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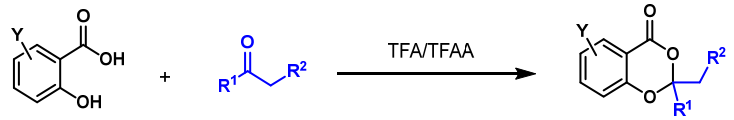
General Experimental

All solvents were purchased as the highest available grade from Energy Chemical, Leyan, Bide and Sinopharm Chemical. All moisture and oxygen sensitive reactions were performed in flame-dried glassware under a slight argon overpressure. All reactions were stirred magnetically. Sensitive solutions, solvents or reagents were transferred via cannula or syringe. Reactions were monitored by thin-layer chromatography (TLC) or ^{1}H NMR of the crude mixture. Thin-layer chromatography was carried out on pre-coated Leyan HPTLC Silica Gel 60 GF254 plate. Evaporations were conducted under reduced pressure at temperatures lower than 35 ºC, unless otherwise noted. Further dryings of the residues were accomplished using a high vacuum pump. Flash column chromatography was performed with silica gel from SiliaFlash (0.040-0.063 μm, 240-400 mesh). All NMR spectra were measured on Bruker Avance III 400 or Avance III 500. Chemical shifts are given in ppm and referenced to the solvent residual peaks (Chloroform-*d* ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.16 ppm; DMSO-d_6 ^{1}H, δ = 2.50 ppm, ^{13}C, δ = 39.52 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet,d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet, br = broad), coupling constant *J*, integration. High-resolution mass spectra were measured on Agilent 1290/6545 UHPLC-QTOF/MS. Melting points were recorded on a SGWX-4A melting point apparatus (Shanghai instrument physical optics instrument Co., LTD.) and are uncorrected.

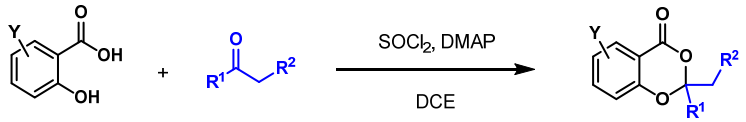
Synthesis of Salicylic Acid Ketals

Method A



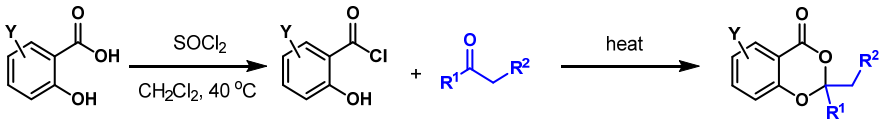
Method A is according to procedures reported in literature.[1,2] To an ice-cold suspension of salicylic acid (1.0 equiv) in TFA were added ketone (2.0 equiv) and trifluoroacetic anhydride. The mixture was warmed slowly to room temperature and kept stirring for 8-24 hours. For substrates that low conversions were observed at room temperature as indicated by TLC, the reaction temperature can be increased. After completion, the reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The organic layer was then dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography to afford the corresponding salicylic acid ketal.

Method B



Method B is according to procedures reported in literature.[3,4] To a flask containing salicylic acid (1.0 equiv) and DMAP (0.1 equiv) were added DME and ketone (1.3 equiv). This solution was cooled to 0 ºC under argon followed by addition of $SOCl_2$ (1.5 equiv) dropwise. The reaction was brought to room temperature and stirred for 18 hours before evacuated under vacuum. The residue was diluted in EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, evaporated and purified by flash column chromatography to afford the corresponding salicylic acid ketal.

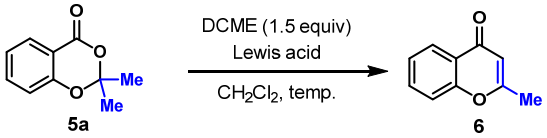
Method C



Method C is according to procedures reported in literature.[5,6] To a suspension of salicylic acid (1.0 equiv) in CH_2Cl_2 was added $SOCl_2$ (2.0 equiv) dropwise at 40 ºC and the resulting mixture was allowed to stir at the same temperature for 6 hours before evacuated under vacuum. Ketone (1.0 equiv) was added and the resulting mixture was heated (120 – 160 ºC) for 5 hours before cooling to room temperature. The residue was purified by flash column chromatography to afford the corresponding salicylic acid ketal.

Optimization Details

Table S1. Evaluation of Lewis Acids

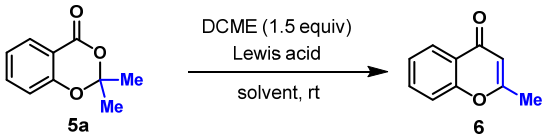


5a 6

Entry[a]	Lewis acid	Yield[b]
1	BF_3•Et_2O (1.0 equiv)	N.D.
2	$AlCl_3$ (1.0 equiv)	trace
3	LiCl (1.0 equiv)	trace
4	LiBr (1.0 equiv)	N.D.
5	$MgCl_2$ (1.0 equiv)	trace
6	$POCl_3$ (1.0 equiv)	N.D.
7	$ZnBr_2$ (1.0 equiv)	65%
8	$ZnCl_2$ (1.0 equiv)	64%
9	$FeCl_3$ (1.0 equiv)	<10%
10	$CeCl_3$ (1.0 equiv)	N.D.
11	$SnCl_4$ (1.0 equiv)	91%
12	AgOTf (3.0 equiv)	92% (89%)[c]
13	$SnCl_4$ (0.5 equiv)	92% (90%)[c]
14	$AgNTf_2$ (3.0 equiv)	91% (90%)[c]
15[d]	$SnCl_4$	N.D.[e]
16[d]	AgOTf	N.D.[f]
17[g]	$SnCl_4$ or AgOTf	N.D.

[a]**Reaction conditions: 5a** (0.25 mmol), DCME (1.5 equiv), Lewis acid, CH_2Cl_2 (1.5 mL), Ar, room temperature. [b]Determined by ^{1}H NMR analysis of crude product using $(CHCl_2)_2$ as the internal standard. [c]Isolated yield. [d]Without DCME. [e]Conversion was 33%. [f]Conversion was <5%. [g]DCME was replaced with trimethyl orthoformate. N.D. = not detected.

Table S2. Evaluation of Solvents

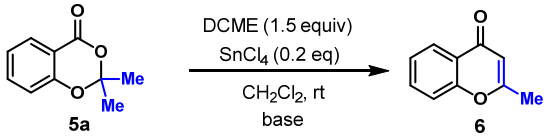


5a 6

Entry[a]	Lewis acid	Solvent	Yield[b]
1	$SnCl_4$ (0.2 equiv)	CH_2Cl_2	68%
2	$SnCl_4$ (0.5 equiv)	cyclohexane	<10%
3	$SnCl_4$ (0.5 equiv)	CH_3CN	37%
4	$SnCl_4$ (0.5 equiv)	EtOAc	41%
5	$SnCl_4$ (0.5 equiv)	acetone	N.D.
6	$SnCl_4$ (0.2 equiv)	PhMe	20%
7	$SnCl_4$ (0.2 equiv)	DCE	50%
8	$SnCl_4$ (0.2 equiv)	$CHCl_3$	47%
9	$SnCl_4$ (0.2 equiv)	CCl_4	20%
10	$SnCl_4$ (0.2 equiv)	CH_2Cl_2 (40 °C)	65%

[a]**Reaction conditions: 5a** (0.25 mmol), DCME (1.5 equiv)**,** Lewis acid, CH_2Cl_2 (1.5 mL), Ar, room temperature. [b]Determined by ^{1}H NMR analysis of crude product using $(CHCl_2)_2$ as the internal standard. N.D. = not detected.

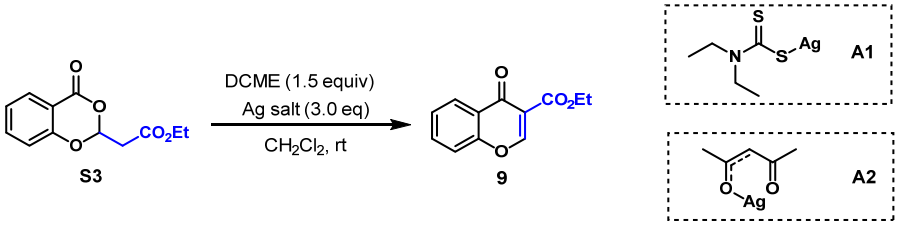
Table S3. Evaluation of Bases



Entry[a]	Base	Yield[b]
1	Et_3N (3.0 equiv)	N.D.
2	DBU (3.0 equiv)	N.D.
3	$NaHCO_3$ (3.0 equiv)	59%
4	K_2CO_3 (3.0 equiv)	58%
5	Na_2HPO_4 (3.0 equiv)	36%

[a]**Reaction conditions: 5a** (0.25 mmol), DCME (1.5 equiv)**,** Lewis acid, CH_2Cl_2 (1.5 mL), Ar, room temperature. [b]Determined by ^1H NMR analysis of crude product using $(CHCl_2)_2$ as the internal standard. N.D. = not detected.

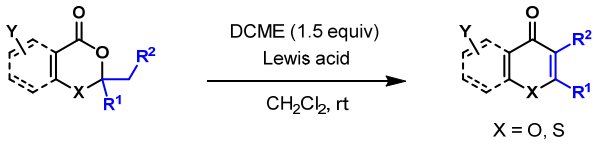
Table S4. Evaluation of Silver Salts



Entry[a]	[Ag] (3.0 equiv)	Yield[b]	Entry	[Ag] (3.0 equiv)	Yield[b]
1	AgOTf	62%[c]	11	PhCOOAg	N.D.
2	Ag_3PO_4	N.D.	12	$AgBF_4$	trace
3	AgF	N.D.	13	CH_3SO_3Ag	N.D.
4	CH_3CO_2Ag	N.D.	14	Silver sulfadiazine	N.D.
5	Ag_2CO_3	N.D.	15	*p*-TsOAg	N.D.
6	Ag_2SO_4	N.D.	16	Ag_2O	N.D.
7	CF_3COOAg	N.D.	17	A1	N.D.
8	$AgClO_4$	N.D.	18	A2	N.D.
9	$AgSbF_6$	N.D.	19	$AgNTf_2$	45%[c]
10	Silver lactate	N.D.			

[a]**Reaction conditions: S3** (1.0 equiv), DCME (1.5 equiv)**,** Lewis acid, CH_2Cl_2, Ar, room temperature. [b]Determined by ^1H NMR analysis of crude product using $(CHCl_2)_2$ as the internal standard. [c]Isolated yield. N.D. = not detected.

General Procedure for the Dehydrative Rearrangement (DHR) reaction

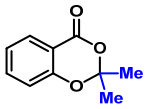


To an oven-dried flask equipped with a magnetic stir bar were added ketal (1.0 equiv), Lewis acid (0.5 equiv of $SnCl_4$, or 3.0 equiv of AgOTf or 3.0 equiv of $AgNTf_2$) and CH_2Cl_2 (0.6 mL per 0.1 mmol) under argon. DCME (1.5 equiv) was added dropwise at room temperature. The reaction mixture was allowed to stir at the same temperature unless otherwise specified. After completion as indicated by TLC (or stirred at room temperature for 12 hours), the reaction mixture was diluted with EtOAc and washed by saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography to afford the corresponding chromone, thiochromone or γ-pyrone.

Experimental Procedures and Characterization Data

Salicylic Acid Ketals

Compound 5a



2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 30.0 mmol scale with salicylic acid and acetone at room temperature for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 3.52 g (66%) of the title compound **5a**.

Physical State: white solid.

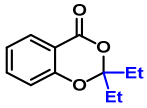
m.p.: 58 - 59 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.0 Hz, 1H), 1.70 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.2, 156.1, 136.5, 129.7, 122.7, 117.2, 113.6, 106.4, 25.8.

Spectroscopic data are in agreement with published values.[7]

Compound S1



2,2-diethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 10.0 mmol scale with salicylic acid and 3-pentanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 0.94 g (45%) of the title compound **S1**.

Physical State: colorless oil.

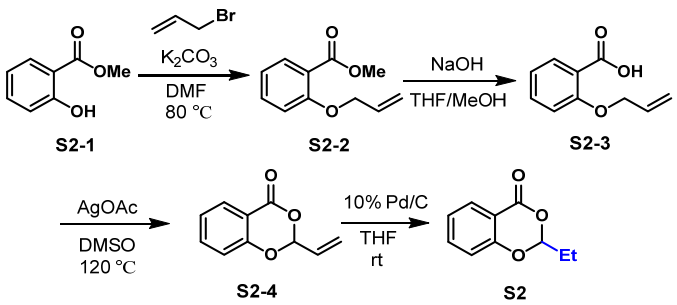
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 – 7.88 (m, 1H), 7.51 (tt, *J* = 7.4, 1.9 Hz, 1H), 7.06 (td, *J* = 7.7, 3.1 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.7 Hz, 1H), 1.97 (qd, *J* = 7.5, 2.8 Hz, 4H), 0.99 (td, *J* = 7.4, 2.5 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 156.1, 136.4, 129.5, 122.4, 117.2, 113.9, 110.3, 28.8, 7.5.

HRMS (ESI) calculated for: $C_{12}H_{15}O_3^+$ ([M+H]$^+$) m/z 207.1016, found 207.1014.

Compound S2

2-ethyl-4H-benzo[d][1,3]dioxin-4-one



*Compound **S2** was prepared according to procedures reported in literature.*[8-10] A mixture of ester **S2-1** (1.4 g, 9.2 mmol, 1.0 equiv), K_2CO_3 (2.54 g, 2.0 equiv), and allyl bromide (1.34 g, 1.2 equiv) in DMF (40 mL) was heated to 80 ºC for 2 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc and washed with brine. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by flash column chromatography to give **S2-2** (1.37 g, 78%).[8]

Compound **S2-2** (0.96 g, 5.0 mmol, 1.0 equiv) was dissolved in THF/MeOH (1/1, 8 mL) and NaOH (aq. 2 M, 7.5 mL, 3.0 equiv) was added. The solution was stirred at room temperature for 6 hours before acidified to pH 2 with 3 N HCl. The layers were separated and the aqueous lay was extracted with EtOAc for three time. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to provide the crude acid **S2-3** (0.88 g, 99%), which was used directly in the next step without further purification.[8]

A mixture of **S2-3** (88 mg, 0.5 mmol, 1.0 equiv) and AgOAc (0.25 g, 3.0 equiv) was stirred in DMSO (6 mL) at 120 ºC for 10 hours. After cooling to room temperature, saturated aqueous NH_4Cl was added, and the mixture was extracted with DCE for three times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated and purified by flash column chromatography to give **S2-4** (53 mg, 61%).[9]

To a solution of **S2-4** (0.3 g, 1.72 mmol, 1.0 equiv) in THF (15 mL) was added Pd/C (60 mg). After exchanging the atmosphere with hydrogen for three times, the reaction mixture was allowed to stir at room temperature under hydrogen balloon for 0.5 hour. The mixture was filtered through celite and rinsed with THF. After evaporation, the residue was purified by flash column chromatography to give **S2** (0.27 g, 90%).

Physical State: yellow oil.

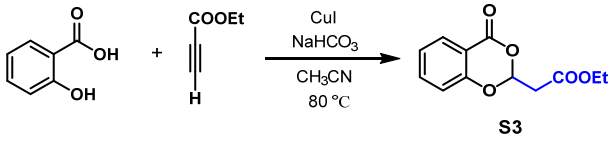
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.53 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 7.01 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.54 (t, *J* = 4.9 Hz, 1H), 2.03 (qd, *J* = 7.5, 4.8 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.4, 158.5, 136.2, 130.2, 123.3, 116.7, 114.5, 102.3, 26.9, 7.2.

Spectroscopic data are in agreement with published values.[10]

Compound S3

ethyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate



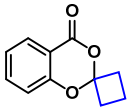
S3

*Compound **S3** was prepared according to procedures reported in literature.*[11] To an oven-dried flask equipped with a magnetic stir bar were added salicylic acid (1.66 g, 12.0 mmol, 1.2 equiv), $NaHCO_3$ (1.08 g, 1.2 equiv), CuI (1.90 g, 1.0 equiv), ethyl propiolate (0.98 g, 1.0 equiv) and CH_3CN (50 mL) successively. The reaction mixture was stirred at 80 ºC. After completion, the reaction mixture was diluted with EtOAc and filtered over celite. After evaporation, the crude product was purified by flash column chromatography to obtain **S3** (1.62 g, 57%).

Physical State: yellow oil.

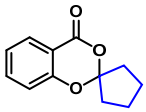
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 7.19 (td, *J* = 7.6, 1.1 Hz, 1H), 7.04 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.05 (t, *J* = 5.5 Hz, 1H), 4.23 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.09 (dd, *J* = 5.5, 3.3 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.7, 161.5, 158.0, 136.5, 130.3, 123.8, 116.8, 114.4, 98.2, 61.4, 39.4, 14.2.
Spectroscopic data are in agreement with published values.[11]

Compound S4



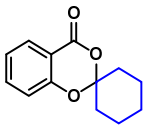
4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclobutan]-4-one
Following Method A on 5.0 mmol scale with salicylic acid and cyclobutanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 40:1 PE:EtOAc) afforded 0.35 g (37%) of the title compound **S4**.
Physical State: yellow oil.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56 (ddd, *J* = 8.7, 7.4, 1.7 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 2.61 – 2.42 (m, 4H), 2.00 – 1.82 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.6, 156.1, 136.5, 130.0, 123.3, 117.6, 114.6, 105.6, 34.5, 11.4.
HRMS (ESI) calculated for: $C_{11}H_{11}O_3^+$ ([M+H]$^+$) m/z 191.0703, found 191.0704.

Compound S5



4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclopentan]-4-one
Following Method A on 0.5 mmol scale with salicylic acid and cyclopentanone at 80 ºC for 4 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 53 mg (48%) of the title compound **S5**.
Physical State: yellow solid.
m.p.: 75 - 77 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.89 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (td, *J* = 7.8, 1.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 2.17 – 2.01 (m, 4H), 1.85 – 1.69 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.7, 156.8, 136.2, 129.7, 122.7, 117.2, 116.2, 114.3, 37.0, 23.2.
HRMS (ESI) calculated for: $C_{12}H_{13}O_3^+$ ([M+H]$^+$) m/z 205.0859, found 205.0864.

Compound 75b



4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

Following Method A on 10.0 mmol scale with salicylic acid and cyclohexanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 1.35 g (62%) of the title compound **75b**.

Physical State: yellow solid.

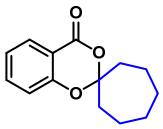
m.p.: 63 - 64 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.7, 7.5, 1.7 Hz, 1H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 6.97 (dd, *J* = 8.3, 0.9 Hz, 1H), 2.06 – 1.93 (m, 4H), 1.74 – 1.63 (m, 4H), 1.57 – 1.41 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 155.8, 136.4, 129.7, 122.6, 117.3, 114.3, 107.0, 34.6, 24.7, 22.3.

HRMS (ESI) calculated for: $C_{13}H_{15}O_3^+$ ([M+H]$^+$) m/z 219.1016, found 219.1012.

Compound S6



4H-spiro[benzo[d][1,3]dioxine-2,1'-cycloheptan]-4-one

Following Method A on 10.0 mmol scale with salicylic acid and cycloheptanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.98 g (62%) of the title compound **S6**.

Physical State: white solid.

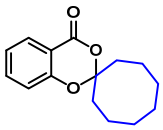
m.p.: 42 - 43 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.92 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 (td, *J* = 7.8, 1.7 Hz, 1H), 7.08 (td, *J* = 7.6, 0.8 Hz, 1H), 6.95 (dd, *J* = 8.3, 0.2 Hz, 1H), 2.26 – 2.13 (m, 4H), 1.66 – 1.60 (m, 8H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 161.3, 156.0, 136.4, 129.6, 122.5, 117.3, 114.2, 111.2, 38.3, 28.8, 21.5.

HRMS (ESI) calculated for: $C_{14}H_{17}O_3^+$ ([M+H]$^+$) m/z 233.1172, found 233.1169.

Compound S7



4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclooctan]-4-one

Following Method A on 0.5 mmol scale with salicylic acid and cyclooctanone at 80 ºC for 4 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 51 mg (41%) of the title compound **S7**.

Physical State: white solid.

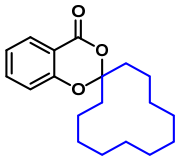
m.p.: 41 - 43 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (td, *J* = 8.2, 1.5 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 2.20 – 2.14 (m, 4H), 1.67 – 1.54 (m, 10H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.1, 155.7, 136.4, 129.5, 122.4, 117.2, 114.0, 110.6, 33.4, 27.6, 24.4, 21.1.

HRMS (ESI) calculated for: $C_{15}H_{19}O_3^+$ ([M+H]$^+$) m/z 247.1329, found 247.1322.

Compound S8



4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclododecan]-4-one

Following Method A on 0.5 mmol scale with salicylic acid and cyclododecanone at 80 ºC for 6 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 23 mg (30%) of the title compound **S8**.

Physical State: white solid.

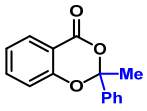
m.p.: 94 - 96 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.94 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.53 (td, *J* = 7.8, 1.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 2.02 (t, *J* = 8.0 Hz, 4H), 1.60 – 1.54 (m, 2H), 1.52 – 1.43 (m, 2H), 1.40 – 1.33 (m, 14H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 156.0, 136.4, 129.7, 122.6, 117.2, 114.5, 110.9, 31.6, 26.0, 25.8, 22.5, 22.1, 19.5.

HRMS (ESI) calculated for: $C_{19}H_{27}O_3^+$ ([M+H]$^+$) m/z 303.1955, found 303.1954.

Compound S9



2-methyl-2-phenyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 10.0 mmol scale with salicylic acid and acetophenone at room temperature for 24 hours. After workup, the crude product was dissolved in MeOH (20 mL) and $NaBH_4$ (0.19 g, 5.0 mmol) was added at 0 ºC to reduce the excess acetophenone. After 30 min, the solvent was removed under vacuum, and the residue was diluted with H_2O and extracted with EtOAc. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.30 g (54%) of the title compound **S9**.

Physical State: yellow solid.

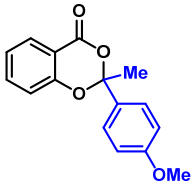
m.p.: 45 - 46 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.35 – 7.27 (m, 3H), 7.08 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.05 – 6.98 (m, 1H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.5, 156.6, 140.6, 136.5, 129.9, 129.0, 128.8, 126.0, 122.9, 117.3, 114.9, 106.9, 30.2.

HRMS (ESI) calculated for: $C_{15}H_{13}O_3^+$ ([M+H]$^+$) m/z 241.0859, found 241.0858.

Compound S10



2-(4-methoxyphenyl)-2-methyl-4H-benzo[d][1,3]dioxin-4-one

Following Method B on 10.0 mmol scale with salicylic acid and 4-methoxyacetophenone at room temperature for 18 hours. After workup, the crude product was dissolved in MeOH (20 mL) and $NaBH_4$ (0.19 g, 5.0 mmol) was added at 0 ºC to reduce the excess 4-methoxy acetophenone. After 30 min, the solvent was removed under vacuum, and the residue was diluted with H_2O and extracted with EtOAc. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.0 g (37%) of the title compound **S10**.

Physical State: white solid.

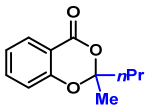
m.p.: 96 - 98 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.80 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.03 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.99 (td, *J* = 7.6, 1.1 Hz, 1H), 6.81 – 6.78 (m, 2H), 3.73 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 161.6, 160.0, 156.6, 136.4, 132.6, 129.8, 127.4, 122.8, 117.3, 114.8, 114.1, 107.0, 55.3, 30.2.

HRMS (ESI) calculated for: $C_{16}H_{15}O_4^+$ ([M+H]$^+$) m/z 271.0965, found 271.0969.

Compound 18-1



2-methyl-2-propyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 10.0 mmol scale with salicylic acid and 2-pentanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.10 g (53%) of the title compound **18-1**.

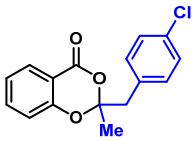
Physical State: yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 (td, *J* = 8.0, 1.7 Hz, 1H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.0 Hz, 1H), 1.96 – 1.91 (m, 2H), 1.64 (s, 3H), 1.58 – 1.49 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 161.2, 156.1, 136.4, 129.6, 122.6, 117.2, 113.8, 108.1, 41.0, 23.7, 16.8, 14.0.

HRMS (ESI) calculated for: $C_{12}H_{15}O_3^+$ ([M+H]$^+$) m/z 207.1016, found 207.1011.

Compound 18-2



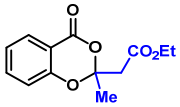
2-(4-chlorobenzyl)-2-methyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with salicylic acid and 4-chlorophenylacetone at 80 ºC for 8 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 25 mg (35%) of the title compound **18-2**.

Physical State: yellow oil.

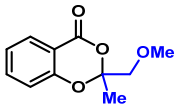
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.30 (AB, *J* = 14.2 Hz, 1H), 3.20 (BA, *J* = 14.2 Hz, 1H), 1.62 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.8, 155.8, 136.8, 133.4, 132.8, 132.1, 129.9, 128.6, 122.9, 117.3, 113.7, 107.1, 44.2, 23.8.
HRMS (ESI) calculated for: $C_{16}H_{14}ClO_3^+$ ([M+H]$^+$) m/z 289.0626, found 289.0629.

Compound 18-3



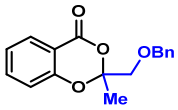
ethyl 2-(2-methyl-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate
To an oven-dried flask equipped with a magnetic stir bar were added salicylic acid (24.0 mmol, 1.2 equiv), CuI (20.0 mmol, 1.0 equiv), Et_3N (24.0 mmol, 1.2 equiv), ethyl 2-butynoate (20.0 mmol, 1.0 equiv) and CH_3CN (50 mL) under argon. The reaction was heated to 80 °C and kept for stirring until completion as indicated by TLC. The reaction mixture was diluted with EtOAc and filtered over celite. After concentration, the crude product was purified by flash column chromatography to obtain compound **18-3** (0.78 g, 16%).
Physical State: yellow oil.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.01 (AB, *J* = 14.4 Hz, 1H), 2.95 (BA, *J* = 14.4 Hz, 1H), 1.85 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.4, 160.1, 155.5, 136.7, 129.7, 123.1, 117.4, 113.5, 105.0, 61.2, 43.4, 24.5, 14.1.
HRMS (ESI) calculated for: $C_{13}H_{15}O_5^+$ ([M+H]$^+$) m/z 251.0914, found 251.0917.

Compound 18-4



2-(methoxymethyl)-2-methyl-4H-benzo[d][1,3]dioxin-4-one
Following Method C on 3.0 mmol scale with salicylic acid and 1-ethoxypropan-2-one at 120 ºC for 6 hours. Purification by flash column chromatography (silica, 100:1 PE:EtOAc) afforded 0.19 g (30%) of the title compound **18-4**.
Physical State: colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H), 7.11 (td, *J* = 7.8, 0.9 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 3.73 (AB, *J* = 10.8 Hz, 1H), 3.63 (BA, *J* = 10.8 Hz, 1H), 3.42 (s, 3H), 1.72 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 160.5, 155.9, 136.6, 129.7, 122.9, 117.2, 113.7, 106.2, 75.1, 60.0, 21.9.
HRMS (ESI) calculated for: $C_{11}H_{13}O_4^+$ ([M+H]$^+$) m/z 209.0808, found 209.0810.

Compound 18-5



2-((benzyloxy)methyl)-2-methyl-4H-benzo[d][1,3]dioxin-4-one

Physical State: colorless oil.

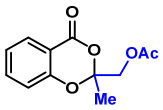
Following Method C on 6.0 mmol scale with salicylic acid and 1-(benzyloxy)propan-2-one at 120 ºC for 4 hours. Purification by flash column chromatography (silica, 100:1 PE:EtOAc) afforded 0.77 g (46%) of the title compound **18-5**.

^{1}H NMR (500 MHz, Chloroform-d): δ 7.93 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.32 – 7.25 (m, 5H), 7.11 (td, *J* = 7.5, 0.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 4.62 – 4.55 (m, 2H), 3.79 (AB, *J* = 10.9 Hz, 1H), 3.69 (BA, *J* = 10.9 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 160.6, 156.0, 137.4, 136.6, 129.7, 128.6, 128.0, 127.8, 122.8, 117.2, 113.8, 106.3, 73.9, 72.4, 22.3.

HRMS (ESI) calculated for: $C_{17}H_{17}O_4^+$ ([M+H]$^+$) m/z 285.1121, found 285.1124.

Compound 18-6



(2-methyl-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)methyl acetate

The **52e** were prepared according to procedures reported in literature.[12] A suspension of Zn-dust (30 mg, 0.45 mmol) in petroleum ether (6 mL) was stirred with **18-5** (0.511 g, 1.8 mmol) and acetyl chloride (0.144 mL, 1.98 mmol) at room temperature under argon for 3 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 0.41 g (97%) of the title compound **18-6**.

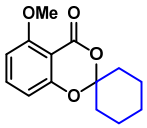
Physical State: colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.56 (td, *J* = 8.3, 1.7 Hz, 1H), 7.14 (td, *J* = 7.8, 0.8 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.40 (AB, *J* = 12.0 Hz, 1H), 4.34 (BA, *J* = 12.0 Hz, 1H), 2.06 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 170.2, 160.1, 155.7, 136.8, 129.8, 123.2, 117.2, 113.4, 104.8, 65.5, 22.4, 20.7.

HRMS (ESI) calculated for: $C_{12}H_{13}O_5^+$ ([M+H]$^+$) m/z 237.0757, found 237.0757.

Compound S11



5-methoxy-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

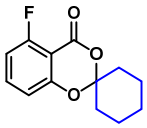
Following Method A on 4.0 mmol scale with 2-hydroxy-6-methoxybenzoic acid and cyclohexanone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 0.36 g (36%) of the title compound **S11**.

Physical State: white solid.

m.p.: 116 - 117 ºC.

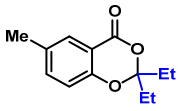
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.42 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 2.02 – 1.87 (m, 4H), 1.73 – 1.54 (m, 4H), 1.52 – 1.37 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 161.5, 158.5, 157.6, 136.5, 109.4, 106.0, 105.5, 103.9, 56.5, 34.4, 24.8, 22.4.
HRMS (ESI) calculated for: $C_{14}H_{17}O_4^+$ ([M+H]$^+$) m/z 249.1121, found 249.1121.

Compound S12



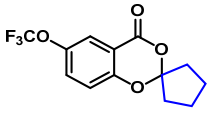
5-fluoro-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one
Following Method A on 4.0 mmol scale with 2-fluoro-6-hydroxybenzoic acid and cyclohexanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 0.27 g (28%) of the title compound **S12**.
Physical State: colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.48 (td, *J* = 8.4, 5.8 Hz, 1H), 6.84 – 6.76 (m, 2H), 2.04 – 1.92 (m, 4H), 1.75 – 1.58 (m, 4H), 1.55 – 1.41 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 162.6 (d, *J* = 265.6 Hz), 157.1 (d, *J* = 4.0 Hz), 156.9 (d, *J* = 1.9 Hz), 136.8 (d, *J* = 11.3 Hz), 113.1 (d, *J* = 3.9 Hz), 110.5 (d, *J* = 20.9 Hz), 107.2, 104.1 (d, *J* = 10.4 Hz), 34.5, 24.6, 22.2.
^{19}F NMR (471 MHz, Chloroform-*d*): δ -107.8 (dd, *J* = 9.3, 6.1 Hz).
HRMS (ESI) calculated for: $C_{13}H_{14}FO_3^+$ ([M+H]$^+$) m/z 237.0921, found 237.0922.

Compound S13



2,2-diethyl-6-methyl-4H-benzo[d][1,3]dioxin-4-one
Following Method A on 0.25 mmol scale with 5-methylsalicylic acid and 3-pentanone at 40 ºC for 10 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 24 mg (44%) of the title compound **S13**.
Physical State: white solid.
m.p.: 56 -58 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.73 (s, 1H), 7.33 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.85 (dd, *J* = 8.6, 1.5 Hz, 1H), 2.32 (s, 3H), 1.97 (qd, *J* = 7.4, 1.8 Hz, 4H), 1.02 – 0.97 (td, *J* = 7.4, 1.4 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.7, 154.0, 137.3, 132.1, 129.4, 117.0, 113.6, 110.3, 28.8, 20.6, 7.6.
HRMS (ESI) calculated for: $C_{13}H_{17}O_3^+$ ([M+H]$^+$) m/z 221.1172, found 221.1168.

Compound S14



6-(trifluoromethoxy)-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclopentan]-4-one

Following Method A on 2.0 mmol scale with 2-hydroxy-5-(trifluoromethoxy)benzoic acid and cyclopentanone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 0.27g (47%) of the title compound **S14**.

Physical State: yellow oil.

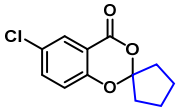
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.38 (dd, *J* = 8.9, 2.9 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 2.19 – 2.09 (m, 4H), 1.88 – 1.76 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.7, 155.4, 143.9, 129.6, 122.3, 120.5 (q, *J* = 259.6 Hz), 119.0, 116.9, 115.1, 37.2, 23.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -58.5.

HRMS (ESI) calculated for: $C_{13}H_{12}F_3O_4^+$ ([M+H]$^+$) m/z 289.0682, found 289.0683.

Compound S15



6-chloro-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclopentan]-4-one

Following Method A on 0.25 mmol scale with 5-chlorosalicylic acid and cyclopentanone at 80 ºC for 12 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 28 mg (47%) of the title compound **S15**.

Physical State: brown solid.

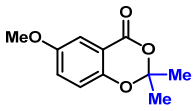
m.p.: 53 - 57 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.91 – 7.83 (m, 1H), 7.49 – 7.42 (m, 1H), 6.92 (dd, *J* = 9.0, 3.5 Hz, 1H), 2.16 – 2.07(m, 4H), 1.86 – 1.75 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.6, 155.4, 136.2, 129.2, 128.1, 118.9, 116.7, 115.4, 37.1, 23.2.

HRMS (ESI) calculated for: $C_{12}H_{12}ClO_3^+$ ([M+H]$^+$) m/z 239.0469, found 239.0468.

Compound S16



6-methoxy-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.5 mmol scale with 5-methoxysalicylic acid and acetone at 80 ºC for 8 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 47 mg (45%) of the title compound **S16**.

Physical State: white solid.

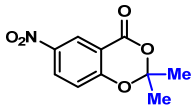
m.p.: 105 - 107 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 (d, *J* = 3.1 Hz, 1H), 7.06 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 3.74 (s, 3H), 1.65 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 154.8, 150.1, 124.7, 118.3, 113.6, 110.9, 106.3, 55.8, 25.6.

HRMS (ESI) calculated for: $C_{11}H_{13}O_4^+$ ([M+H]$^+$) m/z 209.0808, found 209.0812.

Compound S17



2,2-dimethyl-6-nitro-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 10.0 mmol scale with 5-nitrosalicylic acid and acetone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 1.26 g (57%) of the title compound **S17**.

Physical State: white solid.

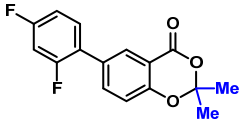
m.p.: 92 - 94 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.76 (d, *J* = 2.8 Hz, 1H), 8.38 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 1H), 1.75 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.3, 158.9, 142.7, 131.2, 125.8, 118.6, 113.3, 107.8, 25.8.

HRMS (ESI) calculated for: $C_{10}H_{10}NO_5^+$ ([M+H]$^+$) m/z 224.0553, found 224.0552.

Compound S18



6-(2,4-difluorophenyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 5.0 mmol scale with diflunisal and acetone at room temperature for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 0.76 g (52%) of the title compound **S18**.

Physical State: white solid.

m.p.: 111 - 113 ºC.

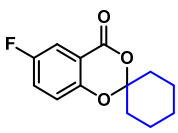
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.39 (q, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.99 – 6.87 (m, 2H), 1.77 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.6 (dd, *J* = 250.5, 11.1 Hz), 161.0, 159.8 (dd, *J* = 251.5,12.1 Hz), 155.6, 137.0 (d, *J* = 4.0 Hz), 131.3 (dd, *J* = 10.1, 5.0 Hz), 129.9 (d, *J* = 3.0 Hz), 129.8, 123.6 (dd, *J* = 13.1, 3.0 Hz), 117.6, 113.8, 112.0 (dd, *J* = 12.1, 3.0 Hz), 106.8, 104.7 (t, *J* = 5.0 Hz), 26.0.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -110.4 (p, *J* = 7.9 Hz), -113.6 (q, *J* = 8.9 Hz).

HRMS (ESI) calculated for: $C_{16}H_{13}F_2O_3^+$ ([M+H]$^+$) m/z 291.0827, found 291.0827.

Compound S19



6-fluoro-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

Following Method A on 0.25 mmol scale with 5-fluorosalicylic acid and cyclohexanone at 80 ºC for 12 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 30 mg (51%) of the title compound **S19**.

Physical State: yellow solid.

m.p.: 79 - 81 ºC.

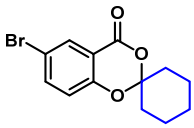
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.63 (dd, *J* = 7.7, 3.1 Hz, 1H), 7.31 – 7.25 (m, 1H), 6.99 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.08 – 1.94 (m, 4H), 1.77 – 1.62 (m, 4H), 1.59 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.4, 157.7 (d, *J* = 244.4 Hz), 152.0 (d, *J* = 3.0 Hz), 123.8 (d, *J* = 24.2 Hz), 118.9 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 24.2 Hz), 115.1 (d, *J* = 8.1 Hz), 107.5, 34.5, 24.6, 22.3.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -119.2 (td, *J* = 7.8, 4.1 Hz).

HRMS (ESI) calculated for: $C_{13}H_{14}FO_3^+$ ([M+H]$^+$) m/z 237.0921, found 237.0920.

Compound S20



6-bromo-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

Following Method A on 0.25 mmol scale with 5-bromosalicylic acid and cyclohexanone at 80 ºC for 12 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 43 mg (58%) of the title compound **S20**.

Physical State: yellow solid.

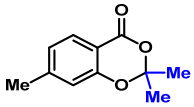
m.p.: 75 - 77 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 1.97 – 1.84 (m, 4H), 1.67 – 1.53 (m, 4H), 1.47 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.6, 154.6, 139.0, 131.8, 119.1, 115.5, 114.6, 107.3, 34.3, 24.3, 22.0.

HRMS (ESI) calculated for: $C_{13}H_{14}BrO_3^+$ ([M+H]$^+$) m/z 297.0121, found 297.0126.

Compound 75a



2,2,7-trimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with 4-methylsalicylic acid and acetone at 40 ºC for 10 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 24 mg (50%) of the title compound **75a**.

Physical State: white solid.

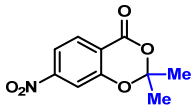
m.p.: 51 - 52 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.70 (s, 1H), 2.32 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.2, 156.0, 148.0, 129.4, 123.7, 117.3, 110.9, 106.2, 25.7, 22.0.

HRMS (ESI) calculated for: $C_{11}H_{13}O_3^+$ ([M+H]$^+$) m/z 193.0859, found 193.0861.

Compound S22



2,2-dimethyl-7-nitro-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with 4-nitrosalicylic acid and acetone at 80 ºC for 30 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 30 mg (54%) of the title compound **S22**.

Physical State: white solid.

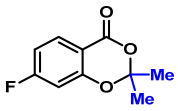
m.p.: 128 - 130 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.83 (d, *J* = 2.1 Hz, 1H), 1.77 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.3, 156.5, 152.8, 131.3, 118.4, 117.2, 113.2, 107.8, 25.9.

HRMS (ESI) calculated for: $C_{10}H_{10}NO_5^+$ ([M+H]$^+$) m/z 224.0553, found 224.0557.

Compound S23



7-fluoro-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with 4-fluorosalicylic acid and acetone at 40 ºC for 4 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 22 mg (45%) of the title compound **S23**.

Physical State: white solid.

m.p.: 75 - 77 ºC.

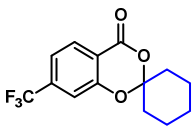
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (dd, *J* = 8.7, 6.3 Hz, 1H), 6.81 (td, *J* = 8.5, 2.4 Hz, 1H), 6.65 (dd, *J* = 9.3, 2.4 Hz, 1H), 1.72 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.6 (d, *J* = 230.3 Hz), 160.3, 157.9 (d, *J* = 14.1 Hz), 132.2 (d, *J* = 11.1 Hz), 110.9 (d, *J* = 23.2 Hz), 110.1 (d, *J* = 3.0 Hz), 107.0, 104.7 (d, *J* = 25.2 Hz), 25.9.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -99.1 (q, *J* = 8.1 Hz).

HRMS (ESI) calculated for: $C_{10}H_{10}FO_3^+$ ([M+H]$^+$) m/z 197.0608, found 197.0611.

Compound S24



7-(trifluoromethyl)-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

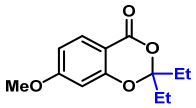
Following Method A on 0.25 mmol scale with 4-(trifluoromethyl)salicylic acid and cyclohexanone at 80 ºC for 10 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 31 mg (43%) of the title compound **S24**.

Physical State: yellow solid.

m.p.: 68 - 69 ºC.

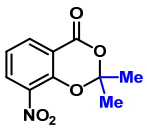
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 1H), 2.07 – 1.94 (m, 4H), 1.78 – 1.63 (m, 4H), 1.58 – 1.43 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.9, 155.8, 137.7 (q, *J* = 33.3 Hz), 130.6, 123.0 (q, *J* = 274.7 Hz), 119.0 (q, *J* = 4.0 Hz), 117.0, 114.8 (q, *J* = 4.0 Hz), 107.8, 34.5, 24.4, 22.2.
^{19}F NMR (471 MHz, Chloroform-*d*): δ -63.7.
HRMS (ESI) calculated for: $C_{14}H_{14}F_3O_3^+$ ([M+H]$^+$) m/z 287.0890, found 287.0890.

Compound S25



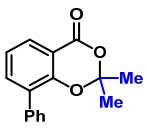
2,2-diethyl-7-methoxy-4H-benzo[d][1,3]dioxin-4-one
Following Method A on 0.25 mmol scale with 4-methoxysalicylic acid and 3-pentanone at 40 ºC for 10 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 27 mg (46%) of the title compound **S25**.
Physical State: colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.84 (d, *J* = 8.8 Hz, 1H), 6.62 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 1.98 (q, *J* = 7.5 Hz, 4H), 1.00 (t, *J* = 7.5 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.4, 161.2, 158.0, 131.2, 110.3, 110.1, 106.5, 101.1, 55.8, 28.8, 7.6.
HRMS (ESI) calculated for: $C_{13}H_{17}O_4^+$ ([M+H]$^+$) m/z 237.1121, found 237.1121.

Compound S26



2,2-dimethyl-8-nitro-4H-benzo[d][1,3]dioxin-4-one
Following Method A on 15.0 mmol scale with 3-nitrosalicylic acid and acetone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.21 g (36%) of the title compound **S26**.
Physical State: yellow solid.
m.p.: 89 - 91 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.25 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 1.81 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.0, 150.0, 138.6, 135.1, 132.0, 122.0, 116.1, 108.2, 26.0.
HRMS (ESI) calculated for: $C_{10}H_{10}NO_5^+$ ([M+H]$^+$) m/z 224.0553, found 224.0553.

Compound S27



2,2-dimethyl-8-phenyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 2.5 mmol scale with 3-phenylsalicylic acid and acetone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 0.27 g (43%) of the title compound **S27**.

Physical State: yellow solid.

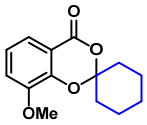
m.p.: 70 - 72 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 1.74 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.4, 153.0, 137.2, 135.9, 130.8, 129.2, 129.0, 128.4, 127.9, 122.7, 114.3, 106.3, 25.9.

HRMS (ESI) calculated for: $C_{16}H_{15}O_3^+$ ([M+H]$^+$) m/z 255.1016, found 255.1015.

Compound S28



8-methoxy-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

Following Method A on 5.0 mmol scale with 3-methoxysalicylic acid and cyclohexanone at room temperature for 24 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 0.74 g (60%) of the title compound **S28**.

Physical State: white solid.

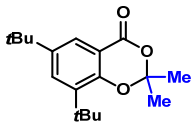
m.p.: 141 - 143 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.49 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.09 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 2.01 (t, *J* = 6.2 Hz, 4H), 1.72 – 1.64 (m, 4H), 1.52 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.1, 148.6, 145.6, 122.1, 120.6, 117.8, 114.9, 107.3, 56.4, 34.5, 24.7, 22.3.

HRMS (ESI) calculated for: $C_{14}H_{17}O_4^+$ ([M+H]$^+$) m/z 249.1121, found 249.1128.

Compound S29



6,8-di-tert-butyl-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 10.0 mmol scale with 3,5-di-*tert*-butylsalicylic acid and acetone at room temperature for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 1.00 g (34%) of the title compound **S29**.

Physical State: white solid.

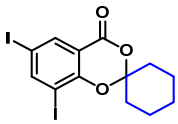
m.p.: 89 - 91 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.82 (d, *J* = 2.4 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 1.73 (s, 6H), 1.36 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.3, 152.4, 144.9, 138.0, 130.9, 123.9, 113.7, 105.3, 34.8, 34.7, 31.4, 29.7, 25.9.

HRMS (ESI) calculated for: $C_{18}H_{27}O_3^+$ ([M+H]$^+$) m/z 291.1955, found 291.1953.

Compound S30



6,8-diiodo-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclohexan]-4-one

Following Method A on 10.0 mmol scale with 3,5-di-iodosalicylic acid and cyclohexanone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 1.20 g (25%) of the title compound **S30**.

Physical State: yellow solid.

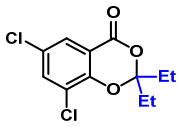
m.p.: 82 - 83 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.20 (d, *J* = 2.1 Hz, 1H), 2.17 – 2.09 (m, 2H), 1.90 – 1.82 (m, 2H), 1.76 – 1.59 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.1, 155.1, 152.6, 138.3, 116.3, 108.5, 86.0, 85.3, 34.5, 24.5, 22.4.

HRMS (ESI) calculated for: $C_{13}H_{13}I_2O_3^+$ ([M+H]$^+$) m/z 470.8949, found 470.8950.

Compound S31



6,8-dichloro-2,2-diethyl-4H-benzo[d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with 3,5-dichlorosalicylic acid and 3-pentanone at 80 ºC for 36 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 22 mg (32%) of the title compound **S31**.

Physical State: yellow solid.

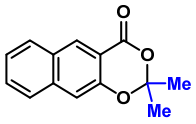
m.p.: 50 - 52 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.83 (d, *J* = 2.6 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 2.02 (qd, *J* = 7.4, 2.9 Hz, 4H), 1.03 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 159.3, 150.8, 136.1, 127.7, 127.7, 123.6, 116.0, 111.9, 28.9, 7.6.

HRMS (ESI) calculated for: $C_{12}H_{13}Cl_2O_3^+$ ([M+H]$^+$) m/z 275.0236, found 275.0239.

Compound S32

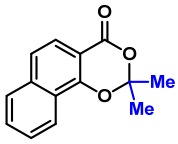


2,2-dimethyl-4H-naphtho[2,3-d][1,3]dioxin-4-one

Following Method A on 0.25 mmol scale with 3-hydroxy-2-naphthoic acid and acetone at 40 ºC for 12 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 29 mg (51%) of the title compound **S32**.

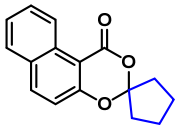
Physical State: white solid.
m.p.: 127 - 128 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.59 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 8.2 Hz, 1H), 7.33 (s, 1H), 1.76 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.6, 151.2, 137.8, 132.3, 129.8, 129.7, 129.2, 127.0, 125.5, 114.3, 112.9, 106.5, 26.3.
HRMS (ESI) calculated for: $C_{14}H_{13}O_3^+$ ([M+H]$^+$) m/z 229.0859, found 229.0864.

Compound S33



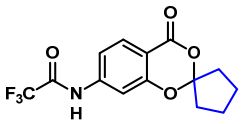
2,2-dimethyl-4H-naphtho[1,2-d][1,3]dioxin-4-one
Following Method A on 0.25 mmol scale with 1-hydroxy-2-naphthoic acid and acetone at 80 ºC for 16 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 35 mg (61%) of the title compound **S33**.
Physical State: white solid.
m.p.: 81 - 83 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.84 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.66 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 1.85 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.5, 154.4, 137.7, 129.9 128.2, 126.8, 124.0, 123.6, 123.0, 122.1, 107.5, 106.8, 25.9.
HRMS (ESI) calculated for: $C_{14}H_{12}NaO_3^+$ ([M+Na]$^+$) m/z 251.0679, found 251.0679.

Compound S34



1'H-spiro[cyclopentane-1,3'-naphtho[2,1-d][1,3]dioxin]-1'-one
Following Method A on 10.0 mmol scale with 2-hydroxy-1-naphthoic acid and cyclopentanone at room temperature for 16 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 1.06 g (42%) of the title compound **S34**.
Physical State: white solid.
m.p.: 96 - 97 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.18 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 2.27 – 2.13 (m, 4H), 1.89 – 1.77 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 158.6, 137.7, 131.8, 129.8, 129.5, 128.7, 125.6, 125.2, 117.3, 115.3, 106.2, 36.9, 23.3.
HRMS (ESI) calculated for: $C_{16}H_{15}O_3^+$ ([M+H]$^+$) m/z 255.1016, found 255.1018.

Compound S35



2,2,2-trifluoro-N-(4-oxo-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclopentan]-7-yl)acetamide

Following Method A on 0.25 mmol scale with 4-aminosalicylic acid, cyclopentanone, TFA (0.25 mL) and TFAA (0.4 mL) at 80 ºC for 12 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 45 mg (57%) of the title compound **S35**.

Physical State: white solid.

m.p.: 132 - 133 ºC.

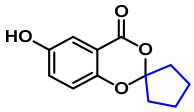
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.74 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.18 – 2.12 (m, 4H), 1.88 – 1.78 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 161.6, 158.1, 155.4 (q, *J* = 15.2 Hz), 142.5, 131.1, 115.5 (q, *J* = 192.9 Hz), 116.9, 114.6, 111.6, 108.7, 37.2, 23.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -75.6.

HRMS (ESI) calculated for: $C_{14}H_{13}F_3NO_4^+$ ([M+H]$^+$) m/z 316.0791, found 316.0798.

Compound S36



6-hydroxy-4H-spiro[benzo[d][1,3]dioxine-2,1'-cyclopentan]-4-one

Following Method A on 0.5 mmol scale with 2,4-di-hydroxybenzoic acid and cyclopentanone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 41 mg (37%) of the title compound **S36**.

Physical State: white solid.

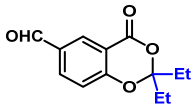
m.p.: 103 - 105 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.48 (d, *J* = 3.1 Hz, 1H), 7.11 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.55 (br s, 1H), 2.17 – 2.11 (m, 4H), 1.87 – 1.75 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.9, 151.7, 150.9, 124.8, 118.5, 116.8, 114.8, 114.5, 37.1, 23.3.

HRMS (ESI) calculated for: $C_{12}H_{12}NaO_4^+$ ([M+H]$^+$) m/z 243.0628, found 243.0627.

Compound S37



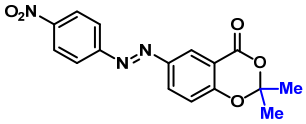
2,2-diethyl-4-oxo-4H-benzo[d][1,3]dioxine-6-carbaldehyde

Following Method A on 10.0 mmol scale with 5-formylsalicylic acid and 3-pentanone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 0.20 g (10%) of the title compound **S37**.

Physical State: yellow oil.

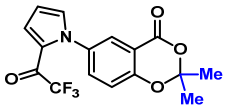
^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.94 (d, *J* = 0.6 Hz, 1H), 8.44 (d, *J* = 2.1 Hz, 1H), 8.10 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 2.02 (q, *J* = 7.6 Hz, 4H), 1.02 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 189.7, 160.7, 160.1, 135.8, 133.4, 131.4, 118.5, 113.9, 111.5, 29.1, 7.5.
HRMS (ESI) calculated for: $C_{13}H_{14}NaO_4^+$ ([M+Na]$^+$) m/z 257.0784, found 257.0778.

Compound S38



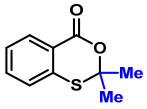
2,2-dimethyl-6-((4-nitrophenyl)diazenyl)-4H-benzo[d][1,3]dioxin-4-one
Following Method A on 5.0 mmol scale with 2-hydroxy-5-((4-nitrophenyl)diazenyl)-benzoic acid and acetone at 80 ºC for 24 hours. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 0.93 g (57%) of the title compound **S38**.
Physical State: orange solid.
m.p.: 156 - 158 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.62 (d, *J* = 2.4 Hz, 1H), 8.41 – 8.37 (m, 2H), 8.21 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.05 – 8.02 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 1.80 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 160.4, 158.9, 155.5, 149.0, 147.7, 130.7, 126.1, 125.0, 123.7, 118.5, 114.0, 107.3, 26.1.
HRMS (ESI) calculated for: $C_{16}H_{14}N_3O_5^+$ ([M+H]$^+$) m/z 328.0928, found 328.0932.

Compound S39



2,2-dimethyl-6-(2-(2,2,2-trifluoroacetyl)-1H-pyrrol-1-yl)-4H-benzo[d][1,3]dioxin-4-one
Following Method A on 2.0 mmol scale with 2-hydroxy-5-(1H-pyrrol-1-yl)benzoic acid, cyclopentanone, TFA (4 mL) and TFAA (4 mL) at 80 ºC for 12 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 0.42 g (62%) of the title compound **S39**.
Physical State: white solid.
m.p.: 111 - 113 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.87 (d, *J* = 2.6 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.19 – 7.16 (m, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 6.47 (dd, *J* = 4.3, 2.6 Hz, 1H), 1.79 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 169.6 (q, *J* = 28.3 Hz), 160.3, 156.0, 134.9, 134.7, 134.4, 126.8, 125.3, 125.1 (q, *J* = 3.0 Hz), 118.1, 116.9 (q, *J* = 233.3 Hz), 113.7, 111.7, 107.2, 26.0.
^{19}F NMR (471 MHz, $CDCl_3$): δ -71.6.
HRMS (ESI) calculated for: $C_{16}H_{13}F_3NO_4^+$ ([M+H]$^+$) m/z 340.0791, found 340.0795.

Compound S40



2,2-dimethyl-4H-benzo[d][1,3]oxathiin-4-one

Following Method A on 16.0 mmol scale with thiosalicylic acid and acetone at room temperature for 24 hours. Purification by flash column chromatography (silica, 100:1 PE:EtOAc) afforded 1.89 g (61%) of the title compound **S40**.

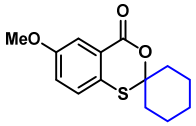
Physical State: colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.14 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1H), 7.25 (td, *J* = 7.9, 1.2 Hz, 2H), 1.79 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.5, 136.9, 133.9, 132.1, 127.9, 126.3, 123.5, 86.2, 29.1.

Spectroscopic data are in agreement with published values.[13]

Compound S41



6-methoxy-4H-spiro[benzo[d][1,3]oxathiine-2,1'-cyclohexan]-4-one

Following Method A on 2.0 mmol scale with 2-mercapto-5-methoxybenzoic acid and cyclohexanone at room temperature for 16 hours. Purification by flash column chromatography (silica, 80:1 PE:EtOAc) afforded 174 mg (33%) of the title compound **S41**.

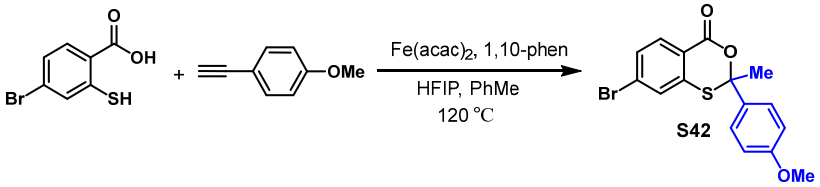
Physical State: colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.67 (d, *J* = 2.9 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.84 (s, 3H), 2.16 - 2.10 (m, 2H), 2.09 – 2.02 (m, 2H), 1.78 – 1.72 (m, 2H), 1.63 – 1.57 (m, 2H), 1.55 – 1.50 (m, 1H), 1.49 – 1.42 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 163.7, 158.3, 129.4, 127.3, 125.1, 122.2, 115.2, 90.1, 55.8, 37.2, 25.1, 22.6.

HRMS (ESI) calculated for: $C_{14}H_{17}O_3S^+$ ([M+H]$^+$) m/z 265.0893, found 265.0893.

Compound S42



7-bromo-2-(4-methoxyphenyl)-2-methyl-4H-benzo[d][1,3]oxathiin-4-one

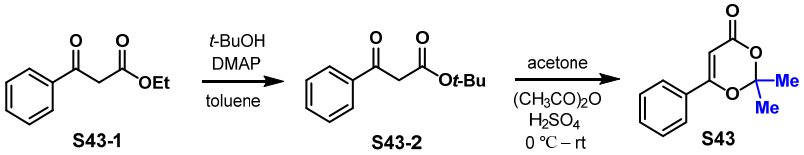
Compound **S42** was prepared according to procedures reported in the literature.[14] A solution of $Fe(acac)_2$ (30 mg, 0.12 mmol) and 1,10-phenanthroline (43 mg, 0.24 mmol) in HFIP (0.6 mL) and anhydrous toluene (0.9 mL) was stirred at room temperature under argon for 10 min. A sealed tube charged with 4-bromo-2-mercaptobenzoic acid (153 mg, 0.66 mmol), 1-ethynyl-4-methoxybenzene (79 mg, 0.6 mmol) and a magnetic stir bar was evacuated and backfilled with argon for three times. The catalyst solution was then transferred to the sealed tube via cannula under argon protection. The sealed tube was heated to 120 ºC and stirred for 16 hours. After cooling the room temperature, the reaction mixture was filtered over celite, evaporated, and purified by flash column chromatography (silica gel, 100:1 PE:EtOAc) to give **S42** (89 mg, 41%).

Physical State: yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.18 (d, *J* = 2.2 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.82 – 6.78 (m, 2H), 3.76 (s, 3H), 2.04 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*): δ 163.0, 159.9, 136.8, 136.0, 134.7, 133.9, 129.0, 127.2, 126.0, 120.0, 114.0, 90.8, 55.4, 31.5.
HRMS (ESI) calculated for: $C_{16}H_{14}BrO_3S^+$ ([M+H]$^+$) m/z 364.9842, found 364.9842.

Compound S43

2,2-dimethyl-6-phenyl-4H-1,3-dioxin-4-one

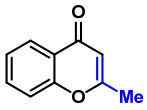


S43-1 S43-2 S43

The **S43** was prepared according to procedures reported in literature.[14-15] To a flask equipped with a Dean-Stark apparatus and a magnetic stir bar were added **S43-1** (1.93 g, 10.0 mmol, 1.0 equiv), *t*-BuOH (4.8 mL, 5.0 equiv), DMAP (0.37 g, 0.3 equiv) and toluene (40 mL). The mixture was heated to reflux and the reaction progress was monitored by TLC. After completion, the reaction mixture was concentrated and purified by flash chromatography to obtain **S43-2** (1.35 g, 61%).[15]
To a stirred solution of **S43-2** (0.40 g, 2.18 mmol, 1.0 equiv) in acetone (1.6 mL, 10.0 equiv) were added acetic anhydride (3.1 mL, 15.0 equiv) and sulfuric acid (0.12 mL, 1.0 equiv) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 1 hour before quenched by addition of Na_2CO_3 (aq., 7.0 g, 30.0 equiv, 20 mL). EtOAc (50 mL) was added to the reaction and the mixture was stirred for another 40 min. The layers were separated and the aqueous layer was extracted with EtOAc for three times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography to afford **S43** (0.20 g, 44%).[16]
Physical State: white solid.
m.p.: 62 - 63 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.40 (m, 3H), 5.88 (s, 1H), 1.79 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 165.1, 161.9, 132.2, 131.1, 128.9, 126.4, 106.7, 91.3, 25.1.
HRMS (ESI) calculated for: $C_{12}H_{13}O_3^+$ ([M+H]$^+$) m/z 205.0859, found 205.0860.

Chromones, Thiochromones, and γ-Pyrones

Compound 6



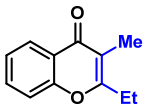
2-methyl-4H-chromen-4-one

Following General Procedure on 0.25 mmol scale with **5** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 36 mg (90%) of the title compound **6**.
Physical State: white solid.
m.p.: 66 - 67 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.18 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.65 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.42 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.38 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.18 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.4, 166.3, 156.6, 133.6, 125.8, 125.1, 123.7, 117.9, 110.7, 20.8.

Spectroscopic data are in agreement with published values.[17]

Compound 7



2-ethyl-3-methyl-4H-chromen-4-one

Following General Procedure on 0.6 mmol scale with **S1** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 103 mg (91%) of the title compound **7**.

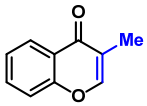
Physical State: yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.20 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.34 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.4, 166.3, 156.1, 133.0, 126.0, 124.6, 122.8, 117.7, 116.2, 25.8, 11.5, 9.7.

HRMS (ESI) calculated for: $C_{12}H_{13}O_2^+$ ([M+H]$^+$) m/z 189.0910, found 189.0915.

Compound 8



3-methyl-4H-chromen-4-one

Following General Procedure on 0.5 mmol scale with **S2** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 62 mg (78%) of the title compound **8**.

Physical State: yellow solid.

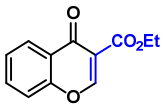
m.p.: 64 - 66 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.79 (s, 1H), 7.63 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.43 – 7.34 (m, 2H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.5, 156.8, 151.9, 133.4, 125.9, 124.9, 123.7, 120.9, 118.1, 11.4.

HRMS (ESI) calculated for: $C_{10}H_9O_2^+$ ([M+H]$^+$) m/z 161.0597, found 161.0593.

Compound 9

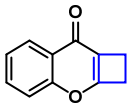


ethyl 4-oxo-4H-chromene-3-carboxylate

Following General Procedure on 0.75 mmol scale with **S3** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 101 mg (62%) of the title compound **9**.

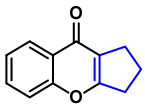
Physical State: yellow solid.
m.p.: 67 - 68 ºC.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.66 (s, 1H), 8.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.70 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 173.6, 163.5, 161.9, 155.8, 134.3, 126.8, 126.4, 125.3, 118.3, 116.5, 61.6, 14.4.
Spectroscopic data are in agreement with published values.[18]

Compound 10



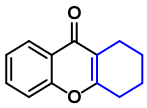
1,2-dihydro-8H-cyclobuta[b]chromen-8-one
Following General Procedure on 0.7 mmol scale with **S4** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 110 mg (90%) of the title compound **10**.
Physical State: white solid.
m.p.: 137 - 138 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.25 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.60 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.46 – 7.36 (m, 2H), 3.28 (t, *J* = 3.3 Hz, 2H), 2.92 (t, *J* = 3.3 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 172.4, 165.3, 157.8, 132.6, 127.3, 126.5, 125.0, 122.1, 118.4, 33.5, 23.9.
HRMS (ESI) calculated for: $C_{11}H_9O_2^+$ ([M+H]$^+$) m/z 173.0597, found 173.0599.

Compound 11



2,3-dihydrocyclopenta[b]chromen-9(1H)-one
Following General Procedure on 1.0 mmol scale with **S5** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 154 mg (83%) of the title compound **11**.
Physical State: yellow solid.
m.p.: 119 - 121 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 3.00 – 2.92 (m, 2H), 2.90 – 2.81 (m, 2H), 2.11 (p, *J* = 7.6 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.3, 169.7, 157.0, 132.8, 125.9, 124.9, 124.2, 121.1, 118.0, 32.3, 26.1, 19.6.
HRMS (ESI) calculated for: $C_{12}H_{11}O_2^+$ ([M+H]$^+$) m/z 187.0754, found 187.0754.
Spectroscopic data are in agreement with published values.[19]

Compound 12



1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.5 mmol scale with **75b** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 90 mg (90%) of the title compound **12**.

Scale up was performed following the General Procedure on 7.3 mmol scale with **75b** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 5:1 PE:EtOAc) afforded 1.22 g (83%) of the title compound **12**.

Physical State: white solid.

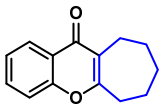
m.p.: 102 - 104 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.16 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.36 – 7.27 (m, 2H), 2.63 (t, *J* = 6.3 Hz, 2H), 2.55 (t, *J* = 6.1 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.77 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.7, 163.9, 155.9, 133.0 125.7, 124.4, 123.2, 118.4, 117.6, 28.2, 21.9, 21.7, 21.0.

Spectroscopic data are in agreement with published values.[20]

Compound 13



7,8,9,10-tetrahydrocyclohepta[b]chromen-11(6H)-one

Following General Procedure on 0.5 mmol scale with **S6** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 77 mg (71%) of the title compound **13**.

Physical State: white solid.

m.p.: 84 - 85 ºC.

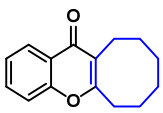
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.19 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 2.86 – 2.82 (m, 2H), 2.81 – 2.77 (m, 2H), 1.88 – 1.81 (m, 2H), 1.77 – 1.71 (m, 2H), 1.59 (p, *J* = 5.8 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 177.1, 169.1, 155.8, 132.9, 126.2, 124.6, 123.1, 122.9, 117.8, 34.9, 32.0, 26.5, 25.0, 22.4.

HRMS (ESI) calculated for: $C_{14}H_{15}O_2^+$ ($[M+H]^+$) m/z 215.1067, found 215.1061.

Spectroscopic data are in agreement with published values.[20]

Compound 14



6,7,8,9,10,11-hexahydro-12H-cycloocta[b]chromen-12-one

Following General Procedure on 0.5 mmol scale with **S7** and AgOTf at room temperature for 3 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 123 mg (94%) of the title compound **14**.

Physical State: yellow solid.

m.p.: 90 - 92 ºC.

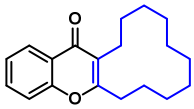
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.17 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.6, 7.1, 1.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.80 – 2.75 (m, 2H), 2.72 – 2.67 (m, 2H), 1.85 – 1.78 (m, 2H), 1.72 – 1.65 (m, 2H), 1.52 – 1.40 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.1, 166.4, 156.1, 132.9, 125.9, 124.5, 123.1, 120.7, 117.8, 31.5, 29.3, 29.1, 26.4, 26.3, 22.9.

HRMS (ESI) calculated for: $C_{15}H_{17}O_2^+$ ([M+H]$^+$) m/z 229.1223, found 229.1223.

Spectroscopic data are in agreement with published values.[20]

Compound 15



6,7,8,9,10,11,12,13,14,15-decahydro-16H-cyclododeca[b]chromen-16-one

Following General Procedure on 0.5 mmol scale with **S8** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 120 mg (85%) of the title compound **15**.

Physical State: white solid.

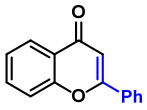
m.p.: 113 - 115 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.77 – 1.70 (m, 2H), 1.53 – 1.46 (m, 6H), 1.43 – 1.36 (m, 4H), 1.33 – 1.28 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.4, 166.1, 156.1, 133.1, 126.0, 124.4, 123.1, 121.5, 117.6, 28.9, 26.5, 25.7, 25.5, 25.2, 24.9, 23.9, 23.2, 23.0, 22.1.

HRMS (ESI) calculated for: $C_{19}H_{25}O_2^+$ ([M+H]$^+$) m/z 285.1849, found 285.1853.

Compound 16



2-phenyl-4H-chromen-4-one

Following General Procedure on 0.5 mmol scale with **S9** and $AgNTf_2$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 102 mg (92%) of the title compound **16**.

Physical State: yellow solid.

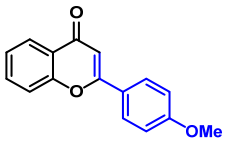
m.p.: 93 - 95 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.69 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.59 – 7.48 (m, 4H), 7.41 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H), 6.82 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.6, 163.5, 156.3, 133.9, 131.8, 131.7, 129.1, 126.4, 125.8, 125.3, 124.0, 118.2, 107.6.

Spectroscopic data are in agreement with published values.[21]

Compound 17



2-(4-methoxyphenyl)-4H-chromen-4-one

Following General Procedure on 0.5 mmol scale with **S10** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 90 mg (71%) of the title compound **17**.

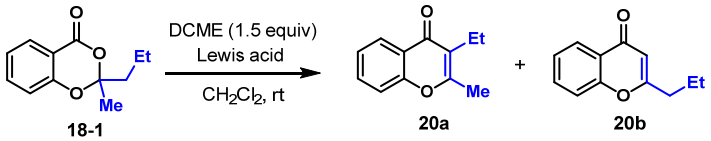
Physical State: white solid.

m.p.: 157 - 158 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.69 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.75 (s, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.6, 163.6, 162.6, 156.4, 133.7, 128.2, 125.8, 125.2, 124.2, 124.1, 118.1, 114.6, 106.4, 55.7.

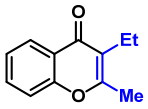
Spectroscopic data are in agreement with published values.[21]



Following General Procedure on 0.2 mmol scale with **18-1** and $SnCl_4$ at room temperature for 3 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 29 mg (77%) of **20a** and 6 mg (16%) of **20b**.

Following General Procedure on 0.65 mmol scale with **18-1** and AgOTf at room temperature for 2 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 66 mg (54%) of **20a** and 38 mg (31%) of **20b**.

Compound 20a



2-ethyl-2-methyl-4H-chromen-4-one

Physical State: white solid.

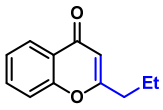
m.p.: 46 - 47 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.35 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.32 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 177.5, 162.1, 156.0, 133.0, 126.0, 124.5, 123.1, 123.0, 117.7, 18.3, 18.1, 13.3.

HRMS (ESI) calculated for: $C_{12}H_{13}O_2^+$ ([M+H]$^+$) m/z 189.0910, found 189.0913.

Compound 20b



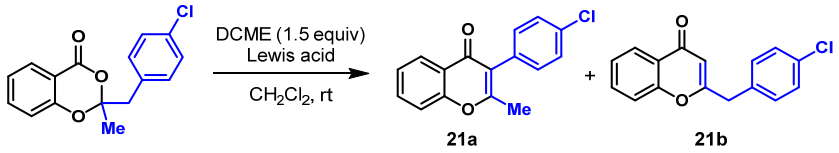
2-propyl-4H-chromen-4-one

Physical State: colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.16 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.40 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.36 (ddd, *J* = 7.6, 0.5 Hz, 1H), 6.16 (s, 1H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.5, 169.7, 156.6, 133.5, 125.7, 125.0, 123.8, 117.9, 110.0, 36.3, 20.3, 13.6.

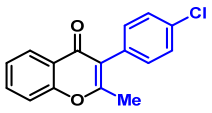
HRMS (ESI) calculated for: $C_{12}H_{13}O_2^+$ ([M+H]$^+$) m/z 189.0910, found 189.0915.



Following General Procedure on 0.3 mmol scale with **18-2** and $SnCl_4$ at room temperature for 3 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 19 mg (23%) of **21a** and 6 mg (7%) of **21b**.

Following General Procedure on 0.57 mmol scale with **18-2** and AgOTf at room temperature for 1 hour. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 91 mg (59%) of **21a** and 53 mg (34%) of **21b**.

Compound 21a



3-(4-chlorophenyl)-2-methyl-4H-chromen-4-one

Physical State: white solid.

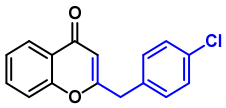
m.p.: 88 - 90 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.66 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.46 – 7.36 (m, 4H), 7.25 – 7.22 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.7, 163.5, 156.0, 133.9, 133.6, 132.0, 131.7, 128.8, 126.3, 125.1, 123.4, 122.7, 117.8, 19.7.

HRMS (ESI) calculated for: $C_{16}H_{12}ClO_2^+$ ([M+H]$^+$) m/z 271.0520, found 271.0525.

Compound 21b



2-(4-chlorobenzyl)-4H-chromen-4-one

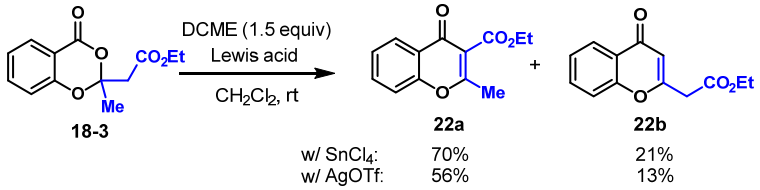
Physical State: white solid.

m.p.: 115 - 117 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.63 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.41 – 7.30 (m, 4H), 7.25 – 7.21 (m, 2H), 6.12 (s, 1H), 3.89 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.4, 167.5, 156.6, 133.8, 133.6, 133.4, 130.7, 129.2, 125.8, 125.2, 123.7, 118.0, 110.9, 40.1.

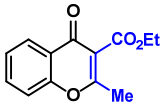
HRMS (ESI) calculated for: $C_{16}H_{12}ClO_2^+$ ([M+H]$^+$) m/z 271.0520, found 271.0518.



Following General Procedure on 0.17 mmol scale with **18-3** and $SnCl_4$ at room temperature for 3 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 28 mg (70%) of **22a** and 8 mg (21%) of **22b**.

Following General Procedure on 0.2 mmol scale with **18-3** and AgOTf at room temperature for 1 hour. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 26 mg (56%) of **22a** and 6 mg (13%) of **22b**.

Compound 22a



ethyl 2-methyl-4-oxo-4H-chromene-3-carboxylate

Physical State: white solid.

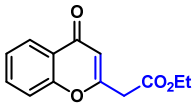
m.p.: 68 - 70 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.18 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.65 (ddd, *J* = 7.8, 1.8 Hz, 1H), 7.43 – 7.35 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 174.5, 166.8, 165.2, 155.7, 134.0, 126.2, 125.6, 123.5, 118.3, 117.8, 61.9, 19.6, 14.3.

HRMS (ESI) calculated for: $C_{13}H_{13}O_4^+$ ([M+H]$^+$) m/z 233.0808, found 233.0807.

Compound 22b



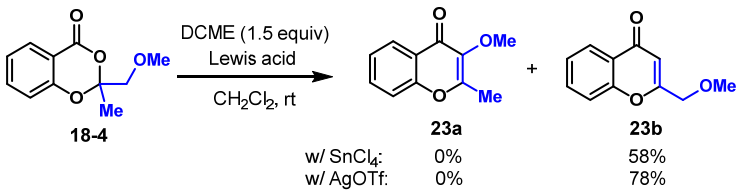
ethyl 2-(4-oxo-4H-chromen-2-yl)acetate

Physical State: yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 6.30 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.2, 167.5, 161.5, 156.6, 133.9, 125.9, 125.4, 123.8, 118.1, 112.5, 62.0, 40.5, 14.2.

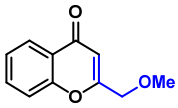
HRMS (ESI) calculated for: $C_{13}H_{13}O_4^+$ ([M+H]$^+$) m/z 233.0808, found 233.0804.



Following General Procedure on 0.13 mmol scale with **18-4** and $SnCl_4$ at room temperature for 2 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 14 mg (58%) of **23b**.

Following General Procedure on 0.13 mmol scale with **18-4** and AgOTf at room temperature for 2 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 19 mg (78%) of **23b**.

Compound 23b



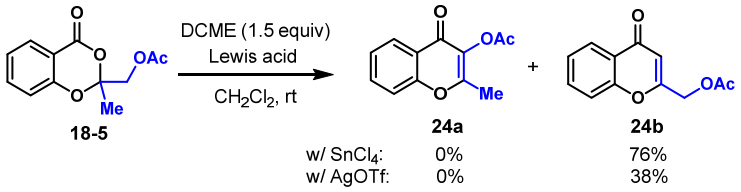
2-(methoxymethyl)-4H-chromen-4-one

Physical State: colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.19 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 4.37 (s, 2H), 3.50 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.2, 165.0, 156.4, 133.9, 125.9, 125.3 124.2, 118.1, 109.8, 70.9, 59.4.

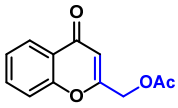
HRMS (ESI) calculated for: $C_{11}H_{11}O_3^+$ ([M+H]$^+$) m/z 191.0703, found 191.0704.



Following General Procedure on 0.3 mmol scale with **18-5** and $SnCl_4$ at room temperature for 1 hour. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 53 mg (76%) of **24b**.

Following General Procedure on 0.3 mmol scale with **18-5** and AgOTf at room temperature for 1 hour. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 27 mg (38%) of **24b**.

Compound 24b



(4-oxo-4H-chromen-2-yl)methyl acetate

Physical State: white solid.

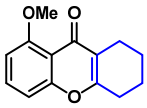
m.p.: 63 - 64 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.19 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 5.02 (s, 2H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.0, 170.1, 162.7, 156.3, 134.1, 126.0, 125.6, 124.1, 118.1, 110.1, 61.8, 20.8.

HRMS (ESI) calculated for: $C_{12}H_{11}O_4^+$ ([M+H]$^+$) m/z 219.0652, found 219.0651.

Compound 25



8-methoxy-1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.3 mmol scale with **S11** and $SnCl_4$ at room temperature for 12 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 59 mg (86%) of the title compound **25**.

Physical State: white solid.

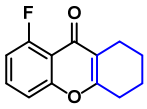
m.p.: 97 - 98 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.47 (t, *J* = 8.4 Hz, 1H), 6.94 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.74 (dd, *J* = 8.3, 1.0 Hz, 1H), 3.96 (s, 3H), 2.60 (tt, *J* = 6.4, 1.7 Hz, 2H), 2.52 (tt, *J* = 6.2, 1.7 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.76 – 1.69 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 177.6, 161.6, 159.9, 158.1, 133.0, 119.6, 114.0, 110.0, 105.7, 56.4, 27.8, 22.0, 21.9, 21.0.

HRMS (ESI) calculated for: $C_{14}H_{15}O_3^+$ ([M+H]$^+$) m/z 231.1016, found 231.1013.

Compound 26



8-fluoro-1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.3 mmol scale with **S12** and $SnCl_4$ at room temperature for 2 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 61 mg (93%) of the title compound **26**.

Physical State: white solid.

m.p.: 137 - 138 ºC.

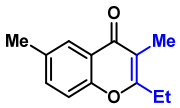
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50 (td, *J* = 8.3, 5.5 Hz, 1H), 7.16 (dt, *J* = 8.5, 1.1 Hz, 1H), 6.97 (ddd, *J* = 10.7, 8.1, 1.0 Hz, 1H), 2.63 (tt, *J* = 6.4, 1.6 Hz, 2H), 2.53 (tt, *J* = 6.1, 1.7 Hz, 2H), 1.88 – 1.82 (m, 2H), 1.77 – 1.70 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 176.1, 163.0, 160.8 (d, *J* = 264.1 Hz), 157.0 (d, *J* = 3.9 Hz), 132.9 (d, *J* = 10.7 Hz), 119.5, 113.7 (d, *J* = 9.7 Hz), 113.6 (d, *J* = 4.4 Hz), 111.2 (d, *J* = 20.9 Hz), 27.9, 21.9, 21.6, 20.9.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -112.3 (dd, *J* = 10.7, 5.5 Hz).

HRMS (ESI) calculated for: $C_{13}H_{12}FO_2^+$ ([M+H]$^+$) m/z 219.0816, found 219.0814.

Compound 27

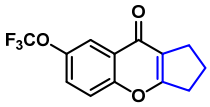


2-ethyl-3,6-dimethyl-4H-chromen-4-one

Following General Procedure on 0.8 mmol scale with **S13** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 148 mg (92%) of the title compound **27**.

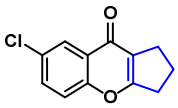
Physical State: white solid.
m.p.: 44 - 46 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.99 – 7.98 (m, 1H), 7.42 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.08 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.4, 166.1, 154.3, 134.3, 134.2, 125.2, 122.3, 117.4, 115.9, 25.8, 21.0, 11.5, 9.7.
HRMS (ESI) calculated for: $C_{13}H_{15}O_2^+$ ([M+H]$^+$) m/z 203.1067, found 203.1067.

Compound 28



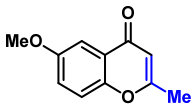
6-(trifluoromethoxy)-2,3-dihydrocyclopenta[b]chromen-9(1H)-one
Following General Procedure on 0.4 mmol scale with **S14** and AgOTf at room temperature for 4 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 96 mg (89%) of the title compound **28**.
Physical State: yellow solid.
m.p.: 85 - 87 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.07 – 8.04 (m, 1H), 7.49 – 7.41 (m, 2H), 2.97 (tt, *J* = 7.1, 1.5 Hz, 2H), 2.84 (tt, *J* = 7.6, 1.5 Hz, 2H), 2.17 – 2.08 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 175.1, 170.3, 155.0, 145.9, 126.1, 125.3, 121.1, 120.7 (q, *J* = 258.5 Hz), 120.0, 117.8, 32.3, 26.1, 19.6.
^{19}F NMR (471 MHz, $CDCl_3$): δ -58.2.
HRMS (ESI) calculated for: $C_{13}H_{10}F_3O_3^+$ ([M+H]$^+$) m/z 271.0577, found 271.0577.

Compound 29



7-chloro-2,3-dihydrocyclopenta[b]chromen-9(1H)-one
Following General Procedure on 0.4 mmol scale with **S15** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 74 mg (84%) of the title compound **29**.
Physical State: white solid.
m.p.: 129 - 130ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.20 (d, *J* = 2.6 Hz, 1H), 7.55 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 2.98 (tt, *J* = 7.6, 1.5 Hz, 2H), 2.86 (tt, *J* = 7.5, 1.5 Hz, 2H), 2.18 – 2.10 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 175.1, 170.1, 155.4, 133.0, 130.9, 125.5, 125.4, 121.3, 119.7, 32.4, 26.2, 19.6.
HRMS (ESI) calculated for: $C_{12}H_{10}ClO_2^+$ ([M+H]$^+$) m/z 221.0364, found 221.0365.

Compound 30



6-methoxy-2-methyl-4H-chromen-4-one

Following General Procedure on 0.8 mmol scale with **S16** and AgOTf at room temperature for 8 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 121 mg (79%) of the title compound **30**.

Physical State: white solid.

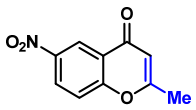
m.p.: 107 - 109 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, *J* = 3.1 Hz, 1H), 7.33 (d, *J* = 9.1 Hz, 1H), 7.21 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.14 (s, 1H), 3.87 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.2, 166.0, 156.8, 151.4, 124.2, 123.5, 119.3, 109.9, 104.9, 56.0, 20.7.

Spectroscopic data are in agreement with published values.[22]

Compound 31



2-methyl-6-nitro-4H-chromen-4-one

Following General Procedure on 0.8 mmol scale with **S17** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 129 mg (79%) of the title compound **31**.

Physical State: white solid.

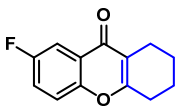
m.p.: 176 - 178 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.03 (d, *J* = 2.8 Hz, 1H), 8.47 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 6.24 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.6, 167.1, 159.4, 144.7, 128.0, 123.8, 122.6, 119.7, 111.2, 20.7.

Spectroscopic data are in agreement with published values.[22]

Compound 32



7-fluoro-1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.5 mmol scale with **S19** and $SnCl_4$ at room temperature for 2 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 98 mg (90%) of the title compound **32**.

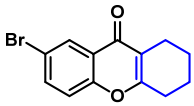
Physical State: yellow solid.

m.p.: 104 - 106 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.80 (dd, *J* = 8.4, 3.0 Hz, 1H), 7.40 – 7.28 (m, 2H), 2.66 (tt, *J* = 6.4, 1.6 Hz, 2H), 2.56 (tt, *J* = 6.6, 1.6 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.79 – 1.72 (m, 2H).

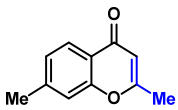
^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.1, 164.4, 159.2 (d, *J* = 245.4 Hz), 152.2, 124.2 (d, *J* = 7.1 Hz), 121.3 (d, *J* = 26.3 Hz), 119.8 (d, *J* = 8.1 Hz), 118.0, 110.5 (d, *J* = 24.2 Hz), 28.2, 21.9, 21.7, 21.1.
^{19}F NMR (471 MHz, Chloroform-*d*): δ -116.5 (td, *J* = 7.9, 4.0 Hz).
Spectroscopic data are in agreement with published values.[23]

Compound 33



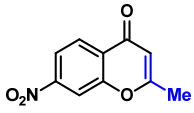
7-bromo-1,2,3,4-tetrahydro-9H-xanthen-9-one
Following General Procedure on 0.8 mmol scale with **S20** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 194 mg (87%) of the title compound **33**.
Physical State: white solid.
m.p.: 150 - 151 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.30 (d, *J* = 2.5 Hz, 1H), 7.67 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 2.66 (tt, *J* = 6.4, 3.1 Hz, 2H), 2.56 (tt, *J* = 6.2, 1.7 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.79 – 1.73 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.5, 164.3, 154.8, 136.0, 128.5, 124.6, 119.8, 118.8, 117.8, 28.3, 21.9, 21.7, 21.1.
Spectroscopic data are in agreement with published values.[19]

Compound 34



2,7-dimethyl-4H-chromen-4-one
Following General Procedure on 0.6 mmol scale with **75a** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 90 mg (86%) of the title compound **34**.
Physical State: white solid.
m.p.: 97 - 98 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.13 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.4, 166.0, 156.8, 144.8, 126.5, 125.5, 121.4, 117.7, 110.6, 21.9, 20.7.
Spectroscopic data are in agreement with published values.[22]

Compound 35



2-methyl-7-nitro-4H-chromen-4-one

Following General Procedure on 0.8 mmol scale with **S22** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 136 mg (83%) of the title compound **35**.

Physical State: yellow solid.

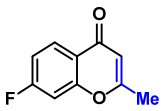
m.p.: 176 - 178 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.34 (d, *J* = 8.7 Hz, 1H), 8.31 (d, *J* = 2.0 Hz, 1H), 8.18 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.26 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.6, 167.9, 155.9, 150.6, 127.8, 127.5, 119.3, 114.3, 111.6, 20.8.

HRMS (ESI) calculated for: $C_{10}H_8NO_4^+$ ([M+H]$^+$) m/z 206.0448, found 206.0445.

Compound 36



7-fluoro-2-methyl-4H-chromen-4-one

Following General Procedure on 0.7 mmol scale with **S23** and $SnCl_4$ at room temperature for 3 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 113 mg (91%) of the title compound **36**.

Physical State: white solid.

m.p.: 101 - 102 ºC.

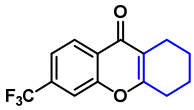
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.20 – 8.13 (m, 1H), 7.11 – 7.06 (m, 2H), 6.13 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.4, 166.5, 165.6 (d, *J* = 254.5 Hz), 157.5 (d, *J* = 14.1 Hz), 128.3 (d, *J* = 10.1 Hz), 120.6, 113.8 (d, *J* = 22.2 Hz), 110.7, 104.6 (d, *J* = 25.2 Hz), 20.6.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -103.4 (q, *J* = 8.0 Hz).

HRMS (ESI) calculated for: $C_{10}H_8FO_2^+$ ([M+H]$^+$) m/z 179.0503, found 179.0501 .

Compound 37



7-(trifluoromethyl)-1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.6 mmol scale with **S24** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 141 mg (88%) of the title compound **37**.

Physical State: white solid.

m.p.: 157 - 158 ºC.

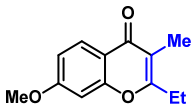
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.54 (dd, *J* = 8.2, 1.6 Hz, 1H), 2,67 (t, *J* = 6.2 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.79 – 1.72 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.7, 164.8, 155.3, 134.6 (q, *J* = 33.3 Hz), 127.1, 123.4 (q, *J* = 273.7 Hz), 125.3, 120.8 (q, *J* = 3.0 Hz), 119.3, 115.7 (q, *J* = 4.0 Hz), 28.2, 21.8, 21.5, 21.1.

^{19}F NMR (471 MHz, Chloroform-*d*): δ -63.0.

HRMS (ESI) calculated for: $C_{14}H_{12}F_3O_2^+$ ([M+H]$^+$) m/z 269.0784, found 269.0786.

Compound 38



2-ethyl-7-methoxy-3-methyl-4H-chromen-4-one

Following General Procedure on 0.5 mmol scale with **S25** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 57 mg (52%) of the title compound **38**.

Physical State: white solid.

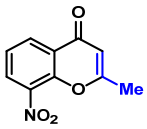
m.p.: 86 - 87 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.07 (d, *J* = 8.9 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.03 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.8, 165.7, 163.6, 157.7, 127.3, 116.7, 115.8, 114.0, 99.7, 55.8, 25.6, 11.5, 9.6.

HRMS (ESI) calculated for: $C_{13}H_{15}O_3^+$ ([M+H]$^+$) m/z 219.1016, found 219.1012.

Compound 39



2-methyl-8-nitro-4H-chromen-4-one

Following General Procedure on 0.5 mmol scale with **S26** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 47 mg (46%) of the title compound **39**.

Physical State: white solid.

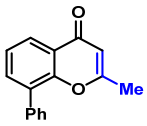
m.p.: 167 - 169 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.44 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.26 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 6.26 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.0, 166.9, 148.7, 138.9, 131.6, 129.6, 125.5, 124.3, 111.4, 20.7.

HRMS (ESI) calculated for: $C_{10}H_8NO_4^+$ ([M+H]$^+$) m/z 206.0448, found 206.0453.

Compound 40

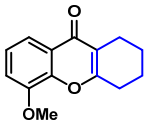


2-methyl-8-phenyl-4H-chromen-4-one

Following General Procedure on 0.4 mmol scale with **S27** and AgOTf at room temperature for 3 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 85 mg (90%) of the title compound **40**.

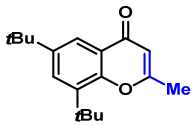
Physical State: yellow solid.
m.p.: 112 - 114 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.20 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.52 – 7.46 (m, 2H), 7.46 – 7.40 (m, 2H), 6.20 (s, 1H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.4, 166.2, 153.4, 136.2, 134.6, 131.4, 129.6, 128.5, 127.0, 125.1, 125.0, 124.1, 110.4, 20.6.
HRMS (ESI) calculated for: $C_{16}H_{13}O_2^+$ ([M+H]$^+$) m/z 237.0910, found 237.0908.

Compound 41



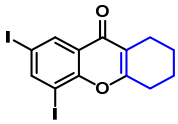
5-methoxy-1,2,3,4-tetrahydro-9H-xanthen-9-one
Following General Procedure on 1.0 mmol scale with **S28** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 143 mg (62%) of the title compound **41**.
Physical State: white solid.
m.p.: 114 - 116 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.74 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.96 (s, 3H), 2.72 (t, *J* = 6.5 Hz, 2H), 2.57 (t, *J* = 6.2 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.79 – 1.71 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 177.7, 163.7, 148.4, 146.4, 124.2, 124.1, 118.6, 116.8, 113.6, 56.4, 28.3, 22.0, 21.7, 21.1.
HRMS (ESI) calculated for: $C_{14}H_{15}O_3^+$ ([M+H]$^+$) m/z 231.1016, found 231.1015.

Compound 42



6,8-di-tert-butyl-2-methyl-4H-chromen-4-one
Following General Procedure on 0.6 mmol scale with **S29** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 139 mg (85%) of the title compound **42**.
Physical State: white solid.
m.p.: 114 - 116 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 6.16 (s, 1H), 2.40 (s, 3H), 1.47 (s, 9H), 1.34 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 179.1, 164.9, 153.4, 147.2, 138.1, 128.5, 123.7, 119.6, 110.0, 35.2, 35.0, 31.4, 30.2, 20.7.
Spectroscopic data are in agreement with published values.[22]

Compound 43



5,7-diiodo-1,2,3,4-tetrahydro-9H-xanthen-9-one

Following General Procedure on 0.3 mmol scale with **S30** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 83 mg (62%) of the title compound **43**.

Physical State: white solid.

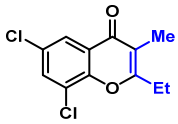
m.p.: decompose before melting.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.46 (d, *J* = 2.2 Hz, 1H), 8.32 (d, *J* = 2.1 Hz, 1H), 2.75 (tt, *J* = 6.4, 1.6 Hz, 2H), 2.55 (tt, *J* = 6.1, 1.6 Hz, 2H), 1.91 – 1.86 (m, 2H), 1.80 – 1.74 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 175.9, 164.9, 154.6, 150.0, 135.3, 125.1, 119.0, 88.7, 86.3, 28.2, 21.9, 21.6, 21.2.

HRMS (ESI) calculated for: $C_{13}H_{11}I_2O_2^+$ ([M+H]$^+$) m/z 452.8843, found 452.8841.

Compound 44



6,8-dichloro-2-ethyl-3-methyl-4H-chromen-4-one

Following General Procedure on 0.6 mmol scale with **S31** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 87 mg (57%) of the title compound **44**.

Physical State: white solid.

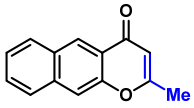
m.p.: 85 - 86 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.03 (d, *J* = 2.5 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.05 (s, 3H), 1.35 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 176.5, 166.6, 150.3, 133.1, 130.0, 124.3, 124.0, 124.0, 116.7, 25.7, 11.3, 9.7.

HRMS (ESI) calculated for: $C_{12}H_{11}Cl_2O_2^+$ ([M+H]$^+$) m/z 257.0131, found 257.0133.

Compound 45



2-methyl-4H-benzo[g]chromen-4-one

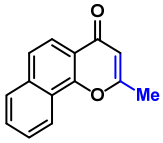
Following General Procedure on 0.8 mmol scale with **S32** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 142 mg (85%) of the title compound **45**.

Physical State: yellow solid.

m.p.: 130 - 132 ºC.

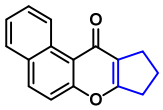
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.76 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.59 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.7, 1.2 Hz, 1H), 6.16 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 179.1, 167.4, 152.9, 135.9, 130.4, 129.8, 128.8, 127.3, 126.9, 126.0, 122.5, 114.1, 109.2, 21.1.
HRMS (ESI) calculated for: $C_{14}H_{11}O_2^+$ ([M+H]$^+$) m/z 211.0754, found 211.0752.

Compound 46



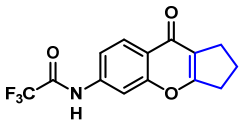
2-methyl-4H-benzo[h]chromen-4-one
Following General Procedure on 0.5 mmol scale with **S33** and AgOTf at -78 ºC for 12 hours. Purification by flash column chromatography (silica, 20:1 PE:EtOAc) afforded 83 mg (79%) of the title compound **46**.
Physical State: white solid.
m.p.: 176 - 177 ºC.
^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.64 (m, 2H), 6.34 (s, 1H), 2.53 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 178.3, 165.4, 154.0, 136.0, 129.3, 128.3, 127.1, 125.2, 124.0, 122.4, 120.9, 120.0, 112.0, 20.6.
HRMS (ESI) calculated for: $C_{14}H_{11}O_2^+$ ([M+H]$^+$) m/z 211.0754, found 211.0755.

Compound 47



9,10-dihydrobenzo[f]cyclopenta[b]chromen-11(8H)-one
Following General Procedure on 0.8 mmol scale with **S34** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 143 mg (76%) of the title compound **47**.
Physical State: white solid.
m.p.: 161 - 164 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 10.16 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.60 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 3.04 (tt, *J* = 7.5, 1.5 Hz, 2H), 2.94 (tt, *J* = 7.4, 1.6 Hz, 2H), 2.17 (p, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 178.7, 166.7, 158.3, 134.5, 131.2, 130.8, 128.9, 128.1, 127.3, 126.4, 124.1, 117.9, 117.3, 32.0, 26.4, 19.8.
HRMS (ESI) calculated for: $C_{16}H_{13}O_2^+$ ([M+H]$^+$) m/z 237.0910, found 237.0909.

Compound 48



2,2,2-trifluoro-N-(9-oxo-1,2,3,9-tetrahydrocyclopenta[b]chromen-6-yl)acetamide

Following General Procedure on 0.5 mmol scale with **S35** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 125 mg (84%) of the title compound **48**.

Physical State: brown solid.

m.p.: decompose before melting.

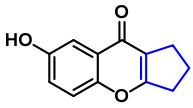
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 11.72 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.72 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.00 (t, *J* = 7.9 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.05 (p, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 174.3, 170.0, 156.7, 155.1 (q, *J* = 34.0 Hz), 140.7, 126.1, 120.7, 120.4, 118.0, 115.6 (q, *J* = 288.5 Hz), 109.1, 31.7, 25.8, 19.0.

^{19}F NMR (471 MHz, CDCl$_3$): δ -69.2.

HRMS (ESI) calculated for: $C_{14}H_{11}F_3NO_3^+$ ([M+H]$^+$) m/z 298.0686, found 298.0684.

Compound 49



6-hydroxy-2,3-dihydrocyclopenta[b]chromen-9(1H)-one

Following General Procedure on 0.4 mmol scale with **S36** and $AgNTf_2$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 60 mg (74%) of the title compound **49**.

Physical State: brown solid.

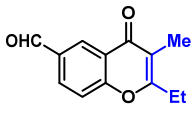
m.p.: decompose before melting.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.93 (s, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 7.16 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.95 (tt, *J* = 8.2, 1.4 Hz, 2H), 2.66 (tt, *J* =7.4, 1.2 Hz, 2H), 2.06 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ 174.8, 169.6, 154.6, 150.1, 124.4, 122.0, 119.5, 119.2, 107.9, 31.6, 25.8, 19.1.

HRMS (ESI) calculated for: $C_{12}H_{11}O_3^+$ ([M+H]$^+$) m/z 203.0703, found 203.0700.

Compound 50



2-ethyl-3-methyl-4-oxo-4H-chromene-6-carbaldehyde

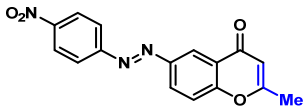
Following General Procedure on 0.5 mmol scale with **S37** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 39 mg (36%) of the title compound **50**.

Physical State: white solid.

m.p.: 112 - 114 ºC.

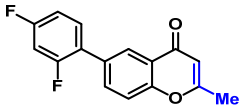
^{1}H NMR (400 MHz, Chloroform-*d*): δ 10.09 (d, *J* = 0.7 Hz, 1H), 8.68 (dd, *J* = 2.1, 0.5 Hz, 1H), 8.16 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.52 (dt, *J* = 8.7, 0.6 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 2.10 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 190.8, 177.6, 166.8, 159.5, 133.0, 131.4, 131.2, 122.7, 119.3, 117.2, 25.7, 11.5, 9.7.
HRMS (ESI) calculated for: $C_{13}H_{12}NaO_3^+$ ([M+Na]$^+$) m/z 239.0679, found 239.0677.

Compound 51



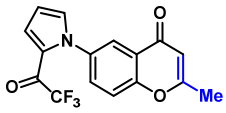
2-methyl-6-((4-nitrophenyl)diazenyl)-4H-chromen-4-one
Following General Procedure on 0.2 mmol scale with **S38** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 40 mg (33%) of the title compound **51**.
Physical State: orange solid.
m.p.: decompose before melting.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.80 (d, *J* = 2.5 Hz, 1H), 8.42 – 8.38 (m, 2H), 8.26 (dd, *J* = 8.9, 2.4 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 6.25 (s, 1H), 2.44 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 177.9, 166.7, 158.6, 155.5, 149.1, 149.1, 126.6, 125.0, 124.3, 123.8, 123.3, 119.4, 111.1, 20.8.
HRMS (ESI) calculated for: $C_{16}H_{12}N_3O_4^+$ ([M+H]$^+$) m/z 310.0822, found 310.0827.

Compound 52



6-(2,4-difluorophenyl)-2-methyl-4H-chromen-4-one
Following General Procedure on 0.6 mmol scale with **S18** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 143 mg (88%) of the title compound **52**.
Physical State: white solid.
m.p.: 160 - 162 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.26 (d, *J* = 1.9 Hz, 1H), 7.79 (dt, *J* = 8.7, 2.2 Hz, 1H), 7.50 – 7.42 (m, 2H), 6.99 – 6.88 (m, 2H), 6.19 (s, 1H), 2.40 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*): δ 178.1, 166.5, 162.8 (dd, *J* = 250.6, 12.1 Hz), 159.9 (d, *J* = 250.6, 12.1 Hz), 156.1, 134.3 (d, *J* = 4.5 Hz), 132.1, 131.7 (q, *J* = 4.5 Hz), 125.7, 123.9 (dd, *J* = 12.1, 4.5 Hz), 123.8, 118.2, 112.0 (dd, *J* = 21.1, 4.5 Hz), 110.8, 104.7 (t, *J* = 25.7 Hz), 20.7.
^{19}F NMR (471 MHz, Chloroform-*d*): δ -110.3 (p, *J* = 8.0 Hz), -113.5 (q, *J* = 9.0 Hz).
HRMS (ESI) calculated for: $C_{16}H_{11}F_2O_2^+$ ([M+H]$^+$) m/z 273.0722, found 273.0723.

Compound 53



2-methyl-6-(2-(2,2,2-trifluoroacetyl)-1H-pyrrol-1-yl)-4H-chromen-4-one

Following General Procedure on 0.22 mmol scale with **S39** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 51 mg (76%) of the title compound **53**.

Physical State: white solid.

m.p.: 156 - 157 ºC.

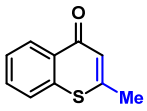
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.07 (d, *J* = 2.6 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.43 – 7.39 (m, 1H), 7.24 – 7.19 (m, 1H), 6.48 (dd, *J* = 4.3, 2.6 Hz, 1H), 6.21 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 177.5, 169.6 (q, *J* = 35.8 Hz), 166.8, 156.0, 136.6, 135.1, 132.0, 125.3, 125.2 (q, *J* = 3.9 Hz), 124.0, 122.6, 118.9, 117.0 (q, *J* = 291.2 Hz), 111.7, 110.8, 20.7.

^{19}F NMR (471 MHz, $CDCl_3$): δ -71.6.

HRMS (ESI) calculated for: $C_{16}H_{11}F_3NO_3^+$ ([M+H]$^+$) m/z 322.0686, found 322.0690.

Compound 54



2-methyl-4H-thiochromen-4-one

Following General Procedure on 0.5 mmol scale with **S40** and $SnCl_4$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 64 mg (73%) of the title compound **54**.

Physical State: brown solid.

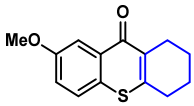
m.p.: 102 - 103 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.47 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.58 – 7.46 (m, 3H), 6.82 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.7, 151.4, 137.7, 131.4, 130.8, 128.6, 127.6, 126.1, 125.0, 23.5.

HRMS (ESI) calculated for: $C_{10}H_9OS^+$ ([M+H]$^+$) m/z 177.0369, found 177.0371.

Compound 55



7-methoxy-1,2,3,4-tetrahydro-9H-thioxanthen-9-one

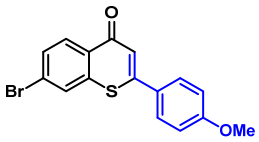
Following General Procedure on 0.2 mmol scale with **S41** and $SnCl_4$ at room temperature for 0.5 hour. Purification by flash column chromatography (silica, 50:1 PE:EtOAc) afforded 42 mg (85%) of the title compound **55**.

Physical State: white solid.

m.p.: 105 - 106 ºC.

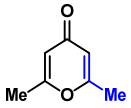
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 2.9 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.91 (s, 3H), 2.72 – 2.67 (m, 4H), 1.88 – 1.80 (m, 4H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 179.7, 159.0, 147.4, 131.7, 130.6, 129.2, 127.0, 121.6, 109.3, 55.8, 31.3, 24.9, 22.4, 22.2.
HRMS (ESI) calculated for: $C_{14}H_{15}O_2S^+$ ([M+H]$^+$) m/z 247.0787, found 247.0787.

Compound 56



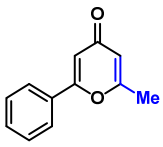
7-bromo-2-(4-methoxyphenyl)-4H-thiochromen-4-one
Following General Procedure on 0.11 mmol scale with **S42** and $SnCl_4$ at room temperature for 3 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 25 mg (71%) of the title compound **56**.
Physical State: white solid.
m.p.: 157 - 159 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.68 (d, *J* = 2.2 Hz, 1H), 7.72 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.21 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*): δ 179.7, 162.2, 153.1, 136.4, 134.7, 132.4, 131.5, 128.7, 128.5, 128.1, 122.2, 122.1, 114.9, 55.7.
HRMS (ESI) calculated for: $C_{16}H_{12}BrO_2S^+$ ([M+H]$^+$) m/z 346.9736, found 346.9734.

Compound 57



2,6-dimethyl-4H-pyran-4-one
Following General Procedure on 1.0 mmol scale with 2,2,6-trimethyl-4H-1,3-dioxin-4-one and AgOTf at room temperature for 7 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 90 mg (73%) of the title compound **57**.
Physical State: white solid.
m.p.: 131 - 133 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (s, 2H), 2.24 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.4, 165.7, 113.9, 19.9.

Compound 58



2-methyl-6-phenyl-4H-pyran-4-one

Following General Procedure on 0.5 mmol scale with **S43** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 70 mg (72%) of the title compound **58**.

Physical State: white solid.

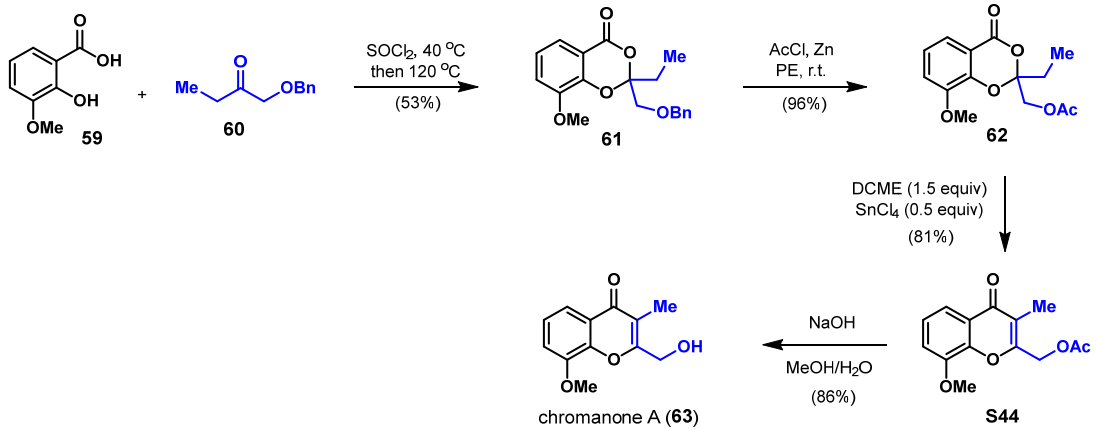
m.p.: 84 - 86 ºC.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.90 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.56 – 7.49 (m, 3H), 6.83 (d, *J* = 2.2 Hz, 1H), 6.19 (s, 1H), 2.35 (s, 3H).

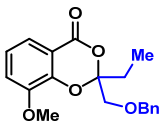
^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 178.8, 165.8, 162.5, 131.3, 131.0, 129.1, 125.8, 113.7, 110.2, 19.2.

HRMS (ESI) calculated for: $C_{12}H_{11}O_2^+$ ([M+H]$^+$) m/z 187.0754, found 187.0753.

Total Synthesis of Chromanone A



Compound 61



2-((benzyloxy)methyl)-2-ethyl-8-methoxy-4H-benzo[d][1,3]dioxin-4-one

Following Method C with 2-hydroxy-3-methoxybenzoic acid (**59**, 5.0 equiv) and 1-(benzyloxy)-butan-2-one (**60**, 0.3 mmol) at 120 ºC for 8 hours. Purification by flash column chromatography (silica, 100:1 PE:EtOAc) afforded 52 mg (53%) of the title compound **61**.

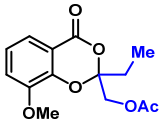
Physical State: yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 7.13 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 4.59 – 4.52 (m, 2H), 3.91 (s, 3H), 3.81 (AB, *J* = 11.0 Hz, 1H), 3.72 (BA, *J* = 11.0 Hz, 1H), 2.26 – 2.06 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 160.7, 148.3, 146.0, 137.5, 128.5, 127.9, 127.7, 122.2, 120.7, 118.0, 114.5, 108.3, 73.6, 70.3, 56.5, 28.3, 7.2.

HRMS (ESI) calculated for: $C_{19}H_{21}O_5^+$ ([M+H]$^+$) m/z 329.1384, found 329.1385.

Compound 62



(2-ethyl-8-methoxy-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)methyl acetate

A suspension of Zn-dust (4 mg, 0.06 mmol) in petroleum ether (2 mL) was stirred with **61** (75 mg, 0.23 mmol) and AcCl (18 µL, 0.25 mmol) at room temperature under argon. After 5 hours, the reaction mixture was directly purified by flash column chromatography (silica, 30:1 PE:EtOAc) to afford 58 mg (96%) of the title compound **62**.

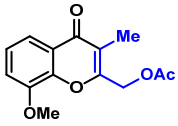
Physical State: colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.53 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.13 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 4.43 (AB, *J* = 12.1 Hz, 1H), 4.35 (BA, *J* = 12.1 Hz, 1H), 3.89 (s, 3H), 2.15 – 2.08 (m, 2H), 2.03 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 170.1, 160.2, 148.4, 145.6, 122.7, 120.7, 118.2, 114.2, 106.8, 63.6, 56.5, 28.6, 20.7, 7.1.

HRMS (ESI) calculated for: $C_{14}H_{16}NaO_6^+$ ([M+H]$^+$) m/z 303.0839, found 303.0840.

Compound S44



(8-methoxy-3-methyl-4-oxo-4H-chromen-2-yl)methyl acetate

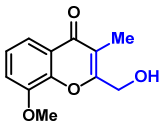
Following General Procedure on 0.15 mmol scale with **62** and $SnCl_4$ at room temperature for 5 hours. Purification by flash column chromatography (silica, 30:1 PE:EtOAc) afforded 32 mg (81%) of the title compound **S44**.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.74 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 2H), 3.97 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 178.3, 170.5, 157.0, 148.8, 146.5, 124.7, 123.7, 119.7, 116.9, 114.2, 61.4, 56.4, 20.8, 9.6.

HRMS (ESI) calculated for: $C_{14}H_{15}O_5^+$ ([M+H]$^+$) m/z 263.0914, found 263.0913.

Compound 63 (chromanone A)



2-(hydroxymethyl)-8-methoxy-3-methyl-4H-chromen-4-one

A solution of NaOH (14 mg, 2.0 equiv) in MeOH/H_2O (1/1, 2 mL) was stirred with **S44** (47 mg, 0.17 mmol) at room temperature. After 1 hour, the reaction mixture was diluted with saturated aqueous NH_4Cl and extracted with EtOAc for three times. Organic layers were combined, dried over anhydrous Na_2SO_4, evaporated and purified by flash column chromatography (silica, 30:1 PE:EtOAc) to afford 30 mg (86%) of chromanone A (**63**).

Physical State: white solid.

m.p.: 172 - 173 ºC.

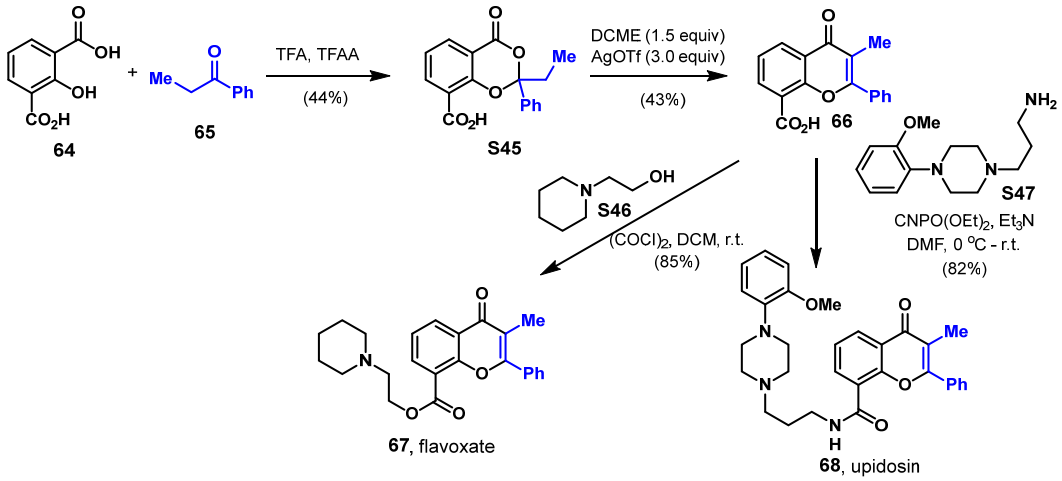
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.74 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.74 (s, 2H), 3.96 (s, 3H), 2.69 (s, 1H), 2.11 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 178.5, 160.7, 148.6, 146.3, 124.6, 123.7, 117.6, 116.9, 114.0, 60.6, 56.3, 9.4.

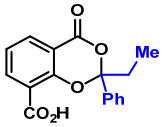
HRMS (ESI) calculated for: $C_{12}H_{13}O_4^+$ ([M+H]$^+$) m/z 221.0808, found 221.0800.

Spectroscopic data are in agreement with published values.[24]

Synthesis of Flavoxate and Upidosin



Compound S45



2-ethyl-4-oxo-2-phenyl-4H-benzo[d][1,3]dioxine-8-carboxylic acid

Following Method A on 0.5 mmol scale with **64** and propiophenone **65** at 80 °C for 6 hours. After completion, the reaction mixture was diluted with EtOAc and washed with saturated aqueous NH_4Cl. The organic layer was then dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography (silica, 7:1 PE:EtOAc) to afford 65 mg (44%) of the title compound **S45**.

Physical State: white solid.

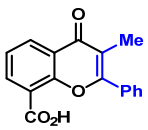
m.p.: 161 - 163 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.25 (dd, *J* = 7.6,1.6 Hz, 1H), 8.07 (dd, *J* = 7.6,1.6 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.33 – 7.28 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 2.32 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 169.1, 160.9, 157.1, 139.4, 138.9, 135.6, 129.4, 128.8 (2C), 126.6 (2C), 122.3, 118.7, 116.4, 109.8, 35.8, 7.5.

HRMS (ESI) calculated for: $C_{17}H_{15}O_5^+$ ([M+H]$^+$) m/z 299.0914, found 299.0912.

Compound 66



3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylic acid

Following General Procedure on 0.2 mmol scale with compound **S45** and AgOTf at room temperature for 1 hour. After completion, the reaction mixture was diluted with EtOAc and washed with saturated aqueous NH_4Cl. The organic layer was then dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography (silica, 50:1 DCM:MeOH) to afford 26 mg (46%) of the title compound **66**.

Physical State: yellow solid.

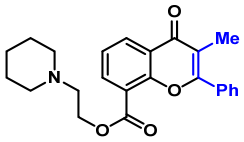
m.p.: 235 - 236 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*/CD_3OD = 10:1): δ 8.37 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.85 (m, 2H), 7.57 – 7.55 (m, 3H), 7.53 (t, *J* = 7.2 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*/CD_3OD = 10:1): δ 178.8, 166.2, 161.4, 154.5, 136.4, 132.7, 130.4 (2C), 129.3 (2C), 128.2 (2C), 124.0, 122.9, 120.9, 117.3, 11.6.

Spectroscopic data are in agreement with published values.[25]

Compound 67



2-(piperidin-1-yl)ethyl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylate

To a solution of compound **66** (42 mg, 0.15 mmol) and a drop of DMF in DCM (1 mL) was added oxalyl chloride (26 µL, 2 equiv) dropwise at 0°C. The mixture was allowed to warm to room temperature and stirred for 1 hour. The mixture was evaporated and redissolved in DCM (1 mL). A solution of 2-(piperidin-1-yl)ethan-1-ol (**S46**, 40 µL, 2 equiv) in DCM (0.5 mL) was added and the resulting mixture was stirred at room temperature for 2 hours. Saturated $NaHCO_3$ (5 mL) was added and the mixture was stirred for 5 min. The organic phase was separated and the aqueous phase was extracted twice with DCM. The organic phases were combined, washed with brine, dried over anhydrous Na_2SO_4, evaporated, and purified by flash column chromatography (silica, 1:2 PE:EtOAc) to afford 50 mg (85%) of the title compound **67**.

Physical State: yellow solid.

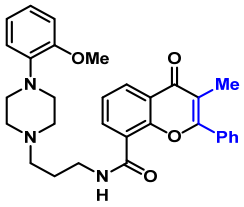
m.p.: 88 - 90 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.43 (d, *J* = 7.9 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 7.76 (dt, *J* = 7.2, 2.0 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 4.46 (t, *J* = 6.3 Hz, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.43 – 2.38 (m, 4H), 2.21 (s, 3H), 1.53 (p, *J* = 5.7 Hz, 4H), 1.38 (p, *J* = 5.8 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ178.3, 164.4, 161.1, 154.5, 136.2, 133.2, 130.8, 130.6, 129.4, 128.5, 124.1, 123.3, 120.8, 117.7, 63.2, 57.2, 54.8, 25.9, 24.1, 11.8.

Spectroscopic data are in agreement with published values.[26]

Compound 68



N-(3-(4-(2-methoxyphenyl)piperazin-1-yl)propyl)-3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxamide

To a solution of compound **66** (28 mg, 0.1 mmol) and amine **S47** (38 mg, 1.5 equiv) in DMF (0.5 mL) was added diethyl cyanophosphonate (90%, 23 µL, 1.4 equiv) and Et_3N (28 µL, 2 equiv) at 0°C. The resulting mixture was allowed to warm to room temperature and stirred for 3 hours. The crude reaction mixture was diluted with EtOAc (10 mL) and brine (10 mL). The organic phase was separated and the aqueous phase was extracted twice with EtOAc. The organic phases were combined, washed with brine, dried over anhydrous Na_2SO_4, evaporated, and purified by flash column chromatography (silica, 2:1 CH_2Cl_2:acetone) to afford 42 mg (82%) of the title compound **68**.

Physical State: white solid.

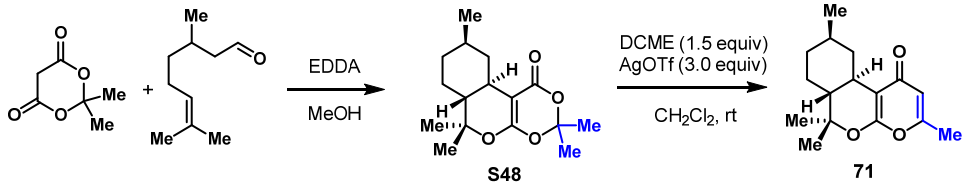
m.p.: 95 - 97 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.29 (d, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 5.5 Hz, 1H), 7.68 (dt, *J* = 7.5, 1.7 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 3.81 (s, 3H), 3.53 (q, *J* = 6.3 Hz, 2H), 2.89 (s, 4H), 2.48 (s, 4H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.15 (s, 3H), 1.72 (p, *J* = 6.8 Hz, 2H).

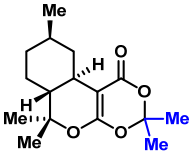
^{13}C NMR (151 MHz, Chloroform-*d*): δ 178.1, 163.9, 160.1, 153.1, 152.2, 141.1, 135.3, 132.9, 130.8, 129.0, 129.0, 128.8, 124.7, 124.3, 123.1, 122.7, 121.0, 118.1, 117.9, 111.2, 56.6, 55.4, 53.3, 50.6, 39.3, 25.9, 11.7.

HRMS (ESI) calculated for: $C_{31}H_{34}N_3O_4^+$ ([M+H]$^+$) m/z 512.2544, found 512.2547.

Synthesis of Polycyclic γ-Pyrones



Compound S48



(6aR,9R,10aR)-3,3,6,6,9-pentamethyl-6a,7,8,9,10,10a-hexahydro-1H,6H-[1,3]dioxino[4,5-c]isochromen-1-one

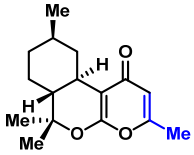
***S48** was prepared according to procedures reported in literature.*[27] To a flask equipped with a magnetic stir bar were added 2,2-dimethyl-1,3-dioxane-4,6-dione (0.40 g, 2.8 mmol), ethylenediammonium diacetate (EDDA, 20 mg, 0.11 mmol) and dry methanol (6 mL) successively. Racemic citronellal (0.39 g, 2.55 mmol) was added under argon while the temperature was kept at 15-20 ºC by cooling the flask with a water bath. The solution was stirred for additional 45 min at room temperature before concentrated under vacuum. The resulting yellow residue was dissolved in Et_2O (100 mL) and washed with water, saturated sodium bicarbonate and brine. The organic layer was then dried over anhydrous Na_2SO_4. Purification by flash column chromatography (silica, 15:1 PE:EtOAc) afforded 0.36 g (51%) of **S48**.

Physical State: white solid.

m.p.: 92 - 93 ºC.

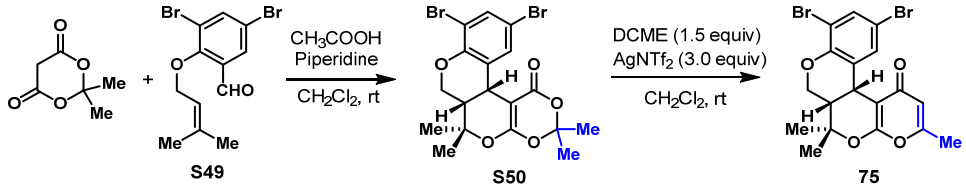
^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.71 (m, 1H), 2.19 – 2.11 (m, 1H), 1.86 – 1.79 (m, 1H), 1.78 – 1.73 (m, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.58 – 1.51 (m, 1H), 1.39 (s, 3H), 1.36 – 1.30 (m, 1H), 1.19 (s, 3H), 1.11 – 0.99 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.63 (q, *J* = 11.5 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.5, 162.5, 105.0, 85.4, 81.6, 49.1, 39.0, 35.3, 33.2, 32.1, 27.6, 27.3, 27.0, 22.3, 22.1, 19.7.
HRMS (ESI) calculated for: $C_{16}H_{25}O_4^+$ ([M+H]$^+$) m/z 281.1747, found 281.1745.

Compound 71

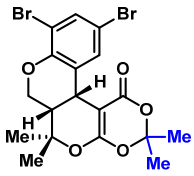


(6aR,9R,10aR)-3,6,6,9-tetramethyl-6a,7,8,9,10,10a-hexahydro-1H,6H-pyrano[2,3-c]isochromen-1-one

Following General Procedure on 0.3 mmol scale with **S48** and AgOTf at room temperature for 6 hours. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded 61 mg (78%) of the title compound **71**.
Physical State: white solid.
m.p.: 116 - 117 ºC.
^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.90 (s, 1H), 3.21 – 3.14 (m, 1H), 2.34 (td, *J* = 11.1, 2.9 Hz, 1H), 2.17 (d, *J* = 0.8 Hz, 3H), 1.85 – 1.75 (m, 2H), 1.63 – 1.54 (m, 1H), 1.43 (s, 3H), 1.37 (td, *J* = 11.2, 10.8, 2.7 Hz, 1H), 1.18 (s, 3H), 1.12 – 1.00 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.56 (q, *J* = 11.6 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.8, 163.1, 159.9, 113.2, 101.2, 84.6, 48.8, 37.2, 35.4, 33.9, 32.4, 27.5, 27.2, 22.4, 19.7, 19.1.
HRMS (ESI) calculated for: $C_{16}H_{23}O_3^+$ ([M+H]$^+$) m/z 263.1642, found 263.1644.



Compound S50



(6aS,12bR)-9,11-dibromo-3,3,6,6-tetramethyl-6a,12b-dihydro-1H,6H,7H-[1,3]dioxino[5',4':5,6]pyrano[3,4-c]chromen-1-one

***S50** was prepared according to procedures reported in literature.*[28] To a solution of benzaldehyde **S49** (348 mg, 1.0 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added 2,2-dimethyl-1,3-dioxane-4,6-dione (159 mg, 1.1 mmol, 1.1 equiv), AcOH (6 µL, 0.1 mmol, 0.1 equiv) and piperidine (9 µL, 0.1 mmol, 0.1 equiv). The mixture was stirred at room temperature for 2 hours, at which point it was diluted with EtOAc (100 mL). The solution was washed with $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, concentrated,

and purified by flash column chromatography (silica, 10:1 PE:EtOAc) to afford 433 mg (91%) of the title compound **S50**.

Physical State: white solid.

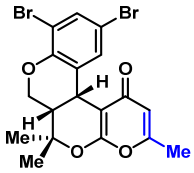
m.p.: 150 - 152 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.83 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 4.54 (dd, *J* = 11.8, 3.9 Hz, 1H), 4.21 (dd, *J* = 11.8, 6.9 Hz, 1H), 4.09 (dd, *J* = 5.9, 0.9 Hz, 1H), 2.21 (ddd, *J* = 6.9, 5.8, 3.9 Hz, 1H), 1.71 (s, 3H), 1.70 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.3, 163.1, 149.5, 134.25, 133.7, 125.4, 112.9, 110.9, 105.7, 83.2, 78.0, 64.8, 38.7, 29.5, 27.4, 26.6, 24.6, 22.8.

HRMS (ESI) calculated for: $C_{18}H_{19}Br_2O_5^+$ ([M+H]$^+$) m/z 472.9594, found 472.9592.

Compound 72



(6aS,12bR)-9,11-dibromo-3,6,6-trimethyl-6a,12b-dihydro-1H,6H,7H-pyrano[3',2':5,6]pyrano[3,4-c]chromen-1-one

Following General Procedure on 0.25 mmol scale with **S50** and $AgNTf_2$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 2:1 PE:EtOAc) afforded 79 mg (69%) of the title compound **72**.

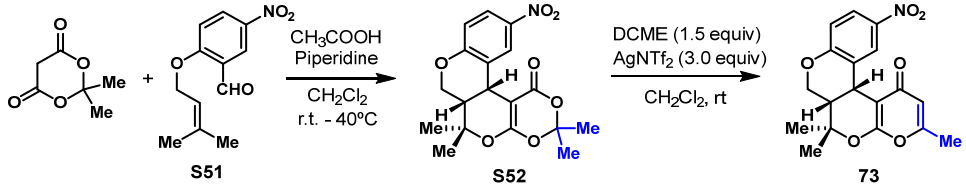
Physical State: yellow solid.

m.p.: 213 - 215 ºC.

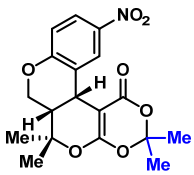
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, *J* = 2.3 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 6.13 (s, 1H), 4.56 – 4.48 (m, 2H), 4.42 (d, *J* = 5.8 Hz, 1H), 2.25 (s, 3H), 2.18 (dt, *J* = 6.2, 3.2 Hz, 1H), 1.62 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.7, 163.3, 161.1, 149.5, 134.0, 132.0, 125.9, 113.3, 112.8, 110.7, 99.6, 84.1, 65.7, 38.6, 29.0, 28.1, 23.6, 19.3.

HRMS (ESI) calculated for: $C_{18}H_{17}Br_2O_4^+$ ([M+H]$^+$) m/z 454.9488, found 454.949.



Compound S52



(6aS,12bR)-3,3,6,6-tetramethyl-11-nitro-6a,12b-dihydro-1H,6H,7H-[1,3]dioxino[5',4':5,6]pyrano[3,4-c]chromen-1-one

***S52** was prepared according to procedures reported in literature.*[28] To a solution of benzaldehyde **S51** (588 mg, 2.5 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added 2,2-dimethyl-1,3-dioxane-4,6-dione (397 mg, 2.75 mmol, 1.1 equiv), AcOH (15 µL, 0.25 mmol, 0.1 equiv) and piperidine (23 µL, 0.25 mmol, 0.1 equiv). The mixture was stirred at 40 ºC for 2 hours, at which point it was diluted with EtOAc (100 mL). The solution was washed with $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, concentrated, and purified by flash column chromatography (silica, 10:1 PE:EtOAc) to afford 548 mg (61%) of the title compound **S52**.

Physical State: white solid.

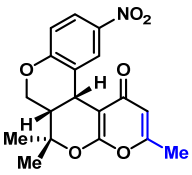
m.p.: 151 - 153 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.72 (d, *J* = 2.7 Hz, 1H), 8.02 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 4.55 (dd, *J* = 11.0, 4.1 Hz, 1H), 4.19 – 4.12 (m, 2H), 2.26 (ddd, *J* = 7.8, 5.7, 4.0 Hz, 1H), 1.72 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.1, 162.9, 158.9, 141.6, 128.9, 124.4, 122.3, 116.8, 105.8, 82.8, 79.8, 64.4, 38.3, 29.3, 27.4, 26.4, 24.9, 22.8.

HRMS (ESI) calculated for: $C_{18}H_{20}NO_7^+$ ([M+H]$^+$) m/z 362.1234, found 362.1237.

Compound 73



(6aS,12bR)-3,6,6-trimethyl-11-nitro-6a,12b-dihydro-1H,6H,7H-pyrano[3',2':5,6]pyrano[3,4-c]chromen-1-one

Following General Procedure on 0.25 mmol scale with **S52** and $AgNTf_2$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 16:1 CH_2Cl_2:acetone) afforded 36 mg (42%) of the title compound **73**.

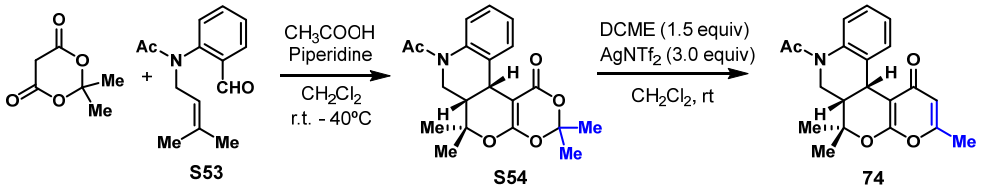
Physical State: yellow solid.

m.p.: 220 - 222 ºC.

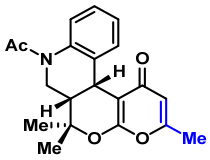
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.44 (d, *J* = 2.8 Hz, 1H), 7.99 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.14 (s, 1H), 4.54 (dd, *J* = 12.3, 3.8 Hz, 1H), 4.47 (dd, *J* = 12.3, 3.3 Hz, 1H), 4.44 (d, *J* = 5.8 Hz, 1H), 2.25 (s, 3H), 2.25 – 2.22 (m, 1H), 1.62 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 180.7, 163.1, 161.2, 158.9, 141.9, 127.3, 124.2, 122.8, 116.6, 112.9, 99.4, 83.7, 65.4, 38.2, 28.8, 27.9, 23.8, 19.3.

HRMS (ESI) calculated for: $C_{18}H_{18}NO_6^+$ ([M+H]$^+$) m/z 344.1129, found 344.1124.



Compound 74



(6aS,12bR)-8-acetyl-3,6,6-trimethyl-6a,7,8,12b-tetrahydro-1H,6H-pyrano[3',2':5,6]pyrano[3,4-c]quinolin-1-one

S54 *was prepared according to procedures reported in literature.*[28] To a solution of benzaldehyde **S53** (462 mg, 2 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added 2,2-dimethyl-1,3-dioxane-4,6-dione (316 mg, 2.2 mmol, 1.1 equiv), AcOH (12 µL, 0.2 mmol, 0.1 equiv) and piperidine (18 µL, 0.2 mmol, 0.1 equiv). The mixture was stirred at room temperature for 4 hours, at which point it was diluted with EtOAc (100 mL). The solution was washed with $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, concentrated, and purified by flash column chromatography (neutral aluminium oxide, 2:1 PE:EtOAc) to afford 250 mg (35%) of compound **S54**.

Following General Procedure on 0.15 mmol scale with **S54** and $AgNTf_2$ at room temperature for 6 hours. Purification by flash column chromatography (silica, 1:2 PE:EtOAc) afforded 37 mg (73%) of the title compound **74**.

Physical State: yellow solid.

m.p.: 254 - 256 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.04 (s, 1H), 4.89 (t, *J* = 11.7 Hz, 1H), 3.86 (d, *J* = 7.0 Hz, 1H), 2.81 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.25 (s, 3H), 2.12 (s, 3H), 1.37 (s, 3H), 0.90 (s, 3H)..

^{13}C NMR (151 MHz, Chloroform-*d*): δ 179.8, 169.9, 163.6, 161.2, 139.8, 134.0, 128.1, 127.1, 126.9, 124.2, 112.5, 97.4, 83.8, 43.7, 41.8, 31.0, 27.7, 22.3, 21.2, 19.3.

HRMS (ESI) calculated for: $C_{20}H_{22}NO_4^+$ ([M+H]$^+$) m/z 340.1543, found 340.1544.

Substrates Where Competing Formylation Was Observed

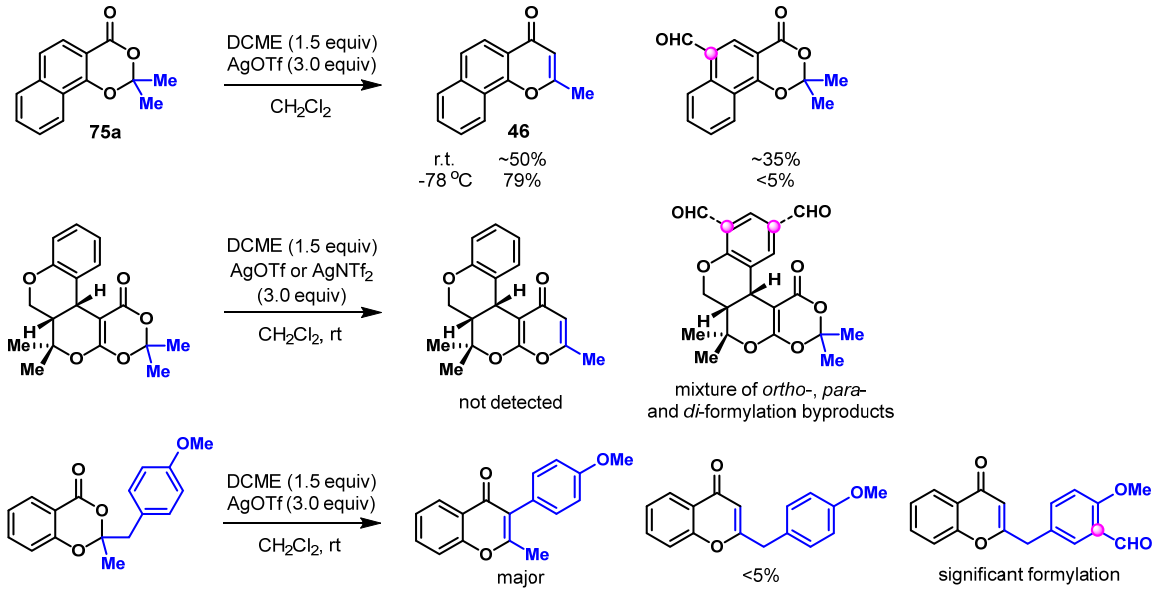
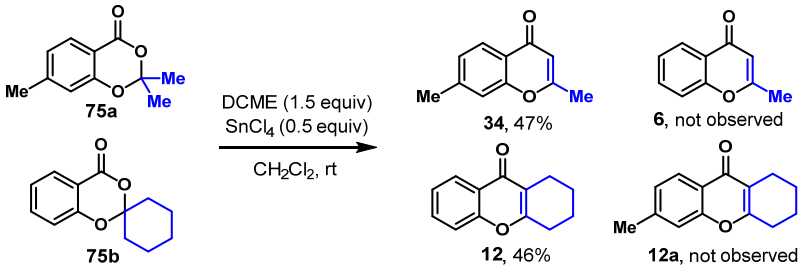


Figure S1. Substrates where competing formylation was observed.

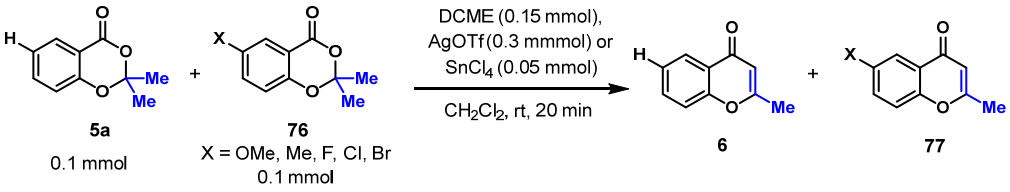
Control Experiments and Kinetic Studies

Crossover Experiments



Following General Procedure with **75a** (0.3 mmol), **75b** (0.3 mmol) and $SnCl_4$ (0.3 mmol) at room temperature. Purification by flash column chromatography (silica, 10:1 PE:EtOAc) afforded compound **34** (49 mg, 47%) and **12** (58 mg, 46%).

Hammett Plot Analysis



Five oven-dried 5 mL tubes was charged with **5a** (0.1 mmol, 1 equiv), 4-substituted salicylic acid ketal **76** (X = OMe, Me, F, Cl, or Br, 0.1 mmol, 1 equiv) and AgOTf (0.3 mmol, 3 equiv) under argon. Anhydrous DCM (0.6 mL) was added to the mixture via a syringe followed by DCME (0.15 mmol, 1.5 equiv). The tube was then stirred for 20 min at room temperature before quenched with saturated aqueous $NaHCO_3$, Brine (20 mL) was added and the crude mixture was extracted with DCM (10 mL × 3). The combined organic phases was dried over Na_2SO_4, concentrated, and analyzed by crude ^1H NMR to determine the ratio of **77/6**. These experiments were repeated, and the average **77/6** ratio was calculated as k_X/k_H (Table S5). The resulting five sets of $\log(k_X/k_H)$ were plotted against σ values of each substituent (σ_p) to obtain the Hammett plot (Figure S2). The obtained ρ value had a negative slope of -2.00.

The same experiments were performed by using $SnCl_4$ (0.05 mmol, 0.5 equiv) instead of AgOTf. The resulting ρ value had a negative slope of -1.96, closely resembling that obtained with AgOTf (Figure S3).

Table S5. Hammett plot data

Entry	Lewis acid	X	σ_p	k_X/k_H	$\log(k_X/k_H)$
1	AgOTf	OMe	-0.268	1.26	0.100
2	AgOTf	Me	-0.17	1.17	0.068
3	AgOTf	H	0	1	0
4	AgOTf	F	0.062	0.29	-0.538
5	AgOTf	Cl	0.227	0.17	-0.770
6	AgOTf	Br	0.232	0.14	-0.854
7	$SnCl_4$	OMe	-0.268	1.5	0.176
8	$SnCl_4$	Me	-0.17	1.28	0.107
9	$SnCl_4$	H	0	1	0
10	$SnCl_4$	F	0.062	0.33	-0.481
11	$SnCl_4$	Cl	0.227	0.16	-0.796
12	$SnCl_4$	Br	0.232	0.21	-0.678

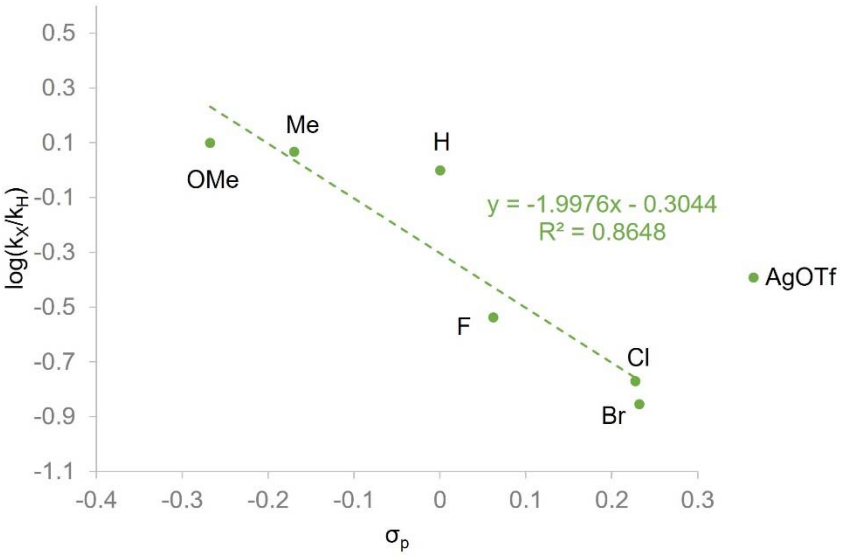


Figure S2. Plots of log(k_X/k_H) against σ_p values of each substituent with AgOTf as Lewis acid.

