Supporting Information

Copper-Catalyzed Sequential Arylation and Intramolecular Annulation of 2-(2-Bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-ones with Amidines

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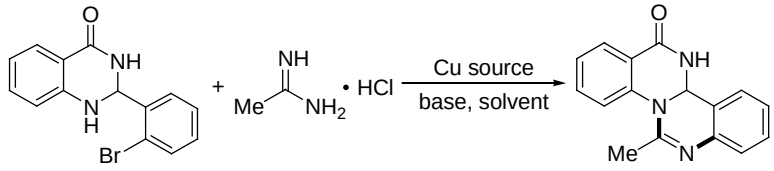
1. General experimental details

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz Bruker spectrometer using DMSO as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. *J* values are in hertz. Organic solvents used were dried by standard methods. The mass analyzer type for the high-resolution mass spectra (HRMS) is quadrupole (for ESI). Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on neutral Al_2O_3 (200−300 mesh).

2. Typical Procedure for copper-catalyzed reaction of 1 with amidines: To a Schlenk reaction tube was added 2-(2-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-ones **1** (0.2 mmol), amidines **2** (0.5 mmol), $Cu(acac)_2$ (10 mol %), and Cs_2CO_3 (0.8 mmol). The reaction tube was placed under high vacuum, backfilled with nitrogen and repeated three times. THF (3 mL) was added using a syringe. The mixture was stirred vigorously at 90 ^{o}C for 24 h. Then the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (neutral Al_2O_3) to afford the desired products **3** or **4**.

3. Screening Optimal Conditions

***Table S1**: Copper-catalyzed synthesis of **3aa** under different reaction parameters*

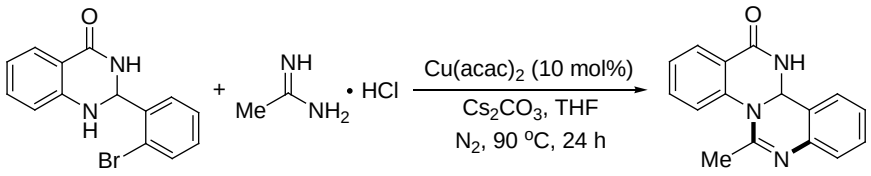


1a **2a** **3aa**

Entry	Cu source	Base	Solvent	Temp. (°C)	Yield (%)
1	copper(II) ethylacetoacetate	Cs_2CO_3	THF	60	29
2	copper(II) hexafluoropentanedionate	Cs_2CO_3	THF	60	35
3	$Cu(acac)_2$	Na_2CO_3	THF	90	trace
4	$Cu(acac)_2$	*t*-BuOK	THF	60	0
5	$Cu(acac)_2$	Cs_2CO_3	CH_2Cl_2	60	45
6	$Cu(acac)_2$	Cs_2CO_3	DMSO	60	21
7	$Cu(acac)_2$	Cs_2CO_3	THF:DMSO (2:1)[b]	60	23
8	$Cu(acac)_2$	Cs_2CO_3	CH_2Cl_2:DMSO (1:3)[b]	60	9
9	$Cu(acac)_2$	Cs_2CO_3	cyclohexane:EtOH (9:1)[b]	60	33

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), indicated Cu source (10 mol %), base (0.5 mmol), solvent (3 mL), 60 °C, 24 h, N_2, isolated yield. [b] Volume ratio for entries 7–9.

***Table S2**: The effect of different molar ratio of substrates on the reaction*

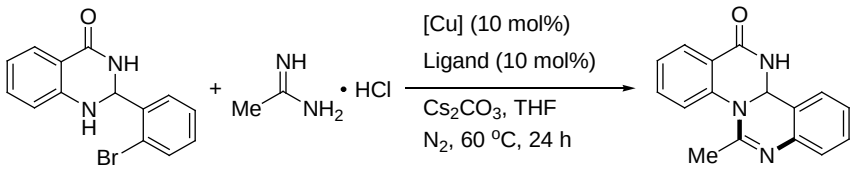


1a **2a** **3aa**

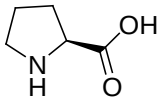
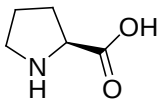
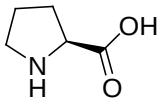
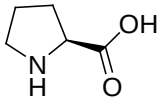
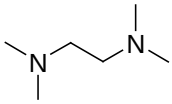
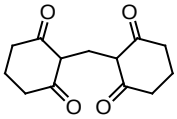
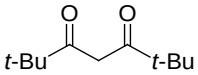
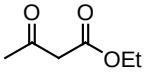
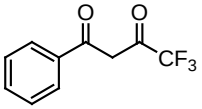
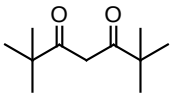
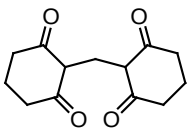
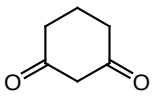
Entry	Molar Ratio (**1a** : **2a** : Cs_2CO_3)	Yield (%)
1	1 : 1 : 2.5	29
2	1 : 1.5 : 3	48
3	1 : 2 : 3.5	69
4	1 : 2.5 : 4	90
5	1 : 3 : 4.5	91
6	1 : 4 : 5.5	88
7	1 : 4 : 7	72

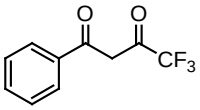
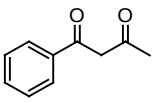
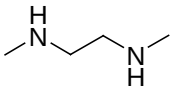
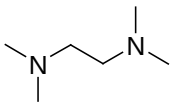
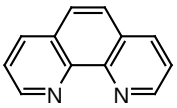
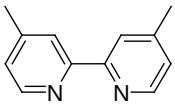
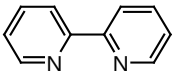
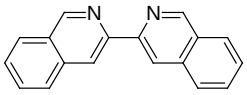
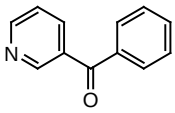
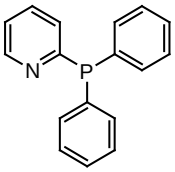
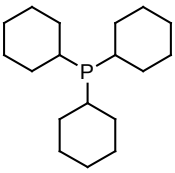
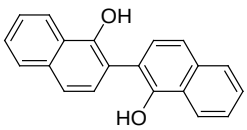
[a] Reaction conditions: $Cu(acac)_2$ (10 mol %), THF (3 mL), 90 °C, 24 h, N_2, GC yield.

***Table S3**: The effect of different ligands on the reaction*[a]



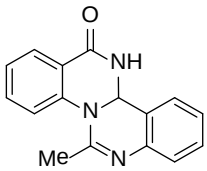
1a **2a** **3aa**

Entry	Cu source	Ligand	Yield (%)
1	CuBr		46
2	CuI		49
3	$Cu(OAc)_2$		16
4	$Cu(acac)_2$		58
5	$Cu(acac)_2$		52
6	$Cu(acac)_2$		54
	$Cu(acac)_2$		34
7	$Cu(acac)_2$		44
8	$Cu(acac)_2$		40
9	$Cu(OAc)_2$		26[b]
10	$Cu(OAc)_2$		38
11	$Cu(OAc)_2$		22

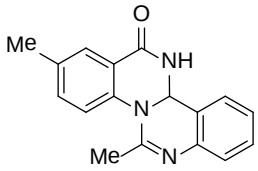
12	$Cu(OAc)_2$		38
13	$Cu(OAc)_2$		13
14	$Cu(OAc)_2$		17
15	$Cu(OAc)_2$		36
16	$Cu(OAc)_2$		11
17	$Cu(OAc)_2$		24
18	$Cu(OAc)_2$		29
19	$Cu(OAc)_2$		12
20	$Cu(OAc)_2$		10
21	$Cu(OAc)_2$		10
22	$Cu(OAc)_2$		11
23	$Cu(OAc)_2$		21

[a] Reaction conditions for entries 1–10: **1a** (0.2 mmol), **2a** (0.3 mmol), indicated Cu source (10 mol %), Cs_2CO_3 (0.5 mmol), THF (3 mL), 60 °C, 24 h, N_2, isolated yield. [b] Reaction conditions for entries 11–32: **1a** (0.2 mmol), **2a** (0.8 mmol), $Cu(OAc)_2$ (10 mol %), Cs_2CO_3 (1.6 mmol), THF (3 mL), 60 °C, 24 h, N_2, GC yield.

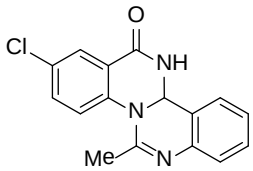
4. Analytical data for all products



6-Methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3aa**) (Table 2, entry 1): White solid, mp 247-249 ^{o}C . ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.11 (s, 3H), 6.21 (d, *J* = 1.3 Hz,1H), 7.17-7.15 (m, 1H), 7.21-7.18 (m, 1H), 7.29-7.27 (m, 1H), 7.38-7.36 (m, 1H), 7.47-7.45 (m, 1H), 7.66-7.61 (m, 2H),7.95 (d, *J* = 7.6 Hz, 1H),8.74 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.4, 63.9, 118.6, 124.0, 124.6, 125.1, 126.5, 126.6, 127.5, 127.6, 129.9, 132.3, 140.8, 141.4, 152.2, 162.2 . IR (KBr): 3043 (N-H), 1675 (C=O) cm^{-1}. HRMS (ESI) for $C_{16}H_{13}N_3O$ $(M+H)^+$: calcd. 264.1131, Found 264.1117.

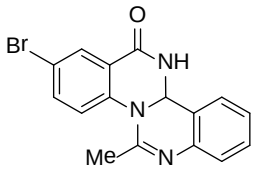


2,6-Dimethyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one(**3ba**) (Table 2, entry 2): White solid, mp 278-280 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.10 (s, 3H), 2.40 (s, 3H), 6.17 (s, 1H), 7.15-7.19 (m, 2H), 7.27-7.28 (m, 1H), 7.38-7.51 (m, 3H), 7.75 (s, 1H), 8.66 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 20.5, 22.3, 63.9, 118.6, 123.9, 124.4, 124.9, 126.2, 127.5, 127.7, 129.9, 132.8, 136.1, 138.9, 140.7, 152.4, 162.2.. IR (KBr): 3034 (N-H), 1663 (C=O) cm^{-1}. HRMS (ESI) for $C_{17}H_{15}N_3O$ $(M+H)^+$: calcd. 278.1288, Found 278.1298.

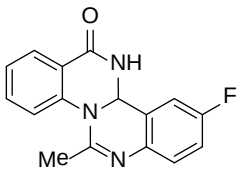


2-Chloro-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one(**3ca**) (Table 2, entry 3): Yellowish solid, mp 106-108 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.12 (s, 3H), 6.23 (d, *J* = 1.4 Hz, 1H), 7.20-7.16 (m, 1H), 7.23-7.21(m, 1H), 7.28-7.27 (m, 1H), 7.41-7.37 (m, 1H), 7.72-7.68 (m, 2H), 7.88 (d, *J* = 1.3 Hz, 1H), 8.89 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.2, 63.8, 118.4, 124.1, 125.2, 126.7, 126.9, 127.5, 128.0, 130.0, 130.9, 132.0, 140.2, 140.6, 151.9, 161.0 . IR (KBr): 3053 (N-H), 1663 (C=O) cm^{-1}.HRMS (ESI) for $C_{16}H_{12}ClN_3O$ $(M+H)^+$: calcd. 298.0742, 300.0713,

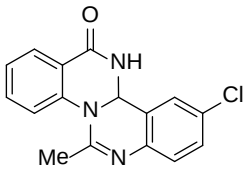
Found 298.0748, 300.0715.



2-Bromo-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3da**) (Table 2, entry 4): Yellowish solid, mp 235-236 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.12 (s, 3H), 6.23 (d, J = 1.3 Hz,1H), 7.18-7.16 (m, 1H), 7.23-7.19 (m, 1H), 7.29-7.27 (m, 1H), 7.40-7.37 (m, 1H), 7.63-7.62 (m, 1H),7.84-7.82 (m, 1H),8.01(d, J = 2.4 Hz, 1H),8.89 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.3, 63.8, 118.4, 119.0, 124.1, 125.2, 127.0, 127.5, 128.3, 129.9, 130.0, 134.9, 140.5, 141.6, 151.8, 160.9. IR (KBr): 3153 (N-H), 1684 (C=O) cm^{-1}. HRMS (ESI) for $C_{16}H_{12}BrN_3O$ $(M+H)^+$: calcd. 342.0237, 344.0217, Found 342.0243, 344.0230.

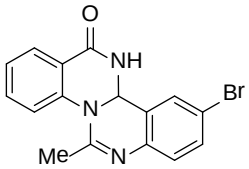


10-Fluoro-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ea**) (Table 2, entry 5): White solid, mp 217-218 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.10 (s, 3H), 6.22 (s,1H), 7.17-7.15 (m, 1H), 7.25-7.19 (m, 2H), 7.48-7.45 (m, 1H), 7.67-7.62 (m, 2H), 7.95 (d, J = 7.5 Hz, 1H),8.79 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.3, 63.6, 113.9, 114.1, 116.8, 117.0, 119.9, 124.7, 126.4, 126.7, 127.6, 132.4, 141.2, 151.8, 159.0 (d, $^{1}J_{CF}$ = 239.5 Hz, 1C), 162.1. IR (KBr): 3130 (N-H), 1703 (C=O) cm^{-1}.HRMS (ESI) for $C_{16}H_{12}FN_3O$ $(M+H)^+$: calcd. 282.1037, Found 282.1033.

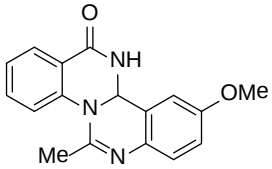


10-Chloro-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3fa**) (Table 2, entry 6): White solid, mp 242-244 ^{o}C . ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.11 (s, 3H), 6.23 (s,1H), 7.18-7.17 (m, 1H), 7.38-7.37 (m, 1H), 7.42-7.41 (m, 1H), 7.49-7.48 (m, 1H), 7.67-7.63 (m, 2H),7.95 (d, J = 7.6 Hz, 1H),8.79 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.4, 63.4, 120.2, 124.7, 125.8, 126.4, 126.8, 127.4, 127.6, 128.4, 129.9,

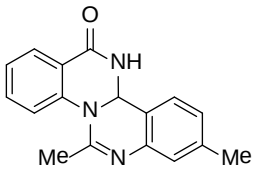
132.4, 139.8, 141.1, 152.9, 162.0 . IR (KBr): 3130 (N-H), 1662 (C=O) cm^{-1}. HRMS (ESI) for $C_{16}H_{12}ClN_3O_1$ $(M+H)^+$: calcd. 298.0742, 300.0713, Found 298.0728, 300.0697.



10-Bromo-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ga**) (Table 2, entry 7): Yellowish solid, mp 263-265 ^oC. ^1H NMR (500 MHz, DMSO-d_6) δ 2.11 (s, 3H), 6.23 (d, *J* = 1.2 Hz,1H), 7.12-7.10 (m, 1H), 7.47-7.45 (m, 1H), 7.51-7.50 (m, 1H), 7.55-7.53 (m, 1H), 7.67-7.62 (m, 2H), 7.96-7.94 (m, 1H), 8.80 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.4, 63.2, 116.5, 120.6, 124.6, 126.1, 126.4, 126.8, 127.7, 130.2, 132.4, 132.8, 140.1, 141.1, 153.0, 162.0. IR (KBr): 3122 (N-H), 1683 (C=O) cm^{-1}. HRMS (ESI) for $C_{16}H_{12}BrN_3O$ $(M+H)^+$: calcd. 342.0237, 344.0217, Found 342.0243, 344.0222.

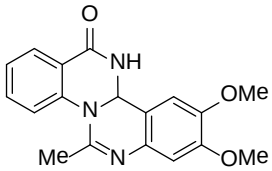


10-Methoxy-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ha**) (Table 2, entry 8): White solid, mp 264-266 ^oC. ^1H NMR (500 MHz, DMSO-d_6) δ 2.08 (s, 3H), 3.76 (s, 3H), 6.15 (s, 1H), 6.88-6.87 (m, 1H), 6.97-6.95 (m, 1H), 7.12-7.11 (m, 1H), 7.46-7.43 (m, 1H), 7.65-7.60 (m, 2H),7.94 (d, *J* = 7.5 Hz, 1H),8.69 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.2, 55.4, 64.1, 112.1, 115.9, 119.4, 124.7, 125.3, 126.3, 126.4, 127.6, 132.3, 134.3, 141.5, 150.0, 156.6, 162.2. IR (KBr): 3159 (N-H), 1676 (C=O) cm^{-1}. HRMS (ESI) for $C_{17}H_{15}N_3O_2$ $(M+H)^+$: calcd. 294.1237, Found 294.1227.

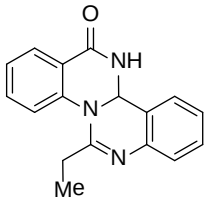


6,9-Dimethyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ia**) (Table 2, entry 9): White solid, mp 270-272 ^oC. ^1H NMR (500 MHz, DMSO-d_6) δ 2.10 (s, 3H), 3.32

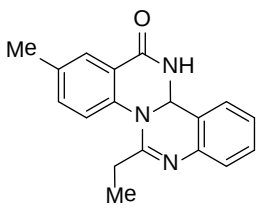
(s, 3H), 6.16 (d, *J* = 1.3 Hz,1H), 7.02-6.99 (m, 2H), 7.16-7.15 (m, 1H), 7.46-7.43 (m, 1H), 7.65-7.60 (m, 2H), 7.95-7.93 (m, 1H), 8.64 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.4, 30.6, 63.8, 114.0, 115.8, 124.4, 125.8, 126.4, 127.2, 125.5, 127.6, 132.2, 139.3, 140.6, 141.5, 152.0, 162.1. IR (KBr): 3098 (N-H), 1680 (C=O) cm^{-1}.HRMS (ESI) for $C_{17}H_{15}N_3O_1$ $(M+H)^+$: calcd. 278.1288, Found 278.1286.



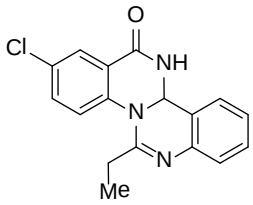
9,10-Dimethoxy-6-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ja**) (Table 2, entry 10): White solid, mp 270-272 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.09 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 6.12 (d, *J* = 1.2 Hz, 1H), 6.77 (s, 1H), 6.88 (s, 1H), 7.46-7.42 (m, 1H), 7.64-7.61 (m, 2H), 7.95-7.93 (m, 1H),8.62 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.2, 55.5, 55.8, 64.1, 107.6, 110.0, 110.4, 124.7, 126.2, 126.4, 127.5, 128.8, 132.2, 141.5, 146.4, 149.9, 150.2, 162.1. IR (KBr): 3098 (N-H), 1676 (C=O) cm^{-1}. HRMS (ESI) for $C_{18}H_{17}N_3O_3$ $(M+H)^+$: calcd. 324.1343, Found 324.1352.



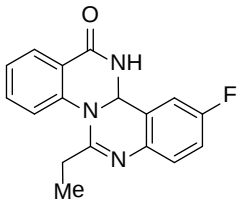
6-Ethyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ab**) (Table 2, entry 11): White solid, mp 203-205 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.94 (t, *J* = 7.4 Hz, 3H), 2.26 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 2.59 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 6.18 (d, *J* = 1.4 Hz, 1H), 7.21-7.18 (m, 2H), 7.28-7.27 (m, 1H), 7.40-7.37 (m, 1H), 7.48-7.44 (m, 1H), 7.66-7.60 (m, 2H), 7.96-7.94 (m, 1H), 8.72 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 10.3, 26.8, 64.1, 118.7, 124.3, 124.7, 125.1, 126.7, 126.8, 127.5, 127.6, 130.0, 132.3, 140.7, 141.3, 155.7, 162.2. IR (KBr): 3096 (N-H), 1680 (C=O) cm^{-1}. HRMS (ESI) for $C_{17}H_{15}N_3O$ $(M+H)^+$: calcd. 278.1288, Found 278.1286.



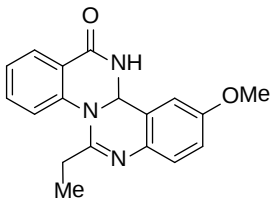
6-Ethyl-2-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one(**3bb**) (Table 2, entry 12: White solid, mp 243-245 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.94 (t, *J* = 7.4 Hz, 3H), 2.24 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 2.40 (s, 3H), 2.56 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 6.13 (d, *J* = 1.5 Hz, 1H), 7.21-7.18 (m, 2H), 7.28-7.26 (m, 1H), 7.40-7.36 (m, 1H), 7.45-7.43 (m, 1H), 7.49-7.48 (m, 1H), 7.76-7.75 (m, 1H), 8.65 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 10.3, 20.5, 26.7, 64.1, 118.7, 124.2, 124.4, 125.0, 126.6, 127.4, 127.7, 129.8, 132.8, 136.2, 138.8, 140.8, 155.9, 162.2. IR (KBr): 3201 (N-H), 1677 (C=O) cm^{-1}. HRMS (ESI) for $C_{18}H_{17}N_3O$ $(M+H)^+$: calcd. 292.1444, Found 292.1444.



