Rh(III)-Catalyzed Selective Mono- and Dual Functionalization/Cyclization of 1-aryl-5-aminopyrazoles with Iodonium Ylides

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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) and DRX500 (^{1}H: 500 MHz, ^{13}C: 125 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).

1-Aryl-5-aminopyrazoles **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®.

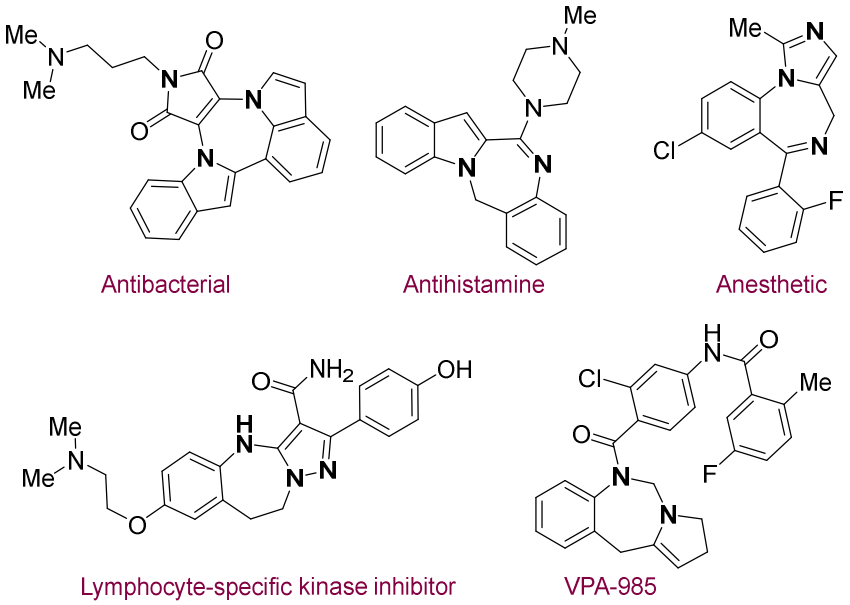
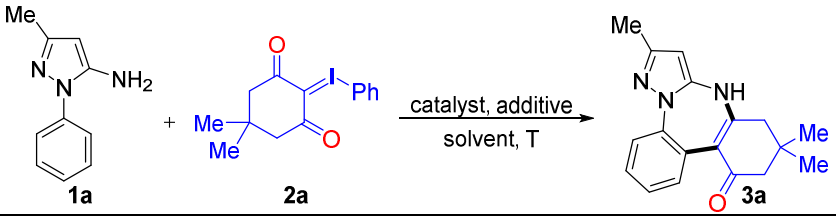


Figure S1. Representative bioactive polycyclic molecules.

2. Optimization of reaction conditions.

Table S1. Optimization of the mono-C-H functionalization/cyclization reaction conditions.[a,b]

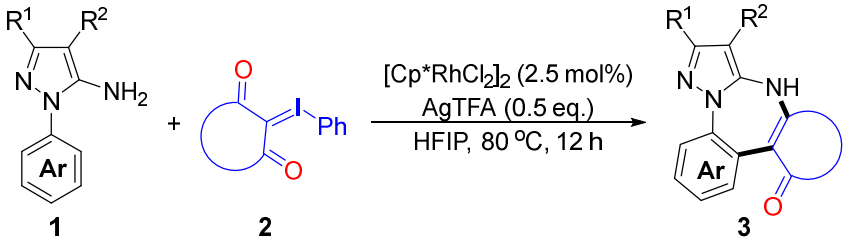


entry[a]	catalyst	additive	solvent	T (°C)	yield (%)
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	TFE	60	48
2	$[Cp^*IrCl_2]_2$	$AgSbF_6$	TFE	60	trace
3	RhI_3	$AgSbF_6$	TFE	60	trace
4	$[RhCl(cod)]_2$	$AgSbF_6$	TFE	60	0
5	$[Cp^*RhCl_2]_2$	-	TFE	60	36
6	$[Cp^*RhCl_2]_2$	AgF	TFE	60	40
7	$[Cp^*RhCl_2]_2$	AgTFA	TFE	60	65
8	$[Cp^*RhCl_2]_2$	$AgNO_3$	TFE	60	32
9	$[Cp^*RhCl_2]_2$	Ag_2CO_3	TFE	60	trace
10	$[Cp^*RhCl_2]_2$	AgOAc	TFE	60	36
11	$[Cp^*RhCl_2]_2$	AgCl	TFE	60	20
12	$[Cp^*RhCl_2]_2$	AgTFA	^{t}BuOH	60	38
13	$[Cp^*RhCl_2]_2$	AgTFA	EtOH	60	63
14	$[Cp^*RhCl_2]_2$	AgTFA	DCE	60	40
15	$[Cp^*RhCl_2]_2$	AgTFA	DMSO	60	48
16	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	60	76
17[c]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	60	64
18[d]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	60	76
19[e]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	60	75
20[f]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	60	70
21	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	40	66
22	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	80	89
23	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	100	78
24[g]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	80	63
25[h]	$[Cp^*RhCl_2]_2$	AgTFA	HFIP	80	89

[a]**1a** (0.3 mmol), **2a** (0.36 mmol, 1.2 equiv), catalyst (2.5 mol%), additive (0.5 equiv), solvent (1.5 mL), at 80 °C for 12 h under air atmosphere; [b]isolated yield; [c]**2a** (1.0 equiv); [d]**2a** (1.5 equiv); [e]O_2 atmosphere; [f]N_2 atmosphere; [g]Catalyst (1.5 mol%); [h]Catalyst (3.5 mol%).

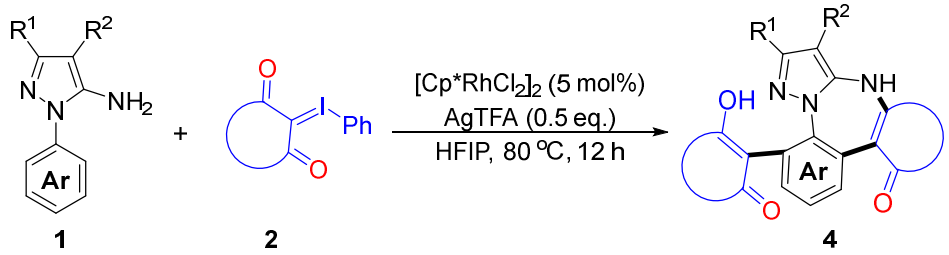
3. General procedure.

3.1 Synthesis of benzo[*f*]pyrazolo[1,5-*a*][1,3]diazepines 3.



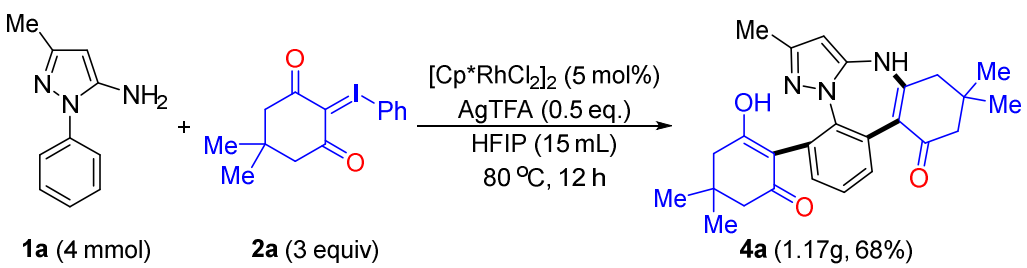
1-Aryl-5-aminopyrazoles **1** (0.3 mmol), iodonium ylides **2** (0.36 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgTFA (0.15 mmol) and HFIP (1.5 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 12.0 h until **1** were completely consumed. The mixture was cooled 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 **3**.

3.2 Synthesis of 4-substituted benzo[*f*]pyrazolo[1,5-*a*][1,3]diazepines 4.



1-Aryl-5-aminopyrazoles **1** (0.4 mmol), iodonium ylides **2** (1.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgTFA (0.2 mmol) and HFIP (2 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 12.0 h until **1** 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 **4**.

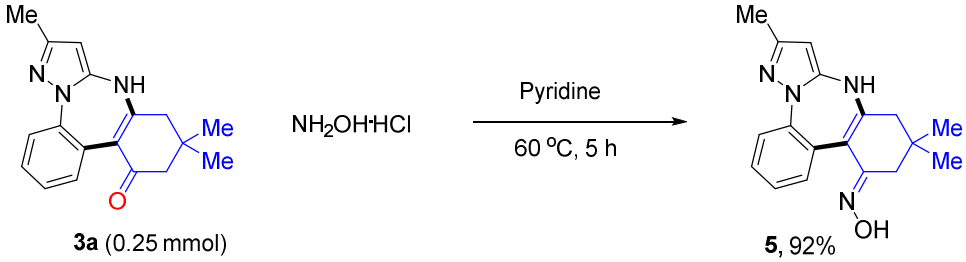
3.3 Gram-scale synthesis of benzo[*f*]pyrazolo[1,5-*a*][1,3]diazepine 4a.



1-Aryl-5-aminopyrazole **1a** (4 mmol), iodonium ylide **2a** (12 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), AgTFA (2 mmol) and HFIP (15 mL) were charged into a 100 mL Ace Glass

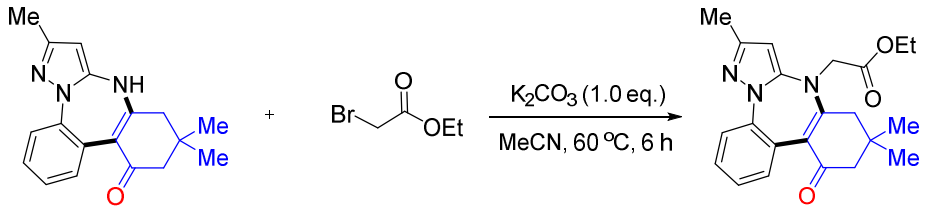
pressure tubes, and the mixture was stirred at 80 °C for 12.0 h until **1** were completely consumed. The mixture was cooled to room temperature, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford **4a** in 68% yield (1.17 g).

3.4 Further transformationf of benzo[*f*]pyrazolo[1,5-*a*][1,3]diazepine 3a.



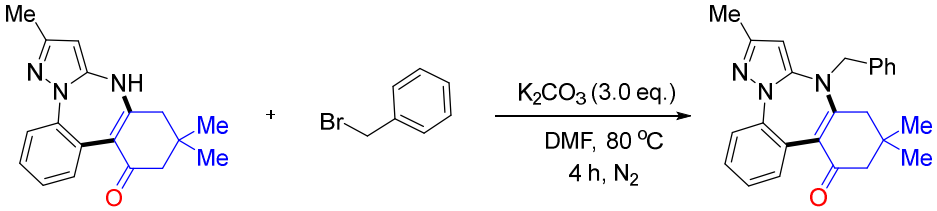
3a (0.25 mmol) **5**, 92%

3a (0.25 mmol), hydrohydrate hydrochloride (1.5 mmol), and pyridine (2 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 60 °C for 5.0 h until **3a** 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 **5** in 92% yield.



3a (0.25 mmol) **6**, 83%

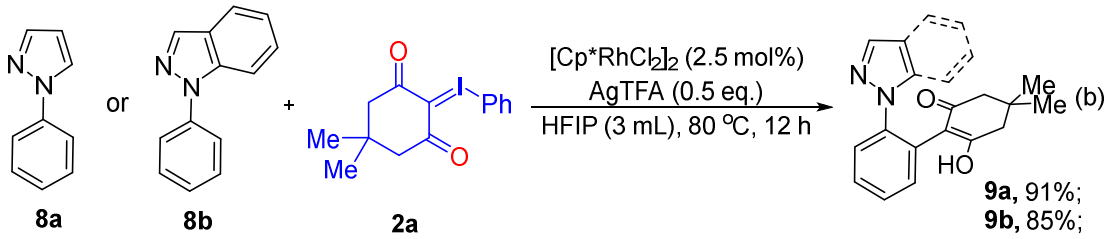
3a (0.25 mmol), ethyl bromoacetate (0.37 mmol), K_2CO_3 (0.25 mmol) and MeCN (2 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 60 °C for 6.0 h until **3a** were completely consumed. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford **6** in 83% yield.



3a (0.25 mmol) **7**, 70%

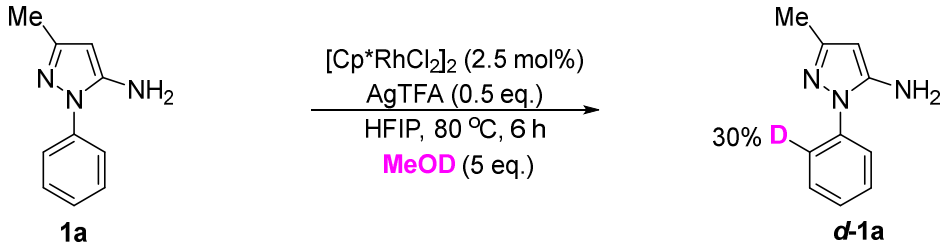
3a (0.25 mmol), benzyl bromide (0.37 mmol), K_2CO_3 (0.75 mmol) and DMF (2 mL) under nitrogen atmosphere were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 4.0 h until **3a** were completely consumed. The mixture was cooled to room temperature, and then EtOAc (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 **7** in 70% yield.

3.5 Control experiment.

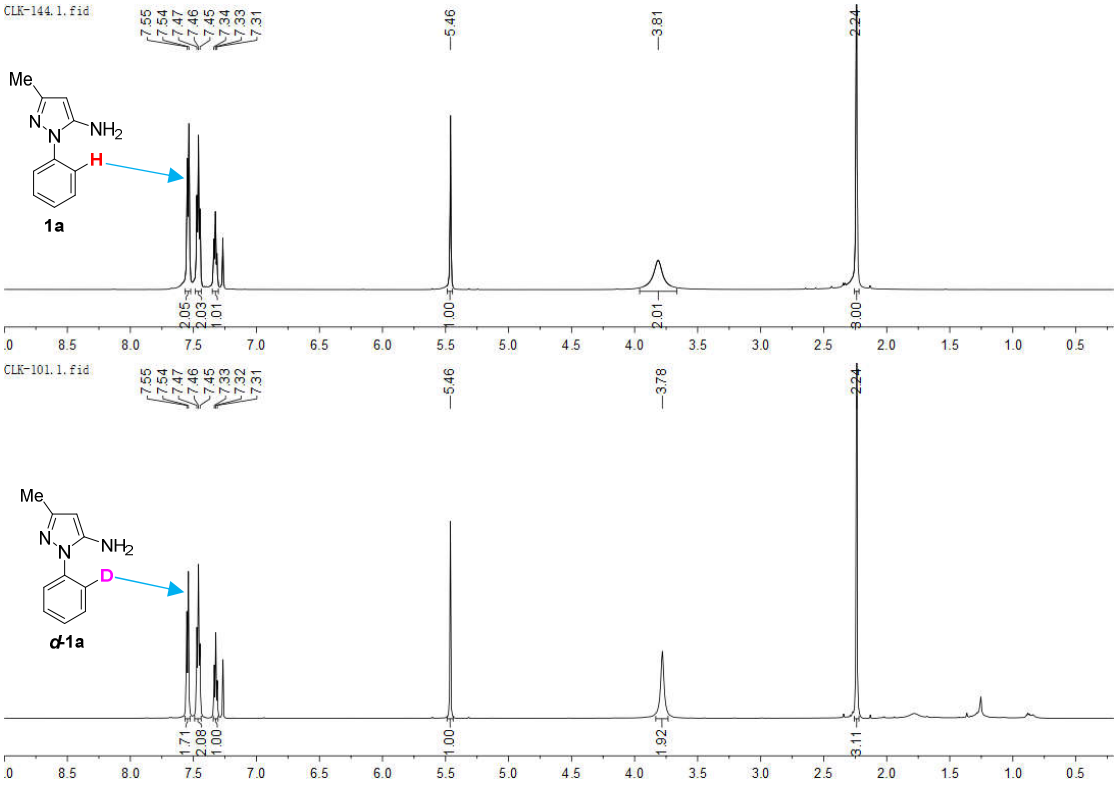


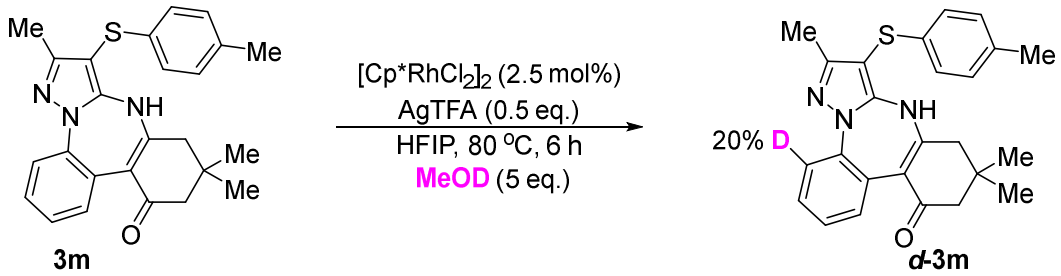
1-Phenylpyrazole **8a** or 1-phenylindazole **8b** (0.5 mmol), iodonium ylides **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgTFA (0.25 mmol) and HFIP (3 mL) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 12.0 h until **8a** or **8b** were completely consumed. 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 **9**.

3.6 H/D Exchange experiment.

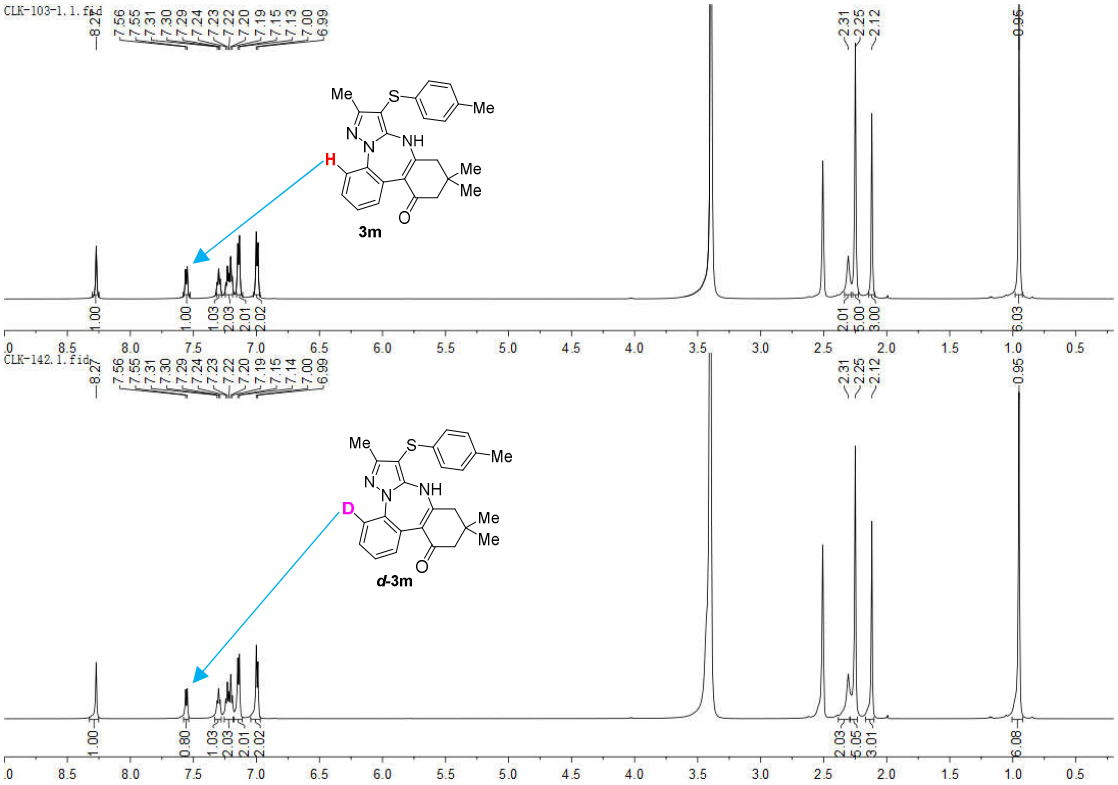


1a (0.3 mmol), $[Cp^*RuCl_2]_2$ (2.5 mol%), AgTFA (0.15 mmol), HFIP (1.5 mL) and MeOD (1.5 mmol) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 6.0 h. The mixture was cooled to room temperature, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford ***d*-1a**.





3m (0.3 mmol), $[Cp^*RuCl_2]_2$ (2.5 mol%), AgTFA (0.15 mmol), HFIP (1.5 mL) and MeOD (1.5 mmol) were charged into a 10 mL Ace Glass pressure tubes, and the mixture was stirred at 80 °C for 6.0 h. 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 ***d*-3m**.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7.15
7.13
7.00
6.99
2.31
2.25
2.12
0.96
Me
S
Me
N
N
NH
H
Me
Me
O
3m
1.00
1.00
1.03
2.03
2.01
2.02
2.01
5.00
3.00
6.03
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7.22
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N
N
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Me
Me
O
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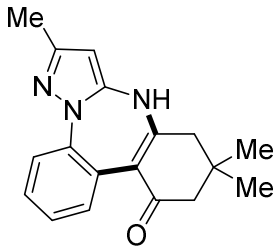
2.02
2.03
5.05
3.01
6.08

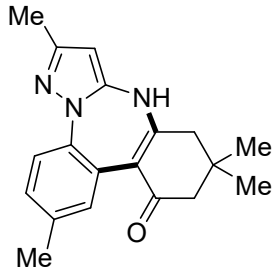
4. Spectroscopic data.

7,11,11- Timethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13 (10*H*)-one (3a)



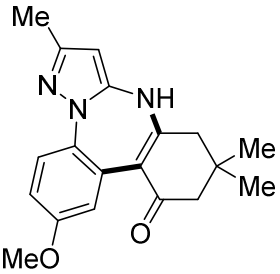
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 78 mg (89%); mp = 296–298 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.83 (s, 1H. NH), 7.50–7.45 (m, 1H, ArH), 7.22–7.18 (m, 1H, ArH), 7.15–7.12 (m, 2H, ArH), 5.60 (s, 1H, C=CH), 2.45 (s, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.12 (s, 2H, CH_2), 1.03 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.4, 164.7, 150.9, 148.9, 139.0, 132.2, 127.5, 126.7, 125.5, 122.3, 114.6, 95.9, 50.8, 44.0, 30.3, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{18}H_{20}N_3O$ $[(M+H)^+]$, 294.1605, found, 294.1594.

2,7,11,11-Tetramethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepi n-13(10*H*)-one (3b)



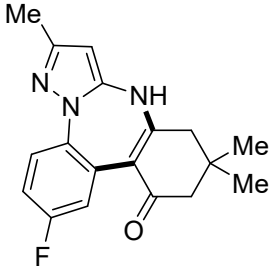
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 85 mg (92%); mp = 272–274 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.76 (s, 1H, NH), 7.37 (d, J = 8.2 Hz, 1H, ArH), 7.01 (d, J = 8.1 Hz, 1H, ArH), 6.96 (s, 1H, ArH), 5.57 (s, 1H, C=CH), 2.44 (s, 2H, CH_2), 2.27 (s, 2H, CH_2), 2.24 (s, 3H, $ArCH_3$), 2.12 (s, 3H, CH_3), 1.03 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.3, 164.6, 150.5, 148.6, 136.7, 134.4, 132.4, 128.1, 126.5, 122.2, 114.7, 95.7, 50.9, 44.1, 30.3, 27.9, 27.9, 20.9, 14.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{22}N_3O$ $[(M+H)^+]$, 308.1757, found, 308.1758.

2-Methoxy-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]d iazepin-13(10*H*)-one (3c)



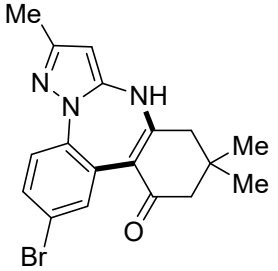
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 4:1, R_f = 0.25; Yellow solid: 91 mg (94%); mp = 285–287 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.81 (s, 1H, NH), 7.40 (d, J = 8.9 Hz, 1H, ArH), 6.83–6.81 (m, 1H, ArH), 6.71 (d, J = 2.6 Hz, 1H, ArH), 5.76 (s, 1H, C=CH), 3.71 (t, J = 3.2 Hz, 3H, $ArOCH_3$), 2.45 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 2.12 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.3, 164.9, 156.8, 150.2, 148.1, 132.4, 127.9, 123.3, 117.3, 114.4, 112.9, 95.5, 55.7, 50.9, 44.2, 30.2, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{22}N_3O_2$ [$(M+H)^+$], 324.1707, found, 324.1705.

2-Fluoro-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3d)



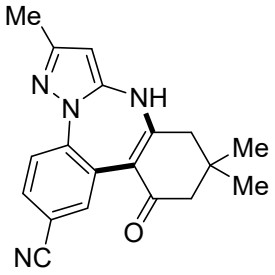
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 78 mg (84%); mp = 275–277 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.98 (s, 1H, NH), 7.51–7.48 (m, 1H, ArH), 7.09–7.06 (m, 1H, ArH), 6.99–6.97 (m, 1H, ArH), 5.61 (s, 1H, C=CH), 2.47 (s, 2H, CH_2), 2.29 (s, 2H, CH_2), 2.13 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.1, 165.4, 159.7 (d, J = 240.9 Hz), 151.0, 148.4, 135.4 (d, J = 2.5 Hz), 128.7 (d, J = 9.0 Hz), 123.9 (d, J = 8.7 Hz), 118.2 (d, J = 24.1 Hz), 114.4 (d, J = 22.6 Hz), 113.4, 96.1, 50.7, 44.2, 30.3, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{18}H_{19}FN_3O$ [$(M+H)^+$], 312.1507, found, 312.1509.

2-Bromo-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3e)



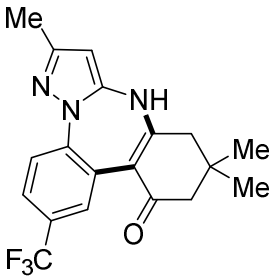
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 100 mg (90%); mp = 323–325 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.04 (s, 1H, NH), 7.43 (t, J = 6.4 Hz, 1H, ArH), 7.39 (d, J = 6.3 Hz, 1H, ArH), 7.33–7.29 (m, 1H, ArH), 5.62 (s, 1H, C=CH), 2.46 (s, 2H, CH_2), 2.29 (s, 2H, CH_2), 2.12 (s, 3H CH_3), 1.02 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.1, 165.5, 151.5, 148.7, 138.3, 134.3, 130.2, 128.5, 124.2, 118.0, 113.1, 96.5, 50.6, 44.1, 30.3, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{18}H_{19}BrN_3O$ [$(M+H)^+$], 372.0706, found, 372.0708.

7,11,11-Trimethyl-13-oxo-10,11,12,13-tetrahydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepine-2-carbonitrile (3f)



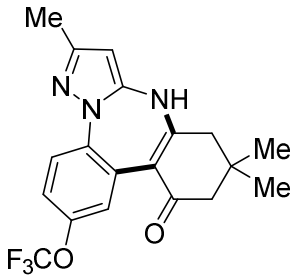
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.25; Yellow solid: 89 mg (94%); mp = 299–301 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.67 (d, J = 8.4 Hz, 1H, ArH), 7.63 (d, J = 8.5 Hz, 1H, ArH), 7.58 (s, 1H, ArH), 5.67 (s, 1H, C=CH), 2.48 (s, 2H, CH_2), 2.31 (s, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.03 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.0, 165.3, 152.7, 149.2, 142.8, 136.4, 131.0, 127.0, 123.1, 119.1, 112.4, 107.9, 97.2, 50.5, 44.1, 30.3, 27.9, 27.9, 14.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{19}N_4O$ [$(M+H)^+$], 319.1553, found, 319.1551.

2-Bromo-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3g)



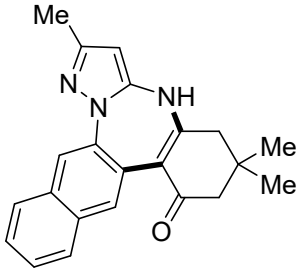
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 94 mg (87%); mp = 267–269 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.12 (s, 1H, NH), 7.70 (d, J = 8.5 Hz, 1H, ArH), 7.55 (d, J = 8.5 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 5.66 (s, 1H, C=CH), 2.48 (s, 2H, CH_2), 2.31 (s, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.03 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.2, 165.4, 152.3, 149.2, 142.2, 129.0 ($J_{C\text{-}F}$ = 3.5 Hz), 126.9, 125.7 ($J_{C\text{-}F}$ = 31.5 Hz), 124.6 ($J_{C\text{-}F}$ = 270.0 Hz), 124.3 ($J_{C\text{-}F}$ = 3.3 Hz), 123.0, 112.9, 96.9, 50.6, 44.1, 30.3, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{19}F_3N_3O$ [$(M+H)^+$], 362.1475, found, 362.1475.

7,11,11-Trimethyl-2-(trifluoromethoxy)-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo [1,5-*a*][1,3]diazepin-13(10*H*)-one (3h)



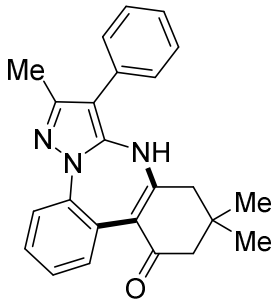
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 99 mg (88%); mp = 240–242 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 9.07 (s, 1H, NH), 7.59 (d, J = 9.0 Hz, 1H, ArH), 7.22 (d, J = 8.7 Hz, 1H, ArH), 7.14 (s, 1H, ArH), 5.64 (s, 1H, C=CH), 2.48 (s, 2H, CH_2), 2.30 (s, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.1, 165.5, 151.6, 148.7, 145.6, 138.0, 128.3, 124.4, 123.8, 120.6 (J = 253.5 Hz), 120.1, 112.9, 96.5, 50.6, 44.2, 30.3, 27.8, 27.8, 14.2; HRMS (TOF ES+): m/z calcd for $C_{19}H_{19}F_3N_3O_2$ [$(M+H)^+$], 378.1424, found, 378.1427.

8,12,12-Trimethyl-12,13-dihydro-10*H*-benzo[*d*]naphtho[2,3-*f*]pyrazolo[1,5-*a*][1,3] diazepin-14(11*H*)-one (3i)



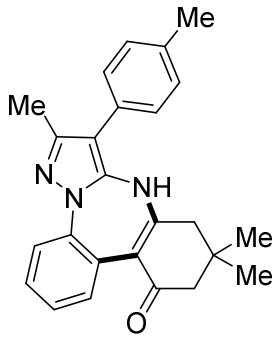
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.25; Yellow solid: 97 mg (95%); mp = 285–287 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 9.07 (s, 1H, NH), 8.01 (s, 1H, ArH), 7.87 (d, J = 7.9 Hz, 1H, ArH), 7.81 (d, J = 7.9 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.45–7.40 (m, 2H, ArH), 5.70 (s, 1H, C=CH), 2.50 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 2.19 (s, 3H, CH_3), 1.08 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 163.1, 151.0, 148.8, 137.6, 132.2, 131.3, 131.2, 128.1, 127.7, 127.0, 126.2, 124.9, 119.5, 114.3, 96.1, 50.9, 44.1, 30.3, 27.9, 27.9, 14.3; HRMS (TOF ES+): m/z calcd for $C_{22}H_{22}N_3O$ [$(M+H)^+$], 344.1757, found, 344.1760.

7,11,11-Trimethyl-8-phenyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3j)



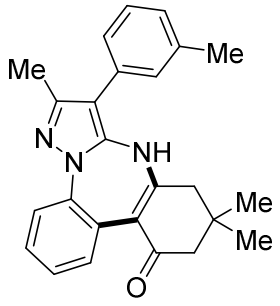
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 90 mg (82%); mp = 242–244 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.74–7.69 (m, 1H, ArH), 7.52–7.46 (m, 2H, ArH), 7.37 (d, *J* = 16.0 Hz, 2H, ArH), 7.30 (d, *J* = 6.8 Hz, 1H, ArH), 7.24 (s, 3H, ArH), 5.44 (s, 1H, NH), 2.40 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.11 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.8, 161.3, 149.2, 143.9, 138.6, 131.8, 131.3, 129.4, 129.4, 129.1, 129.1, 128.1, 127.4, 125.7, 125.5, 122.6, 117.6, 109.6, 50.9, 45.4, 30.6, 27.9, 27.9, 12.9; HRMS (TOF ES+): m/z calcd for $C_{24}H_{24}N_3O$ [$(M+H)^+$], 370.1914, found, 370.1914.

7,11,11-Trimethyl-8-(*p*-tolyl)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3k)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 86 mg (75%); mp = 289–291 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73–7.70 (m, 1H, ArH), 7.38–7.35 (m, 1H, ArH), 7.31–7.27 (m, 3H, ArH), 7.24–7.20 (m, 1H, ArH), 7.14 (d, *J* = 7.8 Hz, 2H, ArH), 5.42 (s, 1H, NH), 2.42 (s, 3H, $ArCH_3$), 2.39 (s, 2H, CH_2), 2.33 (s, 2H, CH_2), 2.26 (s, 3H, CH_3), 1.11 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.7, 161.3, 149.2, 143.8, 138.6, 137.2, 131.7, 130.1, 130.1, 128.9, 128.9, 128.2, 127.9, 125.6, 125.4, 122.5, 117.4, 109.5, 50.9, 45.3, 30.5, 27.9, 27.9, 21.2, 12.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{26}N_3O$ [$(M+H)^+$], 384.2070, found, 384.2071.

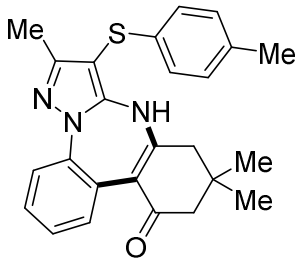
7,11,11-Trimethyl-8-(*m*-tolyl)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3l)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 6:1, R_f = 0.25; White solid: 62 mg (54%); mp = 265–267 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.8 Hz, 1H, ArH), 7.40–7.36 (m, 2H, ArH), 7.31–7.28 (m, 1H, ArH), 7.22 (d, *J* = 7.3 Hz, 1H, ArH), 7.19 (d, *J* = 7.4 Hz, 1H, ArH), 7.08–7.04 (m, 2H, ArH), 5.42 (s, 1H, NH), 2.43 (s, 3H, $ArCH_3$), 2.41 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 2.27 (s, 3H, CH_3), 1.12 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz,

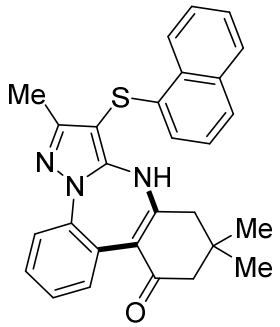
$CDCl_3$) δ = 195.7, 161.2, 149.1, 143.9, 139.1, 138.6, 131.8, 131.2, 129.8, 129.3, 128.1, 128.0, 125.9, 125.6, 125.4, 122.5, 117.5, 109.7, 50.9, 45.4, 30.6, 27.9, 27.9, 21.6, 12.9; HRMS (TOF ES+): m/z calcd for $C_{25}H_{26}N_3O$ [$(M+H)^+$], 384.2070, found, 384.2071.

7,11,11-Trimethyl-8-(*p*-tolylthio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1, 3]diazepin-13(10*H*)-one (3m)



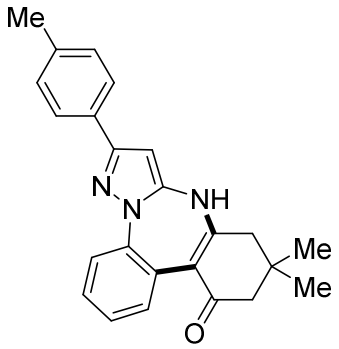
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 95 mg (76%); mp = 165–167 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.9 Hz, 1H, ArH), 7.35 (d, *J* = 7.6 Hz, 1H, ArH), 7.30 (t, *J* = 8.6 Hz, 1H, ArH), 7.27–7.24 (m, 1H, ArH), 7.08 (d, *J* = 7.7 Hz, 2H, ArH), 6.97 (d, *J* = 7.8 Hz, 2H, ArH), 5.68 (s, 1H, NH), 2.34 (s, 2H, CH_2), 2.30 (s, 3H, $ArCH_3$), 2.25 (s, 3H, CH_3), 2.18 (s, 2H, CH_2), 1.05 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.7, 161.3, 154.3, 150.0, 138.4, 135.7, 133.5, 132.0, 130.0, 130.0, 128.2, 126.0, 125.8, 125.8, 125.3, 122.3, 117.4, 94.3, 50.9, 45.2, 30.6, 27.8, 27.8, 20.9, 12.5; HRMS (TOF ES+): m/z calcd for $C_{25}H_{26}N_3OS$ [$(M+H)^+$], 416.1791, found, 416.1798.

7,11,11-Trimethyl-8-(naphthalen-1-ylthio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazol o[1,5-*a*][1,3]diazepin-13(10*H*)-one (3n)



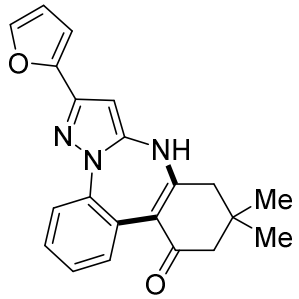
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ =5:1, R_f = 0.25; Yellow solid: 108 mg (80%); mp = 211–213 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.80–7.74 (m, 3H, ArH), 7.67 (d, *J* = 8.0 Hz, 1H, ArH), 7.48–7.39 (m, 3H, ArH), 7.36–7.31 (m, 2H, ArH), 7.26–7.22 (m, 2H, ArH), 5.66 (s, 1H, NH), 2.30 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 2.01 (s, 2H, CH_2), 0.90 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.8, 161.4, 154.4, 150.0, 138.4, 134.7, 133.8, 132.1, 131.6, 129.1, 128.2, 127.8, 127.0, 126.9, 126.2, 125.8, 125.5, 124.1, 123.1, 122.4, 117.5, 93.8, 50.8, 45.1, 30.4, 27.7, 27.7, 12.6; HRMS (TOF ES+): m/z calcd for $C_{28}H_{26}N_3OS$ [$(M+H)^+$], 452.1791, found, 452.1798.

11,11-Dimethyl-7-(*p*-tolyl)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3o)



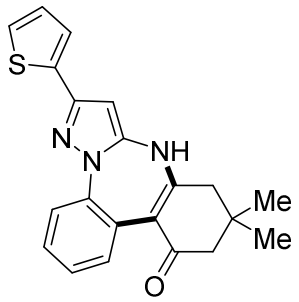
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.25; Yellow solid: 38 mg (35%); mp = 302–304 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.9 Hz, 1H, ArH), 7.69 (d, *J* = 7.8 Hz, 2H, ArH), 7.38 (d, *J* = 7.5 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.22 (d, *J* = 7.9 Hz, 3H, ArH), 5.96 (s, 1H, NH), 5.54 (s, 1H, C=CH), 2.45 (s, 2H, CH_2), 2.40 (s, 2H, CH_2), 2.38 (s, 3H, $ArCH_3$), 1.14 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.7, 161.5, 152.9, 147.8, 138.6, 138.2, 131.7, 129.9, 129.3, 129.3, 127.9, 125.8, 125.7, 125.5, 125.5, 122.9, 117.3, 92.4, 50.9, 45.6, 30.5, 27.9, 27.9, 21.4; HRMS (TOF ES+): m/z calcd for $C_{24}H_{24}N_3O$ $[(M+H)^+]$, 370.1914, found, 370.1912.

7-(Furan-2-yl)-11,11-dimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3p)



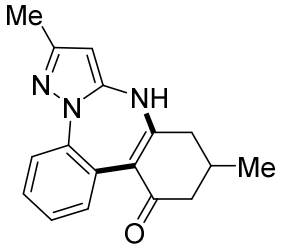
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 47 mg (45%); mp = 276–278 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.97 (s, 1H, NH), 7.75 (s, 1H, C=CH), 7.57 (d, *J* = 8.0 Hz, 1H, C=CH), 7.28–7.25 (m, 1H, ArH), 7.22–7.19 (m, 2H, ArH), 6.84 (d, *J* = 3.0 Hz, 1H, ArH), 6.61–6.59 (m, 1H, C=CH), 6.04 (s, 1H, C=CH), 2.50 (s, 2H, CH_2), 2.30 (s, 2H, CH_2), 1.04 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 164.9, 149.4, 148.1, 145.3, 143.4, 138.7, 132.3, 127.8, 127.1, 126.1, 122.7, 114.9, 112.2, 107.6, 92.9, 50.8, 44.1, 30.4, 27.8, 27.8; HRMS (TOF ES+): m/z calcd for $C_{21}H_{20}N_3O_2$ $[(M+H)^+]$, 346.1550, found, 346.1547.

11,11-Dimethyl-7-(thiophen-2-yl)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3q)



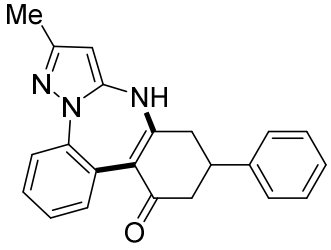
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 52 mg (48%); mp = 284–286 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ =8.97 (s, 1H, NH), 7.54 (m, 2H, C=CH), 7.49–7.47 (m, 1H, ArH), 7.29–7.26 (m, 1H, ArH), 7.21–7.19 (m, 2H, ArH), 7.13–7.10 (m, 1H, C=CH), 6.13 (s, 1H, C=CH), 2.51 (s, 2H, CH_2), 2.31 (s, 2H, CH_2), 1.04 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.4, 164.8, 149.7, 148.5, 138.6, 135.9, 132.3, 128.2, 127.8, 127.0, 126.4, 126.1, 125.7, 122.6, 114.9, 93.2, 50.8, 44.1, 30.4, 27.8, 27.8; HRMS (TOF ES+): m/z calcd for $C_{21}H_{20}N_3OS$ $[(M+H)^+]$, 362.1322, found, 362.1322.

7,11-Dimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3r)



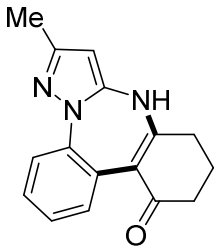
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 48 mg (58%); mp = 294–296 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.86 (s, 1H, NH), 7.48 (d, J = 8.0 Hz, 1H, ArH), 7.21–7.17 (m, 1H, ArH), 7.12 (d, J = 4.2 Hz, 2H, ArH), 5.59 (s, 1H, C=CH), 2.63 (d, J = 15.7 Hz, 1H, CH_2), 2.39 (d, J = 15.2 Hz, 1H, CH_2), 2.28–2.24 (m, 2H, CH_2), 2.13 (s, 3H, CH_3), 2.08–2.05 (m, 1H, CH), 1.01 (d, J = 6.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 165.7, 150.9, 148.8, 139.1, 132.6, 127.5, 126.7, 125.4, 122.2, 115.4, 95.9, 45.6, 38.8, 26.3, 20.4, 14.3; HRMS (TOF ES+): m/z calcd for $C_{17}H_{18}N_3O$ $[(M+H)^+]$, 280.1444, found, 280.1442.

7-Methyl-11-phenyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3s)



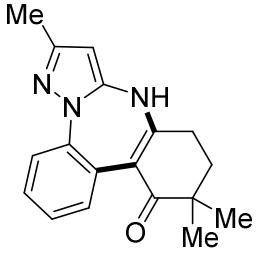
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 82 mg (80%); mp = 216–218 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.97 (s, 1H, NH), 7.51 (d, J = 7.9 Hz, 1H, ArH), 7.38–7.34 (m, 4H, ArH), 7.26 (t, J = 7.0 Hz, 1H, ArH), 7.24–7.20 (m, 1H, ArH), 7.16 (d, J = 6.5 Hz, 2H, ArH), 5.62 (s, 1H, C=CH), 2.82–2.74 (m, 3H, CH_2, CH), 2.56–2.52 (m, 2H, CH_2), 2.14 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 194.9, 165.3, 150.9, 148.7, 143.5, 139.1, 132.7, 129.0, 129.0, 127.6, 127.5, 127.5, 127.2, 126.6, 125.5, 122.3, 115.6, 95.9, 44.4, 38.4, 36.7, 14.3; HRMS (TOF ES+): m/z calcd for $C_{22}H_{20}N_3O$ [$(M+H)^+$], 342.1601, found, 342.1603.

7-Methyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3t)



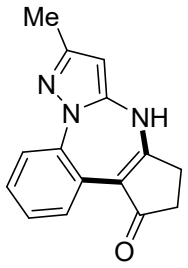
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 29 mg (37%); mp = 284–286 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.90 (s, 1H, NH), 7.48 (d, J = 7.9 Hz, 1H, ArH), 7.22–7.18 (m, 1H, ArH), 7.13–7.10 (m, 2H, ArH), 5.60 (s, 1H, C=CH), 2.56 (t, J = 5.8 Hz, 2H, CH_2), 2.35 (t, J = 6.4 Hz, 2H, CH_2), 2.13 (s, 3H, CH_3), 1.82–1.78 (m, 2H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 166.2, 150.9, 148.8, 139.1, 132.8, 127.5, 126.8, 125.4, 122.2, 115.8, 95.9, 37.6, 30.9, 19.2, 14.2; HRMS (TOF ES+): m/z calcd for $C_{16}H_{16}N_3O$ [$(M+H)^+$], 266.1288, found, 266.1288.

7,12,12-Trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (3u)



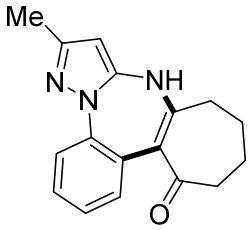
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 33 mg (38%); mp = 243–245 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.82 (s, 1H, NH), 7.48 (d, J = 8.0 Hz, 1H, ArH), 7.19 (t, J = 7.6 Hz, 1H, ArH), 7.11 (t, J = 7.5 Hz, 1H, ArH), 6.99 (d, J = 7.8 Hz, 1H, ArH), 5.59 (s, 1H, C=CH), 2.55 (t, J = 6.0 Hz, 2H, CH_2), 2.12 (s, 3H, CH_3), 1.72 (t, J = 6.0 Hz, 2H, CH_2), 1.06 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 200.9, 164.2, 150.9, 148.9, 139.3, 132.9, 127.5, 127.1, 125.4, 122.2, 114.4, 95.8, 32.7, 27.2, 25.4, 25.4, 25.4, 14.3; HRMS (TOF ES+): m/z calcd for $C_{18}H_{20}N_3O$ [$(M+H)^+$], 294.1601, found, 294.1603.

7-Methyl-10,11-dihydrobenzo[*f*]cyclopenta[*d*]pyrazolo[1,5-*a*][1,3]diazepin-12(9*H*)-one (3v)



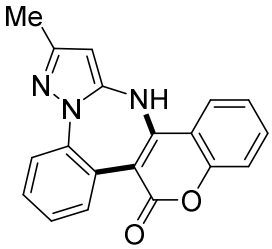
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 2:1, R_f = 0.25; Yellow solid: 47 mg (62%); mp = 259–261 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.03 (s, 1H, NH), 8.18–8.15 (m, 1H, ArH), 7.68–7.65 (m, 1H, ArH), 7.09–7.04 (m, 2H, ArH), 5.59 (s, 1H, C=CH), 3.45 (s, 2H, CH_2), 2.41 (d, J = 5.1 Hz, 2H, CH_2), 2.09 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 201.6, 173.2, 150.9, 145.1, 137.3, 127.3, 126.9, 126.1, 123.9, 122.1, 112.2, 96.5, 34.3, 26.3, 14.1; HRMS (TOF ES+): m/z calcd for $C_{15}H_{14}N_3O$ [$(M+H)^+$], 252.1131, found, 252.1131.

7-Methyl-10,11,12,13-tetrahydrobenzo[*f*]cyclohepta[*d*]pyrazolo[1,5-*a*][1,3]diazepin-14(9*H*)-one (3w)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 21 mg (25%); mp = 221–223 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.79 (s, 1H, NH), 7.41 (d, J = 7.8 Hz, 1H, ArH), 7.17 (t, J = 7.6 Hz, 2H, ArH), 7.14–7.11 (m, 1H, ArH), 5.61 (s, 1H, C=CH), 2.69–2.65 (m, 2H, CH_2), 2.59 (t, J = 6.0 Hz, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.76–1.70 (m, 9.3 Hz, 4H, $2CH_2$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 199.4, 169.5, 150.7, 149.3, 138.9, 132.4, 129.2, 127.1, 125.4, 121.8, 116.8, 95.8, 41.3, 33.5, 22.9, 21.9, 14.3; HRMS (TOF ES+): m/z calcd for $C_{17}H_{18}N_3O$ [$(M+H)^+$], 280.1444, found, 280.1441.

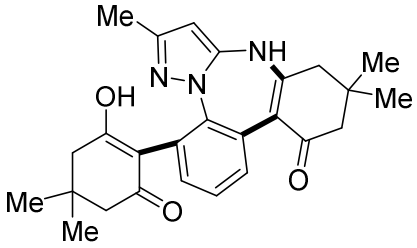
7-Methylbenzo[*f*]chromeno[4,3-*d*]pyrazolo[1,5-a][1,3]diazepin-15(9*H*)-one (3x)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 19 mg (20%); mp = 291–293 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.13 (s, 1H, NH), 8.31 (d, J = 7.5 Hz, 1H,

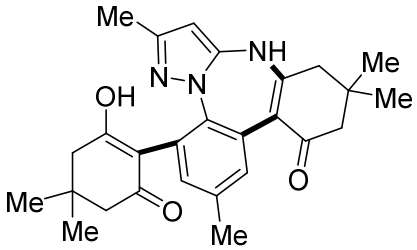
ArH), 7.71 (t, J = 7.7 Hz, 1H, ArH), 7.61 (d, J = 8.1 Hz, 1H, ArH), 7.55 (d, J = 7.9 Hz, 1H, ArH), 7.47–7.44 (m, 2H, ArH), 7.37 (d, J = 7.3 Hz, 1H, ArH), 7.28 (t, J = 7.6 Hz, 1H, ArH), 5.83 (s, 1H, C=CH), 2.18 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 161.1, 155.6, 152.4, 151.5, 148.7, 139.1, 133.4, 132.3, 129.2, 125.9, 125.8, 124.8, 123.5, 122.5, 117.3, 115.9, 107.1, 97.6, 14.4; HRMS (TOF ES+): m/z calcd for $C_{19}H_{14}N_3O_2$ [$(M+H)^+$], 316.1081, found, 316.1081.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4a)



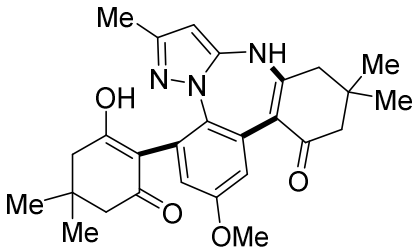
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 155 mg (90%); mp = 318–320 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.44 (s, 1H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.03 (d, J = 7.6 Hz, 1H, ArH), 6.90 (br, 1H, OH), 5.42 (s, 1H, C=CH), 2.47 (s, 2H, CH_2), 2.42 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 2.16 (s, 2H, CH_2), 1.99 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$), 1.00 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 195.5, 167.2, 149.3, 149.3, 148.3, 138.1, 132.1, 130.2, 130.2, 129.7, 124.8, 115.8, 105.5, 95.2, 50.8, 50.8, 43.9, 43.9, 31.7, 30.3, 29.2, 29.2, 28.4, 25.1, 14.5; HRMS (TOF ES+): m/z calcd for $C_{26}H_{30}N_3O_3$ [$(M+H)^+$], 432.2282, found, 432.2273.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2,7,11,11-tetramethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4b)



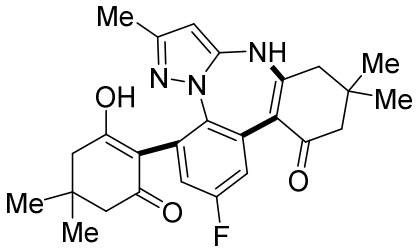
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 167 mg (94%); mp > 330 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.97 (br, 1H, NH), 8.39 (s, 1H, ArH), 6.84 (s, 1H, ArH), 6.67 (br, 1H, OH), 5.40 (s, 1H, C=CH), 2.50–2.24 (m, 6H, $3CH_2$), 2.21 (s, 3H, $ArCH_3$), 2.15 (s, 2H, CH_2), 1.98 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$), 1.00 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 195.5, 166.9, 149.0, 149.0, 147.9, 135.8, 133.5, 132.6, 130.6, 129.8, 129.4, 115.9, 106.8, 94.9, 50.9, 50.9, 43.9, 43.9, 31.7, 30.3, 29.3, 28.4, 28.4, 25.5, 20.9, 14.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{32}N_3O_3$ [$(M+H)^+$], 446.2438, found, 446.2446.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-methoxy-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4c)



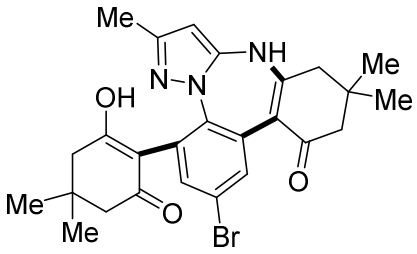
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 167 mg (91%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.22 (br, 1H, NH), 8.43 (s, 1H, ArH), 6.60 (s, 1H, ArH), 6.45 (br, 1H, OH), 5.40 (s, 1H, C=CH), 3.67 (s, 3H, $ArOCH_3$), 2.47–2.34 (m,4H, $2CH_2$), 2.16 (s, 4H, $2CH_2$), 1.98 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$), 1.01 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.4, 195.4, 167.2, 155.9, 155.9, 147.7, 147.7, 131.7, 131.1, 130.7, 117.3, 116.2, 115.4, 107.6, 94.9, 55.6, 50.8, 50.8, 43.9, 43.9, 31.7, 30.28, 29.1, 28.8, 28.8, 28.3, 14.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{32}N_3O_4$ [$(M+H)^+$], 462.2387, found, 462.2395.

2-Fluoro-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4d)



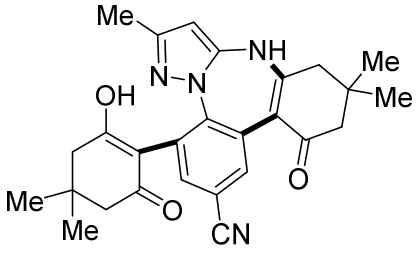
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 149 mg (83%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.29 (br, 1H, NH), 8.60 (s, 1H, ArH), 6.86 (d, J = 12.5 Hz, 1H, ArH), 6.72 (br, 1H, OH), 5.43 (s, 1H, C=CH), 2.47 (s, 2H, CH_2), 2.36 (s, 2H, CH_2), 2.18 (s, 2H, CH_2), 2.12–1.89 (m, 5H, CH_2+CH_3), 1.08 (s, 3H, CH_3), 1.00 (s, 9H, $3CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.3, 195.3, 168.0, 159.02 (d, J = 240.4 Hz), 148.6, 148.6, 148.6, 134.6, 133.4, 132.0 (d, J = 9.2 Hz), 118.3 (d, J = 22.0 Hz), 116.1, 115.9, 107.0, 95.36, 50.7, 50.7, 43.9, 43.9, 31.7, 30.3, 29.2, 29.2, 28.3, 28.3, 14.5; HRMS (TOF ES+): m/z calcd for $C_{26}H_{29}FN_3O_3$ [$(M+H)^+$], 450.2187, found, 450.2187.

2-Bromo-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-Trimethyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4e)



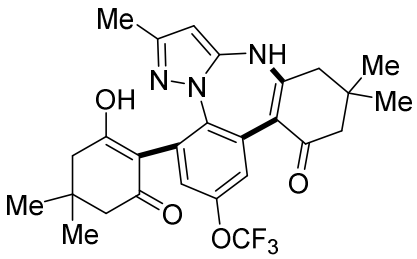
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 177 mg (87%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.34 (br, 1H, NH), 8.65 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.05 (br, 1H, OH), 5.45 (s, 1H, C=CH), 2.46 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 2.18 (s, 2H, CH_2), 2.09–1.88 (m, 5H, CH_2, CH_3), 1.07 (s, 3H, CH_3), 1.02 (s, 6H, $2CH_3$), 1.00 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.3, 195.3, 168.2, 149.0, 149.0, 149.0, 137.5, 134.1, 132.1, 132.1, 131.9, 123.7, 117.6, 114.3, 95.6, 50.6, 50.6, 43.9, 43.9, 31.7, 30.3, 29.1, 28.3, 28.3, 25.5, 14.5; HRMS (TOF ES+): m/z calcd for $C_{26}H_{29}BrN_3O_3$ [$(M+H)^+$], 510.1387, found, 510.1388.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-13-oxo-10,11,12,13-tetrahydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepine-2-carbonitrile (4f)



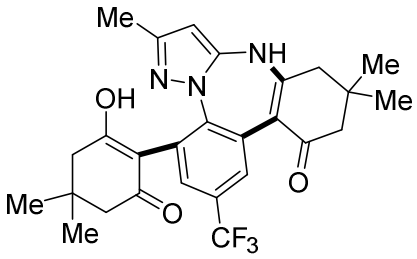
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 150 mg (82%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.34 (br, 1H, NH), 8.65 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.05 (br, 1H, OH), 5.45 (s, 1H, C=CH), 2.5 (d, J = 15.2 Hz, 4H, $2CH_2$), 2.3 (s, 4H, $2CH_2$), 2.0 (s, 3H, CH_3), 1.1 (s, 3H, CH_3), 1.0 (s, 6H, $2CH_3$), 1.0 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.2, 195.2, 168.4, 150.1, 149.7, 142.2, 137.6, 135.3, 133.7, 131.2, 131.1, 128.2, 119.1, 113.9, 107.8, 96.2, 50.5, 50.5, 43.9, 43.9, 31.7, 30.3, 29.2, 29.2, 28.2, 28.2, 14.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{29}N_4O_3$ [$(M+H)^+$], 457.2234, found, 457.2244.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-2-(trifluoromethoxy)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4g)



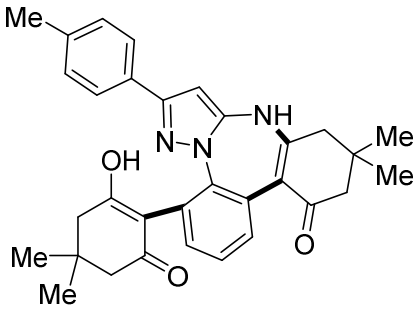
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 167 mg (81%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.50 (br, 1H, NH), 8.69 (s, 1H, ArH), 7.02 (d, J = 2.9 Hz, 1H, ArH), 6.88 (br, 1H, OH), 5.46 (s, 1H, C=CH), 2.48 (s, 2H, CH_2), 2.37 (s, 2H, CH_2), 2.24 (s, 2H, CH_2), 2.10 (s, 2H, CH_2), 2.00 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.00 (s, 9H, 3CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.2, 195.2, 168.3, 155.9, 149.2, 149.2, 145.1, 137.2, 131.9, 131.7, 124.0, 122.0, 120.6 (d, J = 256.1 Hz), 106.8, 114.2, 95.7, 50.6, 50.6, 43.9, 43.9, 31.7, 30.3, 28.9, 28.9, 28.6, 28.6, 14.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{29}F_3N_3O_4$ [$(M+H)^+$], 516.2105, found, 516.2111.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-2-(trifluoromethyl)-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4h)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 180 mg (90%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.45 (br, 1H, NH), 8.72 (s, 1H, ArH), 7.35 (s, 1H, ArH), 7.20 (br, 1H, OH), 5.48 (s, 1H, C=CH), 2.49 (s, 2H, CH_2), 2.31 (s, 4H, 2CH_2), 2.11 (s, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.03 (s, 6H, 2CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.3, 195.3, 168.4, 149.7, 149.6, 141.4, 130.9, 130.9, 129.4, 128.4 (J = 3.1 Hz), 126.6 (J = 3.1 Hz), 125.3 (J = 31.5 Hz), 124.7 (J = 270.0 Hz), 114.39, 105.9, 96.0, 50.6, 50.6, 43.9, 43.9, 31.7, 30.3, 29.1, 29.1, 28.4, 28.4, 14.5; HRMS (TOF ES+): m/z calcd for $C_{27}H_{29}F_3N_3O_3$ [$(M+H)^+$], 500.2156, found, 500.2156.

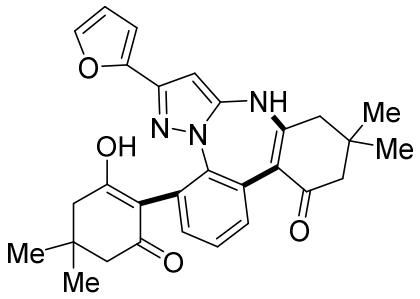
4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-11,11-dimethyl-7-(*p*-tolyl)-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4i)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 162 mg (80%); mp = 327–329 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.63 (s, 1H, ArH), 7.57 (d, J = 7.0 Hz, 2H, ArH), 7.20 (d, J = 7.5 Hz, 2H, ArH), 7.15 (t, J = 7.6 Hz, 1H, ArH), 7.09 (d, J = 7.6 Hz, 1H, ArH), 6.96 (br, 1H, OH), 6.00 (s, 1H, C=CH), 2.54 (s, 2H, CH_2), 2.38 (s, 2H, CH_2), 2.31 (s, 3H, ArCH_3), 2.18 (s, 2H, CH_2), 1.69 (s, 2H, CH_2), 1.04 (s, 6H, 2CH_3),

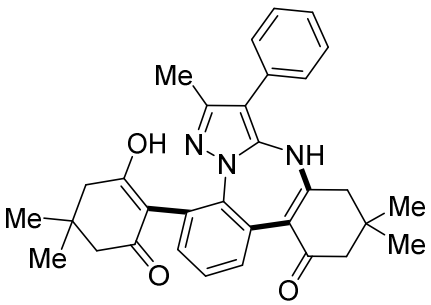
0.94 (s, 3H, CH_3), 0.78 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.6, 195.6, 166.9, 150.5, 150.2, 150.2, 138.0, 137.5, 132.1, 130.8, 130.3, 130.1, 129.8, 129.5, 129.5, 125.3, 125.3, 125.1, 125.1, 115.9, 92.1, 50.8, 50.8, 43.9, 43.9, 31.5, 30.4, 27.2, 27.2, 27.2, 25.5, 21.3; HRMS (TOF ES+): m/z calcd for $C_{32}H_{34}N_3O_3$ [$(M+H)^+$], 508.2595, found, 508.2597.

7-(Furan-2-yl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-11,11-dimethyl-11,12-dihydro-9*H*-dibenzo[d,f]pyrazolo[1,5-a][1,3]diazepin-13(10*H*)-one (4j)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 131 mg (68%); mp = 334–336 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.64 (s, 1H, C=CH), 7.69 (s, 1H, C=CH), 7.16 (d, J = 7.7 Hz, 1H, ArH), 7.07 (d, J = 8.8 Hz, 1H, ArH), 6.97 (br, 1H, OH), 6.60 (d, J = 2.8 Hz, 1H, ArH), 6.55–6.54 (m, 1H, C=CH), 5.86 (s, 1H, C=CH), 2.41 (t, J = 20.1 Hz, 4H, $2CH_2$), 2.17 (d, J = 16.6 Hz, 2H, CH_2), 1.85 (d, J = 68.0 Hz, 2H, CH_2), 1.04 (s, 6H, $2CH_3$), 0.97 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.6, 195.6, 166.9, 150.1, 148.8, 143.5, 142.9, 137.8, 132.2, 130.2, 130.1, 130.1, 129.9, 125.4, 116.1, 111.9, 106.4, 106.4, 92.3, 50.8, 50.8, 43.9, 43.9, 31.5, 30.4, 29.9, 27.5, 27.5, 25.5; HRMS (TOF ES+): m/z calcd for $C_{29}H_{30}N_3O_4$ [$(M+H)^+$], 484.2231, found, 484.2237.