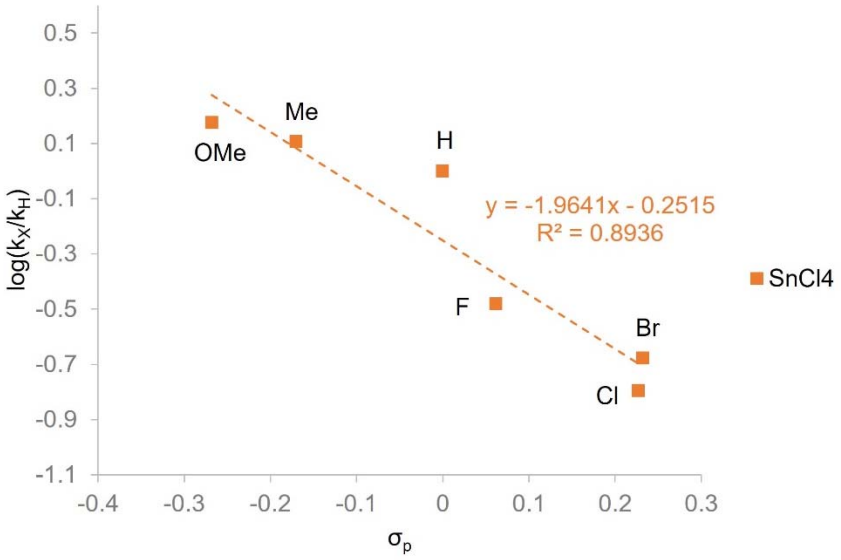
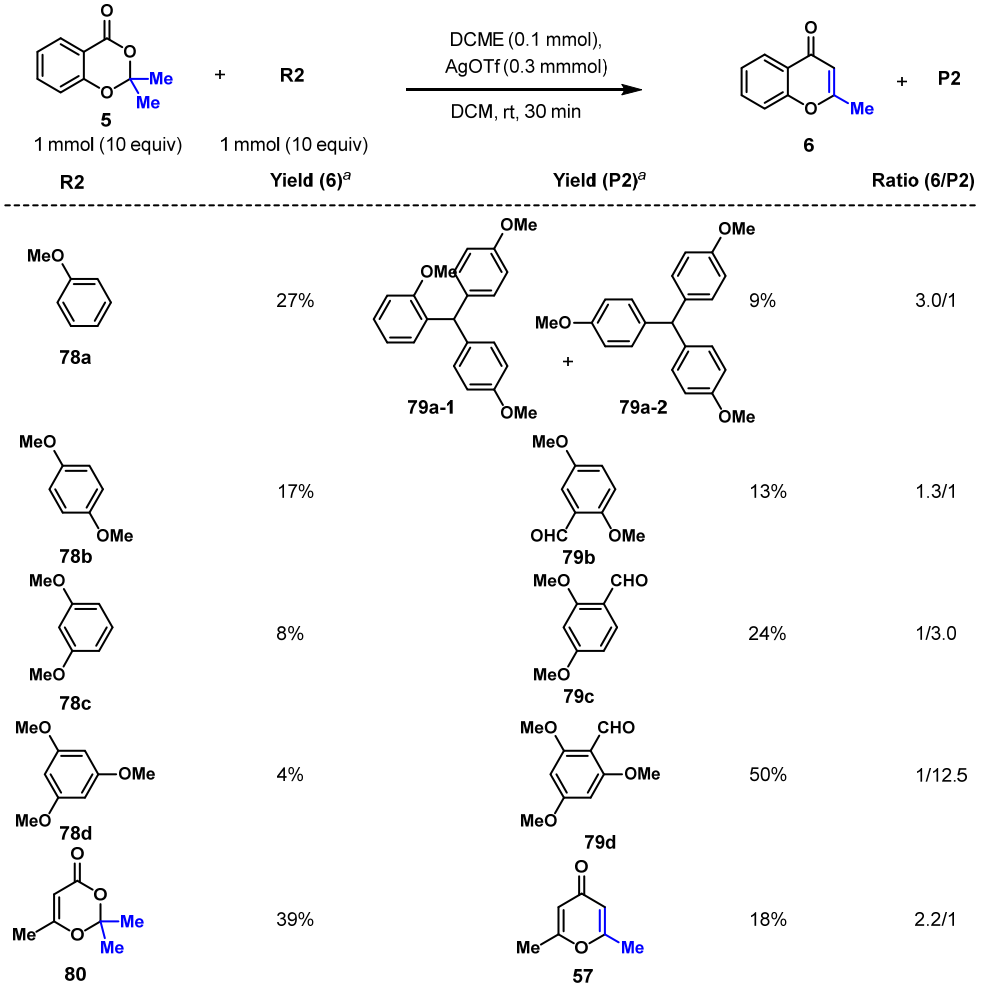


Figure S3. Plots of log(k_X/k_H) against σ_p values of each substituent with $SnCl_4$ as Lewis acid.

DHR Reaction/Formylation Competition Experiments



[a]Determined by ^{1}H NMR analysis of crude product using $(CHCl_2)_2$ as the internal standard.

Five oven-dried 5 mL tubes was charged with AgOTf (0.2 mmol, 2 equiv), **5** (1.0 mmol, 10 equiv), and another reactant (**78a**-**78d**, or **80**, 1.0 mmol, 10 equiv) under argon. Anhydrous DCM (0.6 mL) was added to the mixture via a syringe followed by DCME (0.1 mmol, 1 equiv). The tube was then stirred for 30 min at room temperature before quenched with saturated aqueous $NaHCO_3$, Brine (20 mL) was added and the crude mixture was extracted with DCM (10 mL × 3). The combined organic phases was dried over Na_2SO_4, concentrated, and analyzed by crude ^{1}H NMR using $(CHCl_2)_2$ as the internal standard to determine the yields of the corresponding products.

X-Ray Crystallographic Data

Compound 53

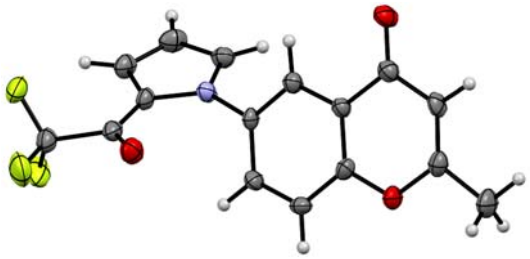


Figure S4. X-Ray Crystallographic Structure for Compound **53**

X-ray information for compound **53** can be obtained free of charge from The Cambridge Crystallographic Data center with number CCDC 2253406.

Table 1 Crystal data and structure refinement for 53.

Identification code	**53**
Empirical formula	$C_{16}H_{10}F_3NO_3$
Formula weight	321.25
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.132(3)
b/Å	13.549(3)
c/Å	8.342(2)
α/°	90
β/°	98.244(9)
γ/°	90
Volume/Å^3	1356.9(6)
Z	4
ρ_{calc}g/cm^3	1.573
μ/mm^{-1}	0.136
F(000)	656.0
Crystal size/mm^3	0.09 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.532 to 52.7
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	2745
Independent reflections	2745 [R_{int} = ?, R_{sigma} = 0.1143]
Data/restraints/parameters	2745/0/209
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0877, wR_2 = 0.1842
Final R indexes [all data]	R_1 = 0.1509, wR_2 = 0.2128
Largest diff. peak/hole / e Å^{-3}	0.39/-0.35

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ZZ. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	36(2)	4482(2)	2464(3)	43.4(7)
F3	1189(2)	5219(2)	1159(3)	48.7(8)
F2	1510(2)	3735(2)	1986(3)	53.1(9)
O1	6227(2)	6226(2)	9414(3)	30.0(7)

O2	3574(2)	6281(2)	11949(3)	34.7(8)
O3	2551(2)	4469(2)	4631(3)	34.3(8)
N1	1998(3)	6423(3)	5862(4)	23.8(8)
C5	4226(3)	6243(3)	9396(5)	22.7(9)
C15	1784(3)	4979(3)	3986(5)	26.0(9)
C7	3077(3)	6247(3)	6789(4)	21.2(9)
C10	5161(3)	6194(3)	8600(5)	24.7(9)
C14	1423(3)	5905(3)	4556(5)	24.6(9)
C6	3173(3)	6265(3)	8454(5)	24.1(9)
C13	459(3)	6439(3)	4051(5)	30.3(10)
C8	4019(3)	6160(3)	6011(5)	25.5(9)
C11	1408(3)	7246(3)	6117(5)	28.7(10)
C1	6371(3)	6320(3)	11070(5)	29.0(10)
C4	4375(3)	6283(3)	11181(5)	27.7(10)
C3	5519(3)	6339(3)	11927(5)	28.2(10)
C12	442(3)	7270(4)	5010(5)	33.7(11)
C9	5060(3)	6129(3)	6909(5)	25.8(9)
C16	1126(3)	4598(3)	2392(5)	31.4(10)
C2	7588(4)	6411(4)	11709(5)	41.3(12)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ZZ. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	30.5(14)	62(2)	35.7(14)	-4.6(13)	-0.9(11)	-17.3(12)
F3	57.1(18)	67(2)	20.3(13)	3.6(13)	-0.6(12)	-24.0(15)
F2	54.6(18)	53(2)	48.0(18)	-24.8(15)	-5.1(14)	-1.0(14)
O1	23.1(15)	46(2)	19.1(14)	-0.3(13)	-4.1(12)	-1.2(13)
O2	29.9(17)	54(2)	19.5(15)	0.4(13)	2.8(13)	5.5(14)
O3	31.6(16)	40(2)	29.6(16)	-1.0(14)	-1.5(13)	4.8(14)
N1	20.9(17)	32(2)	18.1(16)	-1.0(14)	0.7(13)	4.2(14)
C5	21(2)	29(2)	17.6(19)	-1.6(16)	1.8(16)	1.6(16)
C15	22(2)	37(3)	18.7(19)	1.4(18)	1.4(16)	-3.6(19)
C7	19(2)	27(2)	16.4(19)	0.2(15)	-4.3(15)	0.0(16)
C10	18(2)	30(2)	25(2)	-1.5(17)	-1.6(16)	0.3(16)
C14	20(2)	32(2)	20(2)	1.0(17)	-2.7(16)	-2.8(17)
C6	22(2)	30(2)	20(2)	-0.2(16)	1.0(16)	2.2(17)
C13	23(2)	43(3)	23(2)	4.7(19)	-3.7(17)	1.5(18)
C8	24(2)	36(3)	15.9(19)	-0.1(17)	2.8(17)	-1.5(18)
C11	25(2)	34(2)	28(2)	-1.6(18)	5.8(17)	2.8(18)
C1	25(2)	30(2)	29(2)	-1.3(18)	-4.1(18)	-0.3(17)
C4	28(2)	33(3)	22(2)	-0.8(17)	3.8(18)	0.8(18)
C3	30(2)	37(3)	15.3(19)	-1.1(17)	-4.7(17)	2.4(18)
C12	26(2)	41(3)	34(2)	9(2)	3.3(18)	9.8(19)
C9	20(2)	36(3)	23(2)	0.1(17)	7.7(17)	0.6(17)
C16	29(2)	40(3)	24(2)	-0.3(19)	-2.1(18)	-6.5(19)
C2	30(2)	61(3)	29(2)	-2(2)	-9(2)	-4(2)

Table 4 Bond Lengths for ZZ.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C16	1.342(5)	C15	C14	1.432(6)
F3	C16	1.340(5)	C15	C16	1.539(6)
F2	C16	1.320(5)	C7	C6	1.377(5)
O1	C10	1.372(5)	C7	C8	1.399(5)

O1	C1	1.374(5)	C10	C9	1.401(6)
O2	C4	1.238(5)	C14	C13	1.389(6)
O3	C15	1.221(5)	C13	C12	1.383(6)
N1	C7	1.441(5)	C8	C9	1.373(5)
N1	C14	1.396(5)	C11	C12	1.385(6)
N1	C11	1.359(5)	C1	C3	1.339(6)
C5	C10	1.396(6)	C1	C2	1.500(6)
C5	C6	1.401(5)	C4	C3	1.440(6)
C5	C4	1.475(5)			

Table 5 Bond Angles for ZZ.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C10	O1	C1	118.4(3)	C7	C6	C5	120.3(4)
C14	N1	C7	130.5(3)	C12	C13	C14	109.3(4)
C11	N1	C7	120.7(3)	C9	C8	C7	119.9(4)
C11	N1	C14	108.6(3)	N1	C11	C12	109.2(4)
C10	C5	C6	118.2(3)	O1	C1	C2	110.0(4)
C10	C5	C4	119.5(3)	C3	C1	O1	122.8(4)
C6	C5	C4	122.3(3)	C3	C1	C2	127.2(4)
O3	C15	C14	126.9(4)	O2	C4	C5	122.1(4)
O3	C15	C16	117.3(4)	O2	C4	C3	123.8(4)
C14	C15	C16	115.8(3)	C3	C4	C5	114.1(4)
C6	C7	N1	118.5(3)	C1	C3	C4	122.6(4)
C6	C7	C8	120.9(3)	C13	C12	C11	106.6(4)
C8	C7	N1	120.3(3)	C8	C9	C10	119.3(4)
O1	C10	C5	122.4(3)	F1	C16	C15	113.1(3)
O1	C10	C9	116.2(3)	F3	C16	F1	105.8(3)
C5	C10	C9	121.5(4)	F3	C16	C15	111.9(3)
N1	C14	C15	123.8(3)	F2	C16	F1	107.1(3)
C13	C14	N1	106.3(4)	F2	C16	F3	107.4(4)
C13	C14	C15	129.8(4)	F2	C16	C15	111.1(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ZZ.

Atom	*x*	*y*	*z*	U(eq)
H6	2522.6	6291.49	8965.67	29
H13	-101	6261.47	3183.13	36
H8	3939.48	6121.16	4862.91	31
H11	1623.53	7729.28	6927.23	34
H3	5675.61	6390.86	13072.63	34
H12	-123.02	7760.56	4926.19	40
H9	5703.43	6065.53	6389.37	31
H2A	7985.72	5834.27	11376.53	62
H2B	7685.37	6448.59	12894.42	62
H2C	7885.99	7011.07	11274.17	62

Compound 71

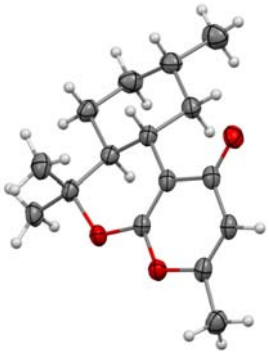


Figure S5. X-Ray Crystallographic Structure for Compound **71**

X-ray information for compound **71** can be obtained free of charge from The Cambridge Crystallographic Data center with number CCDC 2371778.

Table 1 Crystal data and structure refinement for 71.

Identification code	**71**
Empirical formula	$C_{16}H_{22}O_3$
Formula weight	262.33
Temperature/K	170
Crystal system	triclinic
Space group	P-1
a/Å	9.5339(4)
b/Å	9.6176(4)
c/Å	9.7437(4)
α/°	62.587(2)
β/°	72.018(2)
γ/°	65.461(2)
Volume/Å^3	713.80(5)
Z	2
ρ_{calc}g/cm^3	1.221
μ/mm^{-1}	0.663
F(000)	284.0
Crystal size/mm^3	0.16 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.31 to 136.452
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected	6806
Independent reflections	2561 [R_{int} = 0.0814, R_{sigma} = 0.0832]
Data/restraints/parameters	2561/0/176
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.0645, wR_2 = 0.1799
Final R indexes [all data]	R_1 = 0.0892, wR_2 = 0.1996
Largest diff. peak/hole / e Å^{-3}	0.30/-0.46

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_2023724_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	2152.8(15)	3699.1(16)	5458.0(17)	32.1(4)
O3	2769.0(14)	4885.2(15)	6502.1(16)	30.7(4)
O1	4896.2(17)	-922.8(16)	7788.8(17)	37.1(4)

C7	4127(2)	1964(2)	7140(2)	27.8(4)
C8	3080(2)	3431(2)	6429(2)	27.5(4)
C9	4140(2)	505(2)	7026(2)	29.4(4)
C6	5214(2)	1909(2)	8029(2)	28.8(4)
C5	5165(2)	3677(2)	7588(2)	28.7(4)
C10	3203(2)	859(2)	5894(2)	32.1(5)
C13	3480(2)	4841(2)	7682(2)	30.3(5)
C11	2284(2)	2373(2)	5165(2)	32.0(5)
C2	7984(2)	844(3)	8581(2)	36.2(5)
C1	6904(2)	865(2)	7682(2)	33.3(5)
C15	3389(2)	6631(2)	7120(3)	36.6(5)
C3	7868(3)	2611(3)	8218(3)	40.5(5)
C14	2488(3)	4285(3)	9266(3)	41.1(5)
C4	6181(2)	3678(3)	8533(2)	36.3(5)
C12	1290(3)	2915(3)	3979(3)	41.3(5)
C16	9649(3)	-192(3)	8185(3)	48.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_2023724_0m. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	33.2(7)	28.7(7)	37.5(8)	-17.5(6)	-7.1(6)	-6.1(5)
O3	35.5(7)	23.0(7)	35.8(8)	-15.2(6)	-8.2(6)	-5.0(5)
O1	46.0(8)	26.0(7)	38.6(8)	-13.1(7)	-6.0(6)	-10.4(6)
C7	31.2(9)	26.2(9)	27.4(9)	-14.4(8)	1.2(7)	-9.6(7)
C8	27.5(9)	28.3(9)	30.0(9)	-16.8(8)	0.3(7)	-9.1(7)
C9	30.8(9)	27.7(10)	29.6(9)	-14.7(8)	3.1(7)	-10.6(7)
C6	31.8(10)	28.8(9)	28.1(9)	-14.5(8)	-1.5(7)	-9.7(7)
C5	34.3(10)	26.9(10)	26.0(9)	-11.4(8)	-3.1(7)	-10.3(7)
C10	34.4(10)	31.0(10)	38.0(10)	-21.1(9)	1.1(8)	-12.7(7)
C13	37.1(10)	29.0(9)	30.3(10)	-17.3(8)	-3.3(8)	-10.1(7)
C11	30.9(9)	37.4(10)	35.7(10)	-22.9(9)	1.7(7)	-12.8(7)
C2	35.5(10)	36.4(11)	32.8(10)	-11.2(9)	-6.5(8)	-9.2(8)
C1	35.3(10)	29.6(10)	33.3(10)	-15.0(9)	-3.6(8)	-6.8(7)
C15	44.3(11)	27.9(10)	42.0(11)	-20.0(9)	-4.5(8)	-9.5(8)
C3	40.5(11)	40.8(11)	42.7(12)	-13.9(10)	-11.2(9)	-14.3(8)
C14	43.1(11)	42.5(12)	37.7(11)	-21.3(10)	5.6(9)	-15.3(9)
C4	45.0(11)	34.9(10)	36.4(11)	-16.3(9)	-8.8(9)	-14.5(8)
C12	41.0(11)	47.1(12)	45.5(12)	-26.1(11)	-8.3(9)	-12.1(9)
C16	35.6(11)	52.3(14)	50.1(13)	-18.4(12)	-5.8(9)	-10.1(9)

Table 4 Bond Lengths for cu_2023724_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C8	1.359(2)	C5	C13	1.534(3)
O2	C11	1.380(2)	C5	C4	1.529(2)

O3	C8	1.335(2)	C10	C11	1.329(3)
O3	C13	1.482(2)	C13	C15	1.519(3)
O1	C9	1.235(2)	C13	C14	1.524(3)
C7	C8	1.351(3)	C11	C12	1.489(3)
C7	C9	1.453(3)	C2	C1	1.533(3)
C7	C6	1.515(2)	C2	C3	1.530(3)
C9	C10	1.463(3)	C2	C16	1.524(3)
C6	C5	1.533(3)	C3	C4	1.532(3)
C6	C1	1.533(3)			

Table 5 Bond Angles for cu_2023724_0m.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C8	O2	C11	117.85(14)	C11	C10	C9	122.35(16)
C8	O3	C13	116.05(13)	O3	C13	C5	106.57(13)
C8	C7	C9	117.94(16)	O3	C13	C15	102.87(15)
C8	C7	C6	118.91(16)	O3	C13	C14	107.95(16)
C9	C7	C6	123.15(16)	C15	C13	C5	112.38(17)
O3	C8	O2	106.78(14)	C15	C13	C14	111.92(16)
O3	C8	C7	127.91(16)	C14	C13	C5	114.25(17)
C7	C8	O2	125.29(16)	O2	C11	C12	110.68(17)
O1	C9	C7	123.63(17)	C10	C11	O2	121.20(16)
O1	C9	C10	121.94(16)	C10	C11	C12	128.12(18)
C7	C9	C10	114.41(16)	C3	C2	C1	110.39(16)
C7	C6	C5	109.11(15)	C16	C2	C1	109.61(16)
C7	C6	C1	112.57(14)	C16	C2	C3	111.79(19)
C5	C6	C1	108.76(16)	C2	C1	C6	111.58(15)
C6	C5	C13	111.07(16)	C2	C3	C4	111.73(18)
C4	C5	C6	110.53(15)	C5	C4	C3	109.80(15)
C4	C5	C13	114.60(15)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for cu_2023724_0m.

Atom	*x*	*y*	*z*	U(eq)
H6	4846.27	1428.07	9174.45	35
H5	5645.28	4076.28	6467.75	34
H10	3253.85	-26.23	5671.52	38
H2	7638.84	313.42	9724.82	43
H1A	6948.6	-282.88	7974.81	40
H1B	7271.53	1321.27	6546.63	40
H15A	4116.69	6909.09	6152.05	55
H15B	3665.58	6779.28	7921.3	55
H15C	2326.08	7358.46	6924.61	55
H3A	8292.34	3120.65	7107.96	49
H3B	8508.38	2578.16	8869.14	49
H14A	1460.89	5133.01	9264.35	62
H14B	3000.09	4121.18	10084.64	62
H14C	2364.12	3241.72	9468.82	62
H4A	5781.75	3233.83	9660.83	44
H4B	6140.21	4825.28	8235.68	44
H12A	204.26	3444.25	4347.38	62
H12B	1364.25	1950.39	3819.63	62
H12C	1646.6	3705.21	2990.12	62
H16A	9700.6	-1344.17	8546.06	72
H16B	10347.92	-139.42	8702.34	72

H16C	9967.77	241.77	7051.05	72

Compound 72

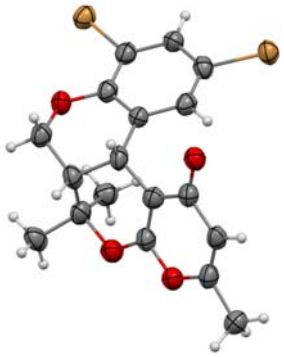


Figure S6. X-Ray Crystallographic Structure for Compound **72**

X-ray information for compound **72** can be obtained free of charge from The Cambridge Crystallographic Data center with number CCDC 2371783.

Table 1 Crystal data and structure refinement for 72.

Identification code	**72**
Empirical formula	$C_{18}H_{16}Br_2O_4$
Formula weight	456.13
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4779(6)
b/Å	17.4082(10)
c/Å	10.9215(7)
α/°	90
β/°	111.049(3)
γ/°	90
Volume/Å^3	1681.73(18)
Z	4
ρ_{calc}g/cm^3	1.802
μ/mm^{-1}	6.290
F(000)	904.0
Crystal size/mm^3	0.19 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.056 to 128.238
Index ranges	-11 ≤ h ≤ 9, -20 ≤ k ≤ 20, -12 ≤ l ≤ 11
Reflections collected	11656
Independent reflections	2750 [R_{int} = 0.0828, R_{sigma} = 0.0613]
Data/restraints/parameters	2750/0/220
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0903, wR_2 = 0.2426
Final R indexes [all data]	R_1 = 0.0922, wR_2 = 0.2467
Largest diff. peak/hole / e Å^{-3}	2.11/-1.29

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for cu_20231315_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	-934.6(8)	6516.9(4)	1422.0(7)	47.0(4)

Br2	411.0(9)	3334.3(4)	1898.0(7)	47.0(4)
O1	2300(6)	6619(3)	1631(5)	45.2(12)
O3	5046(5)	3896(3)	867(4)	45.1(11)
O4	7934(5)	4678(3)	4374(4)	46.7(11)
O2	6865(5)	5790(3)	4204(5)	48.4(12)
C2	448(8)	5700(4)	1586(6)	43.6(15)
C4	990(8)	4360(4)	1781(6)	41.2(14)
C3	-16(8)	4954(4)	1673(6)	42.2(14)
C18	1892(8)	5867(4)	1626(6)	40.8(14)
C5	2415(8)	4501(4)	1783(6)	42.4(15)
C7	4489(8)	5419(4)	1717(6)	43.5(15)
C14	5904(8)	4135(4)	1962(6)	41.5(14)
C16	8100(8)	3955(4)	3943(7)	44.6(15)
C12	5695(8)	4864(4)	2501(6)	42.5(15)
C6	2906(7)	5254(4)	1714(6)	38.9(14)
C15	7183(8)	3686(4)	2801(7)	42.7(14)
C13	6746(8)	5106(4)	3627(6)	41.2(14)
C9	5609(8)	6344(4)	3654(7)	46.7(16)
C11	6374(9)	7113(4)	4068(8)	54.3(18)
C8	4968(8)	6243(4)	2145(7)	44.2(15)
C1	3665(8)	6770(4)	1407(7)	45.6(16)
C10	4540(8)	6174(5)	4379(7)	50.0(17)
C17	9454(9)	3549(5)	4895(7)	49.9(18)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_20231315_0m. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	47.8(6)	39.8(5)	51.6(6)	0.8(3)	15.9(4)	8.1(3)
Br2	49.3(6)	34.2(5)	59.8(6)	-1.0(3)	22.2(4)	-2.8(3)
O1	48(3)	32(2)	54(3)	1.0(18)	17(2)	-0.4(18)
O3	47(3)	37(2)	50(3)	-4.3(19)	16(2)	-2(2)
O4	45(3)	37(2)	53(3)	-2.8(19)	12(2)	-0.6(19)
O2	44(3)	40(3)	57(3)	-5(2)	13(2)	0(2)
C2	48(4)	37(3)	42(3)	1(3)	12(3)	3(3)
C4	48(4)	33(3)	43(3)	-4(3)	16(3)	-4(3)
C3	37(3)	35(3)	51(4)	0(3)	12(3)	1(3)
C18	47(4)	32(3)	41(3)	-2(2)	13(3)	4(3)
C5	46(4)	33(3)	44(3)	-4(2)	12(3)	6(3)
C7	57(4)	26(3)	46(3)	1(3)	17(3)	0(3)
C14	46(4)	34(3)	46(3)	2(3)	19(3)	1(3)
C16	51(4)	32(3)	53(4)	3(3)	20(3)	5(3)
C12	41(4)	39(3)	47(3)	2(3)	16(3)	1(3)
C6	38(3)	33(3)	42(3)	2(2)	9(2)	1(2)
C15	41(4)	31(3)	60(4)	0(3)	22(3)	3(3)
C13	46(4)	31(3)	48(3)	-1(3)	19(3)	0(3)
C9	44(4)	34(3)	61(4)	0(3)	18(3)	7(3)
C11	45(4)	37(4)	78(5)	-12(3)	19(3)	-4(3)
C8	49(4)	30(3)	56(4)	-4(3)	21(3)	-4(3)
C1	49(4)	35(4)	53(4)	1(3)	19(3)	5(3)
C10	43(4)	50(4)	54(4)	-2(3)	14(3)	4(3)
C17	48(4)	46(4)	52(4)	5(3)	14(3)	6(3)

Table 4 Bond Lengths for cu_20231315_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Br1	C2	1.898(7)	C5	C6	1.402(9)
Br2	C4	1.885(6)	C7	C12	1.506(9)
O1	C18	1.364(8)	C7	C6	1.527(10)
O1	C1	1.425(9)	C7	C8	1.526(9)
O3	C14	1.252(8)	C14	C12	1.441(10)
O4	C16	1.371(8)	C14	C15	1.457(9)
O4	C13	1.353(8)	C16	C15	1.324(10)
O2	C13	1.334(8)	C16	C17	1.506(9)
O2	C9	1.481(8)	C12	C13	1.342(9)
C2	C3	1.385(10)	C9	C11	1.513(10)
C2	C18	1.385(10)	C9	C8	1.548(10)
C4	C3	1.383(10)	C9	C10	1.522(11)
C4	C5	1.373(10)	C8	C1	1.517(10)
C18	C6	1.415(9)			

Table 5 Bond Angles for cu_20231315_0m.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C18	O1	C1	116.8(5)	C15	C16	C17	126.3(7)
C13	O4	C16	118.1(5)	C14	C12	C7	121.3(6)
C13	O2	C9	118.1(5)	C13	C12	C7	118.7(6)
C3	C2	Br1	118.9(5)	C13	C12	C14	119.0(6)
C3	C2	C18	121.9(6)	C18	C6	C7	120.1(6)
C18	C2	Br1	119.2(5)	C5	C6	C18	118.6(6)
C3	C4	Br2	120.4(5)	C5	C6	C7	121.4(6)
C5	C4	Br2	118.7(5)	C16	C15	C14	121.2(6)
C5	C4	C3	120.9(6)	O2	C13	O4	107.2(5)
C4	C3	C2	118.8(7)	O2	C13	C12	128.5(6)
O1	C18	C2	118.4(6)	C12	C13	O4	124.3(6)
O1	C18	C6	122.6(6)	O2	C9	C11	103.0(6)
C2	C18	C6	118.9(6)	O2	C9	C8	108.0(6)
C4	C5	C6	120.8(6)	O2	C9	C10	104.6(6)
C12	C7	C6	115.1(5)	C11	C9	C8	112.4(6)
C12	C7	C8	110.3(6)	C11	C9	C10	110.7(6)
C8	C7	C6	111.2(6)	C10	C9	C8	116.9(6)
O3	C14	C12	123.1(6)	C7	C8	C9	113.1(6)
O3	C14	C15	122.0(6)	C1	C8	C7	108.1(6)
C12	C14	C15	114.9(6)	C1	C8	C9	115.4(6)
O4	C16	C17	111.6(6)	O1	C1	C8	114.4(6)
C15	C16	O4	122.1(6)				

Table 6 Torsion Angles for cu_20231315_0m.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Br1	C2	C3	C4	179.4(5)	C12	C7	C6	C18	148.4(6)
Br1	C2	C18	O1	4.2(8)	C12	C7	C6	C5	-32.3(9)
Br1	C2	C18	C6	-178.4(5)	C12	C7	C8	C9	-46.4(8)
Br2	C4	C3	C2	-179.9(5)	C12	C7	C8	C1	-175.4(6)
Br2	C4	C5	C6	-179.2(5)	C12	C14	C15	C16	-2.5(10)
O1	C18	C6	C5	176.1(6)	C6	C7	C12	C14	81.9(8)
O1	C18	C6	C7	-4.6(9)	C6	C7	C12	C13	-109.3(7)
O3	C14	C12	C7	-5.2(11)	C6	C7	C8	C9	82.7(7)
O3	C14	C12	C13	-174.0(7)	C6	C7	C8	C1	-46.4(7)

Table 6 Torsion Angles for cu_20231315_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C14	C15	C16	178.4(7)	C15	C14	C12	C7	175.7(6)
O4	C16	C15	C14	-2.6(11)	C15	C14	C12	C13	7.0(10)
O2	C9	C8	C7	55.1(8)	C13	O4	C16	C15	3.4(10)
O2	C9	C8	C1	-179.7(6)	C13	O4	C16	C17	-178.8(6)
C2	C18	C6	C5	-1.2(9)	C13	O2	C9	C11	-154.6(6)
C2	C18	C6	C7	178.1(6)	C13	O2	C9	C8	-35.5(8)
C4	C5	C6	C18	-0.7(9)	C13	O2	C9	C10	89.7(7)
C4	C5	C6	C7	180.0(6)	C9	O2	C13	O4	-173.7(6)
C3	C2	C18	O1	-175.3(6)	C9	O2	C13	C12	8.0(11)
C3	C2	C18	C6	2.1(10)	C9	C8	C1	O1	-68.1(8)
C3	C4	C5	C6	1.8(10)	C11	C9	C8	C7	168.1(6)
C18	O1	C1	C8	-43.6(8)	C11	C9	C8	C1	-66.8(8)
C18	C2	C3	C4	-1.0(10)	C8	C7	C12	C14	-151.2(7)
C5	C4	C3	C2	-1.0(10)	C8	C7	C12	C13	17.6(9)
C7	C12	C13	O4	-175.8(6)	C8	C7	C6	C18	21.9(8)
C7	C12	C13	O2	2.2(11)	C8	C7	C6	C5	-158.8(6)
C7	C8	C1	O1	59.6(8)	C1	O1	C18	C2	-167.8(6)
C14	C12	C13	O4	-6.8(11)	C1	O1	C18	C6	14.9(9)
C14	C12	C13	O2	171.3(7)	C10	C9	C8	C7	-62.4(8)
C16	O4	C13	O2	-176.9(6)	C10	C9	C8	C1	62.8(8)
C16	O4	C13	C12	1.5(10)	C17	C16	C15	C14	179.9(7)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for cu_20231315_0m.

Atom	*x*	*y*	*z*	U(eq)
H3	-1007.05	4852.78	1657.7	51
H5	3078.37	4082.74	1832.23	51
H7	4427.06	5375.45	786.33	52
H15	7362.26	3190.55	2522.3	51
H11A	6887.39	7121.52	5023.03	81
H11B	5613.98	7522.36	3804.4	81
H11C	7115.25	7193.32	3644.92	81
H8	5811.13	6367.33	1830.22	53
H1A	3973.38	7307.51	1664.65	55
H1B	3463.73	6722.91	456.24	55
H10A	4155.88	5648.5	4185.09	75
H10B	3692.31	6536.46	4094.55	75
H10C	5084.83	6229.23	5325.66	75
H17A	10379.53	3809.45	4917.98	75
H17B	9468.28	3015.38	4612.92	75
H17C	9393.78	3557.27	5771.83	75

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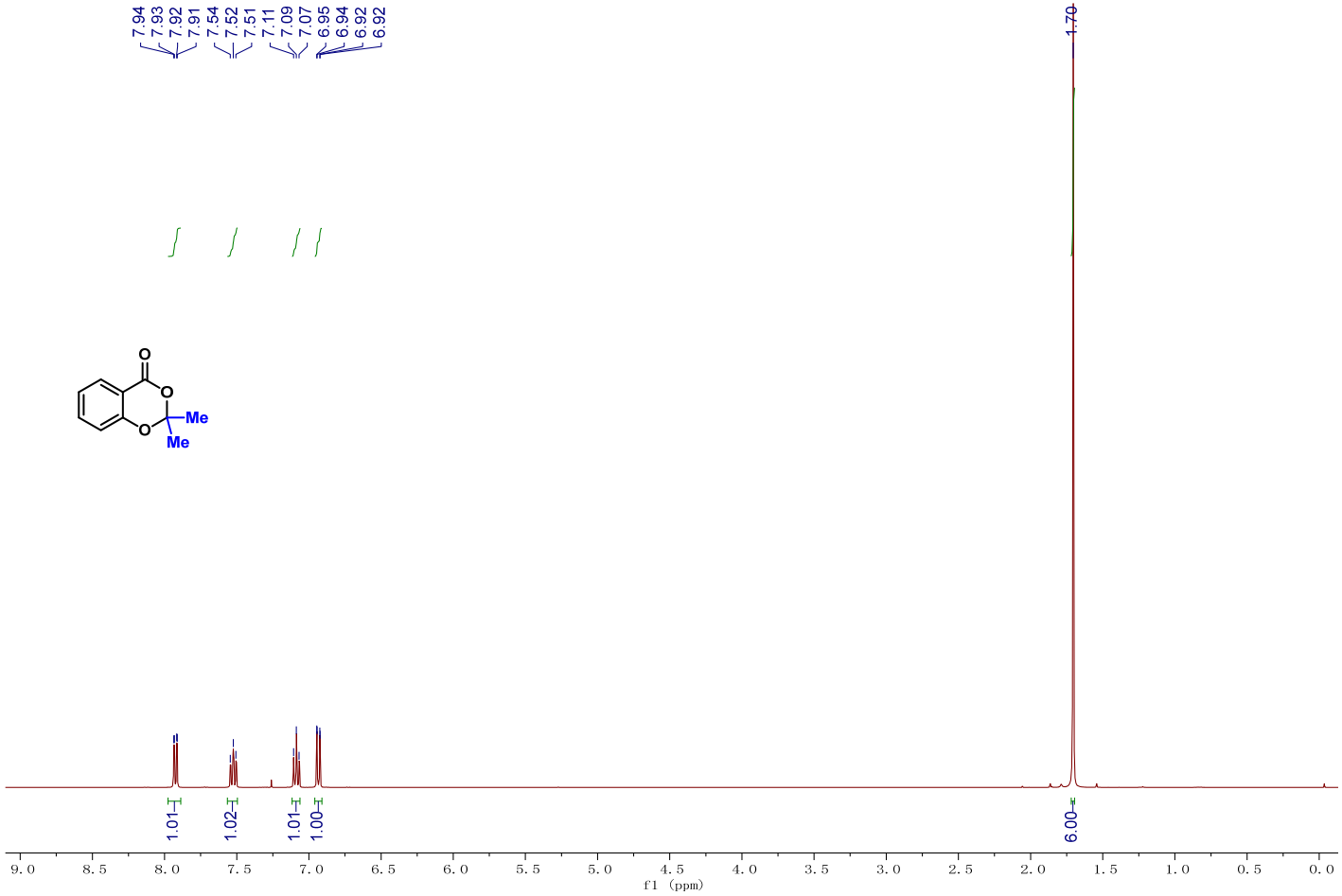
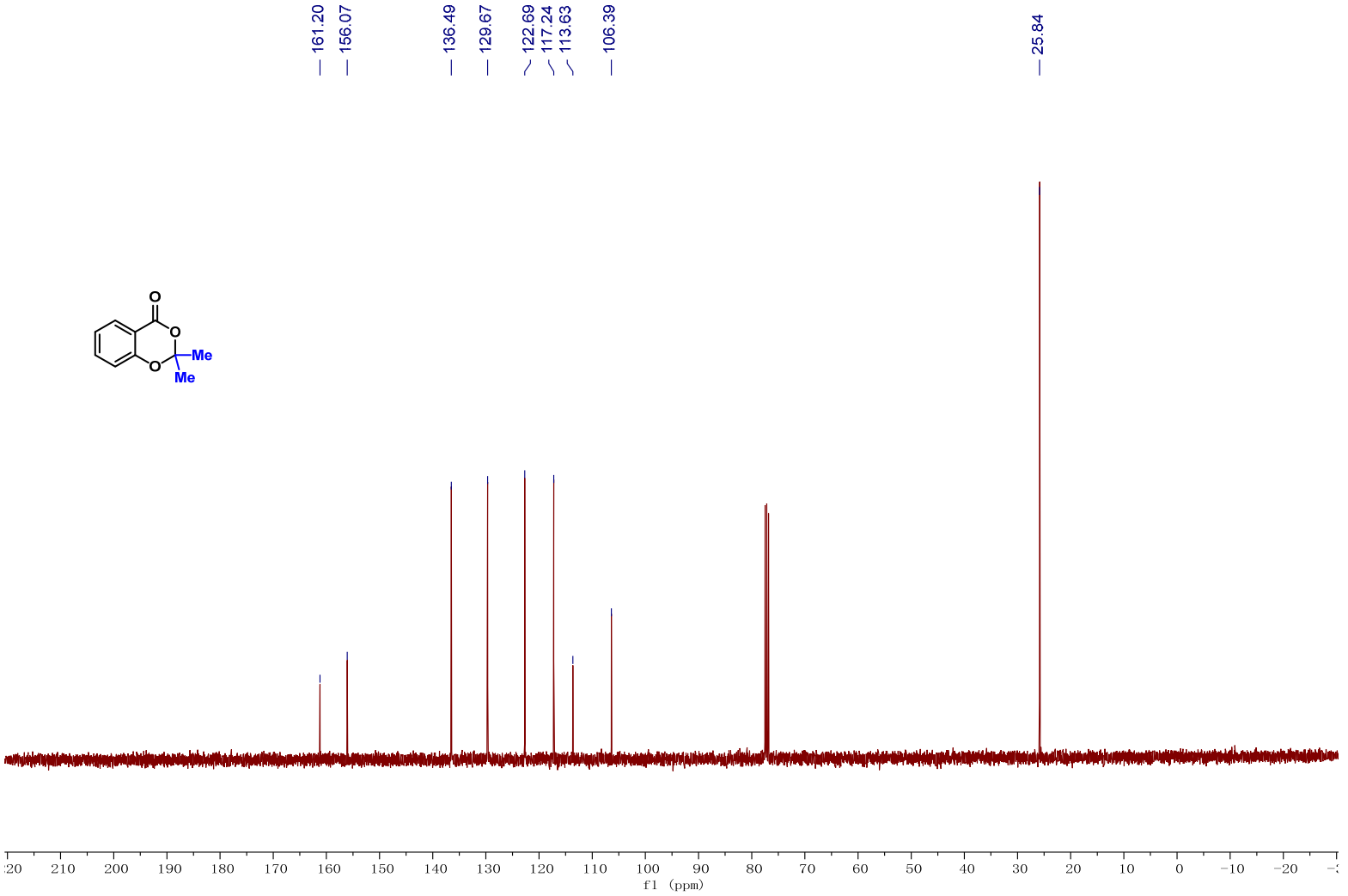
NMR Spectra

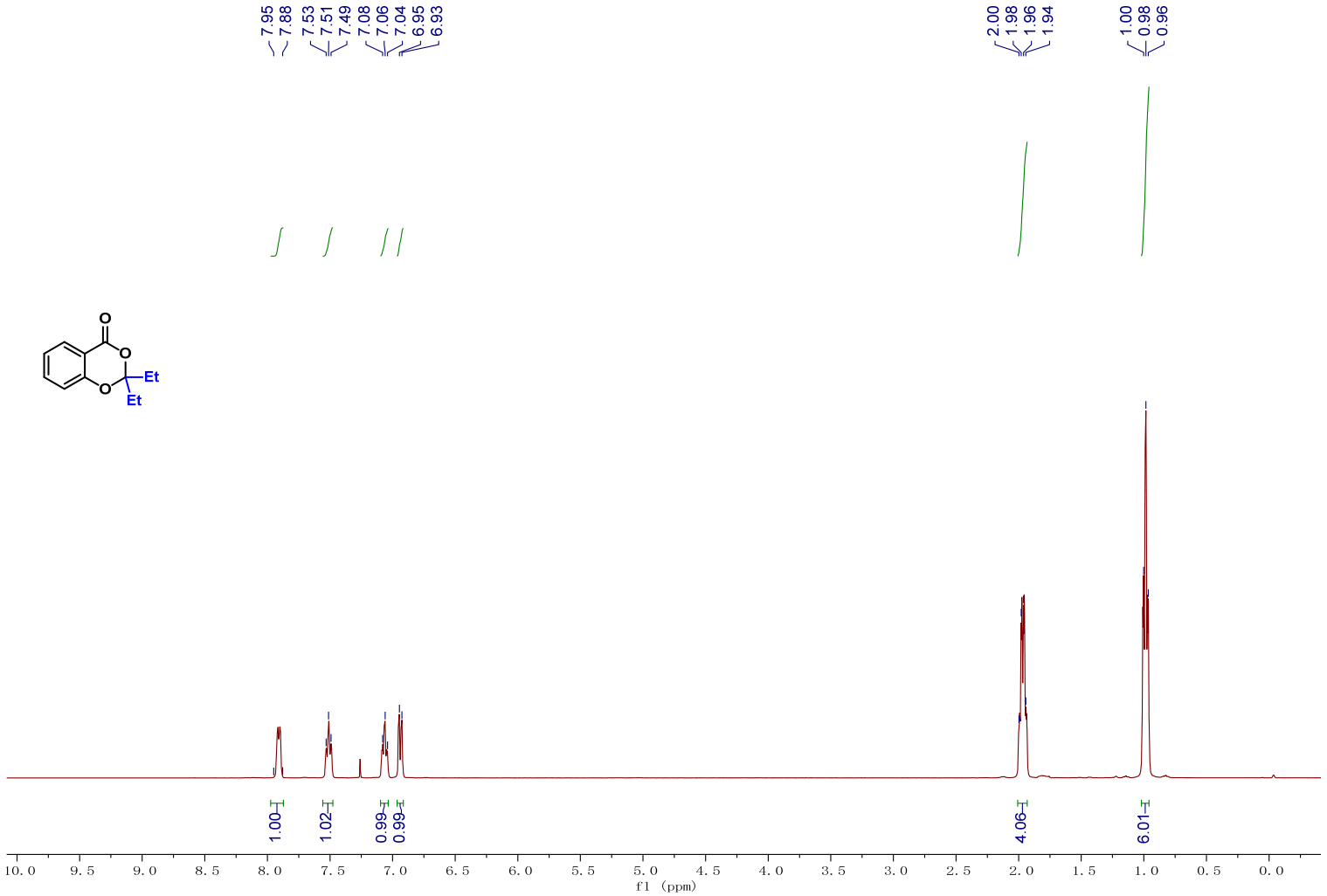
Compound 5a ^{1}H NMR



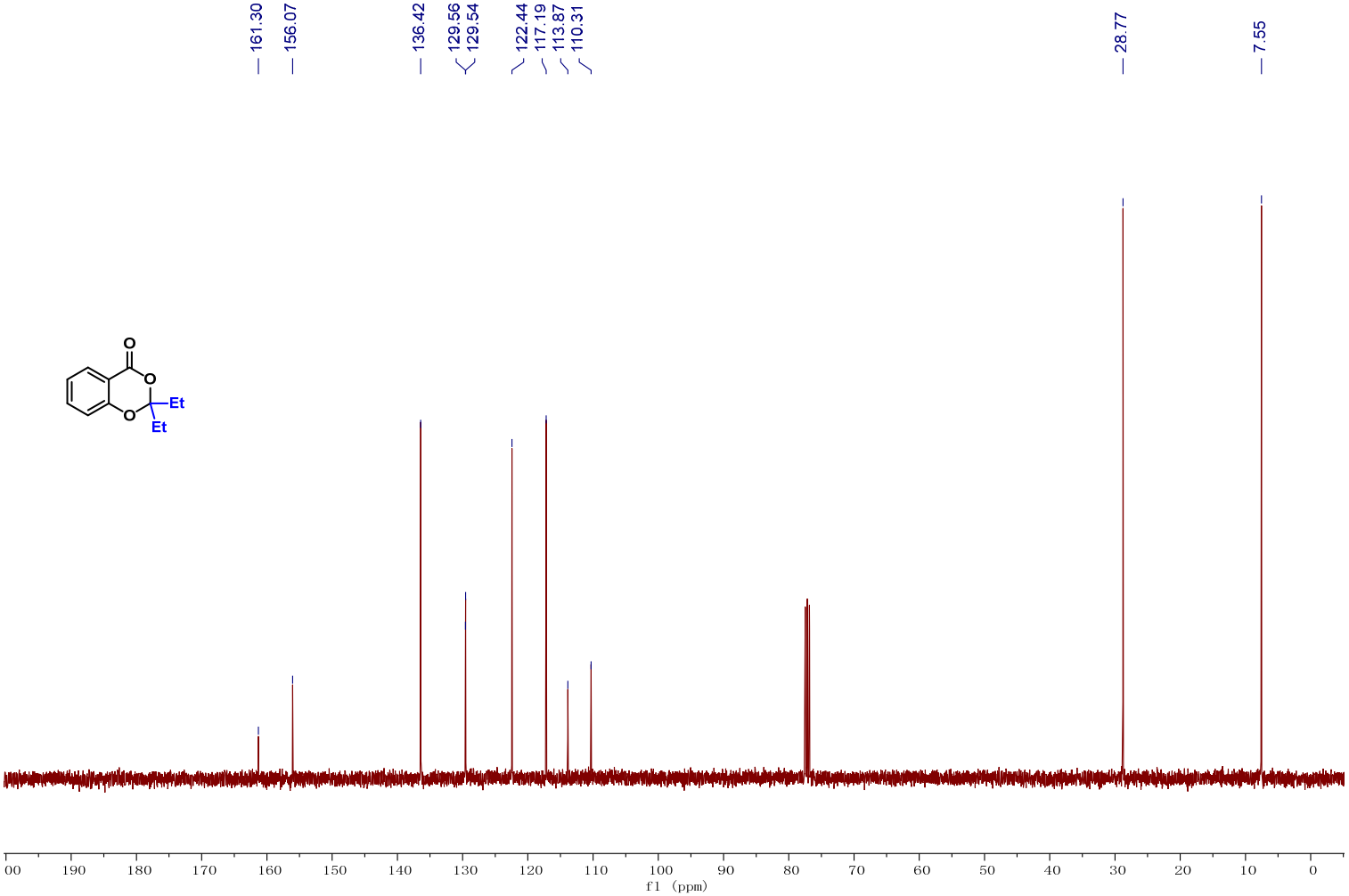
Compound 5a ^{13}C NMR



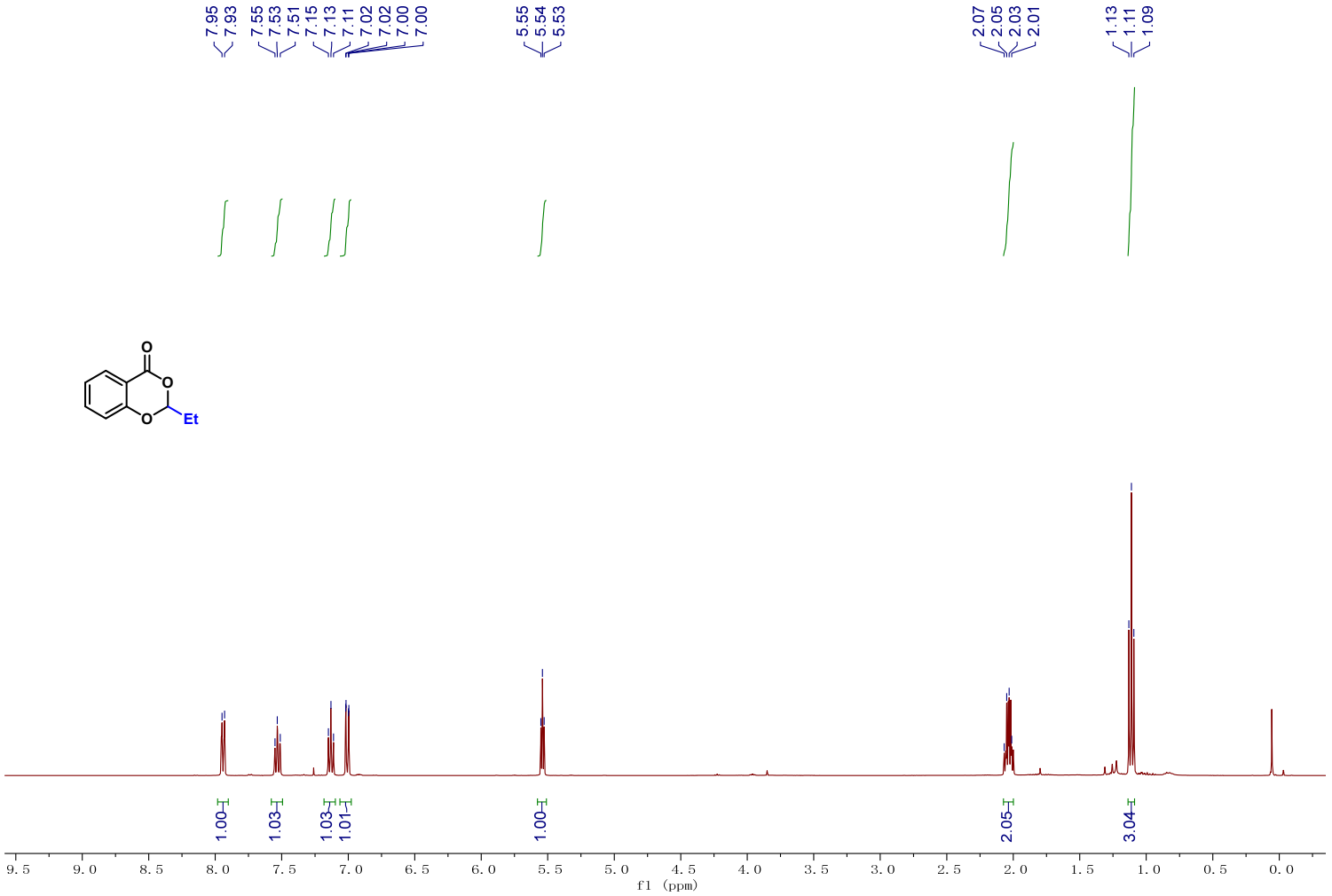
Compound S1 ^{1}H NMR



Compound S1 ^{13}C NMR



Compound S2 ^{1}H NMR



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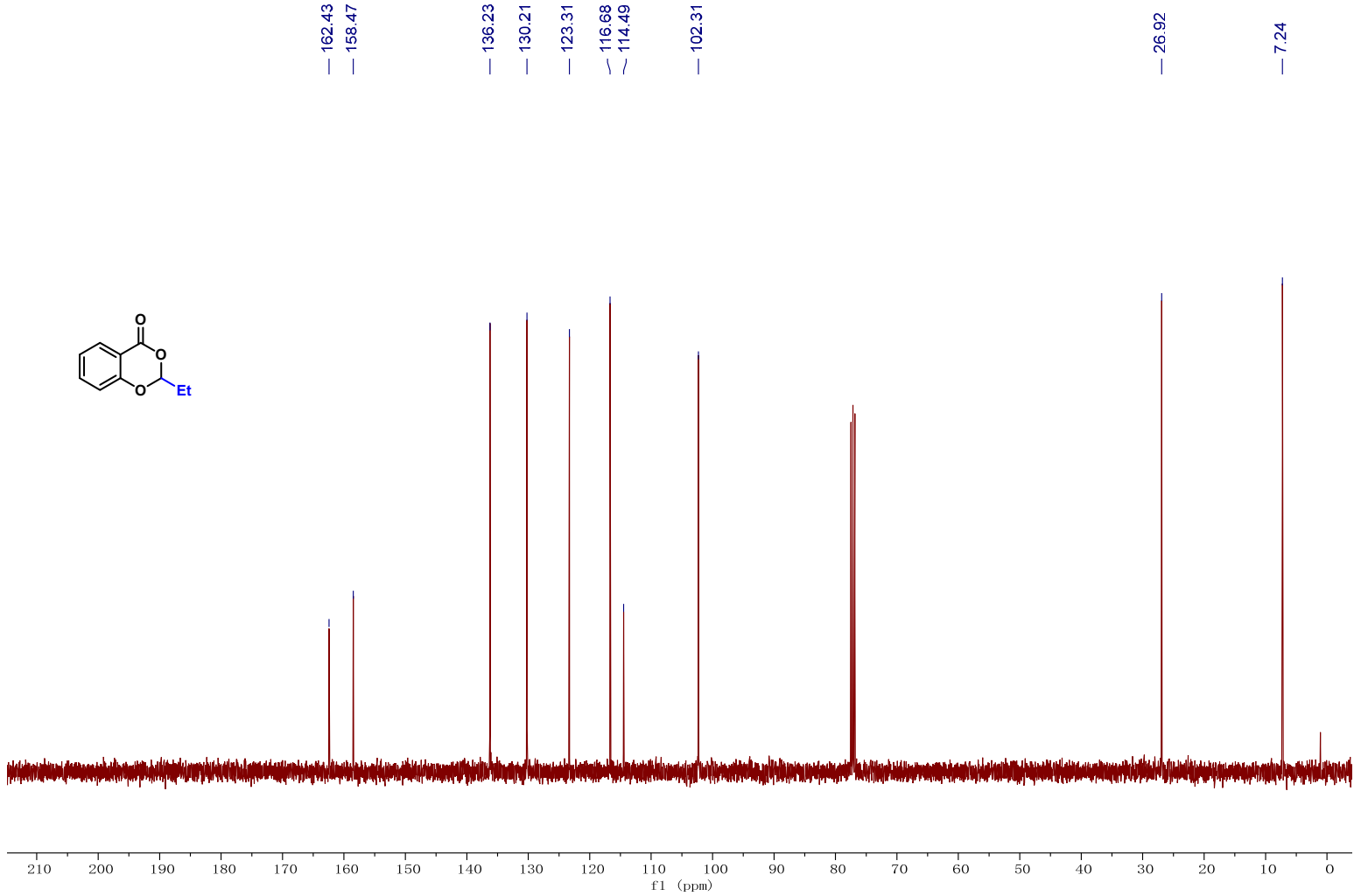
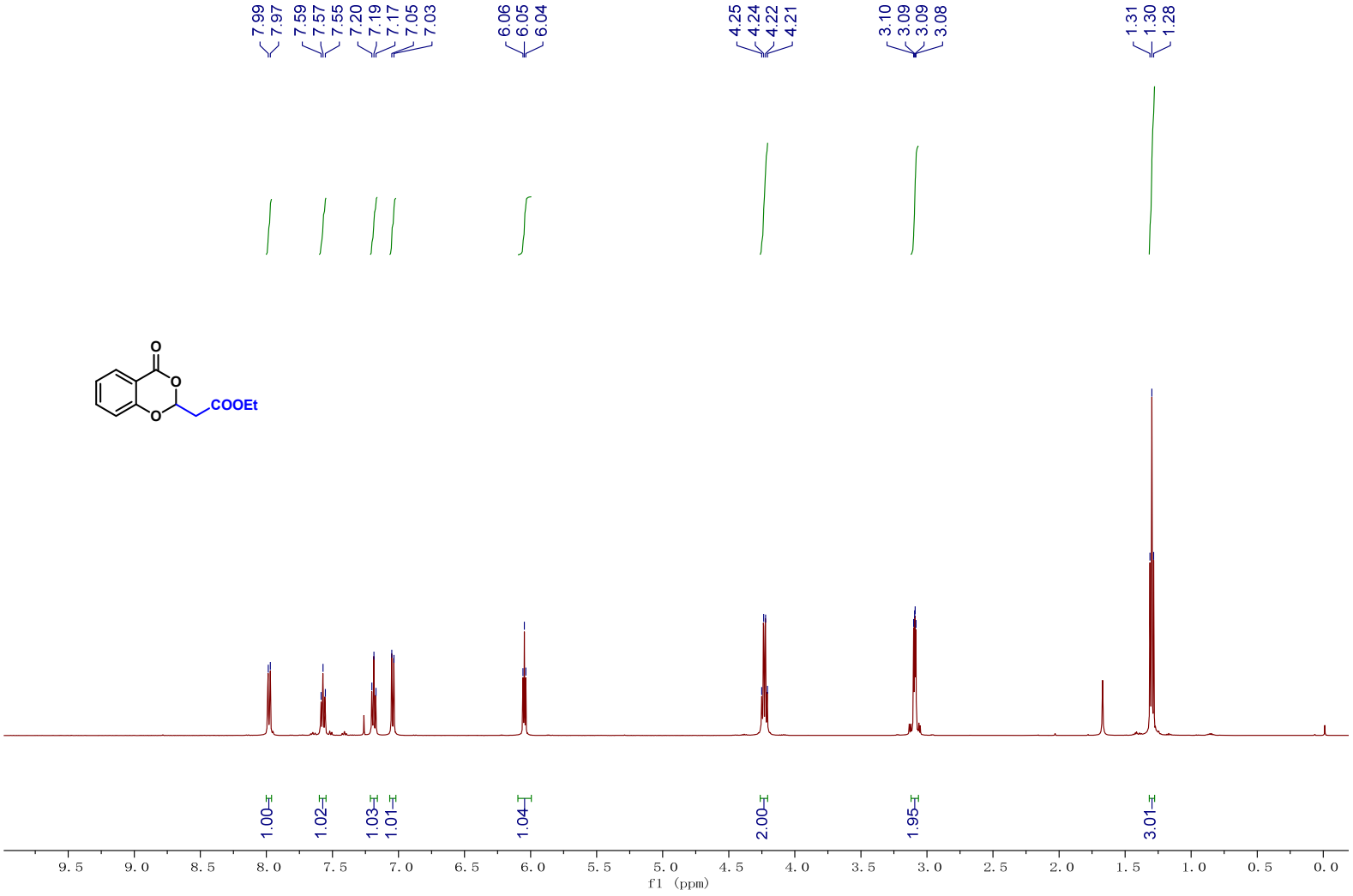


Compound S3 ^{1}H NMR



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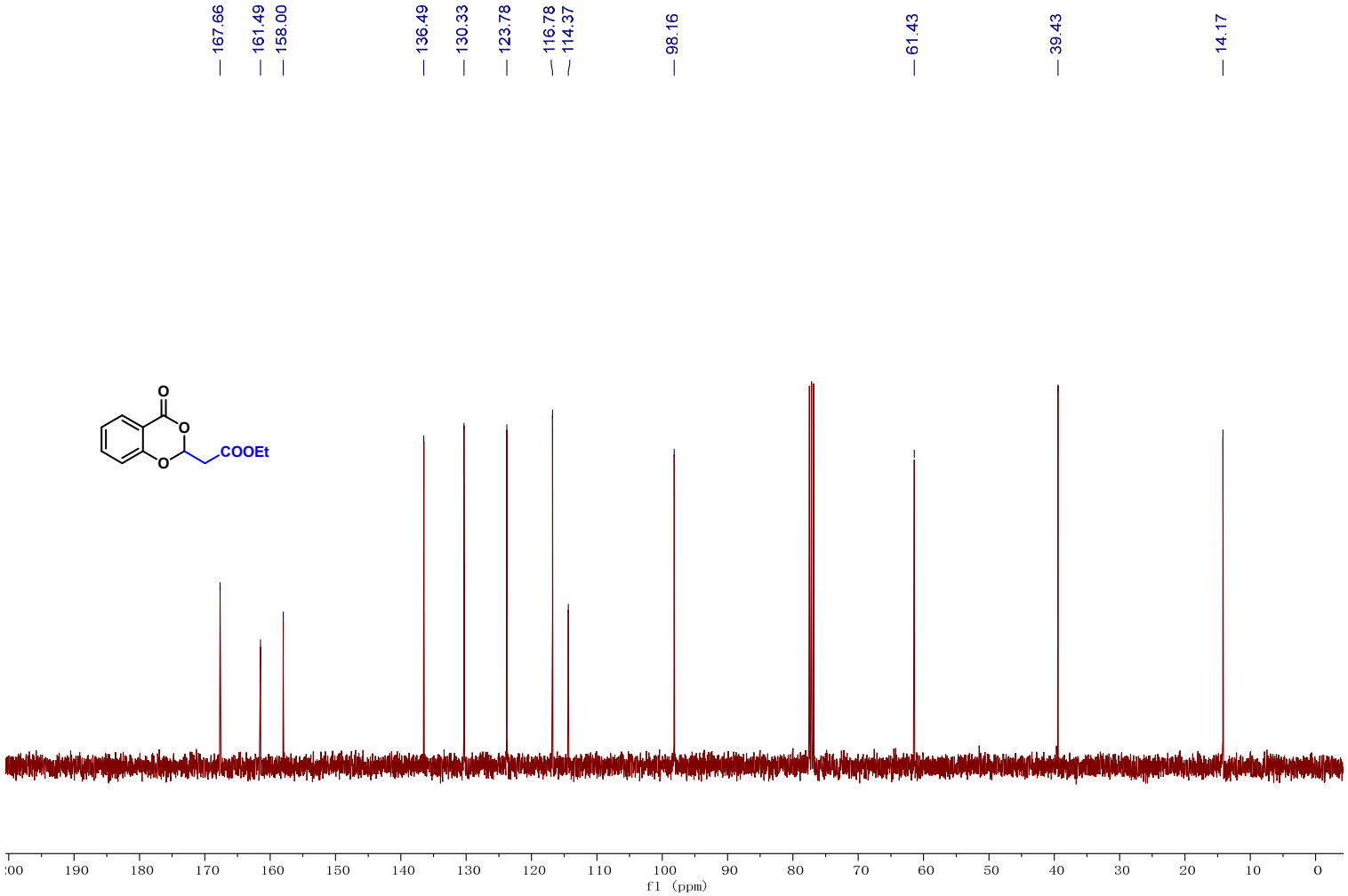

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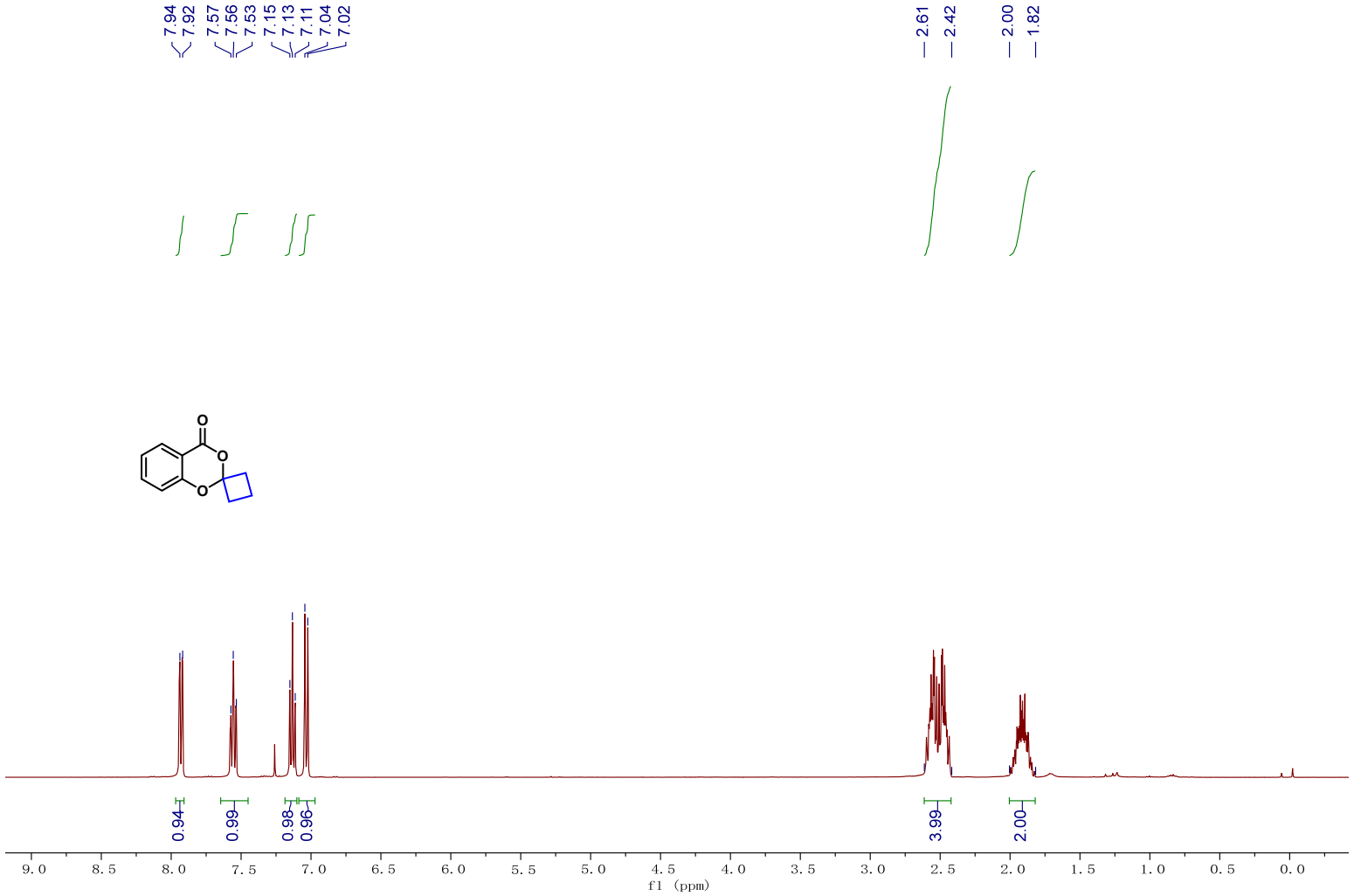

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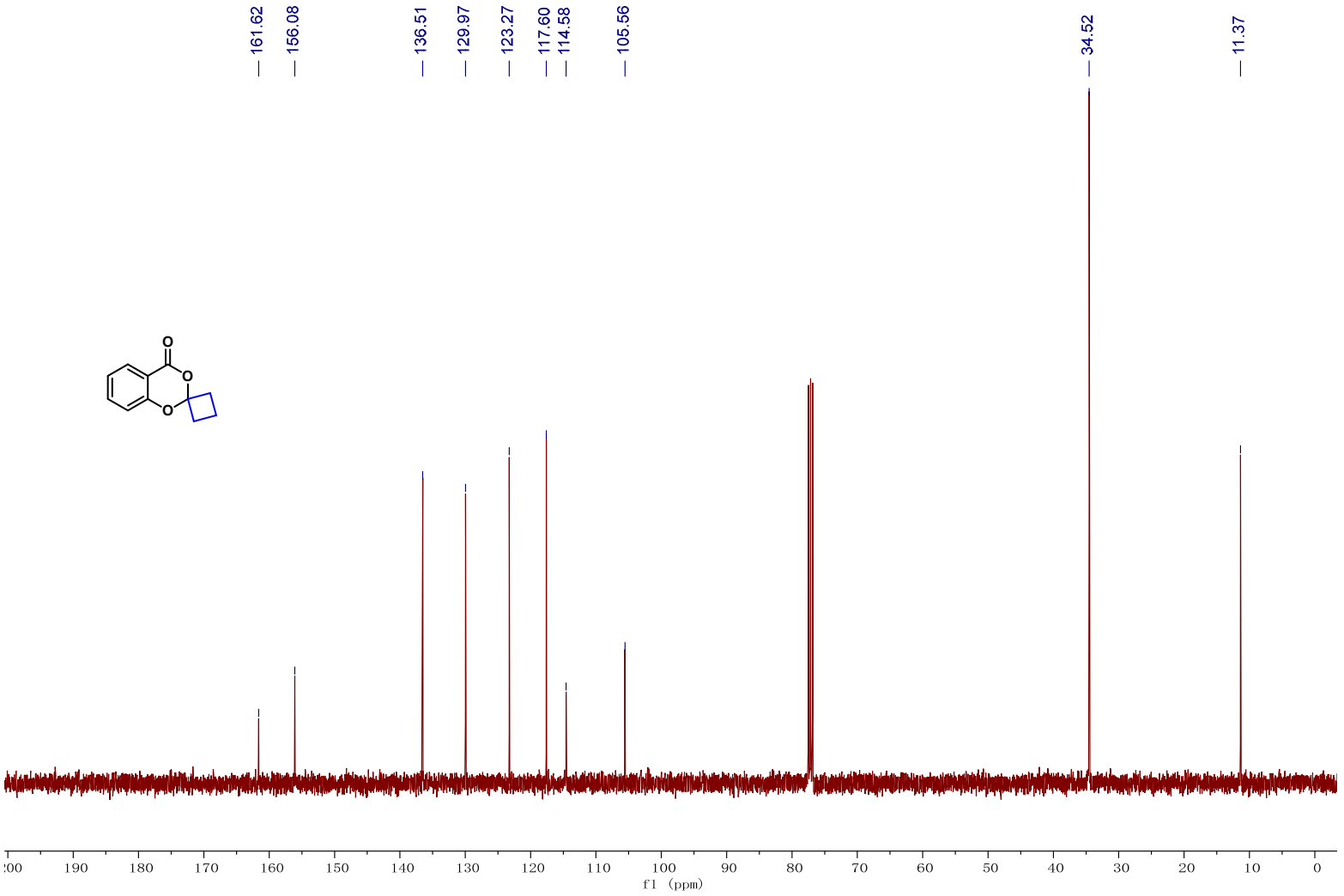

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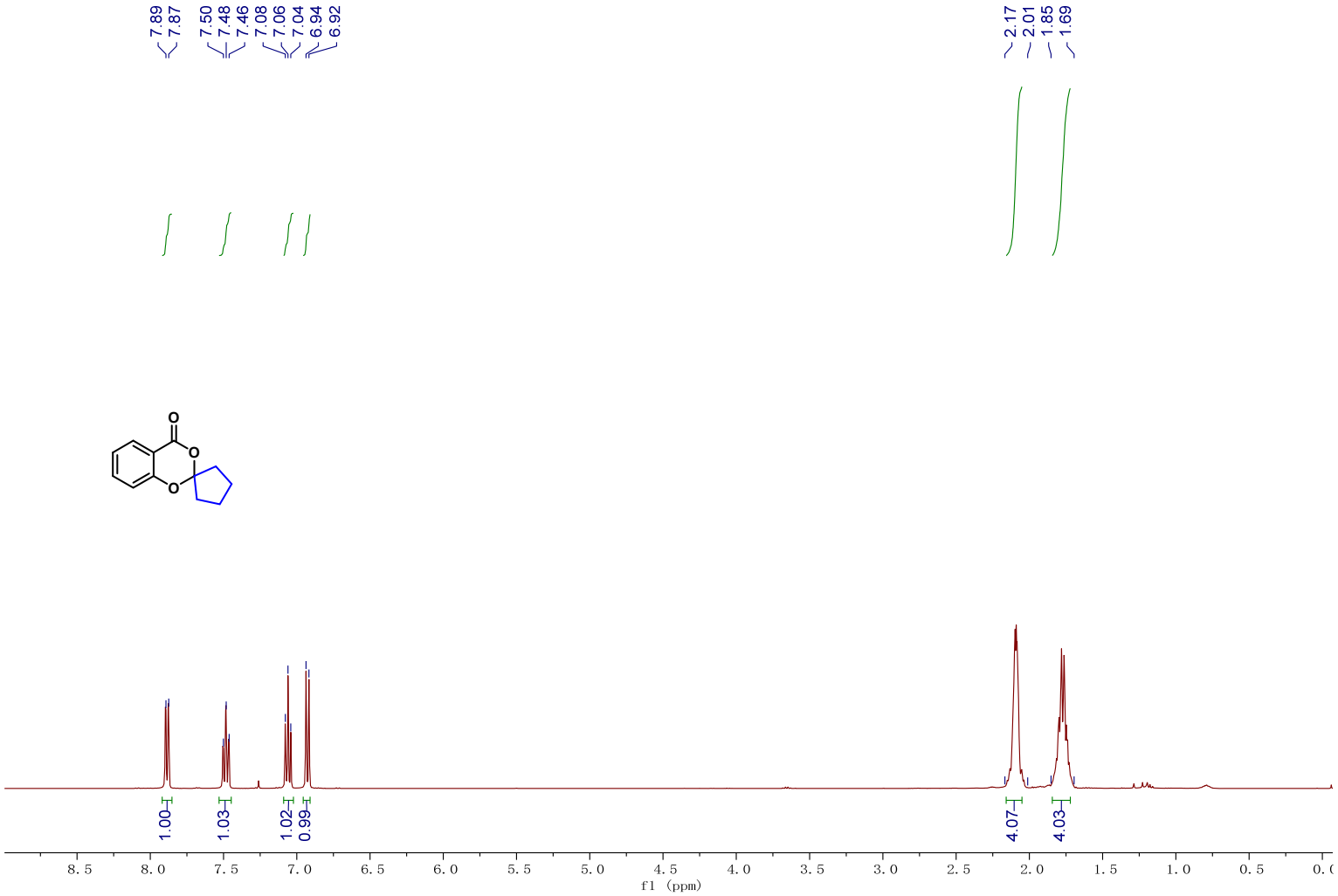
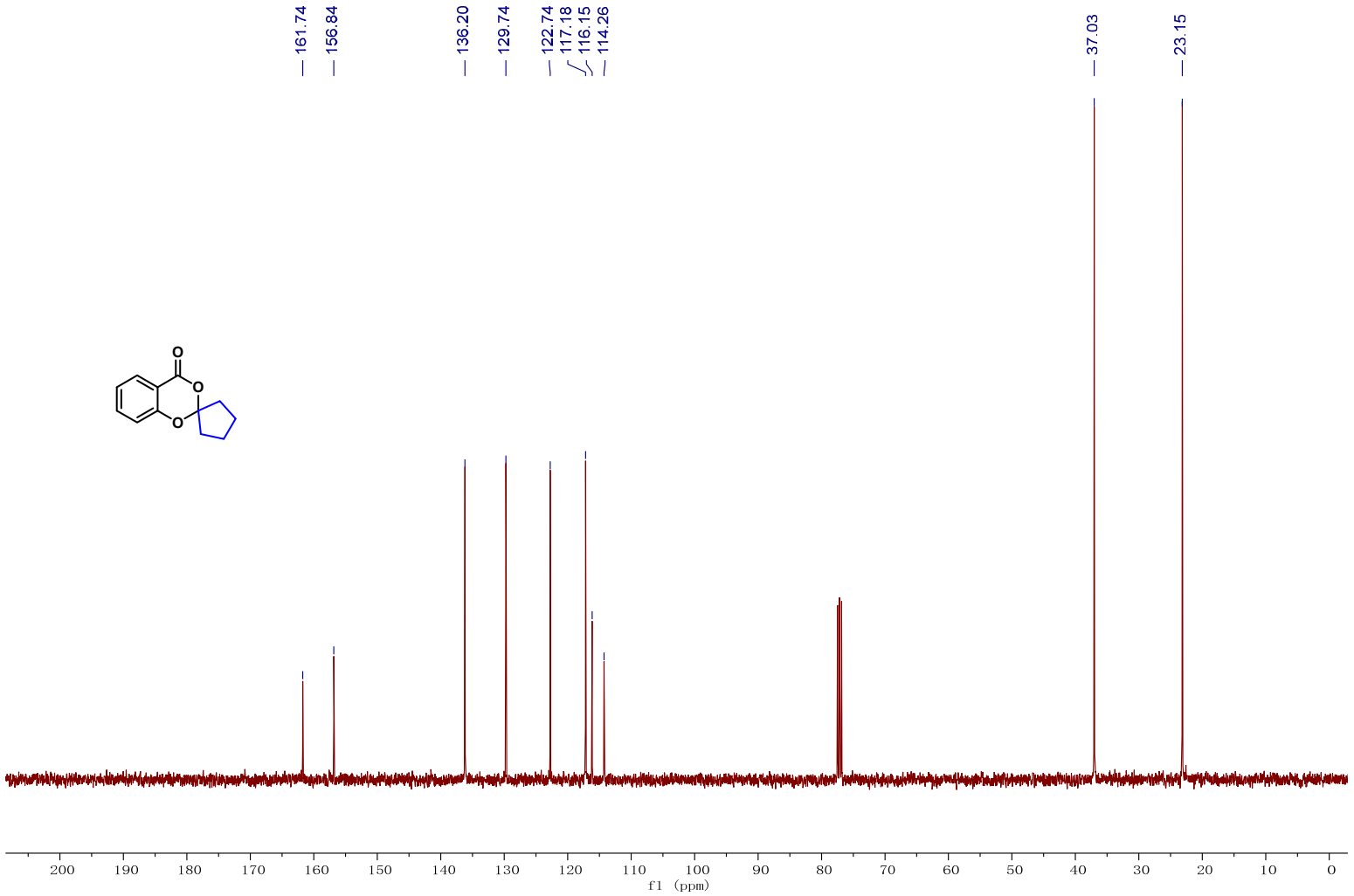
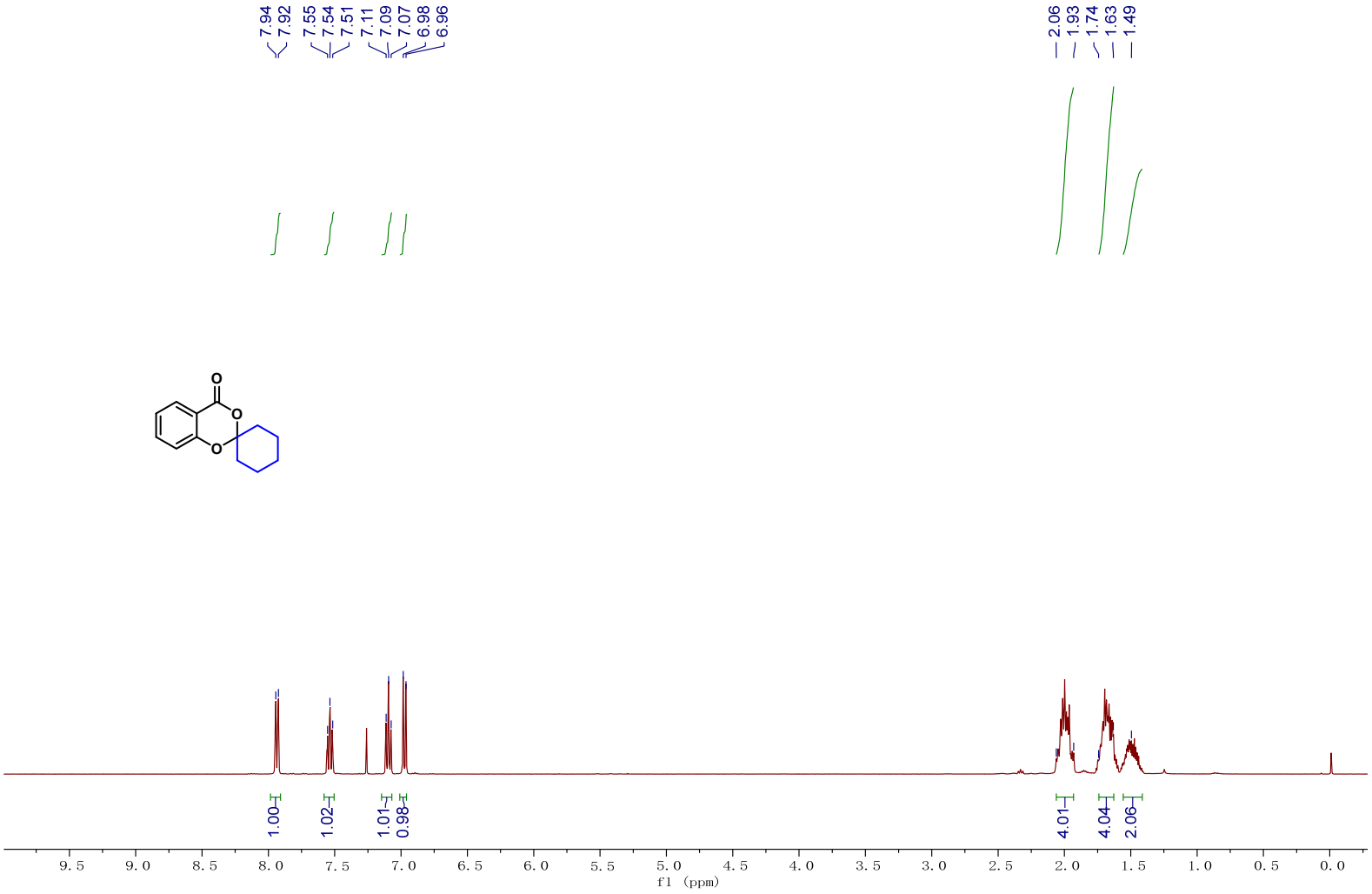


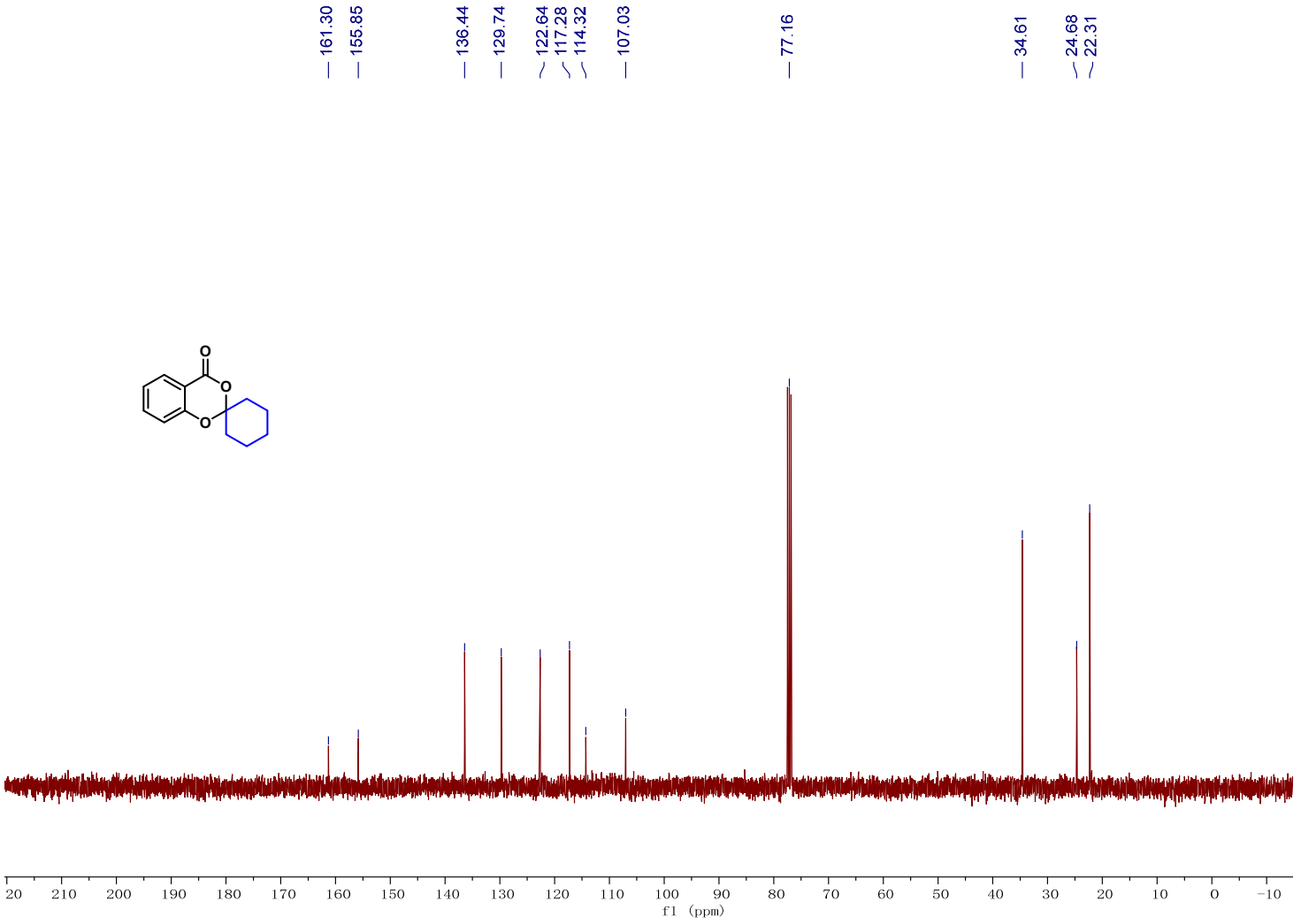
Compound S5 ^{13}C NMR



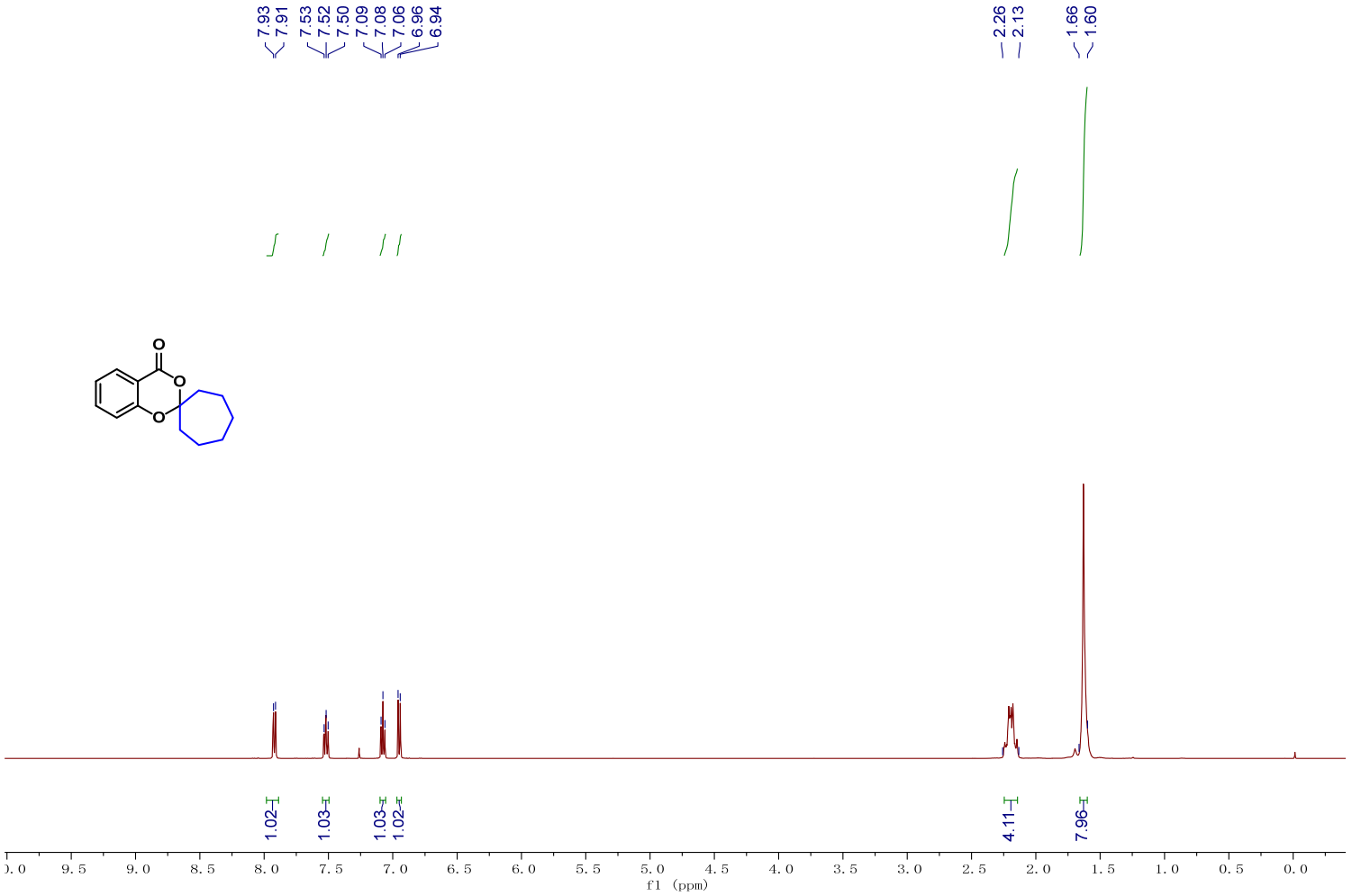
Compound 75b ^{1}H NMR



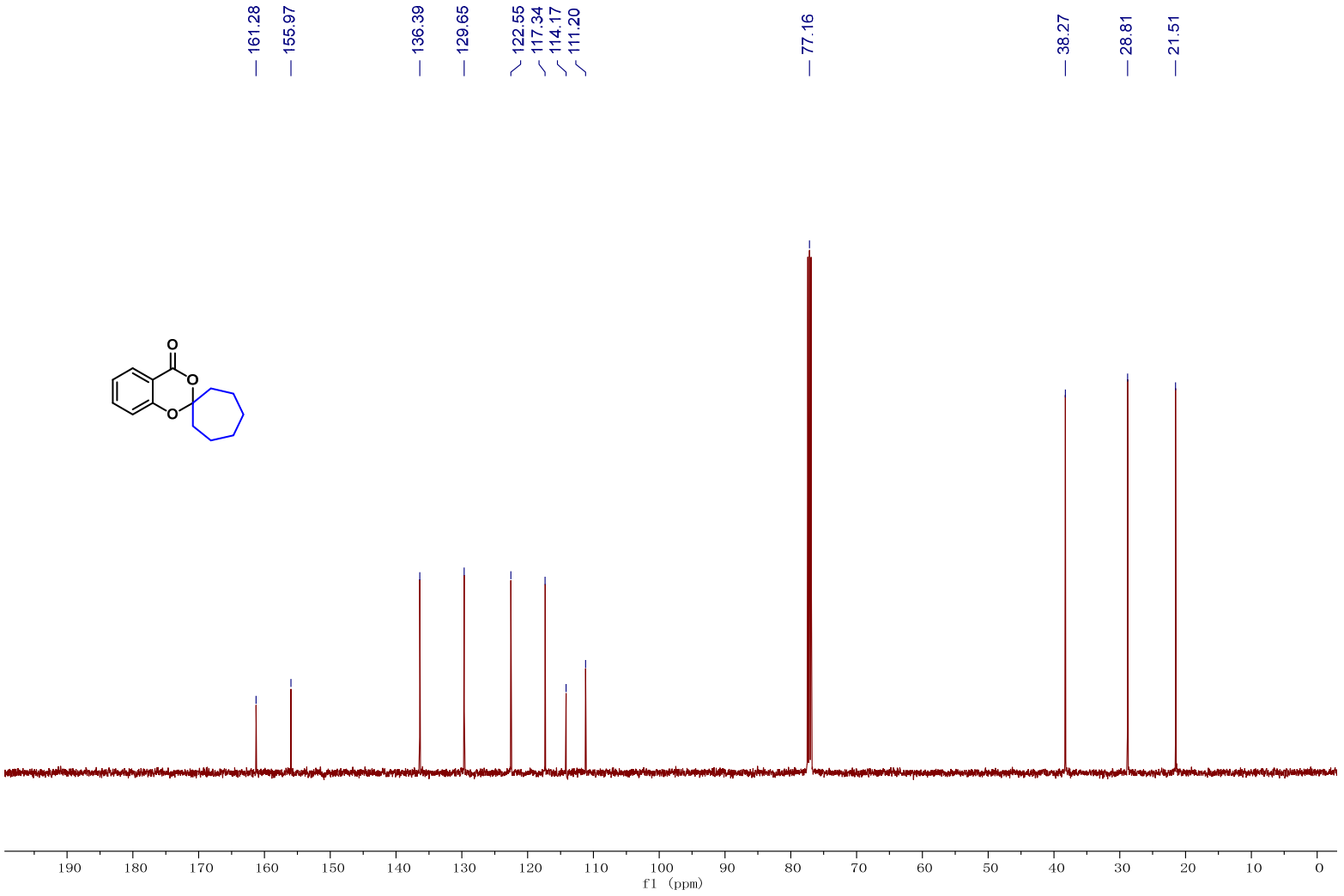
Compound 75b ^{13}C NMR



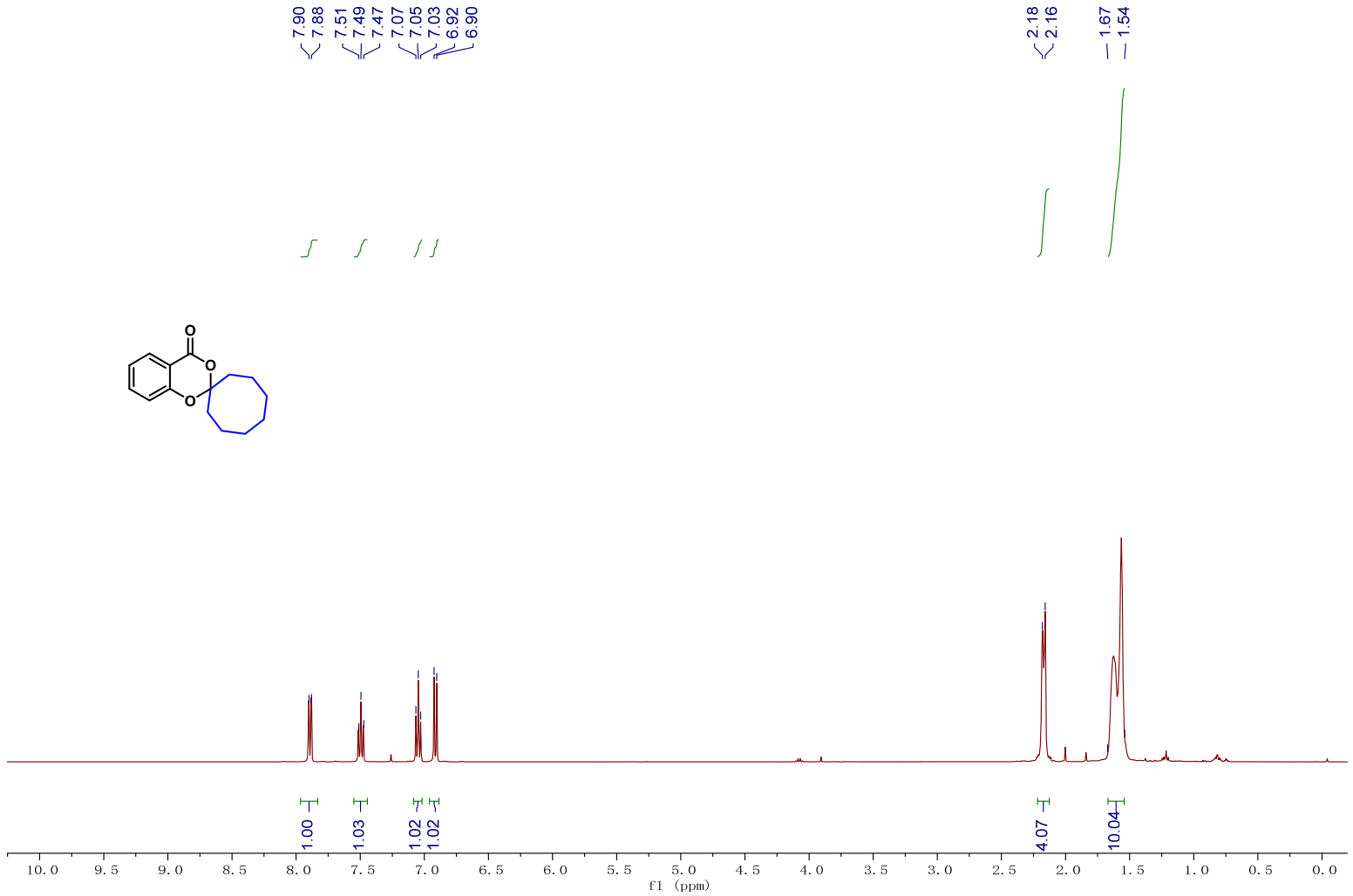
Compound S6 ^{1}H NMR



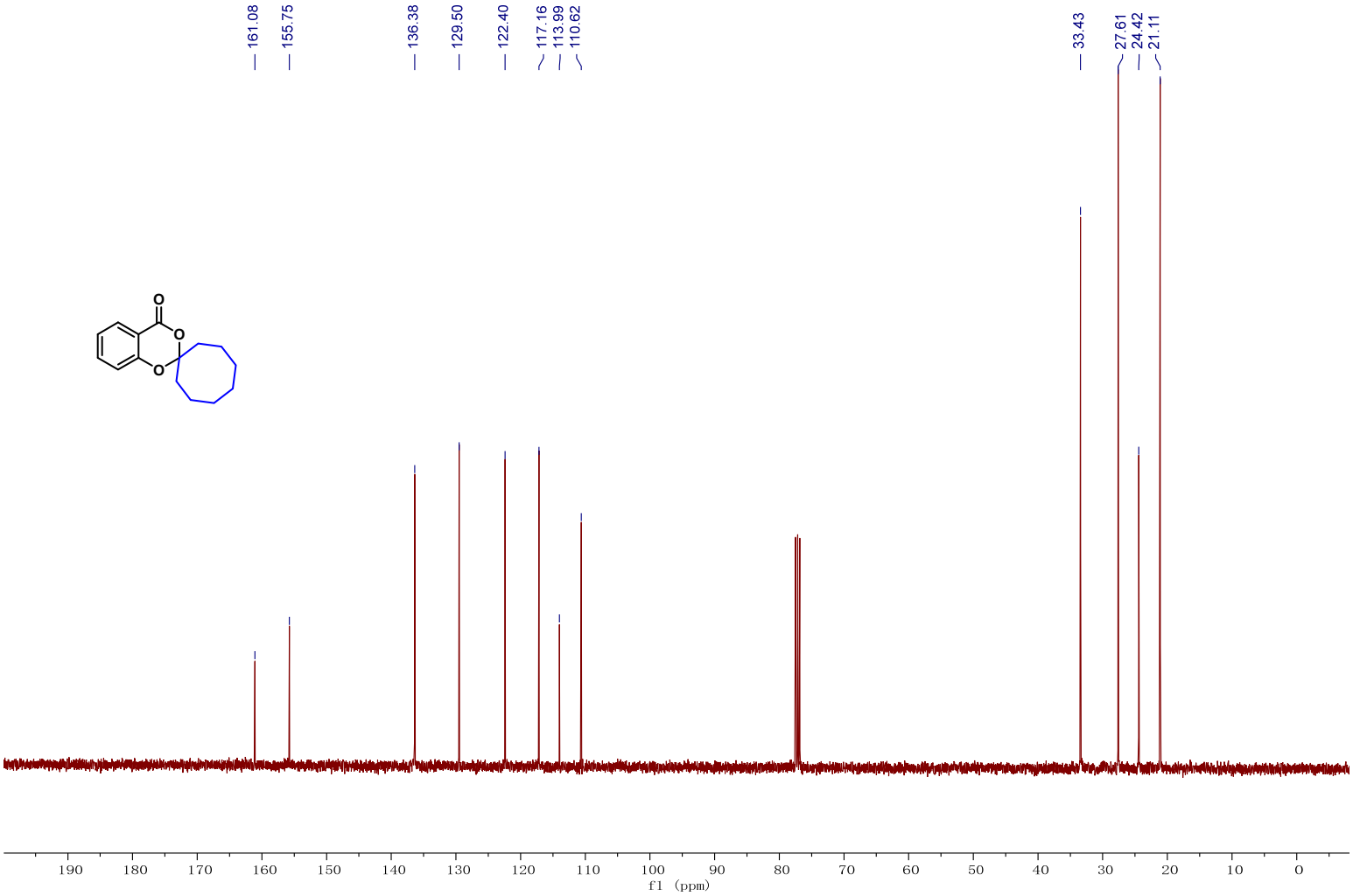
Compound S6 ^{13}C NMR



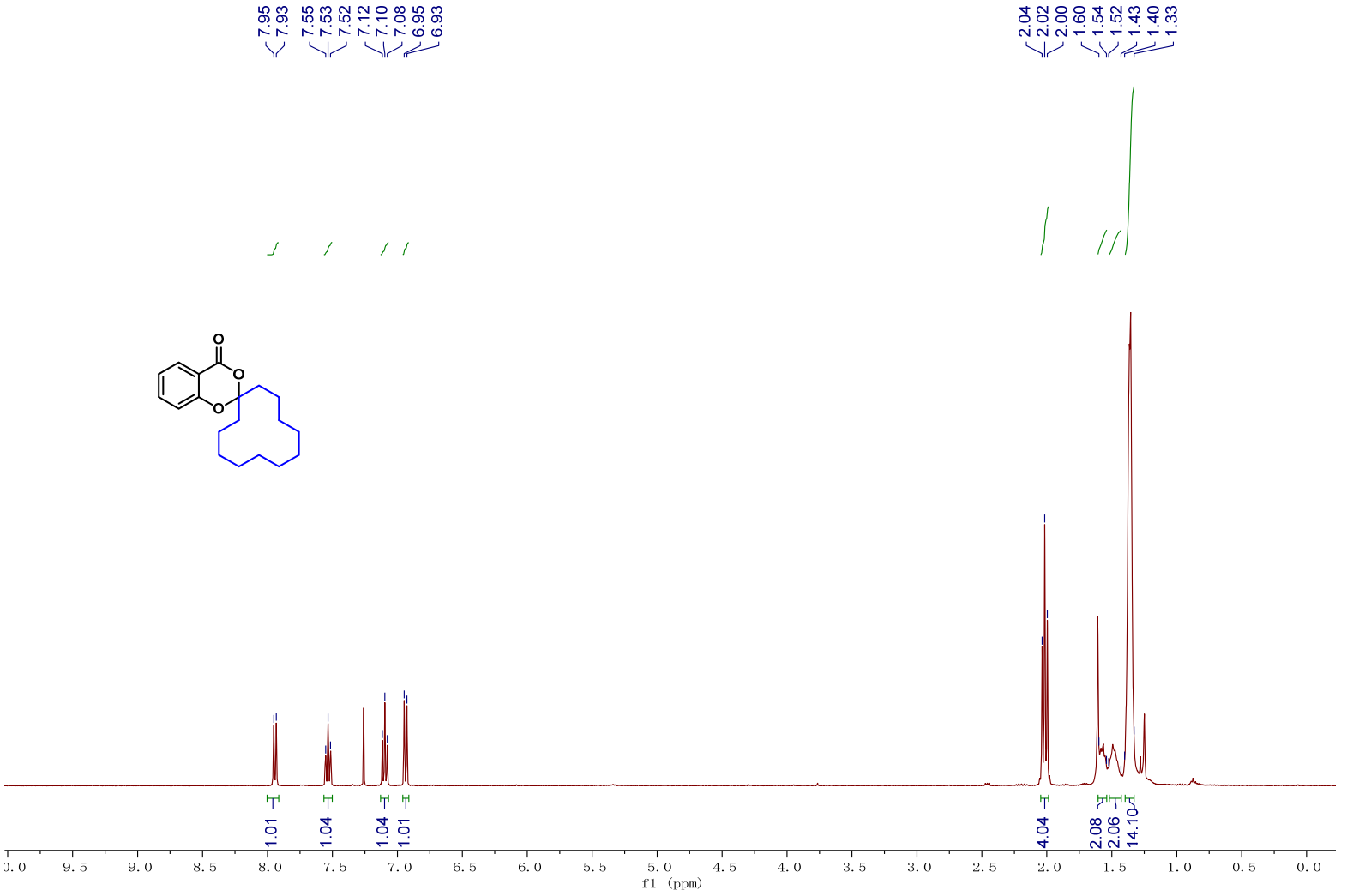
Compound S7 ^{1}H NMR



Compound S7 ^{13}C NMR



Compound S8 ^{1}H NMR



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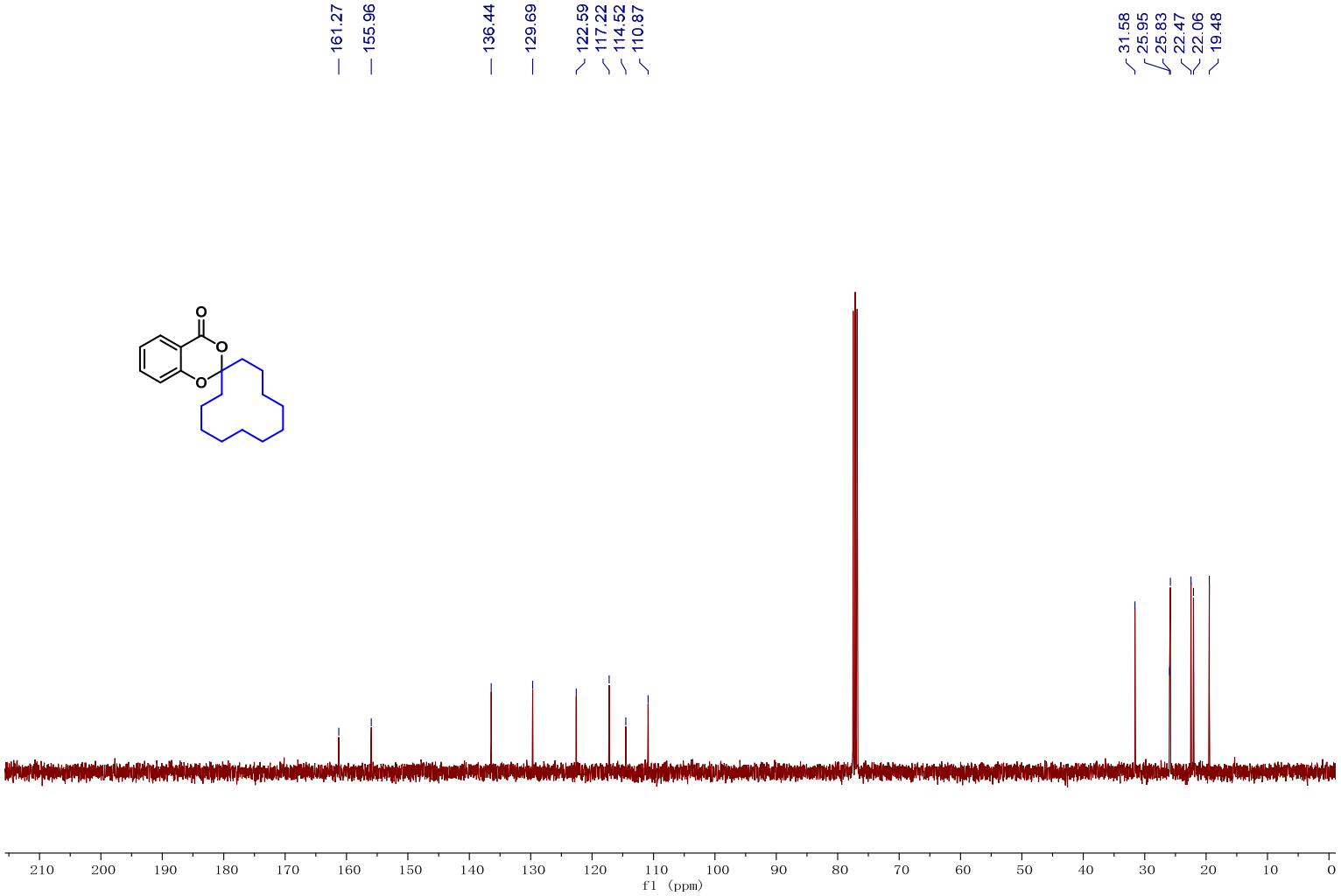

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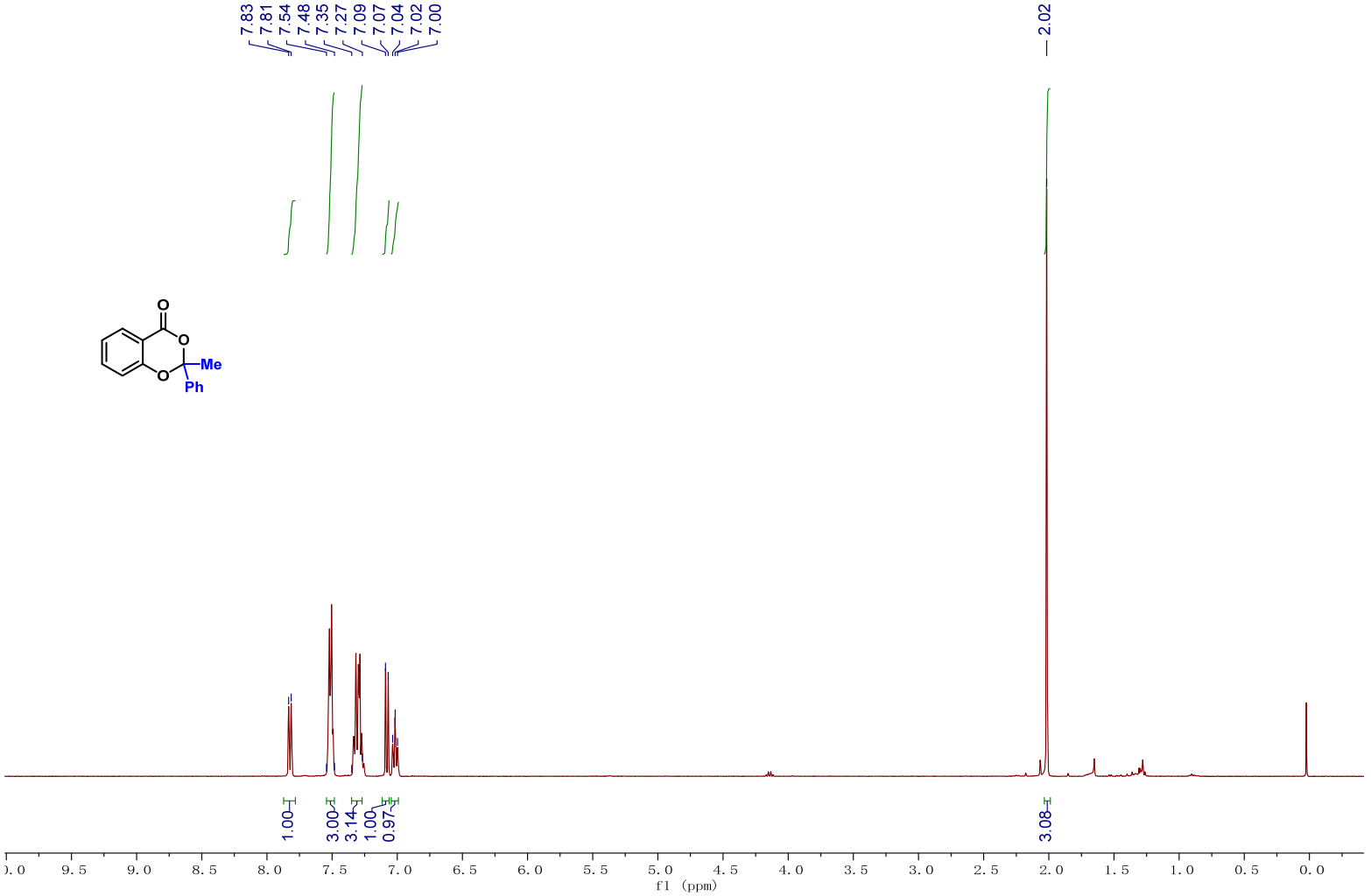
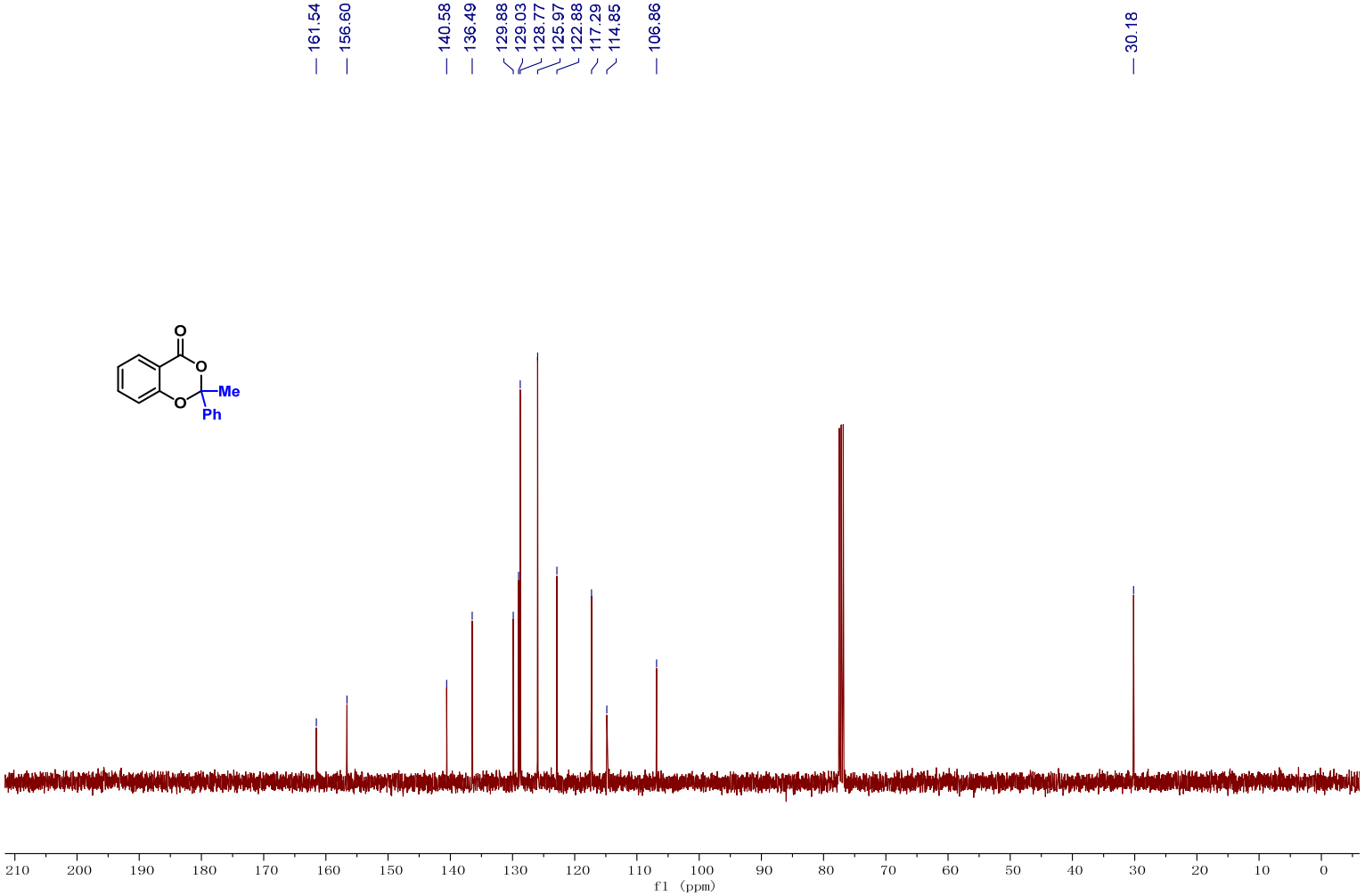
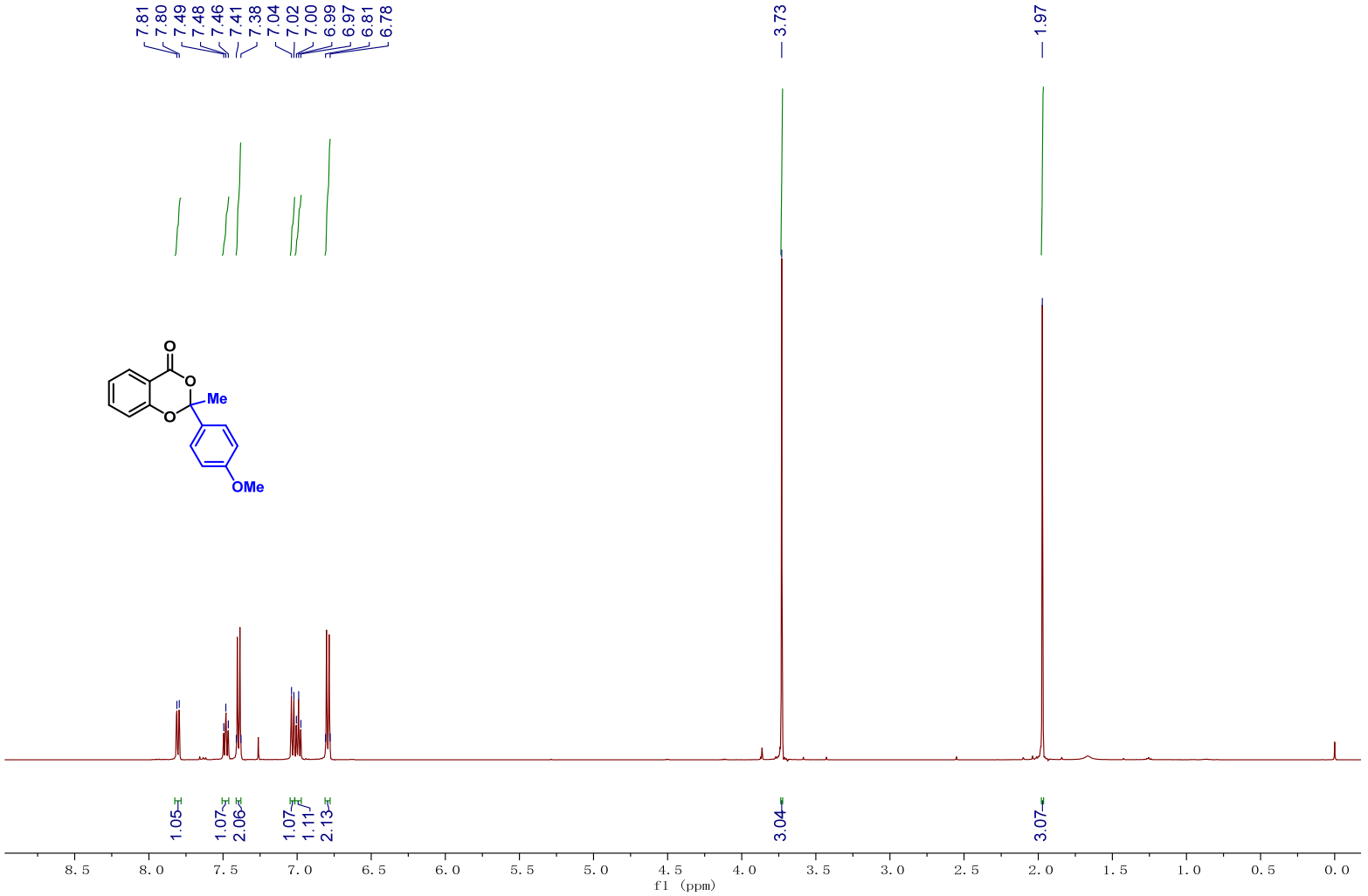


Compound S9 ^{13}C NMR



Compound S10 ^{1}H NMR



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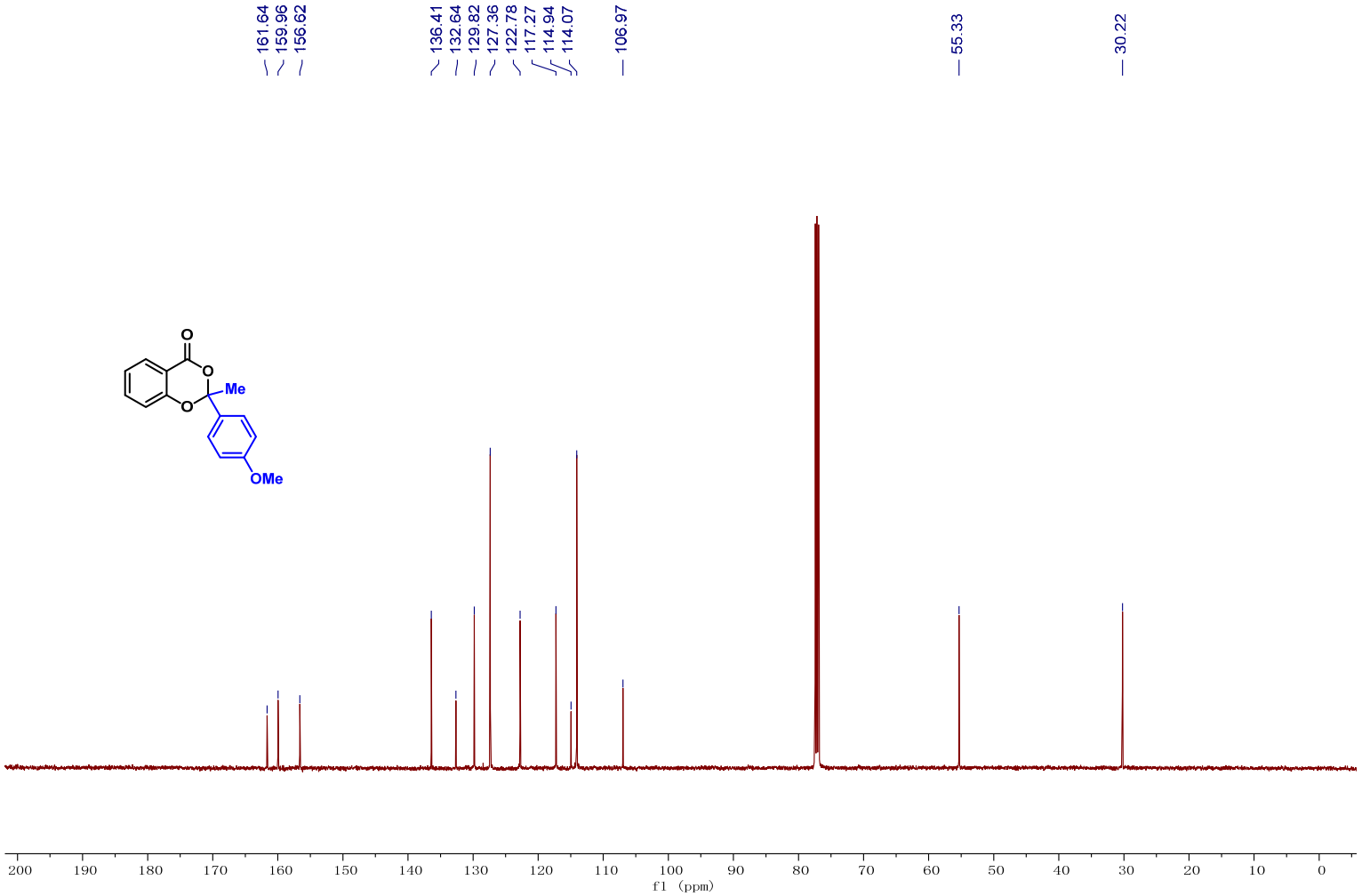
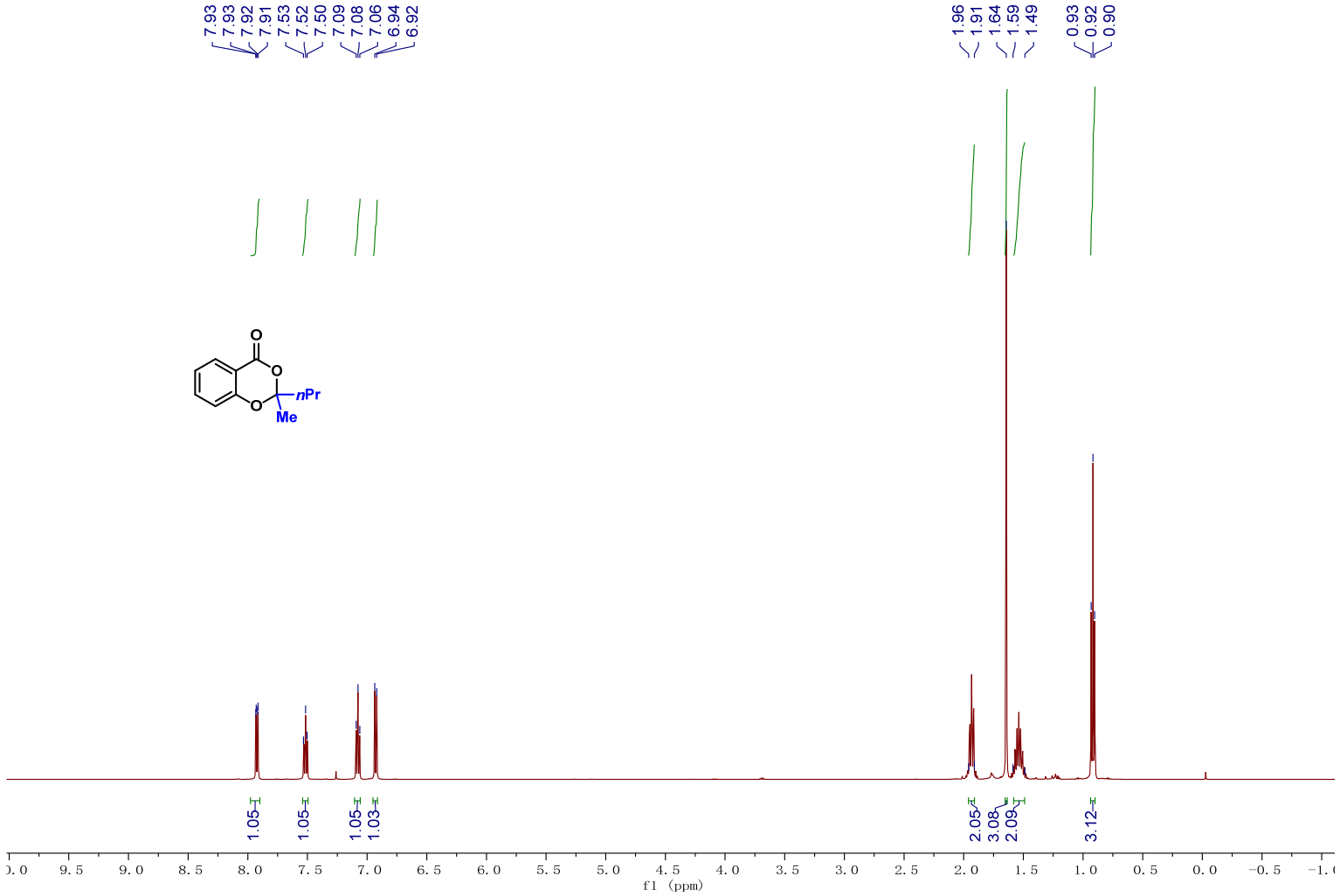
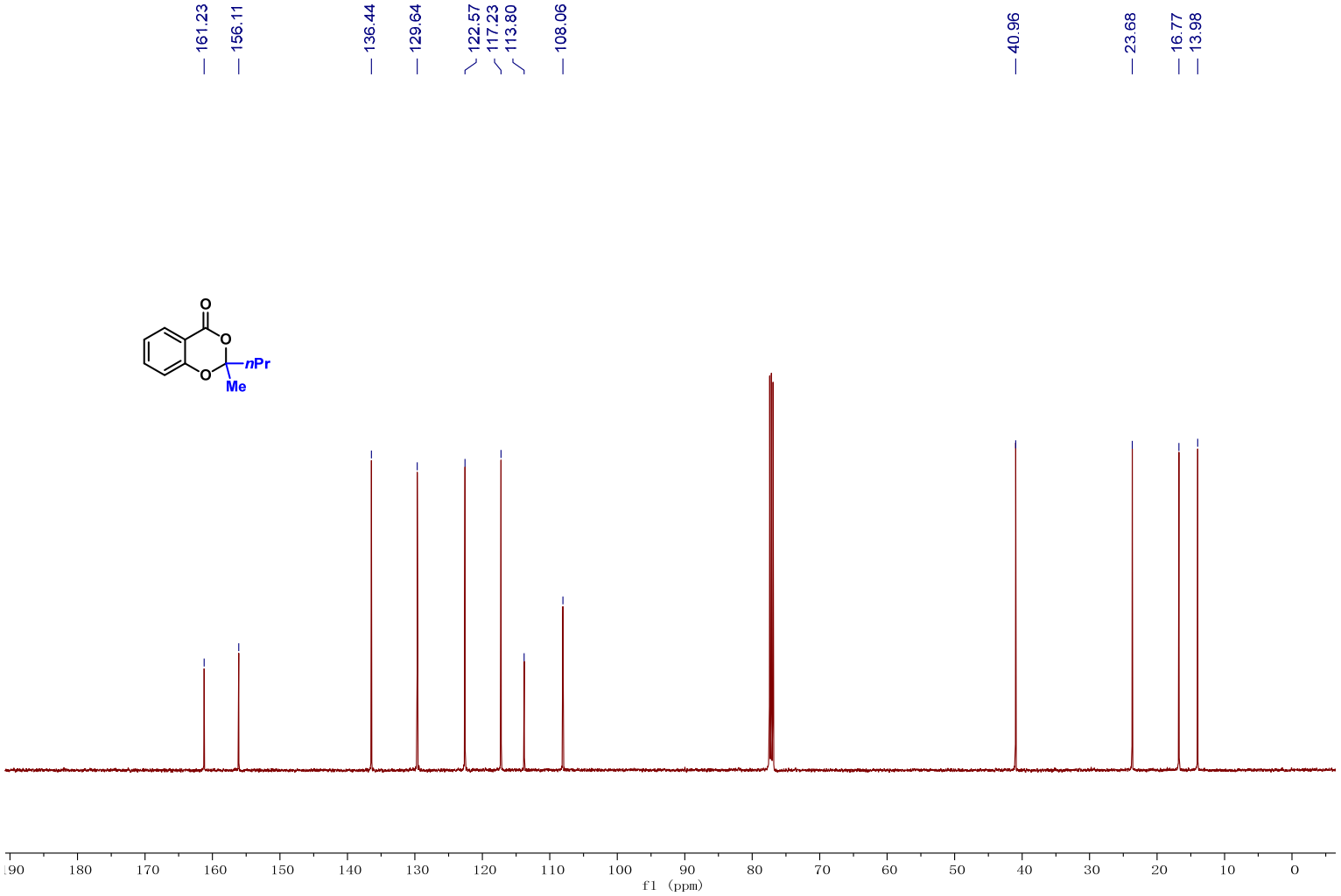


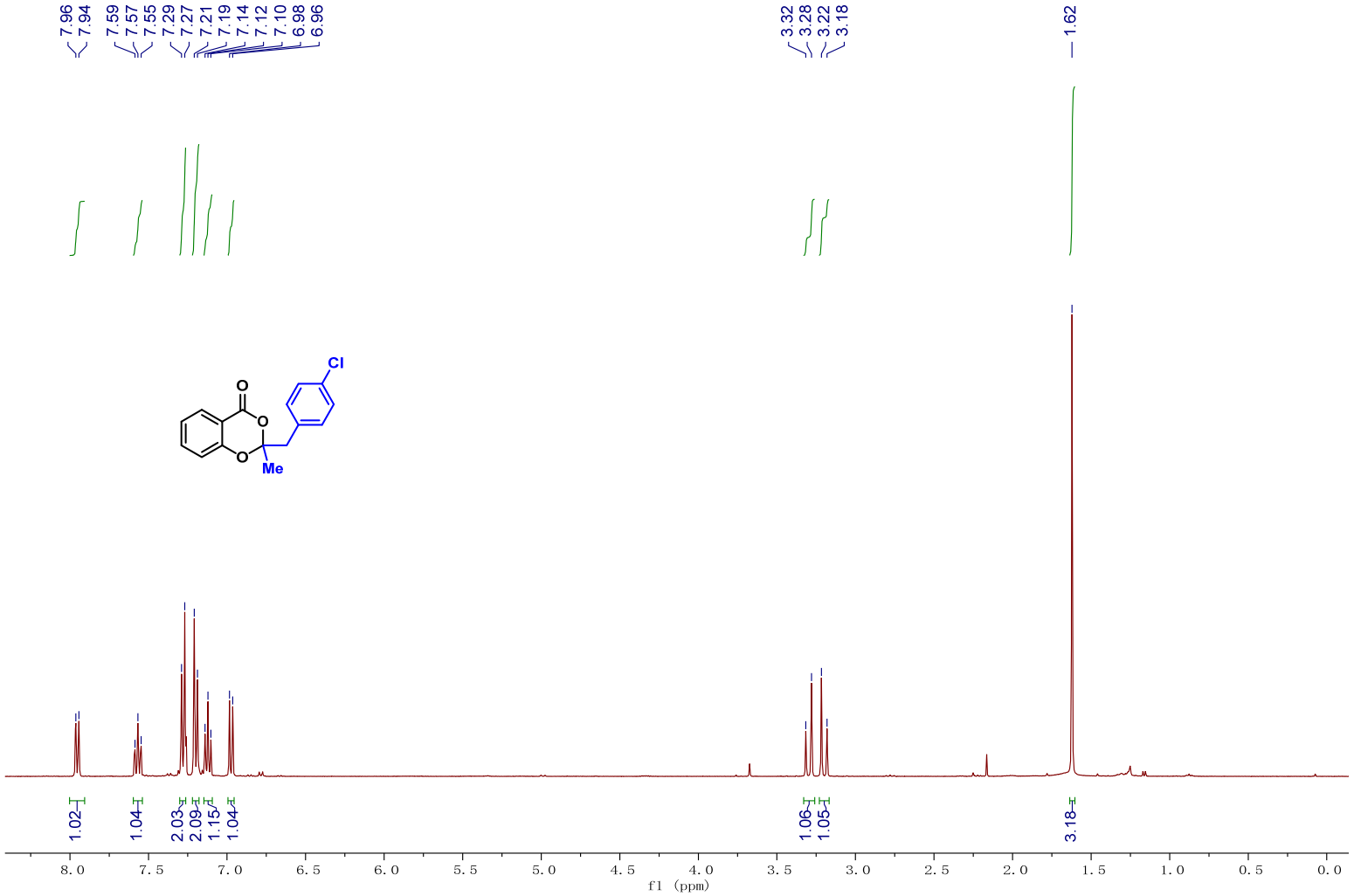
Compound 18-1 ^{1}H NMR



Compound 18-1 ^{13}C NMR



Compound 18-2 ^{1}H NMR



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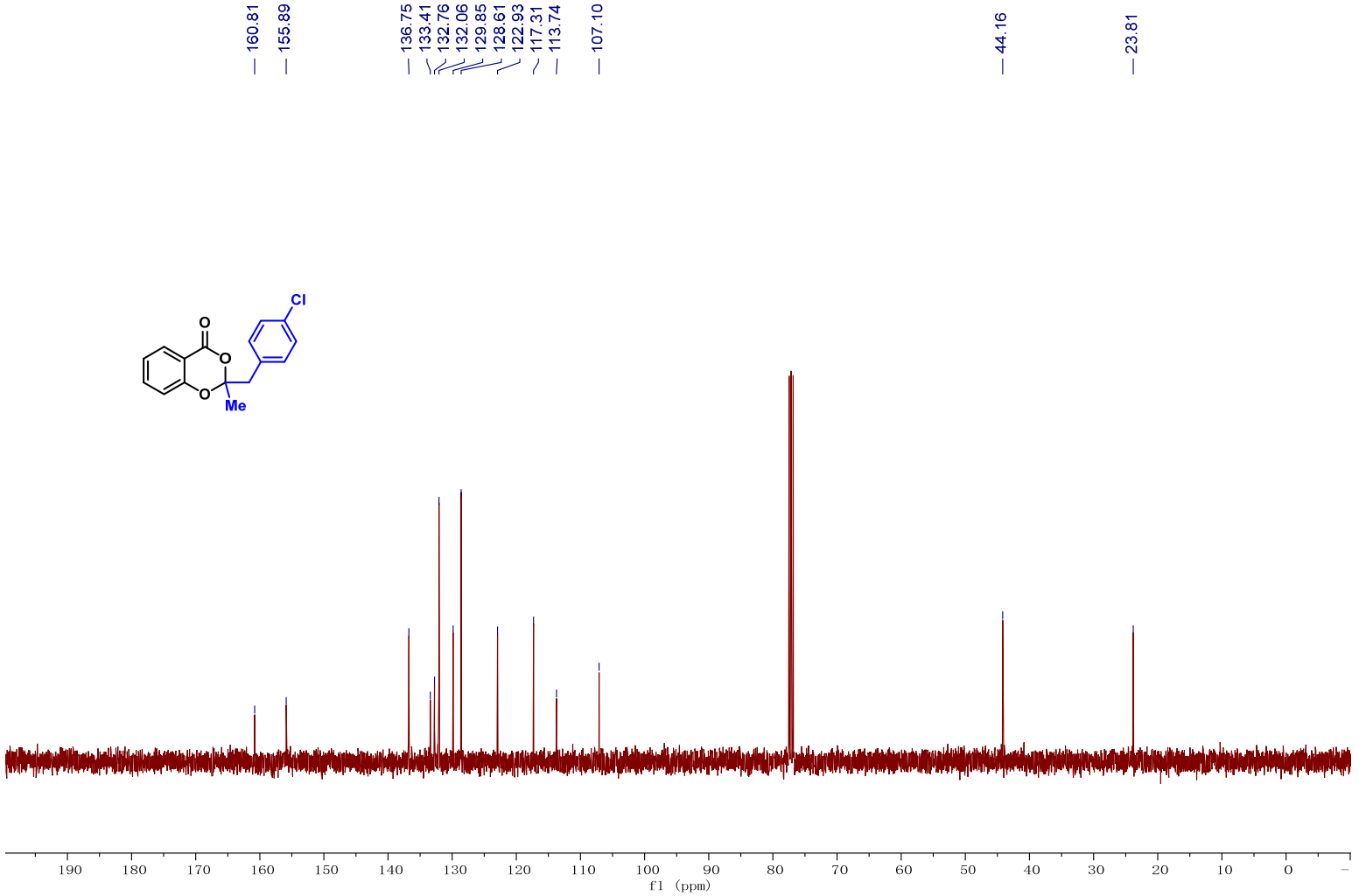
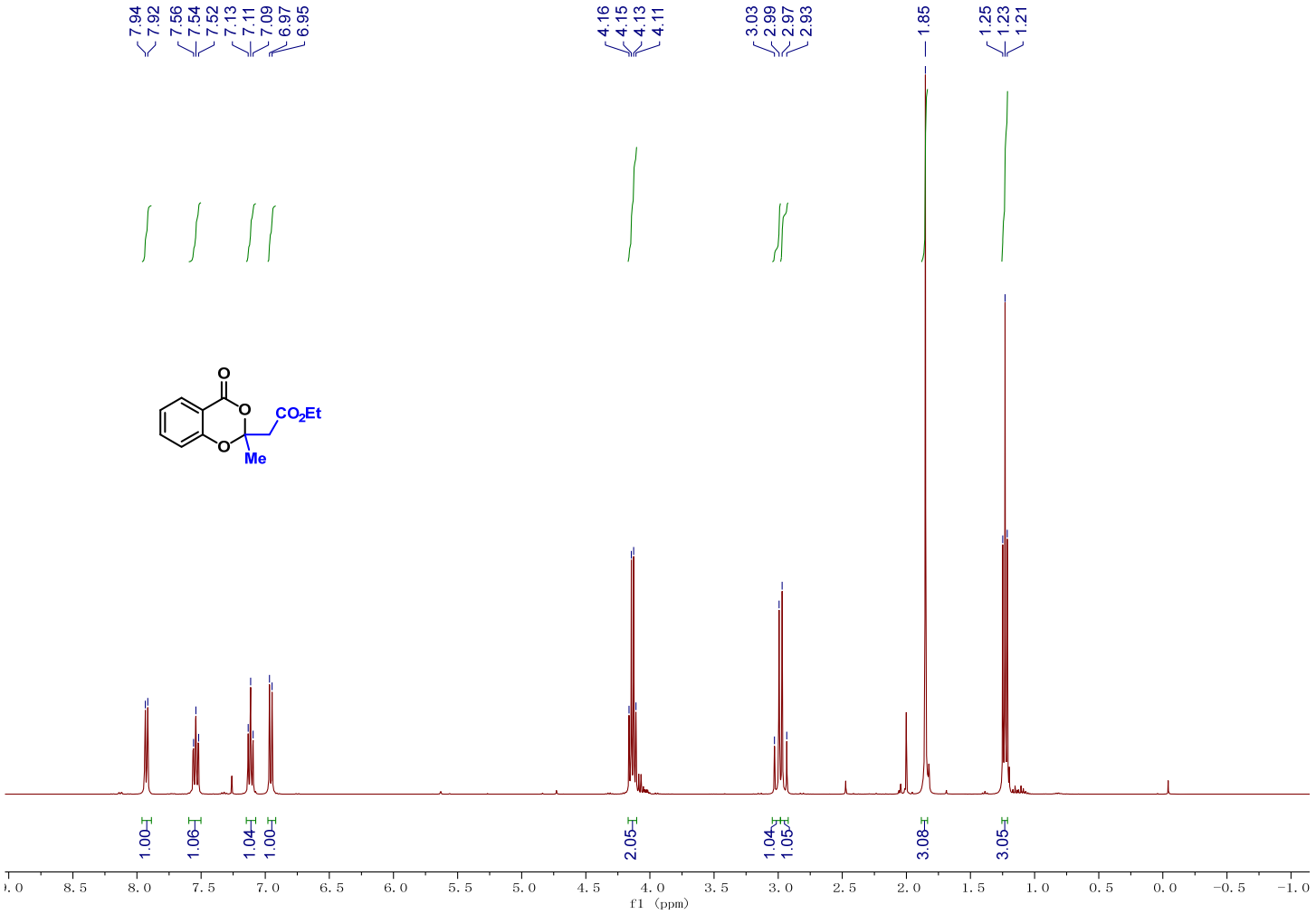
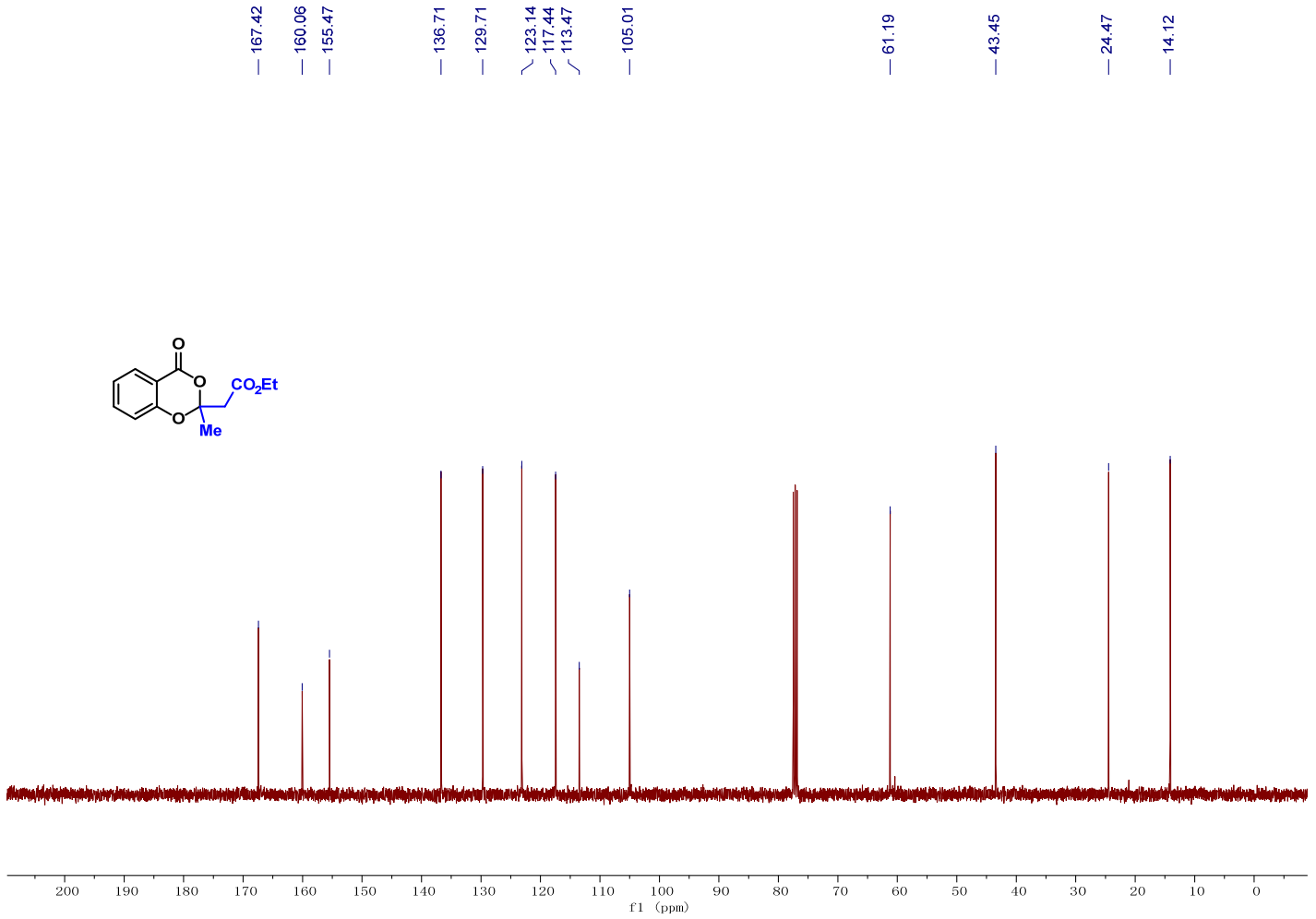


