

SUPPORTING INFORMATION

Copper-Catalyzed One-pot [3+2] Cycloadditions of Ethynyl Indoloxazolidones with 1, 3-Cyclohexanediones

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General

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), EA (MgCl₂), CH₂Cl₂ (CaH₂), toluene (Na), ClCH₂CH₂Cl (CaH₂). The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Anhui Liangchen Silicon Material Company in China. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Varian 500 MHz instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent (CDCl₃ (7.27 ppm), DMSO-*d*₆ (2.50 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for ¹H NMR and the deuterated solvent (CDCl₃ (77.00 ppm), DMSO-*d*₆ (39.51 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for ¹³C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. The MS data were obtained with ESI technique, and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. The X-ray single-crystal determination was performed on a Bruker Smart 1000 CCD X-ray single crystal diffractometer. Compound 1a was prepared according to the reported literature.¹

1. Optimization of the Reaction Conditions.

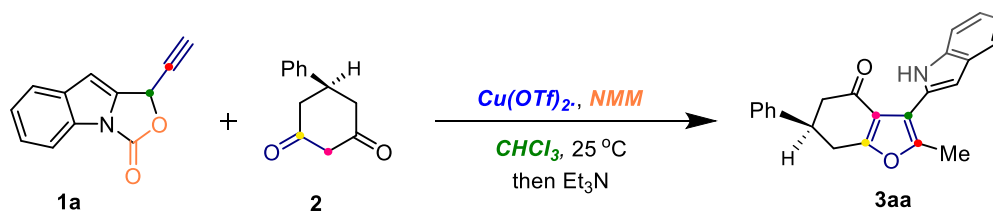
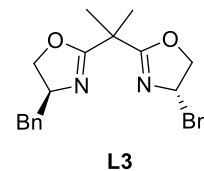
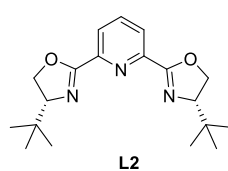
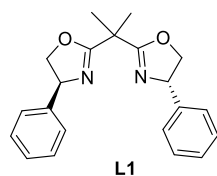


Table 1. Optimization of the Reaction Conditions

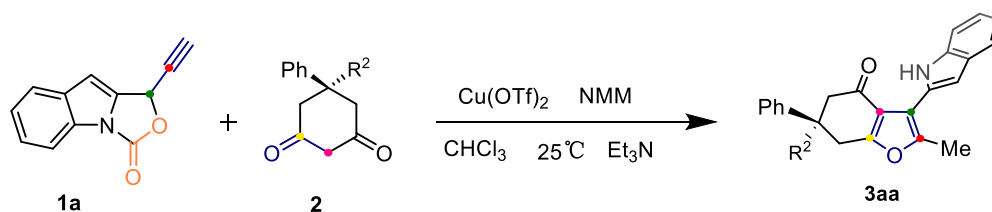
Entry	Cu*L	Base	solvent	T(°C)	Time(h)	additive	yield(%)
1	$\text{Cu}(\text{OTf})_2$	Et_3N	PhCH_3	RT	12	Et_3N	19
2	$\text{Cu}(\text{OTf})_2$	Et_3N	PhCl	RT	12	Et_3N	trace
3	$\text{Cu}(\text{OTf})_2$	Et_3N	CHCl_3	RT	12	Et_3N	43
4	$\text{Cu}(\text{CHCN})_4\text{PF}_6$	Et_3N	CHCl_3	RT	12	Et_3N	37
5	$\text{Cu}(\text{OAc})_2$	Et_3N	CHCl_3	RT	12	Et_3N	40
6	CuI	Et_3N	CHCl_3	RT	12	Et_3N	NR
7	CuCl	Et_3N	CHCl_3	RT	12	Et_3N	NR
8	$\text{Cu}(\text{OTf})_2$	DACH	CHCl_3	RT	12	Et_3N	NR
9	$\text{Cu}(\text{OTf})_2$	TMEDA	CHCl_3	RT	12	Et_3N	47
10	$\text{Cu}(\text{OTf})_2$	DIPEA	CHCl_3	RT	12	Et_3N	46
11	$\text{Cu}(\text{OTf})_2$	DBU	CHCl_3	RT	12	Et_3N	46
12 ^a	$\text{Cu}(\text{OTf})_2$	DBU	CHCl_3	RT	12	Et_3N	NR
13 ^a	$\text{Cu}(\text{OTf})_2$	DBU	CHCl_3	RT	12	Et_3N	44
14 ^a	$\text{Cu}(\text{OTf})_2$	DBU	CHCl_3	RT	12	Et_3N	43
15	$\text{Cu}(\text{OTf})_2$	DBU	CHCl_3	0	12	Et_3N	43
16	CuSO_4	DBU	CHCl_3	0	12	Et_3N	NR
17	CuCl_2	DBU	CHCl_3	0	12	Et_3N	32
18	$\text{Cu}(\text{acac})_2$	DBU	CHCl_3	0	12	Et_3N	40
19	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	Et_3N	56
20	$\text{Cu}(\text{OTf})_2$	NEM	CHCl_3	RT	12	Et_3N	52
21	$\text{Cu}(\text{OTf})_2$	DABCO	CHCl_3	RT	12	Et_3N	41
22 ^b	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	Et_3N	64
23 ^c	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	Et_3N	67
24	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	Et_3N	74
25	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	K_2CO_3	trace
26	$\text{Cu}(\text{OTf})_2$	NMM	CHCl_3	RT	12	DIPA	30

27	Cu(OTf) ₂	NMM	CHCl ₃	RT	12	TMEDA	33
28	Cu(OTf) ₂	NMM	CHCl ₃	5	12	Et ₃ N	55
29	Cu(OTf) ₂	NMM	CHCl ₃	10	12	Et ₃ N	62
30	Cu(OTf) ₂	NMM	CHCl ₃	50	12	Et ₃ N	52

Unless otherwise noted, all reactions were conducted with 0.20 mmol of **1a** (2.0 equiv.), 0.10 mmol of **2** (1.0 equiv.), 20 mmol% of catalyst and 50 mmol% of the base in the solvent (2.0 mL) at 25 °C for the indicated time. Yield of **3aa** by ¹H NMR analysis use internal standards of 1,3,5-trimethoxybenzene (0.4 equiv). Another base of 1 mmol Et₃N (10 equiv.) was added after stirred for 12 hours. ^aligand (L1 for entry 12, L2 for entry 13, L3 for entry 14,15 mol %). ^b0.20 mmol of **1a**. ^c5 mol% of catalyst.



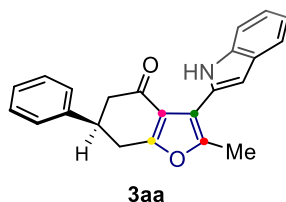
2. General Procedure for the Synthesis of Compound 3 and the Spectroscopic Data for the Compounds



A mixture of **1a** (59.1 mg, 0.30 mmol) and **2** (18.8 mg, 0.10 mmol) was dissolved in CHCl₃ (2.0 mL), to the solution of the mixture was added Cu(OTf)₂ (7.2 mg, 0.02 mmol) and 4-Methylmorpholine (5.0 mg, 0.05 mmol) at 25 °C and stirred for 12 h, Another base of 1 mmol Et₃N (10 equiv.) was added stirred for 5 hours. The reaction mixture was directly purified by flash column chromatography on silica gel [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to give the product **3aa** (25.2 mg, 0.074 mmol) as a solid. (Note: Each 0.1 mmol scale reaction requires about 10 grams of silica gel.)

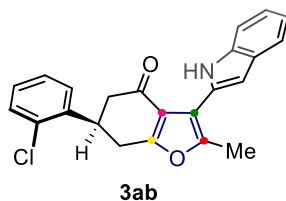
2.6 mmol scale reaction :

A mixture of **1a** (1.50 g, 7.90 mmol) and **2** (0.50 g, 2.60 mmol) was dissolved in CHCl₃ (52.0 mL), to the solution of the mixture was added Cu(OTf)₂ (0.18 g, 0.52 mmol) and 4 - Methylmorpholine (0.13 g, 1.30 mmol) at 25 °C and stirred for 12 h, Another base of 1 mmol Et₃N (10 equiv.) was added stirred for 5 hours. The reaction mixture was directly purified by flash column chromatography on silica gel [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to give the product **3aa** (0.88g, 1.80 mmol) as a solid. (Note: Each 0.1 mmol scale reaction requires about 10 grams of silica gel.)



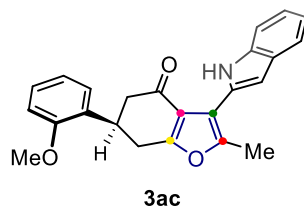
Compound 3aa: (74% yield, 25 mg, 0.074 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 171°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.82 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.29 (dd, J = 16.7, 7.4 Hz, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.60 – 6.57 (m, 1H), 3.56 (tt, J = 10.8, 5.6 Hz, 1H), 3.16 (dd, J = 17.1, 5.1 Hz, 1H), 3.02 (dd, J = 17.1, 11.1 Hz, 1H), 2.89 – 2.85 (m, 2H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.0, 166.3, 149.9, 141.9, 135.5, 129.9, 128.9, 127.4, 126.7, 121.6, 119.8, 119.7, 119.2, 111.8, 111.5, 99.3, 45., 40.7, 31.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3173, 2922, 1655, 1396, 1222, 1049, 700cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₉NO₂: 342.1494; found: 342.1496 [$M + H$]⁺.



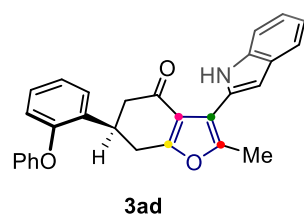
Compound 3ab: (64% yield, 24 mg, 0.064 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 180°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.82 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 5.9 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.20 – 7.16 (m, 1H), 7.11 (d, J = 7.2 Hz, 1H), 6.62 – 6.59 (m, 1H), 4.09 (tt, J = 11.1, 6.3 Hz, 1H), 3.24 (dd, J = 17.0, 5.0 Hz, 1H), 2.98 (dd, J = 17.0, 10.7 Hz, 1H), 2.90 (s, 1H), 2.88 (d, J = 2.9 Hz, 1H), 2.64 ppm (s, 3H).; **¹³C NMR** (126 MHz, CDCl₃) δ = 194.8, 166.1, 150.0, 139.0, 135.5, 133.7, 130.2, 129.9, 128.9, 128.5, 127.4, 127.1, 121.7, 119.9, 119.7, 119.2, 111.8, 111.5, 99.3, 43.9, 37.0, 29.8, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3182, 2918, 1651, 1398, 1224, 1050, 748 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₈ClNO₂: 376.1100; found: 376.1096 [$M + H$]⁺.



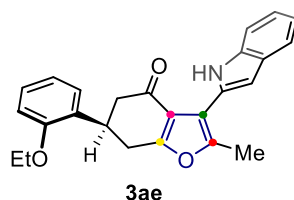
Compound 3ac: (50% yield, 18 mg, 0.050 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 201°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.91 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 – 7.15 (m, 2H), 7.09 (s, 1H), 6.99 – 6.90 (m, 2H), 6.60 – 6.58 (m, 1H), 3.97 – 3.89 (m, 1H), 3.85 (s, 3H), 3.20 – 3.08 (m, 2H), 3.03 – 2.95 (m, 1H), 2.87 (d, J = 3.9 Hz, 1H), 2.63 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 196.0, 167.1, 157.1, 149.6, 135.5, 130.1, 129.9, 128.9, 128.4, 127.1, 121.5, 120.8, 119.8, 119.6, 119.1, 111.8, 111.5, 110.7, 99.1, 55.2, 43.9, 35.2, 29.5, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3173, 2932, 1654, 1491, 1397, 1246, 737 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₄H₂₁NO₃: 372.1600; found: 372.1591 [$M + H$]⁺.



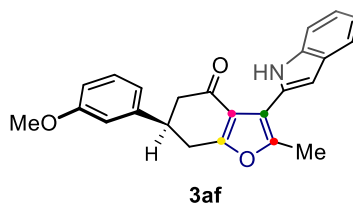
Compound 3ad: (65% yield, 28 mg, 0.065 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 192°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.78 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.33 (dt, J = 15.0, 7.8 Hz, 3H), 7.19 – 7.12 (m, 2H), 7.08 (q, J = 7.1 Hz, 1H), 7.01 (dd, J = 11.8, 8.2 Hz, 3H), 6.96 – 6.90 (m, 2H), 6.58 (s, 1H), 3.54 (tt, J = 10.8, 4.8 Hz, 1H), 3.16 (dd, J = 17.1, 5.0 Hz, 1H), 3.00 (dd, J = 17.0, 11.1 Hz, 1H), 2.91 – 2.79 (m, 2H), 2.62 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.7, 166.1, 157.9, 156.7, 149.9, 144.0, 135.5, 130.2, 129.9, 129.9, 128.9, 123.6, 121.7, 121.3, 119.9, 119.7, 119.3, 119.2, 117.4, 117.0, 111.9, 111.5, 99.3, 45.5, 40.6, 31.2, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3180, 2918, 1652, 1488, 1398, 1259, 776cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₉H₂₃NO₃: 434.1756; found: 434.1751 [$M + H$]⁺.



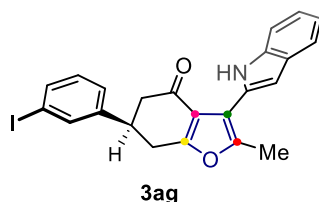
Compound 3ae: (44% yield, 17 mg, 0.044 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 196°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.91 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 3.3 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.09 (d, J = 7.7 Hz, 1H), 6.94 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.59 (s, 1H), 4.08 (q, J = 6.9 Hz, 2H), 3.97 – 3.89 (m, 1H), 3.16 – 3.11 (m, 2H), 3.00 (dd, J = 16.4, 12.3 Hz, 1H), 2.84 (dd, J = 16.4, 3.9 Hz, 1H), 2.63 (s, 3H), 1.42 ppm (t, J = 7.0 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 196.1, 167.2, 156.5, 149.7, 135.6, 130.2, 129.9, 129.0, 128.3, 127.2, 121.6, 120.6, 119.9, 119.6, 119.1, 111.9, 111.6, 111.5, 99.2, 63.5, 44.0, 35.4, 29.5, 14.9, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3171, 2867, 1651, 1399, 1227, 1045, 748cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₃: 386.1756; found: 386.1748 [$M + H$]⁺.



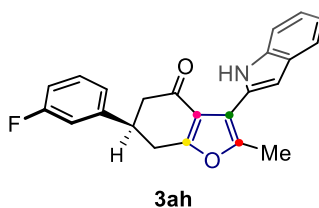
Compound 3af: (62% yield, 23 mg, 0.062 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 166°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.83 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 6.3 Hz, 2H), 6.62 – 6.58 (m, 1H), 3.83 (s, 3H), 3.57 (d, J = 5.1 Hz, 1H), 3.22 (dd, J = 17.1, 5.1 Hz, 1H), 3.11 (d, J = 11.2 Hz, 1H), 2.93 – 2.89 (m, 2H), 2.65 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.0, 166.2, 159.9, 149.9, 143.6, 135.5, 130.0, 129.9, 128.9, 121.6, 119.8, 119.6, 119.3, 118.9, 113.0, 112.2, 111.9, 111.5, 99.3, 55.2, 45.6, 40.8, 31.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3183, 2957, 1651, 1396, 1368, 1049, 791 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₄H₂₁NO₃: 372.1600; found: 372.1594 [$M + H$]⁺.



Compound 3ag: (86% yield, 40 mg, 0.086 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 200°C):

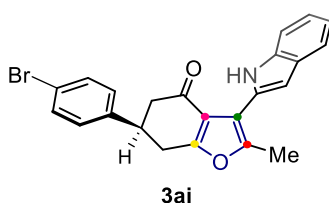
¹H NMR (500 MHz, Chloroform-d) δ = 11.75 (s, 1H), 7.65 – 7.58 (m, 3H), 7.48 (d, J = 8.0 Hz, 1H), 7.18 (q, J = 7.5 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.58 (s, 1H), 3.44 (dt, J = 11.7, 6.7 Hz, 1H), 3.10 – 3.05 (m, 1H), 2.92 – 2.82 (m, 1H), 2.82 – 2.72 (m, 2H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.4, 165.8, 150.0, 144.2, 136.5, 135.9, 135.5, 130.6, 129.9, 128.9, 126.0, 121.7, 119.9, 119.7, 119.2, 111.8, 111.5, 99.3, 94.8, 45.2, 40.2, 31.0, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3173, 1650, 1395, 1223, 1049, 780 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₈INO₂: 468.0460; found: 468.0454 [$M + H$]⁺.



Compound 3ah: (65% yield, 23 mg, 0.065 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 193°C):

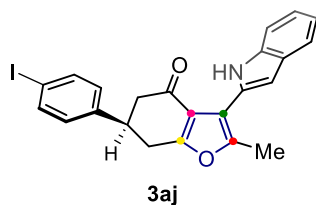
¹H NMR (500 MHz, Chloroform-d) δ = 11.76 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.21 – 7.14 (m, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.99

(t, $J = 8.8$ Hz, 2H), 6.59 (s, 1H), 3.54 (dd, $J = 10.7, 5.7$ Hz, 1H), 3.16 (dd, $J = 17.0, 4.9$ Hz, 1H), 2.98 (dd, $J = 17.0, 11.1$ Hz, 1H), 2.85 (qd, $J = 16.4, 8.2$ Hz, 2H), 2.63 ppm (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 194.5, 165.9, 164.0\text{-}162.0$ (d, $J = 250$ Hz), 150.0, 144.5-144.4 (d, $J = 6.8$ Hz), 135.5, 130.5 (d, $J = 8.3$ Hz), 129.8, 128.9, 122.4 (d, $J = 2.5$ Hz), 121.7, 119.9, 119.7, 119.3, 114.4- 114.3 (d, $J = 21.1$ Hz), 113.9-113.7 (d, $J = 21.7$ Hz), 111.9, 111.5, 99.4, 45.3, 40.4, 31.1, 14.4 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = 112.01$ ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3431, 2921, 1647, 1398, 1221, 1052, 782$ cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{FNO}_2$: 360.1400; found: 360.1390 [$M + \text{H}$] $^+$.



Compound 3ai: (70% yield, 29 mg, 0.070 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. =223°C):

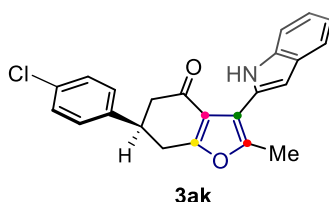
$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 11.77$ (s, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.51 – 7.47 (m, 3H), 7.21 – 7.15 (m, 1H), 7.11 (t, $J = 7.8$ Hz, 3H), 6.61 – 6.57 (m, 1H), 3.50 (s, 1H), 3.11 (s, 1H), 2.96 (d, $J = 11.1$ Hz, 1H), 2.87 – 2.74 (m, 2H), 2.63 ppm (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 194.5, 165.9, 150.0, 140.9, 135.5, 132.0, 129.8, 128.9, 128.5, 121.7, 121.2, 119.9, 119.7, 119.2, 111.8, 111.5, 99.4, 45.3, 40.2, 31.2, 14.4$ ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3207, 2922, 1637, 1492, 1397, 1223, 819$ cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{BrNO}_2$: 420.0599; found: 420.0593 [$M + \text{H}$] $^+$.



Compound 3aj: (50% yield, 23 mg, 0.050 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 200°C):

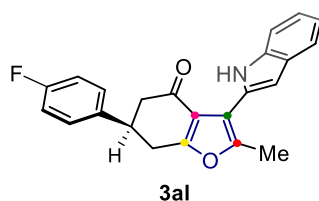
$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 11.77$ (s, 1H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 8.1$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 7.03 (d, $J = 8.3$ Hz, 2H), 6.60 (s, 1H), 3.52 (dd, $J = 10.9, 5.4$ Hz, 1H), 3.15 (d, $J = 5.0$ Hz, 1H), 3.04 – 2.95 (m, 1H), 2.89

– 2.79 (m, 2H), 2.64 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 194.5, 165.9, 150.0, 141.6, 138.0, 135.5, 129.8, 128.9, 128.7, 121.7, 119.9, 119.7, 119.3, 111.9, 111.5, 99.4, 92.6, 45.3, 40.3, 31.2, 14.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3174, 3053, 1651, 1396, 1223, 1049, 780 cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{INO}_2$: 468.0460; found: 468.0457 [$M + \text{H}$] $^+$.



Compound 3ak: (65% yield, 24 mg, 0.065 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 197 $^{\circ}\text{C}$):

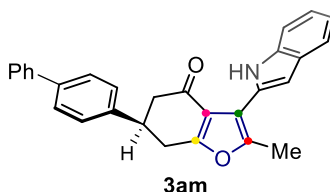
^1H NMR (500 MHz, Chloroform- d) δ = 11.77 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 6.58 (s, 1H), 3.53 – 3.44 (m, 1H), 3.13 – 3.04 (m, 1H), 2.92 (dd, J = 15.9, 10.1 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.62 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 194.6, 165.9, 149.9, 140.3, 135.5, 133.2, 129.9, 129.1, 128.9, 128.1, 121.8, 119.9, 119.7, 119.2, 111.8, 111.5, 99.3, 45.4, 40.1, 31.2, 14.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3179, 2920, 1641, 1493, 1396, 1221, 831 cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{ClNO}_2$: 376.1100; found: 376.1097 [$M + \text{H}$] $^+$.



Compound 3al: (78% yield, 28 mg, 0.078 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 206 $^{\circ}\text{C}$):

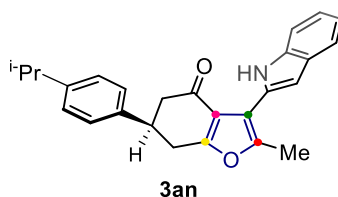
^1H NMR (500 MHz, Chloroform- d) δ = 11.79 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.12 – 7.08 (m, 1H), 7.05 – 6.99 (m, 2H), 6.58 – 6.56 (m, 1H), 3.45 (s, 1H), 3.04 (dd, J = 17.0, 4.9 Hz, 1H), 2.84 (m, 1H), 2.80 – 2.69 (m, 2H), 2.61 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 194.7, 166.1, 162.9–160.9 (d, J = 250.0 Hz), 149.9, 137.7 (d, J = 3.2 Hz), 135.5, 129.9, 128.9, 128.3, 128.2, 121.7, 119.9, 119.7, 119.1, 115.8, 115.6, 111.8, 111.5, 99.3, 45.6, 40.0,

31.4, 14.4 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = 115.03 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3199, 2924, 1652, 1513, 1396, 1218, 832cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₈FNO₂: 360.1400; found: 360.1396 [M+ H]⁺.



Compound 3am: (33% yield, 14 mg, 0.033 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 261°C):

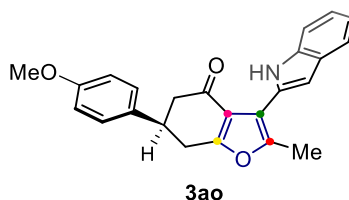
¹H NMR (500 MHz, Chloroform-d) δ = 11.84 (s, 1H), 7.61 (t, J = 8.4 Hz, 5H), 7.51 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (dd, J = 14.9, 7.7 Hz, 3H), 7.18 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.62 (s, 1H), 3.66 (d, J = 4.4 Hz, 1H), 3.27 (dd, J = 17.1, 5.1 Hz, 1H), 3.14 (dd, J = 17.1, 11.0 Hz, 1H), 2.96 (d, J = 8.9 Hz, 2H), 2.66ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.9, 166.2, 149.9, 140.9, 140.5, 140.5, 135.6, 129.9, 128.9, 128.8, 127.7, 127.4, 127.2, 127.0, 121.7, 119.9, 119.7, 119.4, 111.9, 111.5, 99.4, 45.6, 40.5, 31.4, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3398, 2921, 1644, 1396, 1120, 1053, 699cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₉H₂₃NO₂: 418.1807; found: 418.1802 [M + H]⁺.



Compound 3an: (73% yield, 28 mg, 0.073 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 202°C):

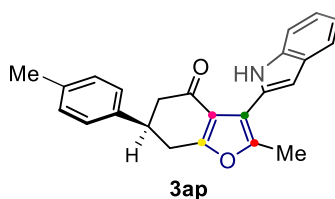
¹H NMR (500 MHz, Chloroform-d) δ = 11.85 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.26 (s, 1H), 7.25 – 7.21 (m, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.60 (s, 1H), 3.57 (dq, J = 10.9, 5.7 Hz, 1H), 3.20 (dd, J = 17.1, 5.0 Hz, 1H), 3.07 (dd, J = 17.1, 11.1 Hz, 1H), 2.95 – 2.87 (m, 3H), 2.64 (s, 3H), 1.27 (s, 3H), 1.26ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.2, 166.5, 149.9, 148.1, 139.3, 135.6, 130.0, 128.9, 126.9, 126.6, 121.6, 119.8, 119.7, 119.3, 111.9, 111.5,

99.3, 45.7, 40.4, 33.7, 31.4, 23.9, 14.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3174, 2956, 1643, 1397, 1221, 1051, 831cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_2$: 384.1964; found: 384.1959 [$M + \text{H}$] $^+$.



Compound 3ao: (76% yield, 28 mg, 0.076 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 187°C):

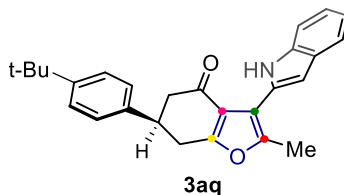
^1H NMR (500 MHz, Chloroform- d) δ = 11.83 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.8 Hz, 3H), 6.86 (d, J = 8.6 Hz, 2H), 6.56 (s, 1H), 3.79 (s, 3H), 3.42 (s, 1H), 3.04 (dd, J = 17.0, 4.9 Hz, 1H), 2.85 (dd, J = 17.0, 11.2 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.60 ppm (s, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ = 195.2, 166.5, 158.8, 149.8, 135.5, 134.1, 130.0, 129.0, 127.7, 121.7, 119.9, 119.7, 119.1, 114.2, 111.8, 111.5, 99.2, 55.3, 45.8, 40.0, 31.5, 14.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3169, 2918, 1647, 1514, 1396, 1233, 783cm^{-1} ; **HRMS** (ESI): m/z calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_3$: 372.1600; found: 376.1594 [$M + \text{H}$] $^+$.



Compound 3ap: (75% yield, 26 mg, 0.075 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 182°C):

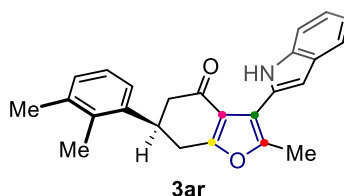
^1H NMR (500 MHz, Chloroform- d) δ = 11.83 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.19 – 7.12 (m, 5H), 7.09 (t, J = 7.4 Hz, 1H), 6.58 (s, 1H), 3.49 (tt, J = 10.8, 5.2 Hz, 1H), 3.10 (dd, J = 17.1, 5.0 Hz, 1H), 2.95 (dd, J = 17.1, 11.2 Hz, 1H), 2.85 – 2.79 (m, 2H), 2.61 (s, 3H), 2.35 ppm (s, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ = 195.2, 166.4, 149.8, 139.0, 137.1, 135.5, 130.0, 129.6, 128.9, 126.6, 121.6, 119.8, 119.7, 119.2, 111.8, 111.5, 99.2, 45.7, 40.4, 31.4, 21.0, 14.4 ppm; **ATR-**

FTIR (cm⁻¹): $\bar{\nu}$ = 3169, 2922, 1648, 1397, 1225, 1051, 751cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₄H₂₁NO₂:356.1651; found: 356.1649 [M + H]⁺.



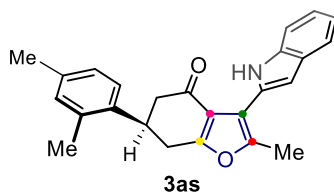
Compound 3aq: (73% yield, 29 mg, 0.073 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 220°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.84 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.61 – 6.57 (m, 1H), 3.58 – 3.50 (m, 1H), 3.17 (dd, *J* = 17.1, 5.1 Hz, 1H), 3.03 (dd, *J* = 17.1, 11.1 Hz, 1H), 2.92 – 2.82 (m, 2H), 2.63 (s, 3H), 1.33 ppm (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.2, 166.5, 150.4, 149.8, 138.9, 135.6, 130.0, 128.9, 126.4, 125.8, 121.7, 119.9, 119.7, 119.3, 111.9, 111.5, 99.3, 45.7, 40.3, 34.5, 31.4, 31.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3181, 2957, 1651, 1394, 1221, 1047, 734 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₇H₂₇NO₂: 398.2120; found: 398.2126 [M + H]⁺.



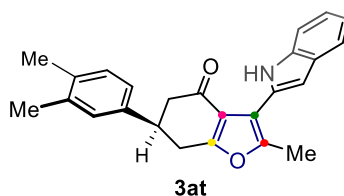
Compound 3ar: (83% yield, 30 mg, 0.082 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 223°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.86 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (ddd, *J* = 10.9, 8.0, 5.5 Hz, 4H), 6.60 – 6.58 (m, 1H), 3.88 (dq, *J* = 11.7, 6.8, 6.0 Hz, 1H), 3.09 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.98 (dd, *J* = 17.1, 11.2 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.63 (s, 3H), 2.33 (s, 3H), 2.27 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.4, 166.6, 149.8, 139.7, 137.6, 135.5, 134.1, 129.9, 128.9, 128.9, 125.9, 123.0, 121.6, 119.8, 119.6, 119.1, 111.9, 111.5, 99.3, 45.3, 36.9, 30.8, 21.0, 14.8, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3167, 2922, 1650, 1395, 1221, 1049, 781cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₂: 370.1807; found: 370.1798 [M + H]⁺.



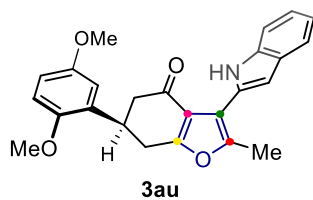
Compound 3as: (86% yield, 32 mg, 0.086 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 214°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.84 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.11 – 7.07 (m, 1H), 7.05 (d, J = 6.7 Hz, 2H), 6.60 – 6.58 (m, 1H), 3.76 (s, 1H), 3.09 (dd, J = 17.1, 5.0 Hz, 1H), 2.99 (dd, J = 17.1, 11.1 Hz, 1H), 2.90 – 2.75 (m, 2H), 2.63 (s, 3H), 2.33 ppm (d, J = 10.7 Hz, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.4, 166.6, 149.8, 136.9, 136.8, 135.5, 135.3, 131.8, 130.0, 128.9, 127.2, 125.2, 121.6, 119.8, 119.6, 119.1, 111.9, 111.5, 99.3, 45.2, 36.4, 30.7, 20.9, 19.3, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3203, 2918, 1651, 1397, 1220, 1047, 777cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₂: 370.1807; found: 370.1825 [$M + H$]⁺.



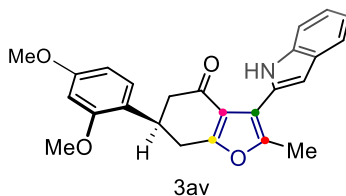
Compound 3at: (72% yield, 26 mg, 0.072 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 217°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.85 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.10 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 5.8 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.59 (s, 1H), 3.55 – 3.47 (m, 1H), 3.15 (dd, J = 17.1, 4.9 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.86 (d, J = 7.8 Hz, 2H), 2.63 (s, 3H), 2.29 (s, 3H), 2.27 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.2, 166.5, 149.8, 139.5, 137.1, 135.7, 135.5, 130.1, 130.0, 128.9, 128.1, 123.9, 121.6, 119.8, 119.6, 119.2, 111.8, 111.5, 99.2, 45.8, 40.4, 31.5, 19.9, 19.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3171, 2949, 1651, 1394, 1222, 1049, 793cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₂: 370.1807; found: 370.1798 [$M + H$]⁺.



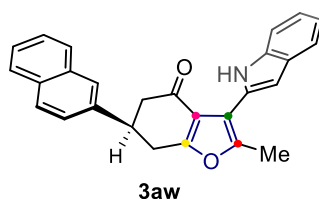
Compound 3au: (80% yield, 32 mg, 0.081 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 182°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.90 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.59 (s, 1H), 3.93 – 3.86 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.21 – 3.06 (m, 2H), 2.98 (dd, J = 16.4, 12.5 Hz, 1H), 2.85 (dd, J = 16.4, 3.8 Hz, 1H), 2.64 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.8, 167.0, 153.6, 151.3, 149.71, 135.5, 131.1, 130.1, 128.9, 121.5, 119.8, 119.6, 119.1, 114.2, 111.9, 111.7, 111.6, 111.5, 99.2, 55.77, 55.7, 43.9, 35.4, 29.5, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3170, 2950, 1655, 1396, 1230, 1050, 781 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₄: 402.1705; found: 402.1698 [$M + H$]⁺.



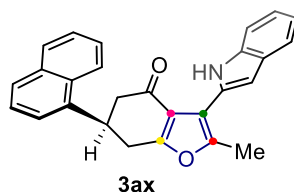
Compound 3av: (72% yield, 29 mg, 0.072 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 214°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.92 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.19 – 7.14 (m, 1H), 7.13 – 7.04 (m, 2H), 6.62 – 6.56 (m, 1H), 6.52 – 6.43 (m, 2H), 3.86 (dd, J = 8.4, 3.6 Hz, 1H), 3.82 (d, J = 9.2 Hz, 6H), 3.16 – 3.10 (m, 2H), 2.97 (d, J = 12.2 Hz, 1H), 2.83 (dd, J = 16.4, 3.8 Hz, 1H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 196.2, 167.2, 160.0, 158.1, 149.6, 135.5, 130.1, 128.9, 127.5, 122.5, 121.5, 119.8, 119.6, 119.1, 111.8, 111.5, 104.1, 99.1, 98.9, 55.4, 55.3, 44.2, 34.9, 29.8, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3165, 2924, 1643, 1505, 1396, 1153, 1048, 835 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₅H₂₃NO₄: 402.1705; found: 402.1694 [$M + H$]⁺.



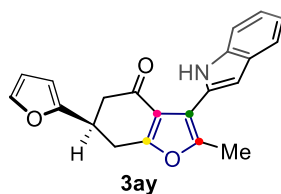
Compound 3aw: (60% yield, 23 mg, 0.060 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 153°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.84 (s, 1H), 7.90 – 7.81 (m, 3H), 7.72 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.50 (qd, J = 5.7, 4.6, 1.6 Hz, 3H), 7.43 – 7.39 (m, 1H), 7.21 – 7.13 (m, 1H), 7.12 – 7.09 (m, 1H), 6.63 – 6.58 (m, 1H), 3.74 (s, 1H), 3.25 (d, J = 5.0 Hz, 1H), 3.17 (d, J = 11.1 Hz, 1H), 3.02 – 2.96 (m, 2H), 2.65 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.0, 166.3, 149.9, 139.3, 135.6, 133.5, 132.7, 130.0, 128.9, 128.7, 127.8, 127.7, 126.5, 126.1, 125.3, 124.9, 121.7, 119.9, 119.7, 119.3, 111.9, 111.5, 99.3, 45.6, 40.9, 31.4, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3181, 2921, 1651, 1398, 1222, 1051, 748cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₇H₂₁NO₂: 392.1651; found: 392.1648 [$M + H$]⁺.



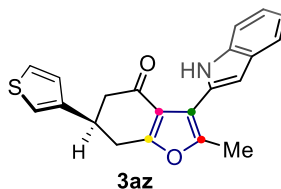
Compound 3ax: (72% yield, 28 mg, 0.072 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 204°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.87 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.41 (d, J = 7.0 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.12 – 7.07 (m, 1H), 6.63 – 6.60 (m, 1H), 4.43 (dt, J = 10.1, 5.1 Hz, 1H), 3.34 (dd, J = 17.1, 4.8 Hz, 1H), 3.14 (dd, J = 17.1, 10.7 Hz, 1H), 3.06 – 3.01 (m, 2H), 2.65 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.4, 166.6, 149.9, 137.6, 135.6, 134.1, 130.9, 130.0, 129.3, 129.0, 128.0, 126.6, 125.9, 125.5, 122.9, 122.4, 121.7, 119.9, 119.7, 119.3, 111.9, 111.6, 99.3, 45.2, 35.9, 31.0, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3208, 2921, 1653, 1397, 1218, 803, 775cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₇H₂₁NO₂: 392.1651; found: 392.1641 [$M + H$]⁺.



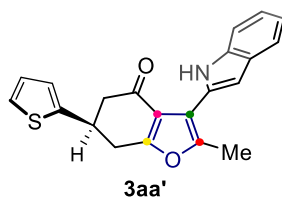
Compound 3ay: (67% yield, 22 mg, 0.067 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 200°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.76 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.58 (s, 1H), 6.34 – 6.30 (m, 1H), 6.12 (d, J = 3.1 Hz, 1H), 3.68 (dt, J = 9.9, 5.0 Hz, 1H), 3.27 (dd, J = 17.1, 5.2 Hz, 1H), 3.12 (dd, J = 17.1, 9.4 Hz, 1H), 2.98 (dd, J = 16.6, 4.3 Hz, 1H), 2.89 (d, J = 10.6 Hz, 1H), 2.62 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.4, 165.4, 155.0, 149.9, 141.8, 135.5, 129.8, 128.9, 121.7, 119.9, 119.7, 119.3, 111.9, 111.5, 110.3, 105.3, 99.3, 42.8, 34.0, 28.7, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3209, 1652, 1397, 1222, 1051, 748cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₁H₁₇NO₃: 332.1287; found: 332.1287 [$M + H$]⁺.



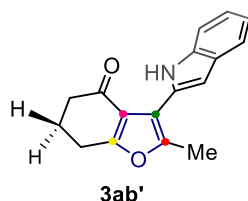
Compound 3az: (50% yield, 16 mg, 0.046 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 220°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.81 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.35 (dd, J = 5.0, 2.9 Hz, 1H), 7.19 – 7.16 (m, 1H), 7.11 – 7.07 (m, 2H), 7.05 (dd, J = 5.0, 1.2 Hz, 1H), 6.60 – 6.57 (m, 1H), 3.69 (dt, J = 11.1, 5.9 Hz, 1H), 3.27 (dd, J = 17.0, 5.0 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.84 (dd, J = 16.4, 11.7 Hz, 1H), 2.64 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.9, 166.0, 149.9, 143.0, 135.5, 129.9, 128.9, 126.6, 126.2, 121.7, 120.4, 119.9, 119.70, 119.4, 111.9, 111.5, 99.3, 45.4, 36.0, 31.1, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3173, 2921, 1650, 1398, 1219, 1049, 786cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₁H₁₇SNO₂: 348.1058; found: 348.1055 [$M + H$]⁺.



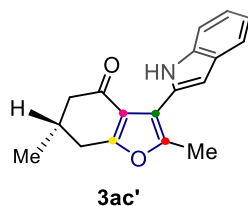
Compound 3aa': (52% yield, 18 mg, 0.052 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 214°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.76 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.22 (d, J = 5.1 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.93 (d, J = 3.4 Hz, 1H), 6.58 (s, 1H), 3.87 (dt, J = 10.5, 5.6 Hz, 1H), 3.32 (dd, J = 17.0, 5.0 Hz, 1H), 3.12 – 3.01 (m, 2H), 2.89 (dd, J = 16.4, 11.4 Hz, 1H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 194.2, 165.5, 150.0, 145.7, 135.5, 129.8, 128.9, 126.9, 123.9, 123.9, 121.7, 119.9, 119.7, 119.4, 111.9, 111.5, 99.4, 46.4, 36.0, 32.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3169, 2918, 1648, 1400, 1222, 1052, 697cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₁H₁₇SNO₂: 348.1058; found: 348.1051 [$M + H$]⁺.



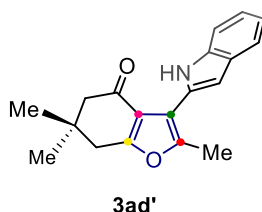
Compound 3ab': (80% yield, 21 mg, 0.080 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 167°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.86 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.57 – 6.53 (m, 1H), 2.85 (t, J = 6.3 Hz, 2H), 2.62 (d, J = 6.3 Hz, 2H), 2.60 (s, 3H), 2.17 ppm (p, J = 6.4 Hz, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ = 196.5, 167.1, 149.4, 135.5, 130.1, 128.9, 121.5, 119.8, 119.6, 119.4, 111.8, 111.5, 99.2, 38.4, 23.7, 22.2, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3170, 2923, 1639, 1397, 1221, 1011, 732cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₇H₁₅NO₂: 266.1181; found: 266.1184 [$M + H$]⁺.



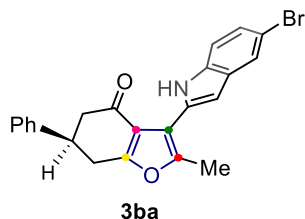
Compound 3ac': (71% yield, 20 mg, 0.071 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 162°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.85 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.10 – 7.05 (m, 1H), 6.58 – 6.53 (m, 1H), 2.92 (dd, J = 16.2, 3.9 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.60 (s, 3H), 2.49 (dd, J = 16.4, 9.7 Hz, 1H), 2.43 (dtd, J = 10.7, 6.3, 5.3, 2.8 Hz, 1H), 2.37 – 2.30 (m, 1H), 1.16 ppm (d, J = 6.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 196.0, 166.8, 149.5, 135.5, 130.1, 128.9, 121.5, 119.8, 119.6, 119.0, 111.8, 111.5, 99.1, 46.8, 31.7, 30.4, 20.8, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3128, 2923, 1654, 1398, 1221, 1048, 780cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₈H₁₇NO₂: 280.1338; found: 280.1338 [$M + H$]⁺.



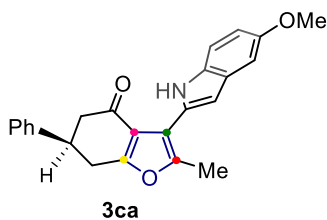
Compound 3ad': (65% yield, 19 mg, 0.065 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 145°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.83 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.18 – 7.13 (m, 1H), 7.10 – 7.05 (m, 1H), 6.58 – 6.55 (m, 1H), 2.70 (s, 2H), 2.60 (s, 3H), 2.47 (s, 2H), 1.15 ppm (s, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.9, 166.2, 149.7, 135.5, 130.1, 129.0, 121.6, 119.8, 119.6, 118.2, 111.7, 111.5, 99.1, 52.6, 37.5, 34.8, 28.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3204, 2961, 1654, 1397, 1223, 1050, 783cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₉H₁₉NO₂: 294.1494; found: 294.1492 [$M + H$]⁺.



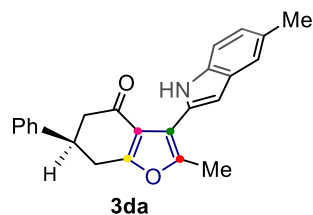
Compound 3ba: (67% yield, 28 mg, 0.067 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 236°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.96 (s, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.37 (dt, J = 16.4, 7.9 Hz, 3H), 7.33 – 7.28 (m, 3H), 7.24 (dd, J = 8.6, 1.9 Hz, 1H), 6.55 – 6.48 (m, 1H), 3.63 – 3.53 (m, 1H), 3.20 (dd, J = 17.1, 5.1 Hz, 1H), 3.06 (dd, J = 17.1, 11.1 Hz, 1H), 2.94 – 2.88 (m, 2H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.1, 166.5, 150.4, 141.8, 134.1, 131.3, 130.7, 129.0, 127.5, 126.7, 124.4, 122.2, 119.2, 112.9, 112.9, 111.5, 98.6, 45.5, 40.8, 31.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3167, 2920, 1651, 1394, 1216, 1050, 699cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₈BrNO₂: 420.0594; found: 420.0606 [$M + H$]⁺.



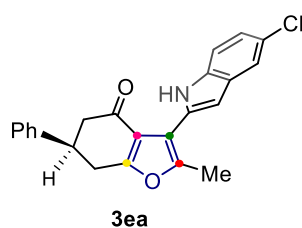
Compound 3ca: (40% yield, 15 mg, 0.040 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 209°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.74 (s, 1H), 7.39 (dd, J = 8.5, 6.1 Hz, 3H), 7.31 (t, J = 7.5 Hz, 3H), 7.07 (d, J = 2.3 Hz, 1H), 6.85 (dd, J = 8.8, 2.4 Hz, 1H), 6.54 – 6.49 (m, 1H), 3.86 (s, 3H), 3.63 – 3.56 (m, 1H), 3.21 (dd, J = 17.1, 5.1 Hz, 1H), 3.07 (dd, J = 17.1, 11.1 Hz, 1H), 2.92 – 2.88 (m, 2H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.0, 166.3, 154.2, 149.7, 141.9, 130.8, 130.6, 129.3, 128.9, 127.4, 126.7, 119.3, 112.2, 112.1, 111.9, 101.5, 99.1, 55.8, 45.6, 40.8, 31.4, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3219, 2952, 1653, 1491, 1396, 1204, 1154, 763 cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₄H₂₁NO₃: 372.1600; found: 372.1591 [$M + H$]⁺.



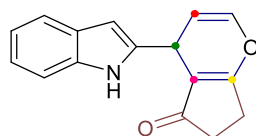
Compound 3da: (57% yield, 20 mg, 0.057 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 257°C):

¹H NMR (500 MHz, Chloroform-d) δ = 11.84 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.19 (s, 4H), 7.16 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.61 – 6.59 (m, 1H), 3.56 (dd, J = 5.9, 3.9 Hz, 1H), 3.18 (dd, J = 17.1, 5.0 Hz, 1H), 3.05 (dd, J = 17.1, 11.1 Hz, 1H), 2.92 – 2.86 (m, 2H), 2.64 (s, 3H), 2.36 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.0, 166.2, 149.7, 142.0, 133.9, 129.9, 129.2, 128.9, 128.8, 127.4, 126.7, 123.4, 119.4, 119.3, 112.0, 111.2, 98.8, 45.6, 40.8, 31., 21.5, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3205, 2920, 1652, 1397, 1182, 1048, 699cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₄H₂₁NO₂: 356.1651; found: 356.1640 [$M + H$]⁺.



Compound 3ea: (66% yield, 25 mg, 0.066 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 221°C):

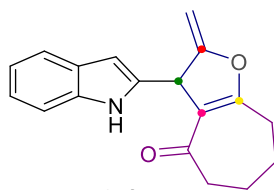
¹H NMR (500 MHz, Chloroform-d) δ = 11.95 (s, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.34 – 7.26 (m, 3H), 7.11 (dd, J = 8.6, 2.0 Hz, 1H), 6.51 (d, J = 1.3 Hz, 1H), 3.58 (dt, J = 10.6, 5.3 Hz, 1H), 3.19 (dd, J = 17.1, 5.1 Hz, 1H), 3.05 (dd, J = 17.1, 11.1 Hz, 1H), 2.91 – 2.86 (m, 2H), 2.63 ppm (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ = 195.1, 166.5, 150.3, 141.8, 133.9, 131.4, 130.0, 129.0, 127.5, 126.7, 125.2, 121.9, 119.2, 119.1, 112.5, 111.6, 98.8, 45.5, 40.8, 31.3, 14.4 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3170, 2914, 1651, 1574, 1396, 1058, 762cm⁻¹; **HRMS** (ESI): m/z calcd for C₂₃H₁₈ClNO₂: 376.1104; found: 376.1099 [$M + H$]⁺.



3ae'

Compound 3ae': (43% yield, 11 mg, 0.043 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. = 184°C):

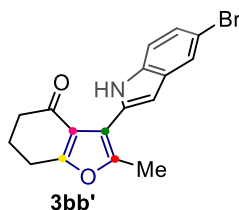
¹H NMR (500 MHz, Chloroform-d) δ = 9.51 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.16 – 7.11 (m, 1H), 7.08 – 7.00 (m, 1H), 6.74 (dd, J = 6.2, 1.6 Hz, 1H), 6.22 – 6.19 (m, 1H), 5.51 (dd, J = 6.2, 3.8 Hz, 1H), 4.63 – 4.59 (m, 1H), 2.63 (ddd, J = 5.8, 4.0, 2.1 Hz, 2H), 2.55 – 2.49 (m, 1H), 2.49 – 2.41 ppm (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ = 205.7, 179.4, 141.0, 140.8, 136.3, 127.8, 121.7, 120.1, 119.5, 116.6, 111.1, 104.9, 98.3, 32.9, 28.0, 25.8 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3285, 2921, 1667, 1613, 1396, 1236, 997, 793cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₆H₁₃NO₂: 252.1025; found: 252.1018[M + H]⁺.



3af'

Compound 3af': (53% yield, 15 mg, 0.053 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. =163°C):

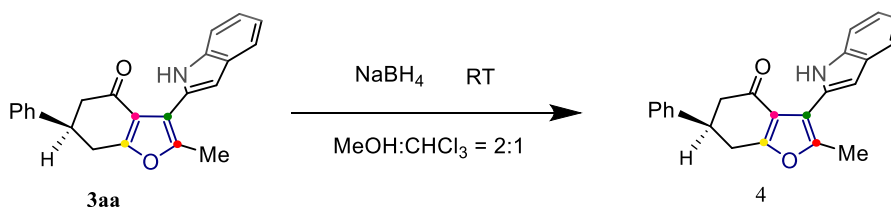
¹H NMR (500 MHz, Chloroform-d) δ = 9.38 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.38 (s, 1H), 5.22 (s, 1H), 5.04 (t, J = 2.5 Hz, 1H), 4.61 (t, J = 2.4 Hz, 1H), 2.74 – 2.56 (m, 4H), 1.98 – 1.76 ppm (m, 4H); **¹³C NMR** (126 MHz, CDCl₃) δ = 198.1, 170.2, 160.4, 138.9, 136.5, 127.8, 121.6, 120.2, 119.7, 119.5, 111.0, 99.3, 90.3, 44.6, 44.3, 30.0, 23.9, 22.6 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3311, 2927, 1602, 1392, 1172, 1066, 927, 737cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₈H₁₇NO₂: 280.1338; found: 280.1332 [M + H]⁺.



Compound 3bb': (54% yield, 18 mg, 0.054 mmol, [20:1 petroleum ether/EtOAc], white crystal, mp. =166°C):

$^1\text{H NMR}$ (500 MHz, Chloroform-d) δ = 12.00 (s, 1H), 7.70 (s, 1H), 7.34 (d, J = 8.6 Hz, 1H), 7.22 (dd, J = 8.6, 1.8 Hz, 1H), 6.49 (d, J = 1.5 Hz, 1H), 2.92 (t, J = 6.3 Hz, 2H), 2.67 – 2.63 (m, 2H), 2.61 (s, 3H), 2.21 ppm (p, J = 6.4 Hz, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl₃) δ = 196.5, 167.3, 149.8, 134.1, 131.4, 130.7, 124.3, 122.2, 119.3, 112.8, 112.8, 111.5, 98.5, 38.4, 23.7, 22.2, 14.3 ppm; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3158, 2922, 1648, 1395, 1011, 769cm⁻¹; **HRMS** (ESI): m/z calcd for C₁₇H₁₄BrNO₂: 344.0286; found: 344.0290 [$M + H$]⁺.