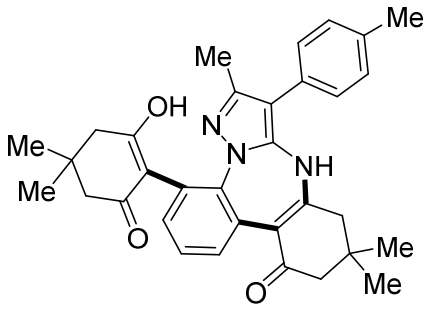
4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-8-phenyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4k)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 180 mg (89%); mp = 312–314 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.93 (s, 1H, ArH), 7.46 (d, J = 7.5 Hz, 2H, ArH), 7.32–7.28 (m, 3H, ArH), 7.13 (d, J = 7.6 Hz, 1H, ArH), 7.08 (d, J = 7.1 Hz, 1H, ArH), 6.96 (br, 1H, OH), 2.59 (d, J = 14.7 Hz, 2H, CH_2), 2.47 (s, 4H, $2CH_2$), 2.16 (d, J = 16.3 Hz, 2H, CH_2), 2.02 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.00 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.9, 195.9, 167.6, 146.6, 146.6, 144.4, 137.8, 132.3, 132.1, 130.7, 130.3, 129.8, 129.7, 129.7,

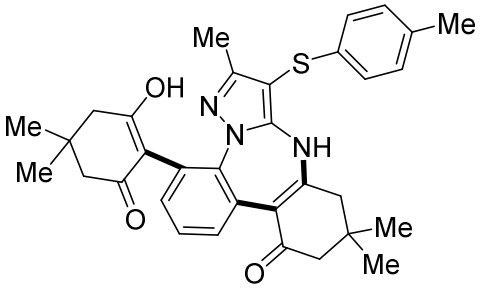
129.1, 129.1, 126.7, 124.9, 116.6, 115.5, 108.9, 50.9, 50.9, 43.5, 43.5, 31.7, 30.4, 29.0, 28.7, 25.5, 19.8, 13.9; HRMS (TOF ES+): m/z calcd for $C_{32}H_{34}N_3O_3$ [$(M+H)^+$], 508.2595, found, 508.2598.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-8-(*p*-tolyl) -11,12-dihydro-9H-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(*10H*)-one (4l)



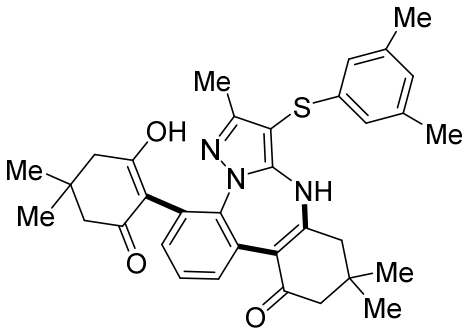
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 179 mg (86%); mp > 330 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.87 (d, J = 50.8 Hz, 1H, ArH), 7.30–7.24 (m, 2H, ArH), 7.21–7.11 (m, 3H, ArH), 7.08 (d, J = 7.8 Hz, 1H, ArH), 6.93 (br, 1H, OH), 2.57 (s, 2H, CH_2), 2.50 (s, 2H, CH_2), 2.46–2.29 (m, 5H, CH_3+CH_2), 2.22–2.11 (m, 2H, CH_2), 2.01 (s, 3H, $ArCH_3$), 1.11 (s, 3H, CH_3), 1.09–0.97 (m, 9H, $3CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.9, 195.9, 167.6, 146.8, 146.6, 144.5, 137.9, 135.9, 131.9, 130.7, 130.1, 129.9, 129.7, 129.7, 129.7, 129.2, 125.1, 124.8, 116.3, 115.3, 108.9, 50.9, 50.4, 43.5, 43.5, 30.4, 30.4, 29.2, 28.9, 28.4, 25.5, 21.2, 13.8; HRMS (TOF ES+): m/z calcd for $C_{33}H_{36}N_3O_3$ [$(M+H)^+$], 522.2715, found, 522.2759.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-8-(*p*-tolylt hio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4m)



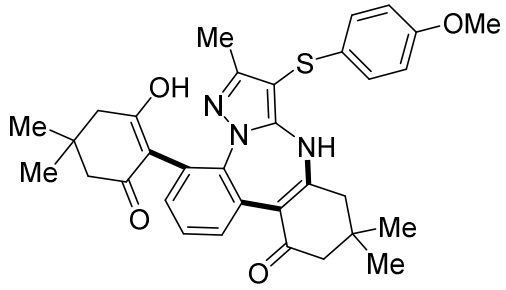
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 190 mg (86%); mp = 277–279 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.09 (s, 1H, ArH), 7.18 (t, J = 7.8 Hz, 1H, ArH), 7.12–7.08 (m, 3H, ArH), 6.96–6.88 (m, 2H, ArH), 2.56 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 2.25 (s, 3H, $ArCH_3$), 2.15 (d, J = 15.6 Hz, 2H, CH_2), 1.95 (s, 5H, CH_3, CH_2), 1.08 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.95 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 195.7, 167.5, 152.1, 152.1, 152.1, 137.7, 135.3, 135.3, 134.8, 132.3, 130.2, 130.2, 130.1, 129.8, 125.5, 125.5, 125.5, 116.9, 105.6, 93.4, 50.8, 50.8, 43.6, 43.6, 31.8, 30.1, 25.5, 25.5, 25.5, 25.5, 20.9, 12.9; HRMS (TOF ES+): m/z calcd for $C_{33}H_{36}N_3O_3S$ [$(M+H)^+$], 554.2472, found, 554.2476.

8-((3,5-Dimethylphenyl)thio)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4n)



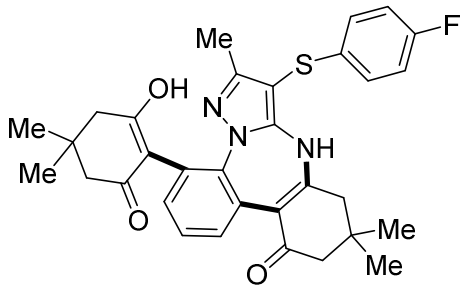
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 186 mg (82%); mp = 316–318 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.41 (br, 1H, NH), 8.08 (d, J = 16.2 Hz, 1H, ArH), 7.18 (t, J = 7.7 Hz, 1H, ArH), 7.08 (d, J = 6.6 Hz, 1H, ArH), 6.75 (s, 1H, ArH), 6.63 (d, J = 56.3 Hz, 2H), 2.64 (d, J = 18.2 Hz, 2H, CH_2), 2.38 (s, 2H, CH_2), 2.21 (s, 6H, $2CH_3$), 2.13 (d, J = 32.8 Hz, 2H, CH_2), 2.02–1.89 (m, 5H, CH_2+CH_3), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.96 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.6, 193.9, 169.4, 167.5, 152.6, 152.1, 138.6, 137.7, 132.3, 130.2, 130.1, 130.1, 129.6, 127.0, 125.5, 122.8, 122.8, 116.9, 115.8, 106.9, 92.9, 50.8, 50.4, 43.7, 43.6, 31.7, 30.2, 29.2, 28.4, 25.5, 25.5, 21.3, 21.3, 12.9; HRMS (TOF ES+): m/z calcd for $C_{34}H_{38}N_3O_3S$ [$(M+H)^+$], 568.2628, found, 568.2629.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-8-((4-methoxyphenyl)thio)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d*,*f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4o)



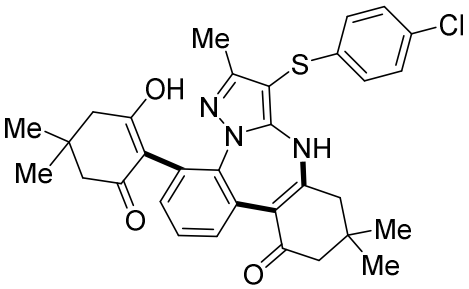
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 177 mg (78%); mp = 289–291 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.40 (br, 1H, NH), 8.10 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.08 (d, J = 6.6 Hz, 1H, ArH), 7.00 (s, 2H, ArH), 6.88 (s, 2H, CH_2), 3.71 (s, 3H, $ArOCH_3$), 2.57 (s, 2H, CH_2), 2.32 (d, J = 68.4 Hz, 2H, CH_2), 2.14 (d, J = 16.0 Hz, 2H, CH_2), 1.97 (d, J = 25.0 Hz, 5H, CH_2,+CH_3), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.95 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.6, 193.9, 167.5, 157.9, 152.3, 151.9, 142.9, 137.7, 132.3, 130.1, 130.1, 129.7, 129.1, 127.4, 125.5, 125.5, 116.8, 115.2, 115.2, 107.9, 94.3, 55.7, 50.8, 50.8, 43.6, 43.6, 31.7, 30.1, 29.2, 28.3, 25.5, 25.5, 12.9; HRMS (TOF ES+): m/z calcd for $C_{33}H_{36}N_3O_4S$ [$(M+H)^+$], 570.2421, found, 570.2428.

8-((4-Fluorophenyl)thio)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4p)



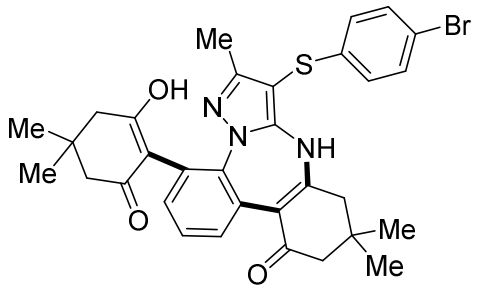
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 167 mg (75%); mp = 310–312 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.14 (d, J = 28.0 Hz, 1H, ArH), 7.20–7.13 (m, 2H, ArH), 7.10–6.99 (m, 4H, ArH), 2.46 (s, 2H, CH_2), 2.31 (s, 2H, CH_2), 2.13 (s, 2H, CH_2), 2.00–1.81 (m, 5H, CH_2+CH_3), 1.03 (s, 6H, $2CH_3$), 0.96 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 194.0, 169.5, 167.3, 160.8 (d, J = 243.5 Hz), 152.9, 151.9, 137.8, 134.4, 132.3 (d, J = 4.5 Hz), 132.3 (d, J = 4.5 Hz), 130.1, 129.7, 127.3 (d, J = 7.5 Hz), 127.3 (d, J = 7.5 Hz), 125.6, 116.4 (d, J = 21 Hz), 116.4 (d, J = 21 Hz), 115.7, 106.9, 93.1, 50.7, 50.7, 43.7, 43.7, 31.7, 30.2, 29.2, 28.1, 25.5, 25.5, 12.7; HRMS (TOF ES+): m/z calcd for $C_{32}H_{33}FN_3O_3S$ [$(M+H)^+$], 558.2221, found, 558.2230.

8-((4-Chlorophenyl)thio)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4q)



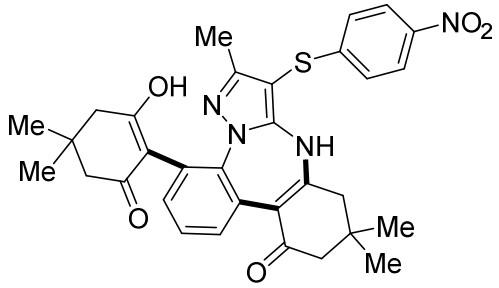
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 165 mg (72%); mp = 302–304 ^oC; ^1H NMR (600 MHz, DMSO-d_6): δ = 8.16 (s, 1H, ArH), 7.36 (d, J = 6.6 Hz, 2H, ArH), 7.19 (t, J = 7.7 Hz, 1H, ArH), 7.14–6.95 (m, 3H, ArH), 2.57 (s, 2H, CH_2), 2.30 (s, 2H, CH_2), 2.17 (s, 2H, CH_2), 2.06 (s, 2H, CH_2), 1.95 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.96 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 195.7, 167.3, 152.0, 152.0, 152.0, 138.3, 137.7, 132.3, 130.2, 130.1, 130.0, 129.8, 129.4, 127.0, 127.0, 127.0, 125.6, 117.1, 105.5, 92.4, 50.8, 50.8, 43.7, 43.7, 31.8, 30.2, 25.5, 25.5, 25.5, 25.5, 12.8; HRMS (TOF ES+): m/z calcd for $C_{32}H_{33}ClN_3O_3S$ [$(M+H)^+$], 574.1926, found, 574.1924.

8-((4-Bromophenyl)thio)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4r)



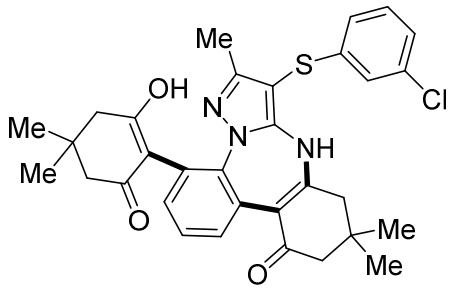
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 197 mg (80%); mp = 311–313 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.17 (s, 1H, ArH), 7.55–7.42 (m, 2H, ArH), 7.18 (t, J = 7.1 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 7.03–7.00 (m, 1H, ArH), 6.92 (s, 1H, ArH), 2.57 (s, 2H, CH_2), 2.36 (d, J = 67.1 Hz, 2H, CH_2), 2.15 (d, J = 15.9 Hz, 2H, CH_2), 2.07–1.87 (m, 5H, CH_2+CH_3), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.96 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 194.1, 167.3, 152.9, 152.1, 152.1, 138.8, 137.8, 132.5, 132.2, 132.1, 130.1, 129.7, 127.4, 127.4, 125.7, 118.2, 117.0, 115.7, 105.2, 92.3, 50.7, 50.7, 43.7, 43.7, 31.7, 30.2, 29.3, 28.1, 25.5, 25.5, 12.8; HRMS (TOF ES+): m/z calcd for $C_{32}H_{33}BrN_3O_3S$ [$(M+H)^+$], 618.1421, found, 618.1430.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-8-((4-nitrophenyl)thio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4s)



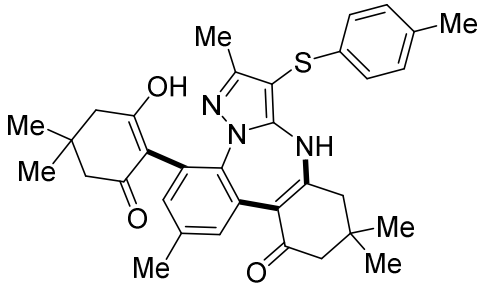
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 180 mg (77%); mp = 321–322 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.52 (br, 1H, NH), 8.28 (s, 1H, ArH), 8.12 (s, 1H, ArH), 7.35 (d, J = 8.5 Hz, 1H, ArH), 7.21 (t, J = 7.7 Hz, 2H, ArH), 7.16–7.05 (m, 2H, ArH), 2.59 (s, 2H, CH_2), 2.42 (d, J = 30.0 Hz, 2H, CH_2), 2.29–2.06 (m, 4H, 2CH_2), 1.96 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 0.97 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.8, 194.3, 169.8, 167.2, 153.7, 151.9, 149.7, 145.2, 137.8, 132.4, 130.2, 130.2, 129.7, 125.8, 125.6, 125.6, 124.9, 124.3, 117.3, 115.7, 90.8, 50.7, 50.7, 43.8, 43.8, 31.7, 30.2, 29.4, 28.0, 25.5, 25.5, 12.8; HRMS (TOF ES+): m/z calcd for $C_{32}H_{33}N_4O_5S$ [$(M+H)^+$], 585.2166, found, 585.2172.

8-((3-Chlorophenyl)thio)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4t)



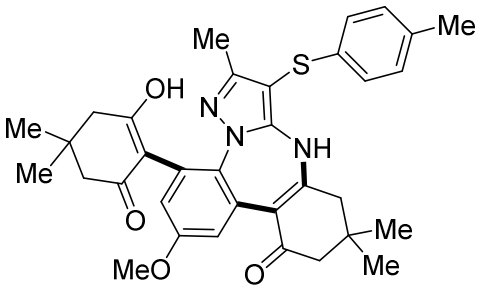
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 153 mg (67%); mp = 290–292 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.23 (s, 1H, ArH), 7.37–7.28 (m, 1H, ArH), 7.19 (t, J = 7.6 Hz, 2H, ArH), 7.10 (d, J = 7.5 Hz, 2H, ArH), 7.03 (s, 1H, ArH), 2.61 (d, J = 17.7 Hz, 2H, CH_2), 2.41–2.32 (m, 2H, CH_2), 2.17 (d, J = 16.1 Hz, 2H, CH_2), 2.07–1.95 (m, 5H, CH_2+CH_3), 1.08 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.96 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 193.9, 167.3, 152.9, 152.2, 141.8, 137.7, 134.5, 132.3, 131.0, 130.2, 130.1, 129.7, 125.7, 125.4, 124.2, 124.0, 117.0, 115.6, 104.9, 91.8, 50.8, 50.8, 43.8, 43.8, 31.7, 30.2, 29.1, 28.4, 25.5, 25.5, 12.8; HRMS (TOF ES+): m/z calcd for $C_{32}H_{33}ClN_3O_3S$ [$(M+H)^+$], 574.1926, found, 574.1933.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2,7,11,11-tetramethyl-8-(*p*-tolylthio)-11,12-dihydro-9H-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4u)



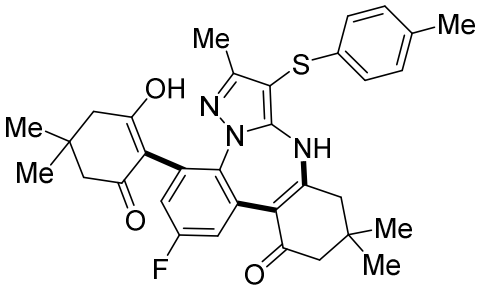
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 188 mg (83%); mp = 319–321 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.05 (s, 1H, ArH), 7.09 (d, J = 7.8 Hz, 2H, ArH), 6.91 (d, J = 29.2 Hz, 3H, ArH), 2.58 (d, J = 18.5 Hz, 2H, CH_2), 2.43 (d, J = 29.7 Hz, 2H, CH_2), 2.25 (d, J = 3.6 Hz, 6H, 2ArCH_3), 2.13 (d, J = 15.8 Hz, 2H, CH_2), 2.04–1.87 (m, 5H, CH_3+CH_2), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.95 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 194.0, 167.3, 152.2, 151.8, 151.8, 135.5, 135.3, 135.3, 134.6, 134.4, 132.8, 130.5, 130.1, 129.9, 129.5, 125.5, 125.5, 116.9, 105.5, 93.1, 50.8, 50.8, 43.6, 43.6, 31.7, 30.2, 28.3, 25.5, 25.5, 25.5, 20.9, 20.8, 12.8; HRMS (TOF ES+): m/z calcd for $C_{34}H_{38}N_3O_3S$ [$(M+H)^+$], 568.2628, found, 568.2630.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-methoxy-7,11,11-trimethyl-8-(*p*-tolylthio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4v)



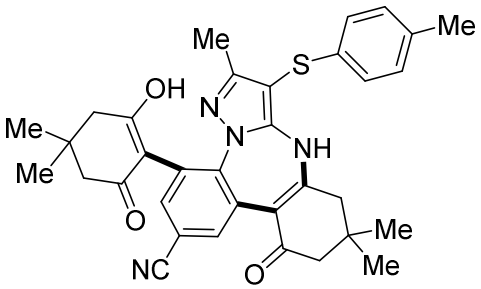
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 189 mg (81%); mp = 294–296 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.44 (br, 1H, NH), 8.09 (s, 1H, ArH), 7.10 (s, 2H, ArH), 6.98–6.87 (m, 2H, ArH), 6.64 (s, 1H, ArH), 3.71 (s, 3H, OMe), 2.57 (s, 2H, CH_2), 2.39 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.14 (d, J = 15.9 Hz, 2H, CH_2), 2.01–1.87 (m, 5H, CH_2+CH_3), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.95 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.6, 193.8, 167.6, 156.4, 156.4, 151.7, 151.7, 135.4, 135.4, 135.4, 134.7, 131.2, 130.1, 125.4, 125.4, 125.4, 117.5, 116.7, 115.2, 105.3, 93.0, 55.7, 50.8, 50.8, 43.7, 43.7, 31.7, 30.1, 29.0, 28.5, 25.5, 25.5, 20.9, 12.8; HRMS (TOF ES+): m/z calcd for $C_{34}H_{38}N_3O_4S$ [(M+H)$^+$], 584.2578, found, 584.2584.

2-Fluoro-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-8-(*p*-tolylthio)-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4w)



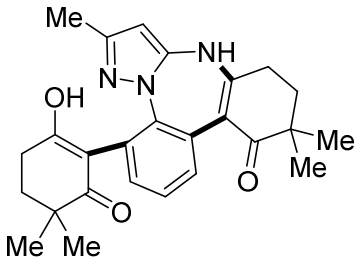
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 182 mg (80%); mp = 285–287 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.68 (br, 1H, NH), 8.27 (s, 1H, ArH), 7.16–7.08 (m, 2H, ArH), 6.91 (d, J = 11.7 Hz, 3H, ArH), 2.59 (s, 2H, CH_2), 2.38 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.15 (d, J = 15.8 Hz, 2H, CH_2), 1.97 (d, J = 44.5 Hz, 5H, CH_2, CH_3), 1.07 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.94 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.5, 193.5, 159.4 (d, J = 241.2 Hz), 158.6, 152.4, 152.4, 152.1, 135.2, 135.2, 134.8, 134.2, 132.2, 131.9, 130.1 (d, J = 7.5 Hz), 125.5, 125.5, 118.6 (d, J = 22.0 Hz), 116.15 (d, J = 23.4 Hz), 115.8, 105.6, 93.6, 50.6, 50.6, 43.7, 43.7, 31.7, 30.1, 28.4, 28.4, 28.3, 28.3, 20.9, 12.8; HRMS (TOF ES+): m/z calcd for $C_{33}H_{35}FN_3O_3S$ [(M+H)$^+$], 572.2378, found, 572.2385.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-7,11,11-trimethyl-13-oxo-8-(*p*-tolylthio)-10,11,12,13-tetrahydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepine-2-carbonitrile (4x)



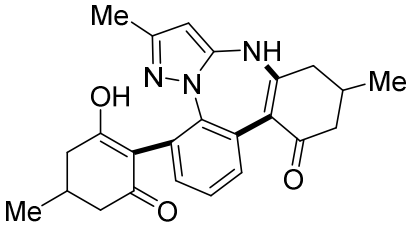
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:1, R_f = 0.25; White solid: 203 mg (88%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.43 (s, 1H, ArH), 7.52 (s, 1H, ArH), 7.12 (d, J = 7.9 Hz, 2H, ArH), 6.94 (s, 2H, ArH), 2.60 (s, 2H, CH_2), 2.32 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 2.03–1.95 (m, 5H, CH_2+CH_3), 1.07 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.95 (s, 6H, 2CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.4, 195.4, 168.8, 153.5, 148.7, 141.6, 135.5, 134.8, 133.7, 131.3, 131.3, 130.2, 130.2, 130.2, 130.2, 125.6, 125.6, 118.9, 115.2, 108.6, 106.2, 94.7, 50.5, 50.5, 43.7, 43.7, 31.8, 30.1, 29.2, 28.2, 25.6, 25.6, 20.9, 12.9; HRMS (TOF ES+): m/z calcd for $C_{34}H_{35}N_4O_3S$ [$(M+H)^+$], 579.2424, found, 579.2430.

4-(2-Hydroxy-5,5-dimethyl-6-oxocyclohex-1-en-1-yl)-7,12,12-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4y)



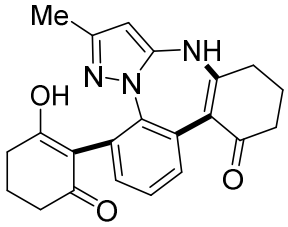
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 124 mg (72%); mp > 330 ºC; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.09 (br, 1H, NH), 8.41 (s, 1H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 6.87 (d, J = 7.7 Hz, 2H, ArH), 5.39 (s, 1H, C=CH), 2.54 (s, 2H, CH_2), 2.00 (s, 3H, CH_3), 1.72 (s, 4H, 2CH_2), 1.1–0.87 (m, 12H, 4CH_3), 0.77 (s, 2H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 201.1, 201.1, 166.4, 149.1, 149.1, 148.2, 138.3, 132.1, 130.8, 130.3, 130.2, 124.8, 115.5, 107.9, 94.7, 34.4, 32.8, 27.1, 27.1, 26.6, 26.6, 25.3, 25.3, 23.9, 23.9, 14.7; HRMS (TOF ES+): m/z calcd for $C_{26}H_{30}N_3O_3$ [$(M+H)^+$], 432.2282, found, 432.2289.

4-(2-Hydroxy-4-methyl-6-oxocyclohex-1-en-1-yl)-7,11-dimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4z)



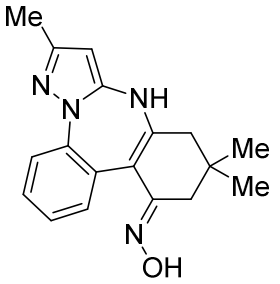
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; Yellow solid: White mg (81%); mp = 317–319 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.12 (br, 1H, NH), 8.50 (s, 1H, ArH), 7.07 (t, J = 7.5 Hz, 1H, ArH), 6.99 (d, J = 6.0 Hz, 1H, ArH), 6.85 (br, 1H, OH), 5.40 (s, 1H, C=CH), 2.63 (d, J = 17.2 Hz, 2H, CH_2), 2.42–2.28 (m, 2H, CH_2), 2.17 (s, 2H, CH_2), 2.10 (s, 2H, CH_2), 2.01 (s, 3H, CH_3), 2.00–1.70 (m, 2H, 2CH), 1.01 (d, J = 5.7 Hz, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 195.7, 168.2, 151.4, 149.8, 148.1, 138.2, 131.9, 130.6, 129.8, 129.5, 124.7, 116.7, 105.6, 94.9, 45.8, 45.8, 38.9, 38.9, 27.9, 26.5, 21.7, 21.1, 14.5; HRMS (TOF ES+): m/z calcd for $C_{24}H_{26}N_3O_3$ [$(M+H)^+$], 404.1969, found, 404.1972.

4-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)-7-methyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (4aa)



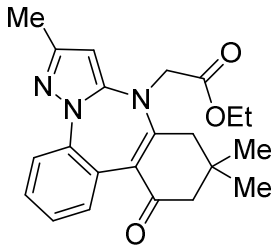
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:2, R_f = 0.25; White solid: 123 mg (82%); mp = 325–327 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.15 (br, 1H, NH), 8.54 (s, 1H, ArH), 7.06 (t, J = 7.5 Hz, 1H, ArH), 6.98 (d, J = 7.3 Hz, 1H, ArH), 6.88 (br, 1H, OH), 5.40 (s, 1H, C=CH), 2.64–2.54 (m, 2H, CH_2), 2.33 (s, 4H, $2CH_2$), 2.02 (s, 3H, CH_3), 1.95–1.65 (m, 6H, $3CH_2$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.7, 195.7, 168.3, 158.7, 149.7, 148.1, 138.2, 131.9, 130.7, 129.8, 129.6, 124.6, 116.9, 104.4, 94.8, 37.6, 37.6, 30.8, 30.8, 20.7, 19.3, 14.4; HRMS (TOF ES+): m/z calcd for $C_{22}H_{22}N_3O_3$ [$(M+H)^+$], 376.1656, found, 376.1660.

(*E*)-7,11,11-trimethyl-11,12-dihydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one oxime (5)



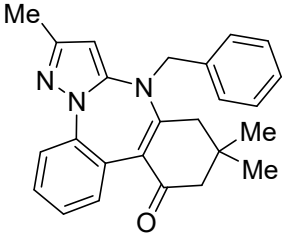
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 3:1, R_f = 0.25; Yellow solid: 71 mg (92%); mp = 275–178 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.56 (s, 1H, NH), 7.71 (s, 1H, ArH), 7.44 (d, J = 7.9 Hz, 1H, ArH), 7.32 (d, J = 7.7 Hz, 1H, ArH), 7.18 (t, J = 7.3 Hz, 1H, ArH), 7.09 (t, J = 7.2 Hz, 1H, ArH), 5.47 (s, 1H, C=CH), 2.38 (s, 2H, CH_2), 2.18 (s, 2H, CH_2), 2.12 (s, 3H, CH_3), 0.99 (s, 6H, $2CH_3$); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 154.8, 152.3, 150.8, 150.7, 139.7, 132.8, 128.8, 127.1, 124.7, 122.4, 112.3, 94.2, 43.4, 36.4, 36.4, 29.3, 29.3, 14.4; HRMS (TOF ES+): m/z calcd for $C_{18}H_{21}N_4O$ [$(M+H)^+$], 309.1710, found, 309.1706.

Ethyl 2-(7,11,11-trimethyl-13-oxo-10,11,12,13-tetrahydro-9*H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-9-yl)acetate (6)



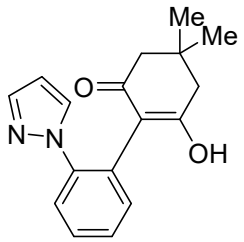
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 79 mg (83%); mp = 213–316 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.50 (d, J = 8.0 Hz, 1H, ArH), 7.31 (t, J = 7.4 Hz, 1H, ArH), 7.22 (t, J = 7.4 Hz, 1H, ArH), 7.16 (d, J = 7.7 Hz, 1H, ArH), 5.81 (s, 1H, C=CH), 4.55 (d, J = 17.9 Hz, 1H, OCH_2), 4.40 (d, J = 17.8 Hz, 1H, OCH_2), 4.10–4.03 (m, 2H, CH_2), 2.64 (d, J = 18.1 Hz, 1H, CH_2), 2.45 (d, J = 18.0 Hz, 1H, CH_2), 2.32 (d, J = 33.3 Hz, 2H, CH_2), 2.16 (s, 3H, CH_3), 1.10 (t, J = 7.0 Hz, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 196.5, 169.3, 166.8, 151.7, 150.6, 138.6, 132.1, 128.1, 126.9, 125.2, 122.0, 120.0, 96.8, 61.3, 51.3, 50.9, 41.1, 31.3, 29.4, 26.6, 14.4, 14.4; HRMS (TOF ES+): m/z calcd for $C_{22}H_{26}N_3O_3$ [$(M+H)^+$], 380.1969, found, 380.1967.

9-Benzyl-7,11,11-trimethyl-11,12-dihydro-*9H*-dibenzo[*d,f*]pyrazolo[1,5-*a*][1,3]diazepin-13(10*H*)-one (7)



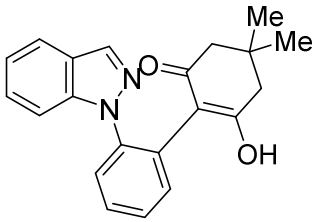
$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.25; Yellow solid: 67 mg (70%); mp = 248–250 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.52 (d, J = 7.9 Hz, 1H, ArH), 7.36 (d, J = 7.1 Hz, 1H, ArH), 7.27 (d, J = 7.2 Hz, 1H, ArH), 7.23 (d, J = 7.5 Hz, 3H, ArH), 7.18 (s, 1H, ArH), 7.13 (d, J = 7.2 Hz, 2H, ArH), 5.91 (s, 1H, C=CH), 4.92 (s, 1H, $ArCH_2$), 4.62 (d, J = 15.4 Hz, 1H, $ArCH_2$), 2.65 (d, J = 18.0 Hz, 1H, CH_2), 2.52 (s, 1H, CH_2), 2.29 (d, J = 25.1 Hz, 2H, CH_2), 2.15 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 0.71 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 196.5, 167.5, 152.3, 150.6, 138.7, 137.9, 131.9, 128.9, 128.9, 128.4, 127.7, 127.3, 127.3, 126.7, 125.3, 121.9, 121.7, 96.9, 52.7, 51.0, 40.9, 31.5, 29.1, 26.3, 14.5; HRMS (TOF ES+): m/z calcd for $C_{25}H_{26}N_3O$ [$(M+H)^+$], 384.2070, found, 384.2066.

6-Hydroxy-4,4-dimethyl-2'-(1*H*-pyrazol-1-yl)-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one (9a)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:3, R_f = 0.25; White solid: 128 mg (91%); mp = 185–187 ^oC; ^1H NMR (500 MHz, DMSO-d_6): δ = 10.52 (br, 1H, OH), 7.52 (d, J = 2.2 Hz, 1H, N-CH), 7.47 (d, J = 1.4 Hz, 1H, N=CH), 7.35–7.33 (m, 1H, ArH), 7.31–7.28 (m, 1H, ArH), 7.27–7.23 (m, 1H, ArH), 7.03–7.02 (m, 1H, ArH), 6.24 (s, 1H, C=CH), 2.21 (s, 2H, CH_2), 2.09 (s, 2H, CH_2), 0.94 (s, 3H, CH_3), 0.85 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 196.0, 171.5, 140.6, 140.1, 133.5, 130.4, 129.7, 128.1, 127.5, 125.4, 113.6, 106.4, 50.0, 43.7, 31.9, 28.9, 28.1; HRMS (TOF ES+): m/z calcd for $C_{17}H_{19}N_2O_2$ [$(M+H)^+$], 283.1441, found, 283.1448.

6-Hydroxy-2'-(1*H*-indazol-1-yl)-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one (9b)



$V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 1:5, R_f = 0.25; White solid: 141 mg (85%); mp = 224–226 ^oC; ^1H NMR (500 MHz, DMSO-d_6): δ = 10.38 (br, 1H, OH), 8.08 (s, 1H, N=CH), 7.69 (d, J = 8.0 Hz, 1H, ArH), 7.37 (d, J = 5.9 Hz, 3H, ArH), 7.24–7.17 (m, 3H, ArH), 7.06 (t, J = 7.1 Hz, 1H, ArH), 2.09 (s, 2H, CH_2), 1.77 (s, 2H, CH_2), 0.85 (s, 3H, CH_3), 0.51 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 195.4, 171.1, 139.8, 139.2, 134.3, 133.9, 131.9, 127.9, 127.7, 126.9, 126.5, 124.1, 121.1, 121.1, 113.4, 110.9, 50.5, 43.1, 31.5, 29.1, 27.4; HRMS (TOF ES+): m/z calcd for $C_{21}H_{21}N_2O_2$ [$(M+H)^+$], 333.1598, found, 333.1599.

5. X-ray Structure and Data[3] of 3j (CCDC 2292416) and 4r (CCDC 2292417).

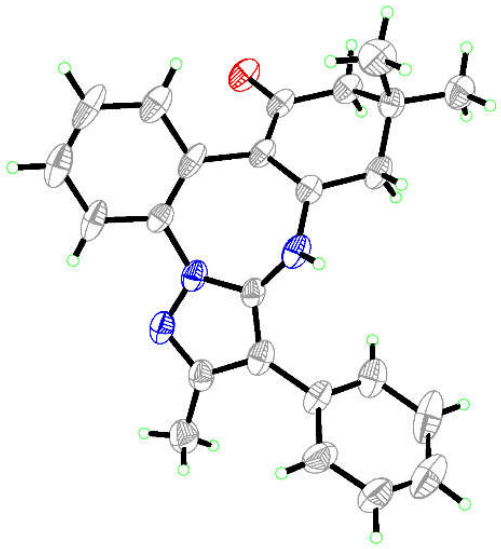


Figure S2 X-Ray crystal structure of 3j.

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

Empirical formula	$C_{24}H_{23}N_3O$
Formula weight	369.45
Temperature	296.15 K
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 6.459(3) A alpha = 90 deg.
	b = 26.872(12) A beta = 98.252(9) deg.
	c = 13.342(5) A gamma = 90 deg.
Volume	2291.7(17) A^3
Z, Calculated density	4, 1.071 Mg/m^3
Absorption coefficient	0.067 mm^-1
F(000)	784.0
Theta range for data collection	6.356 to 49.994 deg.
Limiting indices	-7<=h<=7, -31<=k<=31, -15<=l<=14
Reflections collected / unique	11541 / 4024 [R(int) = 0.0922]
Data/restraints/parameters	4024 / 0 / 256
Goodness-of-fit on F^2	0.917
Final R indices [I>2sigma(I)]	R1 = 0.0755, wR2 = 0.1935
R indices (all data)	R1 = 0.1607, wR2 = 0.2423
Largest diff. peak and hole	0.25 and -0.213 e.A^-3

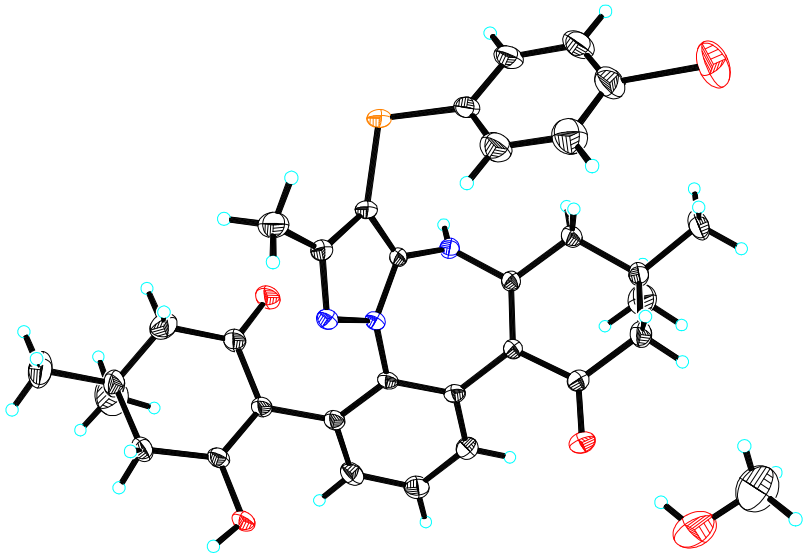


Figure S3 X-Ray crystal structure of 4r.

Table S3 Crystal data and structure refinement for **4r.**

Empirical formula	$C_{33}H_{36}BrN_3O_4S$
Formula weight	650.62
Temperature	296.15 K
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 9.915(3) A alpha = 113.225(5) deg. b = 13.033(4) A beta = 97.316(5) deg. c = 14.176(4) A gamma = 101.109(6) deg.
Volume	1609.4(8) A^3
Z, Calculated density	2, 1.343 Mg/m^3
Absorption coefficient	1.382 mm^-1
F(000)	676.0
Theta range for data collection	5.442 to 55.206 deg.
Limiting indices	-11<=h<=12, -15<=k<=16, -18<=l<=17
Reflections collected / unique	9823 / 7049 [R(int) = 0.0209]
Data/restraints/parameters	7049 / 0 / 387
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0604, wR2 = 0.1434
R indices (all data)	R1 = 0.1135, wR2 = 0.1691
Largest diff. peak and hole	0.78 and -0.84 e.A^-3