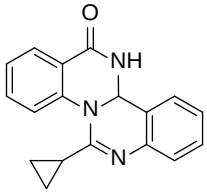
2-Chloro-6-ethyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3cb**) (Table 2, entry 13): White solid, mp 240-241 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.96 (t, *J* = 7.3 Hz, 3H), 2.24 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 2.60 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 6.20 (s, 1H), 7.23-7.19 (m, 2H), 7.29-7.28 (m, 1H), 7.41-7.38 (m, 1H), 7.70-7.69 (m, 2H), 7.88 (d, *J* = 2.0 Hz, 1H), 8.90 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 10.2, 26.7, 64.0, 118.4, 124.4, 125.3, 126.8, 126.9, 127.5, 128.4, 130.0, 131.0, 132.0, 140.1, 140.5, 155.3, 161.0. IR (KBr): 3060 (N-H), 1682 (C=O) cm^{-1}. HRMS (ESI) for $C_{17}H_{14}ClN_3O$ $(M+H)^+$: calcd. 312.0898, 314.0870, Found 312.0906, 314.0884.



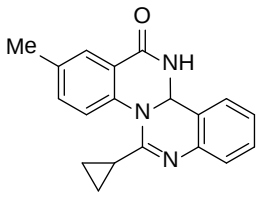
6-Ethyl-10-fluoro-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3eb**) (Table 2, entry 14): White solid, mp 170-172 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.93 (t, *J* = 7.4 Hz, 3H), 2.24 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 2.58 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 6.18 (d, *J* = 1.4 Hz, 1H), 7.17-7.15 (m, 1H), 7.24-7.22 (m, 2H), 7.49-7.45 (m, 1H), 7.66-7.61 (m, 2H), 7.96-7.94 (m, 1H), 8.78 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 10.2, 26.8, 63.7, 114.0 (d, $^{2}J_{CF}$ = 23.6 Hz, 1C), 116.9 (d, $^{2}J_{CF}$ = 22.2 Hz, 1C), 119.9, 120.0, 124.7, 126.7, 126.8, 127.6, 132.4, 137.4, 141.1, 155.3, 159.1 (d, $^{1}J_{CF}$ = 239.9 Hz, 1C), 162.1. IR (KBr): 3045 (N-H), 1676 (C=O) cm^{-1}. HRMS (ESI) for $C_{17}H_{14}FN_3O$ $(M+H)^+$: calcd. 296.1194, Found 296.1195.



6-Ethyl-10-methoxy-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-on (**3hb**) (Table 2, entry 15): Yellowish solid, mp 175-176 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.92 (t, *J* = 7.4 Hz, 3H), 2.22 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 2.57 (dq, *J* = 14.8 Hz, 7.4 Hz, 1H), 3.76 (s, 3H), 6.12 (d, *J* = 1.4 Hz, 1H), 6.88-6.87 (m, 1H), 6.98-6.95 (m, 1H), 7.15-7.14 (m, 1H), 7.47-7.43 (m, 1H), 7.65-7.59 (m, 2H), 7.95-7.94 (m, 1H), 8.67 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 10.3, 26.7, 55.4, 64.3, 112.1.7, 115.8, 119.5, 124.7, 125.5, 126.5, 126.7, 127.5, 132.2, 134.3, 141.4, 153.5, 156.6, 162.2. IR (KBr): 3198 (N-H), 1681 (C=O) cm^{-1}. HRMS (ESI) for $C_{18}H_{17}N_3O_2$ $(M+H)^+$: calcd. 308.1394, Found 308.1398.

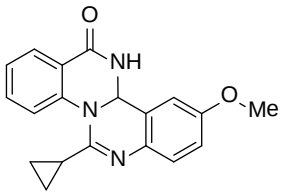


6-Cyclopropyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ac**) (Table 2, entry 16): White solid, mp 215-217 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.71-0.65 (m, 1H), 0.98-0.91 (m, 2H) 1.22-1.17 (m, 1H), 1.59-1.54 (m, 1H), 6.24 (d, *J* = 1.5 Hz, 1H), 7.09-7.07 (m, 1H), 7.17-7.14 (m, 1H), 7.27-7.26 (m, 1H), 7.36-7.33 (m, 1H), 7.48-7.45 (m, 1H), 7.67-7.62 (m, 2H), 7.98-7.96 (m, 1H), 8.78 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 7.3, 10.6, 12.9, 64.3, 118.3, 124.1, 124.7, 124.8, 126.5, 126.7, 127.5, 127.8, 129.9, 132.1, 140.7, 141.2, 155.3, 162.3. IR (KBr): 3199 (N-H), 1696 (C=O) cm^{-1}. HRMS (ESI) for $C_{18}H_{15}N_3O$ $(M+H)^+$: calcd. 290.1288, Found 290.1294.

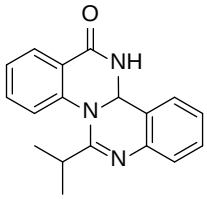


6-Cyclopropyl-2-methyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3bc**) (Table 2, entry 17): White solid, mp 236-238 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.70-0.65 (m, 1H), 0.96-0.89 (m, 2H) 1.23-1.15 (m, 1H), 1.58-1.53 (m, 1H), 2.41 (s, 3H), 6.20 (d, *J* = 1.4 Hz, 1H), 7.08-7.07 (m, 1H), 7.17-7.13 (m, 1H), 7.26-7.25 (m, 1H), 7.34-7.32 (m, 1H), 7.52-7.46 (m, 2H), 7.78-7.77 (m, 1H), 8.70 (s, 1H). ^{13}C NMR

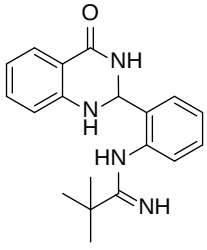
(125 MHz, DMSO-d_6) δ 7.2, 10.5, 12.9, 20.5, 64.3, 118.3, 124.0, 124.5, 124.6, 126.5, 127.4, 127.8, 129.8, 132.7, 136.0, 138.8, 140.8, 155.5, 162.4. IR (KBr): 3091 (N-H), 1679 (C=O) cm^{-1}. HRMS (ESI) for $C_{19}H_{17}N_3O$ $(M+H)^+$: calcd. 341.1397, Found 341.1393.



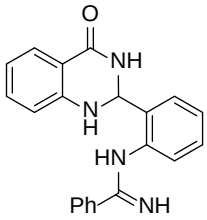
6-Cyclopropyl-10-methoxy-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3hc**) (Table 2, entry 18): Yellowish solid, mp 214-216 ^oC. ^1H NMR (500 MHz, DMSO-d_6) δ 0.67-0.61 (m, 1H), 0.95-0.85 (m, 2H) 1.16-1.11 (m, 1H), 1.56-1.51 (m, 1H), 3.75 (s, 3H), 6.18 (d, J = 1.5 Hz, 1H), 6.87-6.86 (m, 1H), 6.94-6.92 (m, 1H), 7.05-7.03 (m, 1H), 7.47-7.43 (m, 1H), 7.67-7.62 (m, 2H), 7.98-7.96 (m, 1H), 8.71 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 7.0, 10.3, 12.9, 55.3, 64.5, 112.09, 115.8, 119.0, 124.8, 125.3, 126.3, 126.5, 127.7, 132.1, 134.3, 141.3, 153.1, 156.3, 162.4. IR (KBr): 3105 (N-H), 1698 (C=O) cm^{-1}. HRMS (ESI) for $C_{19}H_{17}N_3O_2$ $(M+H)^+$: calcd. 357.1346, Found 357.1346.



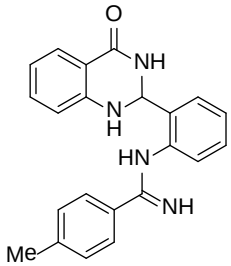
6-Isopropyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**3ad**) (Table 2, entry 19): White solid, mp 232-233 ^oC. ^1H NMR (500 MHz, DMSO-d_6) δ 0.73 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 6.6 Hz, 3H), 3.01-2.93 (m, 1H), 6.17 (d, J = 1.6 Hz, 1H), 7.20-7.18 (m, 2H), 7.28-7.26(m, 1H), 7.40-7.37 (m, 1H), 7.49-7.46 (m, 1H), 7.56-7.55 (m, 1H), 7.67-7.63 (m, 1H), 7.96-7.95 (m, 1H), 8.77 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 19.8, 20.2, 29.2, 64.2, 118.4, 124.3, 124.6, 125.1, 126.7, 127.2, 127.5, 127.6, 129.9, 132.2, 140.7, 141.2, 159.1, 162.3. IR (KBr): 3130 (N-H), 1676 (C=O) cm^{-1}.HRMS (ESI) for $C_{18}H_{17}N_3O$ $(M+H)^+$: calcd. 292.1444, Found 292.1450.



N-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)pivalimidamide (**3ae**) (Table 2, entry 20): White solid, mp 201-203 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21 (s, 9H), 5.71 (s, 2H), 6.72-6.65 (m, 4H), 7.02-6.99 (m, 1H), 7.27-7.22(m, 2H), 7.55-7.53 (m, 1H), 7.12-7.61 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 19.8, 20.2, 29.2, 64.2, 118.4, 124.3, 124.6, 125.1, 126.7, 127.2, 127.5, 127.6, 129.9, 132.2, 140.7, 141.2, 159.1, 162.3. IR (KBr): 3466, 3340, 3301, 3154, (N-H), 1675 (C=O) cm^{-1}. HRMS (ESI) for $C_{19}H_{22}N_4O$ $(M+H)^+$: calcd. 323.1866, Found 323.1870.

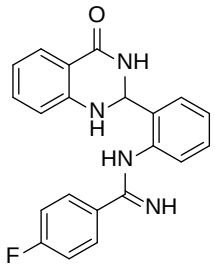


N-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4af**) (Table 3, entry 1): White solid, mp 119-120 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.83 (s, 1H), 6.44 (br s, 2H), 6.69-6.66 (m, 1H), 6.75-6.73 (m, 2H), 6.85-6.84 (m, 1H), 7.10-7.07 (m, 1H), 7.25-7.21 (m, 1H), 7.35-7.32 (m, 1H), 7.48-7.43 (m, 3H), 7.61-7.59 (m, 1H), 7.68-7.66 (m, 1H), 7.74 (s, 1H), 7.99-7.98 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 114.6, 115.0, 117.3, 121.5, 122.2, 127.1, 127.4, 127.8, 128.1, 129.4, 129.5, 130.3, 131.2, 133.2, 135.4, 148.7, 154.4, 163.9. IR (KBr): 3423, 3352, 3323, 3106, (N-H), 1672 (C=O) cm^{-1}. HRMS (ESI) for $C_{21}H_{18}N_4O$ $(M+H)^+$: calcd. 343.1553, Found 343.1545.

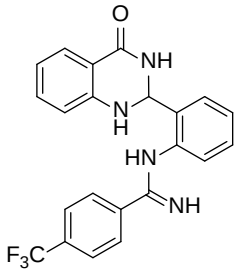


4-Methyl-*N*-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4ag**) (Table 3, entry 2): White solid, mp 158-159 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.34 (s, 3H), 5.81 (s, 1H), 6.36 (br s, 2H), 6.69-6.66 (m, 1H), 6.75-6.73 (m, 2H), 6.84-6.83 (m, 1H), 7.09-7.06 (m, 1H), 7.25-7.21 (m, 3H), 7.33-7.30 (m, 1H), 7.60-7.59 (m, 1H), 7.65-7.64 (m, 1H), 7.72 (s, 1H), 7.89-7.87 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 20.9, 62.6, 114.6, 115.0, 117.3, 121.5, 122.1, 127.0, 127.4, 127.6, 128.6, 129.4, 131.2, 132.6, 133.2, 139.9, 148.6, 148.7, 154.3, 163.9. IR (KBr): 3452, 3384, 3324, 3182, (N-H), 1674 (C=O) cm^{-1}. HRMS (ESI) for $C_{22}H_{20}N_4O$ $(M+H)^+$:

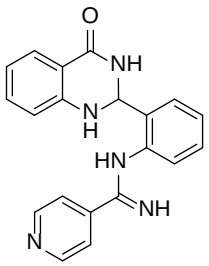
calcd. 35.1710, Found 357.1707.



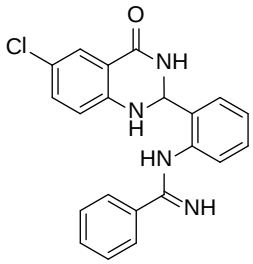
4-Fluoro-*N*-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4ah**) (Table 3, entry 3): Yellowish solid, mp 162-163 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.85 (s, 1H), 6.47 (br s, 2H), 6.70-6.67 (m, 1H), 6.76-6.74 (m, 2H), 6.86-6.85 (m, 1H), 7.11-7.08 (m, 1H), 7.29-7.22 (m, 3H), 7.35-7.32 (m, 1H), 7.62-7.61 (m, 1H), 7.69-7.67 (m, 1H), 7.74 (s, 1H), 8.07-8.05 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 114.6, 114.8, 115.0, 117.3, 121.5, 122.2, 127.4, 127.7, 129.5, 129.6, 131.3, 131.8, 133.2, 148.5, 148.6, 153.5, 163.4 (d, $^{1}J_{CF}$ = 246.2 Hz, 1C), 163.9. IR (KBr): 3450, 3368, 3312, 3179, (N-H), 1680 (C=O) cm^{-1}. HRMS (ESI) for $C_{21}H_{17}FN_4O$ $(M+H)^+$: calcd. 361.1459, Found 361.1462.



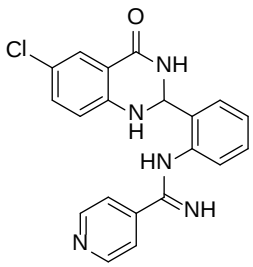
N-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)-4-(trifluoromethyl)benzimidamide (**4ai**) (Table 3, entry 4): Yellowish solid, mp 177-179 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.84 (s, 1H), 6.62 (br s, 2H), 6.69-6.66 (m, 1H), 6.75-6.73 (m, 2H), 6.87-6.86 (m, 1H), 7.13-7.10 (m, 1H), 7.24-7.21 (m, 1H), 7.36-7.33 (m, 1H), 7.60-7.59 (m, 1H), 7.72-7.67 (m, 2H), 7.82-7.80 (m, 2H), 8.19-8.17 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 114.6, 115.0, 117.3, 121.4, 122.5, 125.0, 125.0, 125.2, 127.4, 127.8, 128.0, 129.5, 131.2, 133.2, 139.3, 148.3, 148.6, 153.4, 163.8. IR (KBr): 3441, 3332, 3306, 3178, (N-H), 1666 (C=O) cm^{-1}. HRMS (ESI) for $C_{22}H_{17}F_3N_4O$ $(M+H)^+$: calcd. 411.1427, Found 411.1432.



N-(2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)isonicotinimidamide (**4aj**) (Table 3, entry 5): Yellowish solid, mp 175-176 ^{o}C.^{1}H NMR (500 MHz, DMSO-d_6) δ 5.83 (s, 1H), 6.75-6.66 (m, 5H), 6.87-6.85 (m, 1H), 7.13-7.10 (m, 1H), 7.25-7.21 (m, 1H), 7.36-7.33 (m, 1H), 7.61-7.59 (m, 1H), 7.72-7.67 (m, 2H), 7.92-7.91 (m, 2H), 8.68 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 114.5, 114.9, 117.3, 121.2, 121.3, 122.6, 127.3, 127.7, 129.5, 131.2, 133.2, 142.6, 148.0, 148.5, 149.9, 152.8, 163.8. IR (KBr): 3495, 3377, 3341, 3208, (N-H), 1664 (C=O) cm^{-1}. HRMS (ESI) for $C_{20}H_{17}N_5O$ $(M+H)^+$: calcd. 327.1240, Found 327.1231.

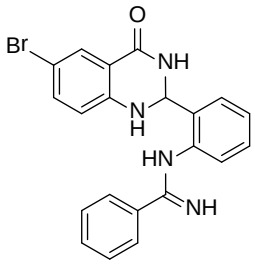


N-(2-(6-chloro-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4cf**) (Table 3, entry 6): White solid, mp 186-187 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.86 (s, 1H), 6.42 (br, 2H), 6.79-6.77 (m, 1H), 6.86-6.85 (m, 1H), 6.99 (s, 1H), 7.11-7.08 (m, 1H), 7.28-7.26 (m, 1H), 7.35-7.33 (m, 1H), 7.48-7.42 (m, 3H), 7.53-7.52 (m, 1H), 7.65-7.63 (m, 1H), 7.94 (s, 1H), 7.99-7.98 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 116.1, 116.6, 120.9, 121.6, 122.2, 126.5, 127.1, 127.4, 127.7, 128.1, 128.2, 129.6, 130.3, 130.9, 132.9, 135.3, 147.3, 148.7, 154.5, 162.7. IR (KBr): 3443, 3328, 3301, 3189, (N-H), 1672 (C=O) cm^{-1}. HRMS (ESI) for $C_{21}H_{17}N_4O$ $(M+H)^+$: calcd. 377.1164, 379.1136, Found 377.1156, 379.1135.

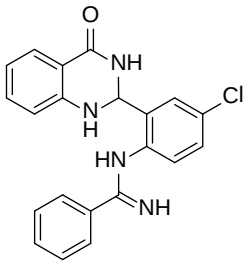


N-(2-(6-chloro-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)isonicotinimidamide

(**4cj**) (Table 3, entry 7): White solid, mp 139-140 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.86 (s, 1H), 6.66 (br s, 2H), 6.78-6.77 (m, 1H), 6.88-6.86 (m, 1H), 6.98 (s, 1H), 7.13-7.10 (m, 1H), 7.27-7.24 (m, 1H), 7.37-7.34 (m, 1H), 7.52-7.52 (m, 1H), 7.65-7.64 (m, 1H), 7.92 (s, 3H), 8.69 (br s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 116.0, 116.5, 120.8, 121.3, 122.6, 126.4, 127.7, 129.6, 131.0, 132.9, 142.5, 147.2, 148.0, 149.8, 152.8, 162.6. IR (KBr): 3450, 3368, 3312, 3179, (N-H), 1692 (C=O) cm^{-1}. HRMS (ESI) for $C_{20}H_{16}ClN_5O$ $(M+H)^+$: calcd. 378.1116, 380.1088, Found 378.1100, 380.1109.

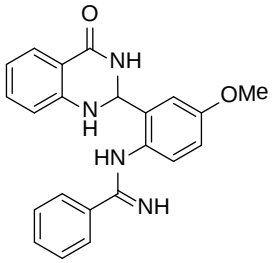


N-(2-(6-bromo-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4df**) (Table 3, entry 8): Yellowish solid, mp 174-176 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.85 (s, 1H), 6.41 (br, 2H), 6.73-6.72 (m, 1H), 6.86-6.85 (m, 1H), 7.00 (s, 1H), 7.10-7.07 (m, 1H), 7.38-7.32 (m, 2H), 7.48-7.42 (m, 3H), 7.65-7.62 (m, 2H), 7.92 (s, 1H), 7.98-7.97 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.5, 108.1, 116.5, 116.9, 118.6, 121.6, 122.2, 127.1, 127.6, 128.0, 129.4, 129.6, 130.2, 135.3, 135.6, 147.6, 148.6, 154.5, 162.6. IR (KBr): 3447, 3377, 3312 (N-H), 1676 (C=O) cm^{-1}. HRMS (ESI) for $C_{21}H_{17}BrN_4O$ $(M+H)^+$: calcd. 421.0659, 423.0639, Found 421.0655, 423.0651.

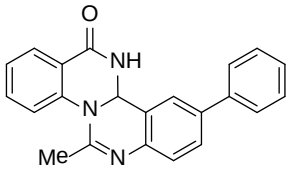


N-(4-chloro-2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4ff**) (Table 3, entry 9): White solid, mp 196-198 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.81 (s, 1H), 6.57 (br, 2H), 6.72-6.69 (m, 1H), 6.79-6.75 (m, 2H), 6.89-6.88 (m, 1H), 7.27-7.24 (m, 1H), 7.37-7.35 (m, 1H), 7.50-7.42 (m, 3H), 7.62-7.58 (m, 2H), 7.77 (s, 1H), 7.98-7.97 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.4, 114.7, 114.9, 117.6, 123.7, 125.9, 127.2, 127.3, 127.4, 128.1, 129.3, 130.4, 133.3, 133.4, 135.1, 147.7,

148.3, 155.1, 163.7. IR (KBr): 3432, 3380, 3342, 3120, (N-H), 1672 (C=O) cm^{-1}. HRMS (ESI) for $C_{21}H_{17}ClN_4O$ $(M+H)^+$: calcd. 377.1164, 379.1136, Found 377.1150, 379.1169.



N-(4-methoxy-2-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenyl)benzimidamide (**4hf**) (Table 3, entry 10): White solid, mp 191-193 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.75 (s, 3H), 5.79 (s, 1H), 6.39 (br, 2H), 6.71-6.68 (m, 1H), 6.81-6.75 (m, 3H), 6.96-6.94 (m, 1H), 7.20-7.19 (m, 1H), 7.26-7.22 (m, 1H), 7.49-7.42 (m, 3H), 7.62-7.60 (m, 1H), 7.75 (s, 1H), 7.99-7.97 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 55.2, 62.8, 112.8, 114.7, 115.0, 115.3, 117.4, 122.5, 127.0, 127.4, 128.1, 130.2, 132.0, 133.2, 135.5, 141.6, 148.6, 154.6, 154.9, 163.9. IR (KBr): 3435, 3378, 3354, 3133, (N-H), 1670 (C=O) cm^{-1}. HRMS (ESI) for $C_{22}H_{20}N_4O_2$ $(M+H)^+$: calcd. 373.1659, Found 373.1680.



