

*Supporting information for*

**Diversity synthesis of indole-derivatives *via* acid-catalyzed  
cyclization reaction of 2-indolylmethanols and  
azonaphthalene**

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Xiaoan Wen\*, Qing-Long Xu\*

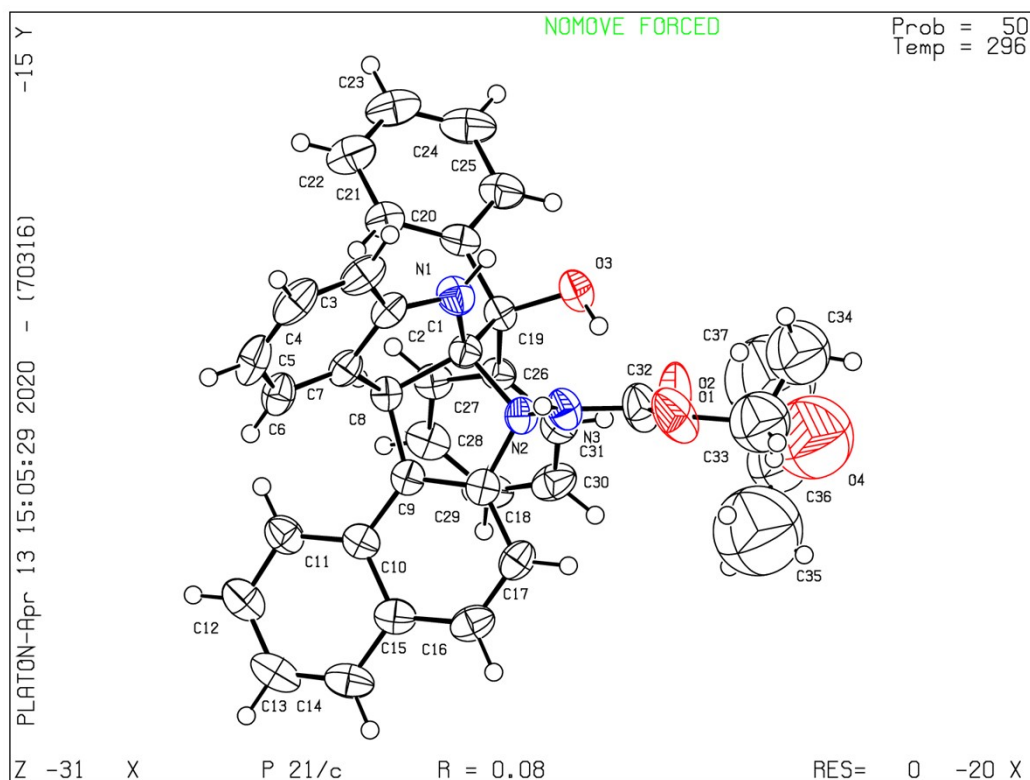
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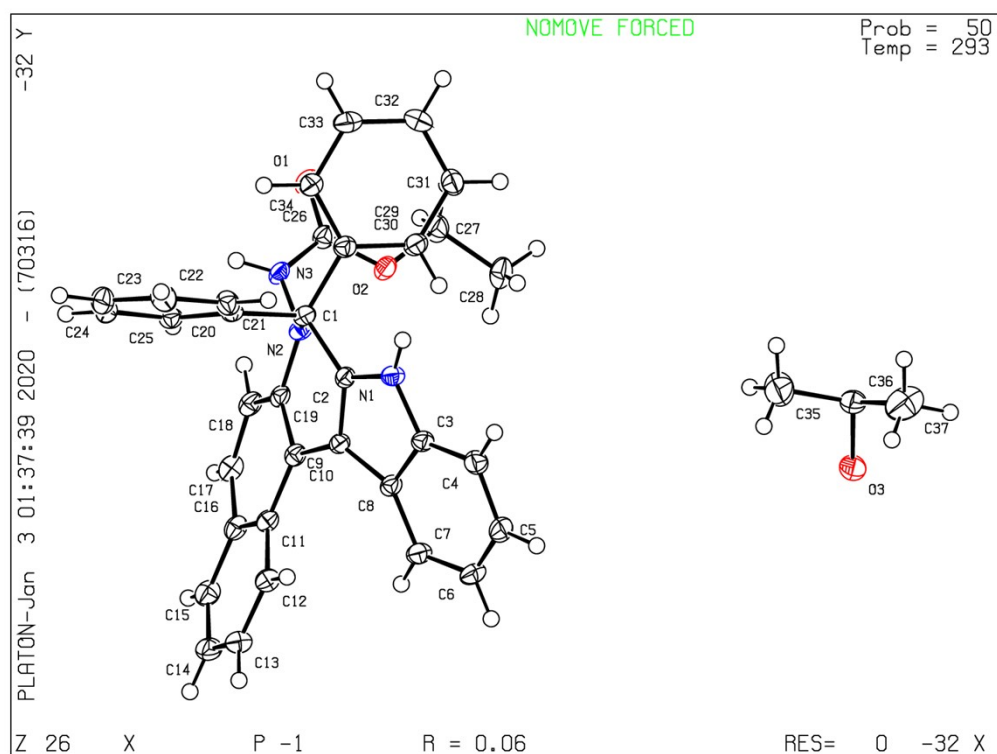
1. X-ray single crystal for compounds **3a,4a,5a**. (Thermal ellipsoids are set at 30% probability, The instrument used for the crystal measurement is ROD synergy-s.) X-ray crystal structure of compounds **3a** (CCDC-2154338). The crystal was grown from CH<sub>3</sub>COCH<sub>3</sub>. 10 mg of **3a** was dissolved in CH<sub>3</sub>COCH<sub>3</sub> (5.5 mL) and the solvent was evaporated slowly in a room atmosphere.



### Single crystal structure of 3a.

Empirical formula	C <sub>37</sub> H <sub>35</sub> N <sub>3</sub> O <sub>4</sub>
Formula weight	585.68
Temperature	296K
Wavelength	0.71073 Å
Space group	P21/C
Unit cell dimensions	a= 15.4317(10) Å    alpha=90. b= 13.3076(8) Å    beta=109.518(3). c= 15.3933(11) Å    gamma=90.
Volume	2979.5(3)
Z	4
Density (calculated)	1.306 Mg/m <sup>3</sup>
Mu (mm-1)	0.085 mm-1
F(000)	1240
h,k,lmax	20,17,20
Nref	6841
Tmin,Tmax	0.760,0.892
Data completeness	0.994

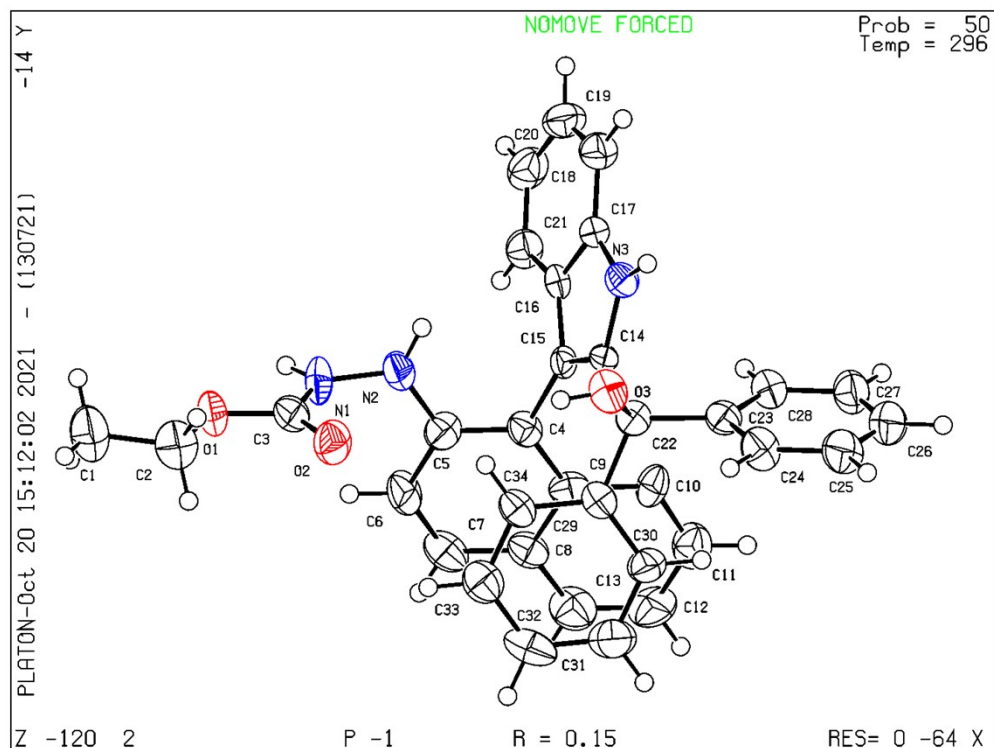
X-ray crystal structure of compounds **4a** (CCDC-2154339). The crystal was grown from CH<sub>3</sub>COCH<sub>3</sub>. 10 mg of **4a** was dissolved in CH<sub>3</sub>COCH<sub>3</sub> (5.5 mL) and the solvent was evaporated slowly in a room atmosphere.



### Single crystal structure of 4a.

Empirical formula	C <sub>37</sub> H <sub>33</sub> N <sub>3</sub> O <sub>3</sub>
Formula weight	567.66
Temperature	293K
Wavelength	1.54178 Å
Space group	P-1
Unit cell dimensions	a=8.9864(5) b=9.7311(5) c=18.0784(9) alpha=78.844(4) beta=81.754(4) gamma=75.670(4)
Volume	1495.17(14)
Z	2
Density (calculated)	1.261 Mg/m <sup>3</sup>
Mu (mm <sup>-1</sup> )	0.639 mm <sup>-1</sup>
F(000)	600
h,k,lmax	10,11,22
Nref	5548
Tmin,Tmax	0.857,1.000
Data completeness	0.967

X-ray crystal structure of compounds **5a** (CCDC-2154340). The crystal was grown from THF. 10 mg of **5a** was dissolved in THF (5.0 mL) and the solvent was evaporated slowly in a room atmosphere.



### Single crystal structure of 5a.

Empirical formula	$C_{34}H_{28}N_3O_3$
Formula weight	526.59
Temperature	296K
Wavelength	0.71073 Å
Space group	P-1
Unit cell dimensions	a=10.3432(10) b=11.855(9) c=12.430(9) alpha=79.657(15) beta=66.16(2) gamma=74.86(4)
Volume	1314.0(14)
Z	2
Density (calculated)	1.304 Mg/m <sup>3</sup>
Mu (mm <sup>-1</sup> )	0.085 mm <sup>-1</sup>
F(000)	554
h,k,lmax	12,14,14
Nref	4691
Tmin,Tmax	0.864,0.864
Data completeness	0.983



## 2. General information

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured at 300 MHz and 75 MHz respectively. The solvents used NMR Spectroscopy were DMSO-*d*<sub>6</sub>, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Analytical grade solvents for the column chromatography were used directly. All starting materials commercially available were used directly.

## 3. General procedure for the synthesis of substrates 1 and 2

In a flame-dried three-necked bottle, phenyl magnesium bromide (100 mL, 1.0 mmol/mL) was added to the bottle under argon. At 0 °C, THF (50 mL) solution of ethyl indole-2-carboxylate (5.7 g, 30 mmol) was added to the bottle dropwise. After the solution added, the reaction was slowly rising to 80 °C and reflux overnight. The mixture was allowed to cool down to room temperature, quenched by saturated ammonium chloride solution, extracted by ethyl acetate three times. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate =10/1) to afford the pure 2-indolylmethanol **1a** in 90% yield.

*(1H-indol-2-yl)diphenylmethanol (1a)*. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.90 (s, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.39-7.18 (m, 11H), 7.08-7.00 (m, 1H), 6.94 (dd, *J* = 10.9, 3.9 Hz, 1H), 6.63 (s, 1H), 5.83 (d, *J* = 1.5 Hz, 1H).

*bis(4-chlorophenyl)(1H-indol-2-yl)methanol (1b)*. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.92 (s, 1H), 7.47-7.24 (m, 10H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 5.85 (s, 1H).

*(1H-indol-2-yl)di-p-tolylmethanol (1c)*. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.77 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.25-7.08 (m, 8H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 5.79 (d, *J* = 0.9 Hz, 1H), 2.28 (s, 6H).

*(1-methyl-1H-indol-2-yl)diphenylmethanol (1d)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.39-7.24 (m, 11H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.92-6.72 (m, 1H), 5.61 (s, 1H), 3.47 (s, 3H).

*(4-methyl-1H-indol-2-yl)diphenylmethanol (1e)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.83 (s, 1H), 7.39-7.21 (m, 10H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 6.9 Hz, 1H), 6.57 (s, 1H), 5.83 (s, 1H), 2.34 (s, 3H).

*(5-methyl-1H-indol-2-yl)diphenylmethanol (1f)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.69 (s, 1H), 7.35-7.17 (m, 12H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.54 (s, 1H), 5.72 (s, 1H), 2.32 (s, 3H).

*(6-methyl-1H-indol-2-yl)diphenylmethanol (1g)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.69 (s, 1H), 7.38-7.20 (m, 11H), 7.13 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 1H), 5.72 (s, 1H), 2.35 (s, 3H).

*(5-fluoro-1H-indol-2-yl)diphenylmethanol (1h)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.97 (s, 1H), 7.37-7.23 (m, 11H), 7.19 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.87 (td, *J* = 9.4, 2.4 Hz, 1H), 6.64 (s, 1H), 5.87-5.81 (m, 1H).

*(5-chloro-1H-indol-2-yl)diphenylmethanol (1i)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 11.09 (s, 1H), 7.48 (s, 1H), 7.39-7.22 (m, 11H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 5.85 (s, 1H).

*(6-chloro-1H-indol-2-yl)diphenylmethanol (1j)* <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 11.09

(s, 1H), 7.48 (s, 1H), 7.39-7.22 (m, 11H), 7.03 (d,  $J = 8.5$  Hz, 1H), 6.68 (s, 1H), 5.85 (s, 1H).

(4,6-dichloro-1H-indol-2-yl)diphenylmethanol (**Ik**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.46 (s, 1H), 7.41-7.23 (m, 11H), 7.11 (d,  $J = 1.4$  Hz, 1H), 6.82 (s, 1H), 5.88 (d,  $J = 1.6$  Hz, 1H).

(4-bromo-1H-indol-2-yl)diphenylmethanol (**Il**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.31 (s, 1H), 7.42-7.23 (m, 11H), 7.16 (d,  $J = 7.5$  Hz, 1H), 6.98 (t,  $J = 7.8$  Hz, 1H), 6.72 (s, 1H), 5.81 (s, 1H).

(5-bromo-1H-indol-2-yl)diphenylmethanol (**Im**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.11 (s, 1H), 7.63 (s, 1H), 7.38-7.22 (m, 11H), 7.15 (d,  $J = 8.5$  Hz, 1H), 6.69 (s, 1H), 5.85 (s, 1H).

(4-methoxy-1H-indol-2-yl)diphenylmethanol (**In**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.87 (s, 1H), 7.39-7.20 (m, 10H), 6.95 (d,  $J = 4.2$  Hz, 2H), 6.55 (s, 1H), 6.44 (m, 1H), 5.76 (d,  $J = 1.7$  Hz, 1H), 3.78 (s, 3H).

(5-methoxy-1H-indol-2-yl)diphenylmethanol (**Io**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.66 (s, 1H), 6.96-6.91 (m, 1H), 6.68 (dd,  $J = 8.6, 2.2$  Hz, 1H), 6.54 (s, 1H), 5.75 (s, 1H), 3.70 (s, 3H).

(6-methoxy-1H-indol-2-yl)diphenylmethanol (**Ip**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.67 (s, 1H), 7.37-7.17 (m, 11H), 6.86 (s, 1H), 6.59 (dd,  $J = 8.4, 1.5$  Hz, 1H), 6.53 (s, 1H), 5.70 (s, 1H), 3.72 (s, 3H).

1-(1H-indol-2-yl)-1-phenylethan-1-ol (**Ir**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.80 (s, 1H), 7.50 (t,  $J = 9.1$  Hz, 3H), 7.33 (t,  $J = 7.2$  Hz, 3H), 7.23 (t,  $J = 7.2$  Hz, 1H), 7.05-6.90 (m, 2H), 6.32 (d,  $J = 1.5$  Hz, 1H), 5.92 (s, 1H), 1.93 (s, 3H).

The corresponding hydrazine hydrochloride (5 g, 25.68 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (20 mL). Pyridine (4.7 mL, 56.51 mmol) was added. The solution was cooled to 0 °C and chloroformate (2.93 mL, 30.81 mmol) was added dropwise under stirring. The reaction mixture was stirred for 15 min at 0 °C and then for 1 h at room temperature. Water (30 mL) was added and the resulting mixture was acidified with HCl (6 M) to pH 4-6. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 20 mL). The combined organic layers were washed with saturated aq.  $\text{NaHCO}_3$  (50 mL), brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated to dryness. The residue products were purified by flash chromatography on silica gel eluted with (petroleum ether/ethyl acetate =15/1) to afford the corresponding products in 70-97% yield. PCC (7.38 g, 34.25 mmol) was added to a solution of corresponding hydrazine carboxylate (31.38 mmol) in 30 mL DCM. The mixture was stirred until hydrazine carboxylate completely consumed (monitored by TLC). The reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified by chromatography on silica gel eluted with (petroleum ether/ethyl acetate =100/1) to afford the corresponding product azonaphthalene **2** in 38-80% yield.

ethyl (*E*)-2-(naphthalen-2-yl)diazene-1-carboxylate (**2a**)  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.76 (d,  $J = 1.4$  Hz, 1H), 8.24 (d,  $J = 7.6$  Hz, 1H), 8.09 (t,  $J = 7.2$  Hz, 2H), 7.86 (dd,  $J = 8.9, 2.0$  Hz, 1H), 7.80-7.66 (m, 2H), 4.50 (q,  $J = 7.1$  Hz, 2H), 1.40 (t,  $J = 7.1$  Hz, 3H).

tert-butyl (*E*)-2-(naphthalen-2-yl)diazene-1-carboxylate (**2b**)  $^1\text{H}$  NMR (300 MHz,

DMSO- $d_6$ )  $\delta$  8.73 (s, 1H), 8.23 (d,  $J = 7.4$  Hz, 1H), 8.08 (t,  $J = 6.9$  Hz, 2H), 7.86 (dd,  $J = 8.9, 1.9$  Hz, 1H), 7.78-7.65 (m, 2H), 1.64 (s, 9H).

*isopropyl (E)-2-(naphthalen-2-yl)diazene-1-carboxylate (2c)*  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.75 (s, 1H), 8.24 (d,  $J = 7.5$  Hz, 1H), 8.08 (t,  $J = 7.0$  Hz, 2H), 7.86 (dd,  $J = 8.9, 1.9$  Hz, 1H), 7.81-7.64 (m, 2H), 5.20 (dq,  $J = 12.4, 6.2$  Hz, 1H), 1.43 (s, 3H), 1.41 (s, 3H).

*butyl (E)-2-(naphthalen-2-yl)diazene-1-carboxylate (2d)*  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.75 (s, 1H), 8.23 (d,  $J = 7.7$  Hz, 1H), 8.07 (t,  $J = 7.1$  Hz, 2H), 7.84 (dd,  $J = 8.9, 1.8$  Hz, 1H), 7.78-7.61 (m, 2H), 4.44 (t,  $J = 6.5$  Hz, 2H), 1.81-1.63 (m, 2H), 1.50-1.32 (m, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H).

*benzyl (E)-2-(naphthalen-2-yl)diazene-1-carboxylate (2e)*  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.74 (s, 1H), 8.21 (d,  $J = 7.7$  Hz, 1H), 8.11-7.99 (m, 2H), 7.83 (dd,  $J = 9.0, 1.6$  Hz, 1H), 7.76-7.61 (m, 2H), 7.59-7.50 (m, 2H), 7.49-7.34 (m, 3H), 5.51 (s, 2H).

*ethyl (E)-2-(6-bromonaphthalen-2-yl)diazene-1-carboxylate (2f)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (m, 1H), 8.06 (d,  $J = 1.1$  Hz, 1H), 7.99-7.84 (m, 2H), 7.79 (d,  $J = 9.0$  Hz, 1H), 7.66 (dd,  $J = 8.7, 1.9$  Hz, 1H), 4.55 (q,  $J = 7.1$  Hz, 2H), 1.49 (t,  $J = 7.1$  Hz, 3H).

*ethyl (E)-2-(6-methylnaphthalen-2-yl)diazene-1-carboxylate (2g)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (s, 1H), 7.90 (dd,  $J = 13.5, 5.0$  Hz, 2H), 7.78 (d,  $J = 9.0$  Hz, 1H), 7.67 (s, 1H), 7.42 (d,  $J = 8.4$  Hz, 1H), 4.54 (q,  $J = 7.1$  Hz, 2H), 1.49 (t,  $J = 7.1$  Hz, 3H).

*benzyl (E)-2-(6-bromonaphthalen-2-yl)diazene-1-carboxylate (2h)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 1H), 8.06 (s, 1H), 7.96-7.84 (m, 2H), 7.78 (d,  $J = 9.0$  Hz, 1H), 7.66 (dd,  $J = 8.7, 1.7$  Hz, 1H), 7.54-7.47 (m, 2H), 7.46-7.32 (m, 3H), 5.49 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  162.14, 149.27, 137.09, 135.19, 132.48, 131.80, 131.69, 131.09, 130.57, 129.59, 129.23, 129.20, 129.11, 123.47, 116.64, 70.02.

*benzyl (E)-2-(6-methylnaphthalen-2-yl)diazene-1-carboxylate (2i)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (s, 1H), 7.96-7.84 (m, 2H), 7.77 (d,  $J = 9.0$  Hz, 1H), 7.66 (s, 1H), 7.51 (d,  $J = 5.9$  Hz, 2H), 7.45-7.33 (m, 4H), 5.49 (s, 2H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  162.29, 148.68, 140.14, 136.40, 135.28, 132.24, 131.38, 130.35, 130.17, 129.63, 129.20, 129.17, 129.10, 127.51, 115.26, 69.87, 21.99.

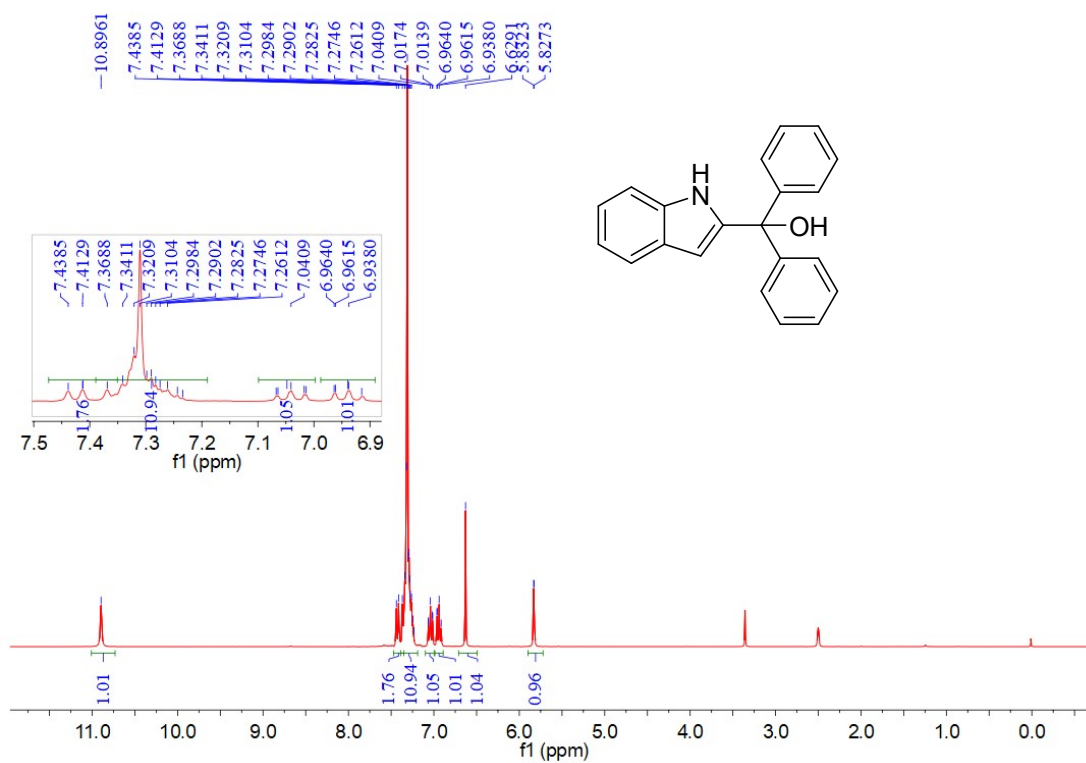
*ethyl (E)-2-(7-bromonaphthalen-2-yl)diazene-1-carboxylate (2j)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.18 (d,  $J = 1.4$  Hz, 1H), 7.95-7.82 (m, 2H), 7.79-7.72 (m, 1H), 7.79-7.65 (m, 1H), 4.55 (q,  $J = 7.1$  Hz, 2H), 1.49 (t,  $J = 7.1$  Hz, 3H).

*ethyl (E)-2-(7-methylnaphthalen-2-yl)diazene-1-carboxylate (2k)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (s, 1H), 7.84 (d,  $J = 1.4$  Hz, 2H), 7.82-7.76 (m, 2H), 7.46 (dd,  $J = 8.4, 1.4$  Hz, 1H), 4.54 (q,  $J = 7.1$  Hz, 2H), 1.49 (t,  $J = 7.1$  Hz, 3H).

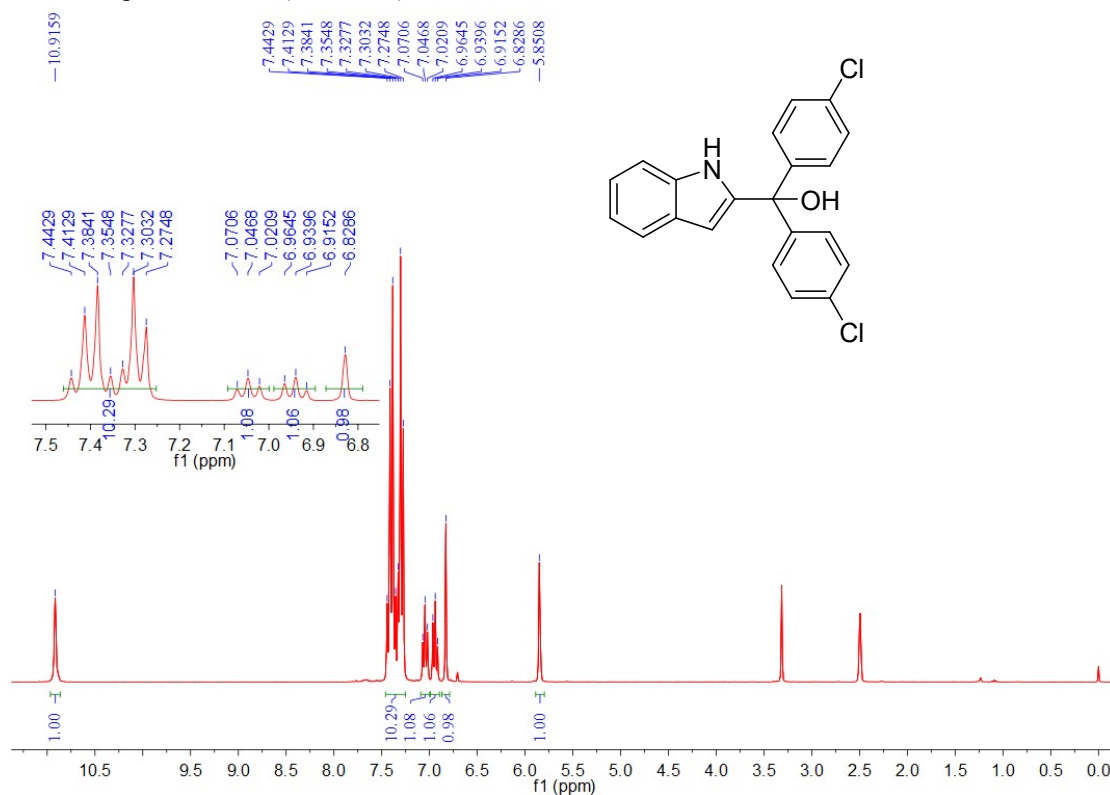
*ethyl (E)-2-(7-methoxynaphthalen-2-yl)diazene-1-carboxylate (2l)*  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (s, 1H), 7.84 (d,  $J = 1.4$  Hz, 2H), 7.82-7.76 (m, 2H), 7.46 (dd,  $J = 8.4, 1.4$  Hz, 1H), 4.54 (q,  $J = 7.1$  Hz, 2H), 2.55 (s, 4H), 1.49 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  162.49, 158.78, 149.58, 134.76, 131.49, 130.48, 130.01, 129.99, 122.12, 112.88, 108.65, 64.76, 55.90, 14.43.

#### 4. NMR spectra of all substrates and products

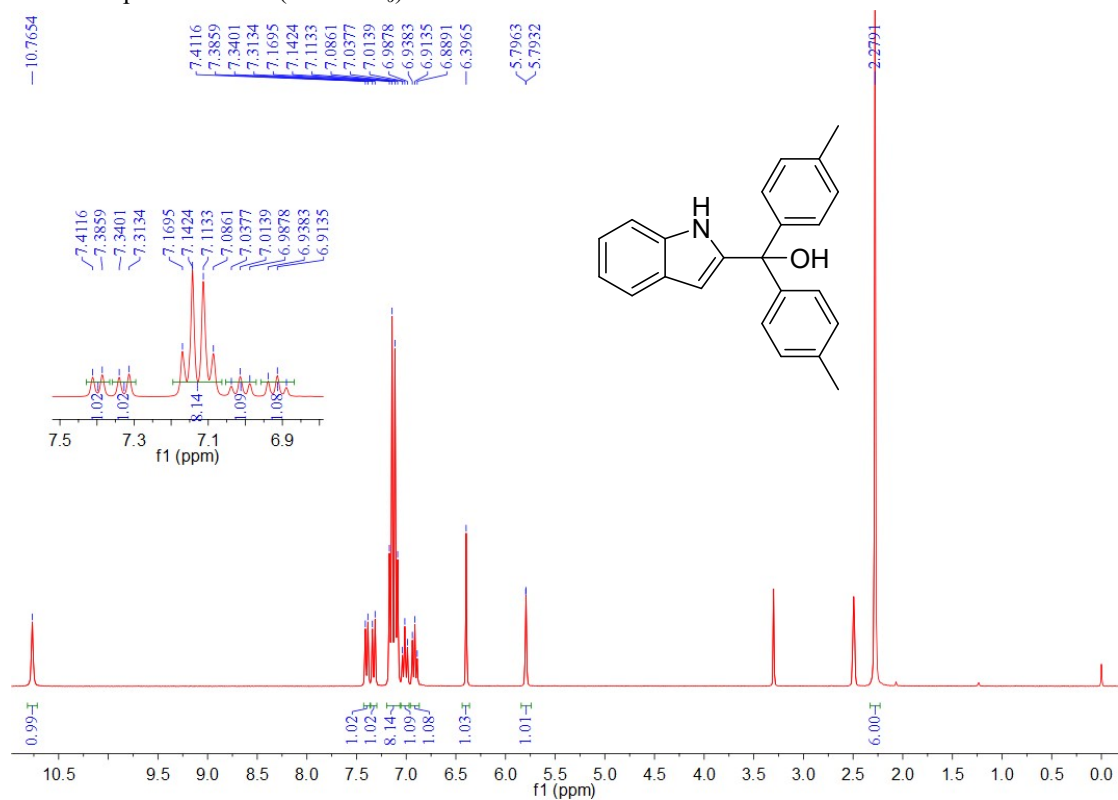
$^1\text{H}$  NMR spectrum of **1a** ( $\text{DMSO-}d_6$ )



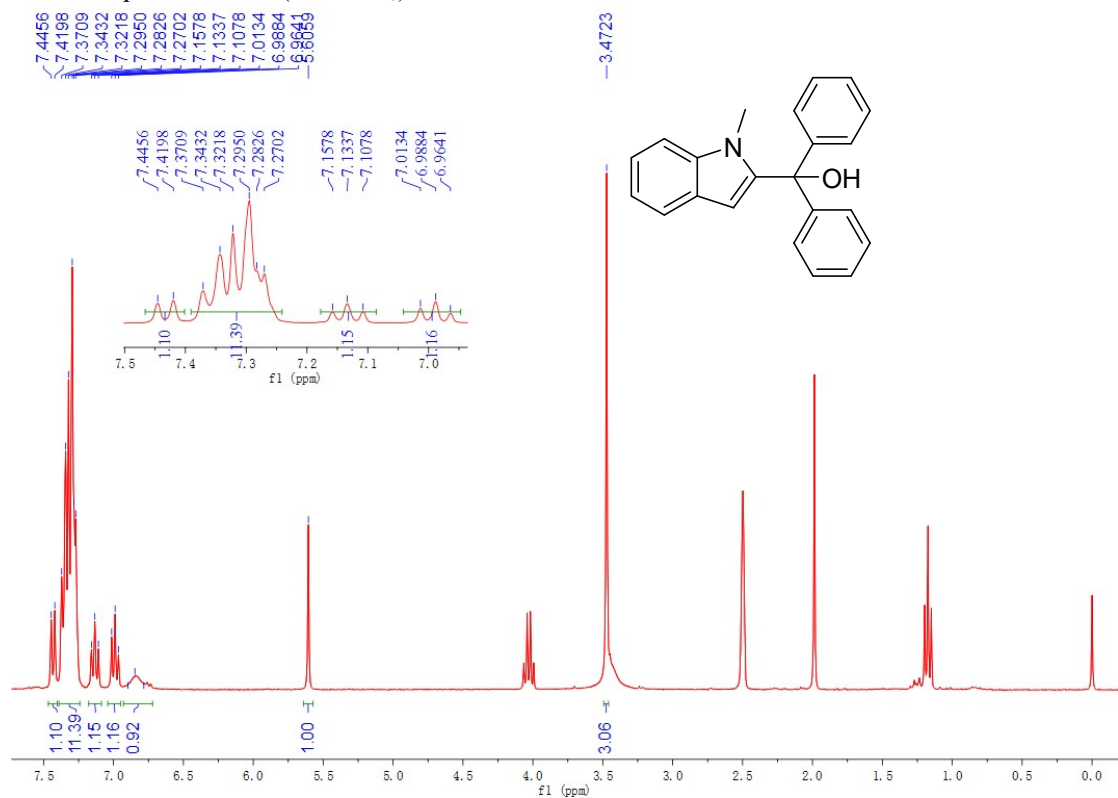
$^1\text{H}$  NMR spectrum of **1b** ( $\text{DMSO-}d_6$ )



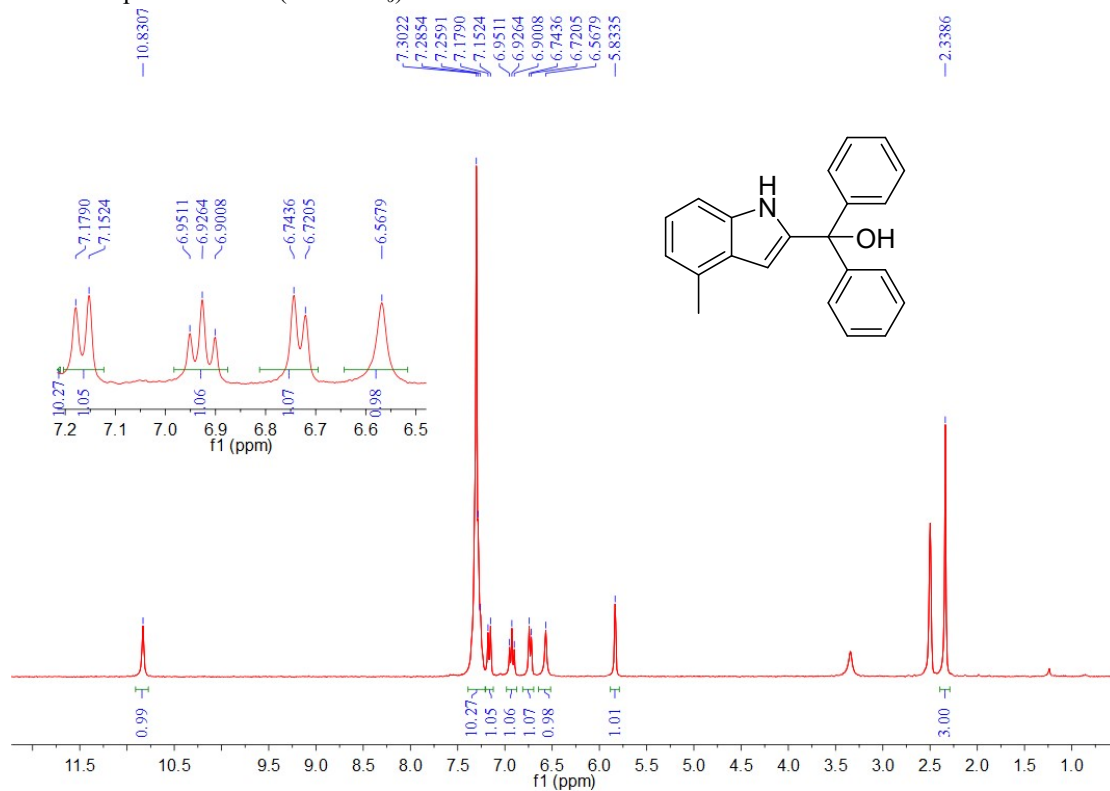
<sup>1</sup>H NMR spectrum of **1c** (DMSO-*d*<sub>6</sub>)