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

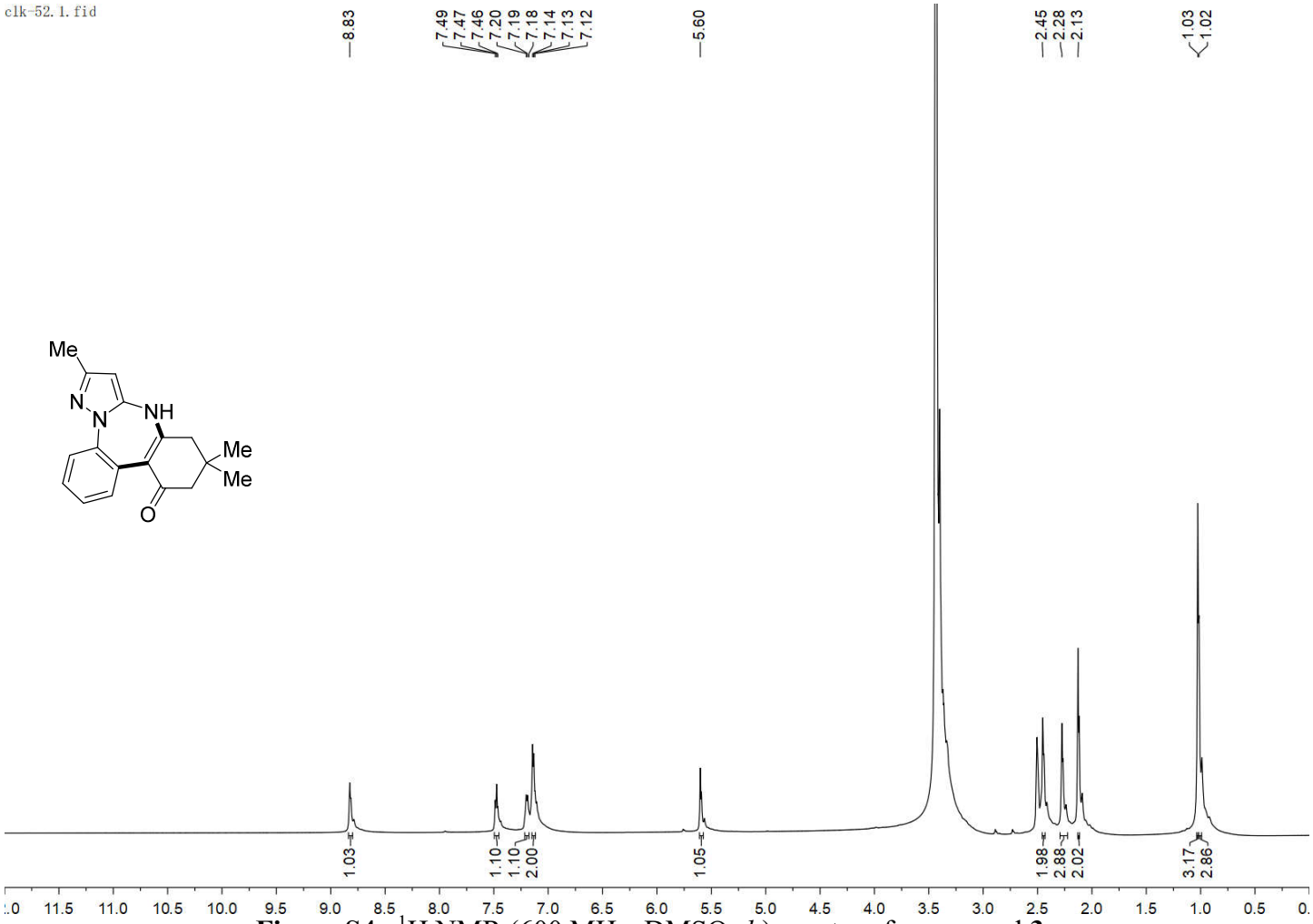


Figure S4. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3a**

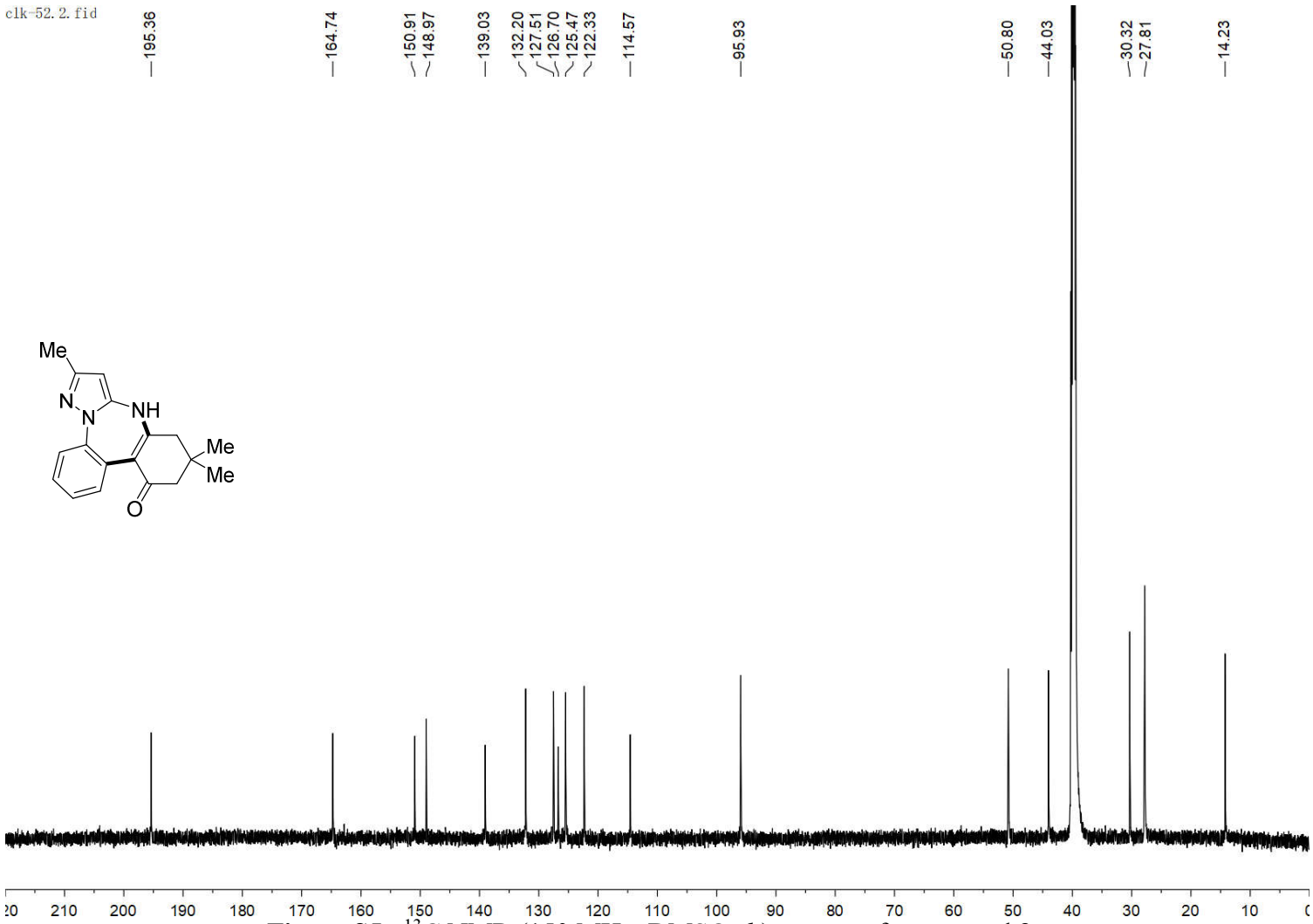


Figure S5. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3a**

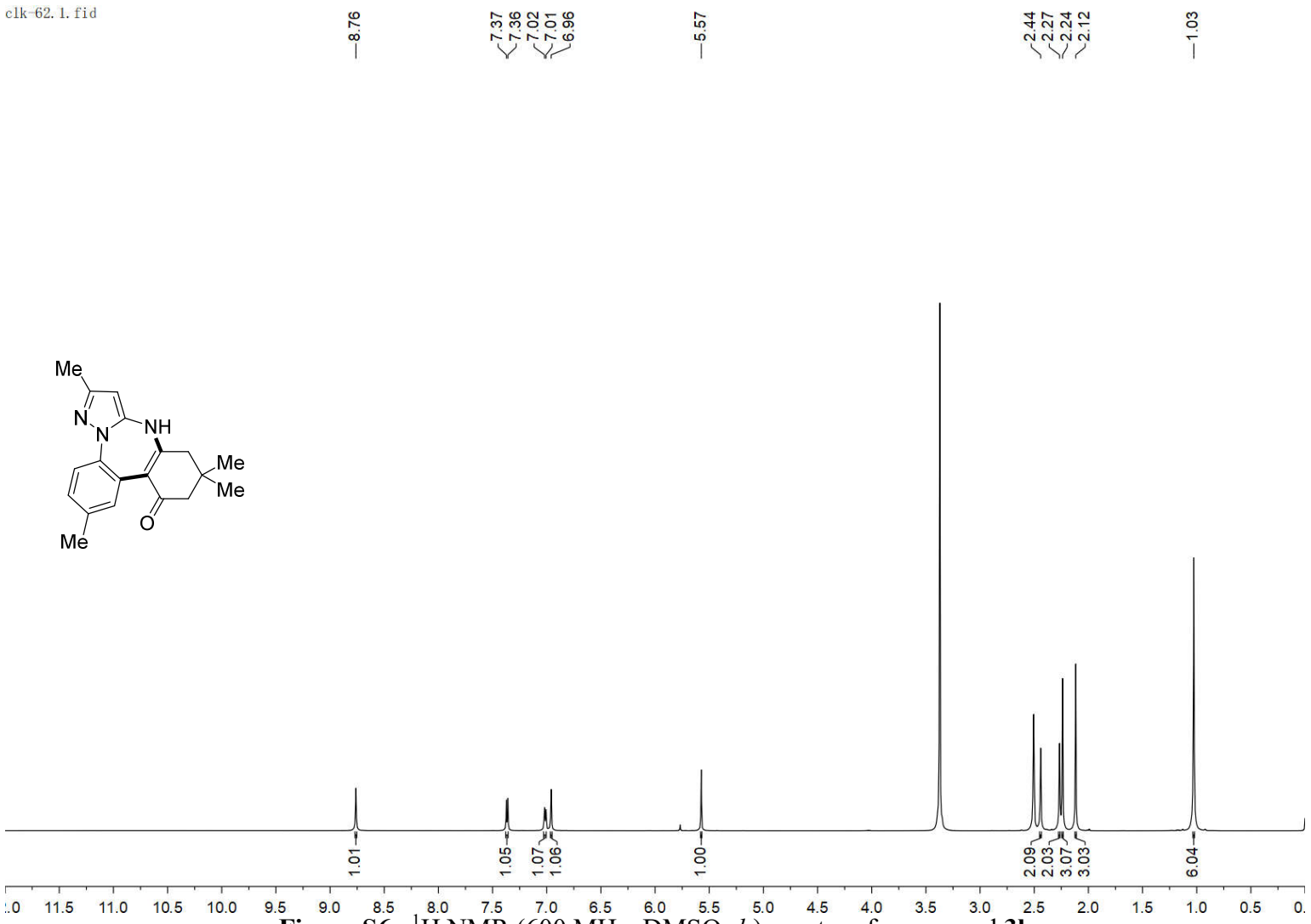


Figure S6. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3b**

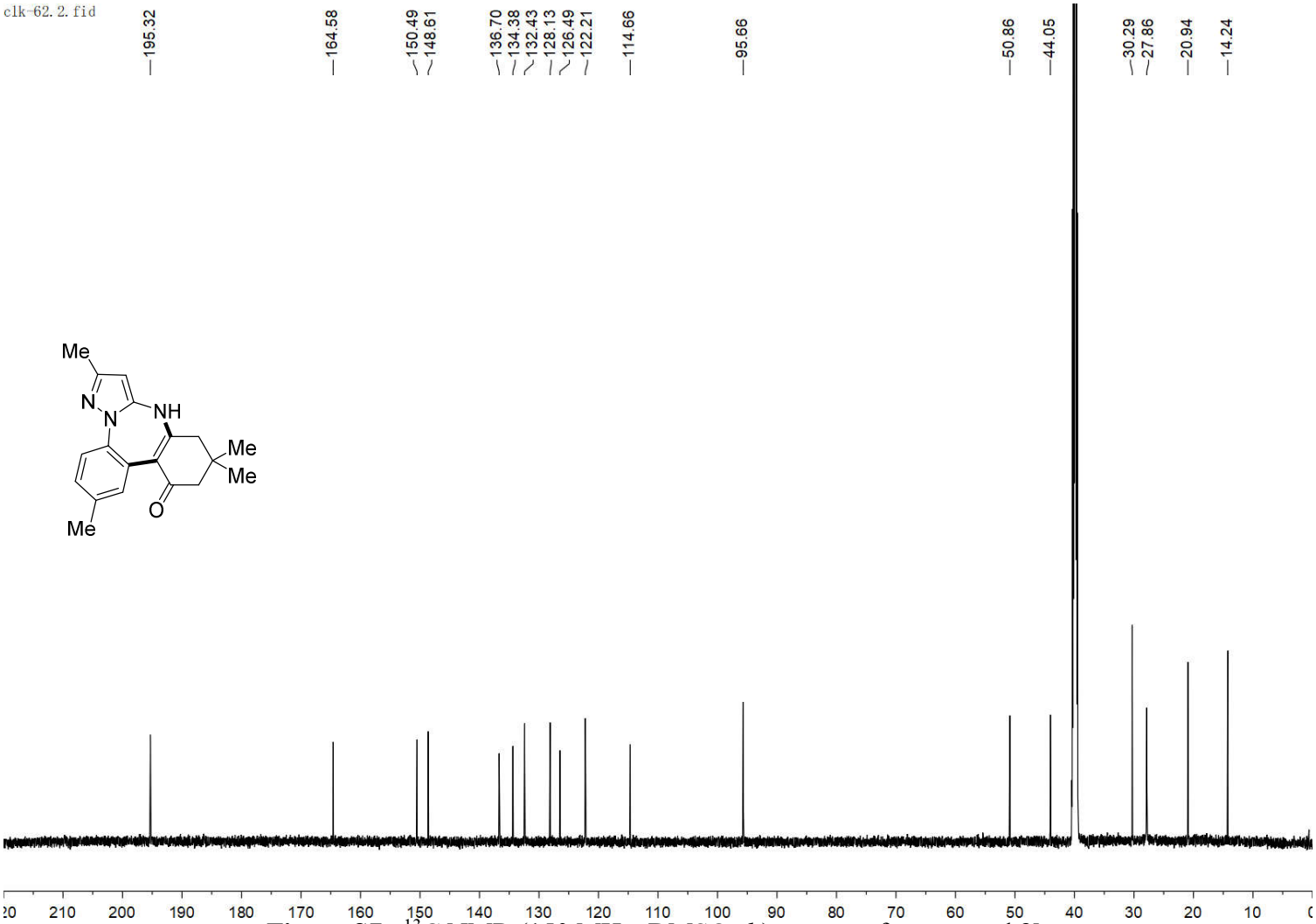


Figure S7. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3b**

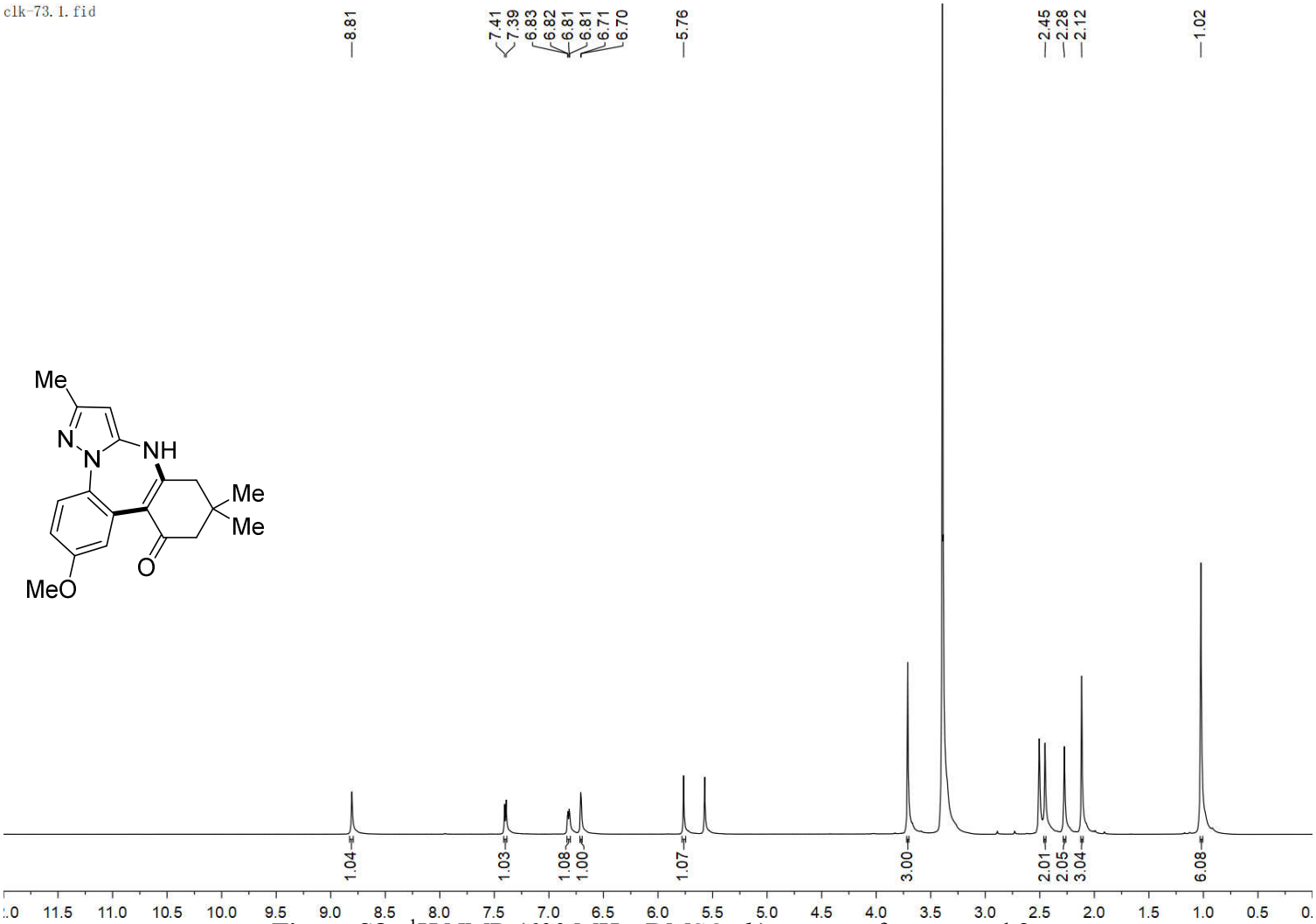


Figure S8. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3c**

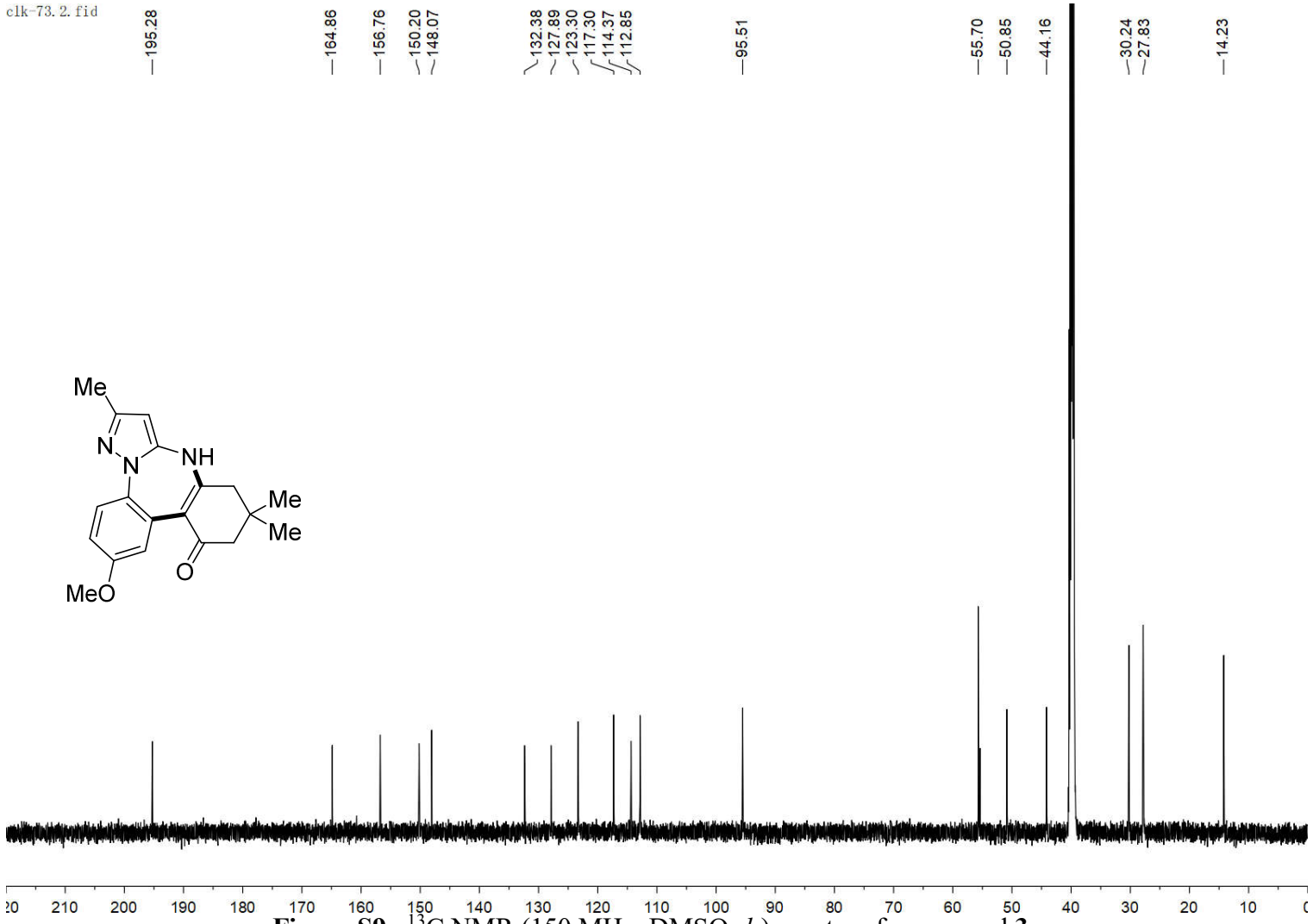


Figure S9. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3c**

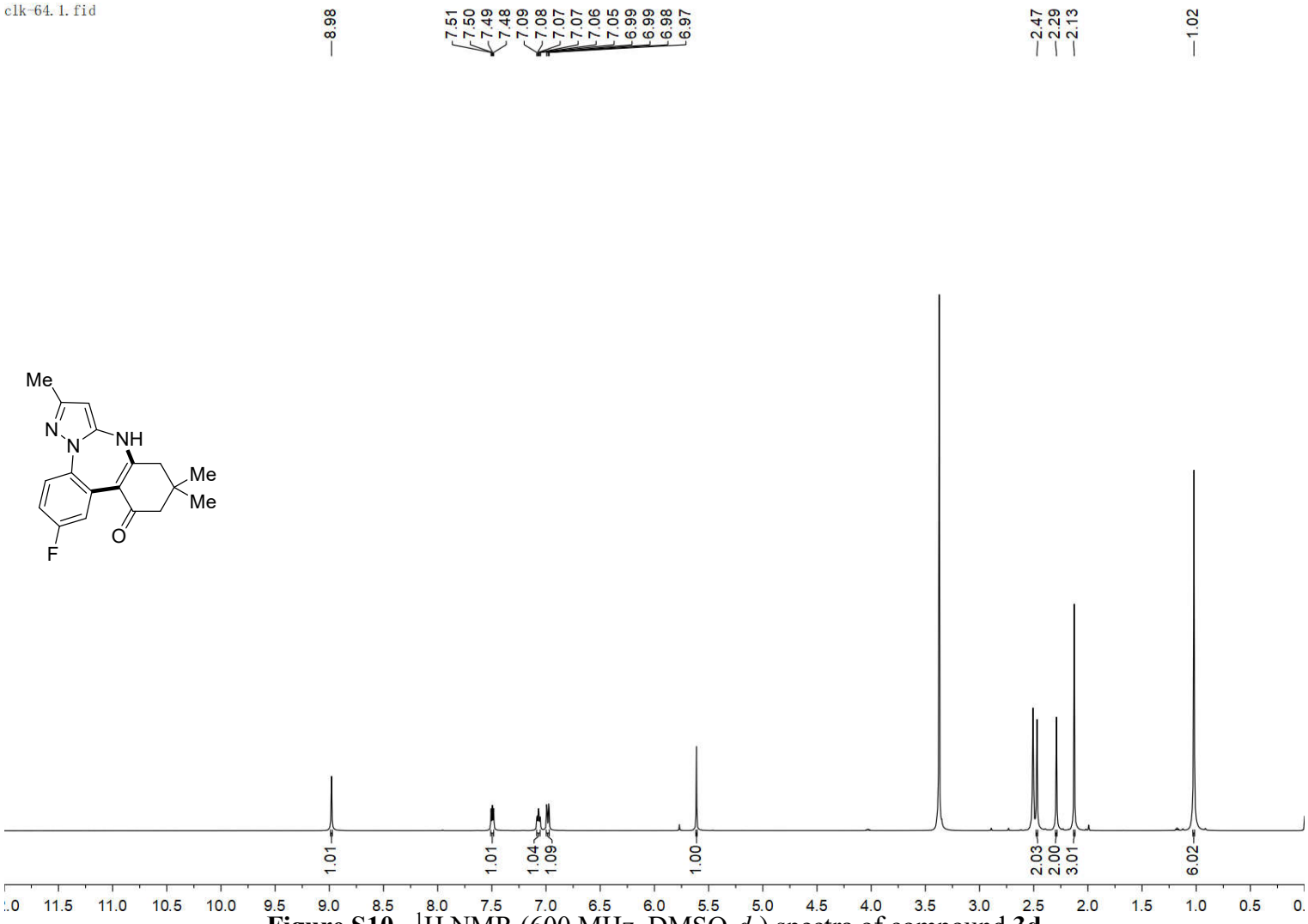


Figure S10. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3d**

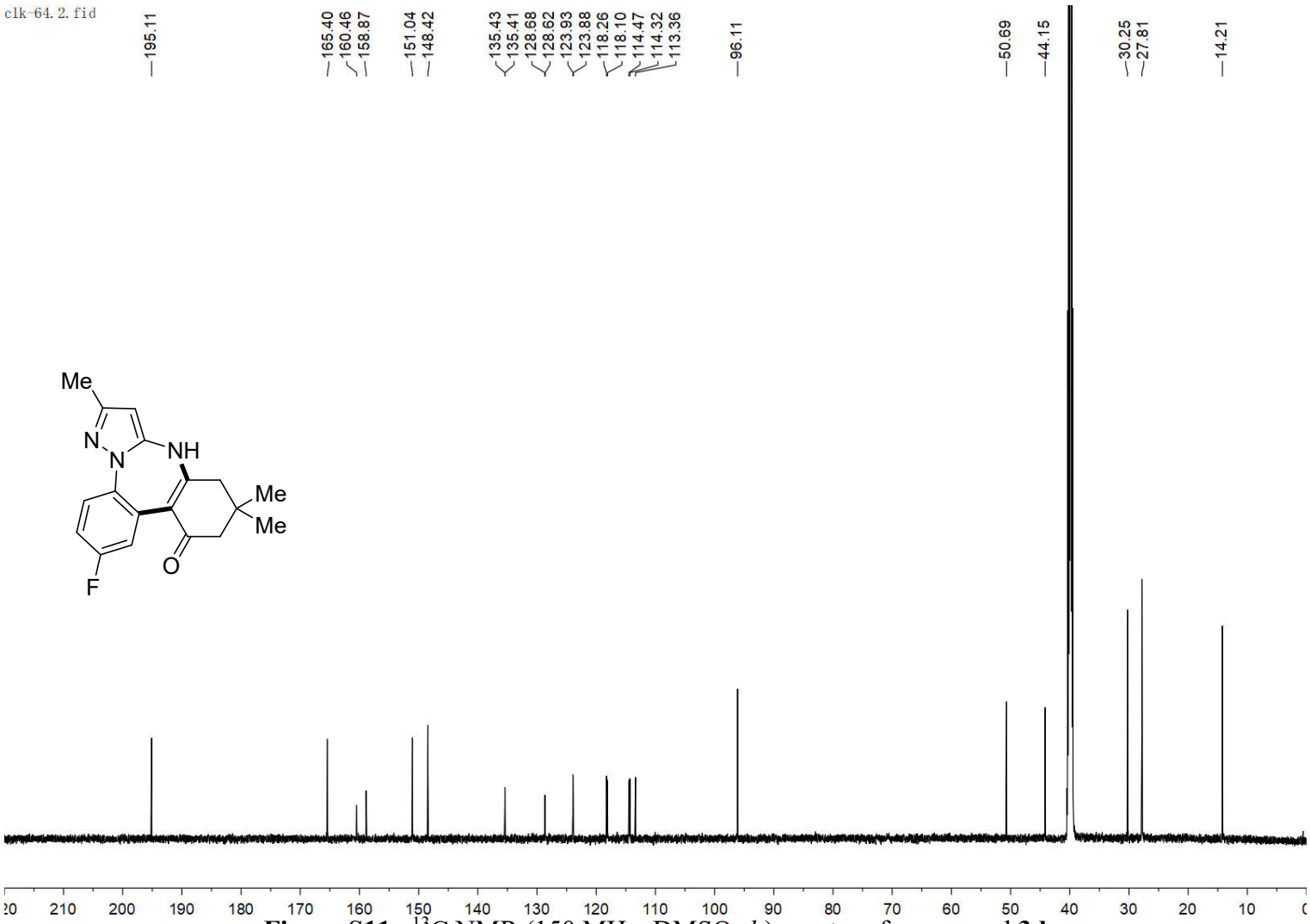


Figure S11. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3d**

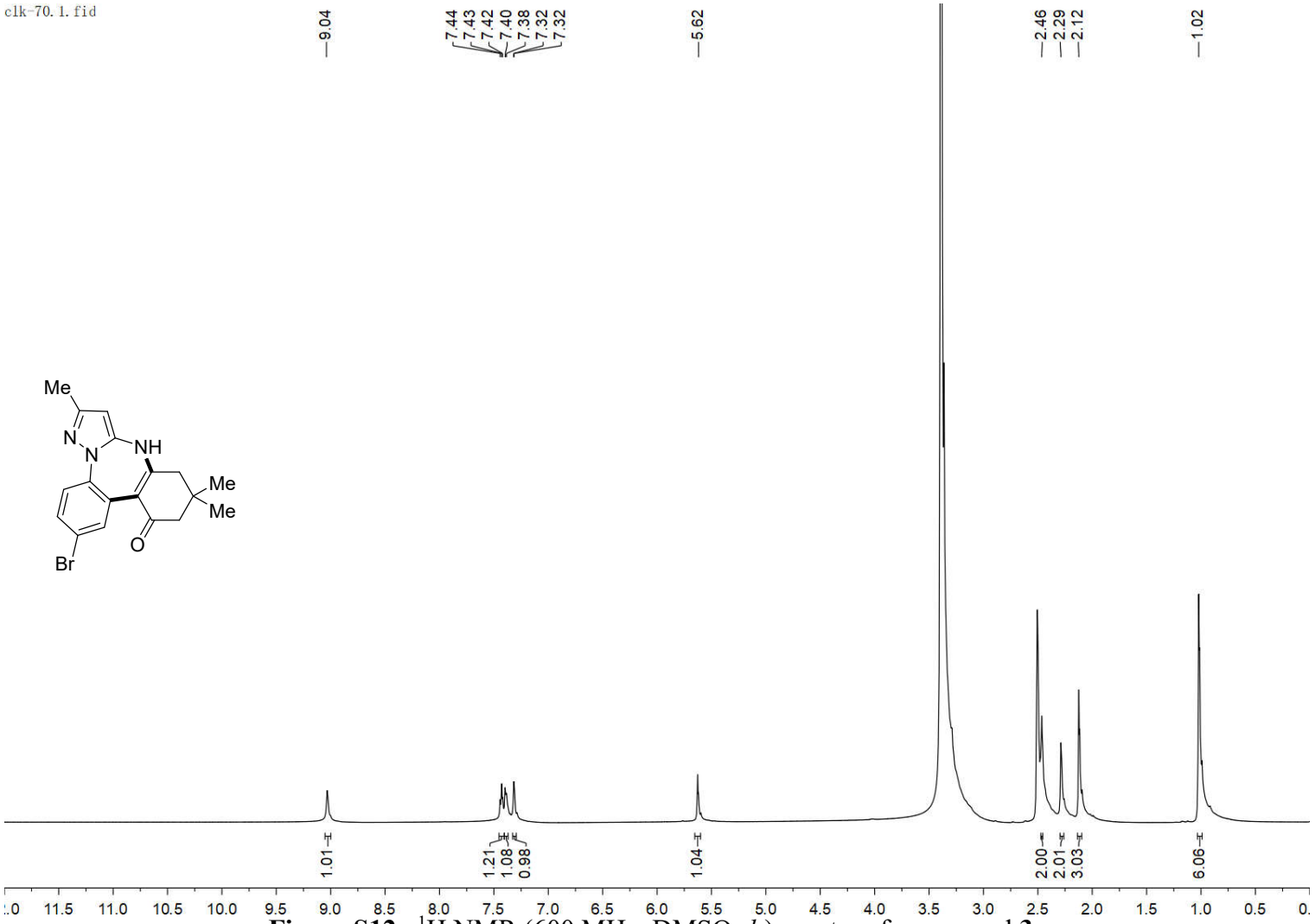


Figure S12. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3e**

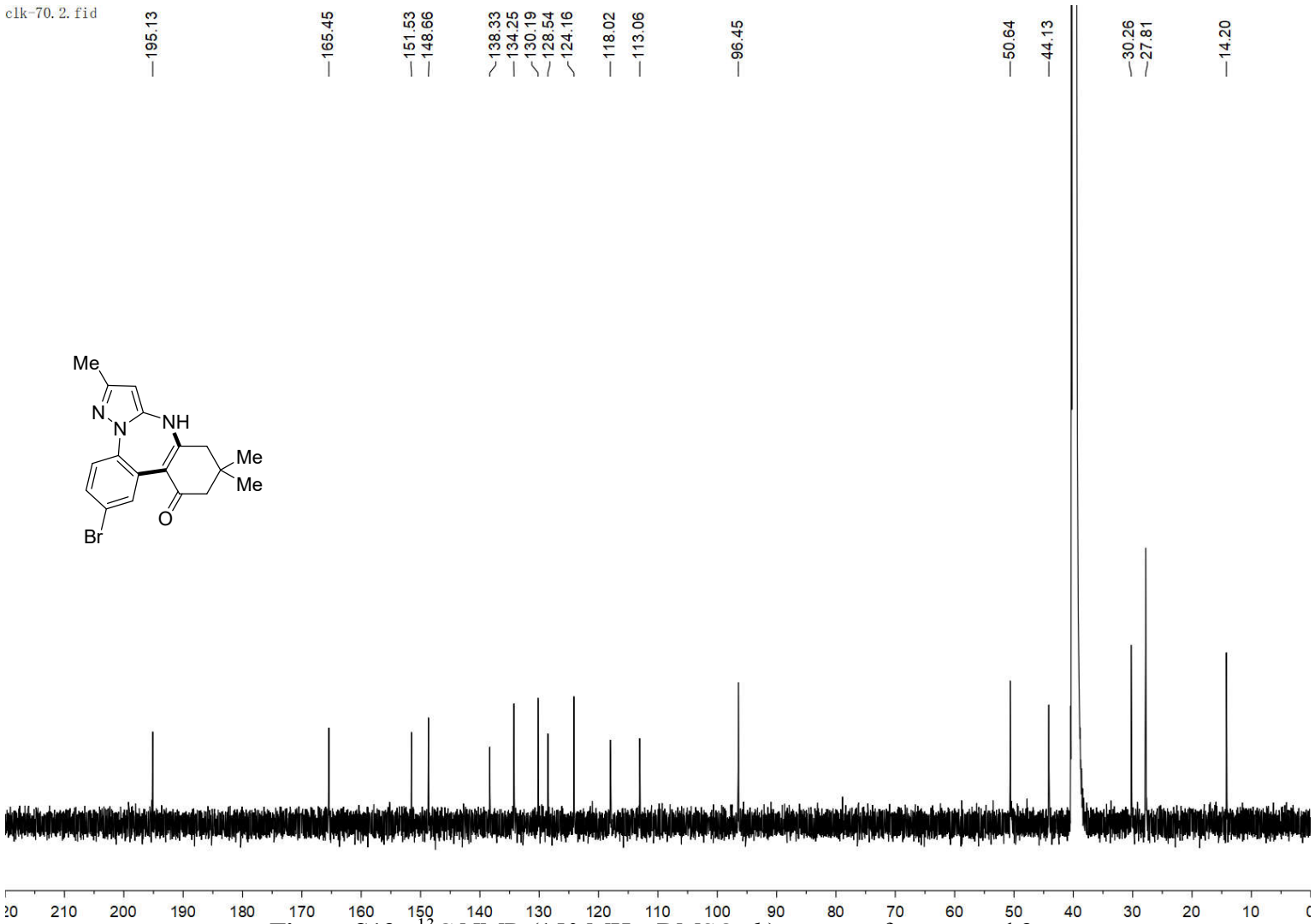


Figure S13. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3e**

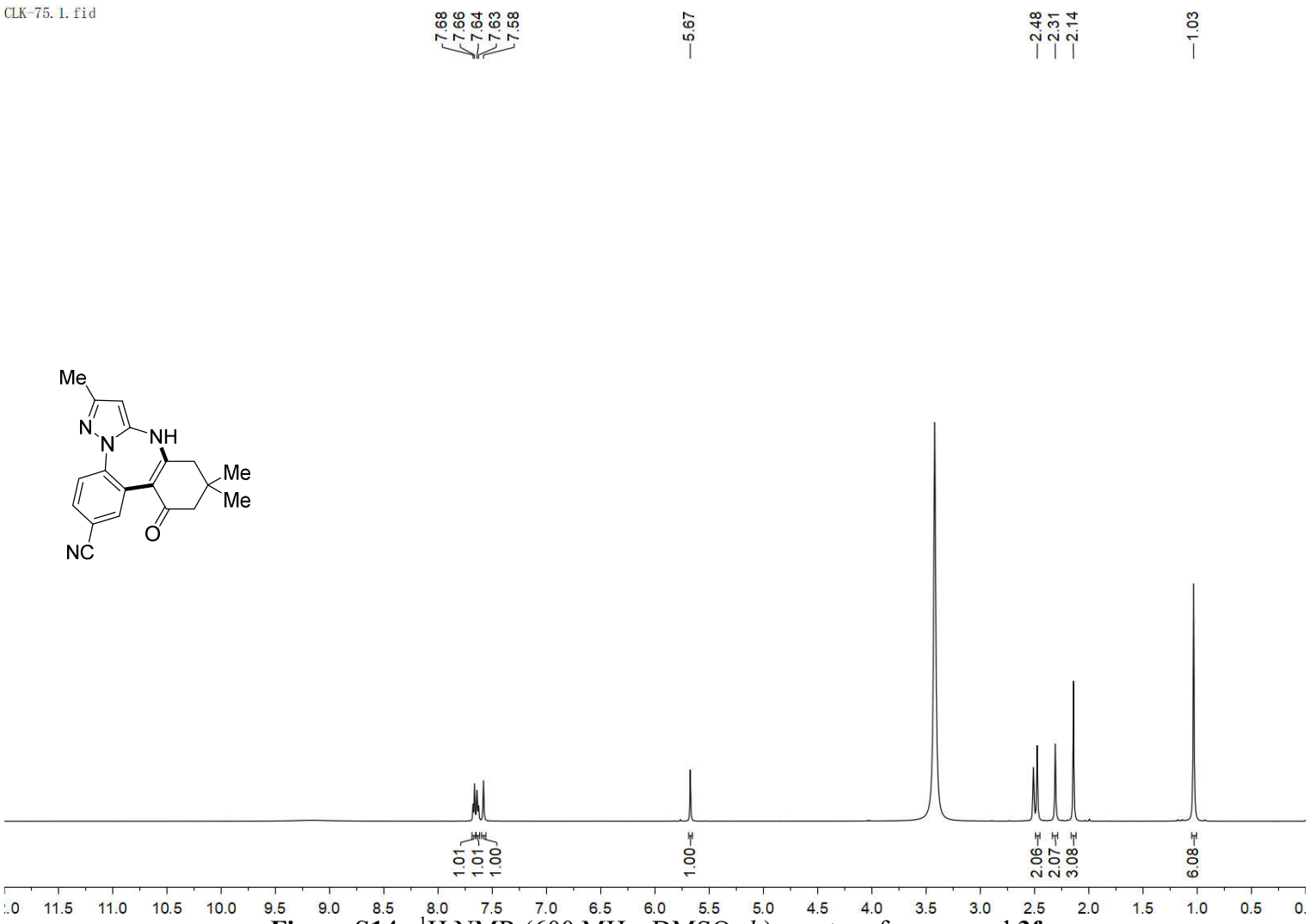


Figure S14. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3f**

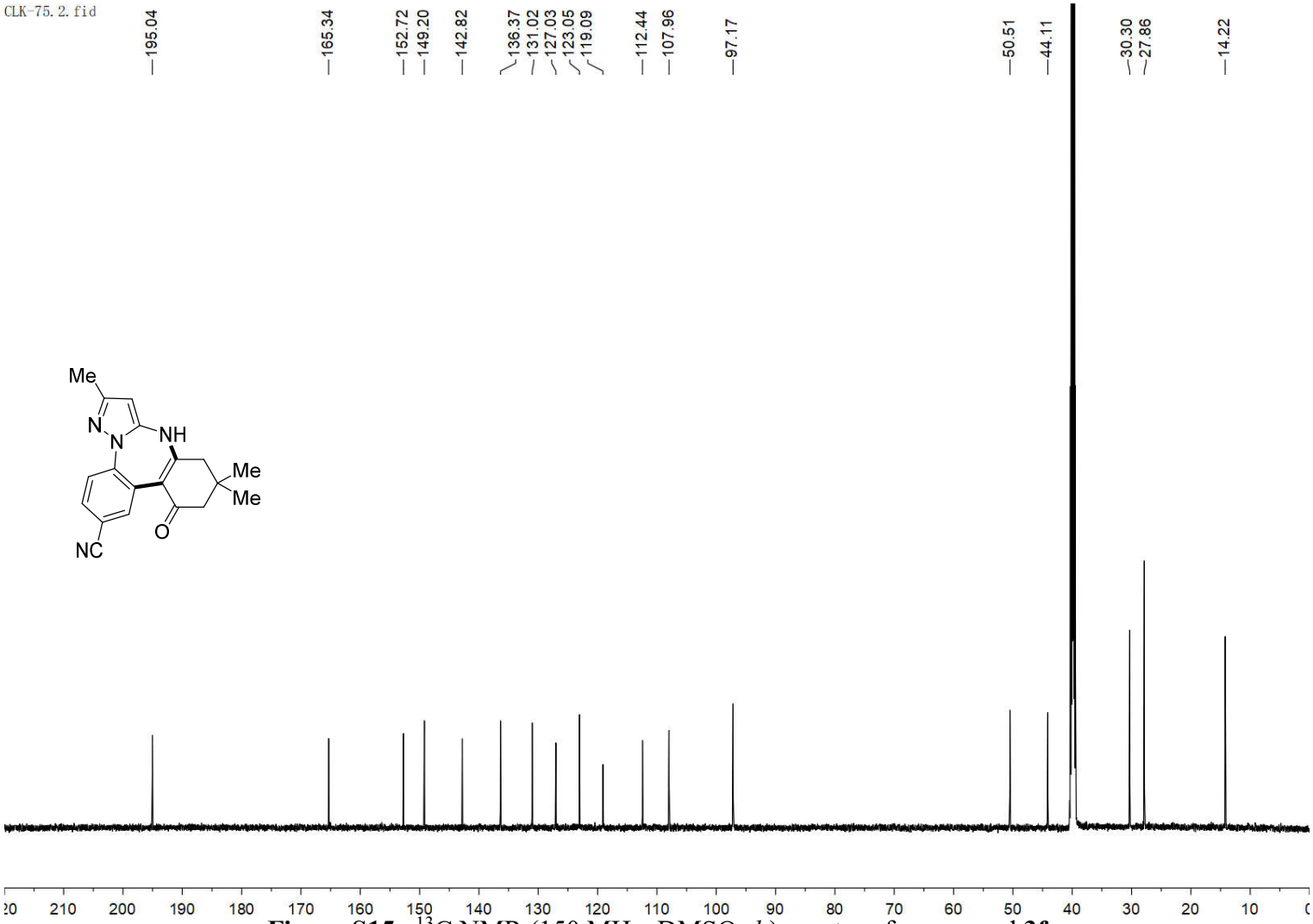


Figure S15. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3f**

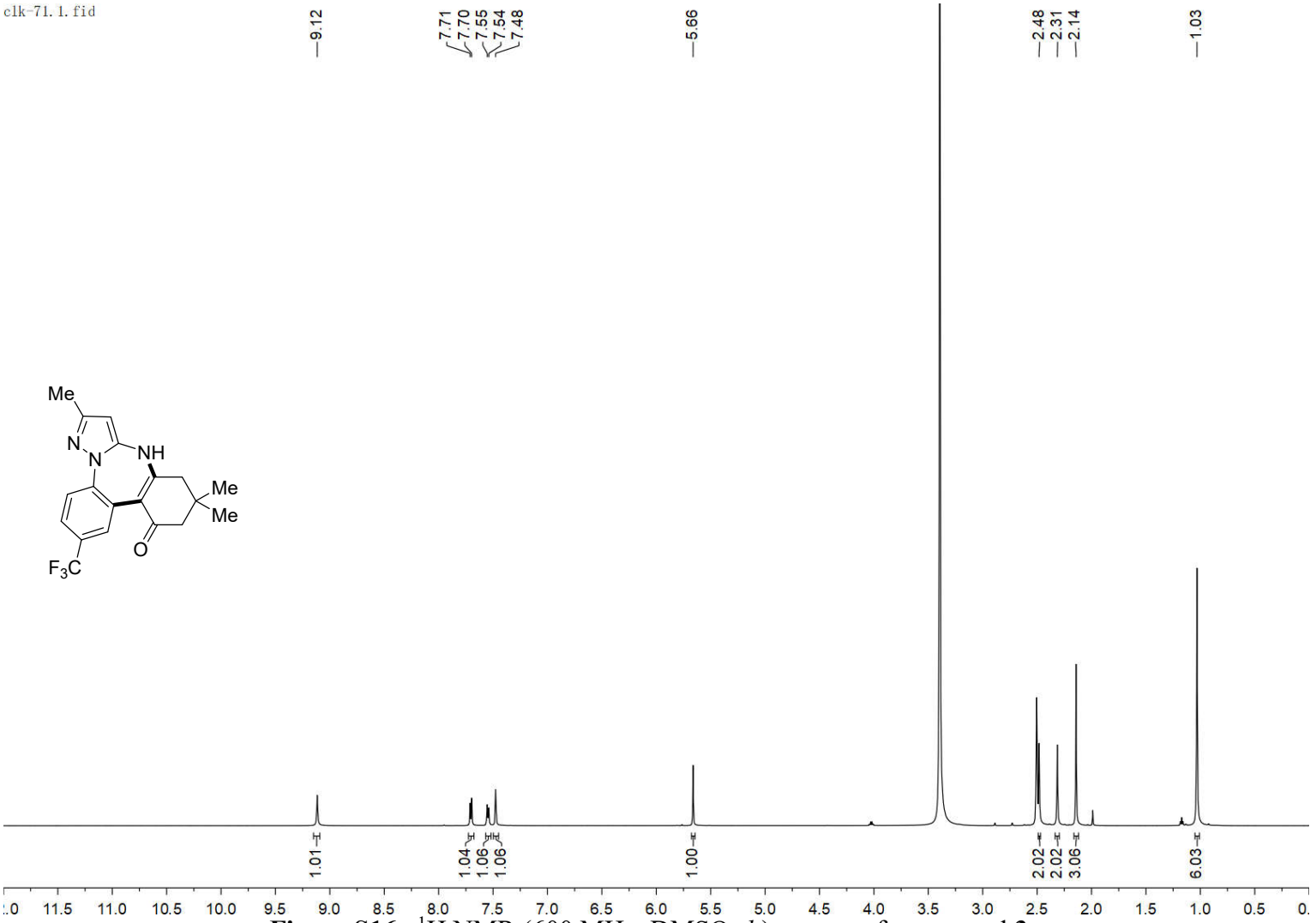


Figure S16. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3g**

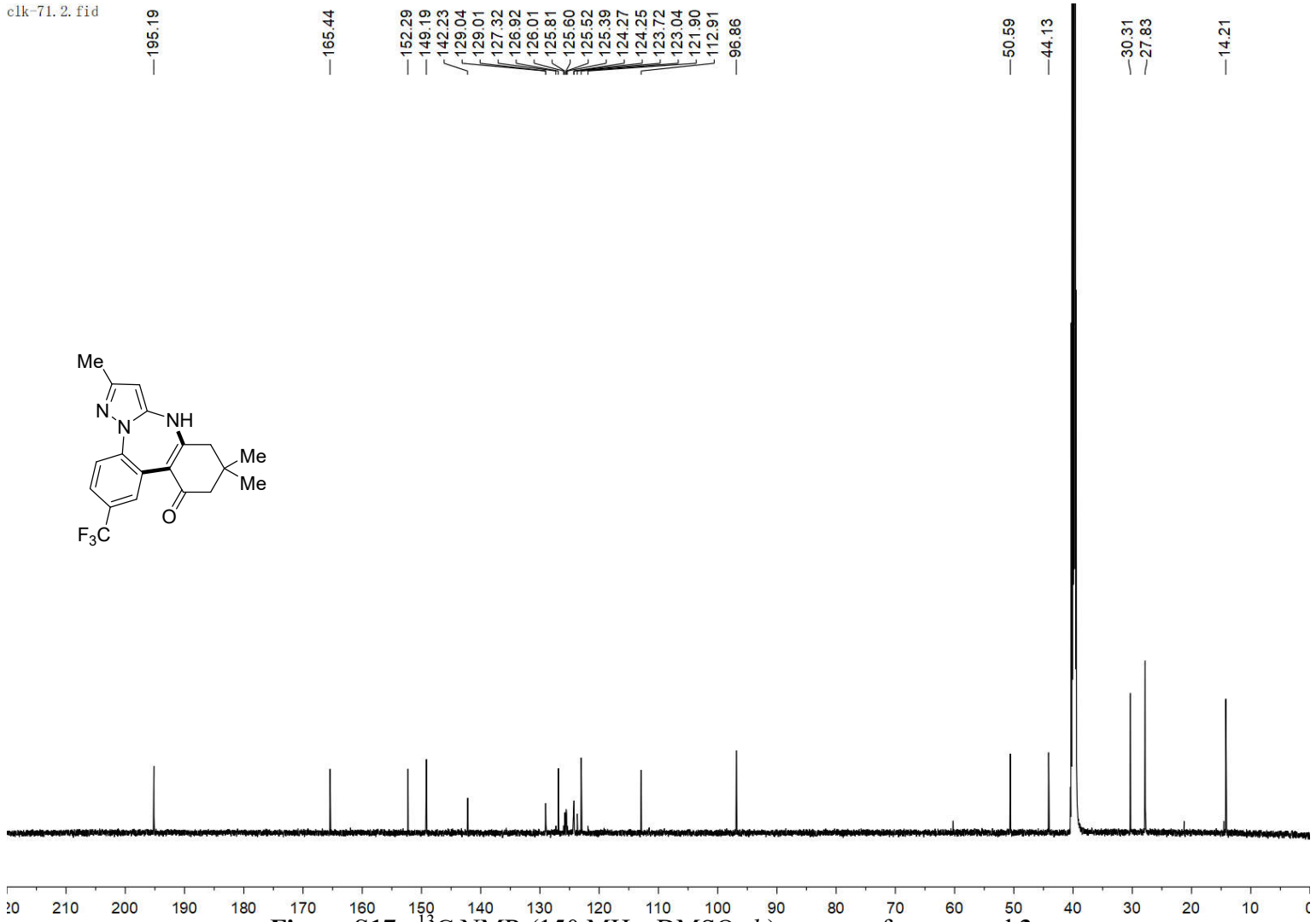


Figure S17. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3g**

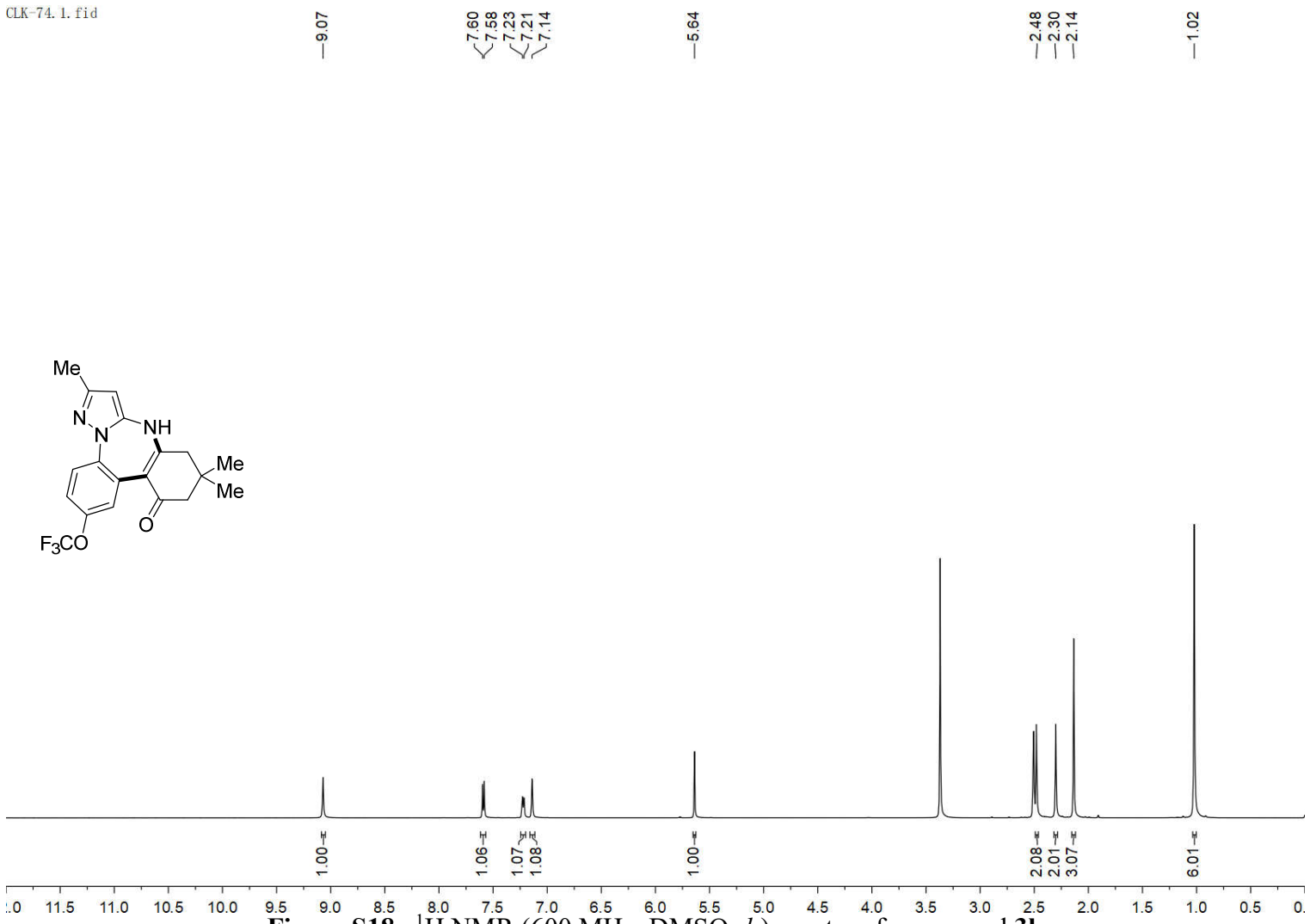


Figure S18. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3h**

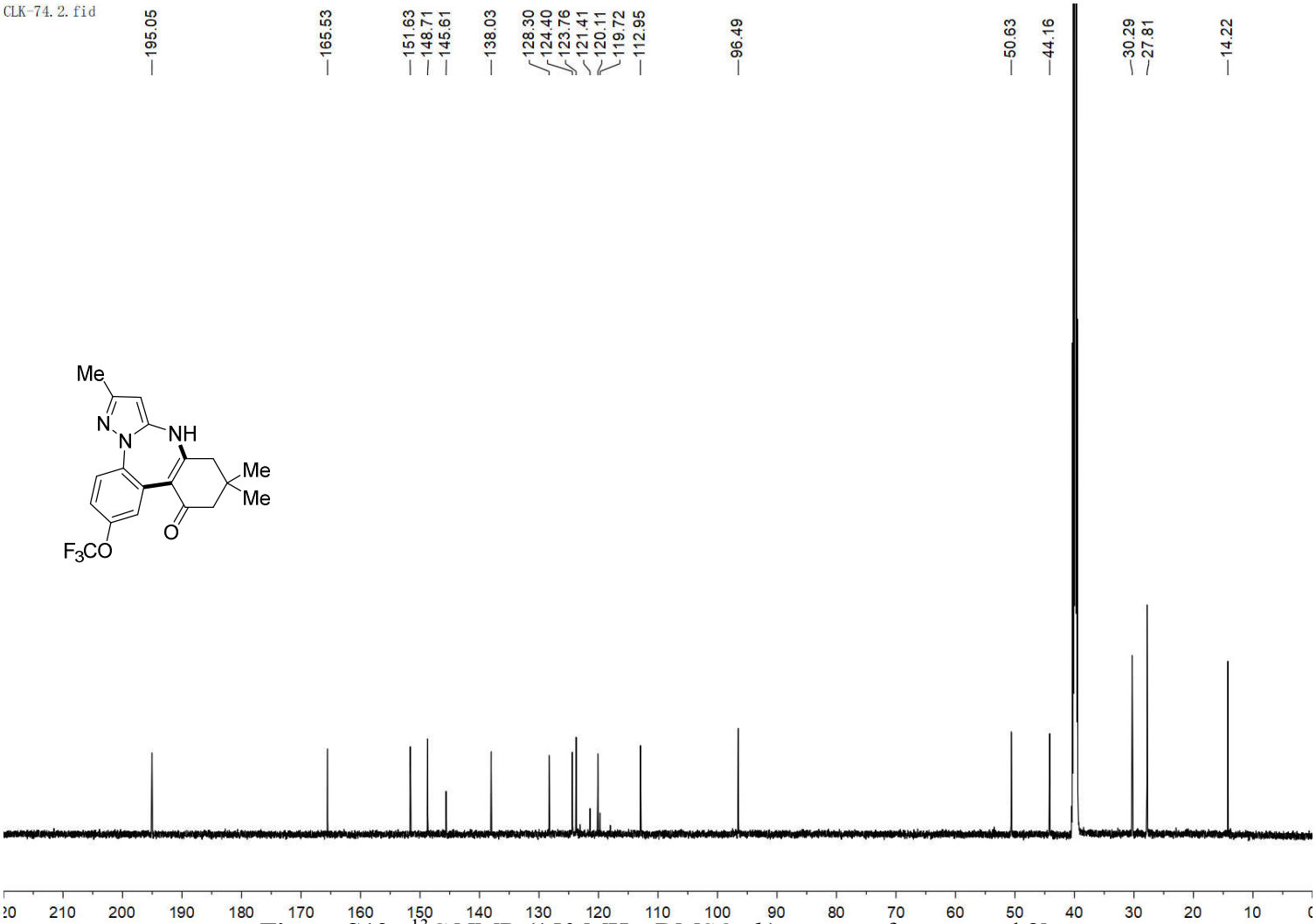


Figure S19. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3h**

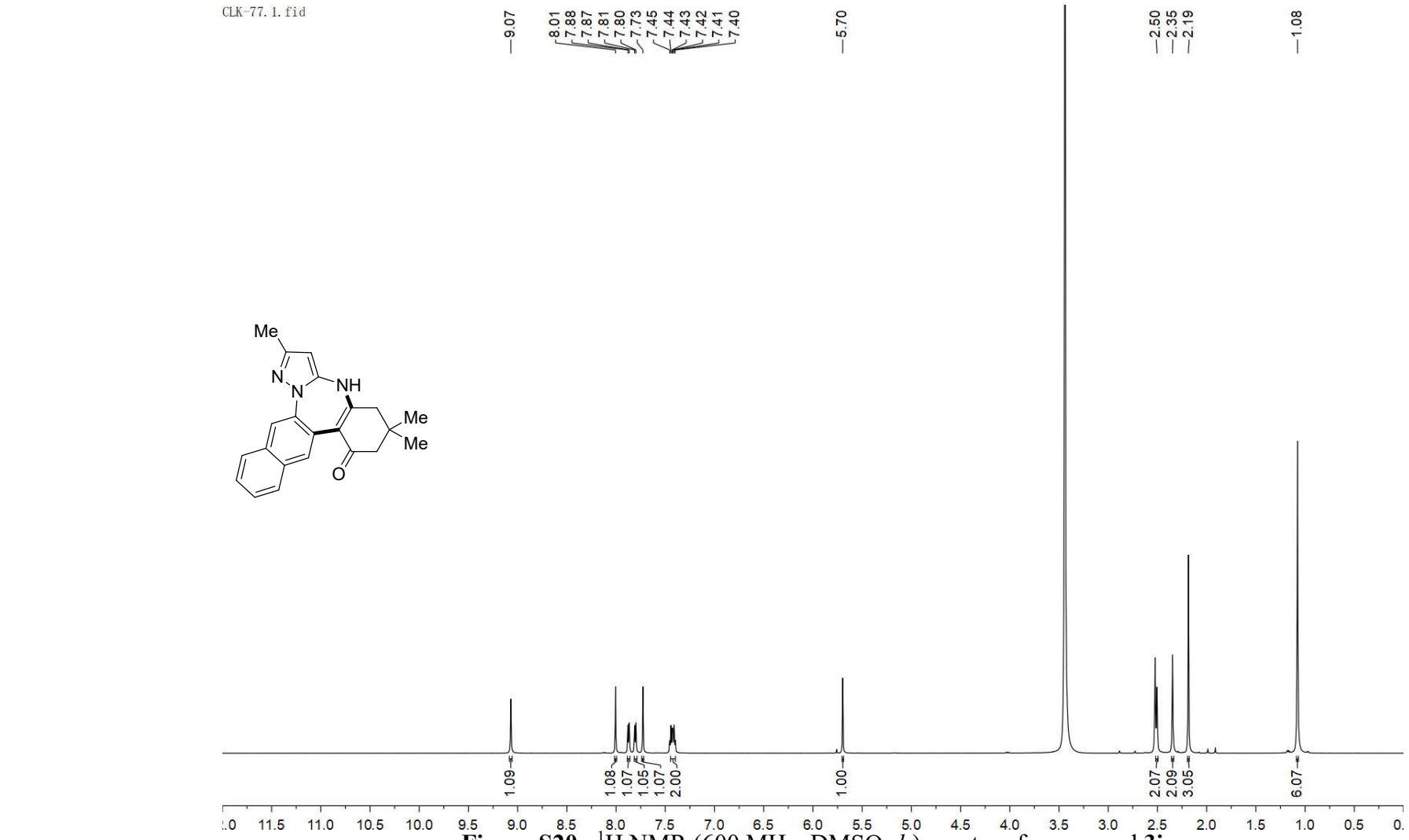


Figure S20. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3i**

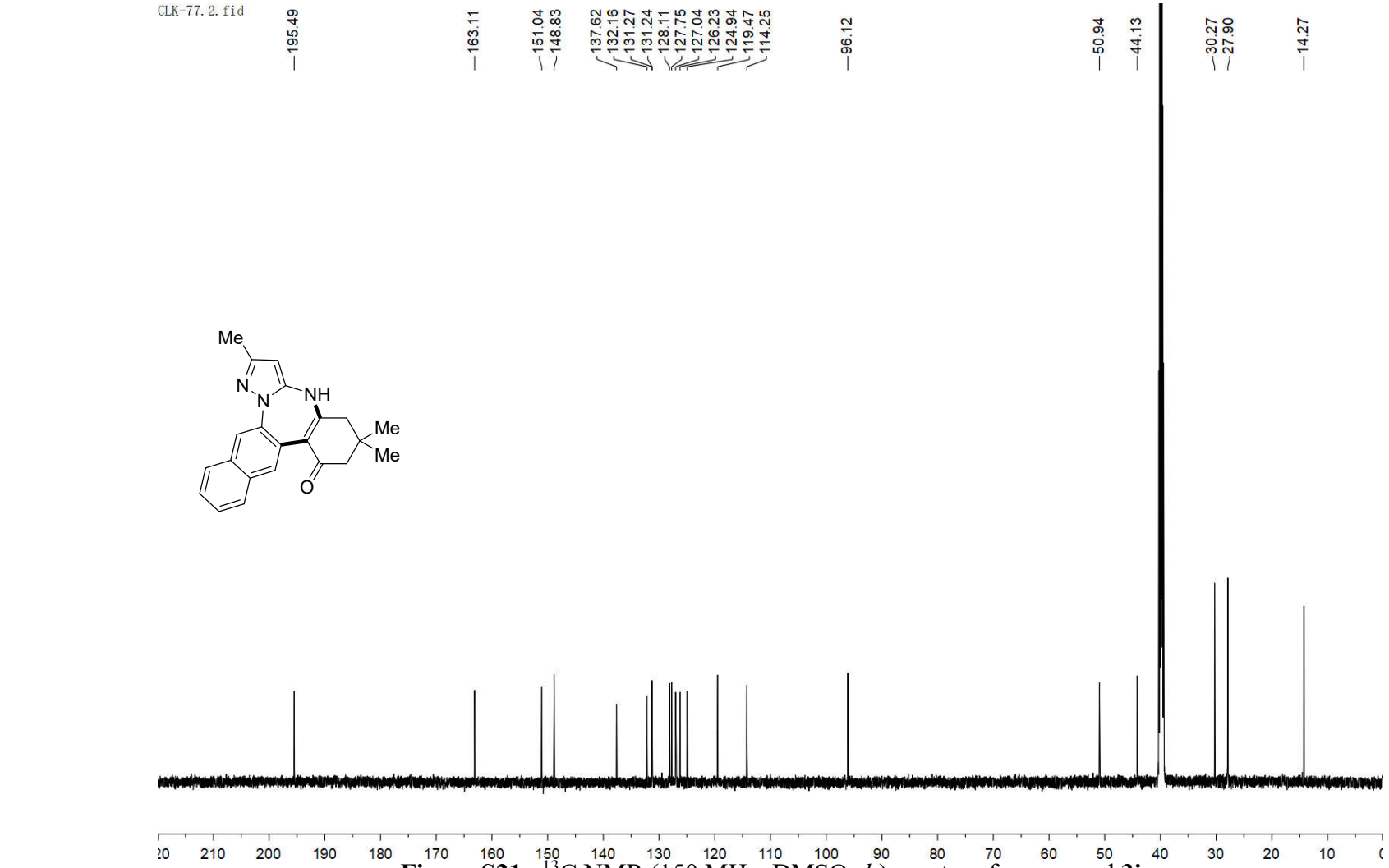


Figure S21. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3i**

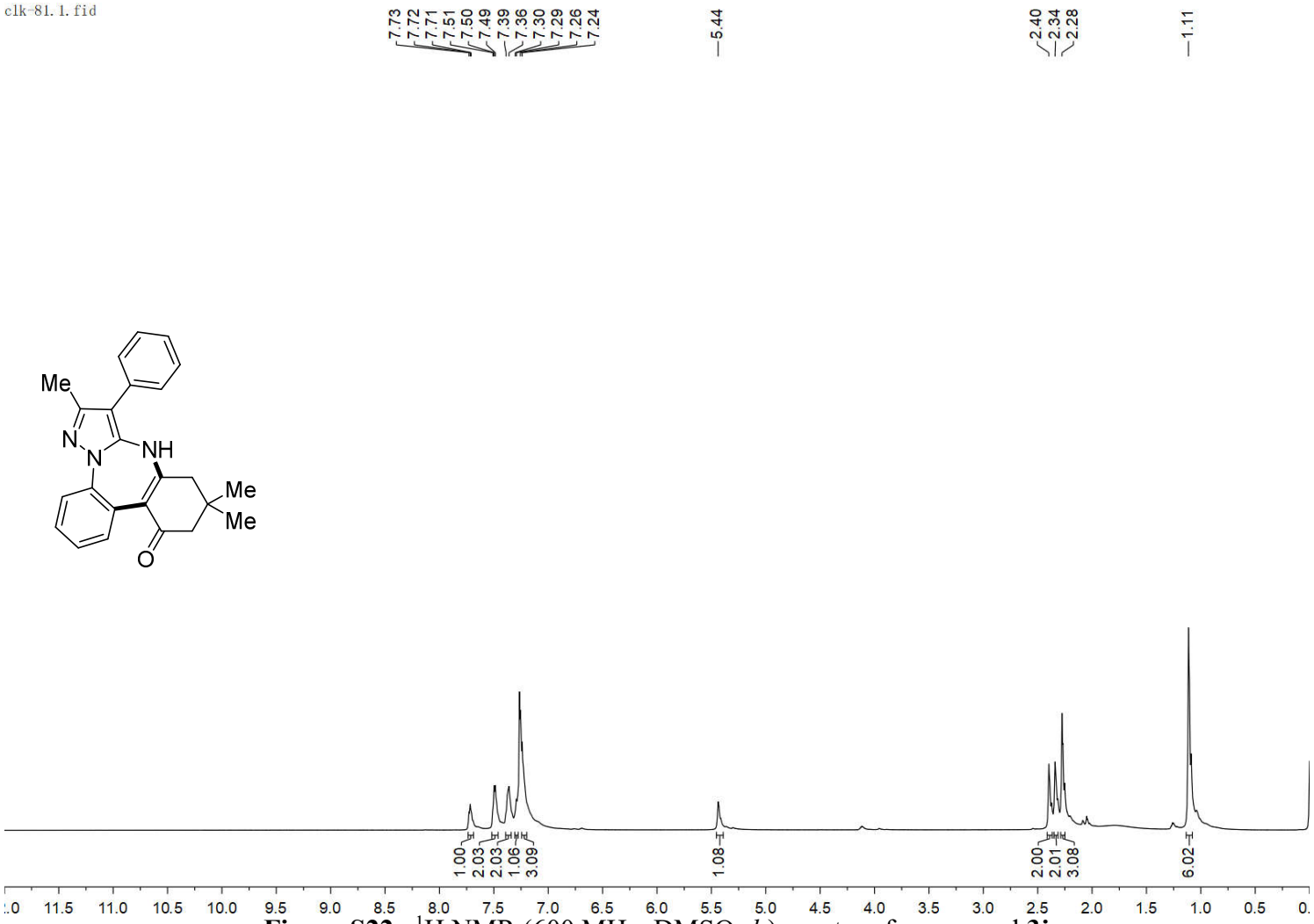


Figure S22. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3j**

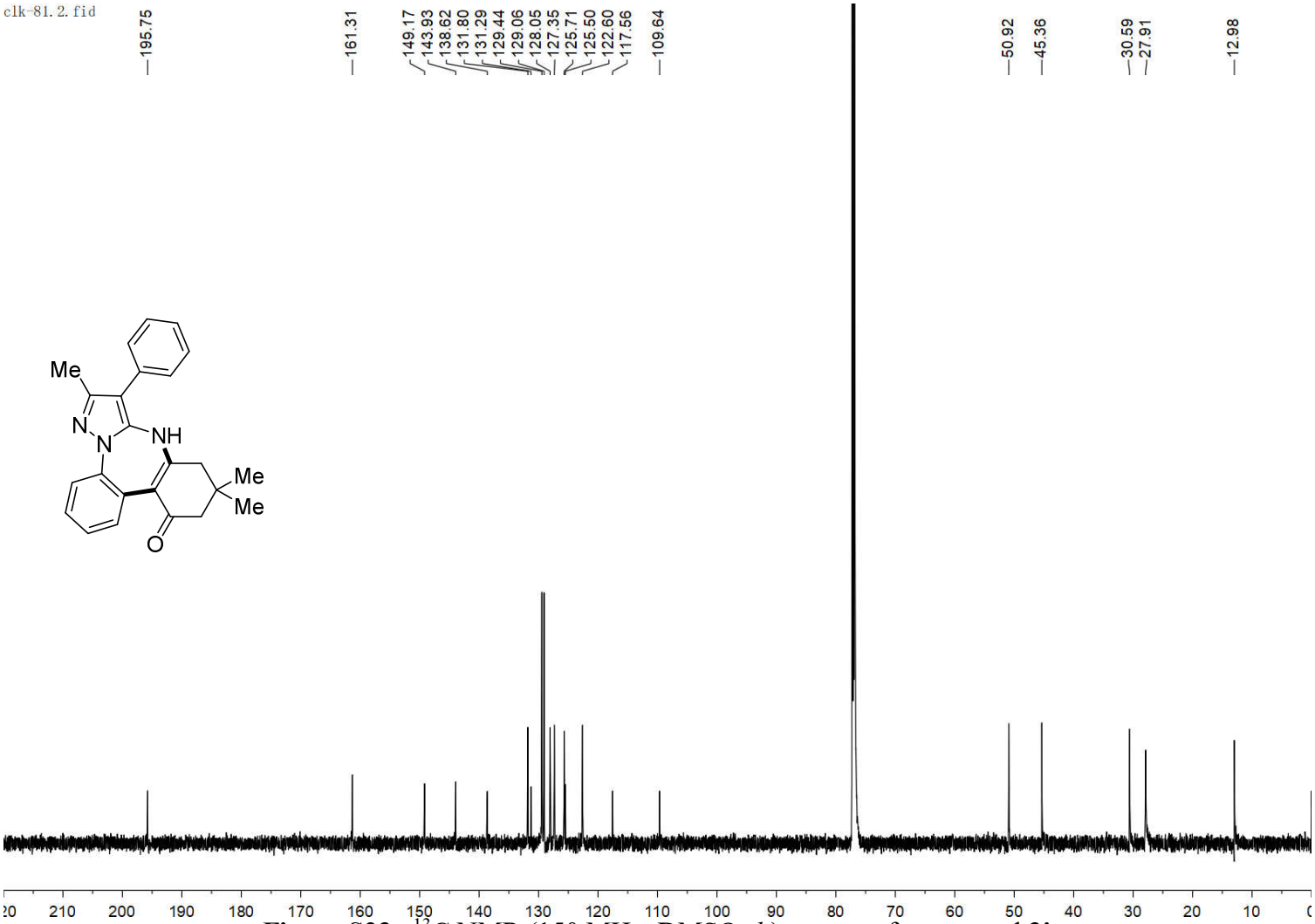


