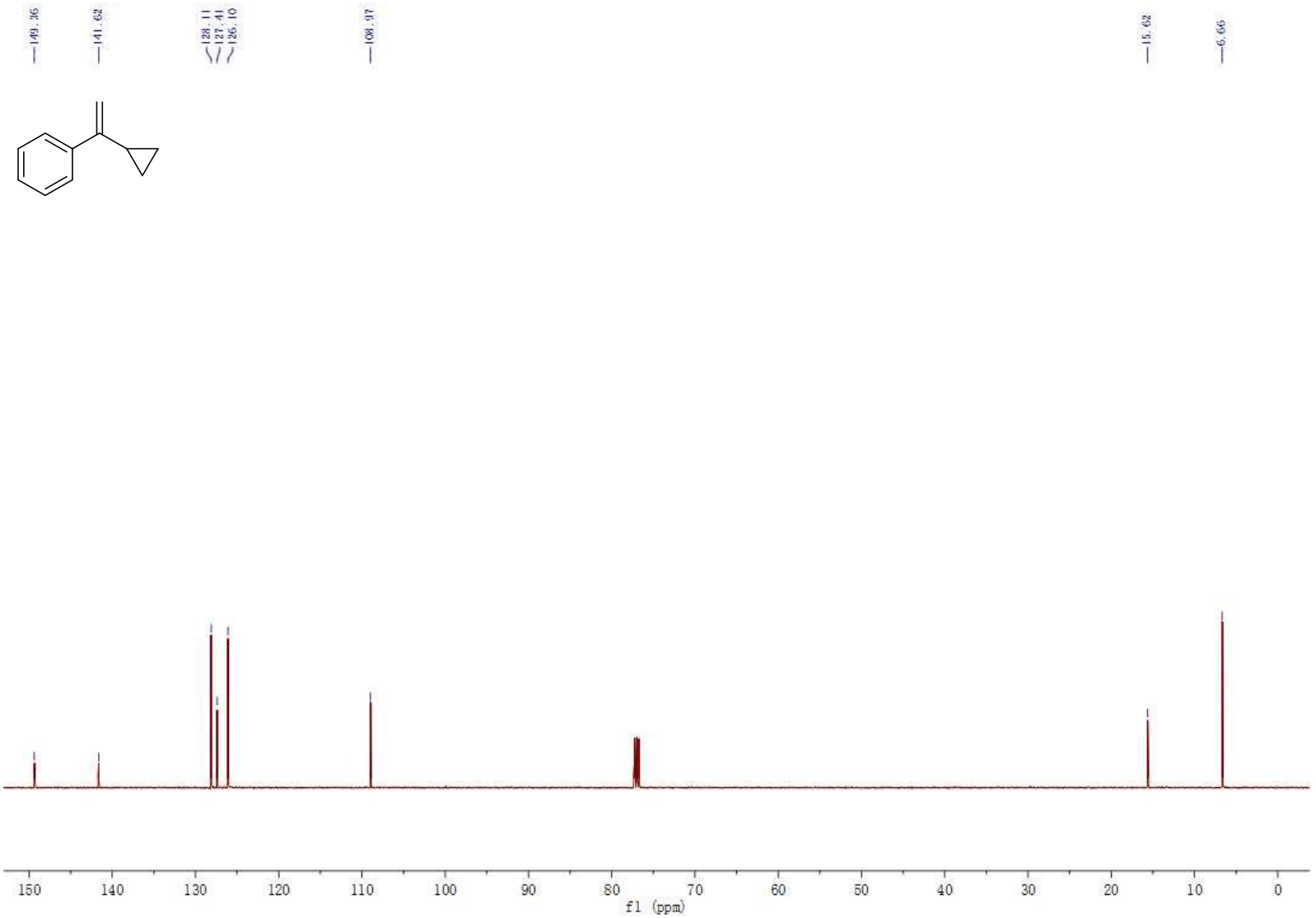

1.08
1.00
1.01
0.96
1.01
1.03
1.05
1.98
0.93
1.00
2.01
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