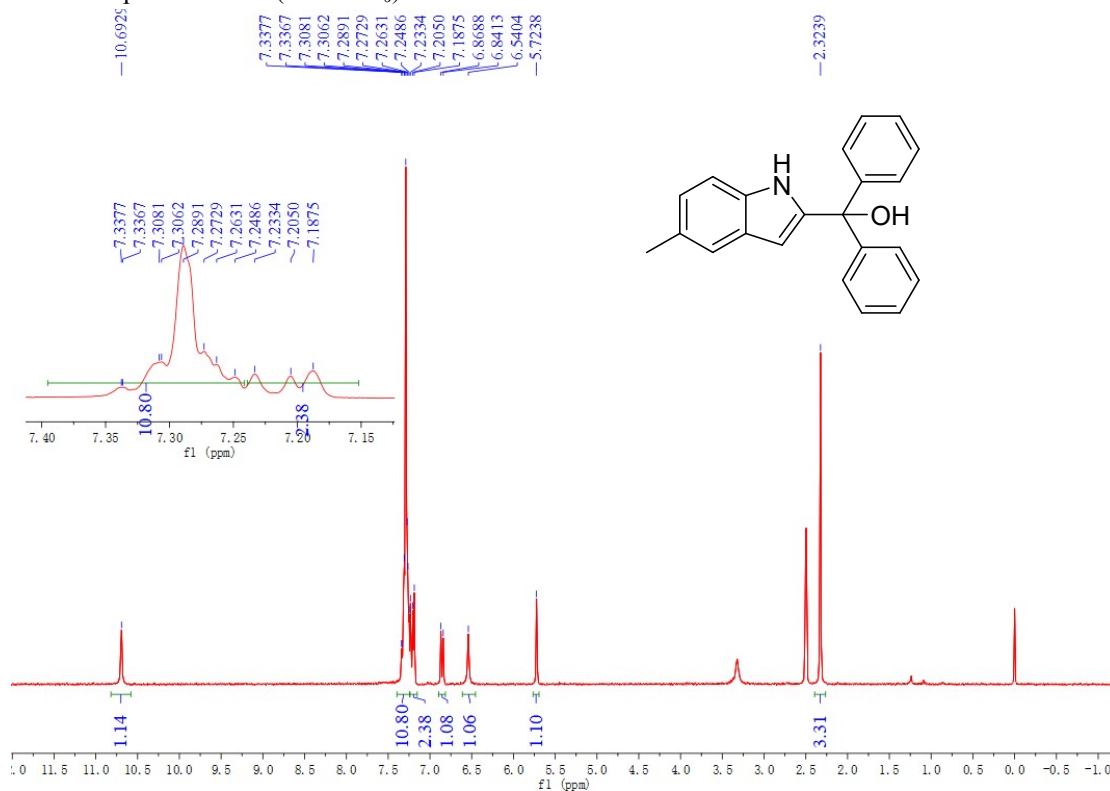
<sup>1</sup>H NMR spectrum of **1d** (DMSO-*d*<sub>6</sub>)



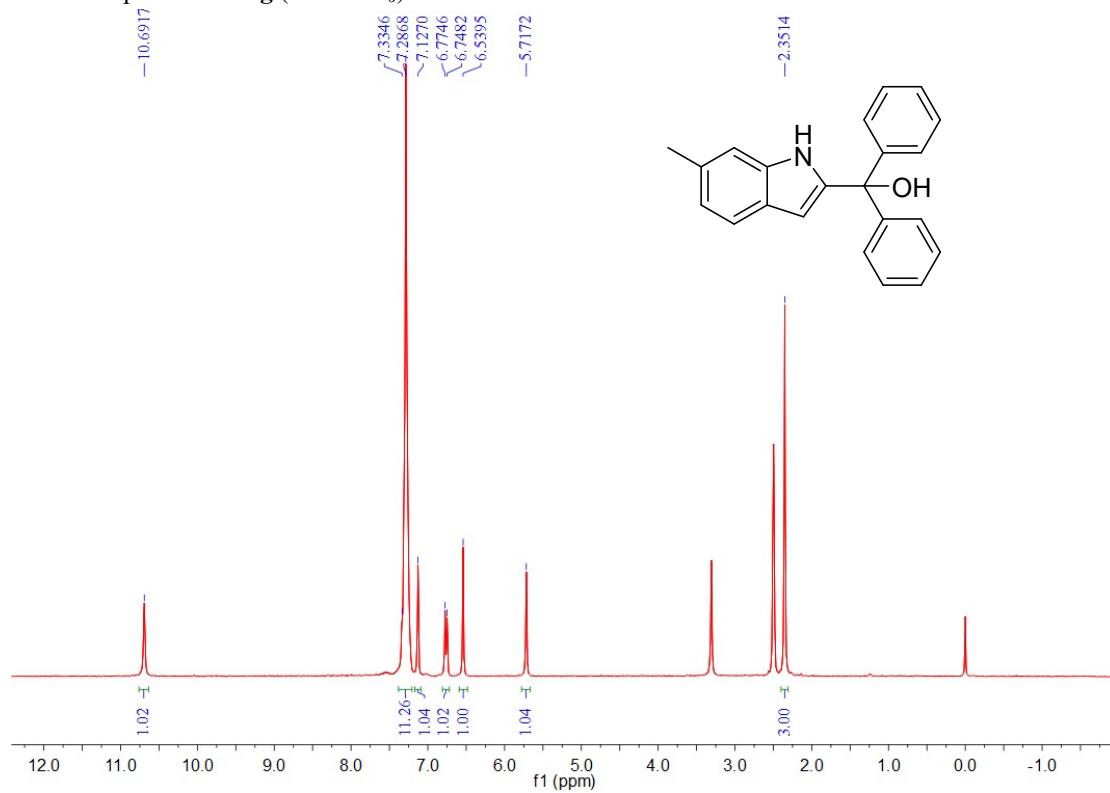
<sup>1</sup>H NMR spectrum of **1e** (DMSO-*d*<sub>6</sub>)



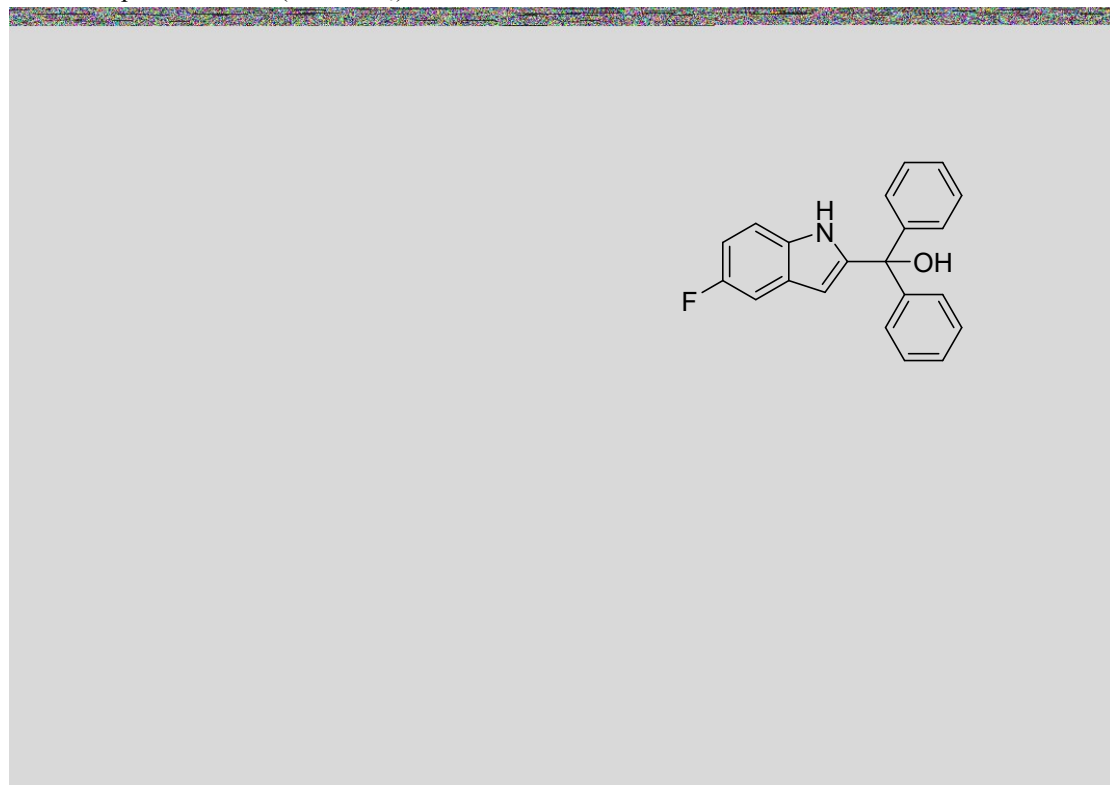
<sup>1</sup>H NMR spectrum of **1f** (DMSO-*d*<sub>6</sub>)



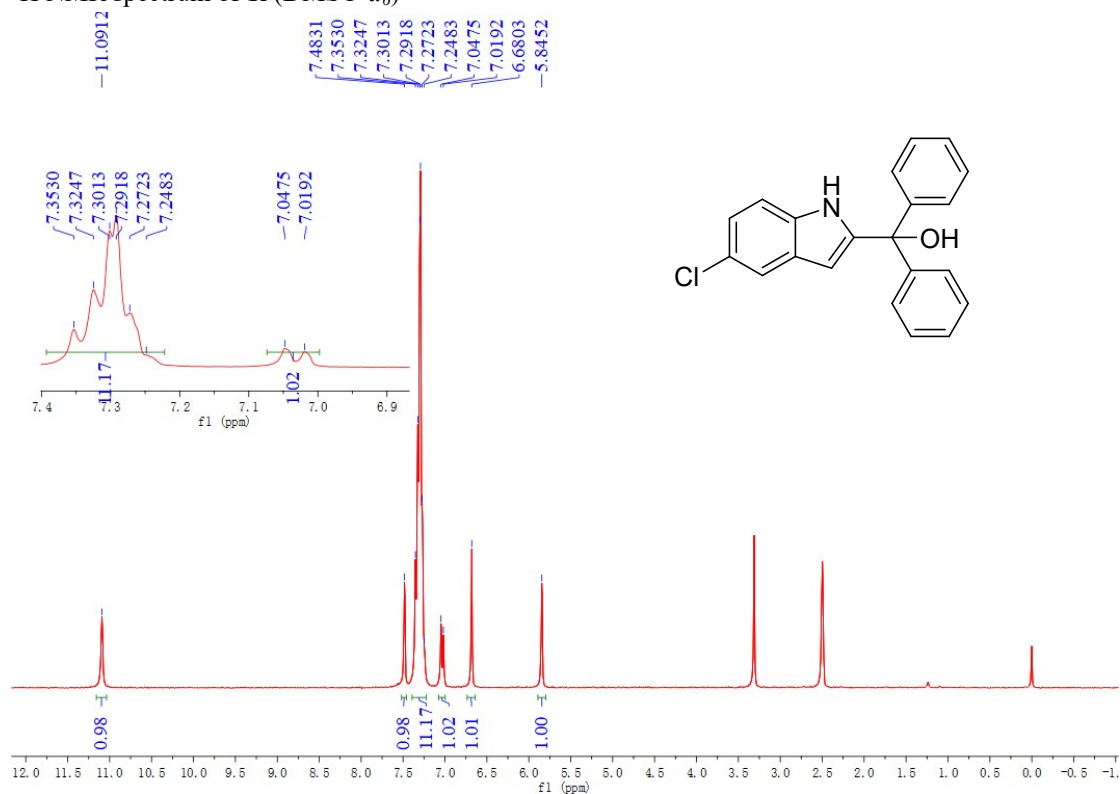
$^1\text{H}$  NMR spectrum of **1g** ( $\text{DMSO-}d_6$ )



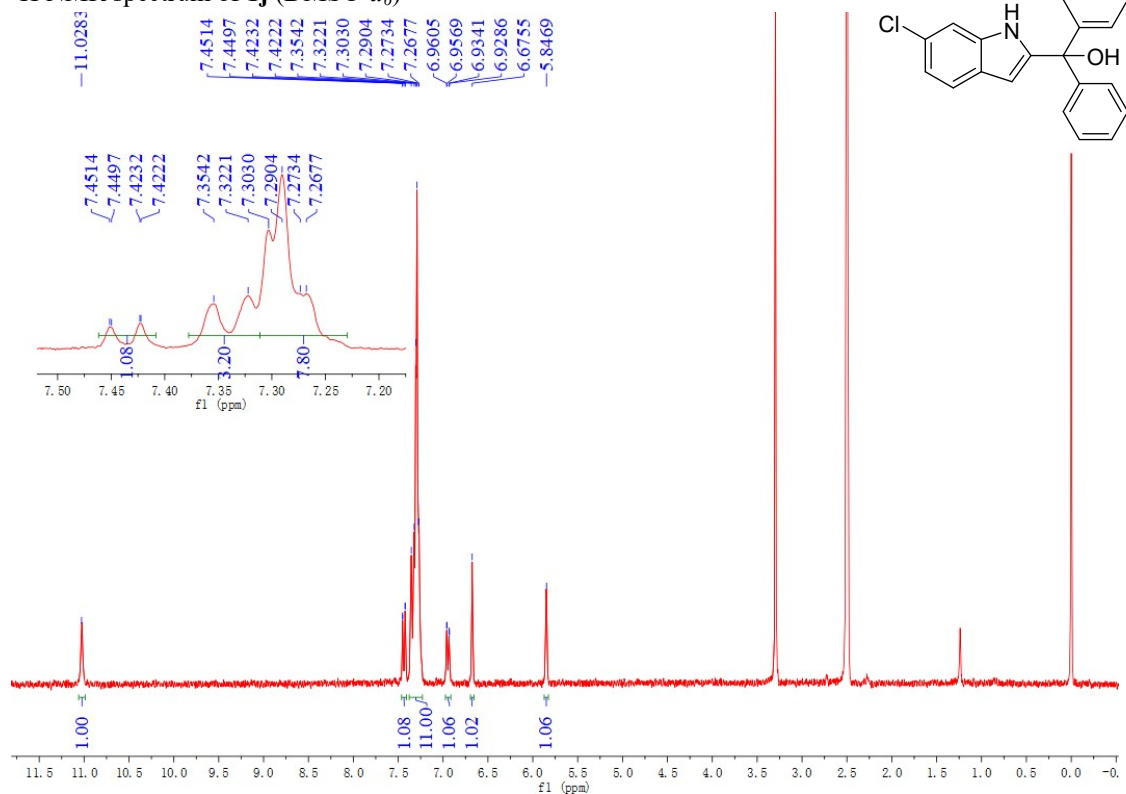
$^1\text{H}$  NMR spectrum of **1h** ( $\text{DMSO-}d_6$ )



<sup>1</sup>H NMR spectrum of **1i** (DMSO-*d*<sub>6</sub>)

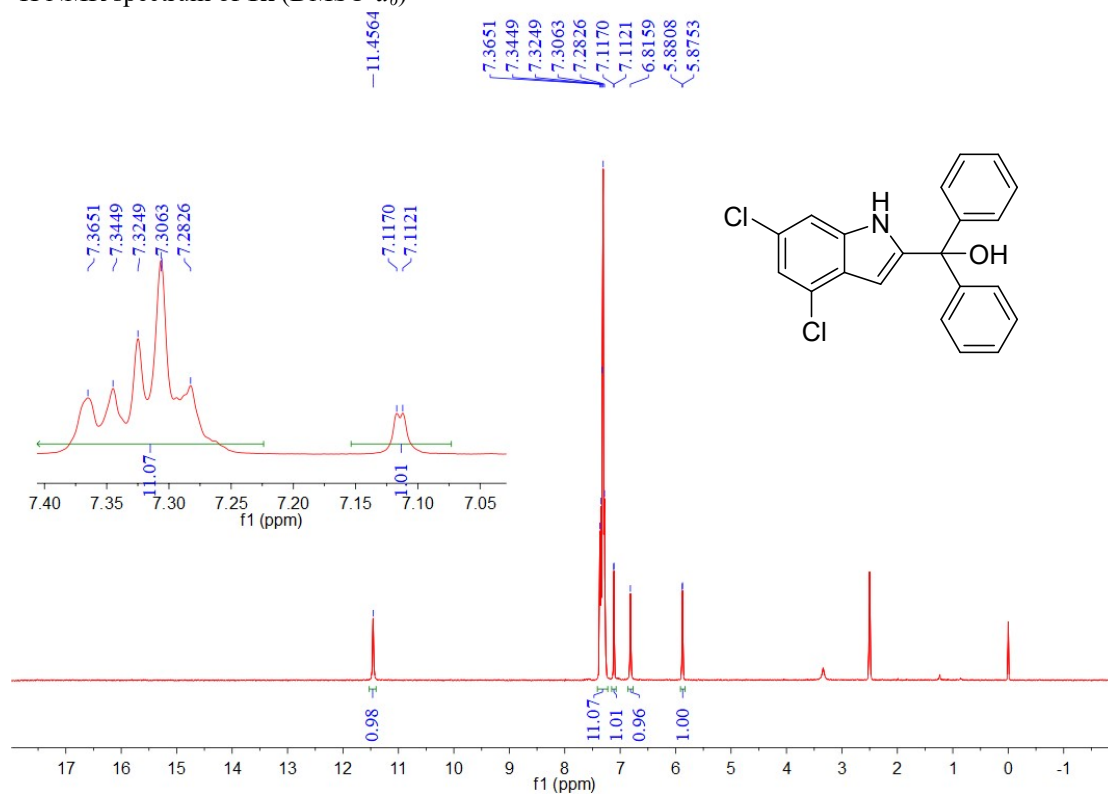


<sup>1</sup>H NMR spectrum of **1j** (DMSO-*d*<sub>6</sub>)

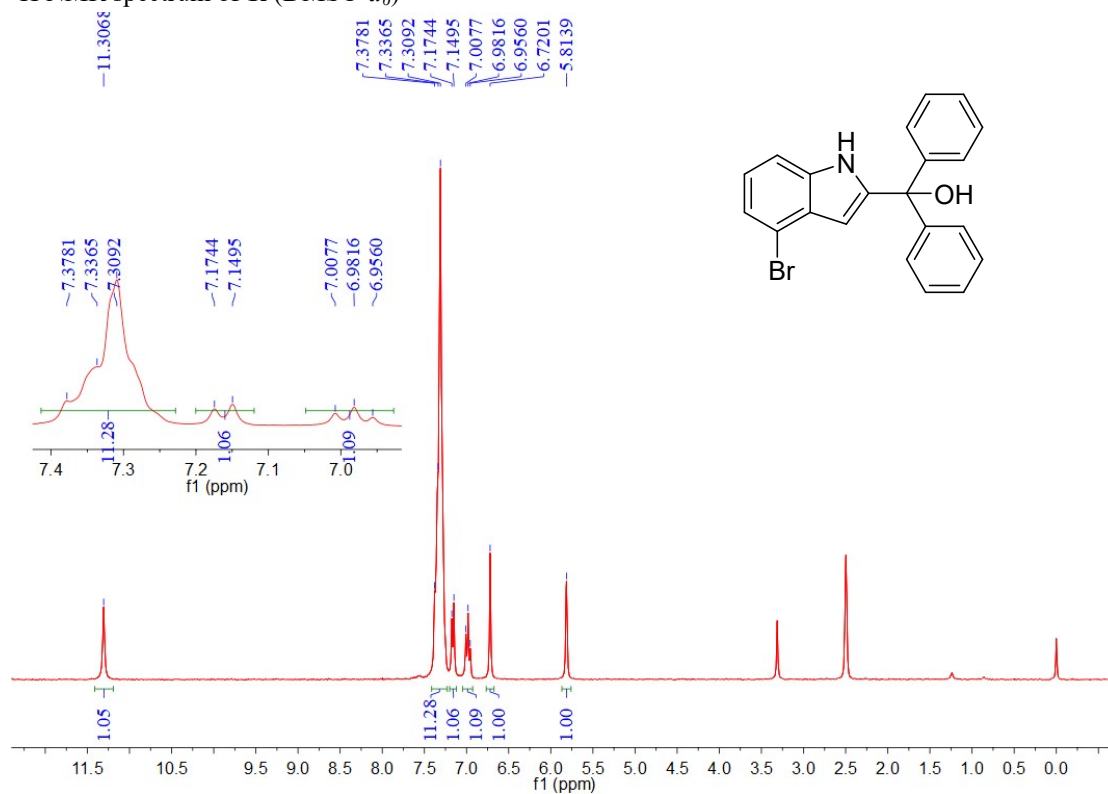




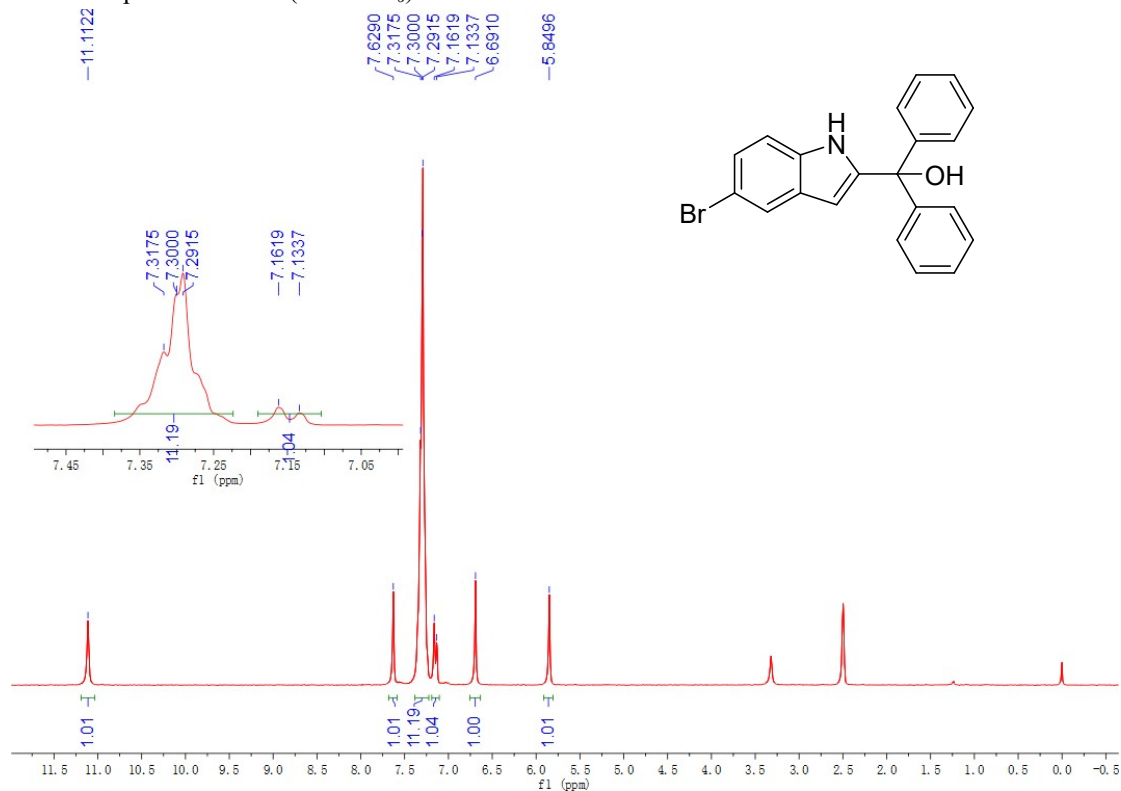
<sup>1</sup>H NMR spectrum of **1k** (DMSO-*d*<sub>6</sub>)



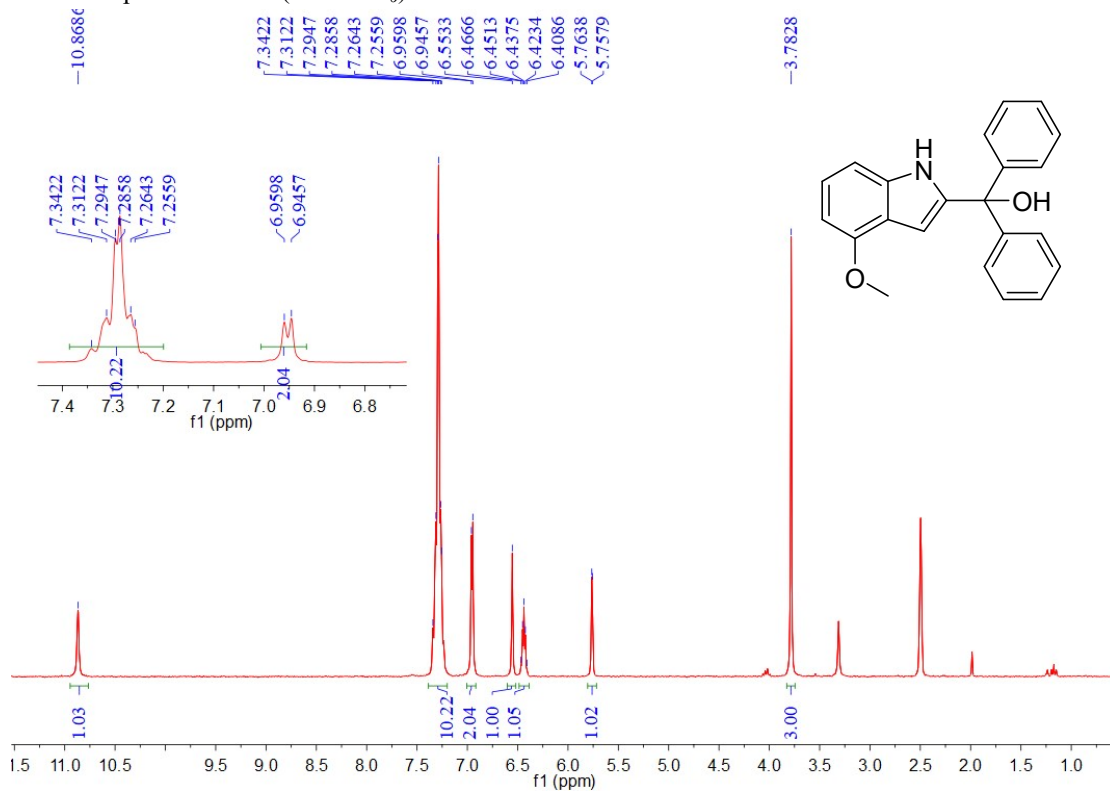
<sup>1</sup>H NMR spectrum of **1l** (DMSO-*d*<sub>6</sub>)



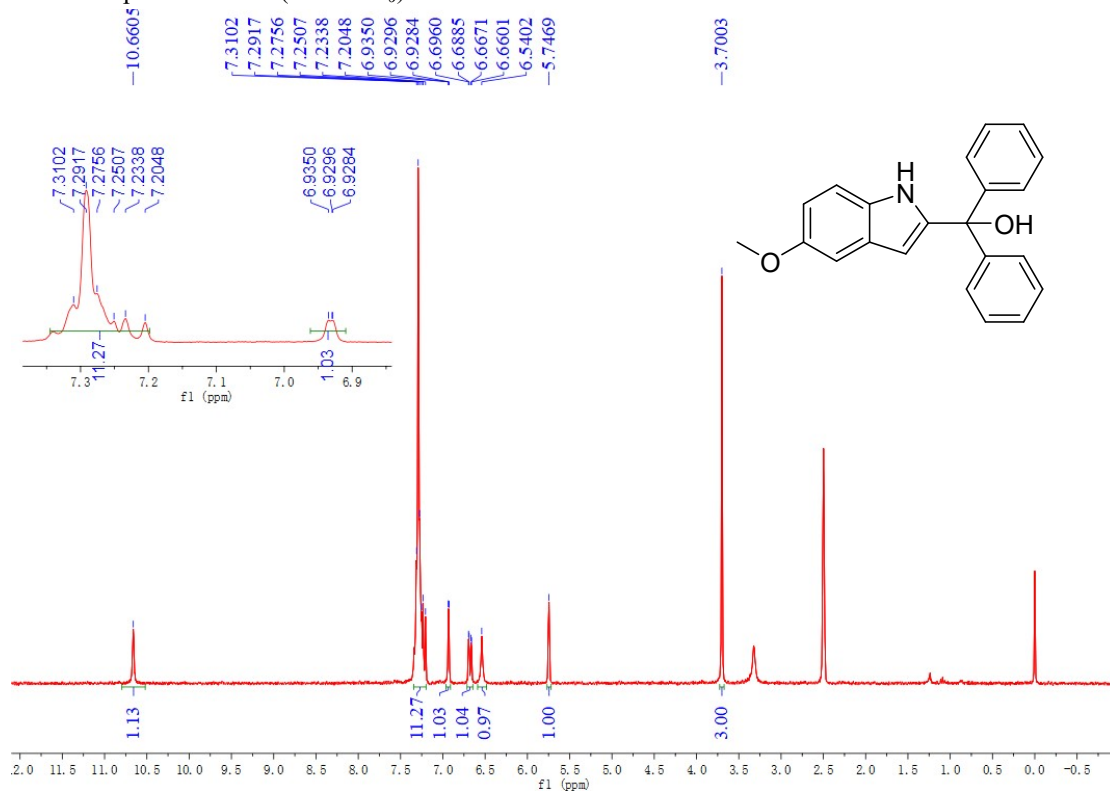
<sup>1</sup>H NMR spectrum of **1m** (DMSO-*d*<sub>6</sub>)



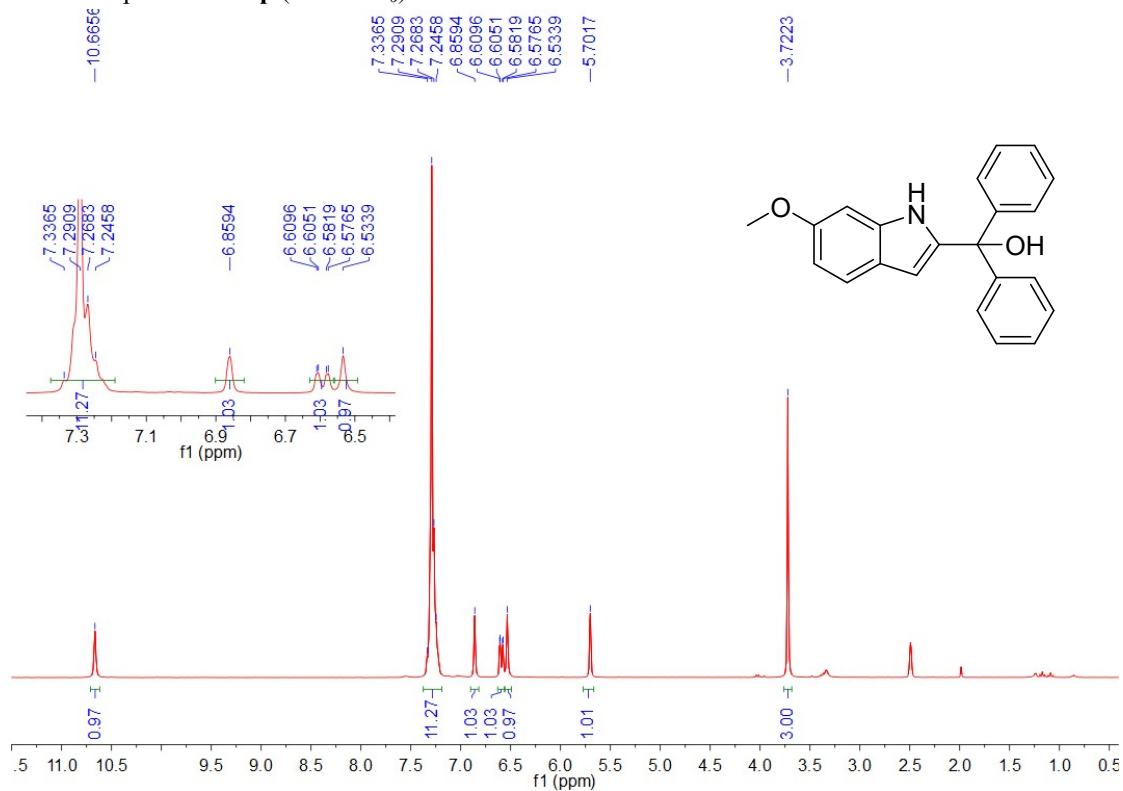
<sup>1</sup>H NMR spectrum of **1n** (DMSO-*d*<sub>6</sub>)



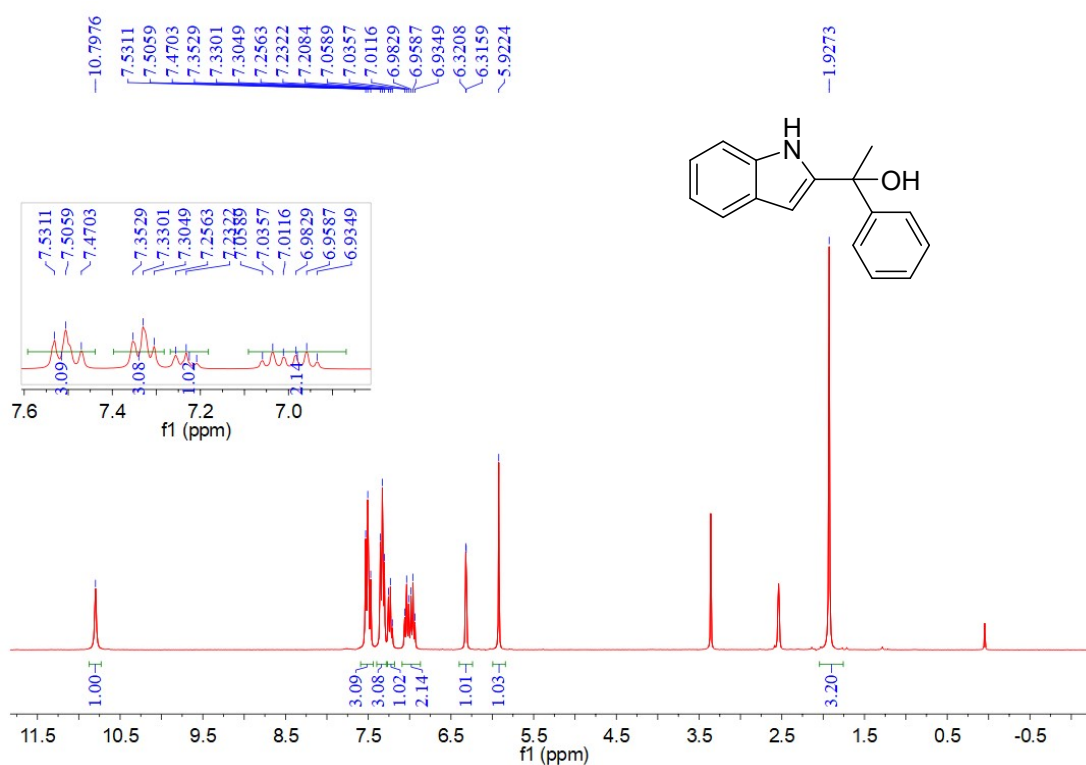
<sup>1</sup>H NMR spectrum of **1o** (DMSO-*d*<sub>6</sub>)



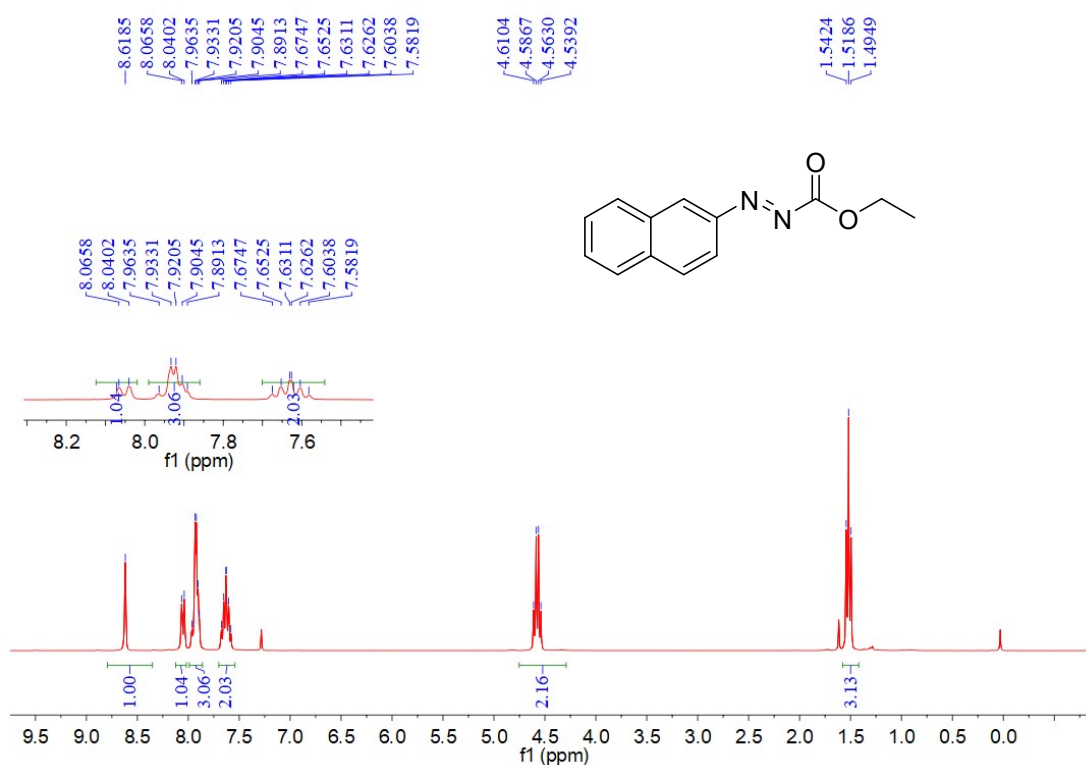
<sup>1</sup>H NMR spectrum of **1p** (DMSO-*d*<sub>6</sub>)



