Supporting Information

For

Regioselective [3+2] cycloaddition reaction of 2-benzylidene-1-indenones with functional olefins to access indanone-fused 2D/3D skeletons

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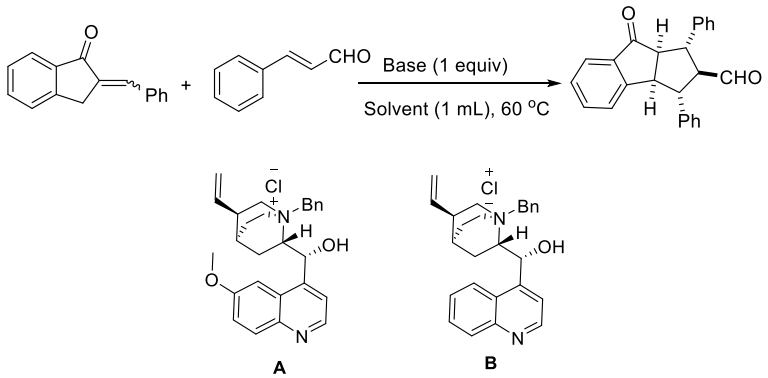
1. General experimental information

Reactions were monitored by TLC and visualization of the developed chromatogram was performed by ultraviolet light. Unless otherwise noted, all reagents including solvents were obtained from commercial supplier without any purification. The forced-flow column chromatography was performed using silica gel eluting with ethyl acetate and petroleum ether. NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ or DMSO-d_6 solutions were recorded either at 400 and 100 MHz or at 500 and 125 MHz (Bruker Avance), respectively and resonances (δ) are given in parts per million (ppm) relatives to tetramethylsilane (TMS). Data for NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. The X-ray crystal-structure determinations of **3fa** and **5o** were obtained on a Bruker APEX DUO system. All melting points are determined on a SGW X-4 melting apparatus and are uncorrected. Cinnamaldehyde **2**, witting reagents, 2-thenoyltrifluoroacetone were obtained from commercial supplier and used directly. 2-Benzylideneinden-1-one **1**, 2-benzylidenebenzofuran-3(2H)-one **4** were prepared according to literature reports.[1]

2. Optimization of the reaction conditions

Table S1. The Screening of solvent and ratio of amount of **1a**:**2a**[a]



Entry	Base	Solvent	Additive	Time (h)	**1a**:**2a**	Yield (%)[b]
1	DBU	DMC	-	80	1.0:1.0	n.r.
2	DMAP	DMC	-	80	1.0:1.0	n.r.
3	Et_3N	DMC	-	80	1.0:1.0	n.r.

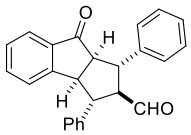
4	PPh_3	DMC	-	80	1.0:1.0	n.r.
5	K_2CO_3	DMC	-	80	1.0:1.0	n.r.
6	Cs_2CO_3	DMC	-	80	1.0:1.0	n.r.
7	Na_2CO_3	DMC	-	80	1.0:1.0	n.r.
8	$NaHCO_3$	DMC	-	80	1.0:1.0	n.r.
9	NaOH	DMC	-	80	1.0:1.0	n.r.
10	EtONa	DMC	-	80	1.0:1.0	n.r.
11	DABCO	Toluene	-	80	1.0:1.0	n.r.
12	DABCO	DCM	-	80	1.0:1.0	n.r.
13	DABCO	CH_3CN	-	80	1.0:1.0	n.r.
14	DABCO	THF	-	80	1.0:1.0	n.r.
15	DABCO	DMF	-	80	1.0:1.0	n.r.
16	DABCO	DMSO	-	80	1.0:1.0	n.r.
17	DABCO	DEC	-	80	1.0:1.0	n.r.
18	DABCO	DMC	-	48	1.5:1.0	40
19	DABCO	DMC	-	48	2.0:1.0	32
20	DABCO	DMC	-	48	1.0:1.5	34
21	DABCO	DMC	-	48	1.0:2.0	34
22[c,d]	DABCO	DMC	-	4	1.5:1.0	23
23[e]	**A**	DCM	--	72	1.5:1.0	n.r.
24[e]	**B**	DCM	--	72	1.5:1.0	n.r.
25[e]	**A**	DCM	Na_2CO_3 (20 mol%)	72	1.5:1.0	n.r.
26[e]	**B**	DCM	Na_2CO_3 (20 mol%)	72	1.5:1.0	n.r.
27[e]	**A**	DCM	Na_2CO_3 (1.0 equiv.)	72	1.5:1.0	n.r.
28[e]	**B**	DCM	Na_2CO_3 (1.0 equiv.)	72	1.5:1.0	n.r.
29[e]	**A**	DCM	K_2CO_3 (1.0 equiv.)	72	1.5:1.0	n.r.
30[e]	**B**	DCM	K_2CO_3 (1.0 equiv.)	72	1.5:1.0	n.r.

[a] Unless otherwise specified the reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), base (1.0 equiv.), solvent (1.0 mL), 60 °C. [b] Yield of isolated **3aa** after purification by silica gel column chromatography. [c] DABCO (2 equiv.). [d] DMC (0.5 mL). [e] 40 °C.

3. General experimental procedures for synthesis of compounds 3

A mixture of DABCO (0.20 mmol, 1.0 equiv.), EtONa (0.20 mmol, 1.0 equiv.), **1** (0.30 mmol, 1.5 equiv.) and **2** (0.20 mmol, 1.0 equiv.) and dimethyl carbonate (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 90 °C for the 1-80 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 10:1 to 5:1) to afford pure products **3**.

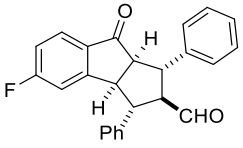
8-oxo-1,3-diphenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3aa)



3aa

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 55.6 mg, 79% yield, m.p. 135.4-136.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 20:1) δ 9.37 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.43 (ddd, *J* = 10.4, 5.8, 2.0 Hz, 3H), 7.38 – 7.27 (m, 7H), 7.27 – 7.22 (m, 1H), 7.22 – 7.16 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.09 (t, *J* = 9.0 Hz, 1H), 3.67 (td, *J* = 11.3, 2.8 Hz, 1H), 3.59 (dd, *J* = 11.1, 8.0 Hz, 1H), 3.45 (t, *J* = 8.3 Hz, 1H), 3.08 (dd, *J* = 11.6, 9.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 199.7, 153.9, 139.9, 138.3, 134.2, 134.1, 128.2, 127.9, 127.5, 126.9, 126.7, 126.6, 126.2, 124.5, 123.6, 68.0, 58.6, 53.8, 51.7, 46.8 ppm. HRMS (ESI) calcd. for $C_{25}H_{21}O_2$ $[M + H]^+$ 353.1536, found: 353.1533.

5-fluoro-8-oxo-1,3-diphenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ba)

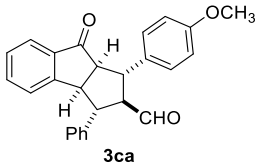


3ba

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 28.9 mg, 39% yield, m.p. 145.8-147.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.46 (d, *J* = 2.7 Hz, 1H), 7.79 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.33 (m, 7H), 7.31 – 7.26 (m, 1H), 7.12 (td, *J* = 8.6, 2.3 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 3.75 (td, *J* = 11.4, 2.7 Hz, 1H), 3.66 (dd, *J* = 11.2, 8.2 Hz, 1H), 3.55 (t, *J* = 8.3 Hz, 1H), 3.17 (dd, *J* = 11.6, 9.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ

204.1, 200.6, 167.3 (d, *J* = 257.6 Hz), 157.7 (d, *J* = 9.9 Hz), 140.6, 138.9, 131.5 (d, *J* = 1.9 Hz), 129.3, 129.0, 127.9, 127.8, 127.7, 127.4, 127.0 (d, *J* = 10.6 Hz), 116.8 (d, *J* = 23.8 Hz), 112.3 (d, *J* = 22.4 Hz), 68.8, 59.8, 54.7, 52.3, 47.9 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}FO_2$ $[M + H]^+$ 371.1442, found: 371.1431.

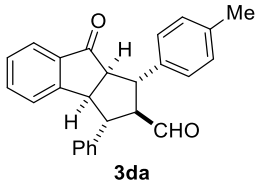
1-(4-methoxyphenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a] indene-2-carbaldehyde (3ca)



3ca

Vicious reddle liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 58.9 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 19:1) δ 9.44 (d, *J* = 2.9 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.51 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.32 (m, 8H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.16 (t, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.71 (dt, *J* = 11.4, 2.9 Hz, 1H), 3.60 (dd, *J* = 11.3, 8.2 Hz, 1H), 3.48 (t, *J* = 8.3 Hz, 1H), 3.18 (dd, *J* = 11.5, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 200.0, 157.7, 154.0, 138.5, 134.2, 134.1, 131.7, 128.1, 127.7, 127.4, 126.9, 126.6, 124.5, 123.5, 113.3, 68.1, 58.7, 54.2, 53.7, 51.5, 46.3 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_3$ $[M + H]^+$ 383.1642, found: 383.1648.

8-oxo-3-phenyl-1-(p-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3da)

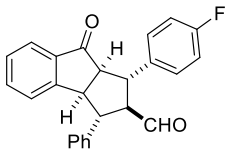


3da

Vicious reddle liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 46.9 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 16:1) δ 9.45 (d, *J* = 2.8 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.52 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.45 – 7.28 (m, 8H), 7.23 – 7.17 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 3.79 – 3.69 (m, 1H), 3.66 – 3.59 (m,

1H), 3.51 (t, *J* = 8.3 Hz, 1H), 3.19 (dd, *J* = 11.6, 9.5 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 199.9, 154.0, 138.4, 136.7, 135.8, 134.2, 134.1, 128.6, 128.1, 127.4, 126.9, 126.6, 126.5, 124.5, 123.6, 68.1, 58.7, 53.7, 51.6, 46.6, 20.0 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1690.

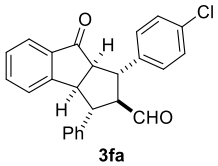
1-(4-fluorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ea)



3ea

Tawny solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 37.8 mg, 51% yield, m.p. 152.7 – 154.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.44 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.52 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 – 7.40 (m, 5H), 7.40 – 7.32 (m, 3H), 7.11 – 7.00 (m, 3H), 4.18 (t, *J* = 9.0 Hz, 1H), 3.76 – 3.61 (m, 2H), 3.47 (t, *J* = 8.2 Hz, 1H), 3.20 – 3.11 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.4, 203.2, 161.6 (d, *J* = 242.8 Hz), 155.9, 140.4, 137.9 (d, *J* = 2.9 Hz),136.0, 135.5, 130.5 (d, *J* = 8.0 Hz), 129.3, 128.9, 128.6, 127.8, 125.7, 124.4, 115.7 (d, *J* = 21.1 Hz), 69.9, 59.5, 54.3, 52.5, 47.1 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}FO_2$ $[M + H]^+$ 371.1442, found: 371.1440.

1-(4-chlorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3fa)

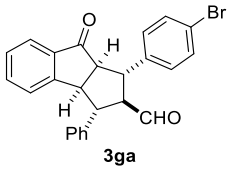


3fa

Tawny solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 29.4 mg, 38% yield, m.p. 161.6 - 162.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.44 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 5H), 7.39 – 7.32 (m,

5H), 7.05 – 7.01 (m, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 3.76 – 3.59 (m, 2H), 3.46 (t, *J* = 8.1 Hz, 1H), 3.15 (dd, *J* = 11.2, 9.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.33, 203.20, 155.91, 140.79, 140.41, 135.99, 135.46, 131.94, 130.51, 129.32, 128.92, 128.89, 128.66, 127.77, 125.74, 124.38, 69.66, 59.41, 54.24, 52.49, 47.10, ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1147.

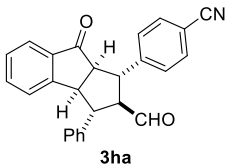
1-(4-bromophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ga)



3ga

Tawny solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 26.7 mg, 31% yield, m.p. 164.0 – 166.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.43 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.46 – 7.32 (m, 8H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 3.73 – 3.56 (m, 2H), 3.46 (t, *J* = 8.2 Hz, 1H), 3.15 (dd, *J* = 11.3, 9.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 199.5, 153.8, 138.8, 138.0, 134.4, 134.0, 131.0, 128.5, 128.2, 127.6, 126.8, 124.5, 123.6, 120.1, 67.7, 58.4, 53.9, 51.5, 46.0 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}BrO_2$ $[M + H]^+$ 431.0641, found: 431.0643.

4-(2-formyl-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]inden-1-yl)benzonitrile (3ha)

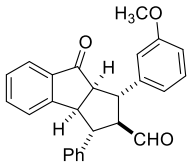


3ha

Light brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 18.9 mg, 25% yield, m.p. 188.8 – 190.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.56 – 7.50 (m, 1H), 7.47 – 7.41 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 4.19

(t, *J* = 9.1 Hz, 1H), 3.78 – 3.68 (m, 2H), 3.51 – 3.44 (m, 1H), 3.13 (td, *J* = 9.4, 2.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 199.0, 153.6, 145.5, 137.6, 134.6, 133.9, 131.7, 128.4, 127.8, 127.7, 127.0, 126.8, 124.6, 123.7, 117.7, 110.1, 67.2, 58.1, 54.2, 51.5, 46.0 ppm. HRMS (ESI) calcd. for $C_{26}H_{19}NO_2$ $[M + H]^+$ 378.1489, found:378.1493.

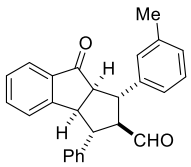
1-(3-methoxyphenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta [a]indene-2-carbaldehyde (3ia)



3ia

Vicious reddle liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 32.1 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 20:1) δ 9.38 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.43 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 1H), 7.03 – 6.96 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.08 (t, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.66 (td, *J* = 11.3, 2.8 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.44 (t, *J* = 8.2 Hz, 1H), 3.07 (dd, *J* = 11.6, 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 199.8, 159.0, 153.9, 141.5, 138.2, 134.2, 134.1, 128.9, 128.2, 127.5, 126.9, 126.7, 124.5, 123.6, 118.7, 112.7, 111.5, 67.8, 58.5, 54.2, 53.8, 51.6, 46.6 ppm. HRMS (ESI) calcd. for $C_{26}H_{22}O_3$ $[M + H]^+$ 383.1642, found: 383.1643.

8-oxo-3-phenyl-1-(m-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ja)

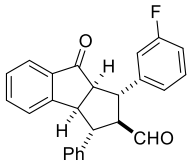


3ja

Yellow viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 49.1 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 20:1) δ 9.45 (d, *J* = 2.9 Hz, 1H), 7.78 (d, *J*

= 7.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.40 – 7.31 (m, 3H), 7.29-7.27 (m, 3H), 7.14 – 7.07 (m, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 4.18 (t, *J* = 9.0 Hz, 1H), 3.74 (td, *J* = 11.4, 2.9 Hz, 1H), 3.62 (dd, *J* = 11.1, 8.2 Hz, 1H), 3.54 (t, *J* = 8.3 Hz, 1H), 3.17 (dd, *J* = 11.7, 9.5 Hz, 1H), 2.39 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 200.9, 155.0, 140.8, 139.4, 138.6, 135.3, 135.2, 129.2, 128.9, 128.5, 128.4, 128.1, 127.9, 127.7, 125.6, 124.5, 124.6, 69.2, 59.7, 54.8, 52.7, 47.9, 21.6 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1690.

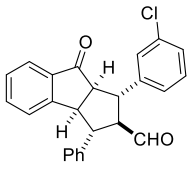
1-(3-fluorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ka)



3ka

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 8.1 mg, 11% yield, m.p. 180.2-180.6 °C. ^{1}H NMR (500 MHz, DMSO-d_6, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.33 (d, *J* = 3.9 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.48 – 7.39 (m, 4H), 7.38 – 7.31 (m, 3H), 7.31 – 7.21 (m, 2H), 7.07 – 7.00 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 4.21 (t, *J* = 8.8 Hz, 1H), 3.66 – 3.52 (m, 3H), 3.22 (t, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.4, 203.2, 162.9 (d, *J* = 243.1 Hz), 155.9, 144.8 (d, *J* = 7.4 Hz), 140.3, 136.0, 135.5, 130.8 (d, *J* = 8.5 Hz), 129.3, 128.9, 128.7, 127.8, 125.7, 124.9, 124.8 (d, *J* = 2.7 Hz), 115.2 (d, *J* = 21.6 Hz), 114.2 (d, *J* = 20.7 Hz), 69.5, 59.4, 54.3, 52.5, 47.3 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}FO_2$ $[M + H]^+$ 371.1442, found: 371.1446.

1-(3-chlorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3la)

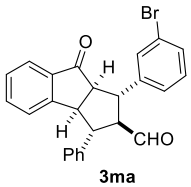


3la

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1

to 5:1), 10.8 mg, 14% yield, m.p. 144.0 – 145.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, *J* = 2.5 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 3H), 7.41 – 7.29 (m, 5H), 7.29 – 7.27 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 4.19 (t, *J* = 9.0 Hz, 1H), 3.77 – 3.56 (m, 2H), 3.50 (t, *J* = 8.1 Hz, 1H), 3.14 (dd, *J* = 11.3, 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 199.3, 153.7, 142.0, 138.0, 134.4, 134.0, 133.8, 129.2, 128.2, 127.6, 126.8, 126.7, 126.5, 125.2, 124.6, 123.6, 67.7, 58.4, 54.0, 51.6, 46.1. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1142.

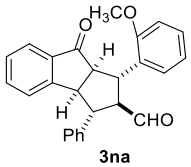
1-(3-bromophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ma)



3ma

Tawny solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 12.1 mg, 14% yield, m.p. 159.33 – 161.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 2.5 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.42 (m, 5H), 7.42 – 7.35 (m, 3H), 7.29 (t, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.21 (t, *J* = 9.1 Hz, 1H), 3.80 – 3.63 (m, 2H), 3.52 (t, *J* = 8.2 Hz, 1H), 3.15 (dd, *J* = 11.3, 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 199.3, 153.7, 142.3, 137.9, 134.4, 134.0, 129.6, 129.5, 129.4, 128.2, 127.6, 126.9, 125.8, 124.6, 123.7, 122.0, 67.7, 58.4, 54.0, 51.5, 46.1. HRMS (ESI) calcd. for $C_{25}H_{20}BrO_2$ $[M + H]^+$ 431.0641, found: 466.0639.

1-(2-methoxyphenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a] indene-2-carbaldehyde (3na)

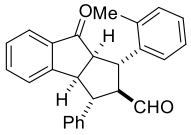


3na

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 43.6 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of

two isomers, the ratio of the two isomers is 12:1) δ 9.42 (d, *J* = 2.8 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.38 – 7.27 (m, 4H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.94 (s, 3H), 3.89 (dd, *J* = 11.5, 2.6 Hz, 1H), 3.86 – 3.76 (m, 2H), 3.14 (dd, *J* = 11.6, 9.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 200.1, 156.1, 154.4, 139.1, 134.2, 134.0, 129.0, 128.0, 127.6, 127.4, 127.3, 126.9, 126.4, 124.5, 123.4, 120.1, 110.1, 67.1, 56.7, 54.3, 53.8, 52.1, 44.1 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_3$ $[M + H]^+$ 383.1642, found: 383.1645.

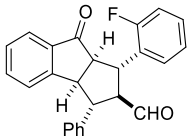
8-oxo-3-phenyl-1-(o-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3oa)



3oa

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 42.5 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 2.2 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.38 (m, 5H), 7.38 – 7.32 (m, 1H), 7.32 – 7.24 (m, 1H), 7.22 – 7.11 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.24 (t, *J* = 9.0 Hz, 1H), 3.97 (dd, *J* = 11.1, 8.1 Hz, 1H), 3.81 - 3.75 (m, 1H), 3.53 (t, *J* = 8.3 Hz, 1H), 3.17 (dd, *J* = 11.8, 9.6 Hz, 1H), 2.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 199.7, 154.0, 138.8, 138.5, 135.6, 134.2, 134.0, 129.8, 128.2, 127.4, 126.8, 126.6, 125.8, 125.7, 125.6, 124.5, 123.5, 70.1, 59.9, 54.0, 51.8, 42.2, 19.1 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1698.

1-(2-fluorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8ahexahydrocyclopenta[a]indene-2-carbaldehyde (3pa)

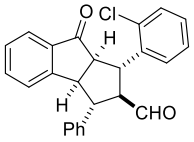


3pa

Reddish brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 20.0 mg, 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ

9.44 (d, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.37 (m, 6H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.19 – 7.08 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 4.25 (t, *J* = 8.6 Hz, 1H), 3.86 (t, *J* = 10.2 Hz, 1H), 3.71 (p, *J* = 8.0 Hz, 2H), 3.11 (t, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 199.5, 160.2 (d, *J* = 245.7 Hz), 154.0, 138.4, 134.2, 134.0, 129.8 (d, *J* = 4.8 Hz), 128.2, 128.1, 127.5, 126.9, 126.7, 124.5, 123.7 (d, *J* = 3.3 Hz), 123.6, 115.2 (d, *J* = 21.9 Hz), 67.3, 57.2, 54.2, 51.7, 42.9 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}FO_2$ $[M + H]^+$ 371.1442, found: 371.1446.

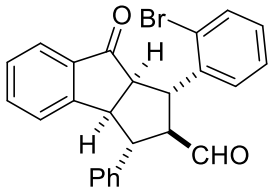
1-(2-chlorophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3qa)



3qa

Yellow viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 43.3 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.27 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.20 (t, *J* = 9.1 Hz, 1H), 3.96 (dd, *J* = 11.1, 7.8 Hz, 1H), 3.91 – 3.81 (m, 1H), 3.70 (t, *J* = 8.1 Hz, 1H), 3.06 (t, *J* = 10.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.9, 202.5, 156.0, 140.4, 138.8, 136.0, 135.3, 133.4, 130.7, 129.9, 129.3, 129.1, 128.9, 128.6, 128.3, 127.8, 125.8, 124.4, 71.1, 59.4, 54.1, 52.4, 44.4 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1145.

1-(2-bromophenyl)-8-oxo-3-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3r)

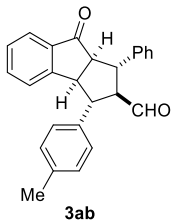


3ra

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 44.9 mg, 52% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.46 (d,

J = 4.3 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.55 – 7.44 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 4.36 (t, *J* = 8.8 Hz, 1H), 4.09 (dd, *J* = 10.9, 8.7 Hz, 1H), 3.76 (t, *J* = 8.5 Hz, 1H), 3.54 (td, *J* = 11.2, 4.3 Hz, 1H), 3.50 – 3.43 (m, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.72, 202.35, 155.98, 140.45, 140.38, 136.03, 135.22, 133.16, 130.85, 129.43, 129.32, 128.94, 128.90, 128.62, 127.78, 125.76, 124.41, 124.37, 71.51, 59.77, 54.08, 52.39, 47.08 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}BrO_2$ $[M + H]^+$ 431.0641, found: 431.0646.

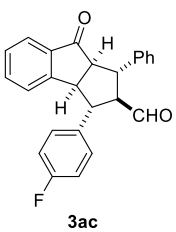
8-oxo-1-phenyl-3-(p-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ab)



3ab

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 21.2 mg, 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 11.8, 7.3 Hz, 3H), 7.37 (dt, *J* = 15.2, 7.4 Hz, 3H), 7.27-7.14 (m, 5H), 7.02 (d, *J* = 7.6 Hz, 1H), 4.12 (t, *J* = 9.1 Hz, 1H), 3.71-3.61 (m, 2H), 3.49 (t, *J* = 8.0 Hz, 1H), 3.09 (t, *J* = 10.2 Hz, 1H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 199.9, 154.0, 139.9, 136.4, 135.2, 134.2, 134.1, 128.8, 127.9, 127.4, 126.7, 126.7, 126.2, 124.6, 123.6, 68.0, 58.6, 53.6, 51.7, 46.7, 20.1 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1695.

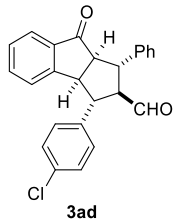
3-(4-fluorophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ac)



3ac

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 34.1 mg, 46% yield, m.p. 145.8-147.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.45 (d, *J* = 2.5 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.41 (dt, *J* = 18.9, 7.6 Hz, 3H), 7.36 – 7.31 (m, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 4.12 (t, *J* = 9.1 Hz, 1H), 3.79 – 3.61 (m, 2H), 3.53 (t, *J* = 8.1 Hz, 1H), 3.16 (t, *J* = 10.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.4, 203.2, 161.9 (d, *J* = 243.1 Hz), 155.7, 141.8, 136.6 (d, *J* = 3.1 Hz), 135.9, 135.5, 130.60 (d, *J* = 8.0 Hz), 129.0, 128.9, 128.5, 127.3, 125.7, 124.4, 116.03 (d, *J* = 21.1 Hz), 69.9, 59.5, 53.5, 52.6, 47.8 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}FO_2$ $[M + H]^+$ 371.1442, found: 371.1445.

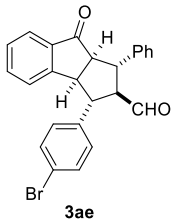
3-(4-chlorophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ad)



3ad

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 63.4 mg, 82% yield, m.p.145.8-147.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.37 (d, *J* = 2.5 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 12.3, 7.0 Hz, 3H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.25 – 7.17 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.04 (t, *J* = 9.1 Hz, 1H), 3.70 – 3.52 (m, 2H), 3.45 (t, *J* = 8.0 Hz, 1H), 3.07 (t, *J* = 10.3 Hz, 1H) ppm. ^{13}C NMR 125 MHz, DMSO-d_6) δ 206.4, 203.1, 155.64, 141.7, 139.5, 136.0, 135.5, 132.3, 130.6, 129.2, 129.0, 128.9, 128.5, 127.3, 125.8, 124.4, 69.8, 59.5, 53.5, 52.5, 47.8 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1150.

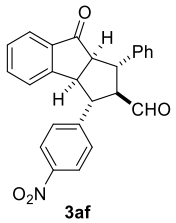
3-(4-bromophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ae)



3ae

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 38.8 mg, 45% yield, m.p. 135.1-136.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.43 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.44 – 7.41 (m, 3H), 7.39 – 7.35 (m, 5H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 3.75 – 3.58 (m, 2H), 3.46 (t, *J* = 8.2 Hz, 1H), 3.15 (dd, *J* = 11.3, 9.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 199.5, 153.8, 138.8, 138.0, 134.4, 134.0, 131.0, 128.5, 128.2, 127.6, 126.8, 126.8, 124.5, 123.6, 120.2, 67.7, 58.4, 53.9, 51.5, 46.0 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}BrO_2$ $[M + H]^+$ 431.0641, found: 431.0640.

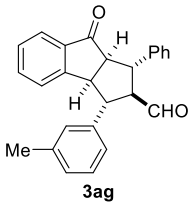
3-(4-nitrophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3af)



3af

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 20.7 mg, 26% yield, m.p. 201.3-202.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 2.4 Hz, 1H), 8.29 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.53 – 7.47 (m, 3H), 7.45 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 4.18 (t, *J* = 8.9 Hz, 1H), 3.77 (dt, *J* = 11.3, 2.4 Hz, 1H), 3.71 – 3.55 (m, 2H), 3.32 (dd, *J* = 11.6, 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 199.9, 153.9, 147.5, 147.3, 140.2, 135.5, 135.1, 129.2, 129.0, 128.9, 127.6, 125.2, 124.9, 124.4, 68.8, 59.6, 53.9, 52.5, 48.3 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}NO_4$ $[M + H]^+$ 398.1387, found: 398.1386.

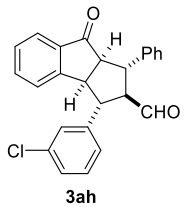
8-oxo-1-phenyl-3-(m-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ag)



3ag

Yellow viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 13.2 mg, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is >20:1) δ 9.37 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.33 (dt, *J* = 15.3, 7.6 Hz, 3H), 7.24 – 7.18 (m, 2H), 7.10 – 7.06 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.10 (t, *J* = 9.0 Hz, 1H), 3.71 – 3.55 (m, 2H), 3.45 (t, *J* = 8.2 Hz, 1H), 3.05 (t, 1H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 199.9, 154.0, 139.8, 138.2, 137.8, 134.2, 134.1, 128.0, 127.9, 127.5, 127.4, 126.7, 126.2, 124.6, 124.0, 123.5, 68.0, 58.6, 53.8, 51.6, 46.7, 20.5 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1697.

3-(3-chlorophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ah)

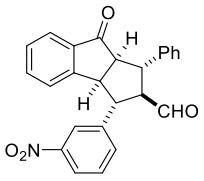


3ah

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 24.8 mg, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 13:1) δ 9.38 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.28 – 7.20 (m, 3H), 7.19 – 7.15 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.07 (t, *J* = 8.9 Hz, 1H), 3.64 (t, *J* = 11.9 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.46 (t, *J* = 8.2 Hz, 1H), 3.08 (t, *J* = 10.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 199.4, 153.5, 140.6, 139.5, 134.4, 134.1, 134.0, 129.4, 128.0, 127.6, 126.9, 126.8,

126.6, 126.4, 125.3, 124.4, 123.7, 67.9, 58.5, 53.1, 51.5, 47.0 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1148.

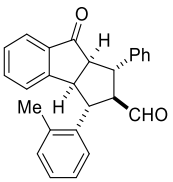
3-(3-nitrophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ai)



3ai

Orange-yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 37.4 mg, 47% yield, m.p. 139.1-141.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 17:1) δ 9.47 (d, *J* = 2.4 Hz, 1H), 8.31 (t, *J* = 2.0 Hz, 1H), 8.24 – 8.16 (m, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 – 7.28 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.22 – 4.15 (m, 1H), 3.78 (td, *J* = 11.3, 2.4 Hz, 1H), 3.71 – 3.53 (m, 2H), 3.34 (dd, *J* = 11.6, 9.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 200.1, 154.1, 148.9, 142.0, 140.2, 135.6, 135.1, 134.6, 130.2, 129.2, 128.9, 127.7, 127.6, 125.2, 124.9, 122.8, 122.5, 68.8, 59.5, 53.7, 52.4, 48.4 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}NO_4$ $[M + H]^+$ 398.1387, found: 398.1392.

8-oxo-1-phenyl-3-(o-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde （3aj）

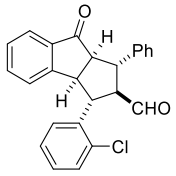


3aj

Orange-yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 18.3 mg, 25% yield, m.p. 145.6-147.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* =

7.1 Hz, 3H), 7.32 (td, *J* = 14.6, 12.4, 8.0 Hz, 4H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 4.11 (t, *J* = 9.0 Hz, 1H), 3.71 (td, *J* = 11.2, 2.1 Hz, 1H), 3.64 (d, *J* = 7.9 Hz, 1H), 3.53 – 3.36 (m, 2H), 2.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 199.7, 154.0, 140.0, 136.9, 135.3, 134.3, 134.0, 129.8, 128.0, 127.5, 126.7, 126.2, 126.12, 126.0, 125.6, 124.2, 123.6, 69.0, 58.8, 52.5, 48.6, 47.0, 19.1 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}O_2$ $[M + H]^+$ 367.1693, found: 367.1697.

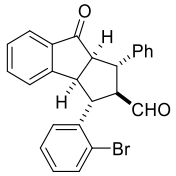
3-(2-chlorophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3ak)



3ak

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 19.3 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 13:1) δ 9.49 (d, *J* = 3.1 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 1H), 6.83 (d, *J* = 15.7 Hz, 1H), 6.35 – 6.19 (m, 1H), 3.90 (t, *J* = 8.8 Hz, 1H), 3.58 (dd, *J* = 11.1, 8.3 Hz, 1H), 3.40-3.33 (m, 2H), 2.89 – 2.70 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 199.7, 153.7, 139.7, 134.5, 133.7, 132.1, 130.4, 128.8, 128.5, 128.0, 127.9, 127.6, 126.6, 126.3, 126.0, 124.6, 123.6, 66.6, 58.6, 51.6, 49.3, 46.5 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClO_2$ $[M + H]^+$ 387.1146, found: 387.1150.

3-(2-bromophenyl)-8-oxo-1-phenyl-1,2,3,3a,8,8a-hexahydrocyclopenta[a]indene-2-carbaldehyde (3al)



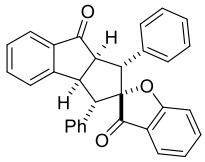
3al

Brown viscous liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1), 14.7 mg, 17% yield. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers, the ratio of the two isomers is 10:1) δ 9.49 (d, *J* = 3.2 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.52 – 7.48 (m, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.10 – 7.05 (m, 1H), 6.79 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.7, 8.6 Hz, 1H), 3.90 (t, *J* = 8.8 Hz, 1H), 3.58 (dd, *J* = 11.0, 8.3 Hz, 1H), 3.43 – 3.31 (m, 2H), 2.84 (q, *J* = 9.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 199.7, 153.7, 139.7, 135.6, 134.5, 132.0, 131.1, 130.6, 128.2, 128.0, 127.6, 126.7, 126.6, 126.3, 124.7, 123.6, 122.5, 66.6, 58.6, 51.5, 49.3, 46.5 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}BrO_2$ $[M + H]^+$ 431.0641, found: 431.0645.

4. General experimental procedures for synthesis of compounds 5

A mixture of DABCO (0.20 mmol, 1.0 equiv.), EtONa (0.20 mmol, 1.0 equiv.), **1** (0.30 mmol, 1.5 equiv.) and **4** (0.20 mmol, 1.0 equiv.) and dimethyl carbonate (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 90 °C for the 1-48 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 8:1 to 5:1) to afford pure products **5**.

1',3'-diphenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5a)

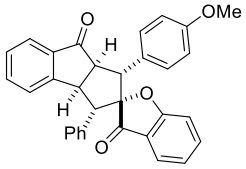


5a

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 73.5 mg, 83% yield, m.p. 213.4-214.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.49 (td, *J* = 7.4, 1.3 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.28 (m, 5H), 7.26 – 7.17 (m, 3H), 7.19 – 7.11 (m, 3H), 7.12 – 7.05 (m, 1H), 7.01 (d, *J* = 7.6

Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 4.70 (dd, *J* = 10.4, 8.3 Hz, 1H), 4.04 (dd, *J* = 10.2, 8.3 Hz, 1H), 3.95 (d, *J* = 10.2 Hz, 1H), 3.67 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 199.2, 171.1, 155.4, 138.0, 135.4, 134.9, 134.8, 129.2, 129.0, 128.5, 128.4, 128.2, 127.8, 127.6, 125.4, 124.7, 123.8, 121.7, 121.5, 112.6, 103.2, 59.7, 56.0, 55.1, 49.4 ppm. HRMS (ESI) calcd. for $C_{31}H_{23}O_3$ $[M + H]^+$ 443.1642, found: 443.1639.

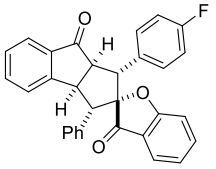
1'-(4-methoxyphenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro [benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5b)



5b

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 72.8 mg, 77% yield, m.p. 95.2-96.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.21 (m, 2H), 7.16 – 7.09 (m, 5H), 7.08 – 7.03 (m, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.66 (dd, *J* = 10.6, 8.4 Hz, 1H), 3.97 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.66 (d, *J* = 10.2 Hz, 1H), 3.51 (s, 3H), 3.38 (d, *J* = 10.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 13C NMR (125 MHz, DMSO-d_6) δ 205.8, 198.9, 171.1, 158.9, 155.8, 139.2, 136.1, 135.5, 135.2, 130.4, 129.4, 129.1, 128.8, 128.2, 127.5, 125.6, 124.5, 123.9, 122.4, 121.5, 113.9, 113.3, 103.3, 59.7, 56.1, 55.3, 54.1, 49.0, 40.4, 40.4, 40.3, 40.2, 40.1, 40.0, 39.9, 39.9, 39.8, 39.6, 39.4. ppm. HRMS (ESI) calcd. for $C_{32}H_{25}O_4$ $[M + H]^+$ 473.1747, found: 473.1742.

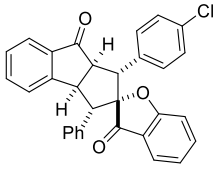
1'-(4-fluorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5c)



5c

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 59.9 mg, 65% yield, m.p. 95.1-96.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.41 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (td, *J* = 7.4, 1.0 Hz, 1H), 7.31 – 7.21 (m, 5H), 7.18 – 7.05 (m, 4H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.86 – 6.74 (m, 3H), 6.67 (t, *J* = 7.4 Hz, 1H), 4.61 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.93 – 3.79 (m, 2H), 3.57 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 199.0, 171.0, 162.2 (d, *J* = 246.0 Hz), 155.4, 138.2, 135.5, 135.3, 134.7, 130.7 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 8.1 Hz), 129.1, 128.6, 128.4, 127.8, 125.4, 124.7, 123.8, 121.7, 121.7, 115.2 (d, *J* = 21.5 Hz), 112.6, 103.1, 59.6, 56.2, 54.3, 49.3 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}FO_3$ $[M + H]^+$ 461.1547, found: 461.1565.

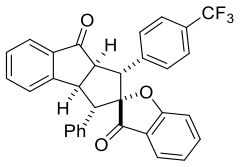
1'-(4-chlorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5d)



5d

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 54.4 mg, 57% yield, m.p. 66.2-67.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.47 – 7.41 (m, 1H), 7.39 – 7.33 (m, 3H), 7.32 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.17 – 7.12 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 4.68 (dd, *J* = 10.3, 8.1 Hz, 1H), 4.04 – 3.78 (m, 2H), 3.64 (d, *J* = 10.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.6, 198.6, 171.0, 155.8, 139.4, 136.2, 135.4, 135.0, 134.7, 132.6, 131.1, 129.4, 129.1, 128.9, 128.6, 128.3, 125.6, 124.5, 123.9, 122.6, 121.4, 113.3, 103.0, 59.6, 55.8, 53.9, 49.0 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}ClO_3$ $[M + H]^+$ 477.1252, found: 477.1257.

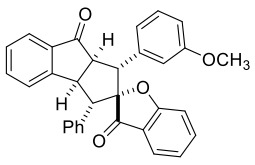
3'-phenyl-1'-(4-(trifluoromethyl)phenyl)-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5e)



5e

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 44.9 mg, 44% yield, m.p. 116.6-117.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 3H), 7.38 – 7.33 (m, 3H), 7.26 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 7.05 – 6.96 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 4.72 (dd, *J* = 10.1, 7.0 Hz, 1H), 4.01 (d, *J* = 6.4 Hz, 2H), 3.66 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 198.7, 170.9, 155.3, 139.2, 138.3, 135.6, 135.2, 134.4, 129.7 (q, *J* = 32.5 Hz), 129.4, 129.1, 128.7, 128.5, 127.9, 125.4, 125.2 (q, *J* = 3.8 Hz), 124.8, 124.0 (q, *J* = 270.5 Hz), 123.9, 121.9, 121.5, 112.6, 102.8, 59.9, 56.1, 54.4, 49.3 ppm. HRMS (ESI) calcd. for $C_{32}H_{22}F_3O_3$ $[M + H]^+$ 511.1516, found: 511.1520.

1'-(3-methoxyphenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5f)

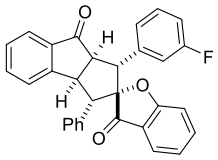


5f

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 66.2 mg, 70% yield, m.p. 84.3-85.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.41 (td, *J* = 7.4, 1.2 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.88 – 6.82 (m, 3H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 8.0, 2.2 Hz, 1H), 4.68 – 4.56 (m, 1H), 3.93 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.62 (s, 3H), 3.57 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 199.1, 171.1, 159.3, 155.4, 138.0, 136.5, 135.4, 134.8, 129.2, 129.1,

128.5, 128.4, 128.4, 127.8, 125.4, 124.7, 123.9, 121.8, 121.6, 121.5, 114.4, 113.4, 112.6, 103.1, 59.8, 56.1, 55.2, 54.9, 49.4 ppm. HRMS (ESI) calcd. for $C_{32}H_{25}O_4$ $[M + H]^+$ 473.1747, found: 473.1746.

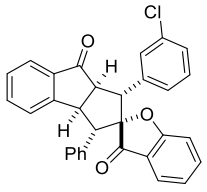
1'-(3-fluorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5g)



5g

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 75.5 mg, 82% yield, m.p. 74.0-74.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.28 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 7.02 – 6.98 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.83 – 6.71 (m, 2H), 4.70 (dd, *J* = 10.4, 8.0 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.65 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 198.8, 171.0, 162.6 (d, *J* = 245.4 Hz), 155.3, 138.2, 137.5 (d, *J* = 7.4 Hz), 135.5, 135.2, 134.6, 129.7 (d, *J* = 8.5 Hz), 129.2, 128.6, 128.5, 127.9, 125.4, 124.9 (d, *J* = 2.7 Hz), 124.7, 123.9, 121.8, 121.6, 115.8 (d, *J* = 22.1 Hz), 114.6 (d, *J* = 21.1 Hz), 112.6, 102.9, 59.7, 56.1, 54.5, 49.3 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}FO_3$ $[M + H]^+$ 461.1547, found: 461.1550.

1'-(3-chlorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5h)

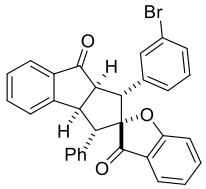


5h

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 14.3 mg, 15% yield, m.p. 85.3-86.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.28 (t, *J* = 8.4 Hz, 3H), 7.20 – 7.15 (m, 1H), 7.16 – 7.04 (m, 4H), 6.99 (d, *J* = 4.6 Hz, 2H), 6.92 (d, *J* = 7.5 Hz,

1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 4.67 – 4.56 (m, 1H), 3.94 – 3.84 (m, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.56 (d, *J* = 10.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 198.8, 171.0, 155.3, 138.3, 137.1, 135.5, 135.2, 134.5, 134.0, 129.5, 129.2, 129.0, 128.6, 128.5, 127.9, 127.8, 127.4, 125.4, 124.7, 123.9, 121.8, 121.6, 112.6, 102.8, 59.66, 56.2, 54.5, 49.4 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}ClO_3$ $[M + H]^+$ 477.1252, found: 477.1251.

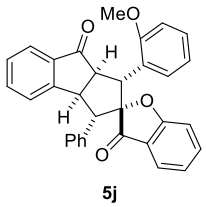
1'-(3-bromophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5i)



5i

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 26.1 mg, 25% yield, m.p. 103.2-104.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.50 (s, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.19 – 7.10 (m, 5H), 7.10 – 7.06 (m, 1H), 6.92 (t, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 4.62 (dd, 1H), 3.87 (dd, *J* = 10.0, 8.4 Hz, 1H), 3.80 (d, *J* = 10.1 Hz, 1H), 3.56 (d, *J* = 10.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 198.7, 171.0, 155.3, 138.3, 137.4, 135.5, 135.2, 134.5, 131.9, 130.7, 129.8, 129.2, 128.6, 128.5, 127.9, 127.9, 125.4, 124.7, 123.9, 122.3, 121.8, 121.6, 112.6, 102.8, 59.6, 56.2, 54.5, 49.4 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}BrO_3$ $[M + H]^+$ 521.0747, found: 521.0753.

1'-(2-methoxyphenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5j)

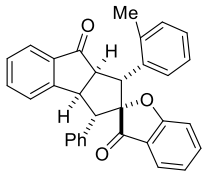


5j

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 68.0 mg, 72% yield, m.p. 181.3-182.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78

(d, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 (td, *J* = 7.5, 1.3 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.40 – 7.35 (m, 2H), 7.33 – 7.26 (m, 1H), 7.25-7.24 (m, , 1H), 7.23 – 7.17 (m, 2H), 7.18 – 7.11 (m, 1H), 7.09 – 7.01 (m, 1H), 7.02 – 6.97 (m, 1H), 6.88 – 6.81 (m, 2H), 6.77 – 6.69 (m, 1H), 6.62 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.74 – 4.55 (m, 2H), 4.02 (dd, *J* = 10.0, 8.4 Hz, 1H), 3.72 (d, *J* = 10.5 Hz, 1H), 3.64 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.3, 198.2, 170.5, 157.3, 155.9, 138.7, 136.1, 135.3, 135.2, 130.0, 129.5, 129.15, 128.8, 128.8, 128.2, 125.6, 124.5, 124.0, 123.6, 122.2, 121.6, 120.4, 113.1, 111.1, 102.4, 60.1, 56.2, 55.7, 49.3, 46.3 ppm. HRMS (ESI) calcd. for $C_{32}H_{25}O_4$ $[M + H]^+$ 473.1747, found: 473.1746.

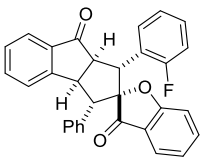
3'-phenyl-1'-(o-tolyl)-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5k)



5k

Brown solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 65.7 mg, 72% yield, m.p. 104.2-105.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.4, 1.3 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.34 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.17 – 7.13 (m, 1H), 7.07 (td, *J* = 8.0, 7.3, 2.2 Hz, 1H), 7.02 – 6.91 (m, 4H), 6.72 (t, *J* = 7.5 Hz, 1H), 4.73 (dd, *J* = 10.6, 8.4 Hz, 1H), 4.41 (d, *J* = 9.9 Hz, 1H), 3.89 (dd, *J* = 9.9, 8.4 Hz, 1H), 3.67 (d, *J* = 10.6 Hz, 1H), 2.32 (s, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 199.4, 171.0, 155.3, 138.0, 137.1, 135.4, 135.3, 134.8, 133.9, 130.3, 129.2, 129.1, 128.5, 128.4, 127.8, 127.1, 125.6, 125.4, 124.6, 123.8, 121.5, 121.5, 112.6, 103.0, 60.2, 58.5, 49.6, 49.0, 20.3 ppm. HRMS (ESI) calcd. for $C_{32}H_{25}O_3$ $[M + H]^+$ 457.1798, found: 457.1806.

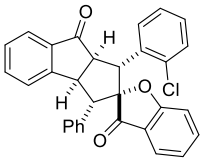
1'-(2-fluorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5l)



5l

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 75.5 mg, 82% yield, m.p. 134.6-135.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.40 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 7.28 – 7.25 (m, 1H), 7.23 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 7.09 – 7.03 (m, 1H), 7.02 – 6.95 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.89 – 6.84 (m, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 4.72 (dd, *J* = 10.5, 8.4 Hz, 1H), 4.34 (d, *J* = 9.9 Hz, 1H), 4.06 (dd, *J* = 9.9, 8.4 Hz, 1H), 3.68 (d, *J* = 10.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 198.5, 170.9, 161.0 (d, *J* = 248.0 Hz), 155.3, 138.0, 135.4, 135.3, 134.7, 130.6 (d, *J* = 3.5 Hz), 129.2, 129.1 (d, *J* = 8.5 Hz), 128.6, 128.4, 127.8, 125.4, 124.7, 123.9, 123.8 (d, *J* = 3.6 Hz), 122.2 (d, *J* = 13.2 Hz), 121.6, 121.4, 115.5 (d, *J* = 23.0 Hz), 112.5, 102.8, 59.7, 55.9, 49.5, 47.4 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}FO_3$ $[M + H]^+$ 461.1547, found: 461.1553.

1'-(2-chlorophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5m)

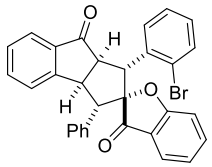


5m

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 73.5 mg, 77% yield, m.p. 227.5-228.3 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 – 7.80 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.32 – 7.21 (m, 5H), 7.22 – 7.10 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 4.85 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.07 (t, *J* = 8.9 Hz, 1H), 3.55 (d, *J* = 10.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.6, 197.9, 170.7, 155.7, 139.2, 136.3, 135.1, 134.9, 133.8, 133.7, 131.81, 129.5, 129.5, 129.4, 129.2, 128.9, 128.3, 127.3, 125.7, 124.6, 124.0, 122.6,

121.2, 113.3, 102.1, 60.0, 58.0, 49.2, 49.2 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}ClO_3$ [M + H]$^+$ 477.1252, found: 477.1249.

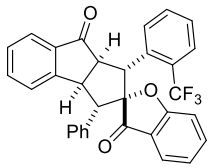
1'-(2-bromophenyl)-3'-phenyl-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5n)



5n

Yellow solid, 54.4 mg, 70 % yield, m.p. 226.6-227.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.42 (m, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.20 – 7.14 (m, 1H), 7.11 – 7.01 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 4.84 (t, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.02 (t, *J* = 9.0 Hz, 1H), 3.53 (d, *J* = 10.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 205.4, 197.8, 170.7, 155.8, 139.2, 136.3, 135.5, 135.1, 134.9, 132.9, 131.9, 129.7, 129.5, 129.3, 128.9, 128.3, 127.8, 125.7, 125.1, 124.6, 124.0, 122.6, 121.2, 113.3, 102.1, 60.1, 58.4, 51.8, 49.8 ppm. HRMS (ESI) calcd. for $C_{31}H_{22}BrO_3$ [M + H]$^+$ 521.0747, found: 521.0744.

3'-phenyl-1'-(2-(trifluoromethyl)phenyl)-1',3',3a',8a'-tetrahydro-3H,8'H-spiro[benzofuran-2,2'-cyclopenta[a]indene]-3,8'-dione (5o)

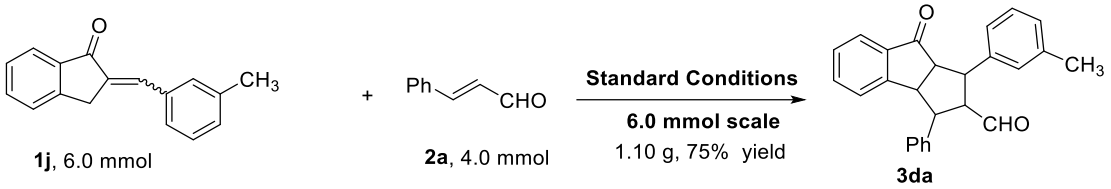


5o

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 5:1), 27.6 mg, 27% yield, m.p. 92.3-93.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$)δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.44 (q, *J* = 6.9 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.40 – 7.30 (m, 1H), 7.22 (dd, *J* = 8.2, 6.3 Hz, 4H), 7.20 – 7.13 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 4.69 (t, *J* = 9.2 Hz, 1H), 4.35 (d, *J* = 9.9 Hz, 1H), 3.90 (t, *J* = 9.1 Hz, 1H), 3.77 (d, *J* = 10.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 204.5, 197.2, 170.4, 155.6, 139.3, 136.3, 134.9, 134.9 (d, *J* = 13.4 Hz), 132.8, 132.4, 129.6, 129.3, 128.9, 128.4, 128.4 (d,

J = 6.6 Hz), 128.2, 126.0, 125.9, 125.7, 124.3 (q, *J* = 549.1, 274.7 Hz), 124.6, 124.0, 122.7, 121.1, 113.3, 101.8, 60.3, 60.0, 49.1, 48.7 ppm. HRMS (ESI) calcd. for $C_{32}H_{22}F_3O_3$ $[M + H]^+$ 511.1516, found: 511.1523.

5. Experimental procedures for gram-scale synthesis of compound 3da.

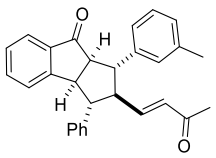


A mixture of DABCO (4.0 mmol, 1.0 equiv.), EtONa (4.0 mmol, 1.0 equiv.), **1j** (6.0 mmol, 1.5 equiv.) and **2a** (4.0 mmol, 1.0 equiv.) and dimethyl carbonate (20.0 mL) were added to a round-bottom flask equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 90 °C for the 24 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 10:1) to afford pure products **3da** in a 75% yield.

6. Experimental procedures for synthesis of compounds 6.

A mixture of **3da** (45 mg, 0.123 mmol, 1.0 equiv.), 1-(triphenylphosphoranylidene) propan-2-one (48.9 mg, 0.148 mmol, 1.2 equiv.) and chloroform (5 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 60 °C for the 12 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 15:1 to 3:1) to afford pure products **6**.

2-(3-oxobut-1-en-1-yl)-3-phenyl-1-(m-tolyl)-2,3,3a,8a-tetrahydrocyclopenta[a] inden-8(1H)-one (6)



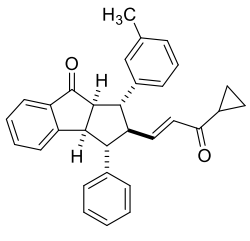
6

Yellow solid, 34.5 mg, 69% yield, m.p. 53.2-54.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.27 – 7.21 (m, 3H), 7.18 (s, 1H), 7.17 – 7.10 (m, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.36 (dd, *J* = 16.0, 7.9 Hz, 1H), 5.58 (d, *J* = 16.6 Hz, 1H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.52 – 3.27 (m, 2H), 3.15 (dd, *J* = 11.0, 8.4 Hz, 1H), 2.74 (dd, *J* = 11.5, 9.6 Hz, 1H), 2.31 (s, 3H), 1.92 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.49, 197.95, 155.49, 145.6, 141.1, 140.0, 138.4, 135.2, 135.1, 132.2, 129.1, 128.8, 128.6, 128.3, 128.0, 127.9, 127.5, 125.6, 124.8, 124.6, 60.7, 59.7, 59.0, 52.7, 52.4, 27.0, 21.6 ppm. HRMS (ESI) calcd. for $C_{29}H_{27}O_2$ $[M + H]^+$ 407.2006, found: 407.2006.

7. Experimental procedures for synthesis of compounds 7.

A mixture of **3da** (45 mg, 0.123 mmol, 1.0 equiv), 1-cyclopropyl-2-(triphenyl-lambda5-phosphanylidene)ethan-1-one (52.9 mg, 0.148 mmol, 1.2 equiv.) and chloroform (5 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 60 °C for the 12 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 20:1 to 8:1) to afford pure products **7**.

2-(3-cyclopropyl-3-oxoprop-1-en-1-yl)-3-phenyl-1-(m-tolyl)-2,3,3a,8a-tetrahydrocyclopenta [a]inden-8(1H)-one (7)



7

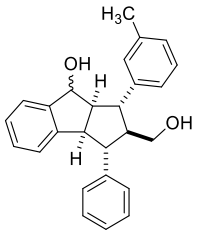
Yellow solid, 20.7 mg, 39% yield, m.p. 51.9-52.5 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 3H), 7.33

(t, *J* = 7.6 Hz, 2H), 7.26 (s, 1H), 7.24 – 7.13 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.56 (dd, *J* = 15.8, 8.7 Hz, 1H), 5.63 (d, *J* = 15.8 Hz, 1H), 4.12 (t, *J* = 9.0 Hz, 1H), 3.56 – 3.38 (m, 2H), 3.12 (dd, *J* = 10.9, 9.0 Hz, 1H), 2.86 (dd, *J* = 11.4, 9.6 Hz, 1H), 2.25 (s, 3H), 2.00 – 1.74 (m, 1H), 0.67 – 0.62 (m, 2H), 0.59 – 0.55 (m, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 206.6, 199.1, 156.4, 146.0, 142.2, 141.4, 137.9, 135.7, 135.5, 131.2, 129.2, 129.2, 128.8, 128.7, 128.7, 127.8, 127.4, 125.8, 125.8, 124.3, 61.3, 59.5, 58.5, 52.6, 52.6, 21.6, 18.5, 11.0, 10.94= ppm. HRMS (ESI) calcd. for $C_{31}H_{28}O_2$ [M + H]$^+$ 433.2162, found: 433.2160.

8. Experimental procedures for synthesis of compounds 8.

Solution of **3da** (45 mg, 0.123 mmol, 1.0 equiv.) in methanol (2 mL) was cooled to 0 ^{o}C. Then, sodium borohydride (14.0 mg, 0.369 mmol, 3 equiv.) was added to the solution at 0 ^{o}C and the resulting mixture was stirred at 0 ^{o}C for 1h, and quenched with saturated NH_4Cl aqueous solution (5 mL). The mixture was extracted with dichloromethane (5 mL x 3) and the combined organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc =15:1 to 5:1) to afford pure products **8**.

2-(hydroxymethyl)-3-phenyl-1-(m-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta [a]inden-8-ol (8)



8

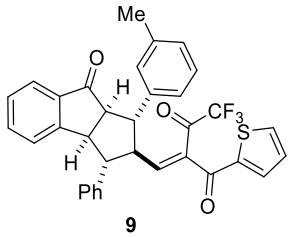
White solid, 44.6 mg, 98% yield, m.p. 167.9-168.9 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 7.23 – 7.09 (m, 6H), 6.97 (d, *J* = 6.9 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 3.77 (t, *J* = 8.7 Hz, 1H), 3.43 (q, *J* = 9.4 Hz, 1H), 3.35 – 3.20 (m, 3H), 2.95 (dd, *J* = 11.3, 8.1 Hz, 1H), 2.56 – 2.37 (m, 1H), 2.29 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 143.7, 143.6, 143.4, 138.5, 128.9, 128.8, 128.8,

128.8, 128.0, 127.5, 127.5, 126.7, 125.3, 125.1, 124.3, 75.4, 61.8, 60.4, 56.5, 56.3, 55.2, 47.1, 21.6 ppm. HRMS (ESI) calcd. for $C_{26}H_{27}O_2$ [M + H]$^+$ 371.2006, found: 371.2011.