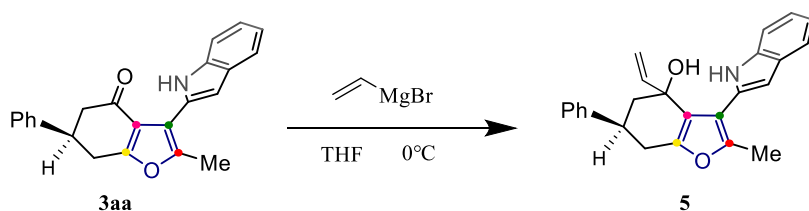
3.General Procedure for the Synthesis derivatives.



Under room temperature, compound **3aa** (34.2 mg, 0.10 mmol) was dissolved in 2.0 mL a mixed solution of methanol and chloroform (MeOH:CHCl₃=2:1), NaBH₄ (11.3 mg, 0.3 mmol) were added to a 25 mL Schlenk tube. The solution was stirred for 0.5 hour until the **3aa** was disappeared. The reaction was quenched with NH₄Cl and extracted with CH₂Cl₂, dried with magnesium sulfate, and evaporated. The residue was purified by chromatography to give **4** (56% yield, 19.2 mg, 0.056 mmol, [20:1 petroleum ether/EtOAc], yellow oil):

$^1\text{H NMR}$ (500 MHz, Chloroform-d) δ = 10.55 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.34 (q, J = 9.7, 8.9 Hz, 4H), 7.27 (d, J = 5.6 Hz, 2H), 7.11 (dt, J = 12.5, 7.0 Hz, 2H), 6.53 – 6.48 (m, 1H), 4.95 (d, J = 7.0

Hz, 1H), 3.13 (ddd, $J = 11.6, 7.2, 2.6$ Hz, 1H), 2.84 (td, $J = 18.3, 17.2, 7.4$ Hz, 2H), 2.58 (s, 3H), 2.53 – 2.46 (m, 1H), 2.02 (d, $J = 9.0$ Hz, 1H), 1.95 ppm (td, $J = 12.1, 7.9$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 149.9, 148.5, 143.9, 135.7, 131.6, 128.9, 128.8, 126.9, 121.3, 119.8, 119.7, 118.5, 113.1, 111.0, 99.1, 65.8, 41.1, 39.5, 30.5, 13.9$ ppm; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3431, 2923, 2851, 1630, 1383, 1107$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2$: 344.1651; found: 344.1650 [$M + \text{H}$] $^+$.



In a 10 mL round bottom flask, **3aa** (34.2 mg, 0.10 mmol) were dissolved in anhydrous THF (3 mL/mmol) under argon atmosphere and cooled to 0 °C. To this solution, ethynyl magnesium bromide (1.5 equiv, 1.0 M in THF) was added dropwise, and the reaction mixture was maintained at 0 °C for 2.0 hours. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The combined organic layer was dried with Na_2SO_4 , and evaporated under reduced pressure. The residue was purified by column chromatography silica gel, affording products **5** as a pale white solid. (60% yield, 22.8 mg, 0.062 mmol, [20:1 petroleum ether/EtOAc], white solid, mp. = 127 °C):

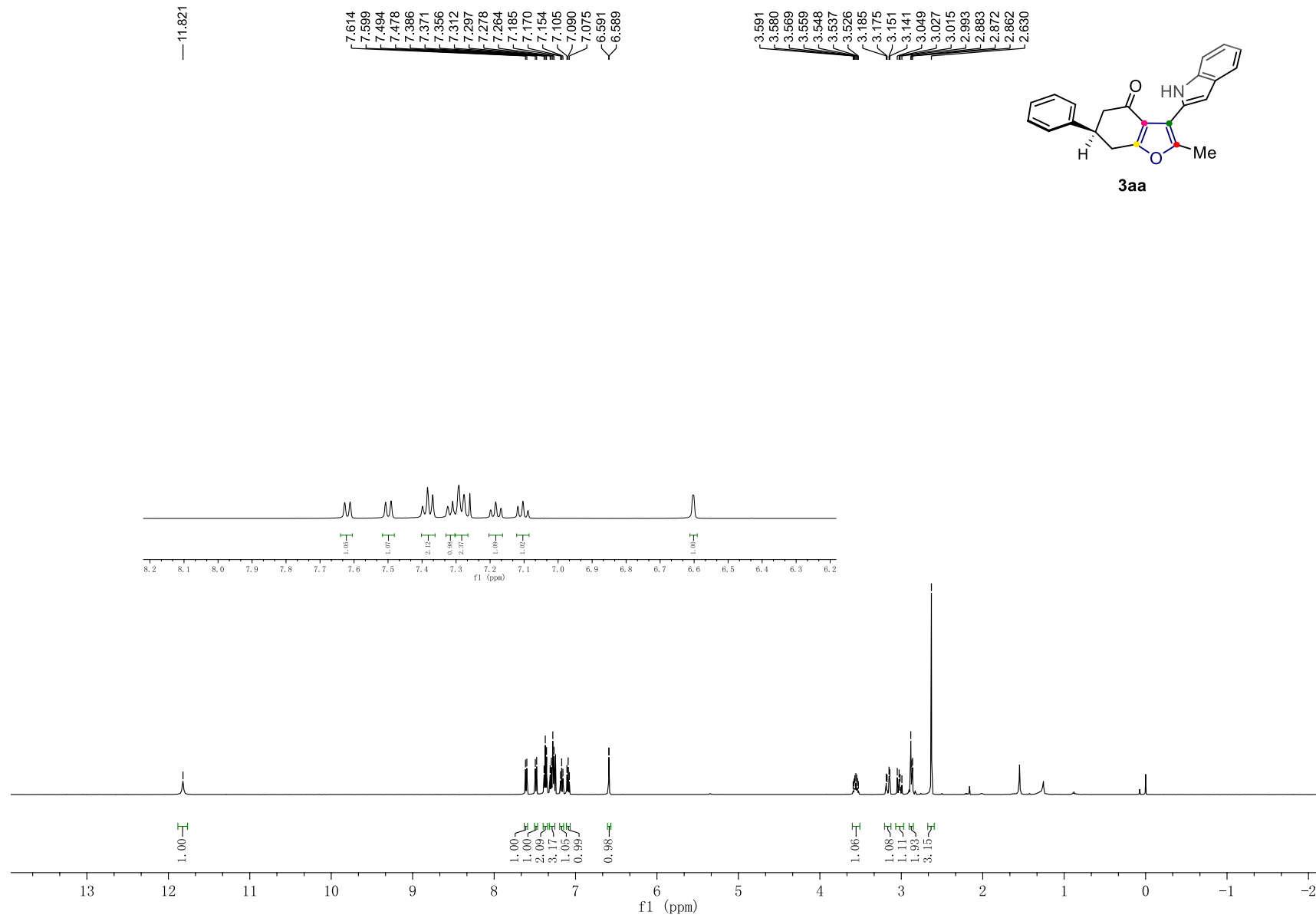
^1H NMR (500 MHz, Chloroform- d) $\delta = 10.34$ (s, 1H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 11.3$ Hz, 1H), 7.24 (s, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.14 – 7.07 (m, 2H), 6.49 – 6.47 (m, 1H), 5.95 (dd, $J = 17.2, 10.5$ Hz, 1H), 5.03 – 4.89 (m, 2H), 3.02 – 2.95 (m, 1H), 2.80 (dd, $J = 16.1, 4.9$ Hz, 1H), 2.66 – 2.60 (m, 1H), 2.59 (s, 3H), 2.20 – 2.14 (m, 2H), 1.91 – 1.83 ppm (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 150.2, 148.9, 143.8, 140.9, 135.6, 131.3, 128.7, 128.7, 126.9, 126.8, 121.2, 119.8, 119.6, 118.5, 116.2, 112.6, 111.0, 99.3, 74.1, 46.7, 38.6, 31.1, 13.9$ ppm; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3408, 3263, 2922, 2851, 1454, 1049, 783, 696$ cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$: 370.1802; found: 370.1807 [$M + \text{H}$] $^+$.

4. References

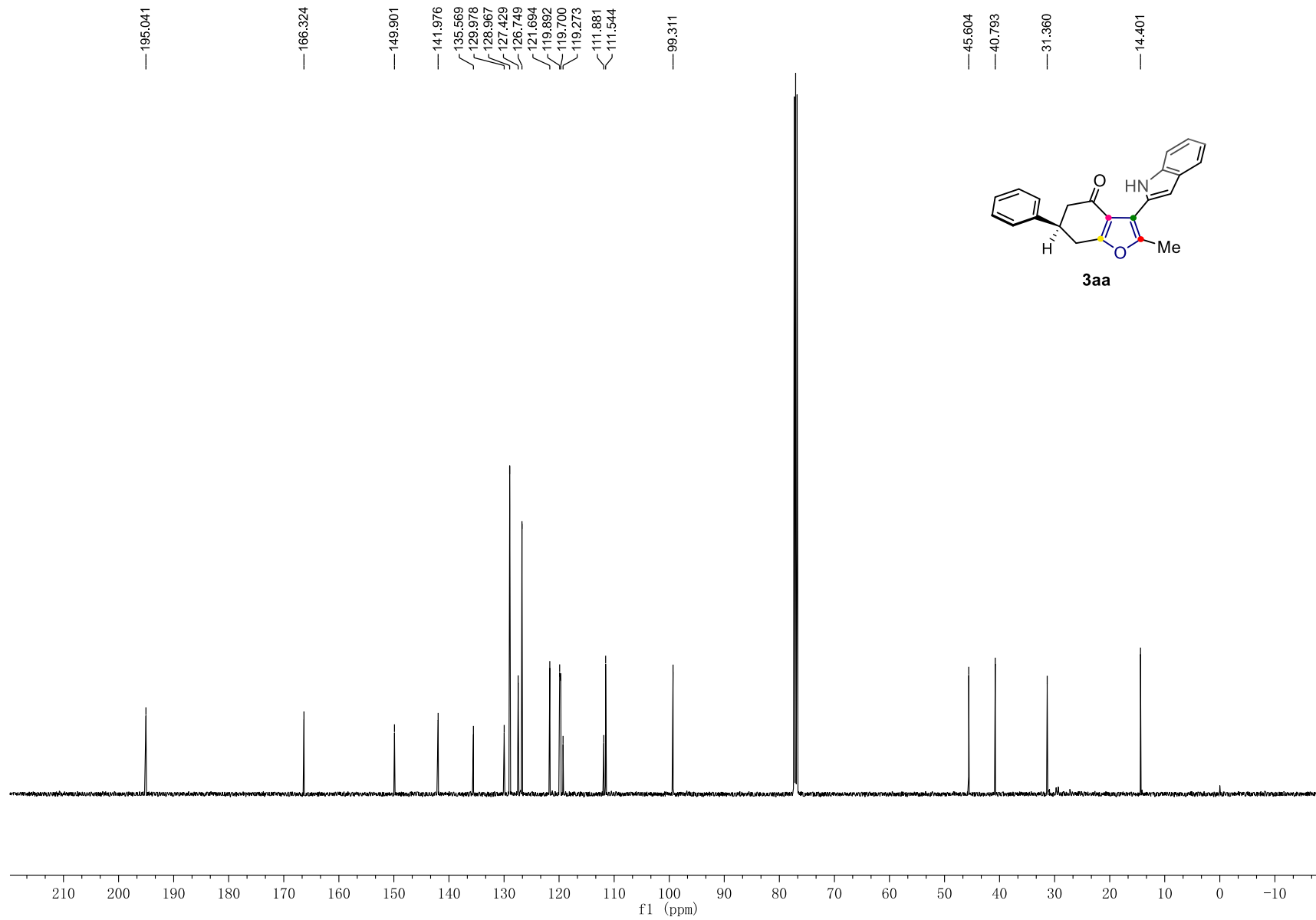
1. J. Zhang, T. Ni, W.-L. Yang and W.-P. Deng, *Org. Lett* , 2020, **22**, 4547-4552.

5. Copies of NMR Spectra

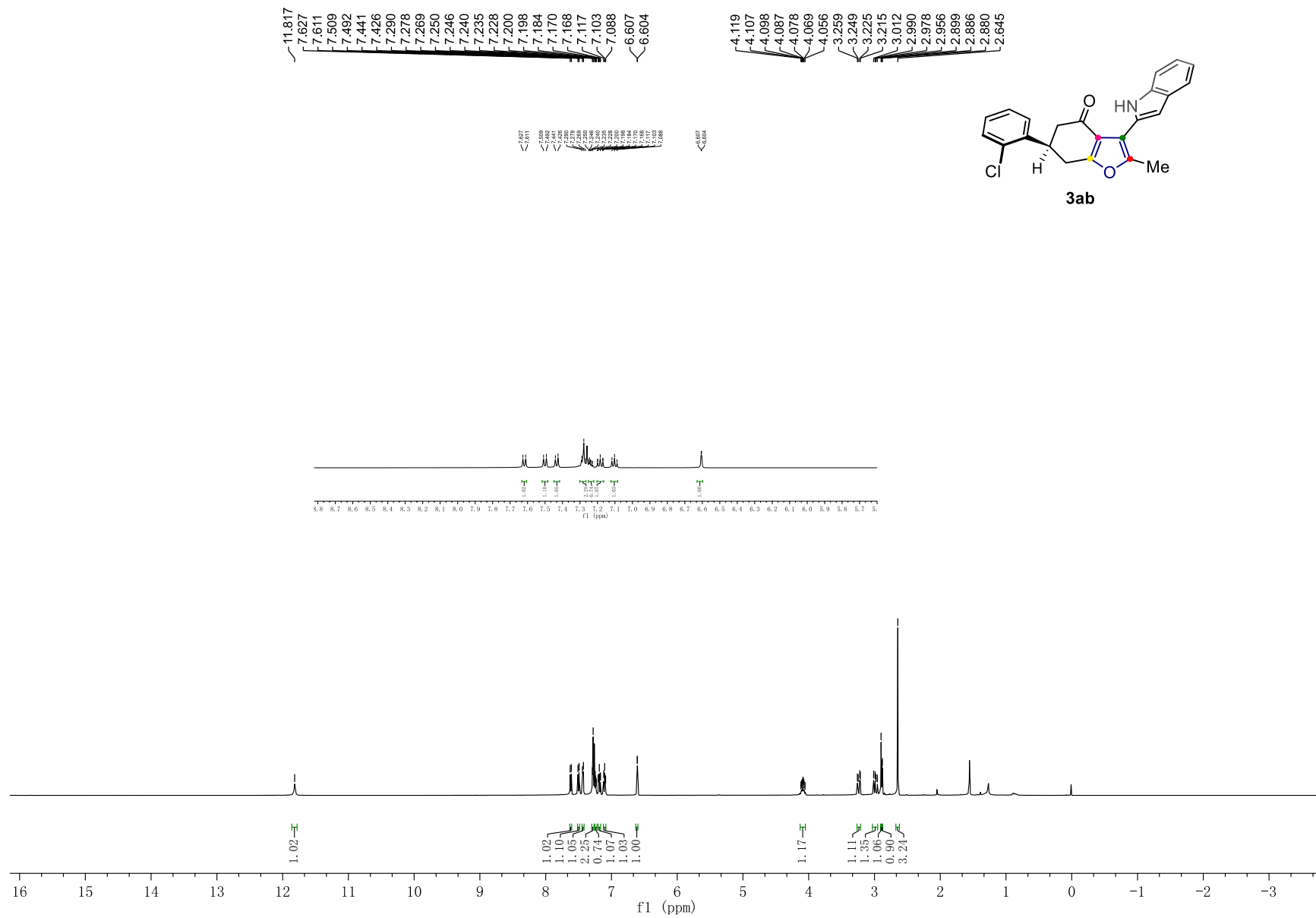
¹H NMR (500 MHz, CDCl₃) of compound **3aa**



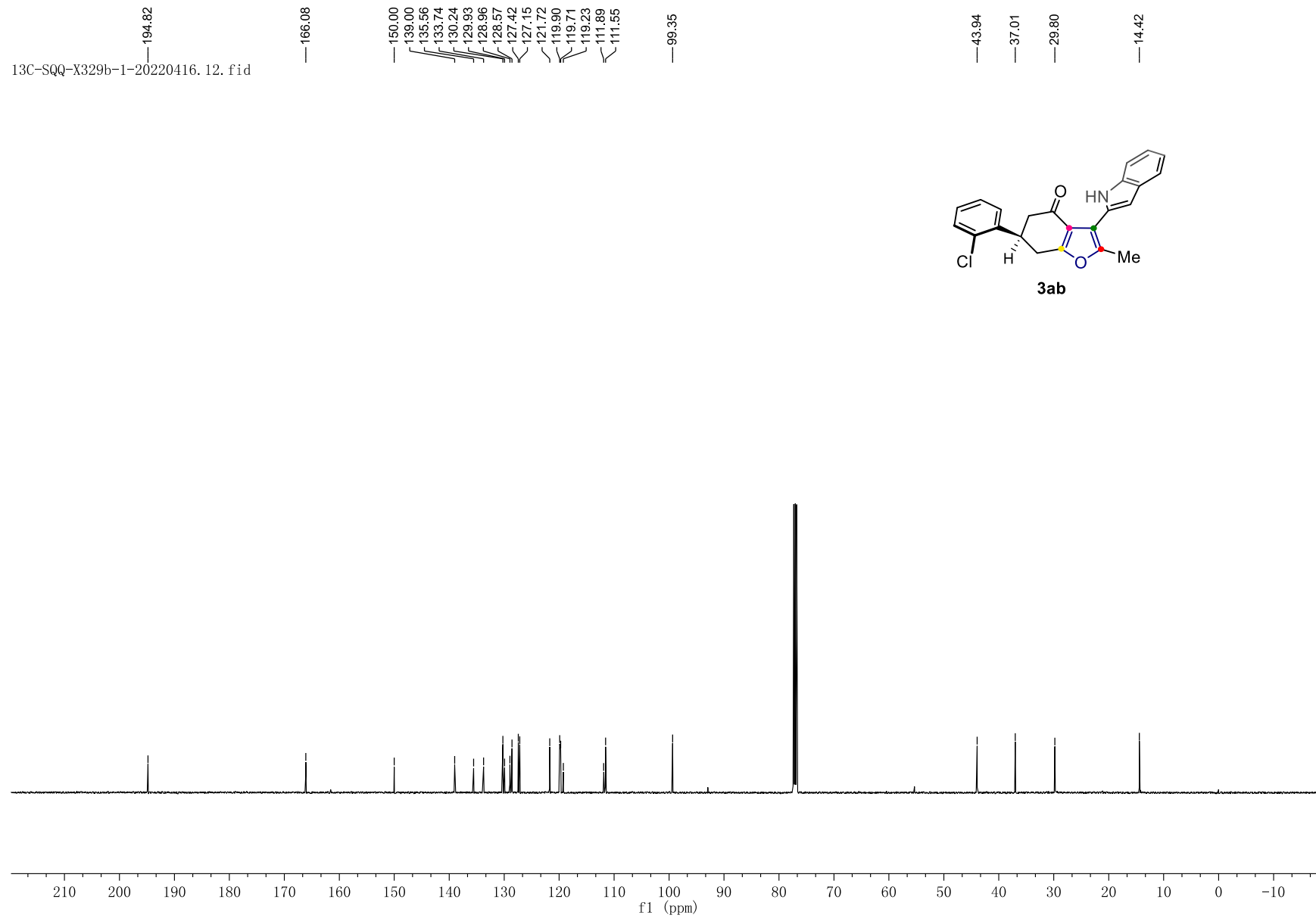
^{13}C NMR (500 MHz, CDCl_3) of compound **3aa**



¹H NMR (500 MHz, CDCl₃) of compound **3ab**



¹³C NMR (500 MHz, CDCl₃) of compound **3ab**

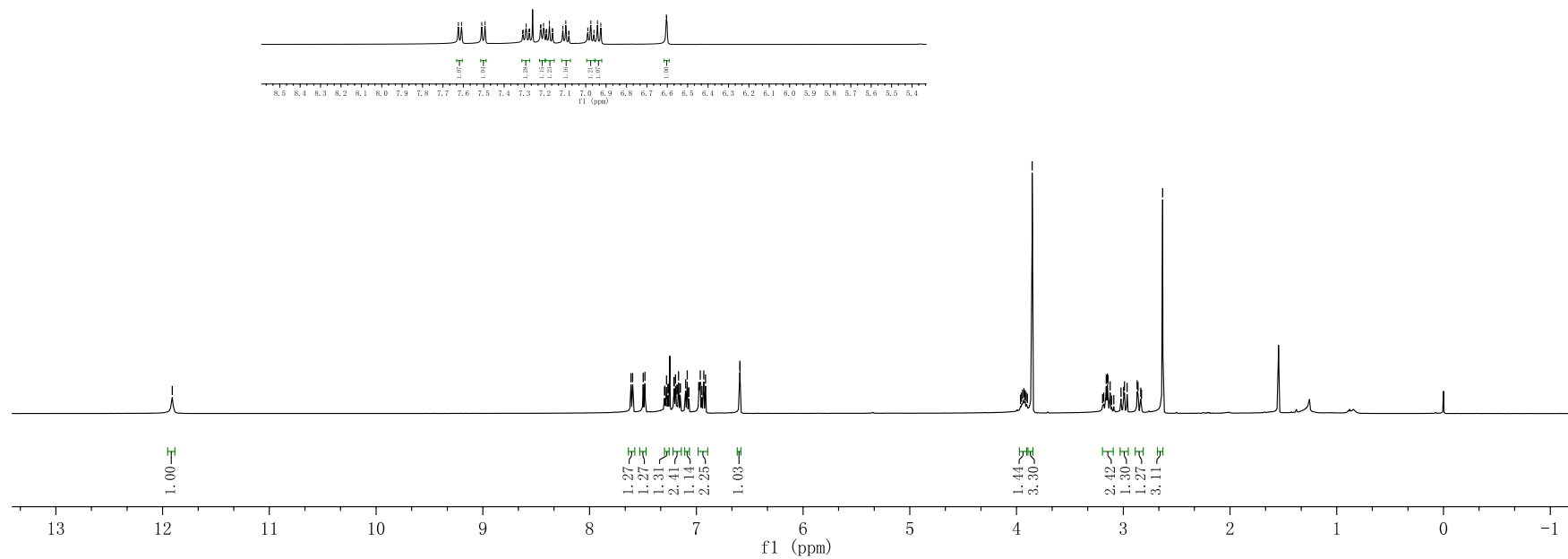
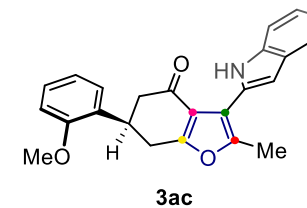


¹H NMR (500 MHz, CDCl₃) of compound **3ac**

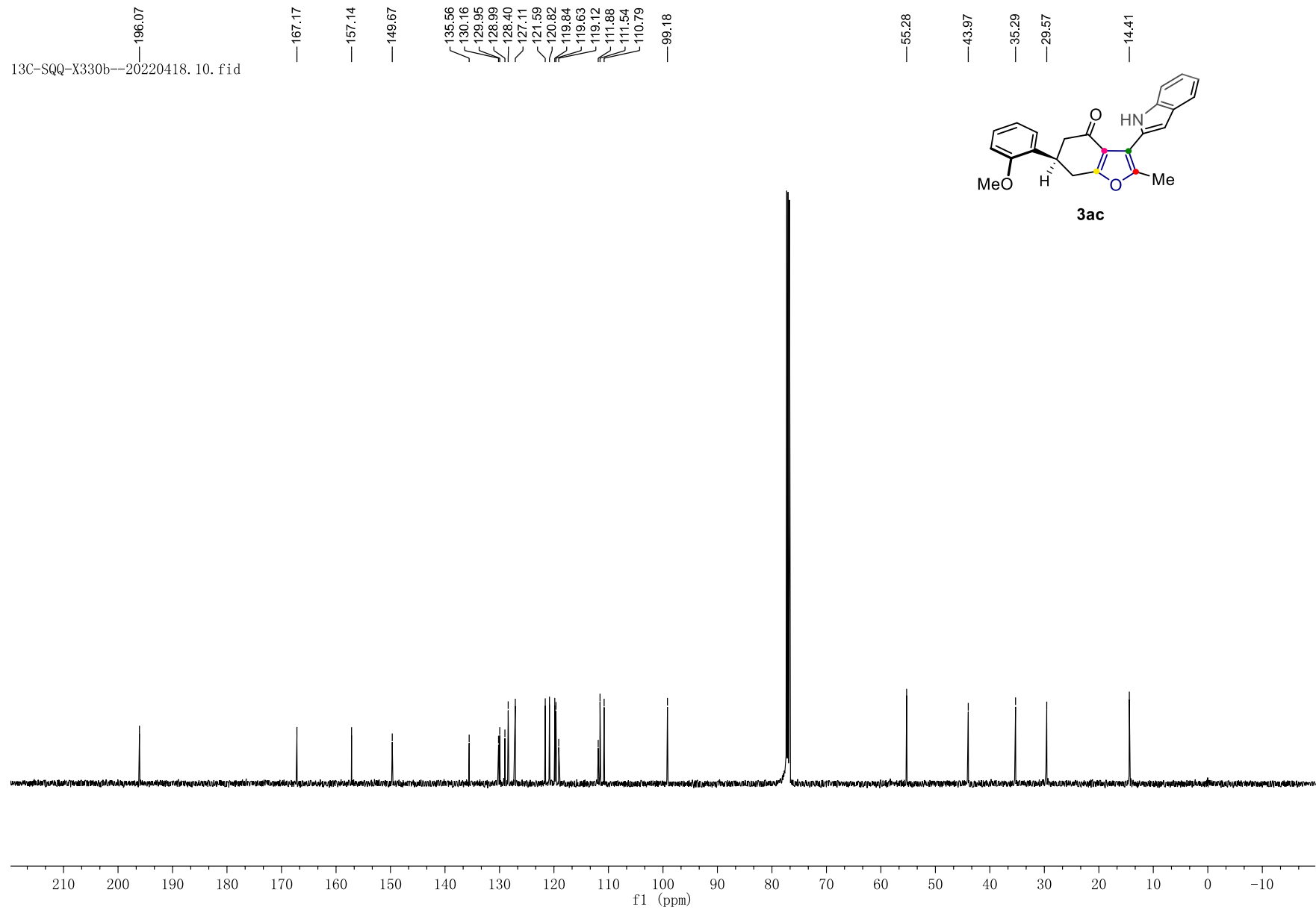
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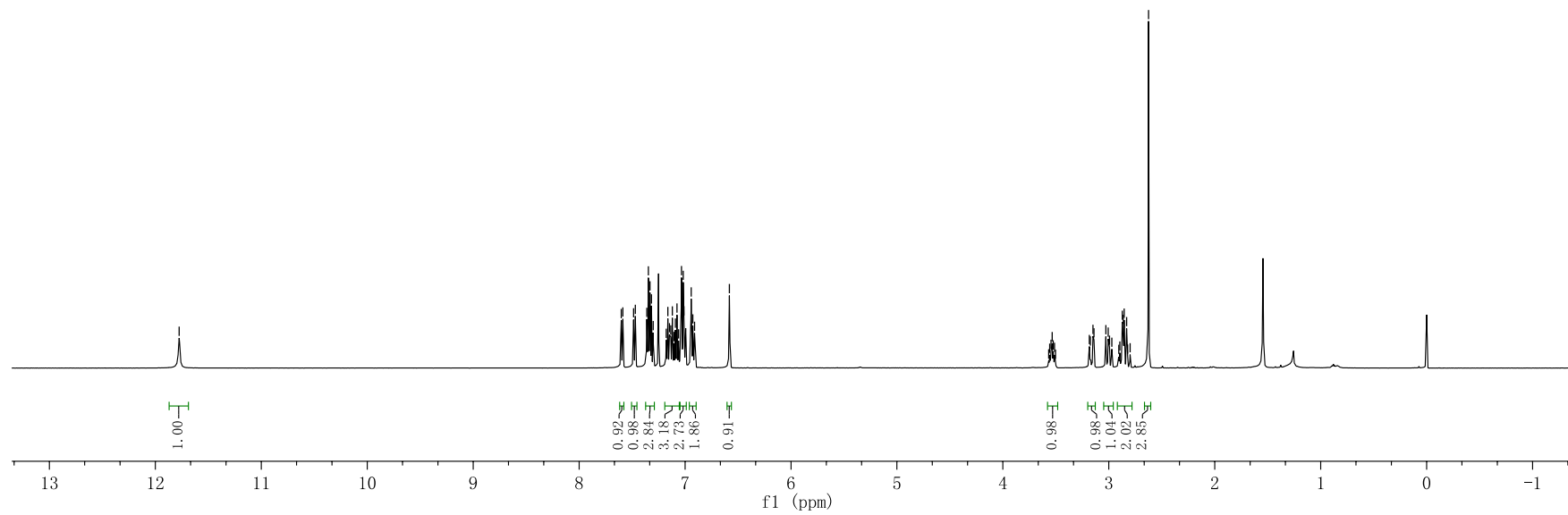
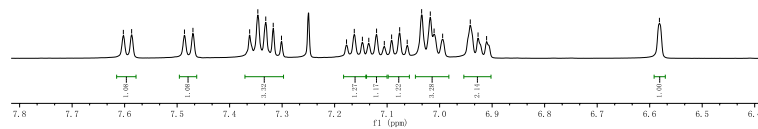
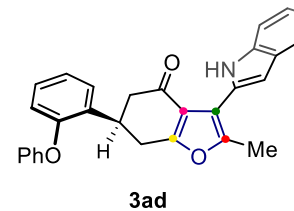
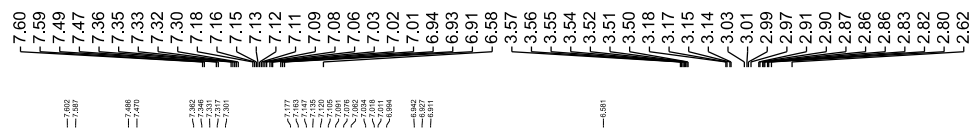


¹³C NMR (500 MHz, CDCl₃) of compound **3ac**

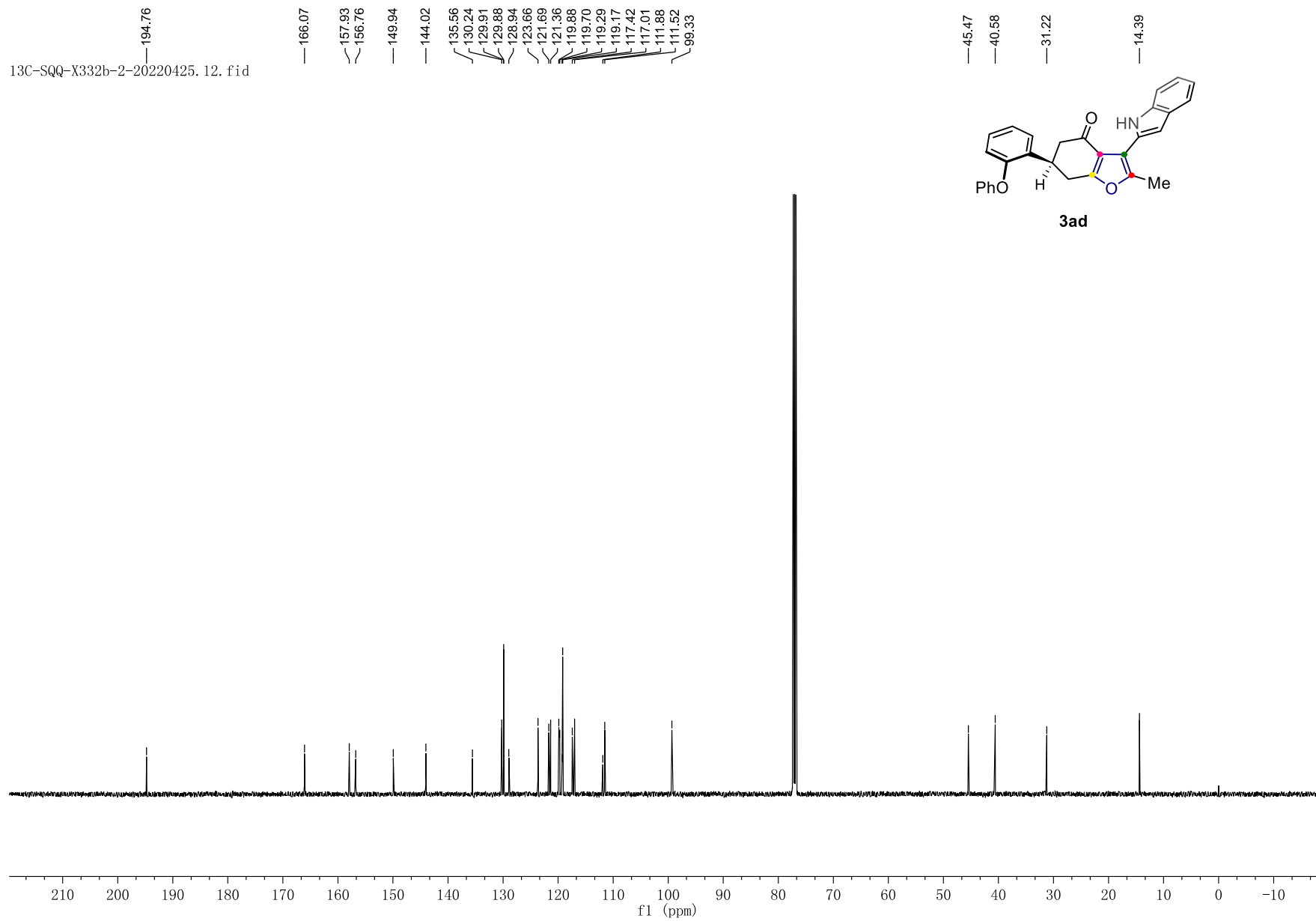


¹H NMR (500 MHz, CDCl₃) of compound **3ad**

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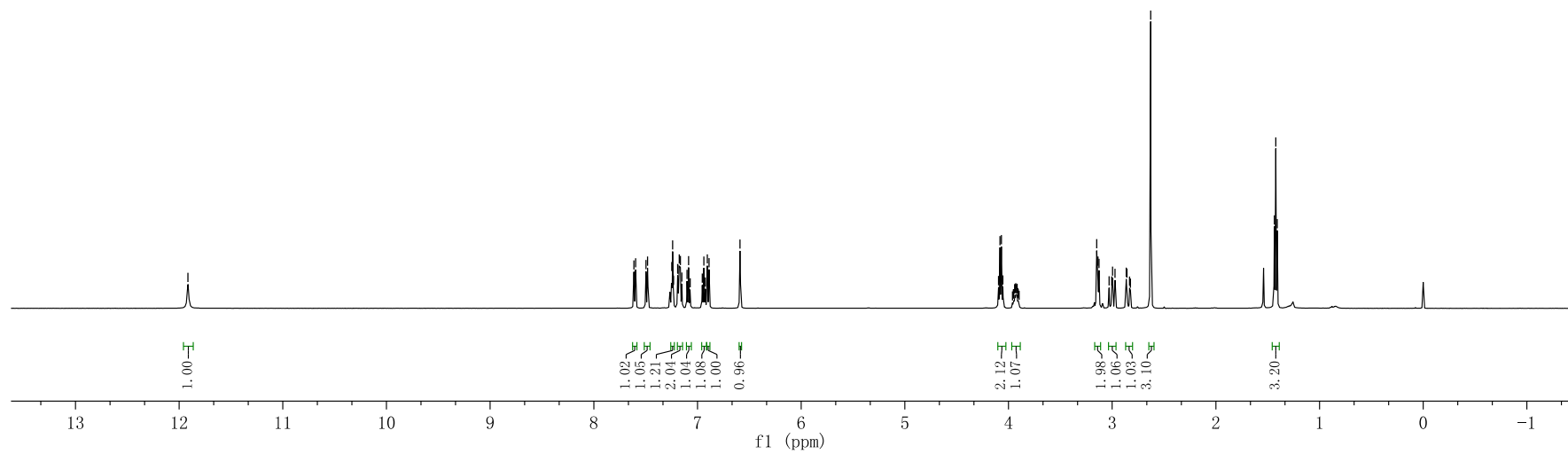
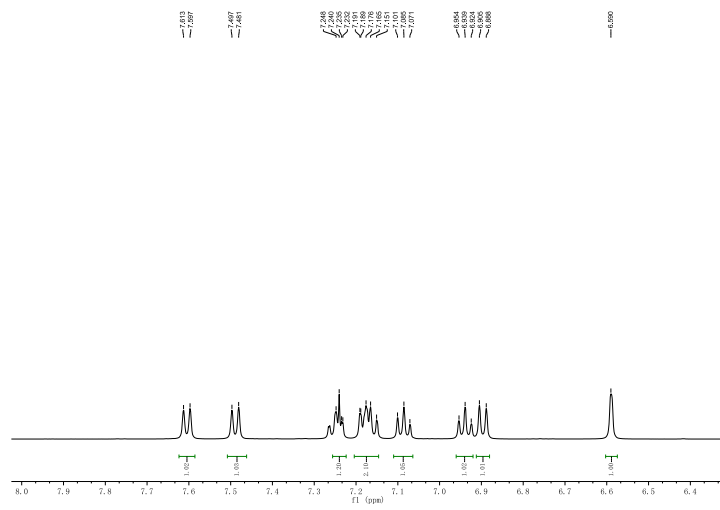


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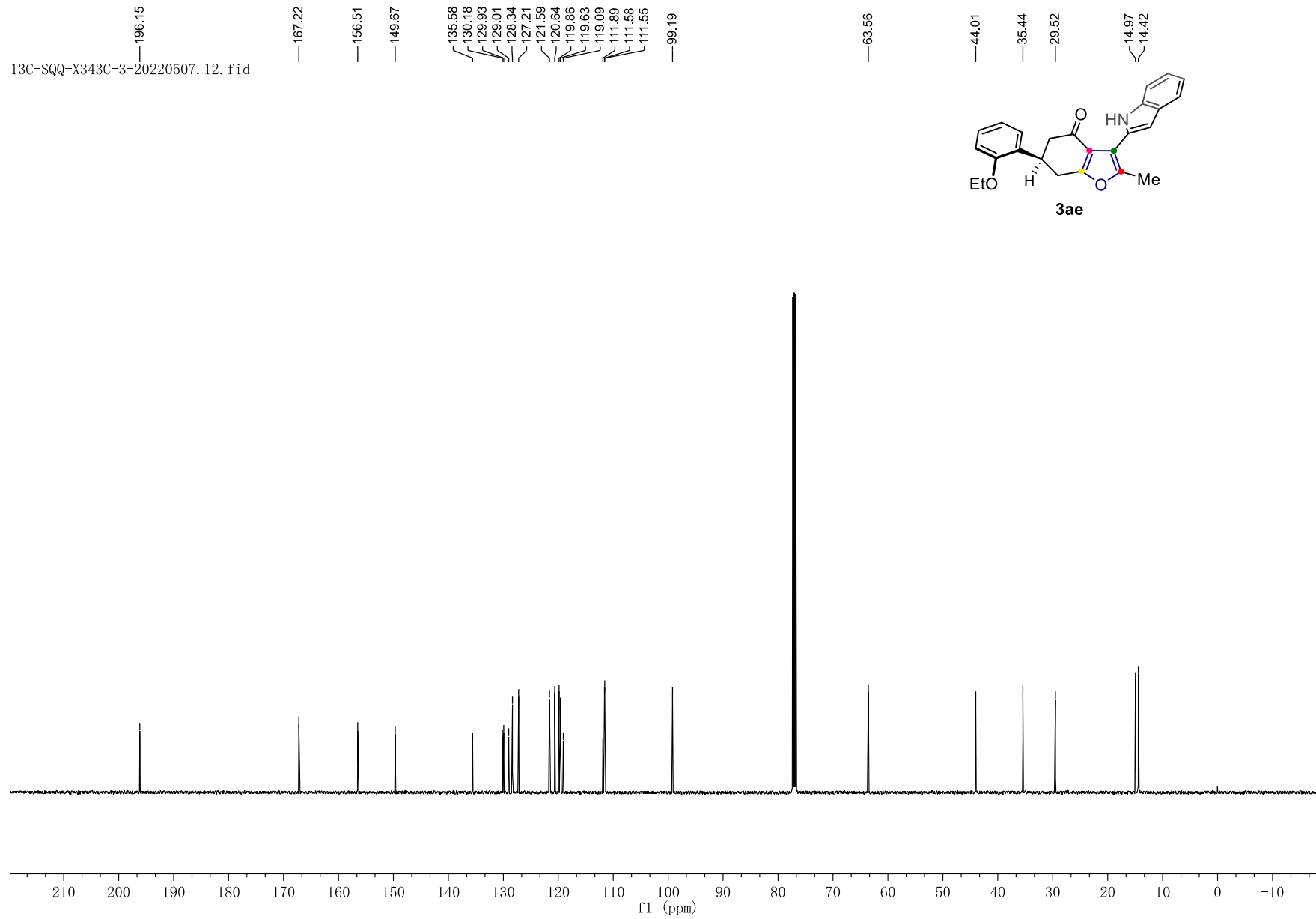


¹H NMR (500 MHz, CDCl₃) of compound **3ae**

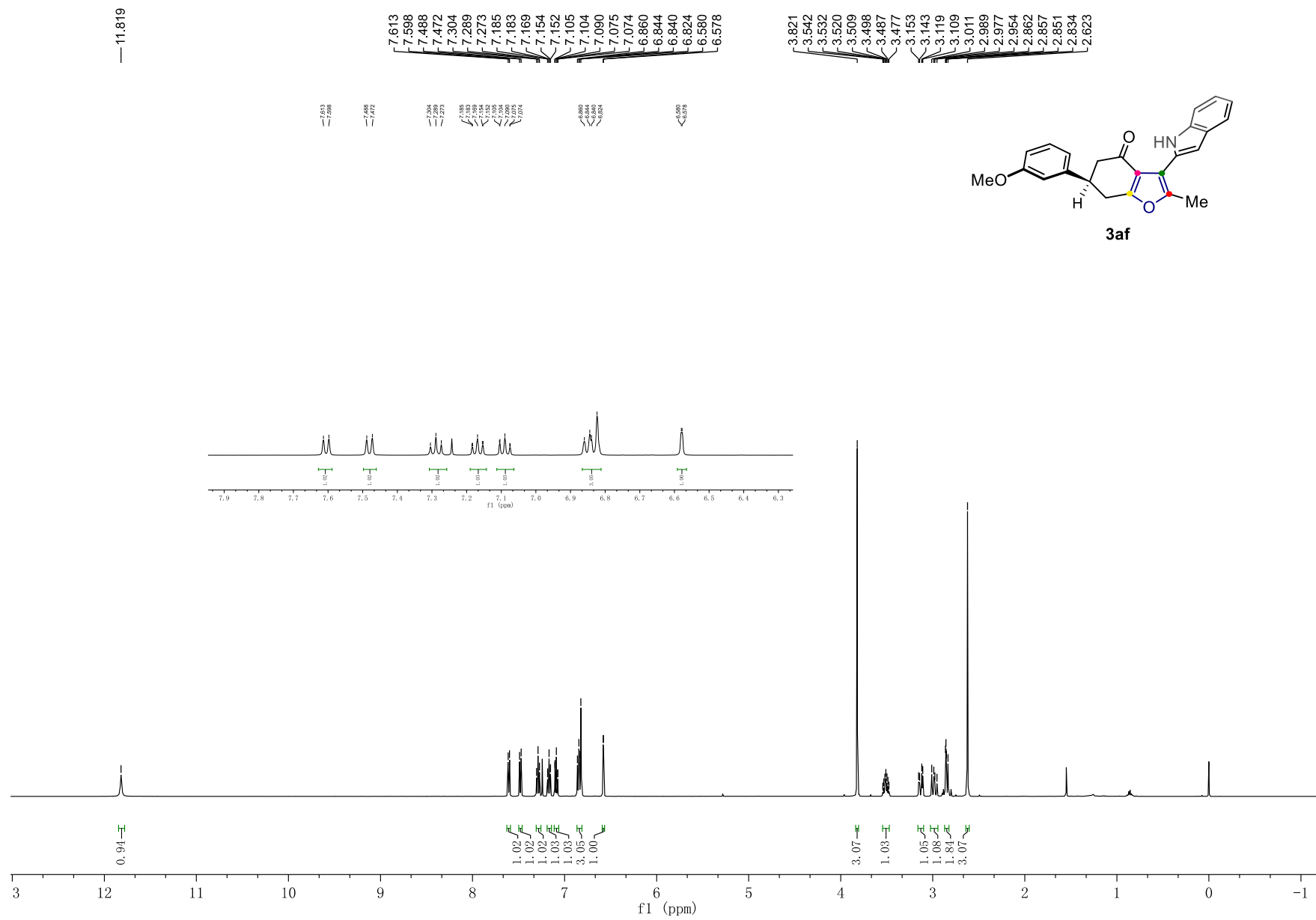
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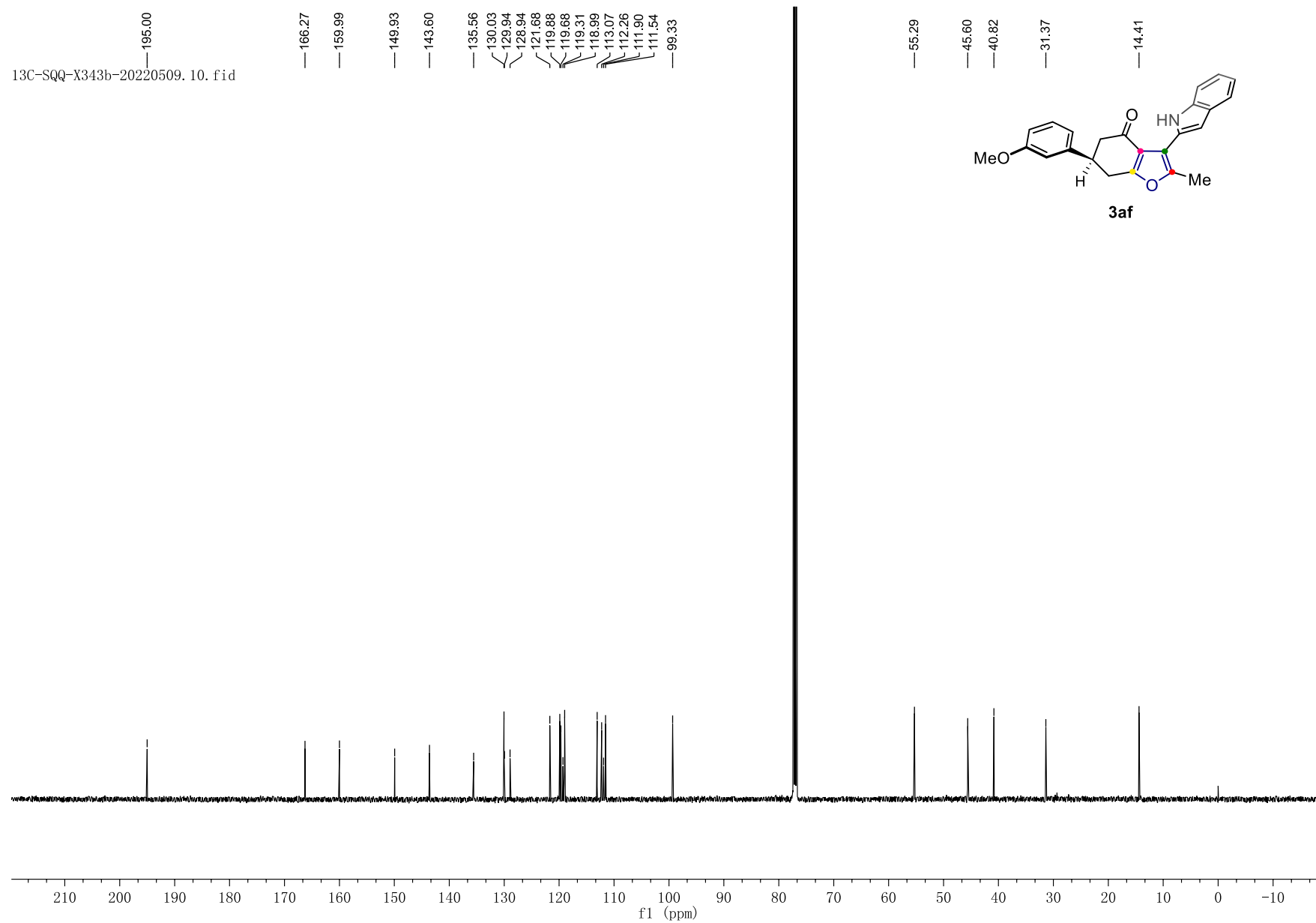
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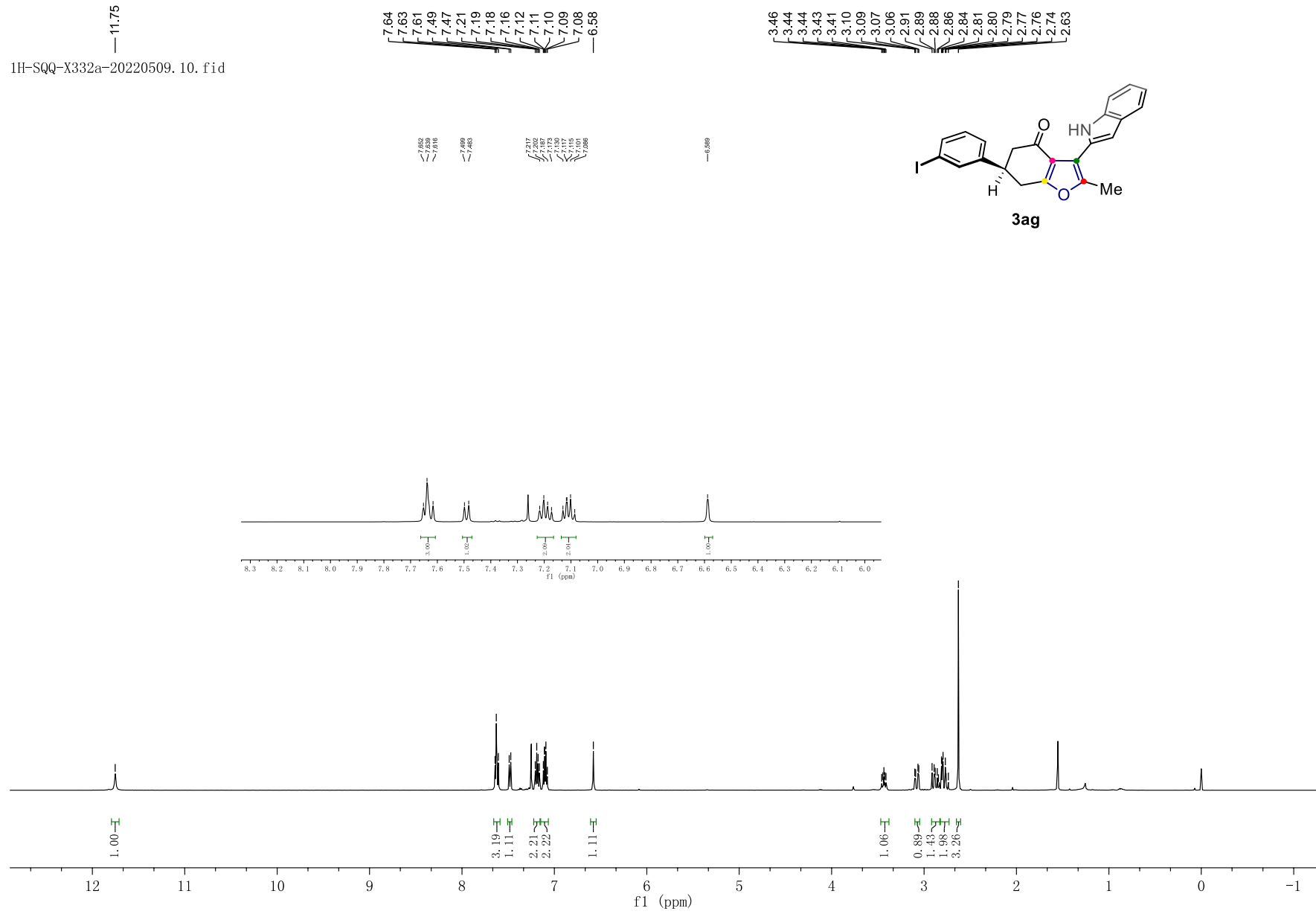
¹H NMR (500 MHz, CDCl₃) of compound **3af**