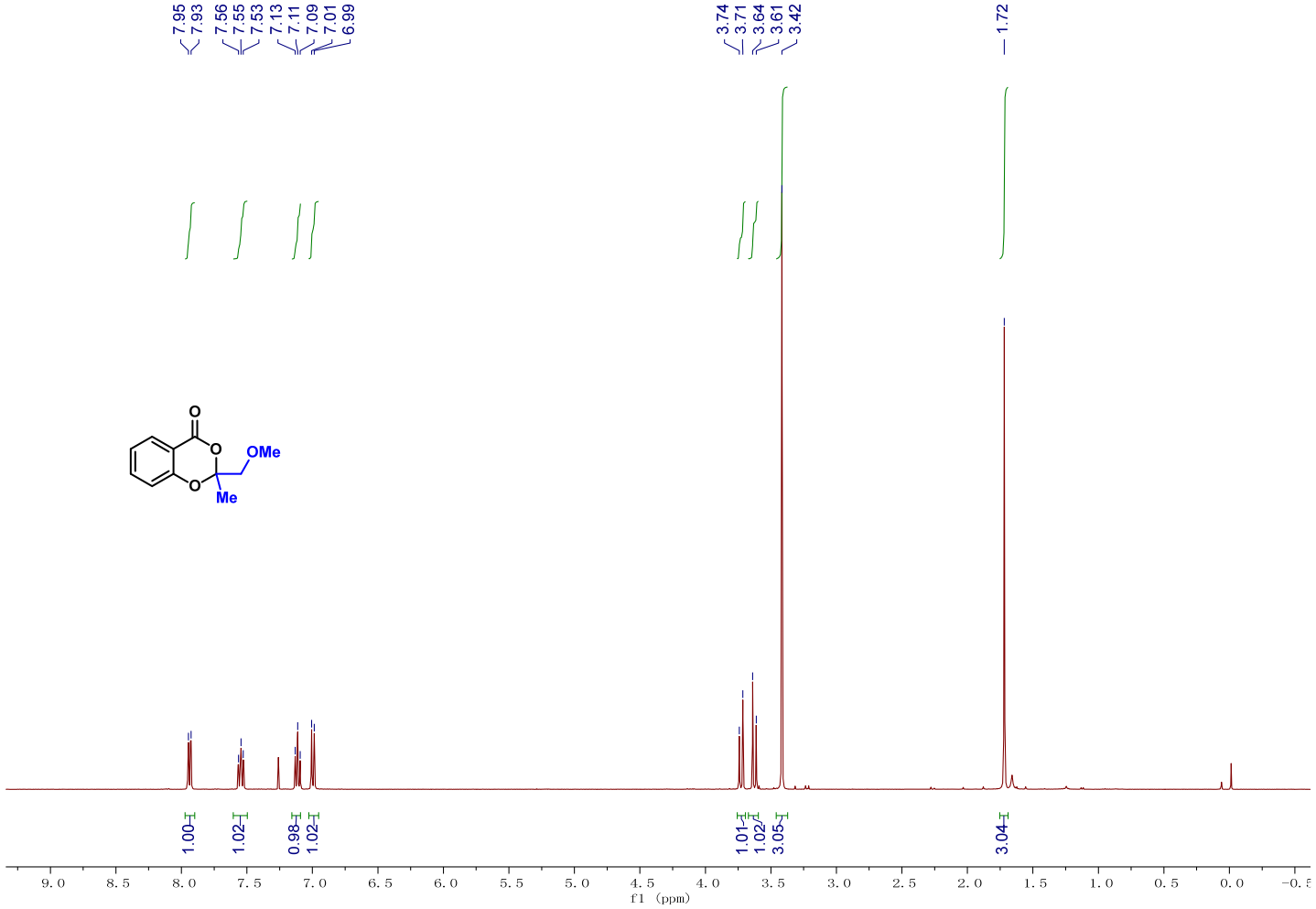
Compound 18-3 ^{1}H NMR



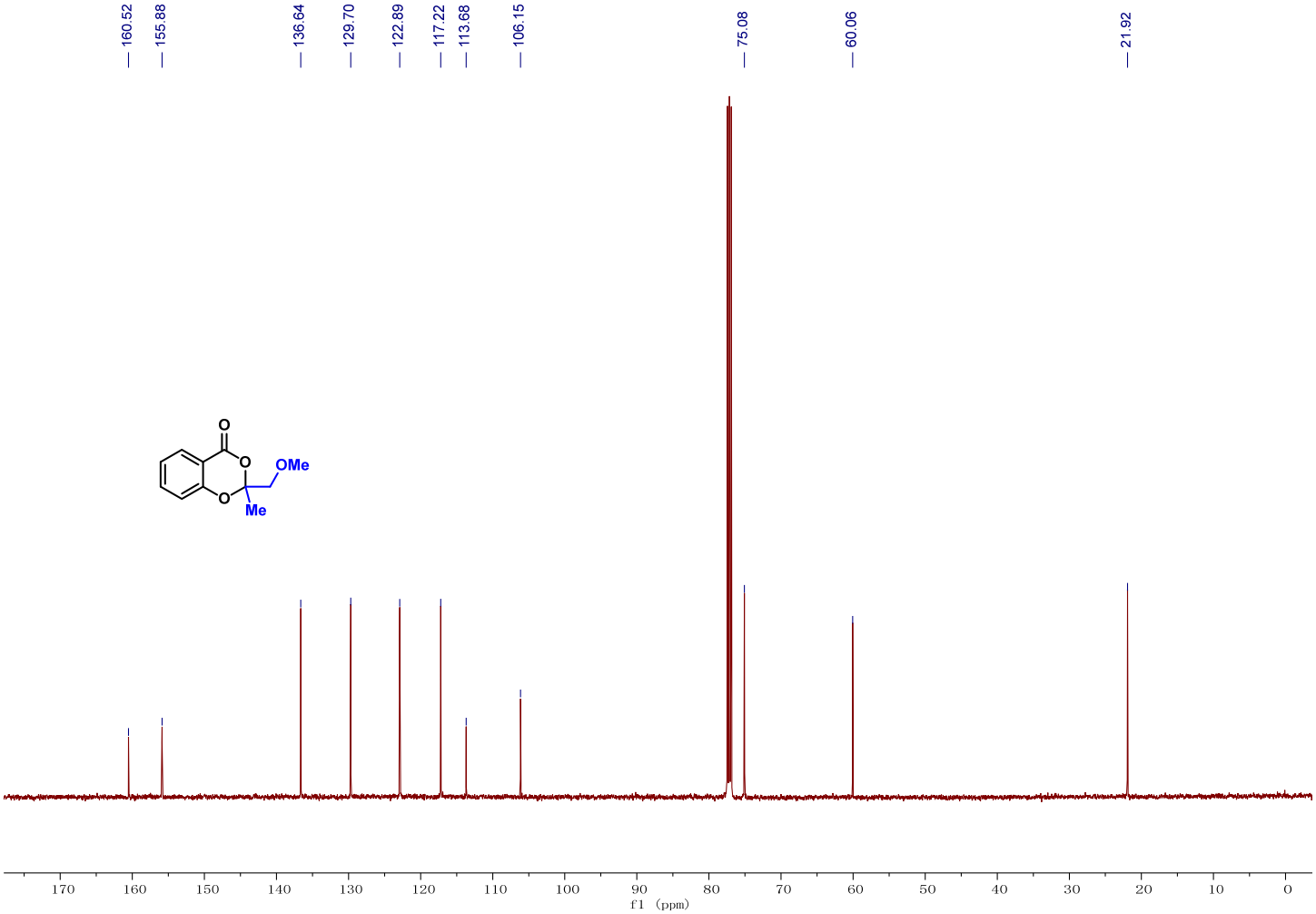
Compound 18-3 ^{13}C NMR



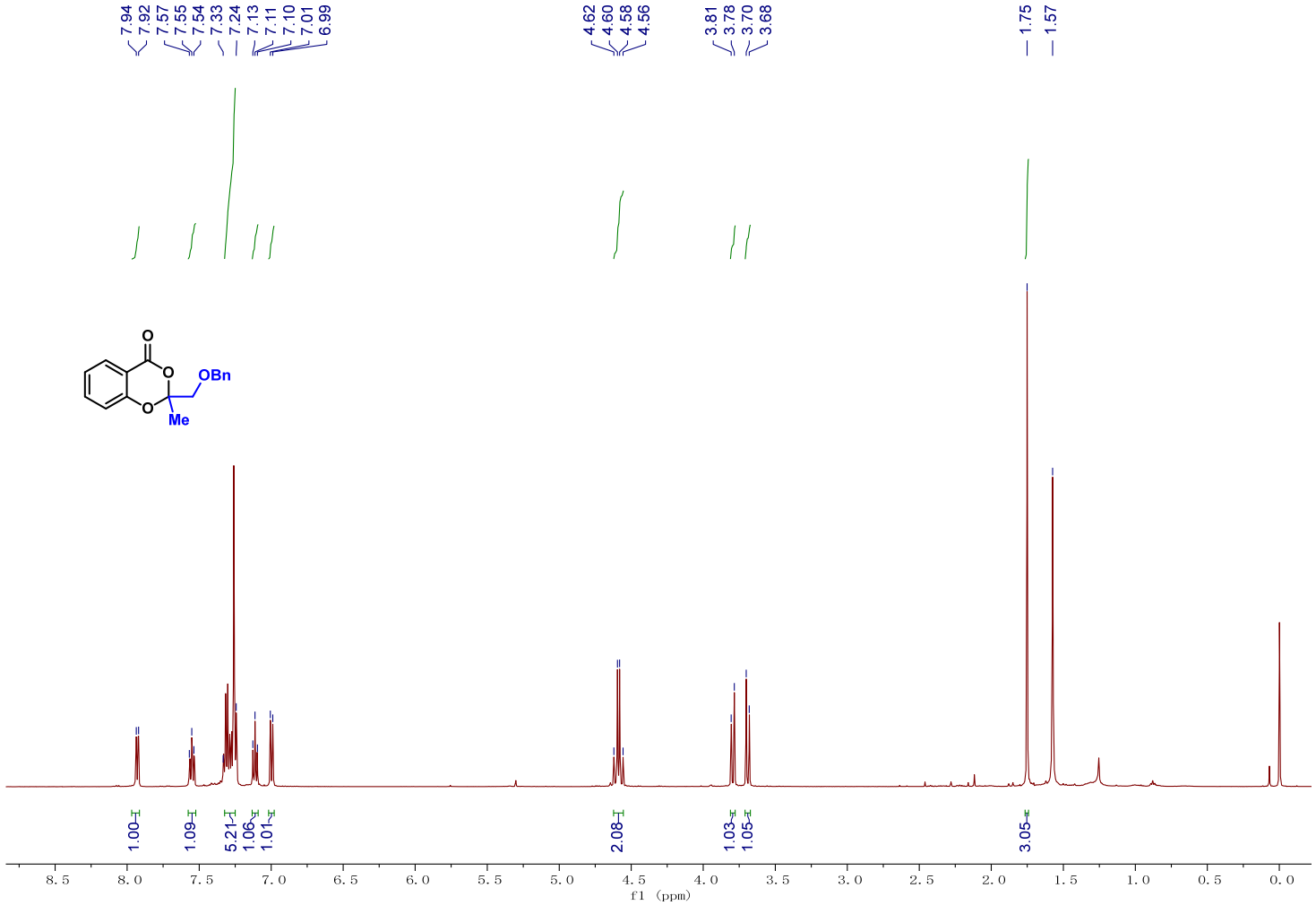
Compound 18-4 ^{1}H NMR



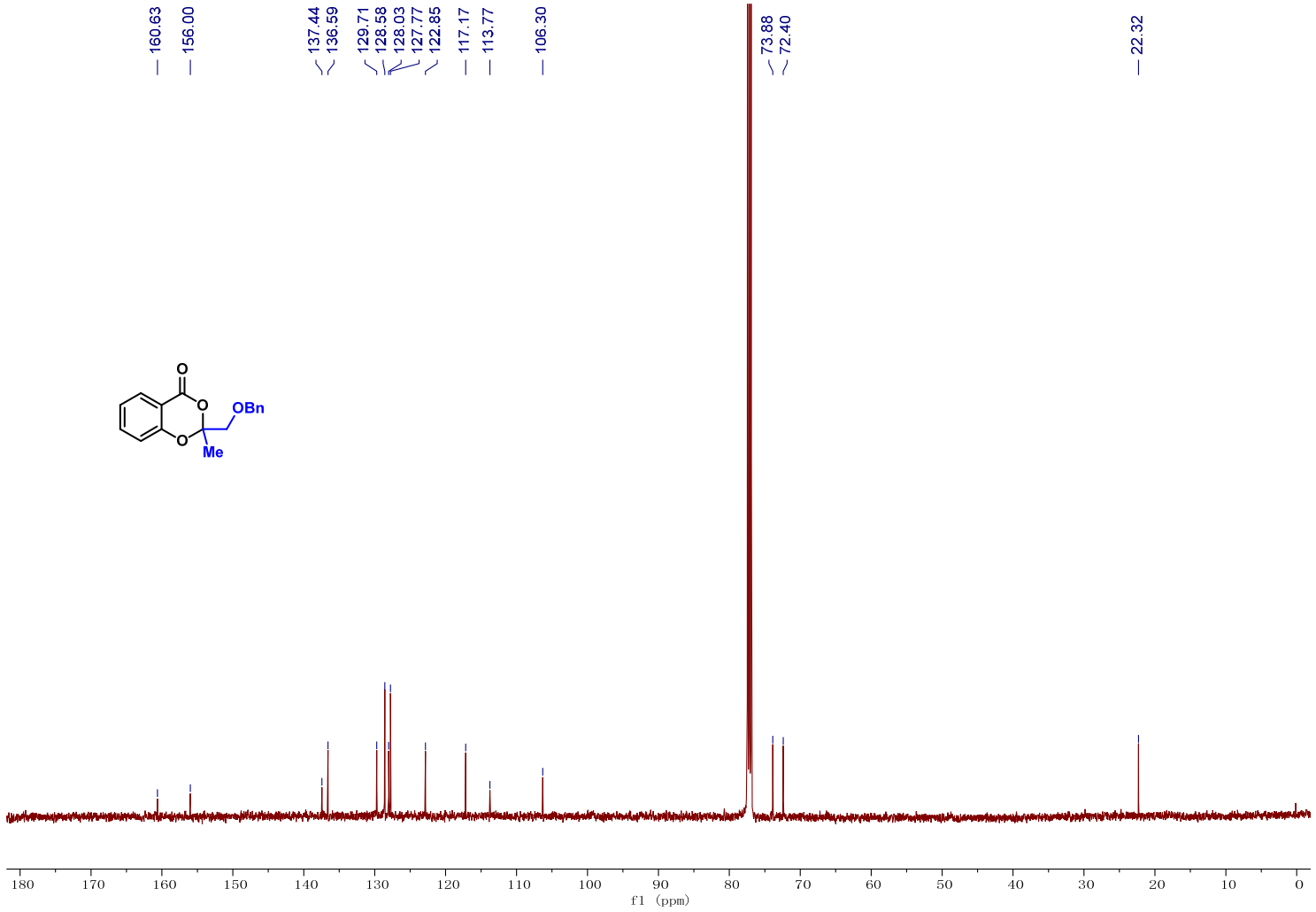
Compound 18-4 ^{13}C NMR



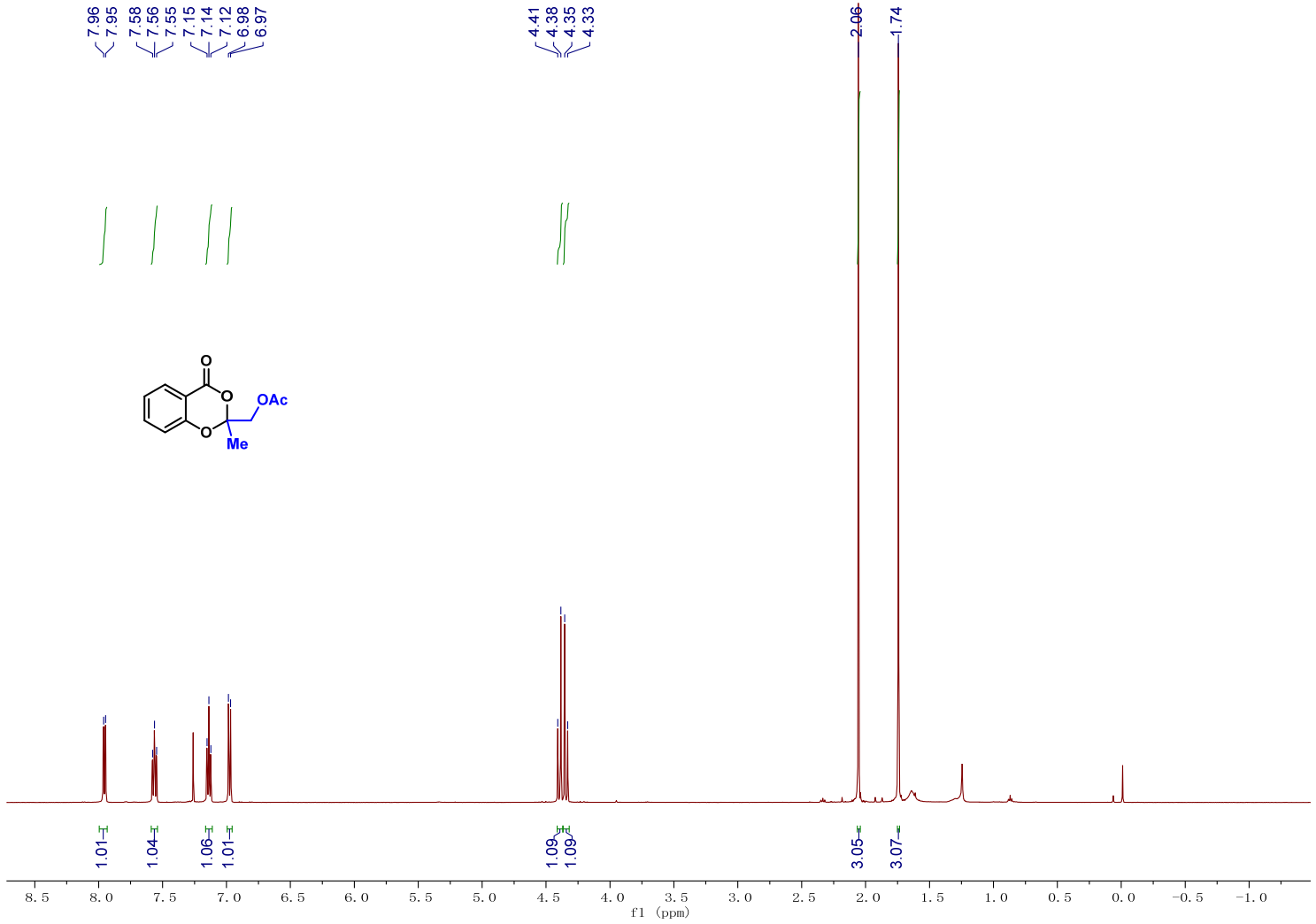
Compound 18-5 ^{1}H NMR



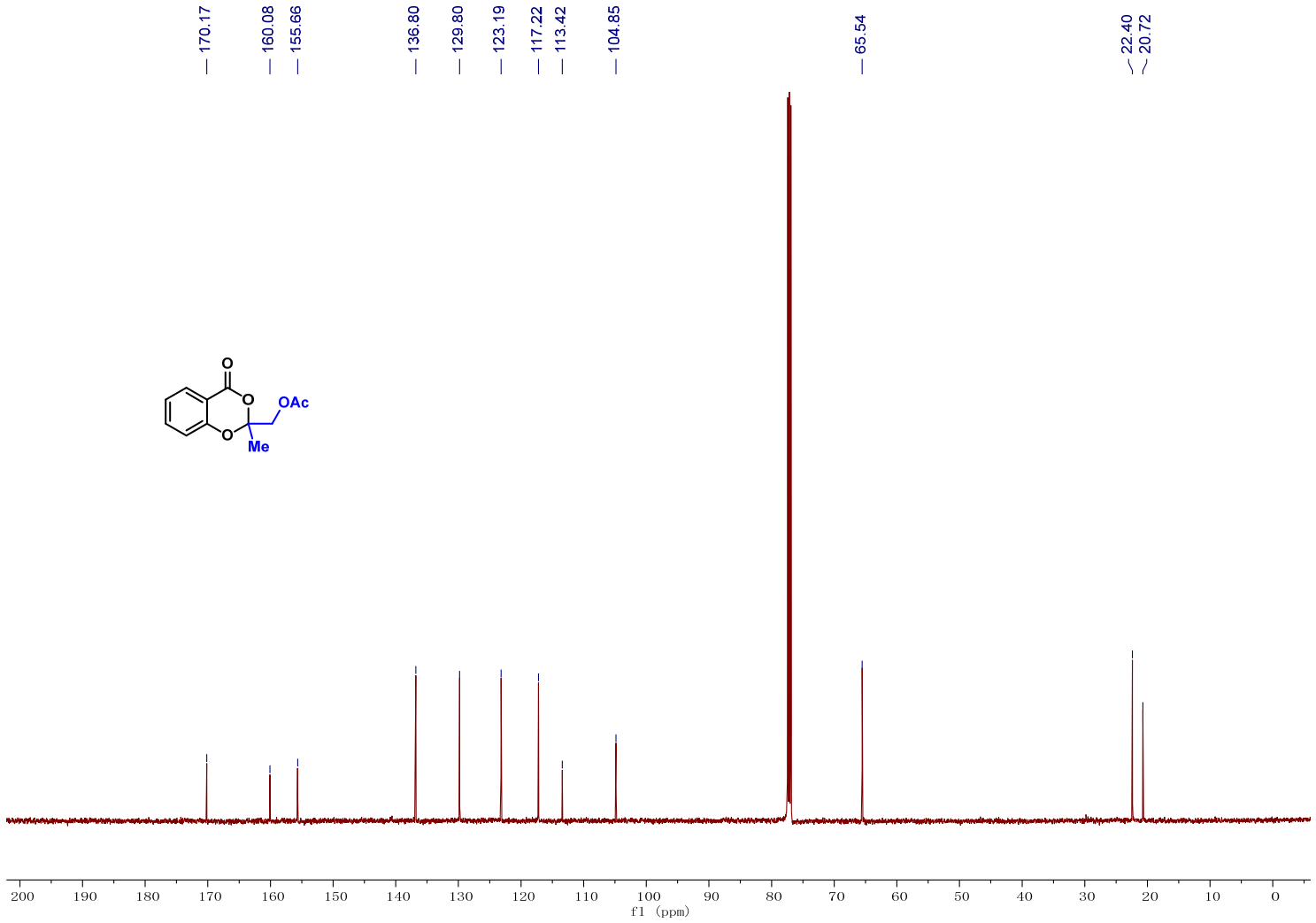
Compound 18-5 ^{13}C NMR



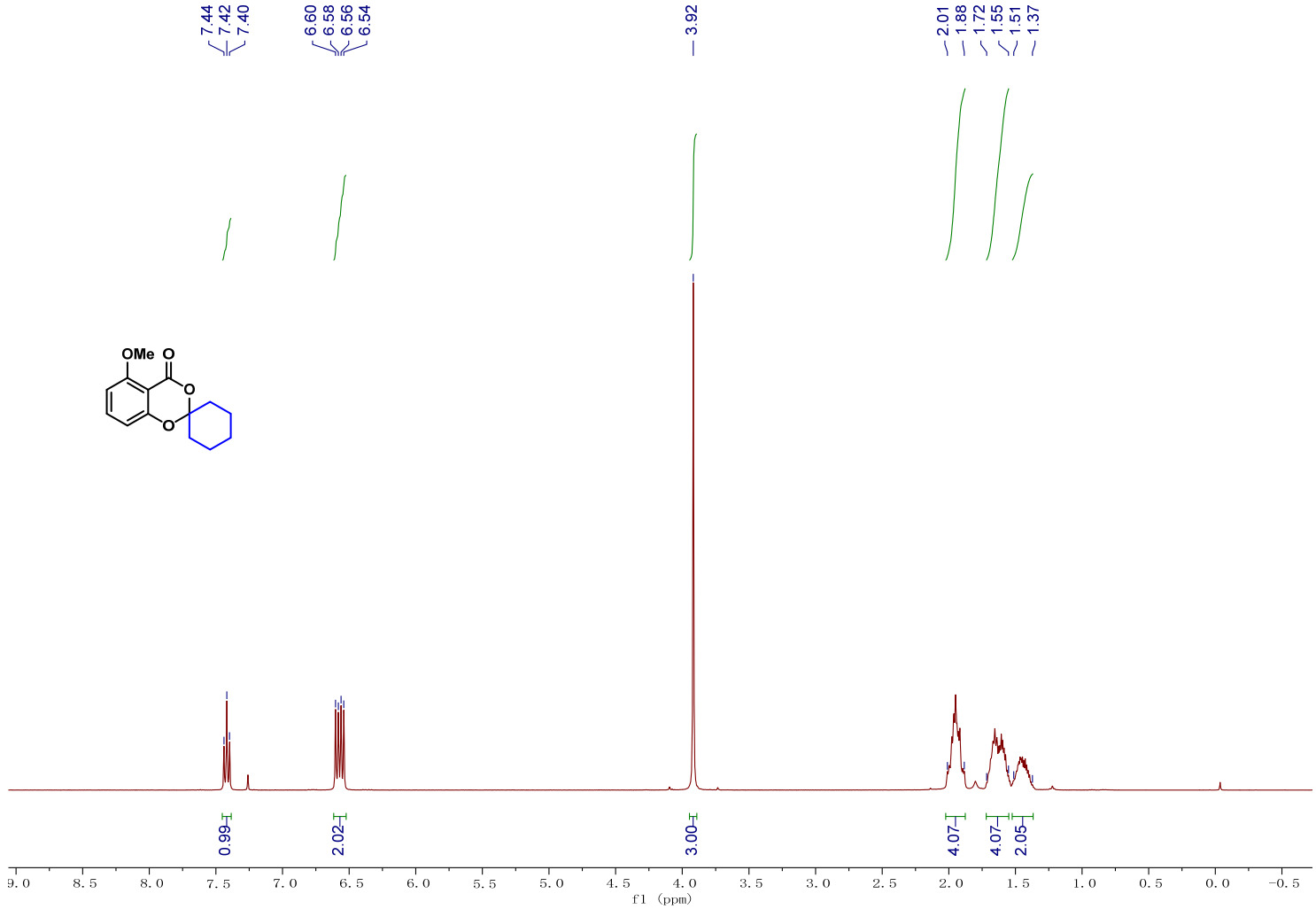
Compound 18-6 ^{1}H NMR



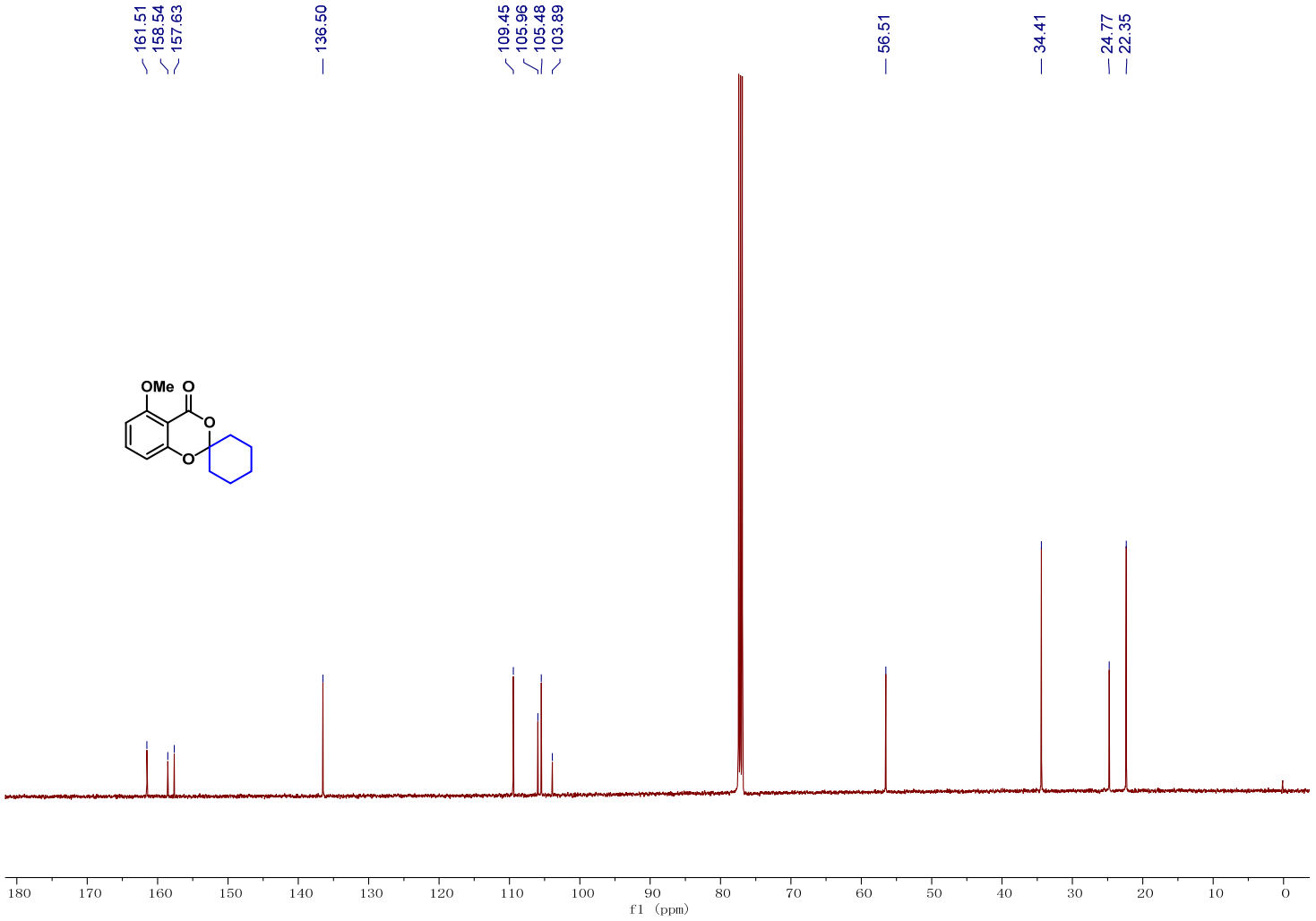
Compound 18-6 ^{13}C NMR



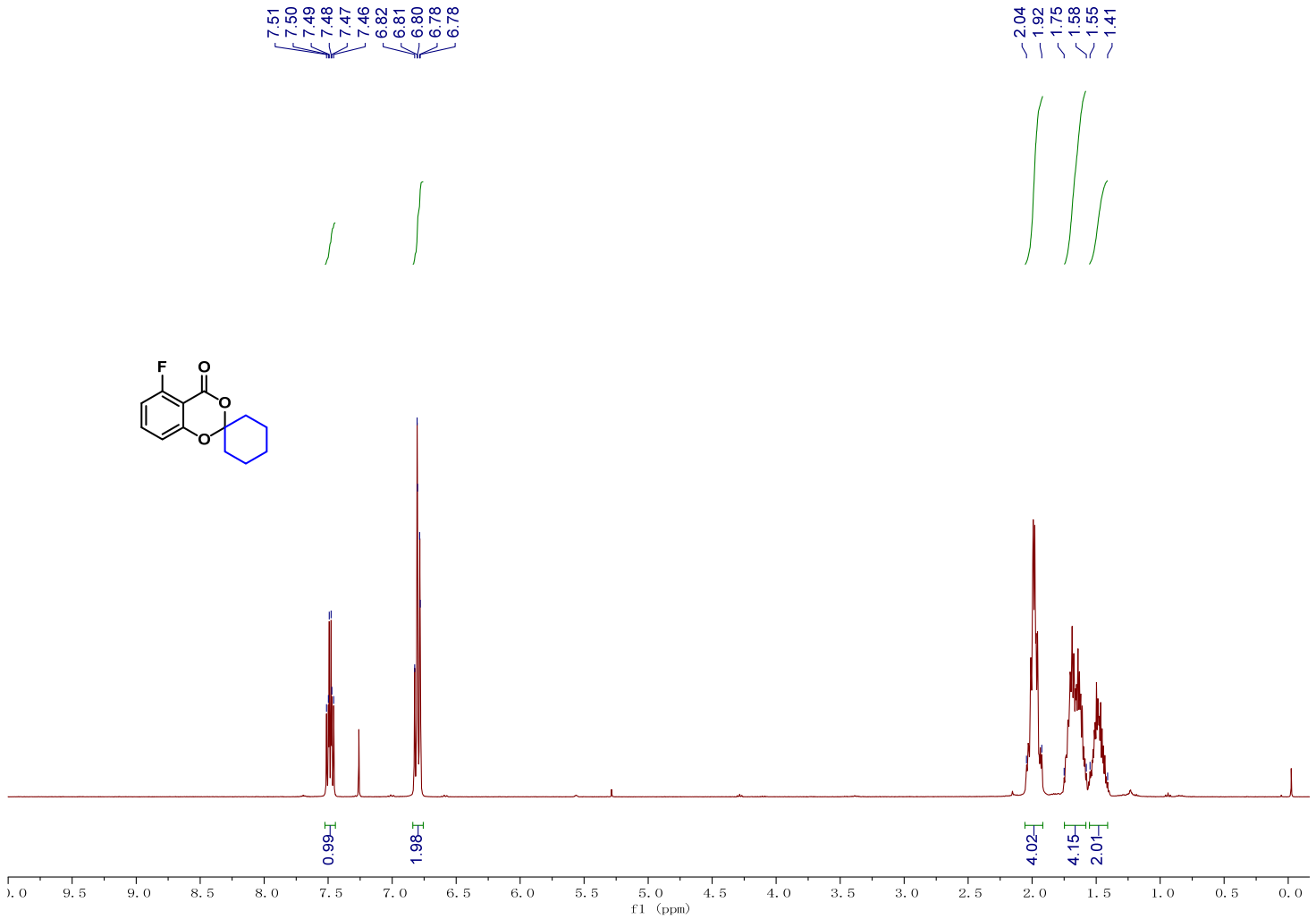
Compound S11 ^{1}H NMR



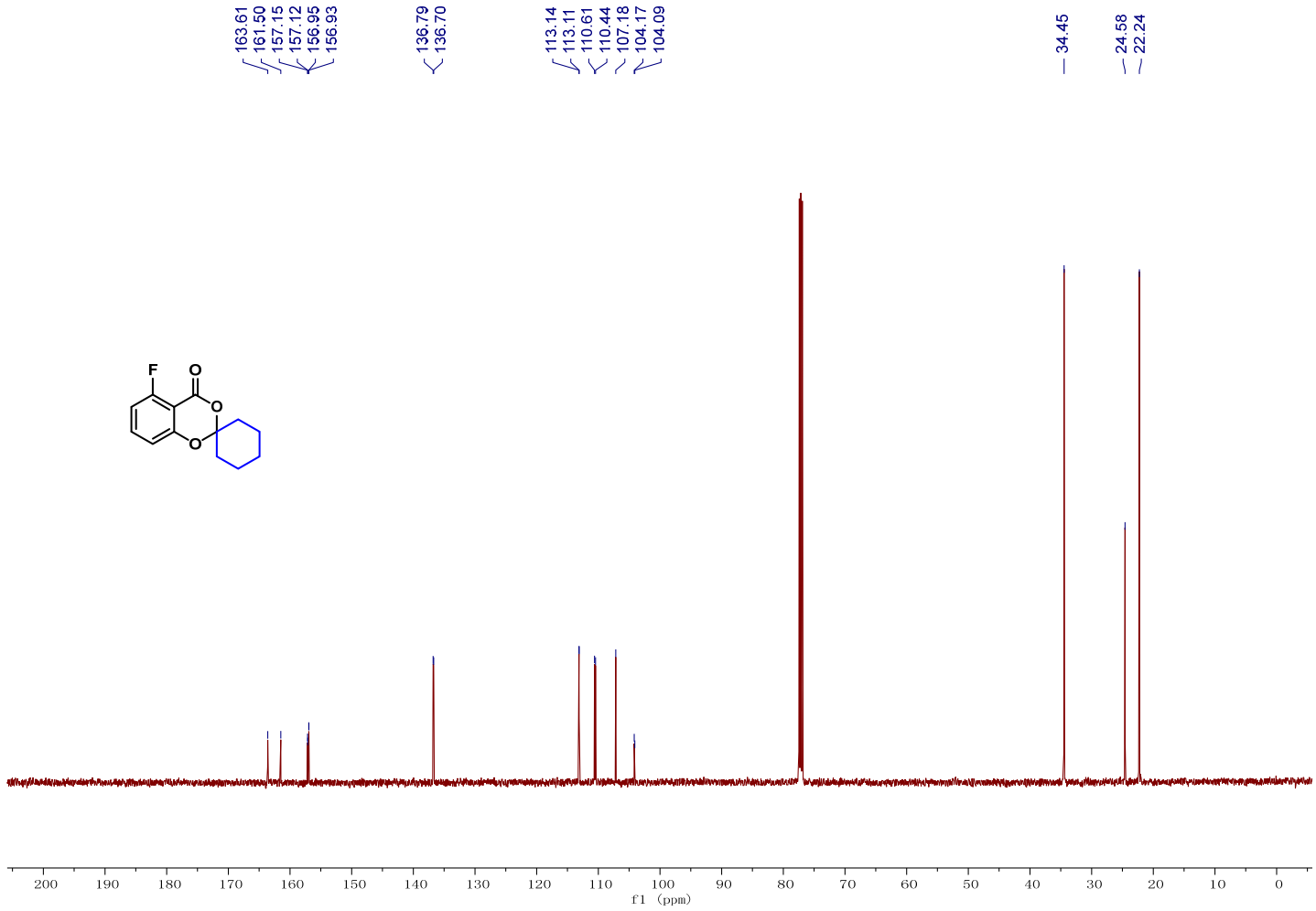
Compound S11 ^{13}C NMR



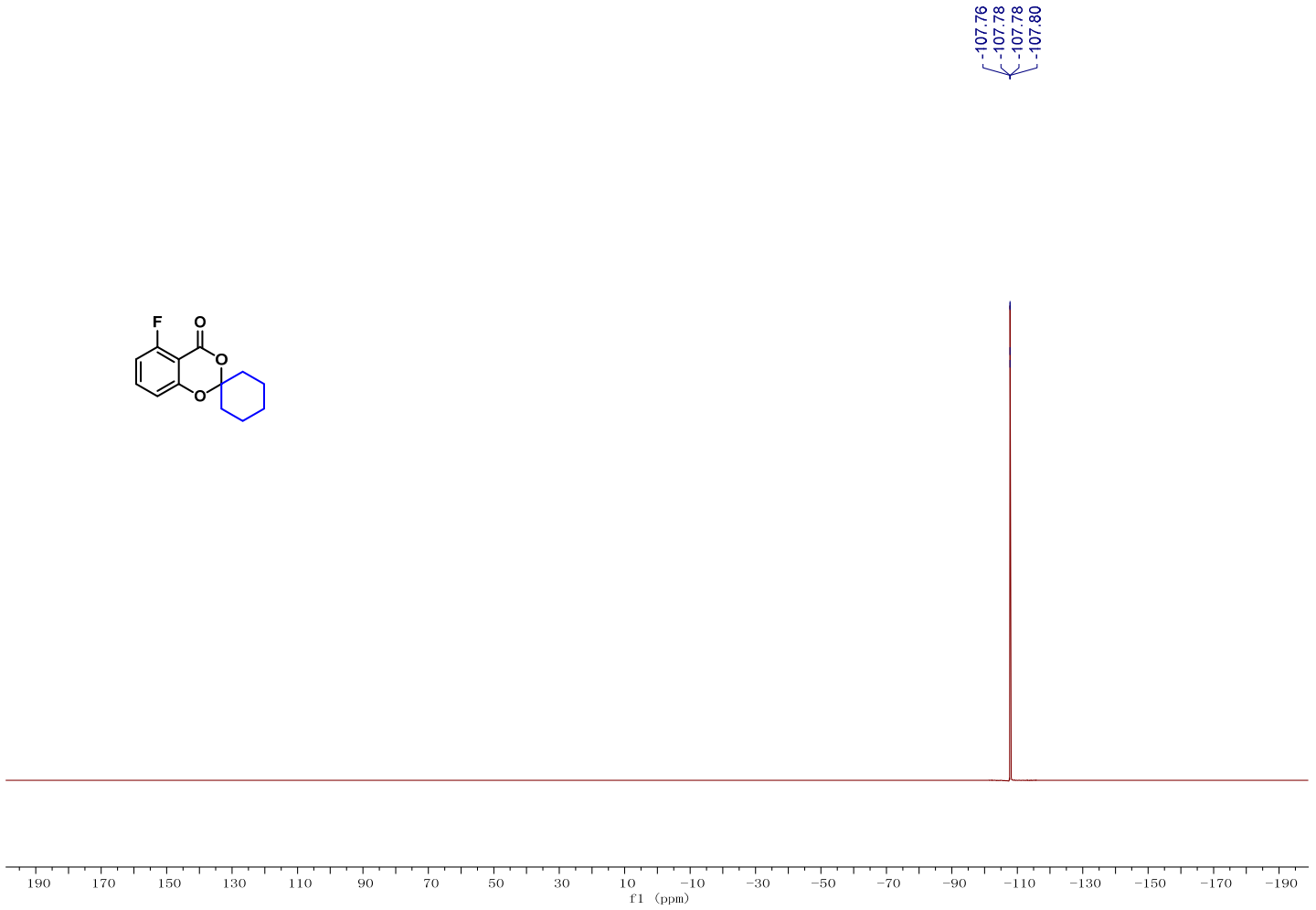
Compound S12 ^{1}H NMR



Compound S12 ^{13}C NMR



Compound S12 ^{19}F NMR



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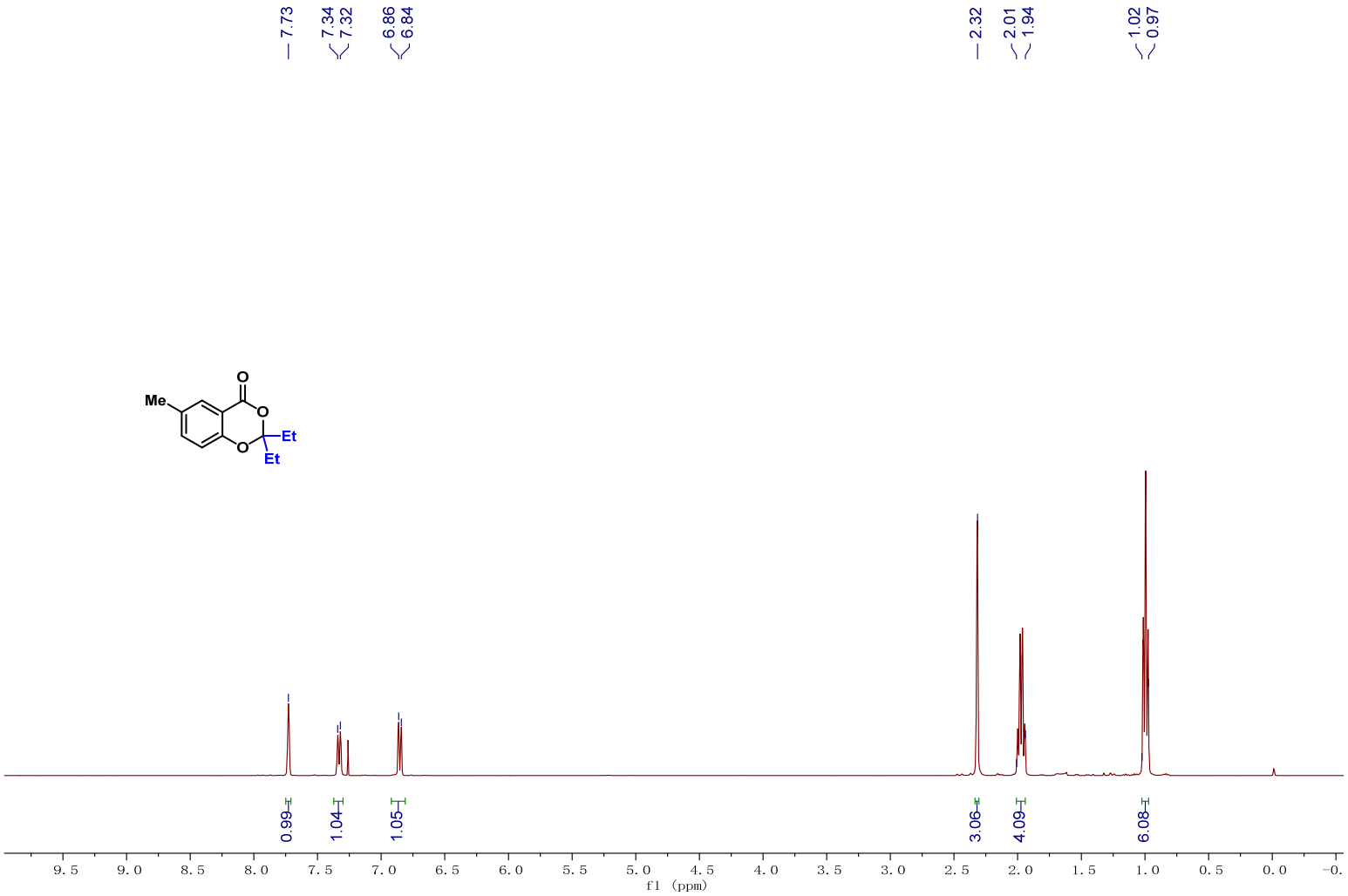
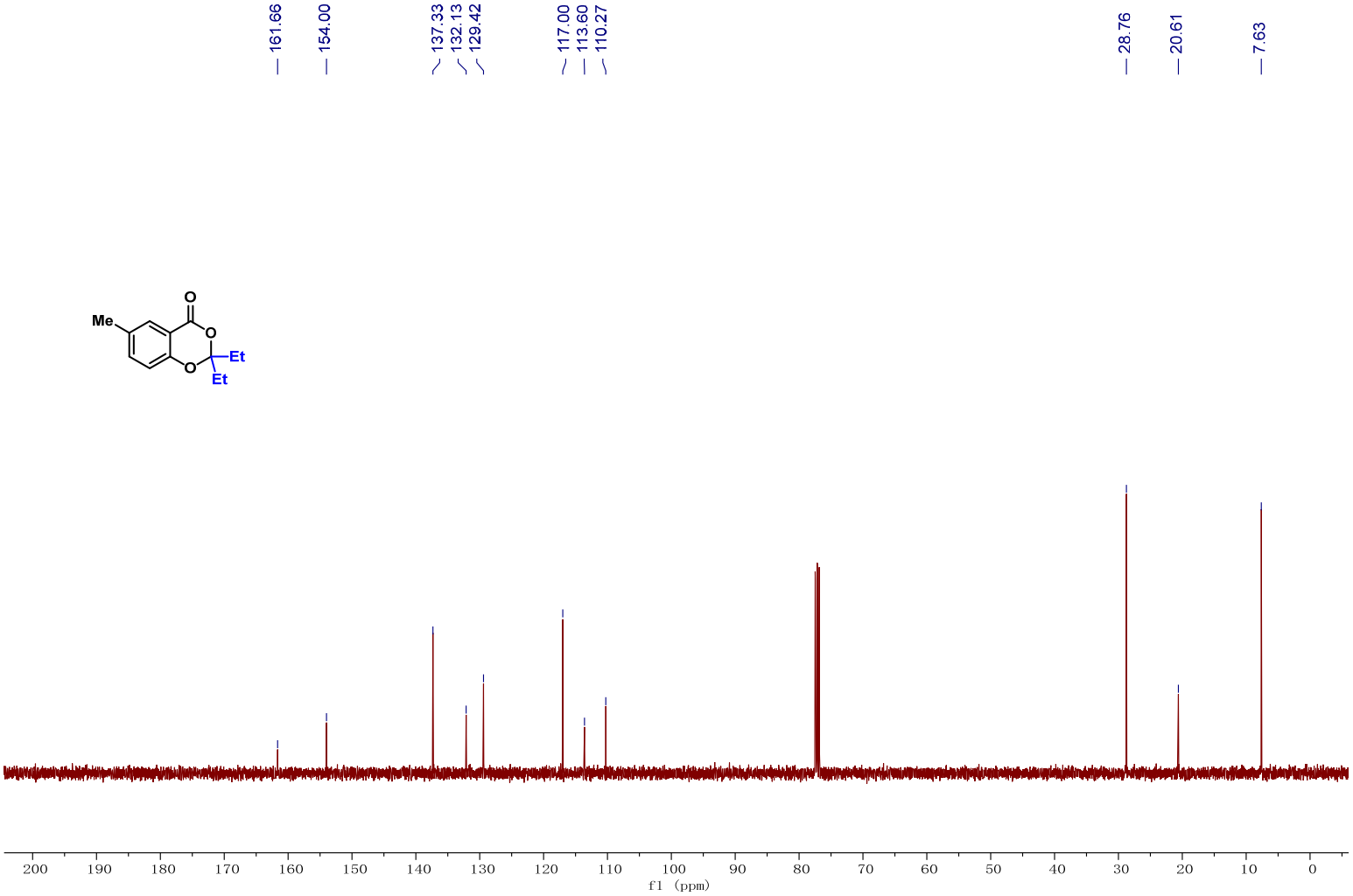
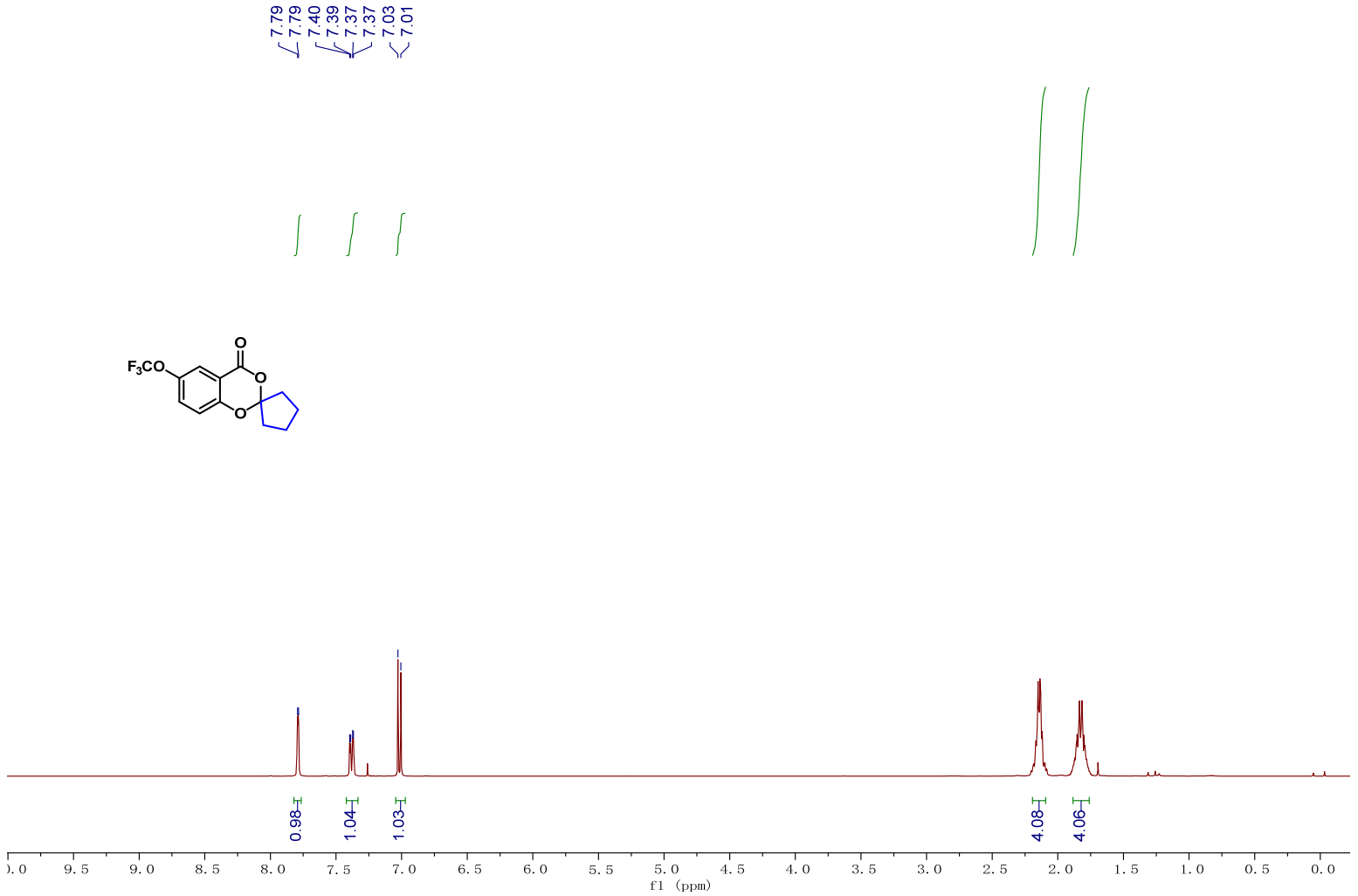