9. Experimental procedures for synthesis of compounds 9.

A mixture of **3da** (45 mg, 0.123 mmol, 1.0 equiv.), 2-thenoyltrifluoroacetone (82.0 mg, 0.369 mmol, 3.0 equiv.), p-toluenesulfonic acid (10.5 mg, 0.061 mmol, 0.5 equiv.) and toluene (10 mL) were added to a sealed reaction tube equipped with a stir bar. The resulting mixture was stirred at 110 ^{o}C for the 10 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:EtOAc = 20:1 to 8:1) to afford pure products **9**.

4,4,4-trifluoro-2-((8-oxo-3-phenyl-1-(m-tolyl)-1,2,3,3a,8,8a-hexahydrocyclopenta [a]inden-2-yl)methylene)-1-(thiophen-2-yl)butane-1,3-dione (9)



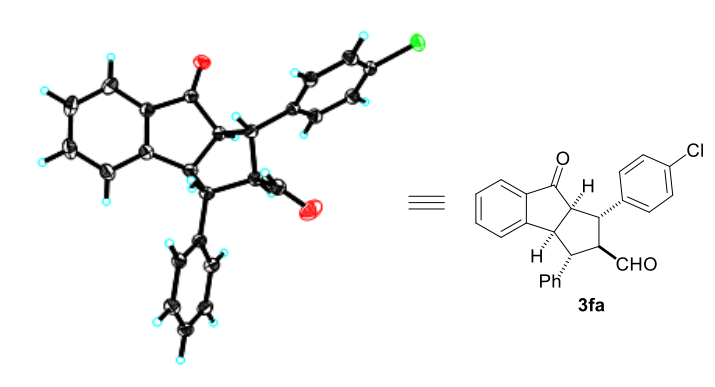
9

Red solid, 32.3 mg, 46% yield, m.p. 68.9-69.6 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 4.7 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.37 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 7.08 (d, J = 6.4 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.01 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.76 (dd, *J* = 15.4, 7.6 Hz, 1H), 6.31 (d, *J* = 15.4 Hz, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 3.59 – 3.45 (m, 2H), 3.27 (dd, *J* = 11.1, 8.5 Hz, 1H), 2.87 (dd, *J* = 11.6, 9.5 Hz, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 180.6, 154.6, 144.8, 143.9, 140.2, 139.2, 137.4, 134.2, 134.1, 132.7, 130.8, 128.0, 127.8, 127.7, 127.3, 127.1, 126.9, 126.9, 126.4, 125.7, 124.6, 123.9, 123.5, 60.0, 58.6, 58.0, 51.5, 51.4, 20.6 ppm. HRMS (ESI) calcd. for $C_{34}H_{26}F_3O_3S$ [M + H]$^+$ 571.1549, found: 571.1542.

10. X-ray crystal structure of compound 3fa

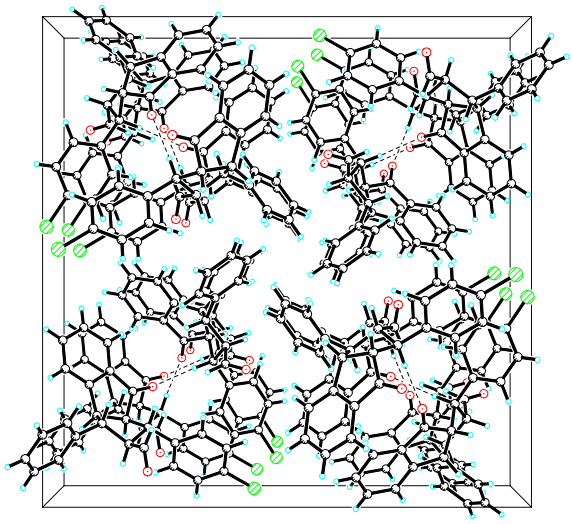
Crystal data for compound **3fa**: $C_{25}H_{19}ClO_2$, *M* = 386.85, *a* = 22.4516(5) Å, *b* =

22.4516(5) Å, c = 7.6085(2) Å, α = 90°, β = 90°, γ = 90°, V = 3835.2(2) Å^3, T = 150.(2) K, space group P-421c, Z = 8, μ(Cu Kα) = 1.900 mm^{-1}, 42858 reflections measured, 3751 independent reflections (R_{int} = 0.3123). The final R_1 values were 0.0466 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0790 ($I > 2\sigma(I)$). The final R_1 values were 0.0773 (all data). The final $wR(F^2)$ values were 0.0880 (all data). The goodness of fit on F^2 was 1.047. Flack parameter = 0.071(18).



View of a molecule of compound **3fa** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of compound **3fa**.

Hydrogen-bonds are shown as dashed lines.

Table S2. Crystal data and structure refinement for compound **3fa**.

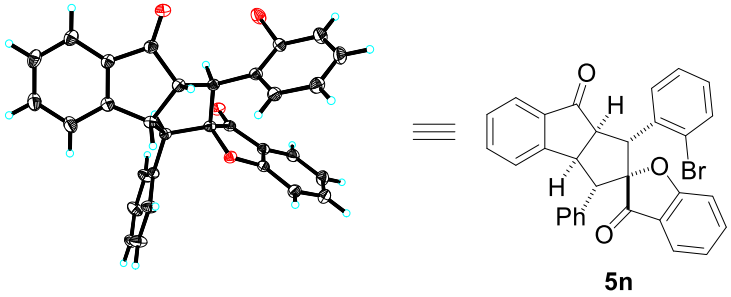
Identification code	global
Empirical formula	C_{25} H_{19} Cl O_2
Formula weight	386.85

Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	P-42$_1$c	
Unit cell dimensions	a = 22.4516(5) Å	α= 90°.
	b = 22.4516(5) Å	β= 90°.
	c = 7.6085(2) Å	γ = 90°.
Volume	3835.2(2) Å^3	
Z	8	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	1.900 mm^{-1}	
F(000)	1616	
Crystal size	0.680 x 0.010 x 0.010 mm^3	
Theta range for data collection	2.78 to 72.38°.	
Index ranges	-27<=h<=27, -27<=k<=27, -9<=l<=7	
Reflections collected	42858	
Independent reflections	3751 [R(int) = 0.3123]	
Completeness to theta = 72.38°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3751 / 0 / 253	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.0790	
R indices (all data)	R1 = 0.0773, wR2 = 0.0880	
Absolute structure parameter	0.071(18)	
Largest diff. peak and hole	0.230 and -0.222 e.Å^{-3}	

11. X-ray crystal structure of compound 5n

rystal data for compound **5n**: $C_{31}H_{21}BrO_3$, M = 521.39, a = 12.3698(5) Å, b = 17.4754(8) Å, c = 12.4146(5) Å, α = 90°, β = 117.668(2)°, γ = 90°, V = 2376.76(18) Å^3,

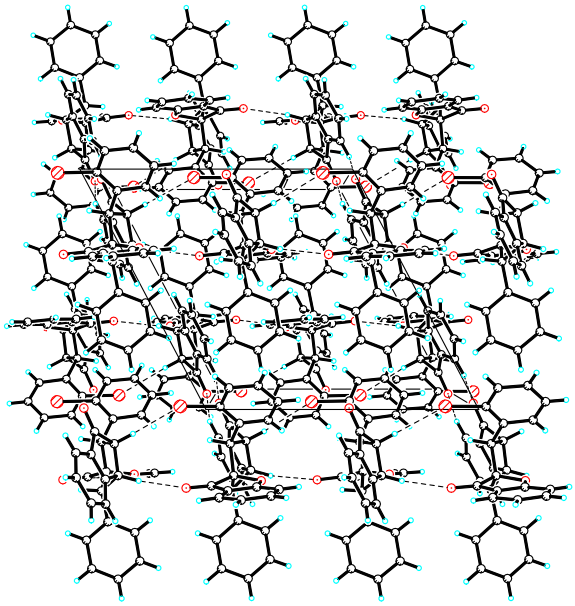
T = 150.(2) K, space group $P121/c1$, Z = 4, μ(Cu Kα) = 2.611 mm^{-1}, 37763 reflections measured, 4381 independent reflections (R_{int} = 0.0679). The final R_1 values were 0.0816 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2020 ($I > 2\sigma(I)$). The final R_1 values were 0.1129 (all data). The final $wR(F^2)$ values were 0.2545 (all data). The goodness of fit on F^2 was 1.200.



5n

View of a molecule of compound **5n** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of compound **5o**.

Hydrogen-bonds are shown as dashed lines.

Table S3. Crystal data and structure refinement for compound **5o**.

Identification code	global
Empirical formula	C_{31} H_{21} Br O_3
Formula weight	521.39

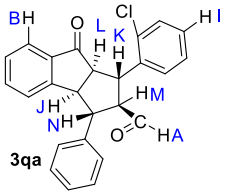
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.3698(5) Å	α= 90°.
	b = 17.4754(8) Å	β= 117.668(2)°.
	c = 12.4146(5) Å	γ = 90°.
Volume	2376.76(18) $Å^3$	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	2.611 mm^{-1}	
F(000)	1064	
Crystal size	0.660 x 0.500 x 0.480 mm^3	
Theta range for data collection	6.47 to 72.14°.	
Index ranges	-14<=h<=15, -21<=k<=21, -15<=l<=14	
Reflections collected	37763	
Independent reflections	4381 [R(int) = 0.0679]	
Completeness to theta = 72.14°	93.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.37 and 0.10	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4381 / 0 / 317	
Goodness-of-fit on F^2	1.200	
Final R indices [I>2sigma(I)]	R1 = 0.0816, wR2 = 0.2020	
R indices (all data)	R1 = 0.1129, wR2 = 0.2545	
Extinction coefficient	0.052(4)	
Largest diff. peak and hole	1.529 and -1.764 $e.Å^{-3}$	

Reference:

1. (a) T. M. Kadayat, S. Banskota, P. Gurung, G. Bist, T. B. T. Magar, A. Shrestha, J.-A. Kim, E.-S. Lee, *Eur. J. Med. Chem*., **2017**, *137*, 575-597; (b) B. Lantaño, J. M. Aguirre, E. V. Drago, M. Bollini, D. J. de la Faba, J. D. Mufato, *Synthetic Commun*., **2017**, *47*, 2202-2214.

12. 2D NMR Analysis of 3qa, 3ra and 5n

Table S4. H NMR signal assignment of **3qa**



No.	δ	No.	δ
A	9.43 (d, *J* = 4.2 Hz, 1H)	**H**	7.34 – 7.28 (m, 2H)
B	7.92 (dd, *J* = 7.9, 1.6 Hz, 1H)	**I**	7.00 (dd, *J* = 7.6, 0.9 Hz, 1H)
C	7.72 – 7.67 (m, 1H)	**J**	4.35 (t, *J* = 8.9 Hz, 1H)
D	7.66 – 7.61 (m, 1H)	**K**	4.11 (dd, *J* = 10.9, 8.7 Hz, 1H)
E	7.53 – 7.49 (m, 3H)	**L**	3.77 (t, *J* = 8.5 Hz, 1H)
F	7.48 – 7.43 (m, 3H)	**M**	3.55 (td, *J* = 11.3, 4.3 Hz, 1H)
G	7.42 – 7.40 (m, 2H)	**N**	3.45 (dd, *J* = 11.6, 9.4 Hz, 1H)

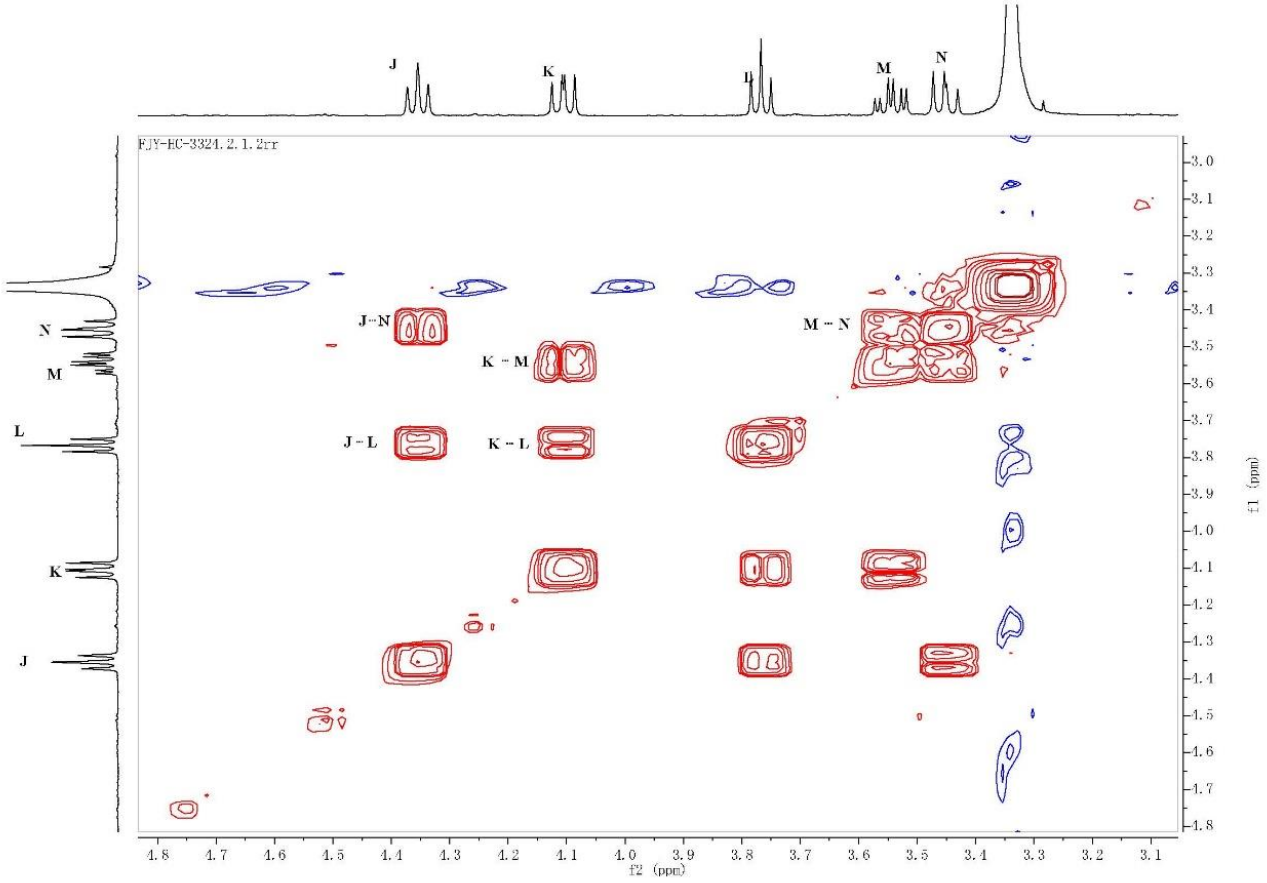


Figure S1. COSY spectrum of **3qa** (500 MHz, DMSO-d_6)

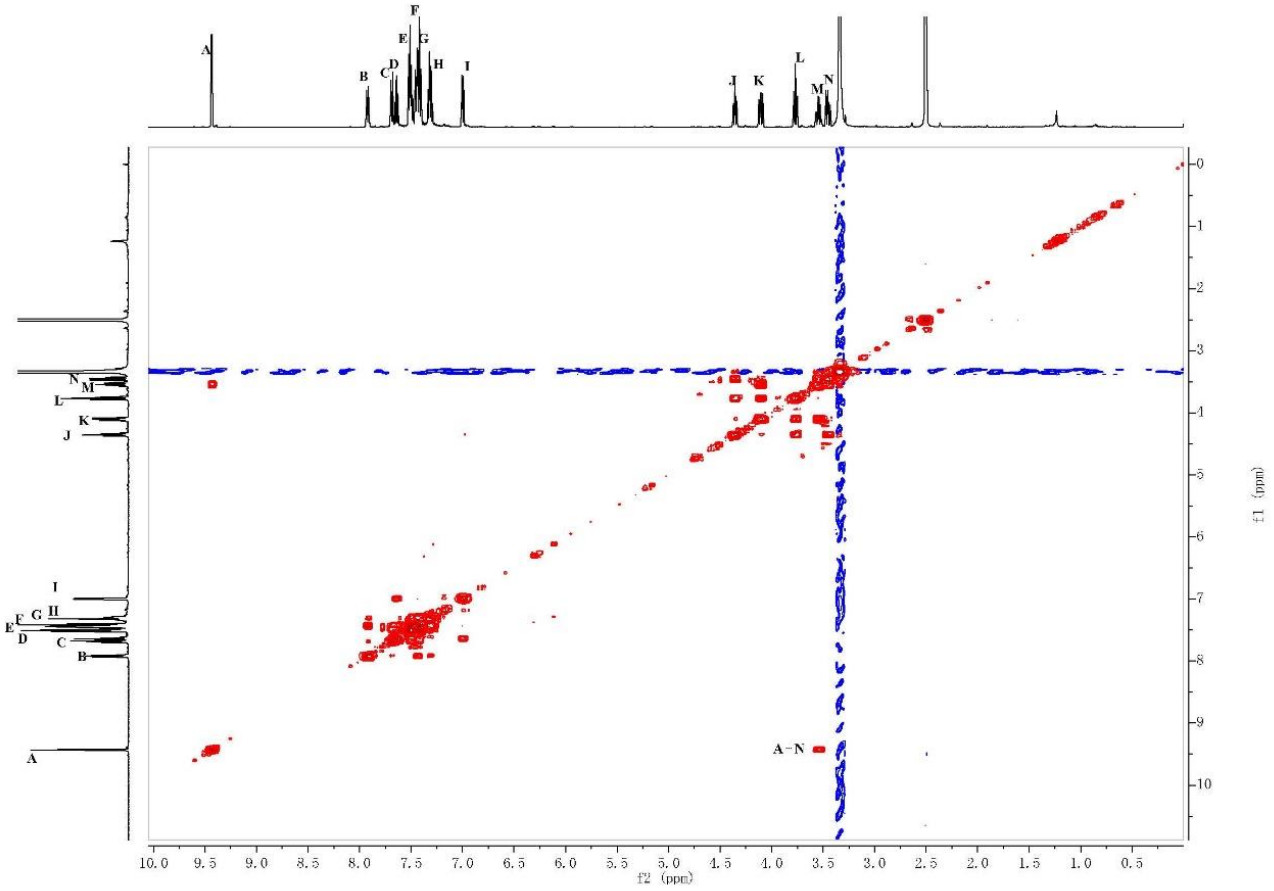
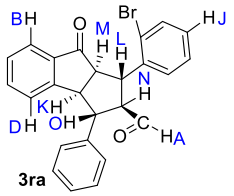


Figure S2. COSY spectrum of **3qa** (500 MHz, DMSO-d_6)

Table S5. H NMR signal assignment of **3ra**



3ra

No.	δ	No.	δ
A	9.46 (d, *J* = 4.2 Hz, 1H)	**H**	7.32 (t, *J* = 7.3 Hz, 1H)
B	7.93 (dd, *J* = 7.9, 1.7 Hz, 1H)	**I**	7.23 (td, *J* = 7.6, 1.6 Hz, 1H)
C	7.69 (d, *J* = 7.6 Hz, 1H)	**J**	7.00 (d, *J* = 7.6 Hz, 1H)
D	7.66 – 7.60 (m, 2H)	**K**	4.36 (t, *J* = 8.9 Hz, 1H)
E	7.55 – 7.51 (m, 2H)	**L**	4.09 (dd, *J* = 10.9, 8.7 Hz, 1H)
F	7.50 – 7.44 (m, 2H)	**M**	3.76 (t, *J* = 8.5 Hz, 1H)
G	7.42 (t, *J* = 7.6 Hz, 2H)	**N**	3.54 (td, *J* = 11.2, 4.3 Hz, 1H)
		O	3.46 (dd, *J* = 11.6, 9.3 Hz, 1H)

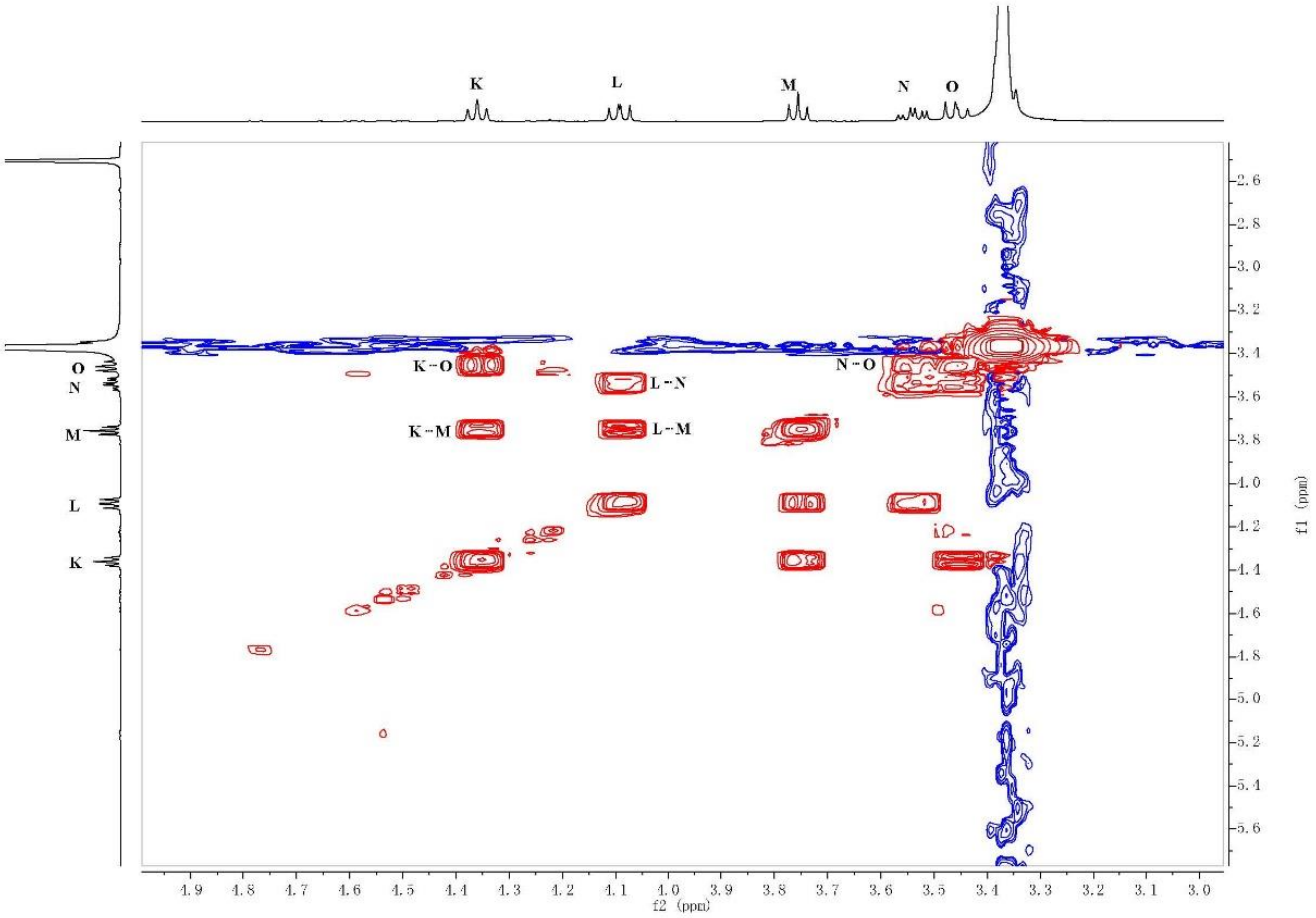


Figure S3. COSY spectrum of **3ra** (500 MHz, DMSO-d_6)

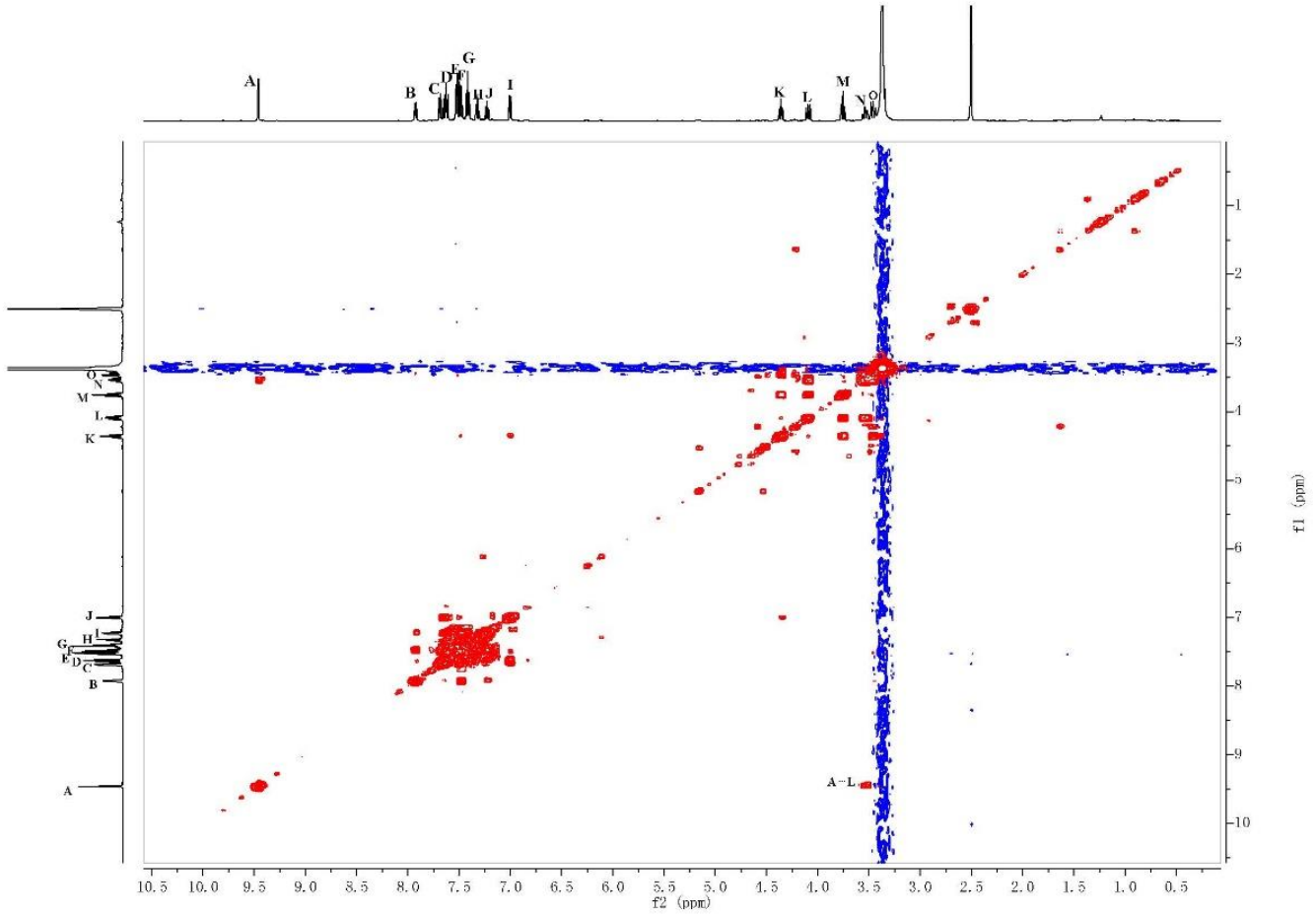
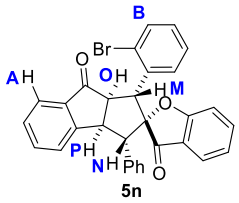


Figure S4. COSY spectrum of **3ra** (500 MHz, DMSO-d_6)

Table S6. H NMR signal assignment of **5n**



5n

No.	δ	No.	δ
A	7.84 (dd, *J* = 8.1, 1.7 Hz, 1H)	**I**	7.20 – 7.13 (m, 1H)
B	7.74 (d, *J* = 7.6 Hz, 1H)	**J**	7.11 – 7.01 (m, 2H)
C	7.63 (td, *J* = 7.5, 1.3 Hz, 1H)	**K**	6.93 (d, *J* = 7.7 Hz, 1H)
D	7.54 (d, *J* = 7.5 Hz, 1H)	**L**	6.84 (t, *J* = 7.4 Hz, 1H)
E	7.52 – 7.46 (m, 1H)	**M**	4.83 (dd, *J* = 10.8, 8.4 Hz, 1H)
F	7.44 (dd, *J* = 8.0, 1.3 Hz, 1H)	**N**	4.53 (d, *J* = 9.6 Hz, 1H)
G	7.39 – 7.36 (m, 2H)	**O**	4.02 (t, *J* = 9.0 Hz, 1H)
H	7.33 – 7.21 (m, 4H)	**P**	3.53 (d, *J* = 10.8 Hz, 1H)

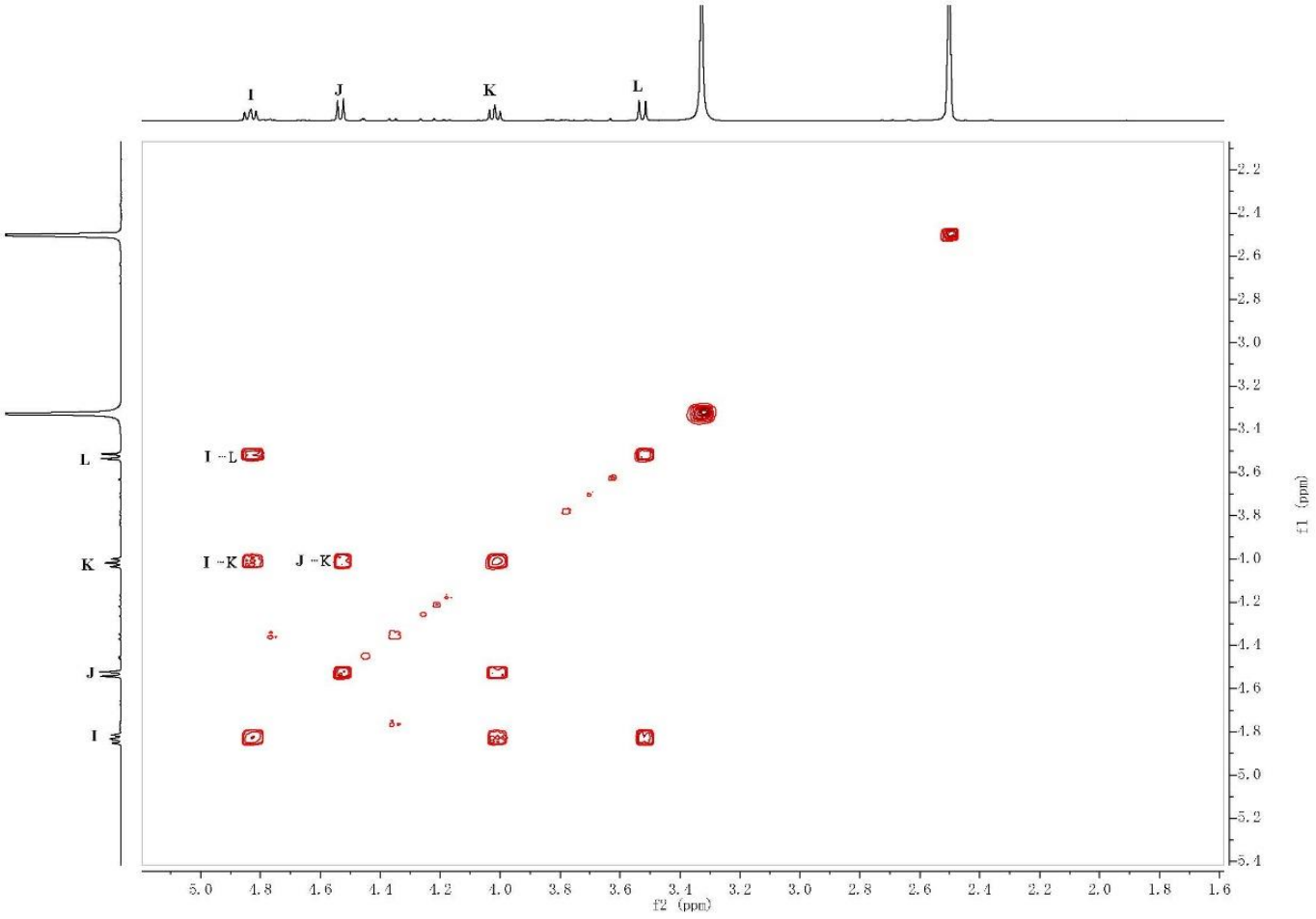

I
J
K
L
I --L
I --K
J --K
f2 (ppm)
f1 (ppm)

Figure S5. COSY spectrum of **5n** (500 MHz, DMSO-d_6)

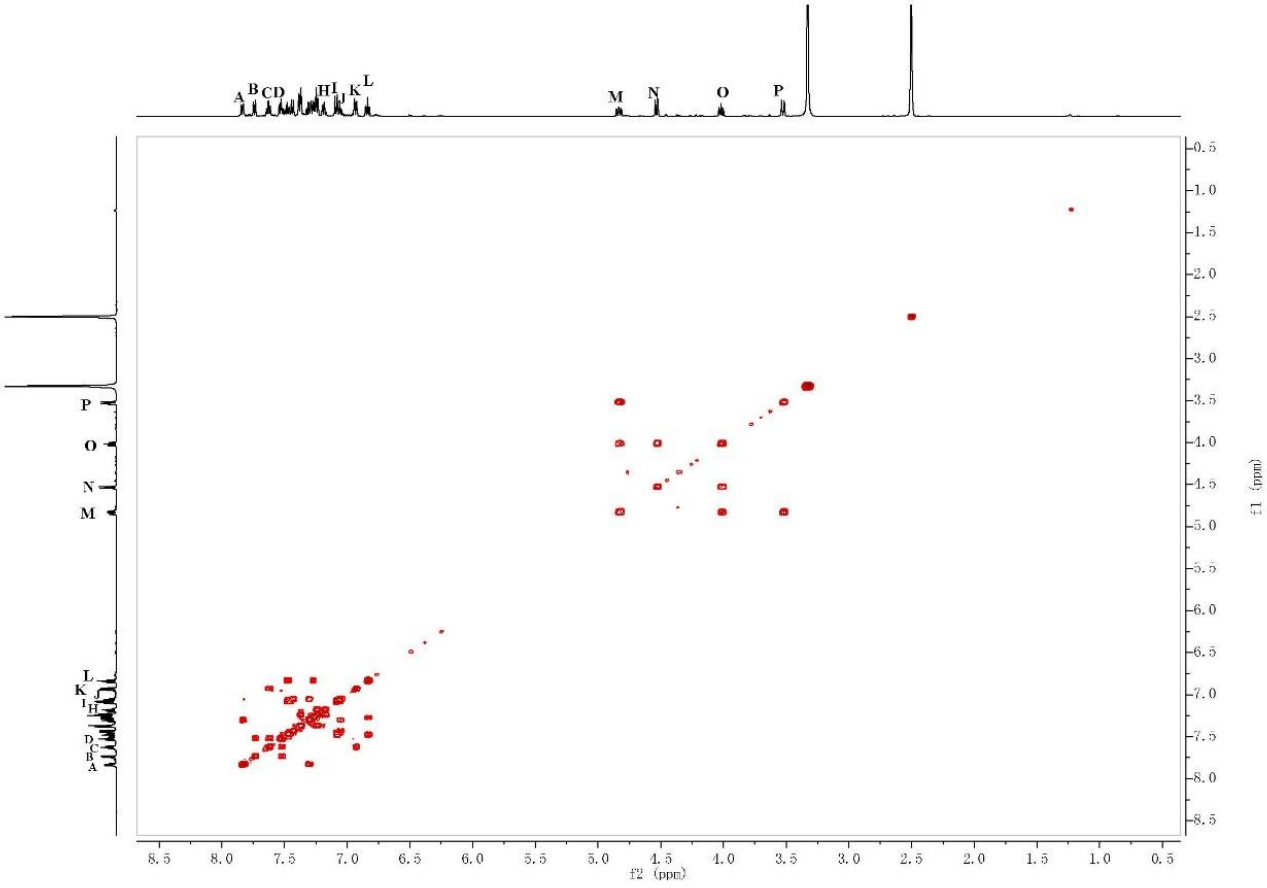
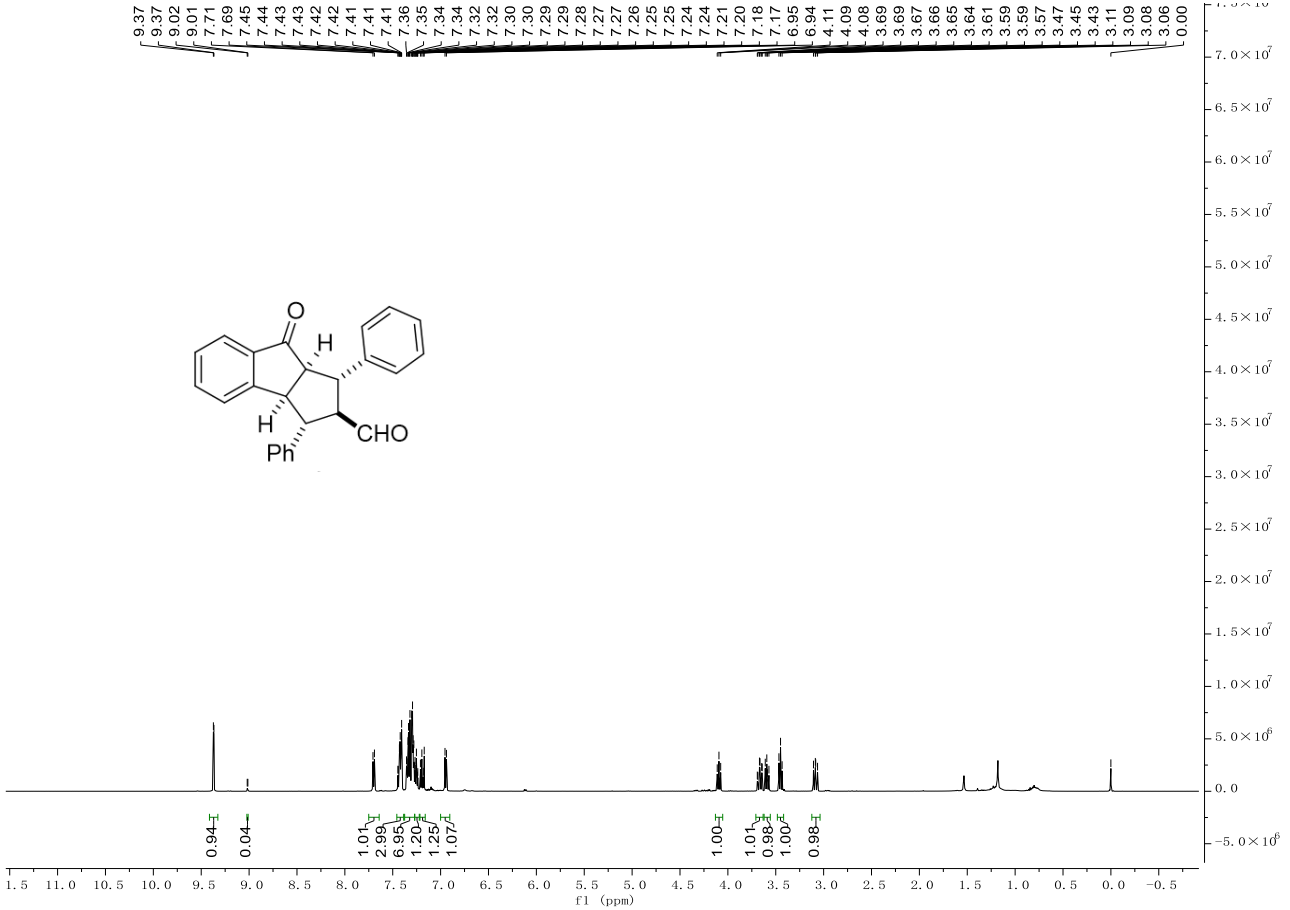


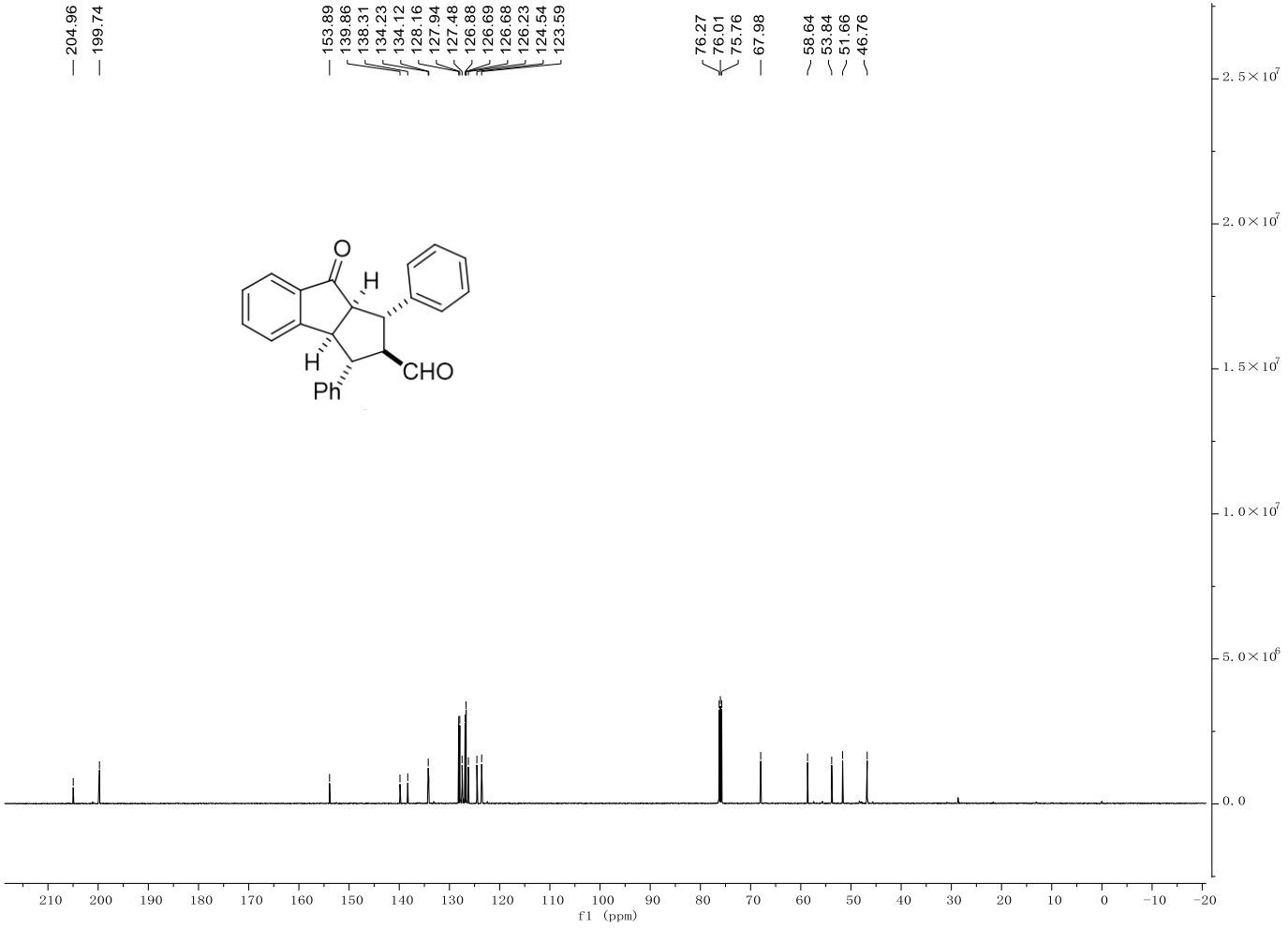
Figure S6. COSY spectrum of **5n** (500 MHz, DMSO-d_6)

13. NMR spectra

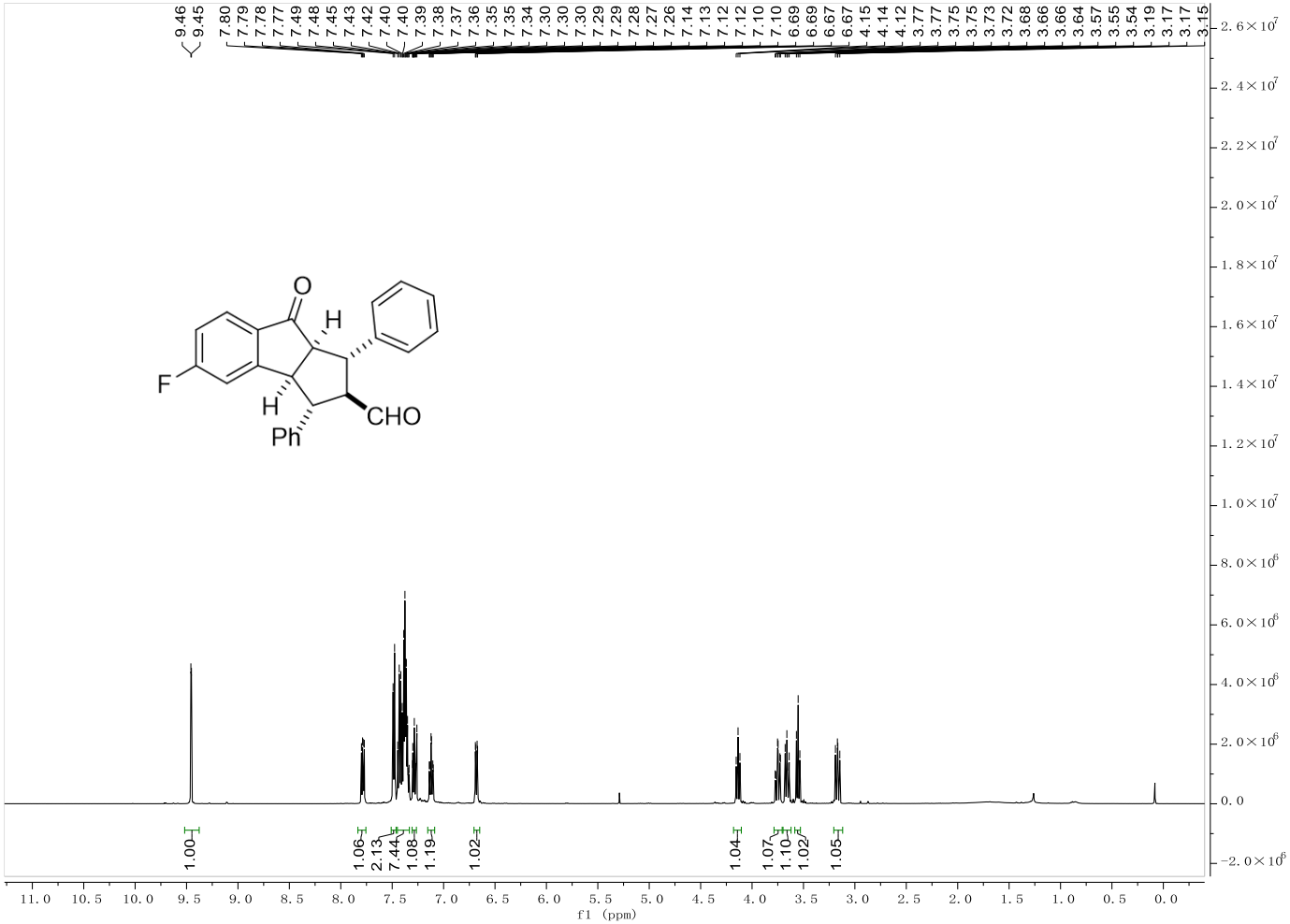
^{1}H NMR spectrum of **3aa** (500 MHz, $CDCl_3$)



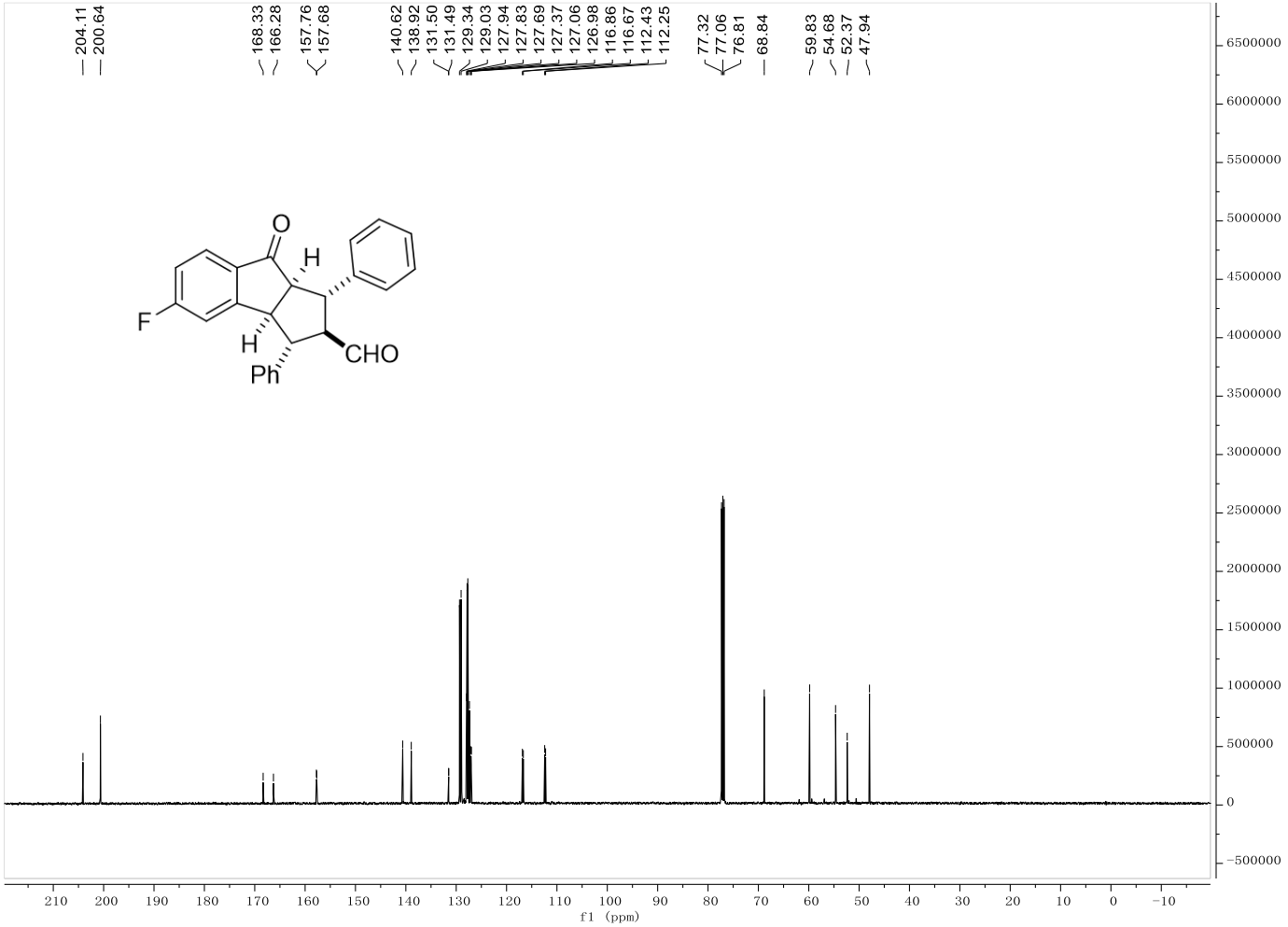
^{13}C NMR spectrum of **3aa** (125 MHz, $CDCl_3$)



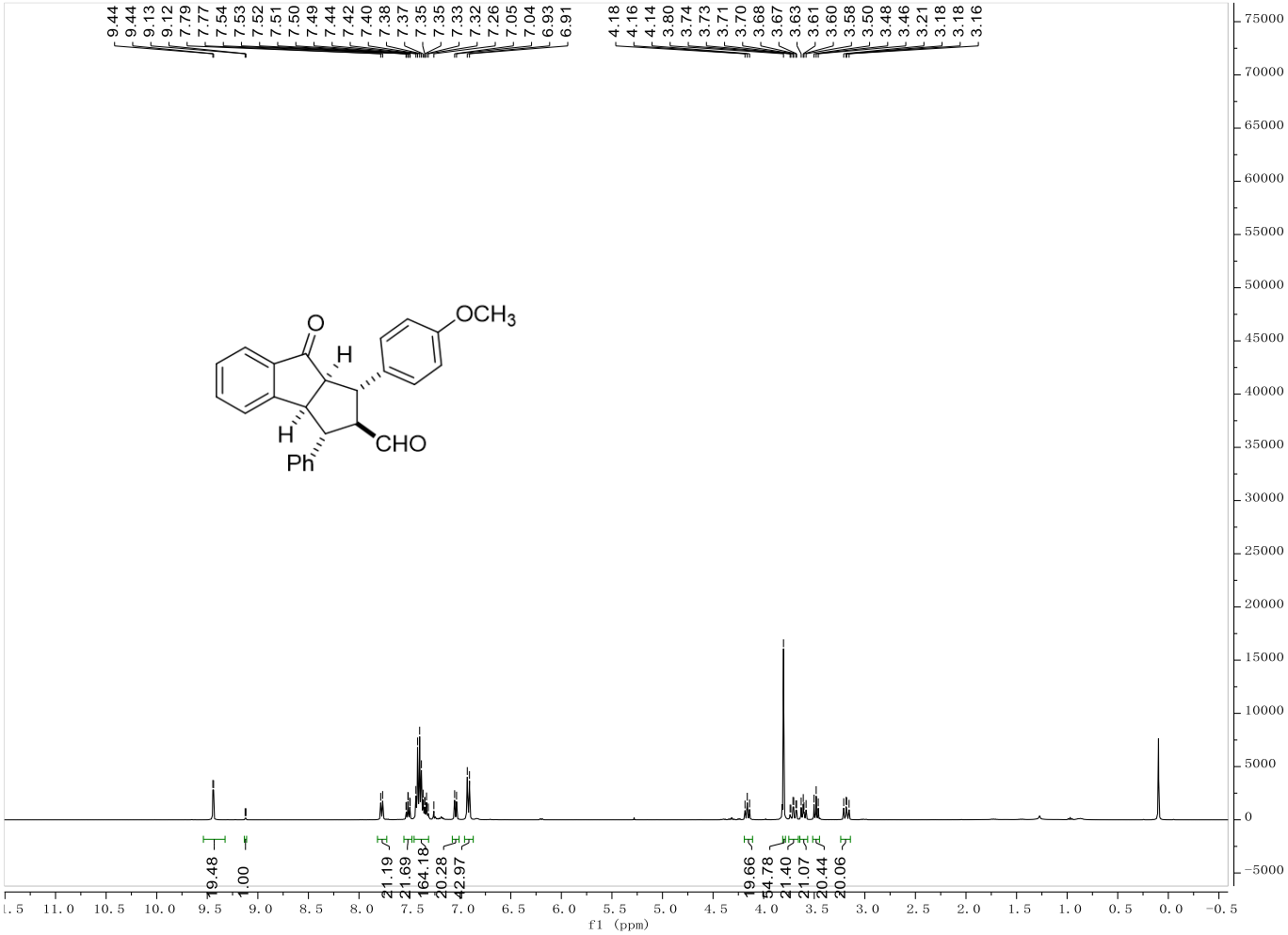
^{1}H NMR spectrum of **3ba** (500 MHz, $CDCl_3$)



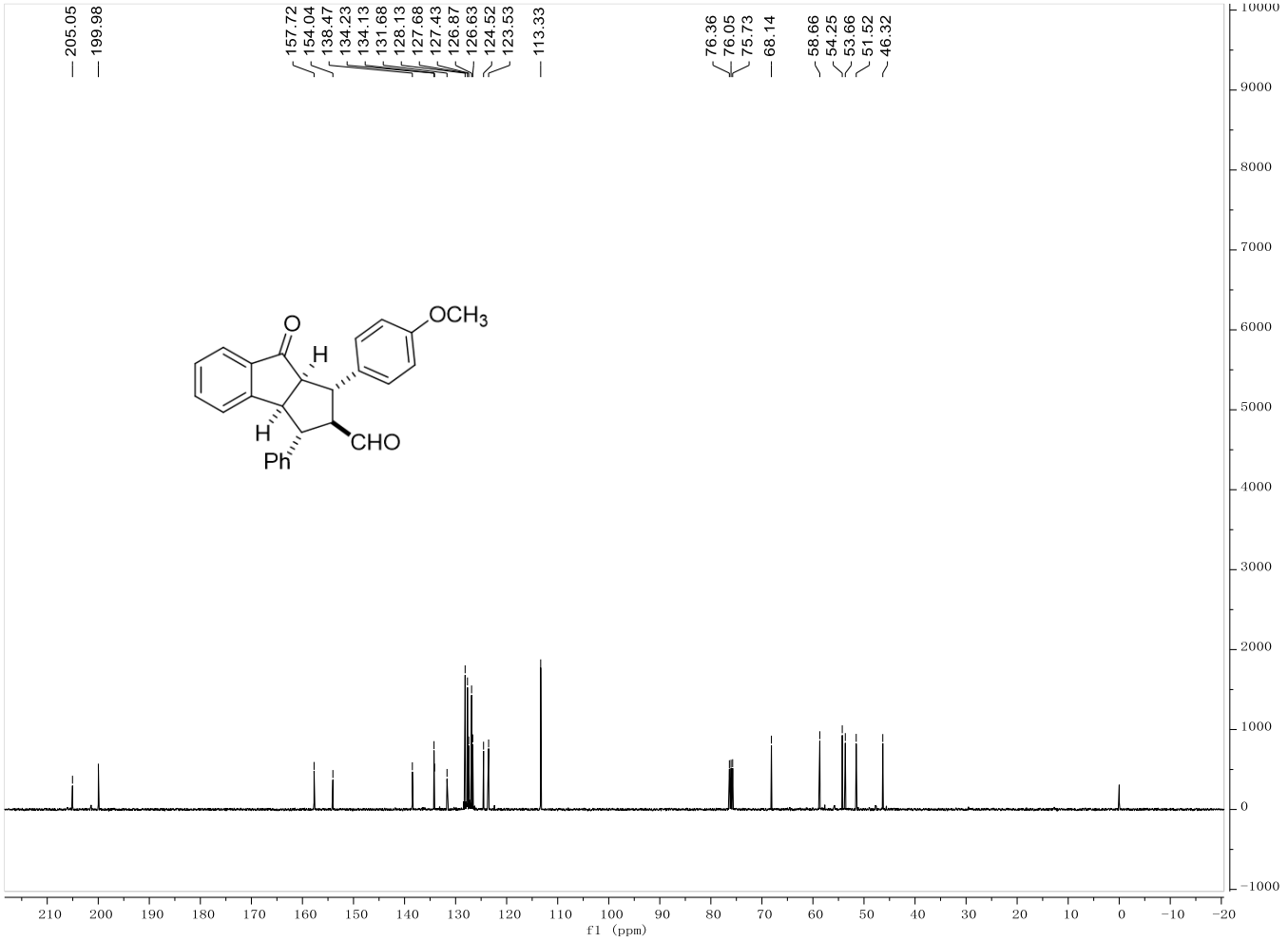
^{13}C NMR spectrum of **3ba** (125 MHz, $CDCl_3$)



