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Supporting Information

$Fe(acac)_2$/TBHP-promoted synthesis of 11-functionalized dibenzodiazepines via alkoxycarbonylation and carboxamidation of *o*-isocyanodiaryl amines

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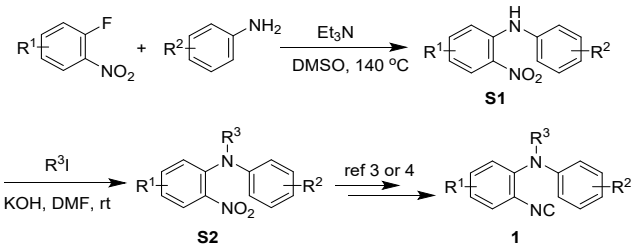
1. General information

All commercial reagents and solvents involved in the reaction could be used directly without further purification unless otherwise noted. All heating reactions were carried out on the IKA heating module. The products were purified by silica gel column chromatography (300−400 mesh silica gel). ^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on Avance 400 spectrometer using $CDCl_3$ as solvent. Chemical shifts were reported in parts per million (ppm) using TMS as internal standard (^{1}H NMR: δ = 7.26 ppm, ^{13}C NMR: δ = 77.16 ppm). IR spectra were recorded on Thermo Scientific Nicolet 6700. High-resolution mass spectrometry (HRMS) data were collected on AB SCIEX TripleTOF 6600. X-ray diffraction data were recorded on Agilent SuperNova E G8910B. Melting points (mp) were recorded on an INESA SGW X-4.

2. General procedure for preparation of substrates

A typical synthesis procedure of substrates **1** was shown below:



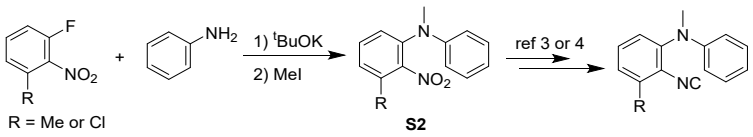
Method A:

Step 1: The *o*-fluoronitrobenzene compounds (30 mmol, 1.0 equiv), arylamines (30 mmol, 1.0 equiv), triethylamine (60 mmol, 2.0 equiv) and DMSO (30 mL) were added sequentially to a round bottom flask. The mixture was stirred at reflux at 140°C for 12 hours. After the reaction was completed, the mixture was cooled to room temperature and then extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA = 100:1) to afford **S1**.[1]

Step 2: To a solution of **S1** (27 mmol, 1.0 equiv) in DMF (30 mL) was added KOH (122 mmol, 4.5 equiv) at room temperature. After ten minutes, R^3I (81 mmol, 3.0 equiv) was slowly added dropwise to the above mixture, and then stirring was continued at room temperature until **S1** was consumed as monitored by TLC. After completion of the reaction, the mixture was quenched with water and extracted three times with ethyl acetate (30 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to obtain the crude product **S2** without further purification.[2]

Step 3 to 5 were prepared according to the literatures.[3,4]

Synthesis procedure of substrate **1k** and **1l**:



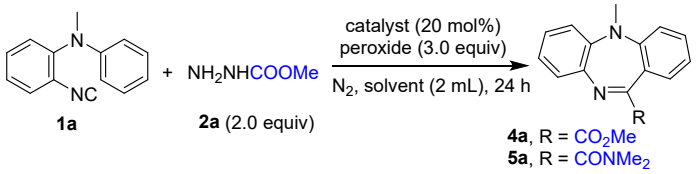
Method B:

Under nitrogen atmosphere, *o*-fluoronitrobenzene compound (30 mmol, 1.0 equiv) was added slowly dropwise to a mixture of potassium *tert*-butoxide (150 mmol, 5.0 equiv), aniline (60 mmol, 2.0 equiv) and DMSO (60 mL) at 0 °C. The mixed reaction solution was stirred at room temperature for 3 h. Then, MeI was slowly added to the above mixture. After 3 h, the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA = 100:1) to afford **S2**.[5]

The formamide reagents, methyl carbazate and ethyl carbazate involved in the reaction were purchased directly, other carbazates were prepared according to the literature.[6]

3. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions.[a]

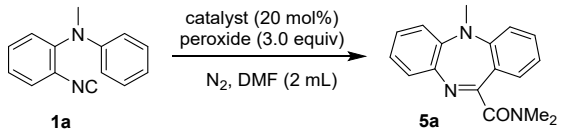


Entry	Catalyst	Peroxide	T (°C)	Solvent	Yield[b] (%)
1	$Fe(acac)_2$	TBHP	80	PhF	34[c]
2	$Fe(acac)_2$	TBHP	80	PhF	67
3	$Fe(acac)_3$	TBHP	80	PhF	65
4	$Fe(OAc)_2$	TBHP	80	PhF	51
5	$FeSO_4·7H_2O$	TBHP	80	PhF	54
6	$Mn(acac)_3$	TBHP	80	PhF	37
7	$Mn(OAc)_3·2H_2O$	TBHP	80	PhF	43
8	TBAI	TBHP	80	PhF	21
9	$Fe(acac)_2$	DTBP	80	PhF	34
10	$Fe(acac)_2$	BPO	80	PhF	trace
11	$Fe(acac)_2$	DCP	80	PhF	25
12	$Fe(acac)_2$	$K_2S_2O_8$	80	PhF	23
13	$Fe(acac)_2$	TBHP	80	DCE	63
14	$Fe(acac)_2$	TBHP	80	1,4-dioxane	0
15	$Fe(acac)_2$	TBHP	80	MeCN	43
16	$Fe(acac)_2$	TBHP	80	THF	0
17	$Fe(acac)_2$	TBHP	80	$PhCF_3$	68
18	$Fe(acac)_2$	TBHP	80	DMF	trace/56[d]
19	$Fe(acac)_2$	TBHP	60	$PhCF_3$	53
20	**$Fe(acac)_2$**	**TBHP**	**100**	**$PhCF_3$**	**70**
21	**$Fe(acac)_2$**	**TBHP**	**80**	**DMF**	**80[d,e]**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), catalyst (20 mol%), peroxide (3.0 equiv), solvent (2 mL), under nitrogen atmosphere for 24 h. [b] Isolated yield. [c] Under air. [d] The product **5a** was obtained. [e] The reaction conducted in the absence of **2a** for 4 h.

Supplementary: Optimization of the reaction conditions for the synthesis of dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide are shown in Table S2.

Table S2 Optimization of the carboxylamidation of *o*-isocyanodiarylamines.[a]

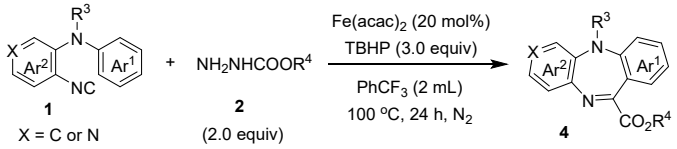


Entry	Catalyst	Peroxide	Base	T (°C)	Yield[b] (%)
1	**$Fe(acac)_2$**	**TBHP**	**/**	**80**	**80**
2	$Fe(acac)_2$	TBHP	/	80	70[c]
3	$Fe(acac)_3$	TBHP	/	80	74
4	$Mn(acac)_3$	TBHP	/	80	48
5	TBAB	TBHP	/	80	45
6	$AgNO_3$	TBHP	/	80	43
7	$FeCl_3$	TBHP	/	80	30
8	$Fe(OAc)_2$	TBHP	/	80	63
9	$Fe(acac)_2$	TBHP	K_2CO_3	80	75
10	$Fe(acac)_2$	$K_2S_2O_8$	/	80	23
11	$Fe(acac)_2$	Oxone	/	80	38
12	$Fe(acac)_2$	DTBP	/	80	0
13	$Fe(acac)_2$	BPO	/	80	0
14	$Fe(acac)_2$	DCP	/	80	trace
15	$Fe(acac)_2$	TBPB	/	80	68
16	$Fe(acac)_2$	TBHP	/	40	72[d]
17	$Fe(acac)_2$	TBHP	/	60	80[d]
18	$Fe(acac)_2$	TBHP	/	100	70
19	$Fe(acac)_2$	TBHP	/	80	71[e]

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (20 mol%), peroxide (3.0 equiv), DMF (2 mL), under nitrogen atmosphere for 4 h. [b] Isolated yield. [c] Under air. [d] The reaction time was extended to 11 h. [e] The loading of TBHP was decreased to 2.0 equiv.

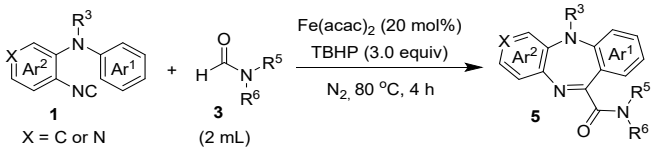
4. General procedure for synthesis of dibenzodiazepines

4.1 The synthesis of dibenzo[*b,e*][1,4]diazepine-11-carboxylates



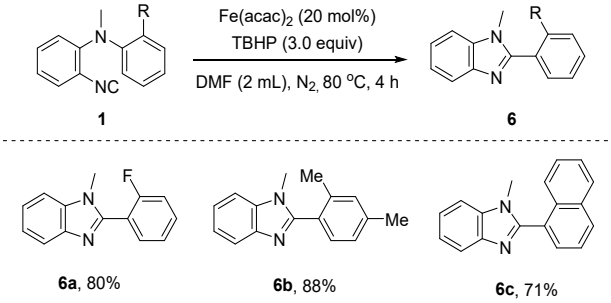
To a Schlenk tube was added a mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $Fe(acac)_2$ (0.04 mmol, 20 mol%), TBHP (0.6 mmol, 3.0 equiv) and $PhCF_3$ (2 mL) under N_2 atmosphere. The mixture was stirred at 100 °C for 24 h. After cooling down, the reaction solution was evaporated under reduced pressure and the residue was purified by flash column chromatography (PE/EA=15:1) to afford dibenzo[*b,e*][1,4]diazepine-11-carboxylates.

4.2 The synthesis of dibenzo[*b*,*e*][1,4]diazepine-11-carboxamides



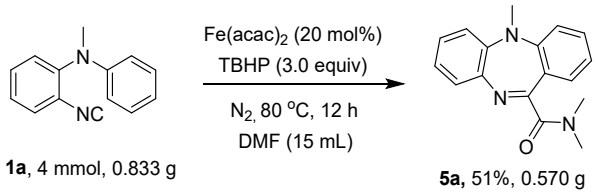
To a Schlenk tube was added a mixture of **1** (0.2 mmol, 1.0 equiv), $Fe(acac)_2$ (0.04 mmol, 20 mol%), TBHP (0.6 mmol, 3.0 equiv) and formamide **3** (2 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 4 h. After cooling down, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA=5:1) to afford dibenzo[*b,e*][1,4]diazepine-11-carboxamides.

5. General procedure for synthesis of 2-arylbenzo[*d*]imidazoles



To a Schlenk tube was added a mixture of *ortho*-substituted substrate **1** (0.2 mmol, 1.0 equiv), $Fe(acac)_2$ (0.04 mmol, 20 mol%), TBHP (0.6 mmol, 3.0 equiv) and DMF (2 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 4 h. After cooling down, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA=20:1) to afford 2-arylbenzo[*d*]imidazoles (**6a**-**6c**).

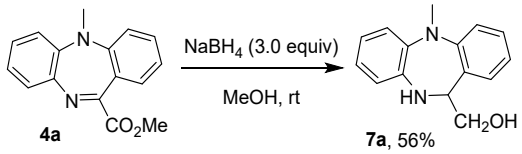
6. Scale-up experiment



To a round-bottomed flask (50 mL) was added a mixture of **1a** (4.0 mmol, 0.833 g), $Fe(acac)_2$ (0.8 mmol, 0.203 g), TBHP (12 mmol, 1.081 g) and DMF (15 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 12 h. After cooling down, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA=5:1) to

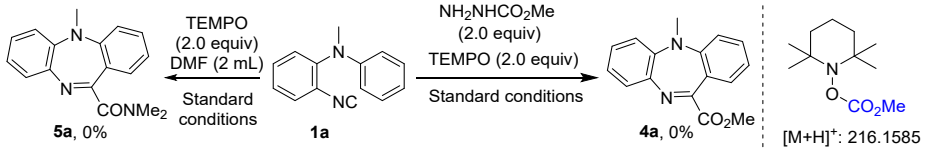
afford **5a** (51%).

7. Derivatization of product 4a

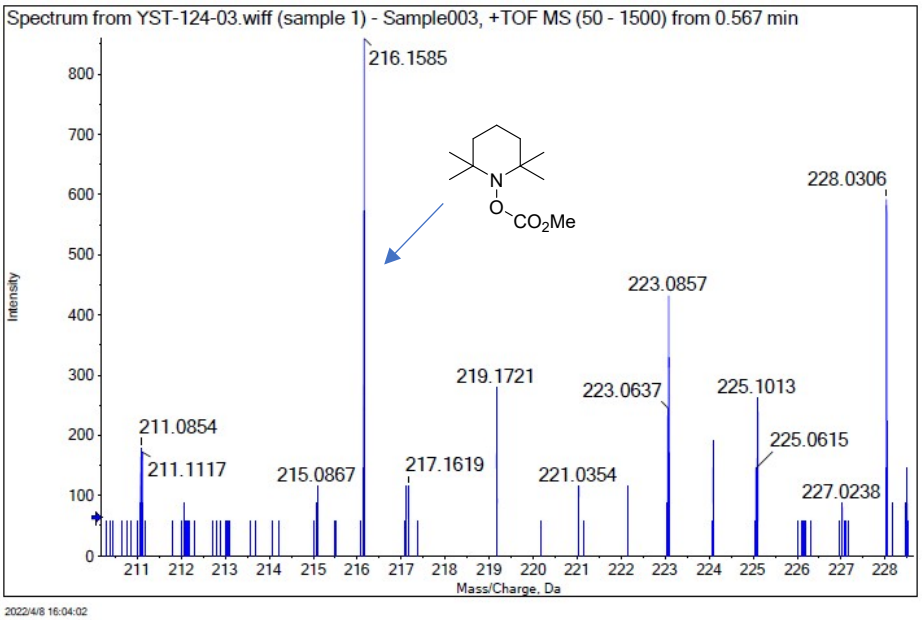


Product **4a** (0.2 mmol, 1.0 equiv) and MeOH (2 mL) were added to the Schlenk tube, and then $NaBH_4$ (0.6 mmol, 3.0 equiv) was slowly added to the mixture under an open-air system. The reaction solution was stirred at room temperature for 2 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (PE/EA = 5:1) to afford **7a**.

8. Radical inhibition experiments

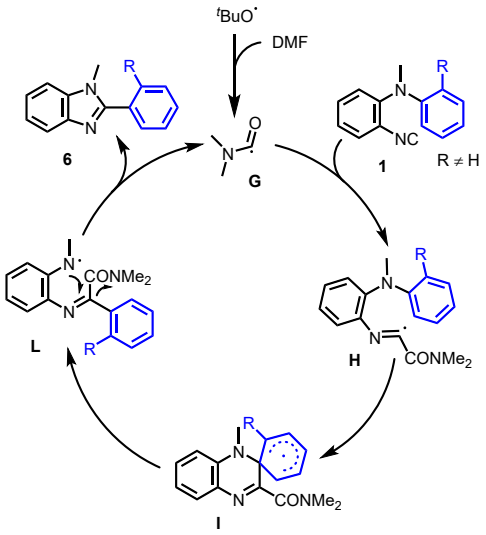


To a Schlenk tube was added a mixture of **1a** (0.2 mmol, 41.7 mg), Methyl carbazate (0.4 mmol, 36.0 mg), $Fe(acac)_2$ (0.04 mmol, 10.2 mg), TBHP (0.6 mmol, 54.1 mg), TEMPO (0.4 mmol, 62.5 mg) and $PhCF_3$ (2 mL) under N_2 atmosphere. The mixture was stirred at 100 °C for 24 h. To another Schlenk tube was added a mixture of **1a** (0.2 mmol, 41.7 mg), $Fe(acac)_2$ (0.04 mmol, 10.2 mg), TBHP (0.6 mmol, 54.1 mg), TEMPO (0.4 mmol, 62.5 mg) and DMF (2 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 4 h. The results of alkoxycarbonylation and carboxamidation experiments of **1a** showed that no target products **4a** and **5a** were observed, while the TEMPO-CO_2Me adduct was detected by HRMS.



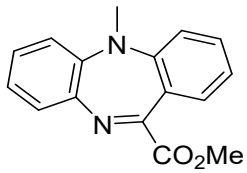
9. Proposed mechanism for the formation of compound 6

A proposed mechanism for the formation of product **6** was shown in Scheme S1, Initially, DMF was deprived of hydrogen by *tert*-butoxyl radical to give the dimethylcarbamic radical **G**. Then, the radical addition of **G** to isocyano group of the substrate **1** (R ≠ H) afforded imidoyl intermediate **H**. The intermediate **H** subsequently underwent aryl migration via intermediacy of spiro-cyclic radical **I** to give aminyl radical **L**.[7] Finally, the radical intermediate **L** underwent intramolecular five-membered cyclization to generate product **6**, accompanied by the generation of dimethylcarbamic radical **G**.

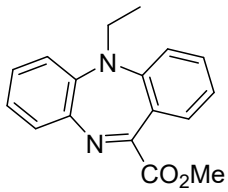


Scheme S1 A proposed mechanism for the formation of product **6**

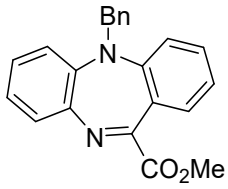
10. Characterization data of products



methyl 5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4a). PE/EA = 15:1, orange solid (37.3 mg, 70%), mp: 112 – 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 3.97 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.5, 158.3, 147.3, 141.3, 132.2, 130.0, 128.8, 128.6, 126.4, 124.2, 123.3, 118.1, 117.7, 53.1, 36.9. IR (KBr): 1724, 1620, 1593, 1575, 1498, 1446, 1320, 1275, 1250. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_2^+$ 267.1128; found 267.1138.

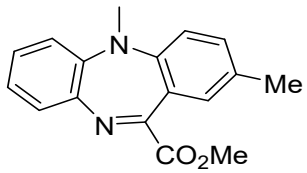


methyl 5-ethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4b). PE/EA = 15:1, orange solid (34.2 mg, 61%), mp: 122 – 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 3H), 7.25 – 7.18 (m, 1H), 7.12 – 7.03 (m, 2H), 7.01 – 6.92 (m, 2H), 3.98 (s, 3H), 3.67 (q, *J* = 6.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.0, 157.1, 145.9, 142.2, 132.0, 129.9, 128.5, 128.4, 127.3, 124.2, 123.3, 119.1, 118.8, 53.1, 42.7, 13.2. IR (KBr): 2957, 2931, 2850, 1725, 1618, 1592,1573, 1490, 1442, 1380, 1273, 1324, 1242. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1287.

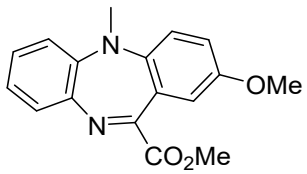


methyl 5-benzyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4c). PE/EA = 10:1, orange solid (36.3 mg, 53%), mp: 126 – 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 3H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.09 (m, 2H), 7.07 – 6.99 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.87 (s, 2H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.2, 156.9, 145.5, 142.1, 136.7, 132.1, 129.9, 128.5, 128.4,

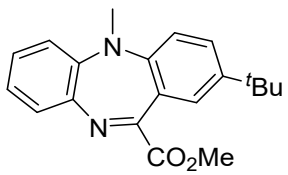
127.9, 127.2, 124.5, 123.6, 119.6, 119.2, 53.3, 52.7. IR (KBr): 2947, 2845, 1726, 1610, 1593, 1572, 1494, 1453, 1327, 1275, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}N_2O_2^+$ 343.1441; found 343.1448.



methyl 2,5-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4d). PE/EA = 15:1, orange solid (28.0 mg, 50%), mp: 128 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.11 (s, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.20 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.6, 155.7, 147.5, 141.2, 132.9, 132.9, 130.1, 128.7, 128.5, 126.2, 124.1, 117.9, 117.5, 53.1, 36.9, 20.6. IR (KBr): 2950, 1722, 1619, 1575, 1559, 1500, 1440, 1380, 1330, 1260, 1228. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1293.

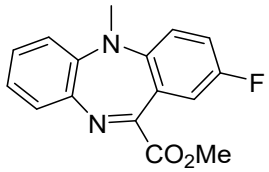


methyl 2-methoxy-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4e). PE/EA = 15:1, orange solid (43.3 mg, 73%), mp: 104 – 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.20 (td, *J* = 8.1, 1.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 – 6.87 (m, 4H), 3.97 (s, 3H), 3.75 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.7, 155.6, 151.1, 147.7, 141.2, 128.7, 128.6, 127.1, 124.0, 118.4, 118.0, 117.7, 114.6, 55.7, 53.1, 36.9. IR (KBr): 1720, 1630, 1603, 1580, 1508, 1453, 1337, 1260, 1247, 1230. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_3^+$ 297.1234; found 297.1244.

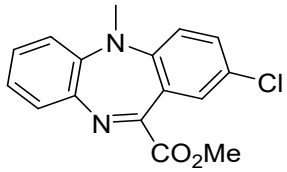


methyl 2-(*tert*-butyl)-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4f).

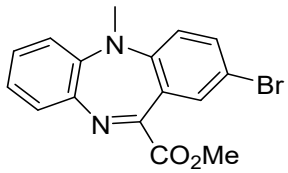
PE/EA = 15:1, orange oil (22.6 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.6, 2.3 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.20 (td, J = 8.0, 1.5 Hz, 1H), 7.07 (td, J = 7.7, 1.0 Hz, 1H), 6.96 – 6.88 (m, 2H), 3.97 (s, 3H), 3.21 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.9, 155.7, 147.5, 146.0, 141.3, 129.2, 128.7, 128.4, 127.0, 125.8, 124.1, 117.9, 117.2, 53.0, 36.8, 34.2, 31.2. IR (KBr): 1725, 1620, 1560, 1502, 1442, 1390, 1365, 1320, 1270, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}N_2O_2^+$ 323.1754; found 323.1761.



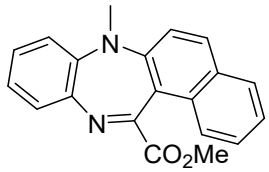
methyl 2-fluoro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4g). PE/EA = 15:1, orange solid (40.9 mg, 72%), mp: 127 – 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.8 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.15 – 7.03 (m, 3H), 6.99 – 6.87 (m, 2H), 3.98 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 158.64 (d, $J_{C\text{-}F}$ = 241.8 Hz), 158.59, 153.9, 147.2, 141.1, 128.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 127.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 124.4, 118.9 (d, $J_{C\text{-}F}$ = 22.7 Hz), 118.8 118.7, 118.0, 116.5 (d, $J_{C\text{-}F}$ = 24.0 Hz), 53.2, 37.0. IR (KBr): 1714, 1620, 1587, 1497, 1442, 1330, 1270, 1250, 1160. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}FN_2O_2^+$ 285.1034; found 285.1042.



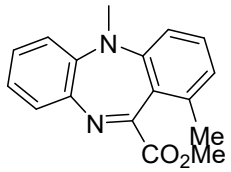
methyl 2-chloro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4h). PE/EA = 15:1, orange solid (40.9 mg, 68%), mp: 136 – 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 3H), 7.25 – 7.17 (m, 1H), 7.15 – 7.05 (m, 1H), 6.96 – 6.86 (m, 2H), 3.98 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 158.8, 156.7, 146.8, 141.0, 132.0, 129.7, 128.9, 128.8, 127.6, 124.5, 118.9, 118.2, 53.3, 36.9. IR (KBr): 1720, 1622, 1587, 1563, 1492, 1447, 1320, 1275, 1245, 820. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}ClN_2O_2^+$ 301.0738; found 301.0745.



methyl 2-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4i). PE/EA = 15:1, orange solid (40.7 mg, 59%), mp: 120 – 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 3.98 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 158.7, 157.2, 146.7, 141.0, 134.9, 132.6, 128.9, 128.8, 128.0, 124.6, 119.3, 118.2, 116.2, 53.3, 36.9. IR (KBr): 1724, 1630, 1580, 1570, 1493, 1450, 1330, 1272, 1247, 730. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}BrN_2O_2^+$ 345.0233; found 345.0242.

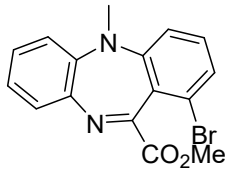


methyl 7-methyl-7*H*-benzo[*b*]naphtho[2,1-*e*][1,4]diazepine-13-carboxylate (4j). PE/EA = 15:1, orange solid (25.3 mg, 40%), mp: 219 – 221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.32 (m, 3H), 7.29 – 7.24 (m, 1H), 7.17 (td, *J* = 7.9, 1.6 Hz, 1H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 162.6, 159.0, 147.7, 142.6, 132.7, 131.8, 130.3, 128.4, 127.9, 127.8, 127.5, 125.0, 124.5, 123.3, 120.3, 118.4, 116.9, 53.1, 36.7. IR (KBr): 1725, 1613, 1570, 1510, 1455, 1310, 1263, 1243. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}N_2O_2^+$ 317.1285; found 317.1294.

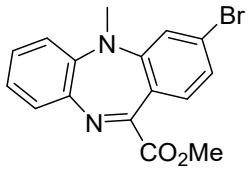


methyl 1,5-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4k). PE/EA = 15:1, orange solid (23.0 mg, 41%), mp: 187 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.21 – 7.14 (m, 1H), 7.12 – 7.06 (m, 1H),

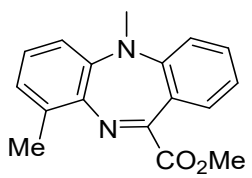
6.97 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 7.8 Hz, 2H), 3.94 (s, 3H), 3.22 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.2, 160.5, 147.1, 141.7, 137.7, 131.3, 127.9, 127.8, 126.2, 125.7, 124.2, 118.0, 114.8, 53.1, 36.8, 19.9. IR (KBr): 2956, 2858, 1720, 1620, 1590, 1578, 1490, 1447, 1380, 1320, 1260, 1224. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1286.



methyl 1-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4l). PE/EA = 15:1, orange solid (31.1 mg, 45%), mp: 184 – 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.8, 1.1 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.02 – 6.94 (m, 2H), 3.95 (s, 3H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 161.6, 161.0, 146.4, 141.5, 132.1, 128.2, 128.1, 126.6, 124.6, 122.6, 118.3, 116.3, 53.3, 36.9. IR (KBr): 1725, 1630, 1575, 1453, 1307, 1263, 1230, 707. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{16}H_{14}BrN_2O_2^+$ 345.0233; found 345.0236.

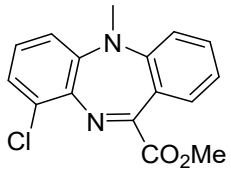


methyl 3-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4l'). PE/EA = 15:1, orange oil (18.0 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 3.96 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 159.4, 159.2, 146.5, 141.2, 131.1, 128.8, 127.2, 126.5, 125.2, 124.7, 121.3, 118.4, 53.2, 37.0. IR (KBr): 1722, 1625, 1577, 1560, 1502, 1440, 1320, 1260, 1245, 708. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{16}H_{14}BrN_2O_2^+$ 345.0233; found 345.0238.

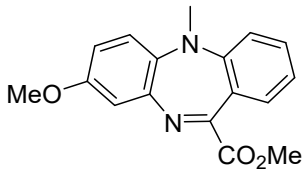


methyl 5,9-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4m). PE/EA =

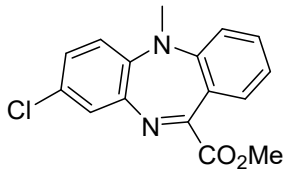
15:1, orange solid (17.9 mg, 32%), mp: 122 – 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.15 – 7.02 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 3.96 (s, 3H), 3.21 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.0, 158.4, 147.6, 139.7, 136.5, 131.9, 129.7, 128.1, 126.8, 125.8, 123.2, 117.7, 115.5, 52.9, 37.0, 18.4. IR (KBr): 2955, 2880, 1722, 1620, 1595, 1575, 1508, 1450, 1380, 1320, 1263, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1291.



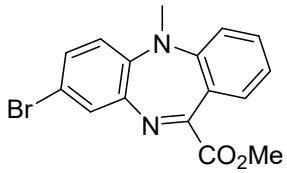
methyl 9-chloro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4n). PE/EA = 15:1, orange oil (34.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.18 – 7.06 (m, 3H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 7.7, 1.4 Hz, 1H), 3.98 (s, 3H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.9, 158.0, 149.3, 138.4, 132.3, 132.2, 130.1, 128.6, 126.7, 125.2, 123.7, 118.1, 116.4, 53.2, 37.2. IR (KBr): 1725, 1630, 1600, 1580, 1492, 1448, 1322, 1263, 1230, 732. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}ClN_2O_2^+$ 301.0738; found 301.0746.



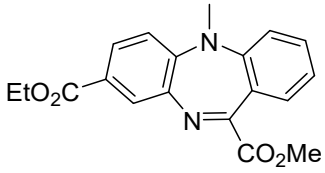
methyl 8-methoxy-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4o). PE/EA = 15:1, orange solid (39.7 mg, 67%), mp: 113 – 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.78 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.97 (s, 3H), 3.76 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 161.0, 158.8, 156.4, 142.1, 140.3, 132.2, 130.0, 126.3, 123.1, 118.6, 117.4, 115.2, 112.4, 55.6, 53.1, 36.9. IR (KBr): 1728, 1637, 1605, 1575, 1508, 1445, 1330, 1275, 1260, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_3^+$ 297.1234; found 297.1240.



methyl 8-chloro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4p). PE/EA = 15:1, orange oil (43.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.16 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.6, 157.9, 145.9, 142.3, 132.5, 130.1, 129.4, 128.2, 128.1, 126.3, 123.6, 119.1, 117.9, 53.2, 37.0. IR (KBr): 1727, 1622, 1593, 1574, 1493, 1450, 1320, 1270, 1247, 755. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}ClN_2O_2^+$ 301.0738; found 301.0742.

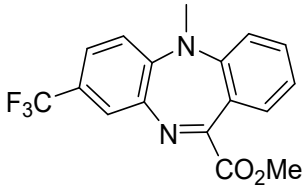


methyl 8-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4q). PE/EA = 15:1, orange oil (41.4 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.44 – 7.38 (m, 1H), 7.35 – 7.27 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.6, 157.9, 146.4, 142.5, 132.5, 131.2, 131.1, 130.1, 126.3, 123.6, 119.5, 117.9, 116.8, 53.2, 36.9. IR (KBr): 1728, 1630, 1594, 1575, 1494, 1452, 1327, 1270, 1247, 630. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}BrN_2O_2^+$ 345.0233; found 345.0240.

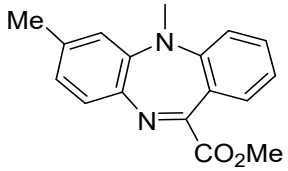


8-ethyl 11-methyl 5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-8,11-dicarboxylate (4r). PE/EA = 8:1, orange solid (43.3 mg, 64%), mp: 84 – 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.89 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.31 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.13 – 7.04 (m, 1H), 7.01 – 6.93 (m, 2H), 4.32 (q, *J* =

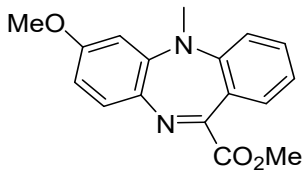
7.0 Hz, 2H), 3.98 (s, 3H), 3.26 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 161.2, 157.2, 151.5, 140.7, 132.5, 130.4, 130.1, 129.9, 126.5, 126.4, 123.8, 118.3, 118.0, 60.9, 53.2, 37.1, 14.3. IR (KBr): 1725, 1625, 1600, 1579, 1560, 1500, 1450, 1330, 1270, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_4^+$ 339.1339; found 339.1344.



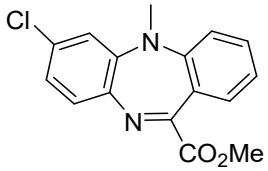
methyl 5-methyl-8-(trifluoromethyl)-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4s). PE/EA = 15:1, orange oil (45.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 1.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.34 (dd, J = 7.7, 1.2 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 8.5 Hz, 2H), 3.98 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 161.8, 157.4, 150.3, 141.2, 132.6, 130.2, 126.6 (q, $J_{C\text{-}F}$ = 32.9 Hz), 126.3, 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.2 (q, $J_{C\text{-}F}$ = 3.5 Hz), 123.9, 121.2 (q, $J_{C\text{-}F}$ = 270.4 Hz), 118.5, 118.2, 53.2, 37.0. IR (KBr): 1725, 1625, 1595, 1575, 1505, 1450, 1335, 1275, 1247, 1123, 1080. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}F_3N_2O_2^+$ 335.1002; found 335.1006.



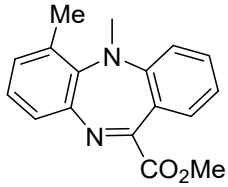
methyl 5,7-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4t). PE/EA = 15:1, orange solid (36.4 mg, 65%), mp: 148 – 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.33 – 7.25 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 3.96 (s, 3H), 3.22 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.7, 158.1, 147.0, 139.0, 138.9, 132.0, 129.9, 128.7, 126.6, 125.0, 123.2, 118.8, 117.7, 53.0, 36.9, 21.2. IR (KBr): 2953, 2882, 1725, 1630, 1600, 1578, 1503, 1450, 1382, 1321, 1262, 1230. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1288.



methyl 7-methoxy-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4u). PE/EA = 15:1, orange solid (29.0 mg, 49%), mp: 87 – 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.64 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 3.96 (s, 3H), 3.79 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.8, 158.2, 157.2, 148.4, 134.8, 132.0, 130.4, 129.9, 126.8, 123.5, 117.9, 108.6, 105.1, 55.5, 53.1, 37.0. IR (KBr): 1732, 1620, 1600, 1575, 1500, 1473, 1330, 1279, 1230, 1062. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_3^+$ 297.1234; found 297.1239.

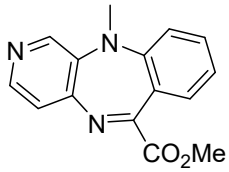


methyl 7-chloro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4v). PE/EA = 15:1, orange oil (37.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.13 – 7.02 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 3.97 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.7, 157.4, 148.0, 139.8, 134.7, 132.4, 130.0, 129.6, 126.4, 124.4, 123.7, 118.7, 118.0, 53.2, 37.0. IR (KBr): 1725, 1620, 1593, 1570, 1495, 1450, 1330, 1270, 1242, 775. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}ClN_2O_2^+$ 301.0738; found 301.0745.

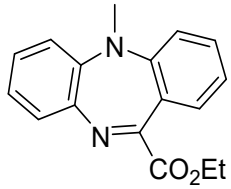


methyl 5,6-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4w). PE/EA = 15:1, orange solid (23.0 mg, 41%), mp: 84 – 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.07 (m, 3H), 3.98 (s, 3H), 3.14 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.8, 156.9, 145.3, 143.5, 136.1,

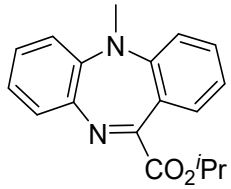
132.6, 131.2, 130.5, 128.9, 126.6, 125.9, 125.5, 124.9, 53.1, 40.0, 18.9. IR (KBr): 2955, 2854, 1725, 1613, 1593, 1574, 1480, 1448, 1378, 1320, 1270, 1244. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1290.



methyl 11-methyl-11*H*-benzo[*e*]pyrido[4,3-*b*][1,4]diazepine-6-carboxylate (4x). PE/EA = 5:1, orange solid (28.3 mg, 53%), mp: 123 – 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.32 (dd, *J* = 7.7 Hz, 1.0 Hz 1H), 7.17 – 6.92 (m, 3H), 3.98 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.0, 156.5, 155.3, 146.9, 136.8, 135.8, 132.8, 129.9, 126.2, 123.4, 119.9, 119.0, 53.3, 35.8. IR (KBr): 3040, 1725, 1630, 1597, 1583, 1500, 1445, 1334, 1257, 1215. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}N_3O_2^+$ 268.1081; found 268.1089.

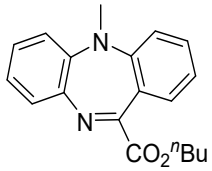


ethyl 5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4y). PE/EA = 15:1, orange solid (40.4 mg, 72%), mp: 108 – 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 1H), 7.12 – 7.01 (m, 2H), 7.00 – 6.92 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.24 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.0, 158.2, 147.2, 141.4, 132.1, 129.9, 128.8, 128.4, 126.5, 124.2, 123.2, 118.1, 117.7, 62.3, 36.9, 14.2. IR (KBr): 2976, 2953, 2883, 2850, 1720, 1618, 1594, 1574, 1495, 1448, 1389, 1320, 1258, 1220. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2^+$ 281.1285; found 281.1292.

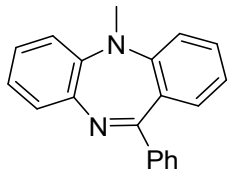


isopropyl 5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4z). PE/EA =

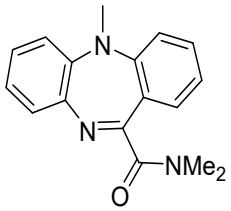
15:1, orange solid (12.4 mg, 21%), mp: 141 – 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.01 (m, 2H), 7.00 – 6.90 (m, 2H), 5.32 – 5.23 (m, 1H), 3.23 (s, 3H), 1.39 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 161.5, 158.1, 147.2, 141.4, 132.0, 129.7, 128.8, 128.3, 126.6, 124.2, 123.1, 118.1, 117.8, 70.1, 37.0, 21.7. IR (KBr): 1718, 1620, 1598, 1575, 1497, 1448, 1386, 1371, 1320, 1259, 1221. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_2^+$ 295.1441; found 295.1445.



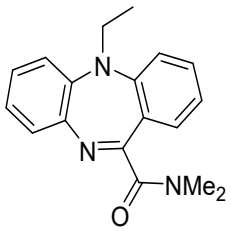
butyl 5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxylate (4za). PE/EA = 15:1, orange oil (26.5 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 1H), 7.24 – 7.14 (m, 2H), 7.13 – 7.05 (m, 1H), 7.00 – 6.90 (m, 2H), 6.89 – 6.79 (m, 2H), 4.26 (t, *J* = 6.9 Hz, 2H), 3.12 (s, 3H), 1.73 – 1.62 (m, 2H), 1.42 – 1.26 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.1, 158.2, 147.2, 141.4, 132.1, 129.8, 128.8, 128.4, 126.5, 124.2, 123.2, 118.1, 117.7, 66.1, 36.9, 30.6, 19.1, 13.7. IR (KBr): 1720, 1622, 1593, 1575, 1497, 1450, 1393, 1360, 1320, 1275, 1249. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}N_2O_2^+$ 309.1598; found 309.1606.



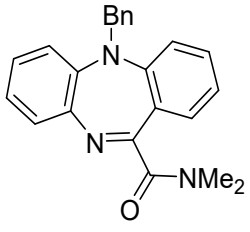
5-methyl-11-phenyl-5*H*-dibenzo[*b,e*][1,4]diazepine (4zb). PE/EA = 50:1, orange solid (11.4 mg, 20%), mp: 127 – 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.8 Hz, 2H), 7.50 – 7.35 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.19 – 7.02 (m, 4H), 6.98 (t, *J* = 7.8 Hz, 2H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 158.0, 146.7, 142.8, 141.0, 131.5, 131.2, 130.1, 129.6, 129.0, 128.0, 127.6, 126.3, 124.0, 122.7, 117.5, 117.3, 36.8. IR (KBr): 1612, 1593, 1560, 1498, 1442, 1320, 1275, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}N_2^+$ 285.1386; found 285.1391.



***N,N*,5-trimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5a)**. PE/EA = 5:1, orange solid (44.7 mg, 80%), mp: 181 – 183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.23 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.18 (td, *J* = 7.7, 1.6 Hz, 1H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 7.01 (dd, *J* = 7.5, 0.7 Hz, 1H), 6.99 – 6.93 (m, 2H), 3.25 (s, 3H), 3.15 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 166.5, 157.5, 147.0, 141.8, 132.5, 129.0, 128.0, 127.7, 126.6, 124.4, 123.5, 118.4, 117.7, 37.8, 37.2, 34.5. IR (KBr): 1638, 1620, 1589, 1487, 1440, 1413, 1398, 1320, 1275, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}N_3O^+$ 280.1444; found 280.1451.

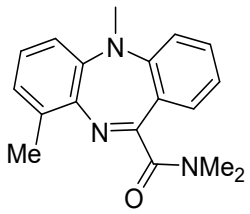


5-ethyl-*N,N*-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5b). PE/EA = 3:1, orange solid (39.9 mg, 68%), mp: 142 – 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.29 – 7.23 (m, 1H), 7.18 (td, *J* = 8.0, 1.5 Hz, 1H), 7.11 – 6.89 (m, 4H), 3.82 – 3.54 (m, 2H), 3.14 (s, 3H), 3.07 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.6, 155.7, 146.0, 142.6, 132.3, 128.9, 127.6, 127.5, 127.4, 124.4, 123.6, 119.2, 118.6, 42.8, 37.6, 34.4, 13.3. IR (KBr): 2978, 2853, 1635, 1610, 1590, 1575, 1510, 1453, 1417, 1397, 1380, 1310, 1277, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O^+$ 294.1601; found 294.1609.

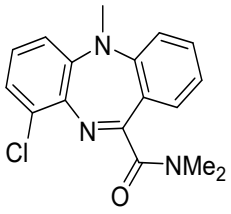


5-benzyl-*N,N*-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5c).

PE/EA = 5:1, orange solid (51.9 mg, 73%), mp: 149 – 151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.18 (m, 3H), 7.18 – 7.07 (m, 3H), 7.06 – 6.93 (m, 3H), 4.87 (s, 2H), 3.11 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.3, 155.6, 145.4, 142.5, 136.8, 132.3, 129.0, 128.39, 128.38, 127.8, 127.6, 127.3, 127.1, 124.6, 123.9, 119.6, 119.2, 52.9, 37.9, 34.5. IR (KBr): 2927, 2855, 1649, 1620, 1593, 1574, 1496, 1454, 1416, 1398, 1332, 1271, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}N_3O^+$ 356.1757; found 356.1763.

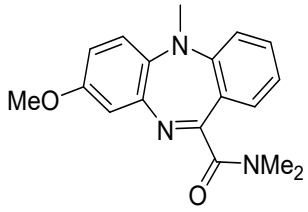


***N,N*,5,9-tetramethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5d)**. PE/EA = 5:1, orange solid (19.9 mg, 34%), mp: 154 – 156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 3.23 (s, 3H), 3.17 (s, 3H), 3.08 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 165.4, 157.7, 147.5, 140.0, 135.9, 132.2, 128.6, 127.3, 127.1, 126.1, 123.4, 117.6, 115.8, 37.9, 37.2, 34.4, 18.5. IR (KBr): 2955, 2860, 1628, 1580, 1560, 1508, 1450, 1410, 1397, 1378, 1310, 1262, 1232. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O^+$ 294.1601; found 294.1605.

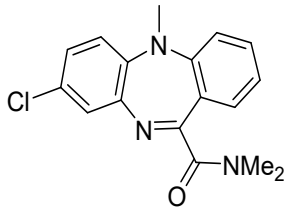


9-chloro-*N,N*,5-trimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5e). PE/EA = 5:1, orange oil (47.7 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.15 – 7.00 (m, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 3.25 (s, 3H), 3.22 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.8, 157.4, 149.1, 138.5, 132.6, 131.8, 128.7, 127.8, 127.4, 125.3, 123.8,

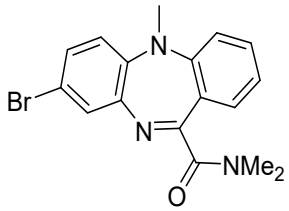
118.1, 116.7, 38.3, 37.4, 34.7. IR (KBr): 1635, 1594, 1560, 1492, 1454, 1427, 1397, 1313, 1263, 1245, 733. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}ClN_3O^+$ 314.1055; found 314.1057.



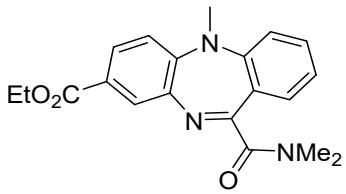
8-methoxy-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5f). PE/EA = 4:1, orange solid (46.4 mg, 75%), mp: 171 – 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.04 – 6.92 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.74 (s, 3H), 3.20 (s, 3H), 3.12 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.2, 157.9, 156.5, 142.6, 140.0, 132.6, 129.1, 126.4, 123.3, 118.9, 117.4, 114.0, 112.0, 55.6, 37.7, 37.2, 34.4. IR (KBr): 1640, 1623, 1605, 1575, 1504, 1445, 1413, 1397, 1319, 1274, 1247, 1228. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O_2^+$ 310.1550; found 310.1551.



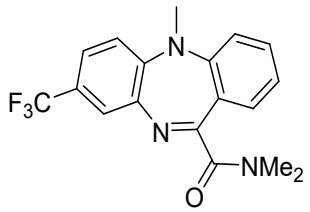
8-chloro-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5g). PE/EA = 5:1, orange solid (41.4 mg, 66%), mp: 151 – 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 3.21 (s, 3H), 3.12 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 157.1, 145.7, 142.8, 132.8, 129.4, 129.1, 127.6, 127.3, 126.5, 123.8, 119.3, 117.8, 37.7, 37.2, 34.5. IR (KBr): 1640, 1630, 1590, 1574, 1508, 1450, 1410, 1397, 1316, 1270, 1250, 749. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}ClN_3O^+$ 314.1055; found 314.1059.



8-bromo-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5h). PE/EA = 5:1, orange solid (36.5 mg, 51%), mp: 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.06 – 6.99 (m, 1H), 6.98 – 6.93 (m, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.21 (s, 3H), 3.14 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.6, 157.1, 146.2, 143.0, 132.8, 130.5, 130.3, 129.1, 126.4, 123.8, 119.7, 117.9, 116.9, 37.8, 37.2, 34.5. IR (KBr): 1638, 1622, 1590, 1573, 1491, 1450, 1414, 1390, 1310, 1270, 1249, 630. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}BrN_3O^+$ 358.0550; found 358.0552.

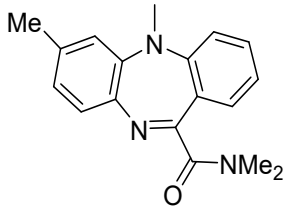


ethyl 11-(dimethylcarbamoyl)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-8-carboxylate (5i). PE/EA = 2:1, orange oil (42.2 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.9 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.91 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 3H), 3.15 (s, 3H), 3.08 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.1, 165.9, 156.5, 151.4, 141.2, 132.8, 129.7, 129.2, 129.1, 126.57, 126.55, 123.9, 118.3, 60.9, 37.8, 37.4, 34.5, 14.3. IR (KBr): 1715, 1645, 1605, 1594, 1574, 1503, 1447, 1412, 1397, 1320, 1272, 1242. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{22}N_3O_3^+$ 352.1656; found 352.1657.

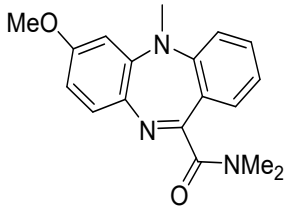


***N*,*N*,5-trimethyl-8-(trifluoromethyl)-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-**

carboxamide (5j). PE/EA = 5:1, orange oil (27.8 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.44 – 7.35 (m, 3H), 7.10 – 6.91 (m, 3H), 3.26 (s, 3H), 3.15 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.5, 156.6, 150.1, 141.8, 133.0, 129.2, 126.6 (q, $J_{C\text{-}F}$ = 32.6 Hz), 126.5, 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.0, 123.9 (q, $J_{C\text{-}F}$ = 270.1 Hz), 118.7, 118.2, 37.8, 37.3, 34.5. IR (KBr): 1650, 1630, 1590, 1575, 1510, 1448, 1415, 1398, 1335, 1271, 1246, 1170, 1120. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}F_3N_3O^+$ 348.1318; found 348.1325.

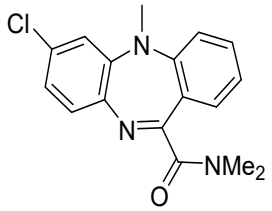


***N,N*,5,7-tetramethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5k)**. PE/EA = 5:1, orange solid (44.6 mg, 76%), mp: 189 – 191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.04 – 6.94 (m, 2H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.75 (s, 1H), 3.24 (s, 3H), 3.14 (s, 3H), 3.08 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 165.8, 157.3, 146.7, 139.3, 137.9, 132.4, 128.9, 127.9, 126.7, 125.0, 123.4, 119.1, 117.7, 37.8, 37.2, 34.5, 21.1. IR (KBr): 2955, 2853, 1643, 1617, 1592, 1576, 1499, 1445, 1382, 1308, 1272, 1244. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O^+$ 294.1601; found 294.1602.