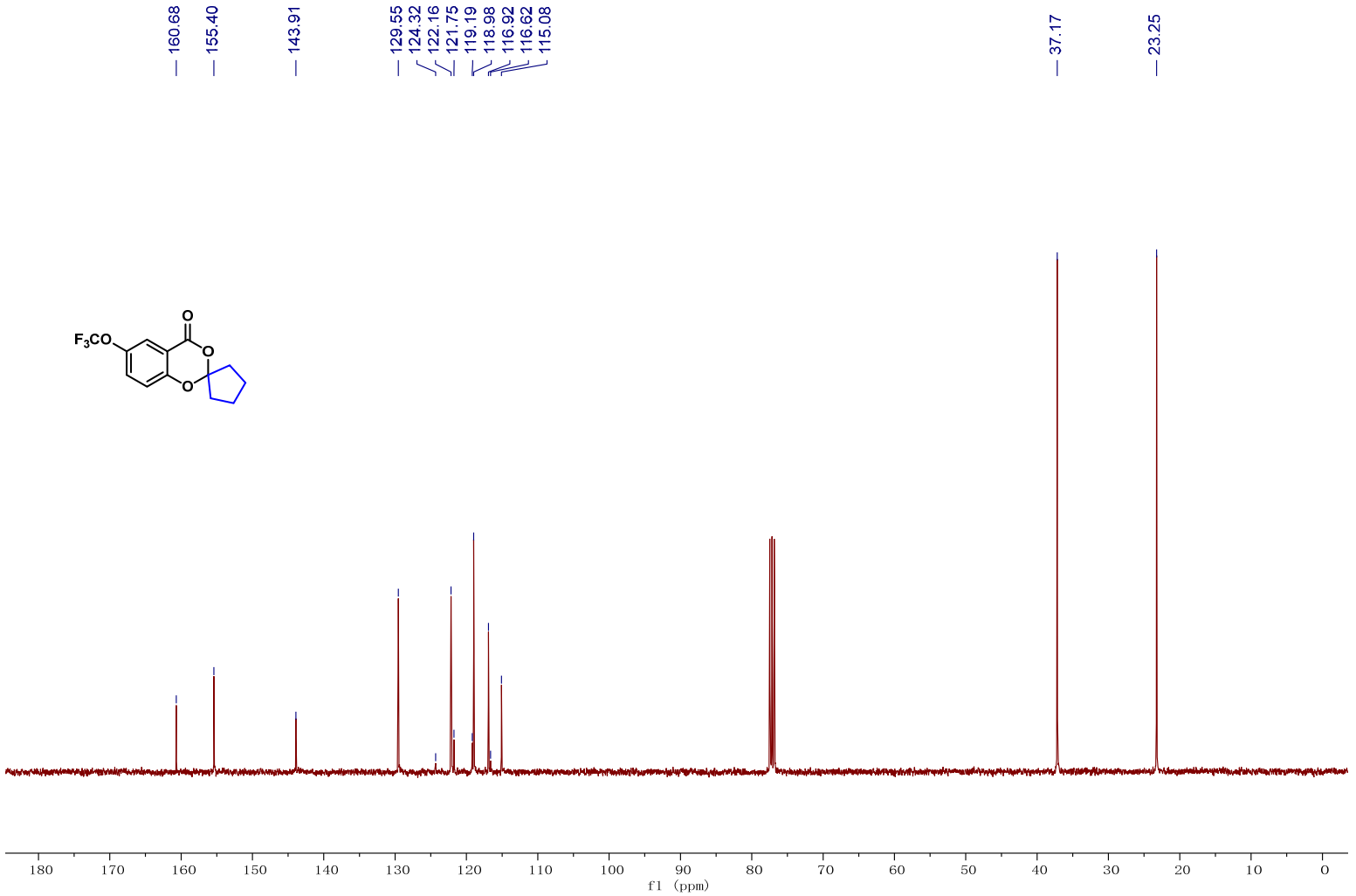
Compound S13 ^{13}C NMR



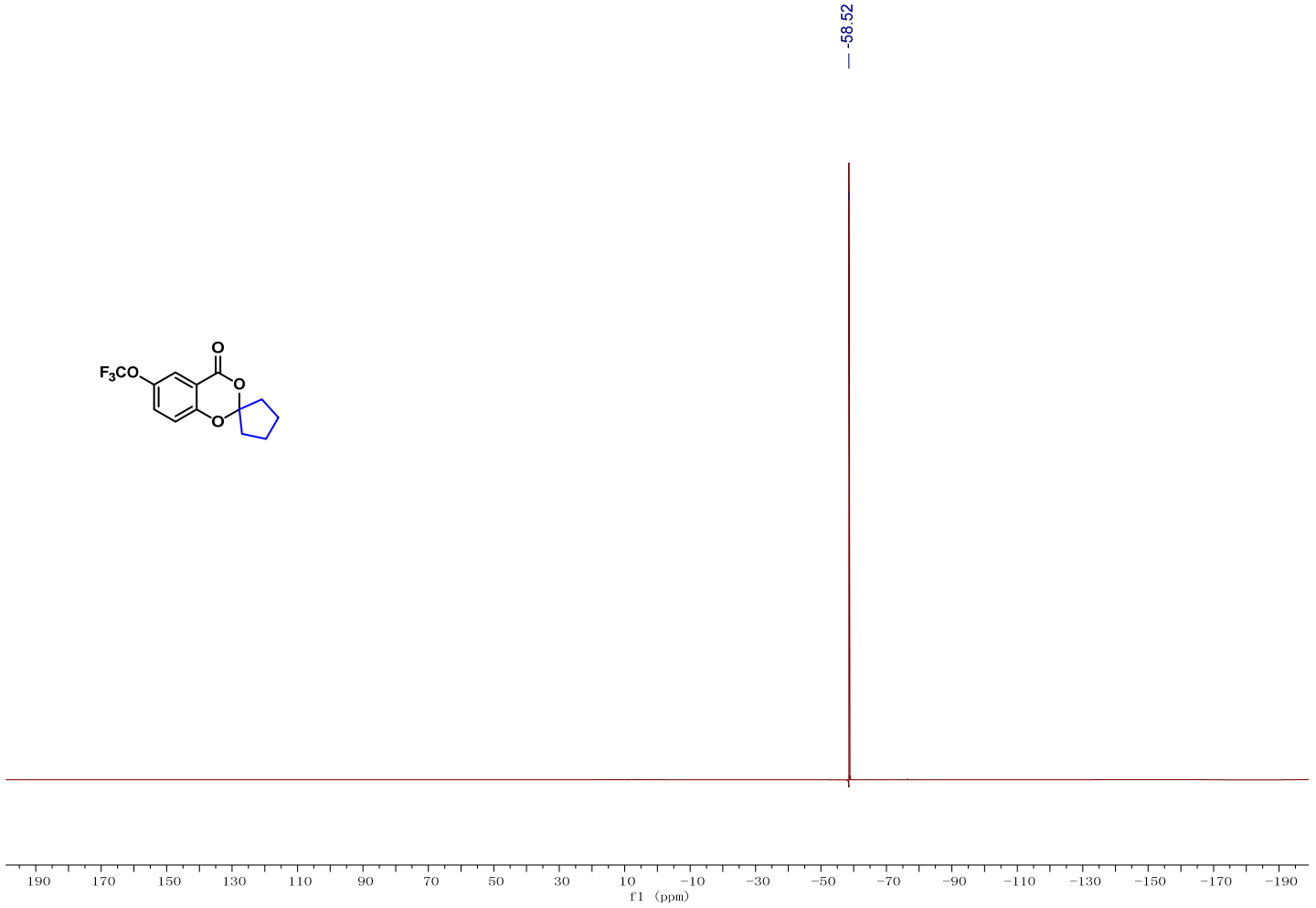
Compound S14 ^{1}H NMR



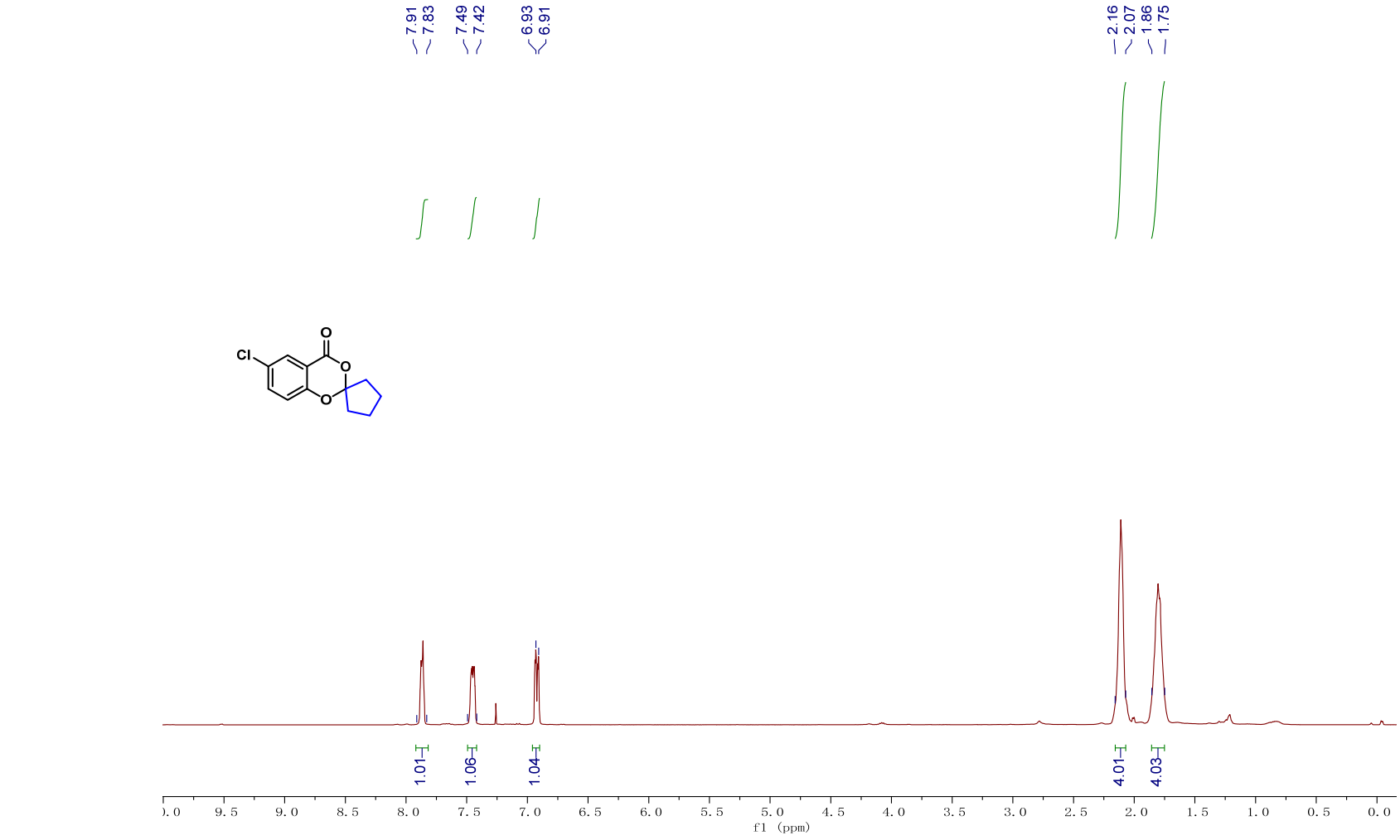
Compound S14 ^{13}C NMR



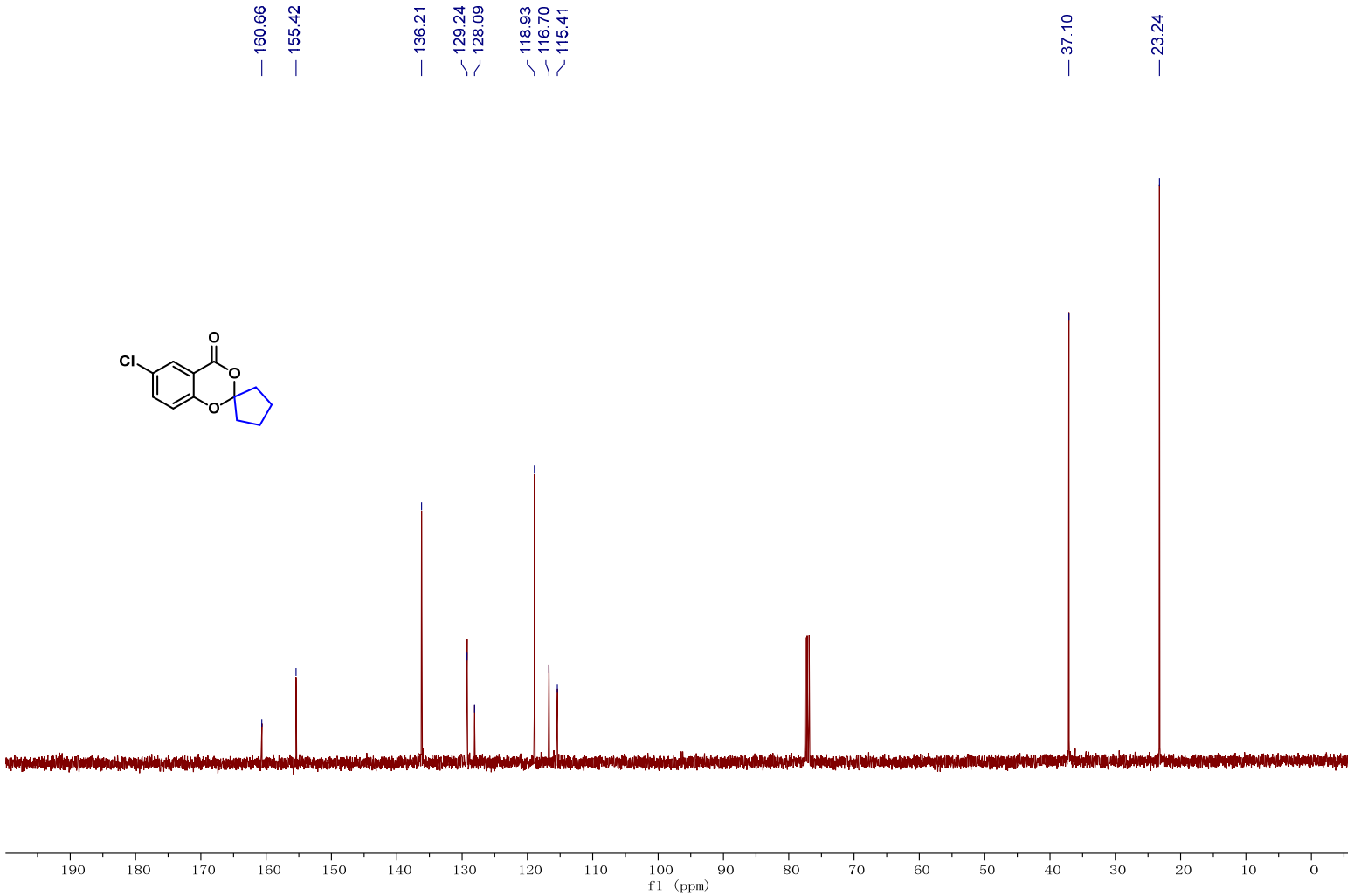
Compound S14 ^{19}F NMR



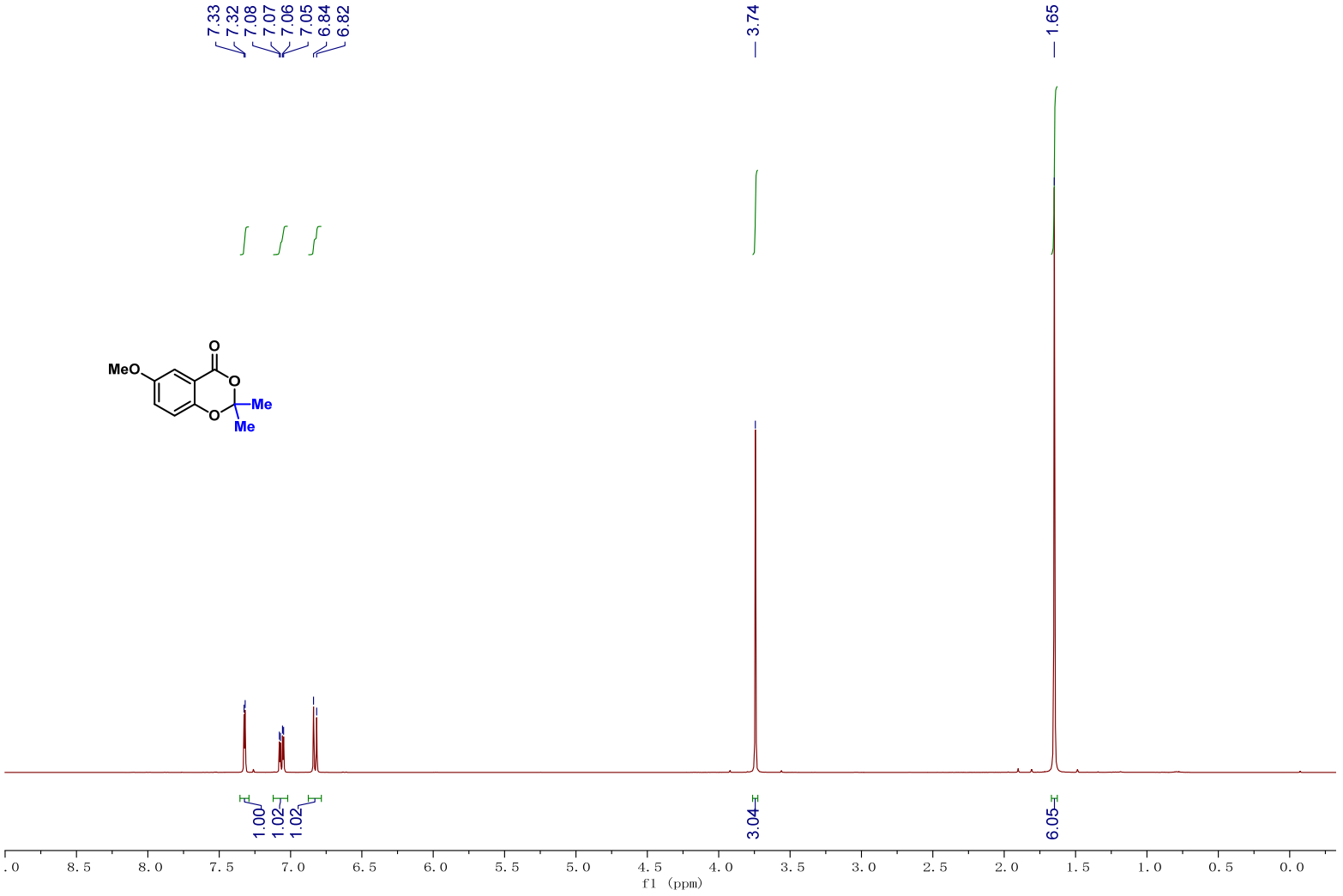
Compound S15 ^{1}H NMR



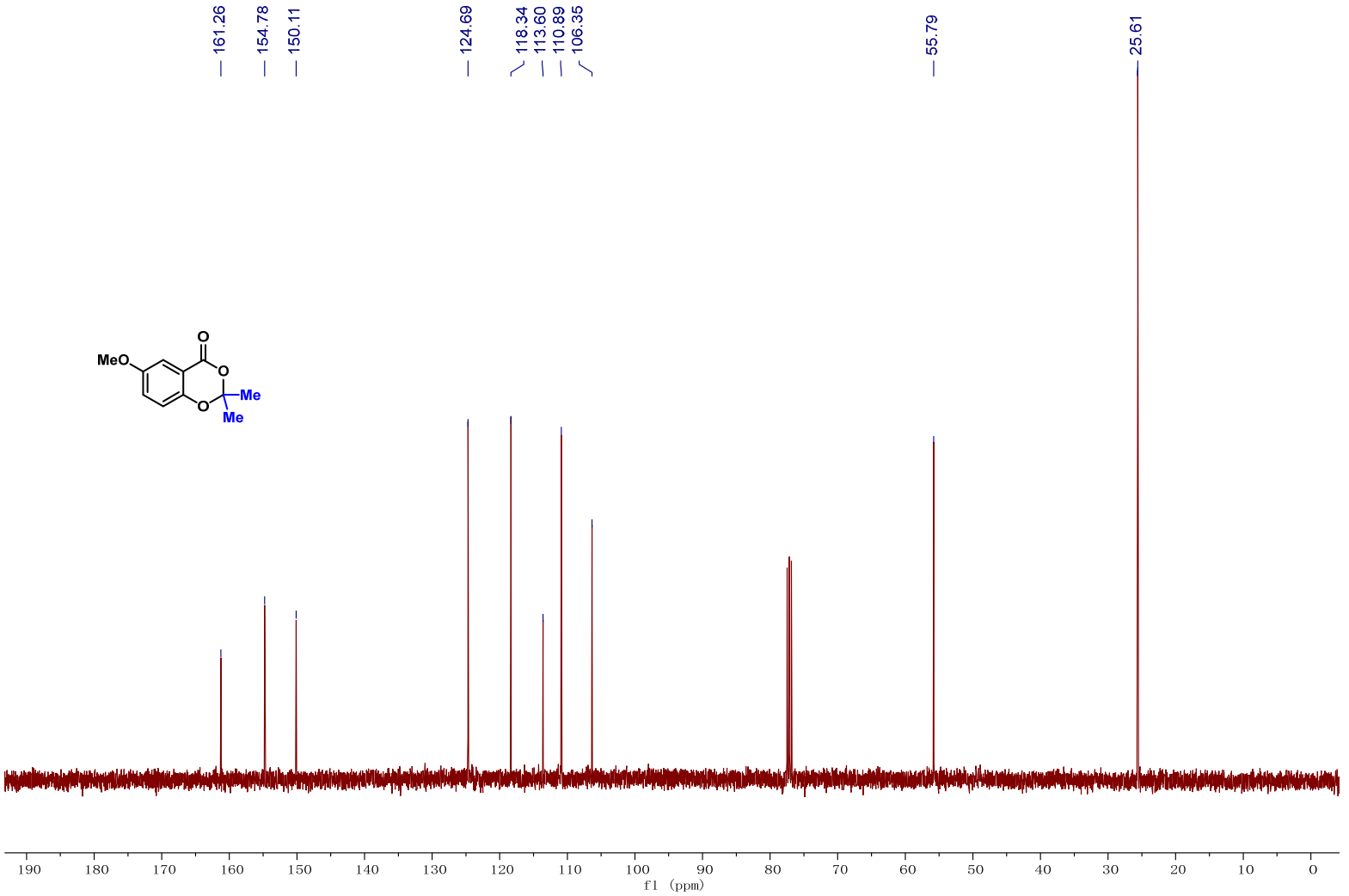
Compound S15 ^{13}C NMR



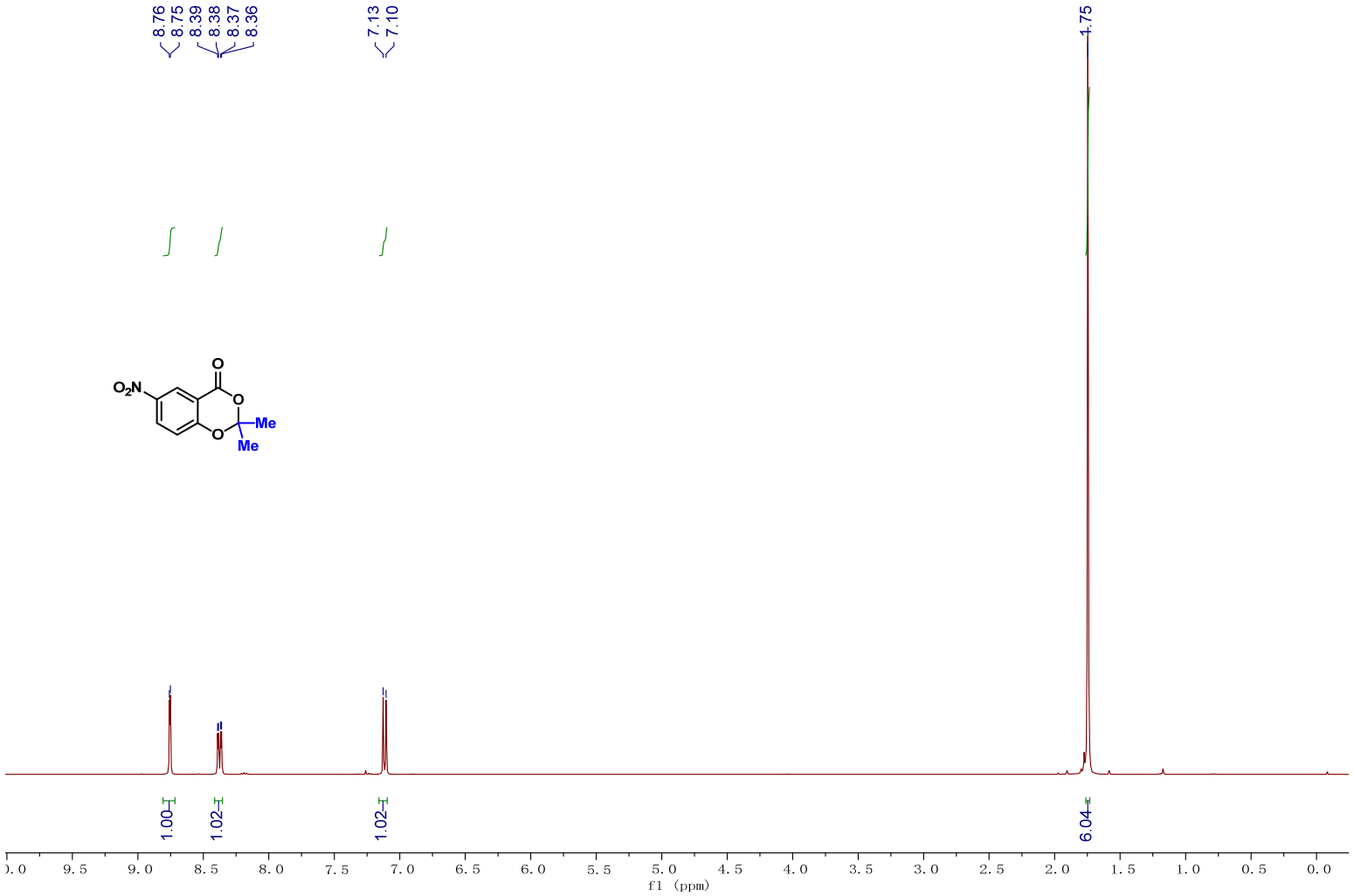
Compound S16 ^{1}H NMR



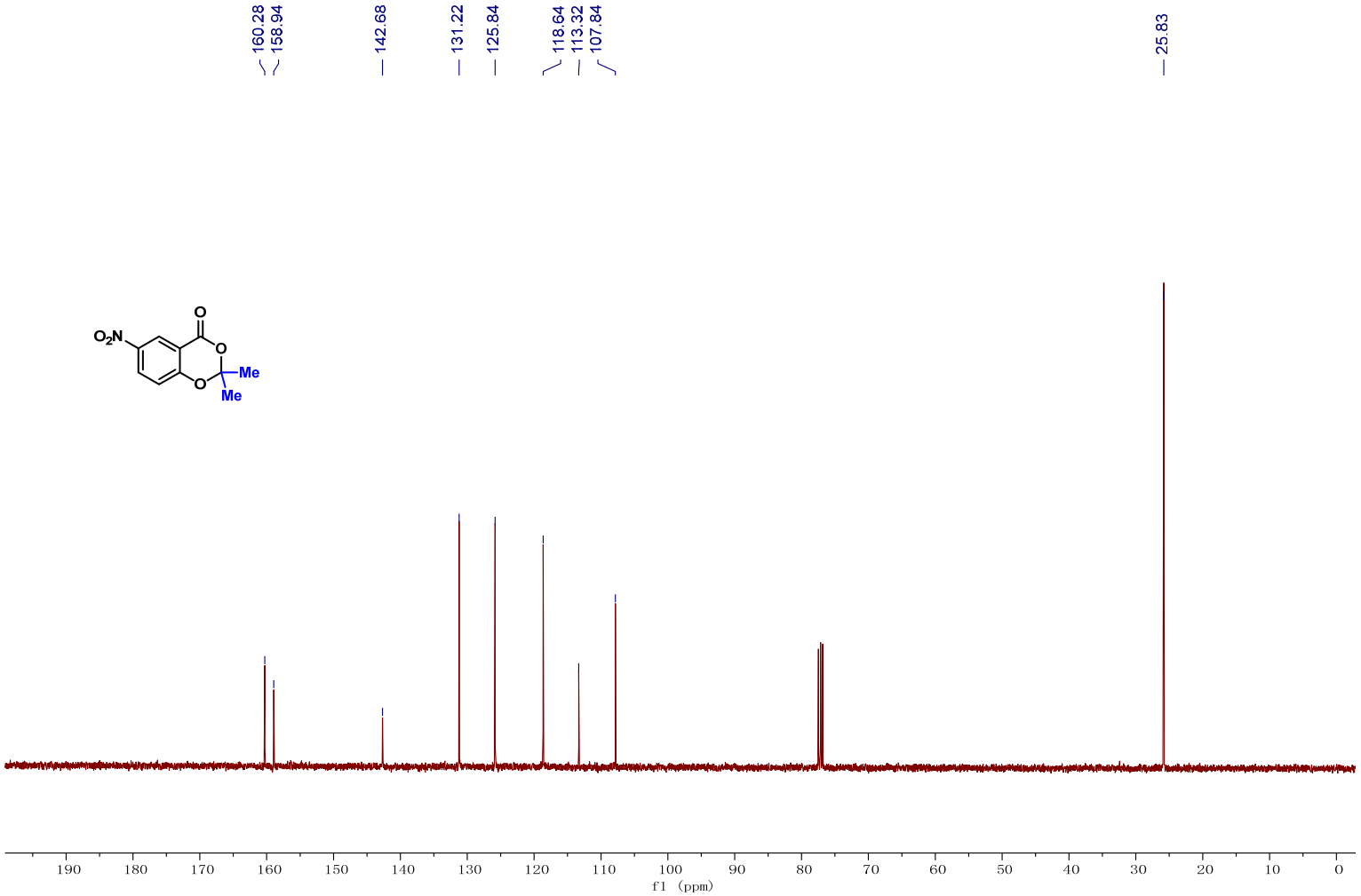
Compound S16 ^{13}C NMR



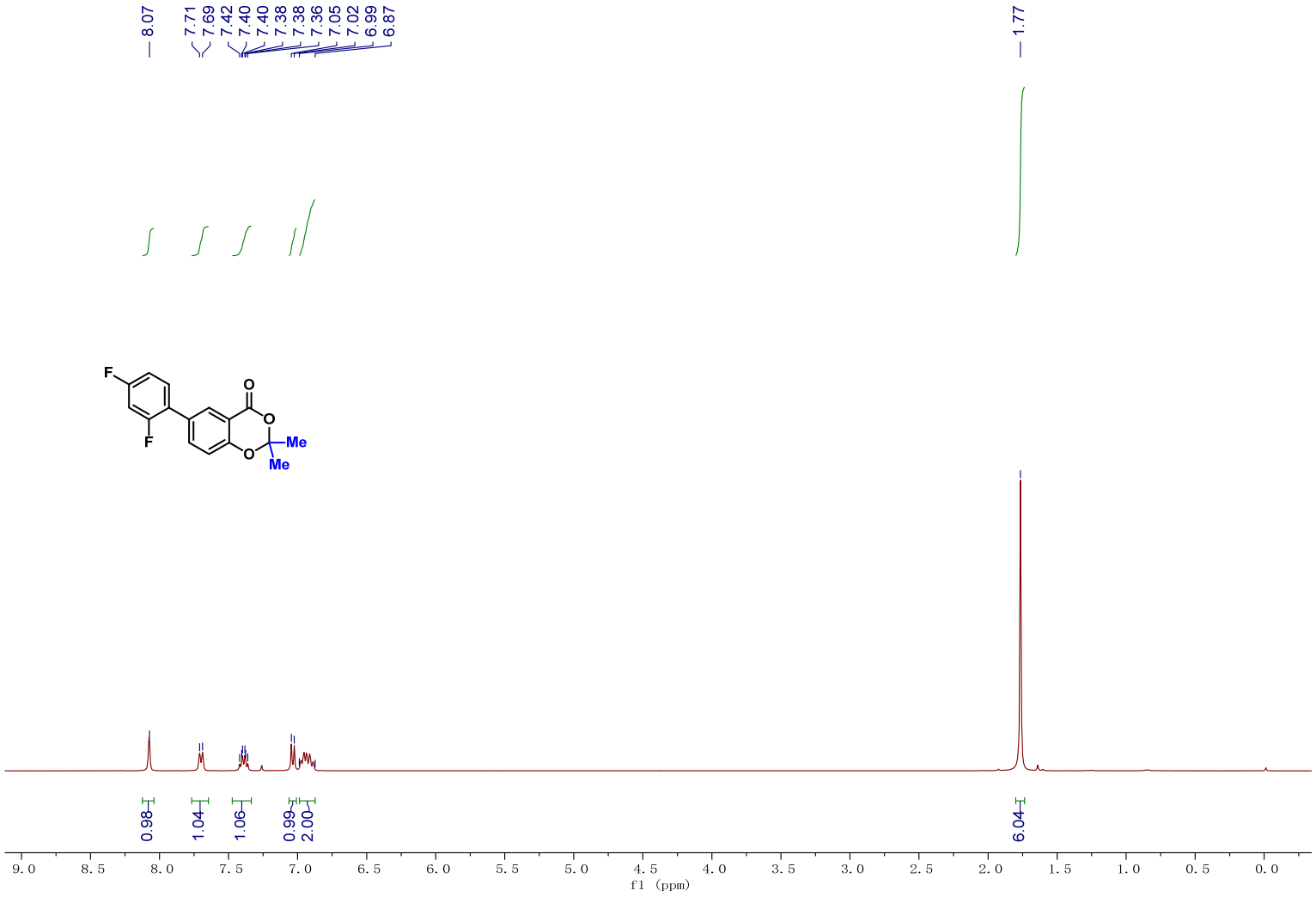
Compound S17 ^{1}H NMR



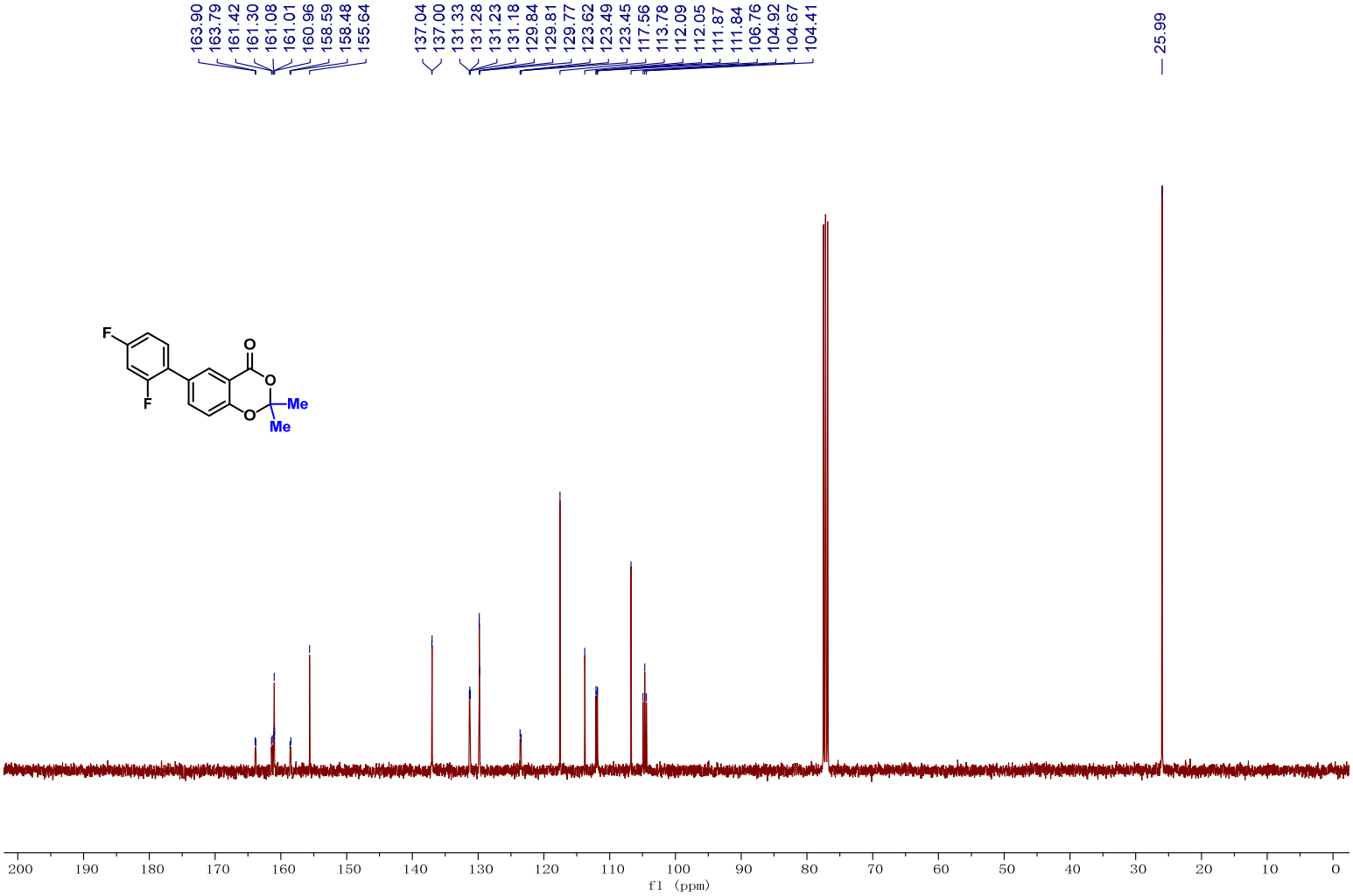
Compound S17 ^{13}C NMR



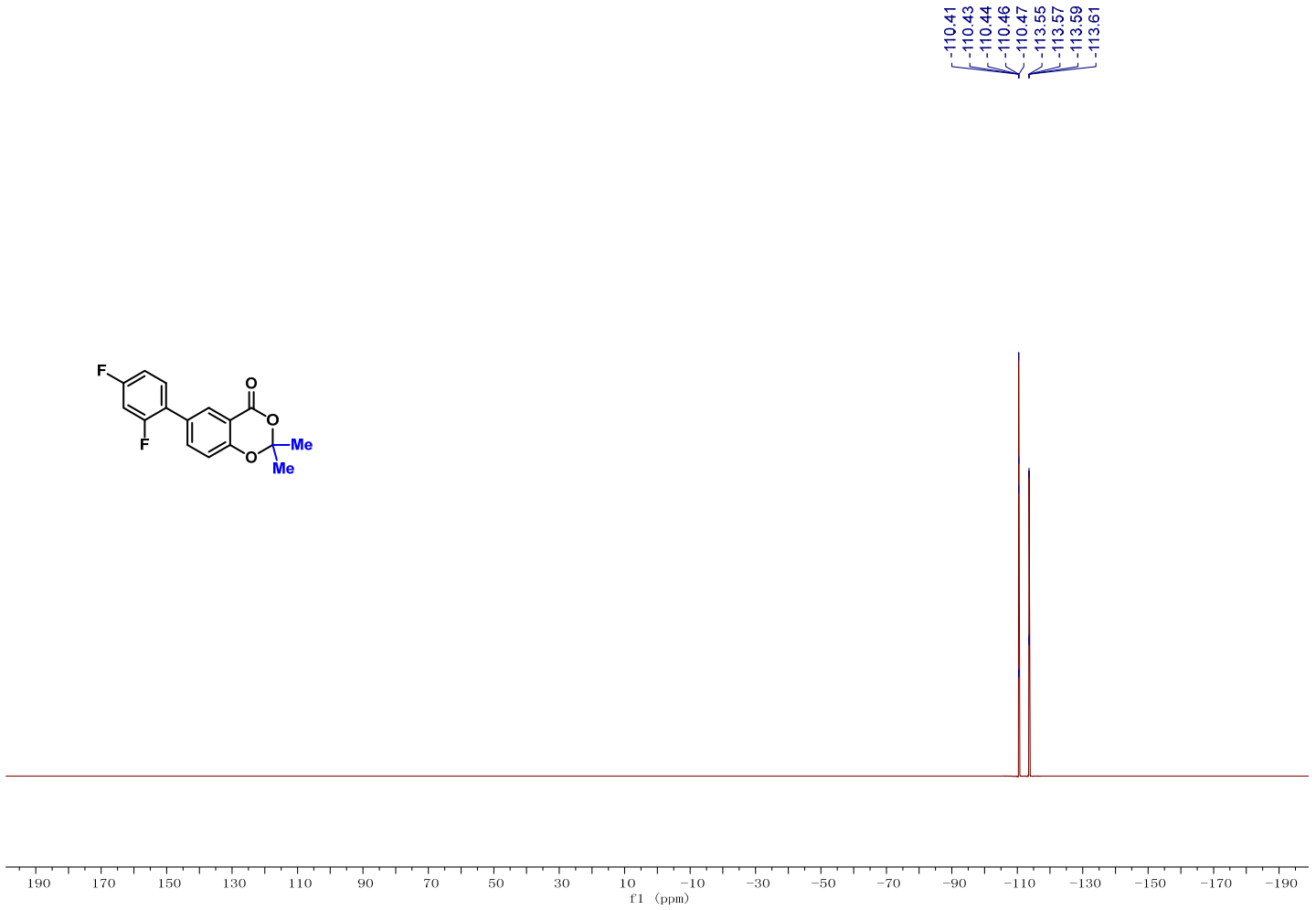
Compound S18 ^{1}H NMR



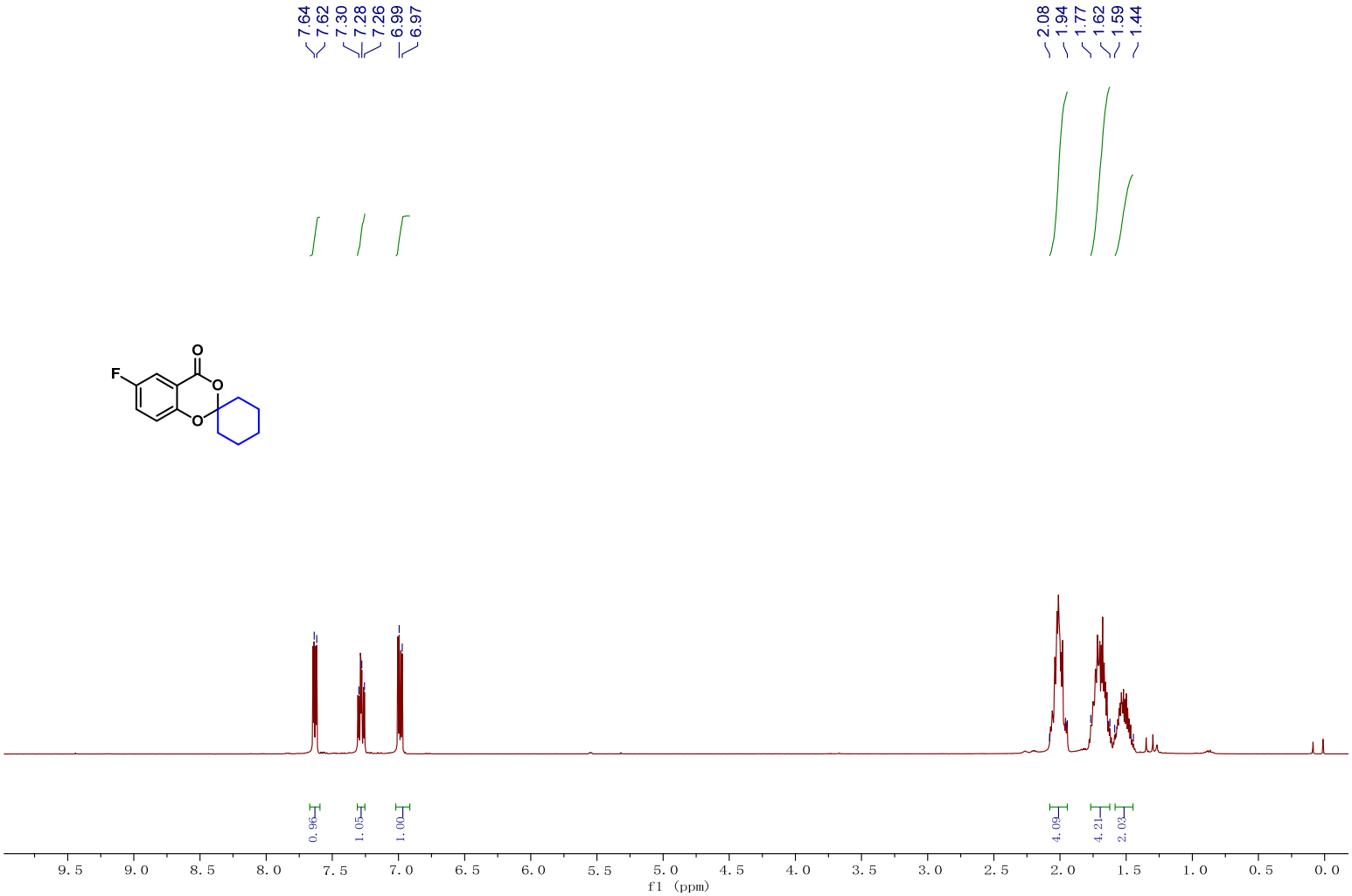
Compound S18 ^{13}C NMR



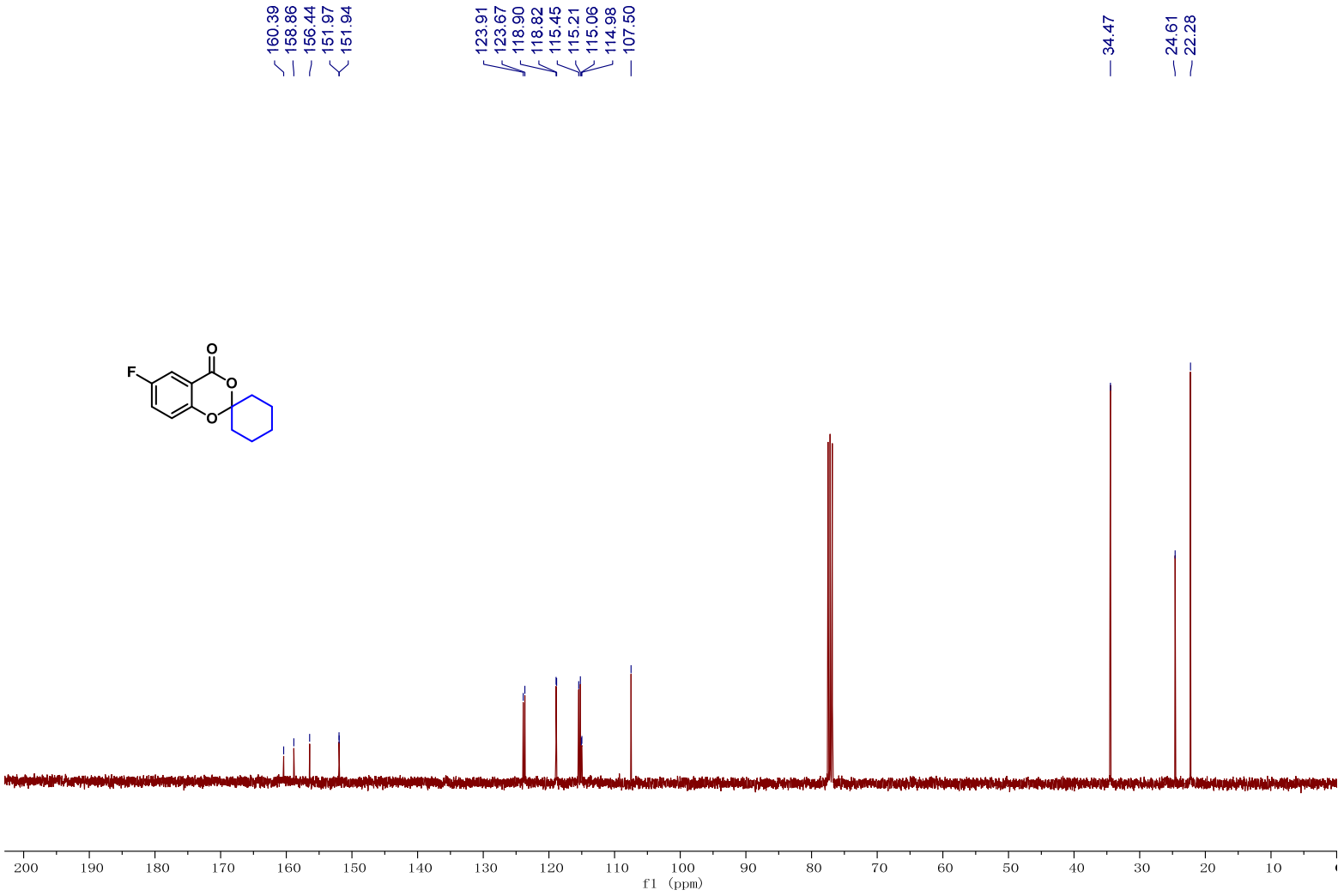
Compound S18 ^{19}F NMR



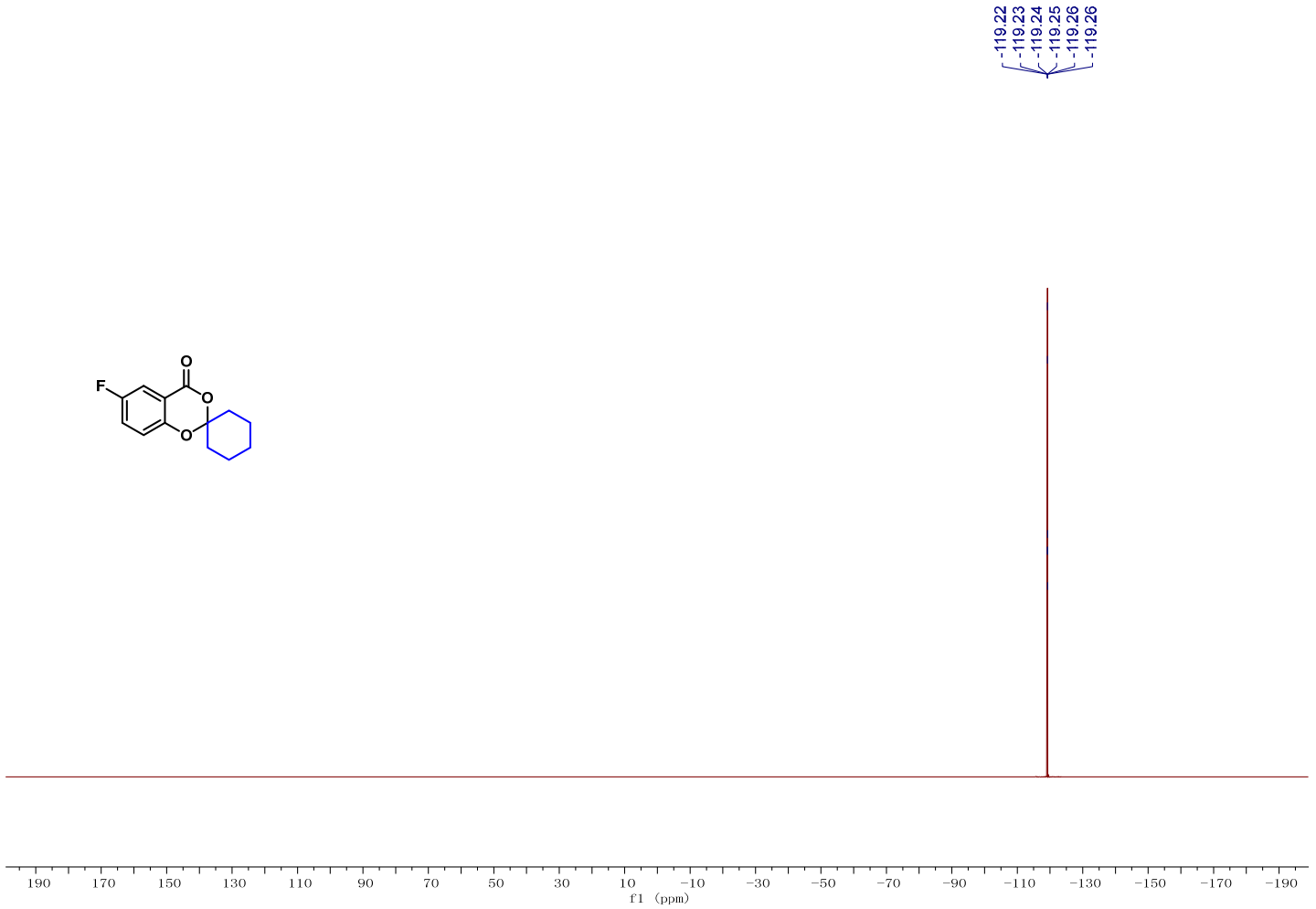
Compound S19 ^{1}H NMR



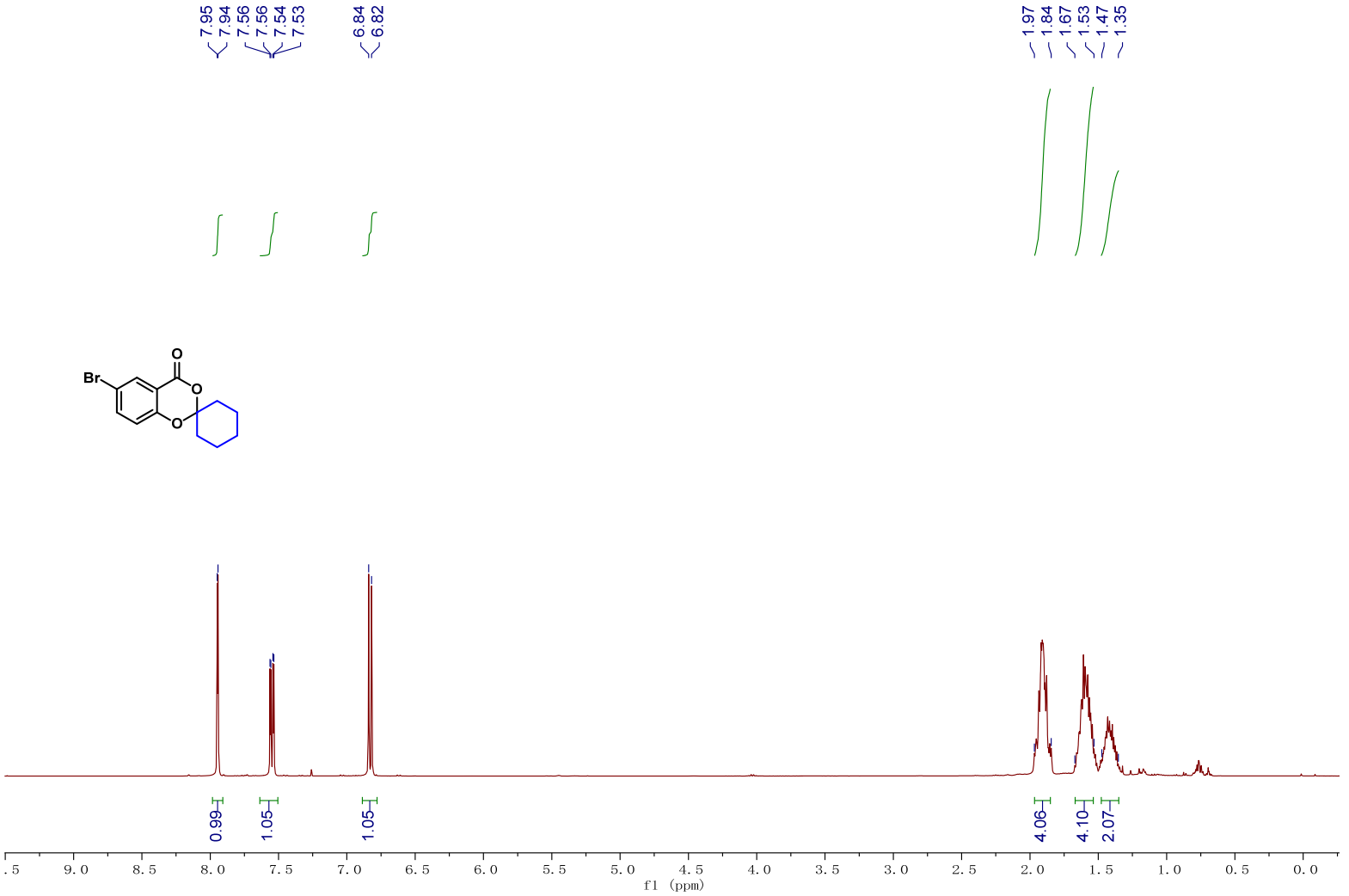
Compound S19 ^{13}C NMR



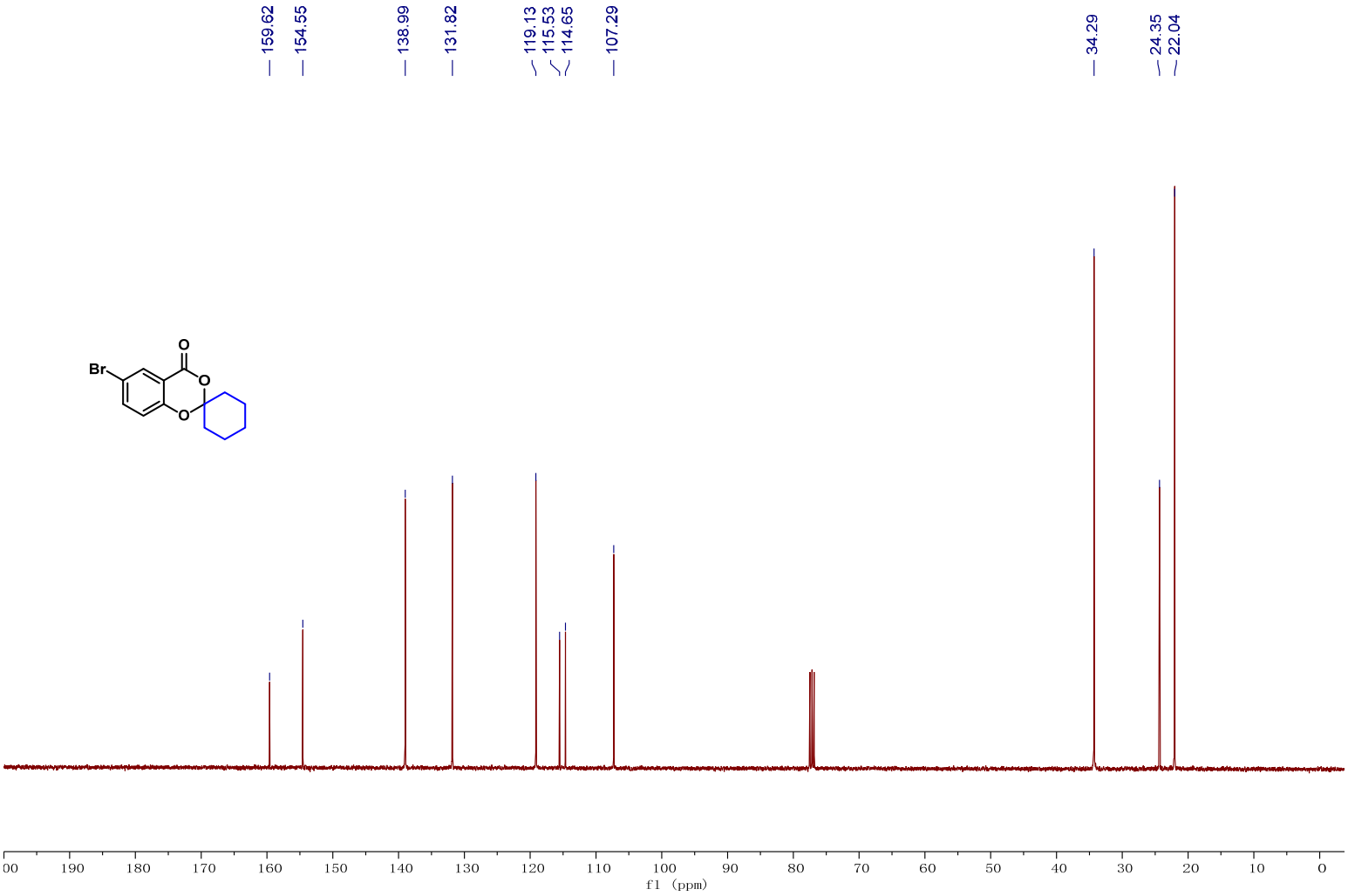
Compound S19 ^{19}F NMR



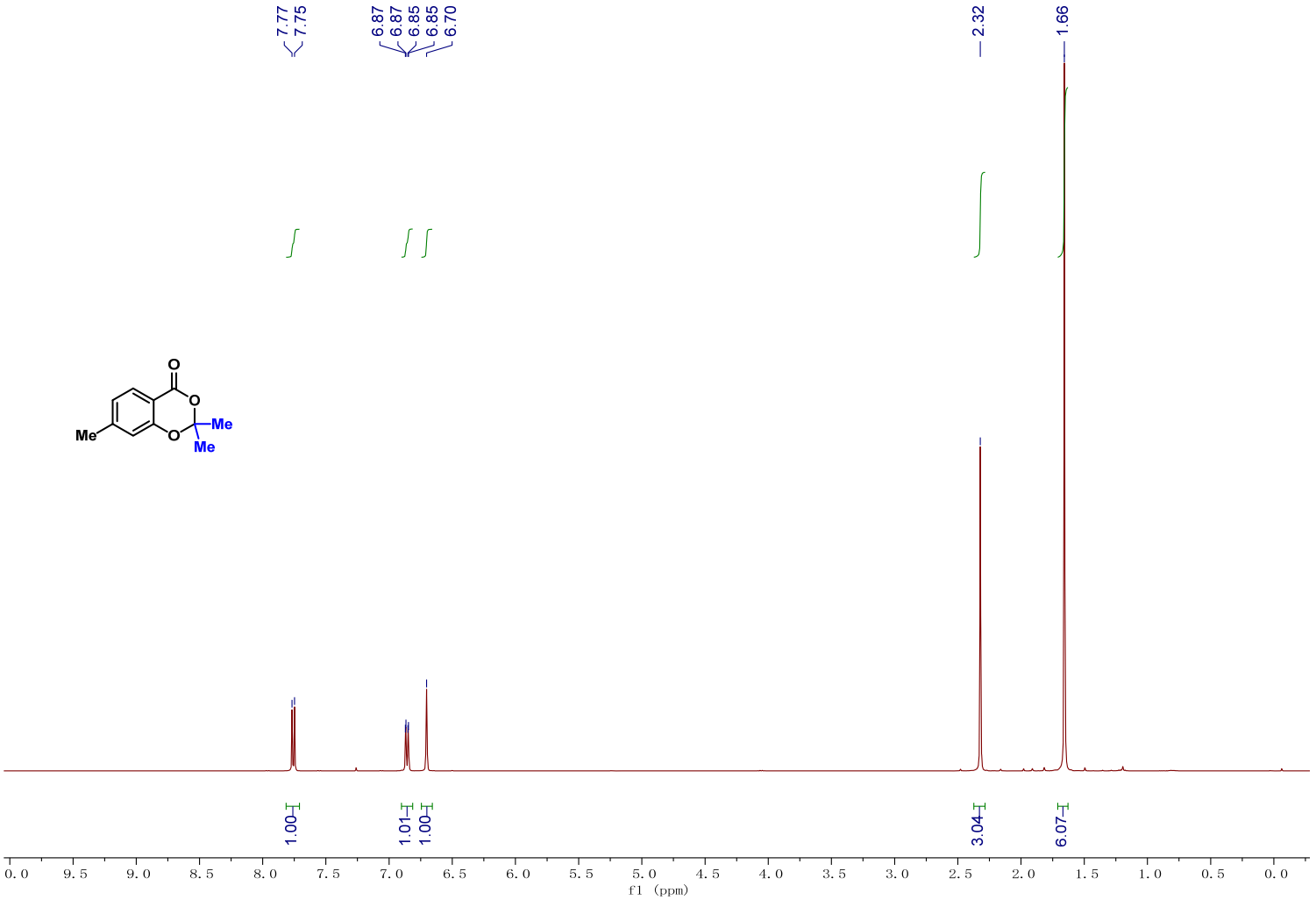
Compound S20 ^{1}H NMR



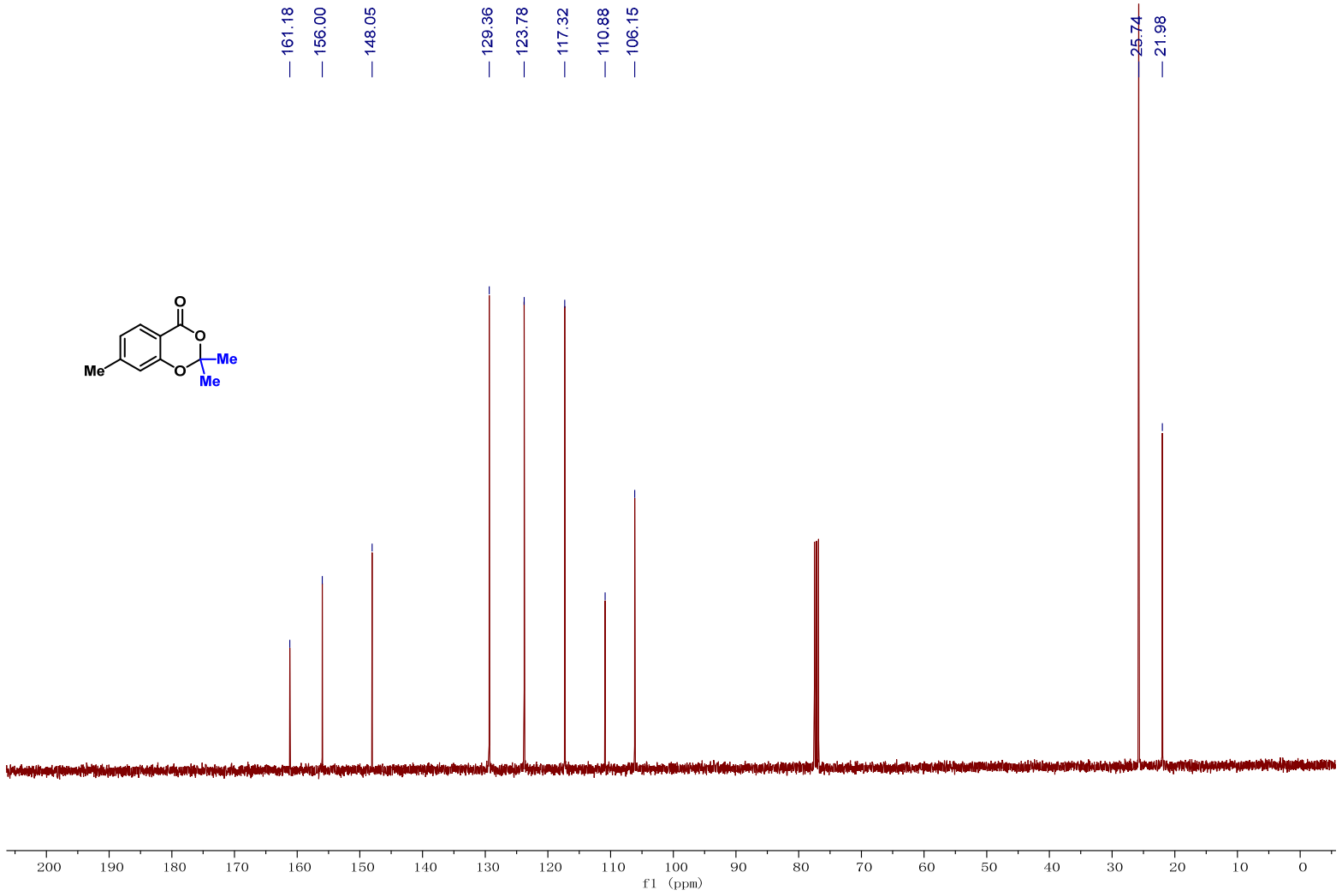
Compound S20 ^{13}C NMR



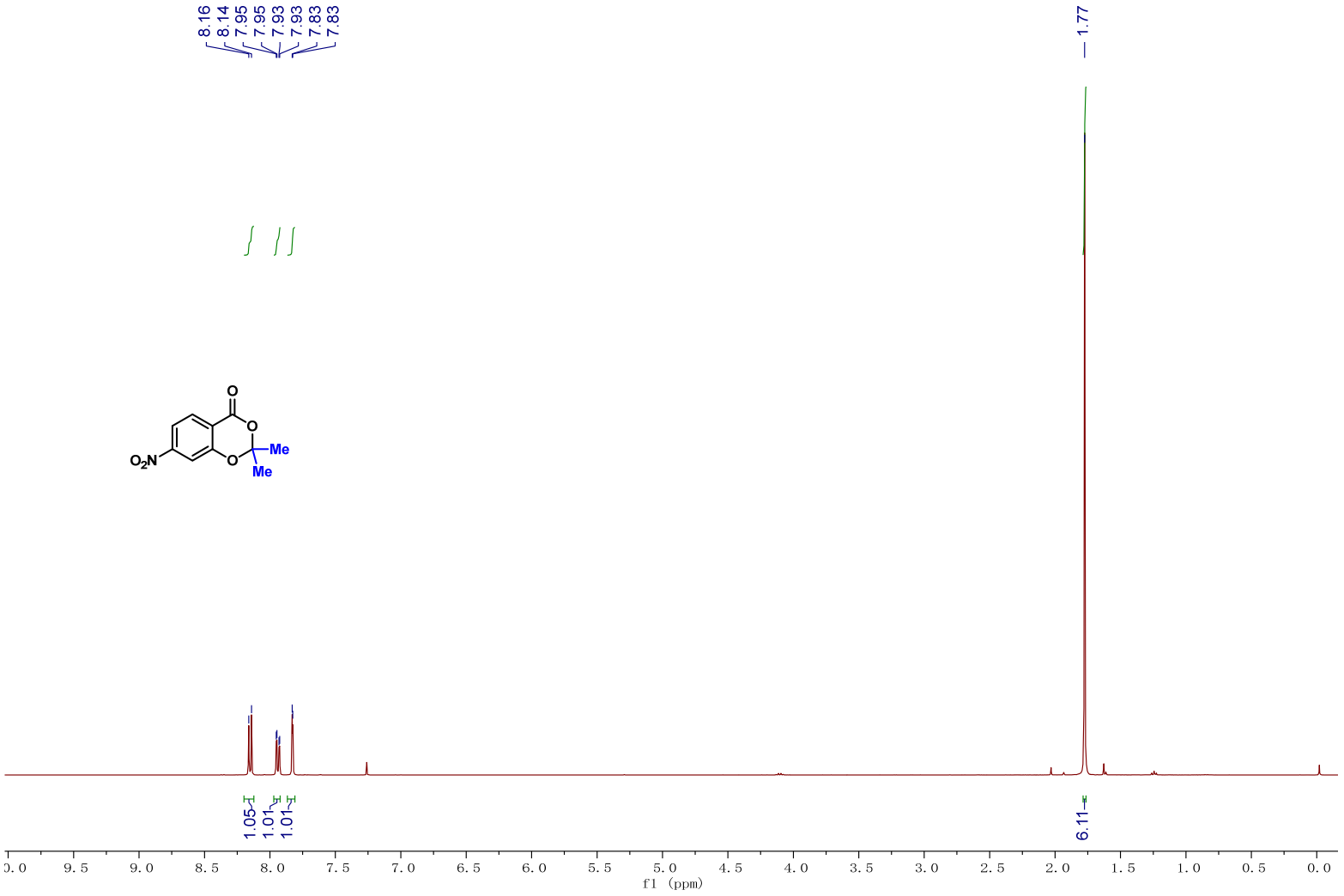
Compound 75a ^{1}H NMR



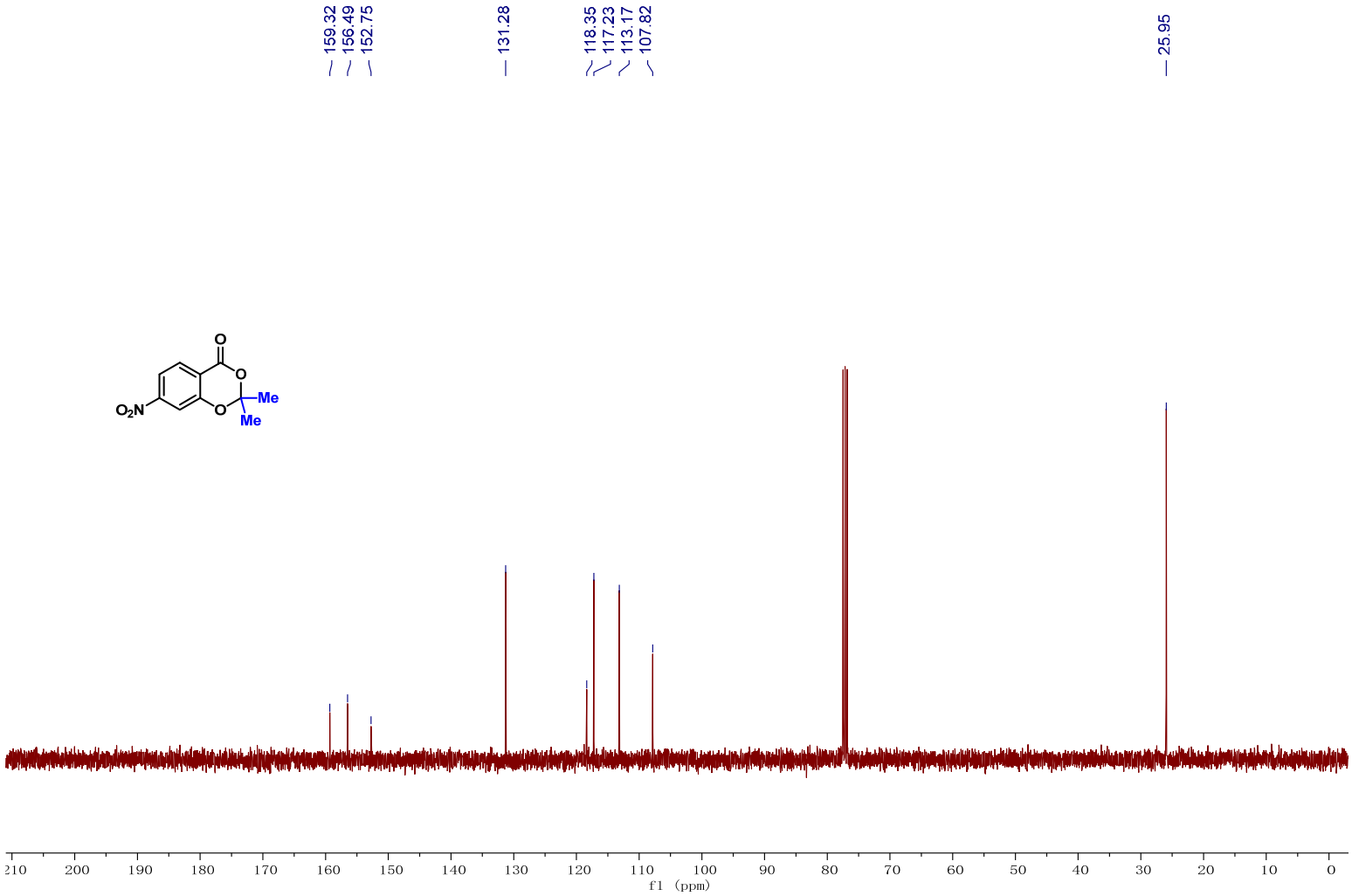
Compound 75a ^{13}C NMR



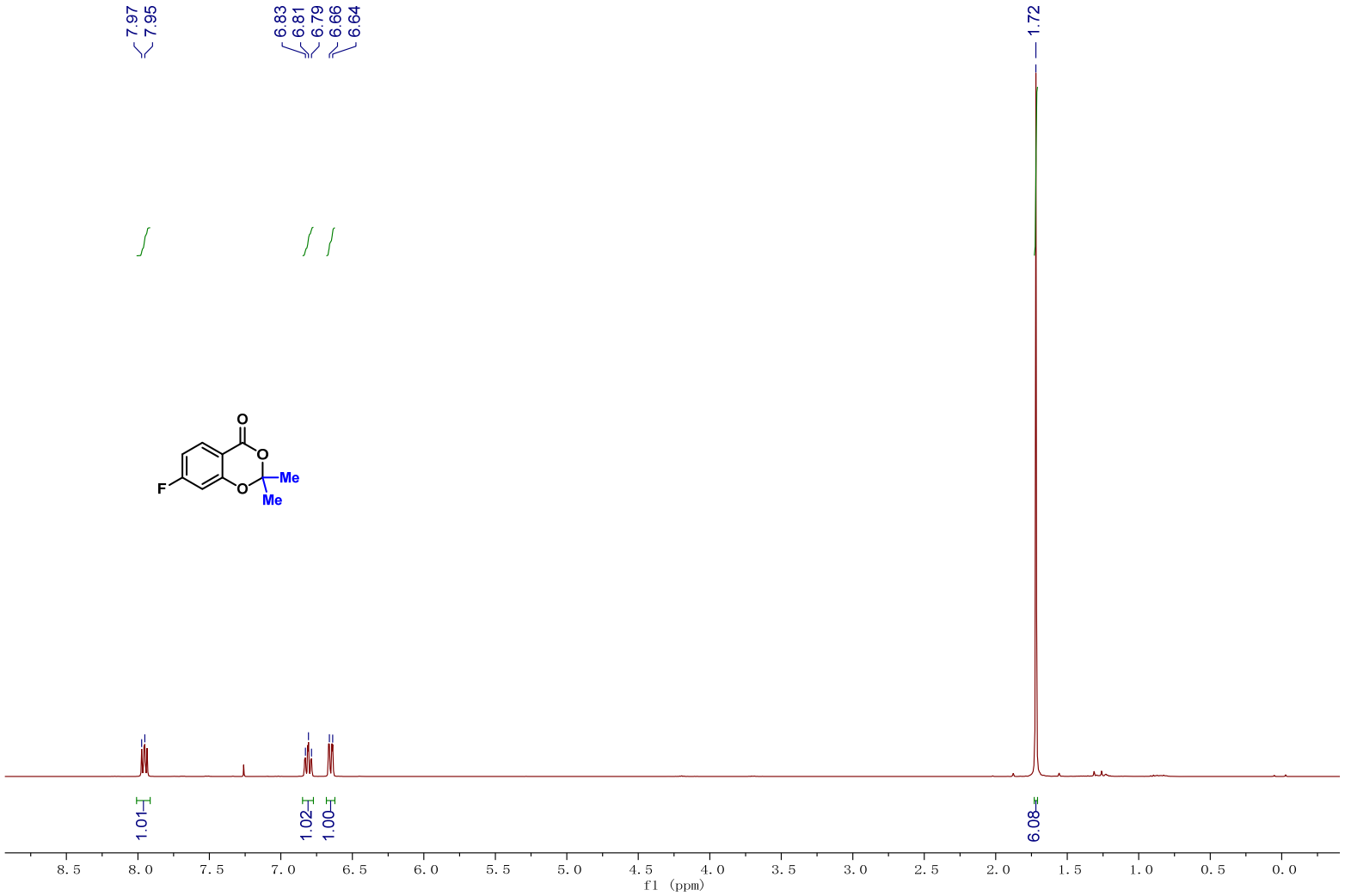
Compound S22 ^{1}H NMR



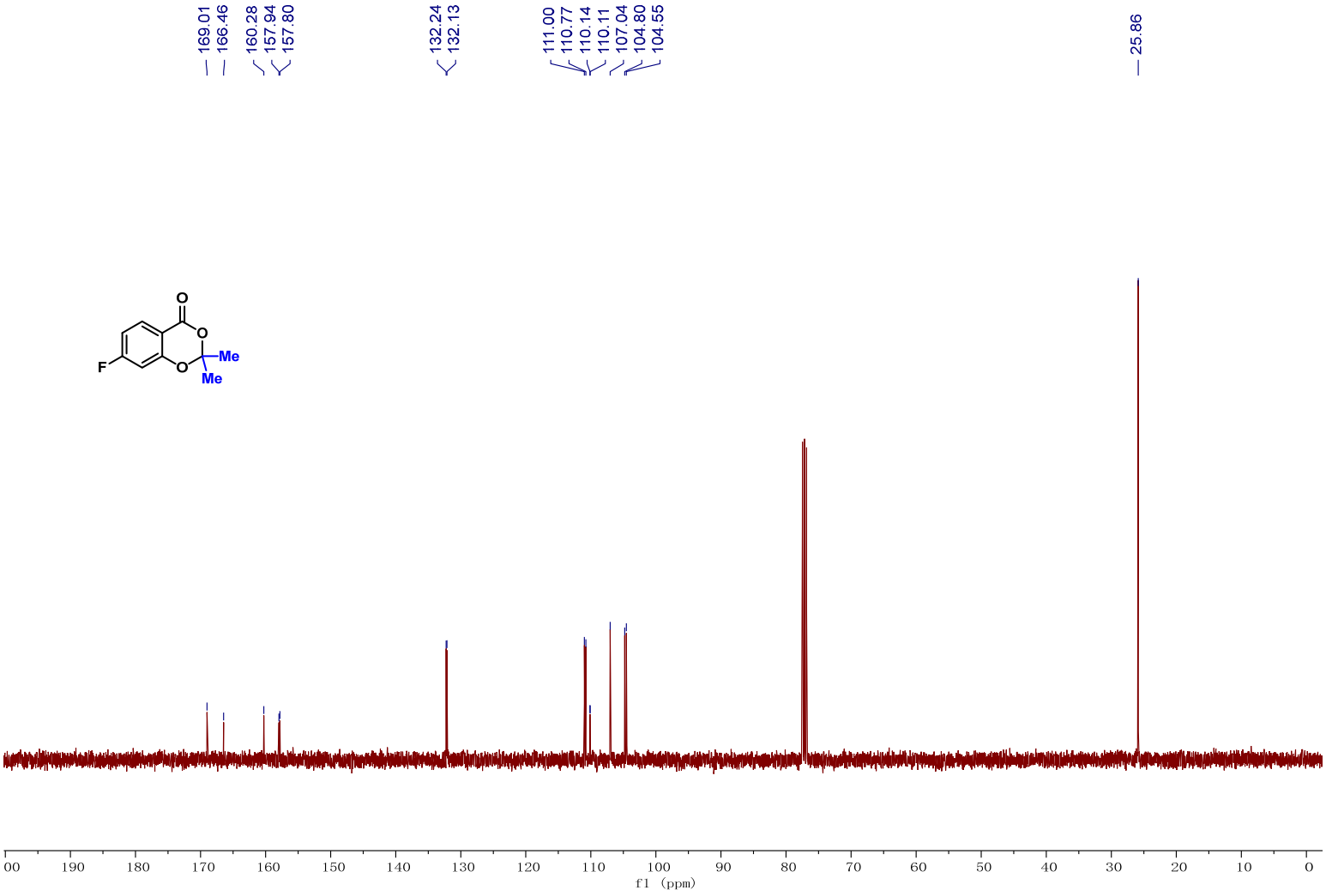
Compound S22 ^{13}C NMR



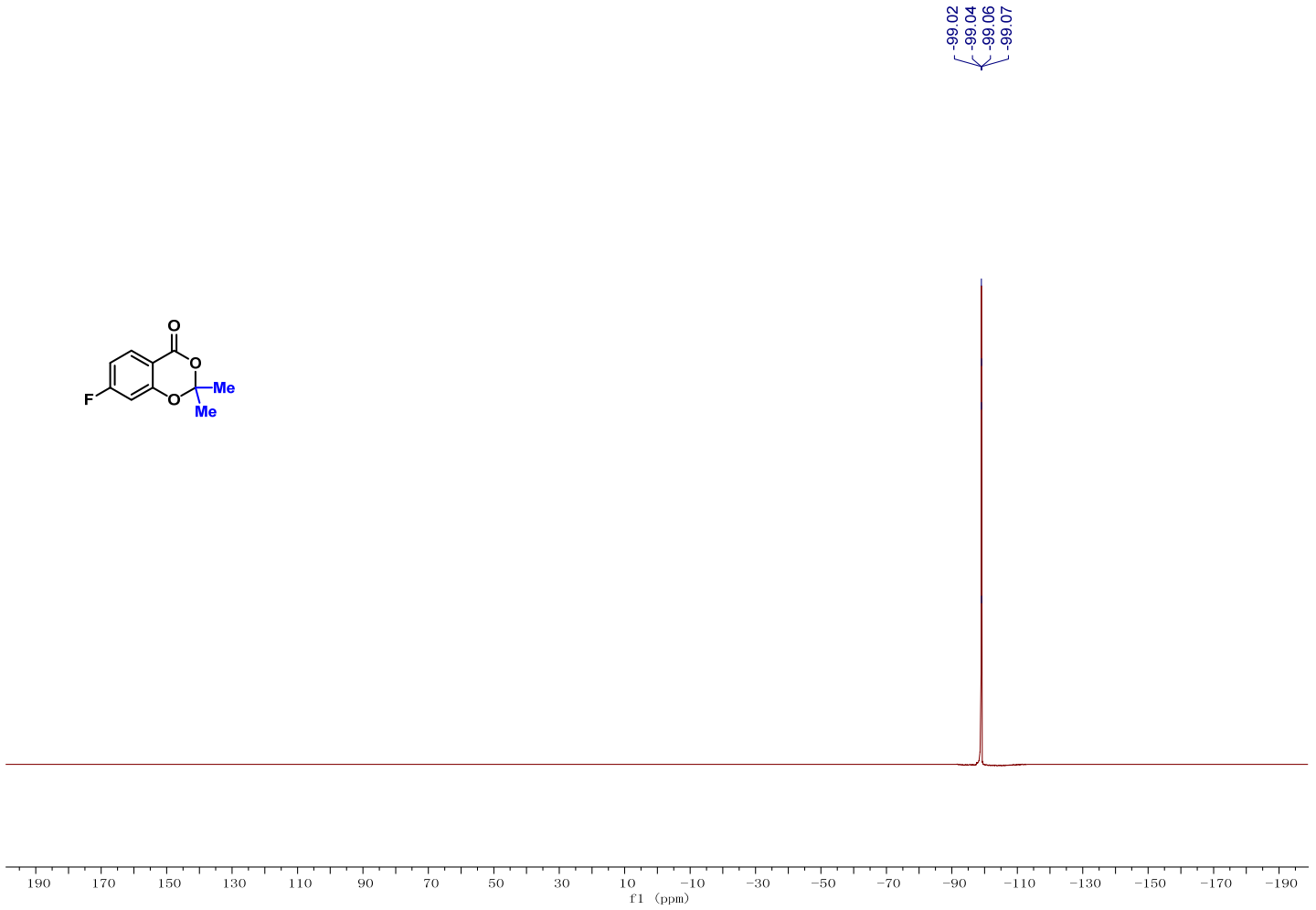
Compound S23 ^{1}H NMR



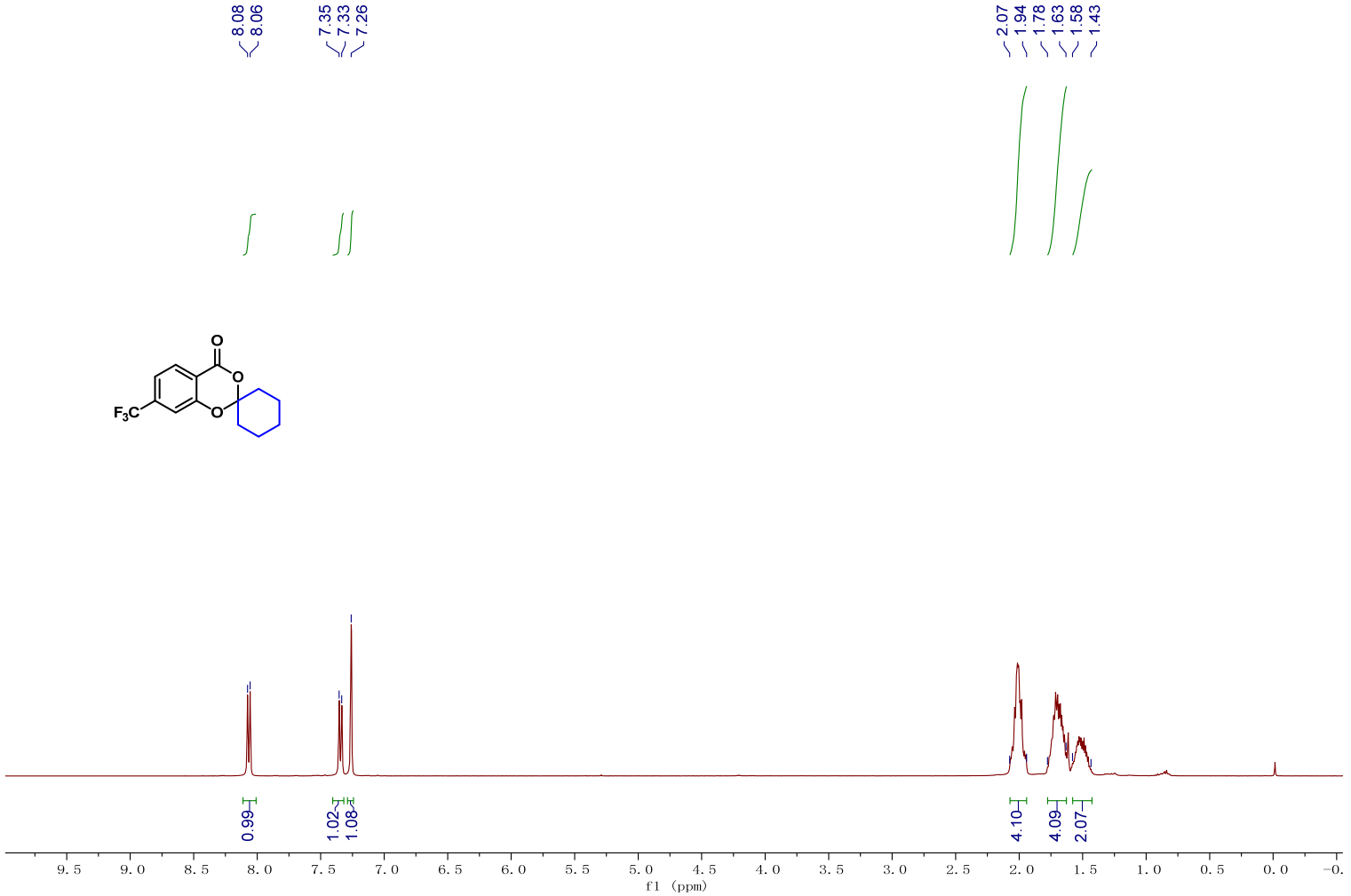
Compound S23 ^{13}C NMR



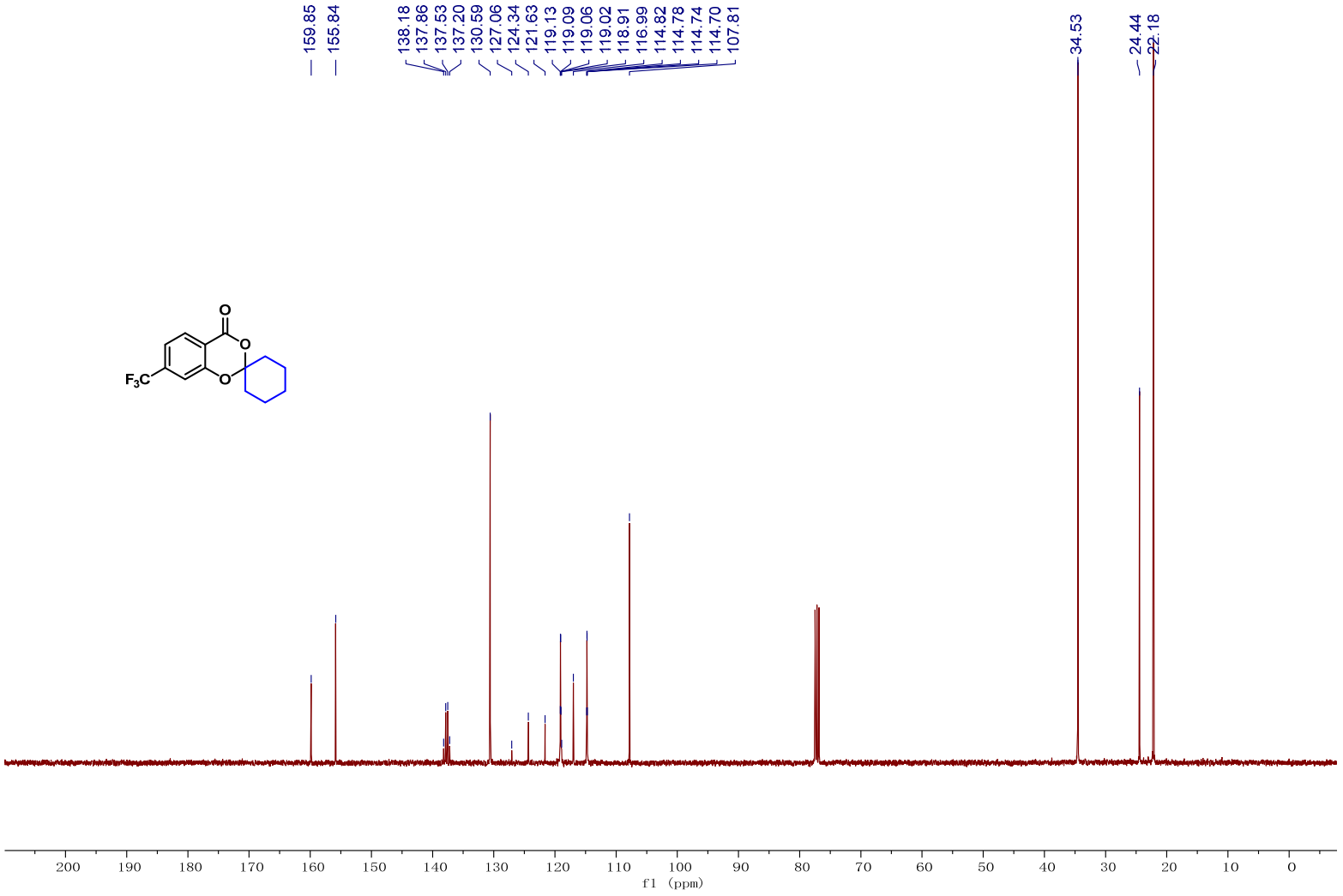
Compound S23 ^{19}F NMR



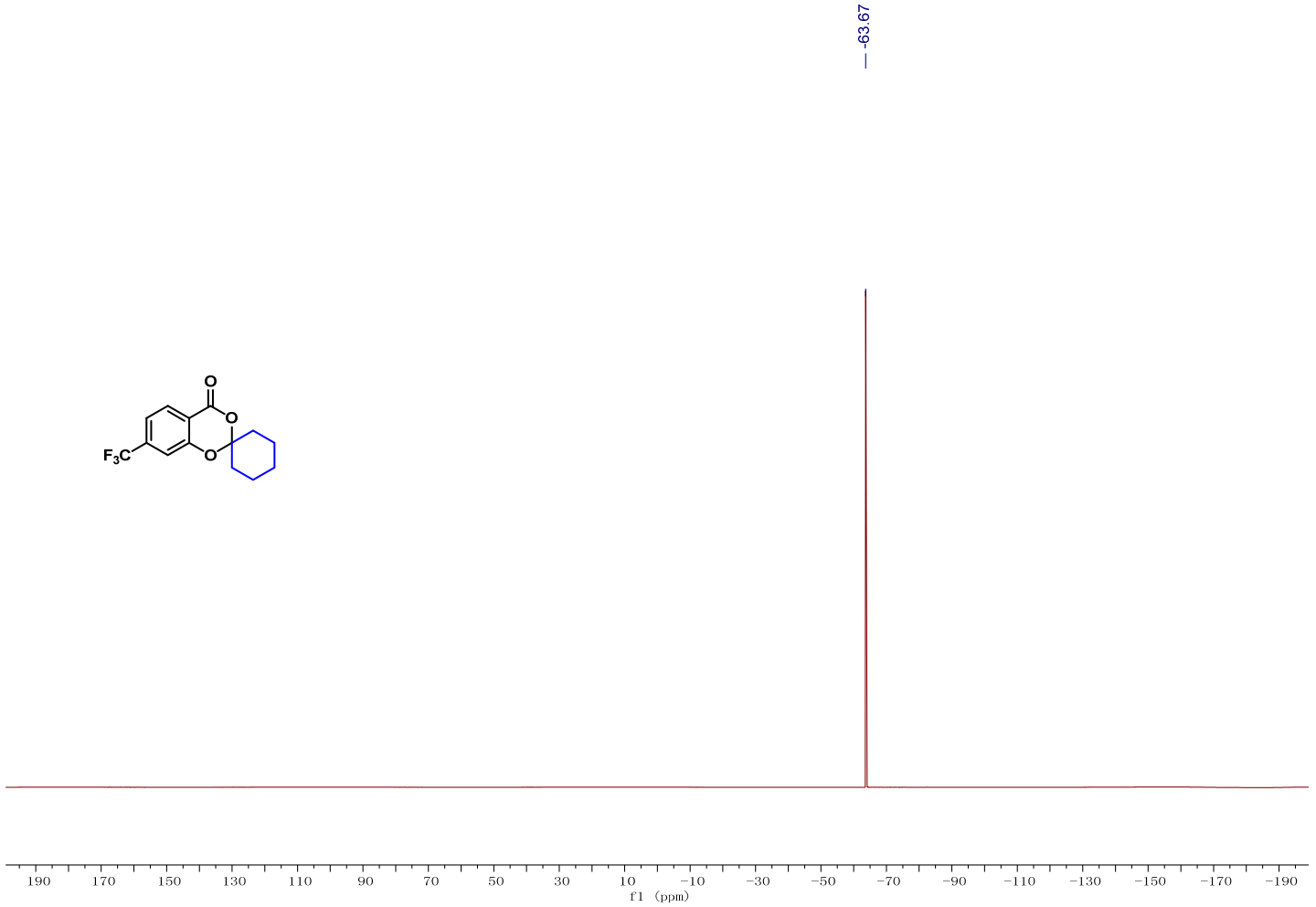
Compound S24 ^{1}H NMR



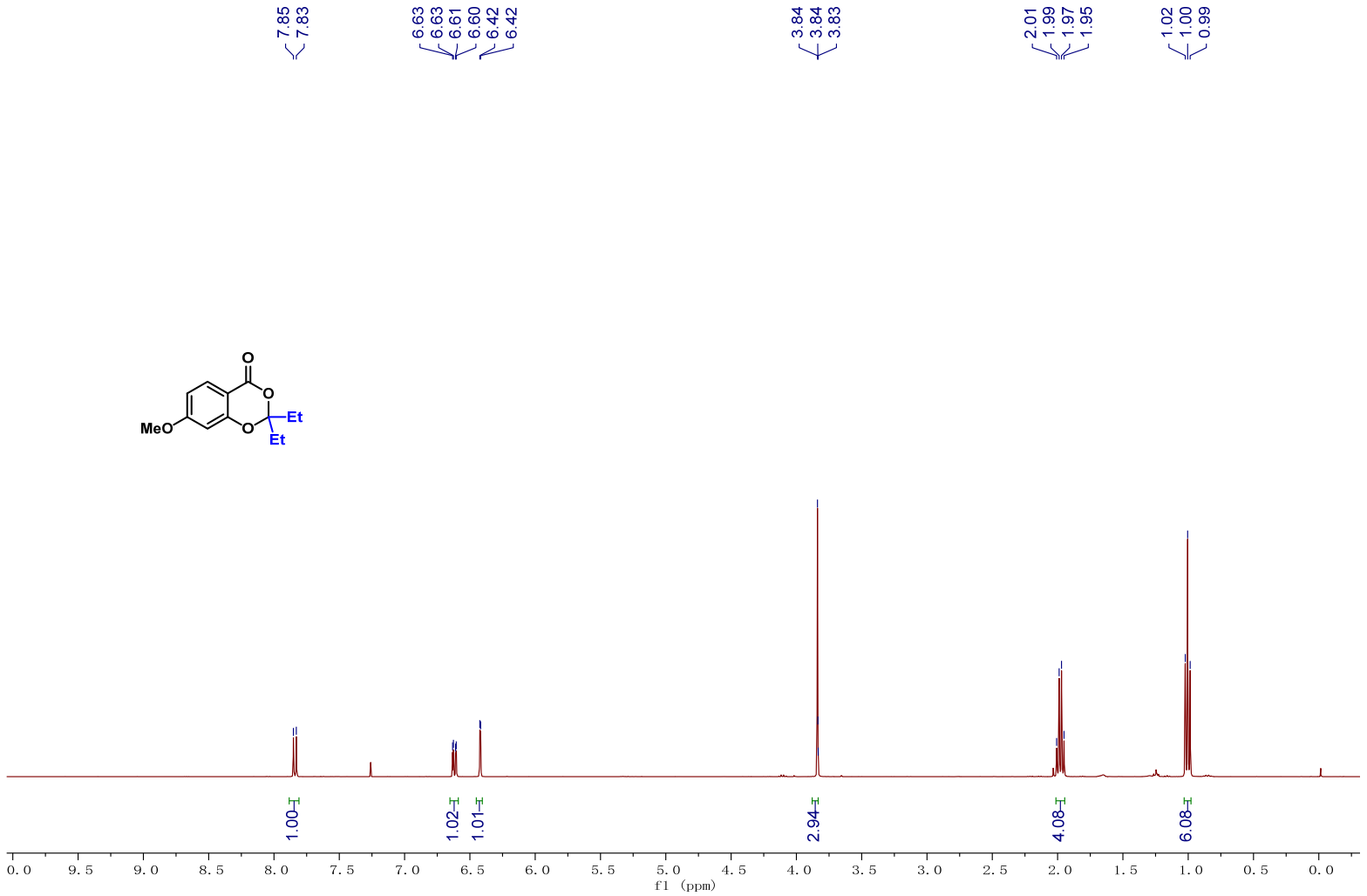
Compound S24 ^{13}C NMR



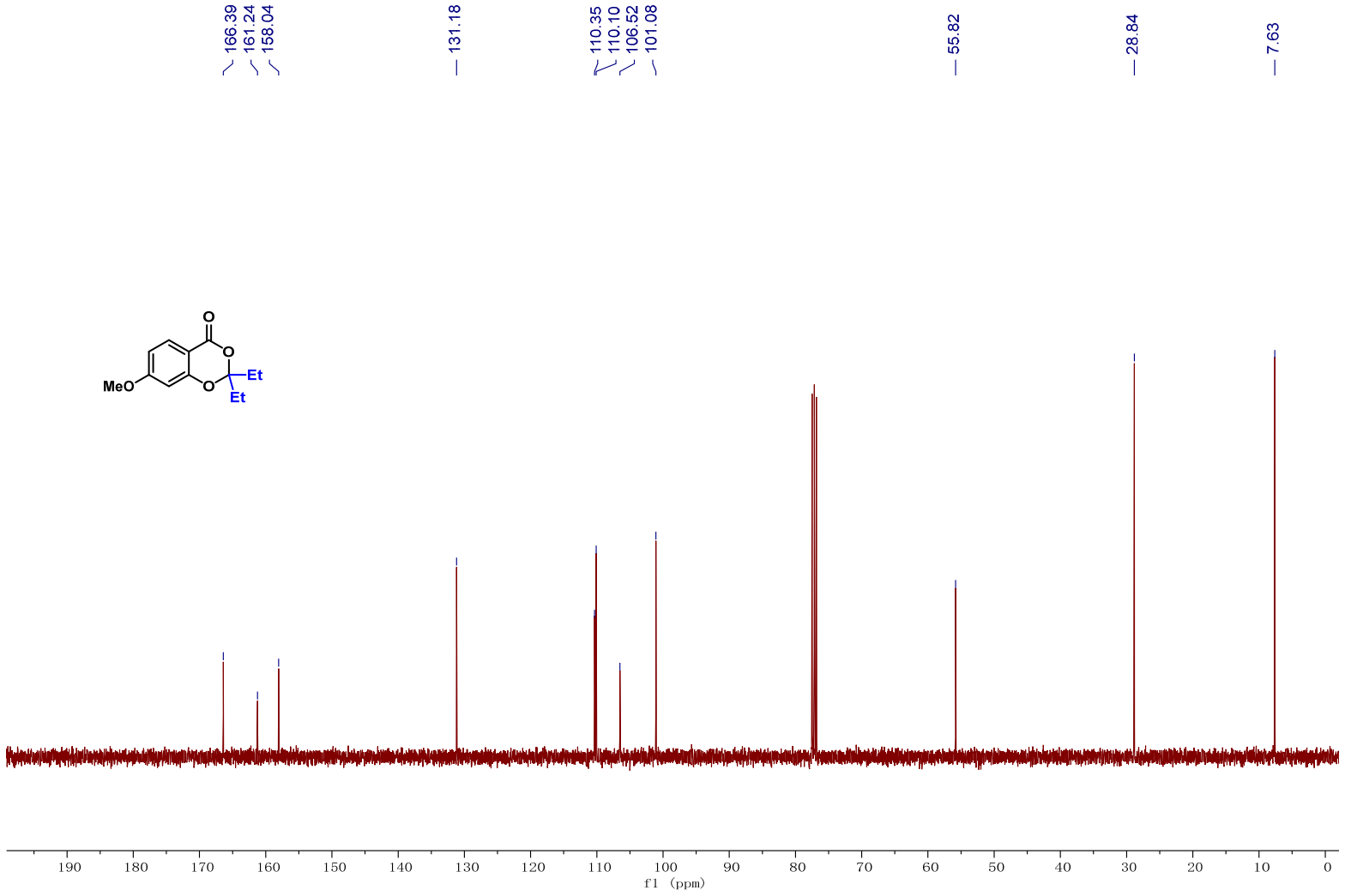
Compound S24 ^{19}F NMR



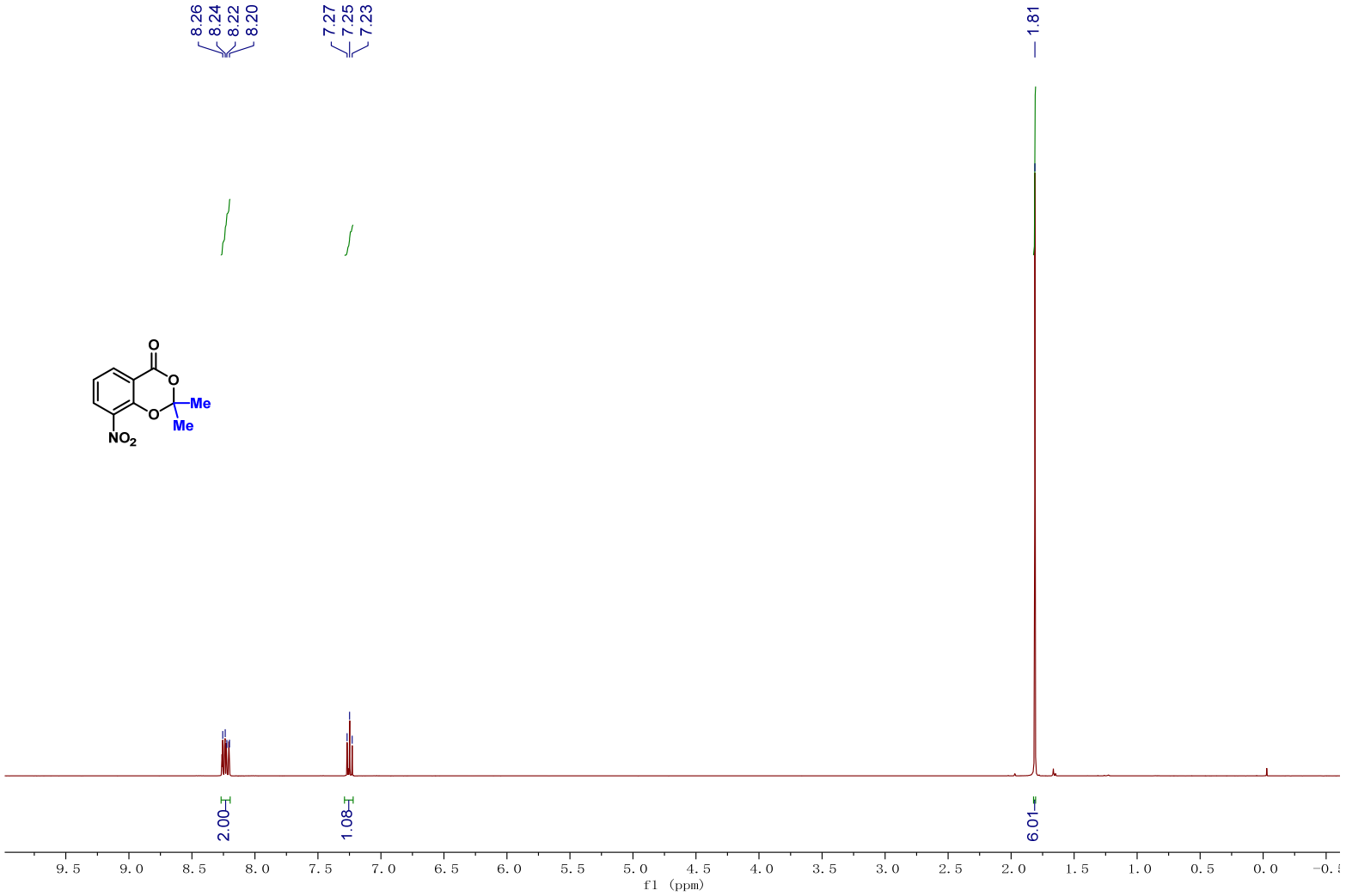
Compound S25 ^{1}H NMR



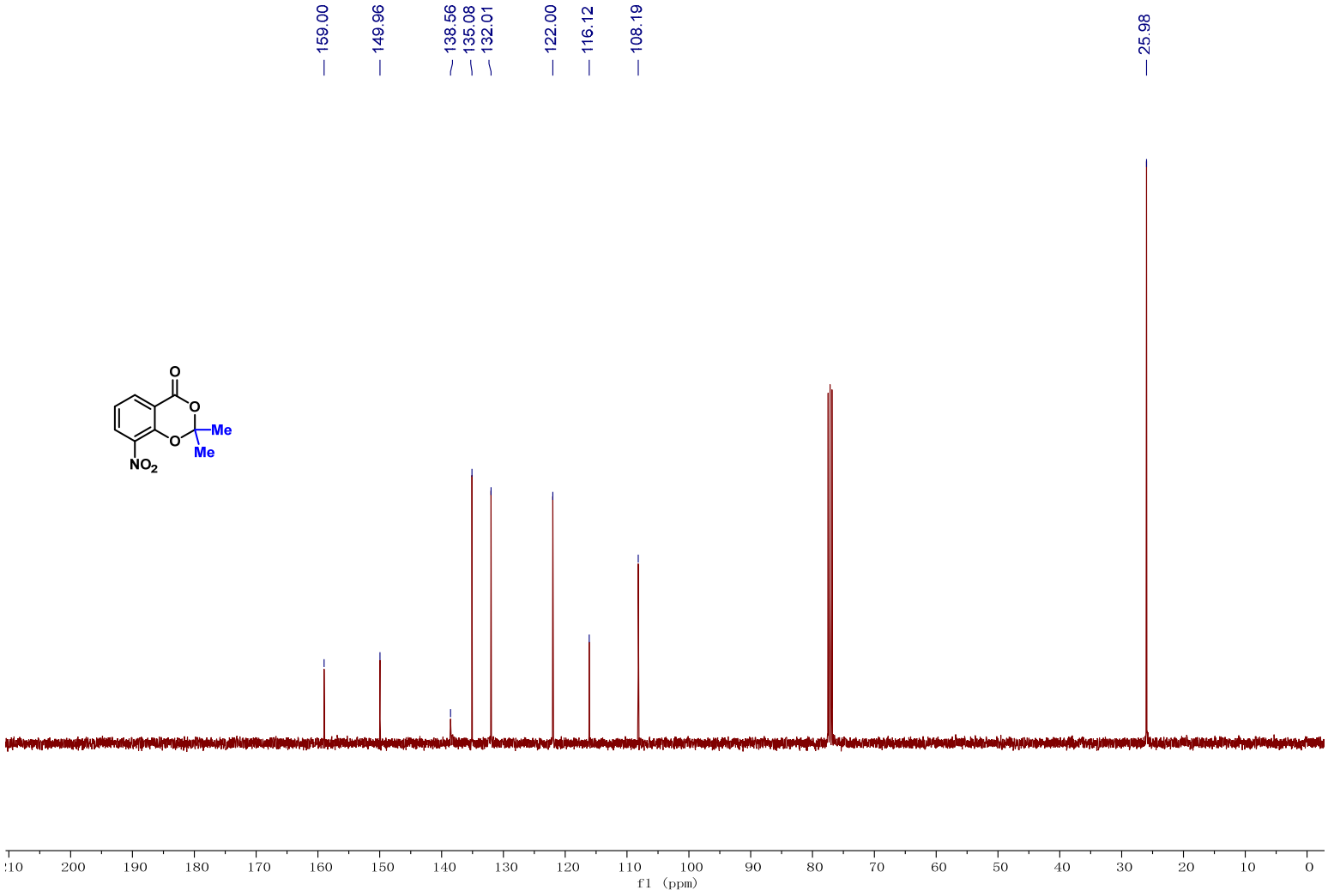
Compound S25 ^{13}C NMR



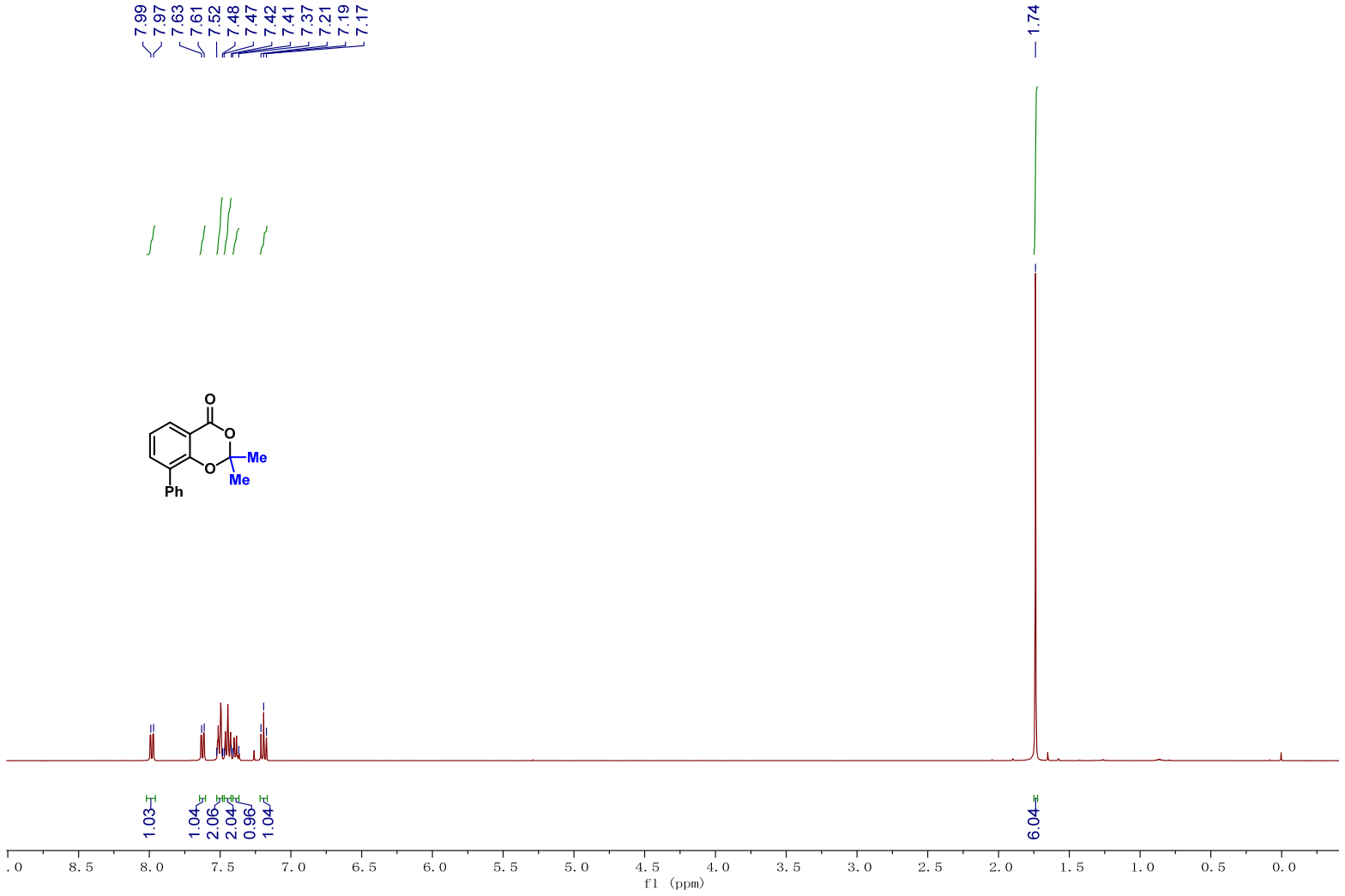
Compound S26 ^{1}H NMR



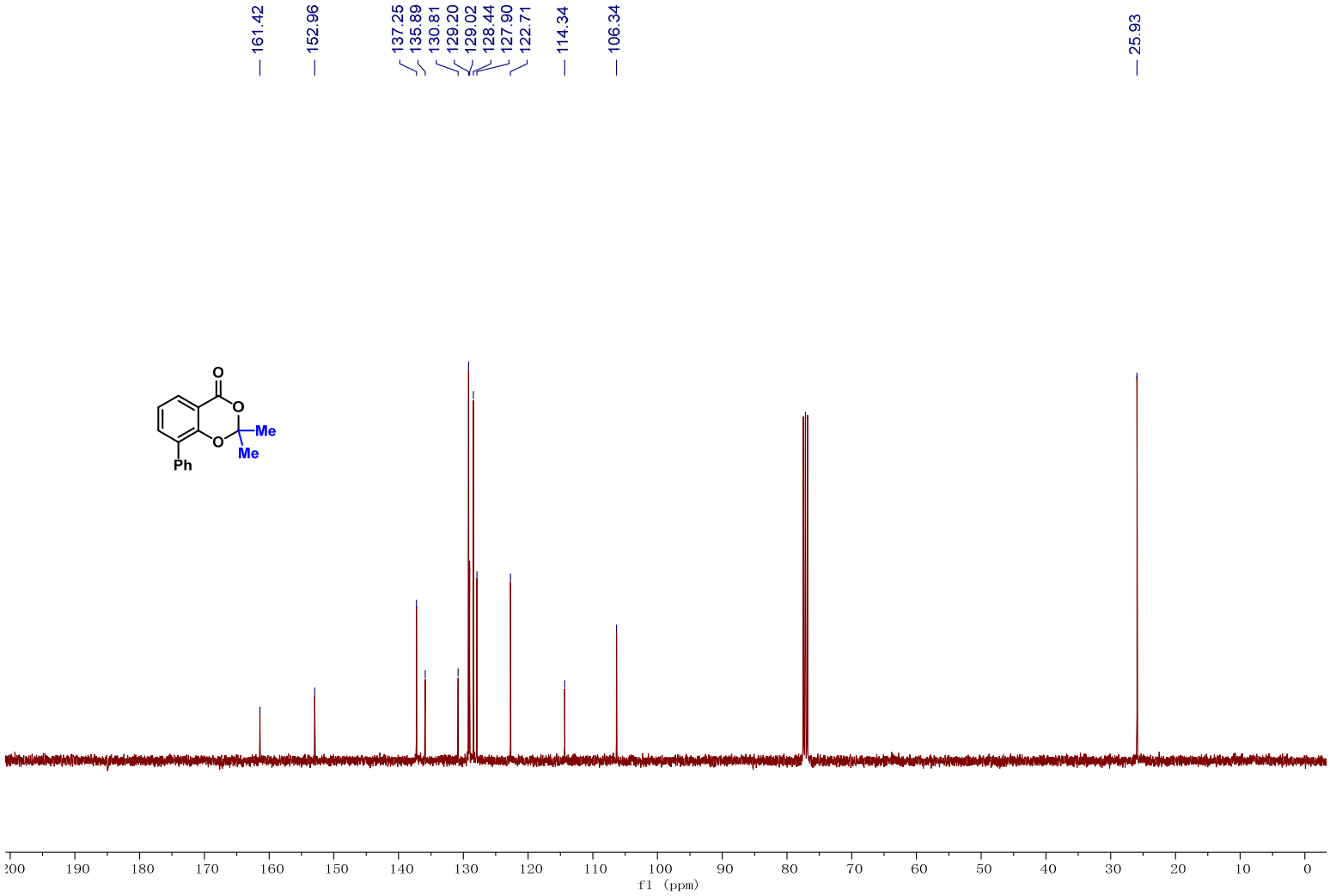
Compound S26 ^{13}C NMR



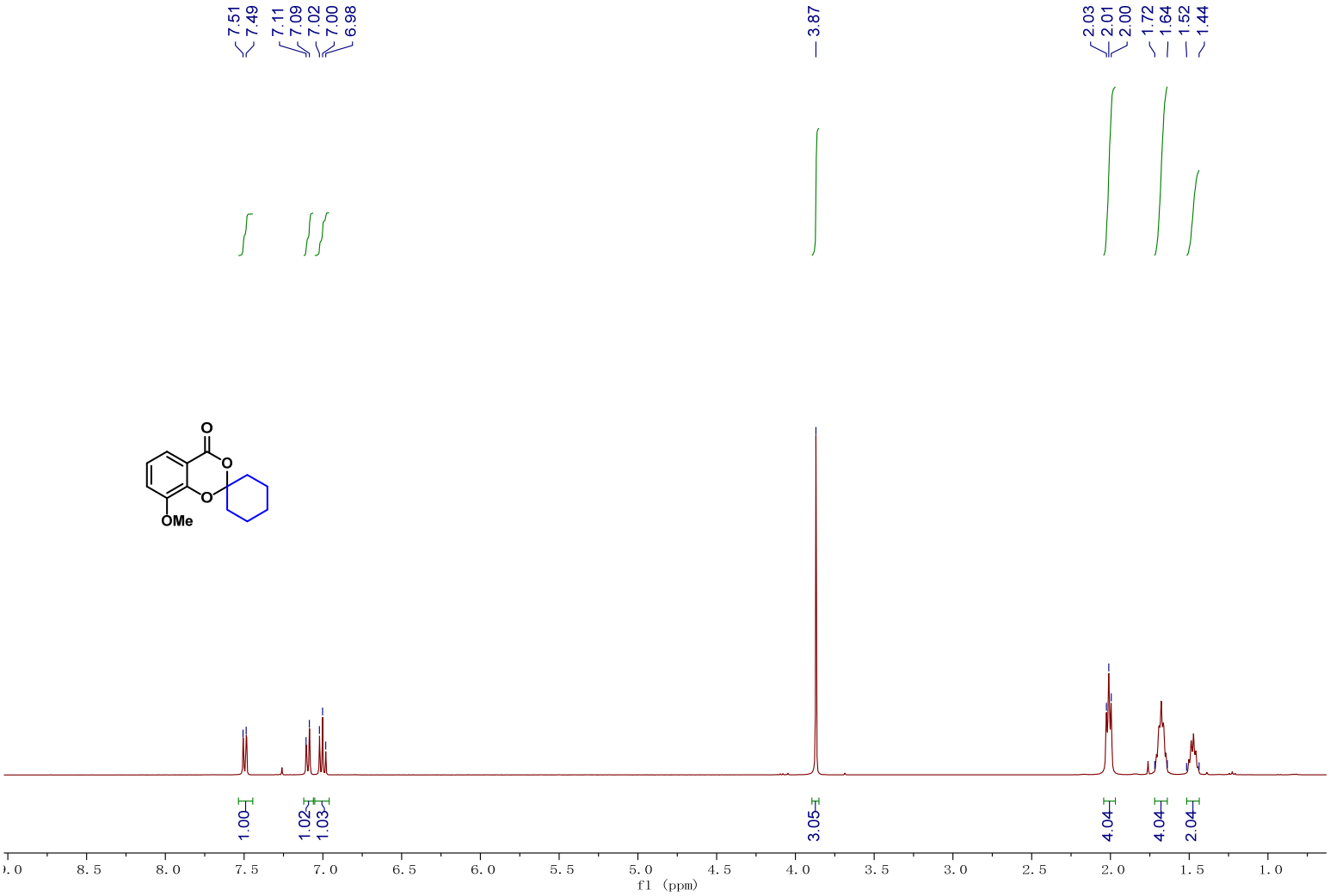
Compound S27 ^{1}H NMR



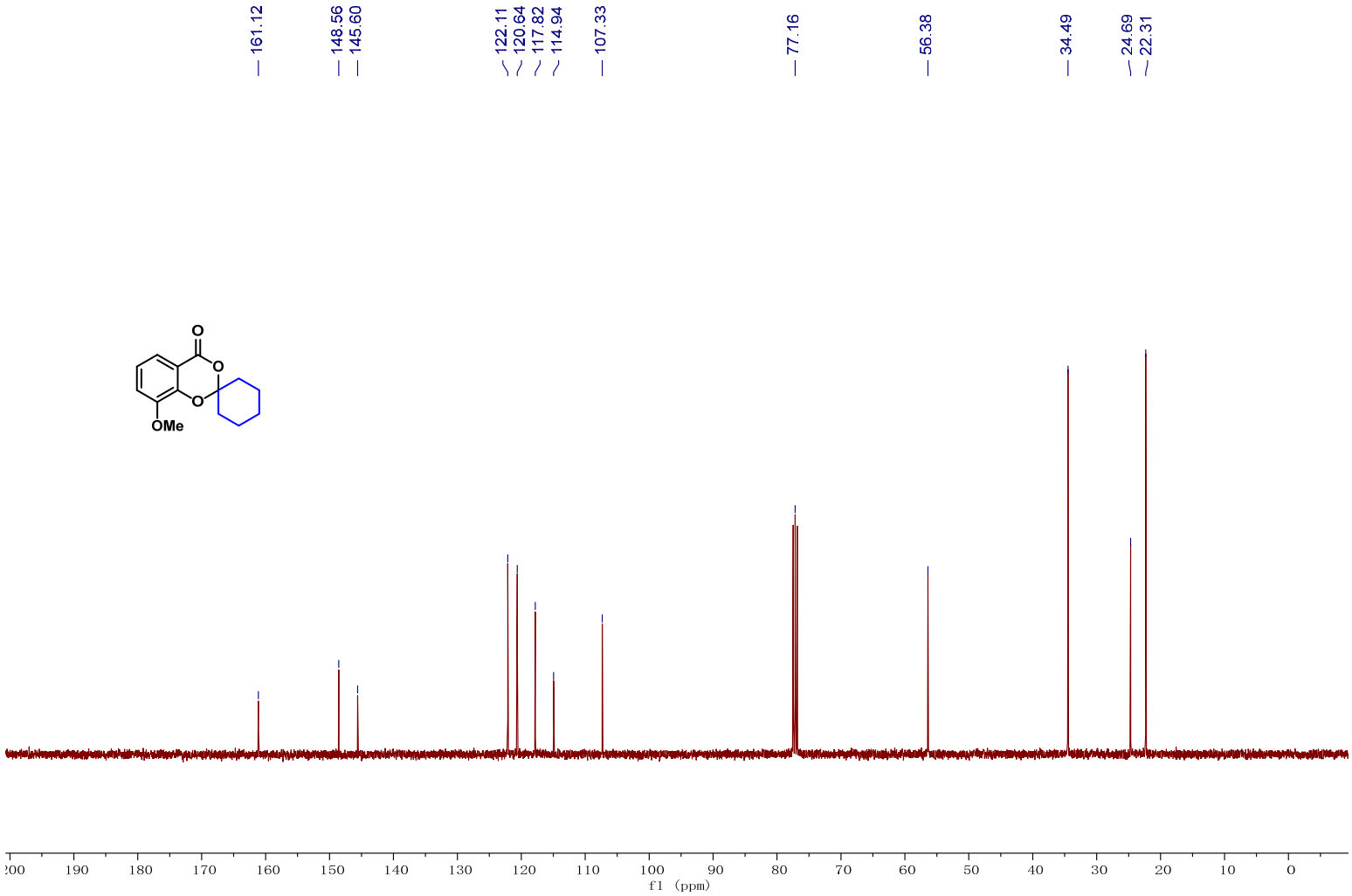
Compound S27 ^{13}C NMR



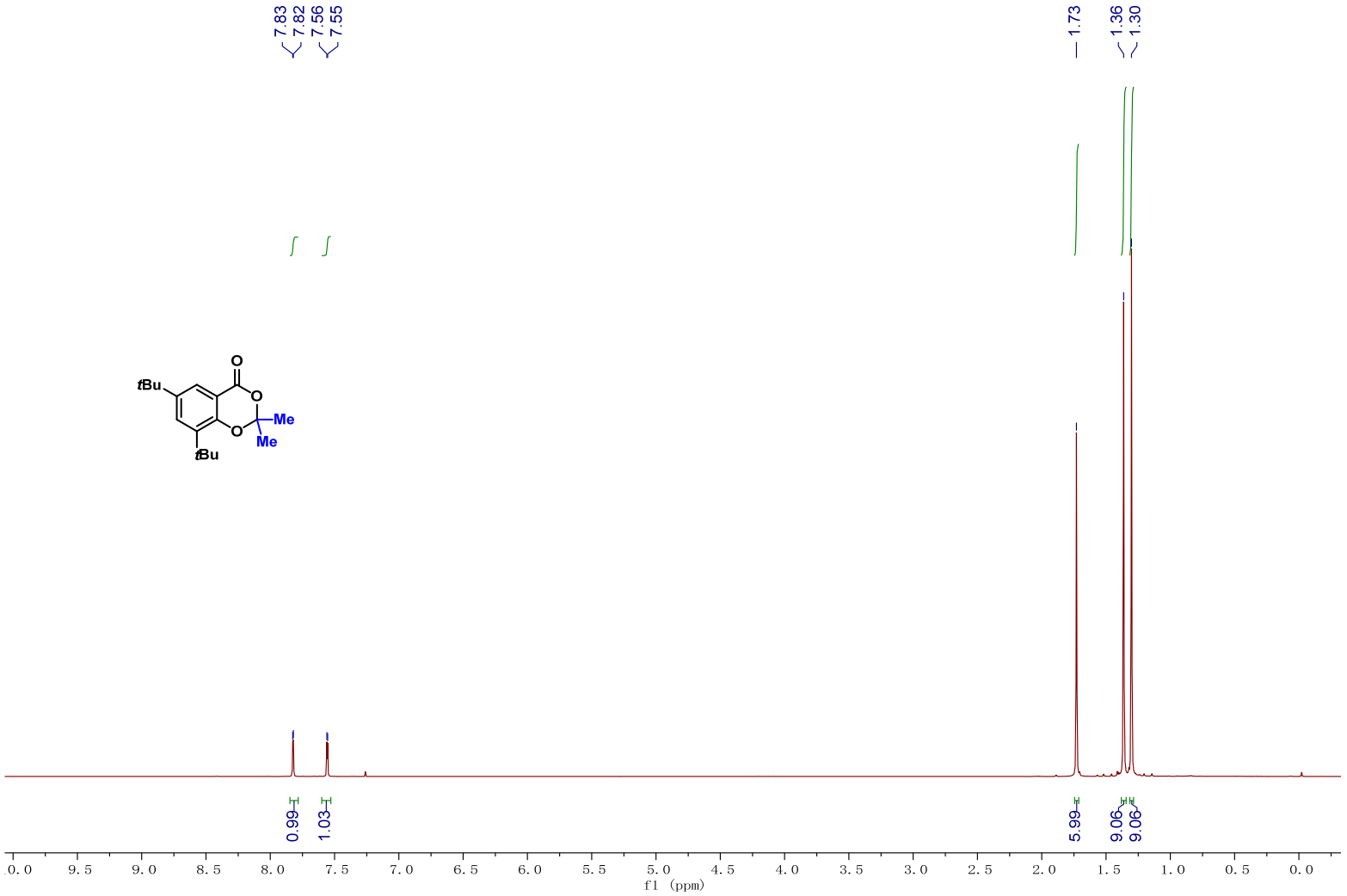
Compound S28 ^{1}H NMR



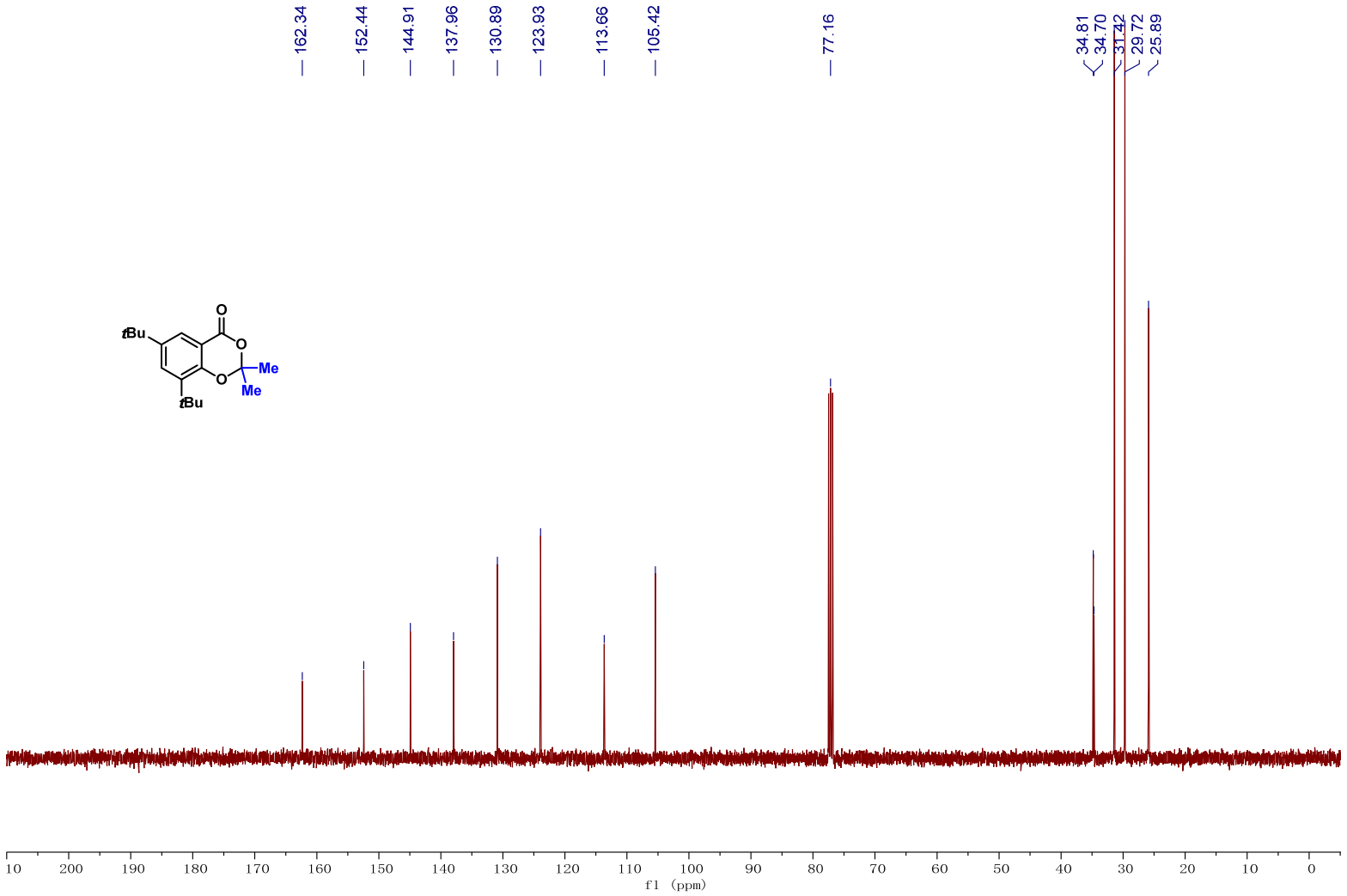
Compound S28 ^{13}C NMR



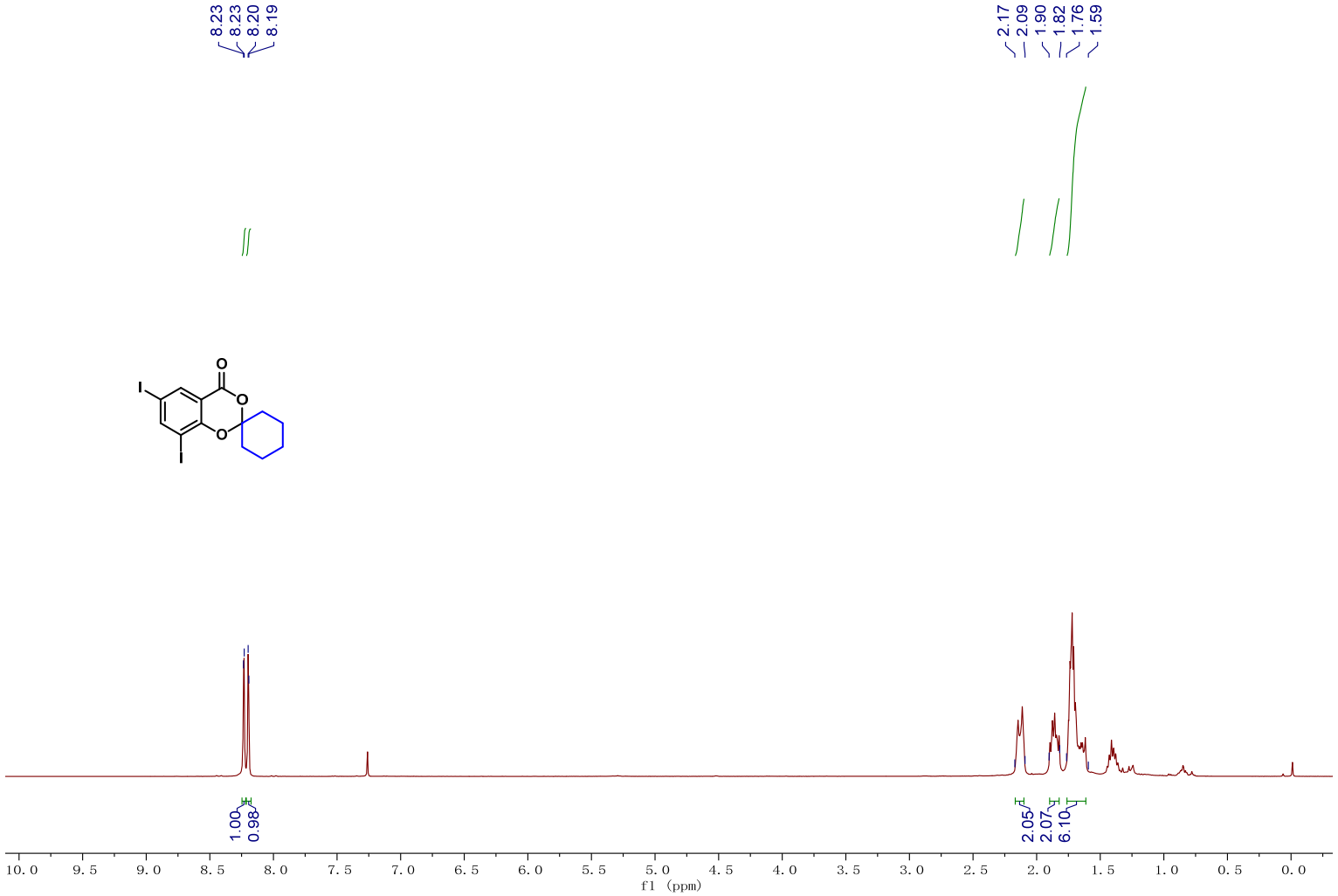
Compound S29 ^{1}H NMR



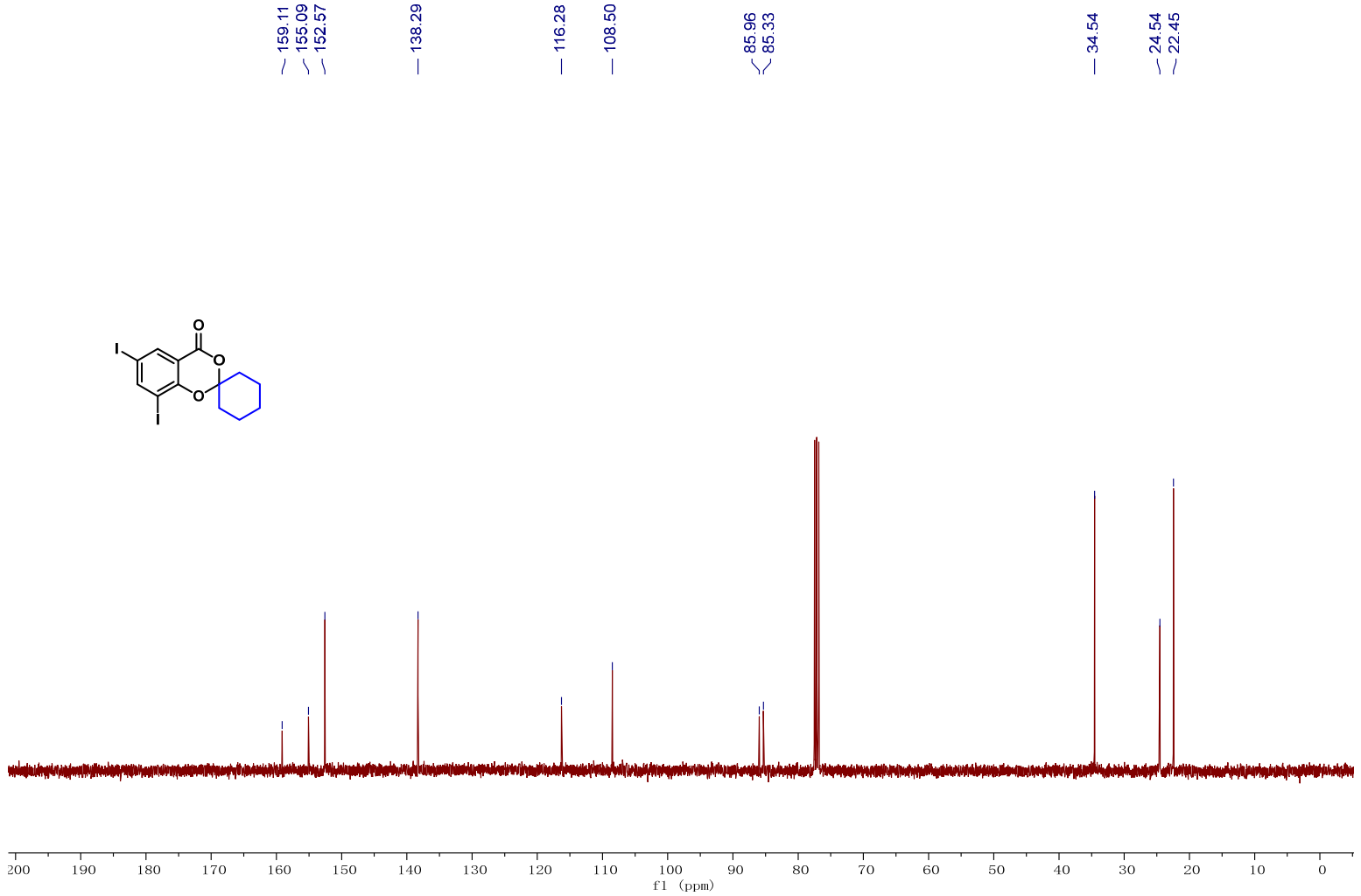
Compound S29 ^{13}C NMR



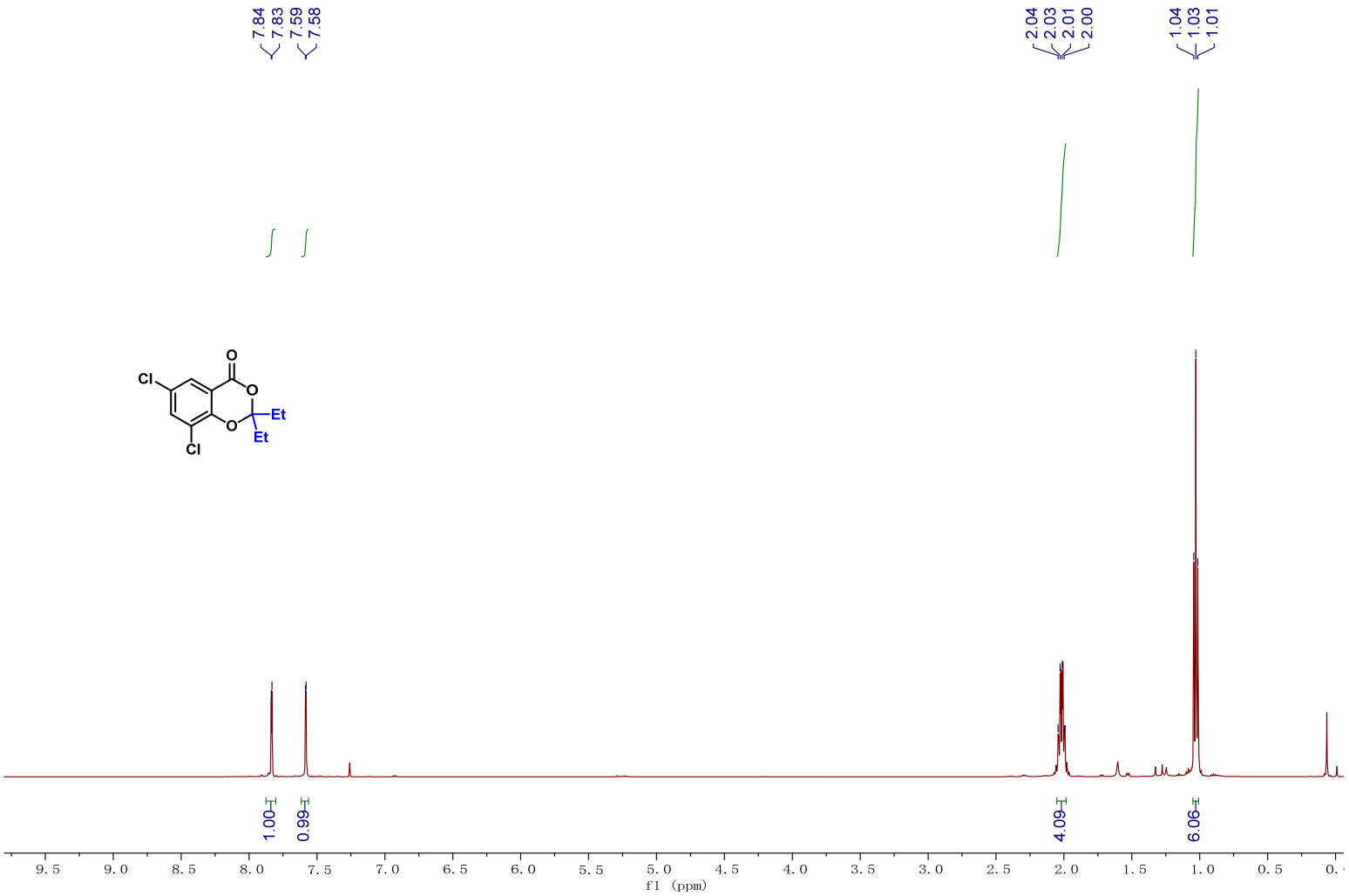
Compound S30 ^{1}H NMR



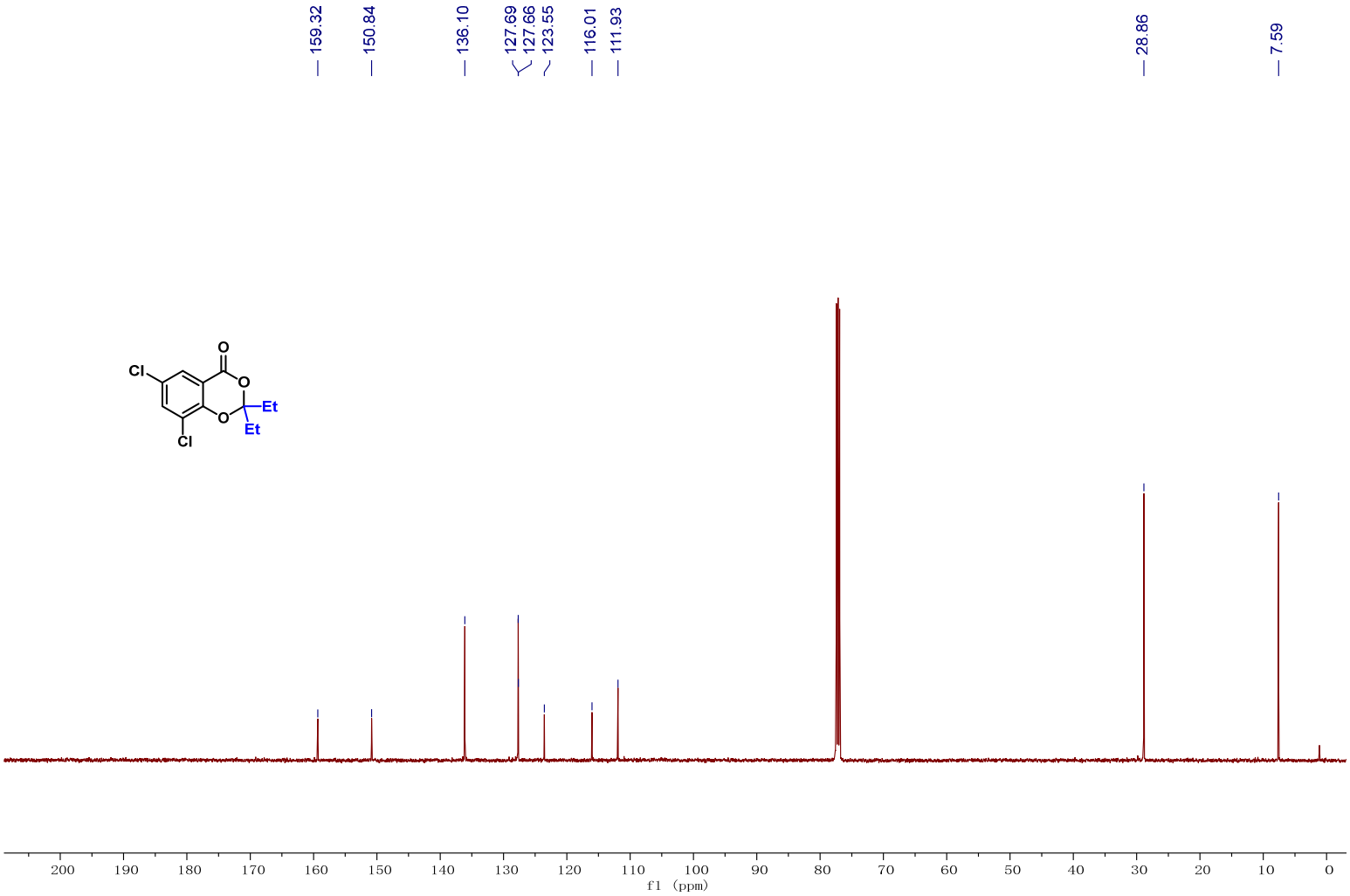
Compound S30 ^{13}C NMR



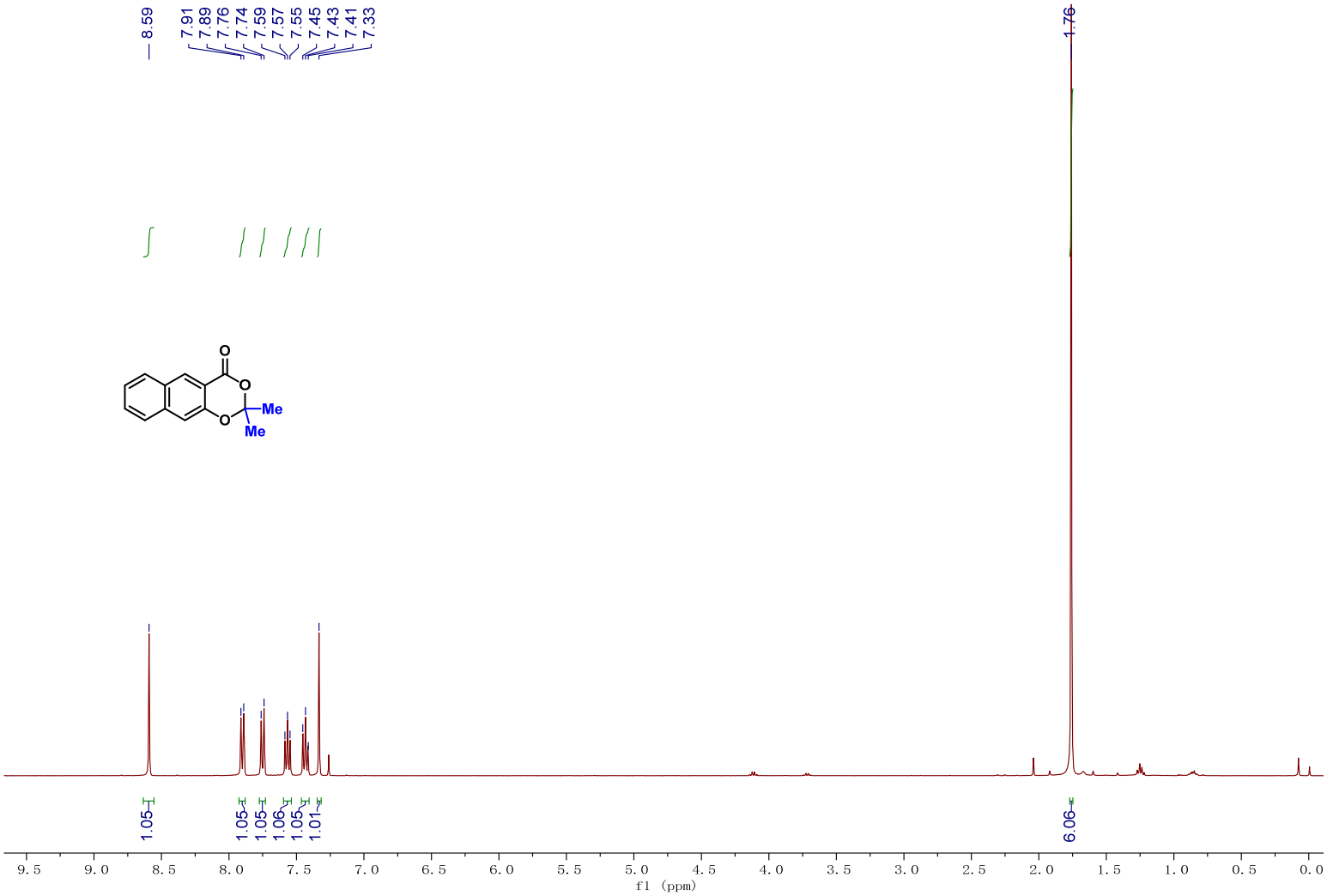
Compound S31 ^{1}H NMR