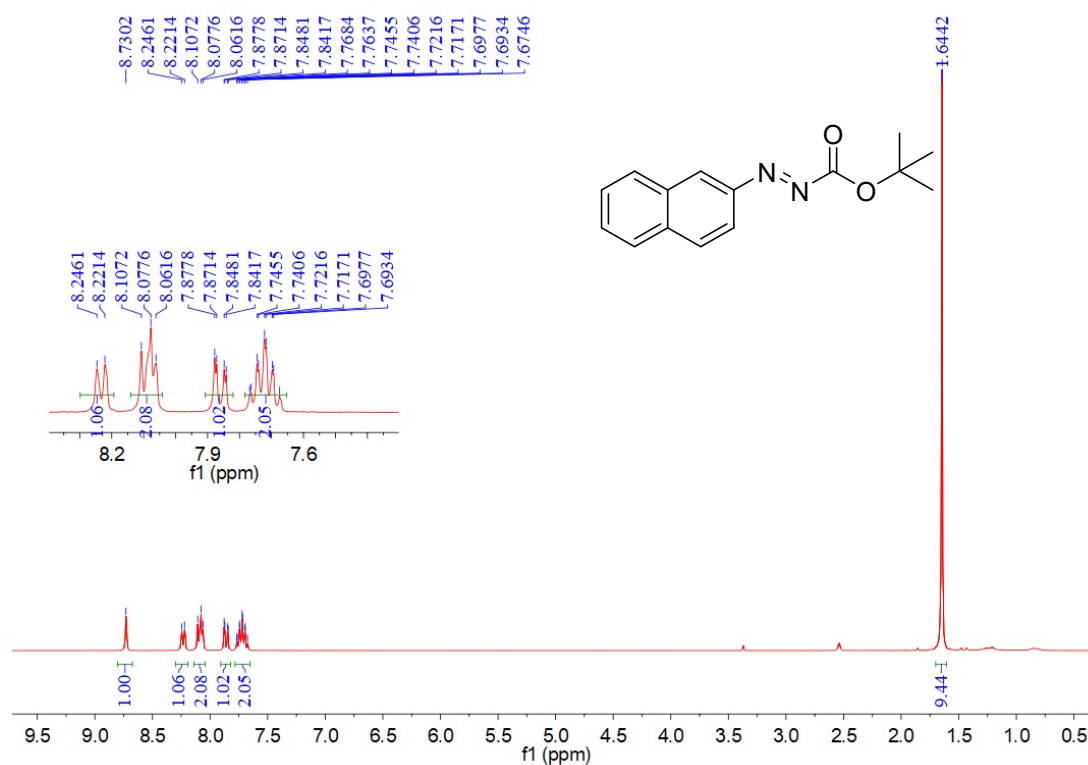
$^1\text{H}$  NMR spectrum of **1q** ( $\text{DMSO-}d_6$ )



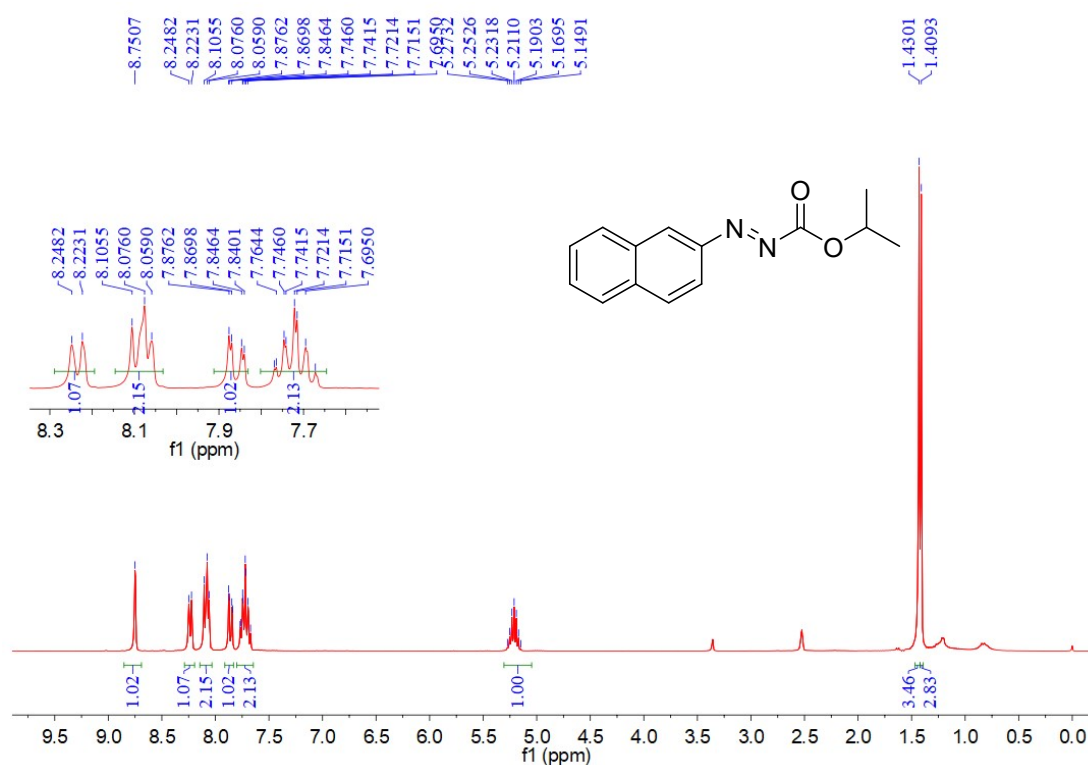
$^1\text{H}$  NMR spectrum of **2a** ( $\text{CDCl}_3$ )



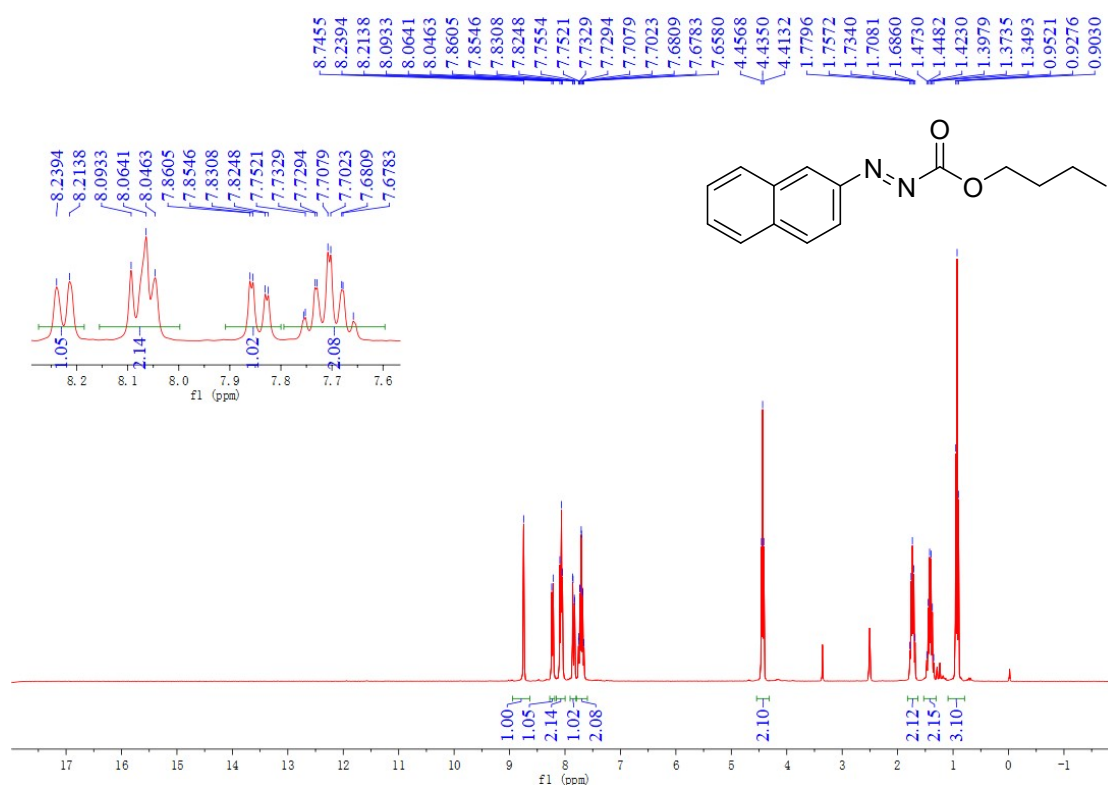
<sup>1</sup>H NMR spectrum of **2b** (DMSO-*d*<sub>6</sub>)



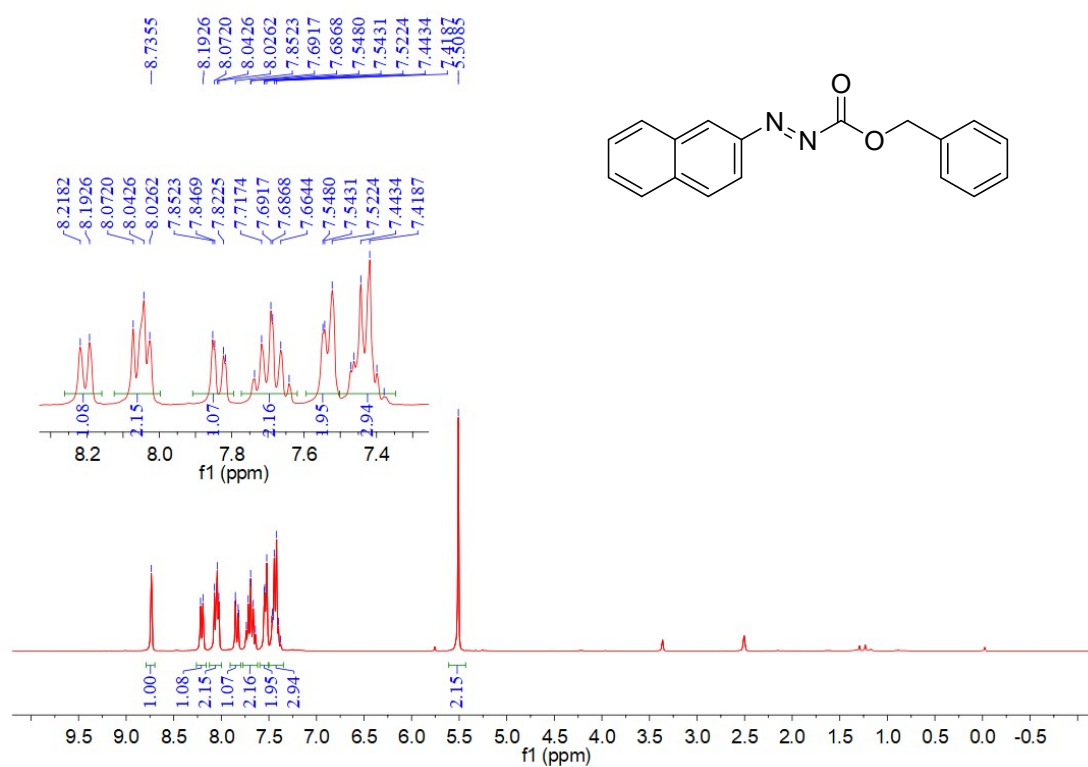
<sup>1</sup>H NMR spectrum of **2c** (DMSO-*d*<sub>6</sub>)



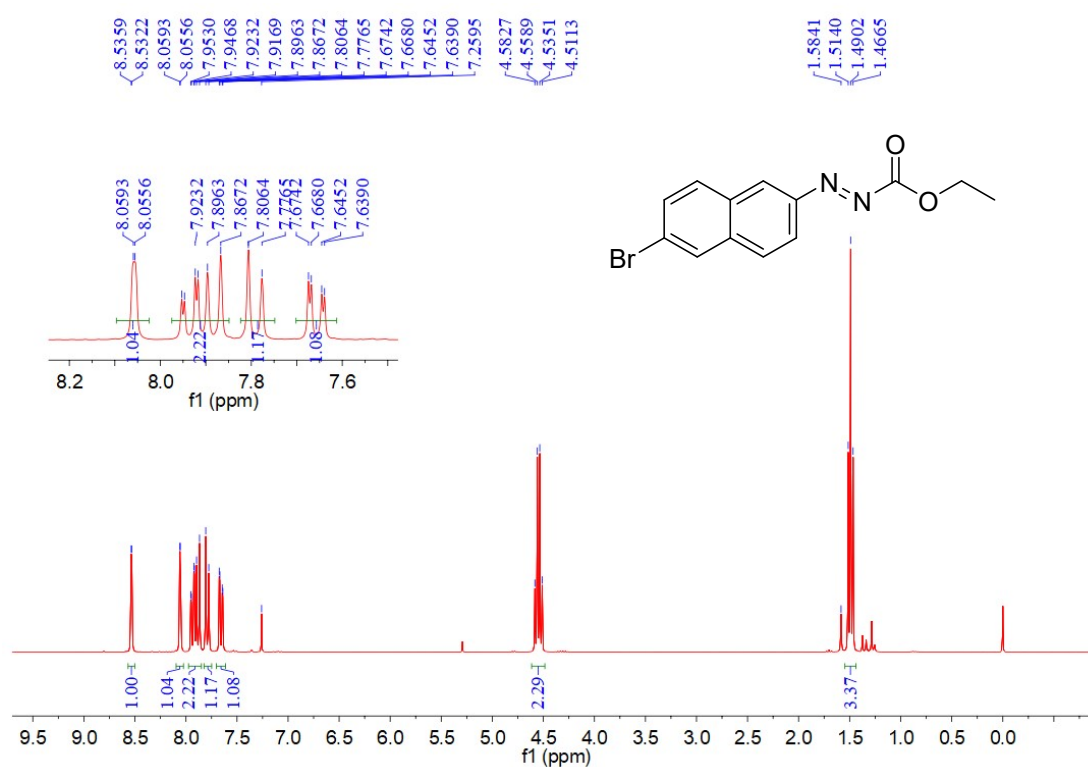
$^1\text{H}$  NMR spectrum of **2d** ( $\text{DMSO}-d_6$ )



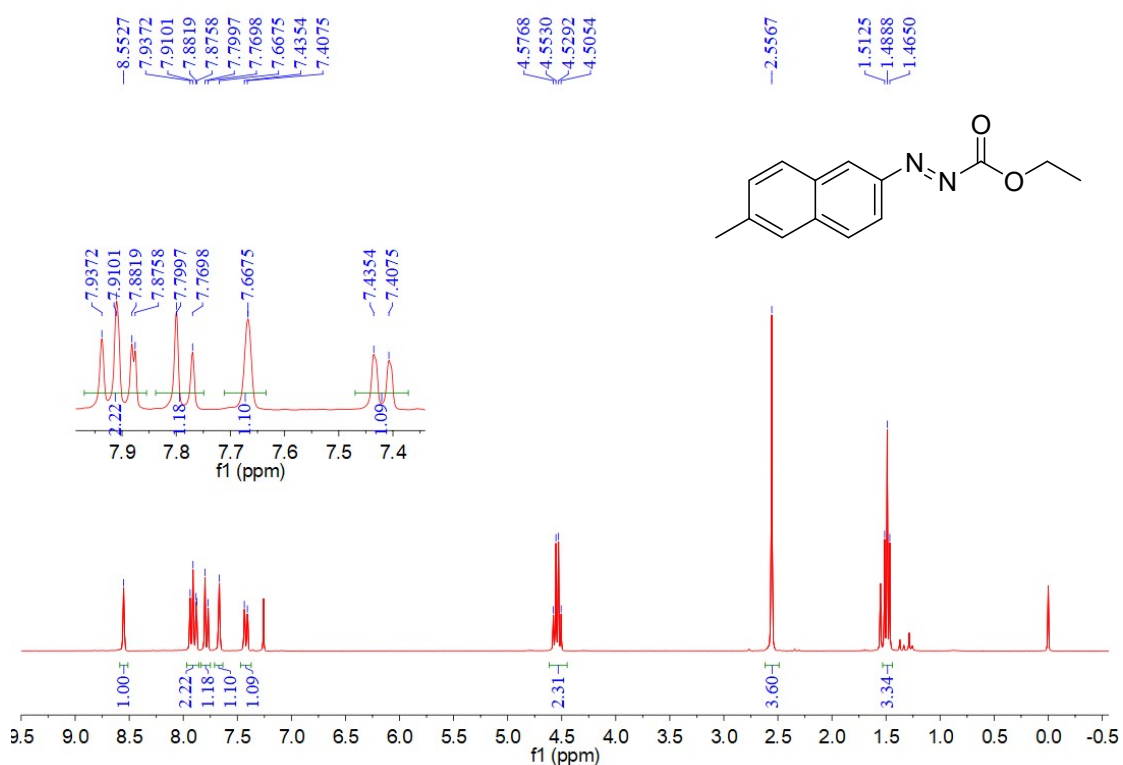
$^1\text{H}$  NMR spectrum of **2e** ( $\text{DMSO}-d_6$ )



$^1\text{H}$  NMR spectrum of **2f** ( $\text{CDCl}_3$ )

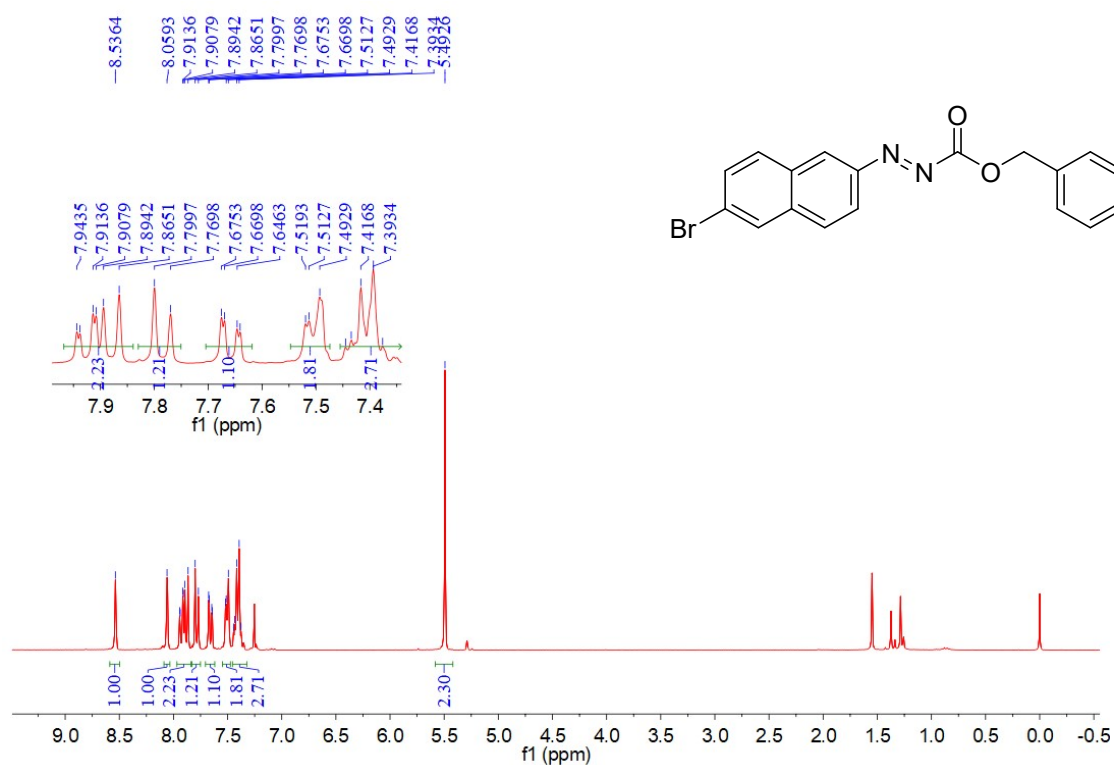


$^1\text{H}$  NMR spectrum of **2g** ( $\text{CDCl}_3$ )

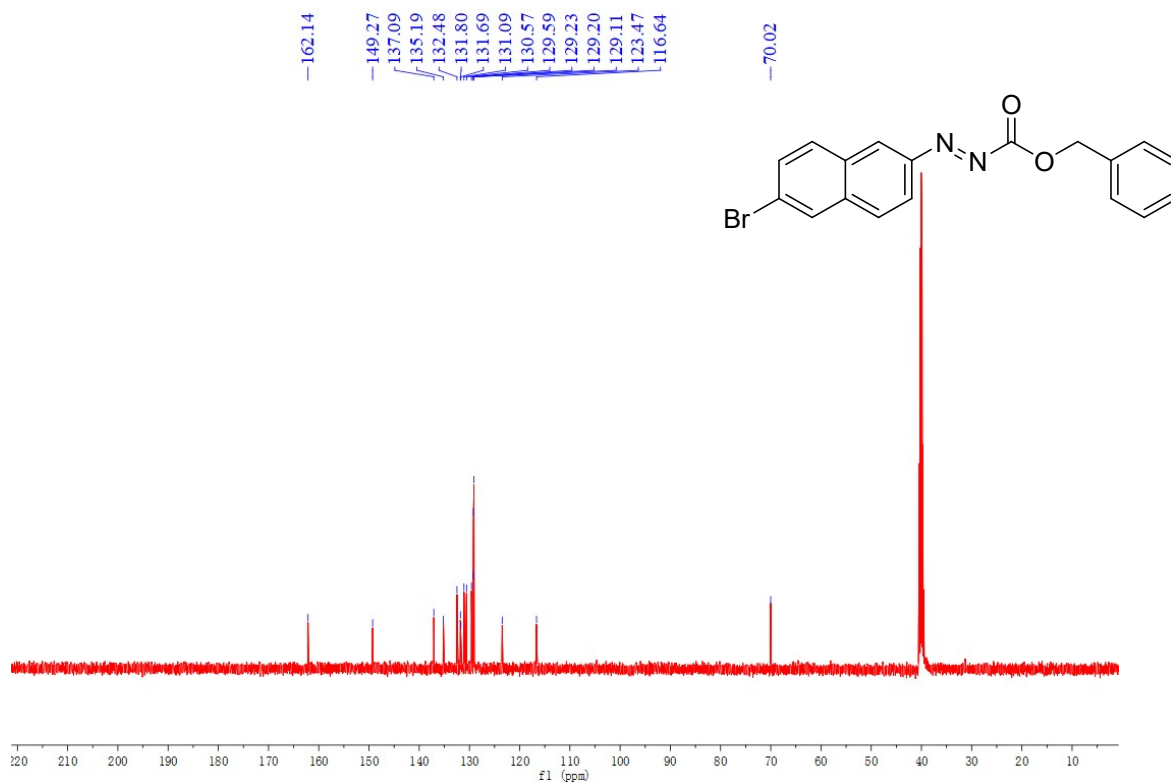




<sup>1</sup>H NMR spectrum of **2h** (CDCl<sub>3</sub>)

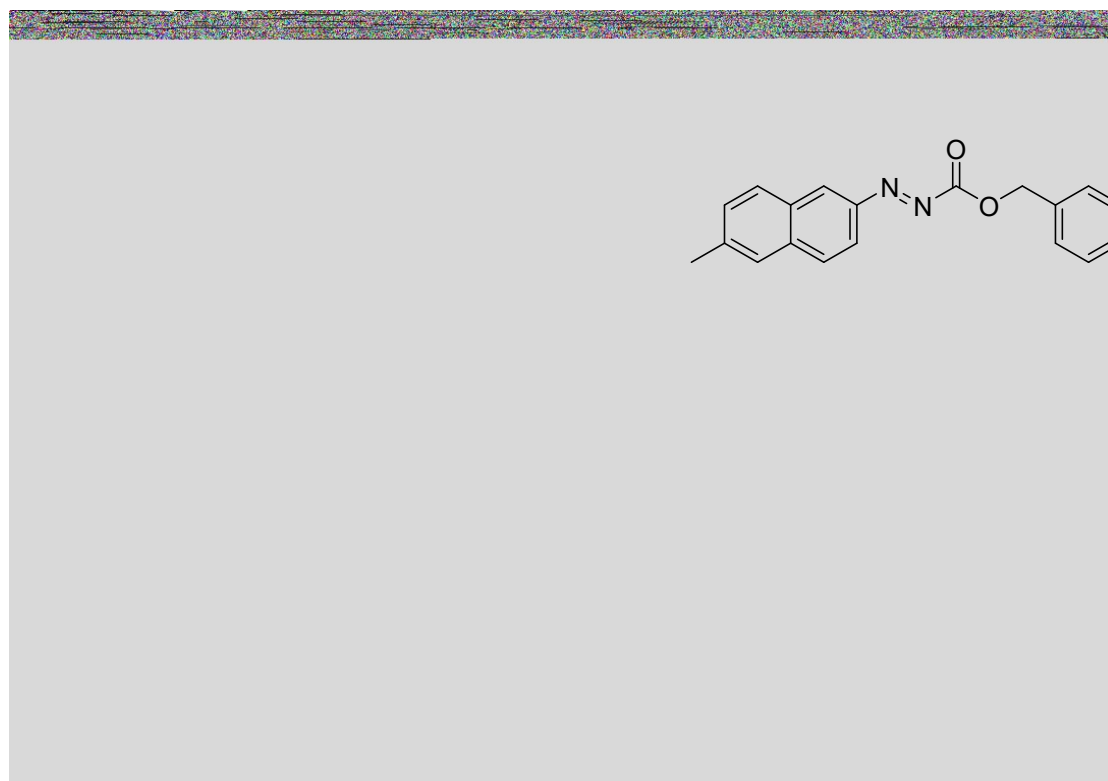


<sup>13</sup>C NMR spectrum of **2h** (DMSO-*d*<sub>6</sub>)

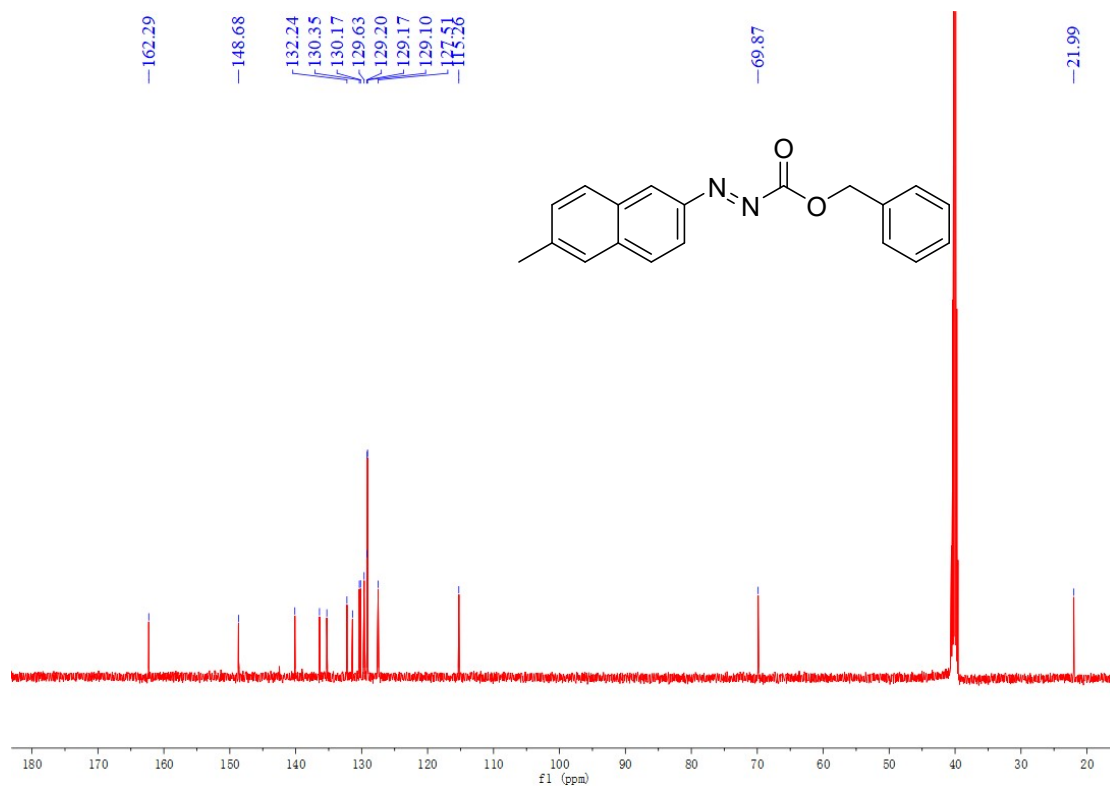




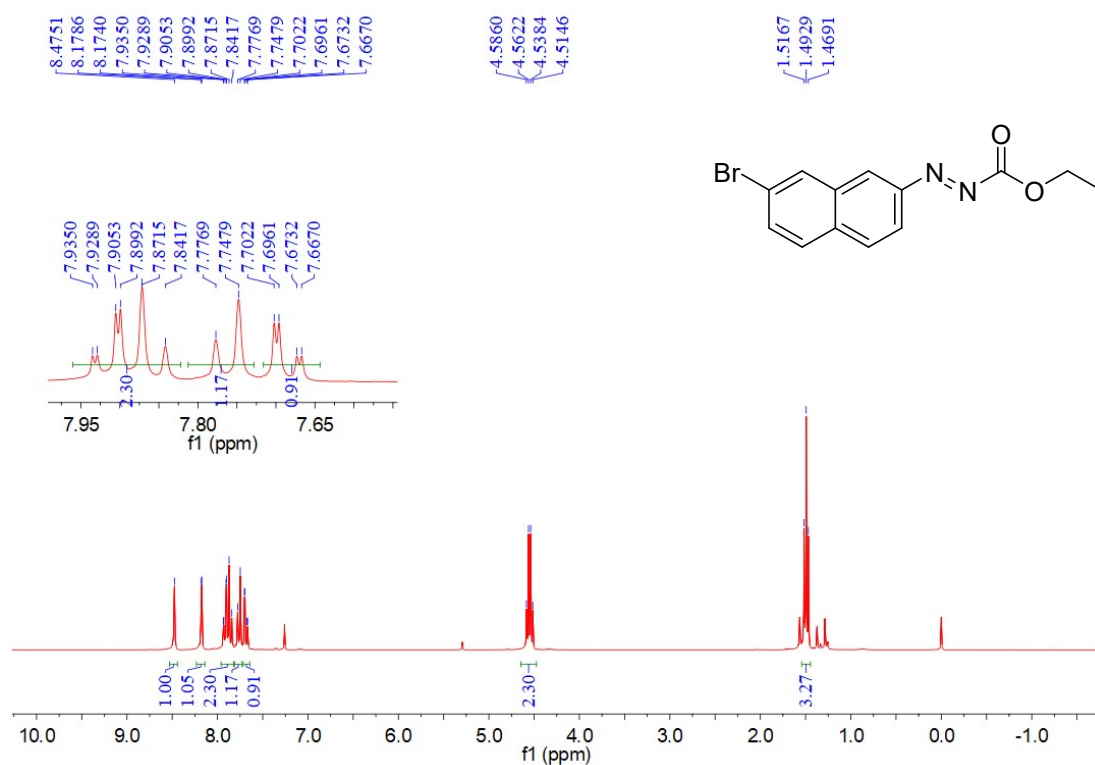
$^1\text{H}$  NMR spectrum of **2i** ( $\text{CDCl}_3$ )



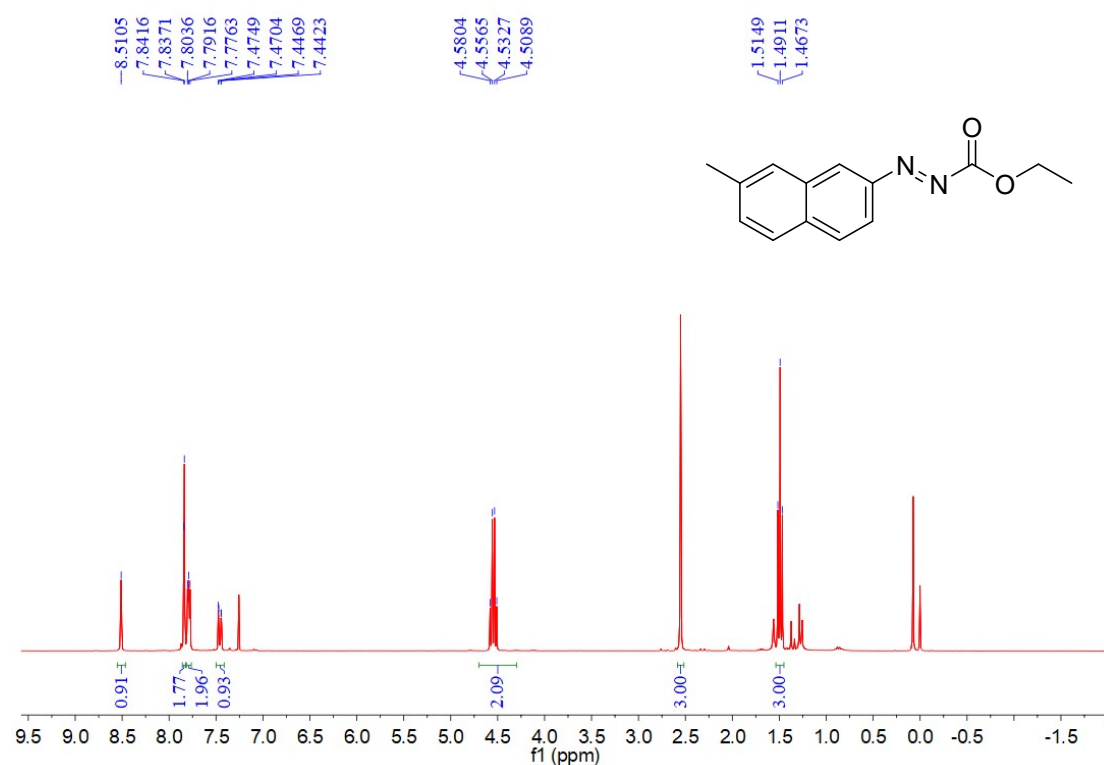
$^{13}\text{C}$  NMR spectrum of **2i** ( $\text{DMSO-}d_6$ )



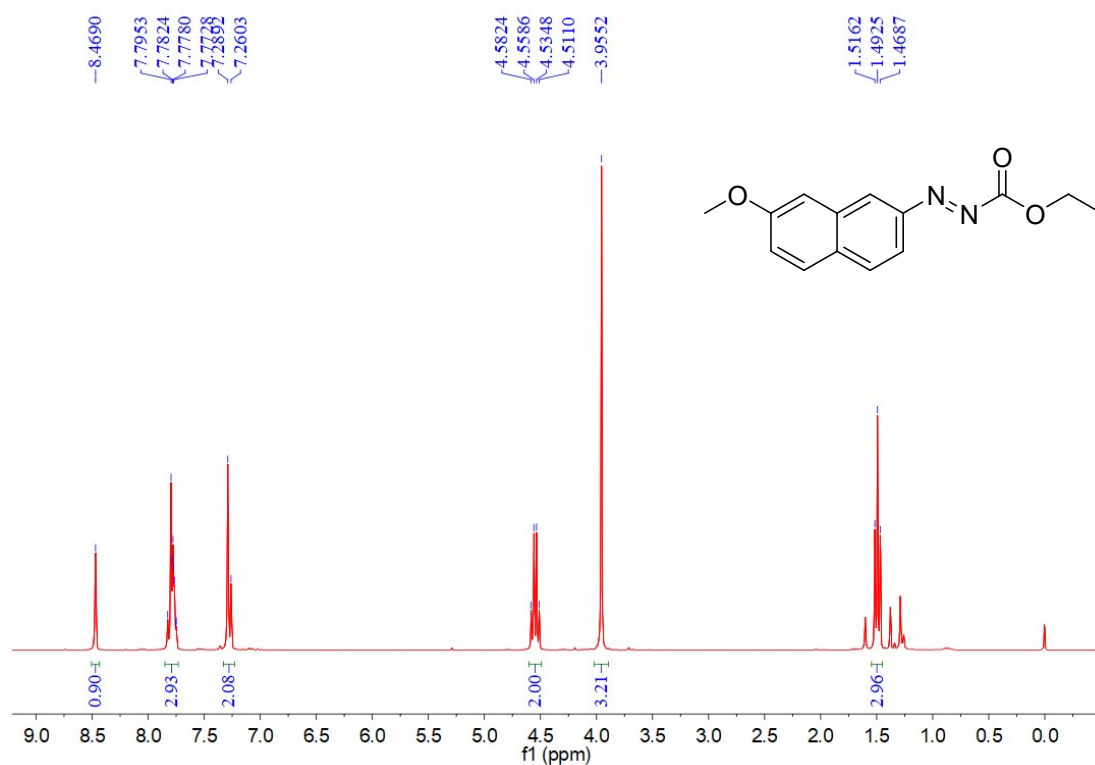
<sup>1</sup>H NMR spectrum of **2j** (CDCl<sub>3</sub>)