6-Methyl-10-phenyl-11b*H*-quinazolino[3,4-*a*]quinazolin-13(12*H*)-one (**5**) (Scheme 2): White solid, mp 277-279 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.10 (s, 3H) 6.07 (s, 1H), 6.80-6.73 (m, 2H), 6.88 (s, 1H), 7.31-7.27 (m, 1H), 7.47-7.44 (m, 2H), 7.64-7.59 (m, 2H), 7.68-7.66 (m, 2H), 7.91-7.90 (m, 1H), 8.02-8.00 (m, 1H), 9.60 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 23.5, 63.2, 114.6, 115.0, 117.6, 126.0, 126.2, 126.4, 127.1, 127.4, 129.0, 129.3, 133.4, 133.8, 134.0, 135.2, 137.0, 139.5, 148.3, 164.0. IR (KBr): 3352 (N-H), 1670 (C=O) cm^{-1}. HRMS (ESI) for $C_{22}H_{17}N_3O$ $(M+H)^+$: calcd. 340.1444, Found 340.1444.

5. ^{1}H NMR and ^{13}C NMR spectra for all products

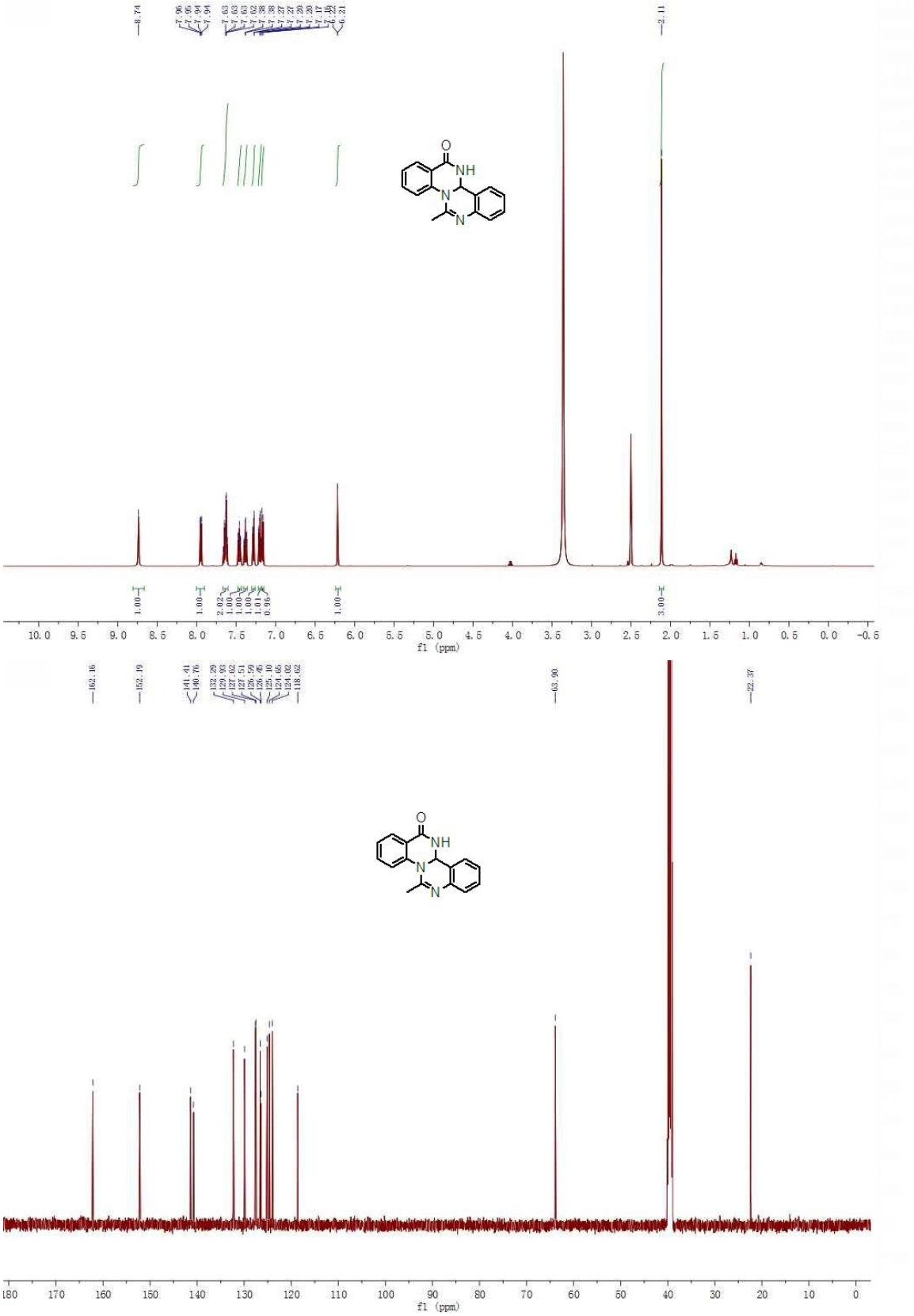


Figure S1. ^{1}H NMR of **3aa** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3aa** (125 MHz, DMSO-d_6).

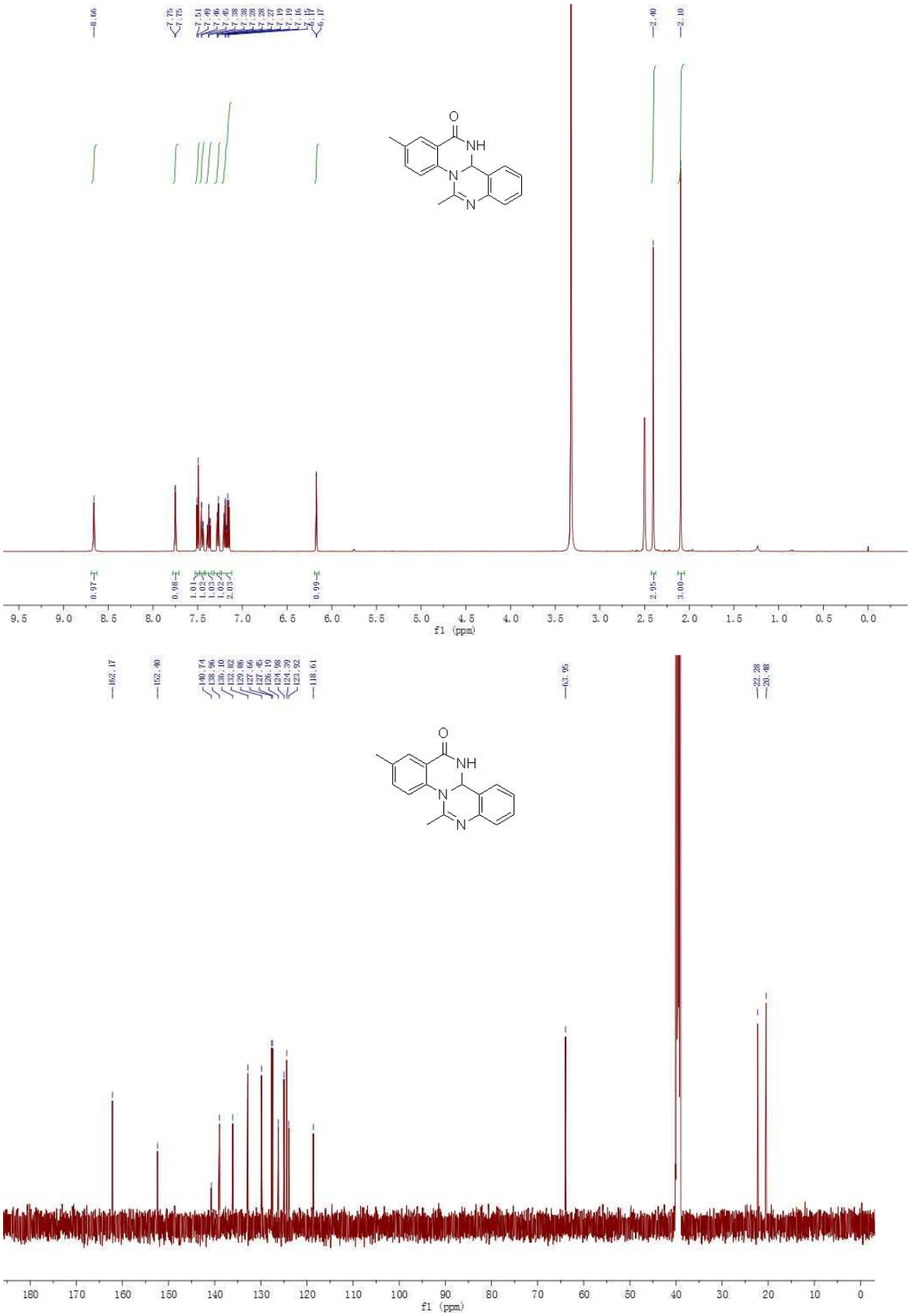


Figure S2. ^{1}H NMR of **3ba** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3ba** (125 MHz, DMSO-d_6).

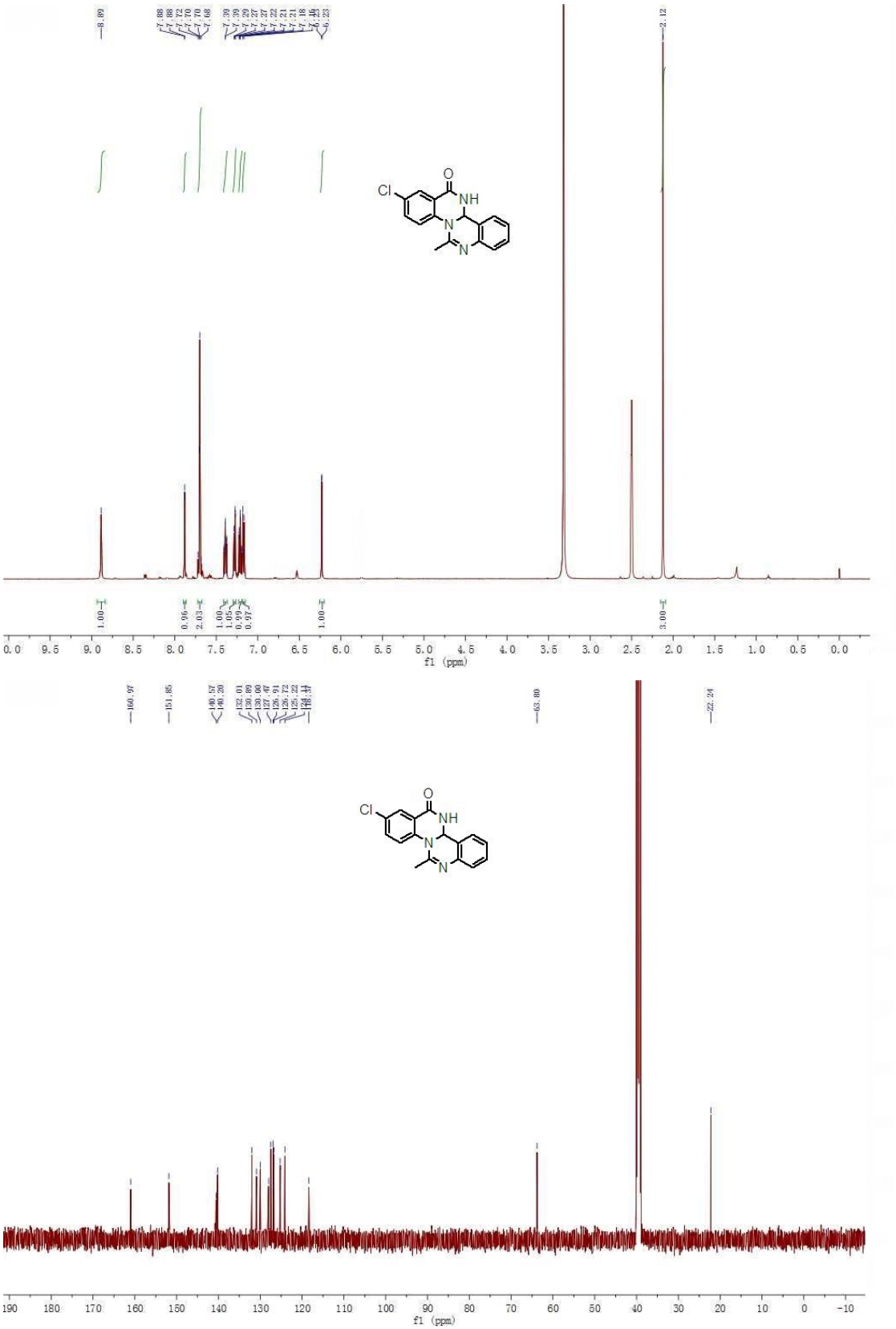


Figure S3. ^{1}H NMR of **3ca** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3ca** (125 MHz, DMSO-d_6).

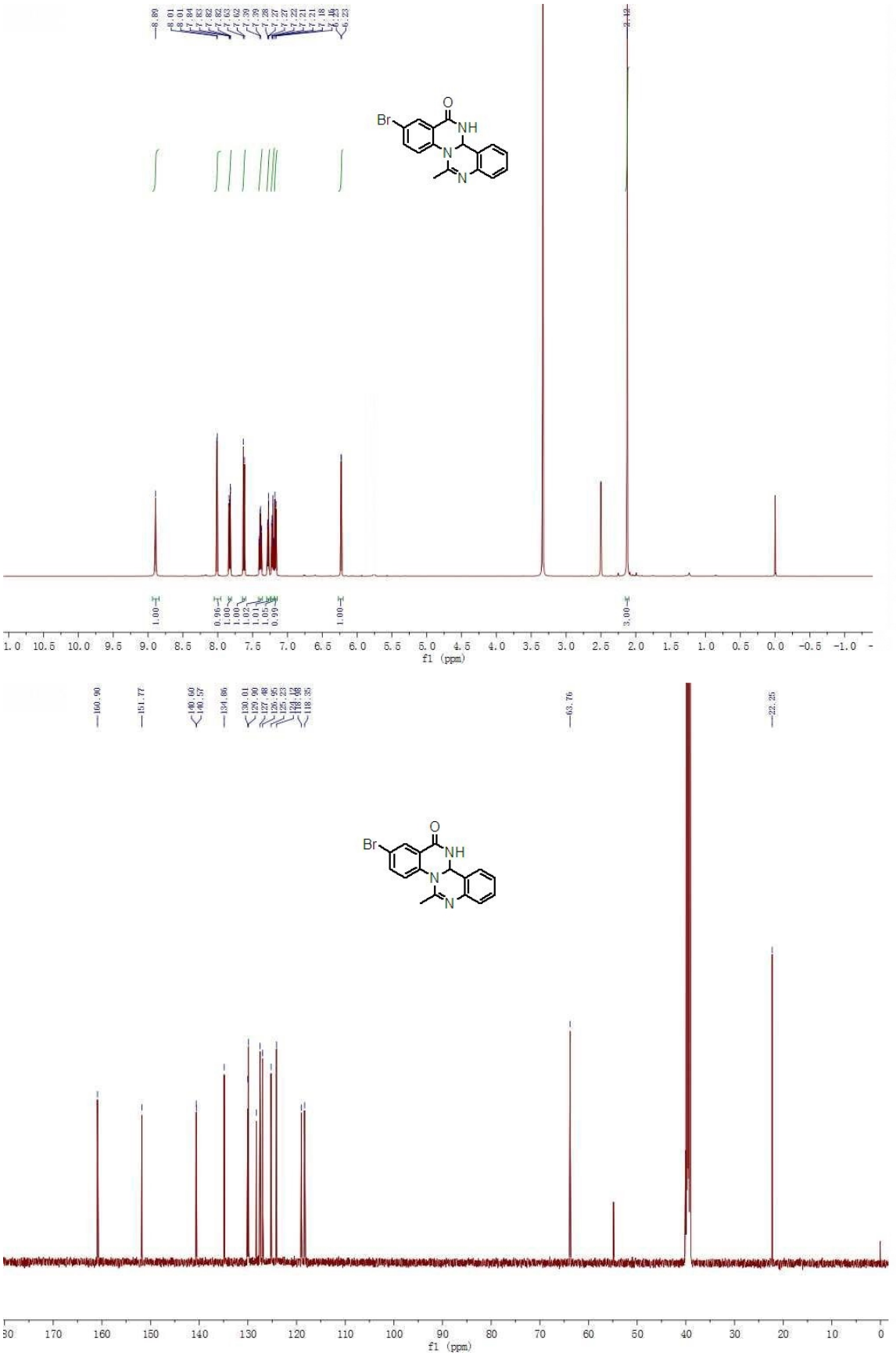


Figure S4. ^{1}H NMR of **3da** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3da** (125 MHz, DMSO-d_6).

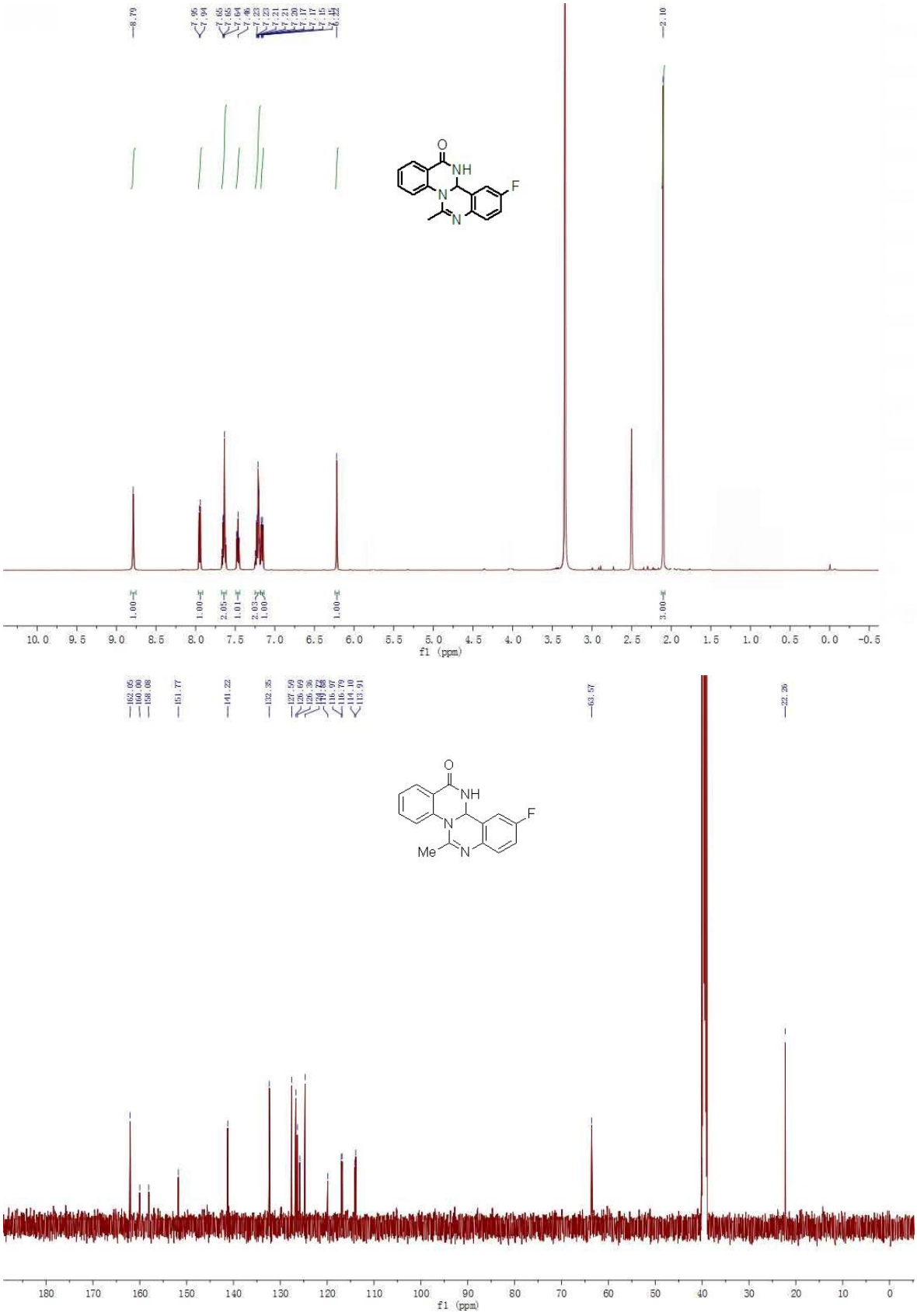


Figure S5. ^{1}H NMR of **3ea** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3ea** (125 MHz, DMSO-d_6).

