Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Unprecedented chemoselective Ru(III)-catalyzed [3+2] annulation of enaminones with iodonium ylides for the synthesis of functionalized 3a,7a-dihydroxy hexahydro-4*H*-indol-4-ones.

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1. General information.

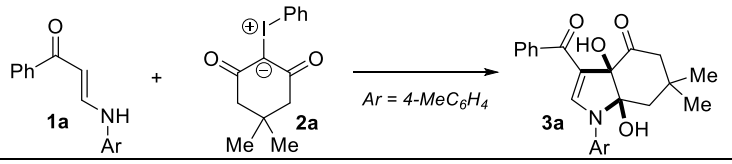
All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a DRX600 (^{1}H: 600 MHz, ^{13}C: 150 MHz), chemical shifts (δ) are expressed in ppm, and J values are given in Hz, and deuterated $CDCl_3$ and DMSO-d_6 were used as solvent. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/MS TOF instrument.

All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

Enaminones **1** were prepared according to the literature[1], iodonium ylides **2** were prepared according to the literature[2]. Other reagents were purchased from Energy Chemical and Adamas-beta®.

2. Optimization of reaction conditions.

Table S1. Optimization of the cascade [3+2] cyclization reaction conditions.[a,b]

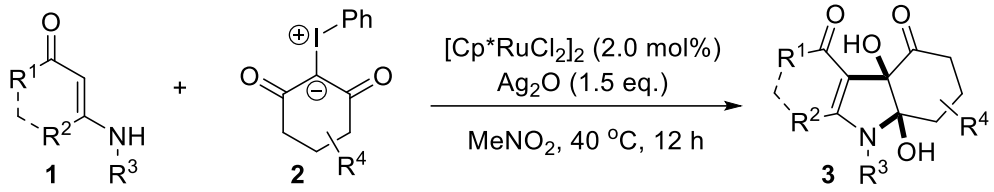


Entry	Catalyst (mol%)	Additive (eq.)	Solvent	T (℃)	Atmosphere	Yield (%)
1	$[Cp^*RhCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	Air	73
2	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	Air	80
3	$[Cp^*IrCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	Air	53
4	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2CO_3 (1.0)	CH_3NO_2	40	Air	70
5	$[Cp^*RuCl_2]_2$ (2.5)	$AgBF_4$ (1.0)	CH_3NO_2	40	Air	56
6	$[Cp^*RuCl_2]_2$ (2.5)	$AgSbF_6$ (1.0)	CH_3NO_2	40	Air	49
7	$[Cp^*RuCl_2]_2$ (2.5)	AgOTf (1.0)	CH_3NO_2	40	Air	48
8	$[Cp^*RuCl_2]_2$ (2.5)	AgOAc (1.0)	CH_3NO_2	40	Air	31
9	$[Cp^*RuCl_2]_2$ (2.5)	$AgNO_3$ (1.0)	CH_3NO_2	40	Air	25
10	$[Cp^*RuCl_2]_2$ (2.5)	AgF (1.0)	CH_3NO_2	40	Air	trace
11	$[Cp^*RuCl_2]_2$ (2.5)	AgTFA (1.0)	CH_3NO_2	40	Air	n.d.
12	$[Cp^*RuCl_2]_2$ (2.5)	$AgVO_3$ (1.0)	CH_3NO_2	40	Air	trace
13	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	DCM	40	Air	47
14	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	EA	40	Air	44
15	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	Toluene	40	Air	32
16	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	DCE	40	Air	23
17	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	Acetone	40	Air	20
18	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	THF	40	Air	n.r.
19	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	MeOH	40	Air	n.d.
20	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	PhCl	40	Air	trace
21	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	DMF	40	Air	n.d.
22	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	$PhCF_3$	40	Air	trace
23	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	rt	Air	68
24	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	60	Air	66
25	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	80	Air	n.d.
26	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	O_2	74
27	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	N_2	70
28	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	4A MS	53
29	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	H_2O	78
30	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (0.8)	CH_3NO_2	40	Air	77
31	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.0)	CH_3NO_2	40	Air	80
32	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (1.5)	CH_3NO_2	40	Air	84
33	$[Cp^*RuCl_2]_2$ (2.5)	Ag_2O (2)	CH_3NO_2	40	Air	82
34	$[Cp^*RuCl_2]_2$ (1.5)	Ag_2O (1.5)	CH_3NO_2	40	Air	76
35	$[Cp^*RuCl_2]_2$ (2.0)	Ag_2O (1.5)	CH_3NO_2	40	Air	84
36	$[Cp^*RuCl_2]_2$ (3)	Ag_2O (1.5)	CH_3NO_2	40	Air	82
37	-	Ag_2O (1.5)	CH_3NO_2	40	Air	18
38	$[Cp^*RuCl_2]_2$ (2.5)	-	CH_3NO_2	40	Air	23

[a]Reacion conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst and catalyst in 2 ml of solvent for 12h. [b]Isolated yield.

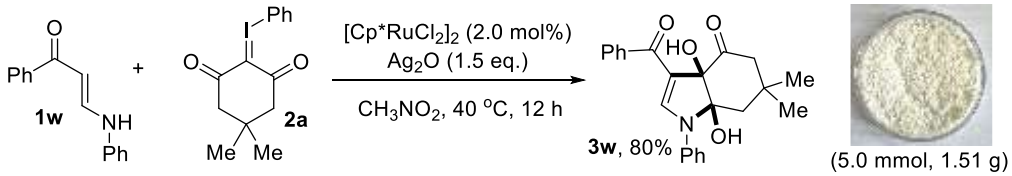
3. General procedure.

3.1 Synthesis of 3a,7a-dihydroxy indoles 3.



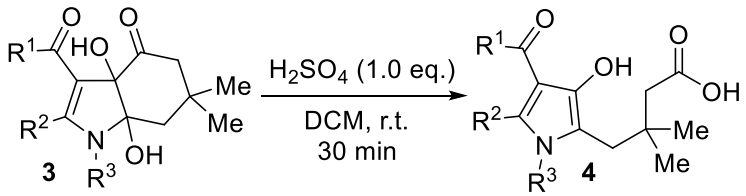
Enaminones **1** (0.5 mmol), iodonium ylides **2** (1.0 mmol), $[Cp^*RuCl_2]_2$ (2.0 mol%), Ag_2O (0.75 mmol) and $MeNO_2$ (2.0 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 40 °C for 12.0 h until enaminones were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL ×2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford 3a,7a-dihydroxy indoles **3**.

3.2 Gram-scale synthesis of 3a,7a-dihydroxy indole 3w.



Enaminone **1w** (5 mmol), iodonium ylide **2a** (10 mmol), $[Cp^*RuCl_2]_2$ (2.0 mol%), Ag_2O (7.5 mmol) and $MeNO_2$ (20 mL) were charged into a 100 mL Ace Glass pressure tubes, and the mixture was stirred at 40 °C for 12.0 h until enaminone were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL ×2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford 3a,7a-dihydroxy indole **3w**.

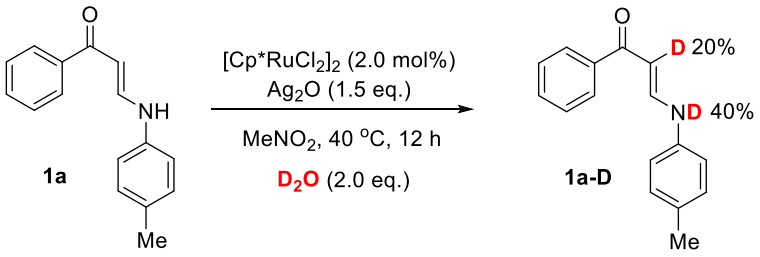
3.3 Further transformations for the construction of 1*H*-pyrrol-3-ol carboxylate derivatives.



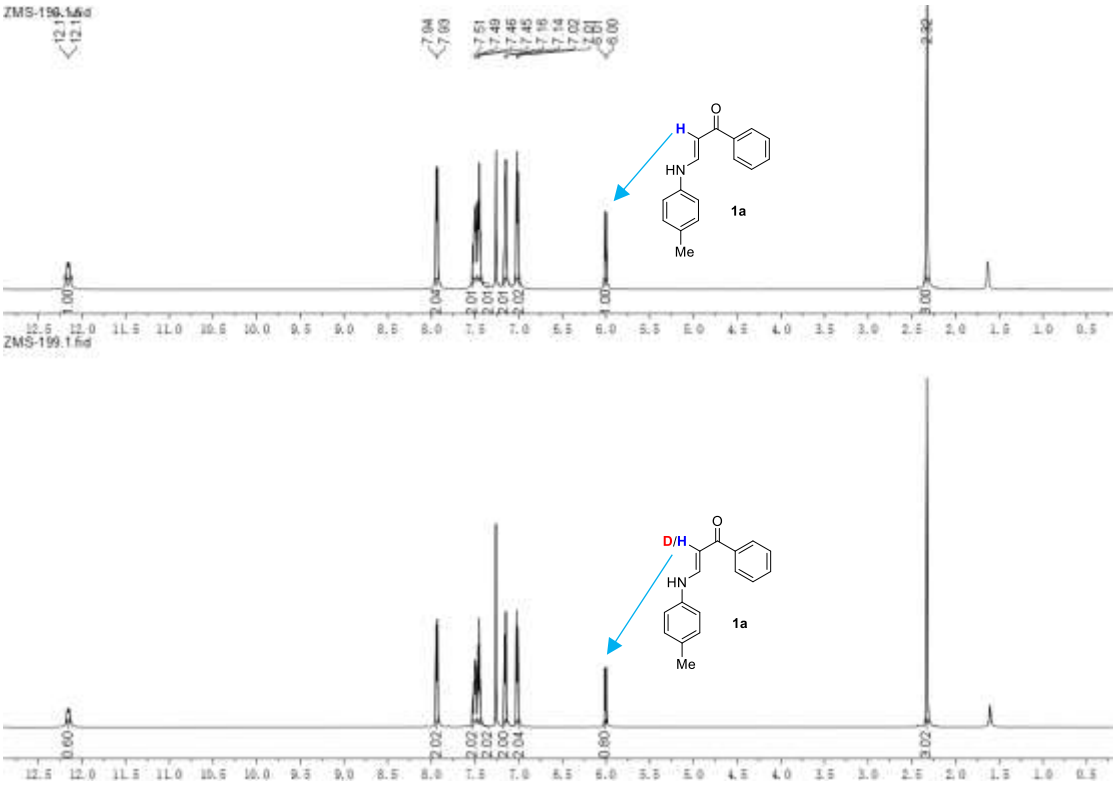
3a,7a-Dihydroxy indoles **3** (0.2 mmol), concentrated sulfuric acid (0.2 mmol, ω 95%), and DCM (2.0 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at room temperature for 20~30 min until **3** were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL ×2)

were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford 1*H*-pyrrol-3-ol carboxylate derivatives **4a**-**4c**.

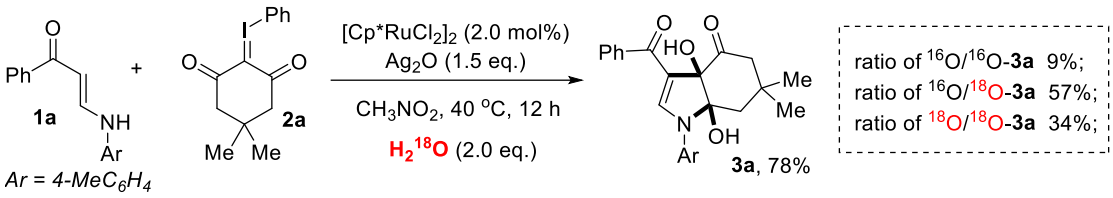
3.4 H/D Exchange experiment.



Enaminone **1a** (0.5 mmol), $[Cp^*RuCl_2]_2$ (2.0 mol%), Ag_2O (0.75 mmol), $MeNO_2$ (2.0 mL) and D_2O (1.0 mmol) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 40 °C for 12.0 h until enaminones were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL ×2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford enaminone **1a**/**1a-D**.



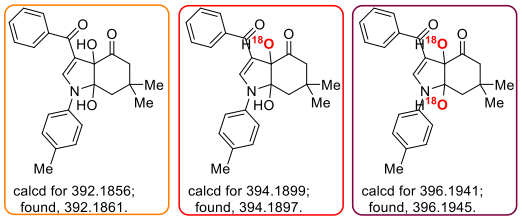
3.5 ^{18}O Iabeling experiment.



Enaminone **1a** (0.25 mmol), iodonium ylide **2a** (0.5 mmol), $[Cp^*RuCl_2]_2$ (2.0 mol%), Ag_2O (0.37 mmol), $H_2{}^{18}O$ (0.5 mmol) and $MeNO_2$ (2.0 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 40 °C for 12.0 h until enaminone were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford 3a,7a-dihydroxy indole **3a**. The ^{18}O content in the structure was identified by HRMS.

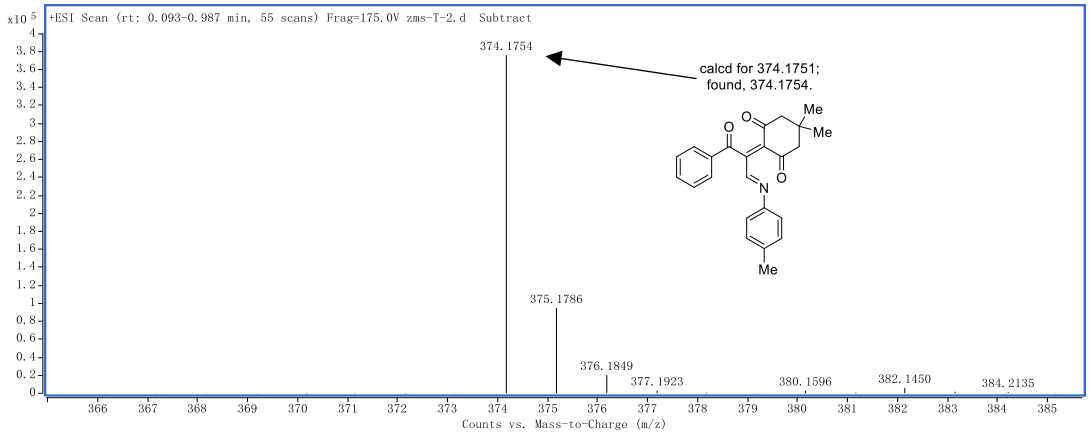
Peak List

m/z	z	Abund
392.1861	1	259058.2
393.1888	1	70692.09
394.1897	1	1593049.5
395.1937	1	463857.13
396.1945	1	954661.19



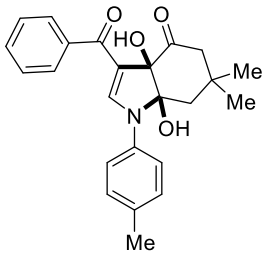
3.6 The mechanistic investigation.

With regard to standard conditions, the intermediate **V** in the Scheme 4 was successfully detected by HRMS during the crude reaction mixture.



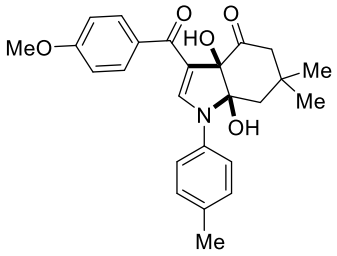
4. Spectroscopic data.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3a)



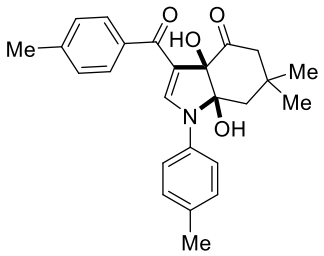
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 165 mg (84%); mp = 147–148 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.67–7.65 (m, 3H, ArH+C=CH), 7.52–7.46 (m, 3H, ArH), 7.35–7.33 (m, 2H, ArH), 7.15–7.13 (m, 2H, ArH), 6.43 (s, 1H, OH), 5.56 (s, 1H, OH), 2.61 (s, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.16–1.90 (m, 3H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.6, 187.5, 150.3, 139.9, 136.5, 134.4, 131.2, 129.9, 129.9, 128.8, 128.1, 128.6, 128.6, 121.9, 121.9, 118.5, 102.9, 83.5, 51.3, 48.1, 35.4, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{24}H_{26}NO_4$ [$(M+H)^+$], 392.1856, found, 392.1861.

3a,7a-Dihydroxy-3-(4-methoxybenzoyl)-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3b)



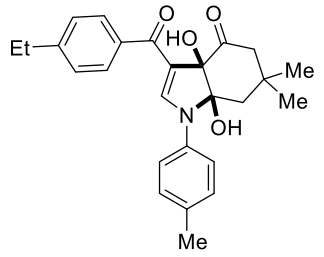
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 173 mg (82%); mp = 97–98 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.69 (d, J = 7.4 Hz, 2H, ArH), 7.67 (s, 1H, C=CH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 7.00 (d, J = 8.2 Hz, 2H, ArH), 6.39 (s, 1H, OH), 5.52 (s, 1H, OH), 3.82 (s, 3H, $ArOCH_3$), 2.61 (d, J = 11.8 Hz, 1H, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.15 (d, J = 11.9 Hz, 1H, CH_2), 2.04 (d, J = 14.3 Hz, 1H, CH_2), 1.90 (d, J = 14.3 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 186.5, 161.9, 149.5, 136.7, 134.2, 132.3, 130.7, 130.7, 129.9, 129.9, 121.7, 121.7, 118.6, 114.0, 114.0, 102.7, 83.7, 55.8, 51.3, 48.0, 35.4, 32.1, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{28}NO_5$ [$(M+H)^+$], 422.1962, found, 422.1965.

3a,7a-Dihydroxy-6,6-dimethyl-3-(4-methylbenzoyl)-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3c)



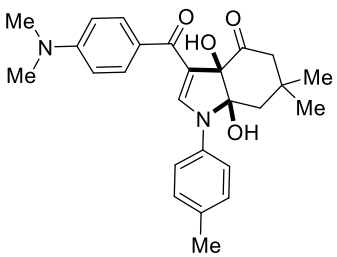
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 166 mg (81%); mp = 179–180 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.66 (s, 1H, C=CH), 7.57 (d, J = 7.4 Hz, 2H, ArH), 7.33 (d, J = 7.5 Hz, 2H, ArH), 7.27 (d, J = 7.6 Hz, 2H, ArH), 7.15 (d, J = 7.9 Hz, 2H, ArH), 6.42 (s, 1H, OH), 5.54 (s, 1H, OH), 2.61 (d, J = 11.3 Hz, 1H, CH_2), 2.36 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$), 2.15 (d, J = 12.1 Hz, 1H, CH_2), 2.05 (d, J = 14.0 Hz, 1H, CH_2), 1.91 (d, J = 14.3 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 187.4, 145.0, 141.2, 137.2, 136.6, 134.4, 129.9, 129.9, 129.4, 129.4, 128.7, 128.7, 121. 8, 121. 8, 118.5, 102.8, 83.6, 51.2, 48.1, 35.4, 32.0, 25.7, 21.5, 20.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{28}NO_4$ [$(M+H)^+$], 406.2013, found, 406.2018.

3-(4-Ethylbenzoyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3d)



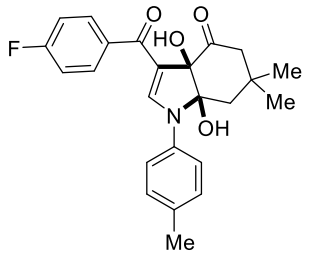
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 166 mg (79%); mp = 157–158 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.68 (s, 1H, C=CH), 7.60 (d, J = 7.8 Hz, 2H, ArH), 7.35 (d, J = 8.1 Hz, 2H, ArH), 7.30 (d, J = 7.8 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.41 (s, 1H, OH), 5.54 (s, 1H, OH), 2.66 (q, J = 7.6 Hz, 2H, CH_2), 2.61 (d, J = 11.9 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.15 (d, J = 11.8 Hz, 1H, CH_2), 2.05 (d, J = 14.1 Hz, 1H, CH_2), 1.91 (d, J = 14.1 Hz, 1H, CH_2), 1.20 (t, J = 7.7 Hz, 3H, CCH_3), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 187.3, 149.9, 147.3, 137.4, 136.6, 134.3, 129.9, 129.9, 128.8, 128.8, 128.2, 128.2, 121.8, 121.8, 118.6, 102.8, 83.6, 51.3, 48.1, 35.4, 32.1, 28.5, 25.7, 20.9, 15.9; HRMS (TOF ES+): m/z calcd for $C_{26}H_{30}NO_4$ [$(M+H)^+$], 420.2169, found, 420.2174.

3-(4-(Dimethylamino)benzoyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3e)



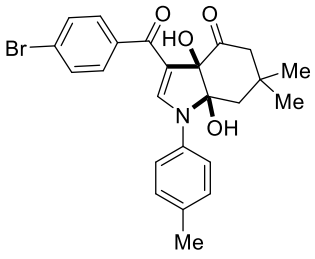
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.2; Yellow solid: 152 mg (70%); mp = 169–170 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.65 (s, 1H, C=CH), 7.58 (d, J = 8.3 Hz, 2H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 6.72 (d, J = 8.5 Hz, 2H, ArH), 6.32 (s, 1H, OH), 5.43 (s, 1H, OH), 2.97 (s, 6H, NCH_3), 2.60 (d, J = 11.8 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.14 (d, J = 11.6 Hz, 1H, CH_2), 2.02 (d, J = 14.2 Hz, 1H, CH_2), 1.85 (d, J = 14.1 Hz, 1H, CH_2), 0.96 (s, 3H, CCH_3), 0.83 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.8, 186.3, 152.7, 148.1, 137.0, 133.9, 130.5, 130.5, 129.9, 129.9, 126.8, 121.4, 121.4, 118.8, 111.4, 111.4, 102.3, 83.9, 51.3, 48.0, 40.2, 40.2, 35.3, 32.1, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{26}H_{31}N_2O_4$ [$(M+H)^+$], 435.2278, found, 435.2280.

3-(4-Fluorobenzoyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3f)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 161 mg (78%); mp = 142–143 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.76–7.73 (m, 2H, ArH), 7.71 (s, 1H, C=CH), 7.36 (d, J = 8.1 Hz, 2H, ArH), 7.27 (t, J = 8.7 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.44 (s, 1H, OH), 5.56 (s, 1H, OH), 2.62 (d, J = 11.8 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.14 (d, J = 11.6 Hz, 1H, CH_2), 2.05 (d, J = 14.2 Hz, 1H, CH_2), 1.93 (d, J = 14.1 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.6, 186.2, 164.0 (C–F, J = 247.8 Hz), 150.5, 136.4 (C–F, J = 4.5 Hz), 134.5, 131.2 (C–F, J = 8.9 Hz), 131.2 (C–F, J = 8.9 Hz), 129.9, 129.9, 121.9, 121.9, 118.3, 115.7 (C–F, J = 21.5 Hz), 115.7 (C–F, J = 21.5 Hz), 102.9, 83.5, 51.2, 48.0, 35.4, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{24}H_{25}FNO_4$ [$(M+H)^+$], 410.1762, found, 410.1765.

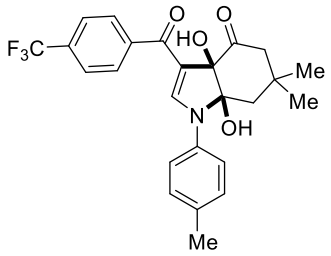
3-(4-Bromobenzoyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(p-tolyl)-1,3a,5,6,7,7a-hexahydro-4H-indol-4-one (3g)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 189 mg (80%); mp = 157–158 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.73 (s, 1H, C=CH), 7.67–7.59 (m, 4H, ArH), 7.36 (d, J = 7.8 Hz, 2H, ArH), 7.15 (d, J = 8.1 Hz, 2H, ArH), 6.45 (s, 1H, OH), 5.58 (s, 1H, OH), 2.62 (d, J = 11.7 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.14 (d, J = 12.0 Hz, 1H, CH_2), 2.06 (d, J = 14.3 Hz, 1H, CH_2), 1.93 (d, J = 14.2 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.6, 186.3, 150.7, 139.0, 136.4, 134.6, 131.8, 131.8, 130.7, 130.7, 129.9, 129.9, 124.7, 121.9,

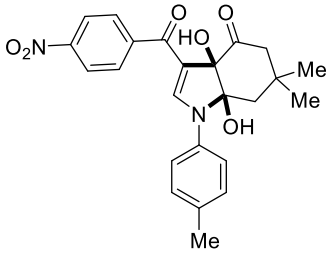
121.9, 118.2, 103.0, 83.4, 51.2, 48.1, 35.4, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{24}H_{25}BrNO_4$ [(M+H)$^+$], 470.0961, found, 470.0967.

3a,7a-Dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-3-(4-(trifluoromethyl)benzoyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3h)



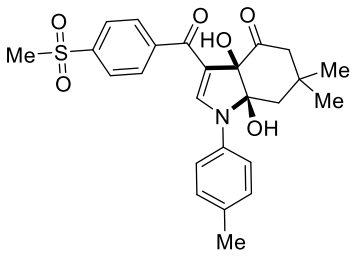
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 177 mg (77%); mp = 188–189 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.86 (d, J = 8.0 Hz, 2H, ArH), 7.82 (d, J = 8.1 Hz, 2H, ArH), 7.78 (s, 1H, C=CH), 7.38 (d, J = 8.3 Hz, 2H, ArH), 7.16 (d, J = 8.0 Hz, 2H, ArH), 6.49 (s, 1H, OH), 5.65 (s, 1H, OH), 2.65 (d, J = 11.8 Hz, 1H, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.16 (d, J = 11.8 Hz, 1H, CH_2), 2.08 (d, J = 14.3 Hz, 1H, CH_2), 1.97 (t, J = 14.9 Hz, 1H, CH_2), 1.00 (s, 3H, CCH_3), 0.85 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.5, 186.2, 151.3, 143.7, 136.3, 134.7, 129.9, 129.9, 129.4, 129.4, 125.8, 125.8, 125.7, 124.5 (C–F, J = 272.5 Hz), 122.1, 122.1, 118.2, 103.2, 83.3, 51.3, 48.1, 35.4, 32.0, 25.71, 20.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{25}F_3NO_4$ [(M+H)$^+$], 460.1730, found, 460.1740.

3a,7a-Dihydroxy-6,6-dimethyl-3-(4-nitrobenzoyl)-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3i)



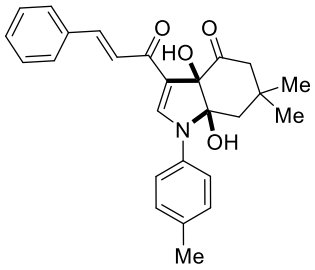
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 171 mg (78%); mp = 168–169 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.29 (d, J = 8.2 Hz, 2H, ArH), 7.89 (d, J = 8.3 Hz, 2H, ArH), 7.78 (s, 1H, C=CH), 7.38 (d, J = 8.1 Hz, 2H, ArH), 7.16 (d, J = 8.0 Hz, 2H, ArH), 6.53 (s, 1H, OH), 5.68 (s, 1H, OH), 2.66 (d, J = 11.8 Hz, 1H, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.16 (d, J = 11.7 Hz, 1H, CH_2), 2.09 (d, J = 14.2 Hz, 1H, CH_2), 1.97 (d, J = 14.0 Hz, 1H, CH_2), 1.01 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.4, 185.6, 151.7, 148.8, 145.8, 136.2, 134.9, 129.9, 129.9, 129.9, 129.9, 124.0, 124.0, 122.1, 122.1, 118.3, 103.4, 83.2, 51.3, 48.1, 35.4, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{24}H_{25}N_2O_6$ [(M+H)$^+$], 437.1707, found, 437.1720.

3a,7a-Dihydroxy-6,6-dimethyl-3-(4-(methylsulfonyl)benzoyl)-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3j)



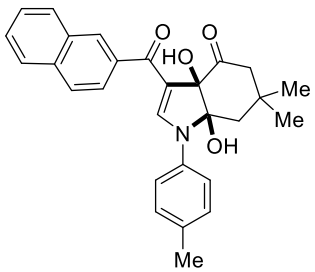
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1 R_f = 0.2; Yellow solid: 146 mg (62%); mp = 142–143 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.99 (d, J = 7.9 Hz, 2H, ArH), 7.88 (d, J = 7.9 Hz, 2H, ArH), 7.76 (s, 1H, C=CH), 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.49 (s, 1H, OH), 5.64 (s, 1H, OH), 3.26 (s, 3H, CH_3), 2.64 (d, J = 12.0 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.15 (d, J = 11.6 Hz, 1H, CH_2), 2.07 (d, J = 14.3 Hz, 1H, CH_2), 1.95 (d, J = 14.2 Hz, 1H, CH_2), 0.99 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.5, 186.0, 151.4, 144.4, 142.5, 136.2, 134.8, 129.9, 129.9, 129.4, 129.4, 127.6, 127.6, 122.1, 122.1, 118.2, 103.3, 83.3, 51.2, 48.1, 43.9, 35.5, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{28}NO_6S$ [$(M+H)^+$], 470.1632, found, 470.1644.

3-Cinnamoyl-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3k)



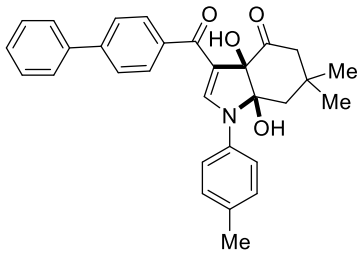
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 173 mg (83%); mp = 197–198°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.65 (s, 1H, C=CH), 7.78 (d, J = 7.4 Hz, 2H, ArH), 7.66 (d, J = 15.5 Hz, 1H, C=CH), 7.48–7.43 (m, 6H, ArH+C=CH), 7.41–7.38 (m, 2H, ArH), 7.22 (d, J = 8.1 Hz, 2H, ArH), 6.45 (s, 1H, OH), 5.48 (s, 1H, OH), 2.54 (d, J = 12.0 Hz, 1H, CH_2), 2.31 (s, 3H, $ArCH_3$), 2.14–2.09 (m, 2H, CH_2), 1.80 (d, J = 14.0 Hz, 1H, CH_2), 0.96 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 180.8, 148.7, 138.7, 136.8, 135.8, 134.1, 130.0, 129.9, 129.9, 129.2, 129.2, 128.7, 128.7, 124.0, 122.0, 121.1, 121.1, 103.1, 83.1, 51.2, 48.1, 35.6, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{26}H_{28}NO_4$ [$(M+H)^+$], 418.2013, found, 418.2028.

3-(2-Naphthoyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3l)



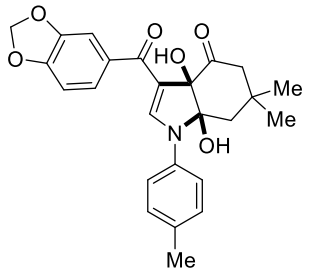
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 158 mg (71%); mp = 119–120 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.31 (s, 1H, C=CH), 8.10 (d, J = 7.9 Hz, 1H, ArH), 7.97 (t, J = 7.2 Hz, 2H, ArH), 7.83 (s, 1H, ArH), 7.71 (d, J = 8.5 Hz, 1H, ArH), 7.63–7.55 (m, 2H, ArH), 7.36 (d, J = 8.1 Hz, 2H, ArH), 7.13 (d, J = 8.1 Hz, 2H, ArH), 6.45 (s, 1H, OH), 5.62 (s, 1H, OH), 2.68 (d, J = 12.0 Hz, 1H, CH_2), 2.26 (s, 3H, $ArCH_3$), 2.18 (d, J = 11.9 Hz, 1H, CH_2), 2.08 (d, J = 14.3 Hz, 1H, CH_2), 1.97 (d, J = 13.9 Hz, 1H, CH_2), 1.01 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 187.4, 150.7, 137.2, 136.6, 134.5, 134.4, 132.7, 129.9, 129.9, 129.6, 128.8, 128.4, 128.0, 127.9, 127.0, 125.7, 121.9, 121.9, 118.7, 103.0, 83.6, 51.3, 48.1, 35.5, 32.1, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{28}H_{28}NO_4$ [$(M+H)^+$], 442.2013, found, 442.2022.

3-([1,1'-Biphenyl]-4-carbonyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3m)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 165 mg (72%); mp = 180–181 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.78–7.76 (m, 5H, ArH+C=CH), 7.74 (d, J = 7.7 Hz, 2H, ArH), 7.51 (t, J = 7.6 Hz, 2H, ArH), 7.42 (t, J = 7.4 Hz, 1H, ArH), 7.38 (d, J = 8.1 Hz, 2H, ArH), 7.16 (d, J = 8.1 Hz, 2H, ArH), 6.46 (s, 1H, OH), 5.59 (s, 1H, OH), 2.65 (d, J = 11.9 Hz, 1H, CH_2), 2.28 (s, 3H, , $ArCH_3$), 2.17 (d, J = 10.8 Hz, 1H, CH_2), 2.07 (d, J = 14.1 Hz, 1H, CH_2), 1.95 (d, J = 14.2 Hz, 1H, CH_2), 1.00 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.7, 187.0, 150.3, 142.8, 139.8, 138.8, 136.5, 134.5, 129.9, 129.9, 129.6, 129.6, 129.4, 129.4, 128.5, 127.3, 127.3, 127.1, 127.1, 121.9, 121.9, 118.6, 102.9, 83.6, 51.3, 48.1, 35.4, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{30}H_{30}NO_4$ [$(M+H)^+$], 468.2169, found, 468.2170.

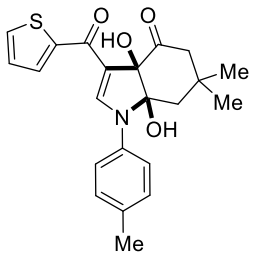
3-(Benzo[*d*][1,3]dioxole-5-carbonyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3n)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 163 mg (75%); mp = 104–105 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.71 (s, 1H, C=CH), 7.36 (d, J = 8.1 Hz, 2H, ArH), 7.27 (d, J = 8.1 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 7.15 (d, J = 8.1 Hz, 2H, ArH), 6.97 (d, J = 8.0 Hz, 1H, ArH), 6.39 (s, 1H, OH), 6.10 (d, J = 2.9 Hz, 2H, OCH_2), 5.51 (s, 1H, OH), 2.59 (s, 1H, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.13 (d, J = 11.5 Hz, 1H, CH_2), 2.04 (d, J = 14.2 Hz, 1H, CH_2), 1.93 (d, J = 14.2 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.6, 186.1, 145.0, 149.8,

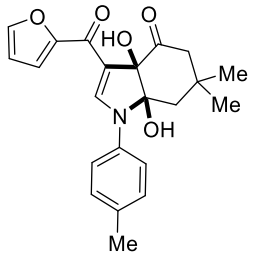
147.7, 136.7, 134.2, 134.2, 129.9, 129.9, 123.8, 121.8, 121.8, 118.3, 108.8, 108.4, 102.7, 102.0, 83.7, 51.3, 48.0, 35.3, 32.0, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{26}NO_6$ [$(M+H)^+$], 436.1755, found, 436.1763.

3a,7a-Dihydroxy-6,6-dimethyl-3-(thiophene-2-carbonyl)-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3o)



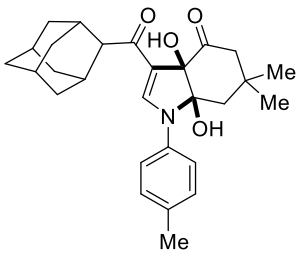
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 159 mg (80%); mp = 159–160 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.10 (s, 1H, C=CH), 7.88 (d, J = 3.8 Hz, 1H, C=CH), 7.82 (d, J = 5.0 Hz, 1H, C=CH), 7.42 (d, J = 8.1 Hz, 2H, ArH), 7.19 (s, 1H, C=CH), 7.17 (t, J = 4.1 Hz, 2H, ArH), 6.43 (s, 1H, OH), 5.54 (s, 1H, OH), 2.59 (d, J = 11.9 Hz, 1H, CH_2), 2.29 (s, 3H, $ArCH_3$), 2.14 (d, J = 11.7 Hz, 1H, CH_2), 2.04 (d, J = 14.2 Hz, 1H, CH_2), 1.90 (d, J = 13.7 Hz, 1H, CH_2), 0.97 (s, 3H, CCH_3), 0.83 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.5, 178.2, 149.0, 144.6, 136.6, 134.5, 131.8, 130.8, 129.9, 129.9, 128.6, 122.1, 122.1, 118.0, 102.6, 83.7, 51.2, 48.1, 35.4, 32.1, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{22}H_{24}NO_4S$ [$(M+H)^+$], 398.1421, found, 398.1427.

3-(Furan-2-carbonyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3p)



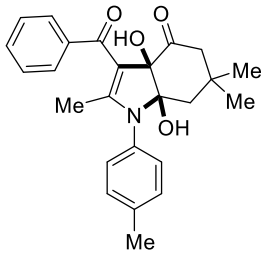
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 156 mg (81%); mp = 179–180 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.31 (s, 1H, C=CH), 7.88 (s, 1H, C=CH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.16 (d, J = 3.6 Hz, 1H, C=CH), 6.65 (s, 1H, C=CH), 6.45 (s, 1H, OH), 5.52 (s, 1H, OH), 2.58 (d, J = 11.7 Hz, 1H, CH_2), 2.30 (s, 3H, $ArCH_3$), 2.13 (d, J = 11.5 Hz, 1H, CH_2), 2.03 (d, J = 14.1 Hz, 1H, CH_2), 1.86 (d, J = 14.0 Hz, 1H, CH_2), 0.96 (s, 3H, CCH_3), 0.82 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.5, 173.1, 153.2, 149.4, 146.1, 136.5, 134.7, 130.0, 130.0, 122.1, 122.1, 117.9, 115.7, 112.4, 102.5, 83.5, 51.1, 48.1, 35.6, 32.0, 25.8, 20.9; HRMS (TOF ES+): m/z calcd for $C_{22}H_{24}NO_5$ [$(M+H)^+$], 382.1649, found, 382.1659.

3-((1*r*,3*r*,5*r*,7*r*)-Adamantane-2-carbonyl)-3a,7a-dihydroxy-6,6-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3q)



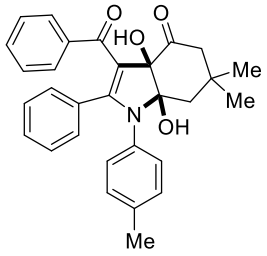
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; White solid: 150 mg (67%); mp = 194–195 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.05 (s, 1H, C=CH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 6.15 (s, 1H, OH), 5.14 (s, 1H, OH), 2.37 (d, J = 11.6 Hz, 1H, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.06 (d, J = 13.0 Hz, 1H, CH_2), 1.98–1.94 (m, 4H, CH_2+CH), 1.89–1.85 (m, 6H, CH_2), 1.74 (d, J = 11.9 Hz, 3H, CH), 1.69–1.64 (m, 4H, CH_2), 0.94 (s, 3H, CCH_3), 0.79 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.9, 198.4, 146.3, 136.7, 134.1, 129.8, 129.8, 122.0, 122.0, 117.6, 101.0, 84.5, 51.0, 48.0, 45.2, 36.6, 36.6, 36.6, 36.6, 35.8, 32.3, 28.4, 28.4, 28.4, 28.4, 28.4, 25.6, 20.9; HRMS (TOF ES+): m/z calcd for $C_{28}H_{36}NO_4$ [$(M+H)^+$], 450.2639, found, 450.2636.

3-Benzoyl-3a,7a-dihydroxy-2,6,6-trimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3r)



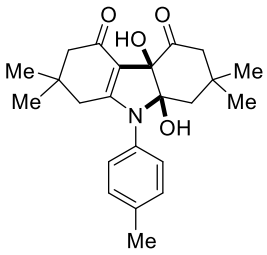
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow oil: 142 mg (70%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.67–7.64 (m, 1H, ArH), 7.57 (d, J = 7.7 Hz, 2H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH), 7.26 (d, J = 7.7 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 6.41 (s, 1H, OH), 5.53 (s, 1H, OH), 2.60 (d, J = 11.9 Hz, 1H, CH_2), 2.35 (s, 3H, $ArCH_3$), 2.27 (s, 3H, CCH_3), 2.14 (d, J = 12.9 Hz, 1H, CH_2), 2.04 (d, J = 14.2 Hz, 1H, CH_2), 1.90 (d, J = 14.1 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.83 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.3, 187.0, 149.6, 140.8, 136.8, 136.2, 134.0, 129.6, 129.6, 129.0, 129.0, 128.4, 128.4, 121.4, 121.4, 118.2, 102.5, 83.2, 50.9, 47.7, 35.1, 31.7, 25.4, 21.2, 20.5; HRMS (TOF ES+): m/z calcd for $C_{25}H_{28}NO_4$ [$(M+H)^+$], 406.2013, found, 406.2013.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-2-phenyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3s)



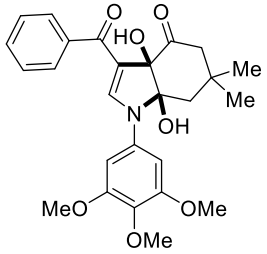
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 166 mg (76%); mp = 118–119 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.11–7.03 (m, 3H, ArH), 6.96–6.85 (m, 11H, ArH), 5.87 (s, 1H, OH), 5.53 (s, 1H, OH), 2.72 (d, J = 9.9 Hz, 1H, CH_2), 2.42 (d, J = 12.9 Hz, 1H, CH_2), 2.16 (s, 5H, CH_2+$ArCH_3$), 1.11 (s, 3H, CCH_3), 0.88 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.8, 190.0, 160.7, 140.8, 135.7, 135.1, 131.1, 130.2, 130.2, 129.8, 129.5, 129.2, 129.2, 128.7, 128.7, 128.3, 128.3, 127.8, 127.8, 127.4, 127.4, 116.8, 101.1, 85.4, 51.3, 49.1, 35.4, 32.3, 25.7, 20.9; HRMS (TOF ES+): m/z calcd for $C_{30}H_{30}NO_4$ [$(M+H)^+$], 468.2169, found, 468.2176.

4a,9a-Dihydroxy-2,2,7,7-tetramethyl-9-(*p*-tolyl)-2,3,4a,6,7,8,9,9a-octahydro-1*H*-carbazole-4,5-dione (3t)



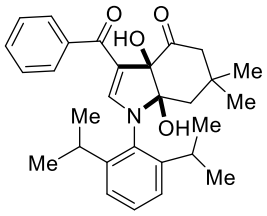
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; White solid: 116 mg (65%); mp = 183–184 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.24 (q, J = 8.1 Hz, 4H, ArH), 6.11 (s, 1H, OH), 5.35 (s, 1H, OH), 2.54 (s, 1H, CH_2), 2.49 (s, 1H, CH_2), 2.32 (s, 3H, $ArCH_3$), 2.22 (d, J = 15.9 Hz, 1H, CH_2), 2.07 (d, J = 11.5 Hz, 1H, CH_2), 1.89 (t, J = 15.4 Hz, 3H, CH_2), 1.68 (d, J = 13.7 Hz, 1H, CH_2), 1.00 (s, 3H, CCH_3), 0.95 (s, 3H, CCH_3), 0.90 (s, 3H, CCH_3), 0.73 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.6, 189.1, 165.7, 137.2, 133.6, 129.8, 129.8, 128.8, 128.8, 112.5, 102.8, 81.2, 51.1, 50.4, 48.2, 37.6, 34.7, 34.3, 32.0, 29.9, 26.9, 25.4, 21.1; HRMS (TOF ES+): m/z calcd for $C_{23}H_{30}NO_4$ [$(M+H)^+$], 384.2169, found, 384.2171.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-(3,4,5-trimethoxyphenyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3u)



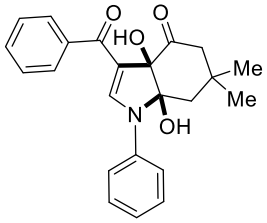
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 196 mg (84%); mp = 177–178°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.69 (s, 1H, C=CH), 7.67 (d, J = 7.7 Hz, 2H, ArH), 7.53 (t, J = 7.4 Hz, 1H, ArH), 7.46 (t, J = 7.5 Hz, 2H, ArH), 6.80 (s, 2H, ArH), 6.49 (s, 1H, OH), 5.57 (s, 1H, OH), 3.76 (s, 6H, $ArOCH_3$), 3.63 (s, 3H, $ArOCH_3$), 2.62 (d, J = 11.7 Hz, 1H, CH_2), 2.16 (d, J = 11.7 Hz, 1H, CH_2), 1.96 (dd, J = 31.2, 13.9 Hz, 2H, CH_2), 1.00 (s, 3H, CCH_3), 0.83 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ =206.8, 187.4, 153.2, 151.2, 139.9, 135.8, 134.9, 131.4, 128.8, 128.8, 128.8, 128.8, 128.8, 128.8, 118.2, 103.1, 101.7, 83.5, 60.5, 56.6, 56.6, 51.4, 47.9, 35.4, 32.1, 25.7; HRMS (TOF ES+): m/z calcd for $C_{26}H_{30}NO_7$ [$(M+H)^+$], 468.2017, found, 468.2023.

3-Benzoyl-1-(2,6-diisopropylphenyl)-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3v)



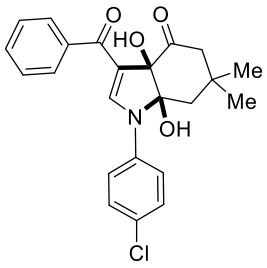
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; White solid: 140 mg (61%); mp = 143–144°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.58–7.56 (m, 2H, C=CH+ArH), 7.49–7.45 (m, 1H, ArH), 7.43–7.39 (m, 2H, ArH, ArH), 7.34 (d, J = 7.6 Hz, 1H, ArH), 7.30 (d, J = 7.6 Hz, 1H, ArH), 7.23 (d, J = 7.6 Hz, 1H, ArH), 5.78 (s, 1H, OH), 5.55 (s, 1H, OH), 3.11–2.99 (m, 2H, C–CH), 2.74 (d, J = 11.9 Hz, 1H, CH_2), 2.29 (d, J = 13.8 Hz, 1H, CH_2), 2.16 (d, J = 11.3 Hz, 1H, CH_2), 1.85 (d, J = 13.2 Hz, 1H, CH_2), 1.30 (d, J = 6.1 Hz, 3H, CCH_3), 1.22 (d, J = 6.3 Hz, 3H, CCH_3), 1.18 (d, J = 6.0 Hz, 3H, CCH_3), 1.05 (s, 3H, CCH_3, CCH_3), 0.92 (d, J = 6.2 Hz, 3H, CCH_3), 0.81 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.9, 186.8, 155.6, 150.6, 147.8, 140.3, 131.8, 131.0, 129.3, 128.6, 128.6, 128.4, 128.4, 124.9, 124.5, 115.2, 104.0, 83.7, 51.3, 46.2, 35.3, 32.0, 29.0, 28.4, 26.5, 25.9, 25.2, 24.0, 23.1; HRMS (TOF ES+): m/z calcd for $C_{29}H_{36}NO_4$ [$(M+H)^+$], 462.2639, found, 462.2634.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-phenyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3w)



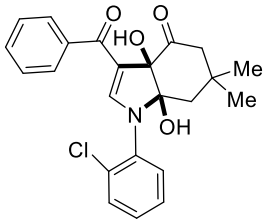
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; White solid: 162 mg (86%); mp = 140–141°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.74 (s, 1H, C=CH), 7.69 (d, J = 7.5 Hz, 2H, ArH), 7.54 (t, J = 7.4 Hz, 1H, ArH), 7.47 (t, J = 7.8 Hz, 4H, ArH), 7.34 (t, J = 7.8 Hz, 2H, ArH), 7.15 (t, J = 7.4 Hz, 1H, ArH), 6.49 (s, 1H, OH), 5.59 (s, 1H, OH), 2.63 (d, J = 11.7 Hz, 1H, CH_2), 2.16 (t, J = 11.7 Hz, 2H, CH_2), 1.97 (d, J = 14.8 Hz, 1H, CH_2), 1.00 (s, 3H, CCH_3), 0.87 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.5, 187.7, 149.9, 139.8, 139.0, 131.3, 129.5, 129.5, 128.8, 128.8, 128.7, 128.7, 124.9, 121.4, 121.4, 118.9, 102.9, 83.6, 51.3, 48.1, 35.5, 32.0, 25.7; HRMS (TOF ES+): m/z calcd for $C_{23}H_{24}NO_4$ [$(M+H)^+$], 378.1700, found, 378.1796.