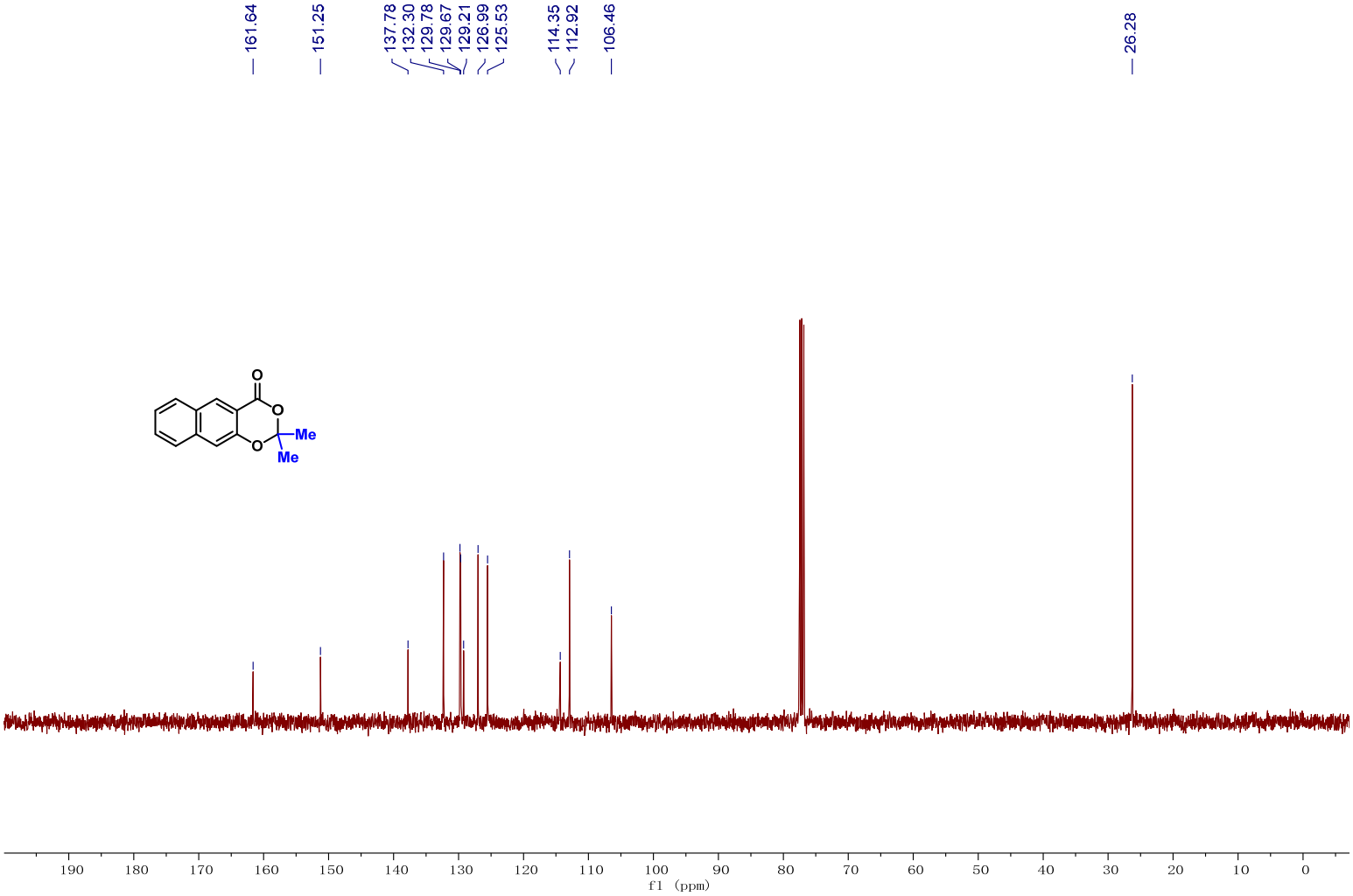
Compound S31 ^{13}C NMR



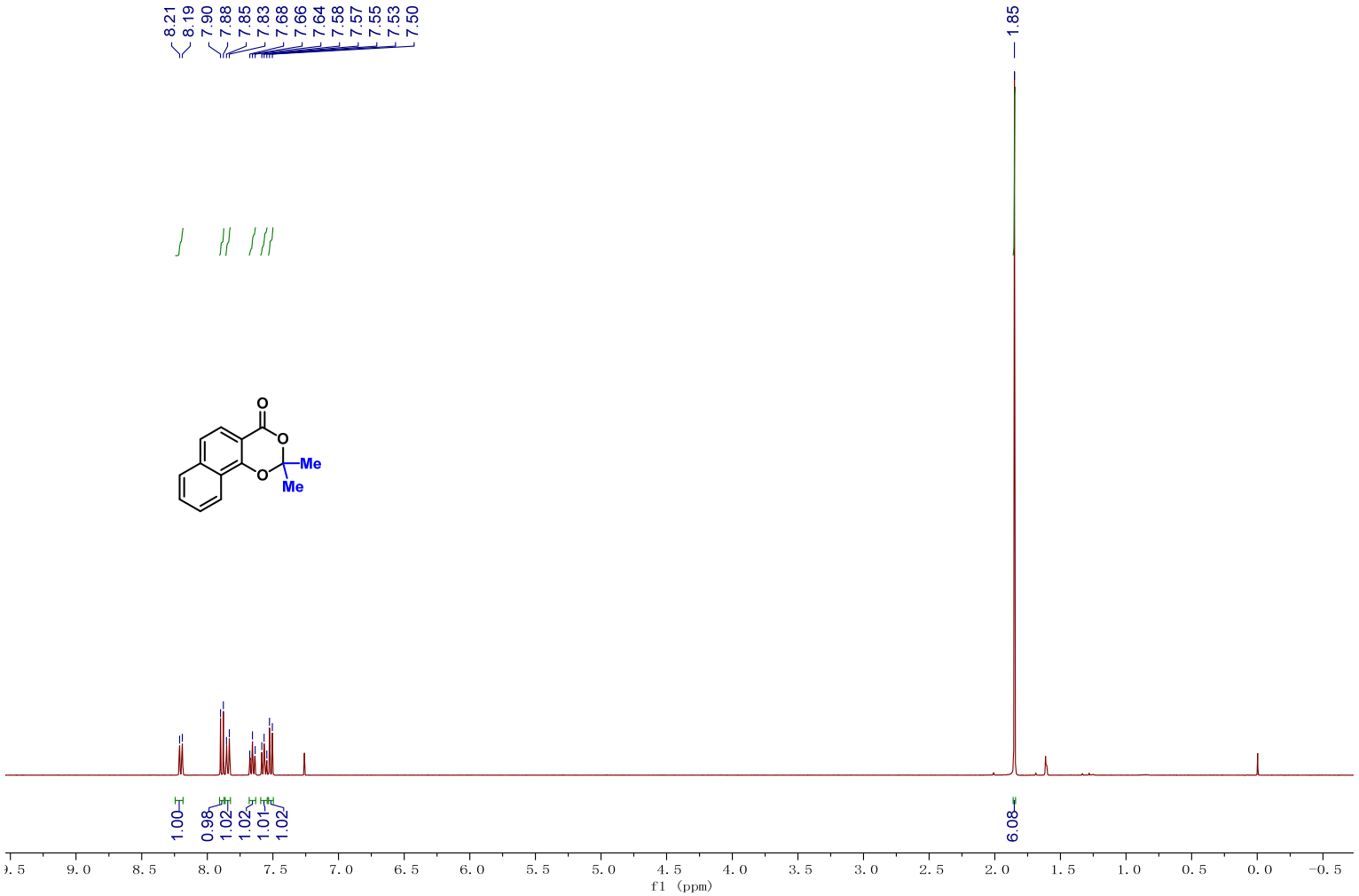
Compound S32 ^{1}H NMR



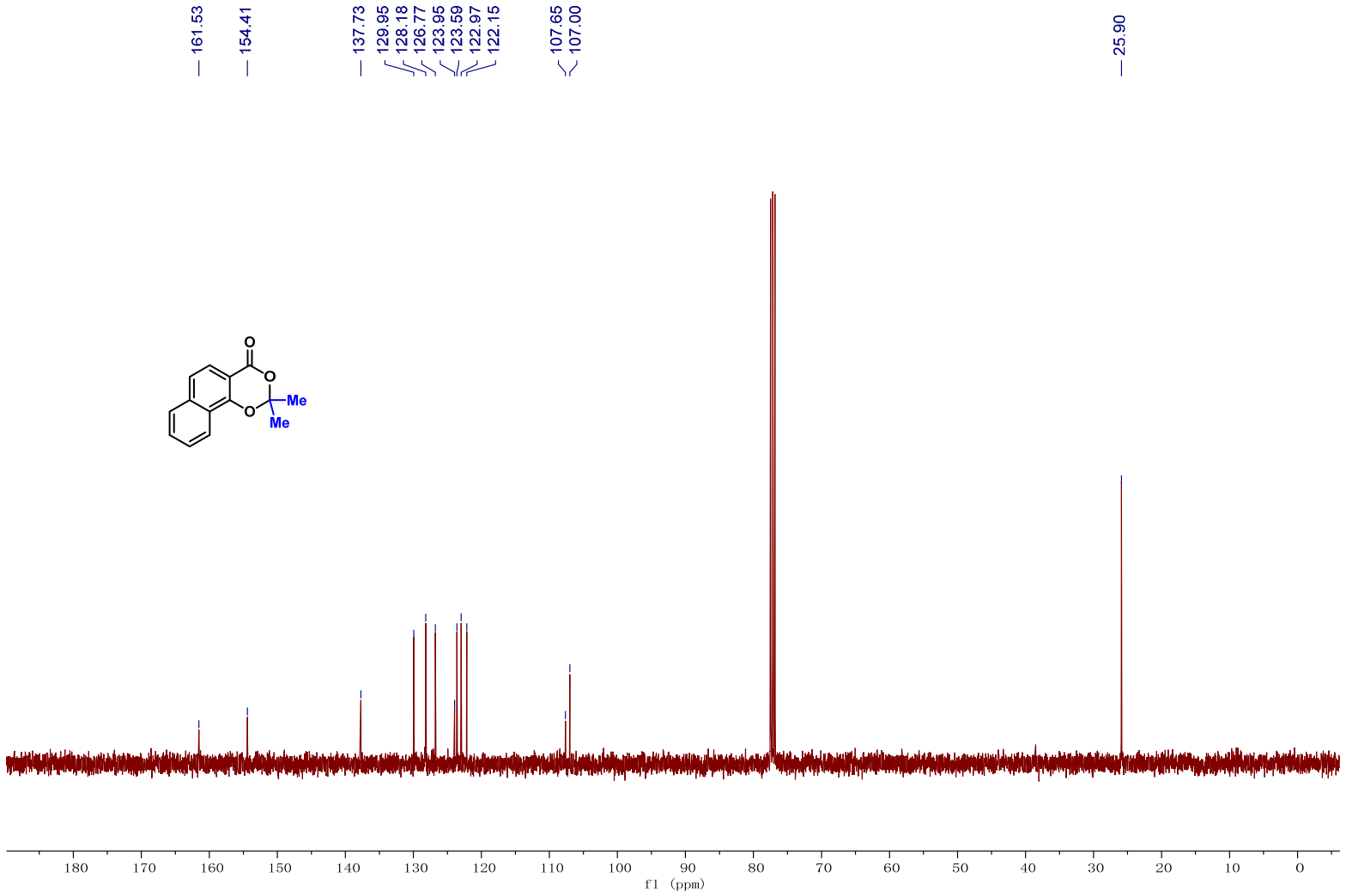
Compound S32 ^{13}C NMR



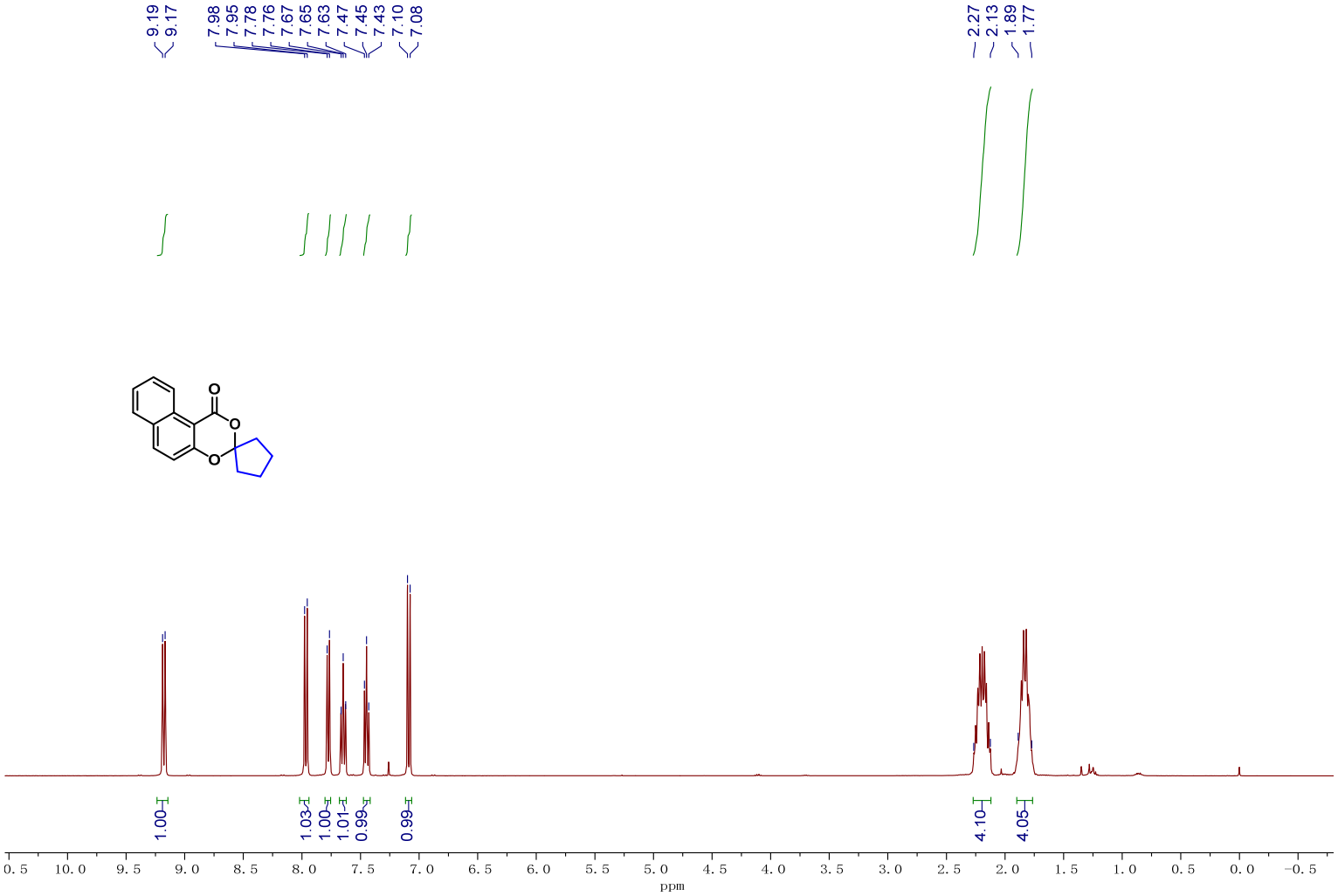
Compound S33 ^{1}H NMR



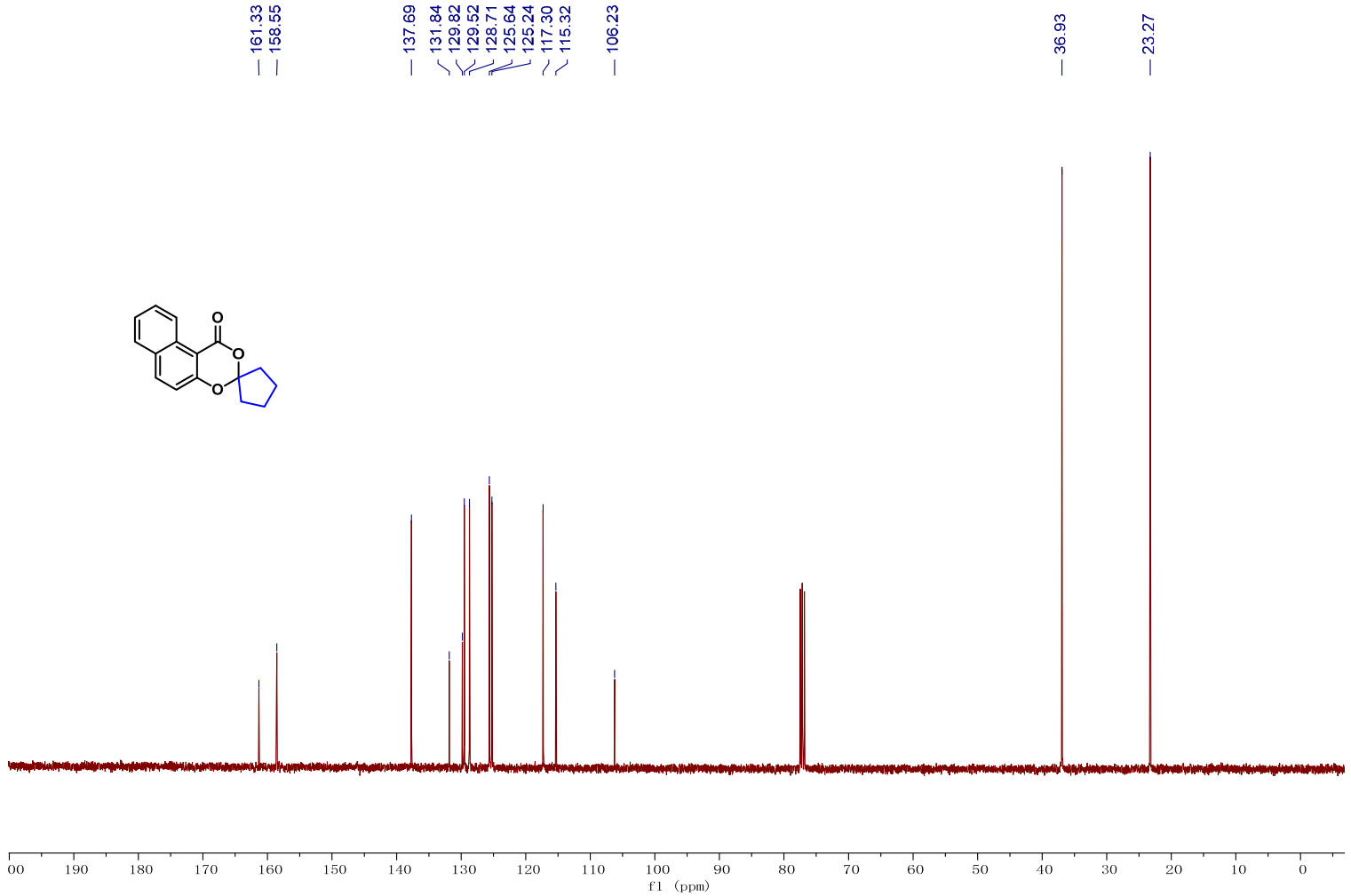
Compound S33 ^{13}C NMR



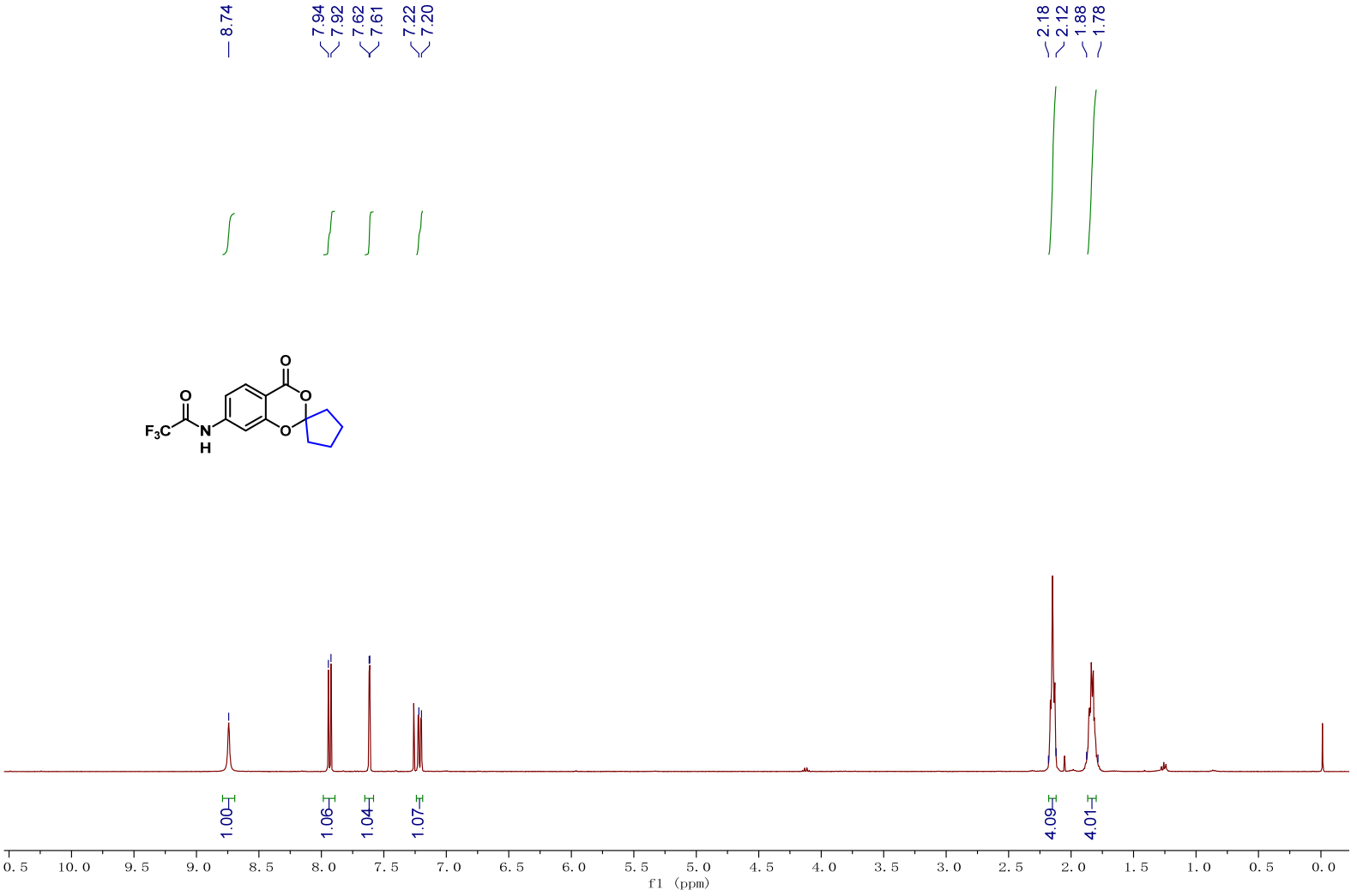
Compound S34 ^{1}H NMR



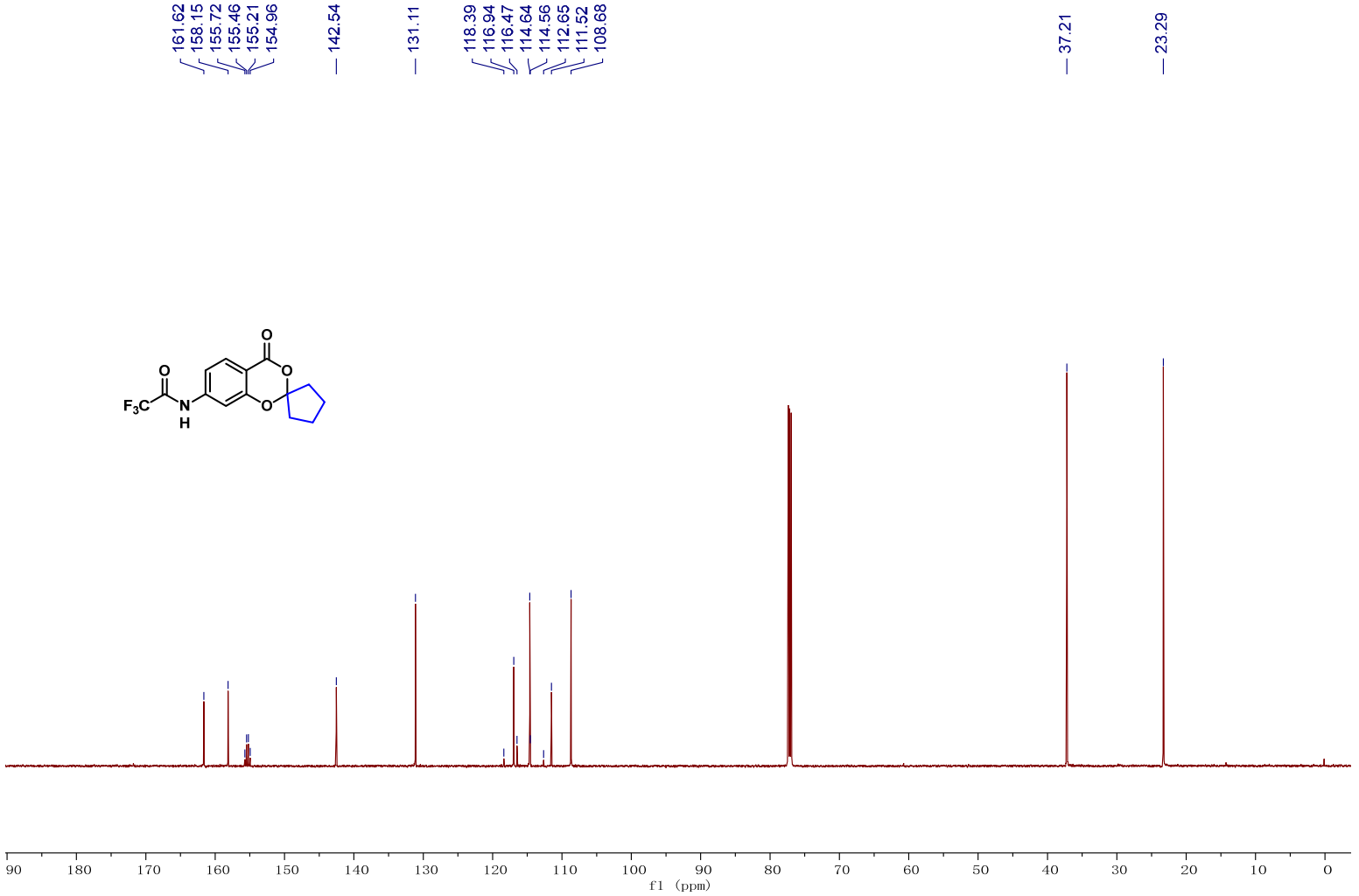
Compound S34 ^{13}C NMR



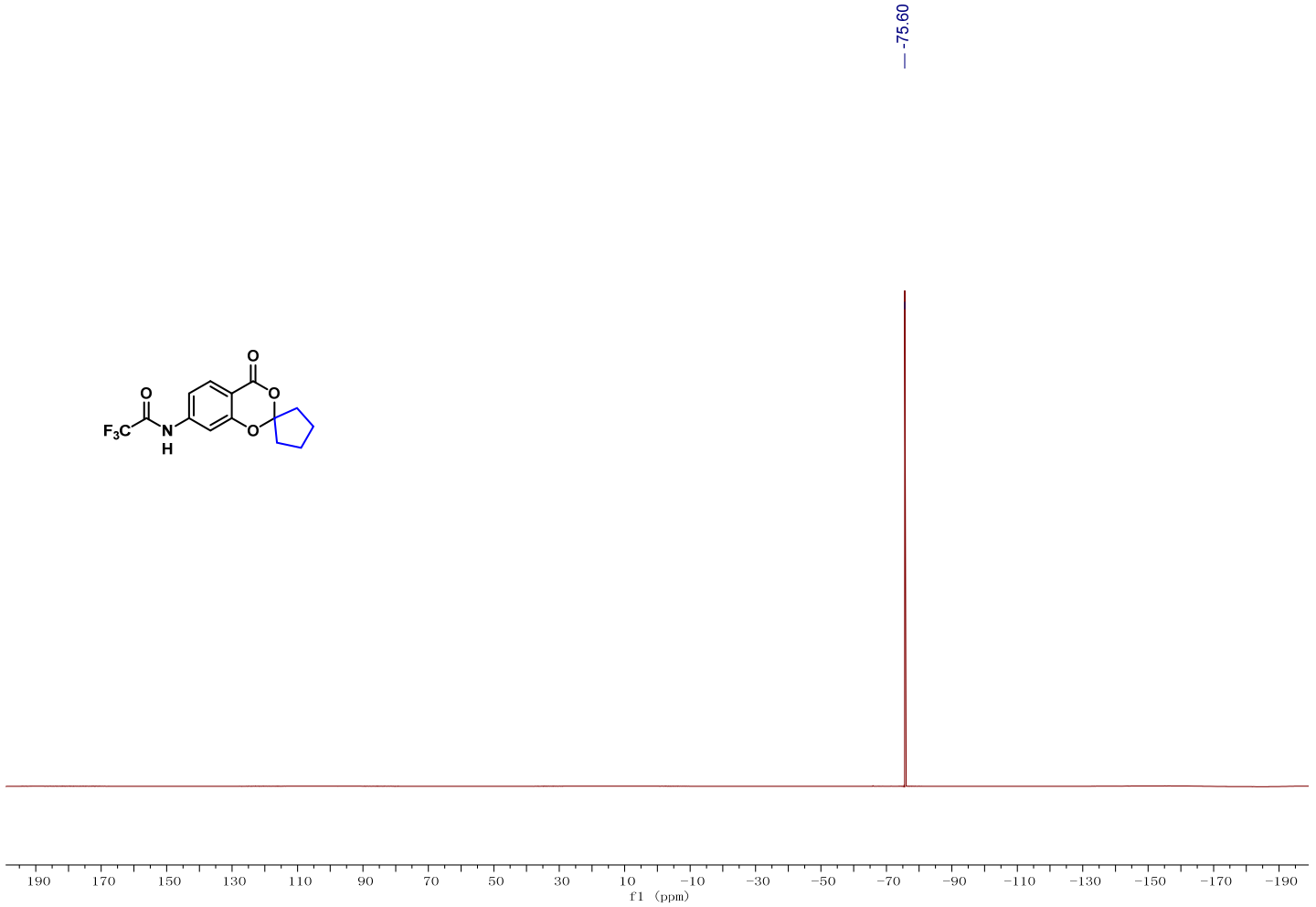
Compound S35 ^{1}H NMR



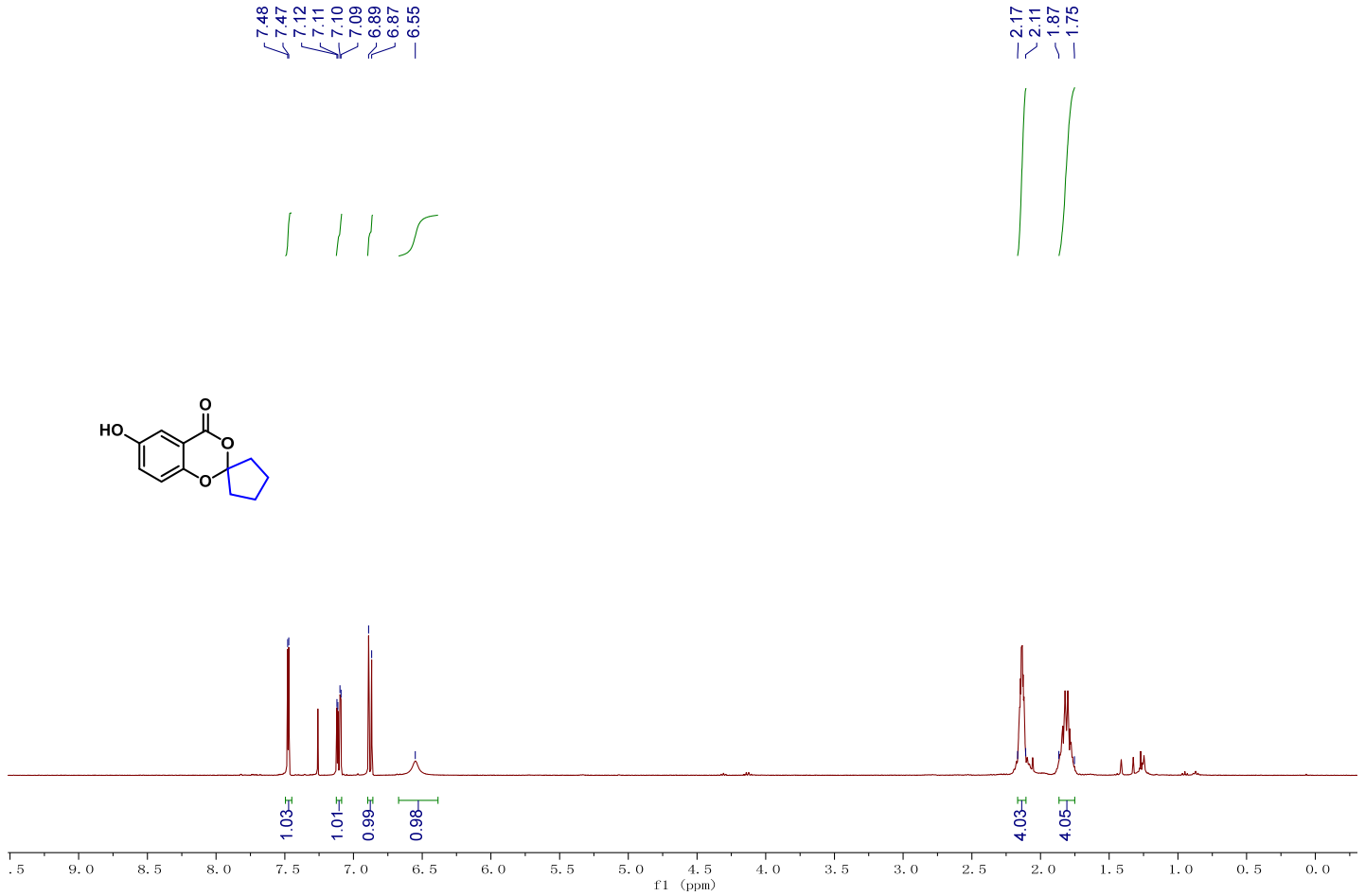
Compound S35 ^{13}C NMR



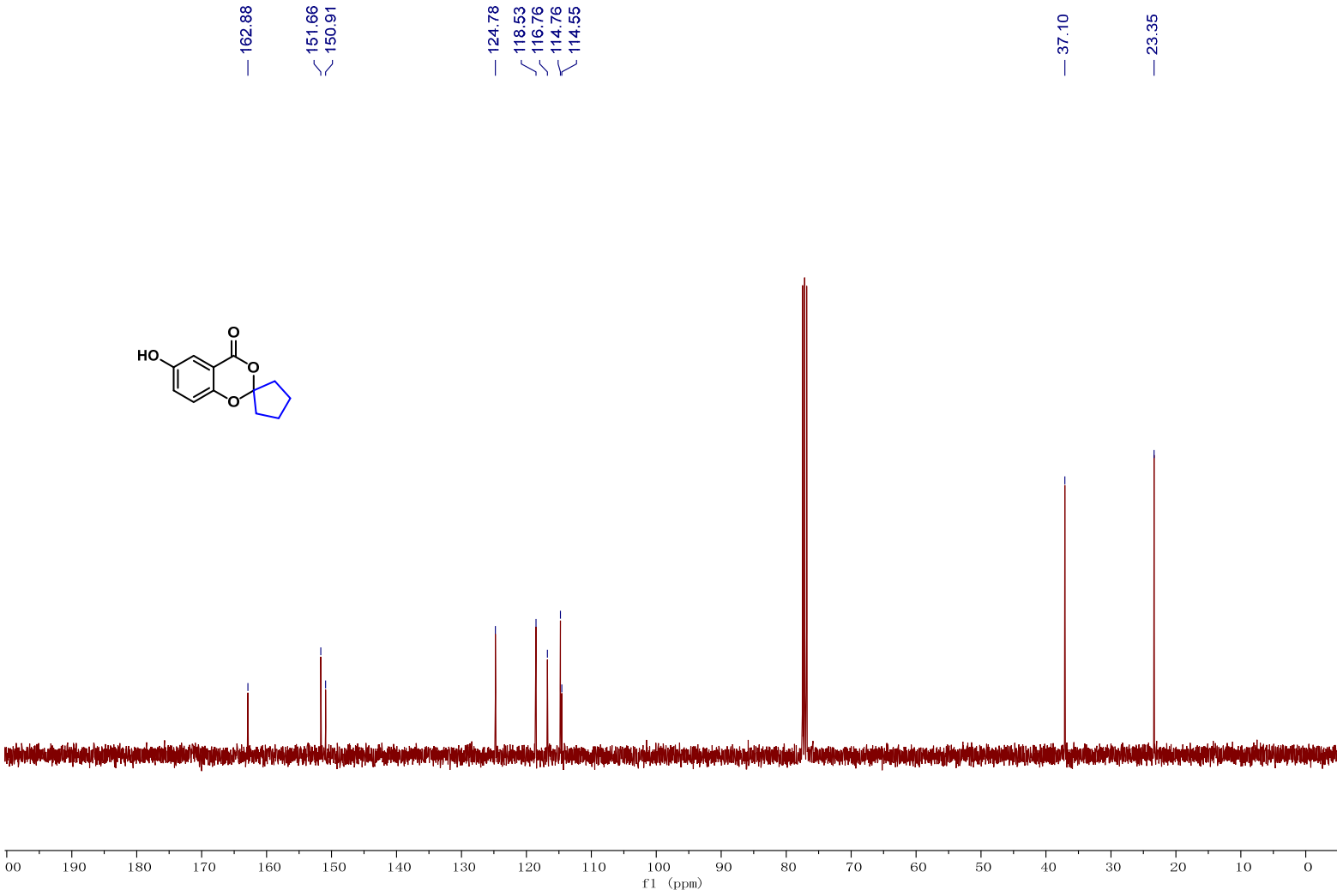
Compound S35 ^{19}F NMR



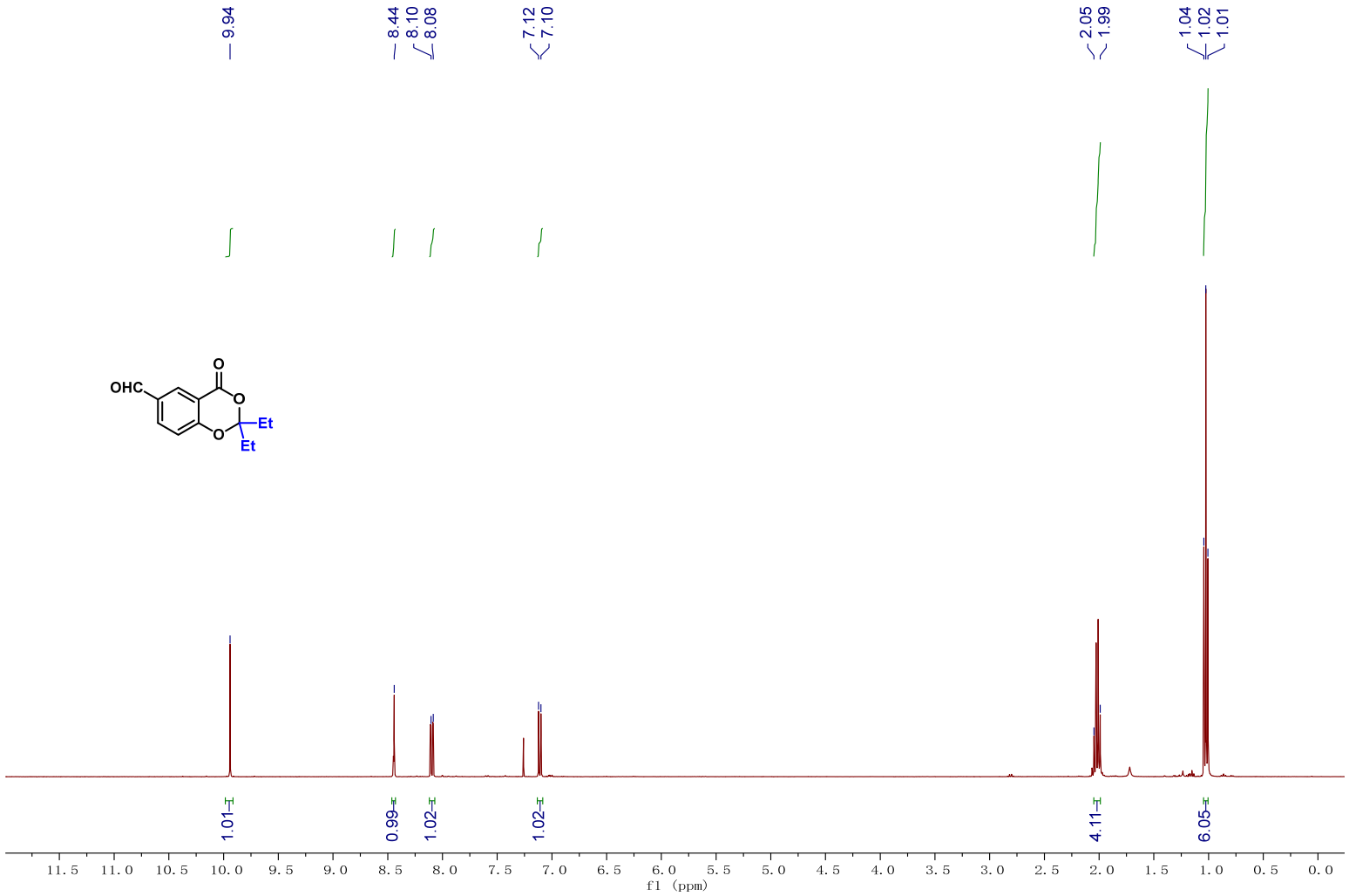
Compound S36 ^{1}H NMR



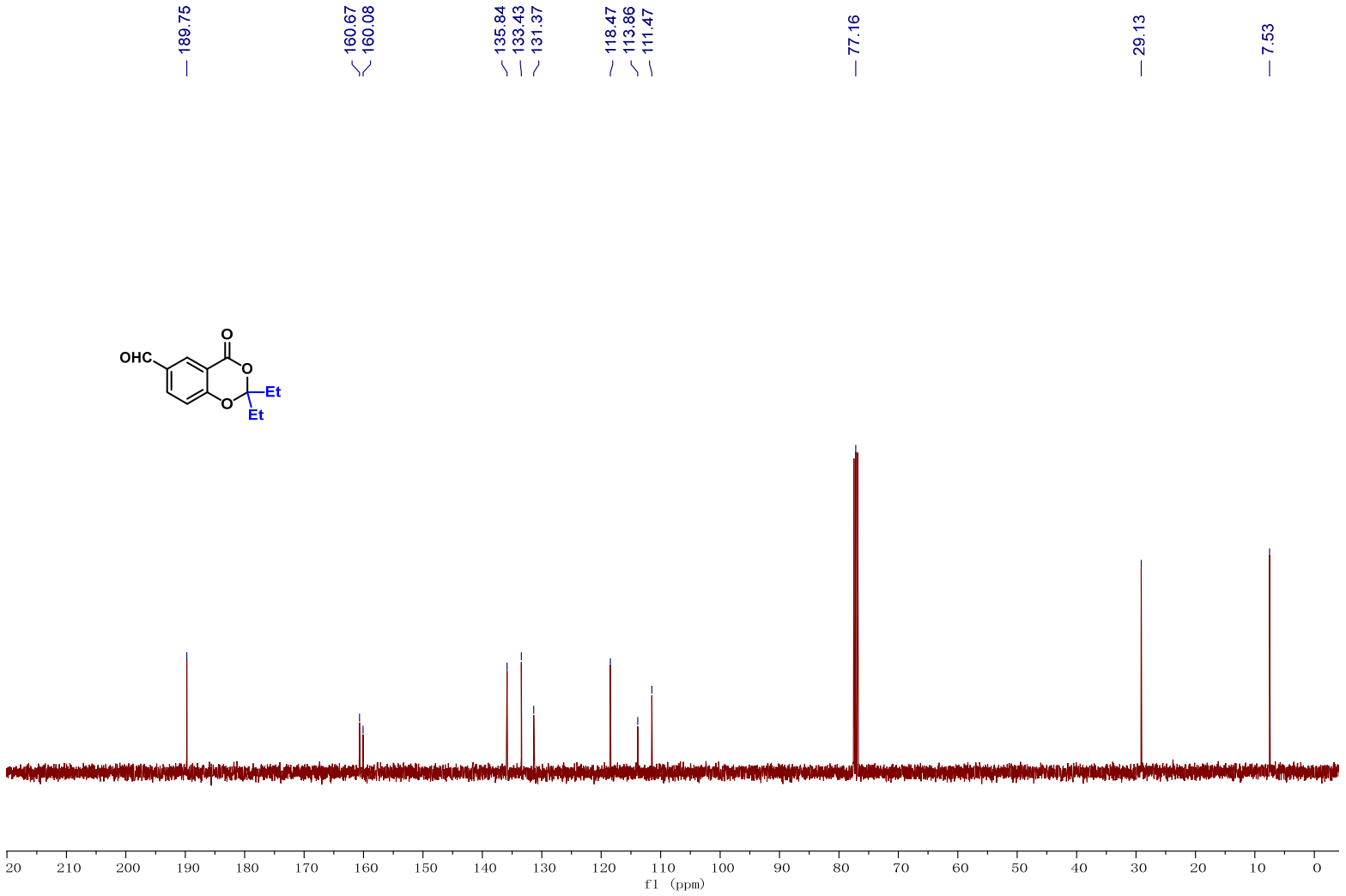
Compound S36 ^{13}C NMR



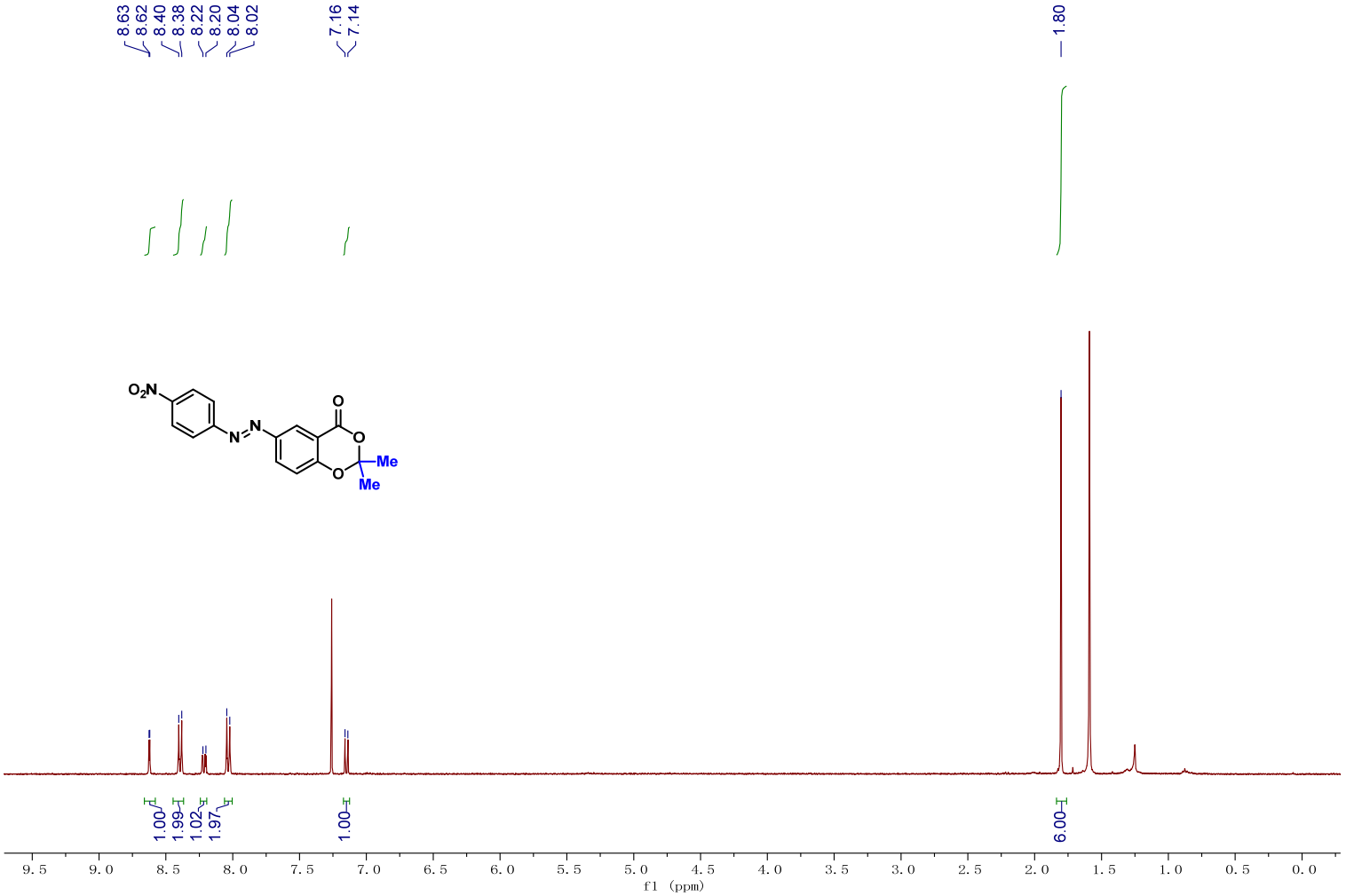
Compound S37 ^{1}H NMR



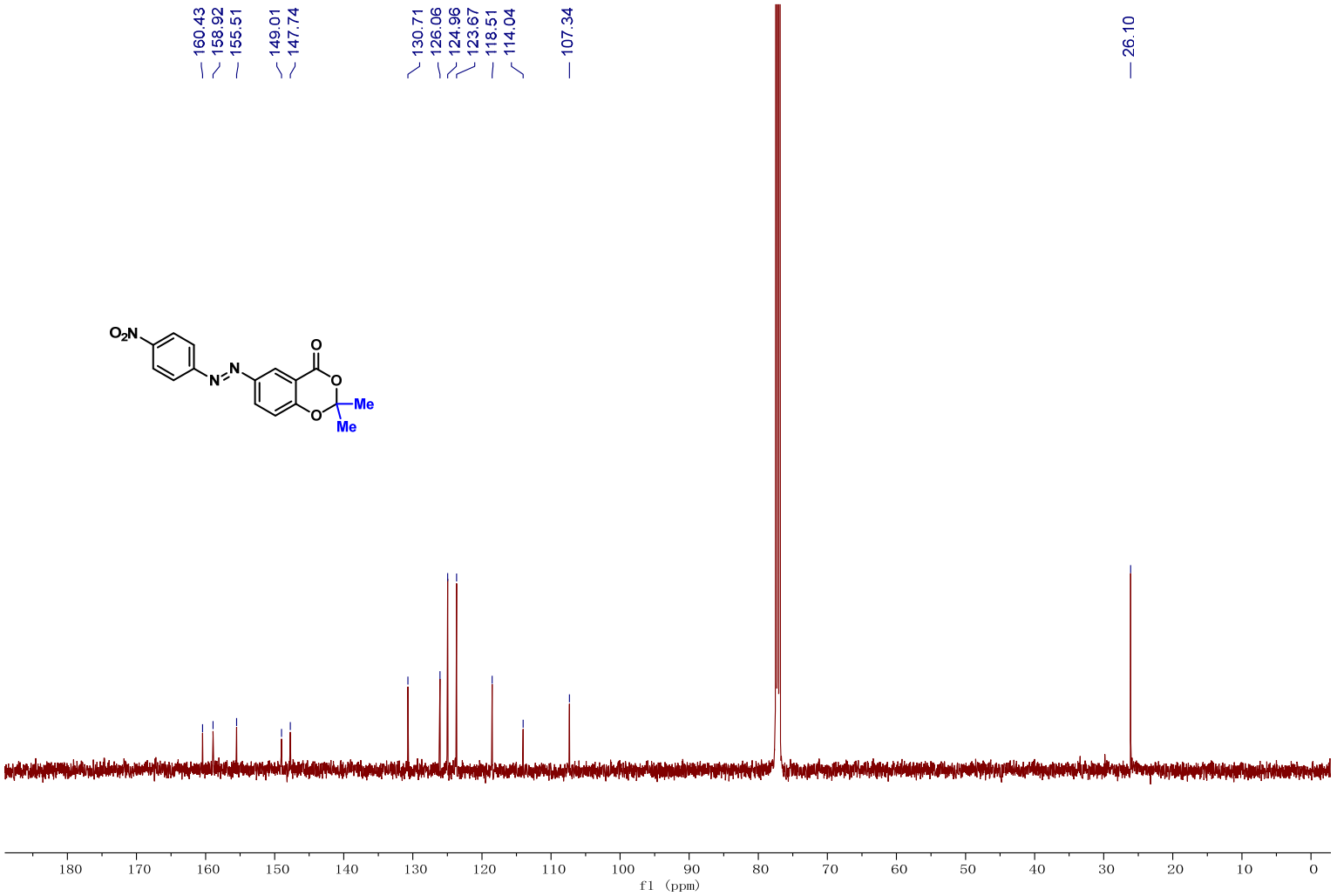
Compound S37 ^{13}C NMR



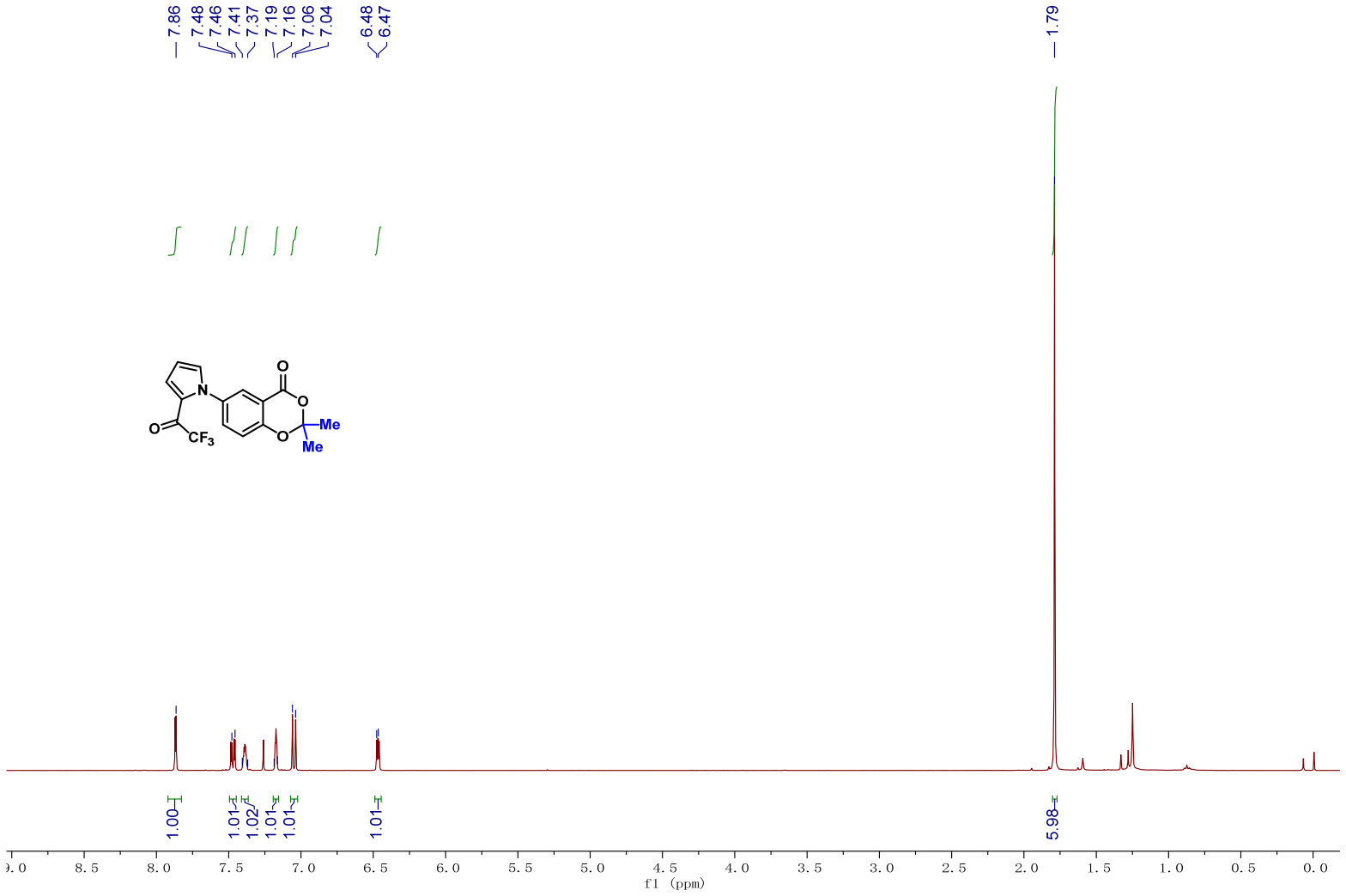
Compound S38 ^{1}H NMR



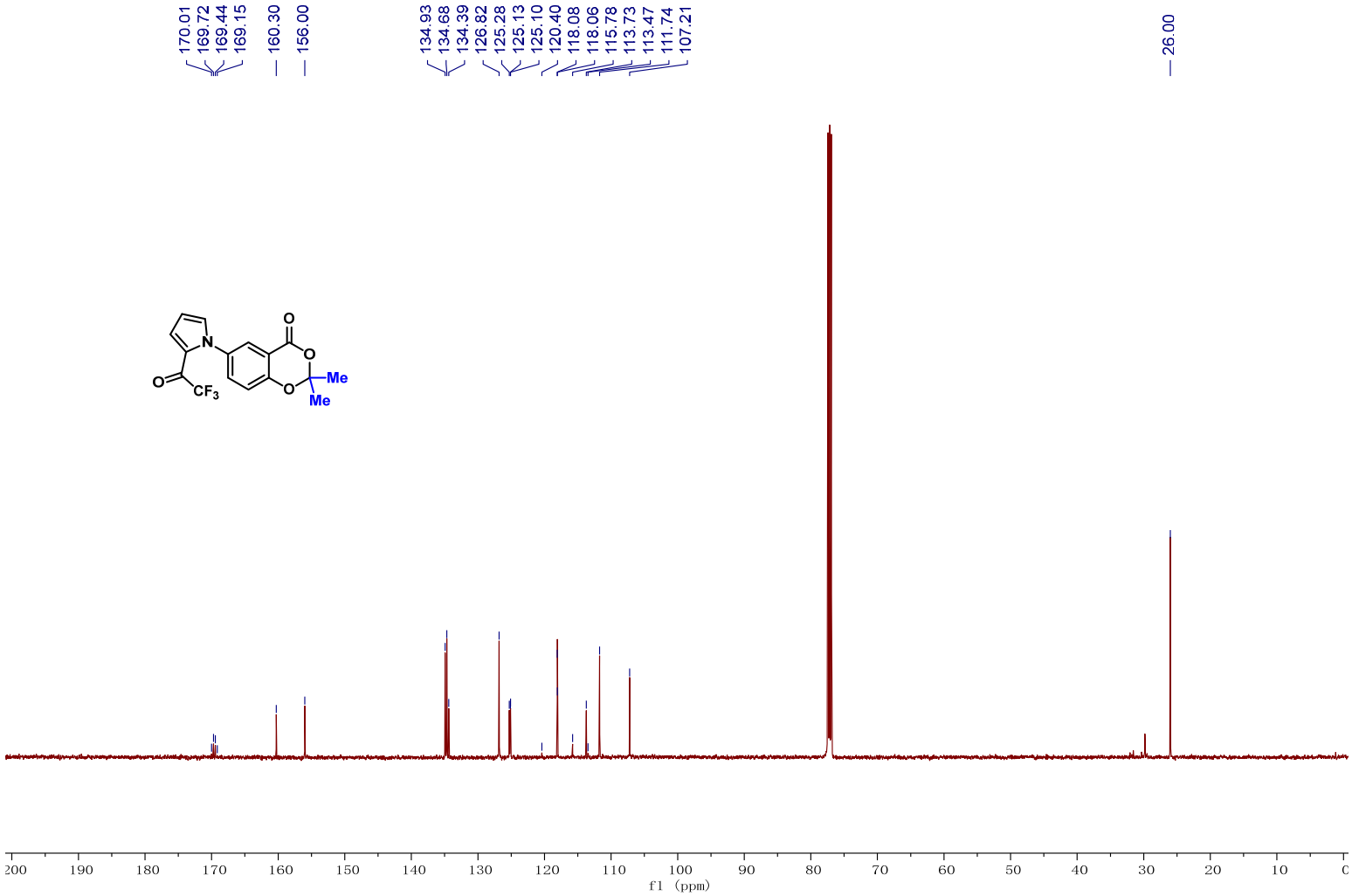
Compound S38 ^{13}C NMR



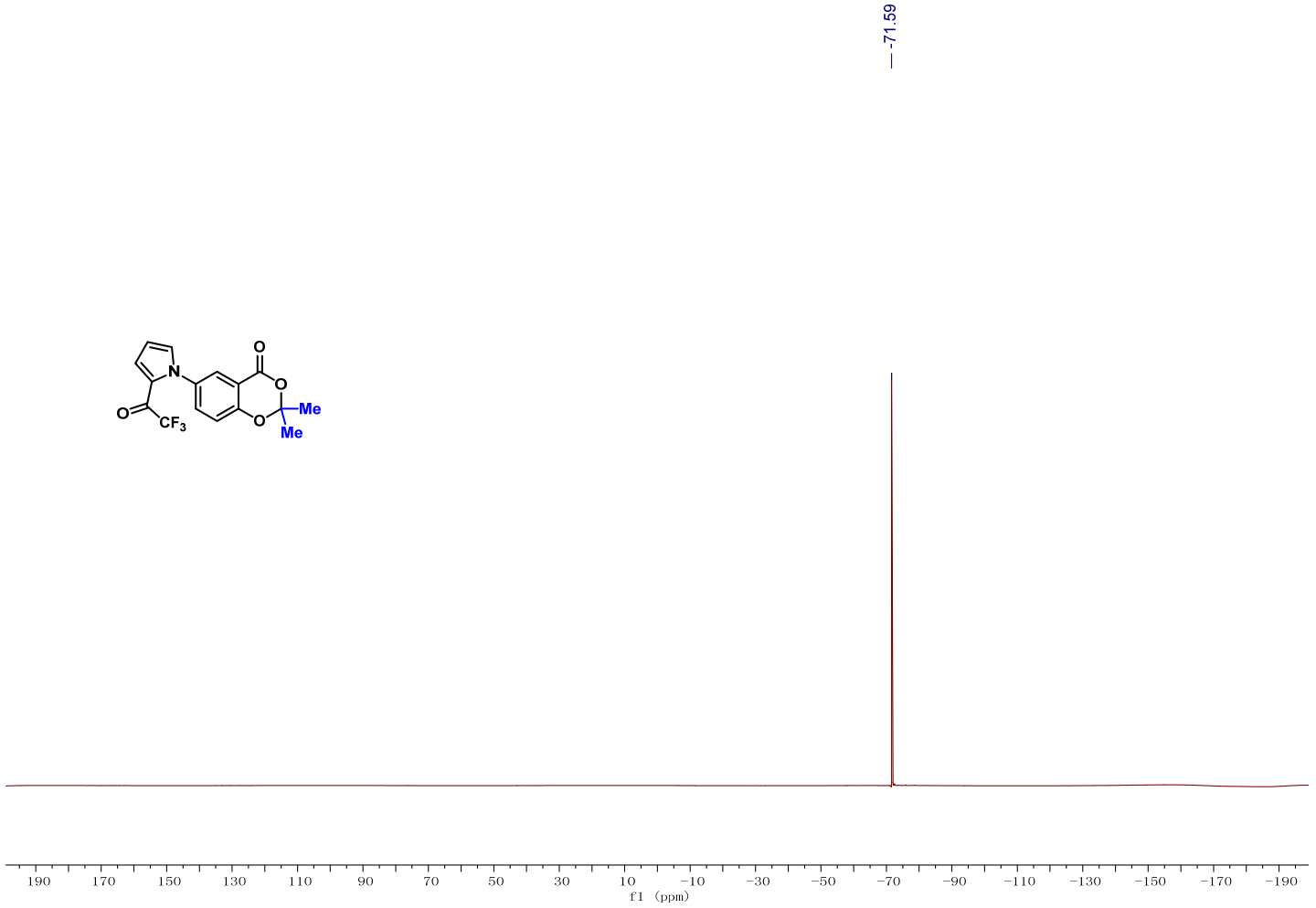
Compound S39 ^{1}H NMR



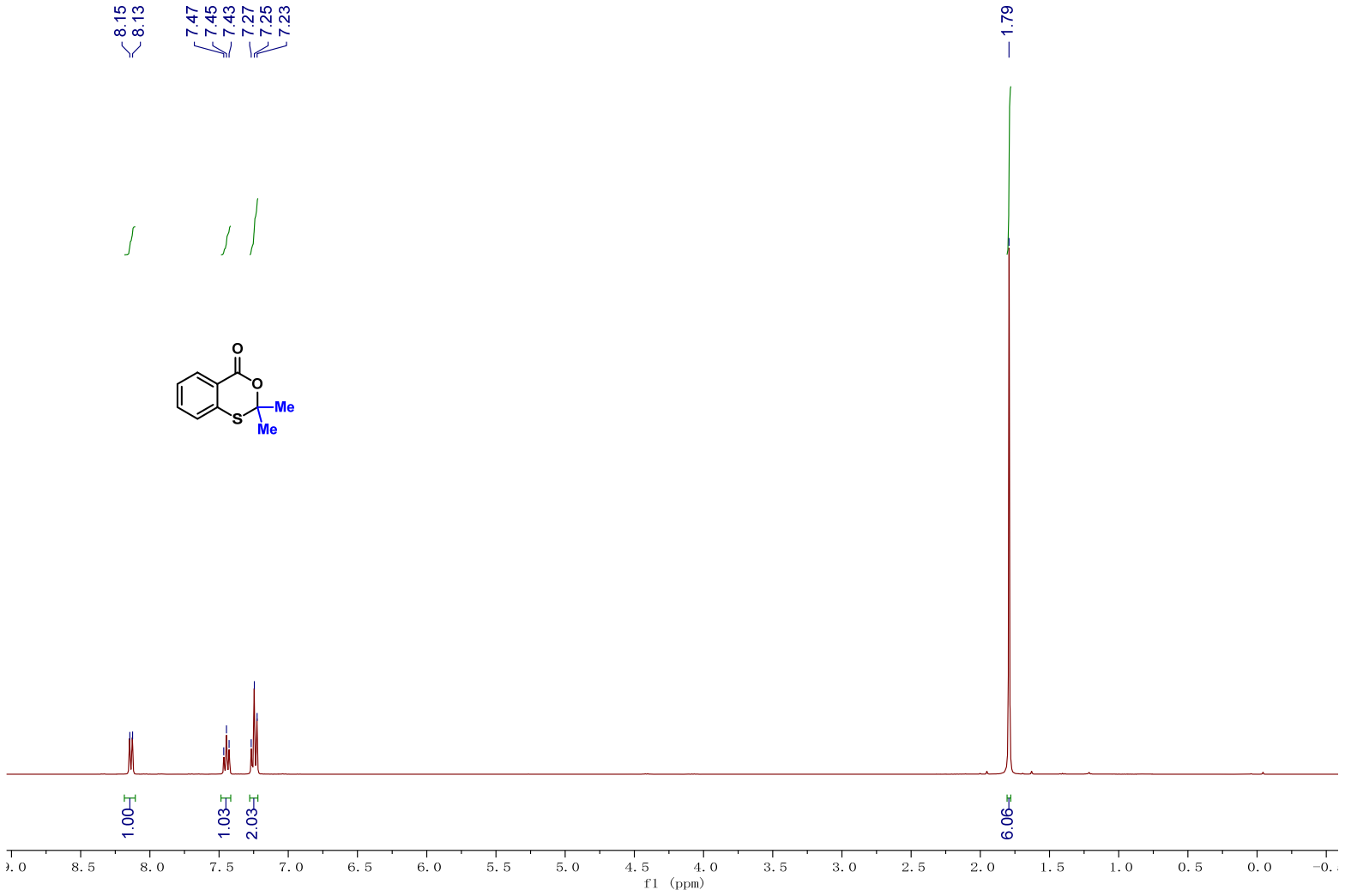
Compound S39 ^{13}C NMR



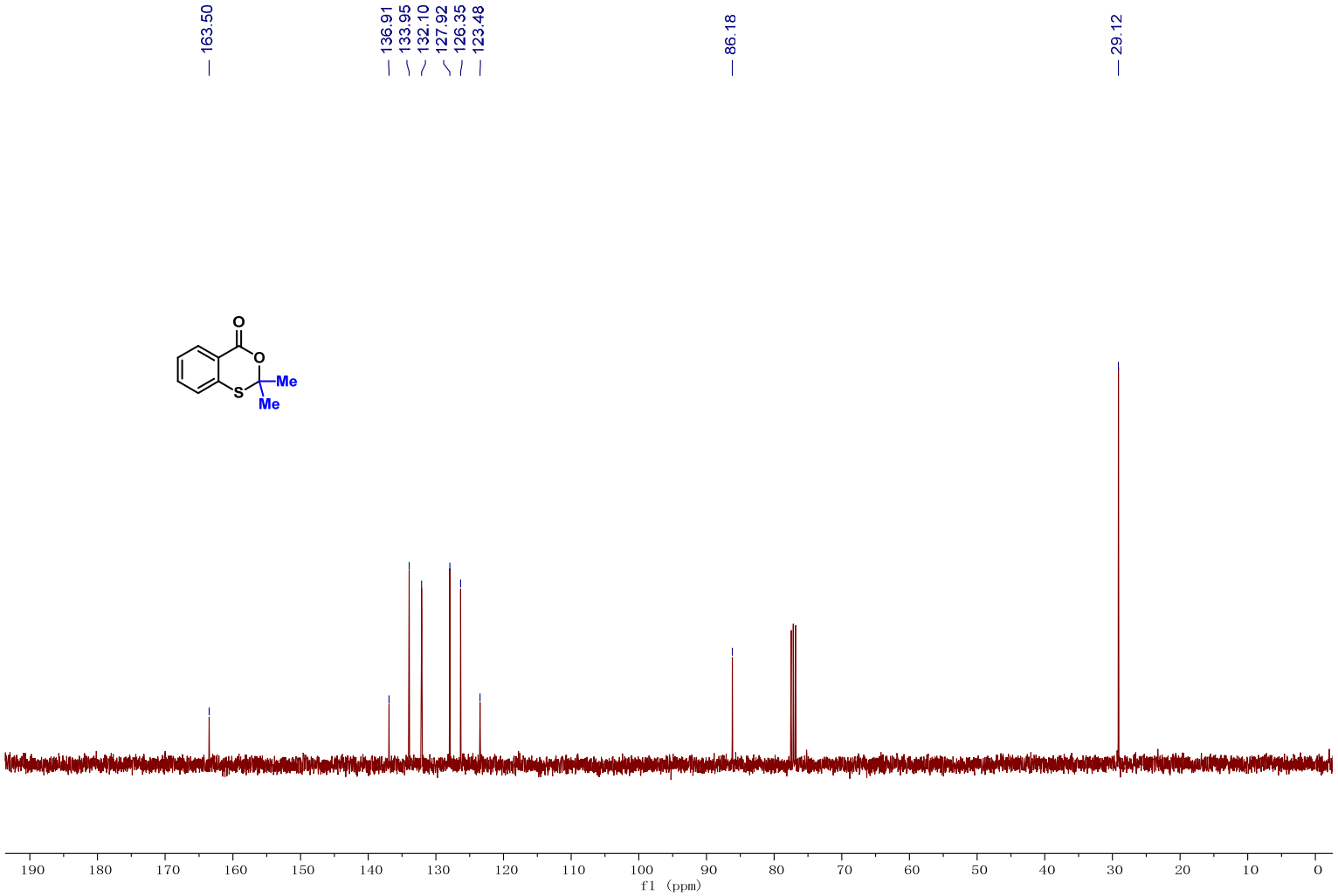
Compound S39 ^{19}F NMR



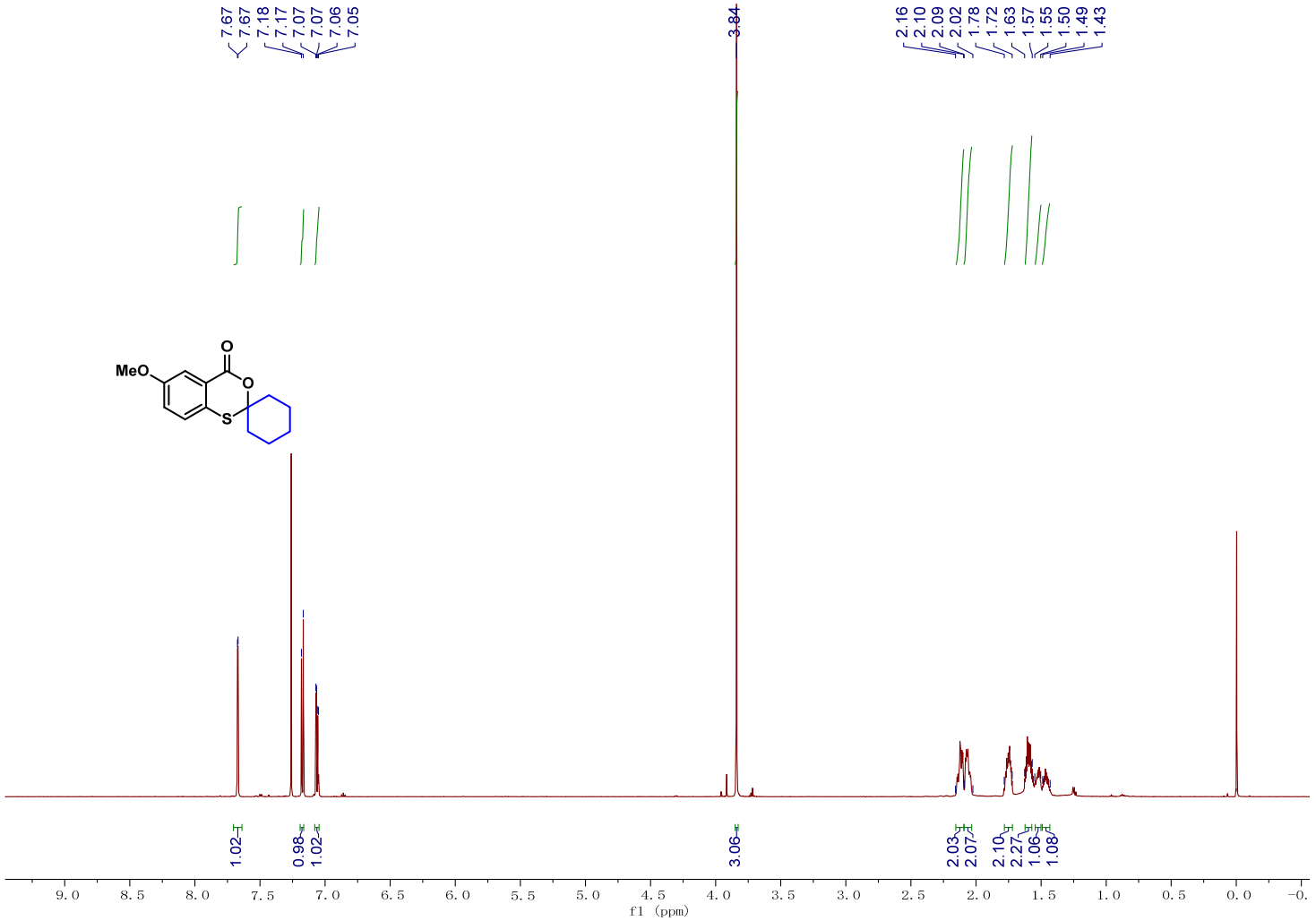
Compound S40 ^{1}H NMR



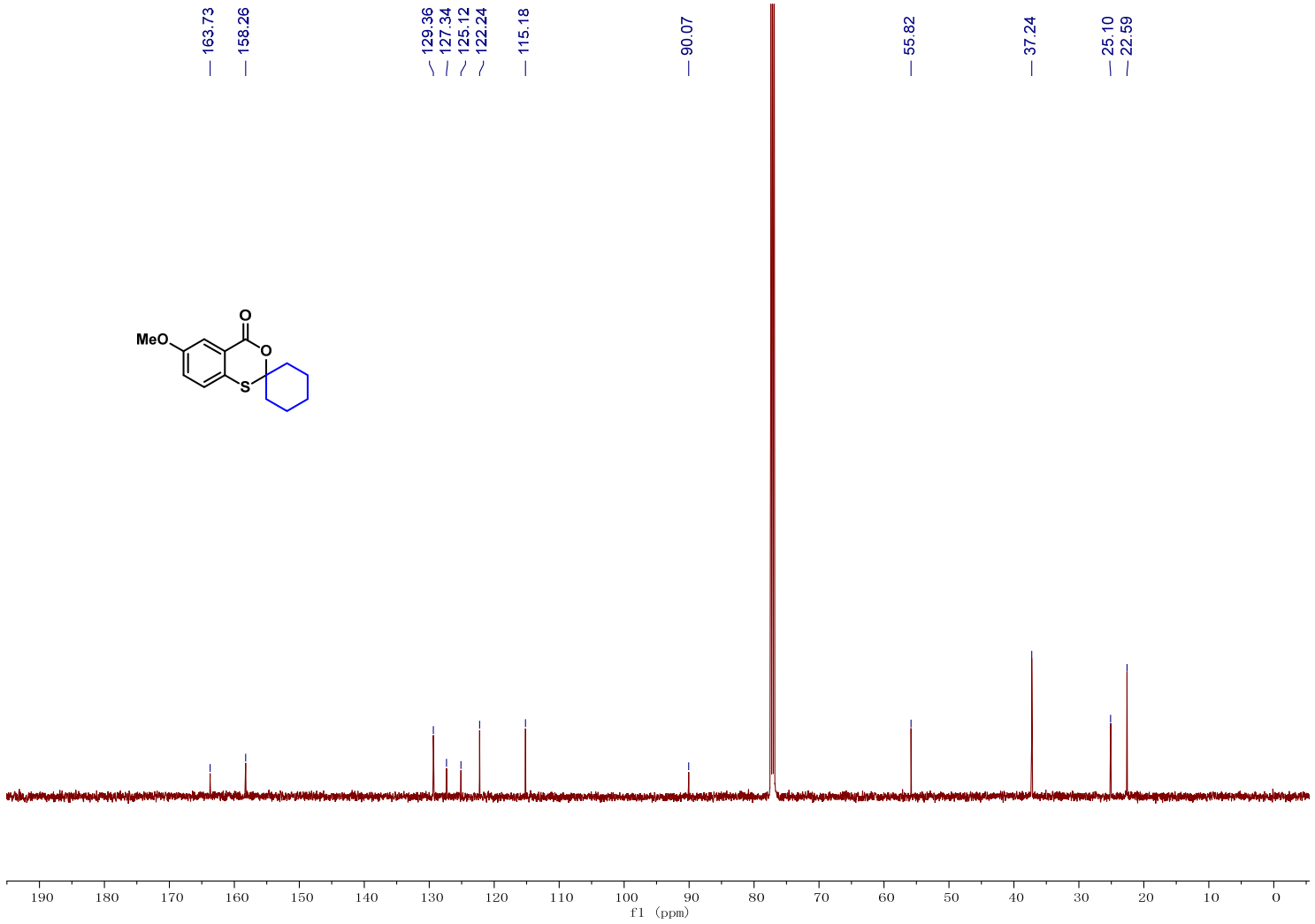
Compound S40 ^{13}C NMR



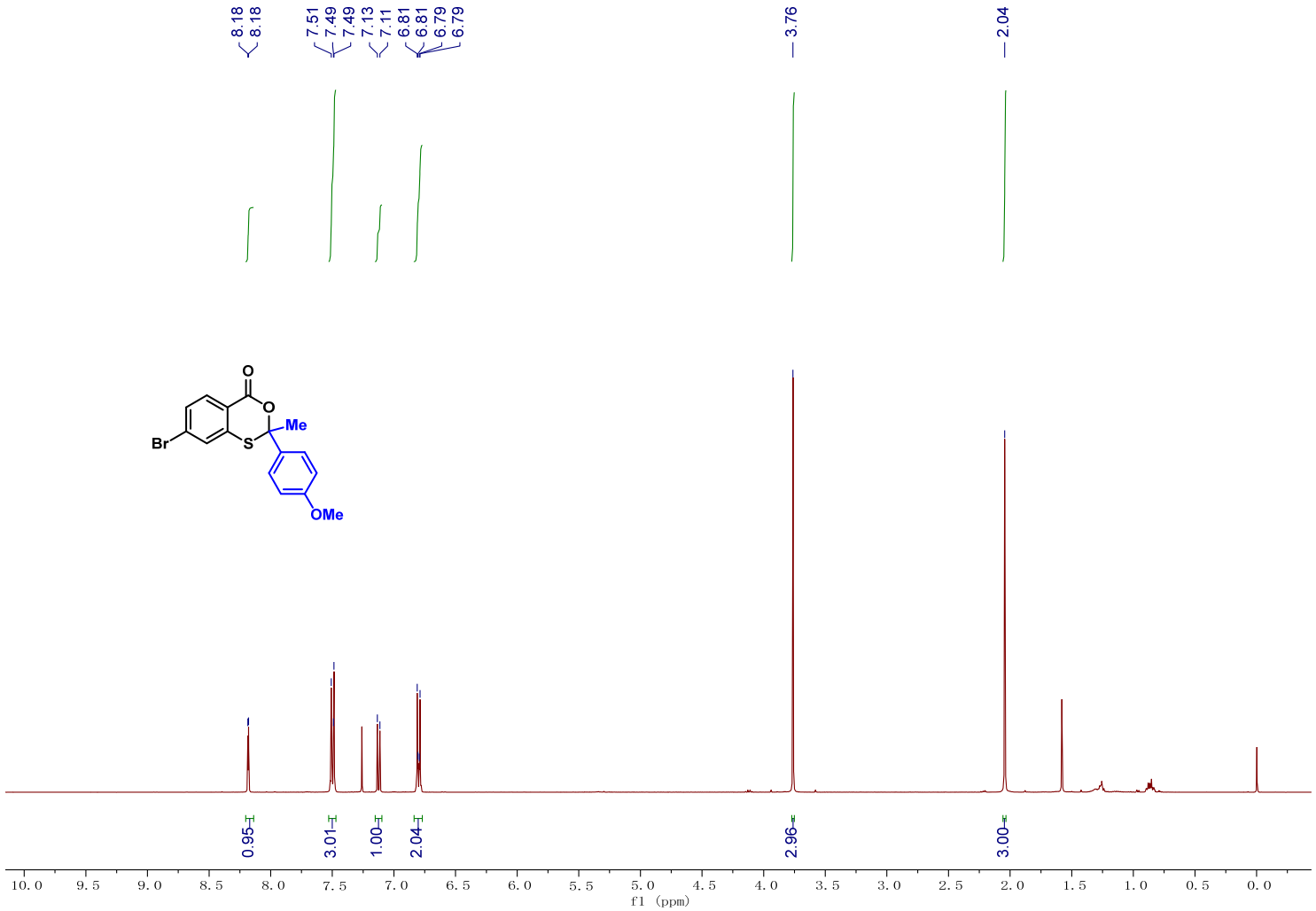
Compound S41 ^{1}H NMR



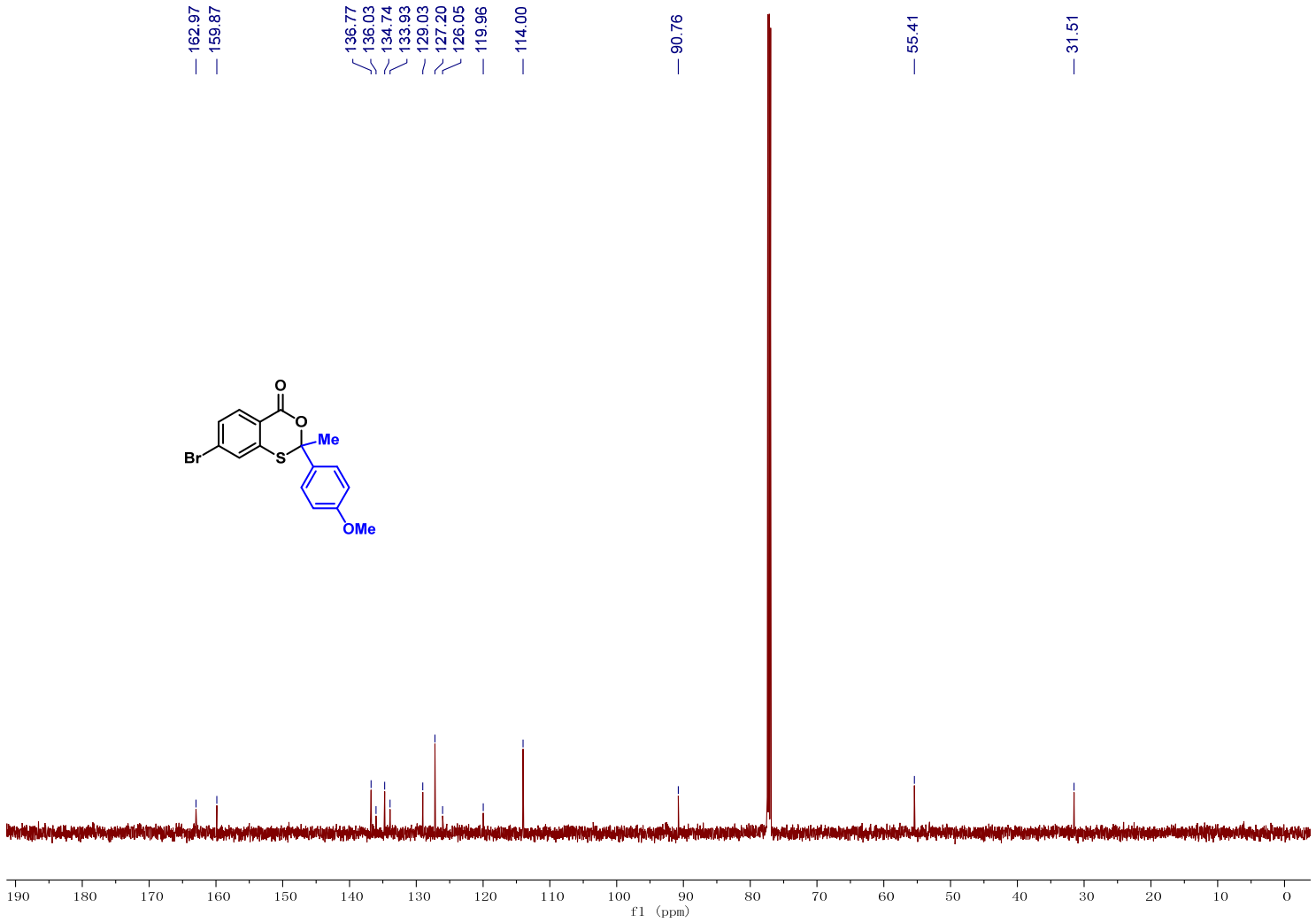
Compound S41 ^{13}C NMR



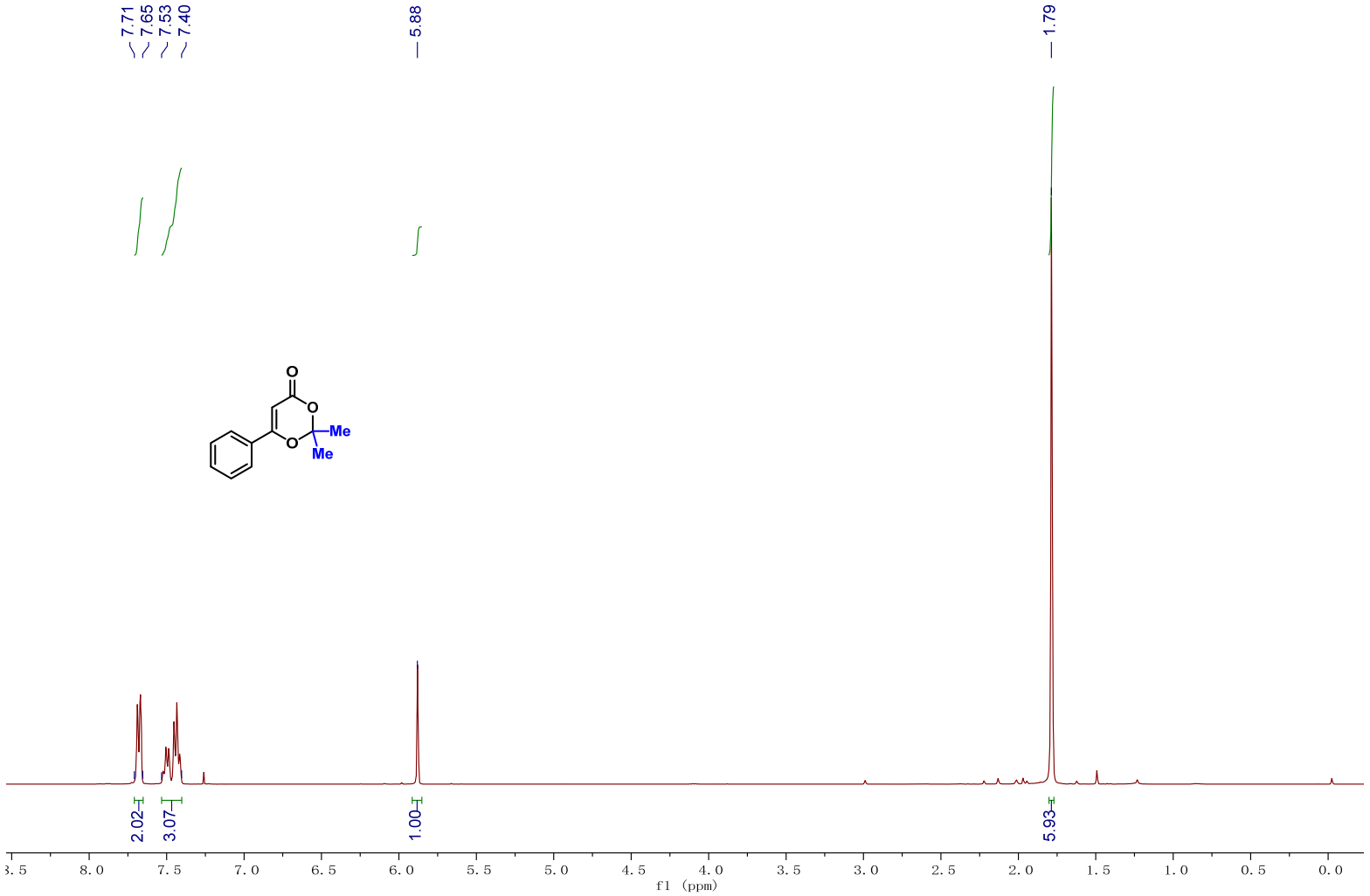
Compound S42 ^{1}H NMR



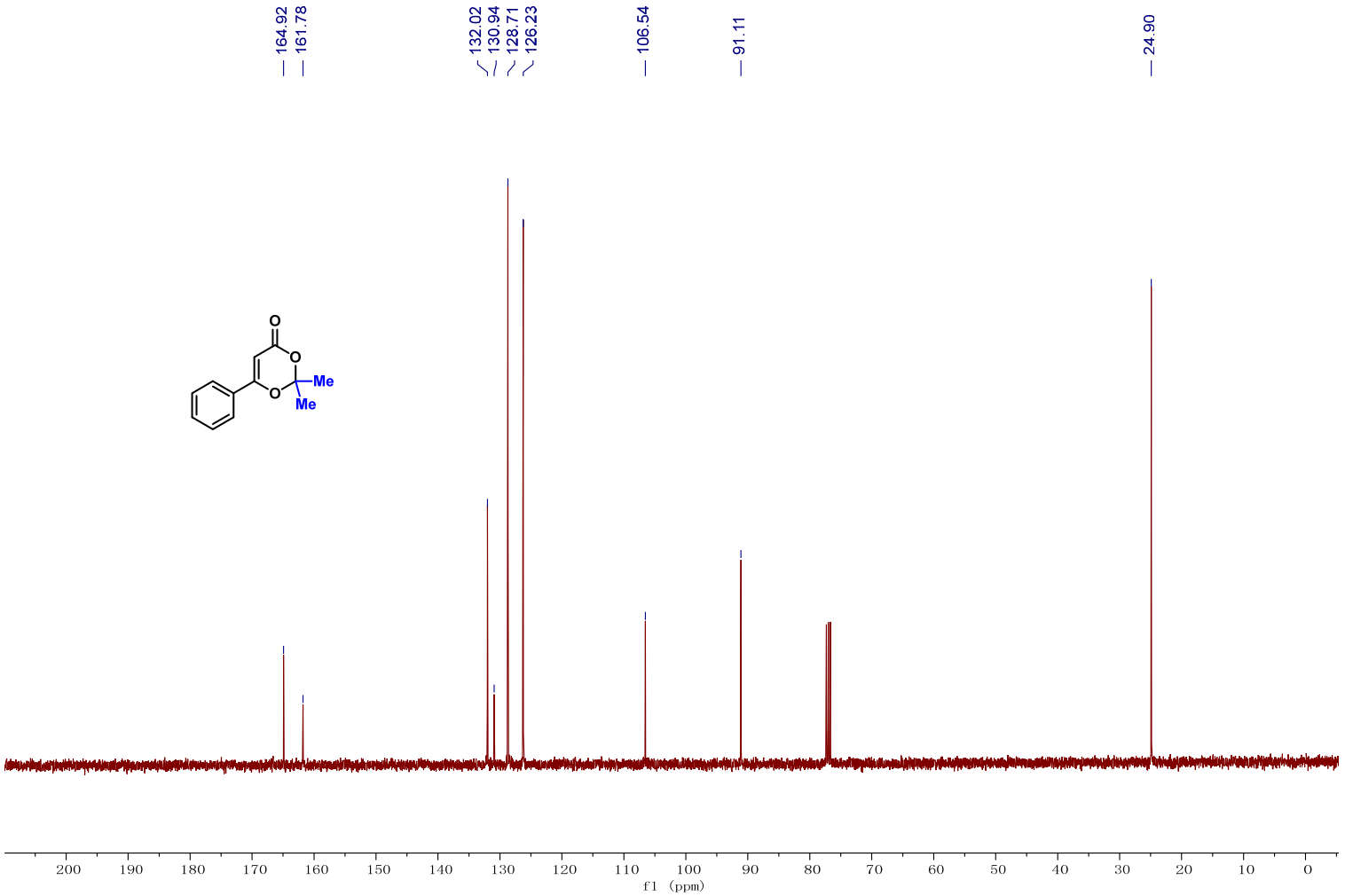
Compound S42 ^{13}C NMR



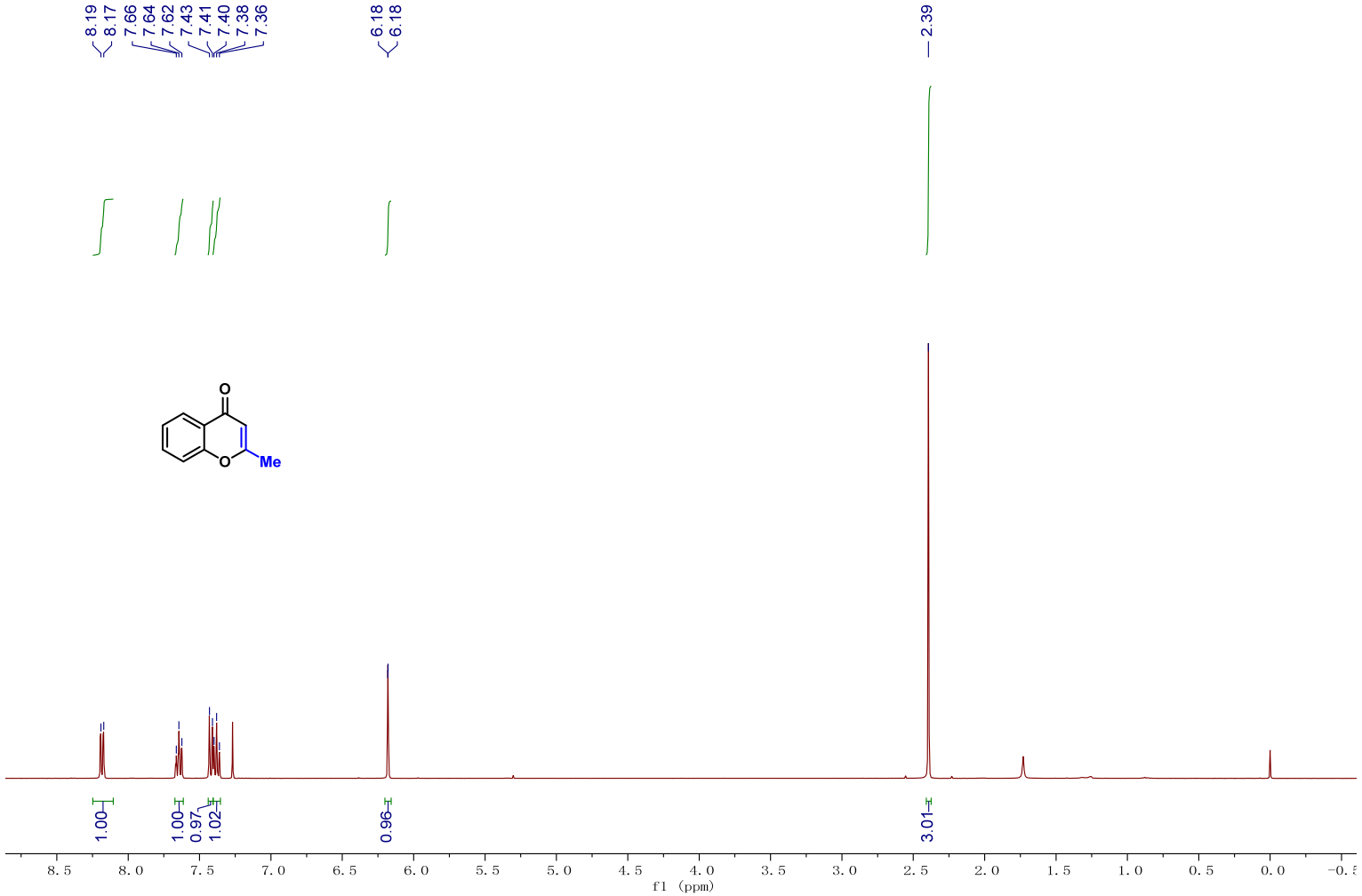
Compound S43 ^{1}H NMR



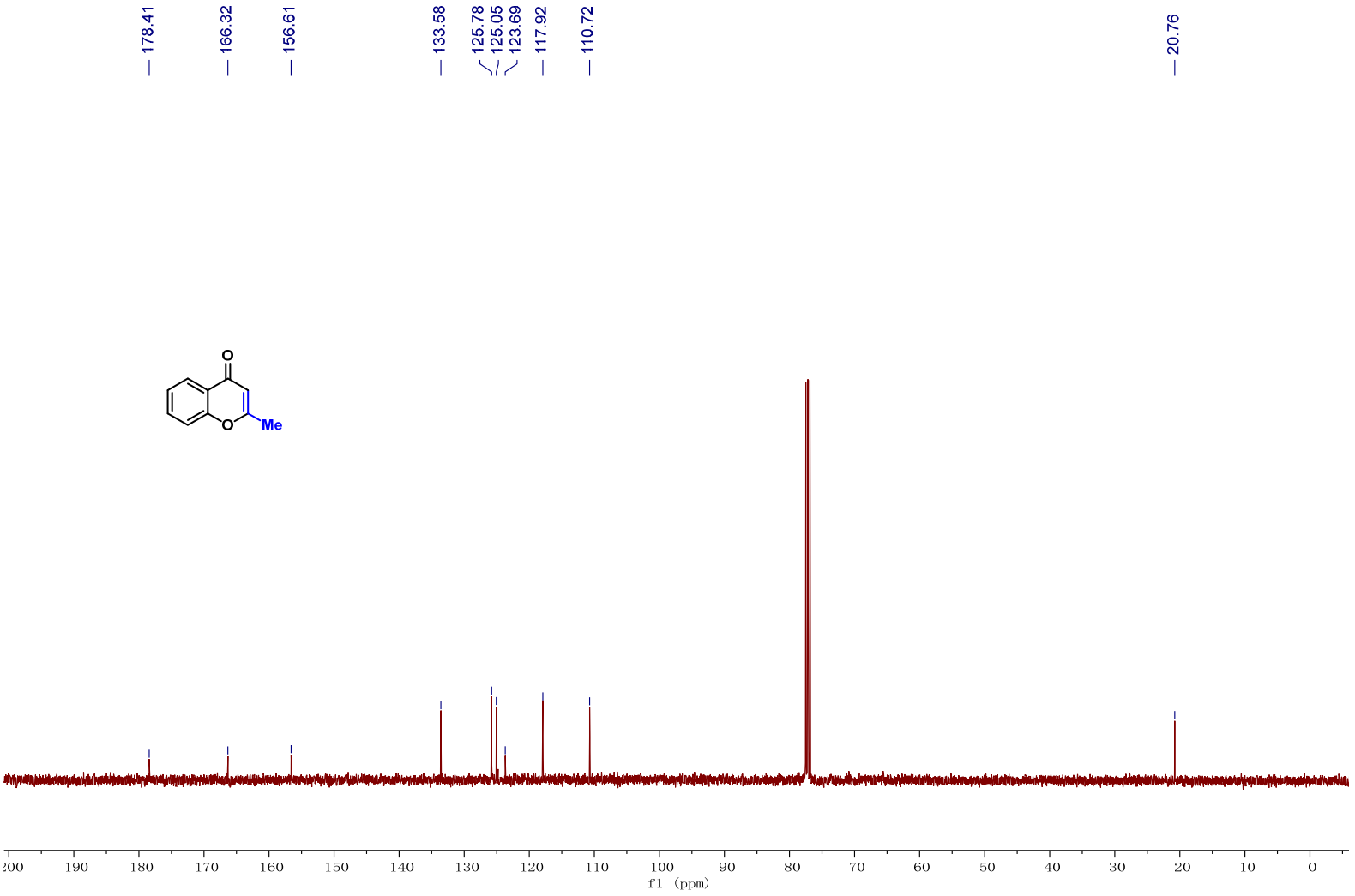
Compound S43 ^{13}C NMR



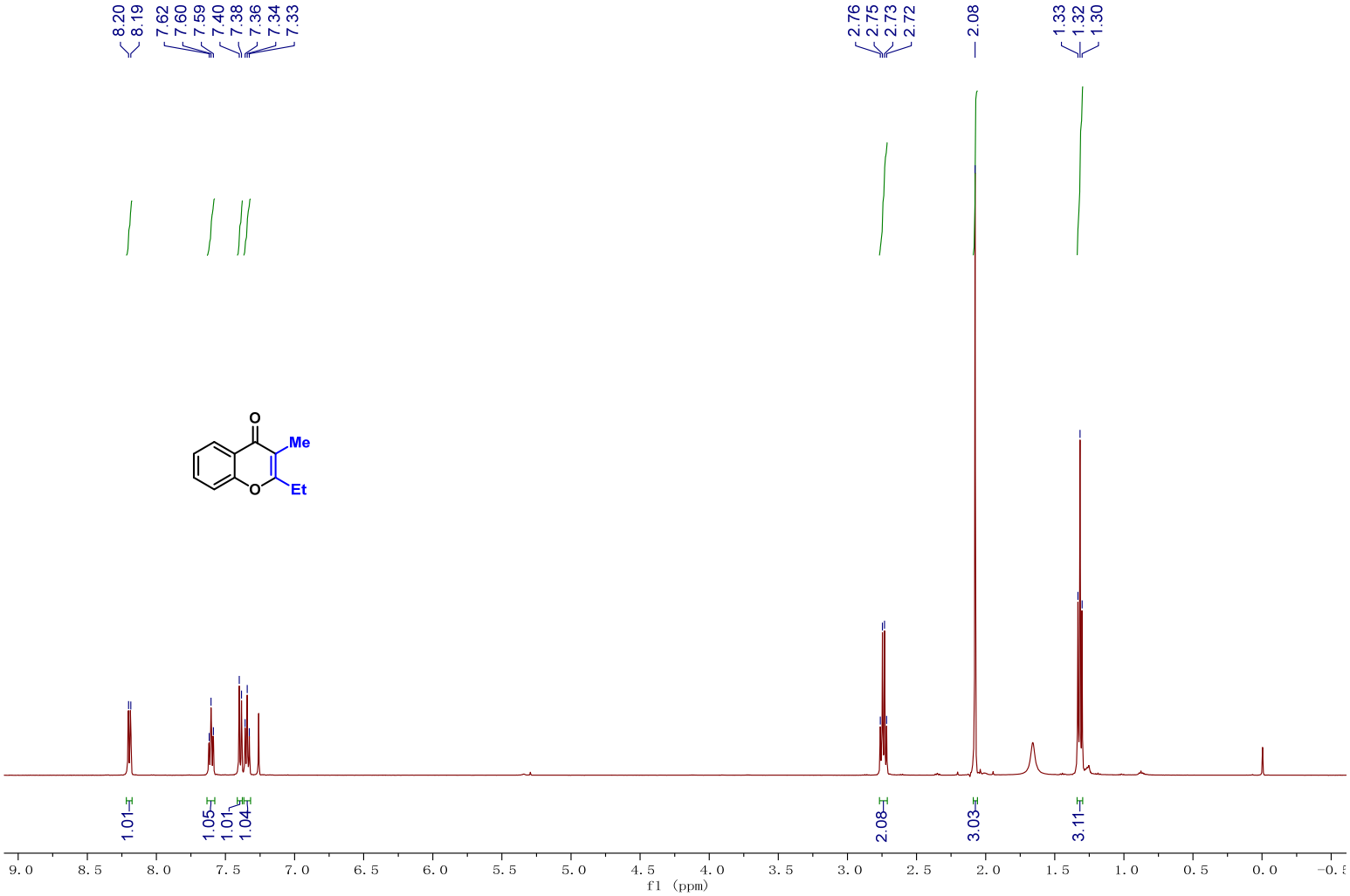
Compound 6 ^{1}H NMR



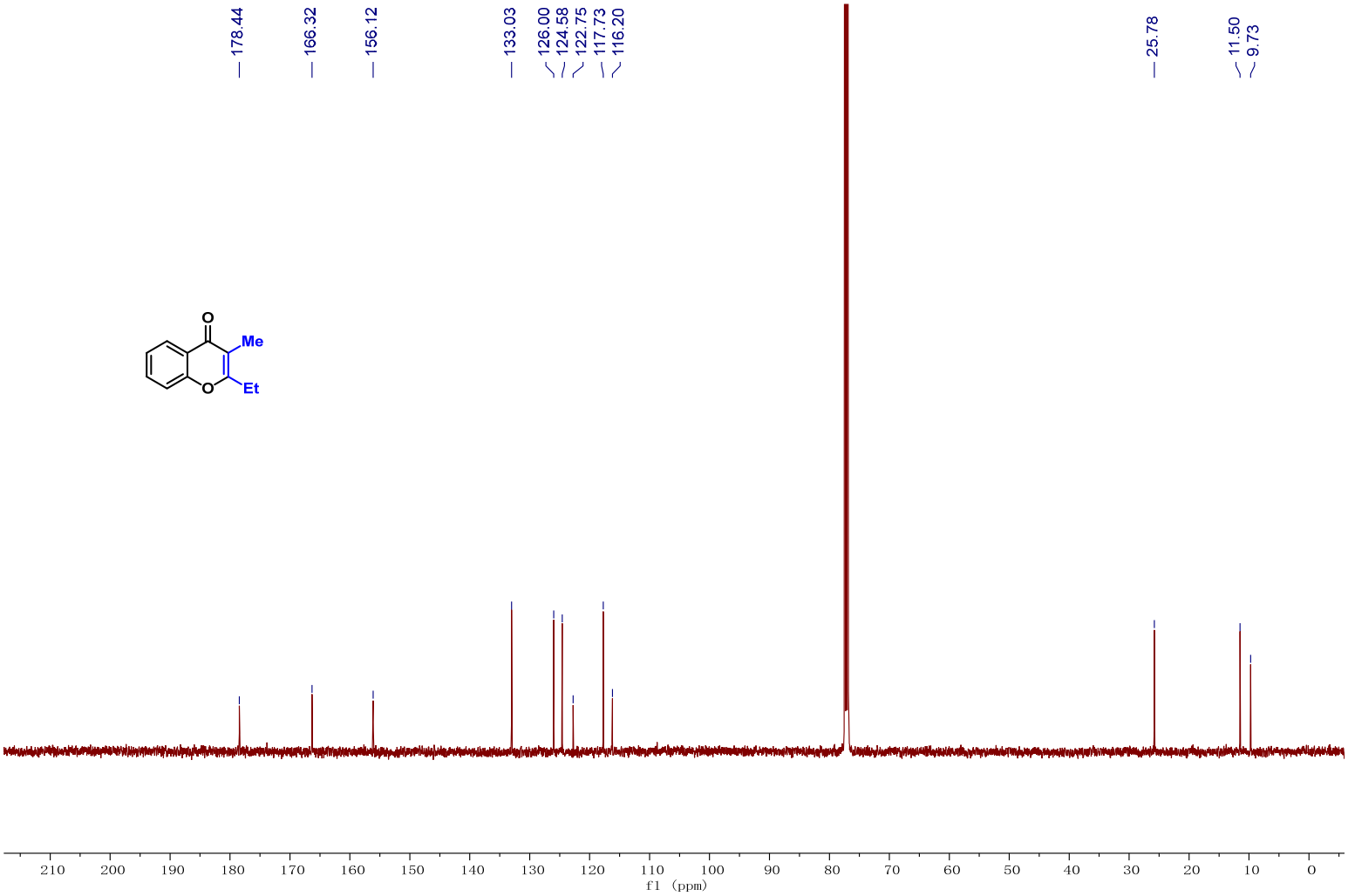
Compound 6 ^{13}C NMR



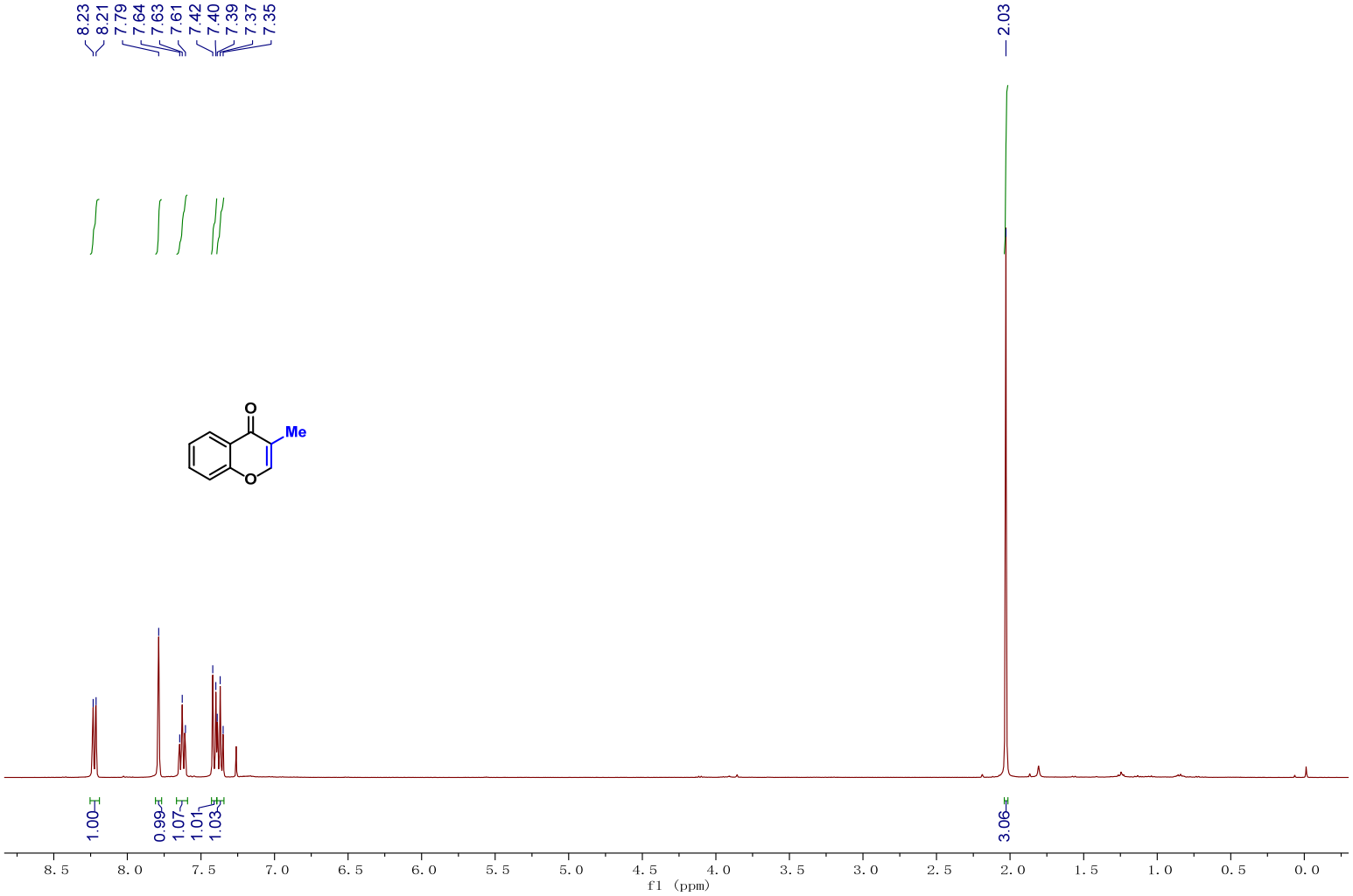
Compound 7 ^{1}H NMR



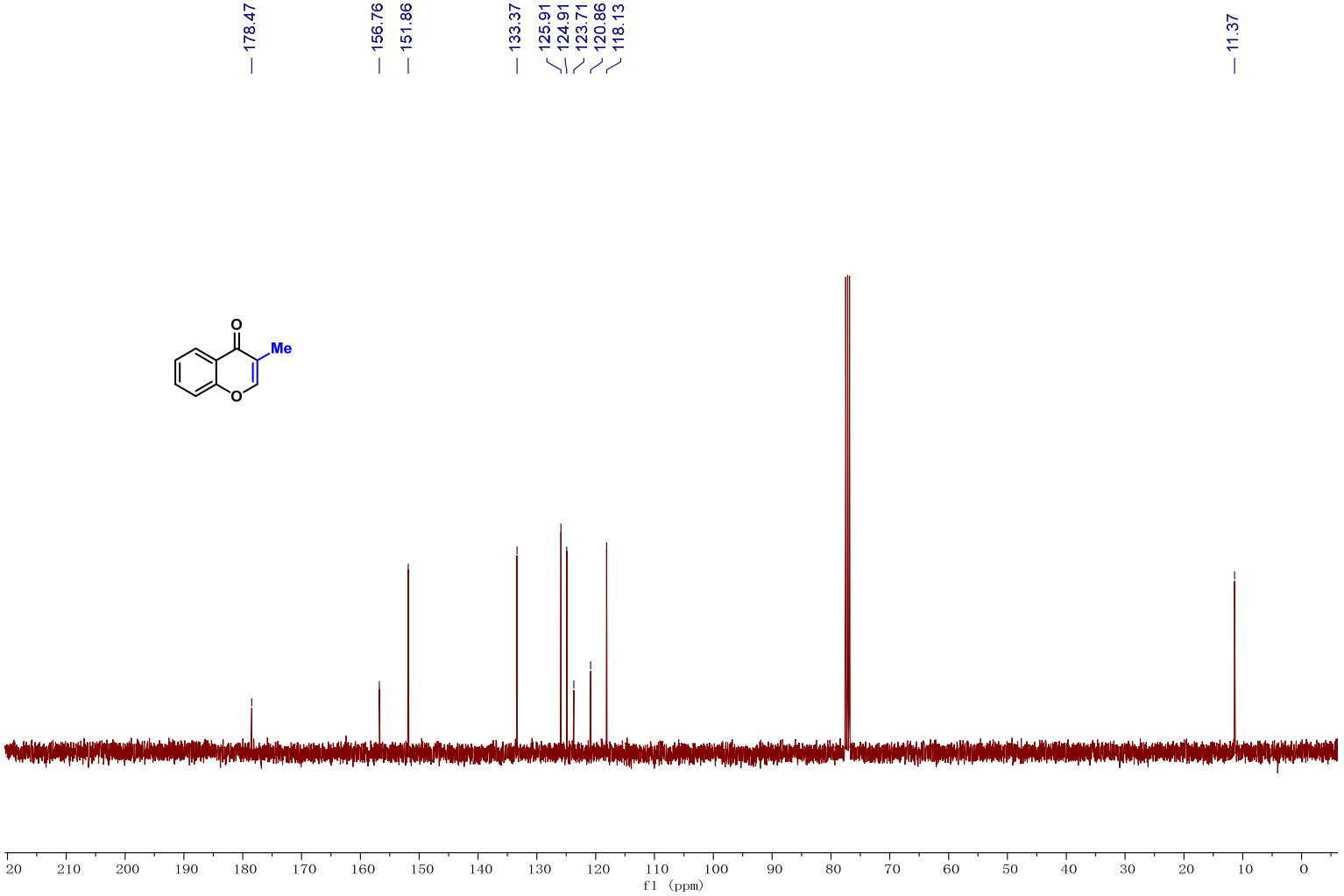
Compound 7 ^{13}C NMR



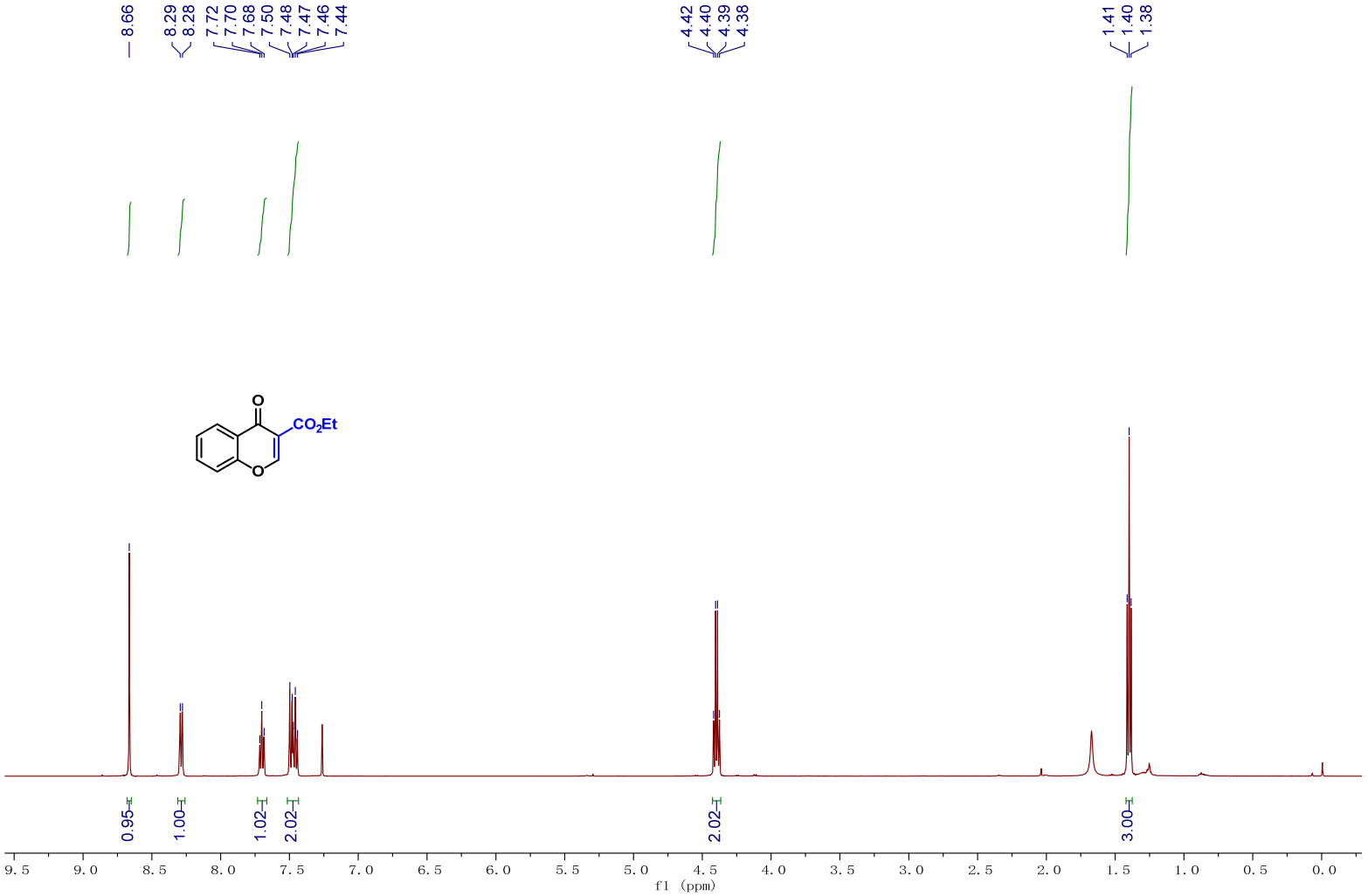
Compound 8 ^{1}H NMR



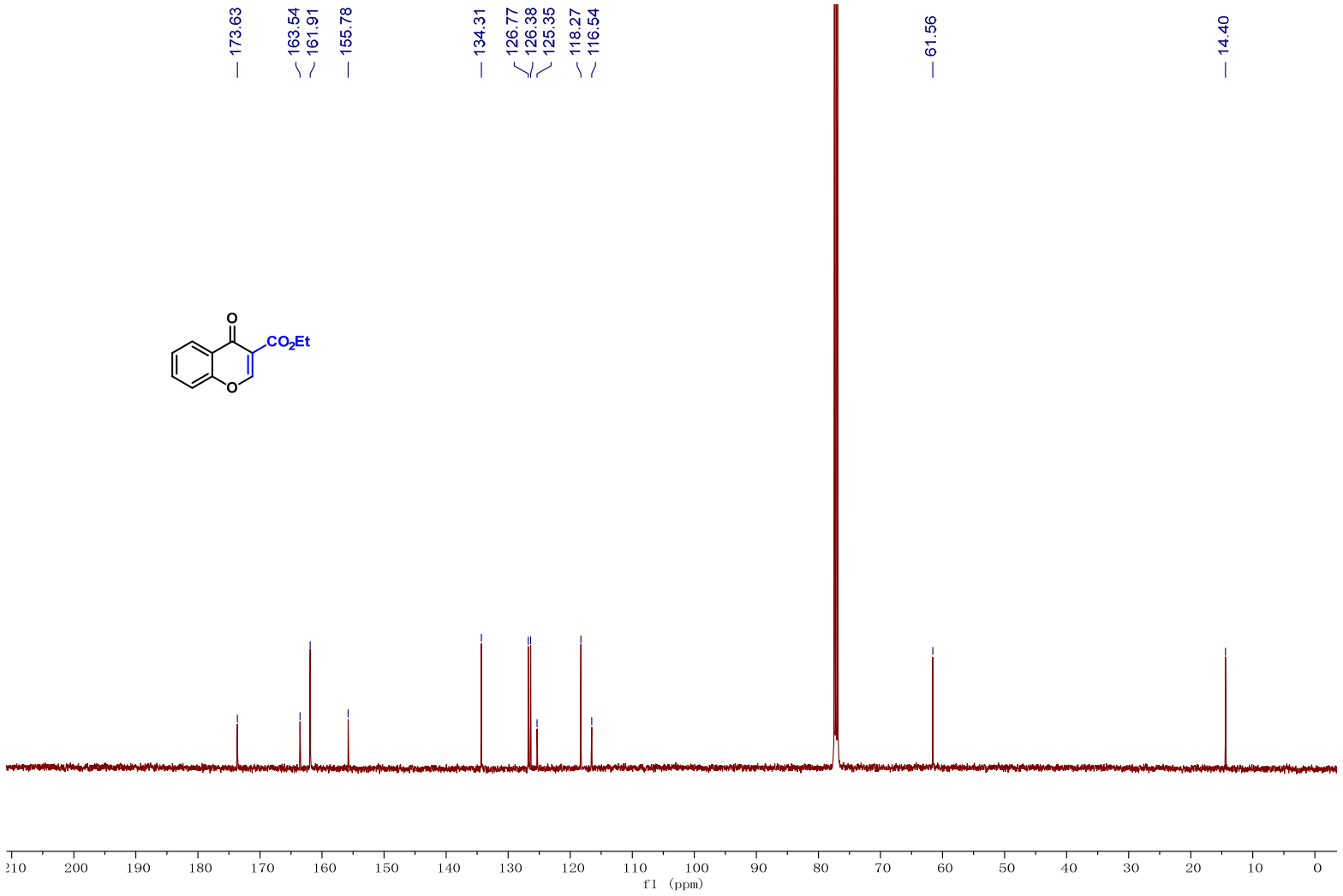
Compound 8 ^{13}C NMR



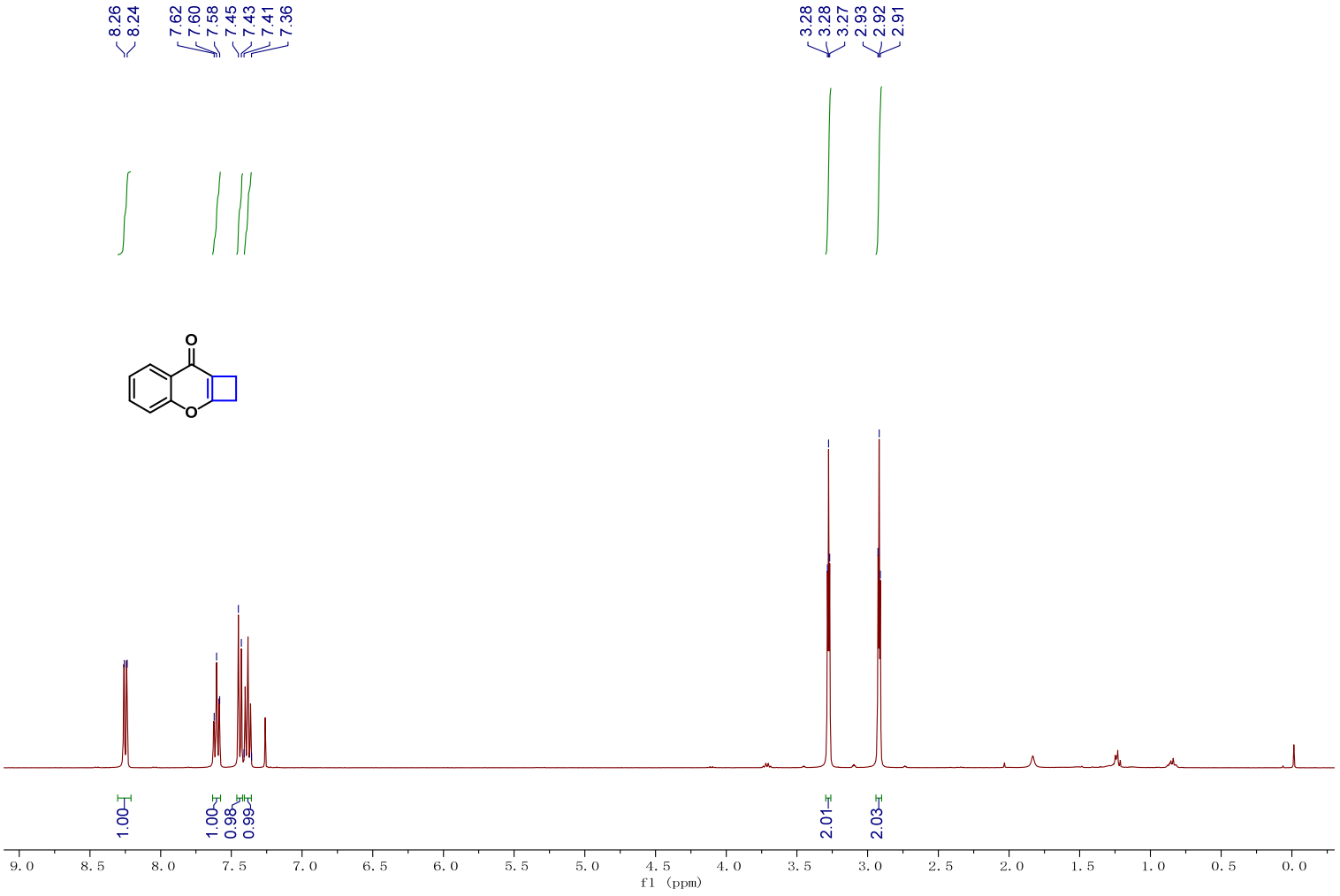
Compound 9 ^{1}H NMR



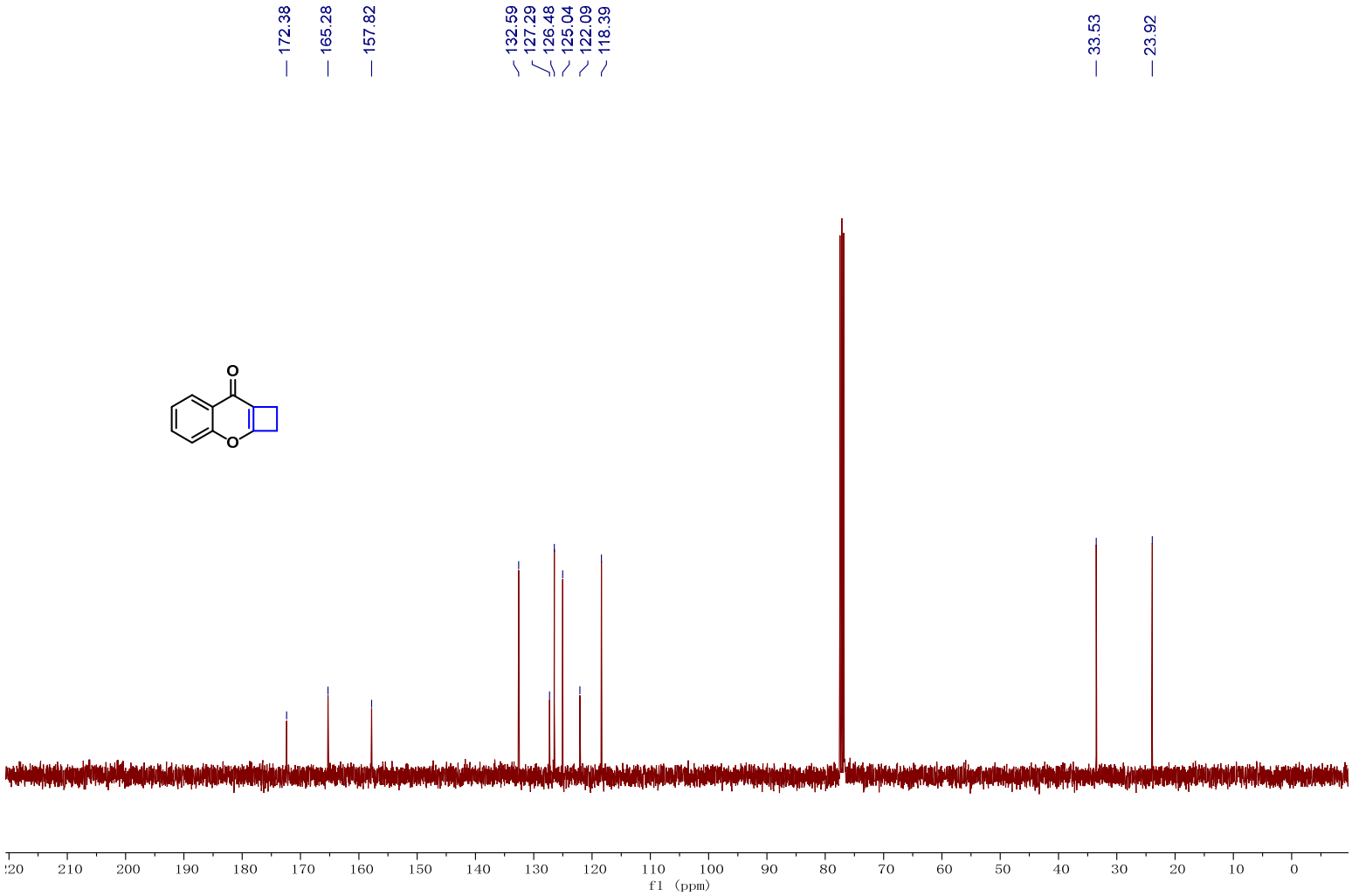
Compound 9 ^{13}C NMR



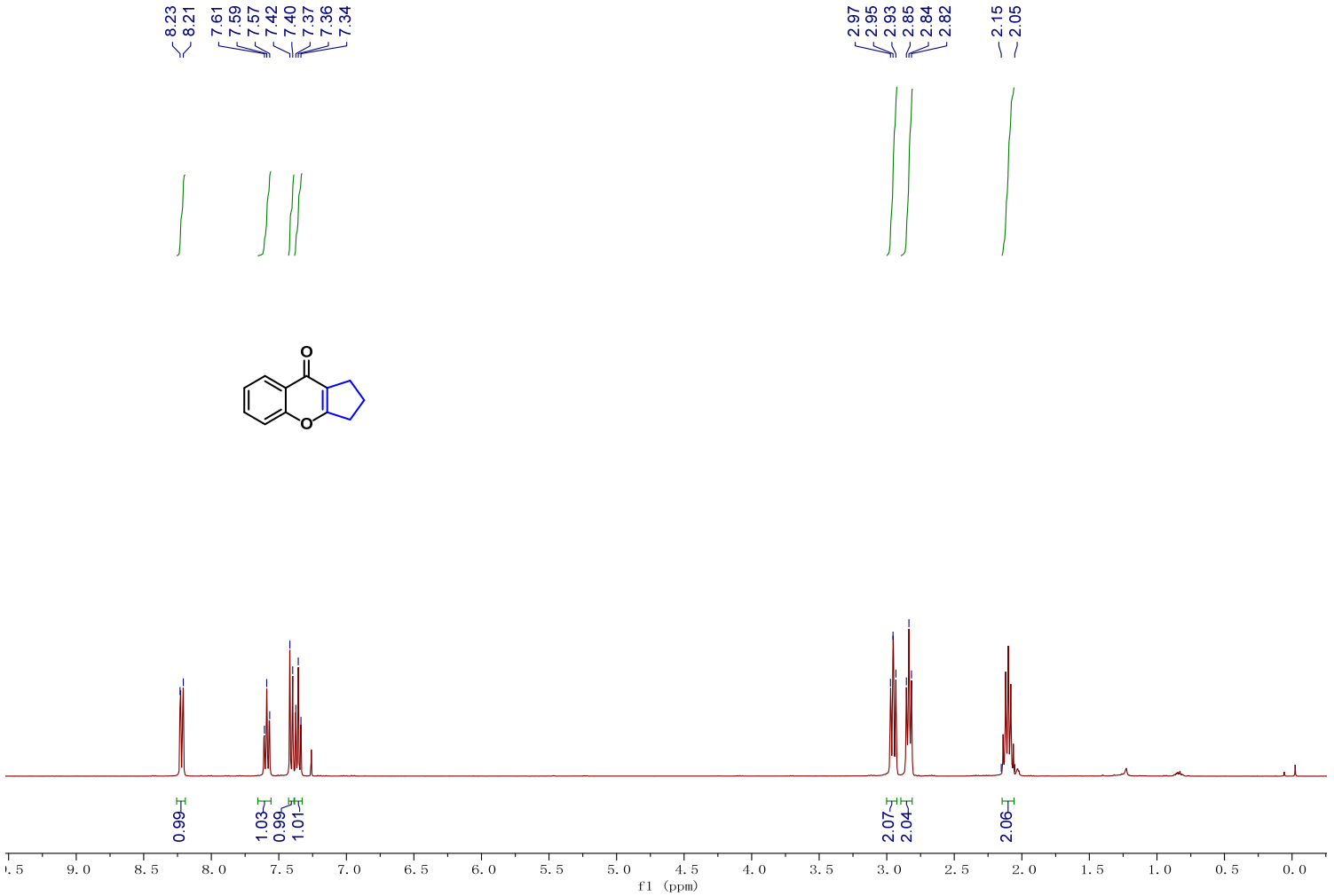
Compound 10 ^{1}H NMR



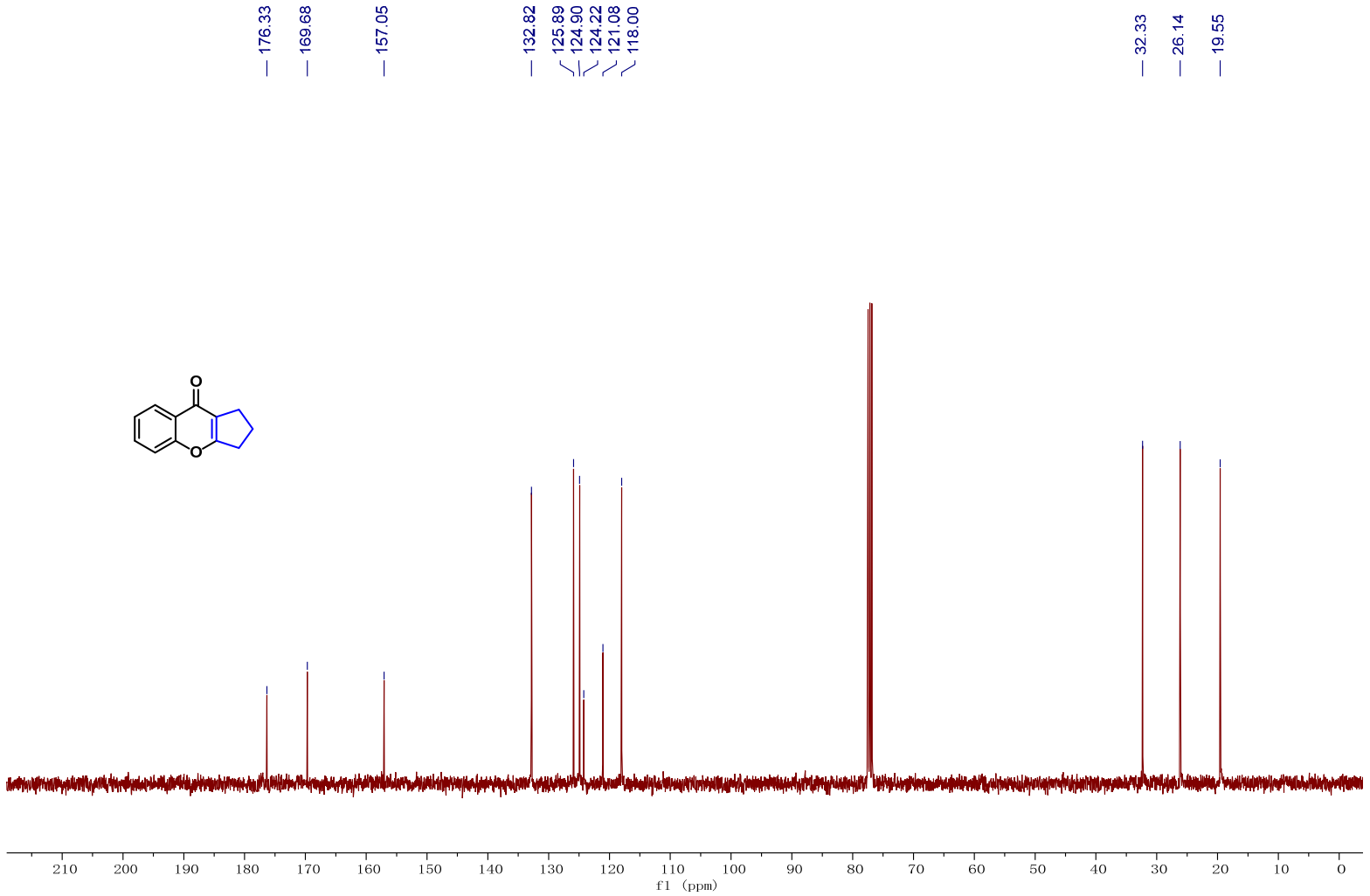
Compound 10 ^{13}C NMR



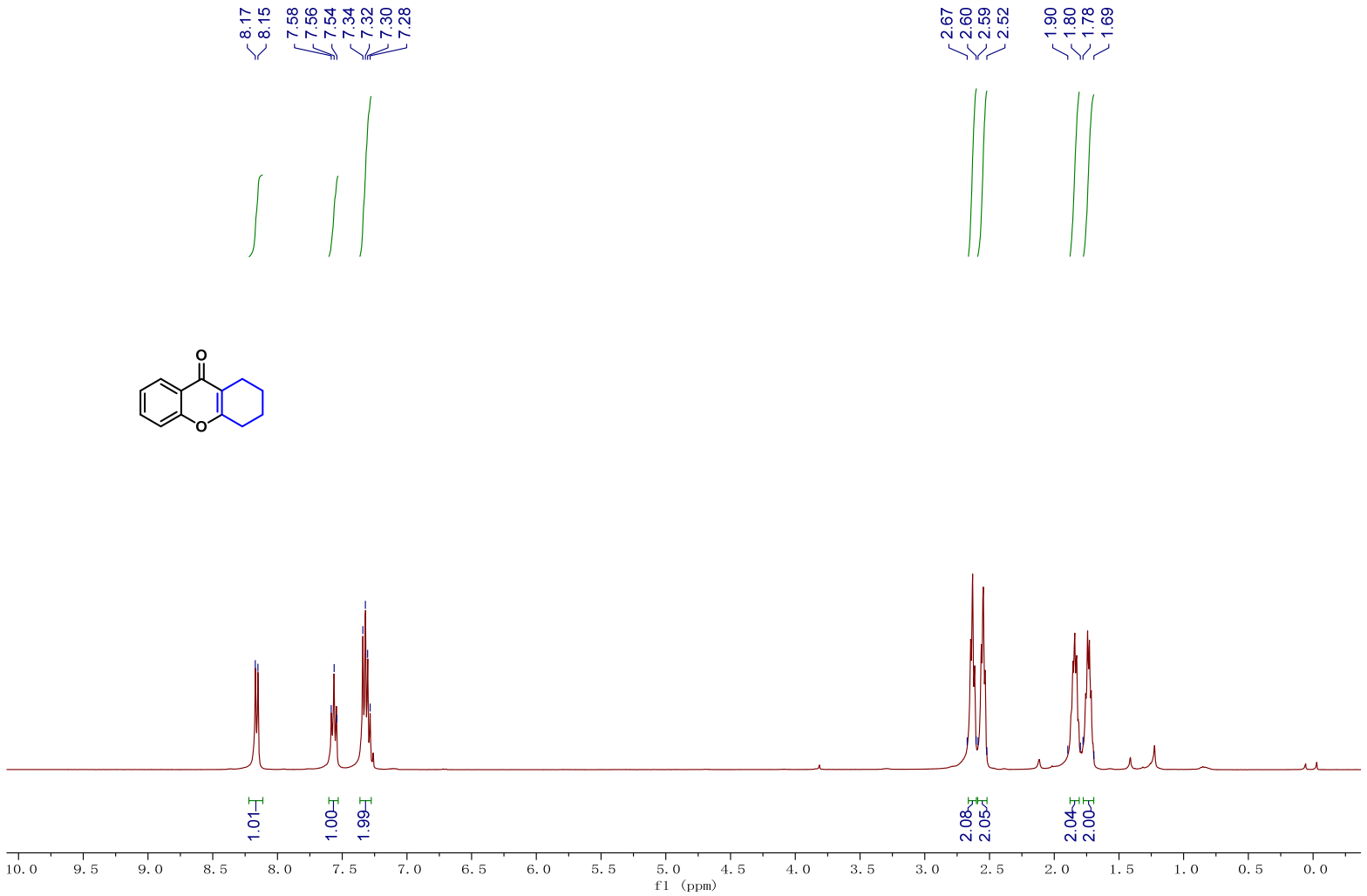
Compound 11 ^{1}H NMR



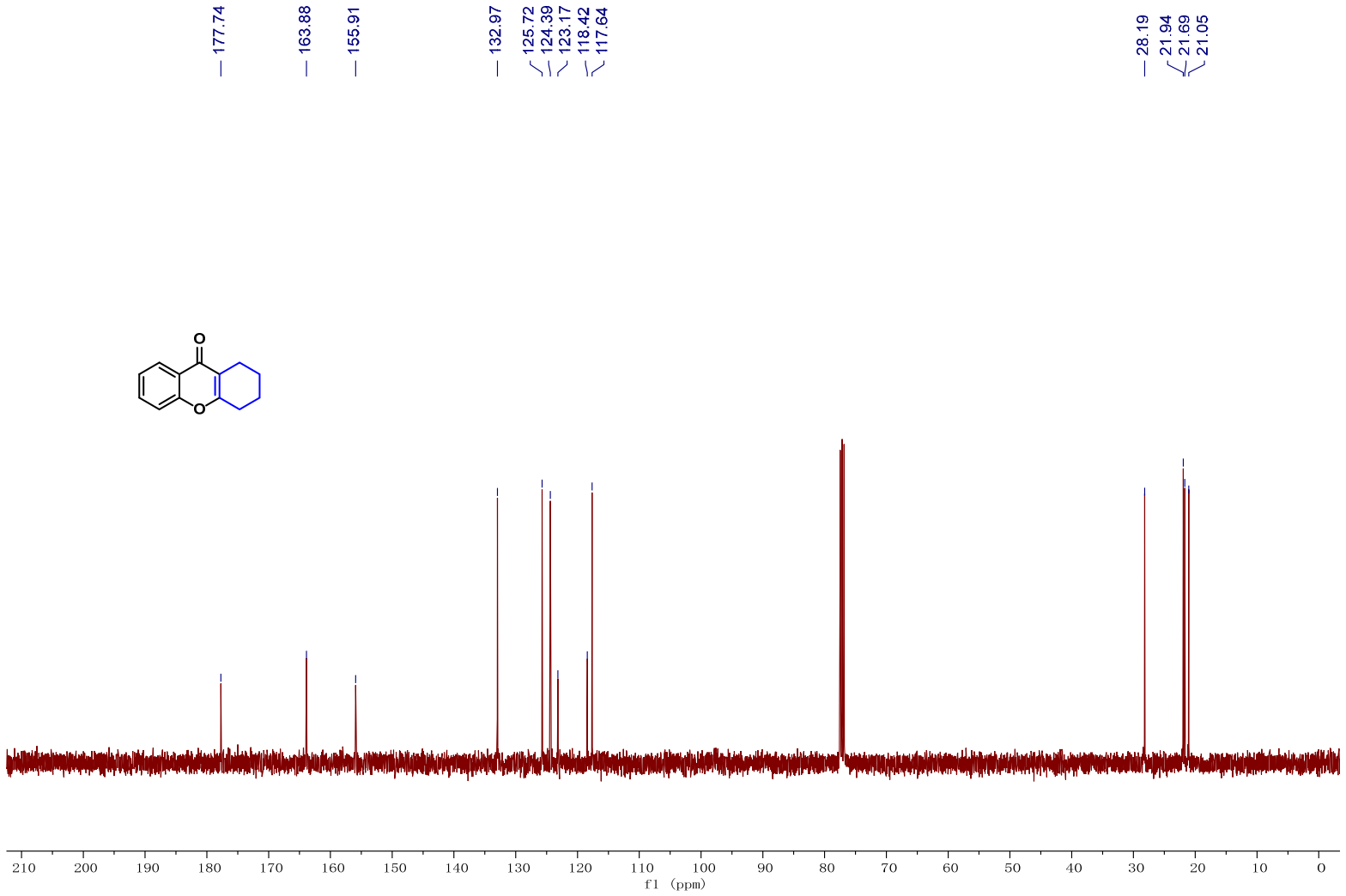
Compound 11 ^{13}C NMR



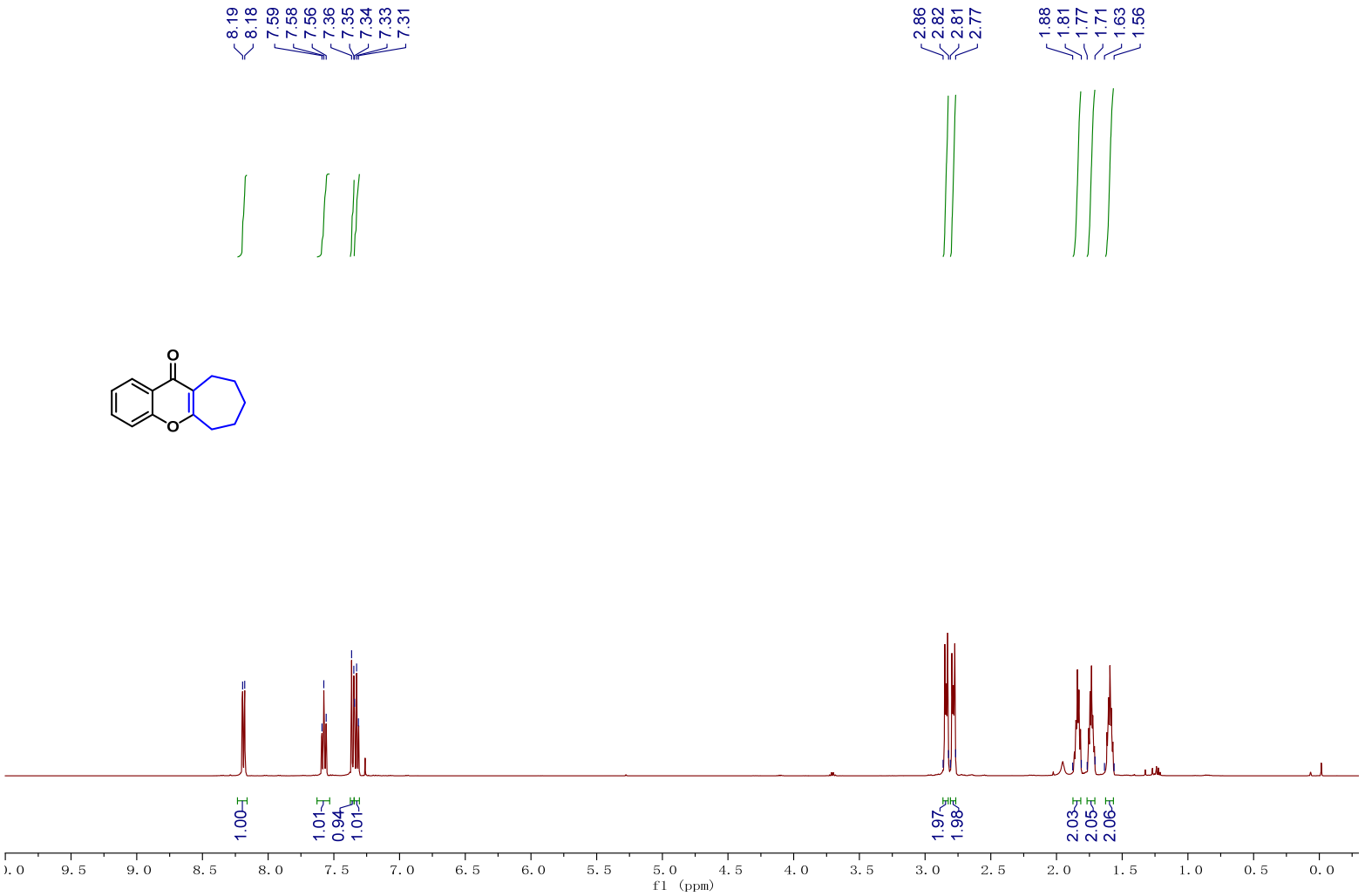
Compound 12 ^{1}H NMR



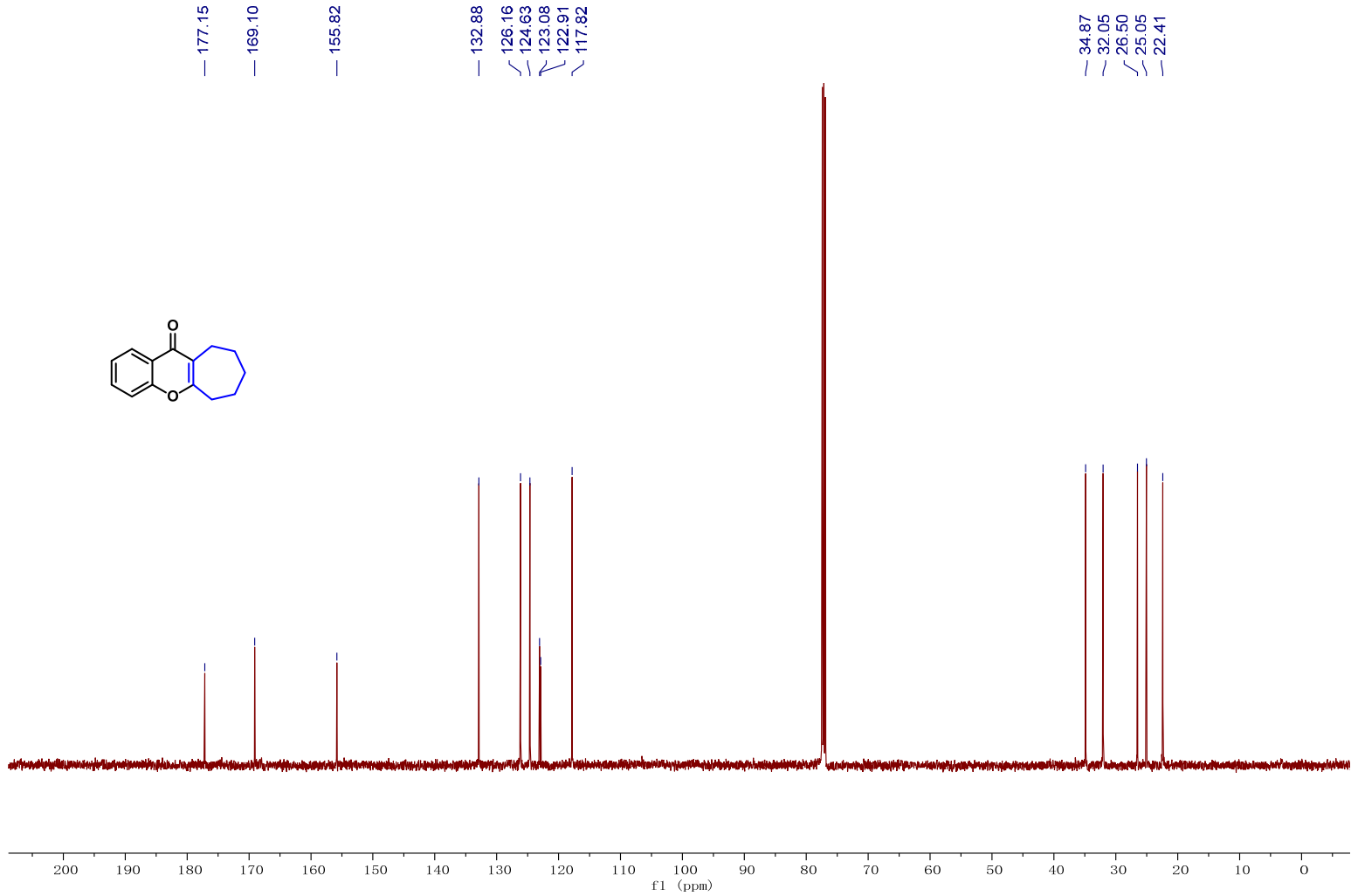
Compound 12 ^{13}C NMR



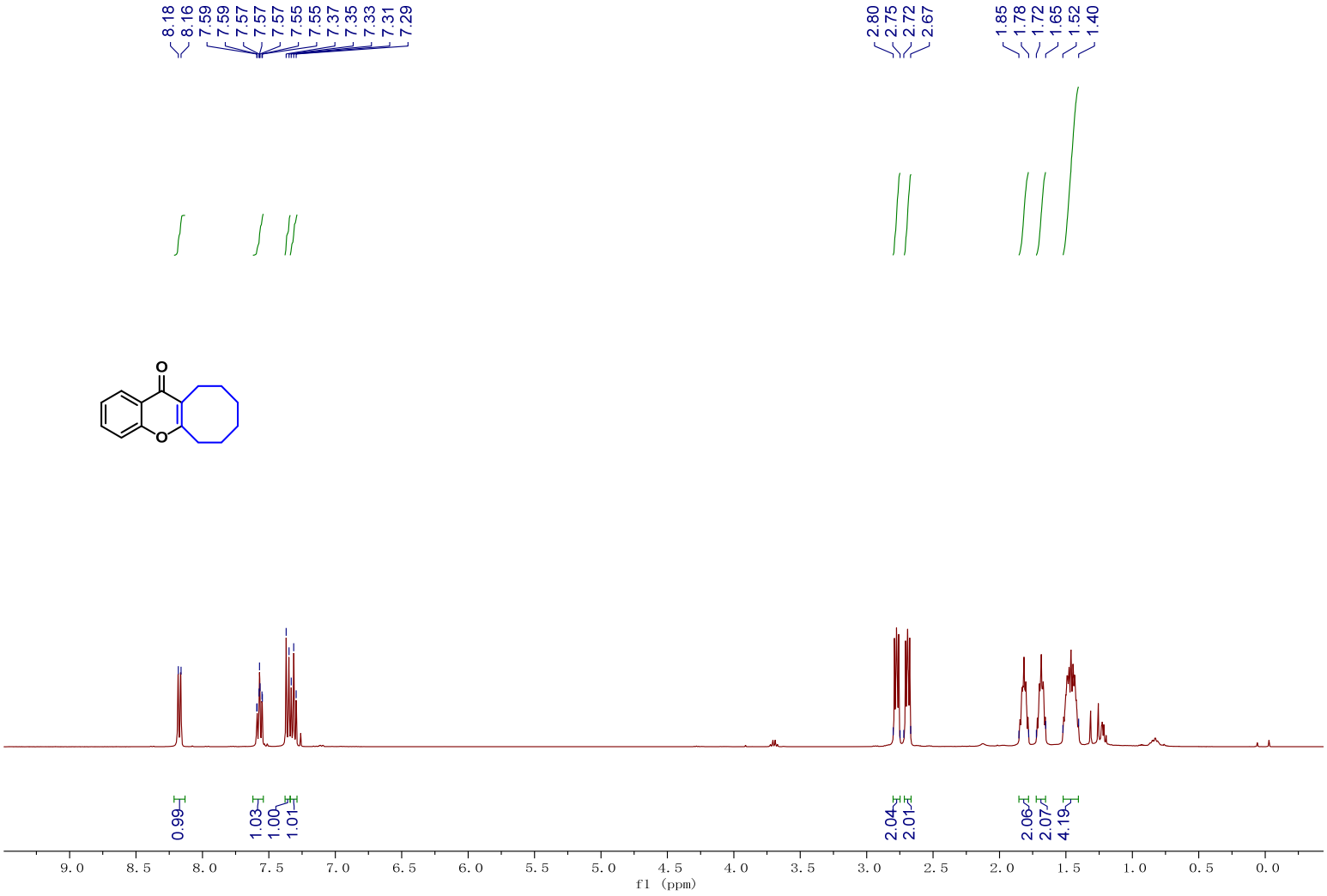
Compound 13 ^{1}H NMR