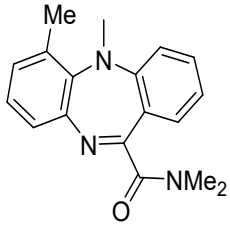


7-methoxy-*N,N*,5-trimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5l). PE/EA = 4:1, orange oil (43.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 3.77 (s, 3H), 3.21 (s, 3H), 3.13 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 164.5, 160.0, 156.5, 148.0, 135.3, 132.3, 129.2, 128.8, 126.8, 123.6, 117.9, 108.4, 105.5, 55.5, 37.8, 37.3, 34.5. IR (KBr): 1637, 1622, 1593, 1577, 1503, 1443, 1397, 1383, 1320, 1264, 1245, 1210.

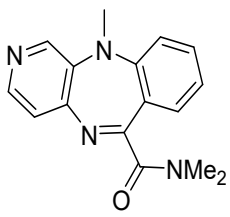
HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O_2^+$ 310.1550; found 310.1551.



7-chloro-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5m). PE/EA = 5:1, orange solid (36.4 mg, 58%), mp: 165 – 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 3.22 (s, 3H), 3.13 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.8, 156.6, 147.8, 140.3, 133.7, 132.8, 129.1, 128.9, 126.5, 124.4, 124.0, 118.9, 118.0, 37.8, 37.3, 34.5. IR (KBr): 1640, 1610, 1594, 1574, 1492, 1450, 1398, 1310, 1280, 1247, 706. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}ClN_3O^+$ 314.1055; found 314.1059.

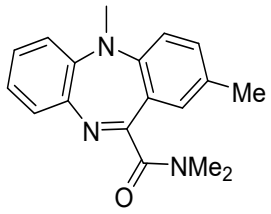


***N*,*N*,5,6-tetramethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5n).** PE/EA = 5:1, orange oil (22.3 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.21 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.17 – 7.05 (m, 4H), 3.26 (s, 3H), 3.12 (s, 3H), 3.11 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 164.5, 156.8, 145.5, 143.3, 135.6, 132.7, 130.7, 129.5, 128.9, 125.9, 125.8, 124.8, 124.2, 40.5, 37.7, 34.6, 19.2. IR (KBr): 2950, 2857, 1640, 1620, 1595, 1567, 1510, 1443, 1409, 1395, 1378, 1324, 1267, 1244. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O^+$ 294.1601; found 294.1603.

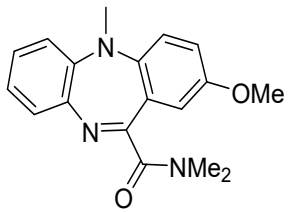


***N*,*N*,11-trimethyl-11*H*-benzo[*e*]pyrido[4,3-*b*][1,4]diazepine-6-carboxamide (5o)**. PE/EA = 2:1, orange solid (36.4 mg, 65%), mp: 68 – 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.12 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.06 – 6.96 (m, 3H), 3.30 (s, 3H), 3.12 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.6, 155.6, 155.3, 146.1, 136.4, 136.1, 133.1, 129.0, 126.2, 123.6, 120.1, 118.8, 37.7, 36.1, 34.5. IR (KBr): 3057, 1636, 1618, 1592, 1577, 1503, 1442, 1425, 1397, 1320, 1267, 1237. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_4O^+$ 281.1397; found 281.1400.

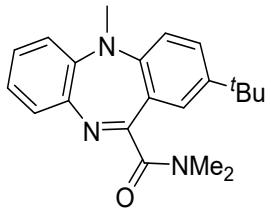


***N,N*,2,5-tetramethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5p)**. PE/EA = 5:1, orange solid (40.5 mg, 69%), mp: 163 – 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 4H), 7.09 – 7.01 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.21 (s, 3H), 3.15 (s, 3H), 3.08 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 166.6, 155.0, 147.3, 141.8, 133.2, 133.1, 129.1, 127.9, 127.6, 126.3, 124.2, 118.1, 117.5, 37.8, 37.1, 34.5, 20.5. IR (KBr): 2953, 2858, 1650, 1623, 1590, 1575, 1503, 1447, 1413, 1402, 1375, 1310, 1275, 1240. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O^+$ 294.1601; found 294.1605.

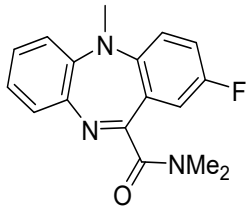


2-methoxy-*N,N*,5-trimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5q). PE/EA = 4:1, orange solid (48.3 mg, 78%), mp: 195 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.17 (td, *J* = 8.0, 1.5 Hz, 1H), 7.07 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.99 – 6.87 (m, 3H), 3.73 (s, 3H), 3.21 (s, 3H), 3.16 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.1, 155.7, 150.5, 147.5, 141.5, 127.9, 127.7, 127.1, 124.2, 118.6, 118.5, 117.9, 113.3, 55.7, 37.8, 37.2, 34.5. IR (KBr): 1640, 1622, 1597, 1575, 1502, 1453, 1417, 1388, 1333, 1270, 1244, 1230. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}N_3O_2^+$ 310.1550; found

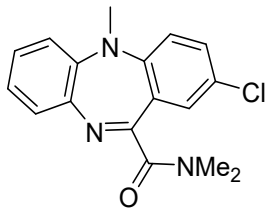
310.1552.



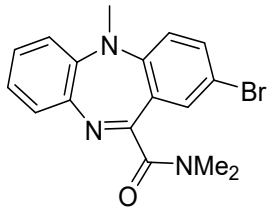
2-(*tert*-butyl)-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5r). PE/EA = 5:1, orange oil (45.6 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.86 (m, 2H), 3.22 (s, 3H), 3.14 (s, 3H), 3.07 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 167.0, 154.8, 147.2, 146.4, 141.8, 129.4, 128.0, 127.6, 126.1, 125.7, 124.2, 118.1, 117.2, 37.8, 37.1, 34.5, 34.2, 31.2. IR (KBr): 1640, 1620, 1603, 1576, 1503, 1447, 1413, 1396, 1364, 1320, 1274, 1250. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}N_3O^+$ 336.2070; found 336.2075.



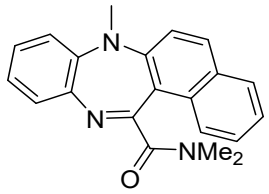
2-fluoro-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5s). PE/EA = 5:1, orange solid (55.9 mg, 94%), mp: 106 – 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 3H), 7.12 – 7.04 (m, 2H), 6.99 – 6.88 (m, 2H), 3.21 (s, 3H), 3.16 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 164.8, 158.7 (d, $J_{C\text{-}F}$ = 242.4 Hz), 153.3, 146.9 141.6, 128.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 127.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 124.5, 119.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 118.9, 118.8, 118.2, 115.4 (d, $J_{C\text{-}F}$ = 23.8 Hz), 37.8, 37.3, 34.5. IR (KBr): 1630, 1610, 1590, 1574, 1503, 1453, 1410, 1394, 1318, 1277, 1261, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}FN_3O^+$ 298.1350; found 298.1354.



2-chloro-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5t). PE/EA = 5:1, orange solid (50.8 mg, 81%), mp: 125 – 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.25– 7.15 (m, 2H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 3.21 (s, 3H), 3.15 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.9, 155.9, 146.6, 141.5, 132.3, 129.0, 128.6, 128.05, 128.02, 127.8, 124.7, 119.0, 118.4, 37.8, 37.3, 34.6. IR (KBr): 1635, 1602, 1575, 1512, 1445, 1415, 1397, 1331, 1260, 1234, 732. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}ClN_3O^+$ 314.1055; found 314.1059.

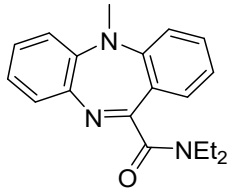


2-bromo-*N*,*N*,5-trimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-11-carboxamide (5u). PE/EA = 5:1, orange solid (51.6 mg, 72%), mp: 160 – 162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.2 Hz, 1H), 7.46 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 3.20 (s, 3H), 3.15 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.8, 156.4, 146.5, 141.5, 135.3, 131.4, 128.2, 128.0, 124.7, 119.4, 118.4, 116.4, 37.9, 37.2, 34.6. IR (KBr): 1637, 1622, 1593, 1578, 1490, 1452, 1413, 1399, 1307, 1260, 1245, 750. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}BrN_3O^+$ 358.0550; found 358.0556.

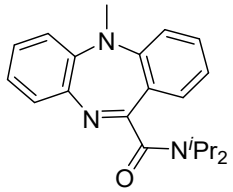


***N*,*N*,7-trimethyl-7*H*-benzo[*b*]naphtho[2,1-*e*][1,4]diazepine-13-carboxamide (5v)**. PE/EA = 3:1, orange solid (34.9 mg, 53%), mp: 247 – 249 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.24 (m, 3H), 7.19 – 7.05 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 3.36 (s, 3H), 3.13 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9,

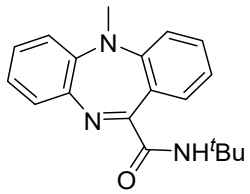
167.5, 158.4, 147.7, 142.8, 132.7, 131.5, 130.4, 128.2, 127.9, 127.2, 127.1, 125.1, 124.6, 124.3, 121.4, 118.3, 116.9, 37.7, 36.9, 35.5. IR (KBr): 1637, 1620, 1590, 1570, 1510, 1447, 1426, 1397, 1337, 1275, 1237. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}N_3O^+$ 330.1601; found 330.1603.



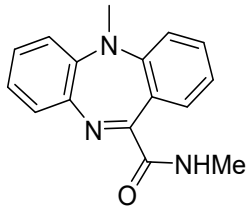
***N,N*-diethyl-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5w)**. PE/EA = 5:1, orange solid (51.0 mg, 83%), mp: 132 – 134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 2H), 7.29 – 7.21 (m, 1H), 7.20 – 7.13 (m, 1H), 7.09 – 6.90 (m, 4H), 3.79 – 3.40 (m, 4H), 3.24 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.9, 157.5, 147.0, 142.0, 132.4, 129.0, 128.1, 127.5, 126.9, 124.3, 123.4, 118.3, 117.6, 42.7, 39.0, 37.1, 13.7, 12.7. IR (KBr): 2970, 2930, 2880, 2827, 1625, 1593, 1574, 1495, 1453, 1380, 1310, 1276, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{22}N_3O^+$ 308.1757; found 308.1762.



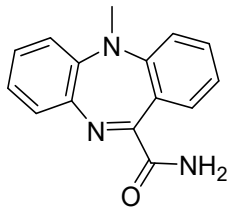
***N,N*-diisopropyl-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5x).** PE/EA = 5:1, orange solid (34.9 mg, 52%), mp: 118 – 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.30 – 7.25 (m, 1H), 7.20 – 7.12 (m, 1H), 7.09 – 6.92 (m, 4H), 4.51 – 4.40 (m, 1H), 3.50 – 3.38 (m, 1H), 3.24 (s, 3H), 1.57 (d, *J* = 6.0 Hz, 3H), 1.49 (d, *J* = 5.7 Hz, 3H), 1.24 (d, *J* = 5.5 Hz, 3H), 0.77 (d, *J* = 4.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.5, 157.6, 147.0, 142.3, 132.2, 128.9, 128.1, 127.2, 127.0, 124.3, 123.3, 118.3, 117.4, 50.5, 45.7, 37.1, 20.7, 19.8. IR (KBr): 1638, 1627, 1589, 1575, 1490, 1443, 1385, 1373, 1313, 1274, 1247. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}N_3O^+$ 336.2070; found 336.2079.



***N*-(*tert*-butyl)-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5y)**. PE/EA = 5:1, orange solid (35.0 mg, 57%), mp: 126 – 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.11 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 3.21 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.2, 158.1, 147.5, 140.9, 131.8, 131.7, 128.1, 127.9, 125.6, 124.0, 123.0, 118.0, 117.5, 51.1, 36.8, 28.6. IR (KBr): 3375, 1680, 1620, 1592, 1575, 1440, 1423, 1394, 1362, 1313, 1277, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{22}N_3O^+$ 308.1757; found 308.1760.

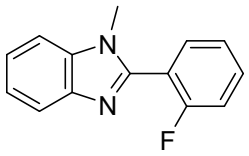


***N*,5-dimethyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5z)**. PE/EA = 5:1, orange solid (24.9 mg, 47%), mp: 131 – 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.24 – 6.15 (m, 2H), 7.11 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 3.21 (s, 3H), 3.00 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 161.6, 157.9, 147.5, 140.9, 132.0, 131.5, 128.3, 128.0, 125.8, 124.1, 123.1, 118.1, 117.6, 36.8, 26.4. IR (KBr): 3255, 1649, 1615, 1597, 1575, 1545, 1498, 1443, 1409, 1385, 1330, 1275, 1250. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}N_3O^+$ 266.1288; found 266.1297.

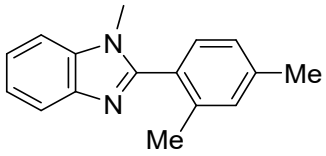


5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepine-11-carboxamide (5za). PE/EA = 10:1, orange solid (14.1 mg, 28%), mp: 106 – 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s,

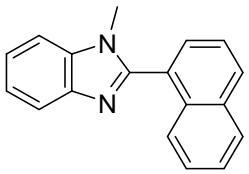
1H), 7.45 (d, J = 6.7 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.29 – 7.16 (m, 2H), 7.12 – 7.04 (m, 2H), 7.02 – 6.92 (m, 2H), 6.23 (s, 1H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 161.0, 158.1, 147.5, 140.9, 132.1, 131.4, 128.5, 128.3, 125.6, 124.1, 123.2, 118.1, 117.8, 36.8. IR (KBr): 3455, 3162, 1670, 1620, 1595, 1574, 1500, 1444, 1403, 1385, 1308, 1265, 1237. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}N_3O^+$ 252.1131; found 252.1138.



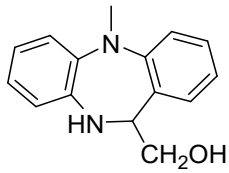
2-(2-fluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (6a). PE/EA = 20:1, white solid (36.2 mg, 80%), mp: 91 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.72 (td, J = 7.5, 1.5 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.28 (m, 3H), 7.27 – 7.18 (m, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, $J_{C\text{-}F}$ = 248.2 Hz), 149.4, 143.2, 136.2, 132.6 (d, $J_{C\text{-}F}$ = 2.6 Hz), 132.11 (d, $J_{C\text{-}F}$ = 8.2 Hz), 124.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 123.0, 122.4, 120.0, 118.6 (d, $J_{C\text{-}F}$ = 14.6 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.5 Hz), 109.7, 31.0 (d, J = 5.6 Hz). IR (KBr): 1610, 1579, 1518, 1457, 1327, 1282, 1263, 1244. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}FN_2^+$ 227.0979; found 227.0982.



2-(2,4-dimethylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (6b). PE/EA = 20:1, white powder (41.6 mg, 88%), mp: 119 – 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 1H), 7.41 – 7.35 (m, 1H), 7.33 – 7.24 (m, 3H), 7.15 (s, 1H), 7.10 (d, J = 7.7 Hz, 1H), 3.59 (s, 3H), 2.39 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.0, 139.8, 137.8, 135.6, 131.2, 130.2, 127.0, 126.5, 122.5, 122.2, 119.8, 109.5, 30.6, 21.4, 19.6. IR (KBr): 2942, 1617, 1576, 1507, 1455, 1378, 1325, 1278, 1245. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_2^+$ 237.1386; found 237.1387.



1-methyl-2-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (6c). PE/EA = 20:1, white solid (36.7 mg, 71%), mp: 126 – 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.98 – 7.87 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.69 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.56 – 7.43 (m, 3H), 7.42 – 7.34 (m, 2H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 143.2, 135.9, 133.6, 132.2, 130.4, 128.9, 128.5, 127.8, 127.2, 126.4, 125.5, 125.0, 122.9, 122.5, 120.1, 109.6, 31.1. IR (KBr): 1622, 1603, 1578, 1505, 1438, 1327, 1260, 1237. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{15}N_2^+$ 259.1230; found 259.1239.



(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)methanol (7a). PE/EA = 20:1, white powder (26.9 mg, 56%), mp: 67 – 69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 1H), 7.12 – 7.02 (m, 2H), 7.00 – 6.90 (m, 2H), 6.82 – 6.71 (m, 2H), 6.62 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.52 – 4.40 (m, 1H), 4.10 – 3.95 (m, 1H), 3.86 (dd, *J* = 10.6, 4.7 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 139.2, 137.6, 131.3, 128.5, 128.2, 122.9, 122.6, 119.5, 119.2, 118.7, 118.5, 66.0, 60.3, 39.4. IR (KBr): 3375, 3255, 1597, 1575, 1493, 1445, 1334, 1273, 1240, 1052. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}N_2O^+$ 241.1335; found 241.1342. [Supplementary Characterization: ^{1}H NMR (400 MHz, DMSO) δ 7.30 – 7.19 (m, 1H), 7.18 – 7.05 (m, 2H), 7.02 – 6.92 (m, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.70 – 6.60 (m, 1H), 6.58 – 6.42 (m, 2H), 5.69 (s, 1H), 4.82 (s, 1H), 4.55 – 4.35 (m, 1H), 3.95 – 3.65 (m, 2H), 3.17 (s, 3H).]

11. X-ray structure of 4a and 5a

(1) X-ray structure of 4a

Product **4a** (30 mg) was dissolved in DCM (0.5 mL) and tightly sealed. The sample was then placed in the refrigerator chill section (3 – 4 °C) until the crystal precipitated.

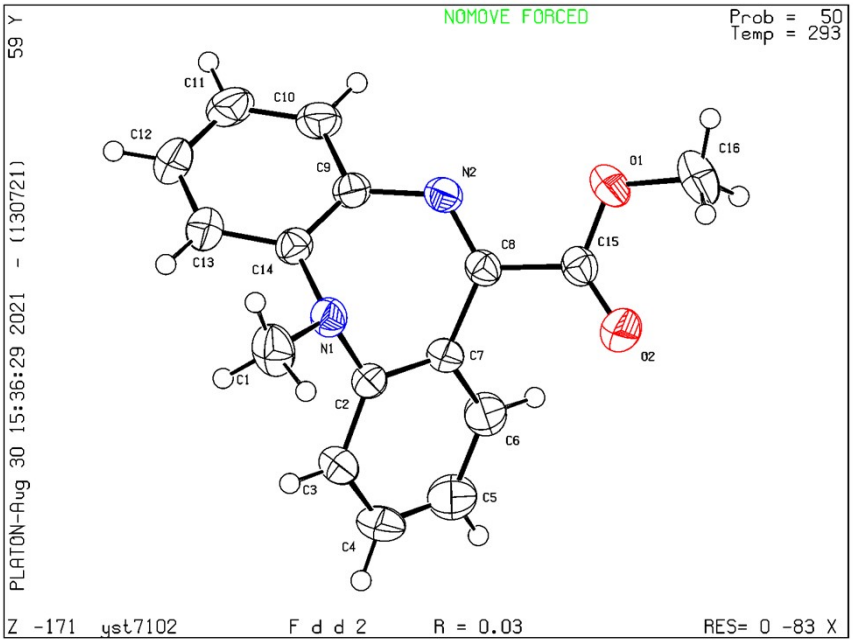


Table 1. Crystal data and structure refinement for yst7102 (CCDC: 2161537).

Identification code	yst7102
Empirical formula	$C_{16}H_{14}N_2O_2$
Formula weight	266.29
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	43.7224(17)
b/Å	14.1940(6)
c/Å	8.7864(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5452.8(4)
Z	16
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.087
F(000)	2240.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.846 to 58.396
Index ranges	$-57 \leq h \leq 53$, $-18 \leq k \leq 19$, $-10 \leq l \leq 11$
Reflections collected	8647
Independent reflections	2909 [R_{int} = 0.0156, R_{sigma} = 0.0150]

Data/restraints/parameters	2909/1/183
Goodness-of-fit on F^2	0.930
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0829
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.17
Flack parameter	0.5

(2) X-ray structure of 5a

Product **5a** (30 mg) was dissolved in DCM (1.5 mL) and layered with petroleum ether (2.0 mL). The crystal of **5a** was slowly grown at room temperature by evaporating the solvent in air.

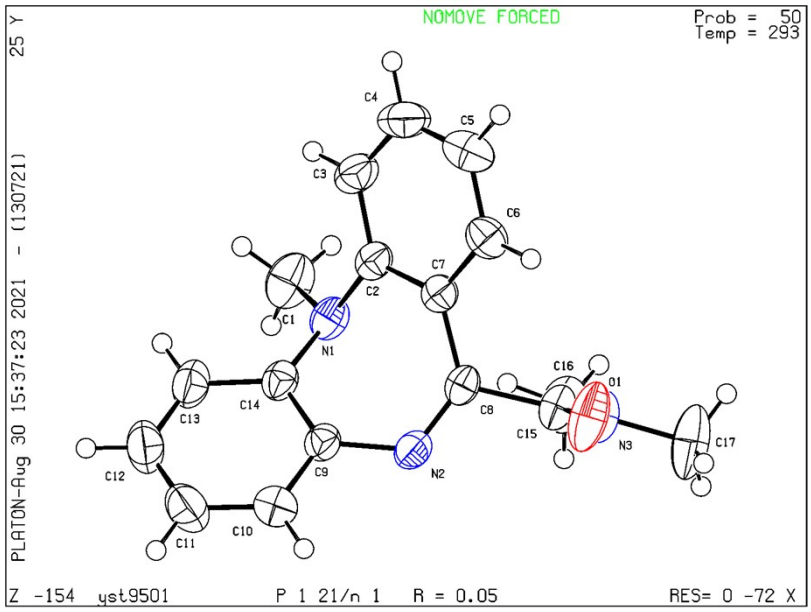


Table 2 Crystal data and structure refinement for yst9501 (CCDC: 2161539).

Identification code	yst9501
Empirical formula	$C_{17}H_{17}N_3O$
Formula weight	279.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.4266(7)
b/Å	13.3424(11)
c/Å	13.1891(12)
α/°	90
β/°	95.252(9)
γ/°	90

Volume/Å^3	1476.6(2)
Z	4
ρ_{calc}g/cm^3	1.256
μ/mm^{-1}	0.081
F(000)	592.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.73 to 58.556
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	12970
Independent reflections	3538 [R_{int} = 0.0225, R_{sigma} = 0.0226]
Data/restraints/parameters	3538/0/193
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1212
Final R indexes [all data]	R_1 = 0.0672, wR_2 = 0.1309
Largest diff. peak/hole / e Å^{-3}	0.19/-0.25

12. Supplementary references

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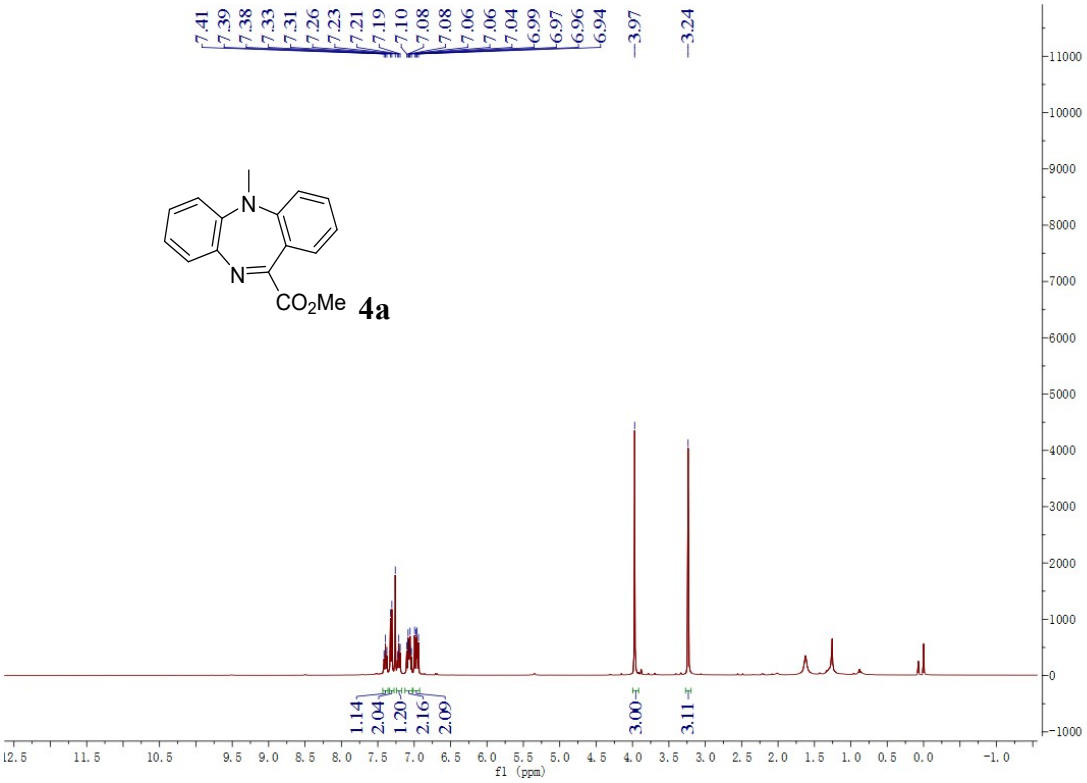
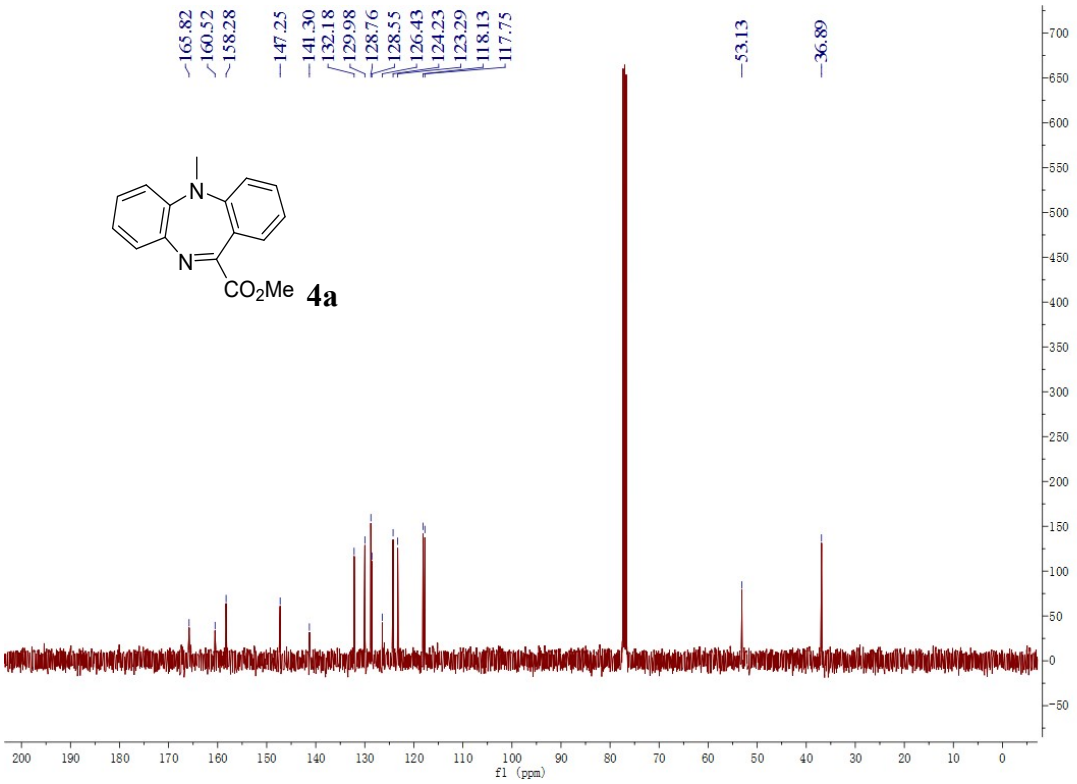
13. The NMR spectra of products

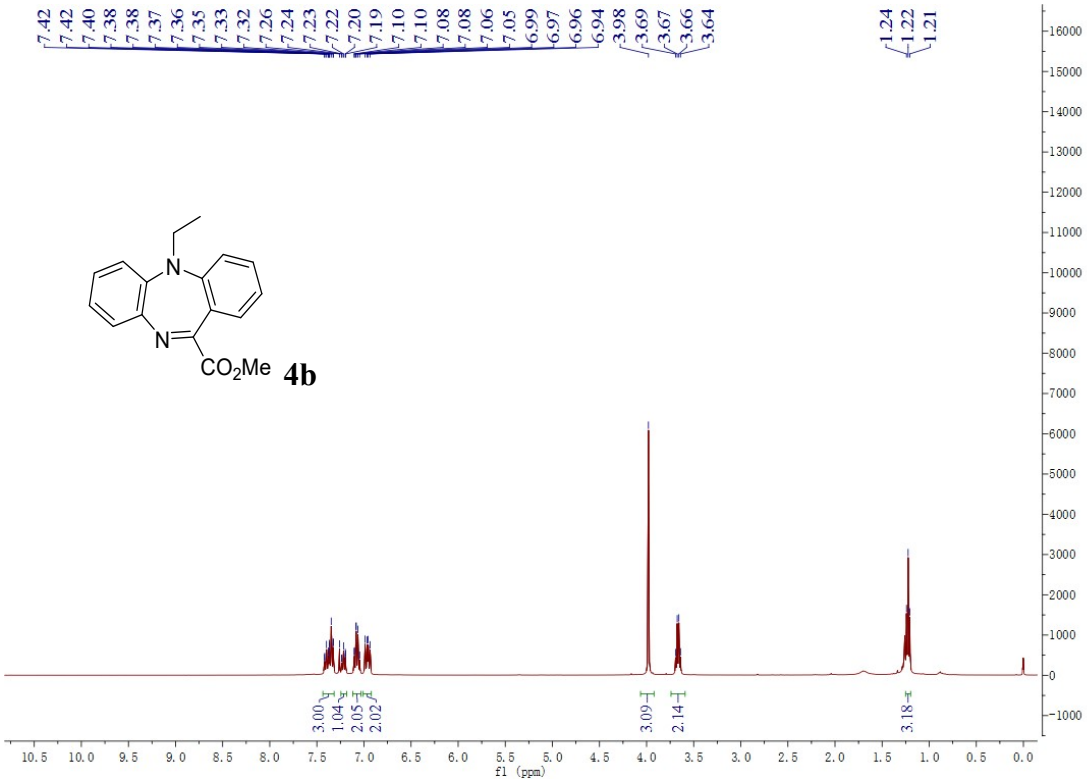
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



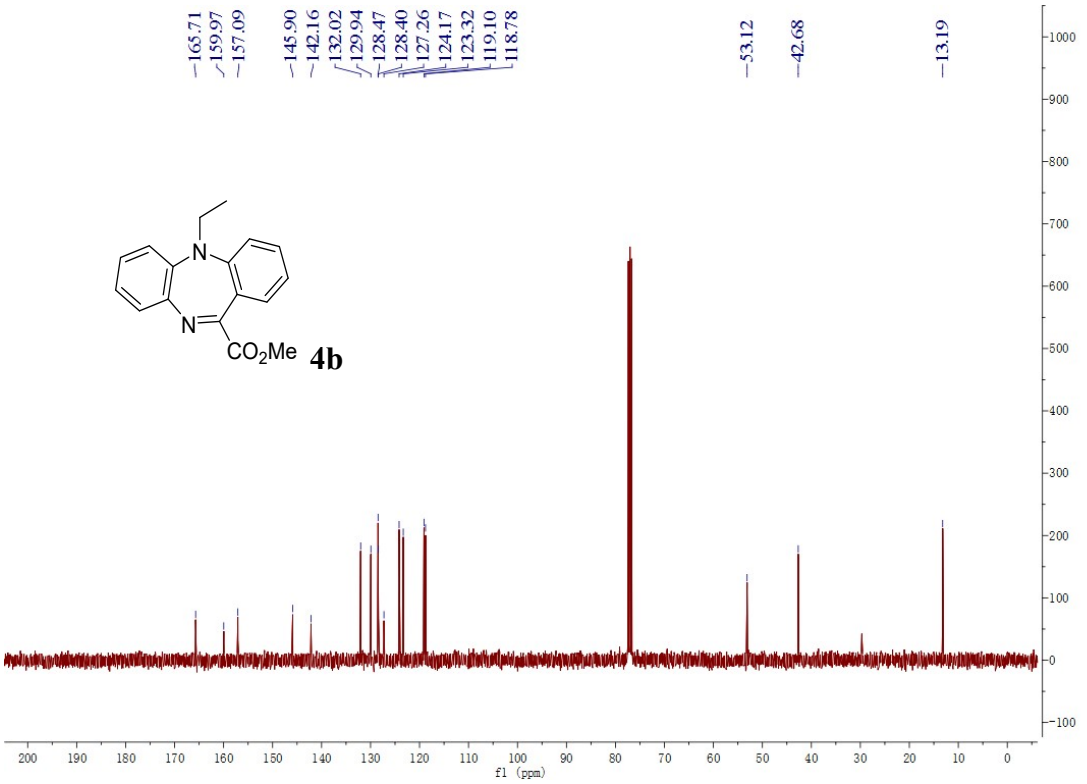
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**



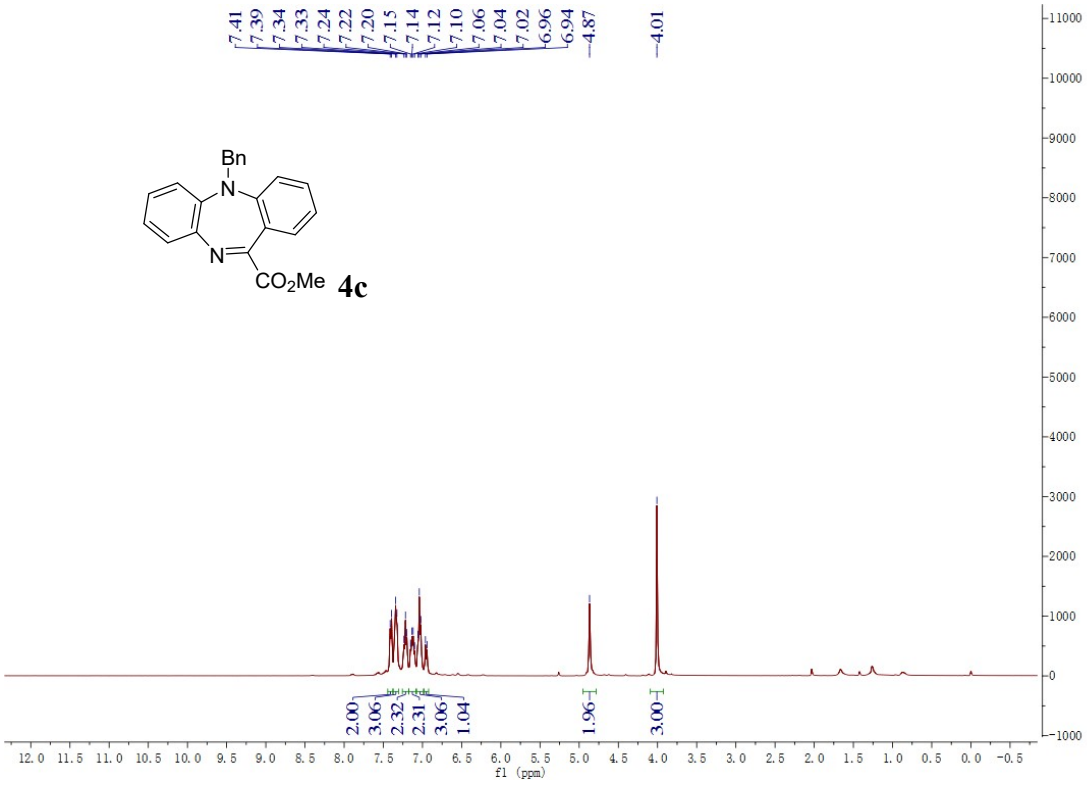
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



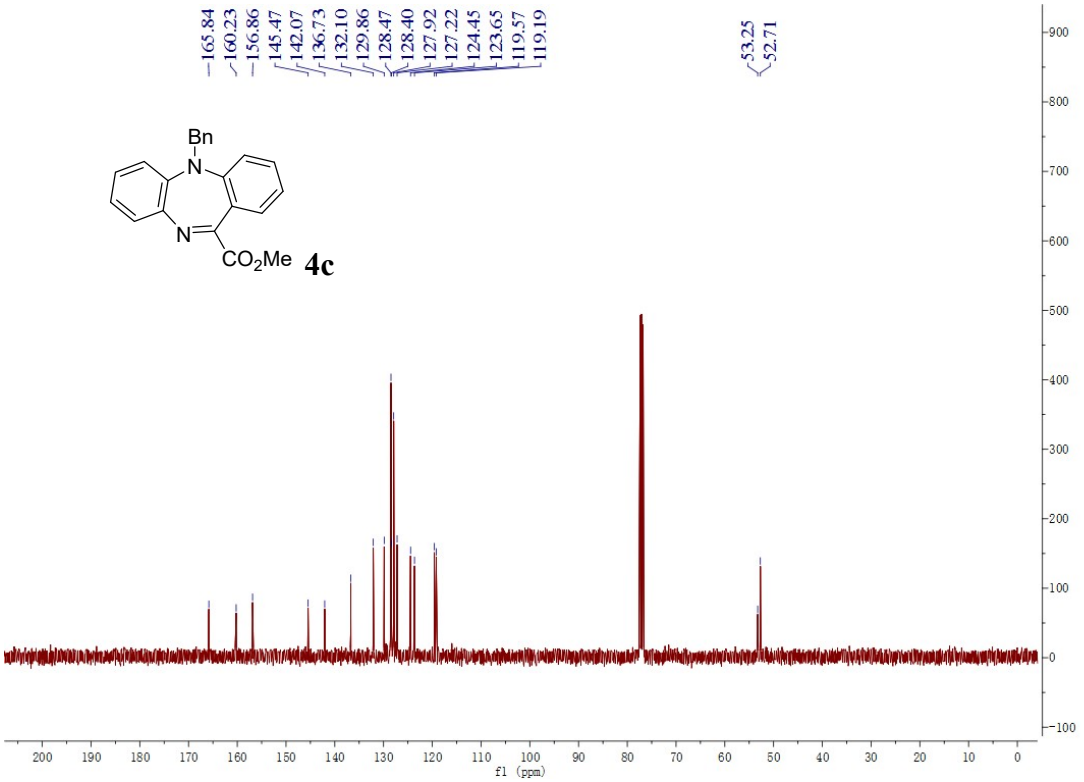
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**



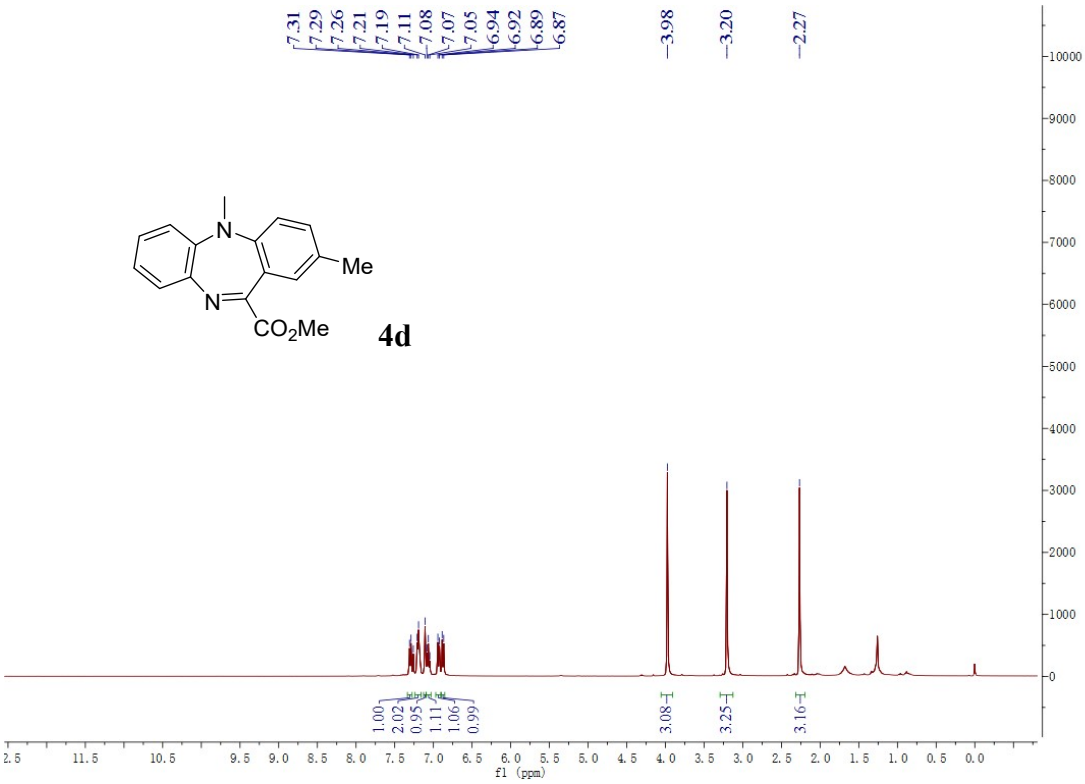
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



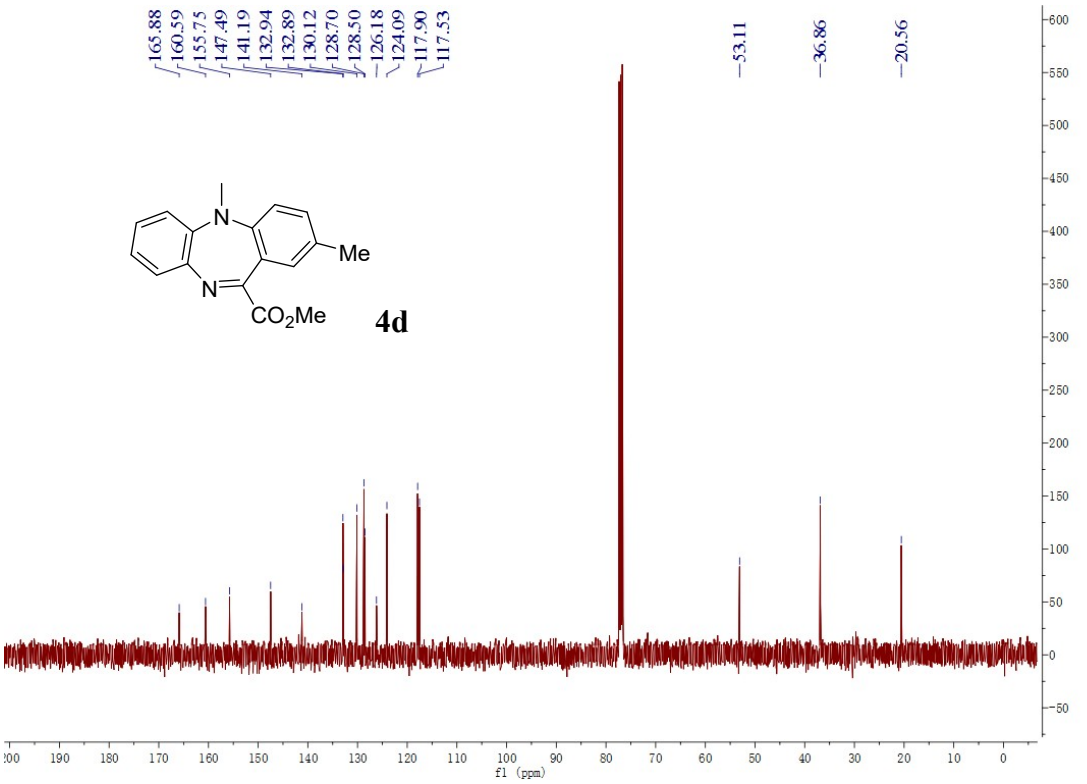
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4c**



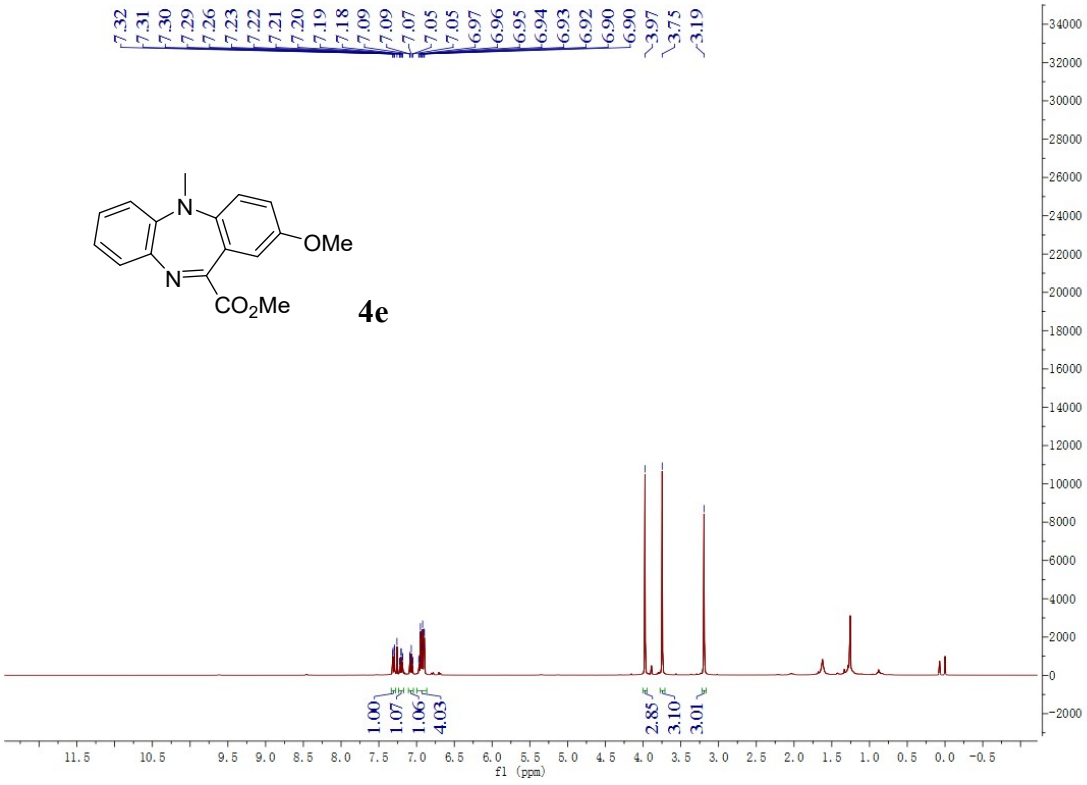
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



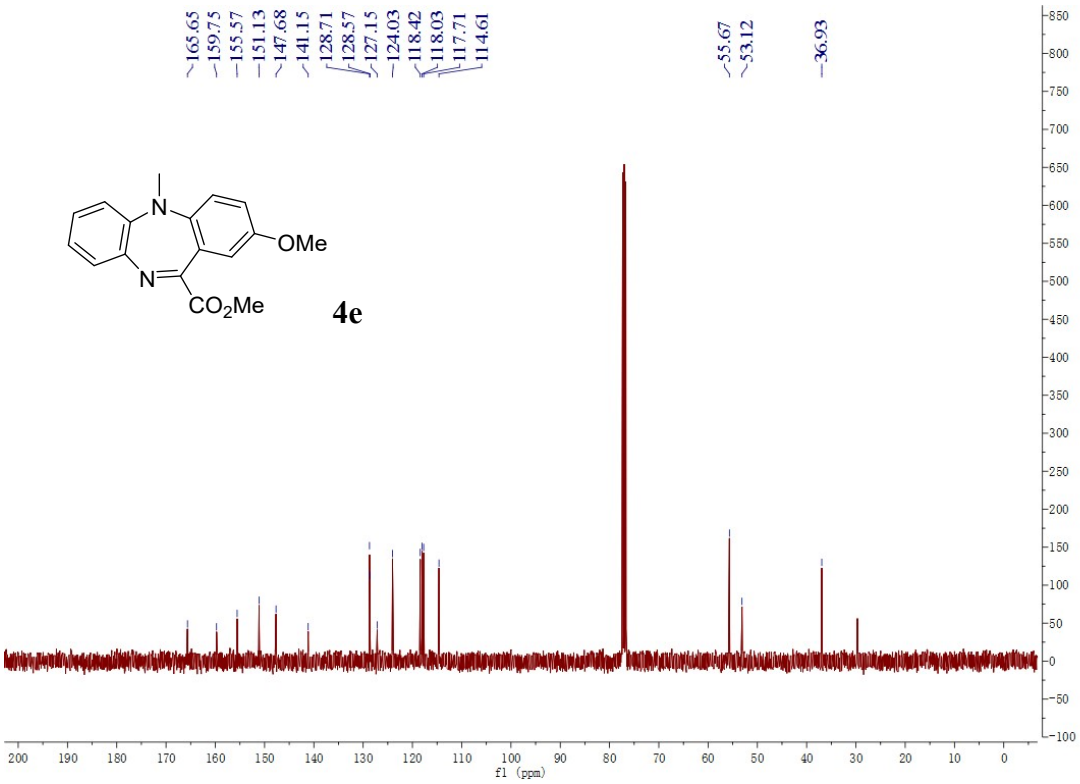
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4d**