3-Benzoyl-1-(4-chlorophenyl)-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3x)



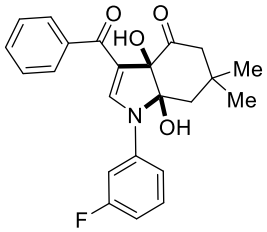
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 160 mg (78%); mp = 155–156°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.77 (s, 1H, C=CH), 7.69 (d, J = 7.5 Hz, 2H, ArH), 7.54 (t, J = 7.4 Hz, 1H, ArH), 7.51–7.46 (m, 4H, ArH), 7.39 (d, J = 8.4 Hz, 2H, ArH), 6.57 (s, 1H, OH), 5.63 (s, 1H, OH), 2.61 (d, J = 11.8 Hz, 1H, CH_2), 2.16 (dd, J = 12.6, 7.7 Hz, 2H, CH_2), 1.96 (t, J = 14.2 Hz, 1H, CH_2), 1.00 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.3, 187.9, 149.5, 139.7, 138.0, 131.4, 129.3, 129.3, 128.9, 128.9, 128.7, 128.7, 128.7, 122.7, 122.7, 119.4, 103.0, 83.4, 51.3, 47.9, 35.4, 32.0, 25.7; HRMS (TOF ES+): m/z calcd for $C_{23}H_{23}ClNO_4$ [$(M+H)^+$], 412.1310, found, 412.1321.

3-Benzoyl-1-(2-chlorophenyl)-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3y)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 100 mg (49%); mp = 77–78°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.75 (s, 1H, C=CH), 7.68 (d, J = 7.1 Hz, 2H, ArH), 7.54 (t, J = 7.3 Hz, 1H, ArH), 7.47 (d, J = 6.3 Hz, 4H, ArH), 7.38 (d, J = 8.9 Hz, 2H, ArH), 6.56 (s, 1H, OH), 5.61 (s, 1H, OH), 2.60 (d, J = 12.0 Hz, 1H, CH_2), 2.18–2.13 (m, 2H, CH_2), 1.94 (d, J = 14.2 Hz, 1H, CH_2), 0.99 (s, 3H, CCH_3), 0.85 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.1, 187.6, 149.2, 139.4, 137.7, 131.2, 129.0, 129.0, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 122.4, 122.4, 119.1, 102.7, 83.2, 51.0, 47.6, 35.2, 31.7, 25.4; HRMS (TOF ES+): m/z calcd for $C_{23}H_{23}ClNO_4$ [$(M+H)^+$], 412.1310, found, 412.1316.

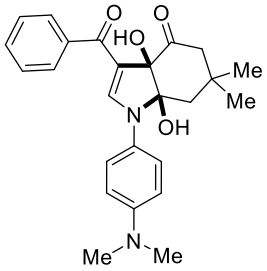
3-Benzoyl-1-(3-chlorophenyl)-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3z)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 162 mg (79%); mp = 169–170°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.83 (s, 1H, C=CH), 7.71 (d, J = 7.4 Hz, 2H, ArH), 7.56 (t, J = 7.4 Hz, 1H, ArH), 7.49 (t, J = 7.5 Hz, 2H, ArH), 7.41 (d, J = 11.4 Hz, 1H, ArH), 7.37–7.32 (m, 2H, ArH),

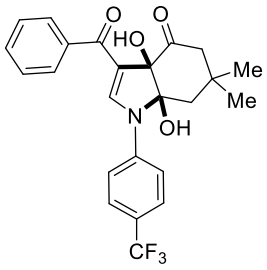
6.95 (t, J = 8.6 Hz, 1H, ArH), 6.60 (s, 1H, OH), 5.66 (s, 1H, OH), 2.61 (d, J = 11.3 Hz, 1H, CH_2), 2.23 (d, J = 13.9 Hz, 1H, CH_2), 2.17 (d, J = 11.4 Hz, 1H, CH_2), 1.97 (d, J = 14.2 Hz, 1H, CH_2), 1.01 (s, 3H, CCH_3), 0.88 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.2, 188.0, 162.8 (C–F, J = 242.1 Hz), 149.2, 140.8 (C–F, J = 10.7 Hz), 139.6, 131.5, 131.0 (C–F, J = 9.5 Hz), 128.9, 128.9, 128.8, 128.8, 119.6, 116.5, 110.9 (C–F, J = 21.1 Hz), 107.7 (C–F, J = 25.5 Hz), 103.0, 83.5, 51.3, 47.8, 35.5, 32.0, 25.7; HRMS (TOF ES+): m/z calcd for $C_{23}H_{23}FNO_4$ [$(M+H)^+$], 396.1606, found, 396.1606.

3-Benzoyl-1-(4-(dimethylamino)phenyl)-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3a′)



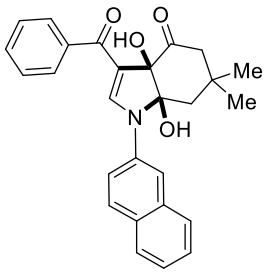
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 140 mg (66%); mp = 157–158^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.65 (d, J = 7.5 Hz, 2H, ArH), 7.53 (s, 1H, C=CH), 7.50 (d, J = 7.3 Hz, 1H, ArH), 7.45 (t, J = 7.5 Hz, 2H, ArH), 7.27 (d, J = 8.5 Hz, 2H, ArH), 6.69 (d, J = 8.6 Hz, 2H, ArH), 6.33 (s, 1H, OH), 5.50 (s, 1H, OH), 2.88 (s, 6H, NCH_3), 2.63 (d, J = 11.8 Hz, 1H, CH_2), 2.14 (d, J = 11.5 Hz, 1H, CH_2), 1.92–1.84 (m, 2H, CH_2), 0.98 (s, 3H, CCH_3), 0.82 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.0, 186.8, 151.6, 149.1, 140.2, 131.0, 128.8, 128.8, 128.5, 128.5, 128.1, 124.8, 124.8, 117.5, 112.9, 112.9, 102.9, 83.4, 51.3, 48.1, 40.7, 40.7, 35.4, 32.1, 25.7; HRMS (TOF ES+): m/z calcd for $C_{25}H_{29}N_2O_4$ [$(M+H)^+$], 421.2122, found, 421.2117.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-(4-(trifluoromethyl)phenyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3b′)



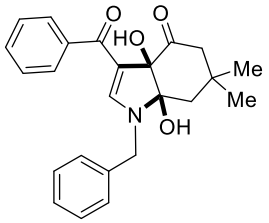
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; Yellow oil: 138 mg (59%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.87 (s, 1H, C=CH), 7.86 (s, 1H, ArH), 7.84–7.80 (m, 3H, ArH), 7.49 (d, J = 7.9 Hz, 2H, ArH), 7.35 (t, J = 7.8 Hz, 2H, ArH), 7.17 (t, J = 7.3 Hz, 1H, ArH), 6.54 (s, 1H, OH), 5.66 (s, 1H, OH), 2.65 (d, J = 11.7 Hz, 1H, CH_2), 2.16 (d, J = 12.8 Hz, 2H, CH_2), 2.00 (d, J = 11.4 Hz, 1H, CH_2), 1.01 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.4, 186.4, 151.0, 143.6, 138.7, 129.4, 129.4, 129.4, 129.4, 125.8, 125.8, 125.2, 124.5(C–F, J = 270 Hz), 121.6, 121.6, 118.6, 103.2, 83.4, 51.3, 48.1, 35.5, 32.0, 25.7; HRMS (TOF ES+): m/z calcd for $C_{24}H_{23}F_3NO_4$ [$(M+H)^+$], 446.1574, found, 446.1584.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-(naphthalen-2-yl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3c′)



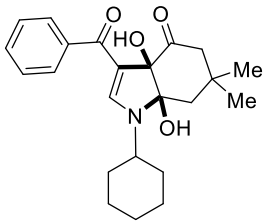
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 176 mg (82%); mp = 107–108°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.12–8.10 (m, 1H, ArH), 7.98–7.96 (m, 2H, ArH), 7.76–7.51 (m, 7H, ArH+C=CH), 7.43 (d, J = 34.8 Hz, 3H, ArH), 6.14 (s, 1H, OH), 5.68 (s, 1H, OH), 2.75 (d, J = 11.8 Hz, 1H, CH_2), 2.35 (d, J = 13.9 Hz, 1H, CH_2), 2.19 (d, J = 11.8 Hz, 1H, CH_2), 1.94 (d, J = 14.0 Hz, 1H, CH_2), 1.04 (s, 3H, CCH_3), 0.79 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.9, 187.1, 155.1, 134.0, 134.9, 134.5, 131.0, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 127.3, 126.8, 126.6, 126.0, 124.6, 117.6, 104.0, 83.5, 51.4, 47.9, 35.4, 32.1, 25.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{26}NO_4$ [$(M+H)^+$], 428.1856, found, 428.1858.

3-Benzoyl-1-benzyl-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3d′)



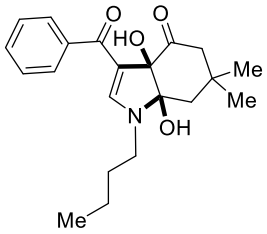
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; White solid: 141 mg (72%); mp = 145–146°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.50–7.48 (m, 1H, ArH), 7.48 (s, 1H, C=CH), 7.45 (d, J = 7.1 Hz, 1H, ArH), 7.40 (d, J = 7.3 Hz, 2H, ArH), 7.37–7.33 (m, 5H, ArH), 7.28 (d, J = 6.8 Hz, 1H, ArH), 5.82 (s, 1H, OH), 5.36 (s, 1H, OH), 4.52–4.40 (m, 2H, CH_2), 2.58 (d, J = 11.8 Hz, 1H, CH_2), 2.11 (d, J = 11.6 Hz, 1H, CH_2), 2.01 (d, J = 14.0 Hz, 1H, CH_2), 1.77 (d, J = 14.0 Hz, 1H, CH_2), 0.98 (s, 3H, CCH_3), 0.82 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.3, 186.1, 154.3, 140.5, 138.3, 130.7, 129.0, 129.0, 128.7, 128.7, 128.6, 128.6, 128.2, 128.2, 127.9, 115.6, 101.2, 83.2, 51.2, 48.0, 46.4, 35.3, 32.1, 25.7; HRMS (TOF ES+): m/z calcd for $C_{24}H_{26}NO_4$ [$(M+H)^+$], 392.1856, found, 392.1857.

3-Benzoyl-1-cyclohexyl-3a,7a-dihydroxy-6,6-dimethyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3e′)



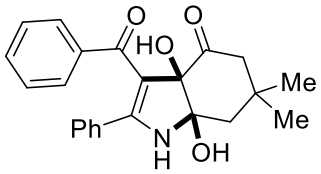
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow oil: 100 mg (52%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.51 (s, 1H, C=CH), 7.50 (d, J = 1.6 Hz, 1H, ArH), 7.47–7.42 (m, 4H, ArH), 5.78 (s, 1H, OH), 5.23 (s, 1H, OH), 3.33–3.29 (m, 1H), 2.58 (d, J = 11.7 Hz, 1H, C–CH), 2.13–2.07 (m, 2H, CH_2), 1.85 (d, J = 11.7 Hz, 1H, CH_2), 1.77–1.70 (m, 4H, CH_2), 1.56 (d, J = 7.5 Hz, 1H, CH_2), 1.38–1.21 (m, 4H, CH_2), 1.38–1.21 (m, 1H, CH_2), 1.02 (s, 3H, CCH_3), 0.82 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.5, 185.5, 151.1, 140.8, 130.5, 128.7, 128.7, 128.3, 128.25, 115.0, 101.6, 83.4, 52.0, 51.1, 48.6, 35.4, 34.3, 33.7, 32.2, 25.9, 25.9, 25.6, 25.0; HRMS (TOF ES+): m/z calcd for $C_{23}H_{30}NO_4$ [(M+H)$^+$], 384.2169, found, 384.2168.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-1-propyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3f′)



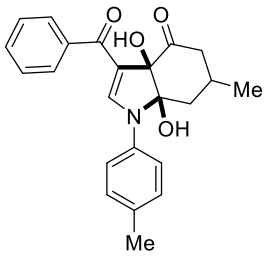
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; Yellow oil: 86 mg (50%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.53–7.51 (m, 2H, ArH), 7.47 (d, J = 7.2 Hz, 1H, ArH), 7.43 (d, J = 7.6 Hz, 2H, ArH), 7.41 (s, 1H, C=CH), 5.75 (s, 1H, OH), 5.25 (s, 1H, OH), 3.25–3.22 (m, 2H, CH_2), 2.58 (d, J = 12.0 Hz, 1H, CH_2), 2.11–2.07 (m, 2H, CH_2), 1.74 (d, J = 13.7 Hz, 1H, CH_2), 1.57–1.53 (m, 2H, CH_2), 1.02 (s, 3H, CCH_3), 0.88 (t, J = 7.4 Hz, 3H, CCH_3), 0.83 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.5, 185.7, 154.4, 140.7, 130.5, 128.6, 128.6, 128.2, 128.2, 114.9, 101.1, 83.3, 51.1, 48.0, 43.0, 35.4, 32.3, 25.7, 20.0, 14.1; HRMS (TOF ES+): m/z calcd for $C_{20}H_{26}NO_4$ [(M+H)$^+$], 344.1856, found, 344.1861.

3-Benzoyl-3a,7a-dihydroxy-6,6-dimethyl-2-phenyl-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3g′)



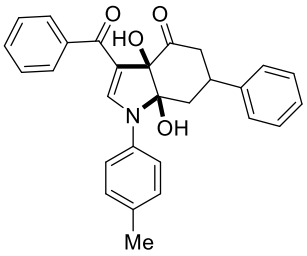
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.2; Yellow solid: 125 mg (66%); mp = 214–215ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.15 (s, 1H, NH), 7.58 (t, J = 8.1 Hz, 3H, ArH), 7.52 (d, J = 7.4 Hz, 2H, ArH), 7.48 (d, J = 8.1 Hz, 3H, ArH), 7.39 (t, J = 7.8 Hz, 2H, ArH), 2.48 (s, 1H, CH_2), 2.39 (d, J = 14.1 Hz, 1H, CH_2), 2.24 (d, J = 16.3 Hz, 1H, CH_2), 2.18 (d, J = 14.0 Hz, 1H, CH_2), 1.24 (s, 3H, CCH_3), 1.12 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 208.0, 193.5, 189.4, 180.8, 139.2, 132.5, 132.3, 130.5, 129.5, 129.5, 129.0, 129.0, 128.9, 128.9, 128.4, 128.4, 107.6, 79.6, 52.5, 46.3, 33.8, 29.3, 29.2; HRMS (TOF ES+): m/z calcd for $C_{23}H_{24}NO_4$ [(M+H)$^+$], 378.1700, found, 378.1702.

3-Benzoyl-3a,7a-dihydroxy-6-methyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3h′)



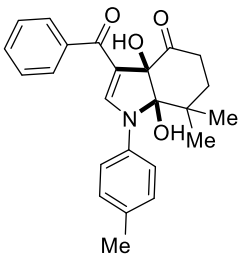
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; White solid: 157 mg (83%); mp = 156–157°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.71 (s, 1H, C=CH), 7.68 (d, J = 7.5 Hz, 2H, ArH), 7.53 (t, J = 7.4 Hz, 1H, ArH), 7.47 (t, J = 7.5 Hz, 2H, ArH), 7.34 (d, J = 8.1 Hz, 2H, ArH), 7.15 (d, J = 8.1 Hz, 2H, ArH), 6.54 (s, 1H, OH), 5.49 (s, 1H, OH), 2.37 (d, J = 11.2 Hz, 2H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.21 (d, J = 12.4 Hz, 1H, C-CH), 1.78–1.69 (m, 2H, CH_2), 0.97 (d, J = 6.0 Hz, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.4, 187.5, 150.4, 139.8, 136.5, 134.4, 131.3, 129.9, 129.9, 128.8, 128.8, 128.6, 128.6, 121.7, 121.7, 118.3, 102.6, 83.6, 46.9, 44.2, 30.4, 21.5, 20.9; HRMS (TOF ES+): m/z calcd for $C_{23}H_{24}NO_4$ [$(M+H)^+$], 378.1700, found, 378.1763.

3-Benzoyl-3a,7a-dihydroxy-6-phenyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3i′)



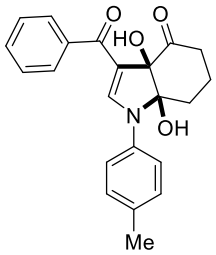
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow solid: 165 mg (75%); mp = 100–101°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.75 (d, J = 8.3 Hz, 3H, ArH+C=CH), 7.54 (d, J = 7.3 Hz, 1H, ArH), 7.49 (t, J = 7.5 Hz, 2H, ArH), 7.34 (d, J = 7.9 Hz, 2H, ArH), 7.29–7.27 (m, 4H, ArH), 7.22–7.20 (m, 1H, ArH), 7.12 (d, J = 8.0 Hz, 2H, ArH), 6.76 (s, 1H, OH), 5.64 (s, 1H, OH), 3.03–2.83 (m, 1H, C-CH), 2.52 (d, J = 23.6 Hz, 3H, CH_2), 2.28 (d, J = 18.0 Hz, 1H, CH_2), 2.24 (s, 3H, $ArCH_3$); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 205.9, 187.6, 150.6, 143.1, 139.8, 136.5, 134.5, 131.3, 129.9, 129.9, 129.1, 129.1, 128.8, 128.8, 128.7, 128.7, 127.3, 127.2, 127.2, 121.8, 121.8, 118.4, 102.1, 83.9, 45.9, 44.3, 40.4, 20.9; HRMS (TOF ES+): m/z calcd for $C_{28}H_{26}NO_4$ [$(M+H)^+$], 440.1856, found, 440.1868.

3-Benzoyl-3a,7a-dihydroxy-7,7-dimethyl-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3j′)



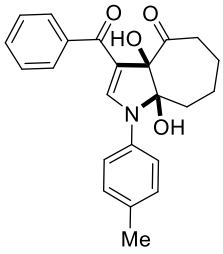
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; Yellow oil: 151 mg (77%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.68–7.66 (m, 3H, ArH+C=CH), 7.52–7.46 (m, 3H, ArH), 7.35–7.33 (m, 2H, ArH), 7.16–7.14 (m, 2H, ArH), 6.44 (s, 1H, OH), 5.57 (s, 1H, OH), 2.62 (d, J = 11.8 Hz, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.16–1.90 (m, 3H, CH_2), 0.98 (s, 3H, CCH_3), 0.84 (s, 3H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 206.3, 187.1, 150.0, 139.5, 136.1, 134.1, 130.9, 129.5, 129.5, 128.5, 128.5, 128.3, 128.3, 121.6, 121.6, 118.1, 102.6, 83.1, 50.9, 47.7, 35.1, 31. 7, 25.4, 20.5; HRMS (TOF ES+): m/z calcd for $C_{24}H_{26}NO_4$ [$(M+H)^+$], 392.1856, found, 392.1857.

3-Benzoyl-3a,7a-dihydroxy-1-(*p*-tolyl)-1,3a,5,6,7,7a-hexahydro-4*H*-indol-4-one (3k′)



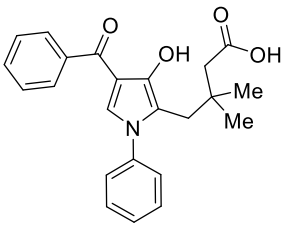
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.2; White solid: 155 mg (85%); mp = 151–152°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.80 (s, 1H, C=CH), 7.64 (d, J = 7.4 Hz, 2H, ArH), 7.53 (t, J = 7.2 Hz, 1H, ArH), 7.46 (t, J = 7.4 Hz, 2H, ArH), 7.39 (d, J = 8.2 Hz, 2H, ArH), 7.15 (d, J = 8.2 Hz, 2H, ArH), 6.68 (s, 1H, OH), 5.54 (s, 1H, OH), 2.57–2.53 (m, 1H, CH_2), 2.41–2.36 (m, 1H, CH_2), 2.27 (s, 3H, $ArCH_3$), 2.00–1.96 (m, 1H, CH_2), 1.86–1.81 (m, 1H, CH_2), 1.71–1.67 (m, 1H, CH_2), 1.60–1.54 (m, 1H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 207.9, 187.5, 151.7, 140.0, 136.4, 134.7, 131.3, 130.0, 130.0, 128.9, 128.9, 128.6, 128.6, 122.0, 122.0, 116.5, 101.4, 84.4, 37.4, 34.3, 20.9, 19.3; HRMS (TOF ES+): m/z calcd for $C_{22}H_{22}NO_4$ [$(M+H)^+$], 364.1543, found, 364.1545.

3-Benzoyl-3a,8a-dihydroxy-1-(*p*-tolyl)-3a,5,6,7,8,8a-hexahydrocyclohepta[*b*]pyrrol-4(1*H*)-one (3l′)



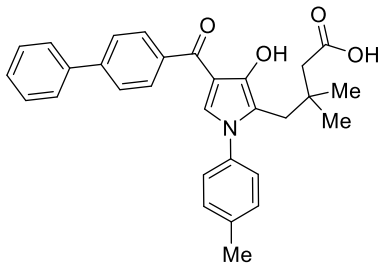
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; Yellow oil: 80 mg (42%); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.79 (s, 1H, C=CH), 7.56–7.46 (m, 5H, ArH), 7.42–7.37 (m, 3H, ArH), 7.30 (s, 1H, ArH), 7.28 (s, 1H, OH), 6.47 (s, 1H, OH), 2.35 (s, 3H, $ArCH_3$), 2.10–2.02 (m, 1H, CH_2), 1.82–1.76 (m, 1H, CH_2), 1.71–1.63 (m, 2H, CH_2), 1.53 (d, J = 12.1 Hz, 1H, CH_2), 1.42–1.34 (m, 2H, CH_2), 1.23–1.16 (m, 1H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 209.8, 187.3, 152.3, 134.0, 137.0, 135.0, 131.4, 130.1, 130.1, 128.6, 128.6, 128.2, 128.2, 122.6, 122.6, 116.5, 95.4, 87.6, 36.0, 26.7, 22.1, 20.9, 14.6; HRMS (TOF ES+): m/z calcd for $C_{23}H_{24}NO_4$ [$(M+H)^+$], 378.1700, found, 378.1706.

4-(4-Benzoyl-3-hydroxy-1-phenyl-1*H*-pyrrol-2-yl)-3,3-dimethylbutanoic acid (4a)



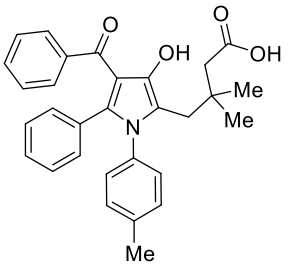
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; Yellow solid: 55 mg (76%); mp = 140–141 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 11.92 (br, 1H, OH), 8.97 (br, 1H, COOH), 7.88 (d, J = 7.6 Hz, 2H, ArH), 7.61 (t, J = 7.4 Hz, 1H, ArH), 7.51 (d, J = 7.7 Hz, 4H, ArH), 7.44 (d, J = 8.1 Hz, 3H, ArH), 7.29 (s, 1H, C=CH), 2.69 (s, 2H, CH_2), 1.93 (s, 2H, CH_2), 0.67 (s, 6H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 192.4, 173.5, 145.6, 139.8, 138.9, 132.5, 129.8, 129.8, 129.1, 129.1, 128.9, 128.9, 128.5, 127.0, 127.0, 125.9, 114.2, 111.6, 46.2, 35.9, 34.9, 27.0, 27.0; HRMS (TOF ES+): m/z calcd for $C_{23}H_{25}NO_4$ [(M+H)$^+$], 378.1700, found, 378.1705.

4-(4-([1,1'-Biphenyl]-4-carbonyl)-3-hydroxy-1-(*p*-tolyl)-1*H*-pyrrol-2-yl)-3,3-dimethylbutanoic acid (4b)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.2; Yellow solid: 66 mg (73%); mp = 165–166 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 11.94 (br, 1H, OH), 9.08 (br, 1H, COOH), 7.97 (d, J = 8.0 Hz, 2H, ArH), 7.81 (d, J = 8.3 Hz, 2H, ArH), 7.73 (d, J = 7.7 Hz, 2H, ArH), 7.50 (t, J = 7.6 Hz, 2H, ArH), 7.42 (t, J = 7.3 Hz, 1H, ArH), 7.32 (s, 4H), 7.30 (s, 1H, C=CH), 2.68 (s, 2H, CH_2), 2.37 (s, 3H, $ArCH_3$), 1.94 (s, 2H, CH_2), 0.69 (s, 6H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 191.3, 173.3, 145.1, 143.6, 139.2, 137.5, 137.4, 137.0, 129.8, 129.8, 129.3, 129.3, 129.2, 129.2, 128.3, 127.0, 127.0, 126.9, 126.9, 126.4, 126.4, 125.4, 113.9, 111.2, 46.0, 35.6, 34.5, 26.7, 26.7, 20.7; HRMS (TOF ES+): m/z calcd for $C_{30}H_{31}NO_4$ [(M+H)$^+$], 468.2169, found, 468.2177.

4-(4-Benzoyl-3-hydroxy-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-2-yl)-3,3-dimethylbutanoic acid (4c)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:4, R_f = 0.2; Yellow solid: 57 mg (64%); mp = 199–200 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 11.94 (br, 1H, OH), 8.70 (br, 1H, COOH), 7.39 (d, J = 7.6 Hz, 2H, ArH), 7.26 (t, J = 7.4 Hz, 1H, ArH), 7.14–7.10 (m, 3H, ArH), 7.08 (d, J = 7.6 Hz, 1H, ArH), 7.01 (d, J =

7.9 Hz, 2H, ArH), 6.92 (t, *J* = 7.3 Hz, 1H, ArH), 6.86 (t, *J* = 7.5 Hz, 2H, ArH), 6.82 (d, *J* = 7.3 Hz, 2H, ArH), 2.57 (s, 2H, CH_2), 2.25 (s, 3H, $ArCH_3$), 1.99 (s, 2H, CH_2), 0.75 (s, 6H, CCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 194.0, 173.4, 143.6, 138.8, 137.5, 134.9, 134.7, 131.2, 131.2, 131.2, 131.0, 129.6, 129.6, 129.17, 129.2, 128. 7, 128.7, 127.5, 127.5, 127.2, 127.2, 127.1, 114.9, 111.7, 46.1, 35.4, 35.4, 27.0, 27.0, 20.7; HRMS (TOF ES+): m/z calcd for $C_{30}H_{31}NO_4$ [$(M+H)^+$], 468.2169, found, 468.2169.

5. X-ray Structure and Data[3] of 3i (CCDC 2215066).

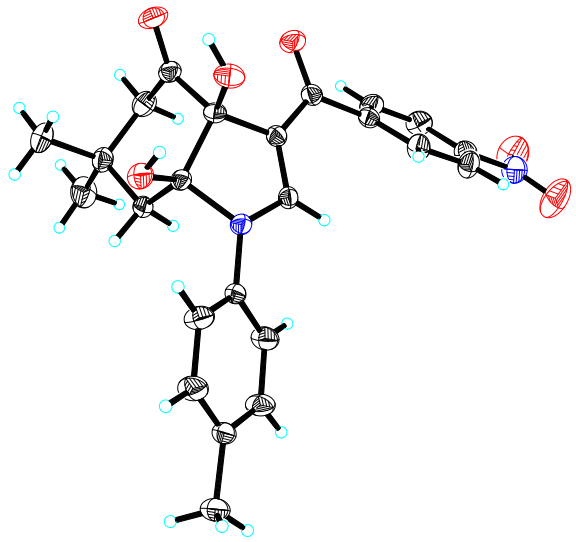


Figure S1 X-Ray crystal structure of 3i.

Table S2 Crystal data and structure refinement for **3i.**

Empirical formula	$C_{24}H_{24}N_2O_6$
Formula weight	436.45
Temperature	296.15 K
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 17.4676(18) A alpha = 90 deg.
	b = 13.5988(13) A beta = 93.711(2) deg.
	c = 9.4095(10) A gamma = 90 deg.
Volume	2230.4(4) A^3
Z, Calculated density	4, 1.300 Mg/m^3
Absorption coefficient	0.094 mm^-1
F(000)	920.0
Theta range for data collection	2.336 to 55.112 deg.
Limiting indices	-22<=h<=18, -11<=k<=17, -12<=l<=11
Reflections collected / unique	13236 / 5025 [R(int) = 0.0295]
Data/restraints/parameters	5025 / 0 / 293
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1393
R indices (all data)	R1 = 0.0888, wR2 = 0.1658
Largest diff. peak and hole	0.27 and -0.37 e.A^-3

6. ^{1}H NMR and ^{13}C NMR spectra for spectroscopic data.