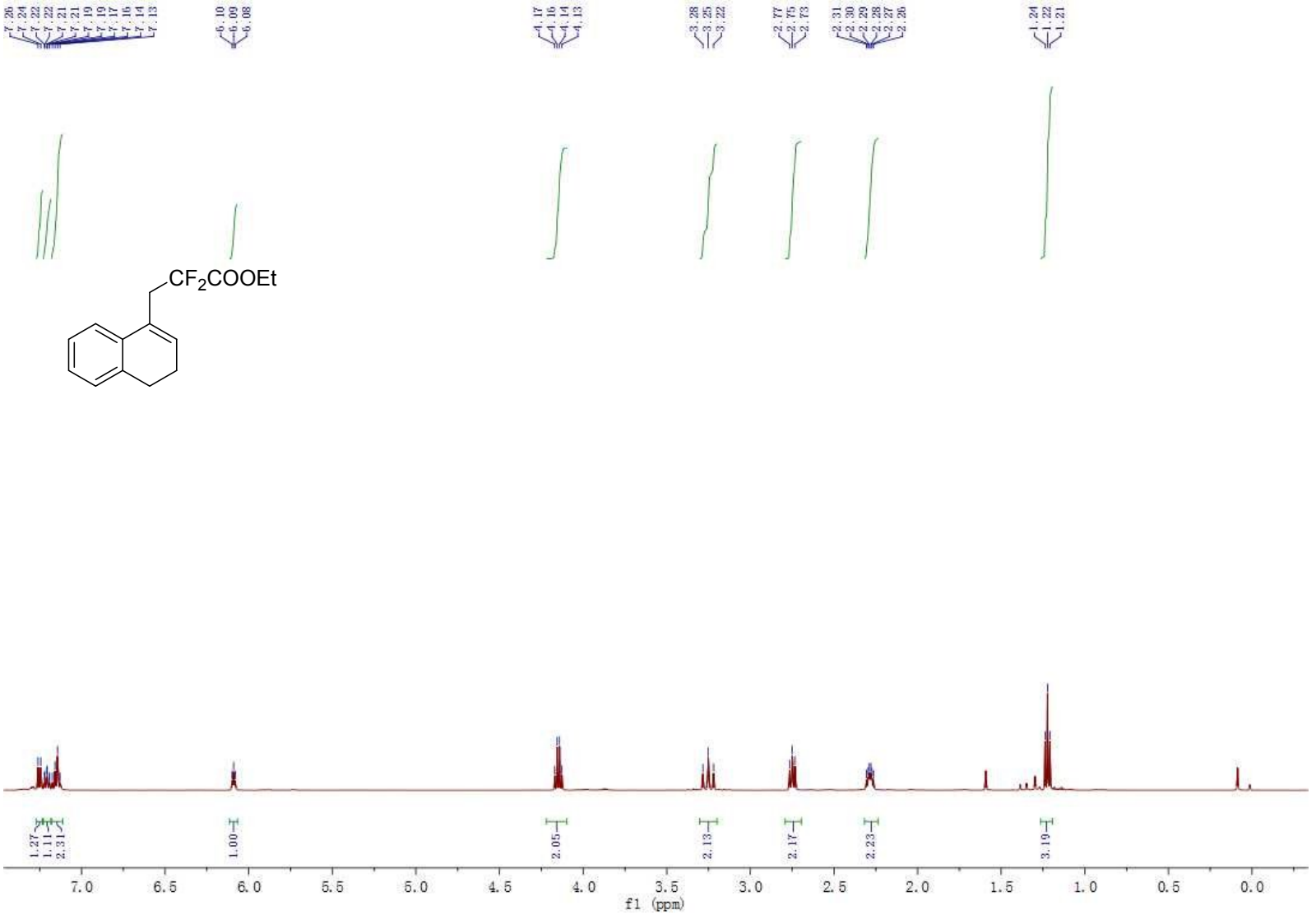

Cl
Cl
O
F
F
N
O
HN
O
O
S
S
166.20
165.97
165.73
162.54
141.01
140.95
140.02
138.30
135.28
134.70
134.20
133.54
133.11
131.41
129.80
128.34
128.11
128.01
126.52
125.39
124.45
120.95
112.44
110.48
108.52
44.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