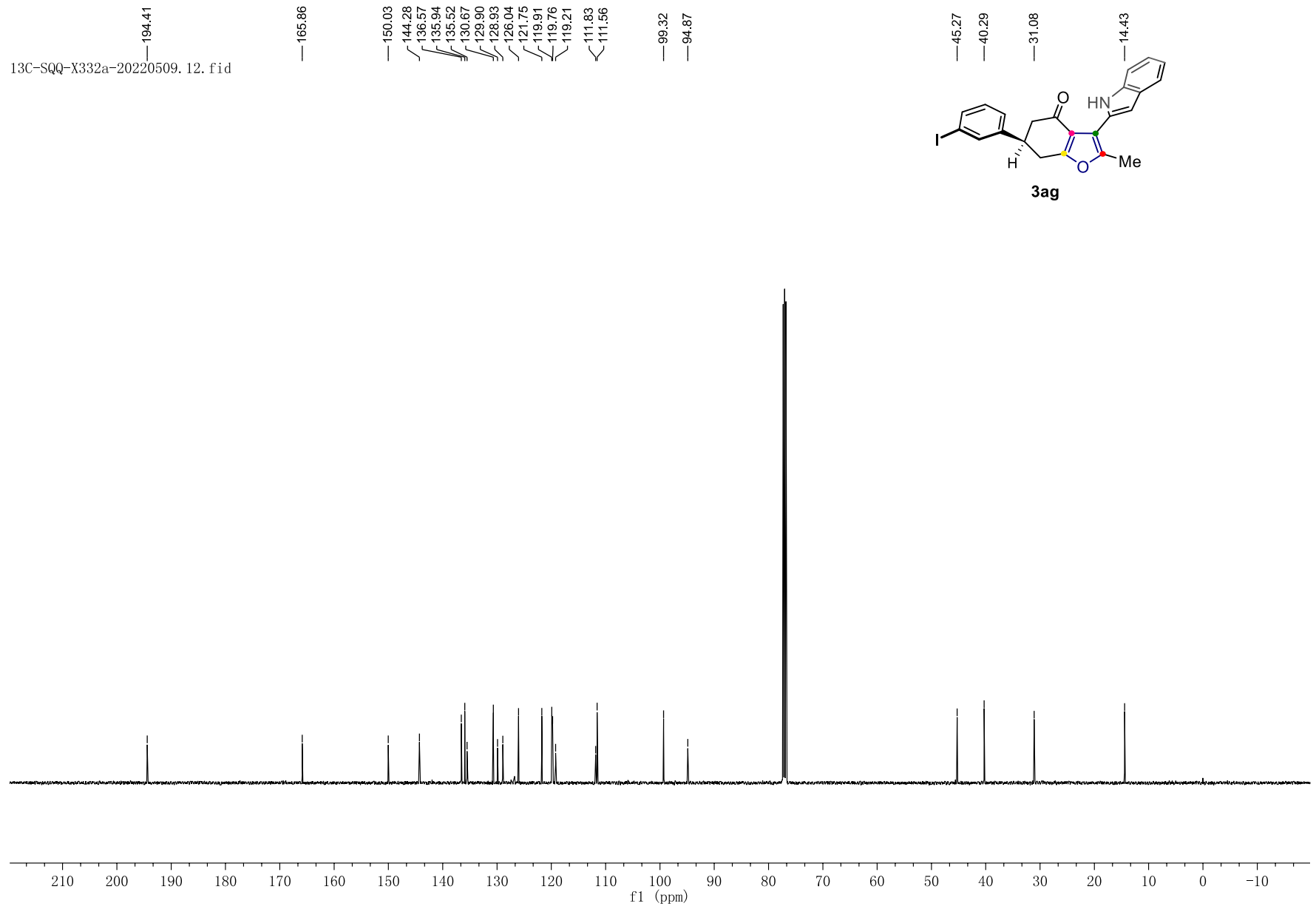
^{13}C NMR (500 MHz, CDCl_3) of compound **3af**



¹H NMR (500 MHz, CDCl₃) of compound **3ag**



¹³C NMR (500 MHz, CDCl₃) of compound **3ag**

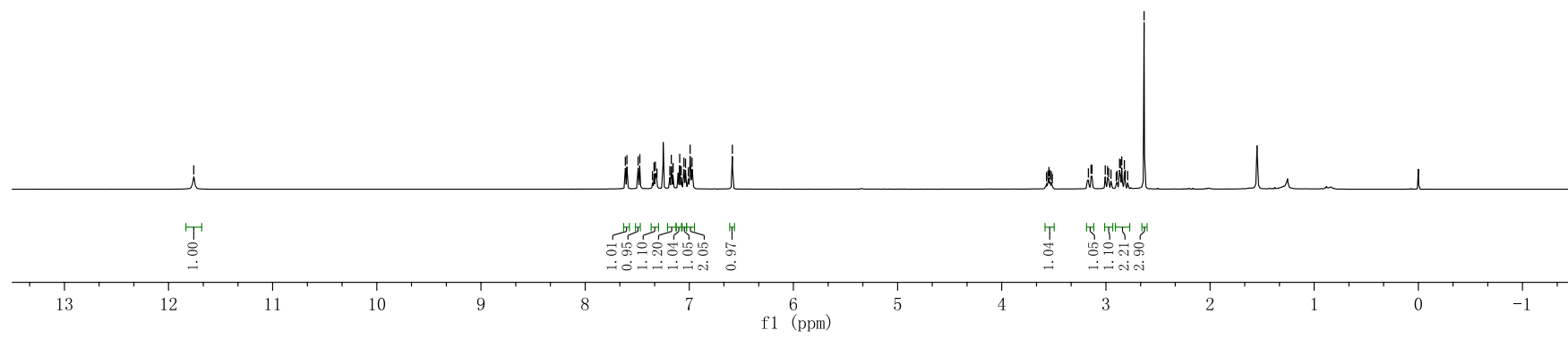
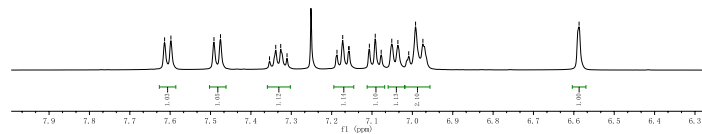
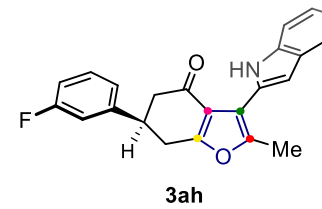


¹H NMR (500 MHz, CDCl₃) of compound **3ah**

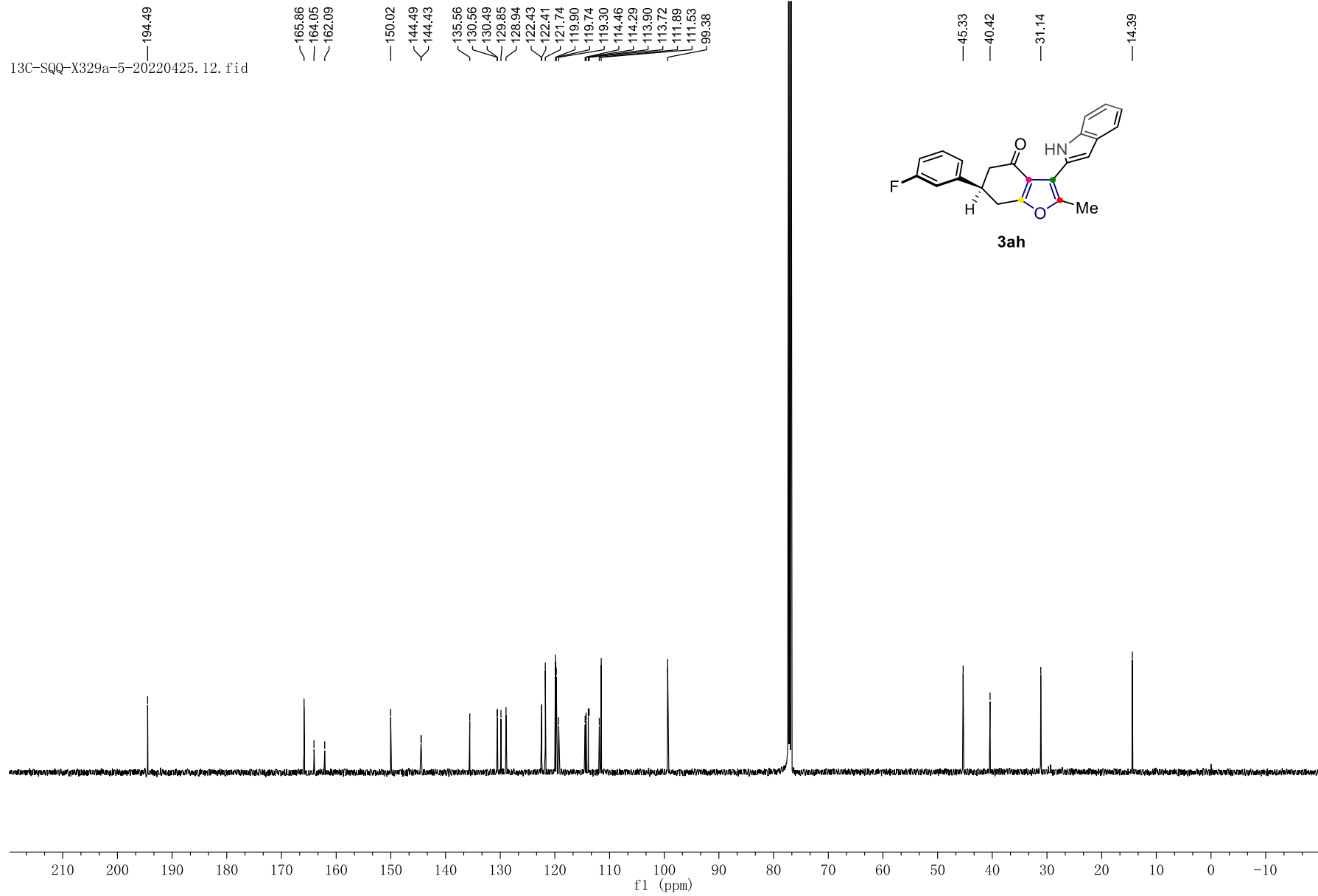
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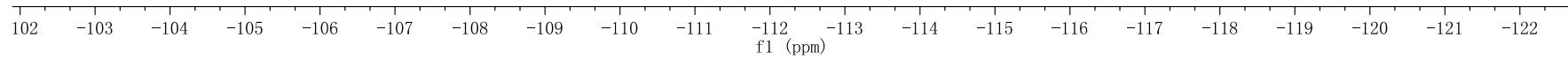
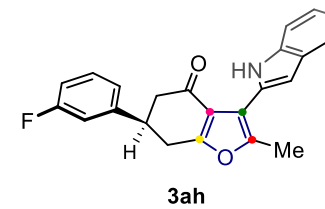
¹³C NMR (500 MHz, CDCl₃) of compound **3ah**



^{19}F NMR (500 MHz, CDCl_3) of compound **3ah**

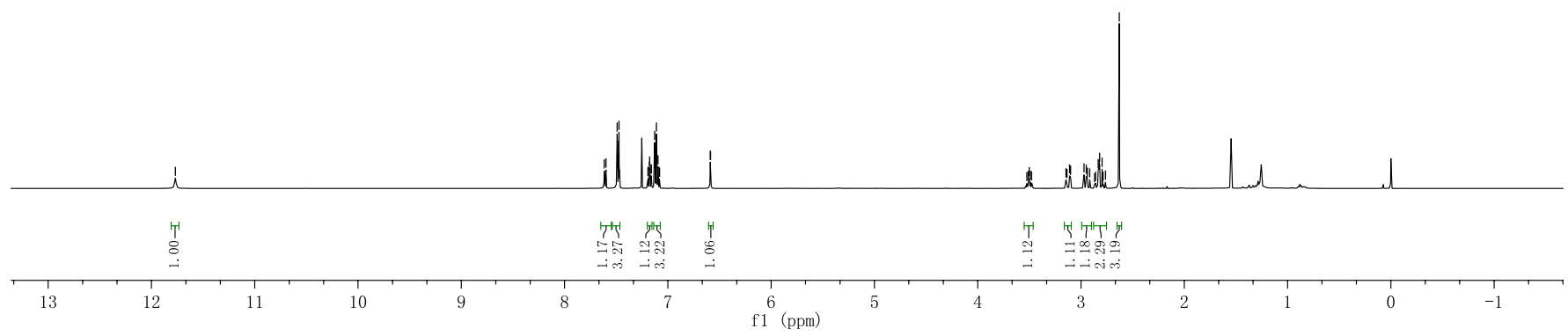
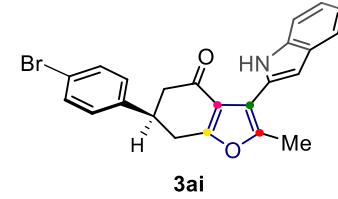
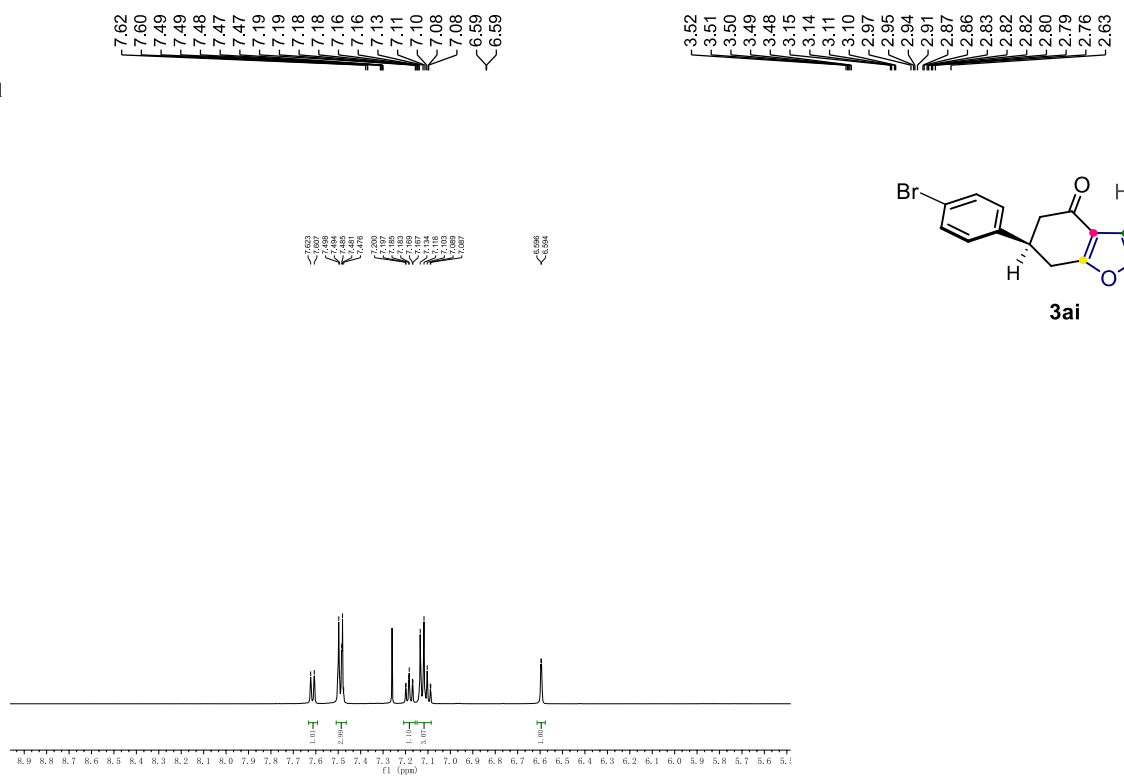
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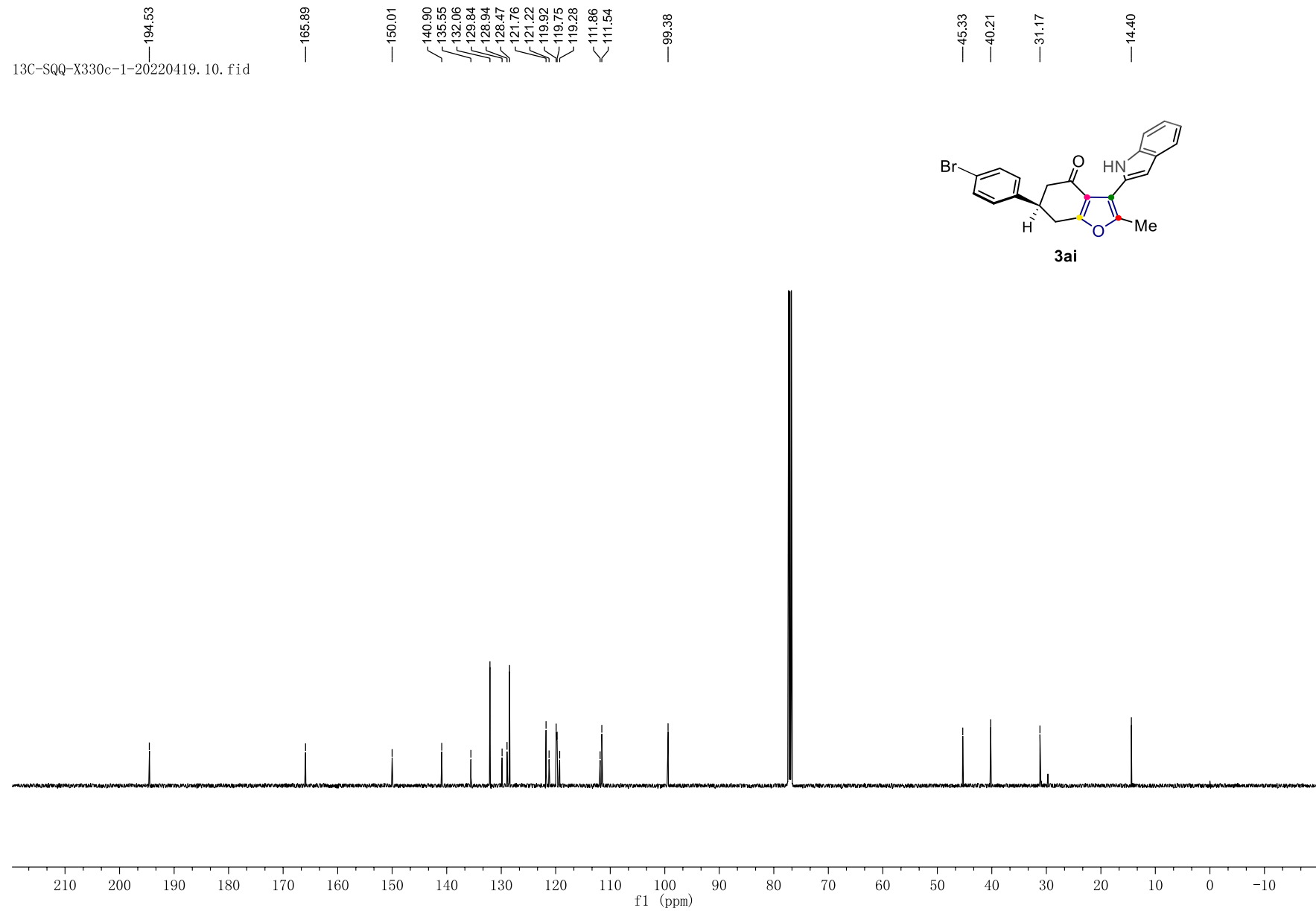


¹H NMR (500 MHz, CDCl₃) of compound **3ai**

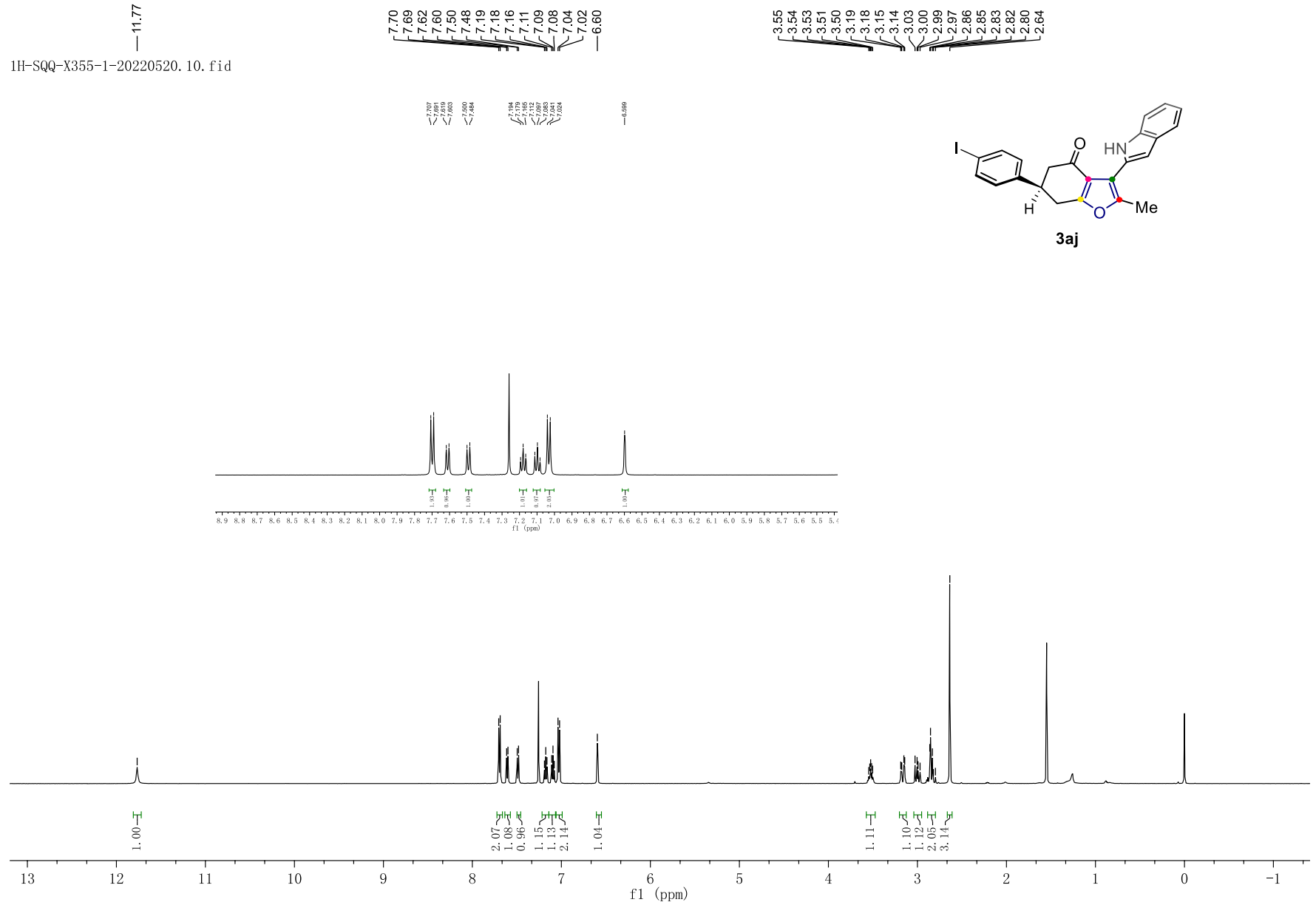
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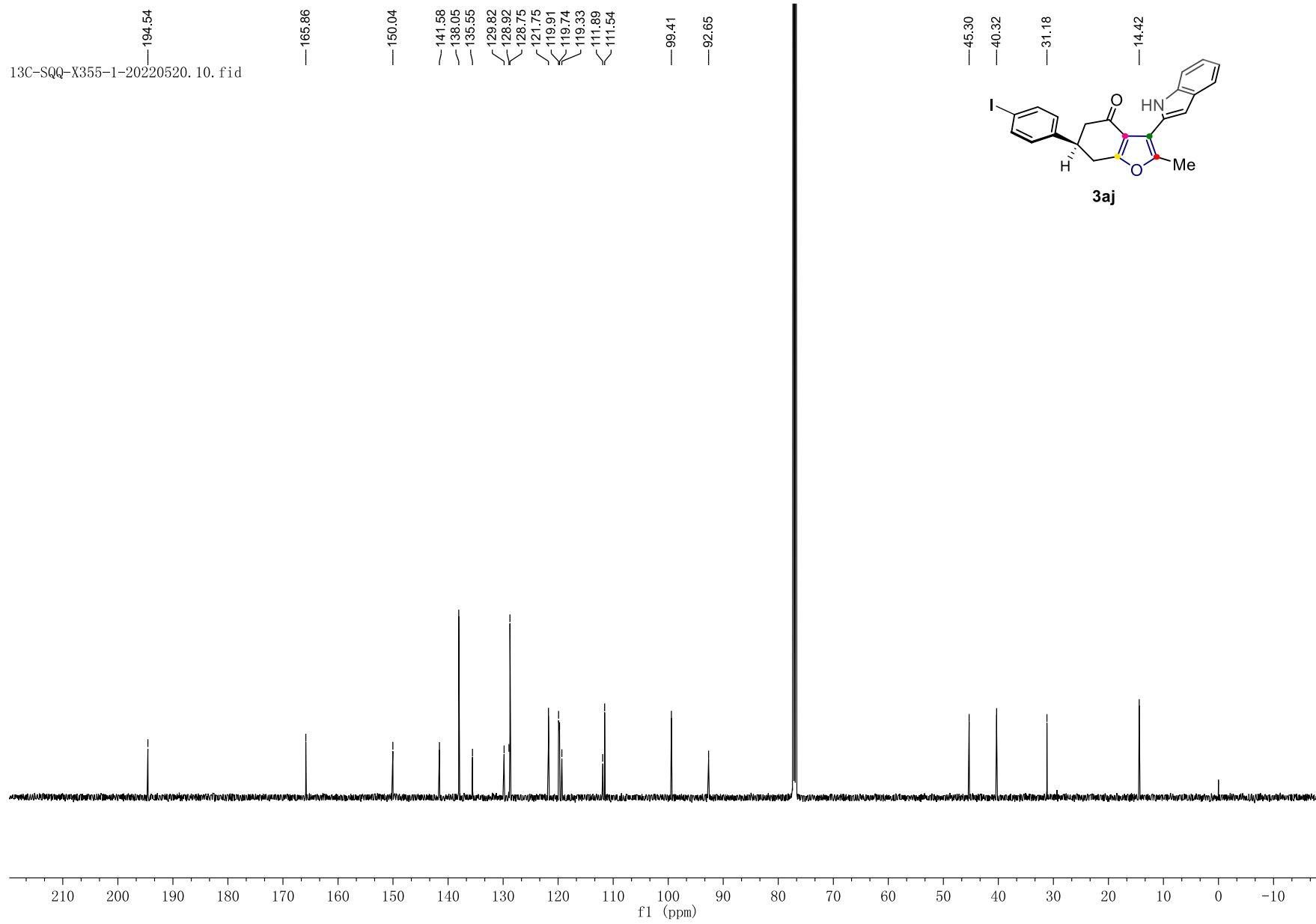
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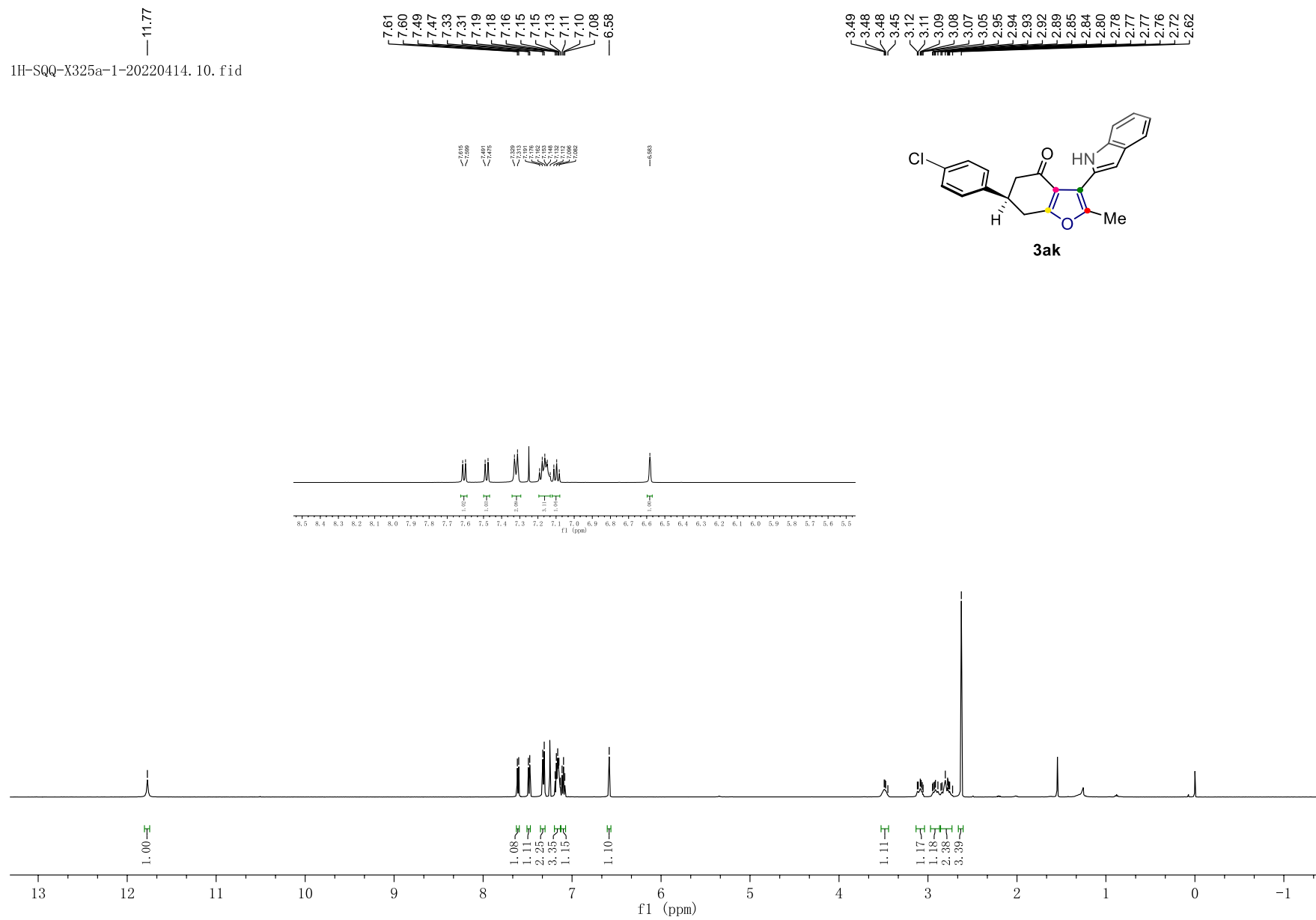
¹H NMR (500 MHz, CDCl₃) of compound **3aj**



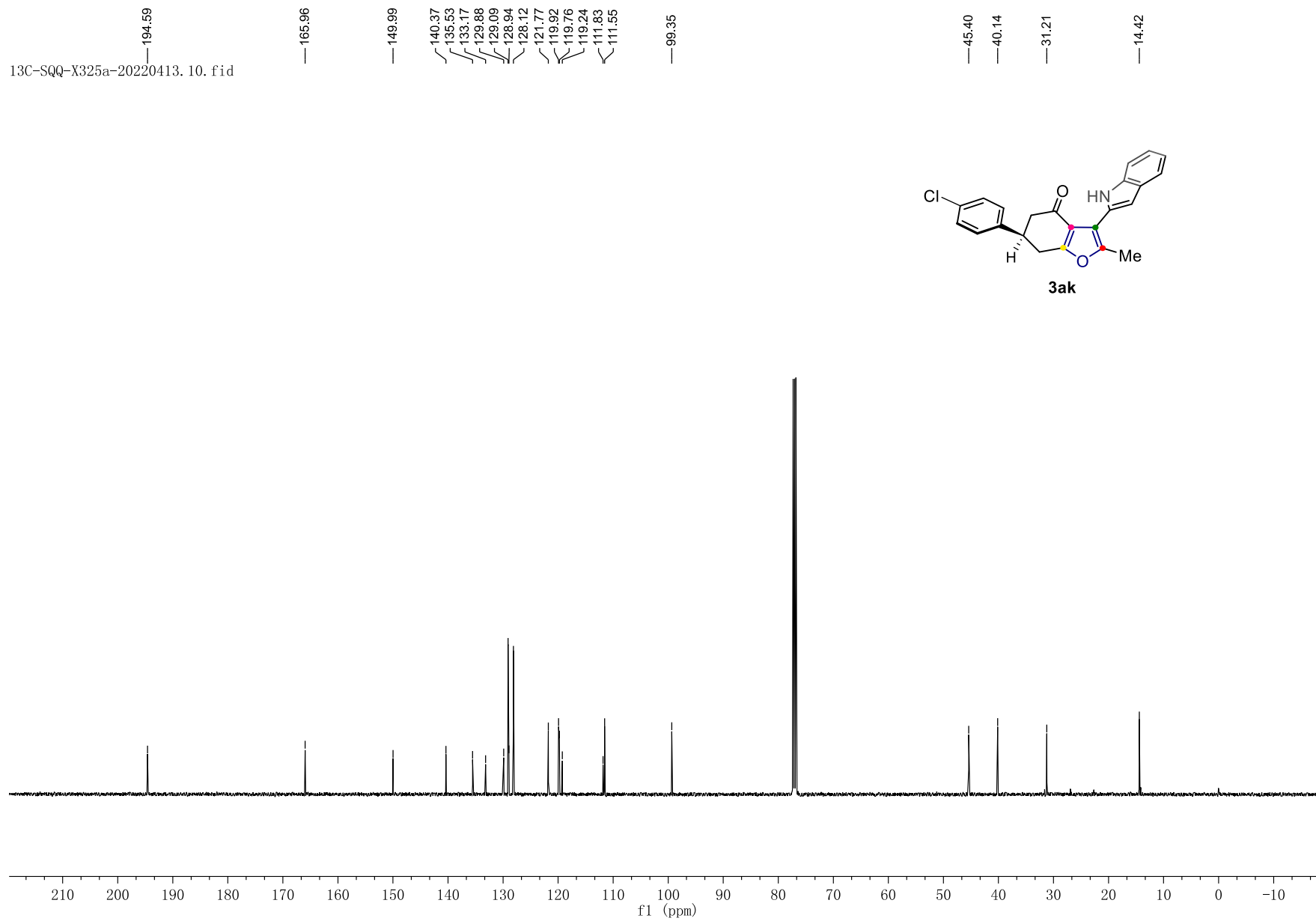
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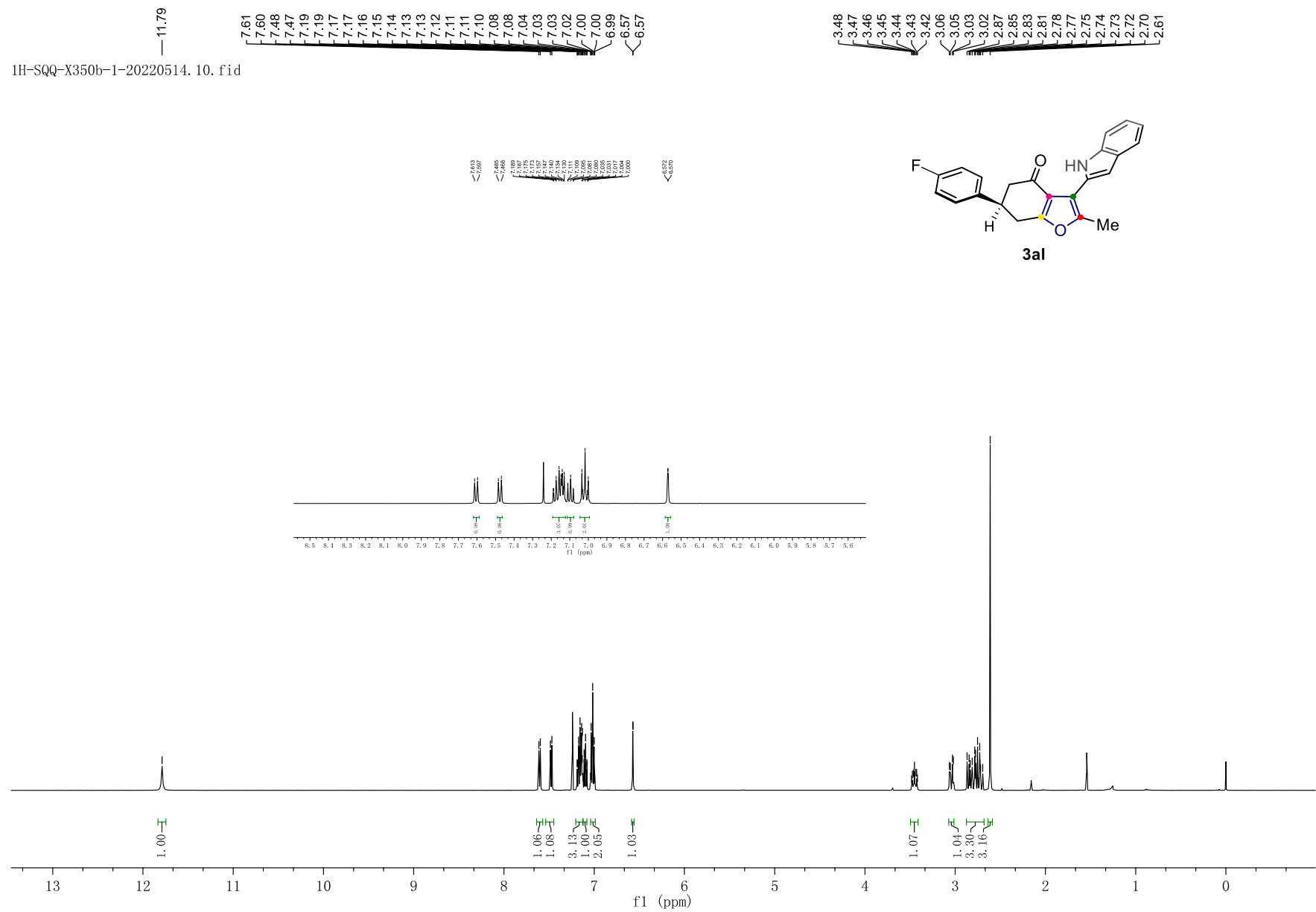
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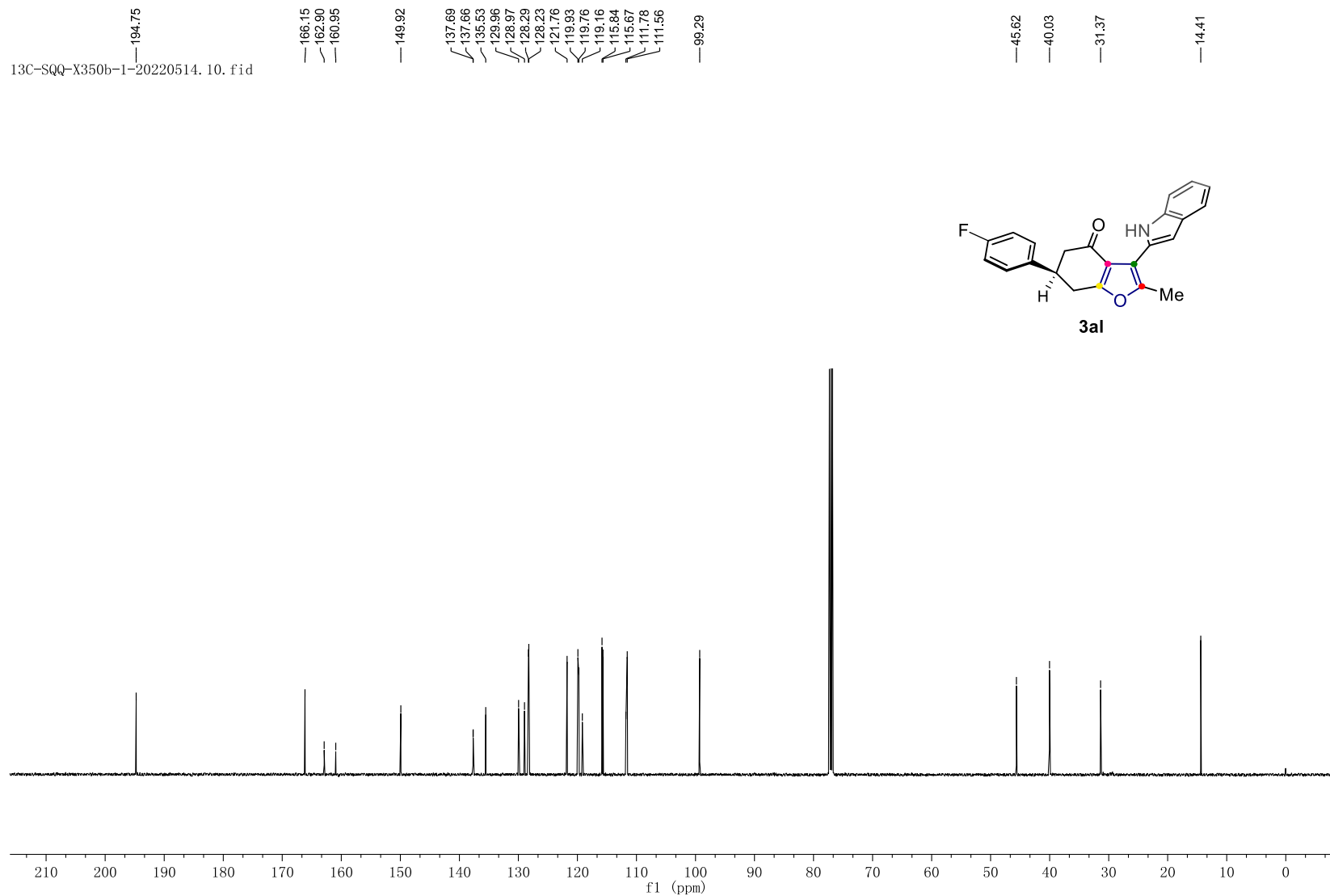
¹³C NMR (500 MHz, CDCl₃) of compound **3ak**



¹H NMR (500 MHz, CDCl₃) of compound **3al**

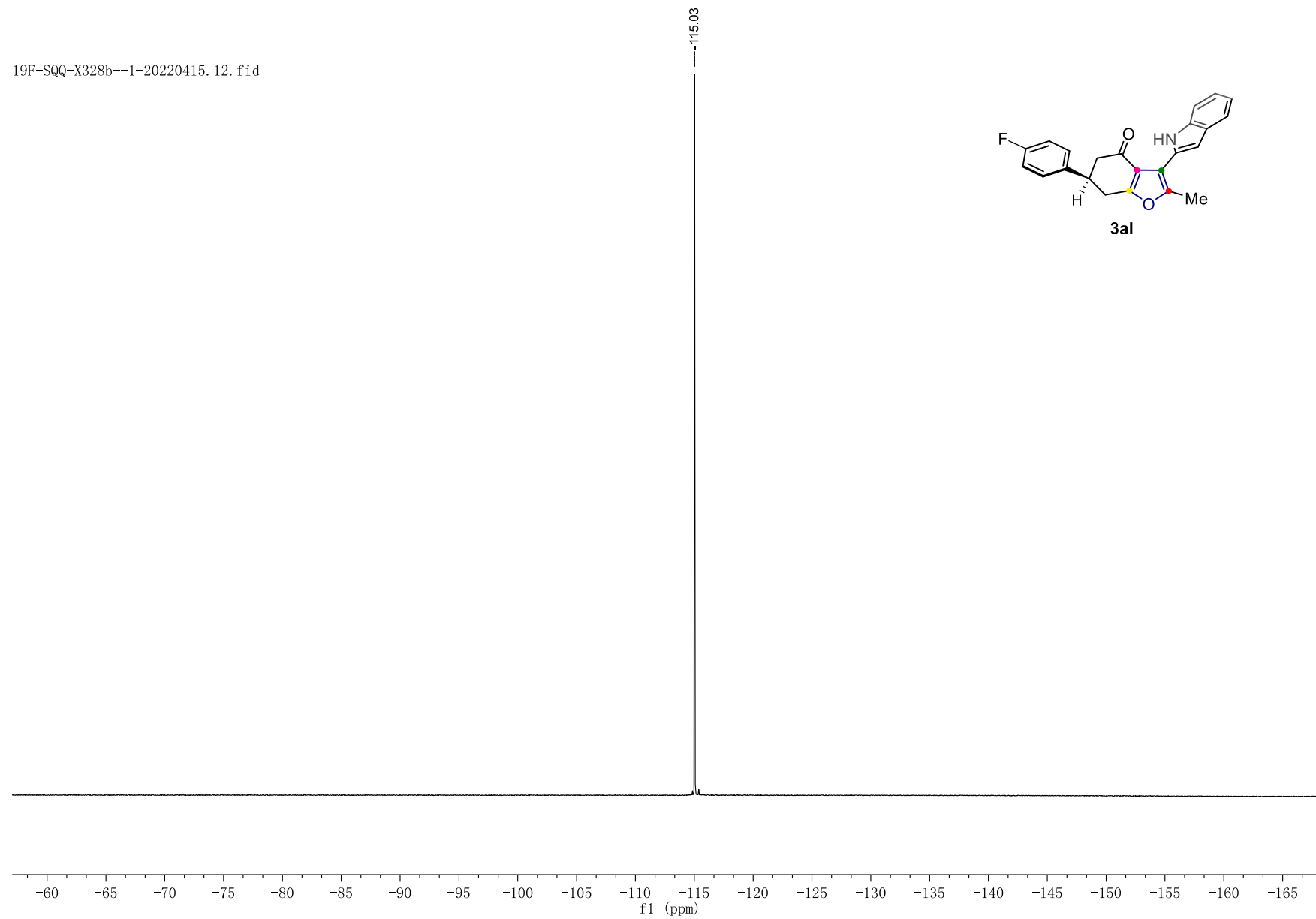
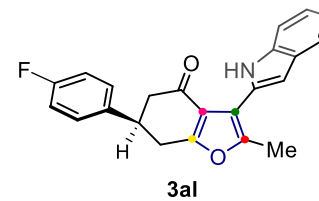