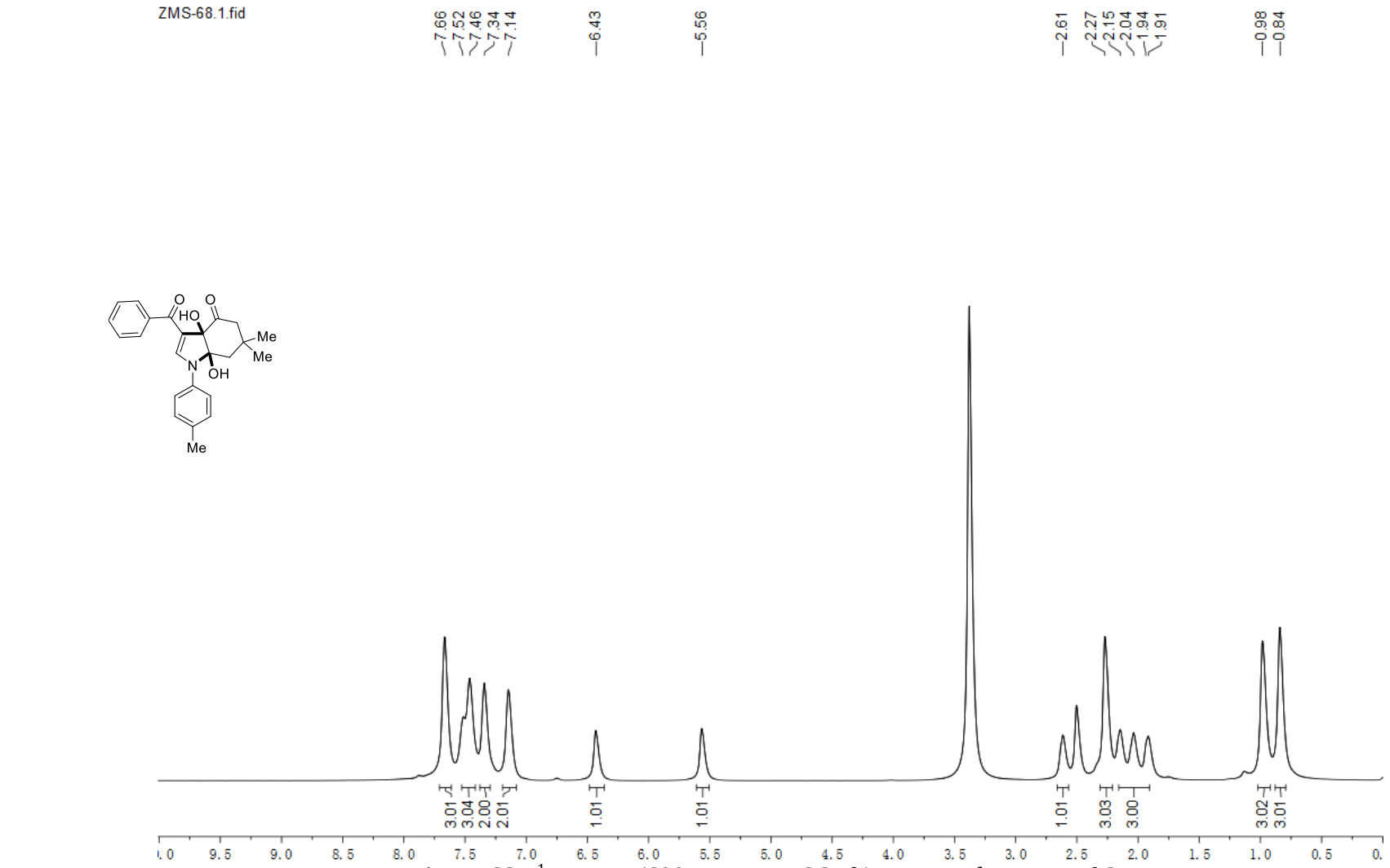


Figure S2. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3a**

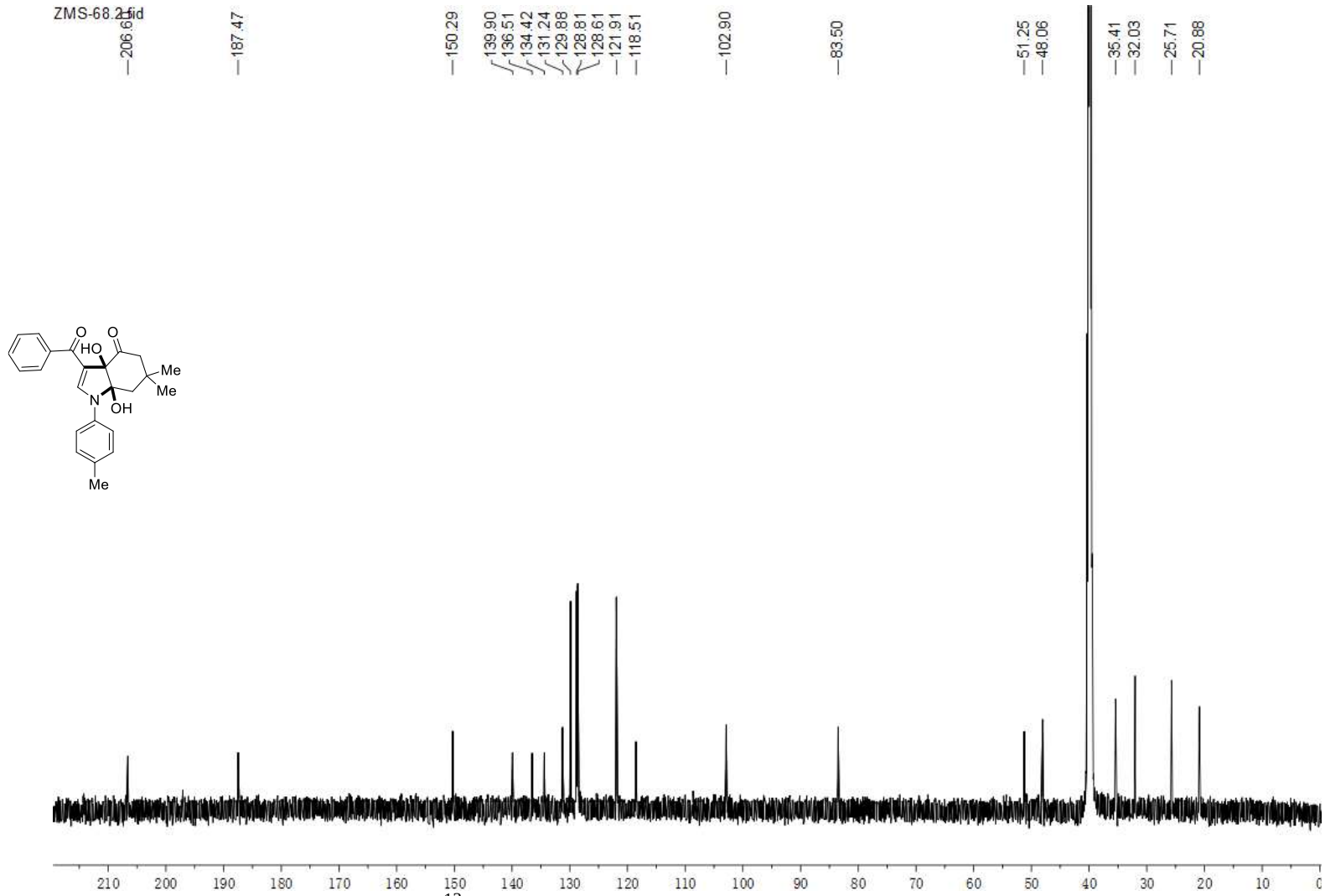


Figure S3. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3a**

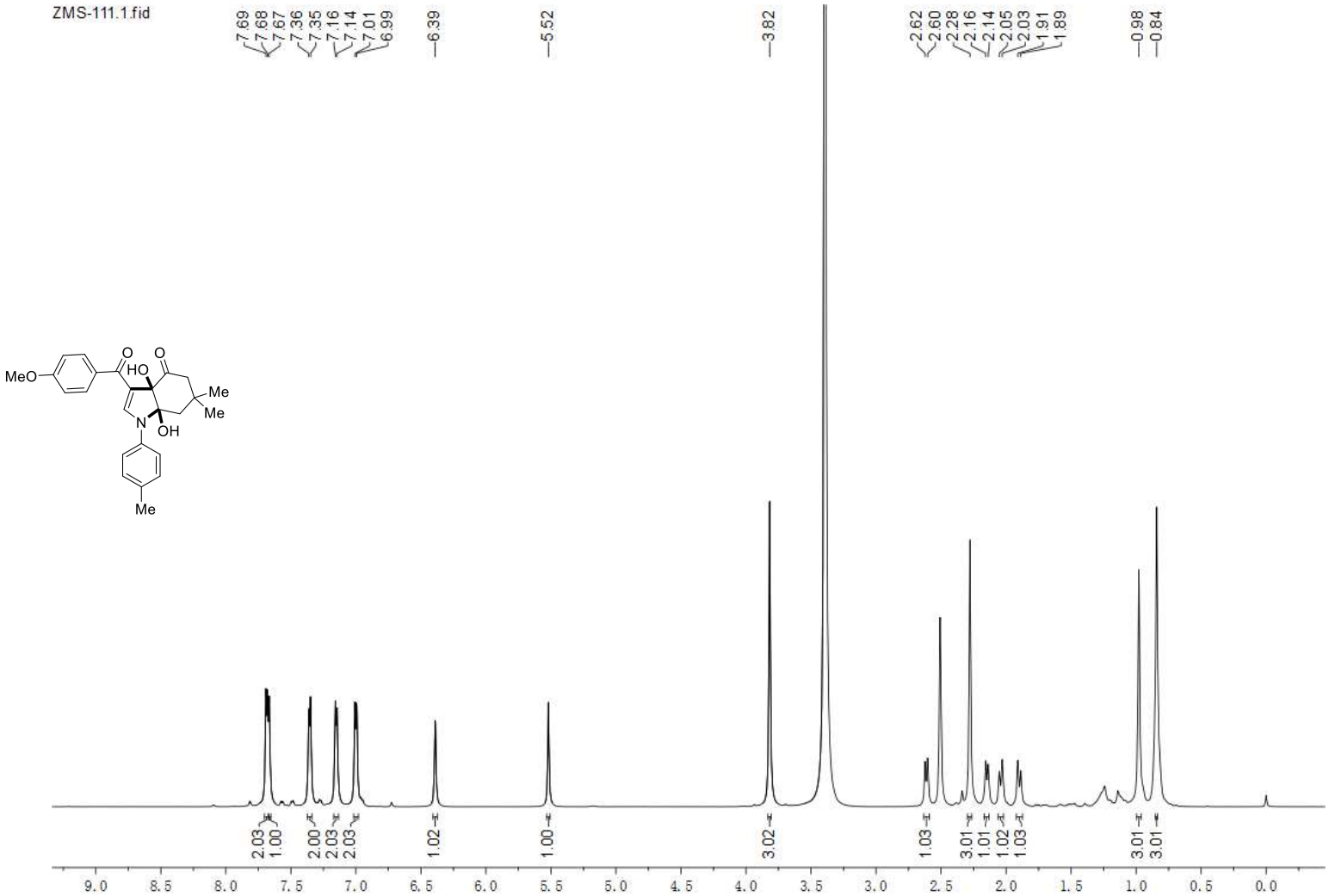


Figure S4. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3b**

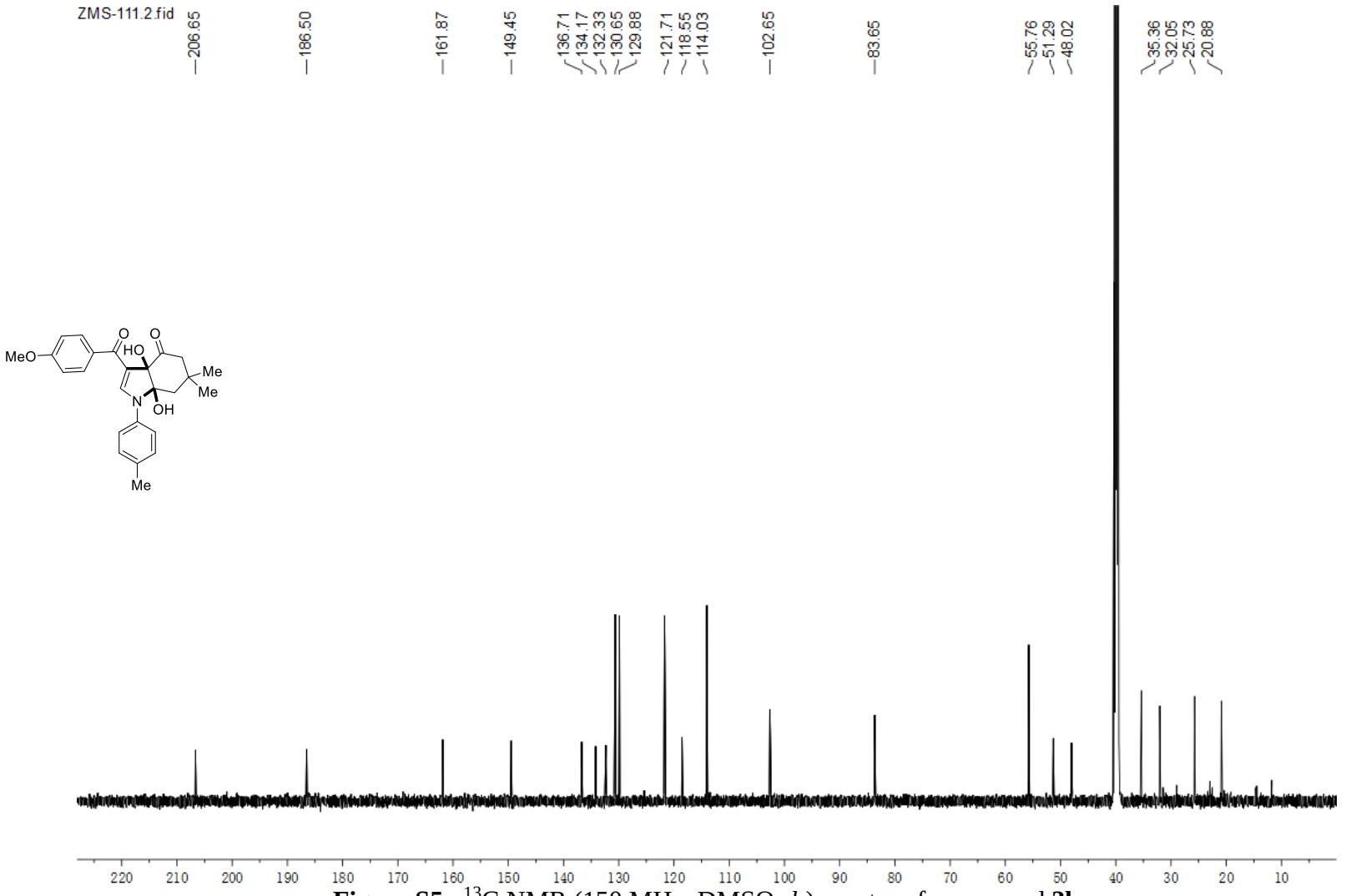


Figure S5. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3b**

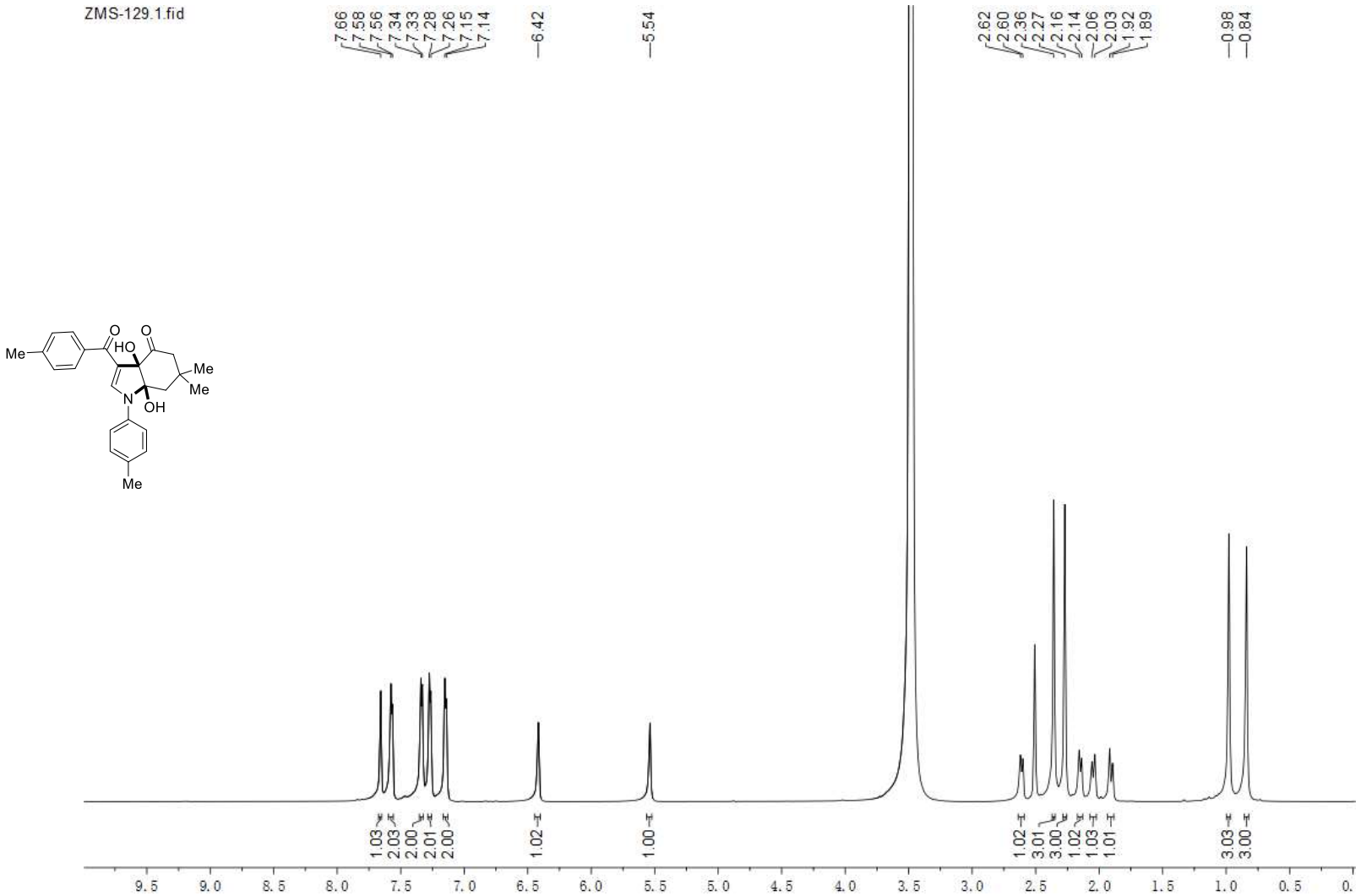


Figure S6. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3c**

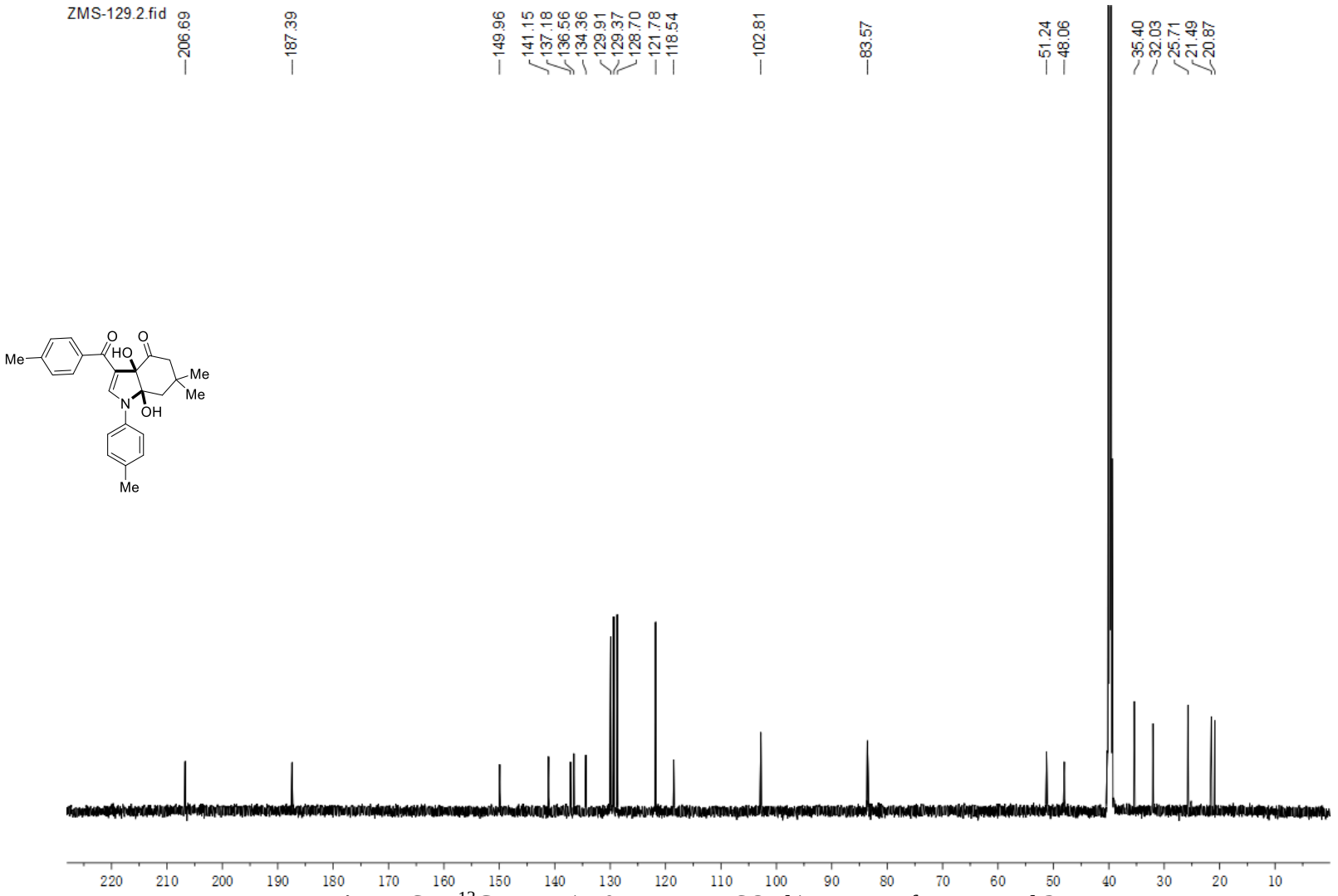


Figure S7. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3c**

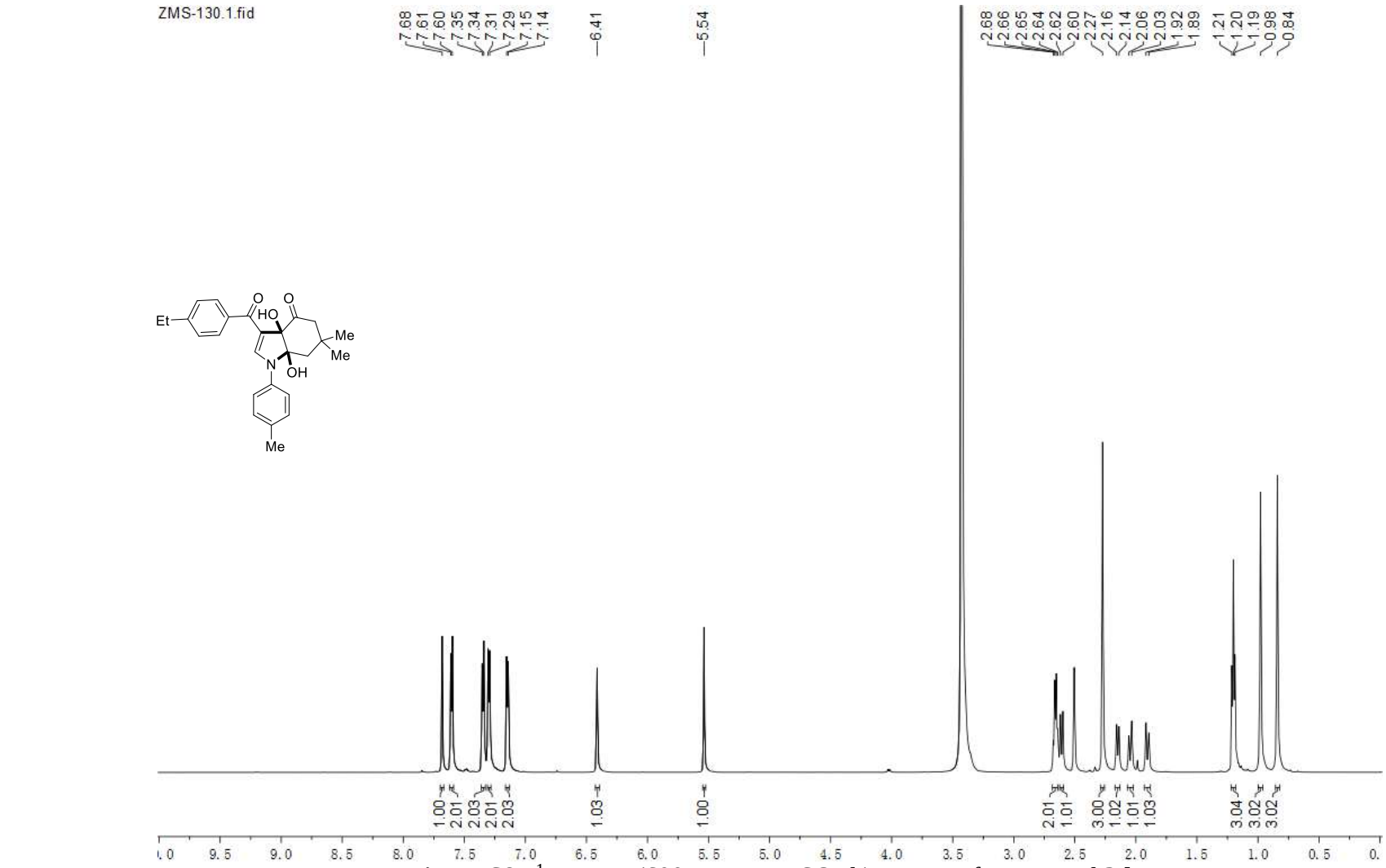


Figure S8. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3d**

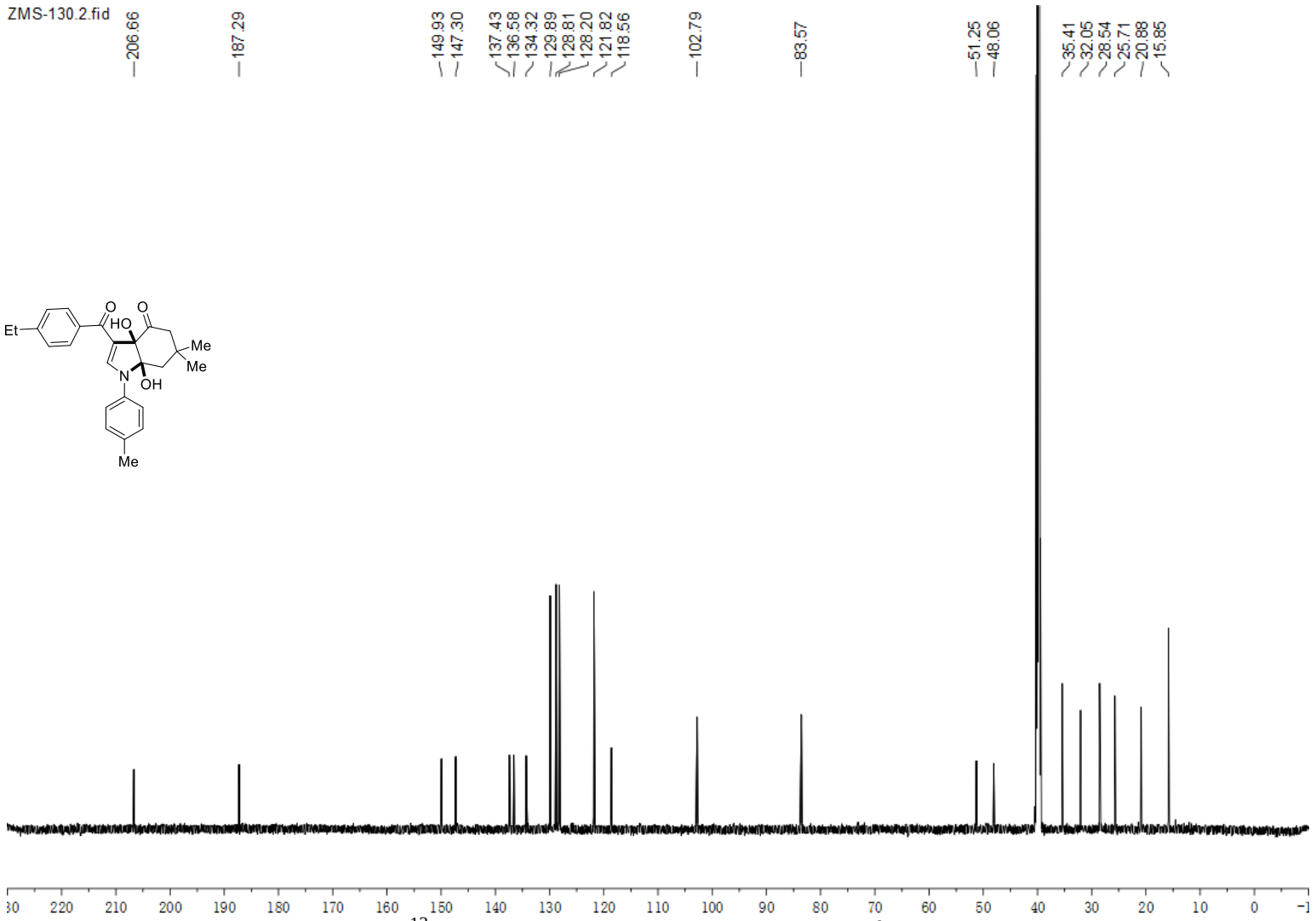


Figure S9. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3d**

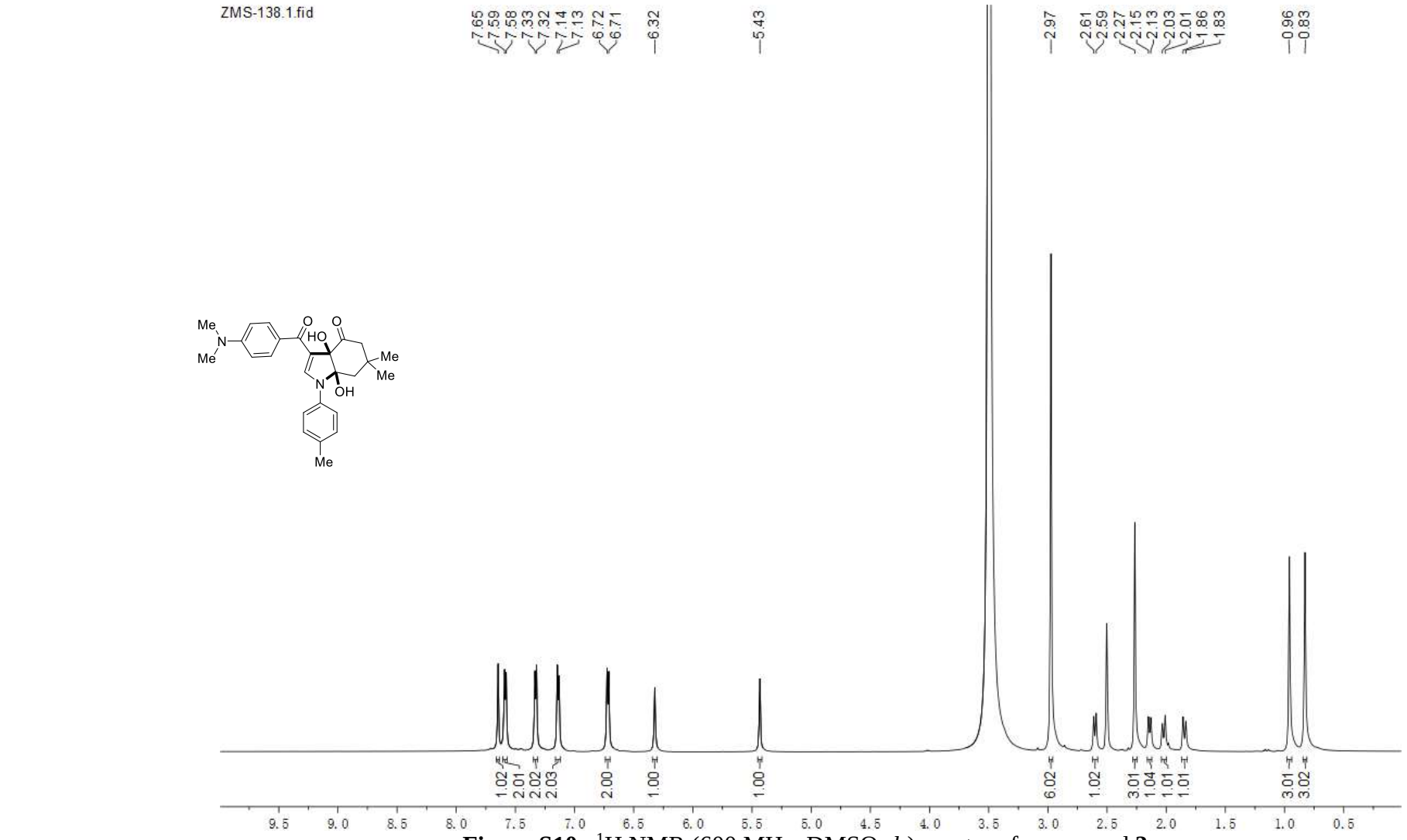


Figure S10. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3e**

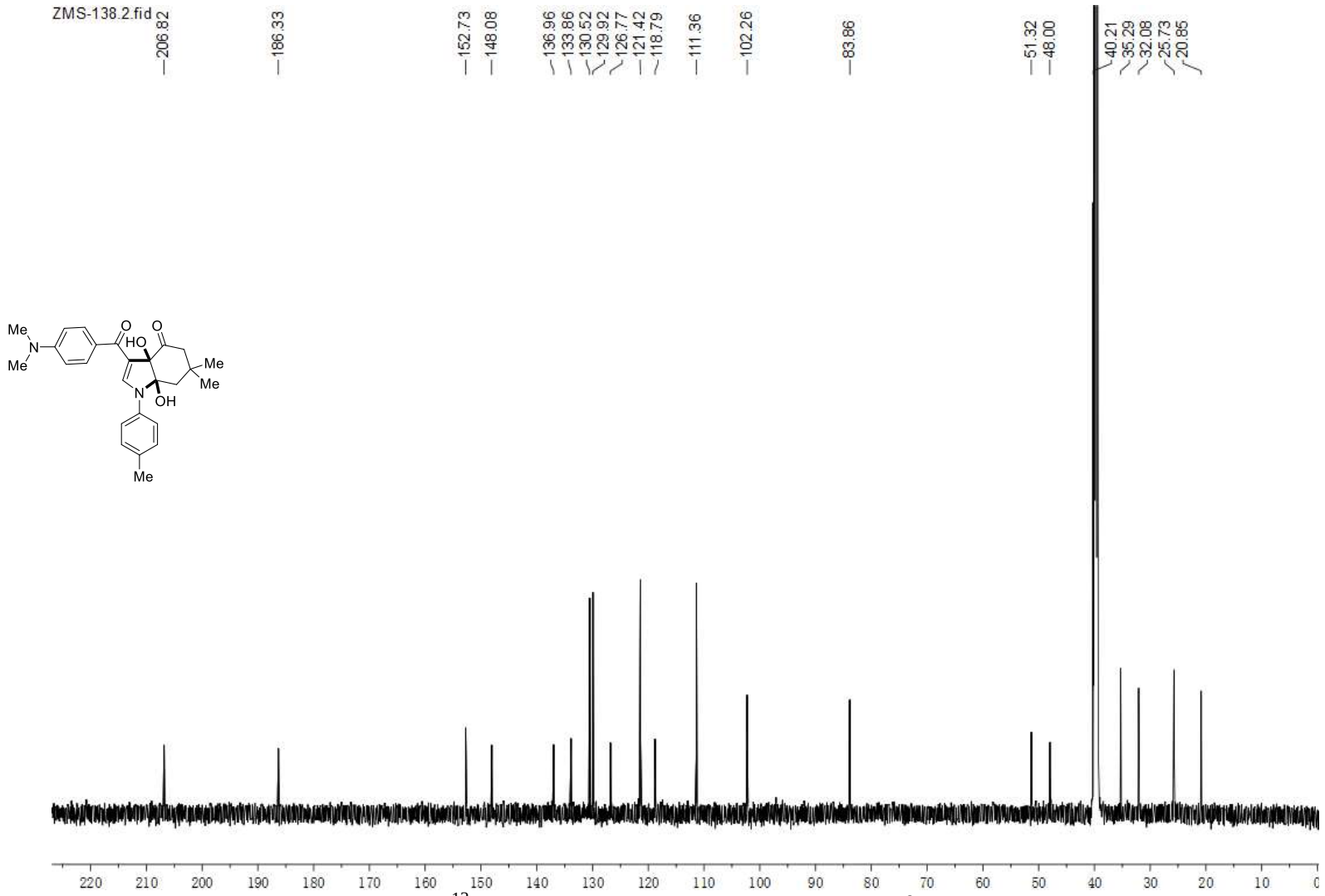


Figure S11. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3e**

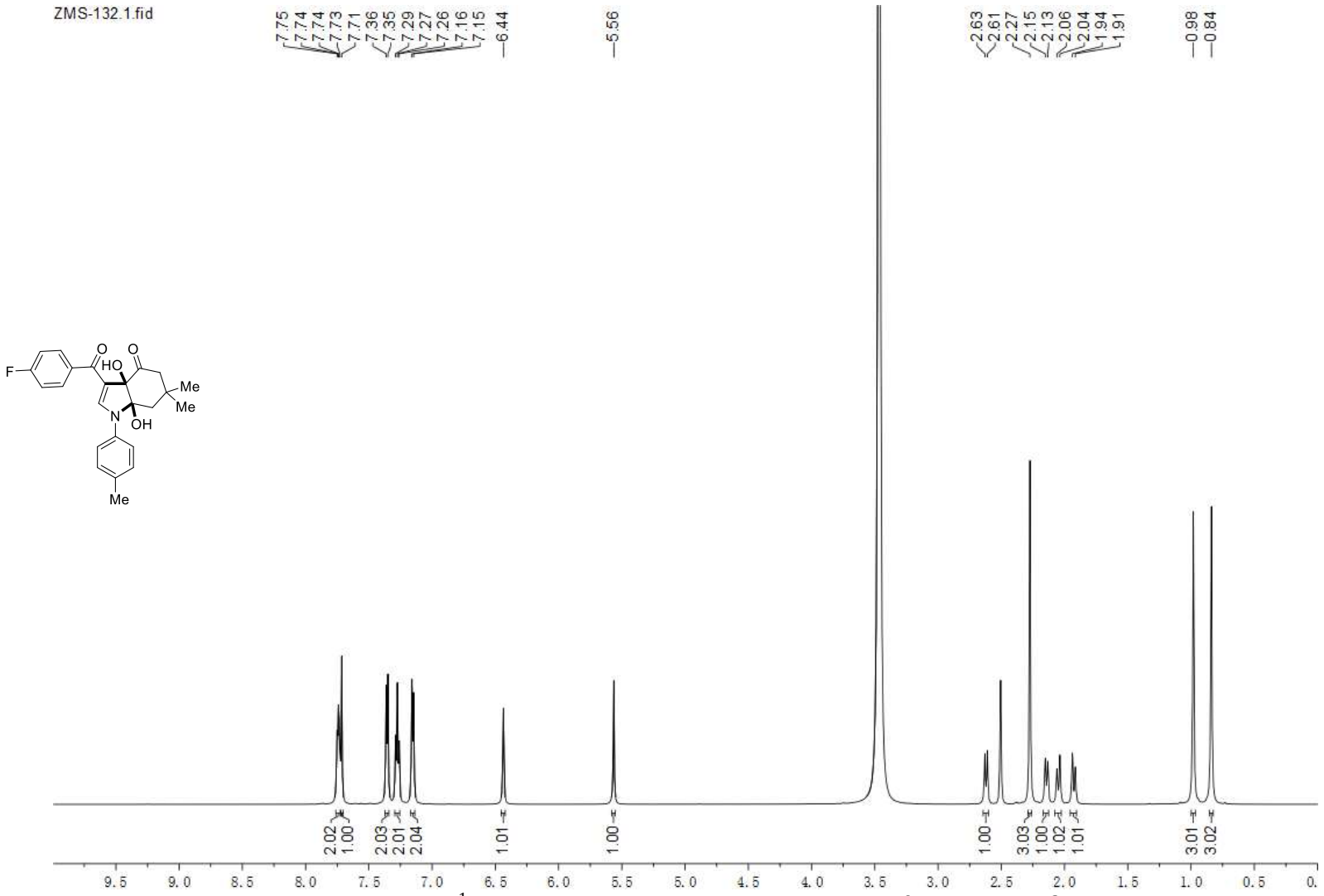


Figure S12. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3f**

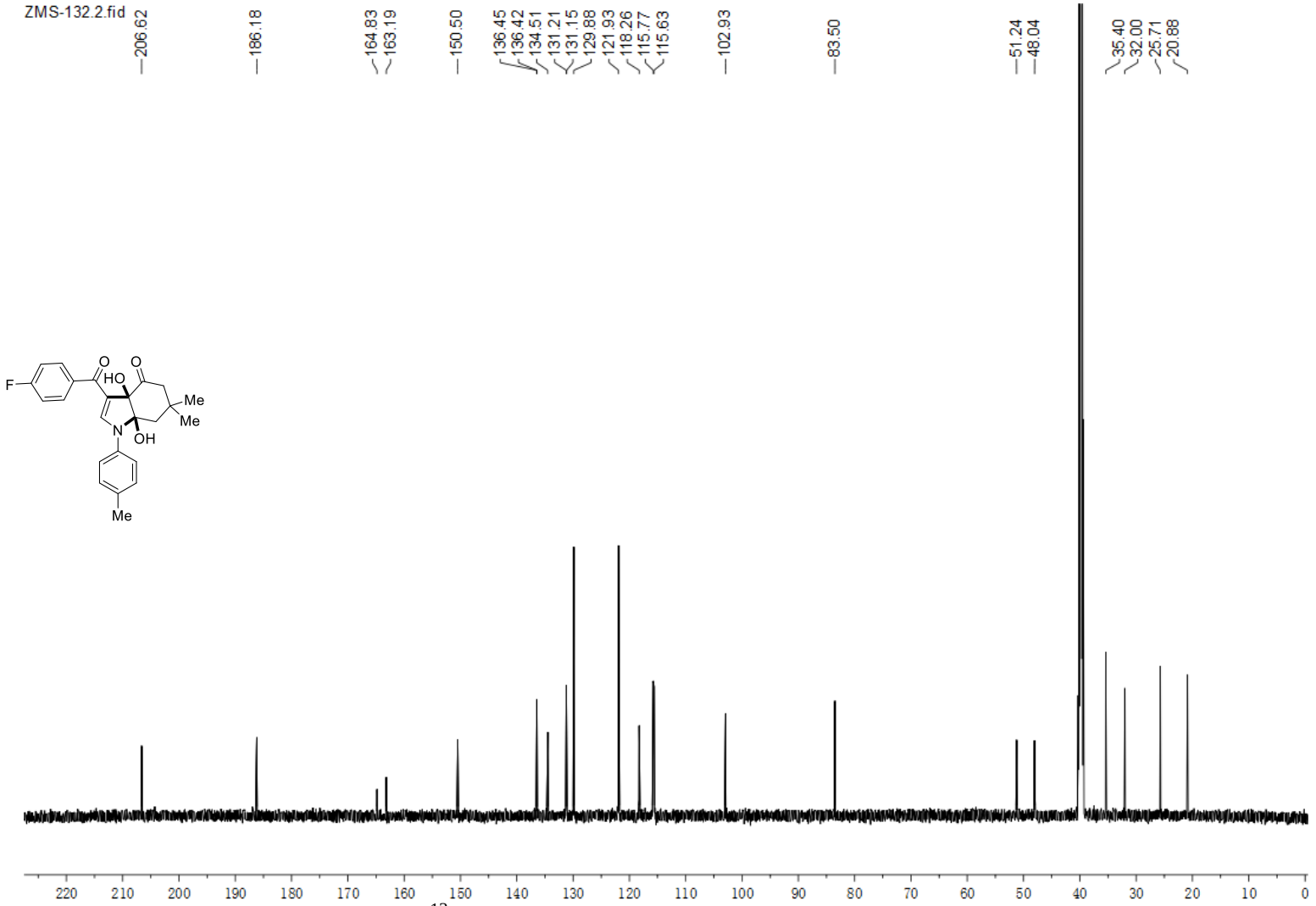


Figure S13. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3f**

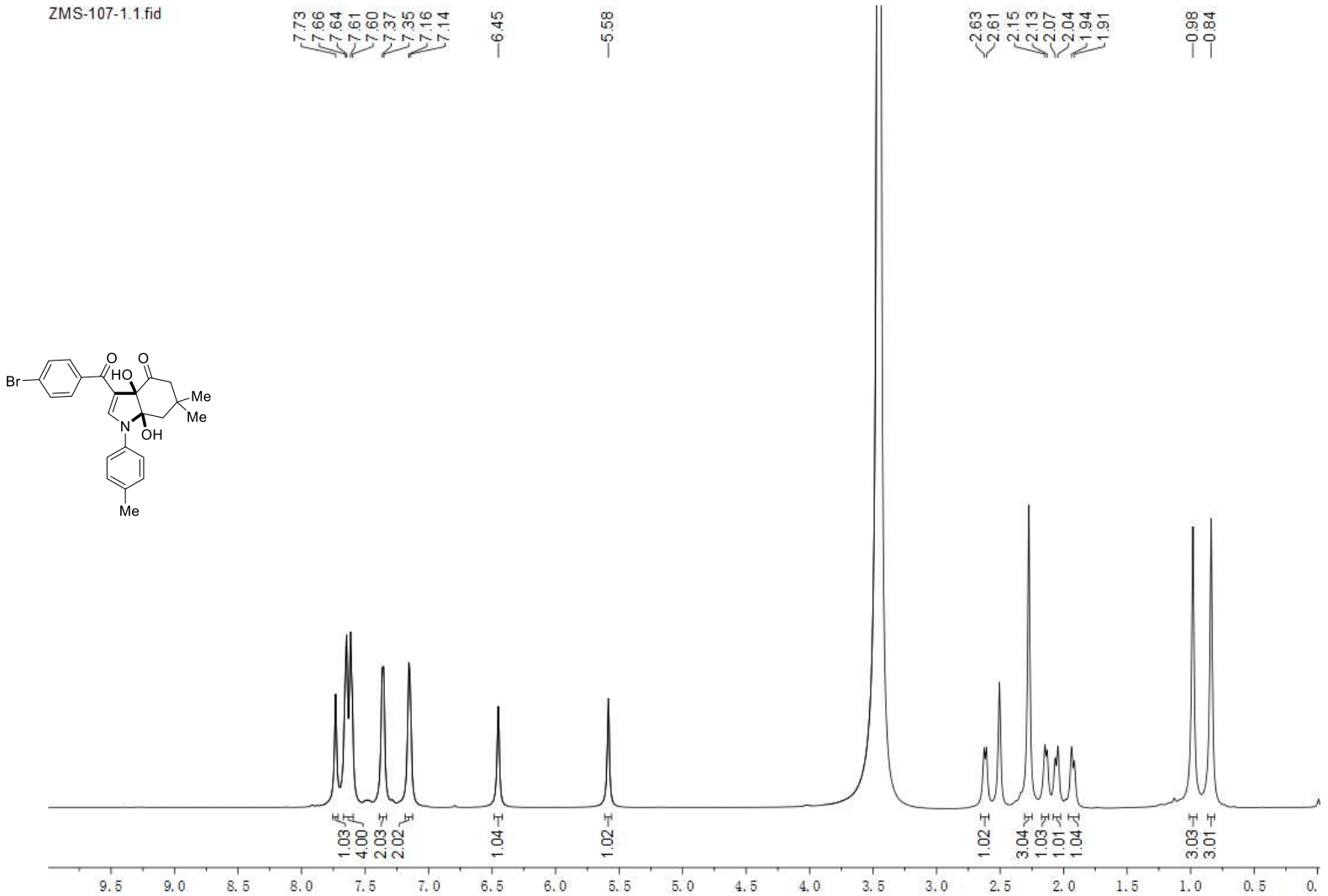


Figure S14. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3g**

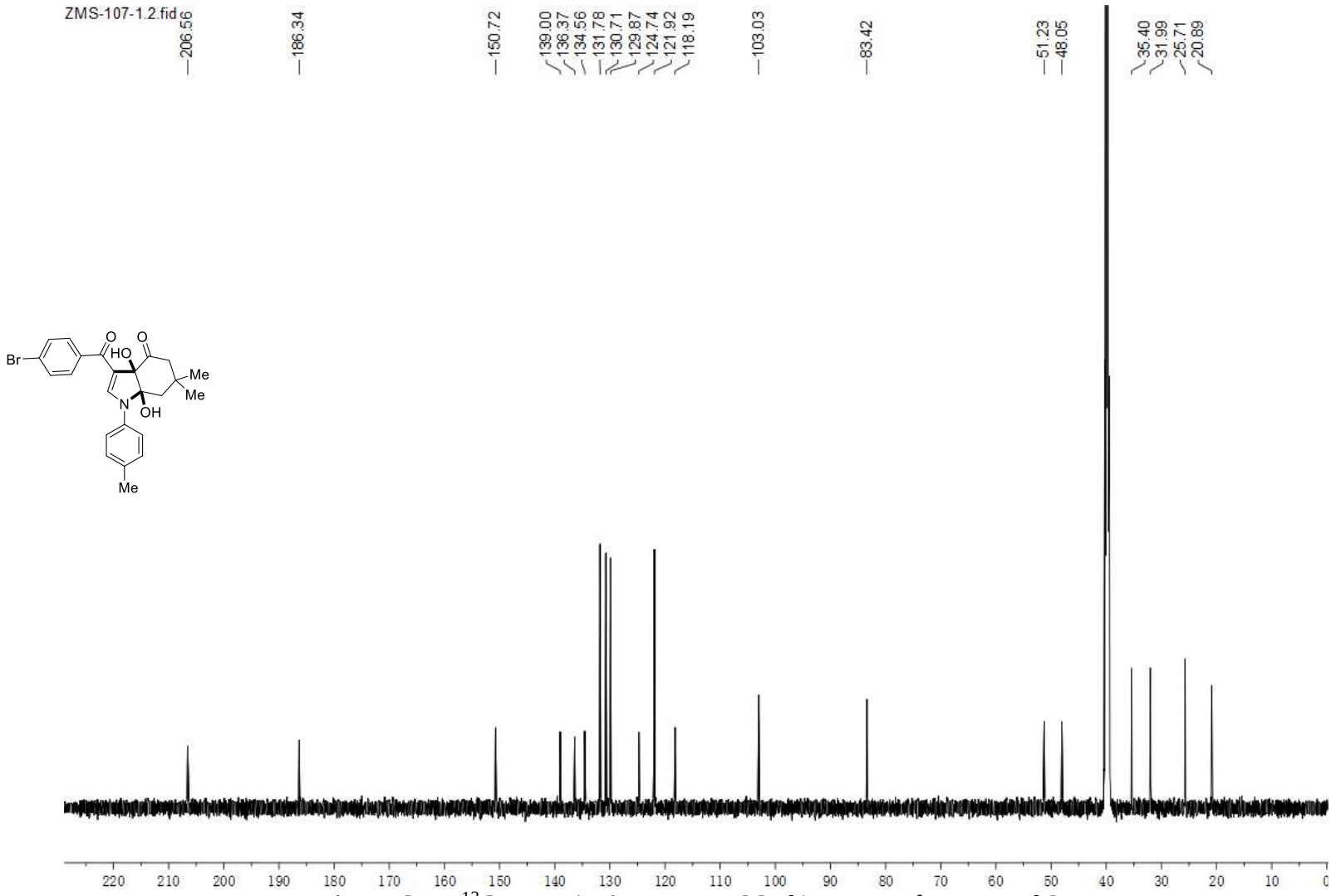


Figure S15. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3g**

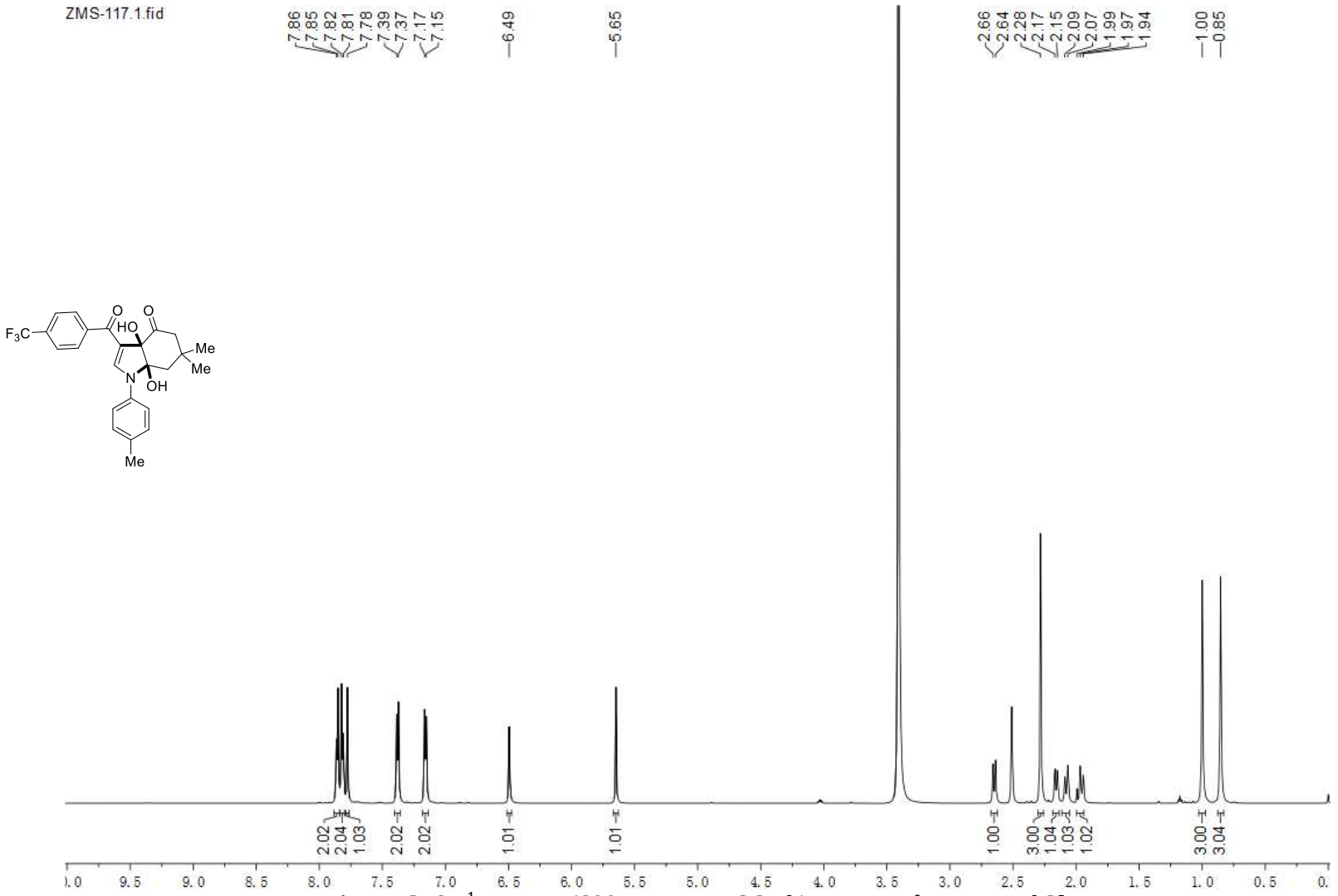


Figure S16. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3h**