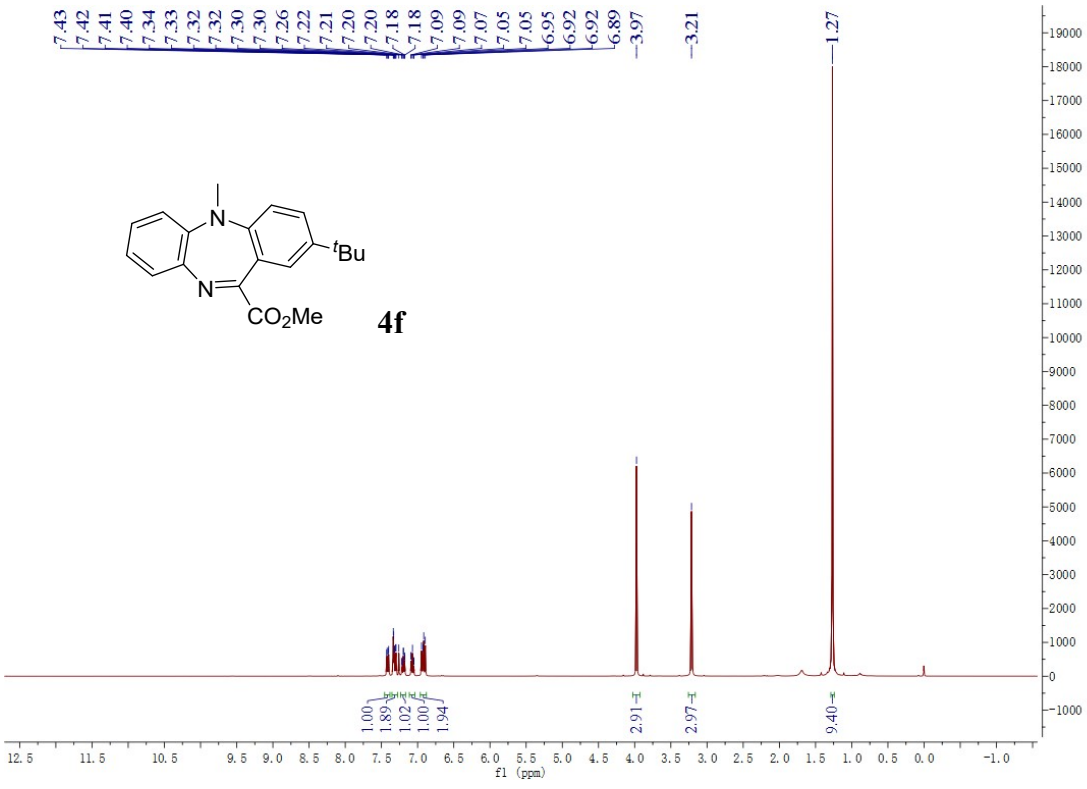
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



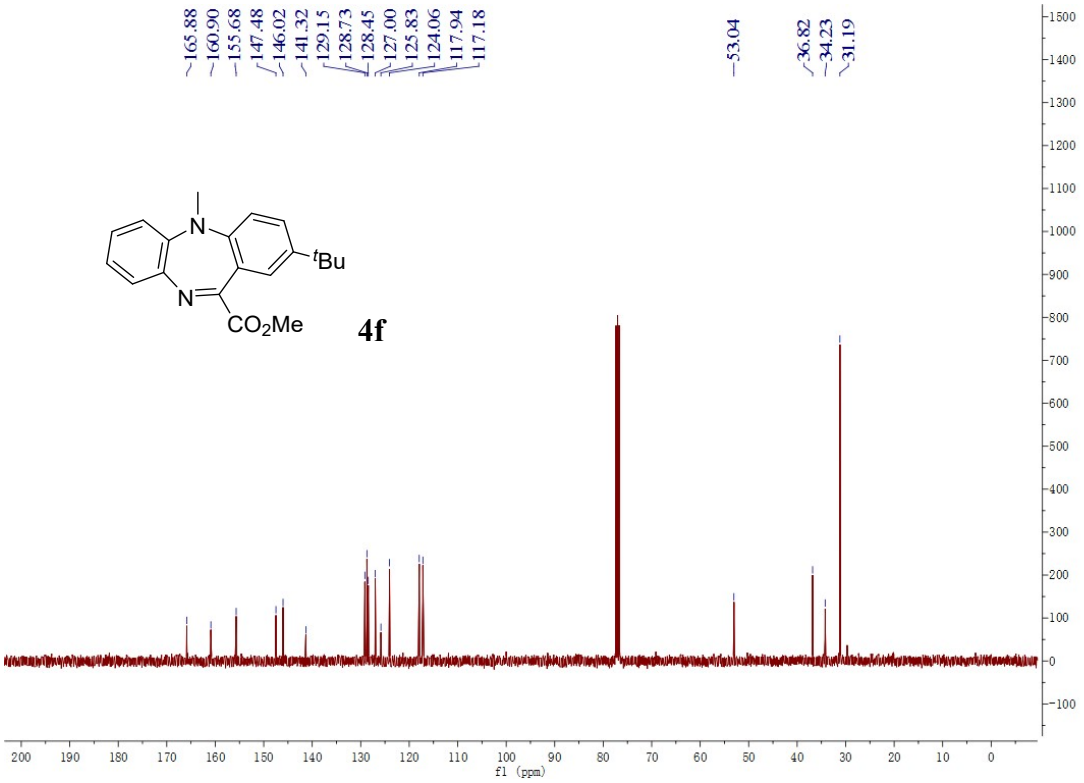
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4e**



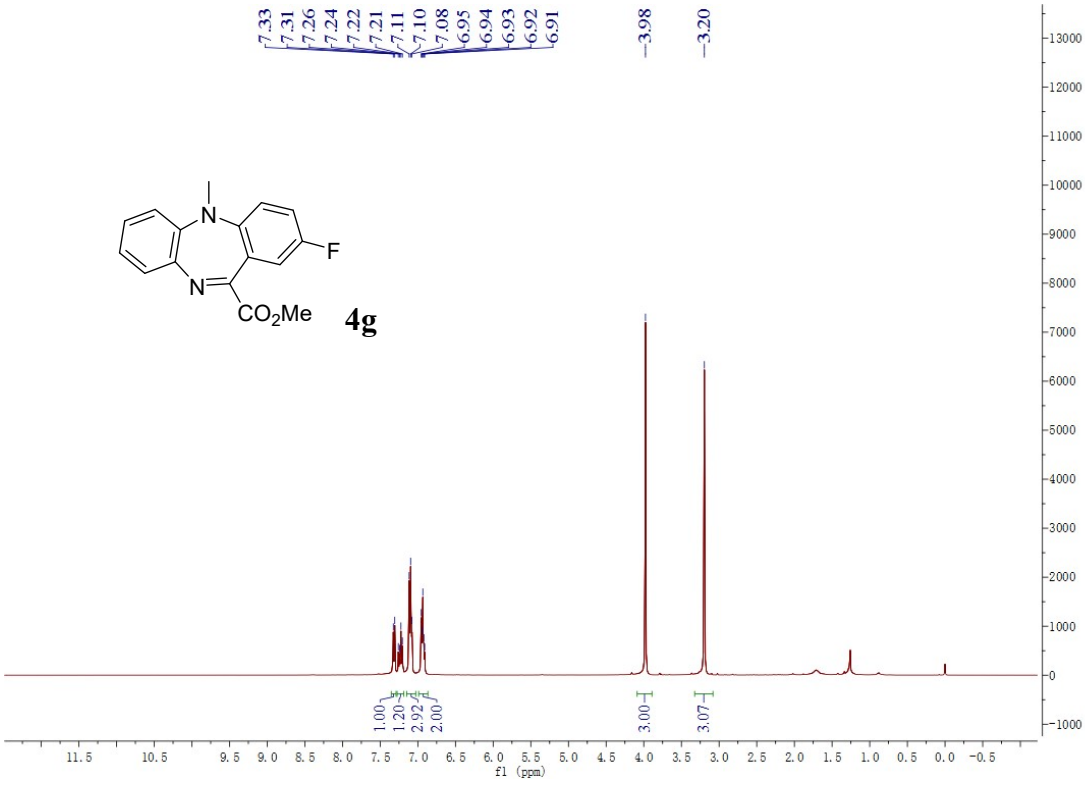
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**



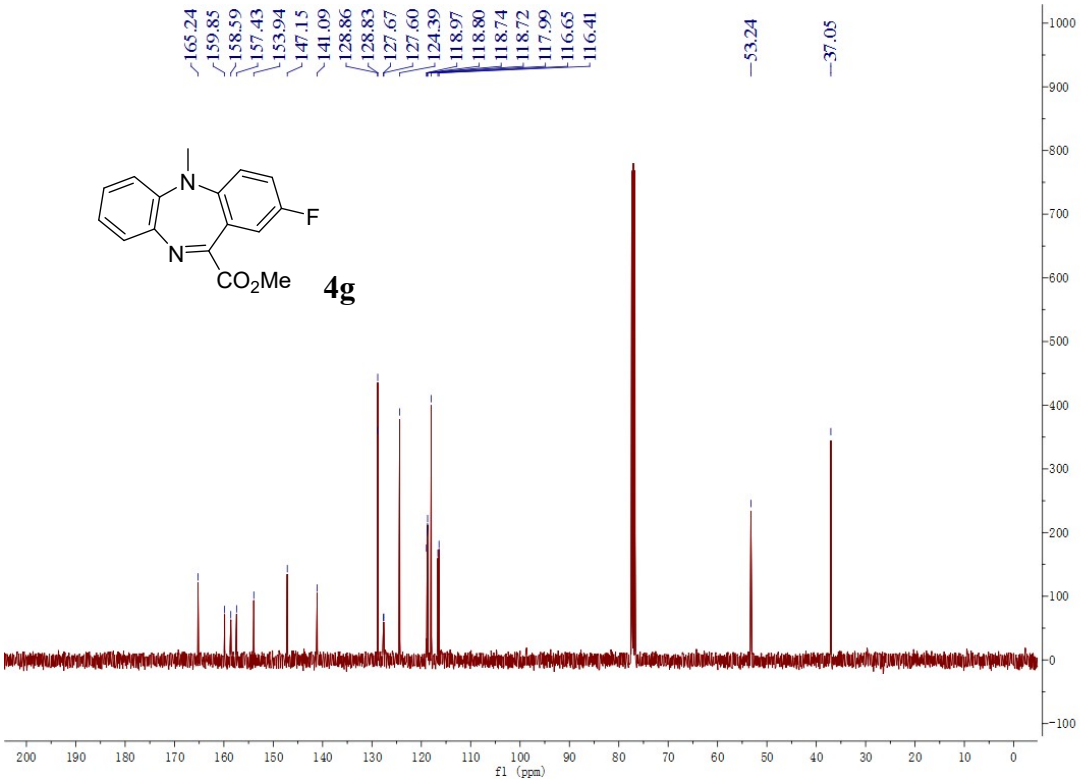
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4f**



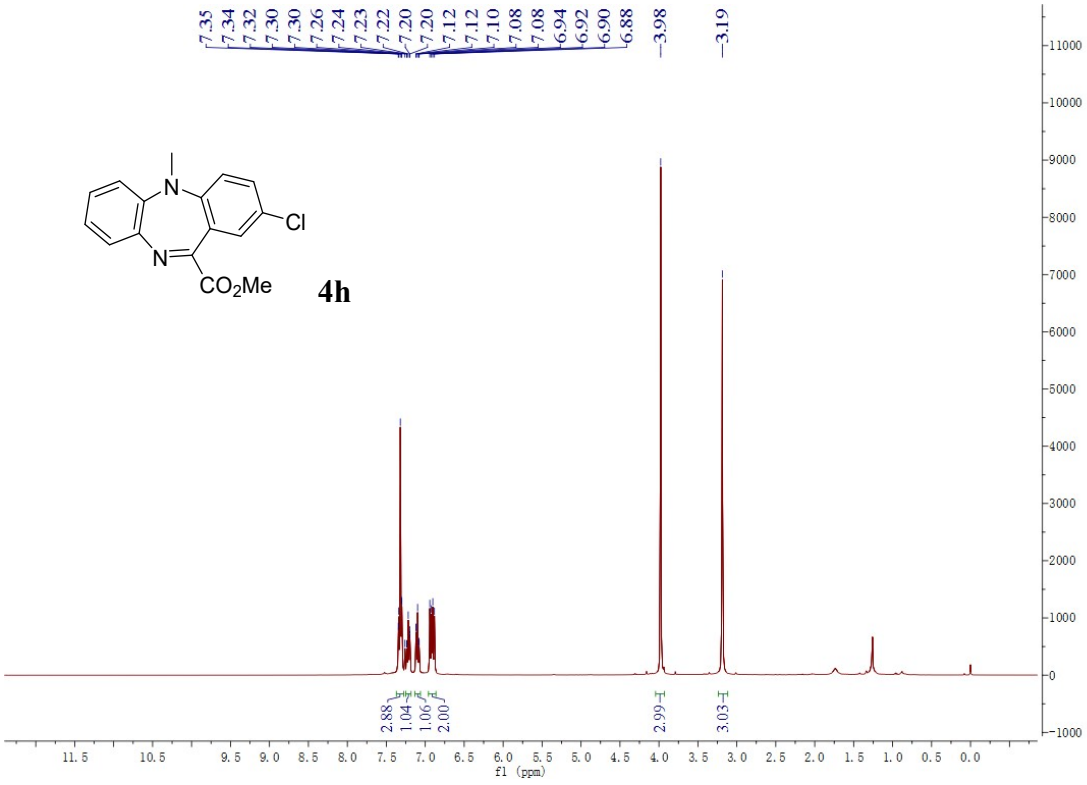
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**



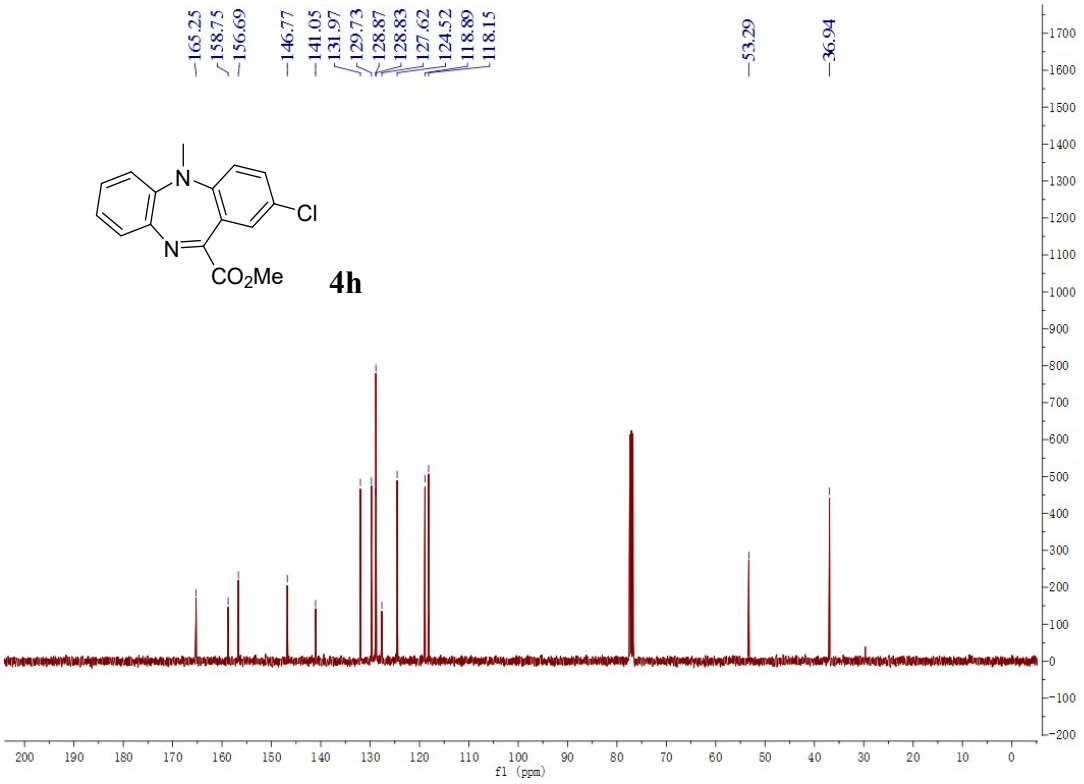
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4g**



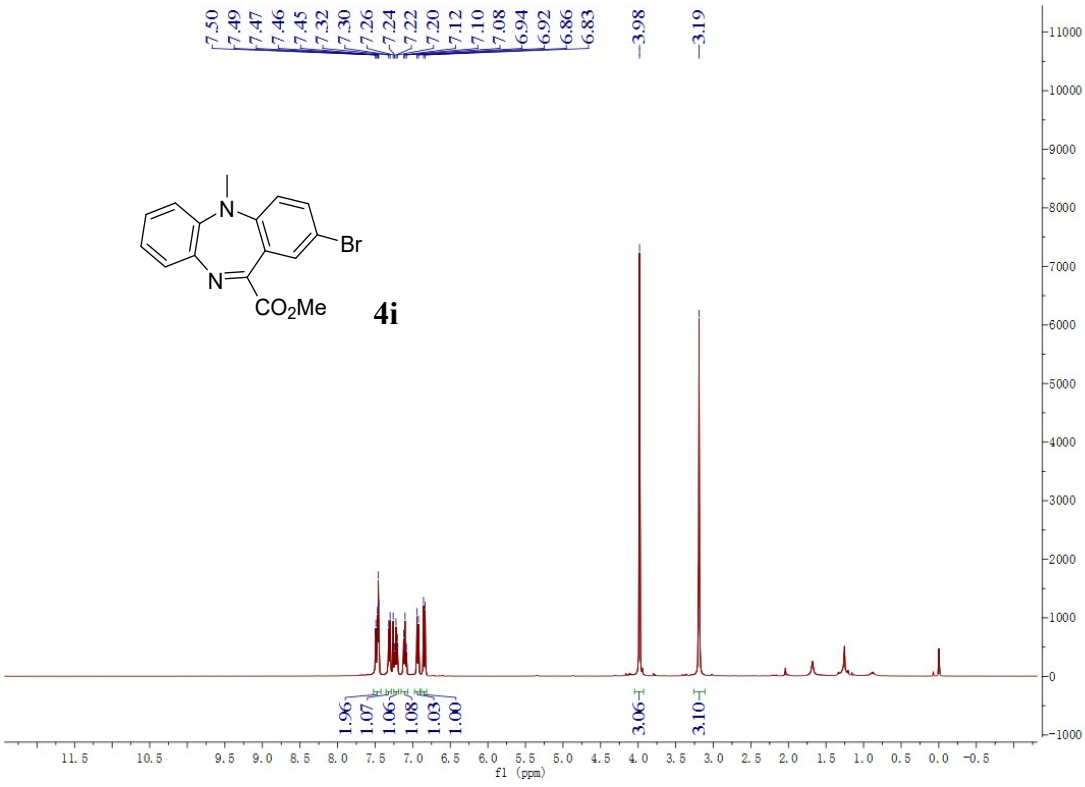
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



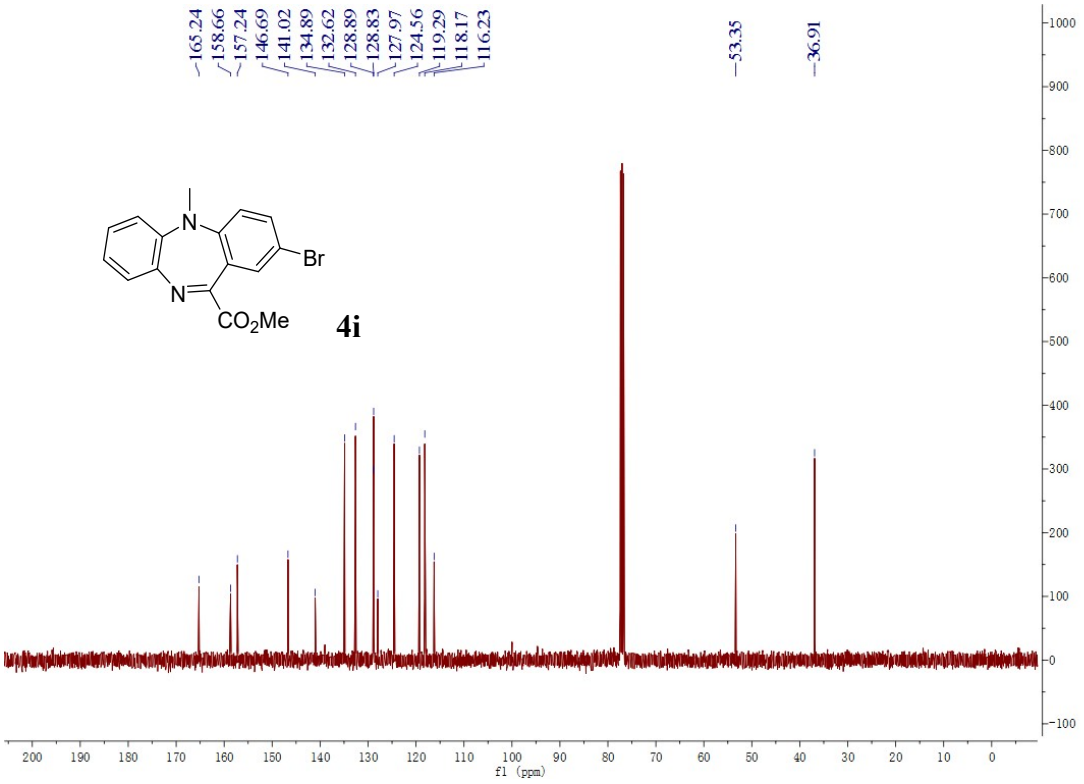
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4h**



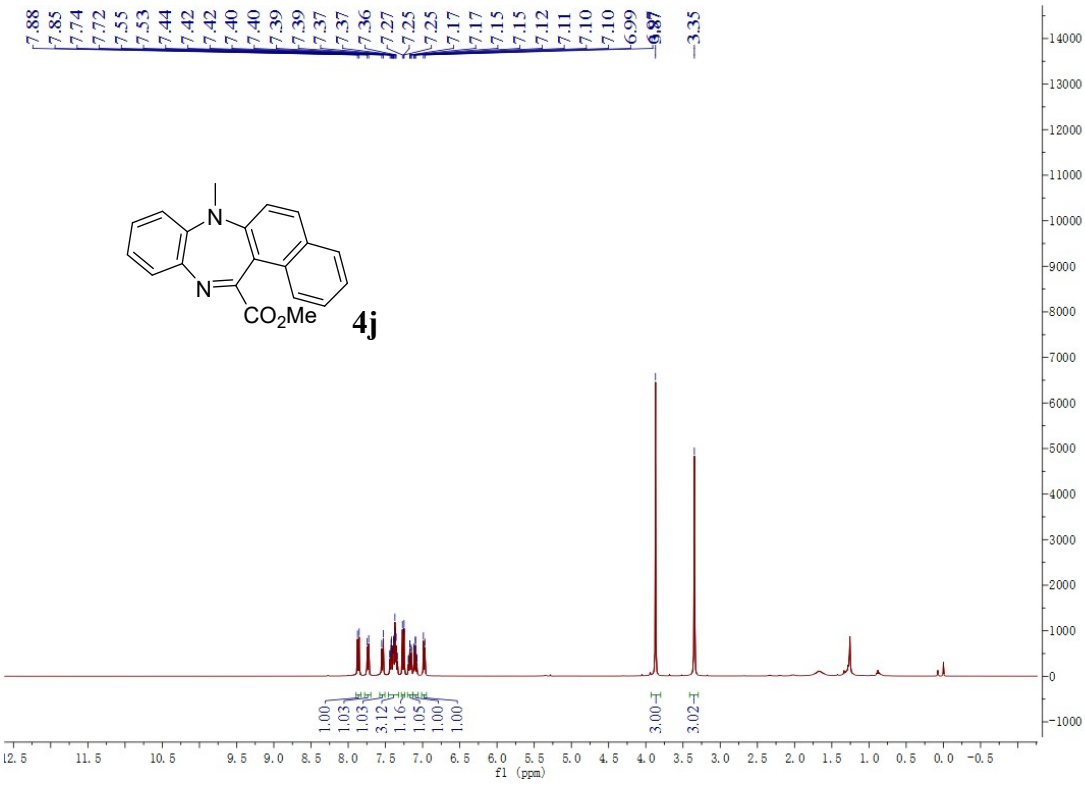
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



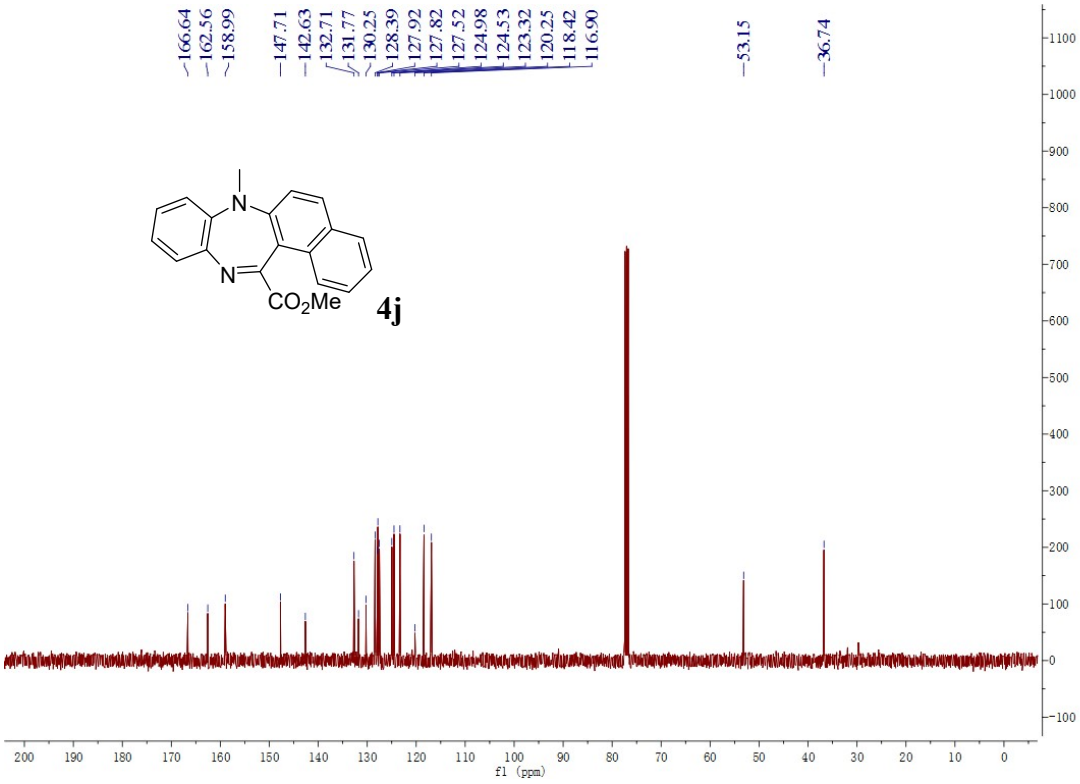
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4i**



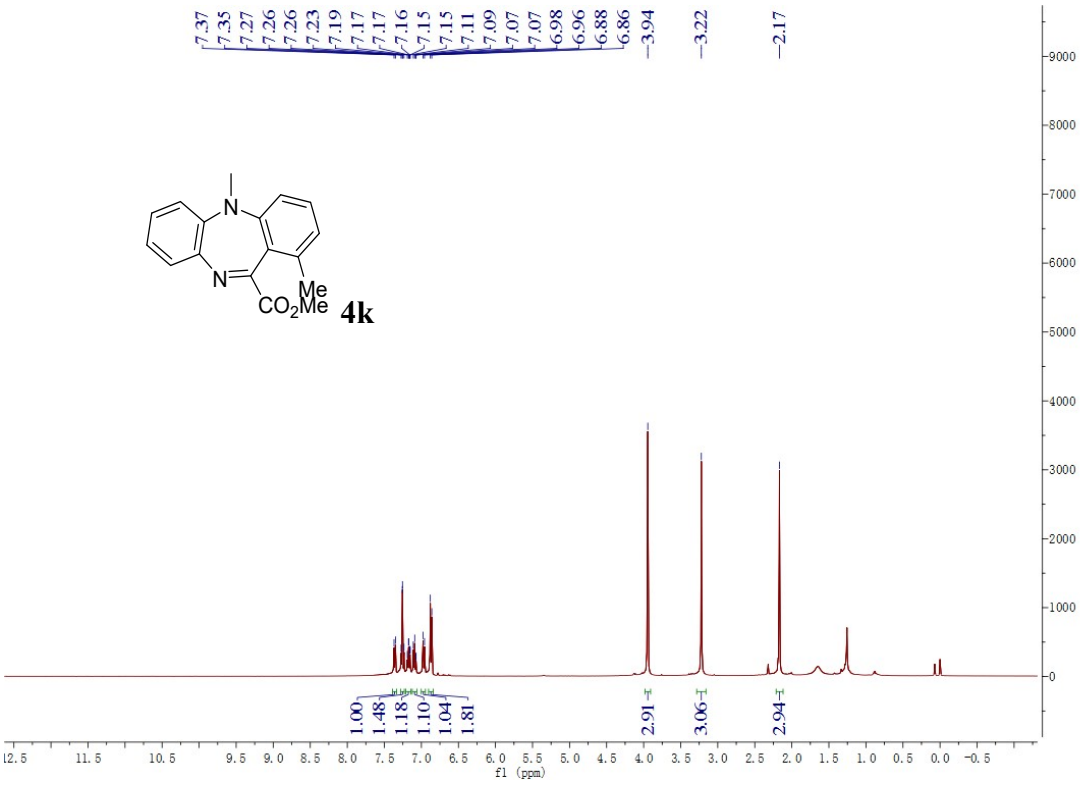
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**



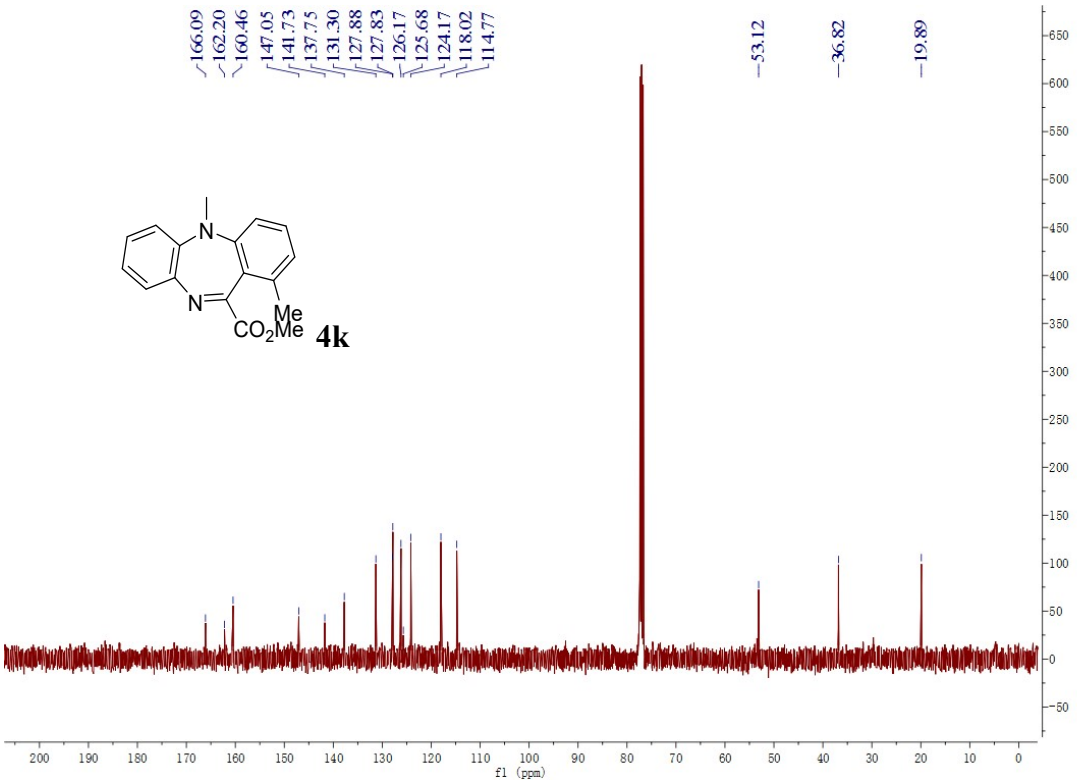
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4j**



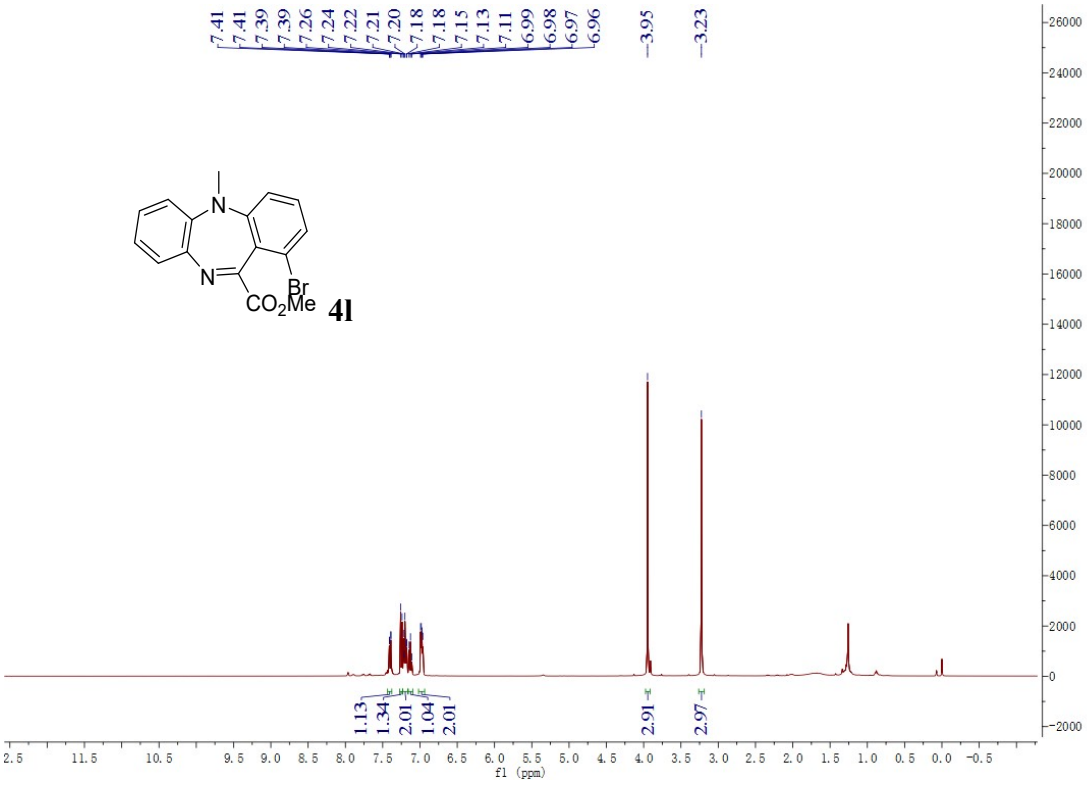
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**



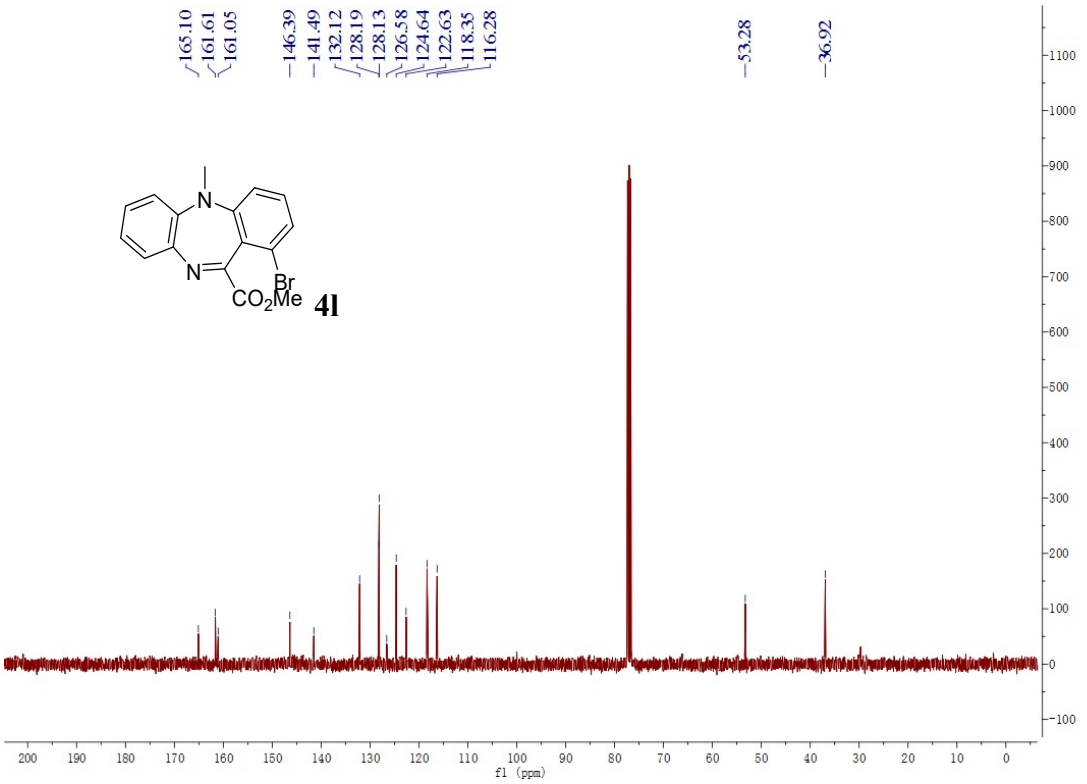
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4k**



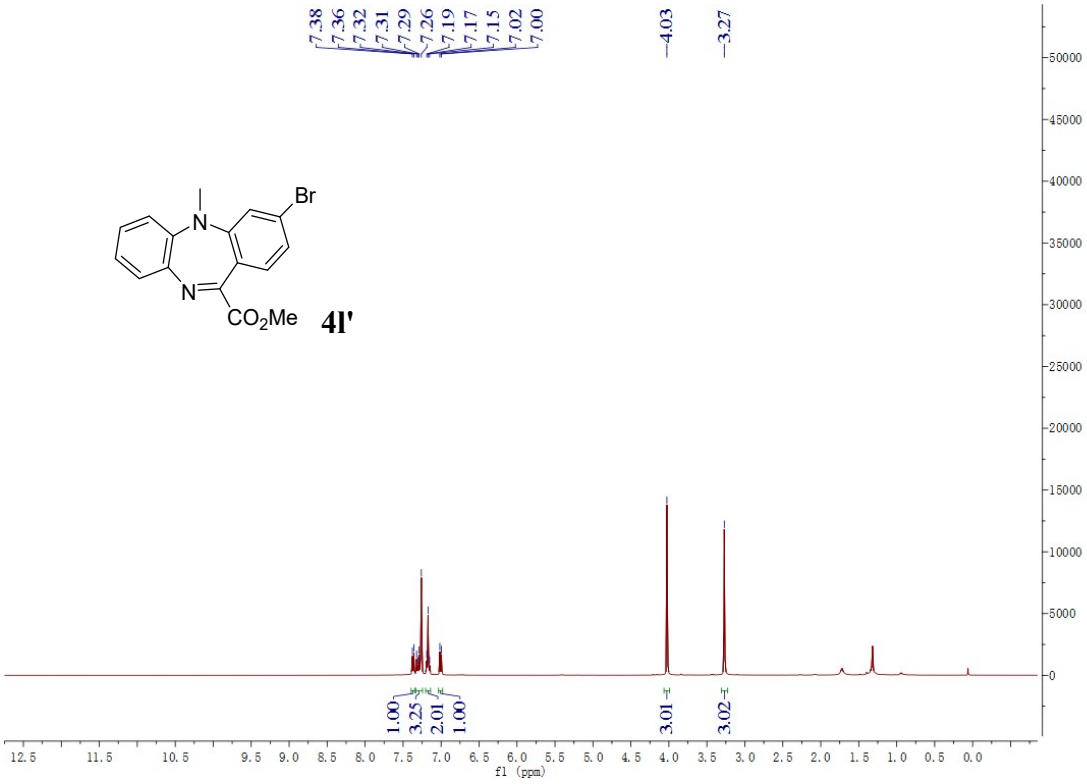
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l**



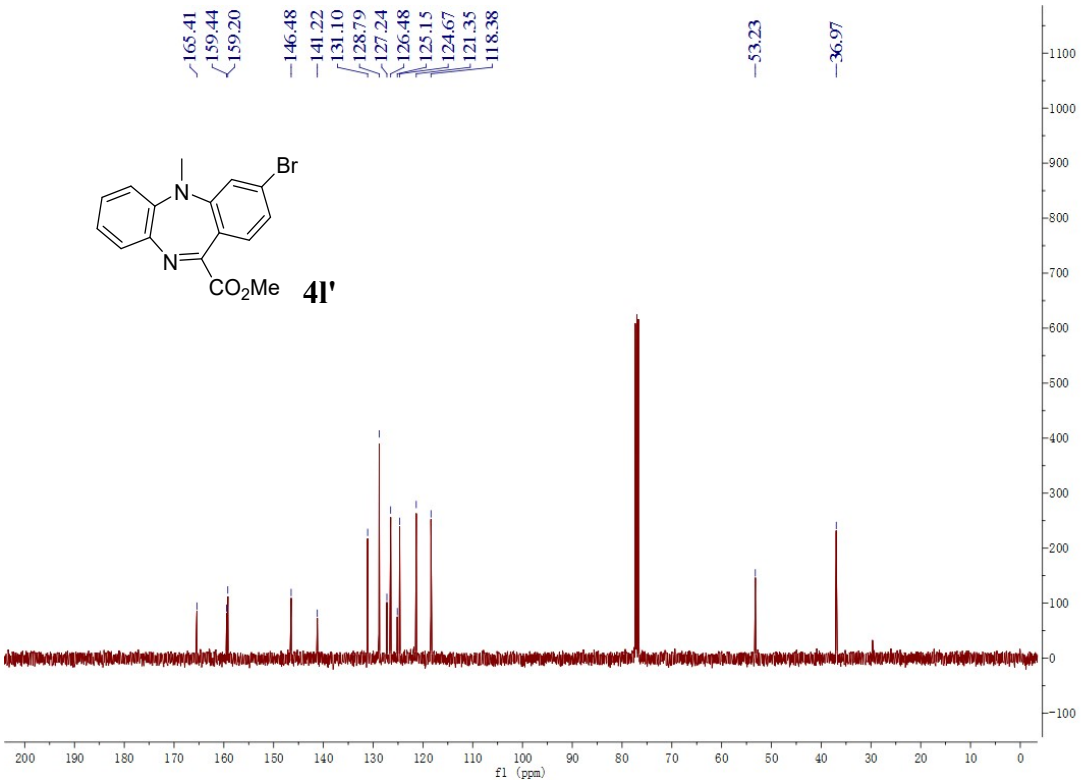
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4l**



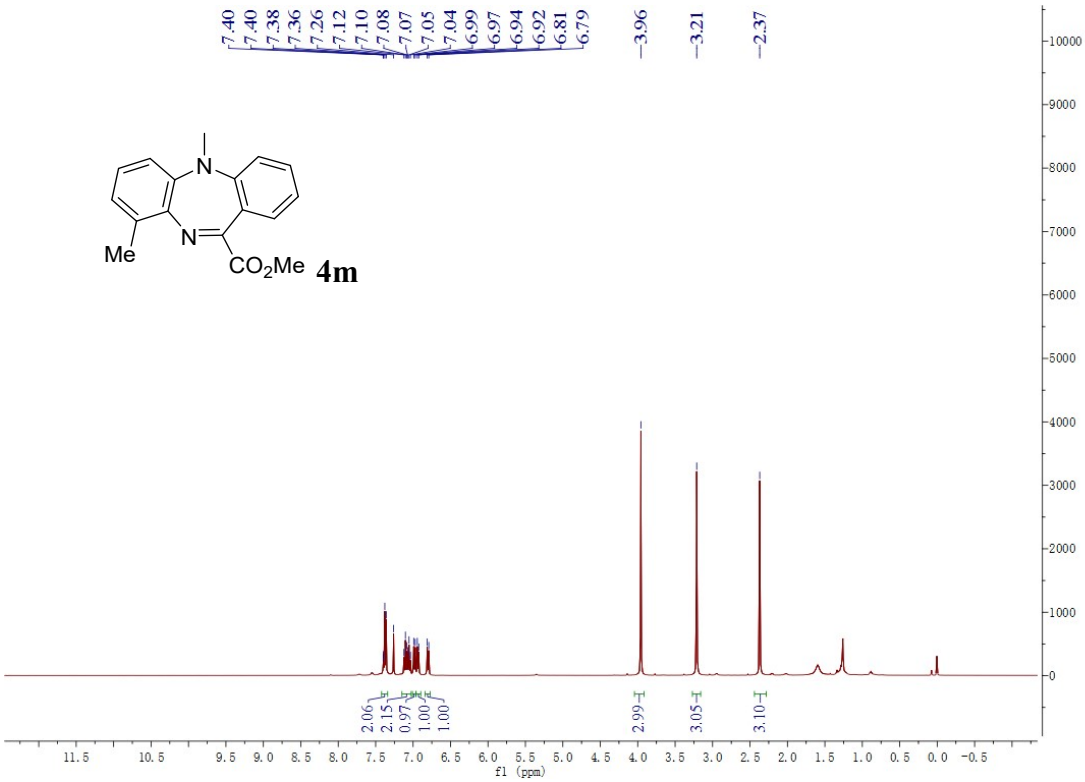
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4l'**



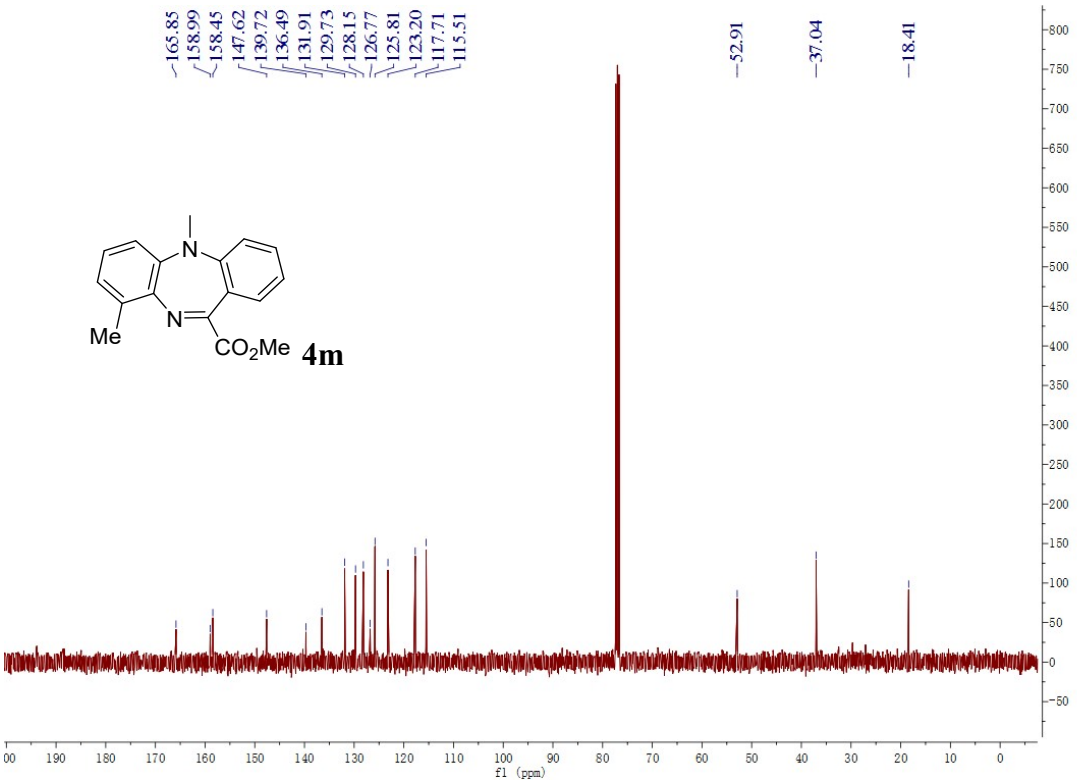
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4l'**



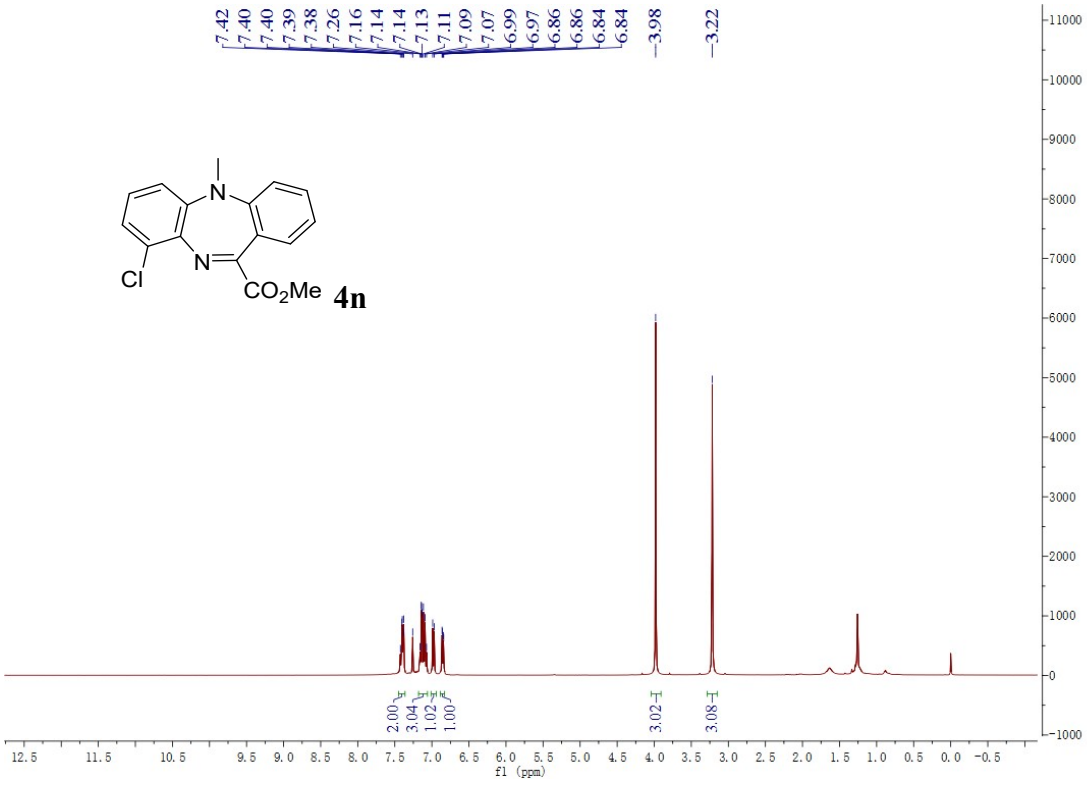
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4m**