^{13}C NMR (500 MHz, CDCl_3) of compound **3al**

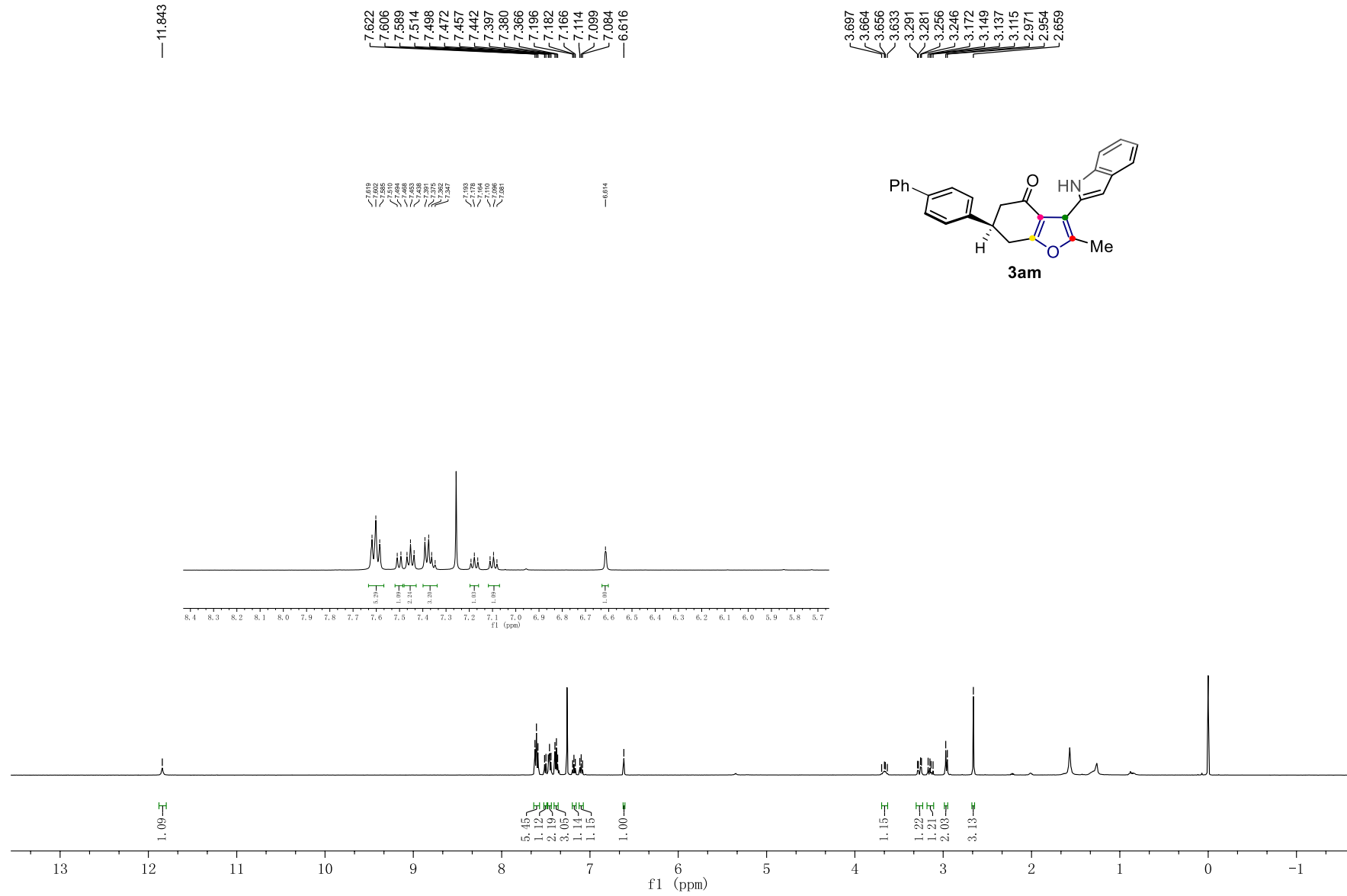


^{19}F NMR (500 MHz, CDCl_3) of compound **3al**

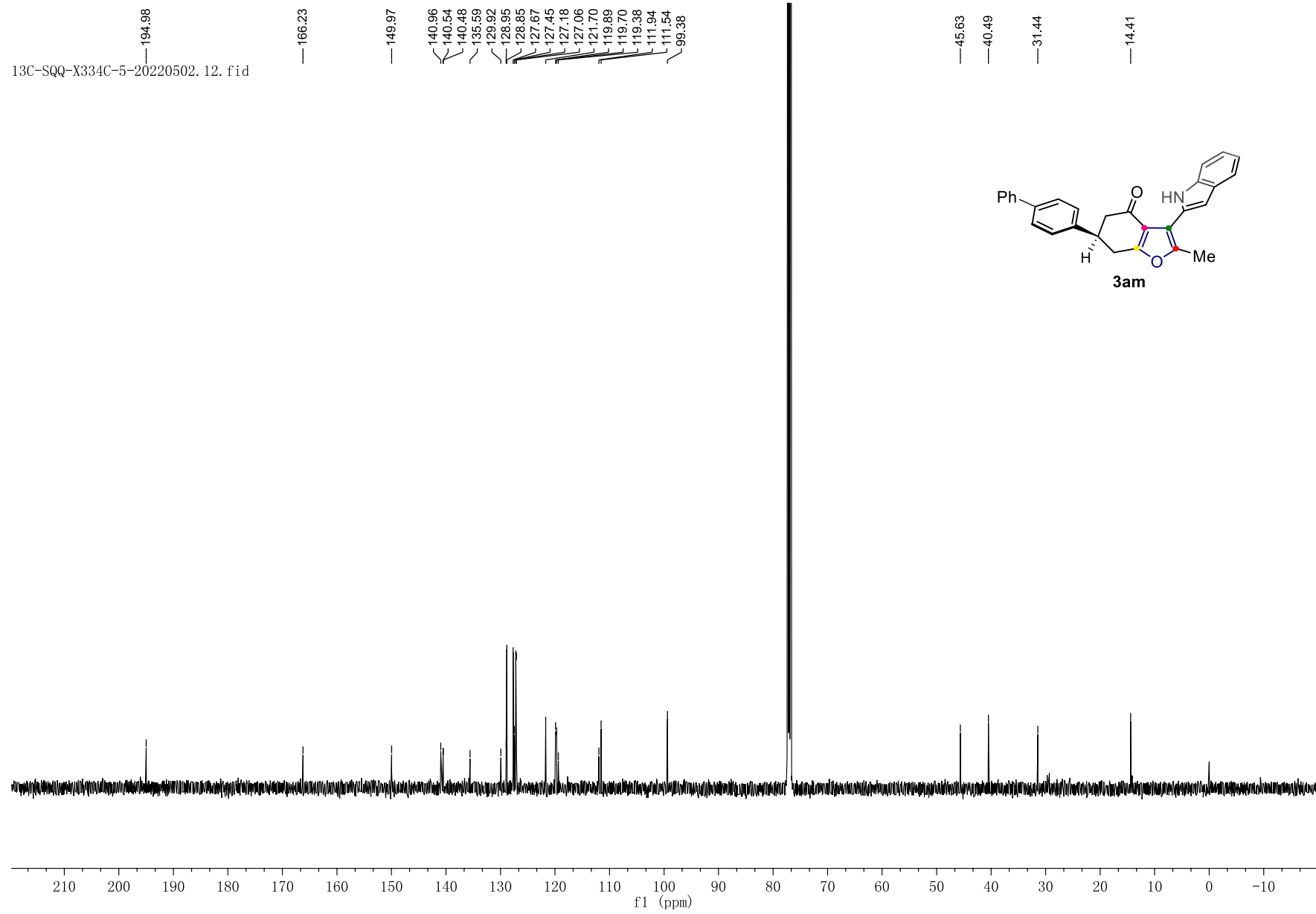
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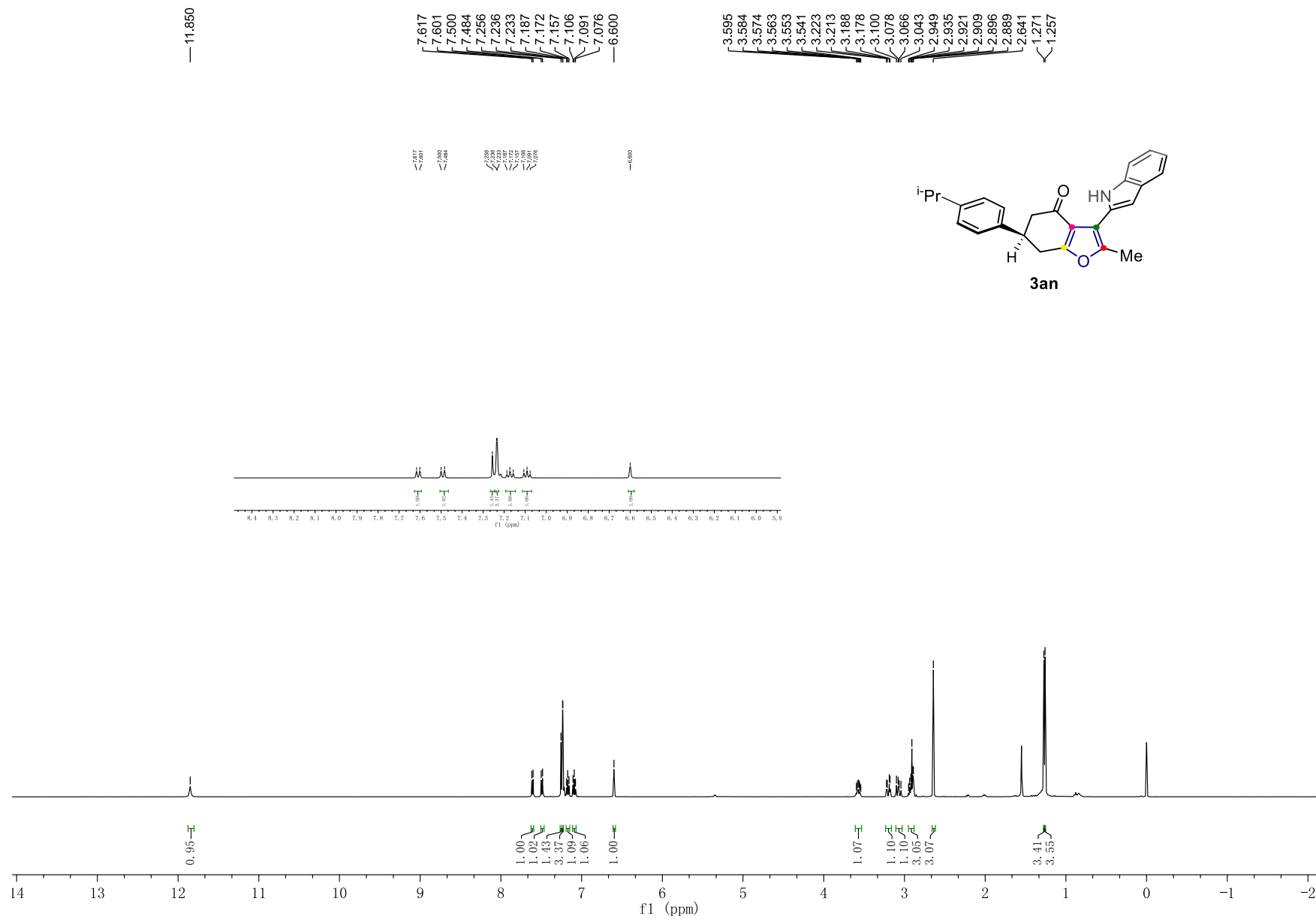
¹H NMR (500 MHz, CDCl₃) of compound **3am**



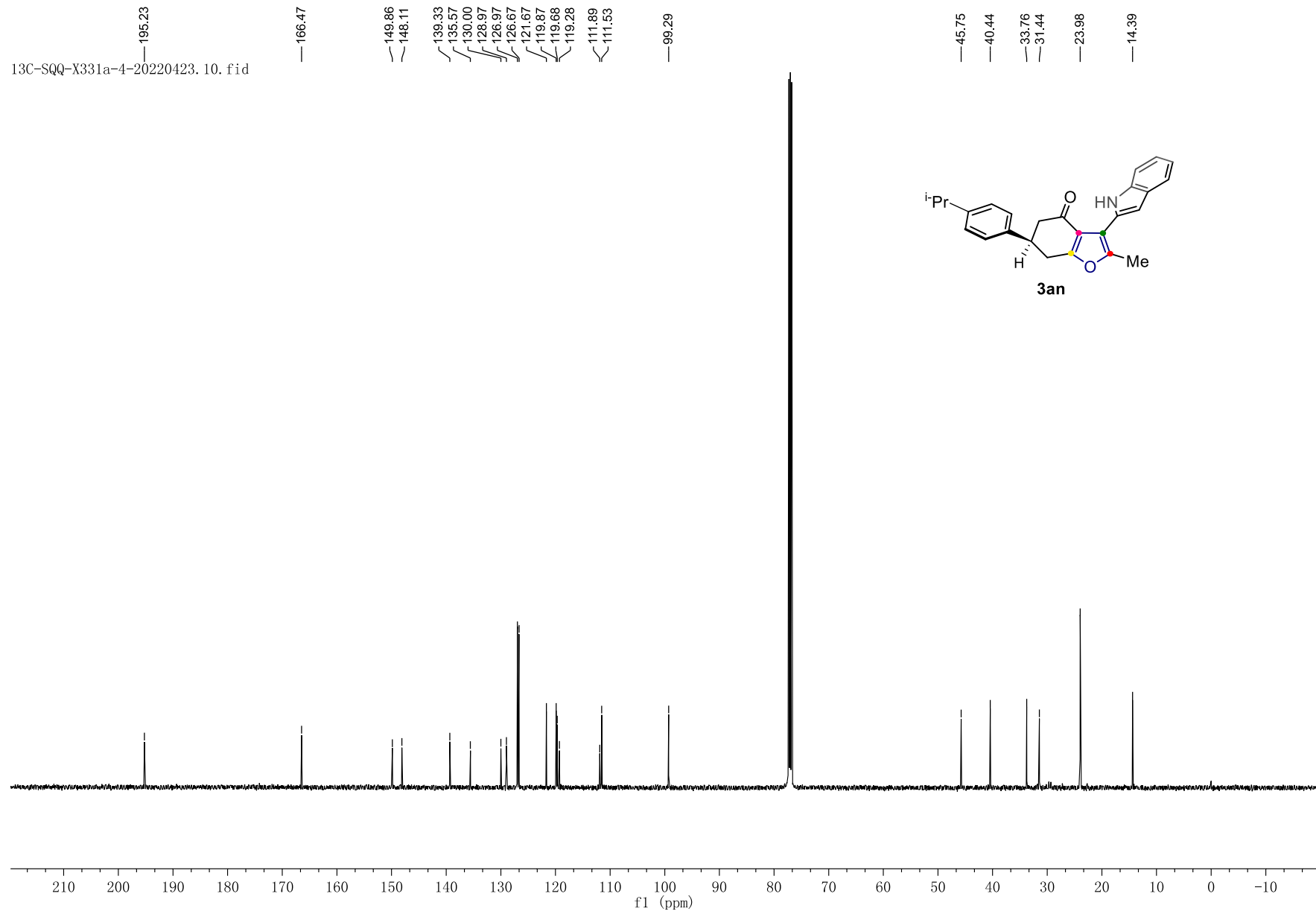
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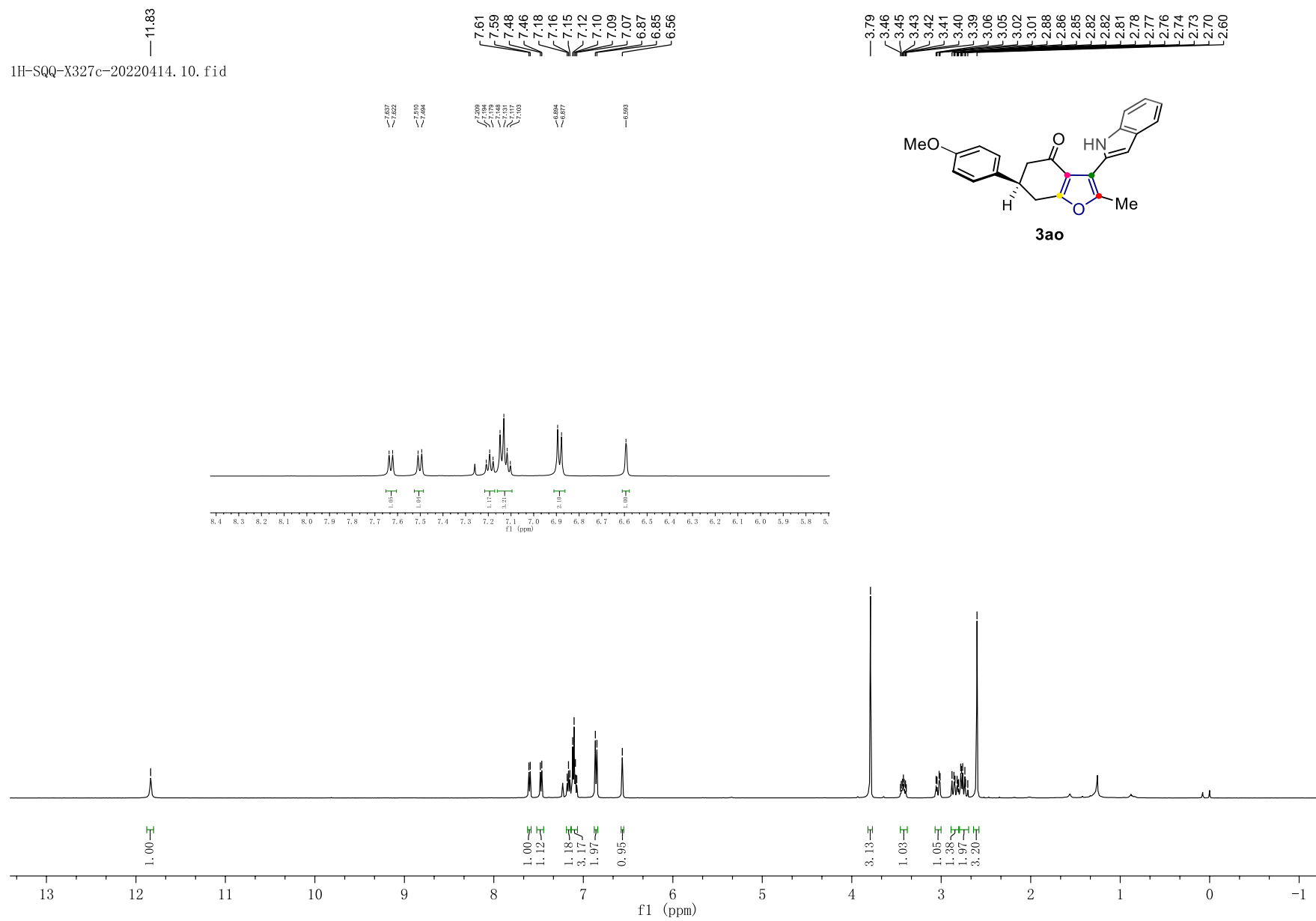
¹H NMR (500 MHz, CDCl₃) of compound **3an**



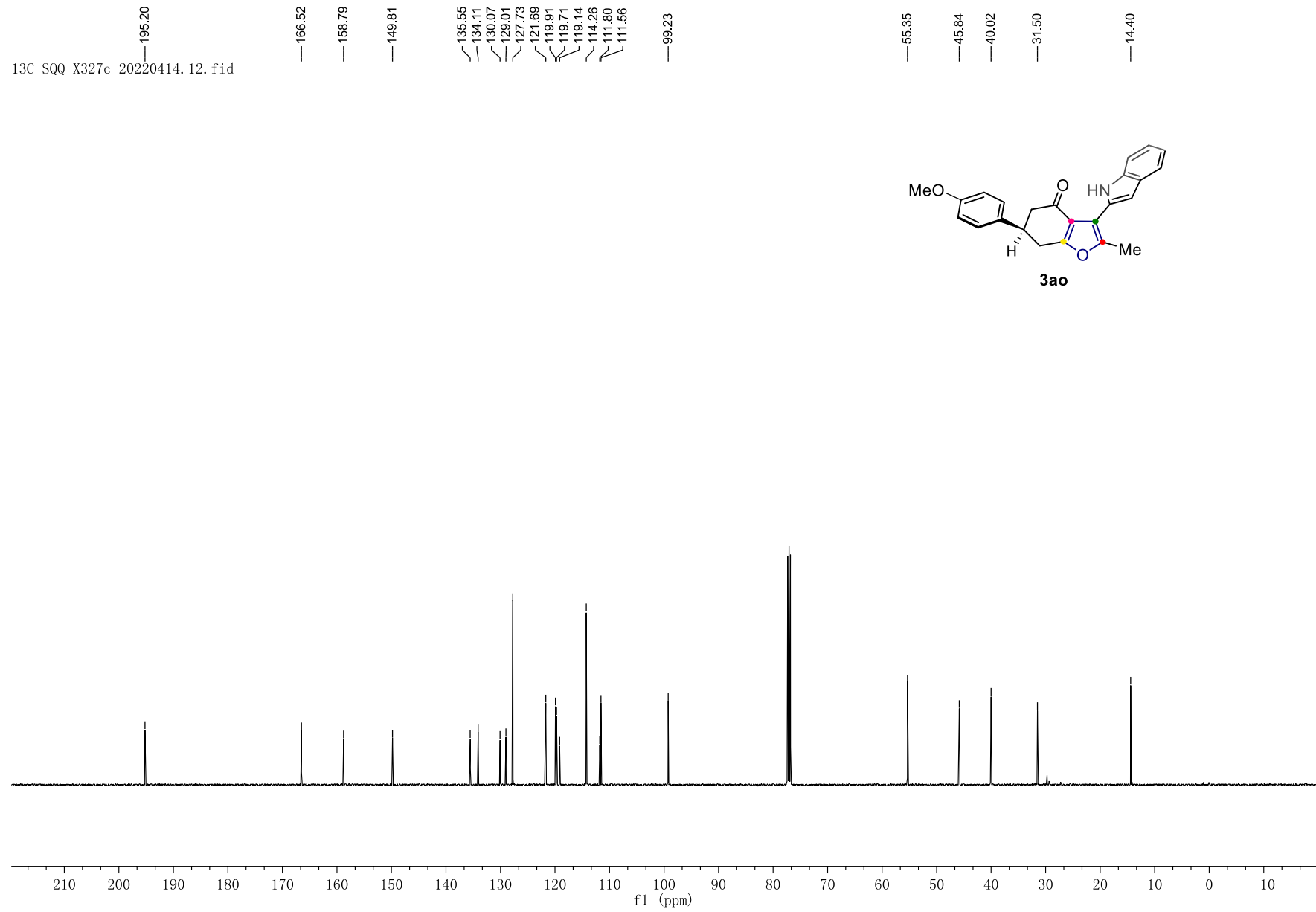
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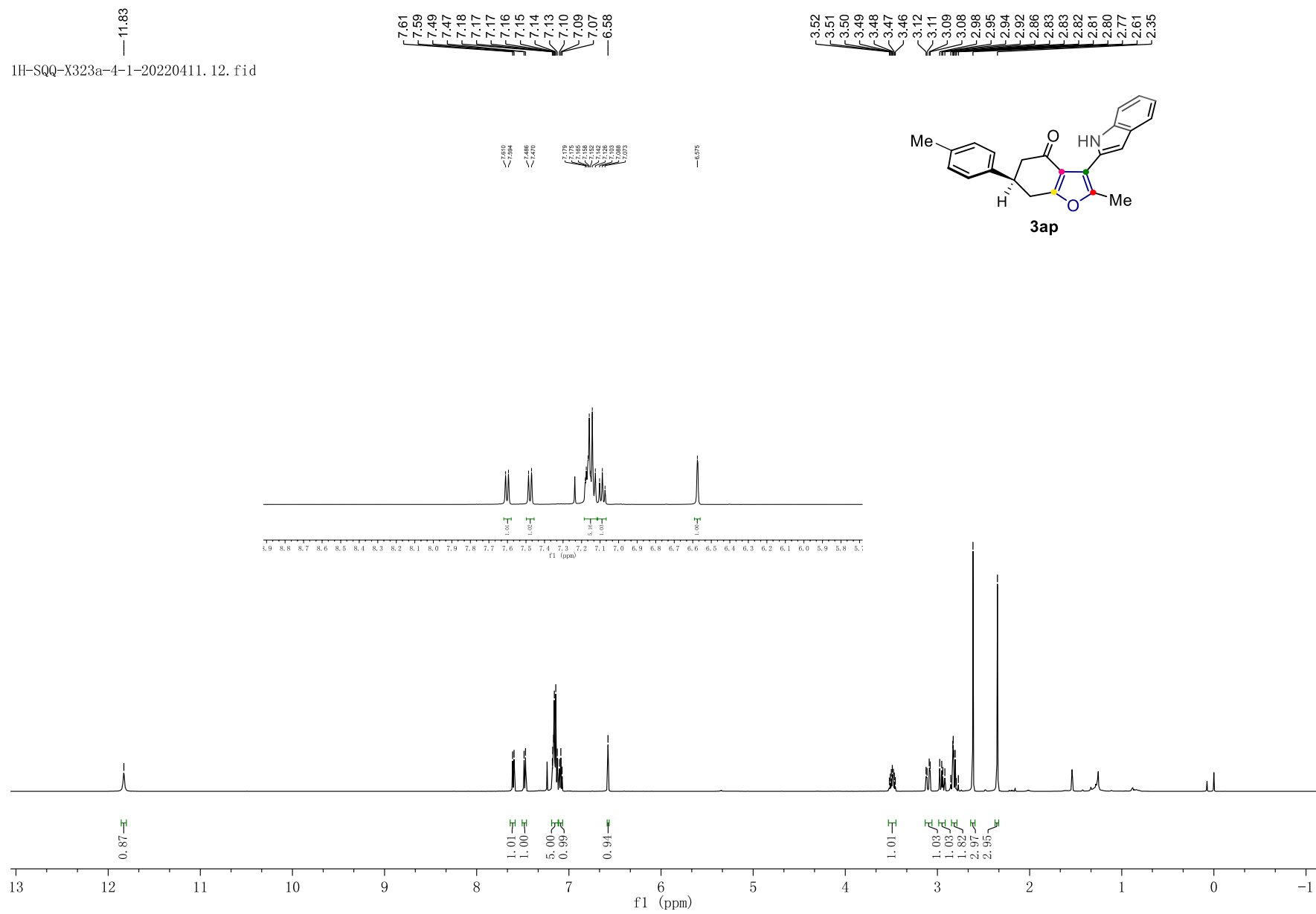
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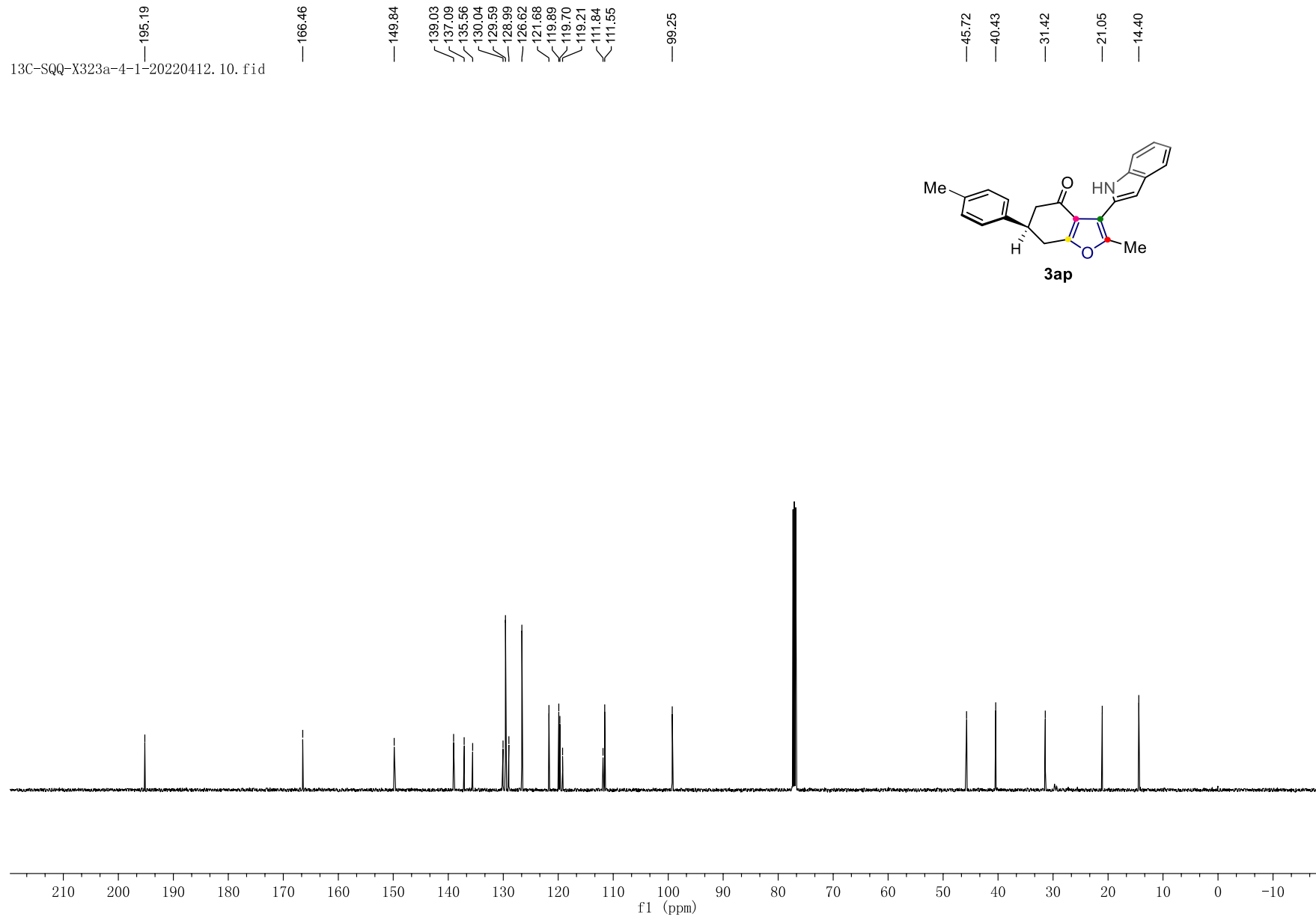
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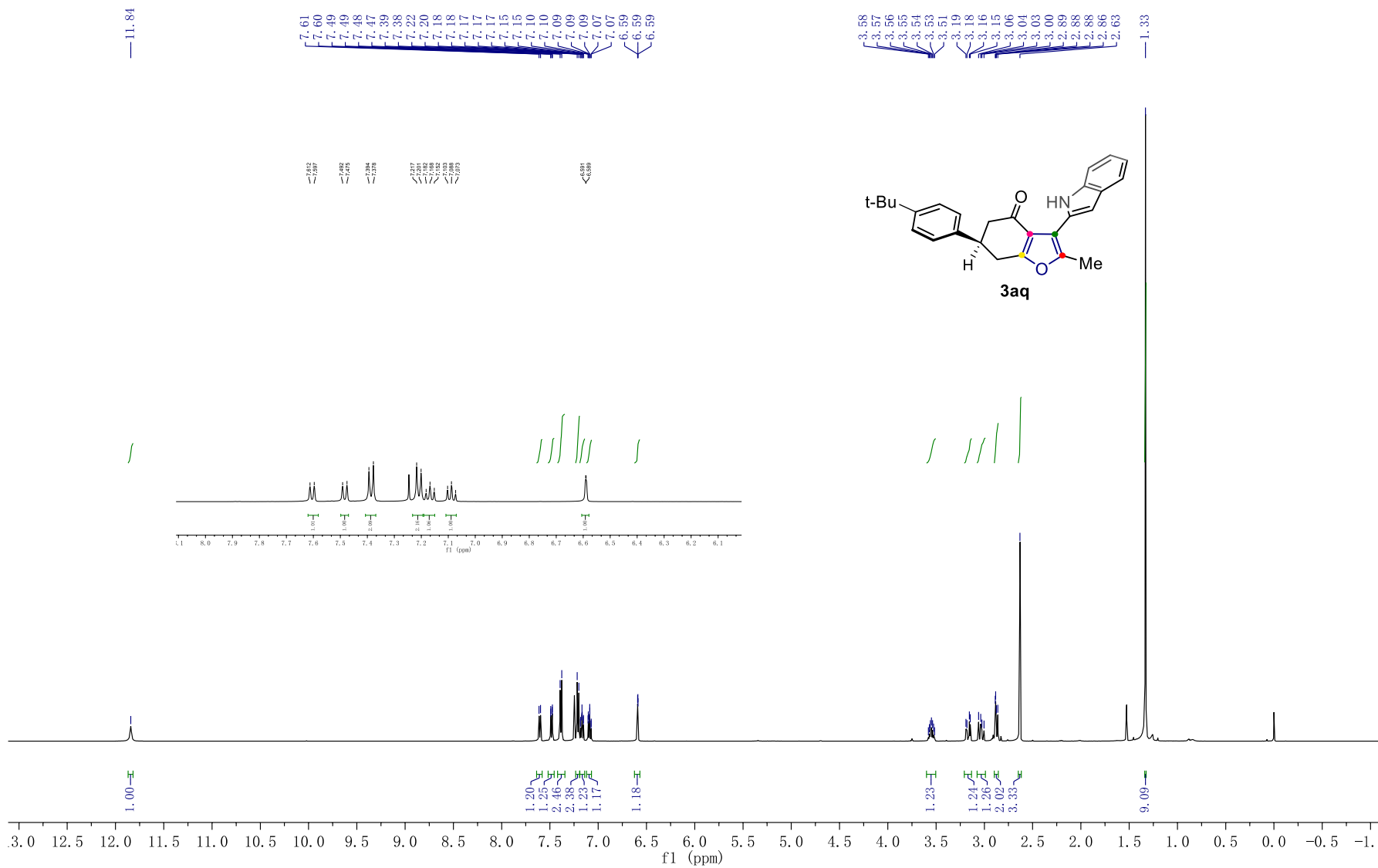


¹H NMR (500 MHz, CDCl₃) of compound **3ap**

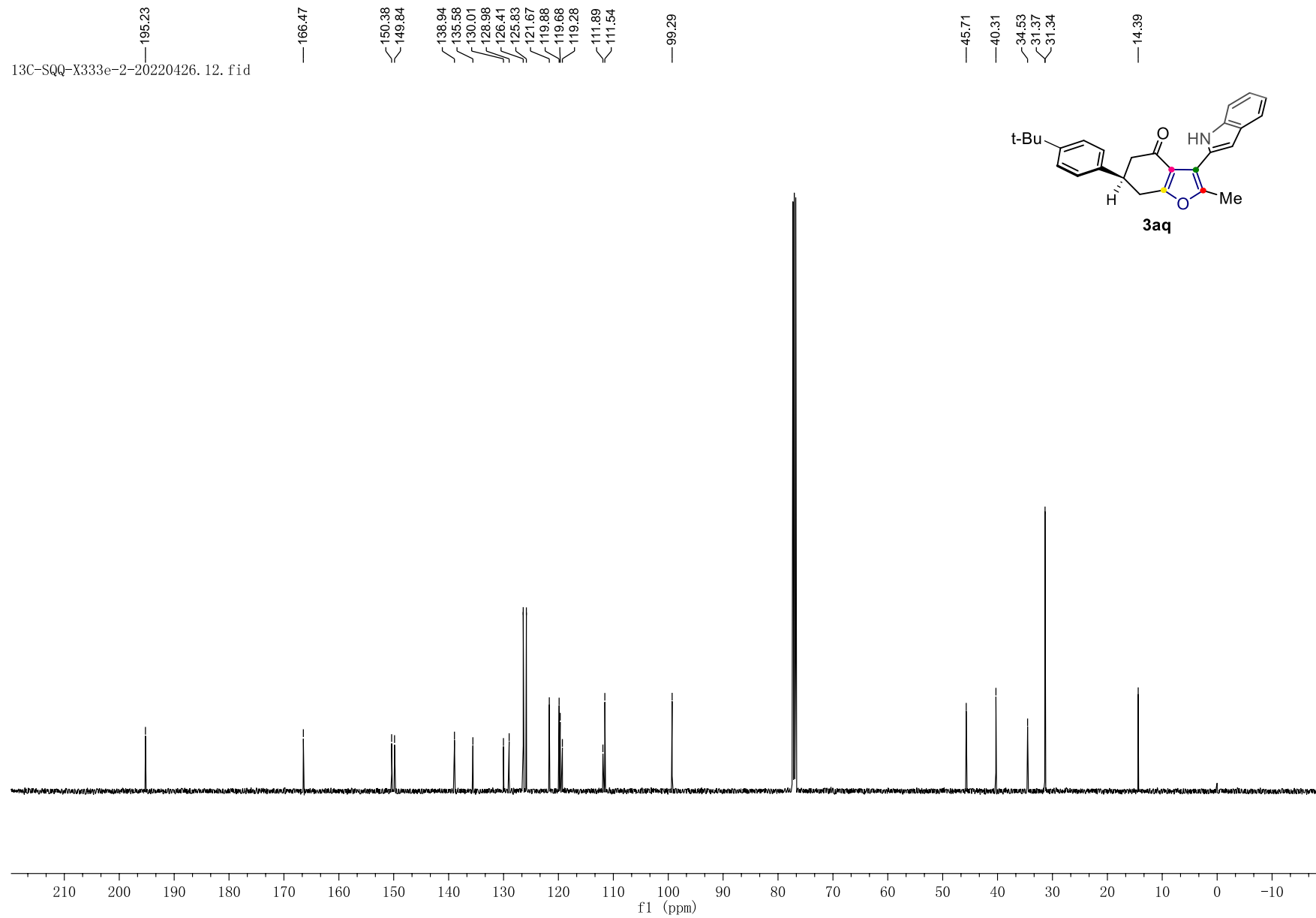


¹³C NMR (500 MHz, CDCl₃) of compound **3ap**

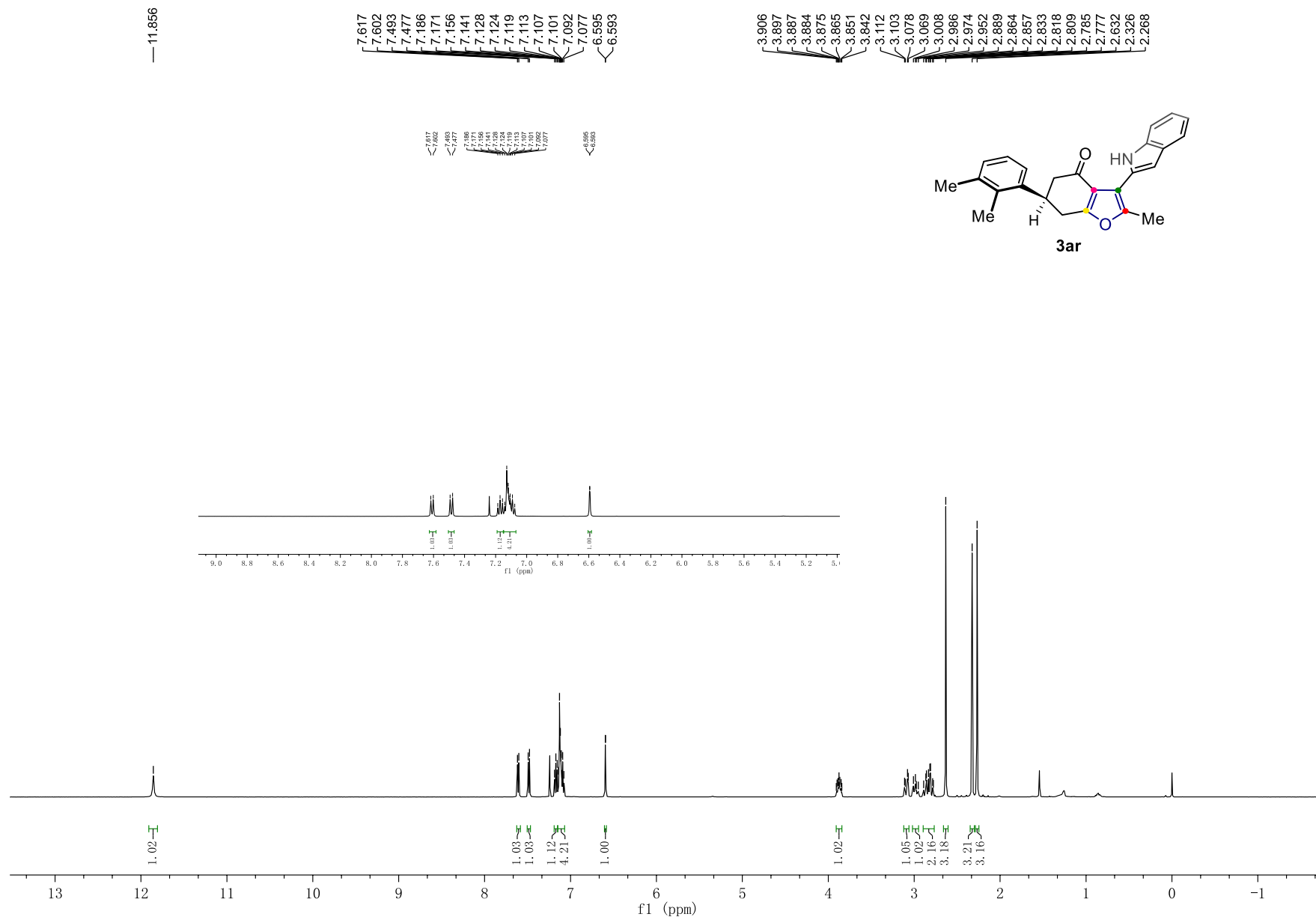


¹H NMR (500 MHz, CDCl₃) of compound **3aq**

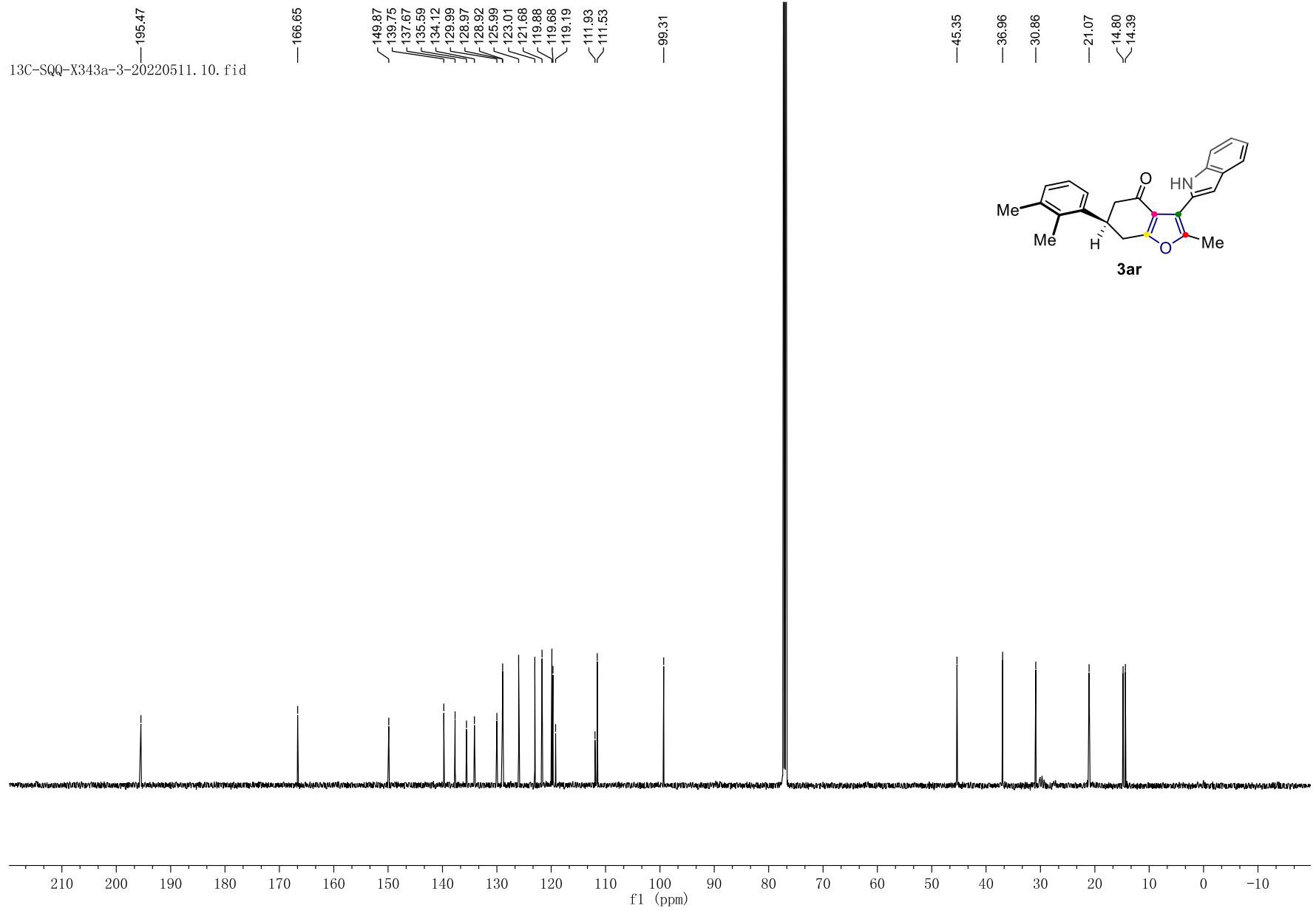
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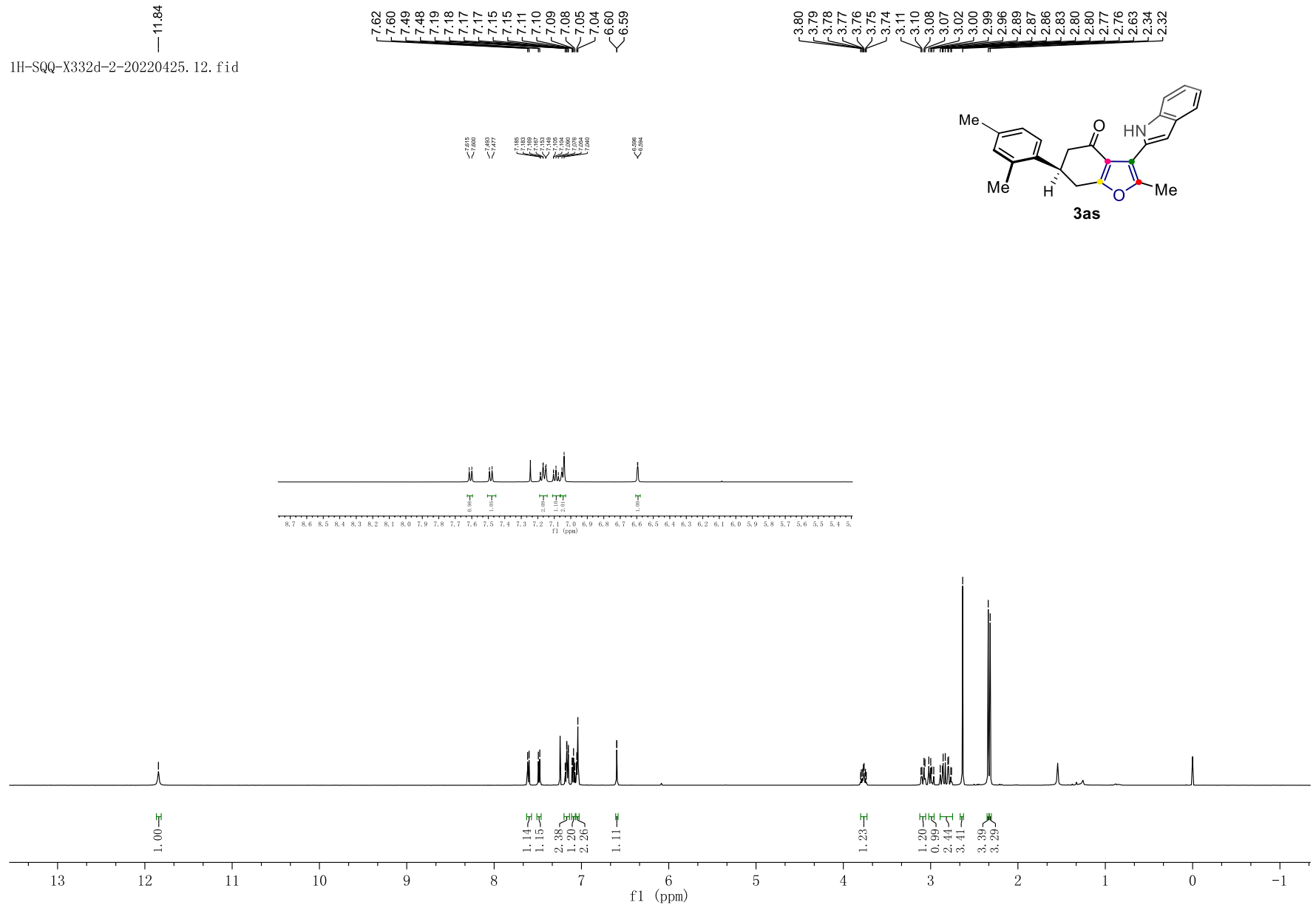
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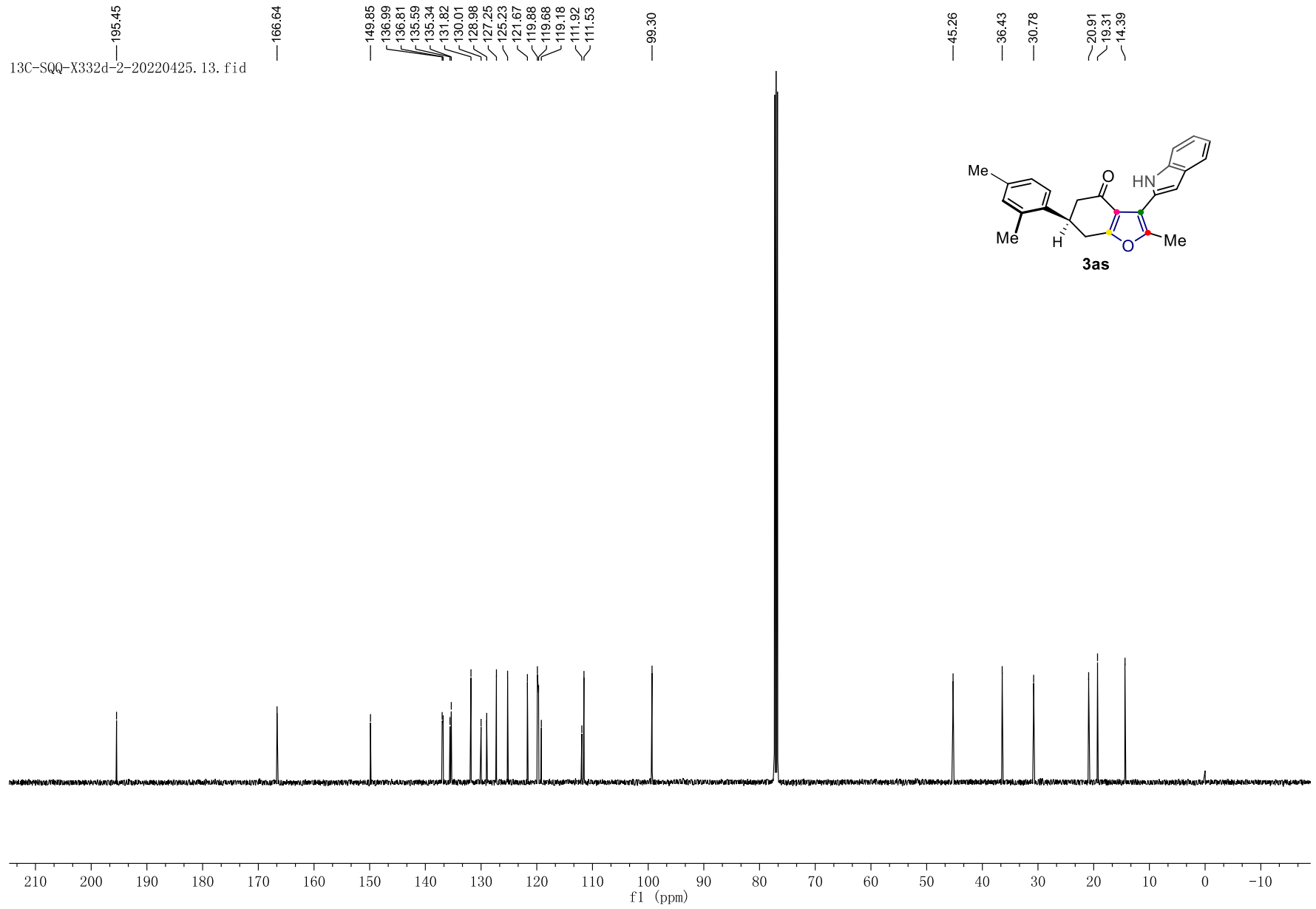
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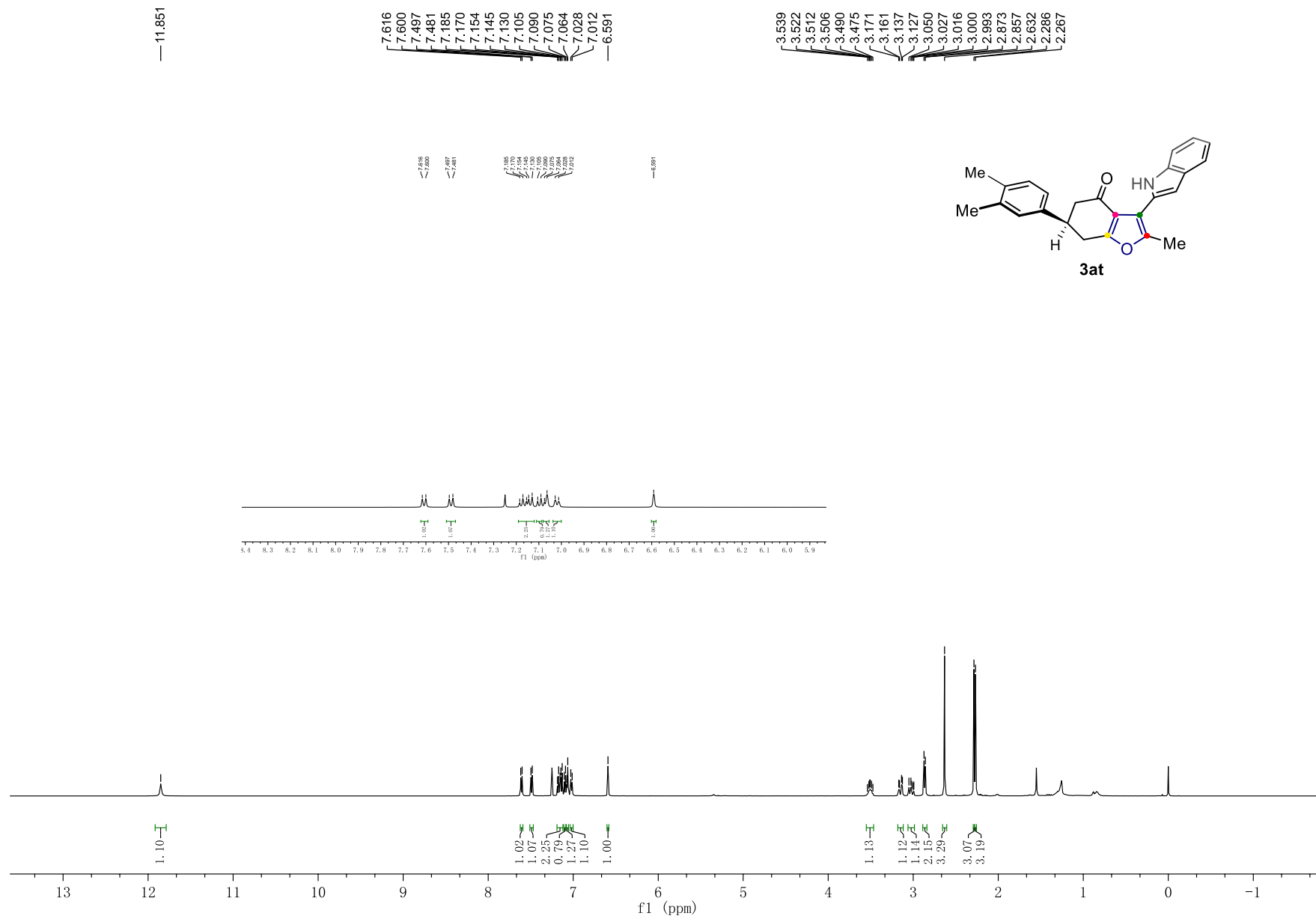
¹H NMR (500 MHz, CDCl₃) of compound **3as**