Figure S23. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3j**

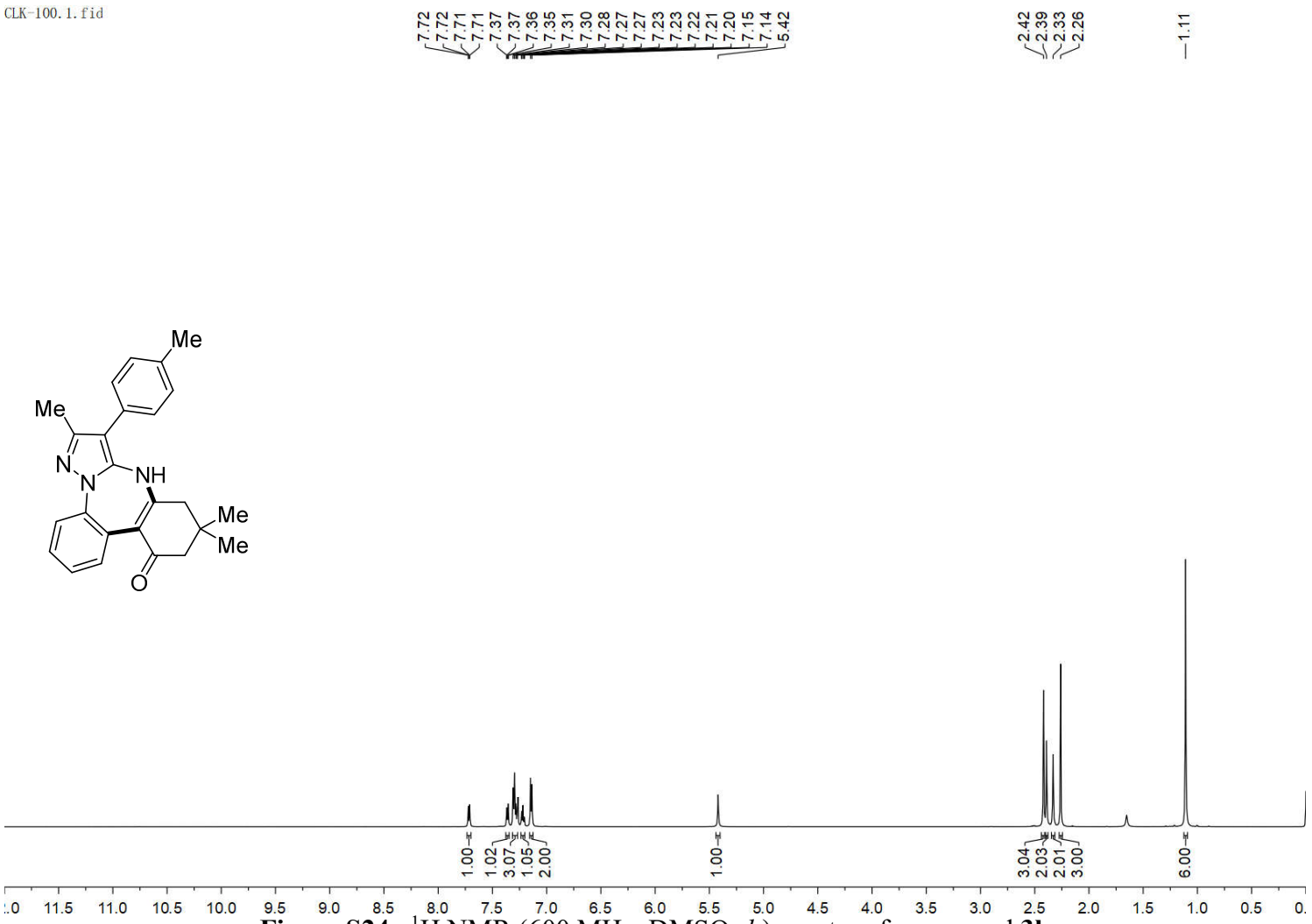


Figure S24. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3k**

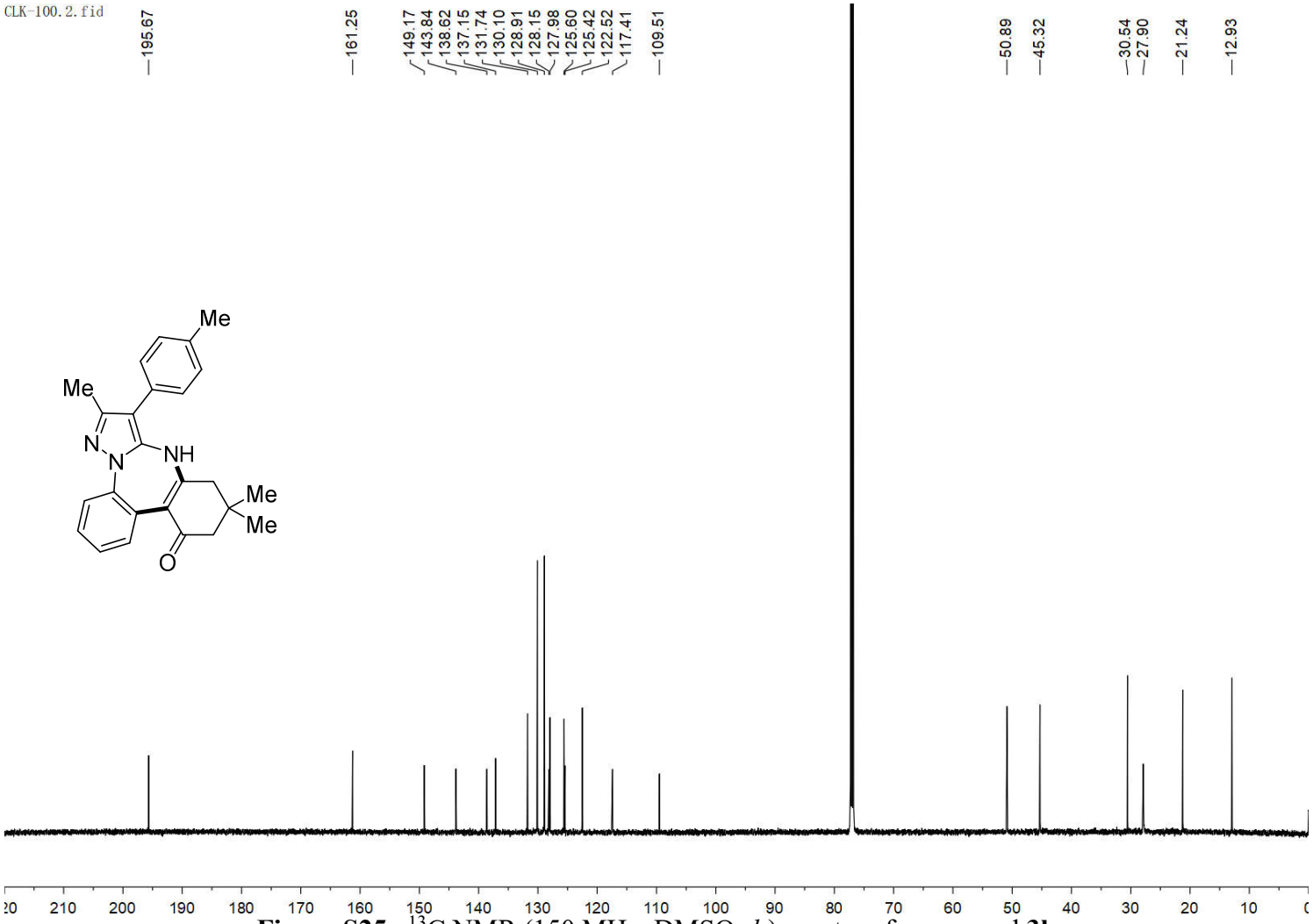


Figure S25. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3k**

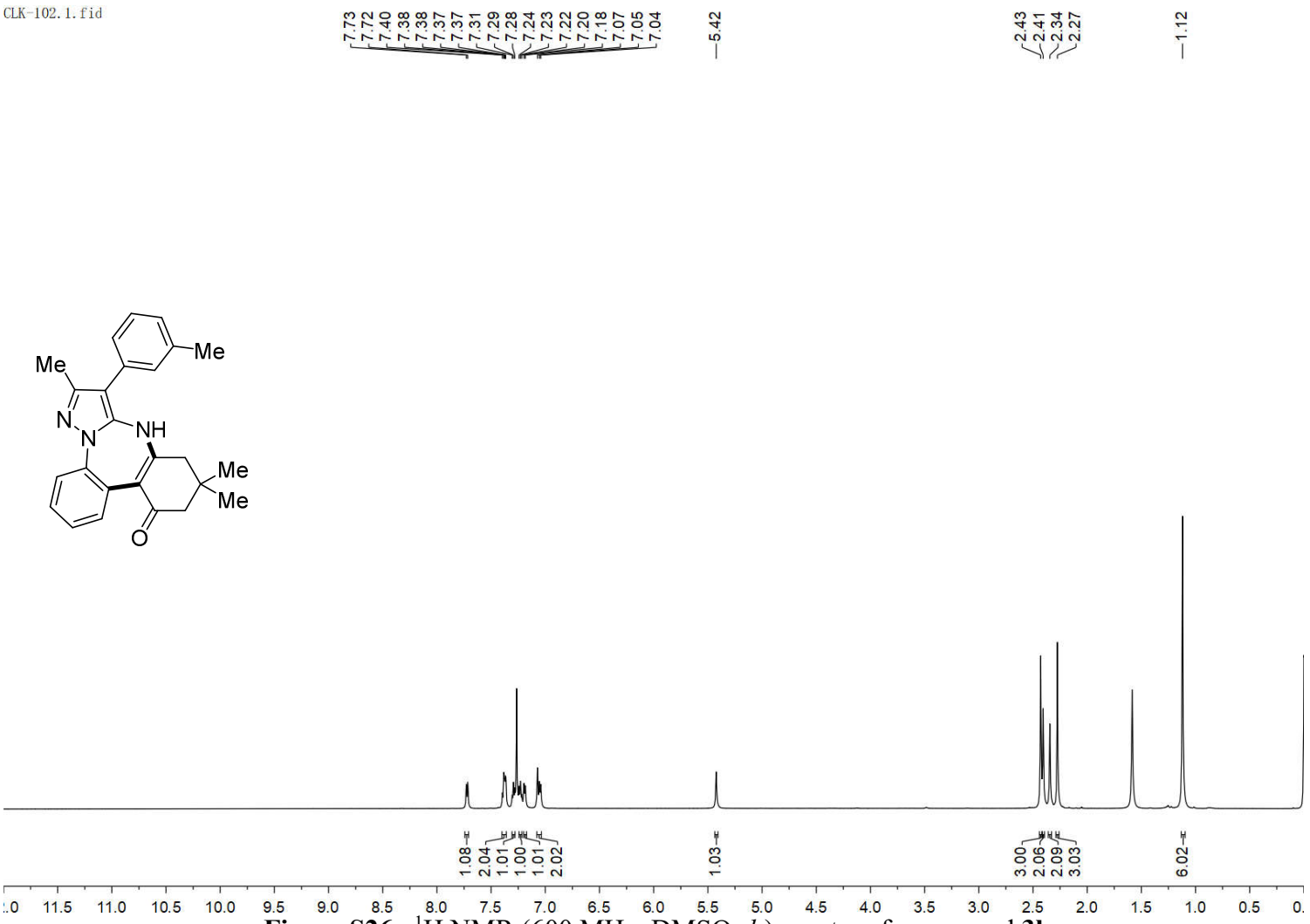


Figure S26. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3l**

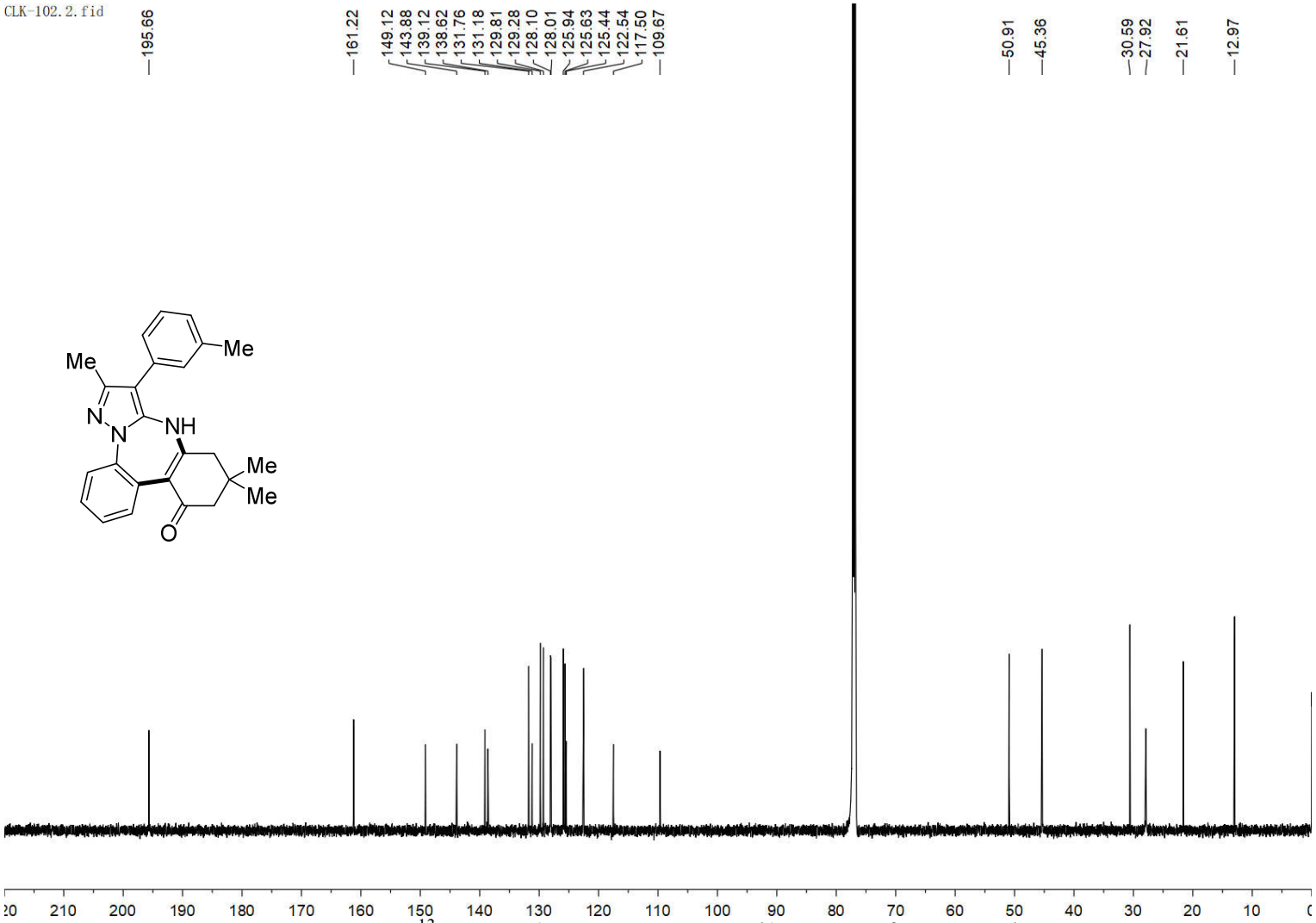


Figure S27. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3l**

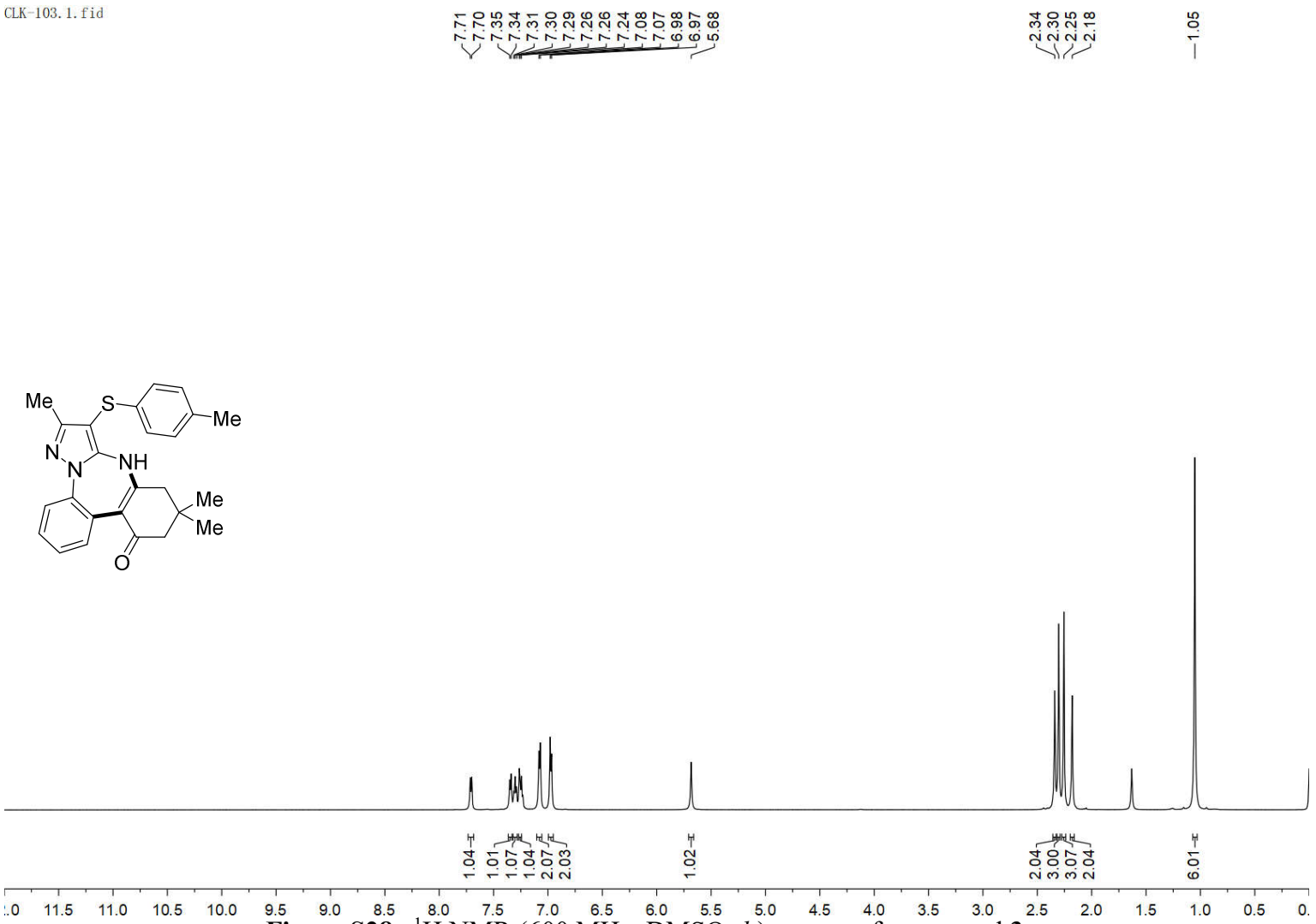


Figure S28. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3m**

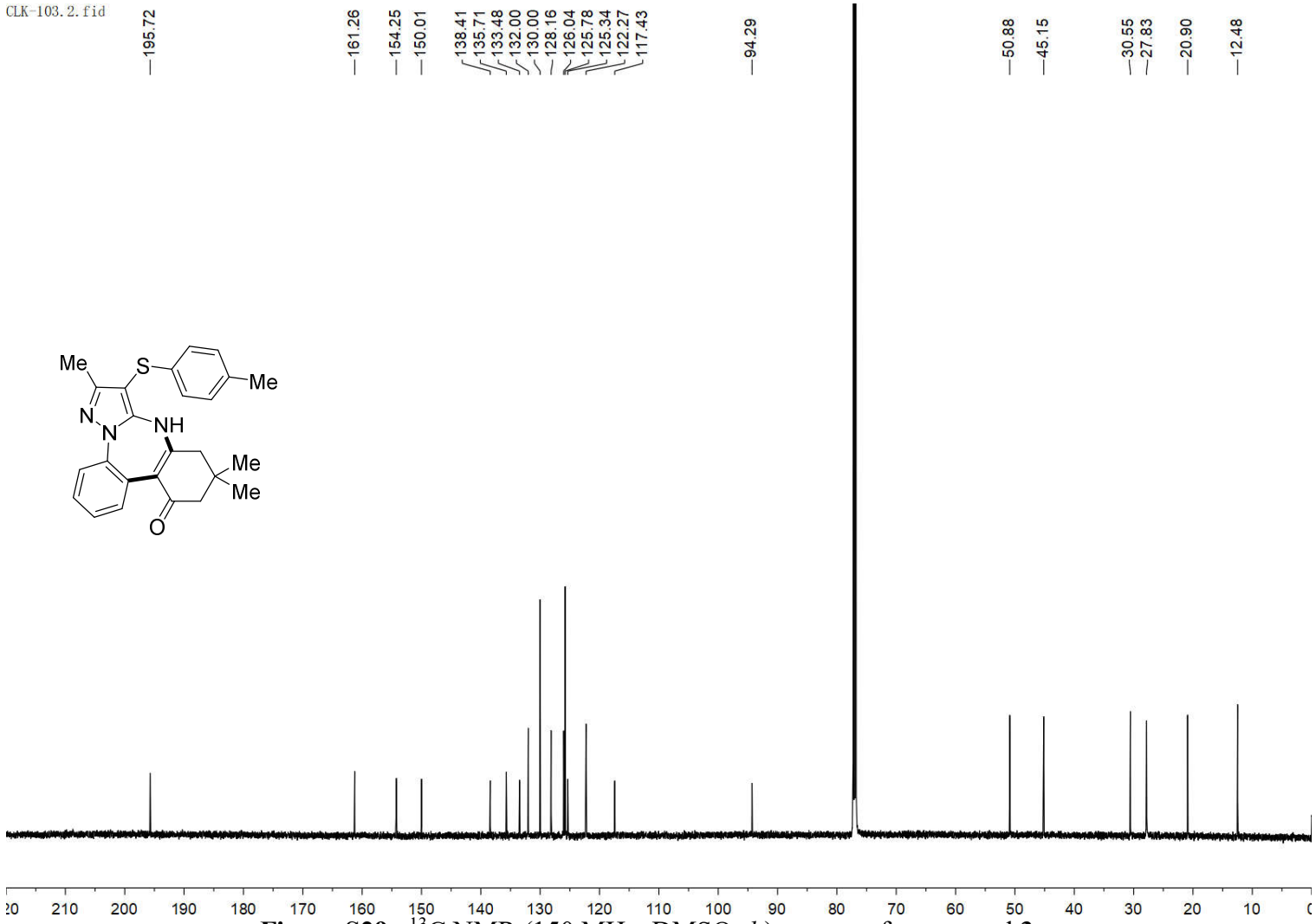


Figure S29. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3m**

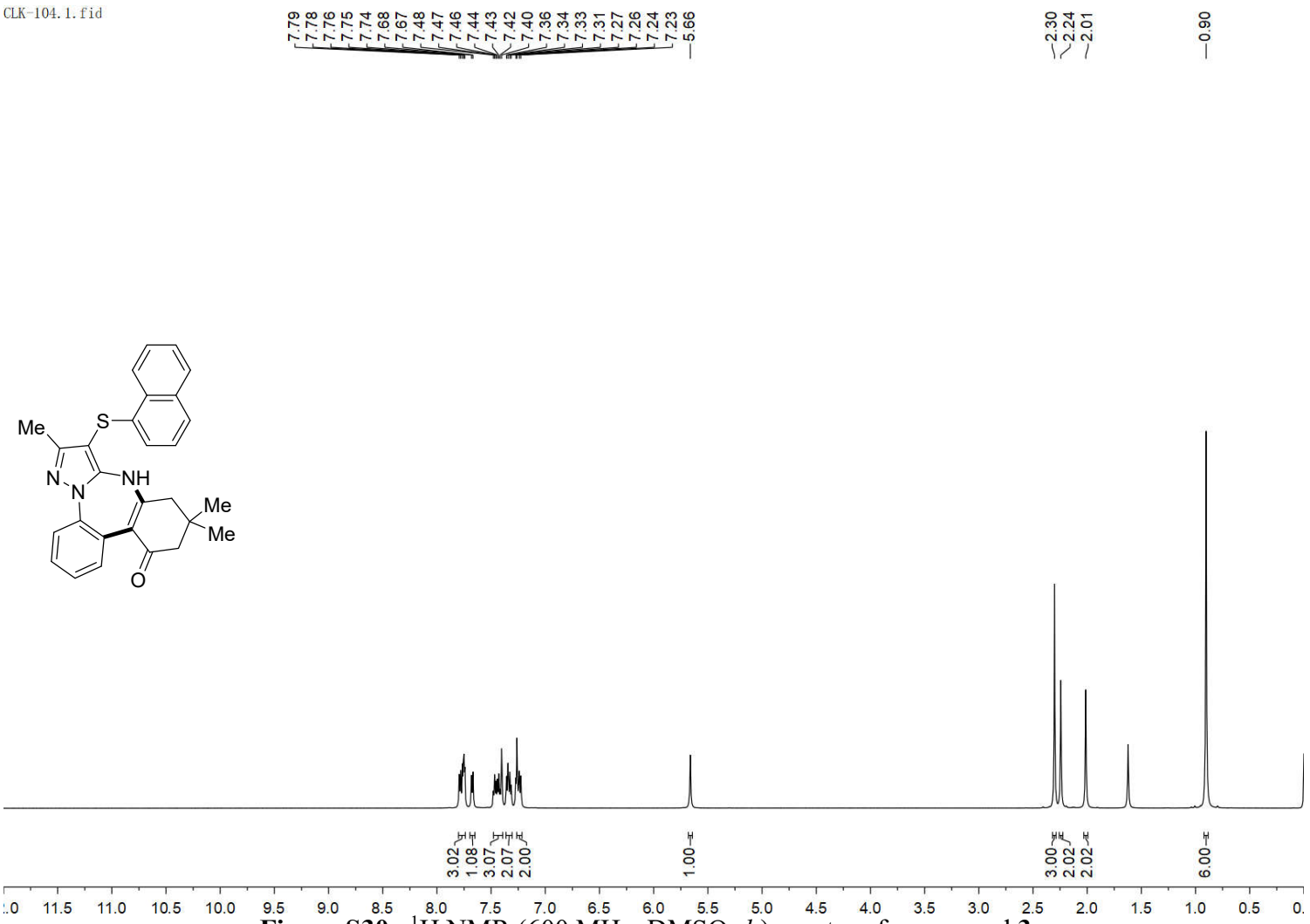


Figure S30. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3n**

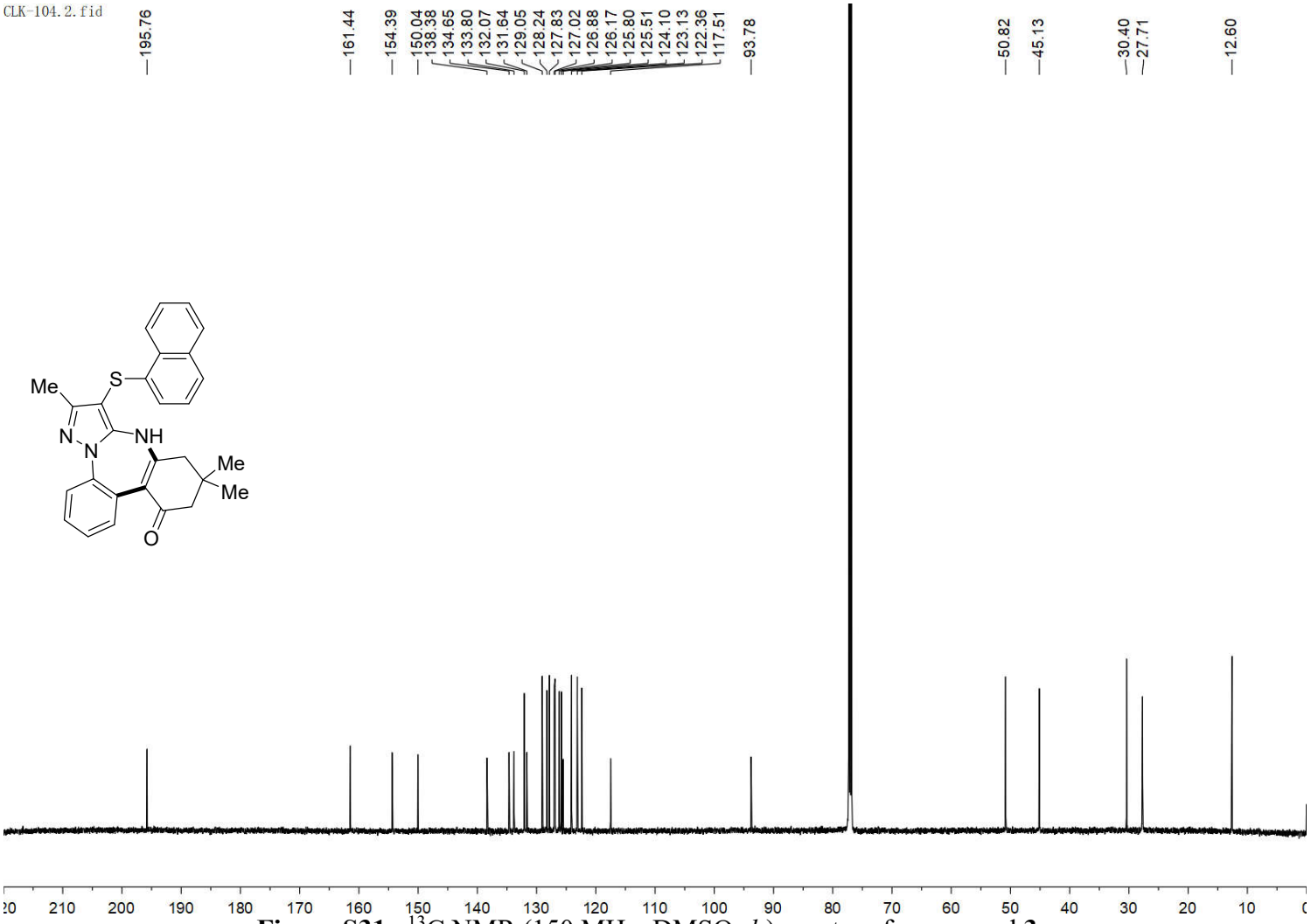


Figure S31. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3n**

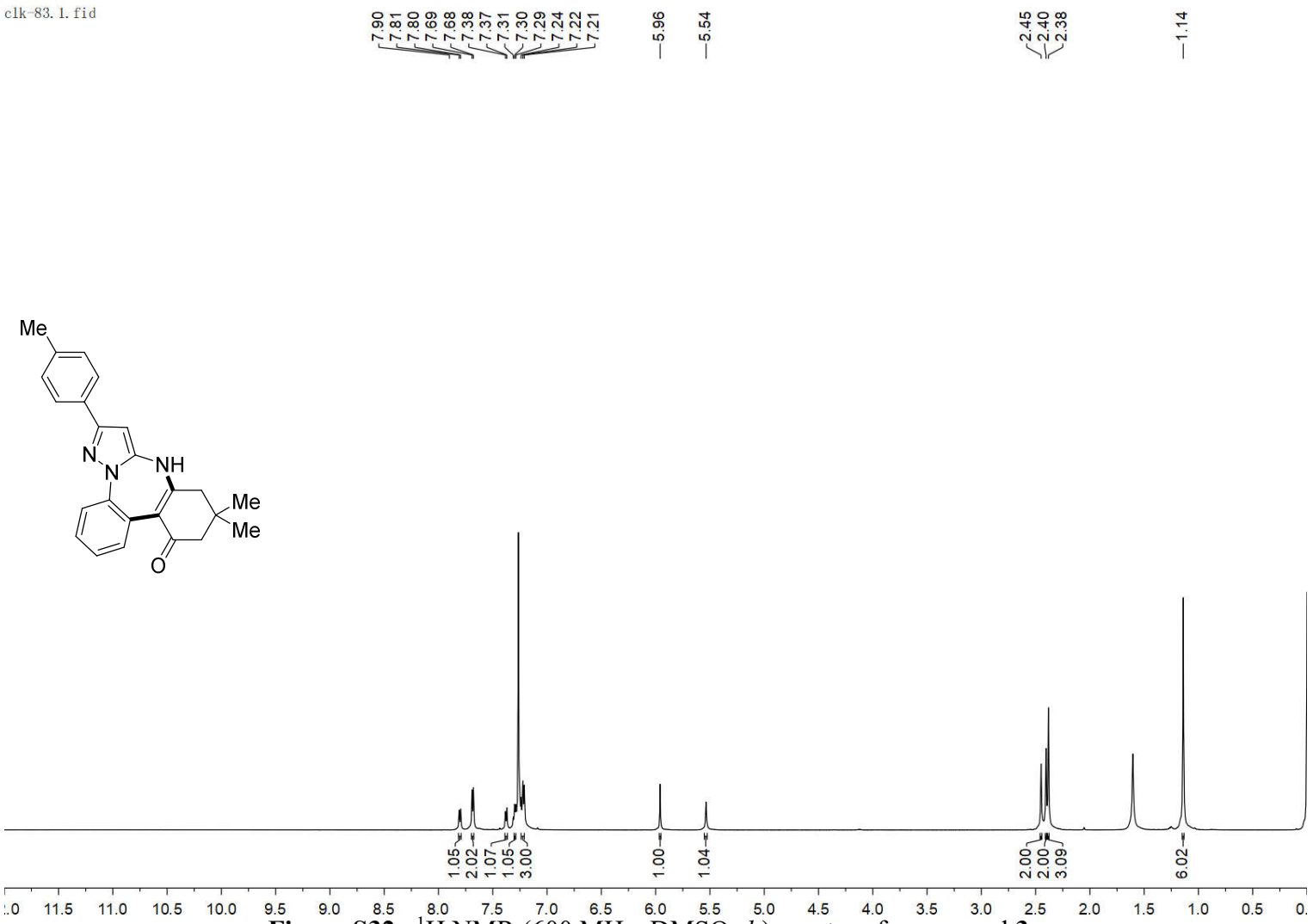


Figure S32. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3o**

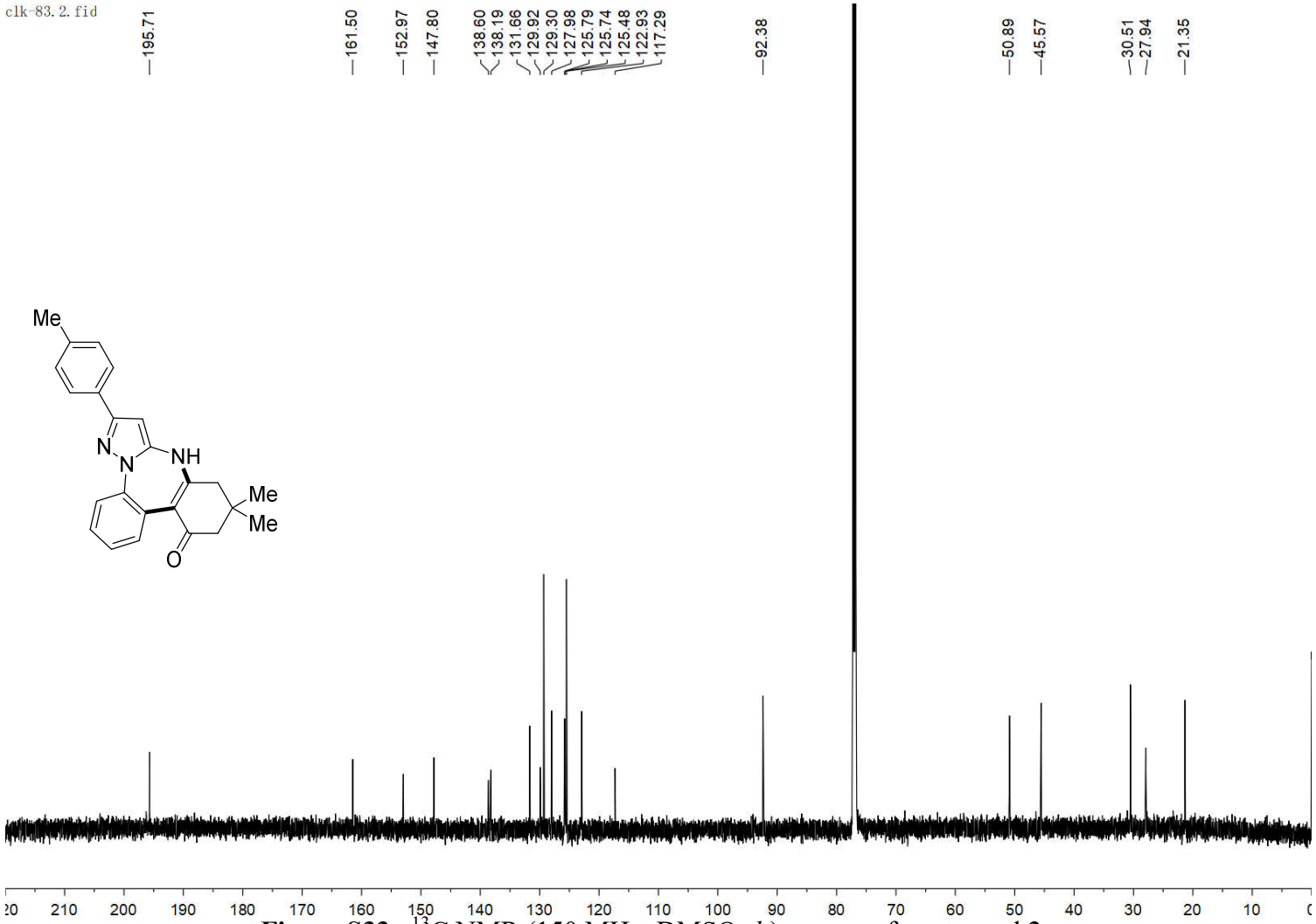


Figure S33. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3o**

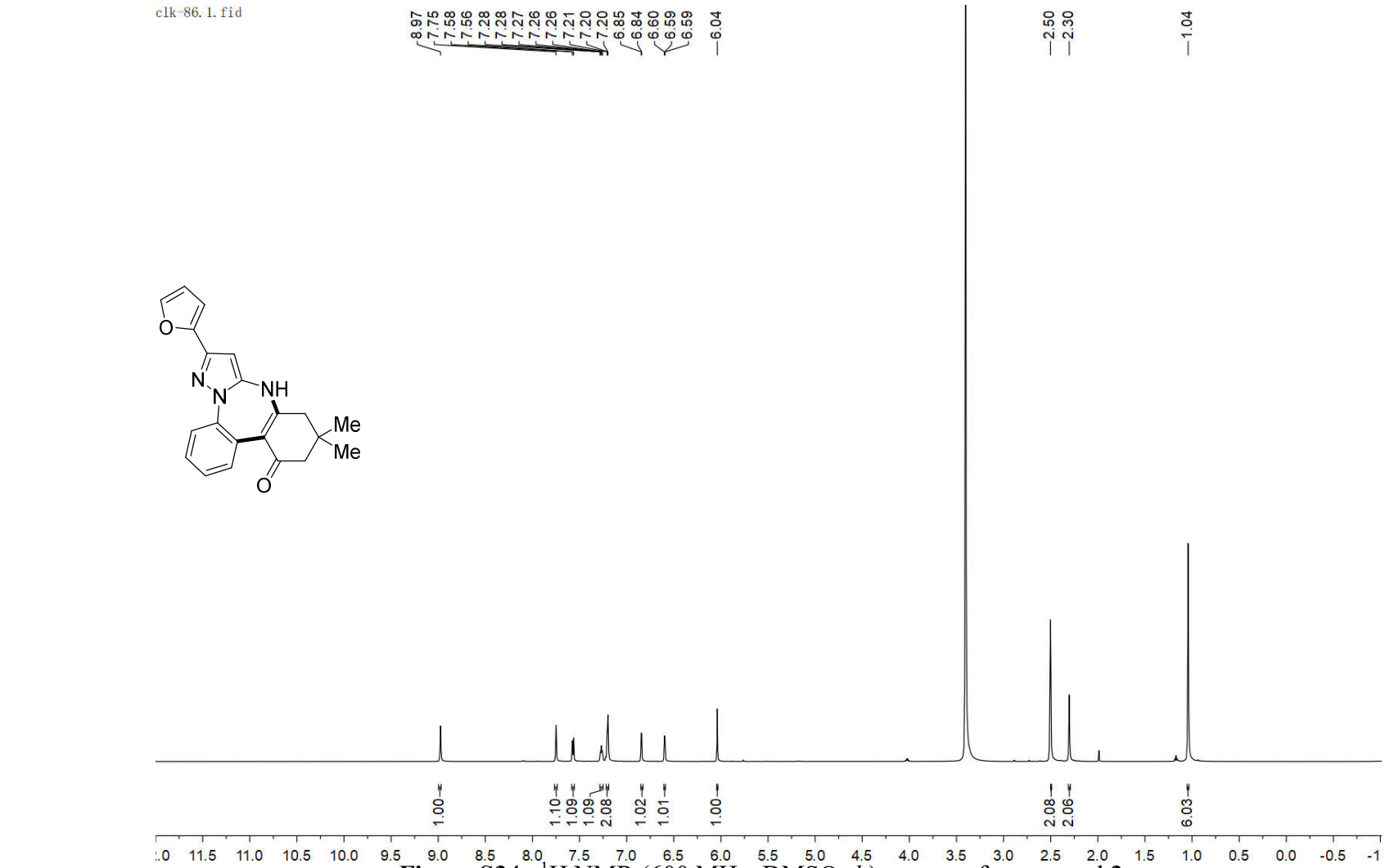


Figure S34. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3p**

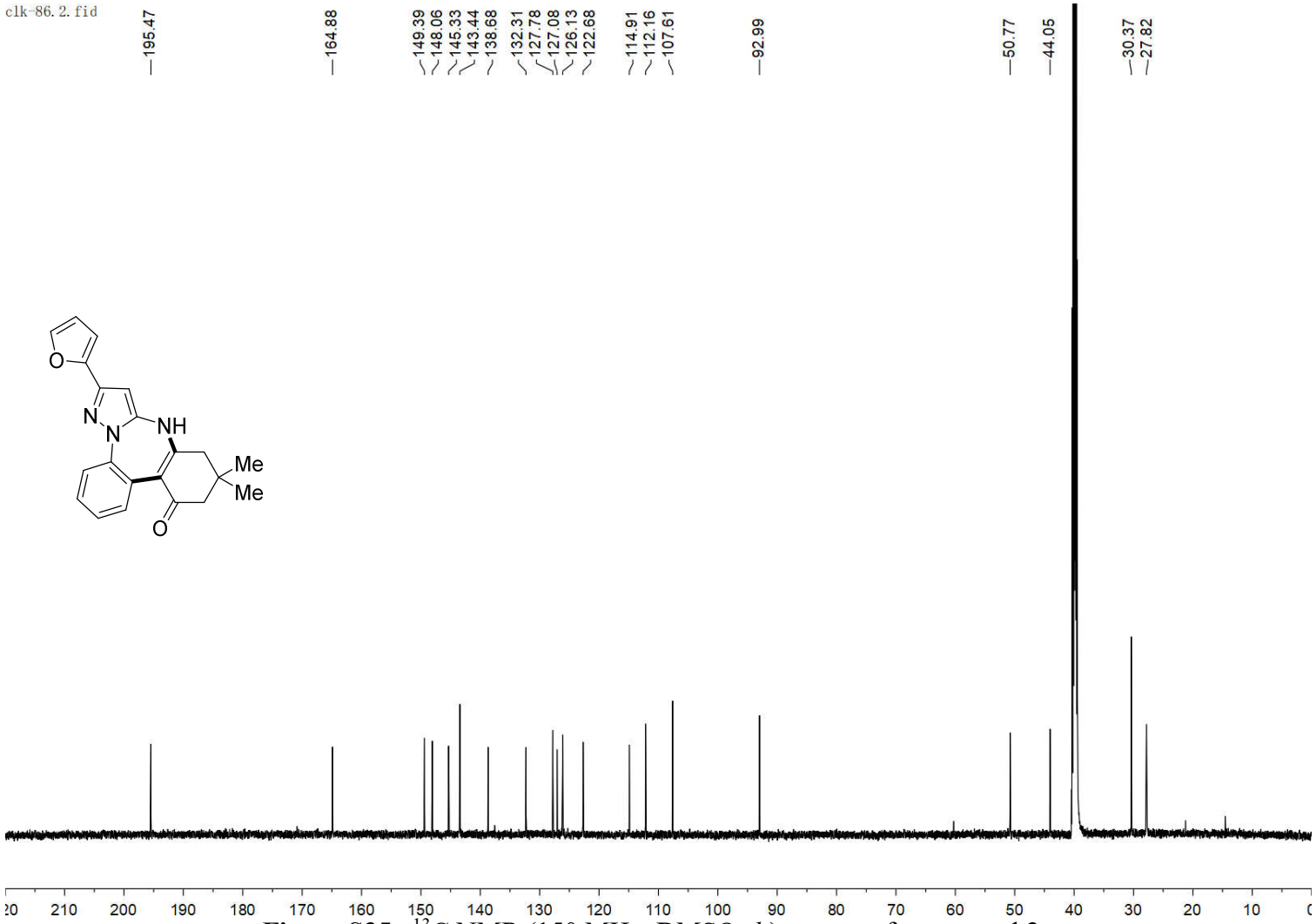


Figure S35. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3p**

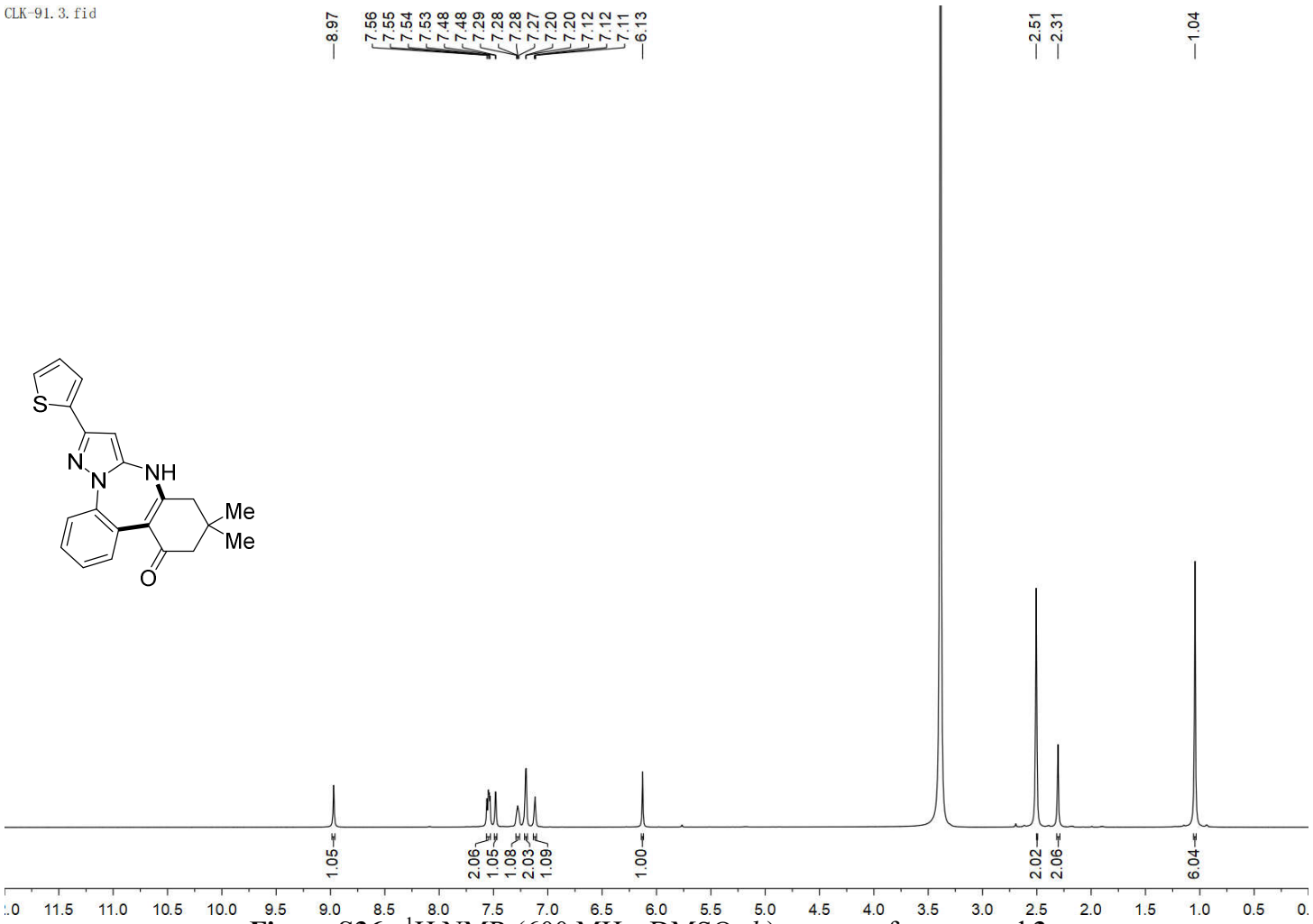


Figure S36. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3q**

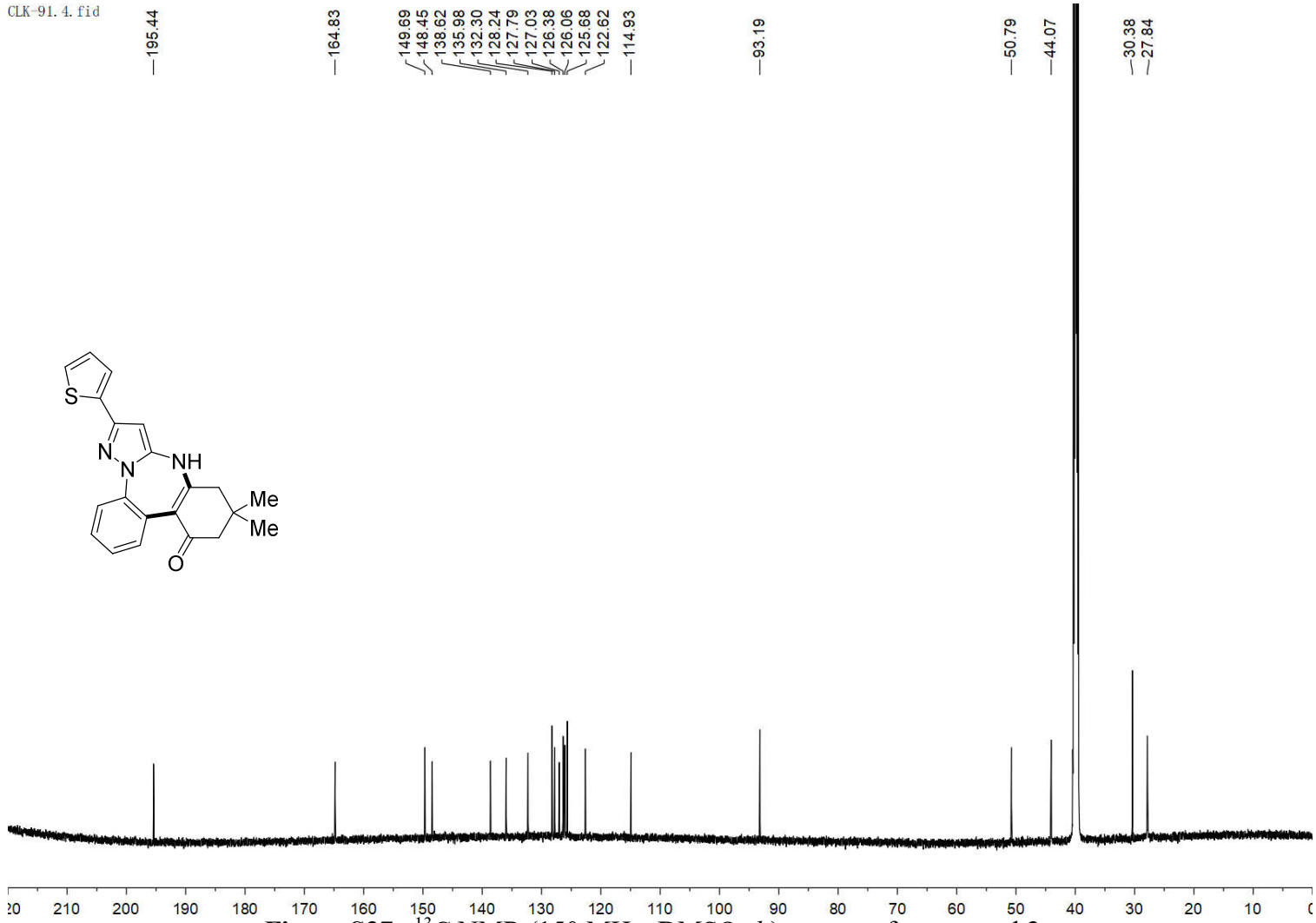


Figure S37. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3q**

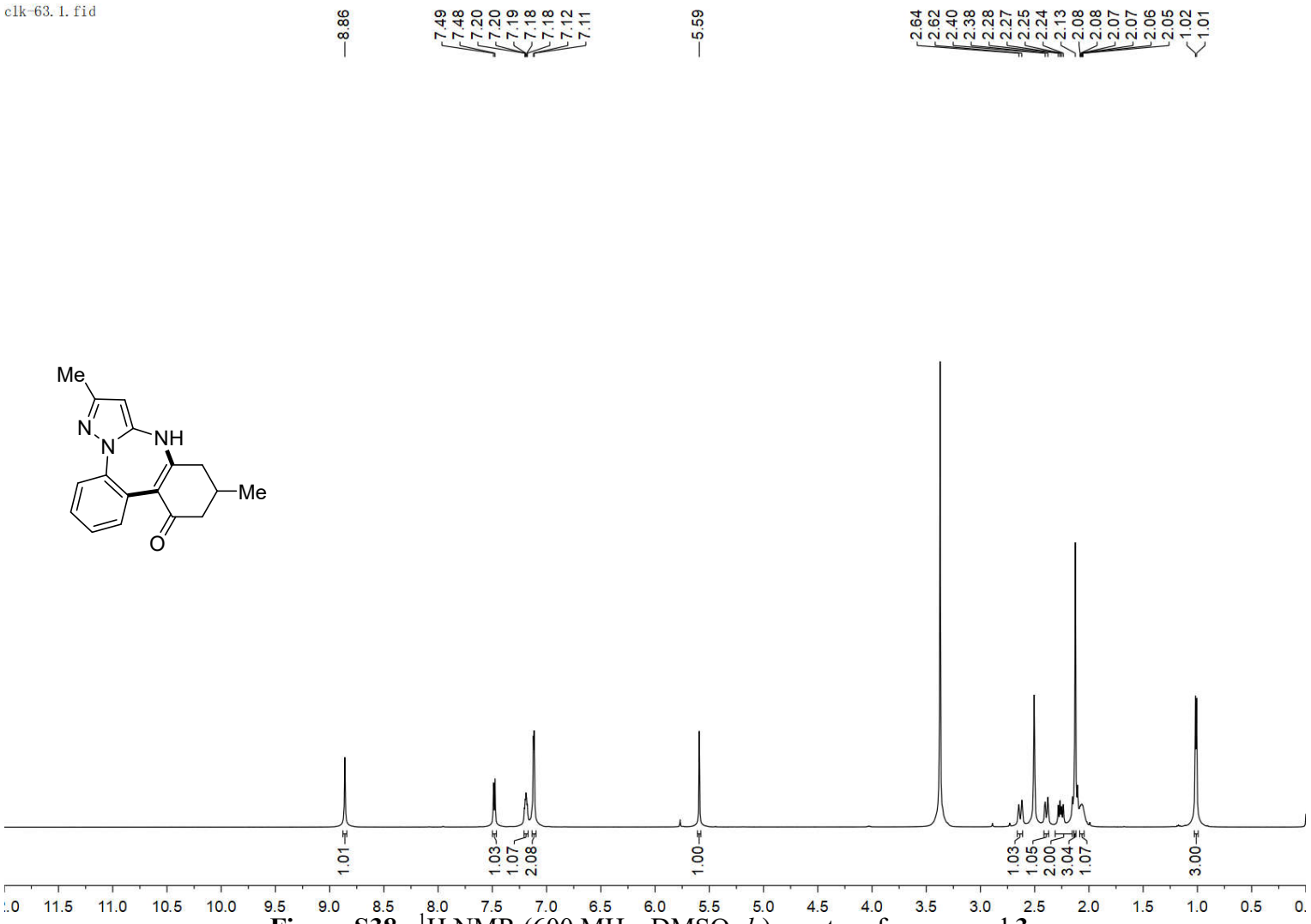


Figure S38. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3r**

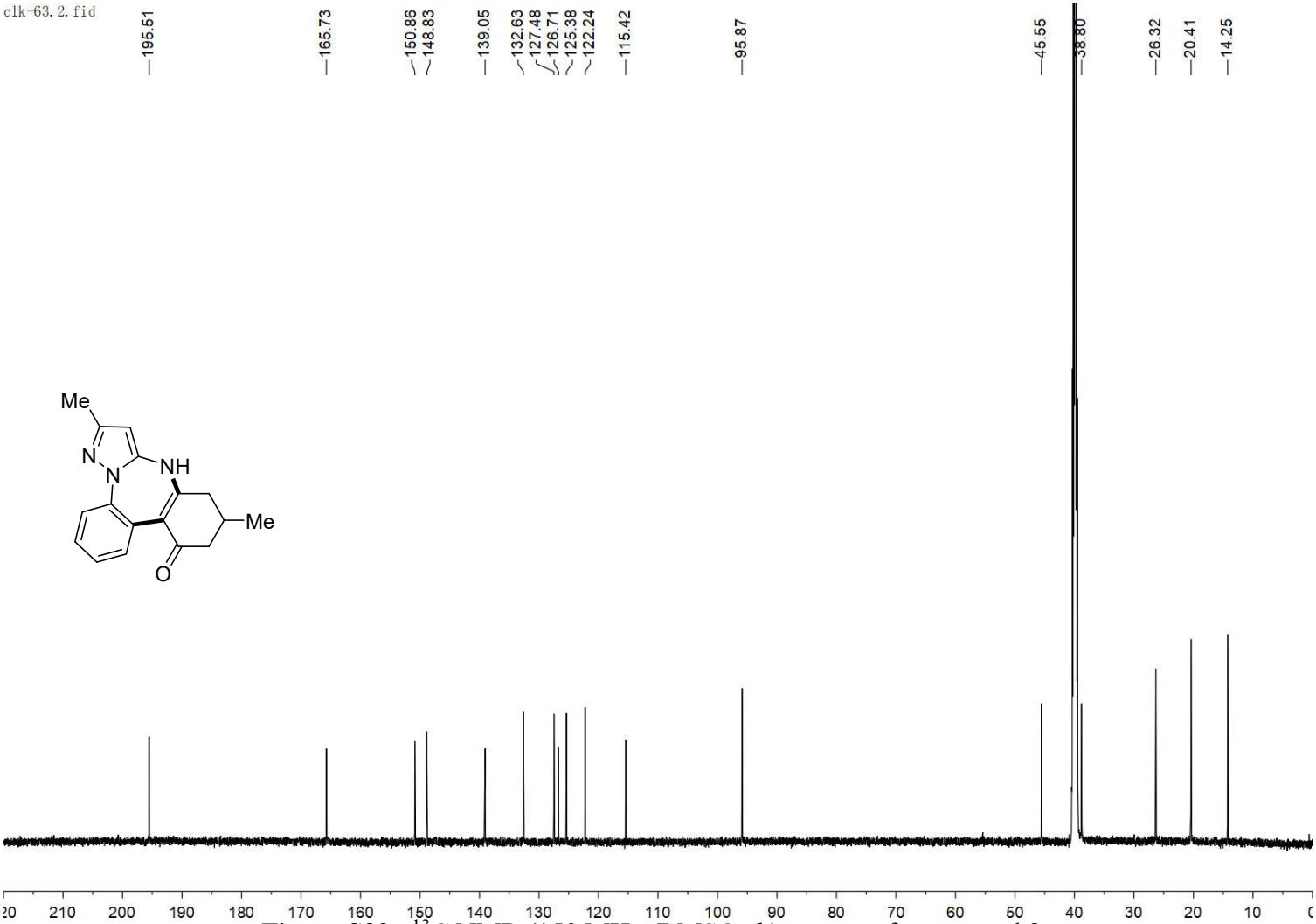


Figure S39. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3r**

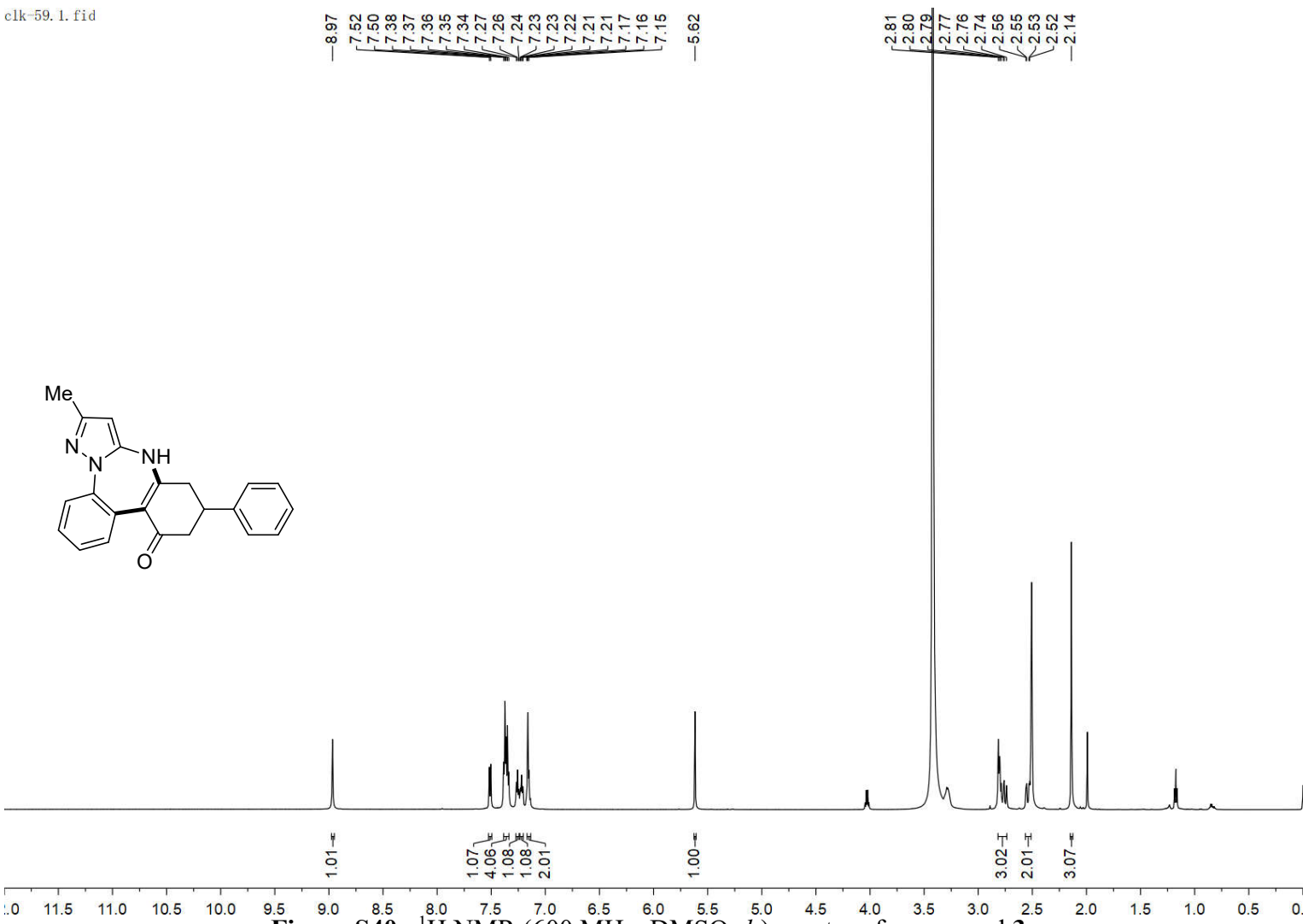


Figure S40. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3s**

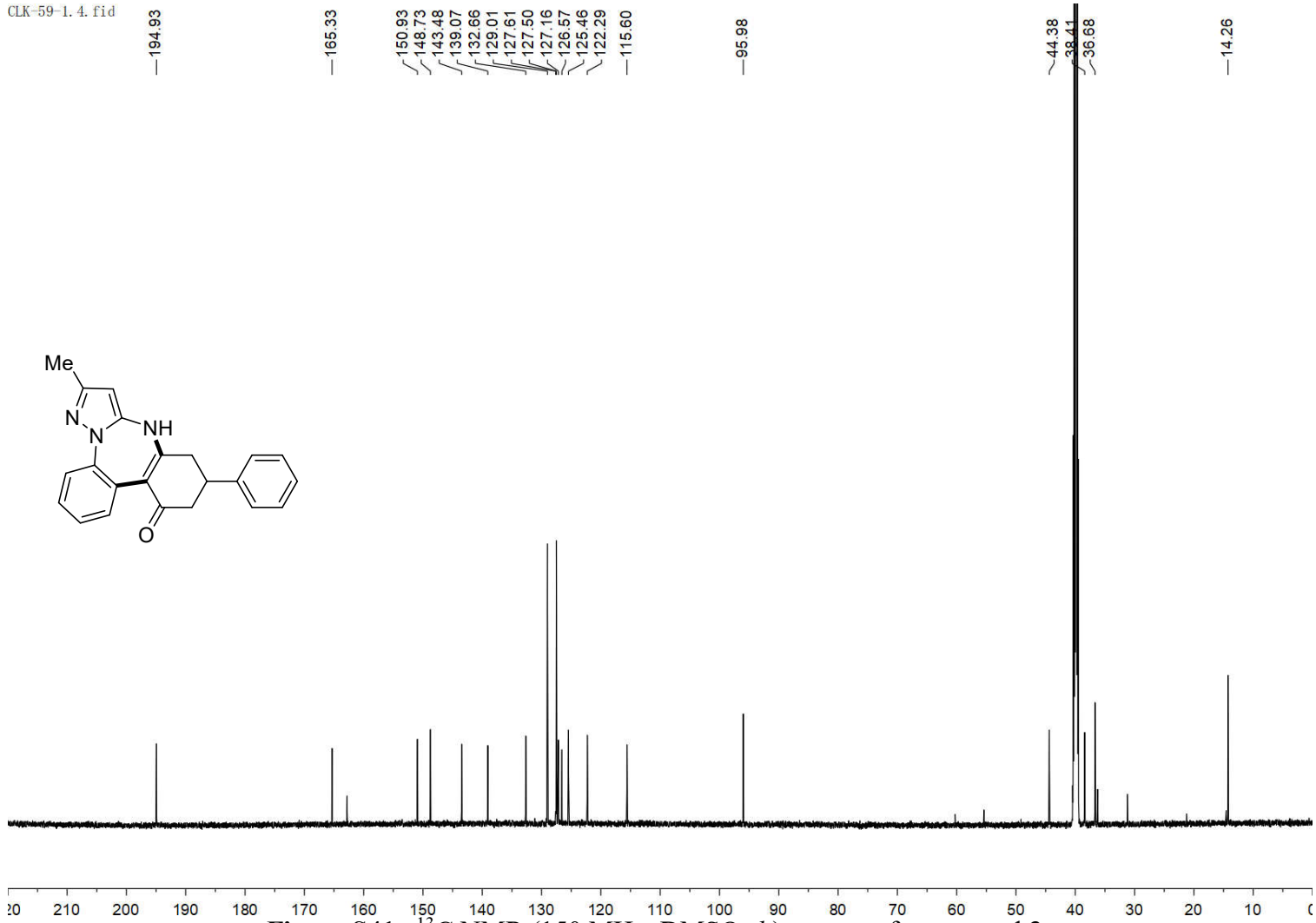


Figure S41. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3s**

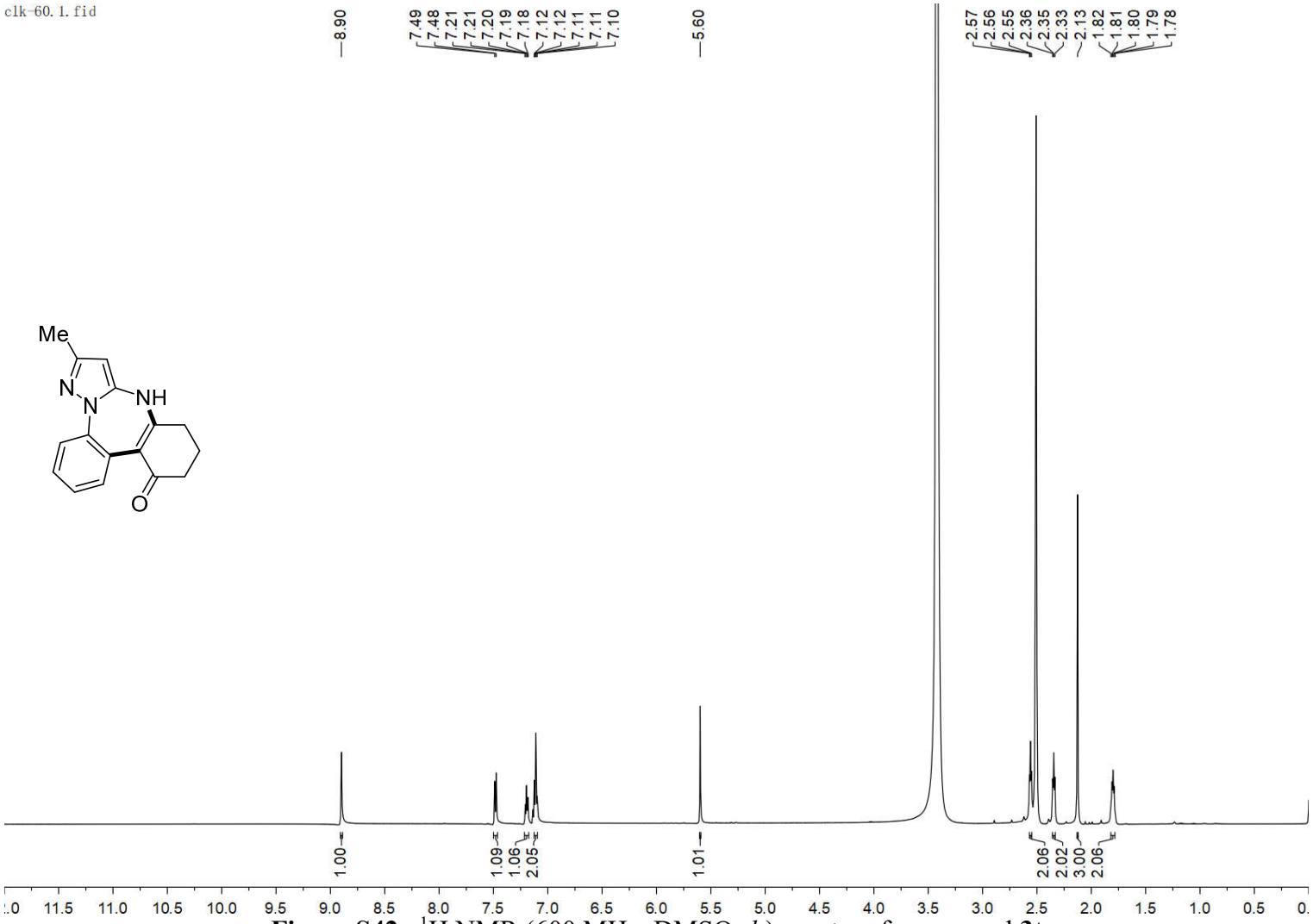


Figure S42. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3t**