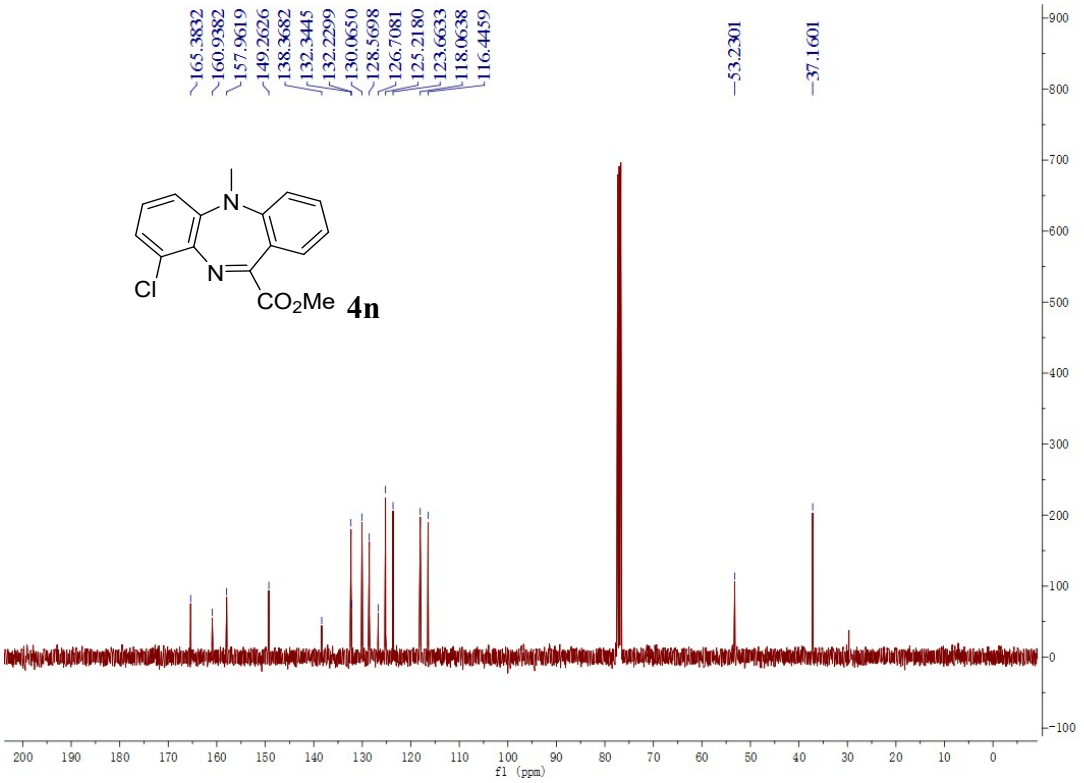
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4m**



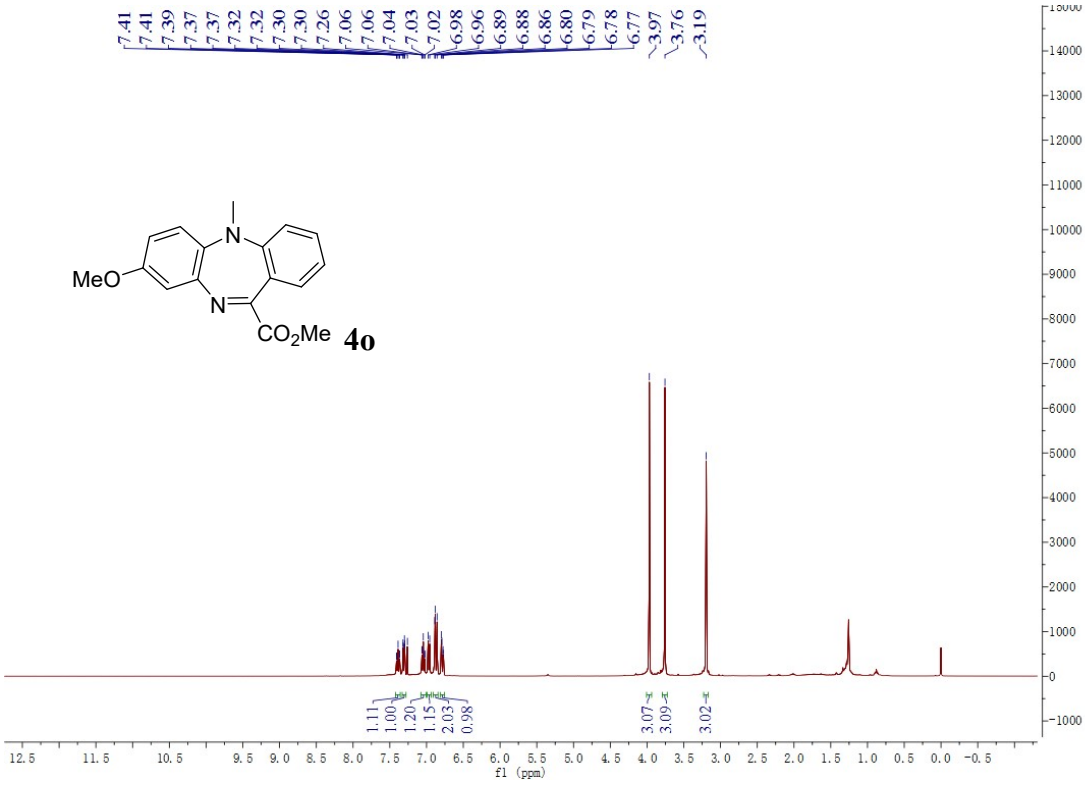
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4n**



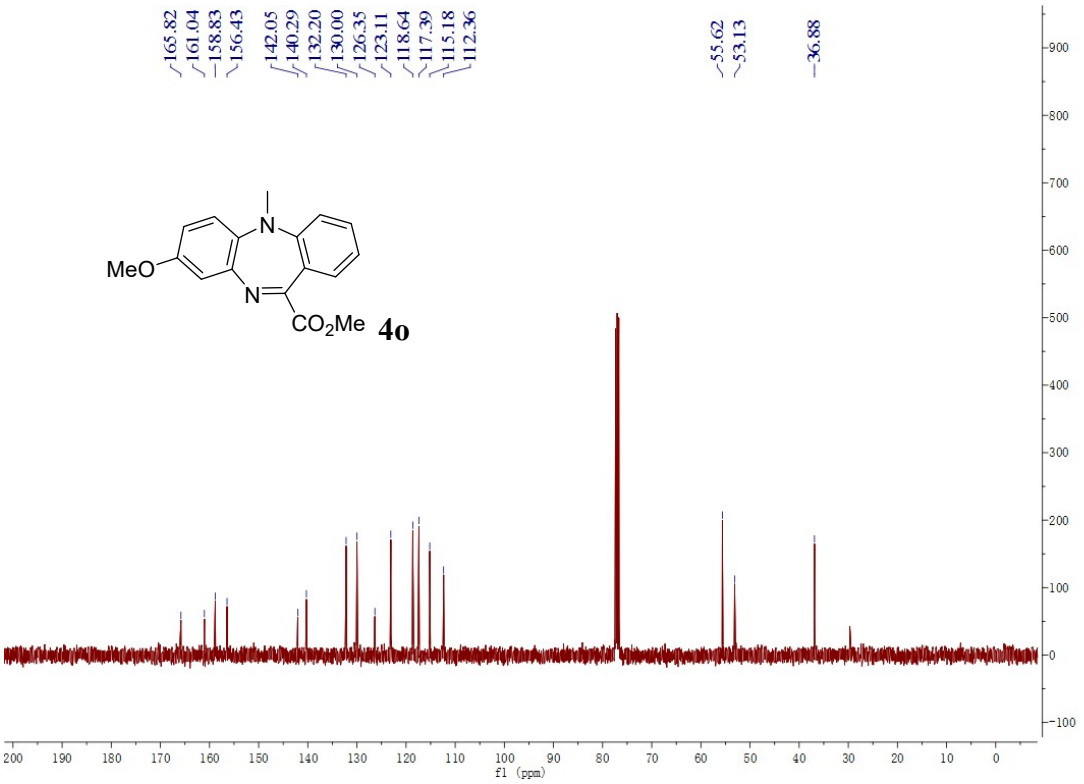
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4n**



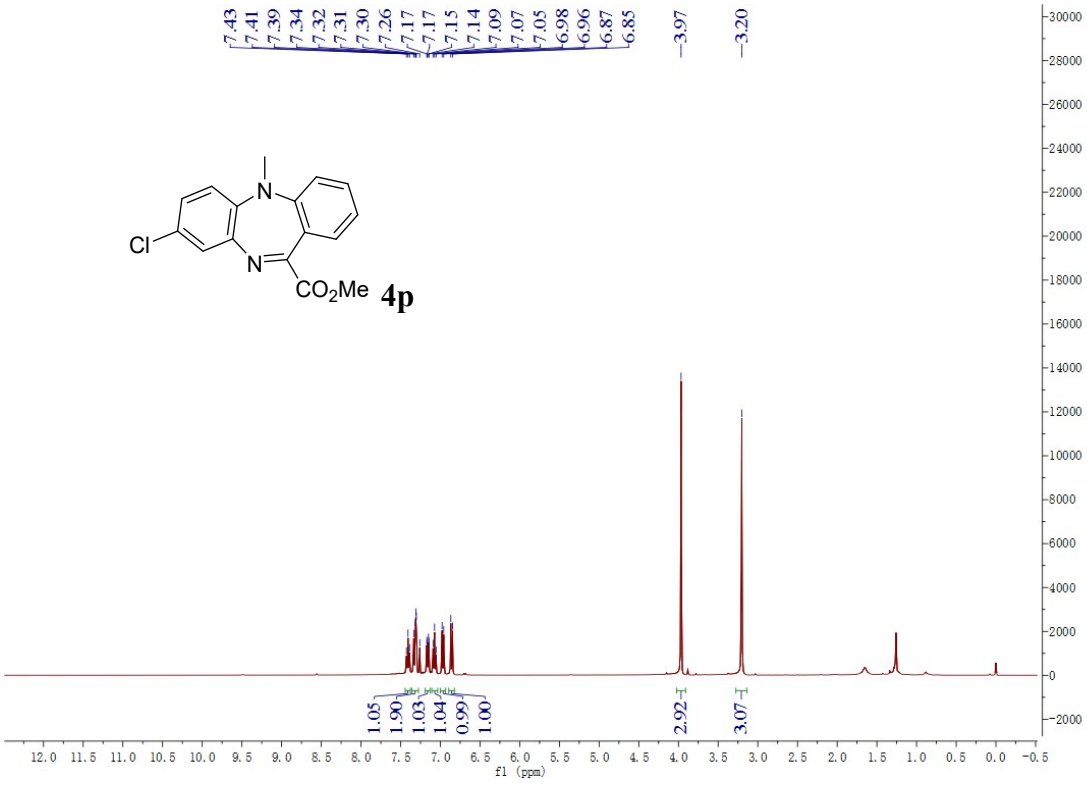
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o**



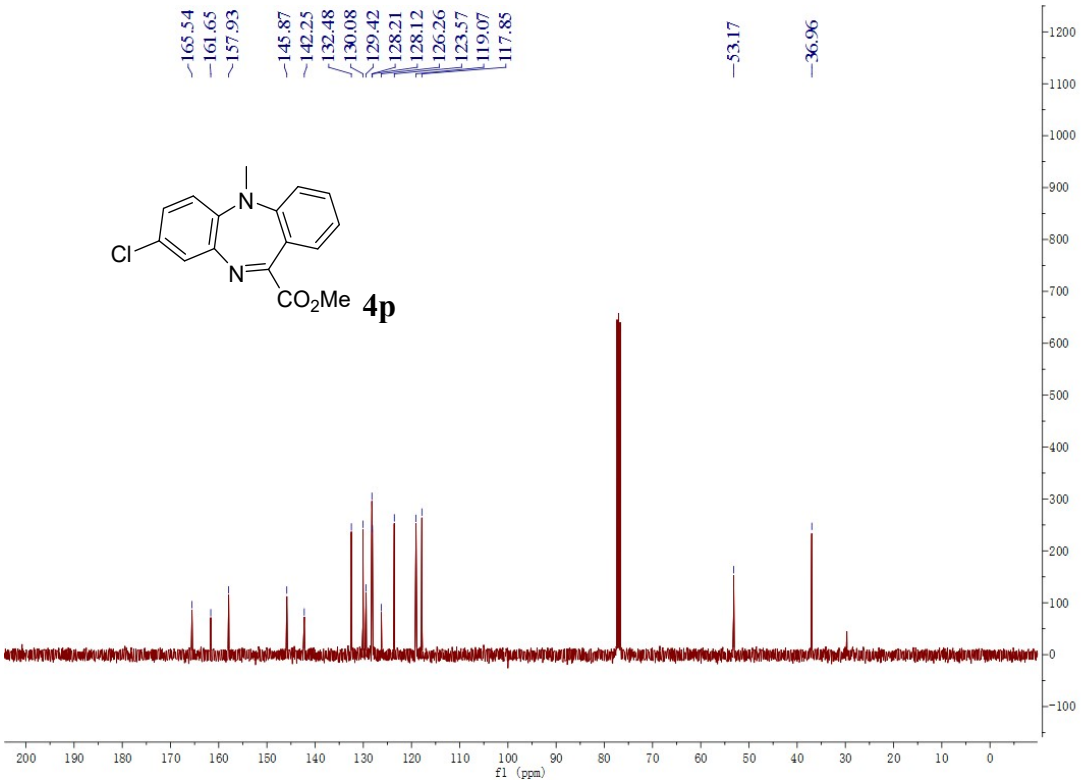
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4o**



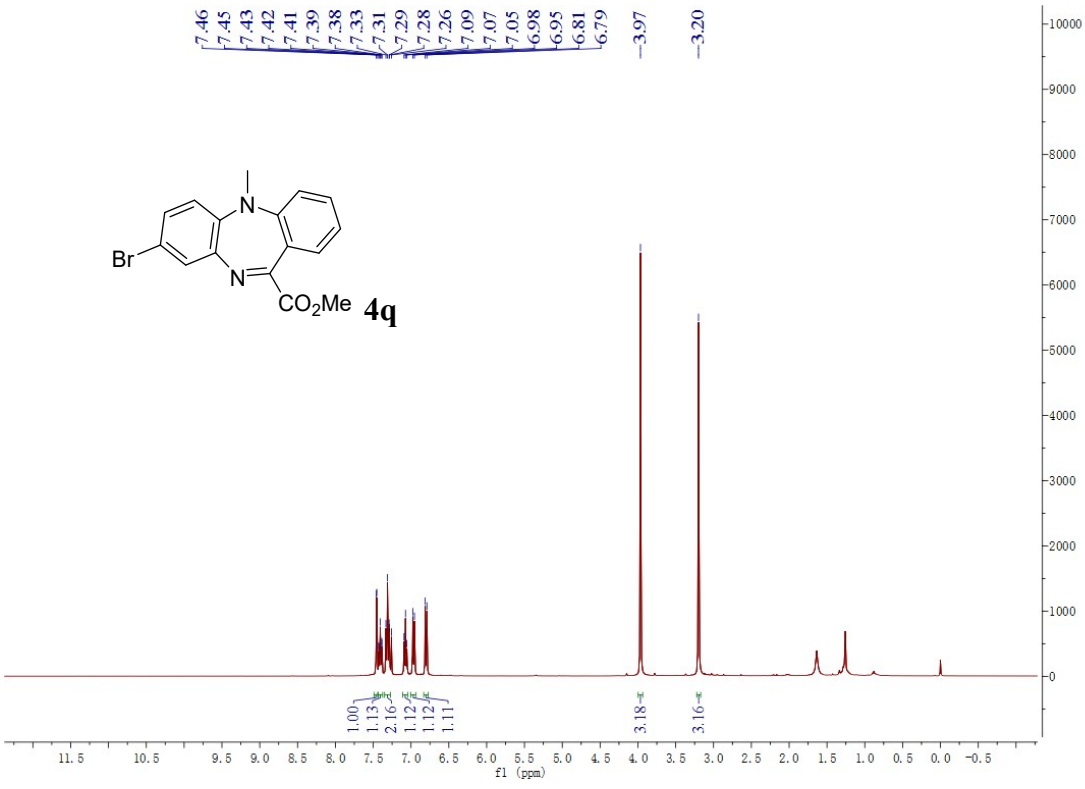
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4p**



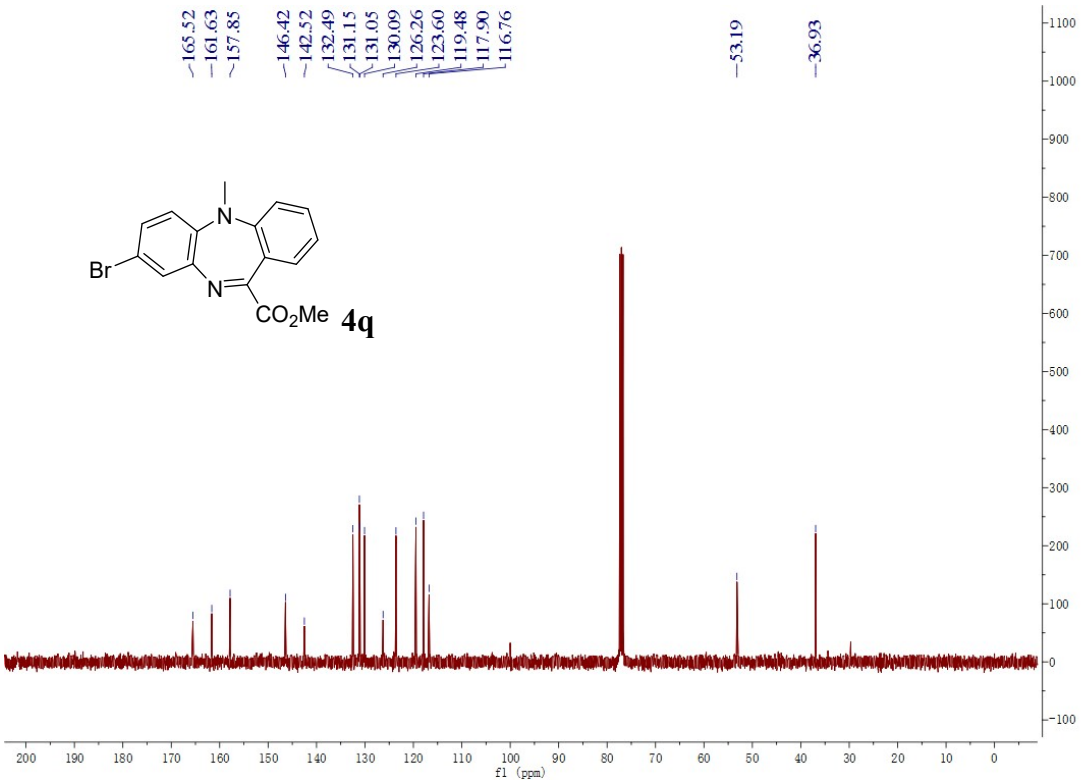
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4p**



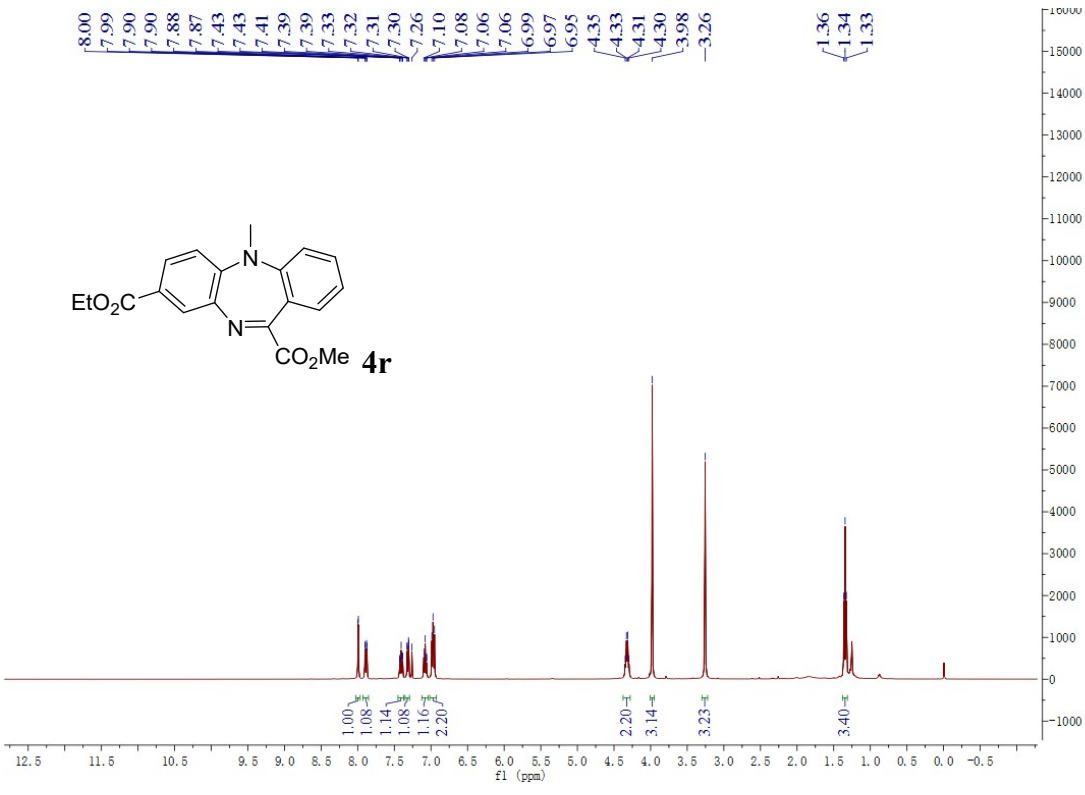
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4q**



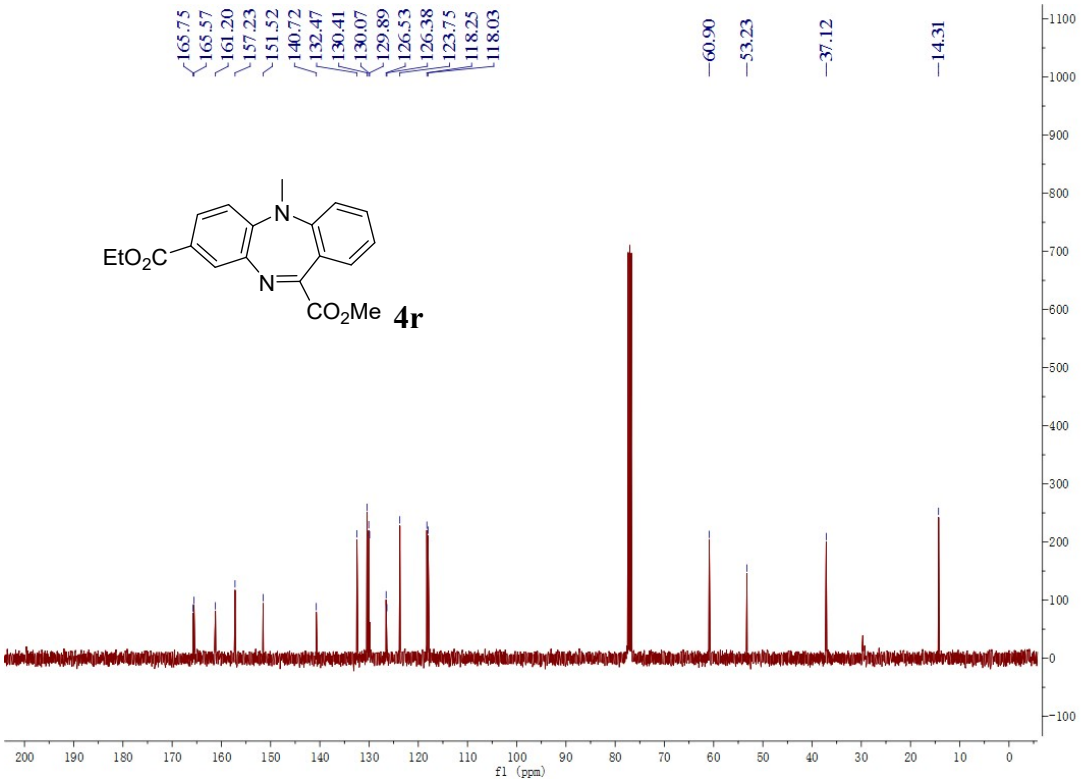
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4q**



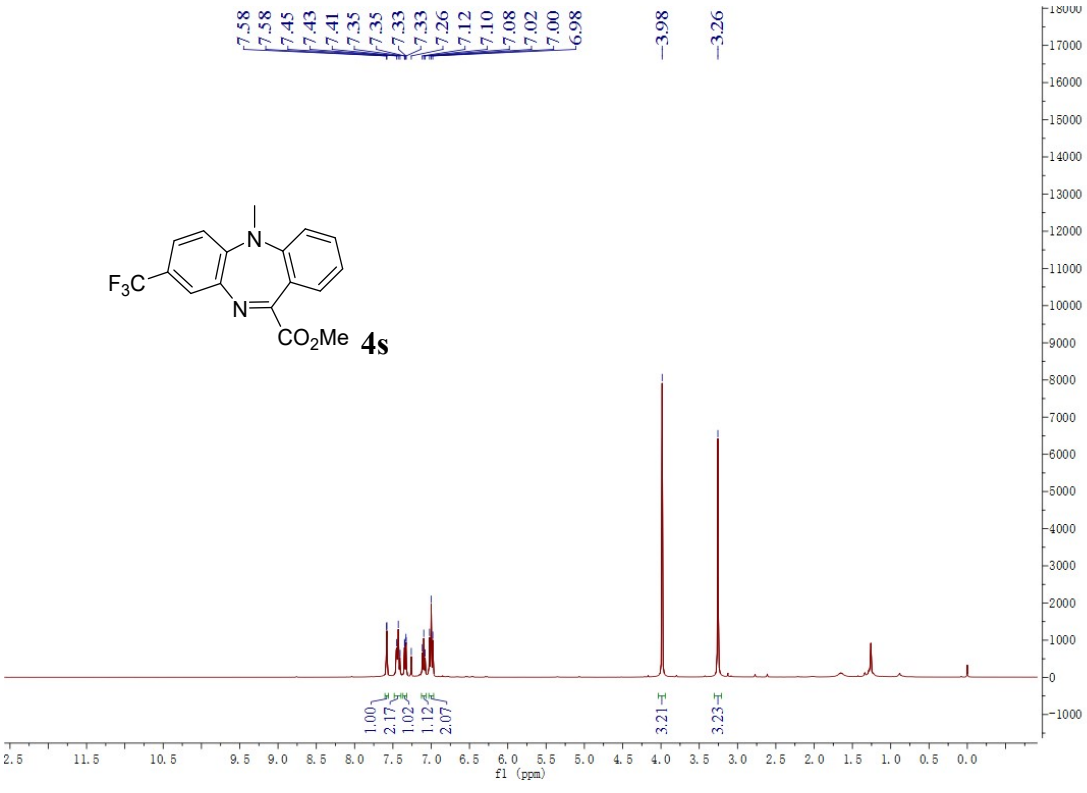
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**



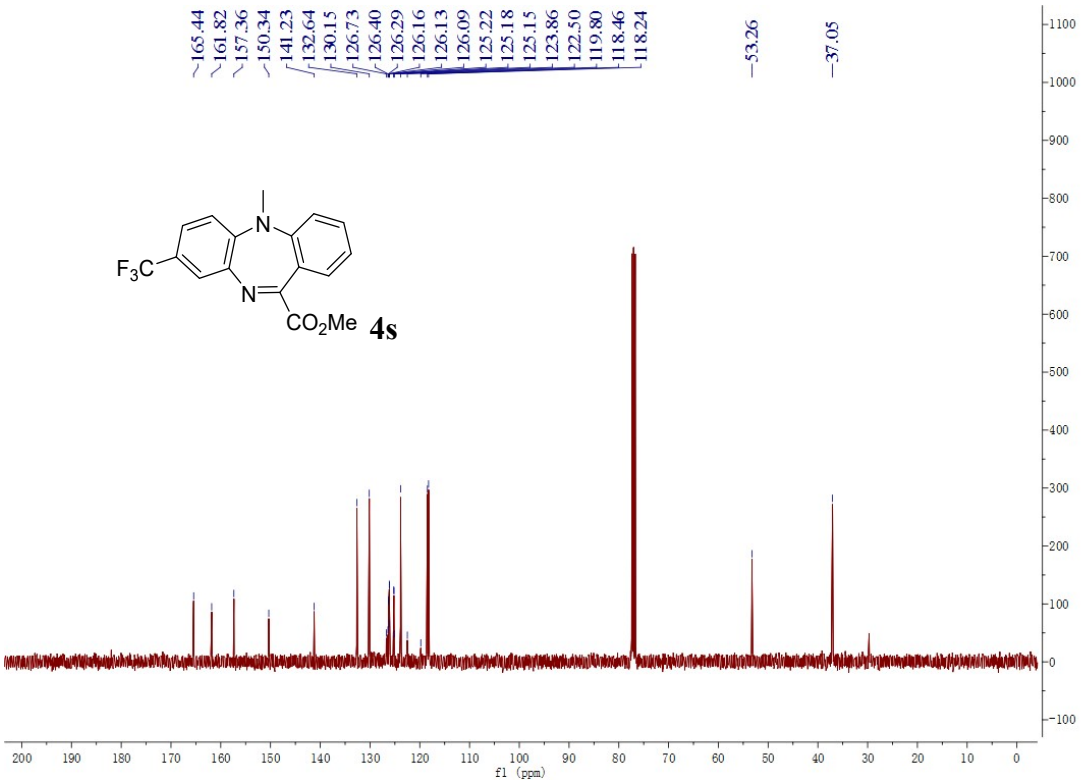
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4r**



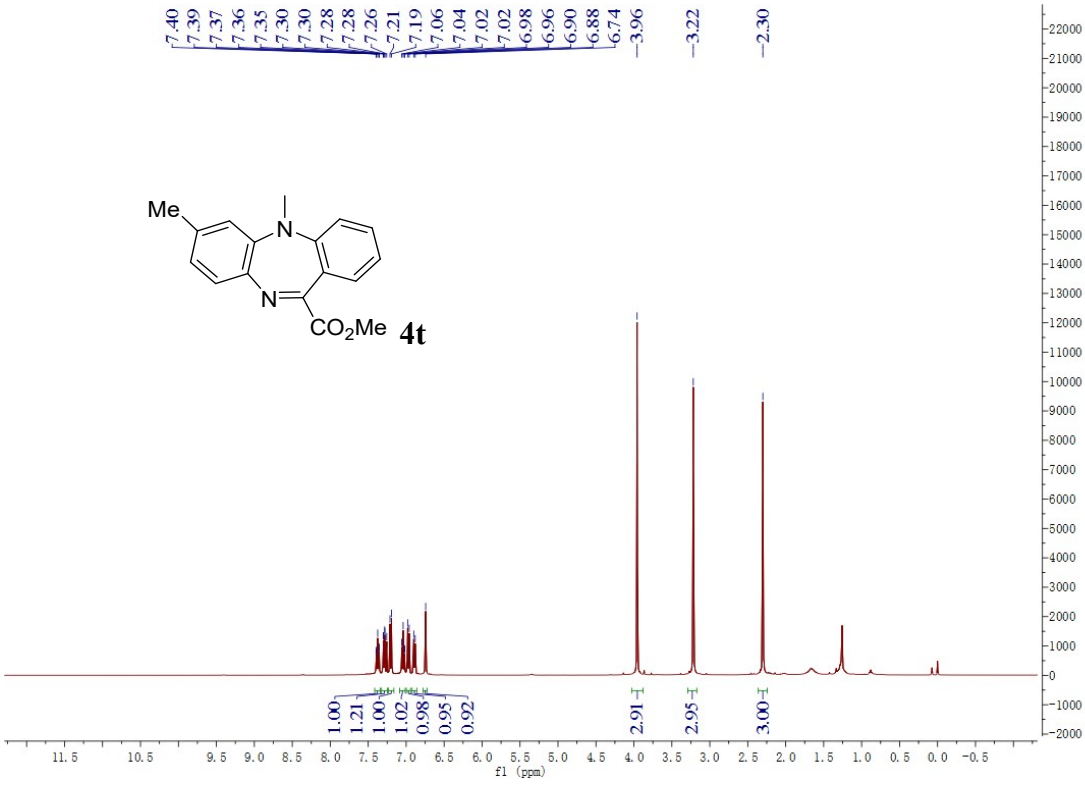
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4s**



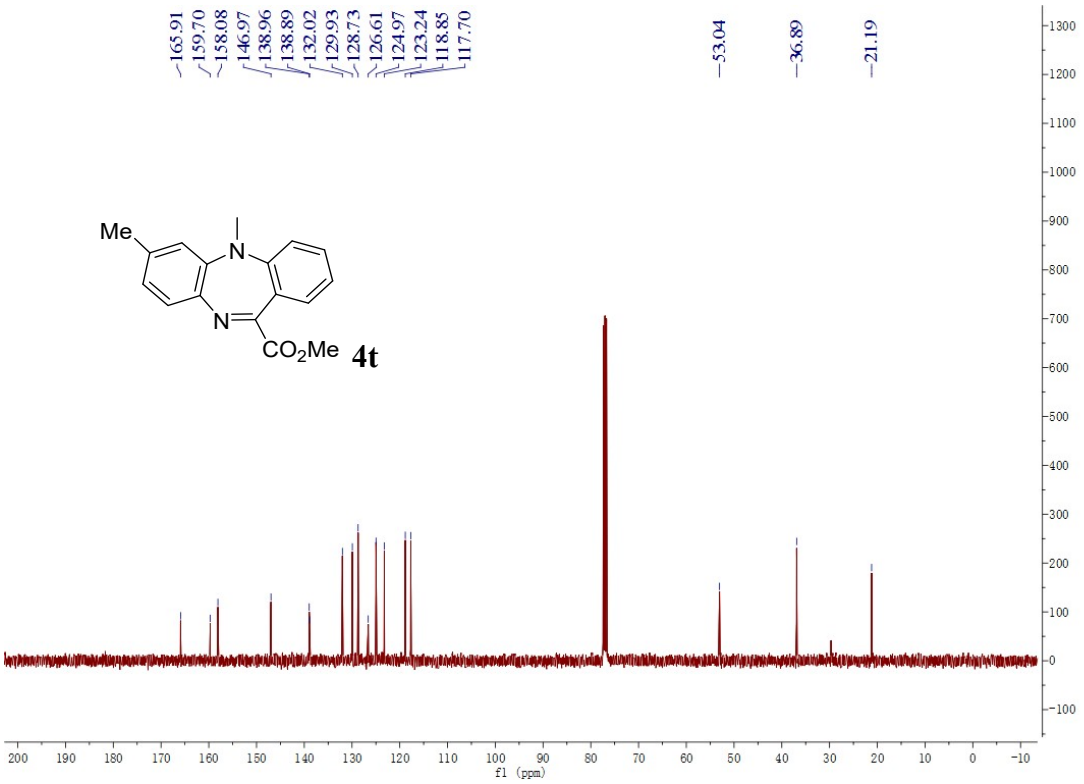
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4s**



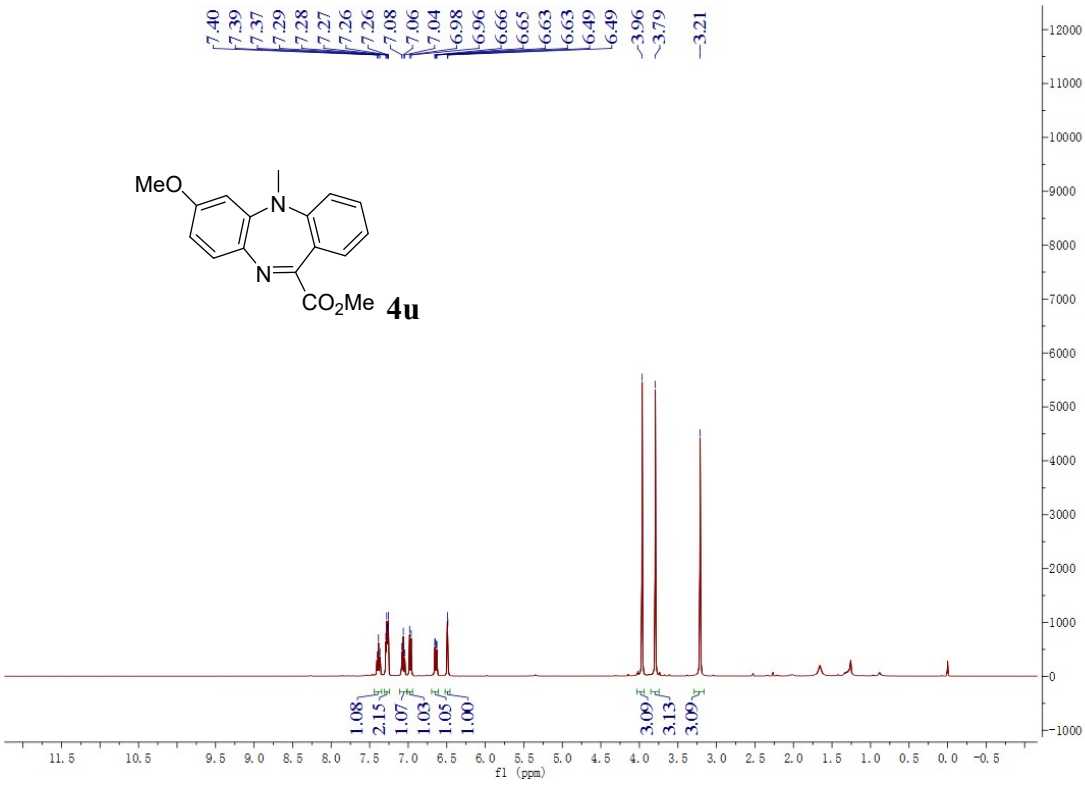
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4t**



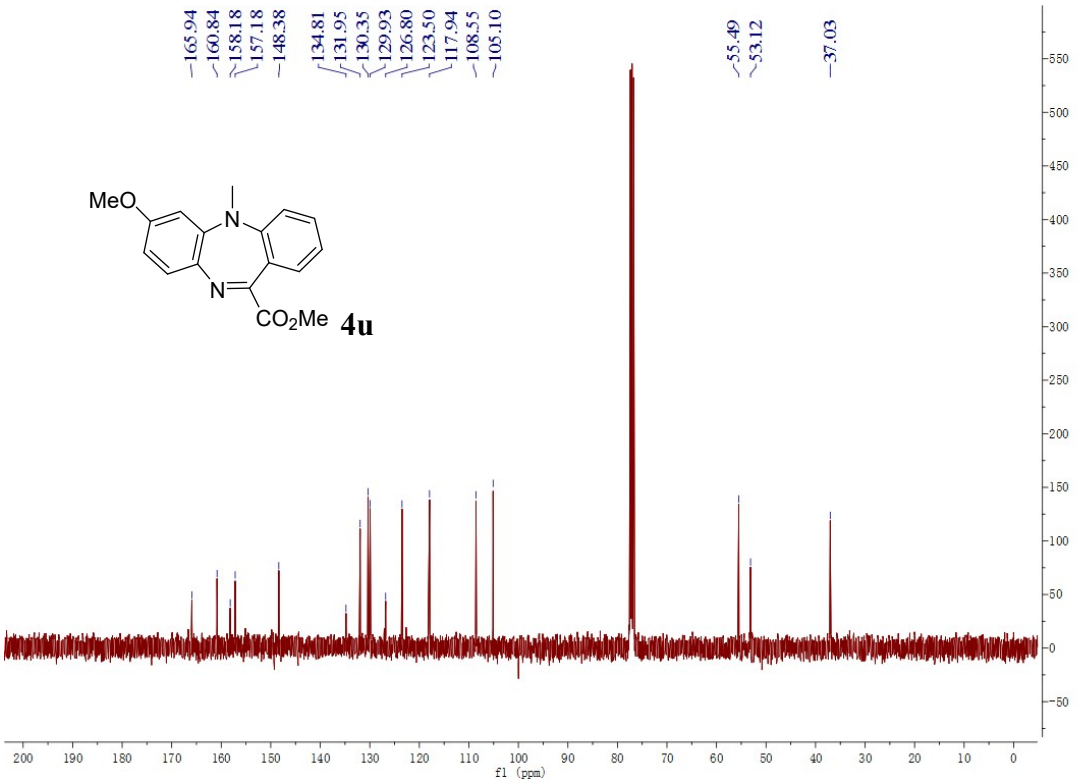
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4t**



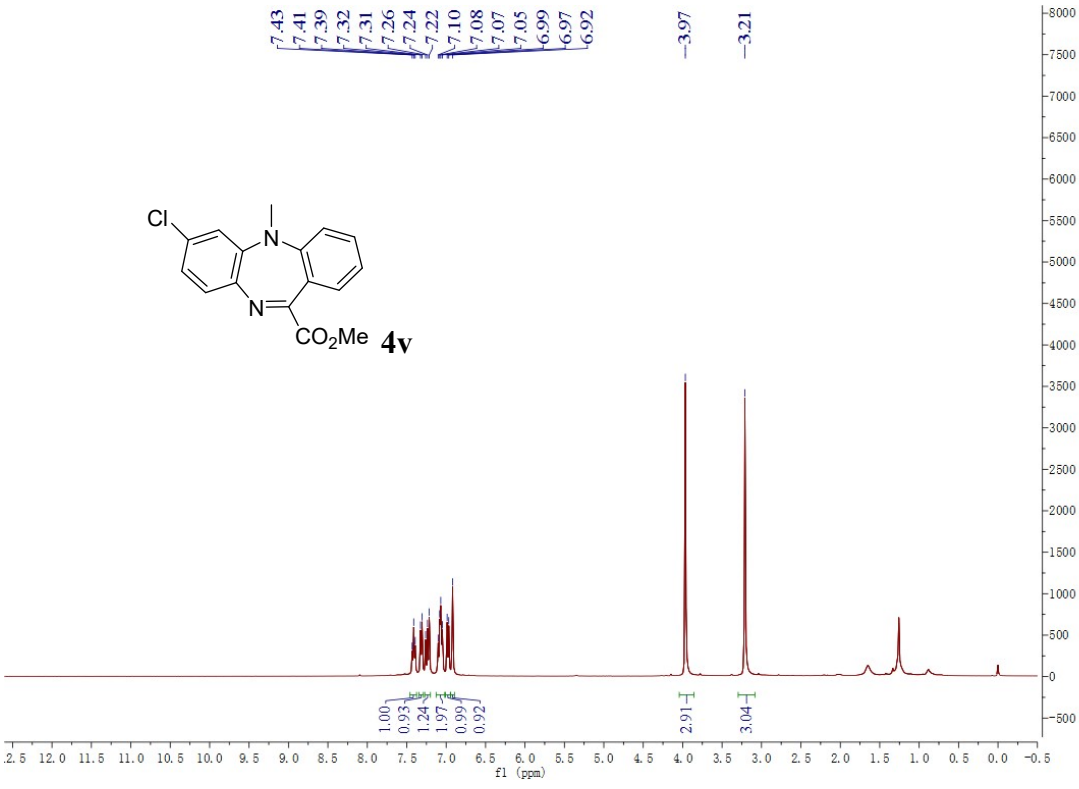
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4u**



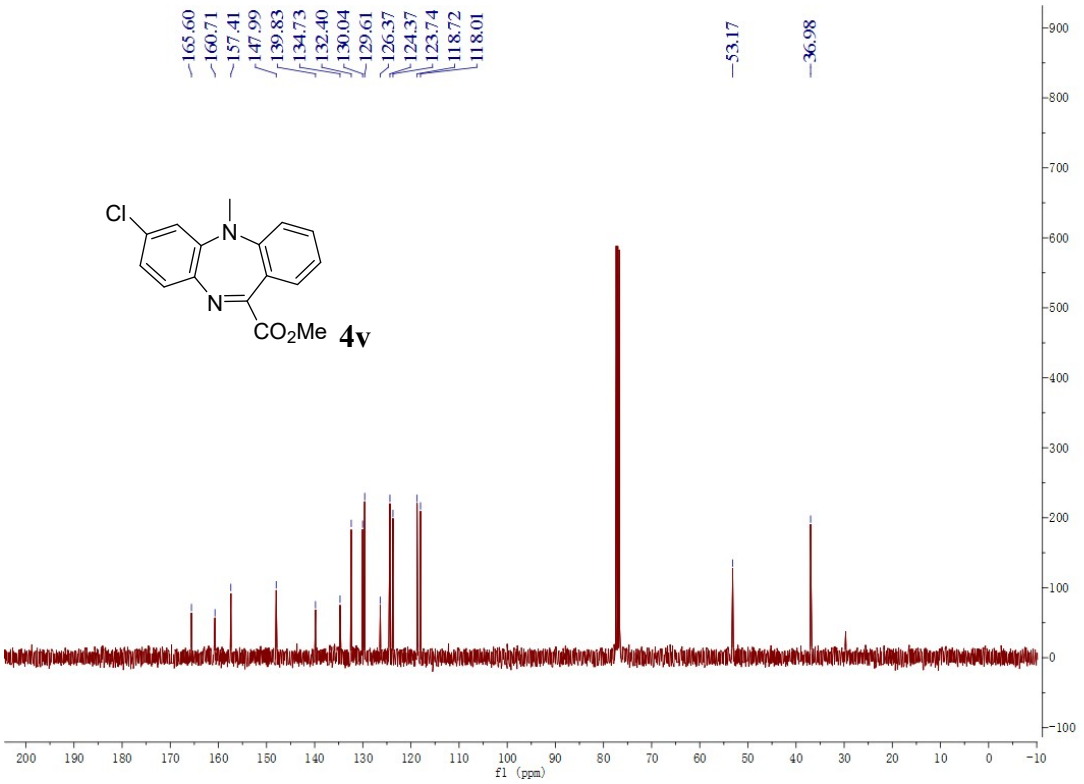
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4u**



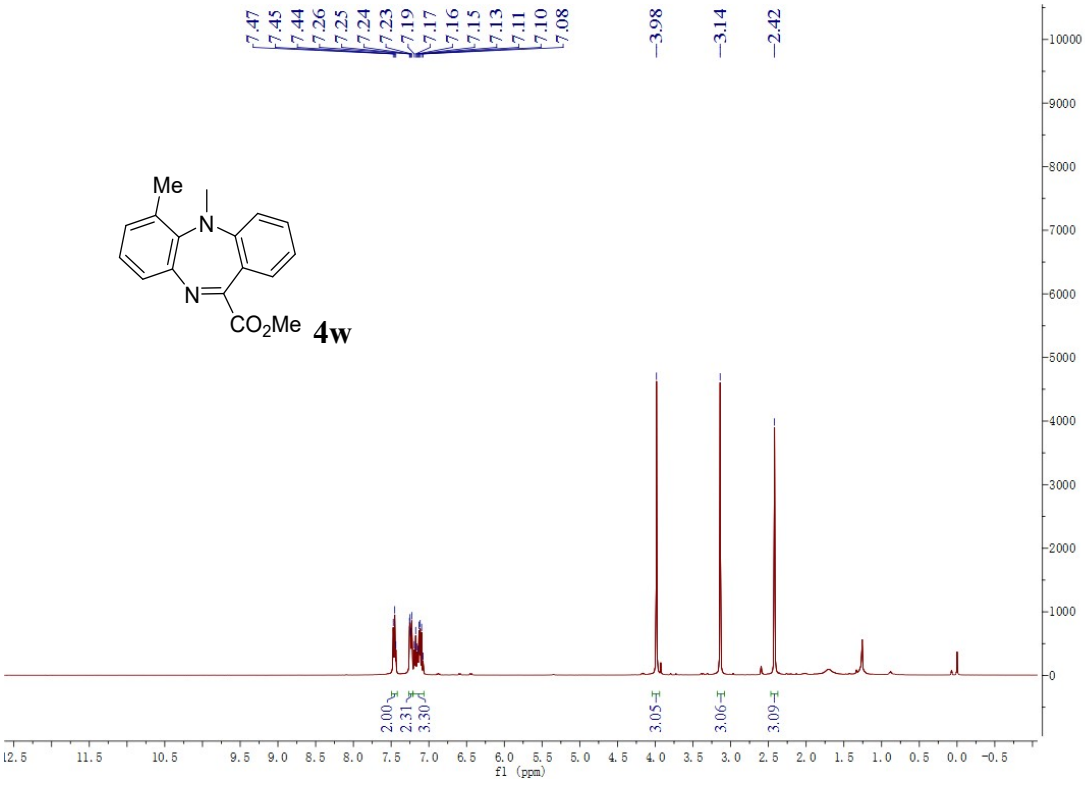
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4v**