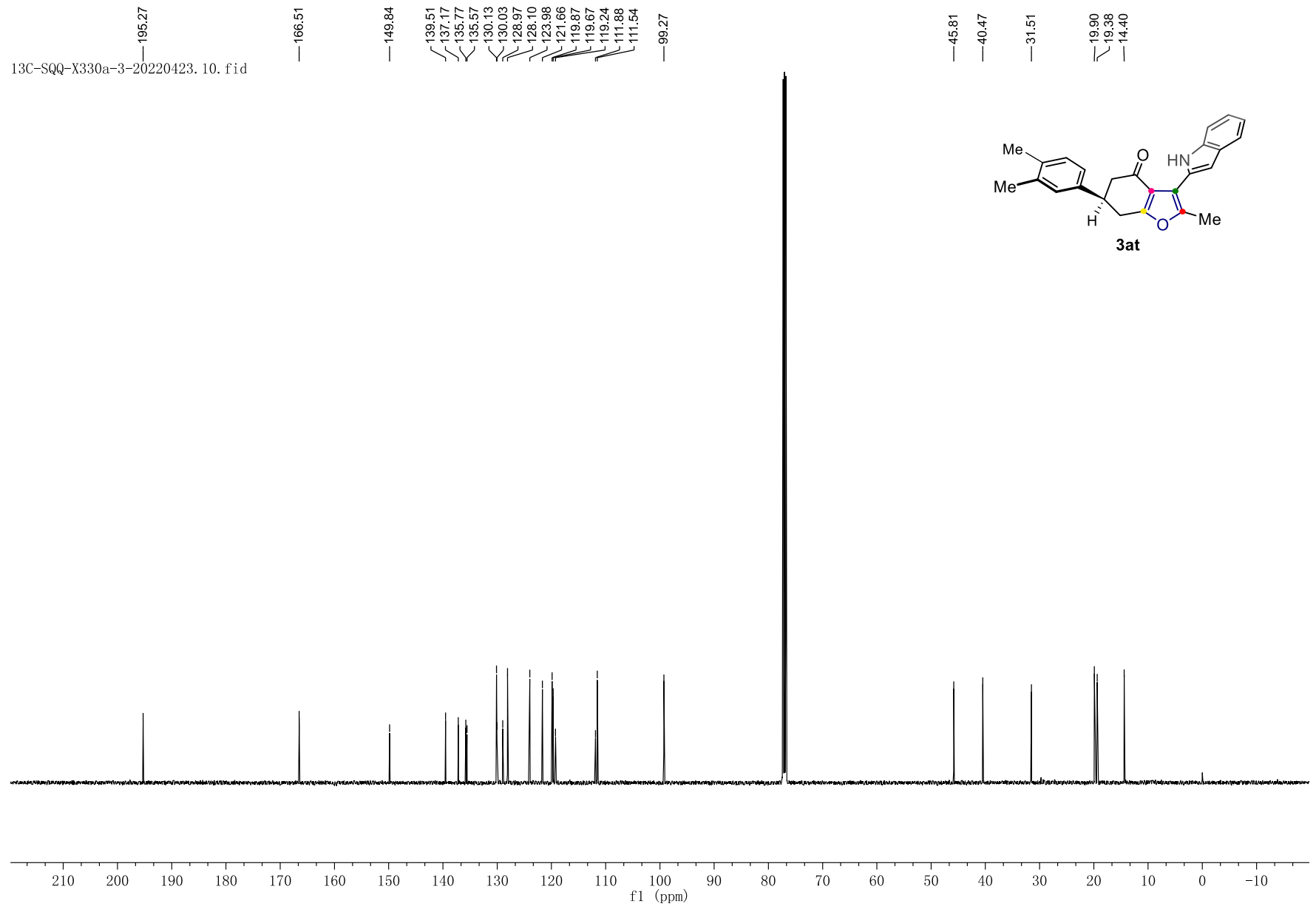
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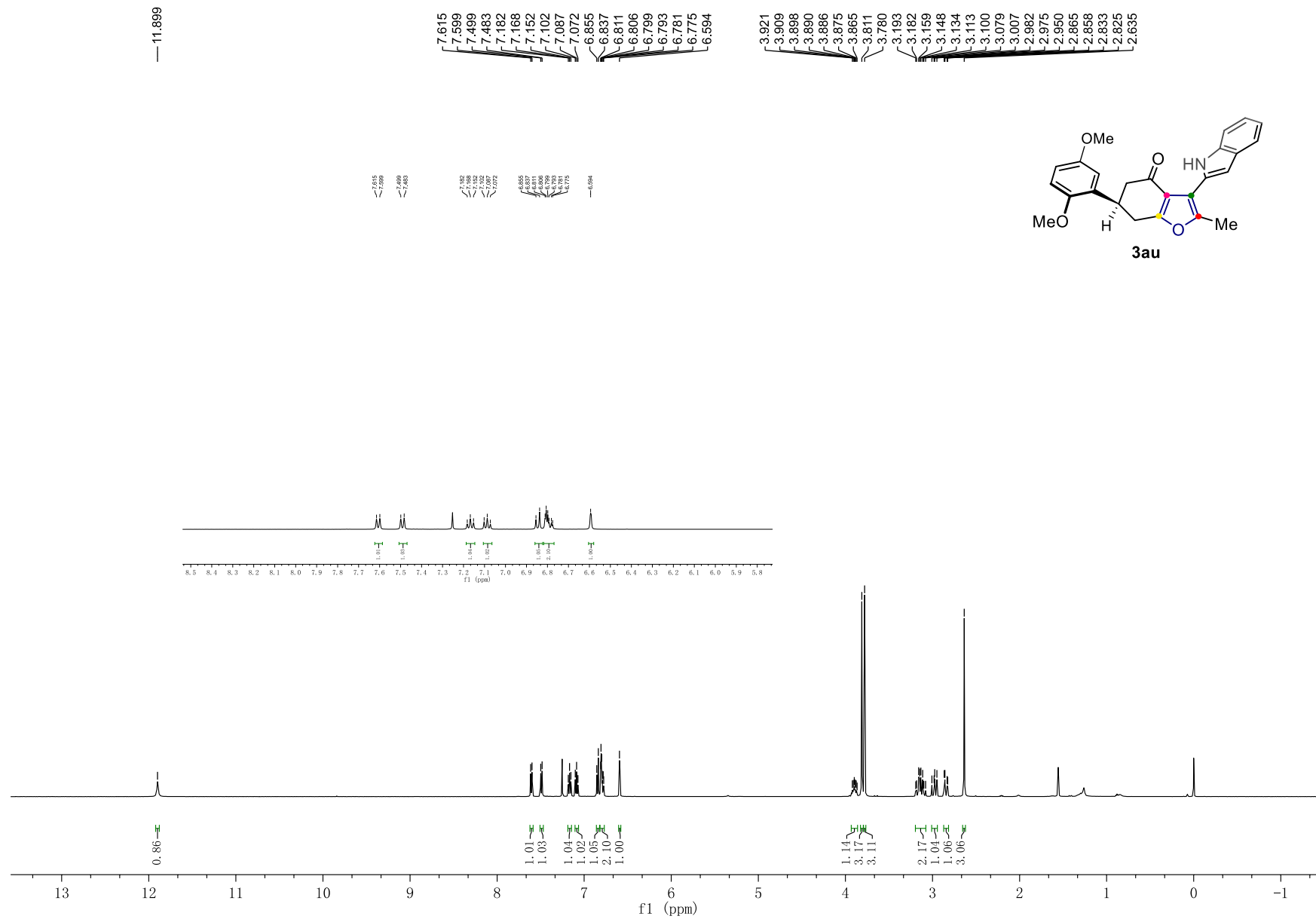
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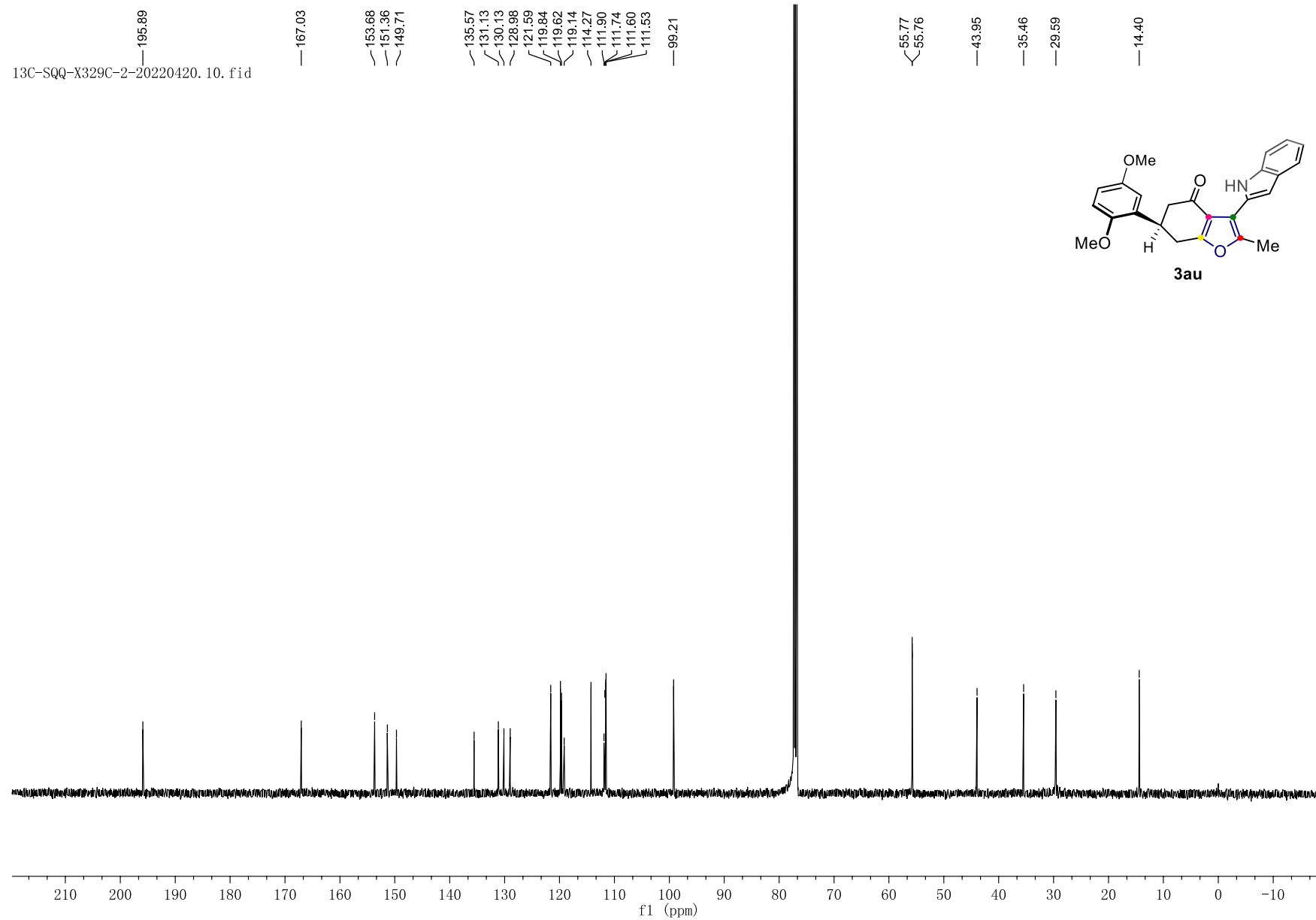
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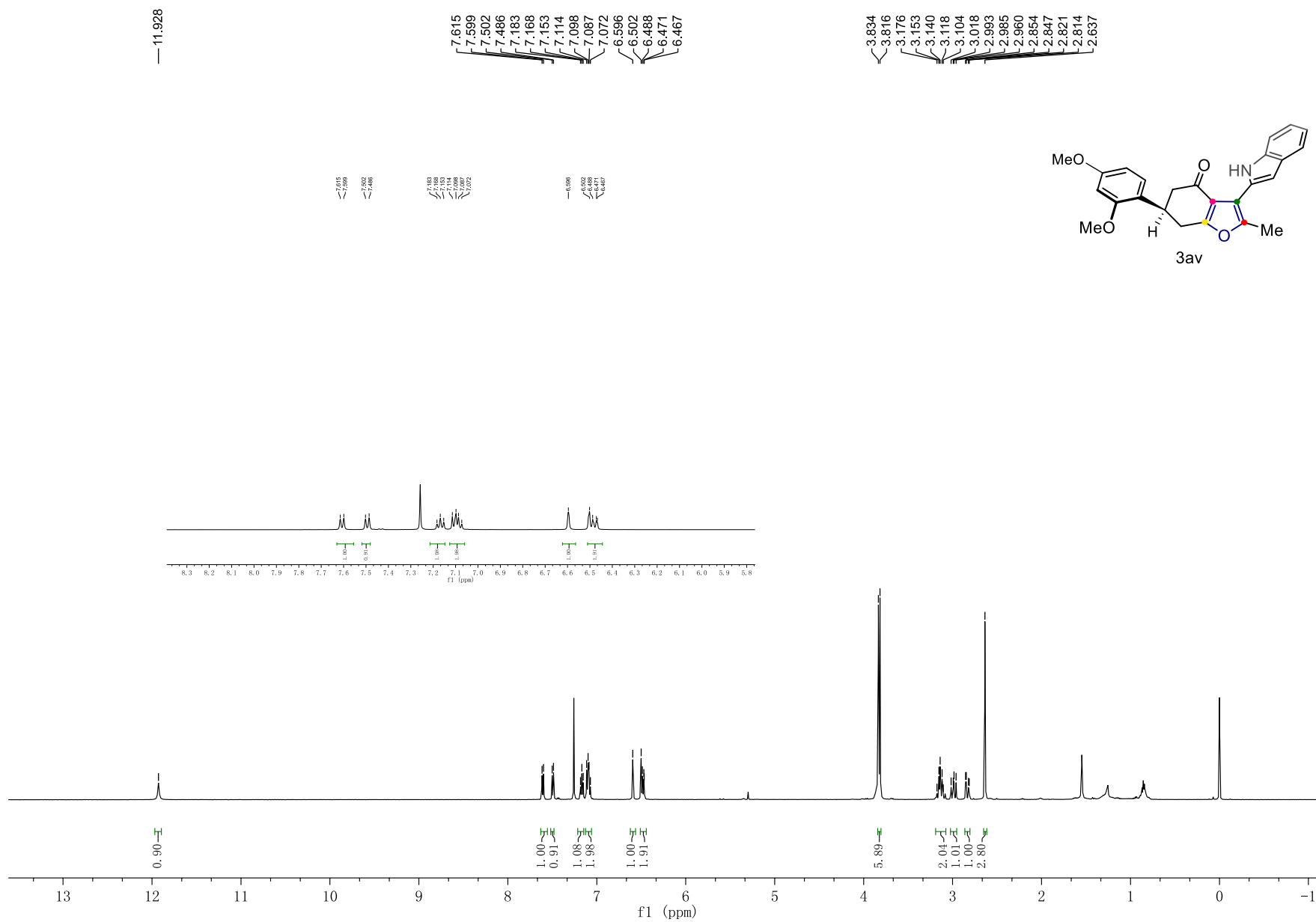
¹H NMR (500 MHz, CDCl₃) of compound **3au**



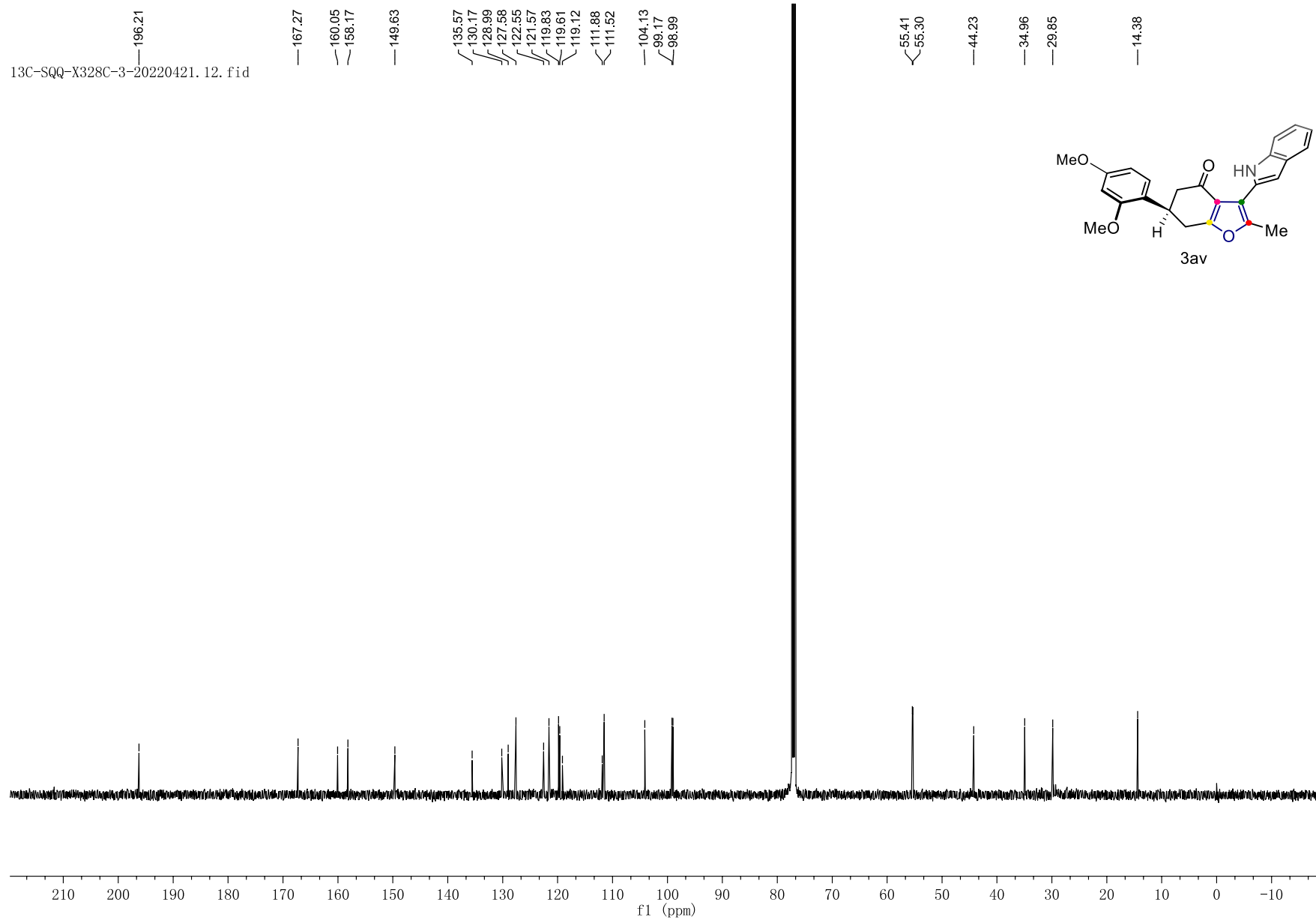
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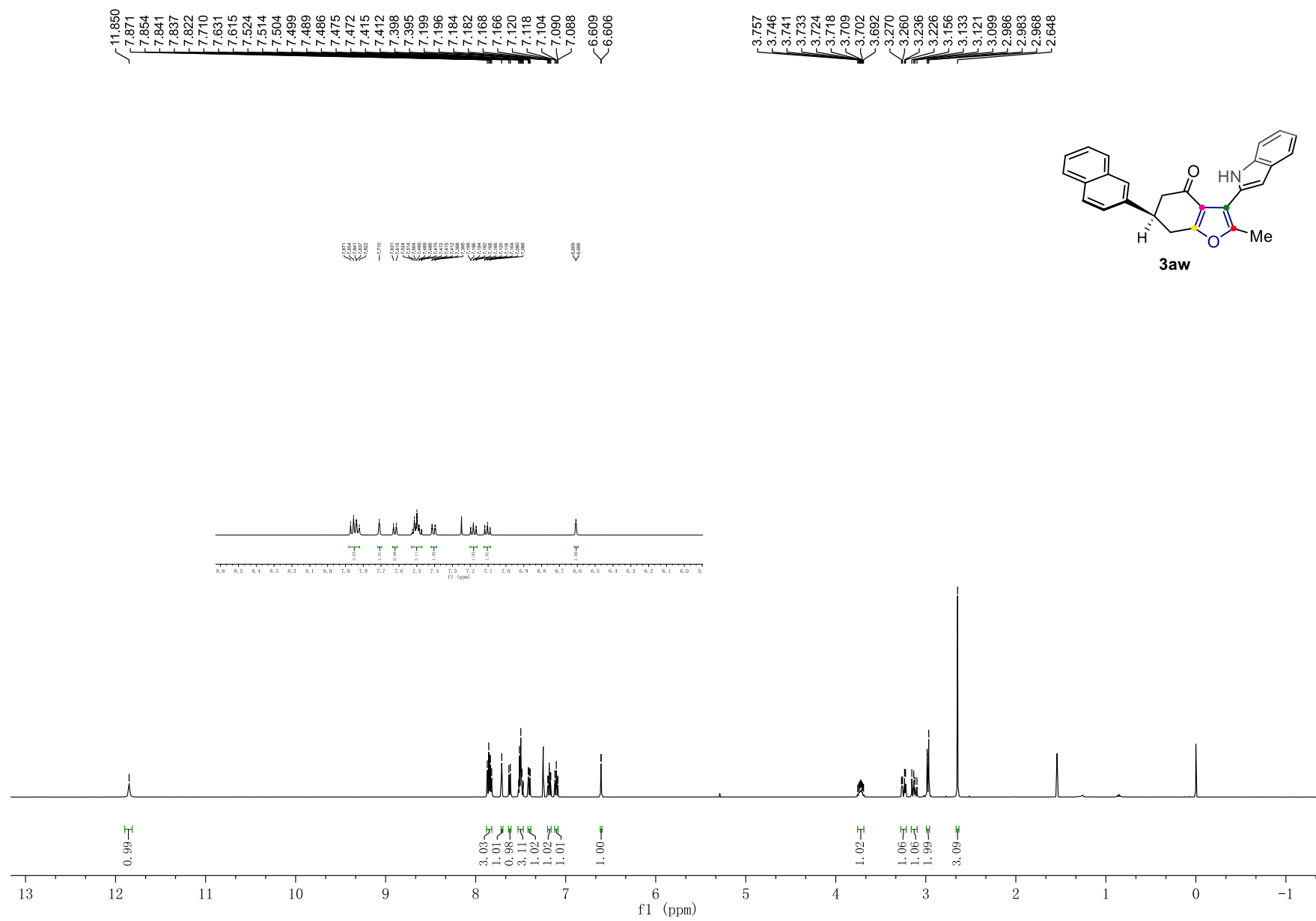
¹H NMR (500 MHz, CDCl₃) of compound **3av**



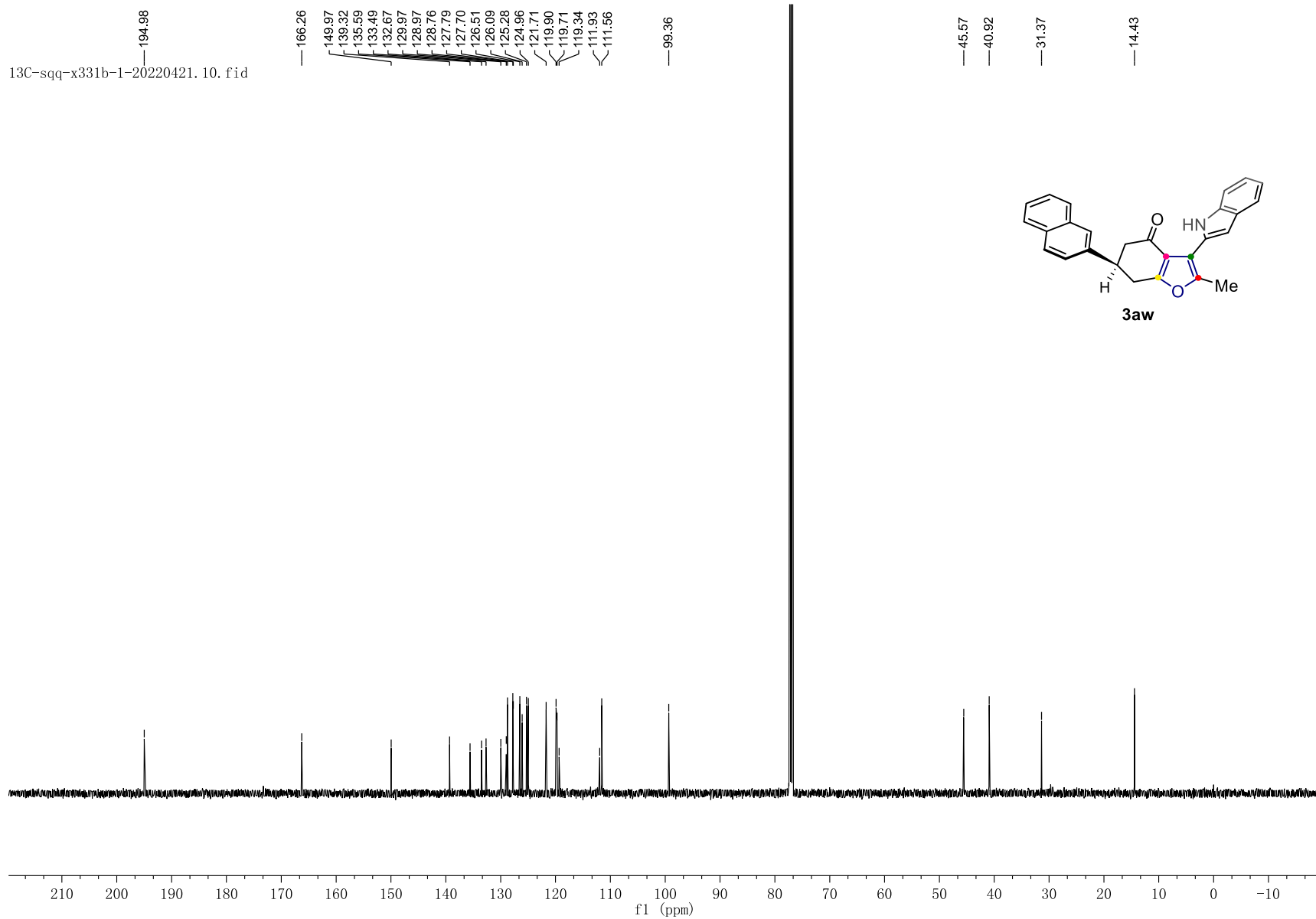
¹³C NMR (500 MHz, CDCl₃) of compound **3av**



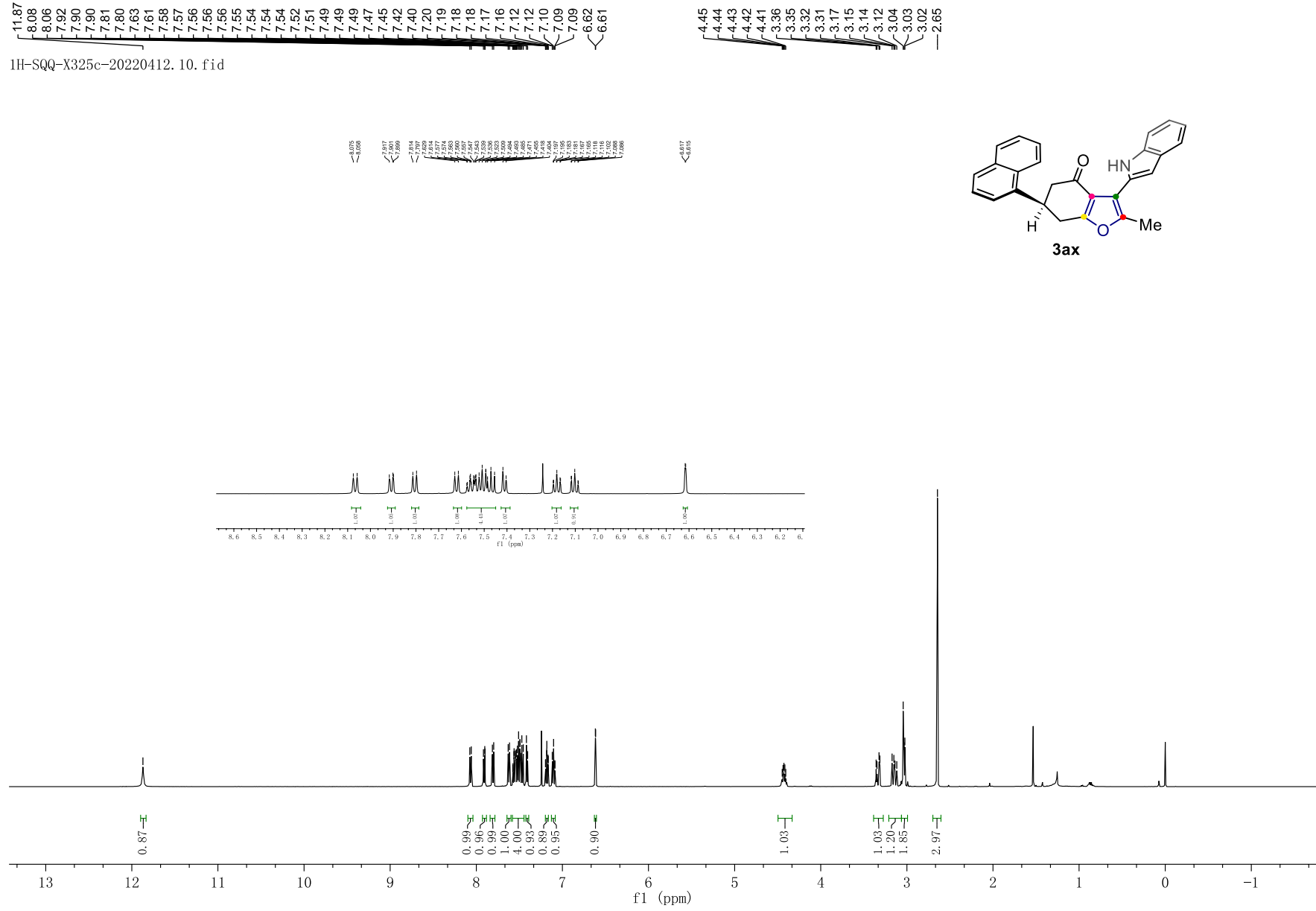
¹H NMR (500 MHz, CDCl₃) of compound **3aw**



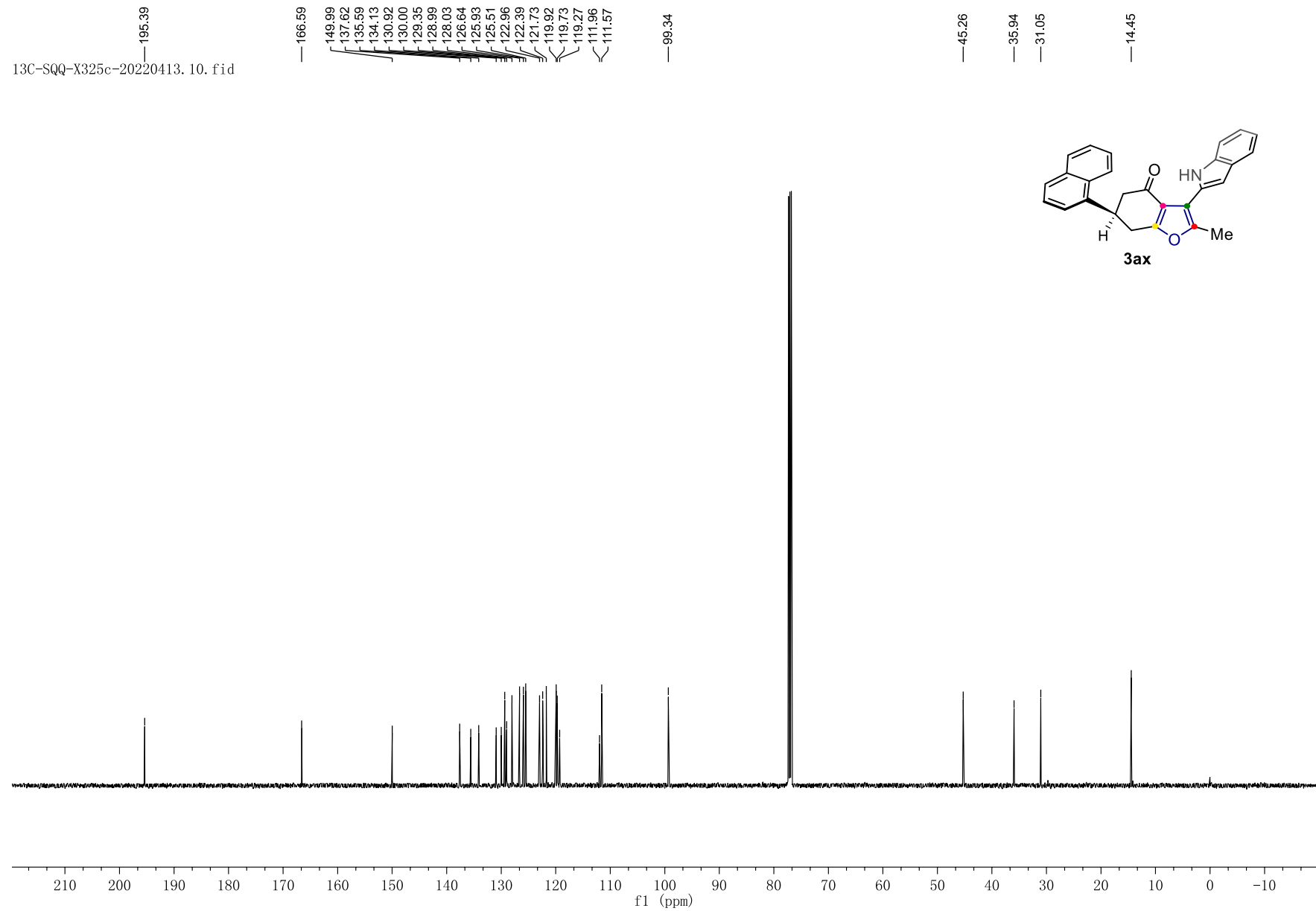
¹³C NMR (500 MHz, CDCl₃) of compound **3aw**



¹H NMR (500 MHz, CDCl₃) of compound **3ax**



¹³C NMR (500 MHz, CDCl₃) of compound **3ax**



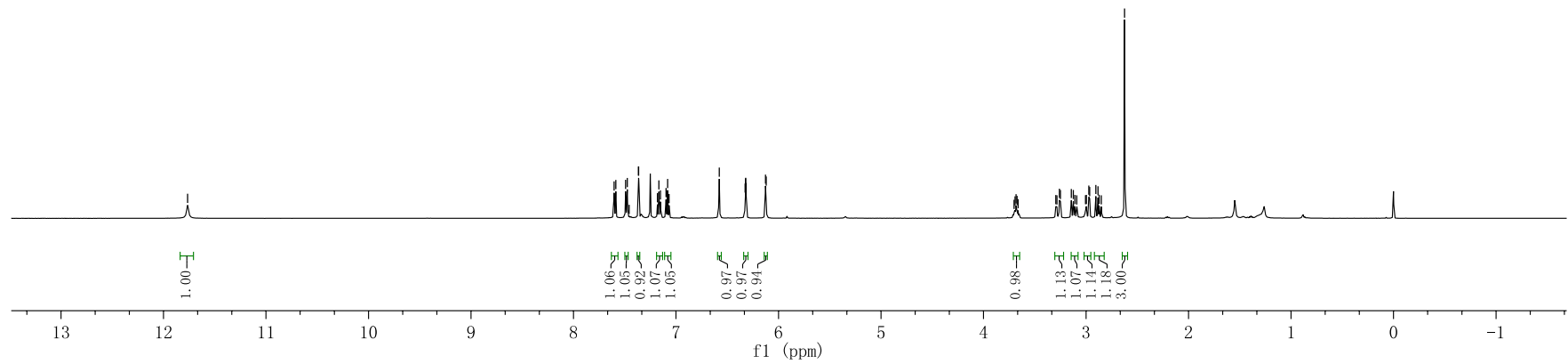
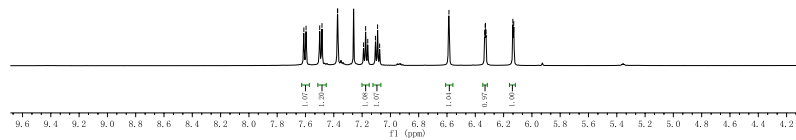
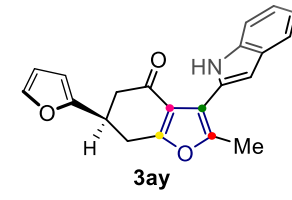
¹H NMR (500 MHz, CDCl₃) of compound **3ay**

1H-SQQ-X337a-5-20220502. 10. fid
11.76

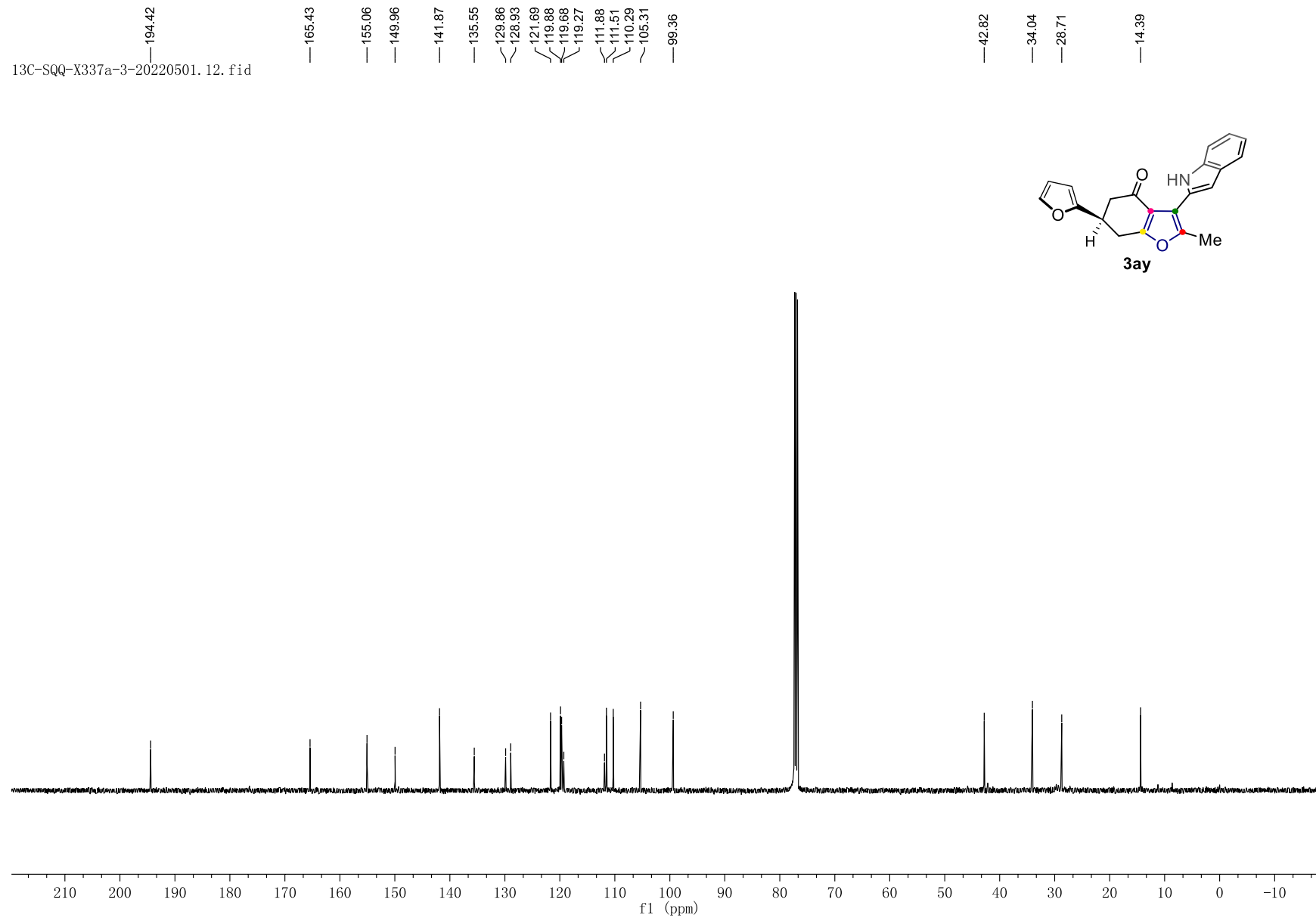
7.60
7.59
7.49
7.48
7.46
7.37
7.36
7.18
7.17
7.15
7.10
7.08
7.07
6.58
6.33
6.32
6.32
6.13
6.12

3.70
3.69
3.68
3.67
3.66
3.29
3.28
3.26
3.25
3.14
3.12
3.11
3.09
3.01
3.00
2.97
2.96
2.90
2.88
2.87
2.85
2.62

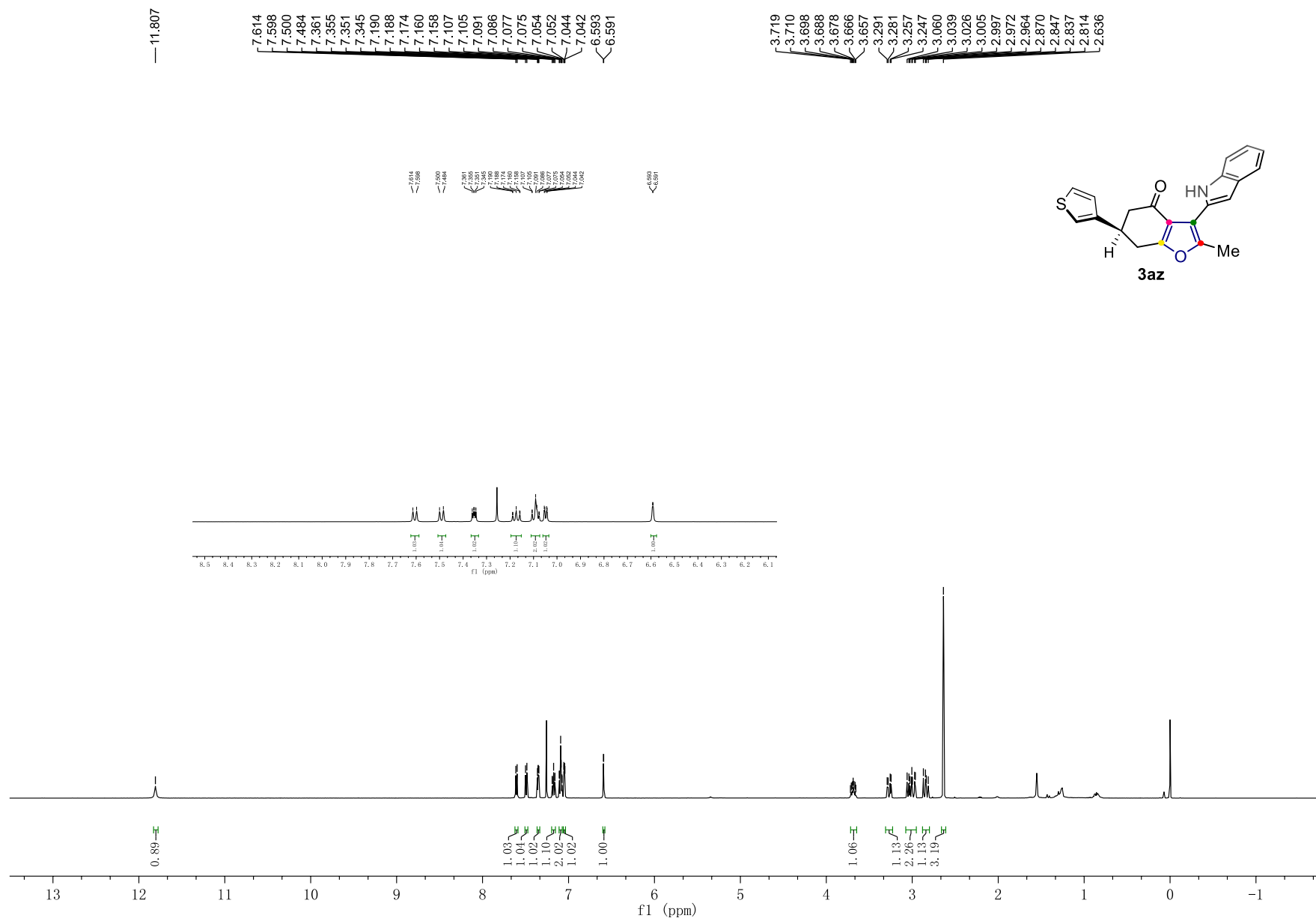
7.512
7.506
7.493
7.473
7.373
7.186
7.091
7.074
6.586
6.334
6.328
6.324
6.128



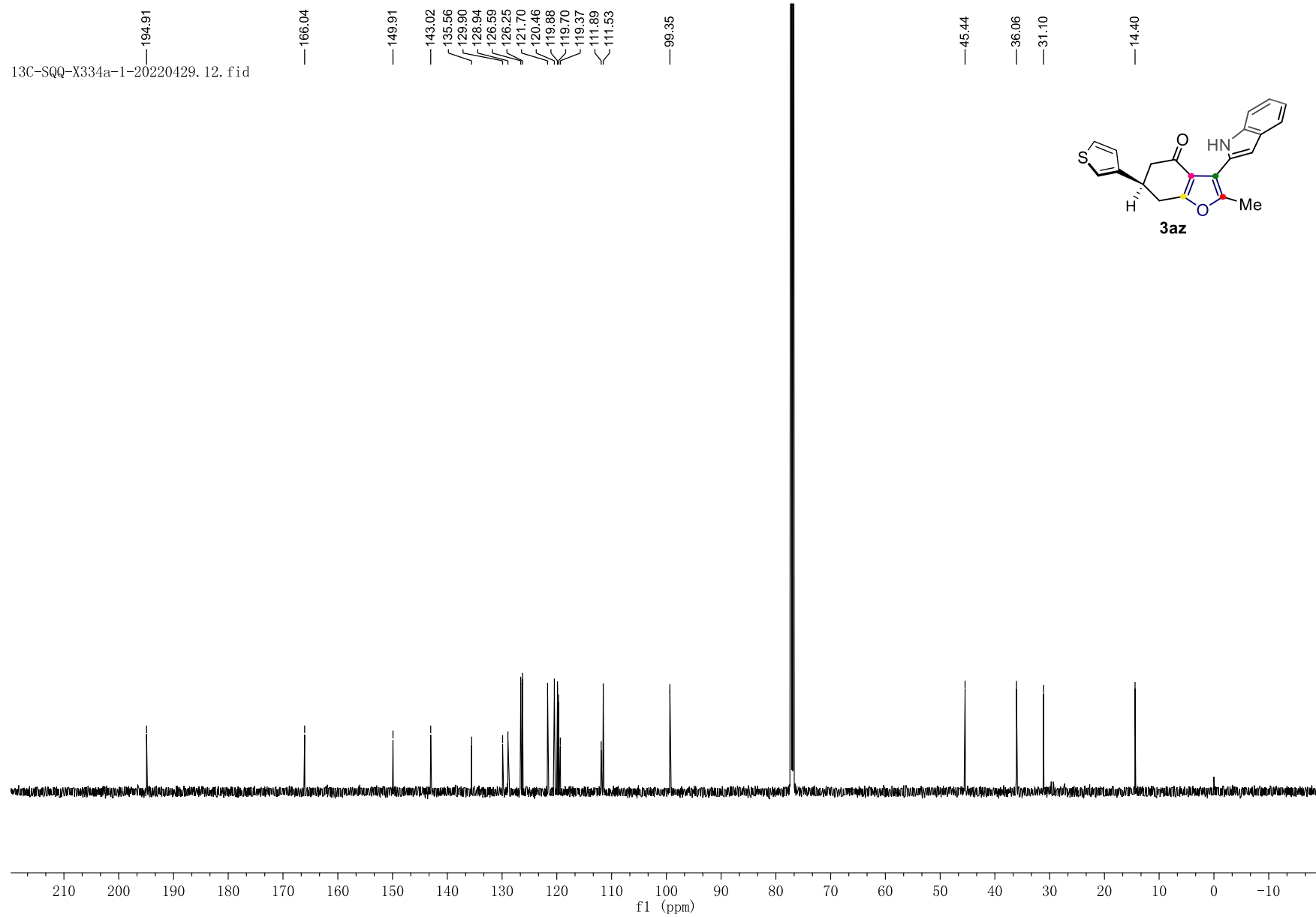
¹³C NMR (500 MHz, CDCl₃) of compound **3ay**