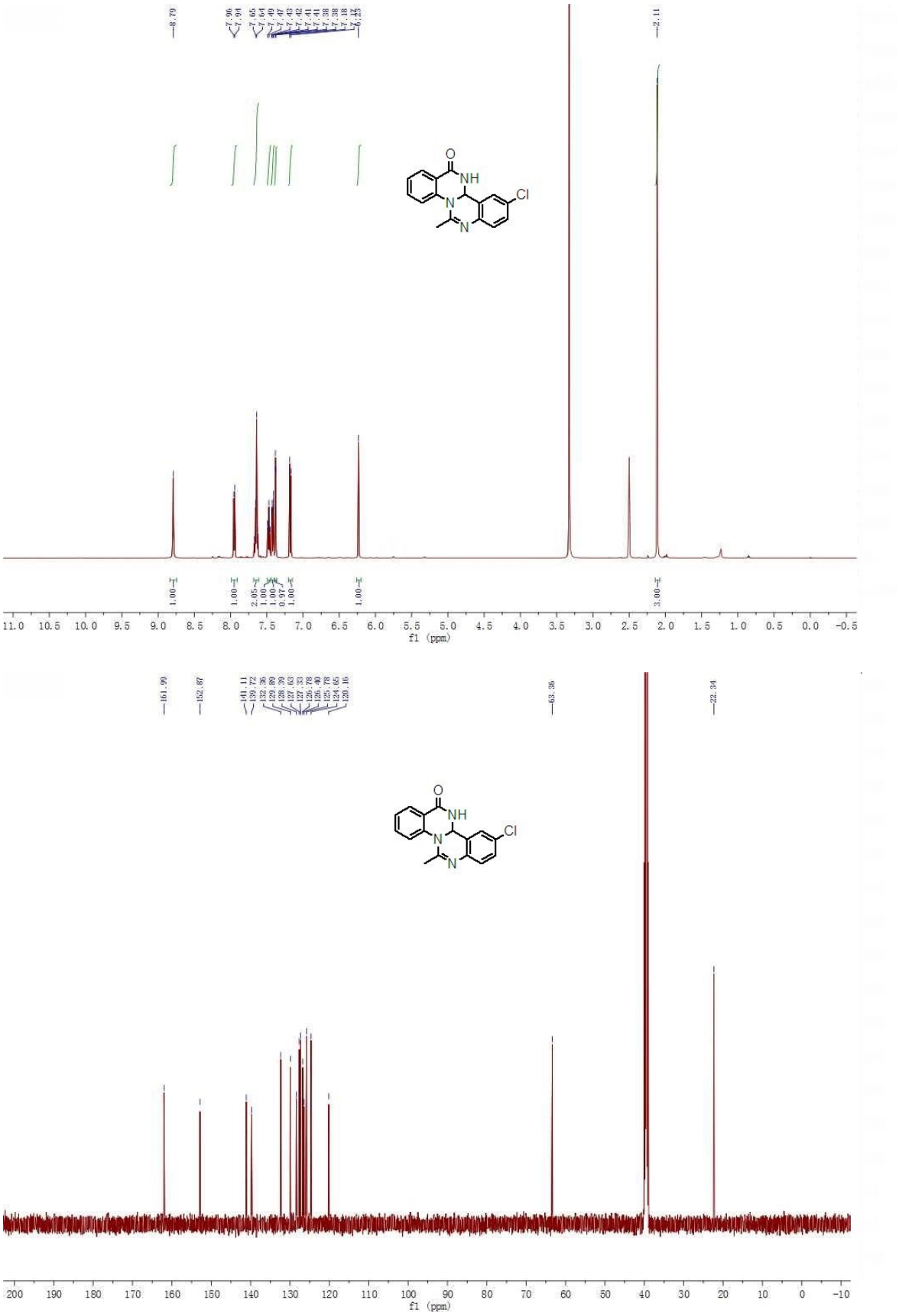


Figure S6. ^{1}H NMR of **3fa** (500 MHz, DMSO-d6) and ^{13}C NMR of **3fa** (125 MHz, DMSO-d6).

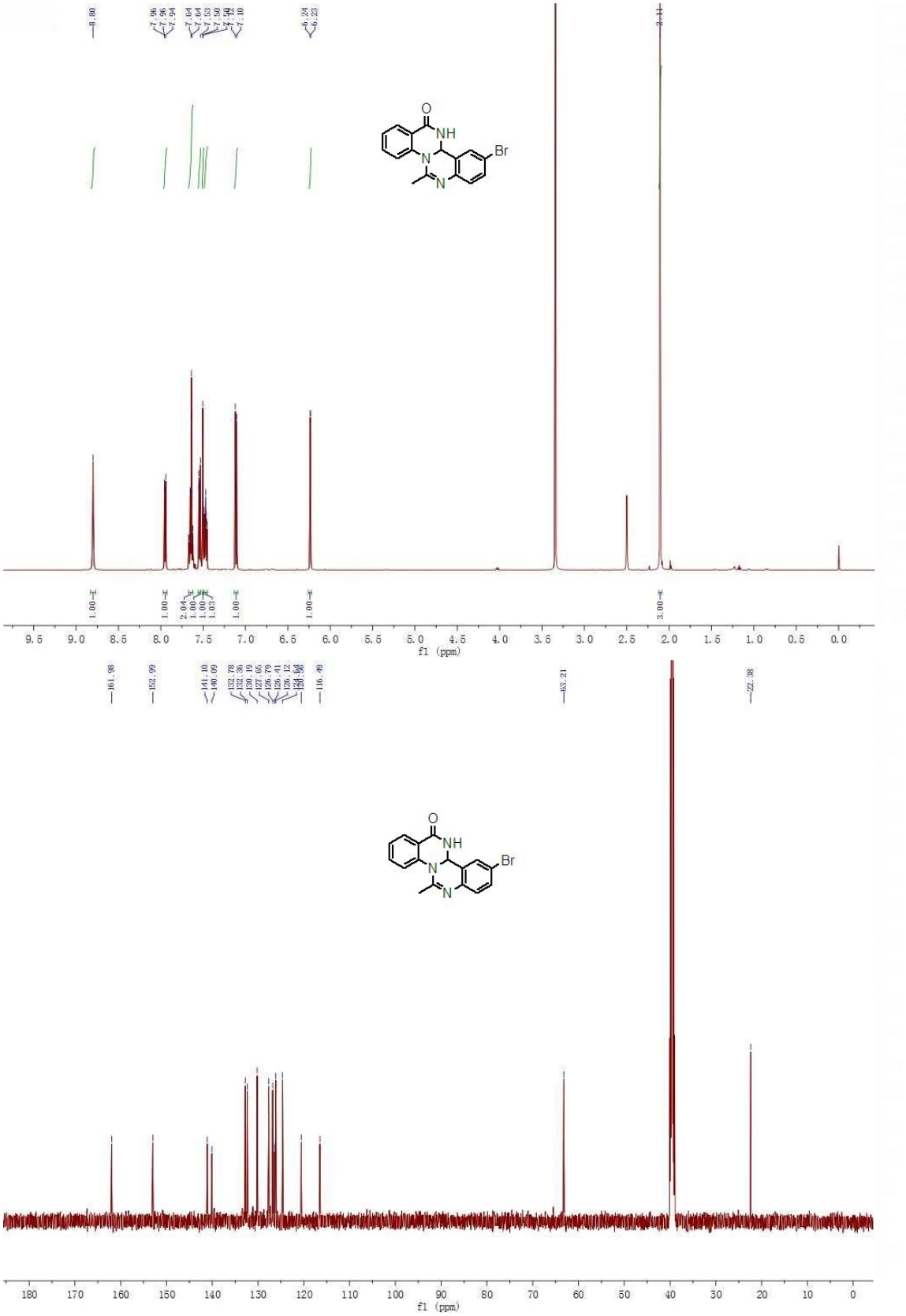


Figure S7. ^{1}H NMR of **3ga** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ga** (125 MHz, DMSO-d6).

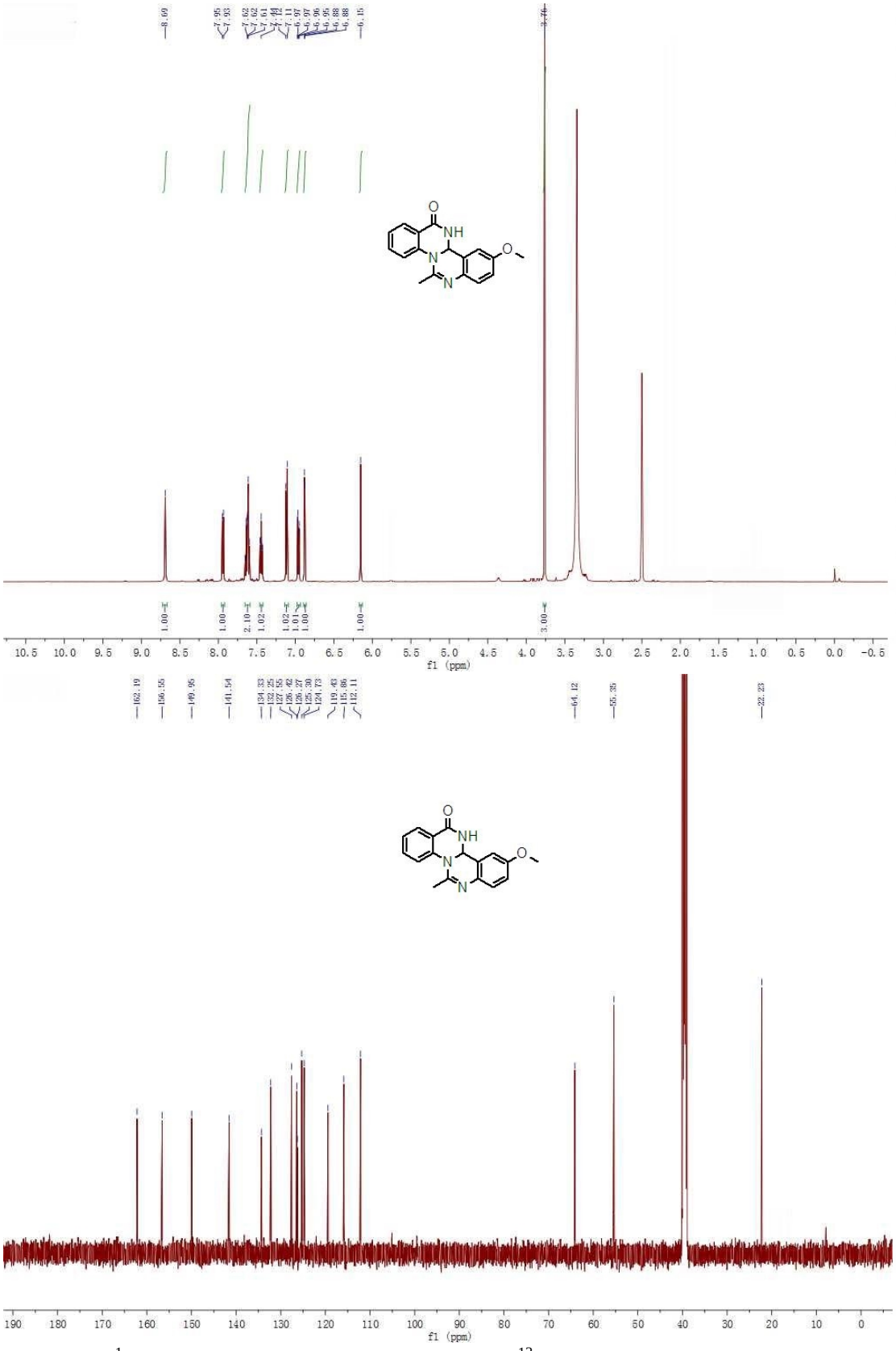


Figure S8. ^{1}H NMR of **3ha** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ha** (125 MHz, DMSO-d6).

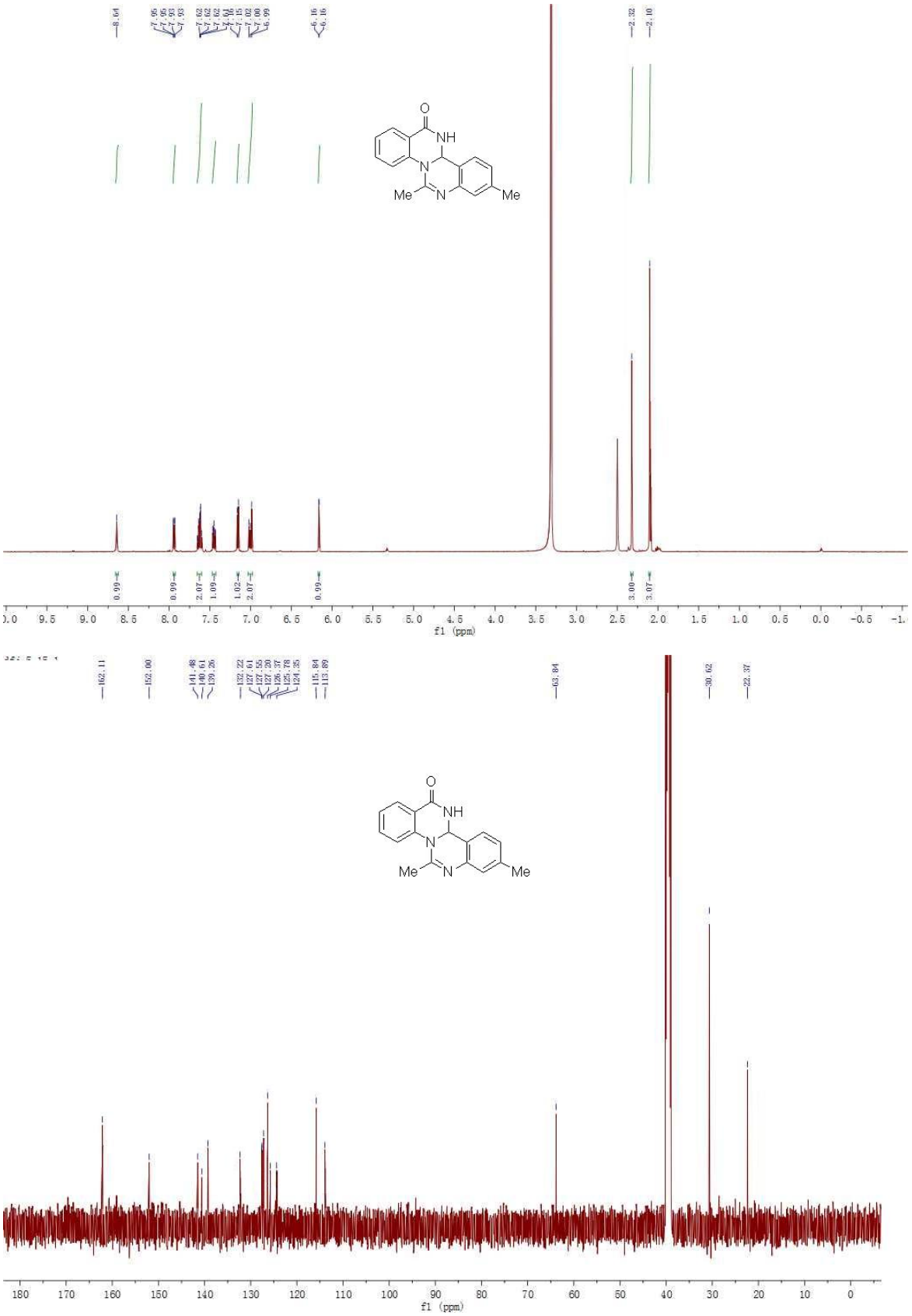


Figure S9. ^{1}H NMR of **3ia** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ia** (125 MHz, DMSO-d6).

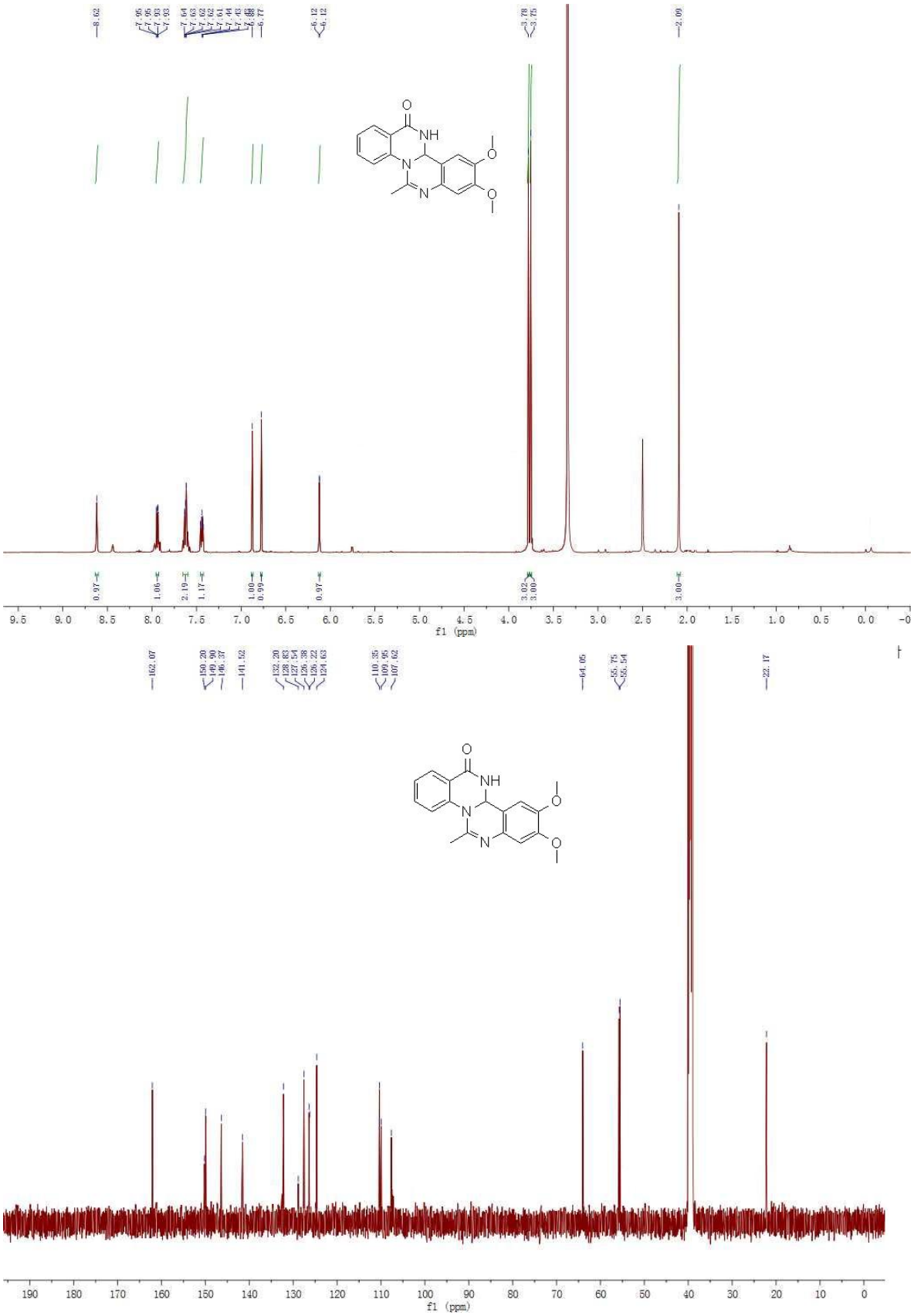


Figure S10. ^{1}H NMR of **3ja** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ja** (125 MHz, DMSO-d6).

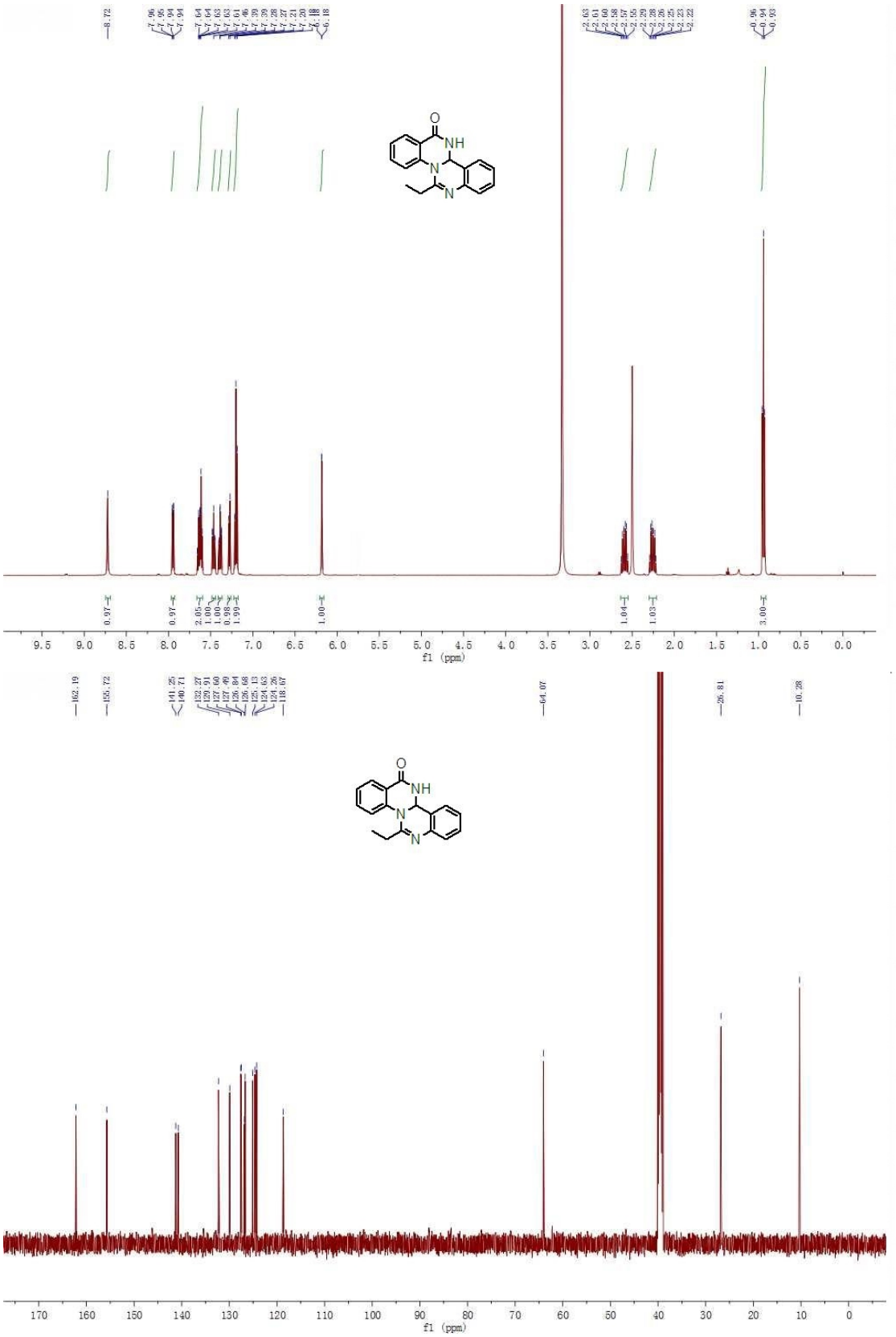


Figure S11. ^{1}H NMR of **3ab** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ab** (125 MHz, DMSO-d6).