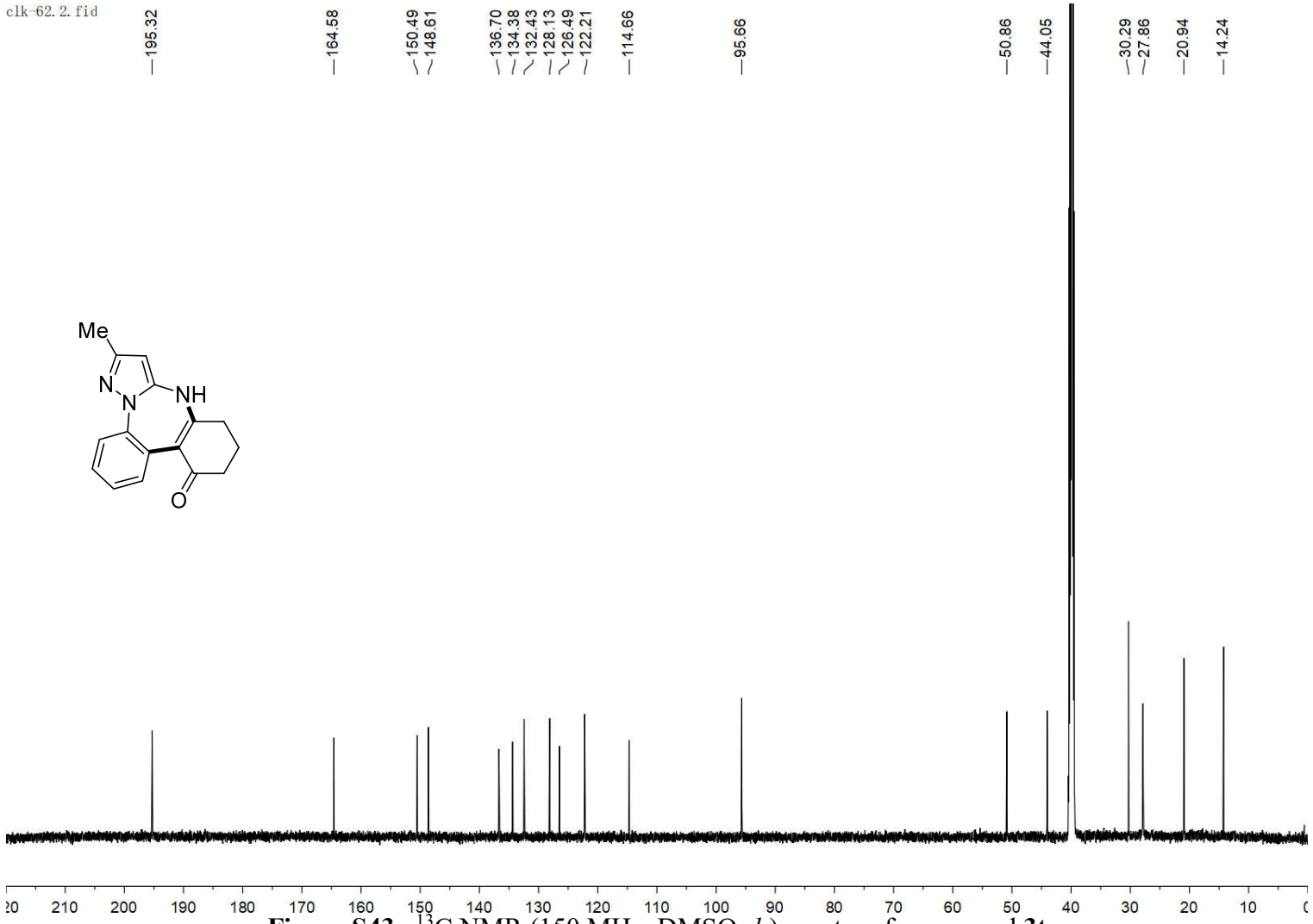


Figure S43. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3t**

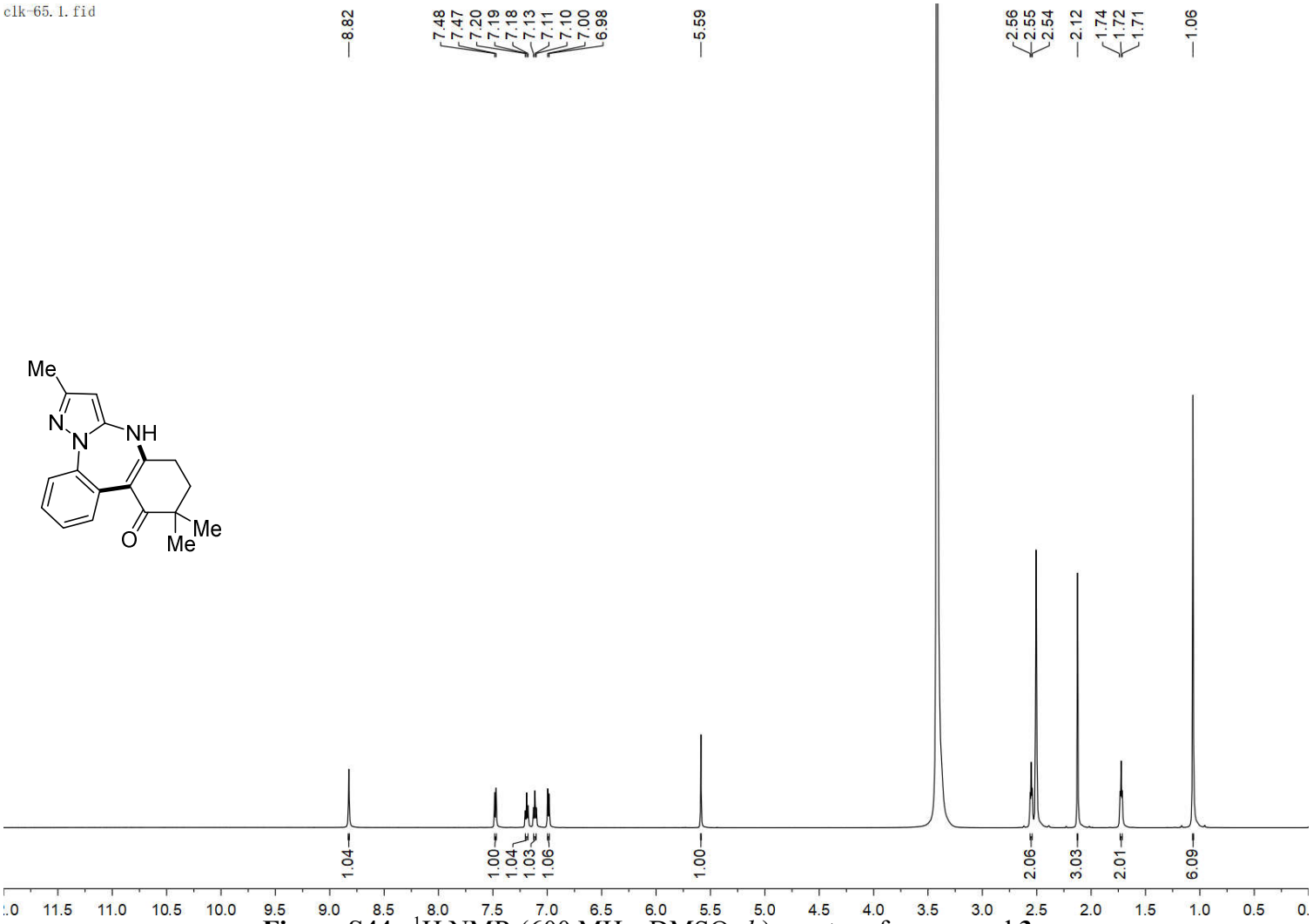


Figure S44. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3u**

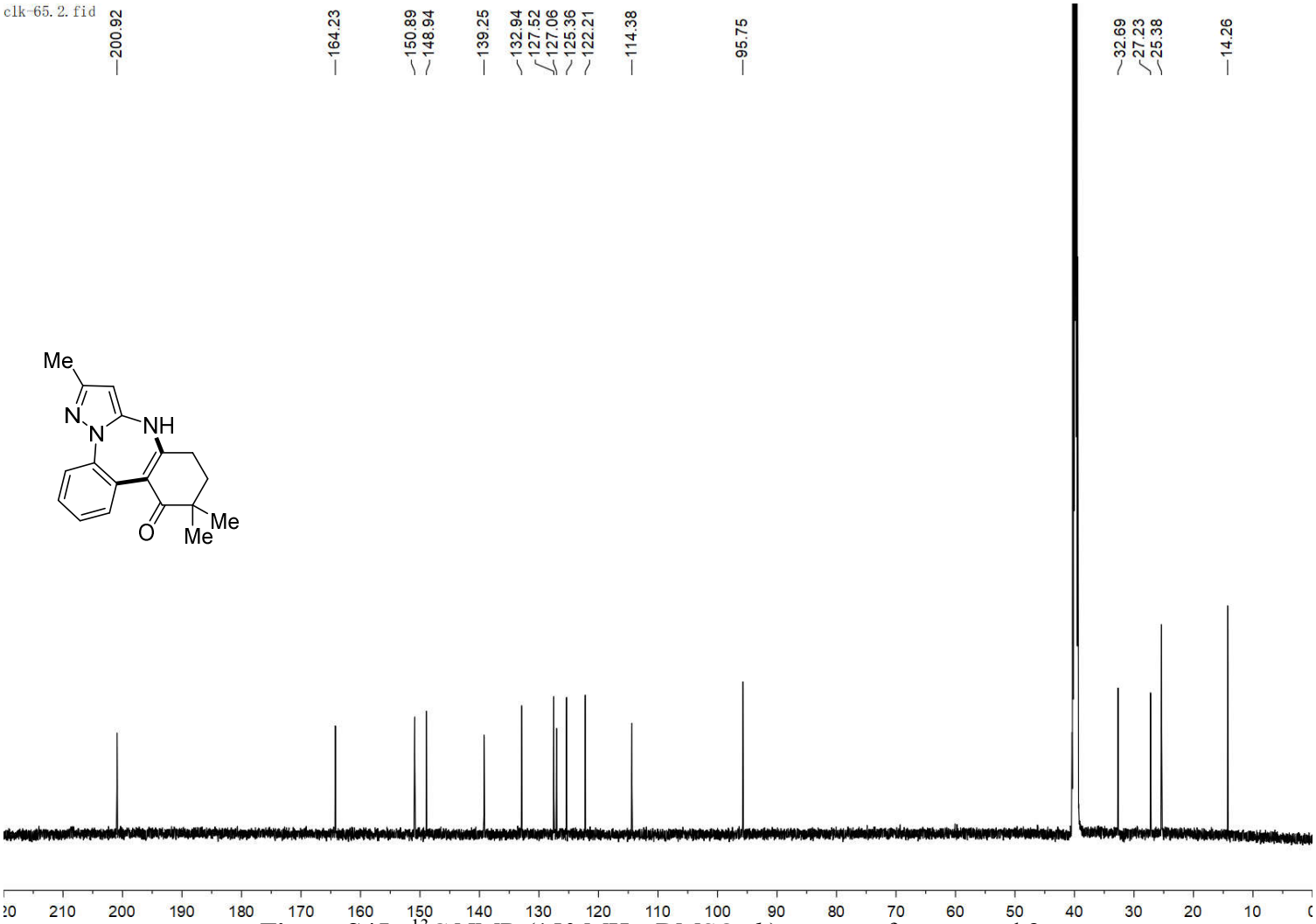


Figure S45. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3u**

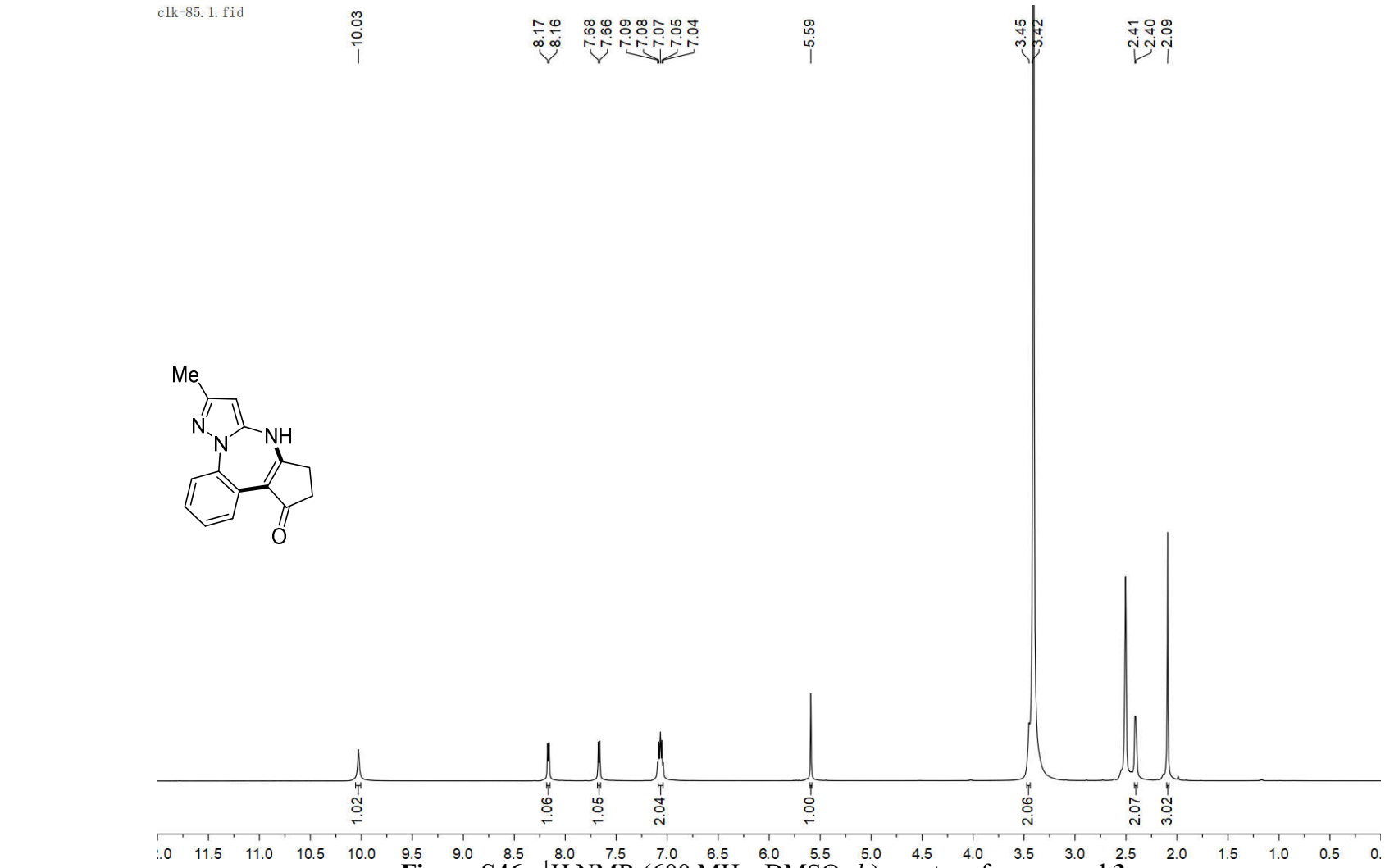


Figure S46. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3v**

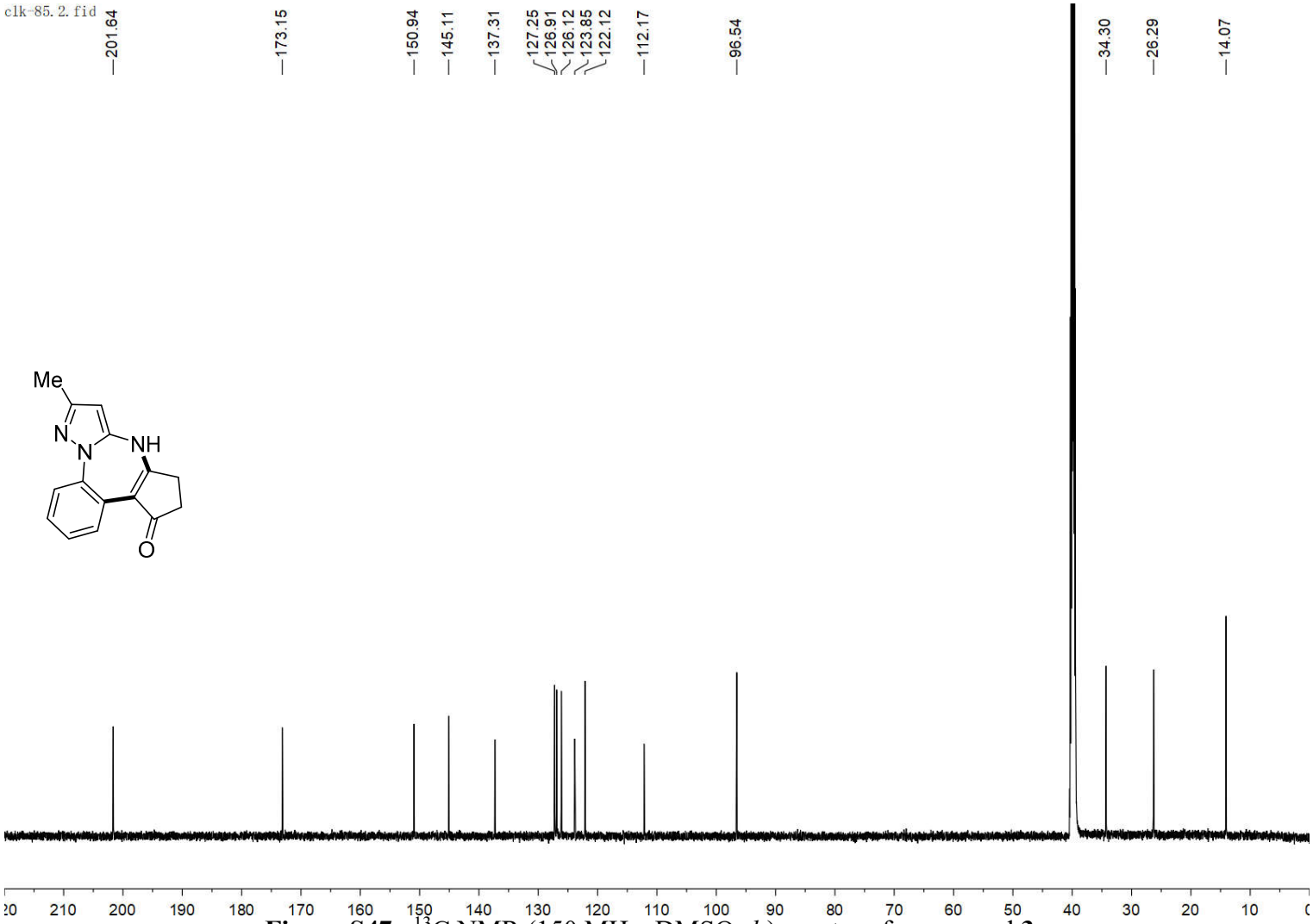


Figure S47. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3v**

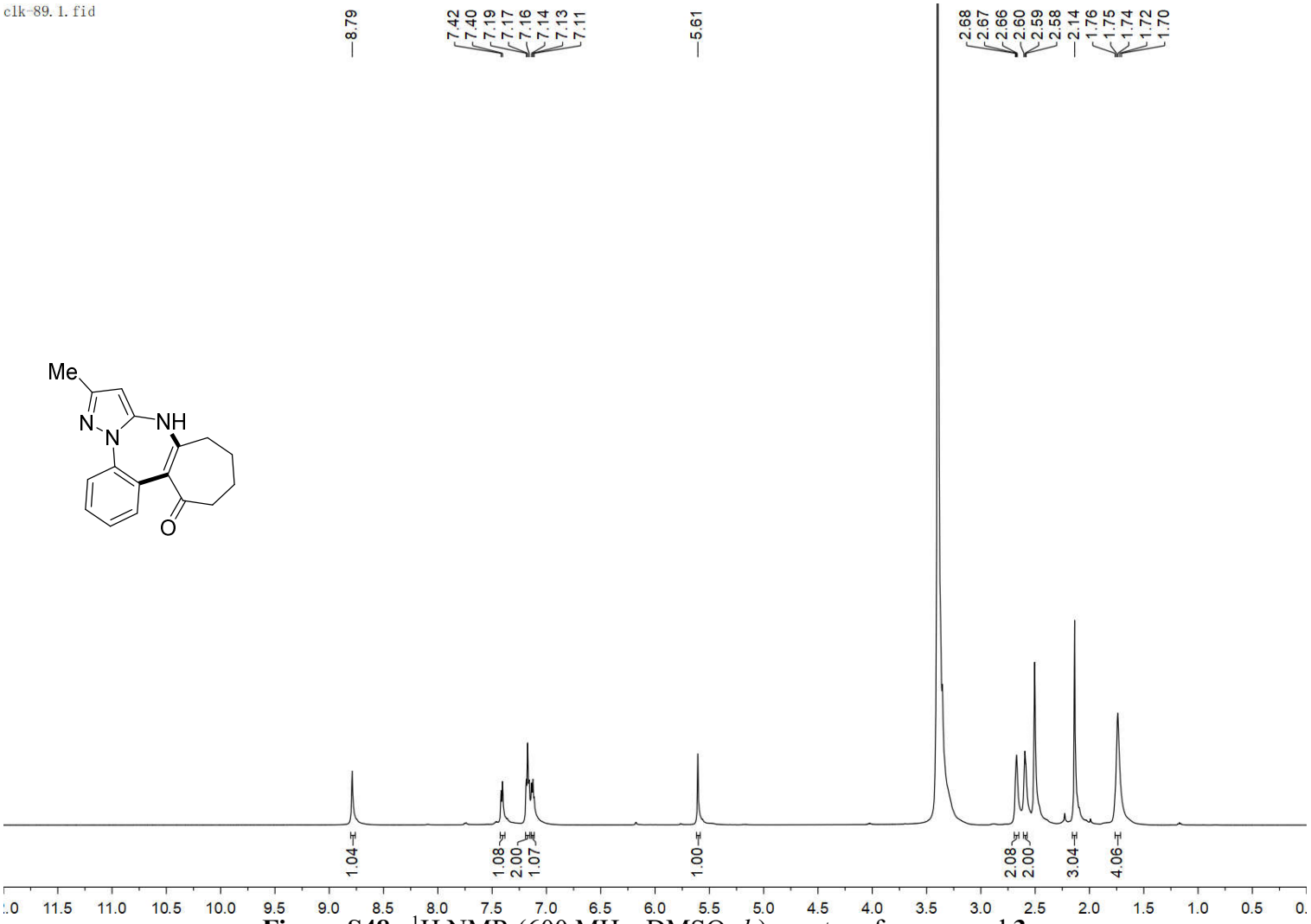


Figure S48. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3w**

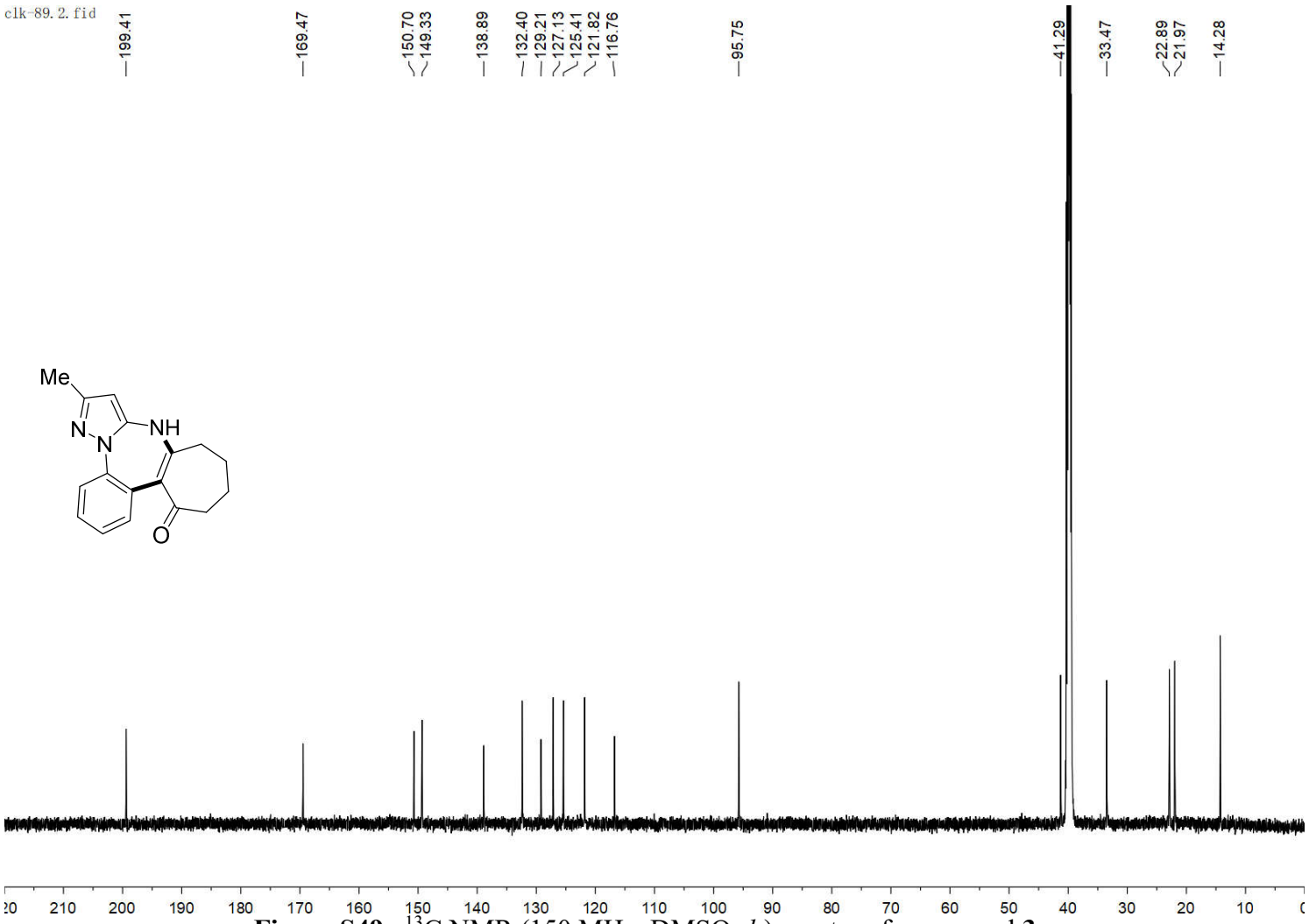


Figure S49. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3w**

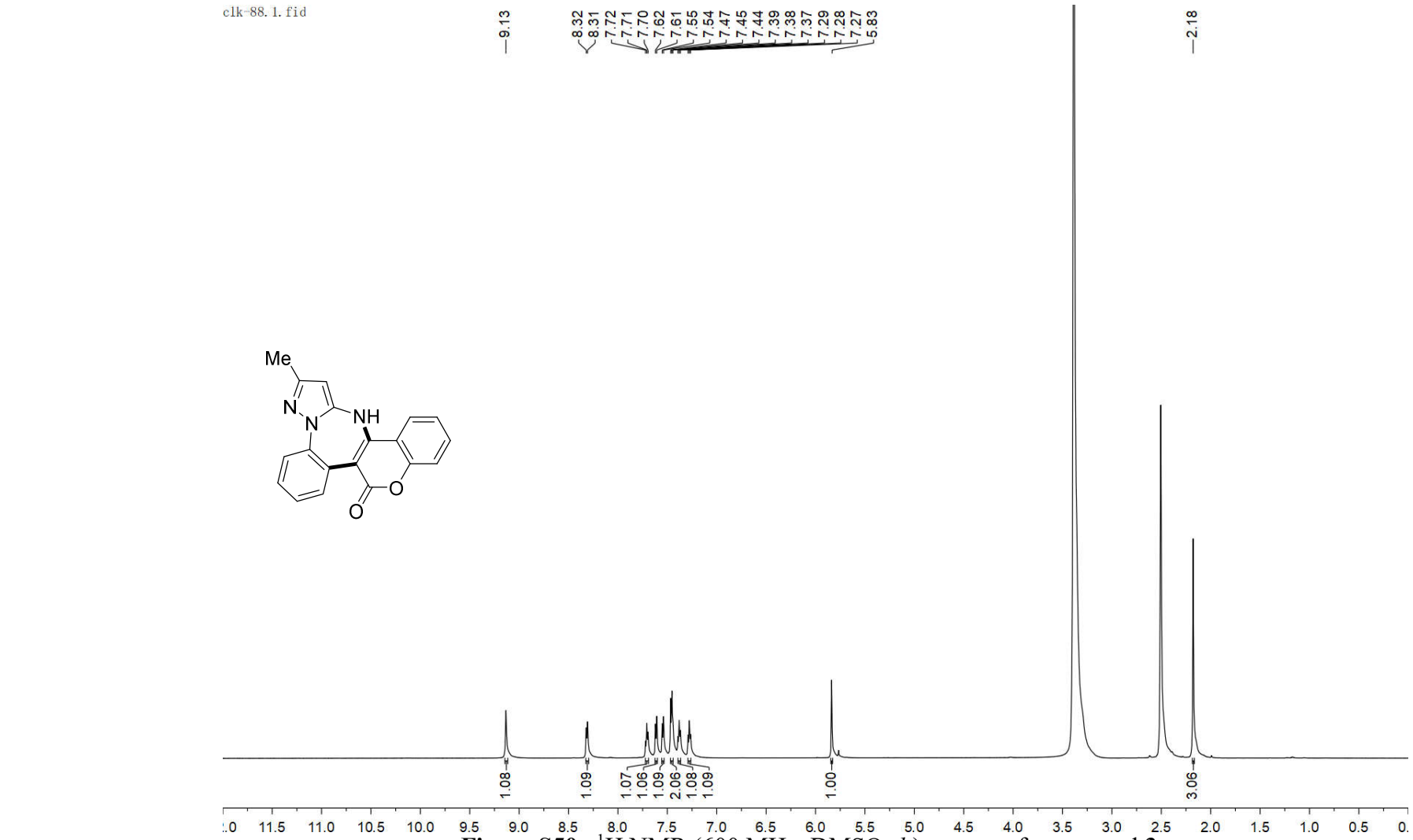


Figure S50. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3x**

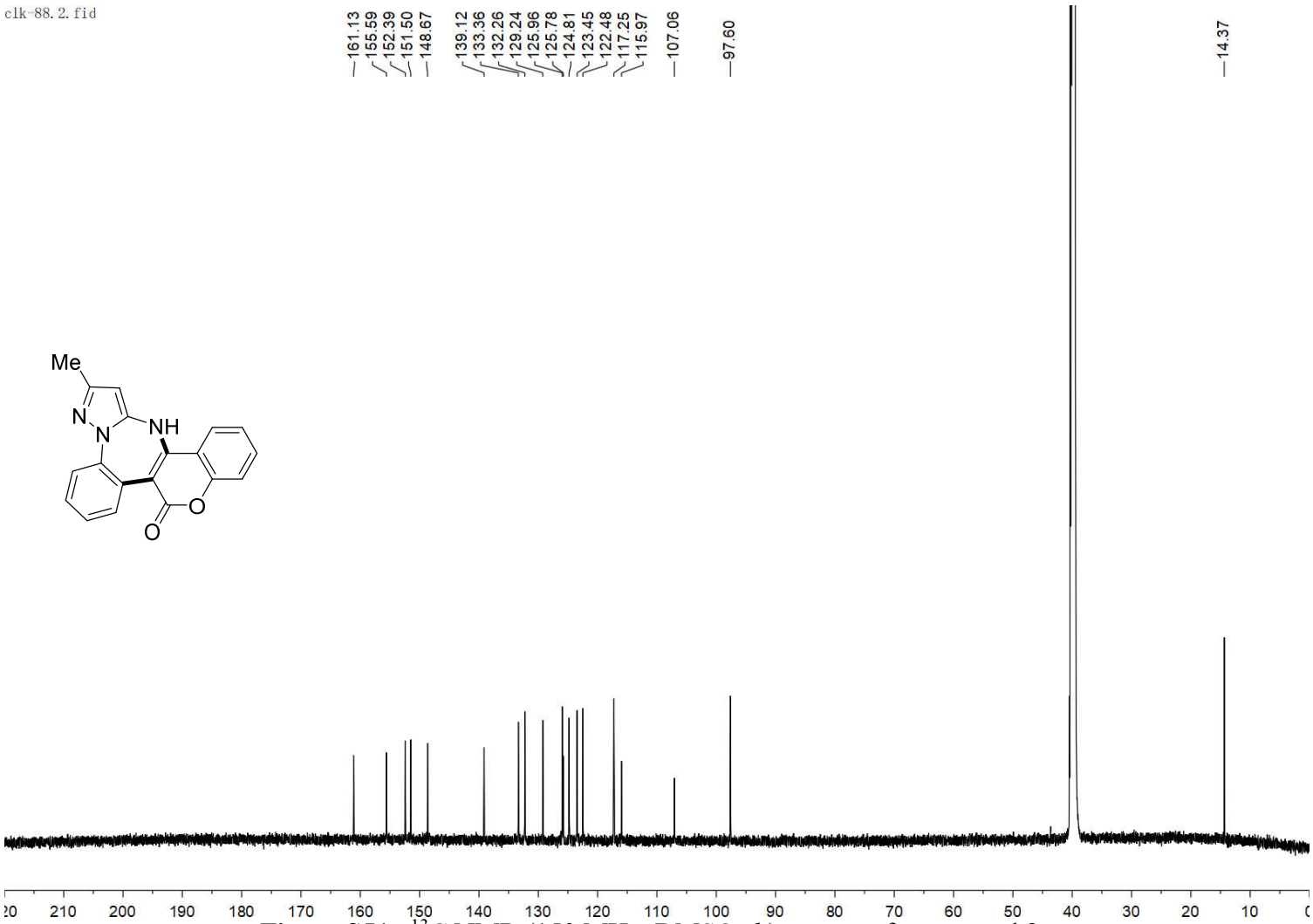


Figure S51. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3x**

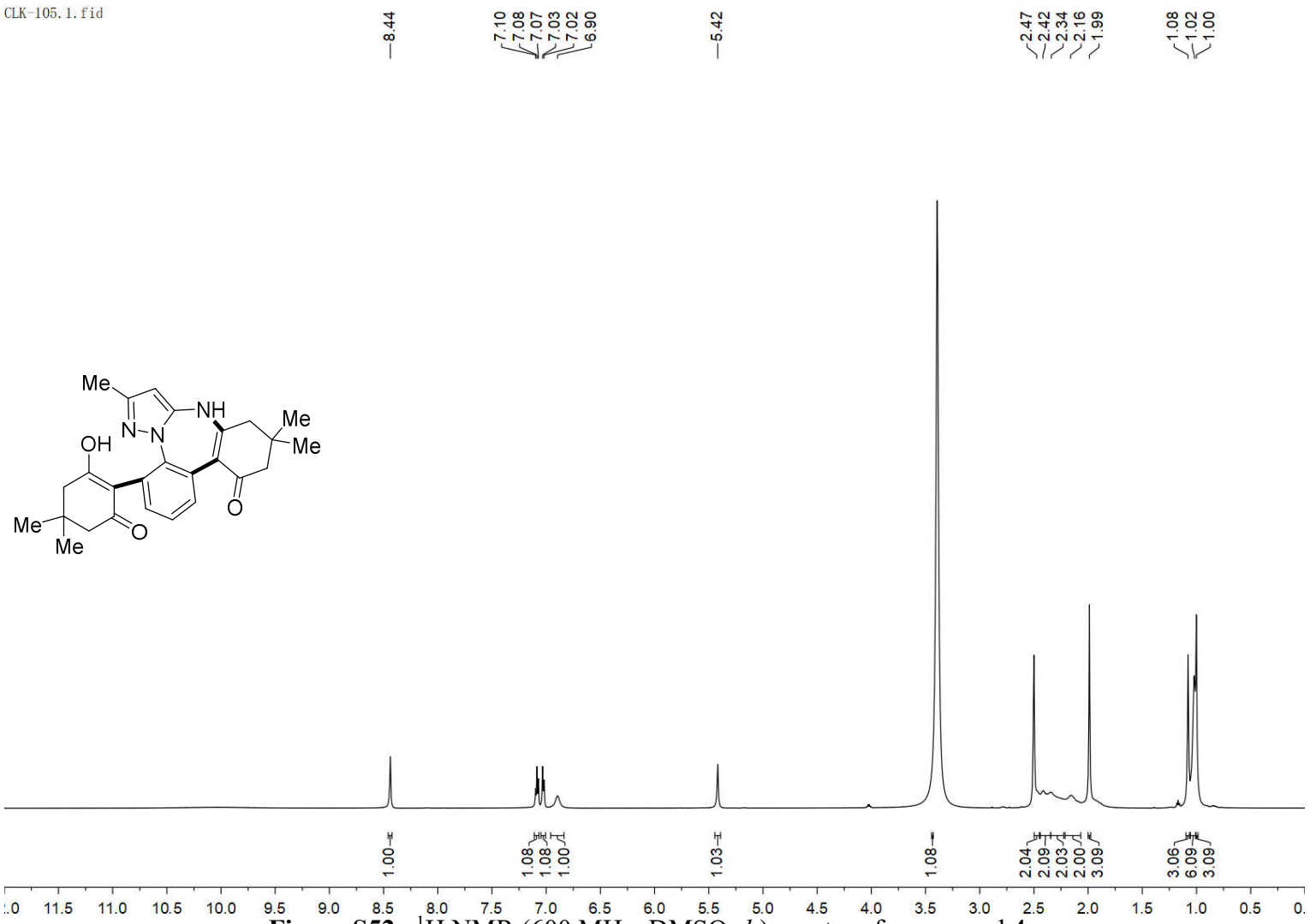


Figure S52. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4a**

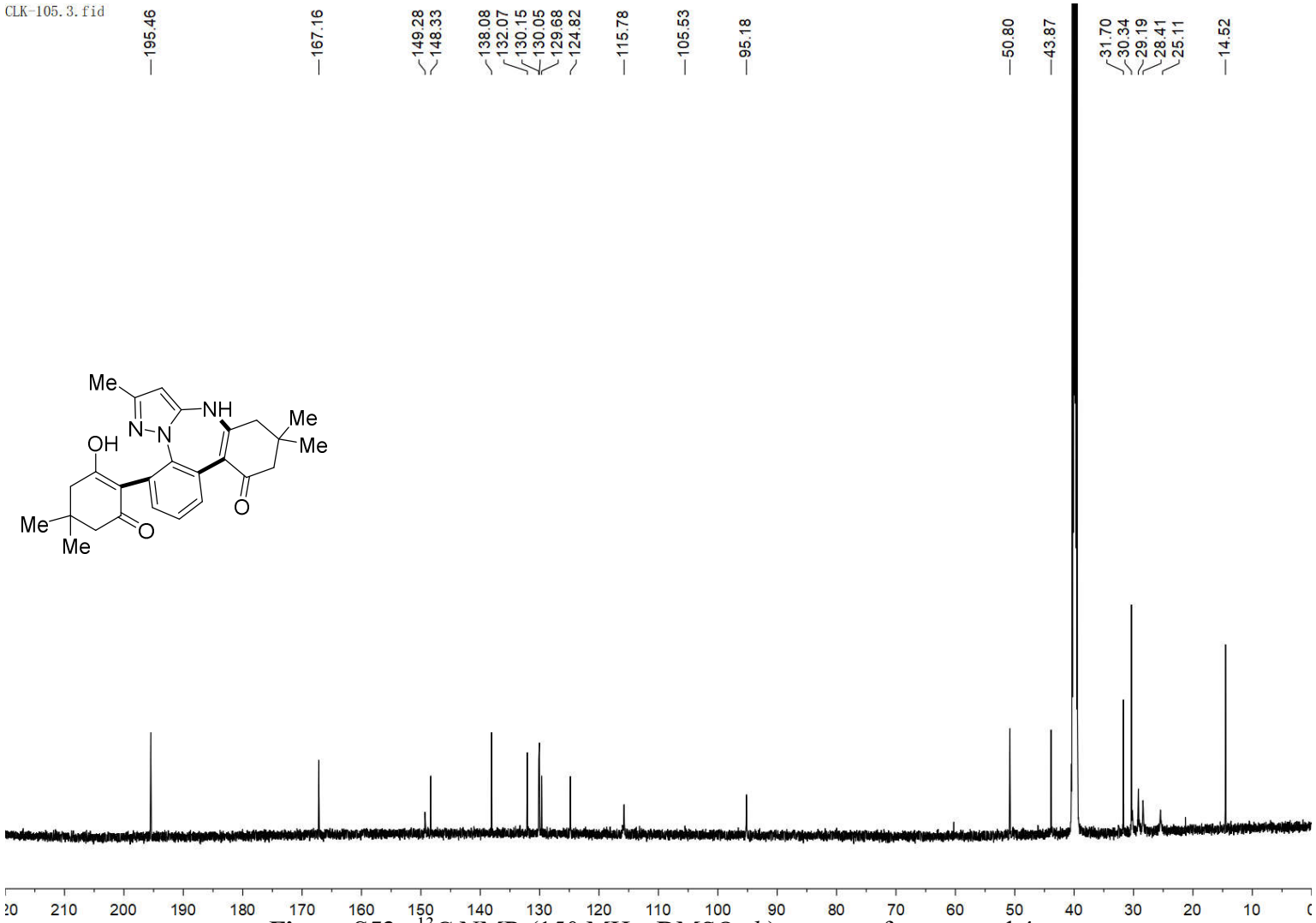


Figure S53. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4a**

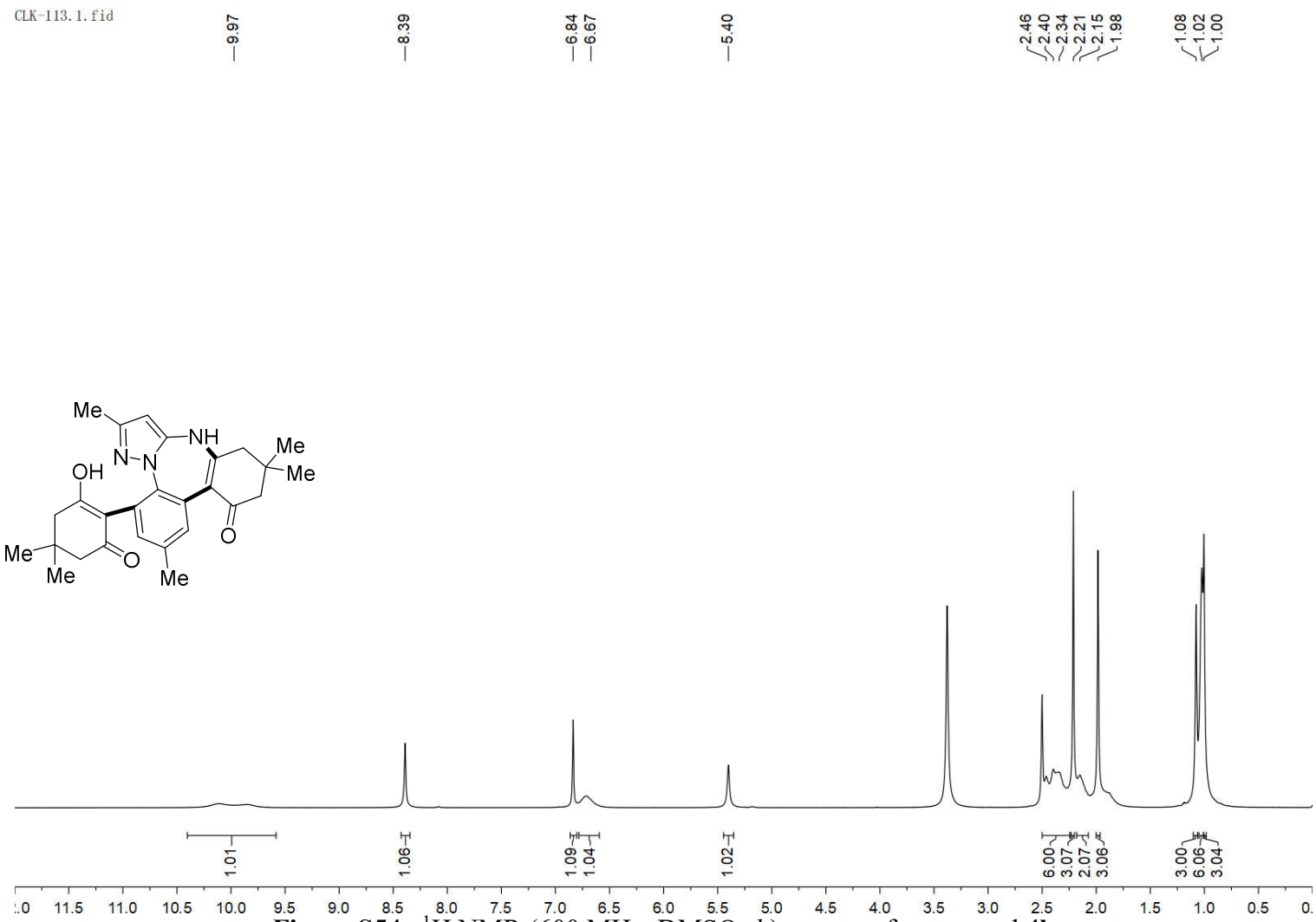


Figure S54. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4b**

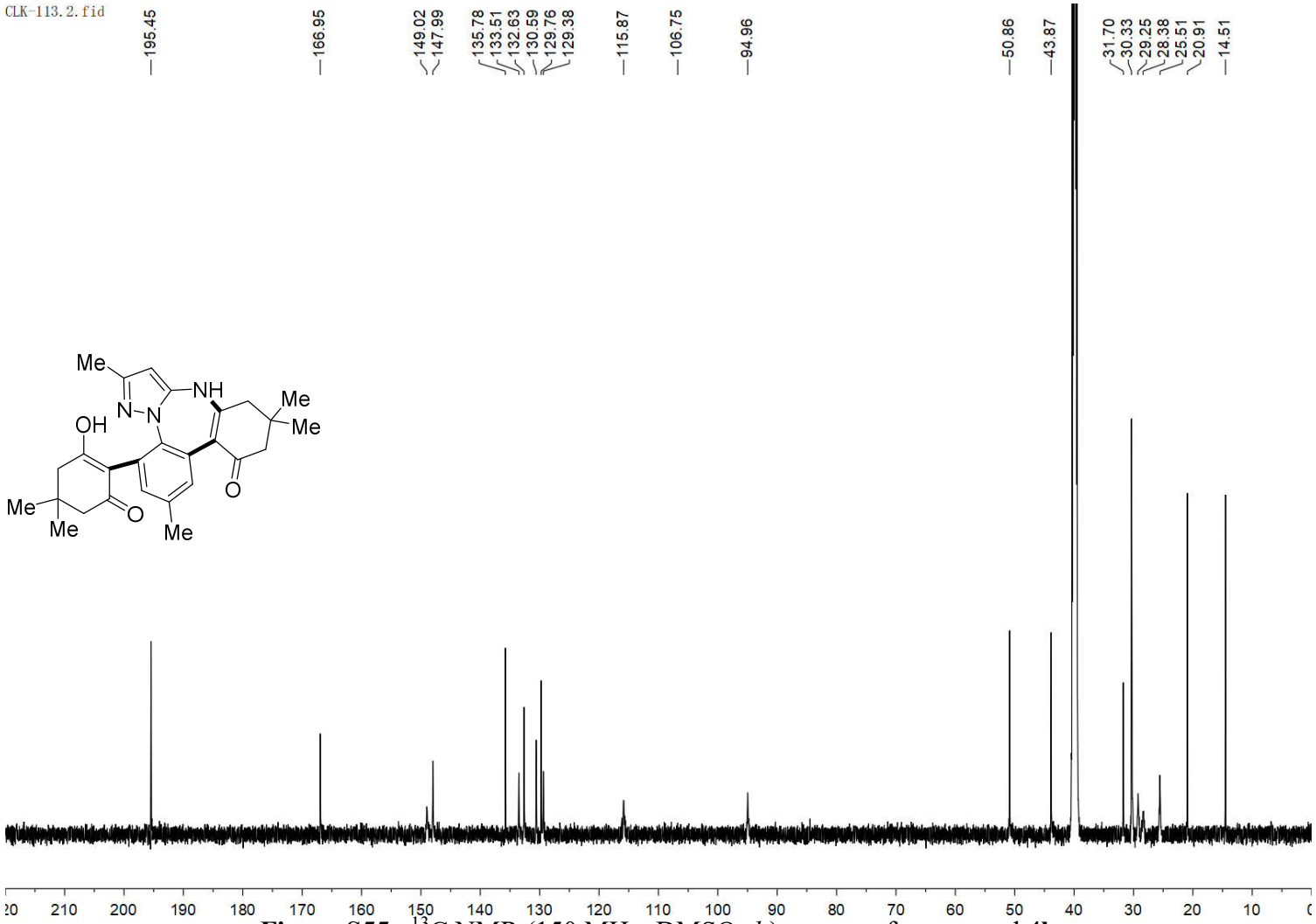


Figure S55. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4b**

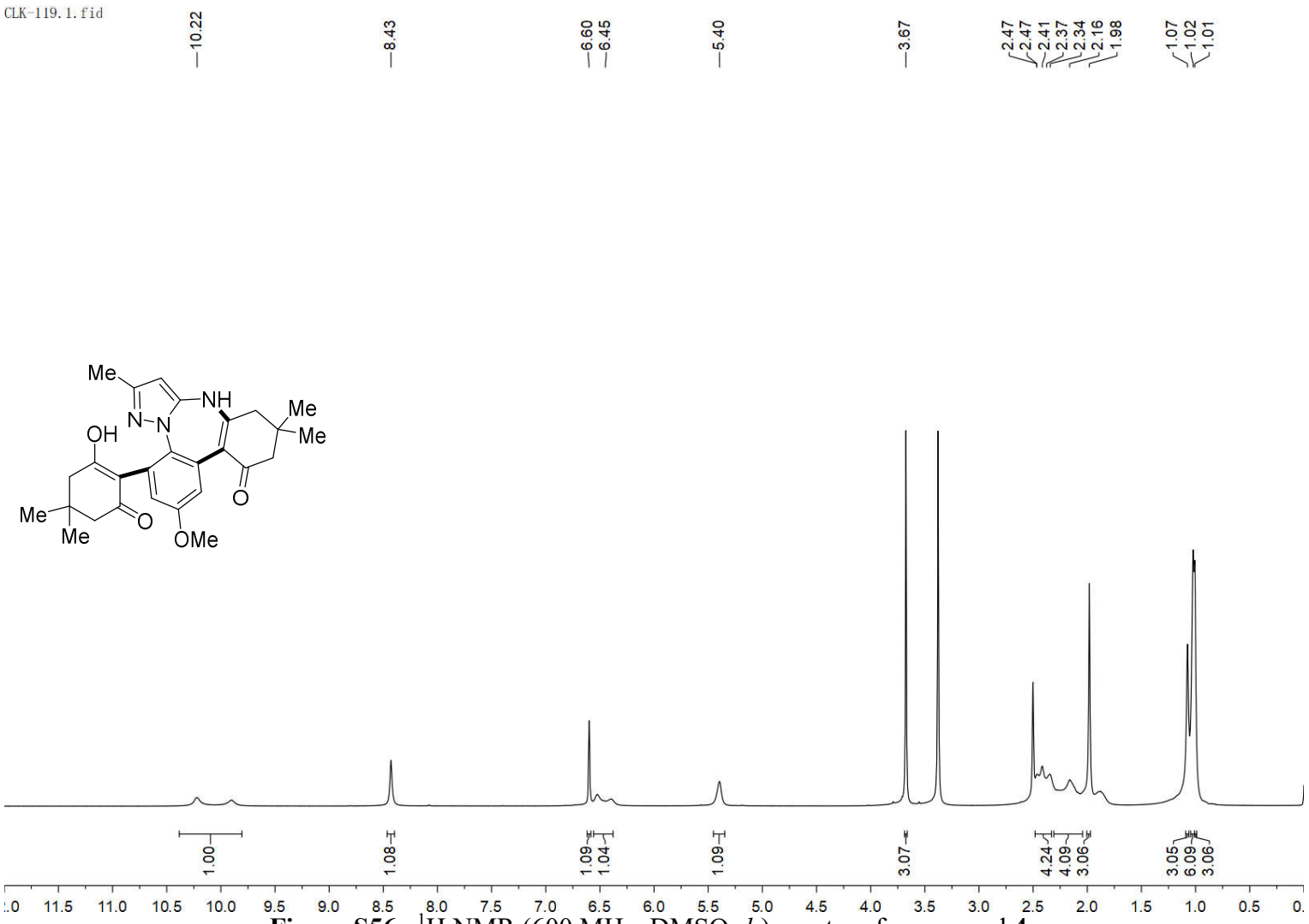


Figure S56. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4c**

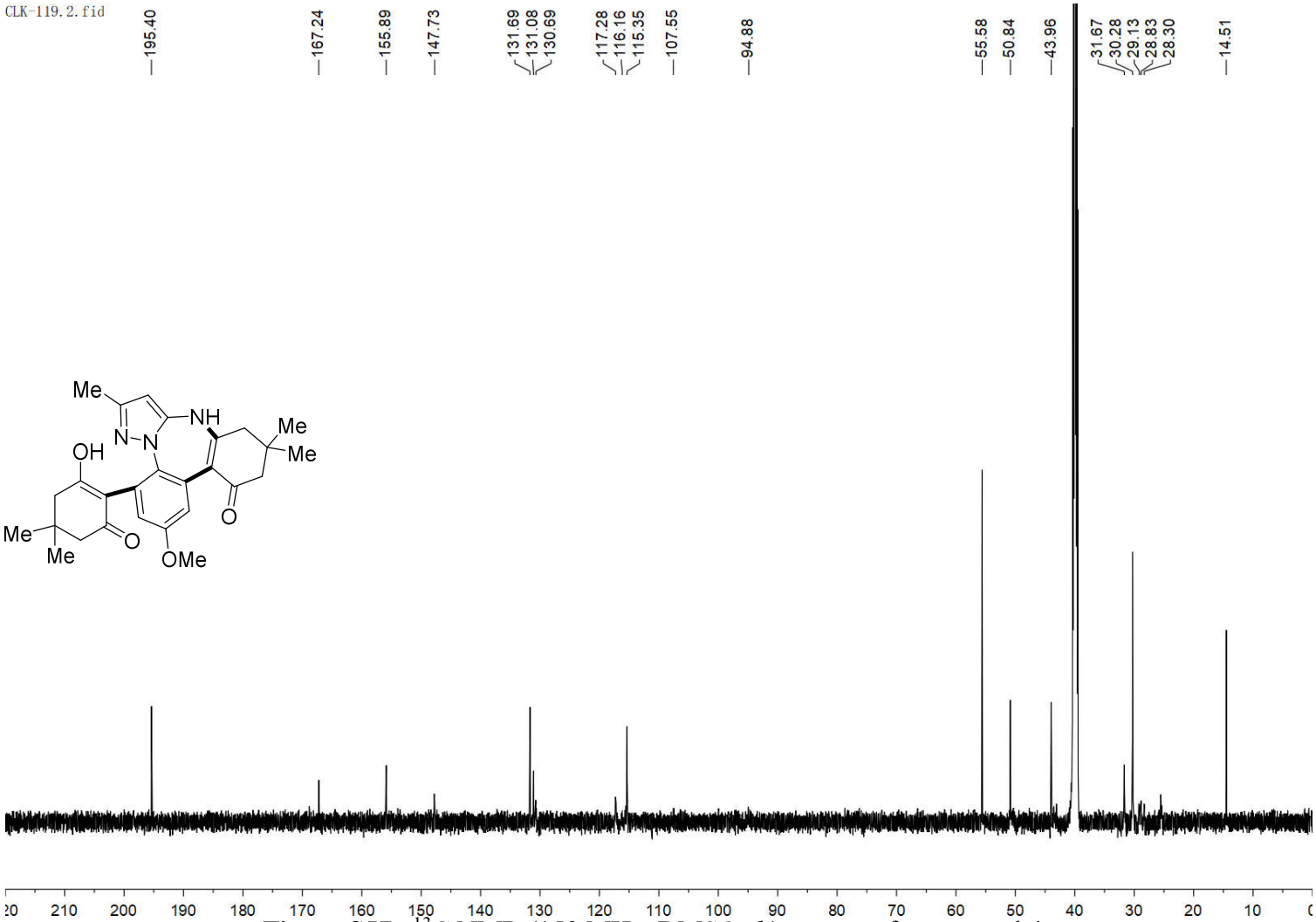


Figure S57. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4c**

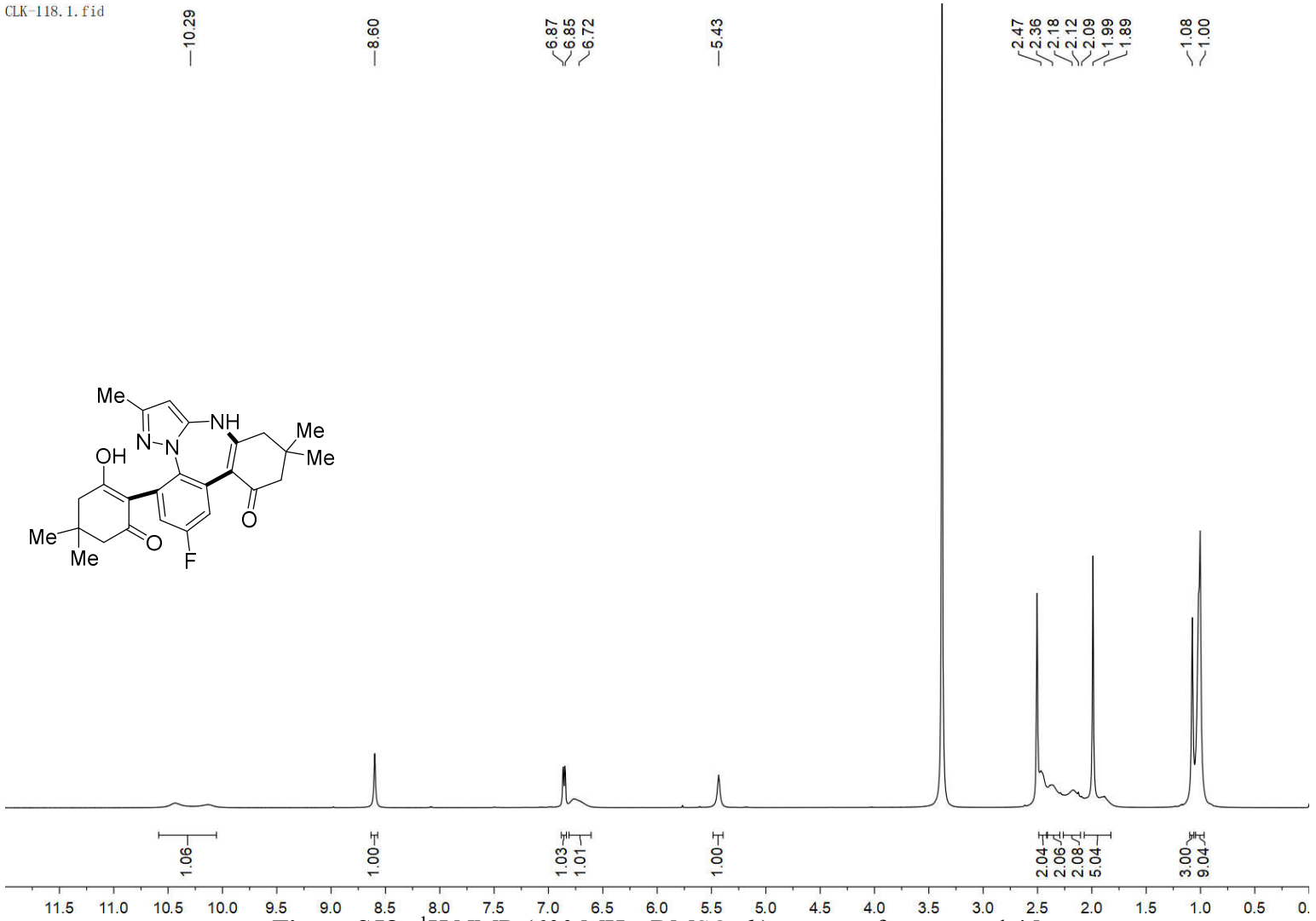


Figure S58. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4d**

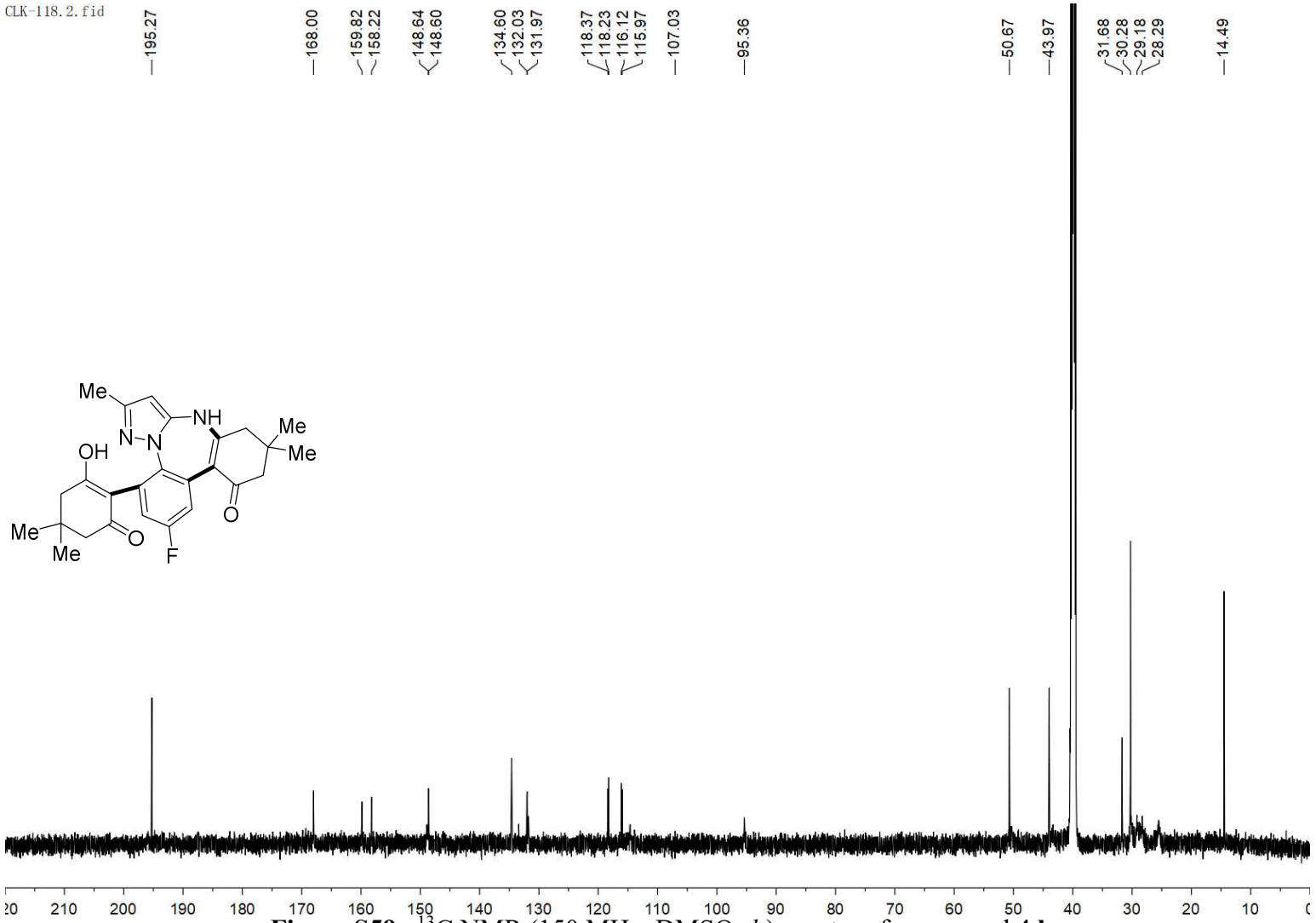


Figure S59. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4d**

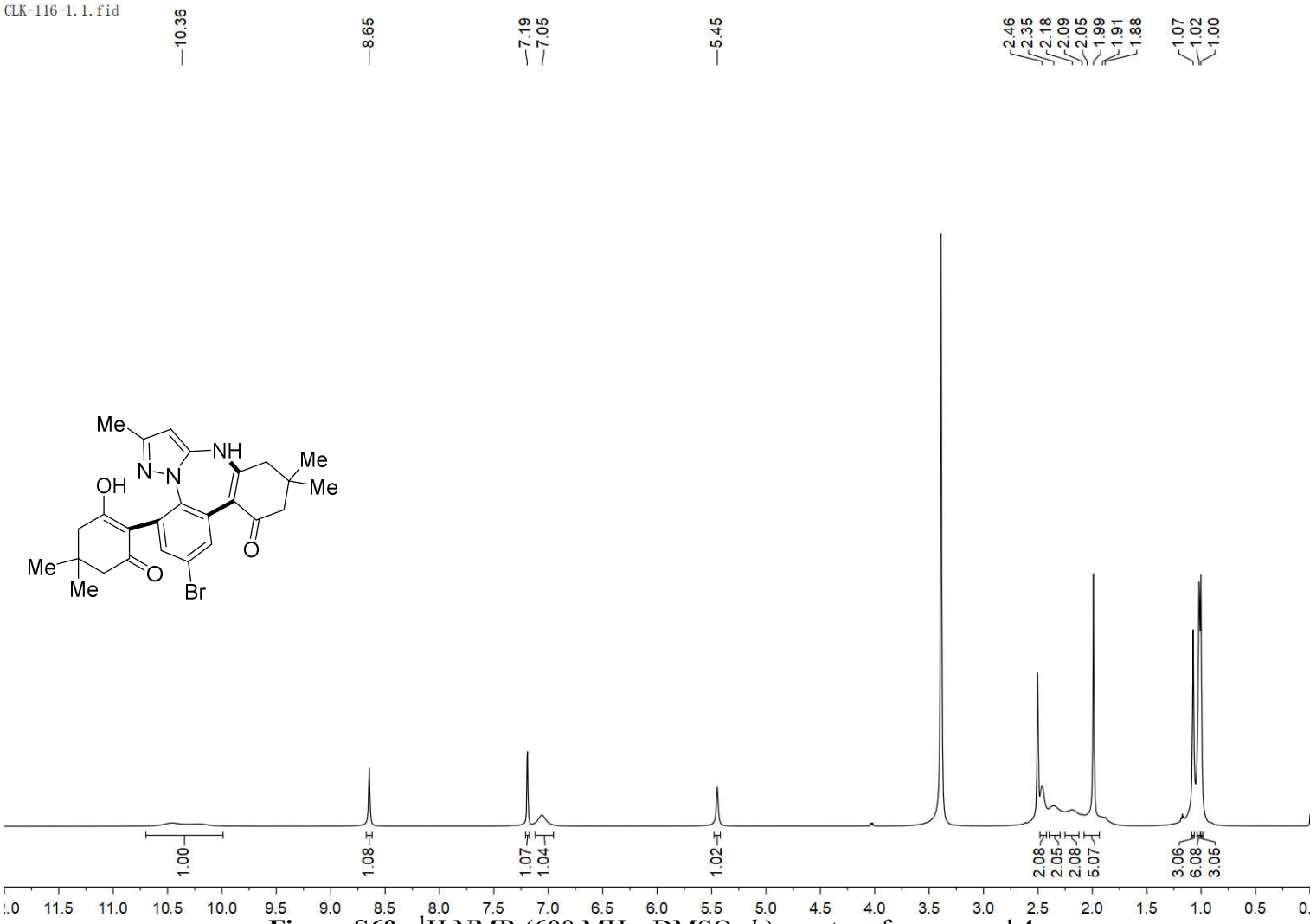


Figure S60. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4e**

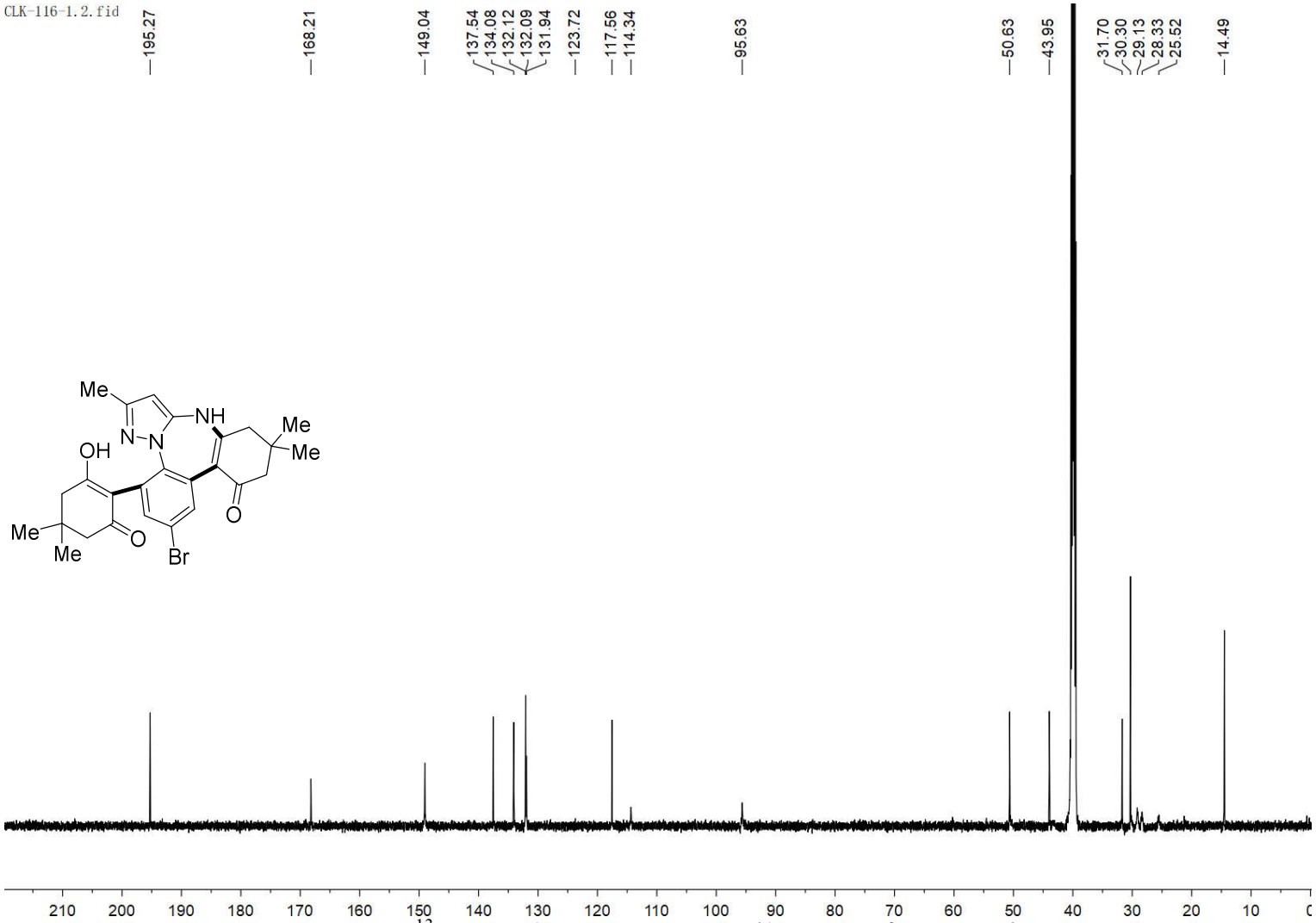


Figure S61. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4e**

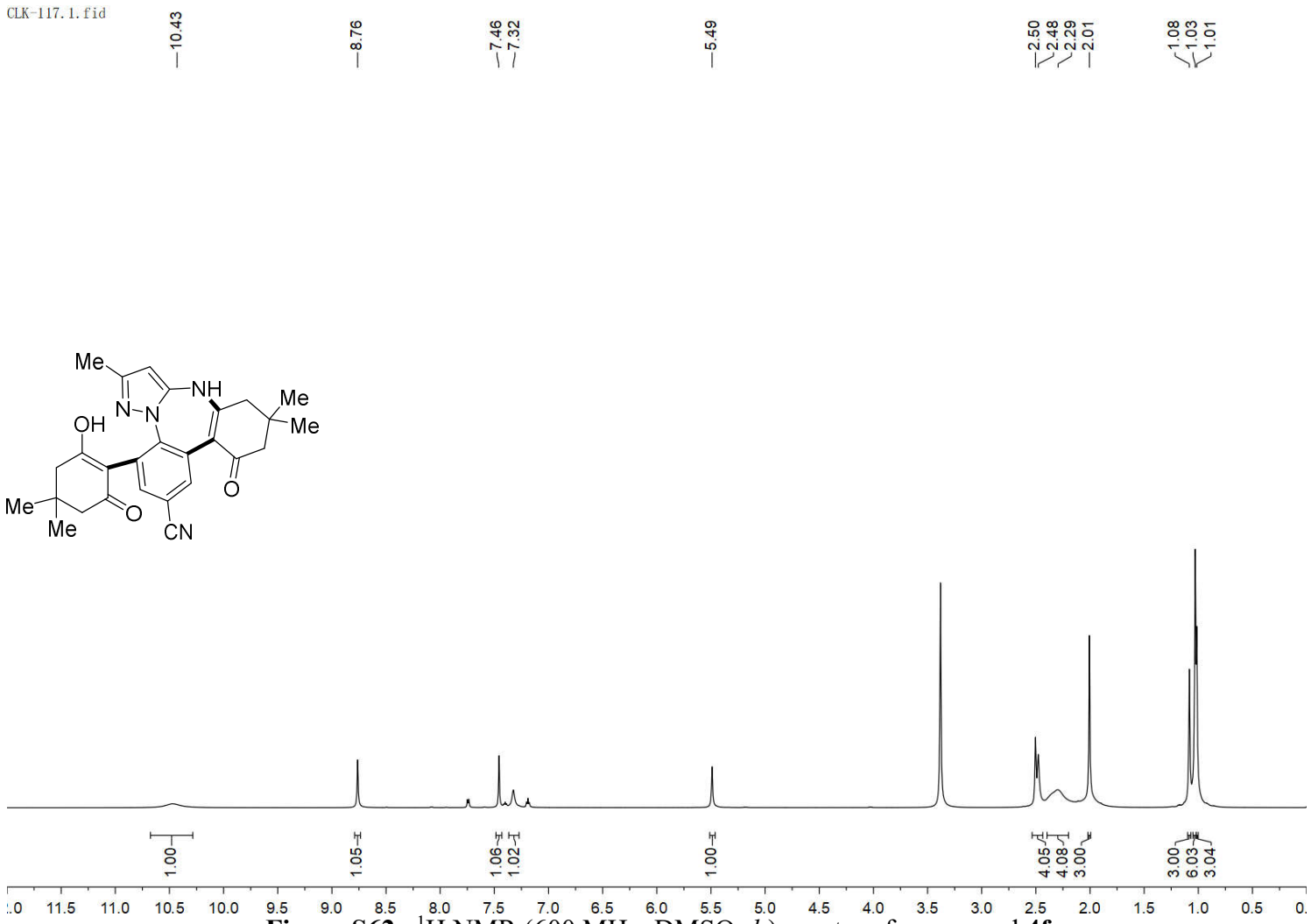


Figure S62. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4f**