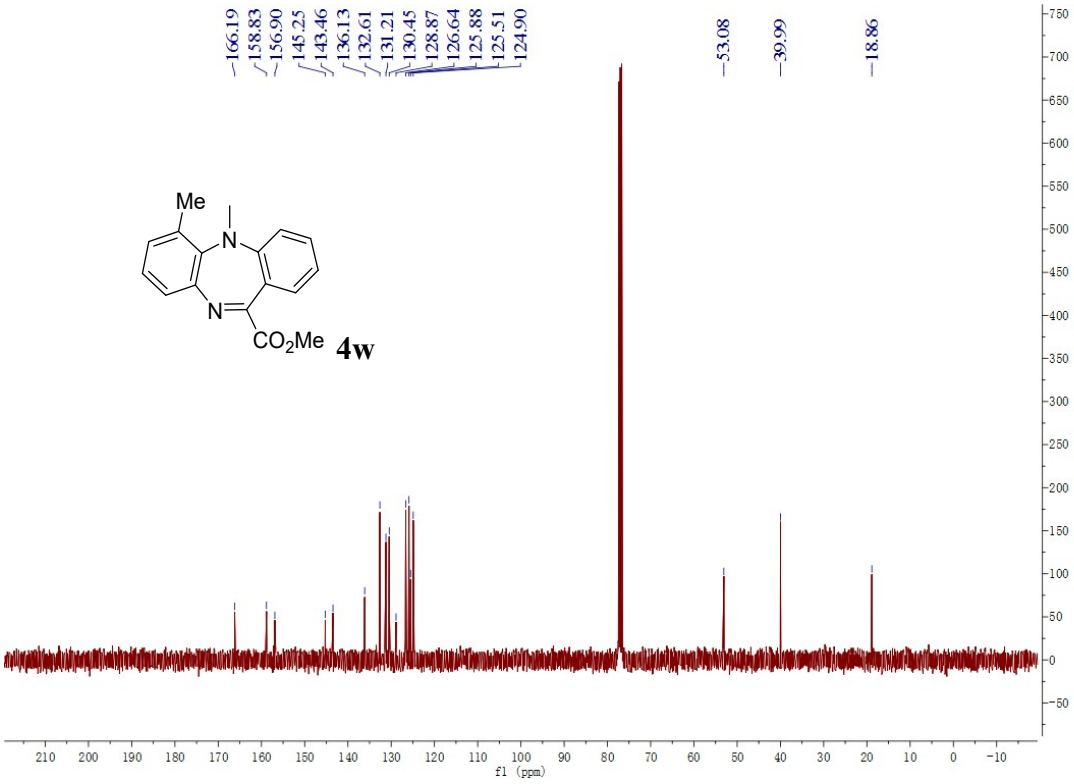
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4v**



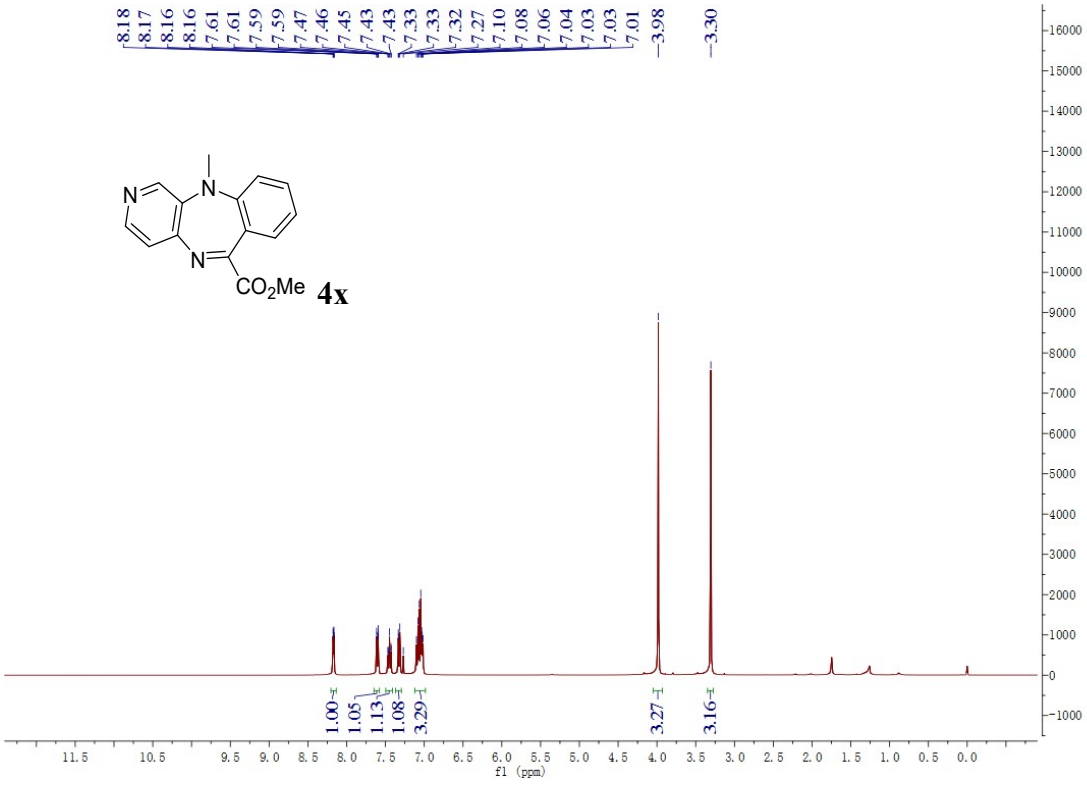
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4w**



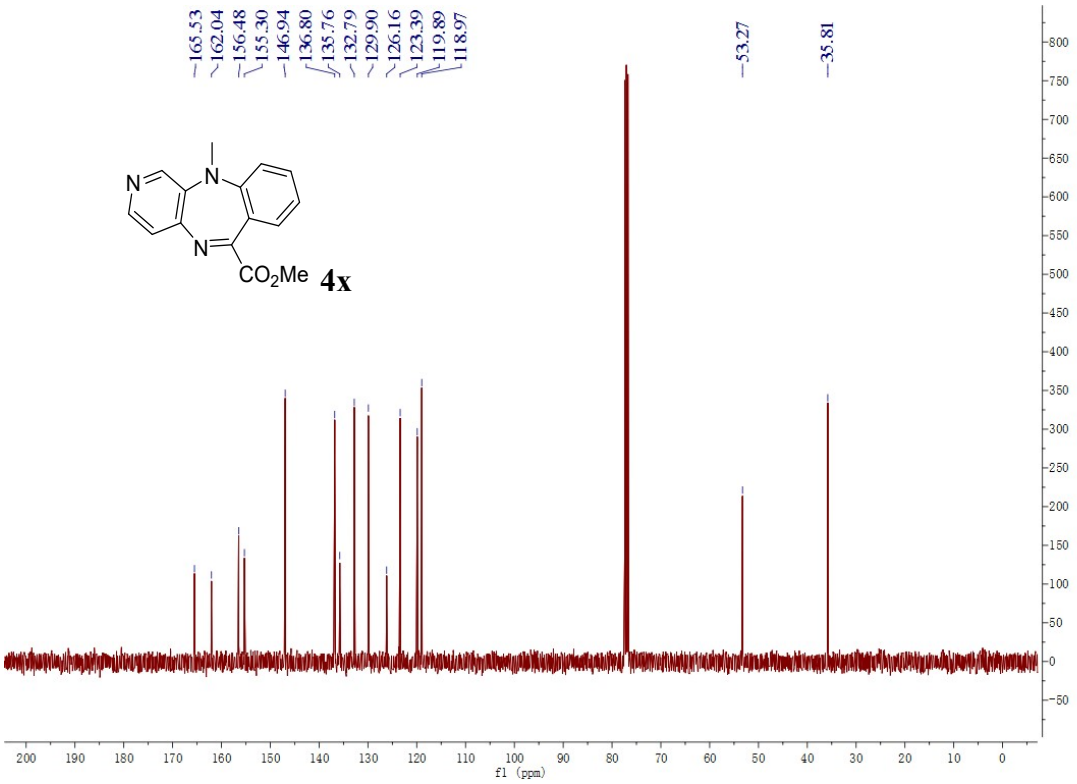
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4w**



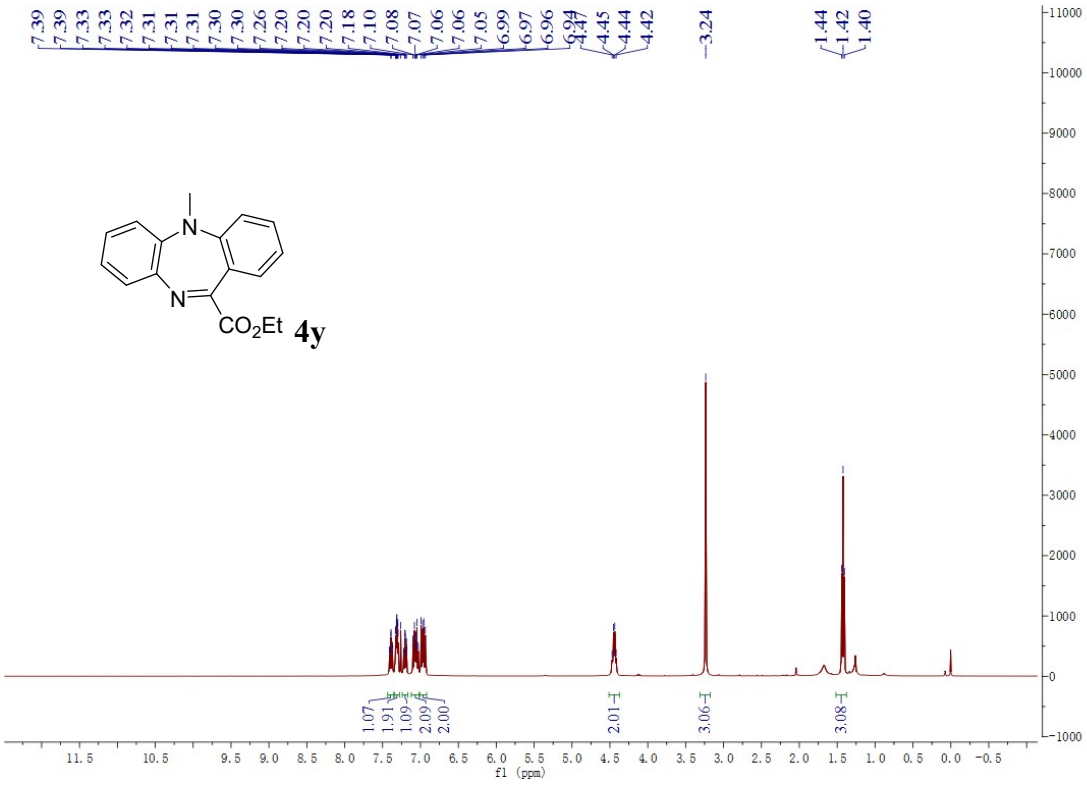
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4x**



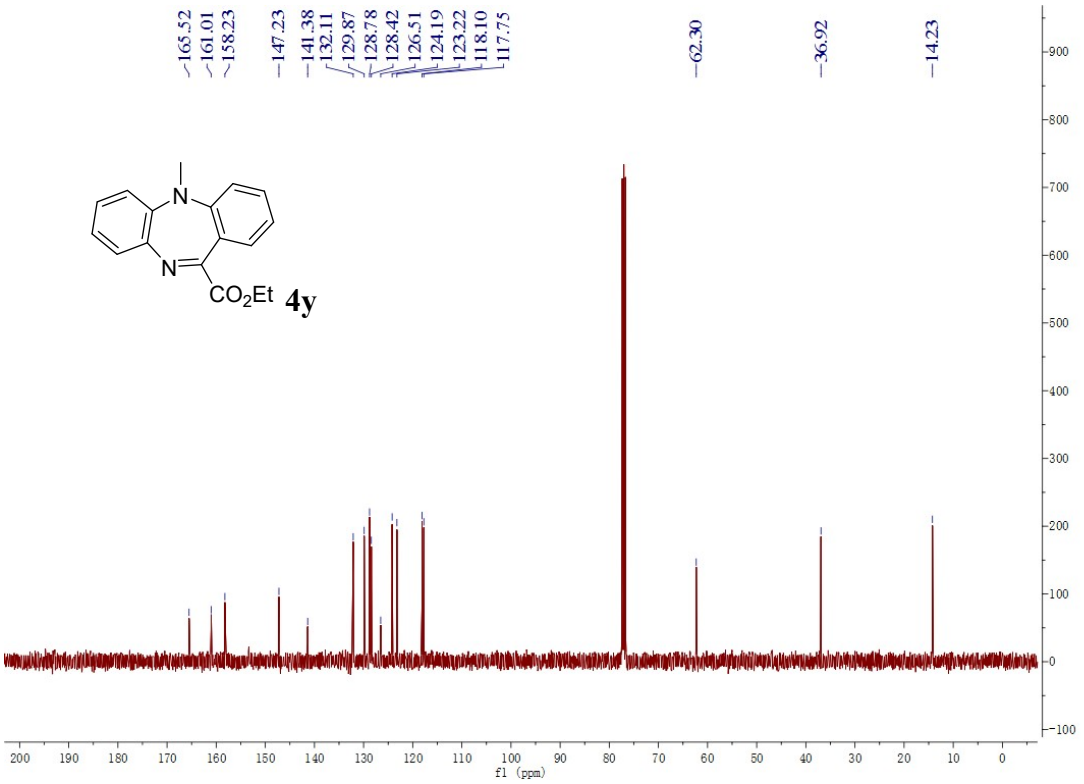
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4x**



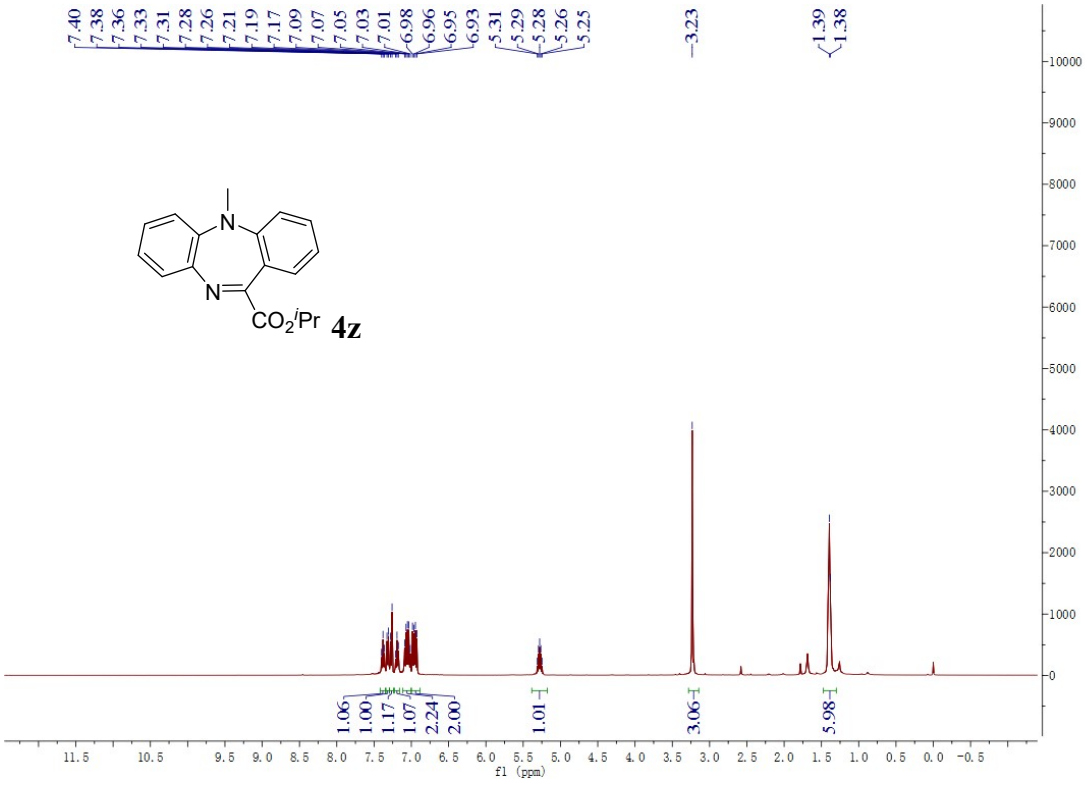
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4y**



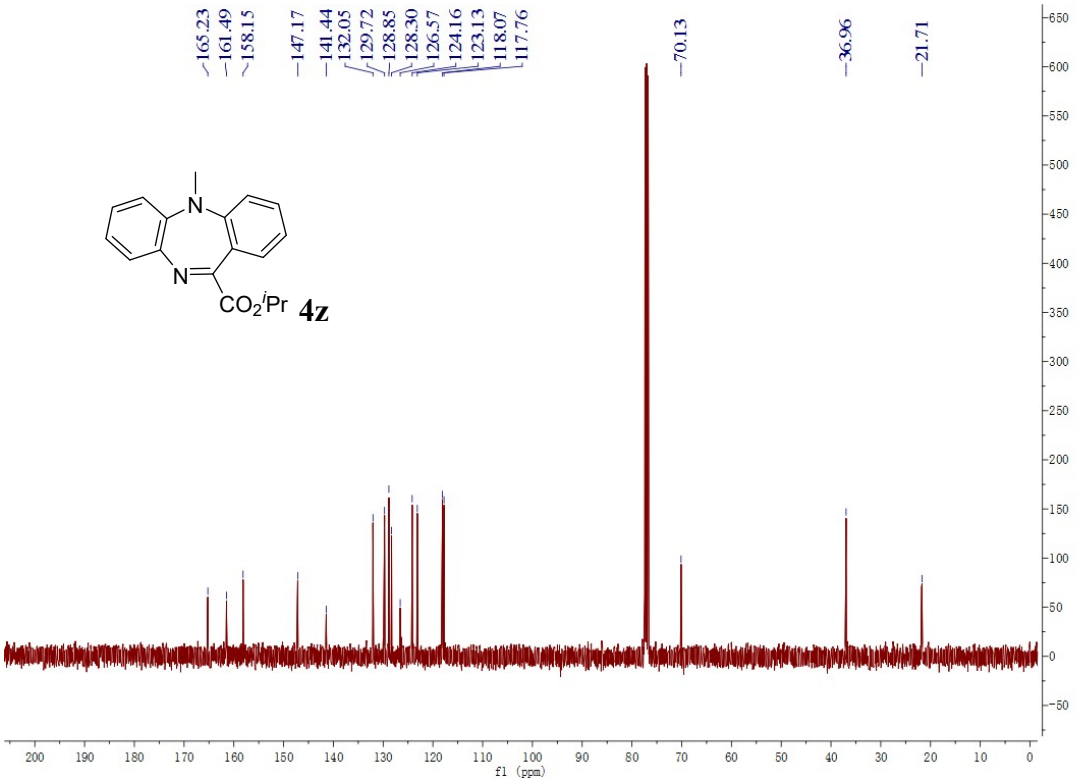
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4y**



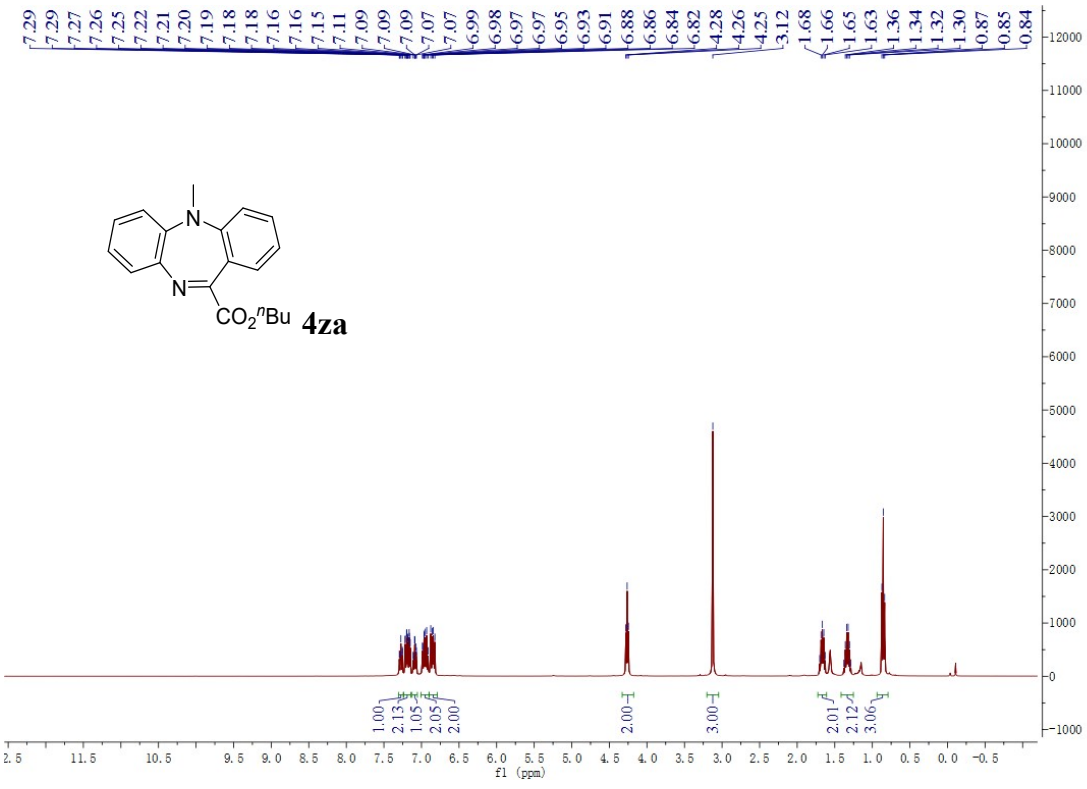
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4z**



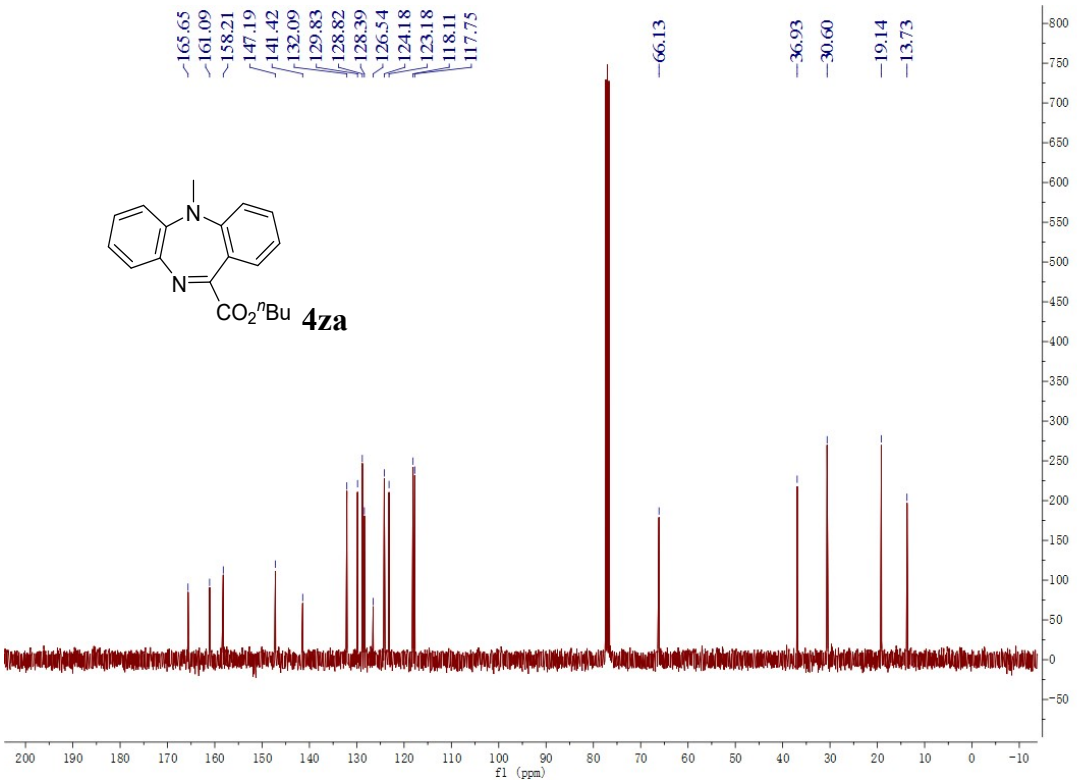
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4z**



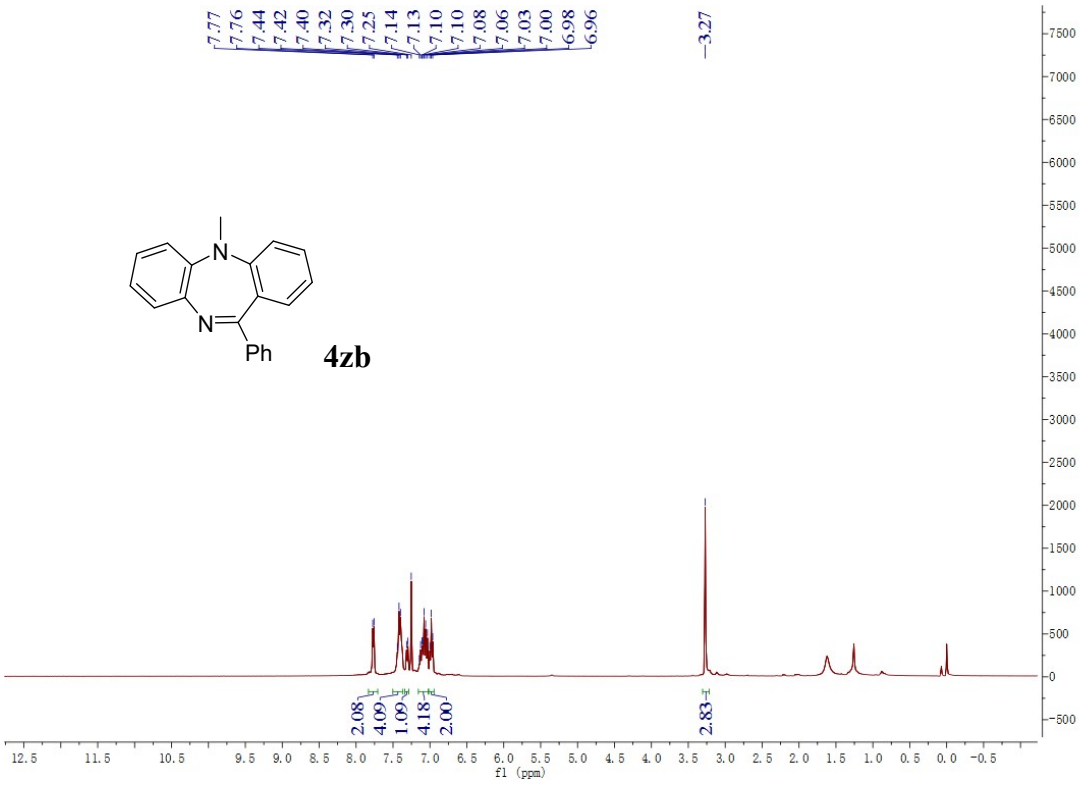
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4za**



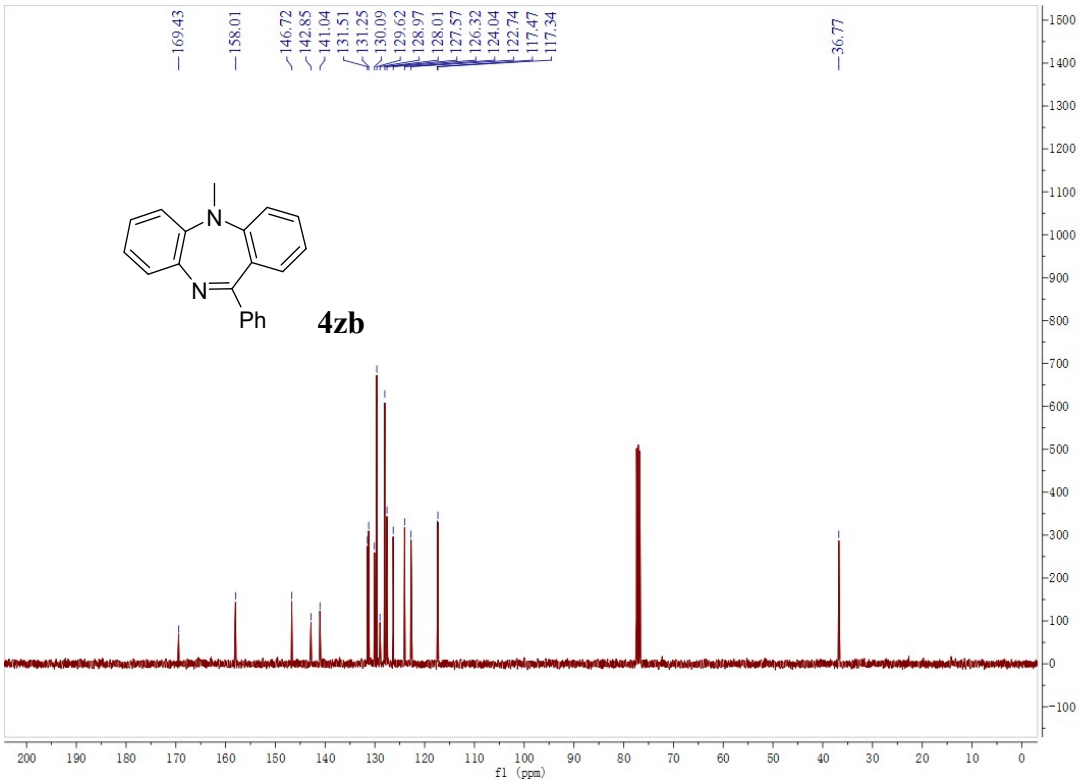
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4za**



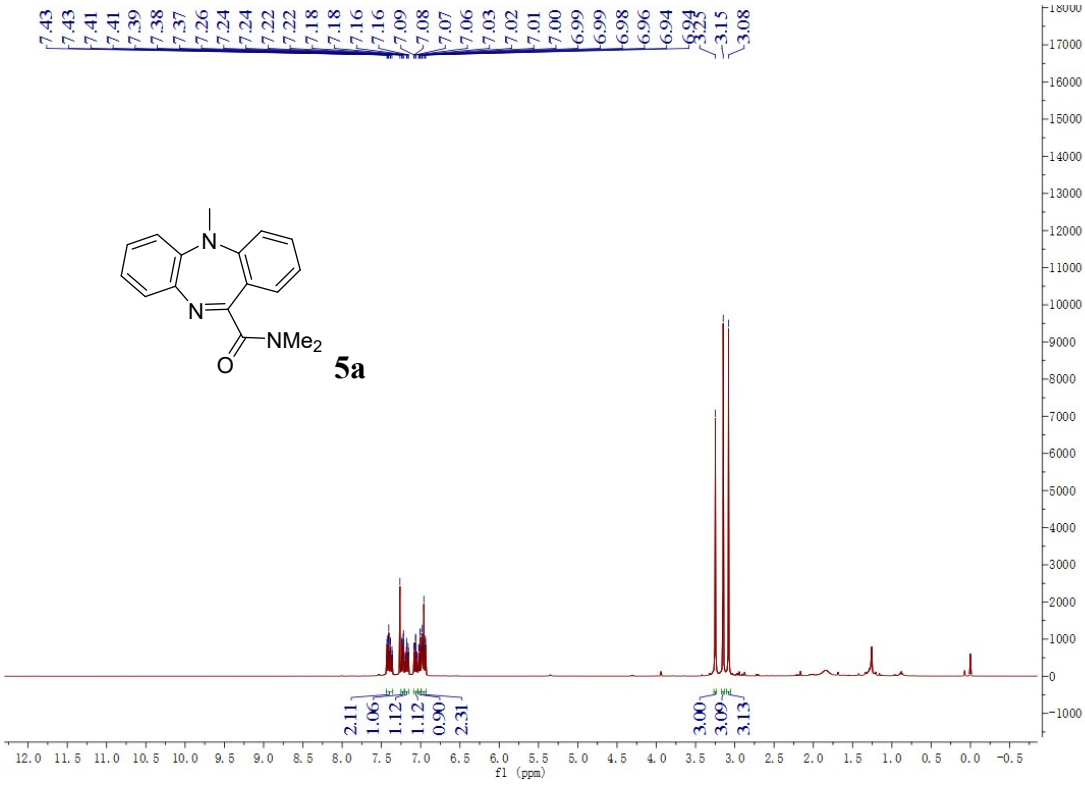
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4zb**



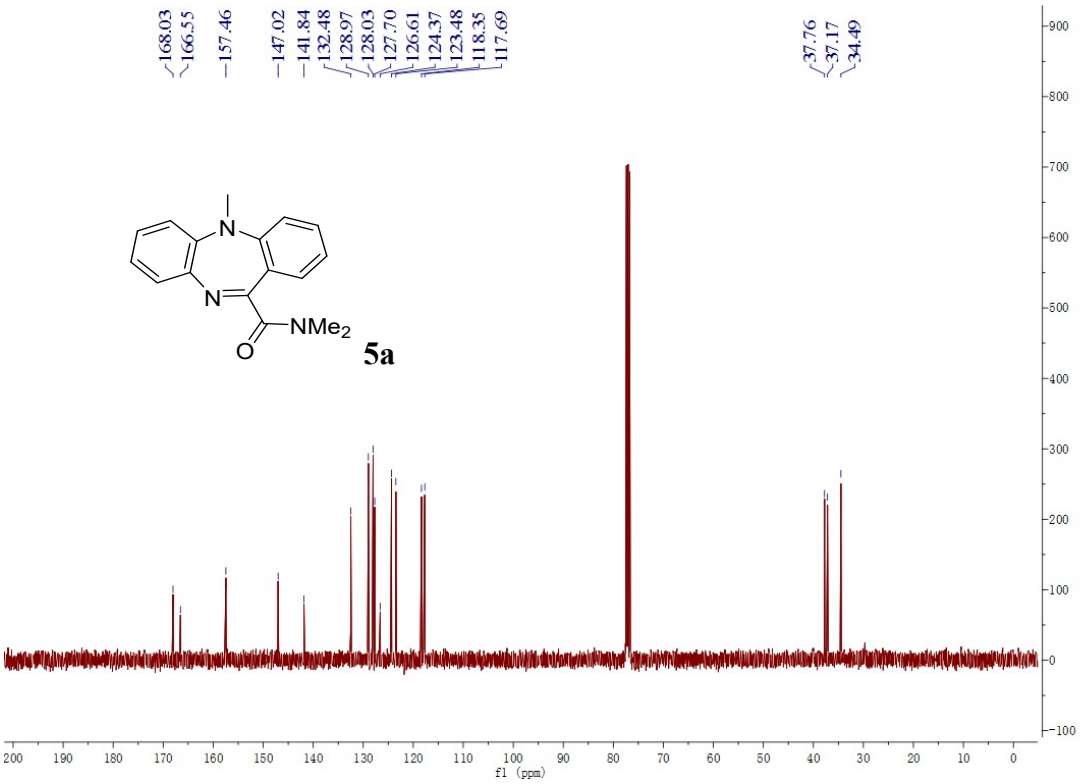
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4zb**



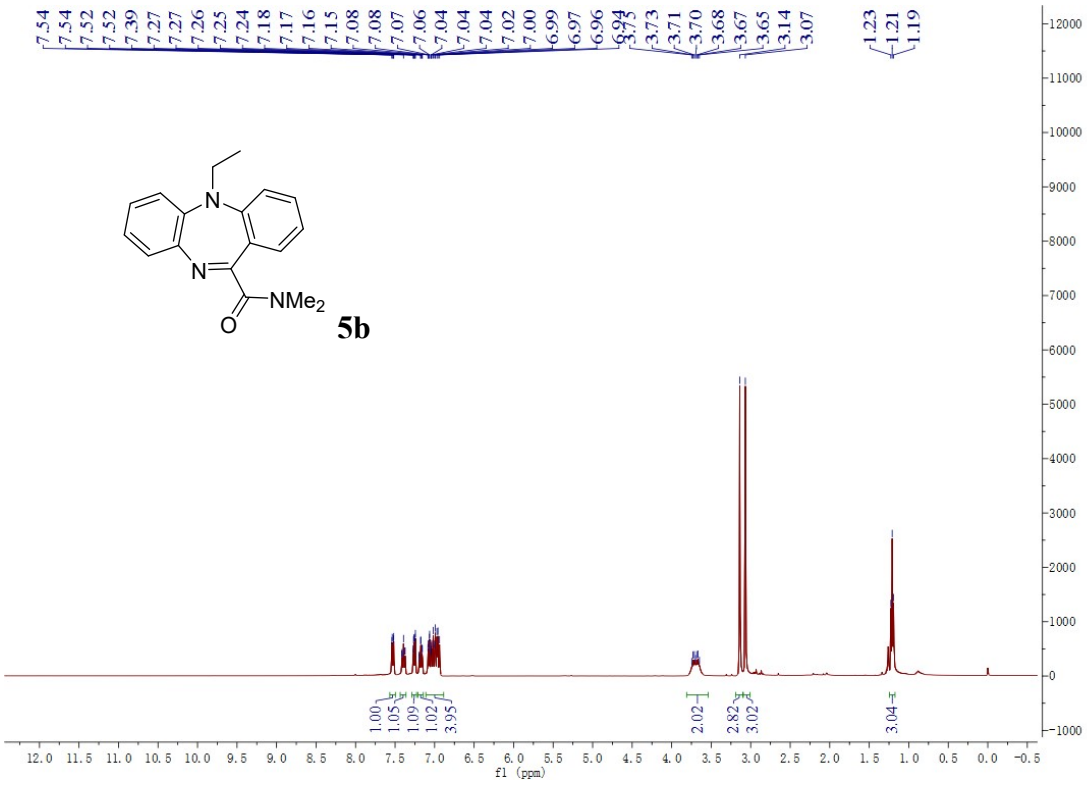
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**



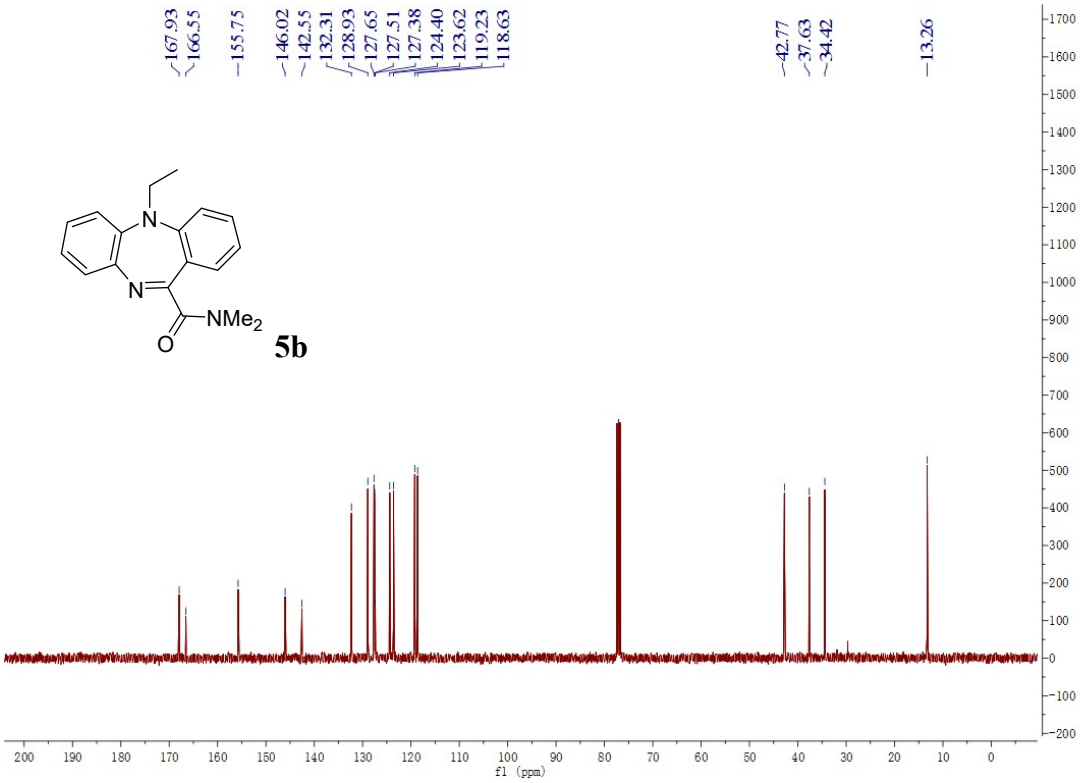
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5a**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

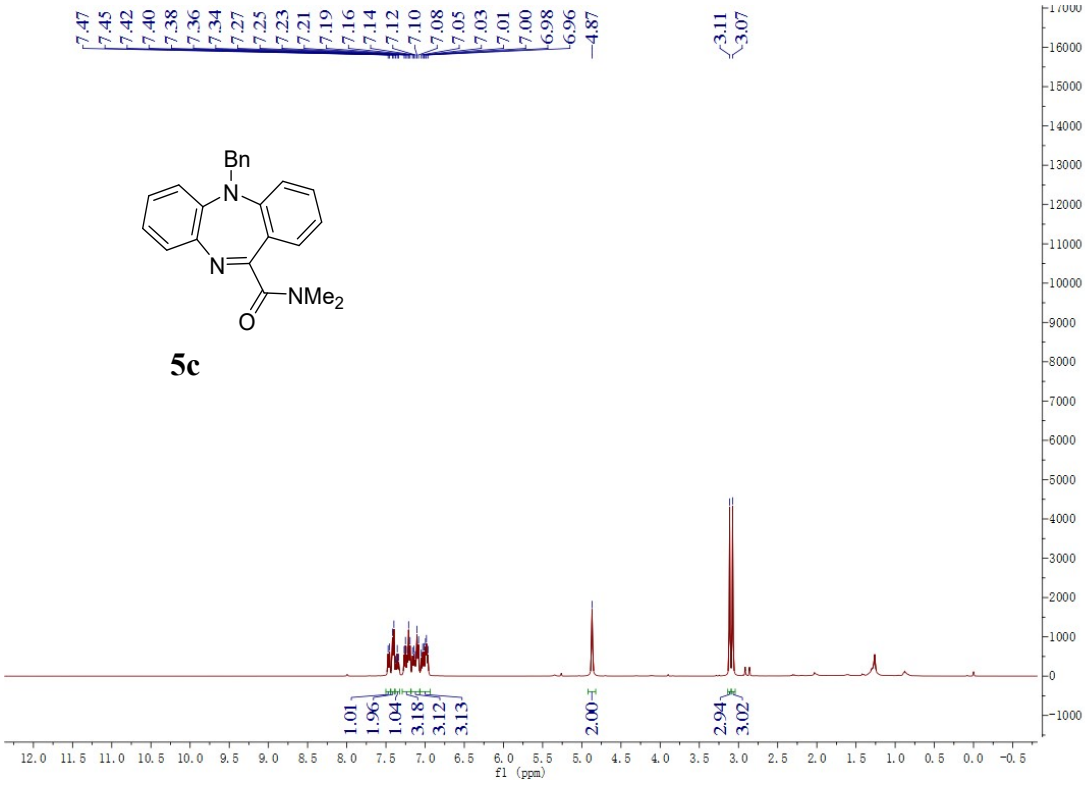


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5b**



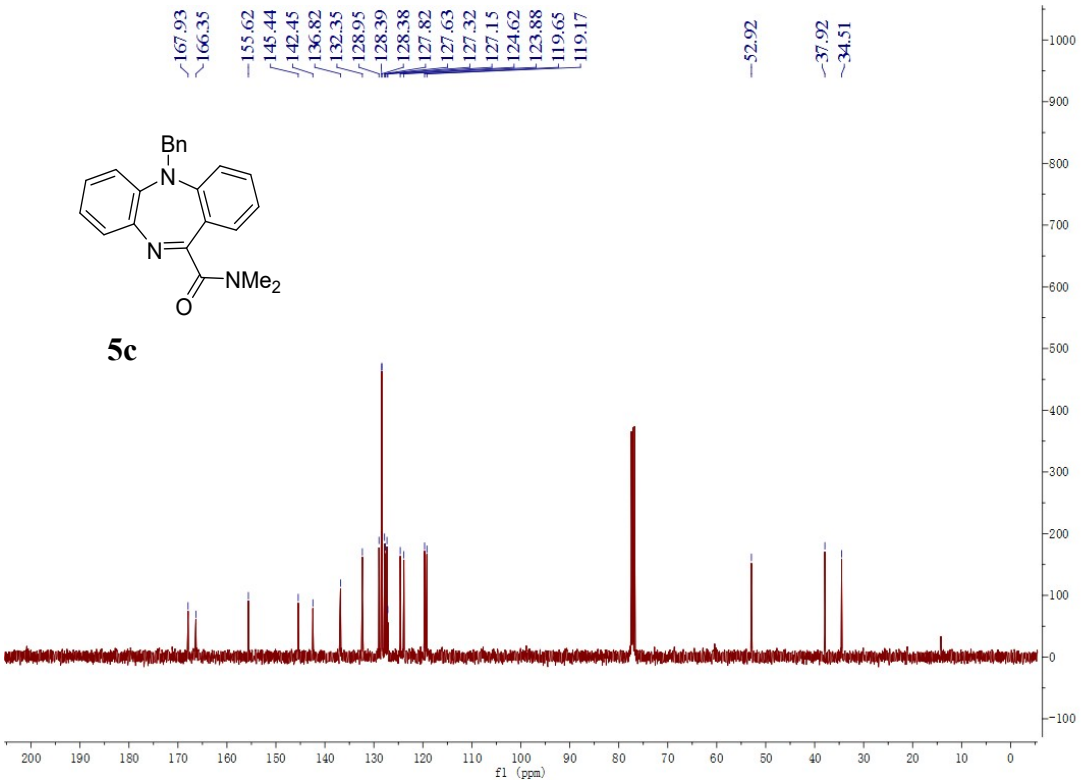
5b

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5c**

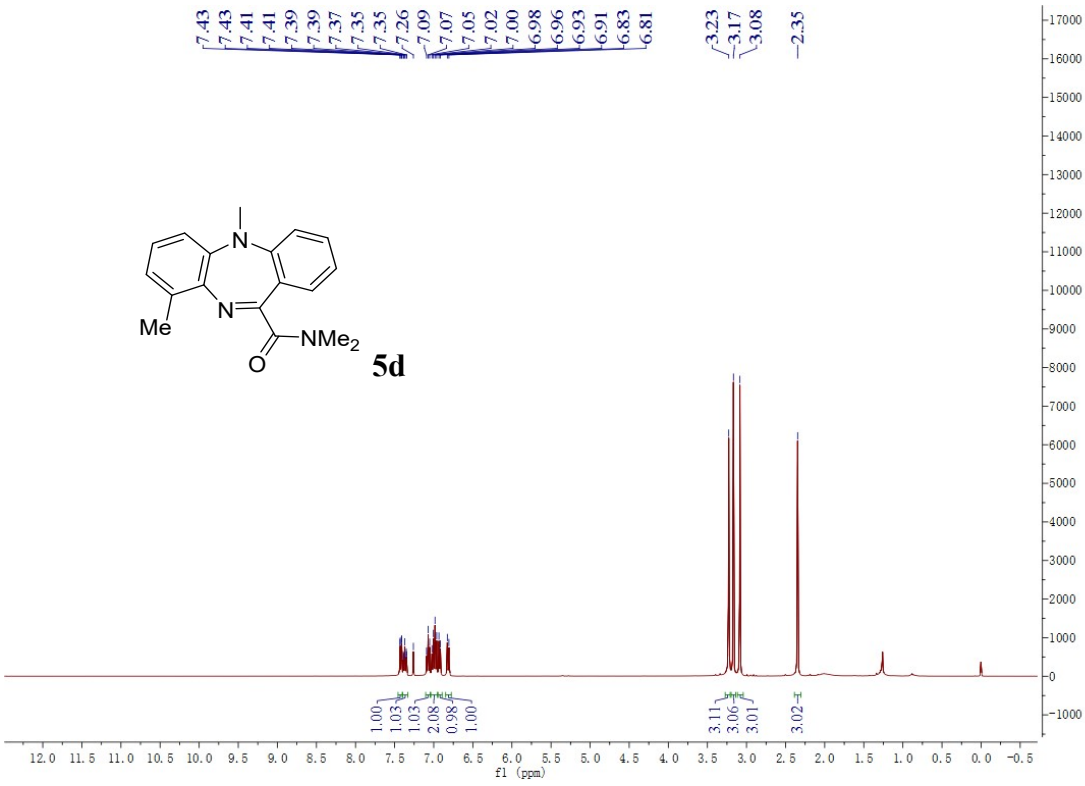


5c

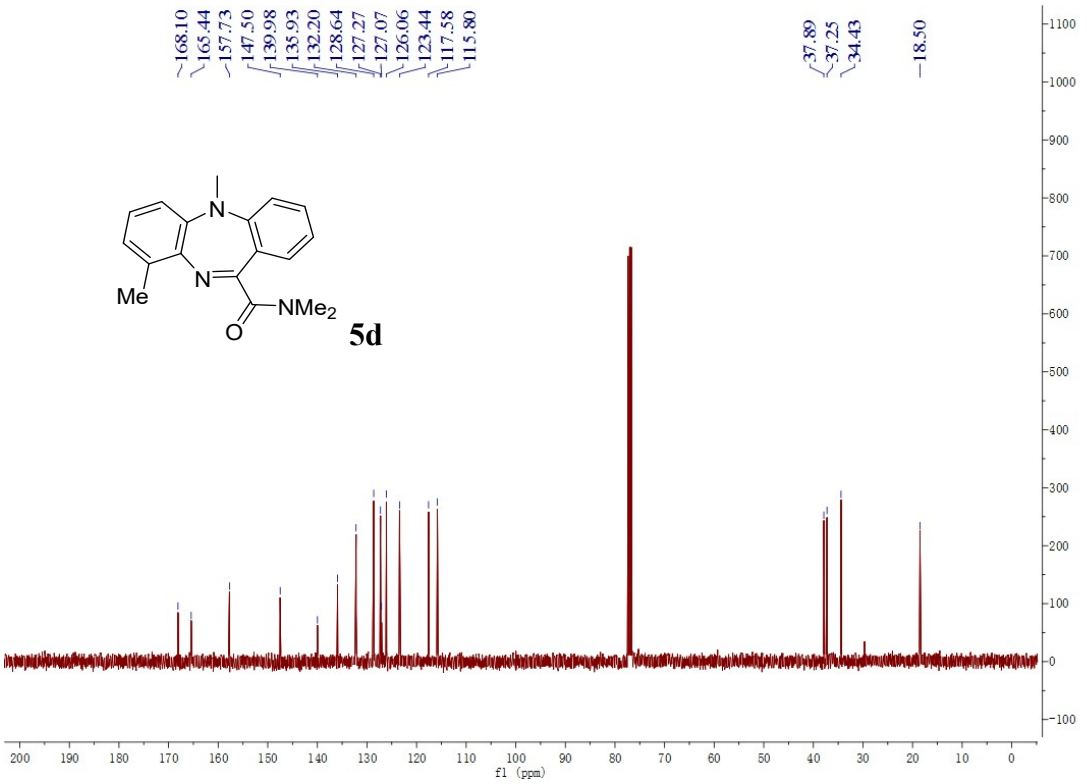
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5c**