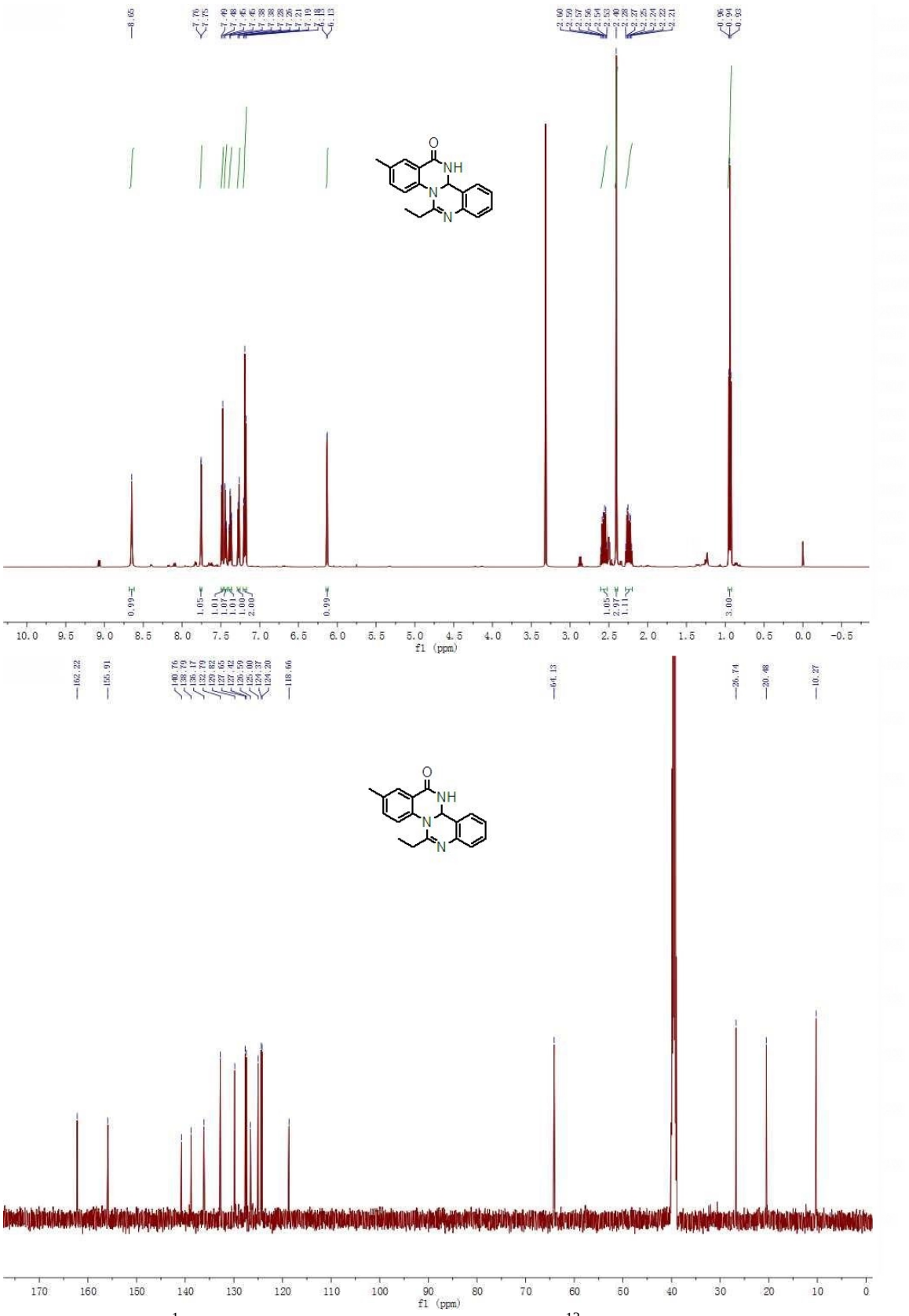


Figure S12. ^{1}H NMR of **3bb** (500 MHz, DMSO-d6) and ^{13}C NMR of **3bb** (125 MHz, DMSO-d6).

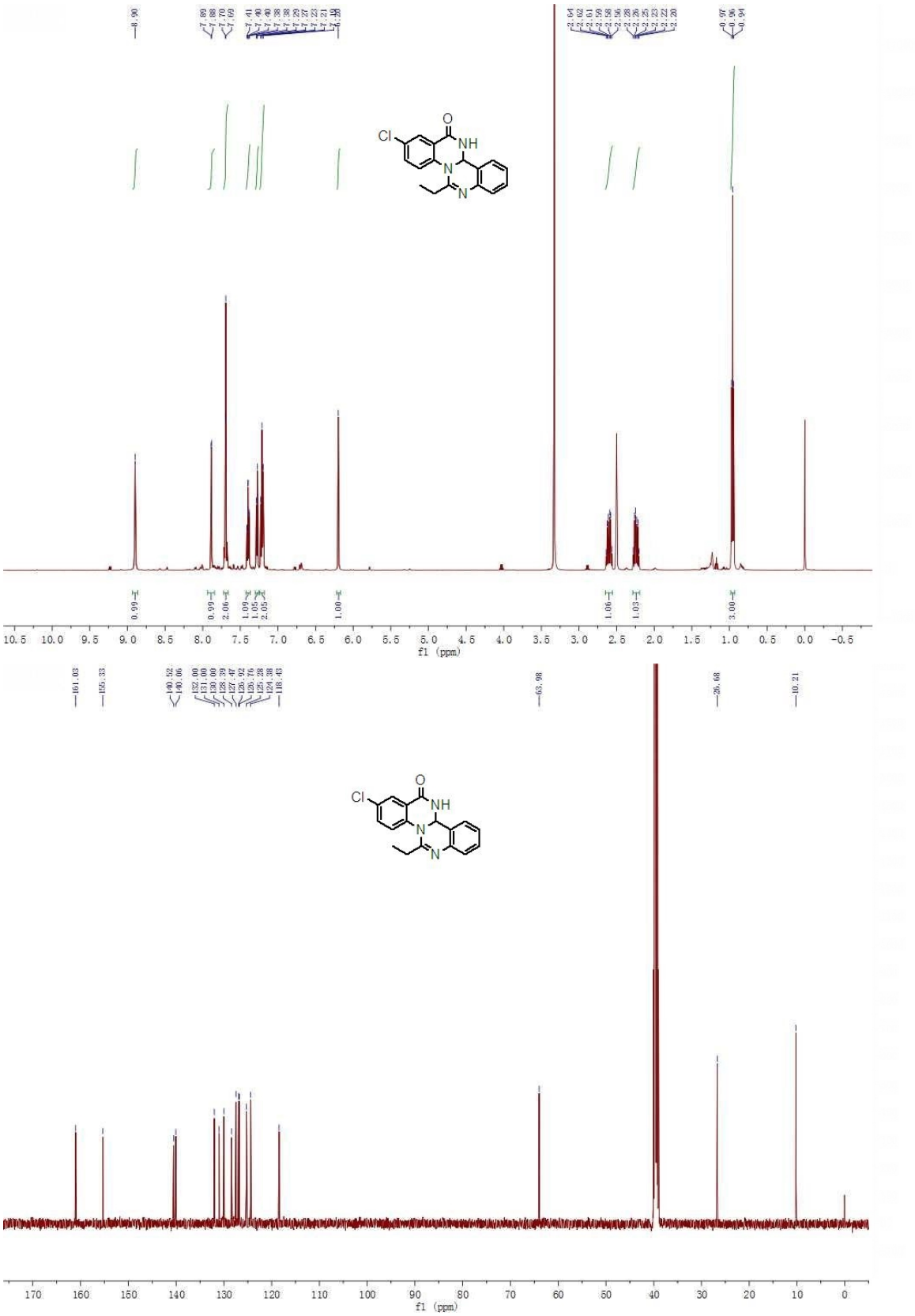


Figure S13. ^{1}H NMR of **3cb** (500 MHz, DMSO-d6) and ^{13}C NMR of **3cb** (125 MHz, DMSO-d6).

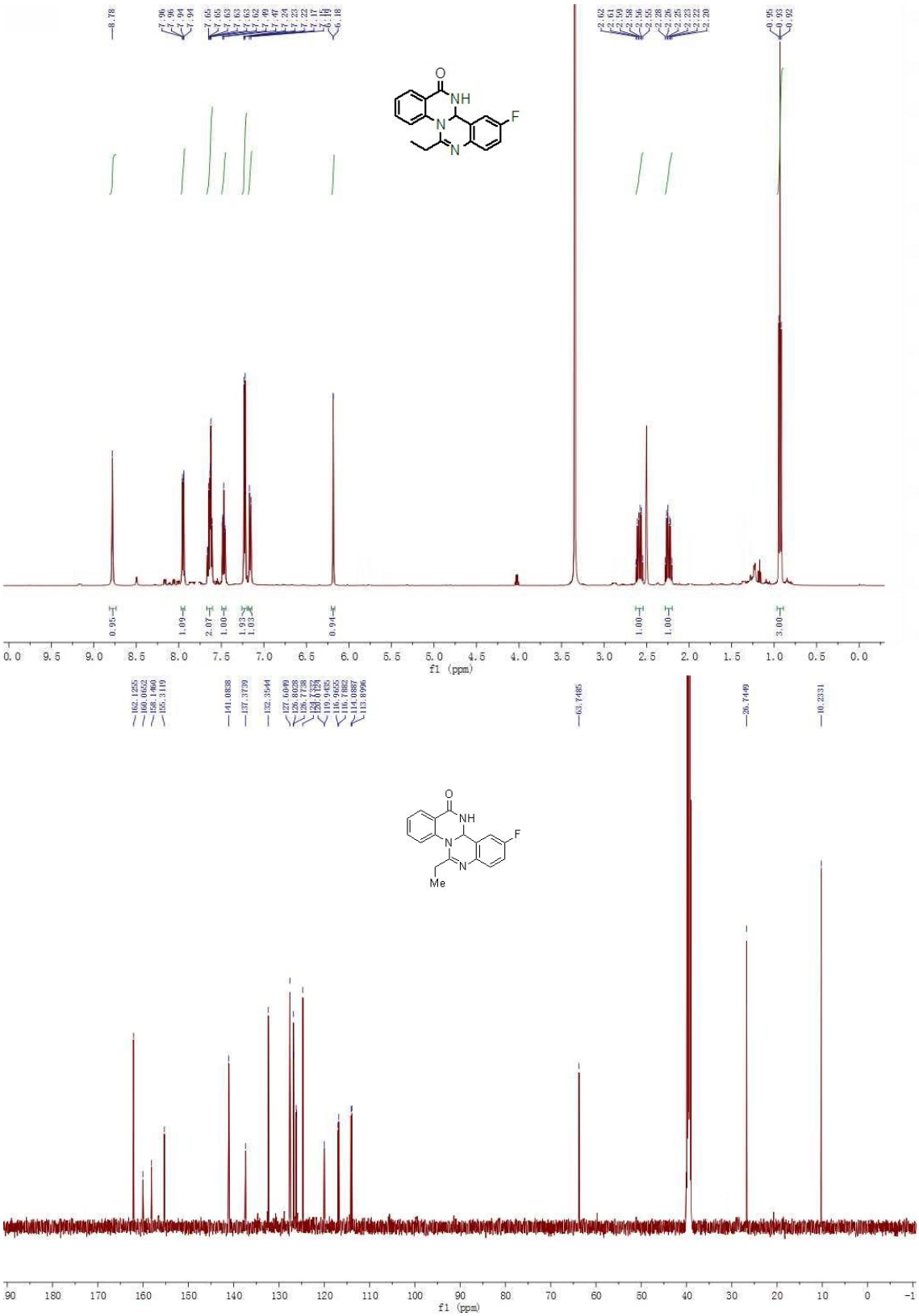


Figure S14. ^{1}H NMR of **3eb** (500 MHz, DMSO-d6) and ^{13}C NMR of **3eb** (125 MHz, DMSO-d6).

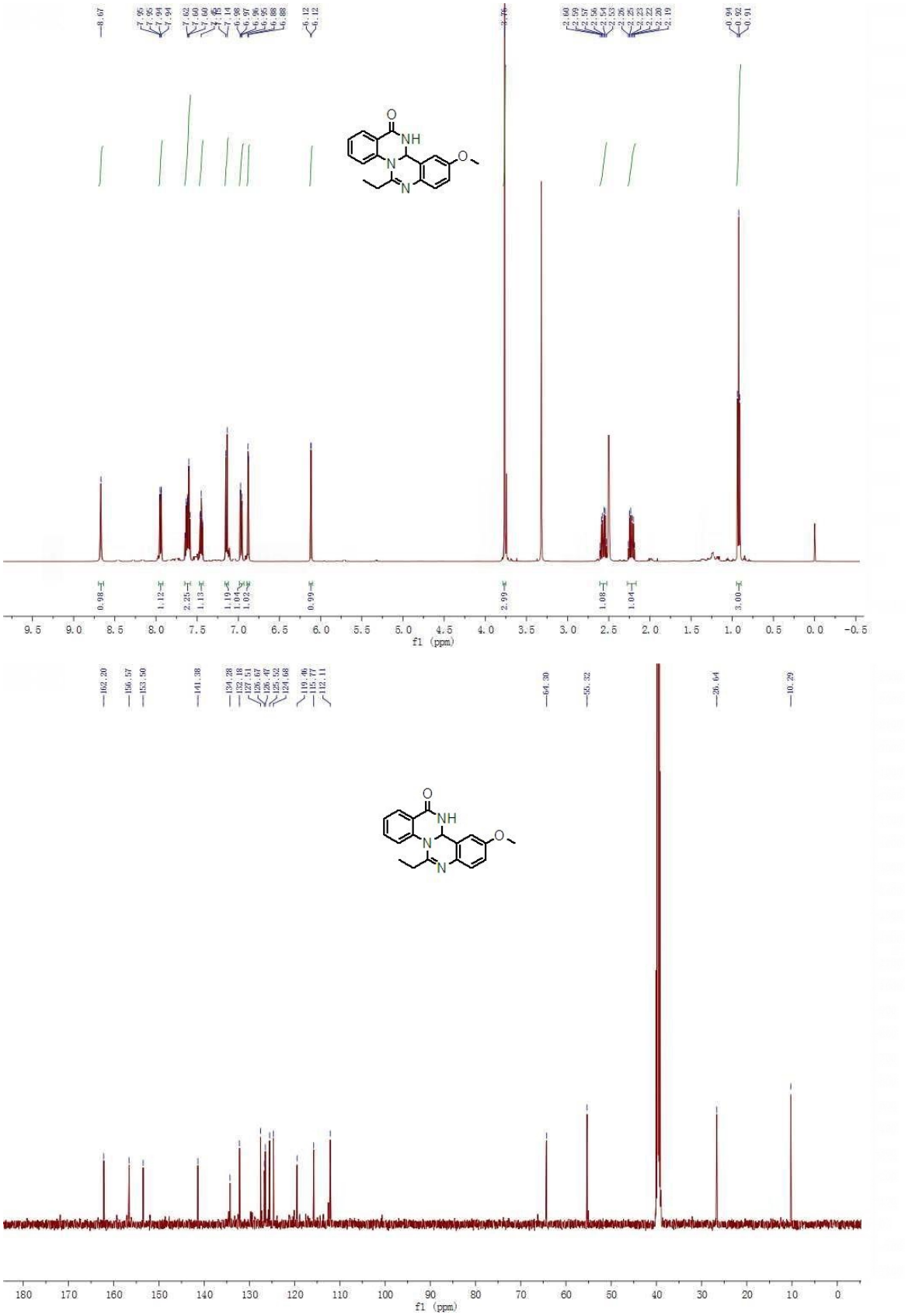


Figure S15. ^{1}H NMR of **3hb** (500 MHz, DMSO-d6) and ^{13}C NMR of **3hb** (125 MHz, DMSO-d6).

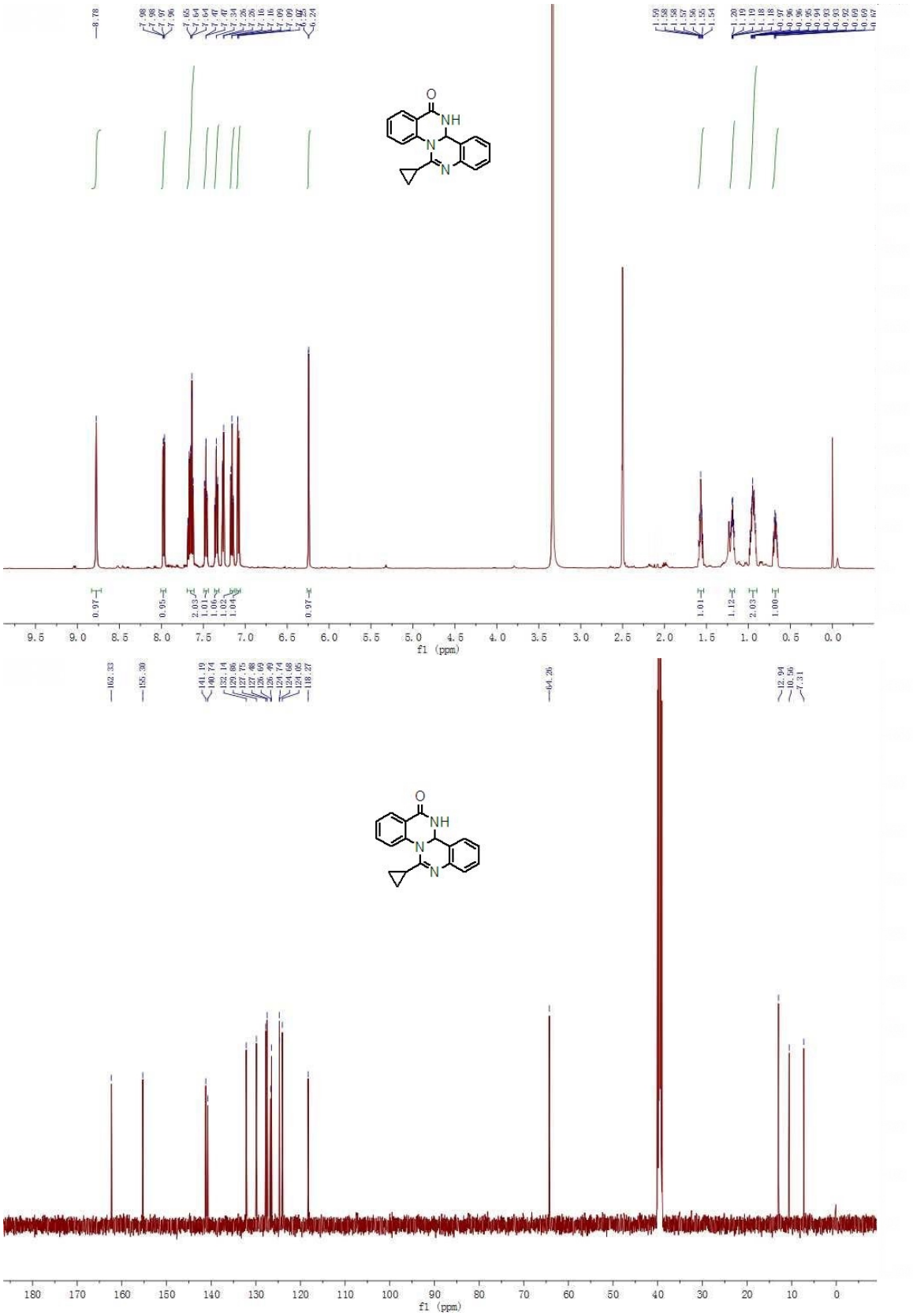


Figure S16. ^{1}H NMR of **3ac** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ac** (125 MHz, DMSO-d6).