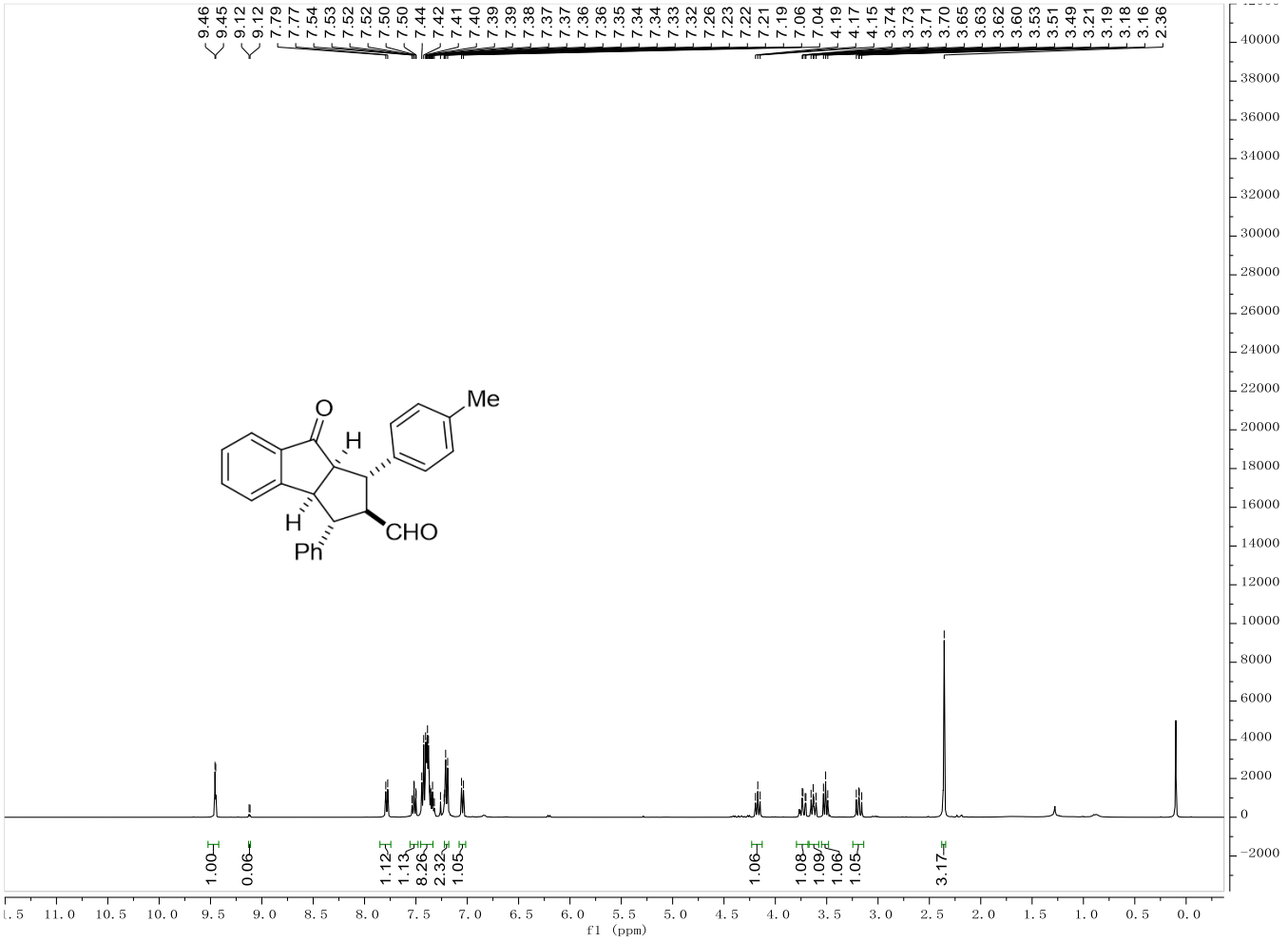
^{1}H NMR spectrum of **3ca** (400 MHz, $CDCl_3$)



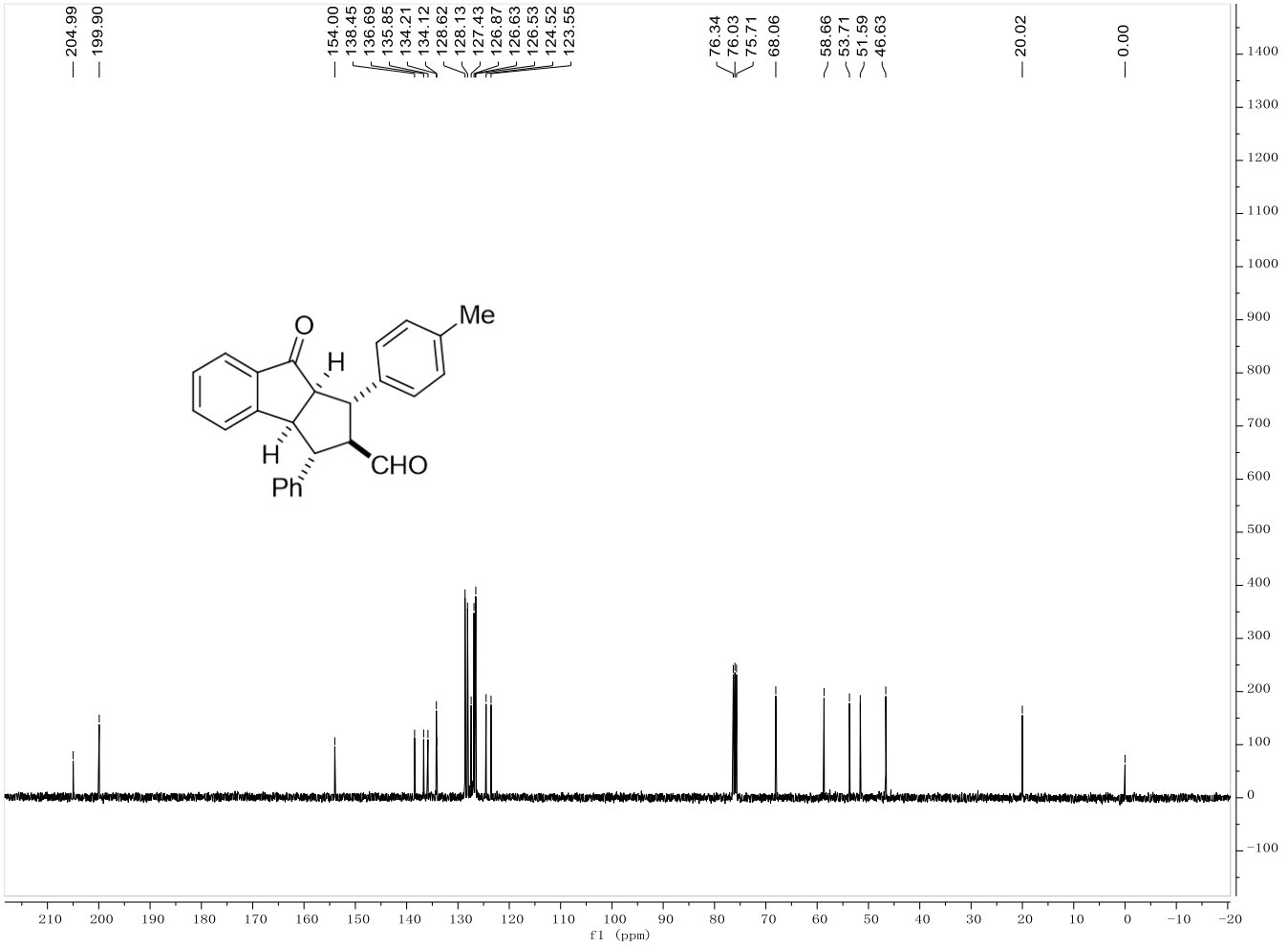
^{13}C NMR spectrum of **3ca** (100 MHz, $CDCl_3$)



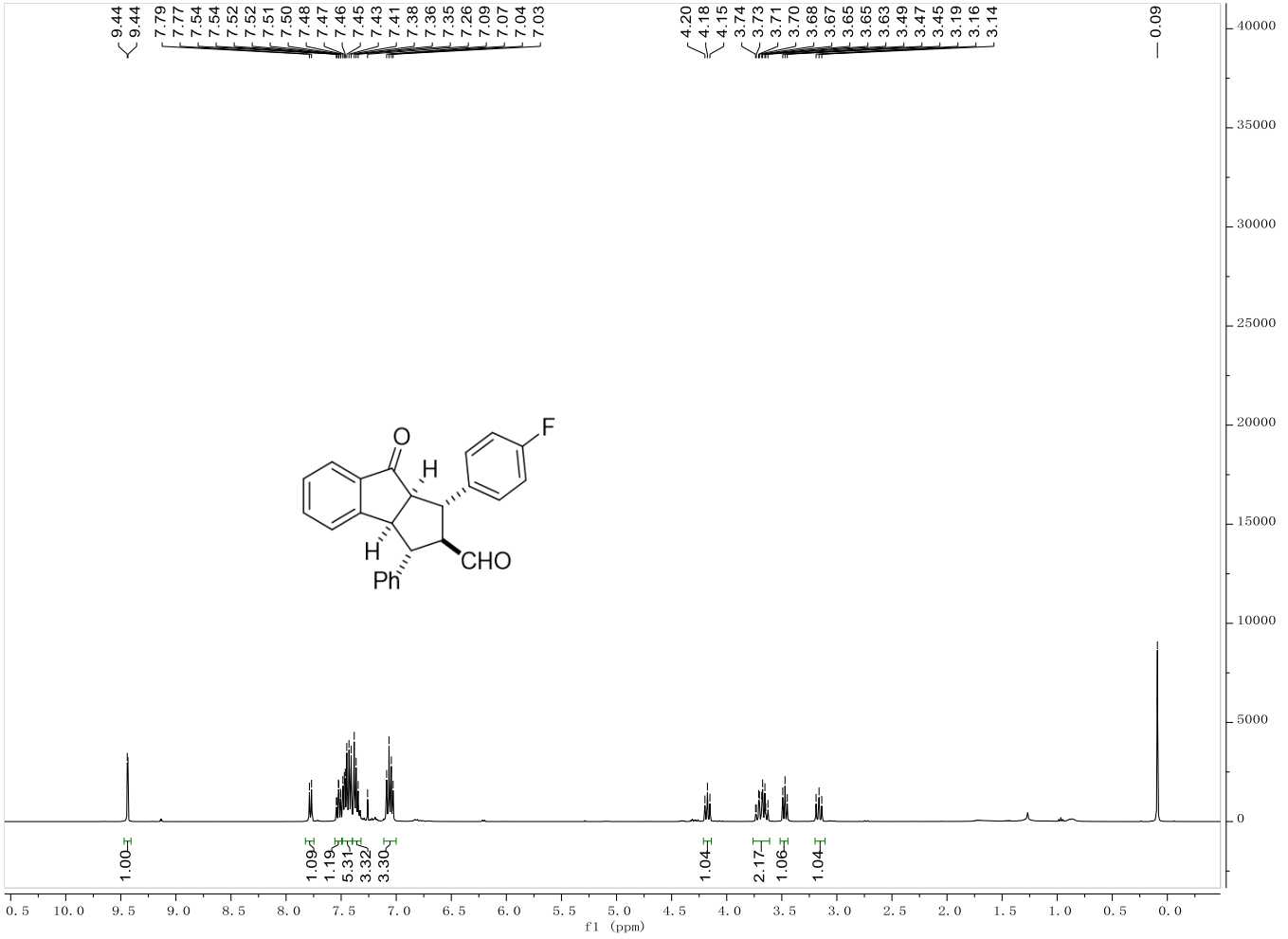
^{1}H NMR spectrum of **3da** (400 MHz, $CDCl_3$)



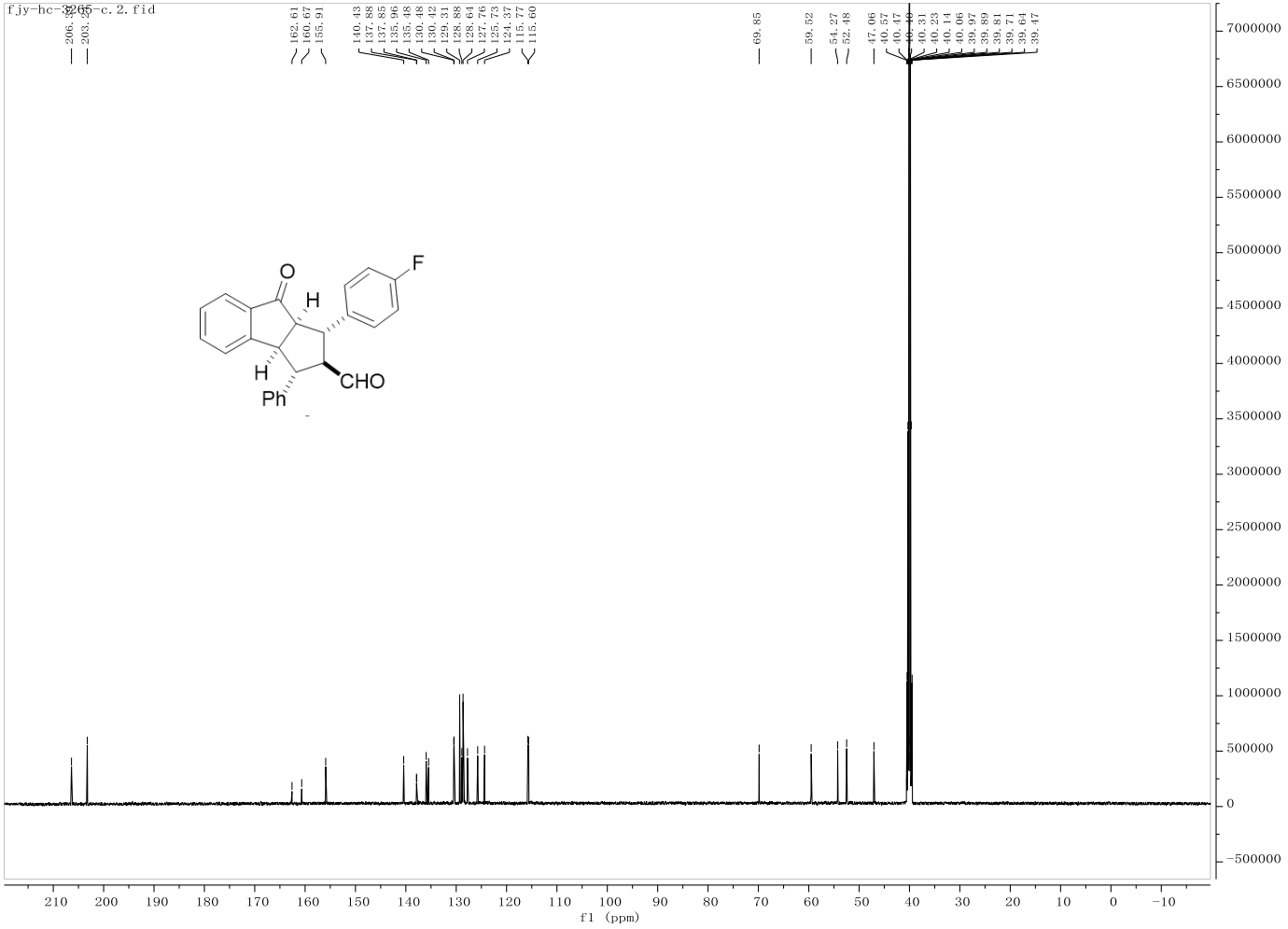
^{13}C NMR spectrum of **3da** (100 MHz, $CDCl_3$)



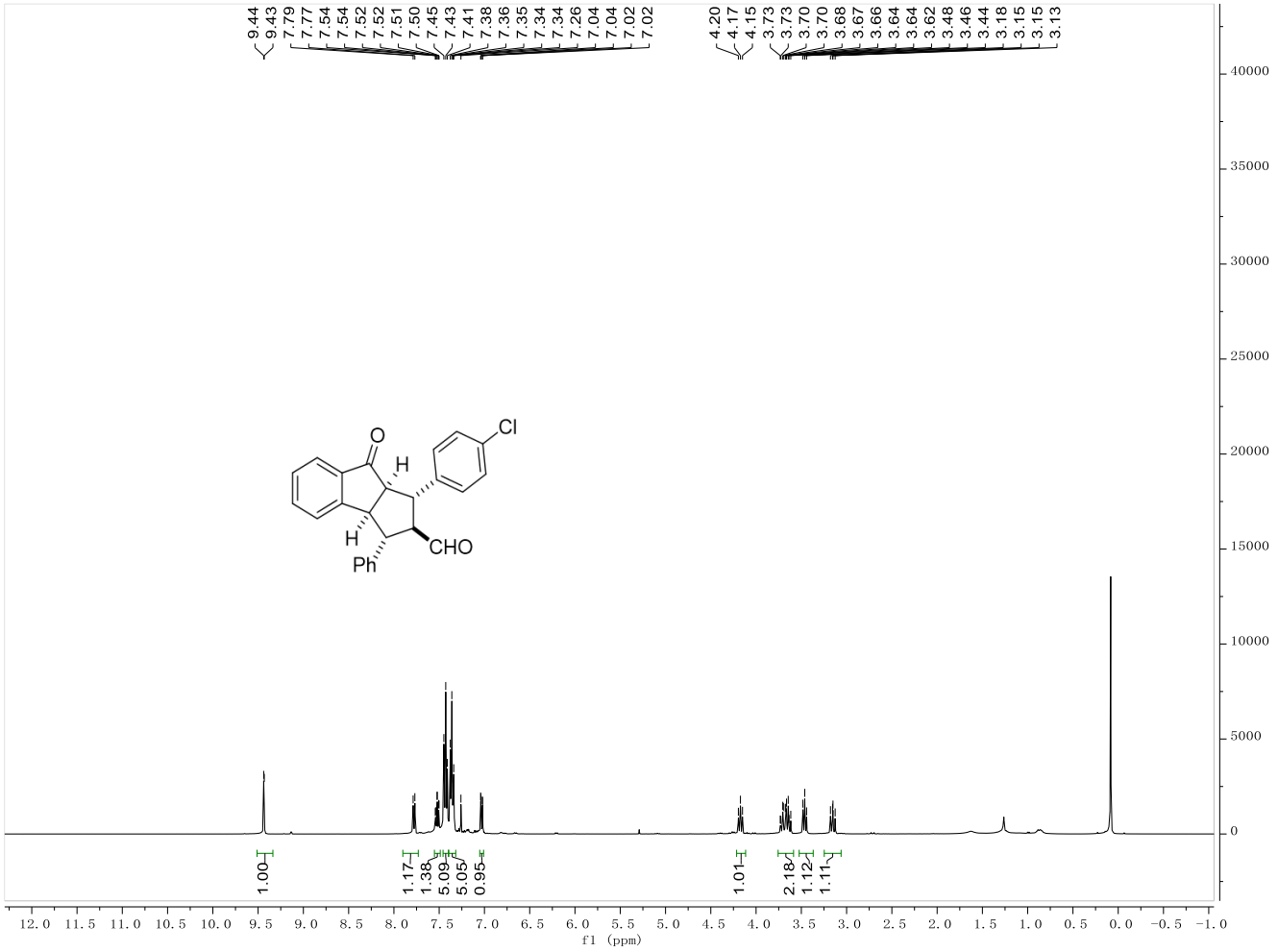
^{1}H NMR spectrum of **3ea** (400 MHz, $CDCl_3$)



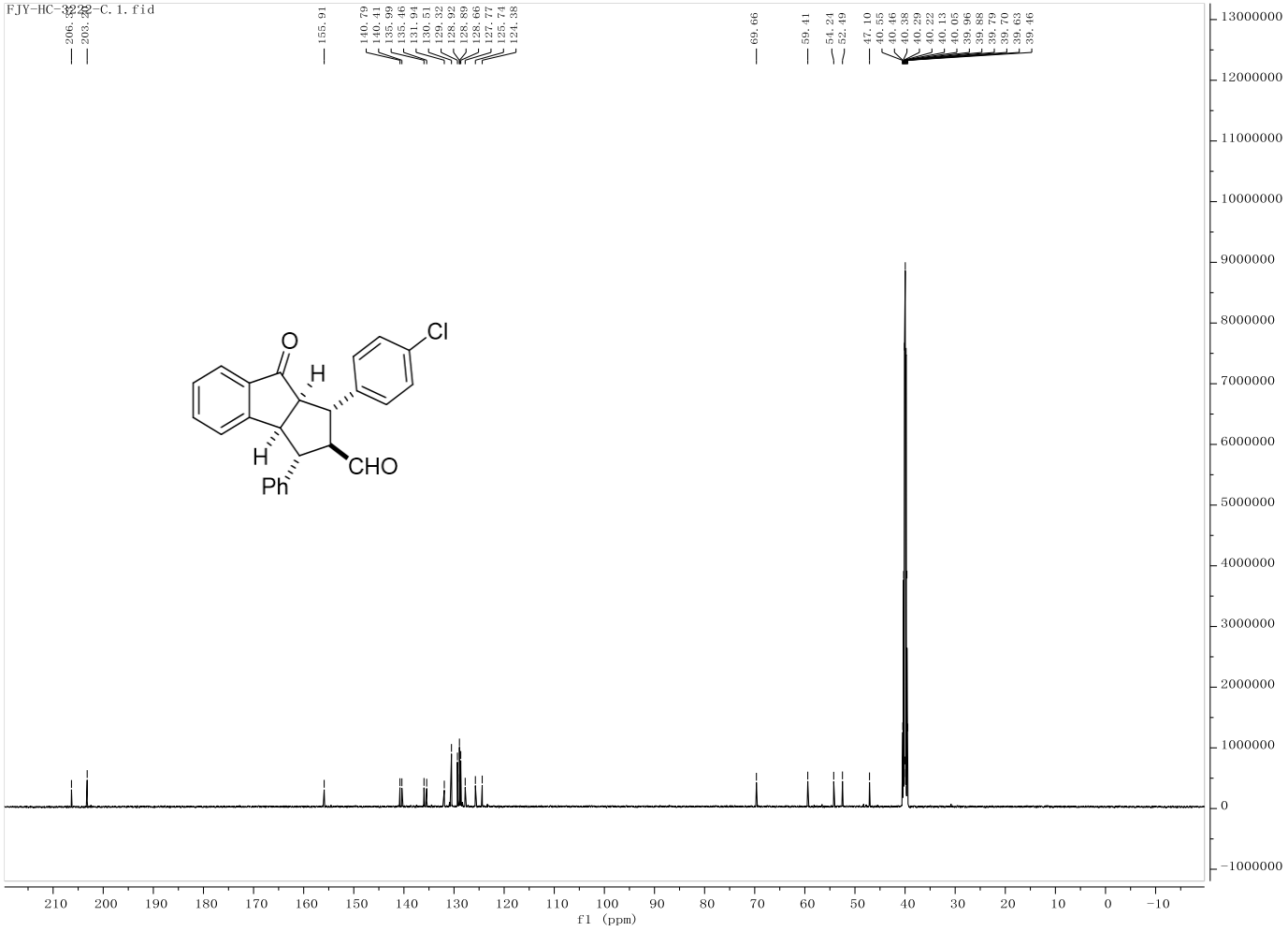
^{13}C NMR spectrum of **3ea** (125 MHz, DMSO-d_6)



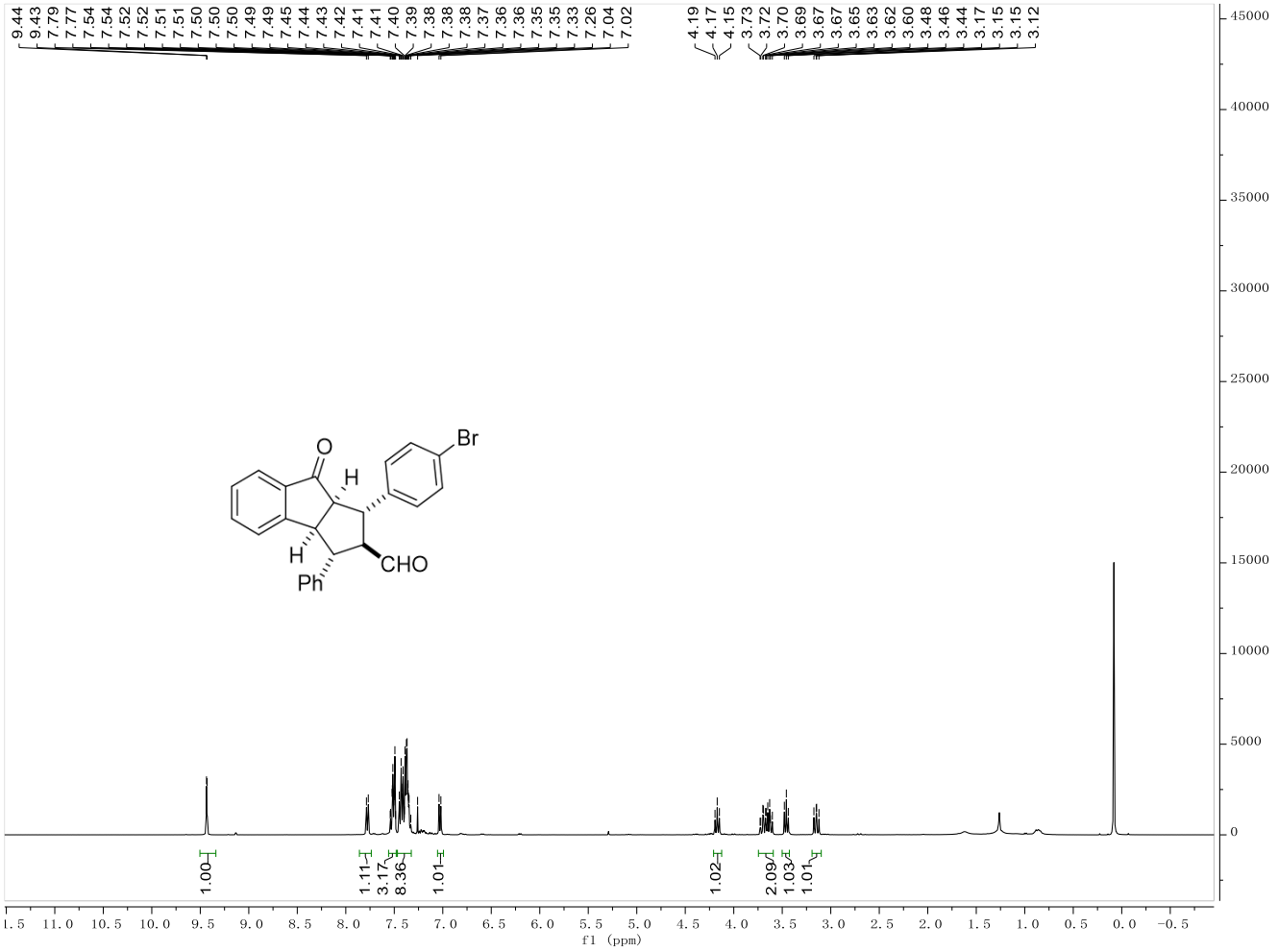
^{1}H NMR spectrum of **3fa** (400 MHz, $CDCl_3$)



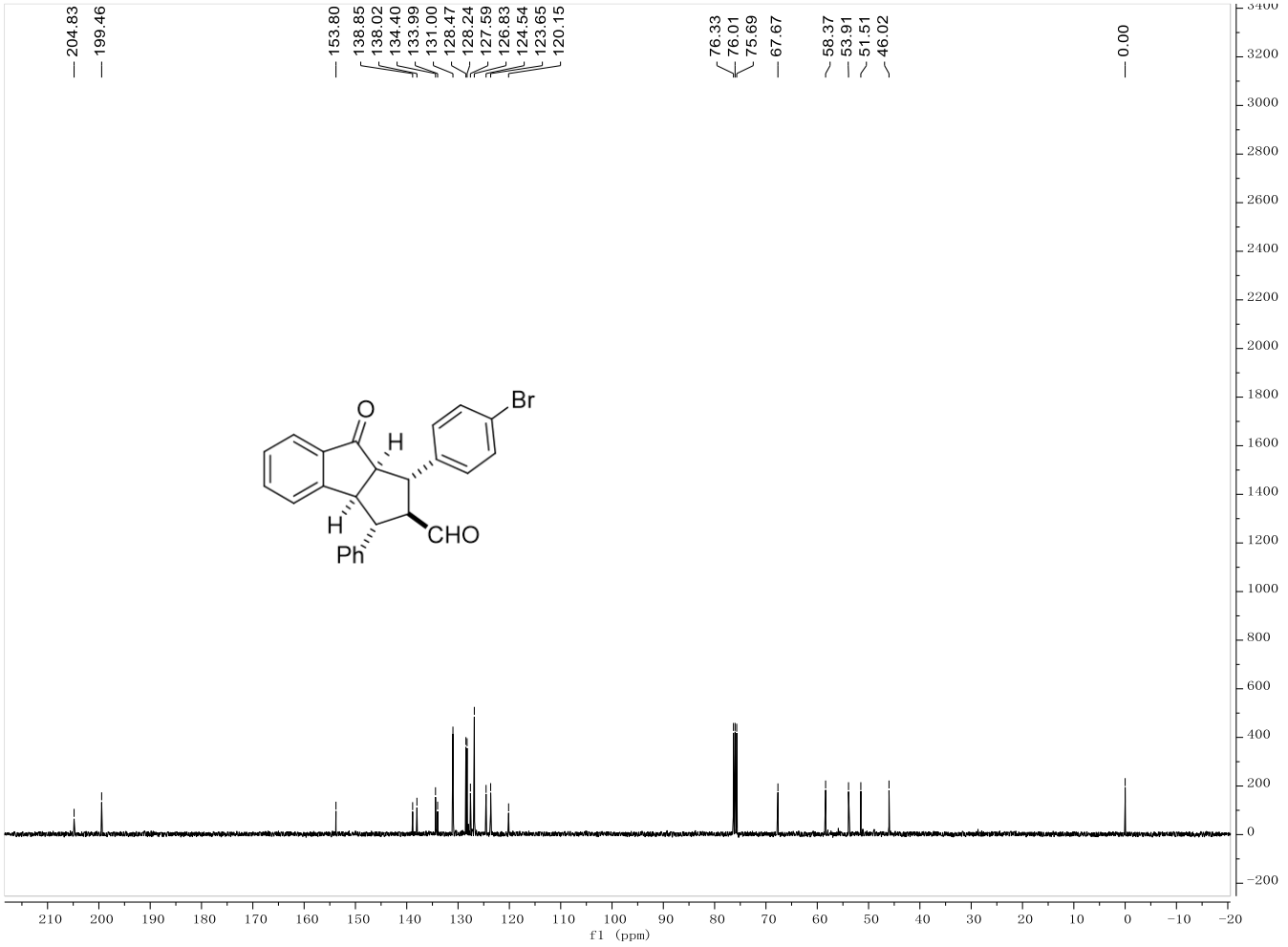
^{13}C NMR spectrum of **3fa** (125 MHz, DMSO-d_6)



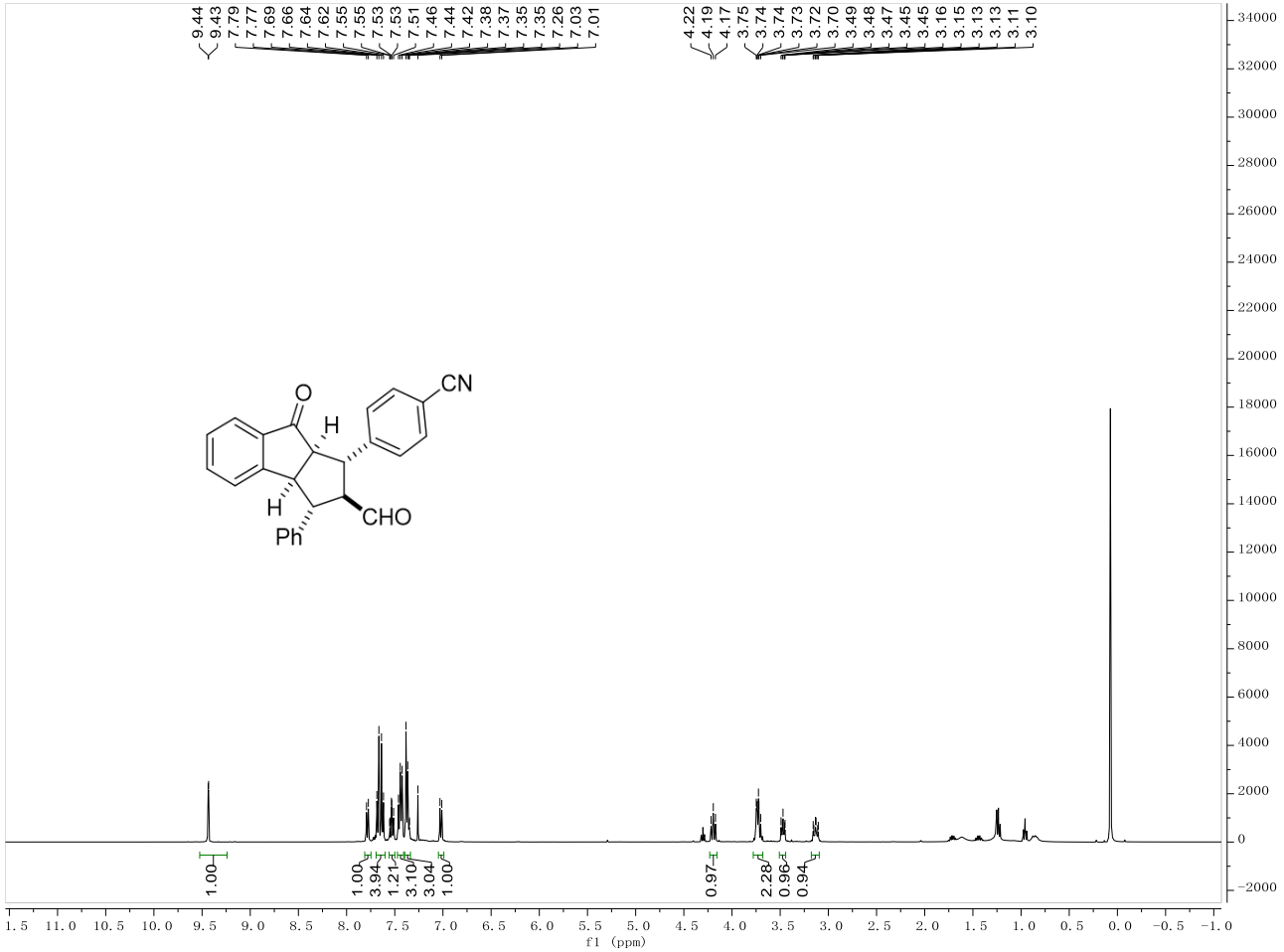
^{1}H NMR spectrum of **3ga** (400 MHz, $CDCl_3$)



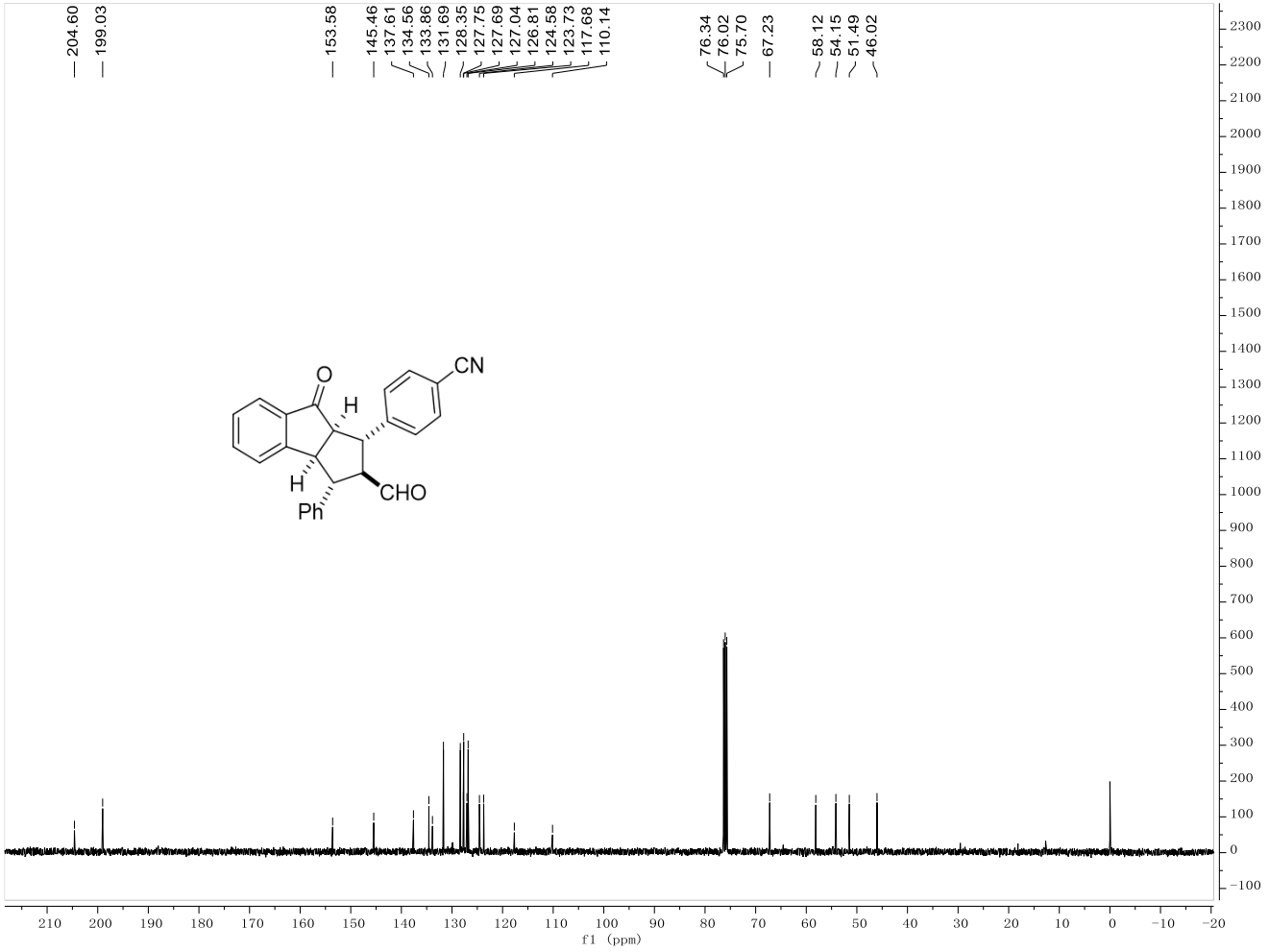
^{13}C NMR spectrum of **3ga** (100 MHz, $CDCl_3$)



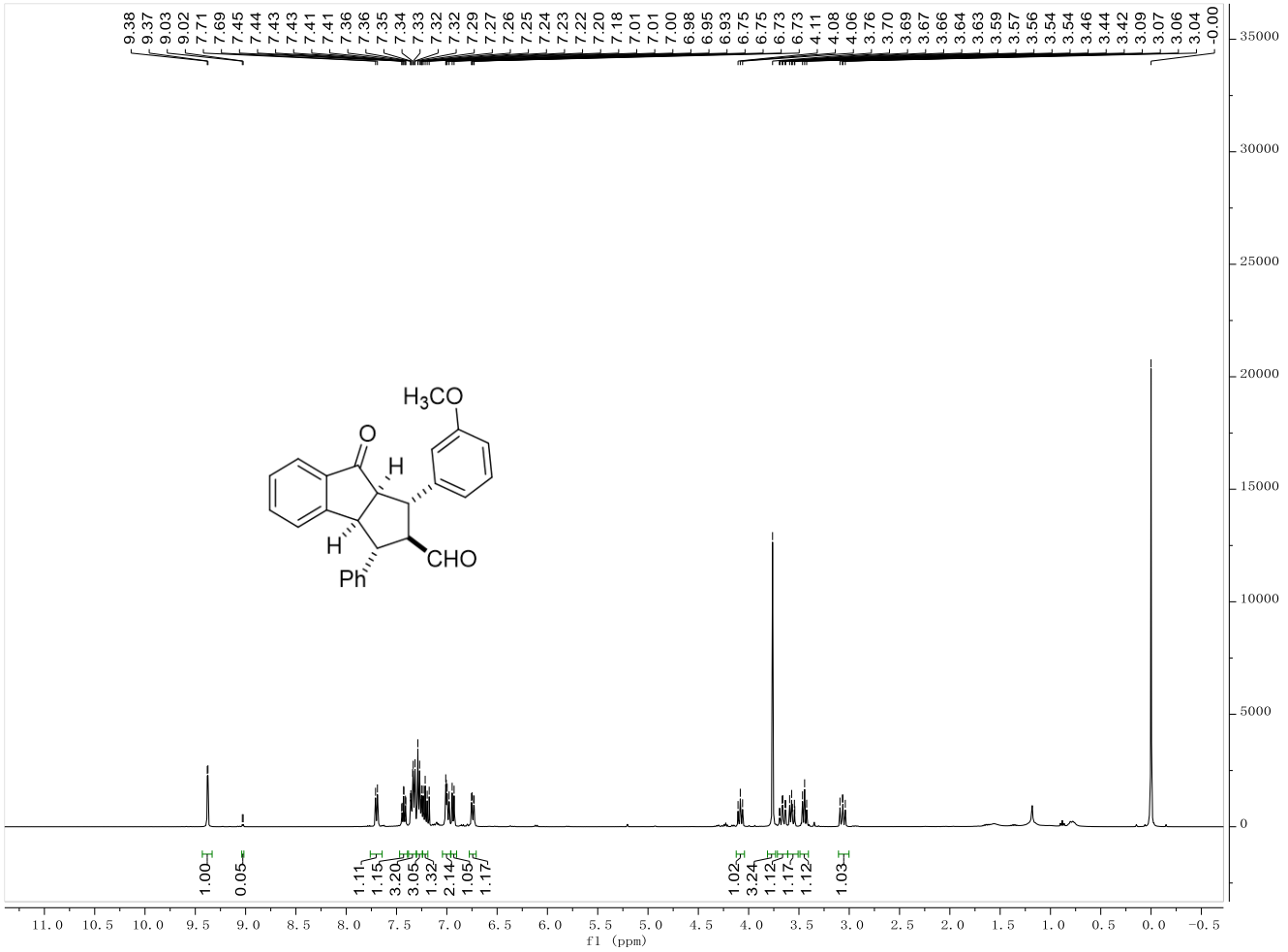
^{1}H NMR spectrum of **3ha** (400 MHz, $CDCl_3$)



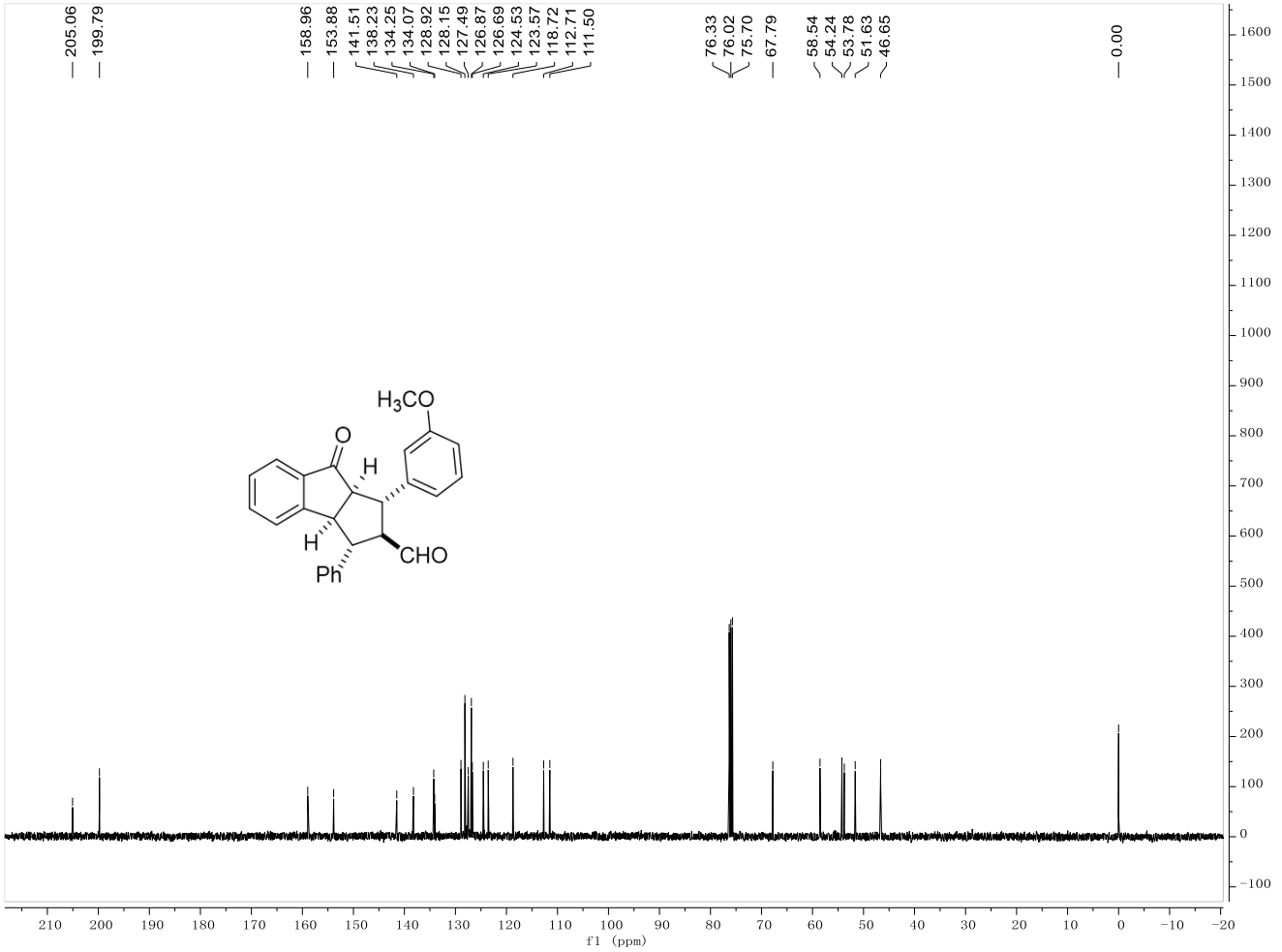
^{13}C NMR spectrum of **3ha** (100 MHz, $CDCl_3$)



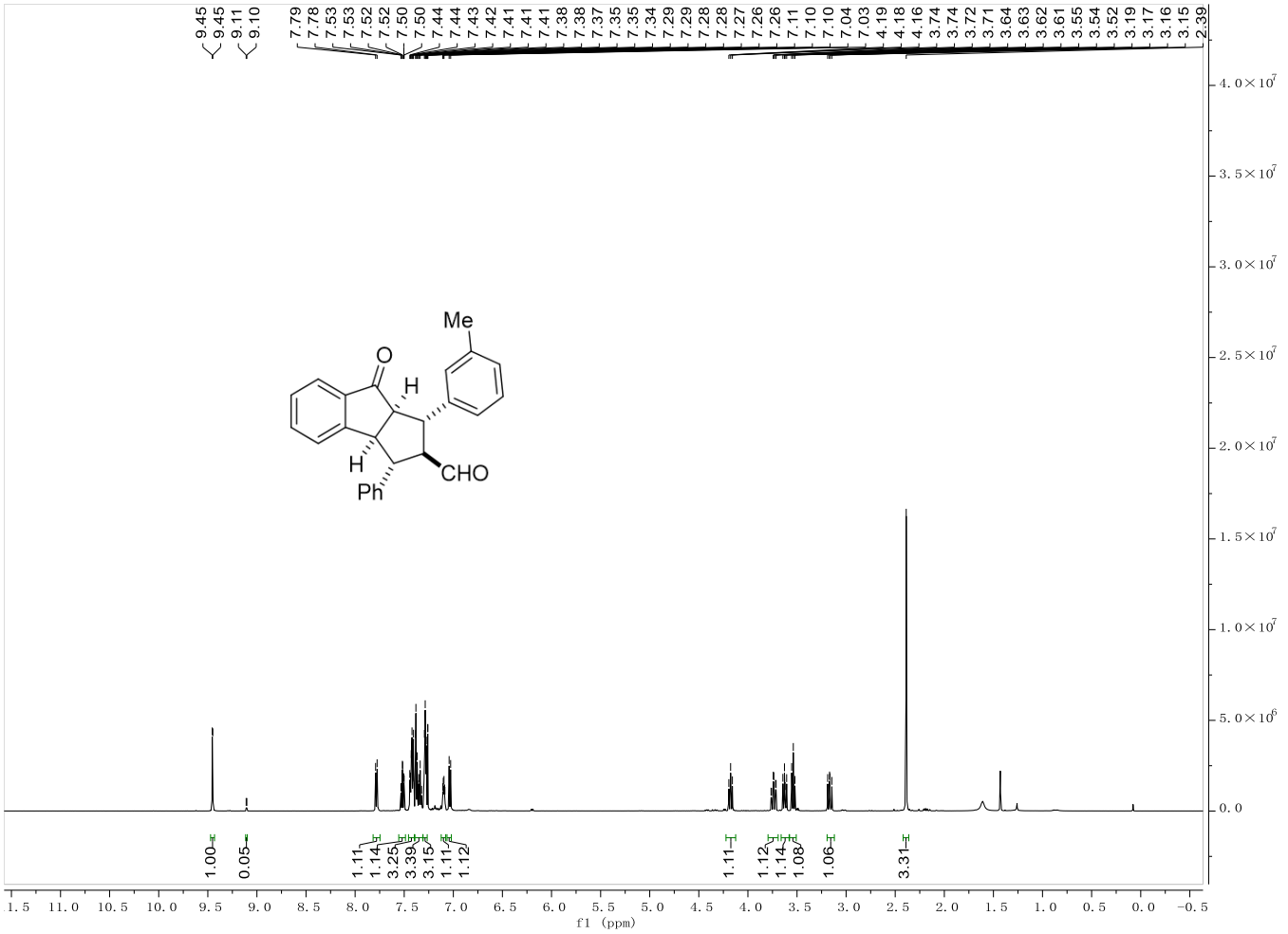
^{1}H NMR spectrum of **3ia** (400 MHz, $CDCl_3$)



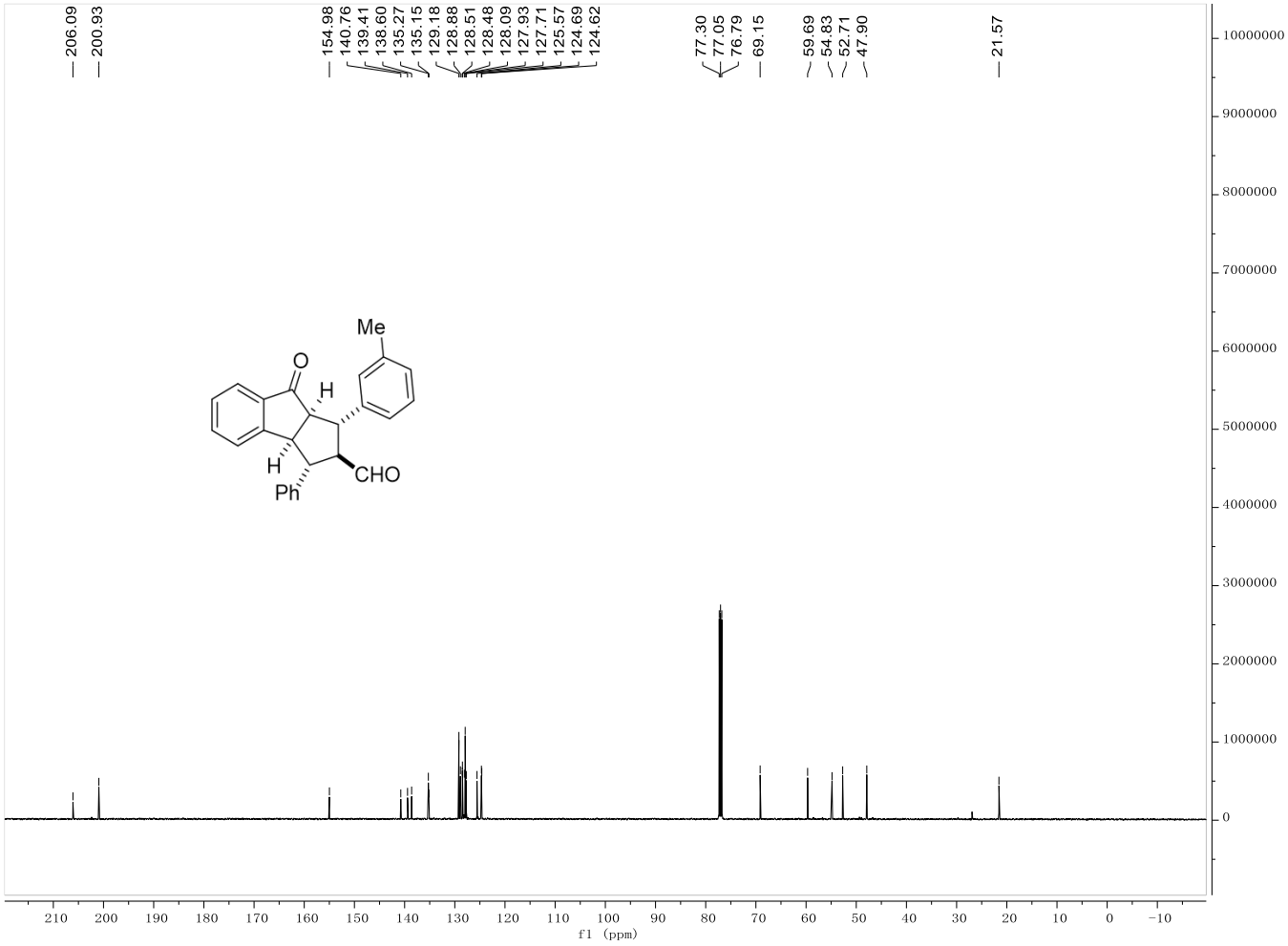
^{13}C NMR spectrum of **3ia** (100 MHz, $CDCl_3$)