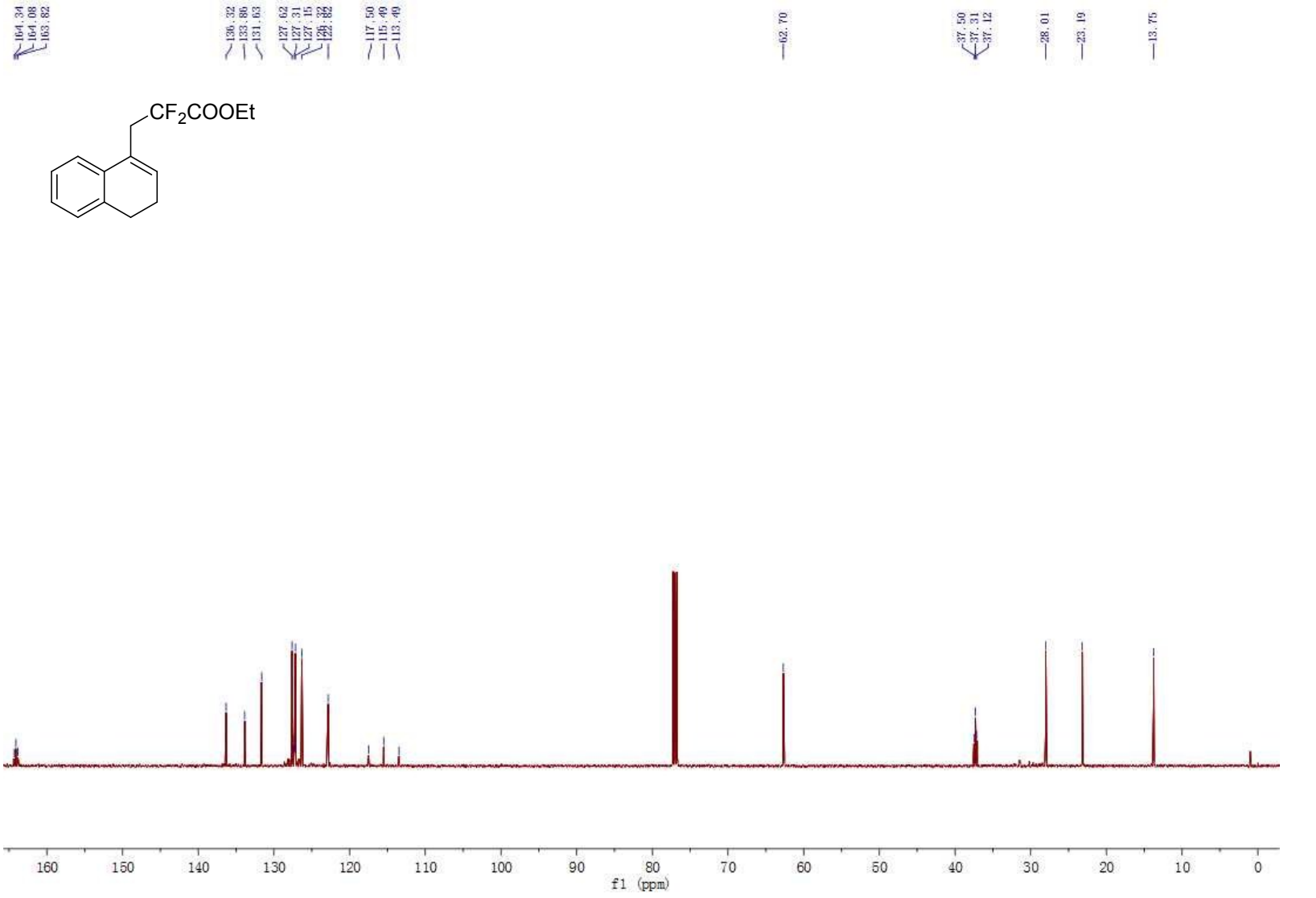

Cl
Cl
O
F
F
N
O
HN
O
S
O
S

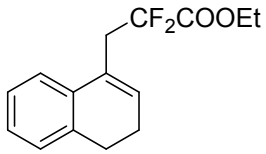
-109.94
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.65
7.63
7.40
7.38
7.37
7.34
7.32
7.31
7.26
5.32
4.98
1.73
1.71
1.71
1.70
1.69
1.67
0.90
0.89
0.87
0.86
0.65
0.64
2.00
1.08
1.04
2.14
0.99
2.03
2.00
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)