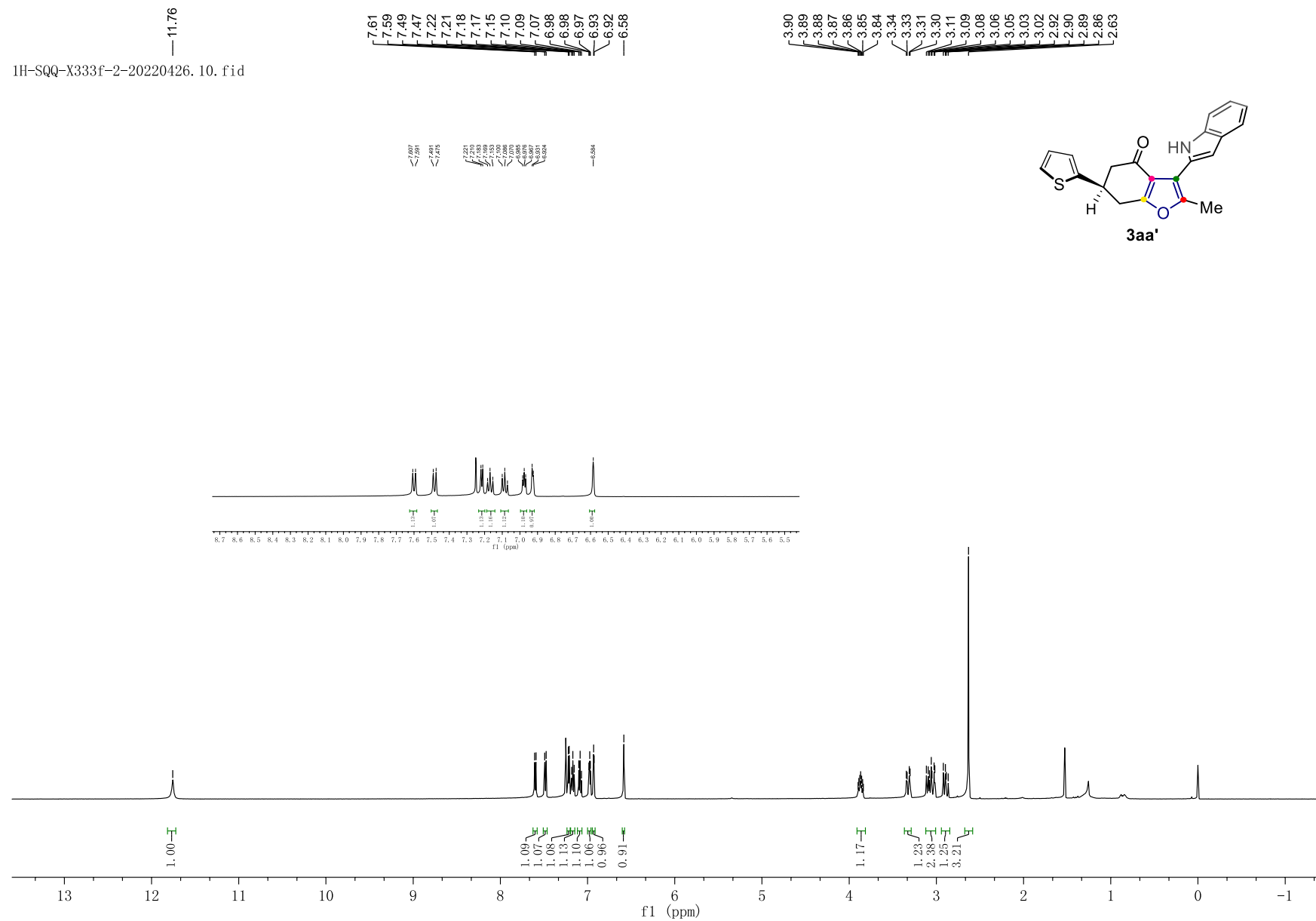
¹H NMR (500 MHz, CDCl₃) of compound **3az**



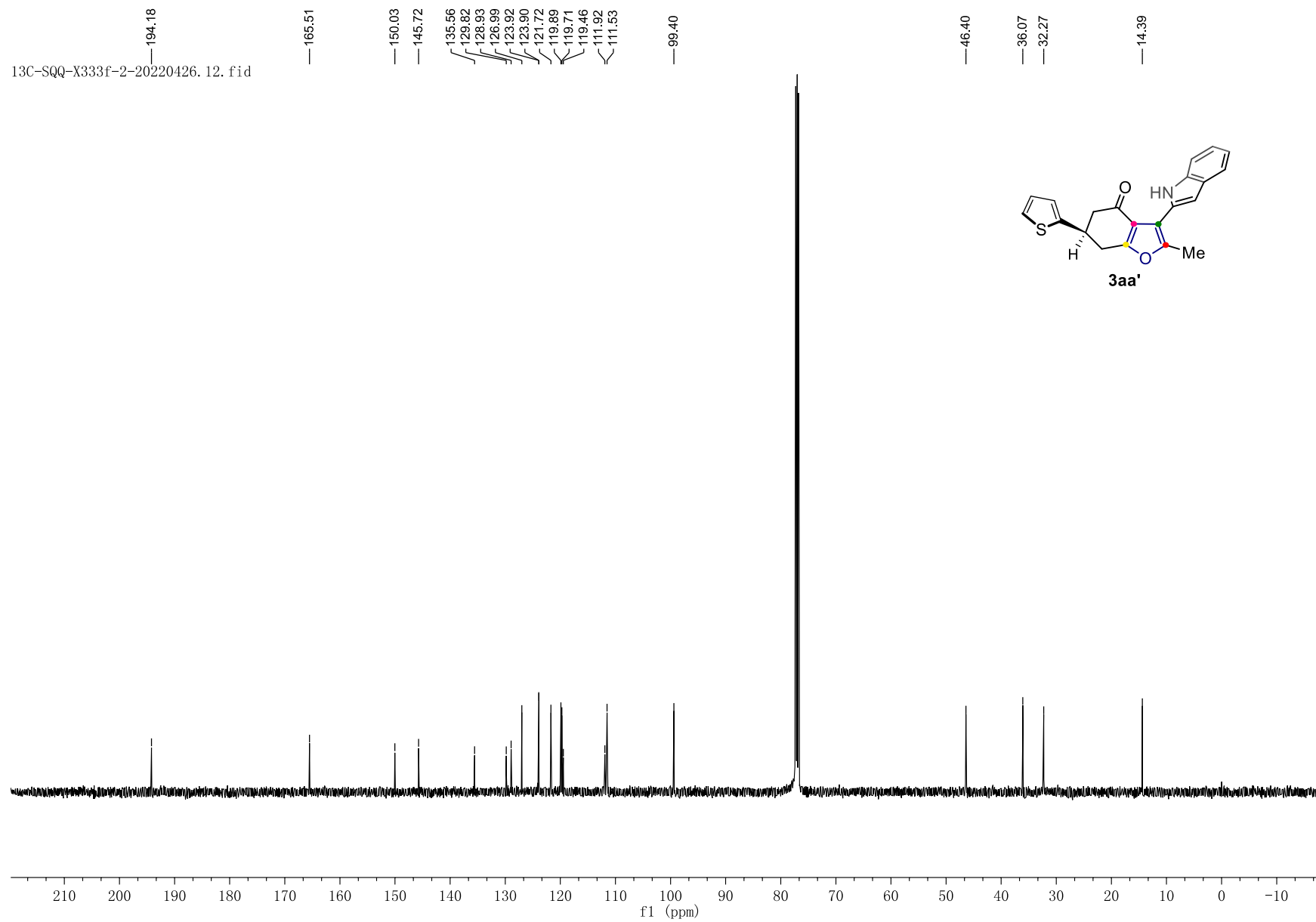
¹³C NMR (500 MHz, CDCl₃) of compound **3az**



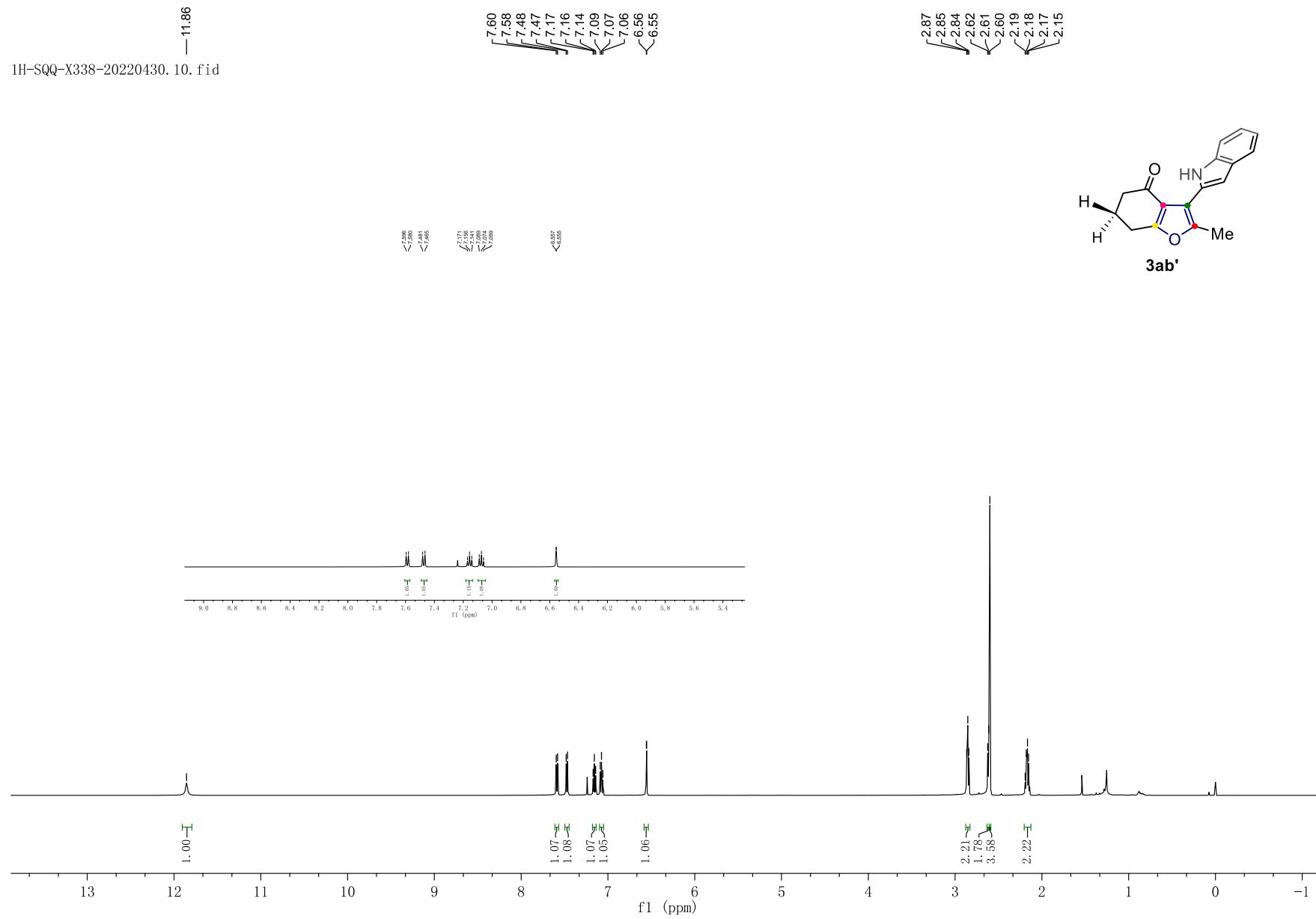
¹H NMR (500 MHz, CDCl₃) of compound **3aa'**



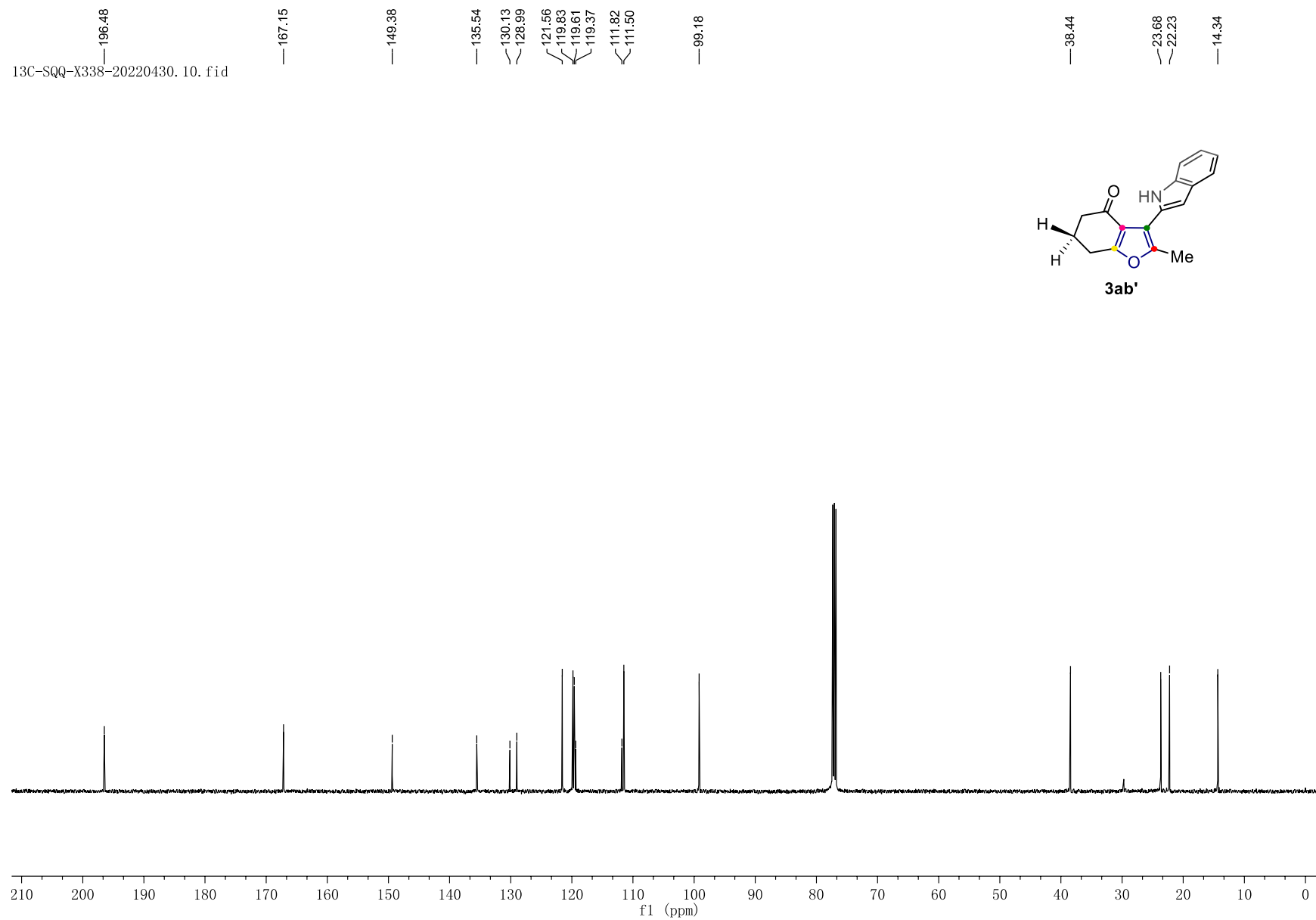
¹³C NMR (500 MHz, CDCl₃) of compound **3aa'**



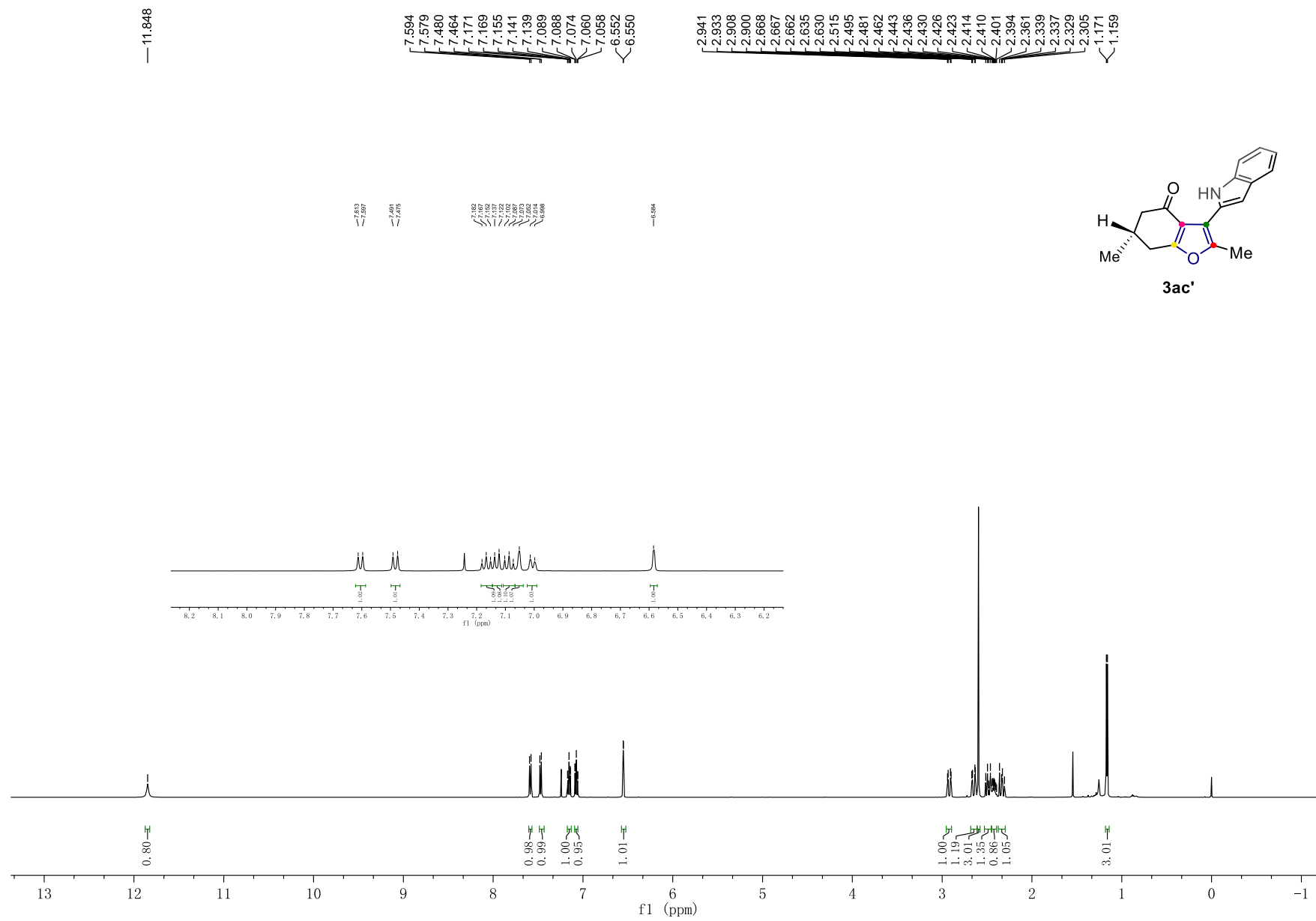
¹H NMR (500 MHz, CDCl₃) of compound **3ab'**



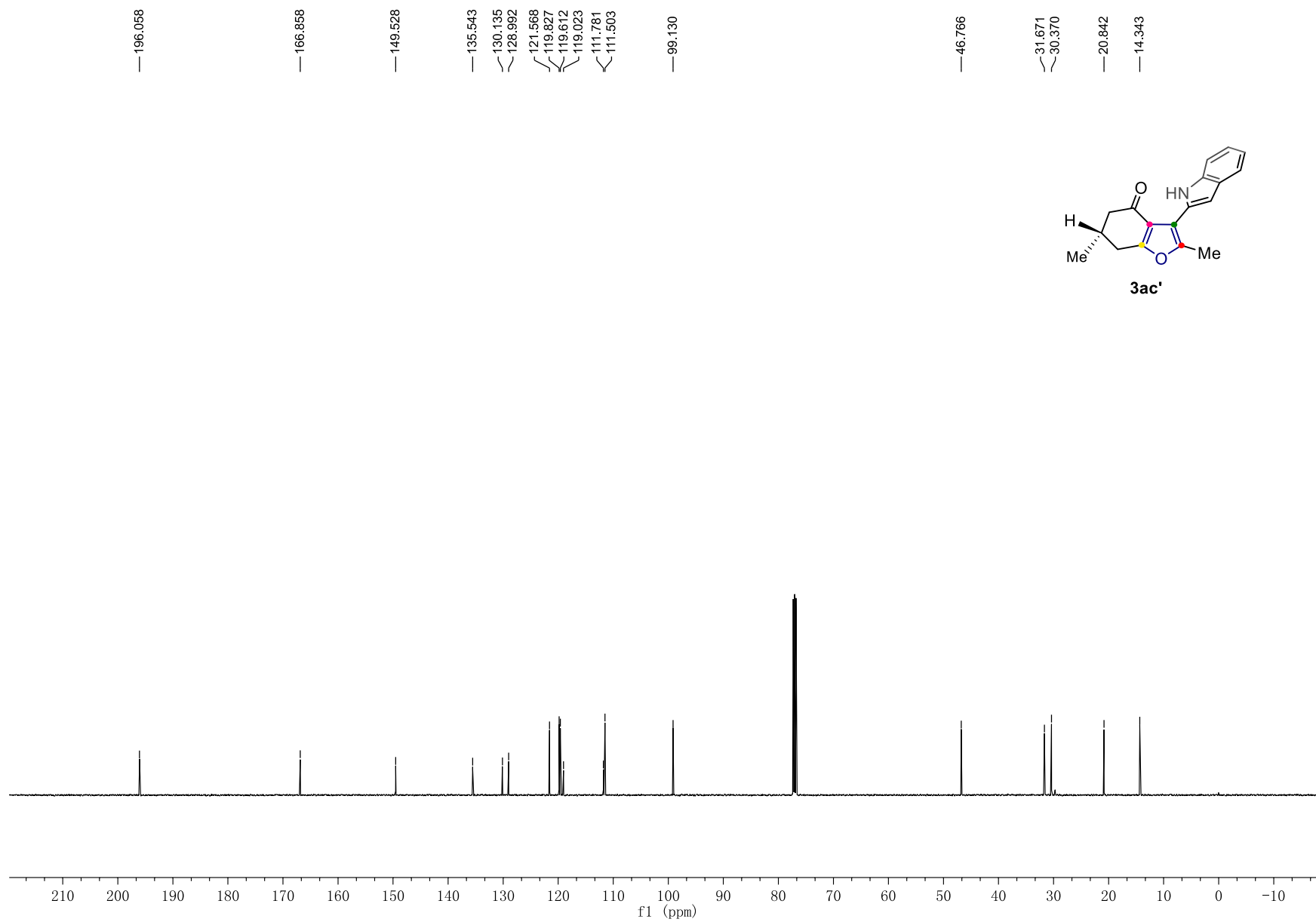
¹³C NMR (500 MHz, CDCl₃) of compound **3ab'**



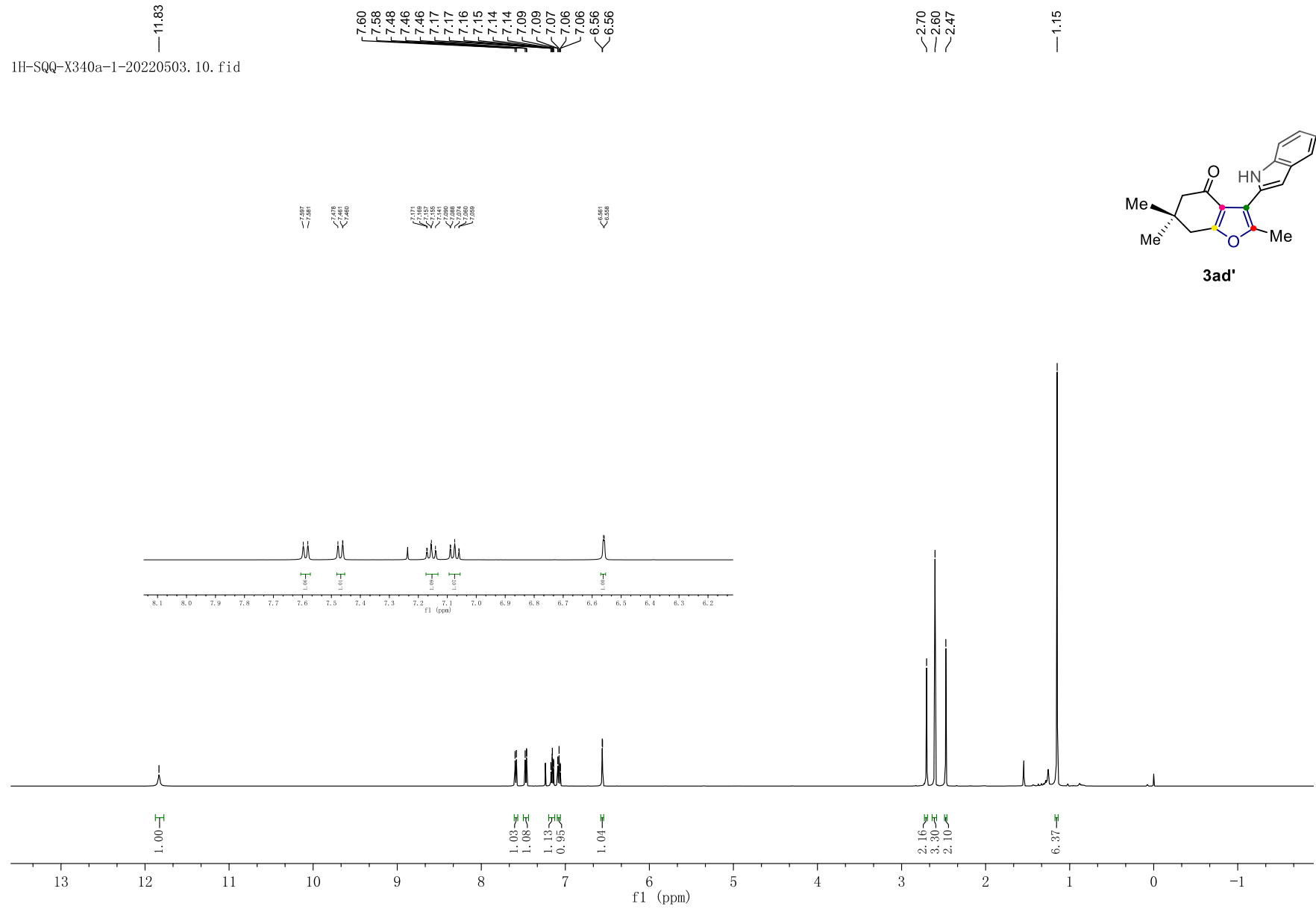
¹H NMR (500 MHz, CDCl₃) of compound **3ac'**



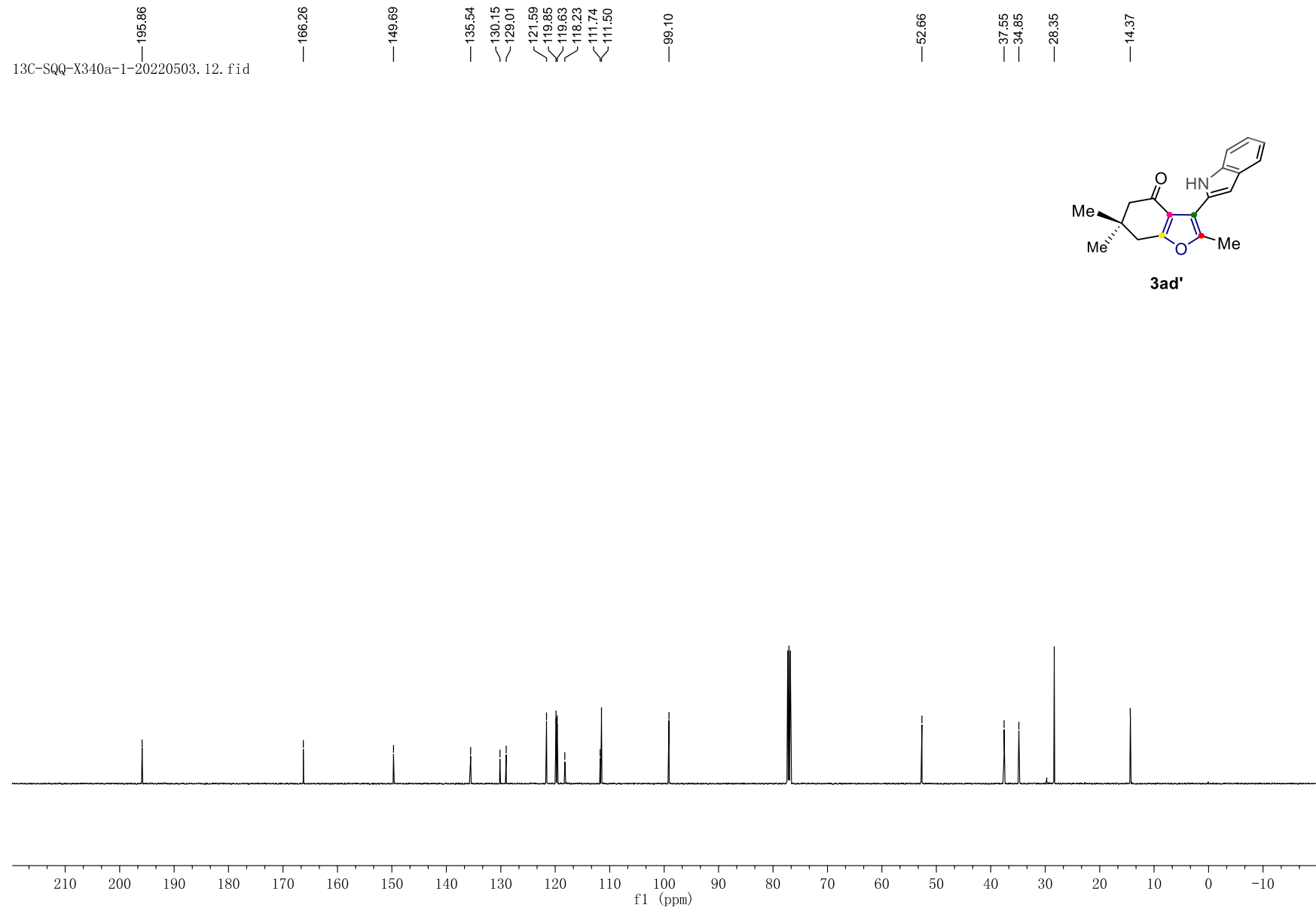
^{13}C NMR (500 MHz, CDCl_3) of compound **3ac'**



¹H NMR (500 MHz, CDCl₃) of compound **3ad'**



¹³C NMR (500 MHz, CDCl₃) of compound **3ad'**

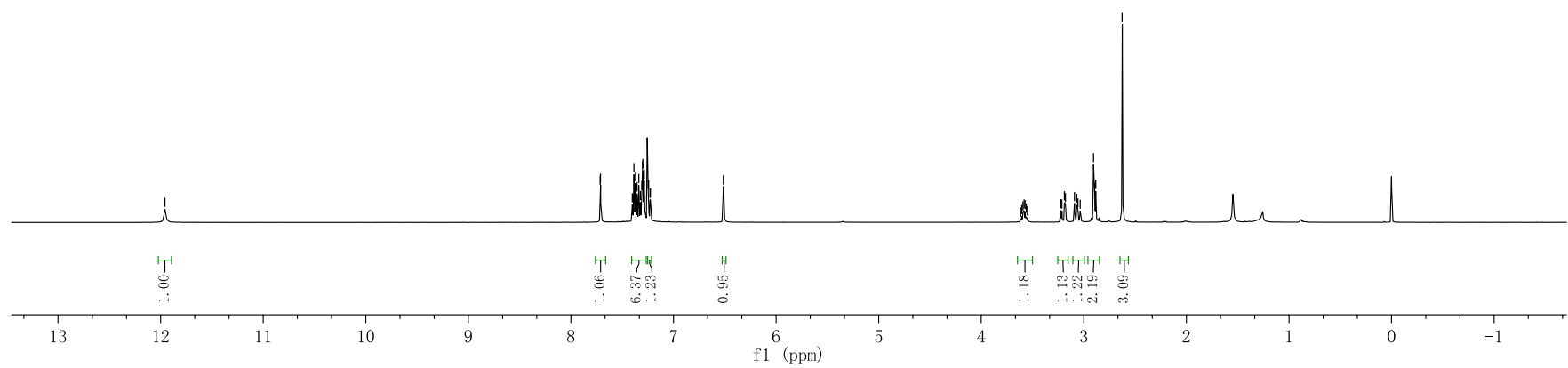
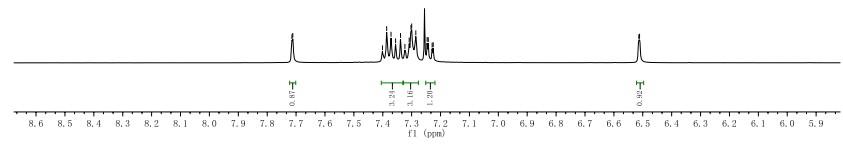
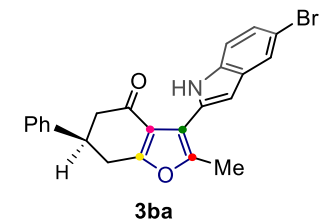


¹H NMR (500 MHz, CDCl₃) of compound **3ba**

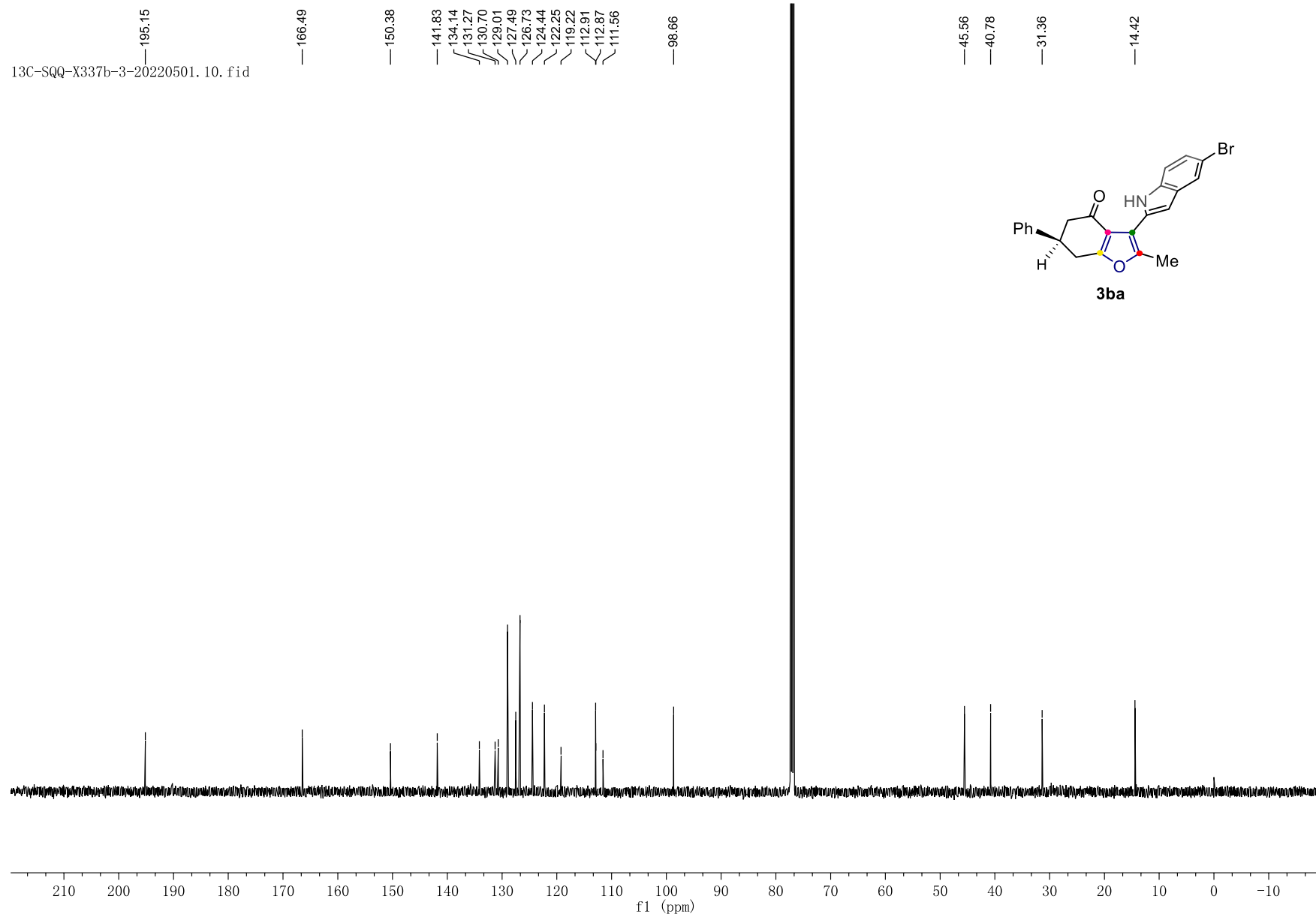
1H-SQQ-X337b-5-20220502. 10. fid
11.96

7.71, 7.71, 7.40, 7.39, 7.37, 7.36, 7.34, 7.32, 7.31, 7.30, 7.30, 7.29, 7.25, 7.24, 7.23, 6.51, 6.51, 3.62, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.22, 3.21, 3.19, 3.18, 3.09, 3.07, 3.06, 3.03, 2.91, 2.89, 2.88, 2.63

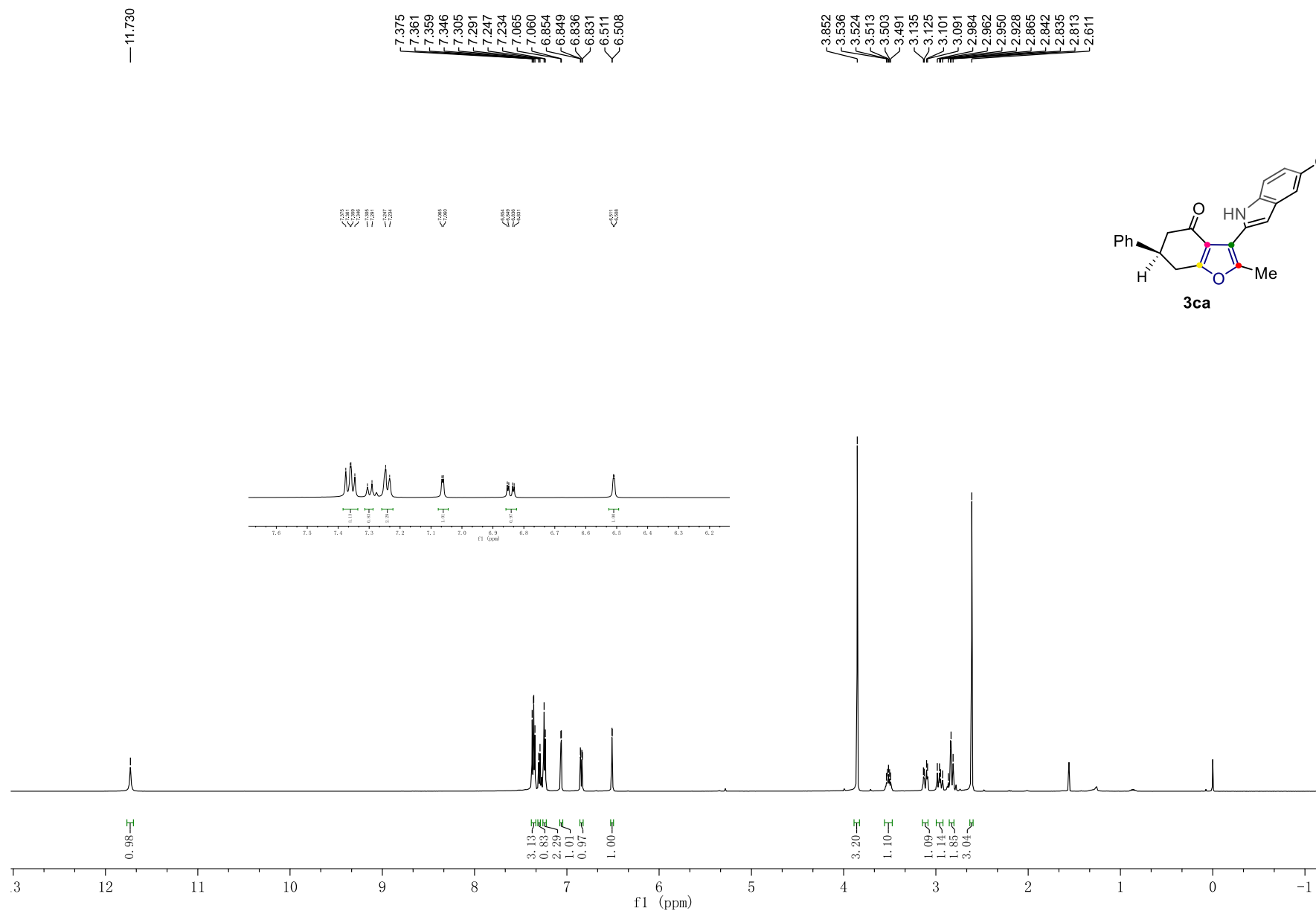
7.714, 7.401, 7.391, 7.386, 7.353, 7.303, 7.292, 7.282, 7.280, 7.246, 7.229, 6.514, 6.511



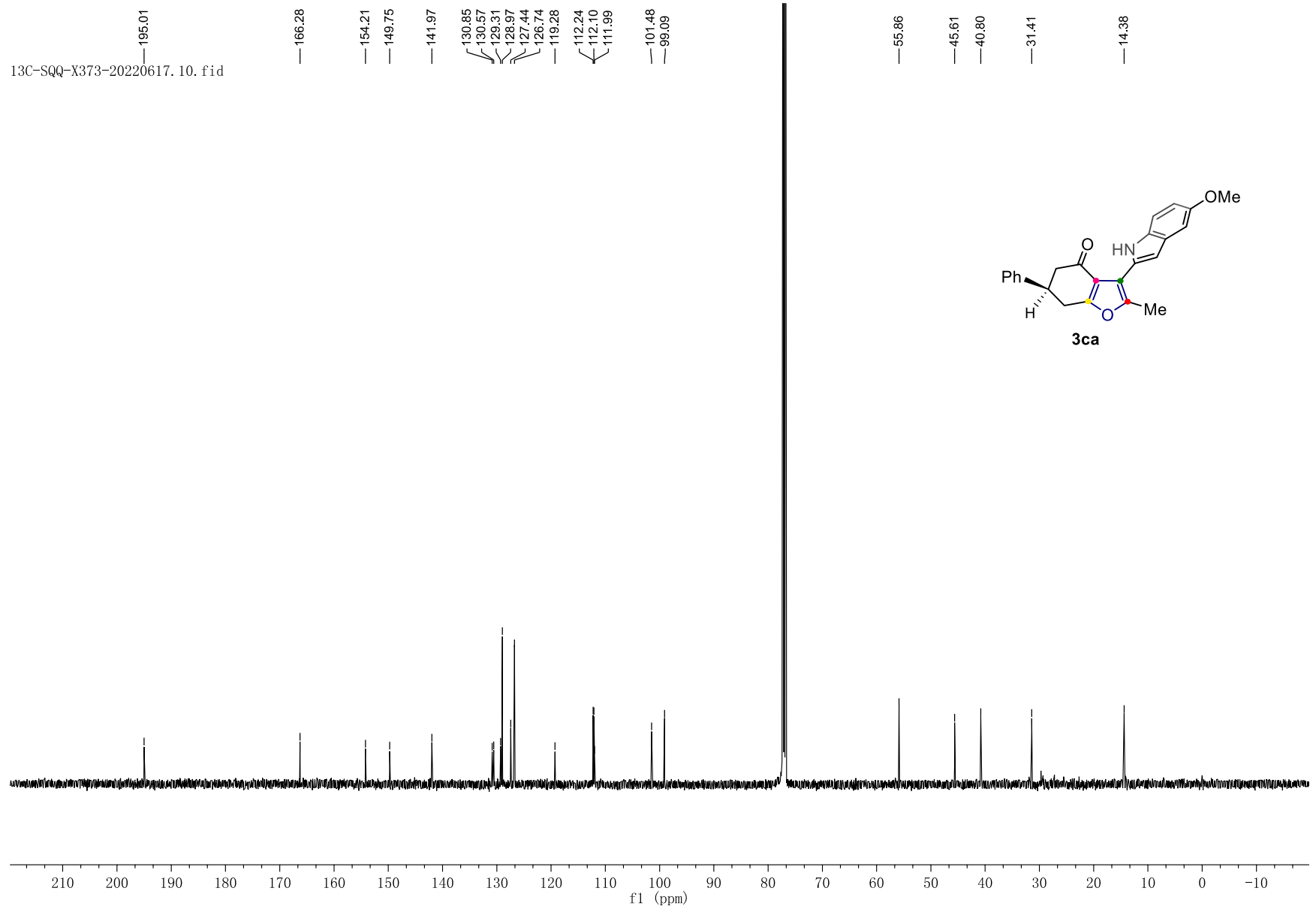
¹³C NMR (500 MHz, CDCl₃) of compound **3ba**



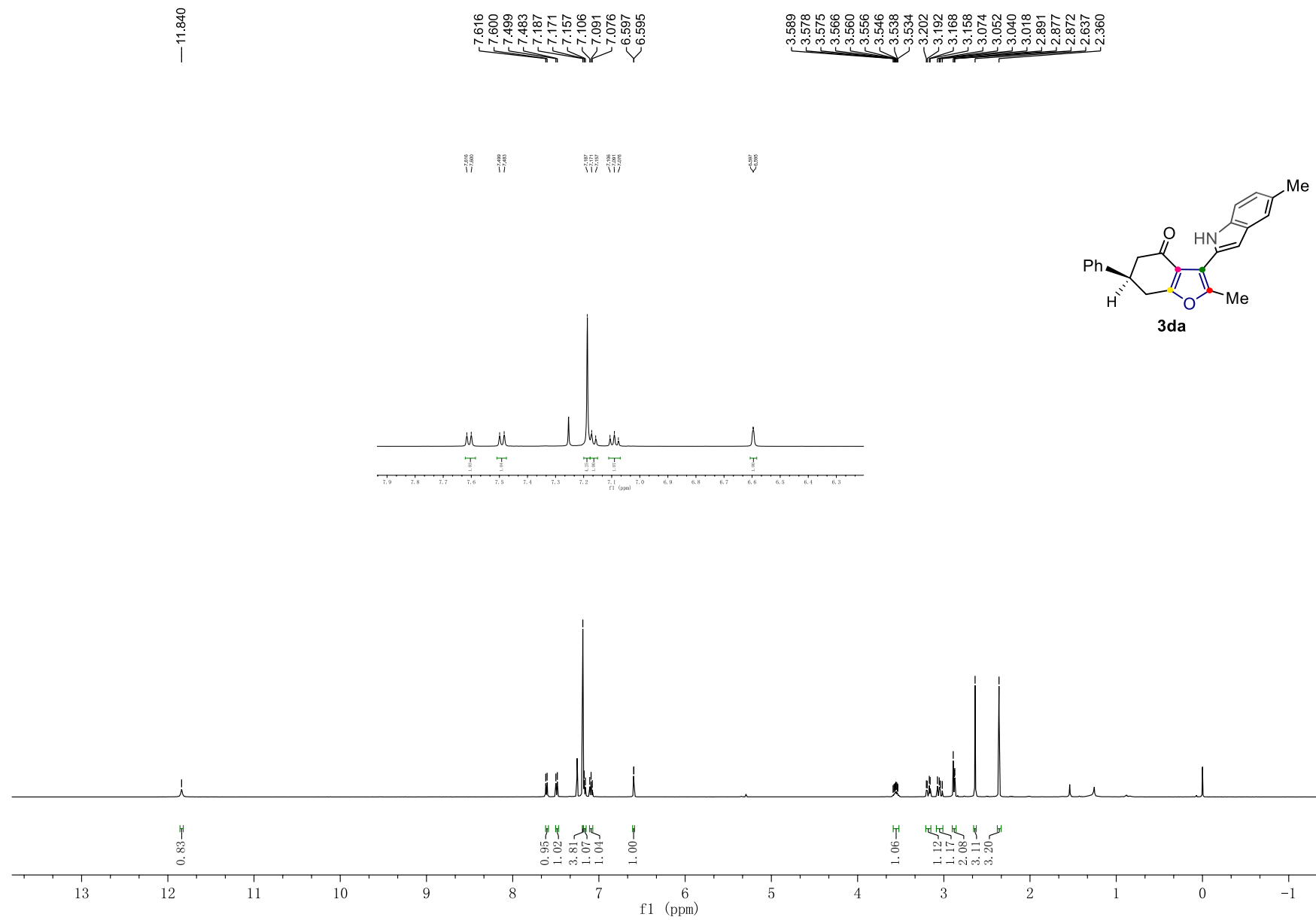
¹H NMR (500 MHz, CDCl₃) of compound **3ca**