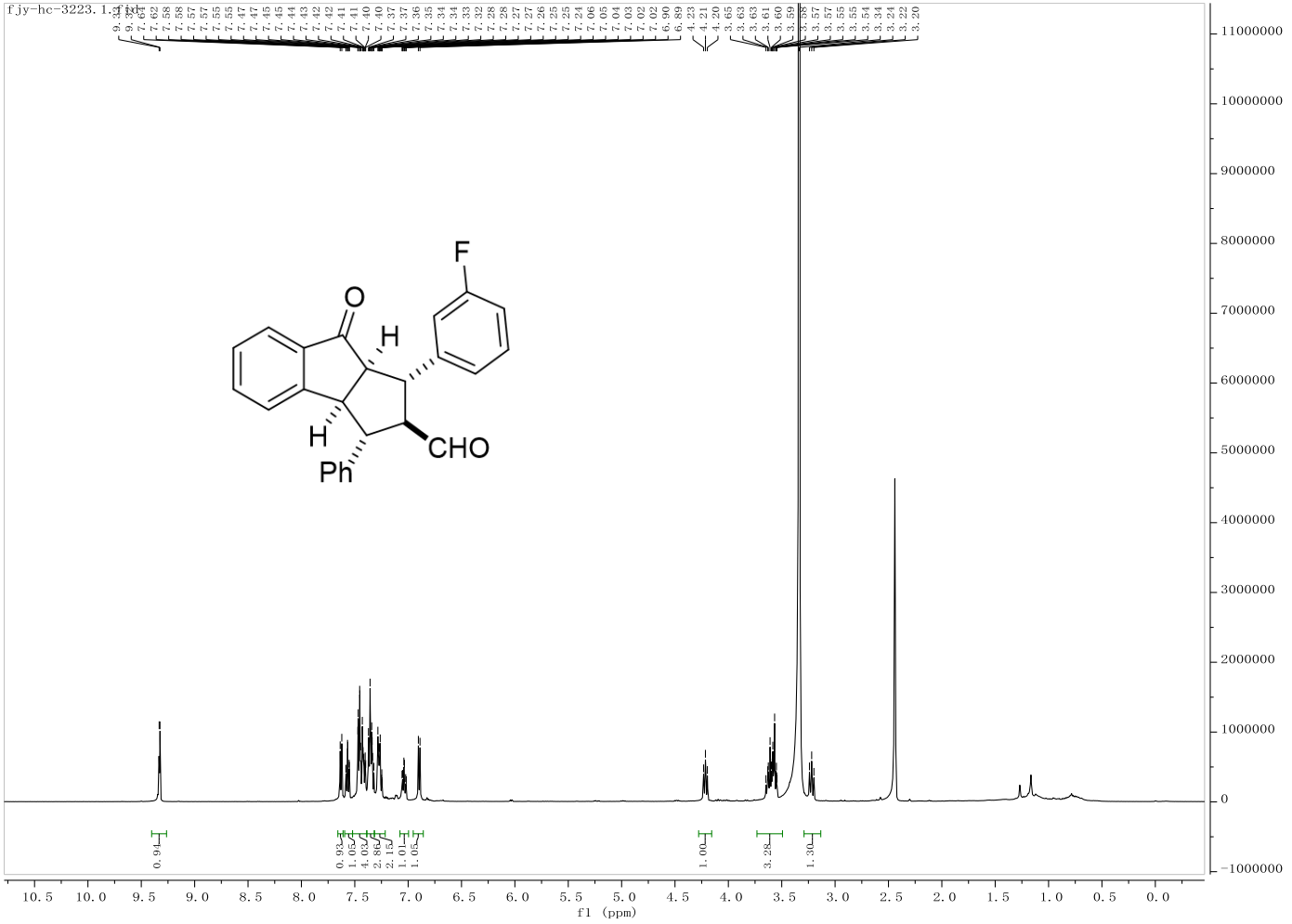
^{1}H NMR spectrum of **3ja** (500 MHz, $CDCl_3$)



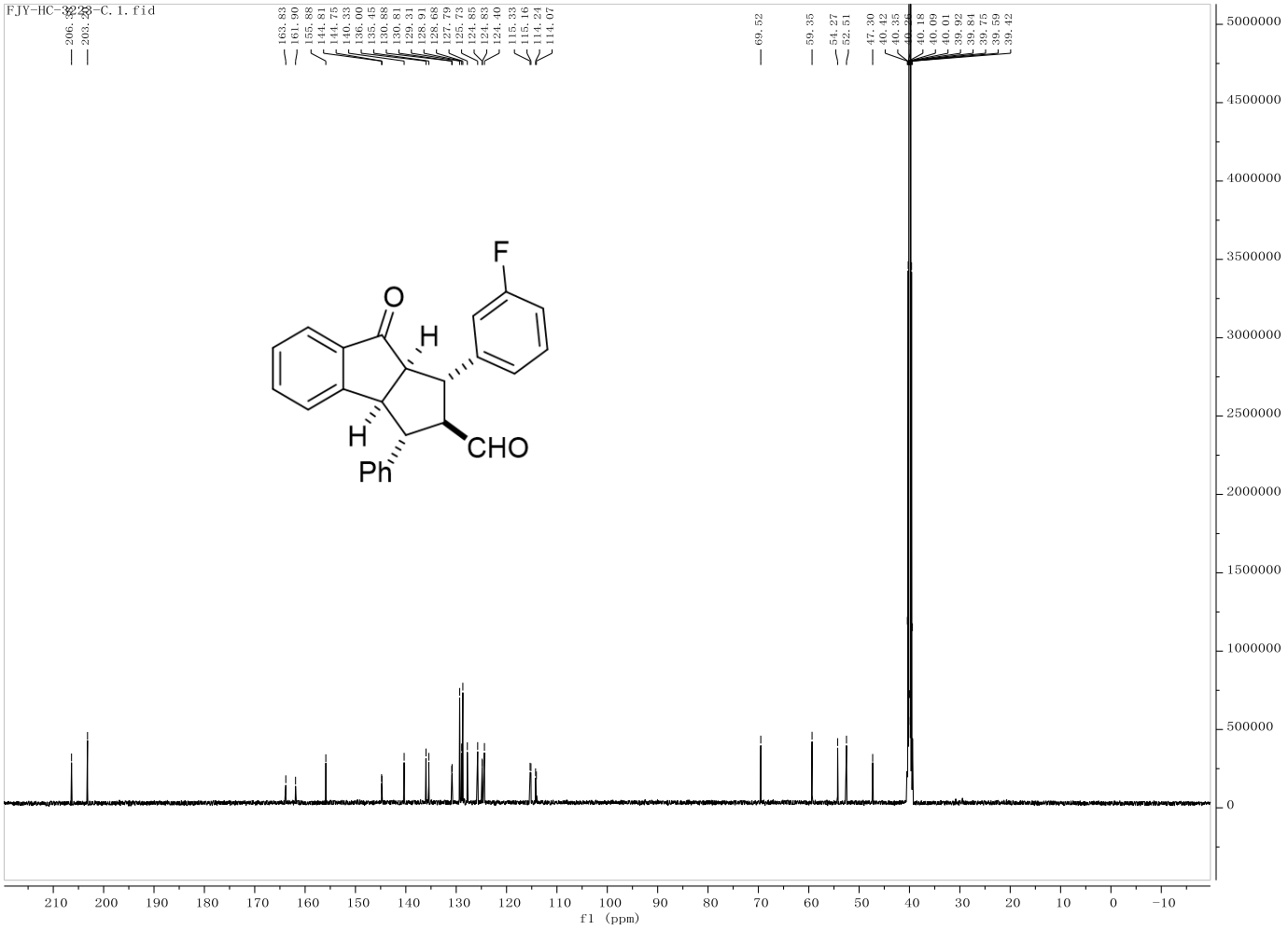
^{13}C NMR spectrum of **3ja** (125 MHz, $CDCl_3$)



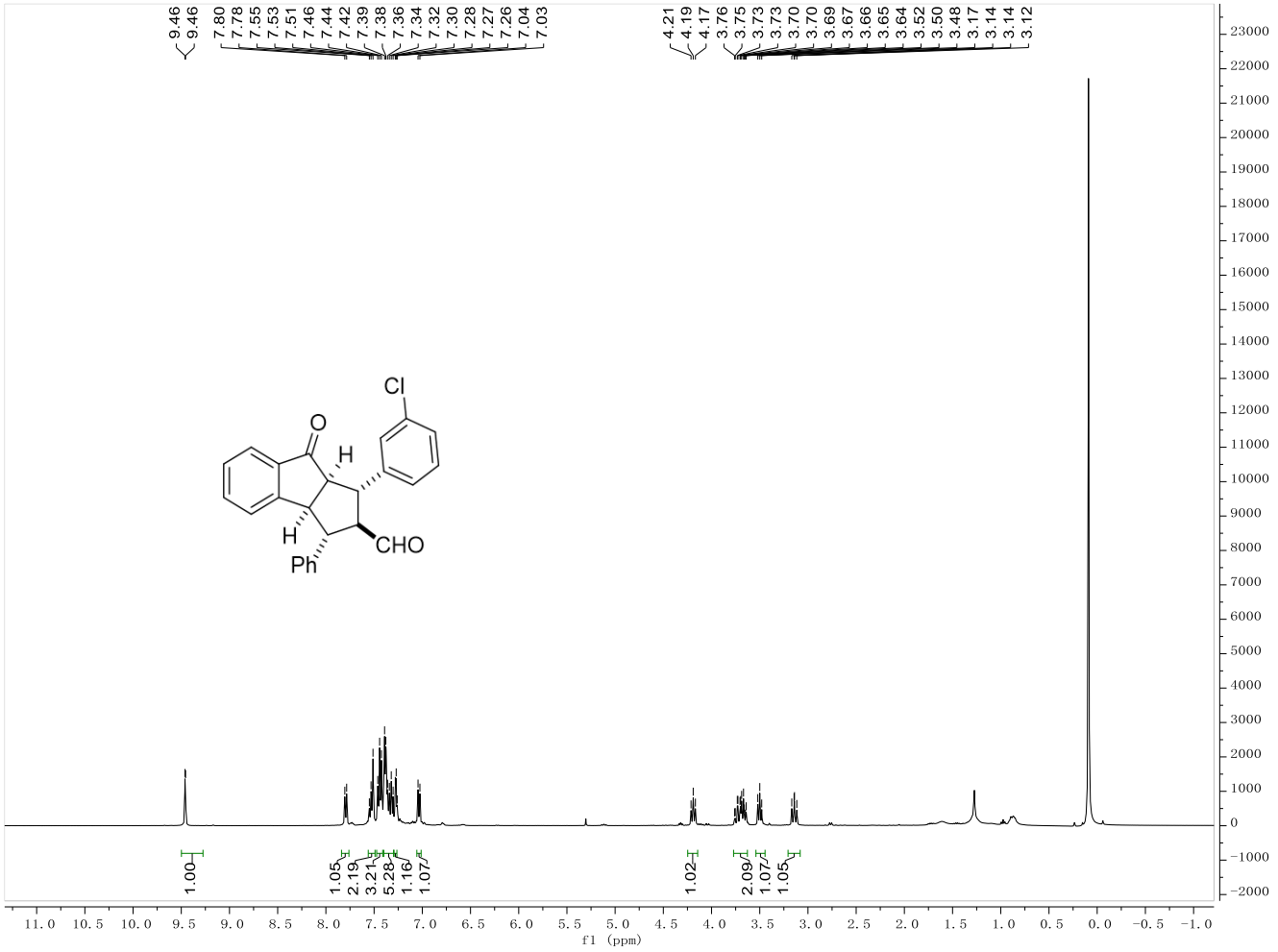
^{1}H NMR spectrum of **3ka** (500 MHz, DMSO-d_6)



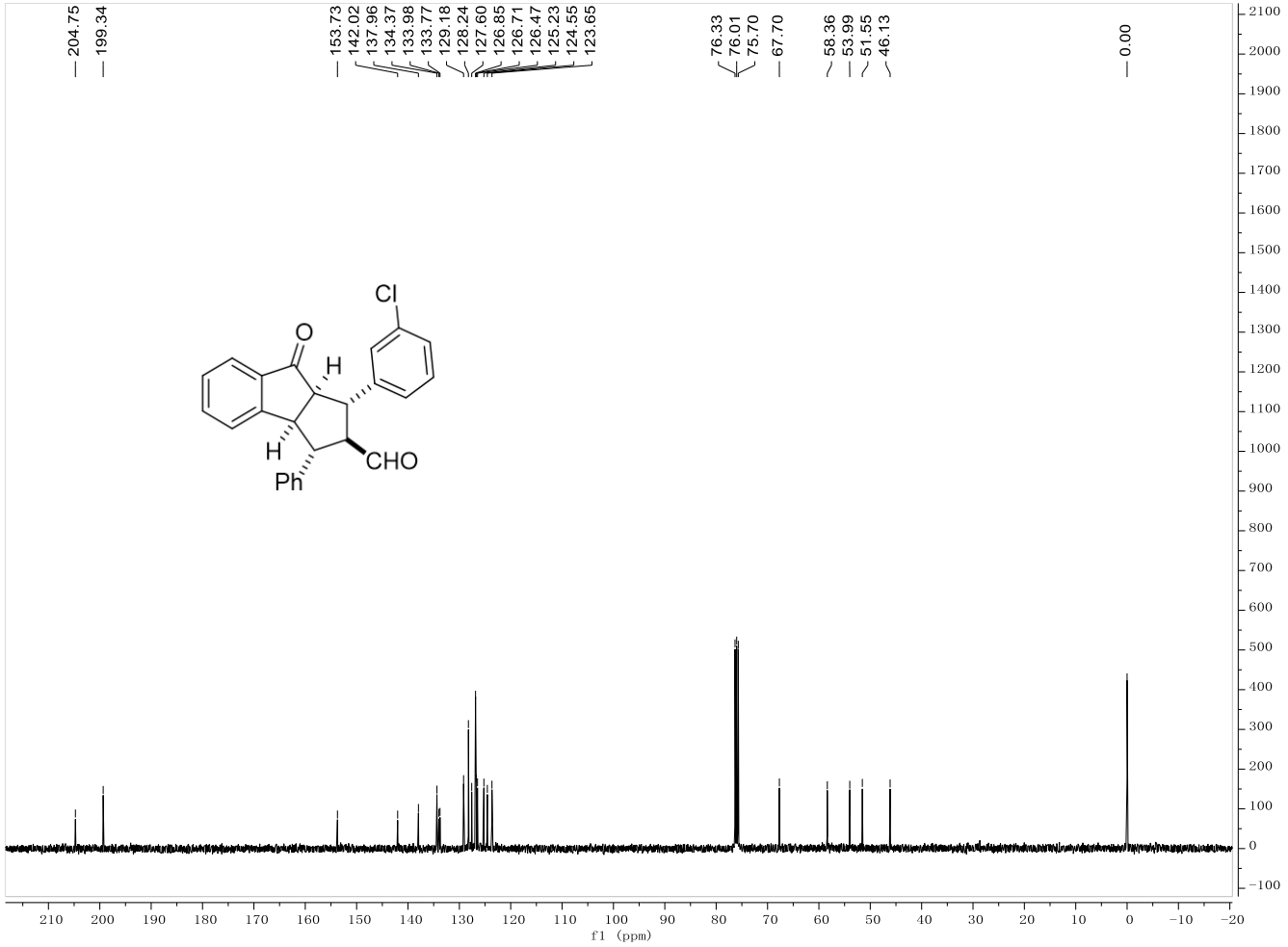
^{13}C NMR spectrum of **3ka** (125 MHz, DMSO-d_6)



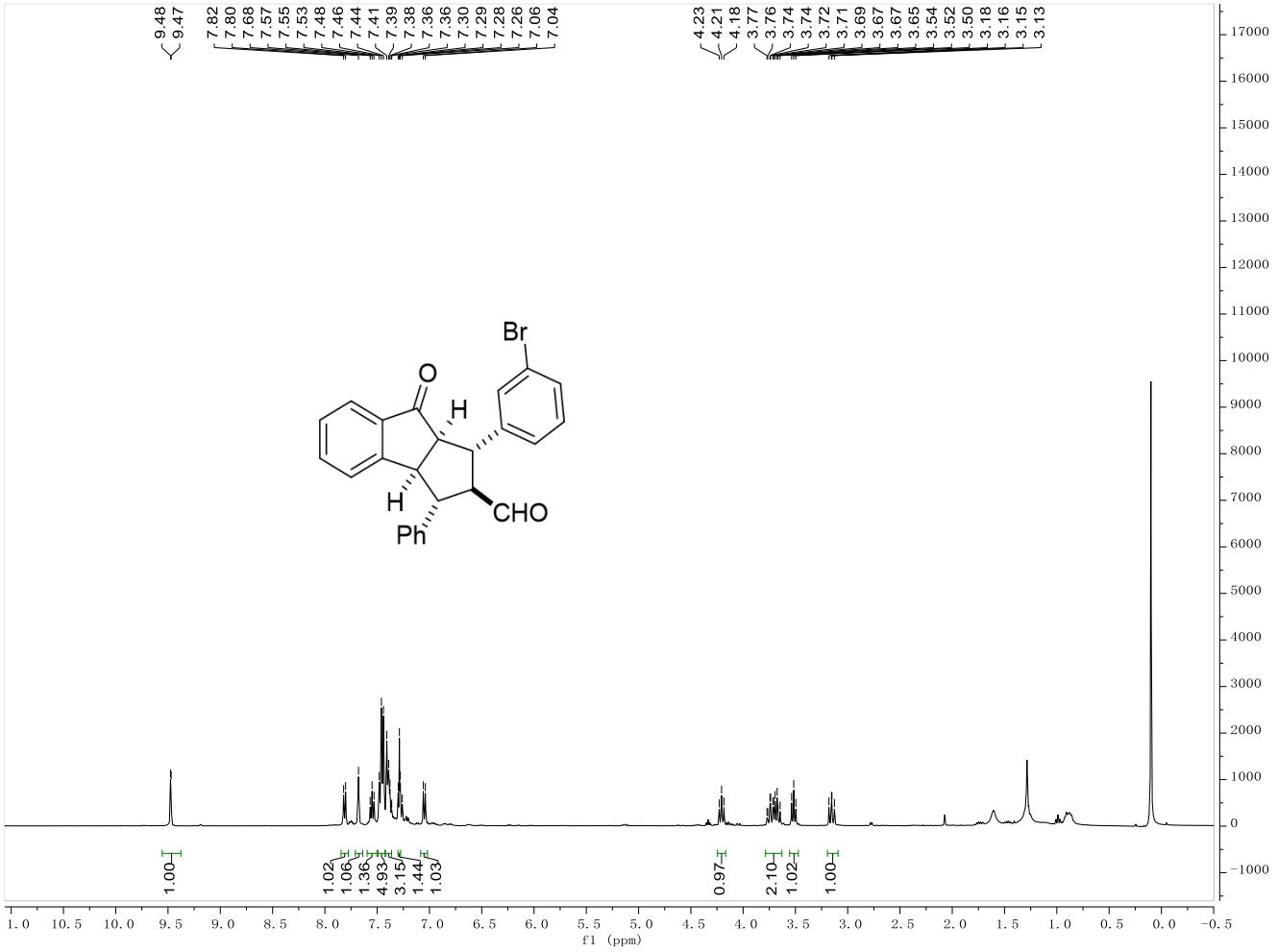
^{1}H NMR spectrum of **3la** (400 MHz, $CDCl_3$)



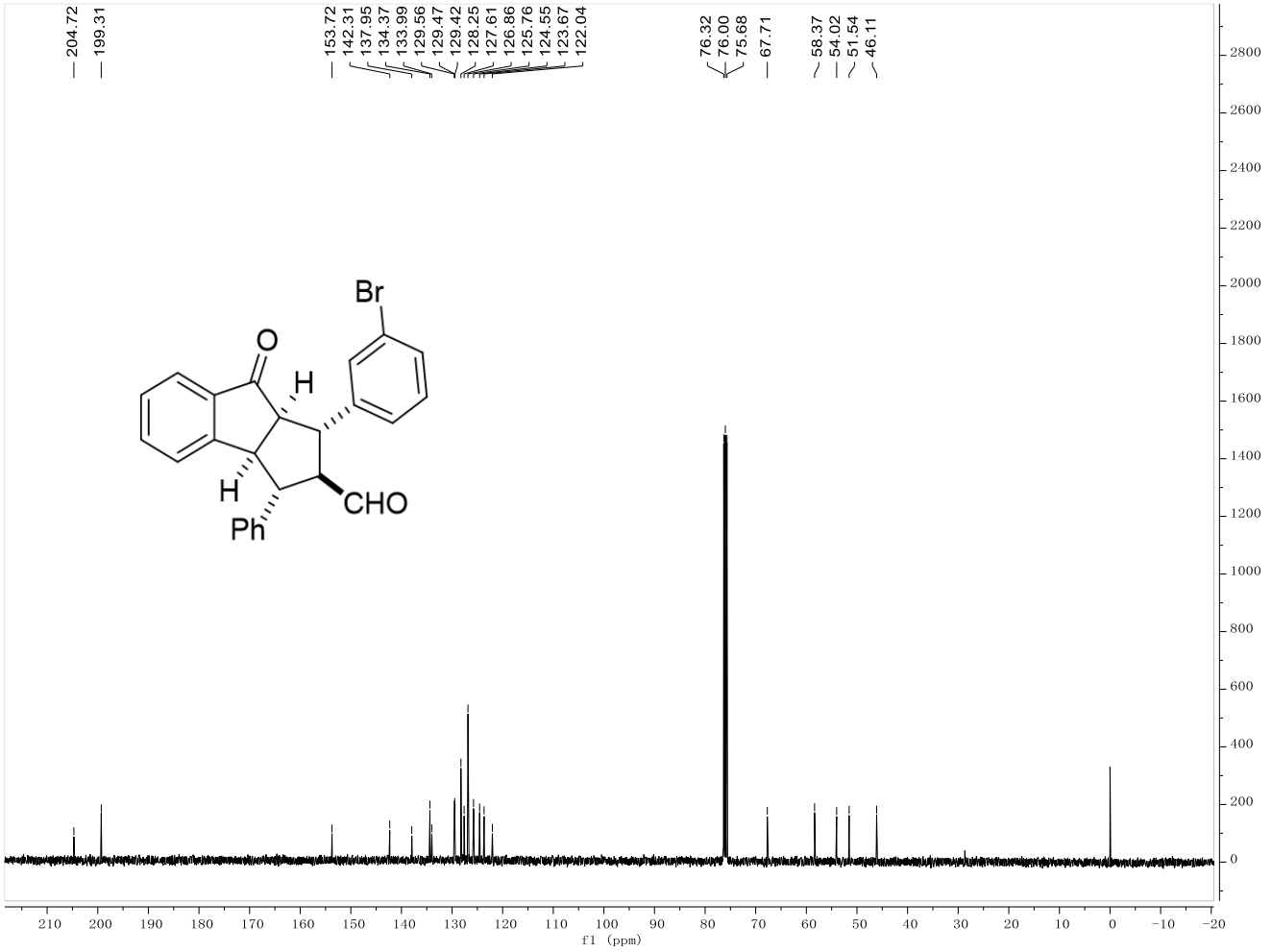
^{13}C NMR spectrum of **3la** (100 MHz, $CDCl_3$)



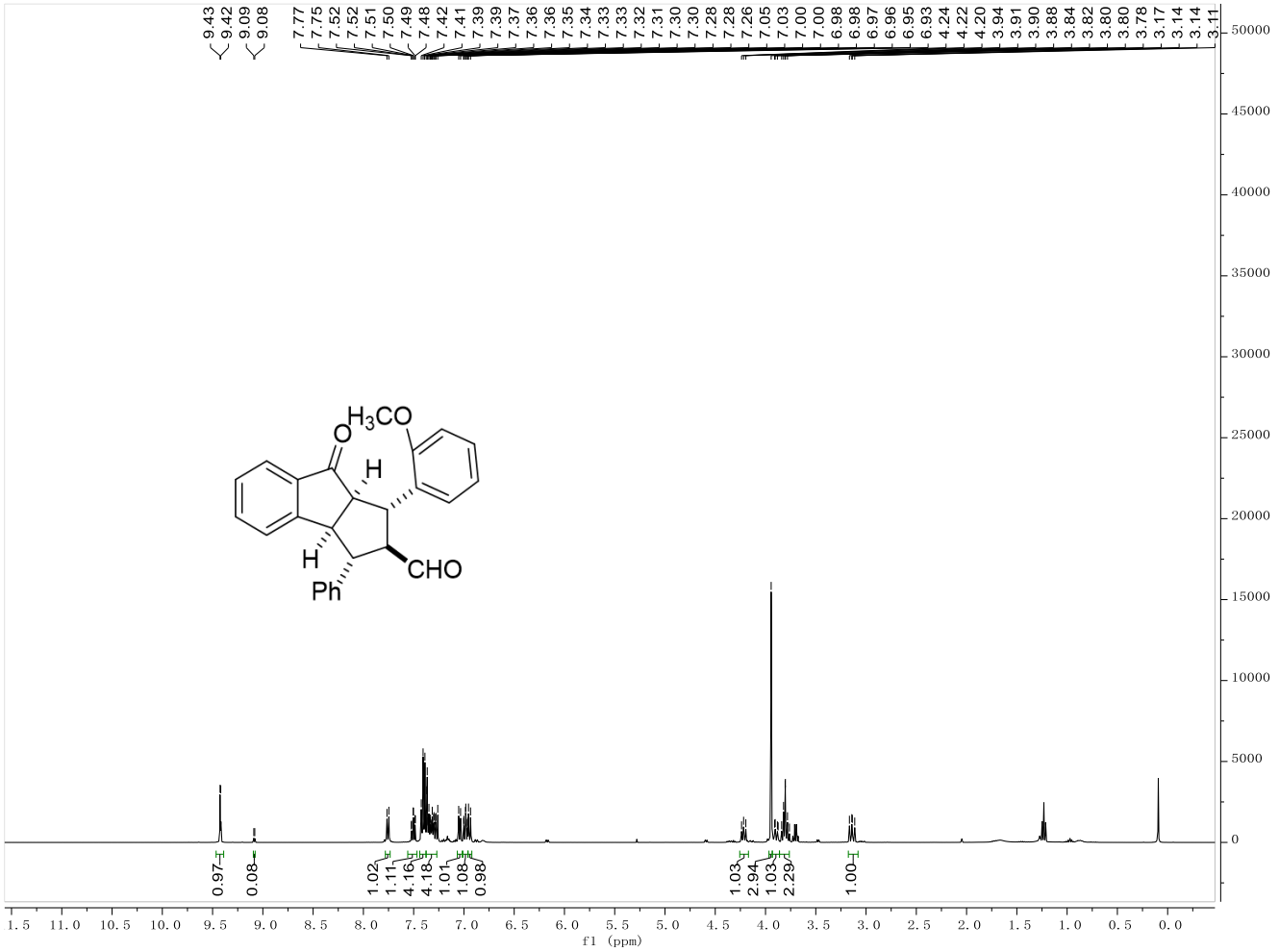
^{1}H NMR spectrum of **3ma** (400 MHz, $CDCl_3$)



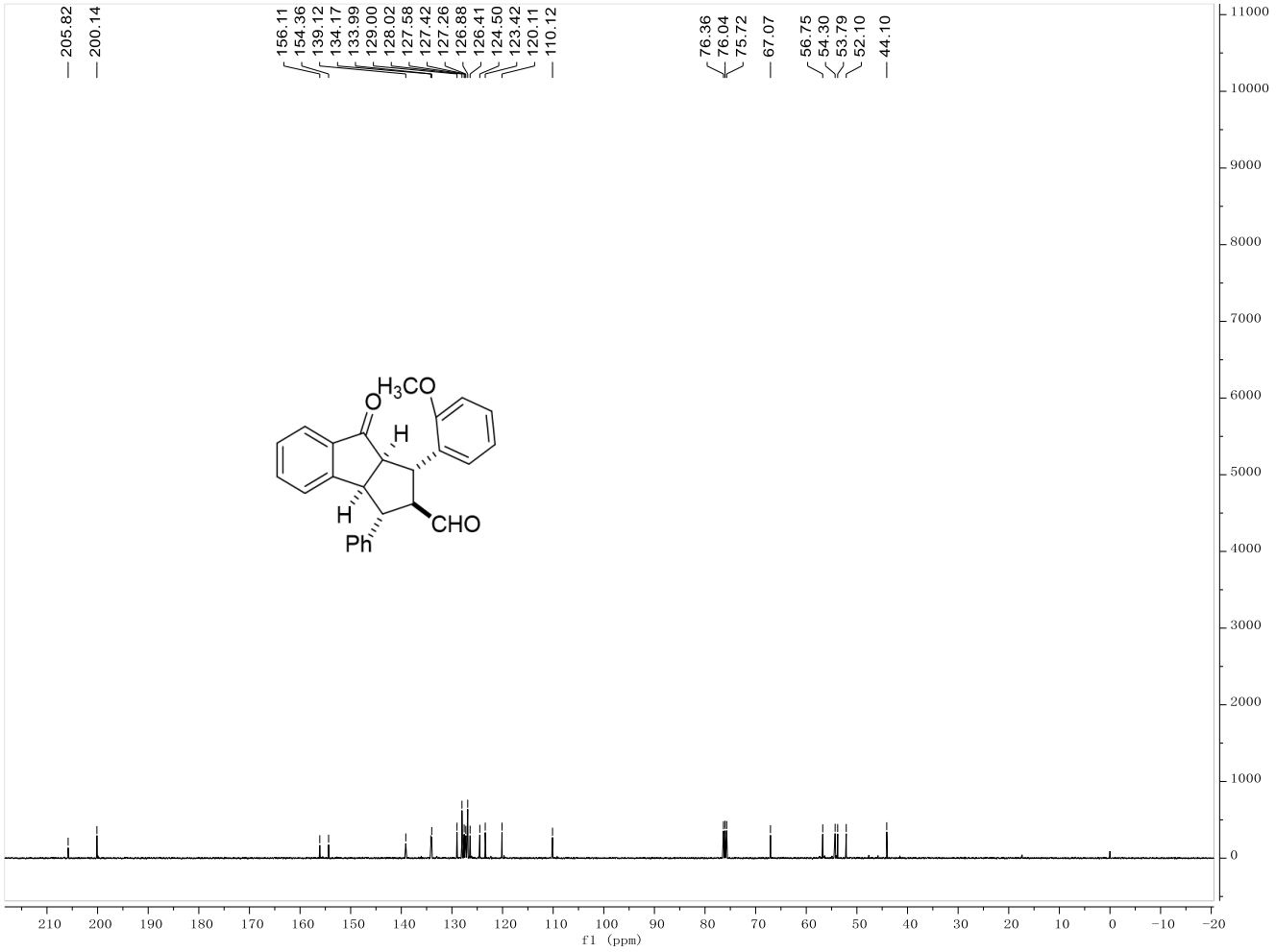
^{13}C NMR spectrum of **3ma** (100 MHz, $CDCl_3$)



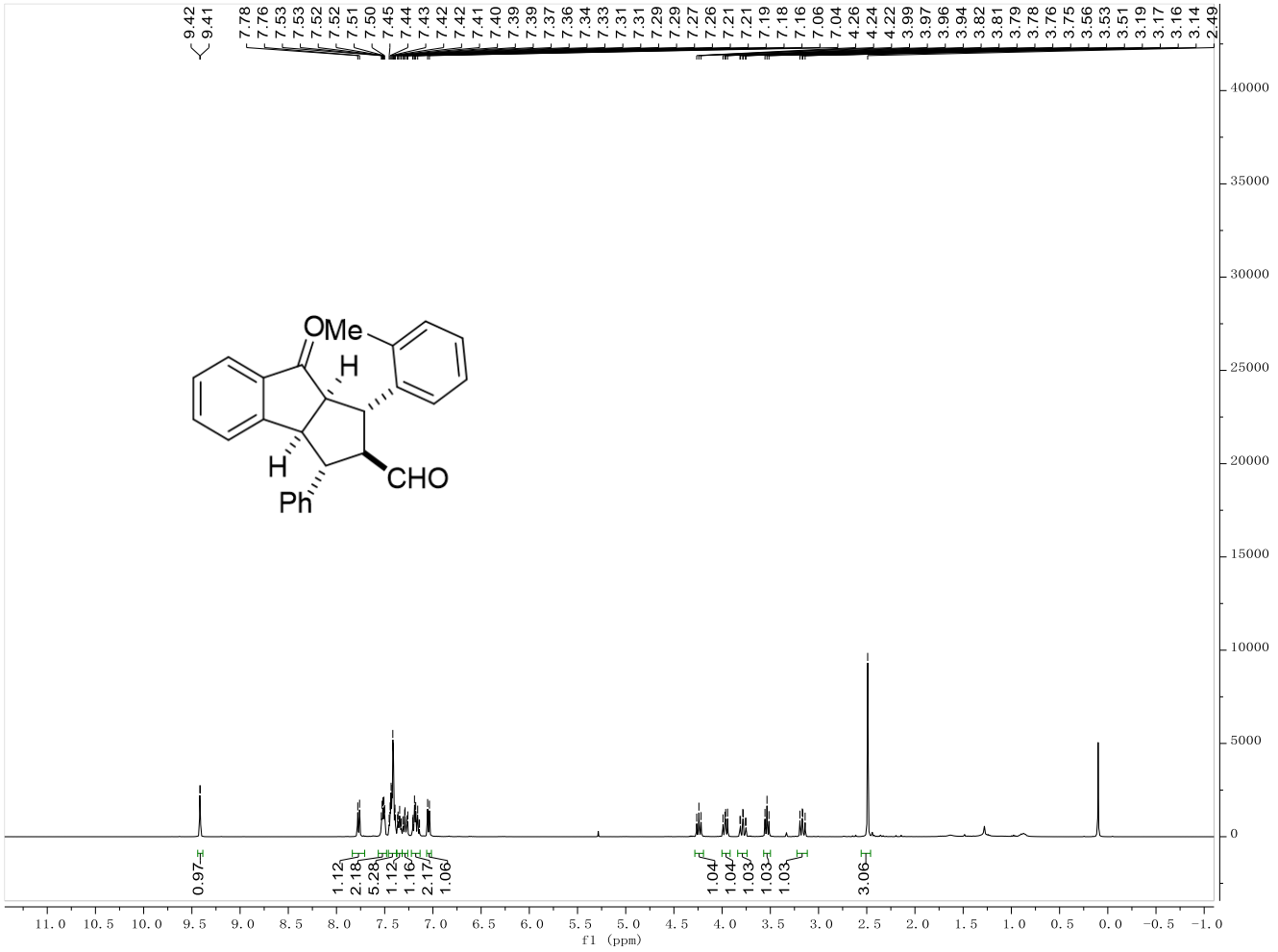
^{1}H NMR spectrum of **3na** (400 MHz, $CDCl_3$)



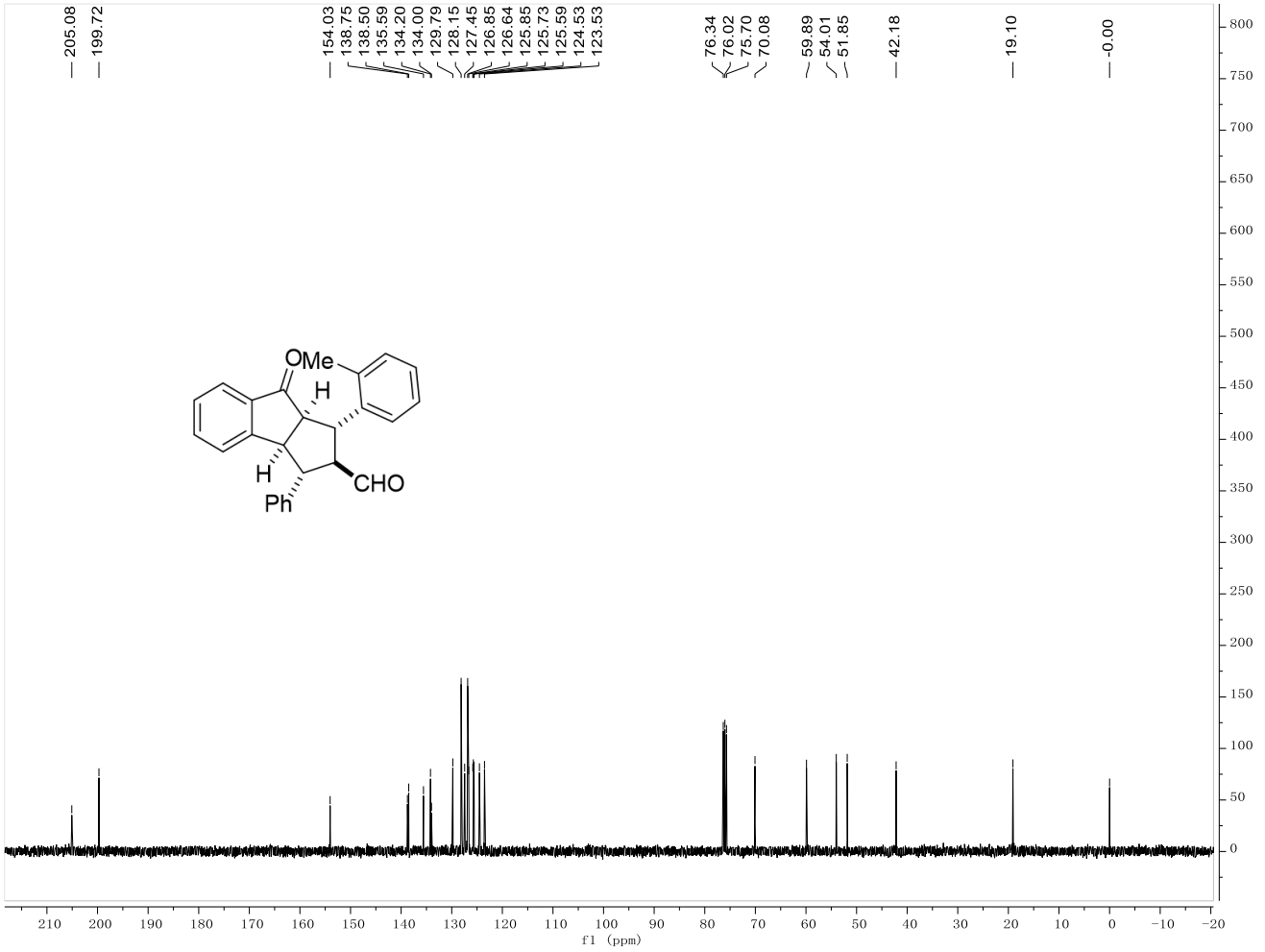
^{13}C NMR spectrum of **3na** (100 MHz, $CDCl_3$)



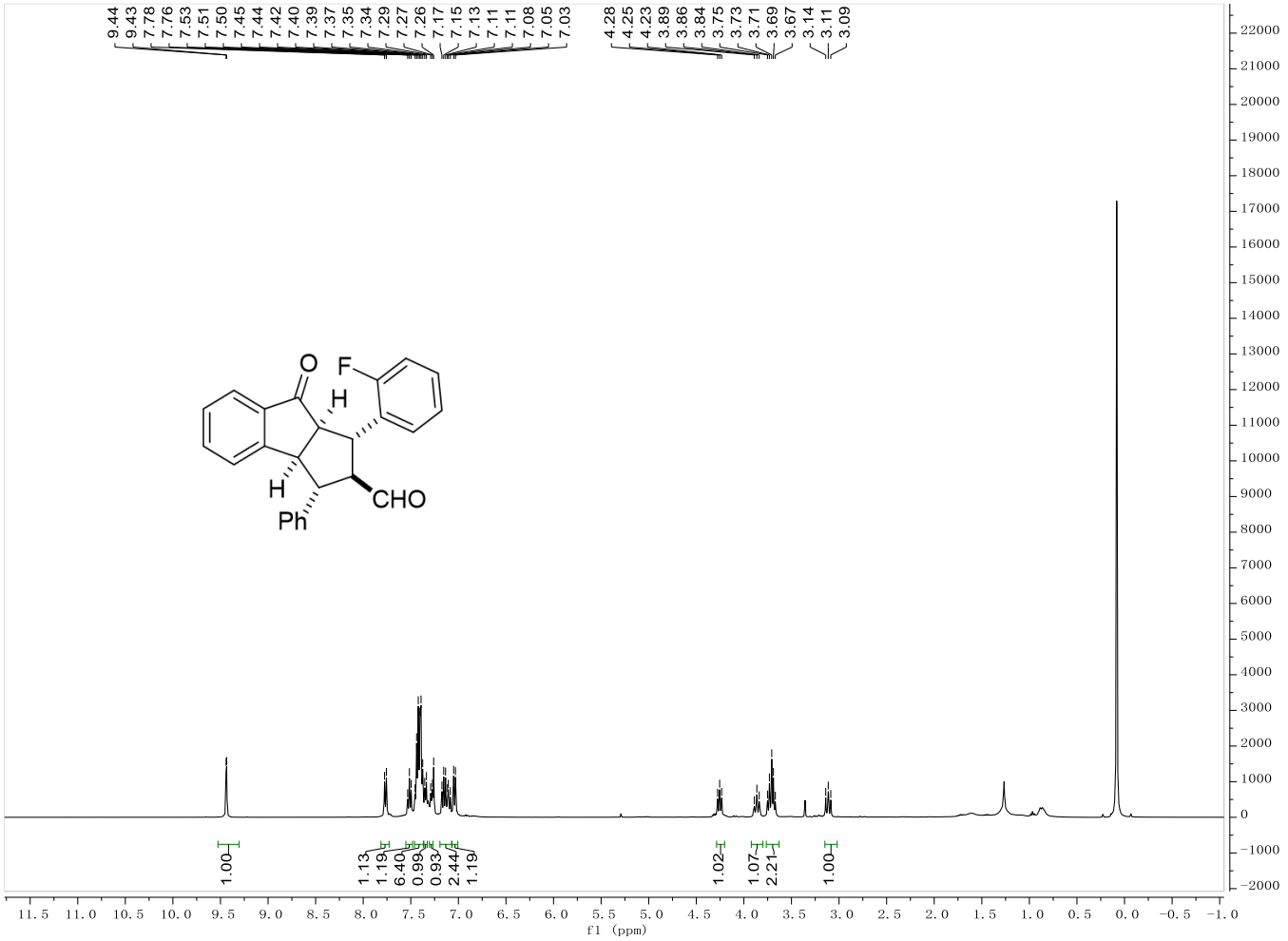
^{1}H NMR spectrum of **3oa** (400 MHz, $CDCl_3$)



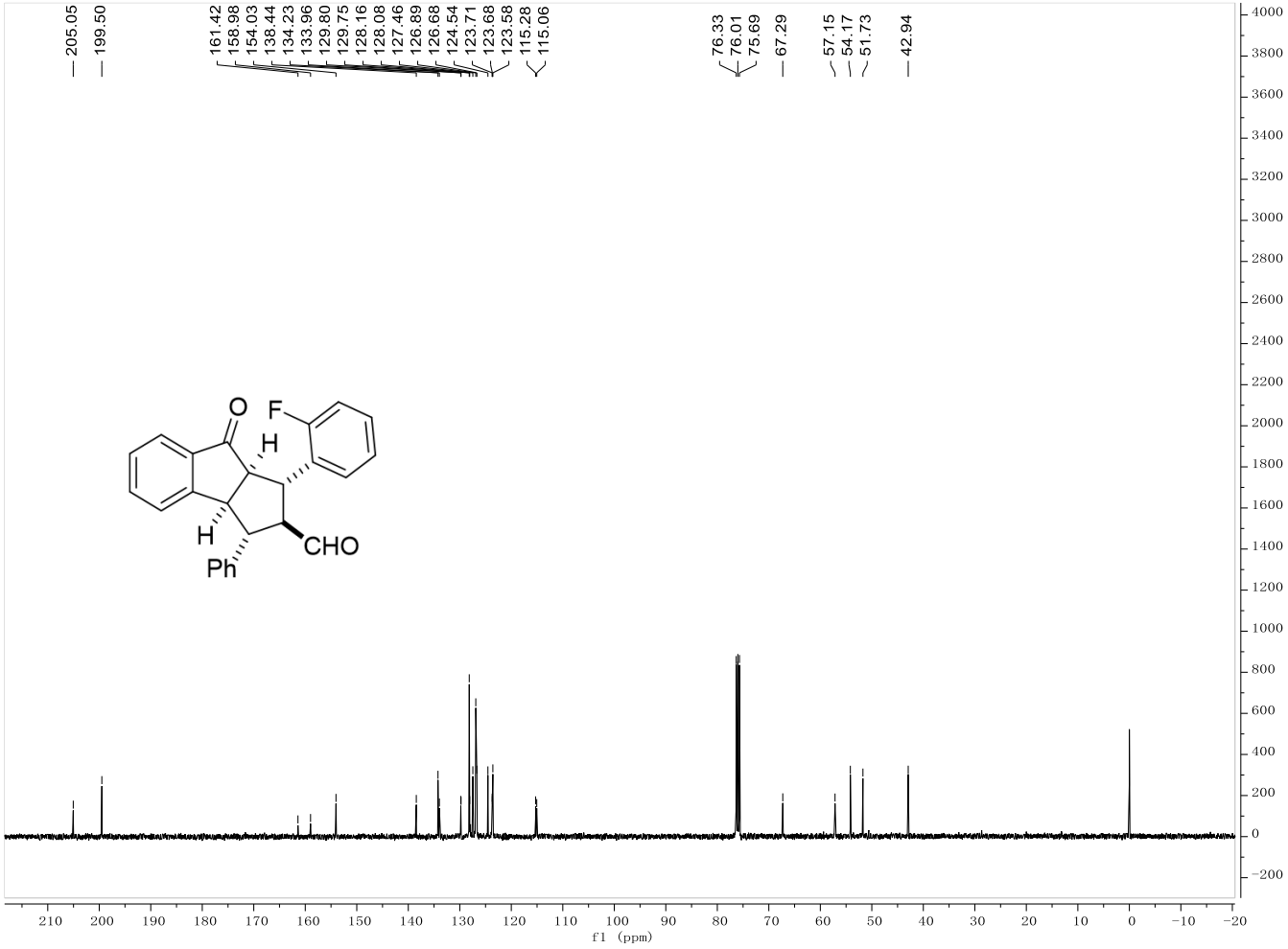
^{13}C NMR spectrum of **3oa** (100 MHz, $CDCl_3$)



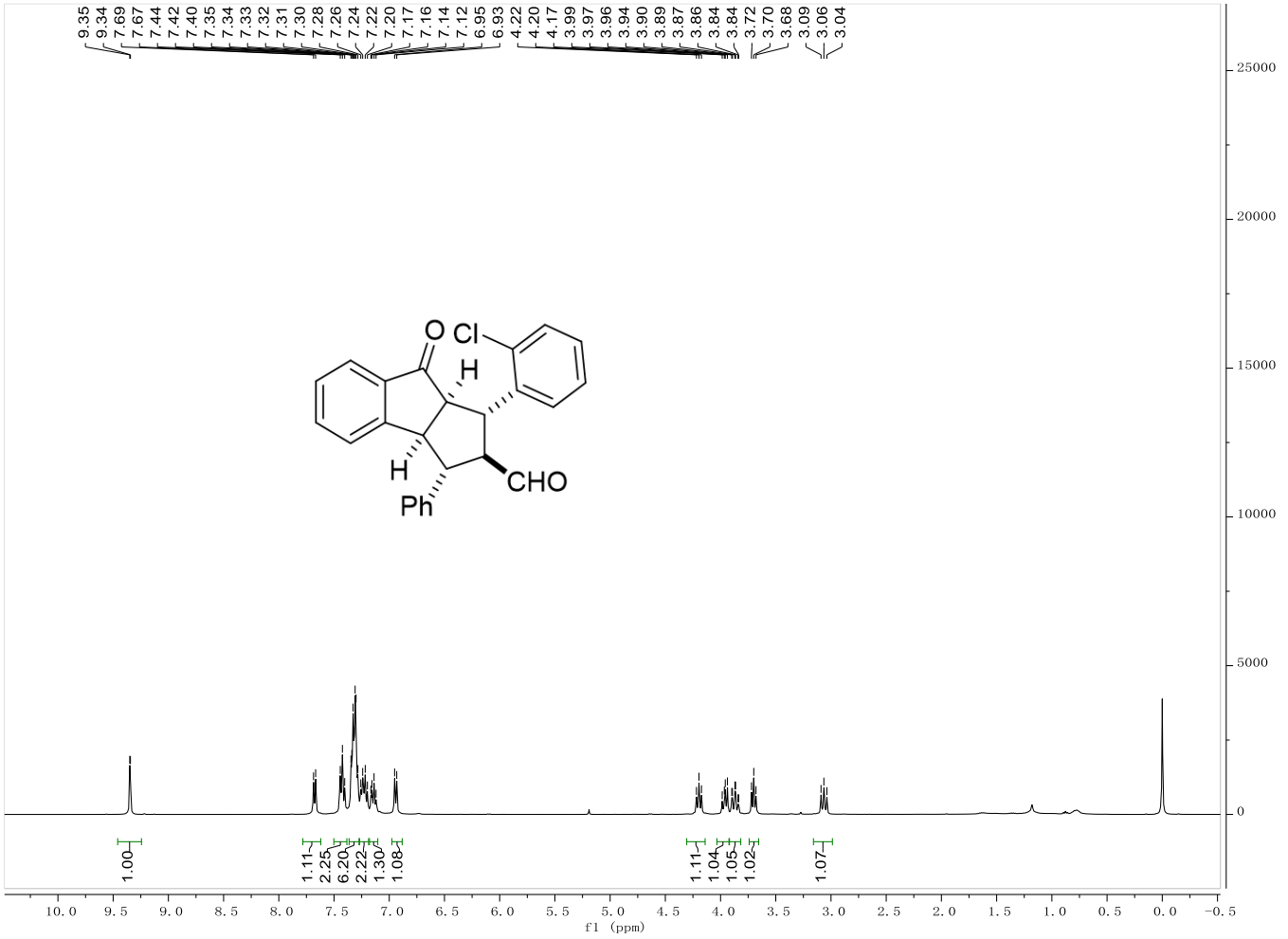
^{1}H NMR spectrum of **3pa** (400 MHz, $CDCl_3$)



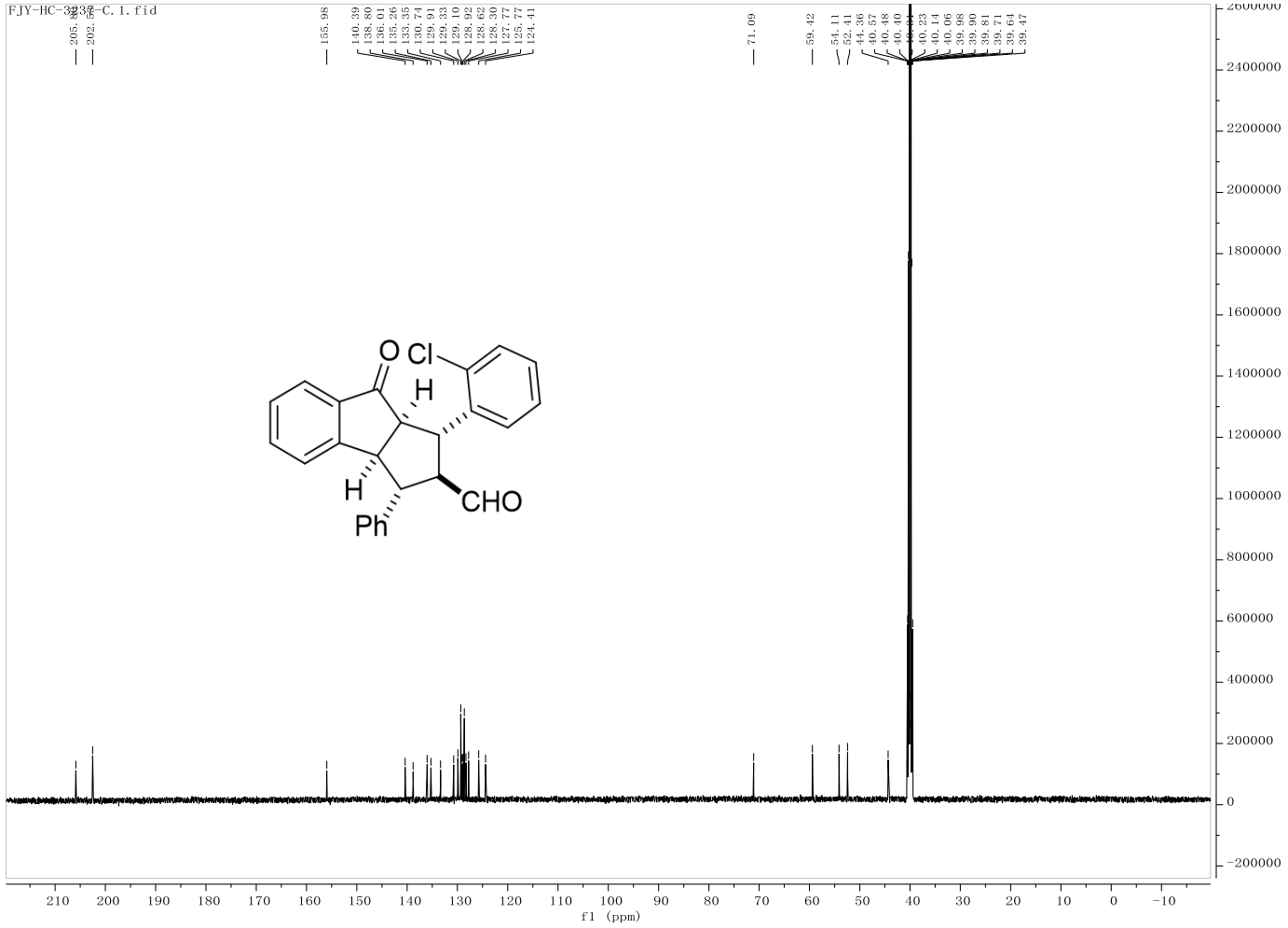
^{13}C NMR spectrum of **3pa** (100 MHz, $CDCl_3$)



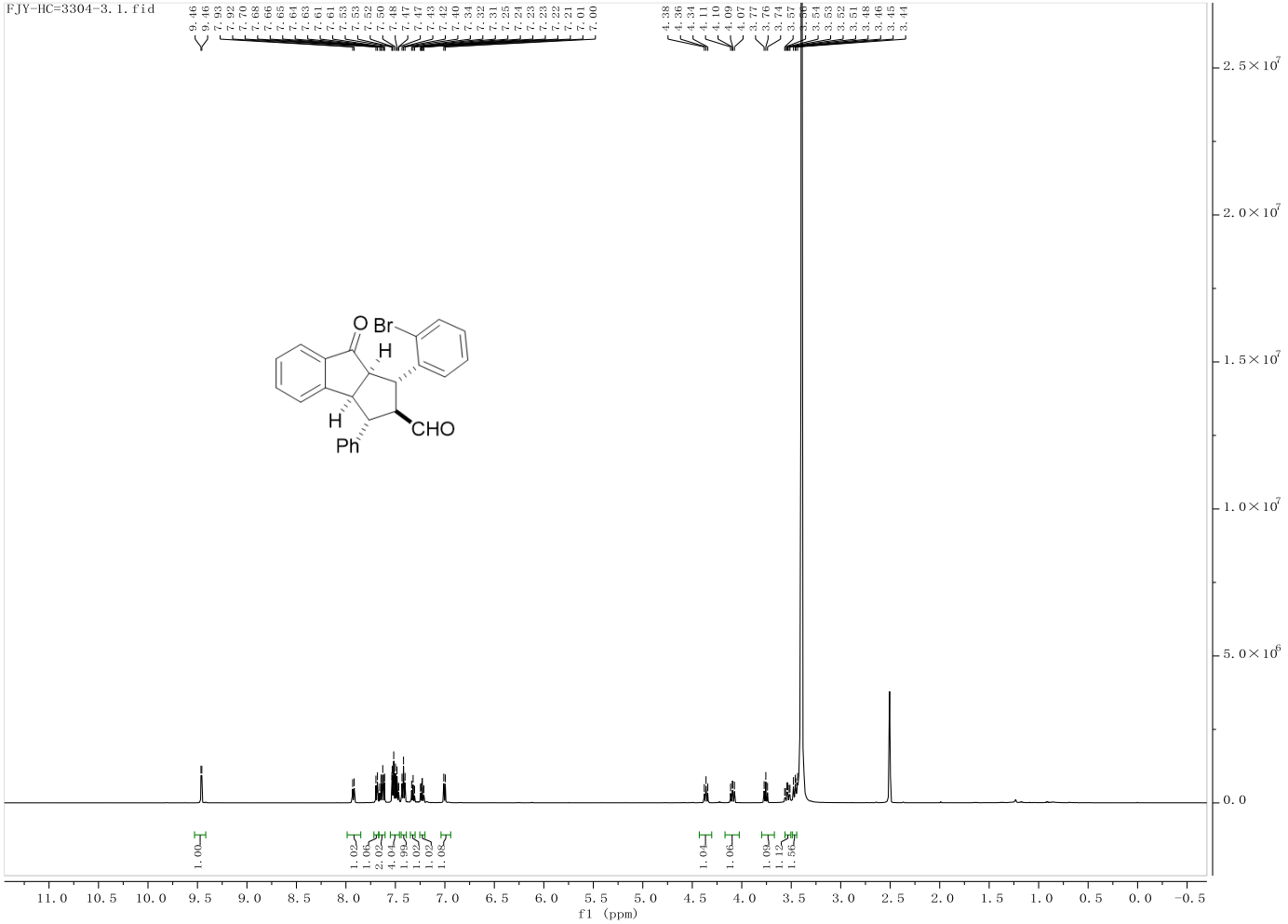
^{1}H NMR spectrum of **3qa** (400 MHz, $CDCl_3$)