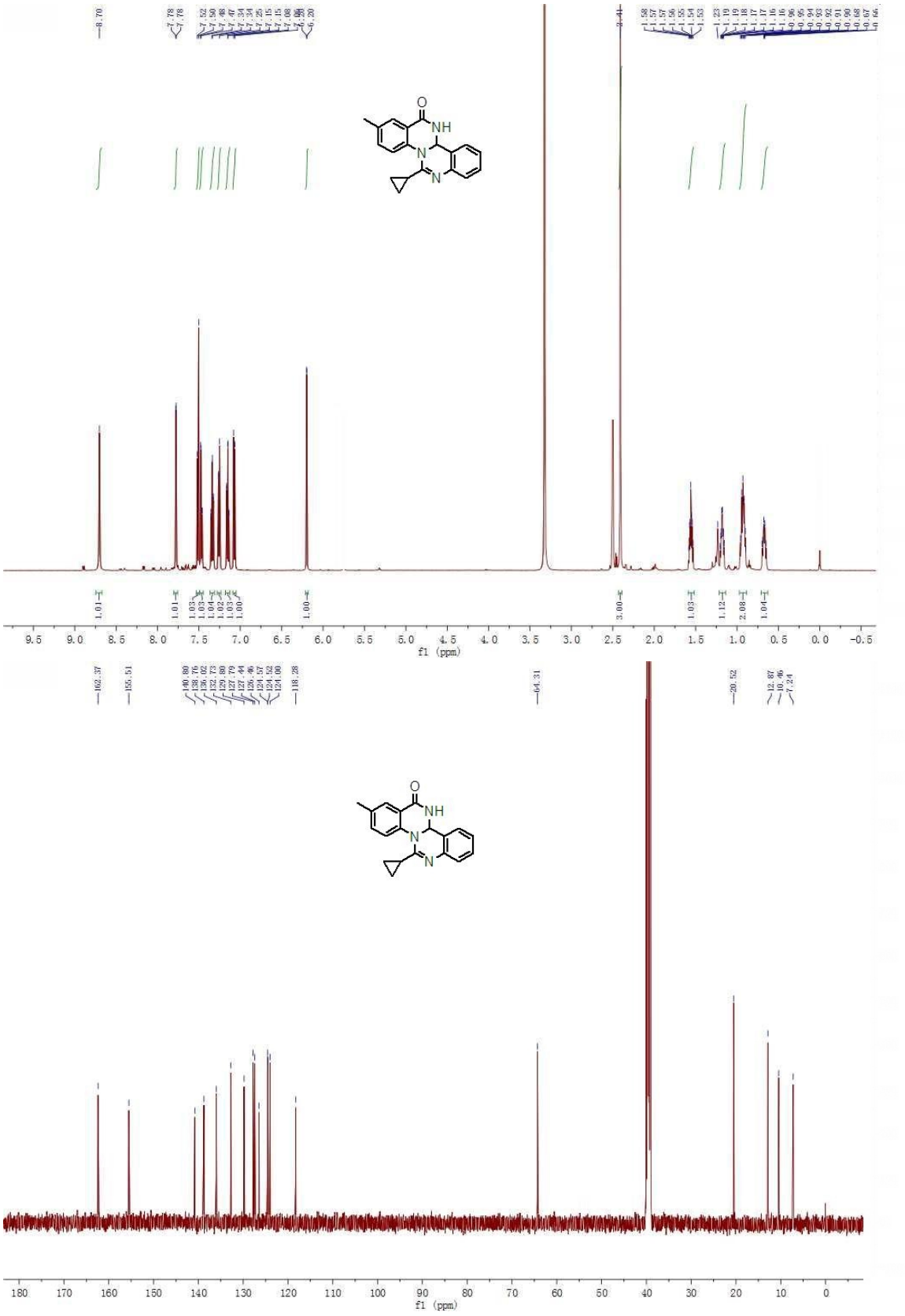


Figure S17. ^{1}H NMR of **3bc** (500 MHz, DMSO-d6) and ^{13}C NMR of **3bc** (125 MHz, DMSO-d6).

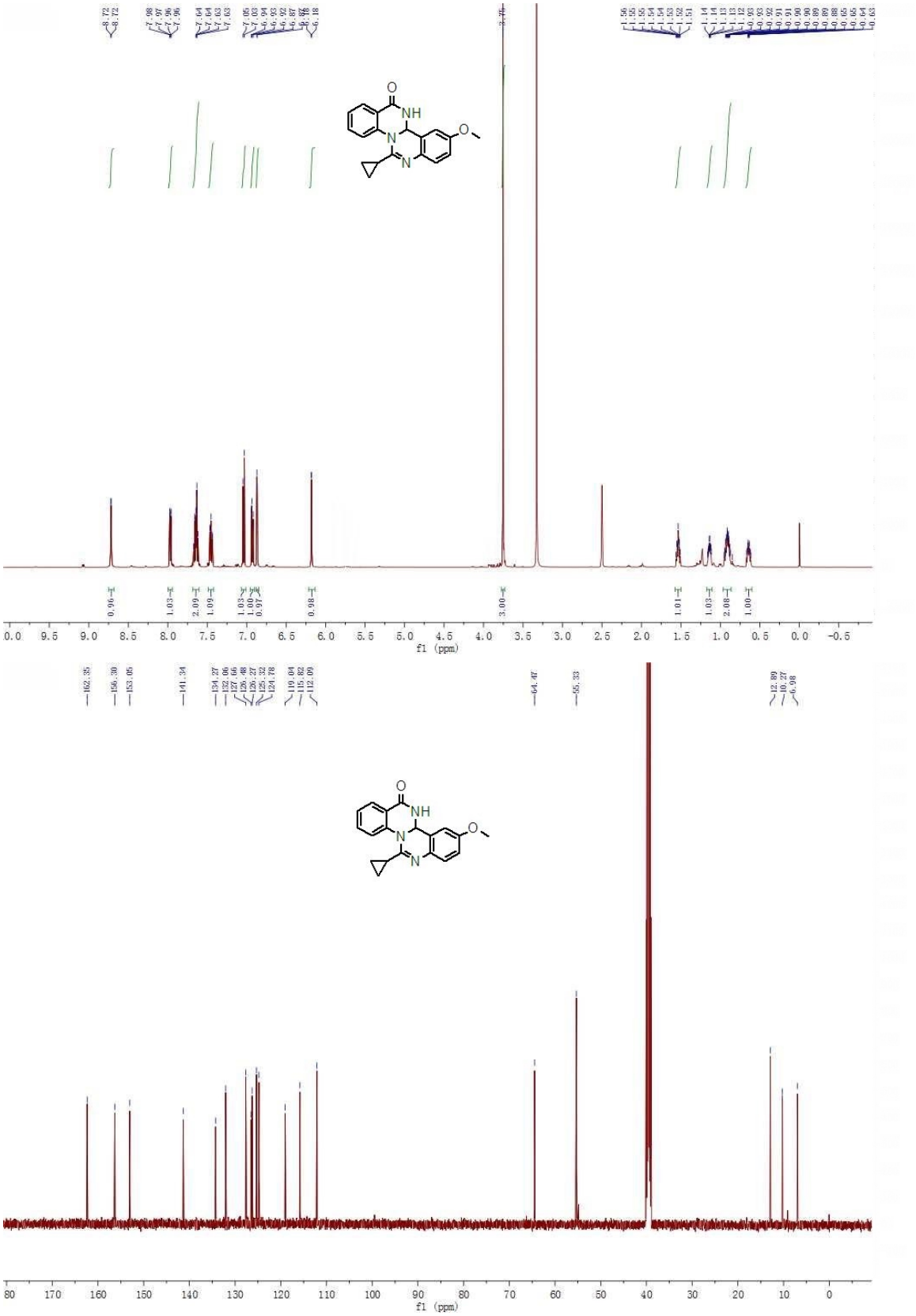


Figure S18. ^{1}H NMR of **3hc** (500 MHz, DMSO-d6) and ^{13}C NMR of **3hc** (125 MHz, DMSO-d6).

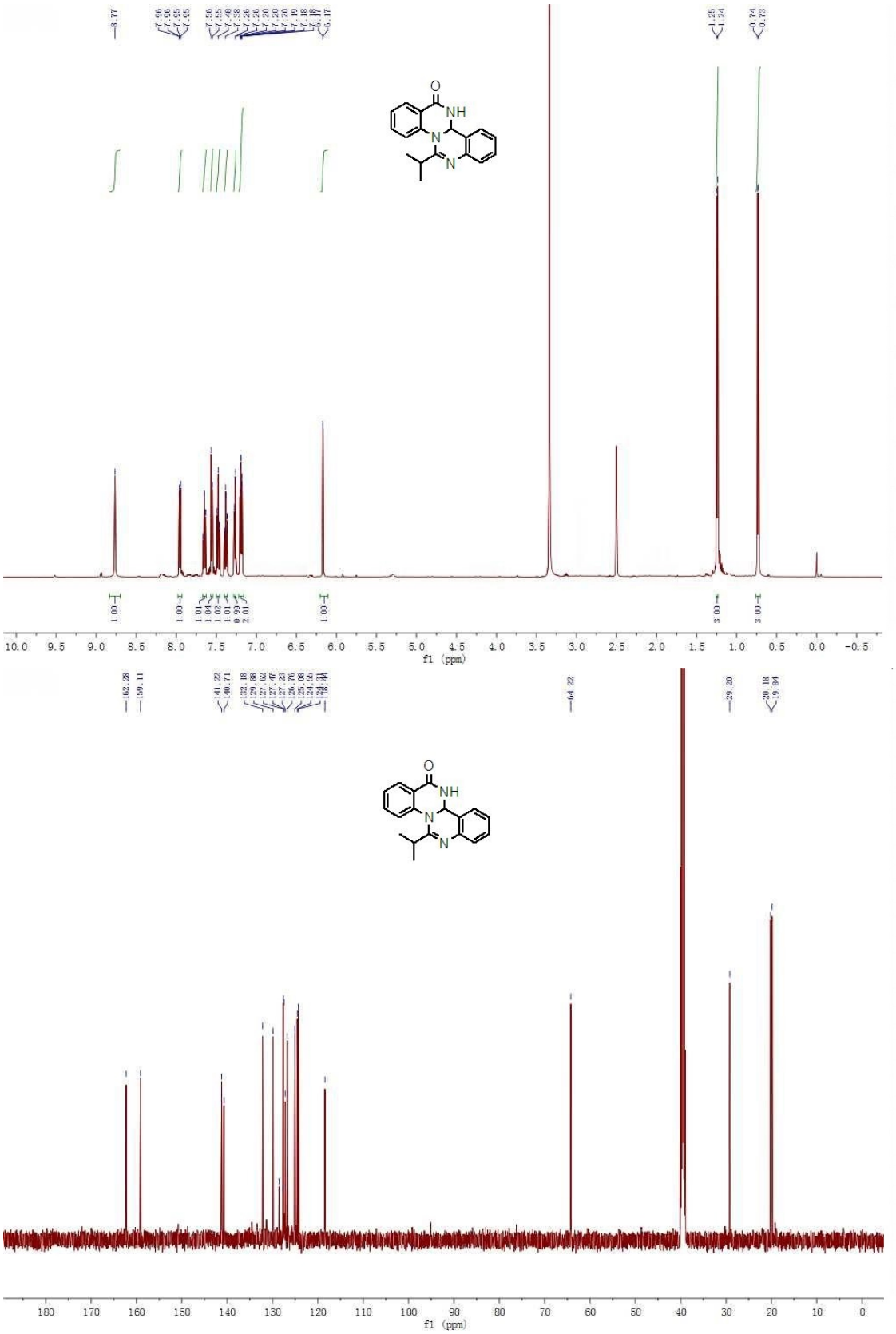


Figure S19. ^{1}H NMR of **3ad** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ad** (125 MHz, DMSO-d6).

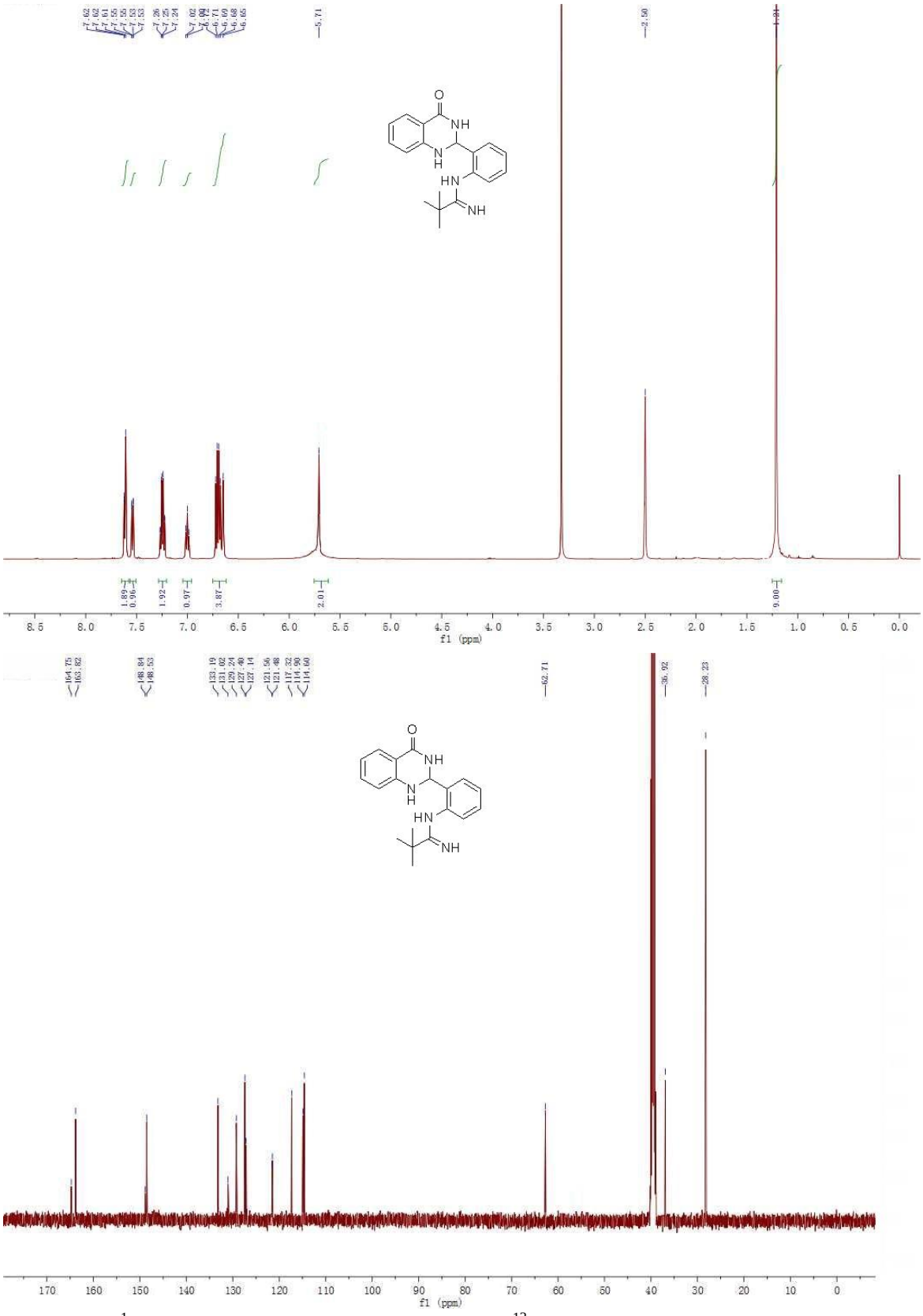


Figure S20. ^{1}H NMR of **3ae** (500 MHz, DMSO-d6) and ^{13}C NMR of **3ae** (125 MHz, DMSO-d6).

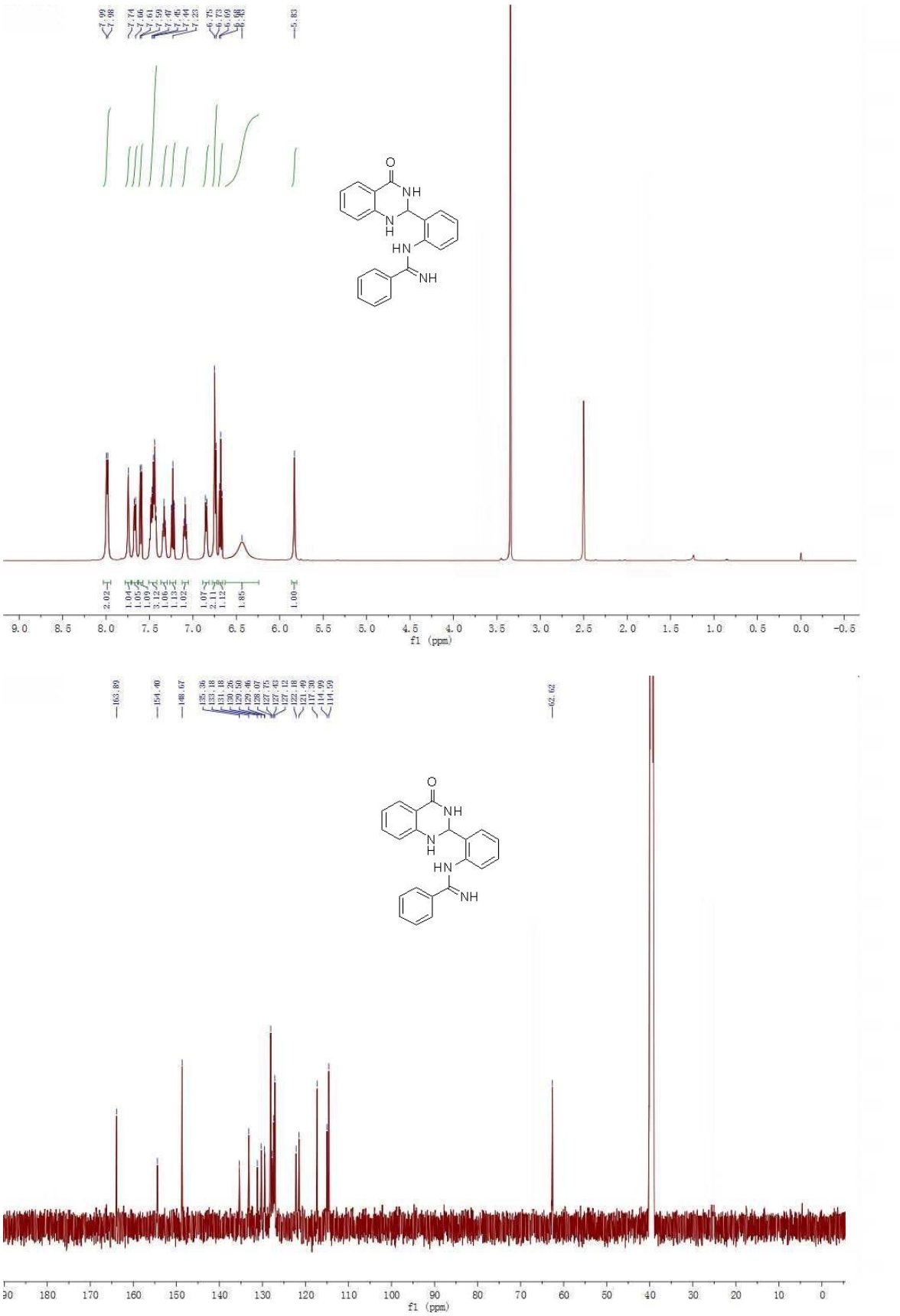


Figure S21. ^{1}H NMR of **4af** (500 MHz, DMSO-d6) and ^{13}C NMR of **4af** (125 MHz, DMSO-d6).

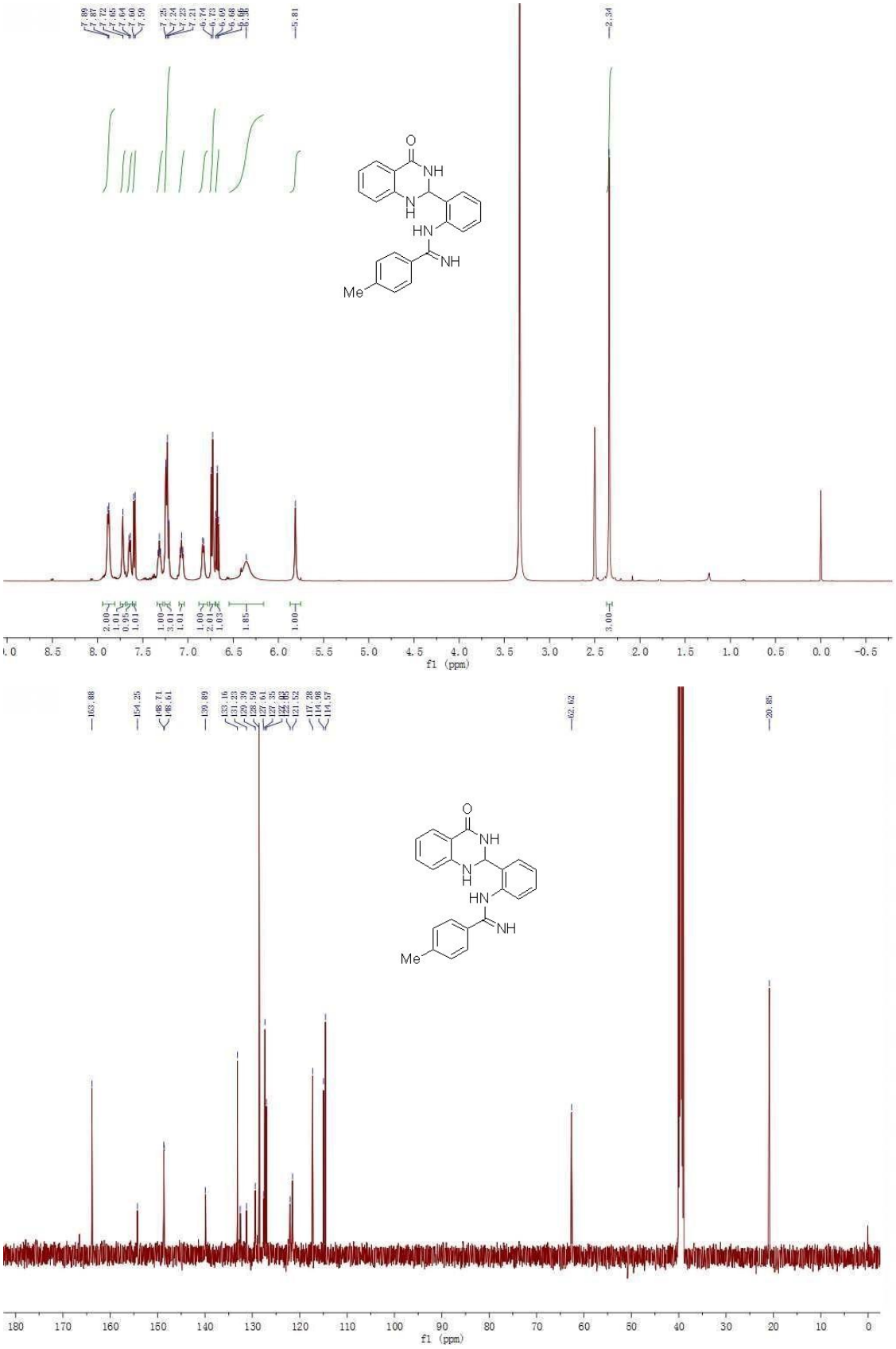


Figure S22. ^{1}H NMR of **4ag** (500 MHz, DMSO-d6) and ^{13}C NMR of **4ag** (125 MHz, DMSO-d6).