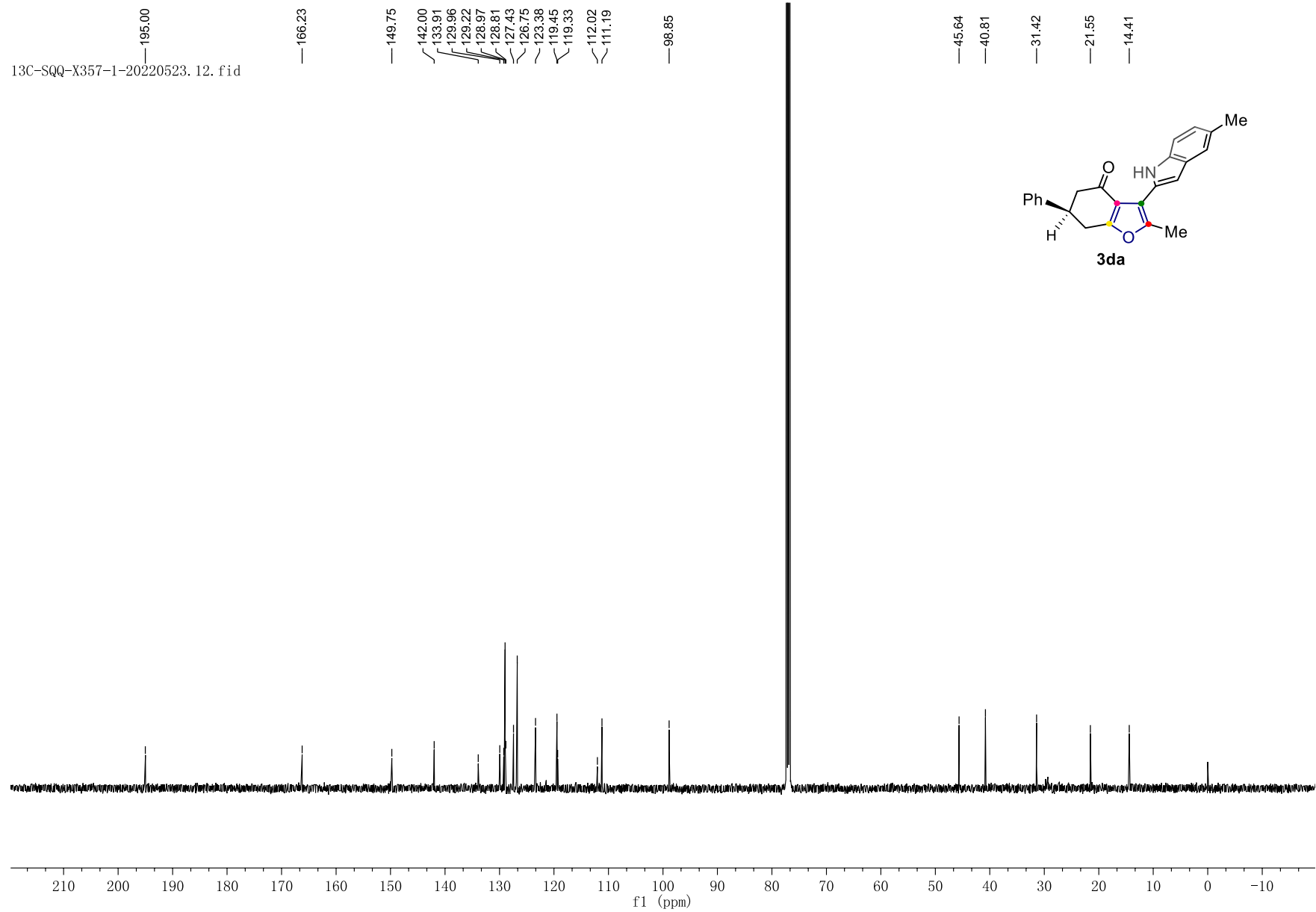
¹³C NMR (500 MHz, CDCl₃) of compound **3ca**



¹H NMR (500 MHz, CDCl₃) of compound **3da**



¹³C NMR (500 MHz, CDCl₃) of compound **3da**

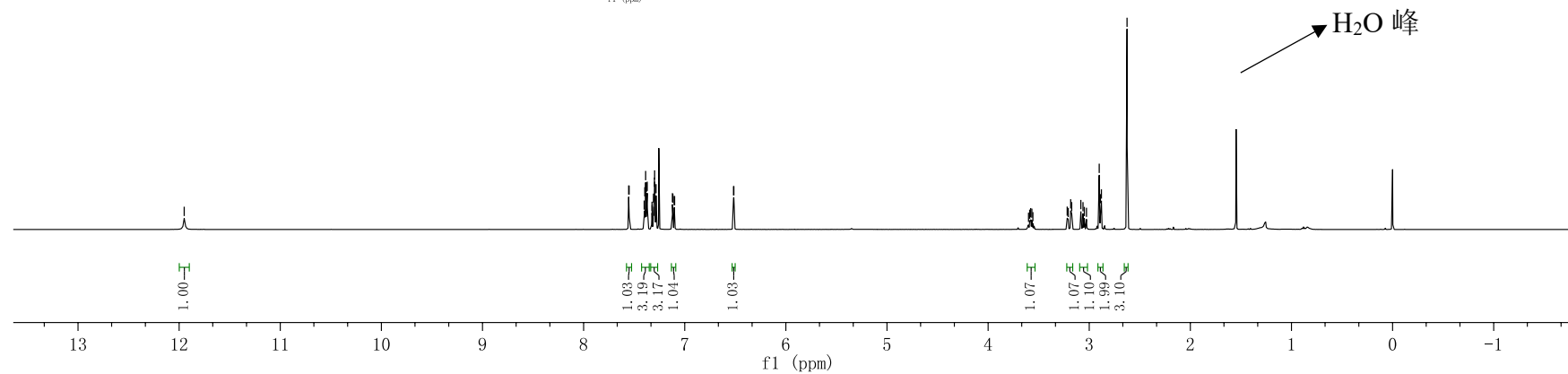
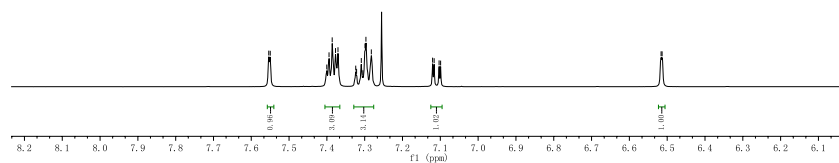
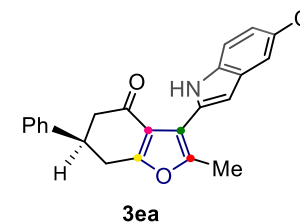


¹H NMR (500 MHz, CDCl₃) of compound **3ea**

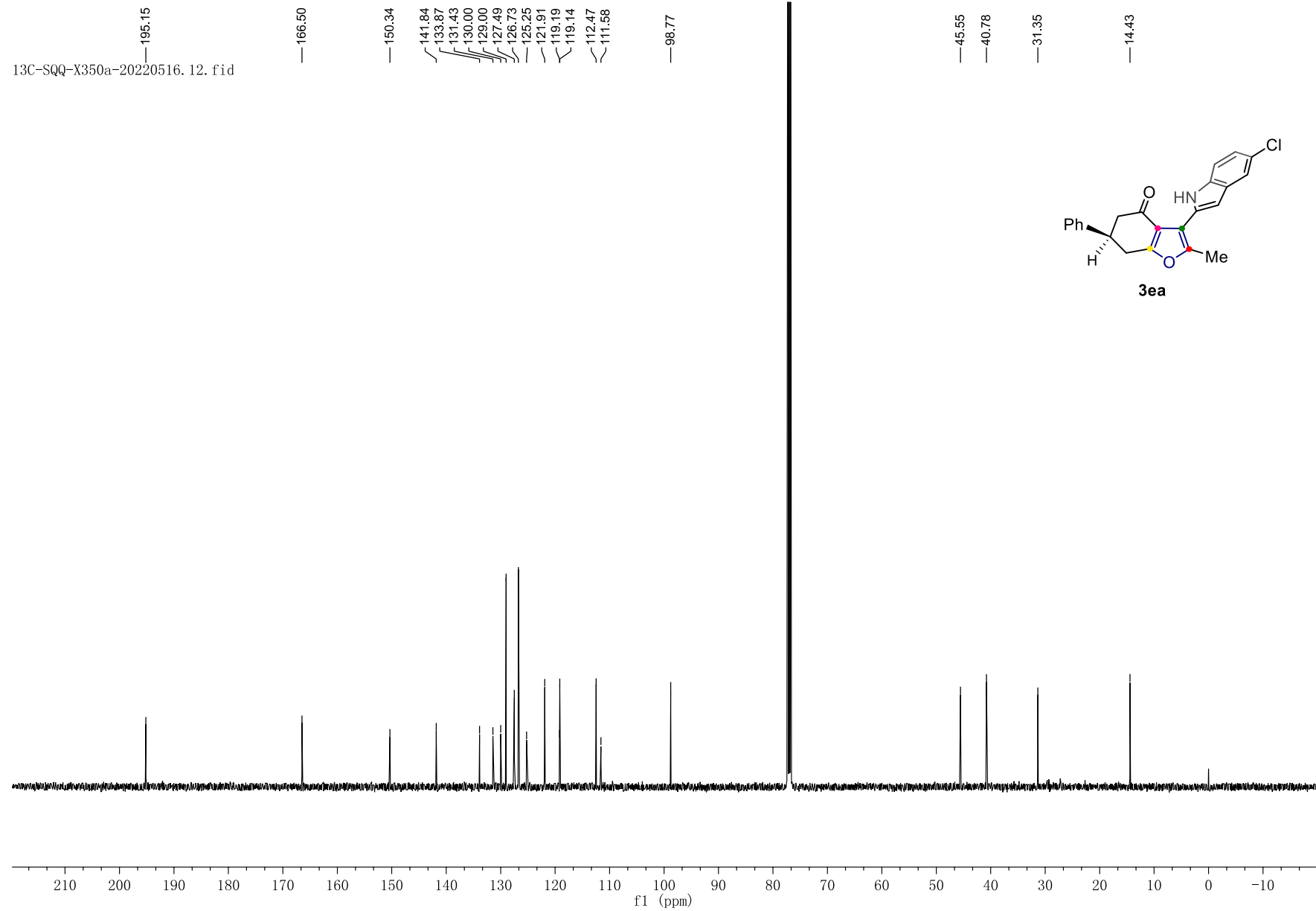
1H-SQQ-X350a-20220516. 10. fid
11.95

7.55, 7.40, 7.39, 7.38, 7.37, 7.32, 7.31, 7.30, 7.30, 7.28, 7.12, 7.10, 6.52, 6.51, 3.60, 3.59, 3.58, 3.57, 3.56, 3.22, 3.21, 3.18, 3.17, 3.08, 3.06, 3.05, 3.03, 2.90, 2.89, 2.88, 2.63

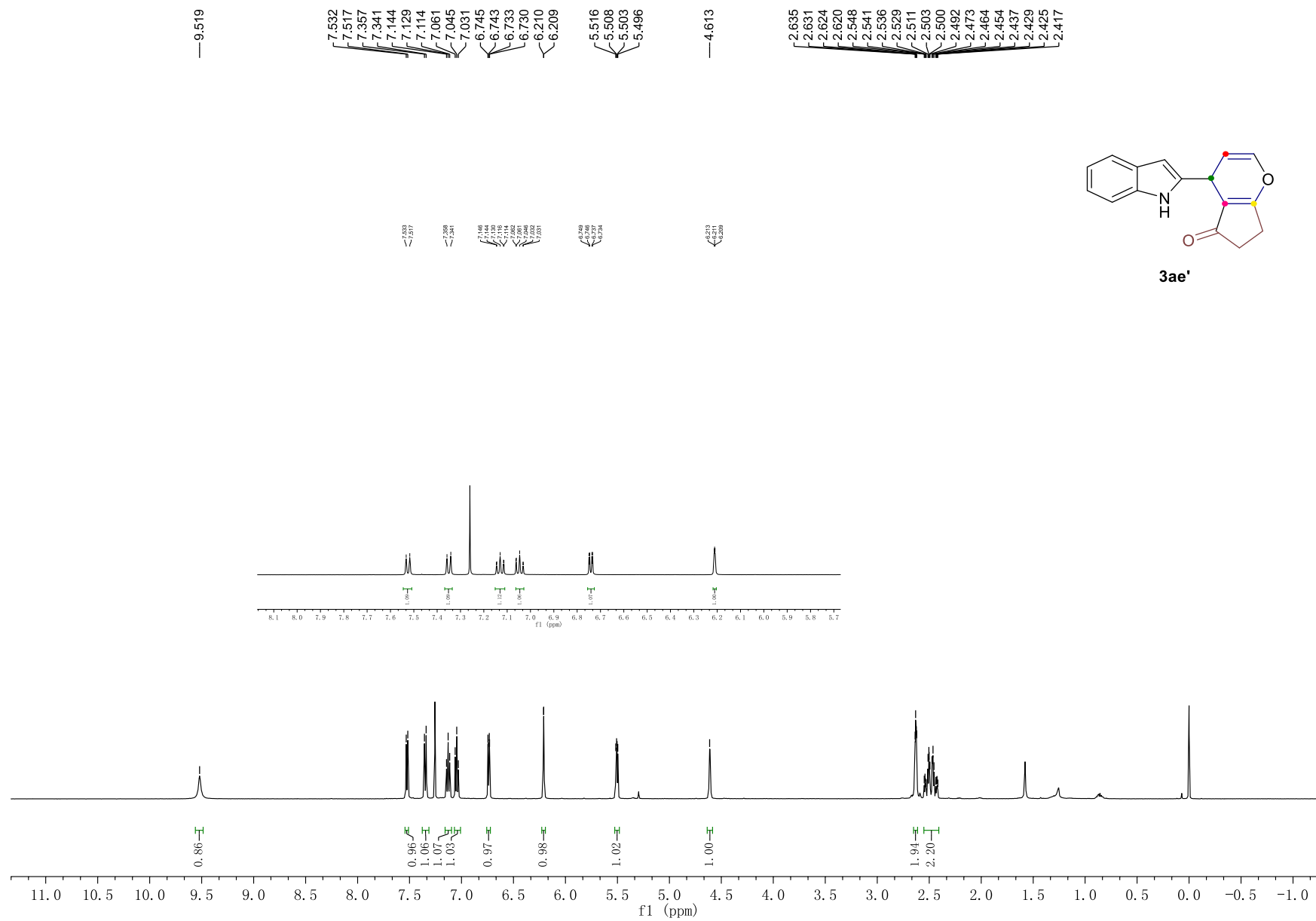
7.554, 7.400, 7.394, 7.377, 7.374, 7.324, 7.322, 7.310, 7.306, 7.297, 7.283, 7.100, 7.103, 6.514



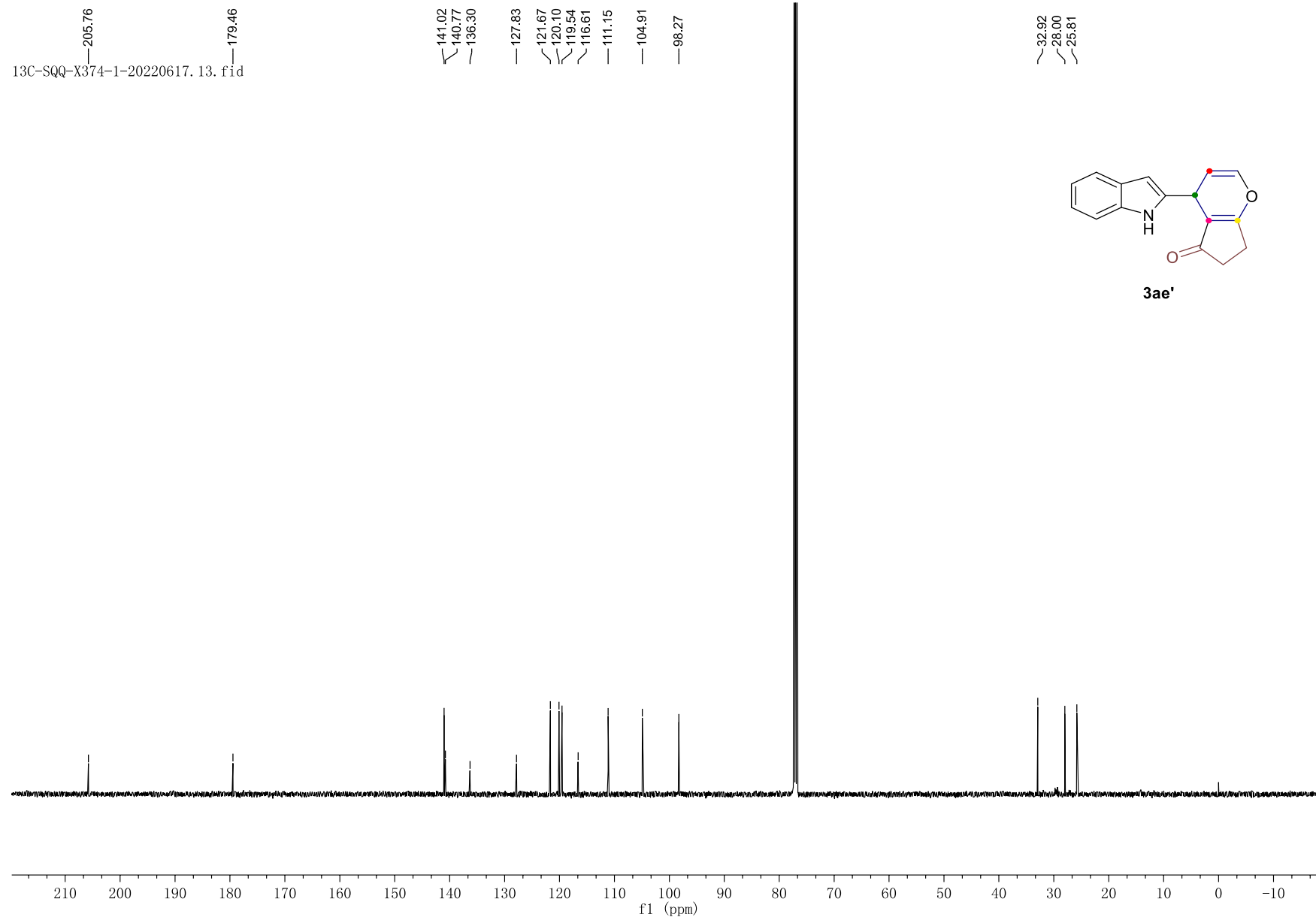
¹³C NMR (500 MHz, CDCl₃) of compound **3ea**



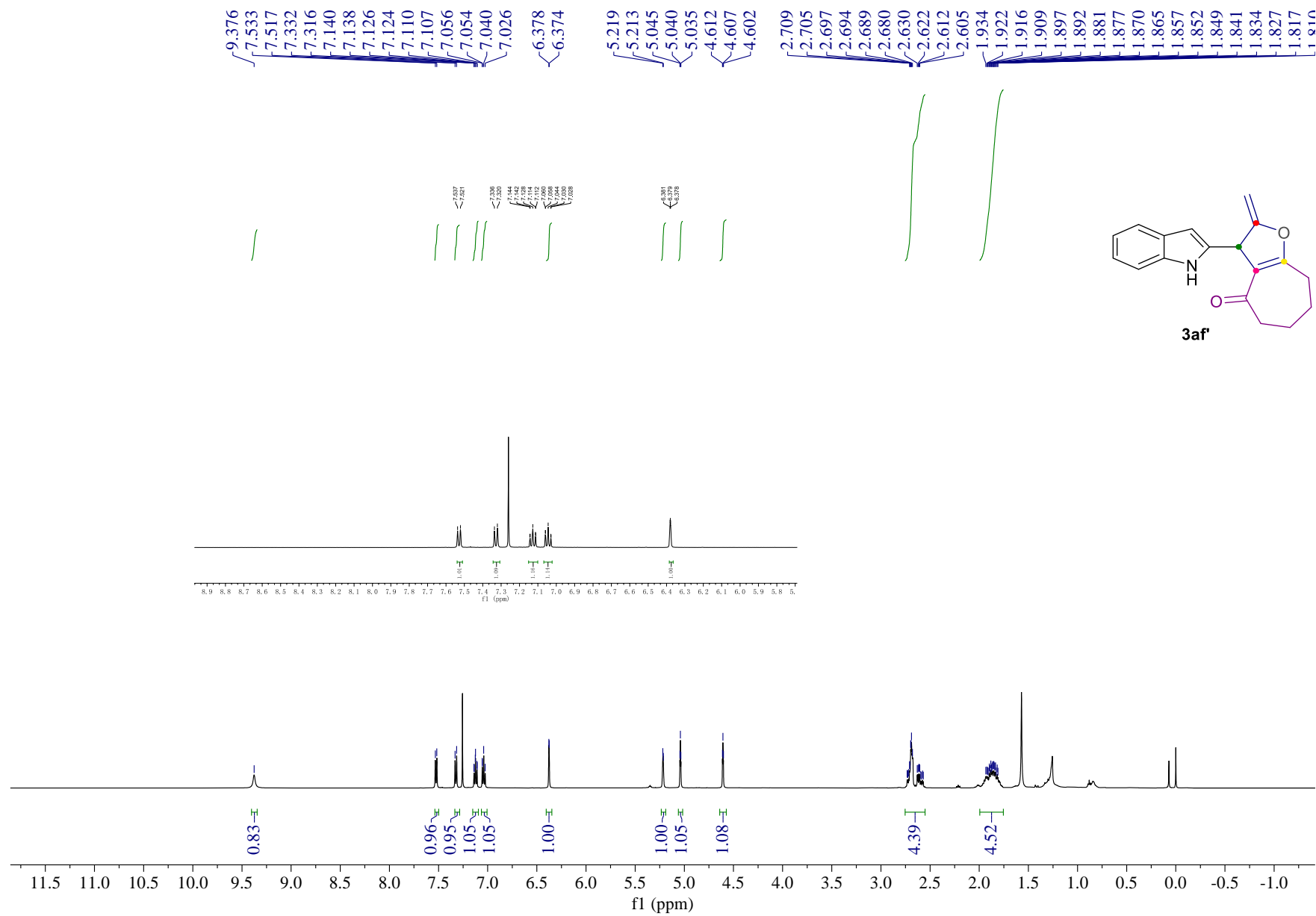
¹H NMR (500 MHz, CDCl₃) of compound **3ae'**



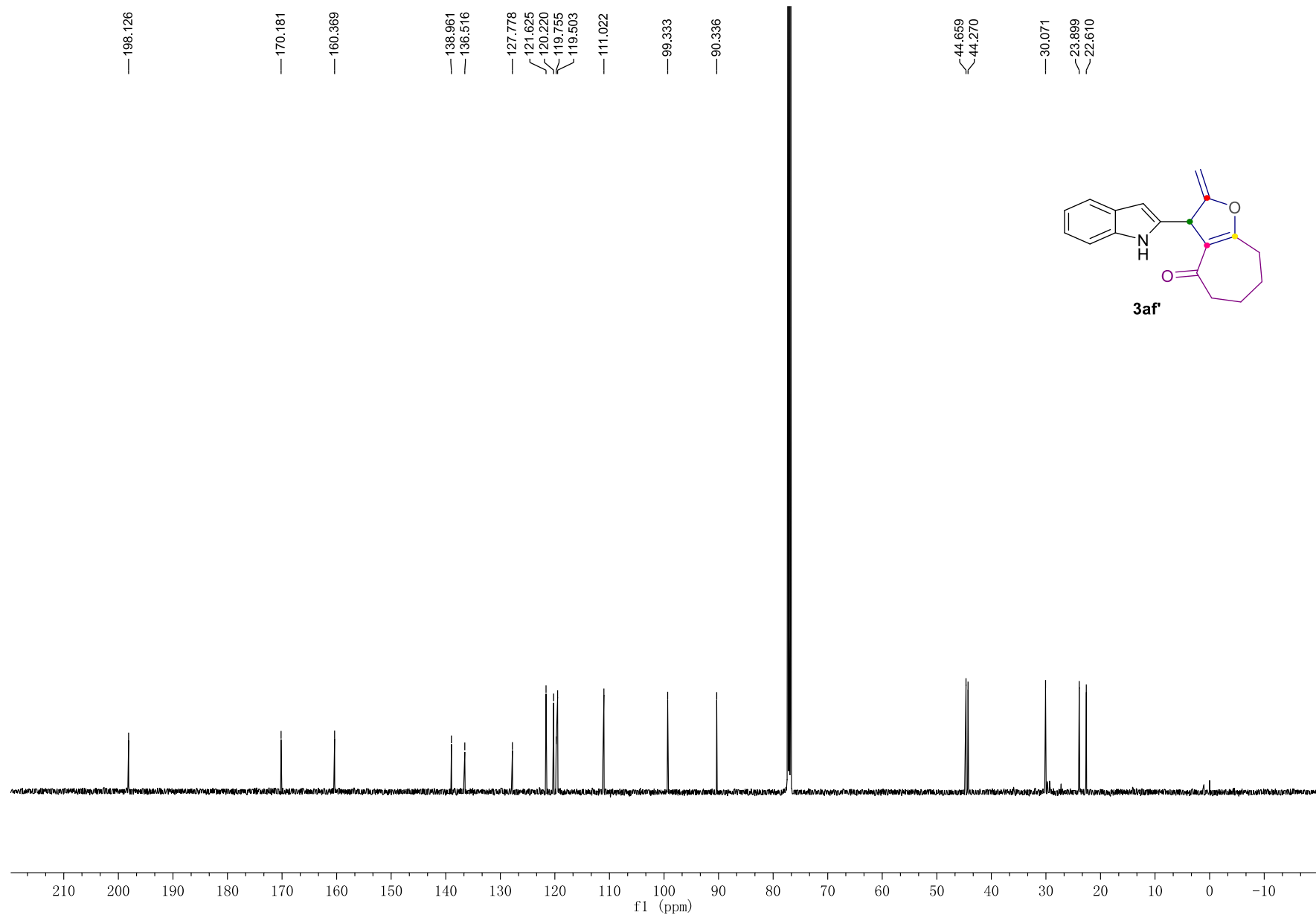
¹³C NMR (500 MHz, CDCl₃) of compound **3ae'**



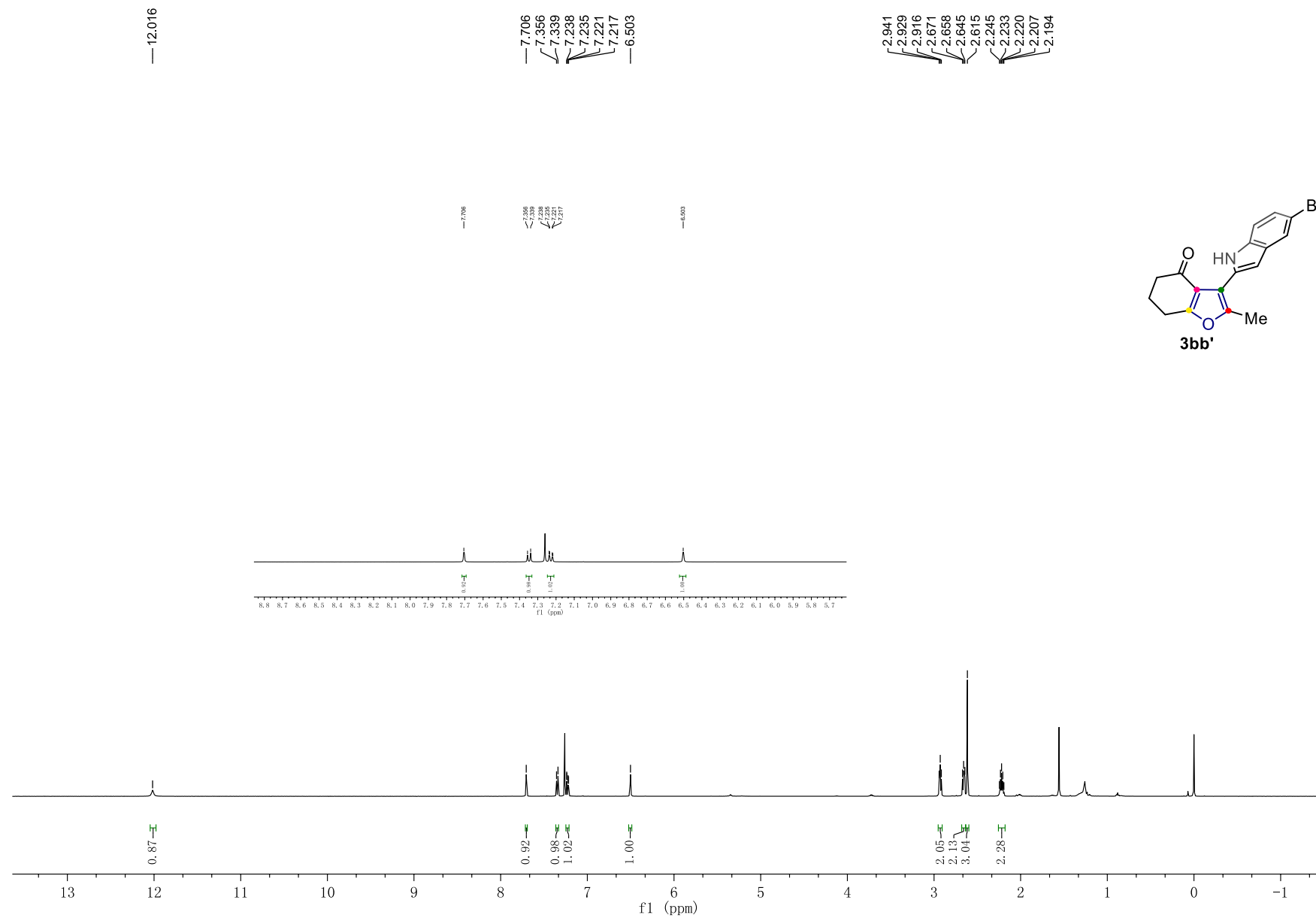
¹H NMR (500 MHz, CDCl₃) of compound **3af**



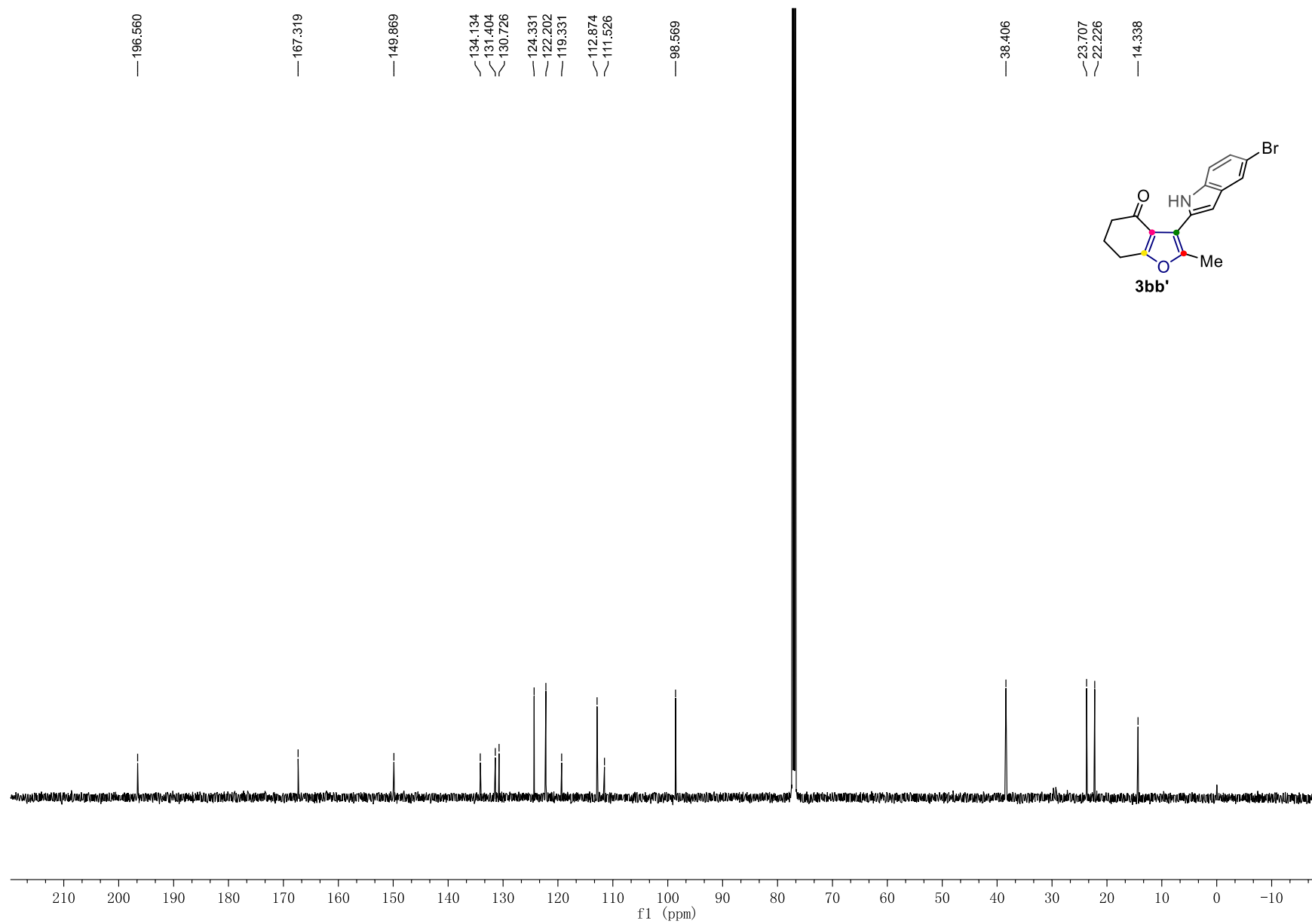
^{13}C NMR (500 MHz, CDCl_3) of compound **3af**



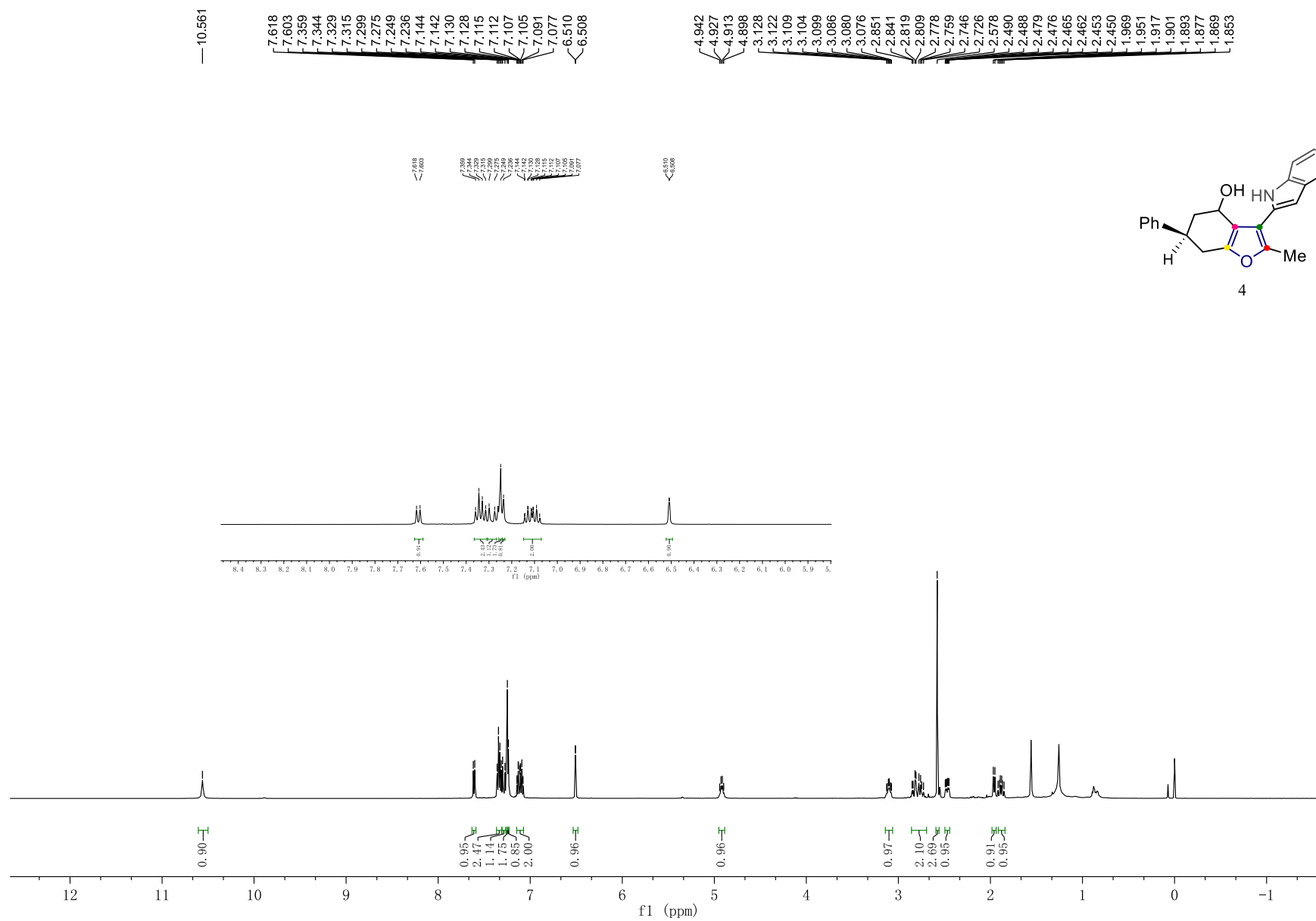
^1H NMR (500 MHz, CDCl_3) of compound **3bb'**



^{13}C NMR (500 MHz, CDCl_3) of compound **3bb'**



¹H NMR (500 MHz, CDCl₃) of compound **4**



¹³C NMR (500 MHz, CDCl₃) of compound **4**

149.988
148.552
143.915
135.764
131.604
128.966
128.821
126.883
121.298
119.833
119.671
118.470
113.093
111.072

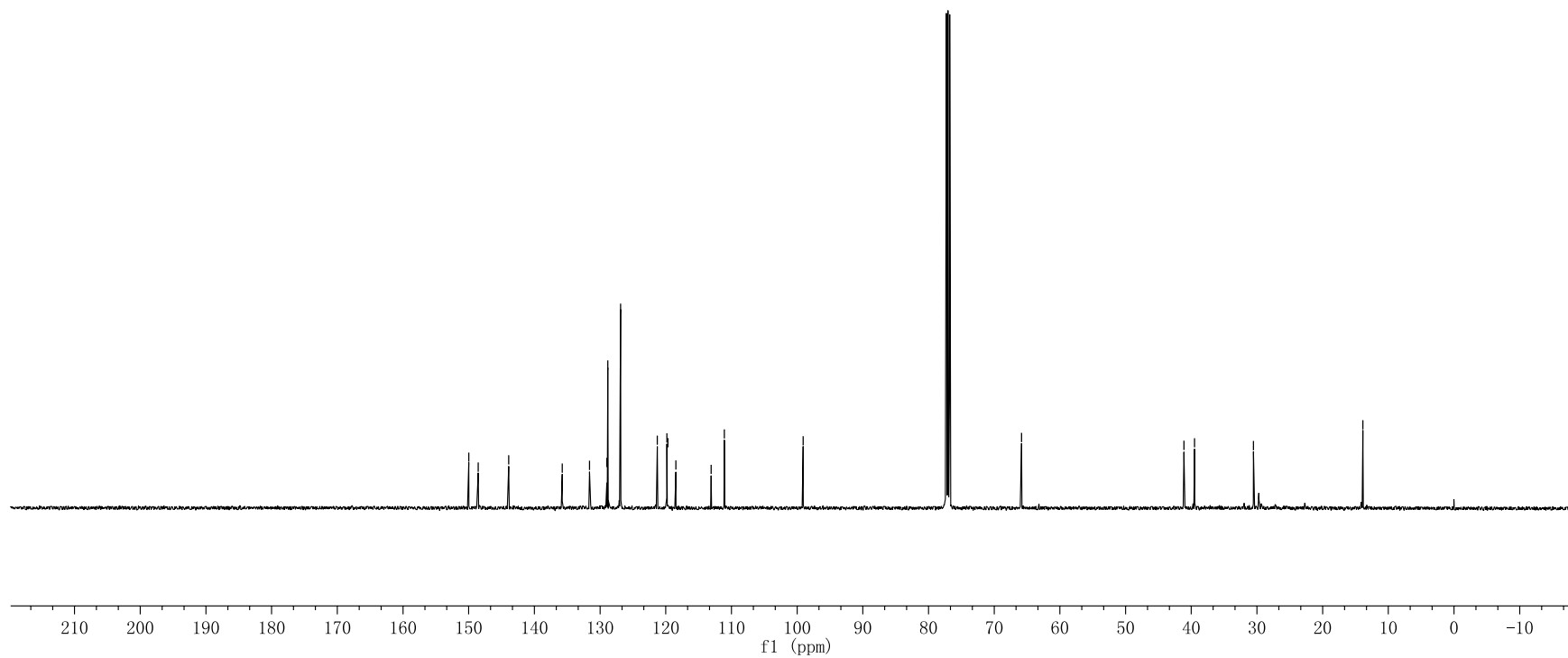
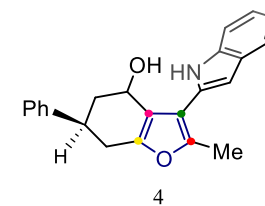
99.093

65.832

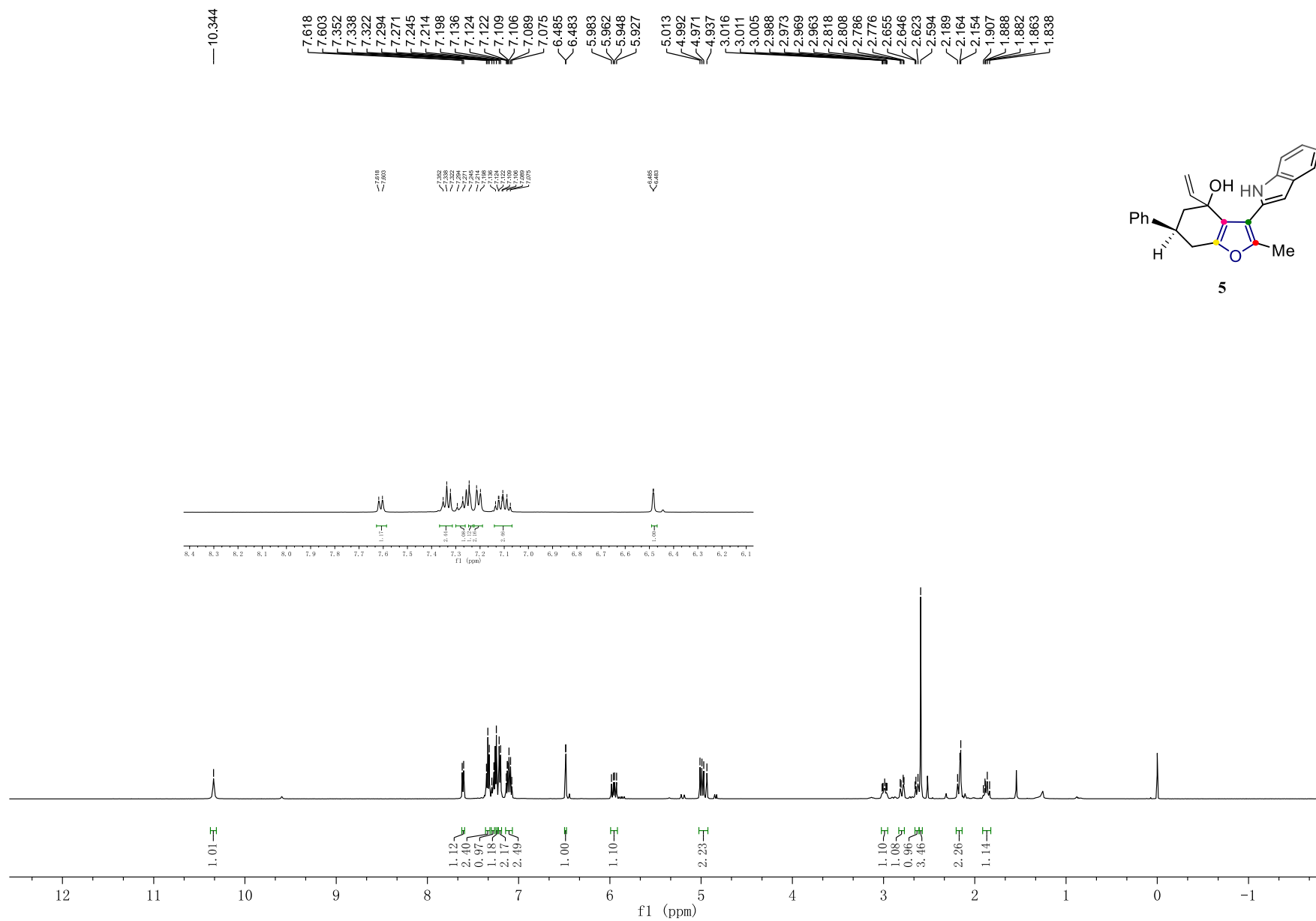
41.111
39.496

30.528

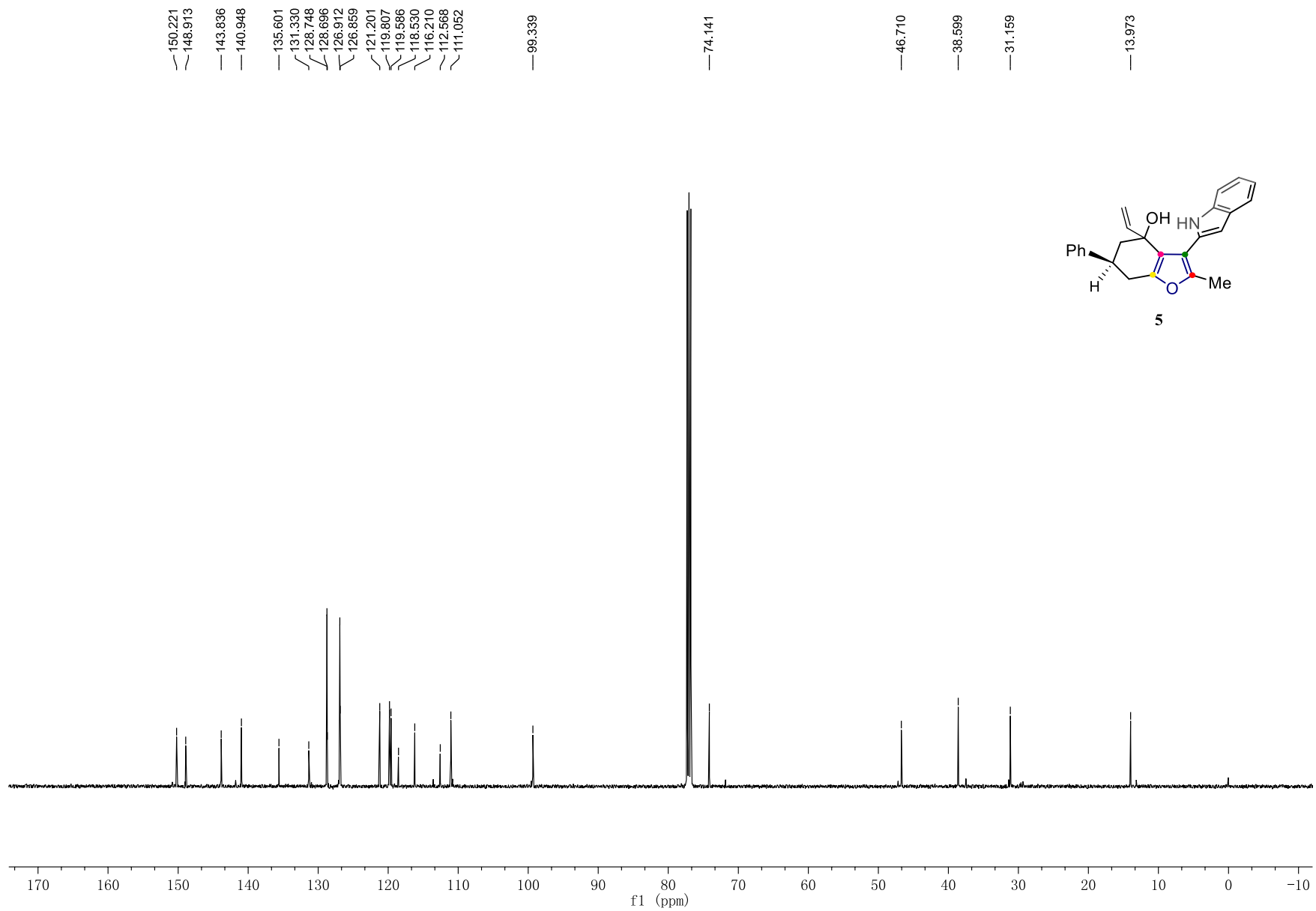
13.868



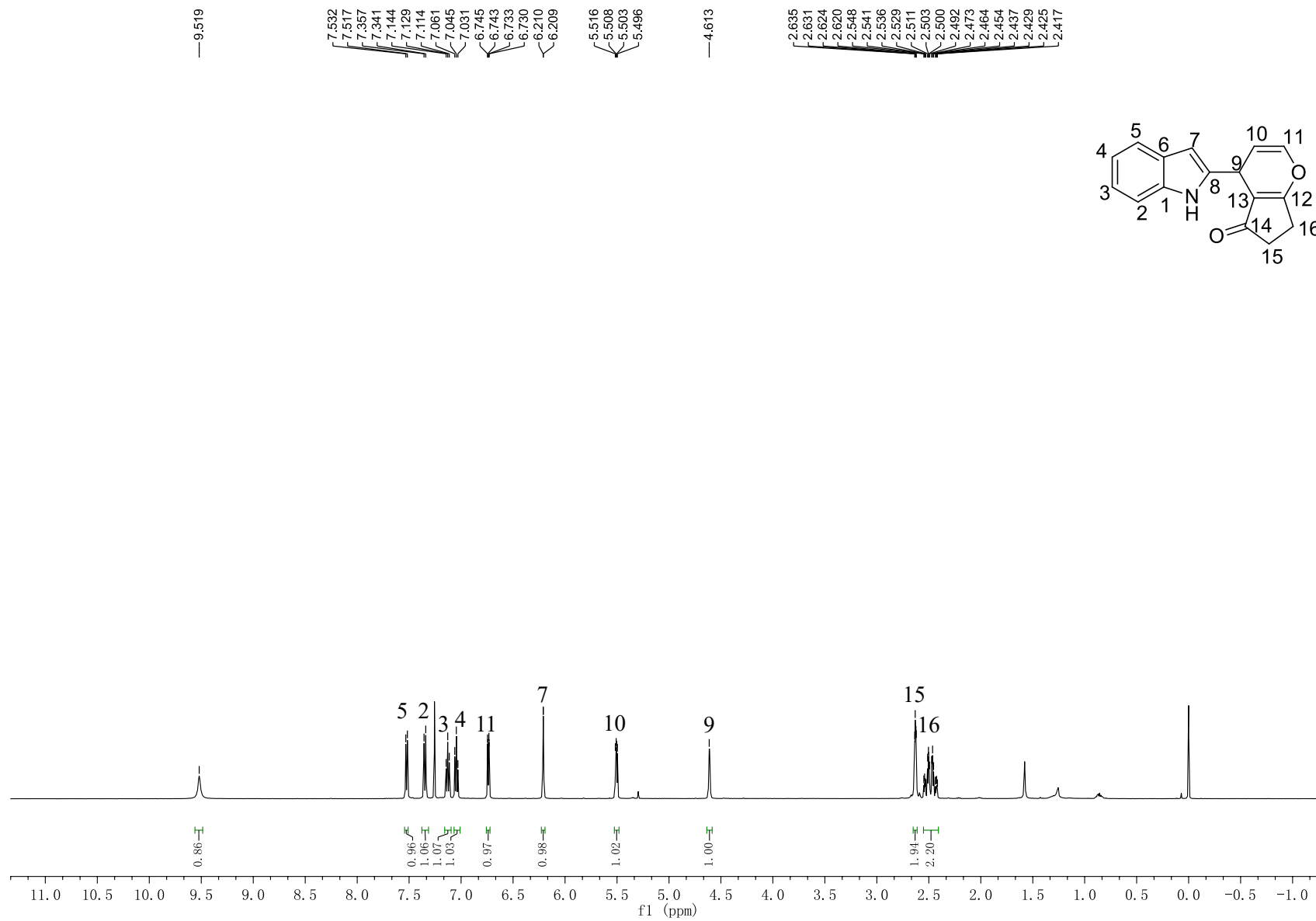
¹H NMR (500 MHz, CDCl₃) of compound **5**