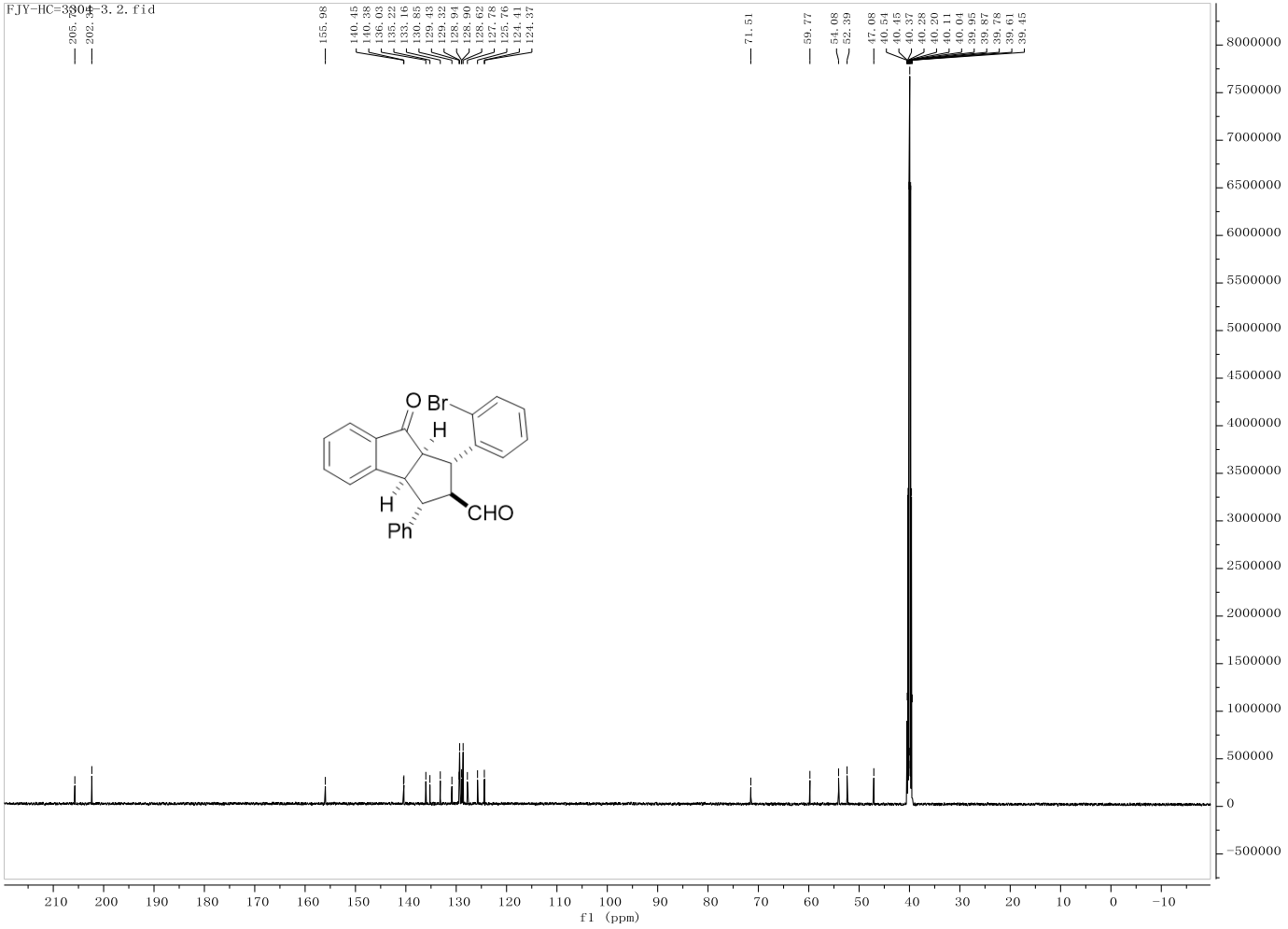
^{13}C NMR spectrum of **3qa** (125 MHz, DMSO-d_6)



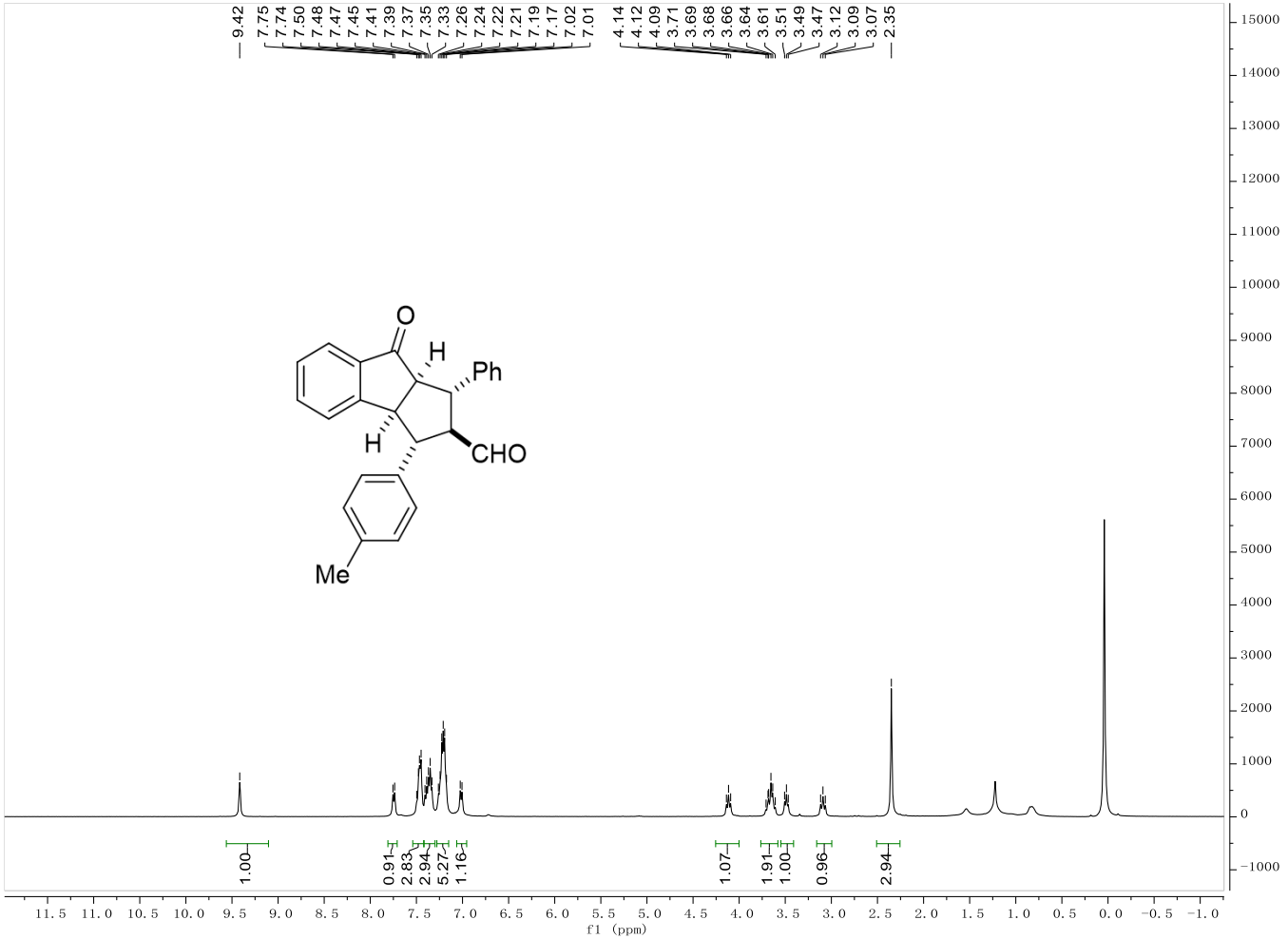
^{1}H NMR spectrum of **3ra** (500 MHz, DMSO-d_6)



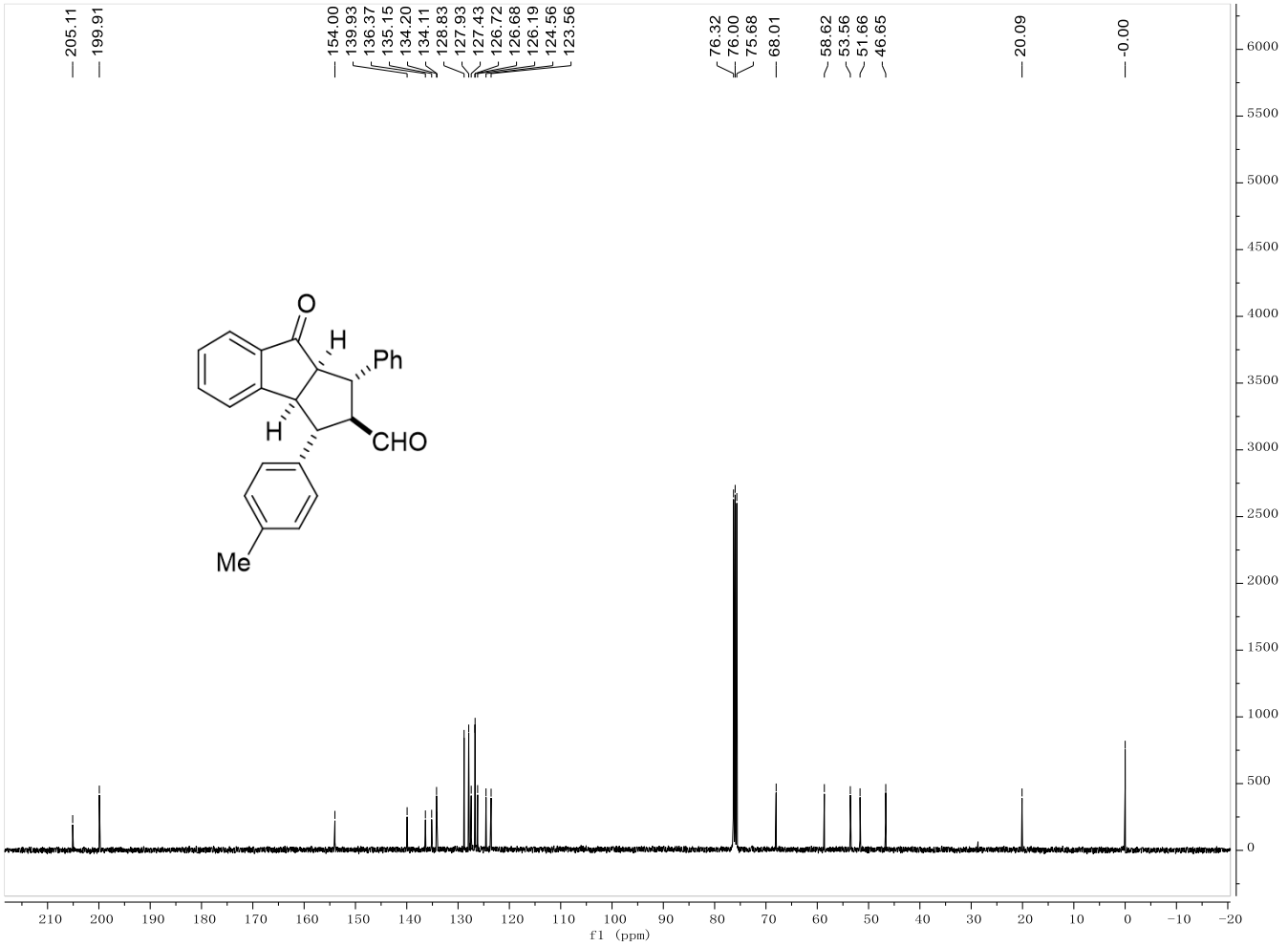
^{13}C NMR spectrum of **3ra** (125 MHz, DMSO-d_6)



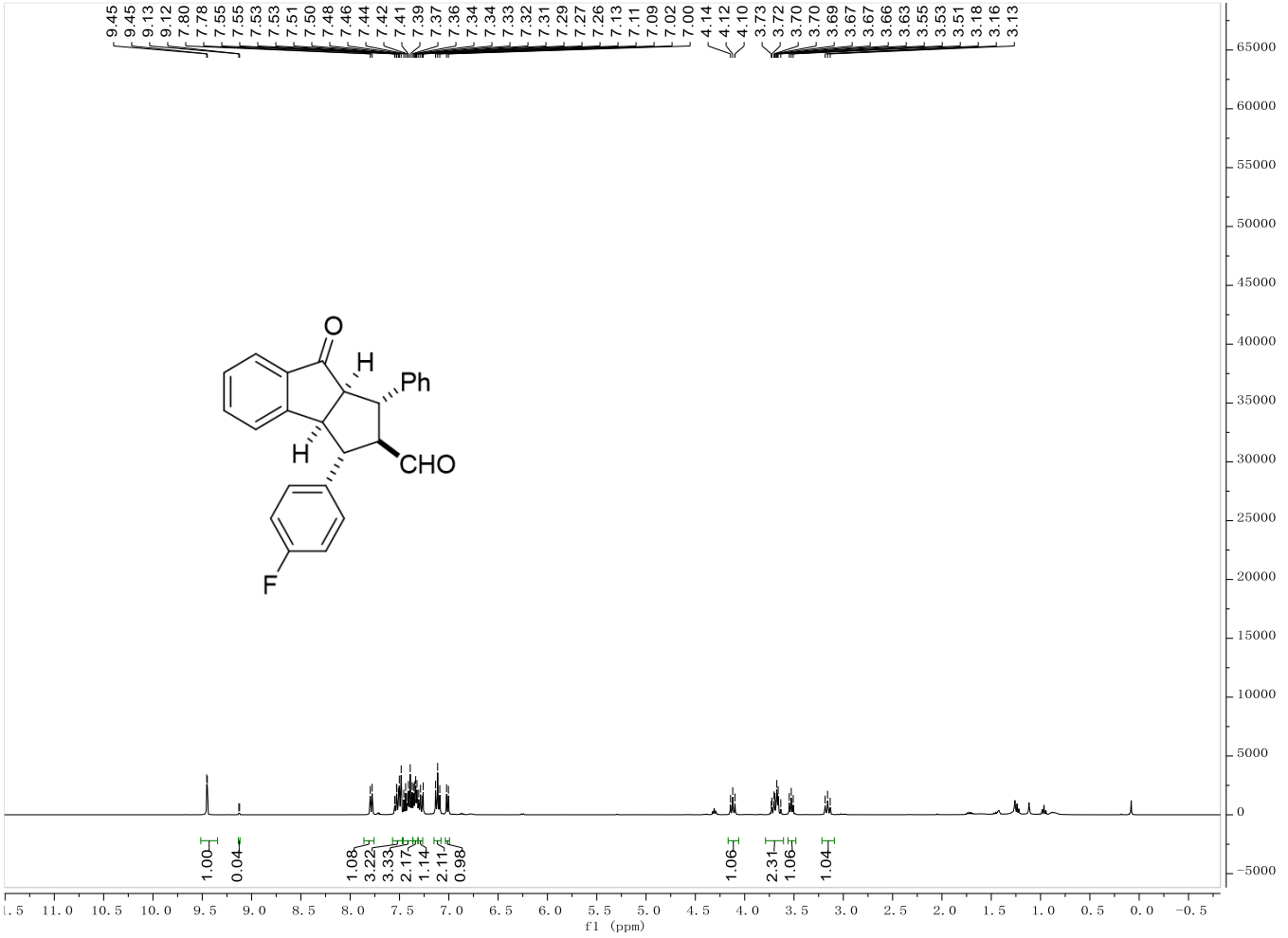
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)



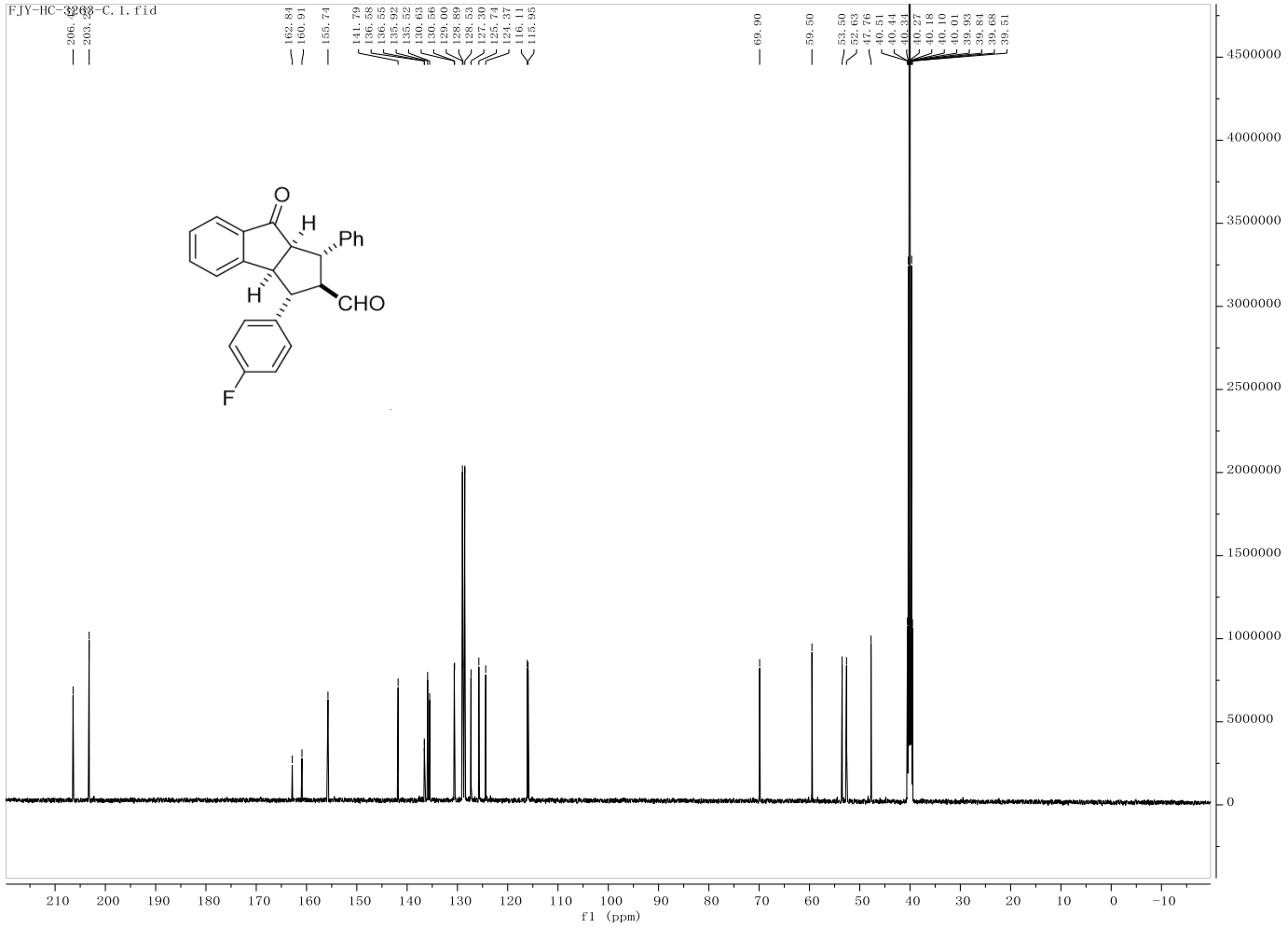
^{13}C NMR spectrum of **3ab** (100 MHz, $CDCl_3$)



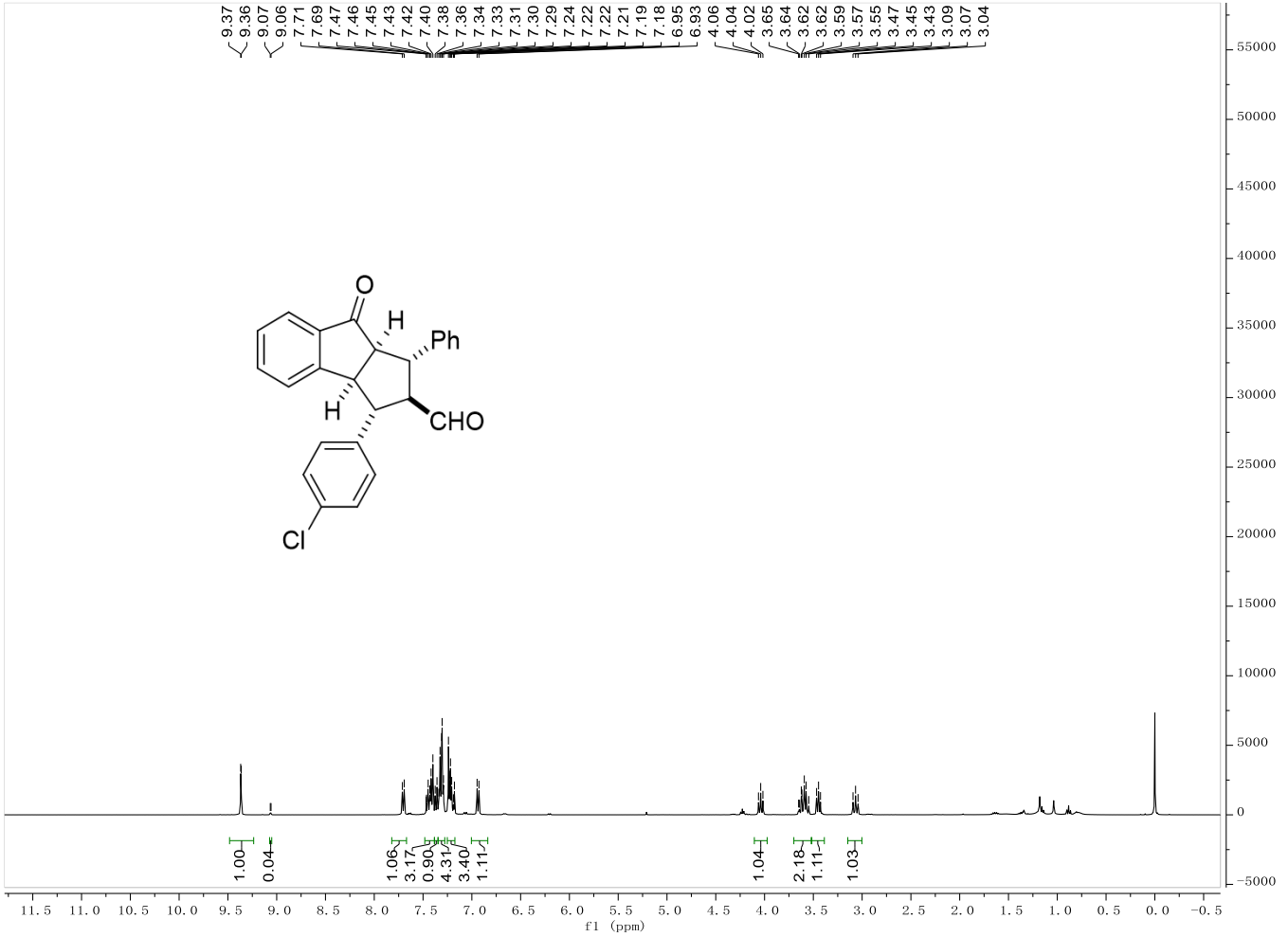
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



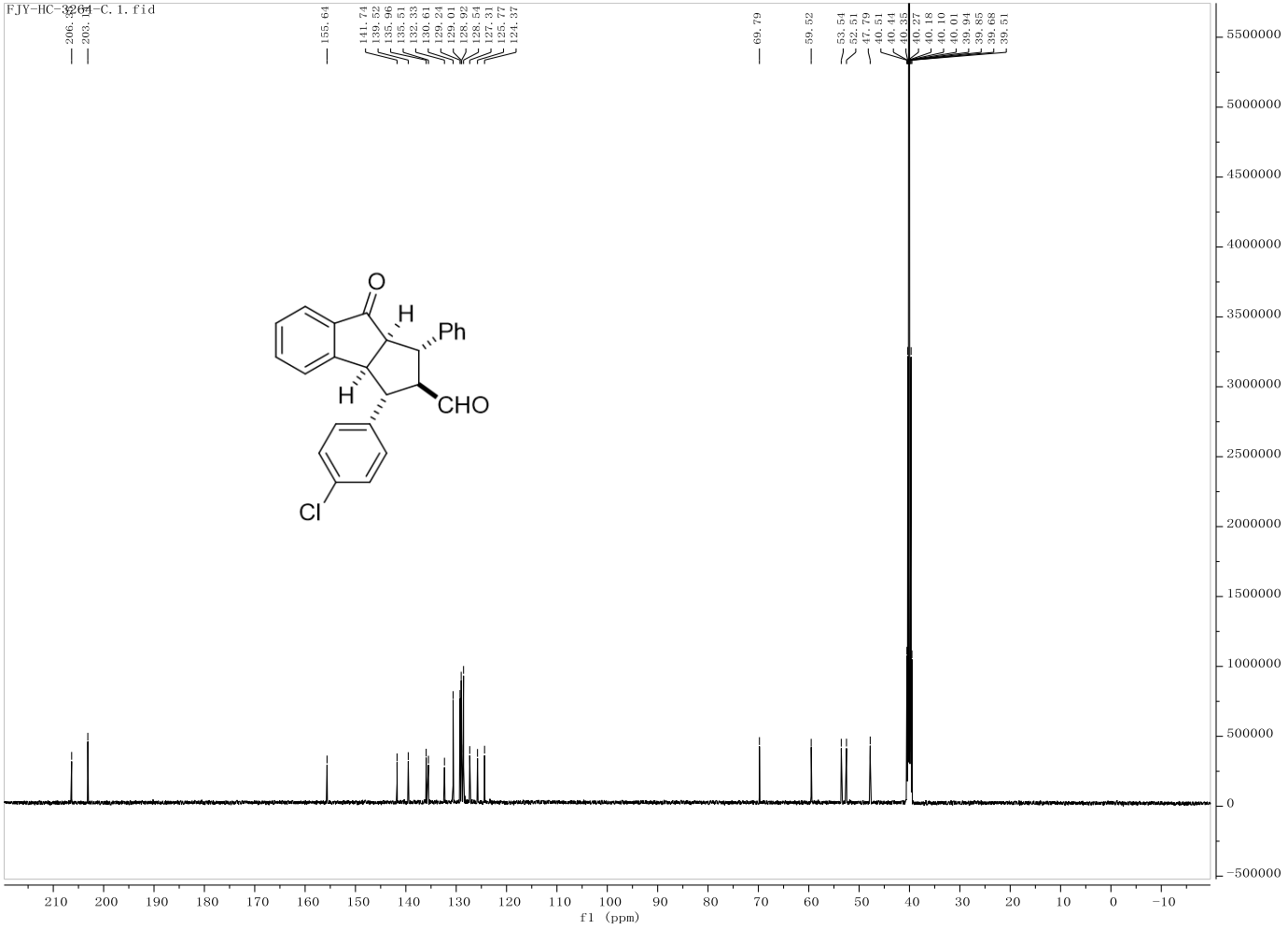
^{13}C NMR spectrum of **3ac** (125 MHz, DMSO-d_6)



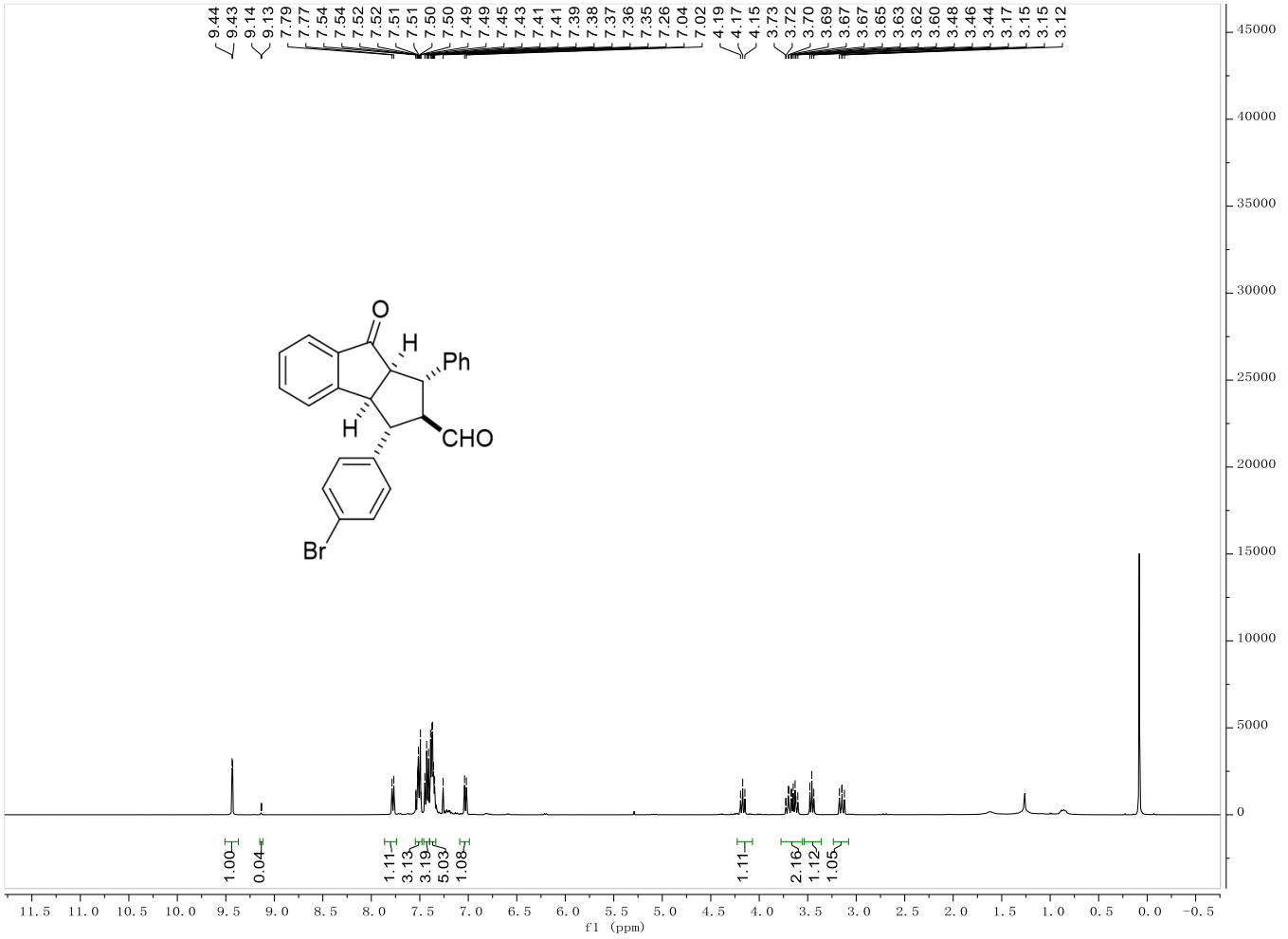
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



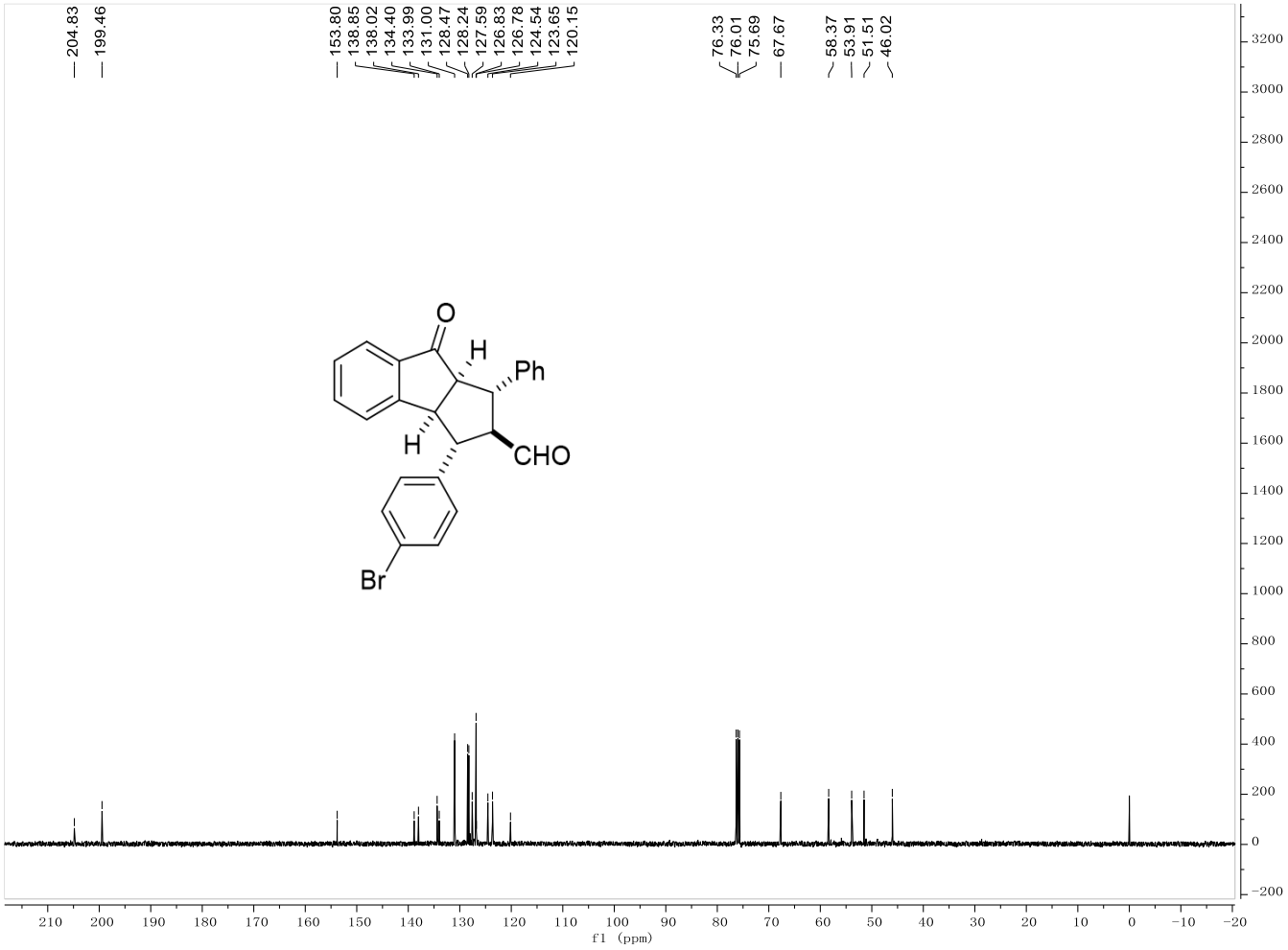
^{13}C NMR spectrum of **3ad** (125 MHz, DMSO-d_6)



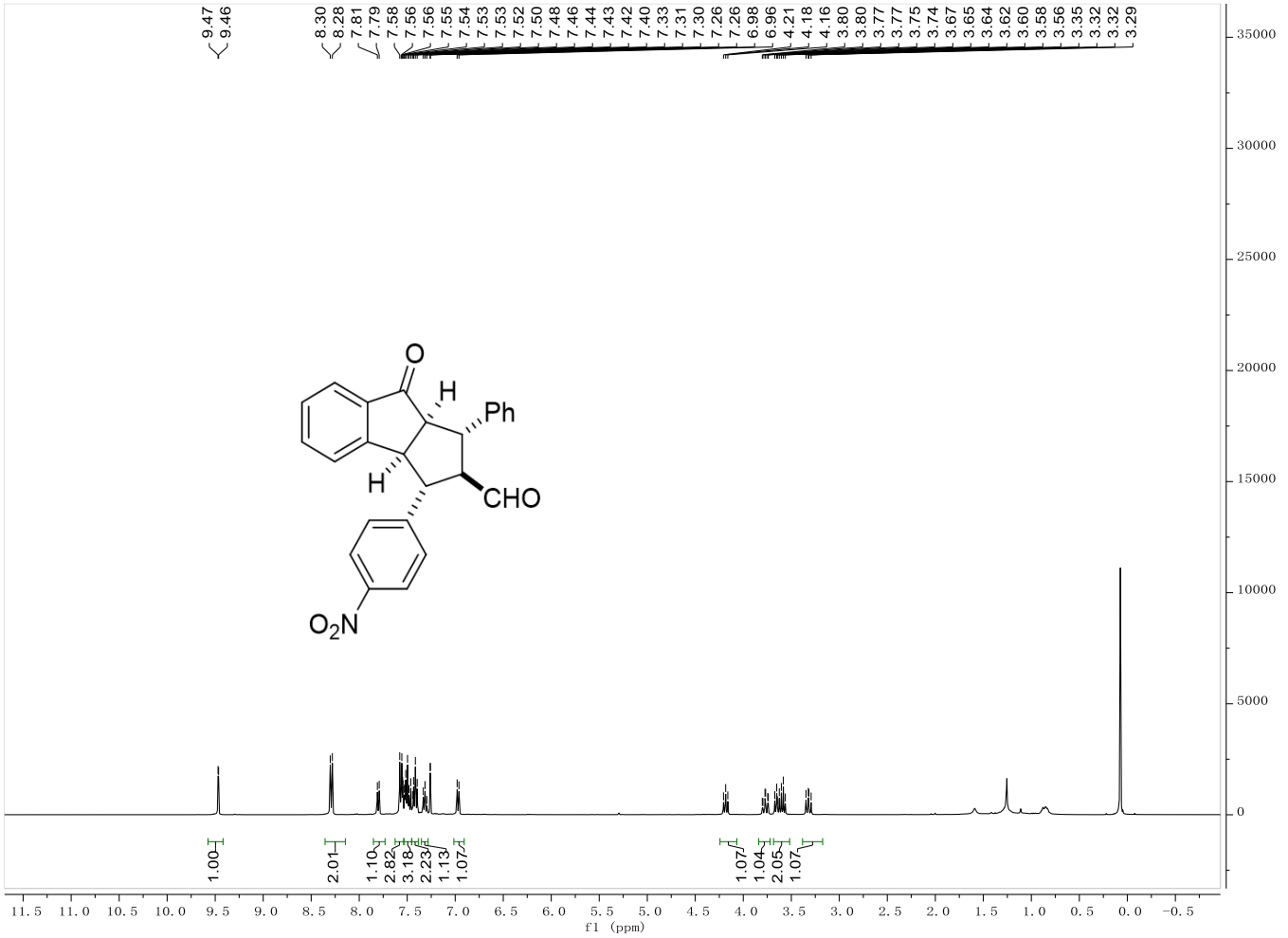
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



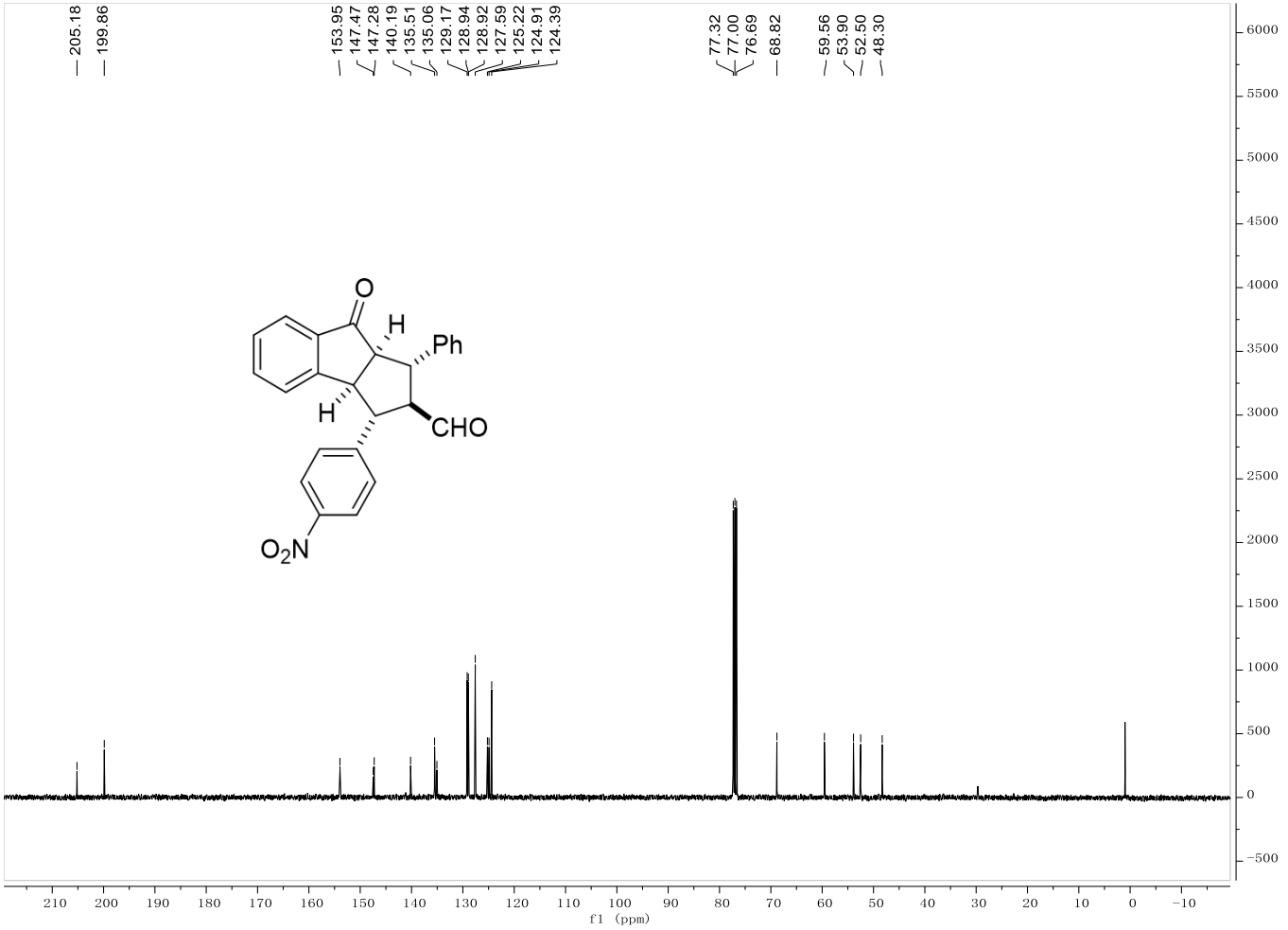
^{13}C NMR spectrum of **3ae** (100 MHz, $CDCl_3$)



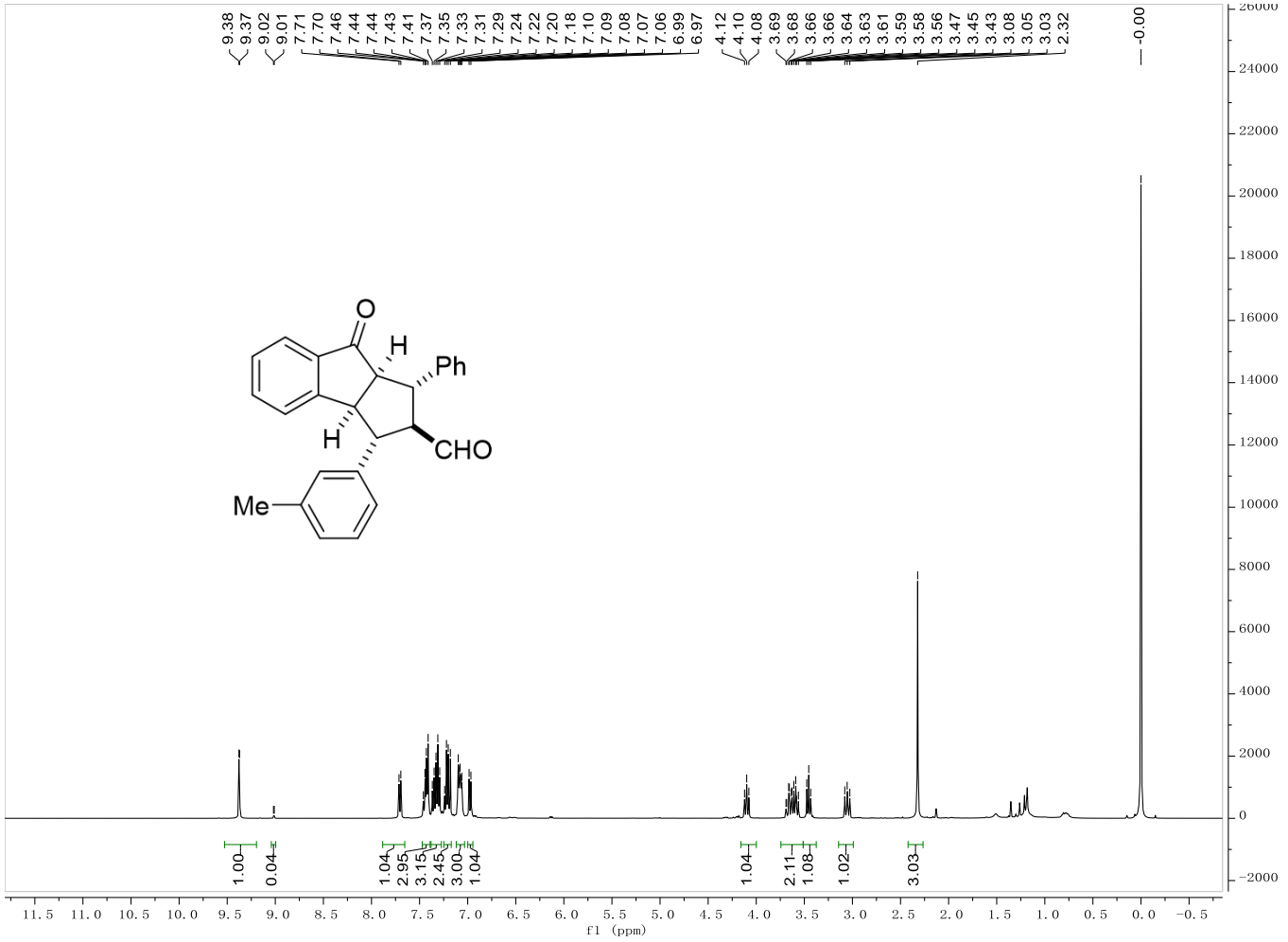
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



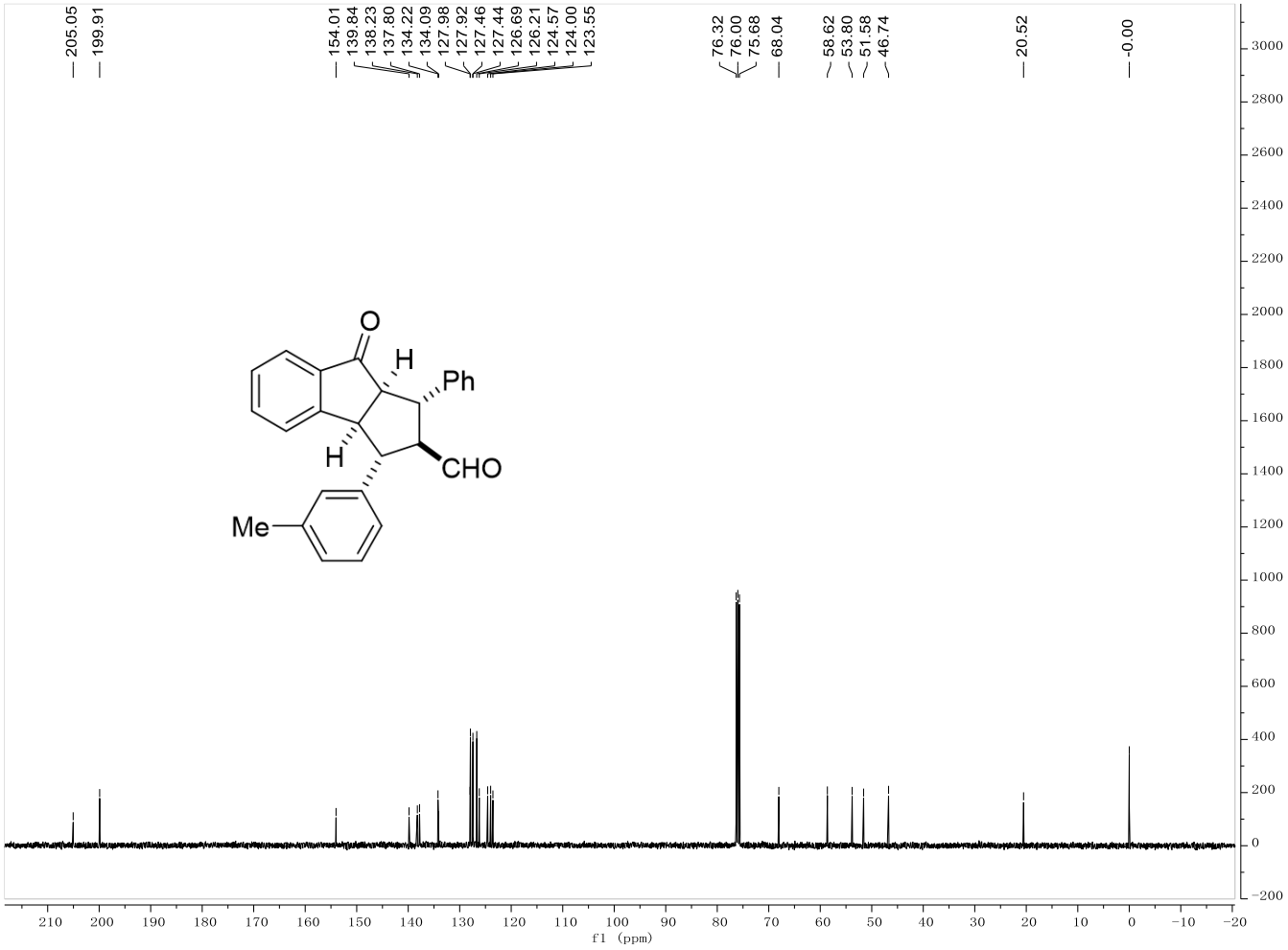
^{13}C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



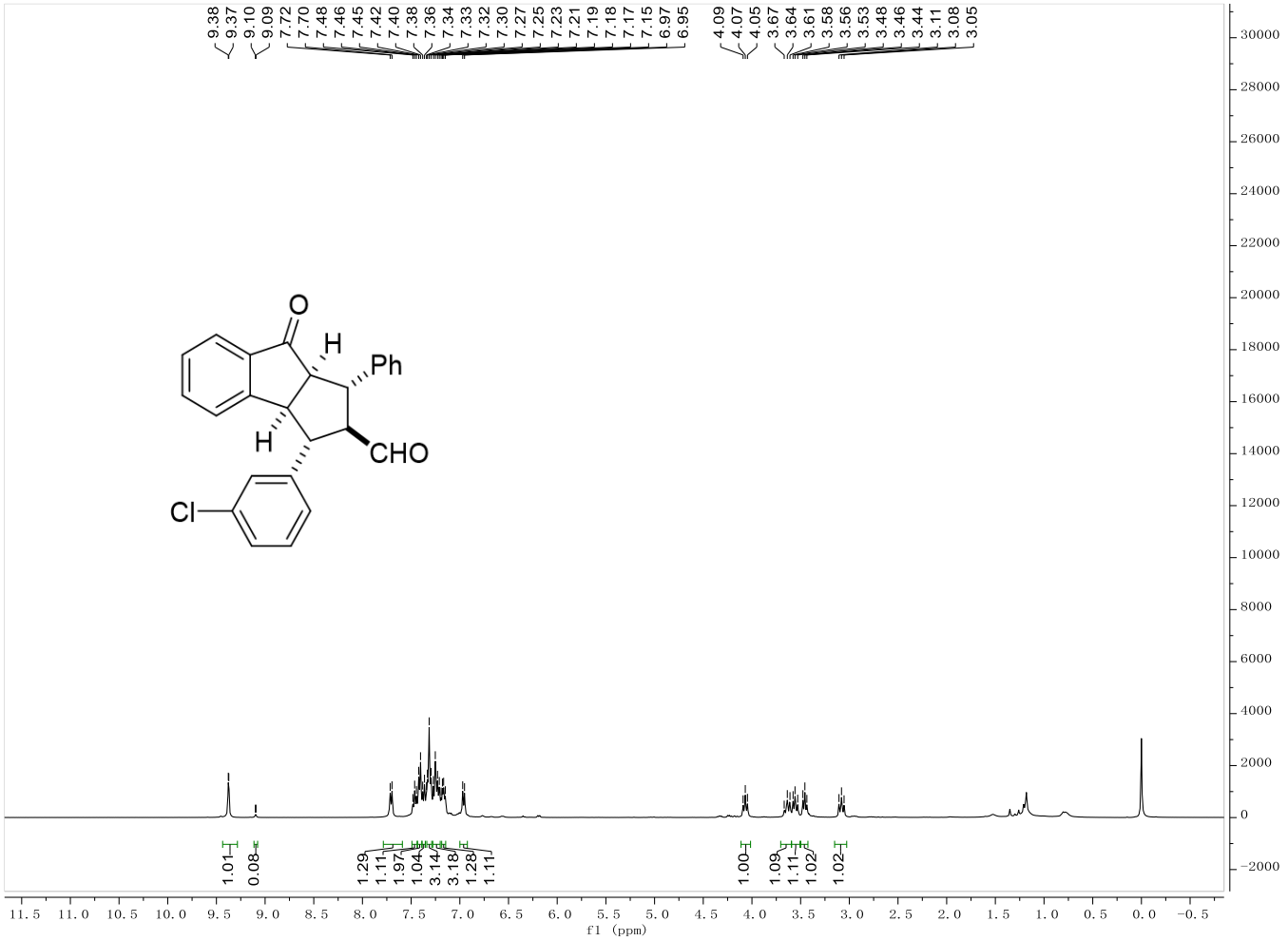
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



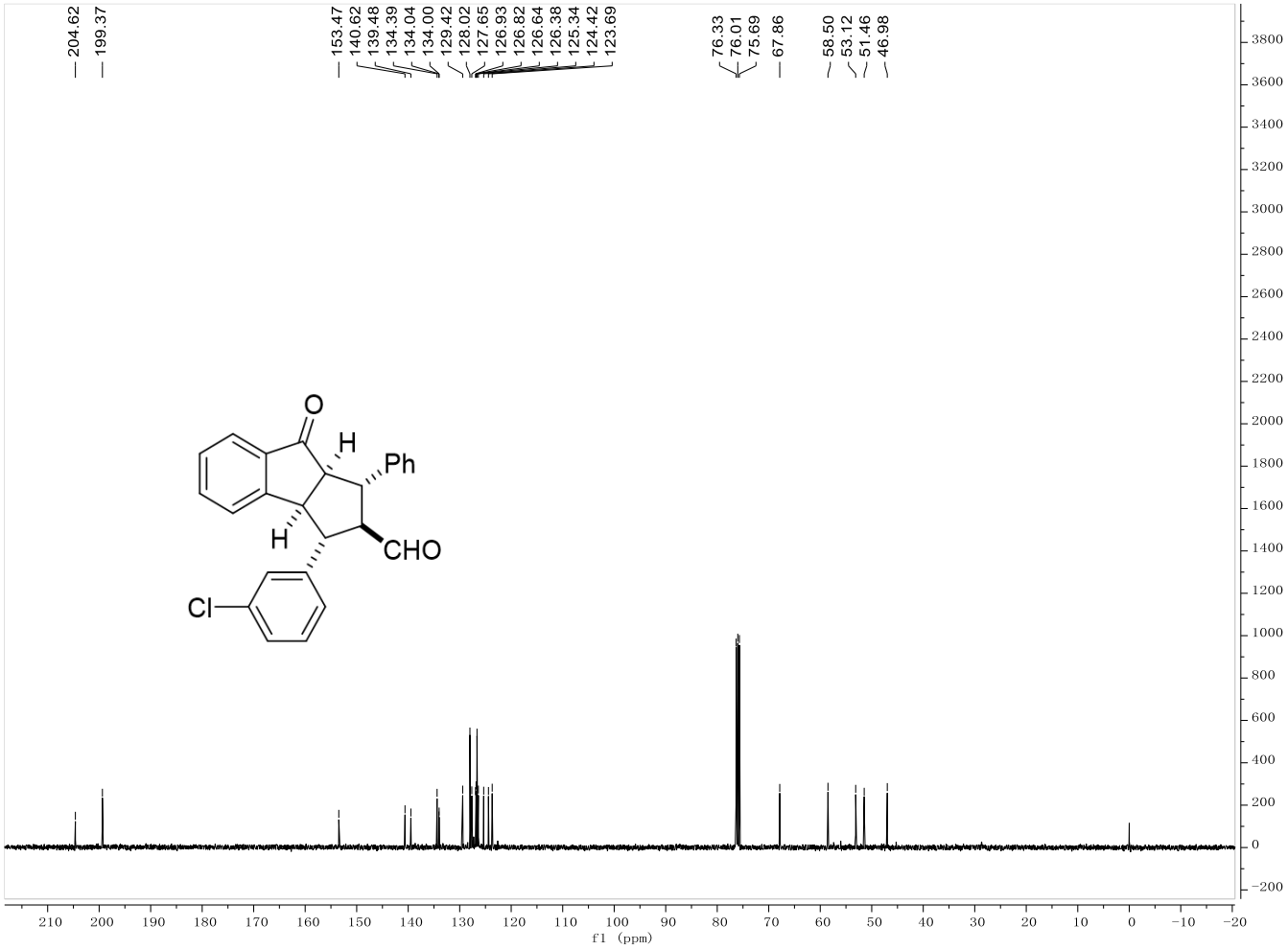
^{13}C NMR spectrum of **3ag** (100 MHz, $CDCl_3$)