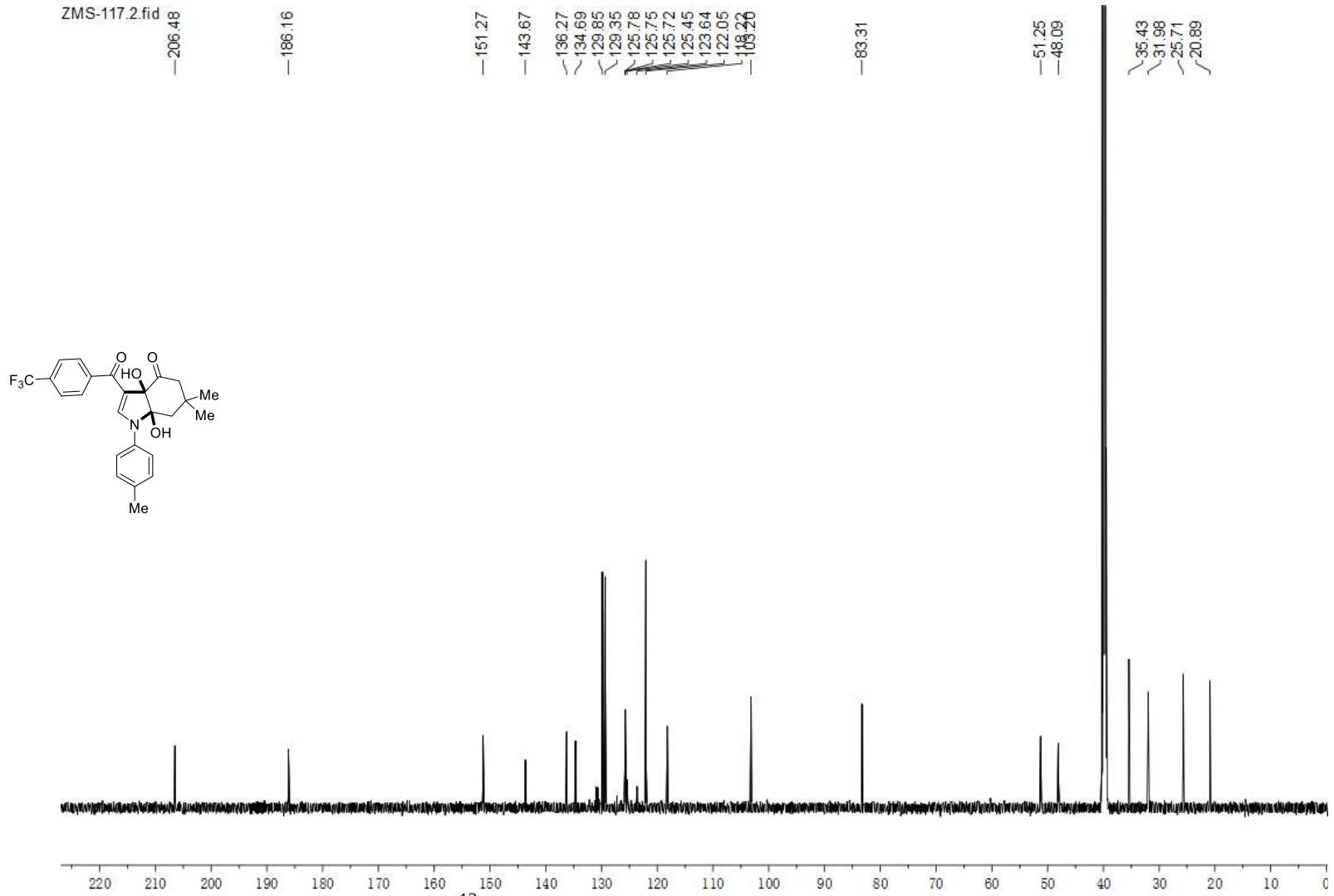


Figure S17. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3h**

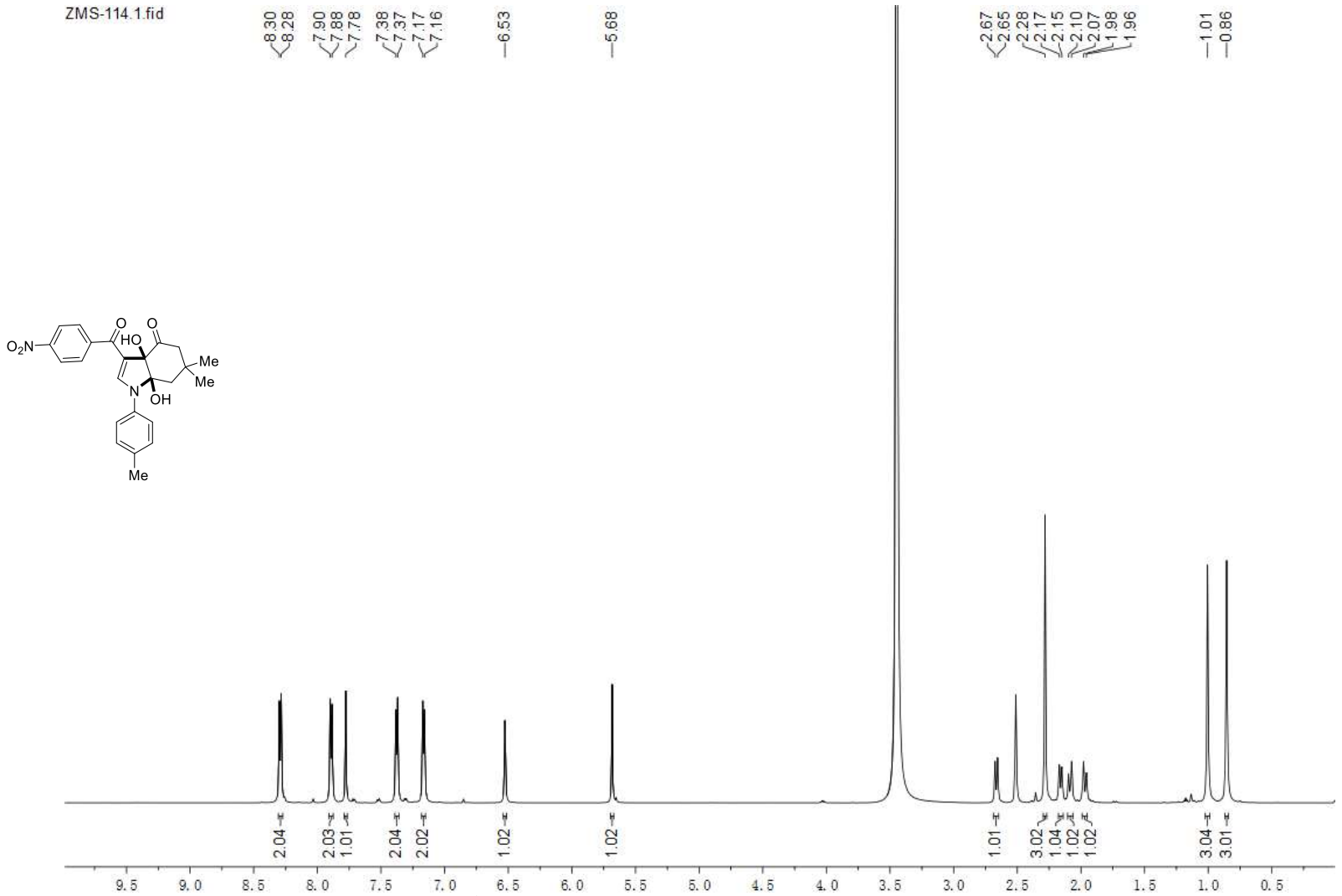


Figure S18. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3i**

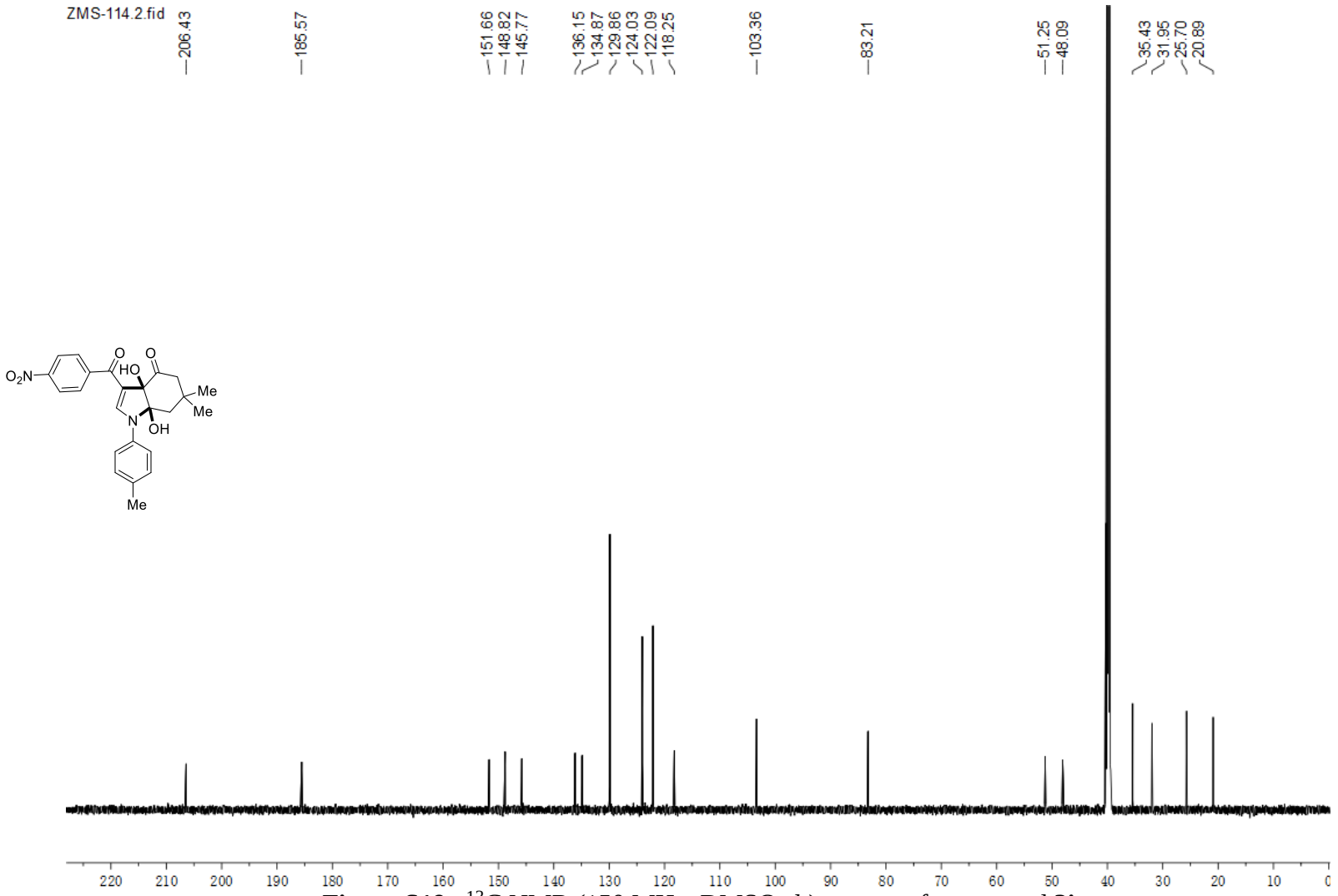


Figure S19. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3i**

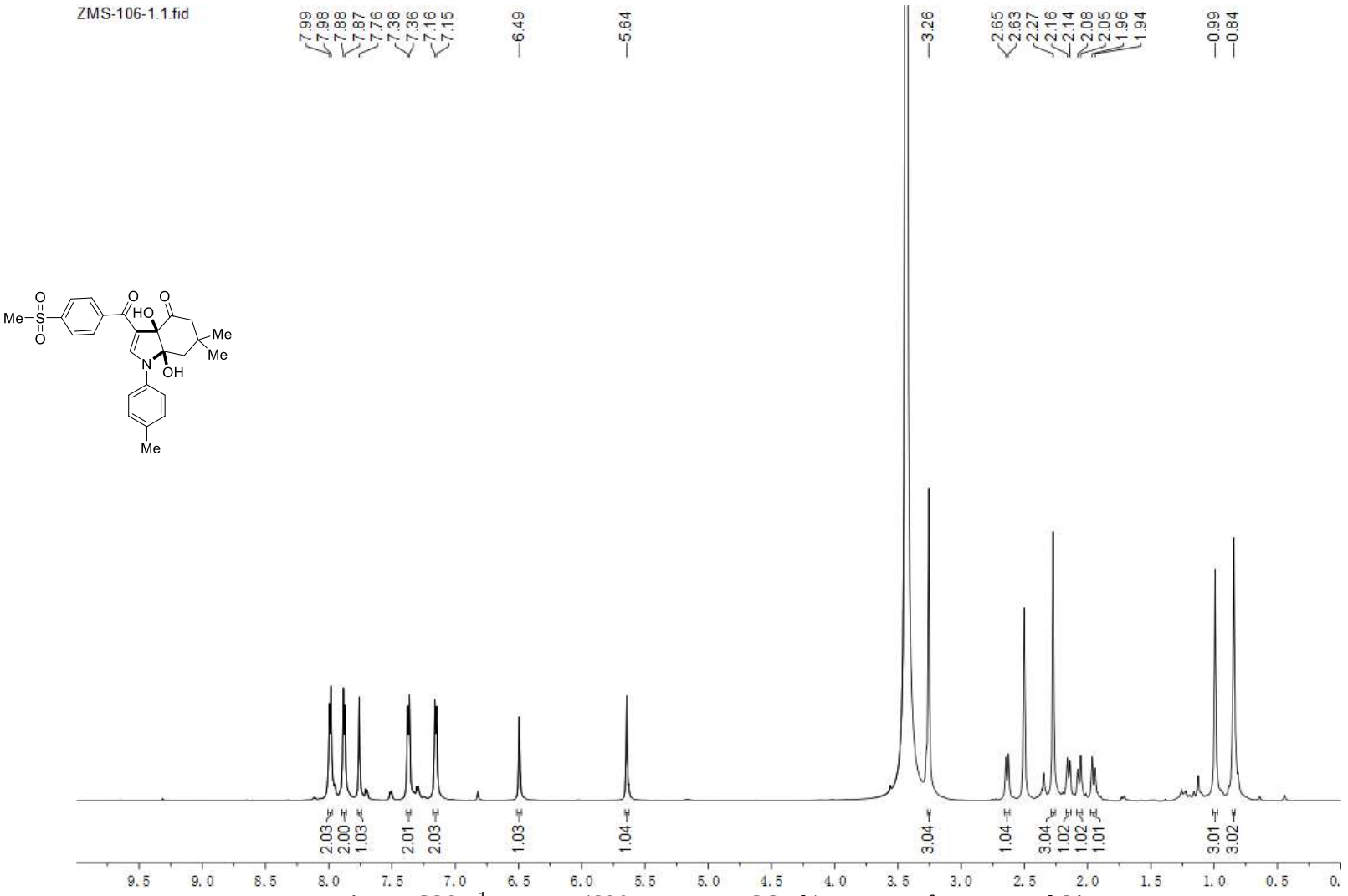


Figure S20. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3j**

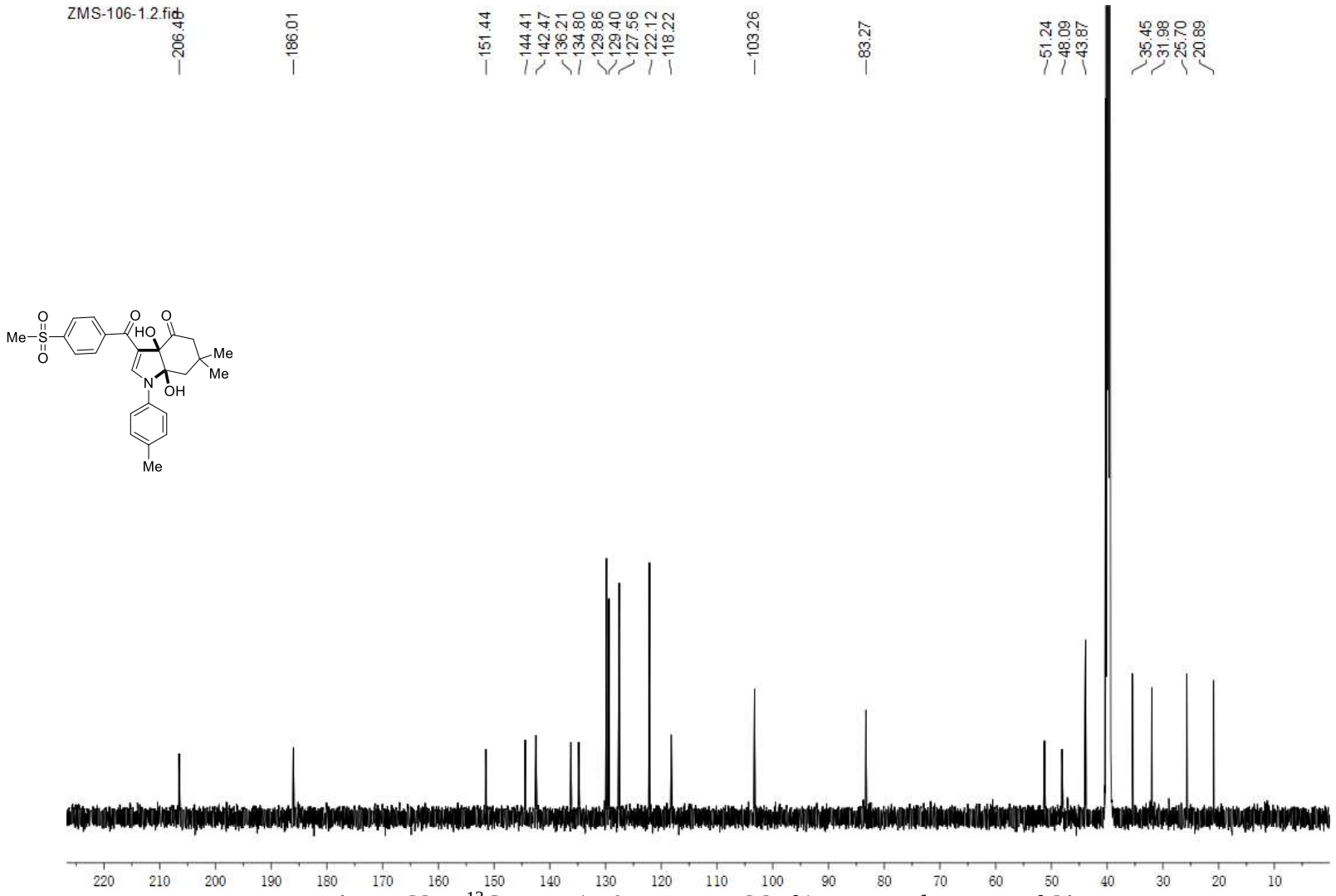


Figure S21. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3j**

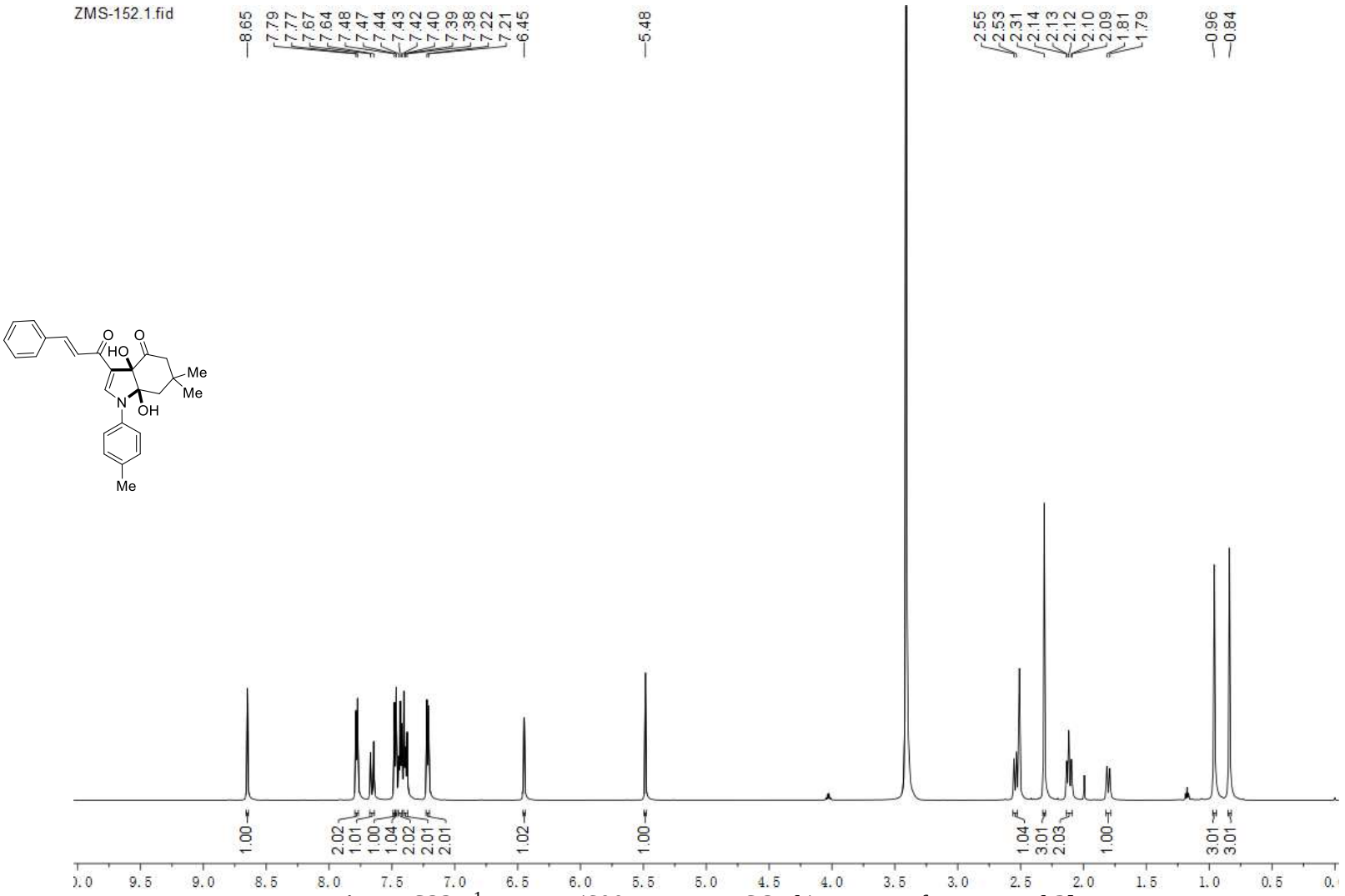


Figure S22. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3k**

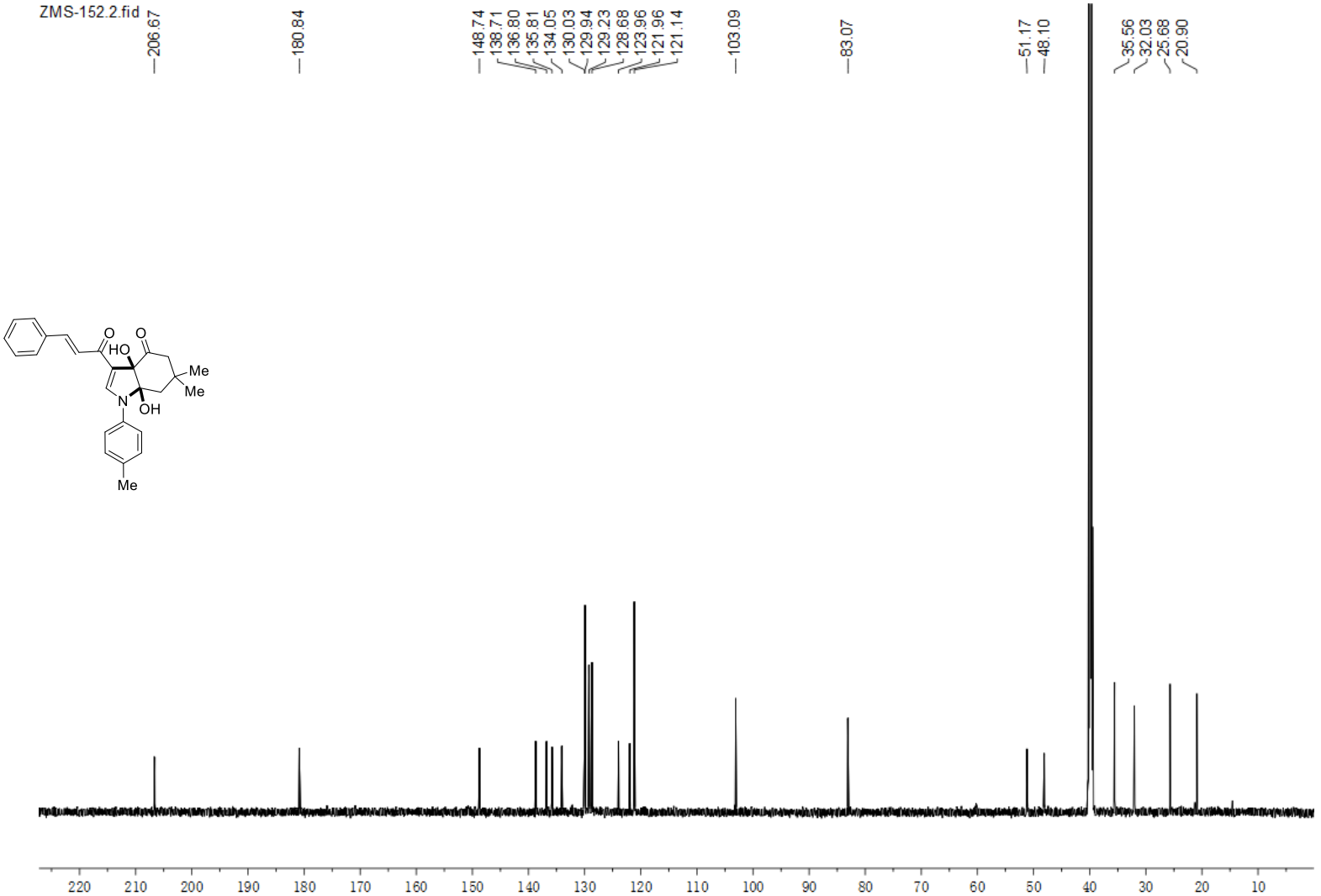


Figure S23. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3k**

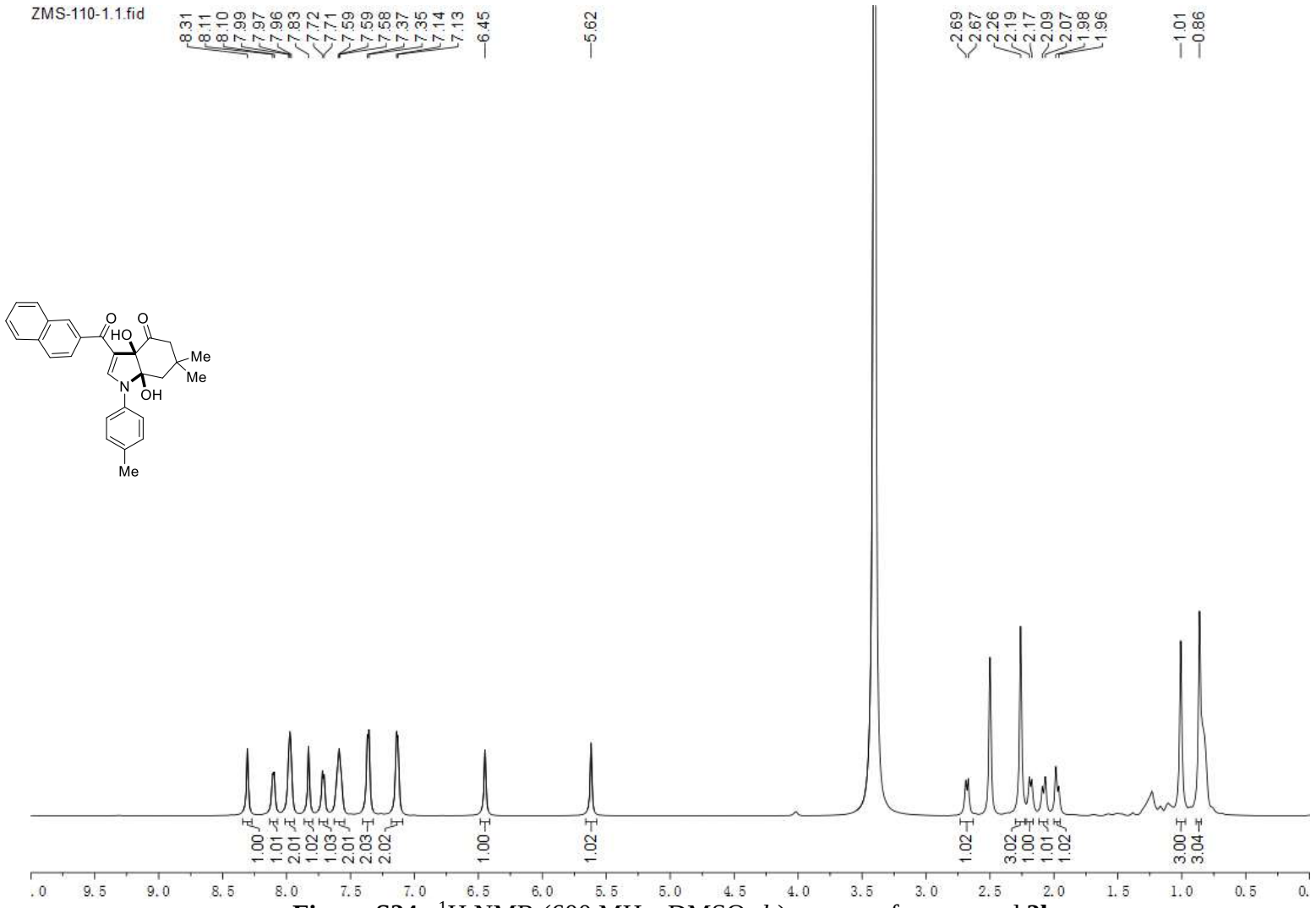


Figure S24. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3l**

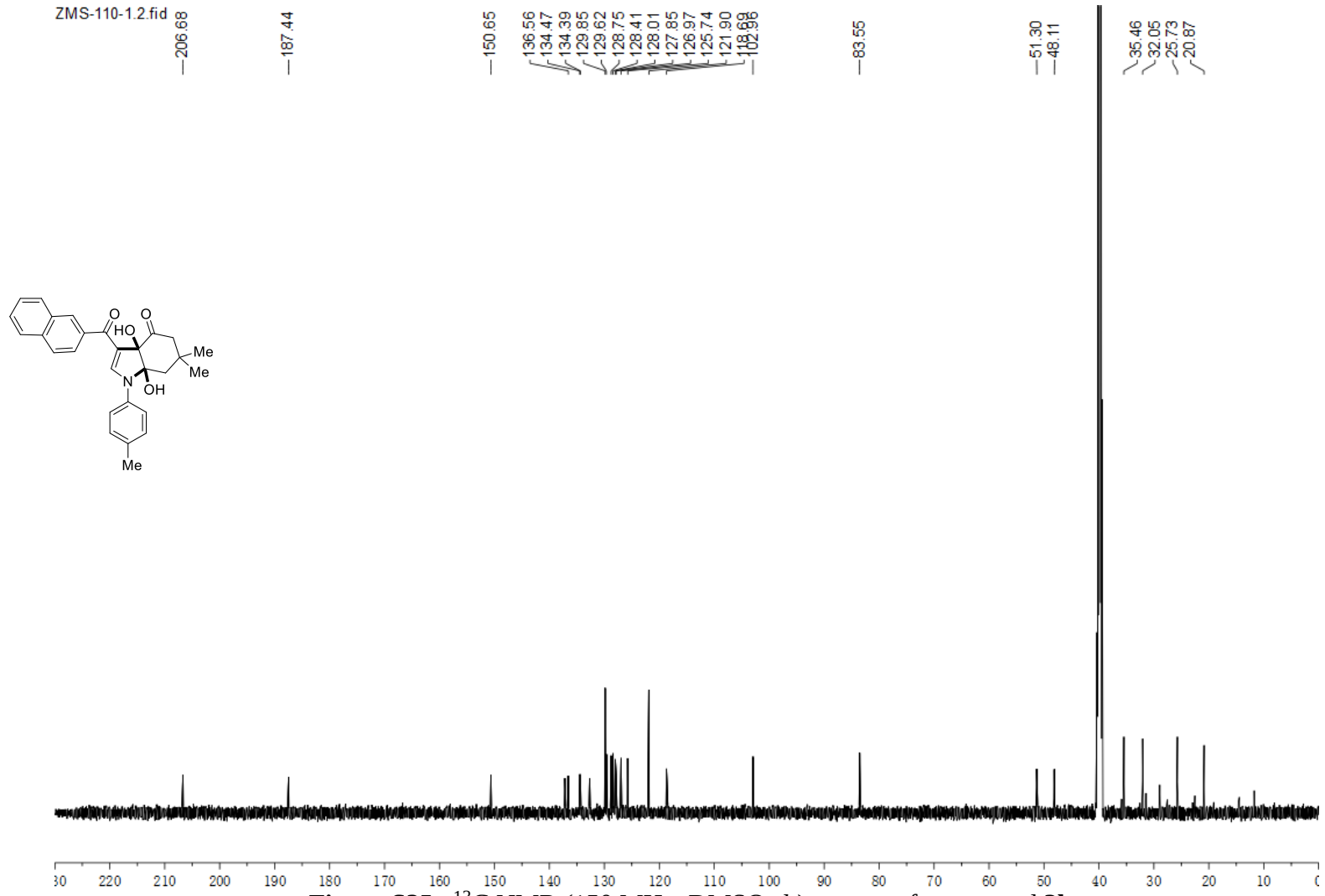


Figure S25. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3l**

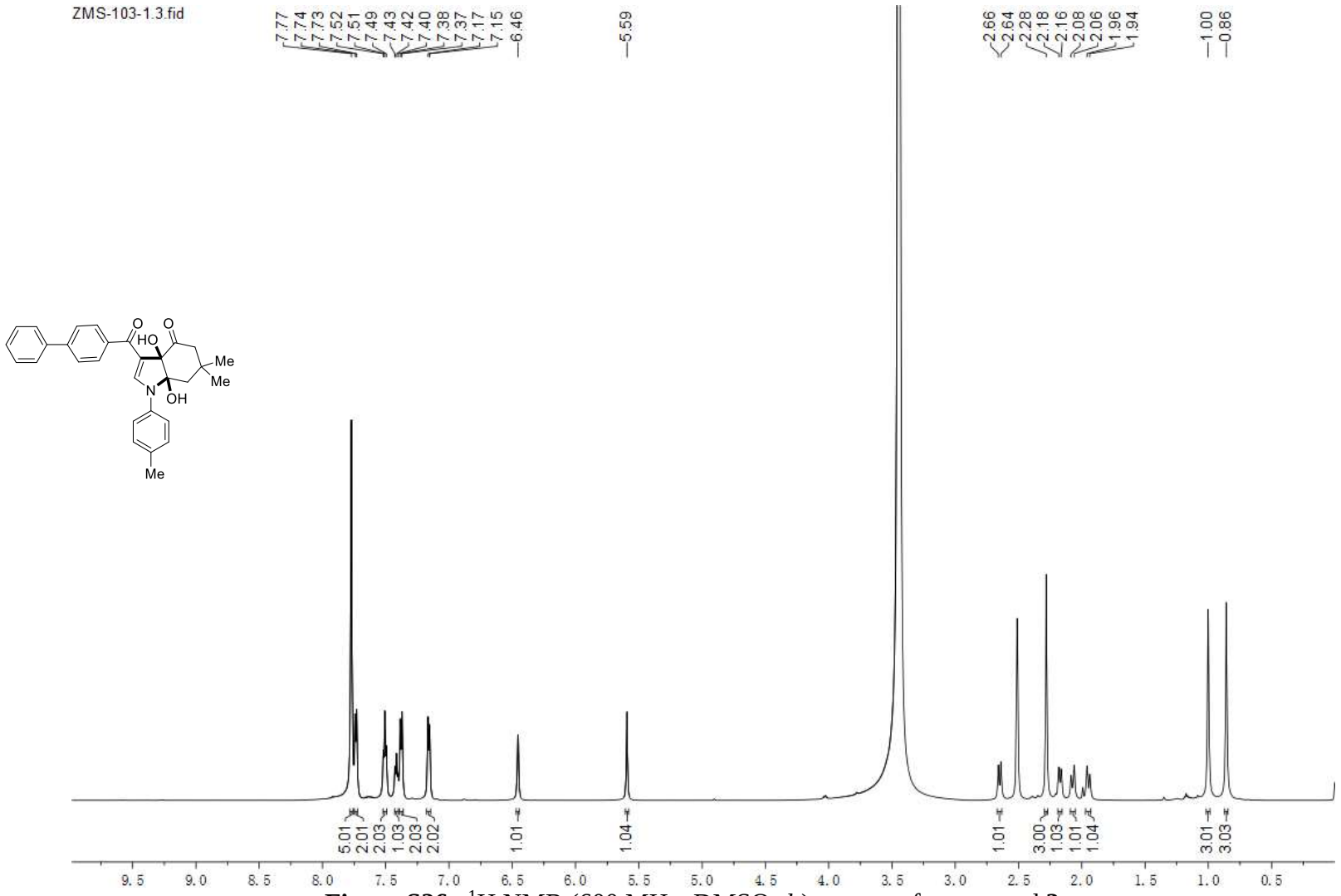


Figure S26. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3m**

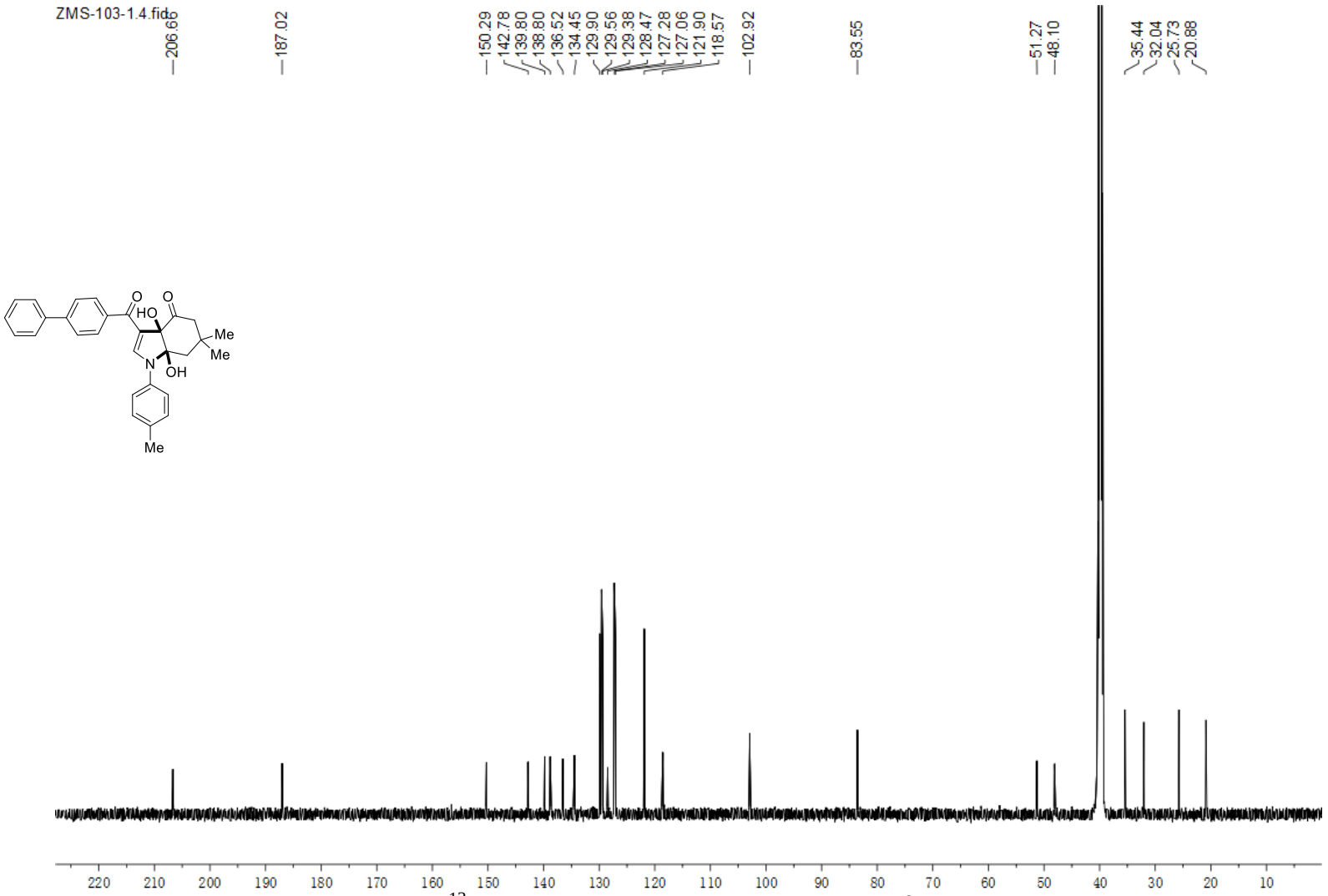


Figure S27. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3m**

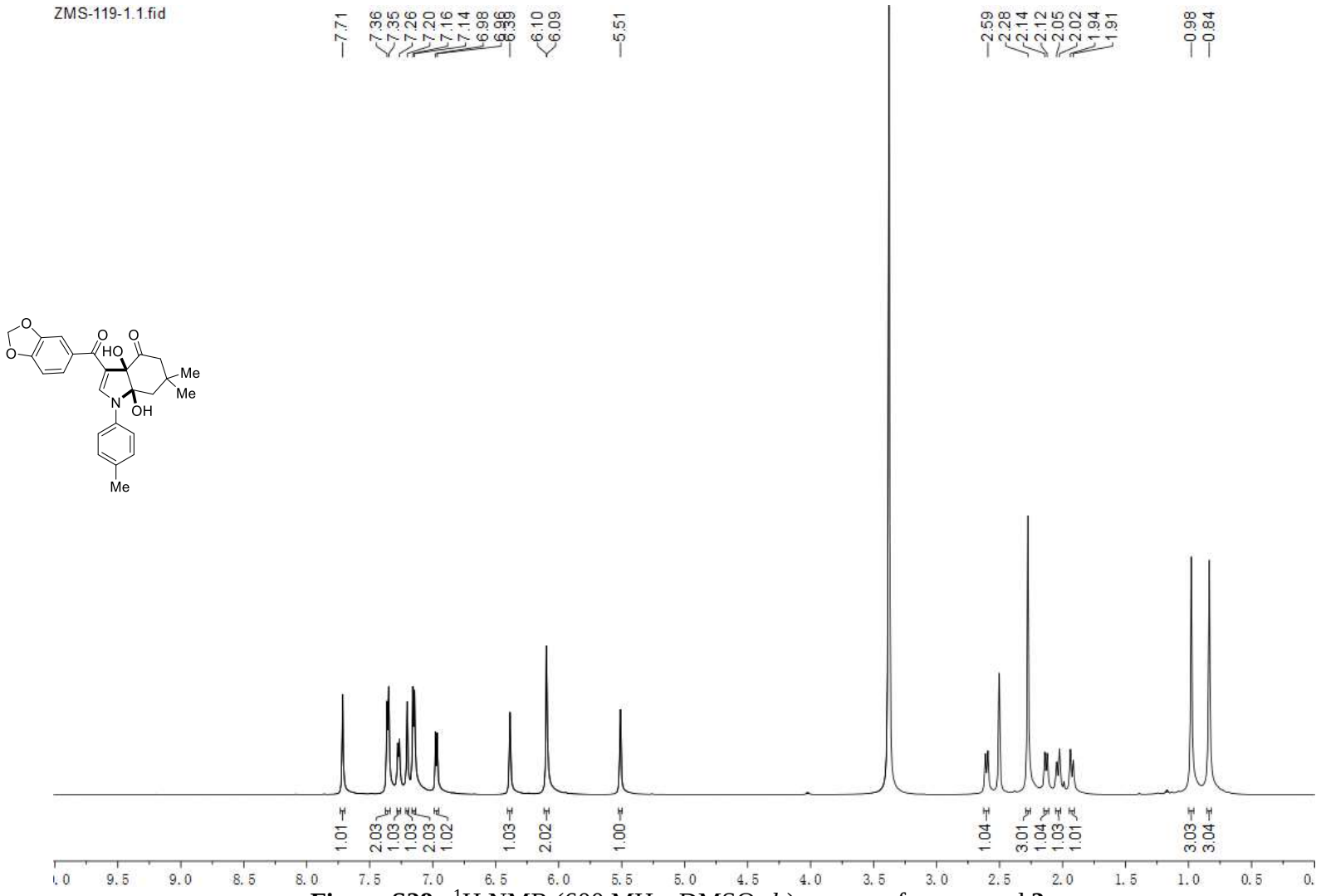


Figure S28. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3n**

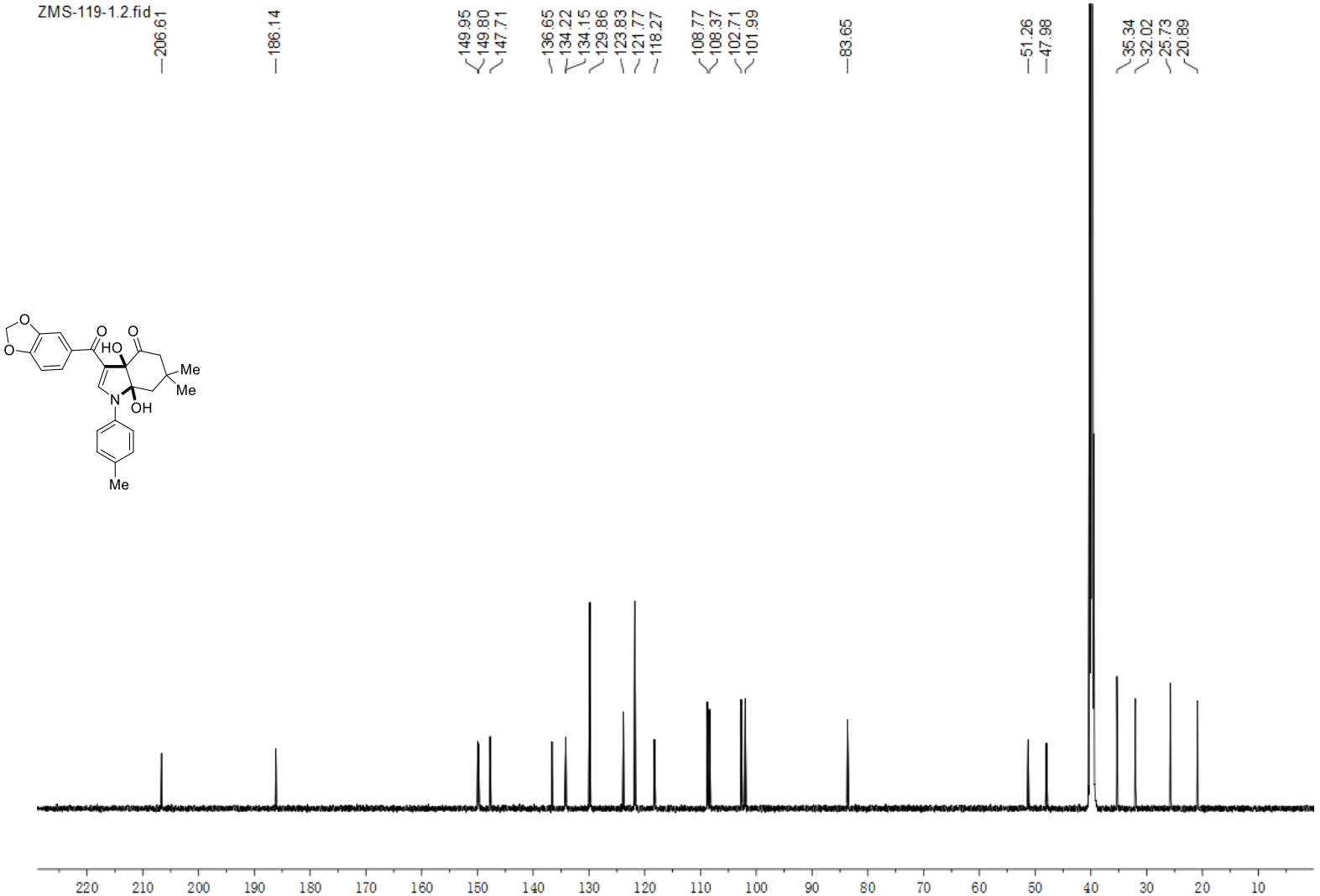


Figure S29. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3n**

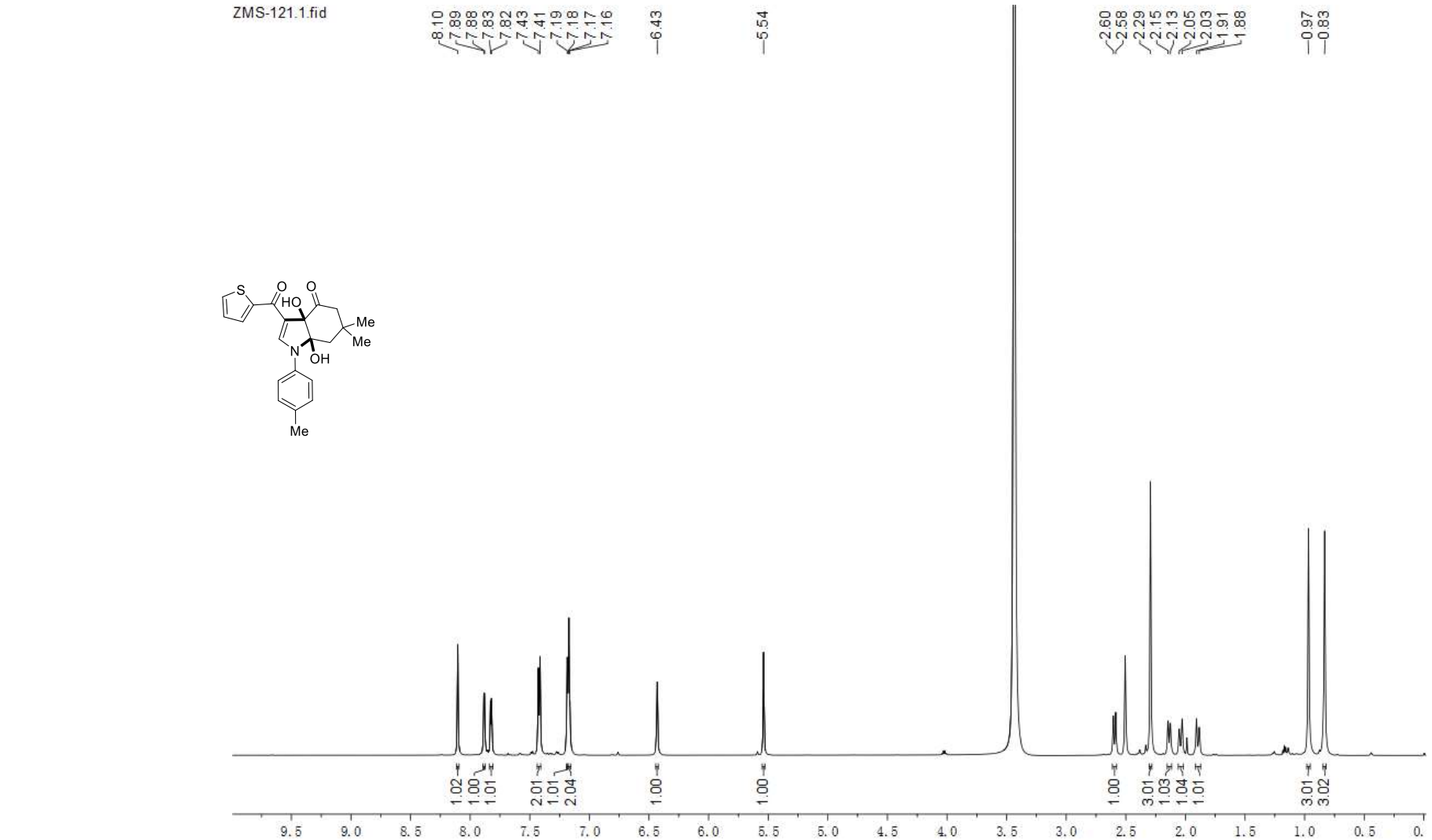


Figure S30. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3o**

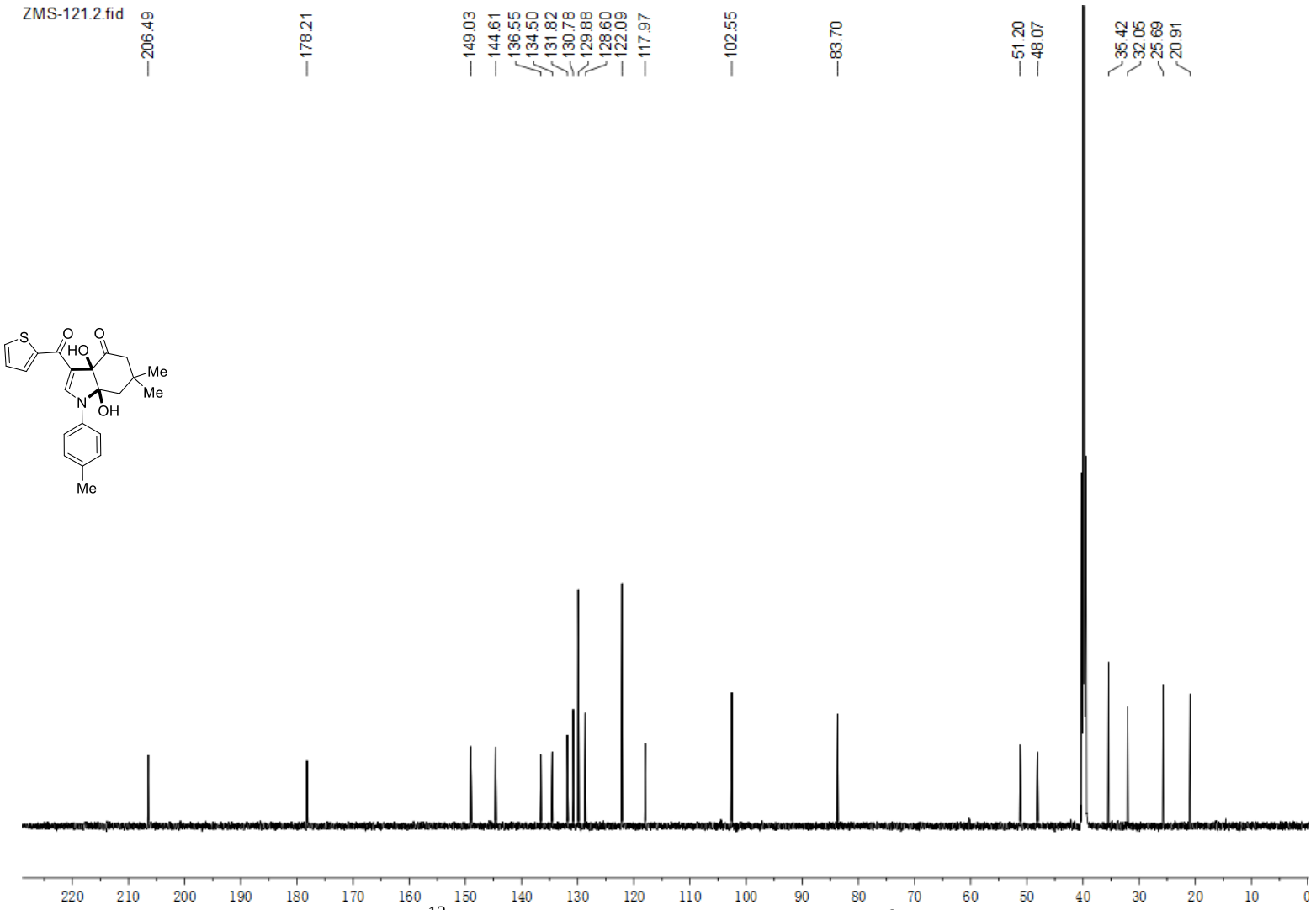