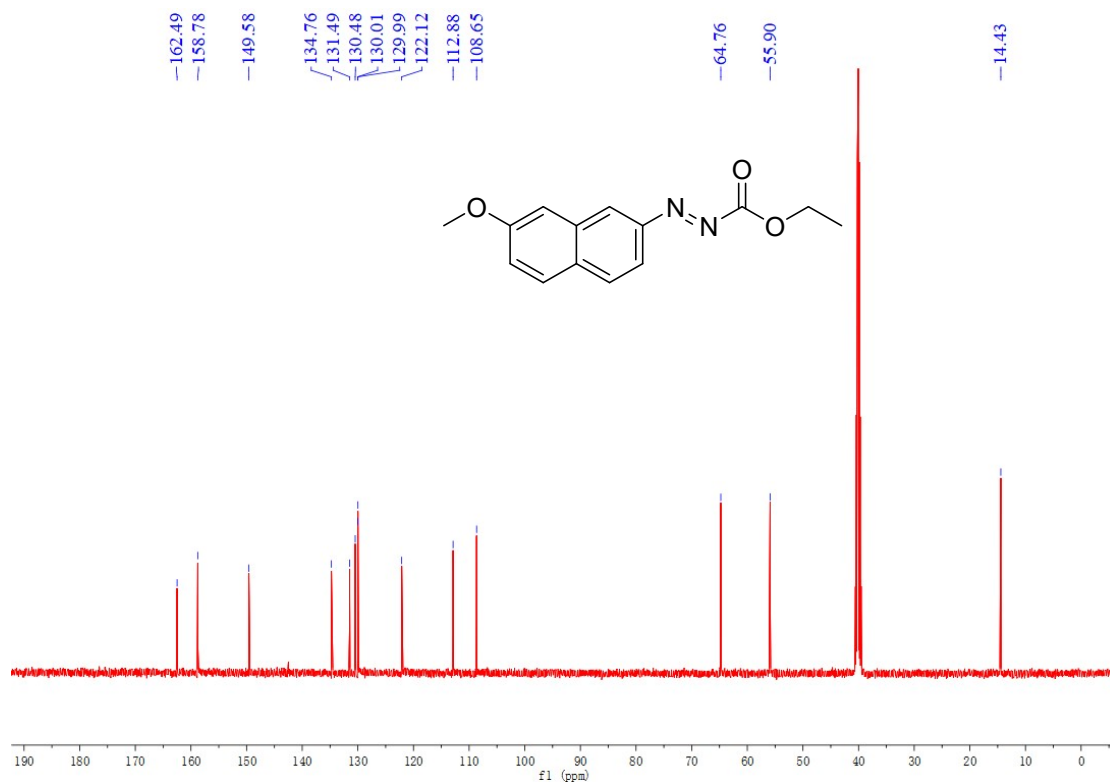
<sup>1</sup>H NMR spectrum of **2k** (CDCl<sub>3</sub>)



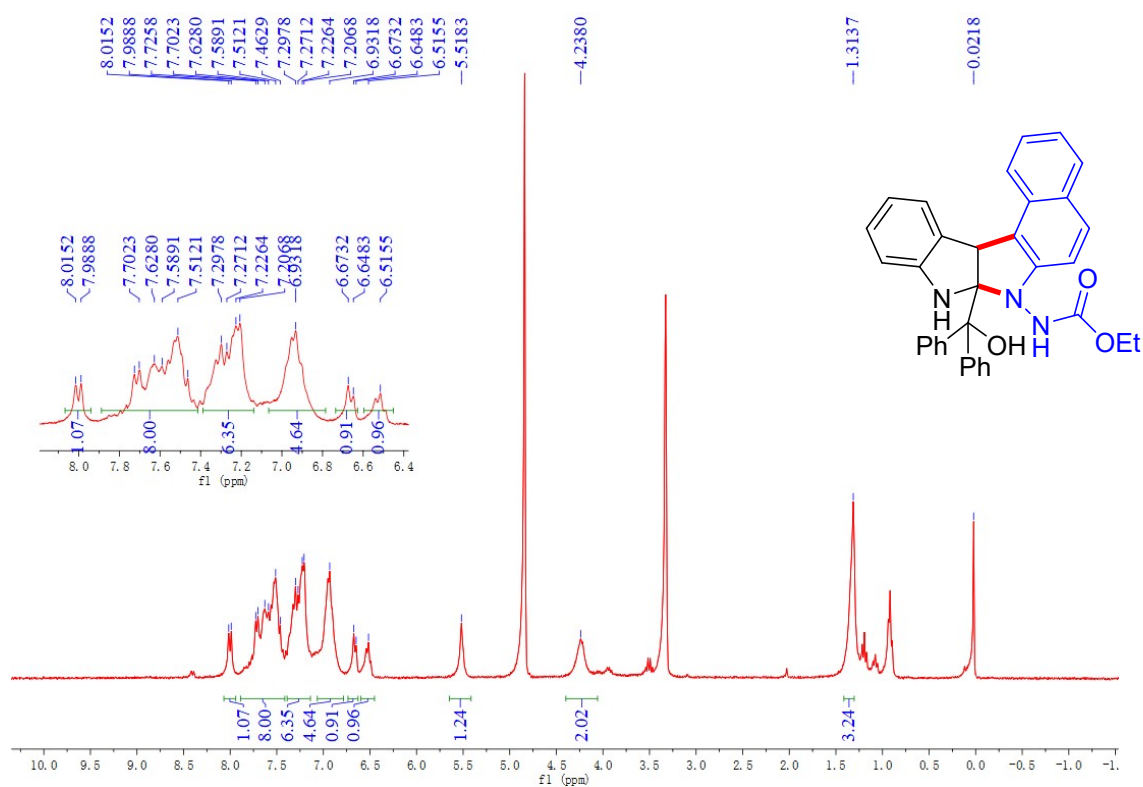
<sup>1</sup>H NMR spectrum of **21** (CDCl<sub>3</sub>)



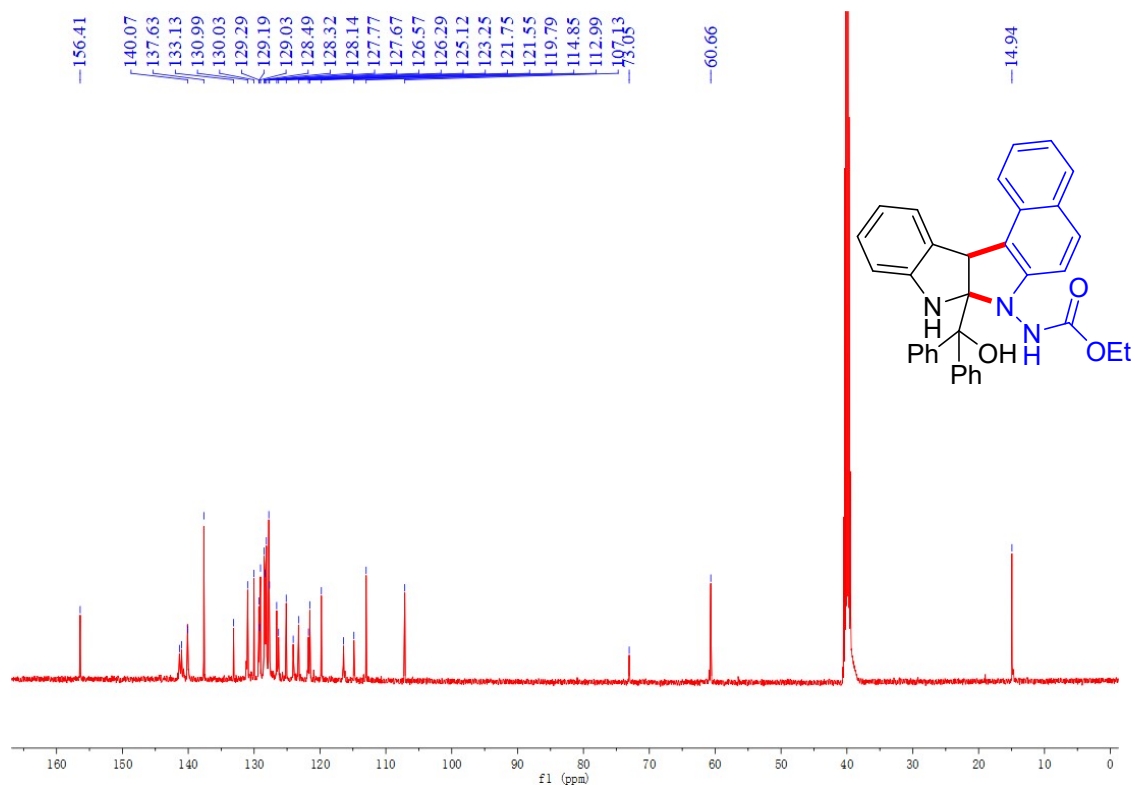
<sup>13</sup>C NMR spectrum of **21** (DMSO-*d*<sub>6</sub>)



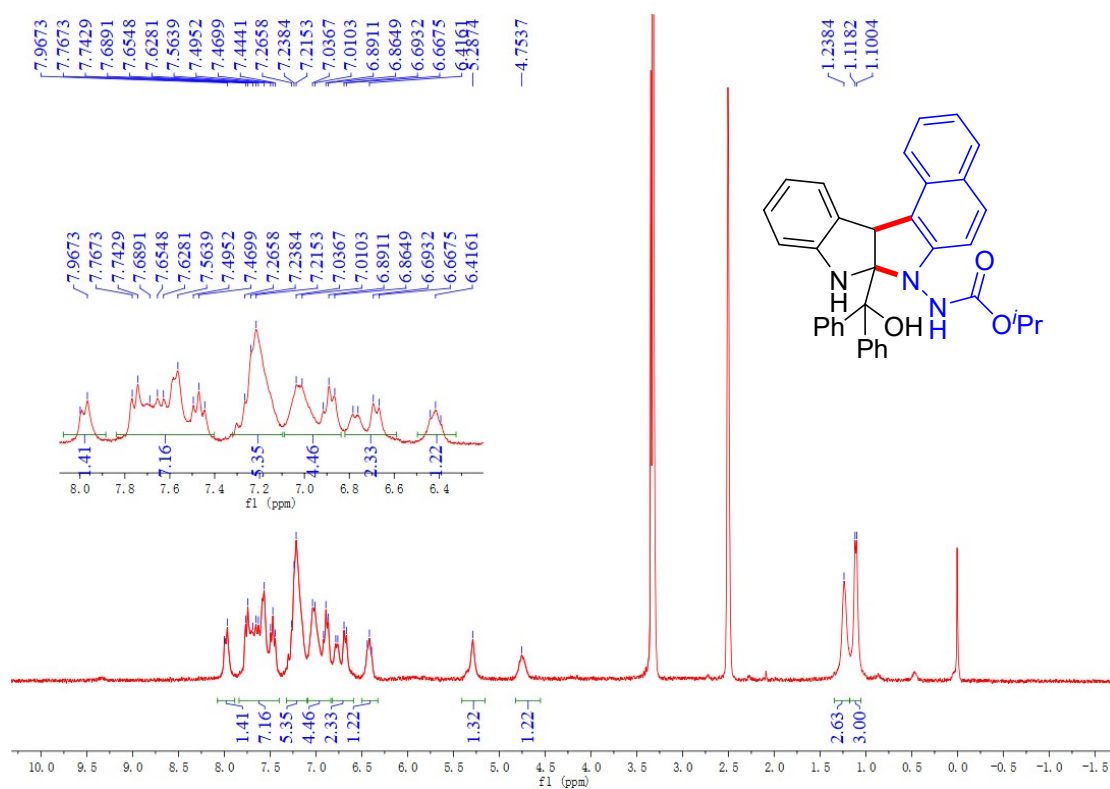
<sup>1</sup>H NMR spectrum of **3a** (CD<sub>3</sub>OD)



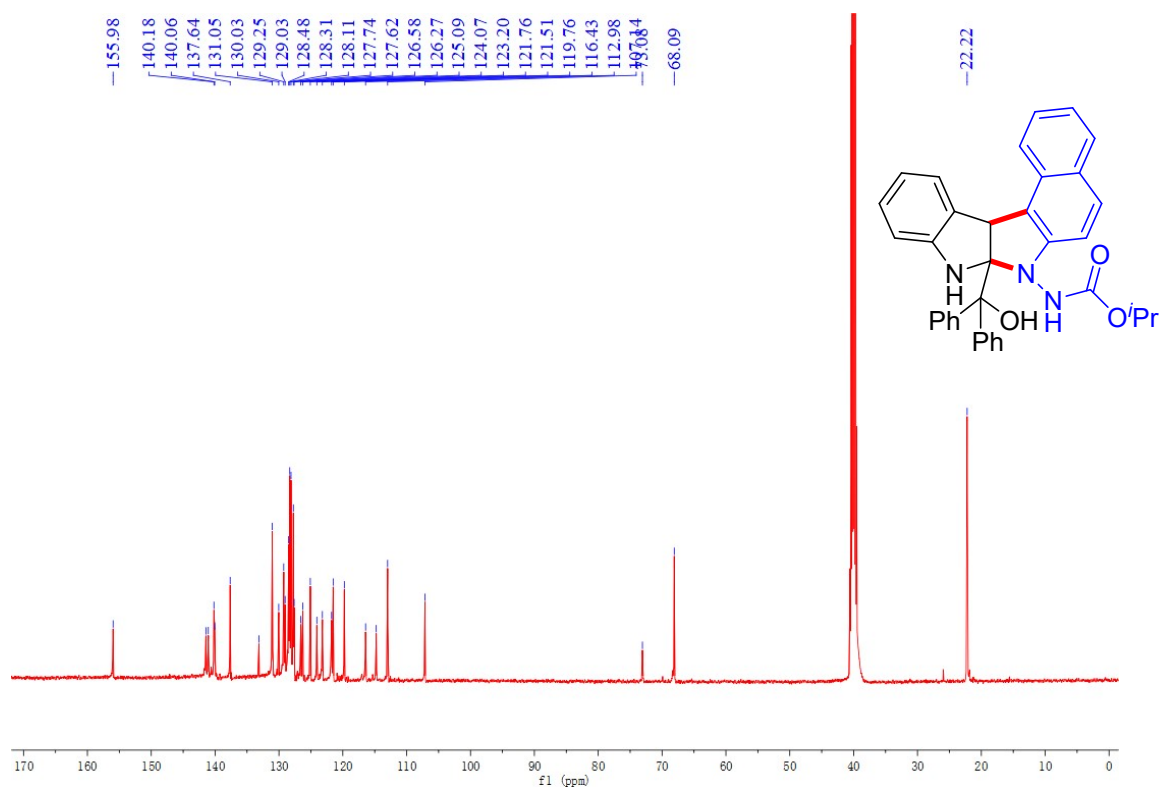
<sup>13</sup>C NMR spectrum of **3a** (DMSO-*d*<sub>6</sub>)



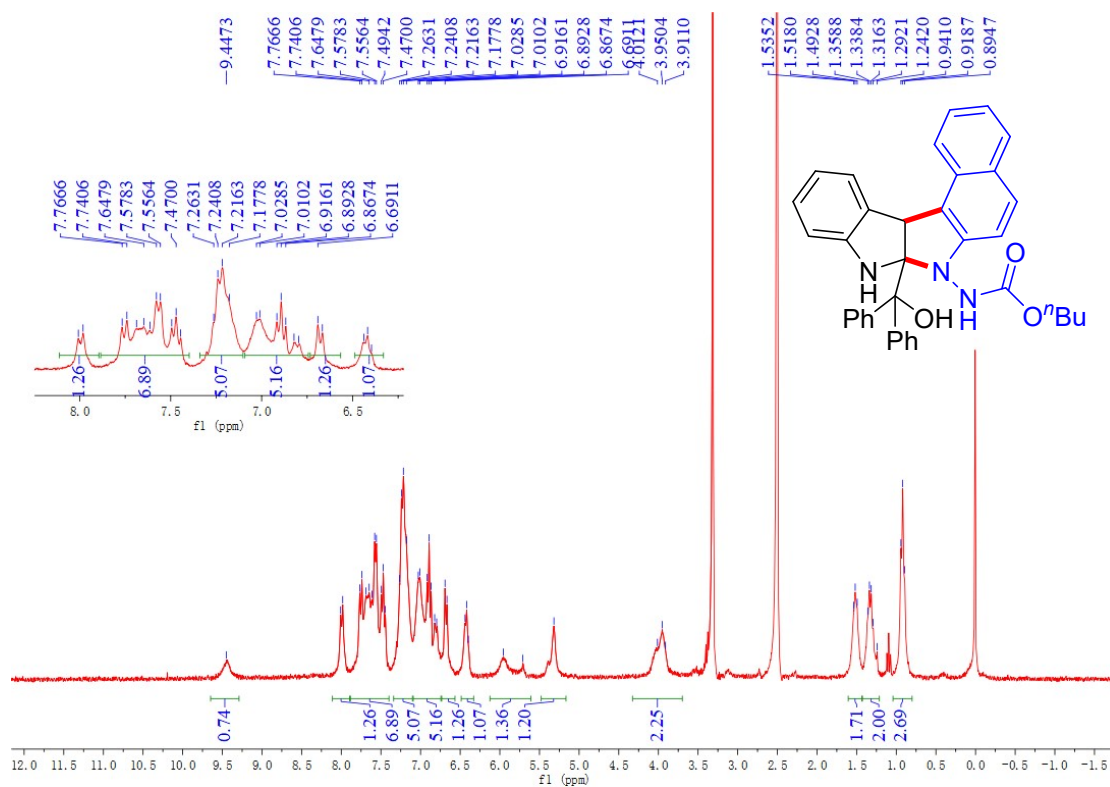
<sup>1</sup>H NMR spectrum of **3b** (DMSO-*d*<sub>6</sub>+D<sub>2</sub>O)



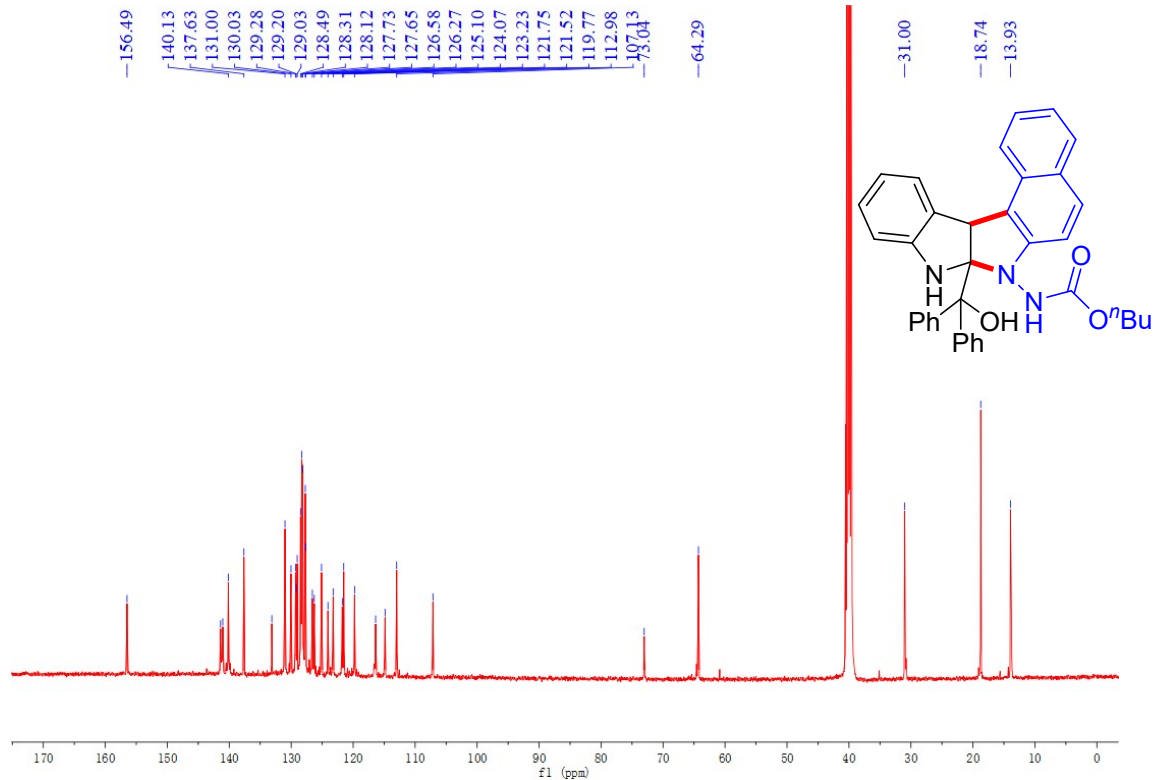
<sup>13</sup>C NMR spectrum of **3b** (DMSO-*d*<sub>6</sub>)



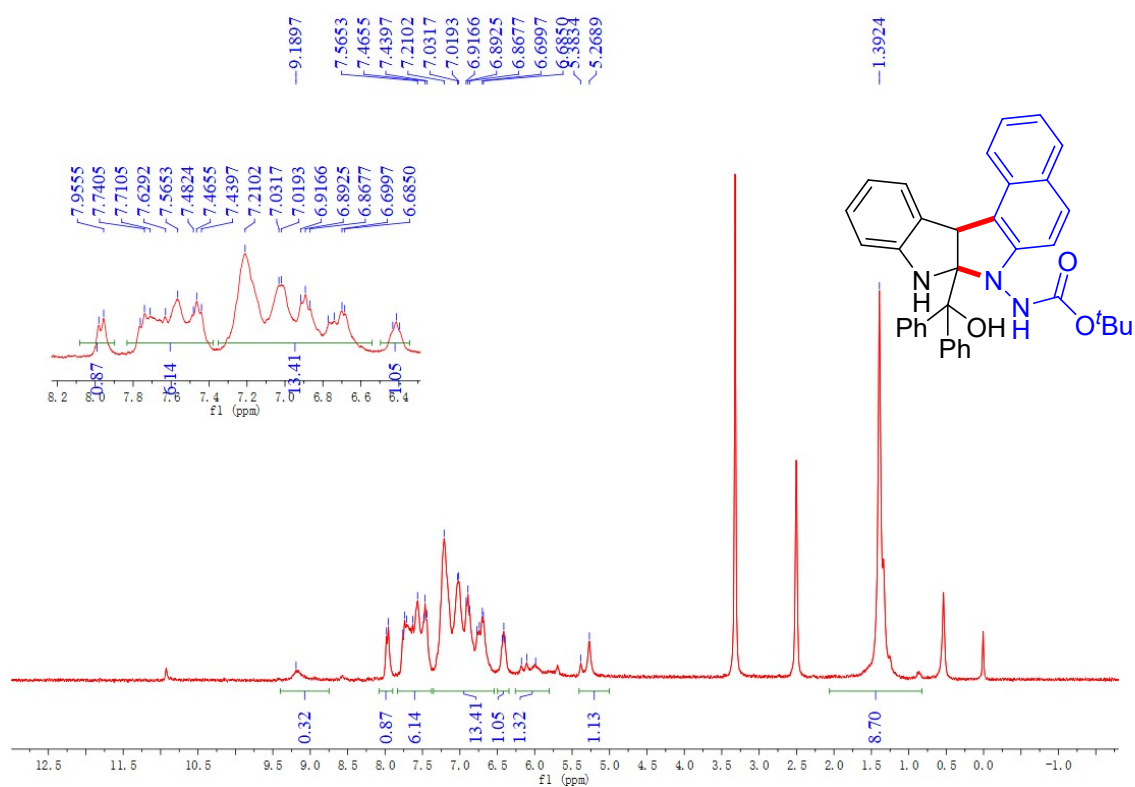
<sup>1</sup>H NMR spectrum of **3c** (DMSO-*d*<sub>6</sub>)



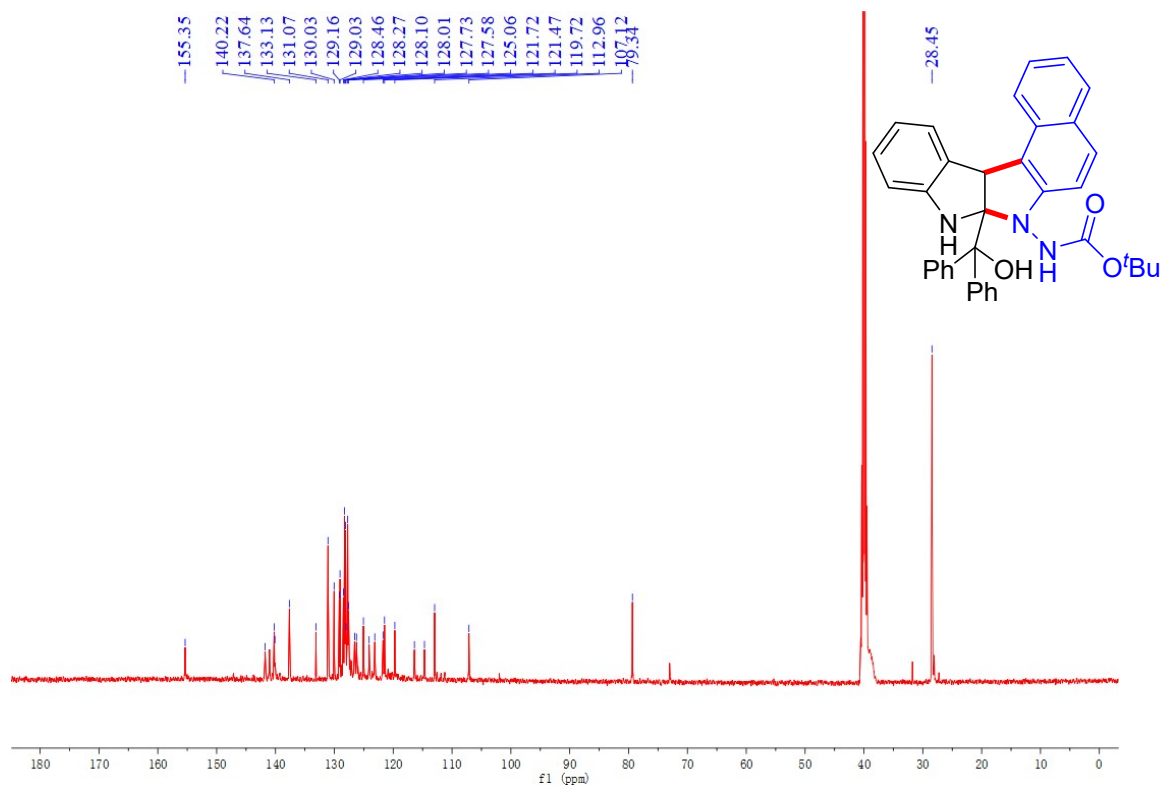
<sup>13</sup>C NMR spectrum of **3c** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **3d** (DMSO-*d*<sub>6</sub>)

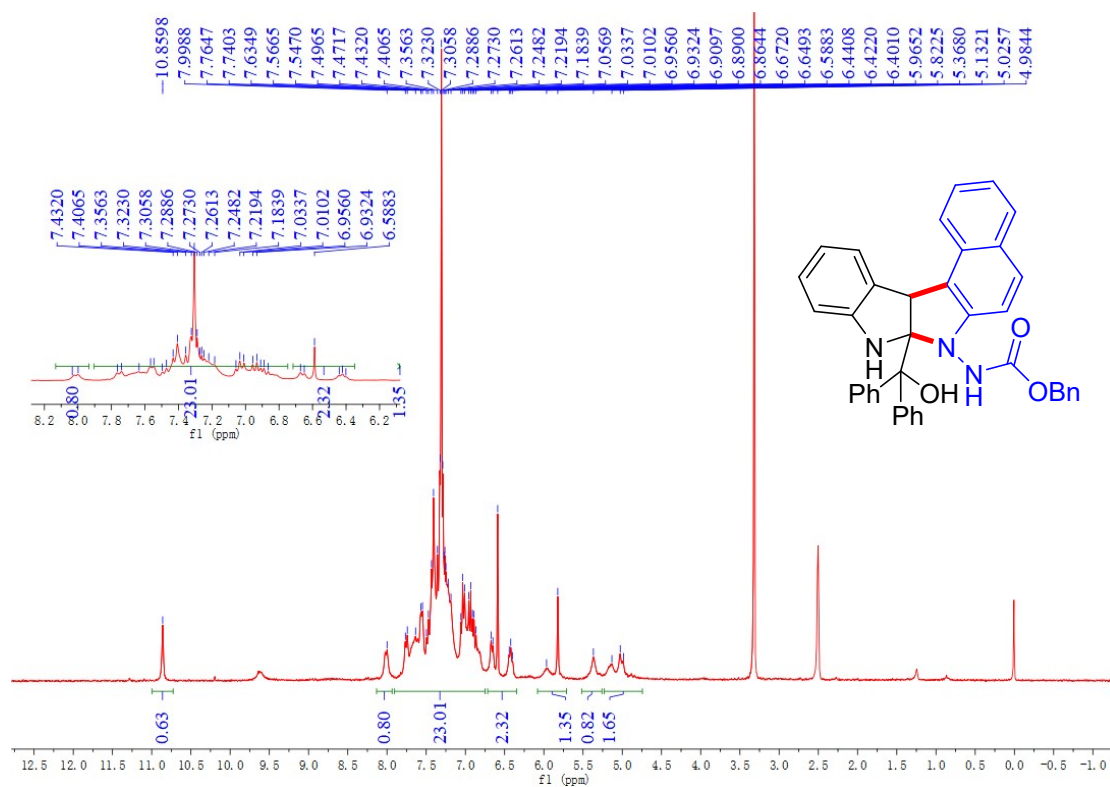


<sup>13</sup>C NMR spectrum of **3d** (DMSO-*d*<sub>6</sub>)

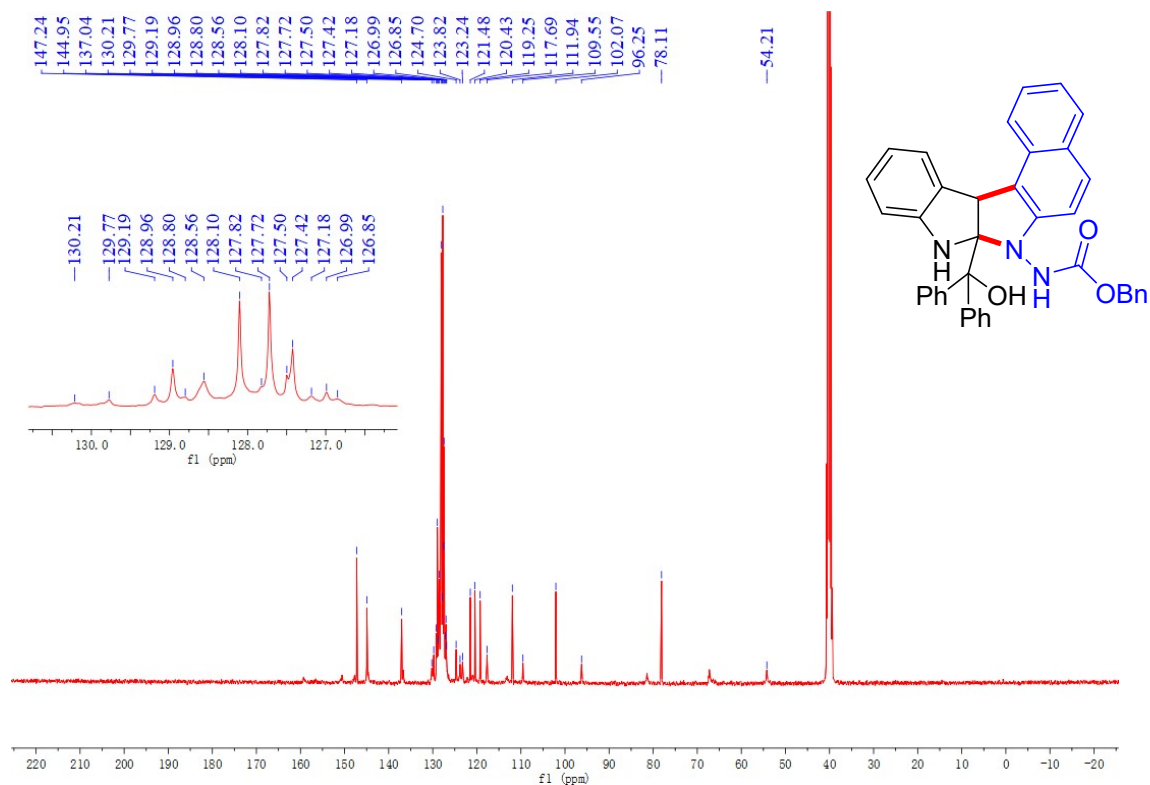




<sup>1</sup>H NMR spectrum of **3e** (DMSO-*d*<sub>6</sub>)

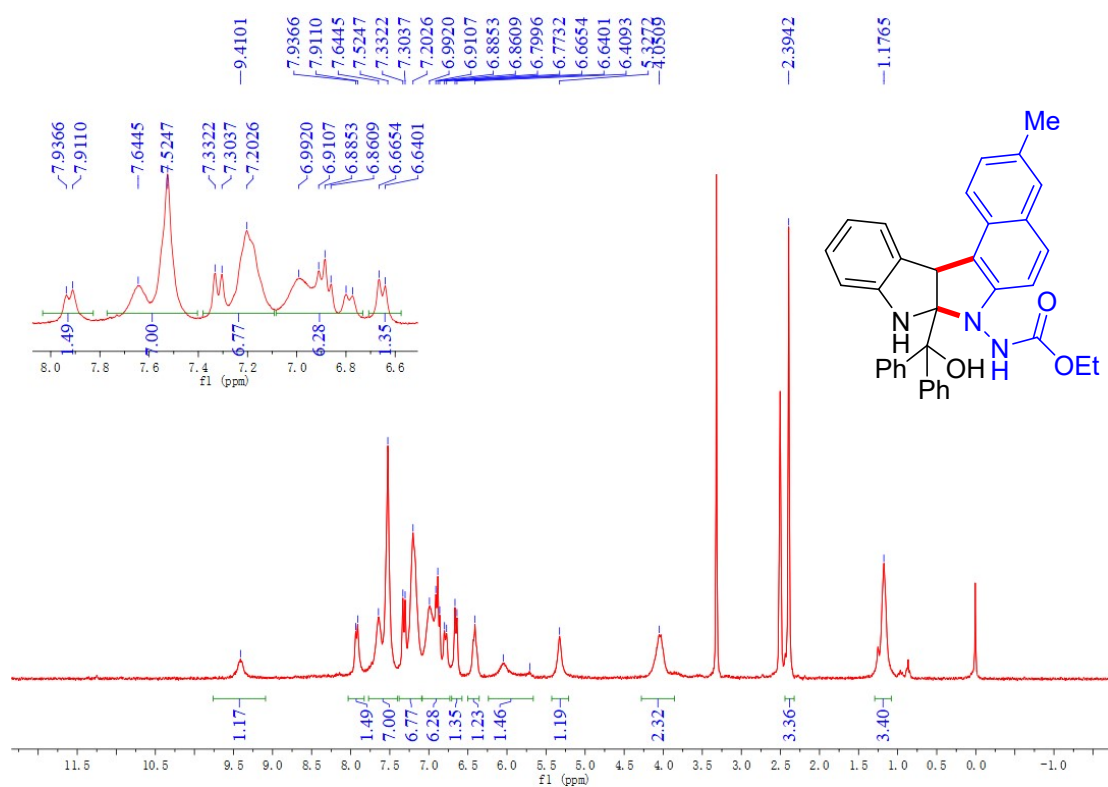


<sup>13</sup>C NMR spectrum of **3e** (DMSO-*d*<sub>6</sub>)