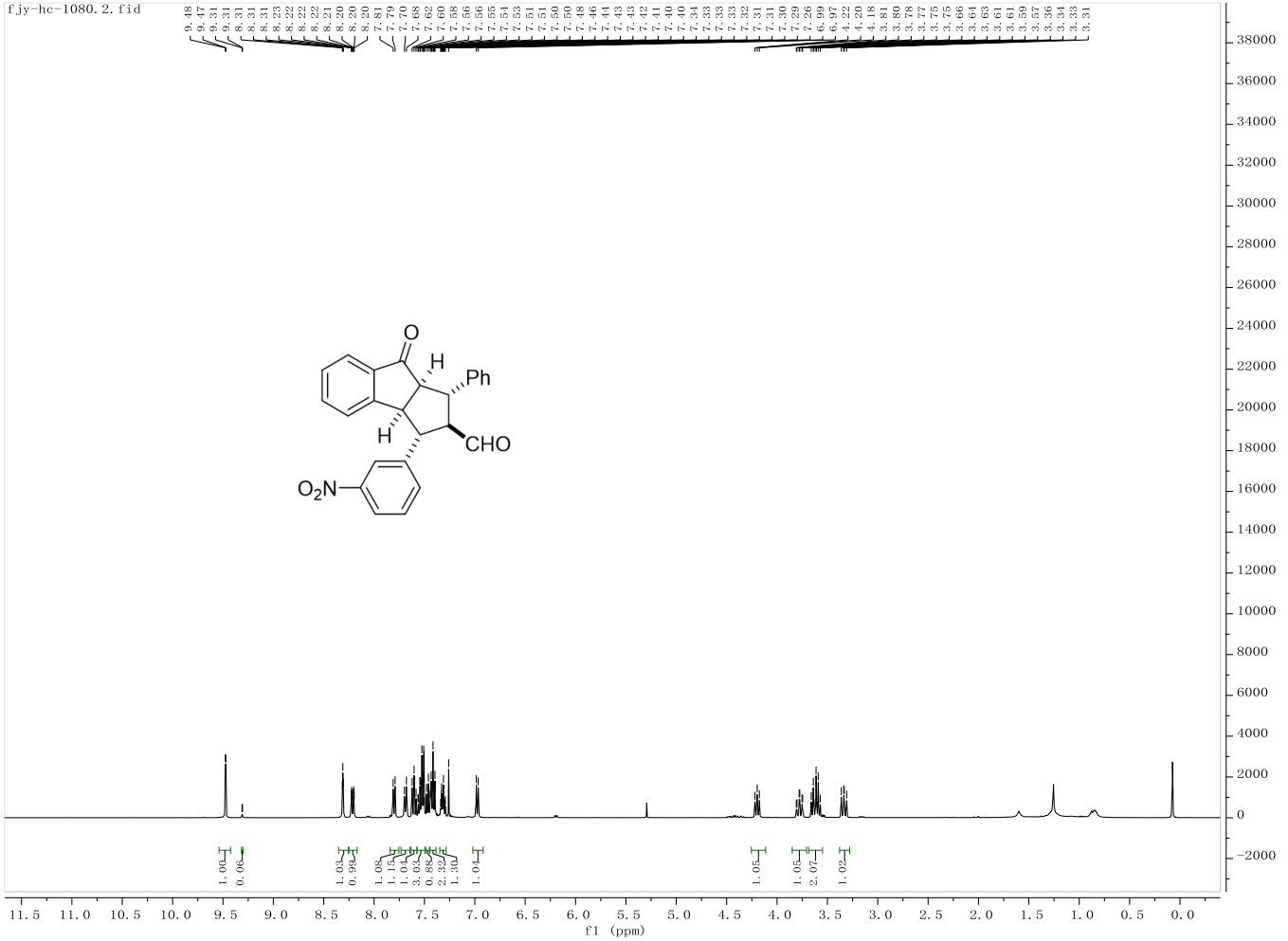
^{1}H NMR spectrum of **3ah** (400 MHz, $CDCl_3$)



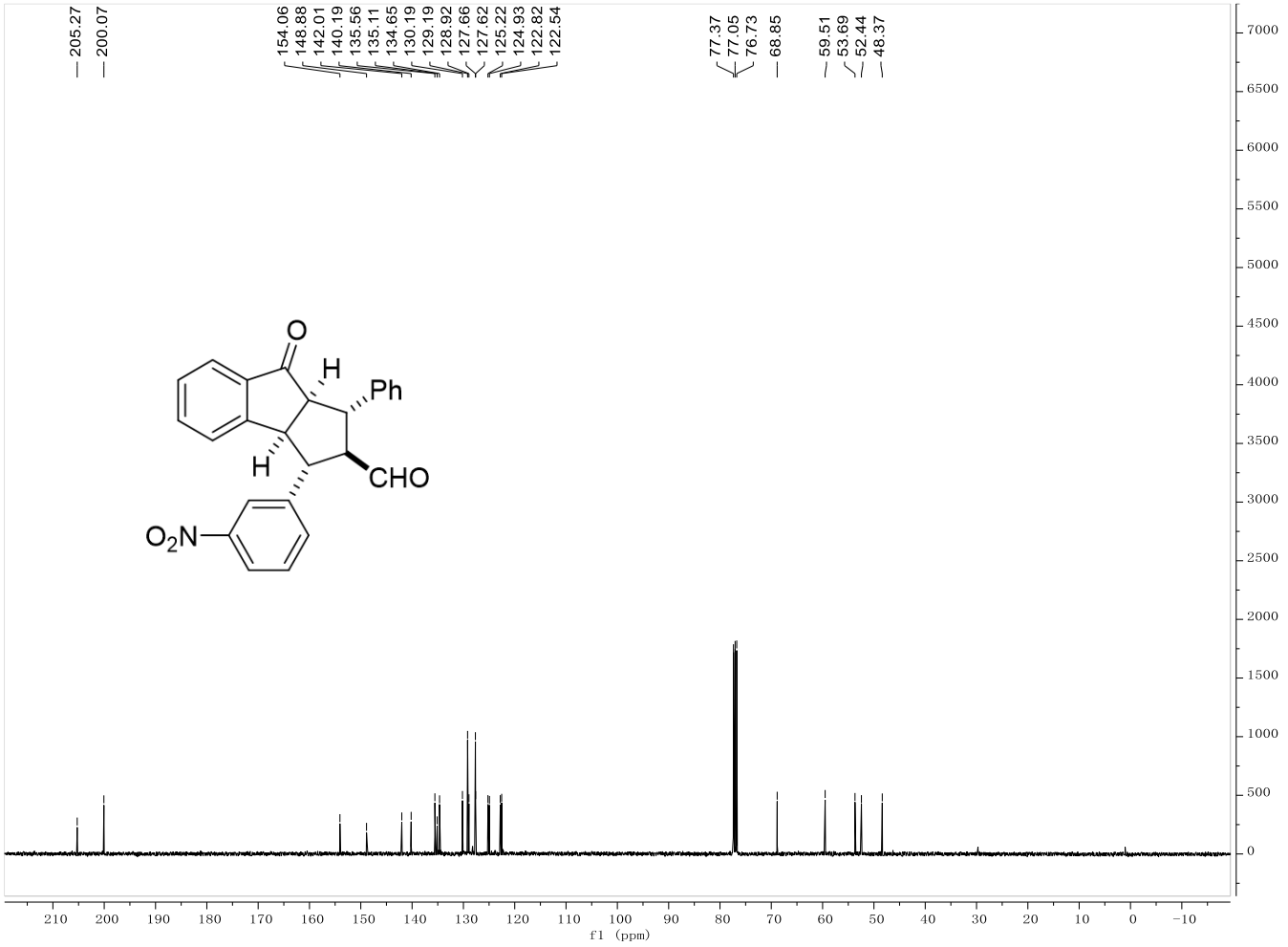
^{13}C NMR spectrum of **3ah** (100 MHz, $CDCl_3$)



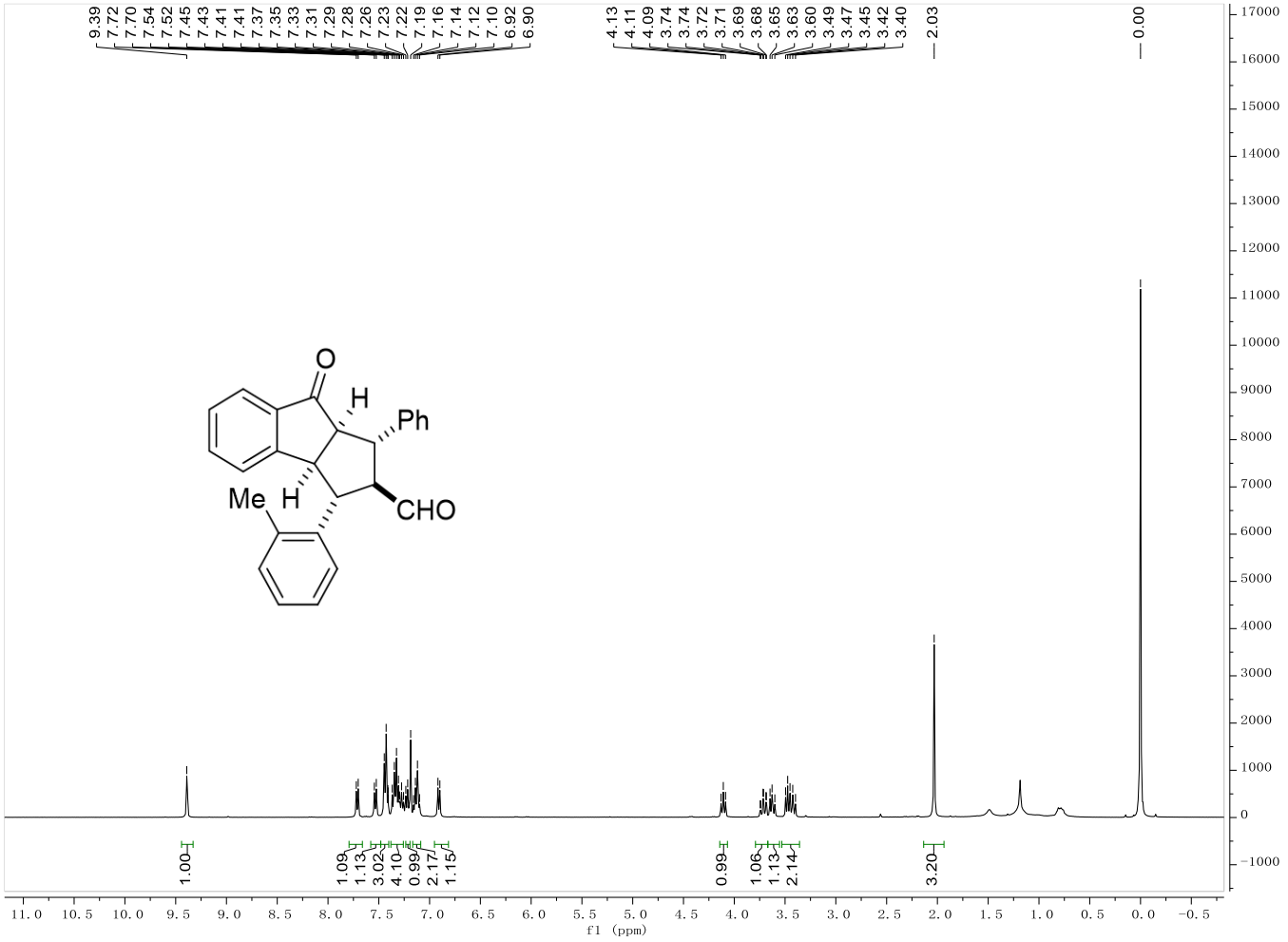
^{1}H NMR spectrum of **3ai** (40s0 MHz, $CDCl_3$)



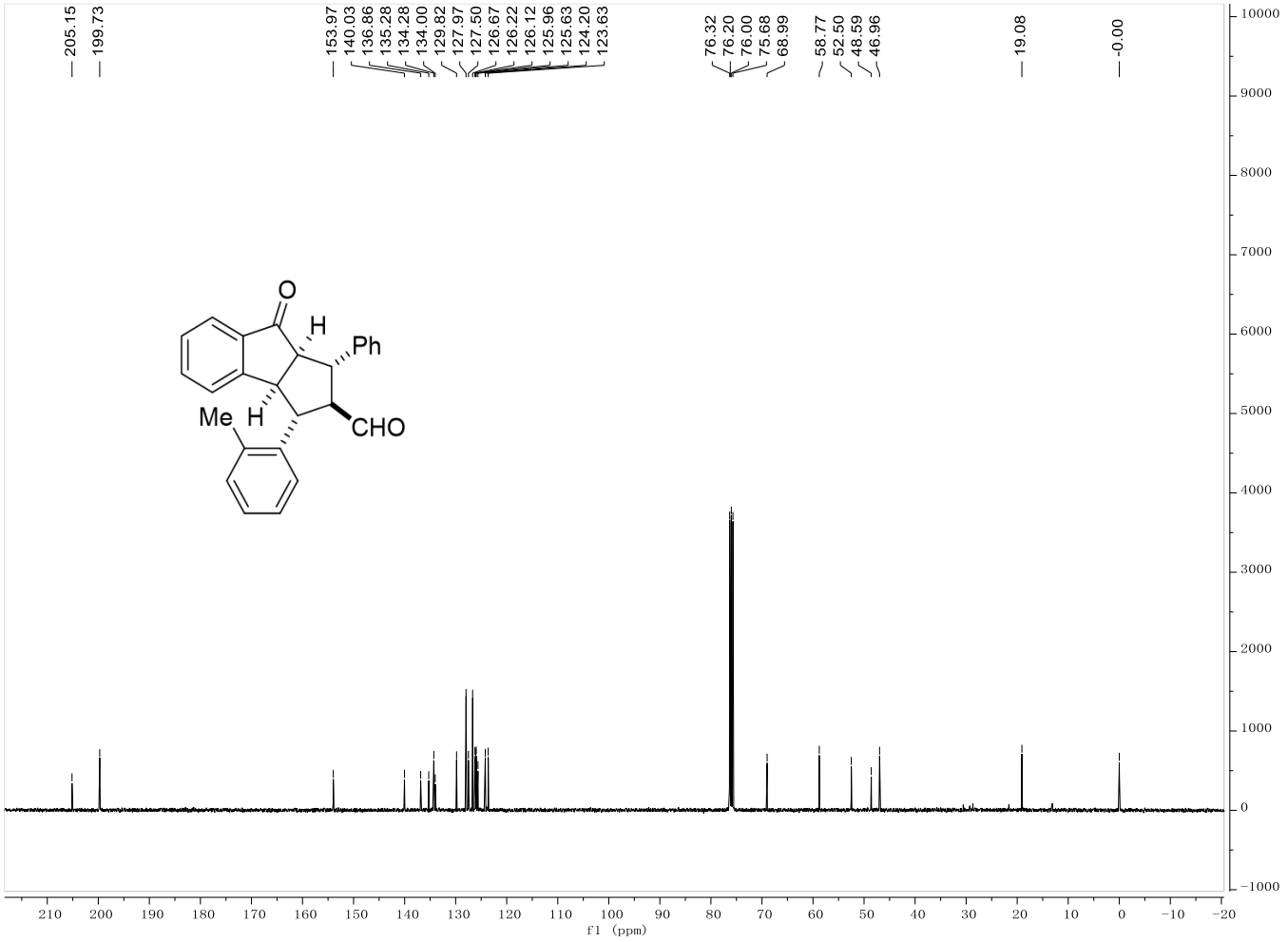
^{13}C NMR spectrum of **3ai** (100 MHz, $CDCl_3$)



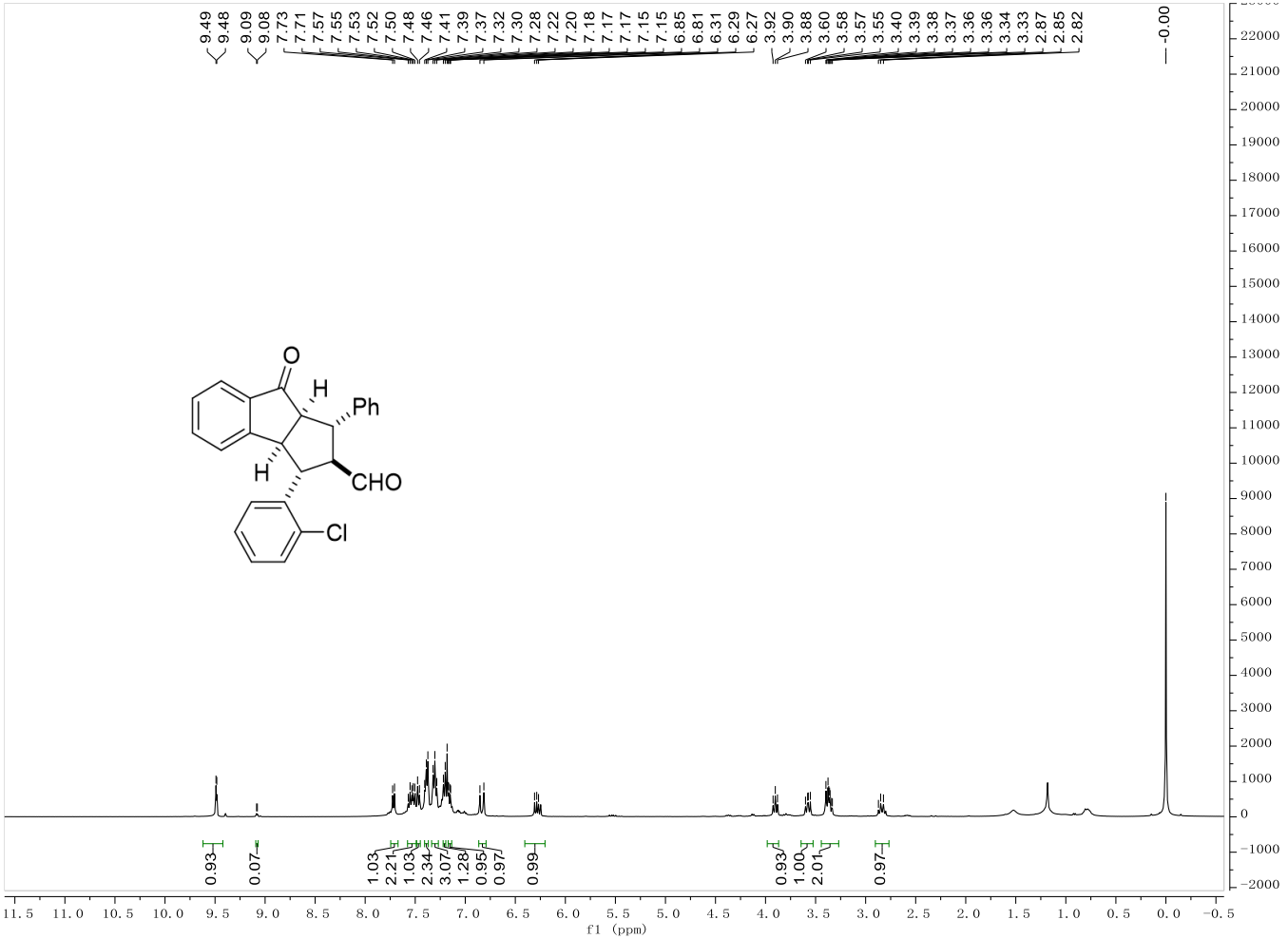
^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$)



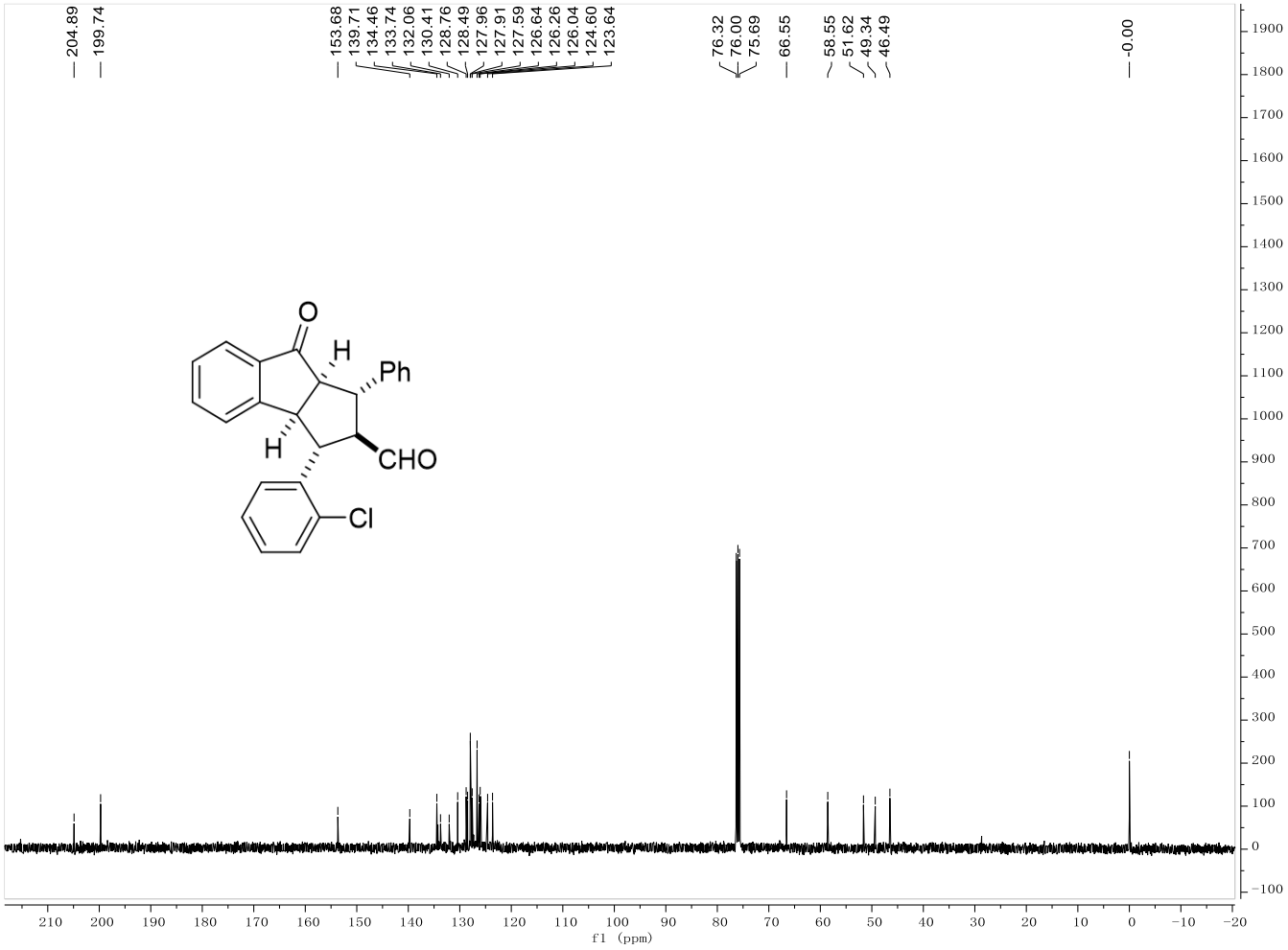
^{13}C NMR spectrum of **3aj** (100 MHz, $CDCl_3$)



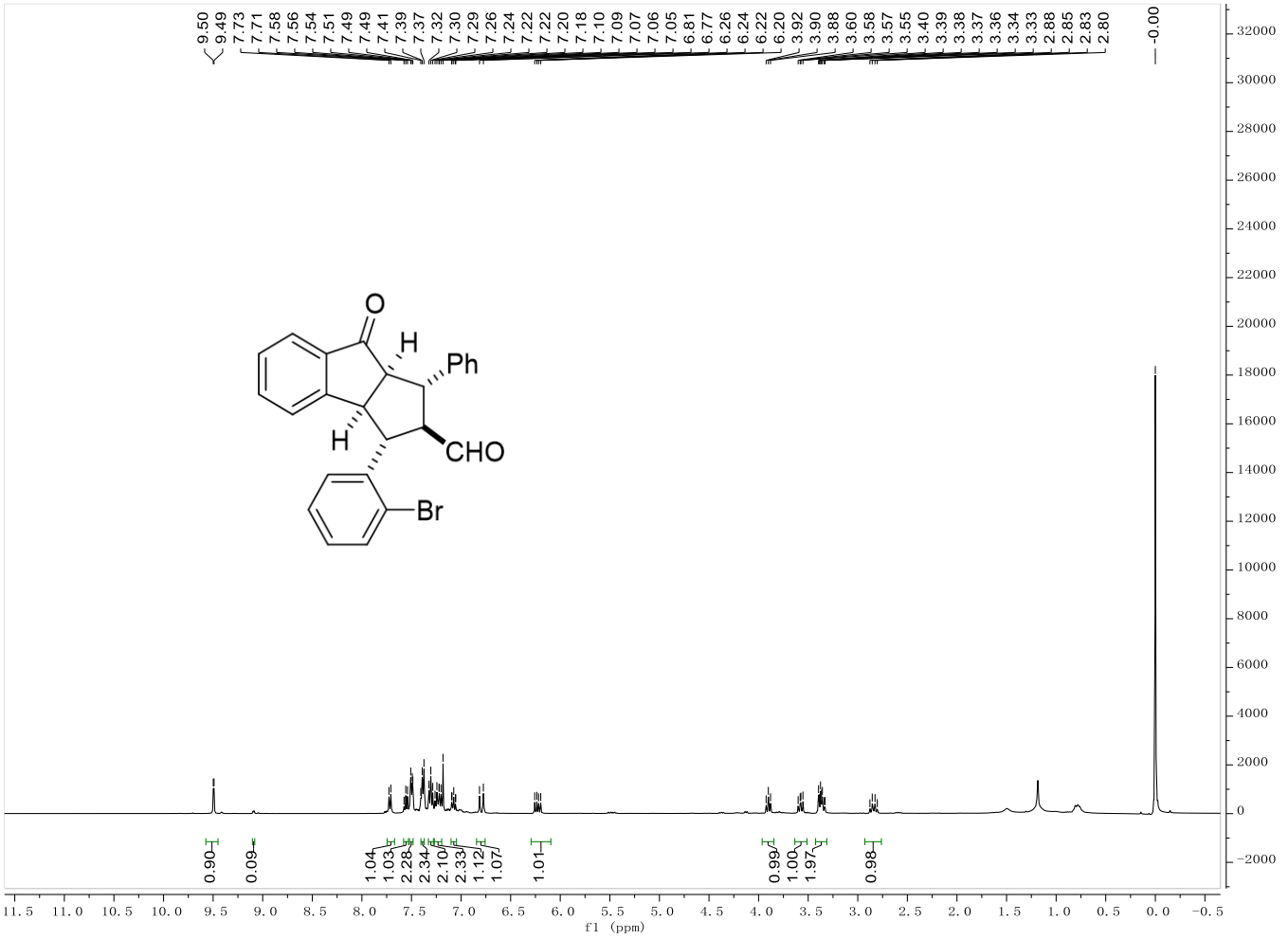
^{1}H NMR spectrum of **3ak** (400 MHz, $CDCl_3$)



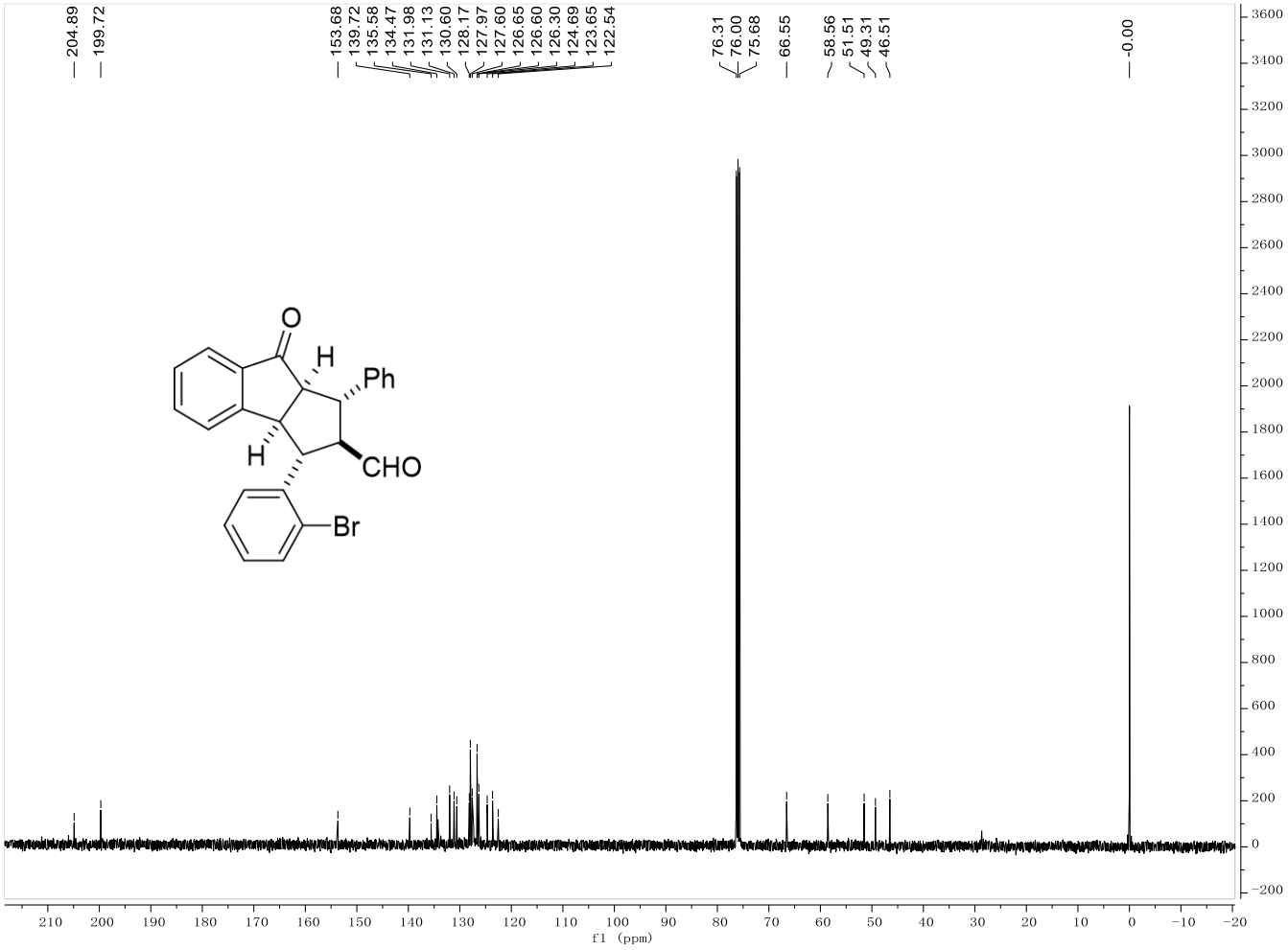
^{13}C NMR spectrum of **3ak** (100 MHz, $CDCl_3$)



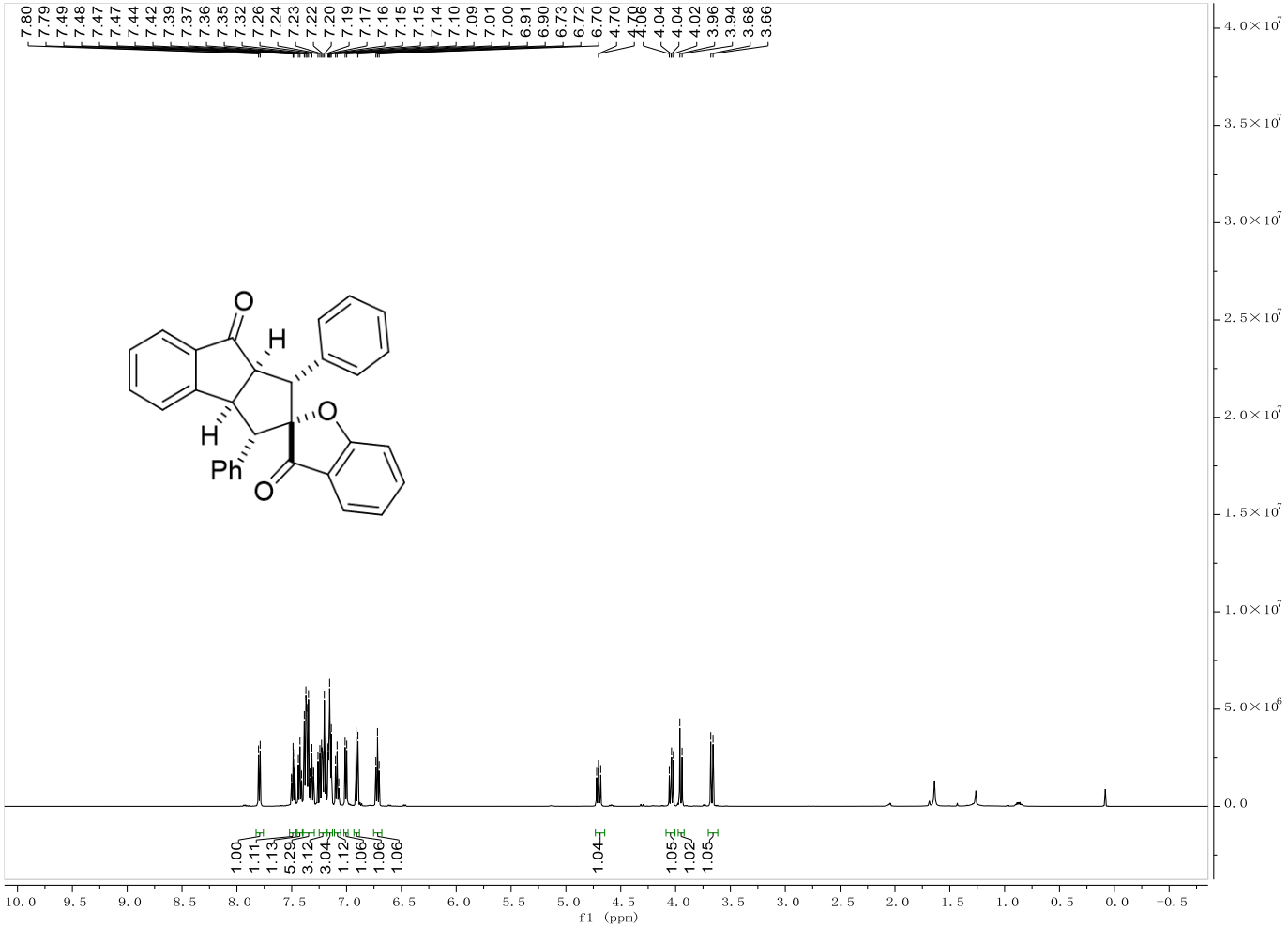
^{1}H NMR spectrum of **3al** (400 MHz, $CDCl_3$)



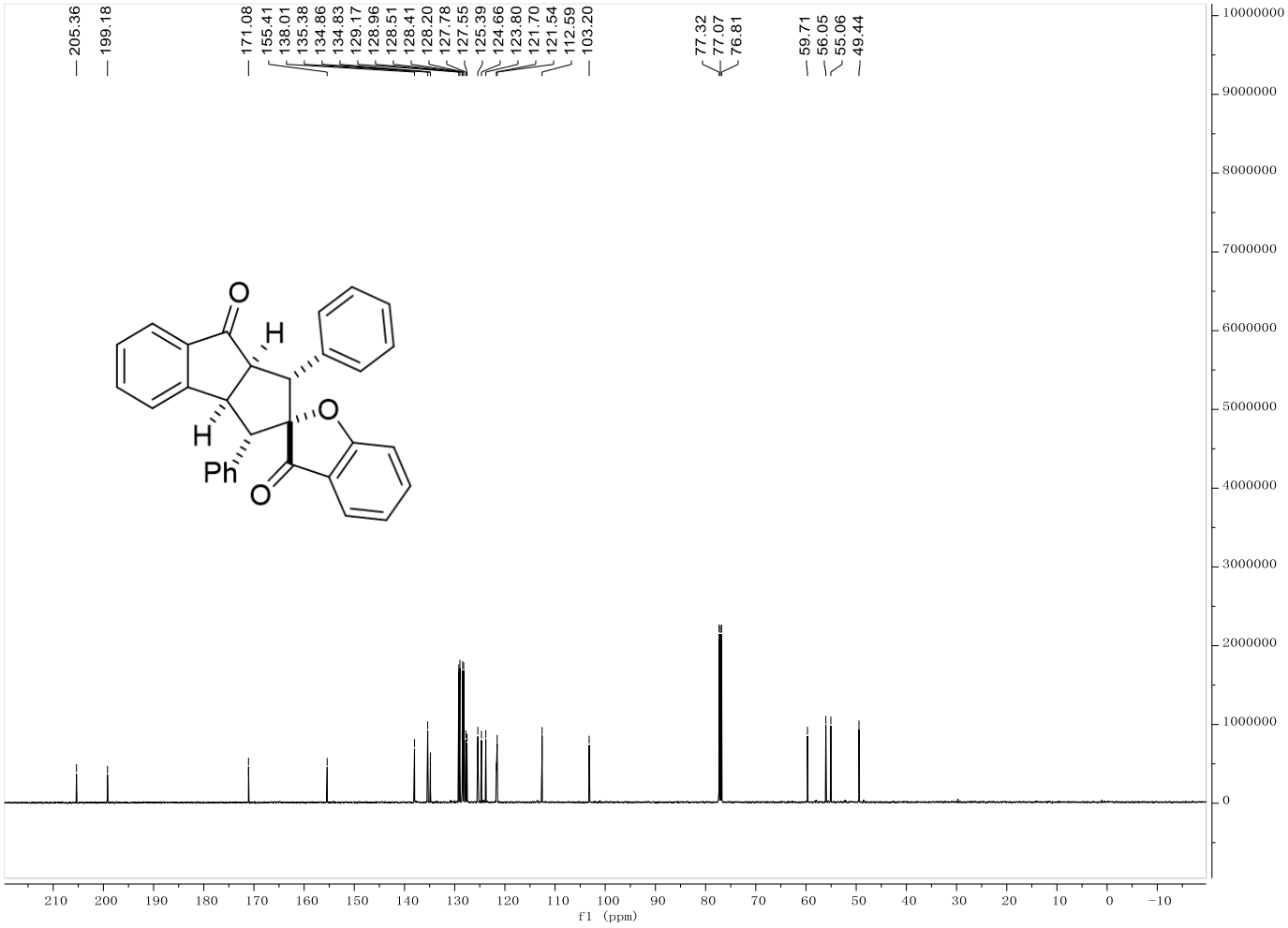
^{13}C NMR spectrum of **3al** (100 MHz, $CDCl_3$)



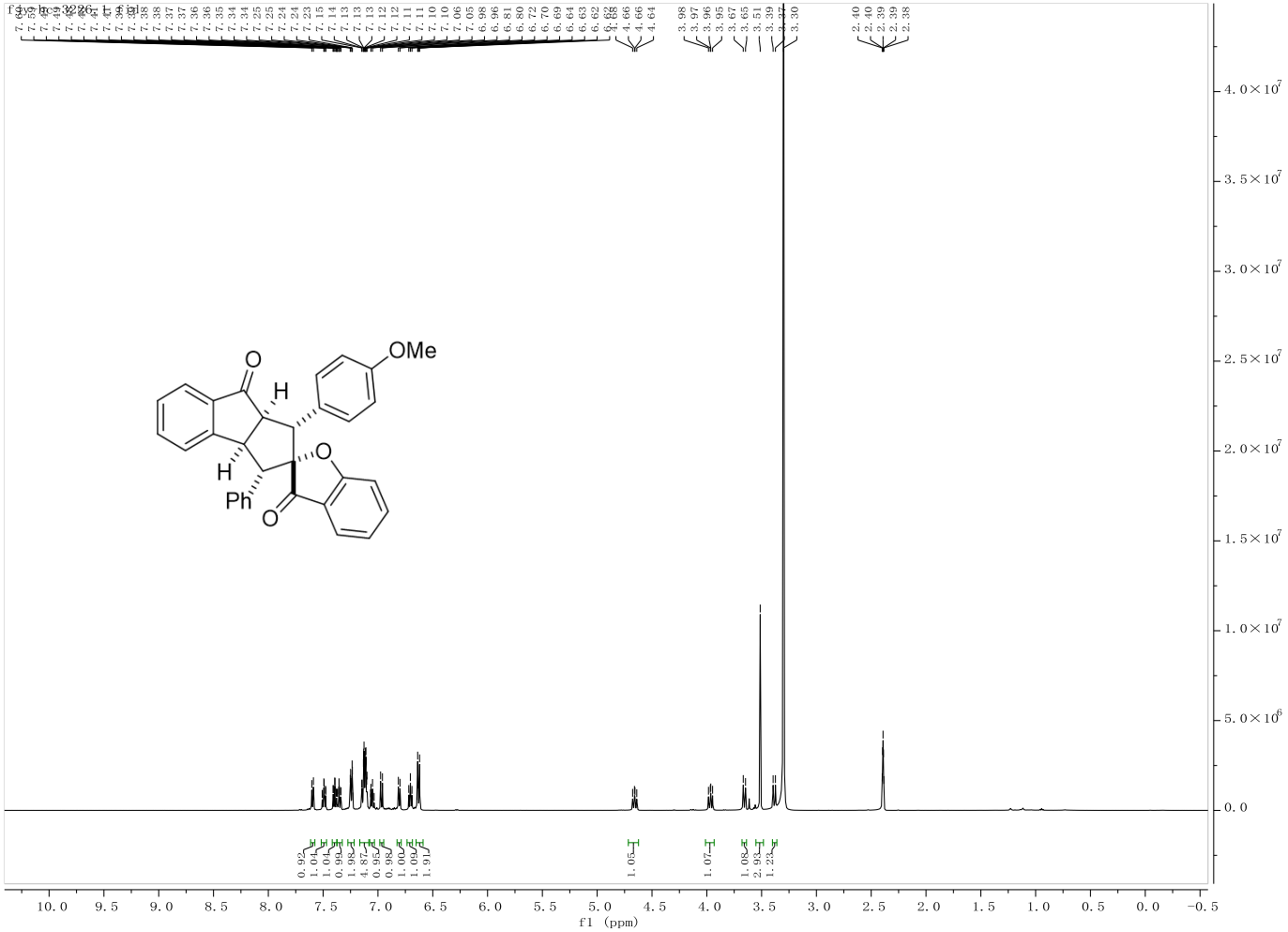
^{1}H NMR spectrum of **5a** (500 MHz, $CDCl_3$)



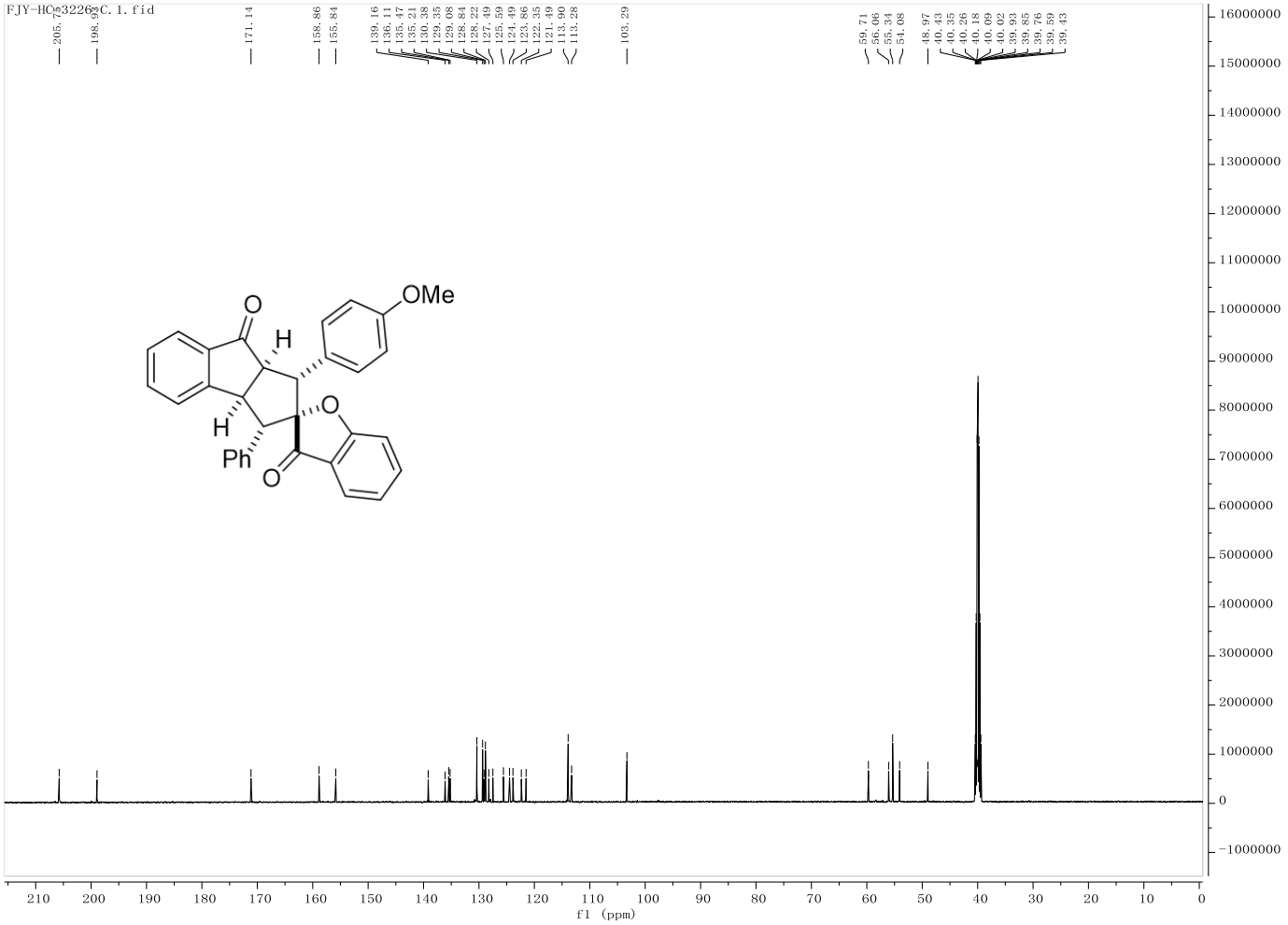
^{13}C NMR spectrum of **5a** (125 MHz, $CDCl_3$)



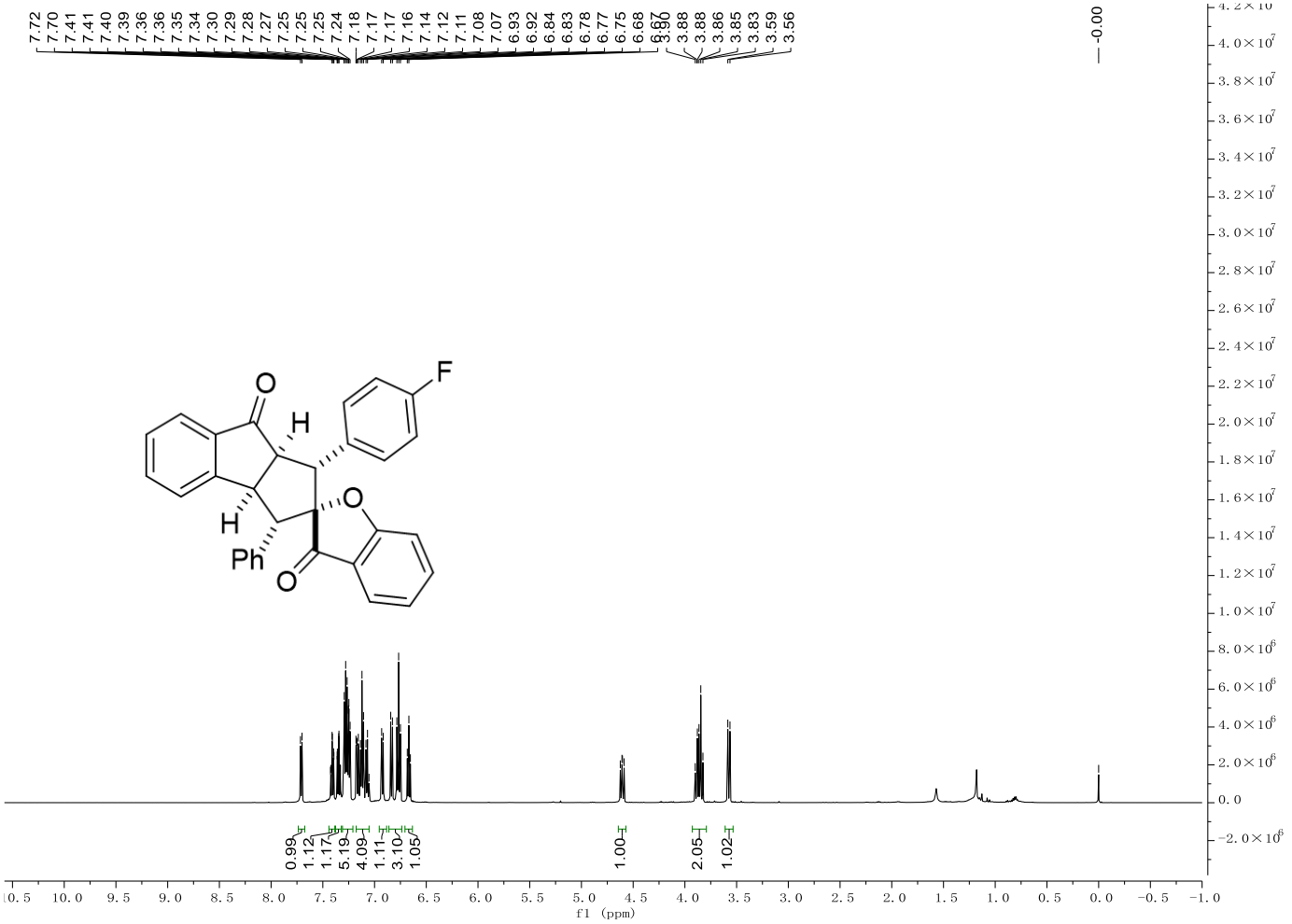
^{1}H NMR spectrum of **5b** (500 MHz, DMSO-d_6)



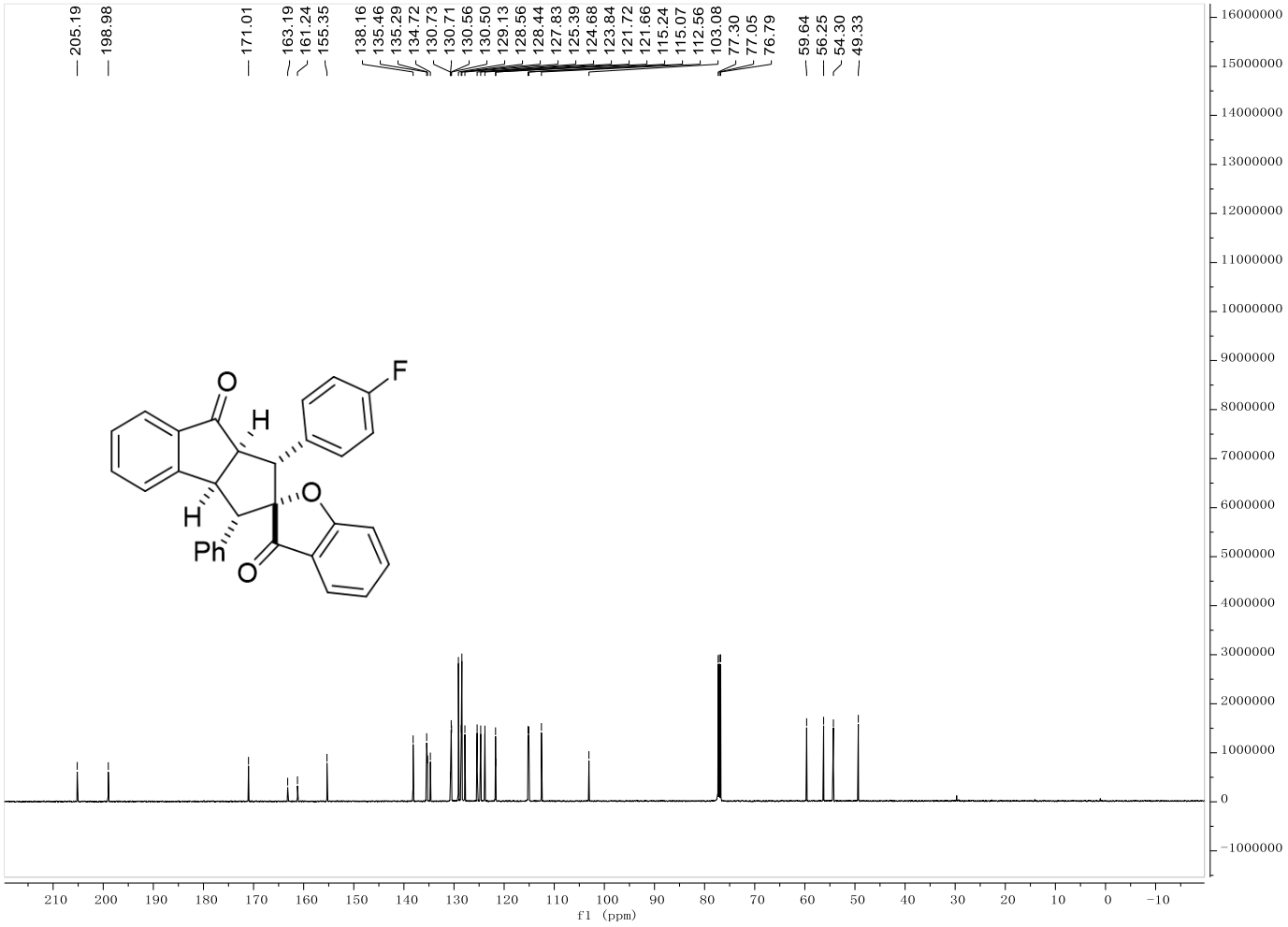
^{13}C NMR spectrum of **5b** (125 MHz, DMSO-d_6)



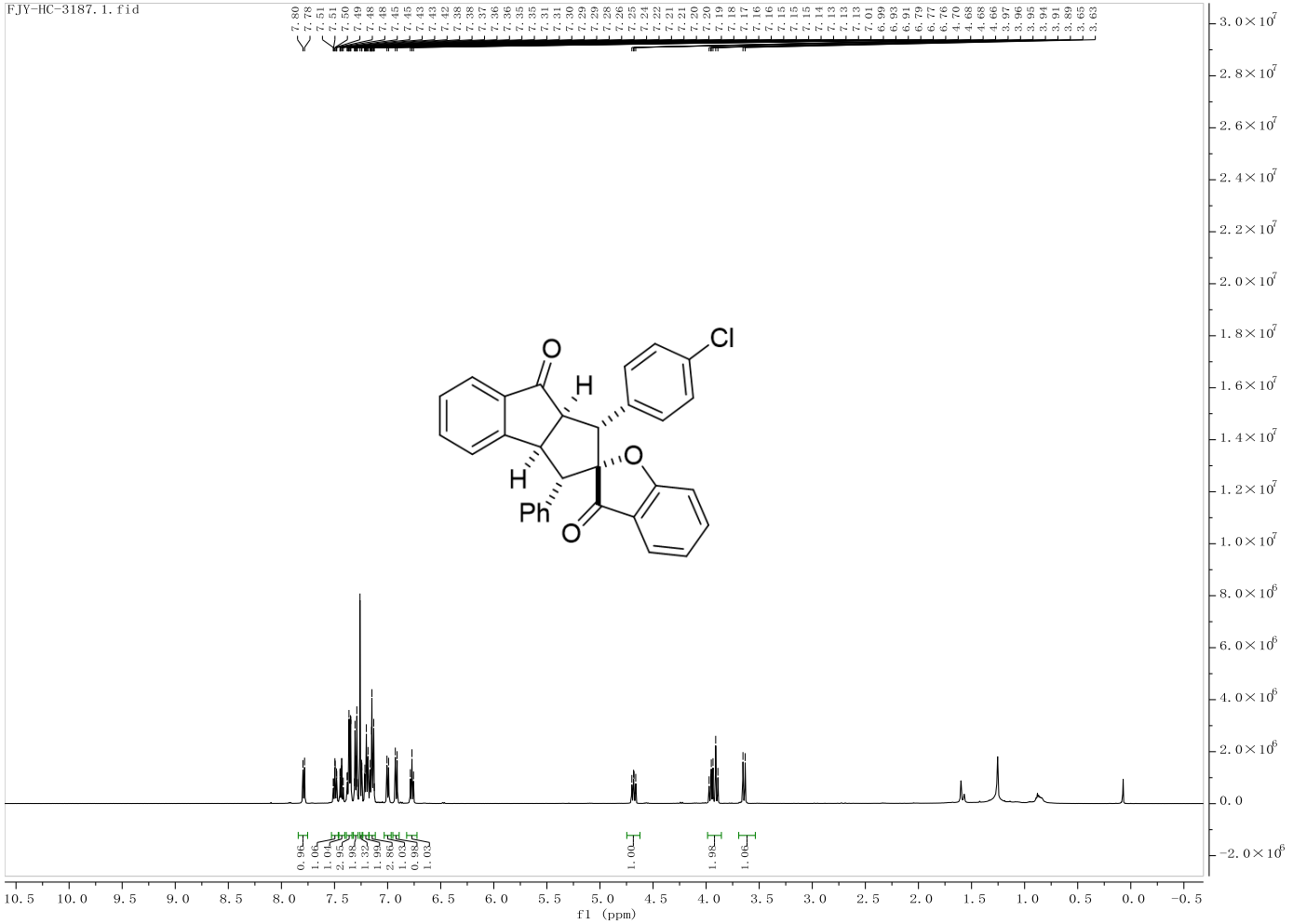
^{1}H NMR spectrum of **5c** (500 MHz, $CDCl_3$)