Figure S31. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3o**

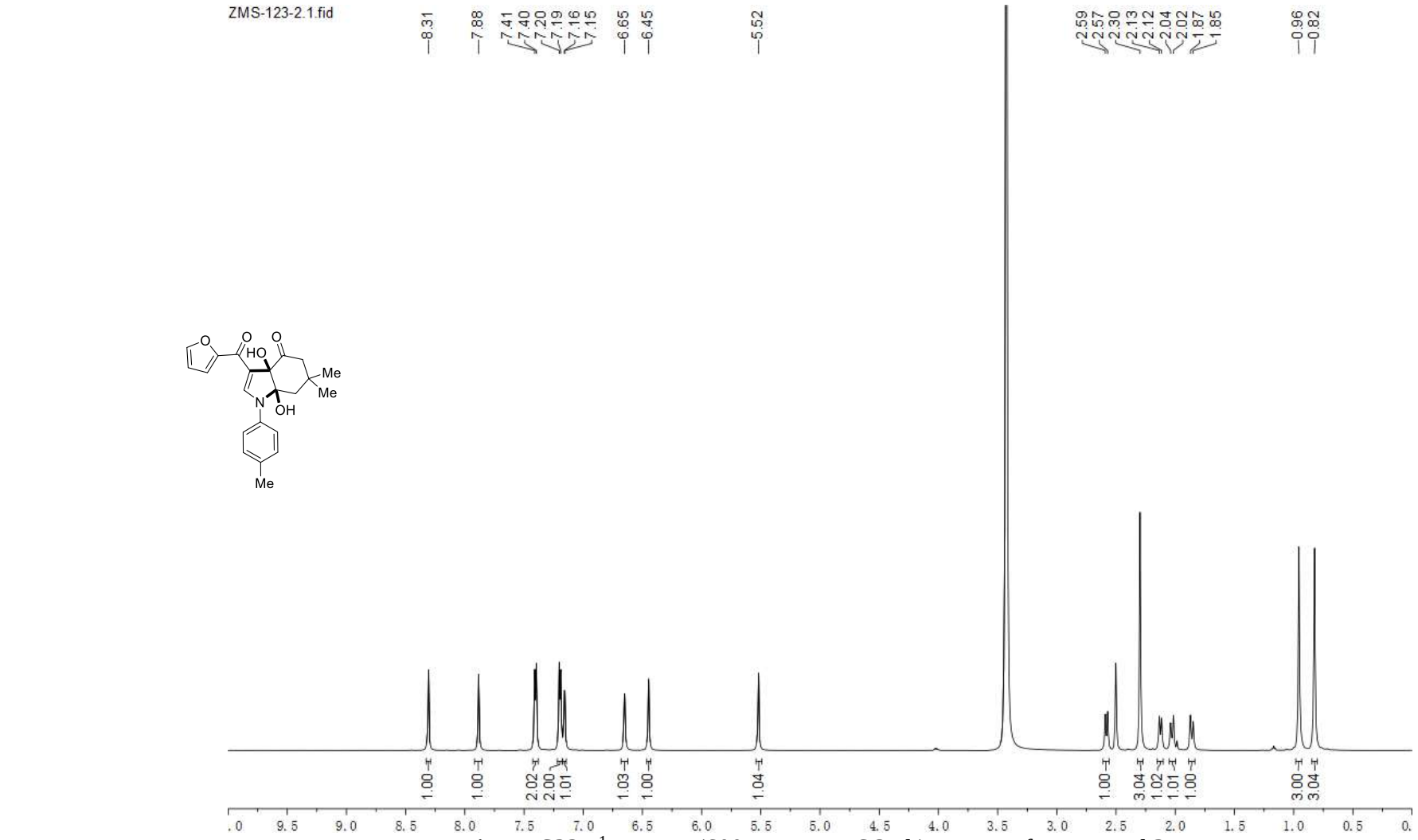


Figure S32. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3p**

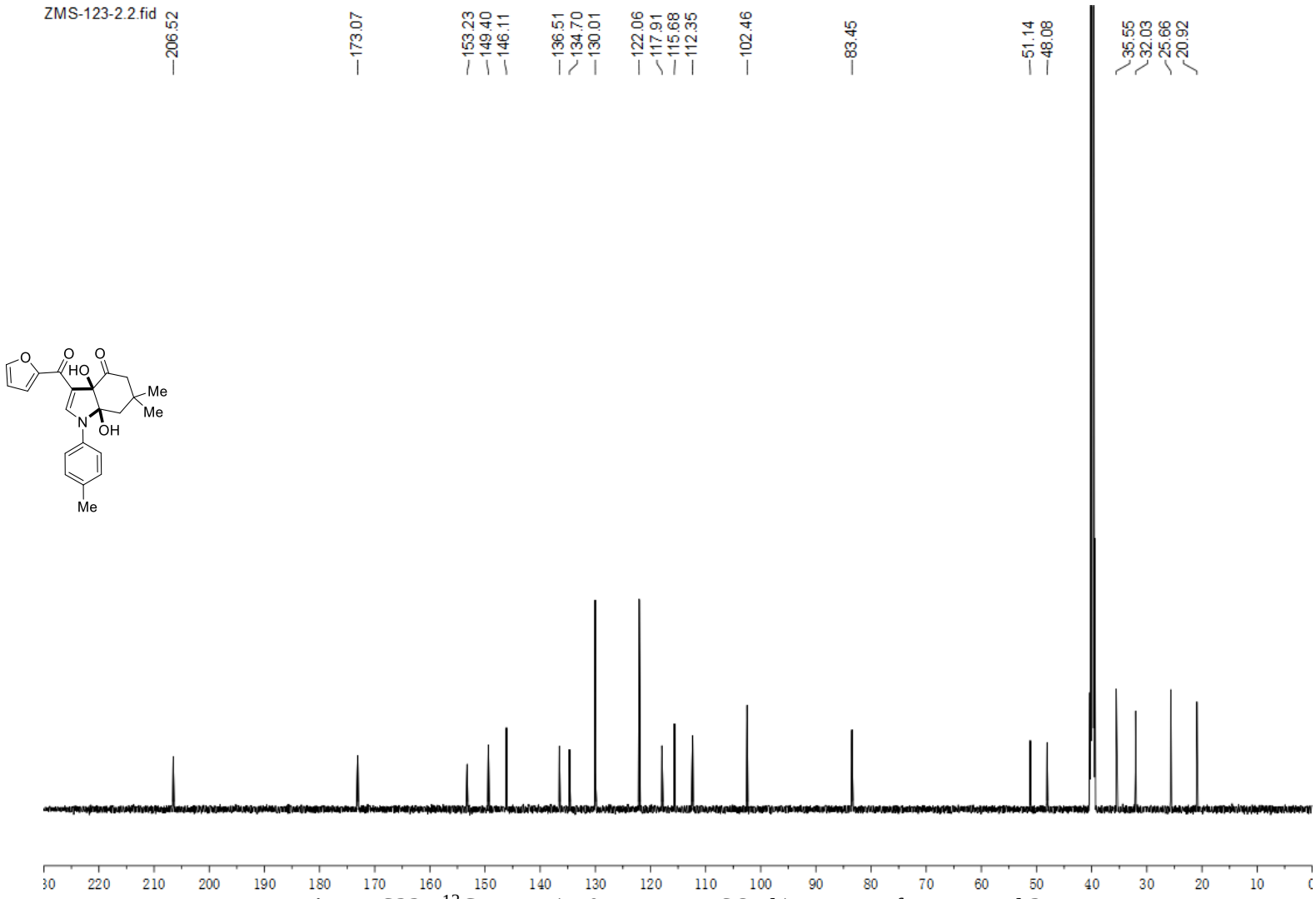


Figure S33. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3p**

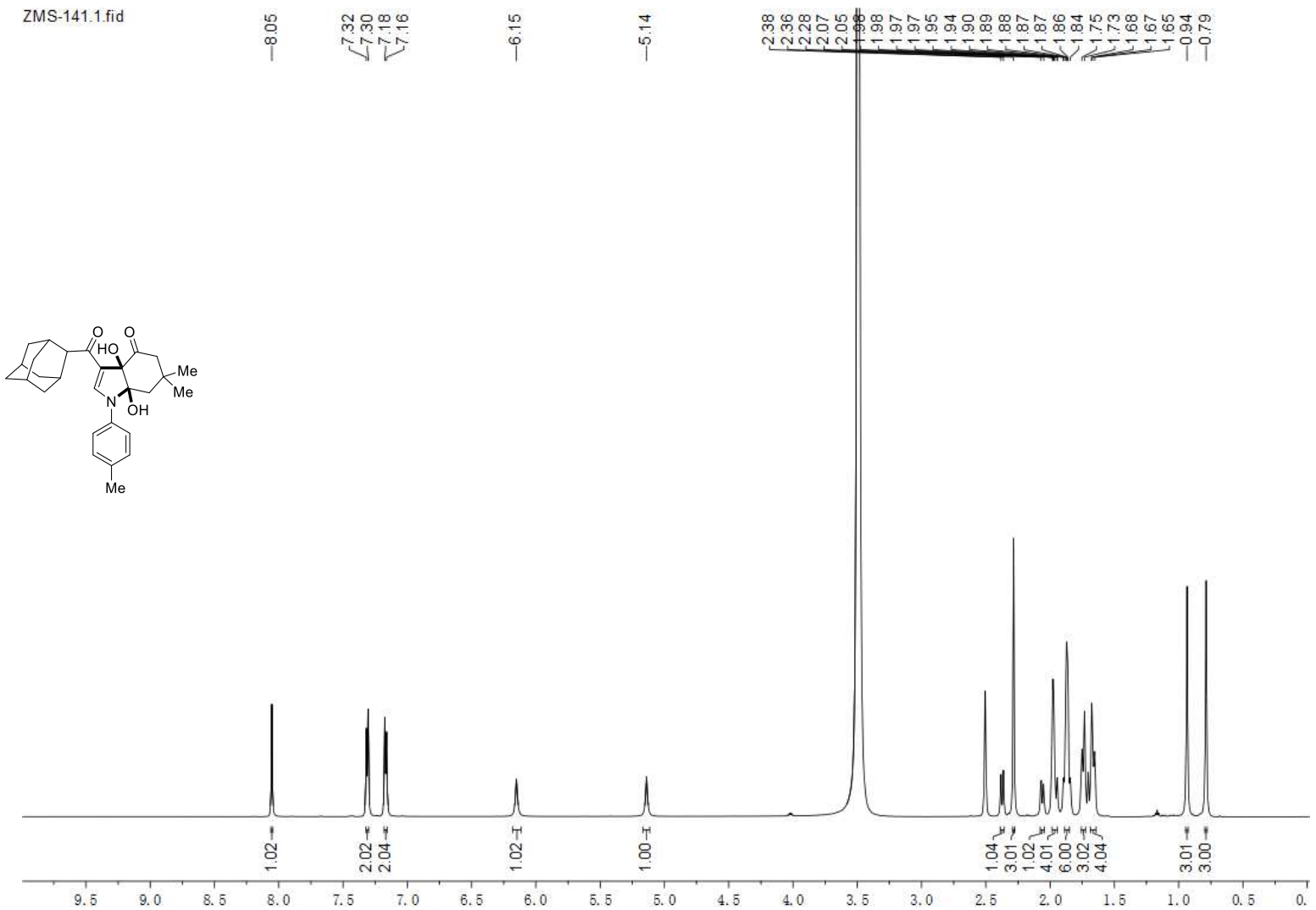


Figure S34. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3q**

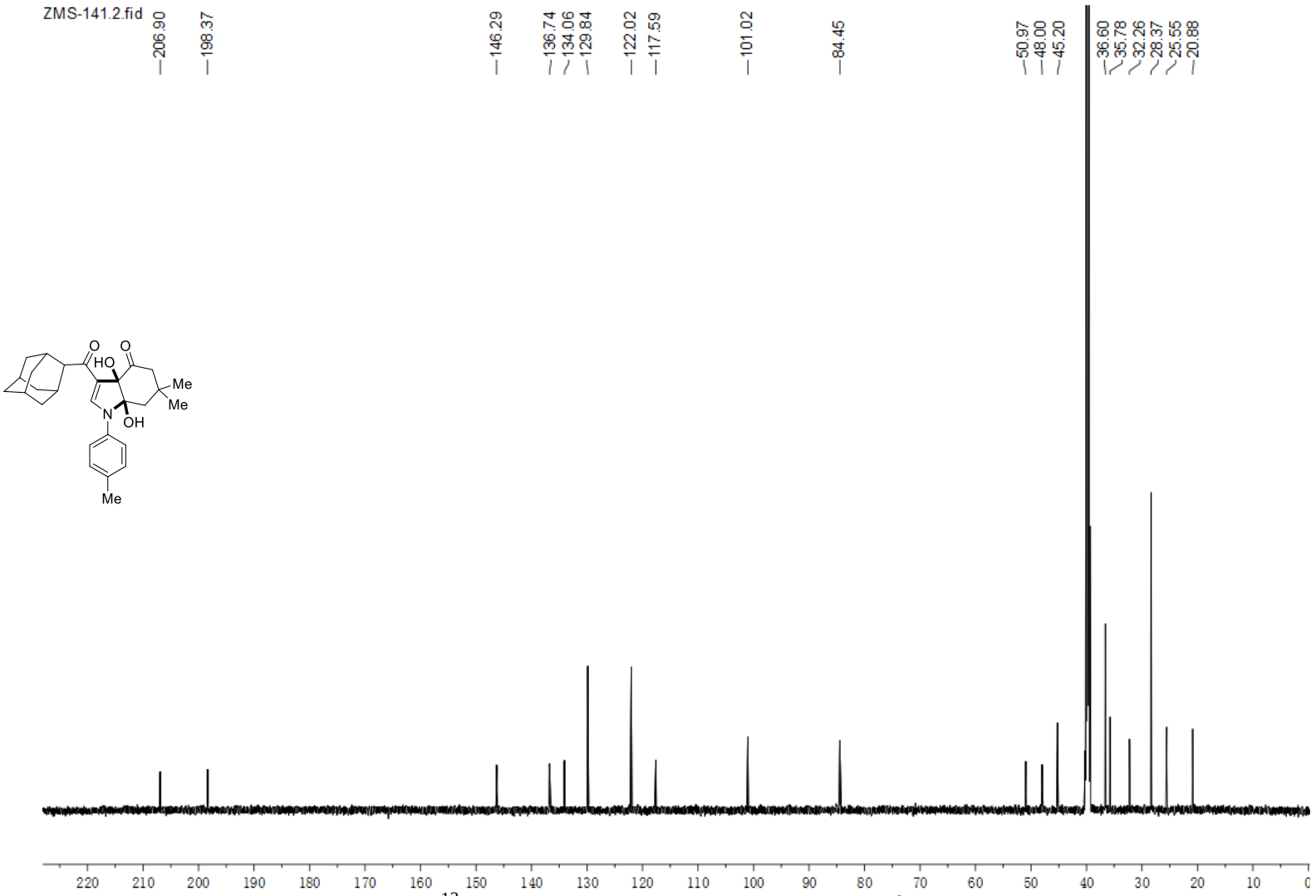


Figure S35. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3q**

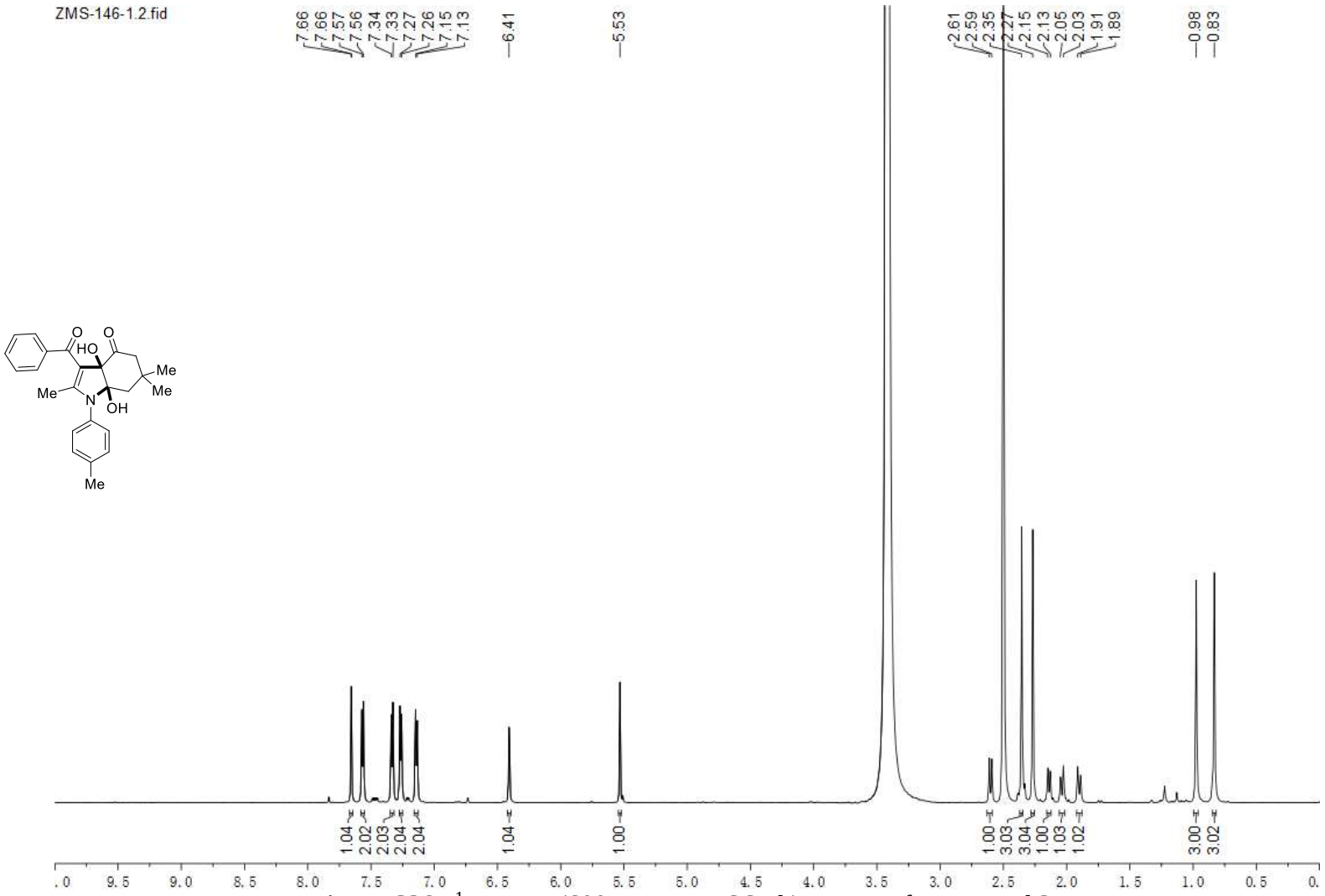


Figure S36. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3r**

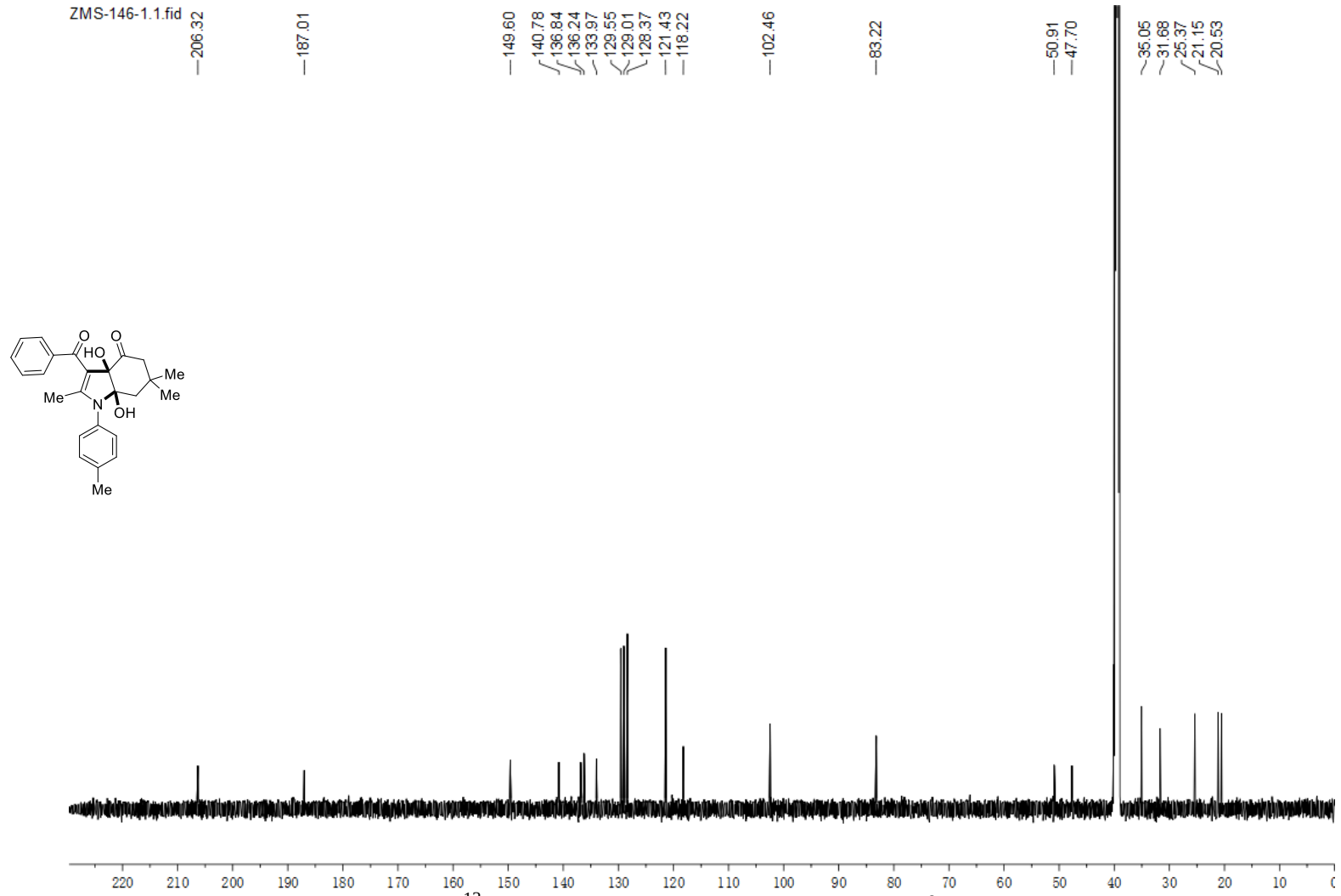


Figure S37. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3r**

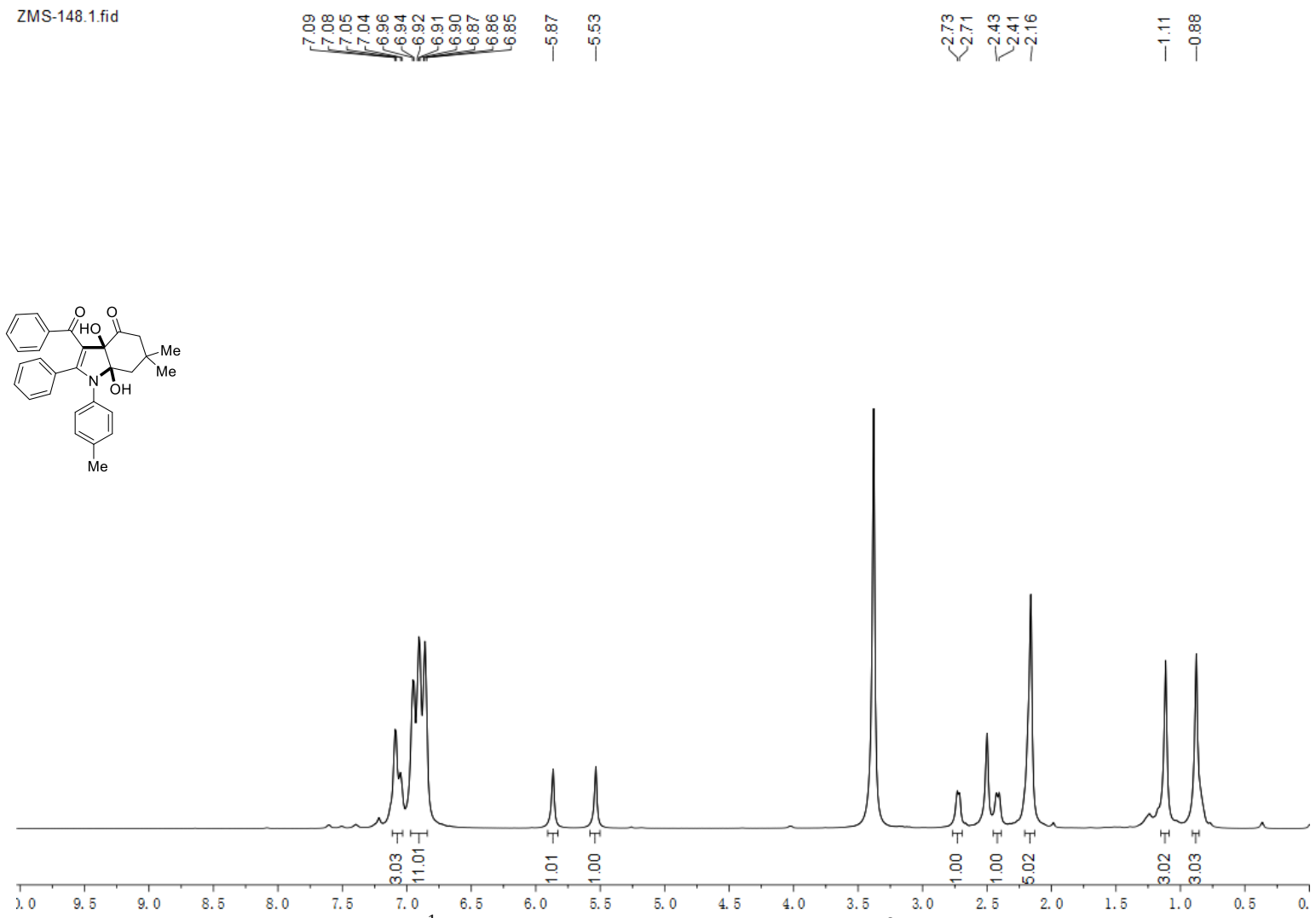


Figure S38. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3s**

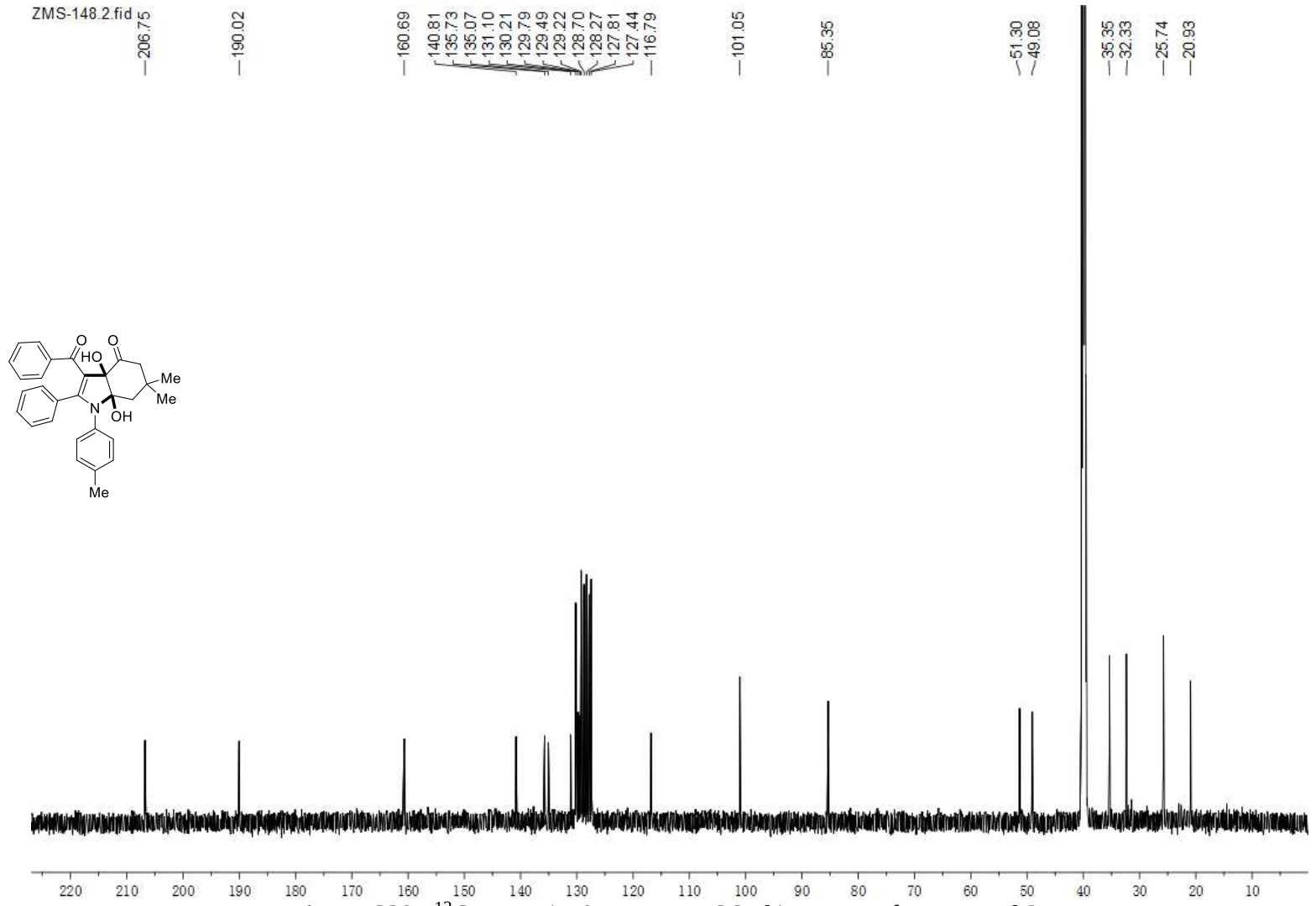


Figure S39. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3s**

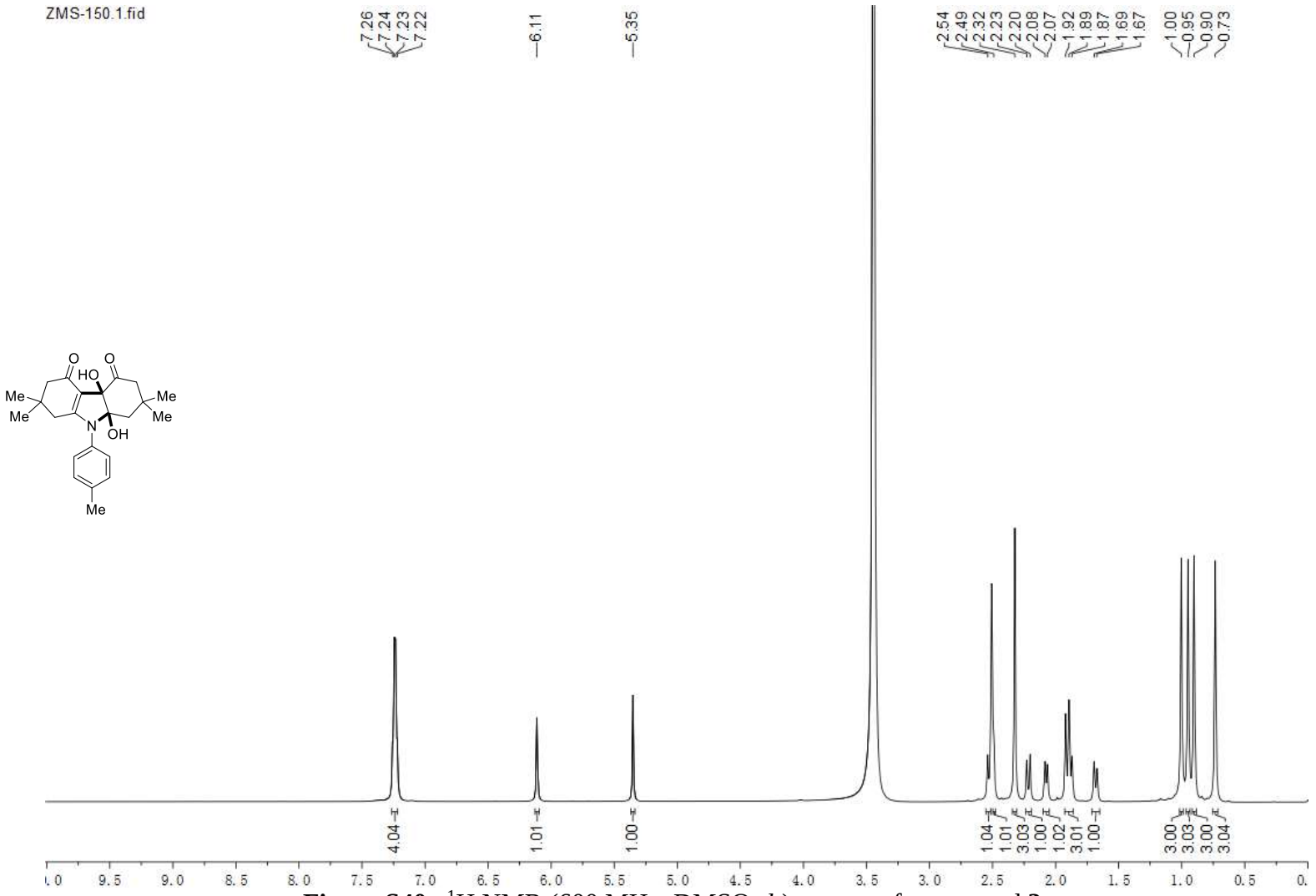


Figure S40. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3t**

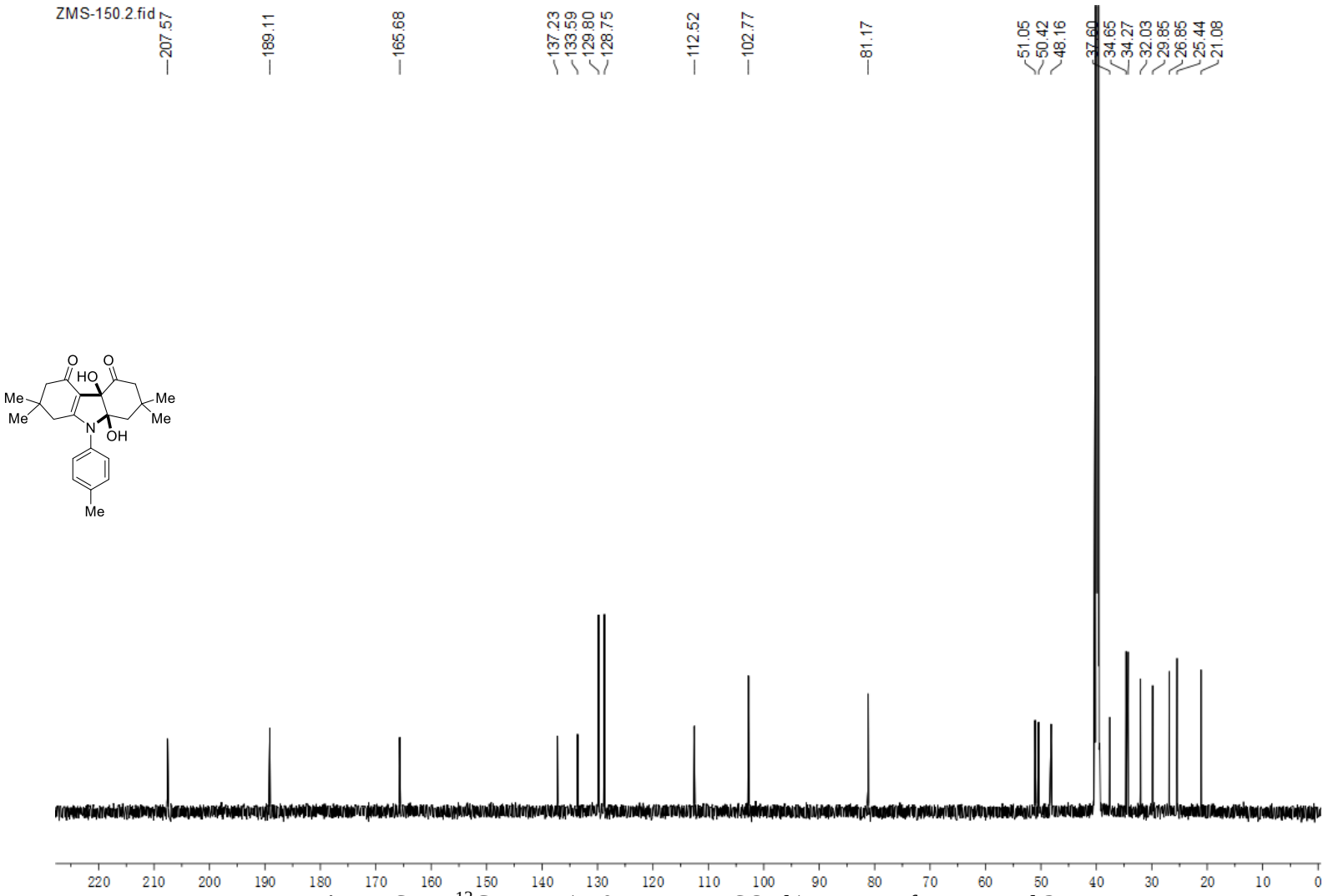


Figure S41. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3t**

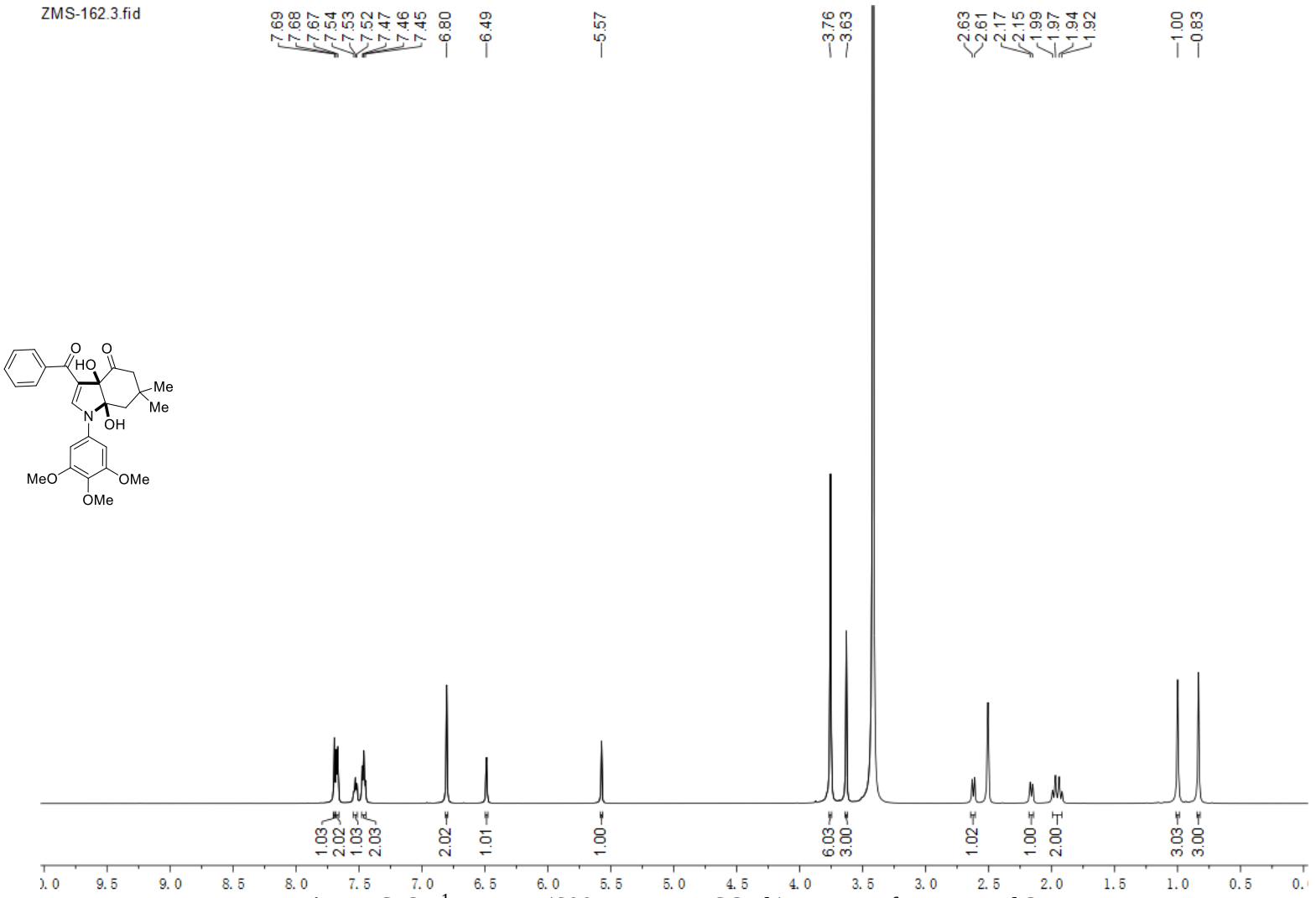


Figure S42. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3u**

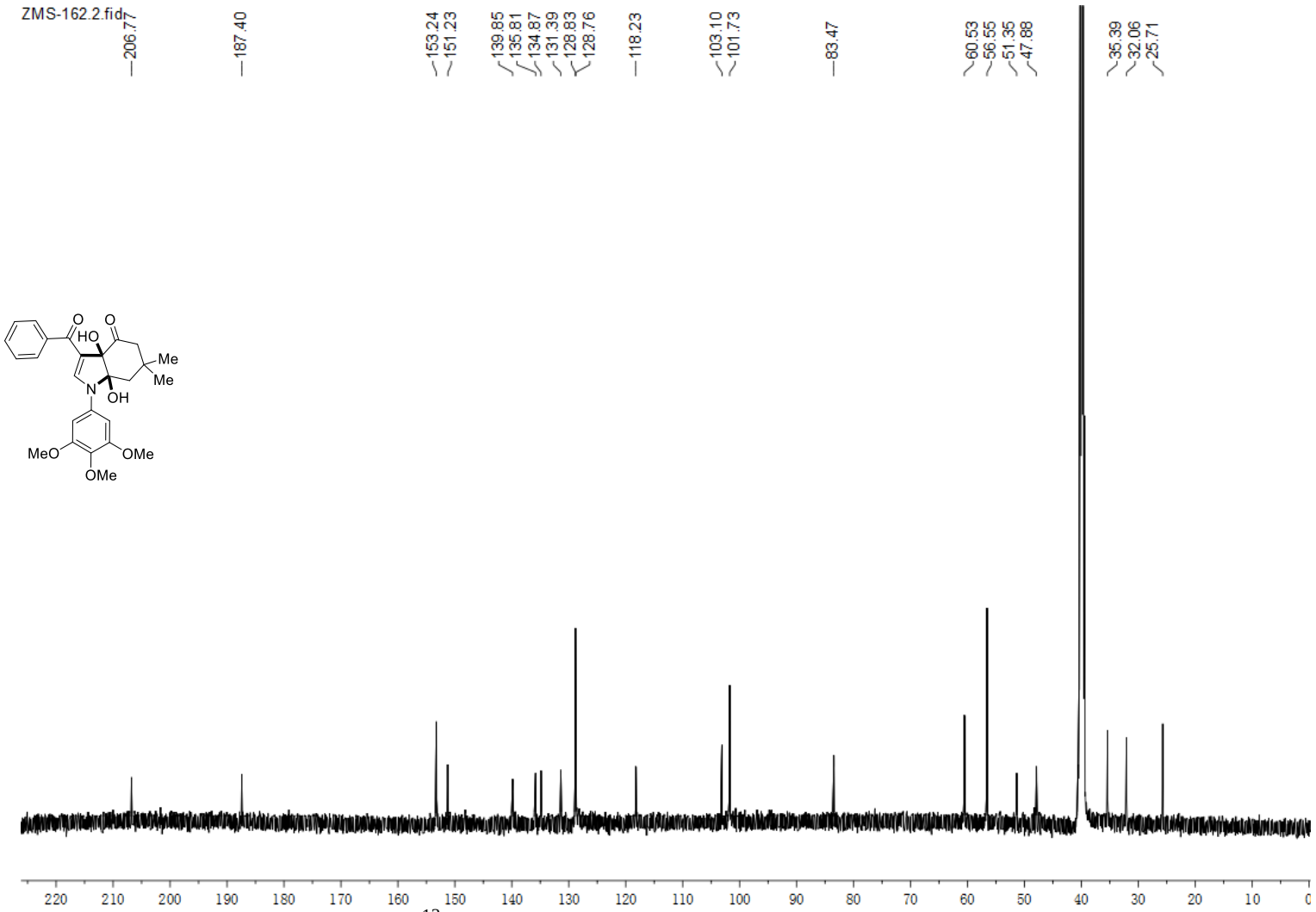


Figure S43. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3u**

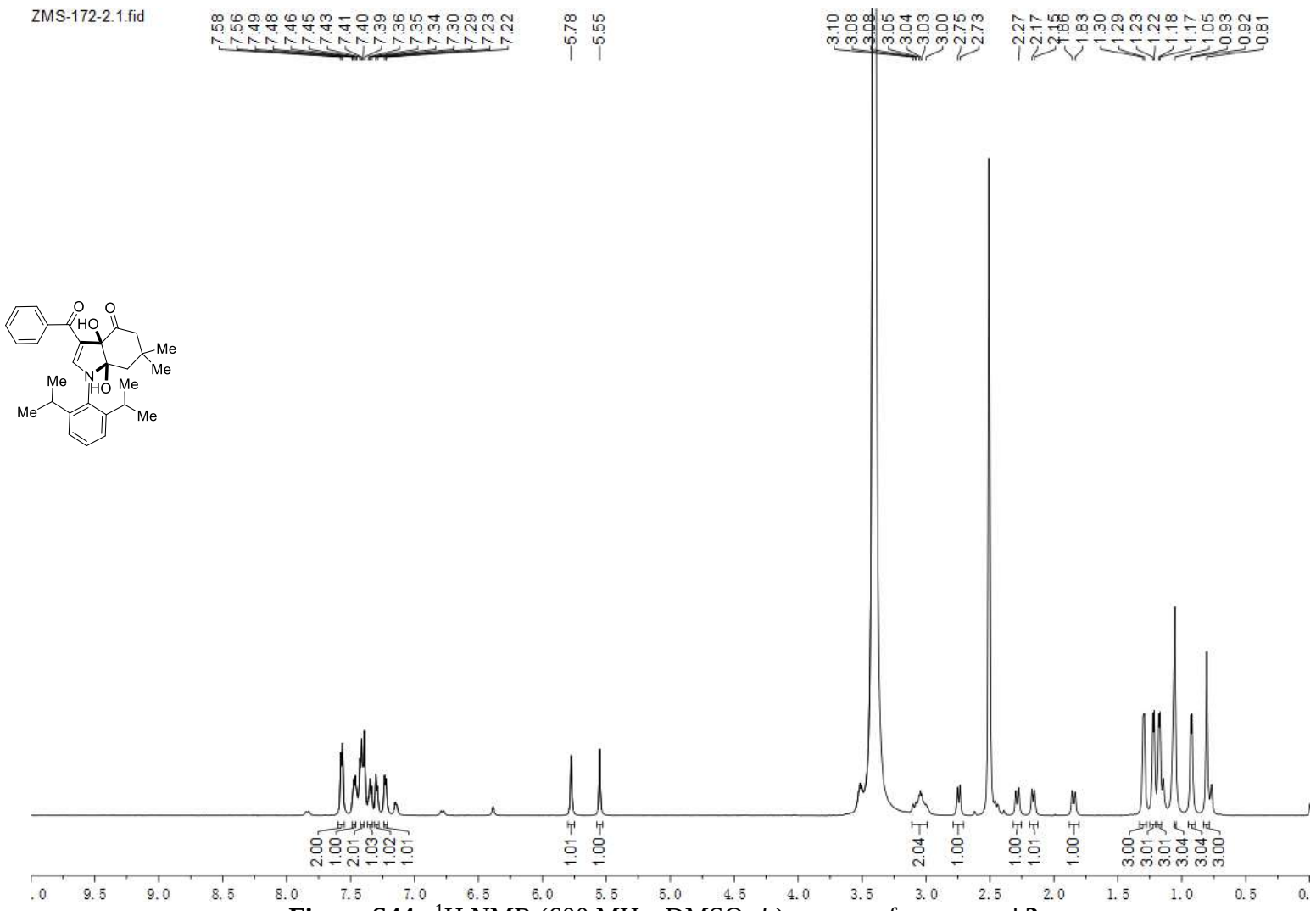


Figure S44. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3v**

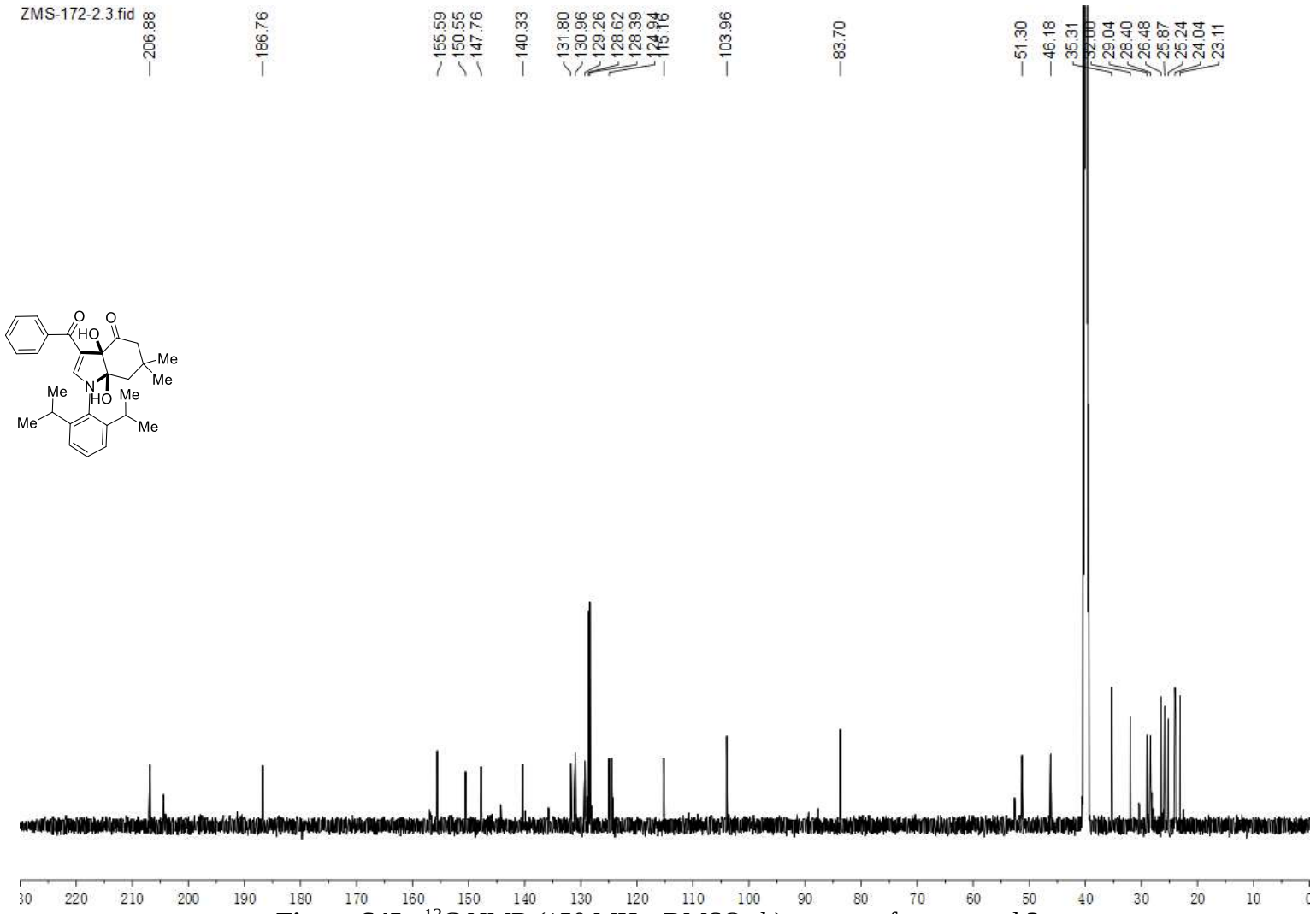


Figure S45. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3v**

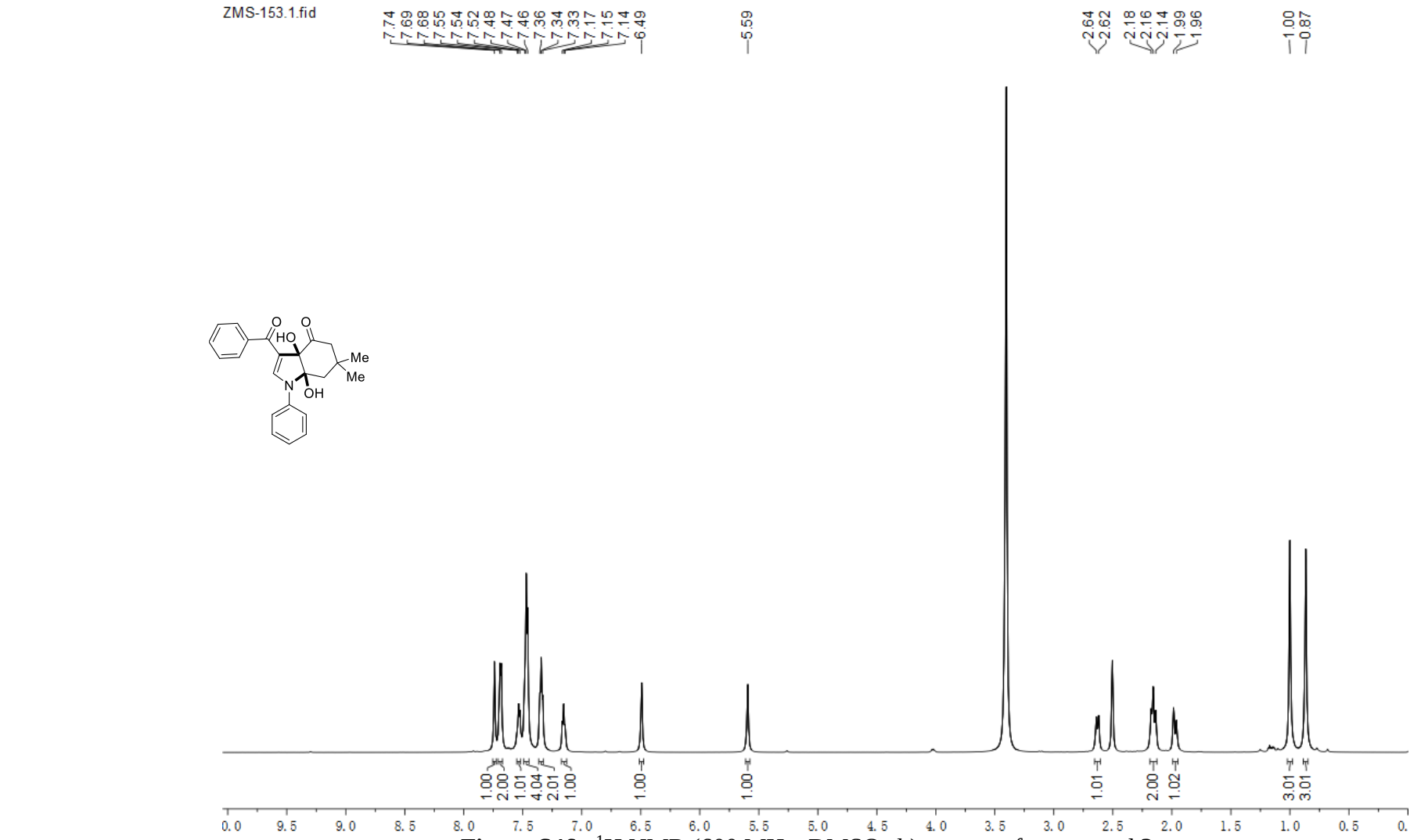