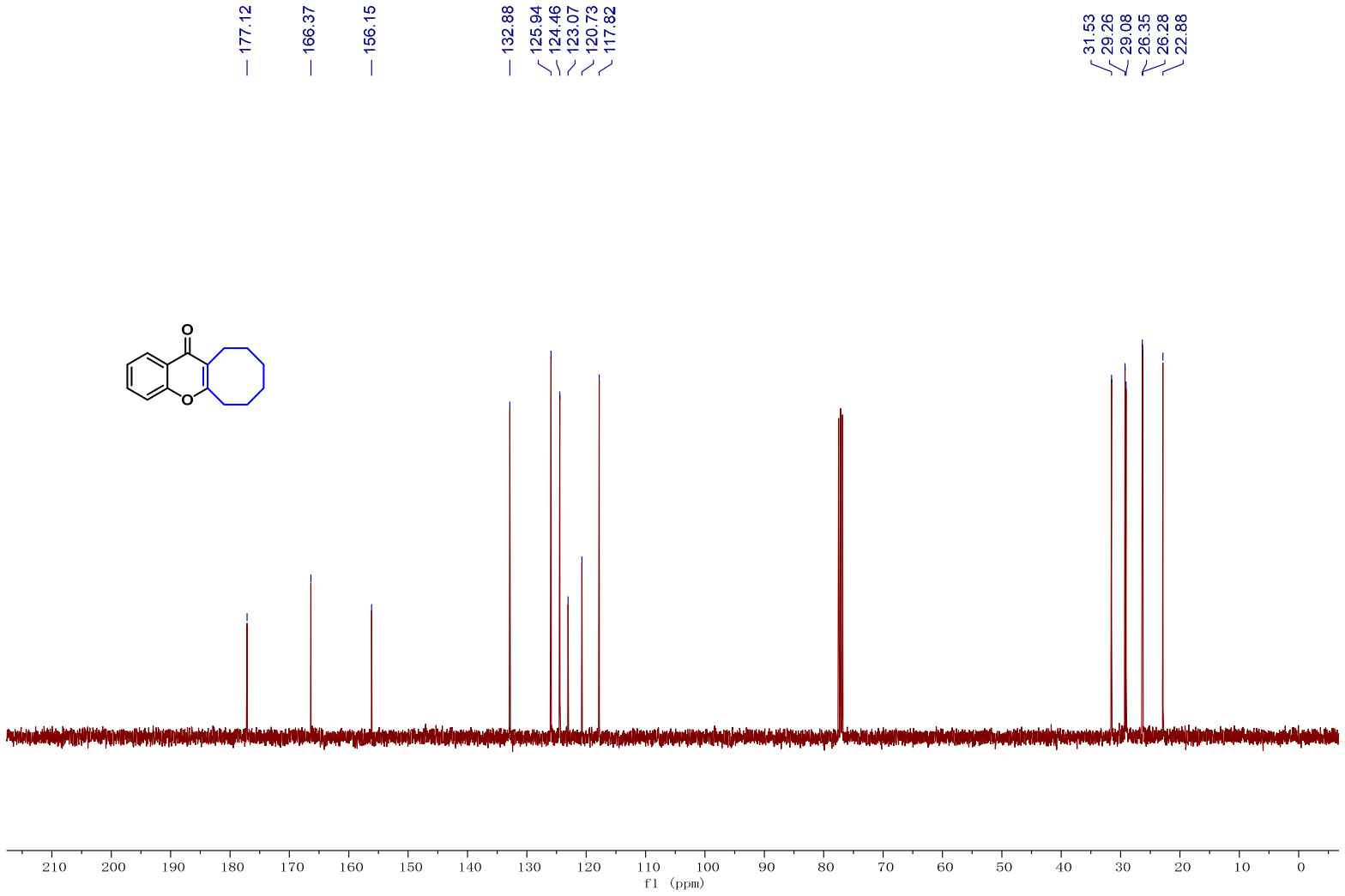
Compound 13 ^{13}C NMR



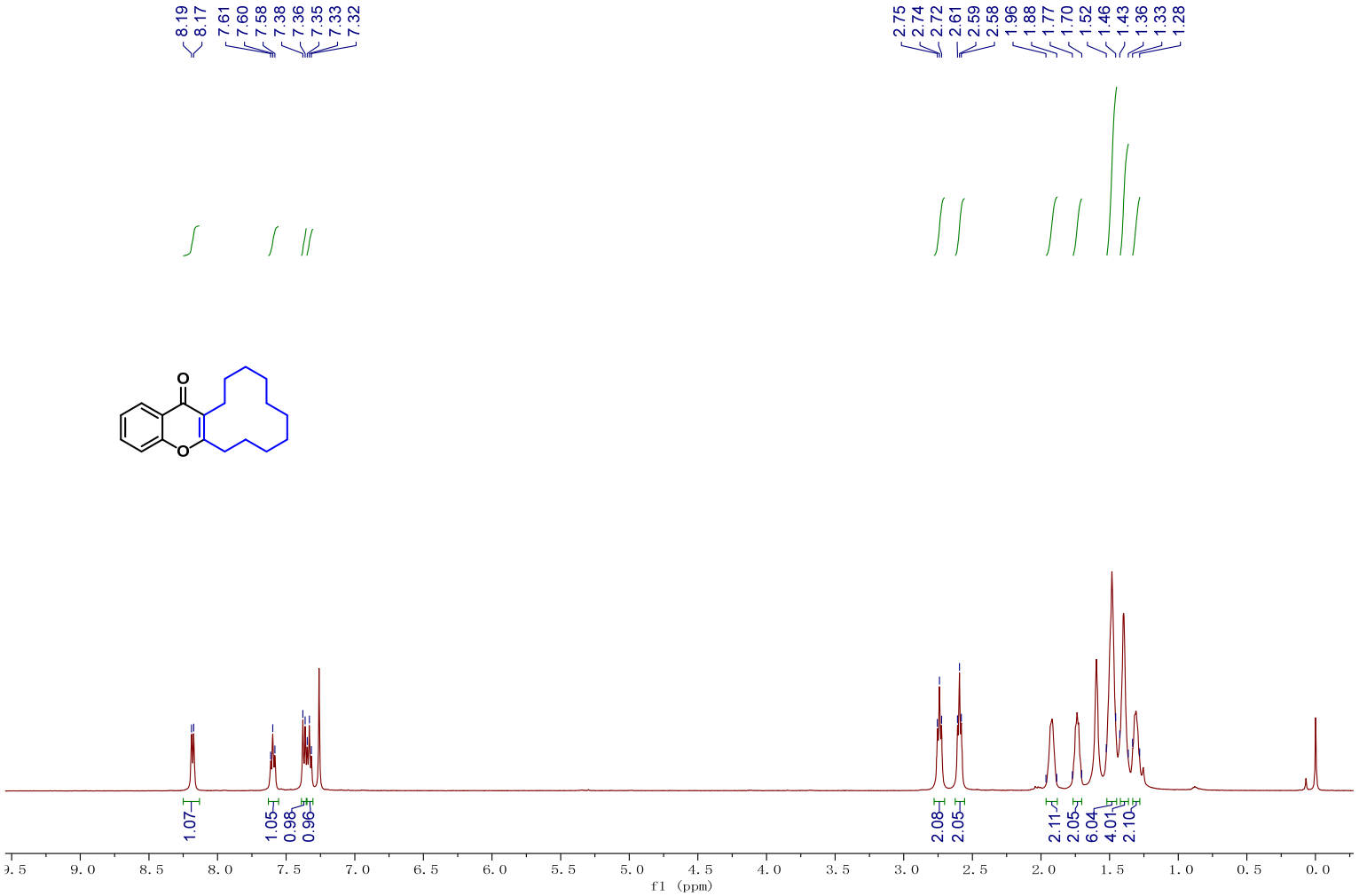
Compound 14 ^{1}H NMR



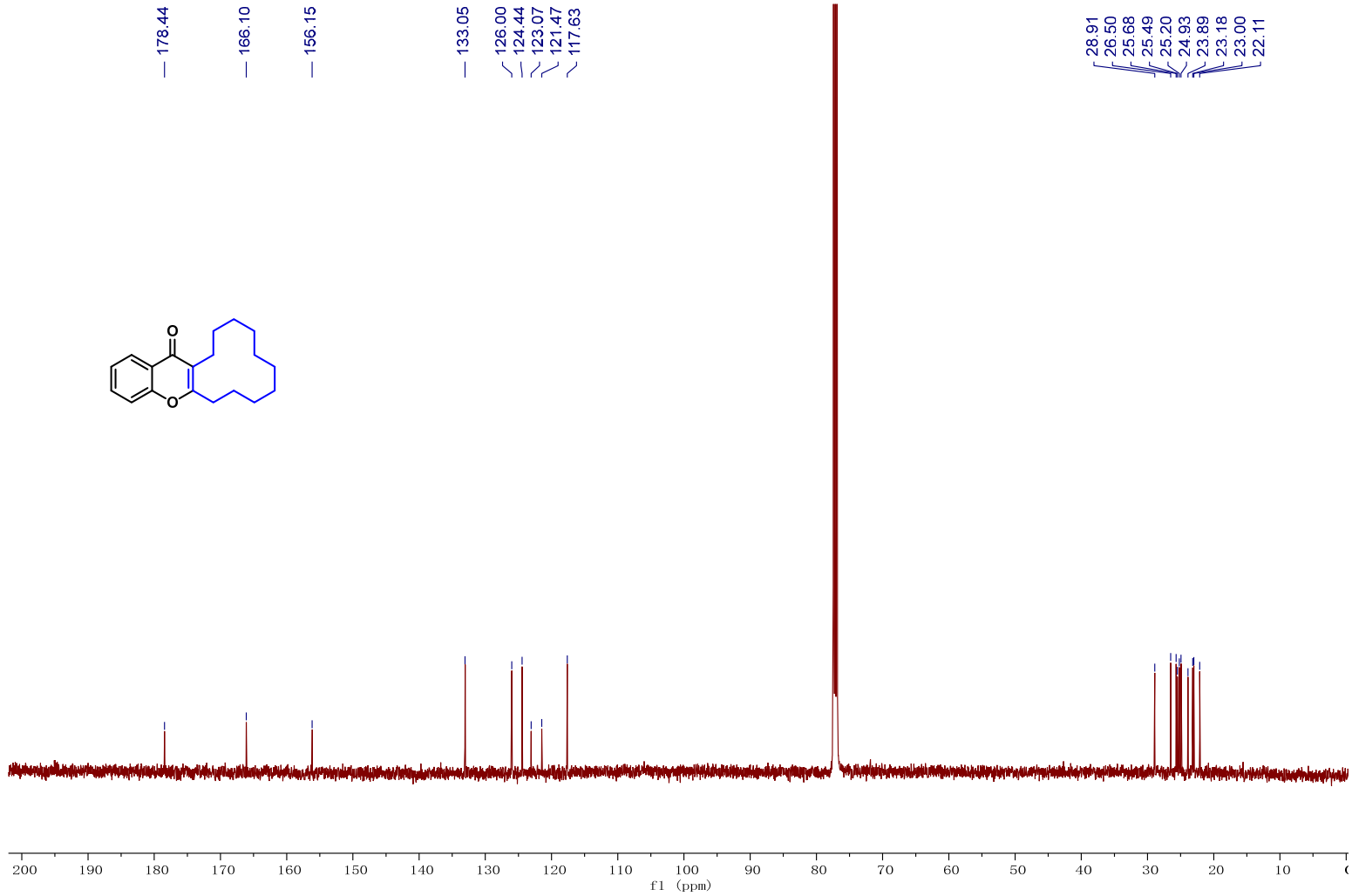
Compound 14 ^{13}C NMR



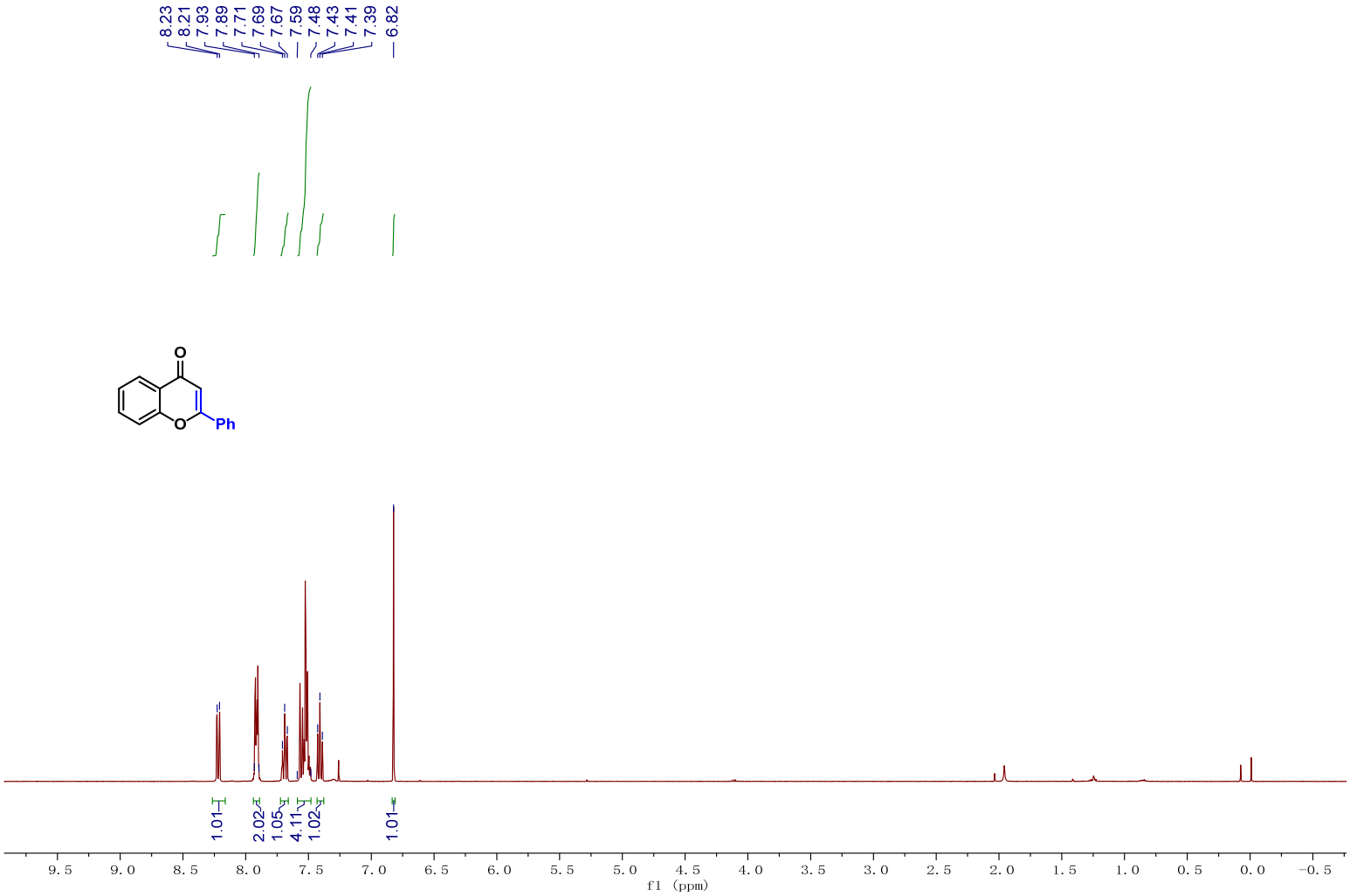
Compound 15 ^{1}H NMR



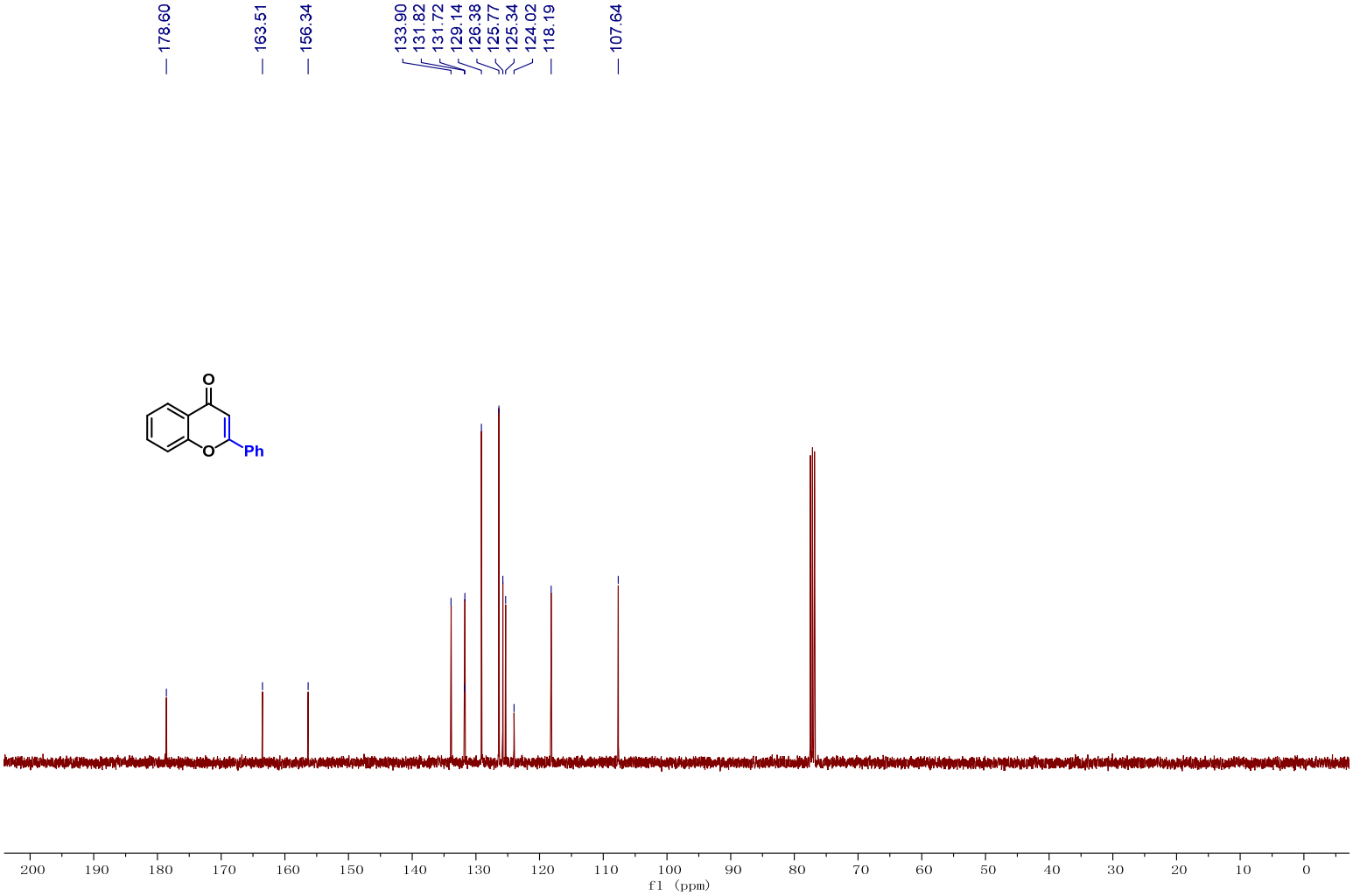
Compound 15 ^{13}C NMR



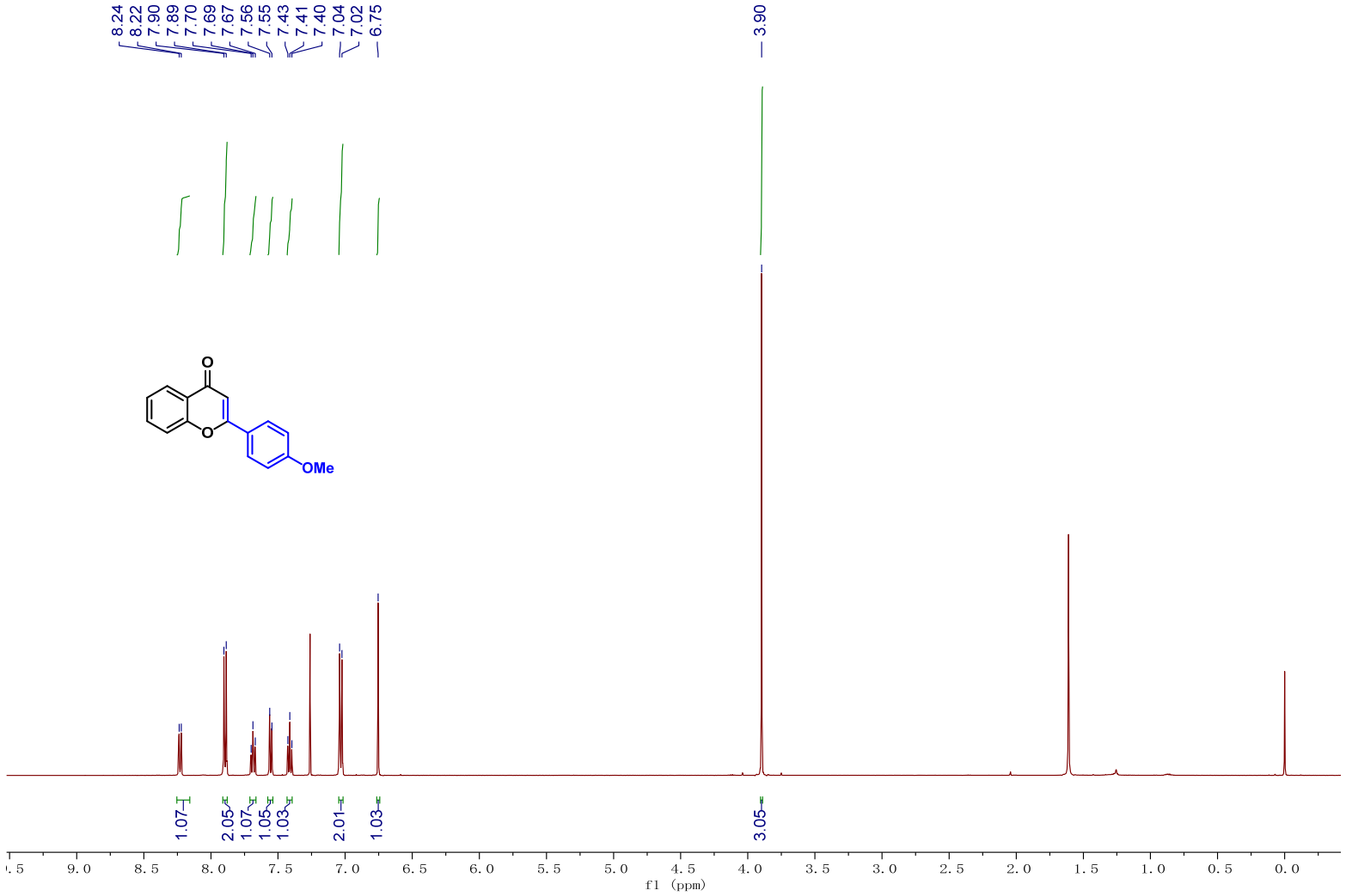
Compound 16 ^{1}H NMR



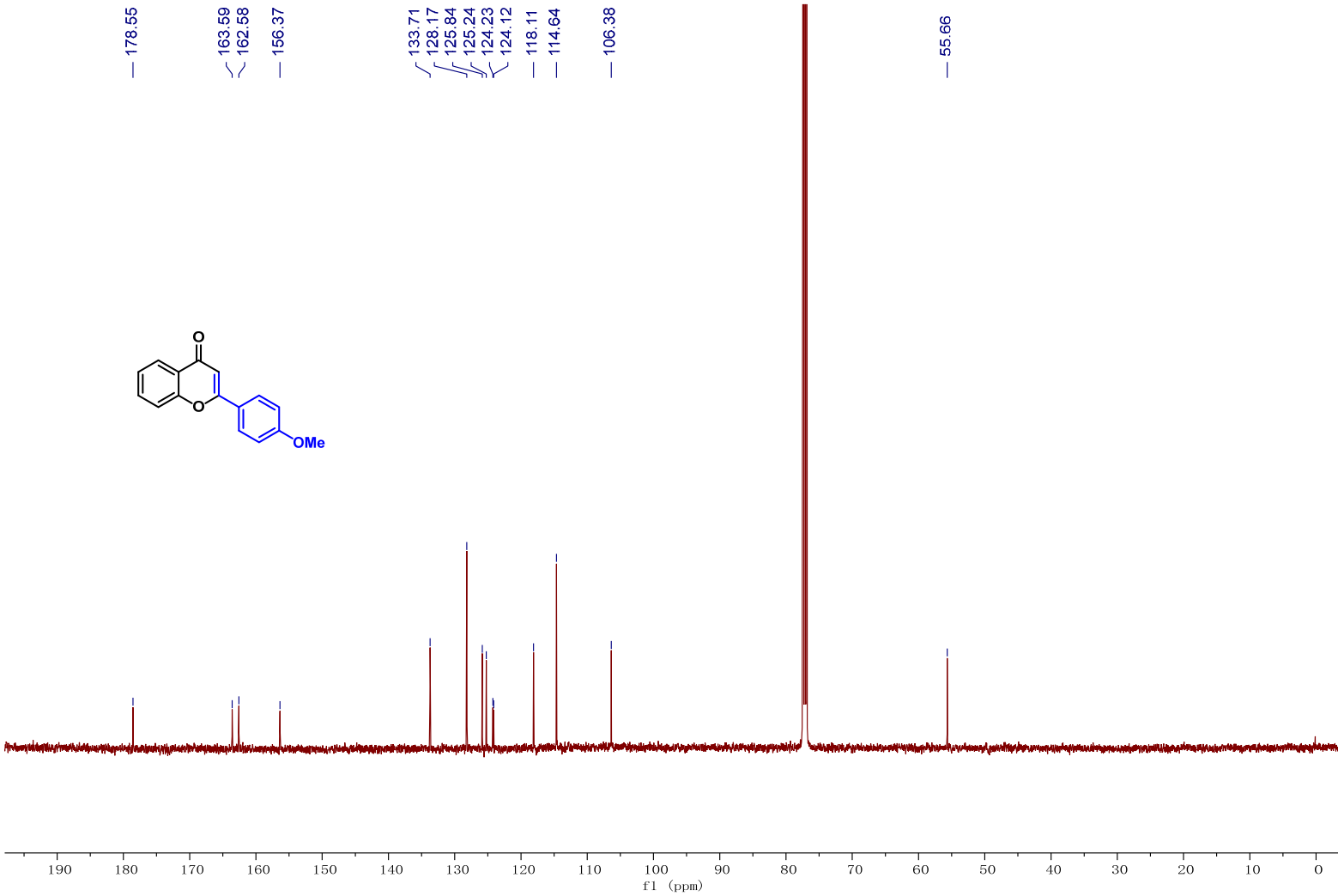
Compound 16 ^{13}C NMR



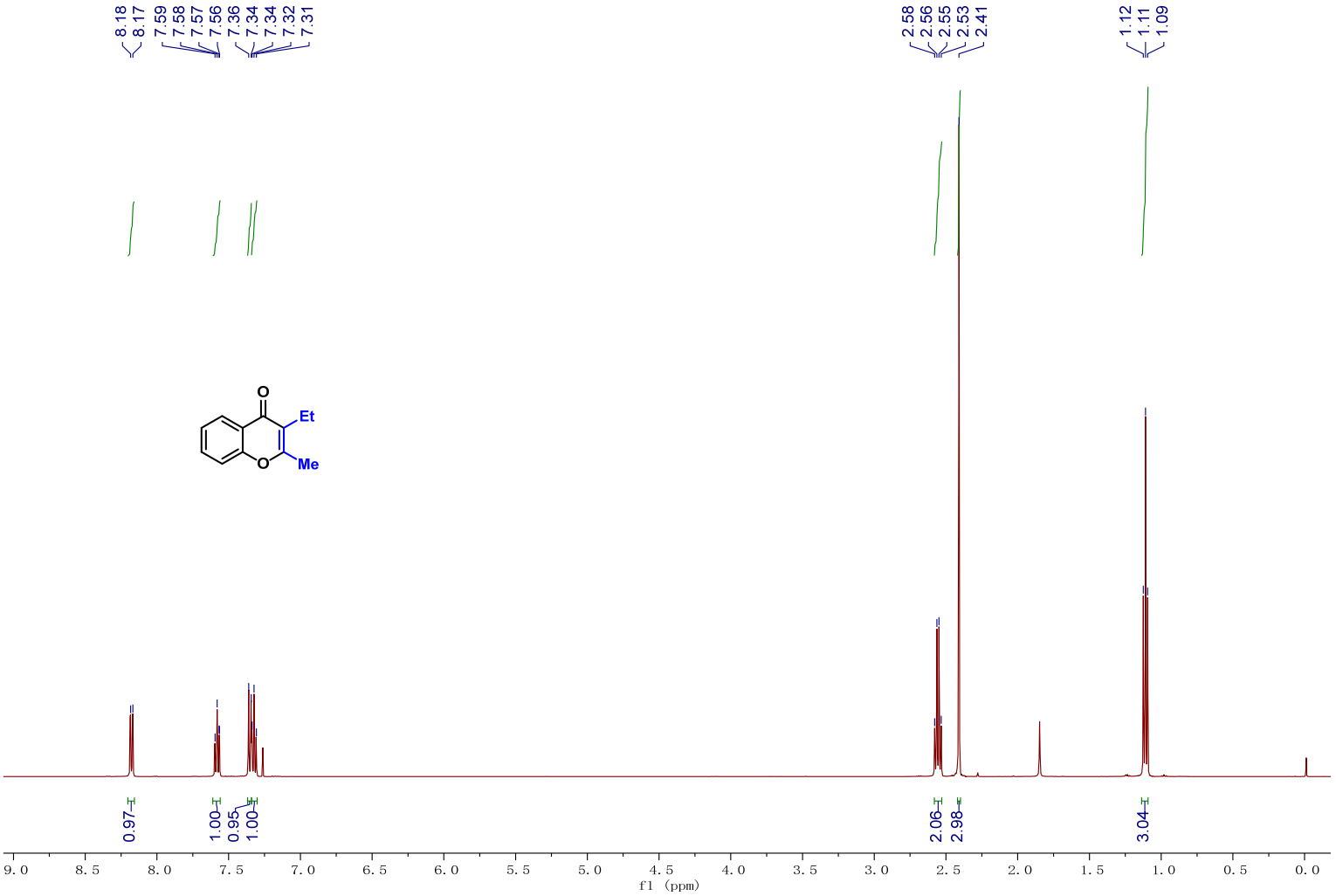
Compound 17 ^{1}H NMR



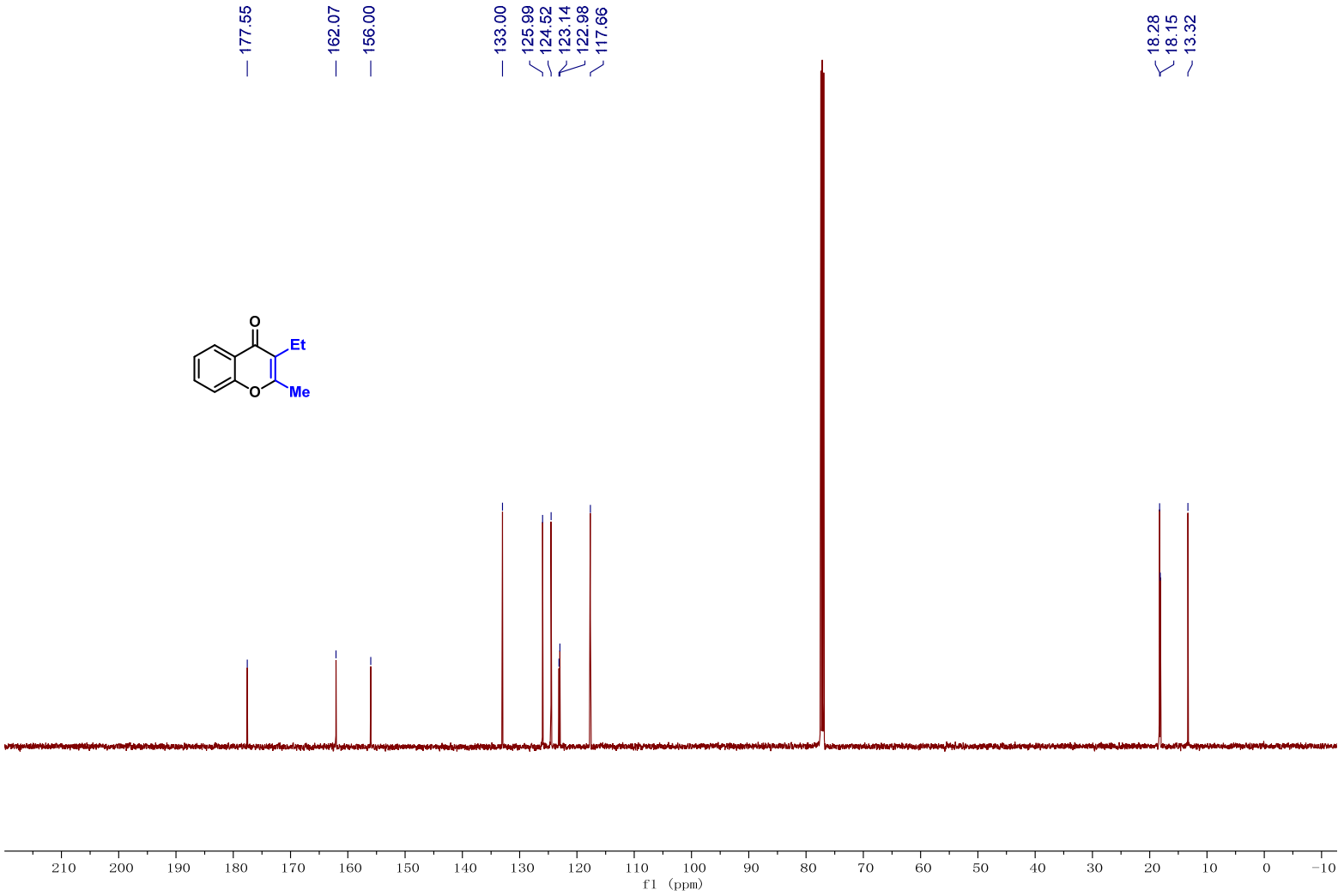
Compound 17 ^{13}C NMR



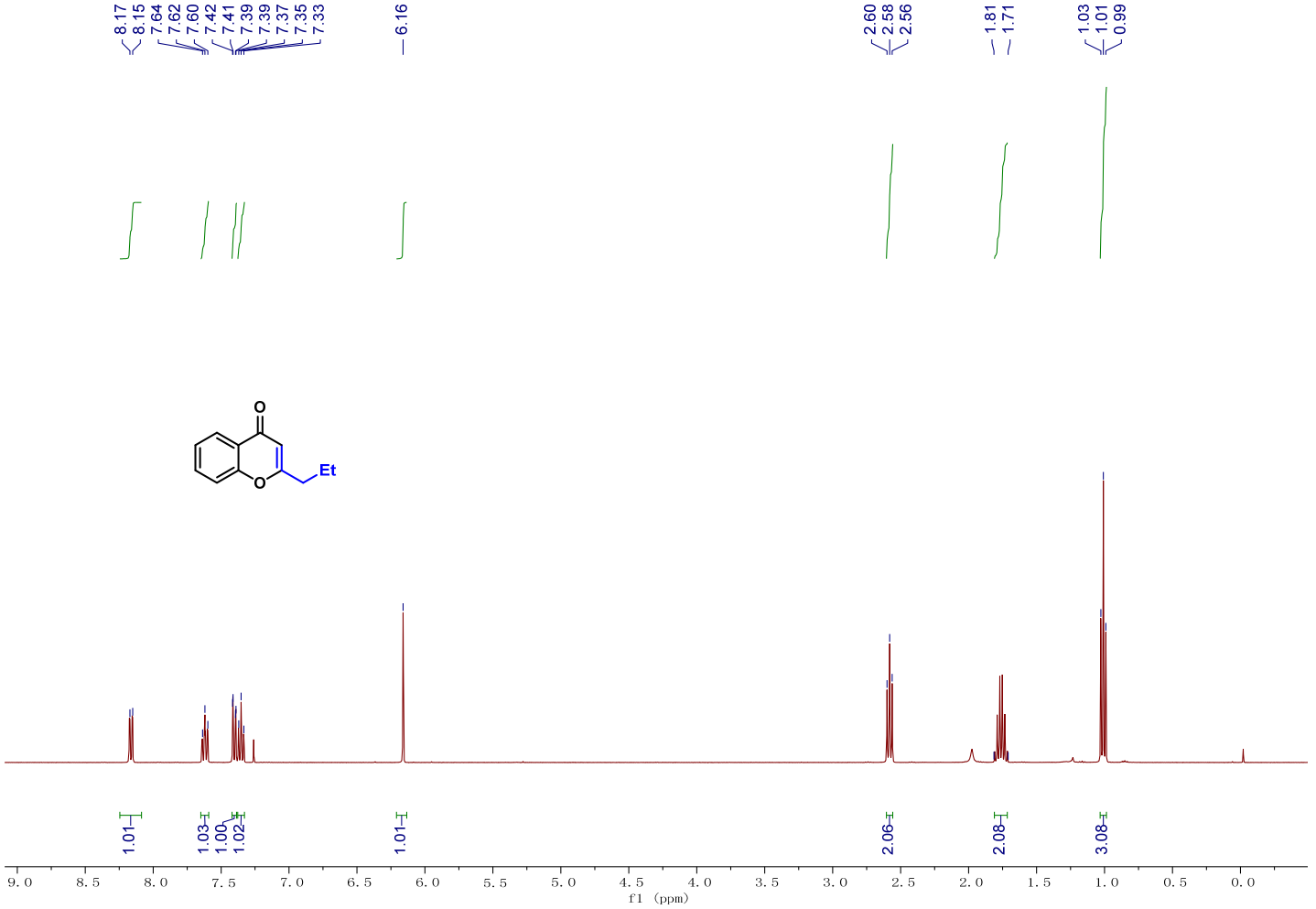
Compound 20a ^{1}H NMR



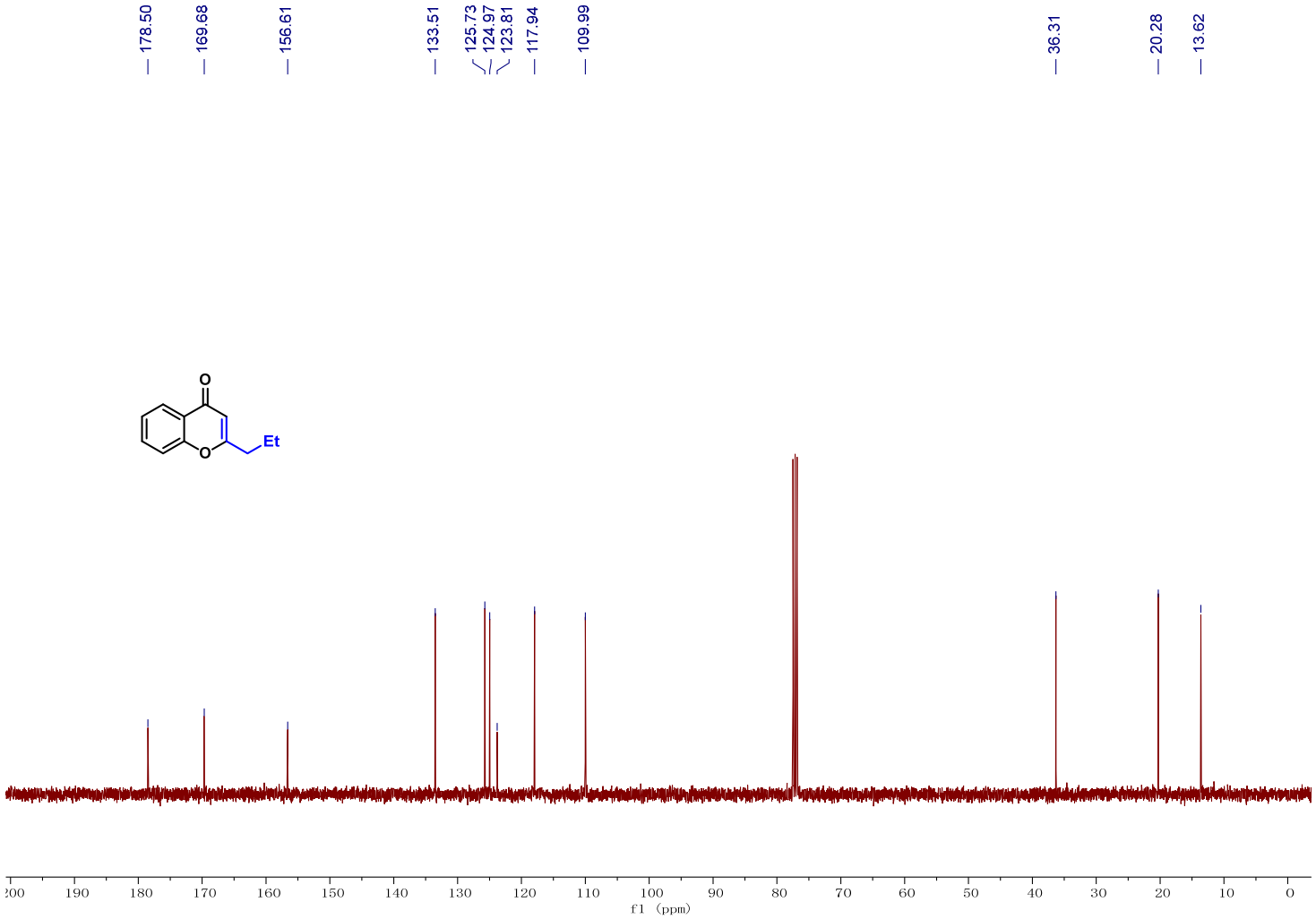
Compound 20a ^{13}C NMR



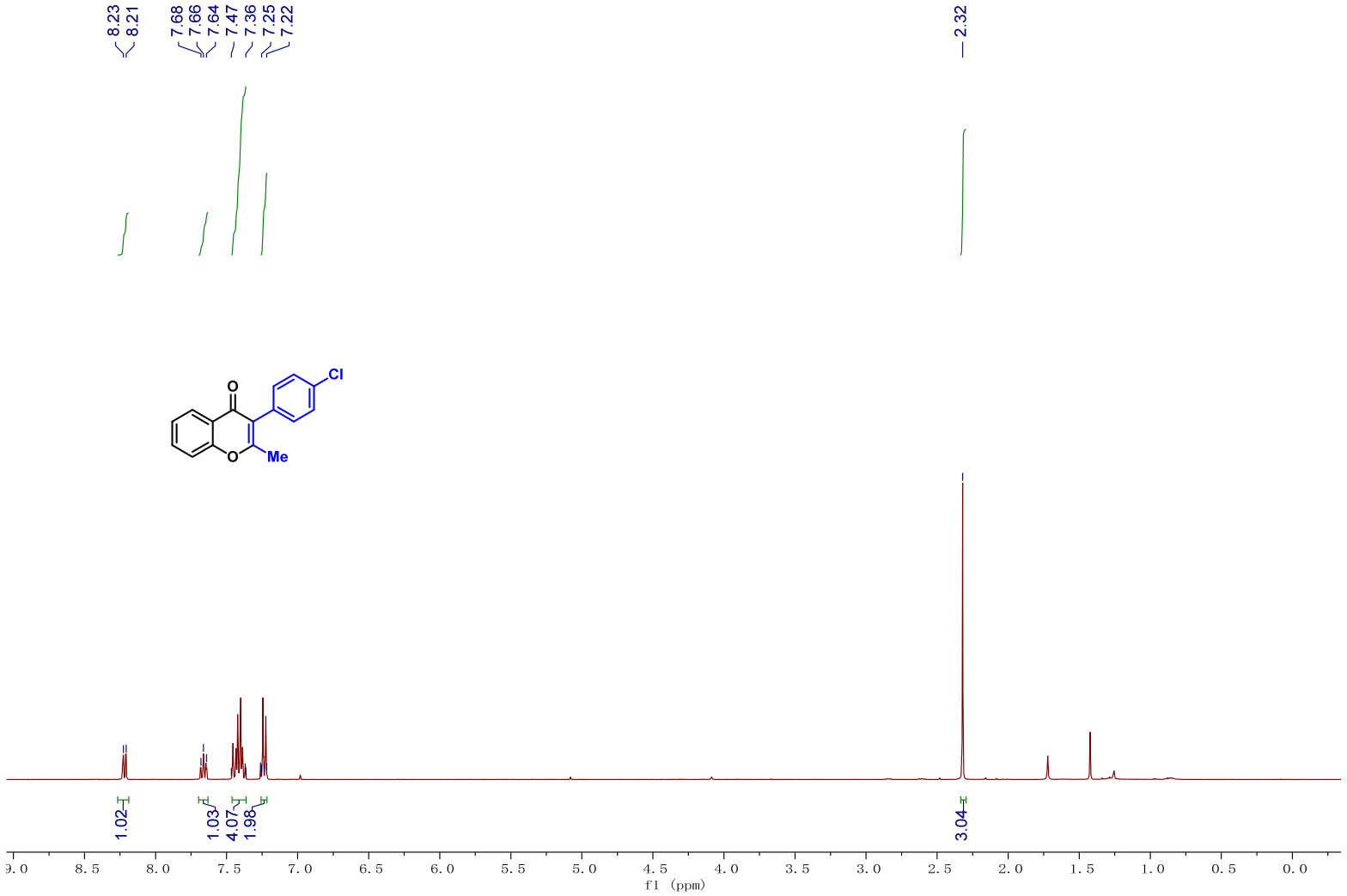
Compound 20b ^{1}H NMR



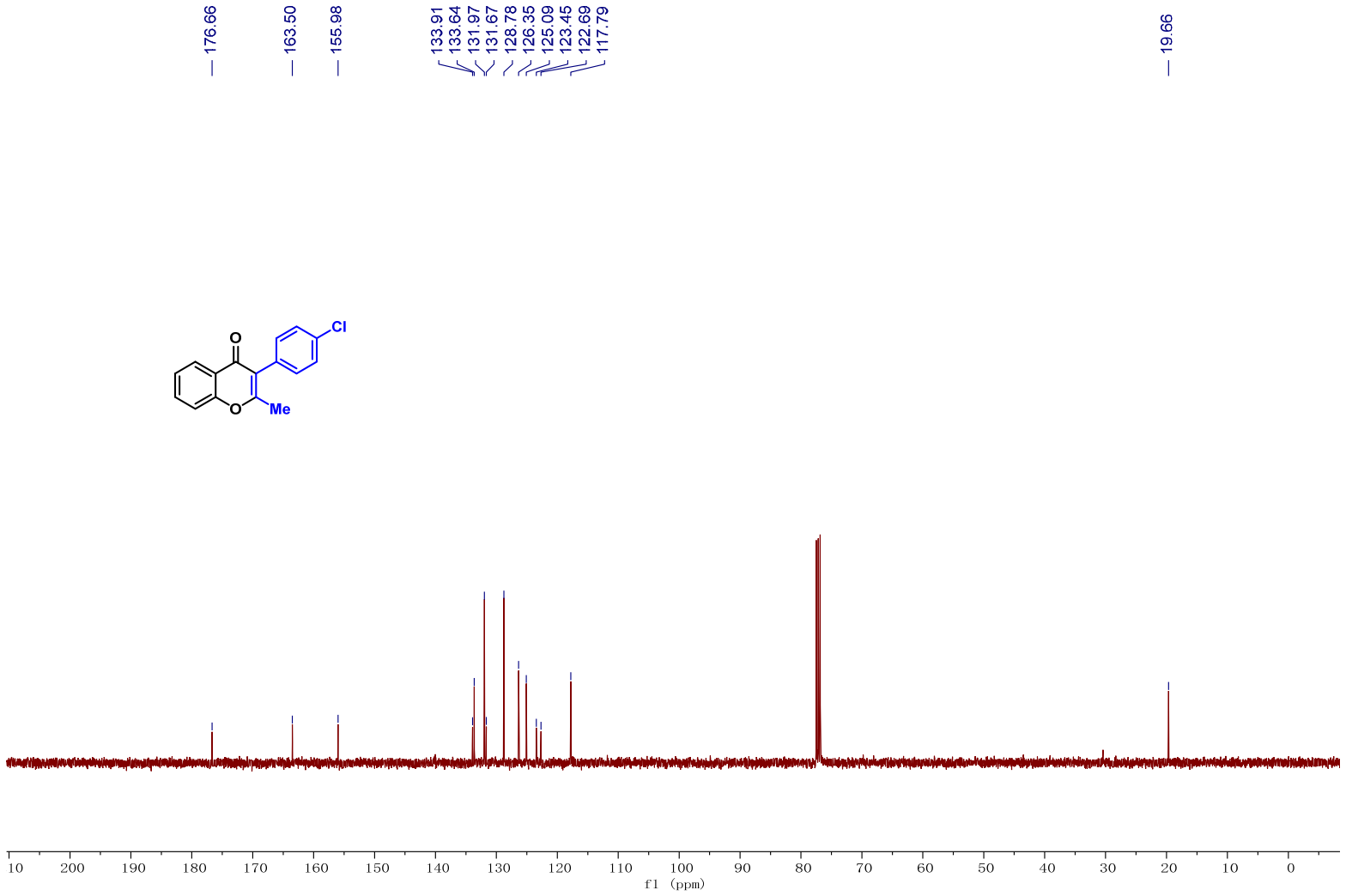
Compound 20b ^{13}C NMR



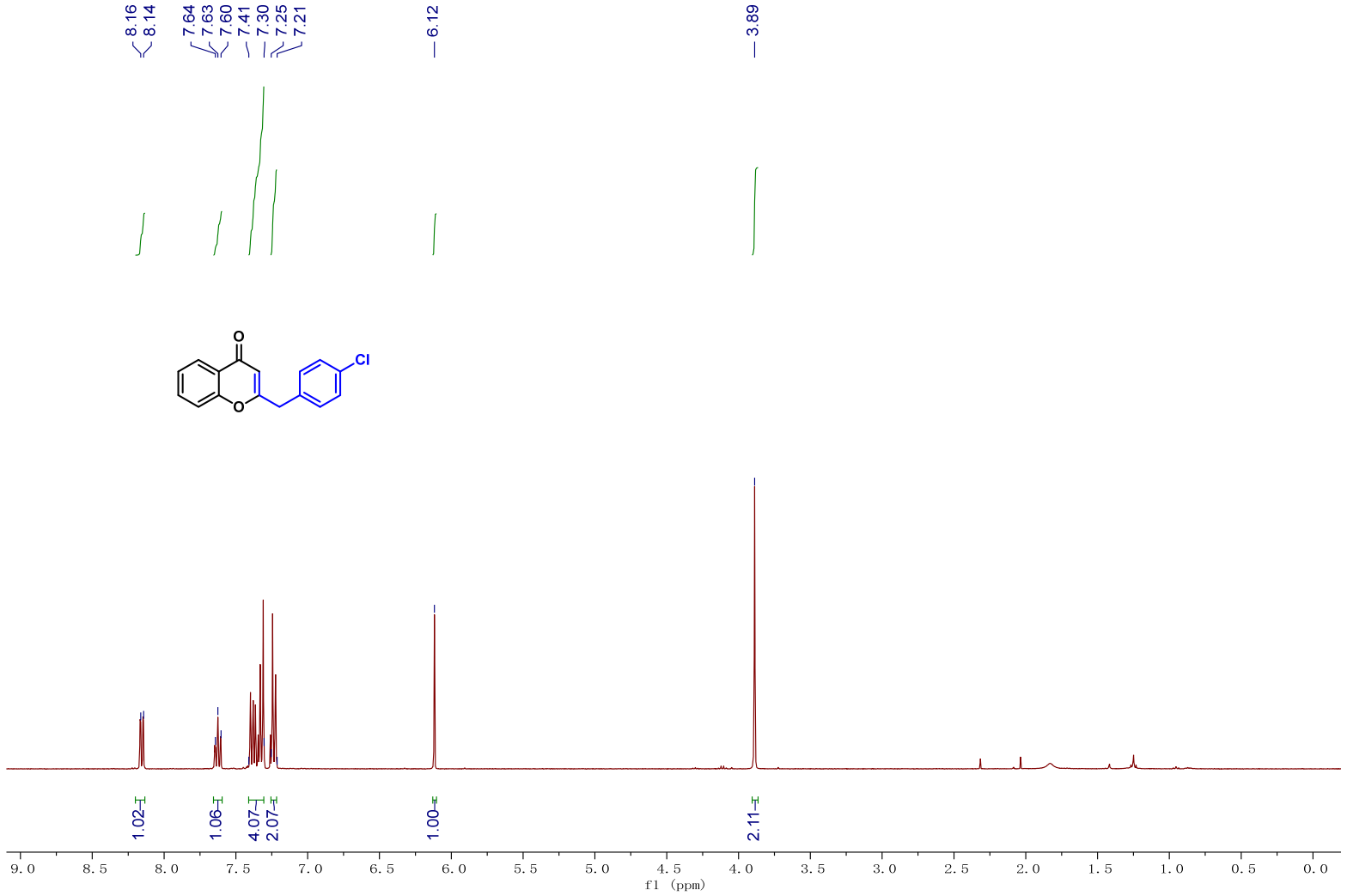
Compound 21a ^{1}H NMR



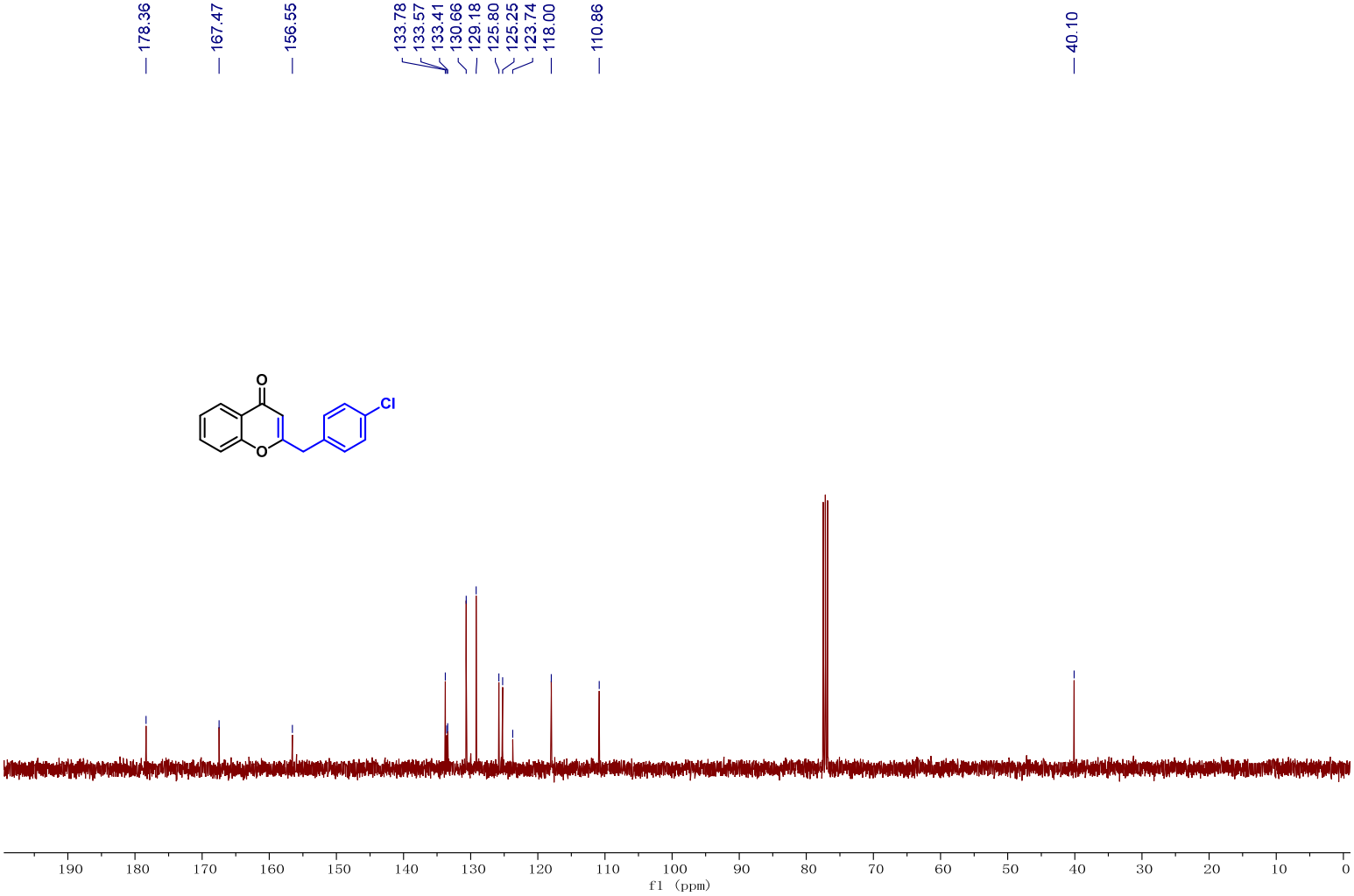
Compound 21a ^{13}C NMR



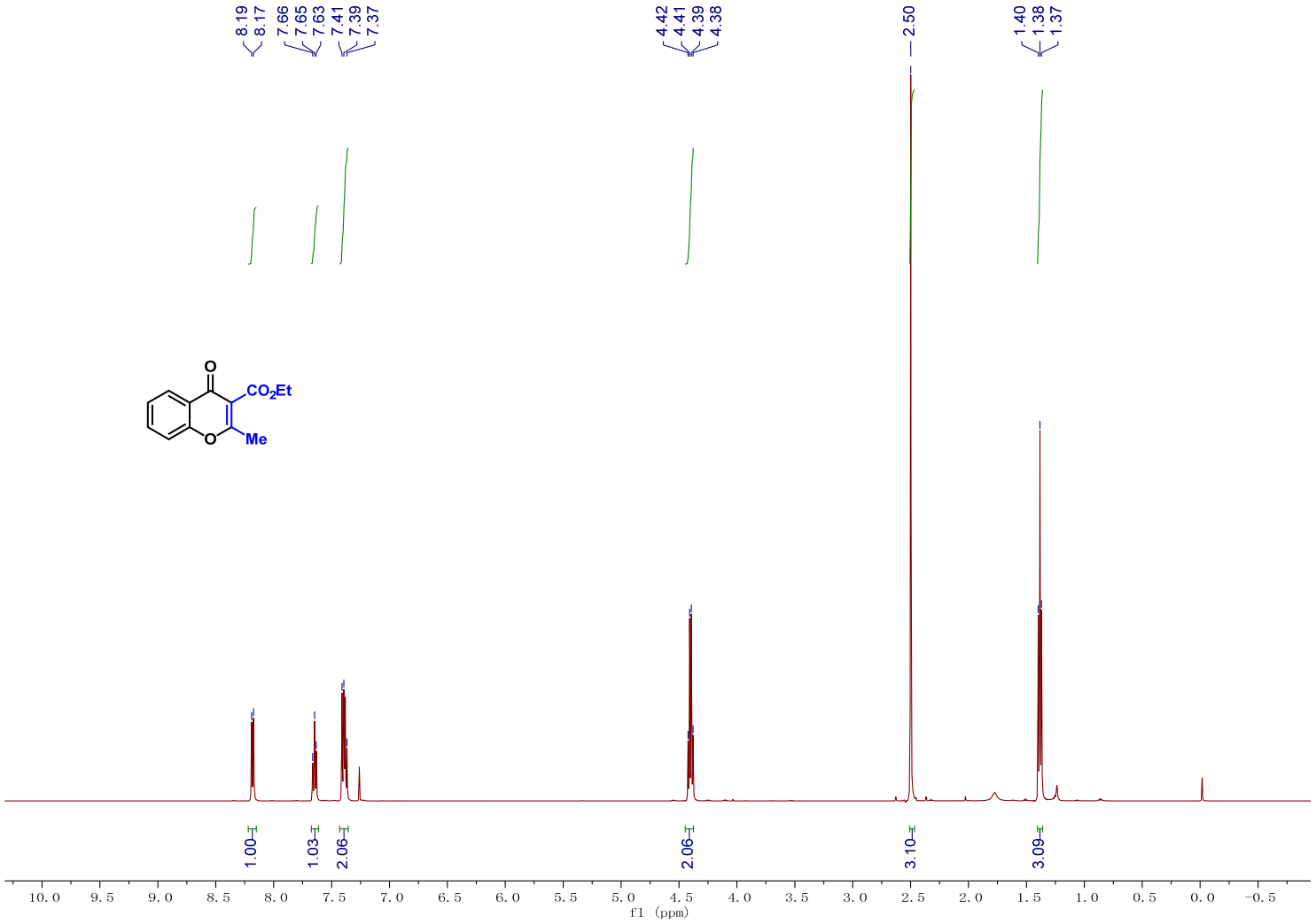
Compound 21b ^{1}H NMR



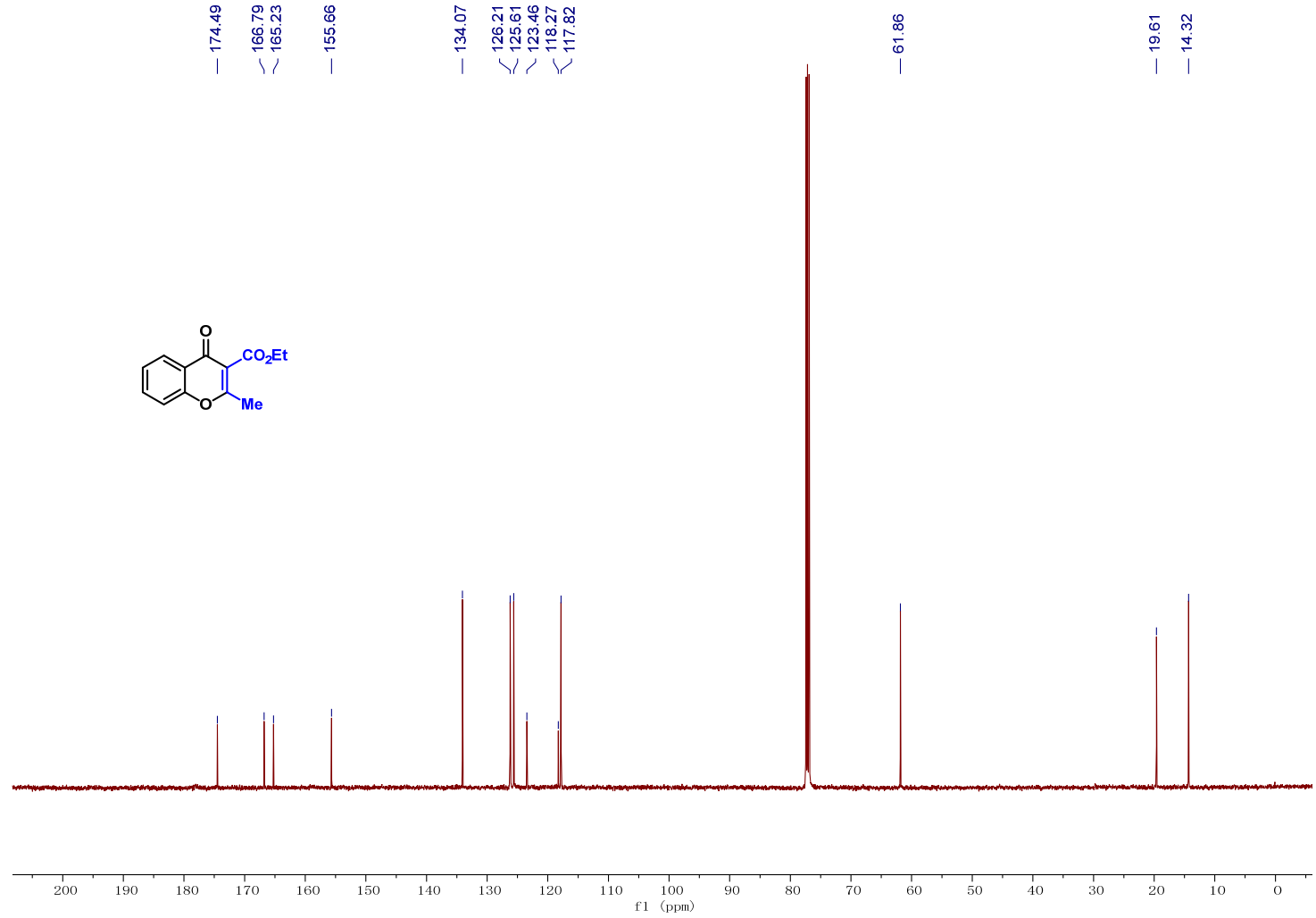
Compound 21b ^{13}C NMR



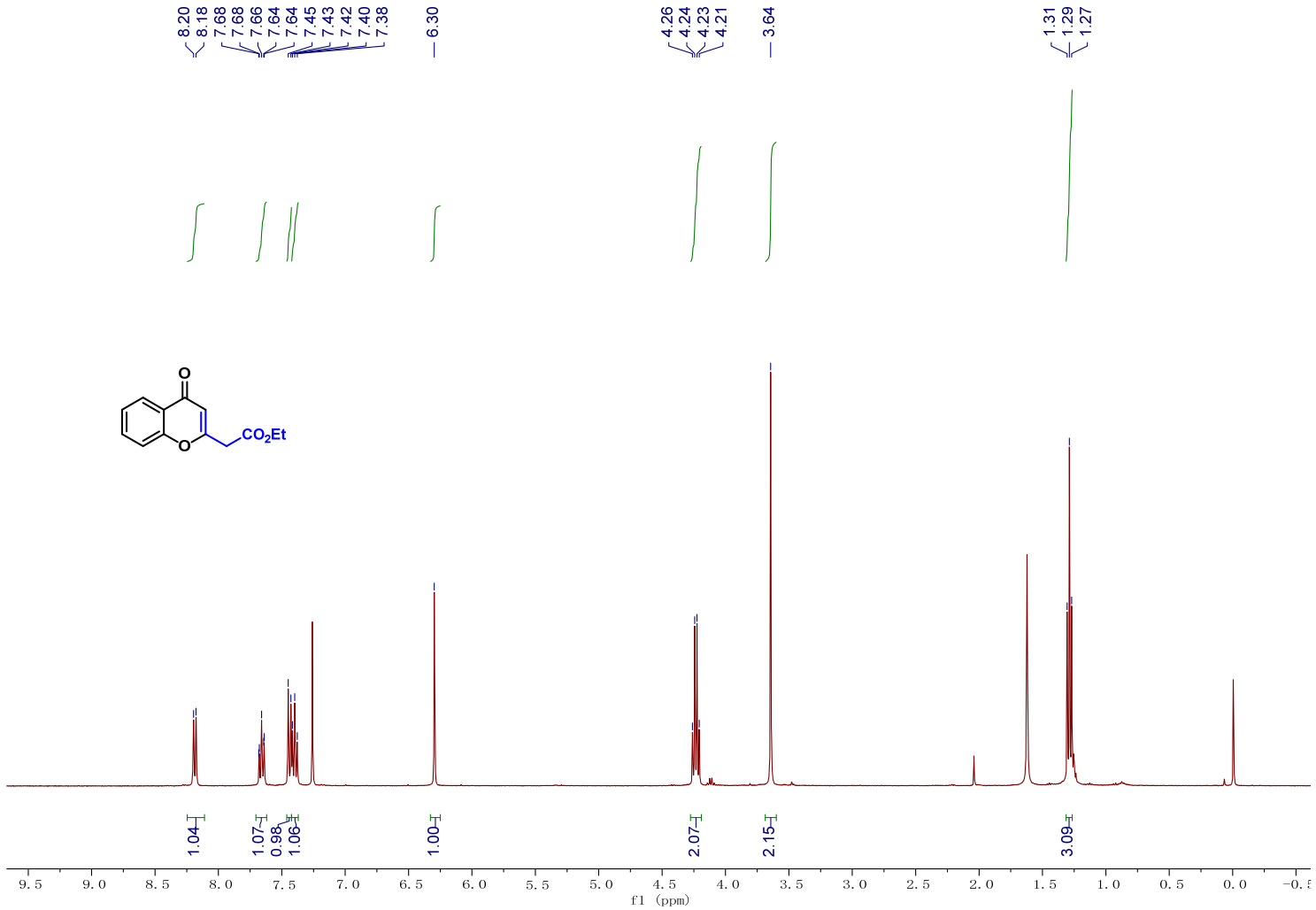
Compound 22a ^{1}H NMR



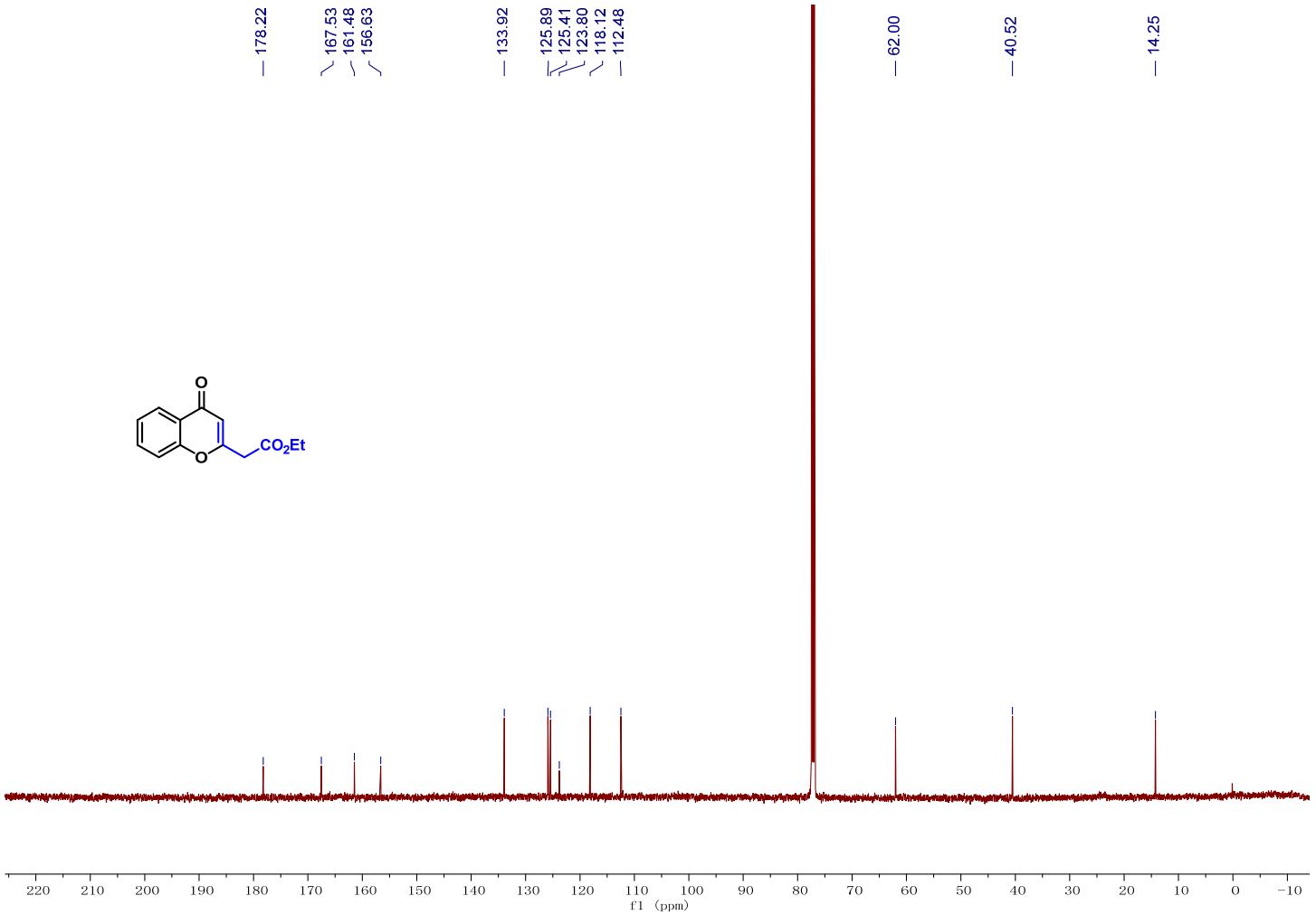
Compound 22a ^{13}C NMR



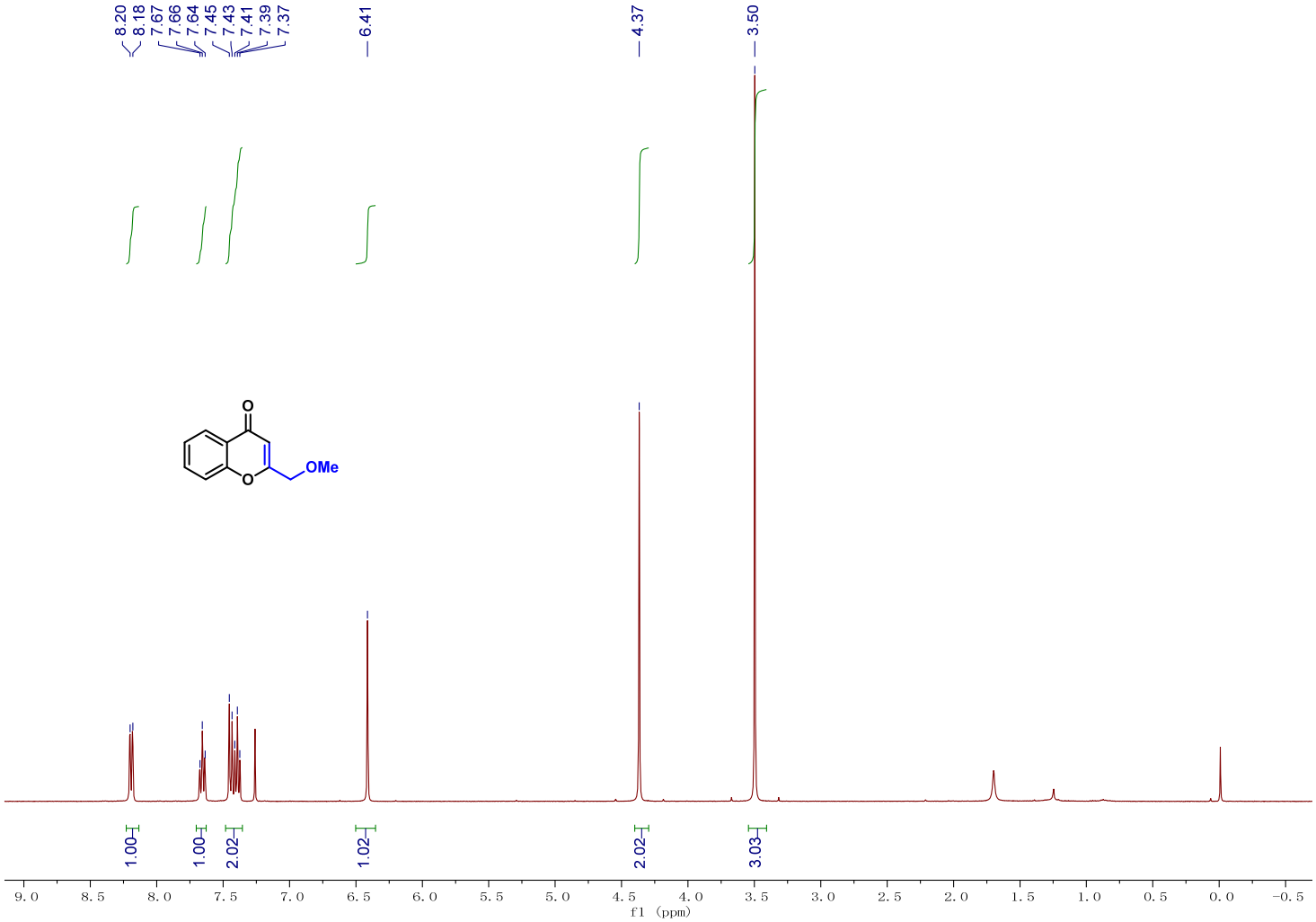
Compound 22b ^{1}H NMR



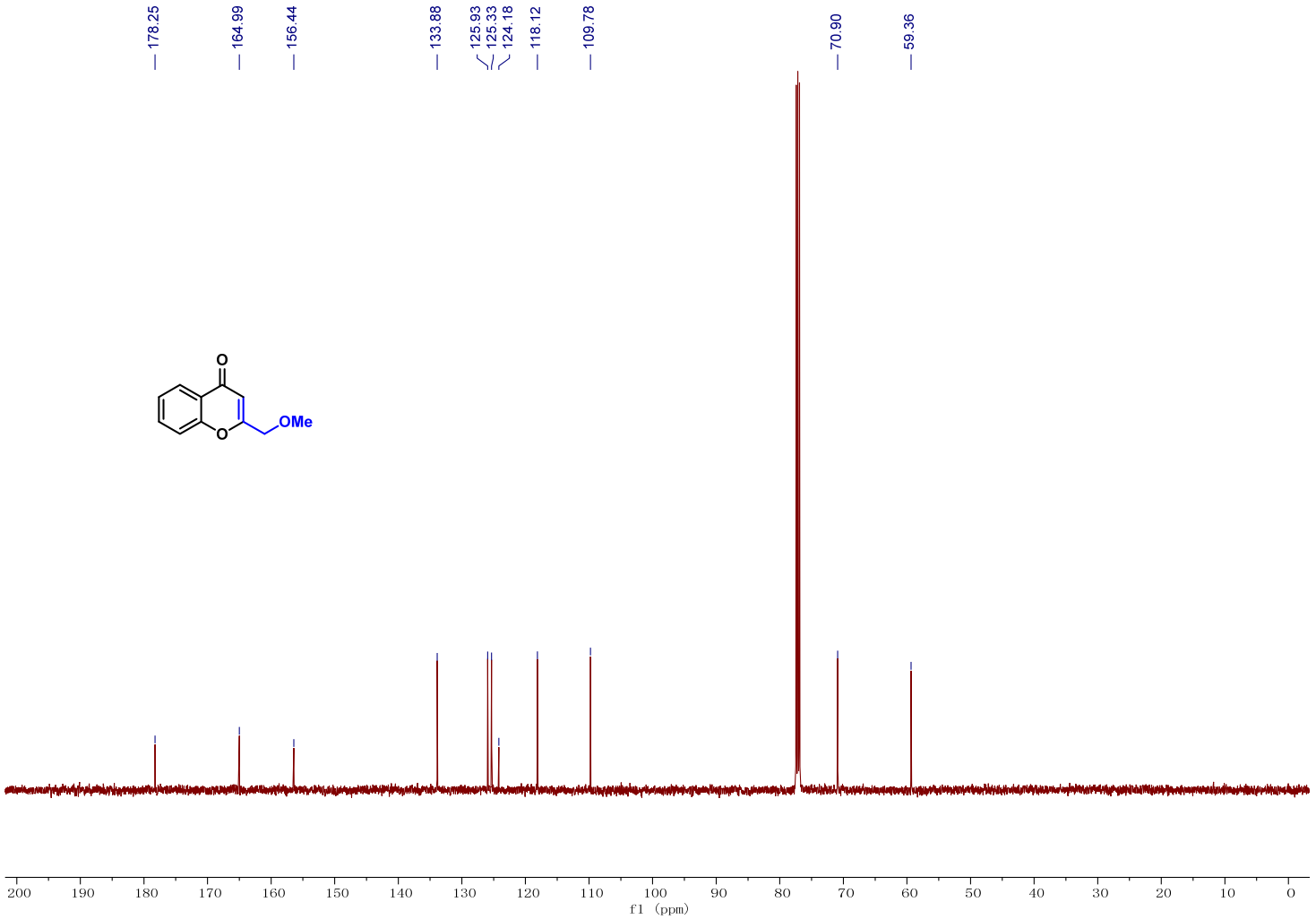
Compound 22b ^{13}C NMR



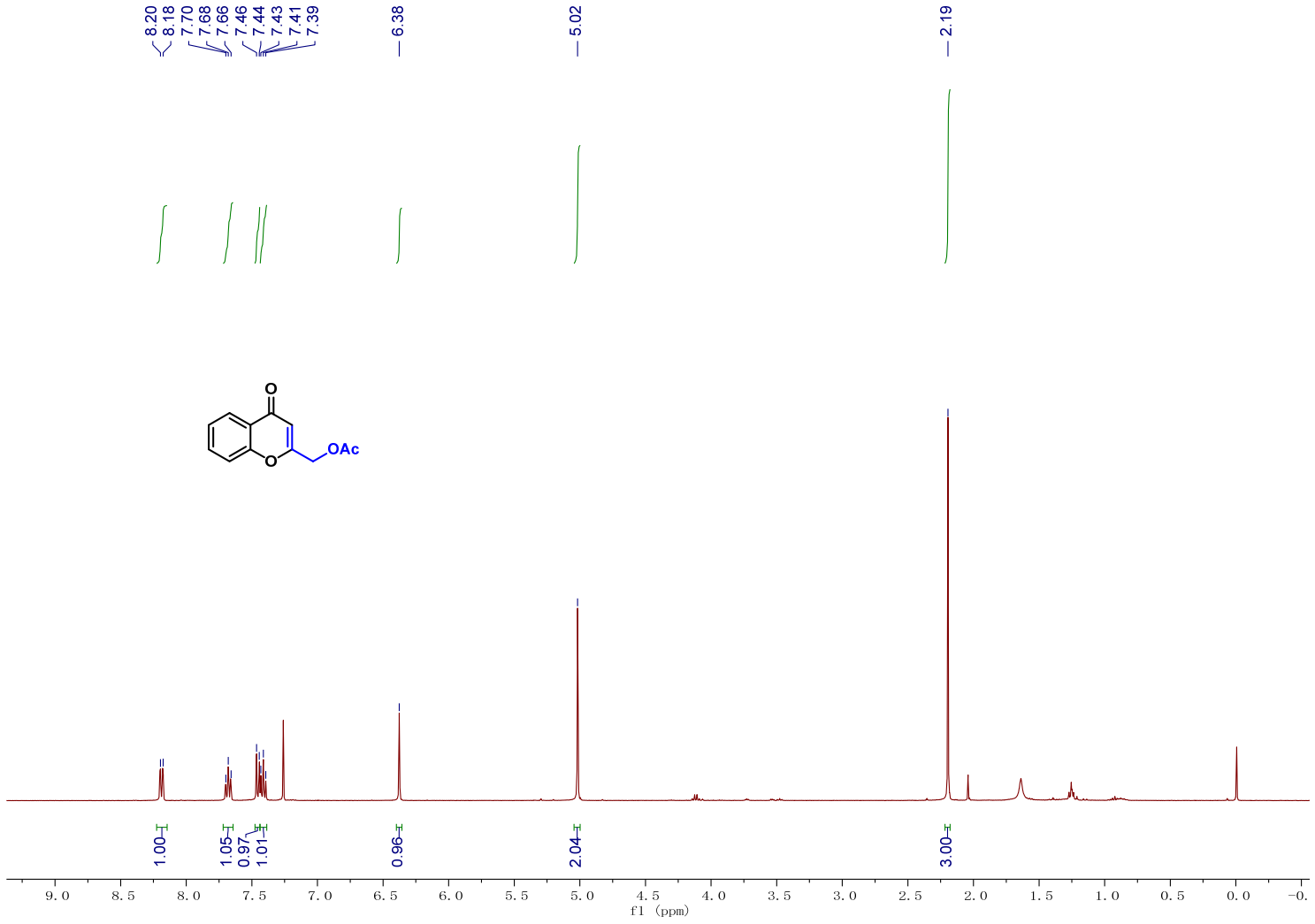
Compound 23b ^{1}H NMR



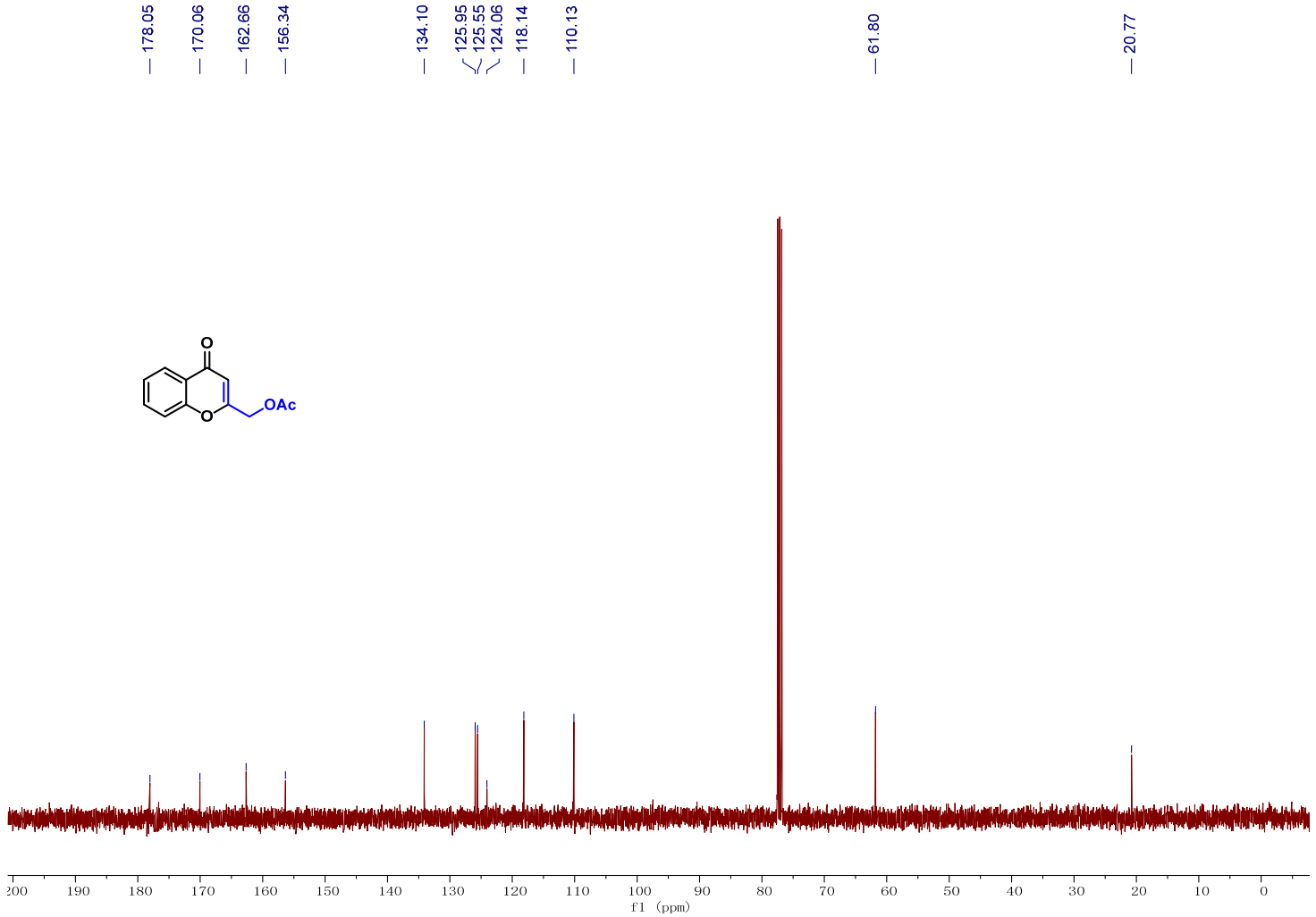
Compound 23b ^{13}C NMR



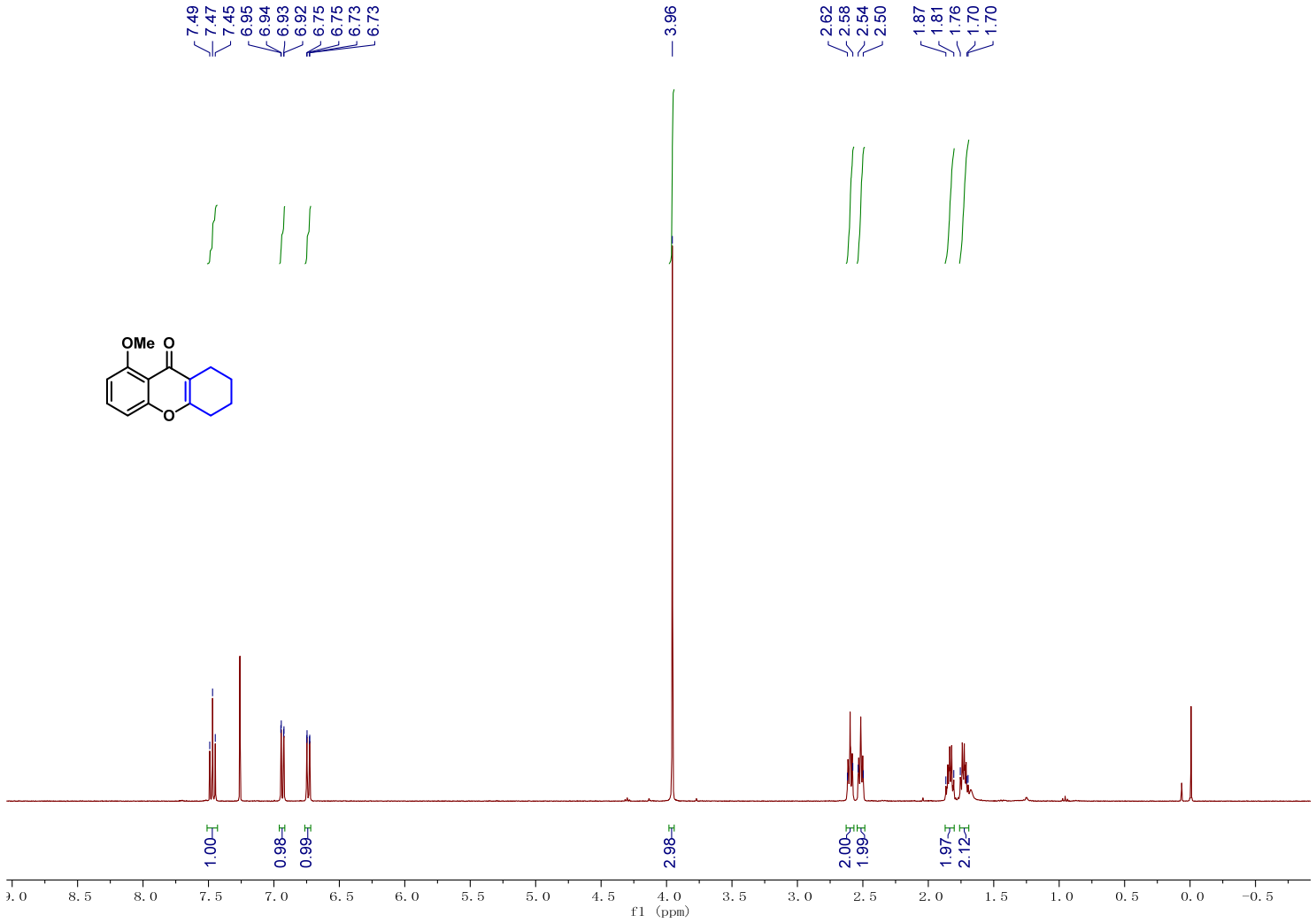
Compound 24b ^{1}H NMR



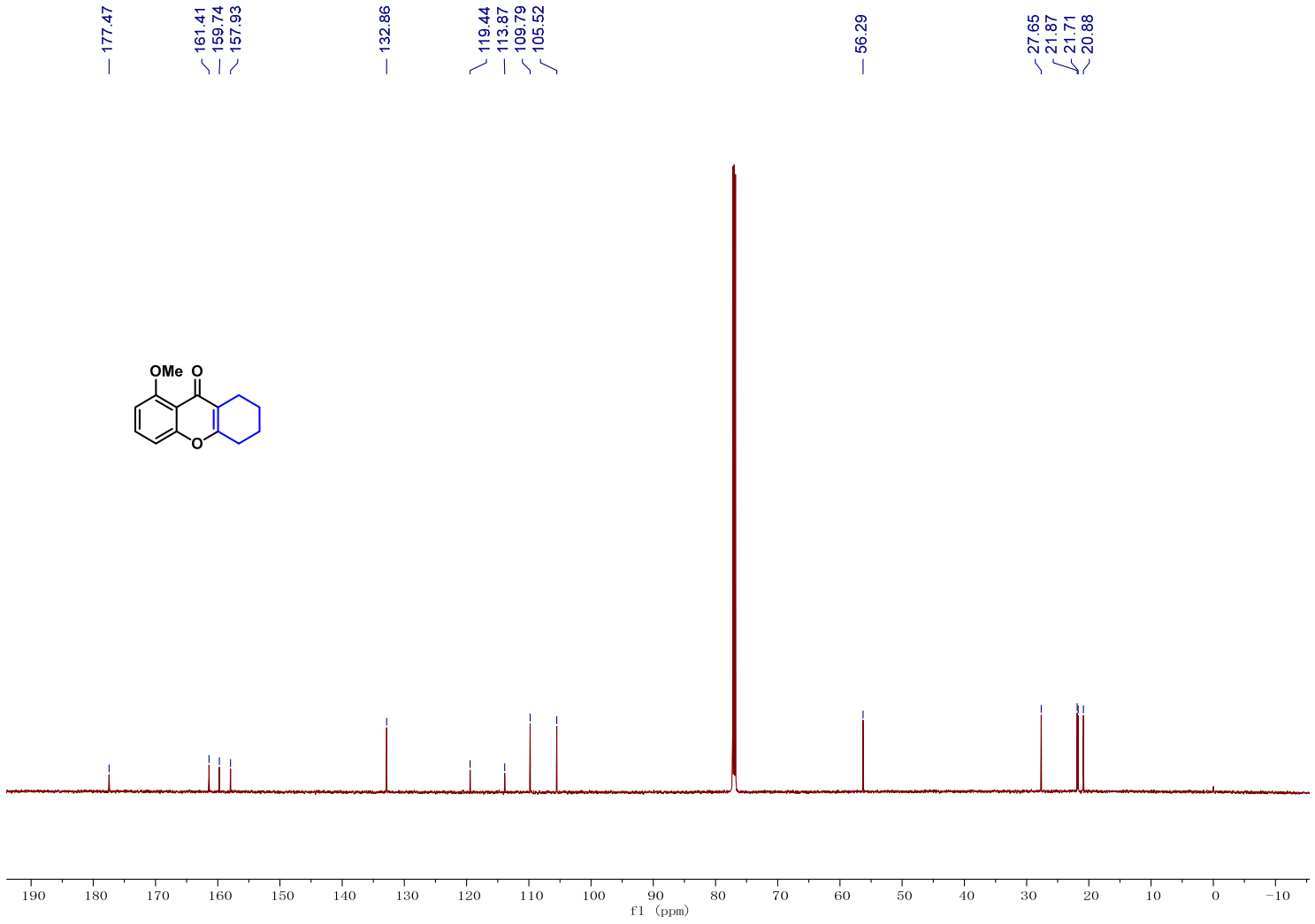
Compound 24b ^{13}C NMR



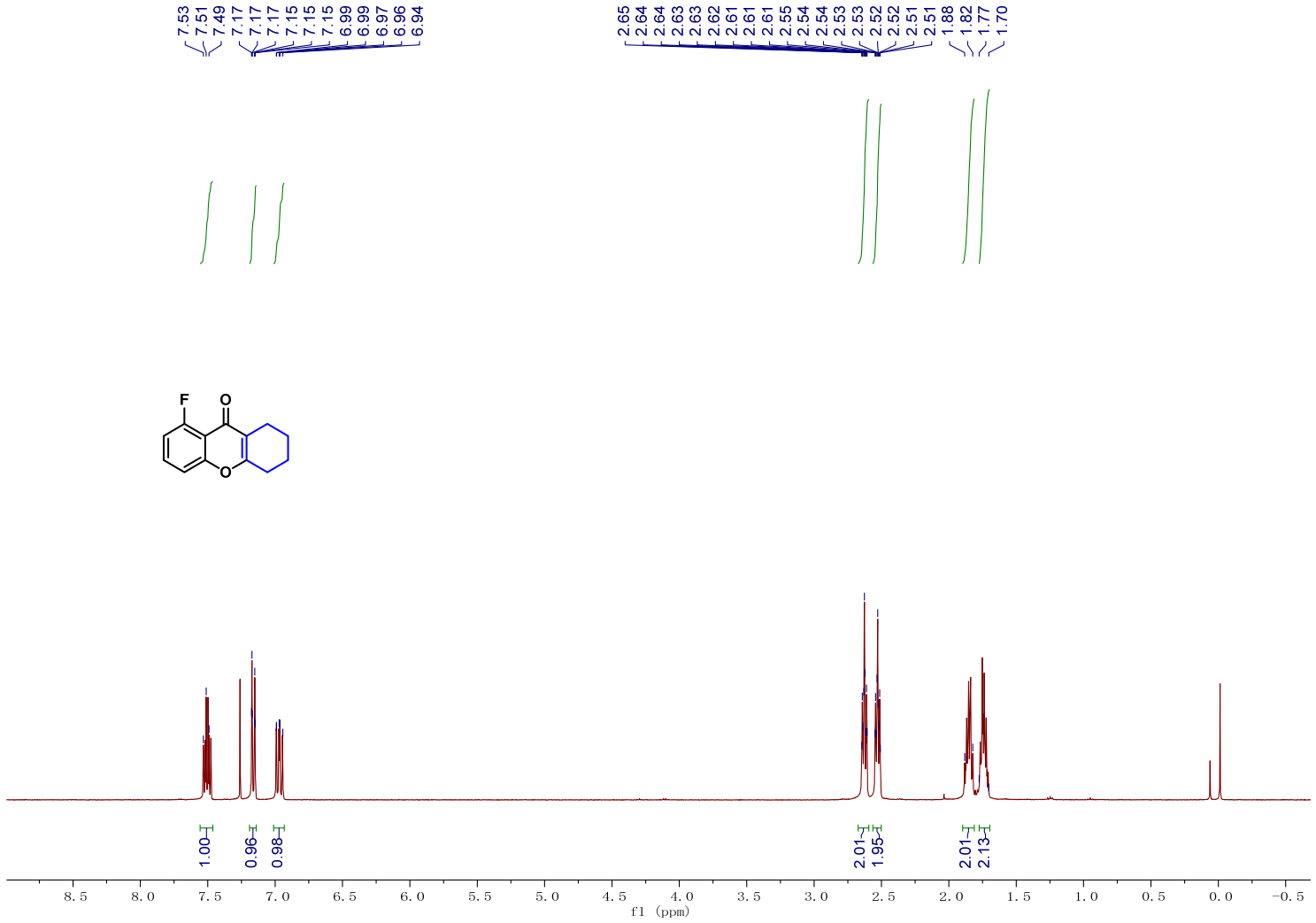
Compound 25 ^{1}H NMR



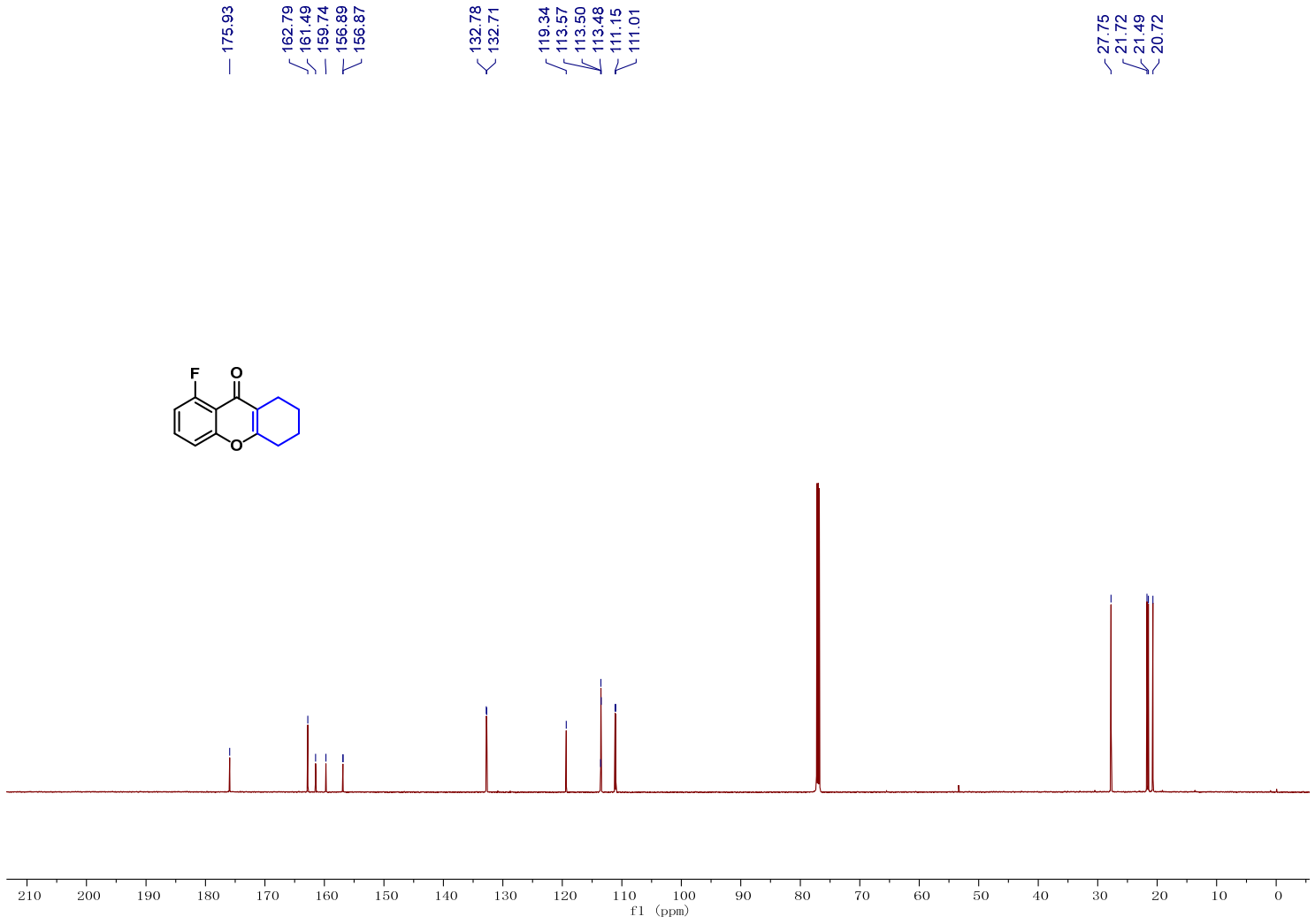
Compound 25 ^{13}C NMR



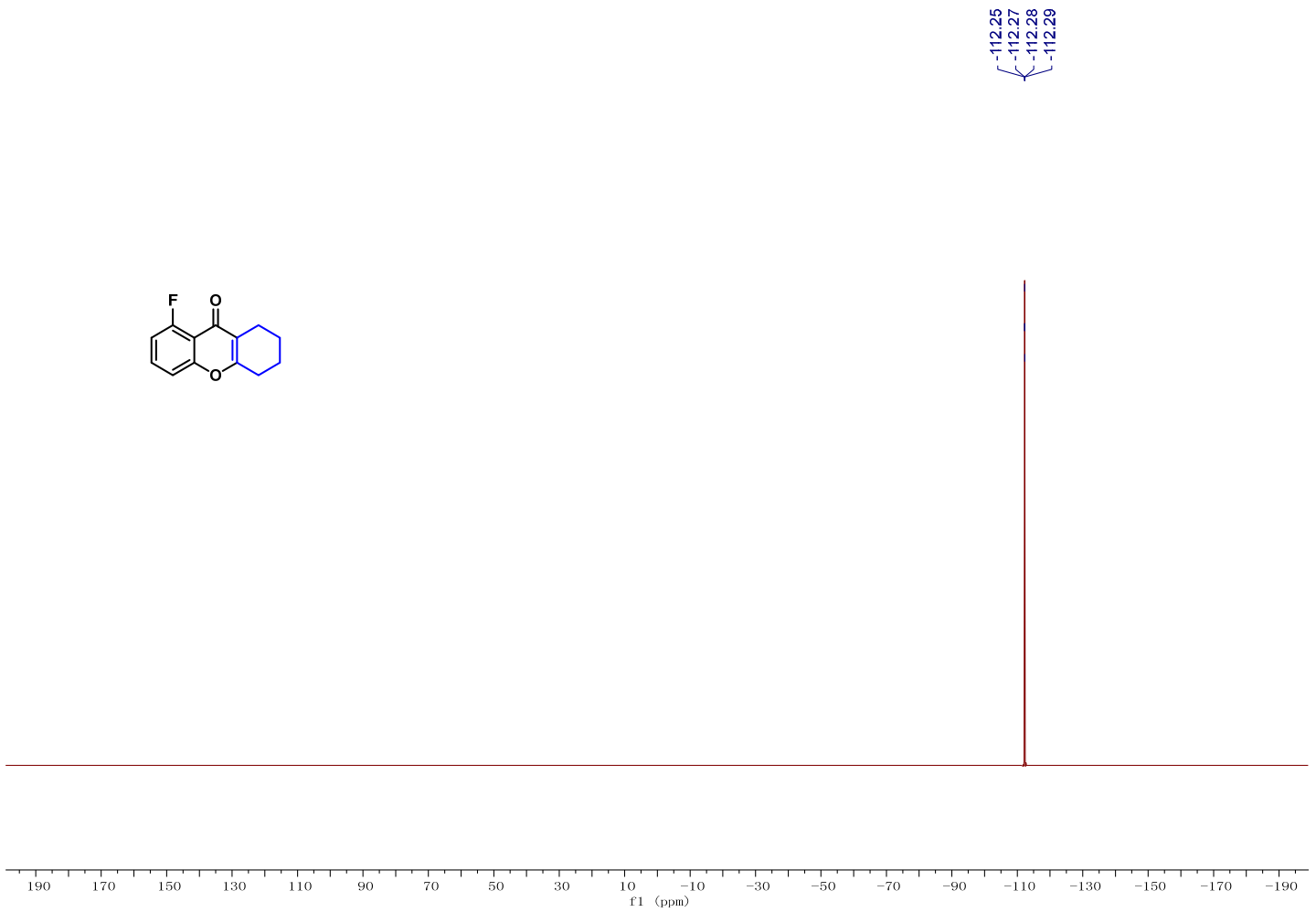
Compound 26 ^{1}H NMR



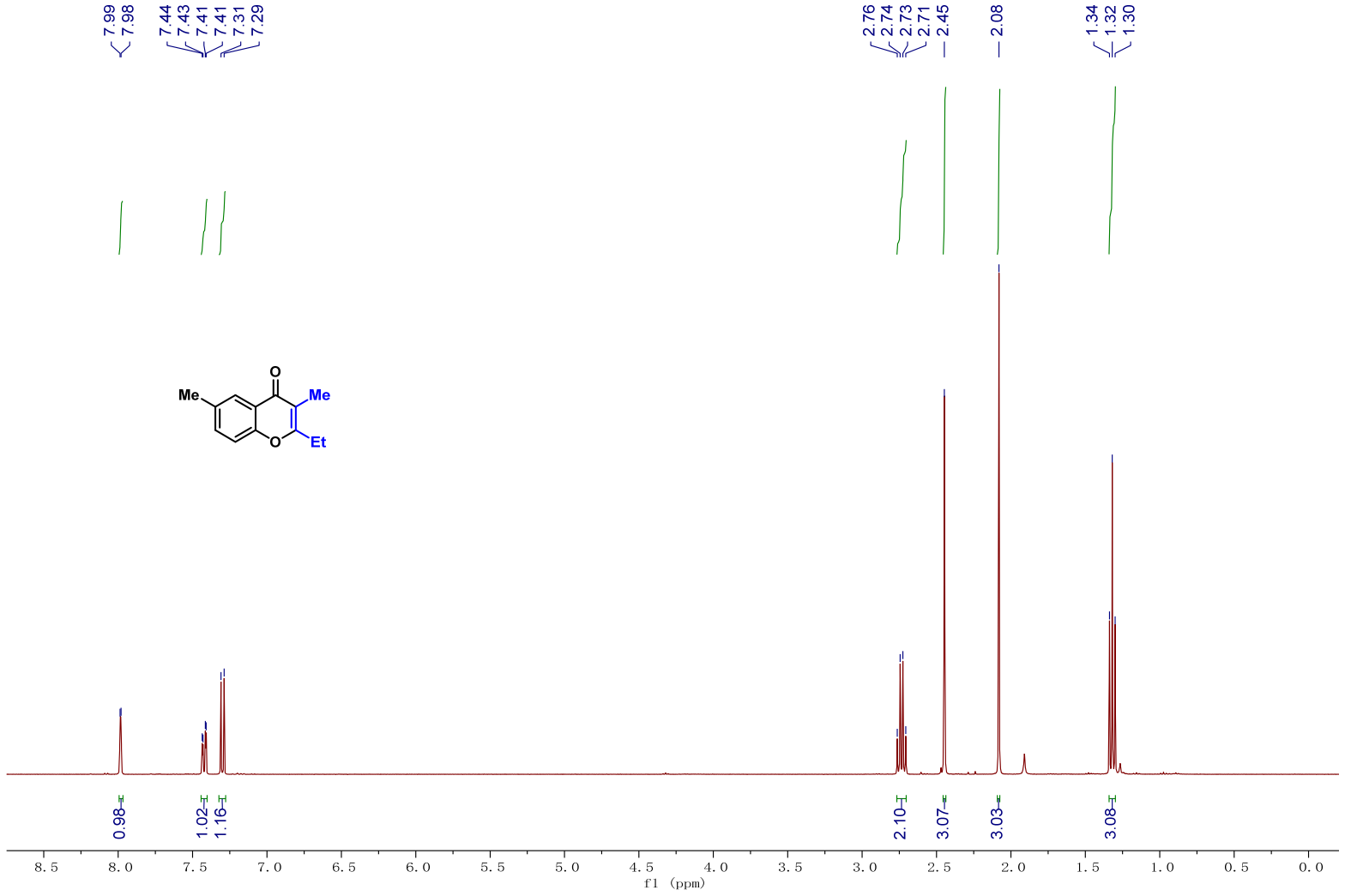
Compound 26 ^{13}C NMR



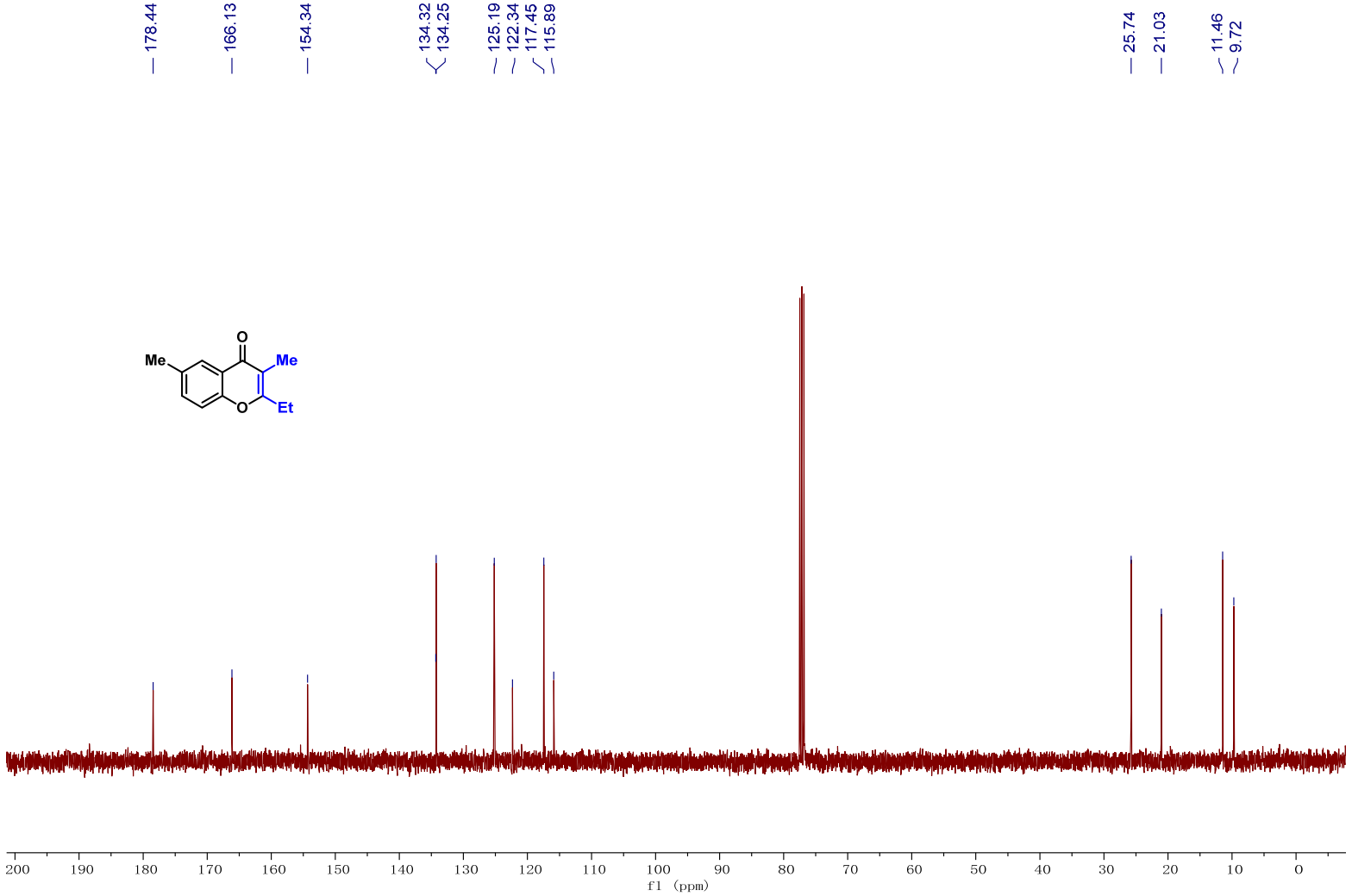
Compound 26 ^{19}F NMR



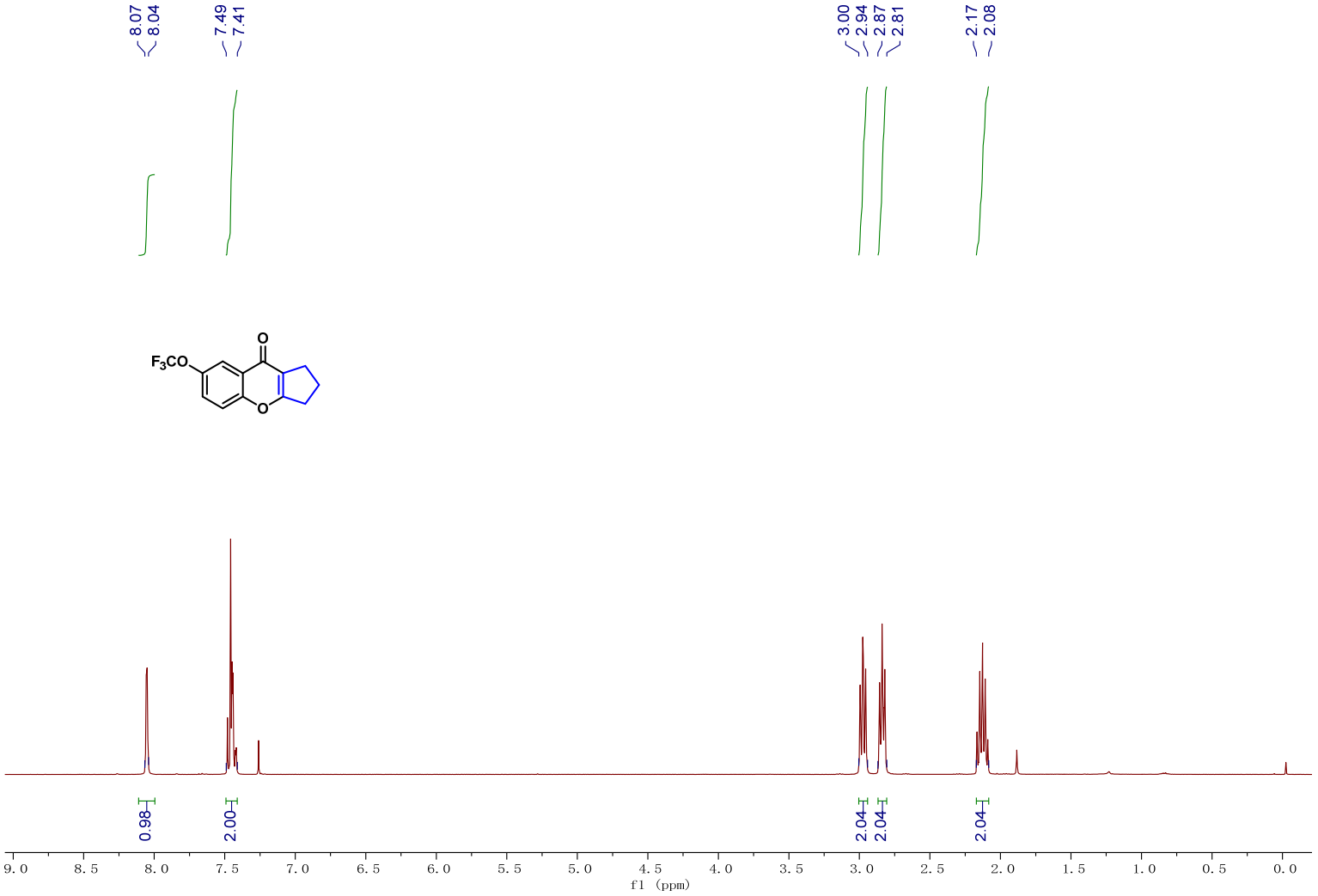
Compound 27 ^{1}H NMR



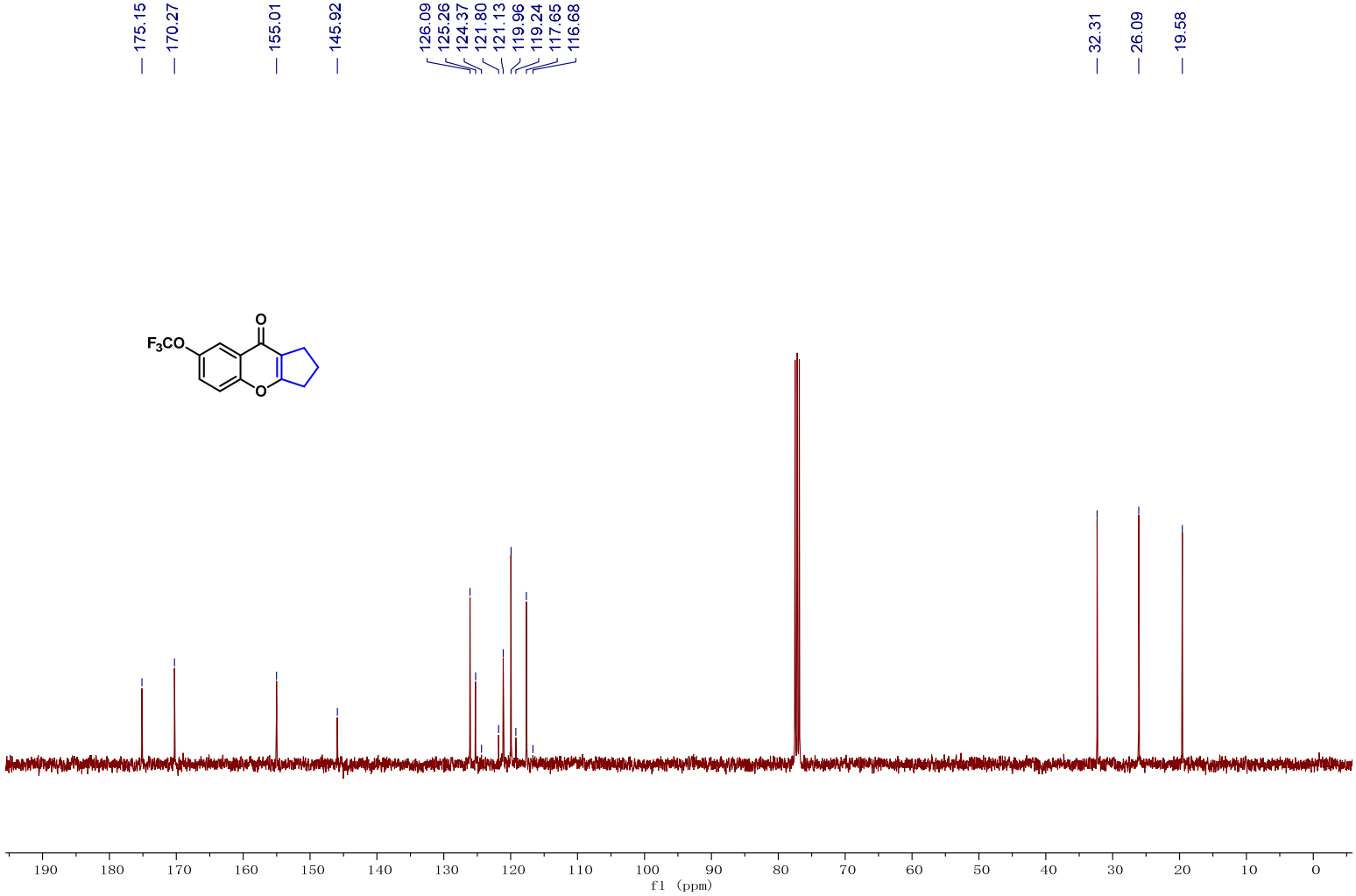
Compound 27 ^{13}C NMR



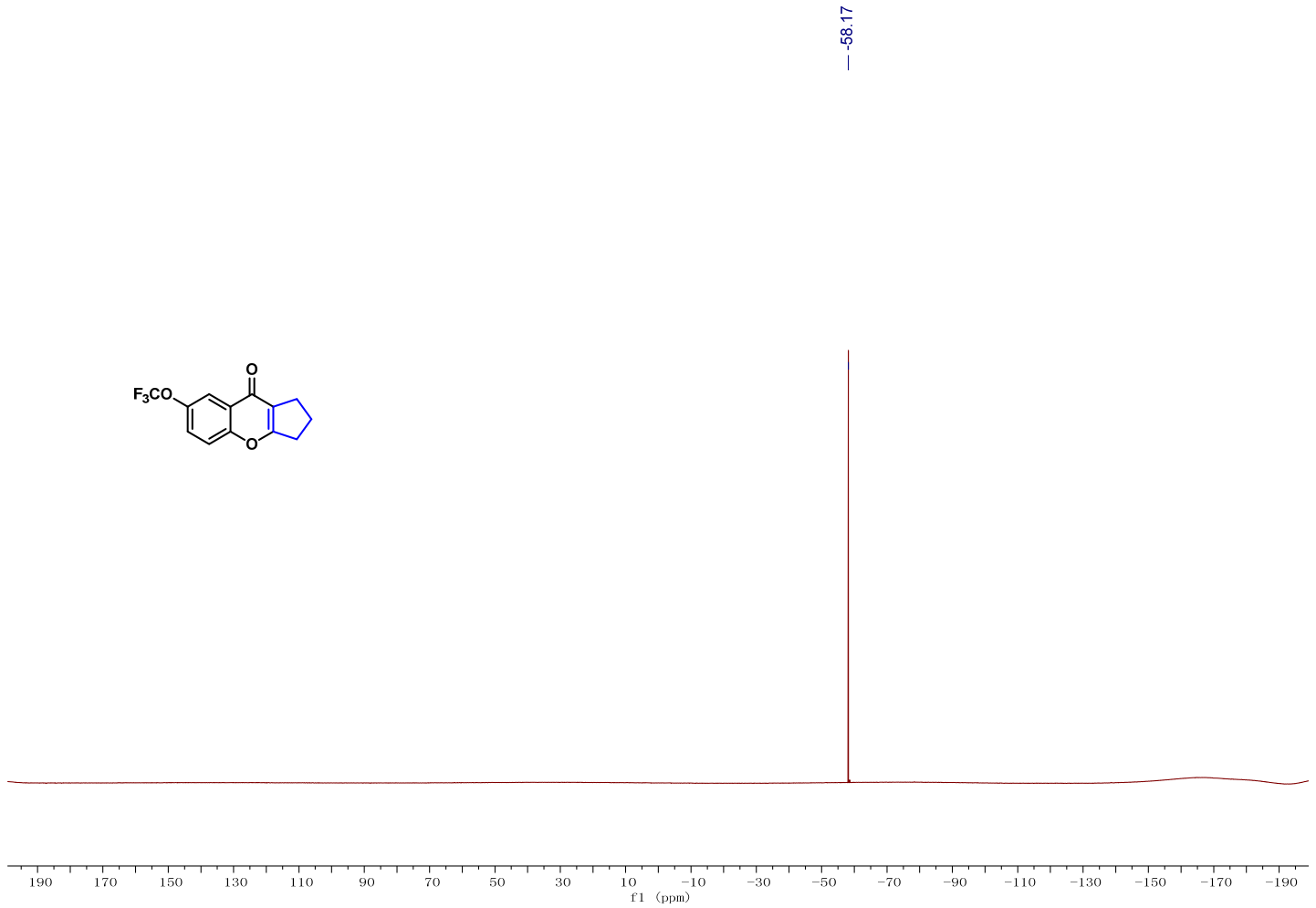
Compound 28 ^{1}H NMR



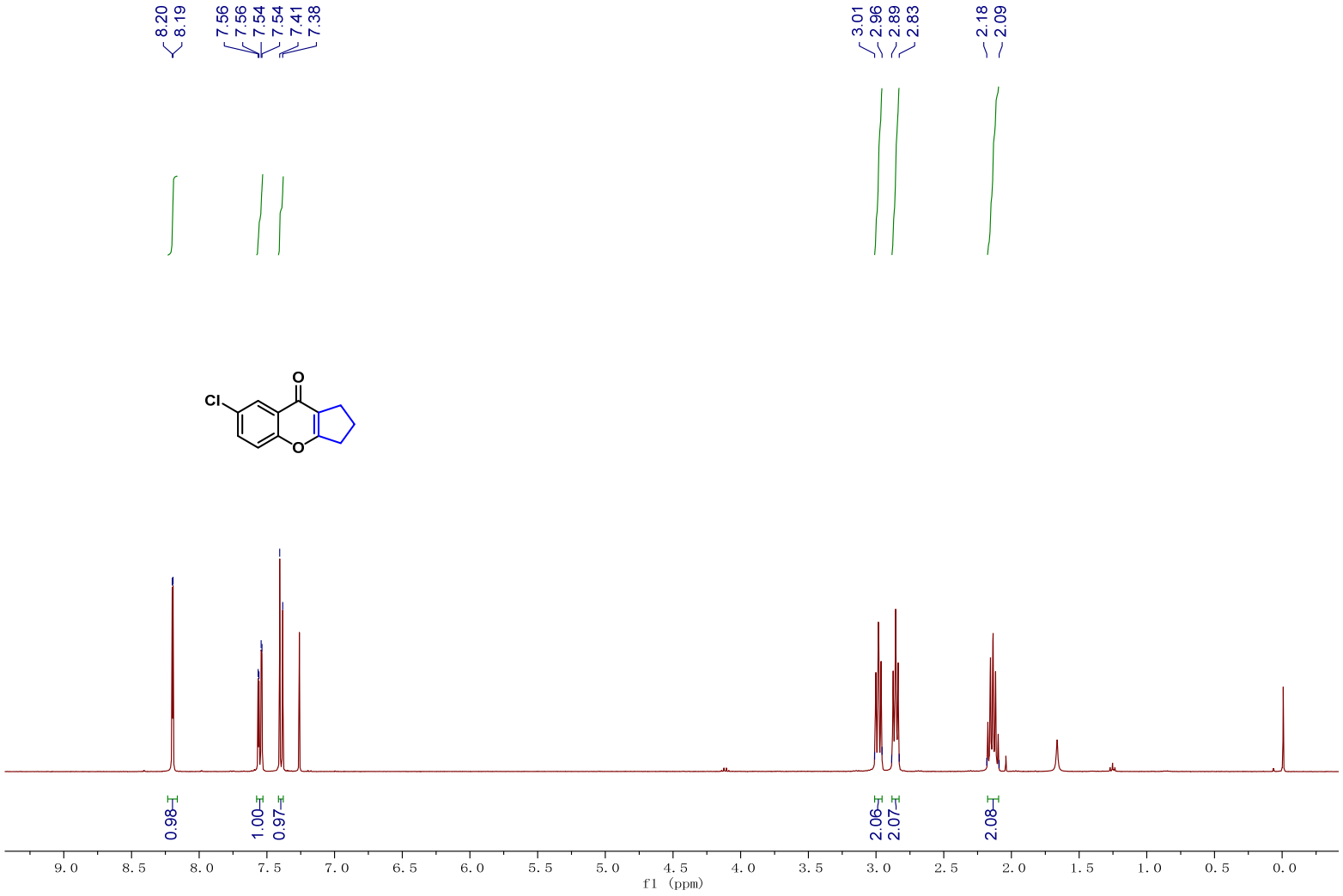
Compound 28 ^{13}C NMR



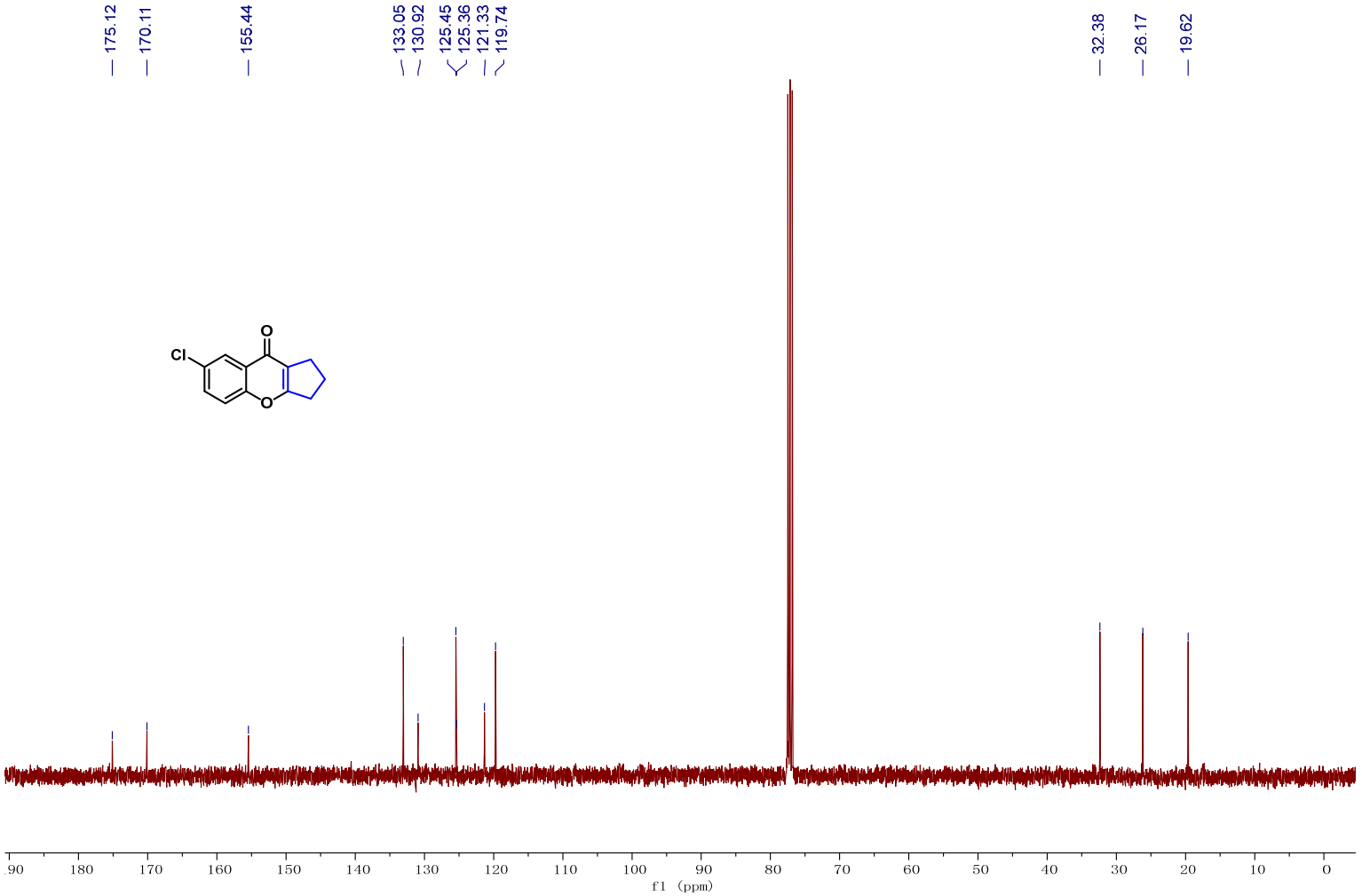
Compound 28 ^{19}F NMR



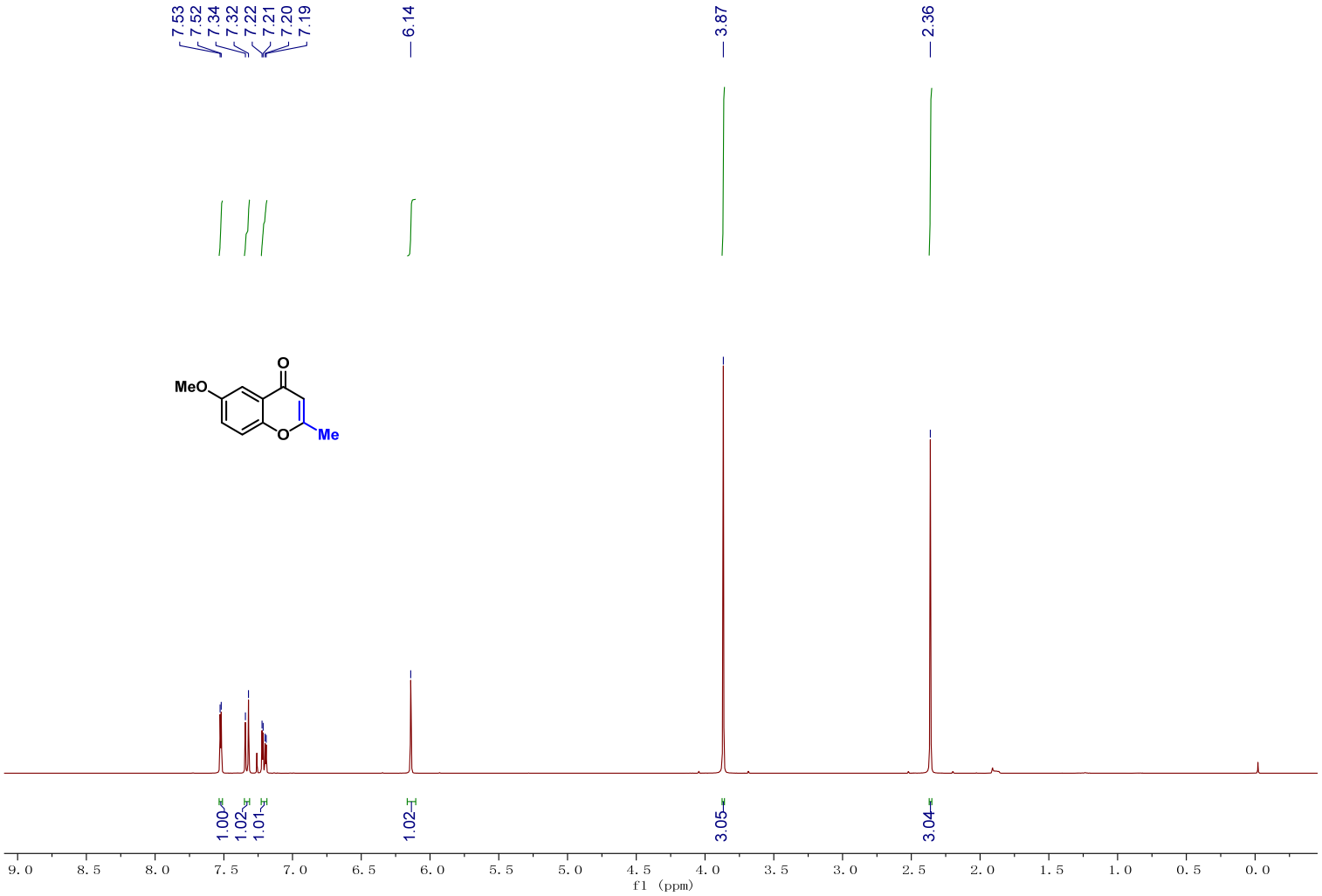
Compound 29 ^{1}H NMR



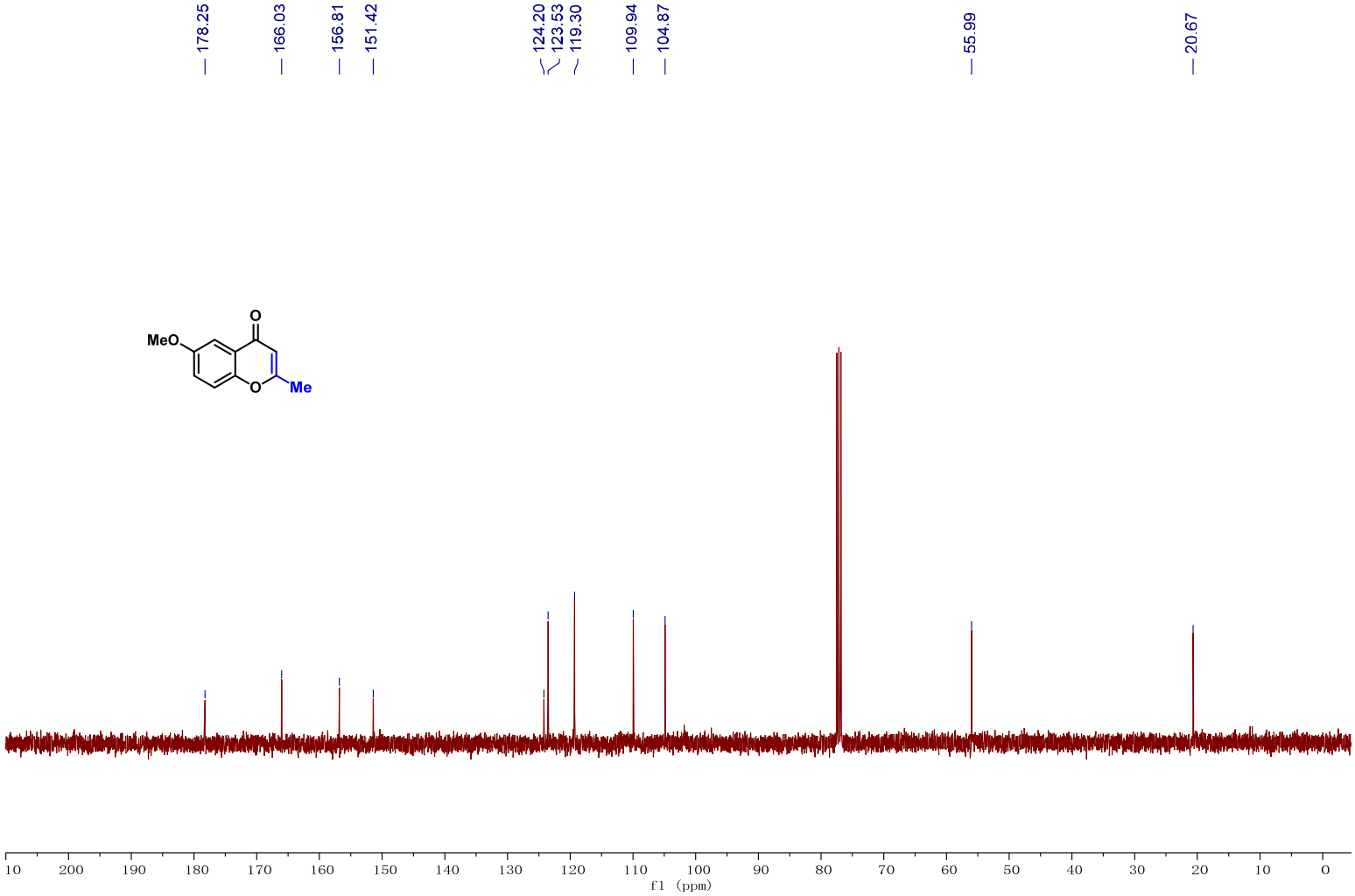
Compound 29 ^{13}C NMR



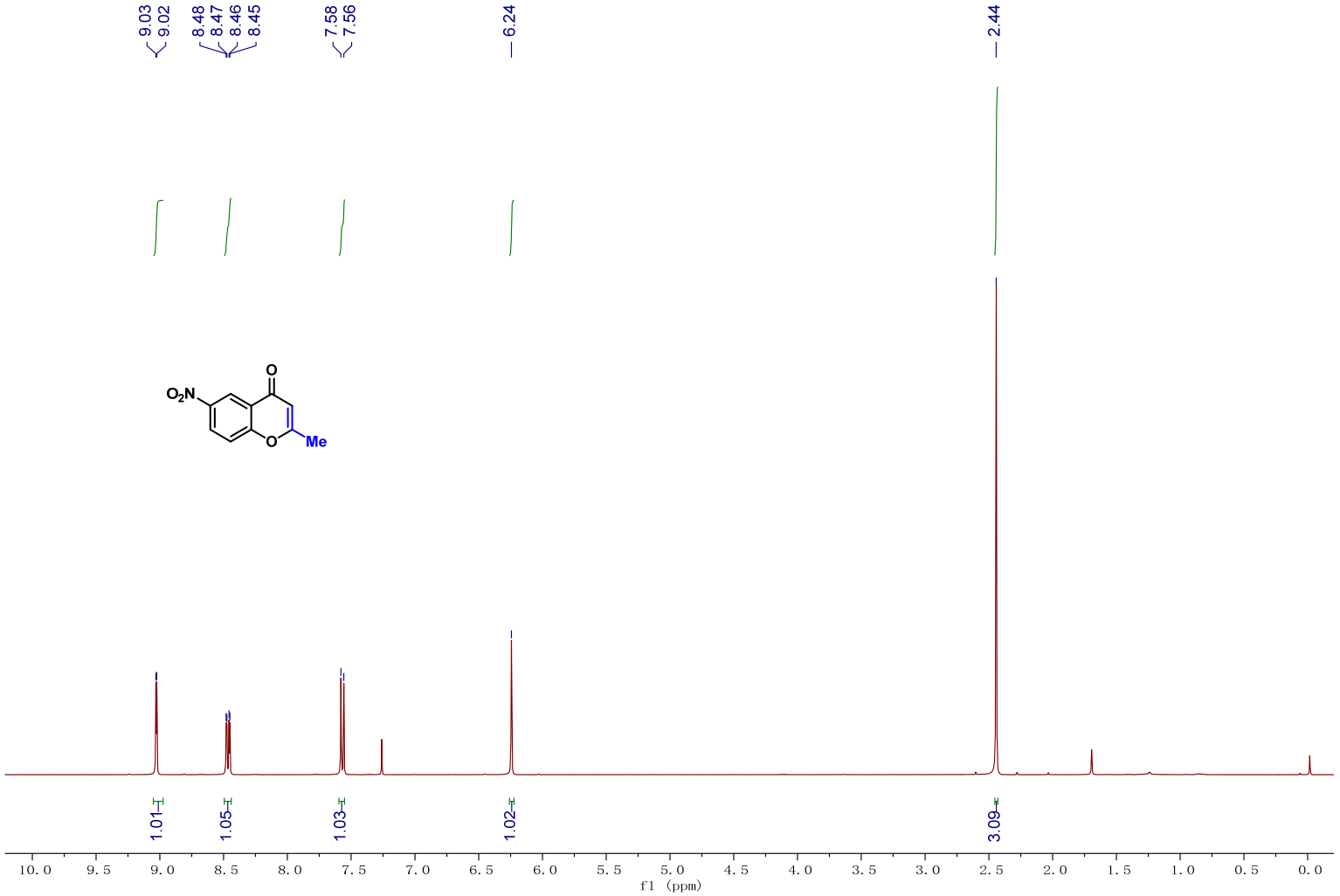
Compound 30 ^{1}H NMR



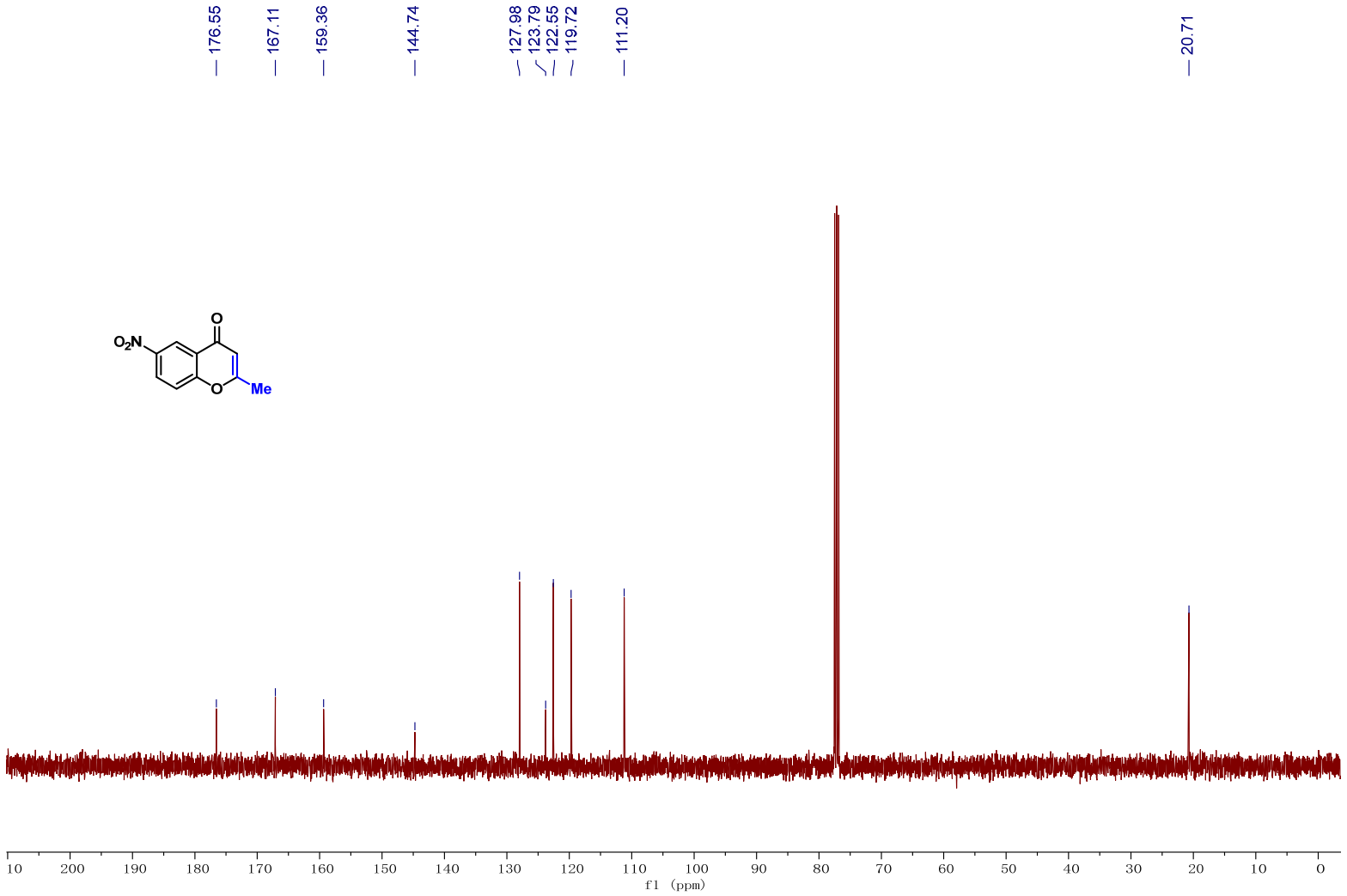
Compound 30 ^{13}C NMR



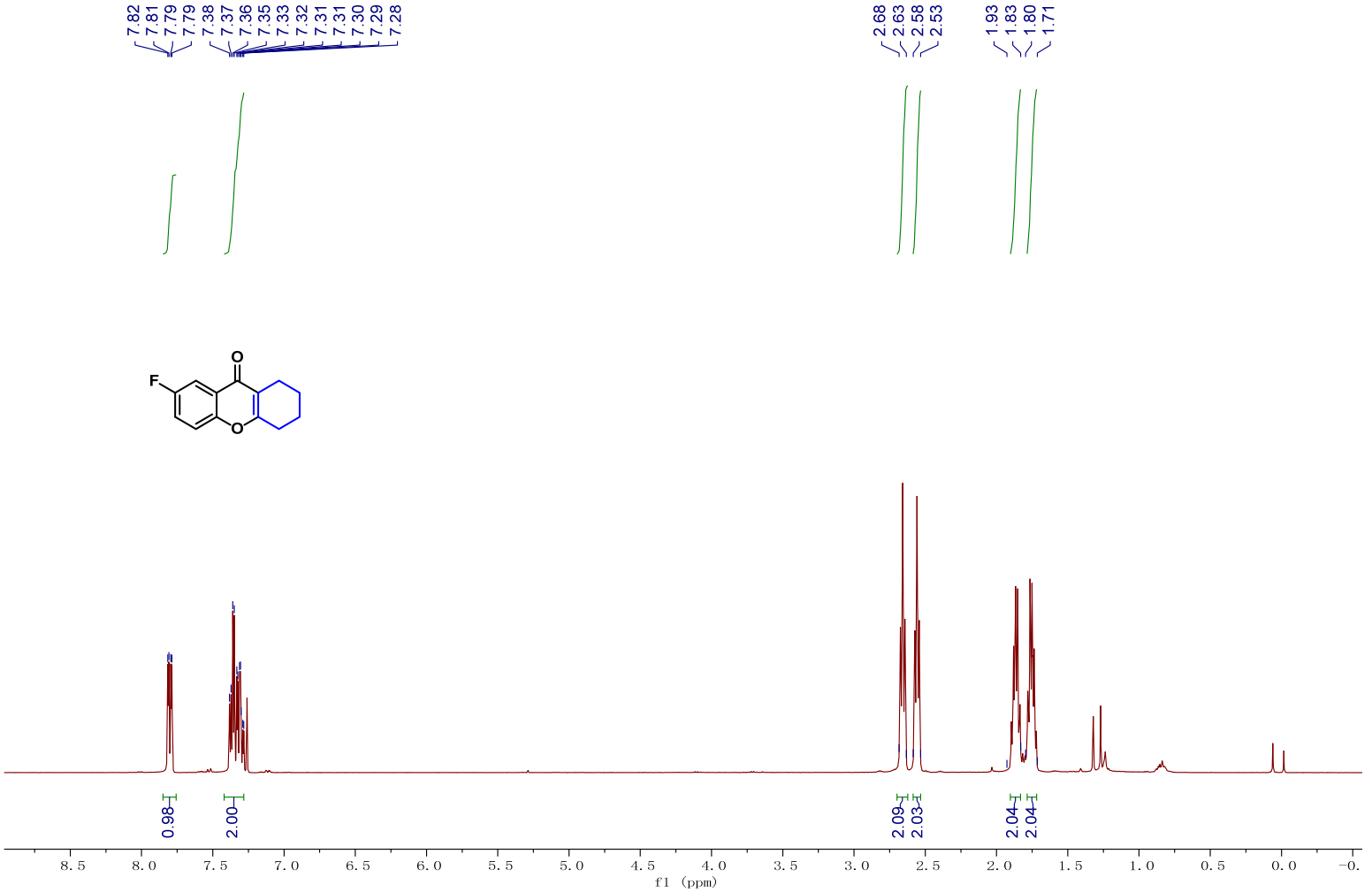
Compound 31 ^{1}H NMR



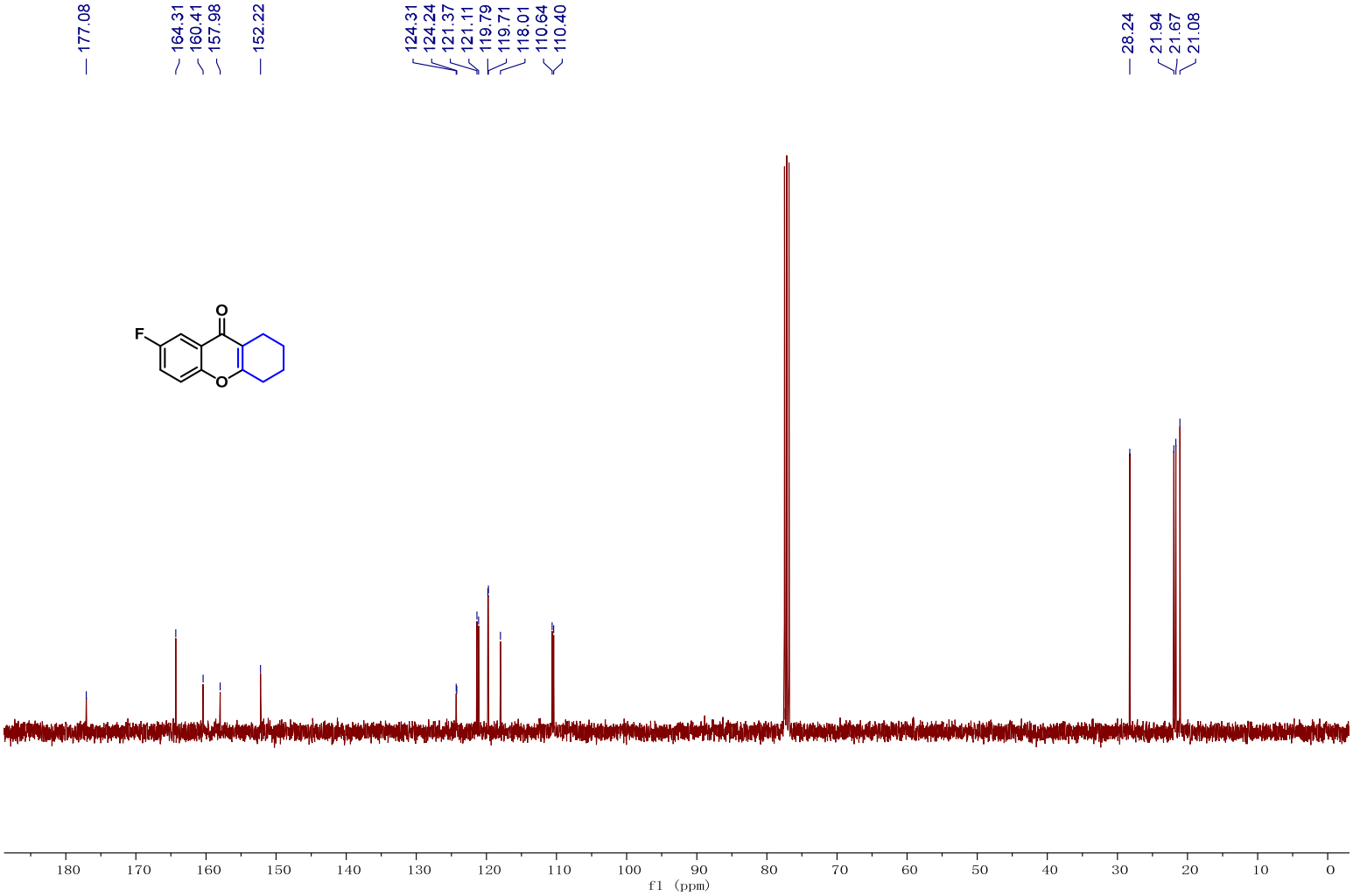
Compound 31 ^{13}C NMR



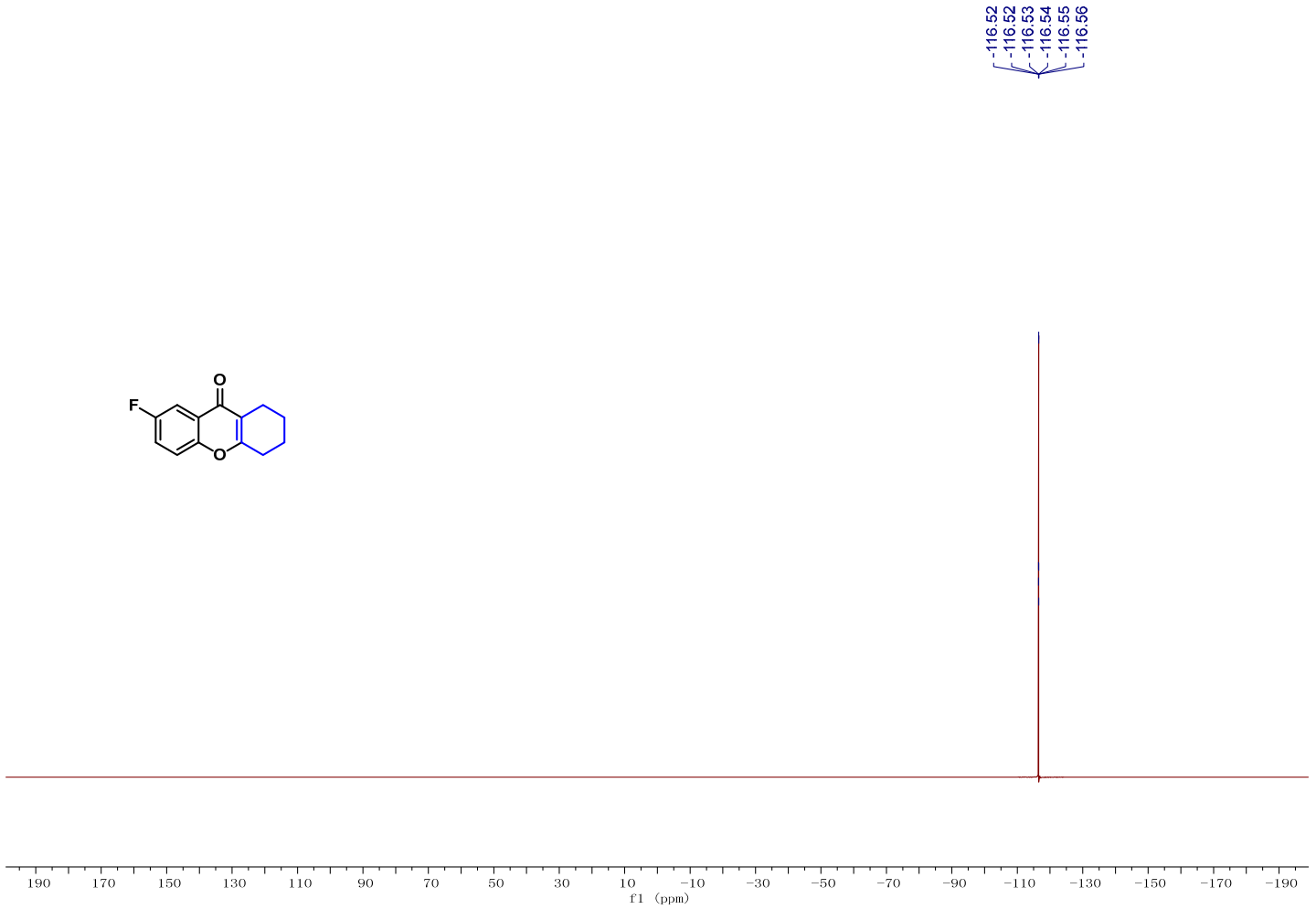