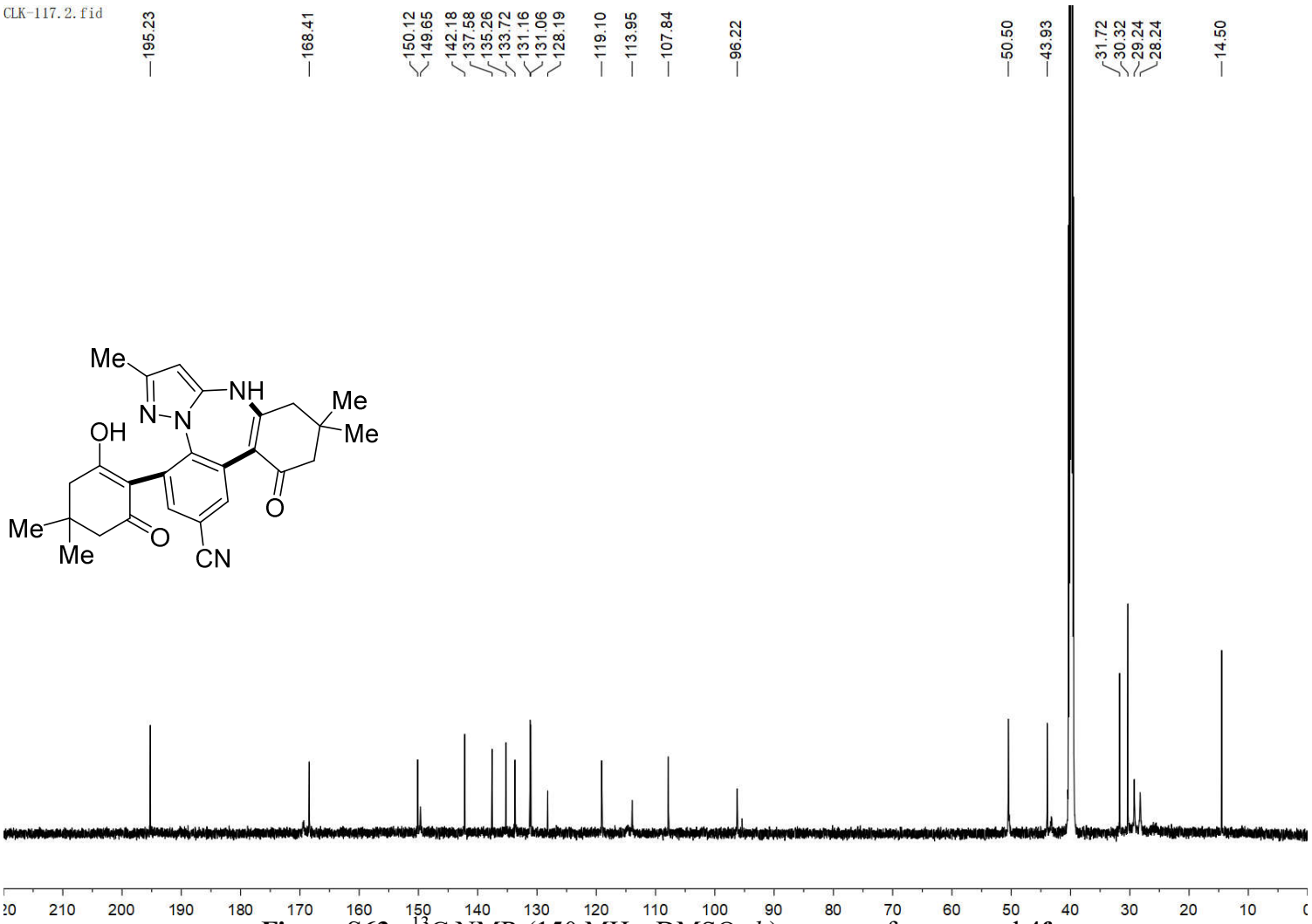


Figure S63. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4f**

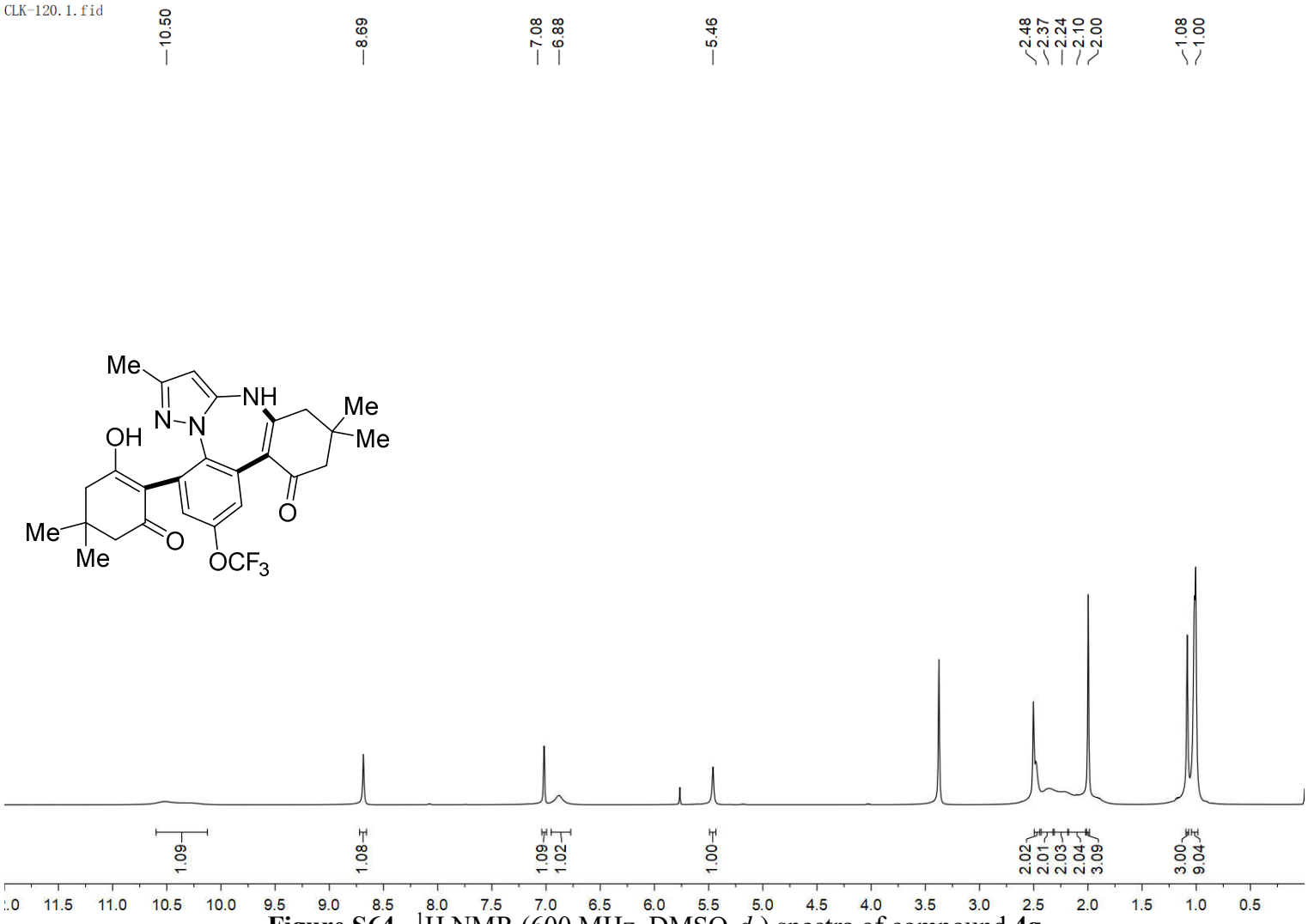


Figure S64. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4g**

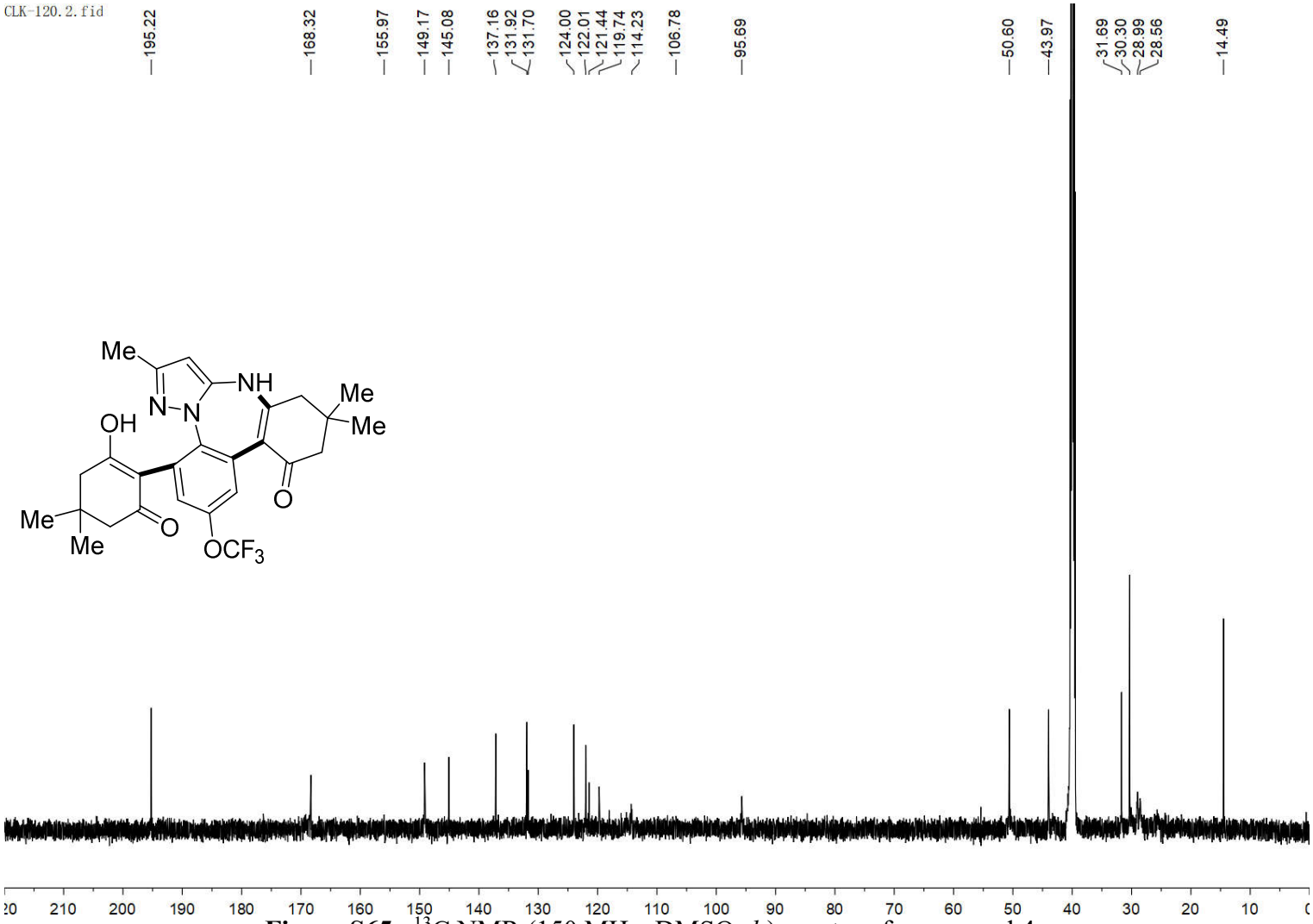


Figure S65. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4g**

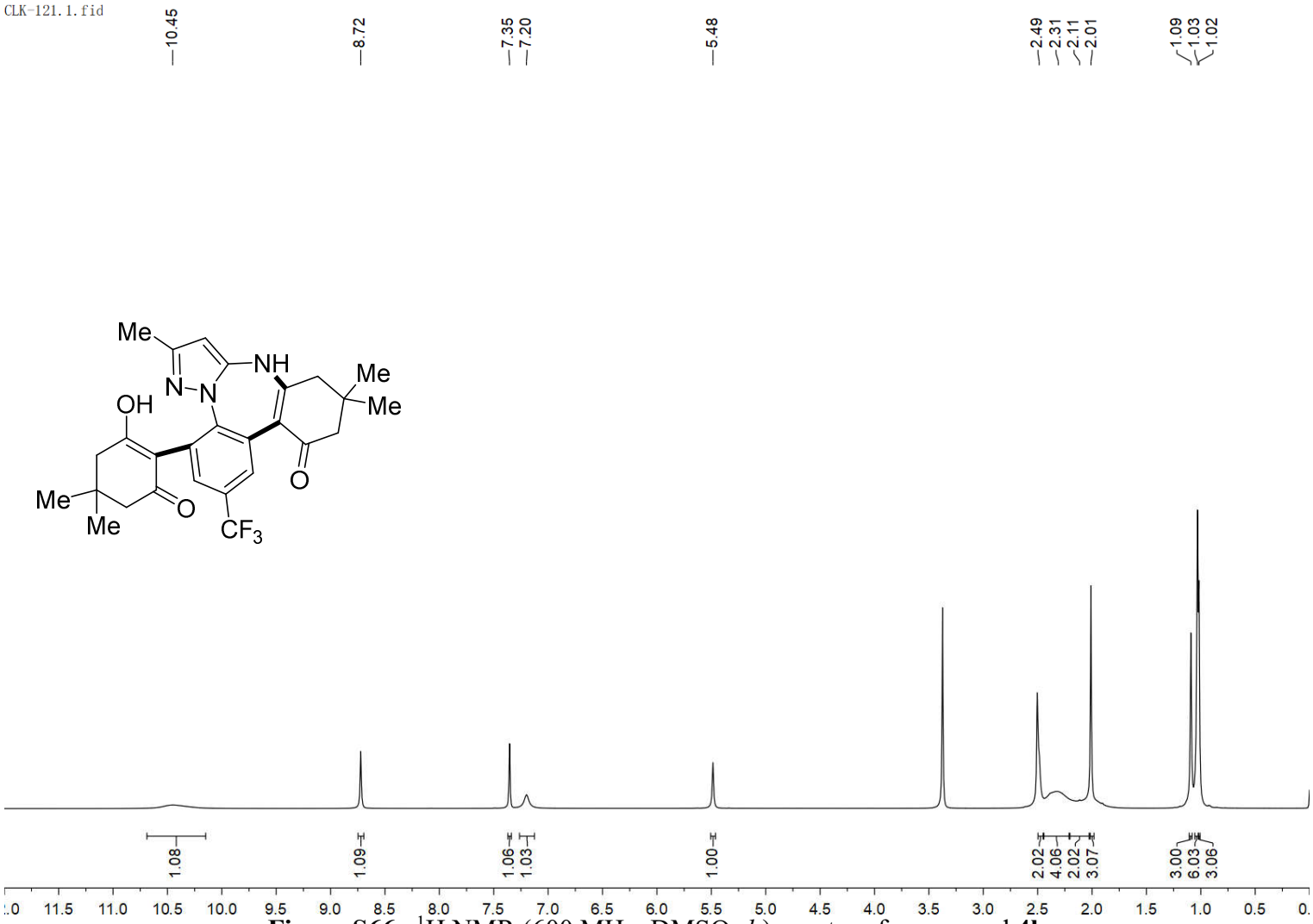


Figure S66. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4h**

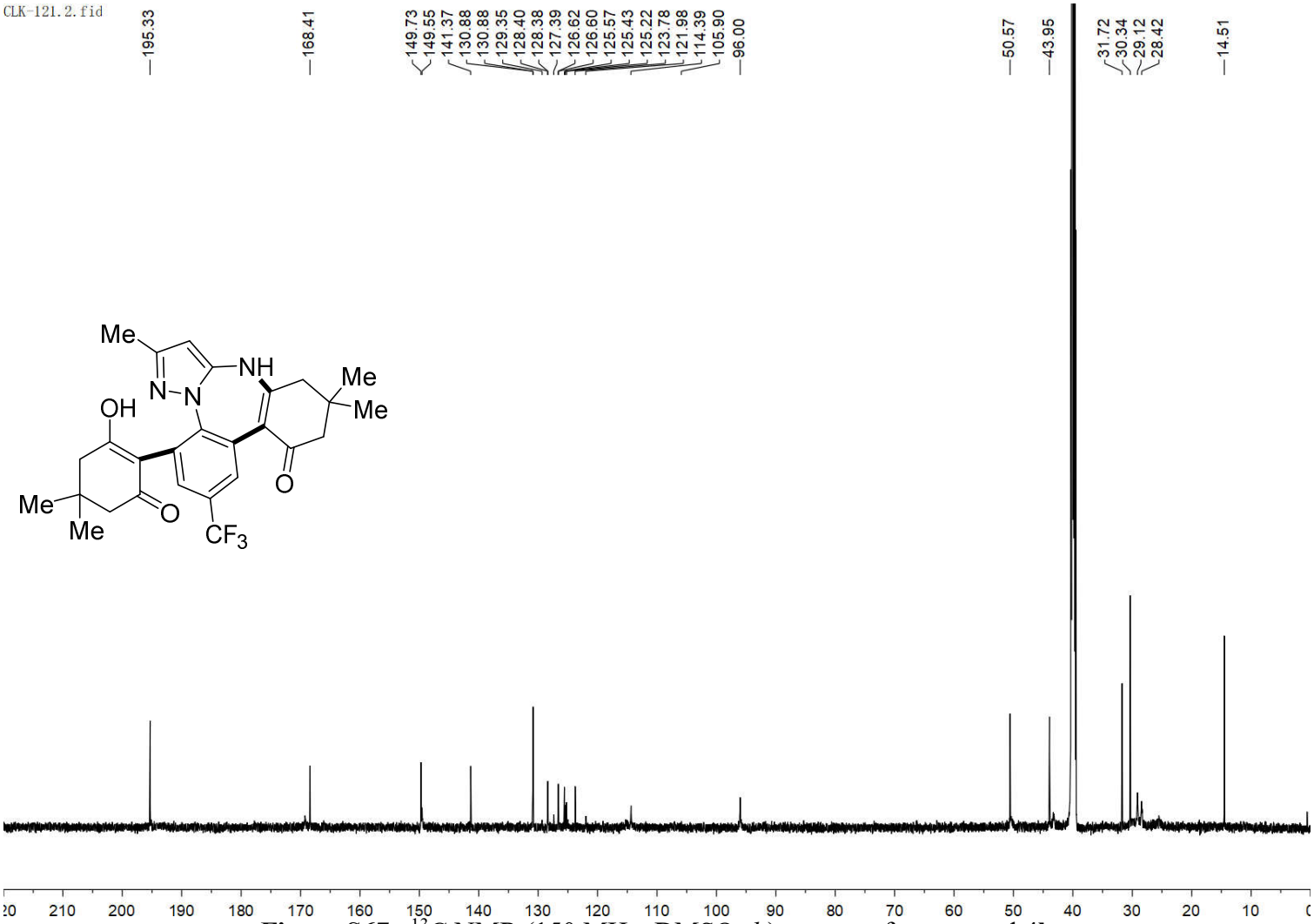


Figure S67. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4h**

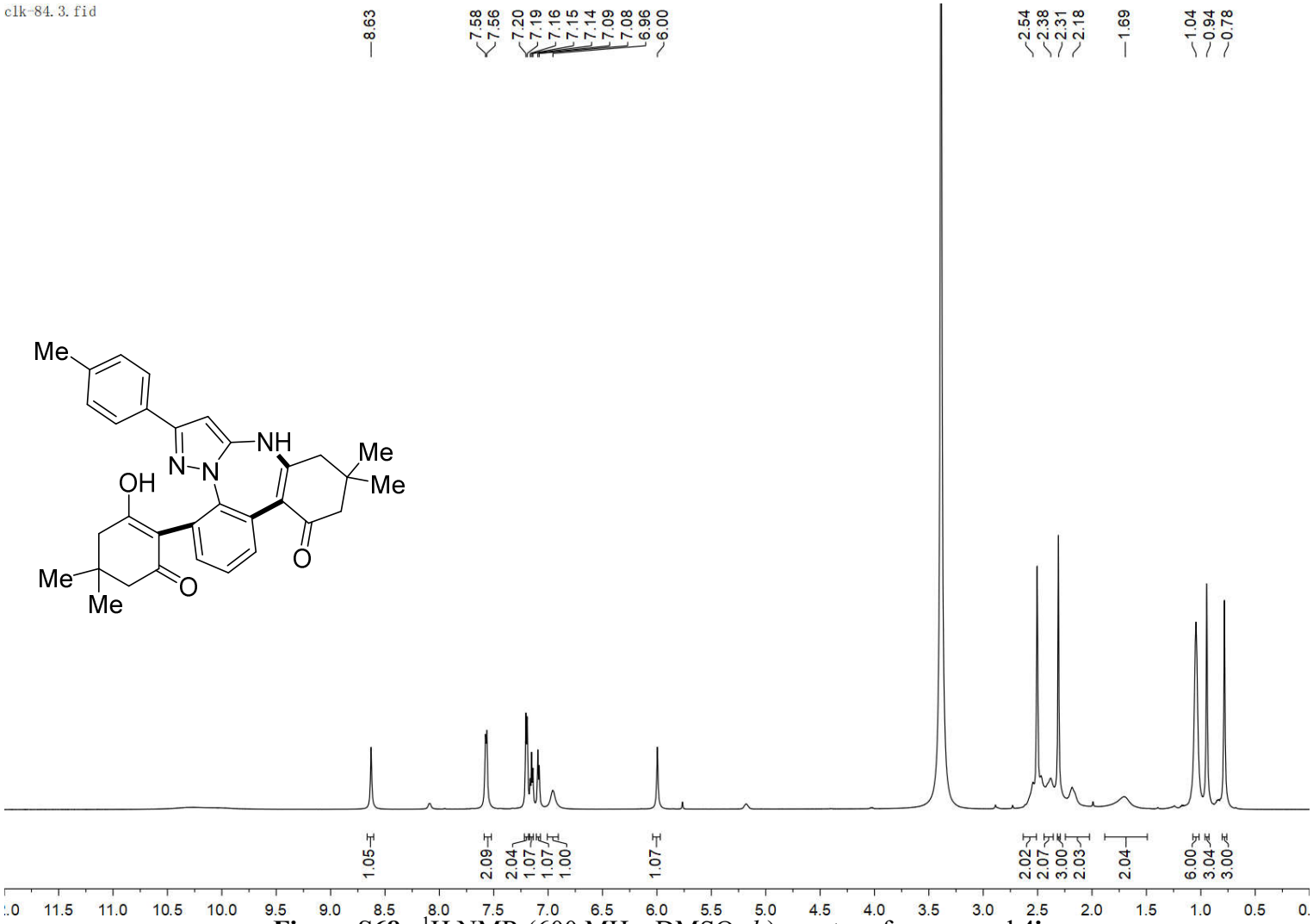


Figure S68. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4i**

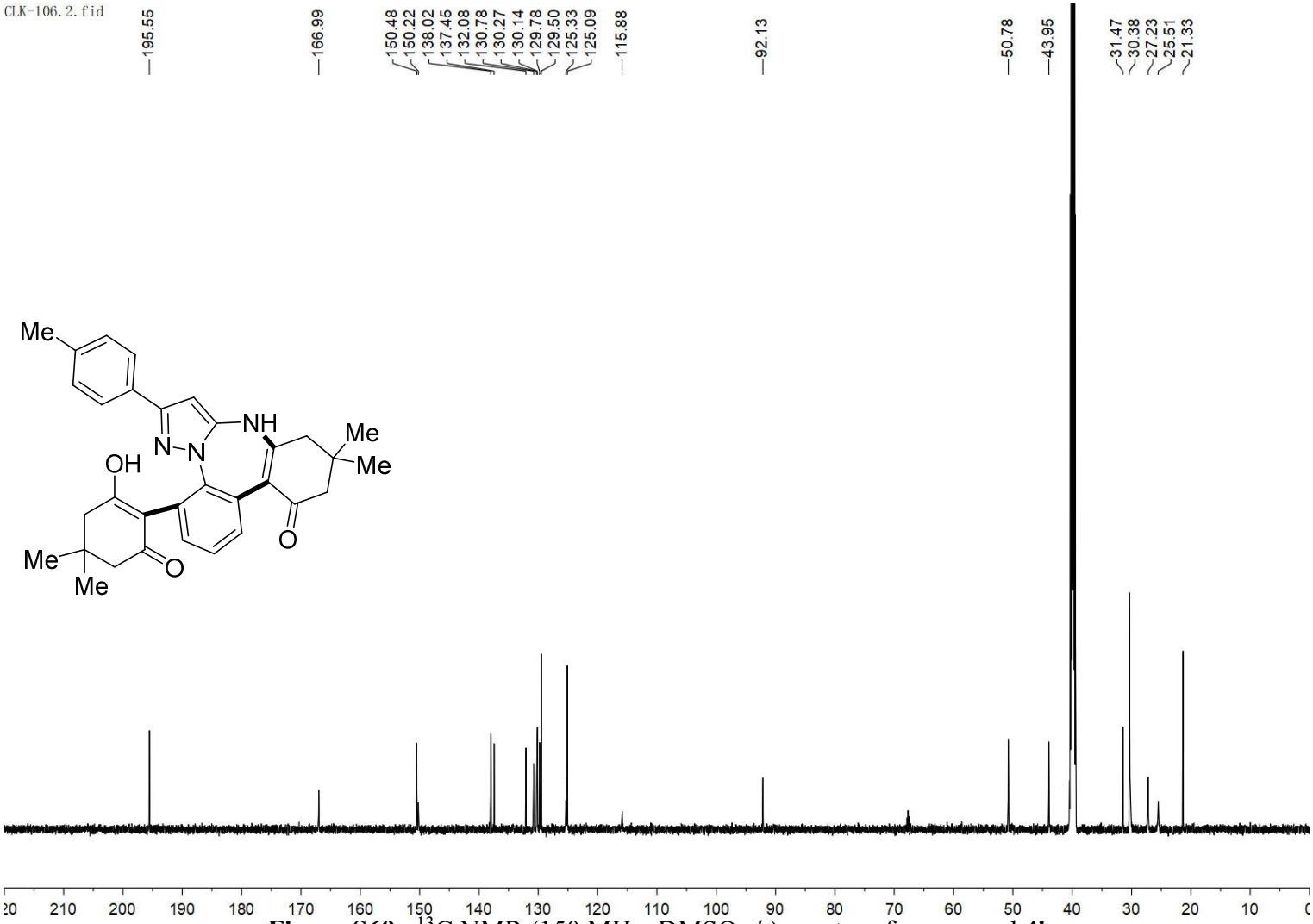


Figure S69. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4i**

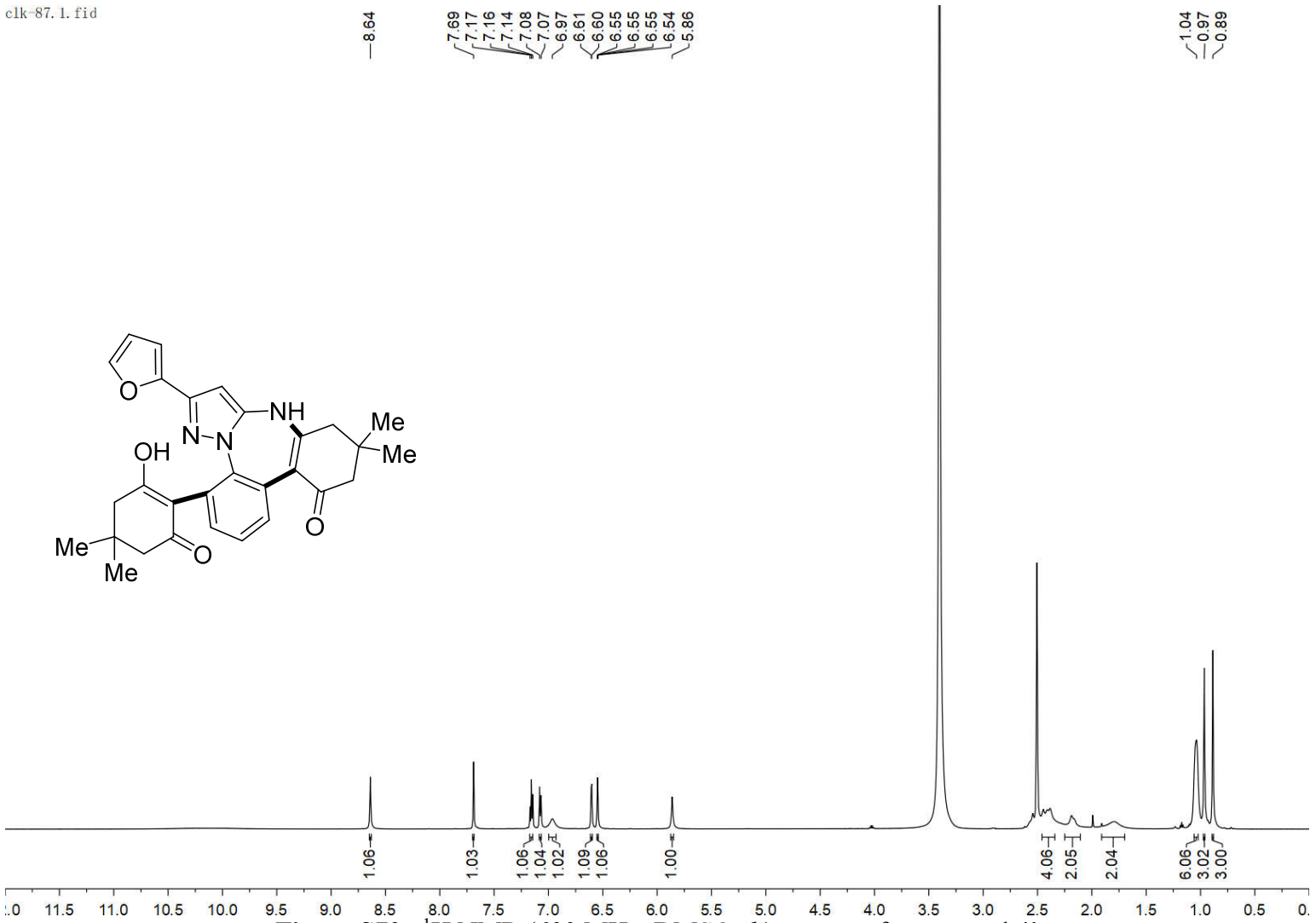


Figure S70. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4j**

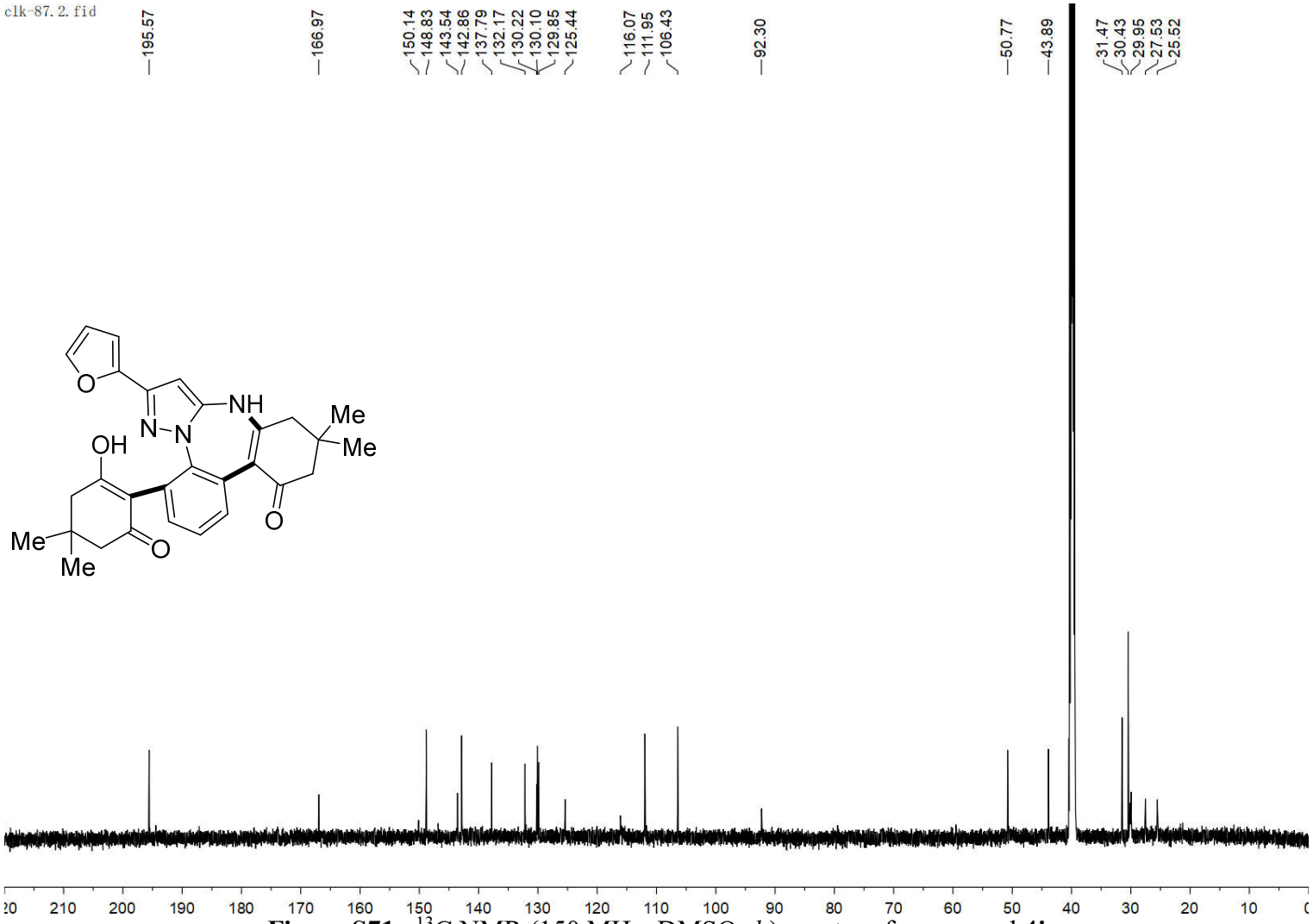


Figure S71. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4j**

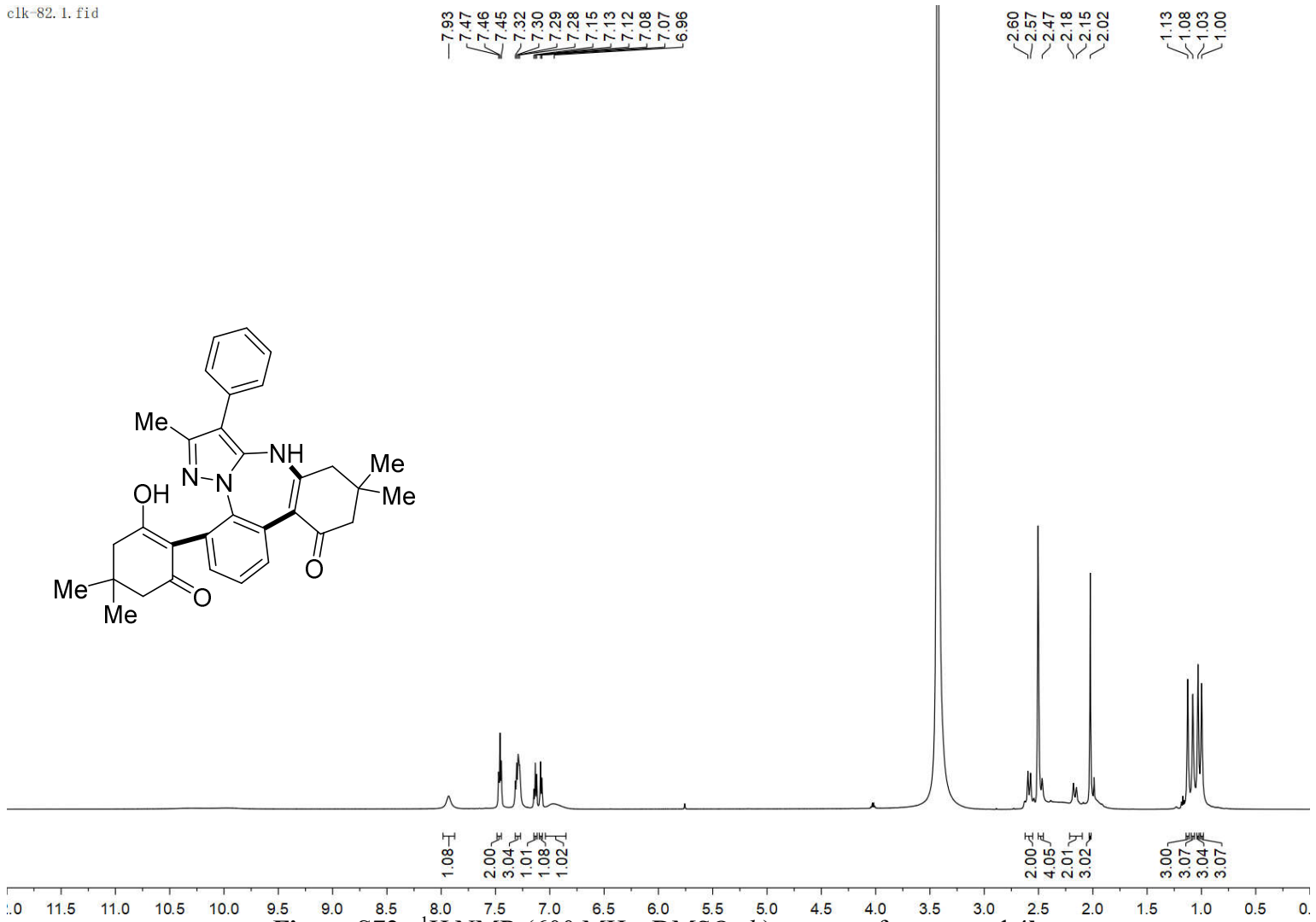


Figure S72. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4k**

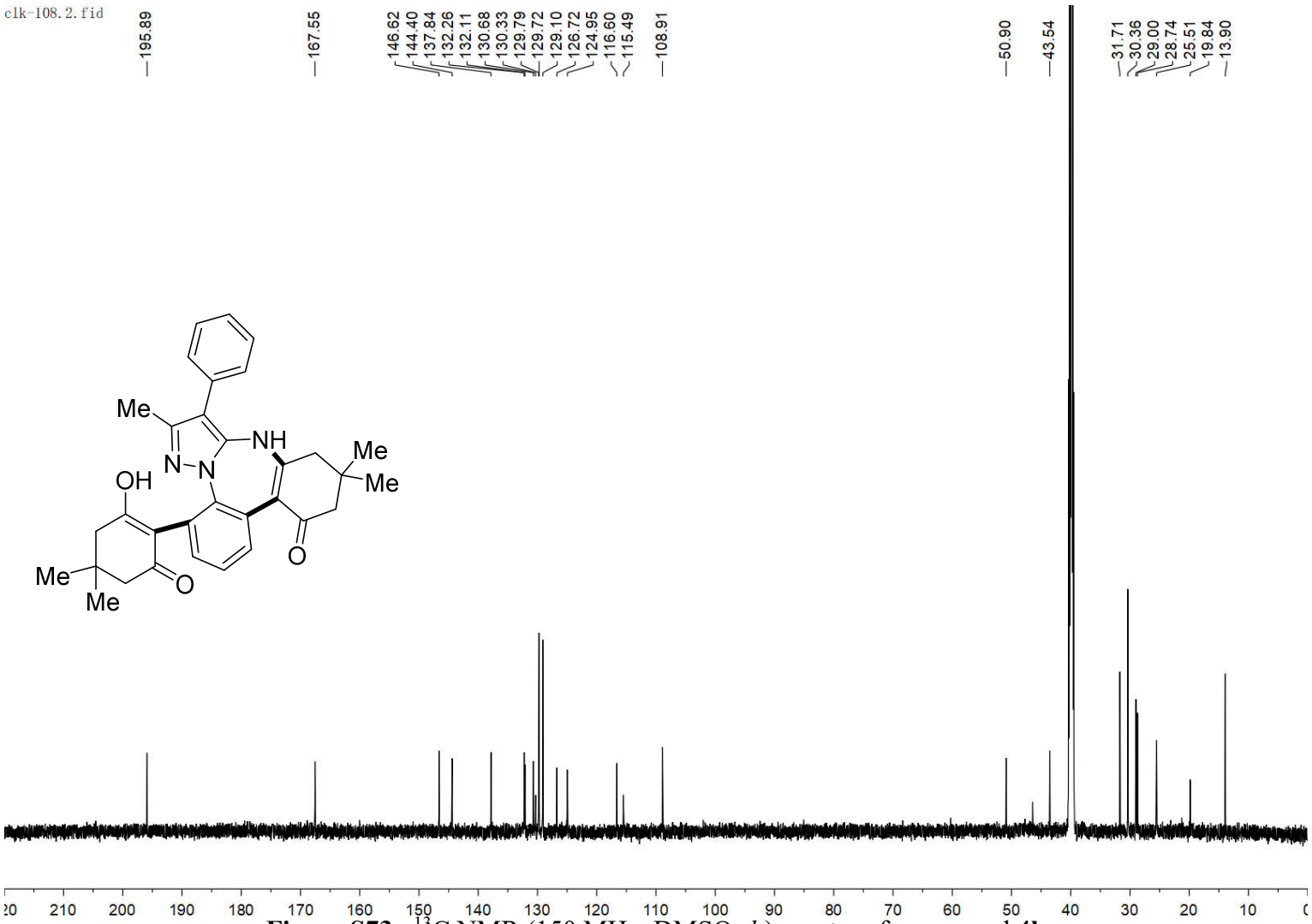


Figure S73. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4k**

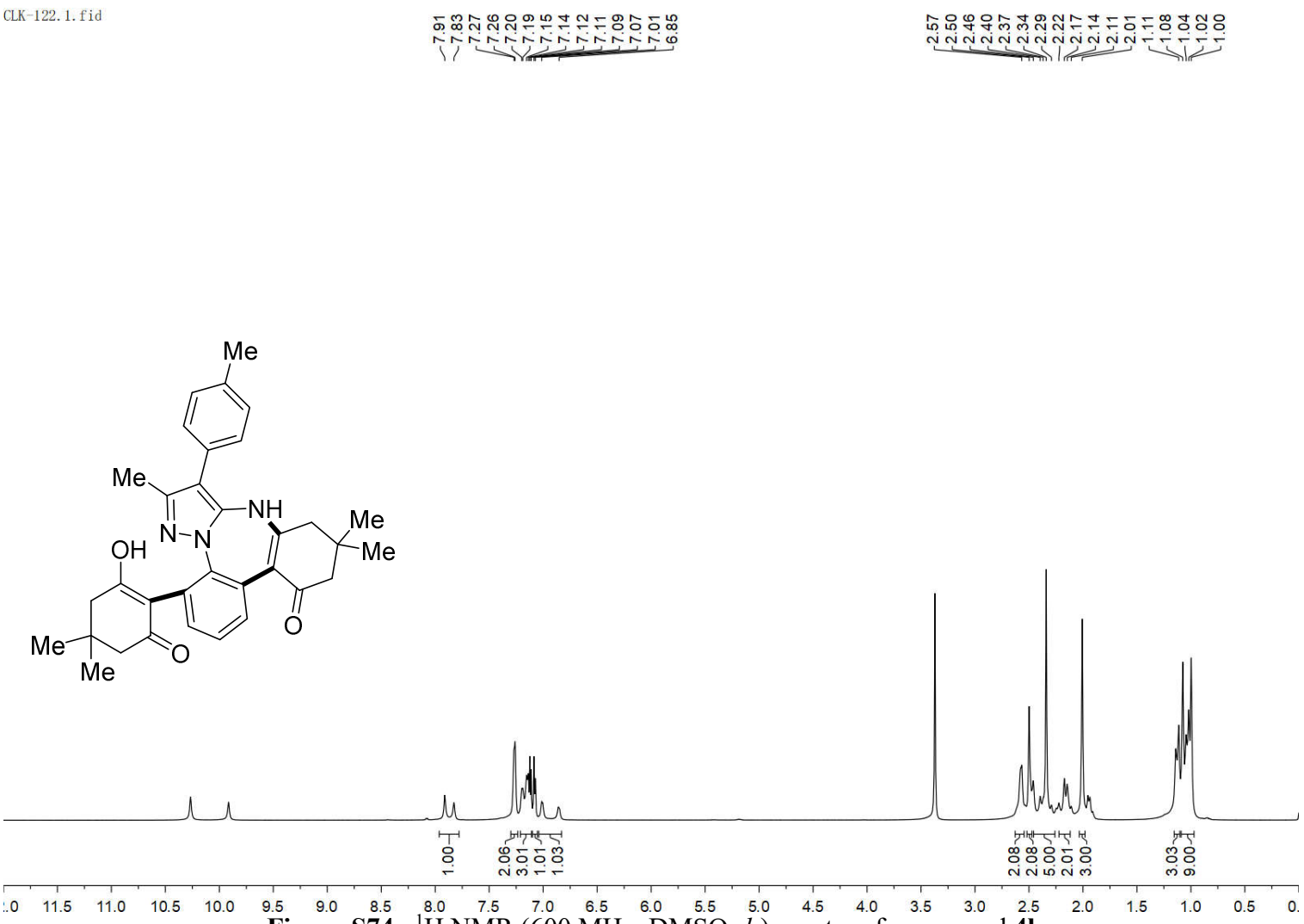


Figure S74. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4l**

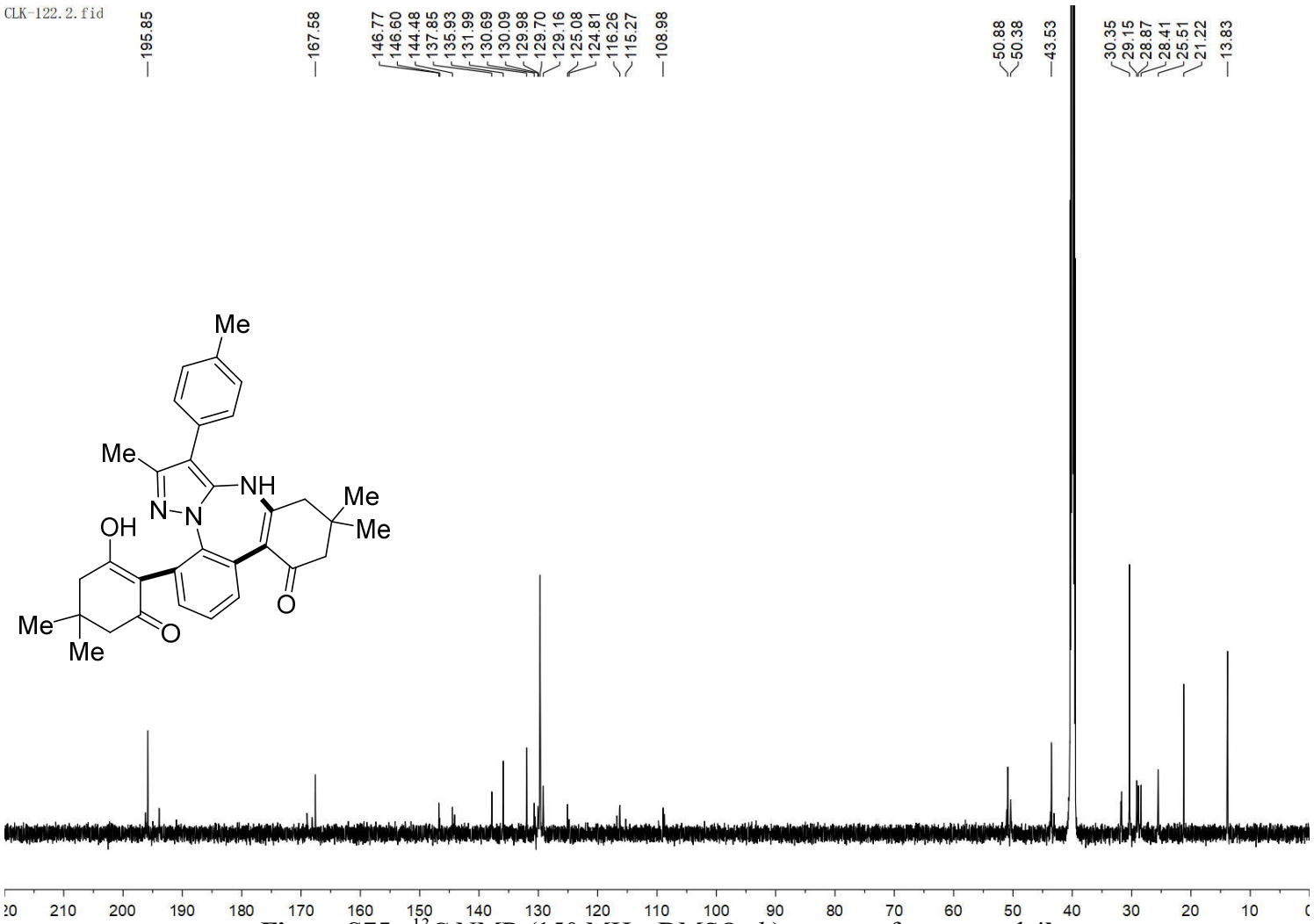


Figure S75. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4l**

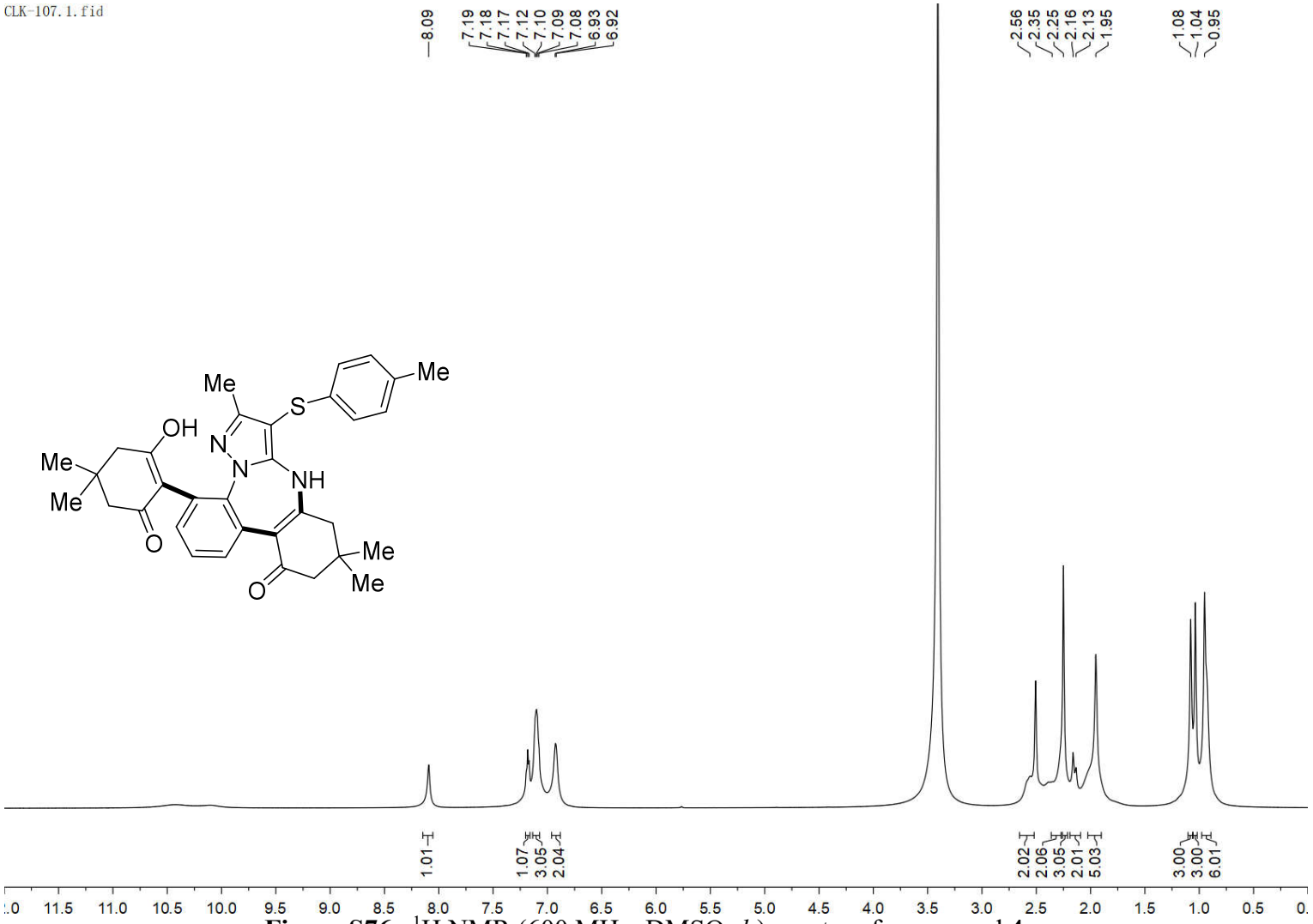


Figure S76. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4m**

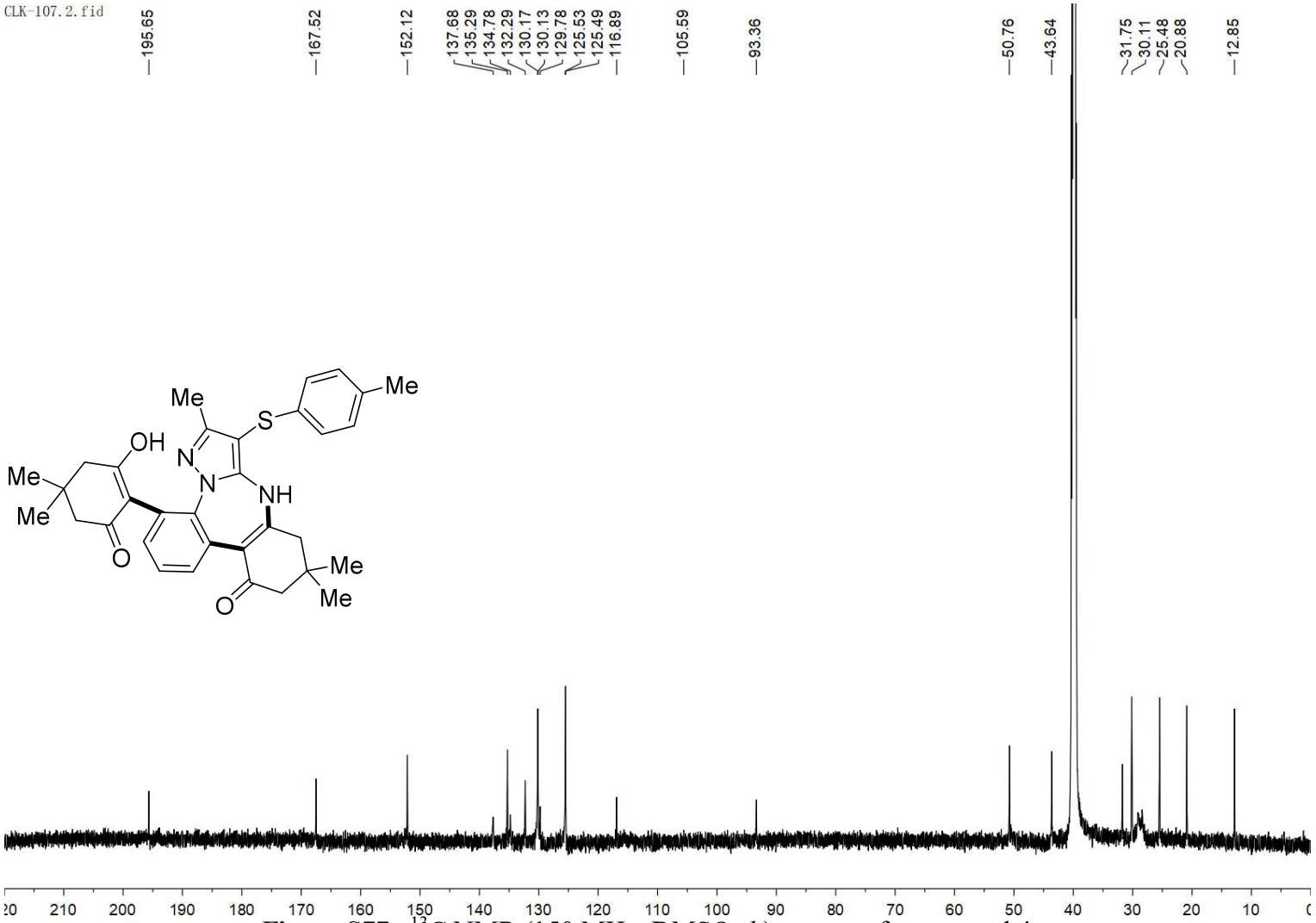


Figure S77. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4m**

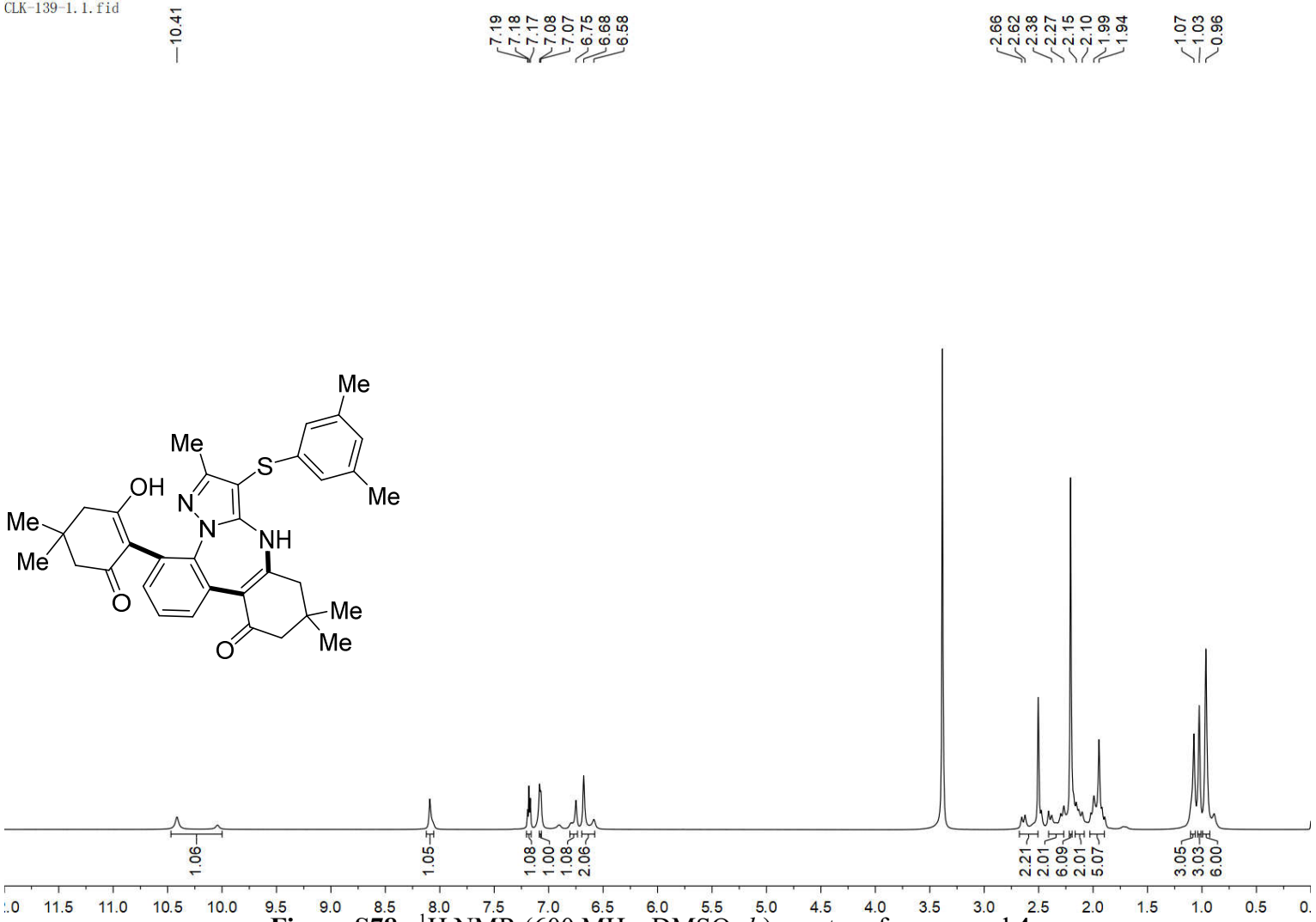


Figure S78. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4n**

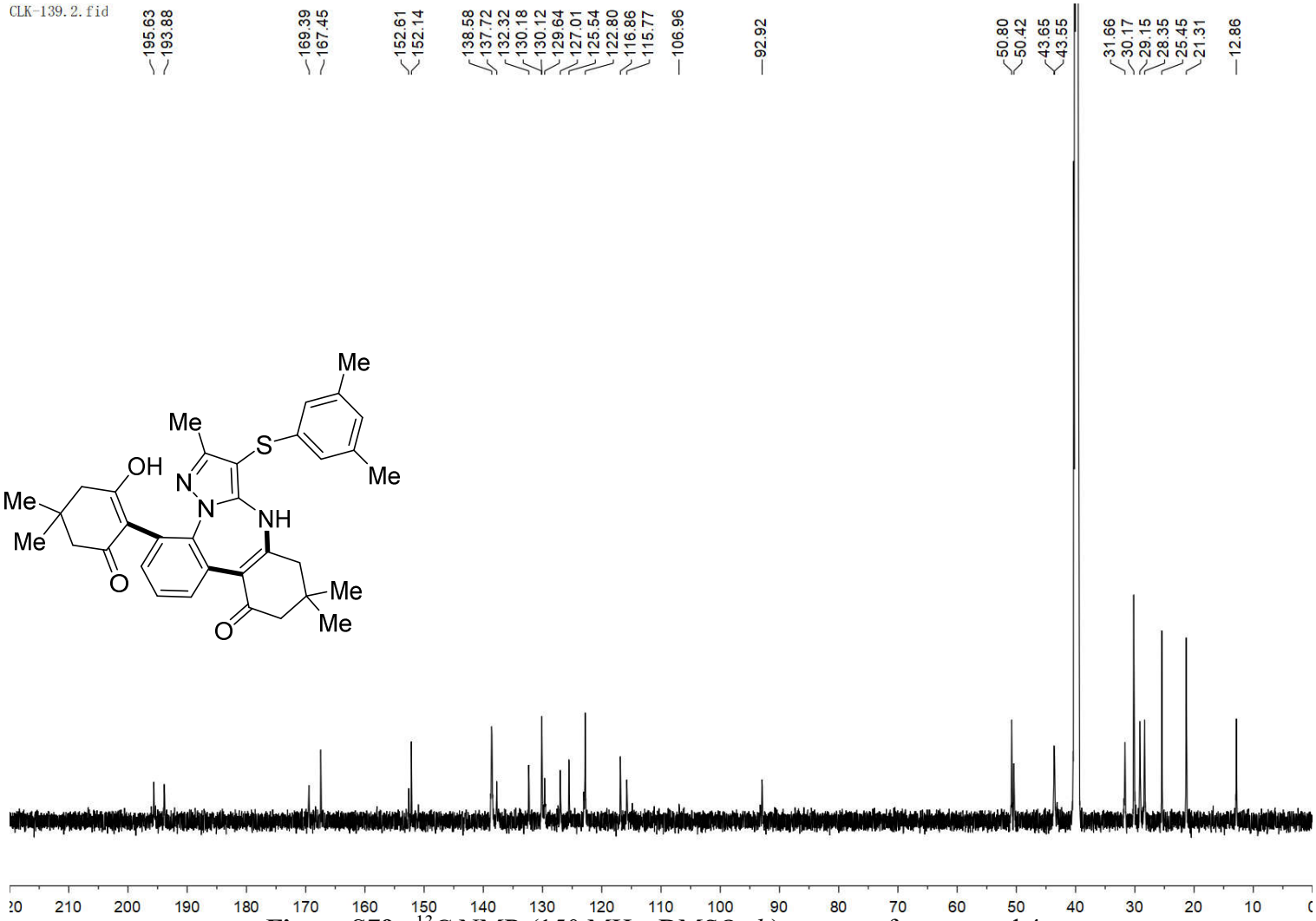


Figure S79. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4n**

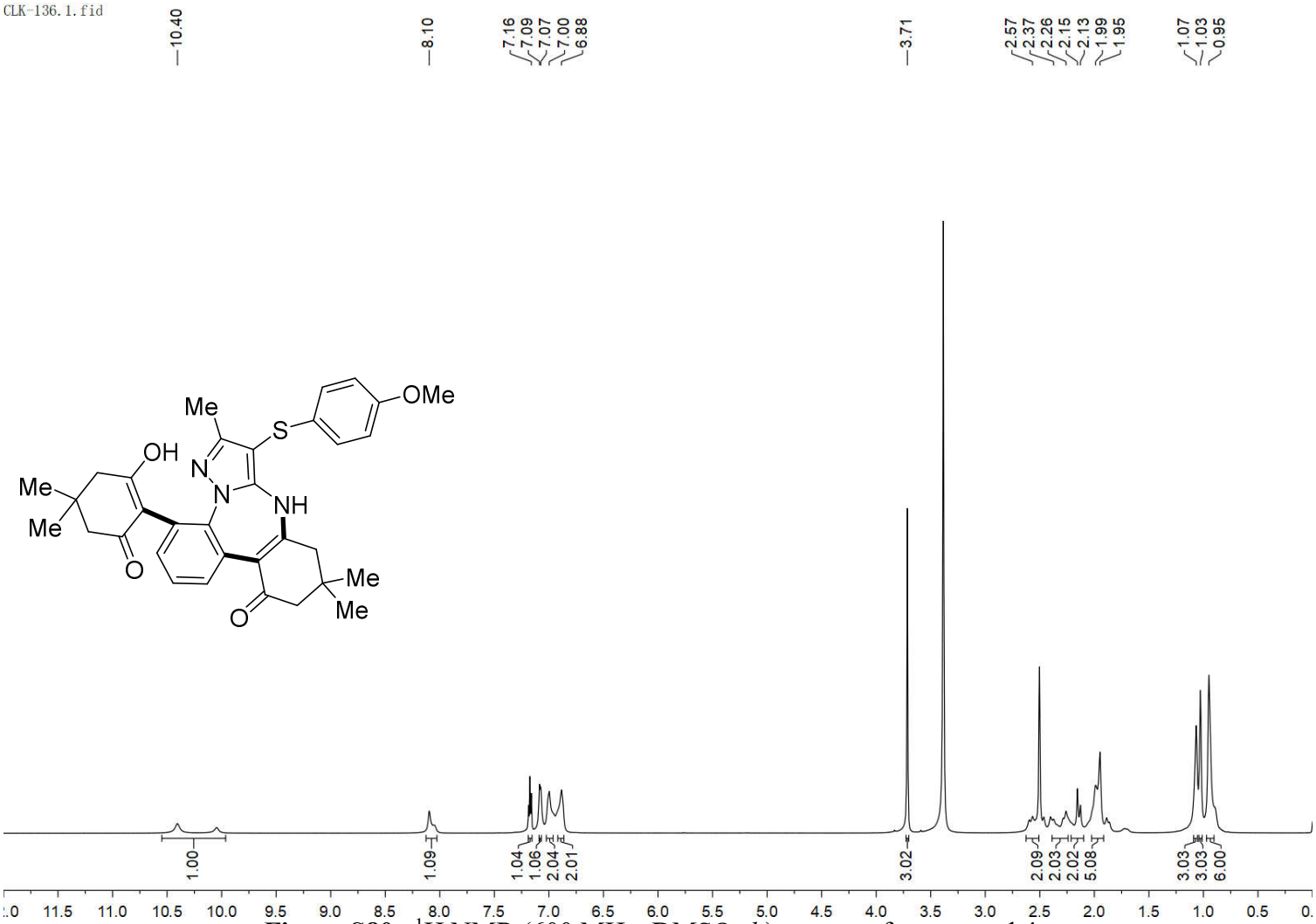


Figure S80. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4o**

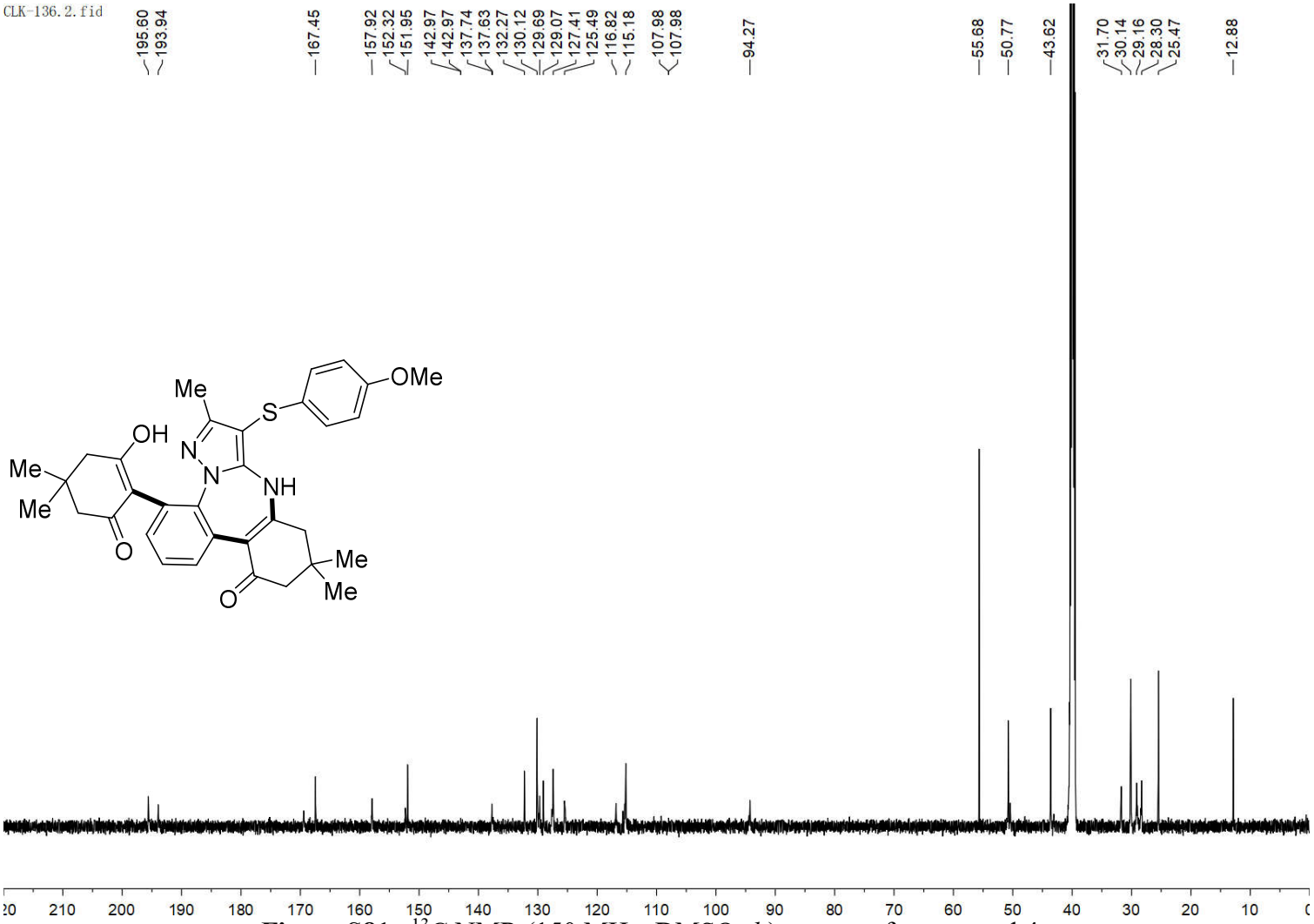


Figure S81. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4o**

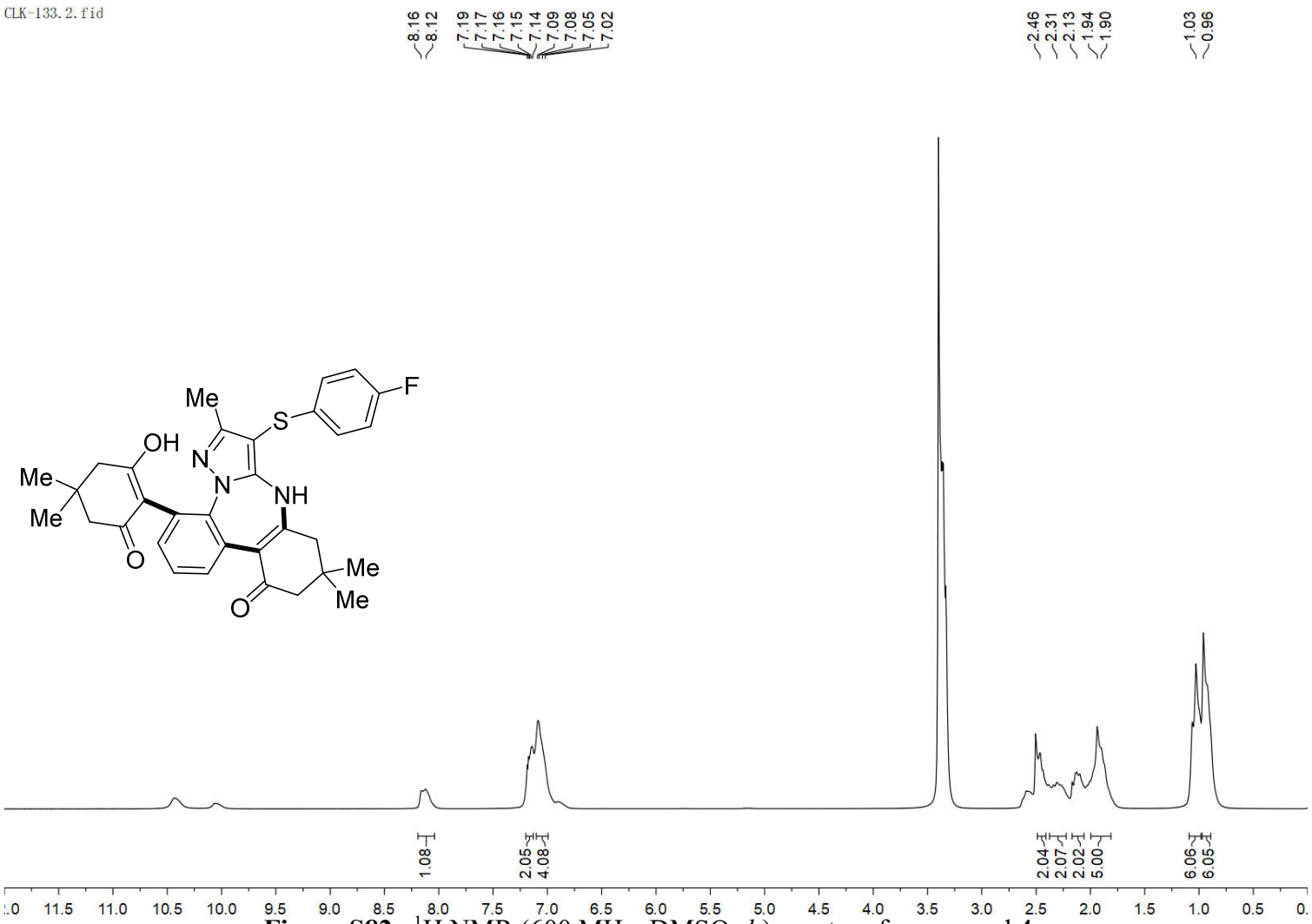