Figure S46. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3w**

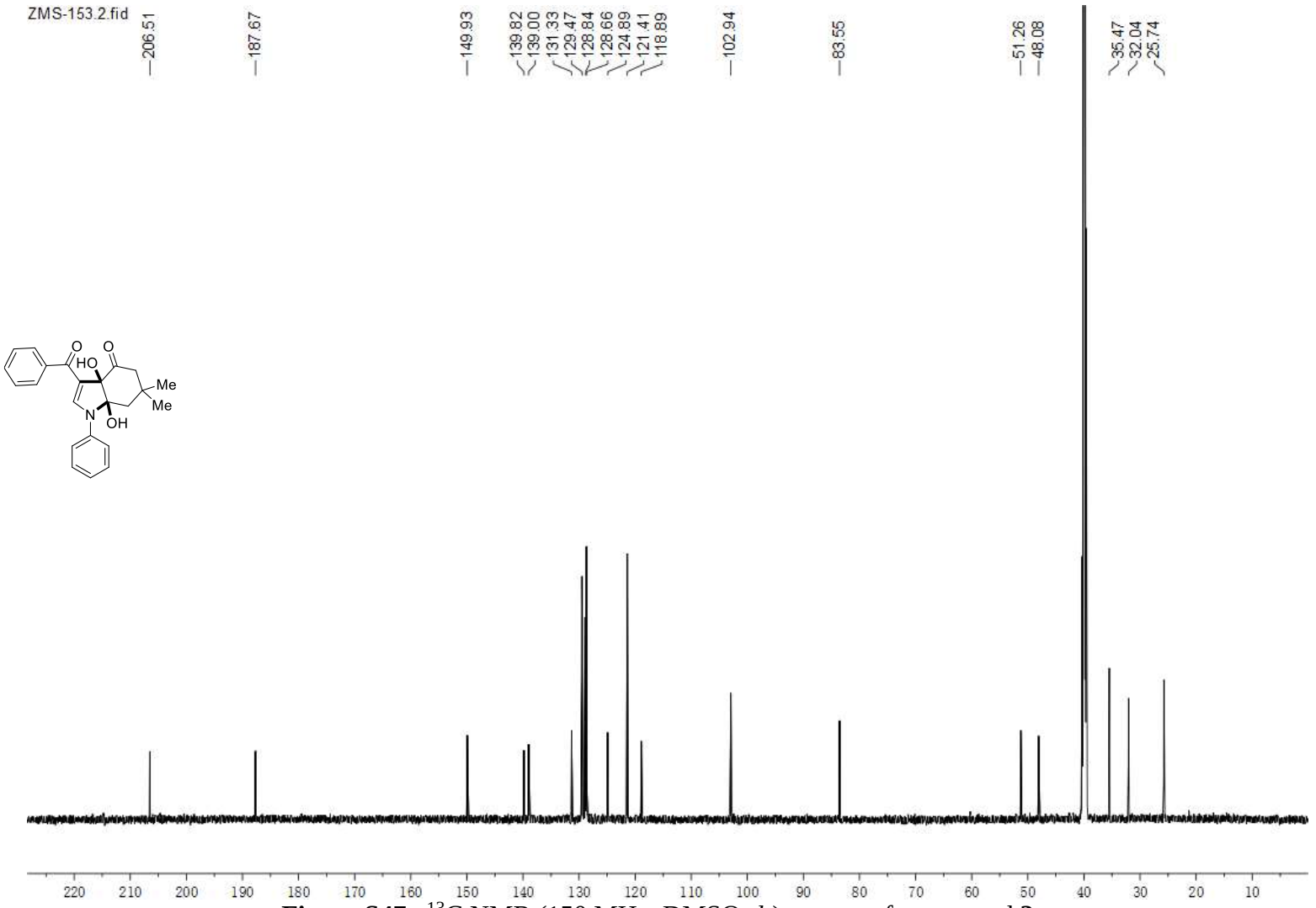


Figure S47. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3w**

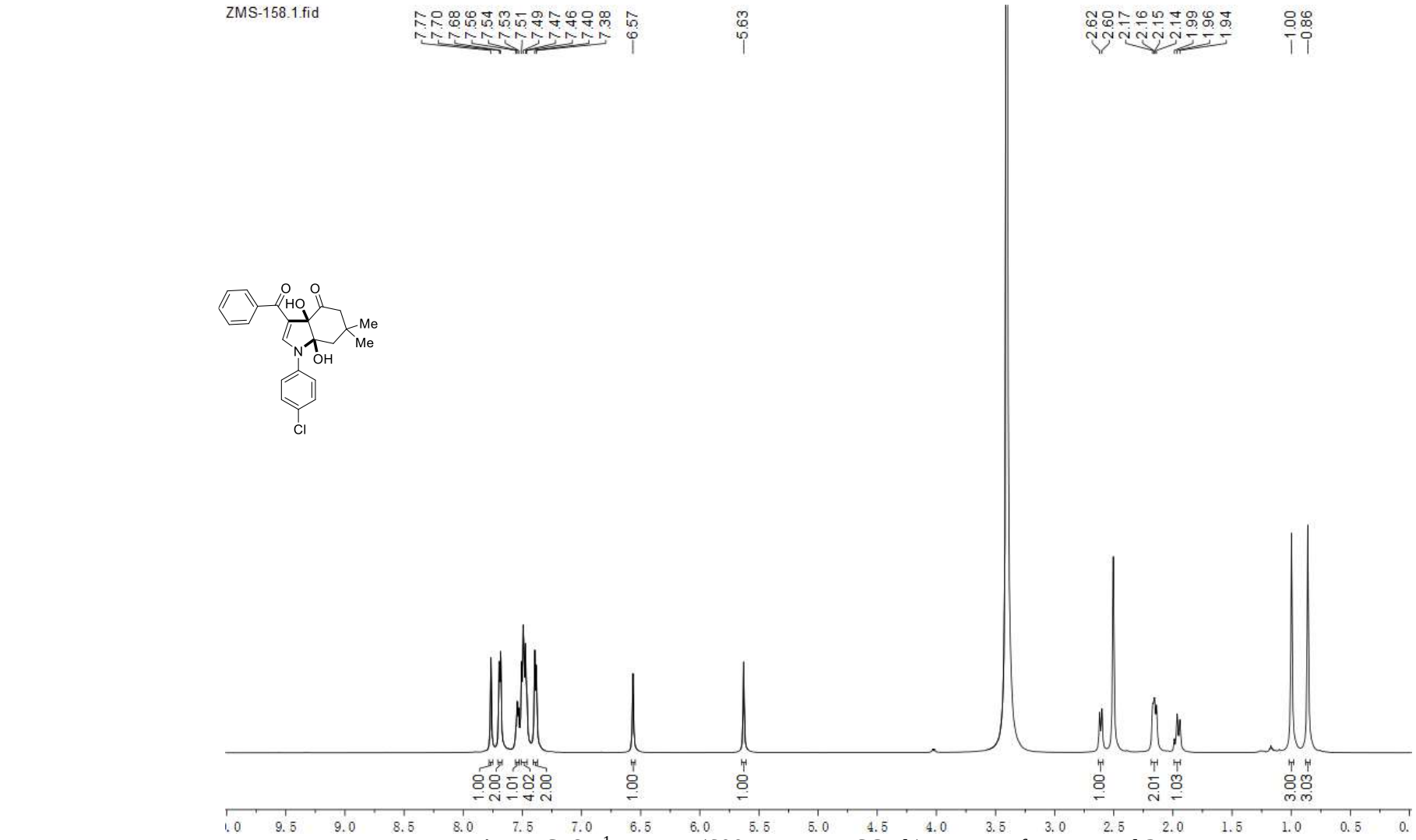


Figure S48. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3x**

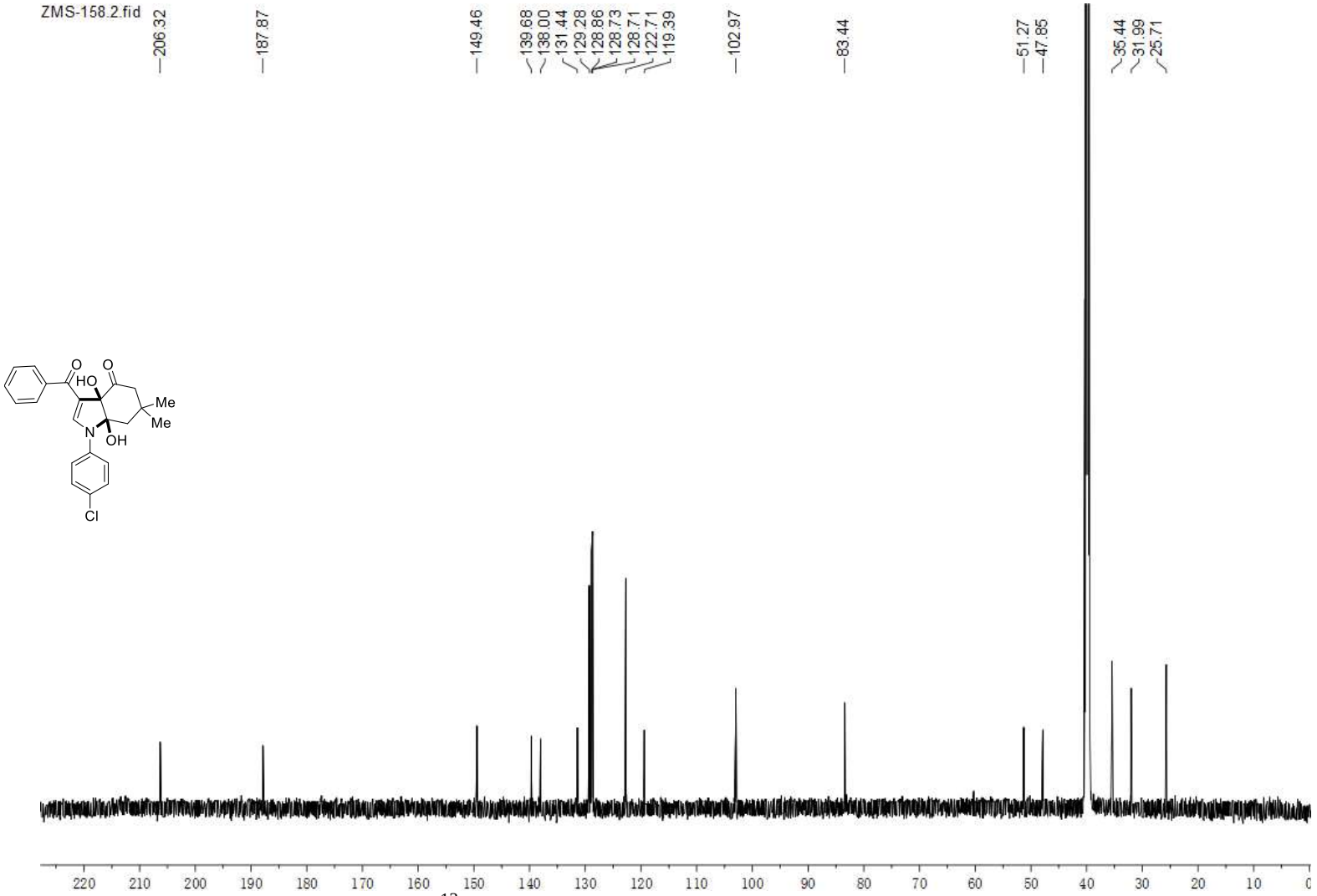


Figure S49. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3x**

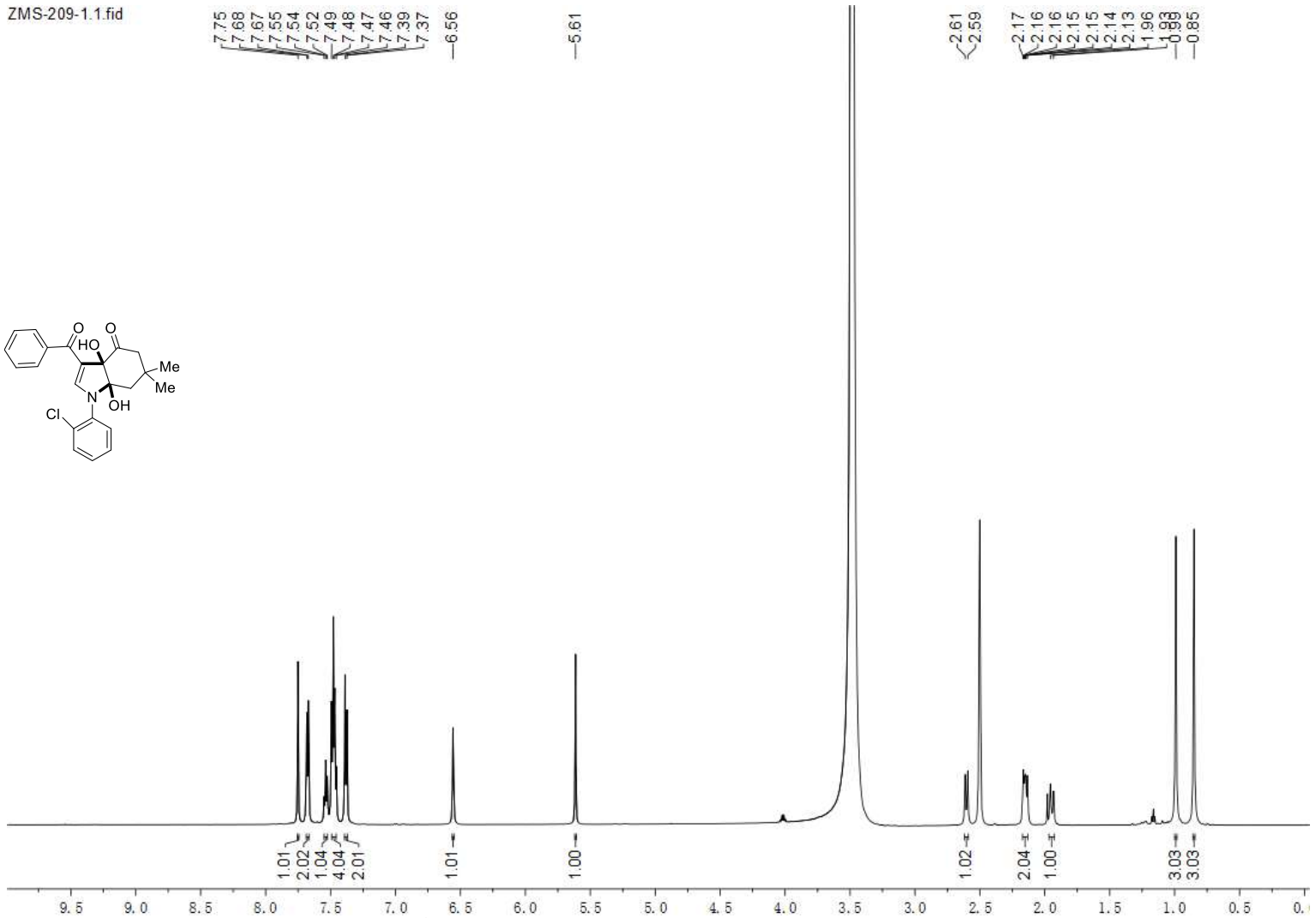


Figure S50. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3y**

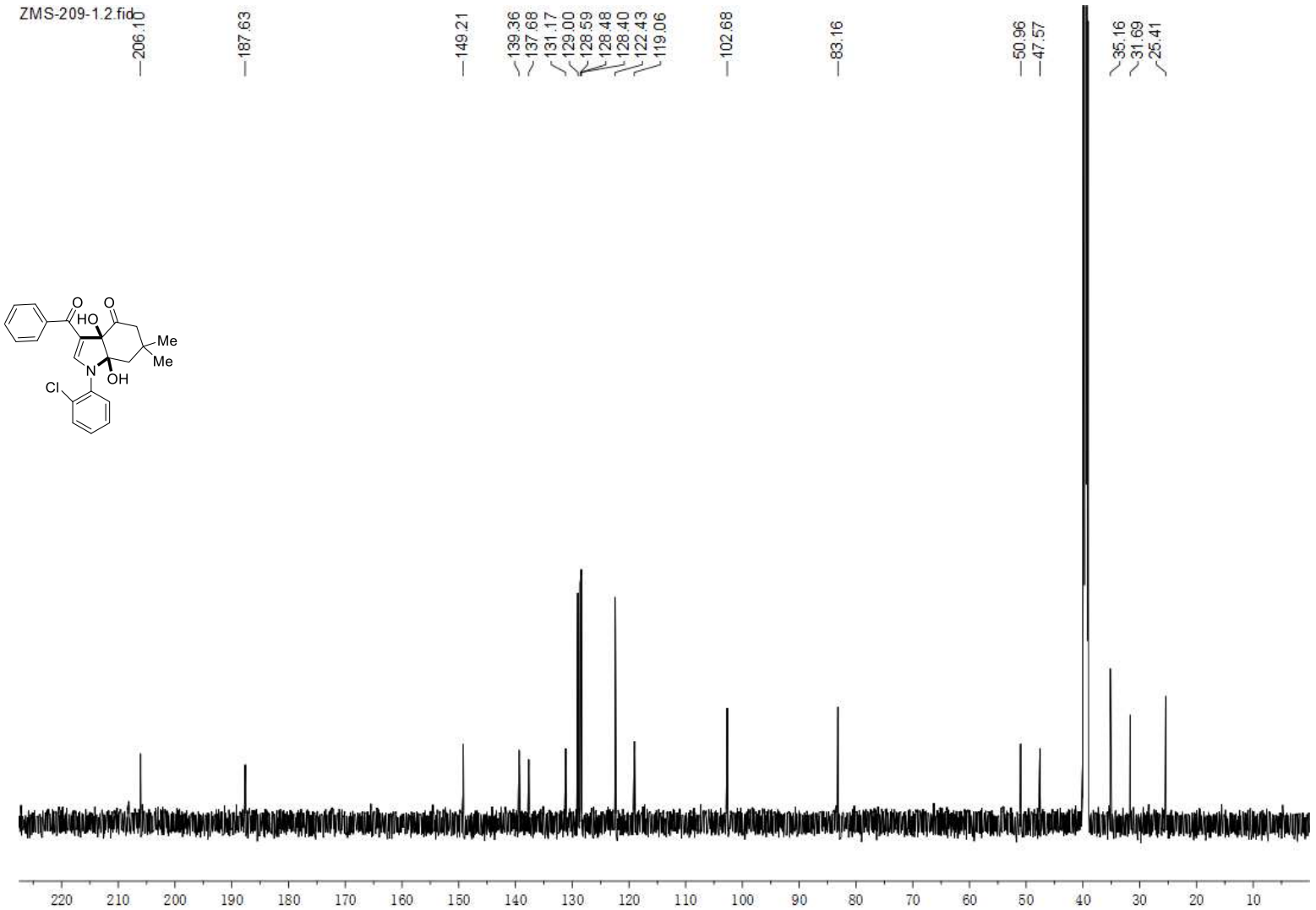


Figure S51. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3y**

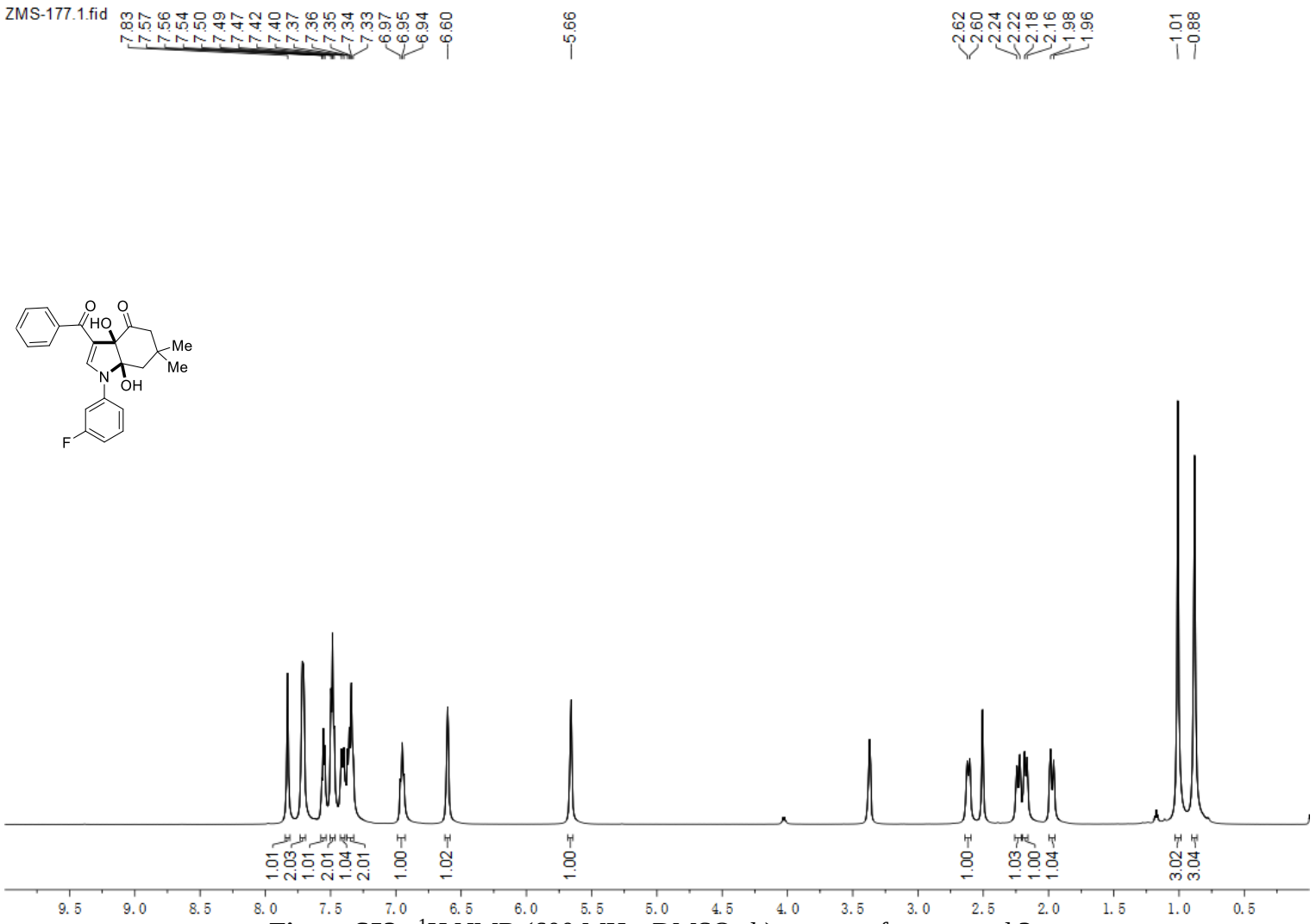


Figure S52. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3z**

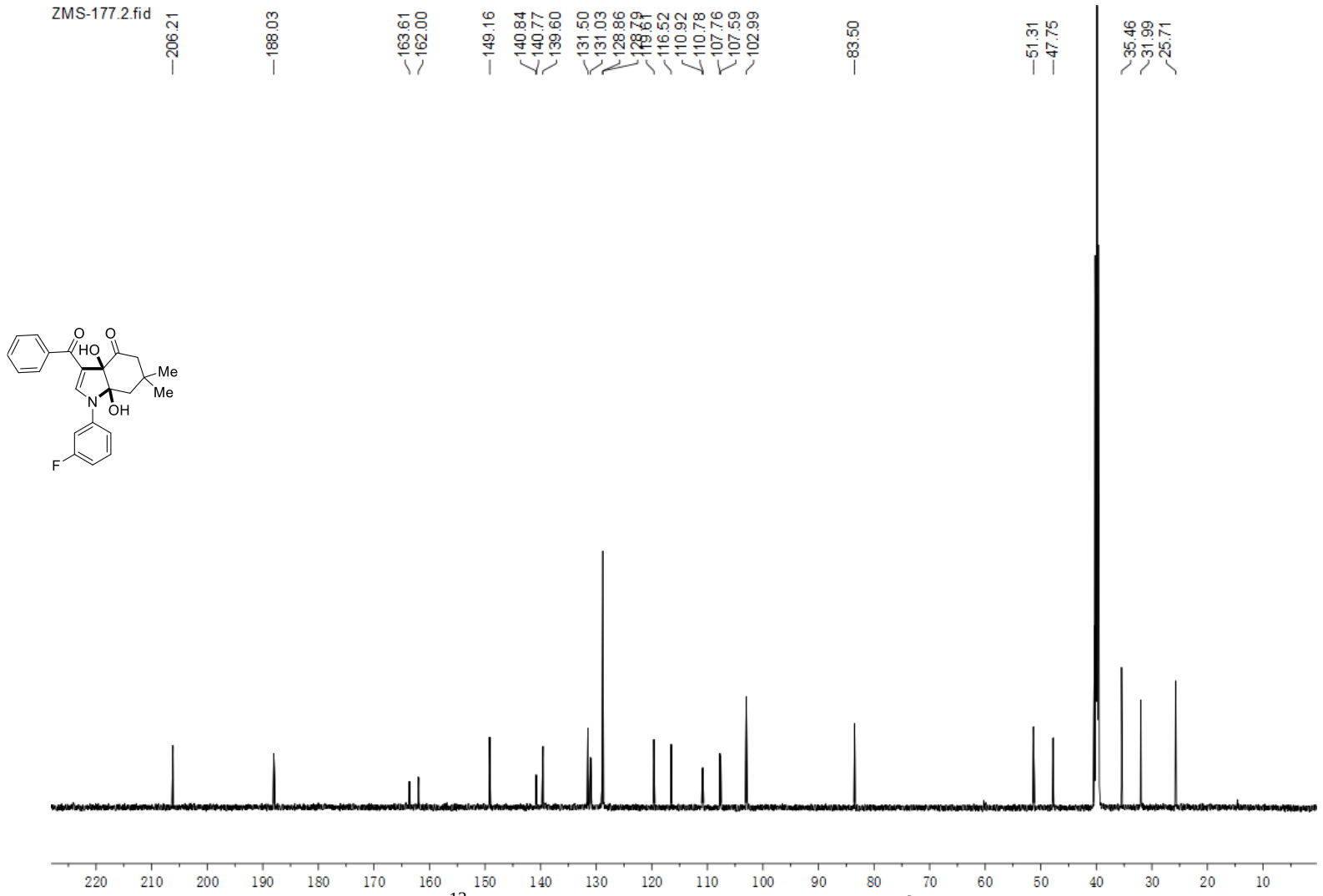


Figure S53. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3z**

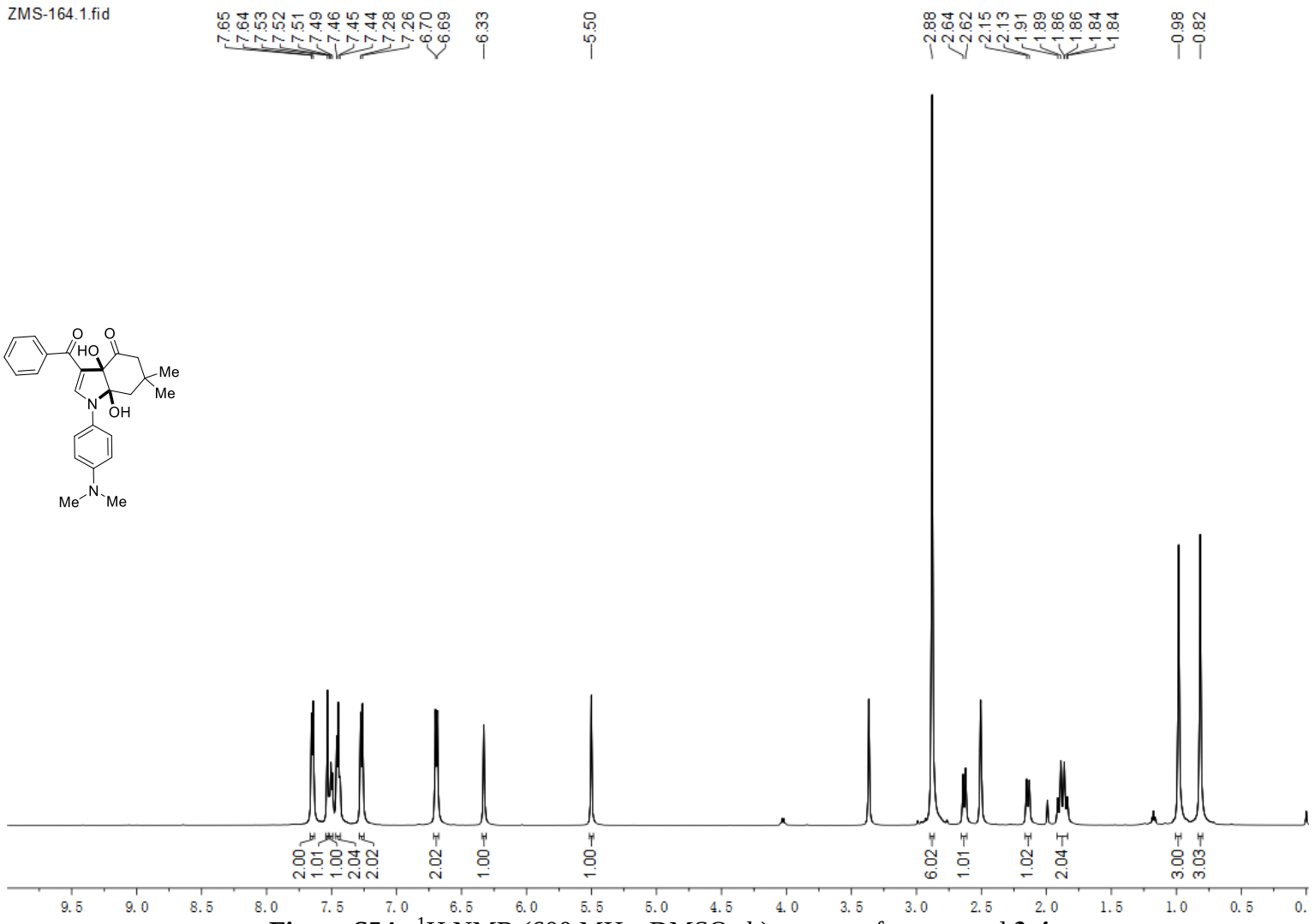


Figure S54. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3a′**

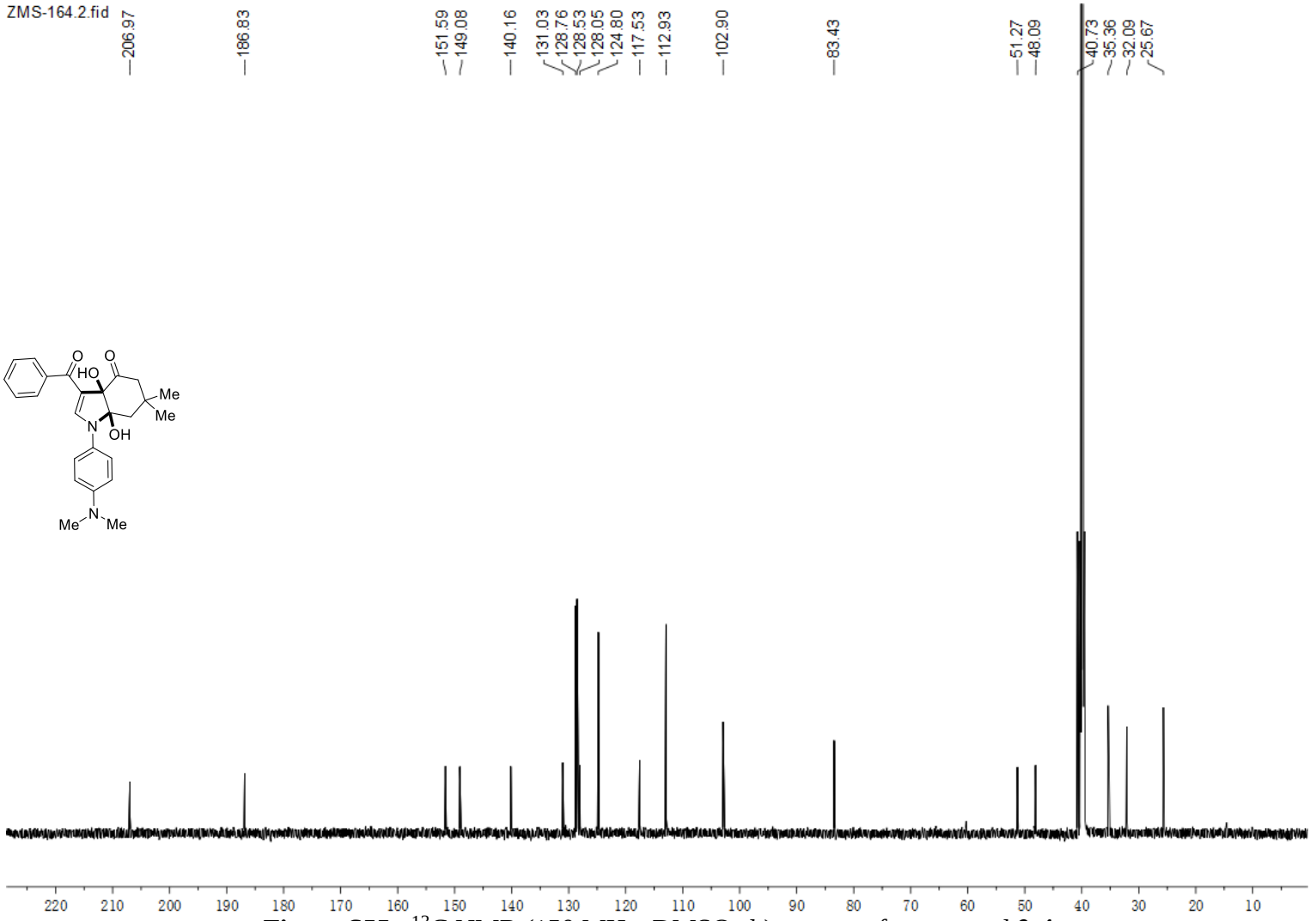


Figure S55. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3a′**

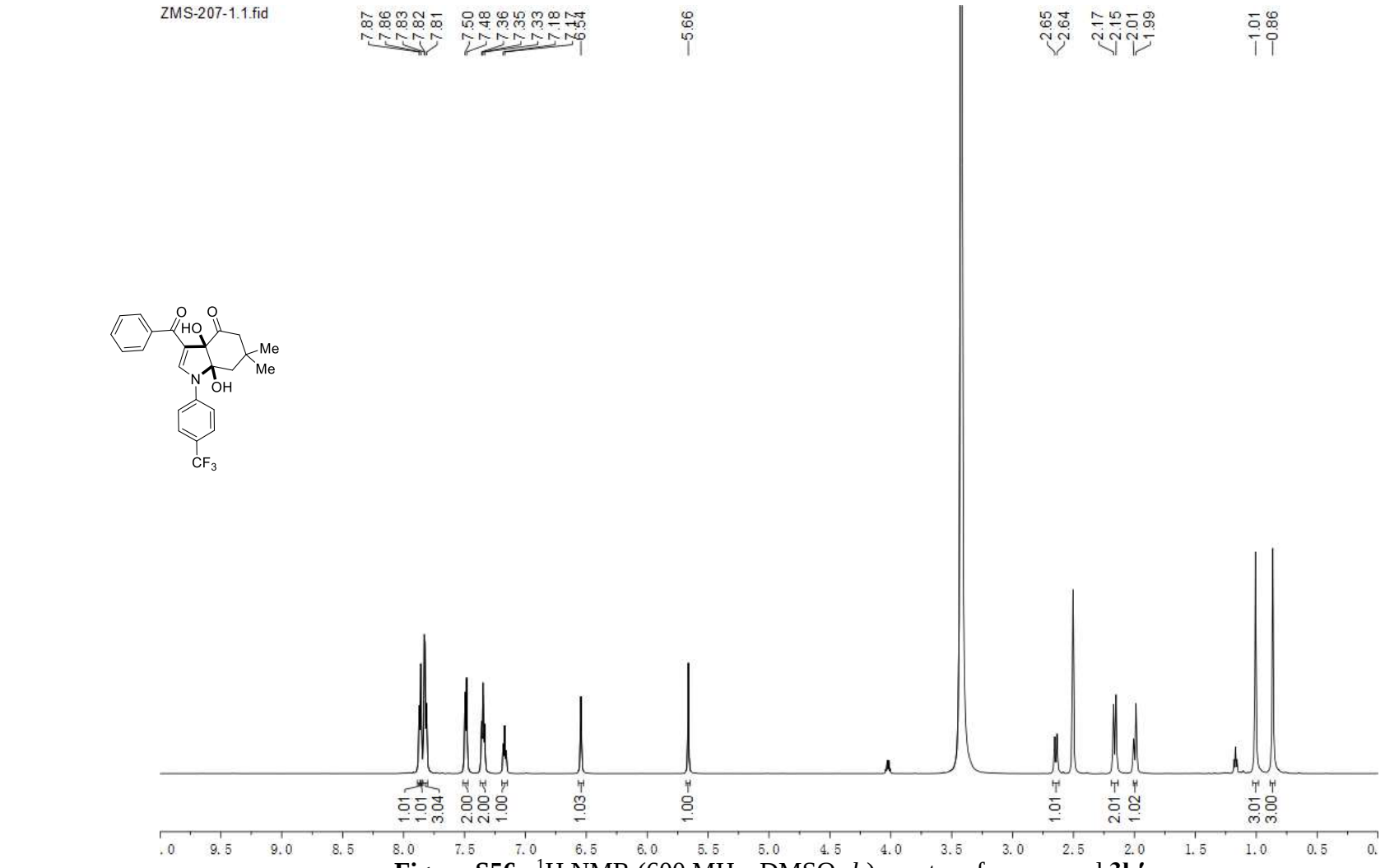


Figure S56. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3b′**

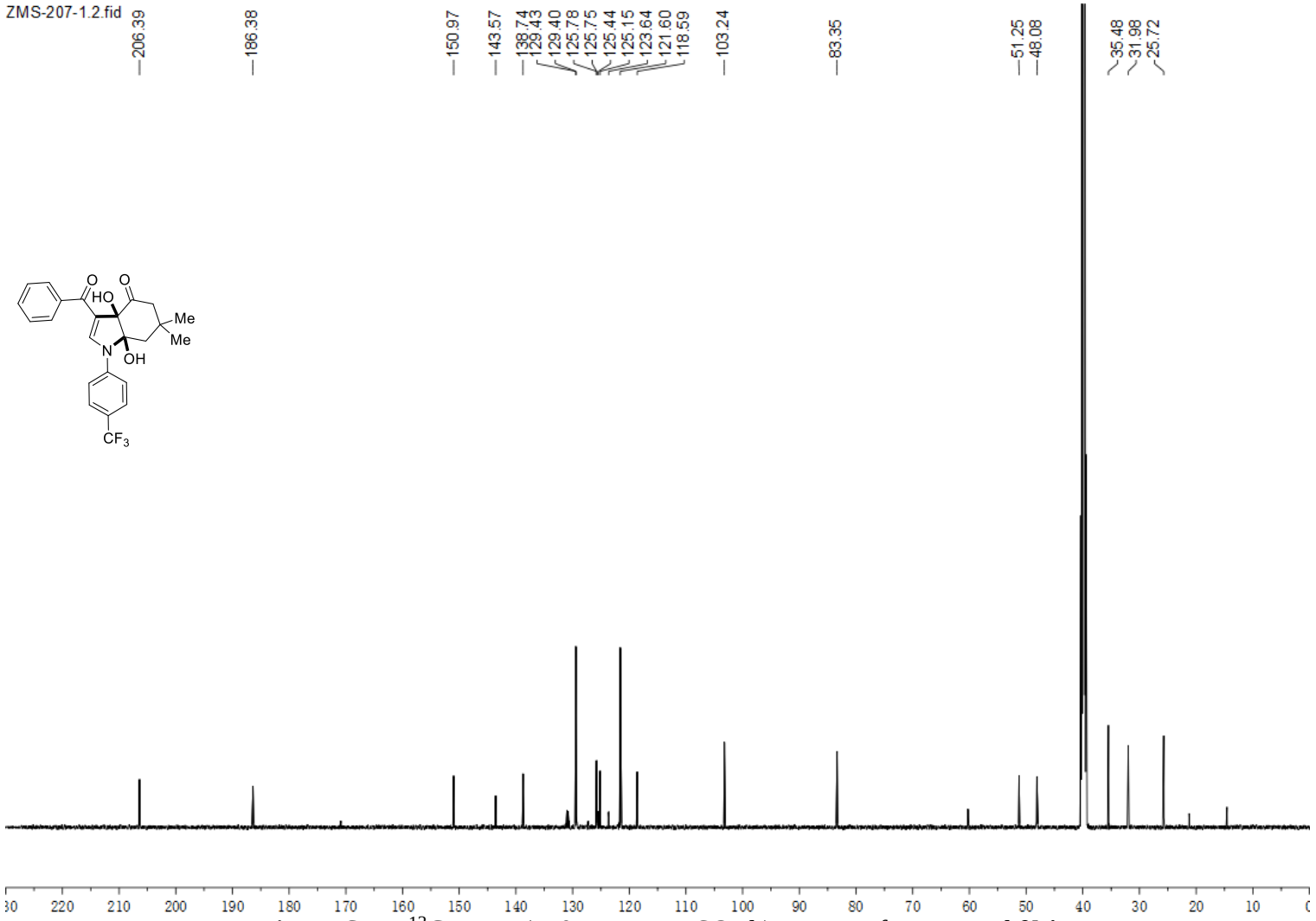


Figure S57. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3b′**

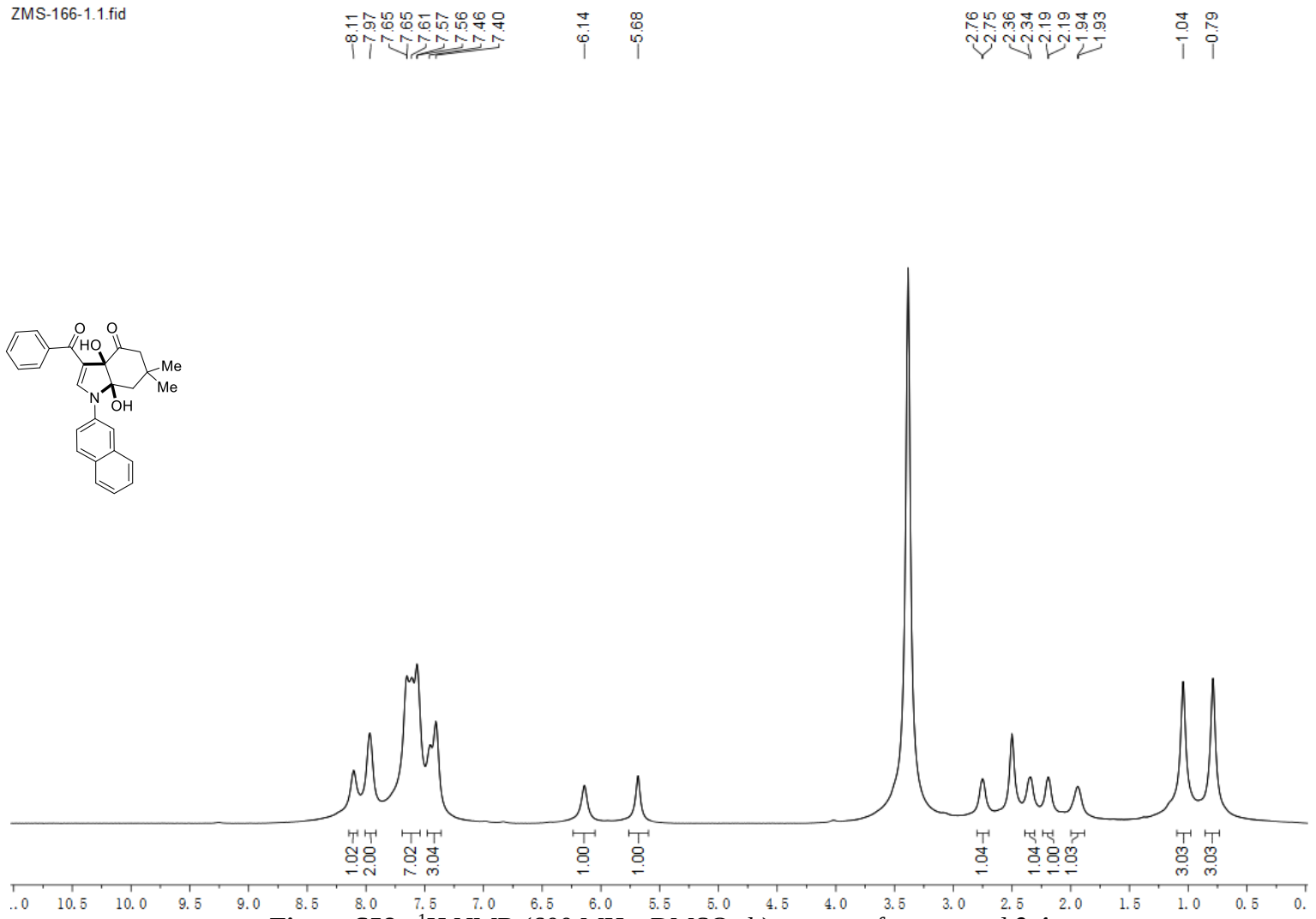


Figure S58. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3c′**

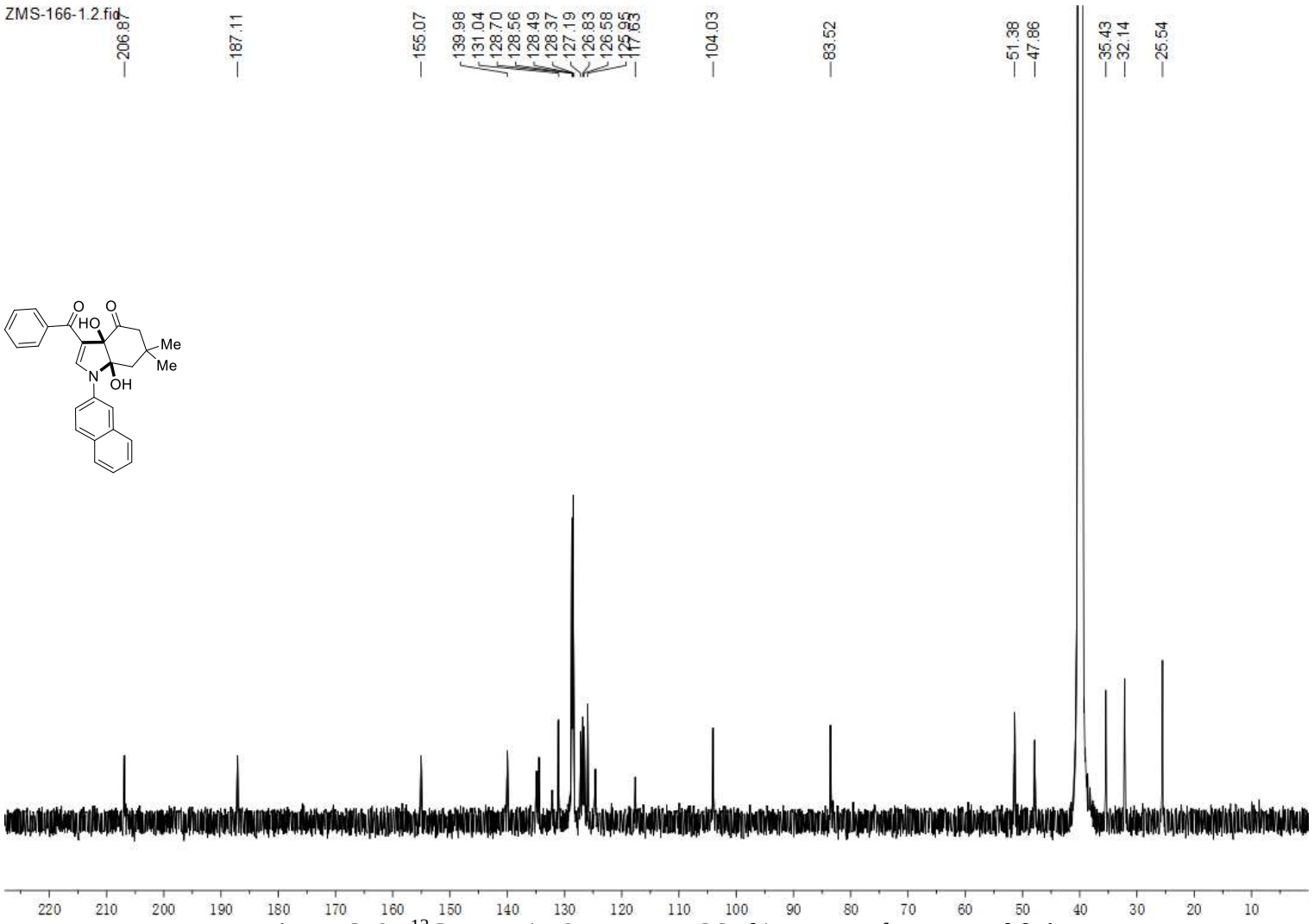


Figure S59. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3c′**

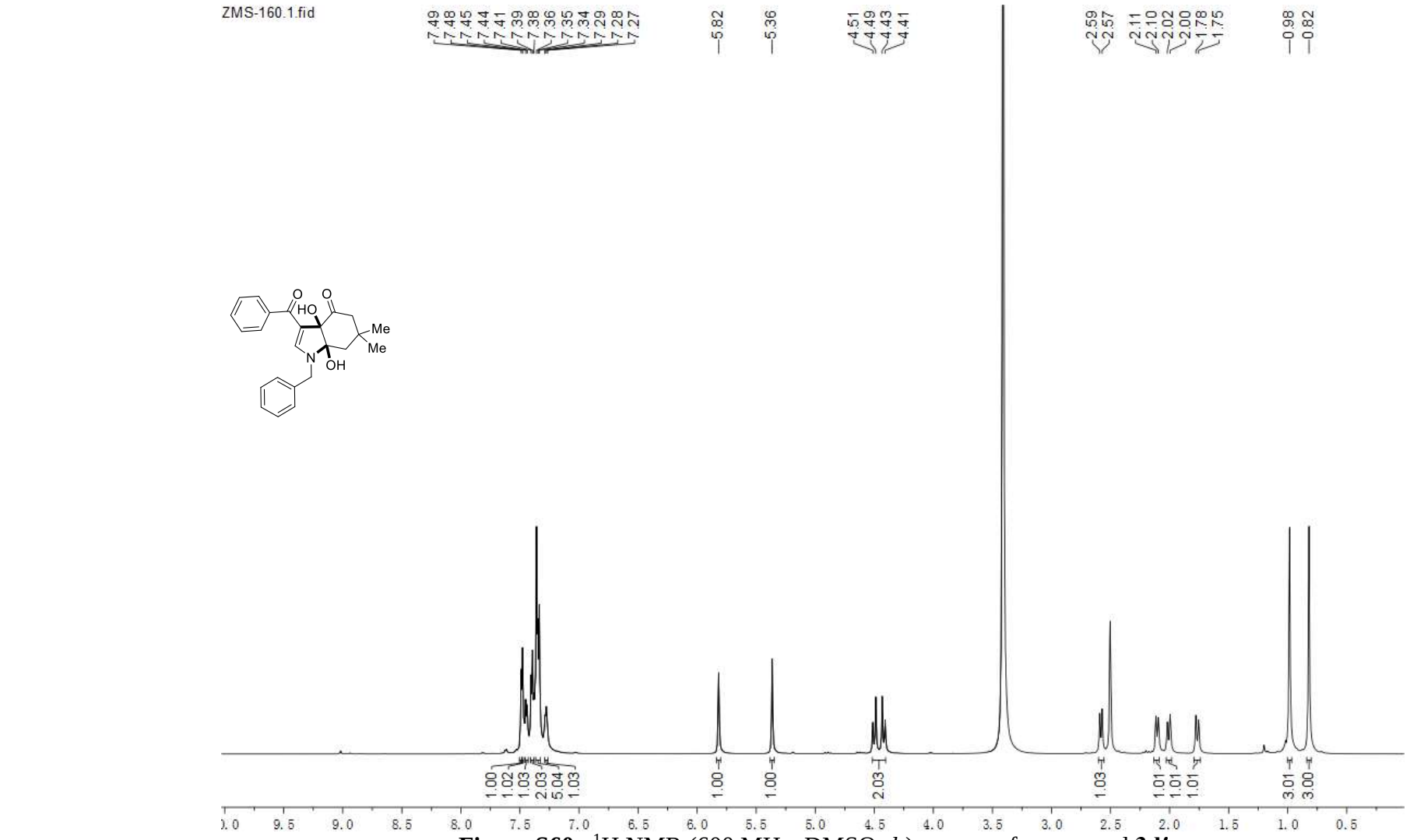


Figure S60. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3d′**

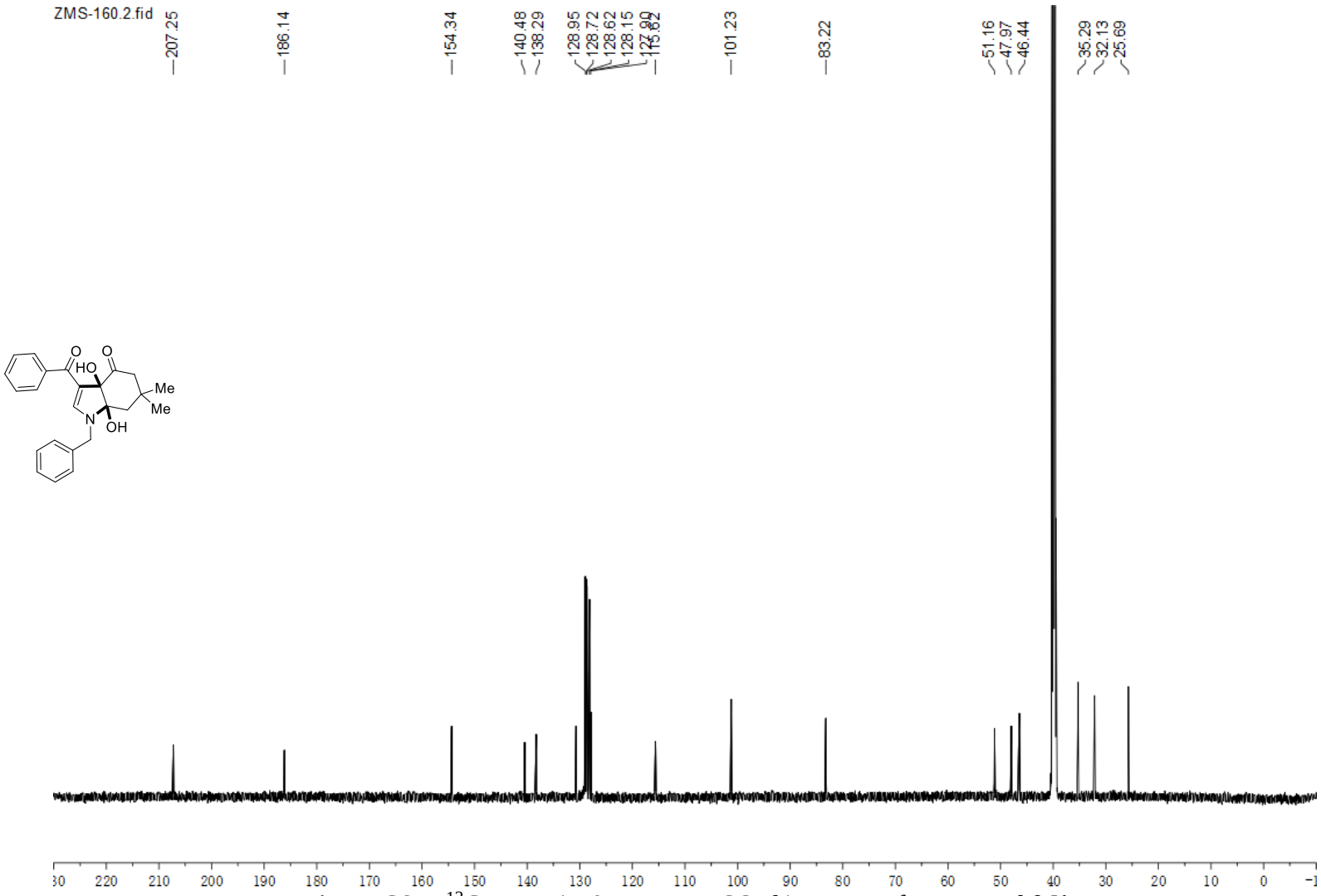