Compound 32 ^{1}H NMR



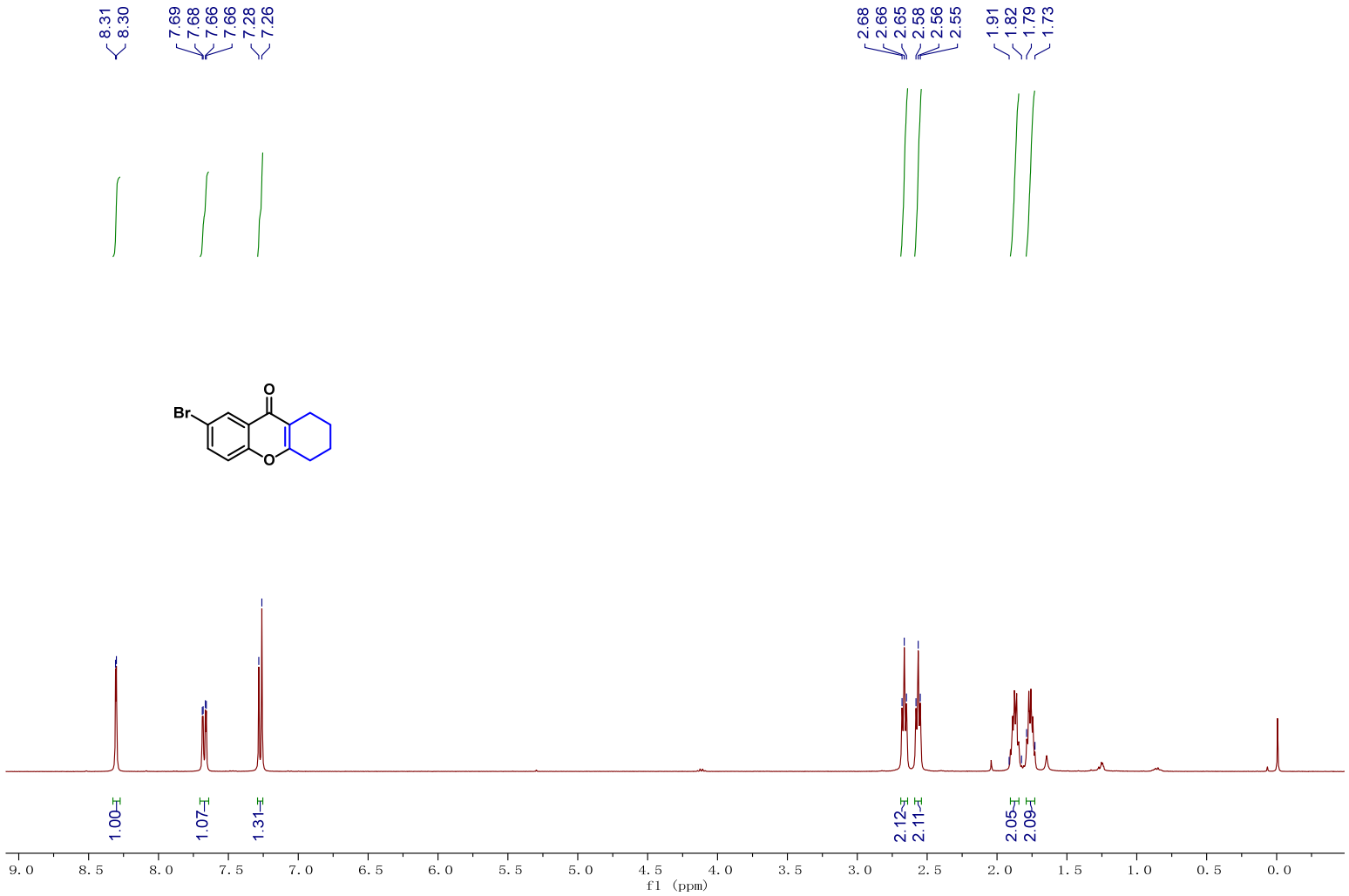
Compound 32 ^{13}C NMR



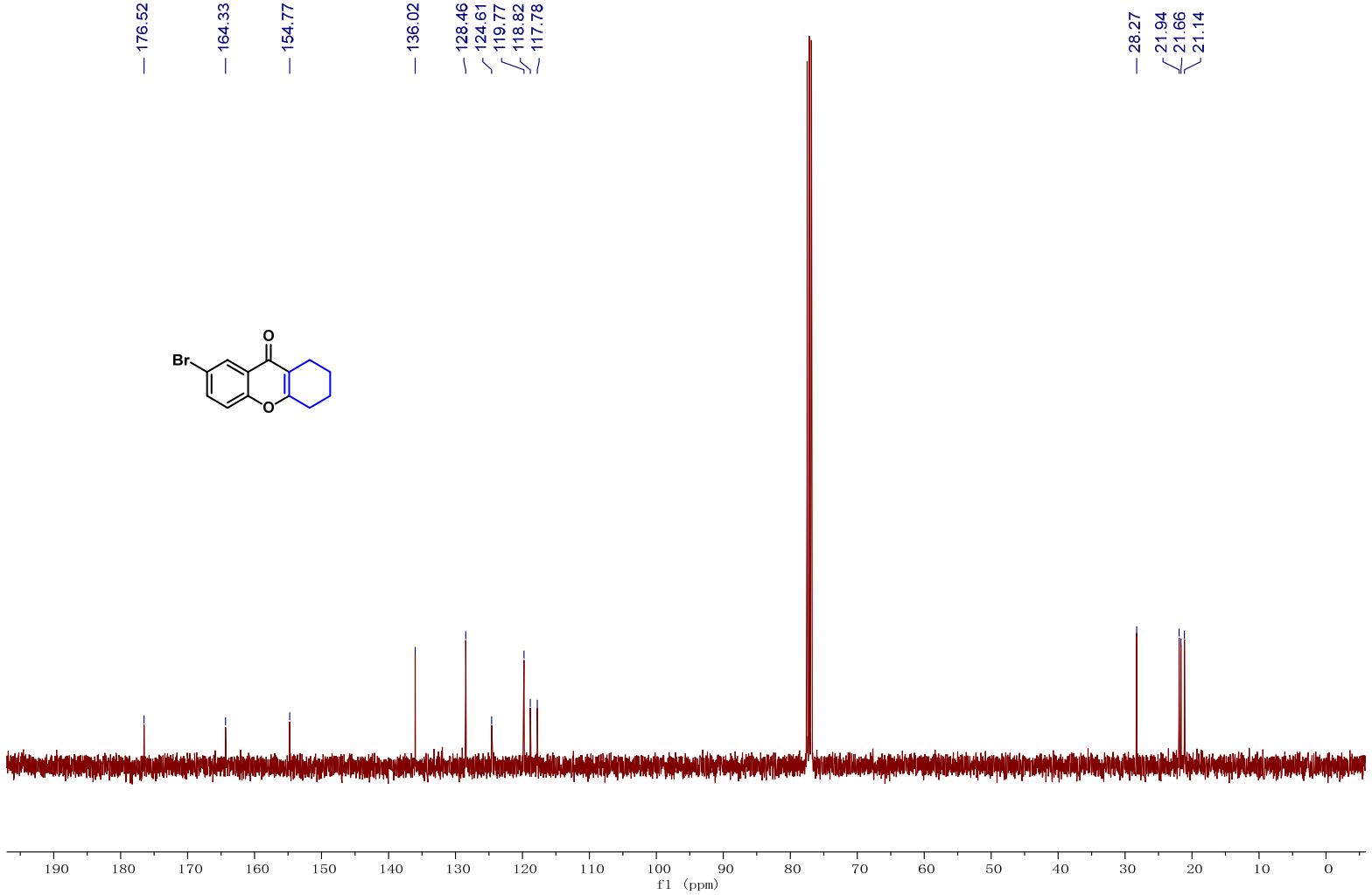
Compound 32 ^{19}F NMR



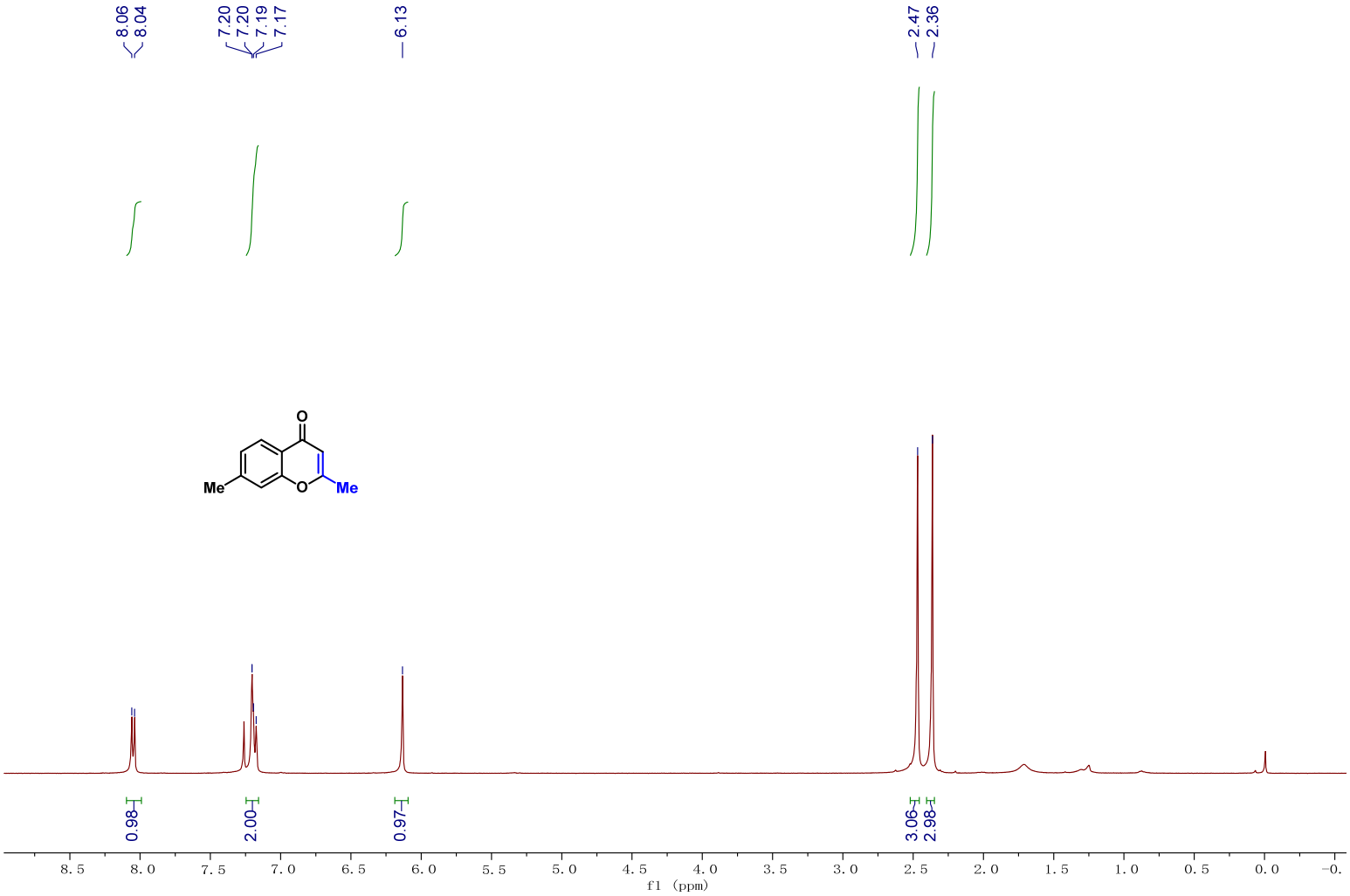
Compound 33 ^{1}H NMR



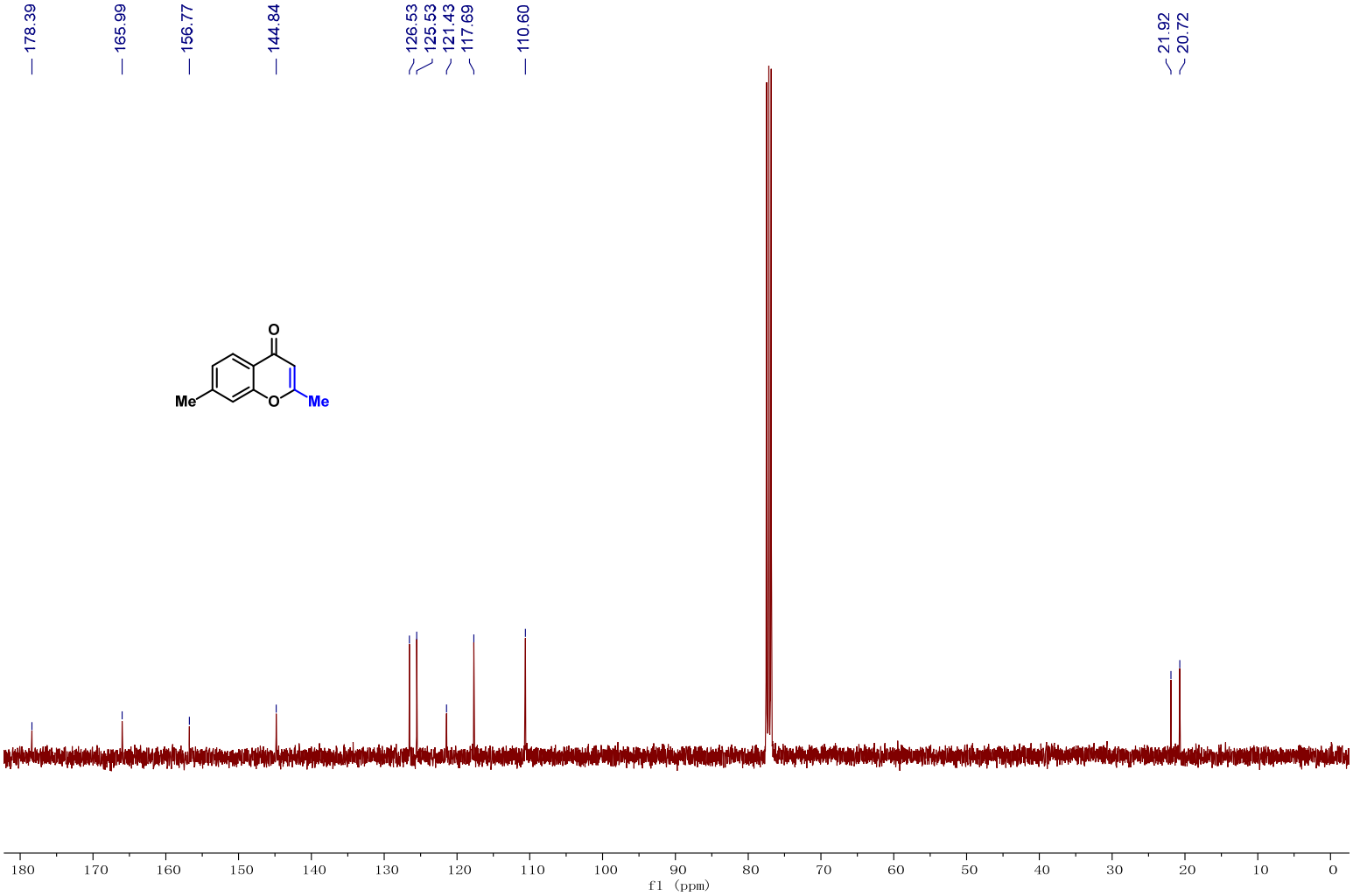
Compound 33 ^{13}C NMR



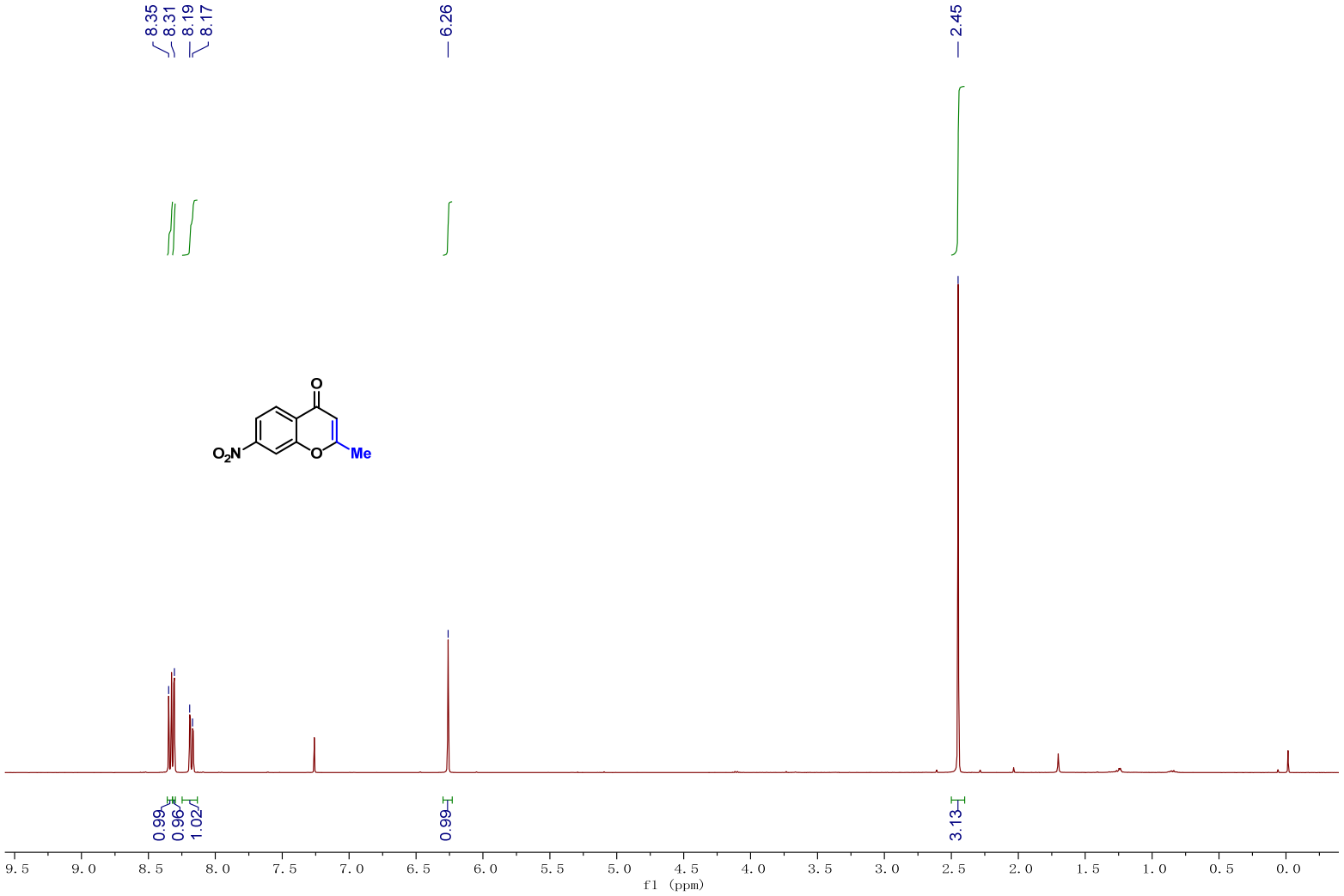
Compound 34 ^{1}H NMR



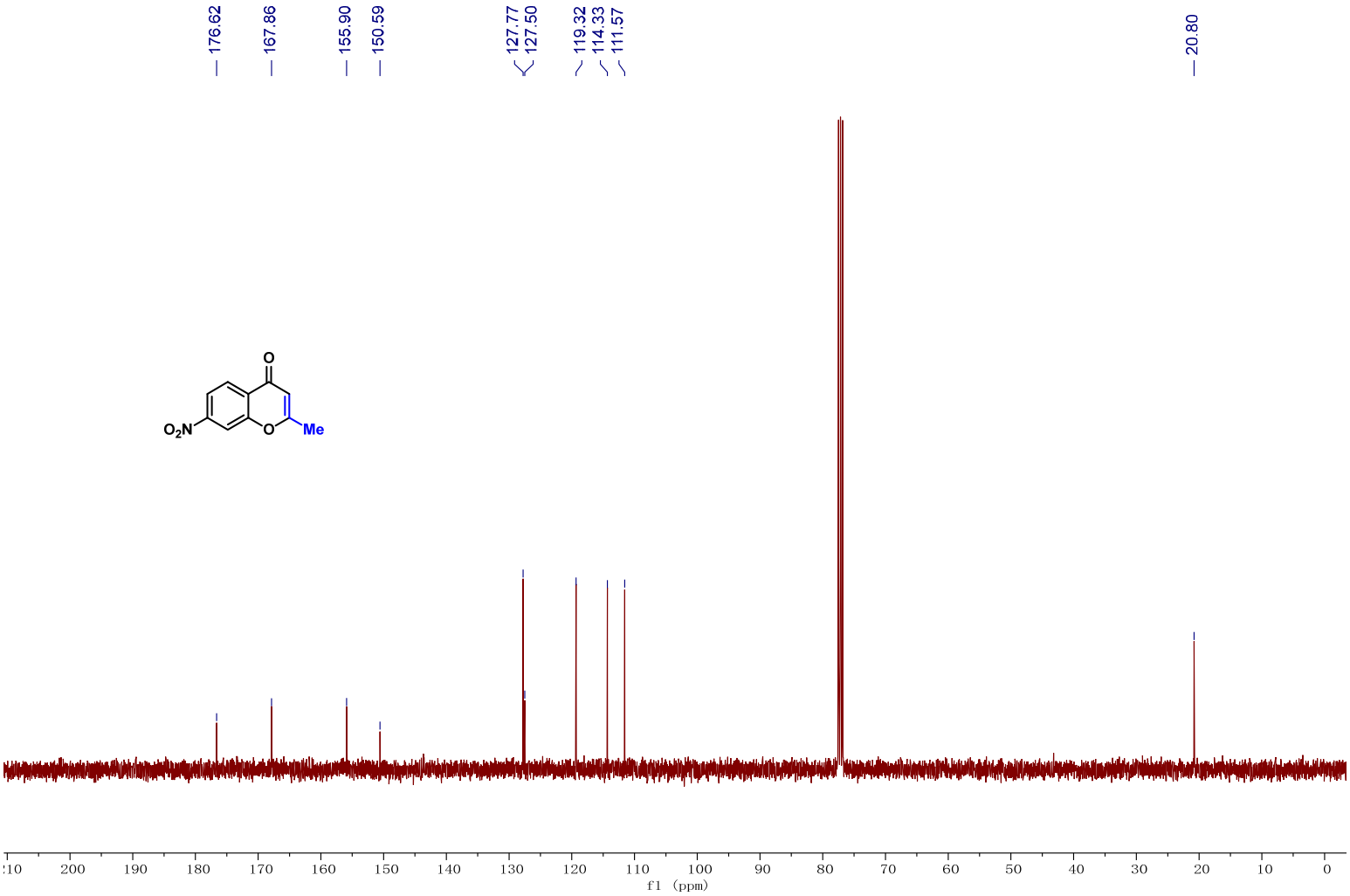
Compound 34 ^{13}C NMR



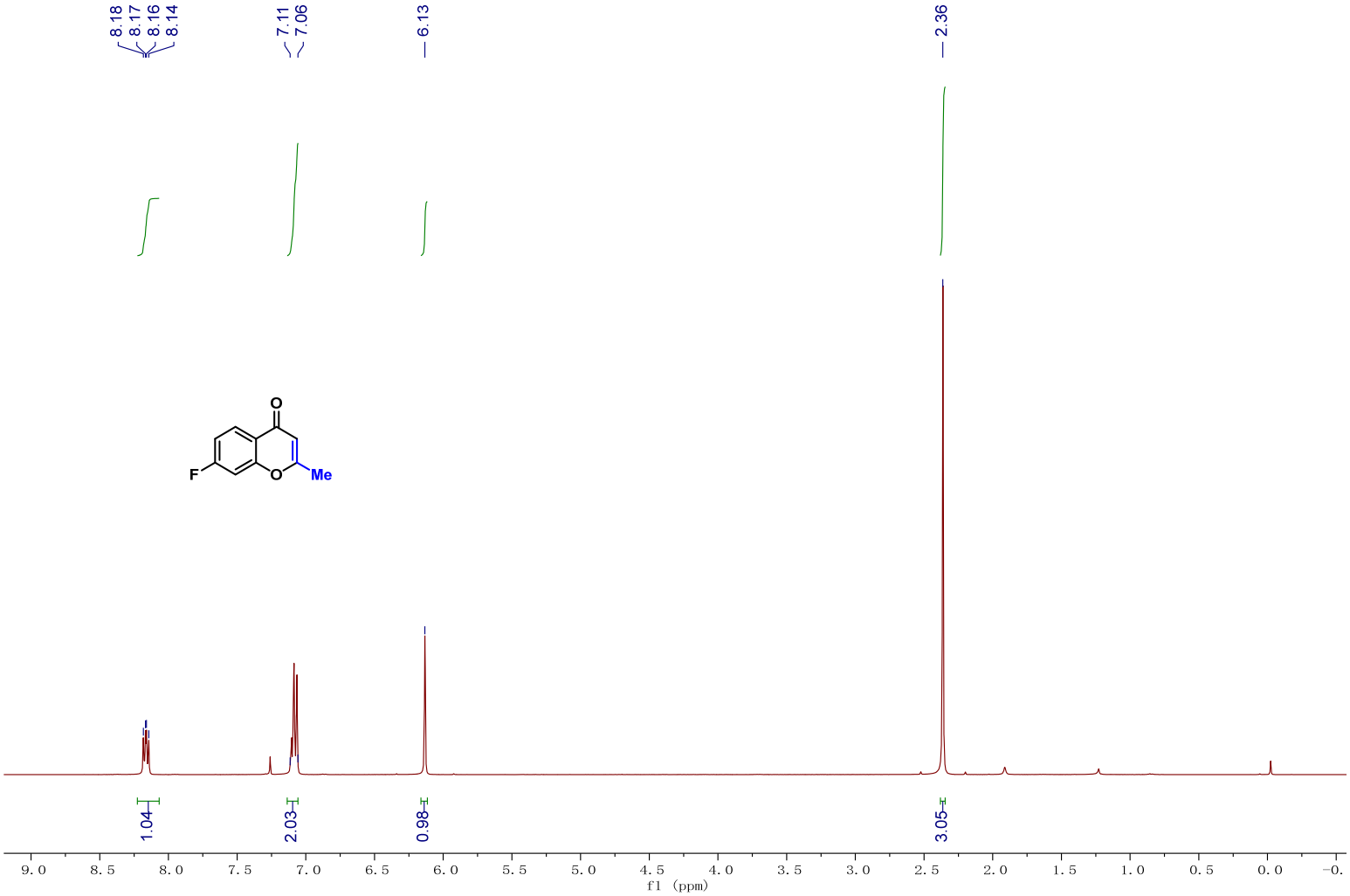
Compound 35 ^{1}H NMR



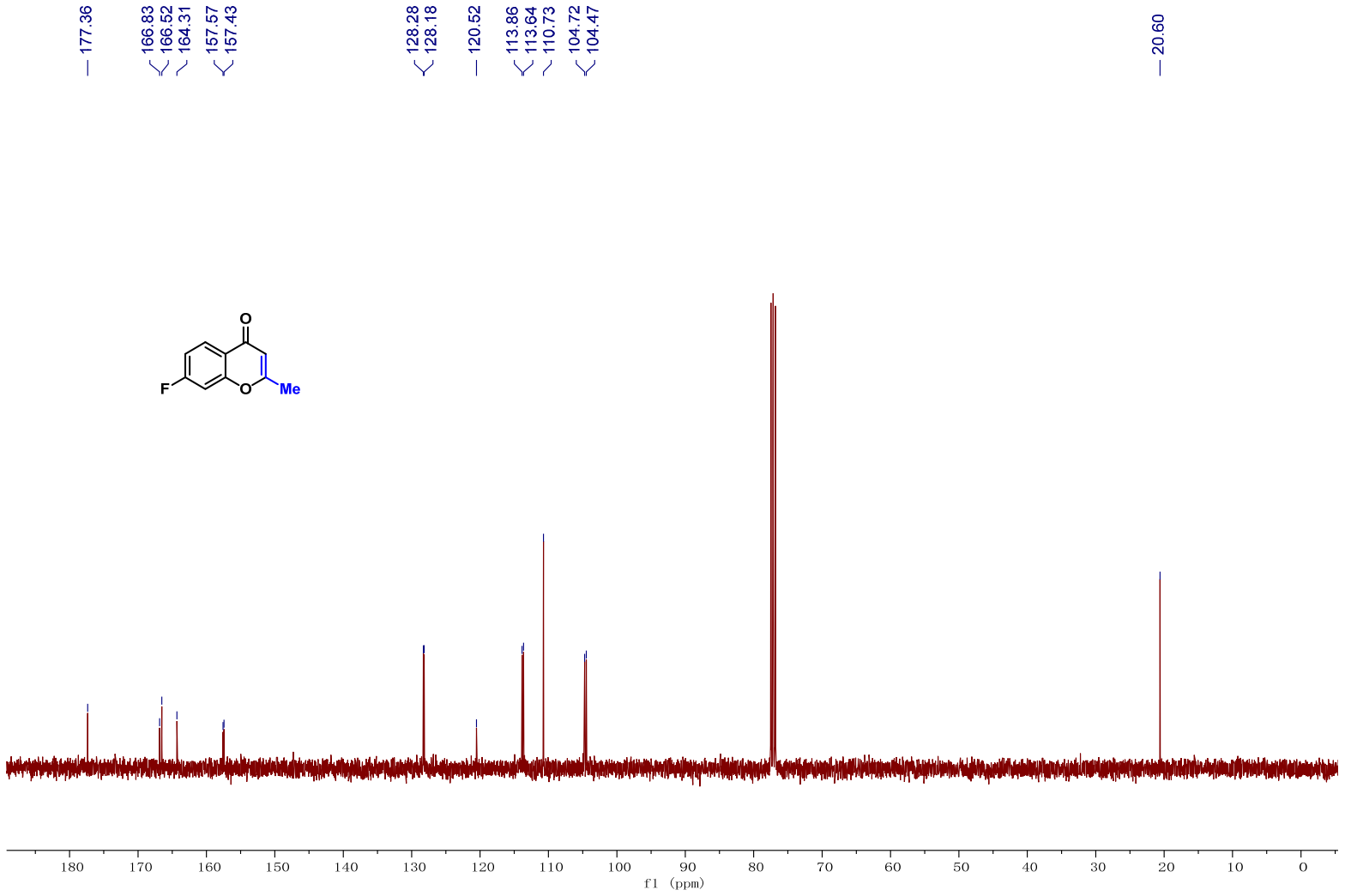
Compound 35 ^{13}C NMR



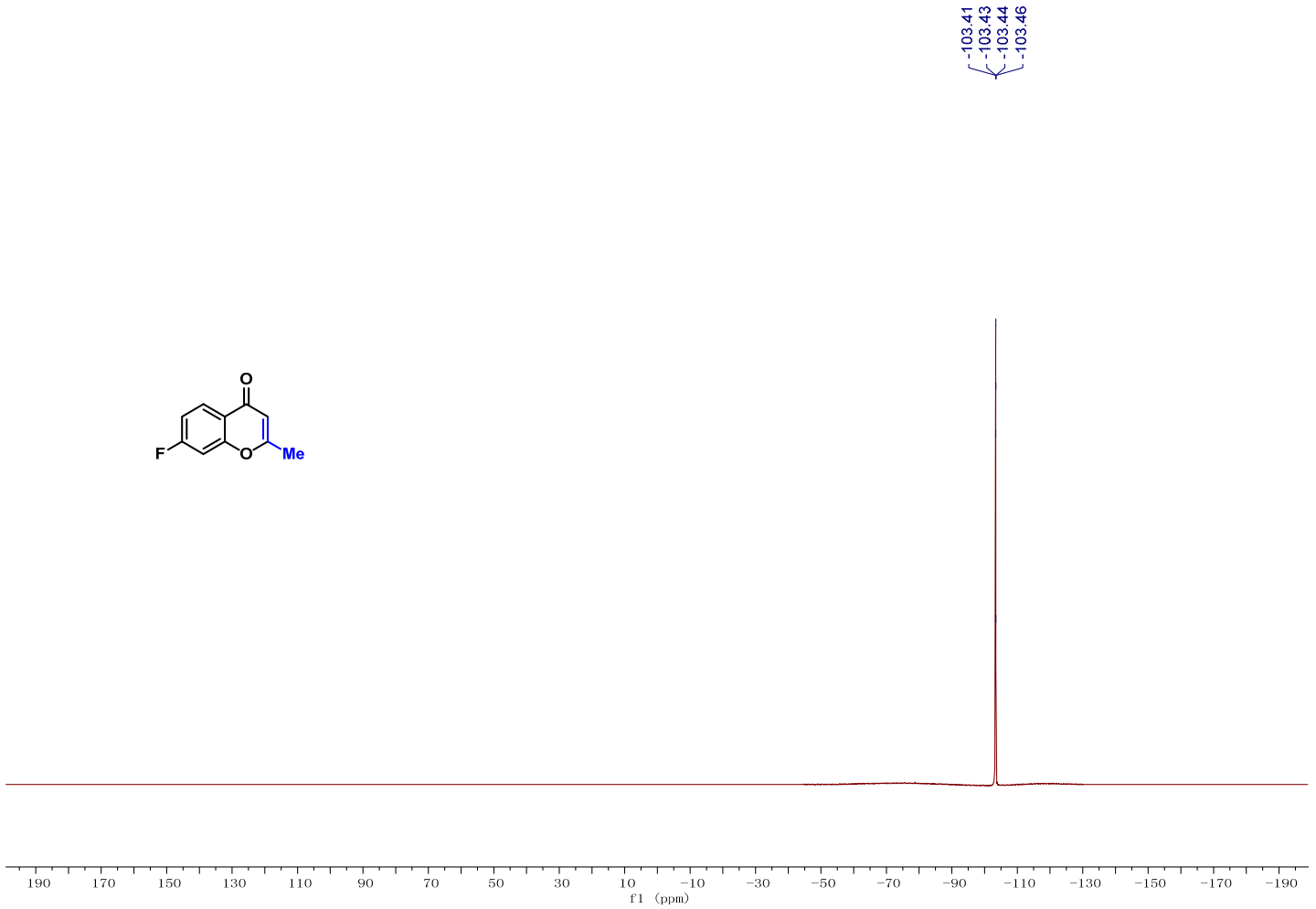
Compound 36 ^{1}H NMR



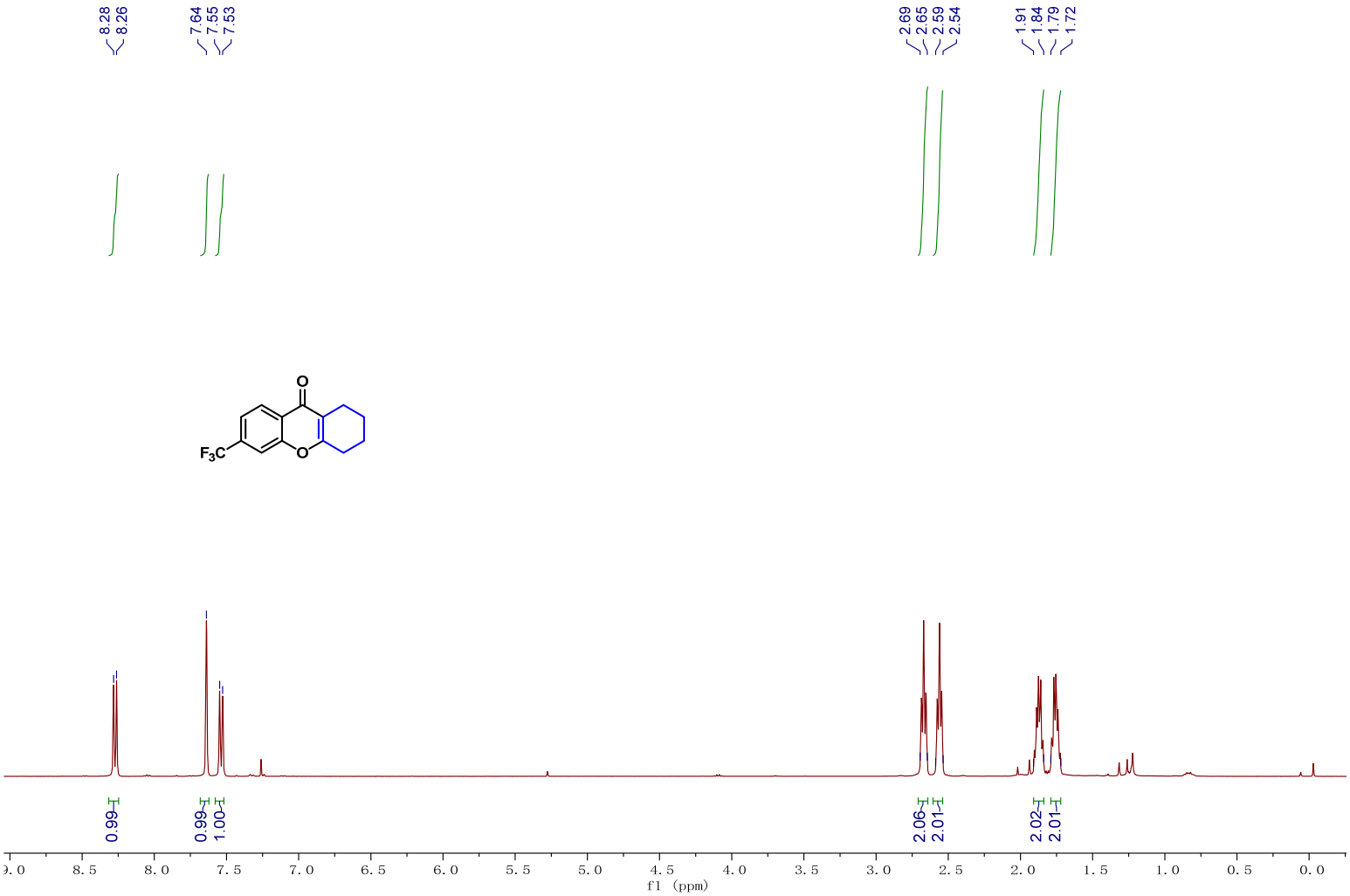
Compound 36 ^{13}C NMR



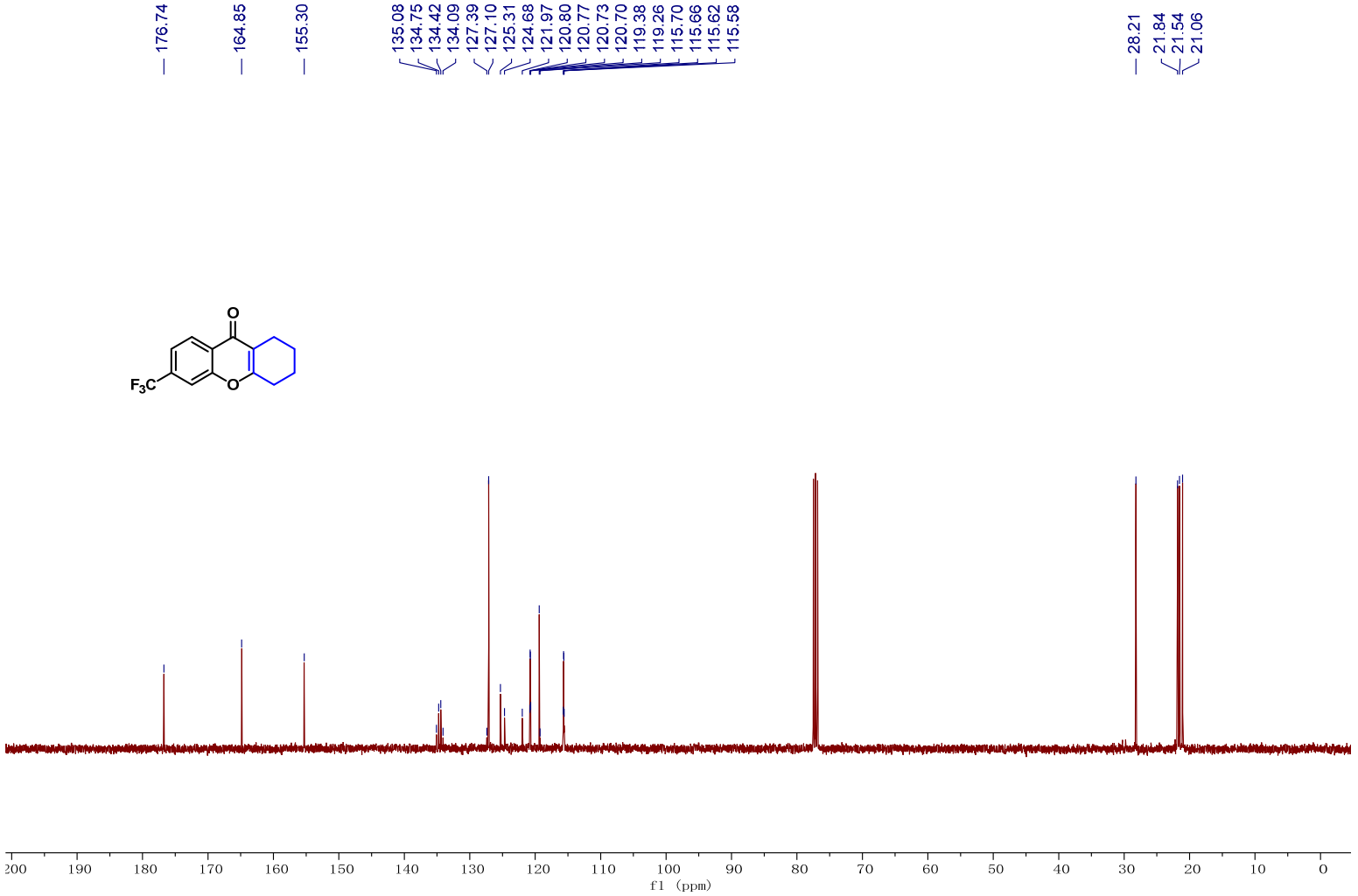
Compound 36 ^{19}F NMR



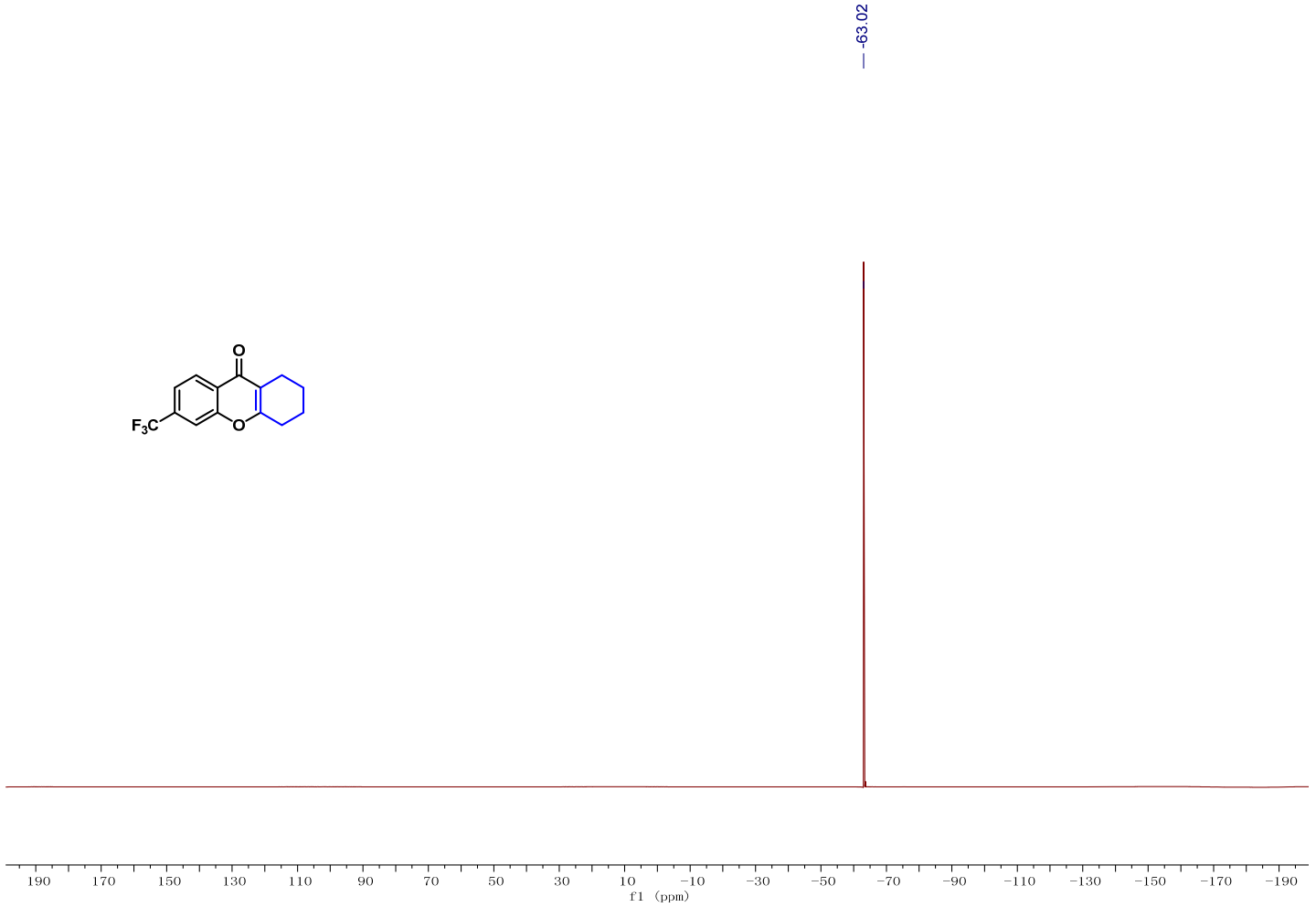
Compound 37 ^{1}H NMR



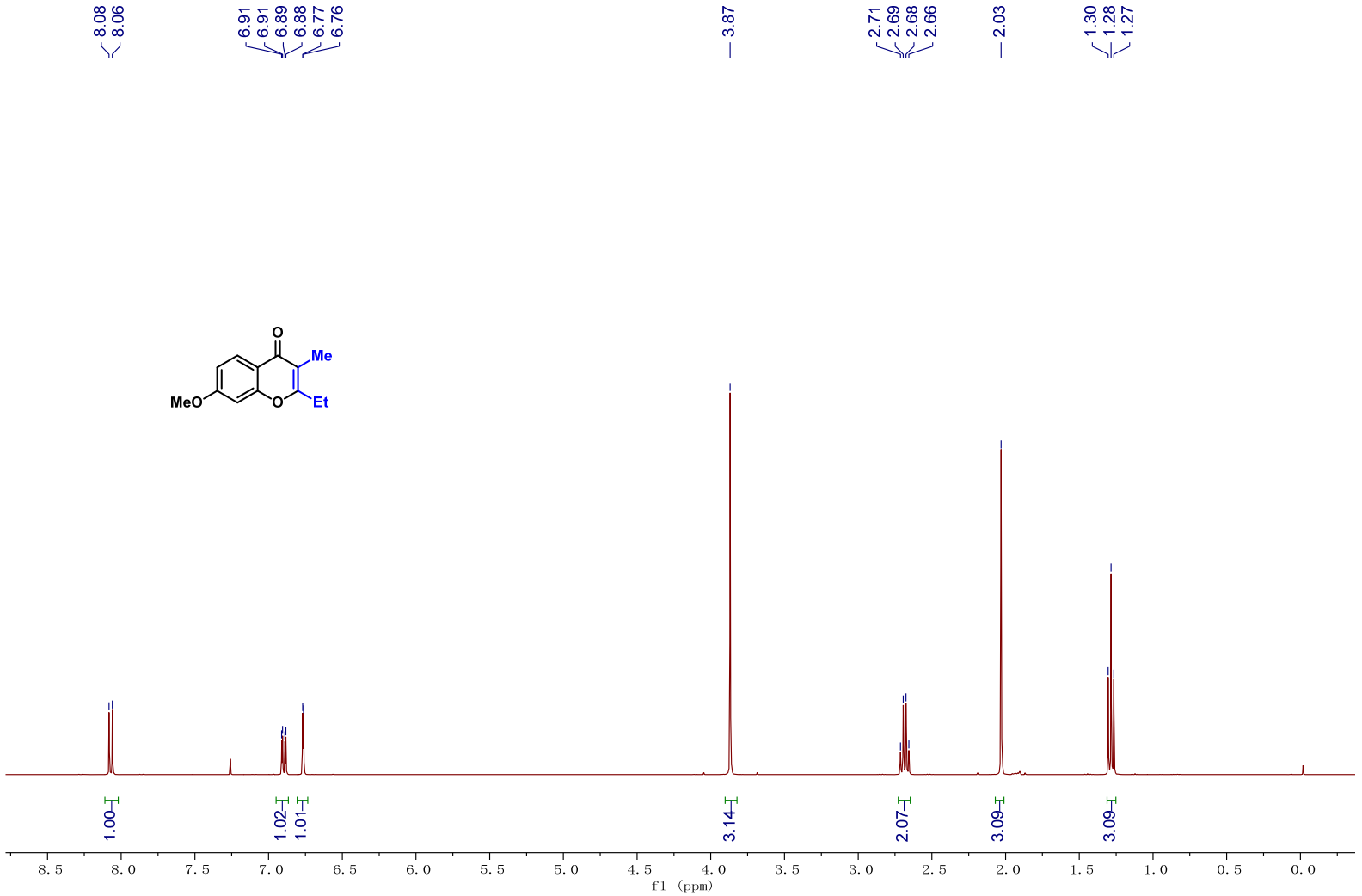
Compound 37 ^{13}C NMR



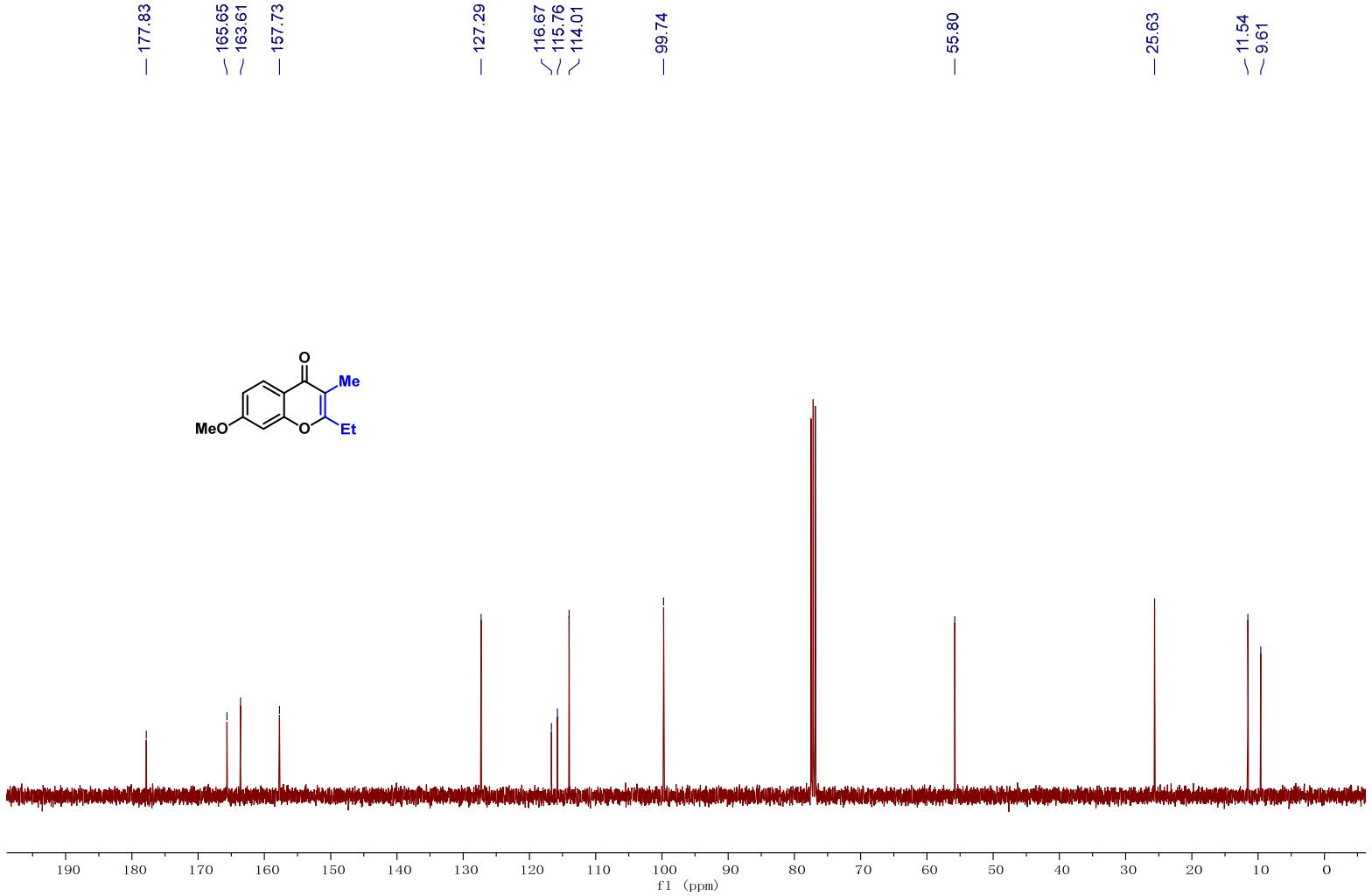
Compound 37 ^{19}F NMR



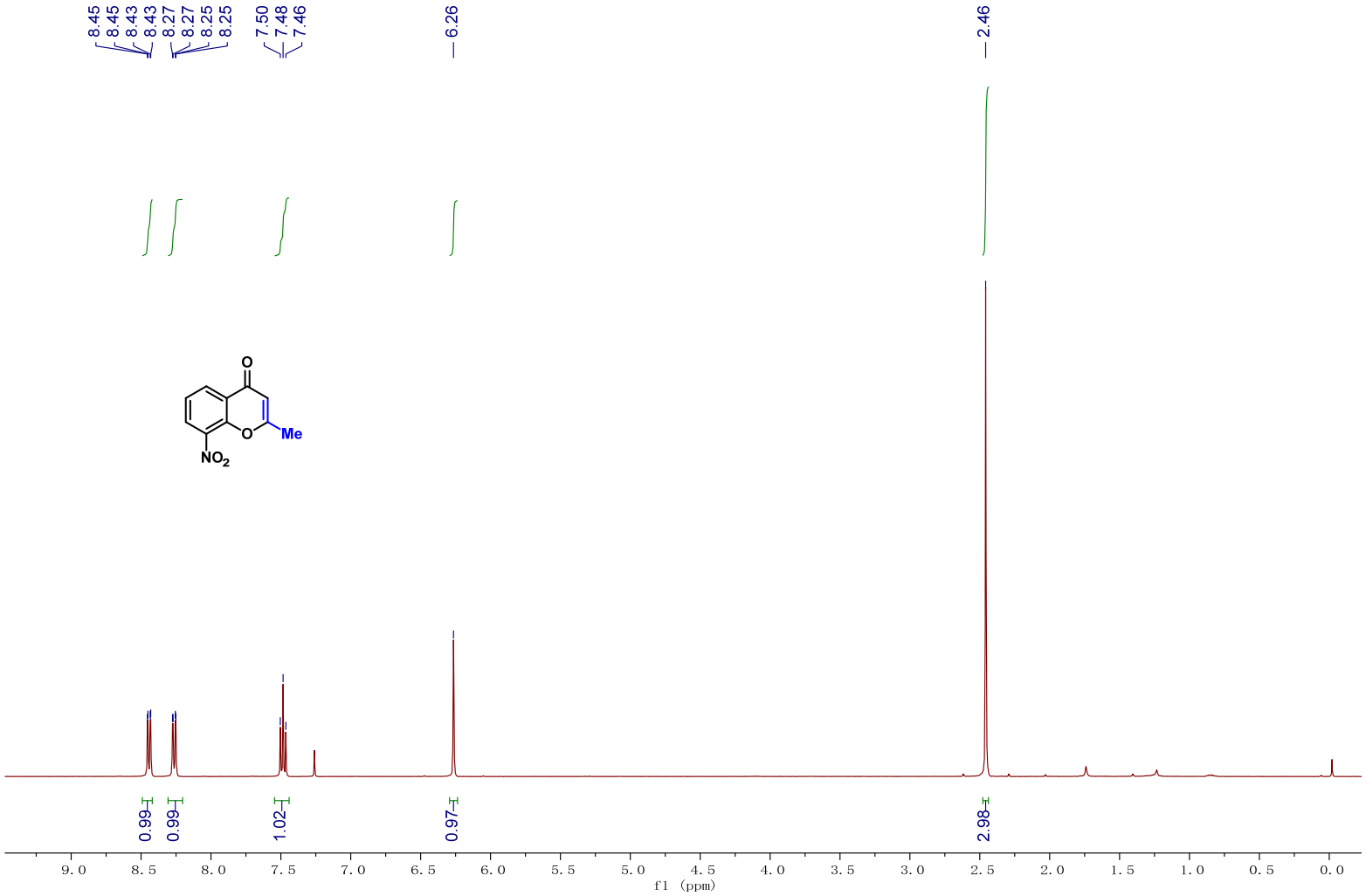
Compound 38 ^{1}H NMR



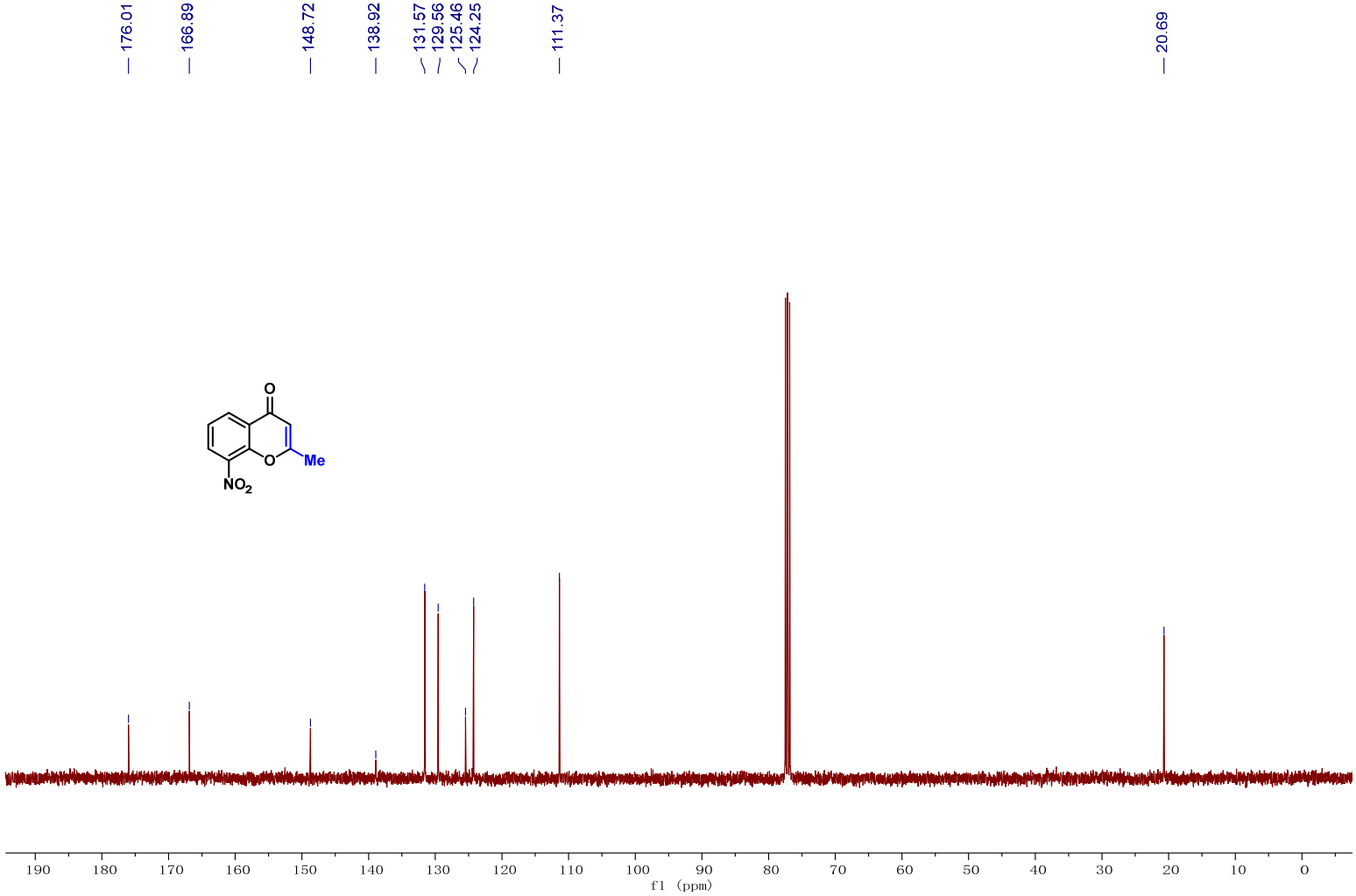
Compound 38 ^{13}C NMR



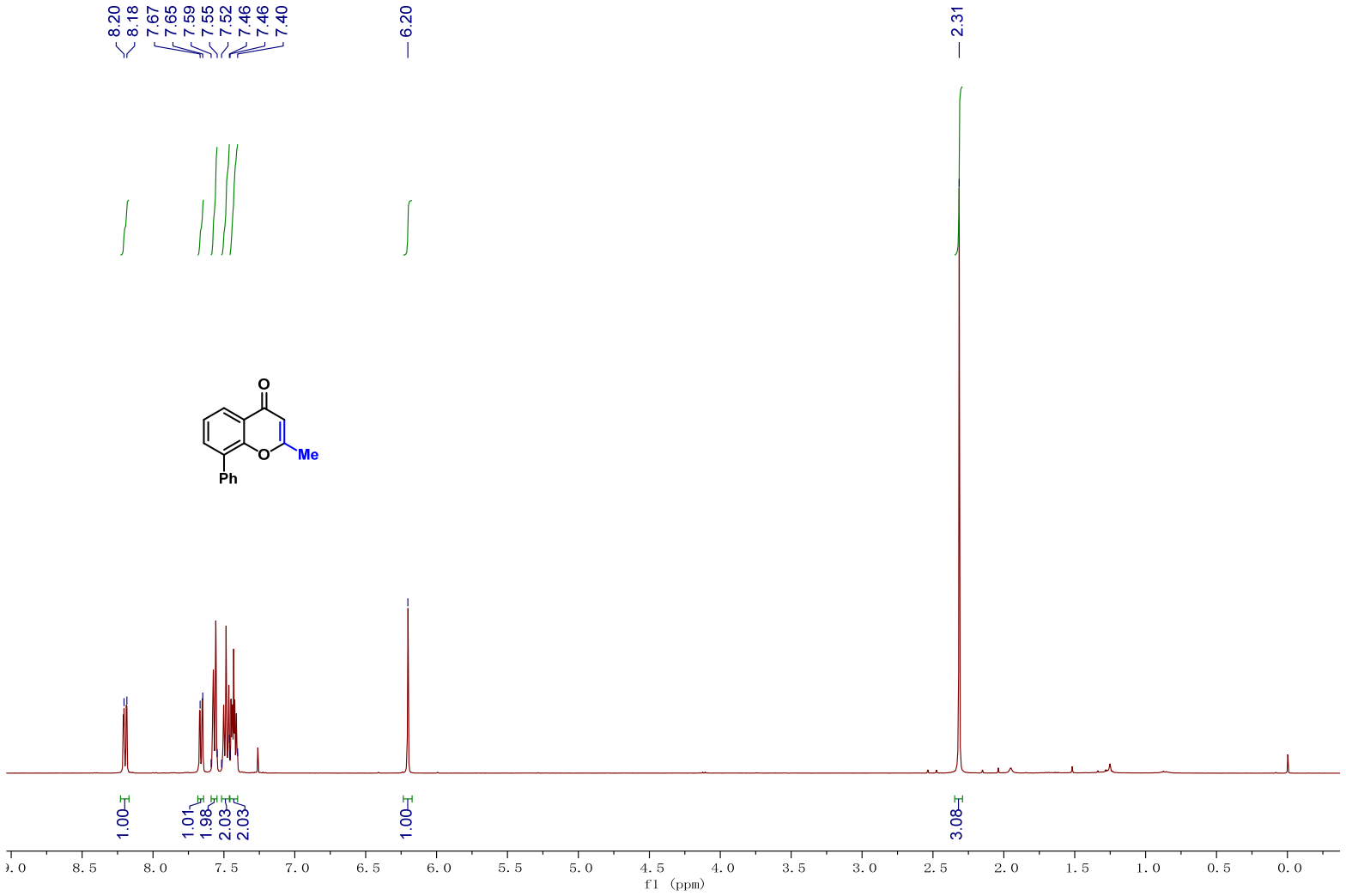
Compound 39 ^{1}H NMR



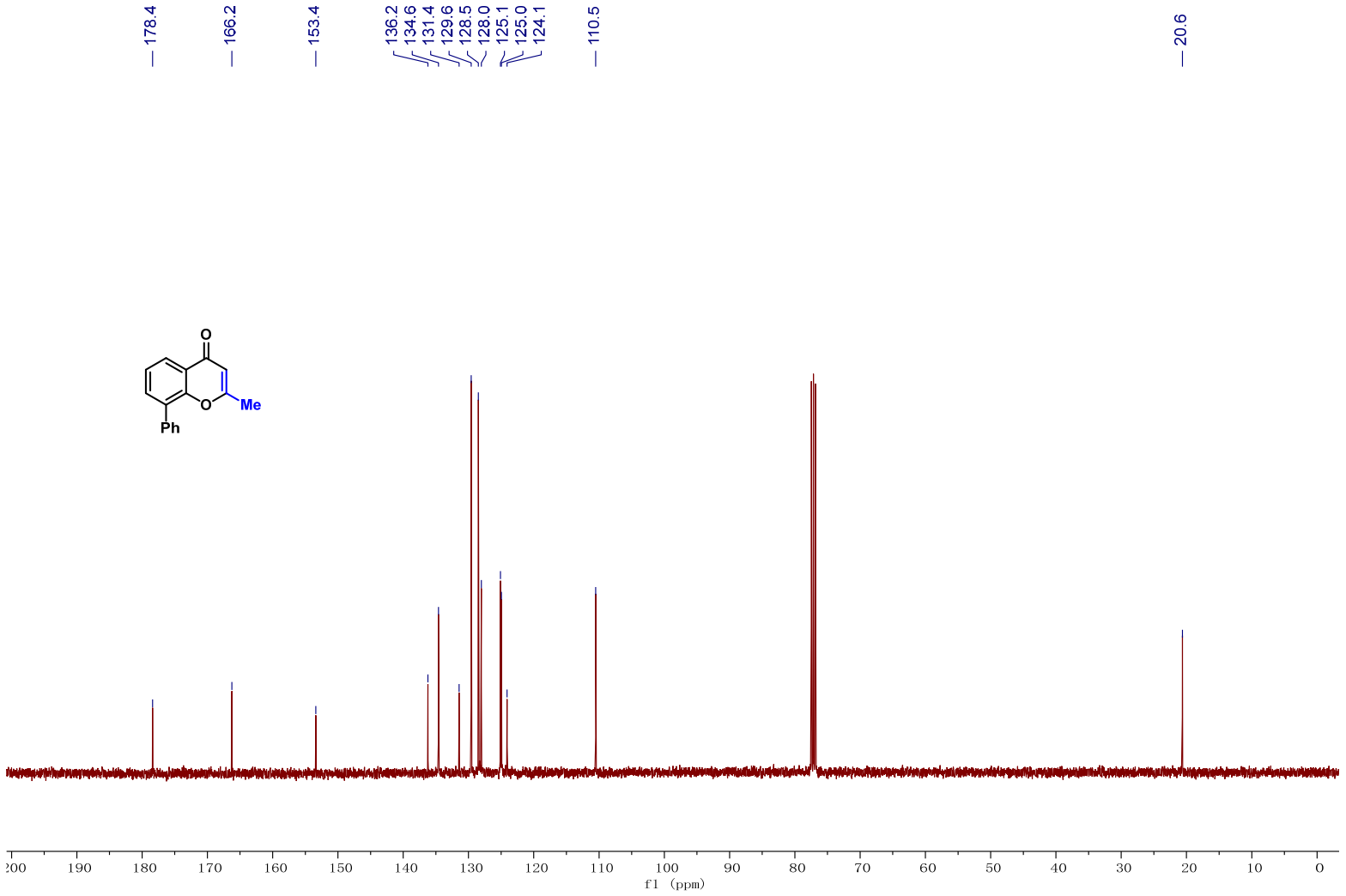
Compound 39 ^{13}C NMR



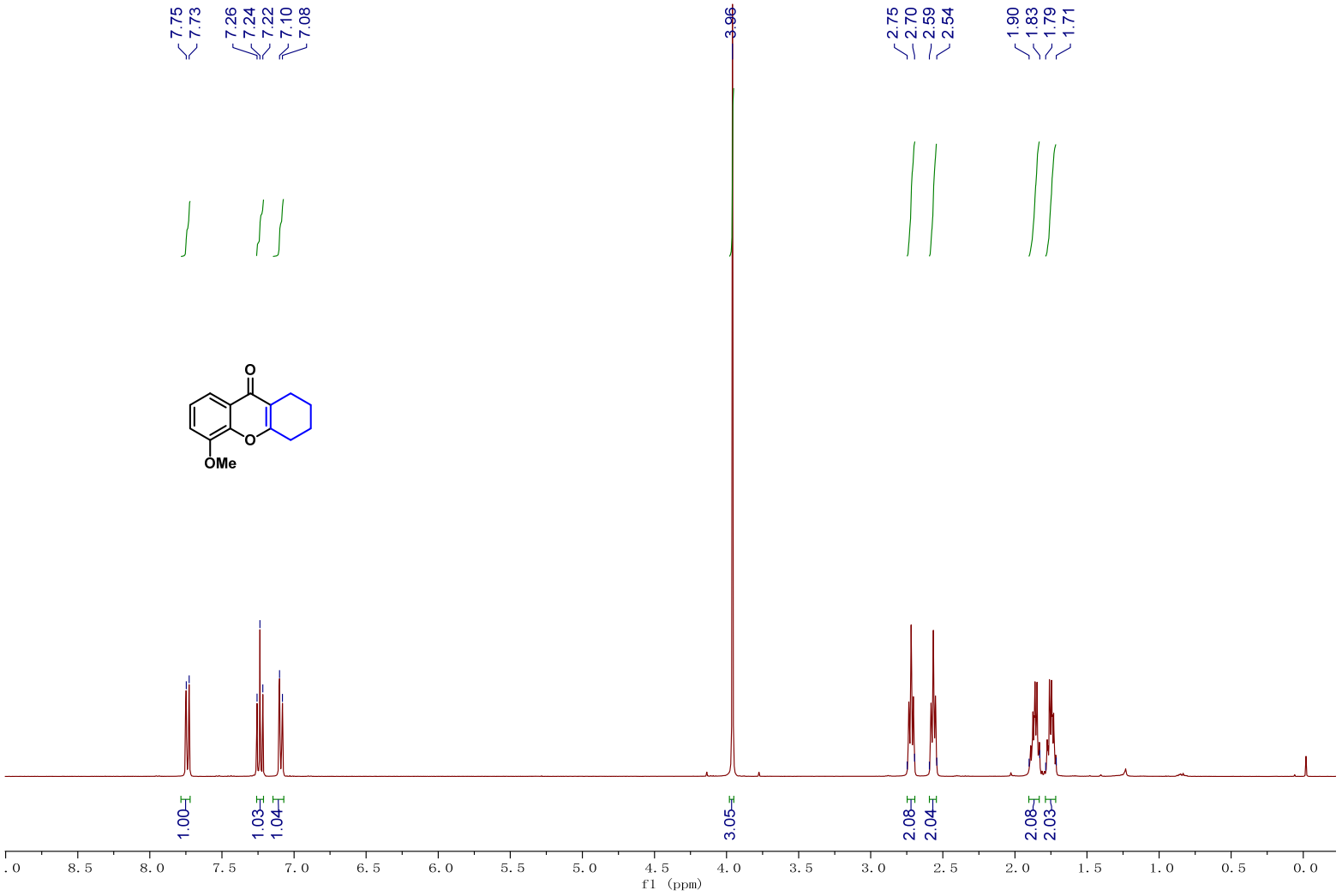
Compound 40 ^{1}H NMR



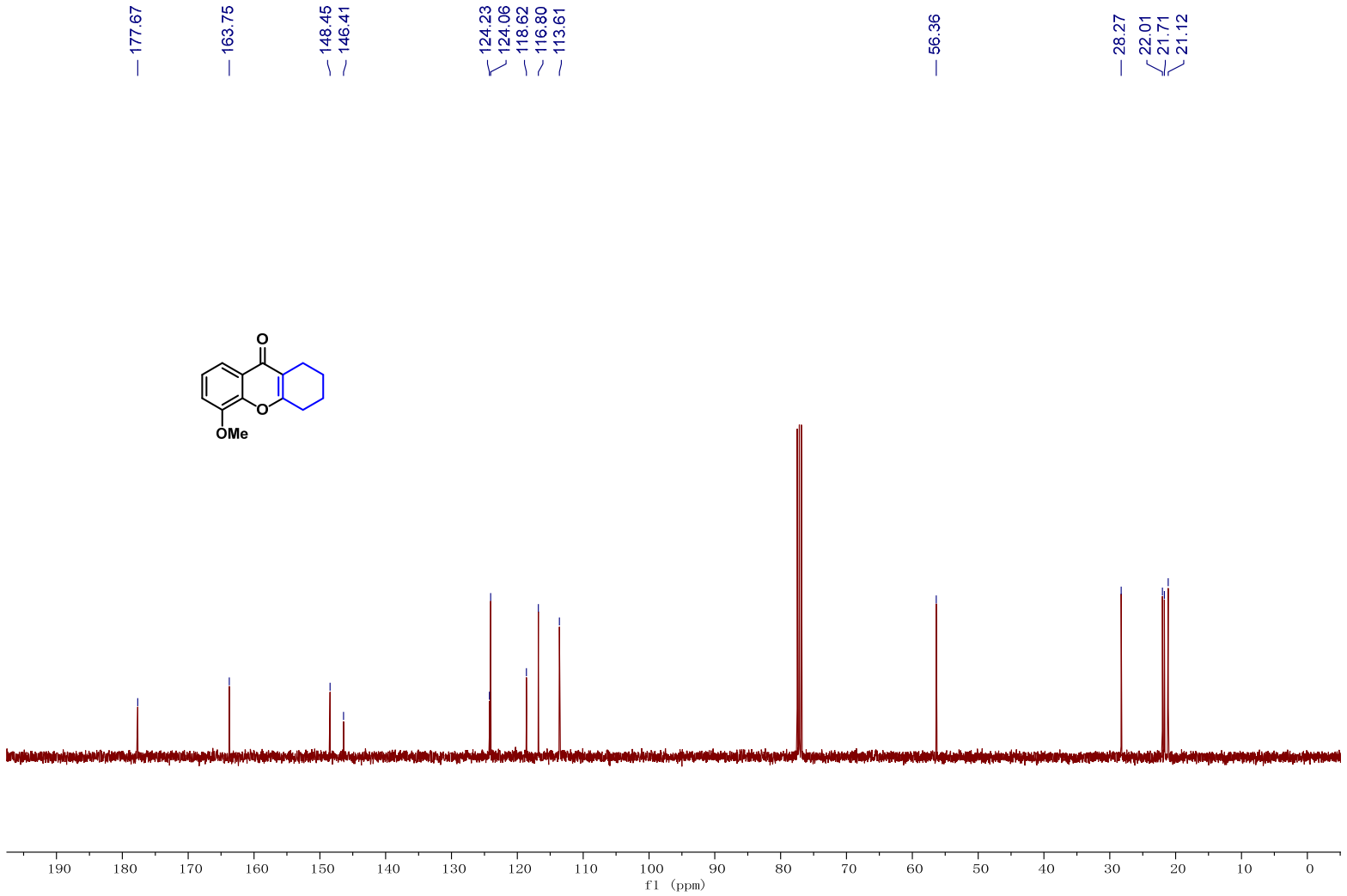
Compound 40 ^{13}C NMR



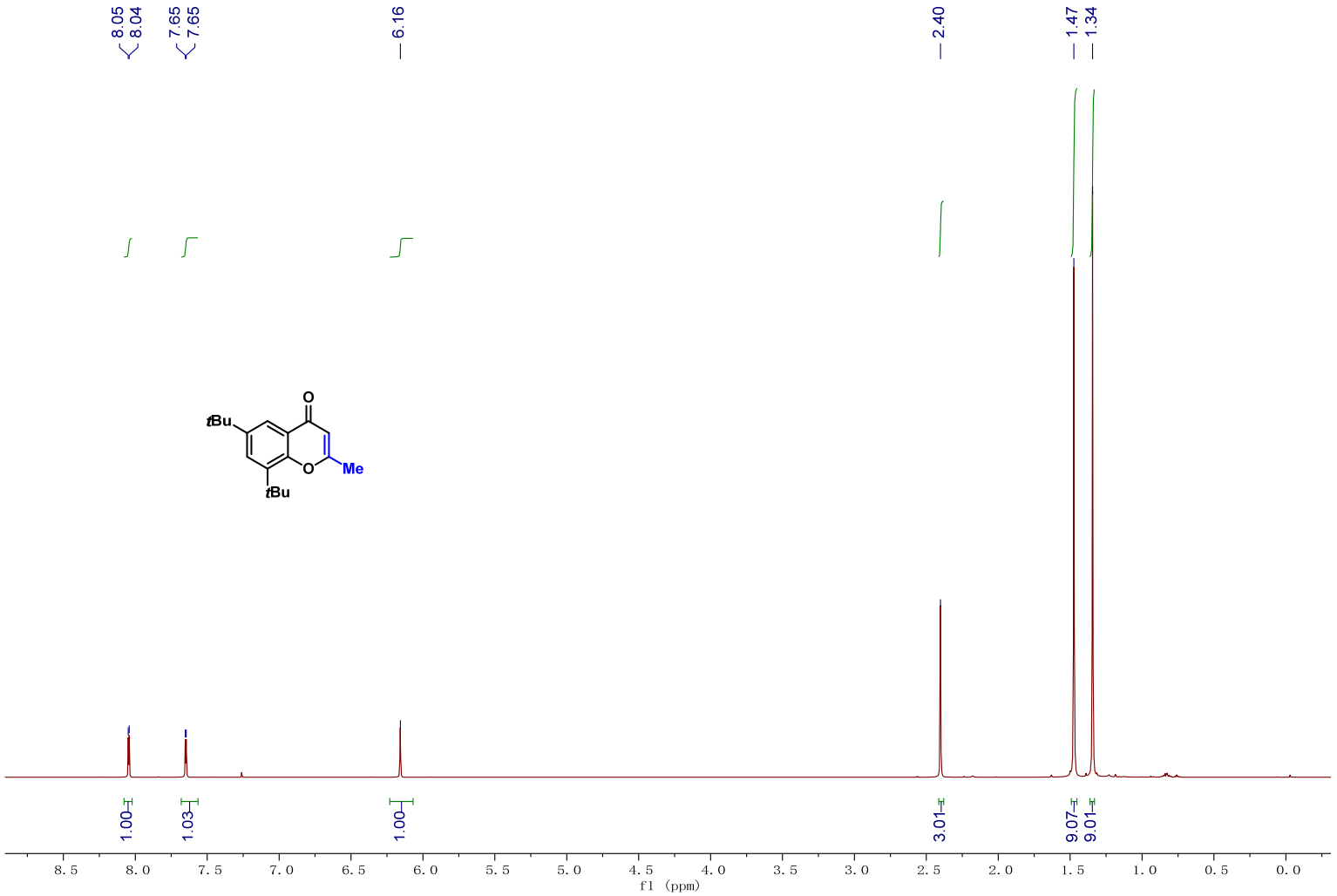
Compound 41 ^{1}H NMR



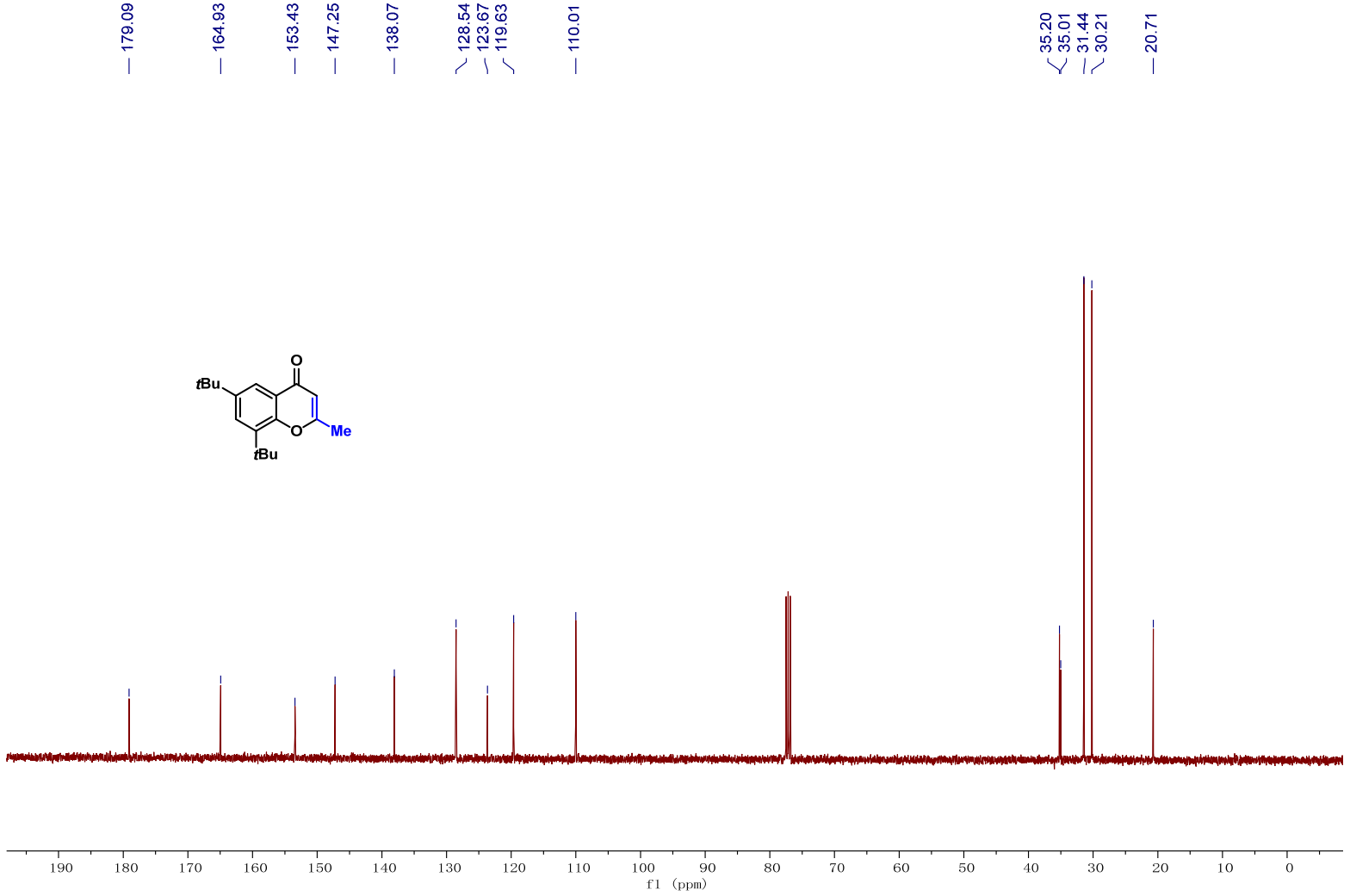
Compound 41 ^{13}C NMR



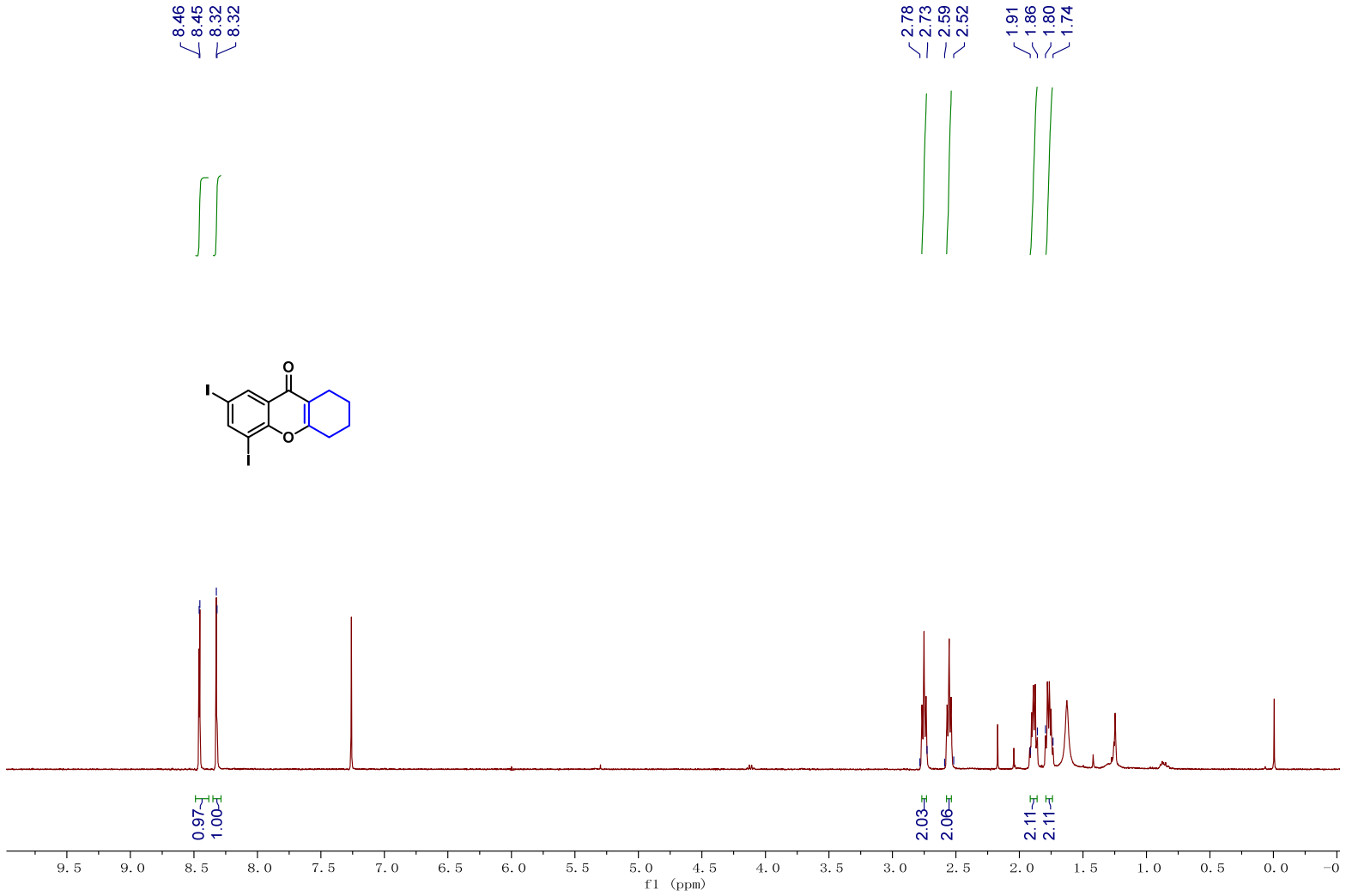
Compound 42 ^{1}H NMR



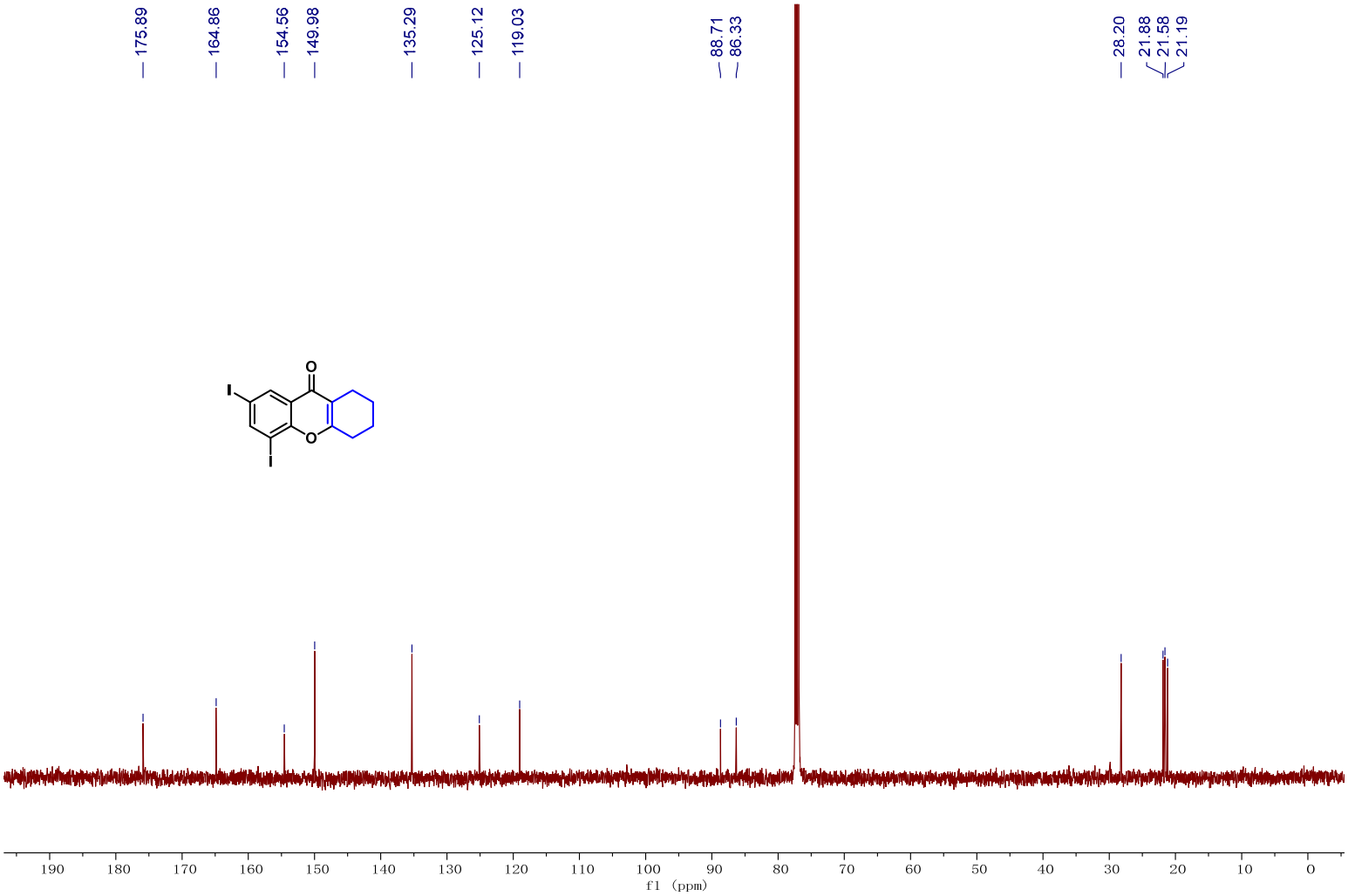
Compound 42 ^{13}C NMR



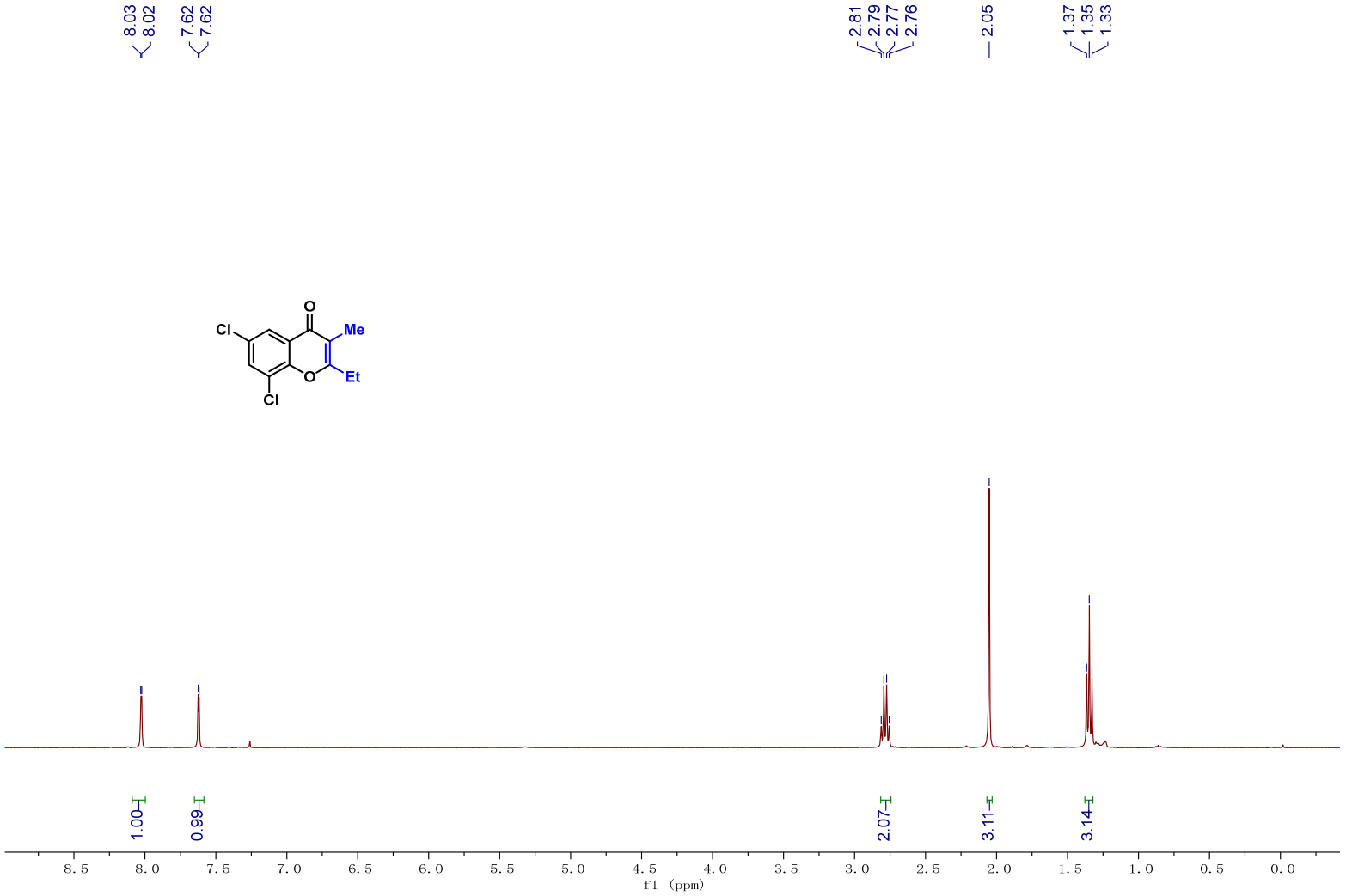
Compound 43 ^{1}H NMR



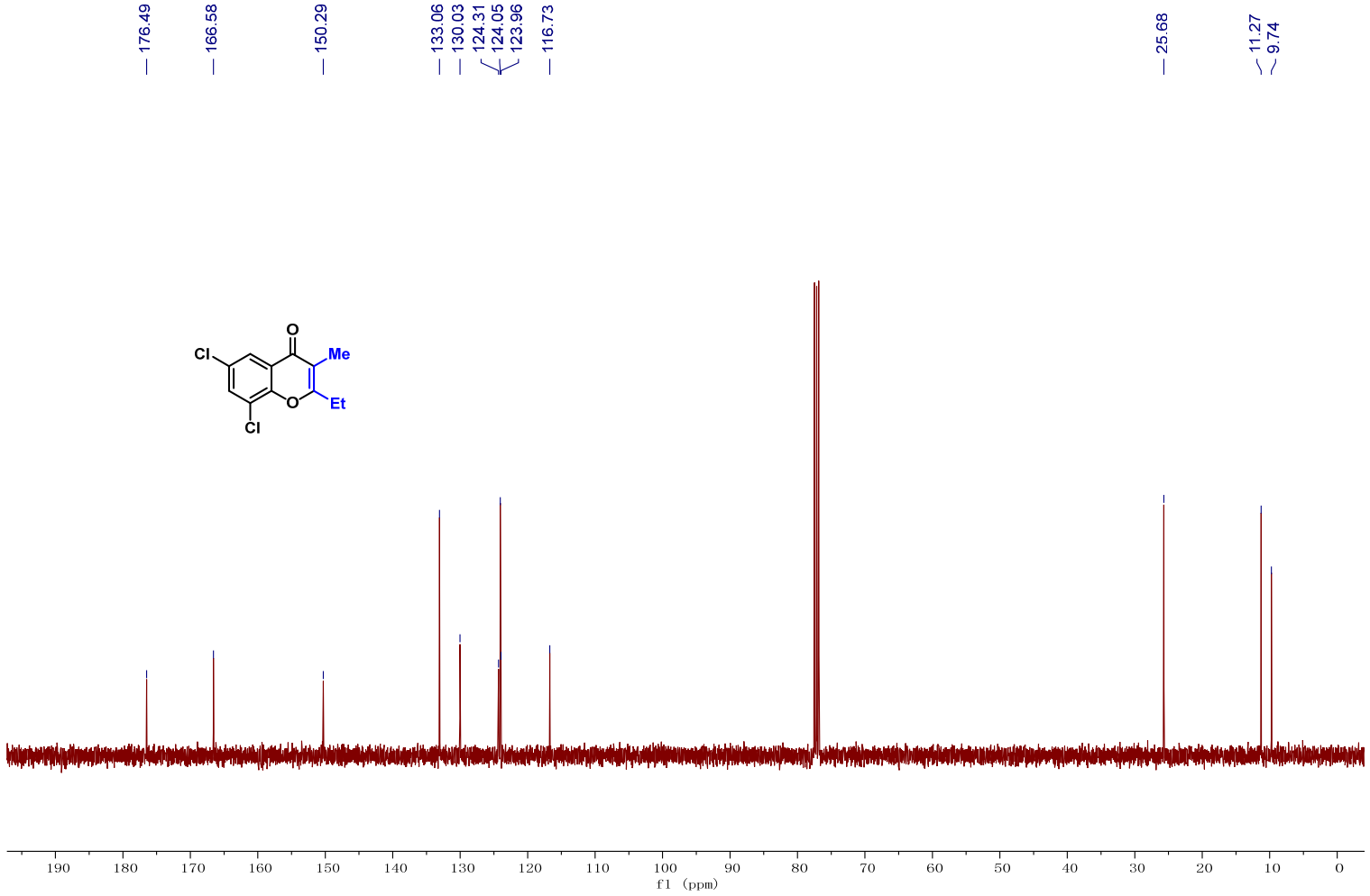
Compound 43 ^{13}C NMR



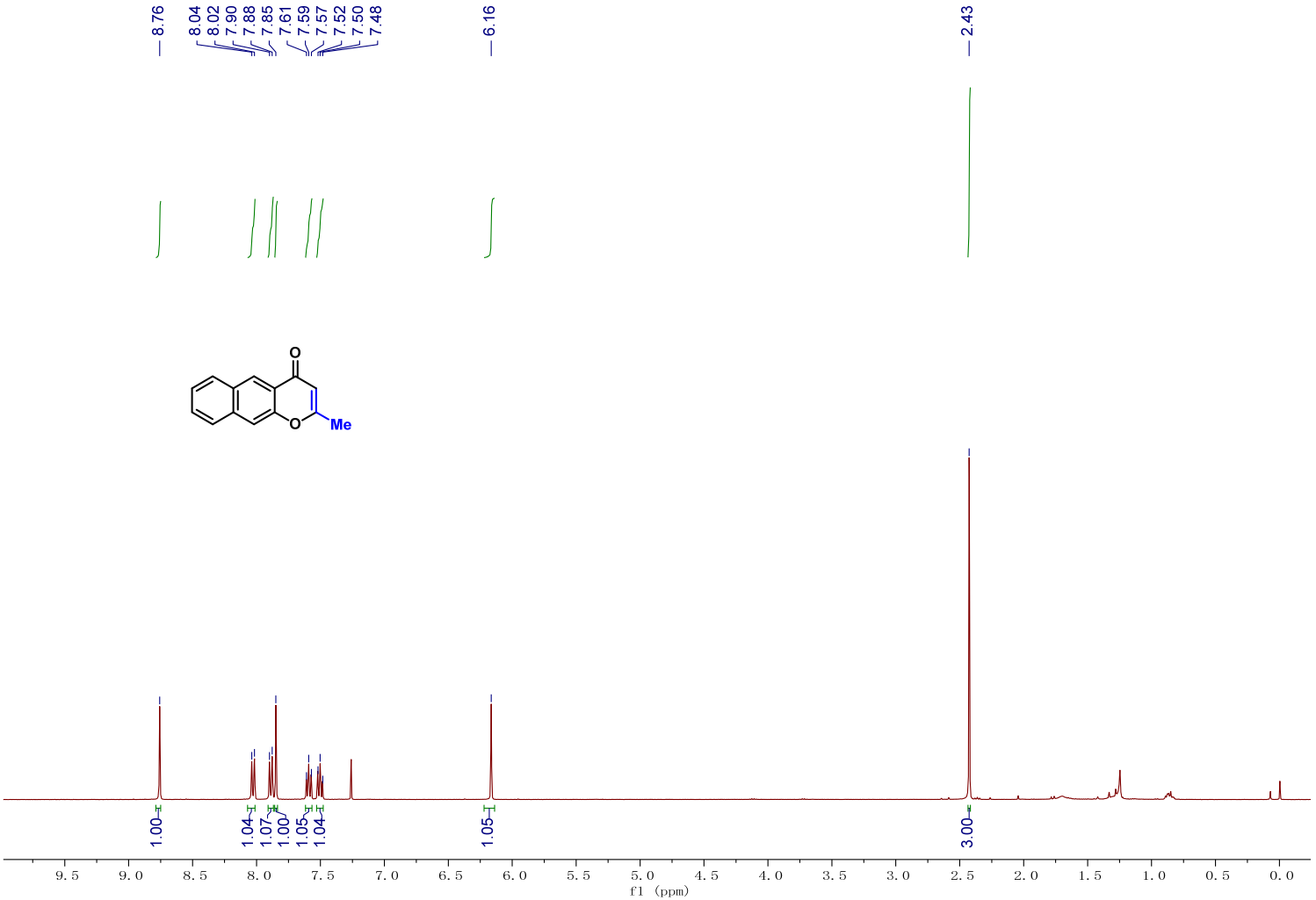
Compound 44 ^{1}H NMR



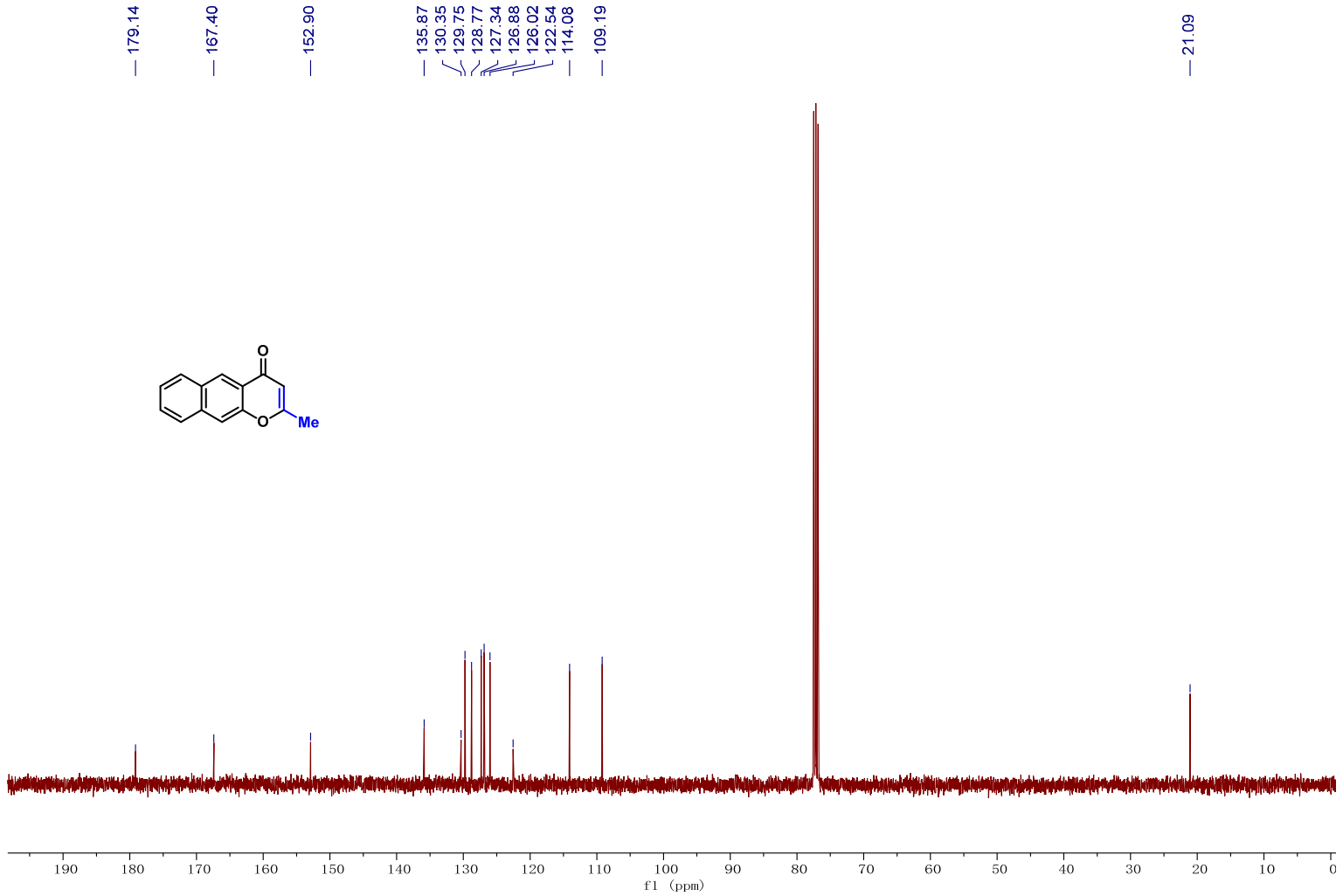
Compound 44 ^{13}C NMR



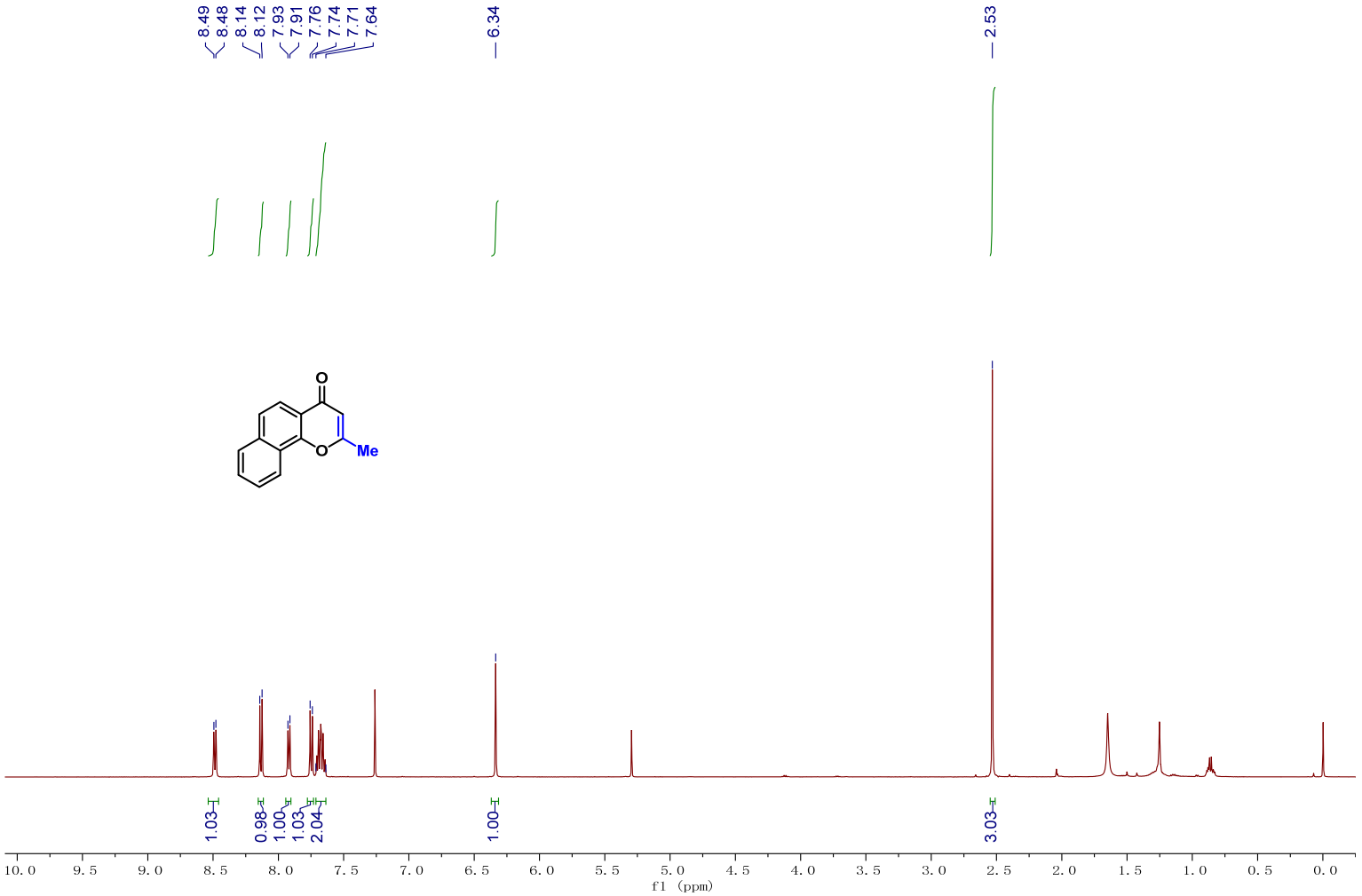
Compound 45 ^{1}H NMR



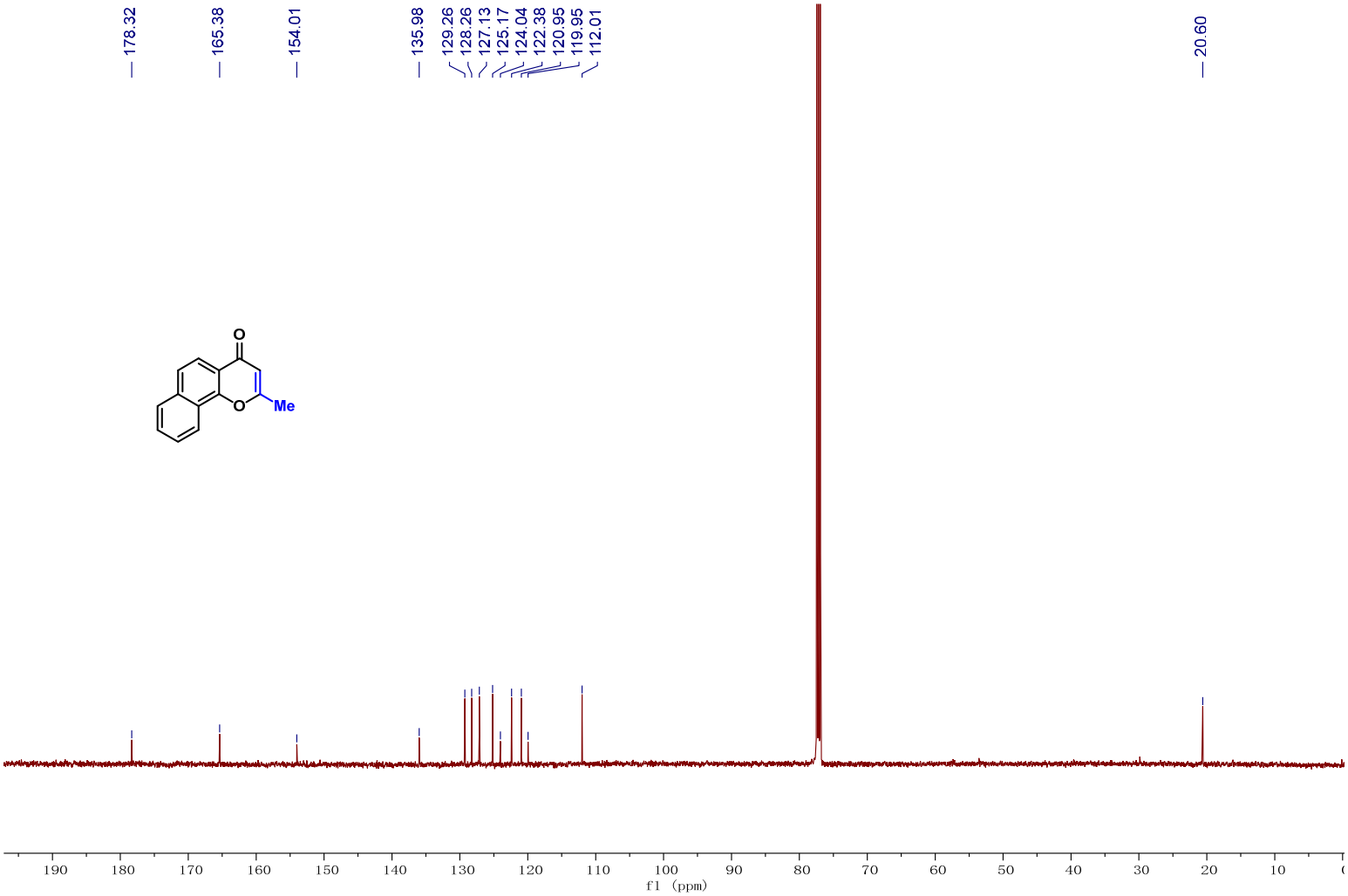
Compound 45 ^{13}C NMR



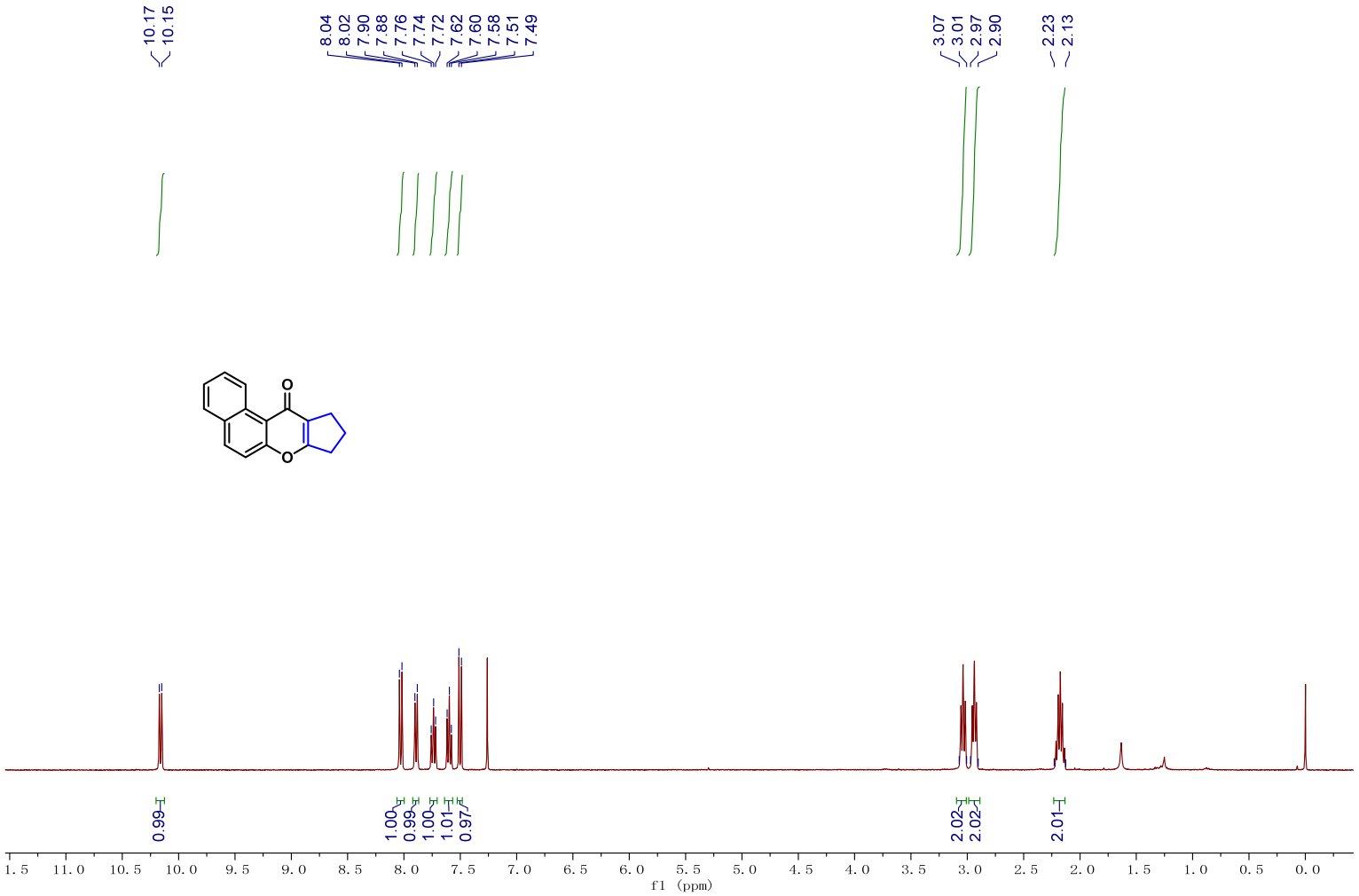
Compound 46 ^{1}H NMR



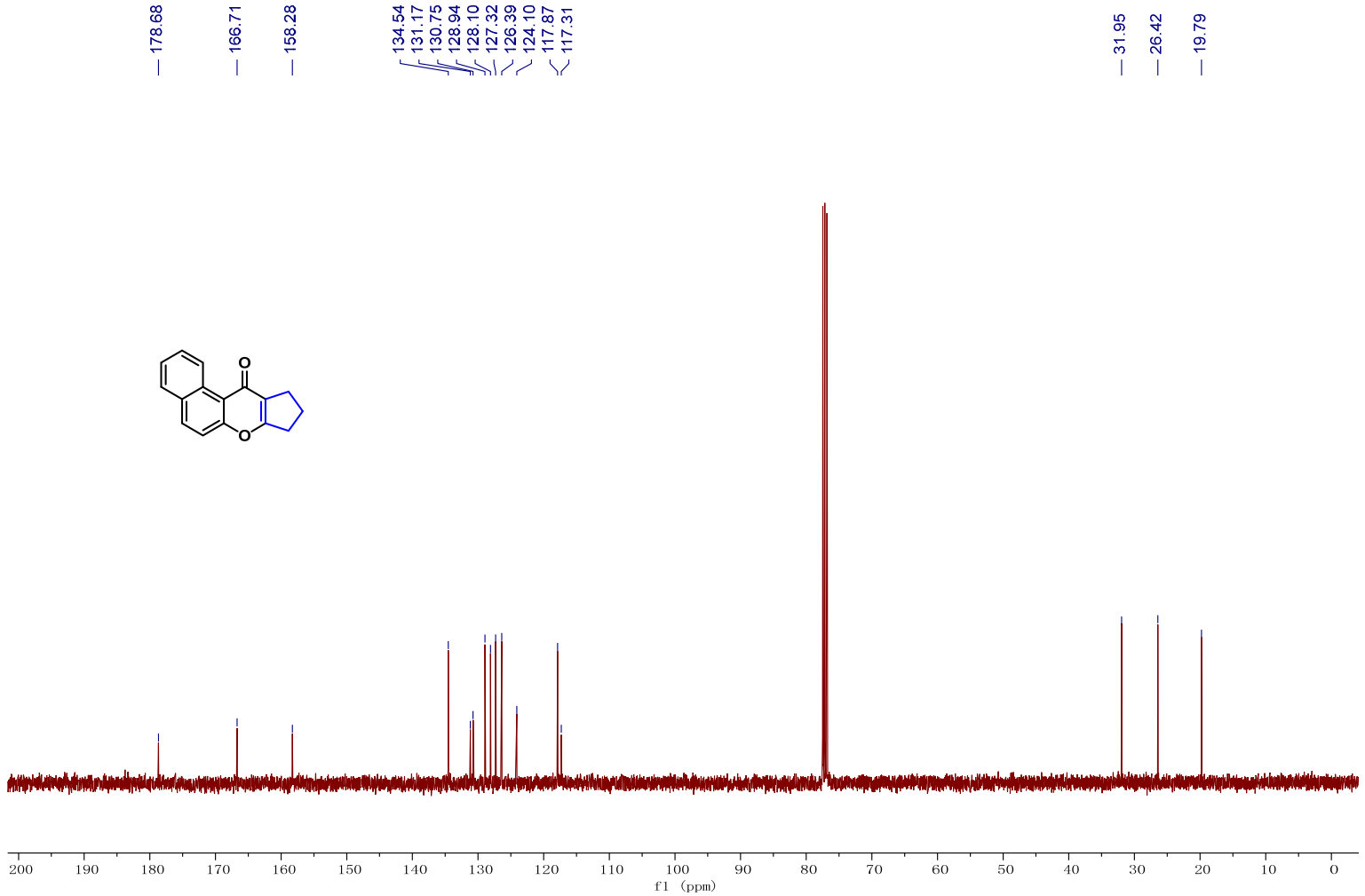
Compound 46 ^{13}C NMR



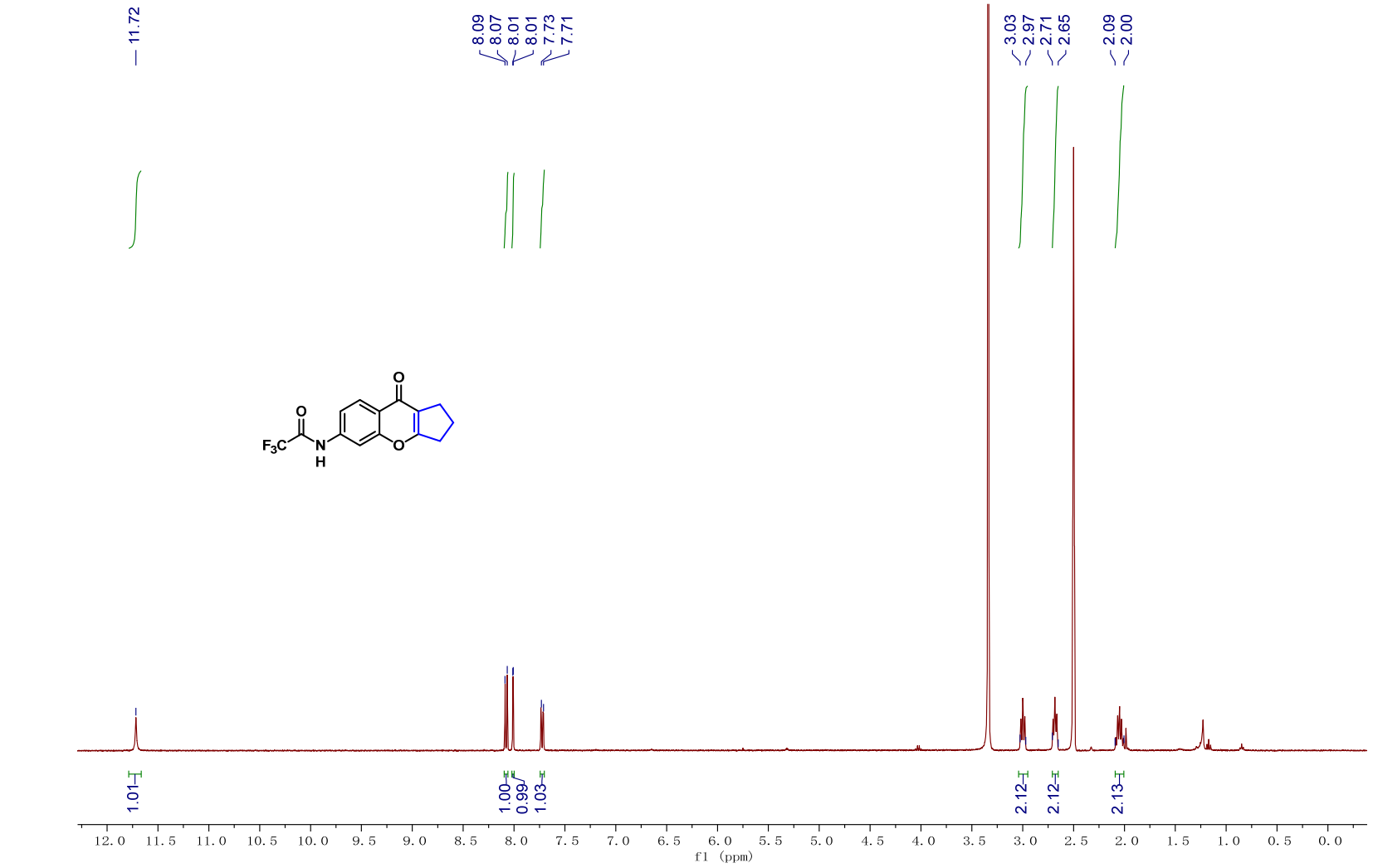
Compound 47 ^{1}H NMR



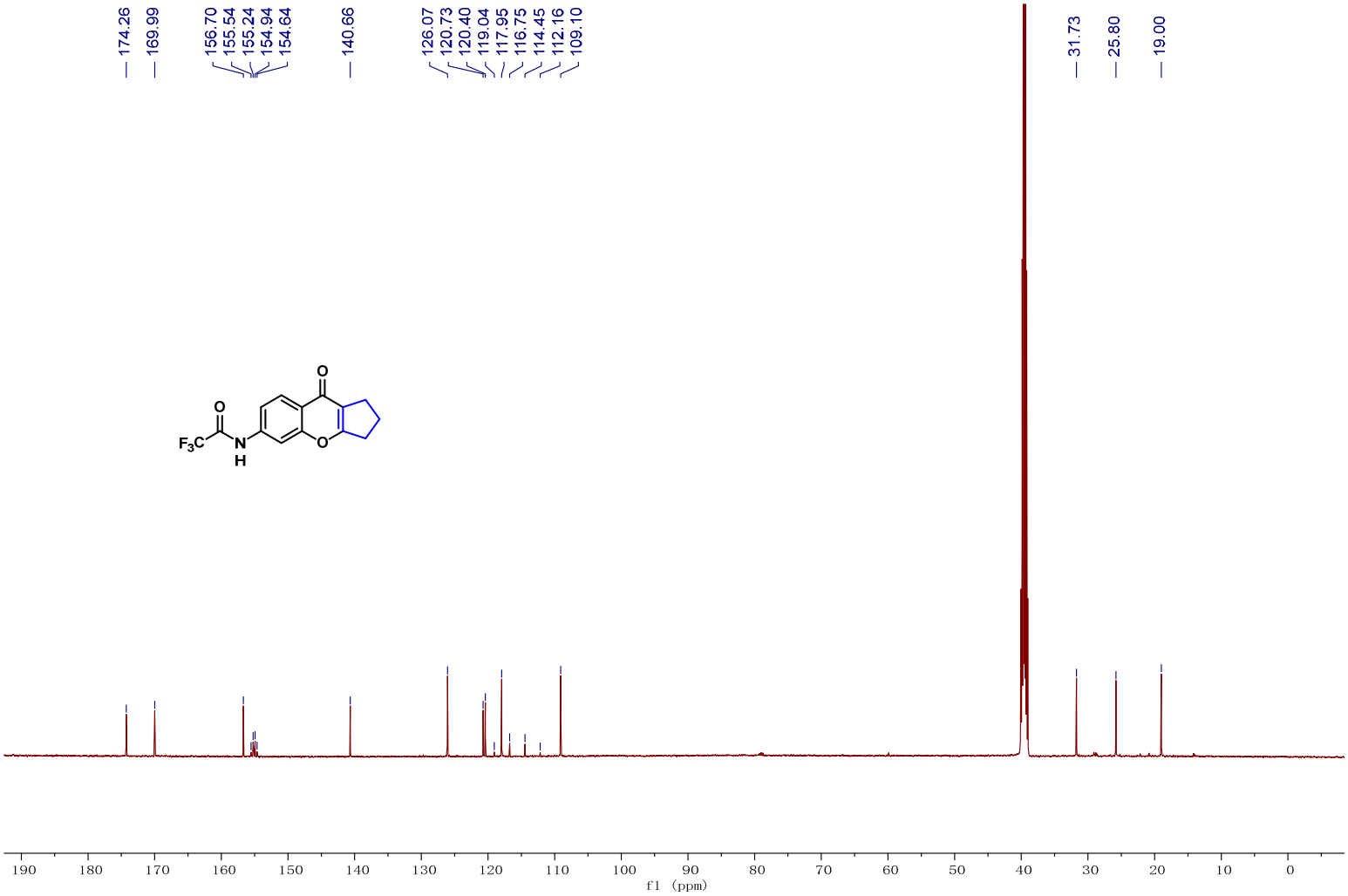
Compound 47 ^{13}C NMR



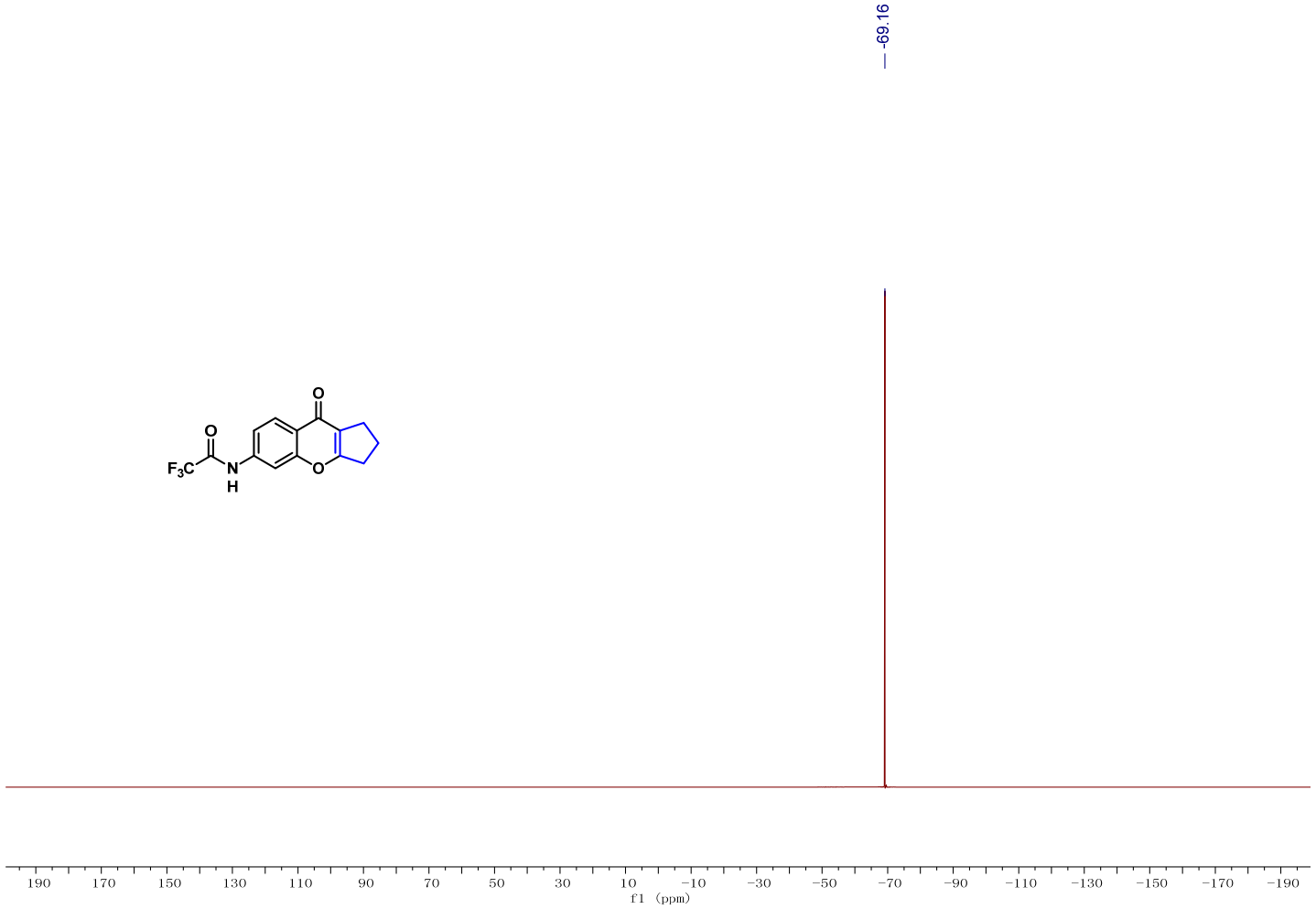
Compound 48 ^{1}H NMR



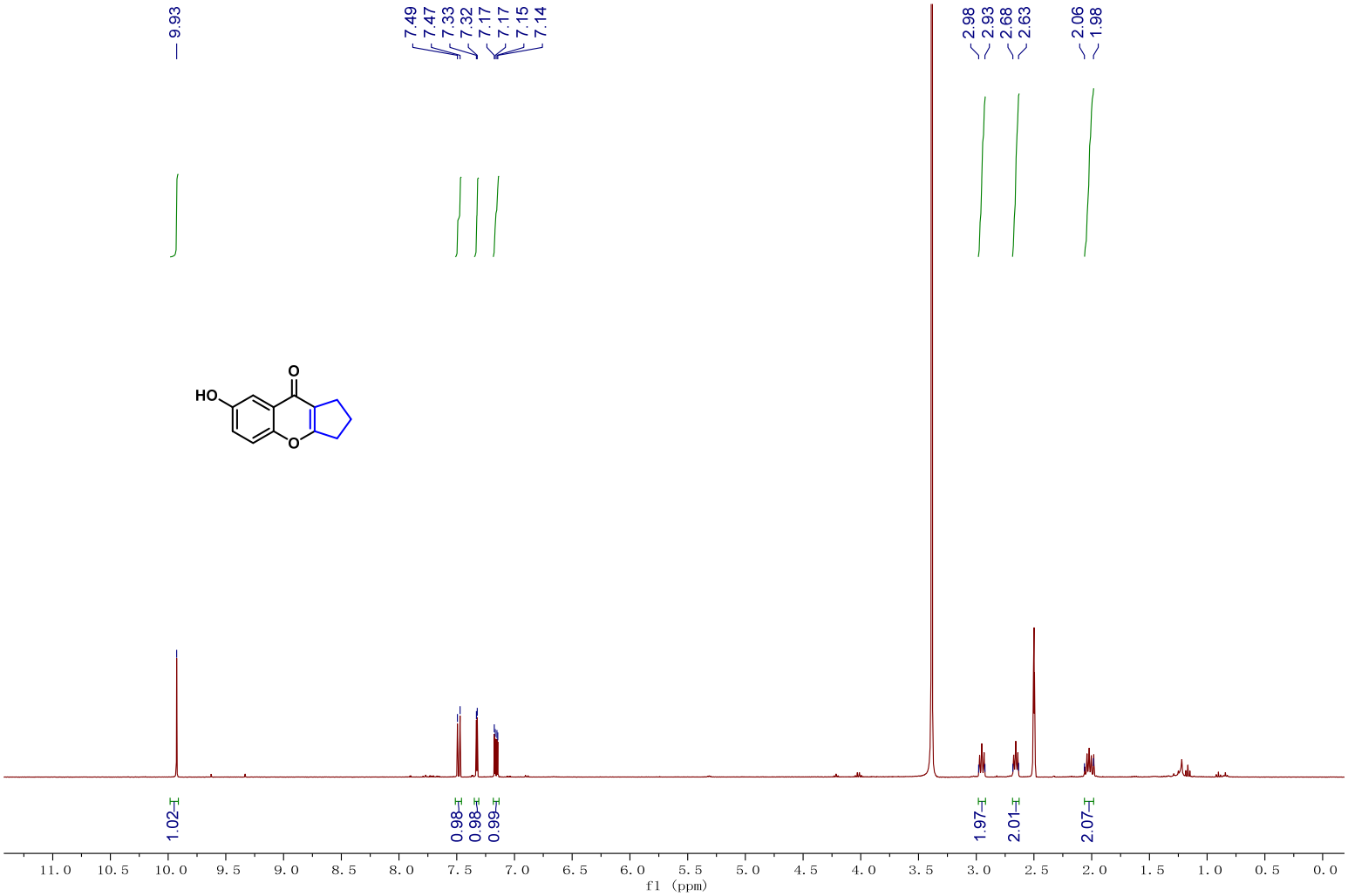
Compound 48 ^{13}C NMR



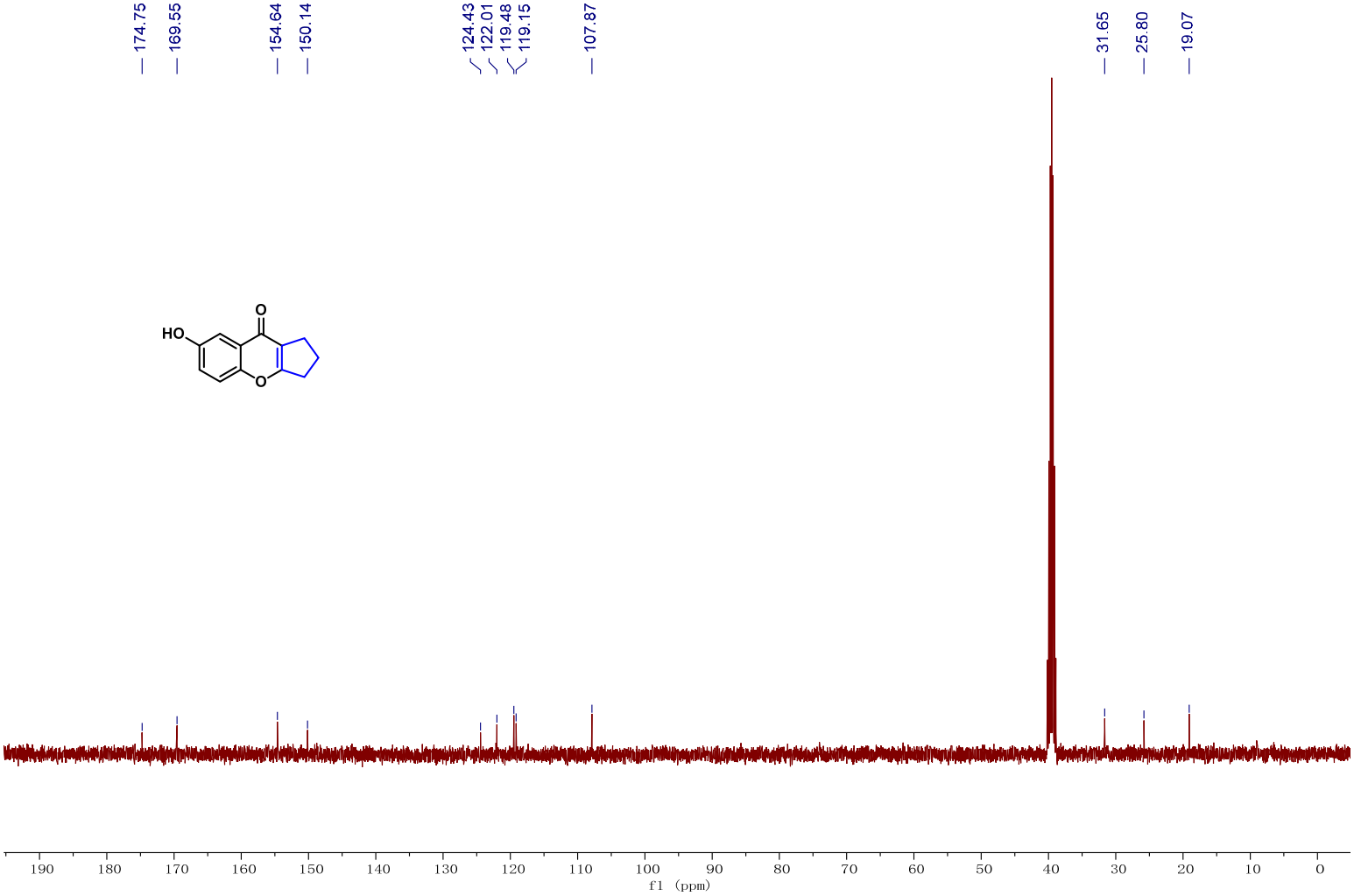
Compound 48 ^{19}F NMR



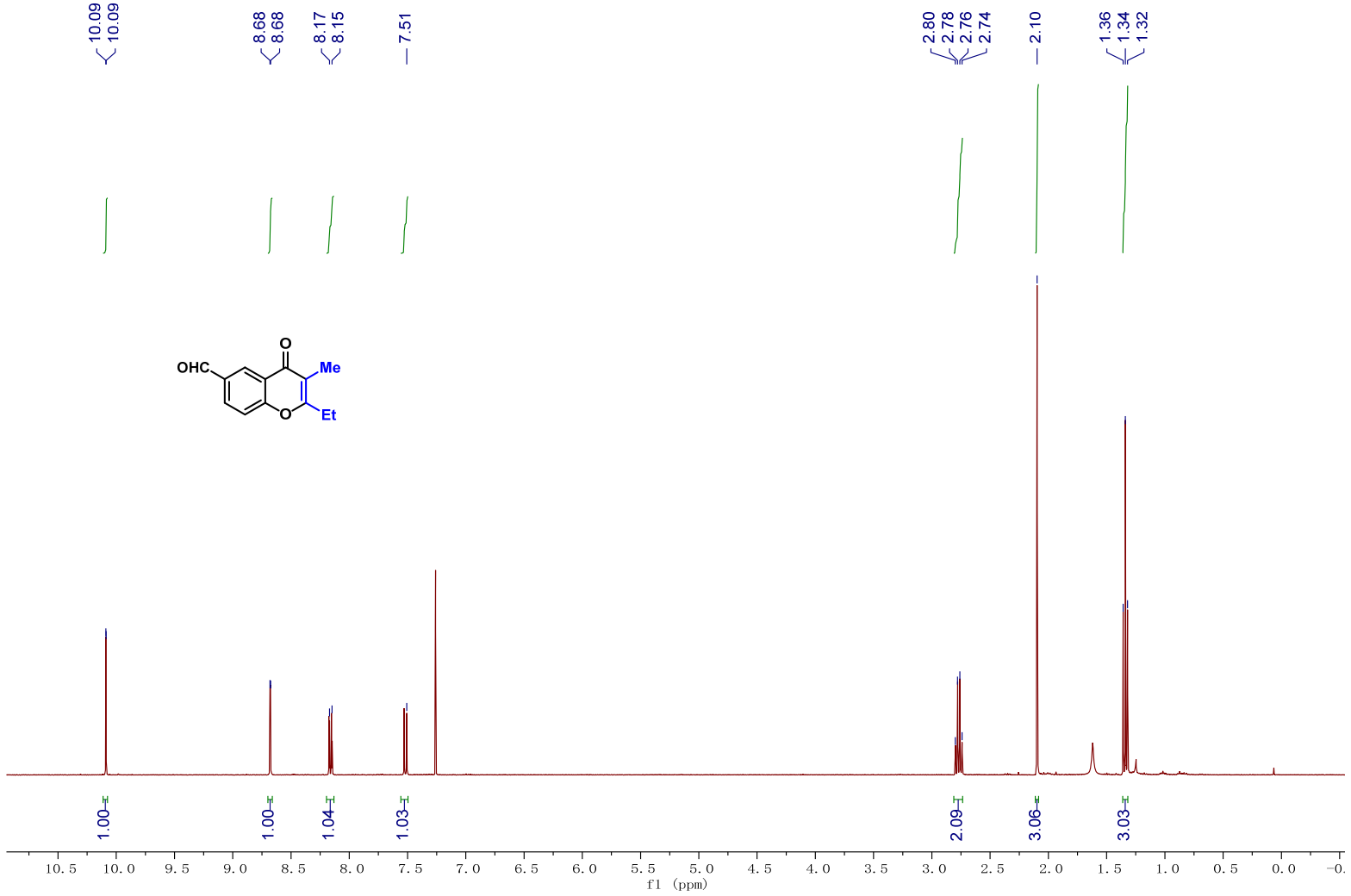
Compound 49 ^{1}H NMR



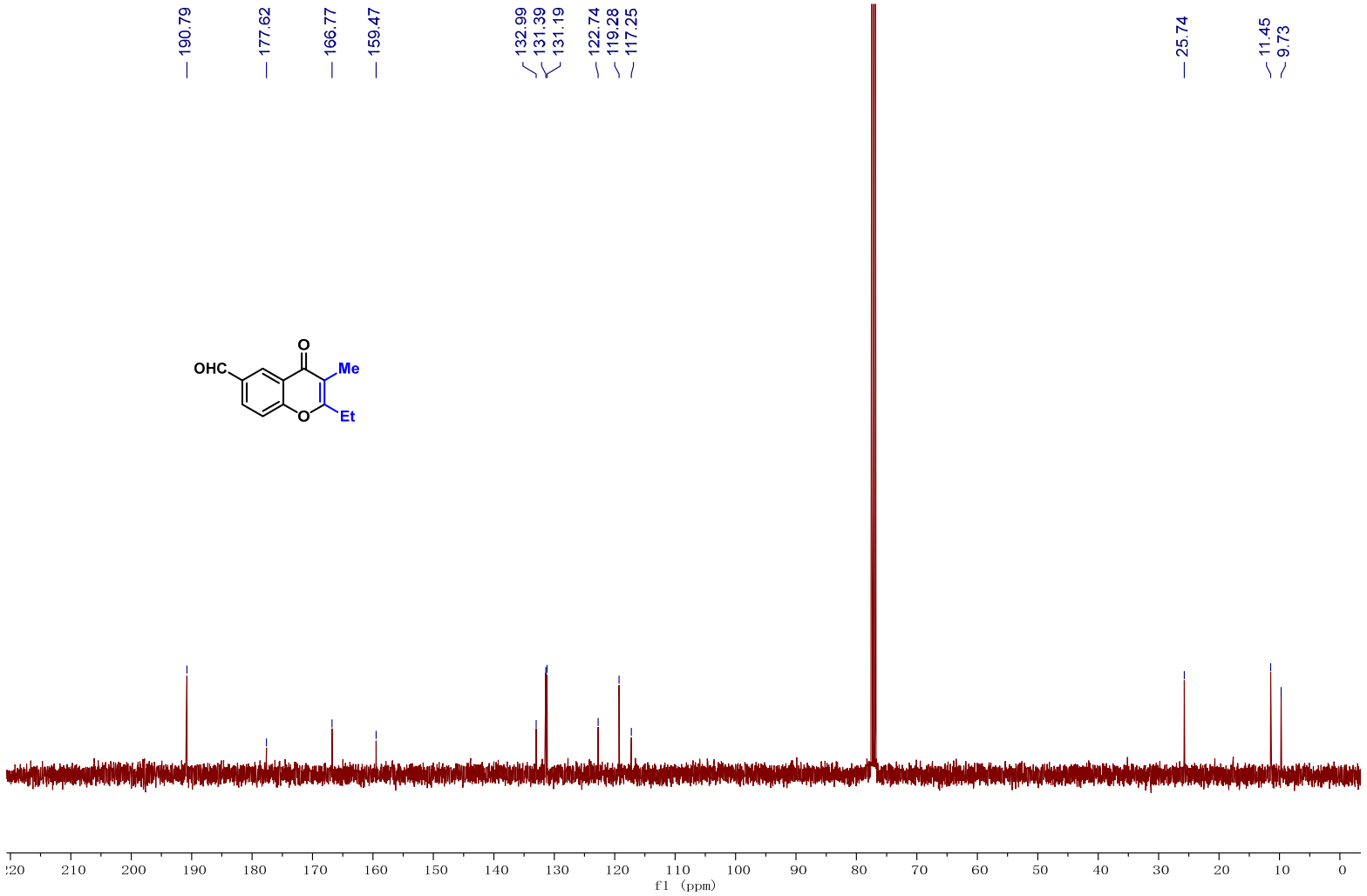
Compound 49 ^{13}C NMR



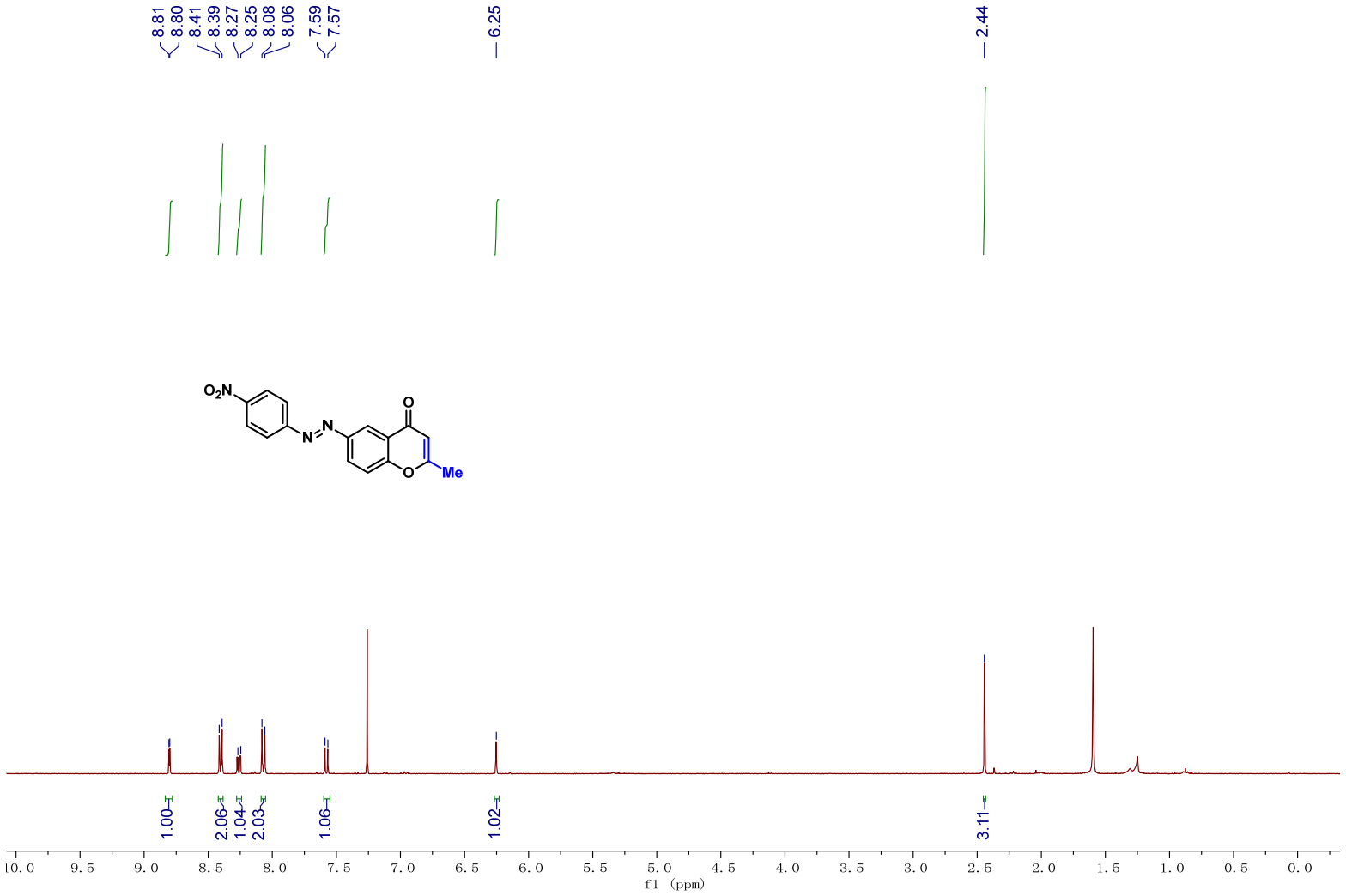
Compound 50 ^{1}H NMR



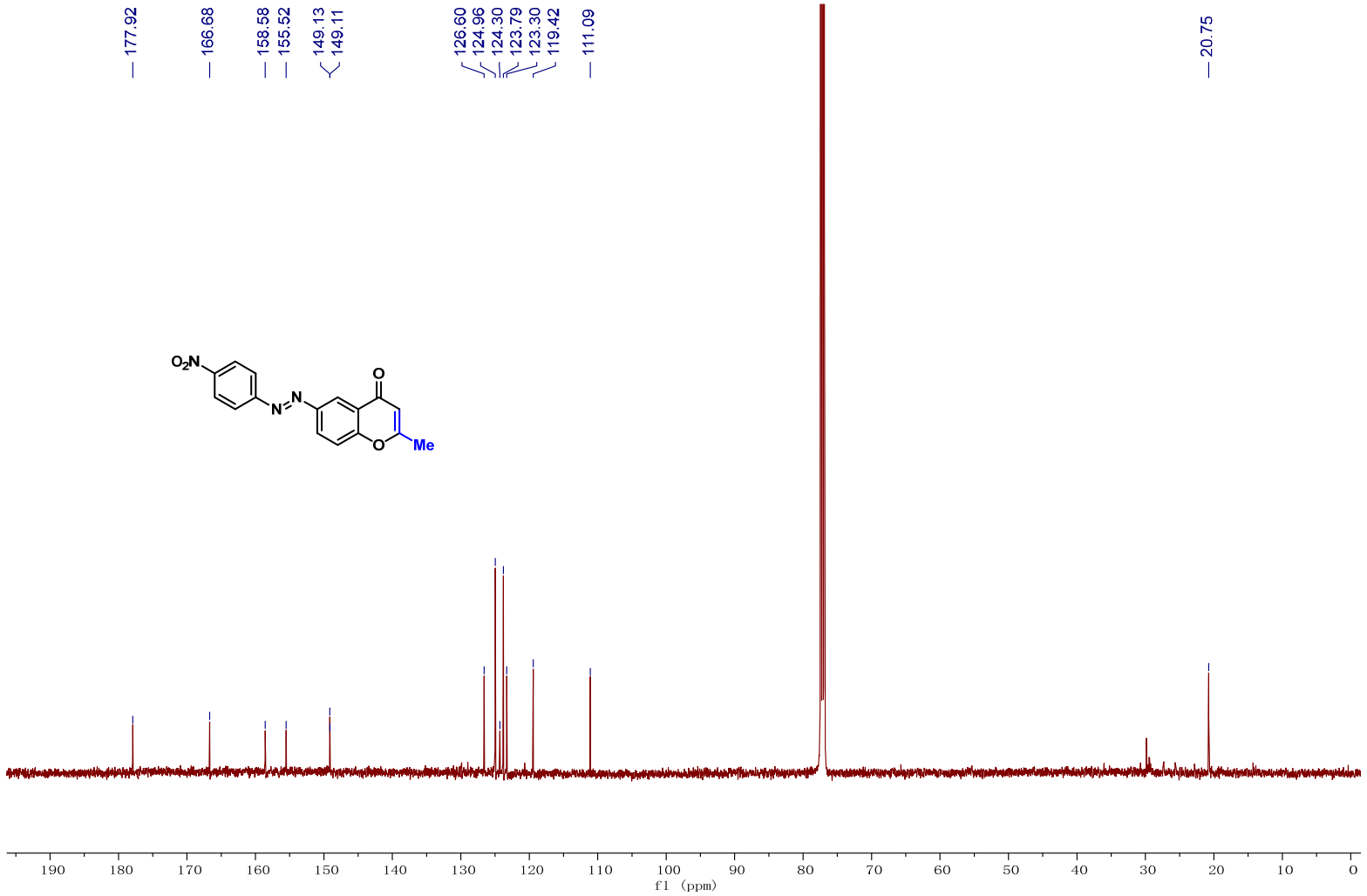
Compound 50 ^{13}C NMR