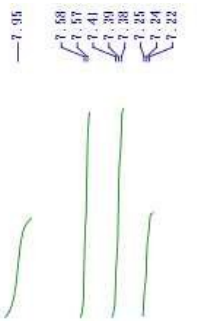

149.36
141.62
128.11
127.41
126.10
108.97
15.62
6.66
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

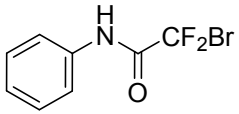

7.26
7.24
7.22
7.22
7.21
7.21
7.19
7.19
7.17
7.16
7.14
7.13
6.10
6.09
6.08
4.17
4.16
4.14
4.13
3.28
3.25
3.22
2.77
2.75
2.73
2.31
2.30
2.29
2.28
2.27
2.26
1.24
1.22
1.21
CF2COOEt
1.27
1.11
2.31
1.00
2.05
2.13
2.17
2.23
3.19
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

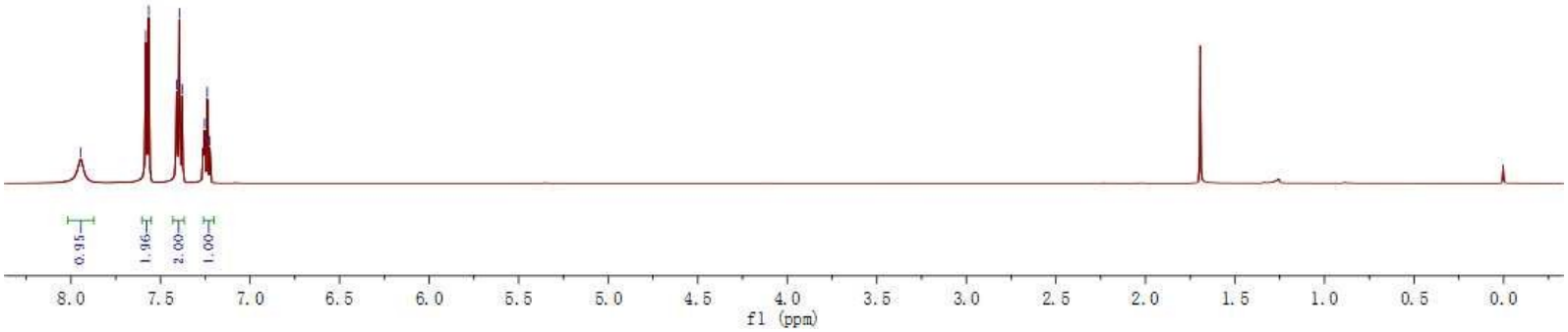

164.34
164.08
163.82
136.32
133.86
131.63
127.62
127.31
127.15
117.50
115.49
113.49
62.70
37.50
37.31
37.12
28.01
23.19
13.75
CF2COOEt
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CF2COOEt

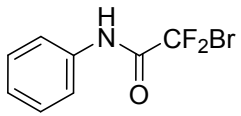
-103.33
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