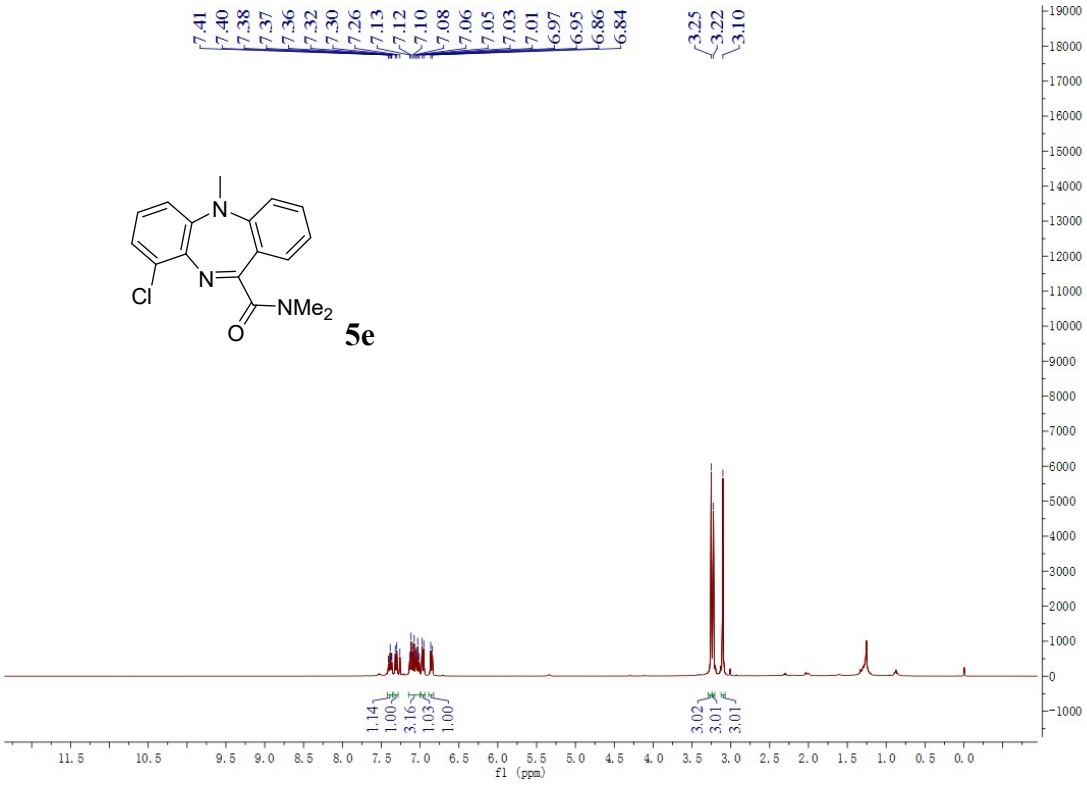
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**



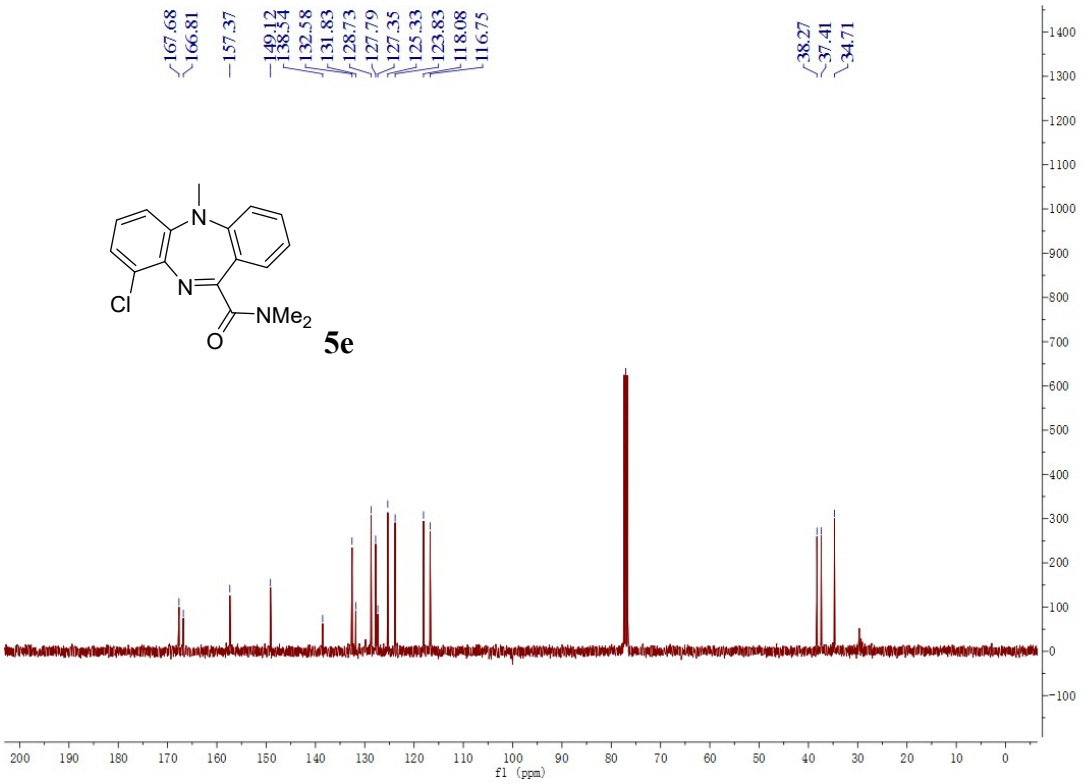
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5d**



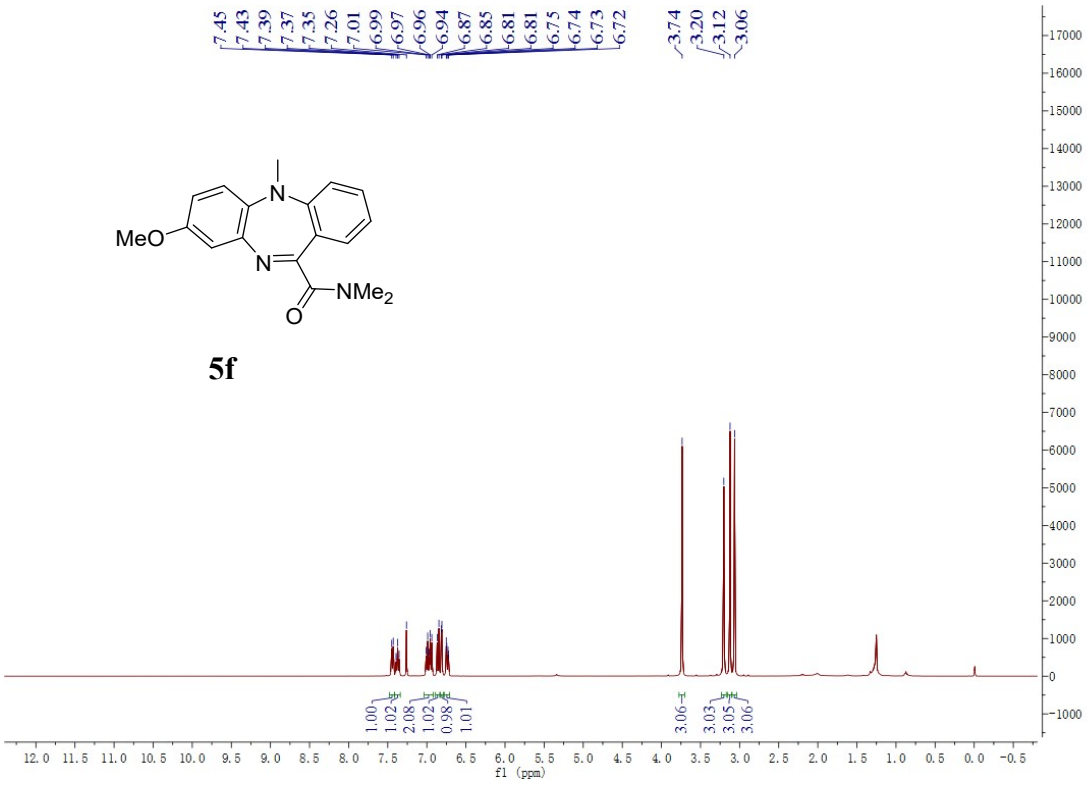
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**



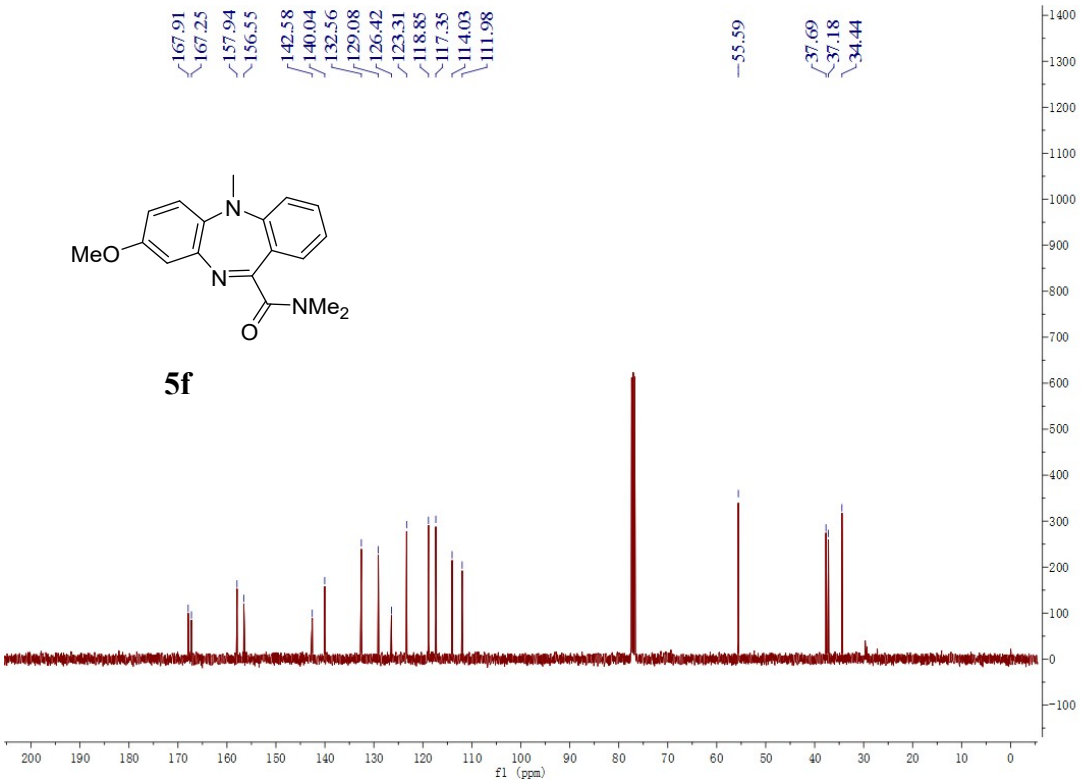
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5e**



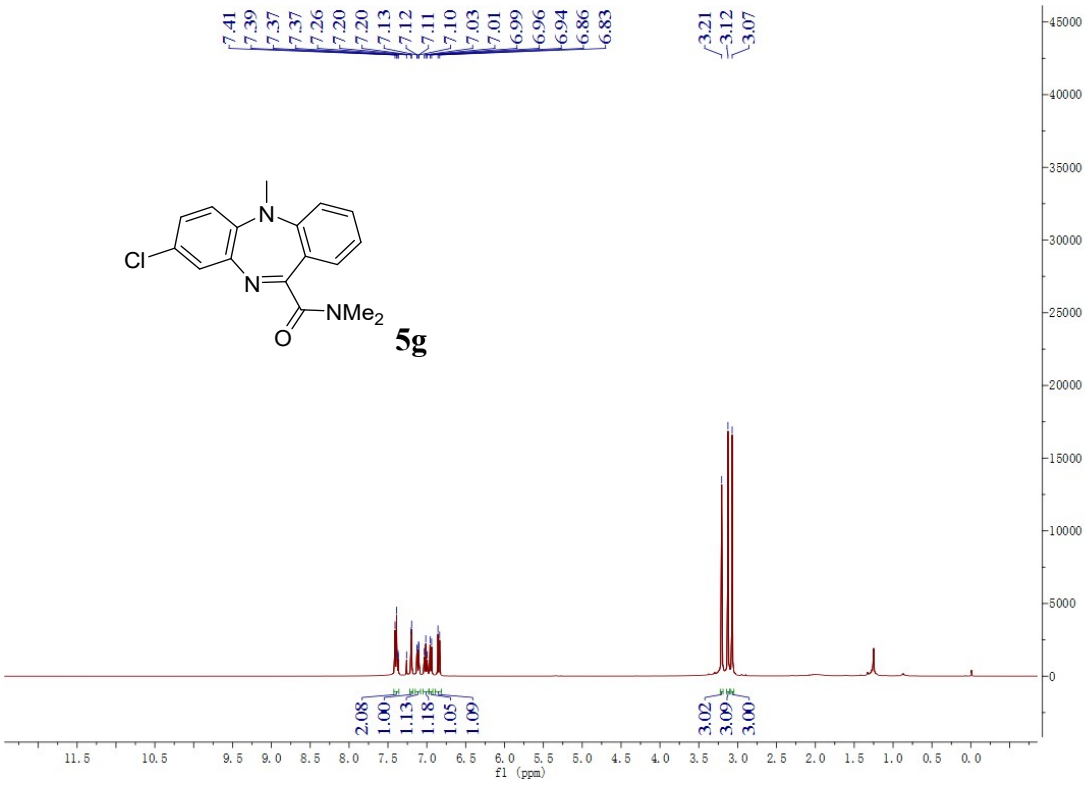
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5f**



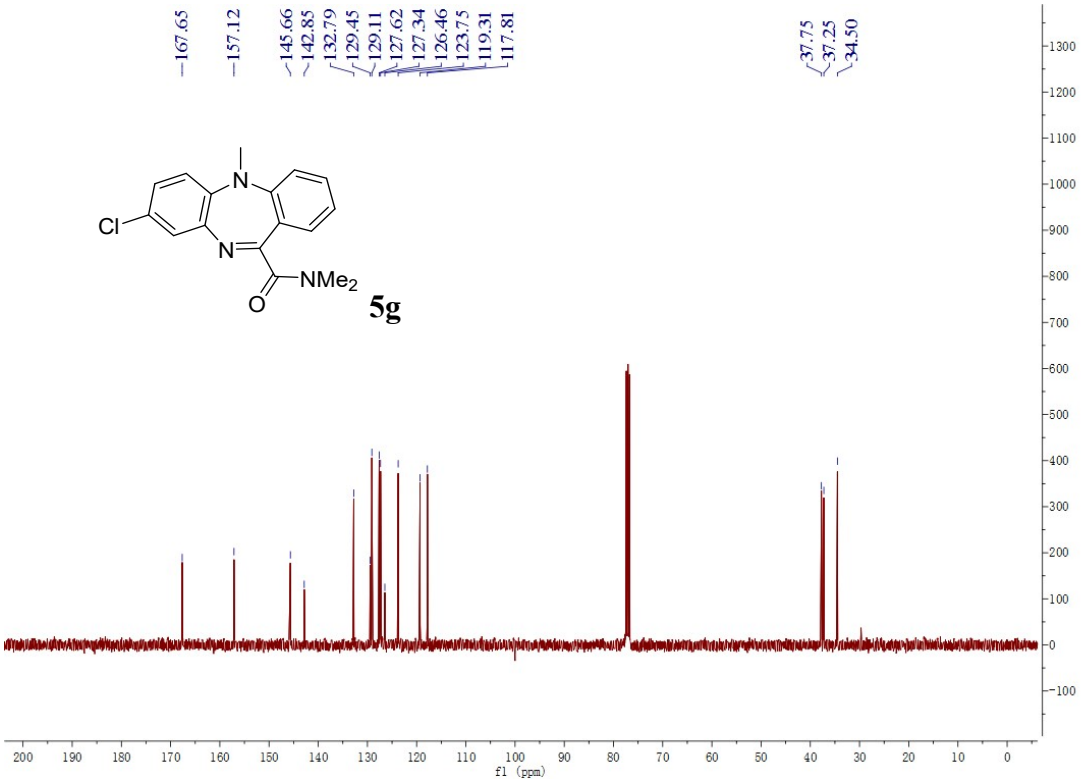
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5f**



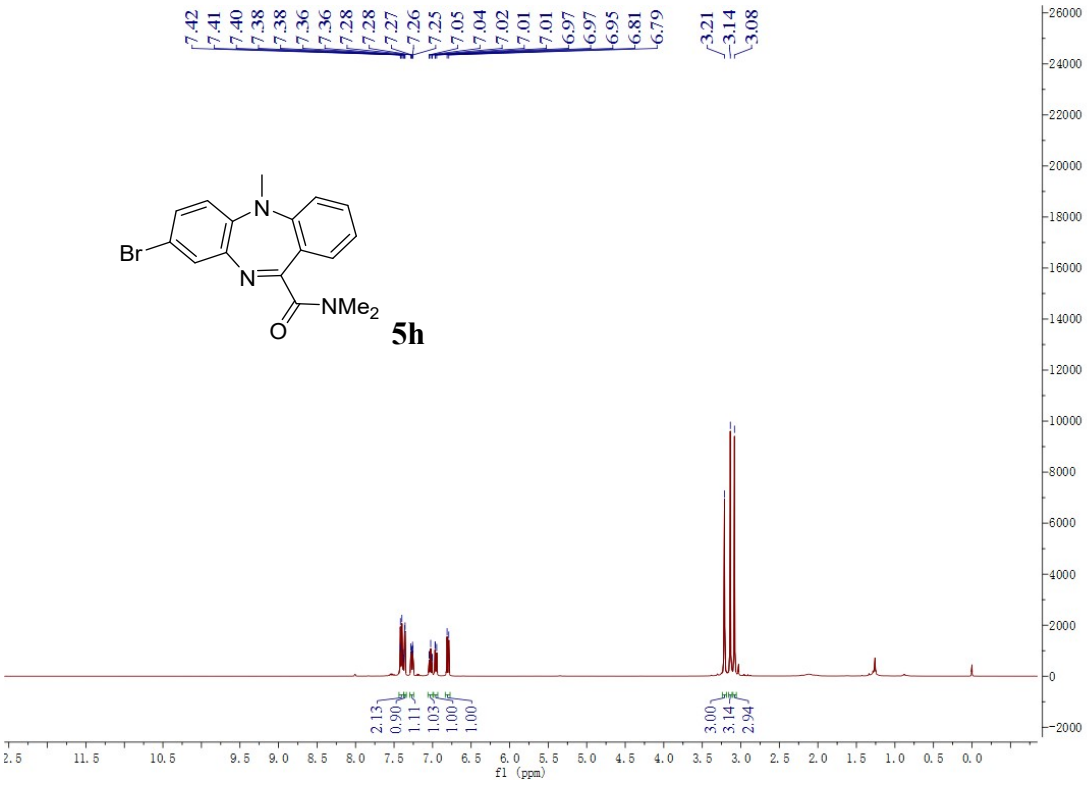
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5g**



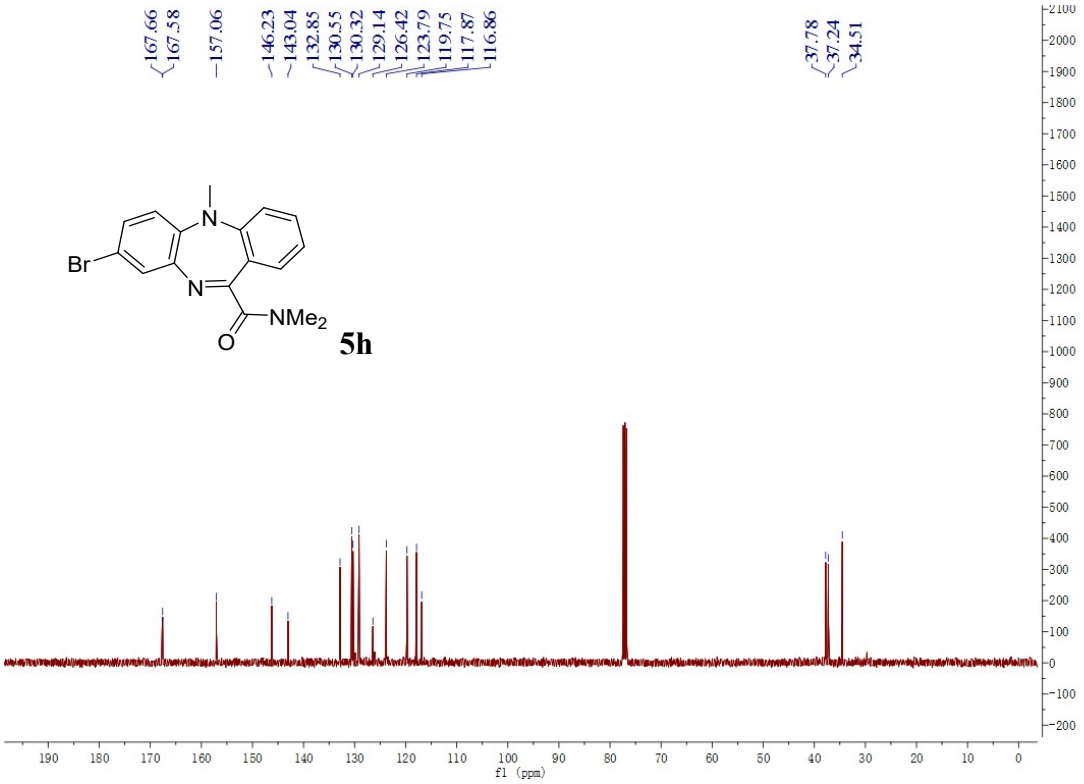
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5g**



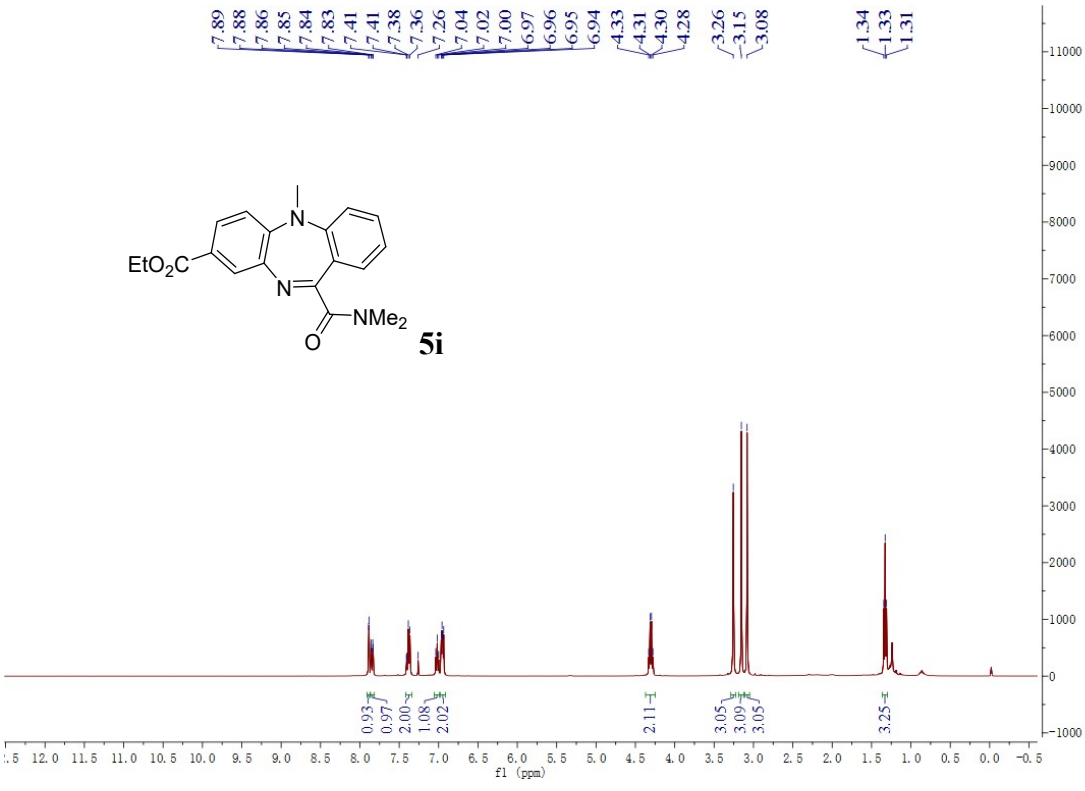
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5h**



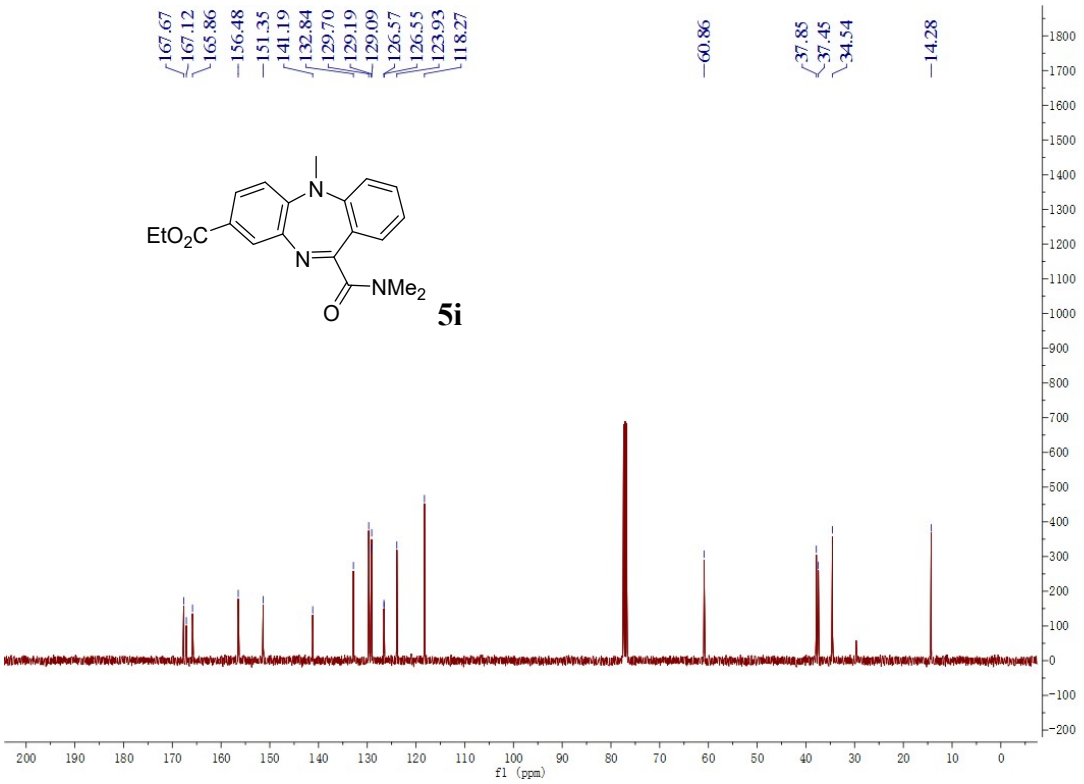
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5h**



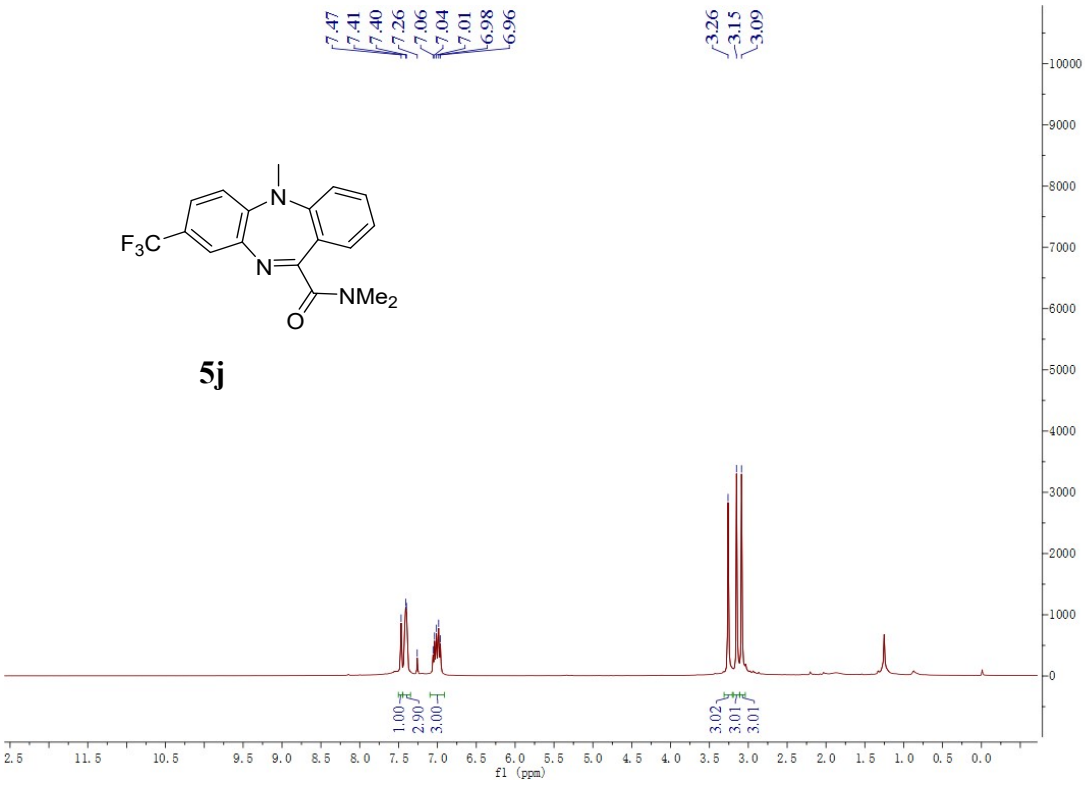
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5i**



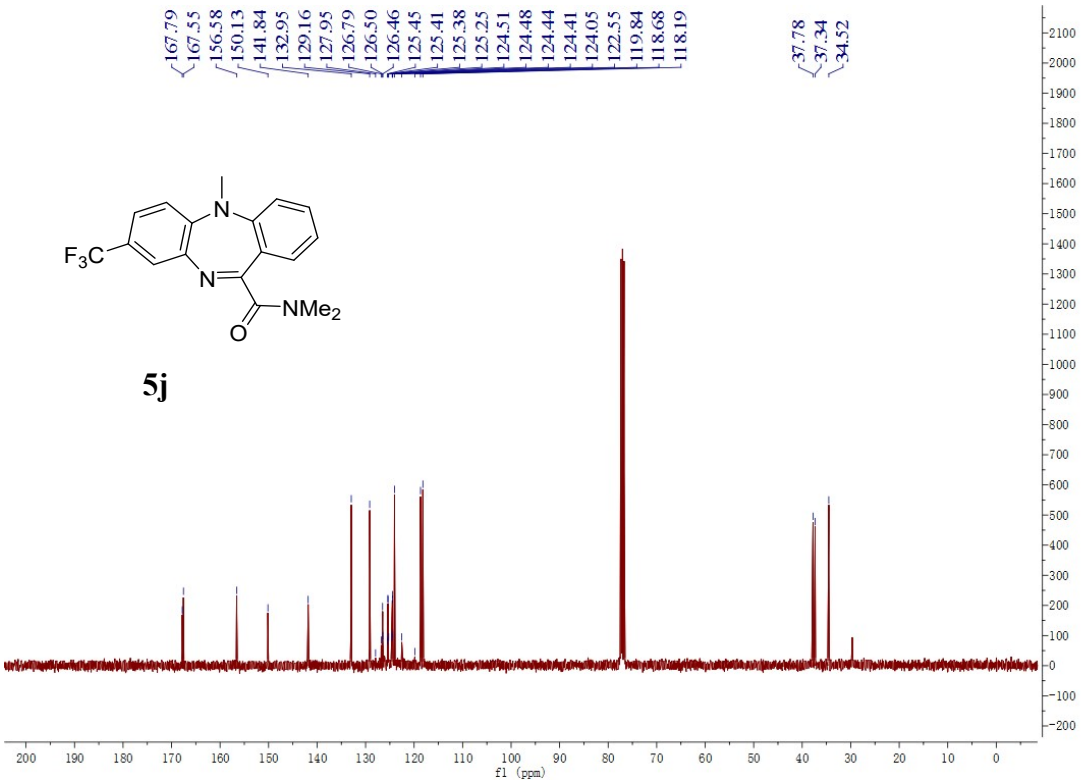
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5i**



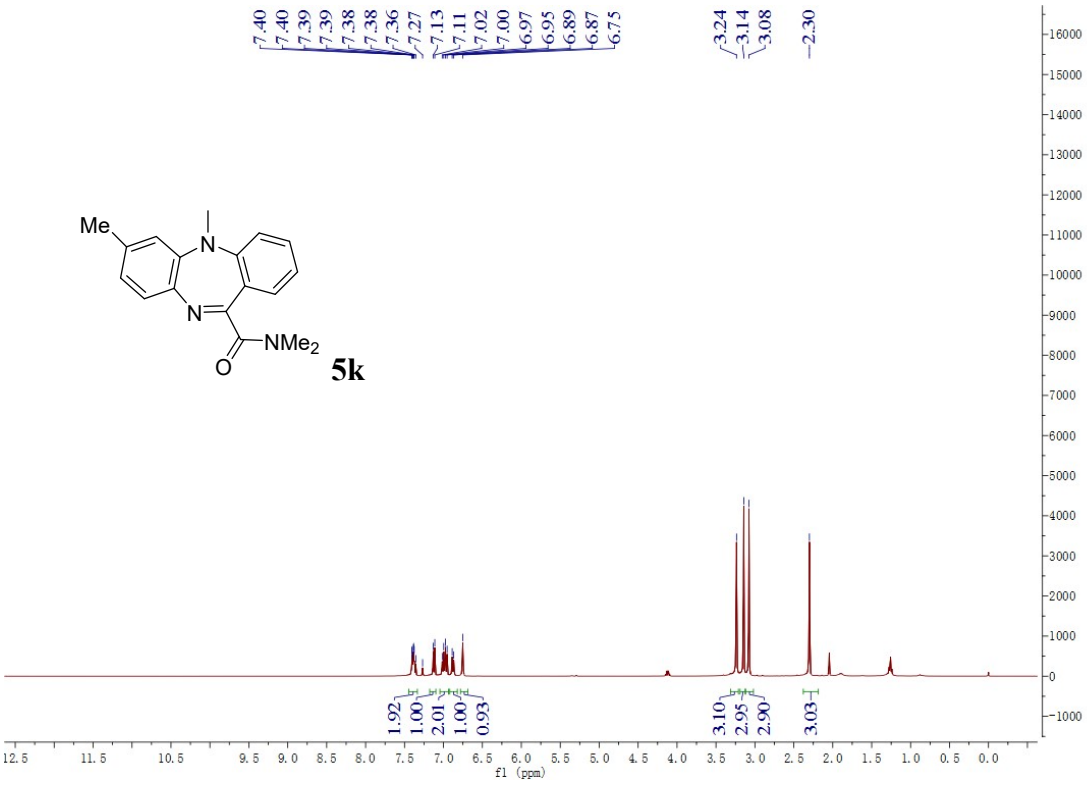
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5j**



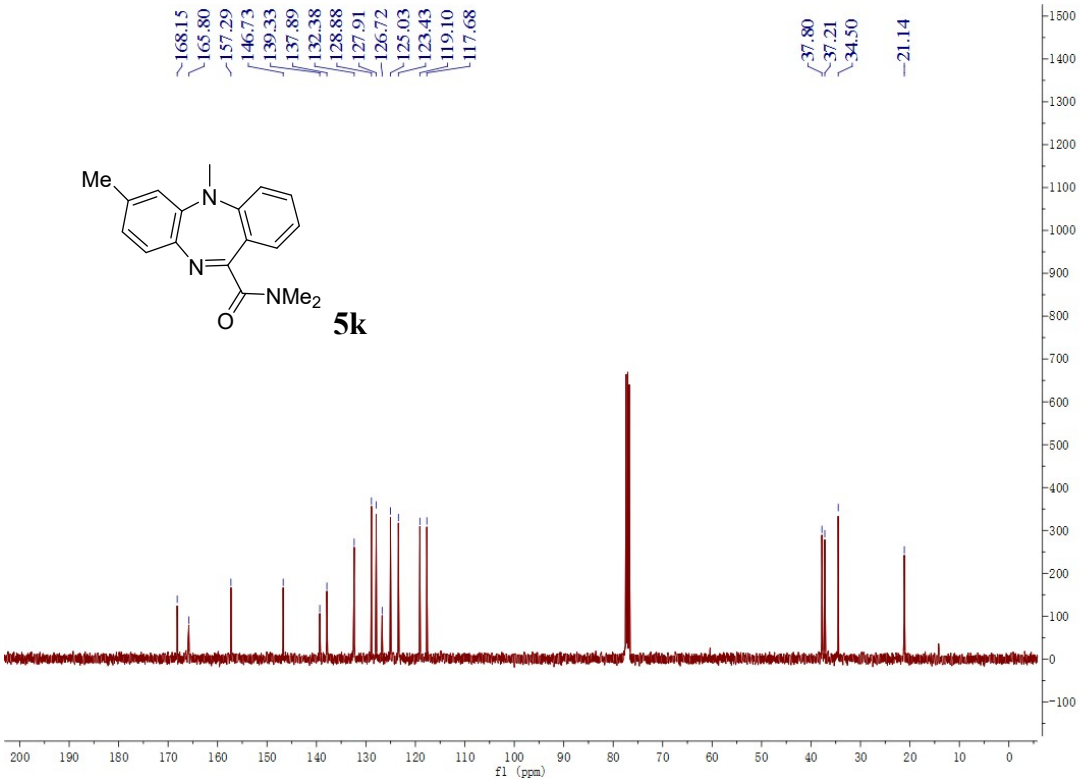
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5j**



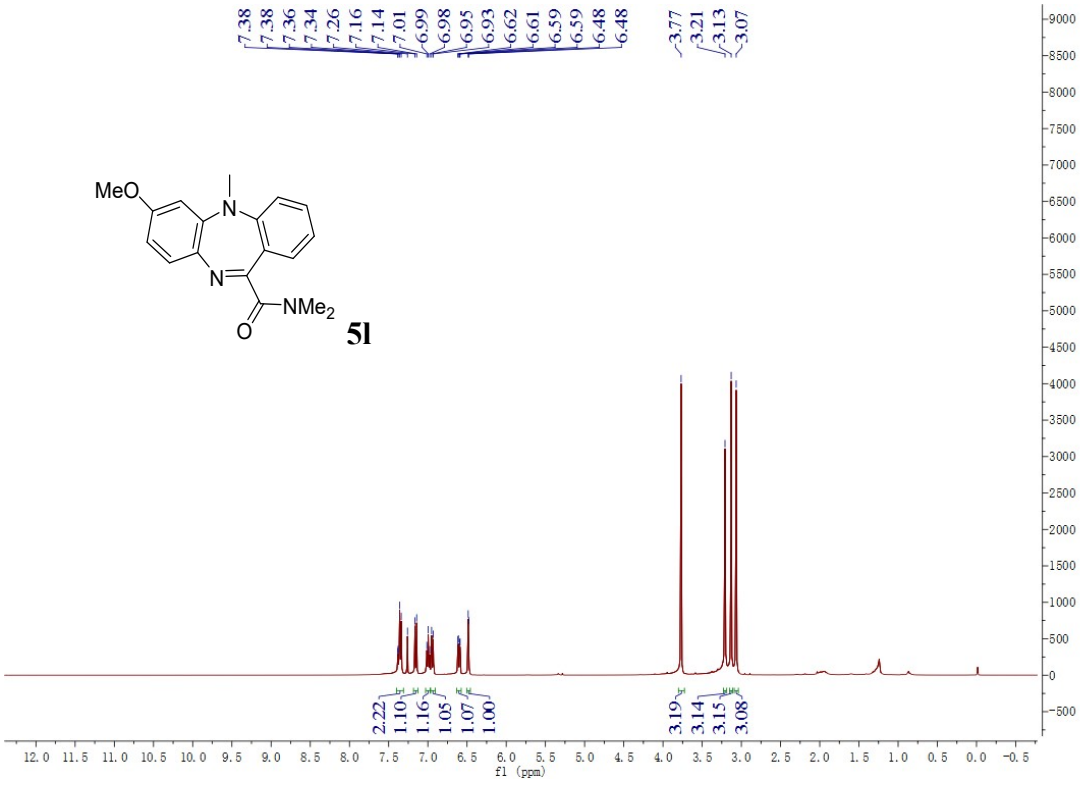
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5k**



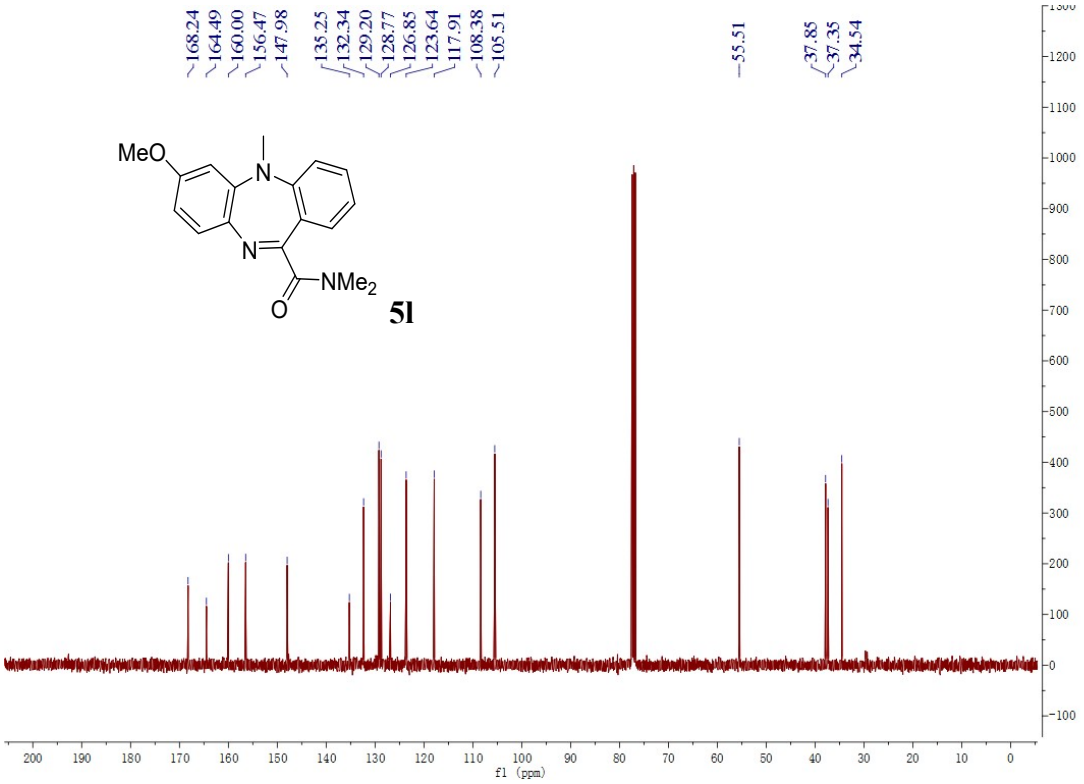
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5k**



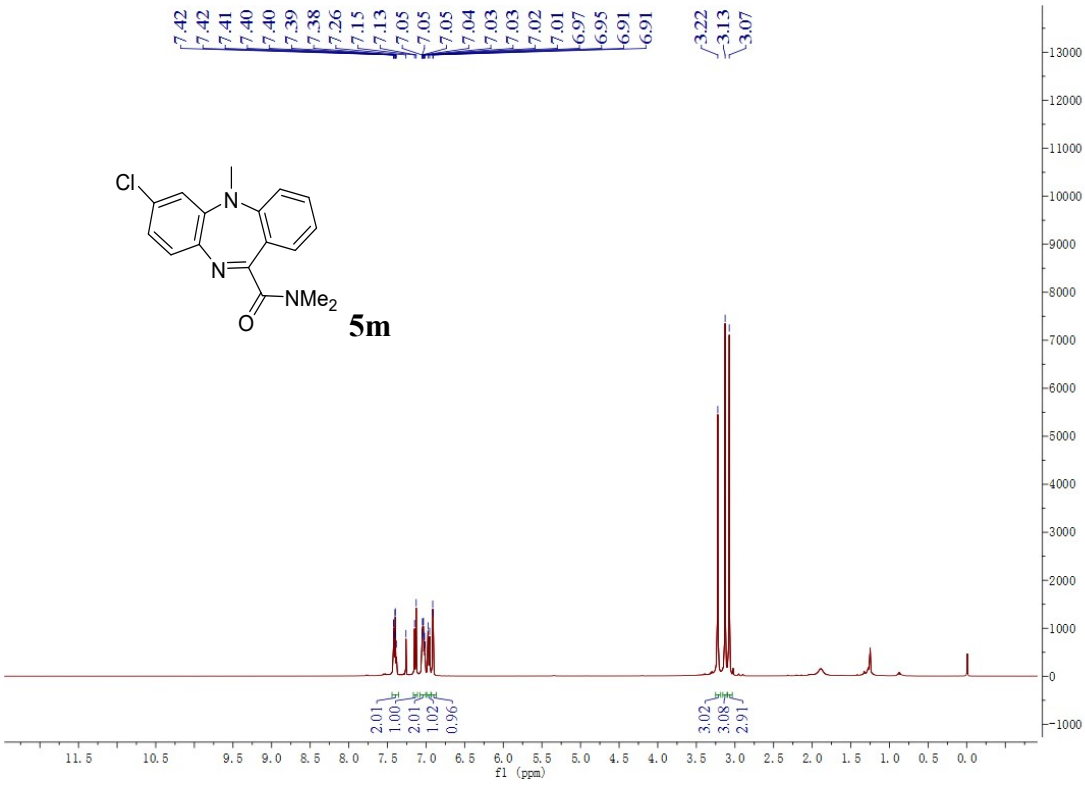
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5l**