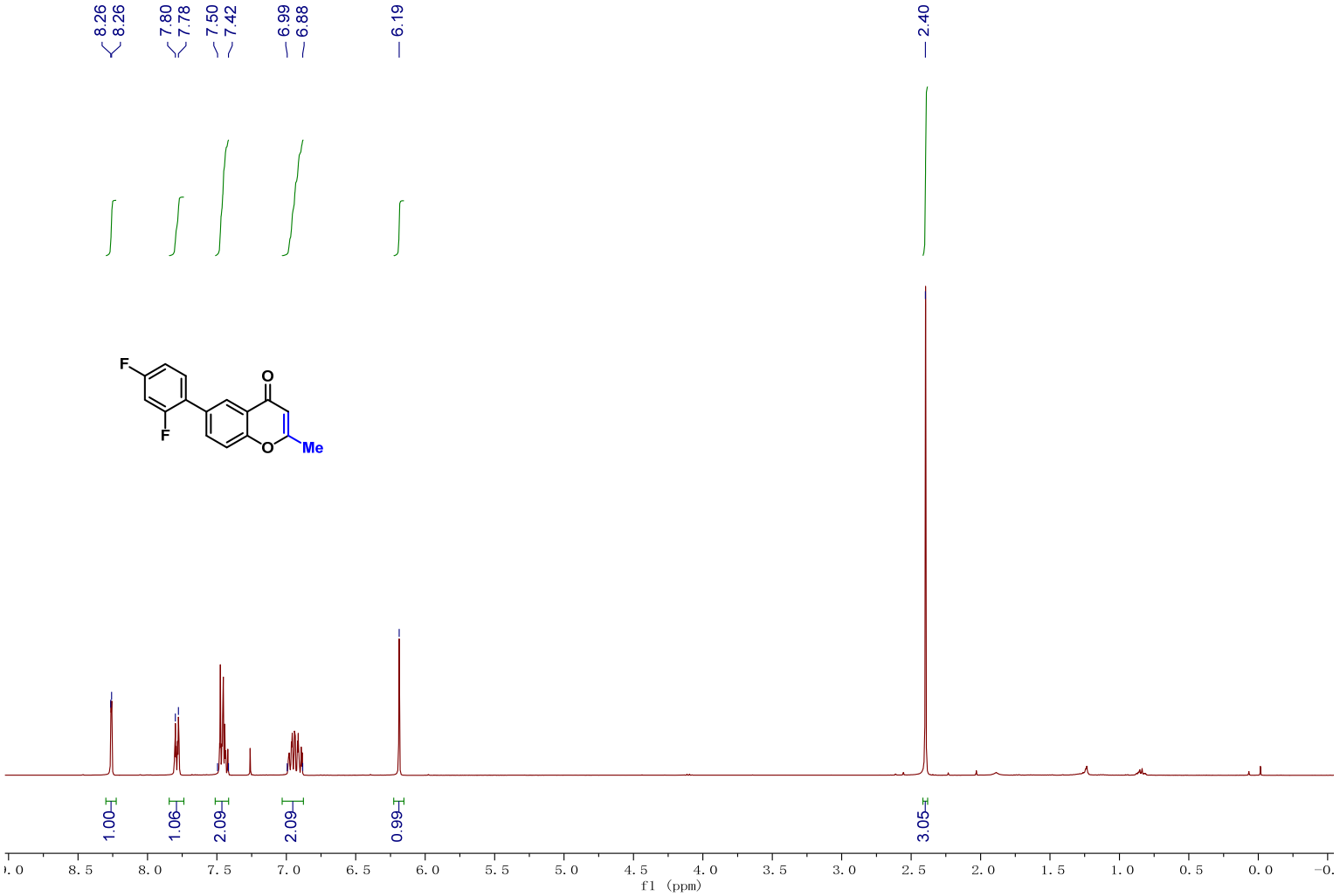
Compound 51 ^{1}H NMR



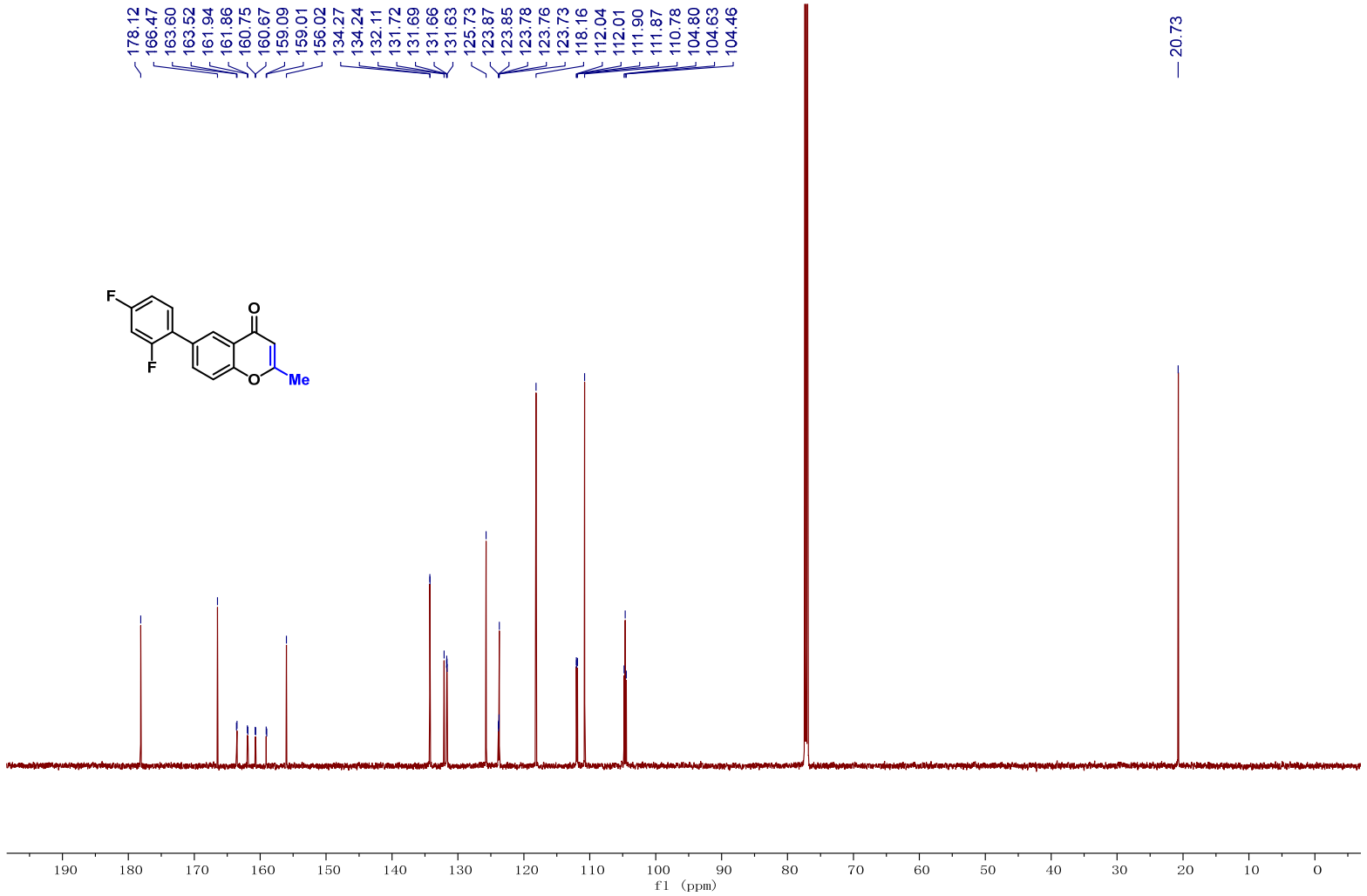
Compound 51 ^{13}C NMR



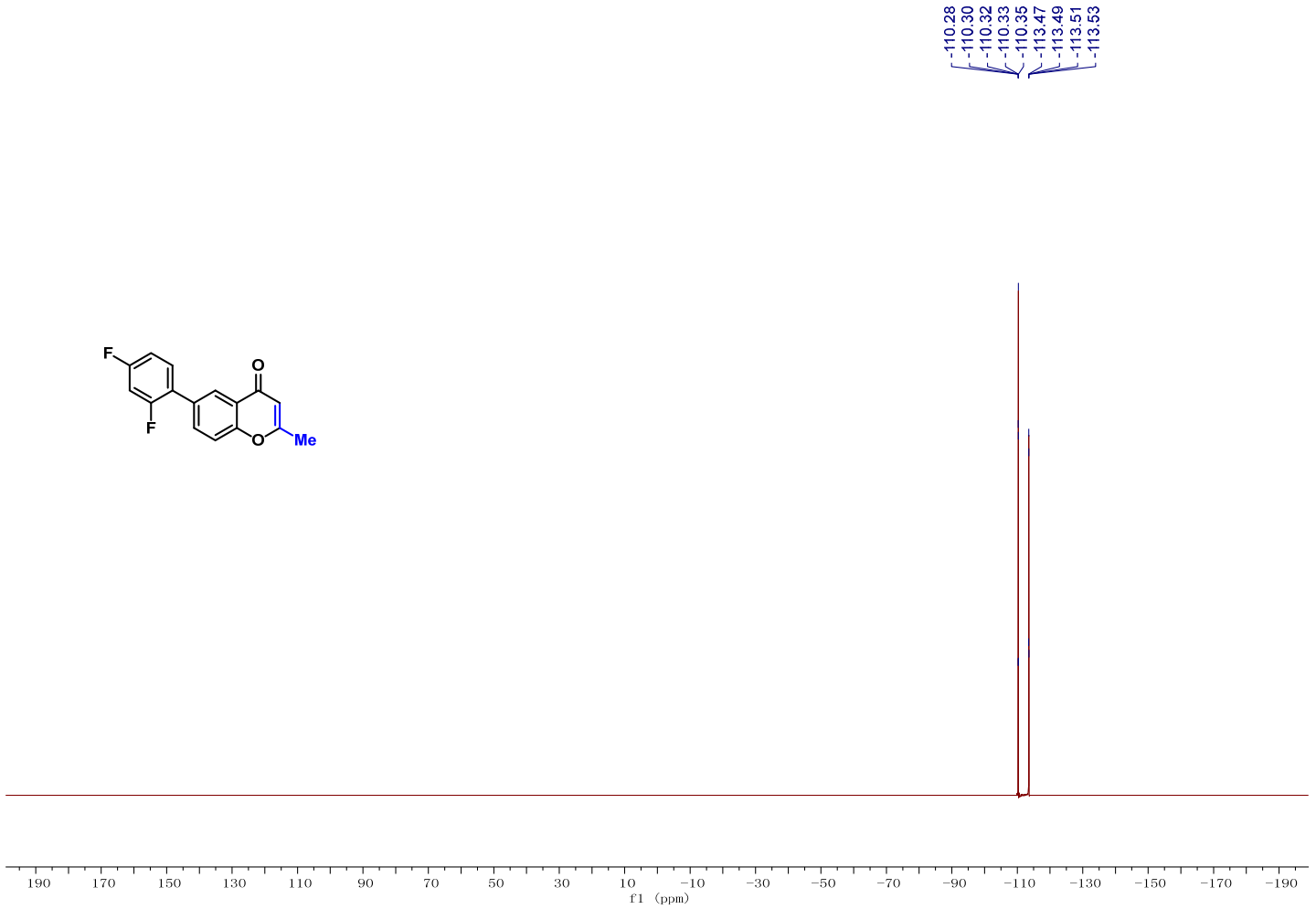
Compound 52 ^{1}H NMR



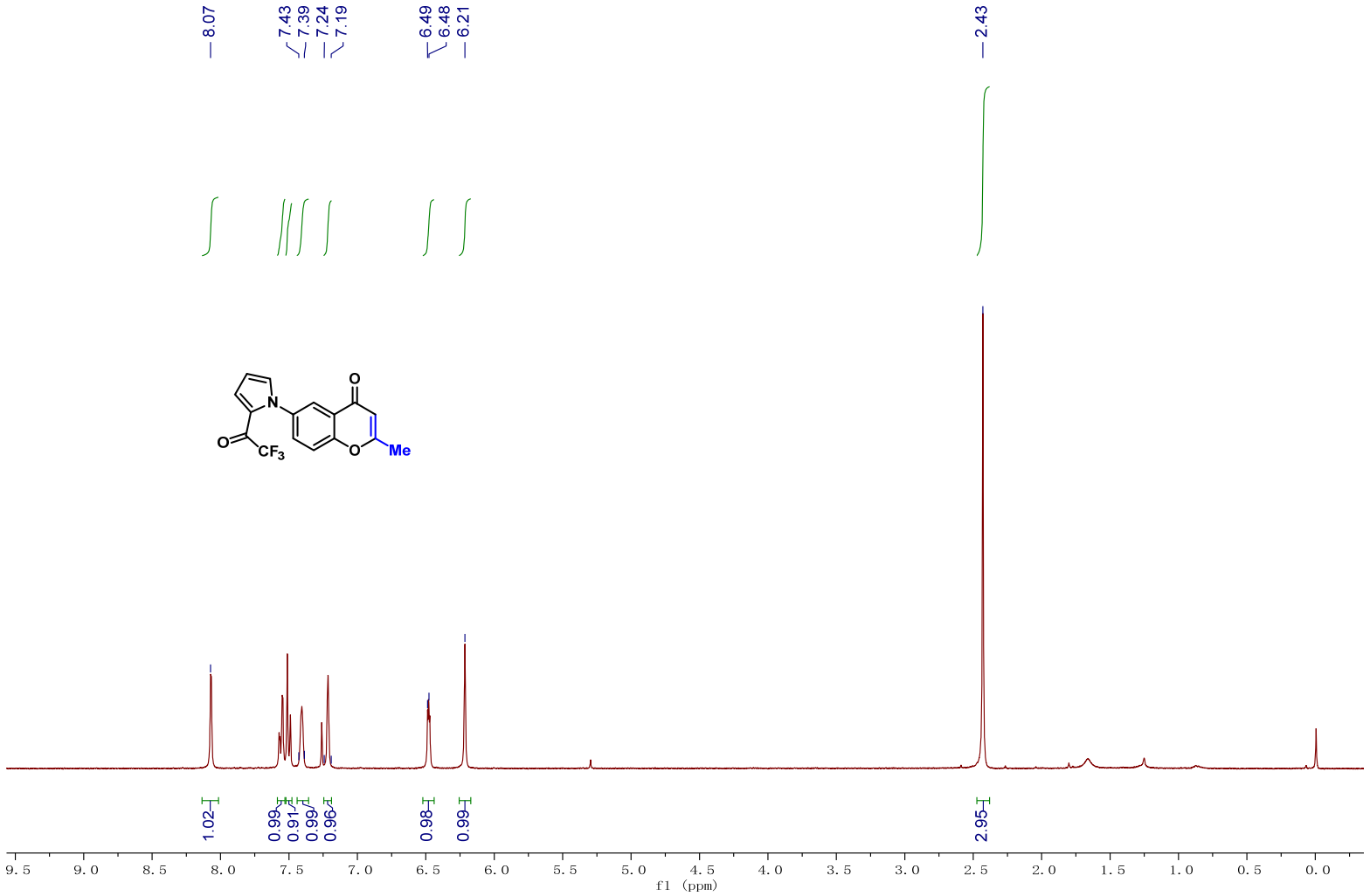
Compound 52 ^{13}C NMR



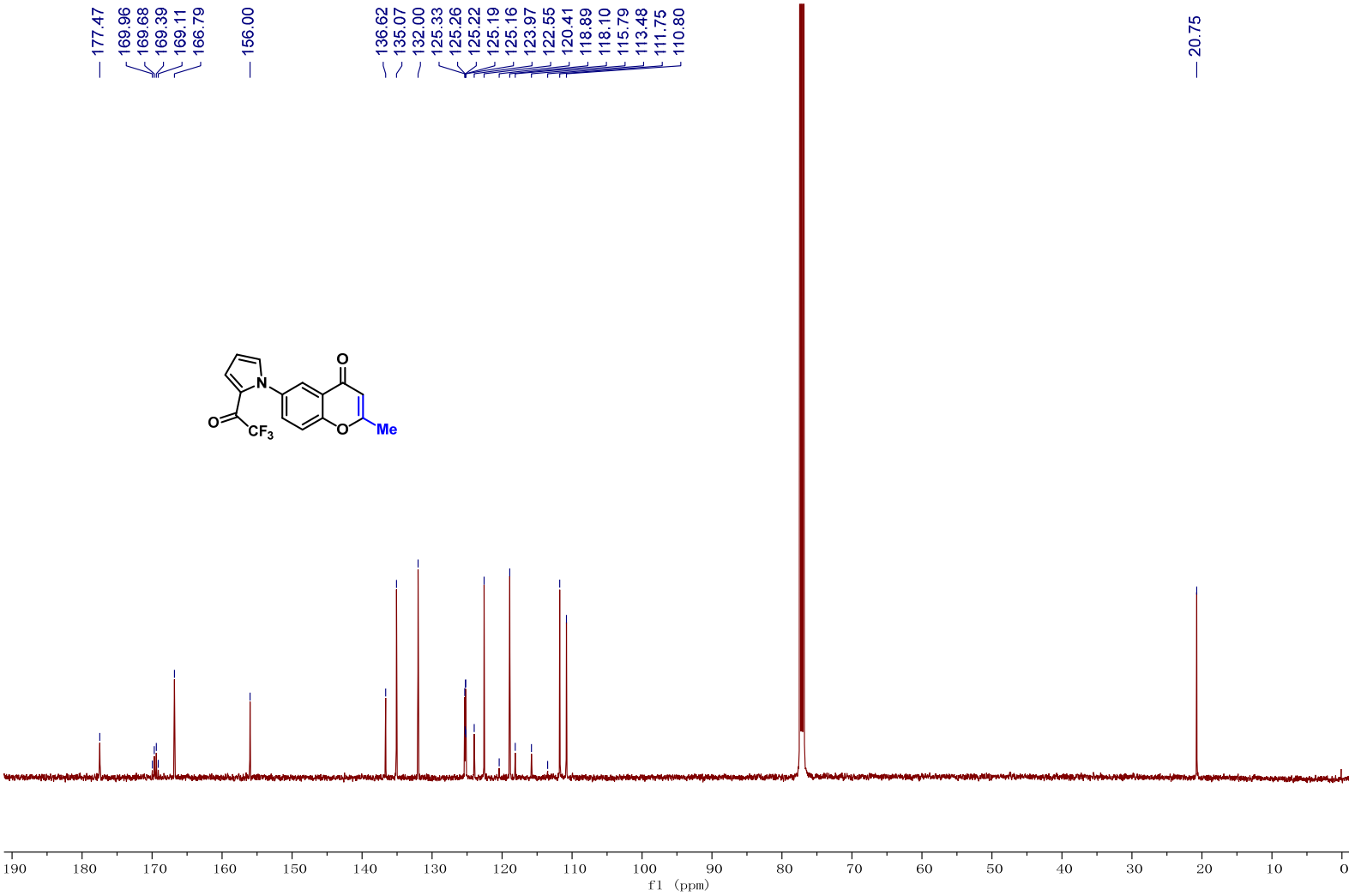
Compound 52 ^{19}F NMR



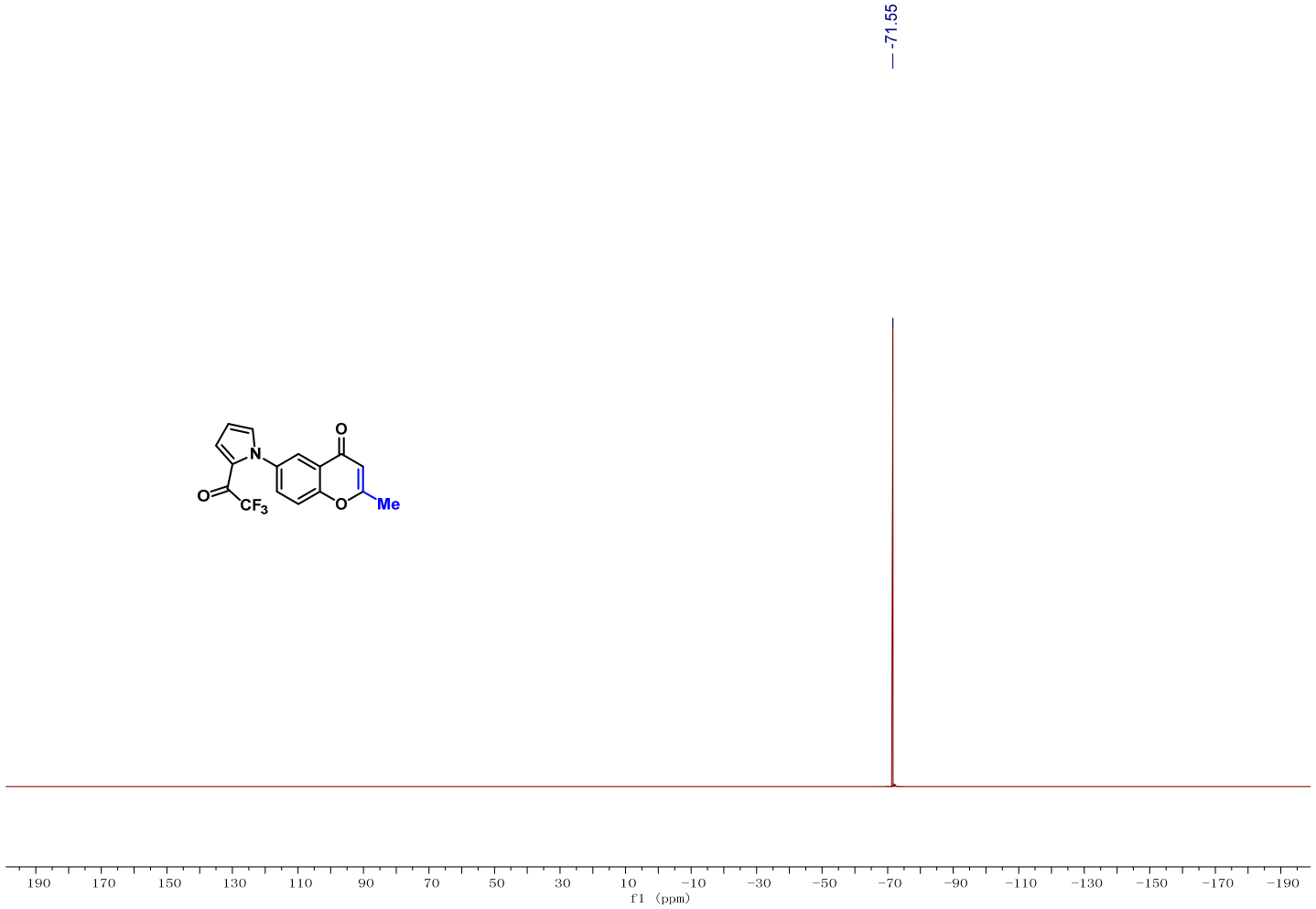
Compound 53 ^{1}H NMR



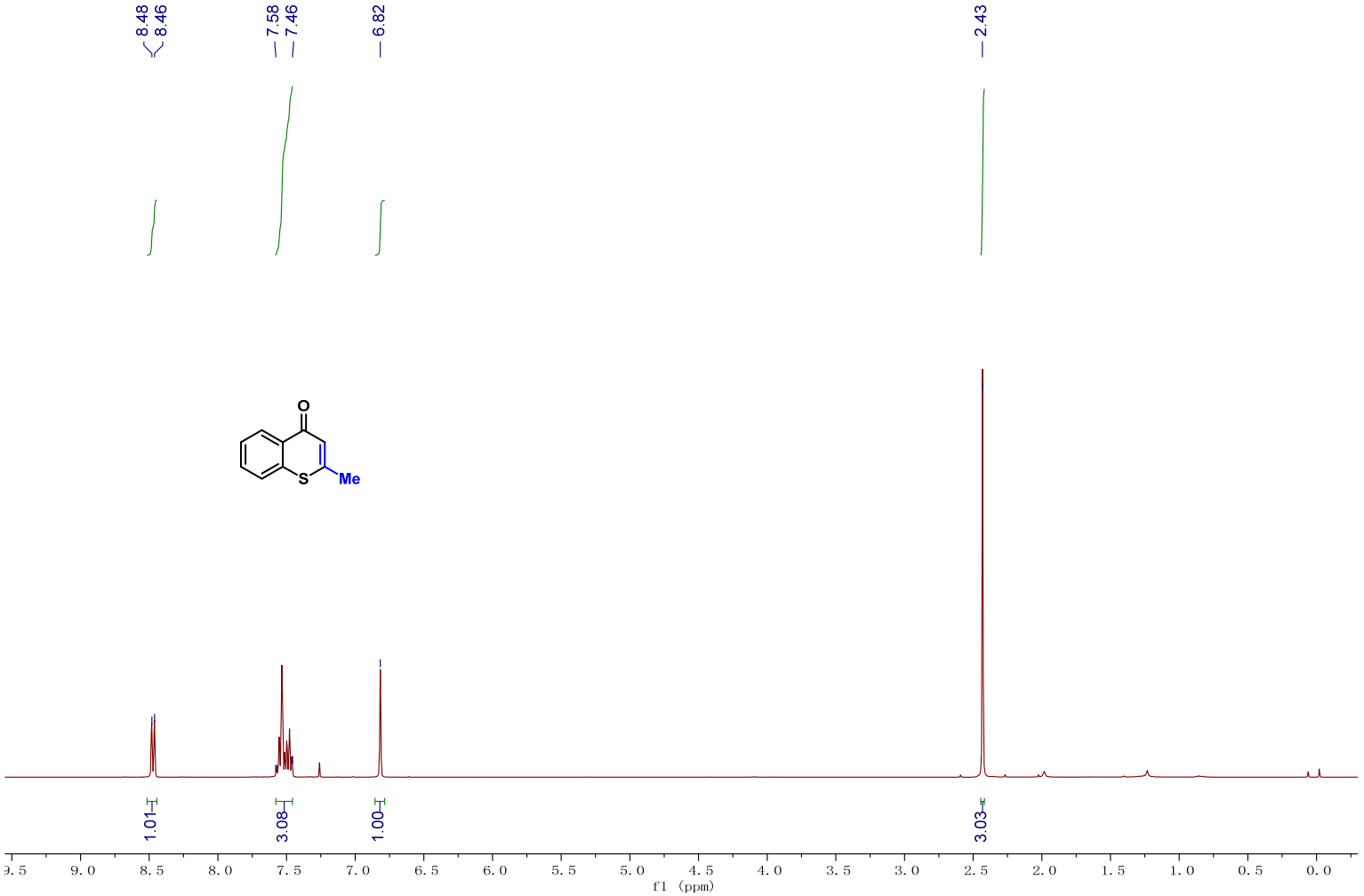
Compound 53 ^{13}C NMR



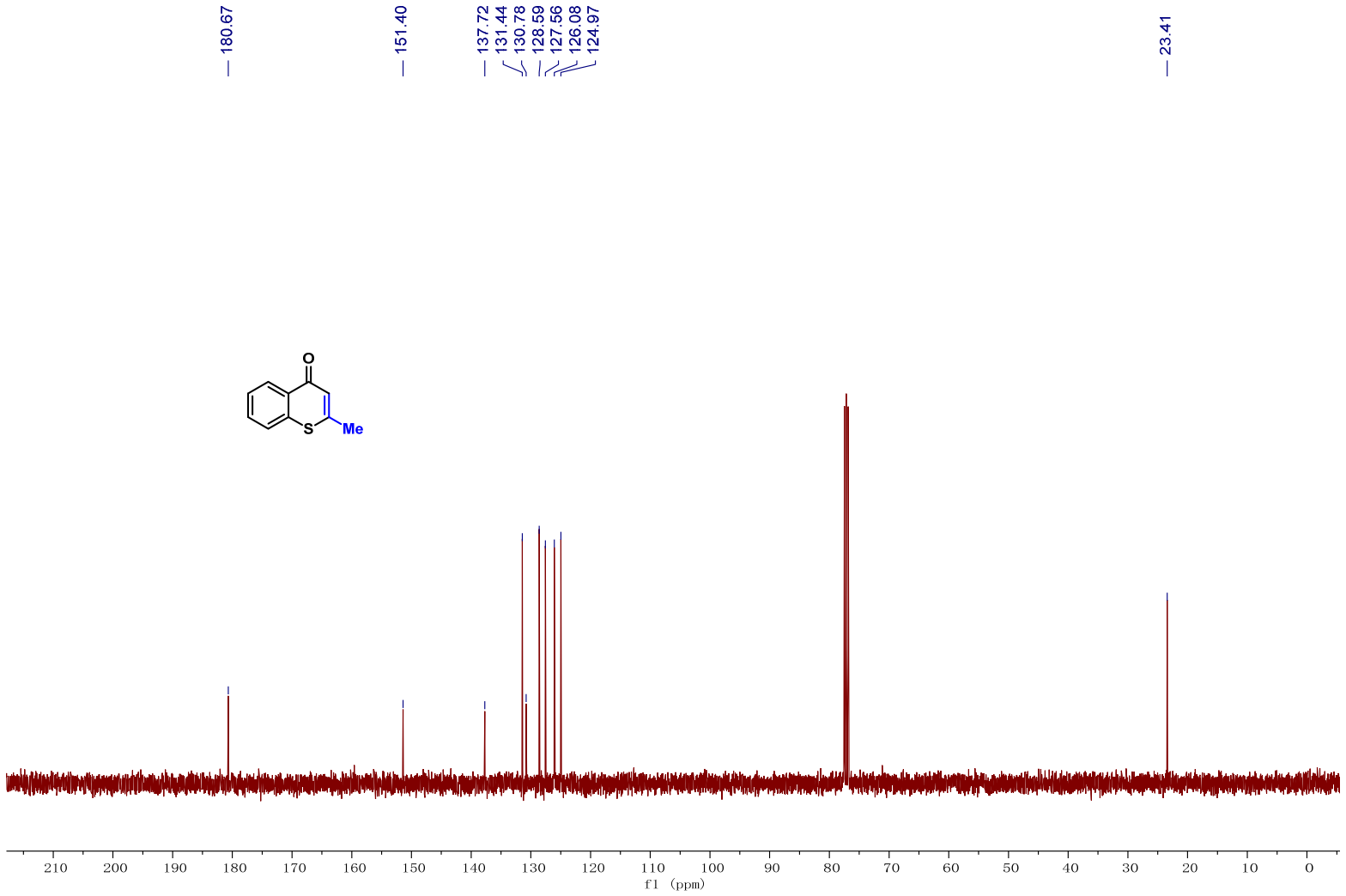
Compound 53 ^{19}F NMR



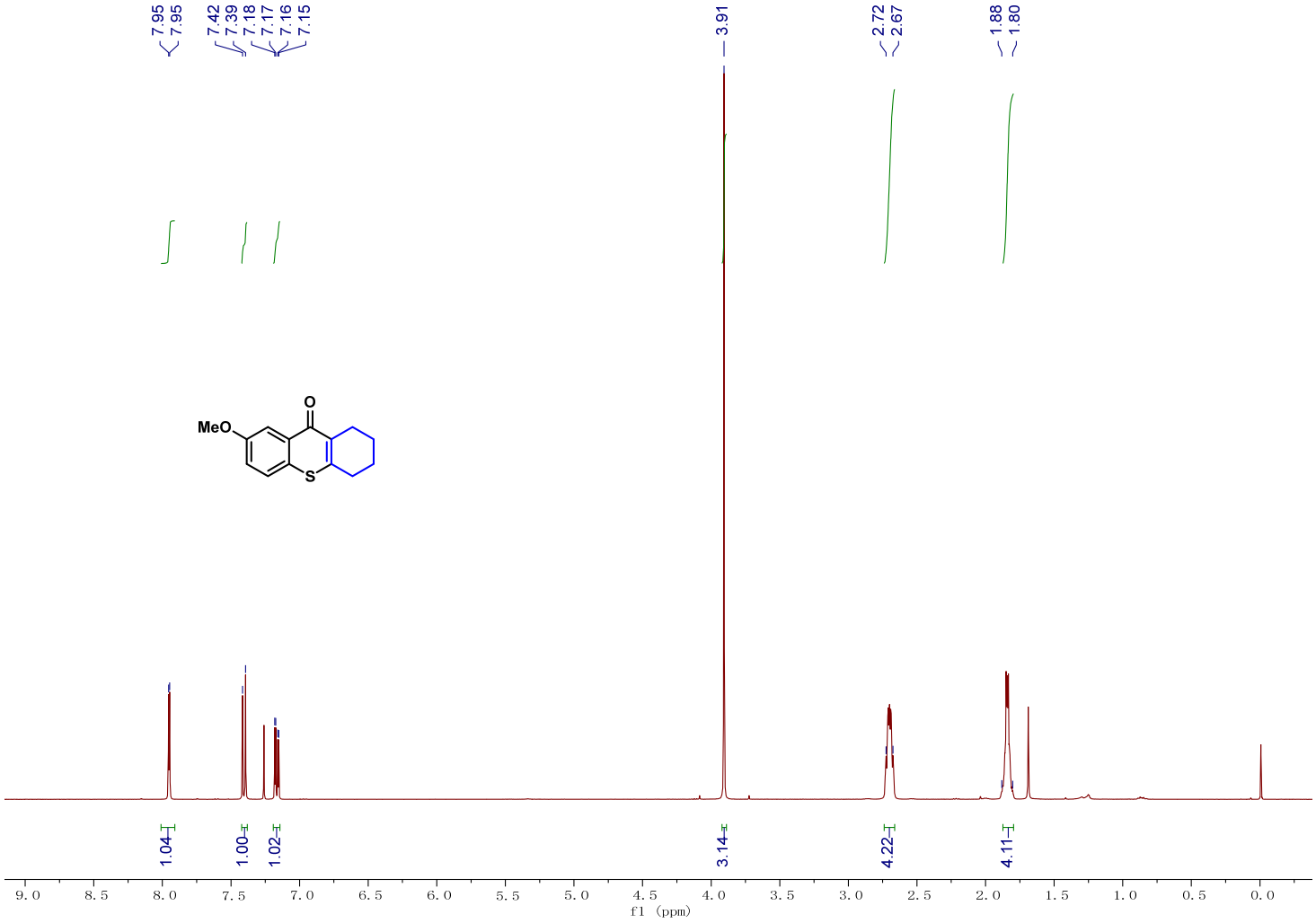
Compound 54 ^{1}H NMR



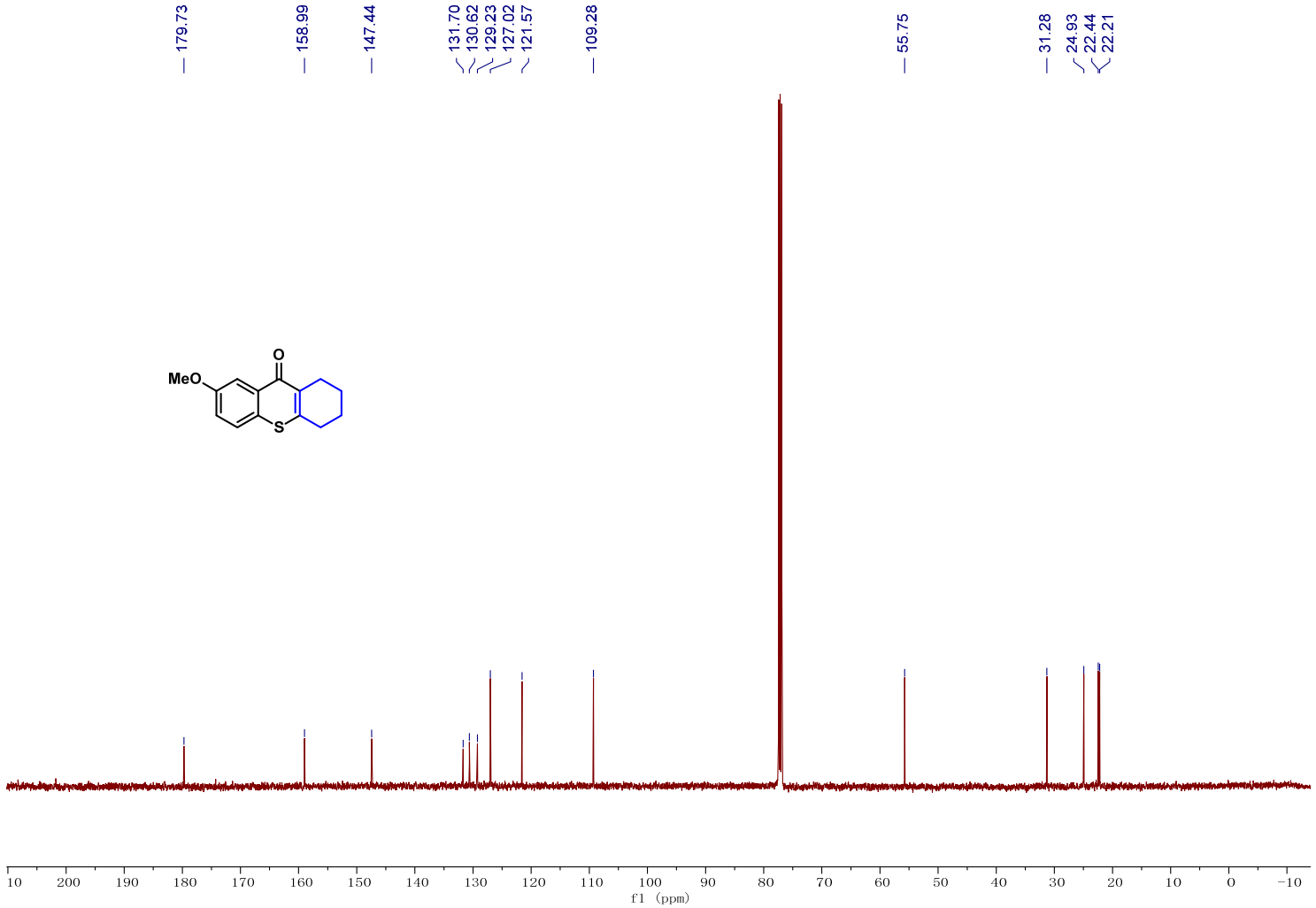
Compound 54 ^{13}C NMR



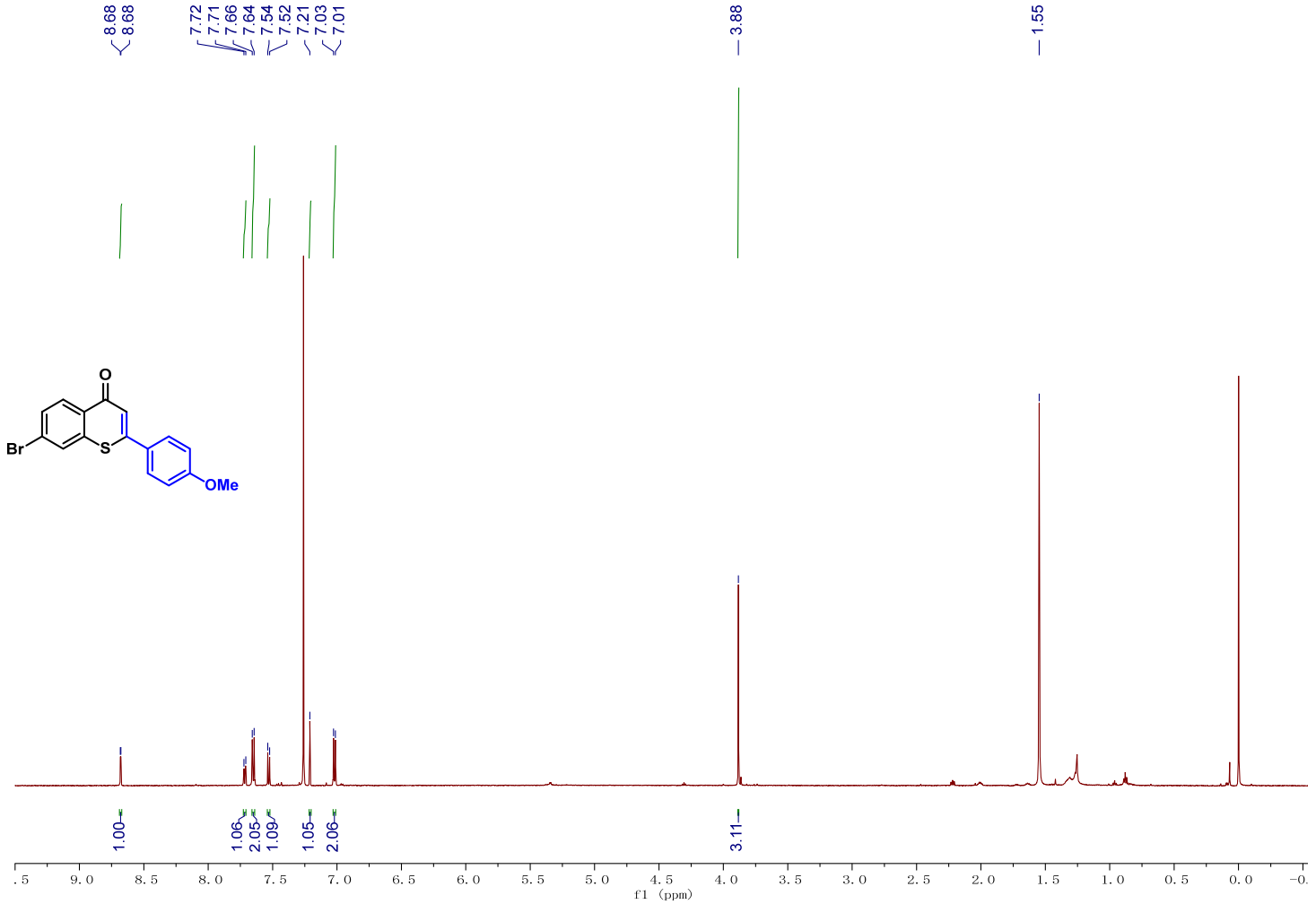
Compound 55 ^{1}H NMR



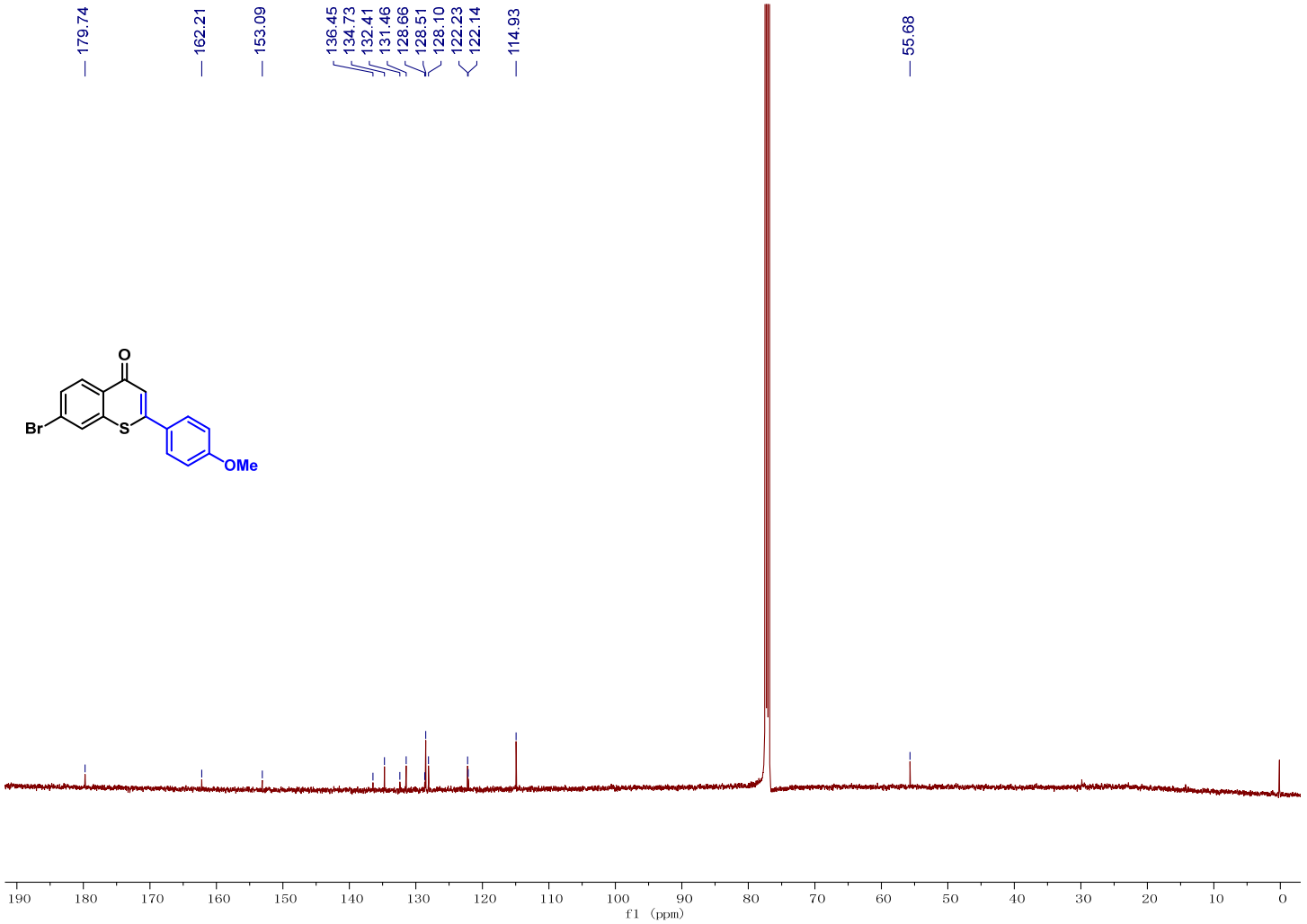
Compound 55 ^{13}C NMR



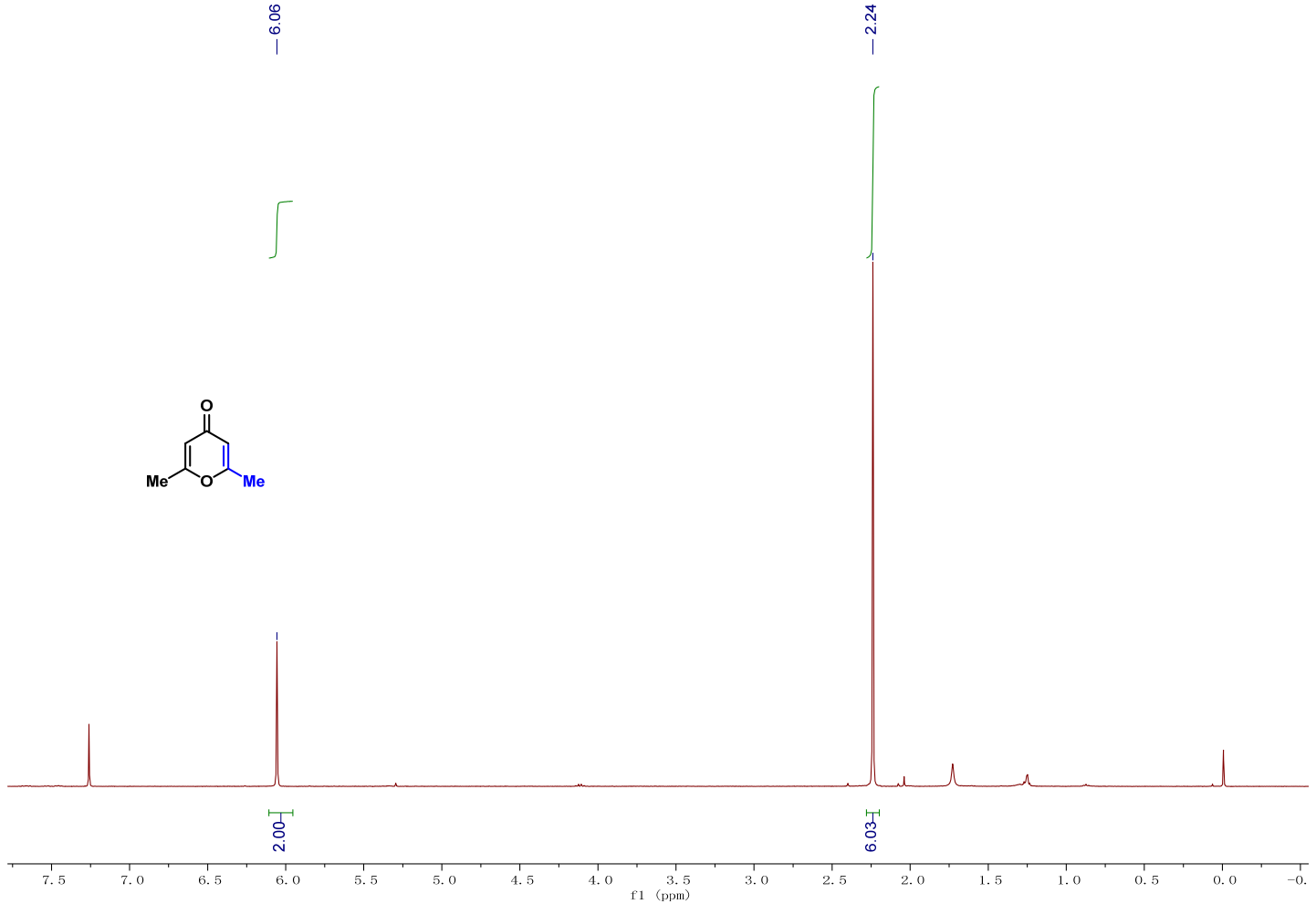
Compound 56 ^{1}H NMR



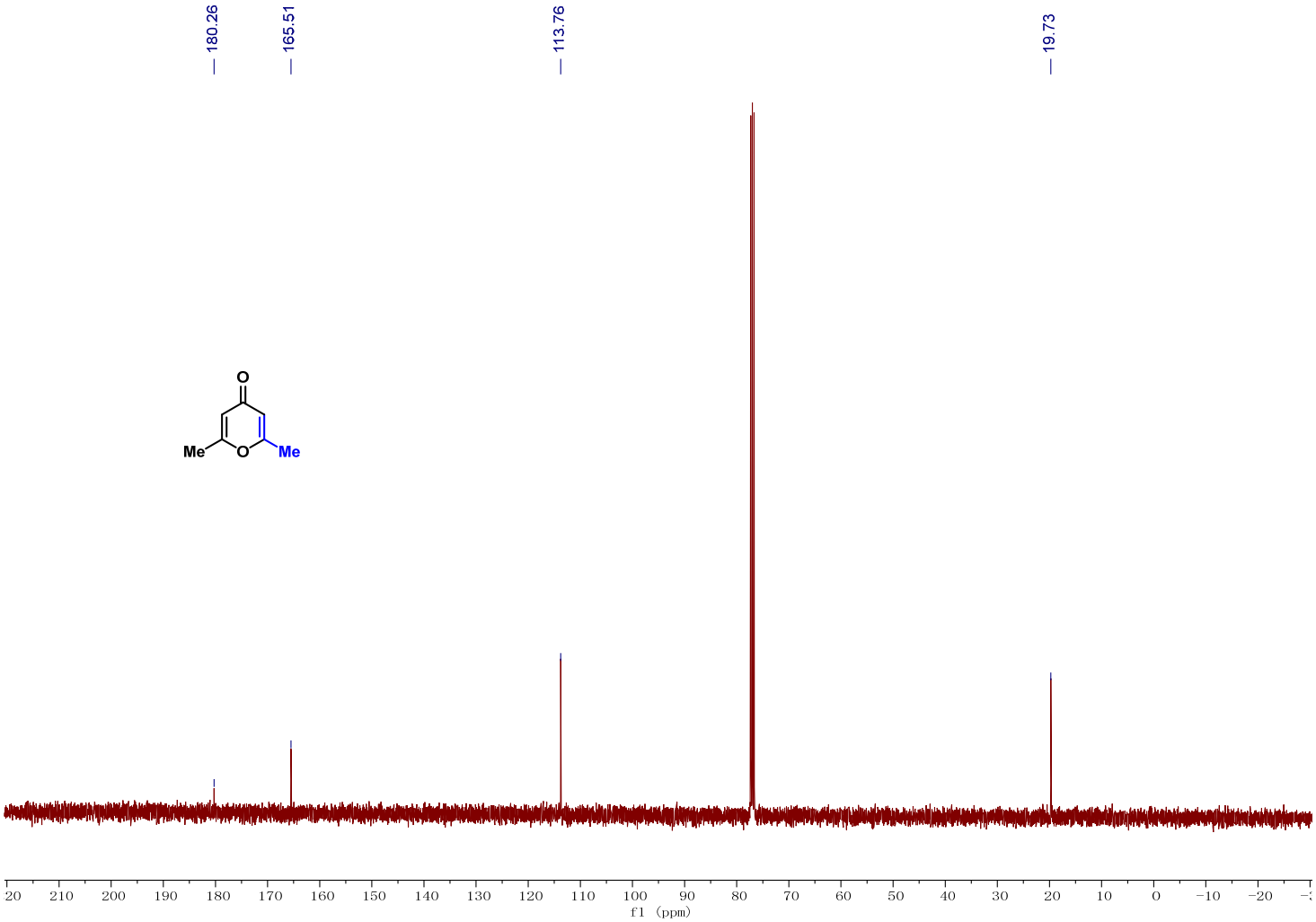
Compound 56 ^{13}C NMR



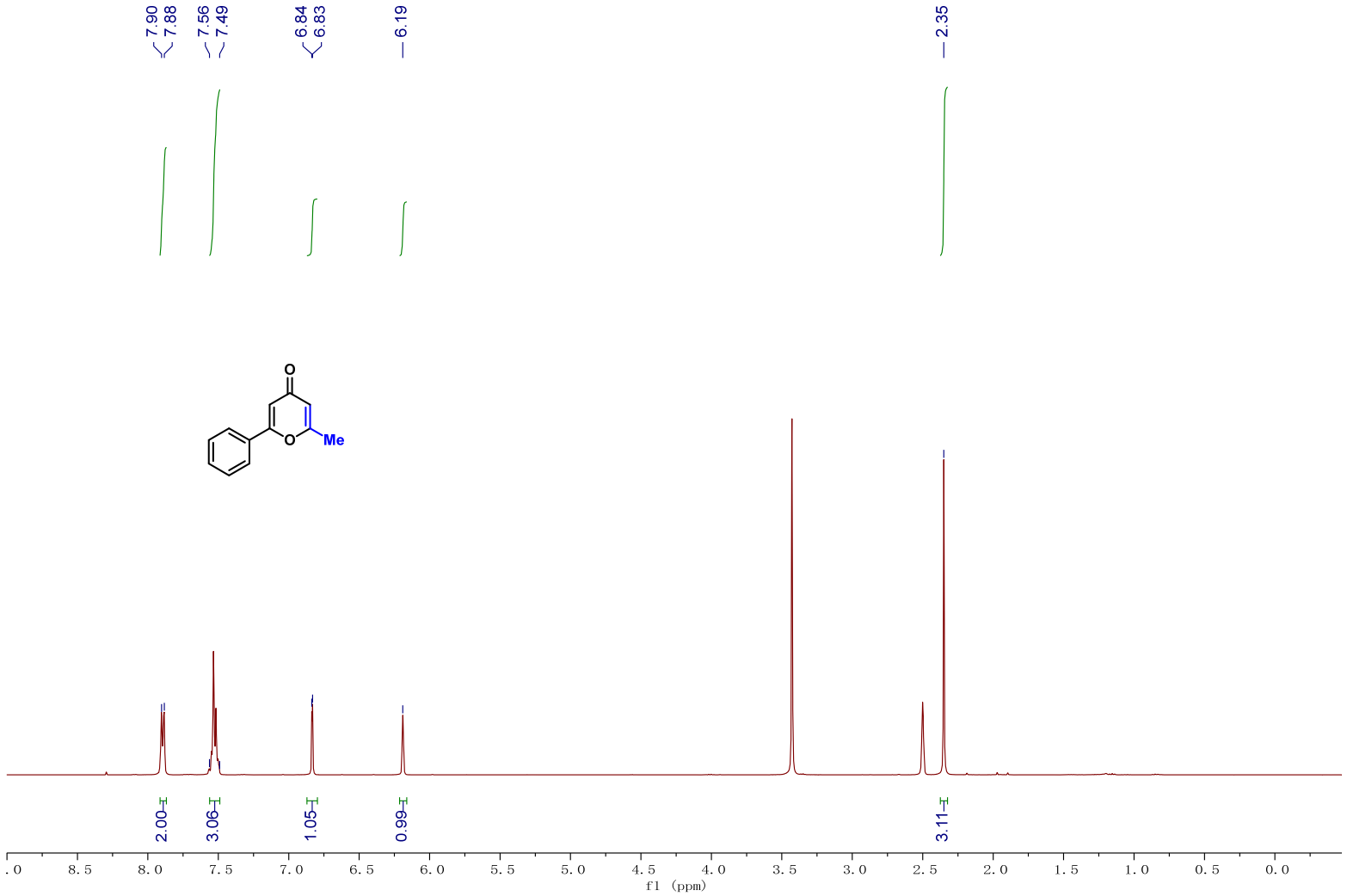
Compound 57 ^{1}H NMR



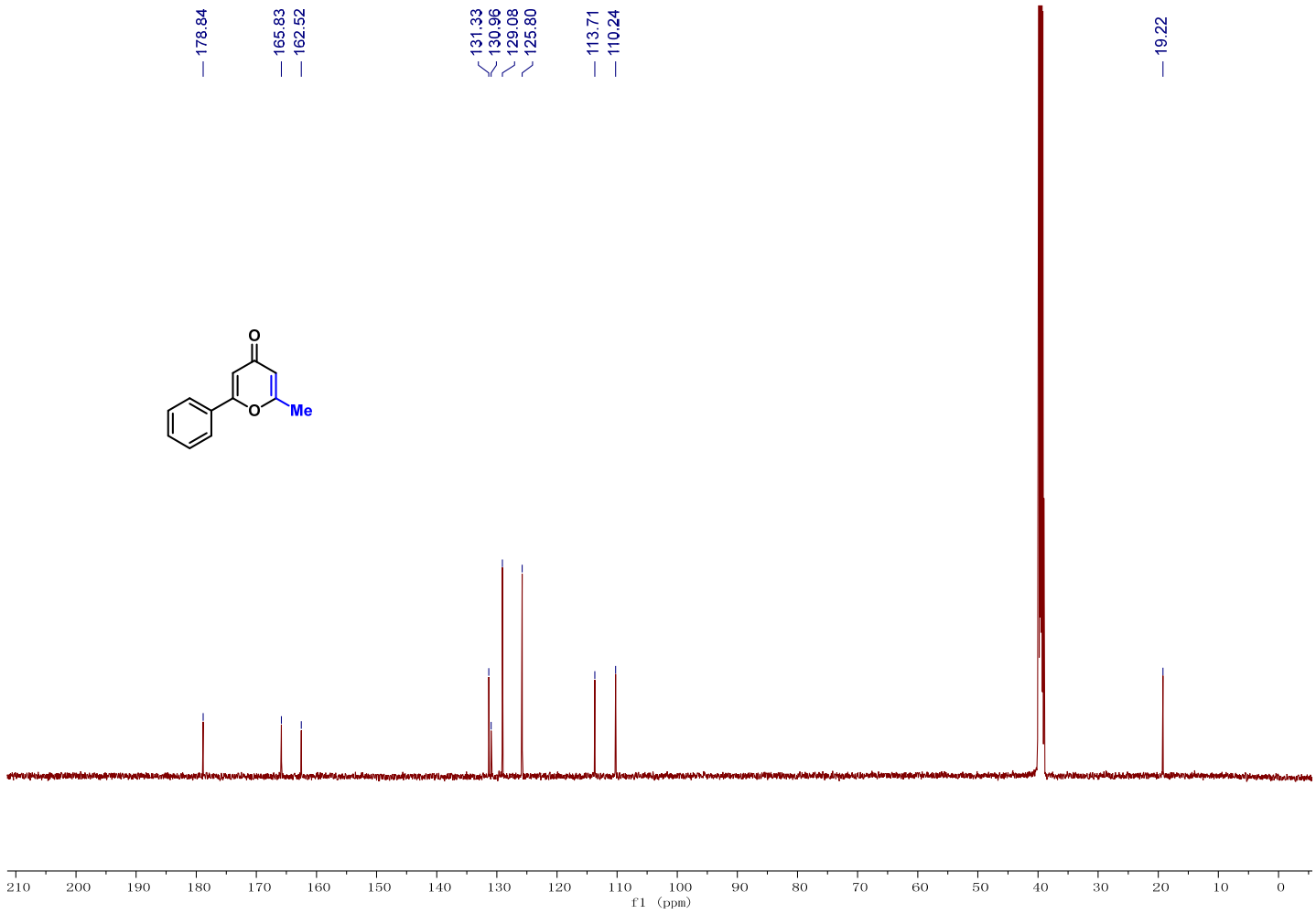
Compound 57 ^{13}C NMR



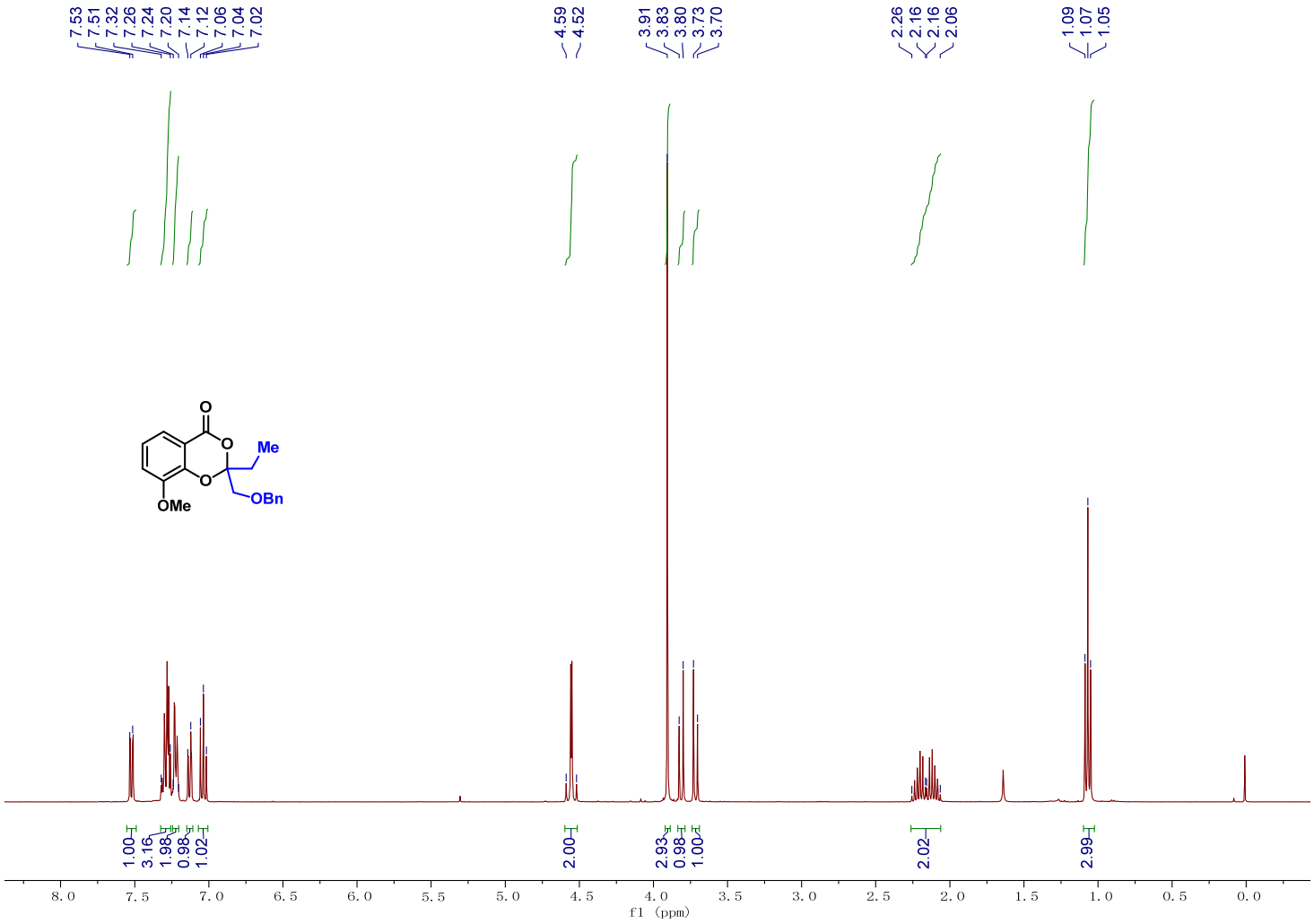
Compound 58 ^{1}H NMR



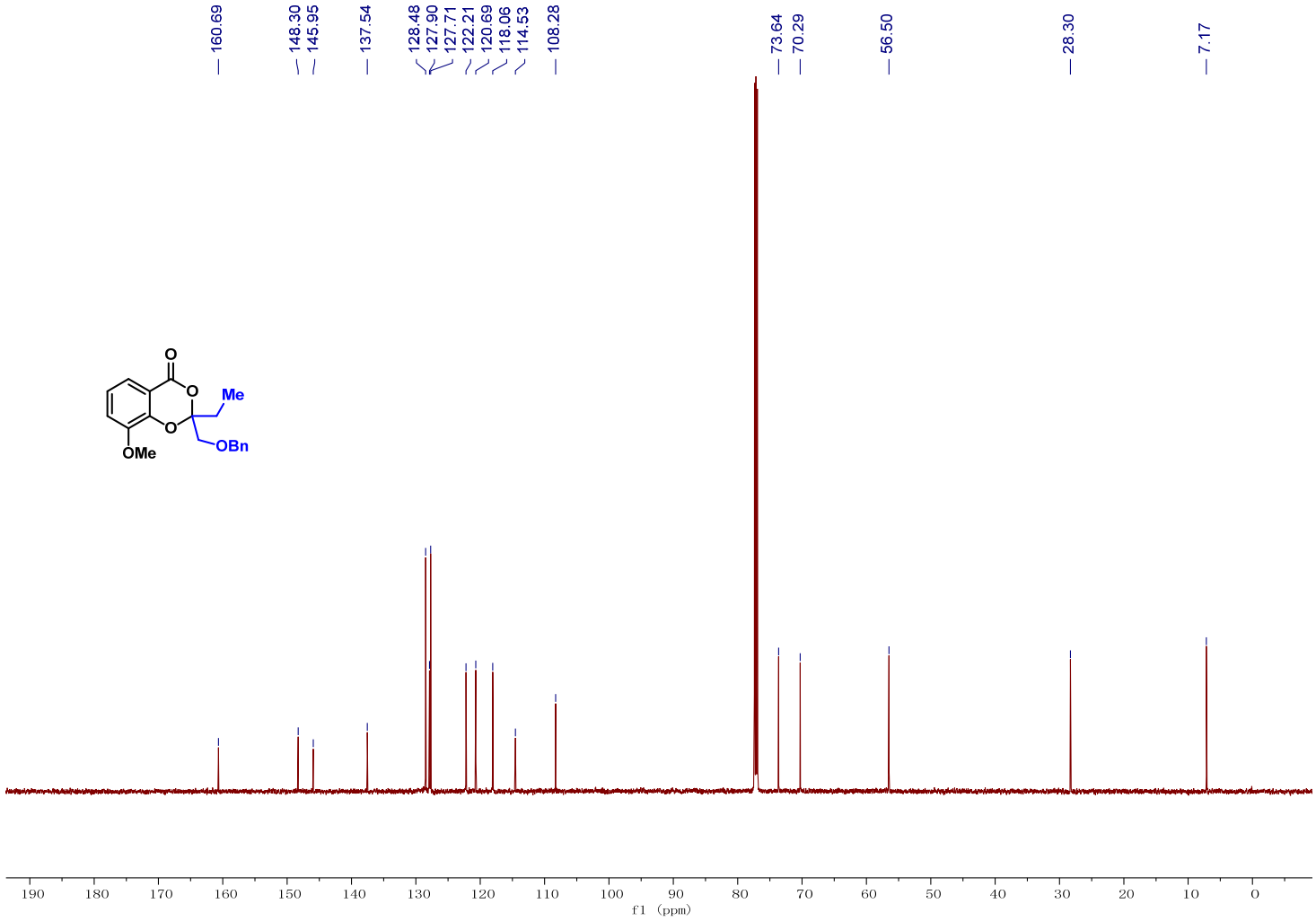
Compound 58 ^{13}C NMR



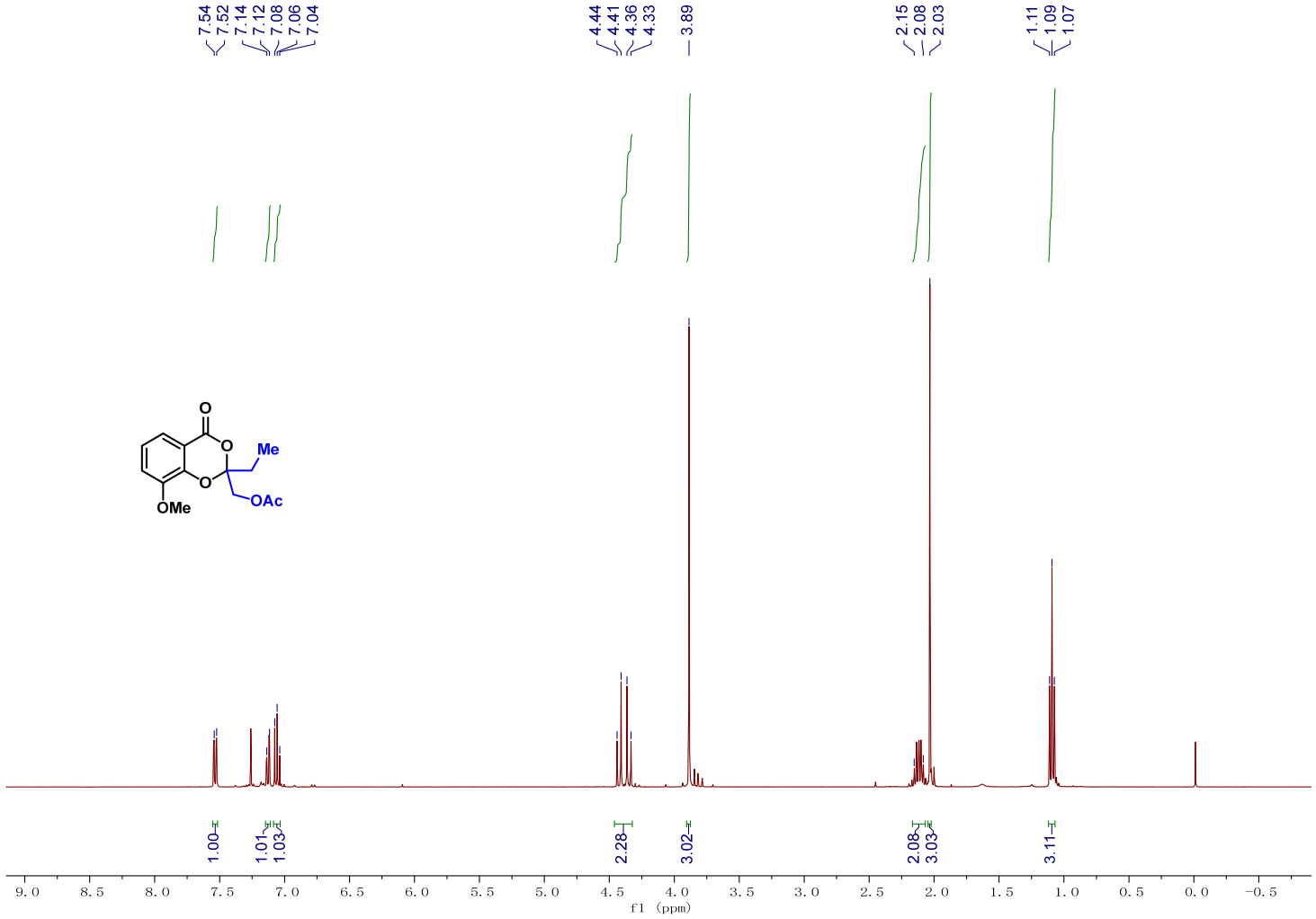
Compound 61 ^{1}H NMR



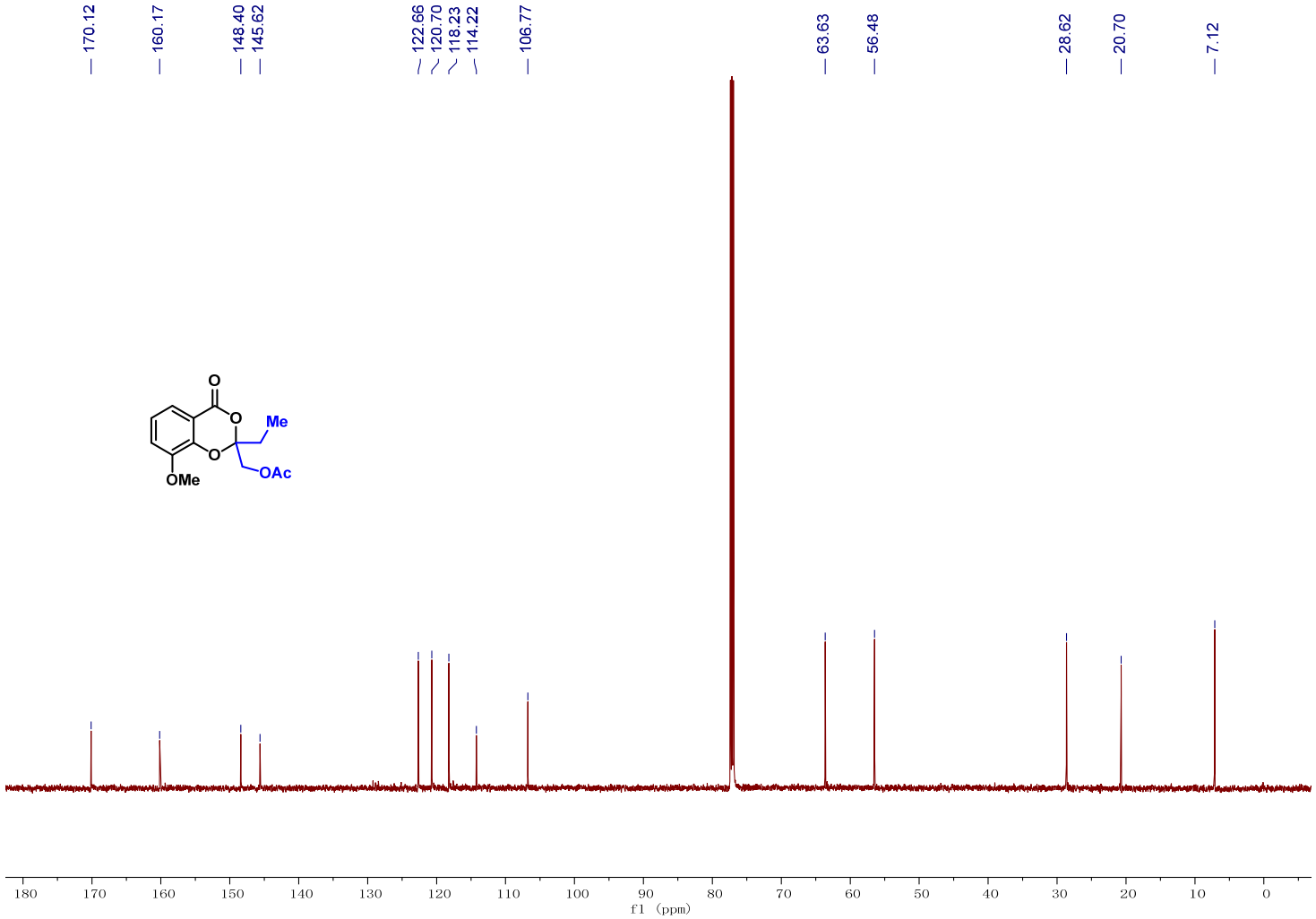
Compound 61 ^{13}C NMR



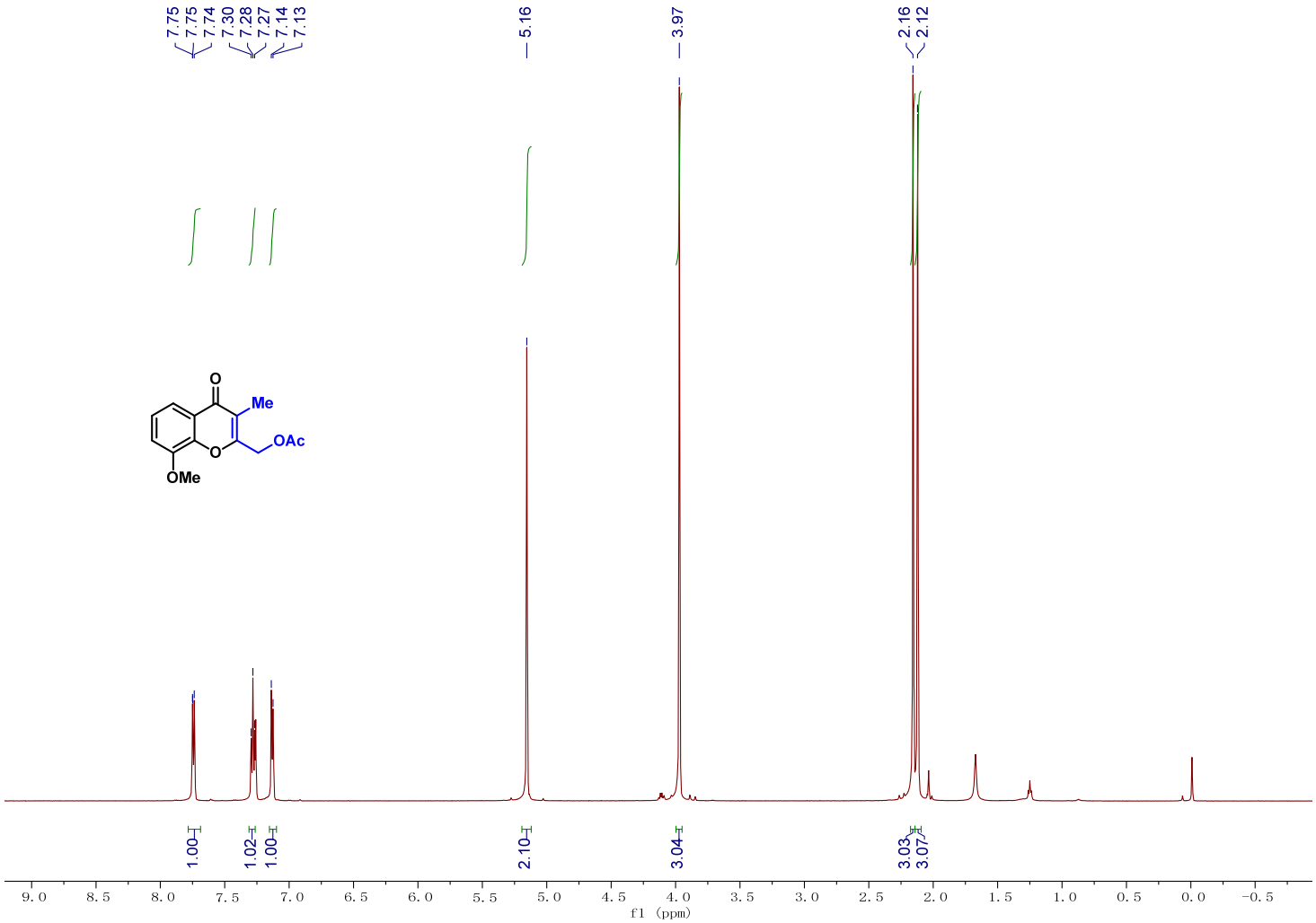
Compound 62 ^{1}H NMR



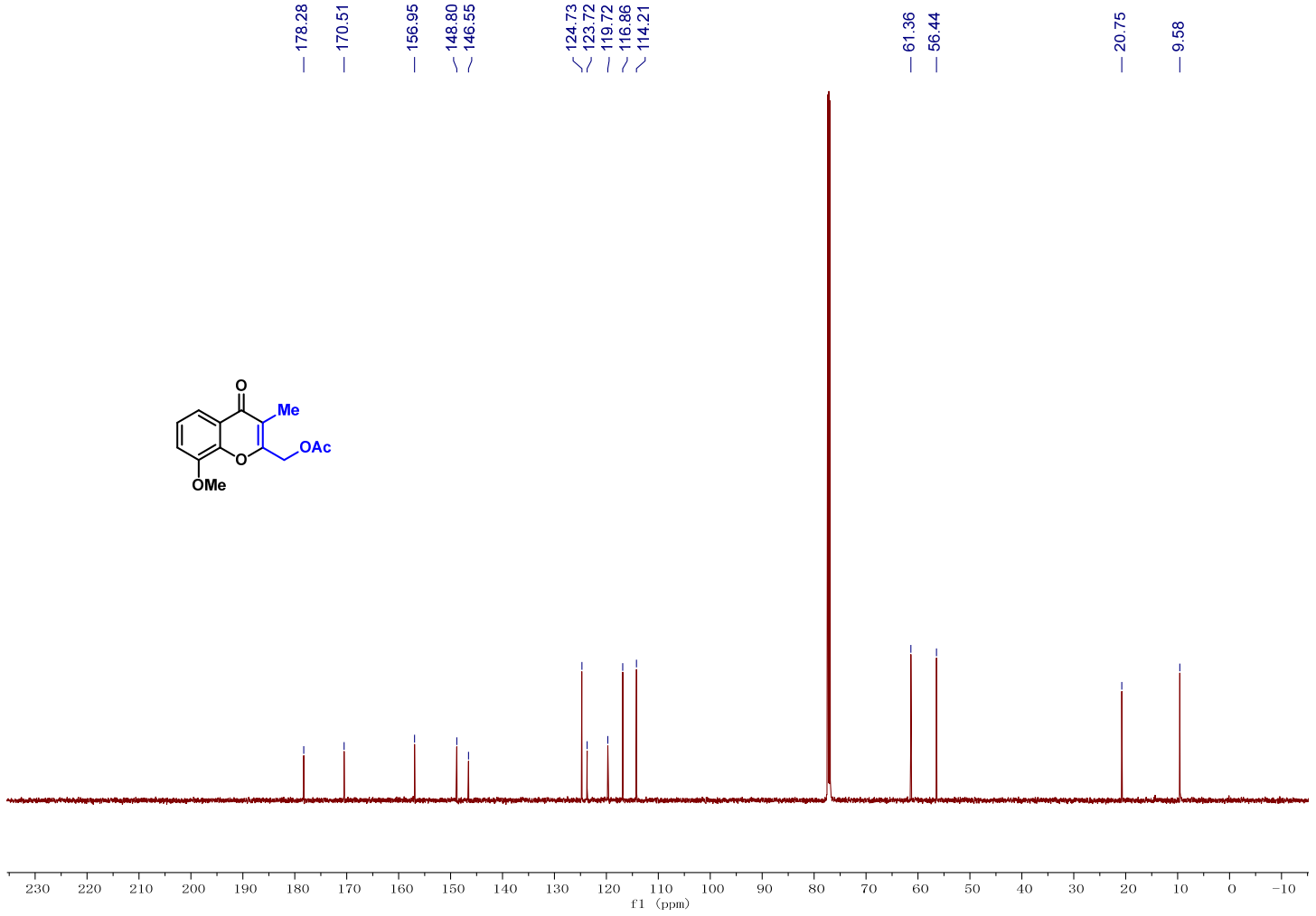
Compound 62 ^{13}C NMR



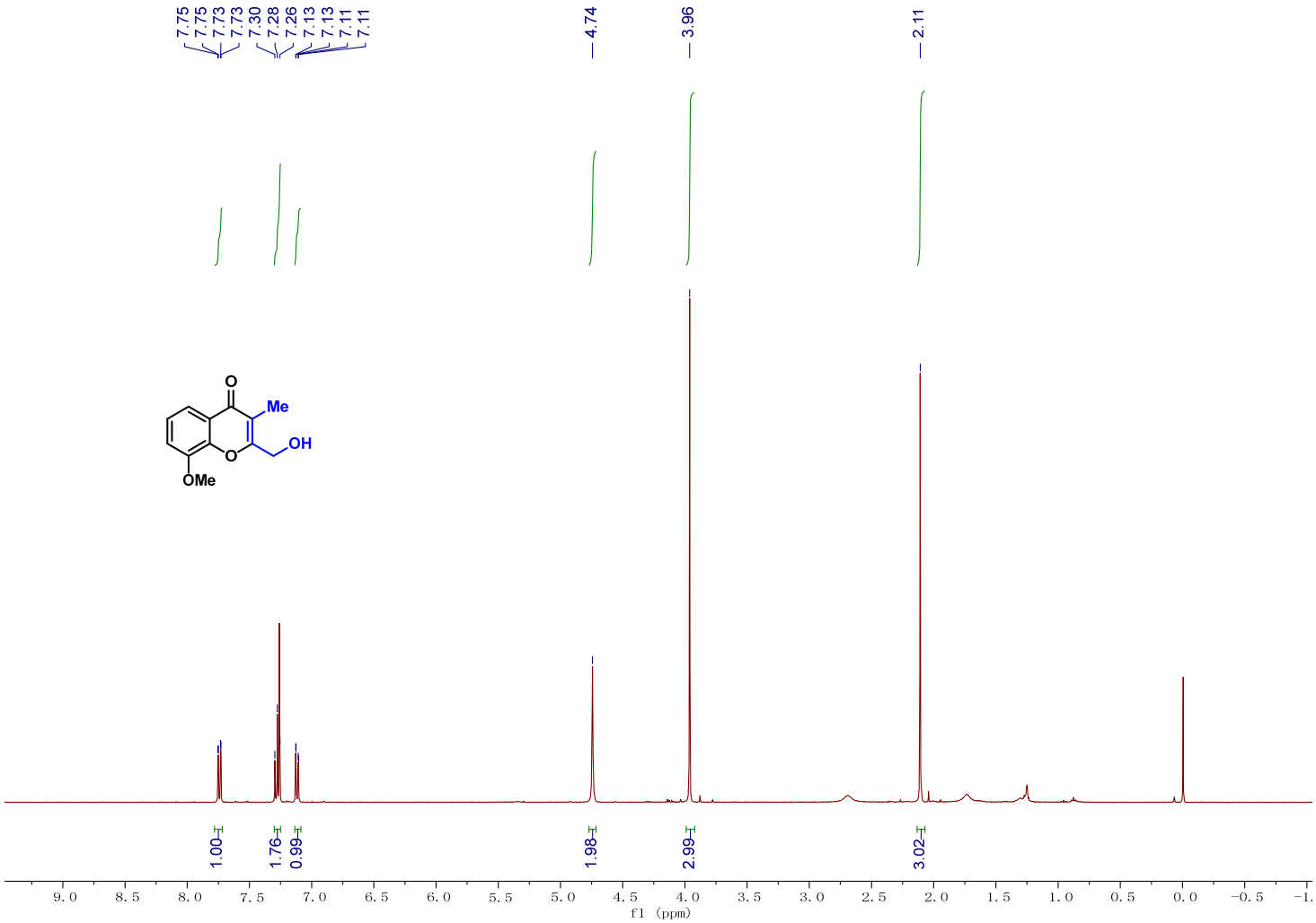
Compound S44 ^{1}H NMR



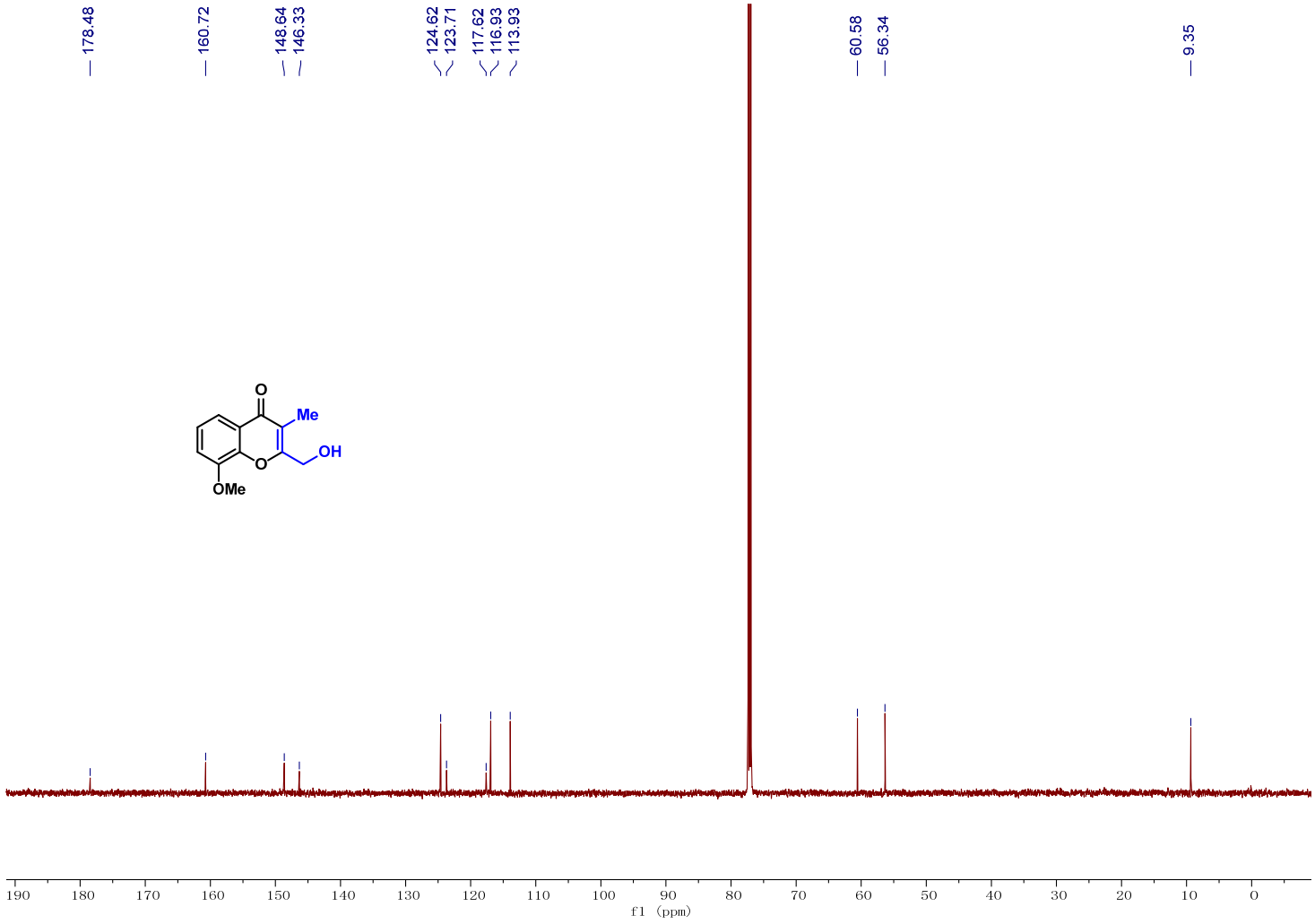
Compound S44 ^{13}C NMR



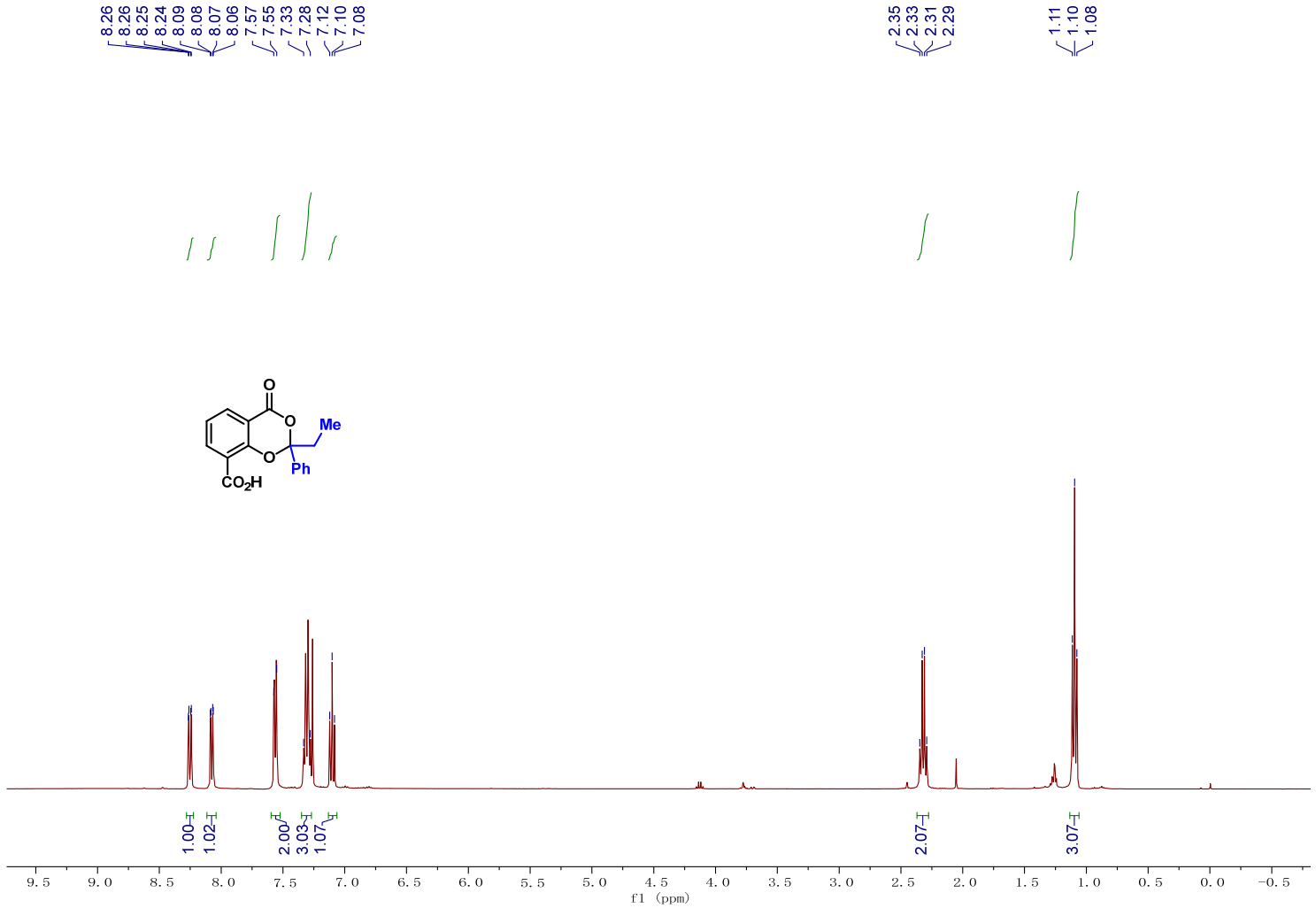
Compound 63 ^{1}H NMR



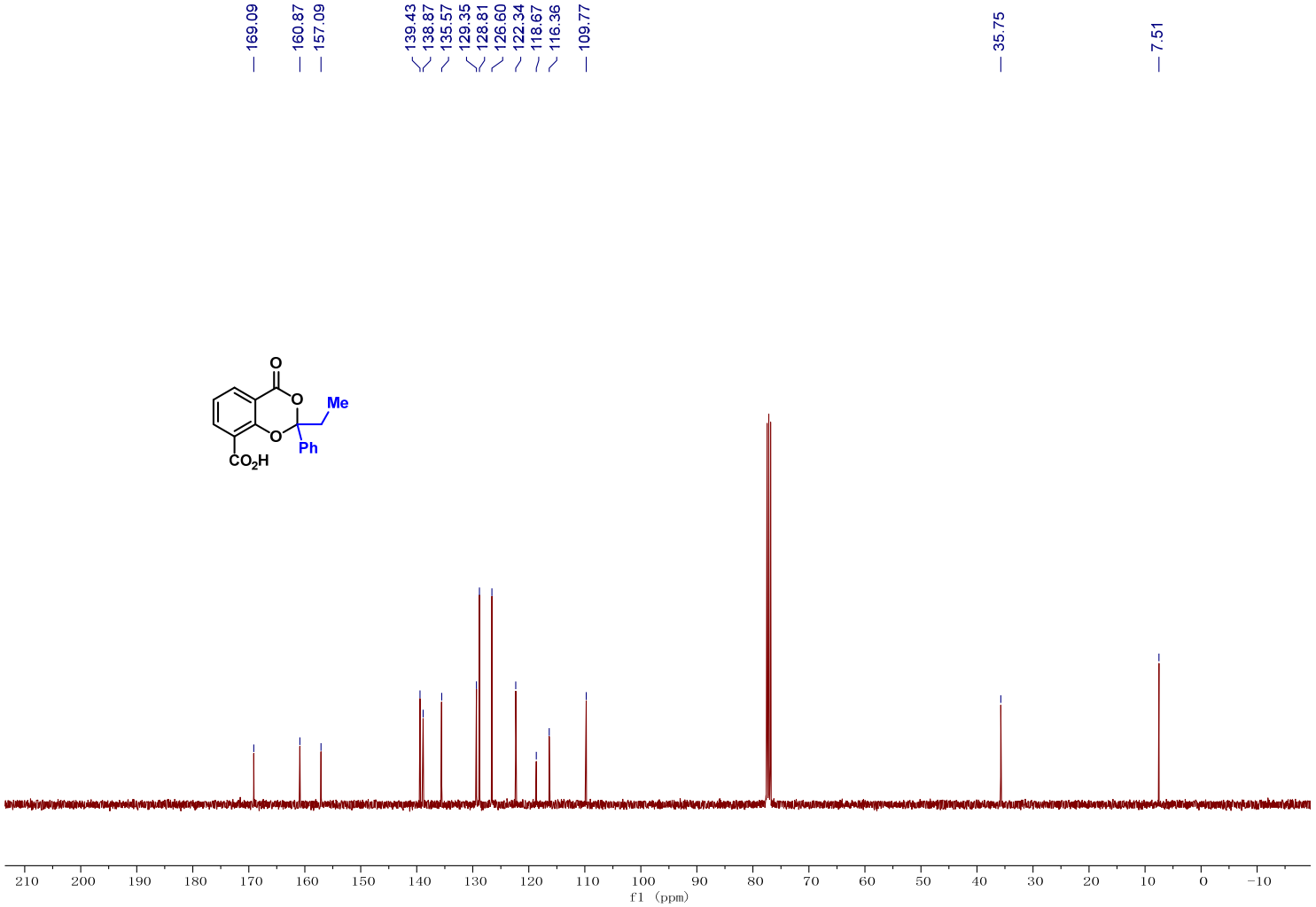
Compound 63 ^{13}C NMR



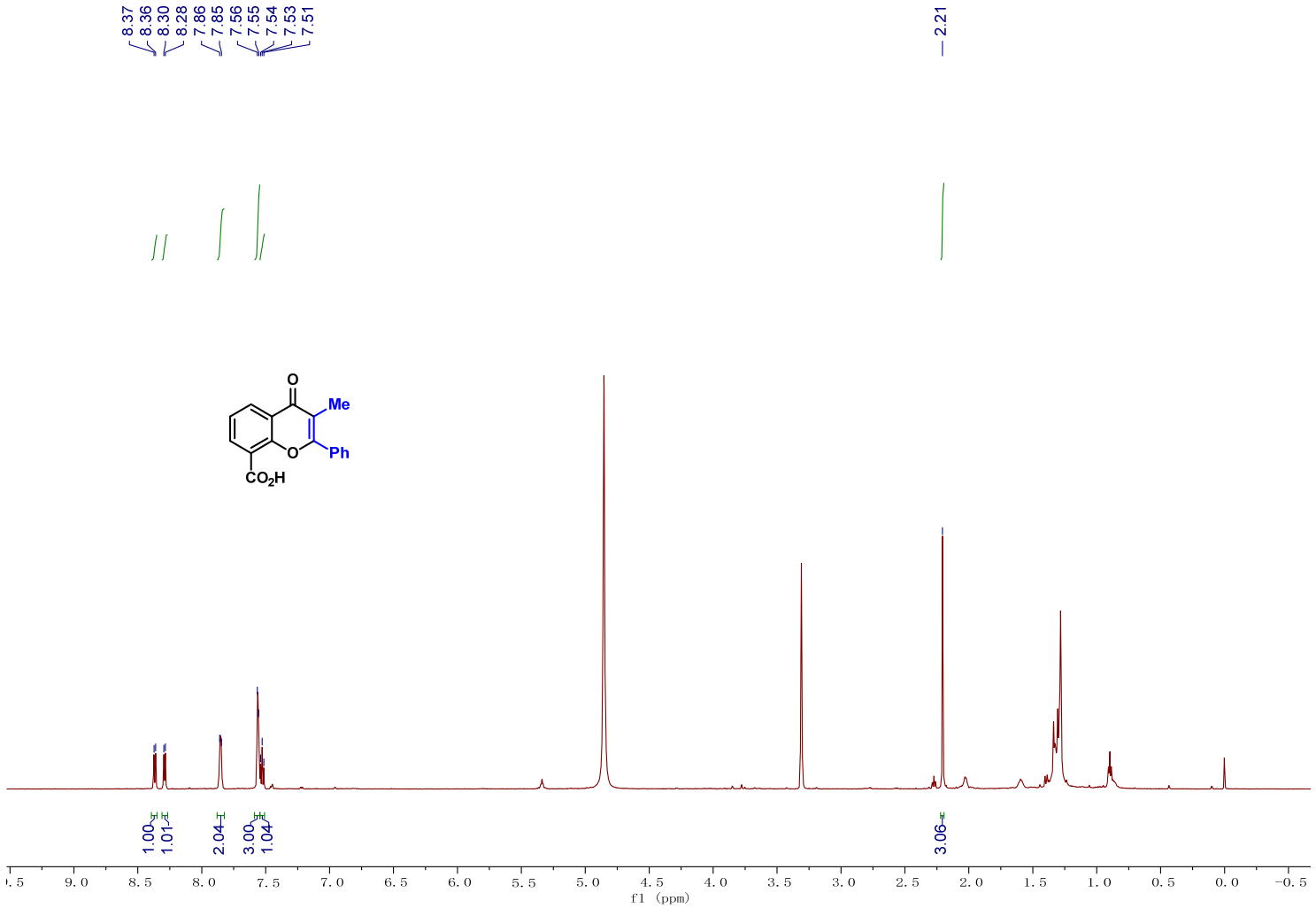
Compound S45 ^{1}H NMR



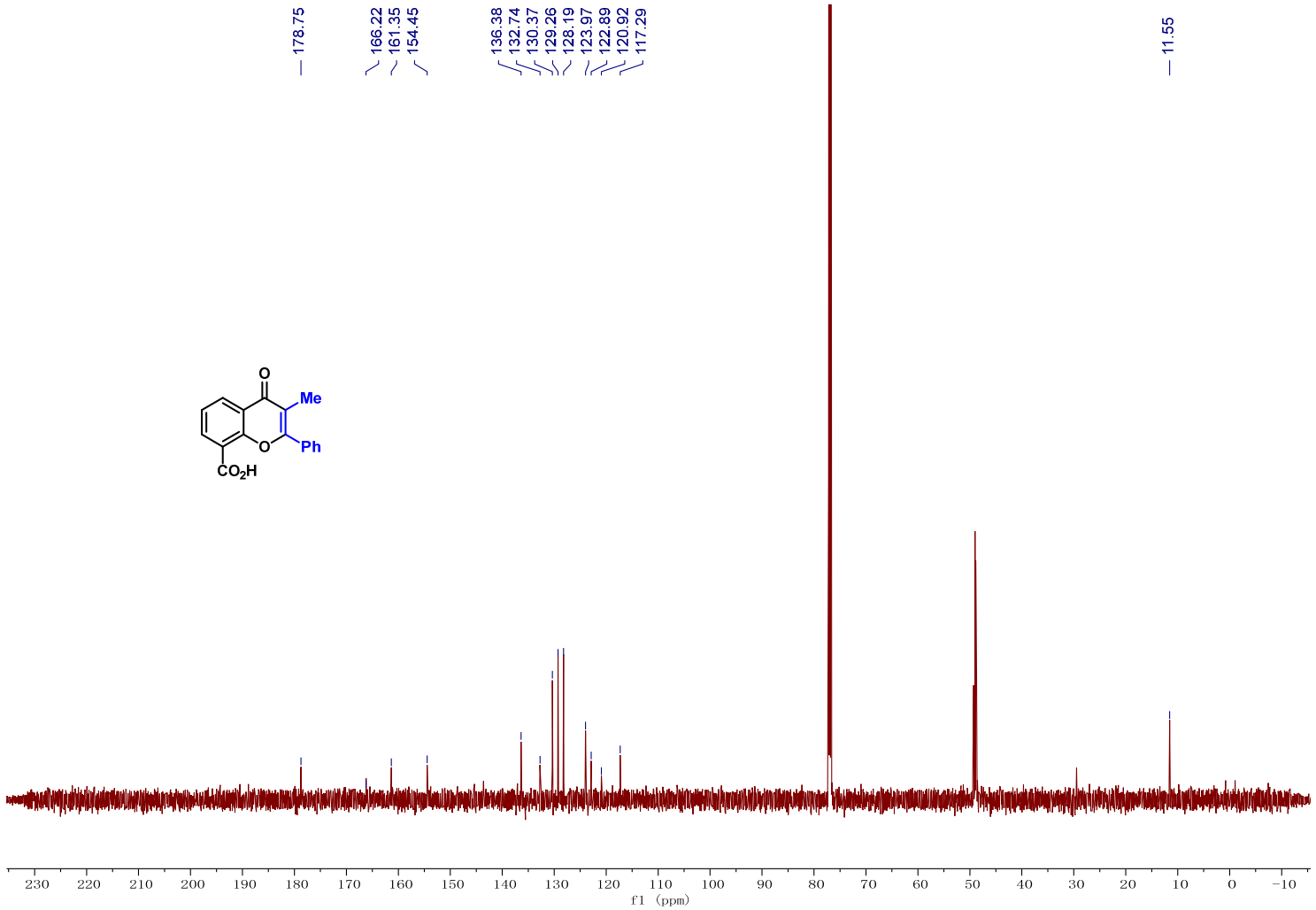
Compound S45 ^{13}C NMR



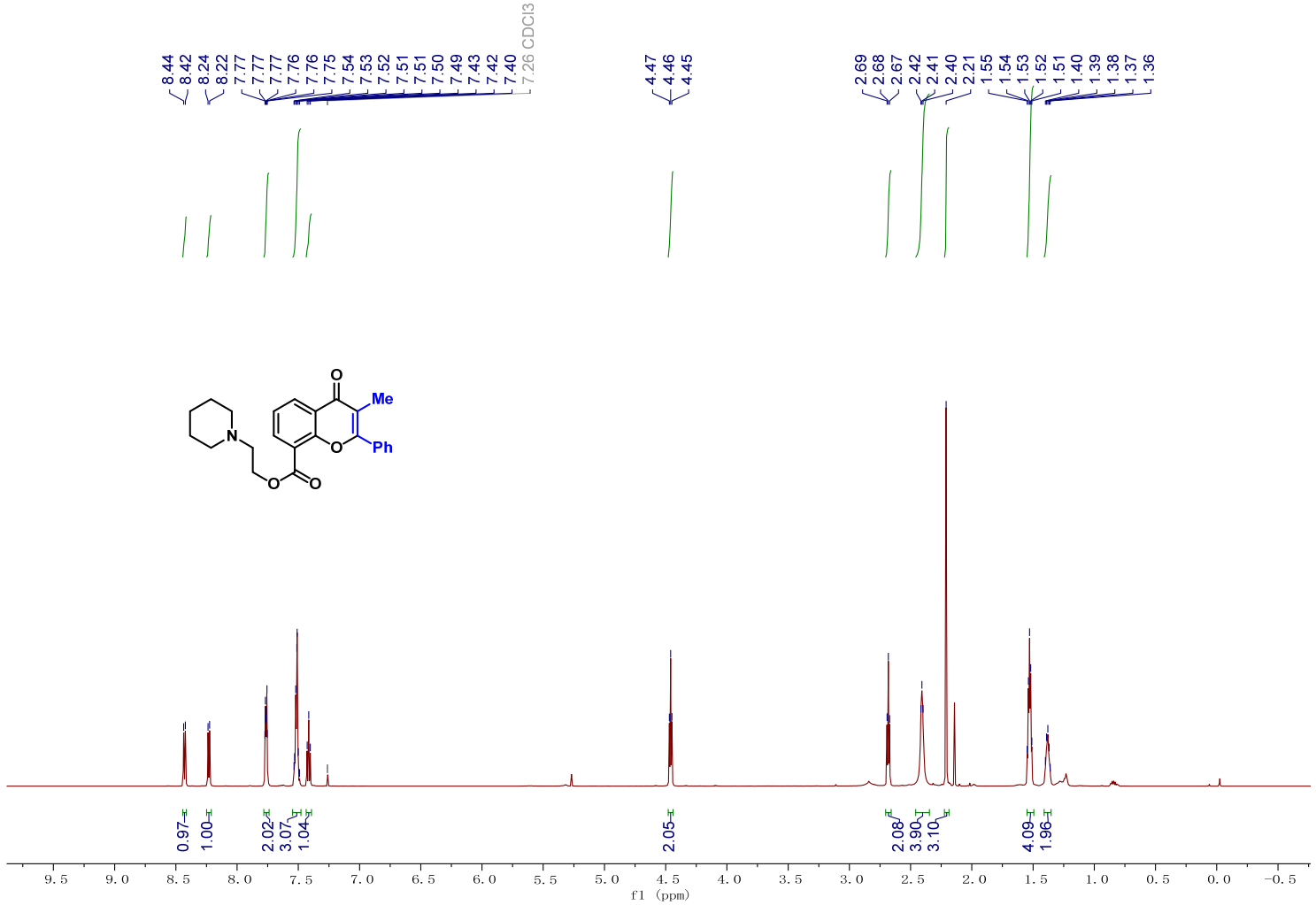
Compound 66 ^{1}H NMR



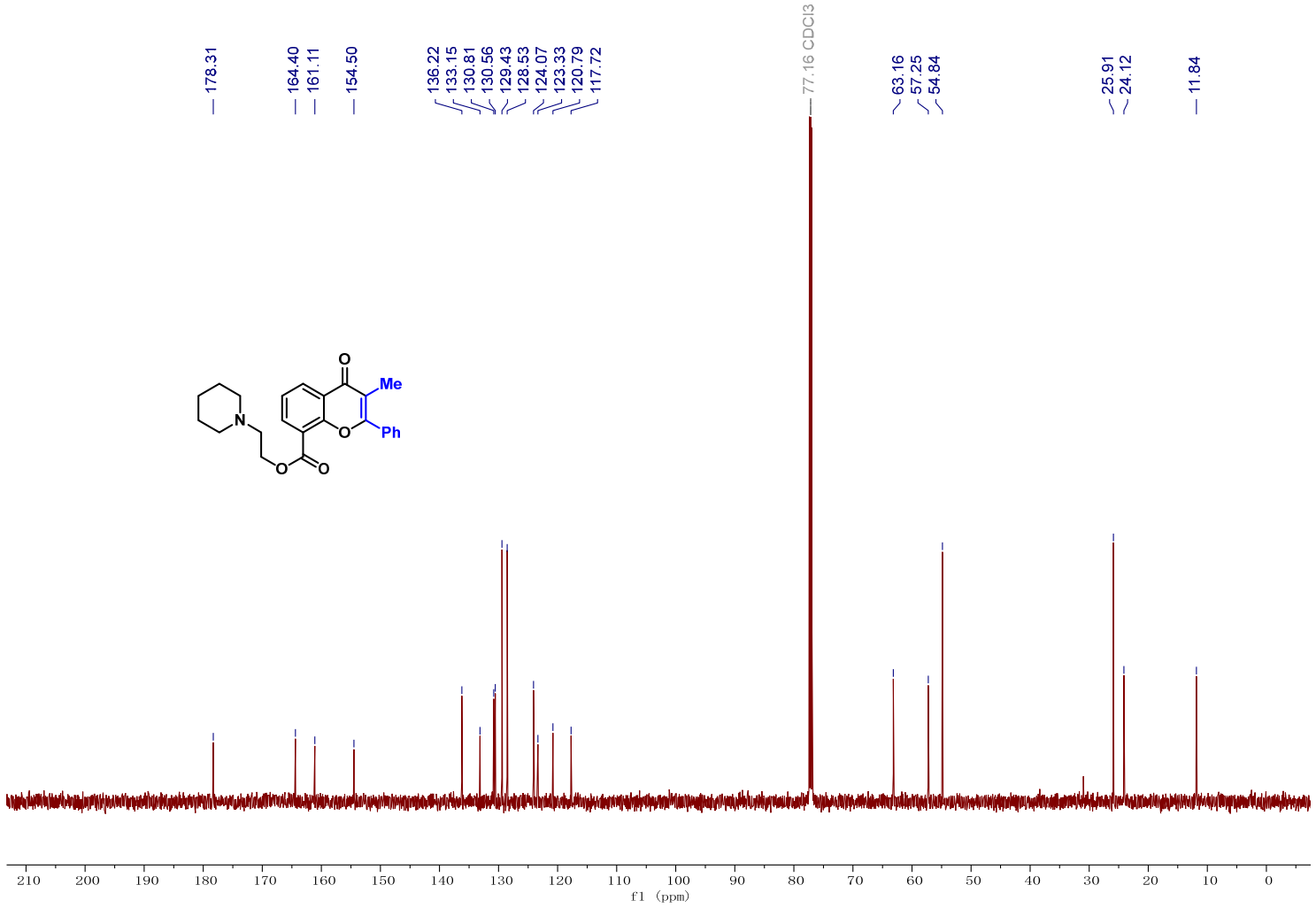
Compound 66 ^{13}C NMR



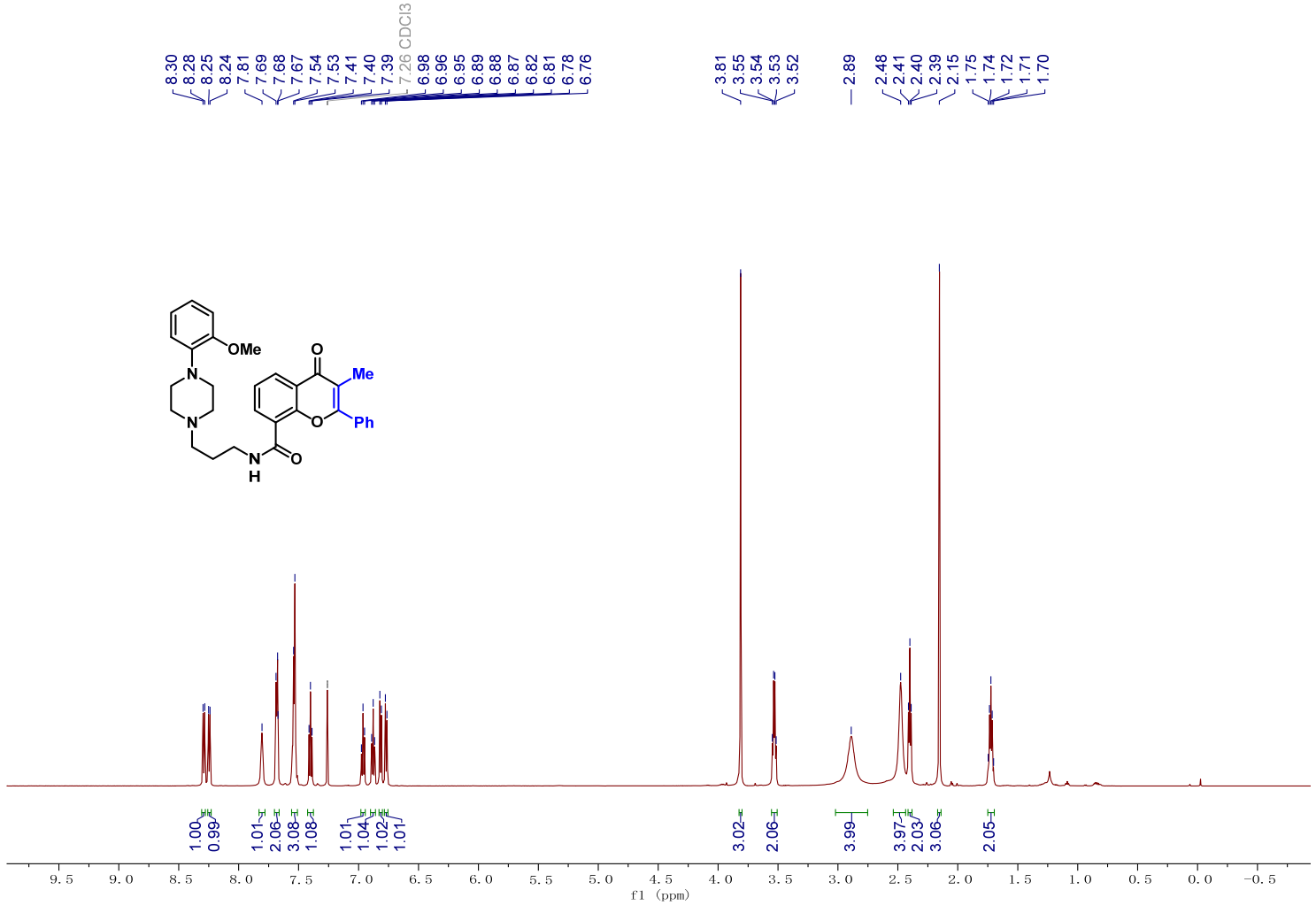
Compound 67 ^{1}H NMR



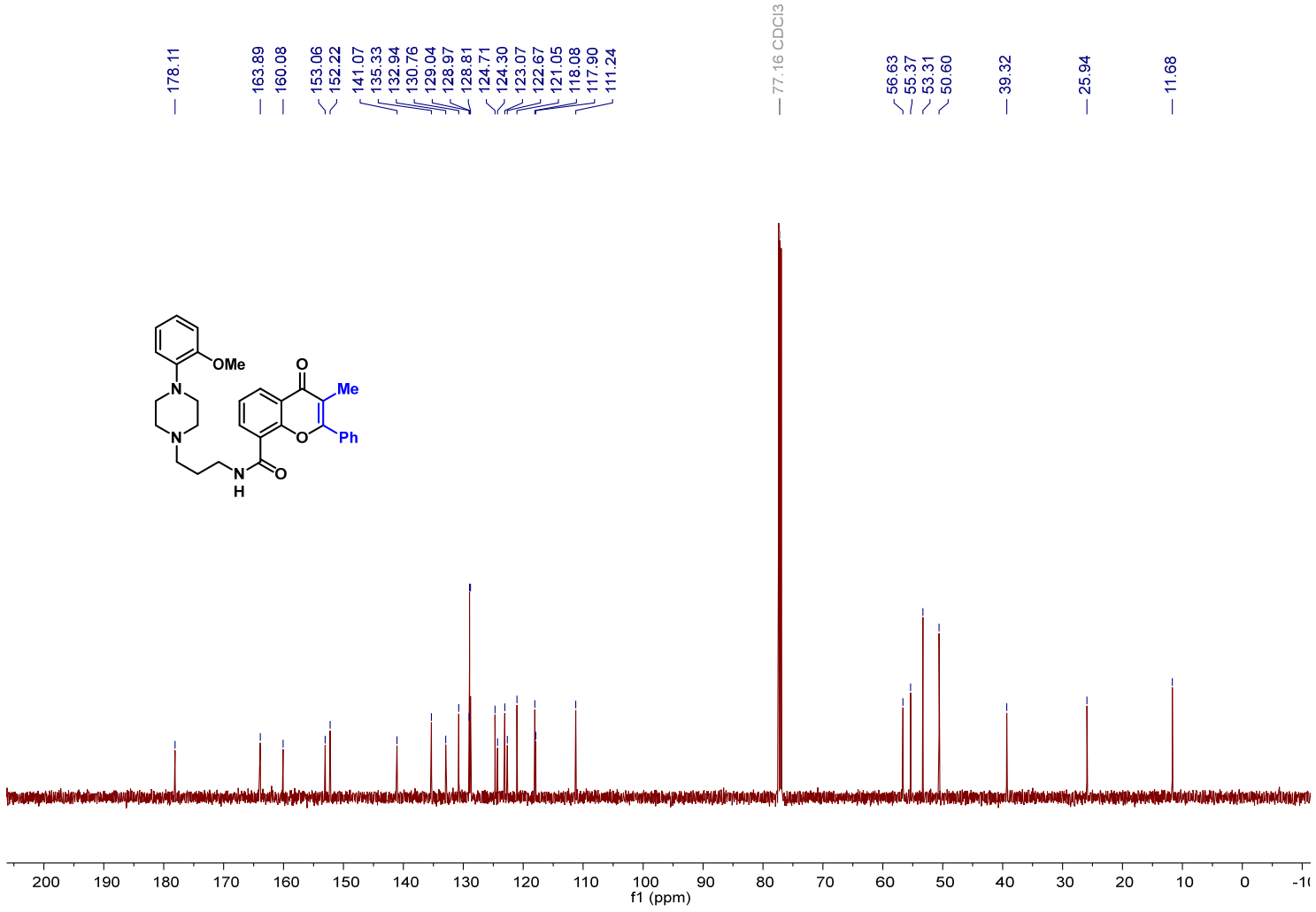
Compound 67 ^{13}C NMR



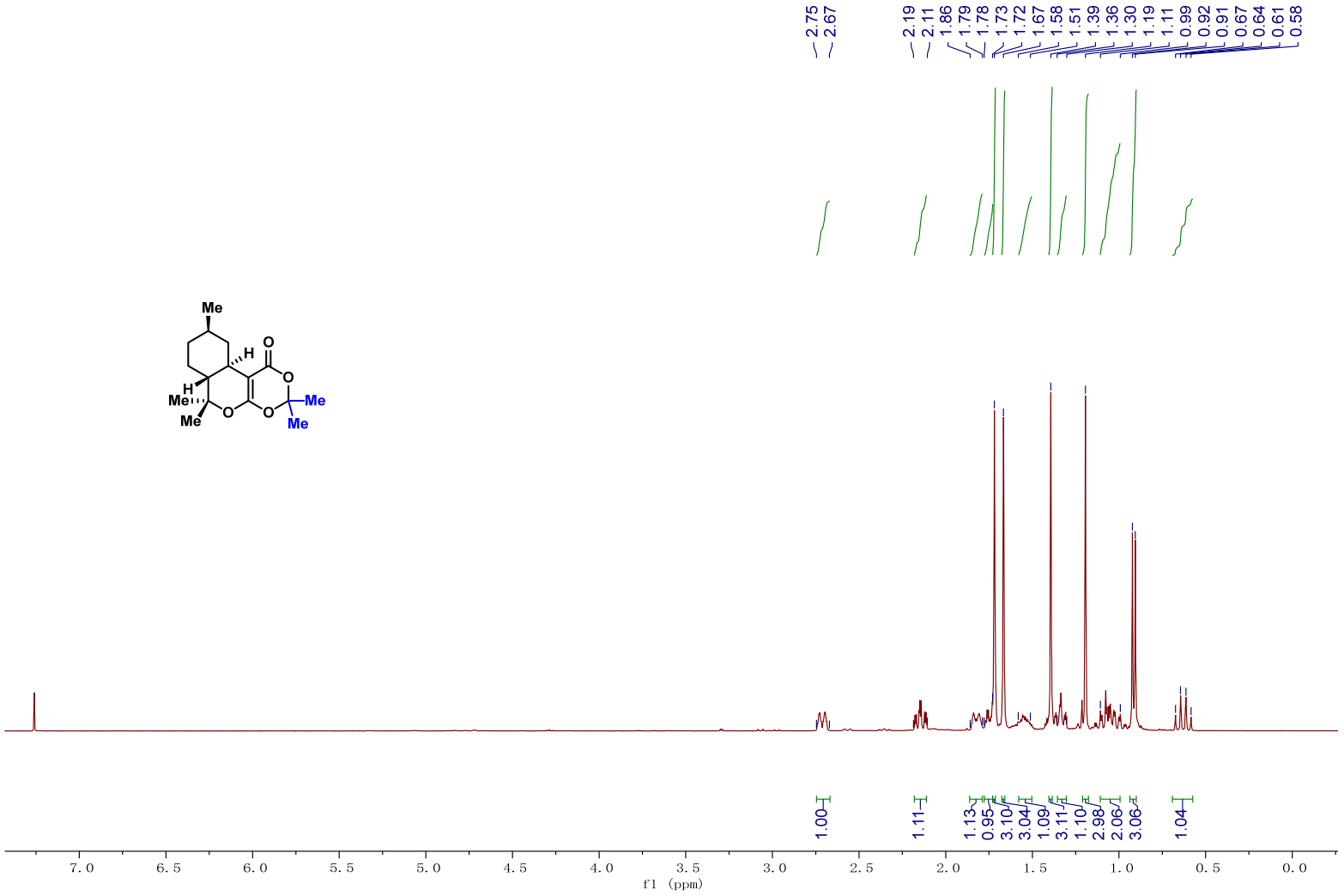
Compound 68 ^{1}H NMR



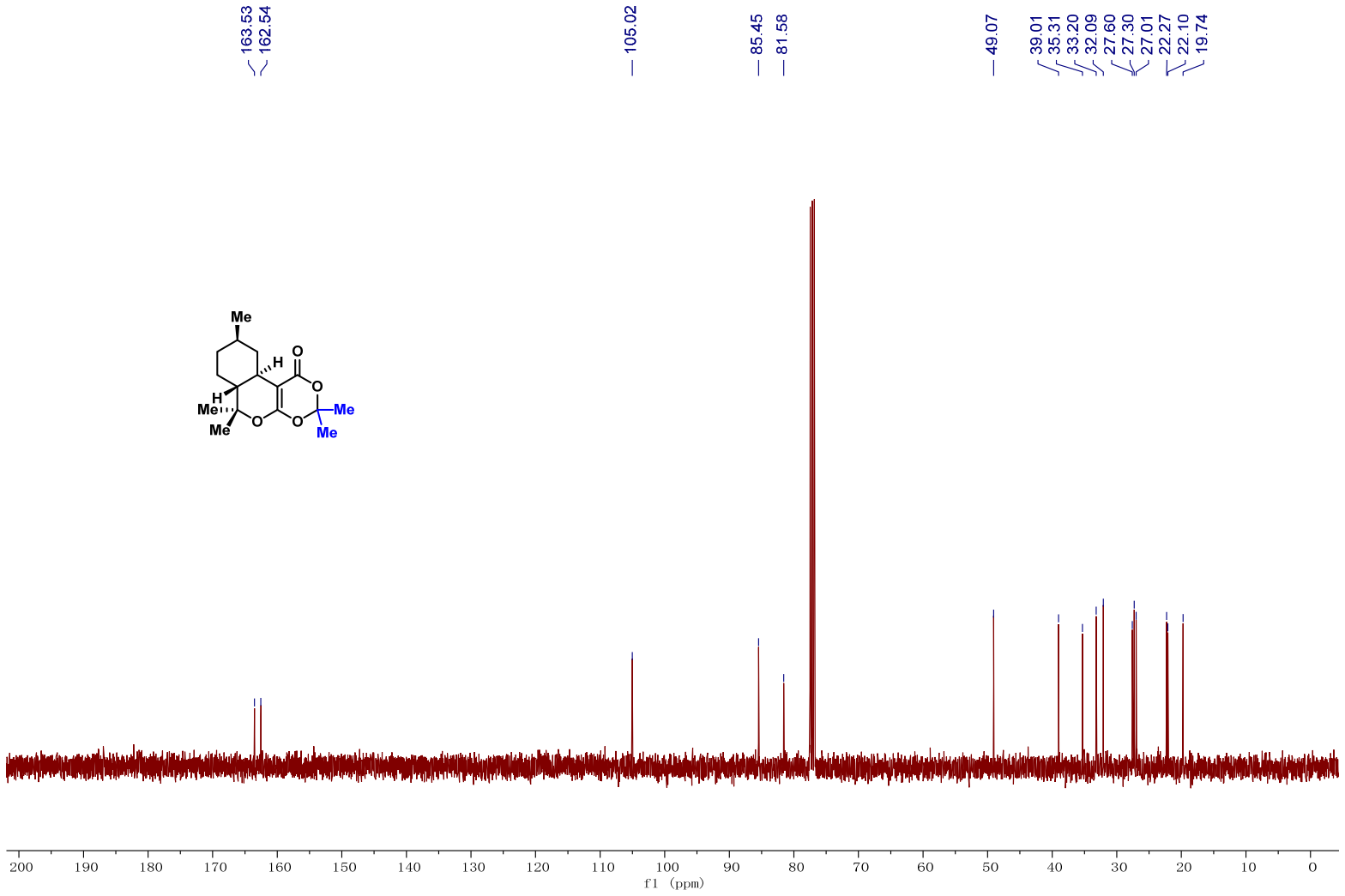
Compound 68 ^{13}C NMR



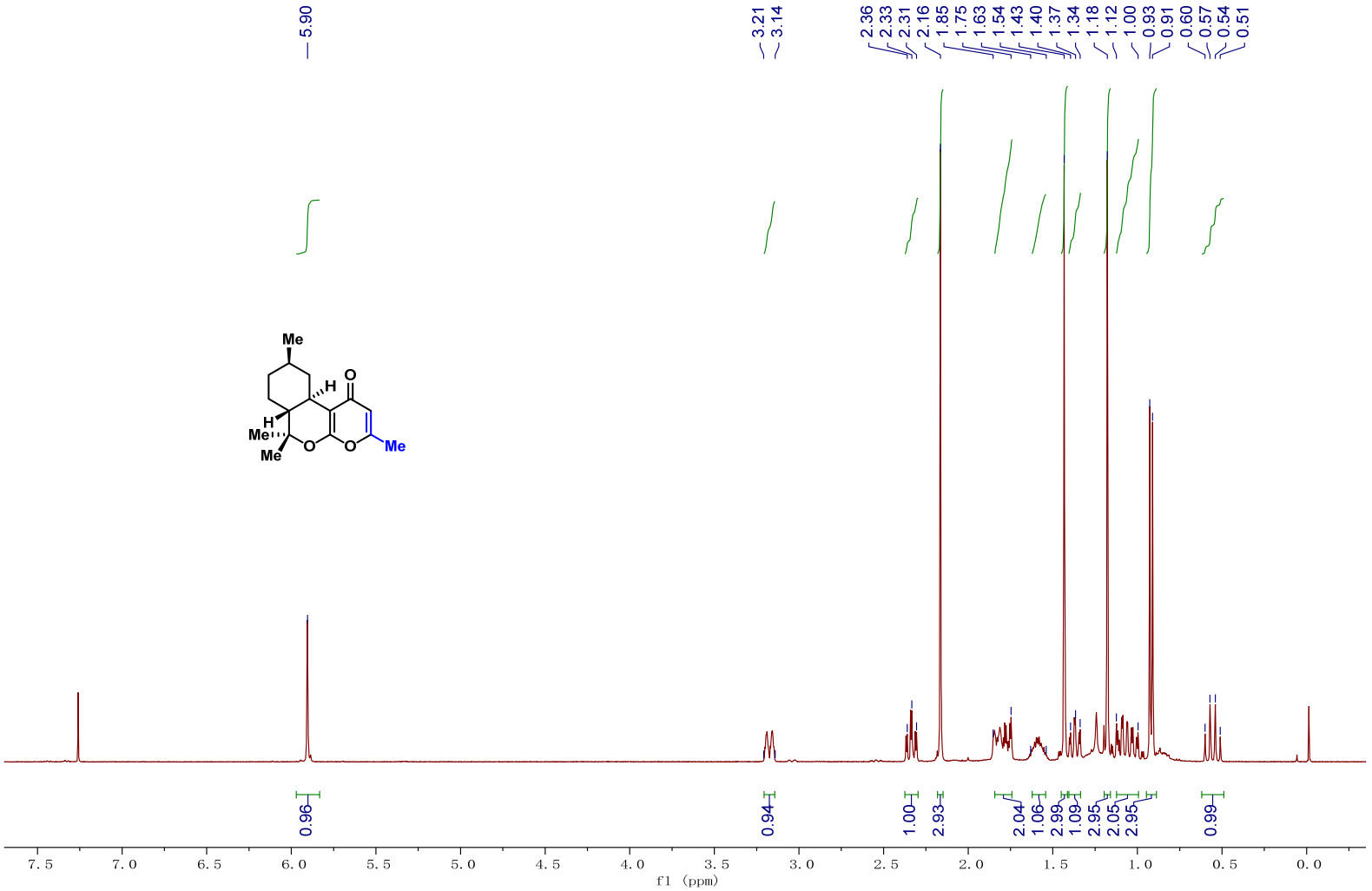
Compound S48 ^{1}H NMR



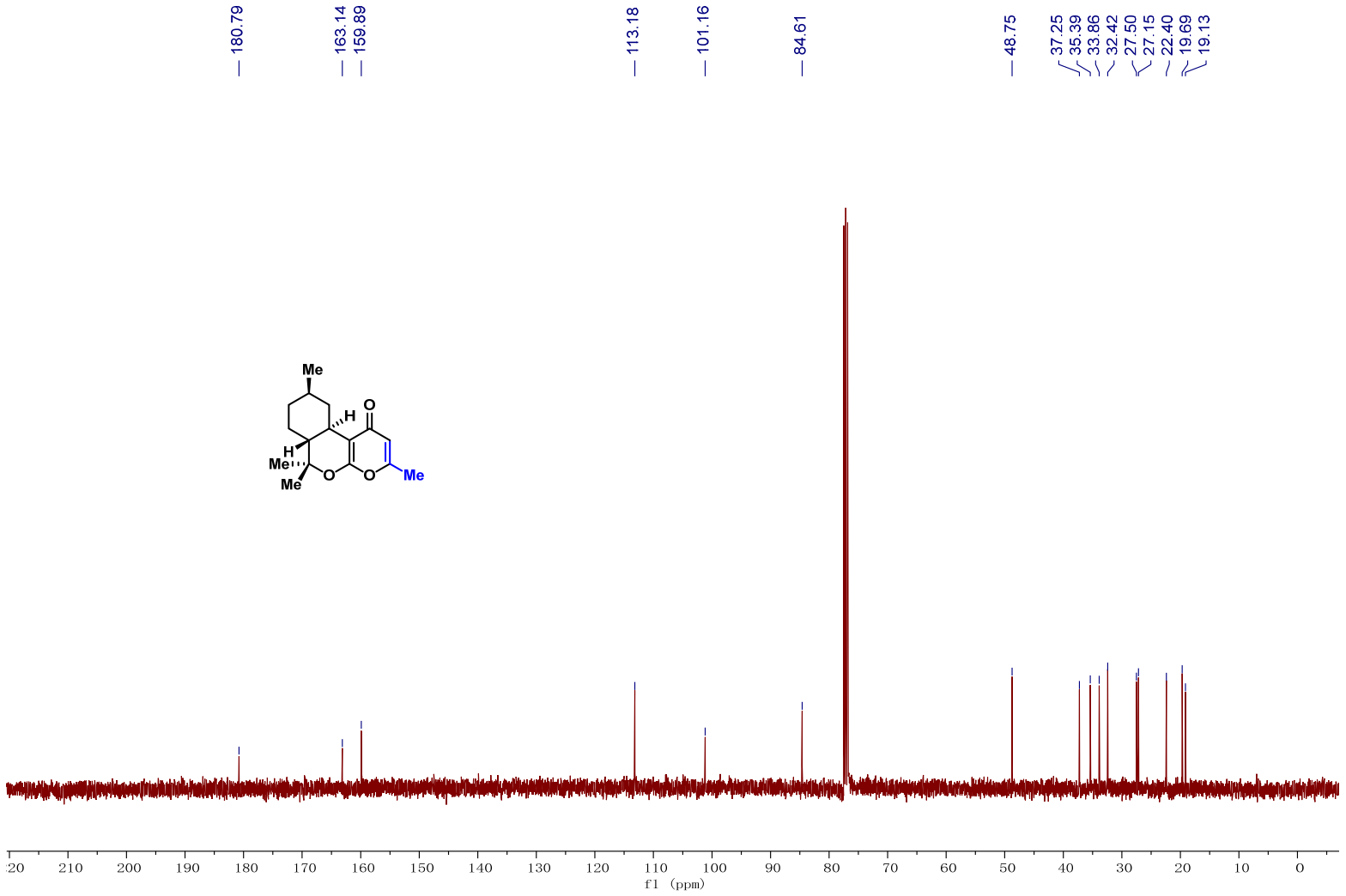
Compound S48 ^{13}C NMR



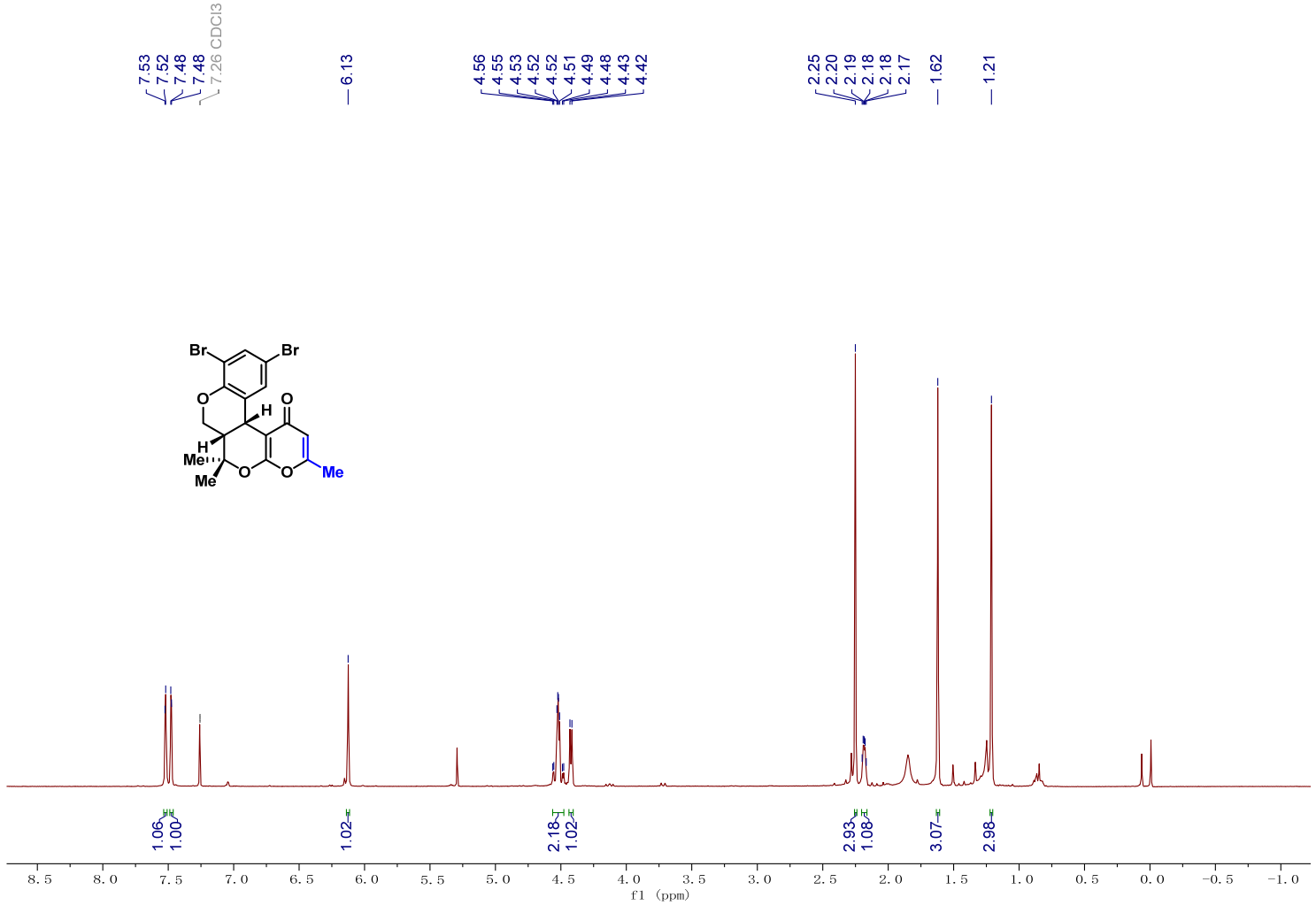
Compound 71 ^{1}H NMR



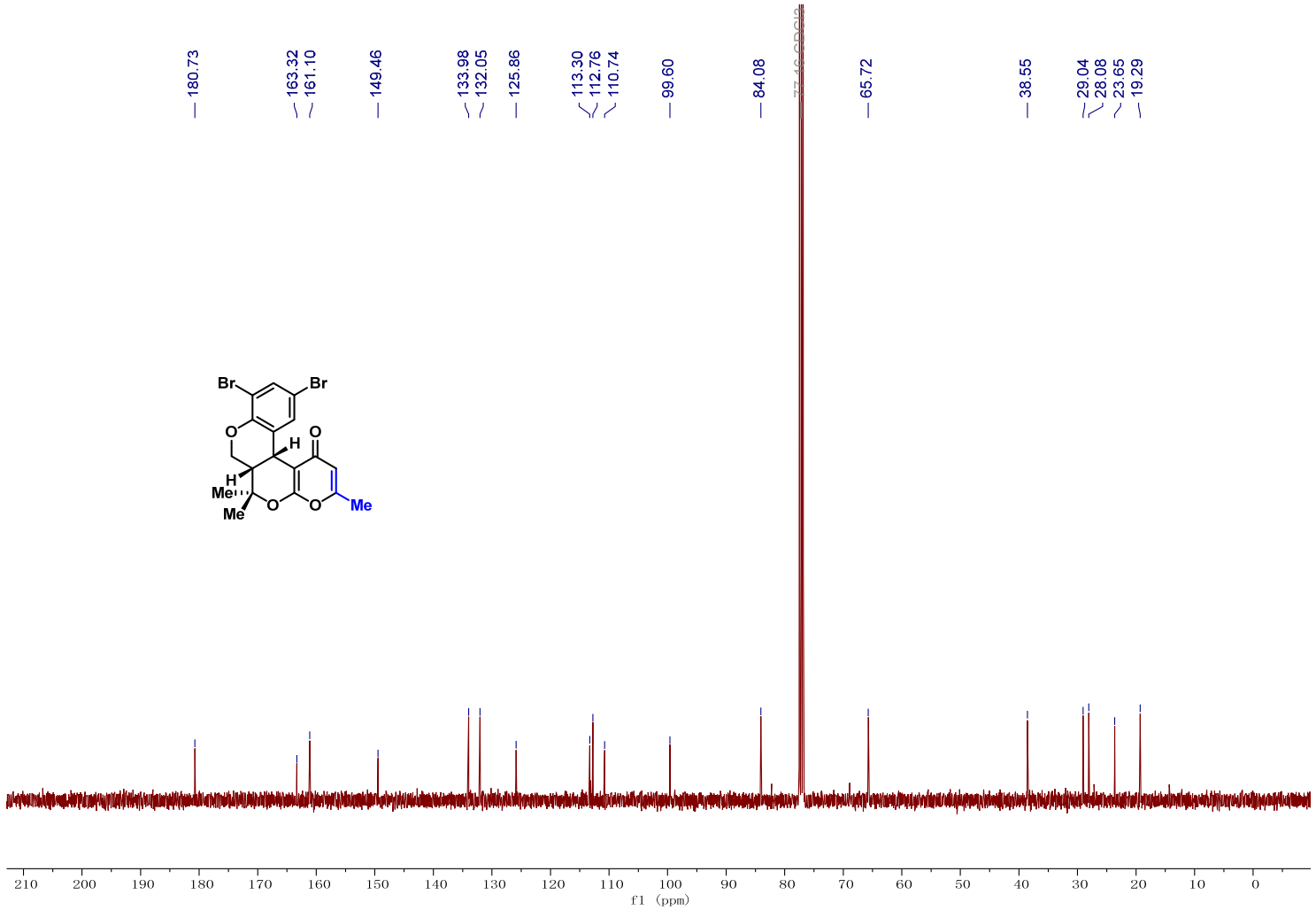
Compound 71 ^{13}C NMR



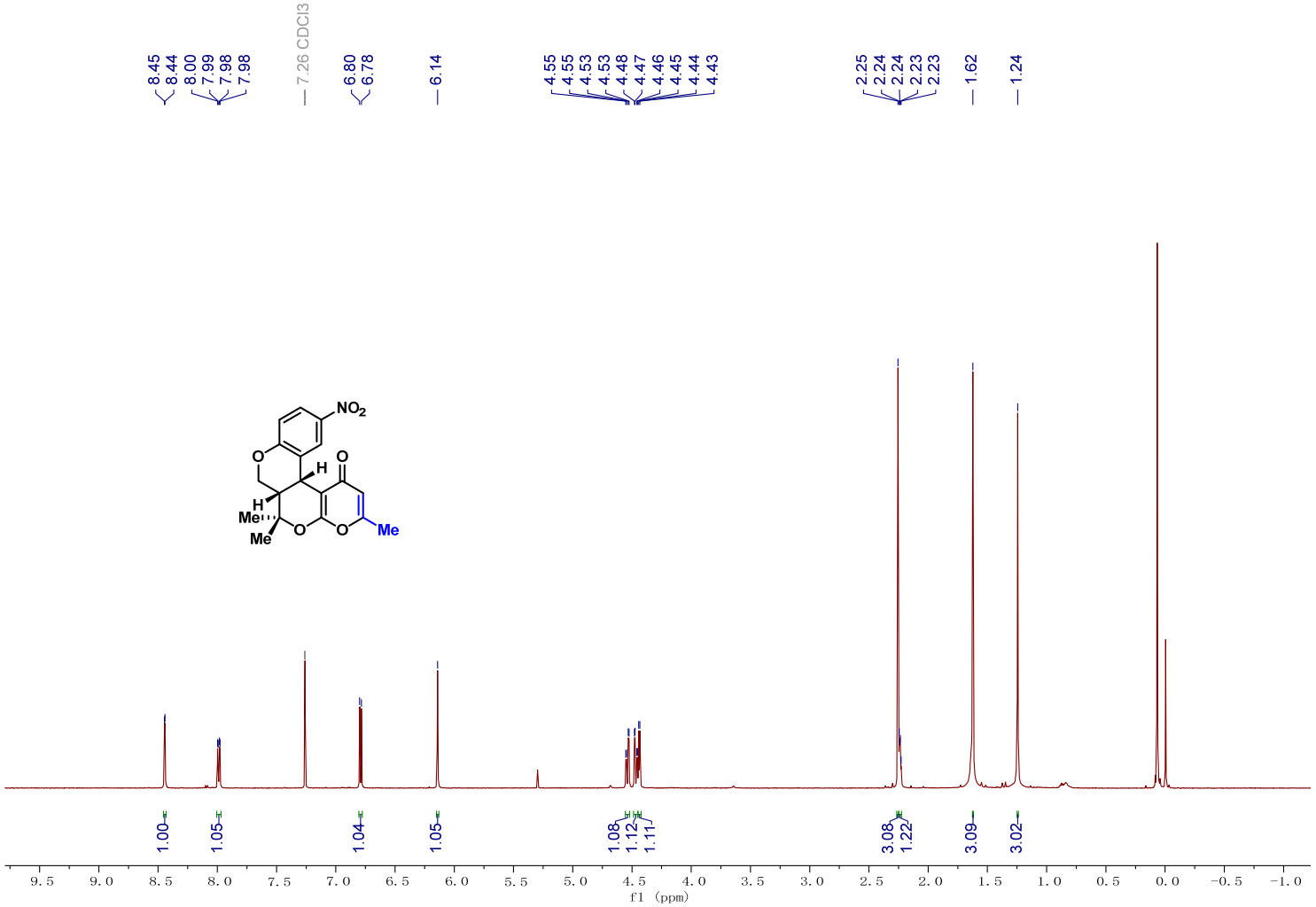
Compound 72 ^{1}H NMR



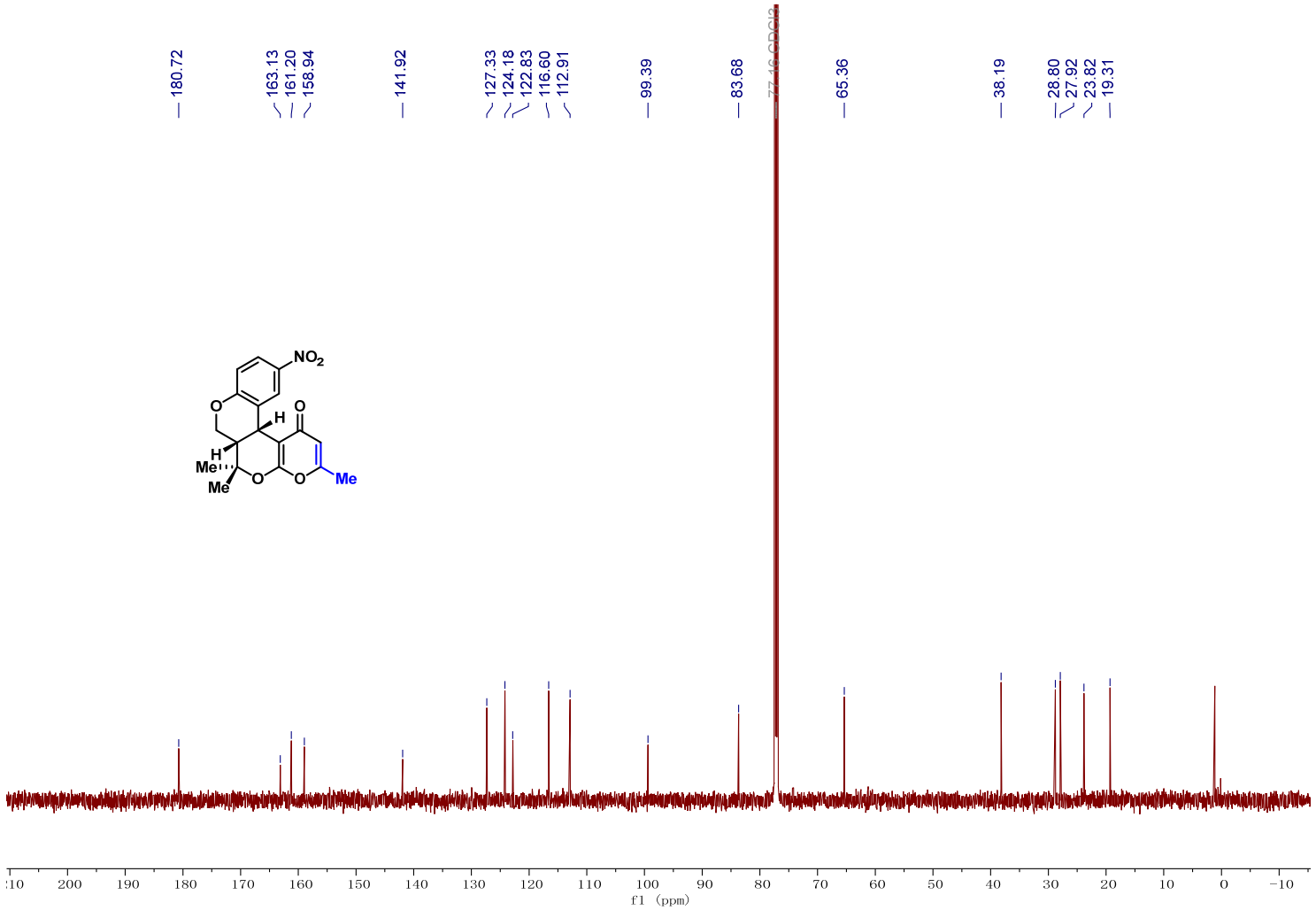
Compound 72 ^{13}C NMR



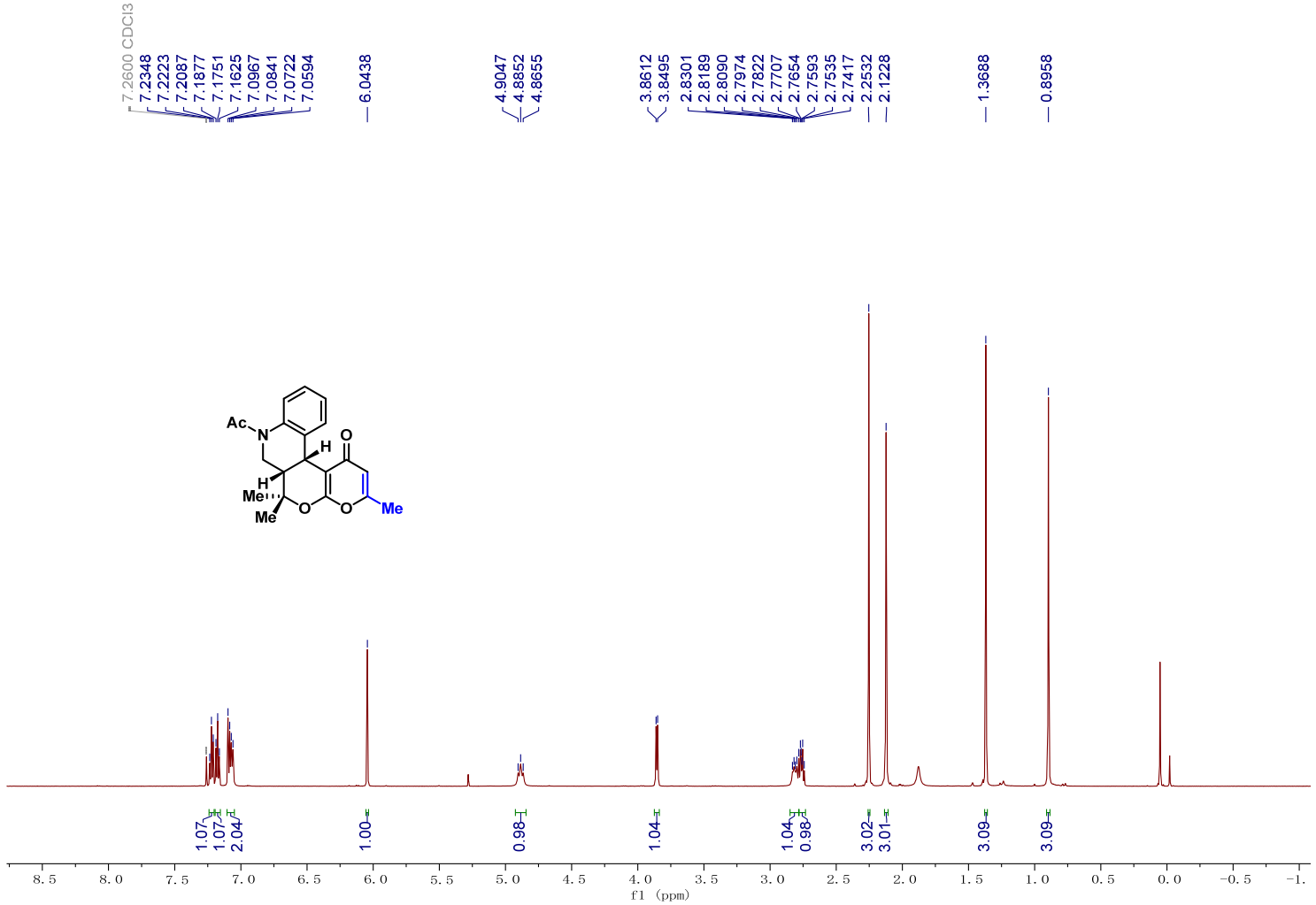
Compound 73 ^{1}H NMR



Compound 73 ^{13}C NMR



Compound 74 ^{1}H NMR



Compound 74 ^{13}C NMR