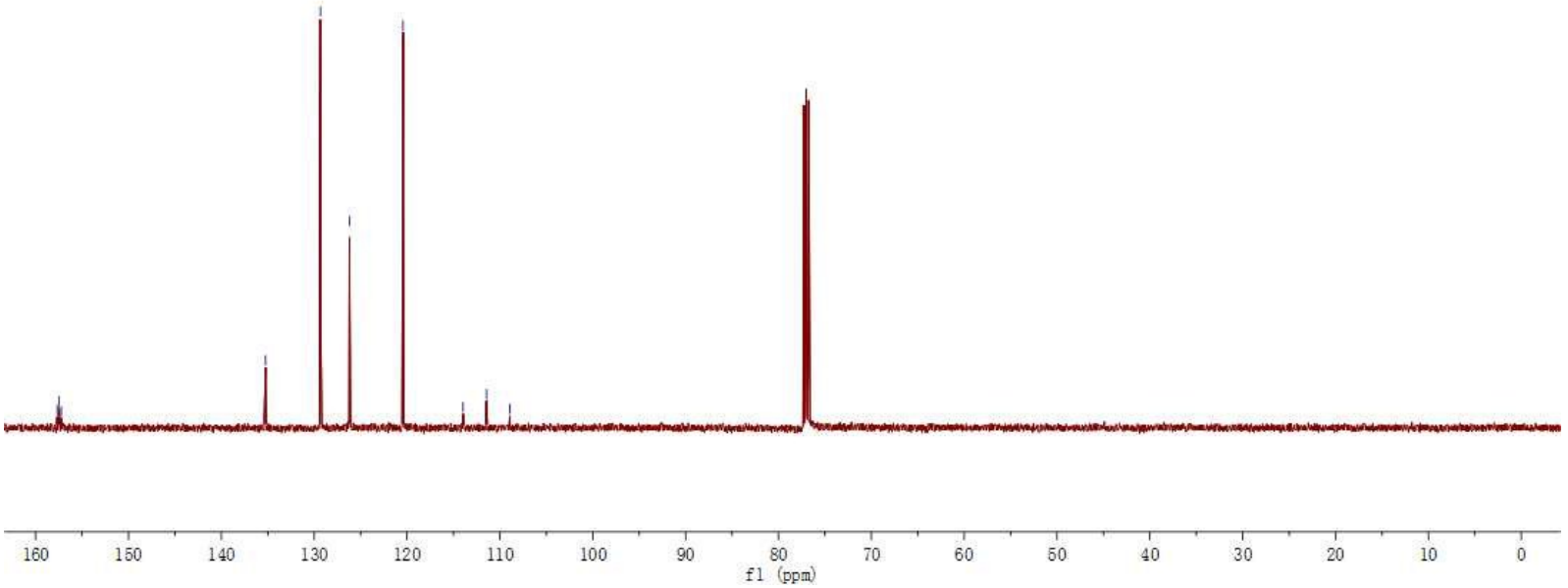

7.95
7.58
7.57
7.41
7.39
7.38
7.25
7.24
7.22

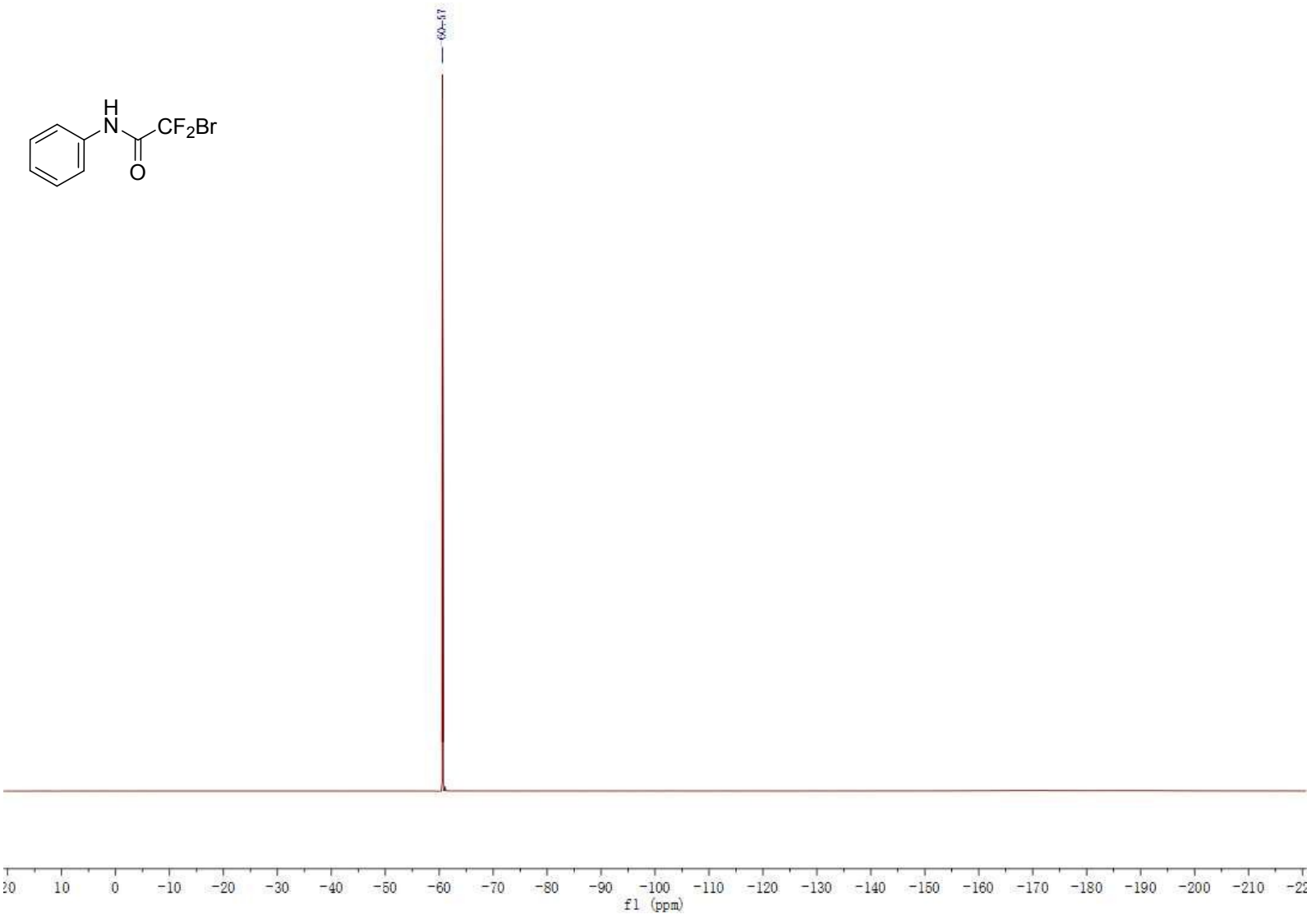

H
N
CF2Br
O

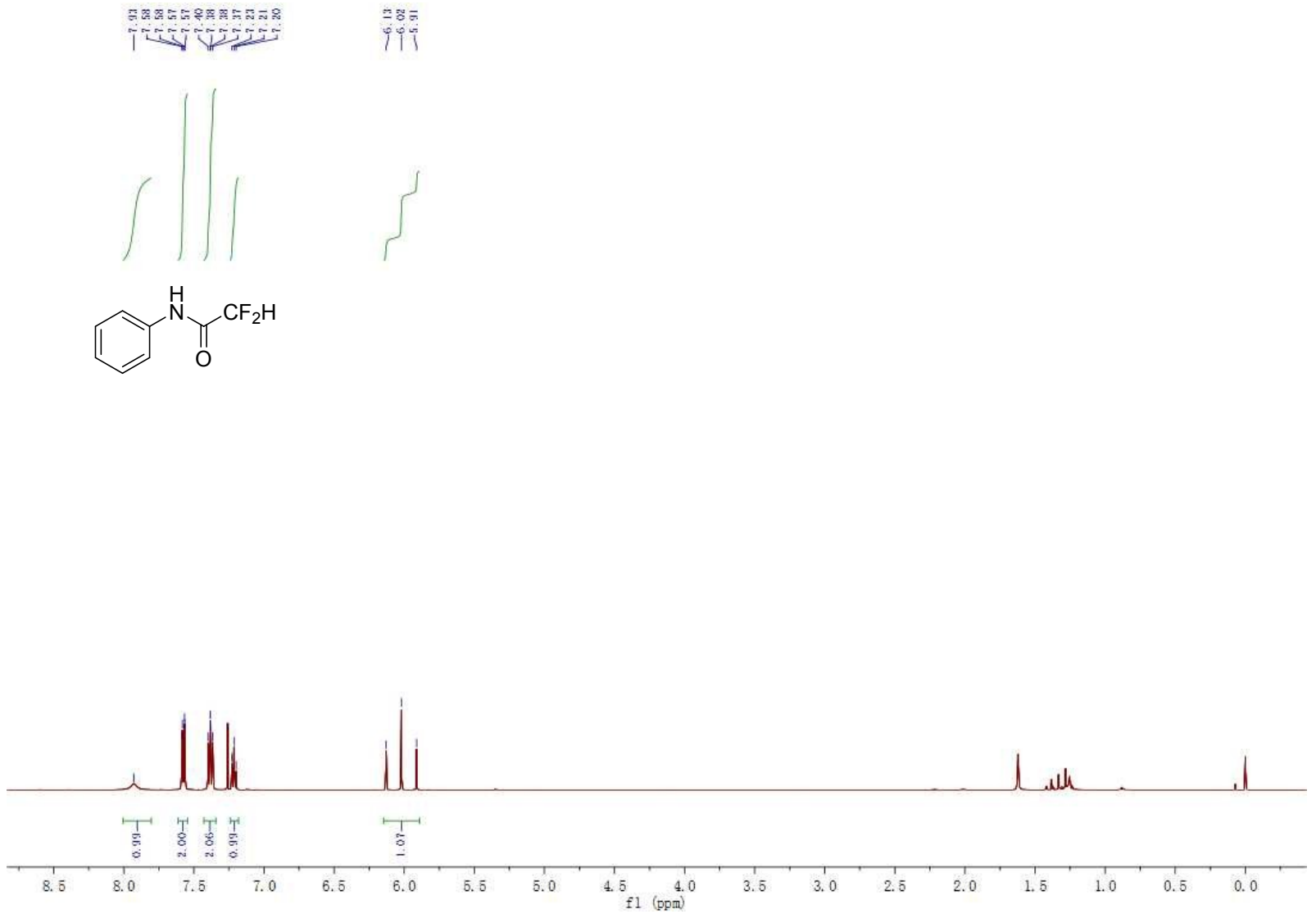

0.95
1.96
2.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

157.68
157.46
157.24
135.23
129.33
126.21
120.43
113.96
111.44
108.93






H
N
CF2Br
O
60-57
20
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)


7.93
7.58
7.58
7.57
7.57
7.40
7.38
7.38
7.37
7.23
7.21
7.20
6.13
6.02
5.91
H
N
CF2H
O
0.99
2.00
2.06
0.99
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