Figure S82. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4p**

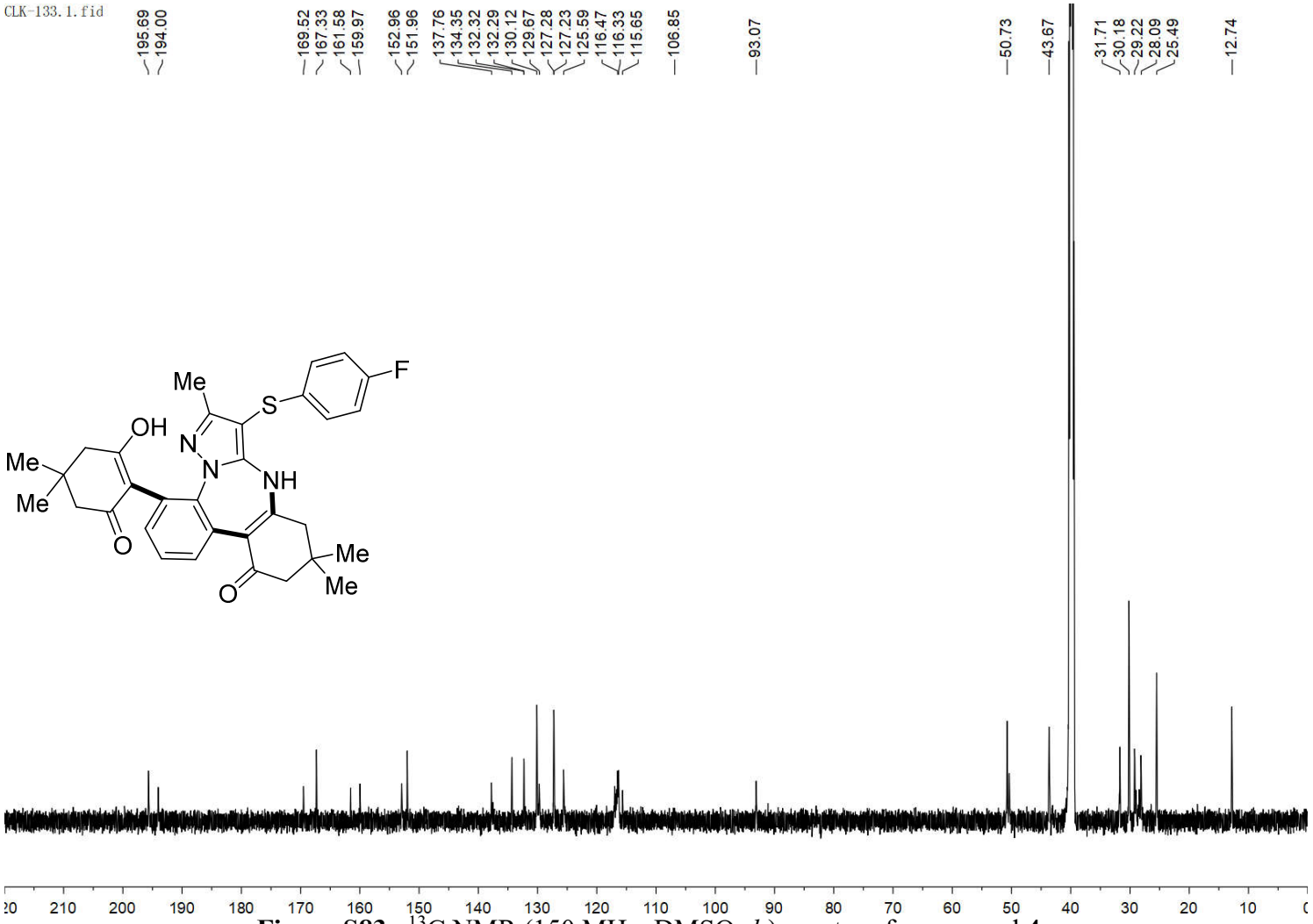


Figure S83. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4p**

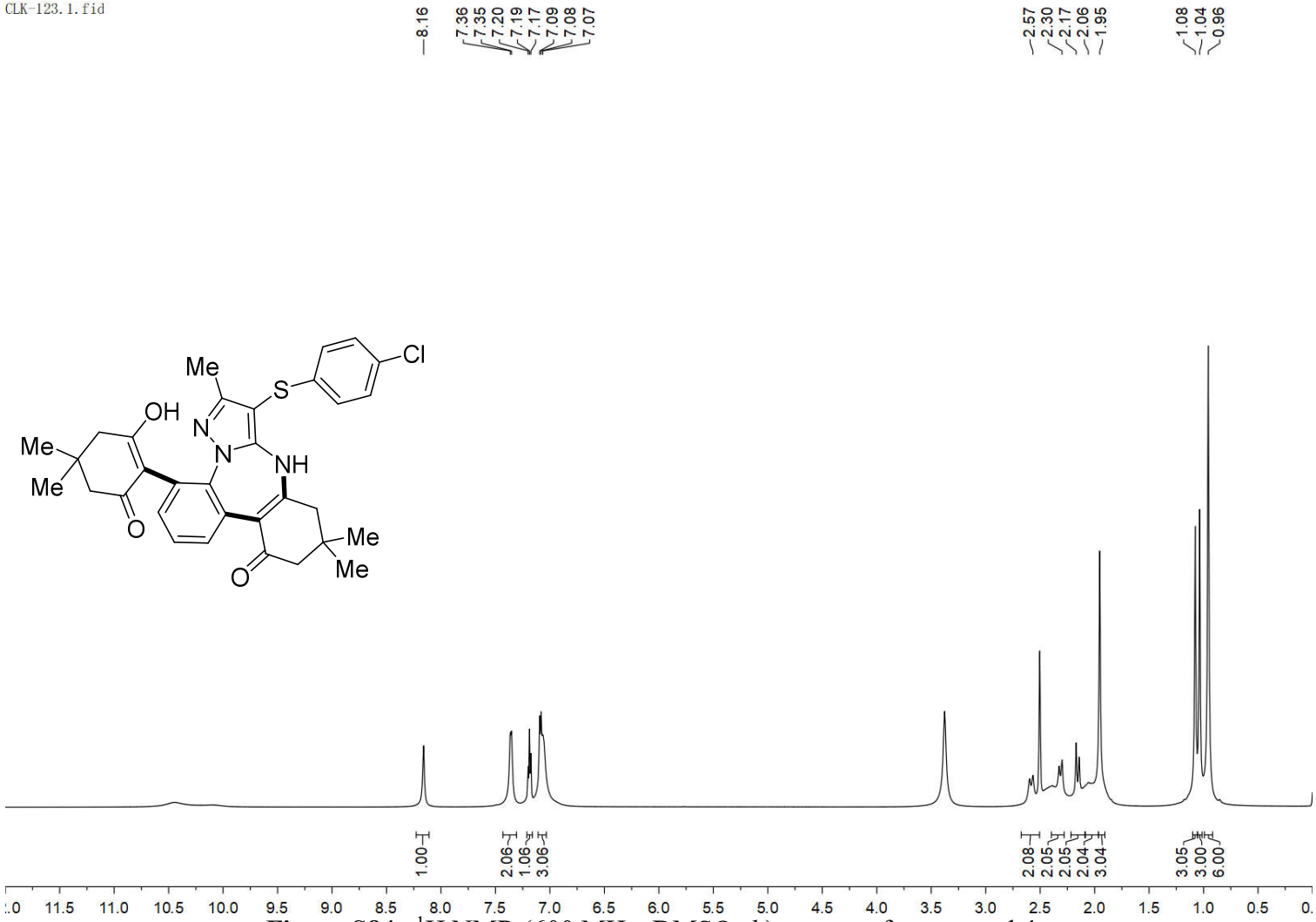


Figure S84. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4q**

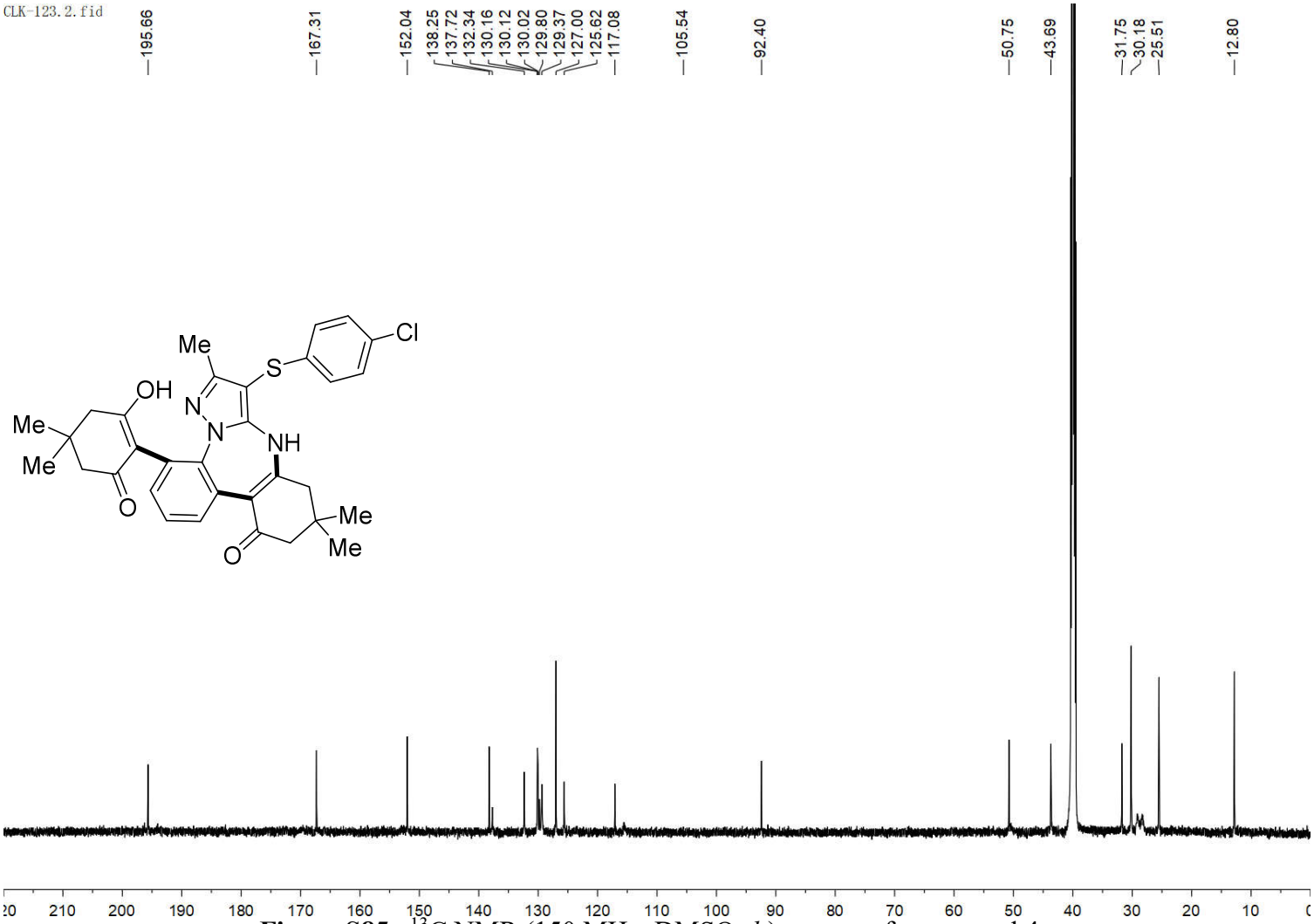


Figure S85. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4q**

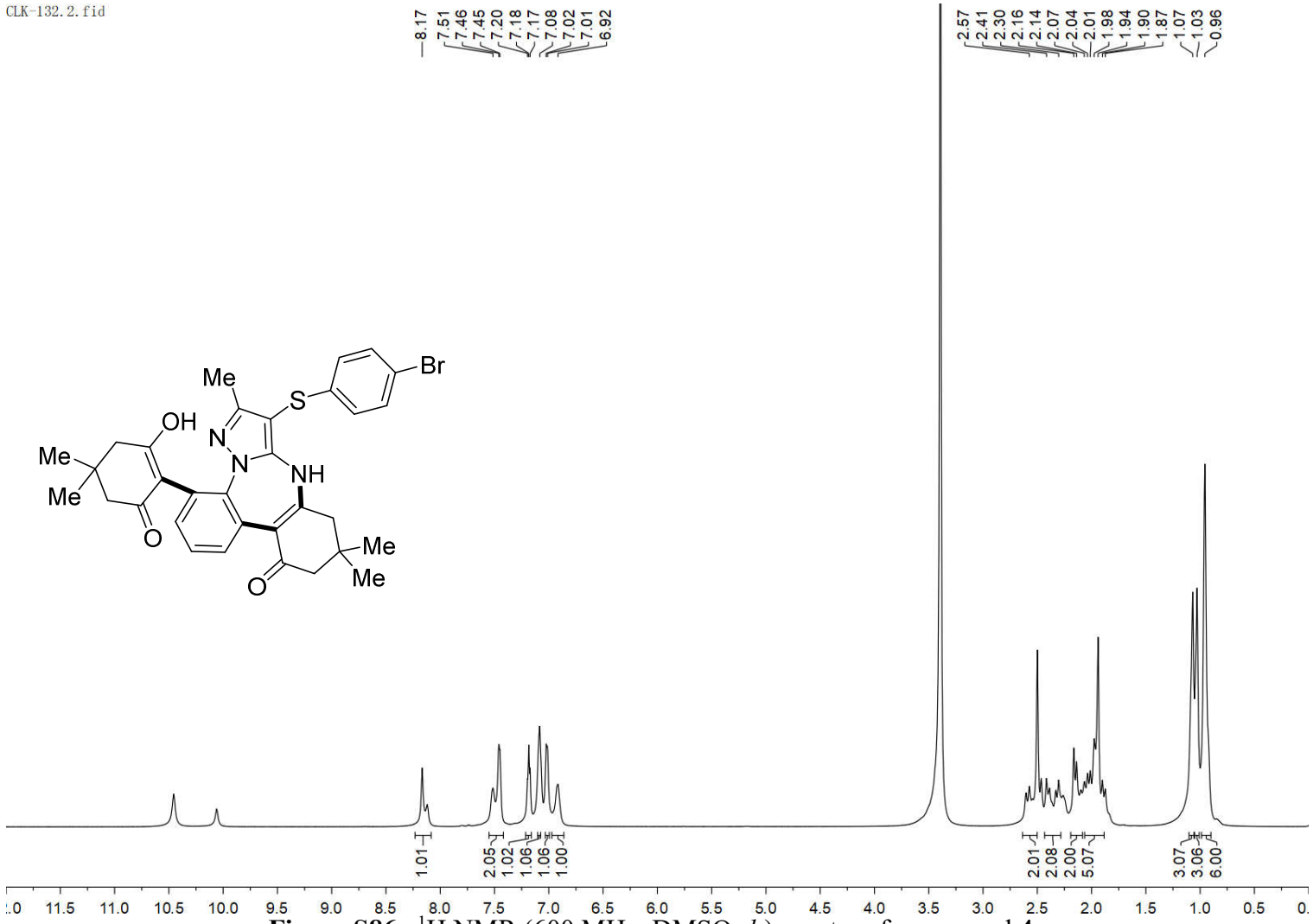


Figure S86. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4r**

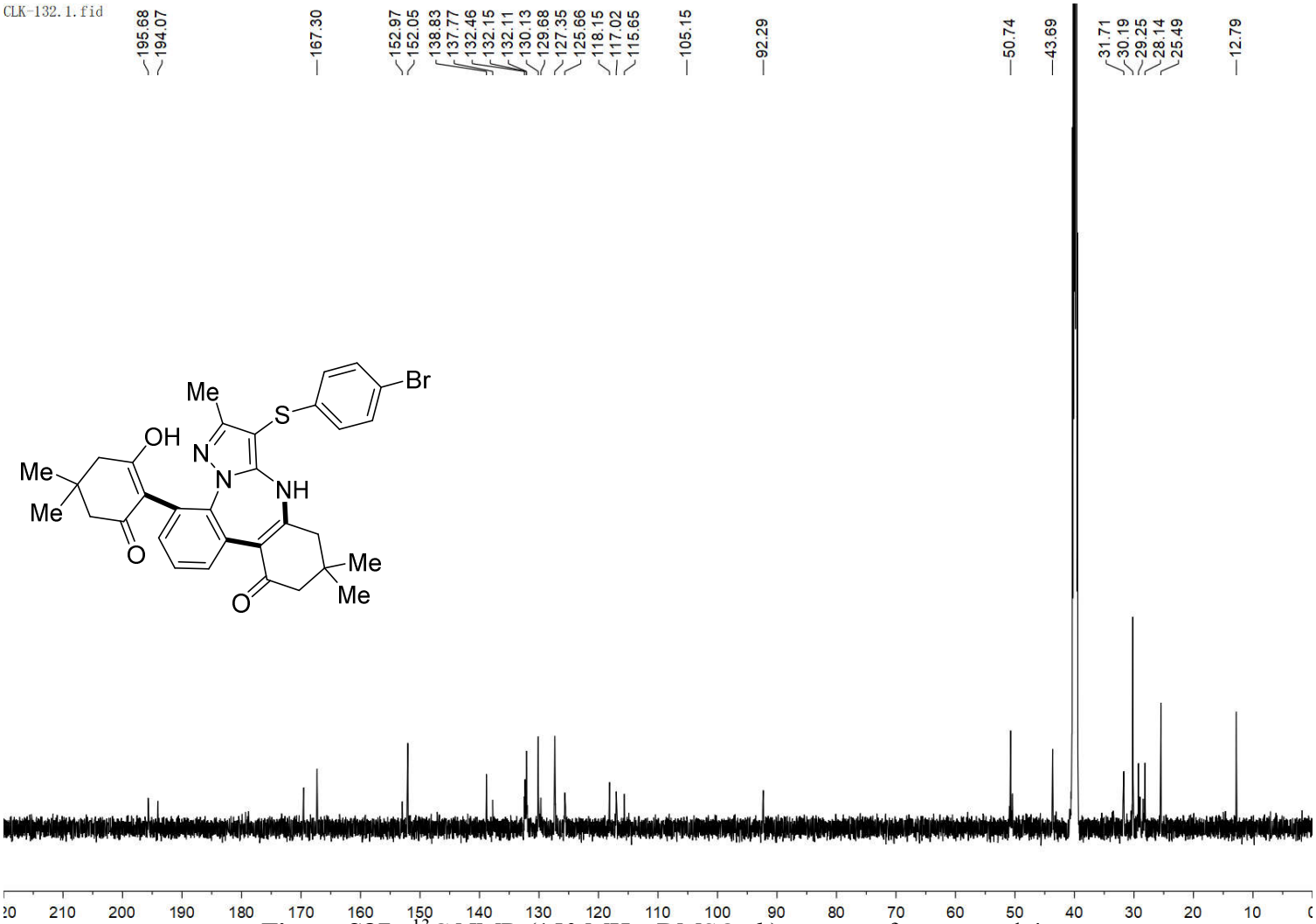


Figure S87. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4r**

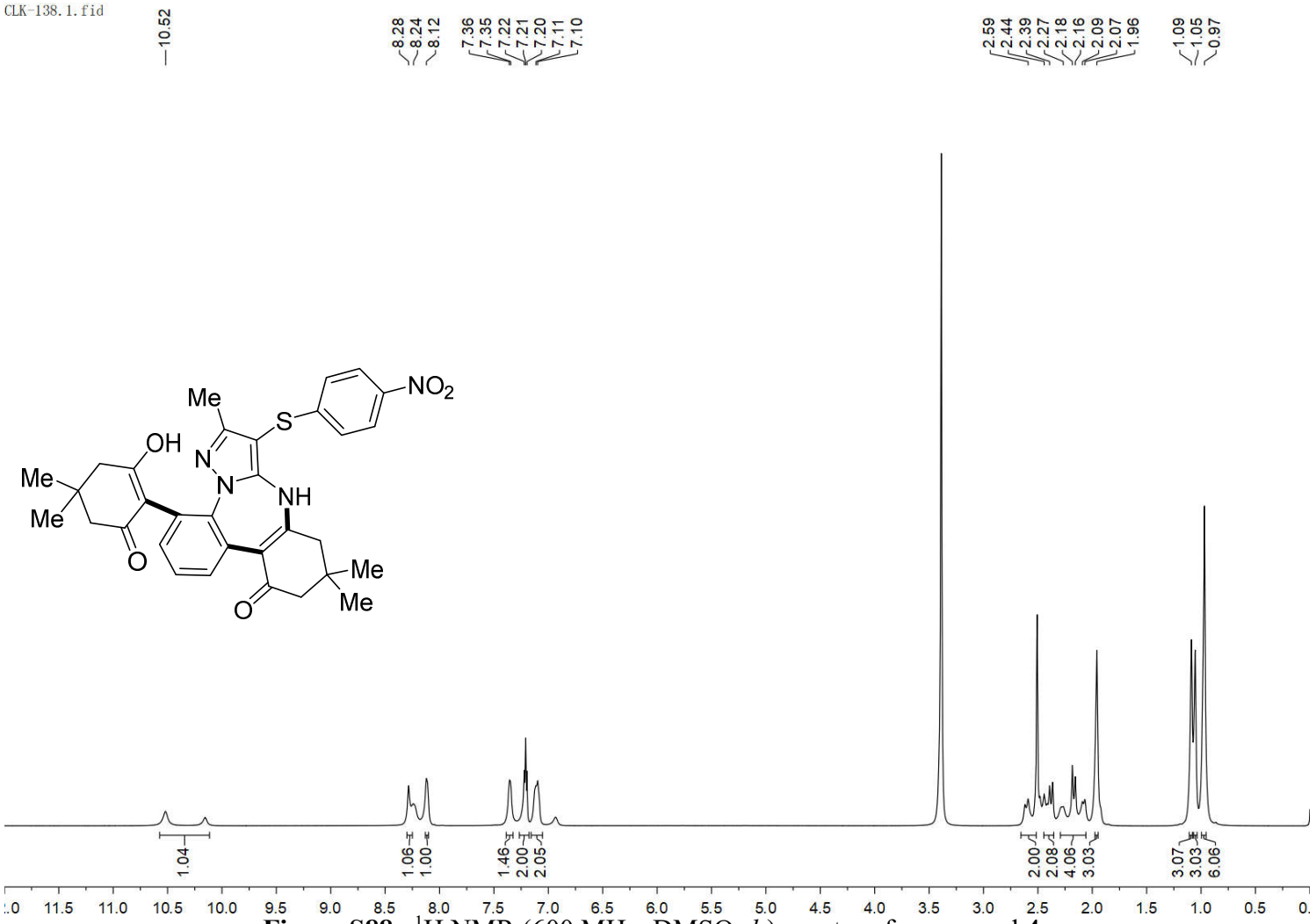


Figure S88. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4s**

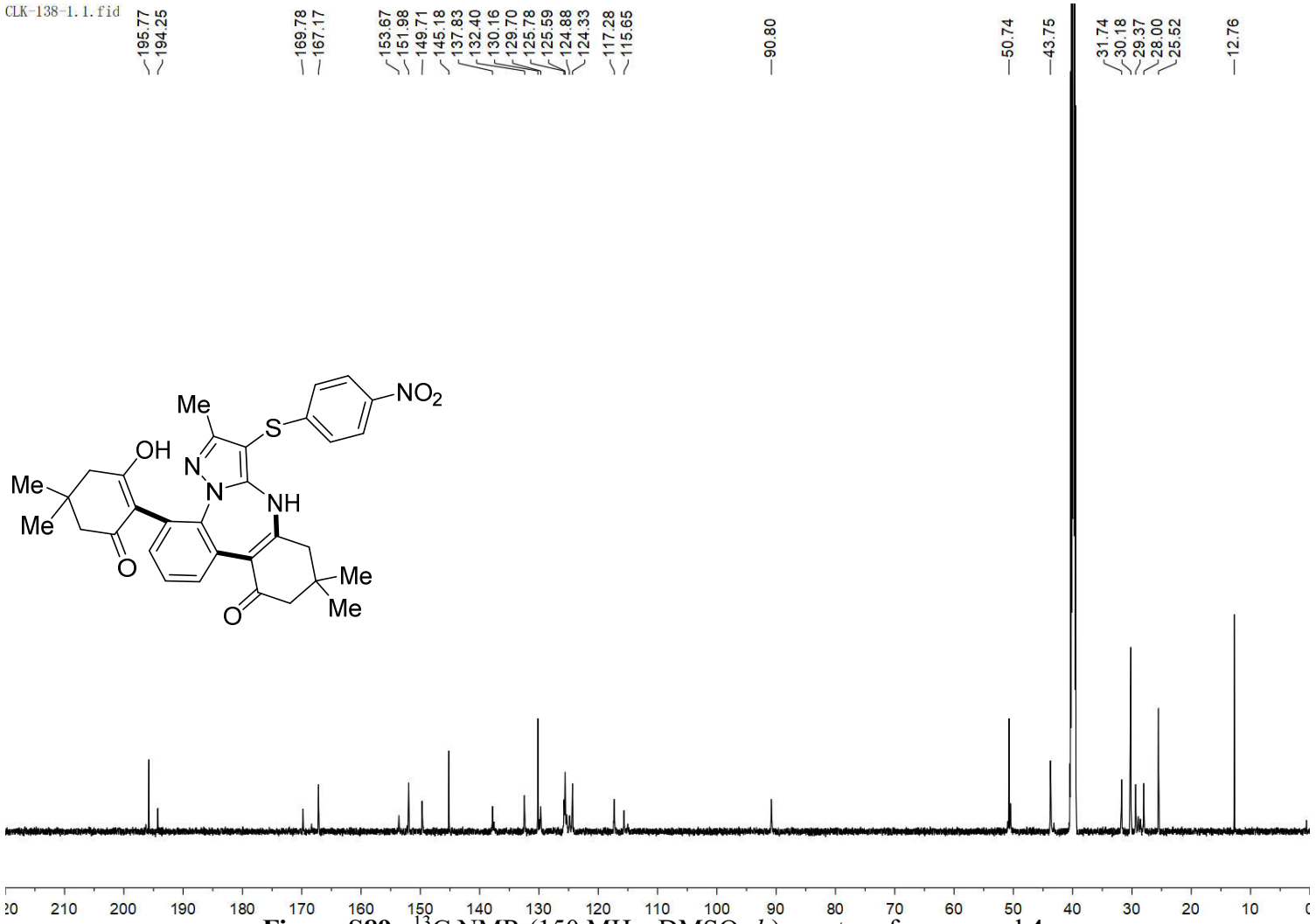


Figure S89. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4s**

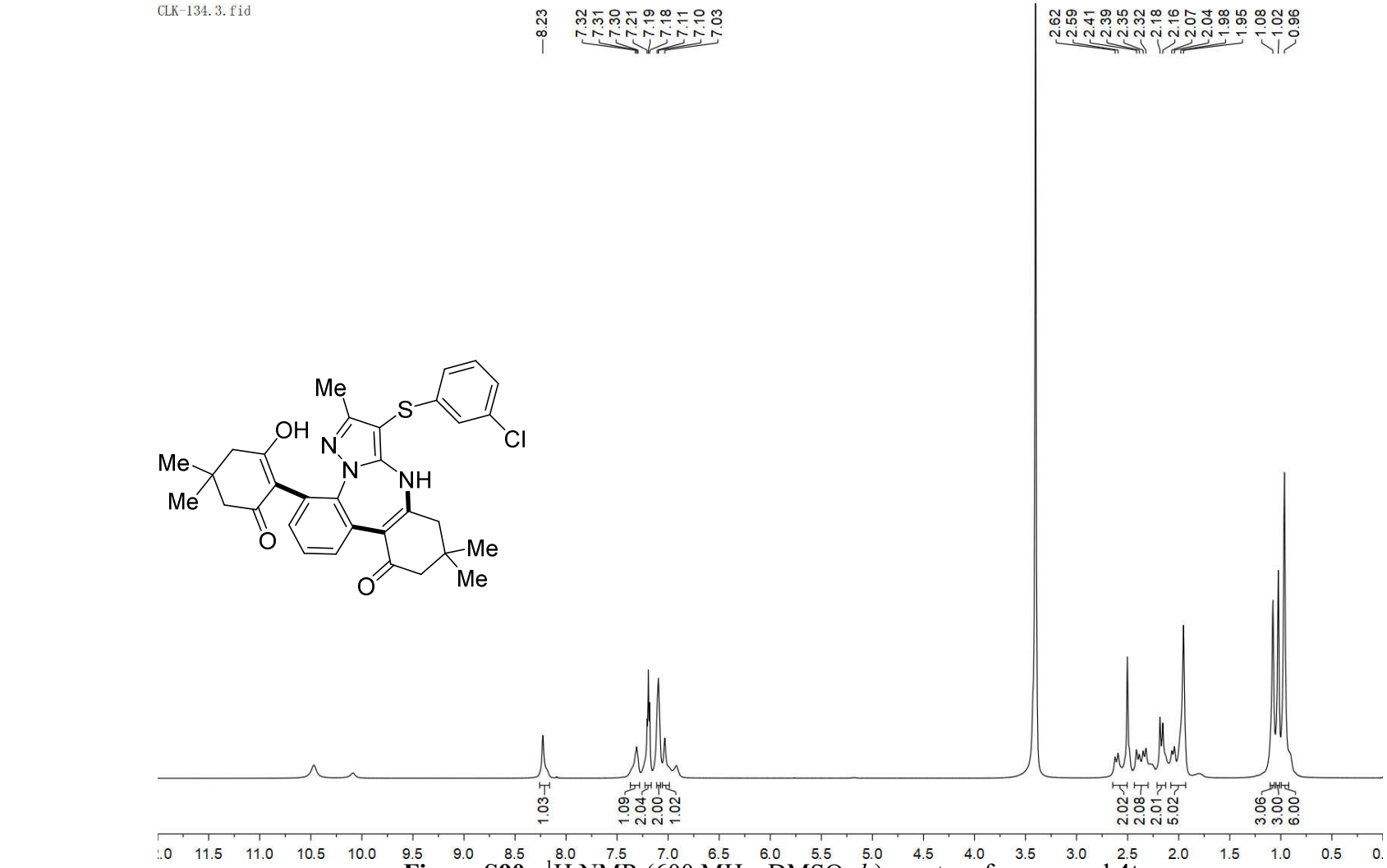


Figure S90. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4t**

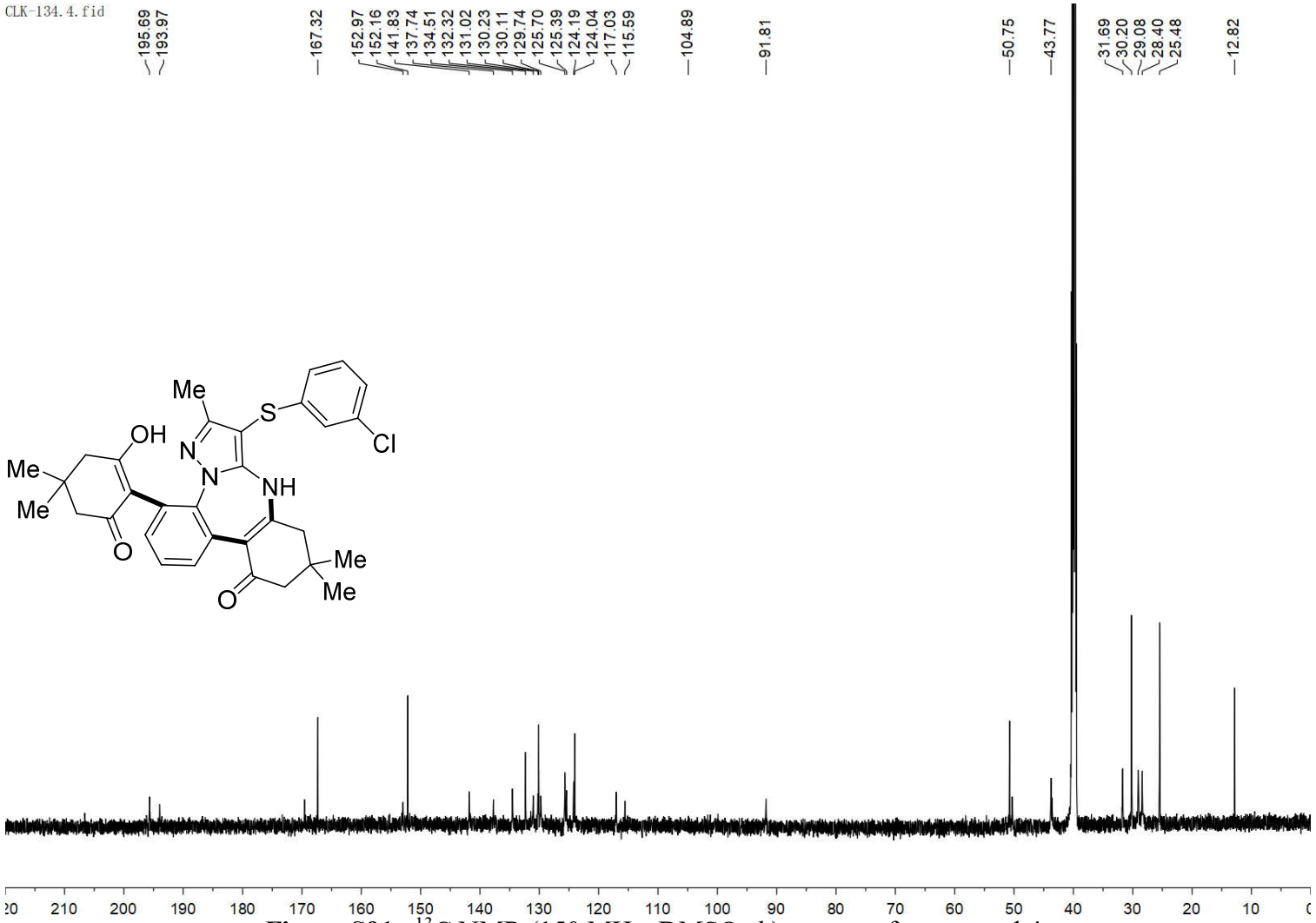


Figure S91. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4t**

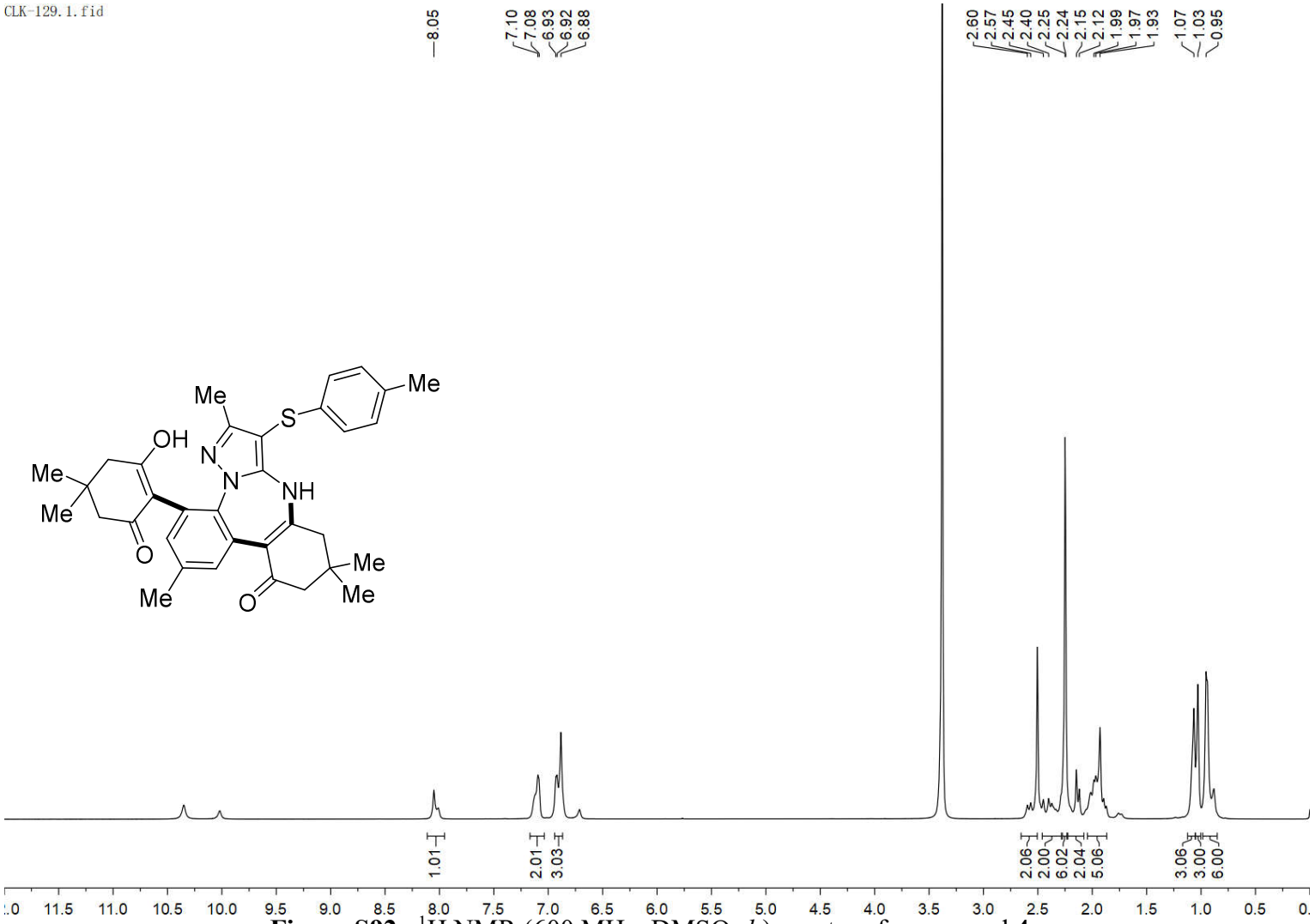


Figure S92. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4u**

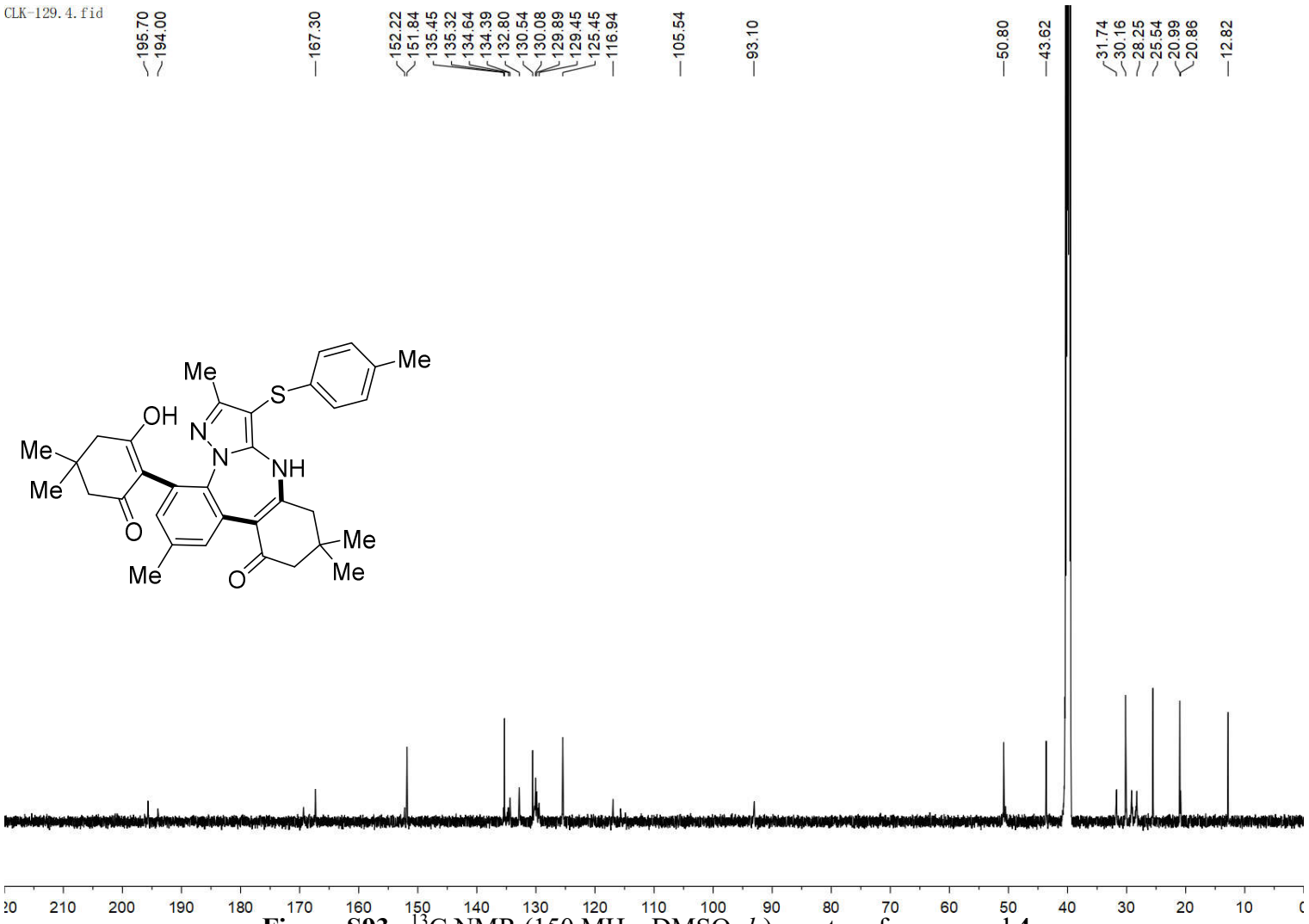


Figure S93. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4u**

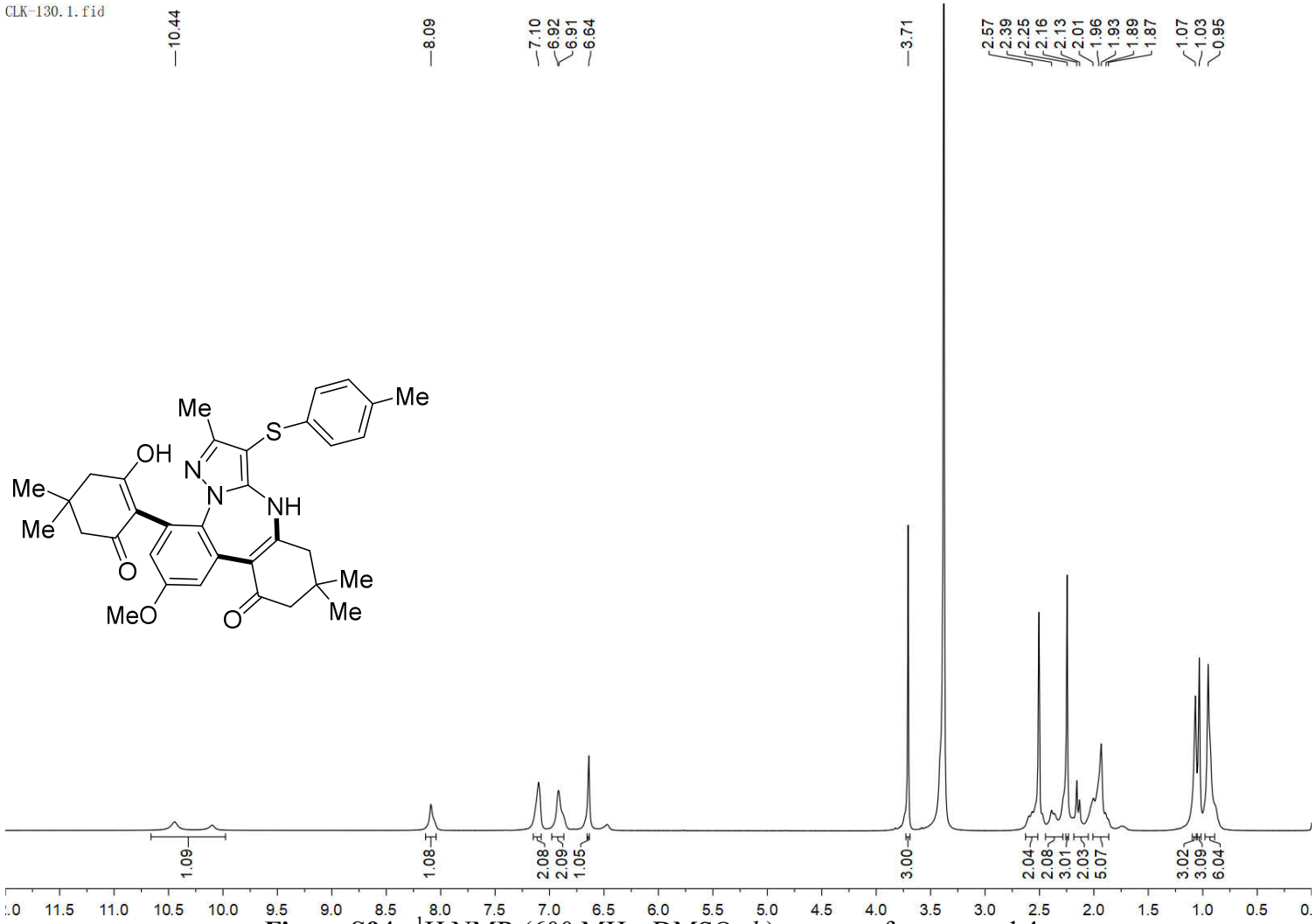


Figure S94. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4v**

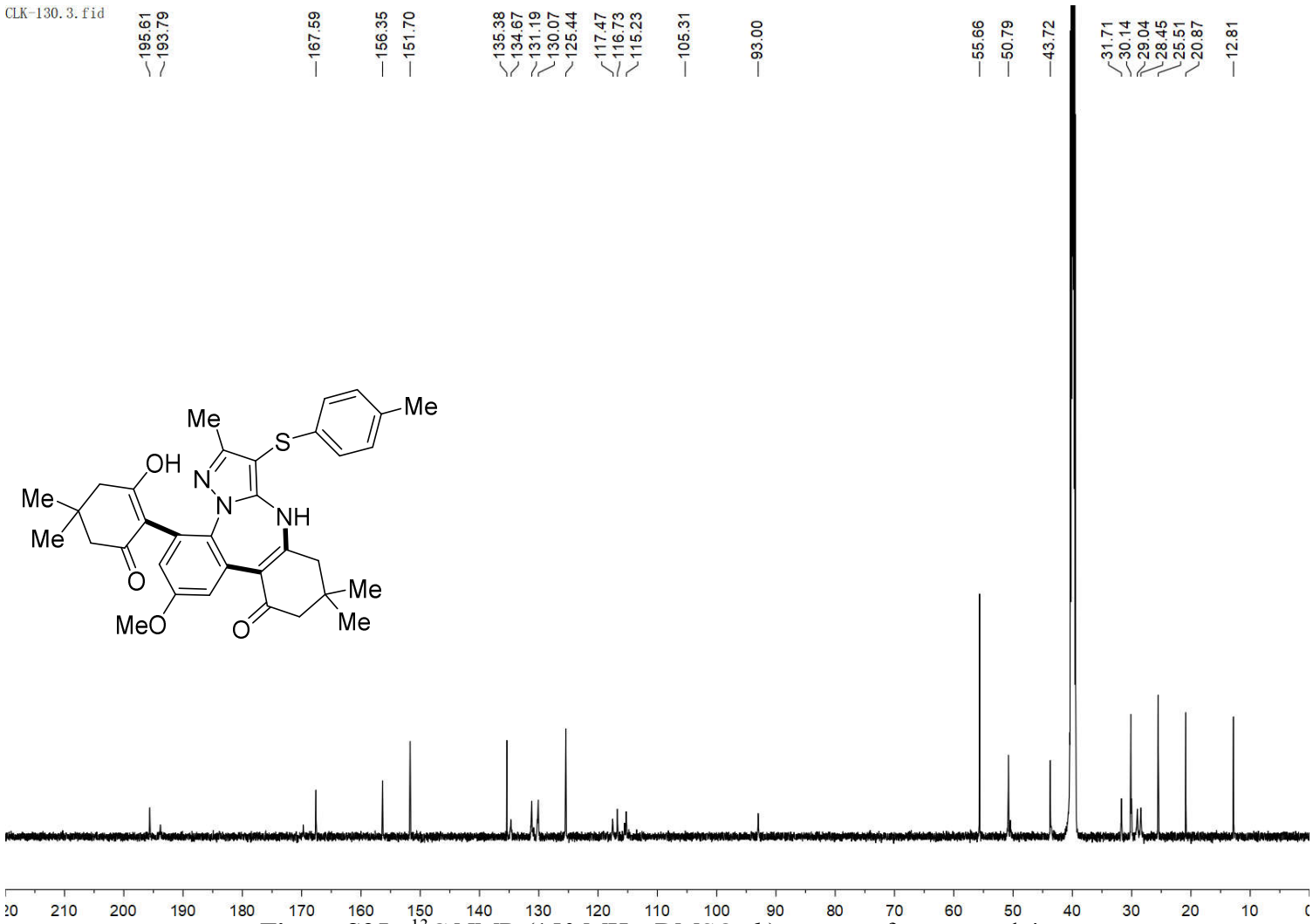


Figure S95. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4v**

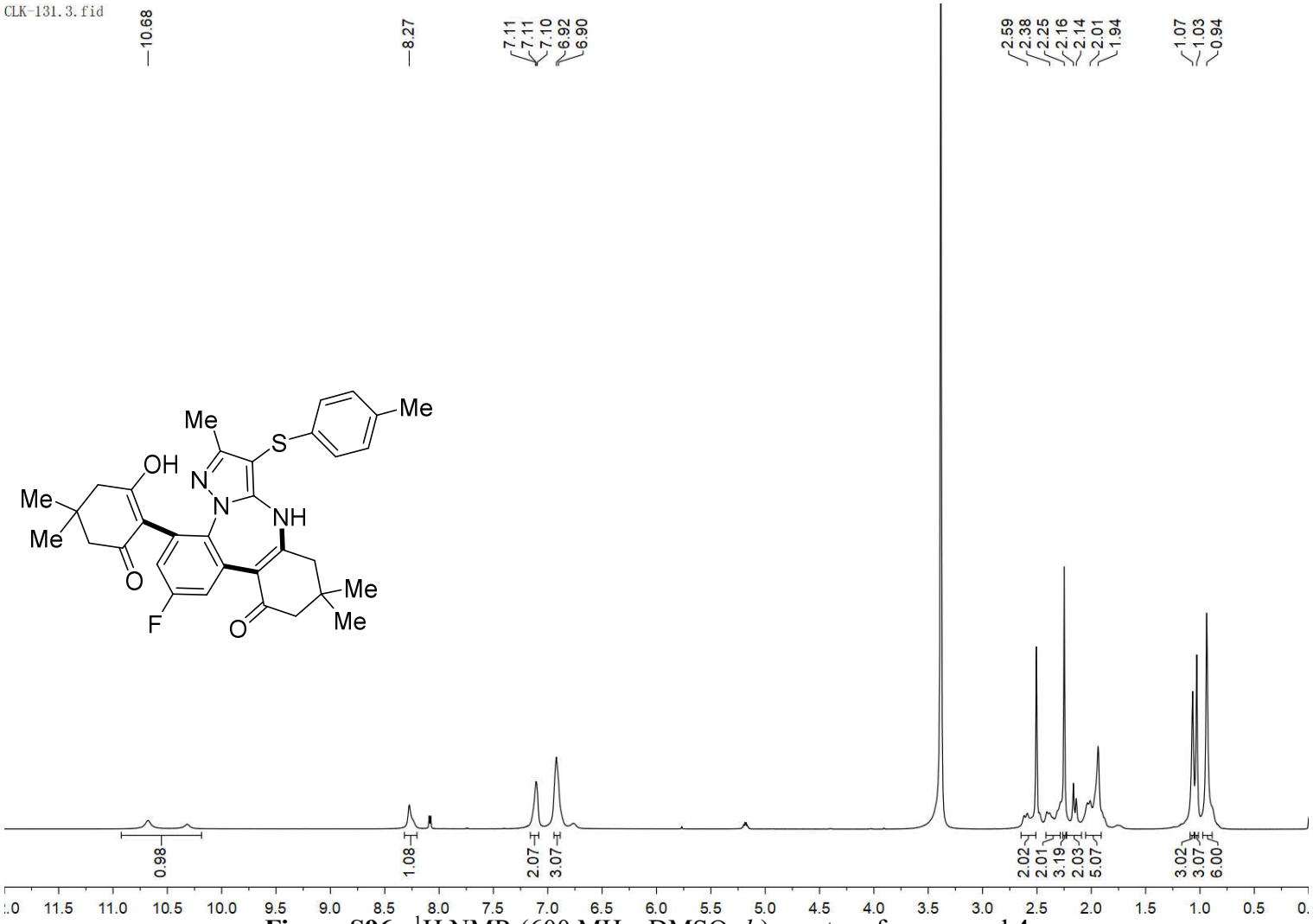


Figure S96. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4w**

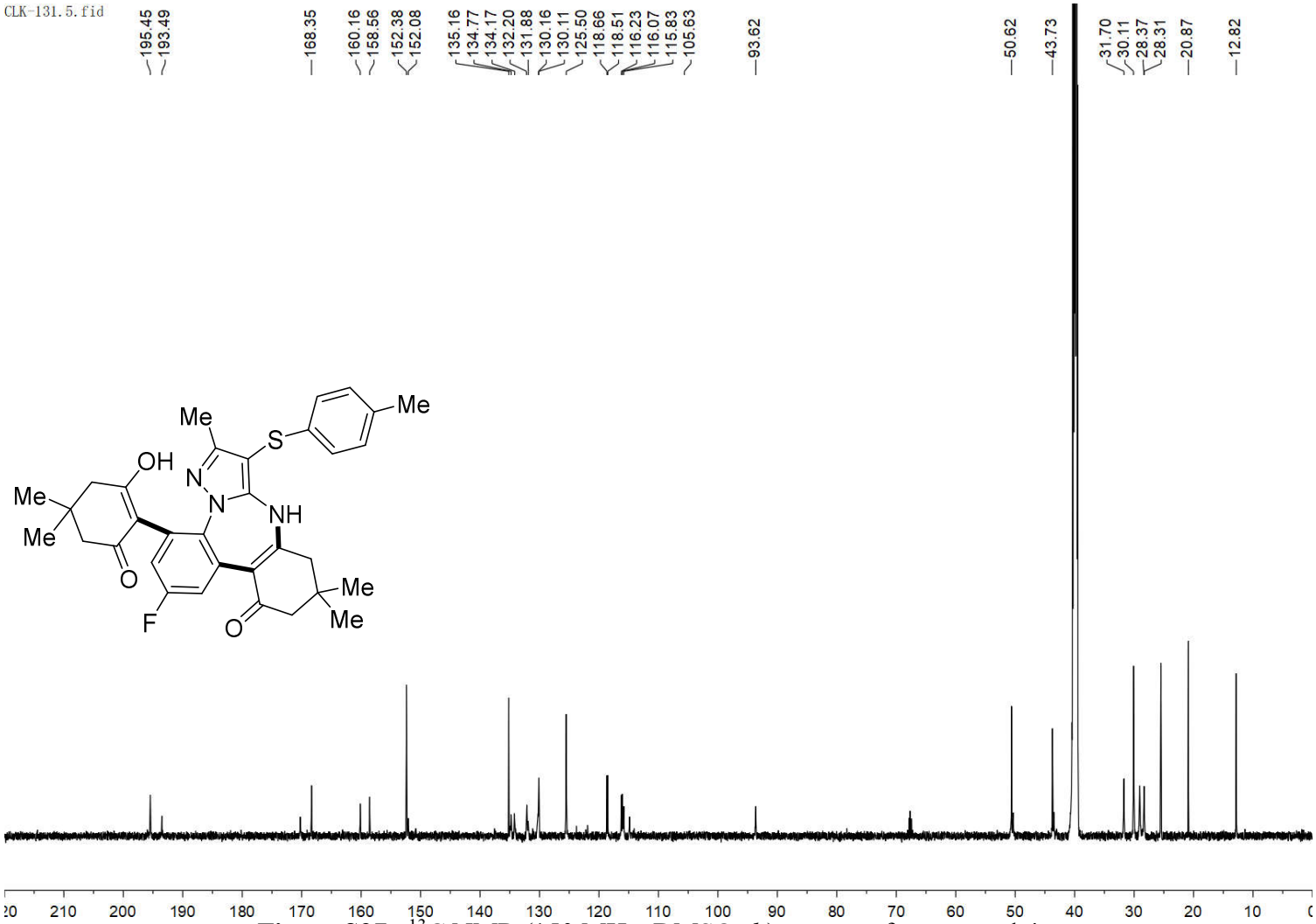


Figure S97. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4w**

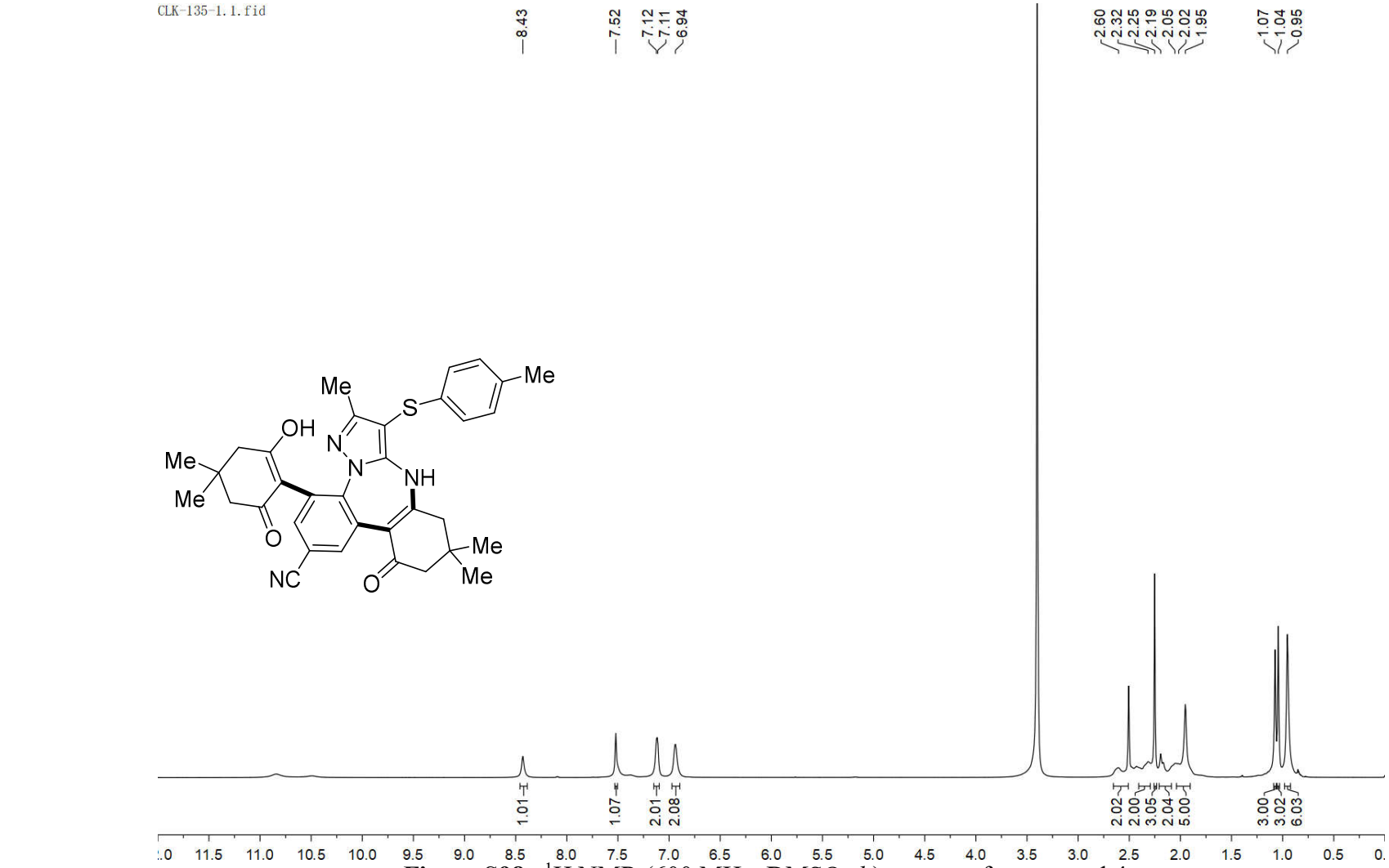


Figure S98. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4x**

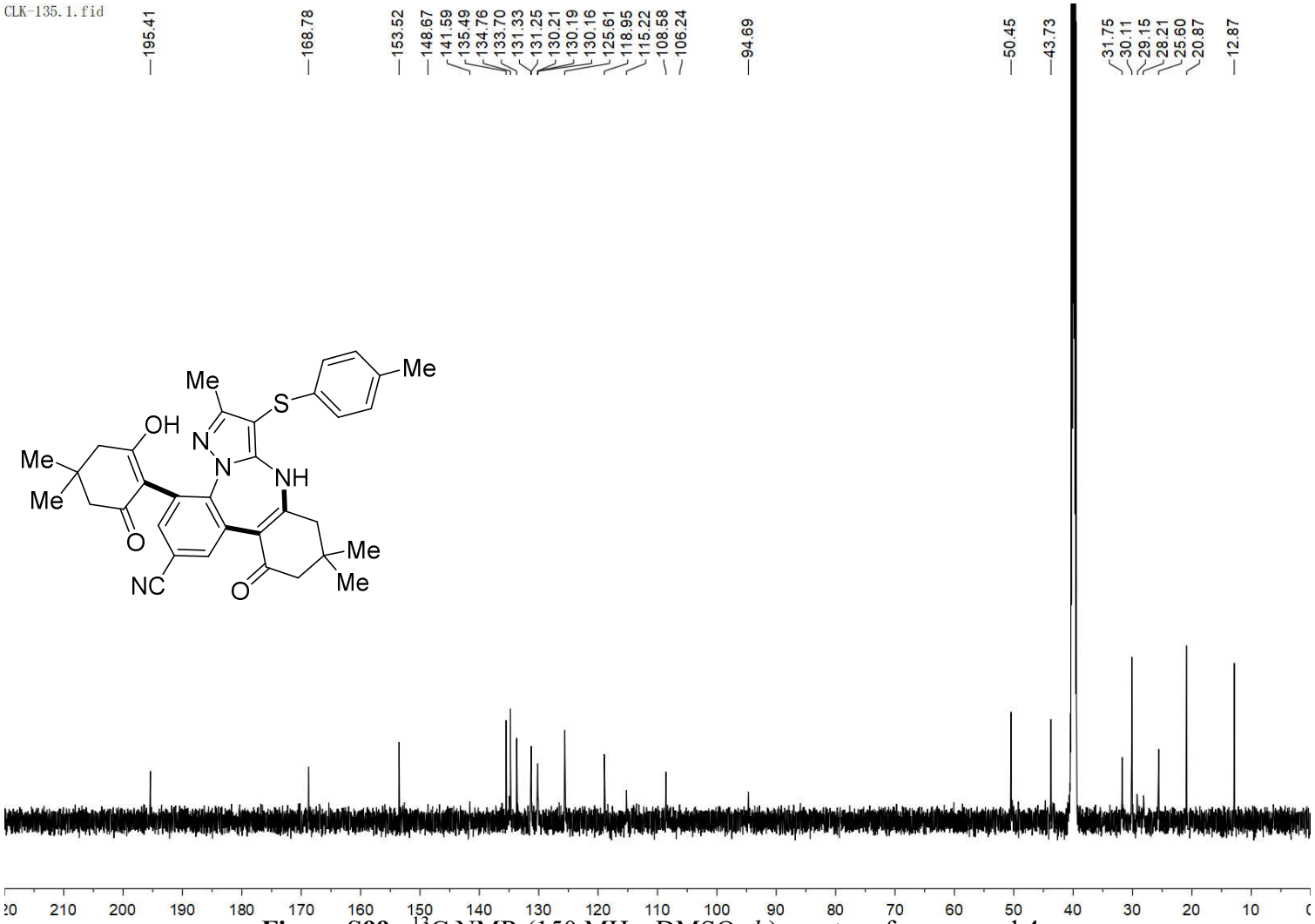


Figure S99. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4x**

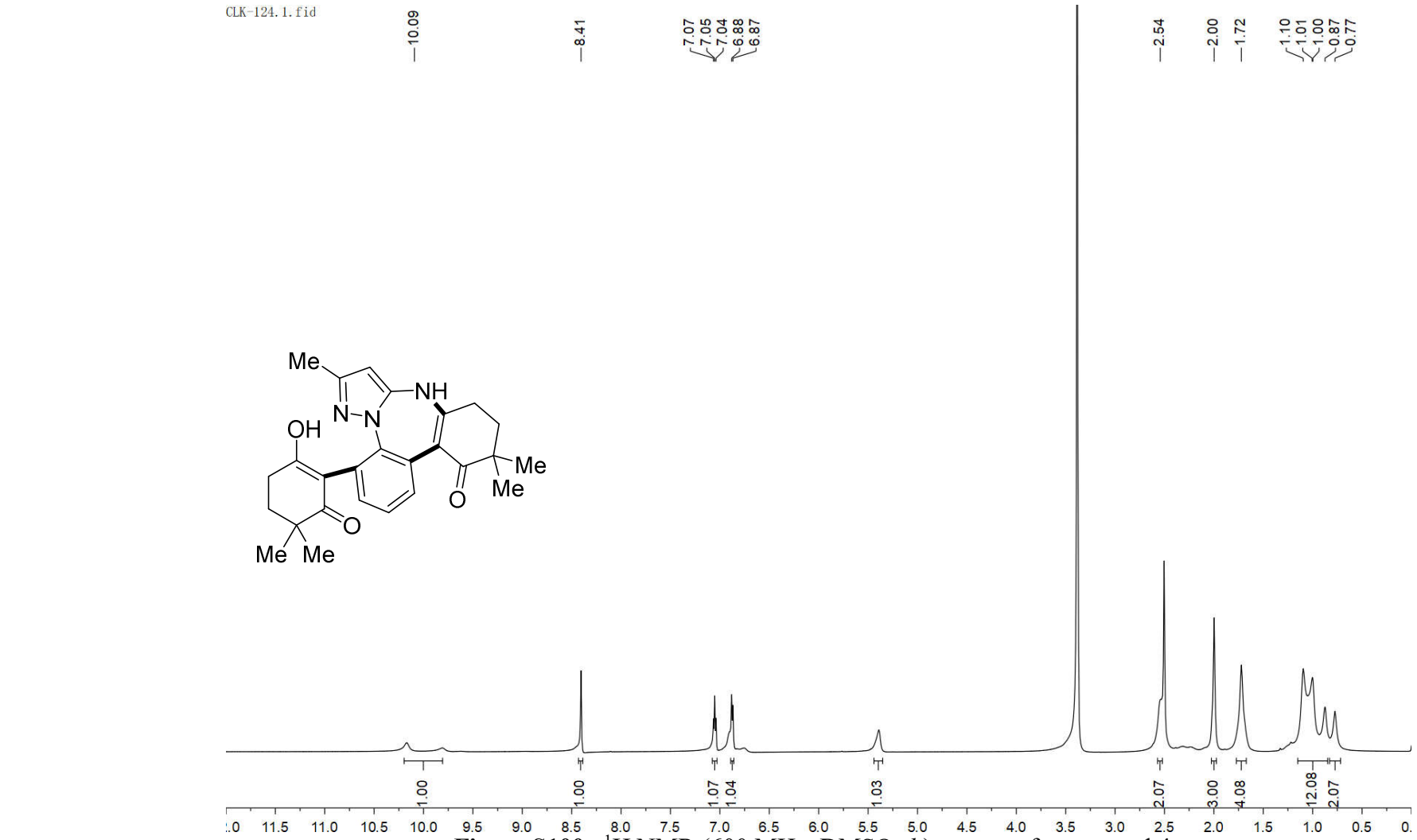


Figure S100. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4y**

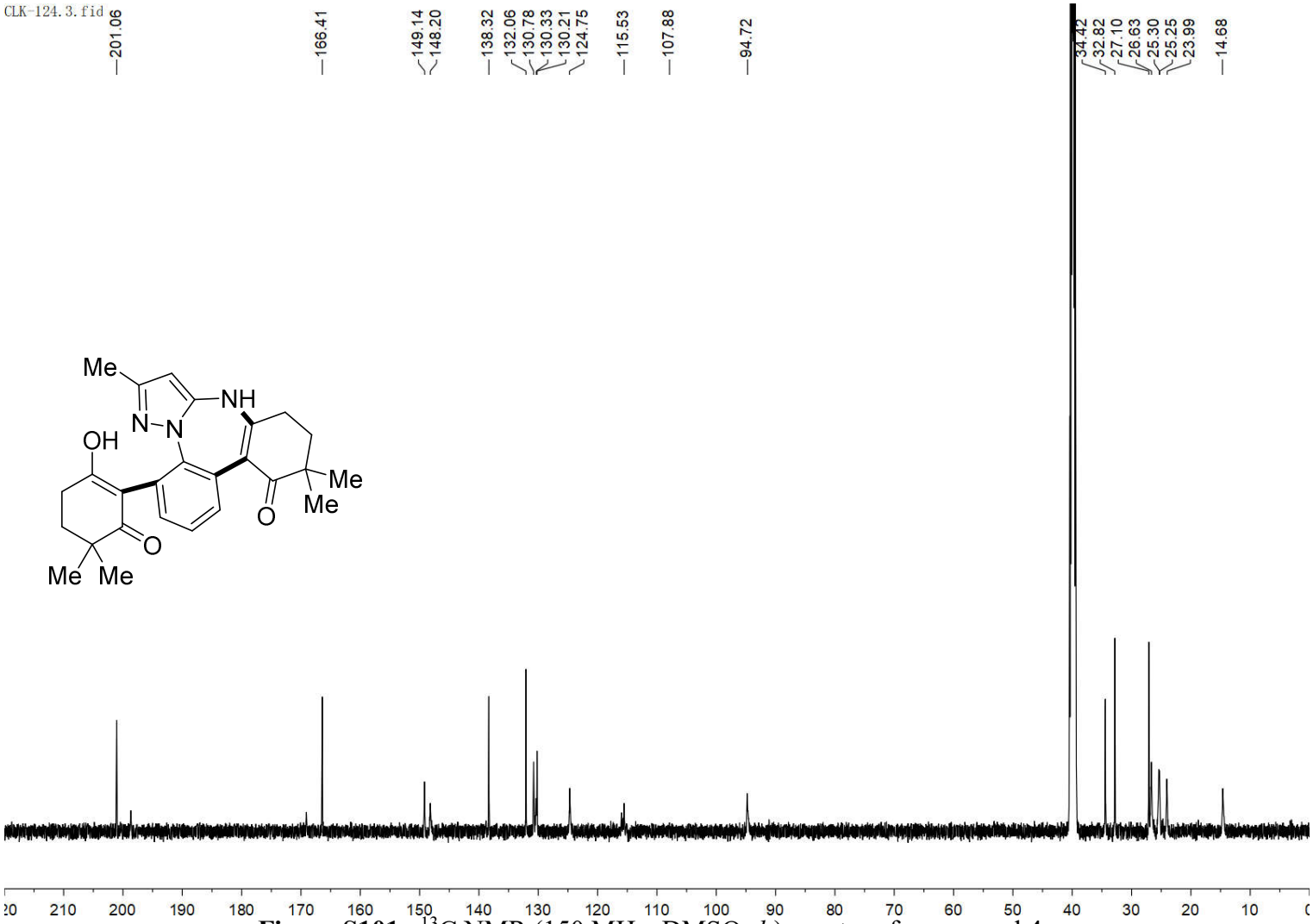


Figure S101. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4y**

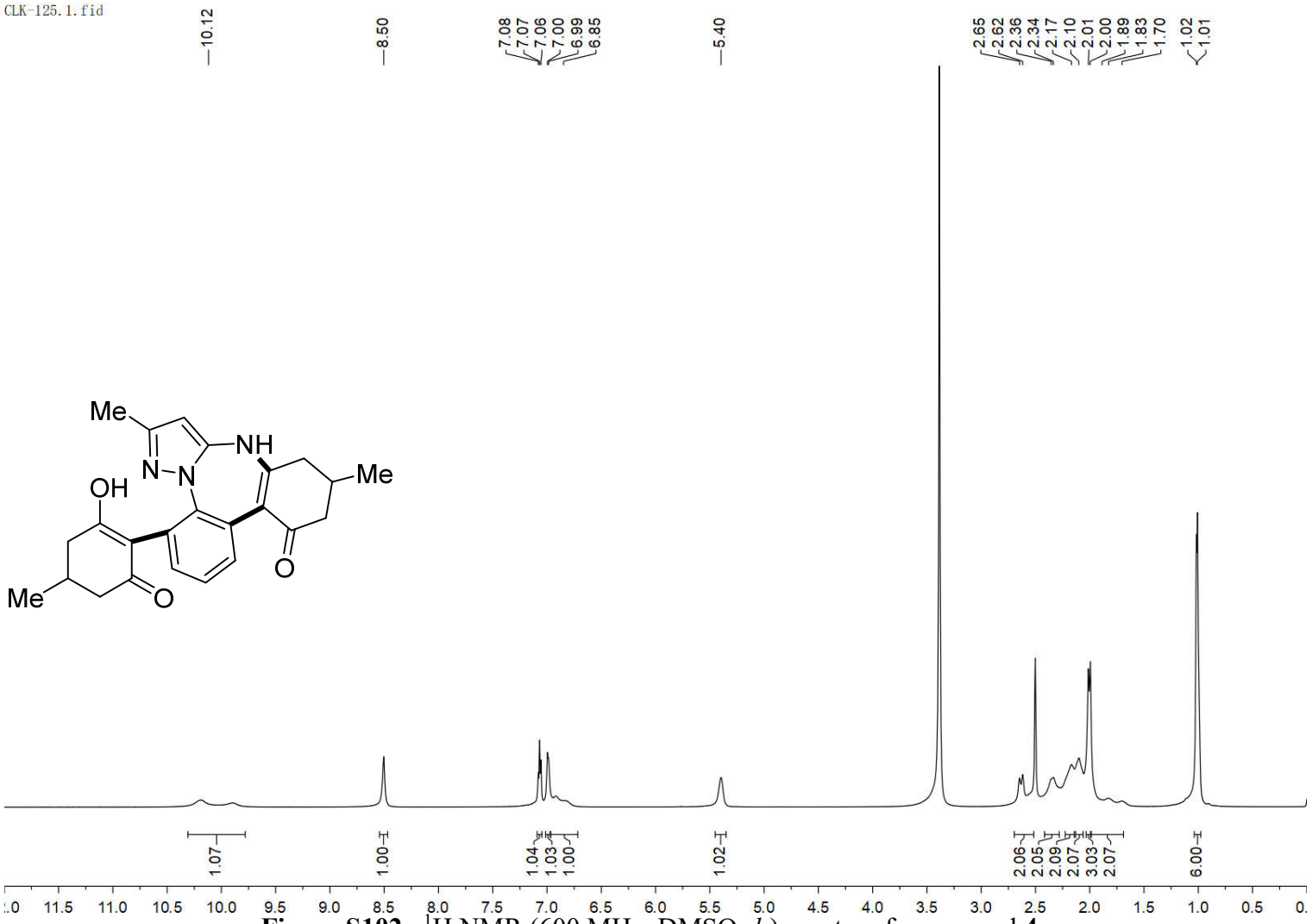