Figure S61. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3d′**

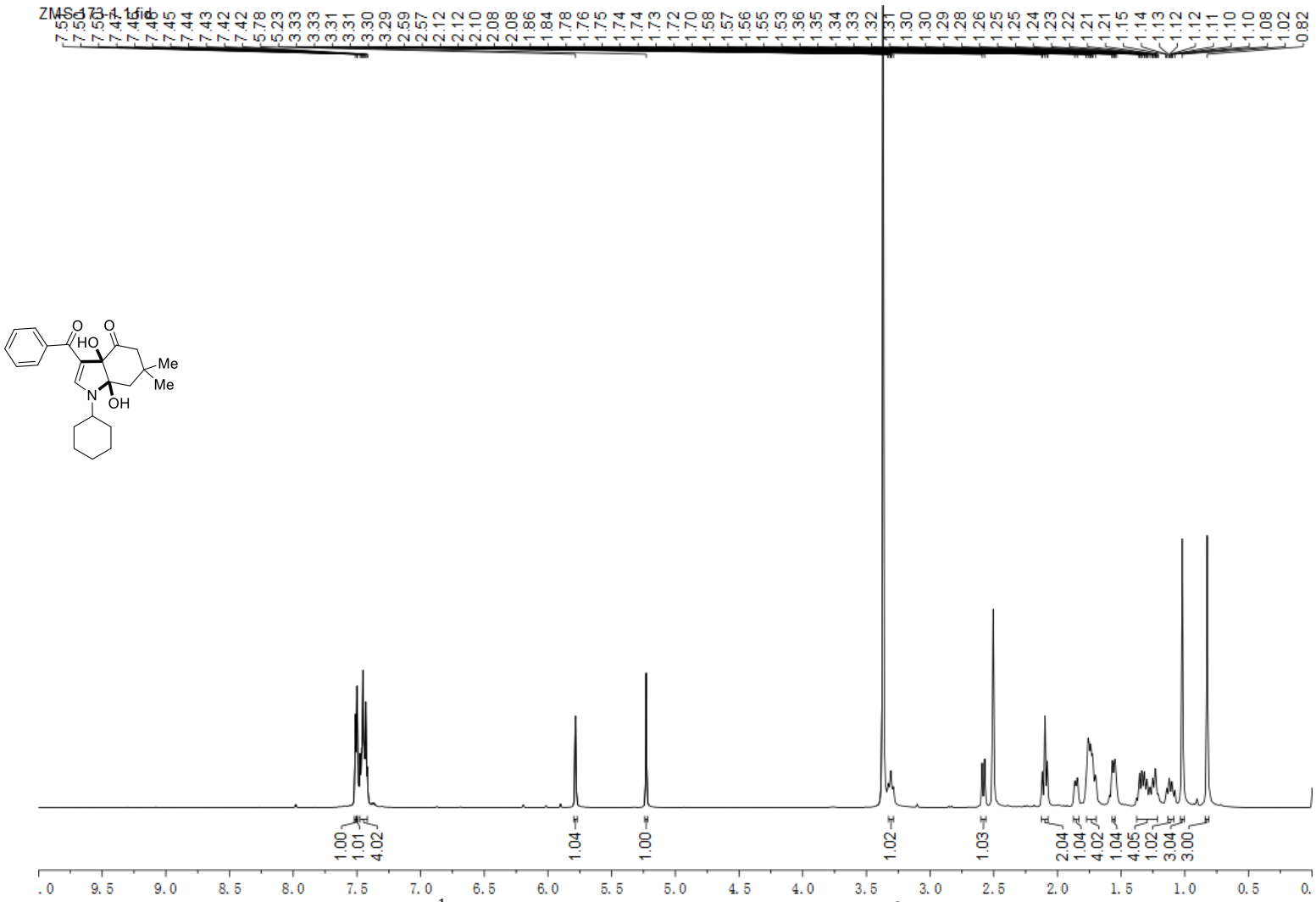


Figure S62. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3e′**

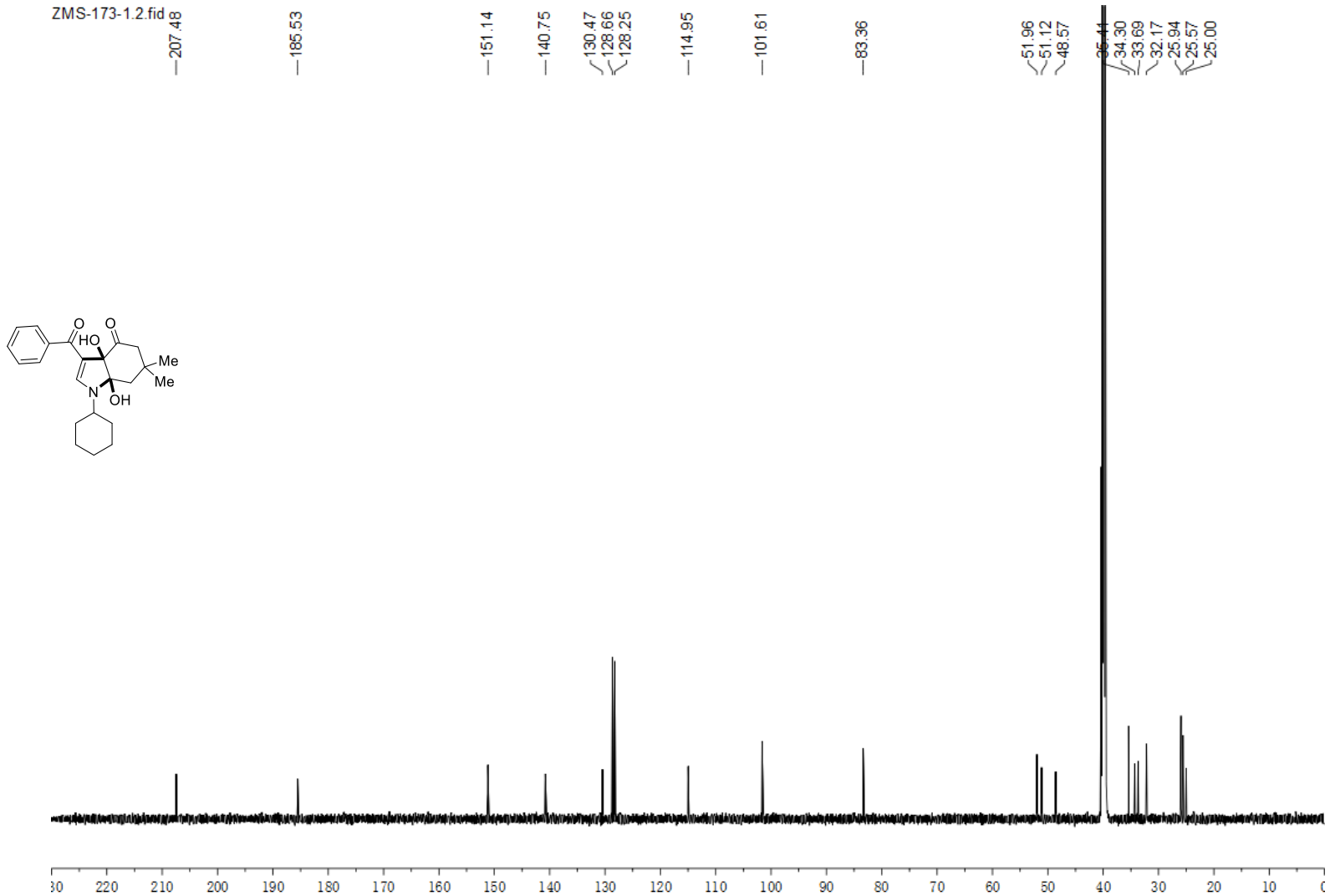


Figure S63. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3e′**

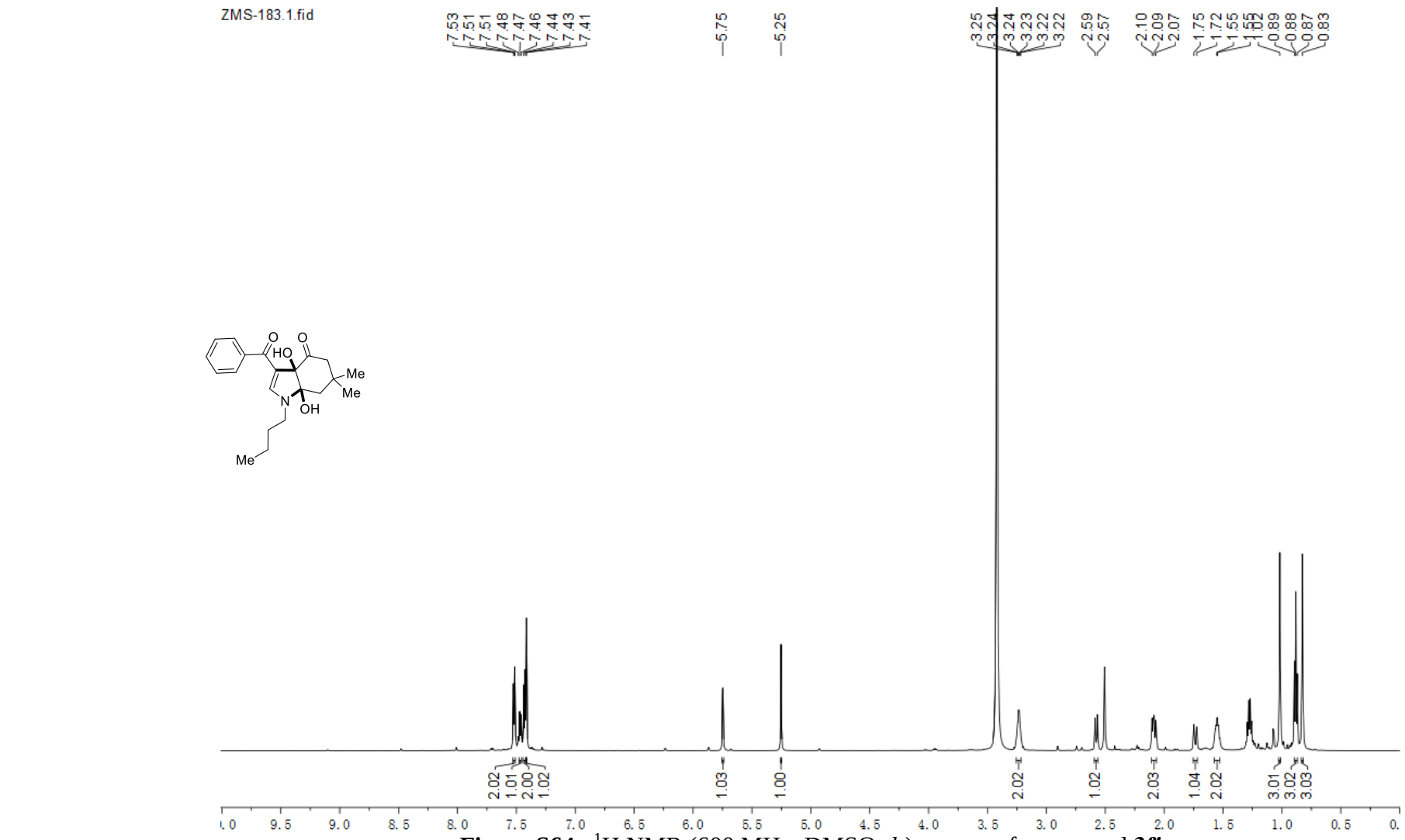


Figure S64. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3f′**

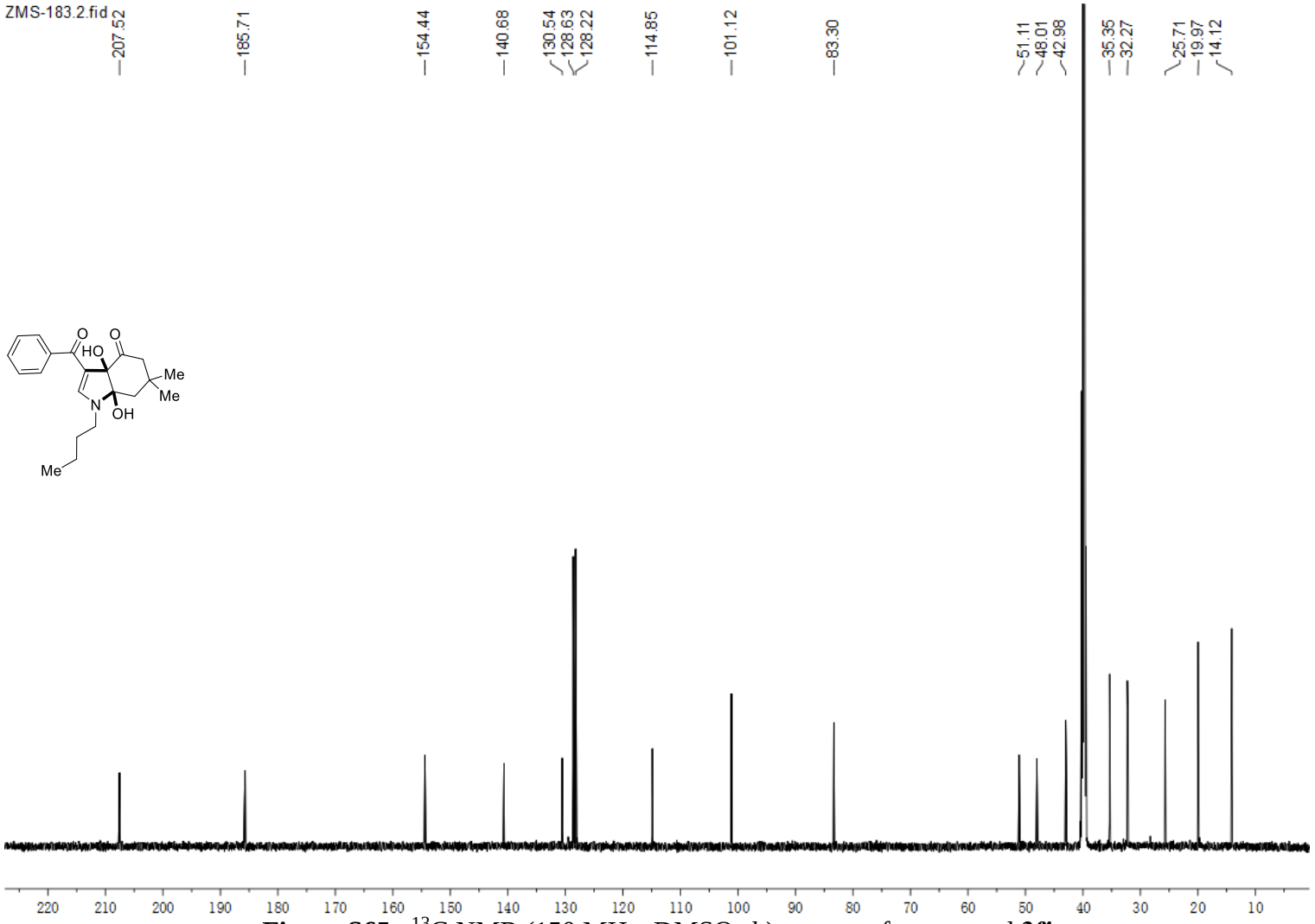


Figure S65. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3f′**

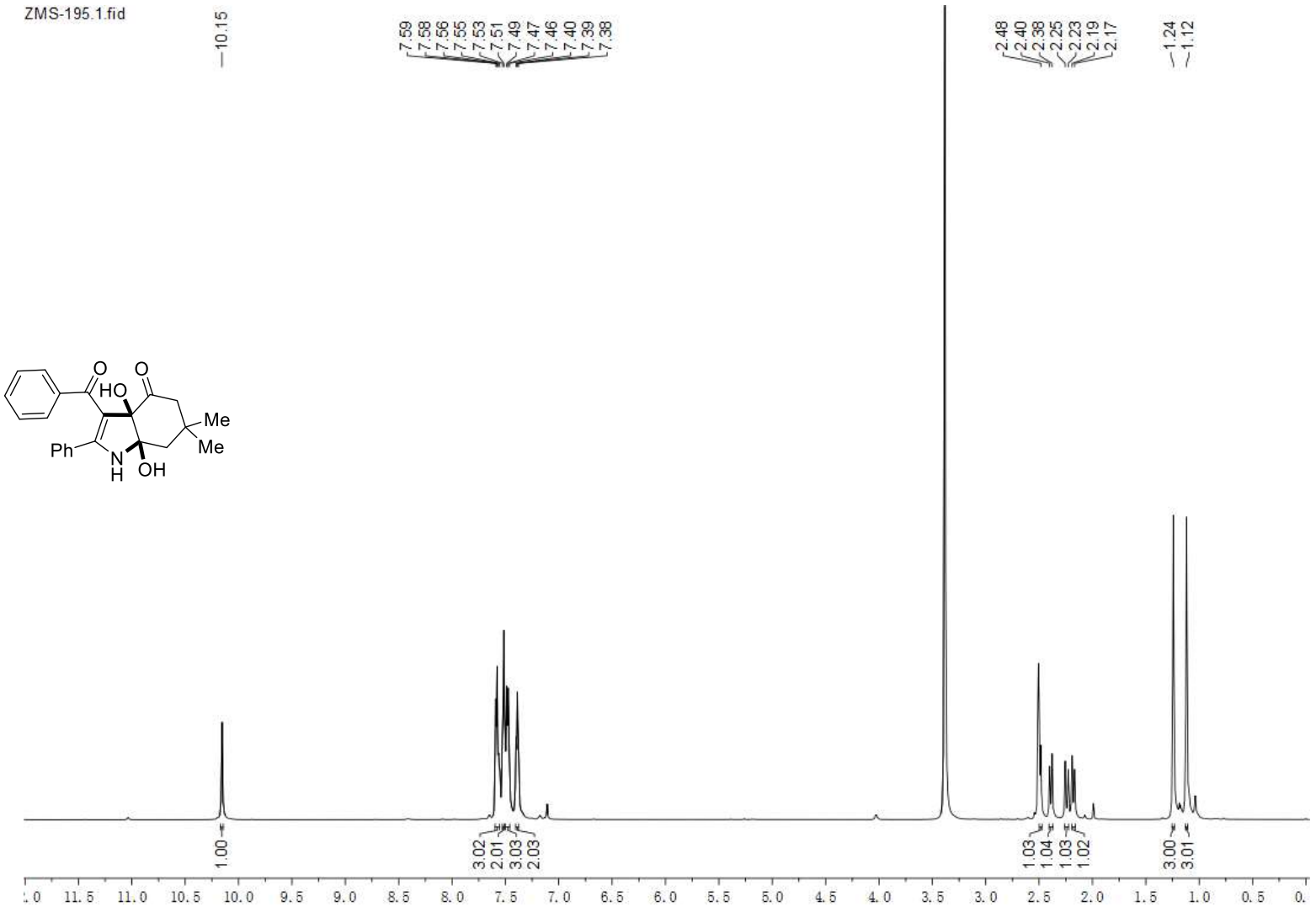


Figure S66. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3g′**

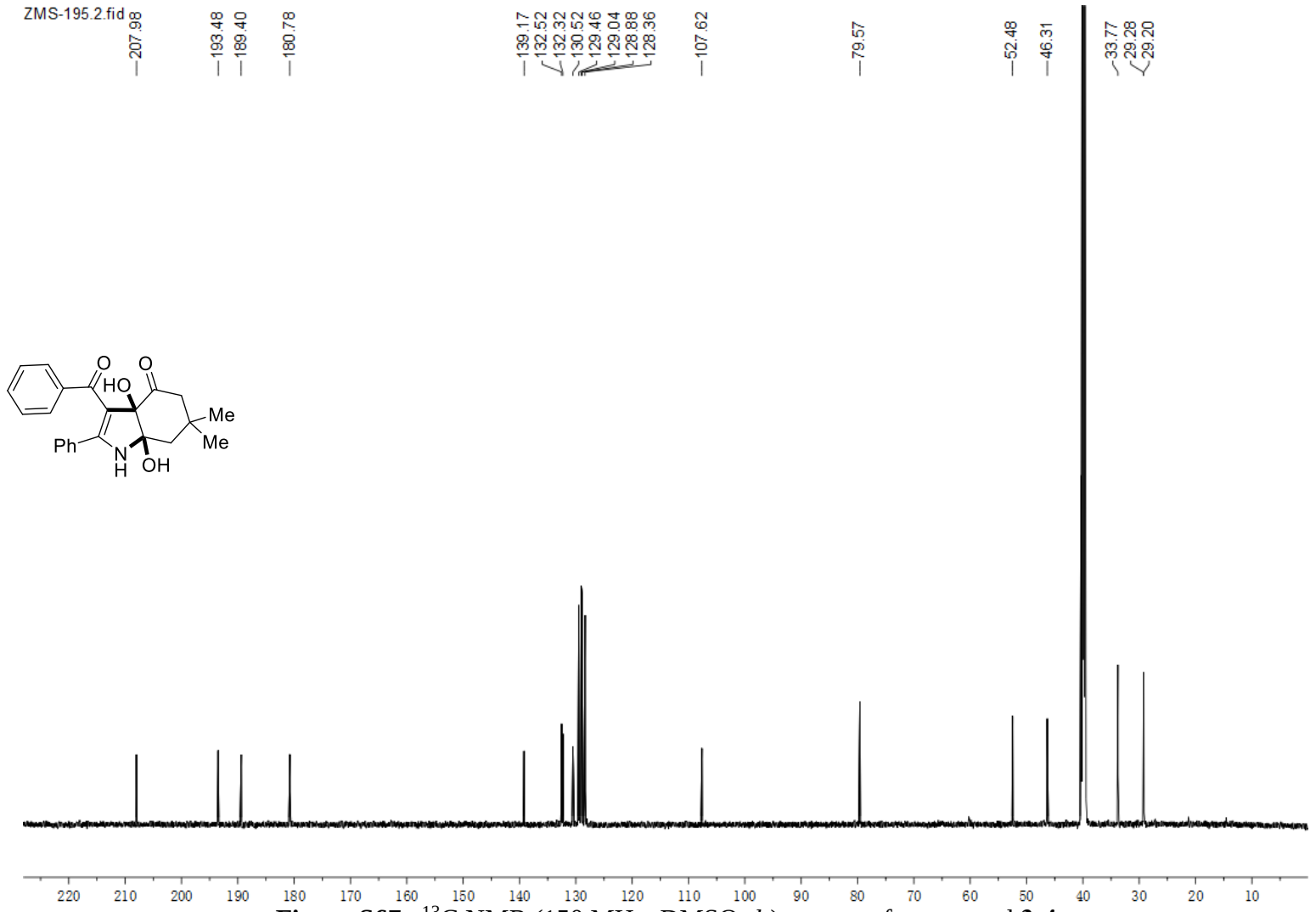


Figure S67. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3g′**

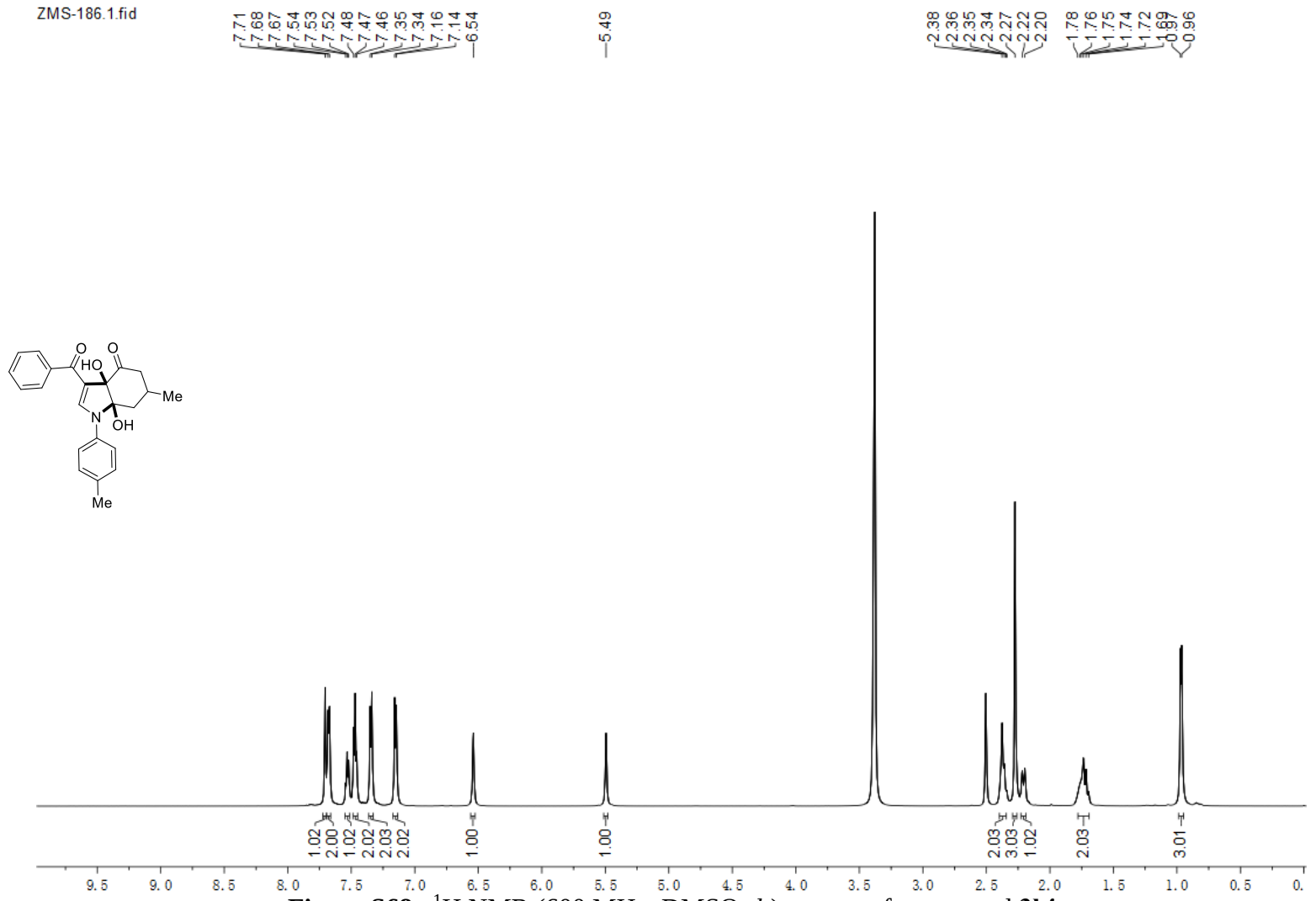


Figure S68. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3h′**

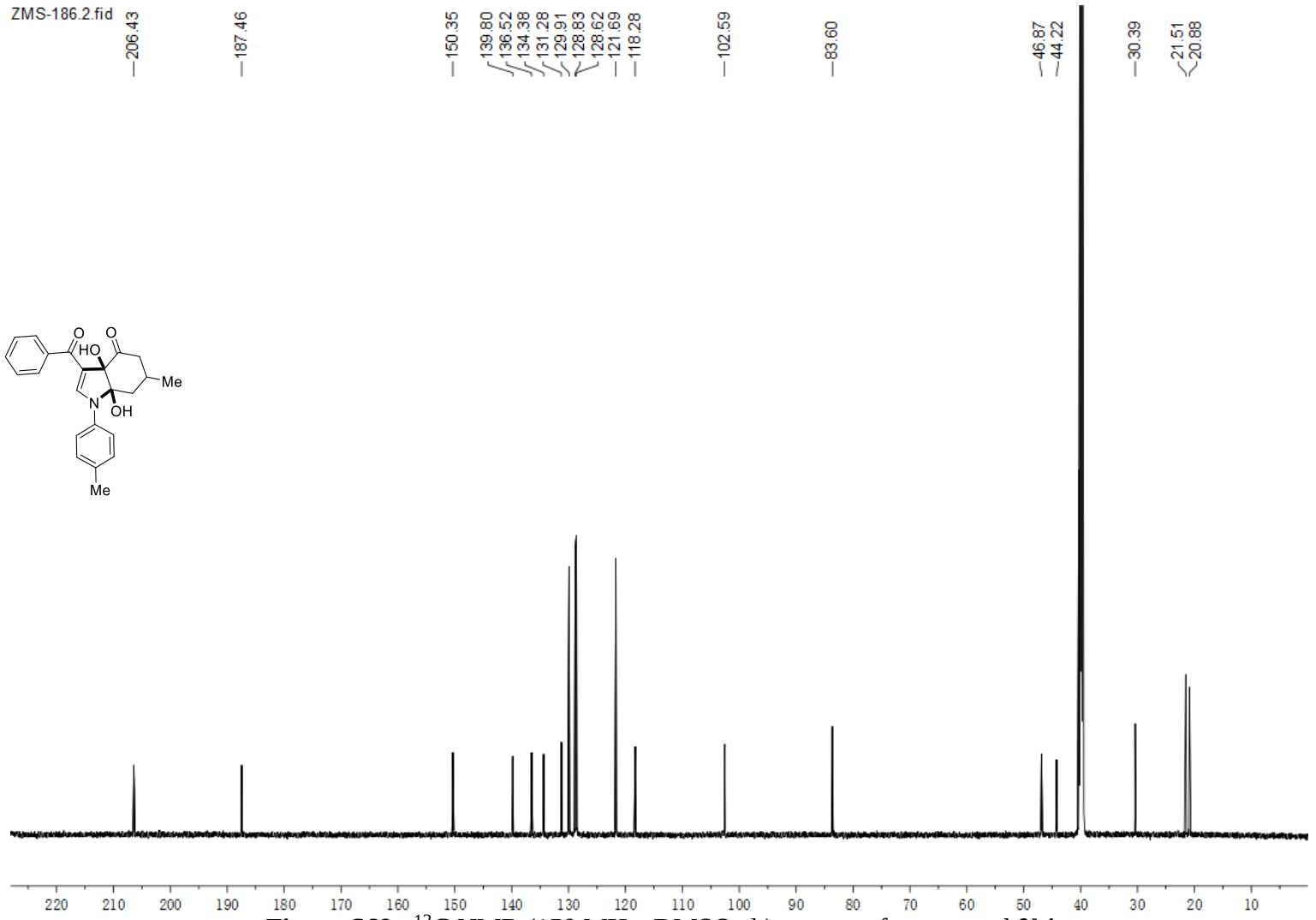


Figure S69. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3h′**

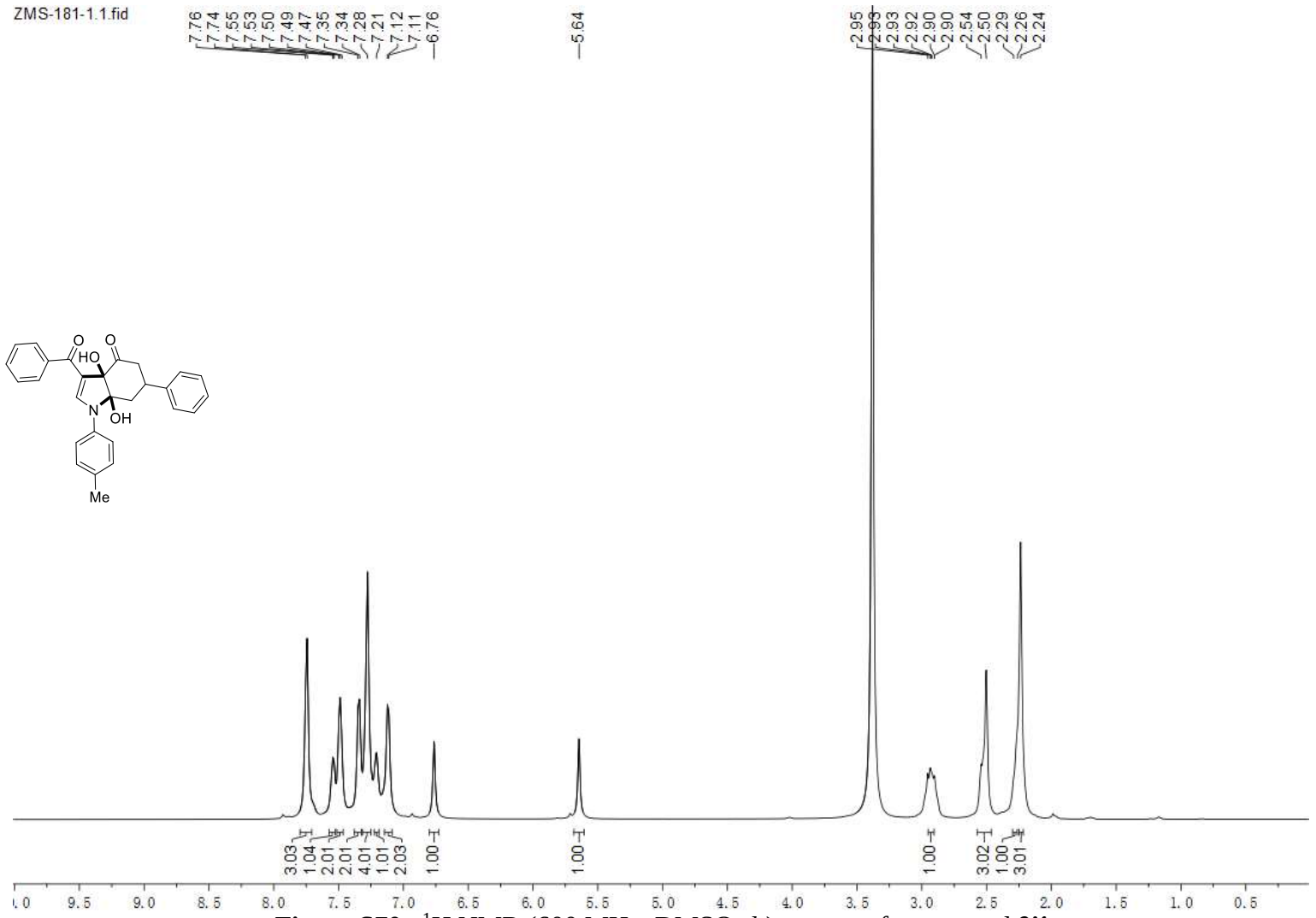


Figure S70. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3i′**

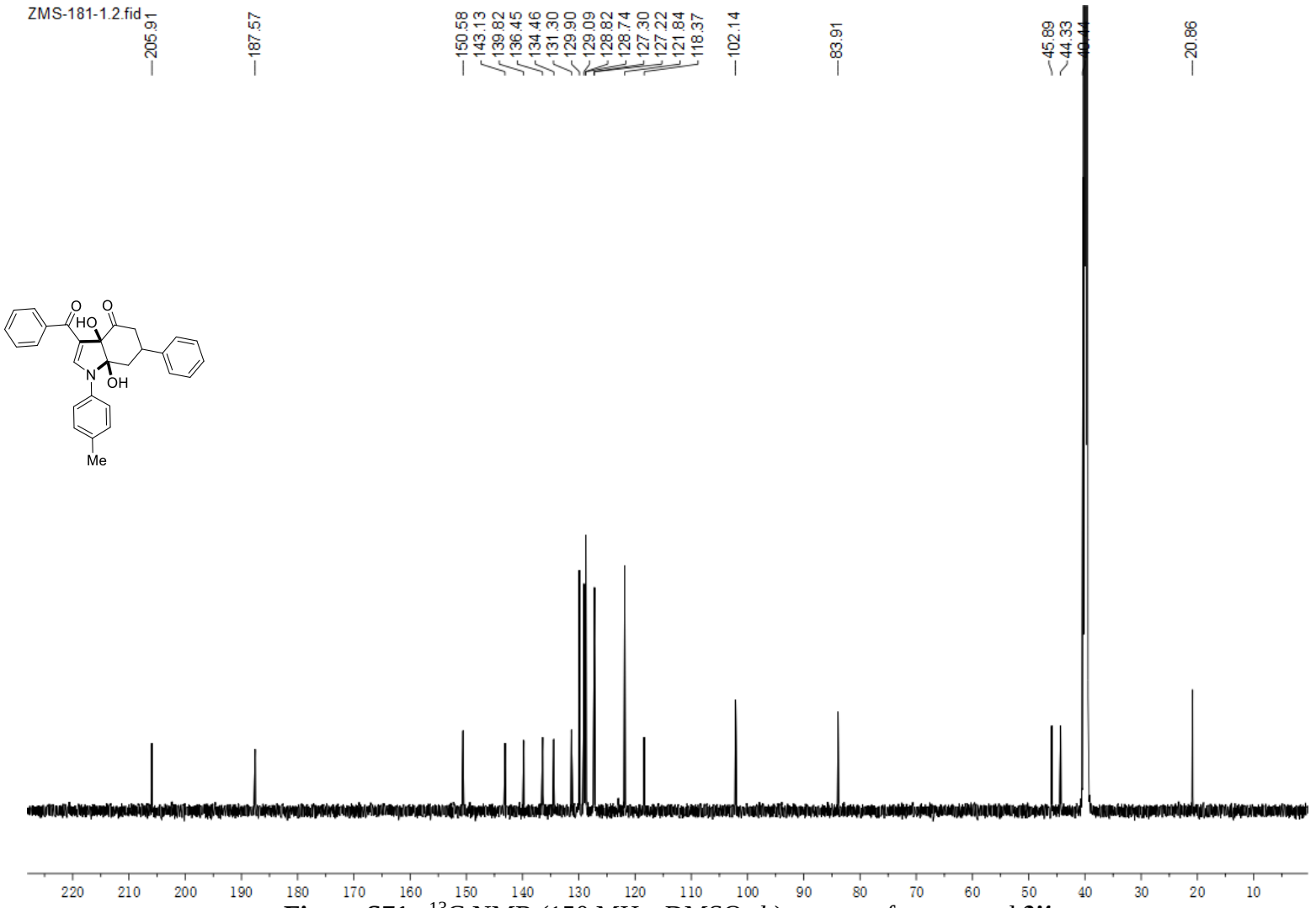


Figure S71. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3i′**

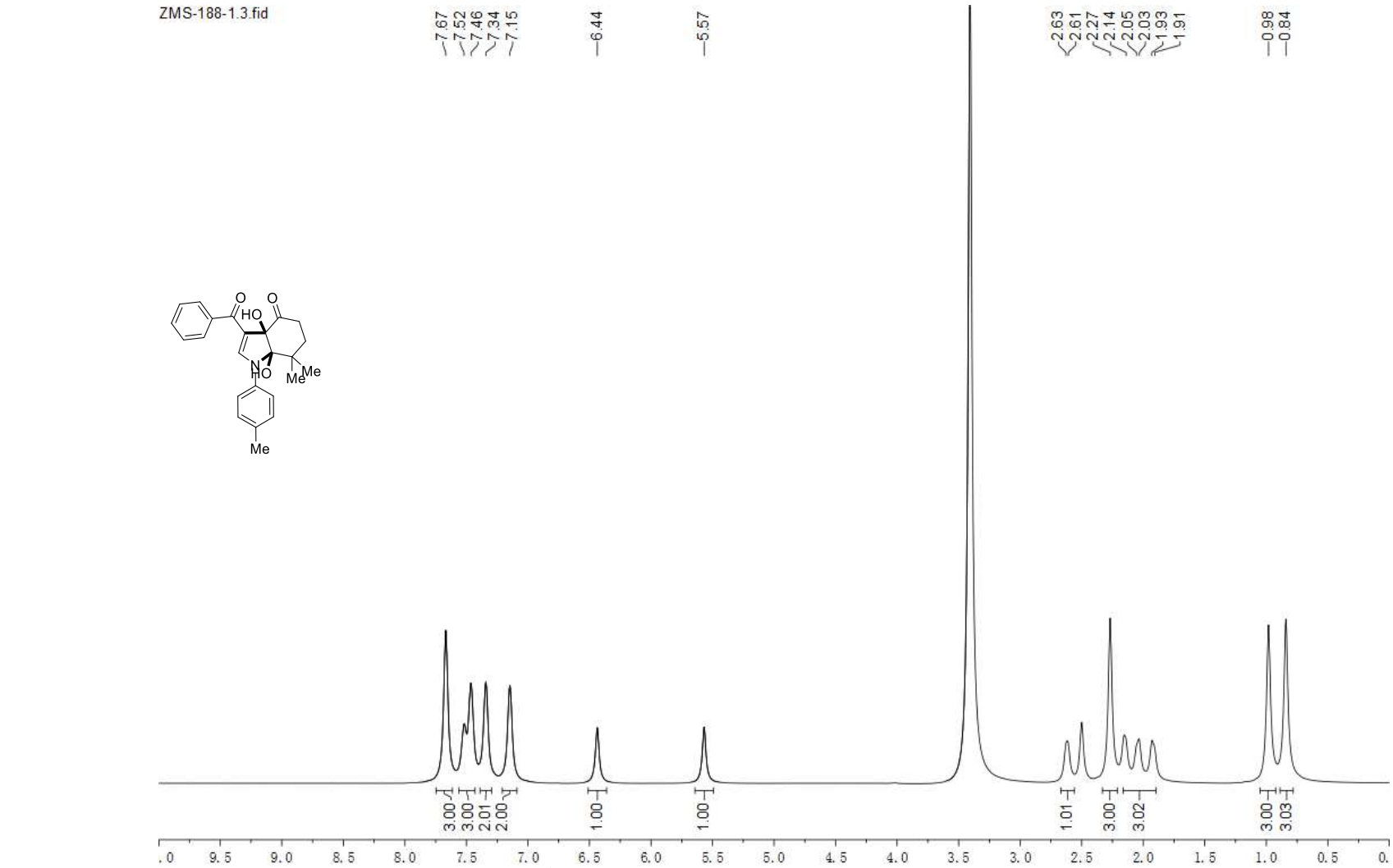


Figure S72. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3j′**

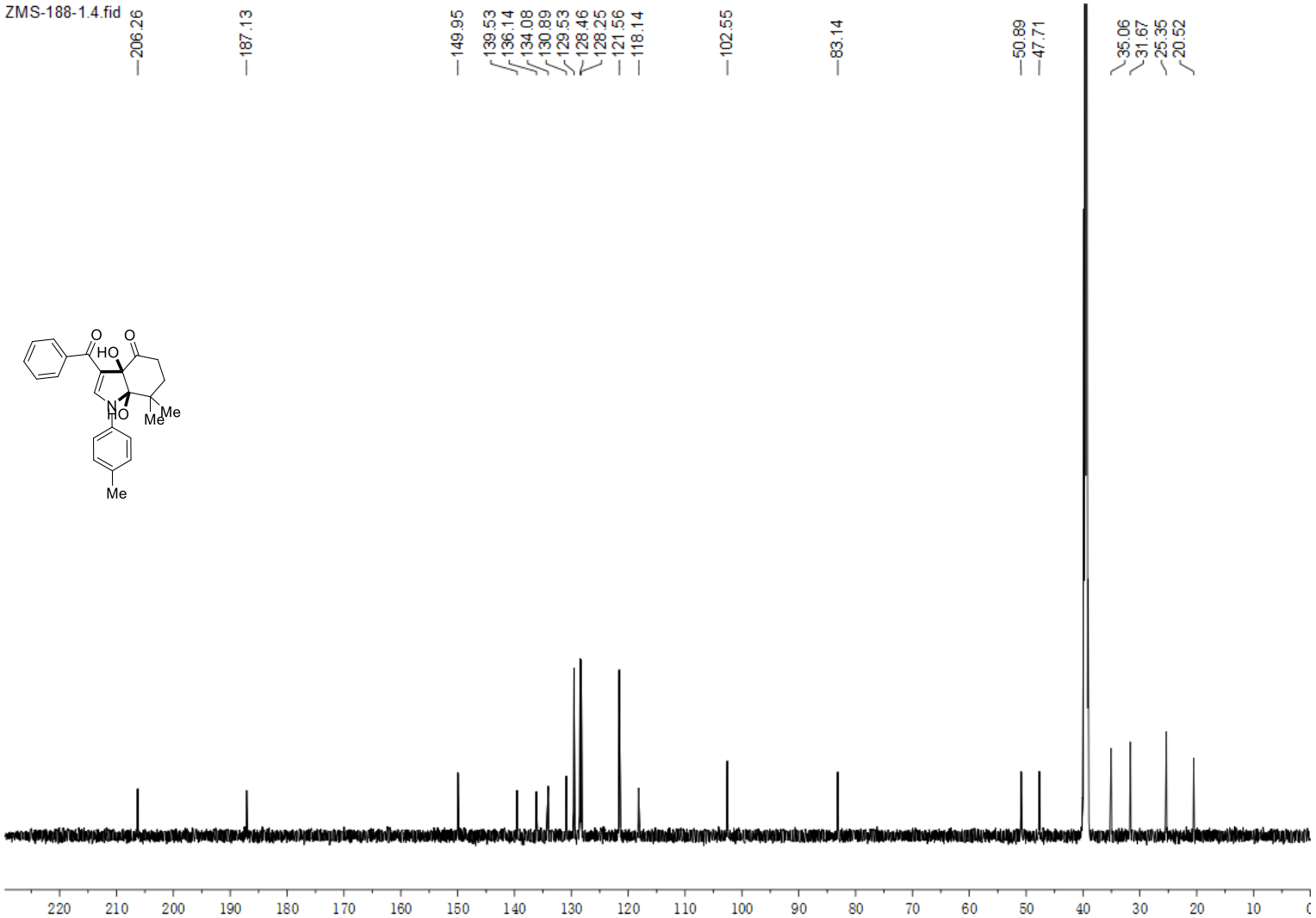


Figure S73. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3j′**

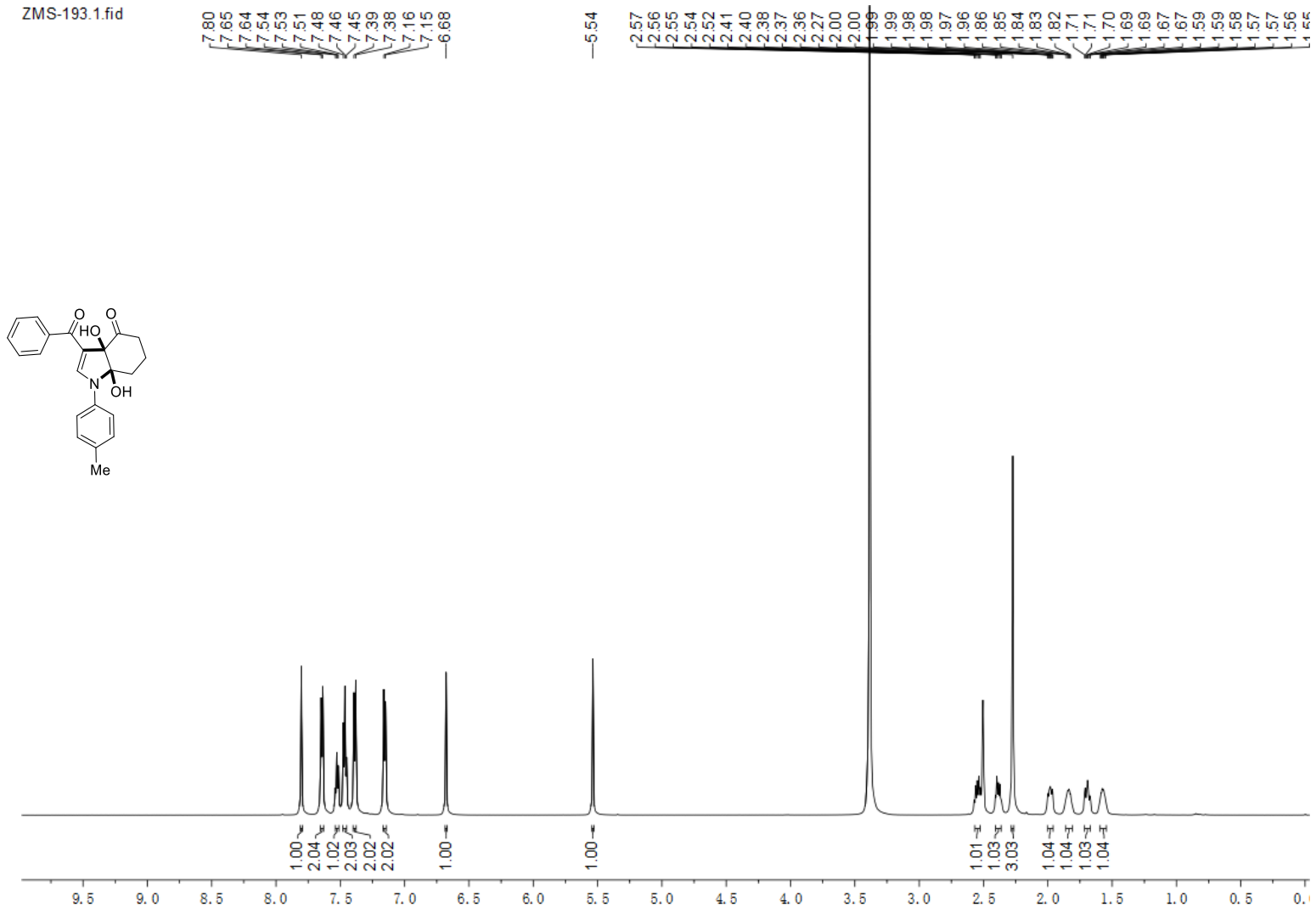


Figure S74. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3k′**

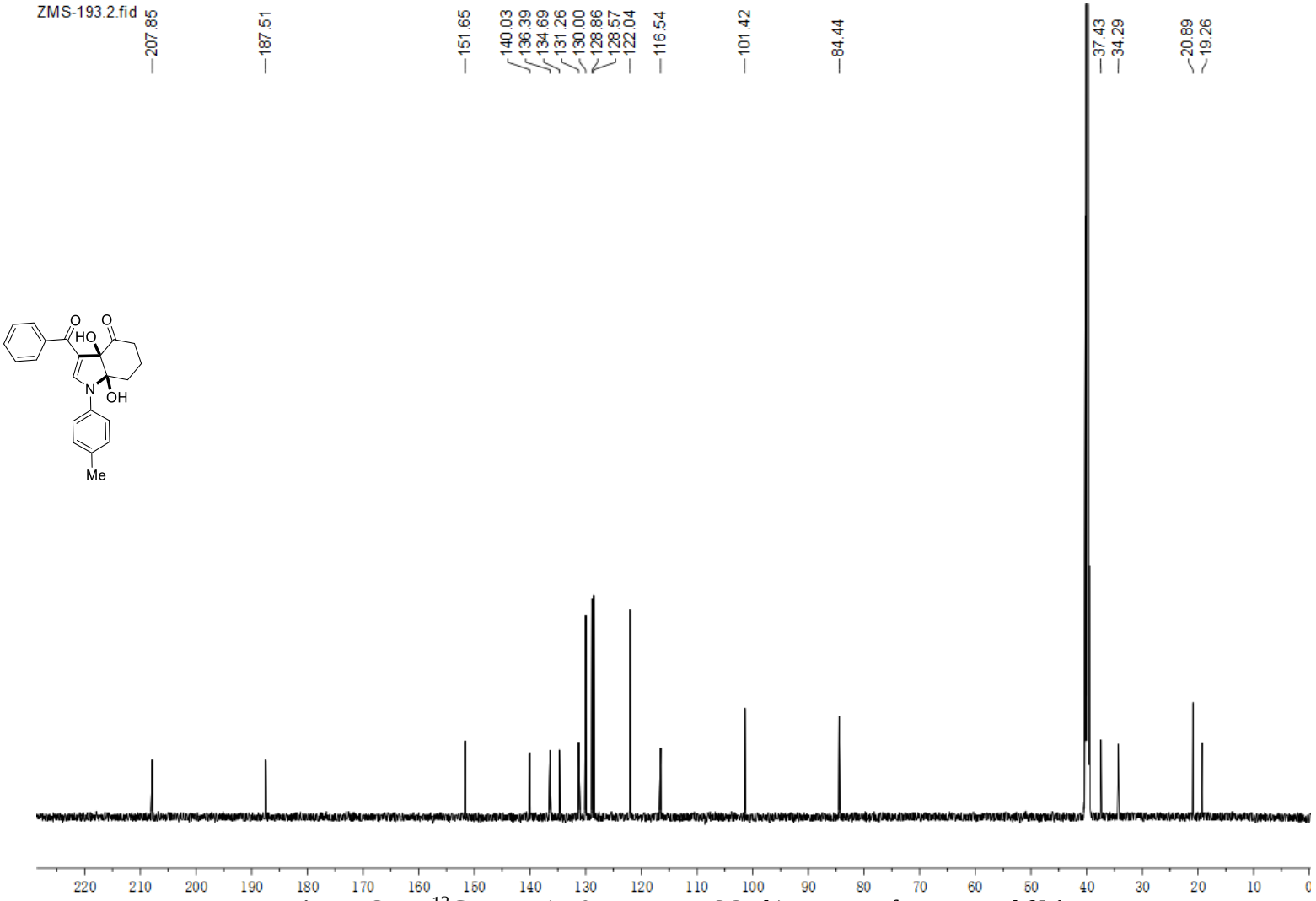


Figure S75. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3k′**