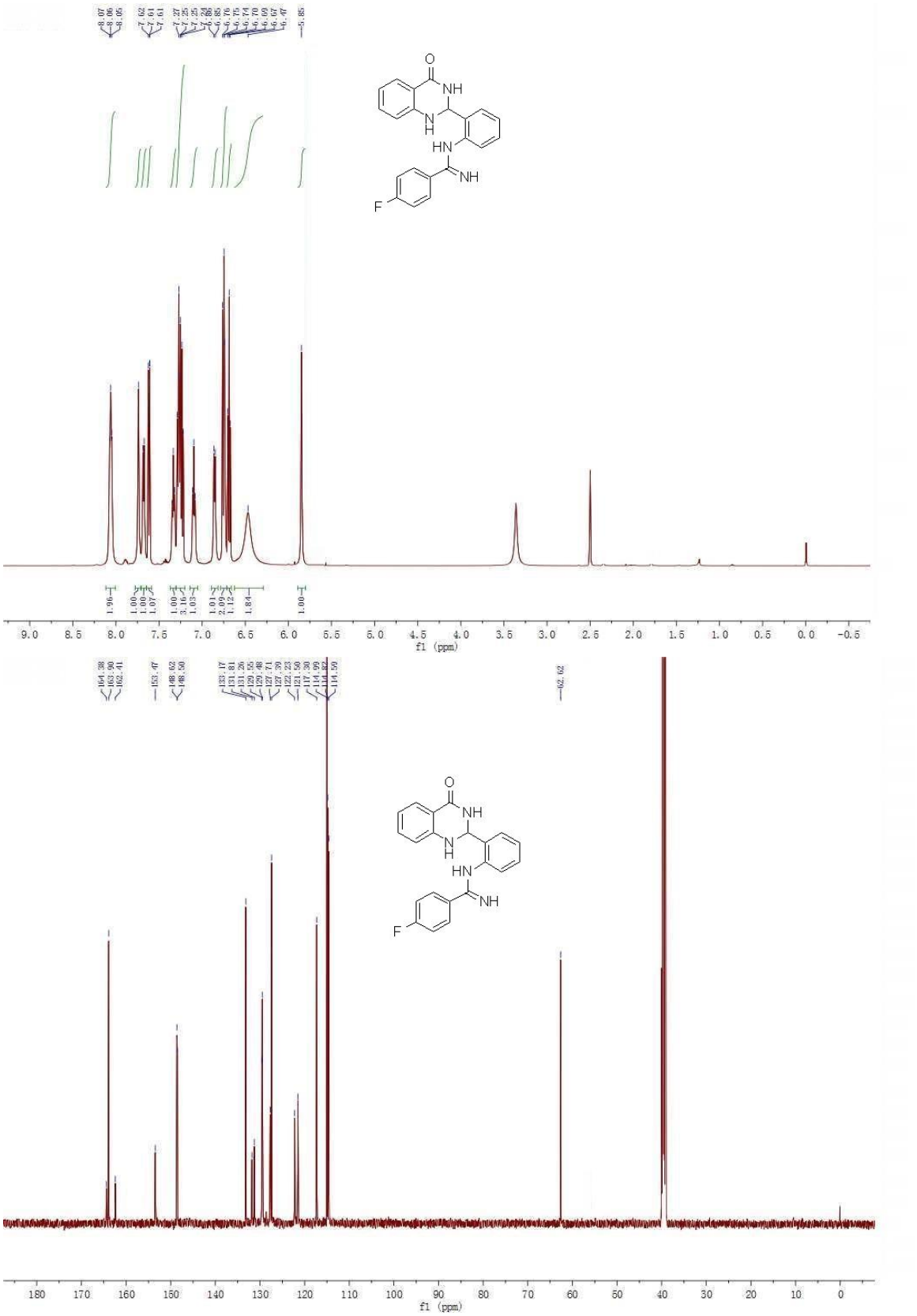


Figure S23. ^{1}H NMR of **4ah** (500 MHz, DMSO-d6) and ^{13}C NMR of **4ah** (125 MHz, DMSO-d6).

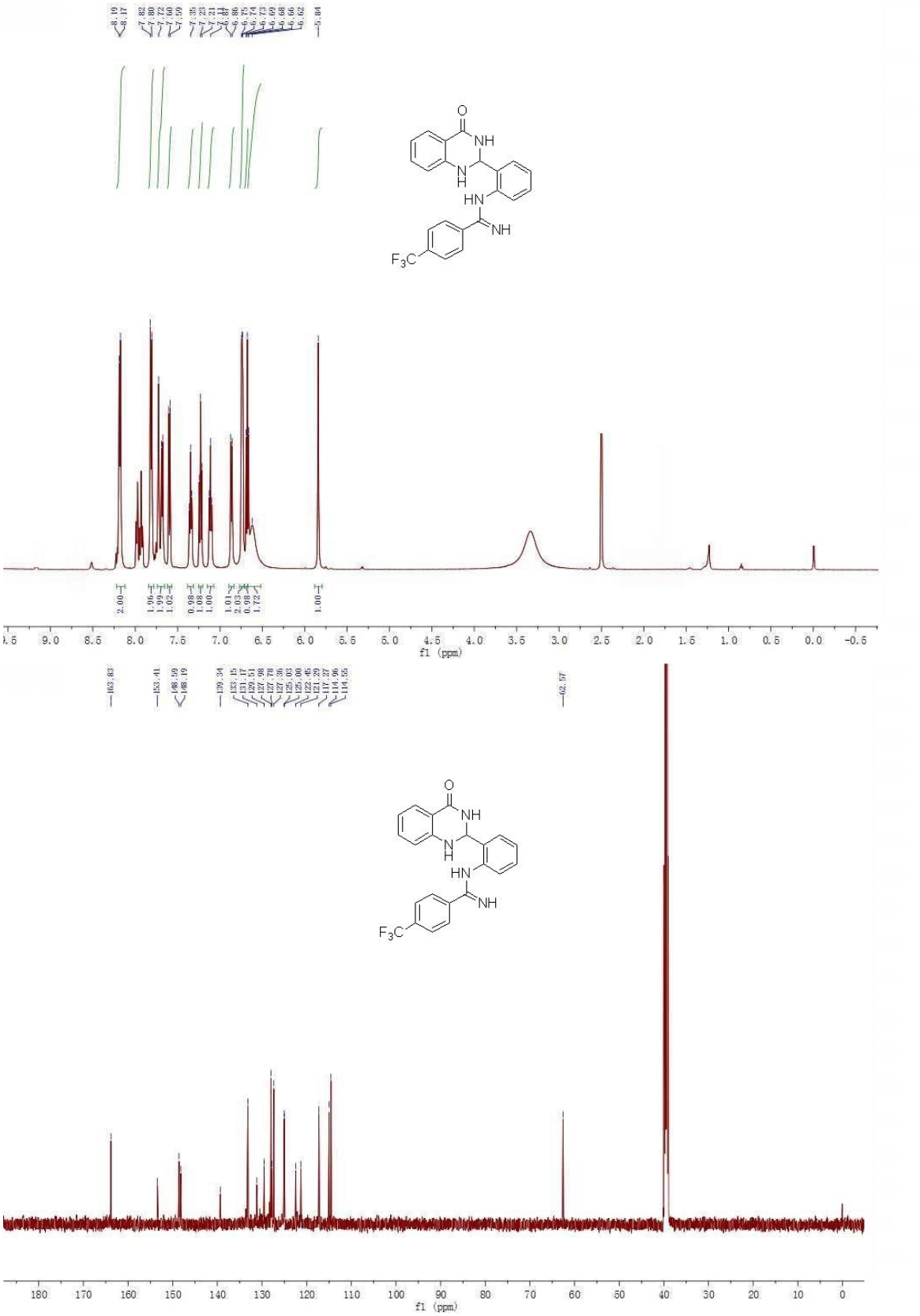


Figure S24. ^{1}H NMR of **4ai** (500 MHz, DMSO-d6) and ^{13}C NMR of **4ai** (125 MHz, DMSO-d6).

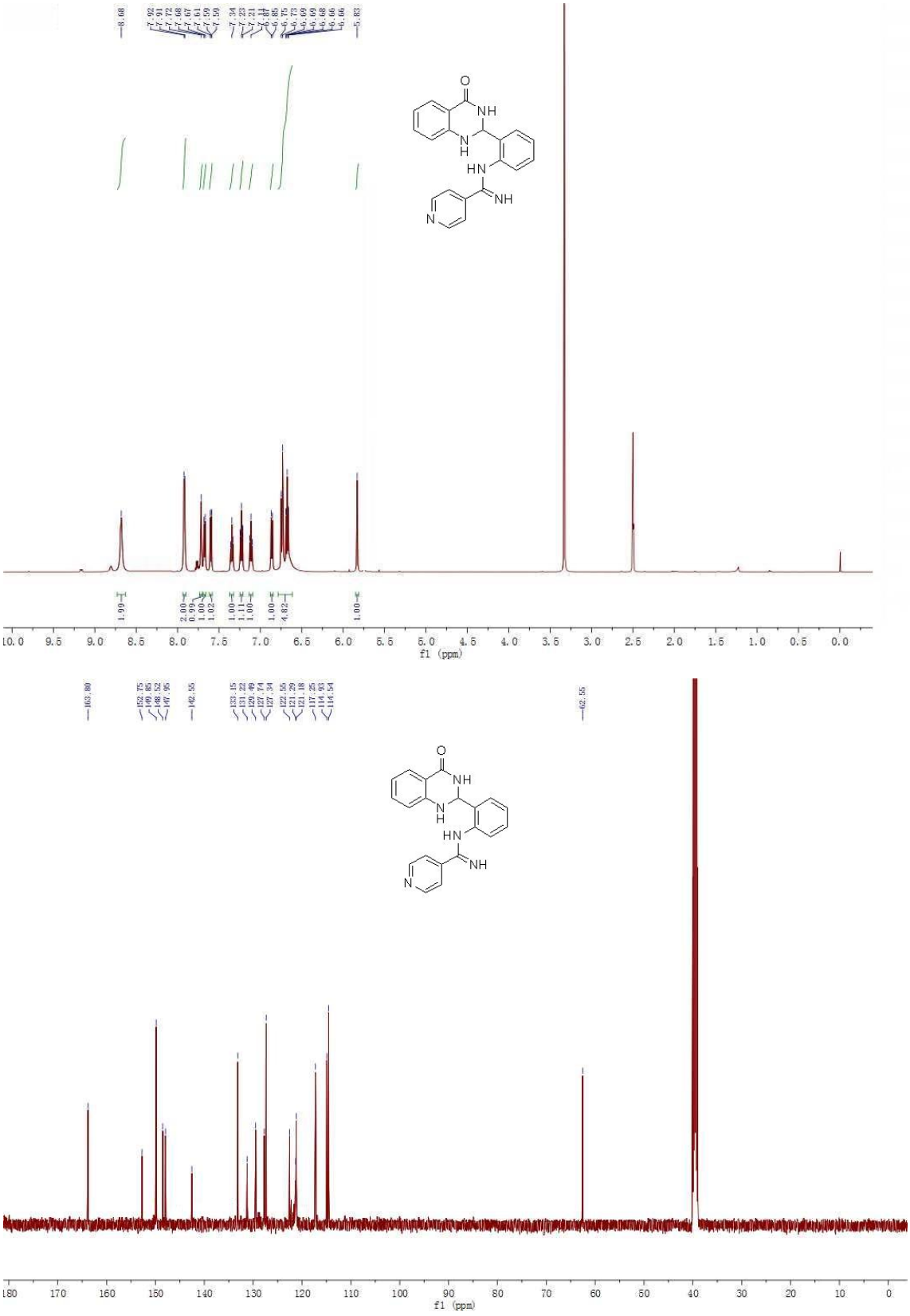


Figure S25. ^{1}H NMR of **4aj** (500 MHz, DMSO-d6) and ^{13}C NMR of **4aj** (125 MHz, DMSO-d6).

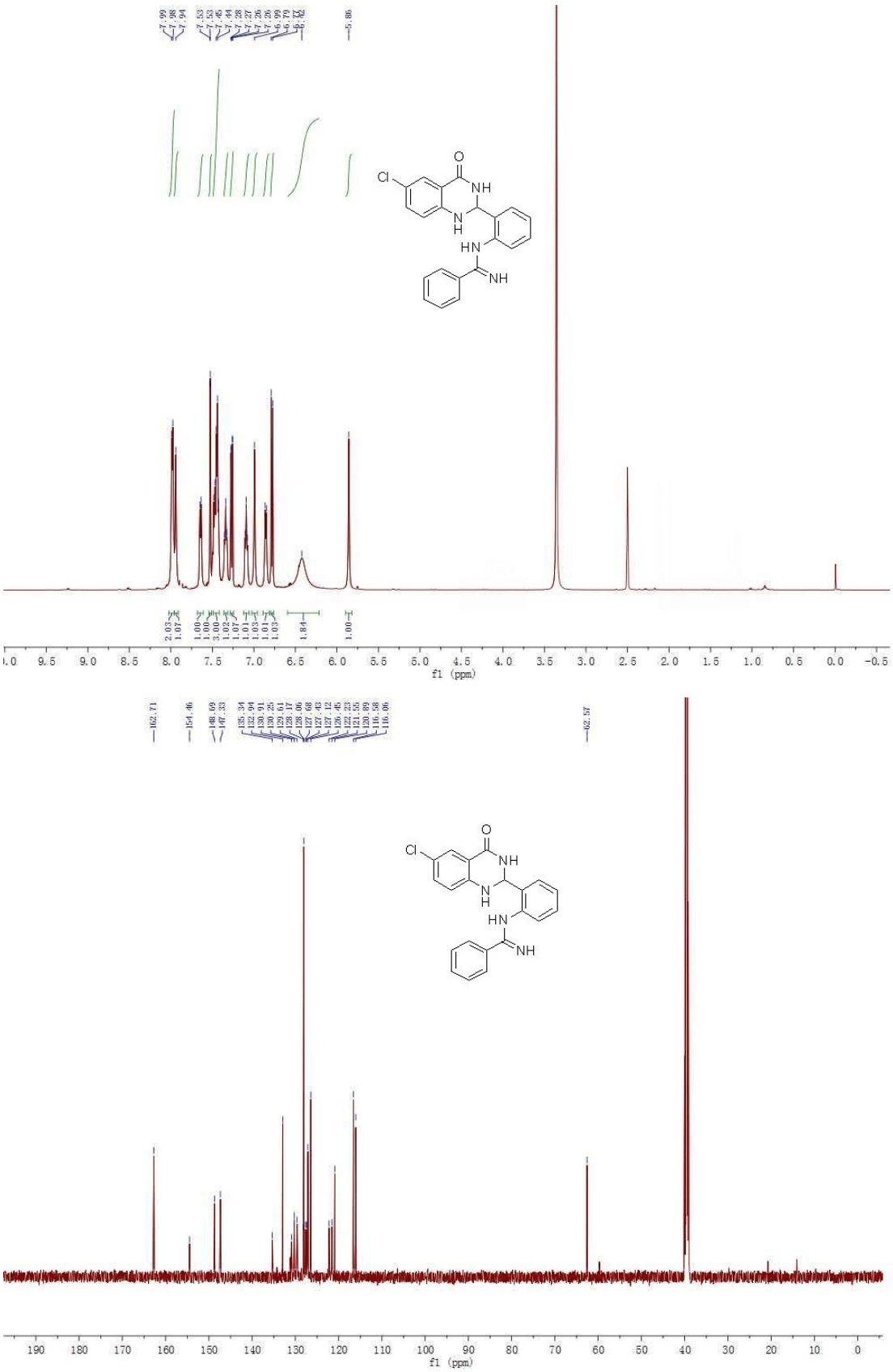


Figure S26. ^{1}H NMR of **4cf** (500 MHz, DMSO-d6) and ^{13}C NMR of **4cf** (125 MHz, DMSO-d6).

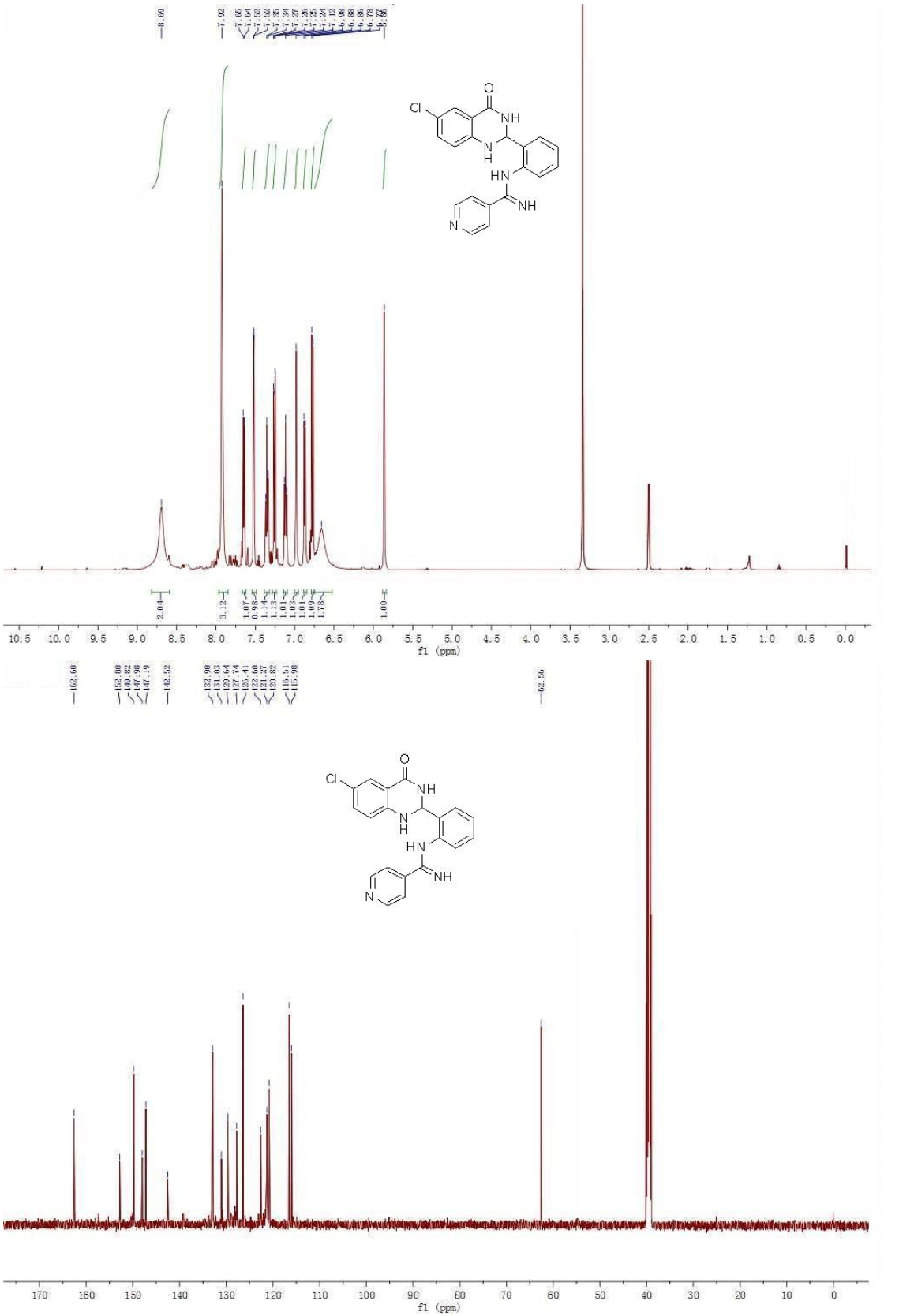


Figure S27. ^{1}H NMR of **4cj** (500 MHz, DMSO-d6) and ^{13}C NMR of **4cj** (125 MHz, DMSO-d6).