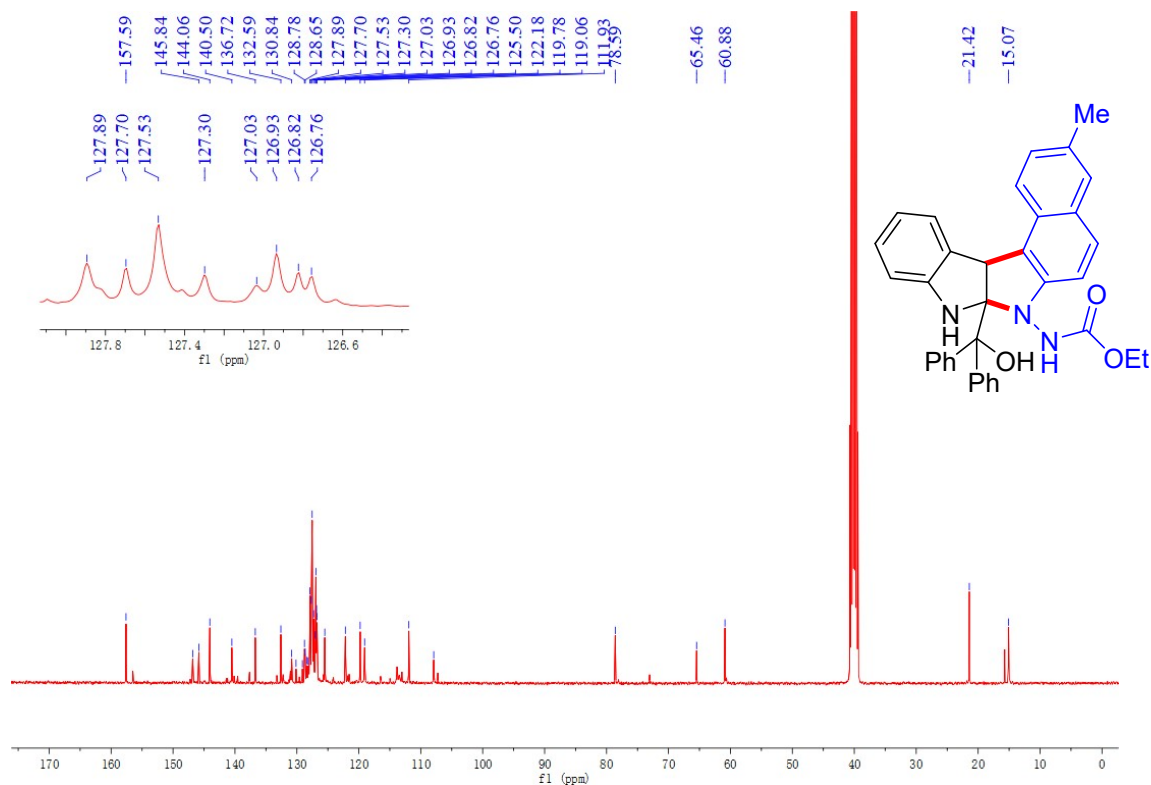




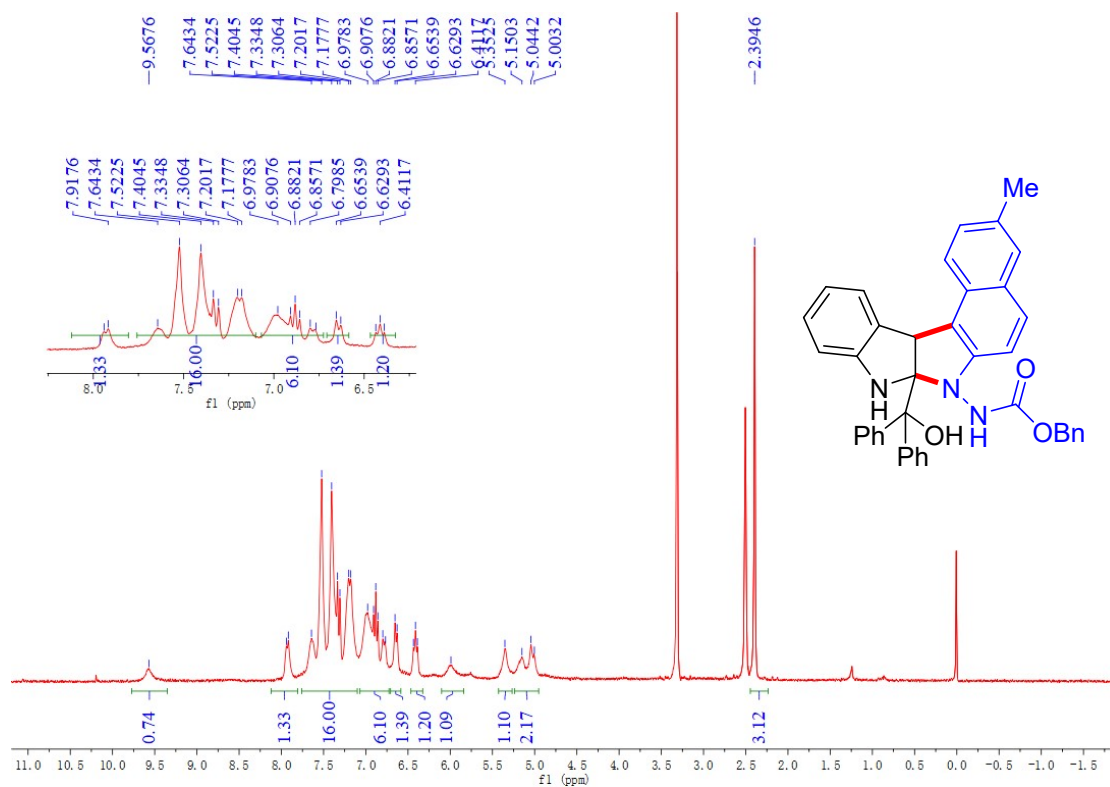
<sup>1</sup>H NMR spectrum of **3f** (DMSO-*d*<sub>6</sub>)



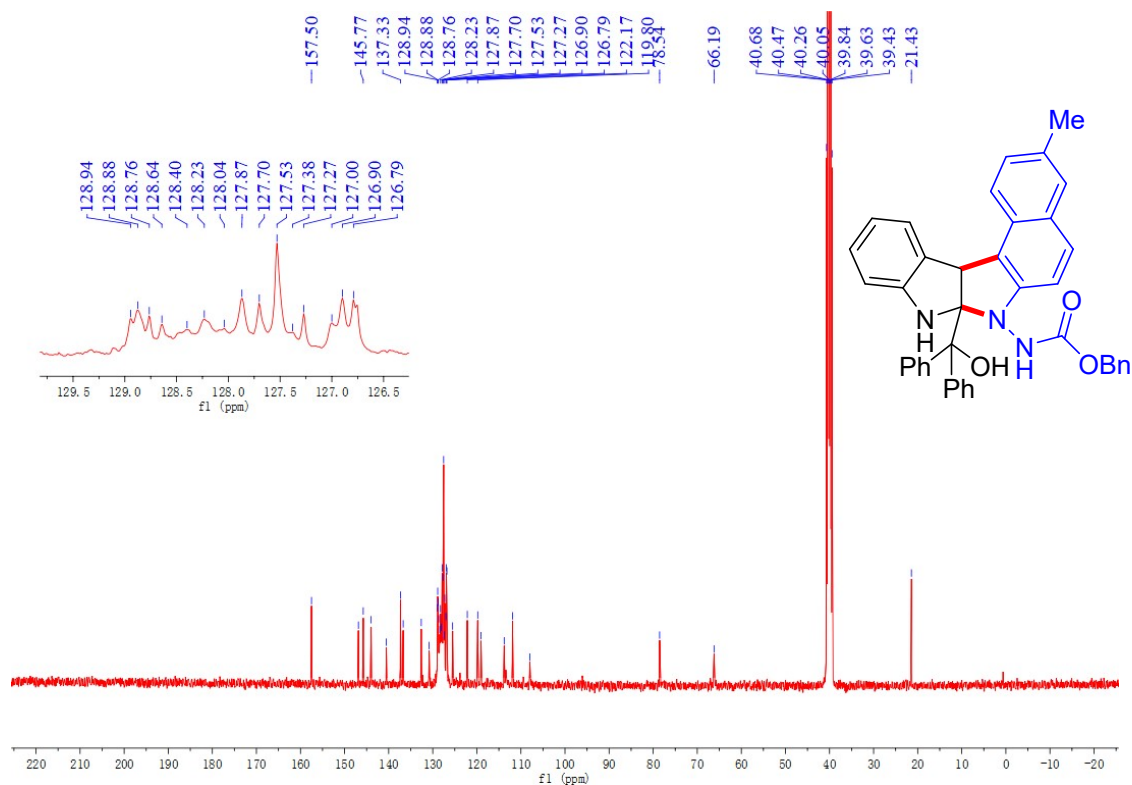
<sup>13</sup>C NMR spectrum of **3f** (DMSO-*d*<sub>6</sub>)



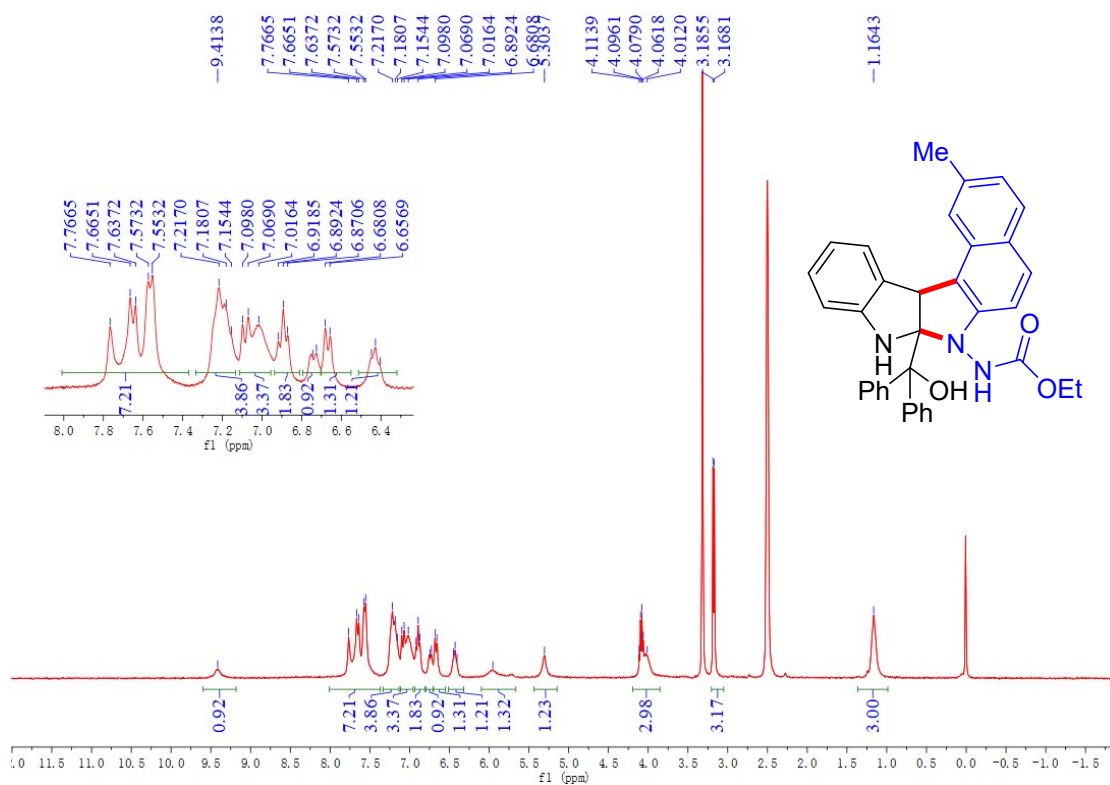
<sup>1</sup>H NMR spectrum of **3g** (DMSO-*d*<sub>6</sub>)



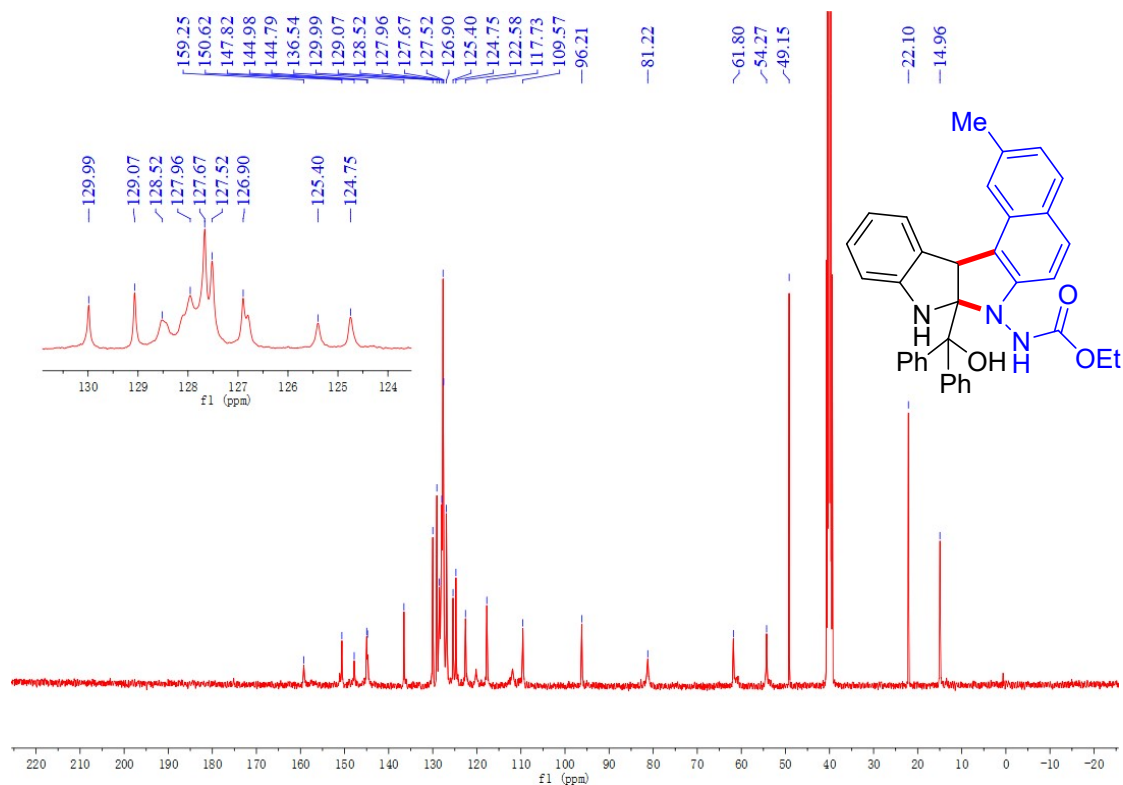
<sup>13</sup>C NMR spectrum of **3g** (DMSO-*d*<sub>6</sub>)



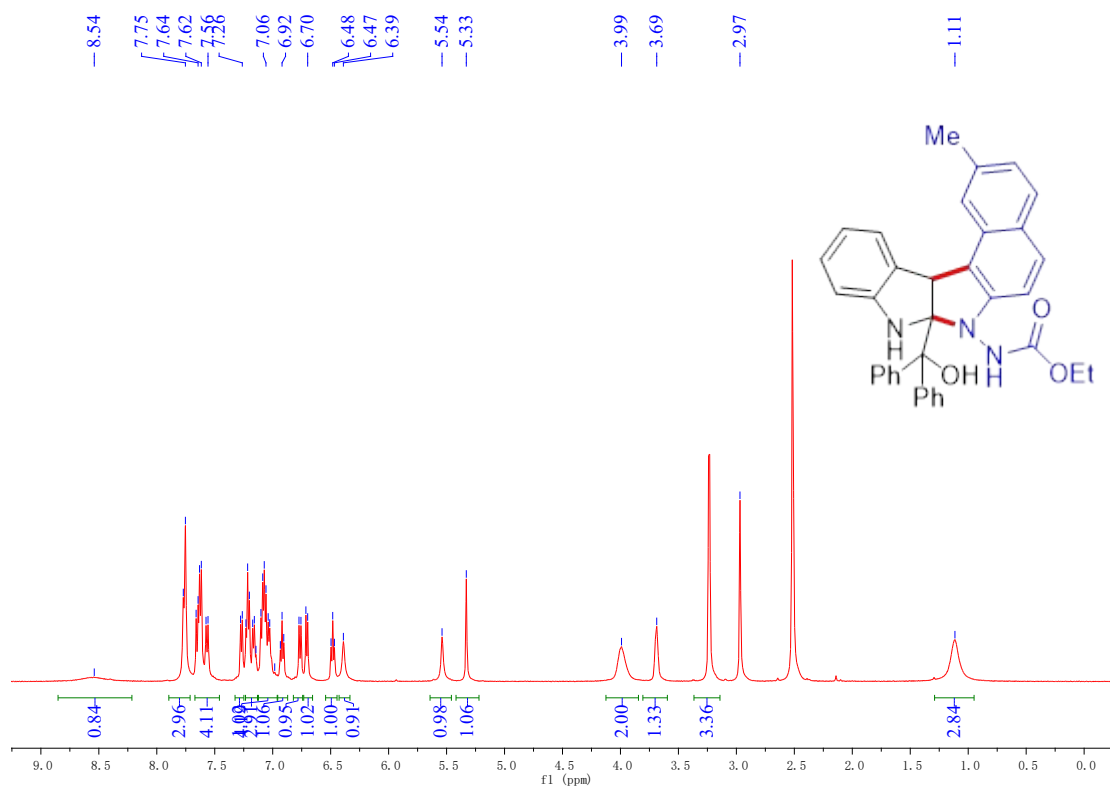
$^1\text{H}$  NMR spectrum of **3h** ( $\text{DMSO-}d_6$ )



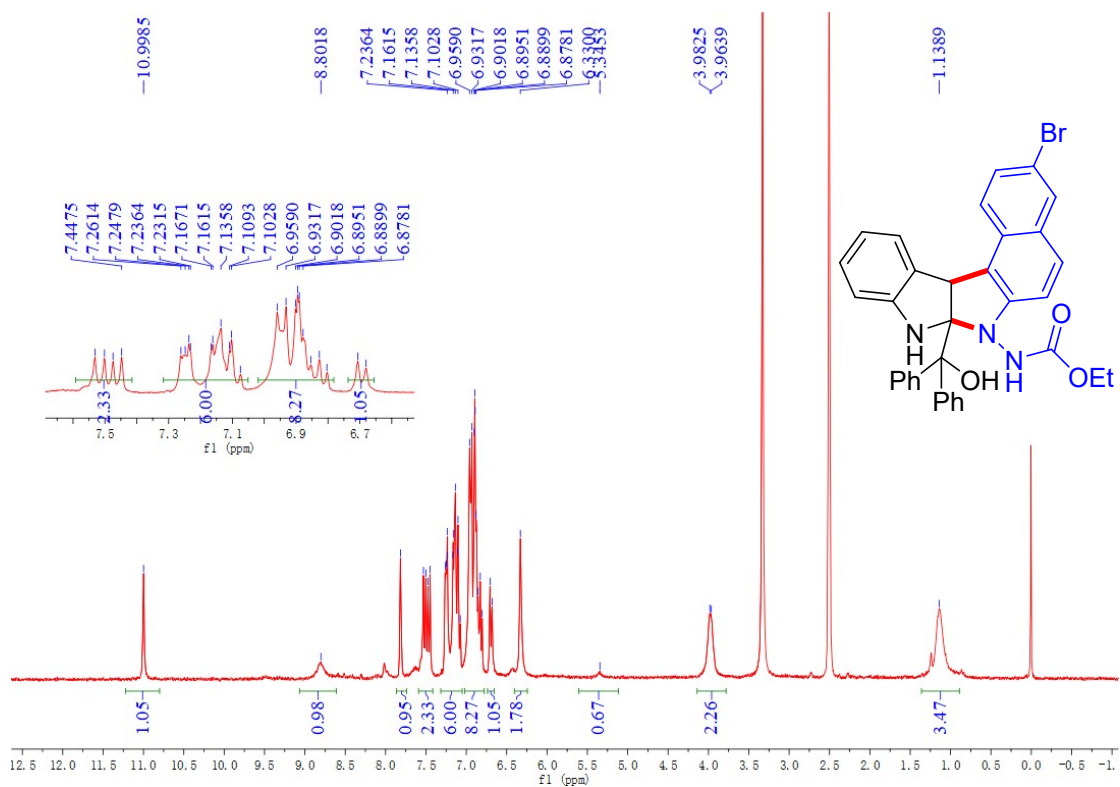
$^{13}\text{C}$  NMR spectrum of **3h** ( $\text{DMSO-}d_6$ )



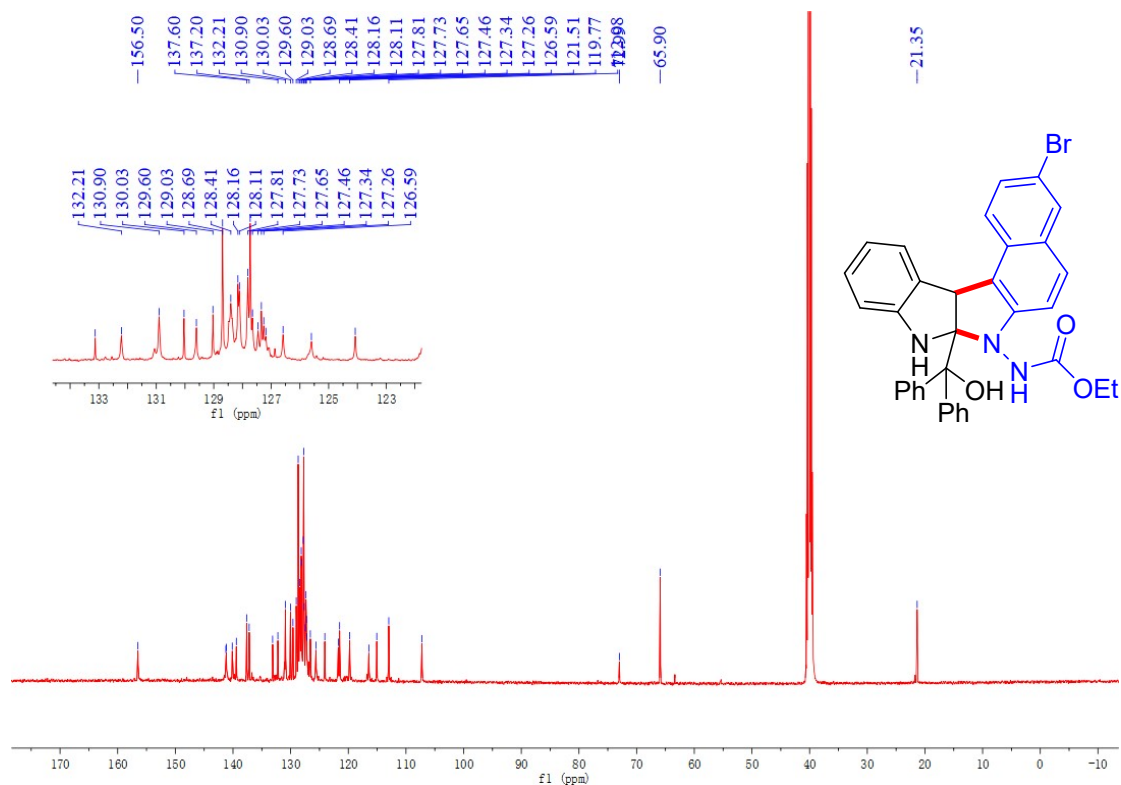
$^1\text{H}$  NMR spectrum of **3h** ( $\text{DMSO-}d_6$ ),  $80\text{ }^\circ\text{C}$



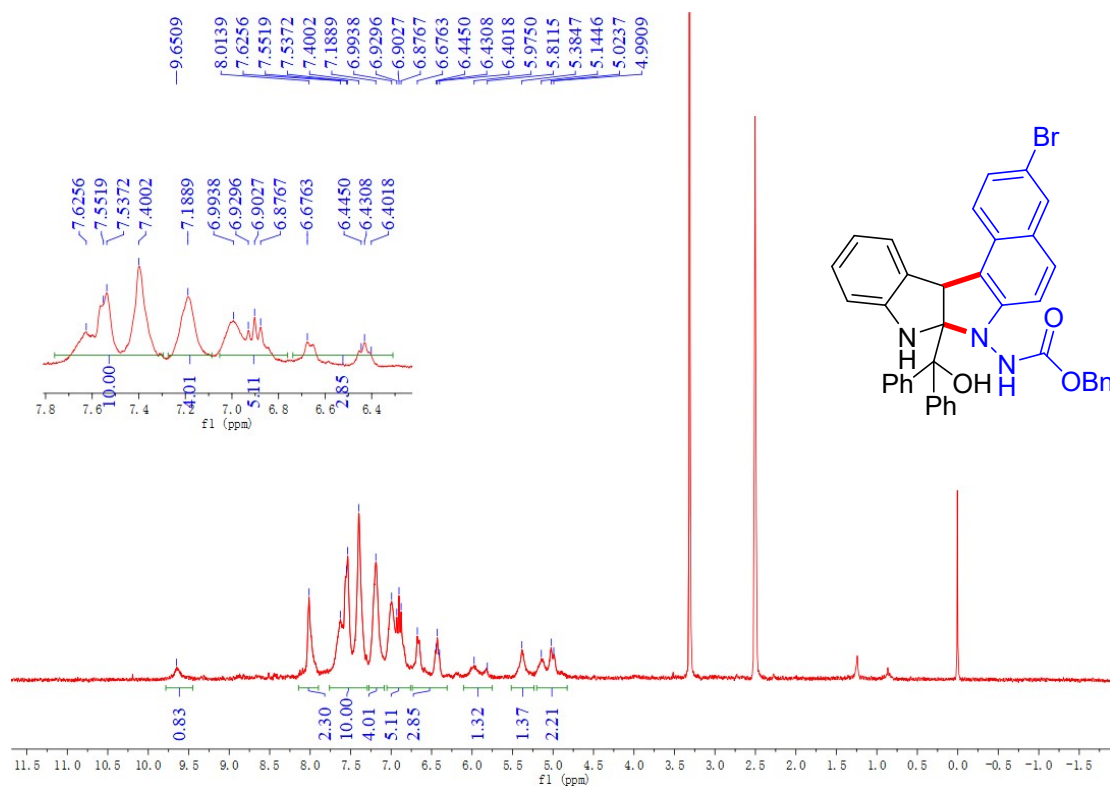
<sup>1</sup>H NMR spectrum of **3i** (DMSO-*d*<sub>6</sub>)



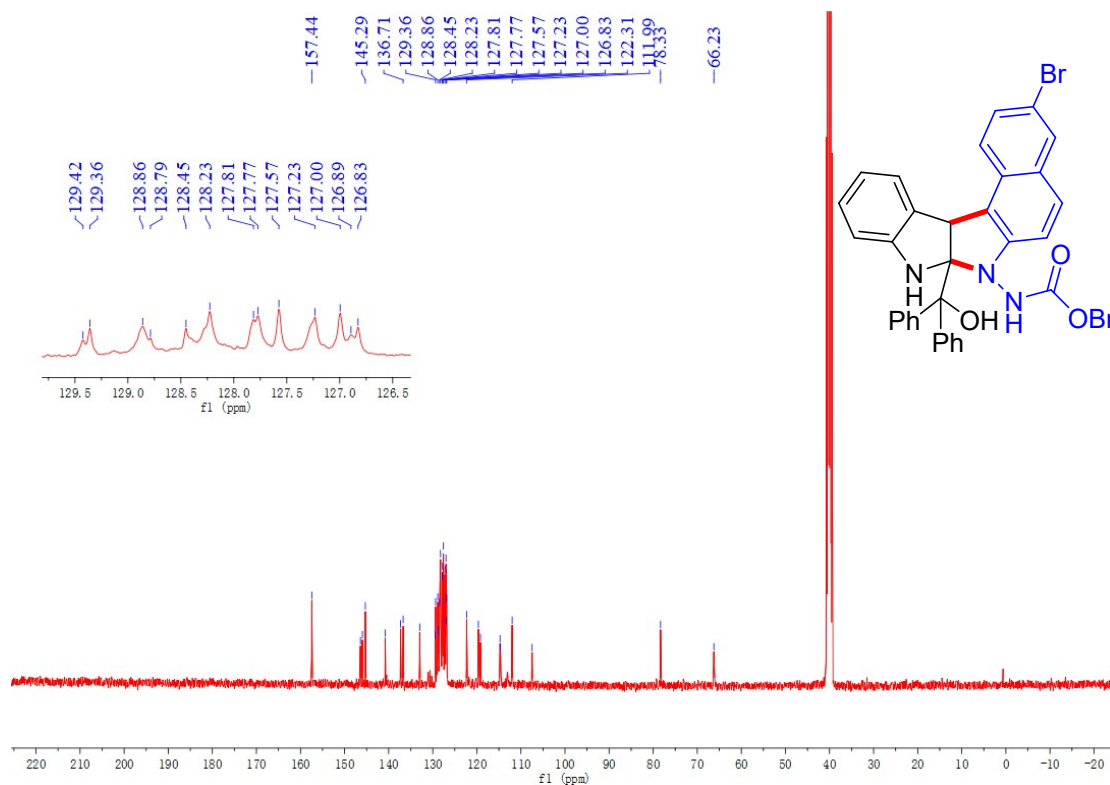
<sup>13</sup>C NMR spectrum of **3i** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **3j** (DMSO-*d*<sub>6</sub>)

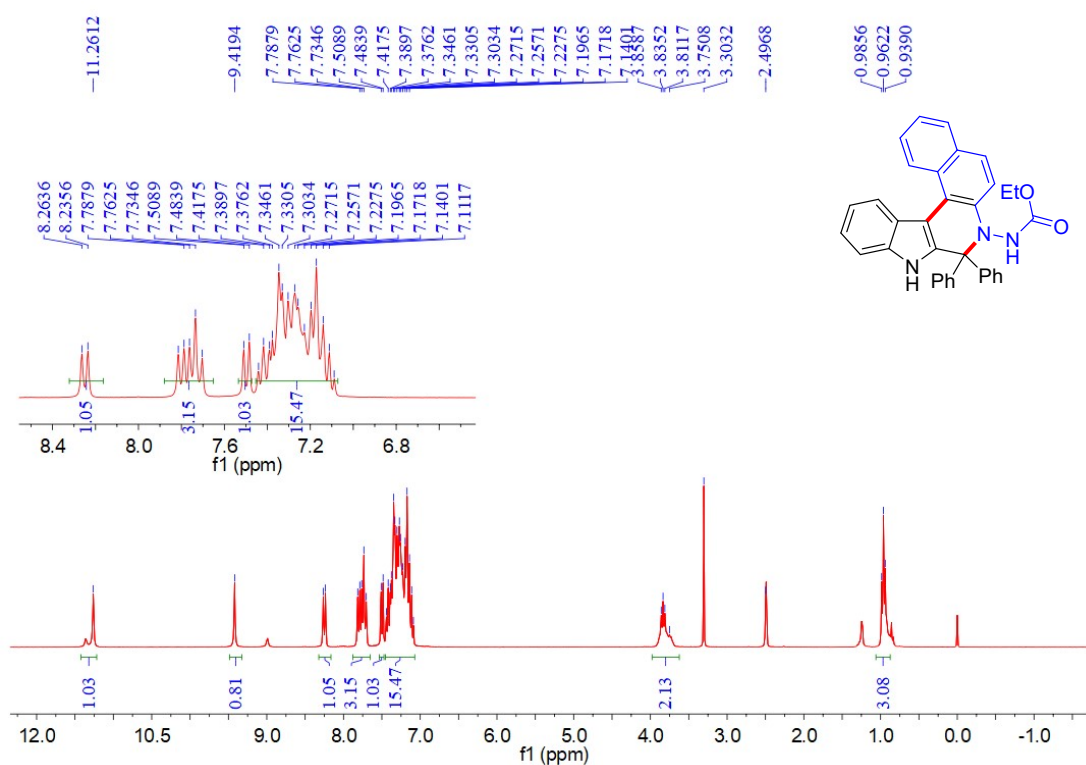


<sup>13</sup>C NMR spectrum of **3j** (DMSO-*d*<sub>6</sub>)

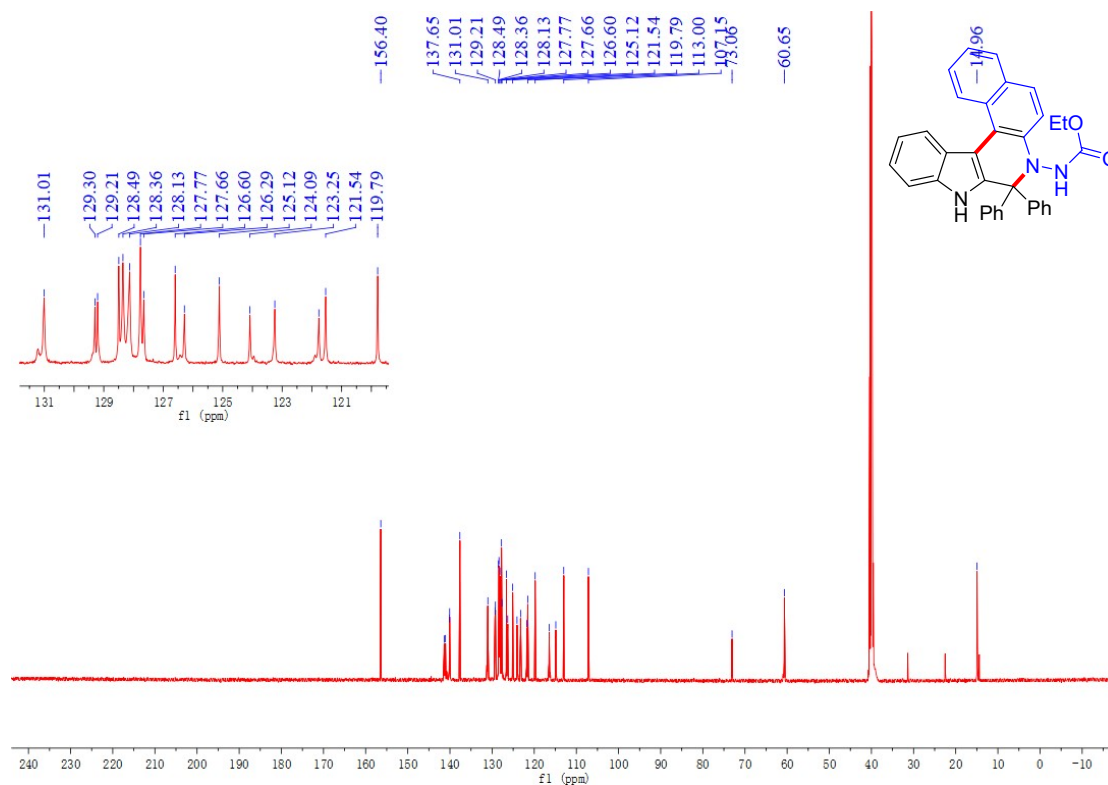




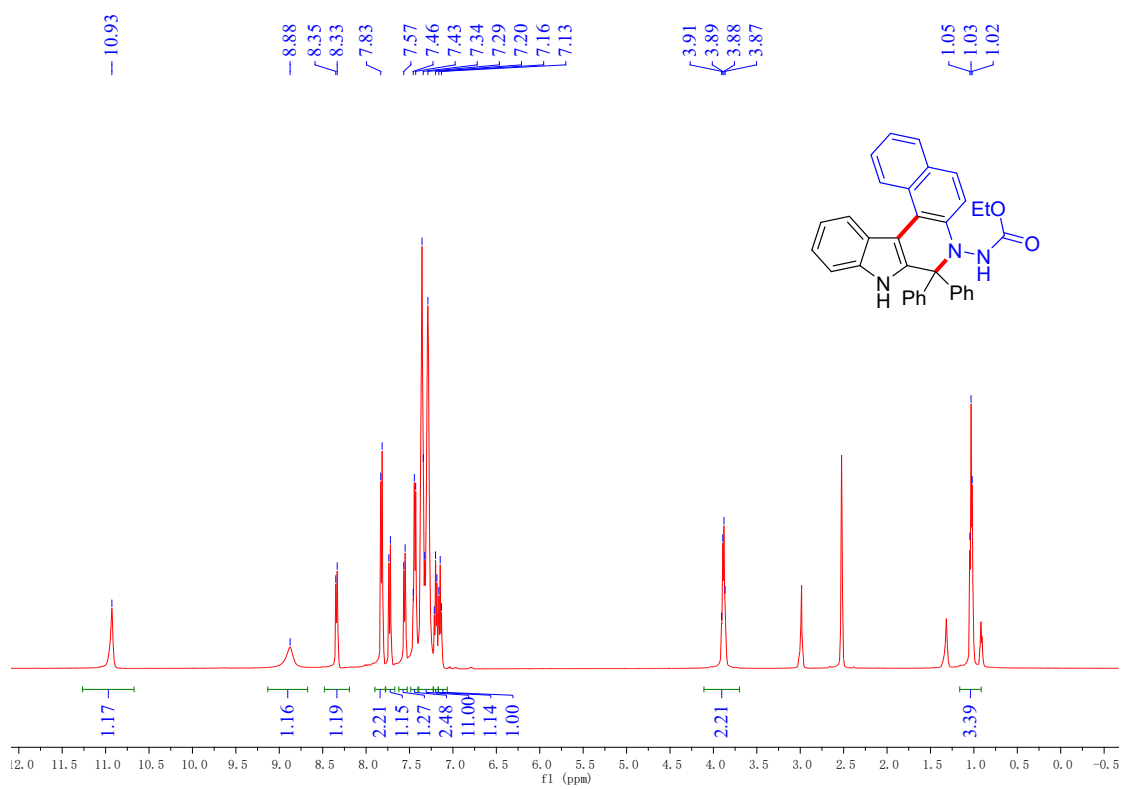
<sup>1</sup>H NMR spectrum of **4a** (DMSO-*d*<sub>6</sub>)



<sup>13</sup>C NMR spectrum of **4a** (DMSO-*d*<sub>6</sub>)

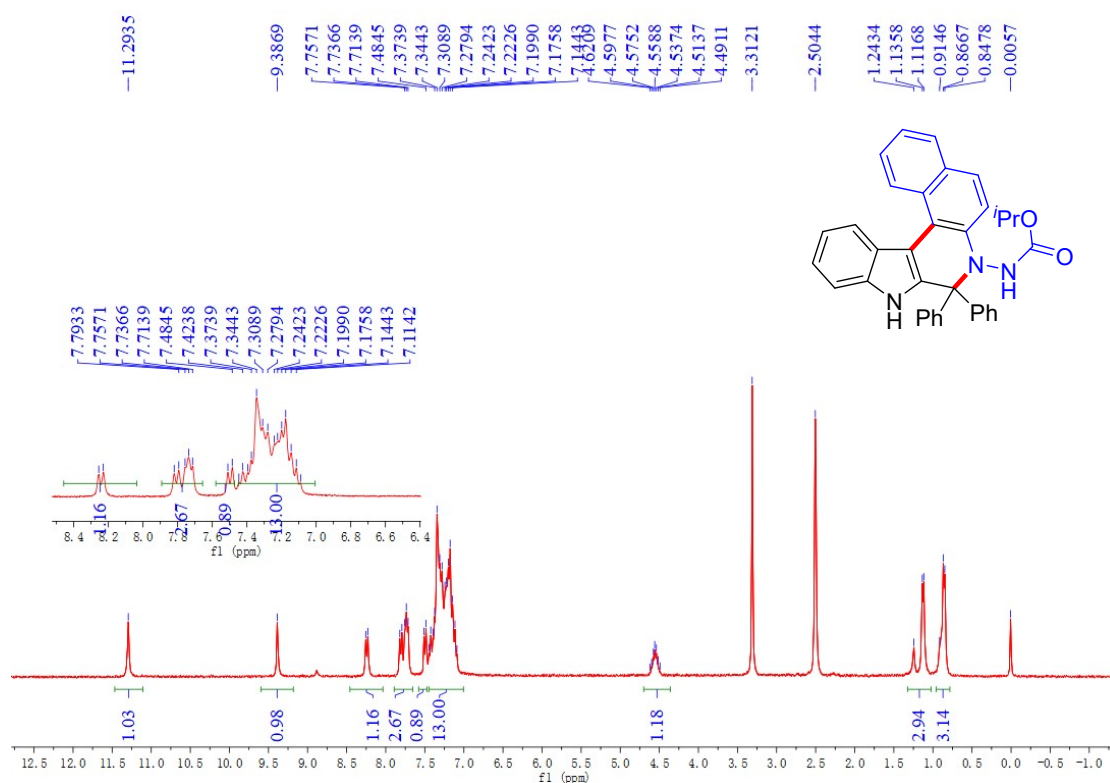


$^1\text{H}$  NMR spectrum of **4a** ( $\text{DMSO-}d_6$ ),  $80\text{ }^\circ\text{C}$