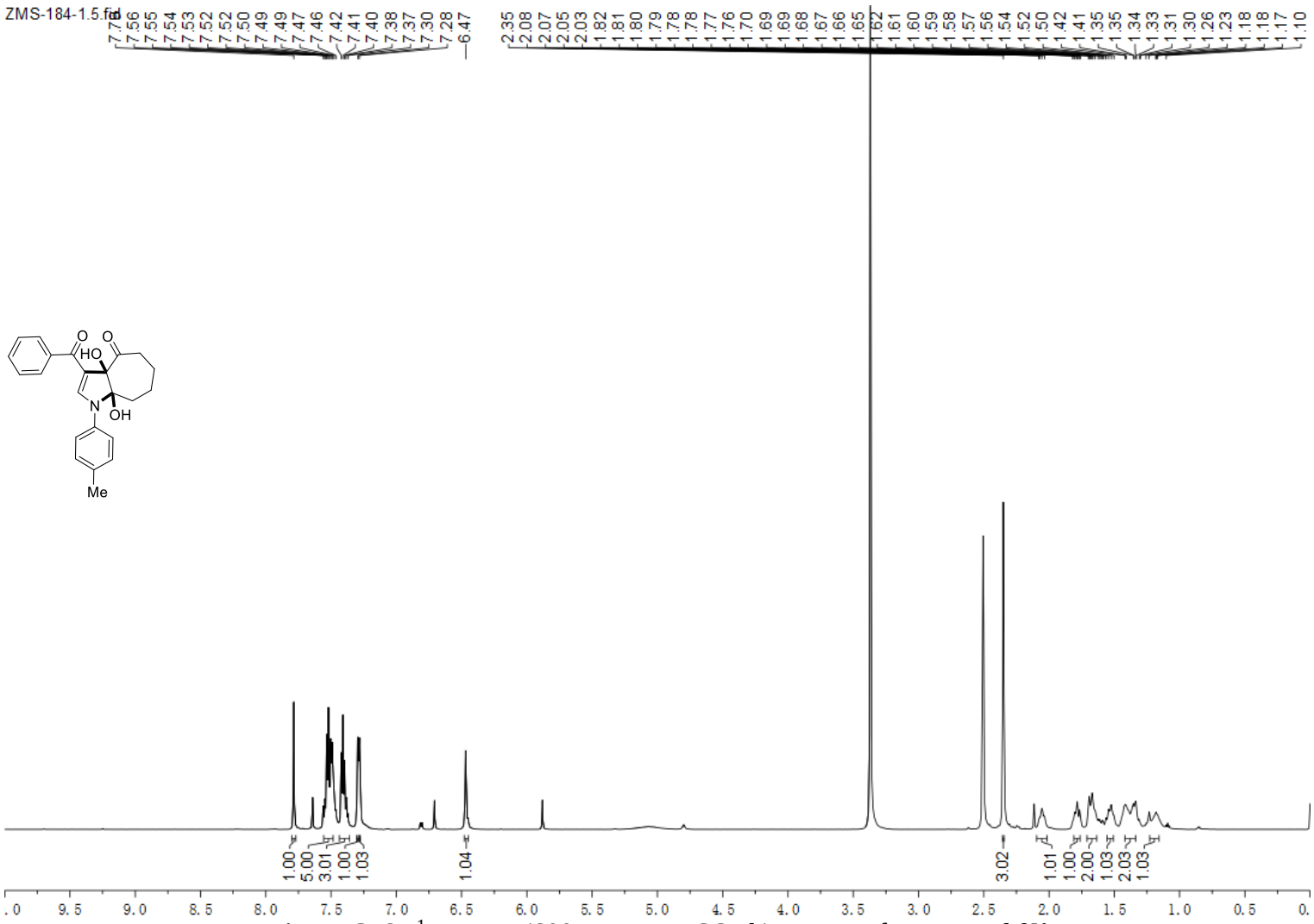


Figure S76. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3l′**

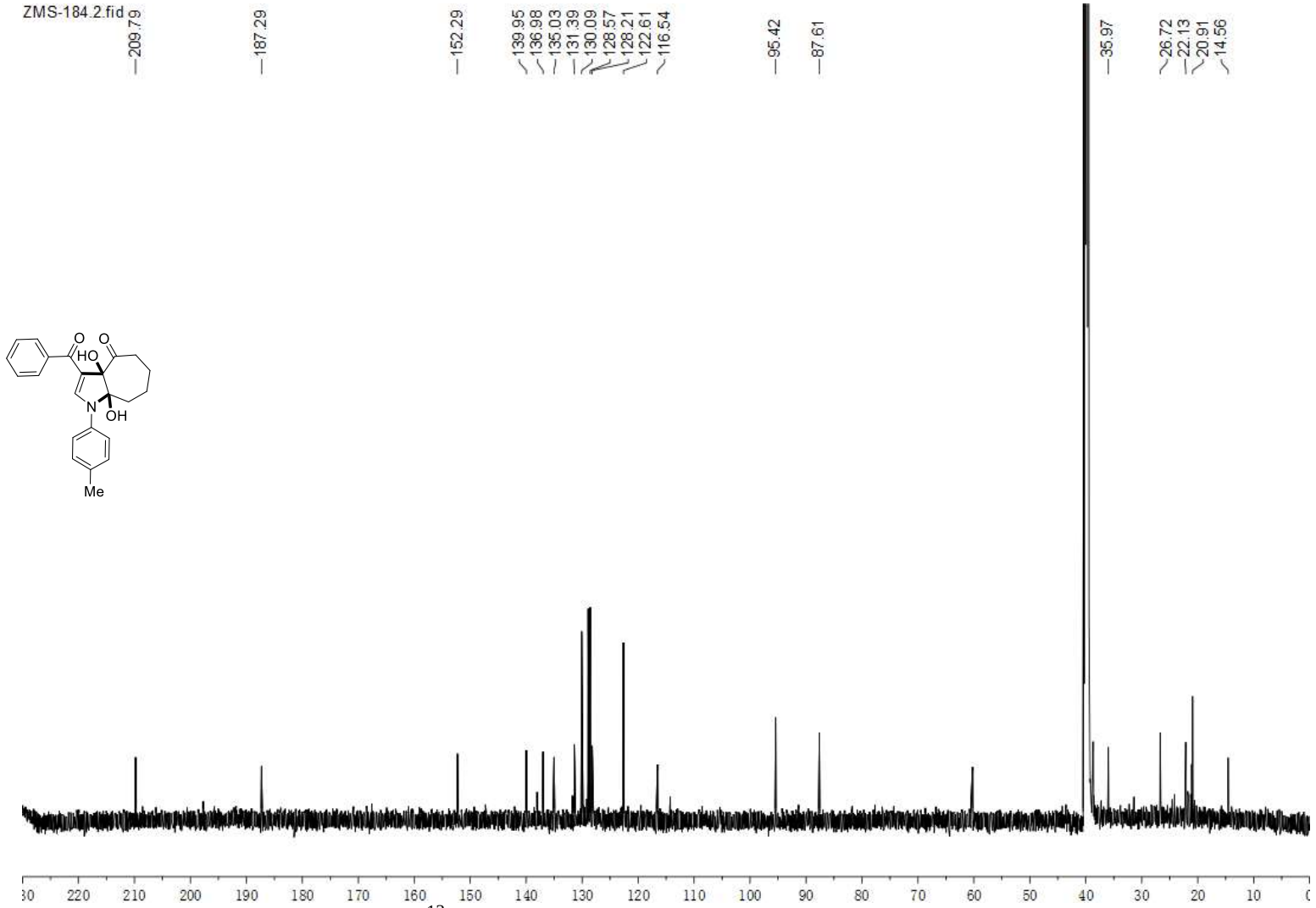


Figure S77. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3l′**

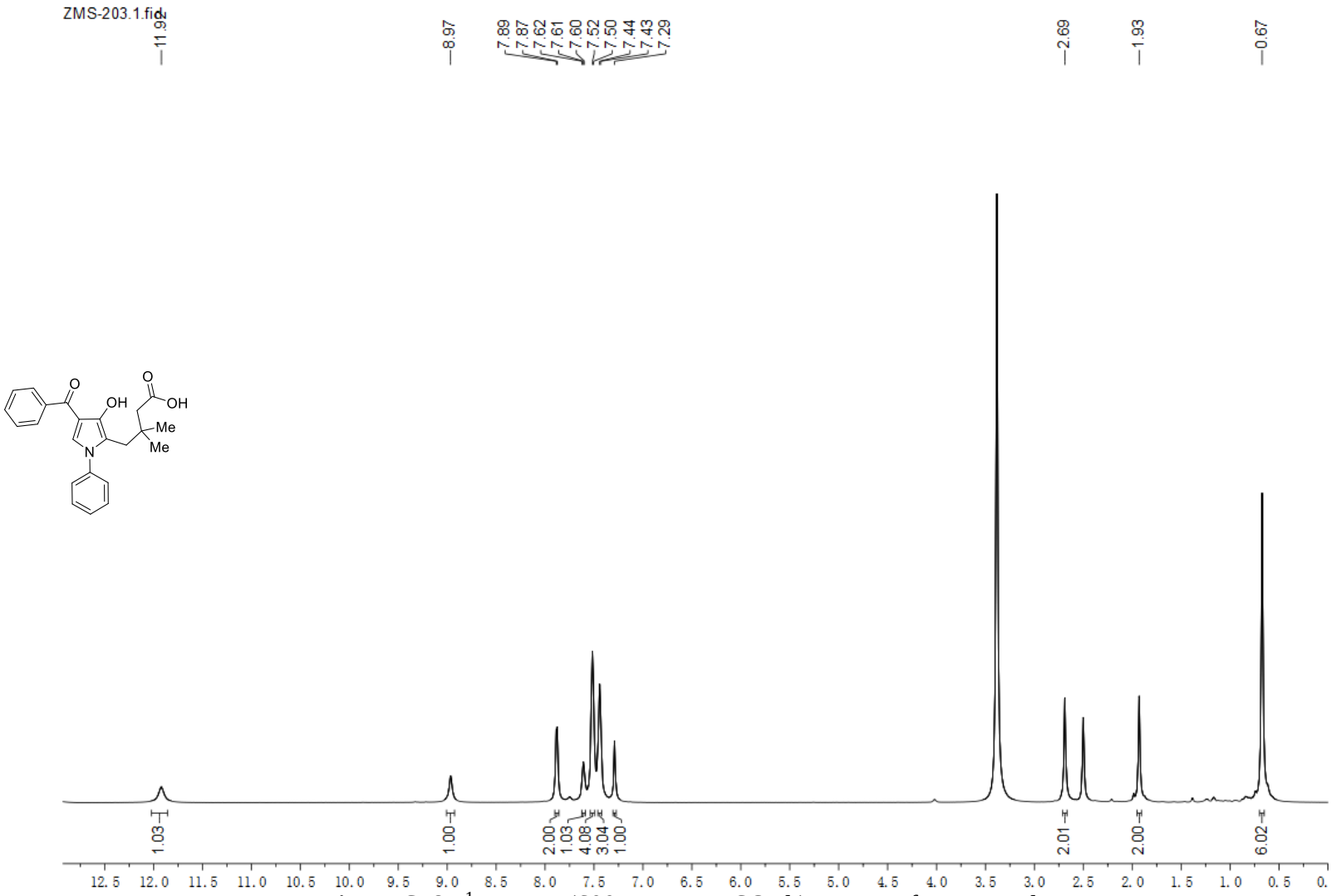


Figure S78. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4a**

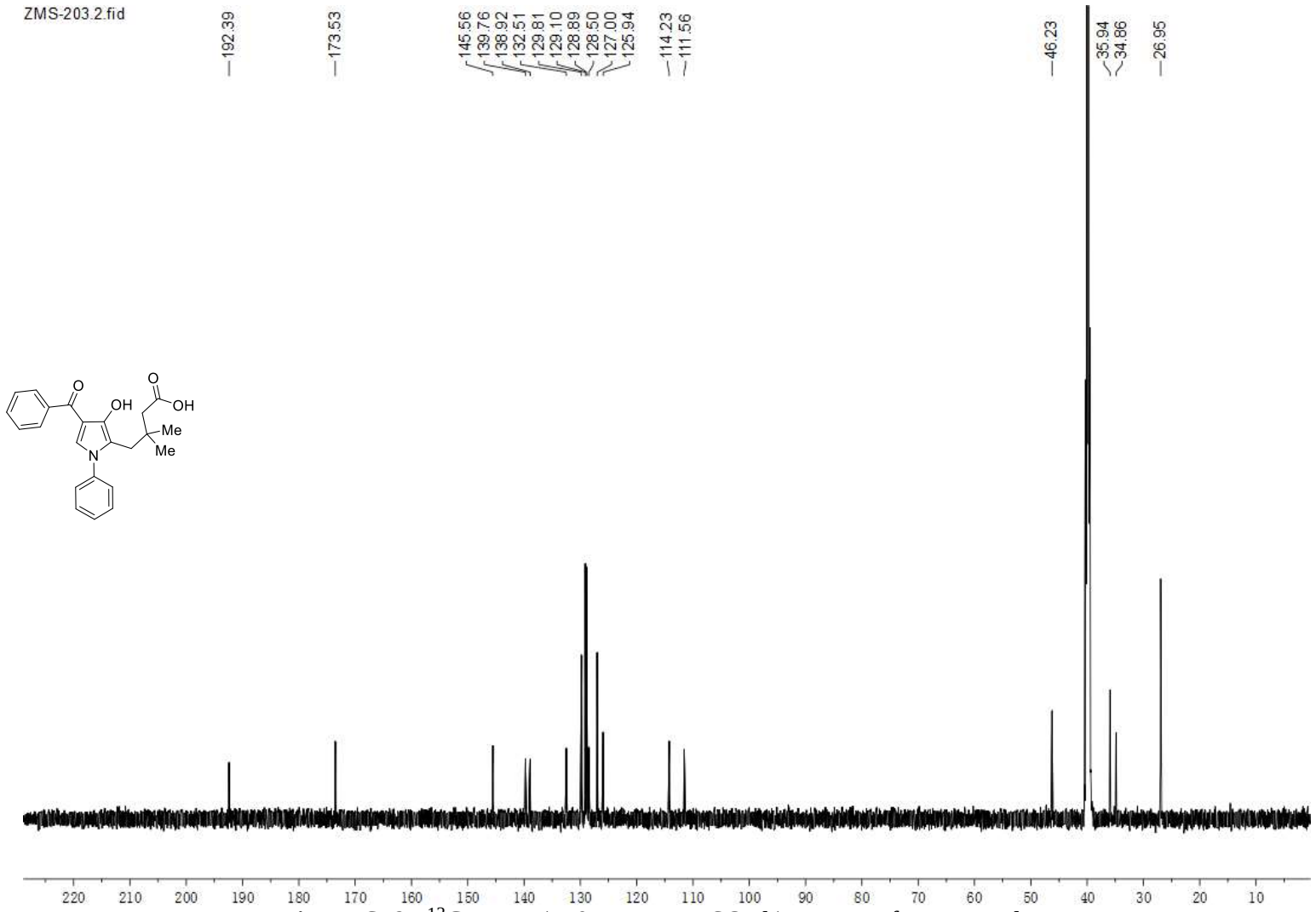


Figure S79. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4a**

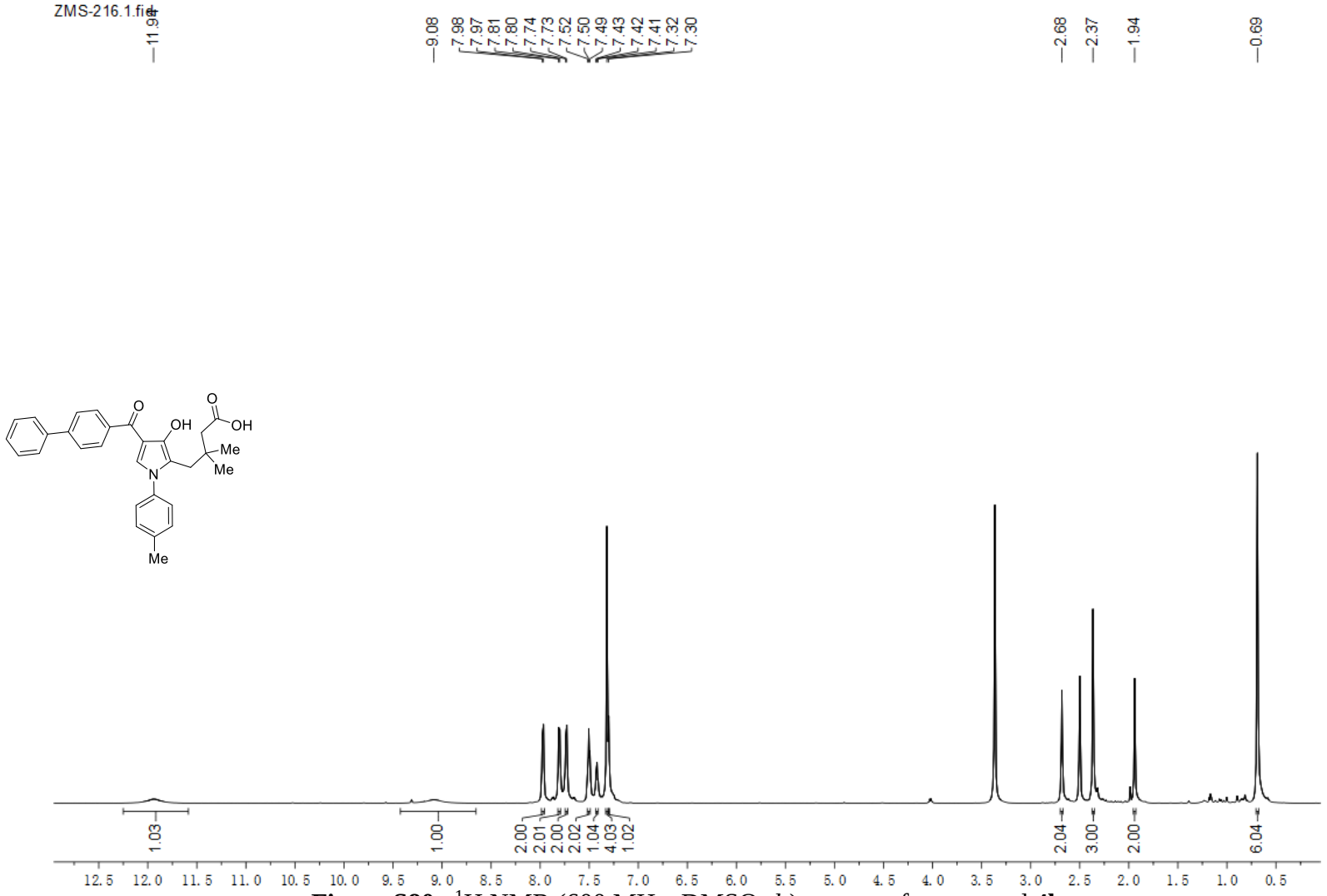


Figure S80. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4b**

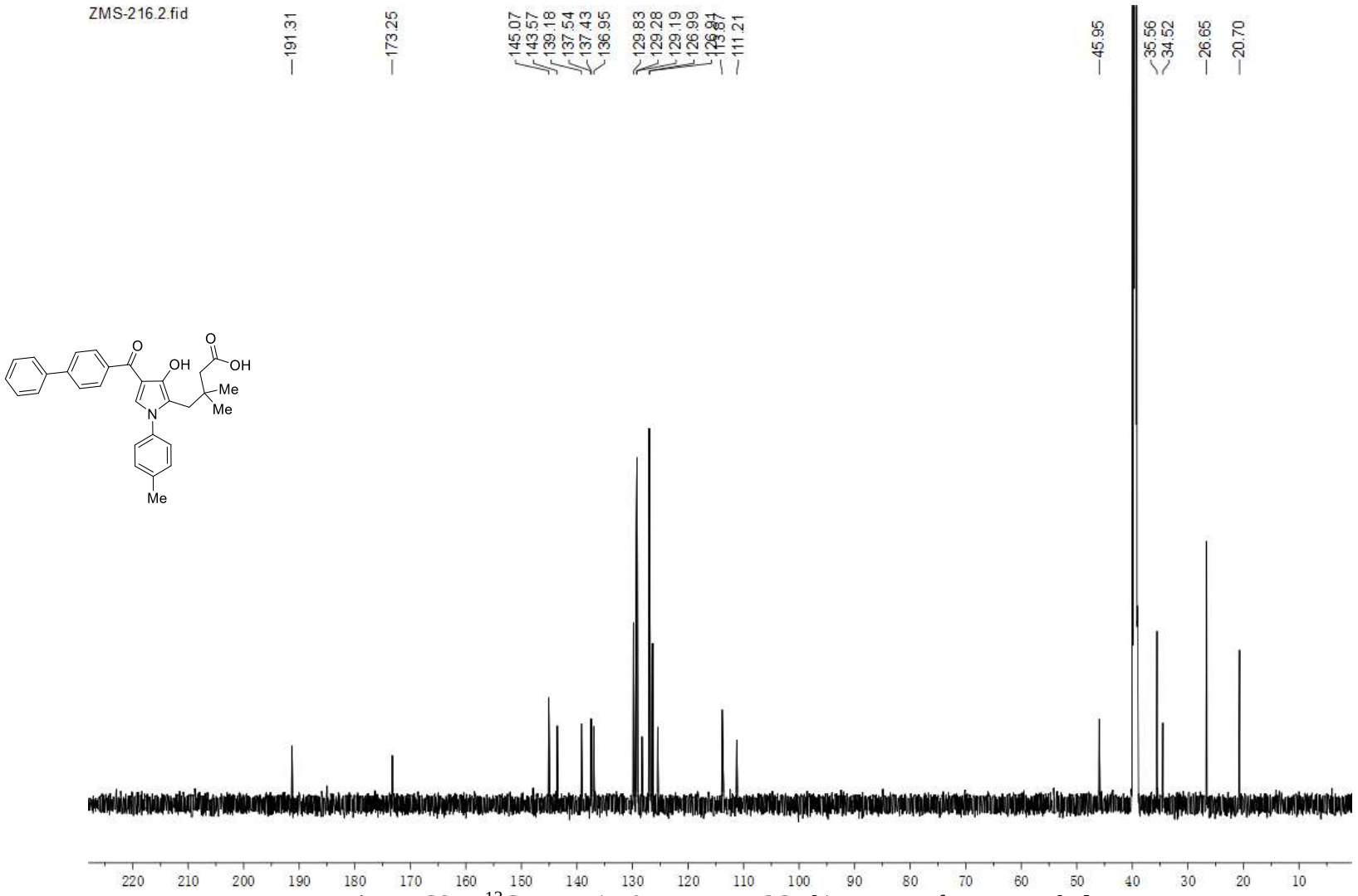


Figure S81. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4b**

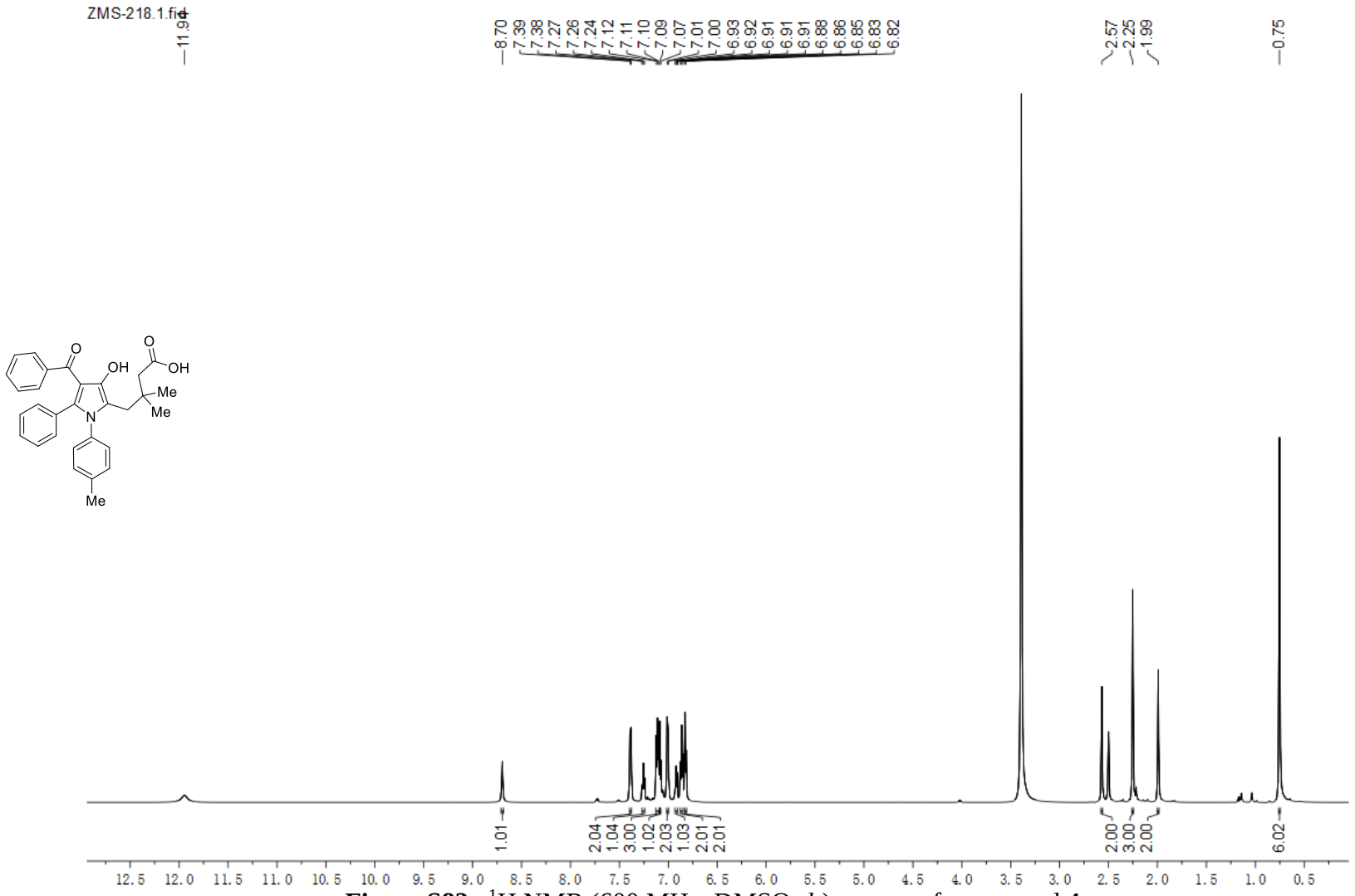


Figure S82. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4c**

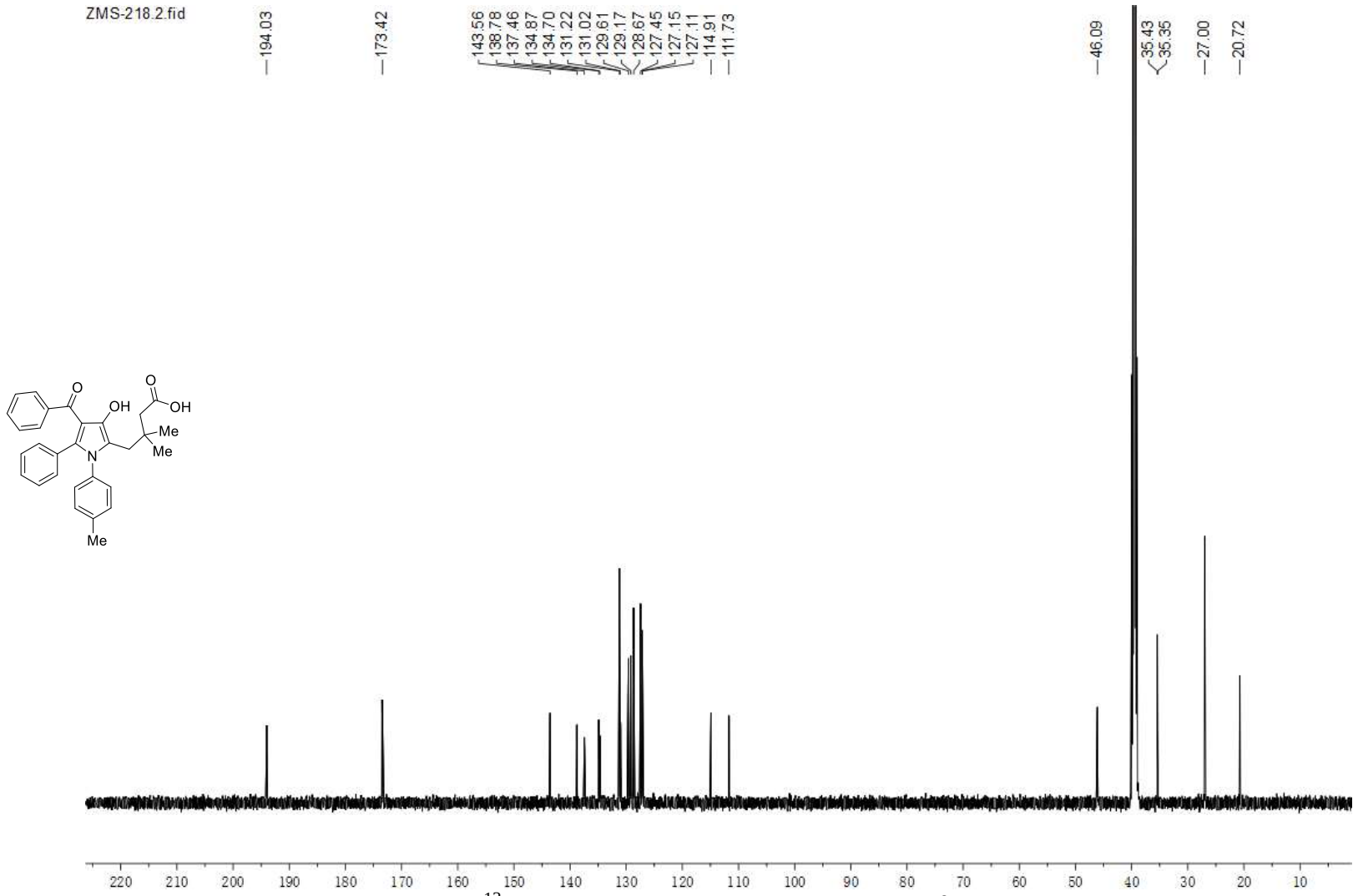


Figure S83. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4c**

7. References and notes.

1. (a) Liu, Y.; Zhou, R..; Wan, J.-P. *Synth. Commun.*, **2013**, *43*, 2475. (b) Zhou, Z.-Z.; Liu, F.-S.; Shen, D.-S.; Tan, C.; Luo, L.-Y. *Inorg. Chem. Commun.*, **2011**, *14*, 659. (c) Larina, N. A.; Lokshin, V.; Berthet, J.; Delbaere, S.; Vermeersch, G.; Khodorkovsky, V. *Tetrahedron*, **2010**, *66*, 8291. (d) Zhou, P.; Hu, B.; Rao, K.; Li, L.; Yang, J.; Gao, C.; Wang, F.; Yu, F. *Synlett*, **2018**, *29*, 519.
2. (a) Mayakrishnan, S.; Tamizmani, M.; Maheswari, N. U. *Chem. Commun.*, **2020**, *56*, 15462. (b) Yang, L.; Pi, C.; Wu, Y.; Cui, X. *Org. Lett.*, **2022**, *24*, 7502.
3. CCDC 2215066 contain the supplementary crystallographic data for compound **3i**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.