Figure S102. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4z**

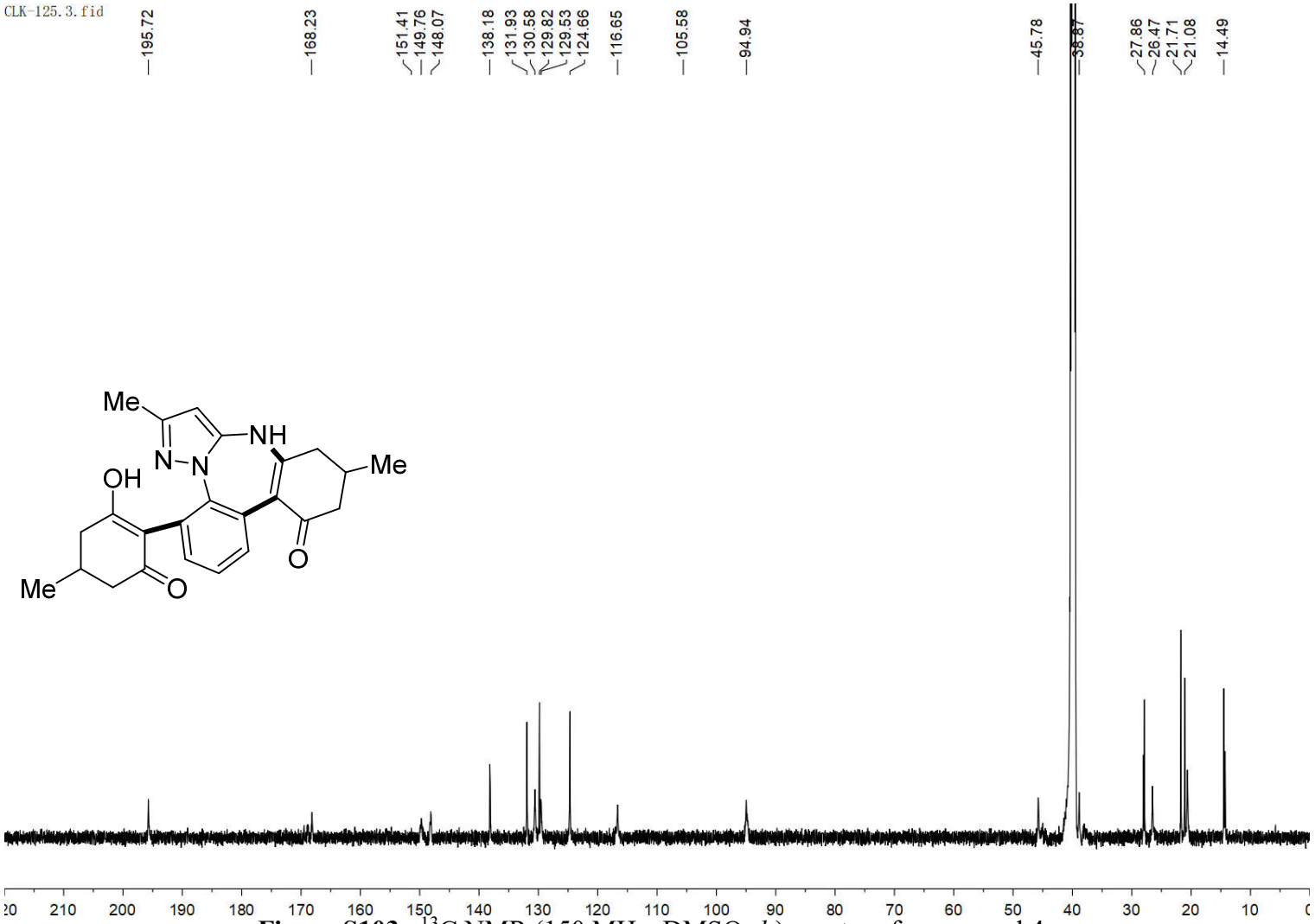


Figure S103. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4z**

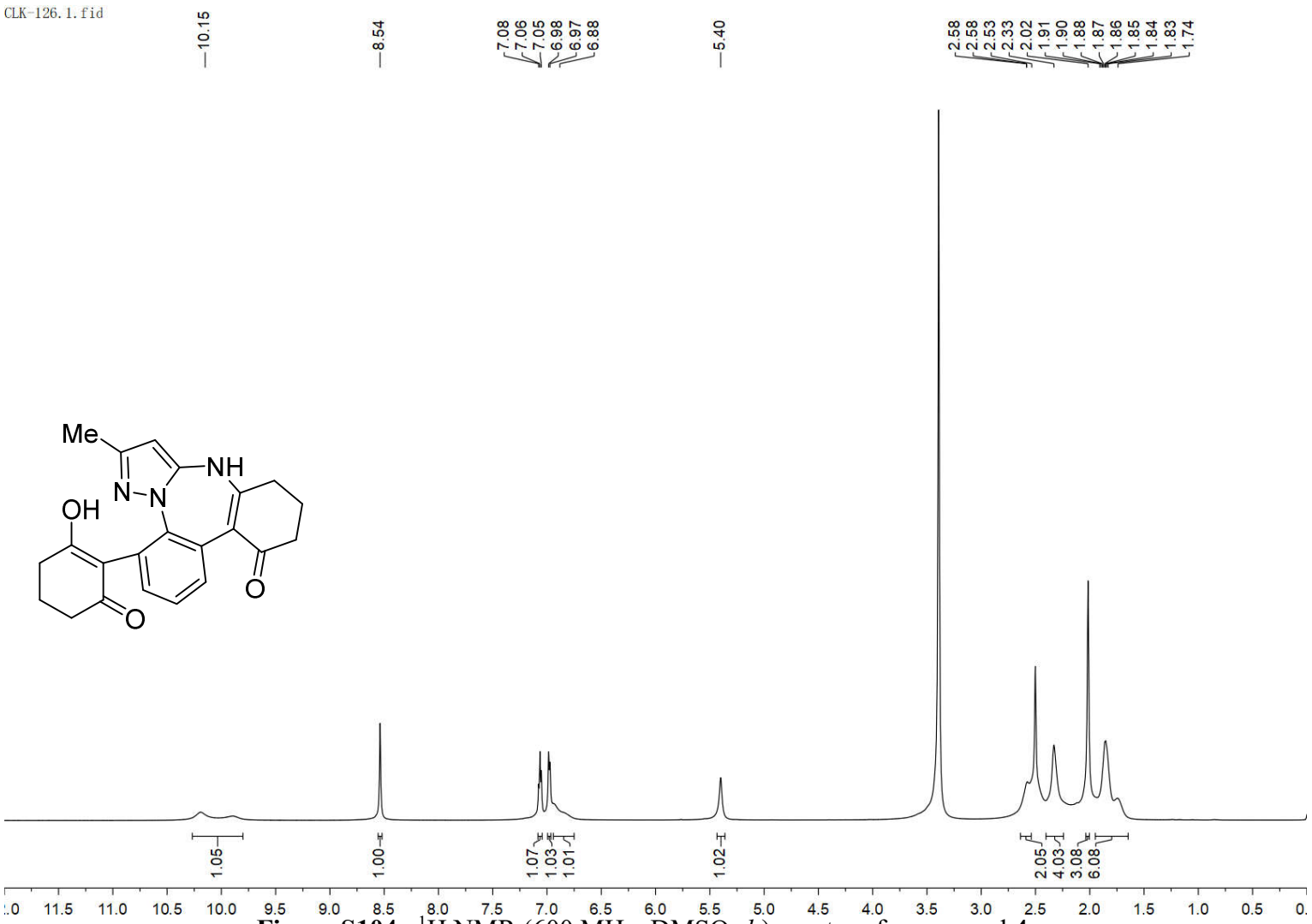


Figure S104. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4aa**

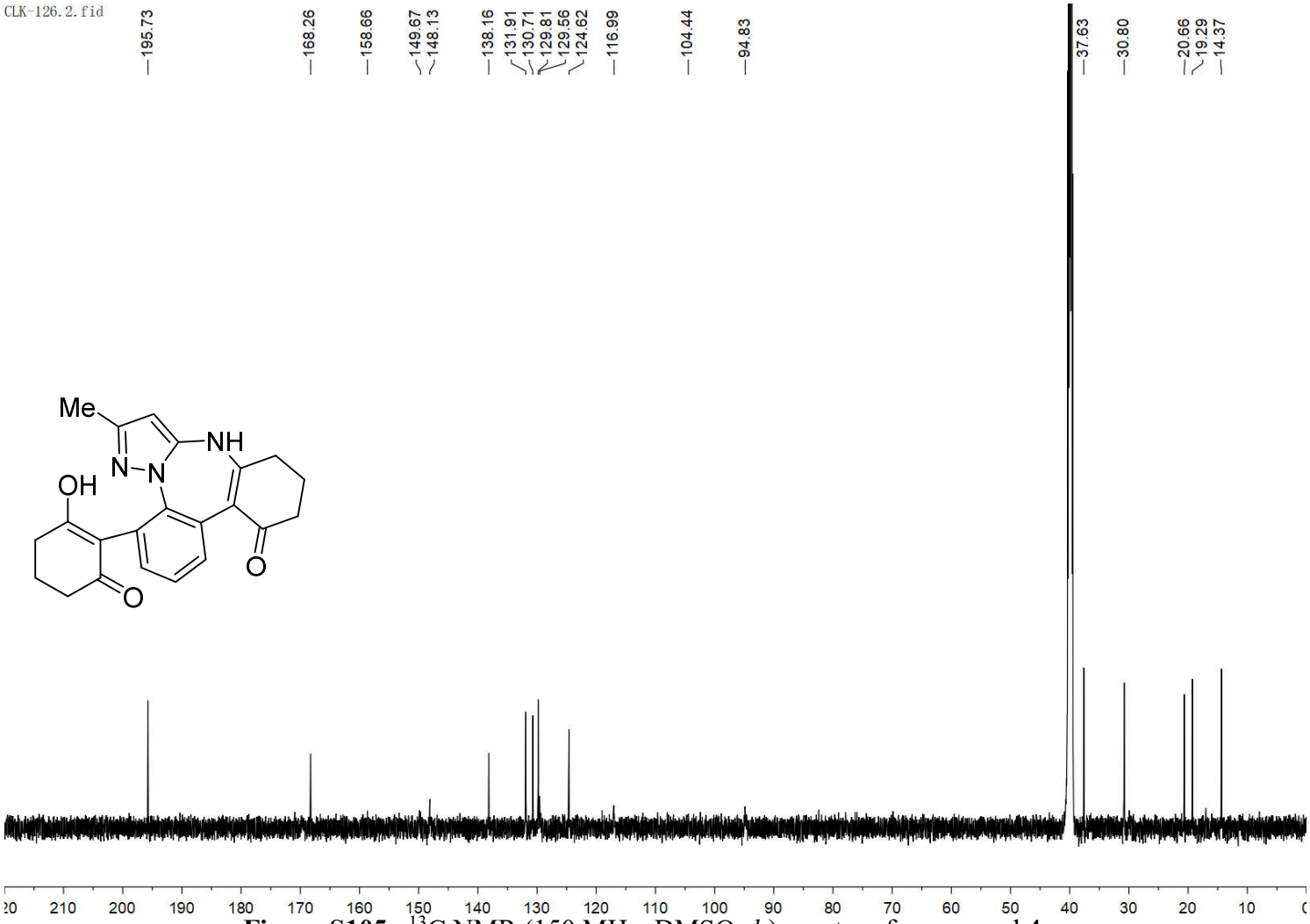


Figure S105. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4aa**

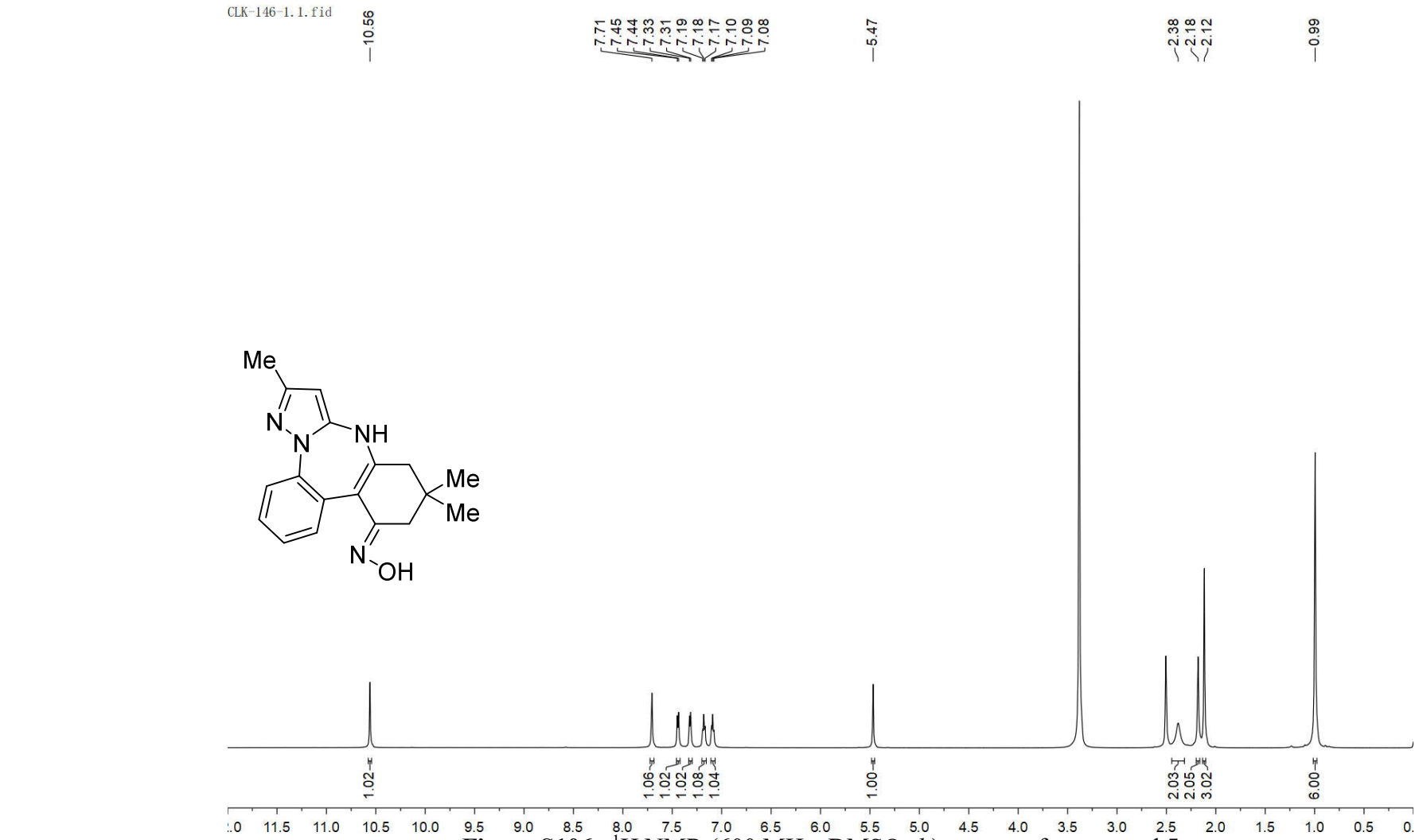


Figure S106. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **5**

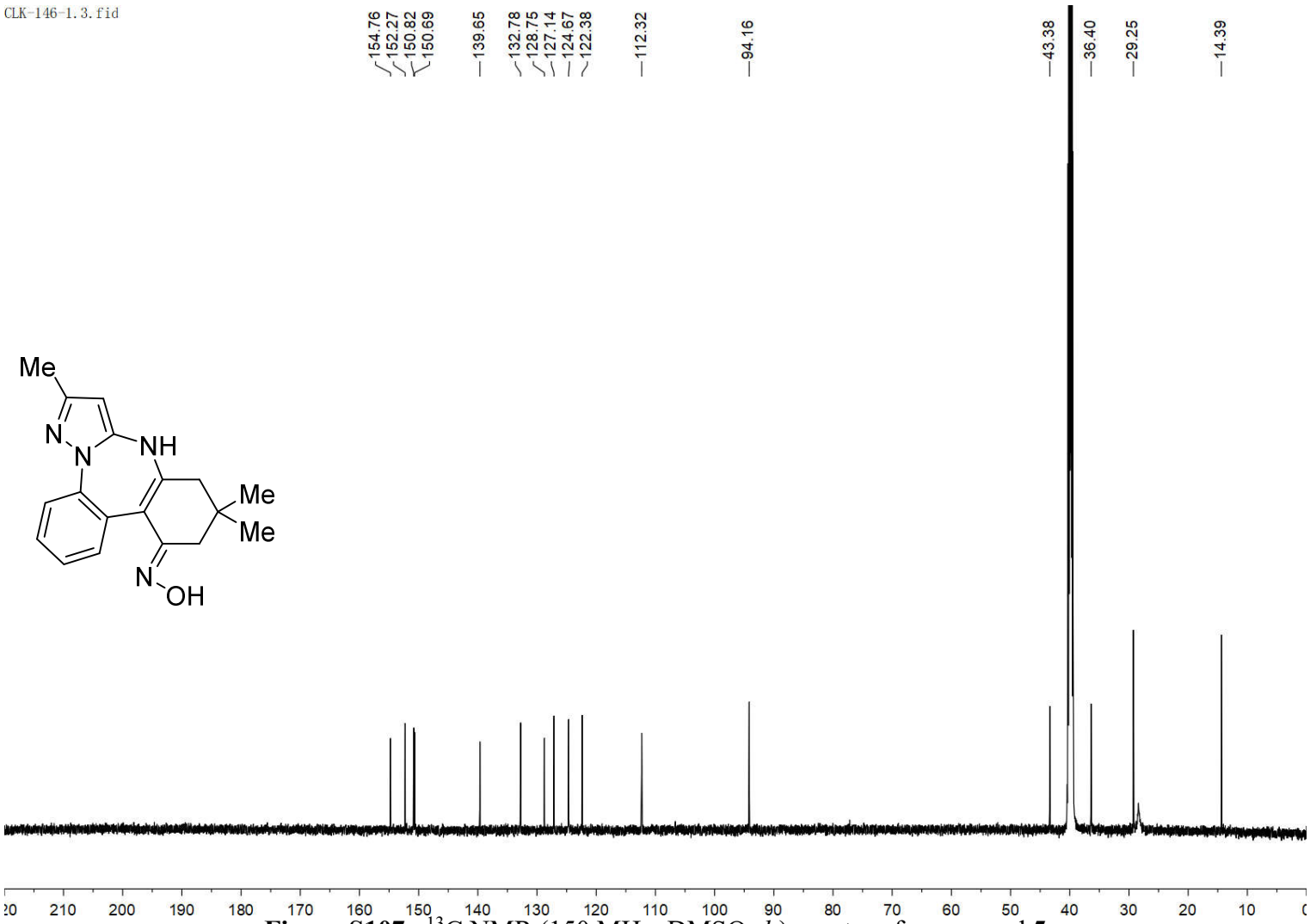


Figure S107. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **5**

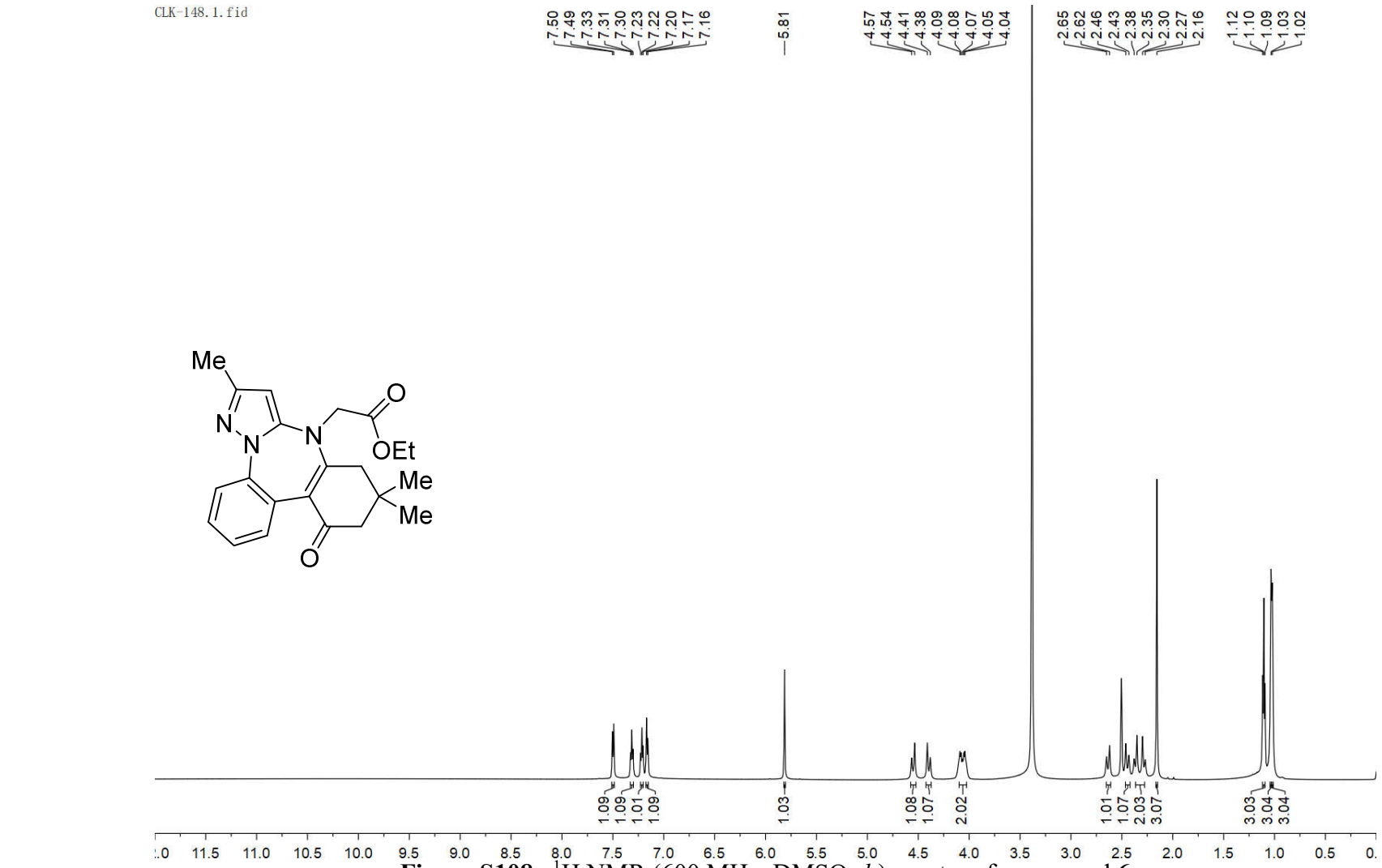


Figure S108. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **6**

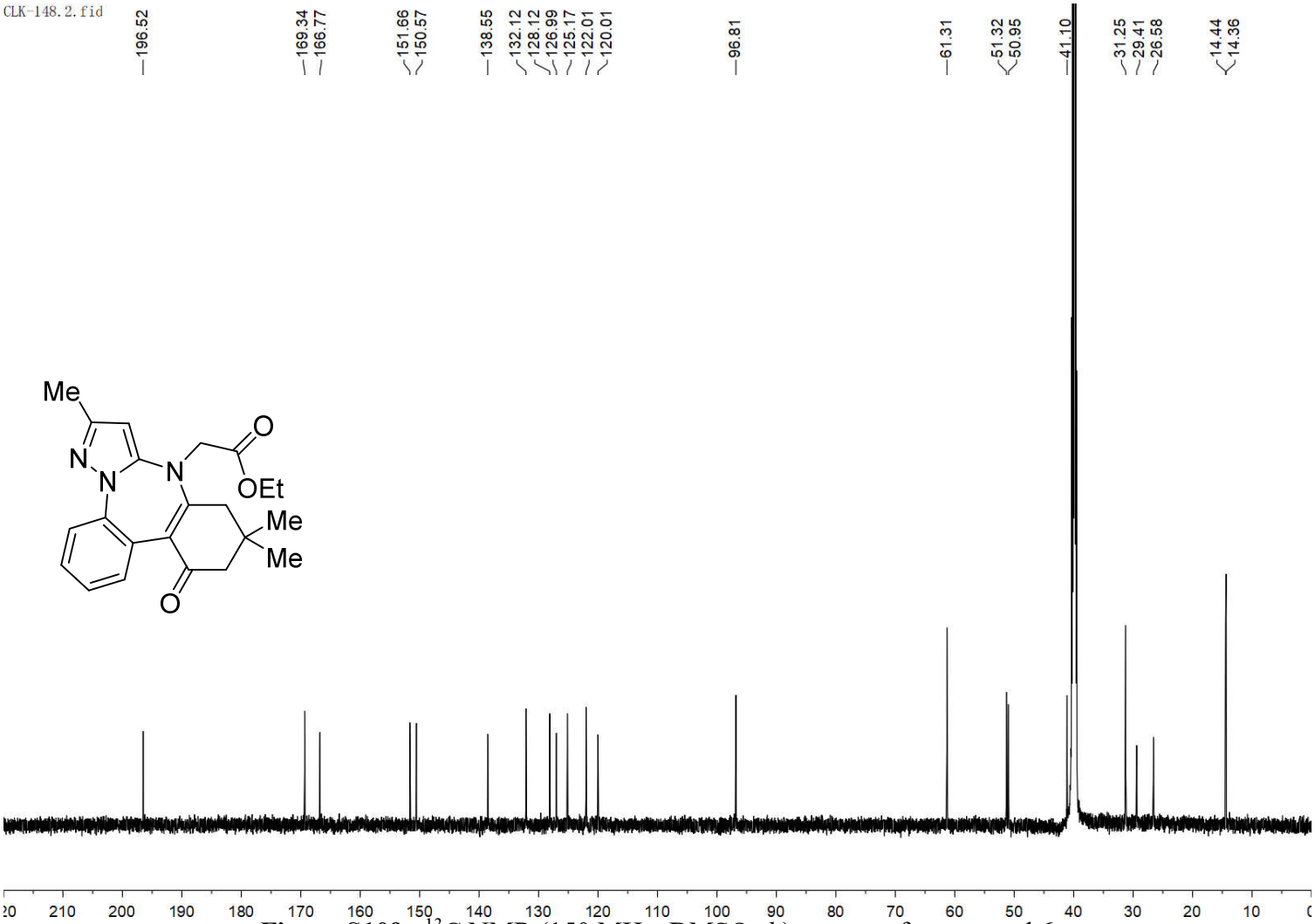


Figure S109. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **6**

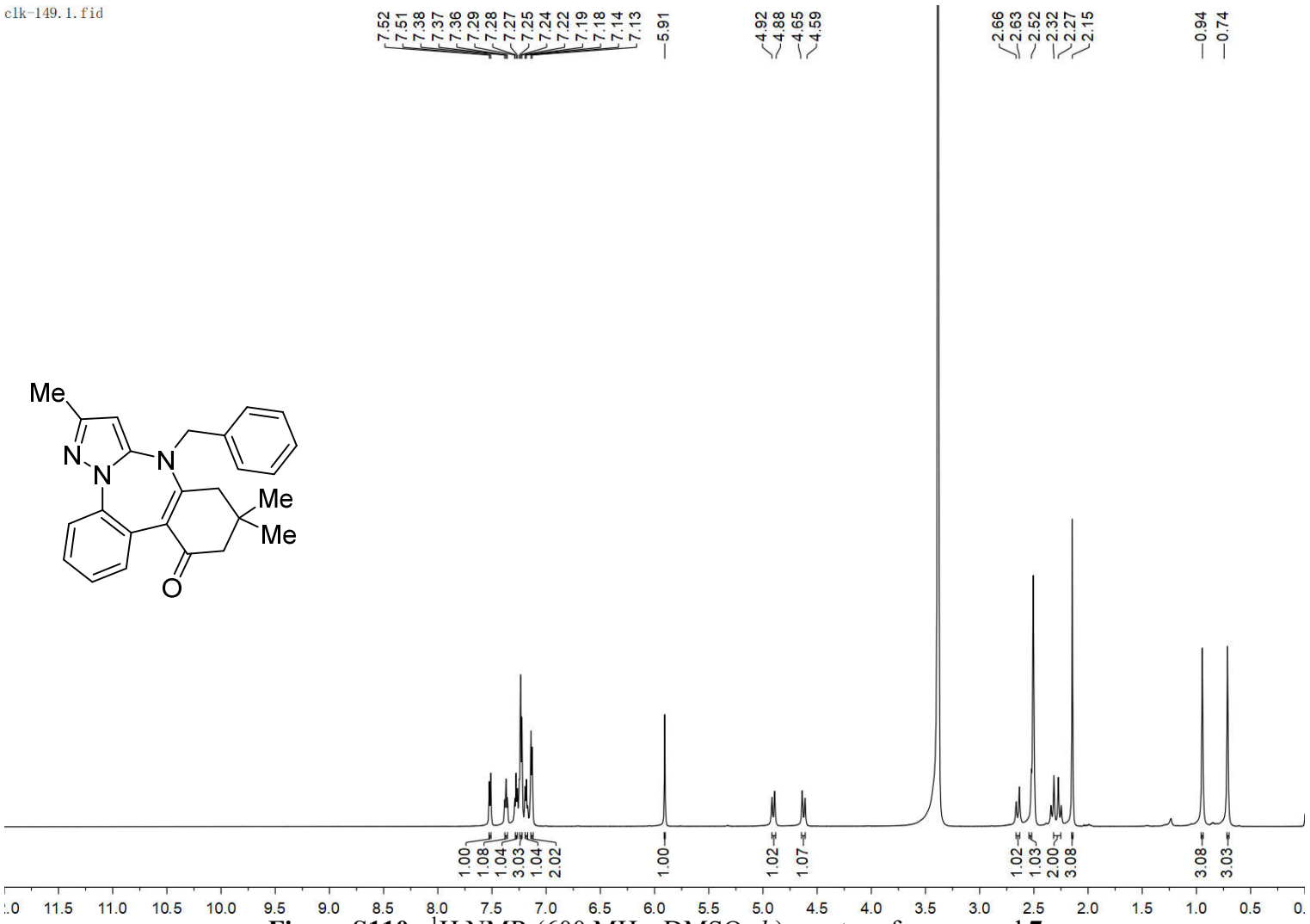


Figure S110. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **7**

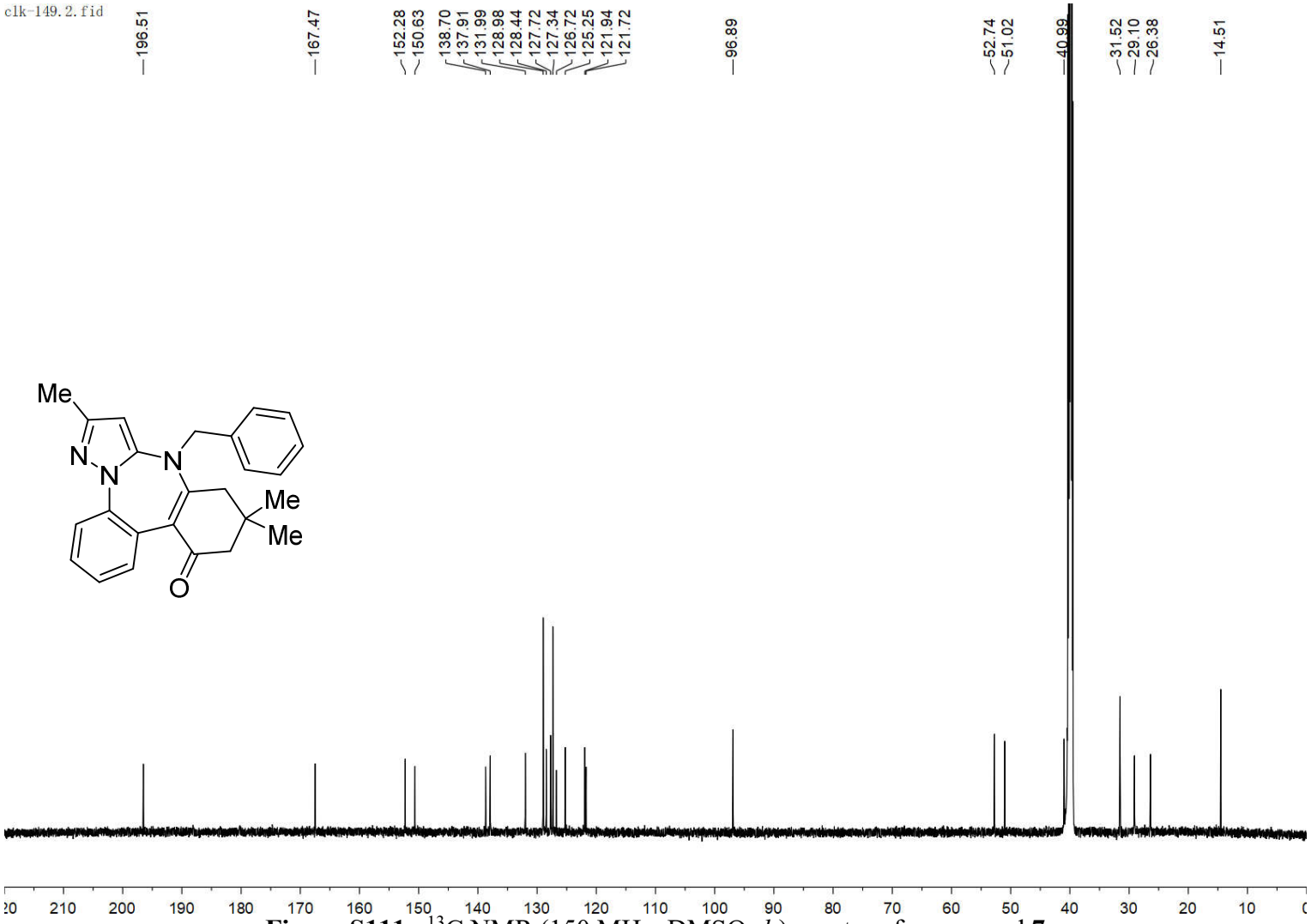


Figure S111. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **7**

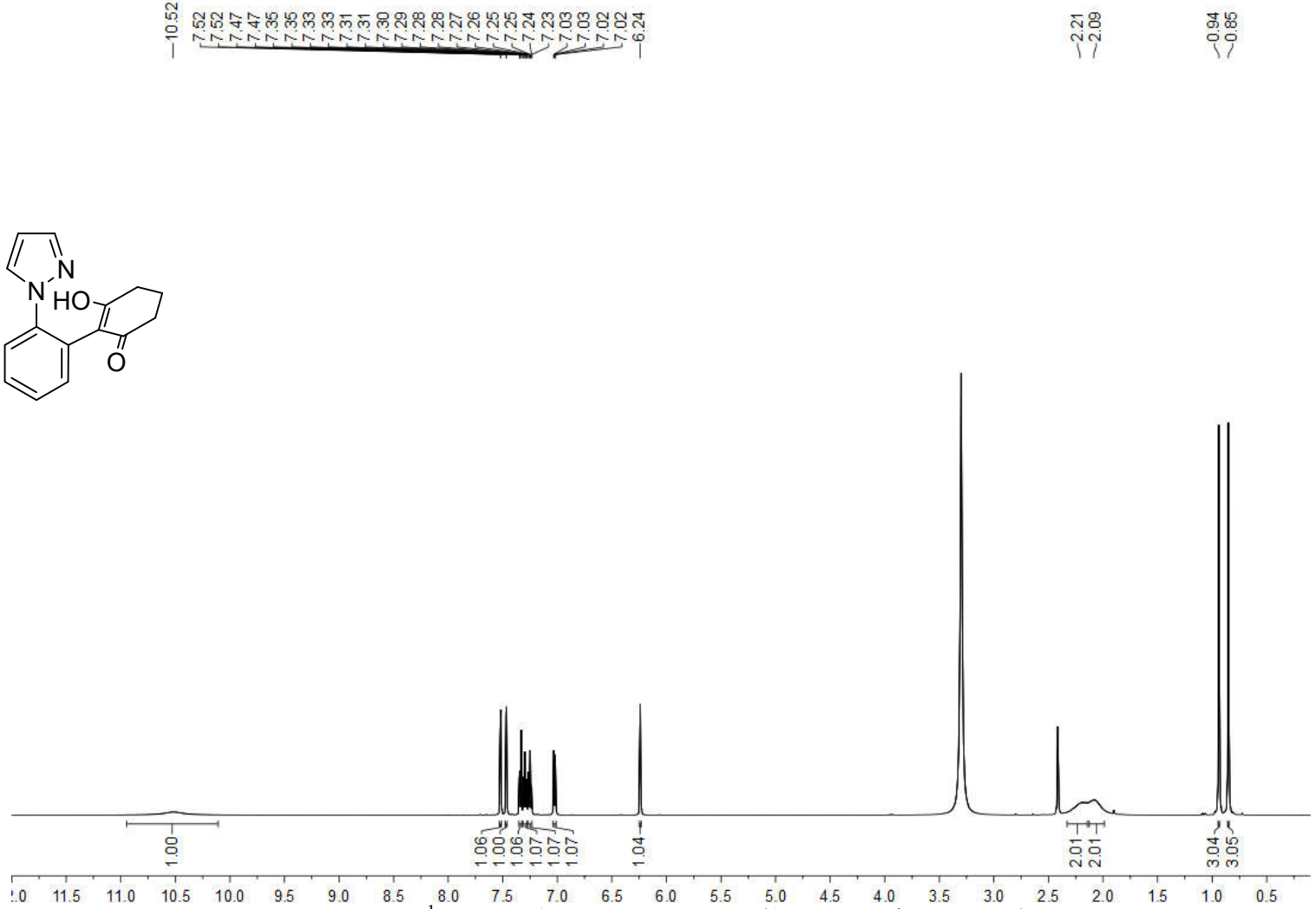


Figure S112. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **9a**

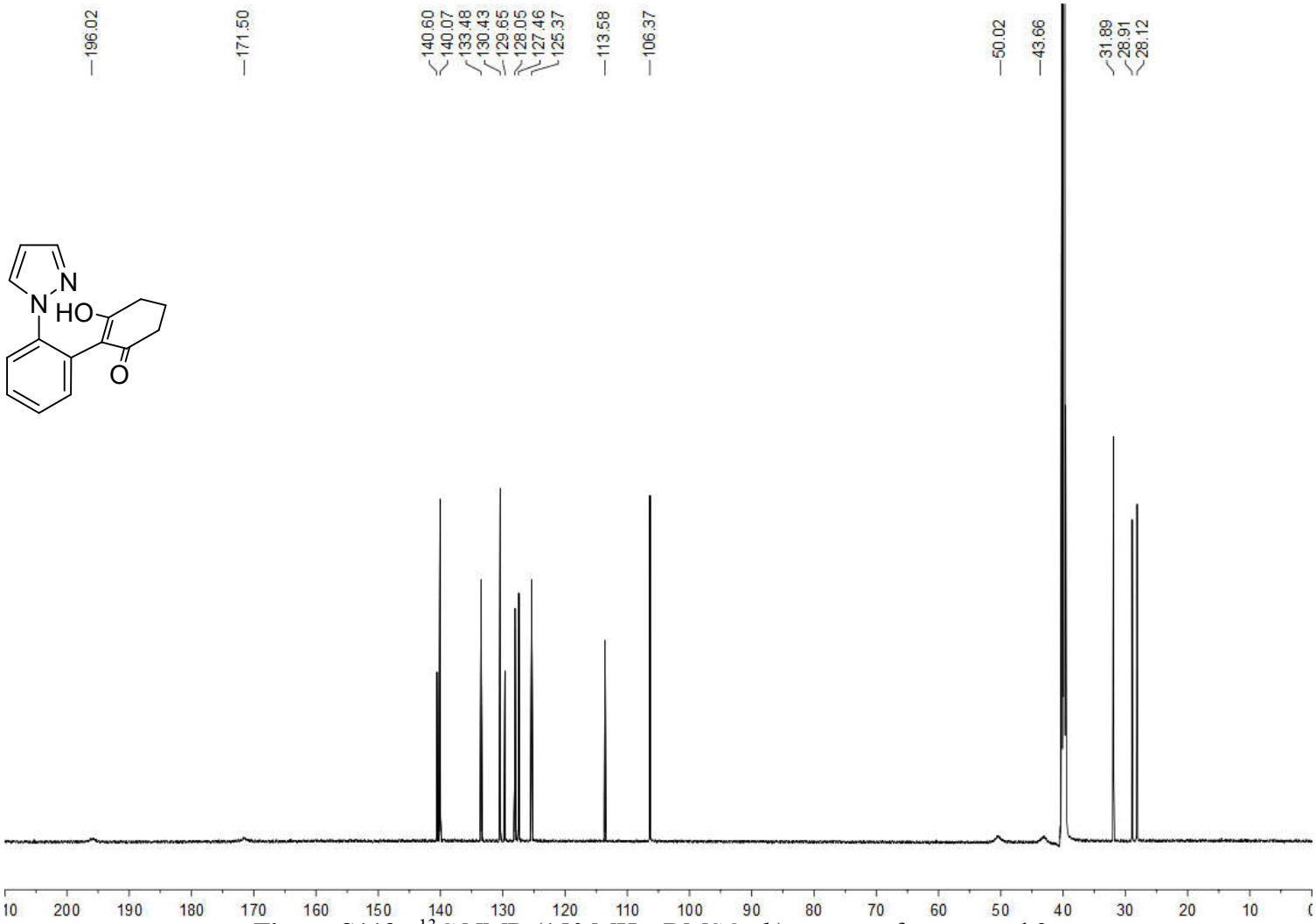


Figure S113. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **9a**

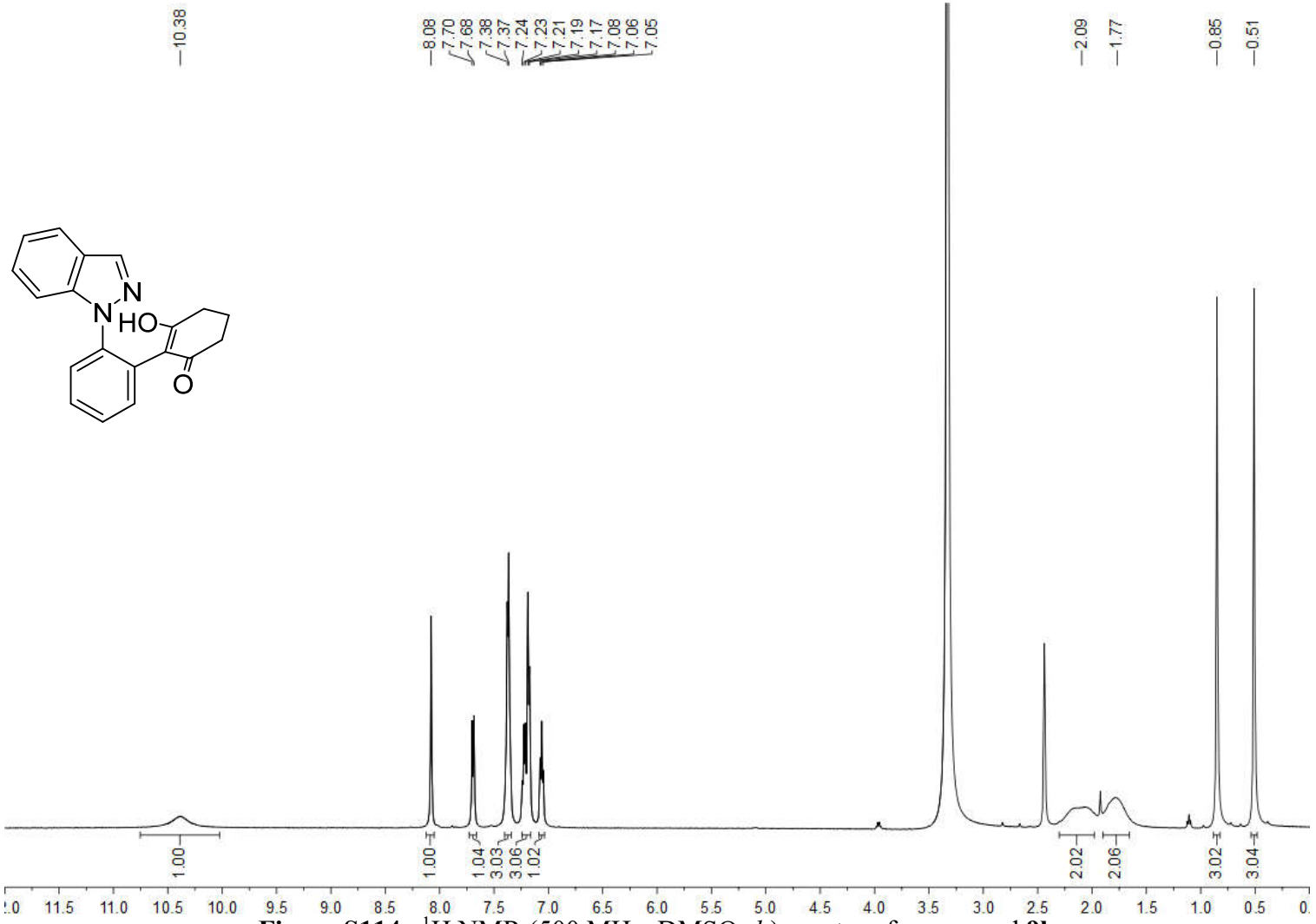


Figure S114. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **9b**

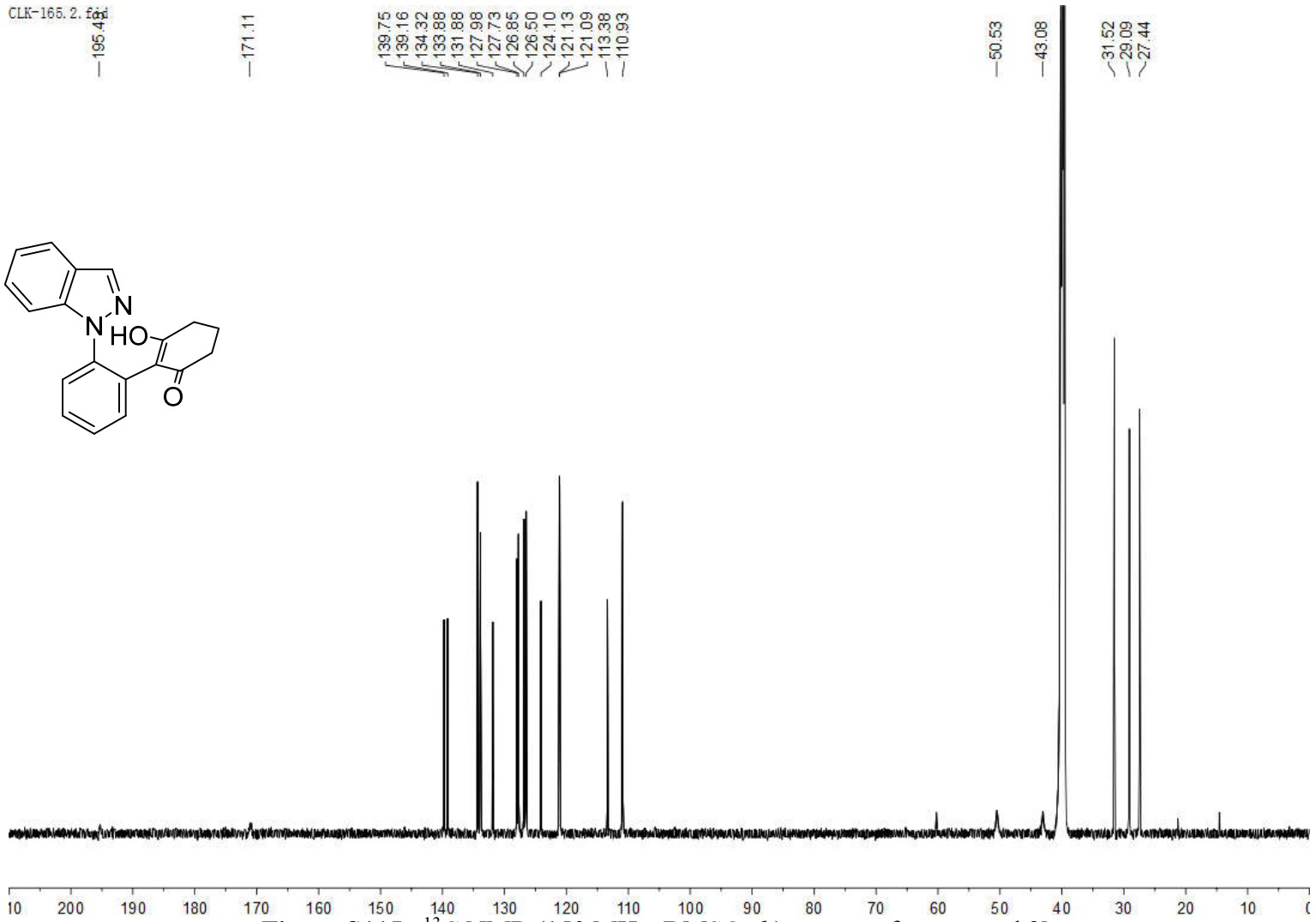


Figure S115. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **9b**

7. References and notes.

1. (a) Rimland, J.; Dunne, A.; Hunjan, S. S.; Sasse, R.; Uings, I.; Montanari, D.; Caivano, M.; Shah, P.; Standing, D.; Gray, D.; Brown, D.; Cairns, W.; Trump, R.; Smith, P. W.; Bertheleme, N.; D'Alessandro, P.; Gul, S.; Vimal, M.; Smith, D. N.; Watson, S. P. *Bioorg. Med. Chem. Lett.*, **2010**, *20*, 2340. (b) Saritha, R.; Annes, S. B.; Perumal, K.; Shankar, B.; Ramesh, S. *J. Org. Chem.,* **2022**, *87*, 13856.
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 2292416 and 2292417 contain the supplementary crystallographic data for compound **3j** and **4r**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.