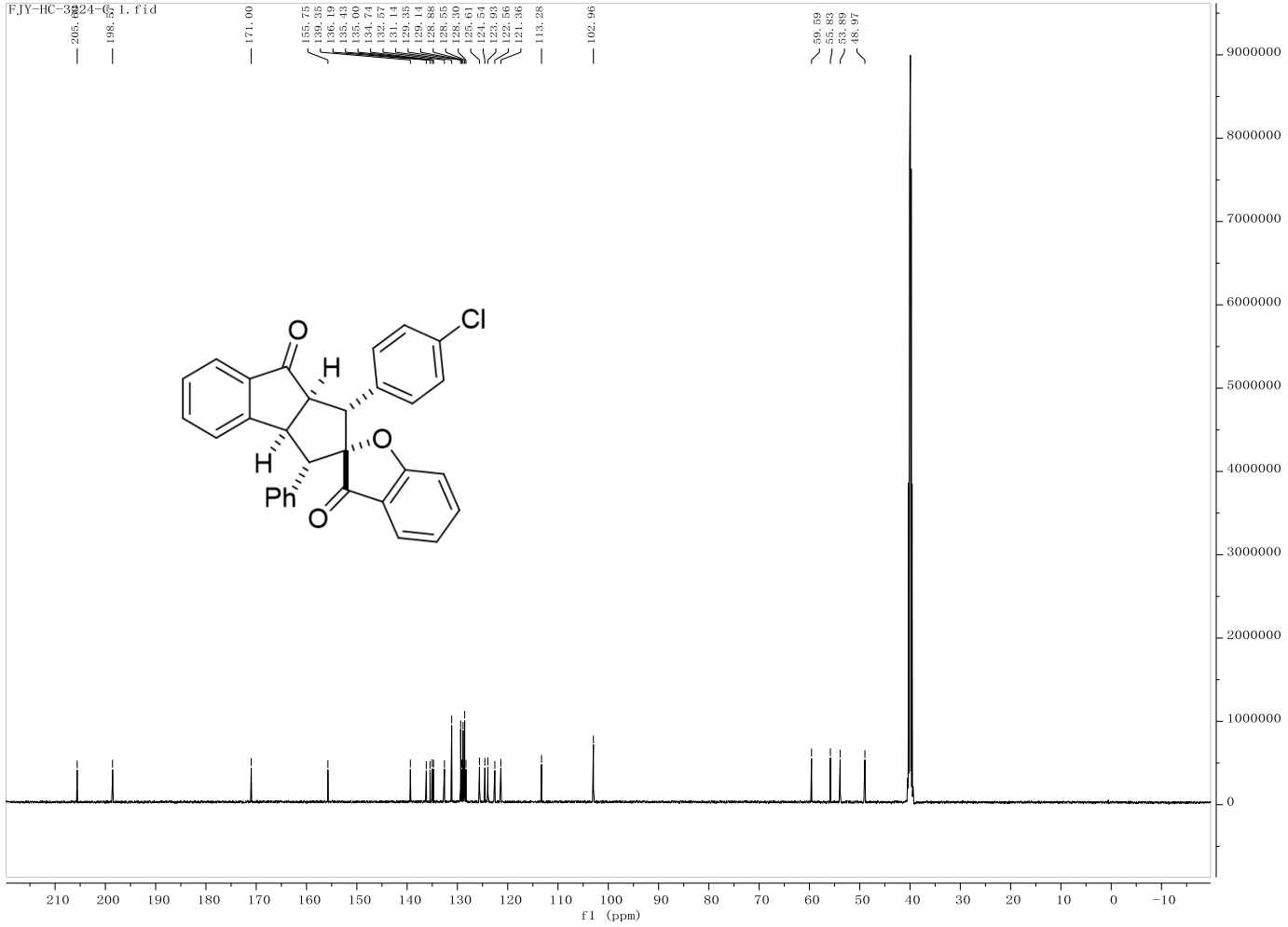
^{13}C NMR spectrum of **5c** (125 MHz, $CDCl_3$)



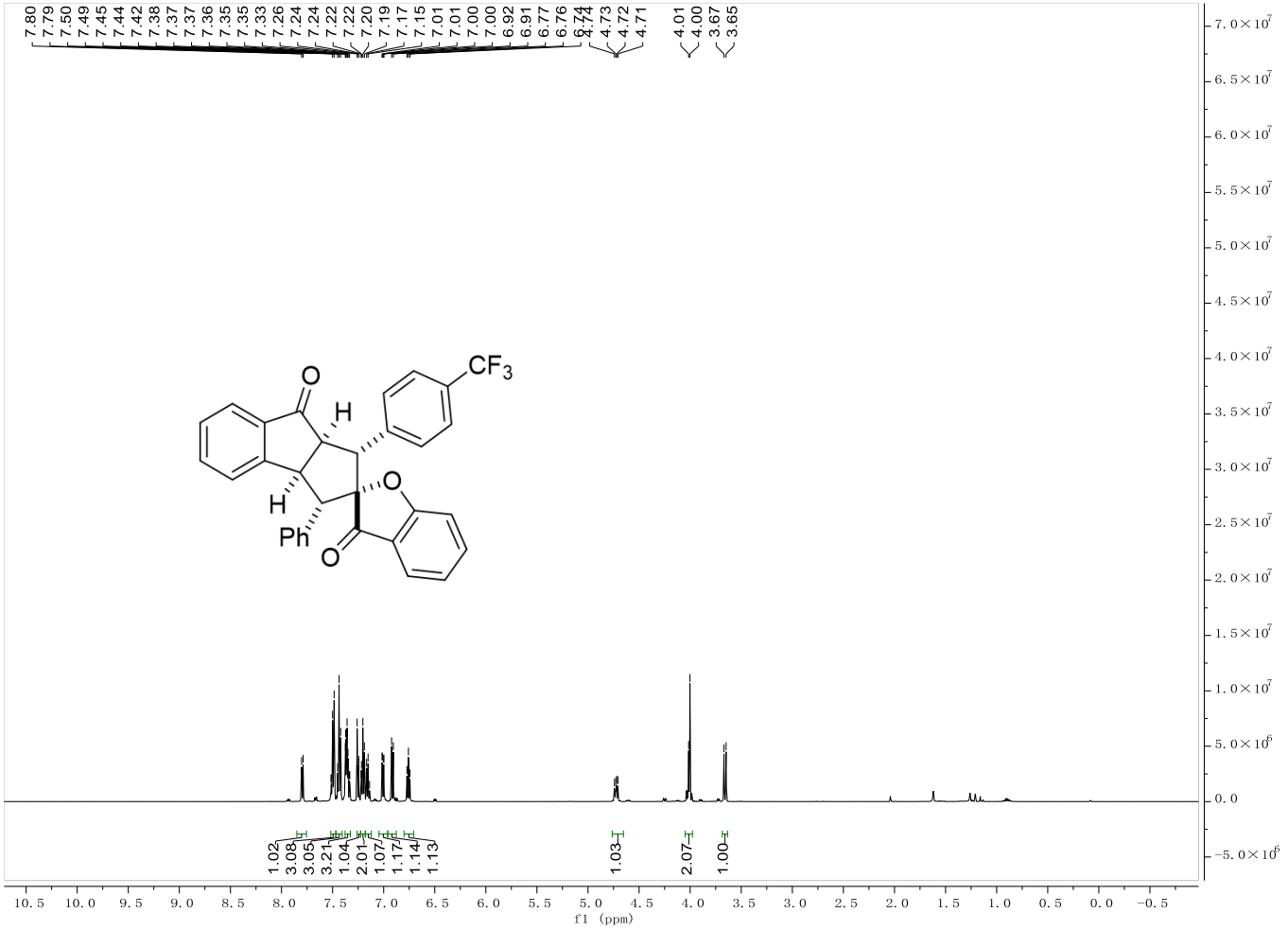
^{1}H NMR spectrum of **5d** (500 MHz, $CDCl_3$)



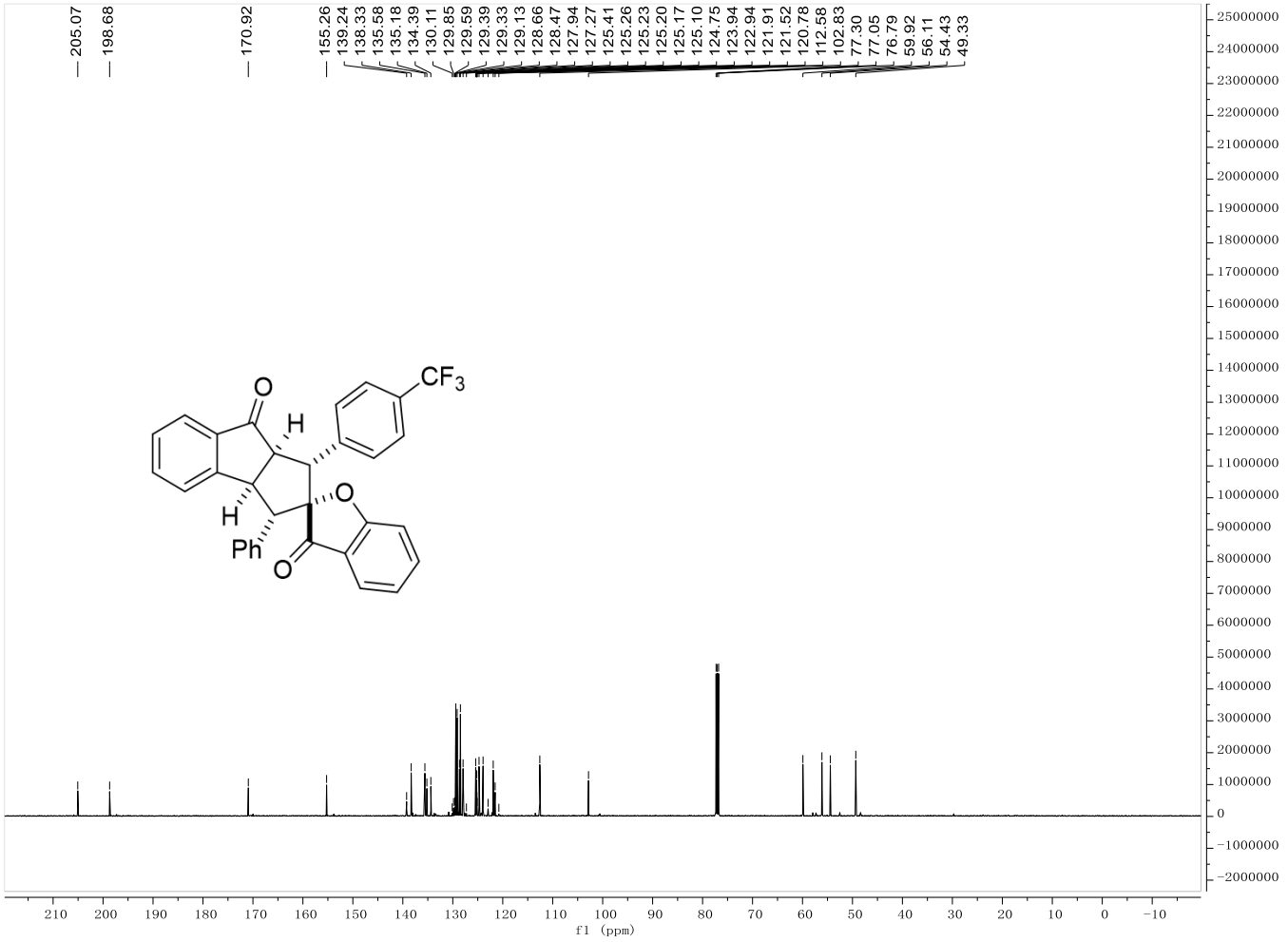
^{13}C NMR spectrum of **5d** (125 MHz, DMSO-d_6)



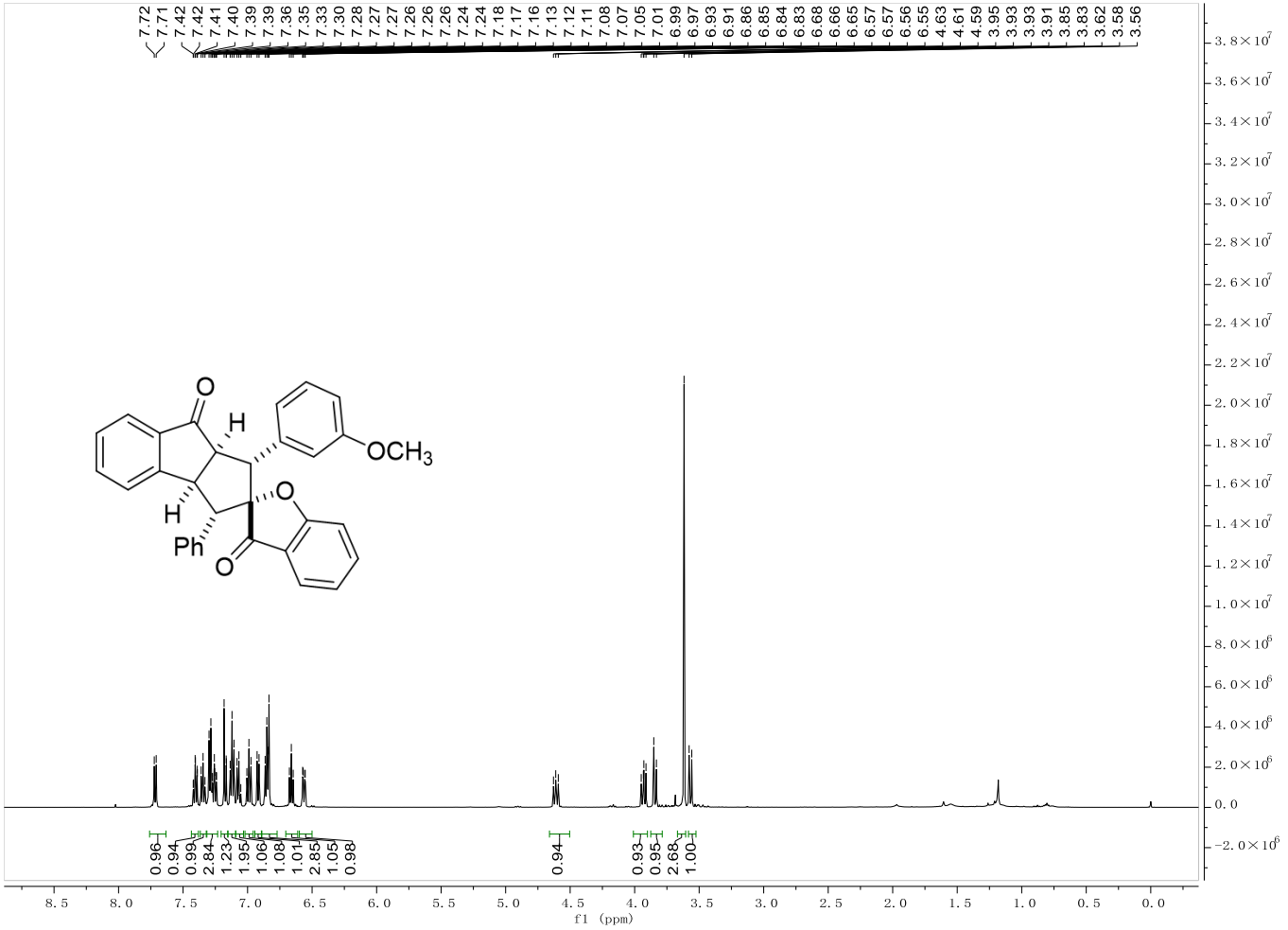
^{1}H NMR spectrum of **5e** (500 MHz, $CDCl_3$)



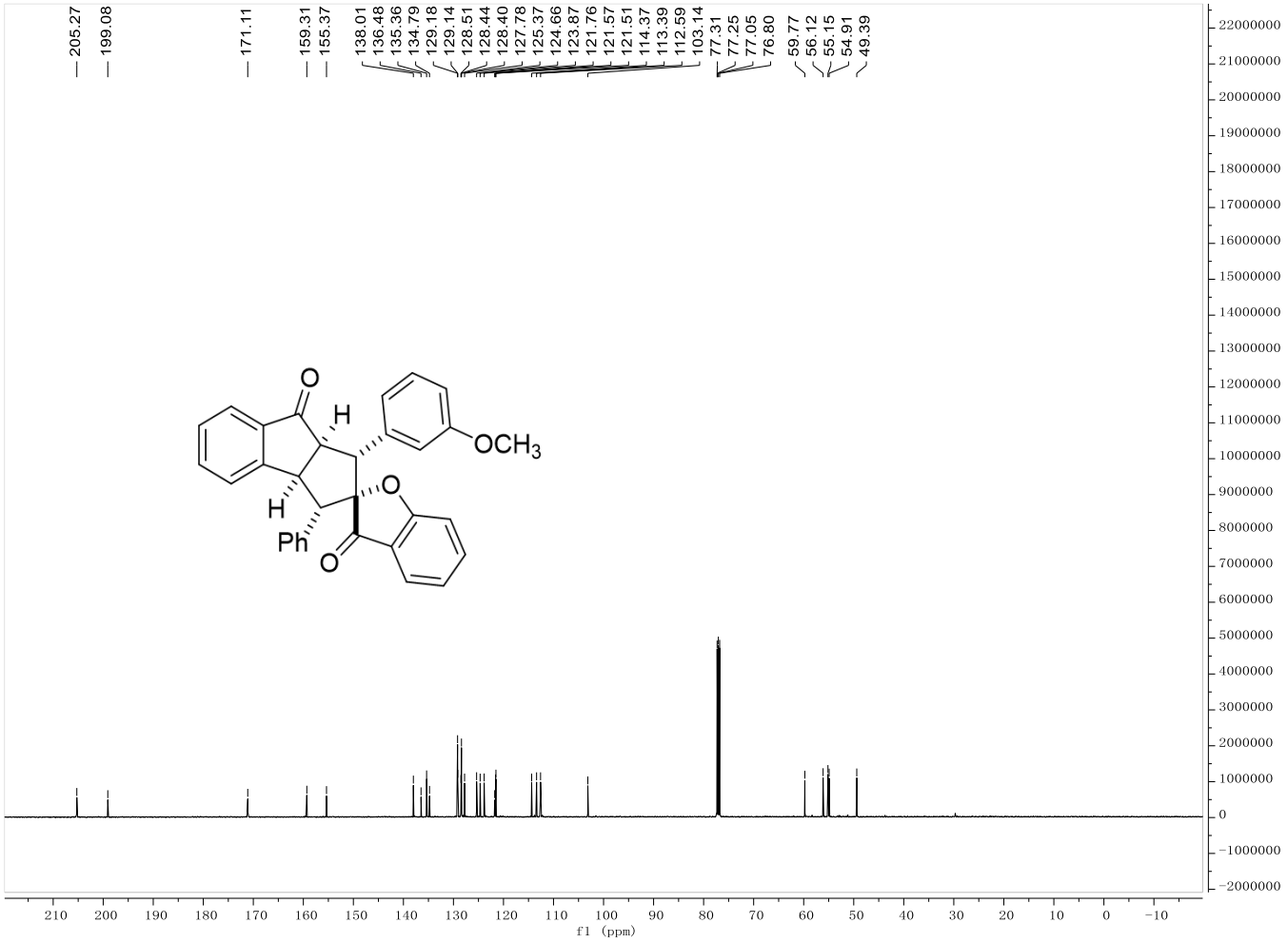
^{13}C NMR spectrum of **5e** (125 MHz, $CDCl_3$)



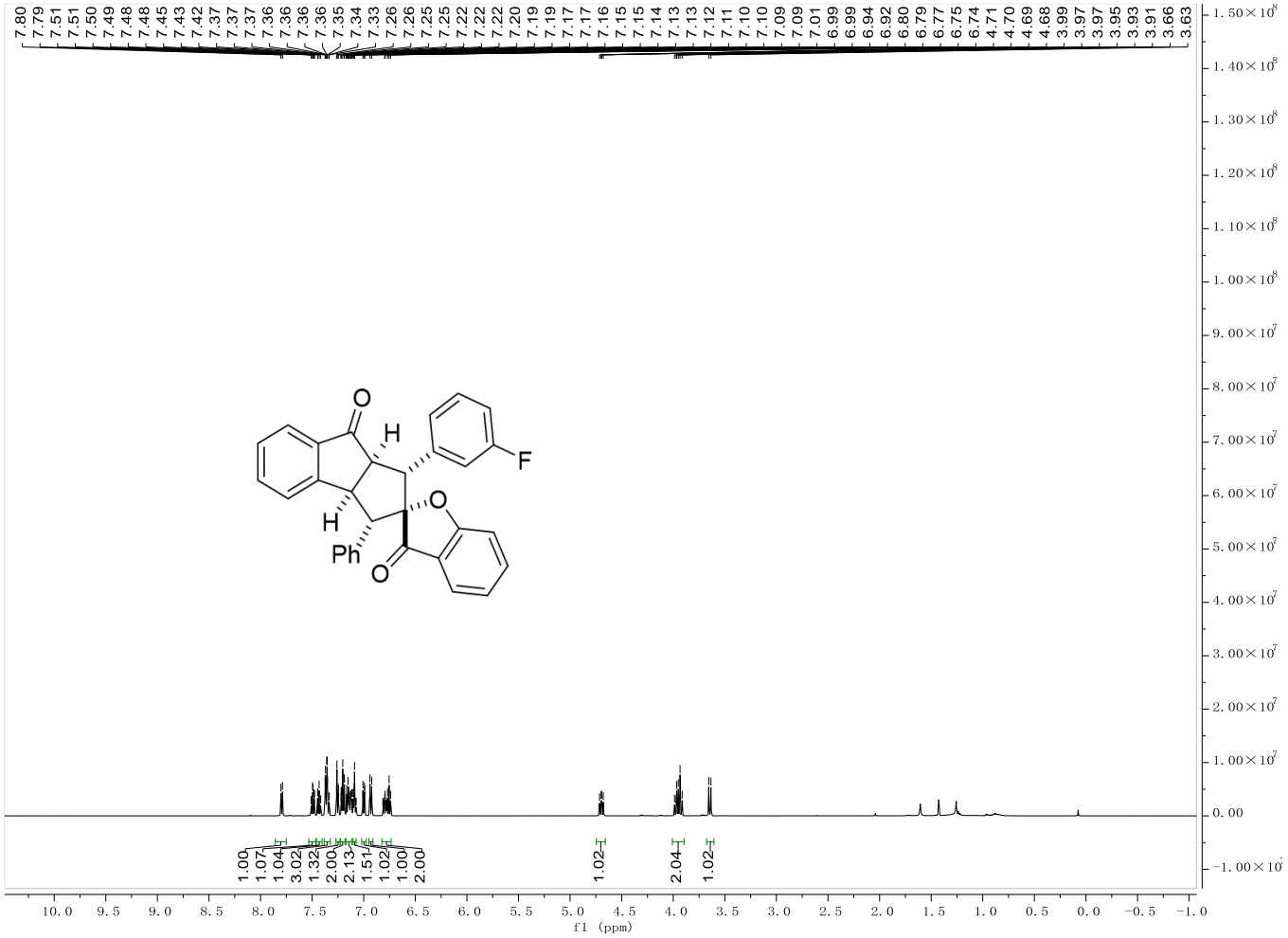
^{1}H NMR spectrum of **5f** (500 MHz, $CDCl_3$)



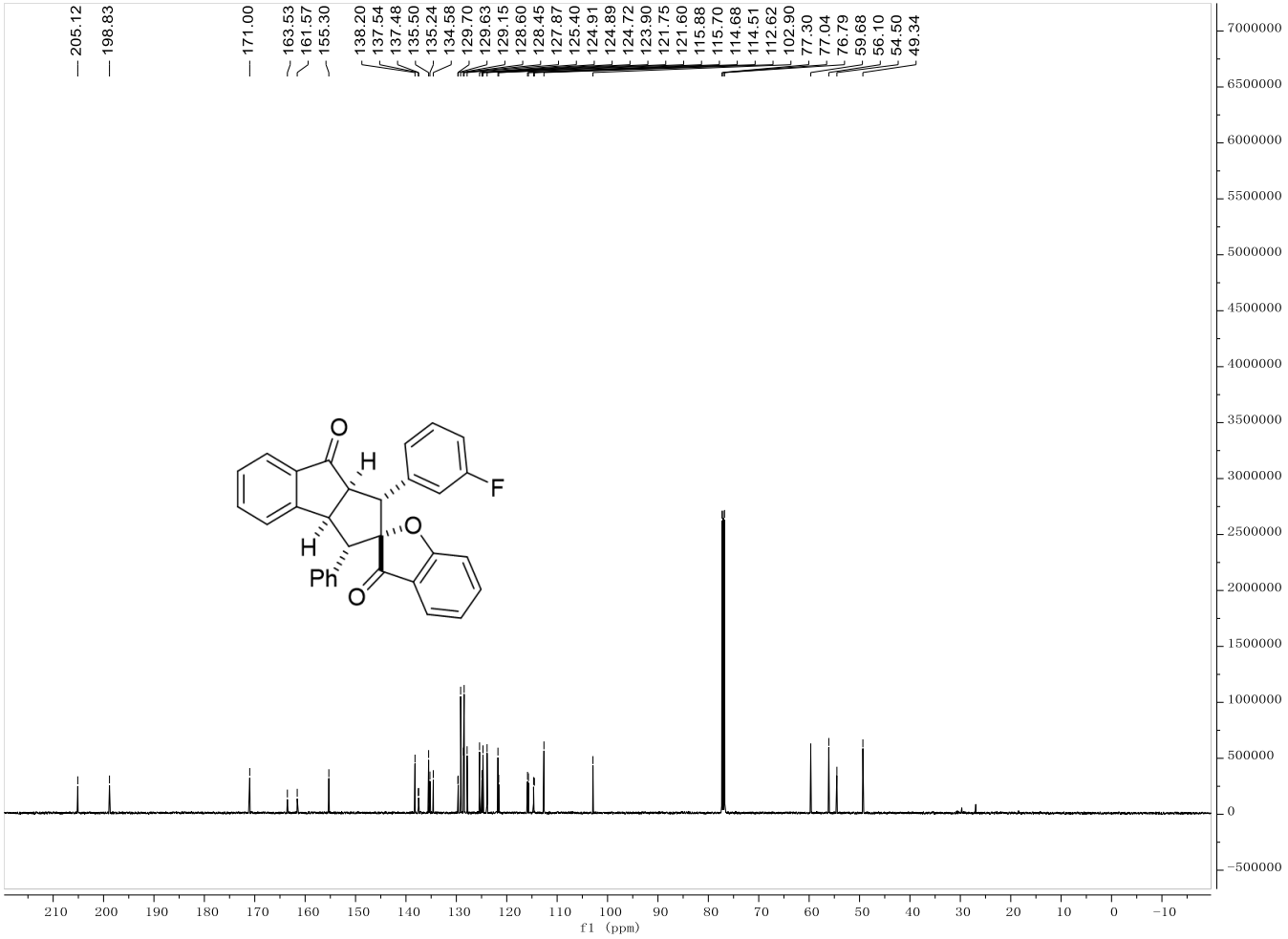
^{13}C NMR spectrum of **5f** (125 MHz, $CDCl_3$)



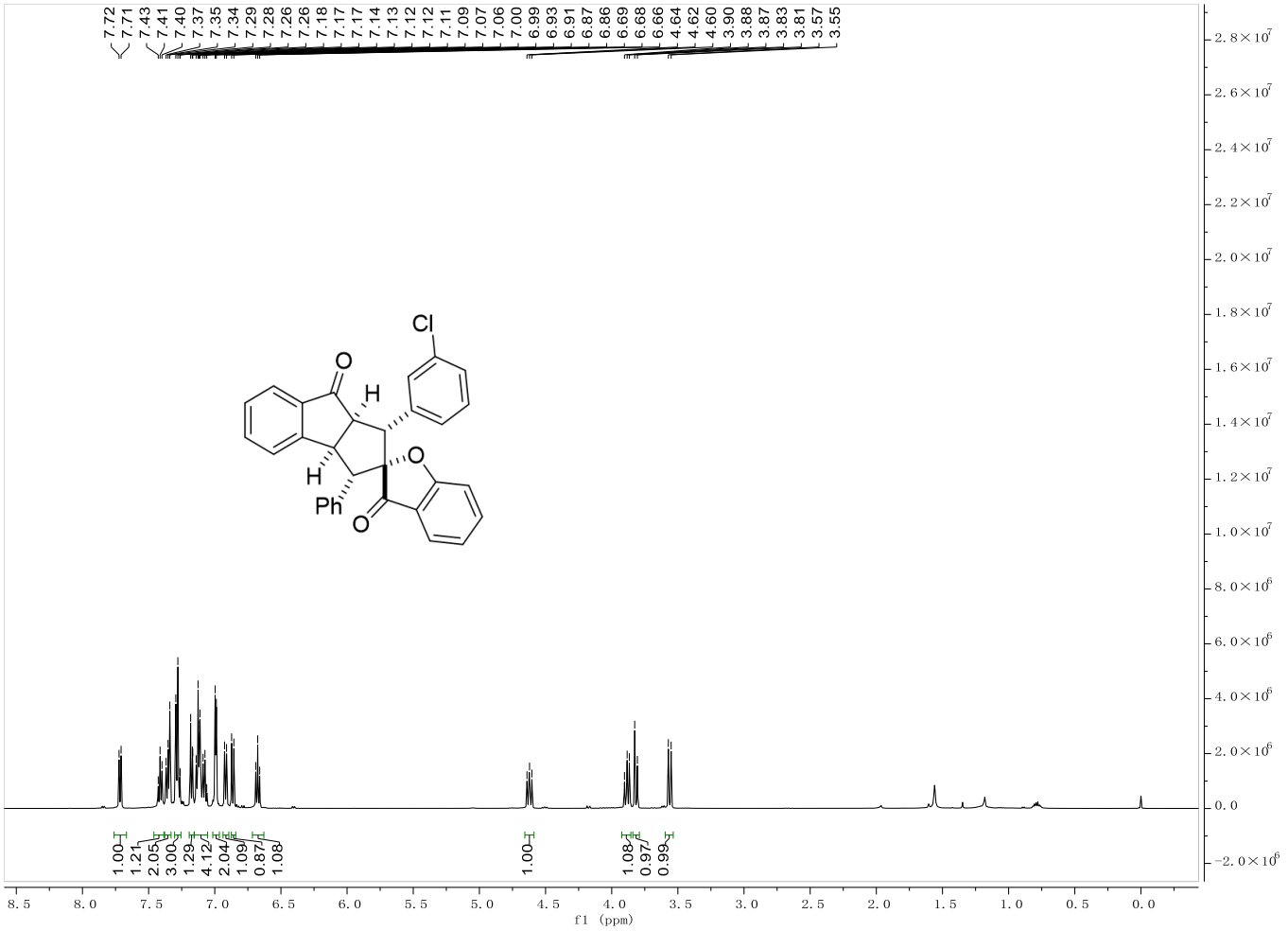
^{1}H NMR spectrum of **5g** (500 MHz, $CDCl_3$)



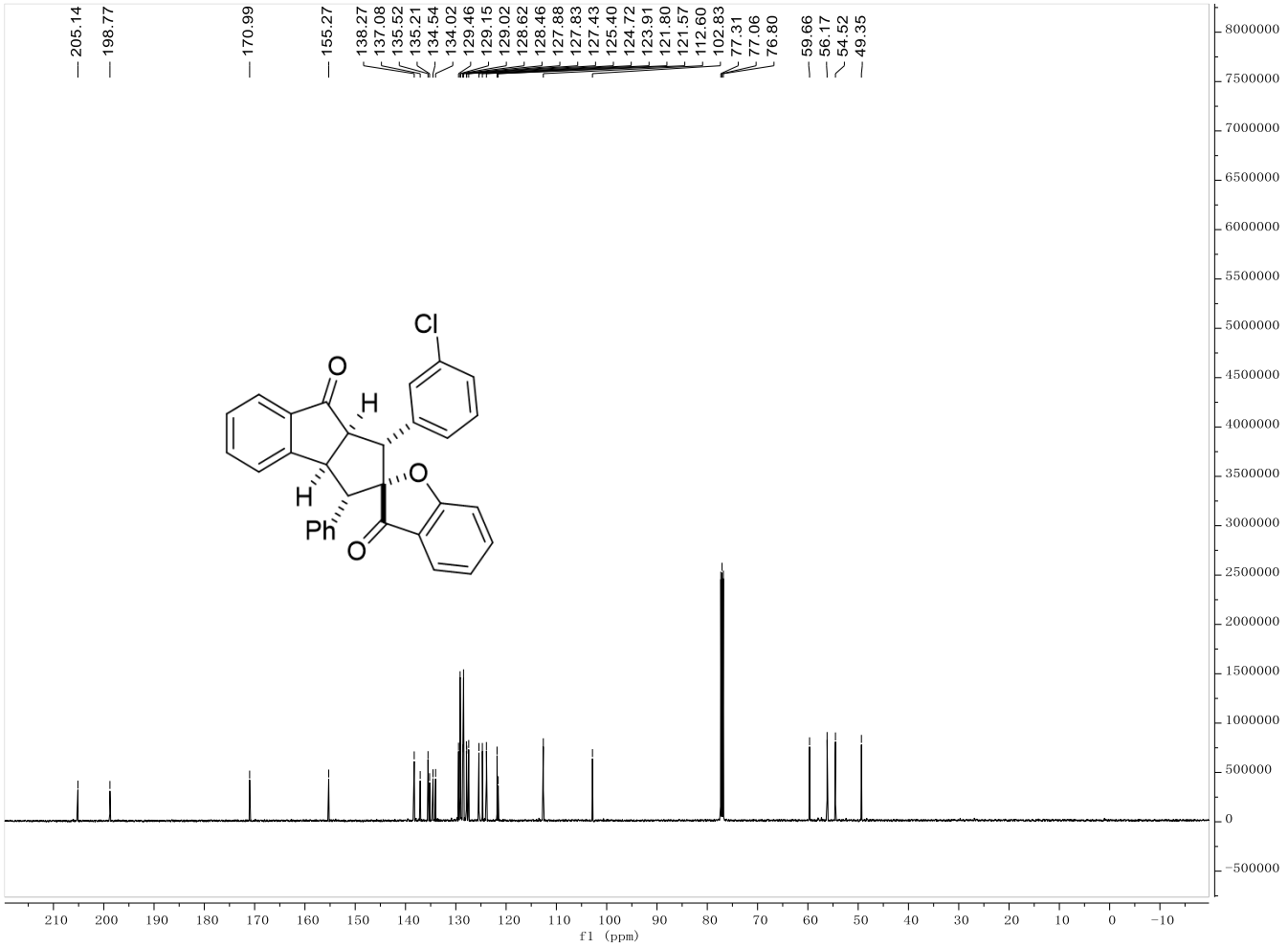
^{13}C NMR spectrum of **5g** (125 MHz, $CDCl_3$)



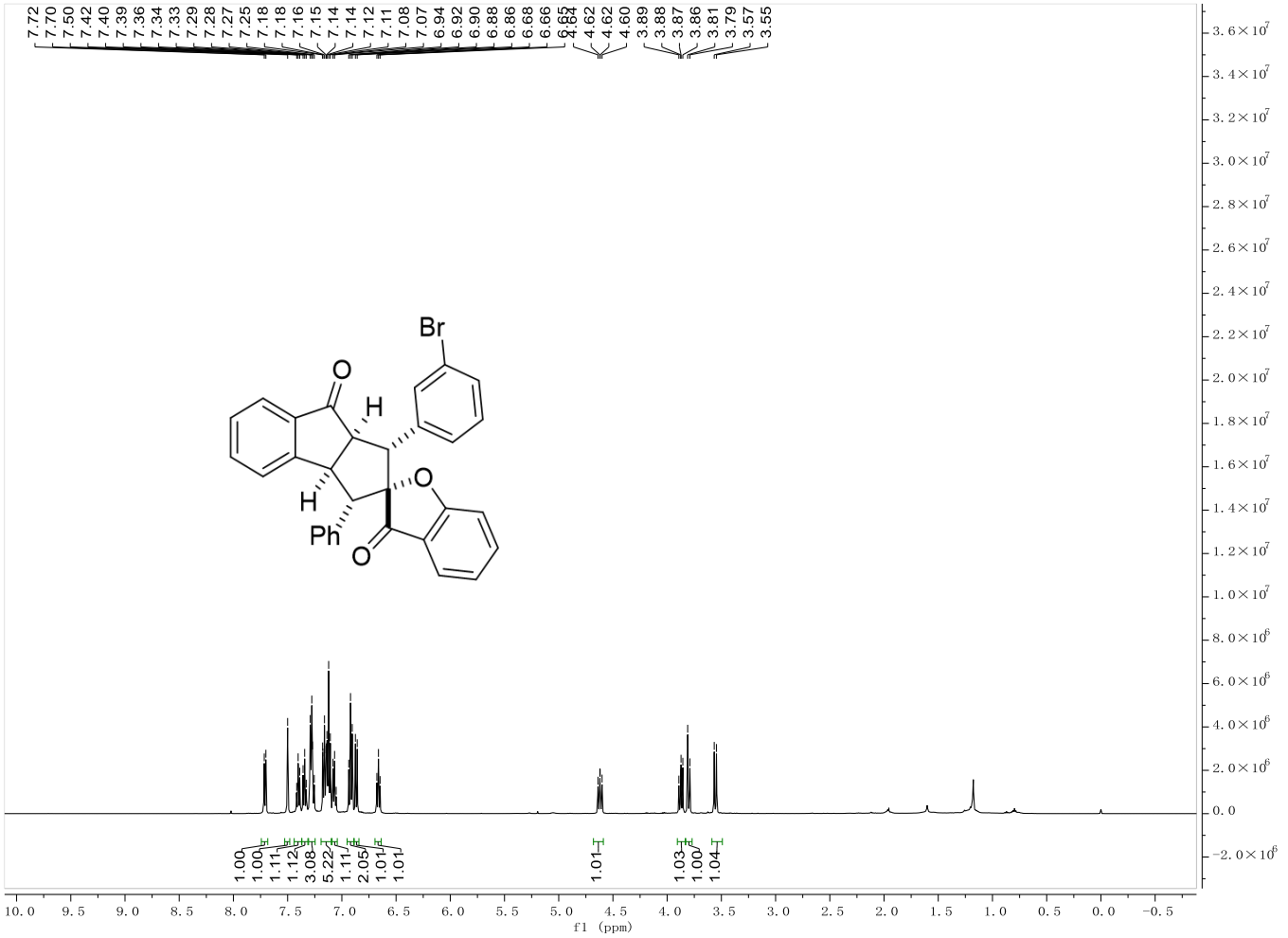
^{1}H NMR spectrum of **5h** (500 MHz, $CDCl_3$)



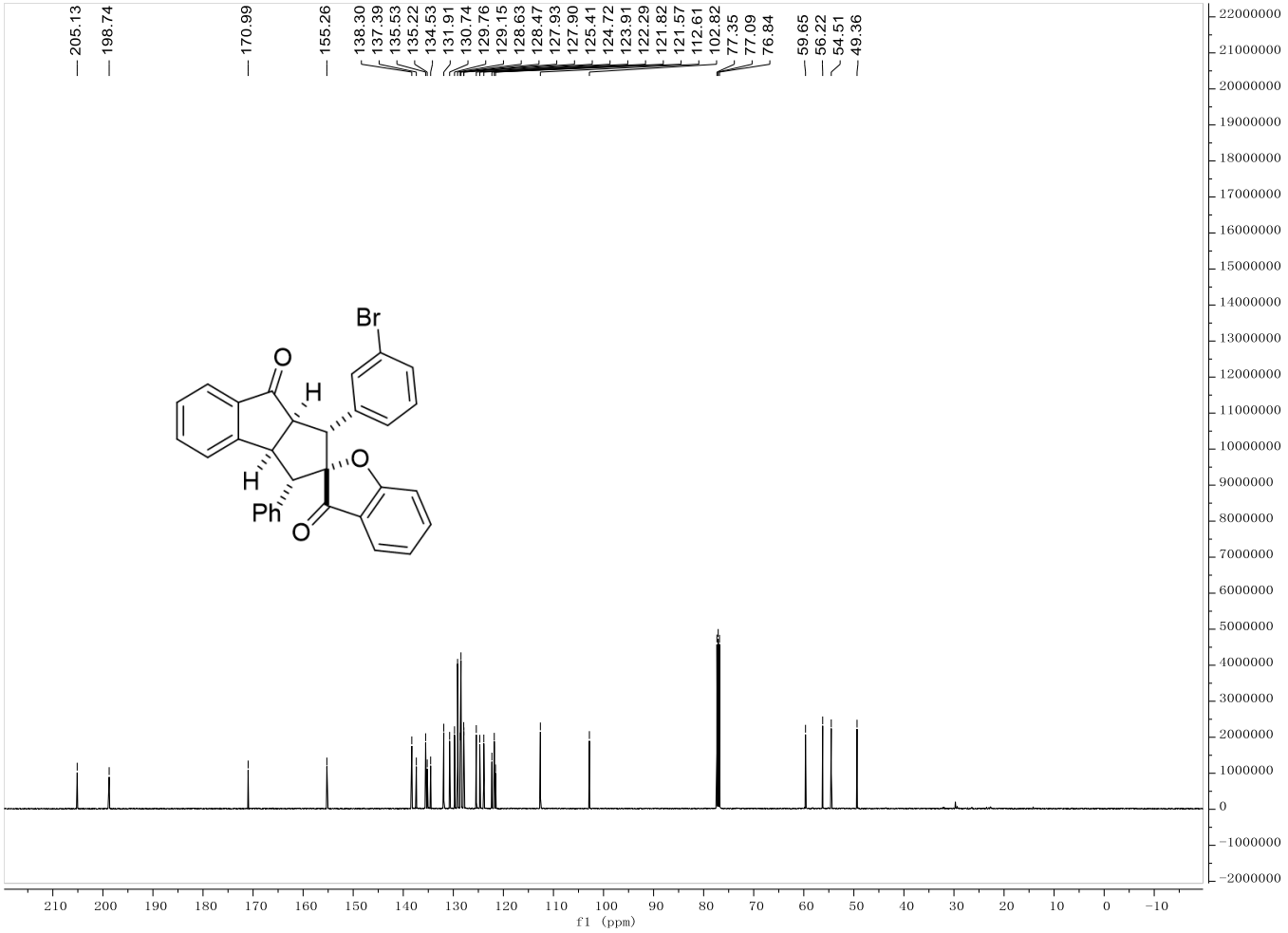
^{13}C NMR spectrum of **5h** (125 MHz, $CDCl_3$)



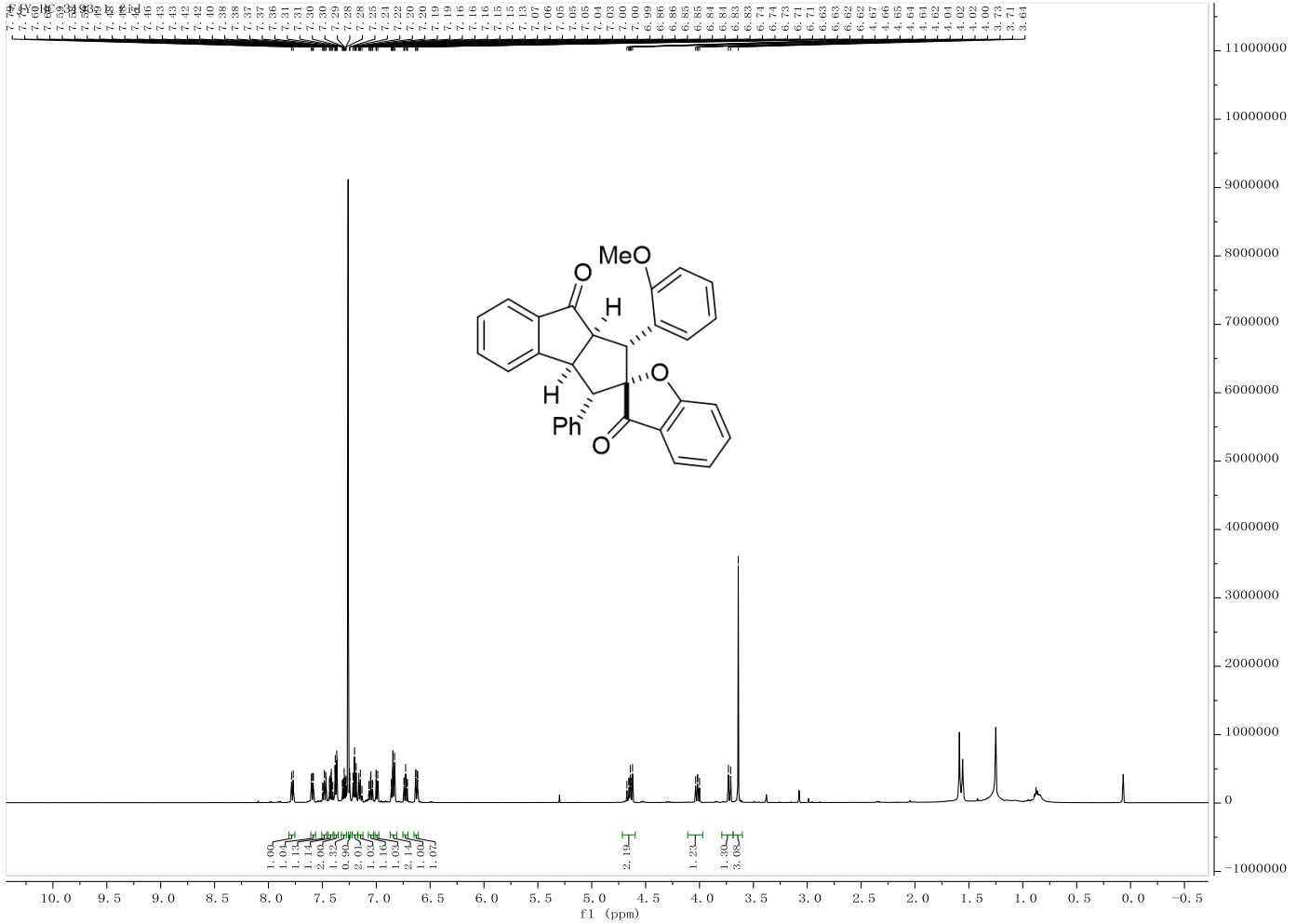
^{1}H NMR spectrum of **5i** (500 MHz, $CDCl_3$)



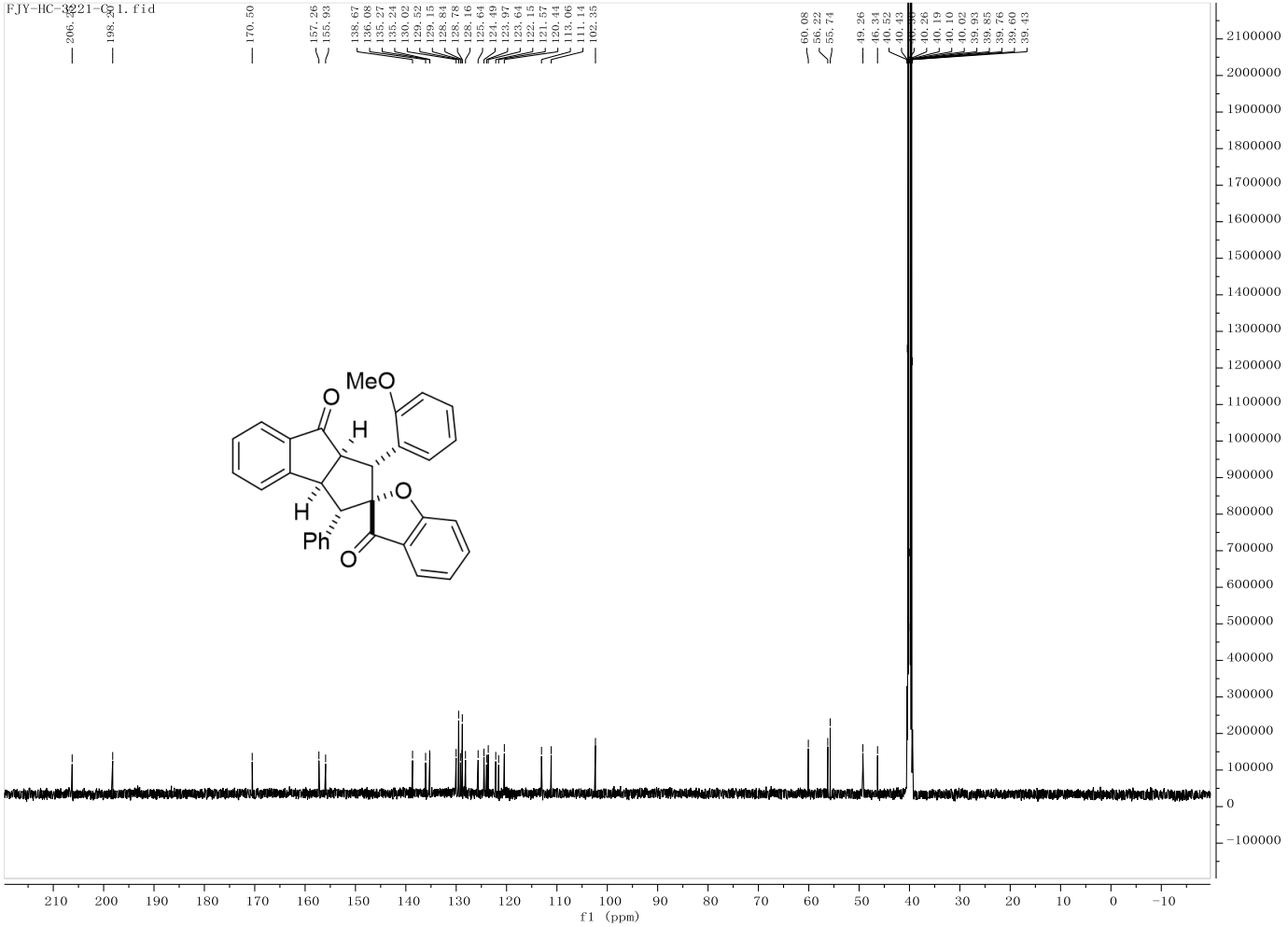
^{13}C NMR spectrum of **5i** (125 MHz, $CDCl_3$)



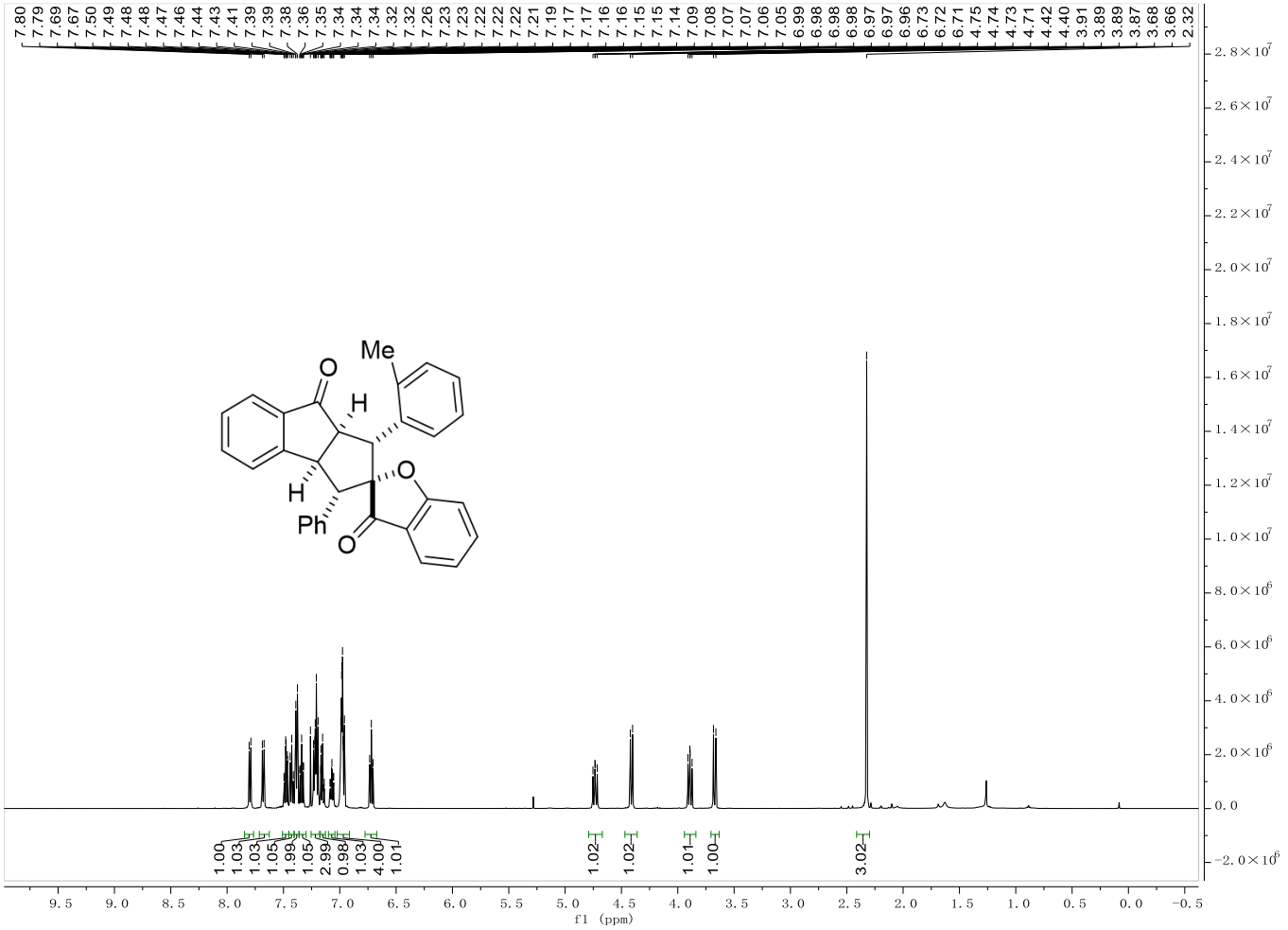
^{1}H NMR spectrum of **5j** (125 MHz, $CDCl_3$)



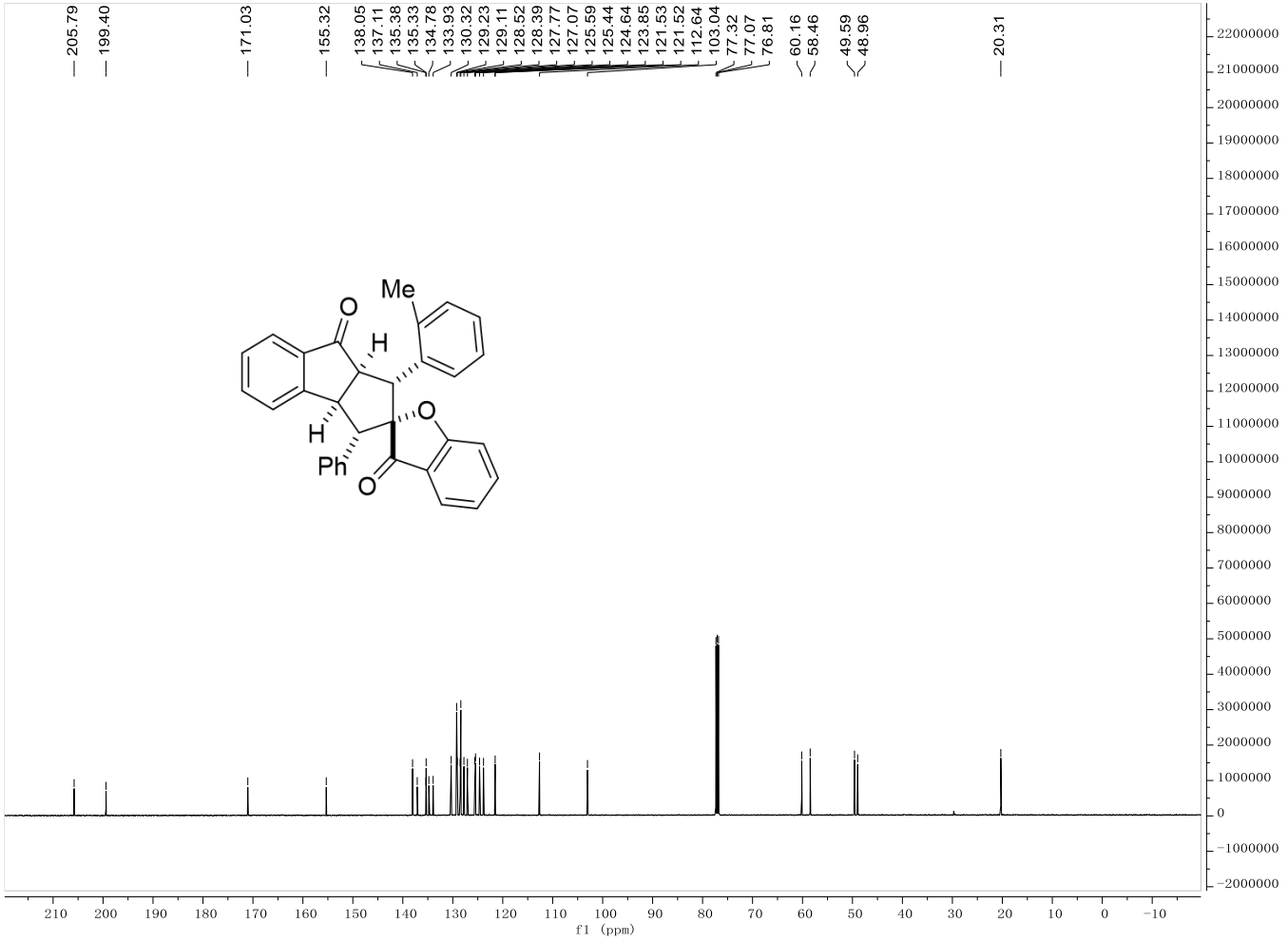
^{13}C NMR spectrum of **5j** (125 MHz, DMSO-d_6)