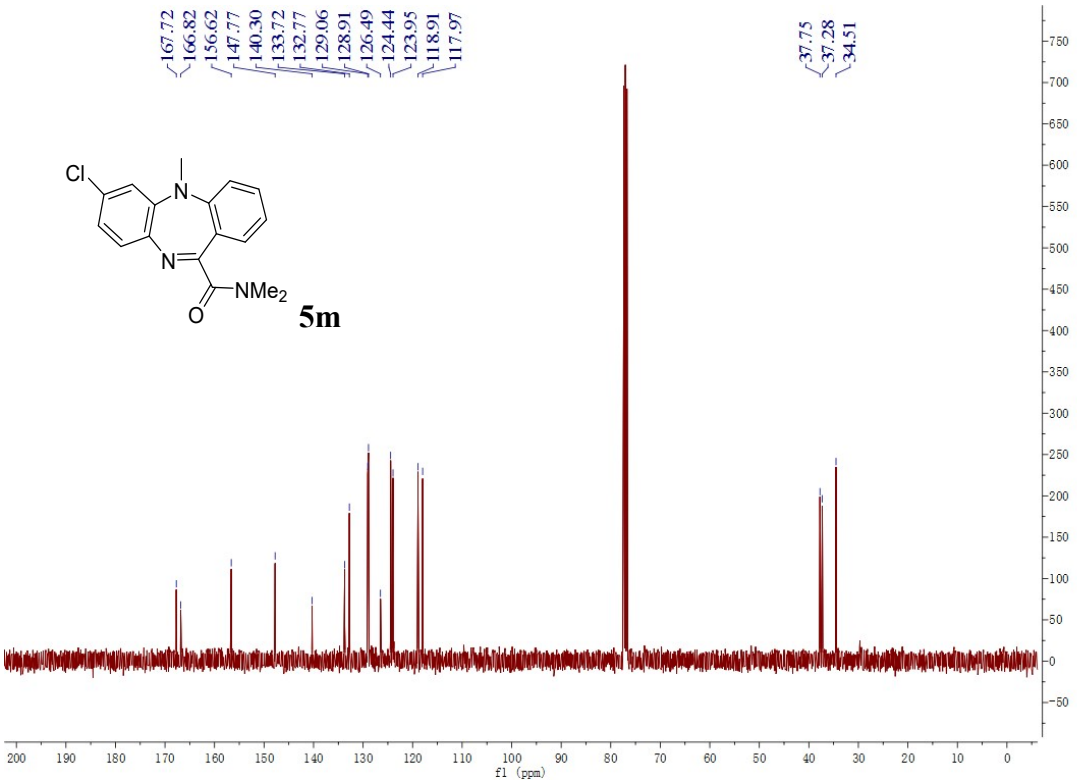
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5l**



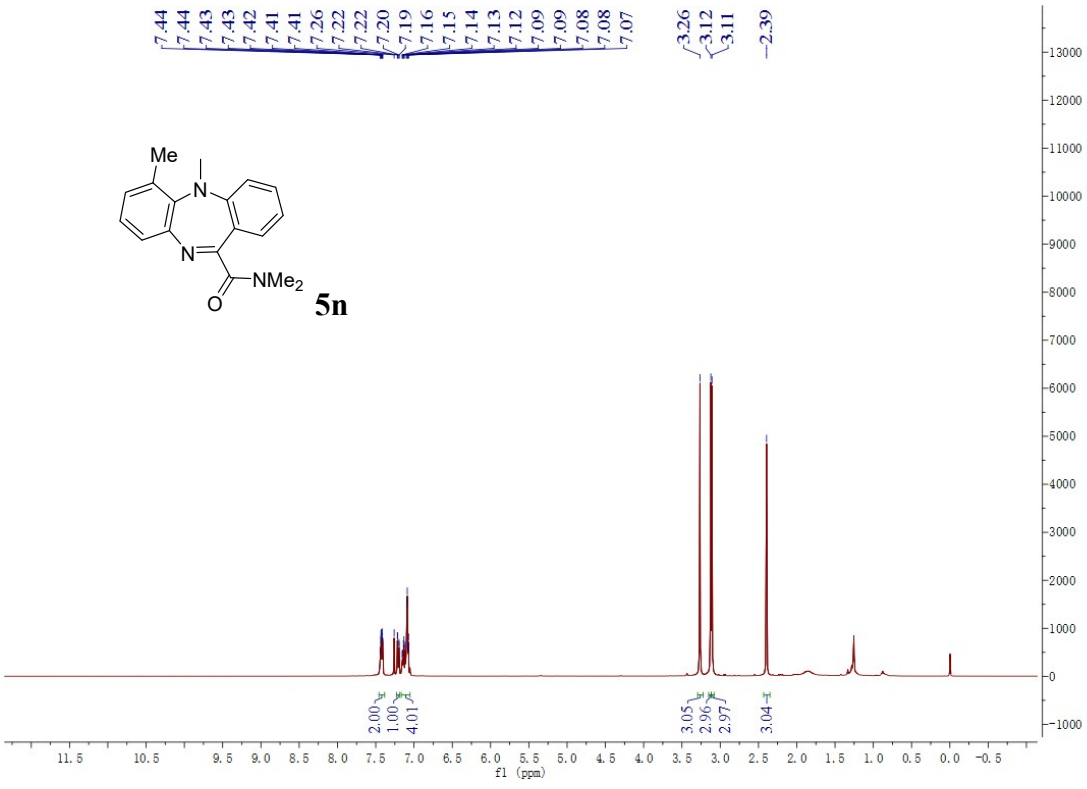
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5m**



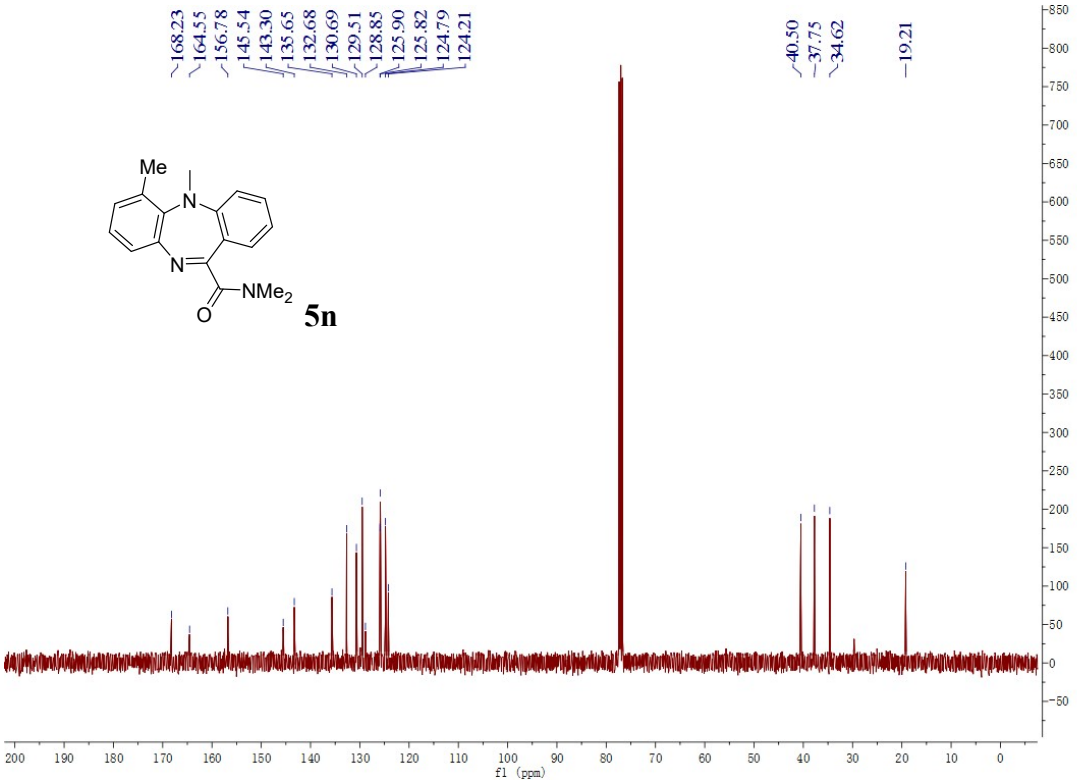
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5m**



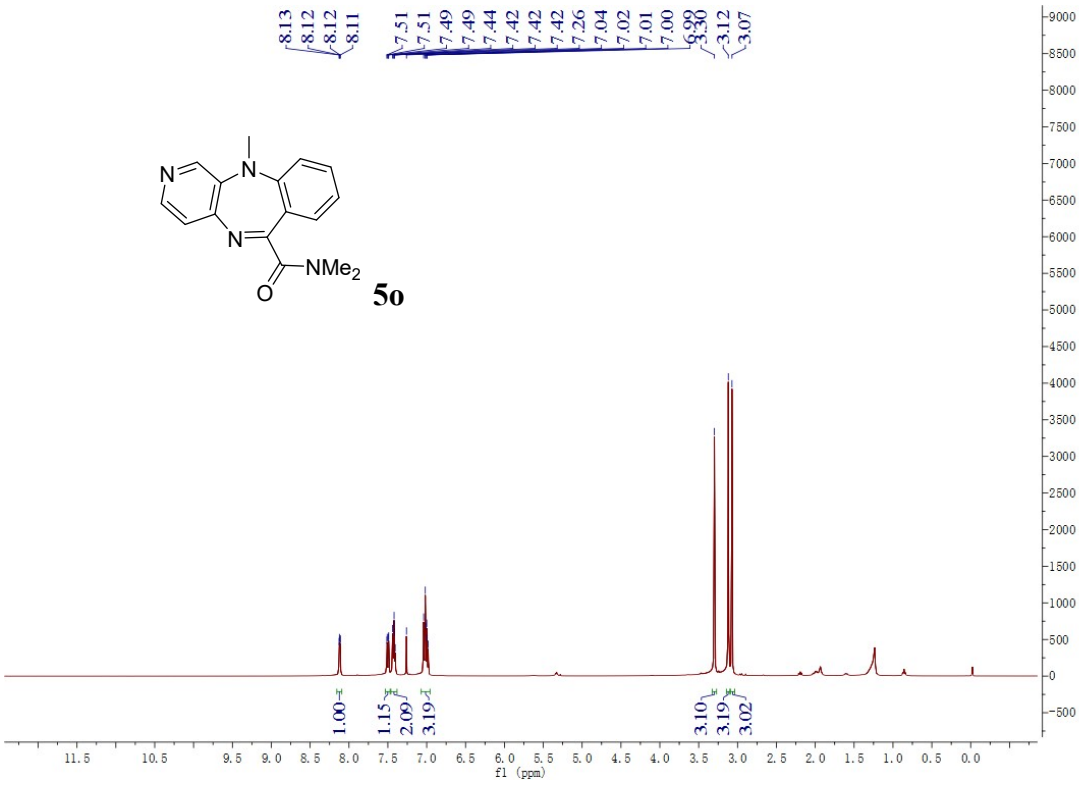
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5n**



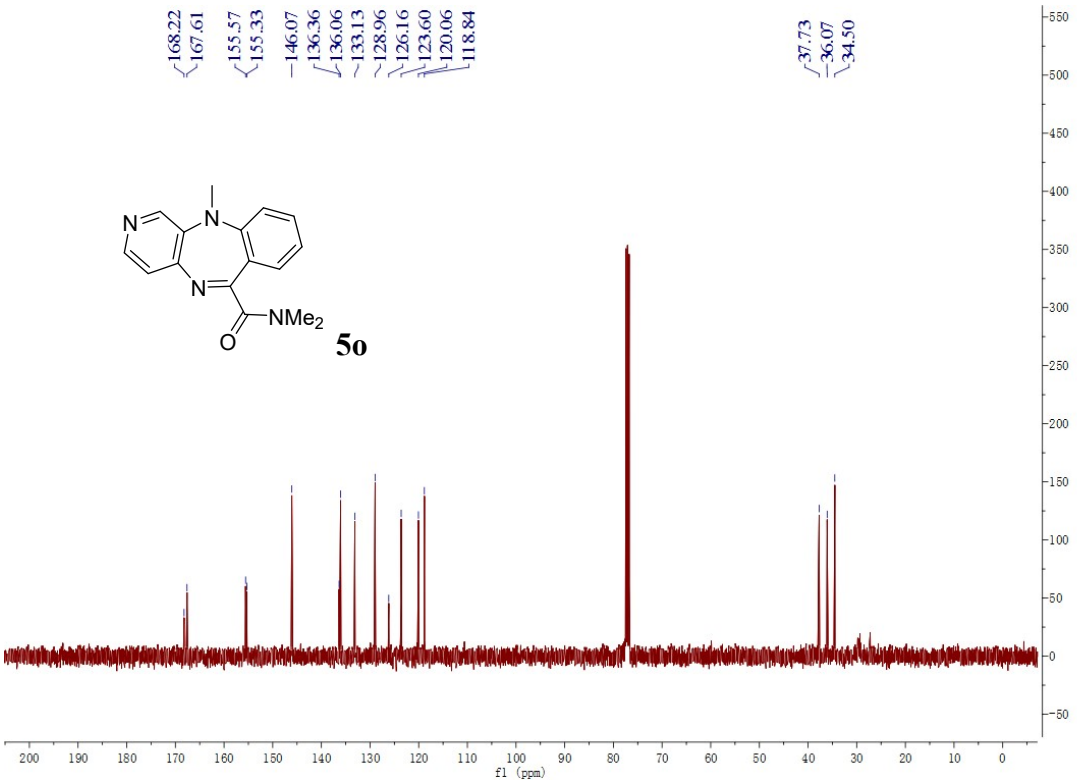
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5n**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5o**

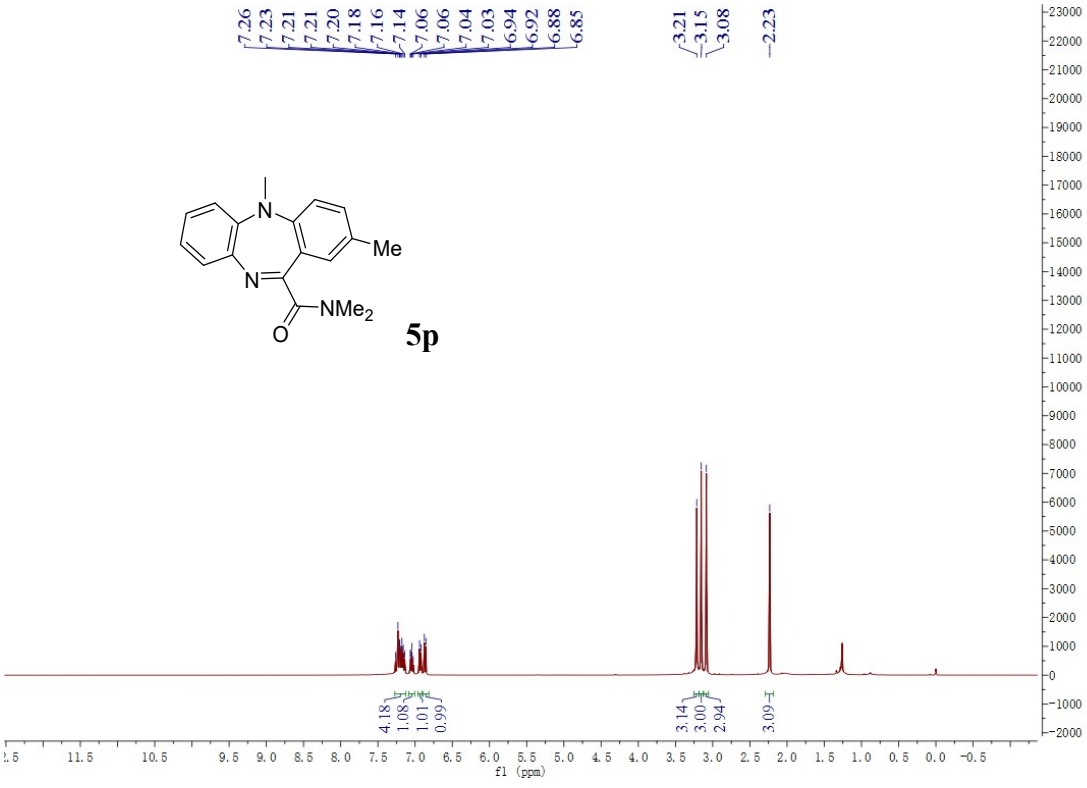


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5o**



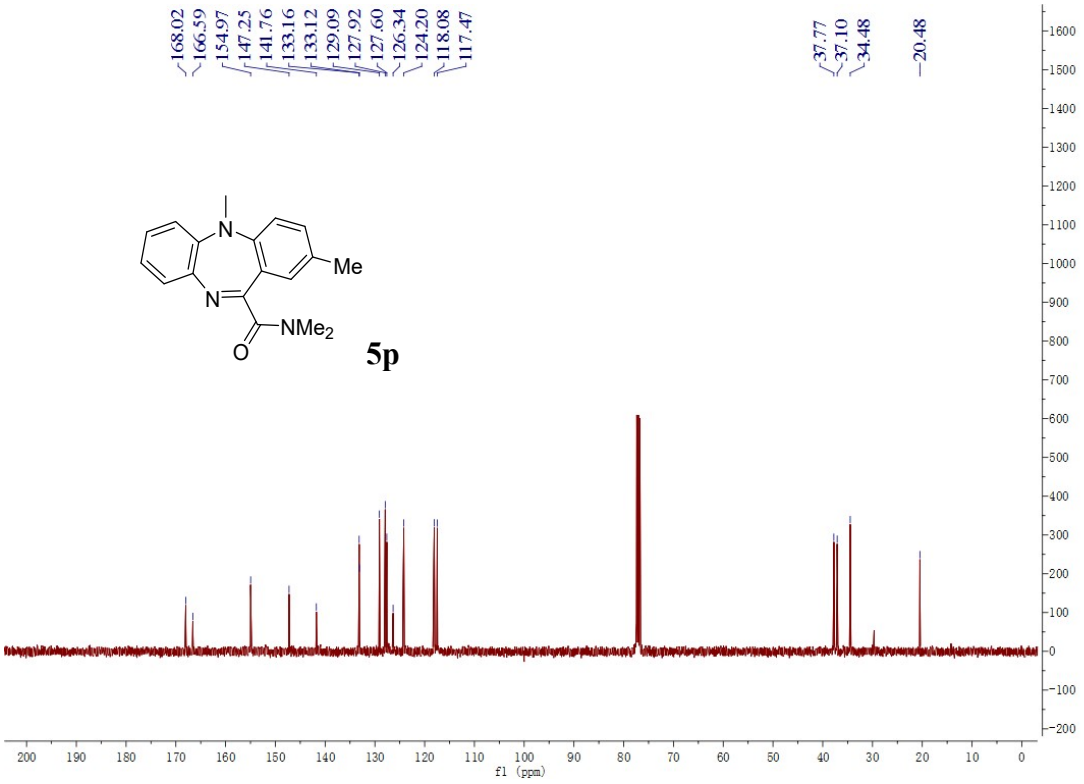
5o

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5p**



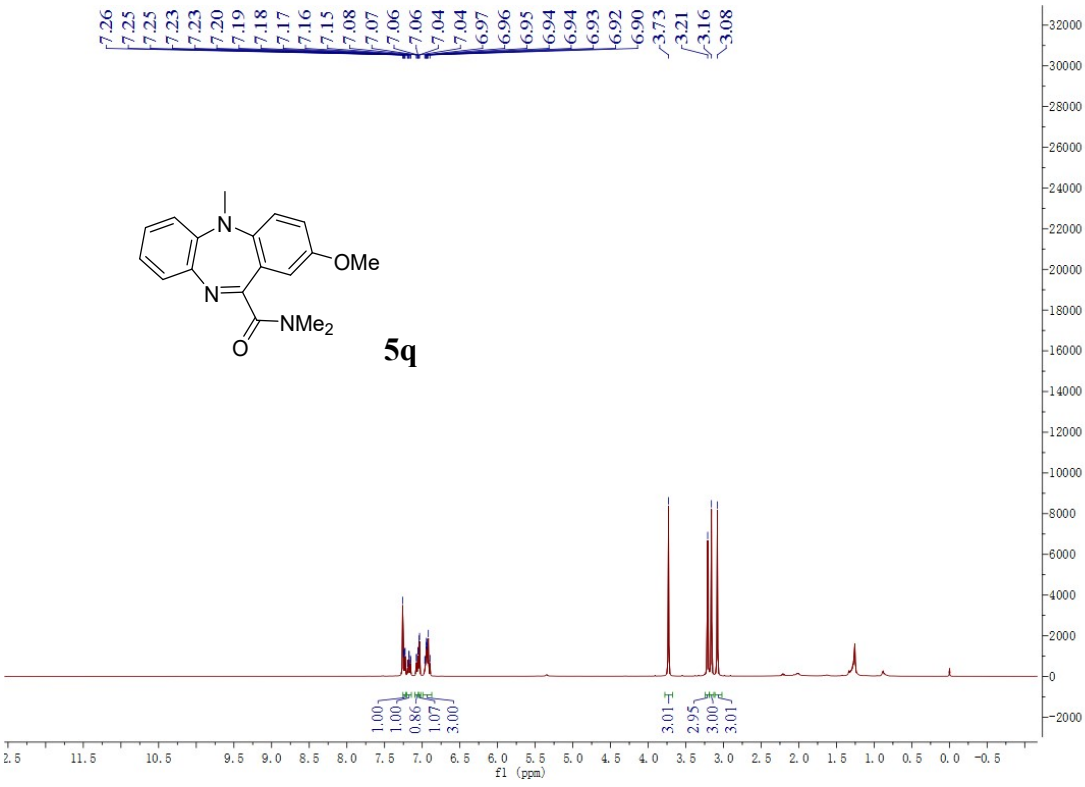
5p

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5p**



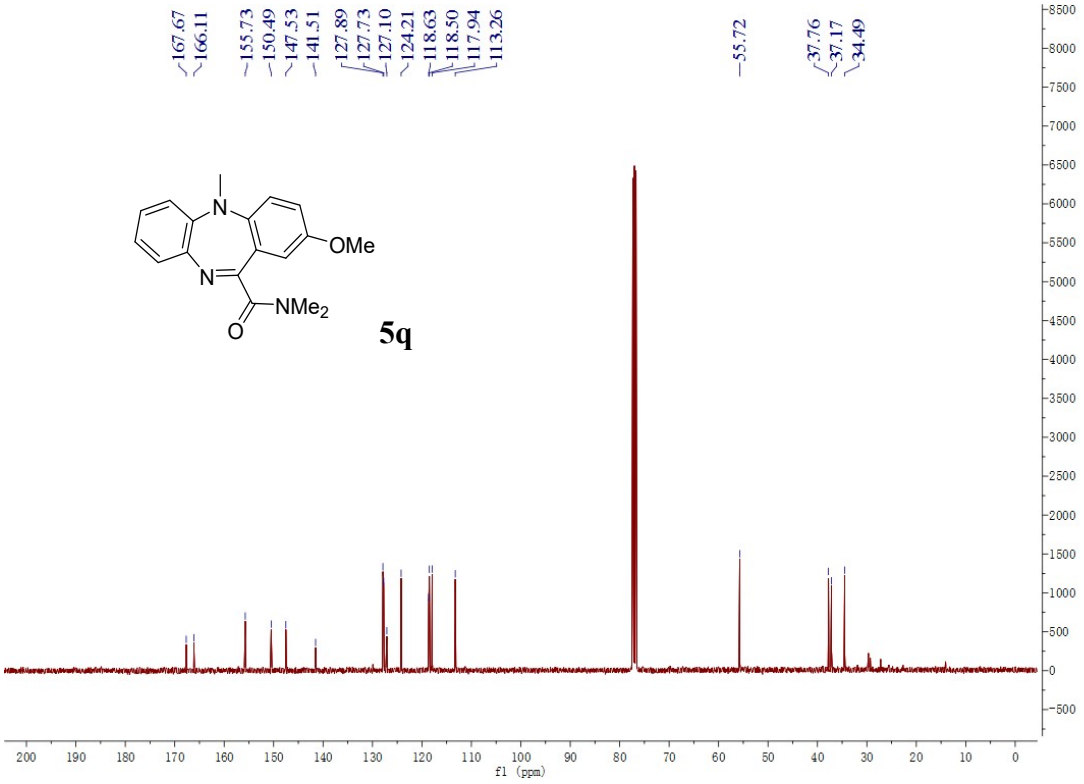
5p

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5q**

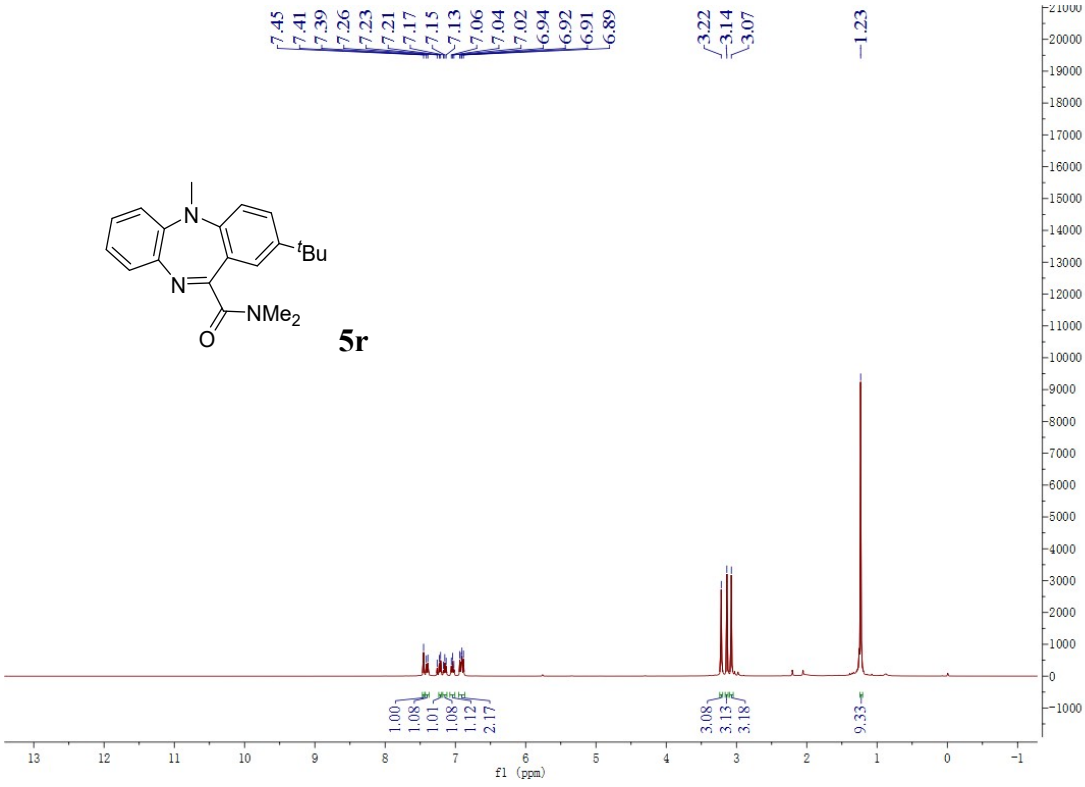


5q

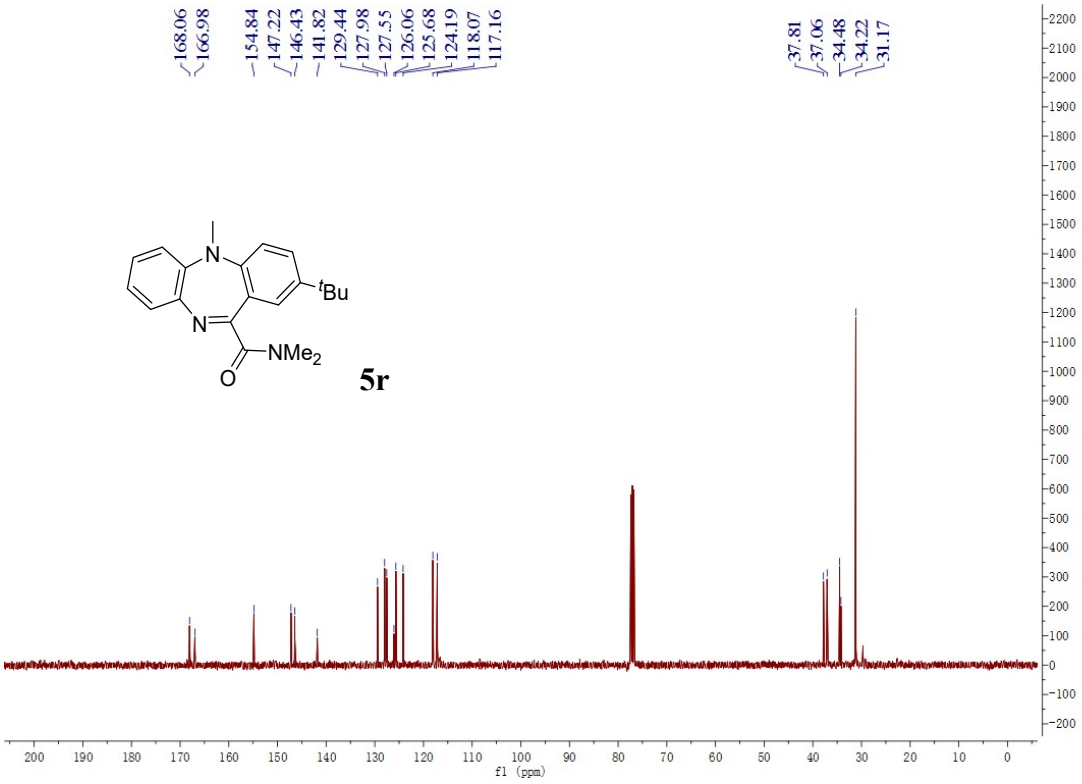
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5q**



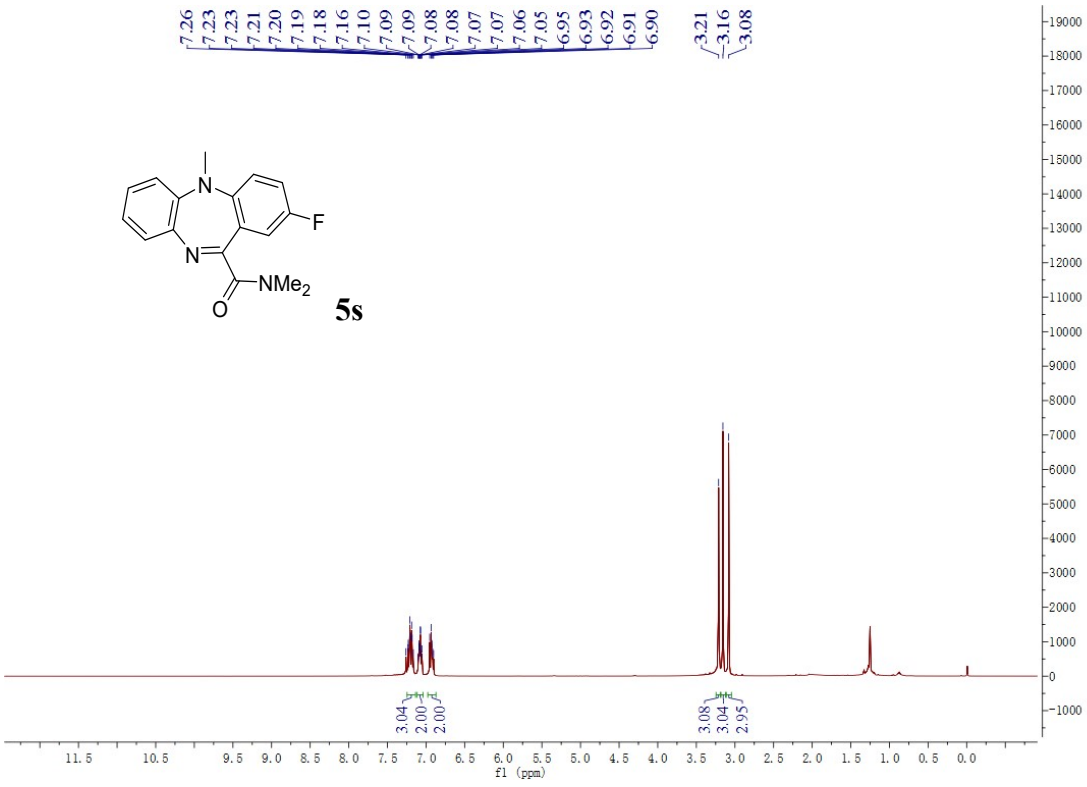
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5r**



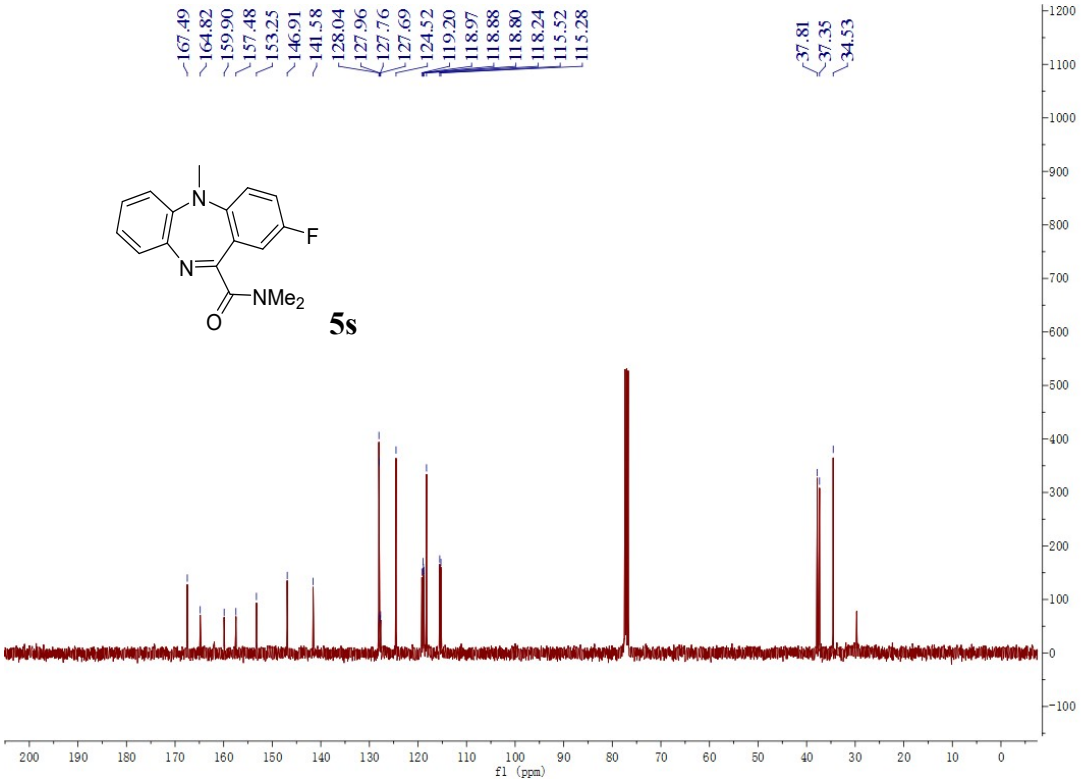
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5r**



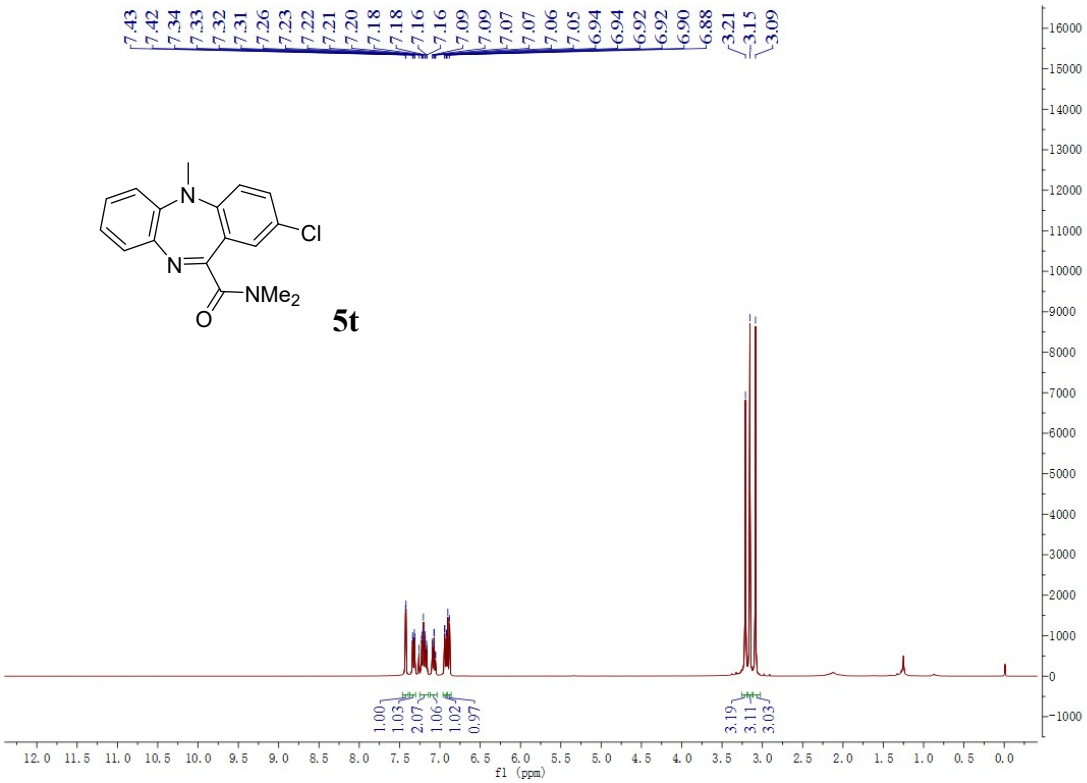
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5s**



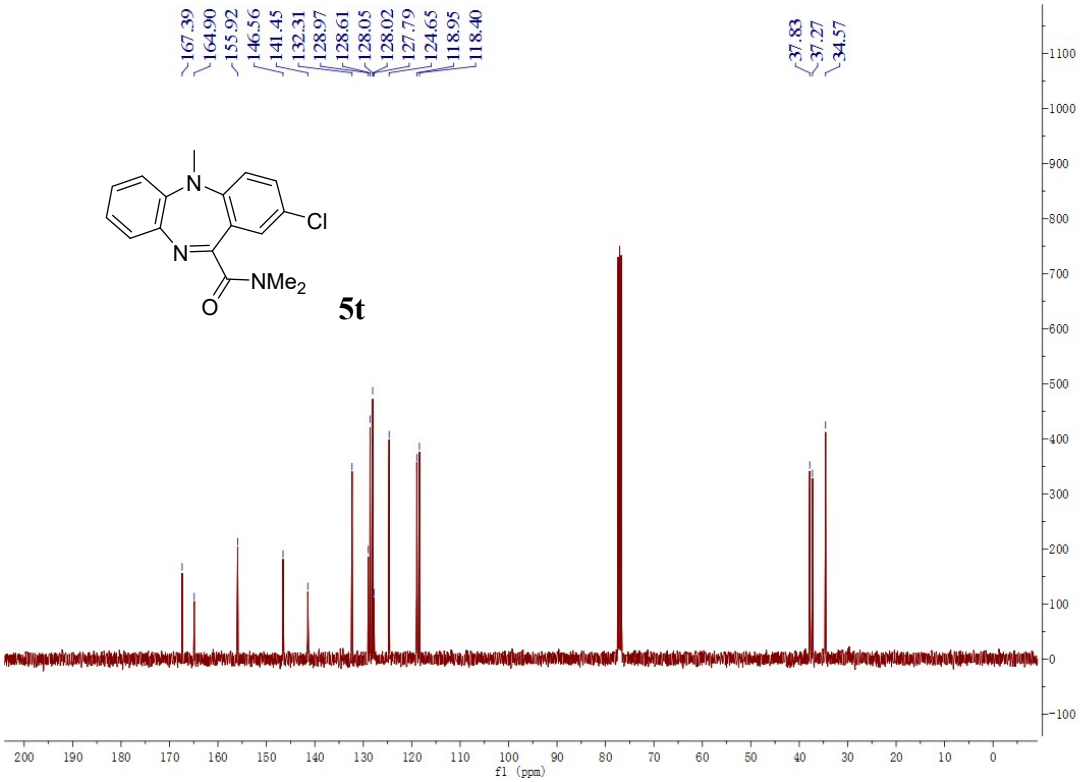
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5s**



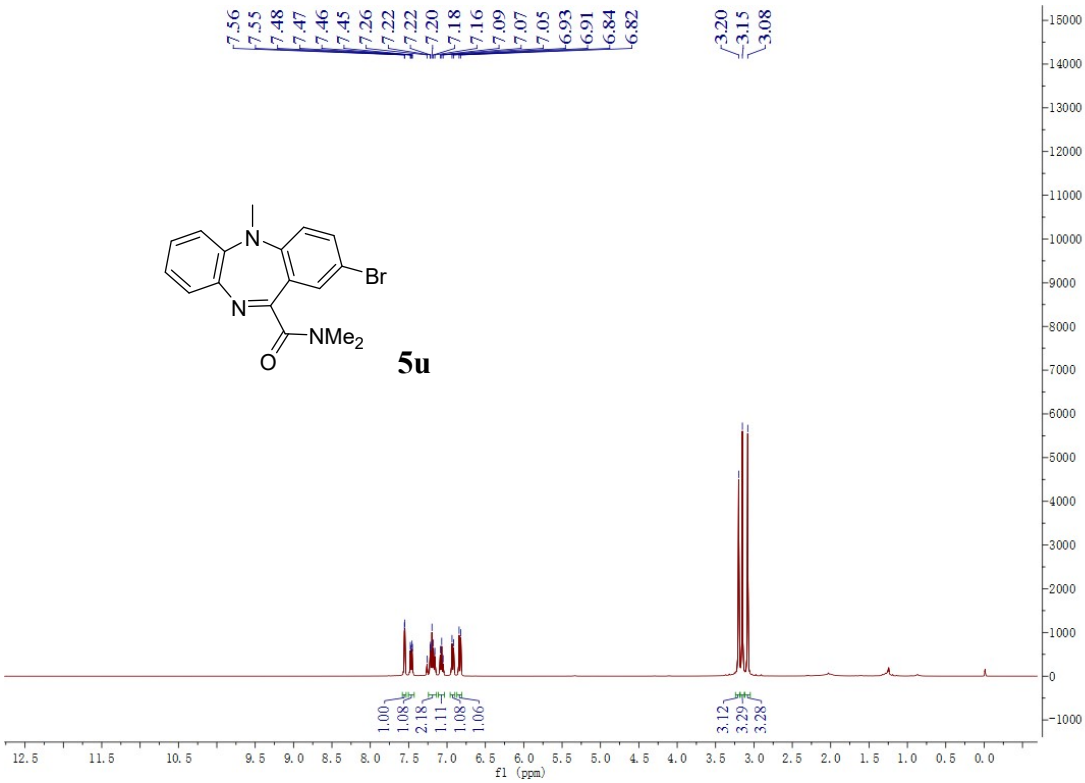
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5t**



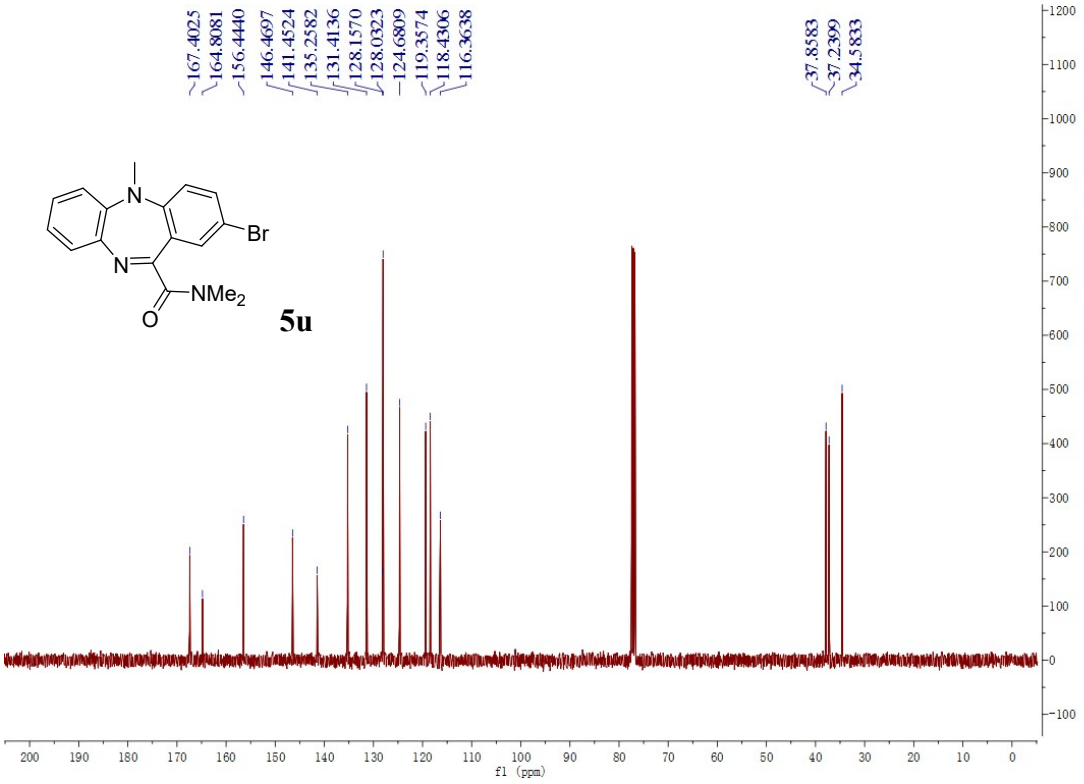
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5t**



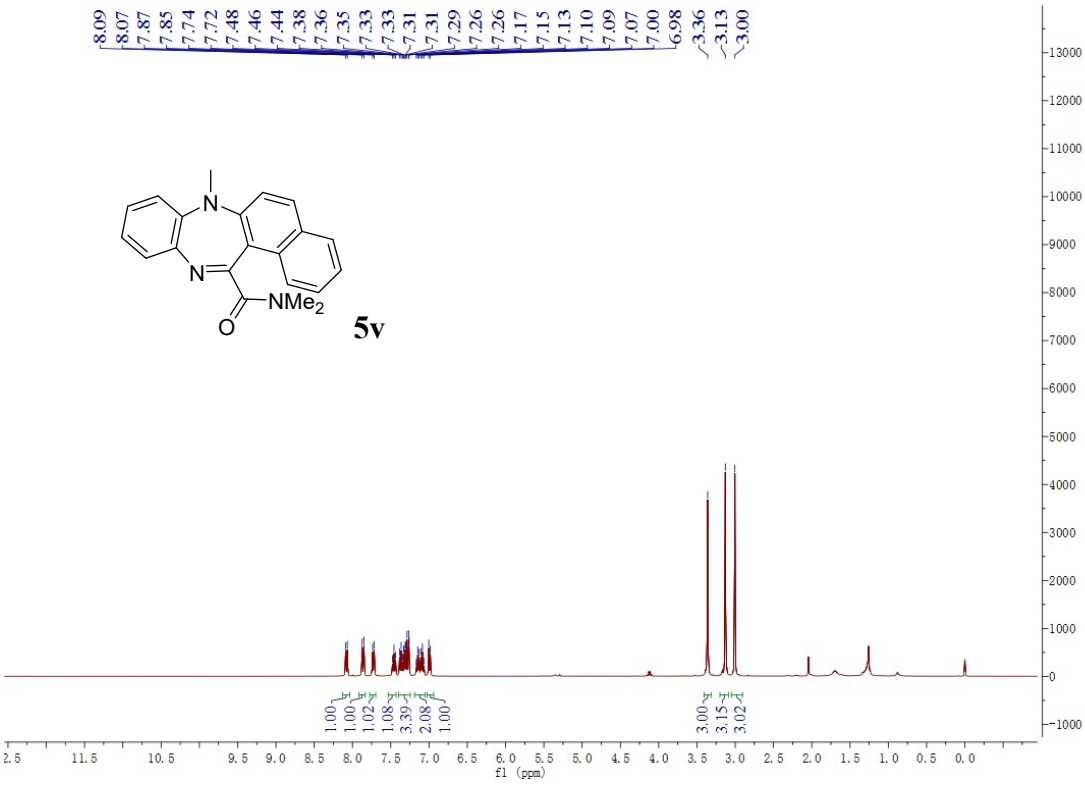
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5u**



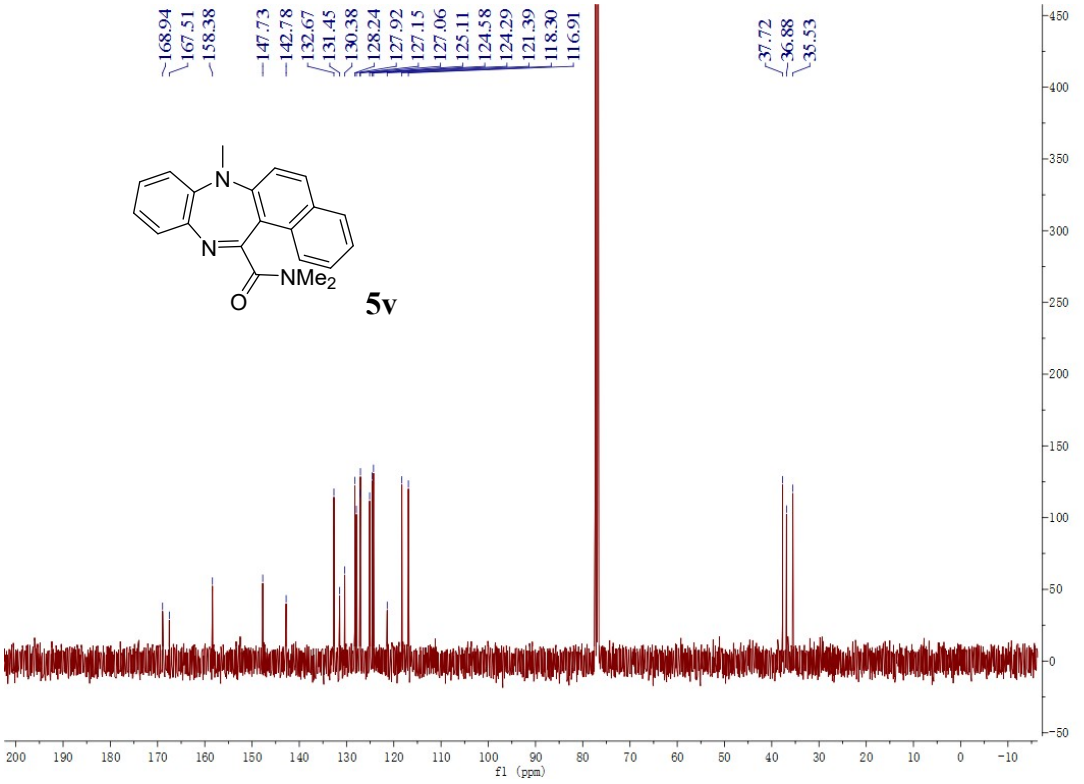
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5u**