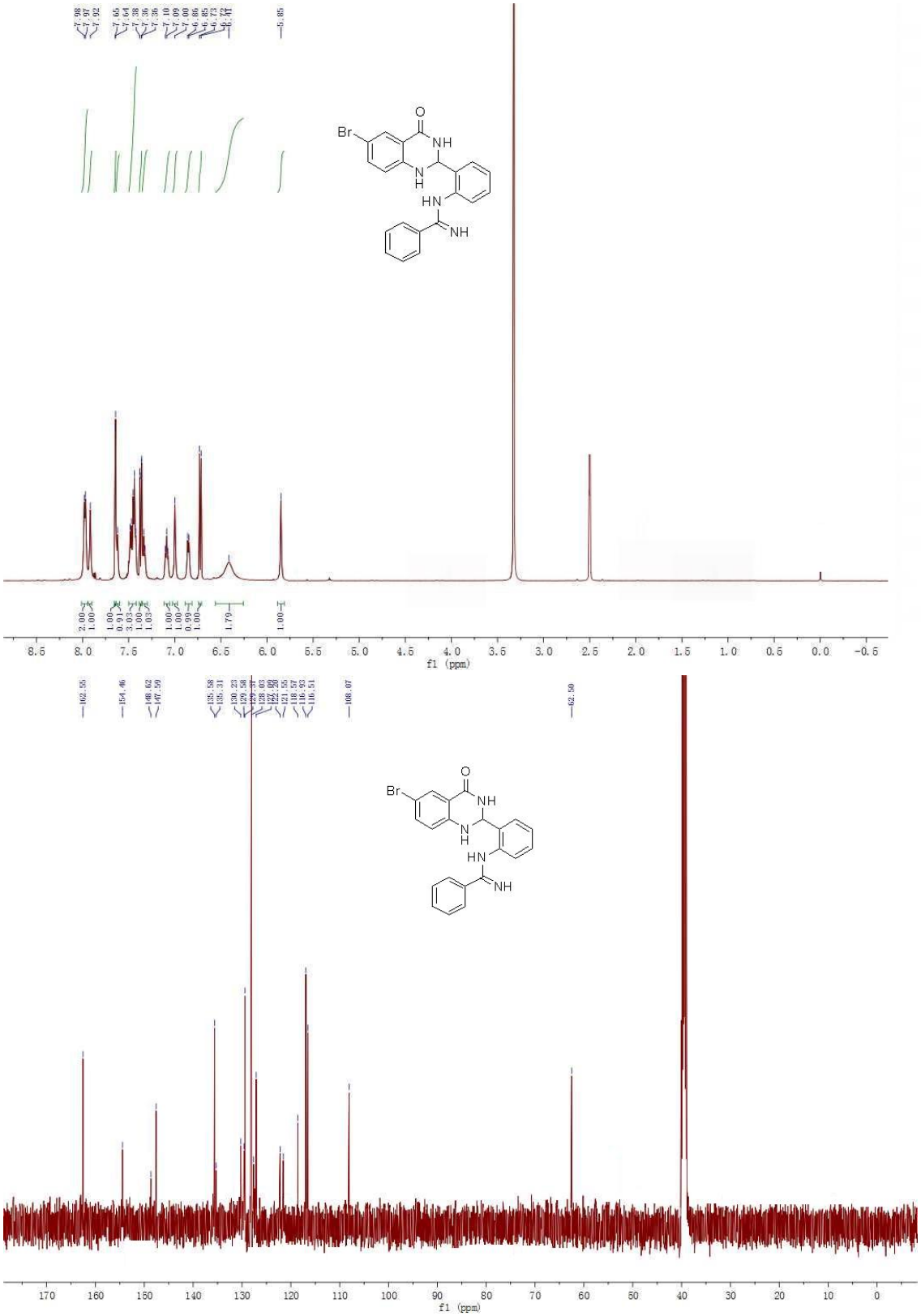


Figure S28. ^{1}H NMR of **4df** (500 MHz, DMSO-d6) and ^{13}C NMR of **4df** (125 MHz, DMSO-d6).

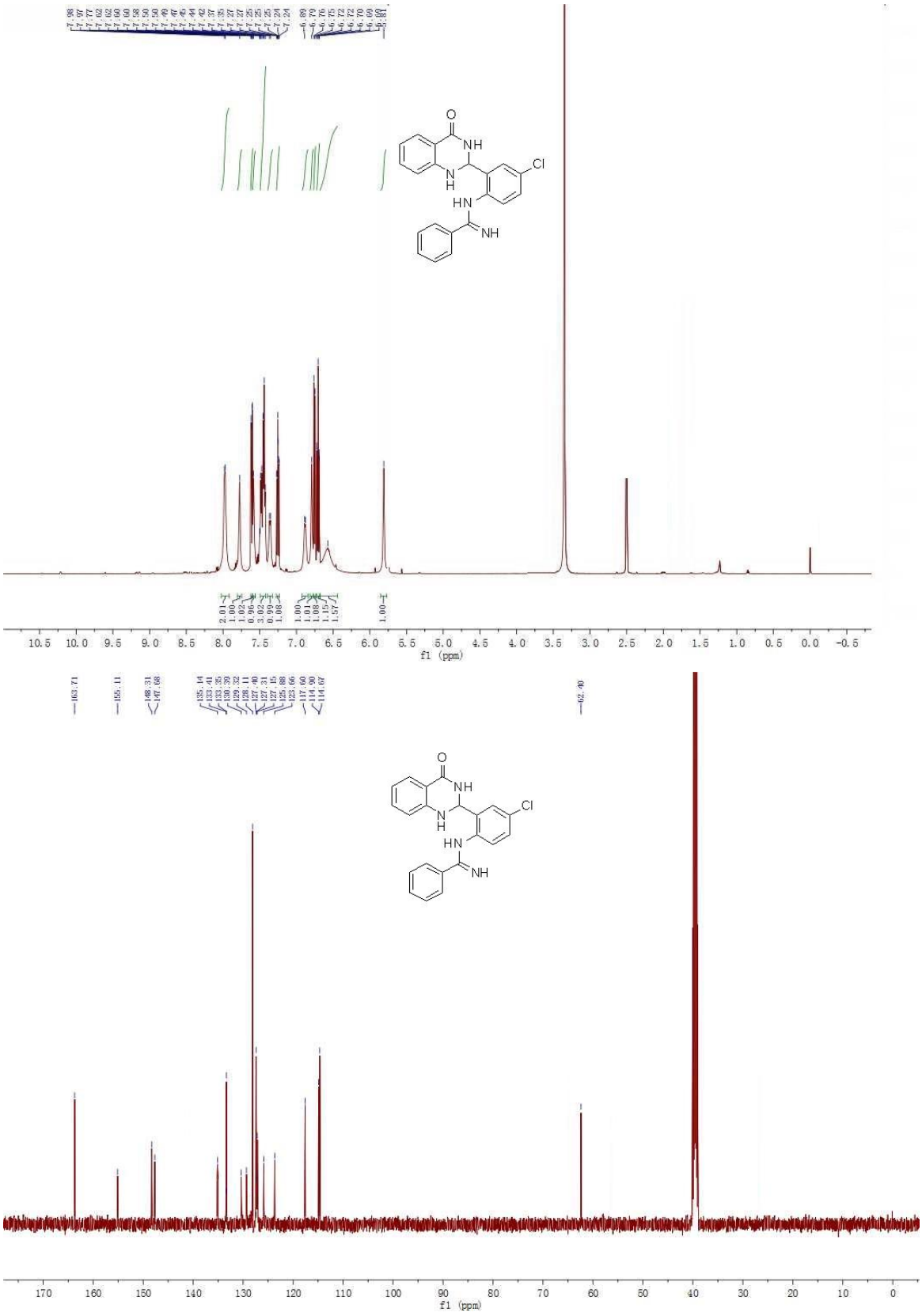


Figure S29. ^{1}H NMR of **4ff** (500 MHz, DMSO-d6) and ^{13}C NMR of **4ff** (125 MHz, DMSO-d6).

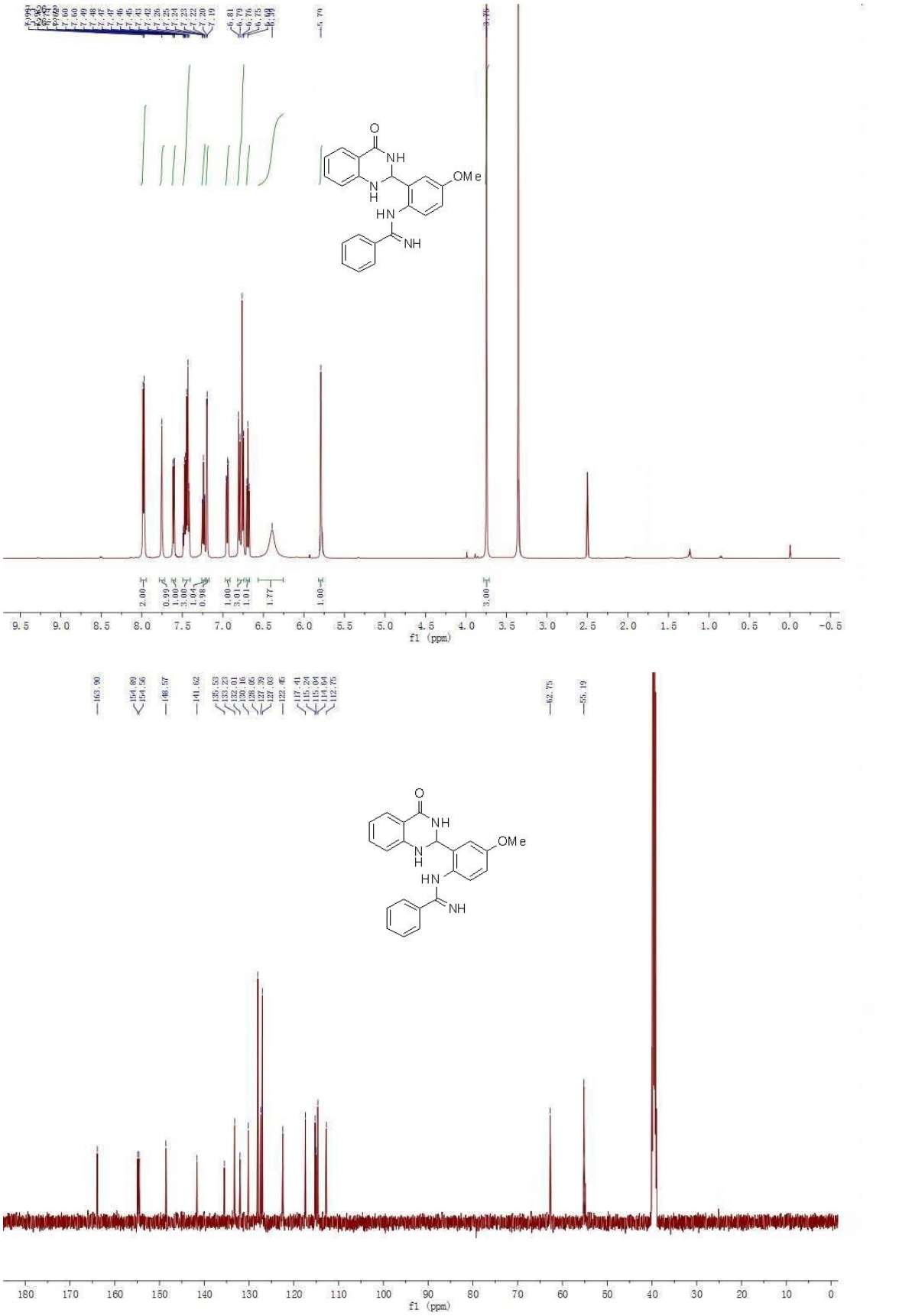


Figure S30. ^{1}H NMR of **4hf** (500 MHz, DMSO-d6) and ^{13}C NMR of **4hf** (125 MHz, DMSO-d6).

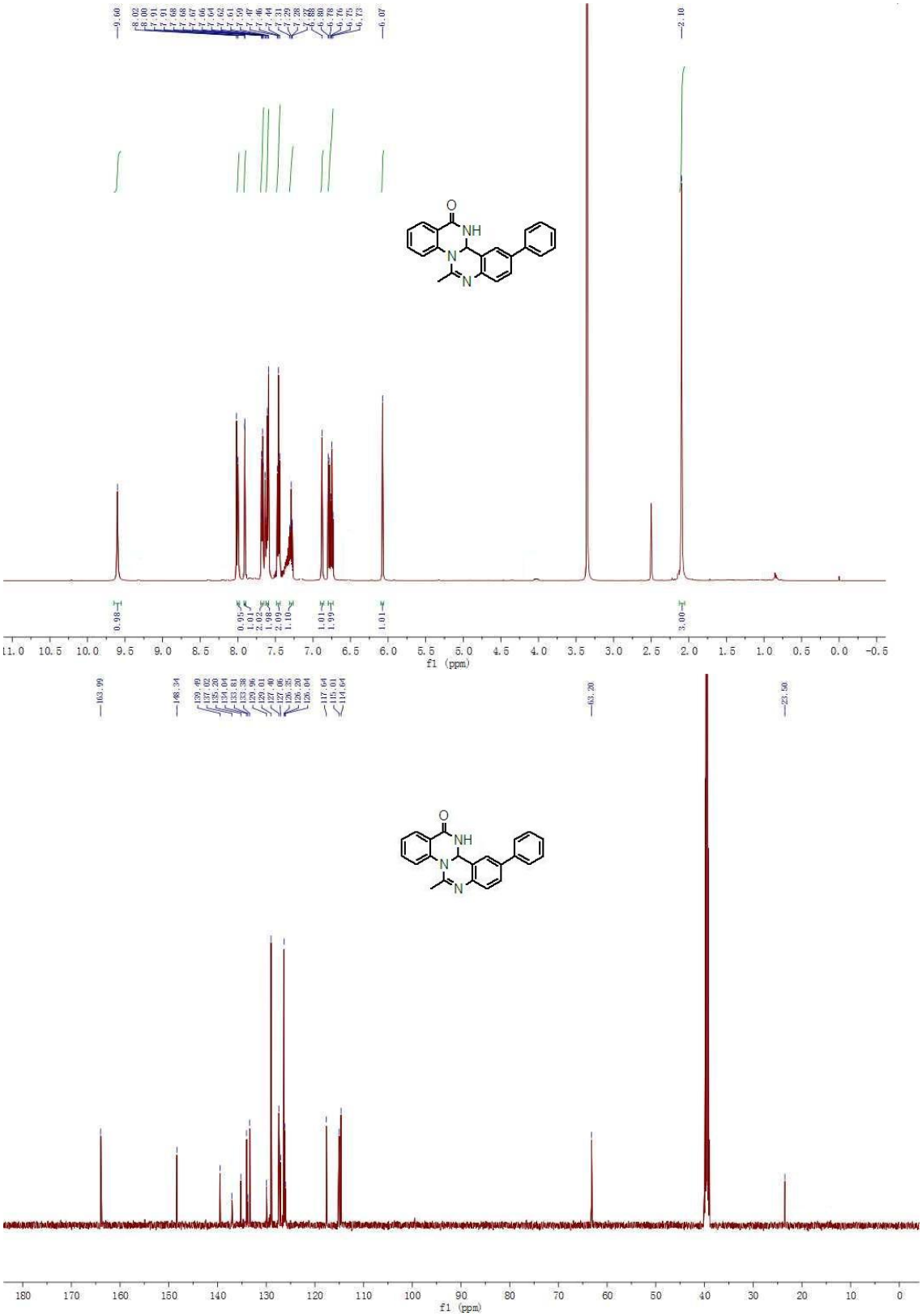


Figure S31. ^{1}H NMR of **5** (500 MHz, DMSO-d6) and ^{13}C NMR of **5** (125 MHz, DMSO-d6).

6. ORTEP Diagram and X-ray data for 3aa, 3ae, 3hc, and 4af

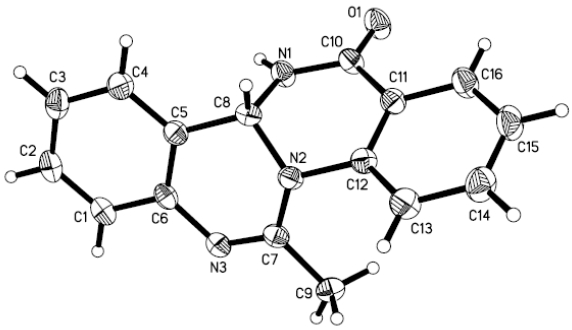


Figure S32 ORTEP Diagram of the single-crystal X-ray structure of **3aa**

Table 1. Crystal data and structure refinement for mo_20110604C_0m.

Identification code	mo_20110604c_0m
Empirical formula	C16 H13 N3 O
Formula weight	263.29
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P b c a
Unit cell dimensions	a = 8.5996(13) A alpha = 90 deg.
	b = 14.555(2) A beta = 90 deg.
	c = 20.633(3) A gamma = 90 deg.
Volume	2582.6(6) A^3
Z, Calculated density	8, 1.354 Mg/m^3
Absorption coefficient	0.088 mm^-1
F(000)	1104
Crystal size	0.18 x 0.15 x 0.11 mm
Theta range for data collection	1.97 to 25.10 deg.
Limiting indices	-10<=h<=10, -17<=k<=12, -24<=l<=22
Reflections collected / unique	10484 / 2292 [R(int) = 0.0825]
Completeness to theta = 25.10	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9904 and 0.9844
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2292 / 0 / 183
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1391
R indices (all data)	R1 = 0.1025, wR2 = 0.1744
Extinction coefficient	0.0045(14)
Largest diff. peak and hole	0.337 and -0.285 e.A^-3

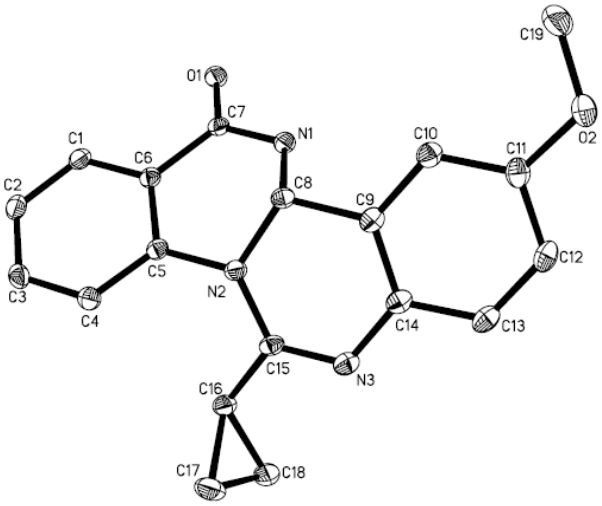


Figure S33 ORTEP Diagram of the single-crystal X-ray structure of **3hc**

Table 1. Crystal data and structure refinement for mo_20120729B_0m.

Identification code	mo_20120729b_0m
Empirical formula	C19 H17 N3 O2
Formula weight	319.36
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 5.2403(4) A alpha = 90 deg.
	b = 16.3094(12) A beta = 94.9210(10) deg.
	c = 17.8420(13) A gamma = 90 deg.
Volume	1519.3(2) A^3
Z, Calculated density	4, 1.396 Mg/m^3
Absorption coefficient	0.093 mm^-1
F(000)	672
Crystal size	0.24 x 0.21 x 0.15 mm
Theta range for data collection	1.69 to 25.50 deg.
Limiting indices	-6<=h<=6, -19<=k<=17, -20<=l<=21
Reflections collected / unique	11496 / 2811 [R(int) = 0.0197]
Completeness to theta = 25.50	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9862 and 0.9780
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2811 / 0 / 218
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.1027
R indices (all data)	R1 = 0.0416, wR2 = 0.1073
Largest diff. peak and hole	0.205 and -0.185 e.A^-3

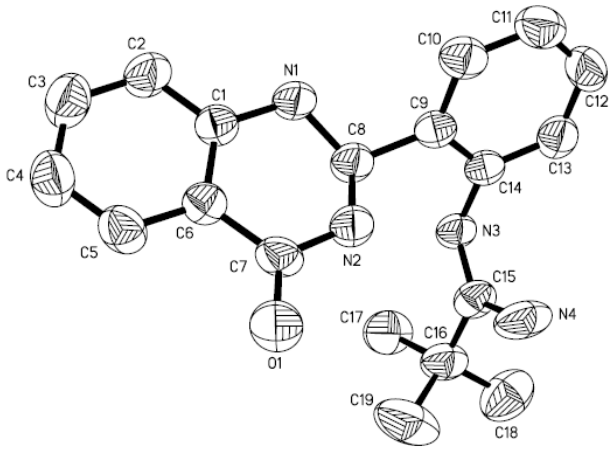


Figure S34 ORTEP Diagram of the single-crystal X-ray structure of **4ae**

Table 1. Crystal data and structure refinement for mo_20111101A_0m.

Identification code	mo_20111101a_0m
Empirical formula	C19 H22 N4 O
Formula weight	322.41
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 9.666(10) A alpha = 90 deg.
	b = 10.849(11) A beta = 100.738(19) deg.
	c = 15.997(16) A gamma = 90 deg.
Volume	1648(3) A^3
Z, Calculated density	4, 1.299 Mg/m^3
Absorption coefficient	0.083 mm^-1
F(000)	688
Crystal size	0.23 x 0.21 x 0.15 mm
Theta range for data collection	2.14 to 25.50 deg.
Limiting indices	-11<=h<=11, -9<=k<=13, -16<=l<=19
Reflections collected / unique	10051 / 3039 [R(int) = 0.0403]
Completeness to theta = 25.50	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9876 and 0.9811
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3039 / 0 / 220
Goodness-of-fit on F^2	1.101
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1773
R indices (all data)	R1 = 0.0896, wR2 = 0.2063
Largest diff. peak and hole	0.339 and -0.330 e.A^-3

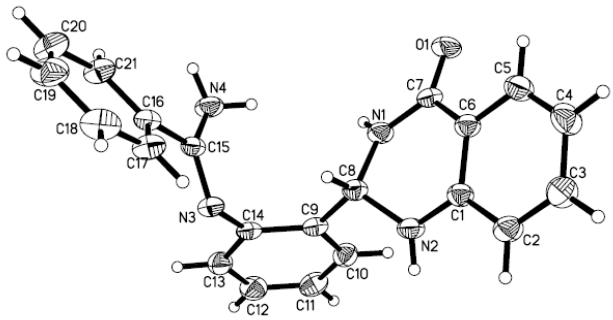


Figure S35 ORTEP Diagram of the single-crystal X-ray structure of **4af**

Table 1. Crystal data and structure refinement for mo_20120422A_0m.

Identification code	mo_20120422a_0m
Empirical formula	C25 H26 N4 O2
Formula weight	414.50
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 11.692(4) A alpha = 90 deg.
	b = 11.309(4) A beta = 91.039(8) deg.
	c = 17.125(6) A gamma = 90 deg.
Volume	2264.0(13) A^3
Z, Calculated density	4, 1.216 Mg/m^3
Absorption coefficient	0.079 mm^-1
F(000)	880
Crystal size	0.28 x 0.22 x 0.15 mm
Theta range for data collection	2.09 to 25.10 deg.
Limiting indices	-13<=h<=13, -12<=k<=13, -15<=l<=20
Reflections collected / unique	12799 / 4004 [R(int) = 0.0750]
Completeness to theta = 25.10	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9882 and 0.9782
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4004 / 0 / 281
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.2025
R indices (all data)	R1 = 0.1318, wR2 = 0.2386
Extinction coefficient	0.012(3)
Largest diff. peak and hole	0.340 and -0.371 e.A^-3