160.46
160.27
160.07

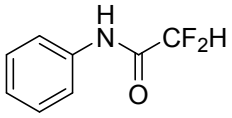
135.61

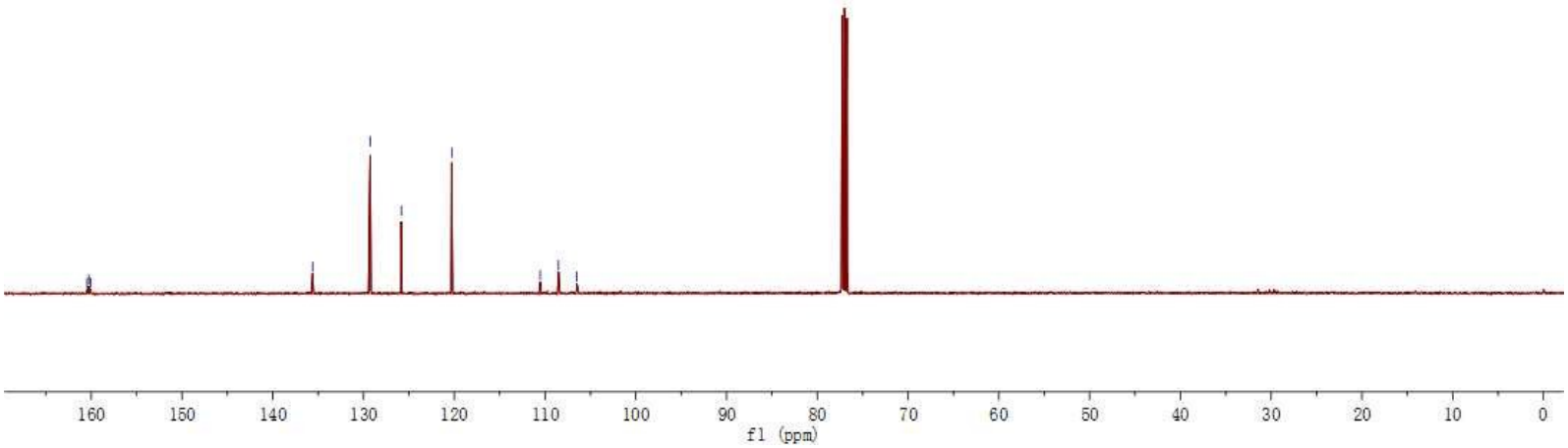
129.26

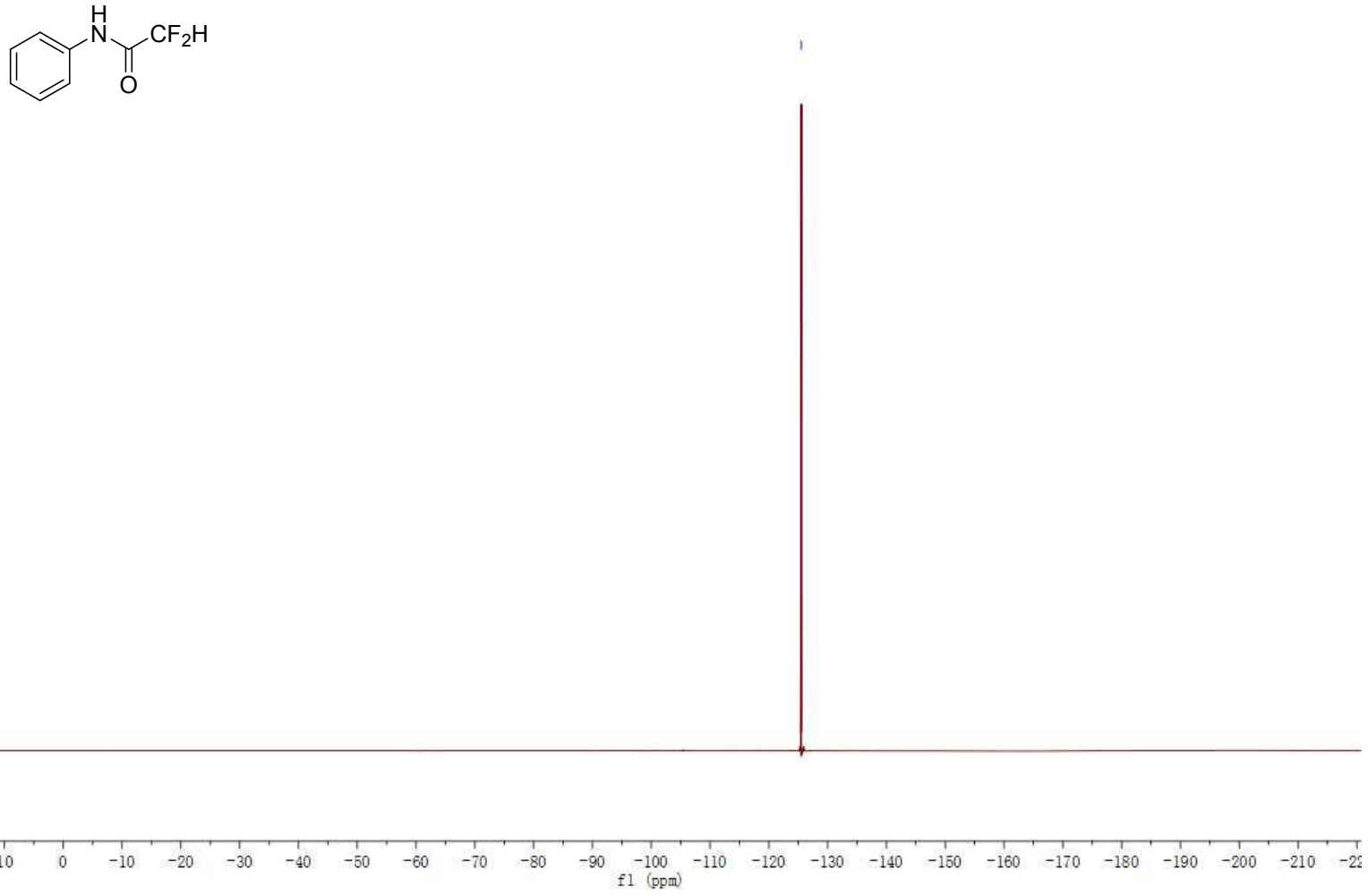
125.83

120.27

110.54
108.52
106.49






H
N
O
CF_2H
-125.53
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)