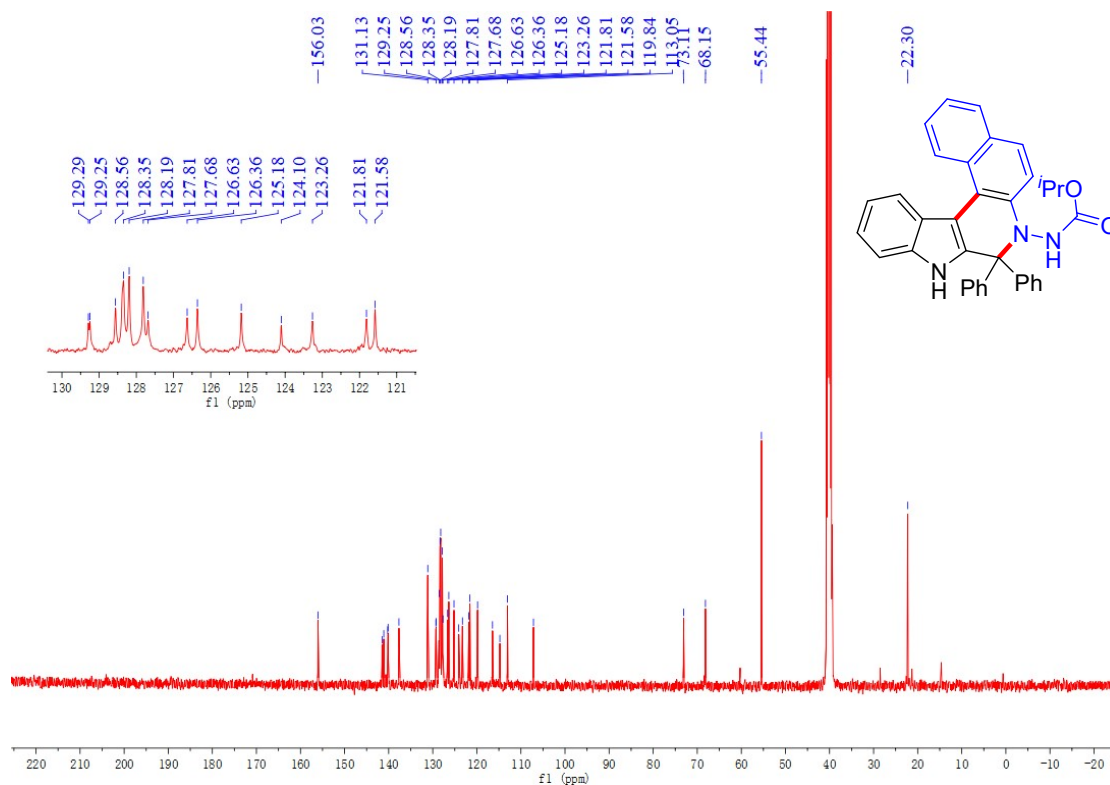




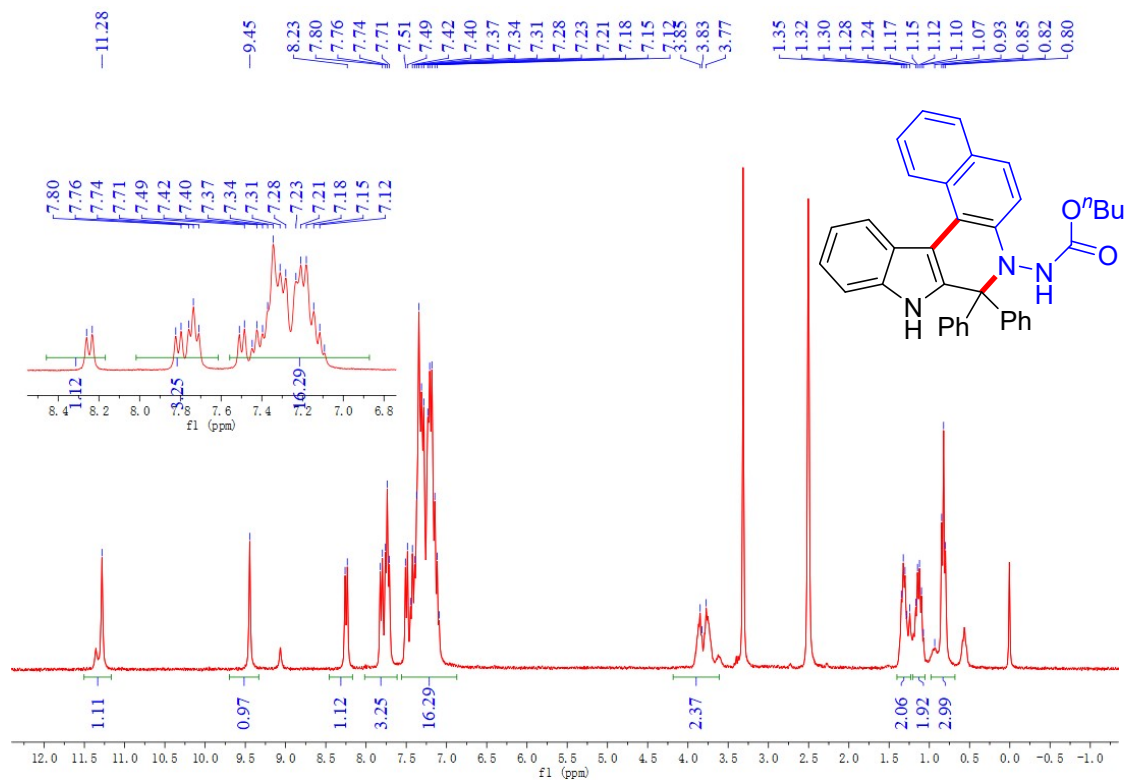
<sup>1</sup>H NMR spectrum of **4b** (DMSO-*d*<sub>6</sub>)



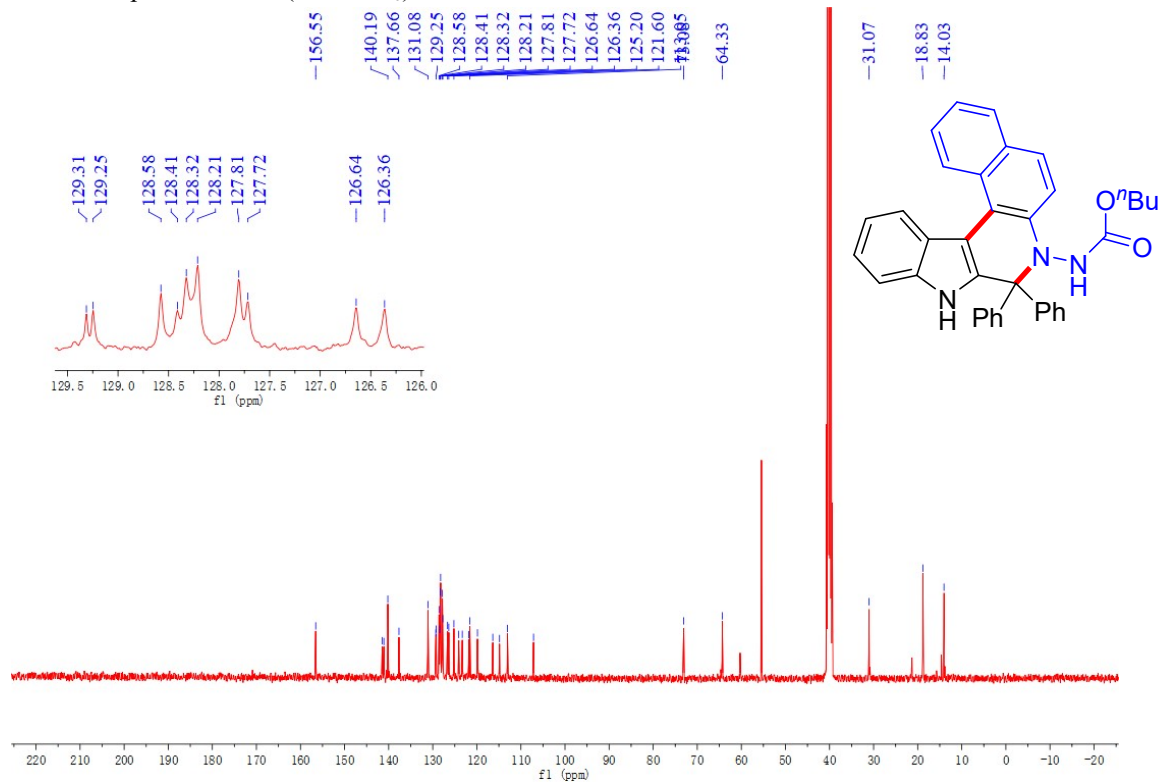
<sup>13</sup>C NMR spectrum of **4b** (DMSO-*d*<sub>6</sub>)



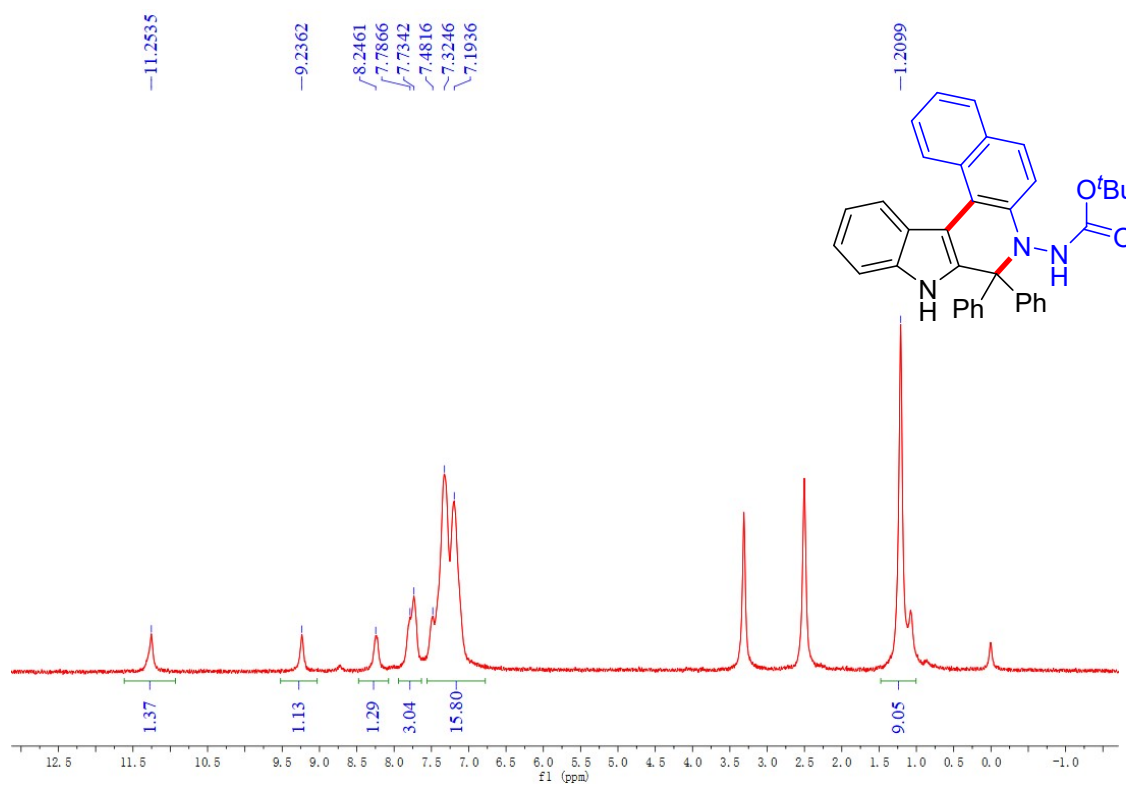
<sup>1</sup>H NMR spectrum of **4c** (DMSO-*d*<sub>6</sub>)



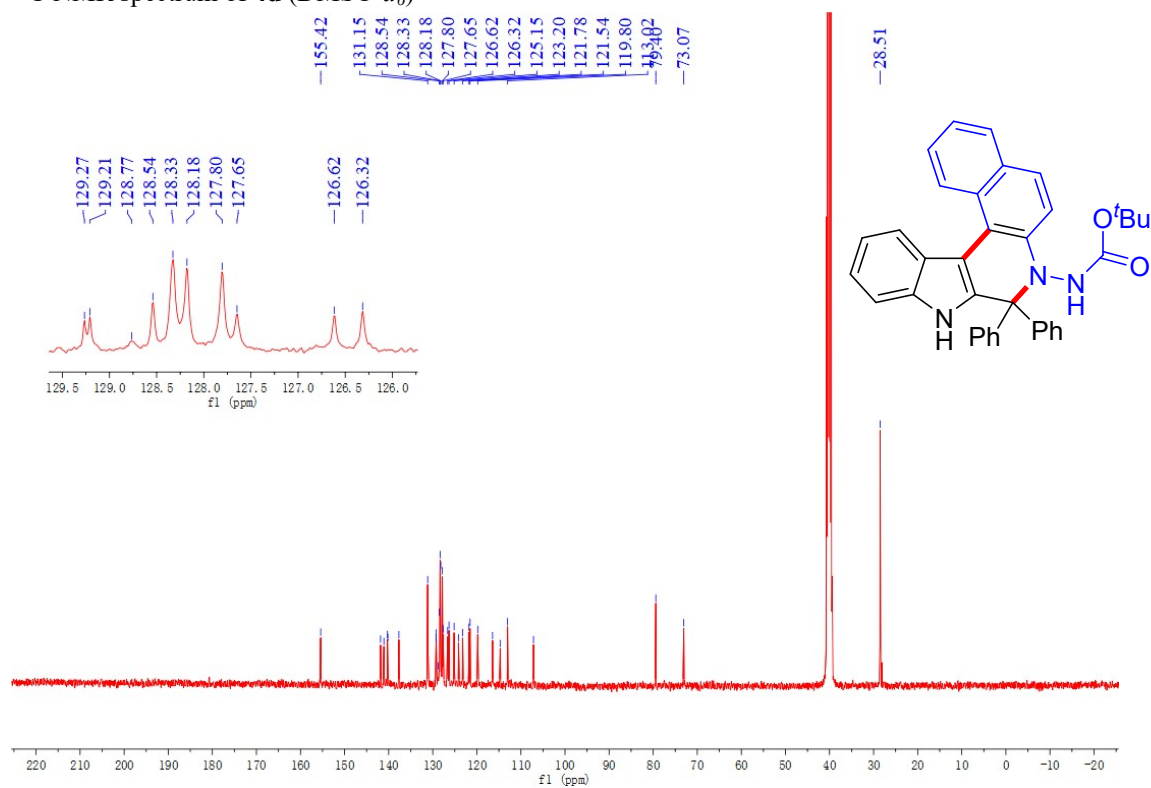
<sup>13</sup>C NMR spectrum of **4c** (DMSO-*d*<sub>6</sub>)



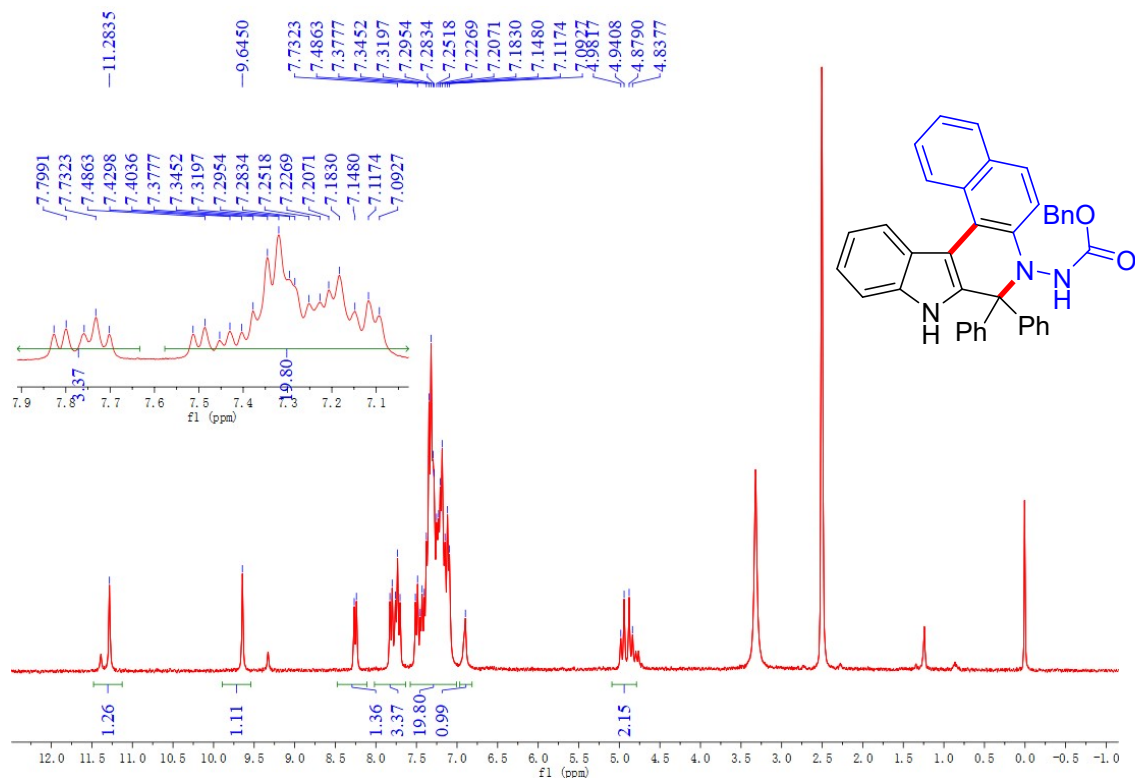
<sup>1</sup>H NMR spectrum of **4d** (DMSO-*d*<sub>6</sub>)



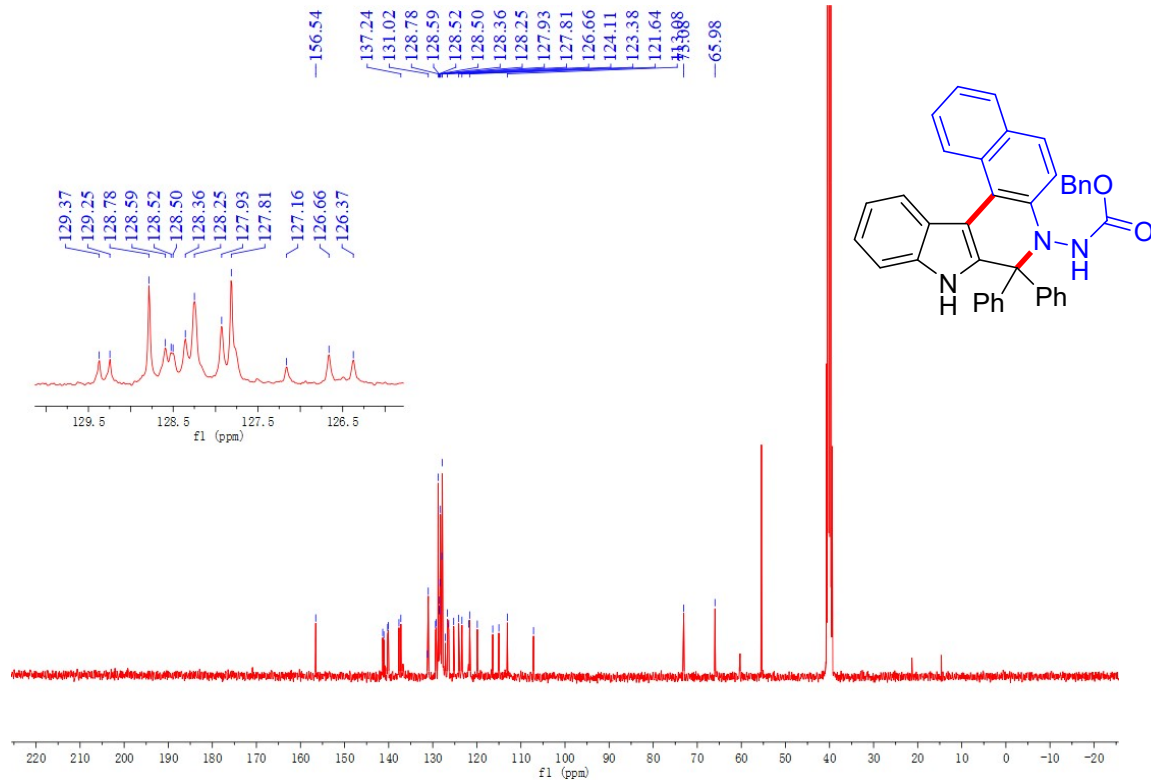
<sup>13</sup>C NMR spectrum of **4d** (DMSO-*d*<sub>6</sub>)



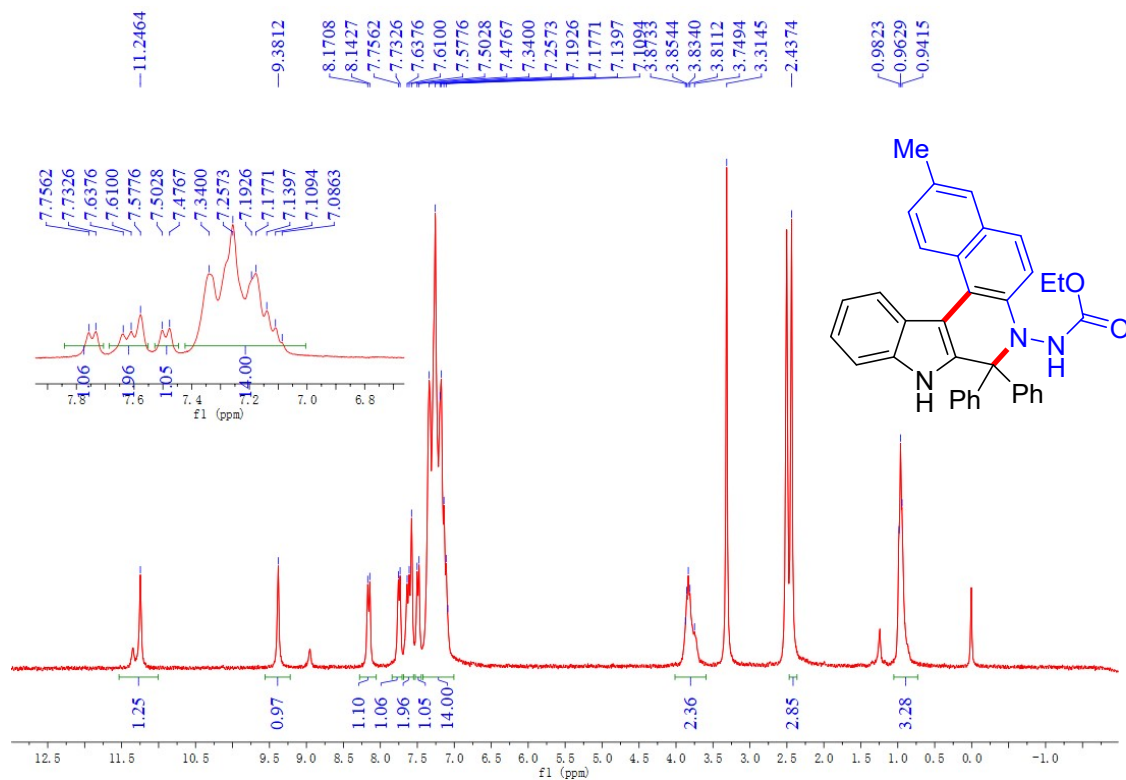
<sup>1</sup>H NMR spectrum of **4e** (DMSO-*d*<sub>6</sub>)



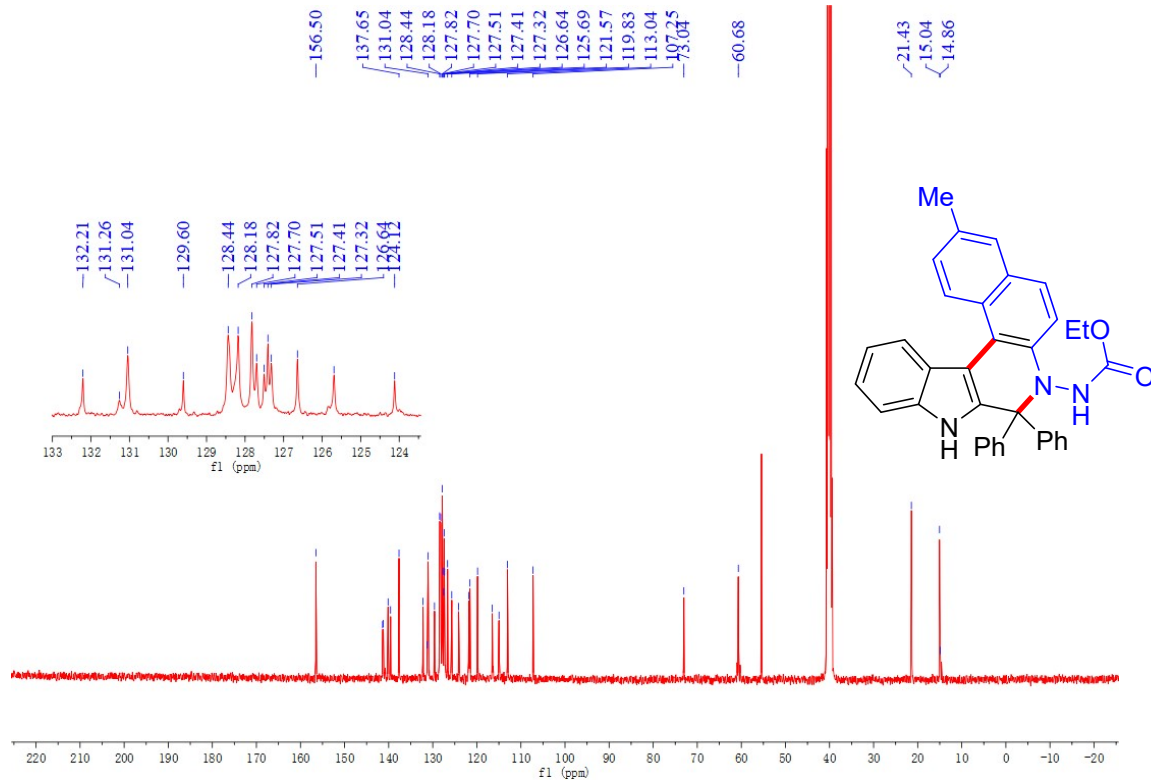
<sup>13</sup>C NMR spectrum of **4e** (DMSO-*d*<sub>6</sub>)



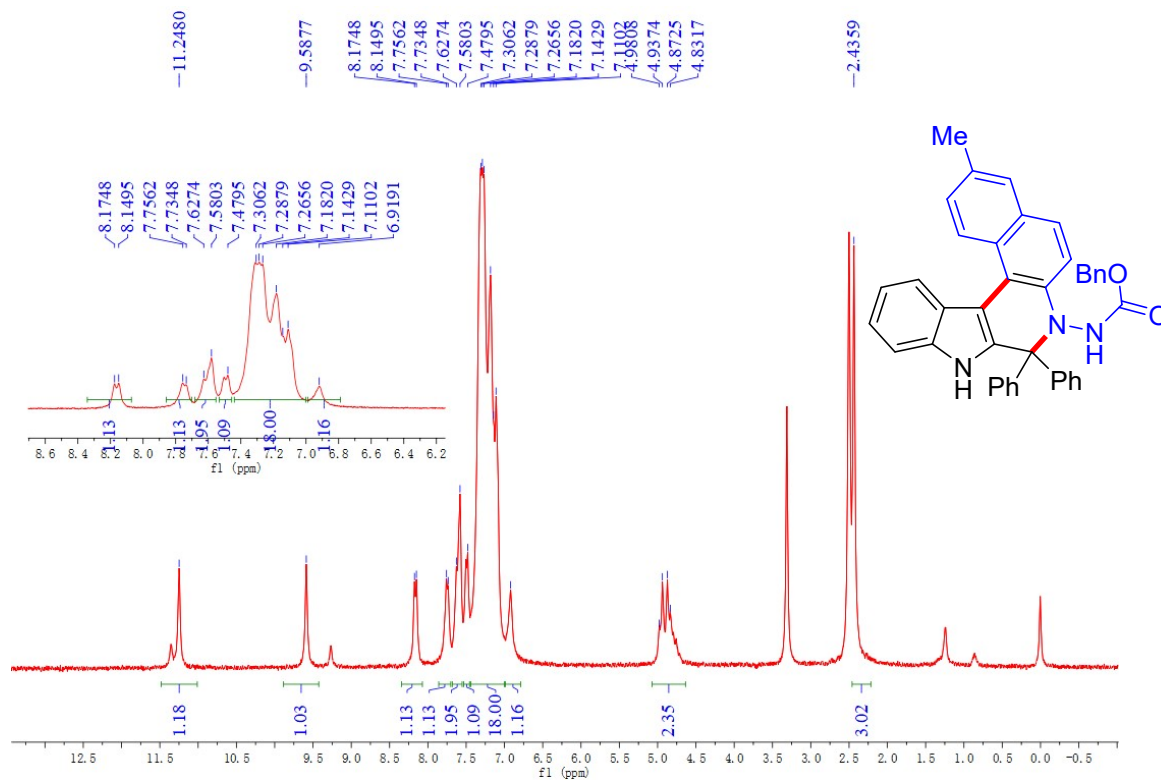
<sup>1</sup>H NMR spectrum of **4f** (DMSO-*d*<sub>6</sub>)



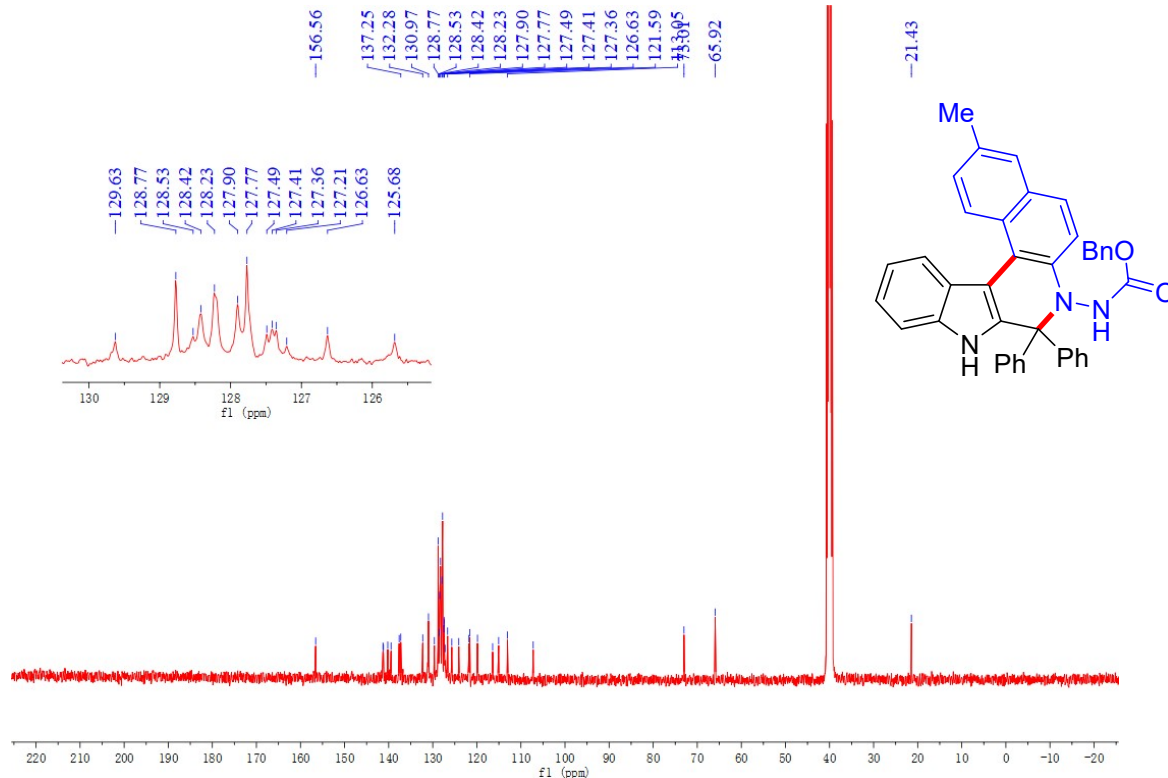
<sup>13</sup>C NMR spectrum of **4f** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4g** (DMSO-*d*<sub>6</sub>)

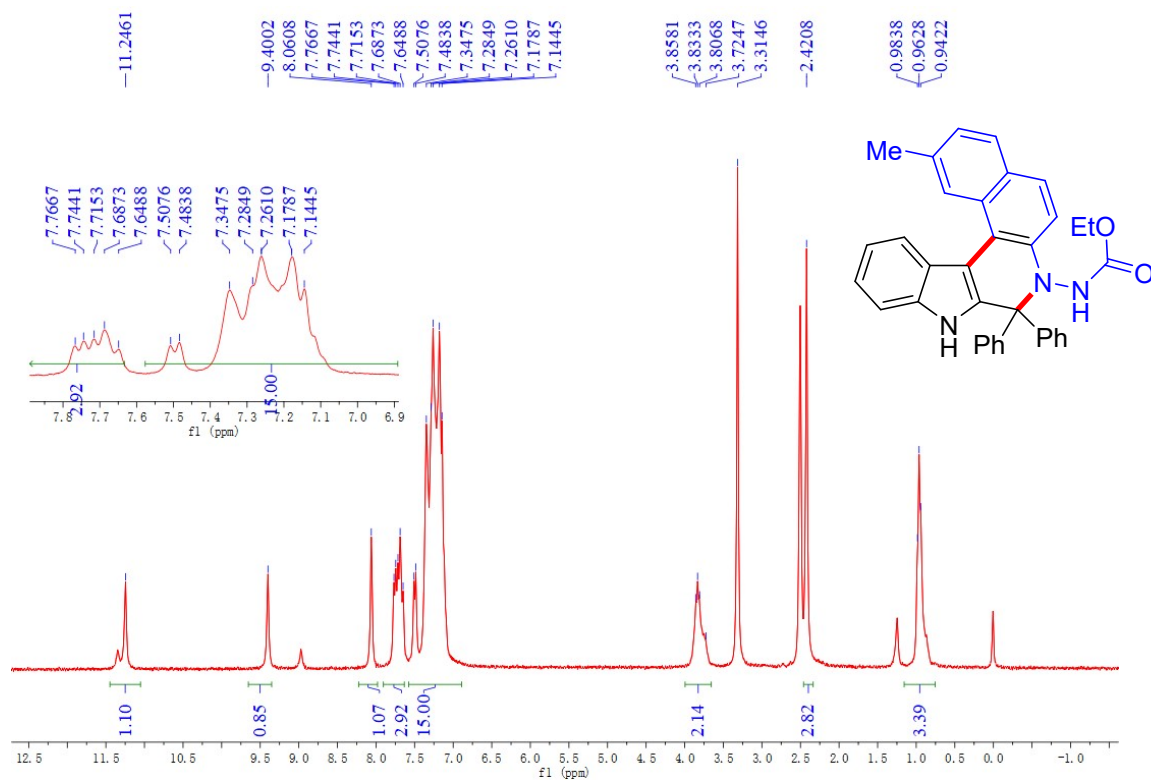


<sup>13</sup>C NMR spectrum of **4g** (DMSO-*d*<sub>6</sub>)