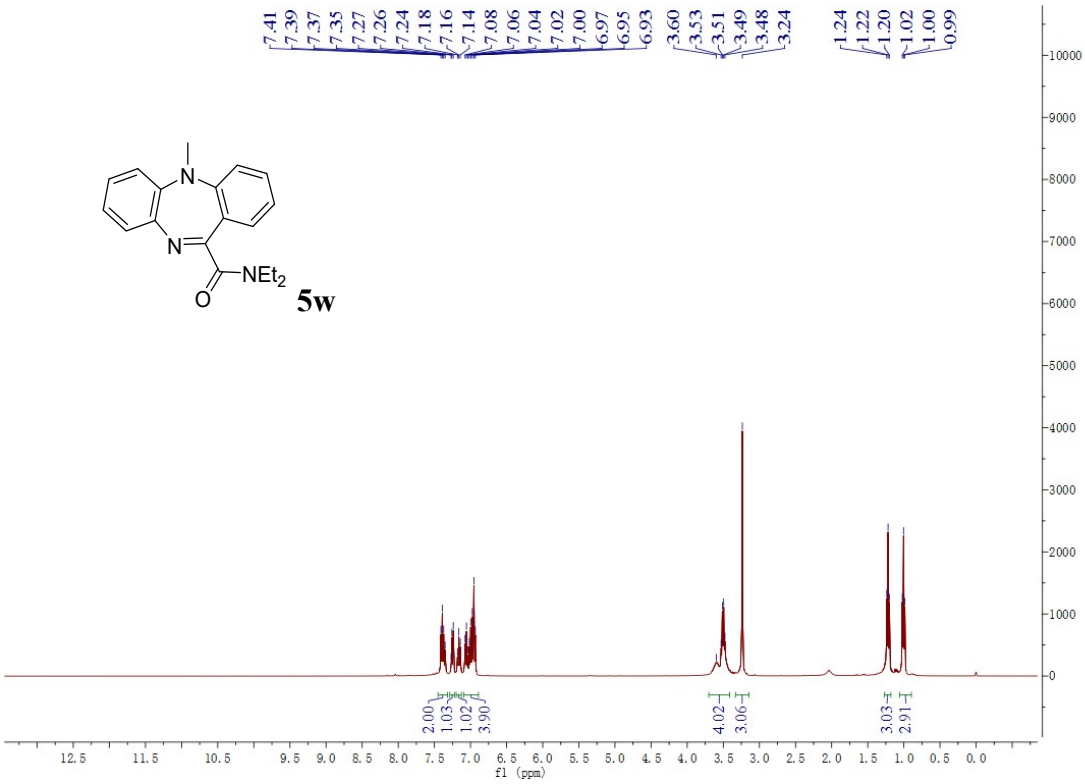
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5v**



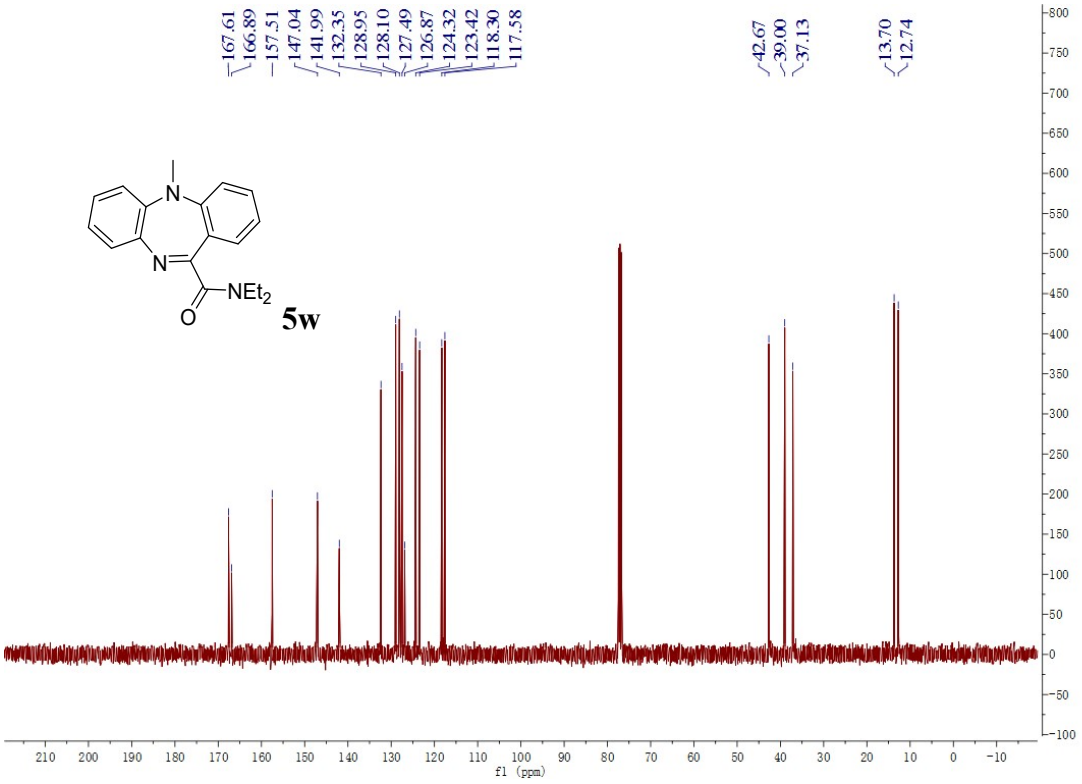
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5v**



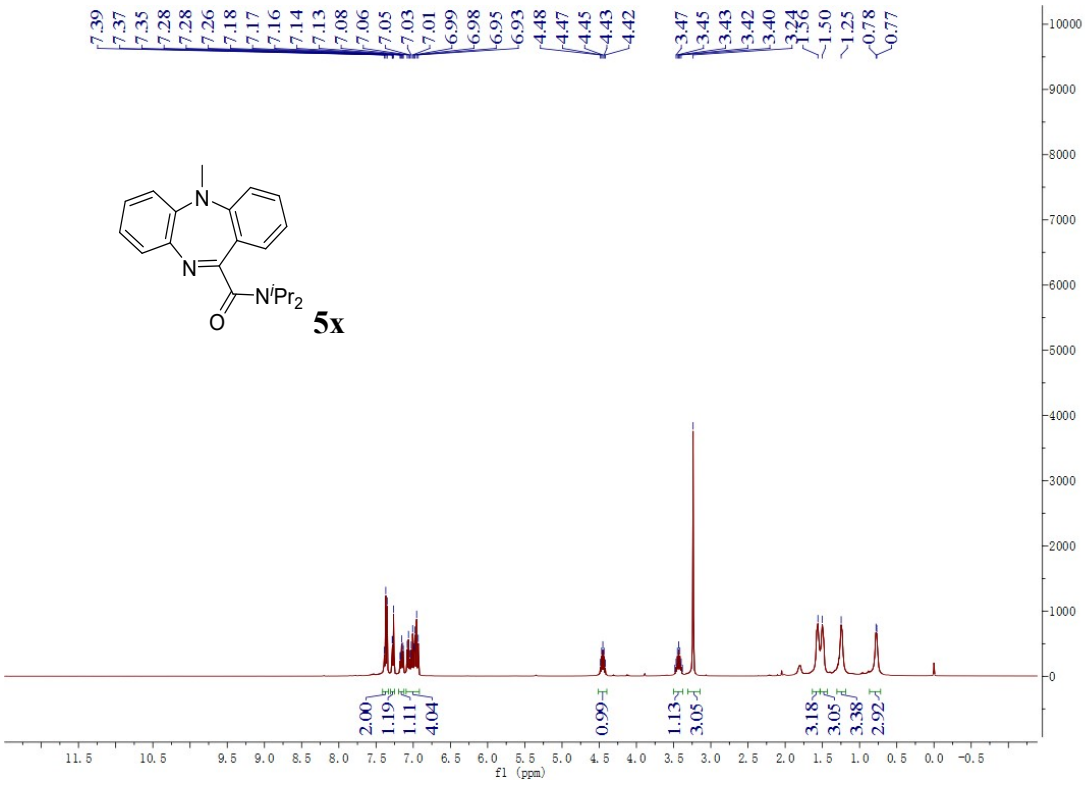
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5w**



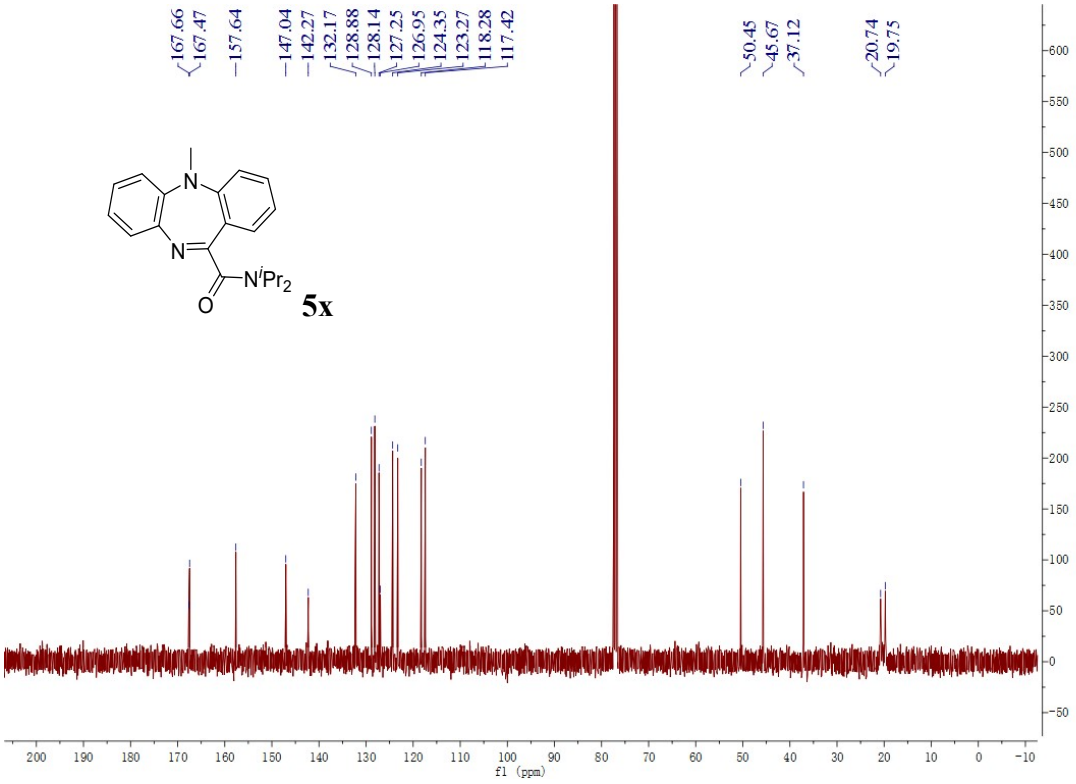
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5w**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5x**

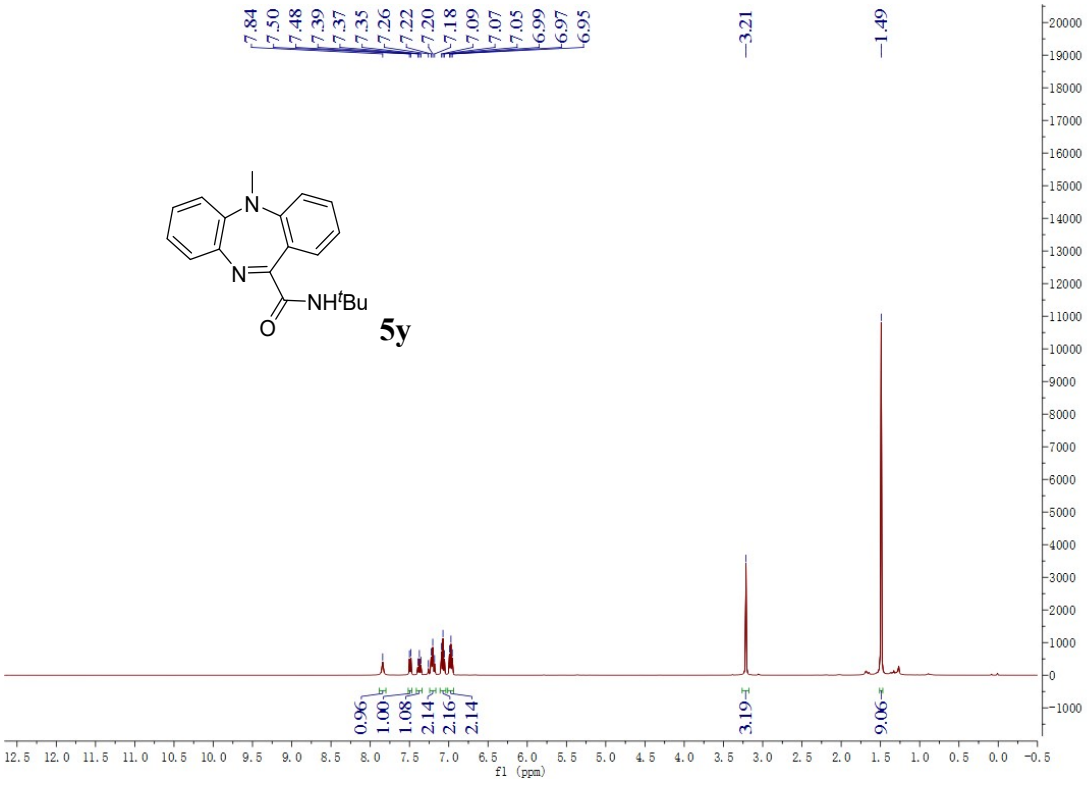


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5x**



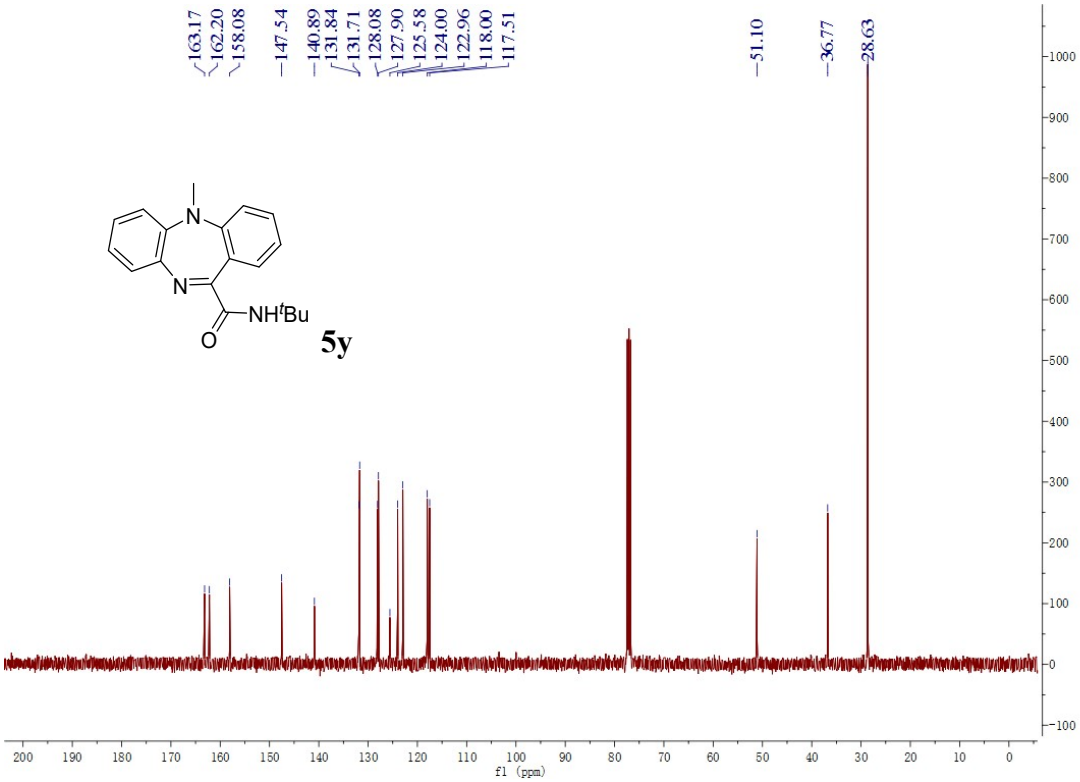
5x

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5y**

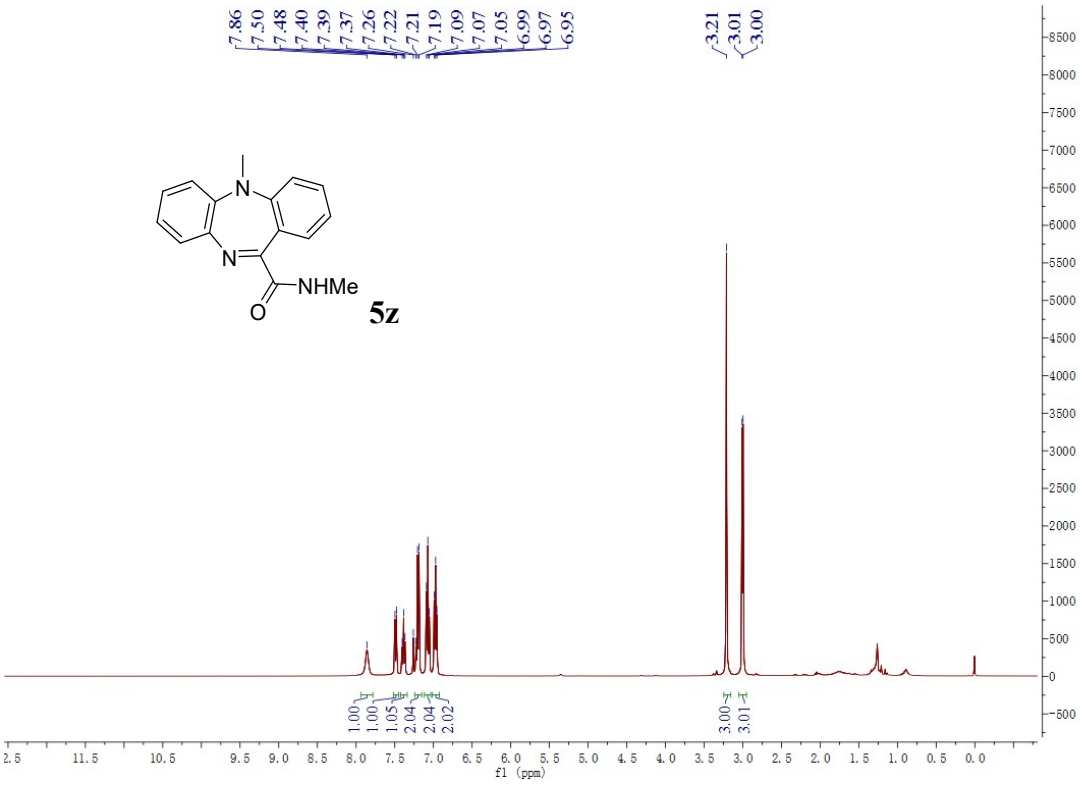


5y

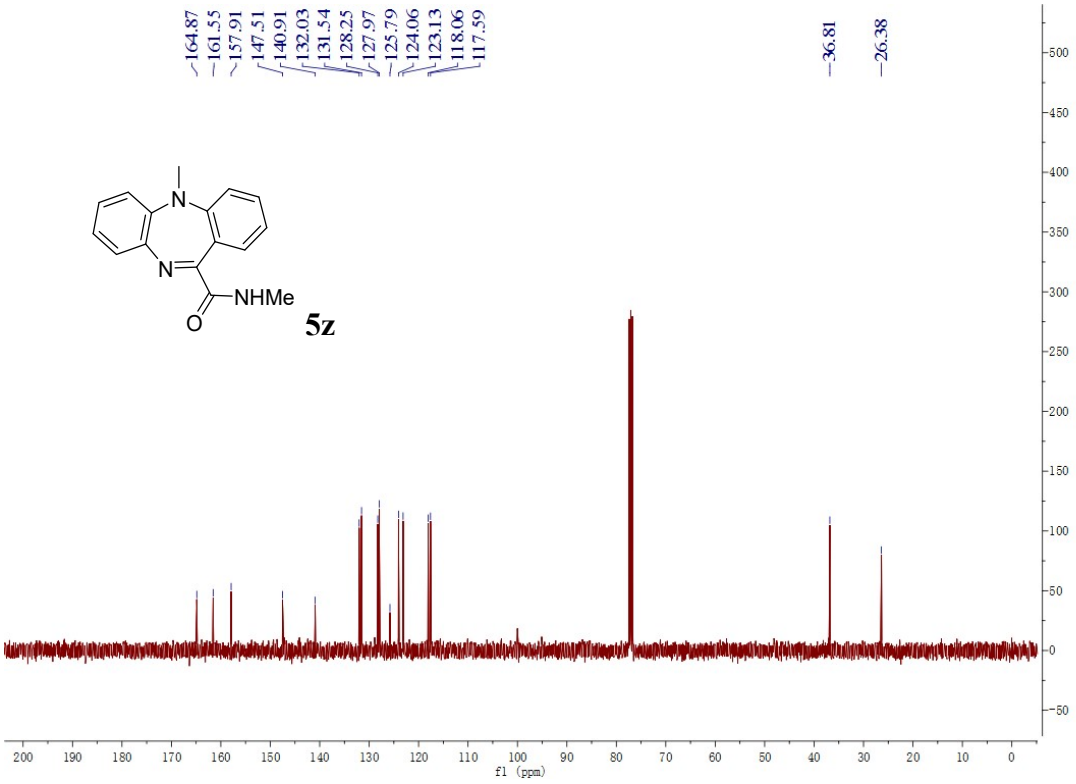
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5y**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5z**

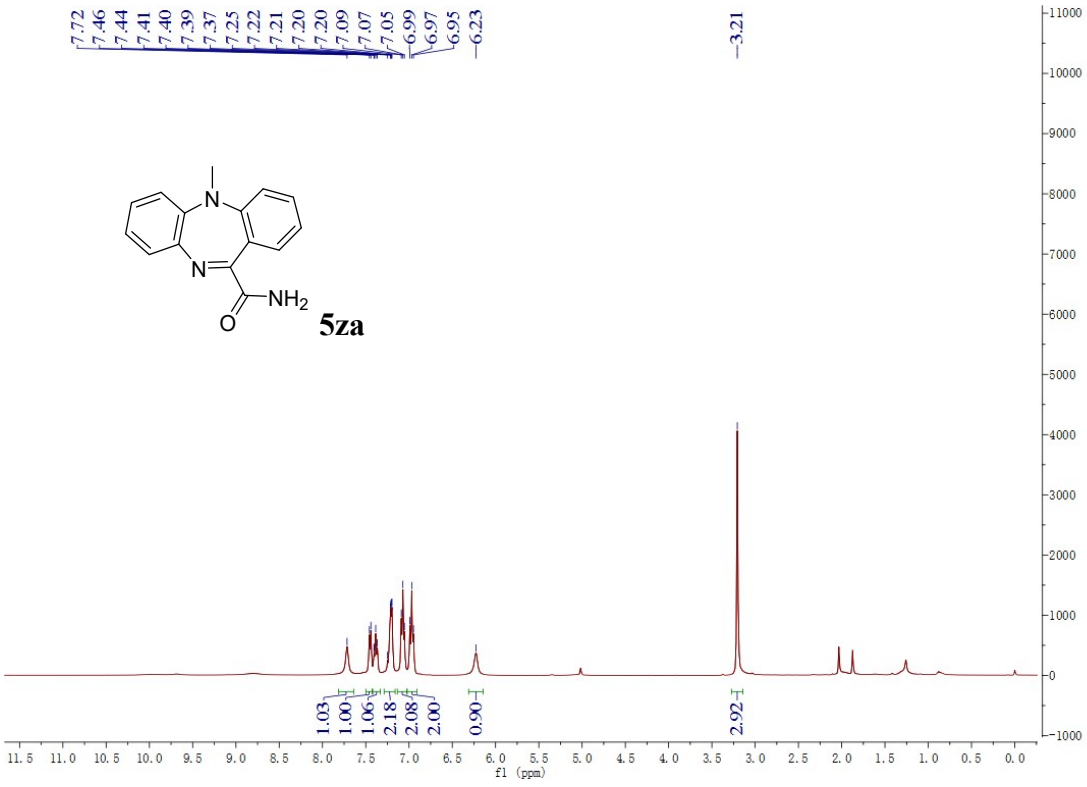


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5z**



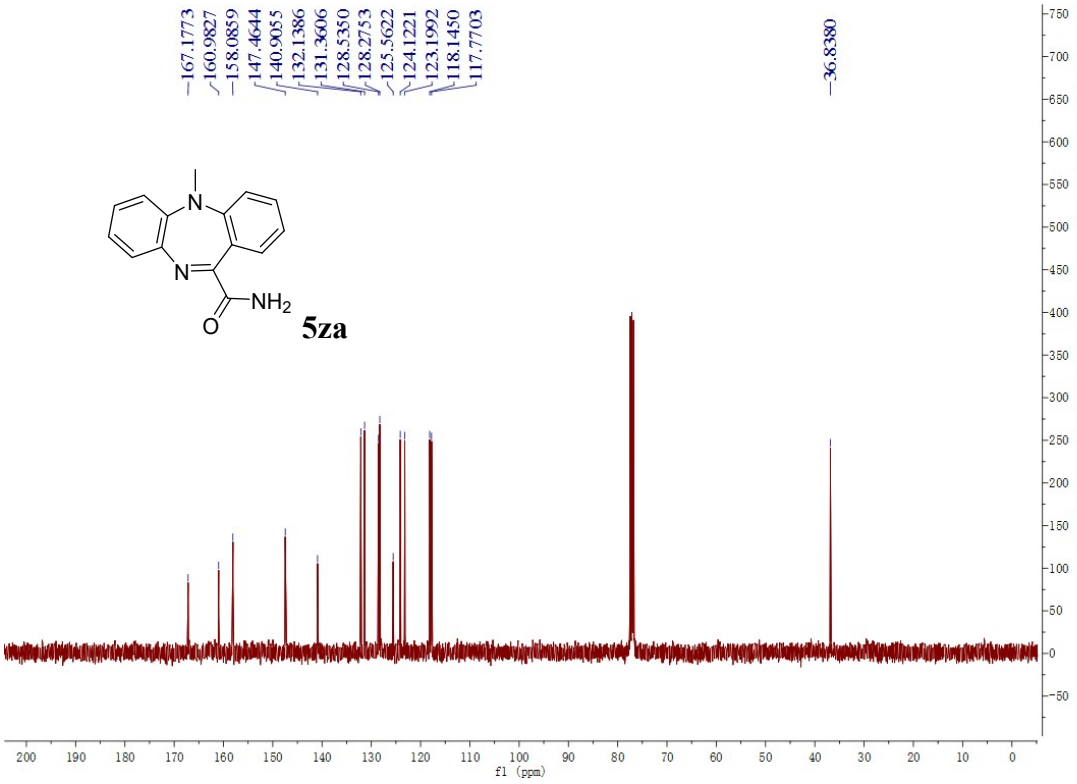
5z

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5za**

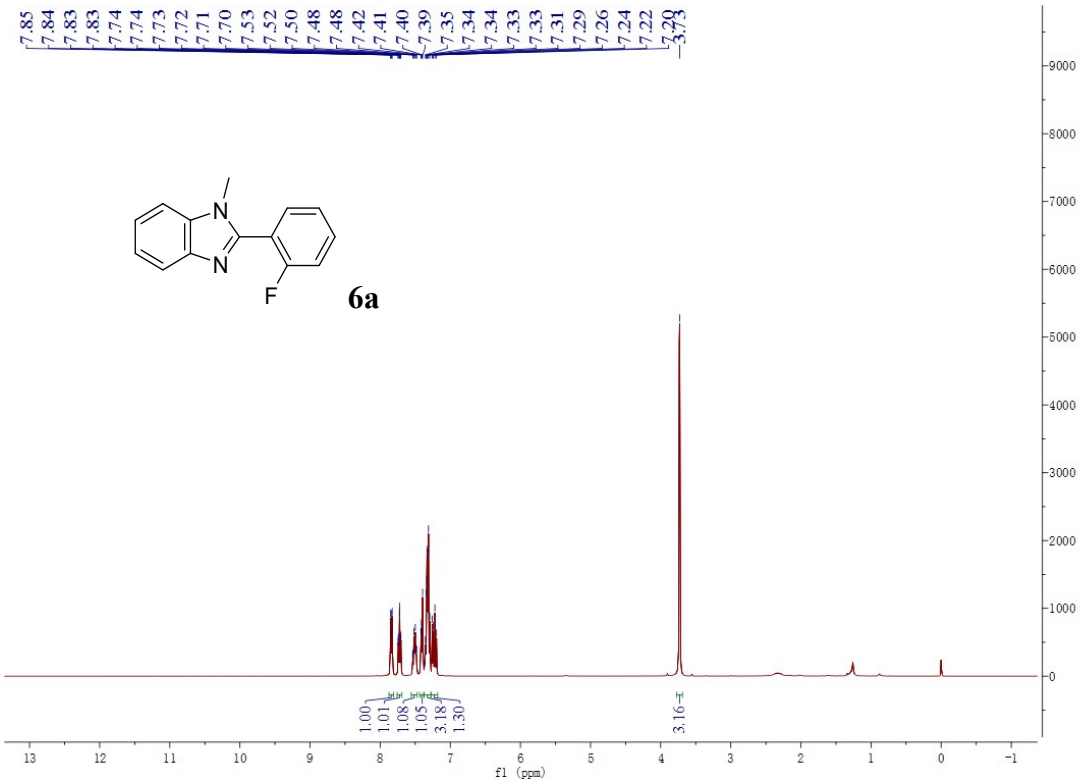


5za

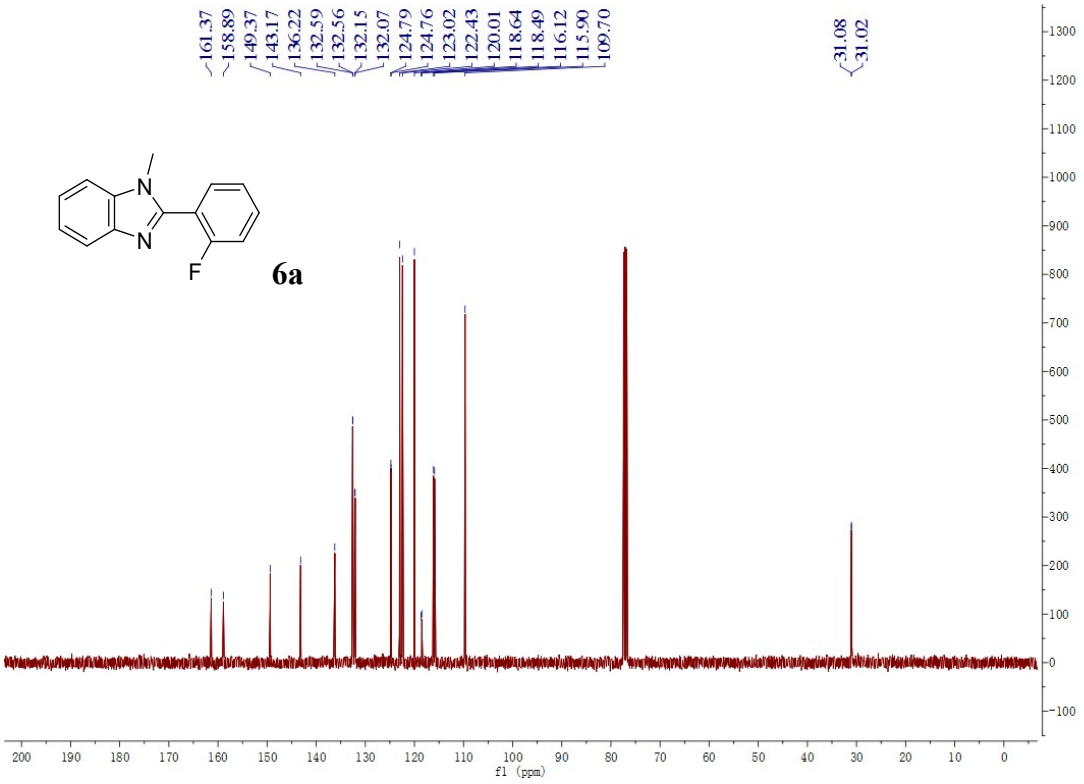
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5za**



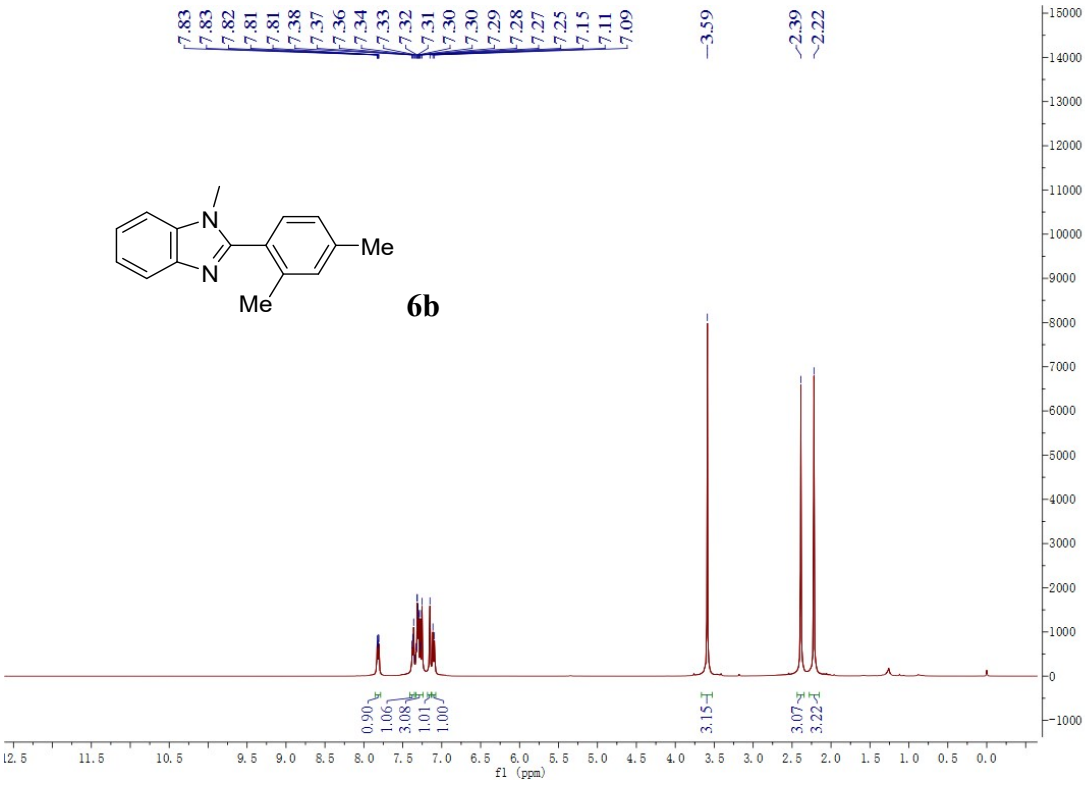
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6a**



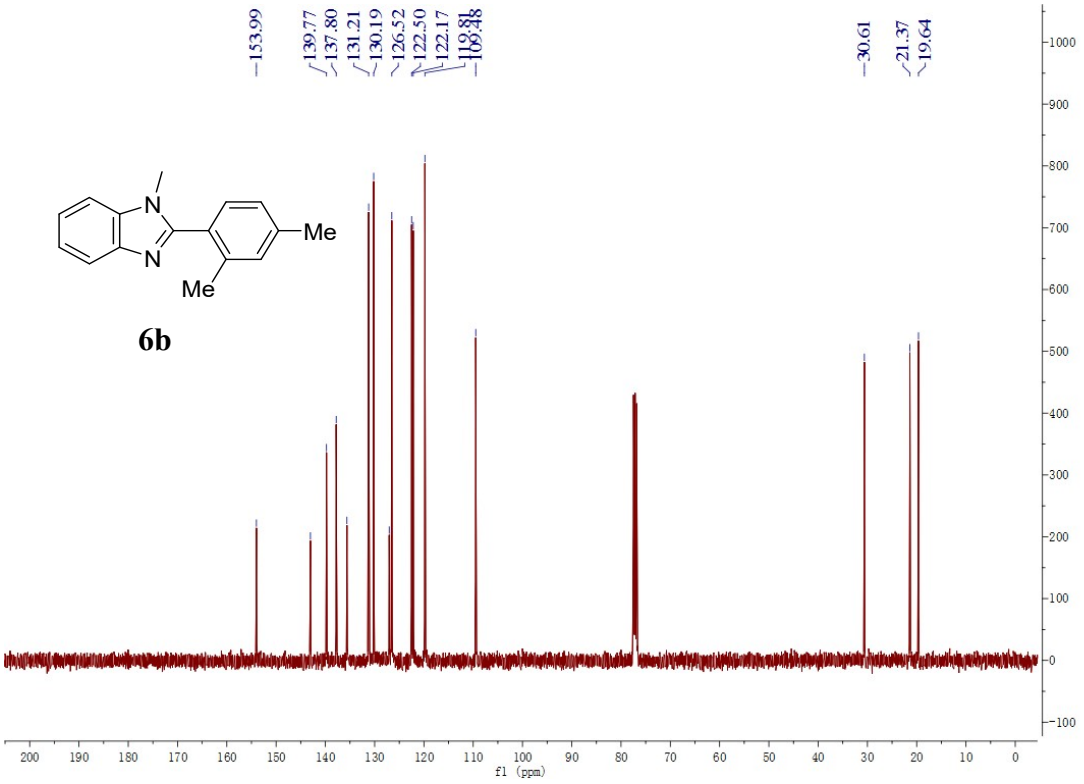
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6a**



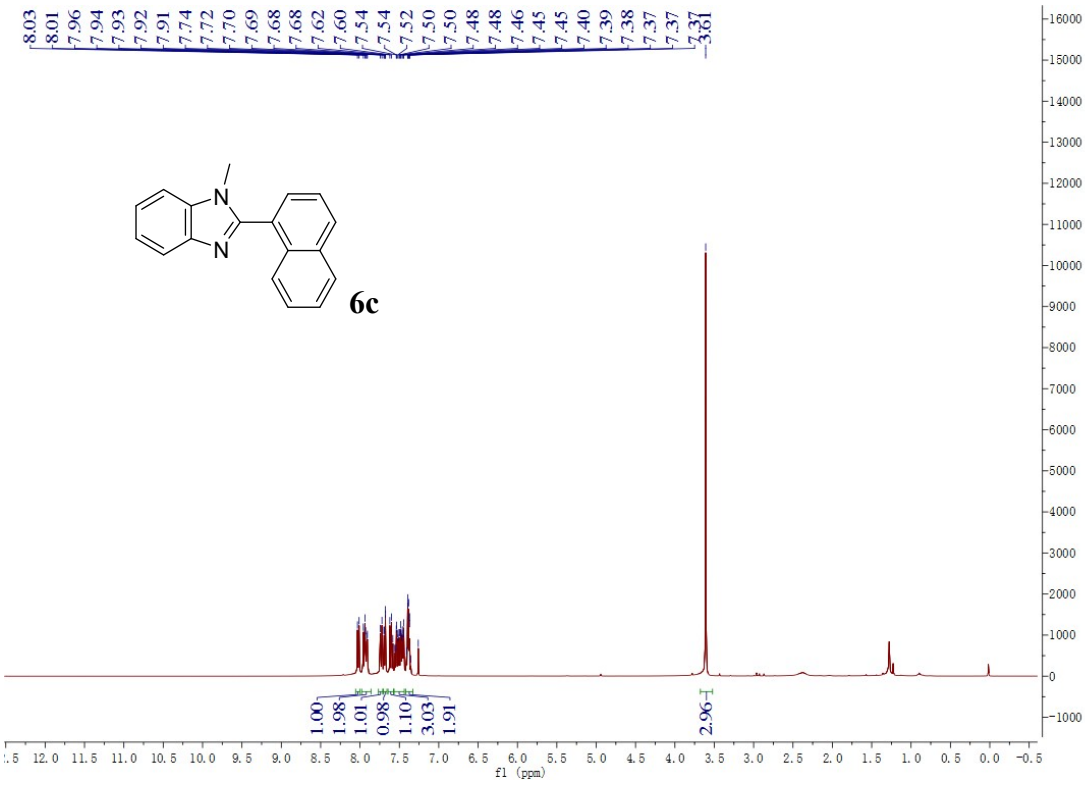
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6b**



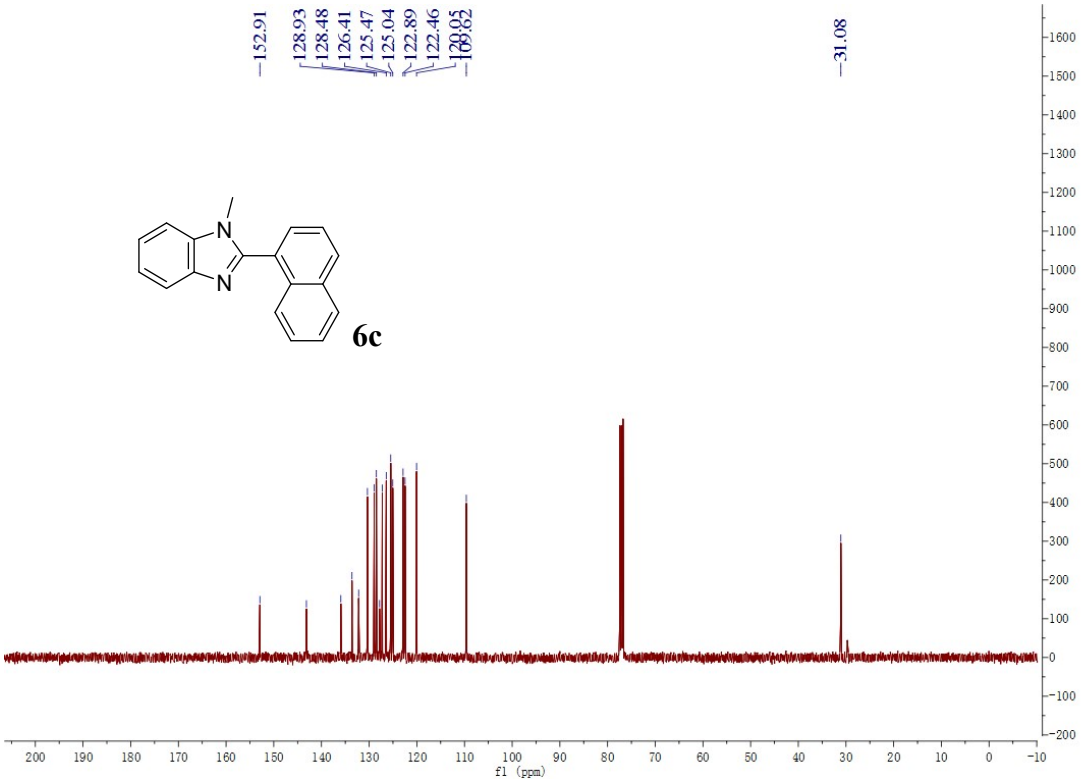
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6b**



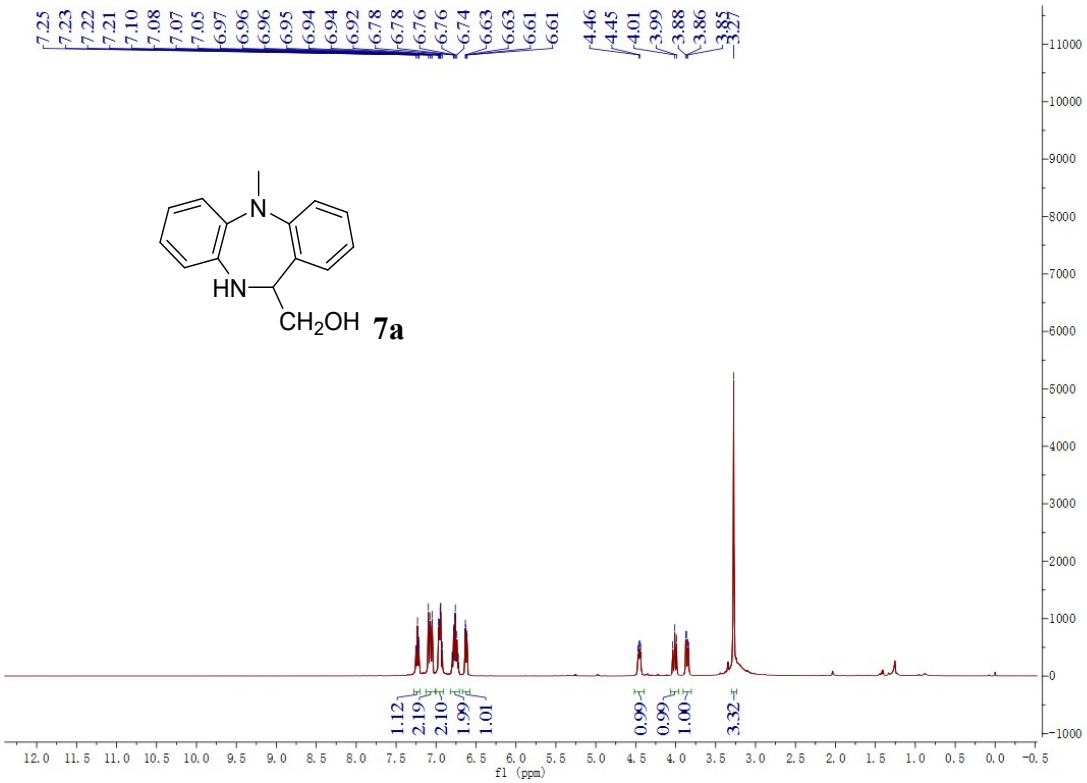
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6c**



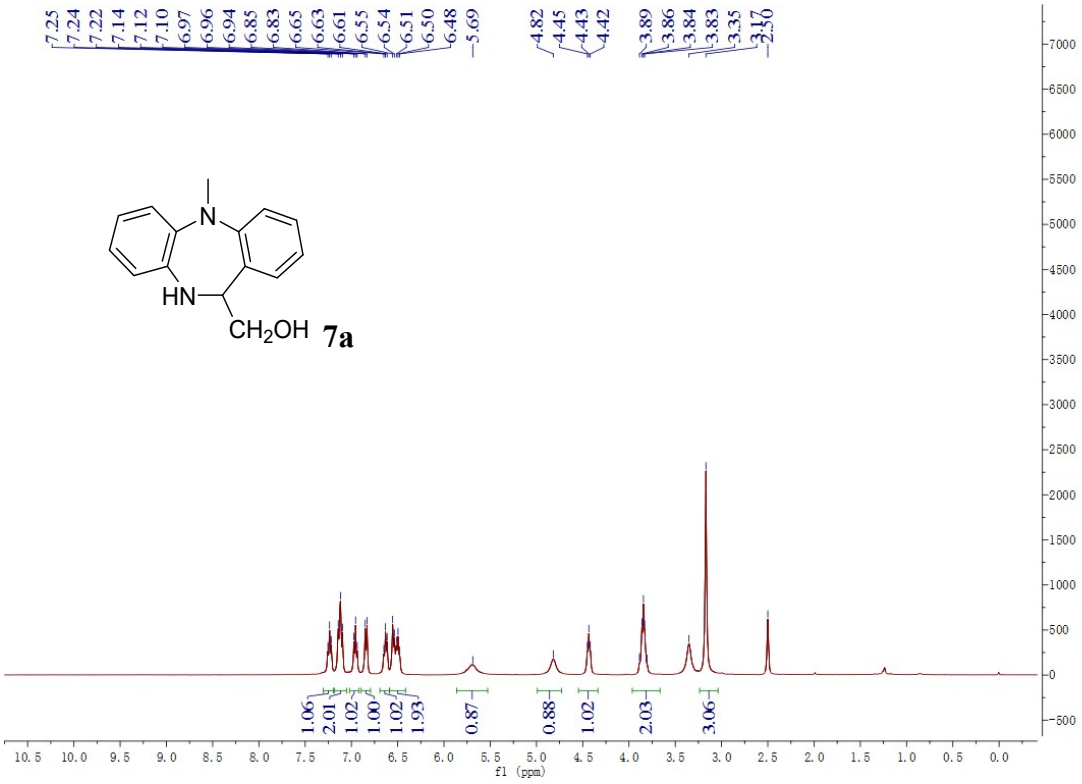
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6c**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7a**



^{1}H NMR (400 MHz, DMSO) spectrum of **7a**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7a**