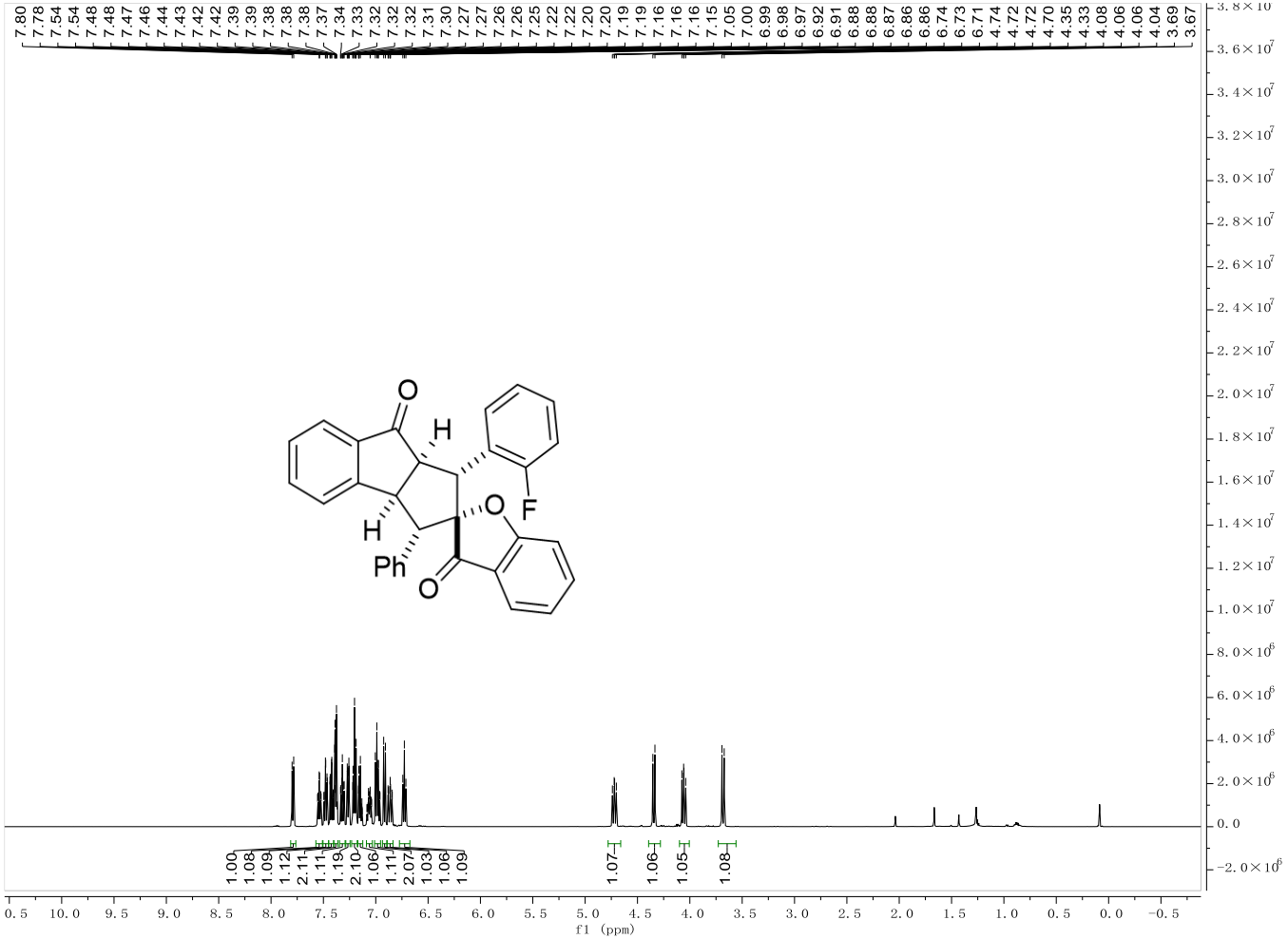
^{1}H NMR spectrum of **5k** (500 MHz, $CDCl_3$)



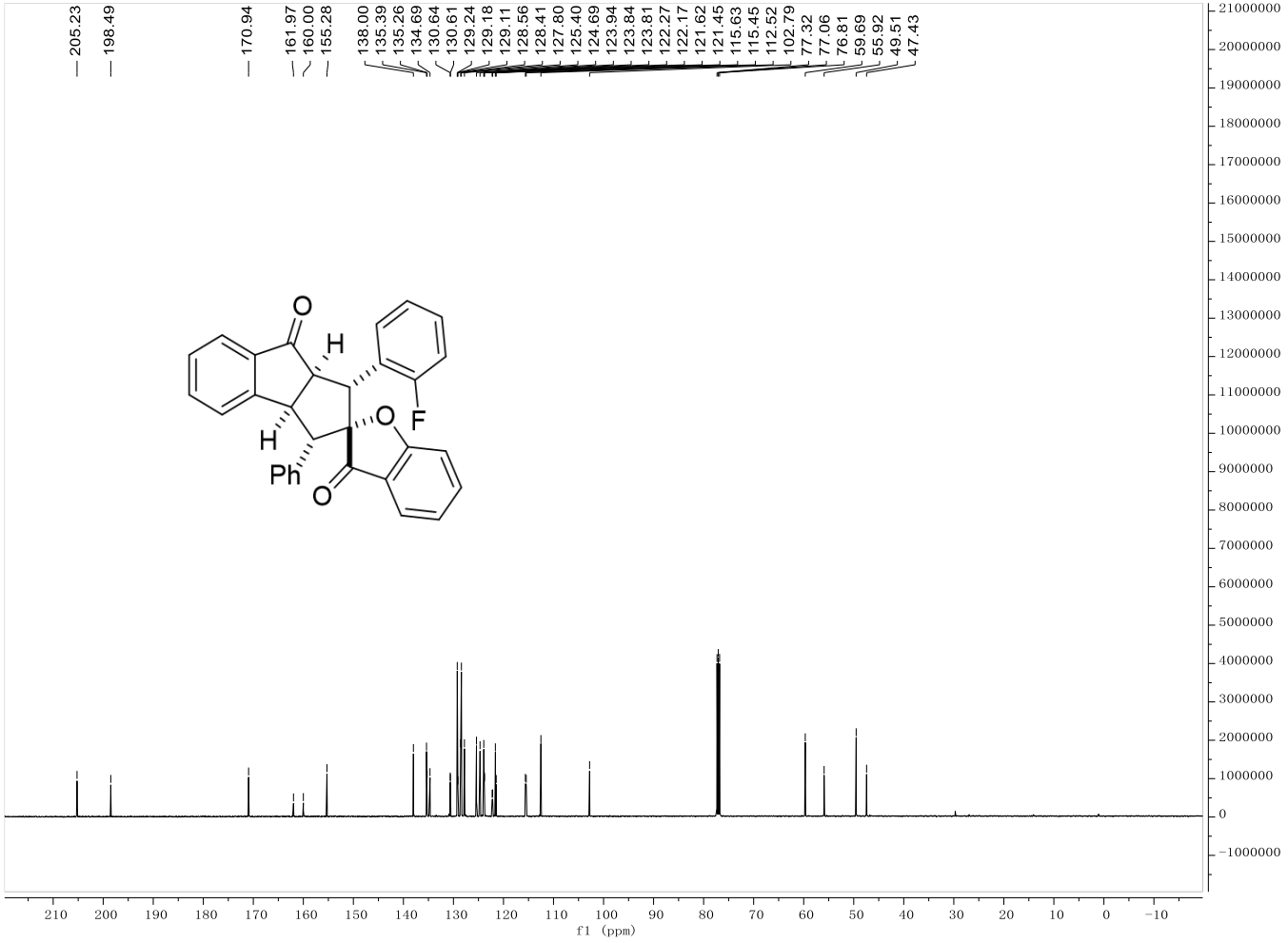
^{13}C NMR spectrum of **5k** (125 MHz, $CDCl_3$)



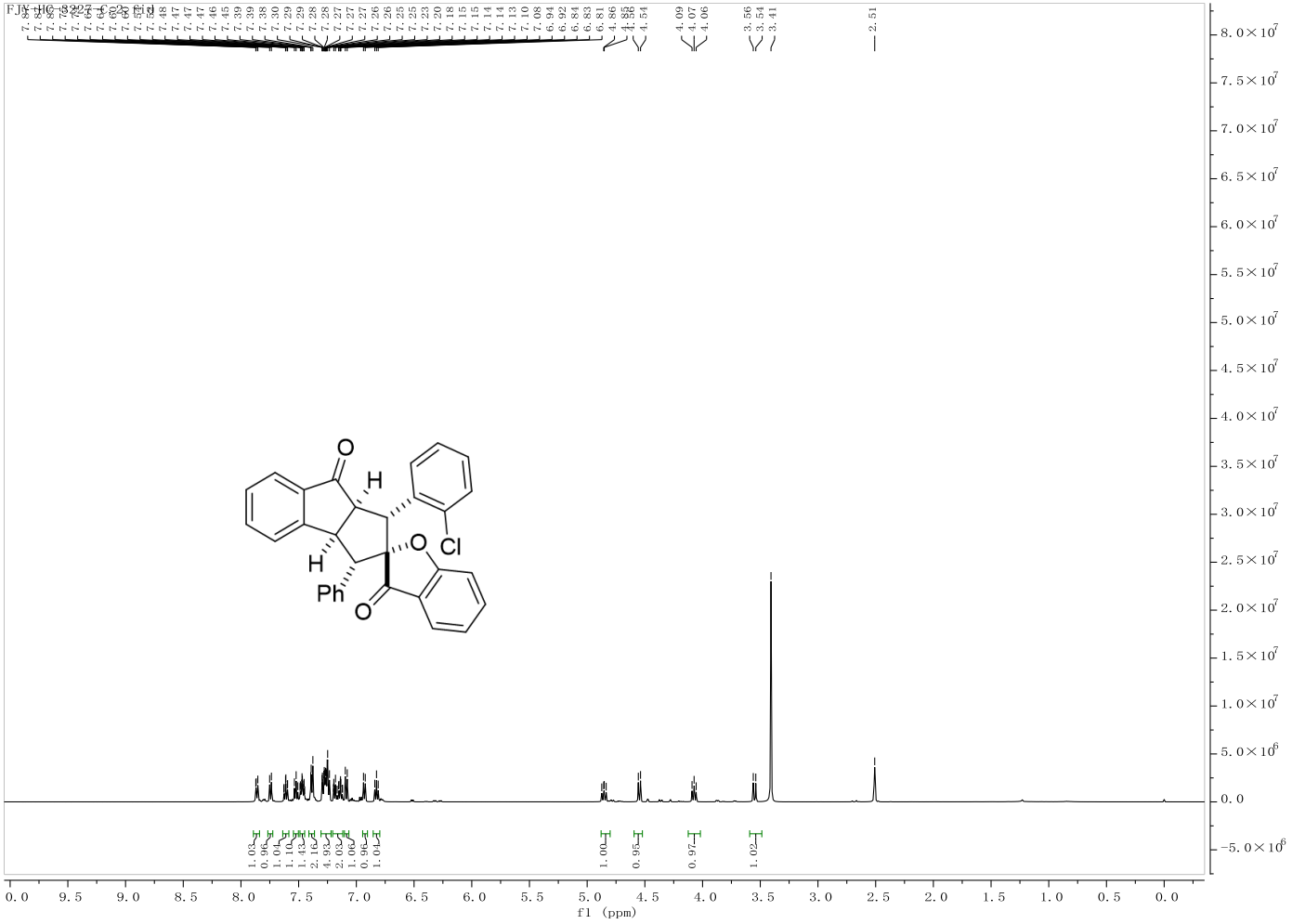
^{1}H NMR spectrum of **5l** (500 MHz, $CDCl_3$)



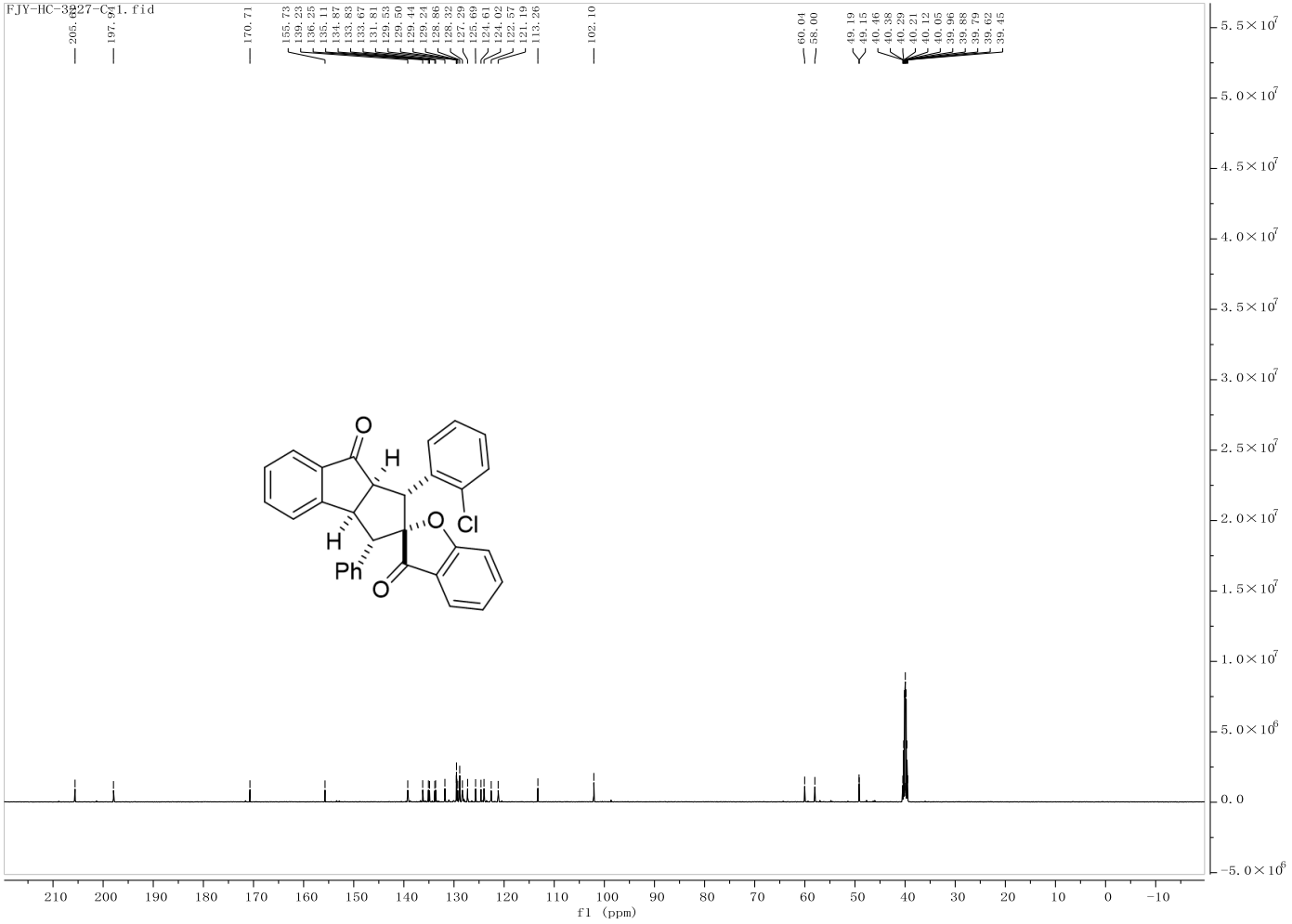
^{13}C NMR spectrum of **5l** (125 MHz, $CDCl_3$)



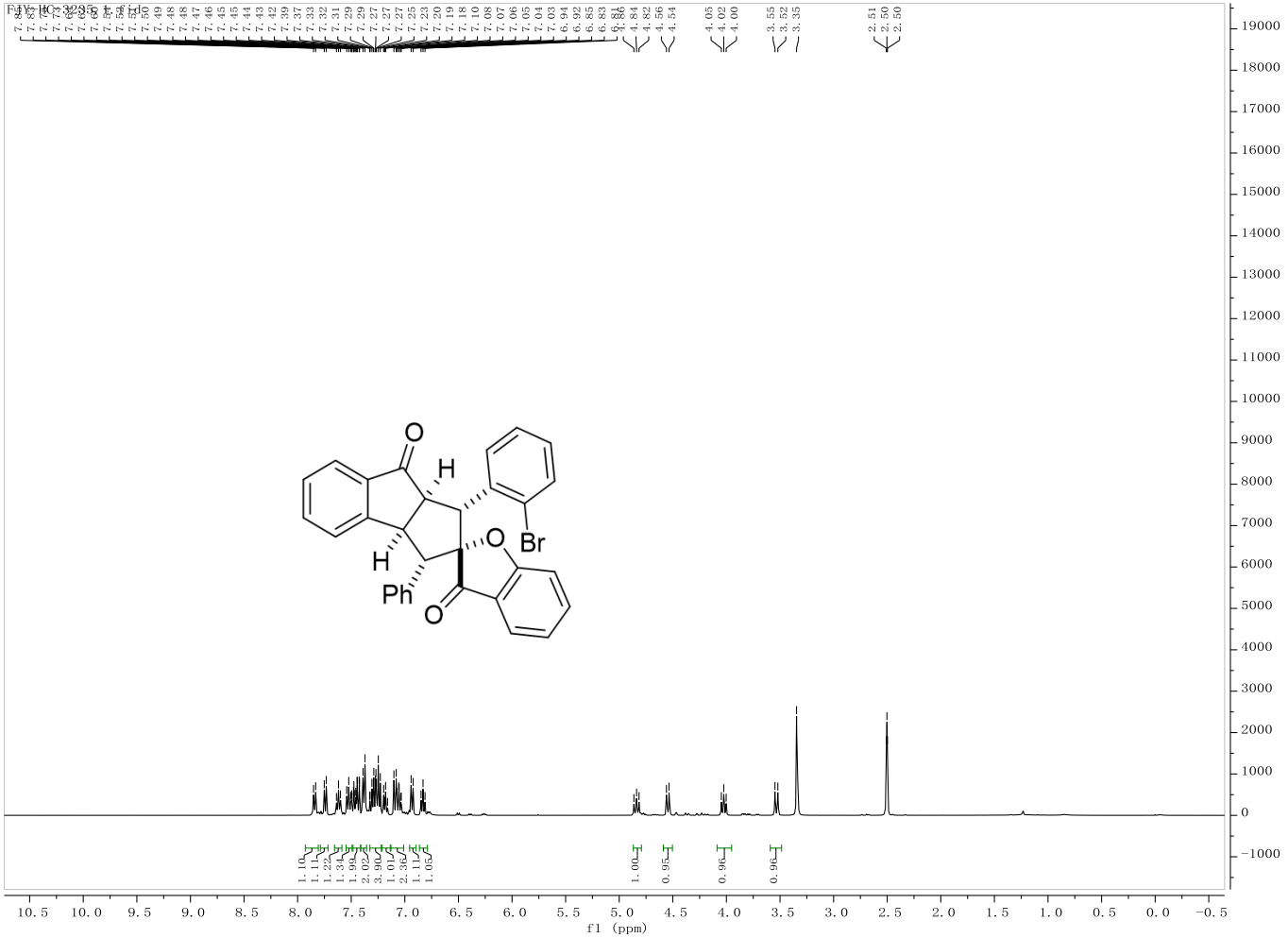
^{1}H NMR spectrum of **5m** (500 MHz, DMSO-d_6)



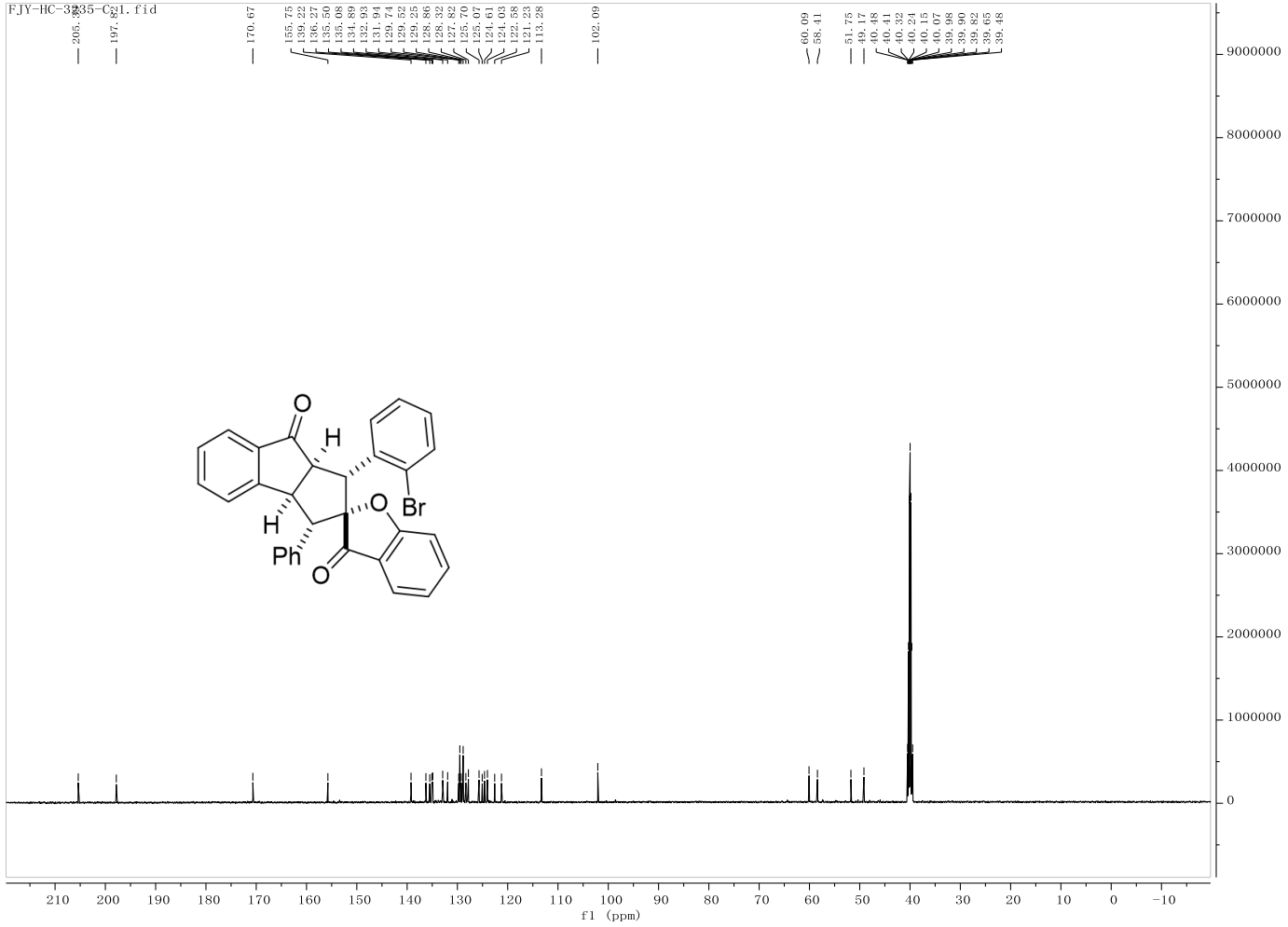
^{13}C NMR spectrum of **5m** (125 MHz, DMSO-d_6)



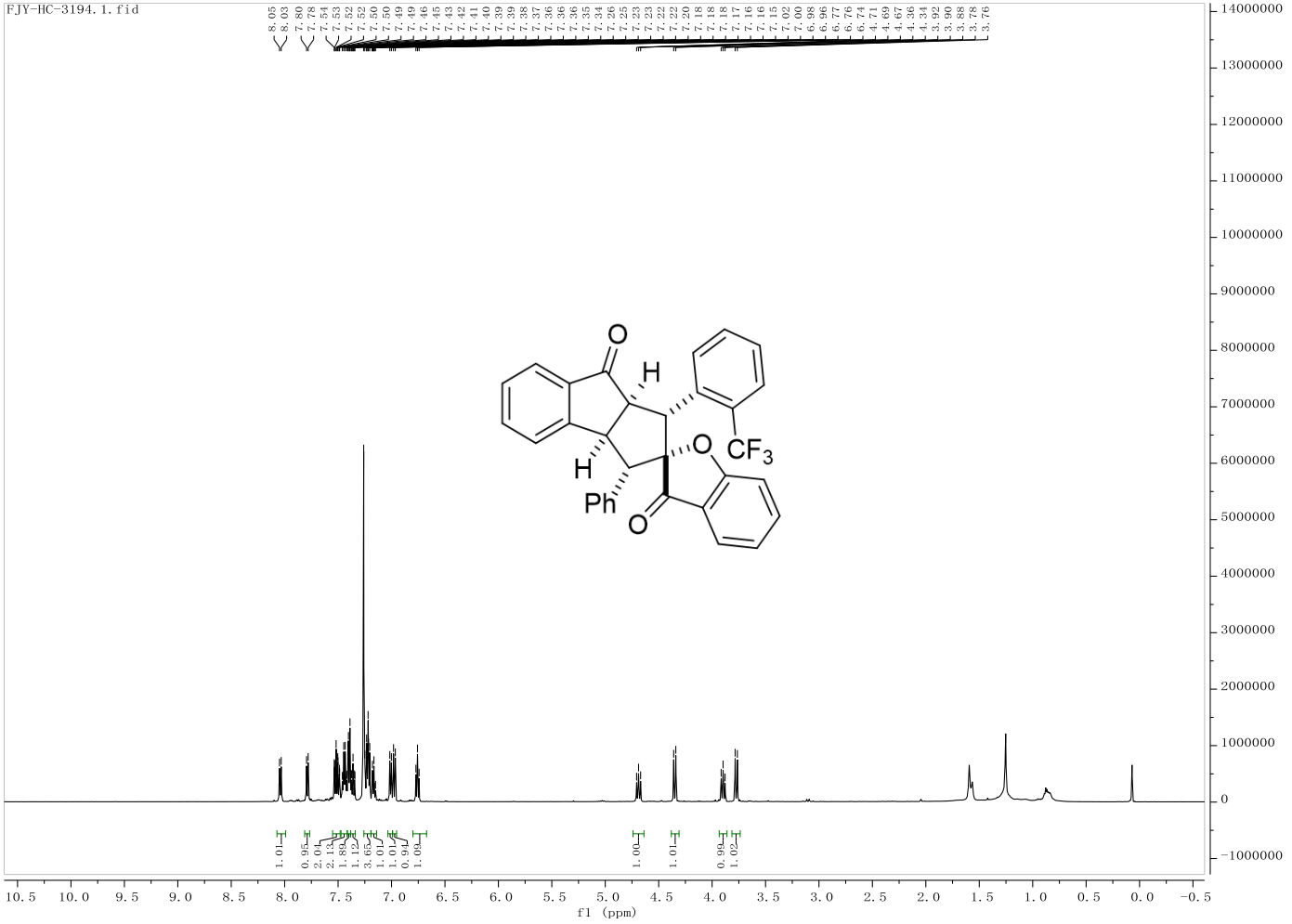
^{1}H NMR spectrum of **5n** (400 MHz, DMSO-d_6)



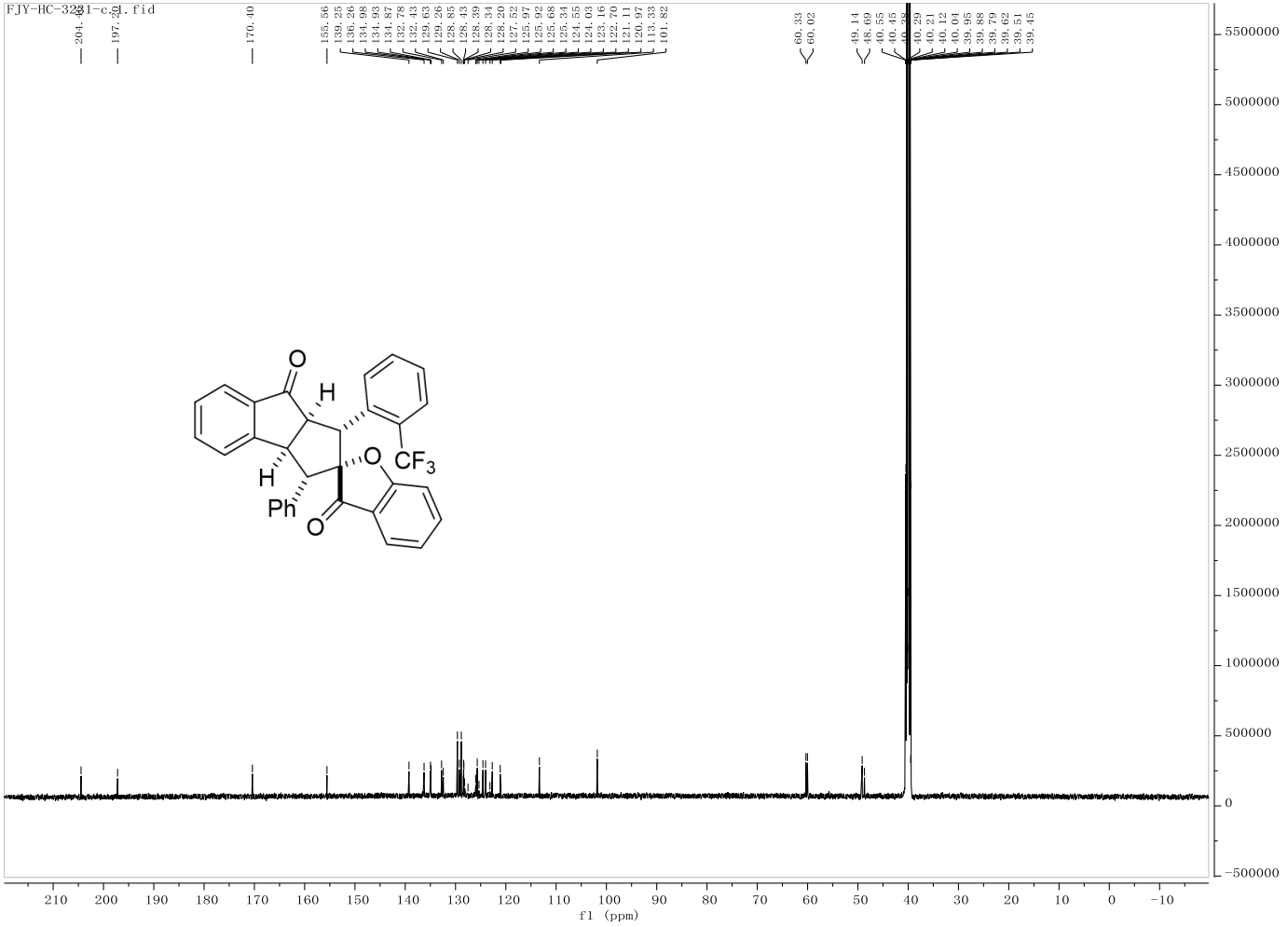
^{13}C NMR spectrum of **5n** (125 MHz, DMSO-d_6)



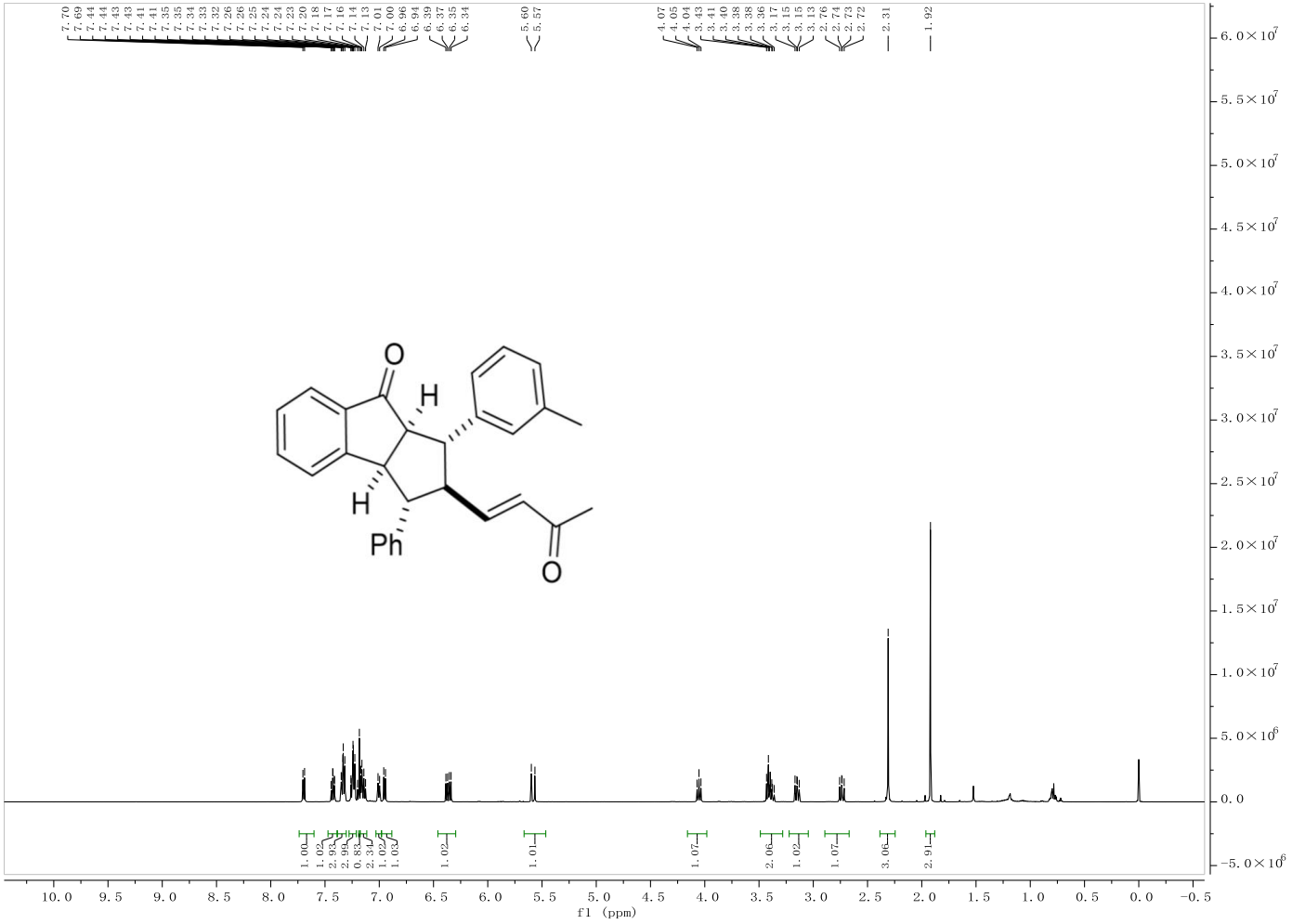
^{1}H NMR spectrum of **5o** (500 MHz, $CDCl_3$)



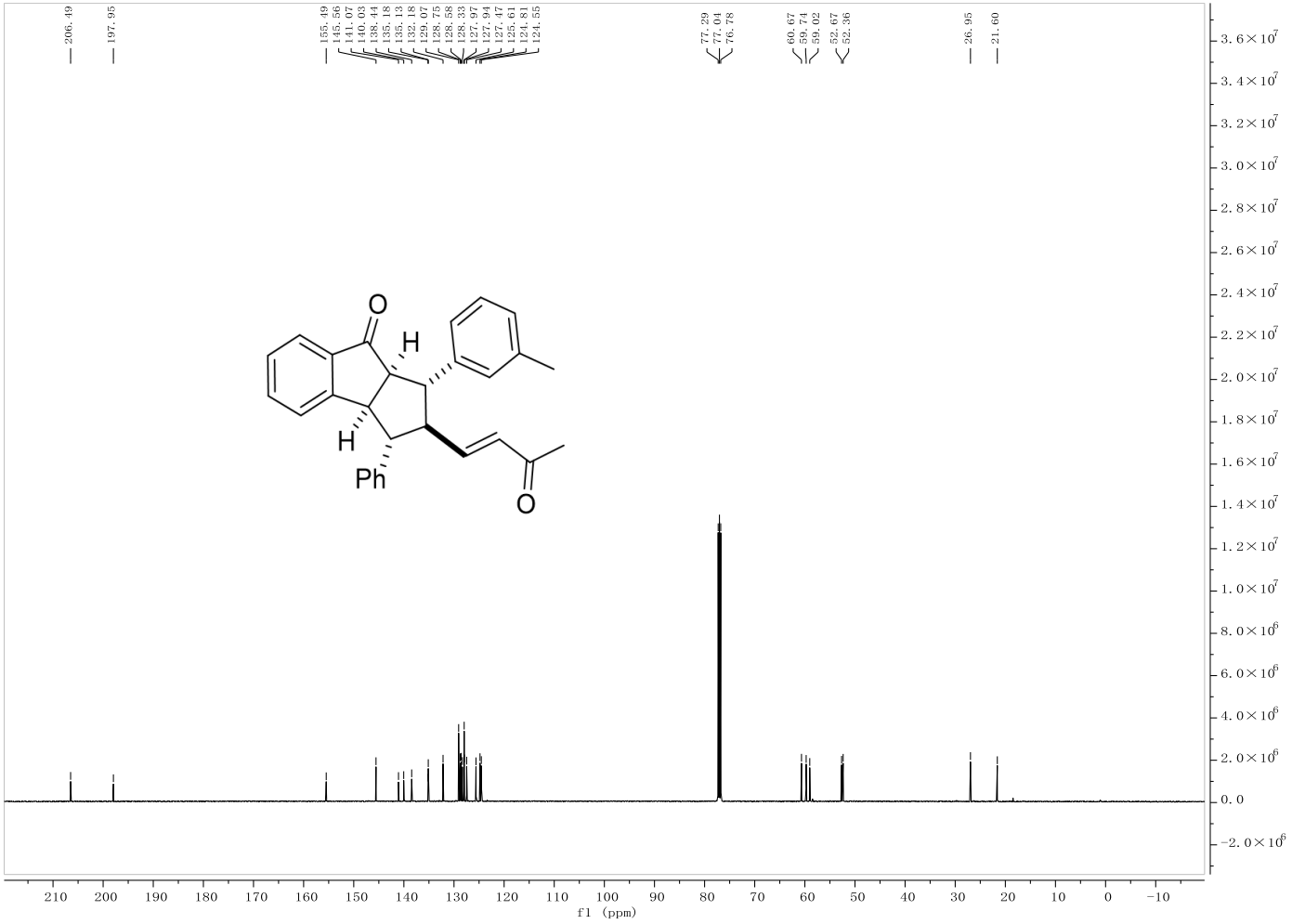
^{13}C NMR spectrum of **5o** (125 MHz, DMSO-d_6)



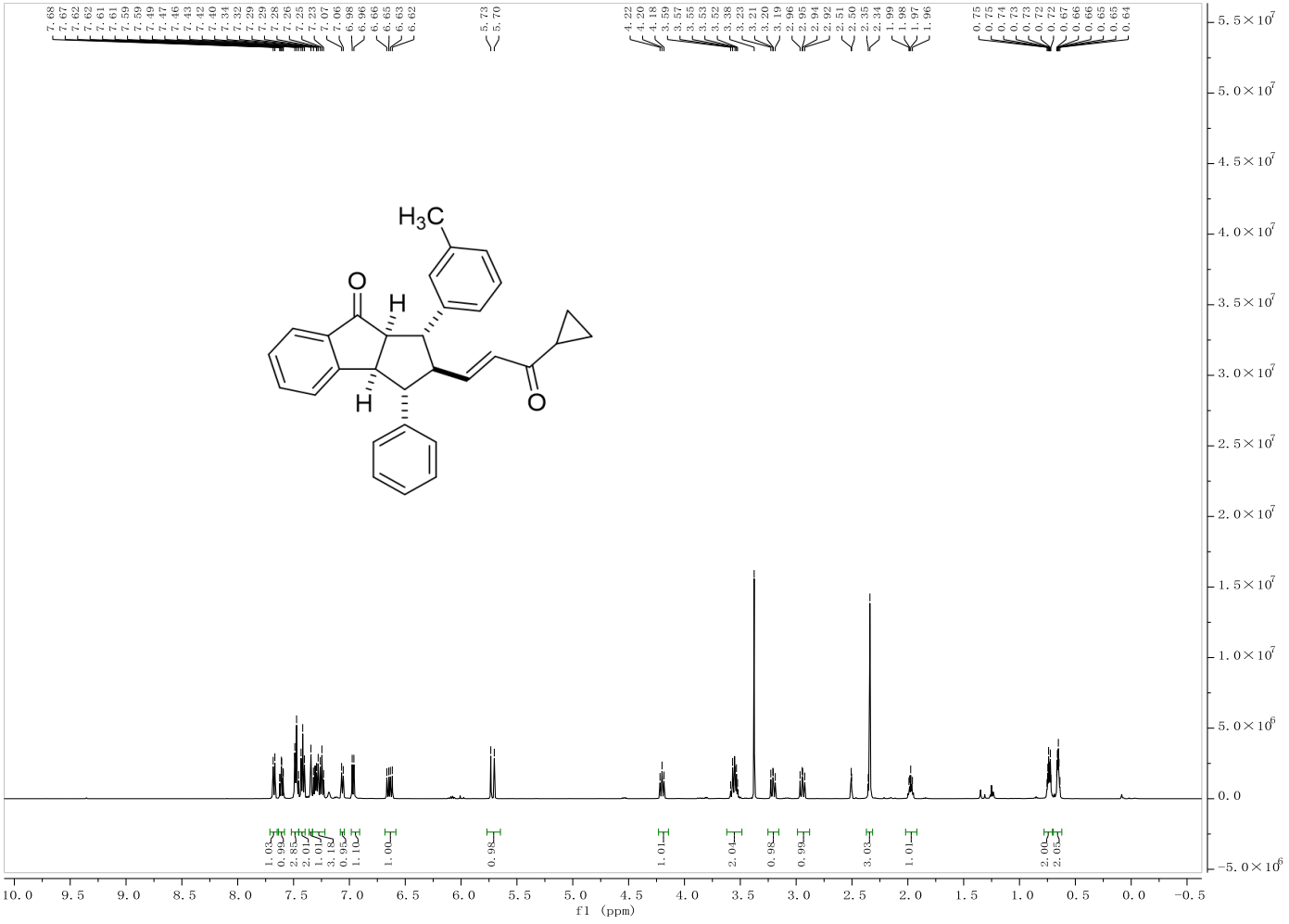
^{1}H NMR spectrum of **6** (500 MHz, $CDCl_3$)



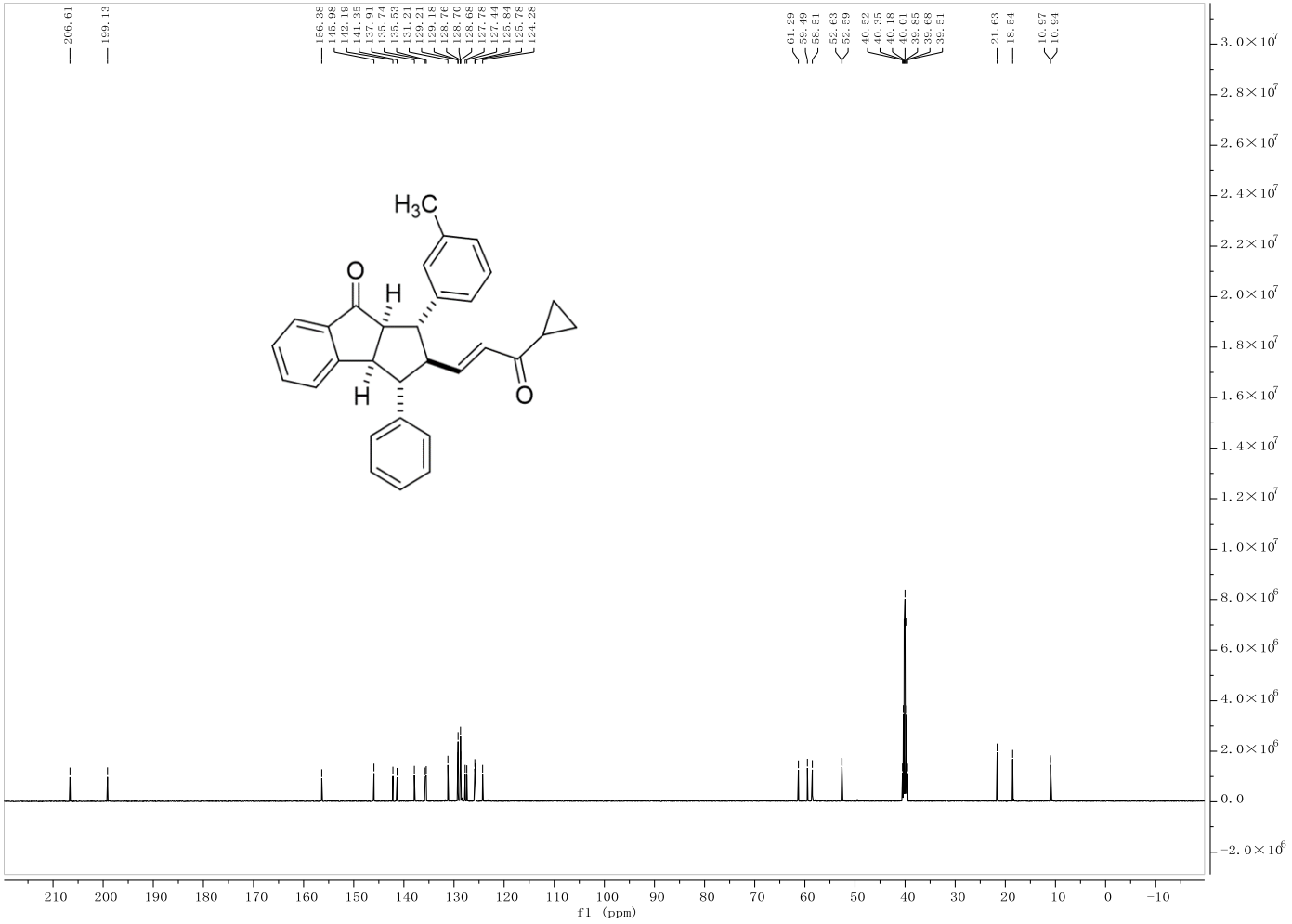
^{13}C NMR spectrum of **6** (125 MHz, $CDCl_3$)



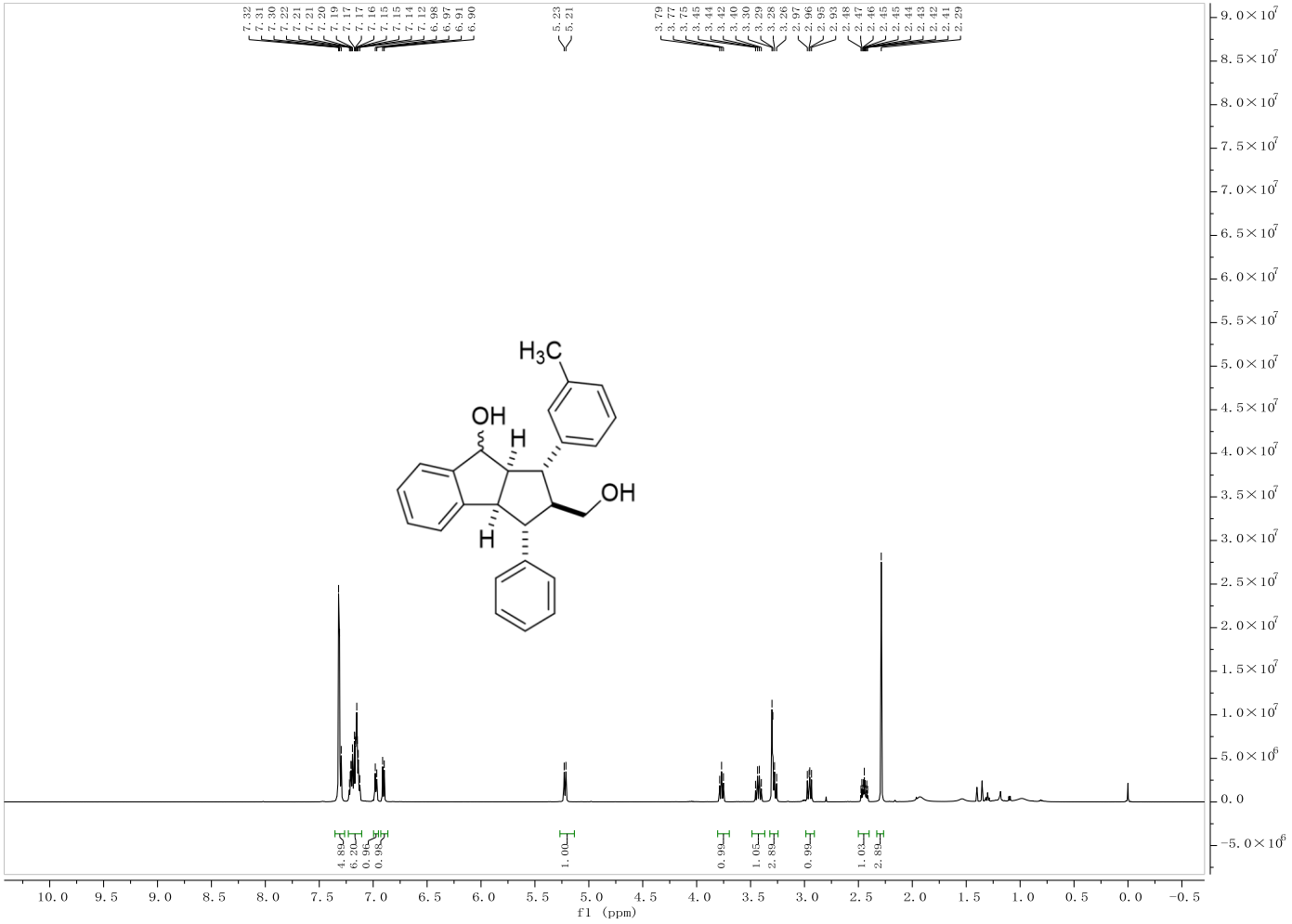
^{1}H NMR spectrum of **7** (500 MHz, DMSO-d_6)



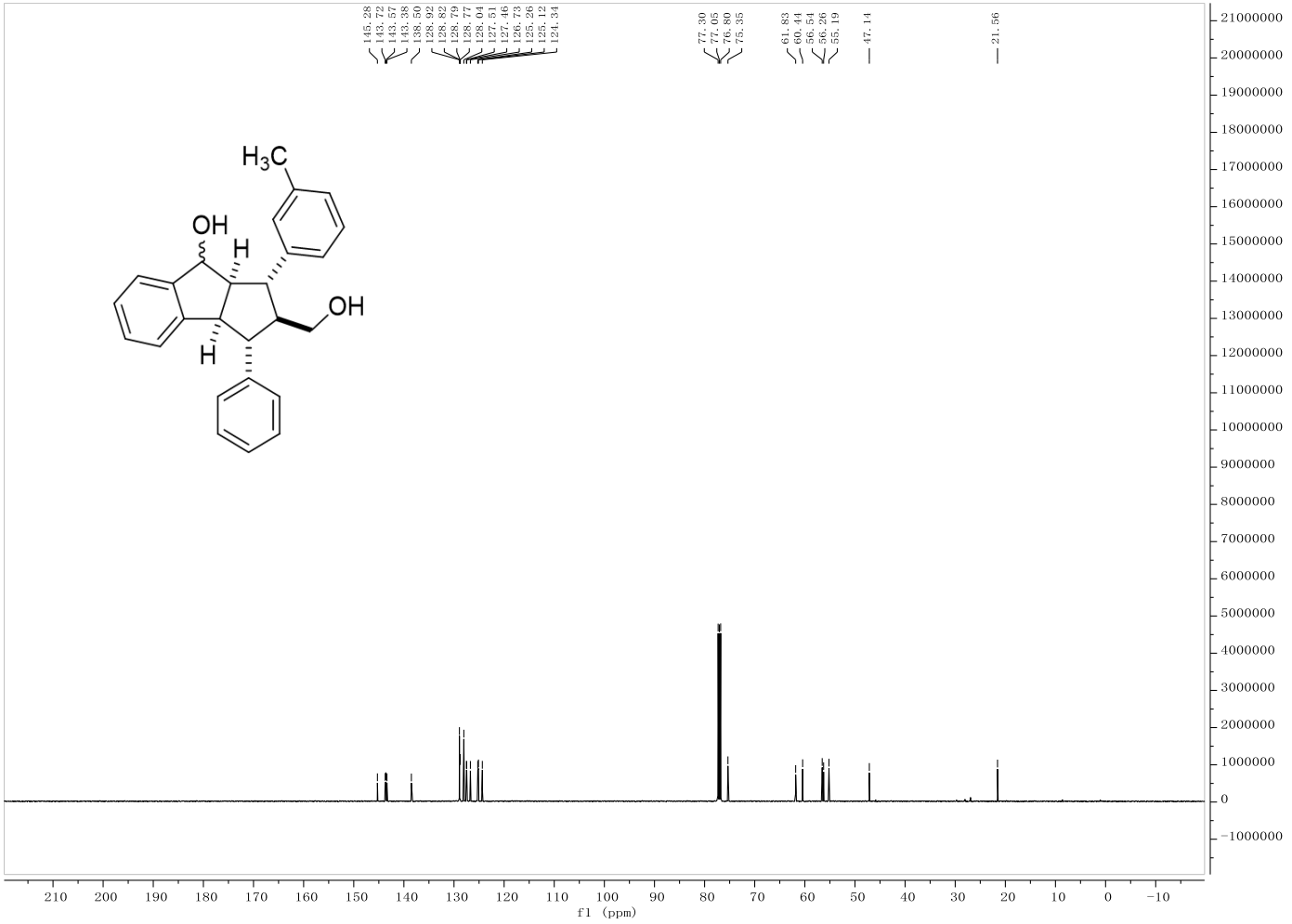
^{13}C NMR spectrum of **7** (125 MHz, DMSO-d_6)



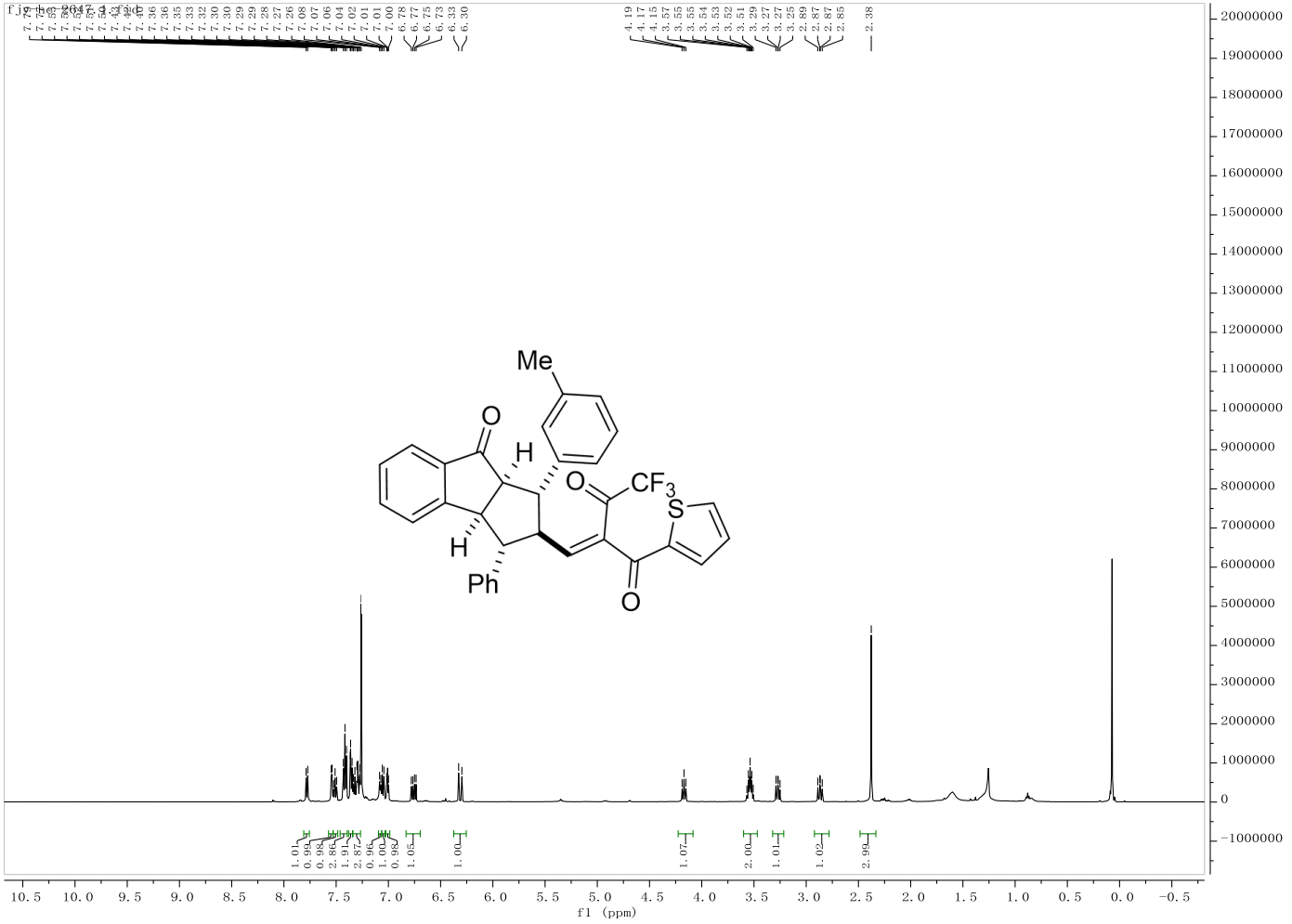
^{1}H NMR spectrum of **8** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **8** (125 MHz, $CDCl_3$)



^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **9** (125 MHz, $CDCl_3$)