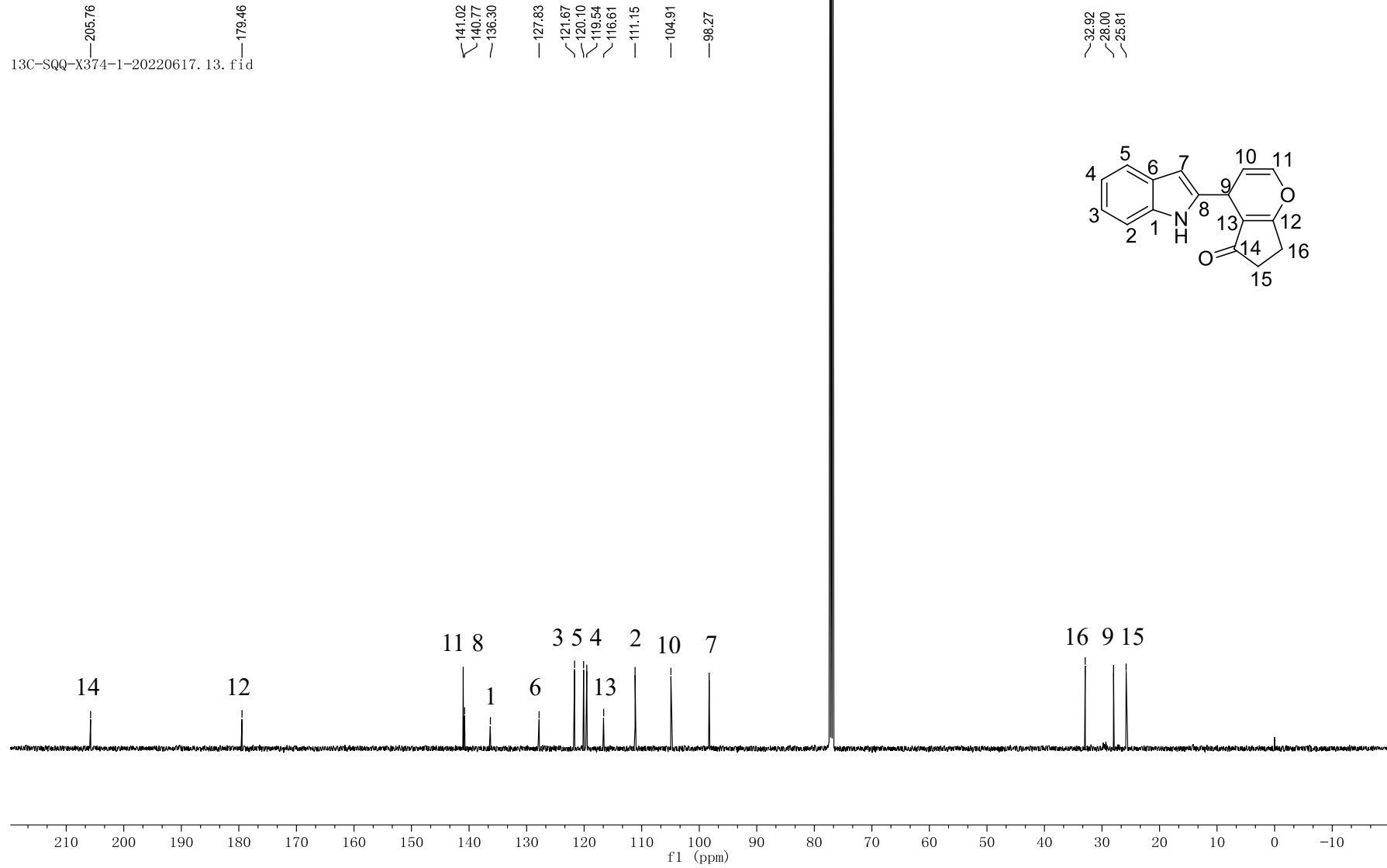
¹³C NMR (500 MHz, CDCl₃) of compound **5**



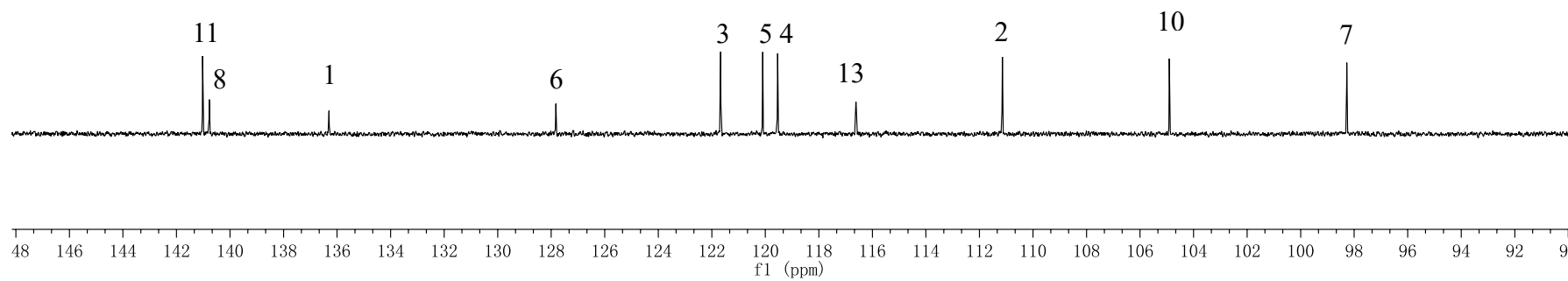
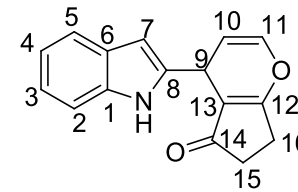
¹H NMR (500 MHz, CDCl₃) of compound **3ae'**



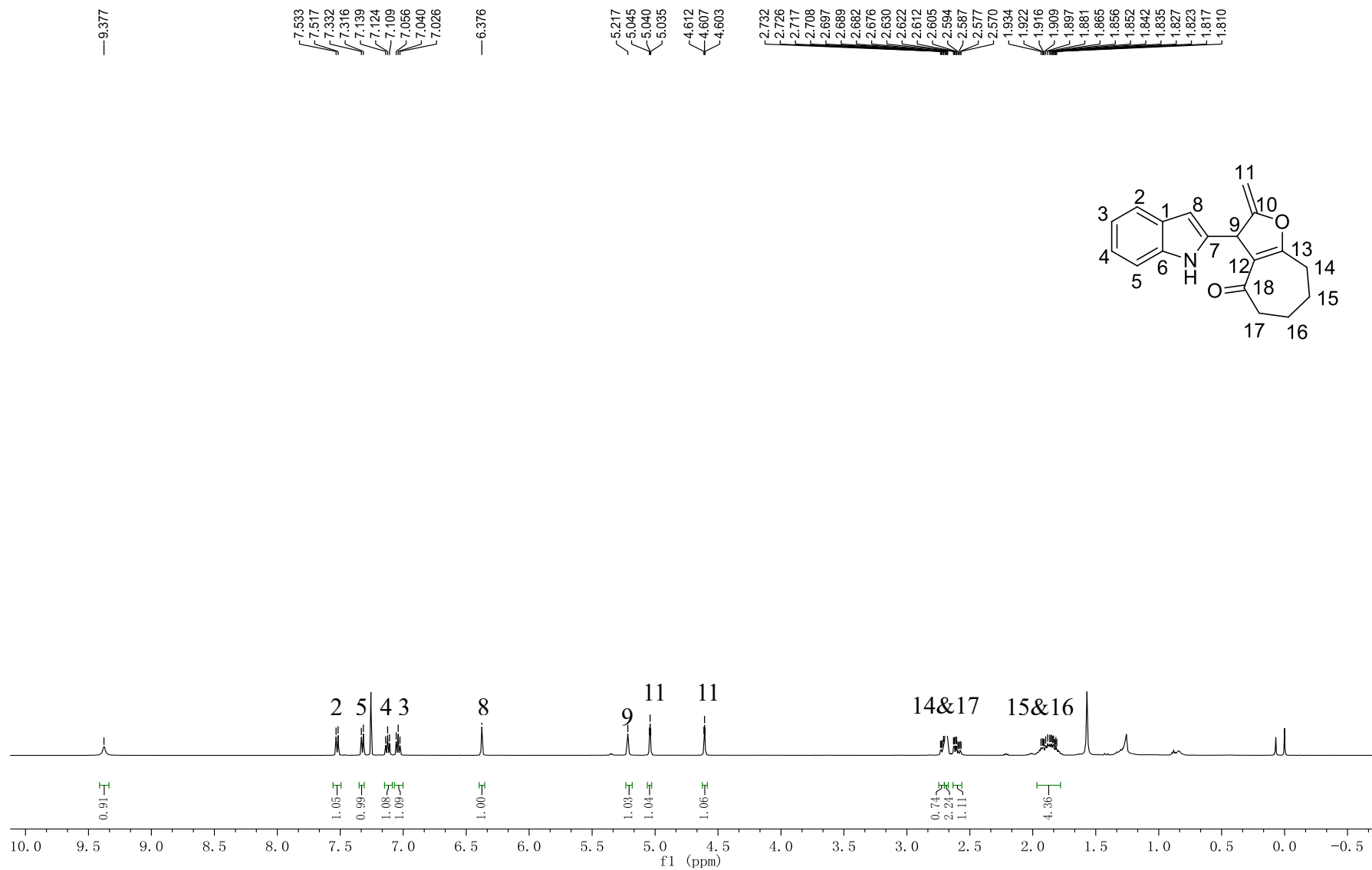
¹³C NMR (500 MHz, CDCl₃) of compound **3ae'**



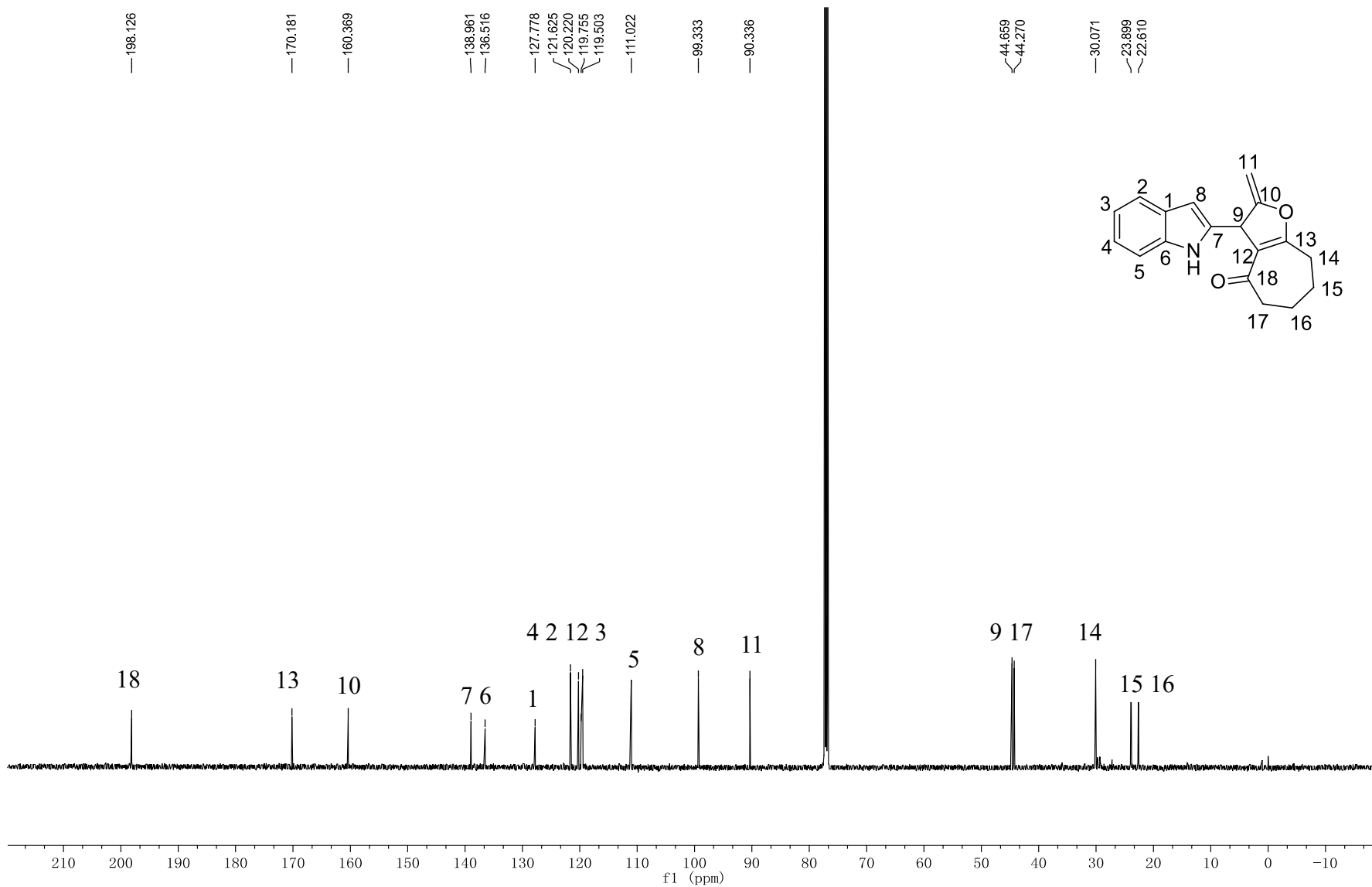
^{13}C NMR (500 MHz, CDCl_3) of compound **3ae'**



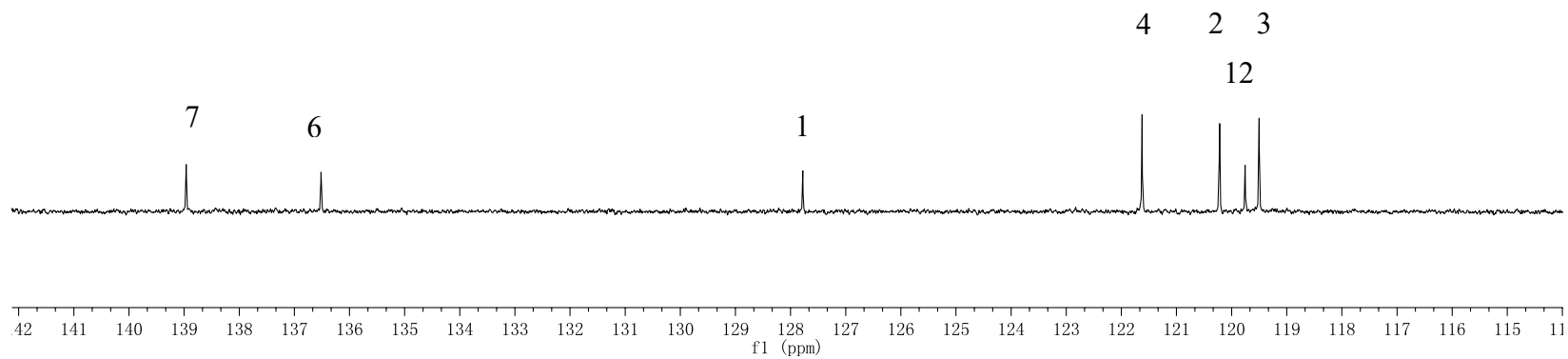
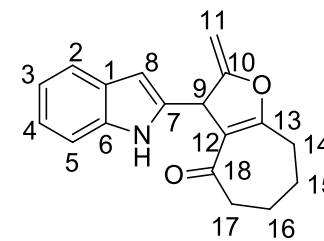
^1H NMR (500 MHz, CDCl_3) of compound **3af**



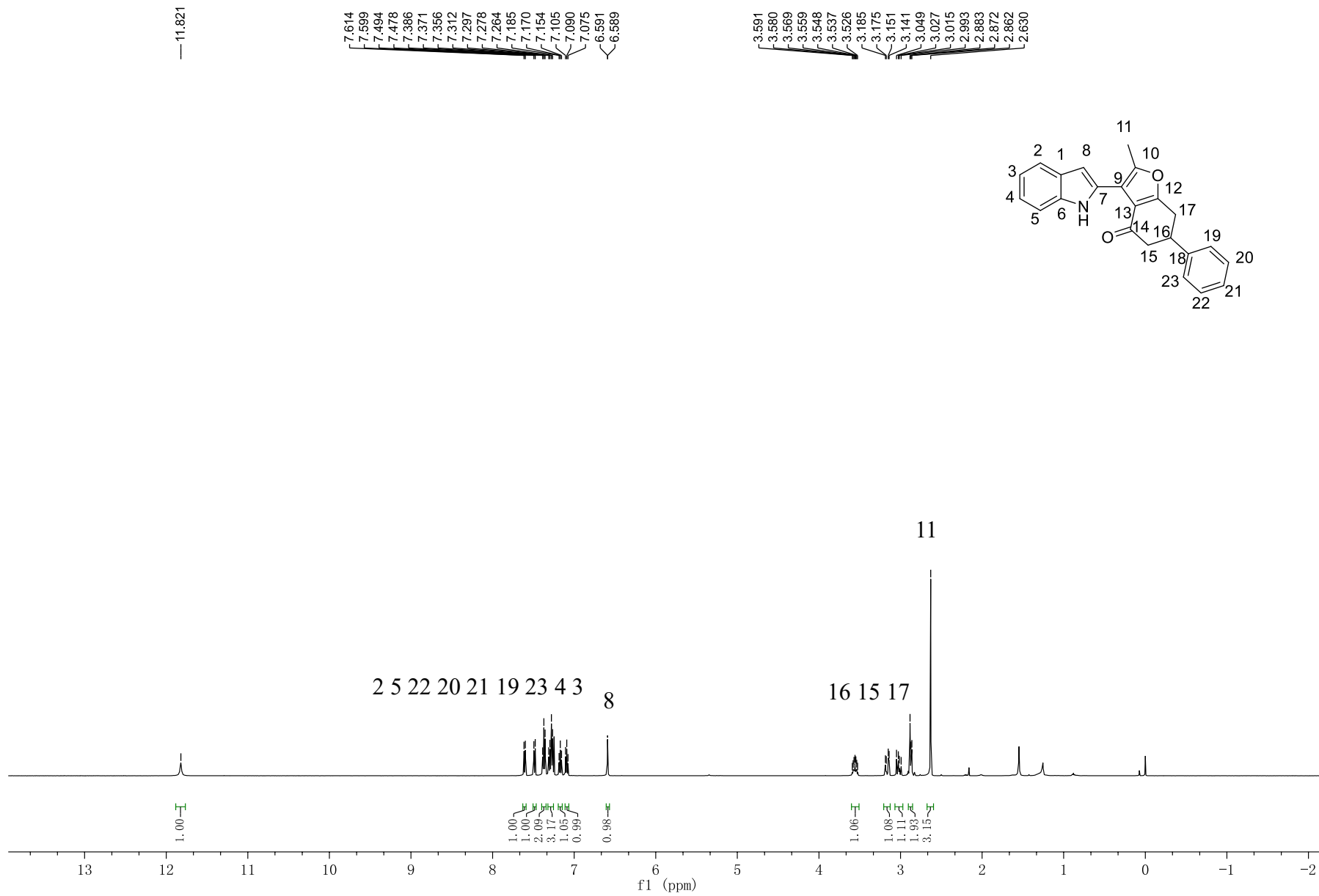
¹³C NMR (500 MHz, CDCl₃) of compound **3af**



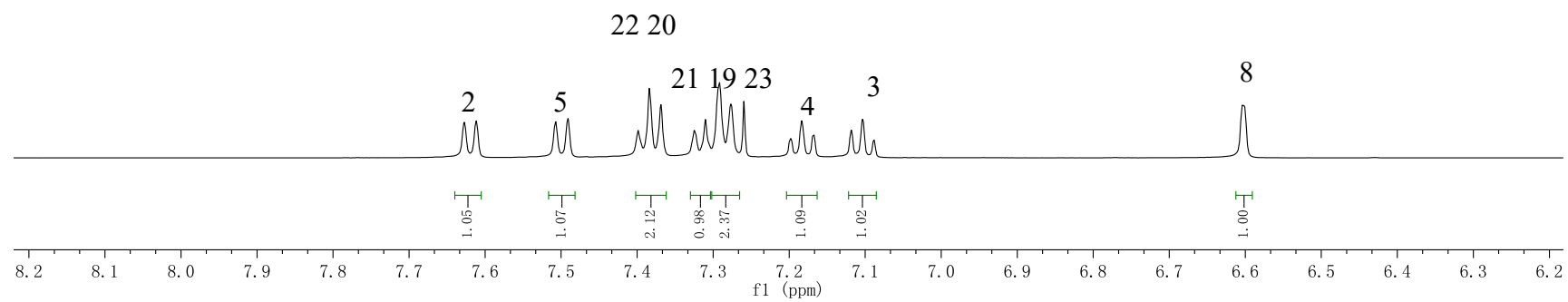
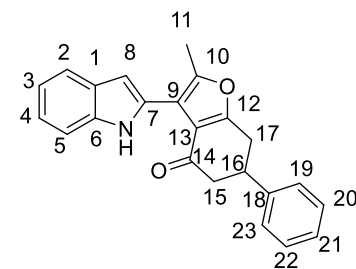
^{13}C NMR (500 MHz, CDCl_3) of compound **3af**



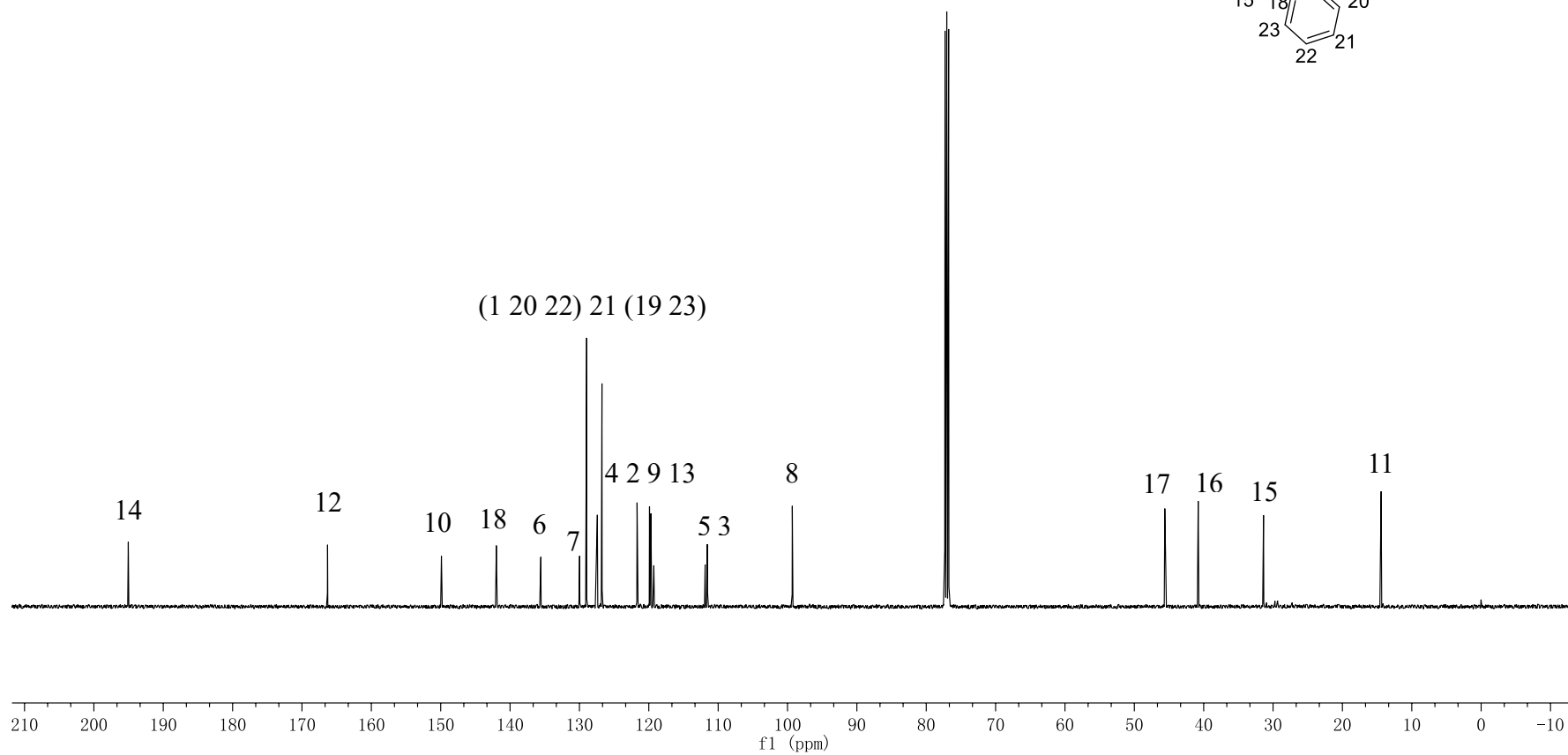
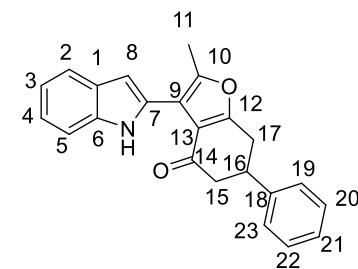
¹H NMR (500 MHz, CDCl₃) of compound **3aa**



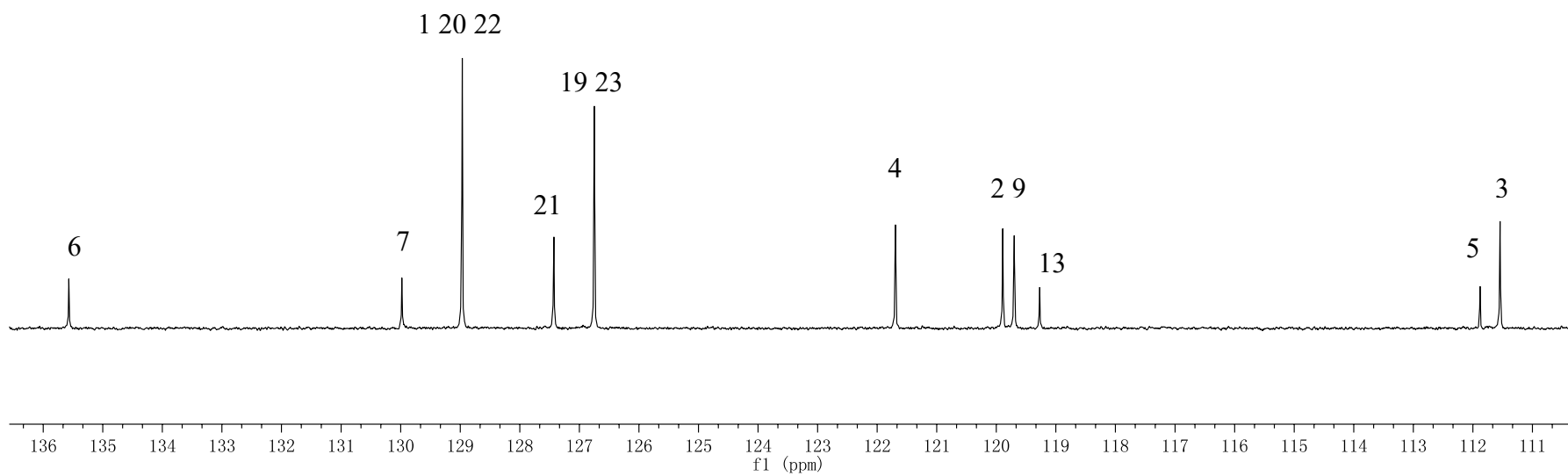
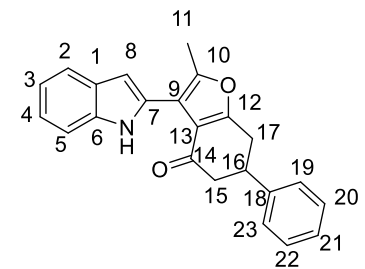
¹H NMR (500 MHz, CDCl₃) of compound **3aa**



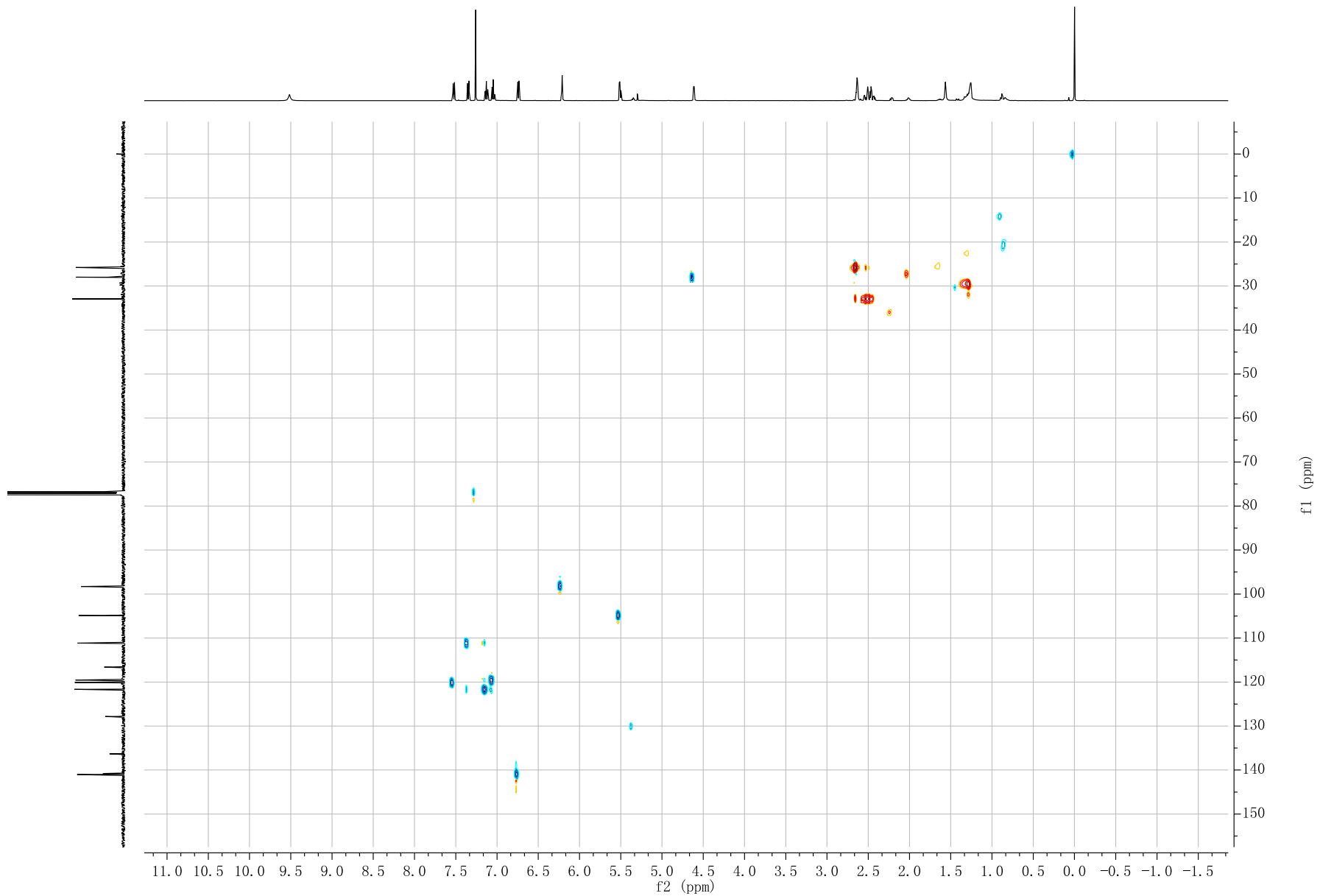
^{13}C NMR (500 MHz, CDCl_3) of compound **3aa**



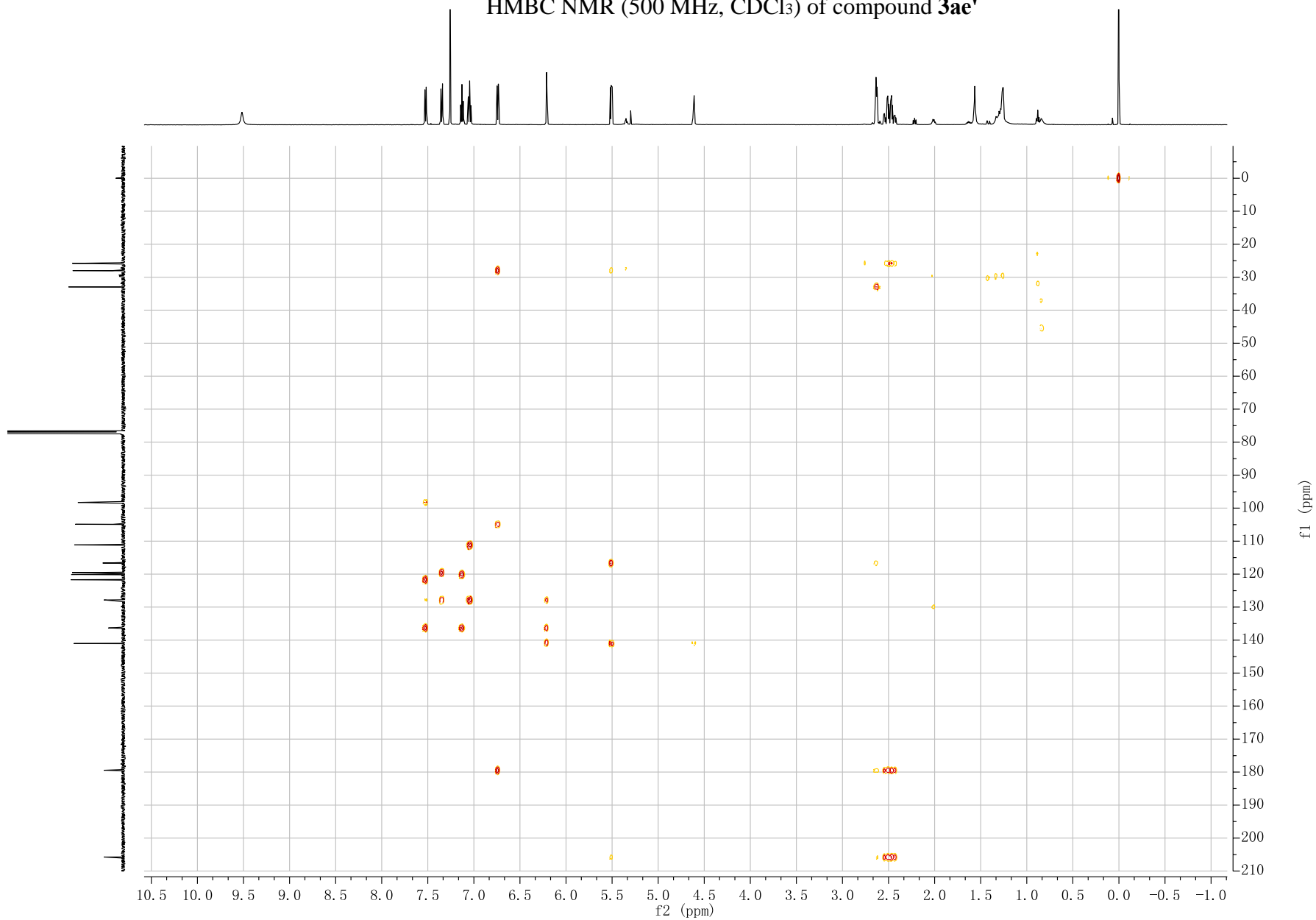
^{13}C NMR (500 MHz, CDCl_3) of compound **3aa**



HSQC NMR (500 MHz, CDCl₃) of compound **3ae'**



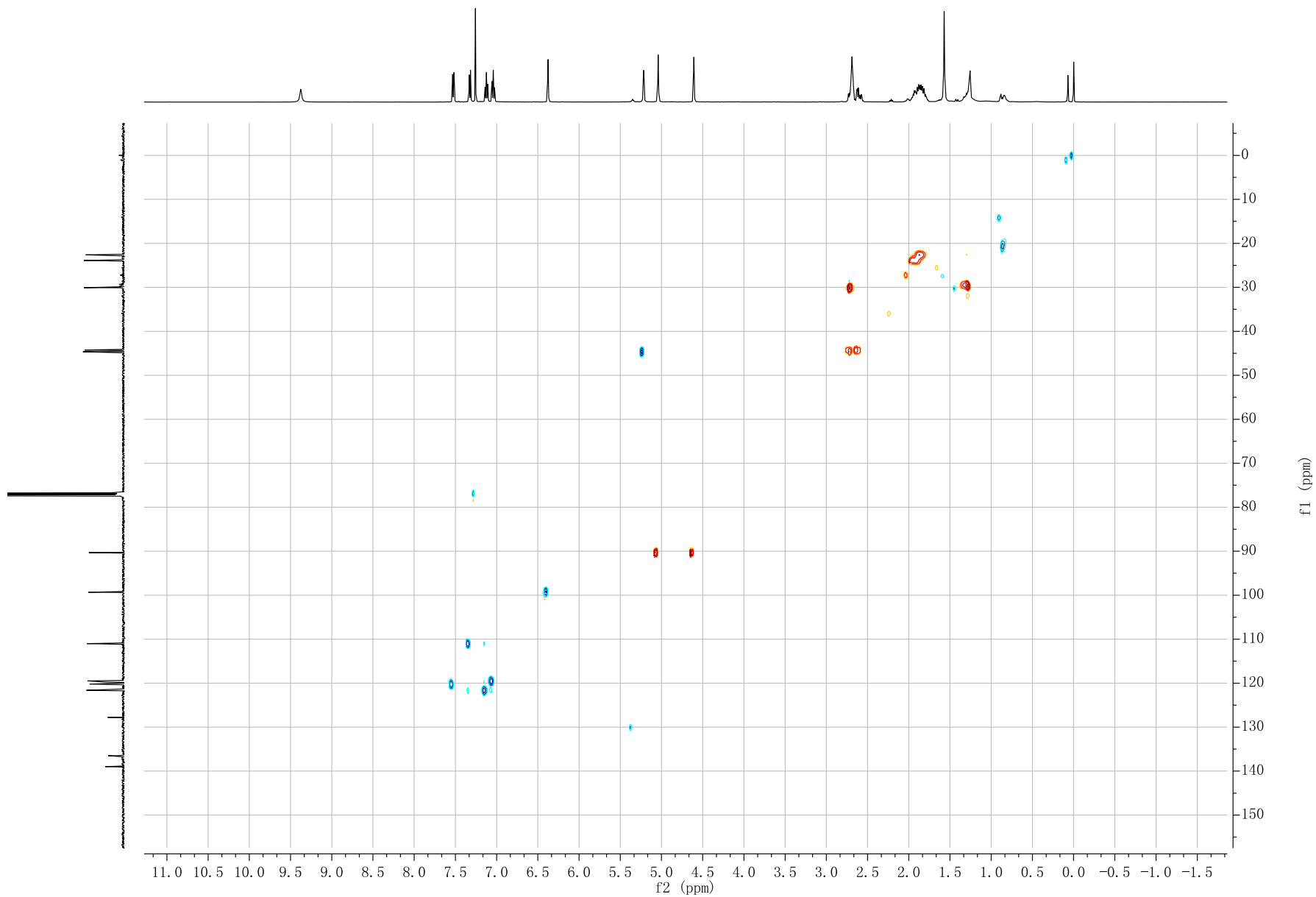
HMBC NMR (500 MHz, CDCl₃) of compound **3ae'**



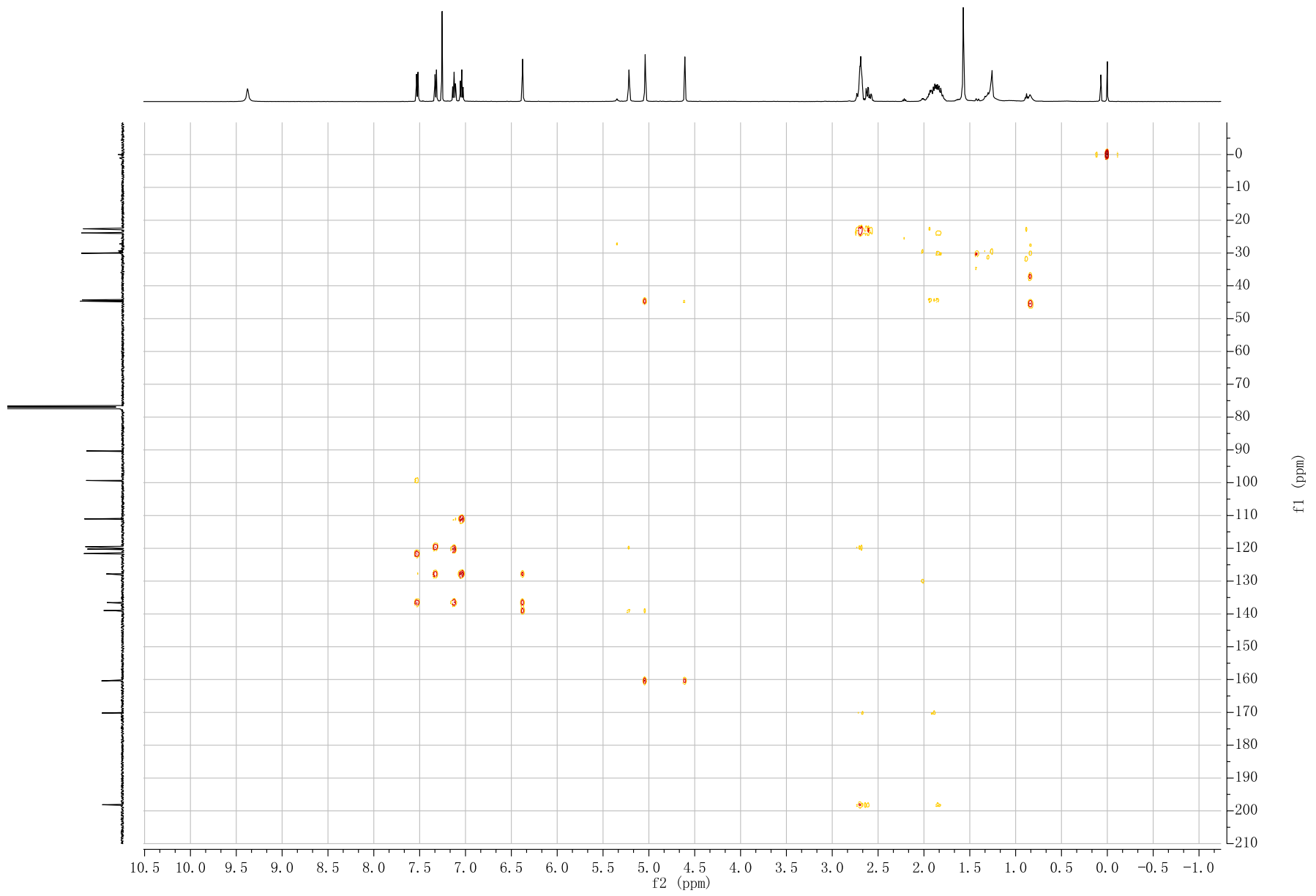
COSY NMR (500 MHz, CDCl₃) of compound **3ae'**



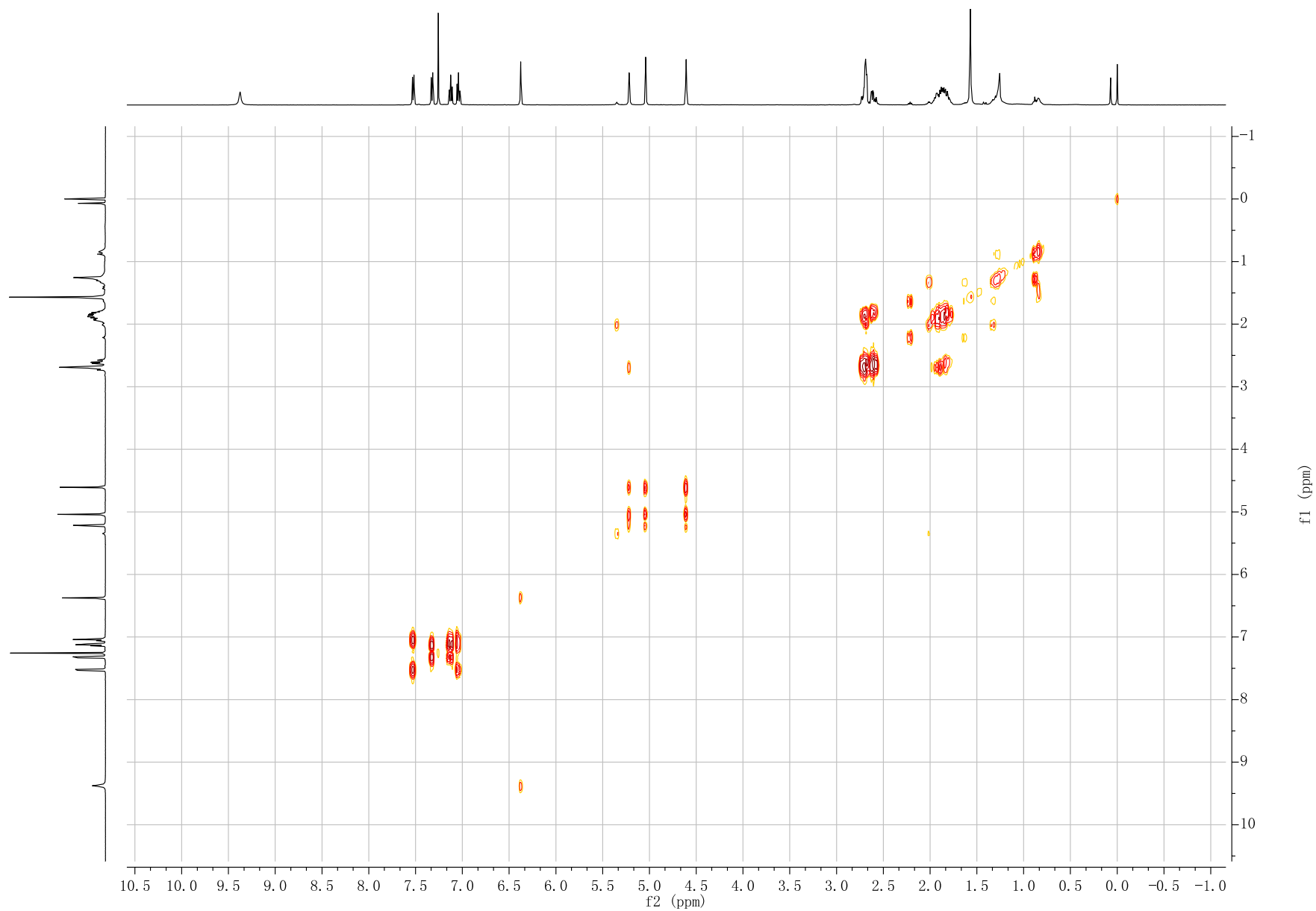
HSQC NMR (500 MHz, CDCl₃) of compound **3af**



HMBC NMR (500 MHz, CDCl₃) of compound **3af**



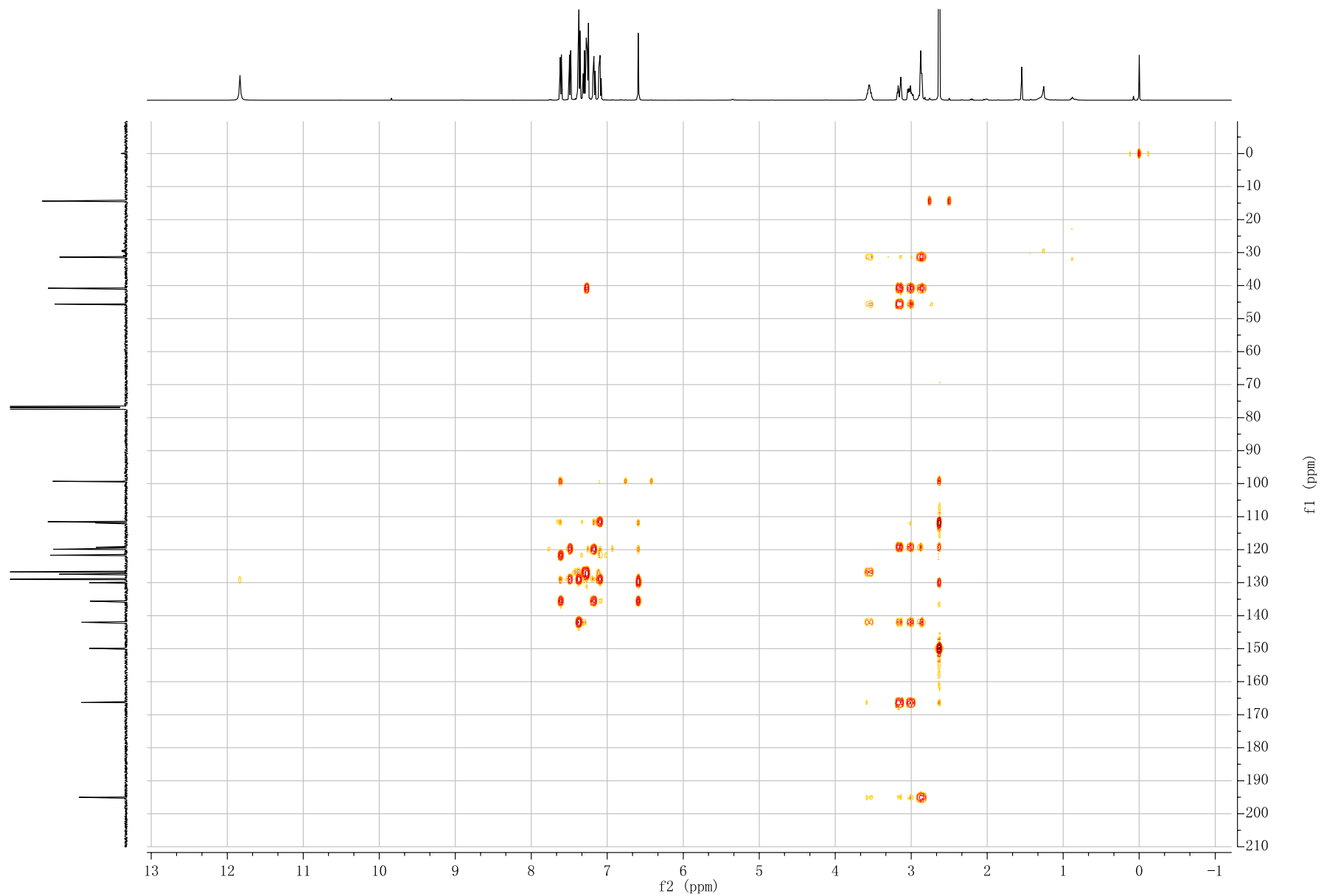
COSY NMR (500 MHz, CDCl₃) of compound **3af**



HSQC NMR (500 MHz, CDCl₃) of compound **3aa**



HMBC NMR (500 MHz, CDCl₃) of compound **3aa**



COSY NMR (500 MHz, CDCl₃) of compound **3aa**