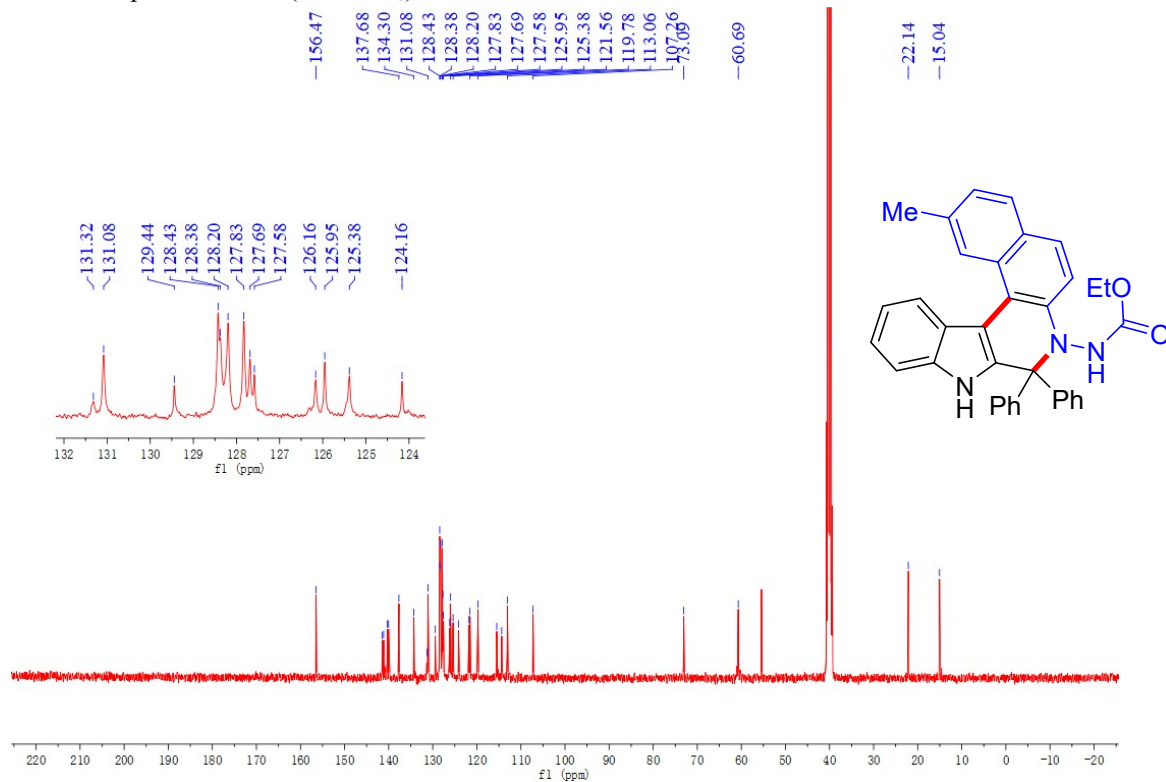




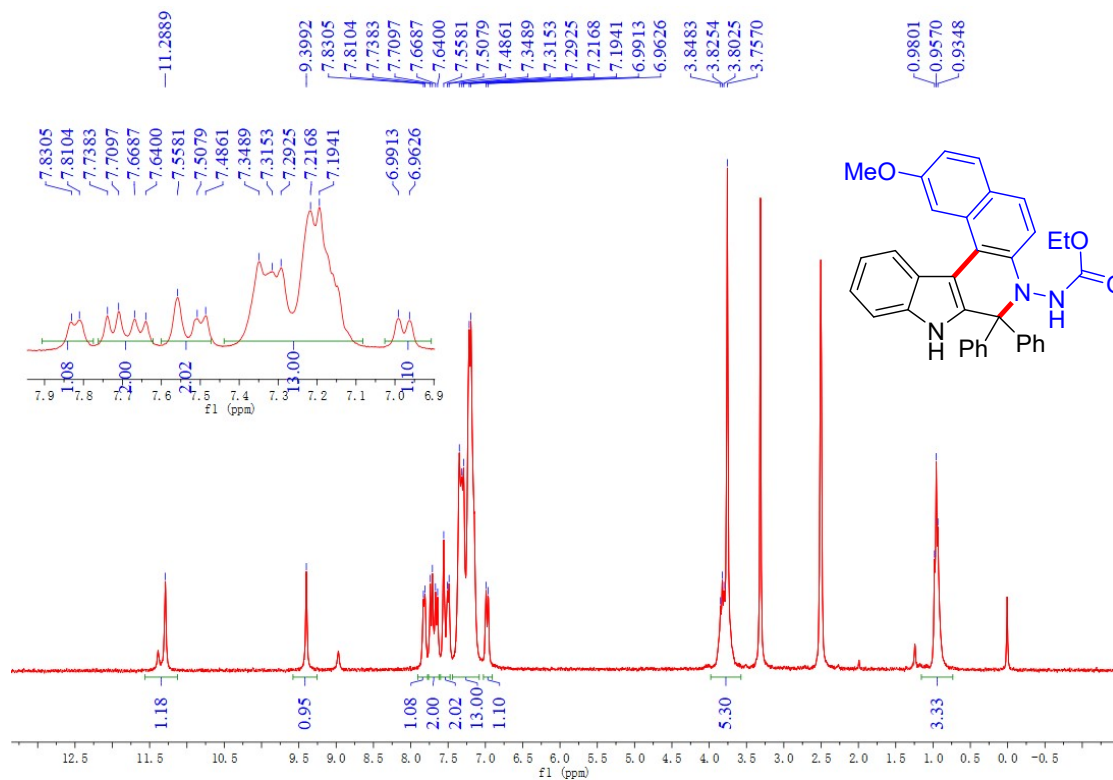
<sup>1</sup>H NMR spectrum of **4h** (DMSO-*d*<sub>6</sub>)



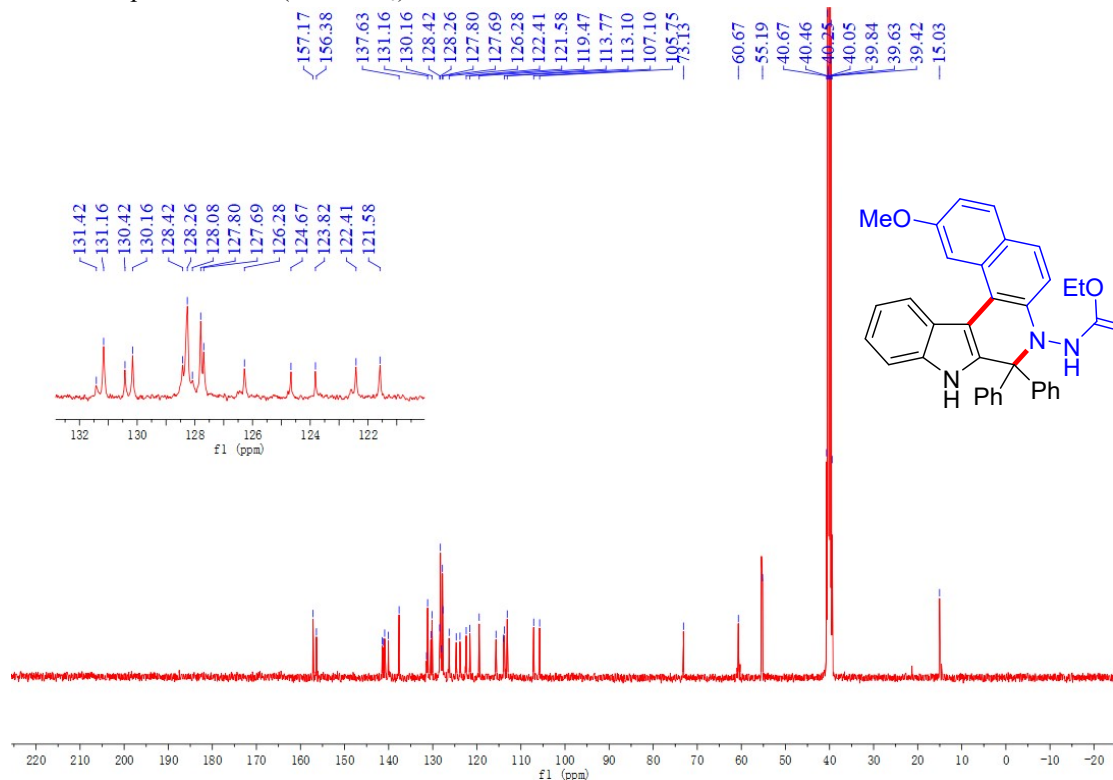
<sup>13</sup>C NMR spectrum of **4h** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4i** (DMSO-*d*<sub>6</sub>)

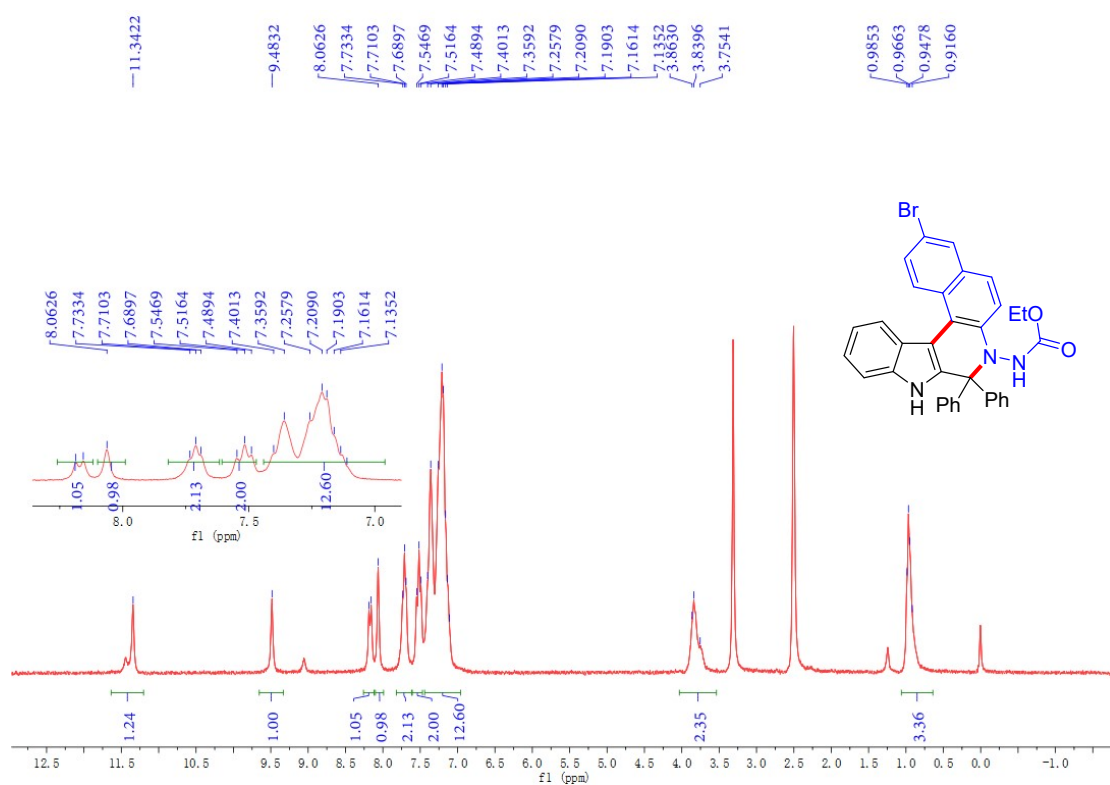


<sup>13</sup>C NMR spectrum of **4i** (DMSO-*d*<sub>6</sub>)

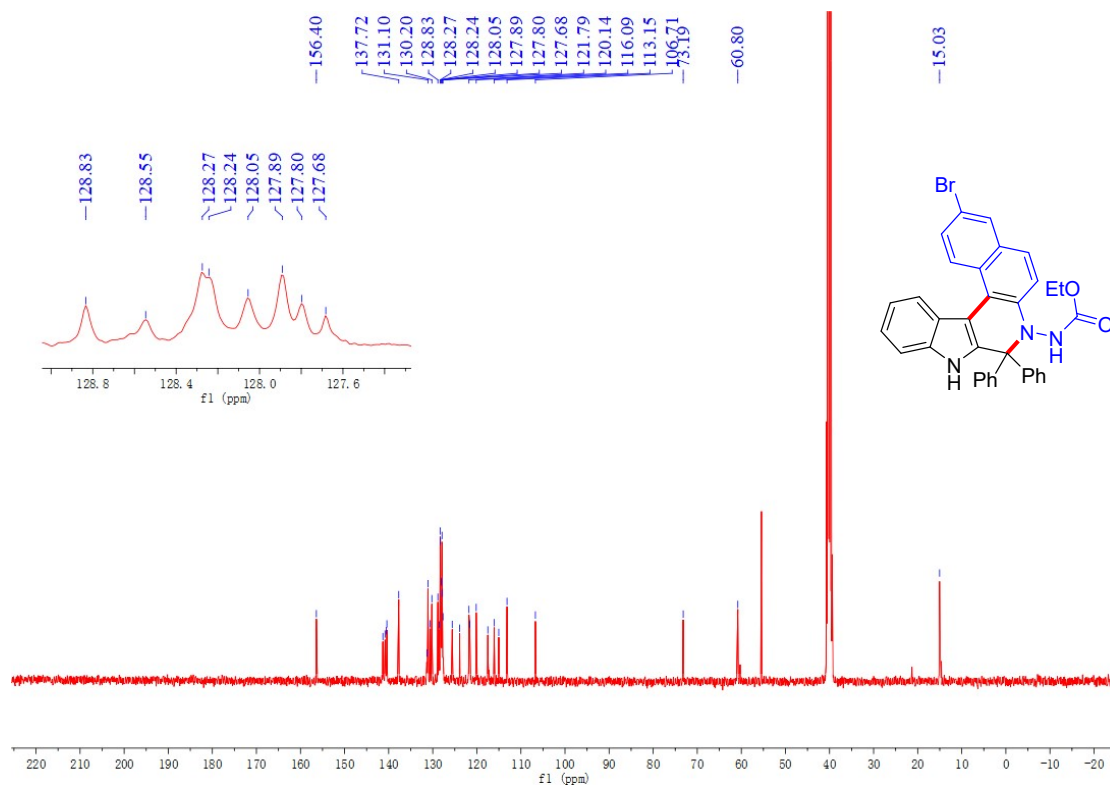




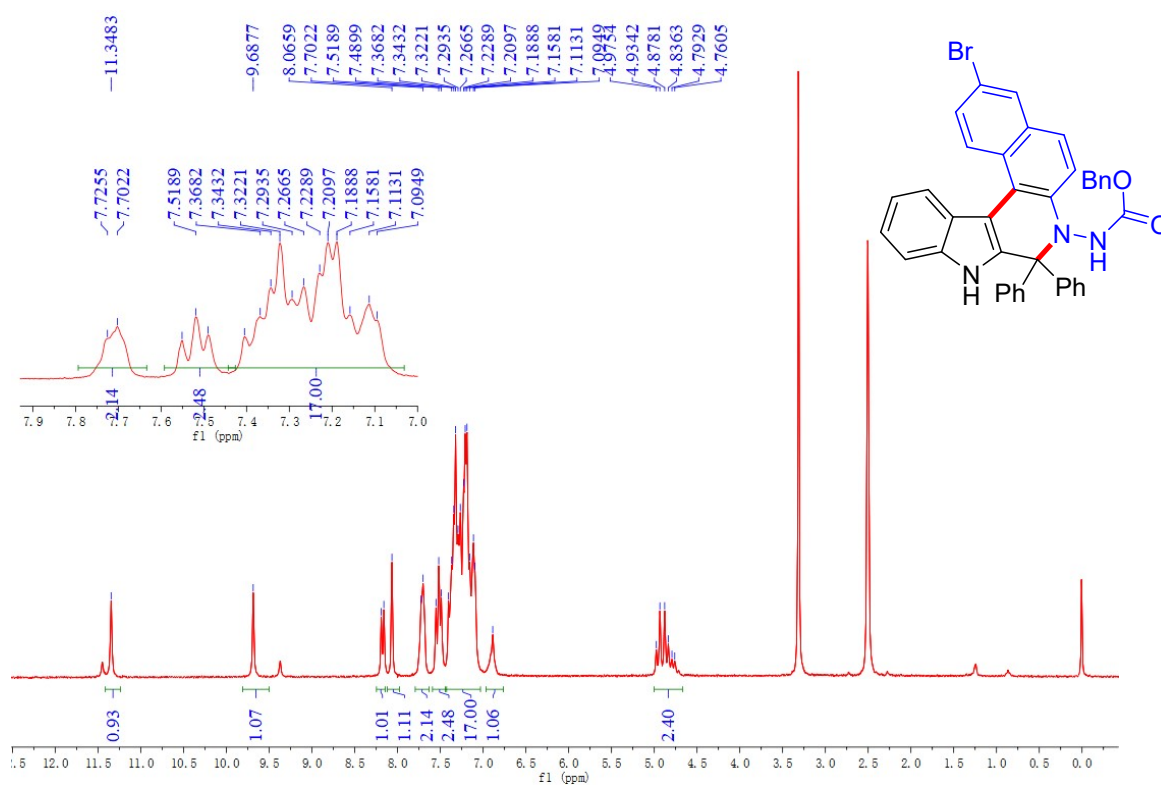
<sup>1</sup>H NMR spectrum of **4j** (DMSO-*d*<sub>6</sub>)



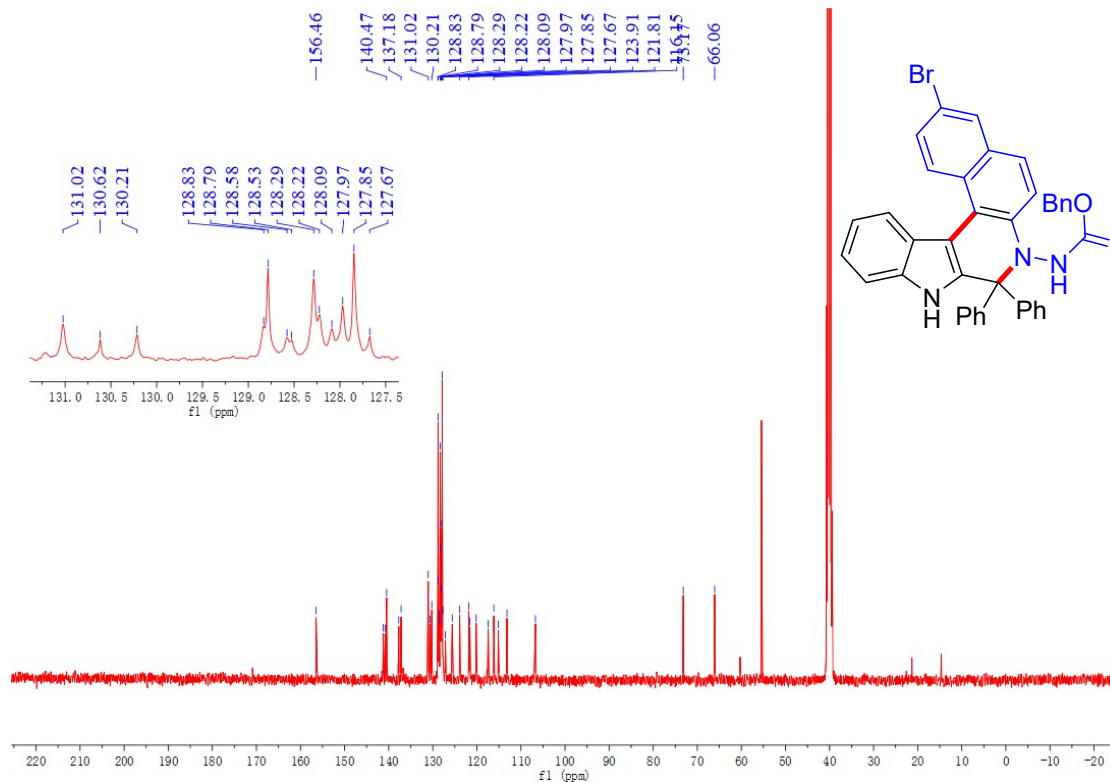
<sup>13</sup>C NMR spectrum of **4j** (DMSO-*d*<sub>6</sub>)



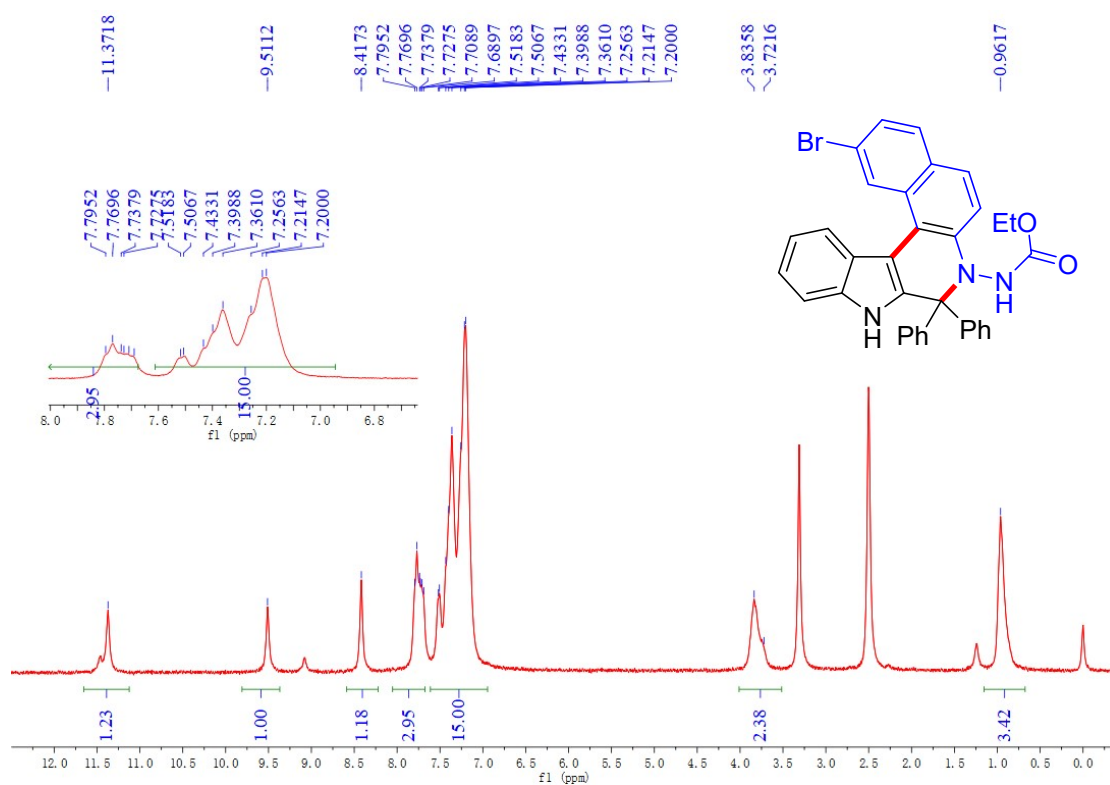
<sup>1</sup>H NMR spectrum of **4k** (DMSO-*d*<sub>6</sub>)



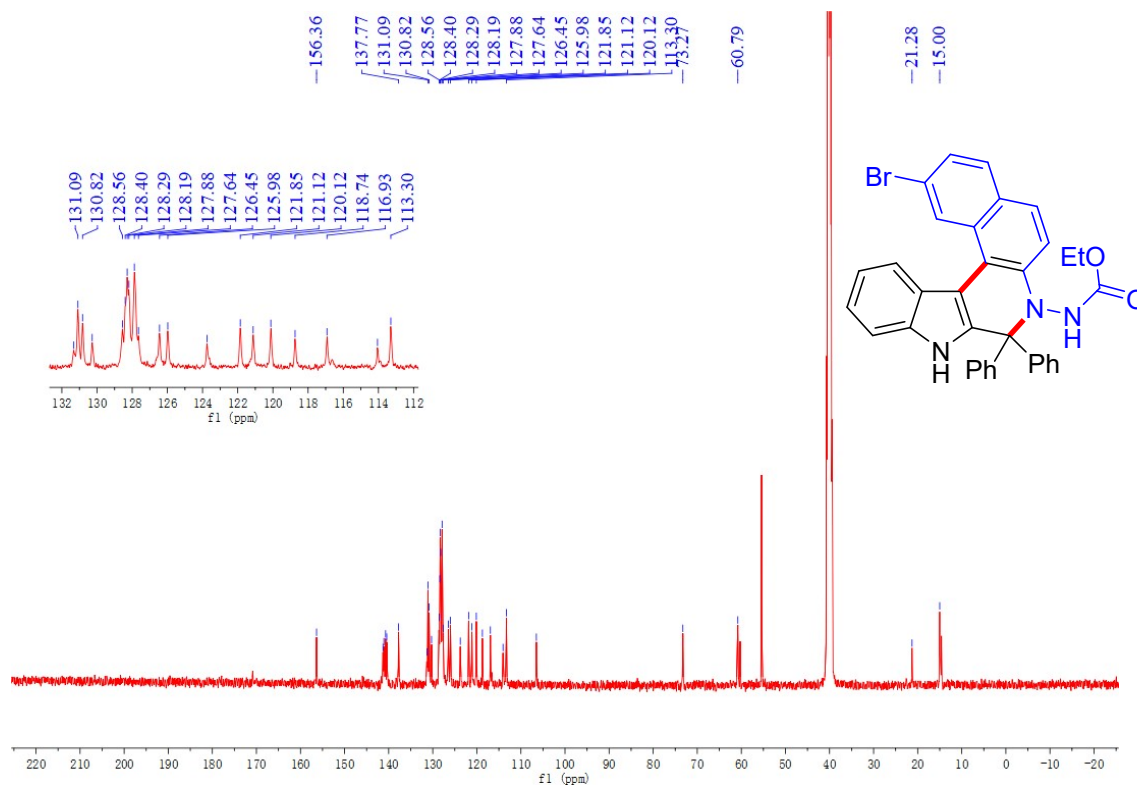
<sup>13</sup>C NMR spectrum of **4k** (DMSO-*d*<sub>6</sub>)



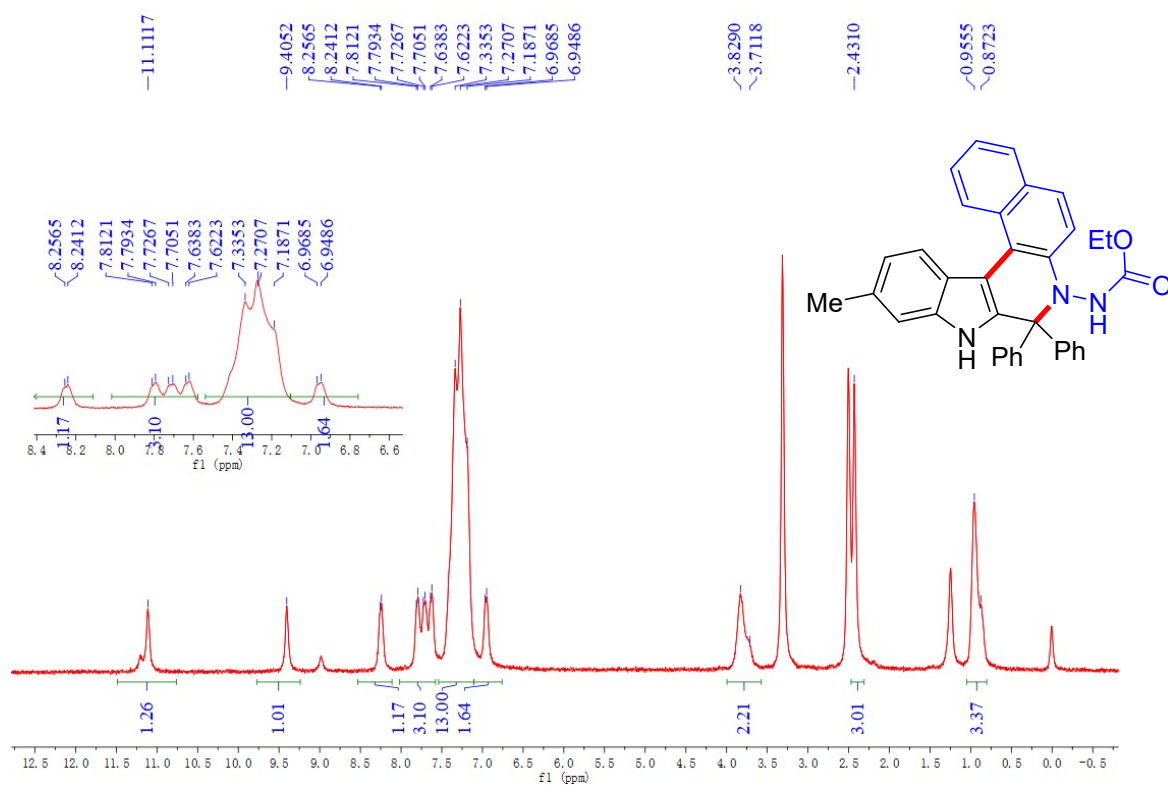
<sup>1</sup>H NMR spectrum of **41** (DMSO-*d*<sub>6</sub>)



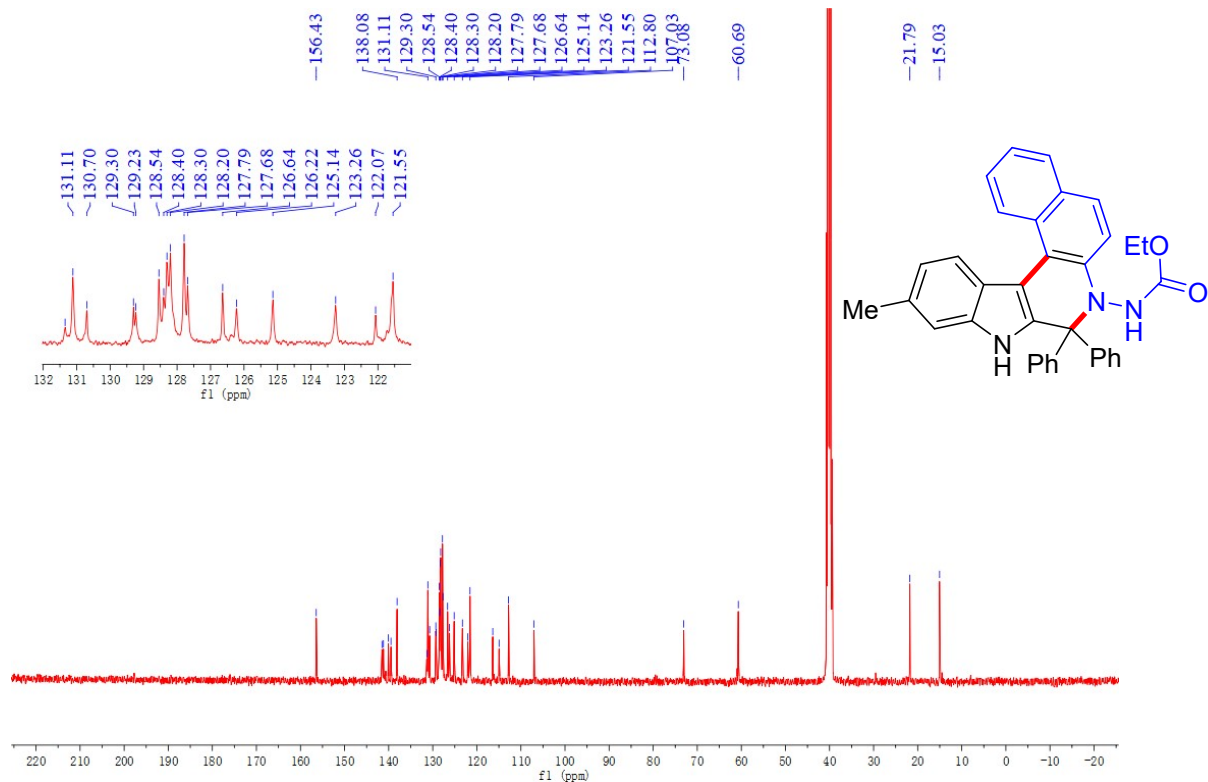
<sup>13</sup>C NMR spectrum of **41** (DMSO-*d*<sub>6</sub>)



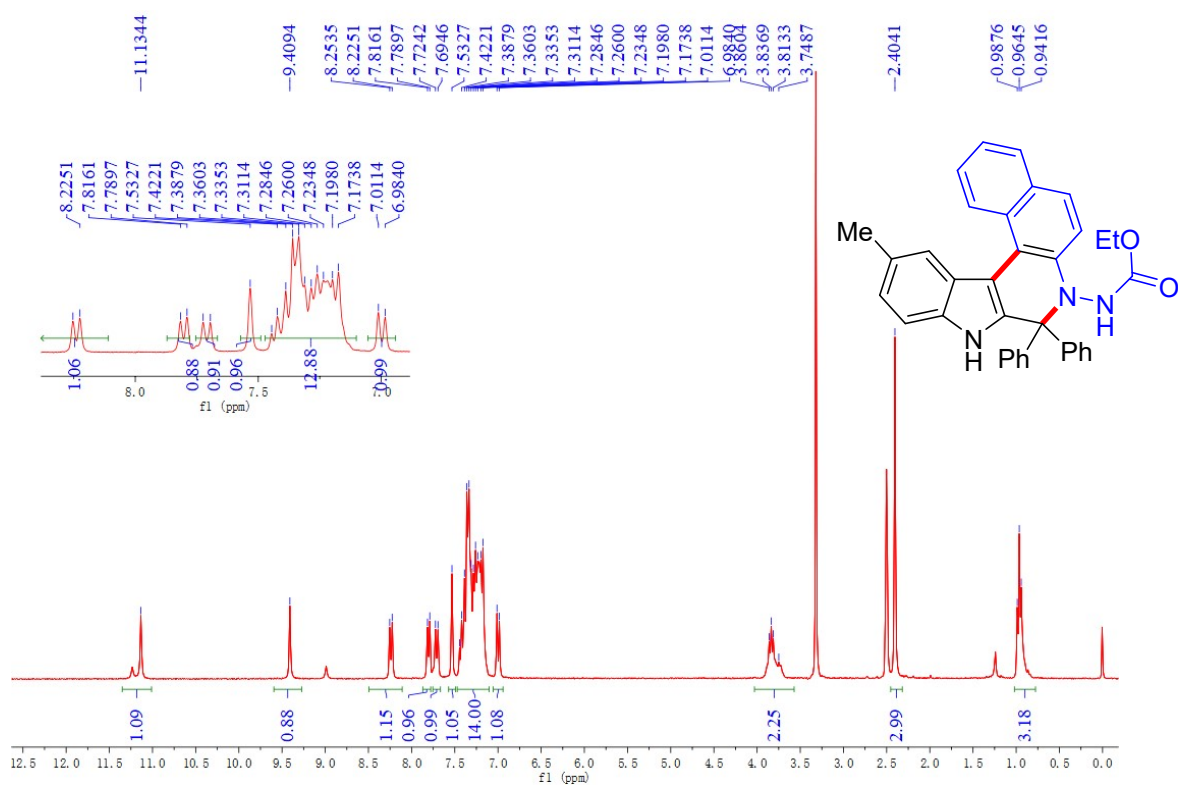
<sup>1</sup>H NMR spectrum of **4m** (DMSO-*d*<sub>6</sub>)



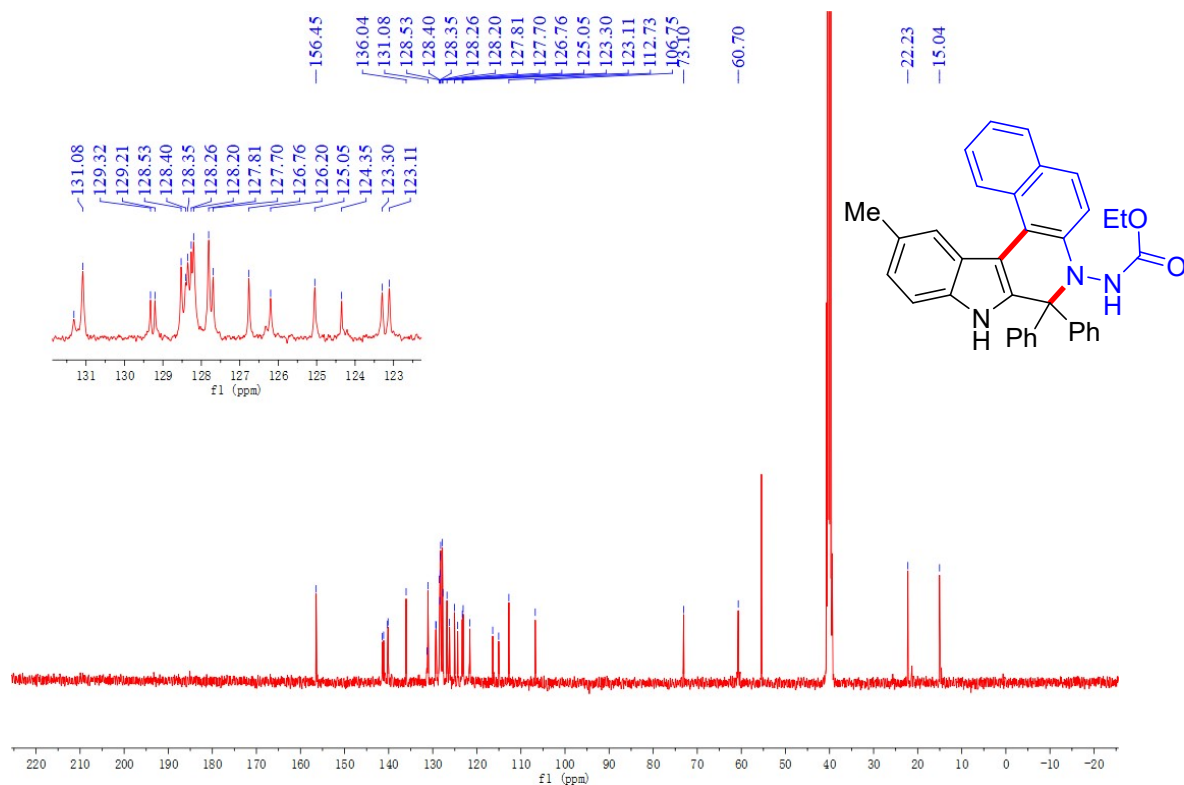
<sup>13</sup>C NMR spectrum of **4m** (DMSO-*d*<sub>6</sub>)



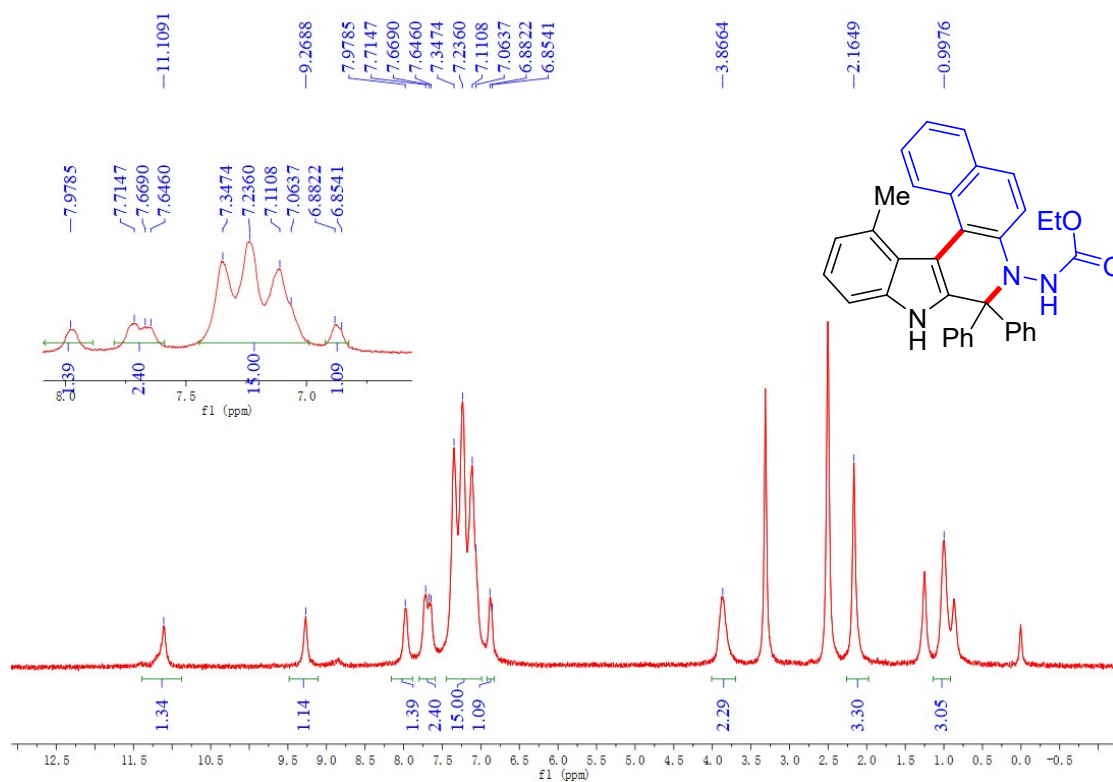
<sup>1</sup>H NMR spectrum of **4n** (DMSO-*d*<sub>6</sub>)



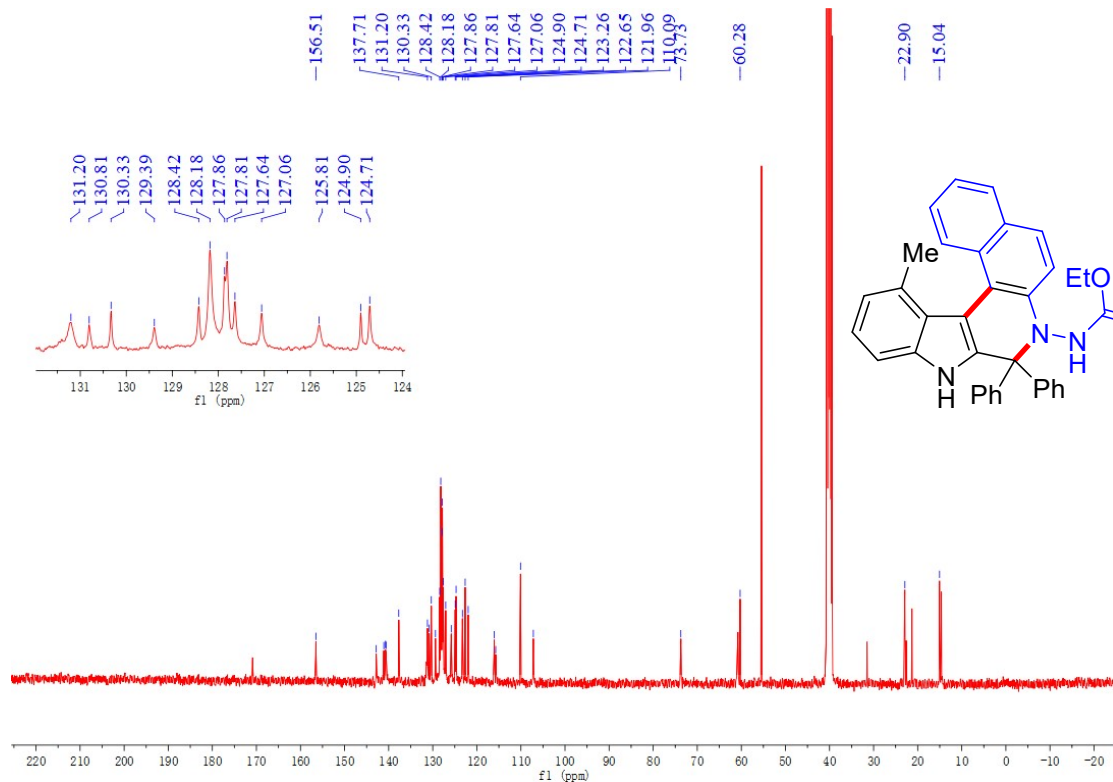
<sup>13</sup>C NMR spectrum of **4n** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4o** (DMSO-*d*<sub>6</sub>)

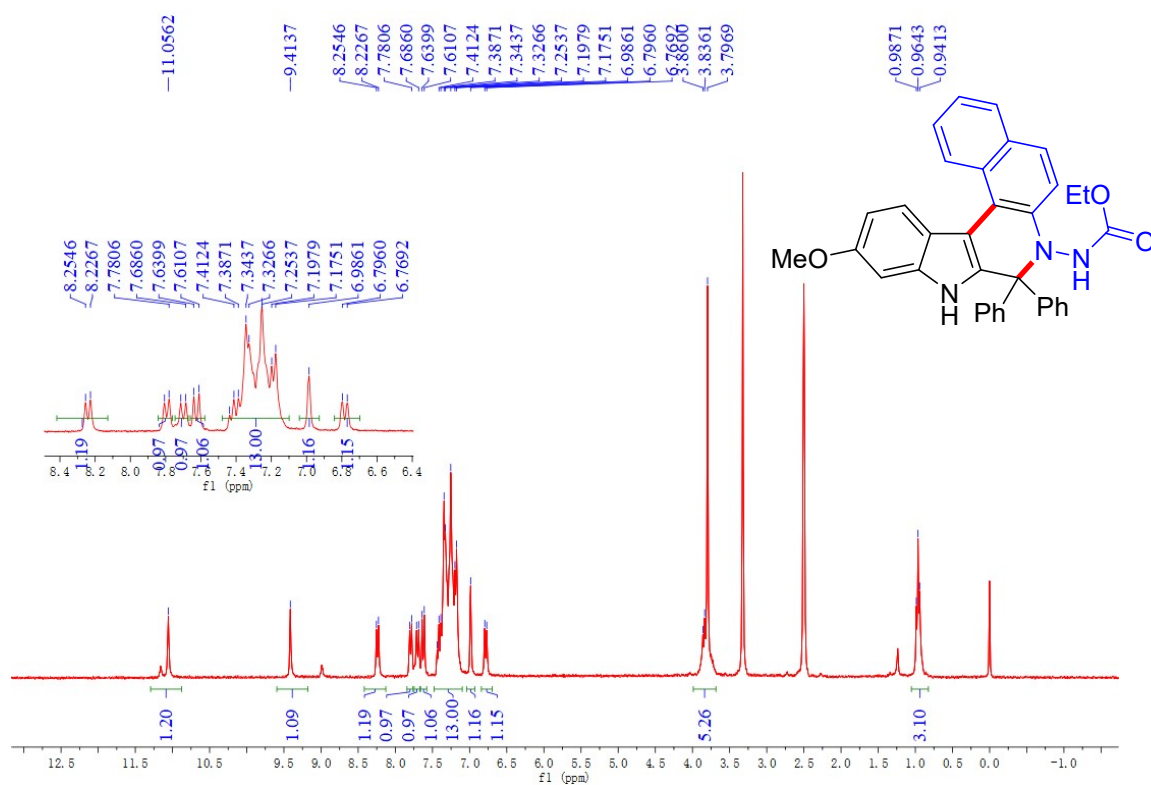


<sup>13</sup>C NMR spectrum of **4o** (DMSO-*d*<sub>6</sub>)

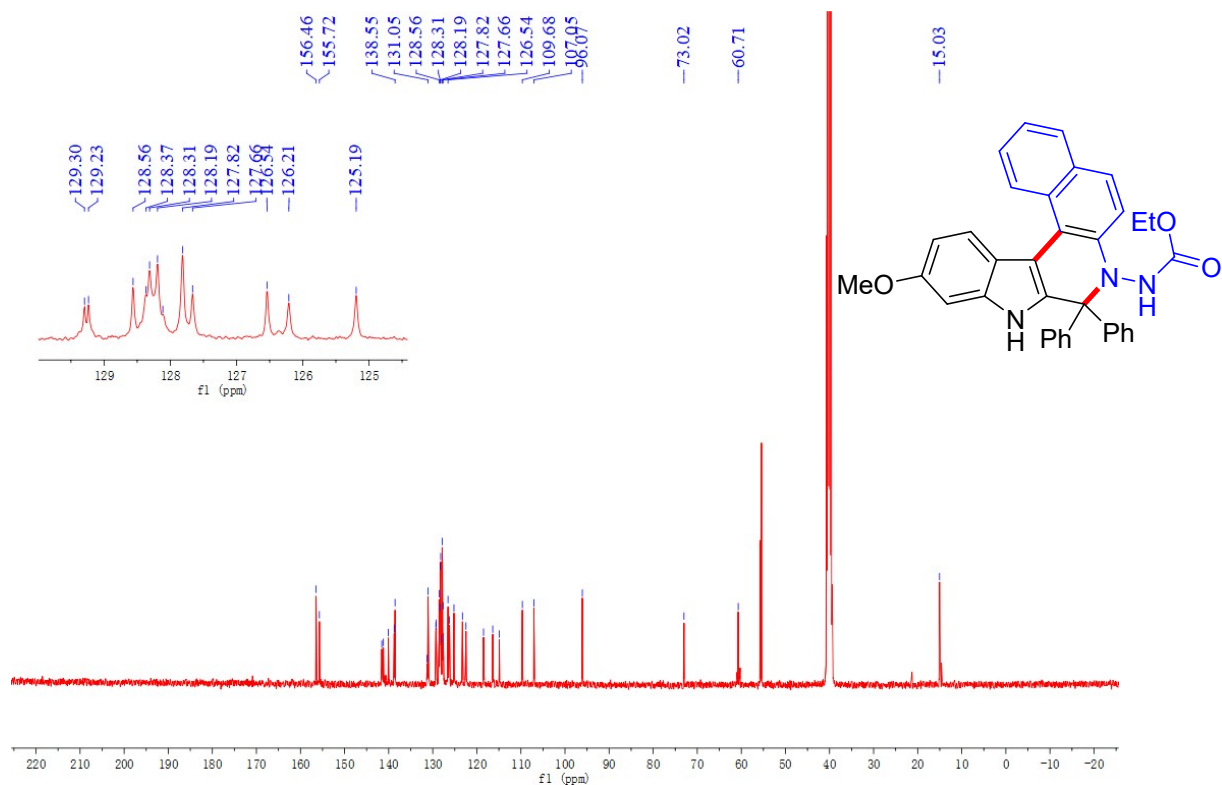




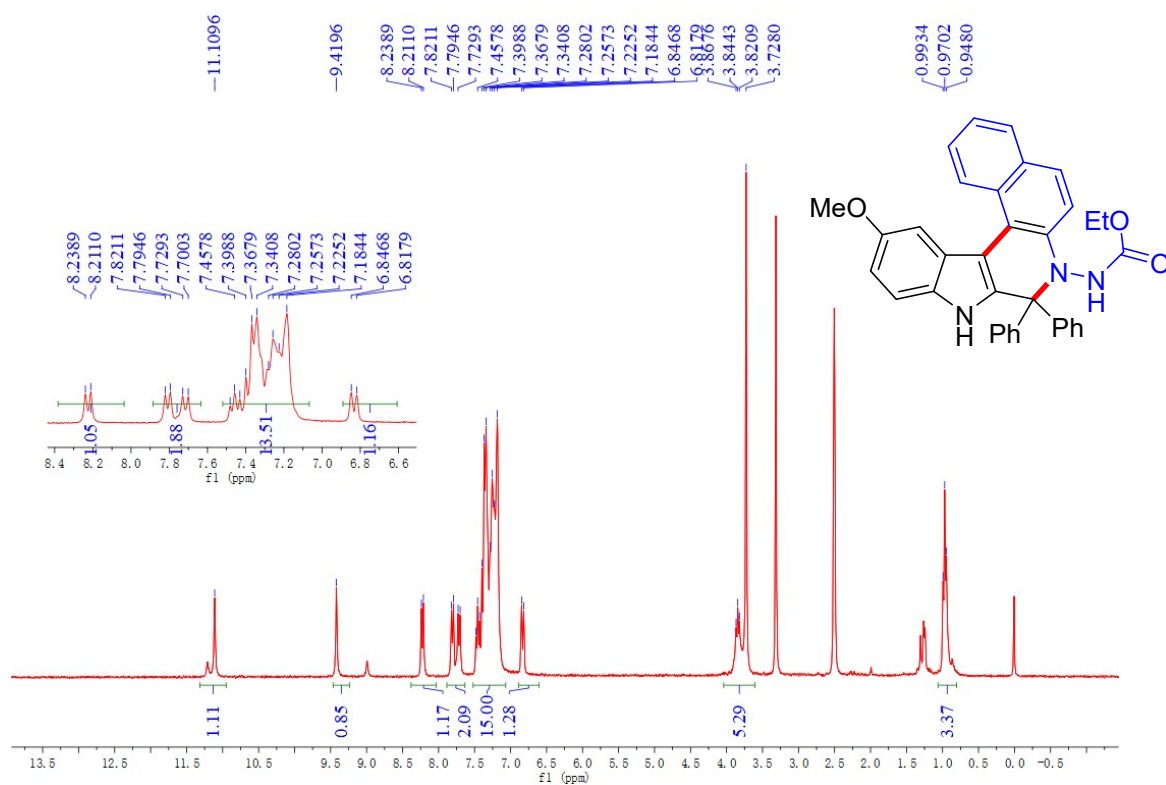
<sup>1</sup>H NMR spectrum of **4p** (DMSO-*d*<sub>6</sub>)



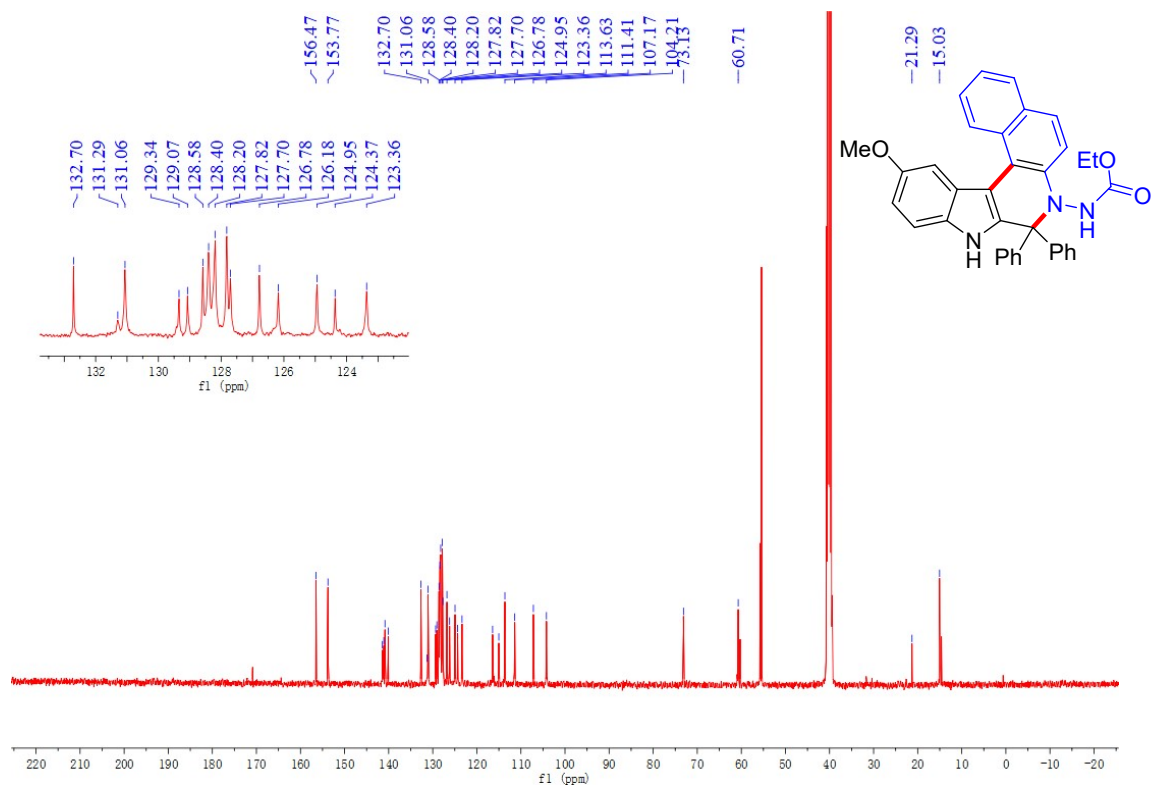
<sup>13</sup>C NMR spectrum of **4p** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4q** (DMSO-*d*<sub>6</sub>)

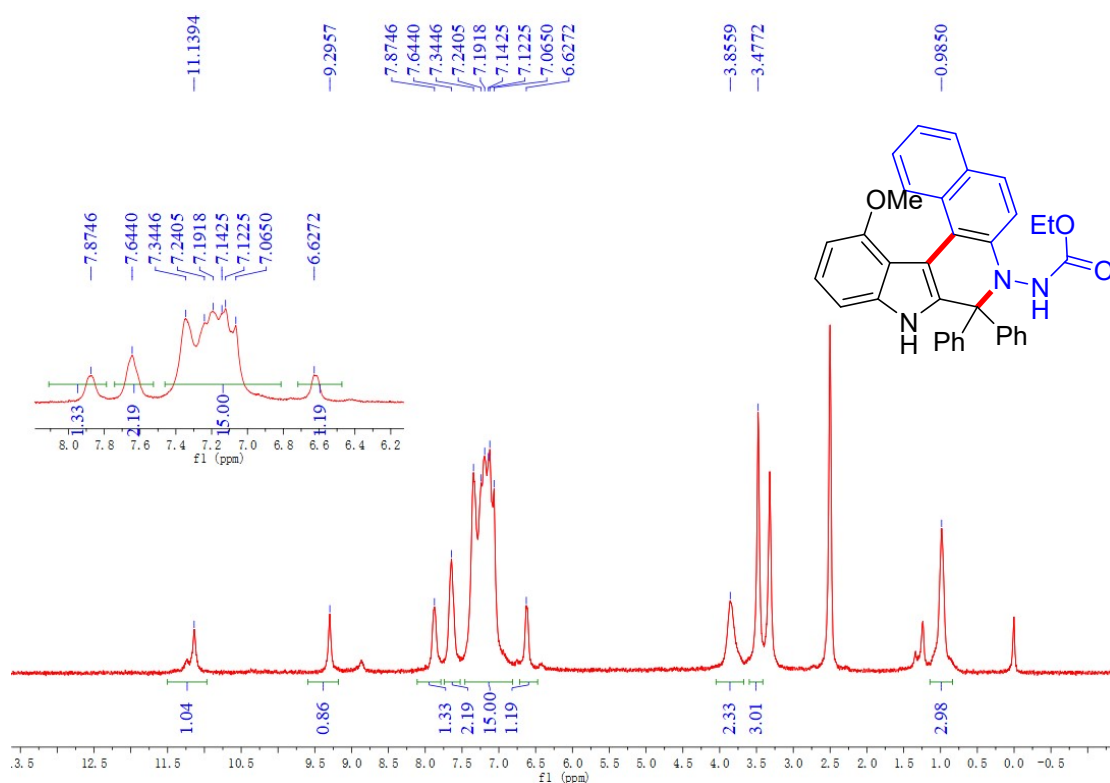


<sup>13</sup>C NMR spectrum of **4q** (DMSO-*d*<sub>6</sub>)

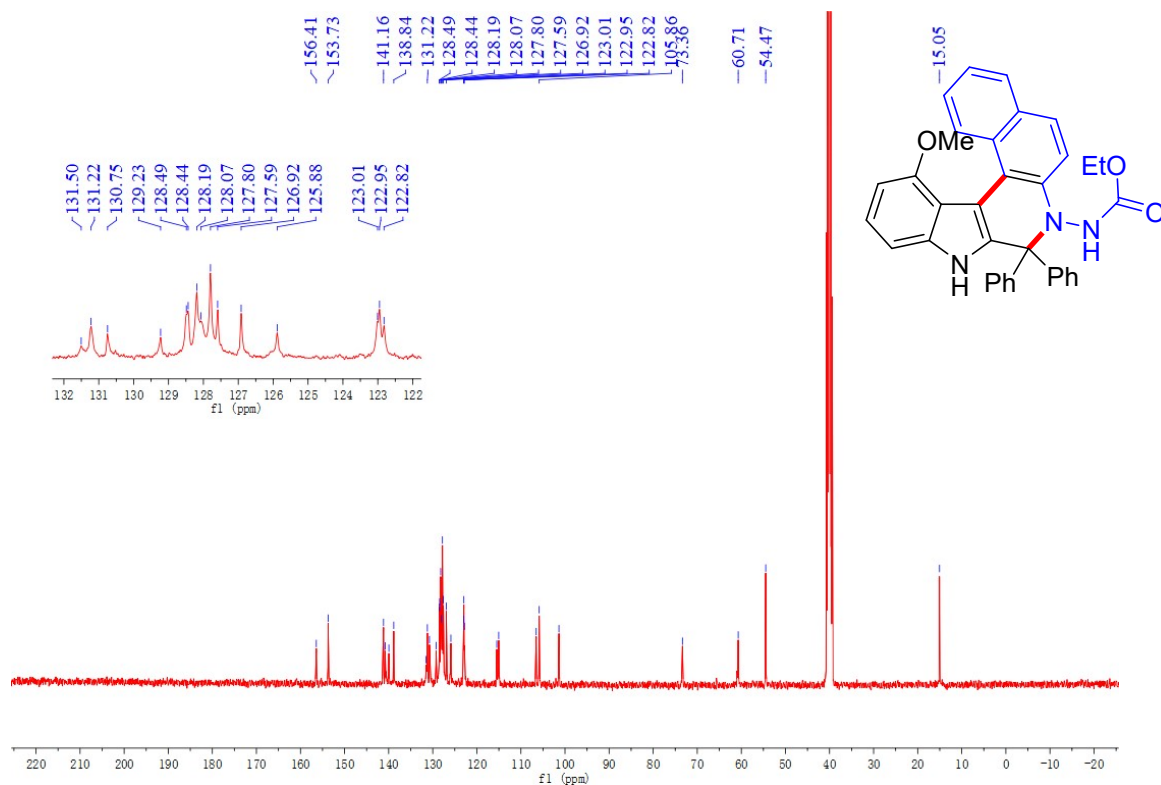




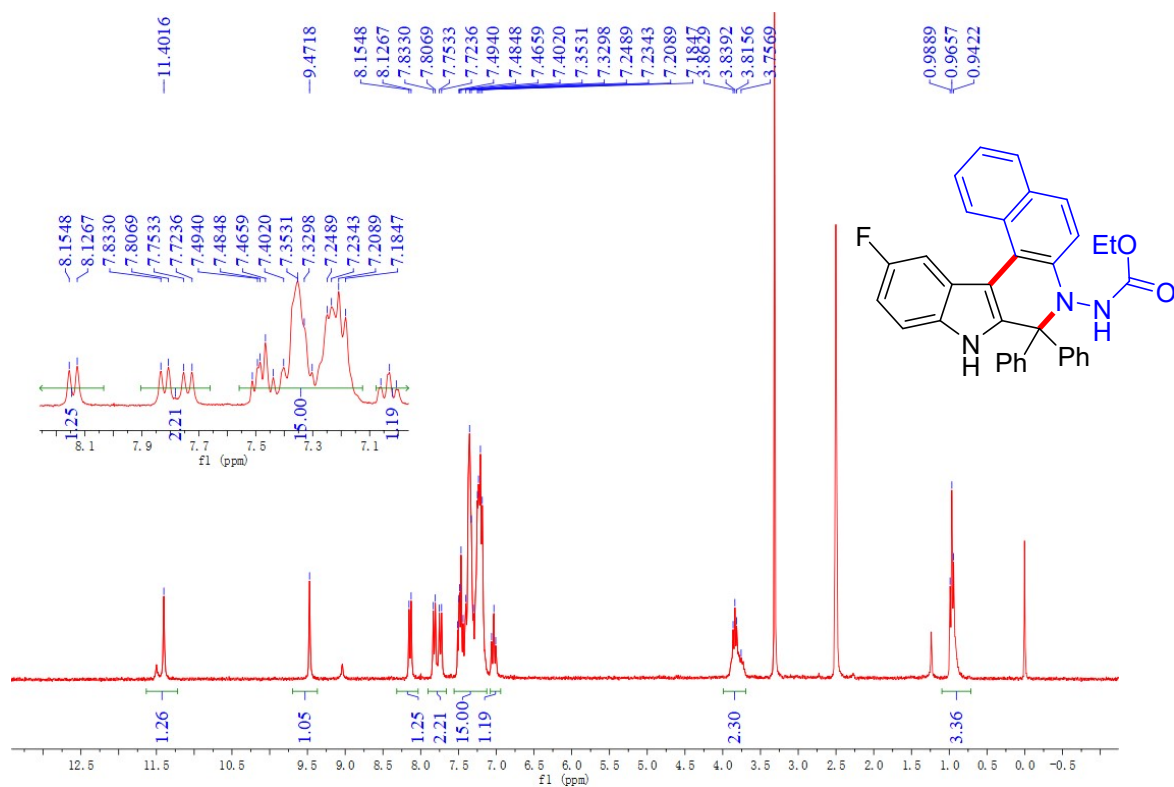
<sup>1</sup>H NMR spectrum of **4r** (DMSO-*d*<sub>6</sub>)



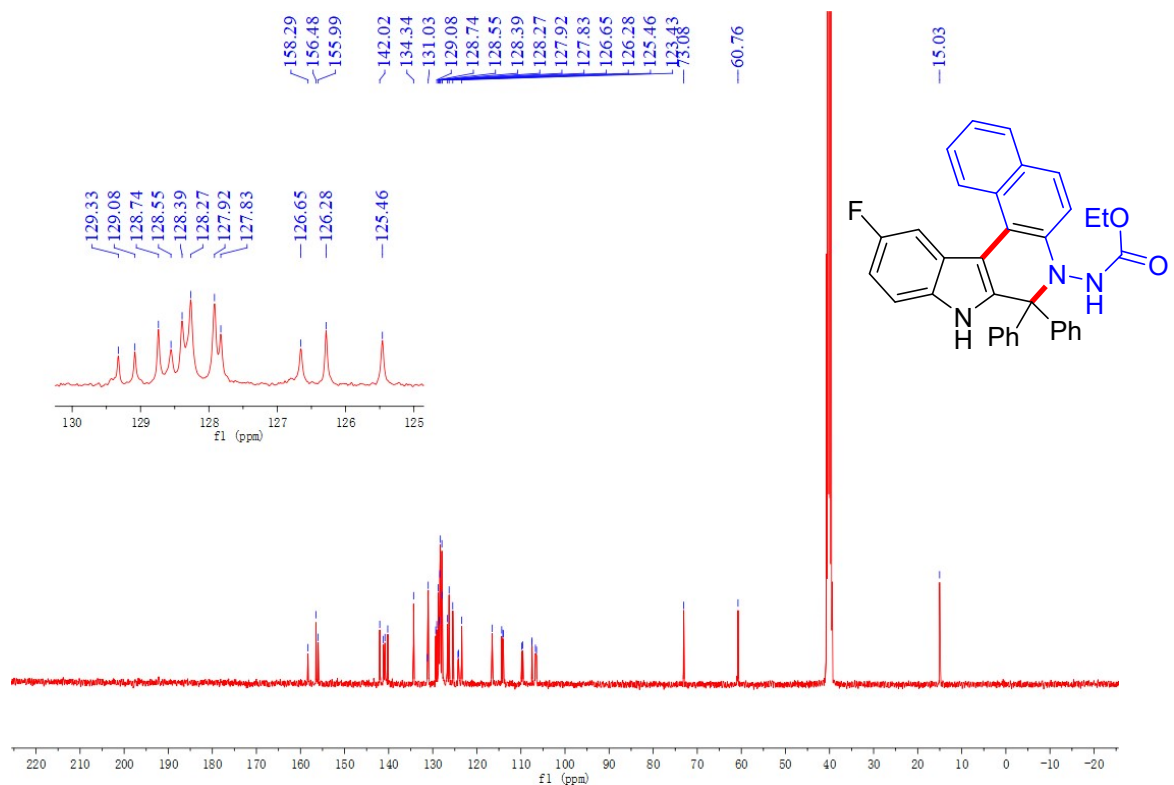
<sup>13</sup>C NMR spectrum of **4r** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4s** (DMSO-*d*<sub>6</sub>)

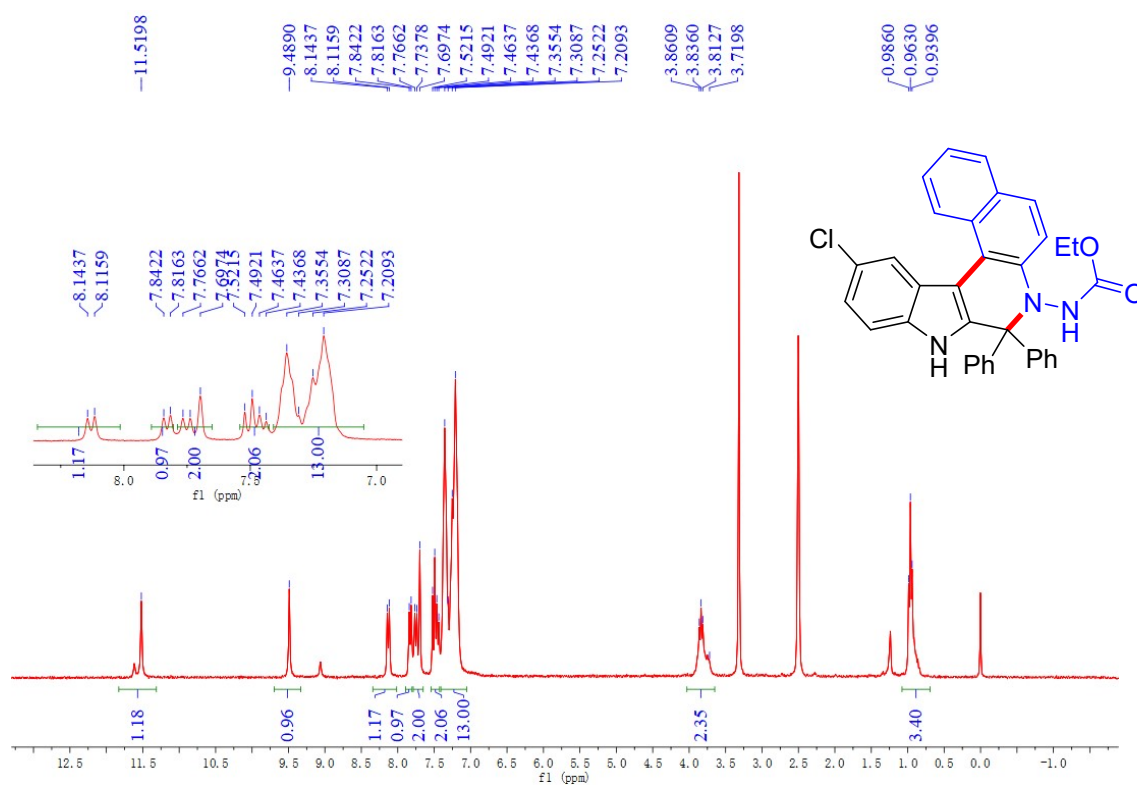


<sup>13</sup>C NMR spectrum of **4s** (DMSO-*d*<sub>6</sub>)

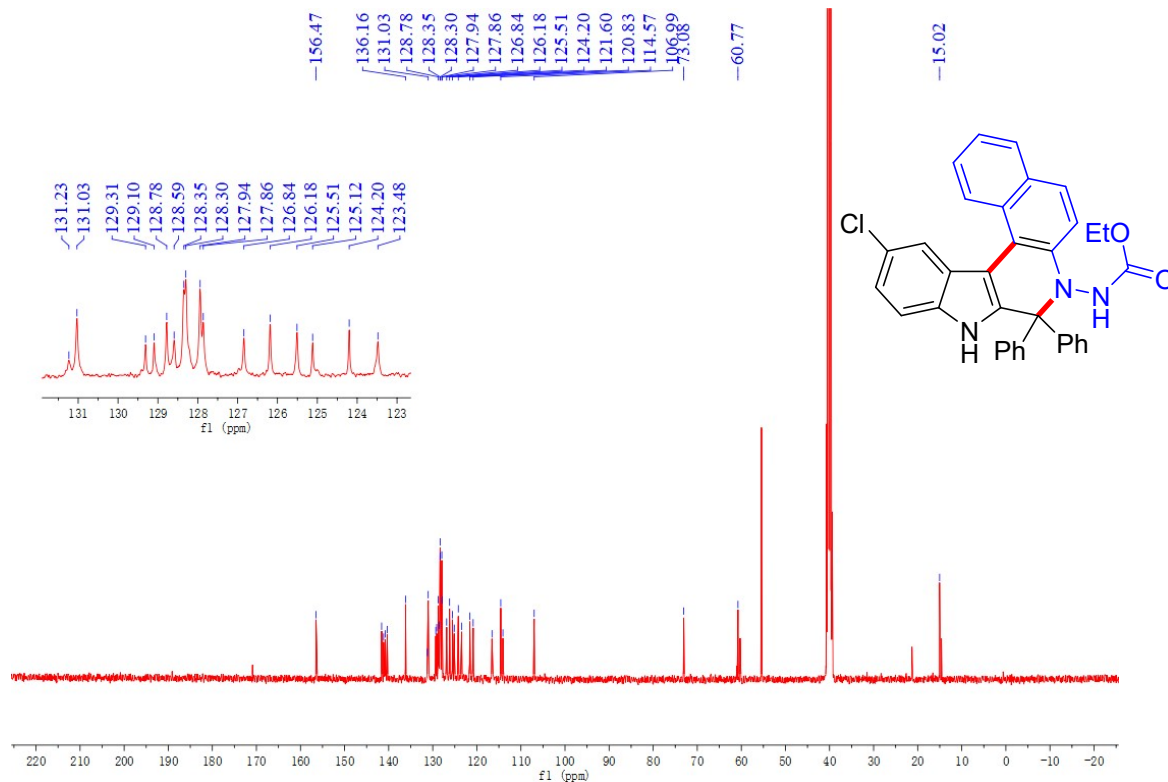




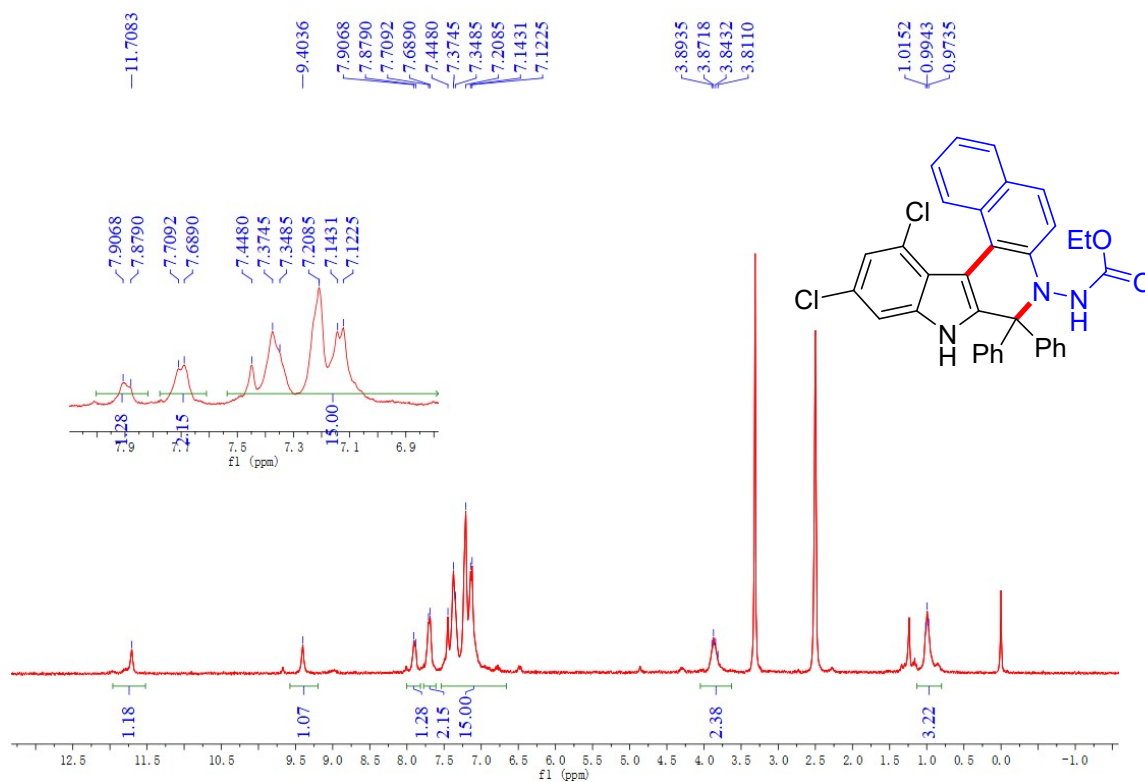
<sup>1</sup>H NMR spectrum of **4u** (DMSO-*d*<sub>6</sub>)



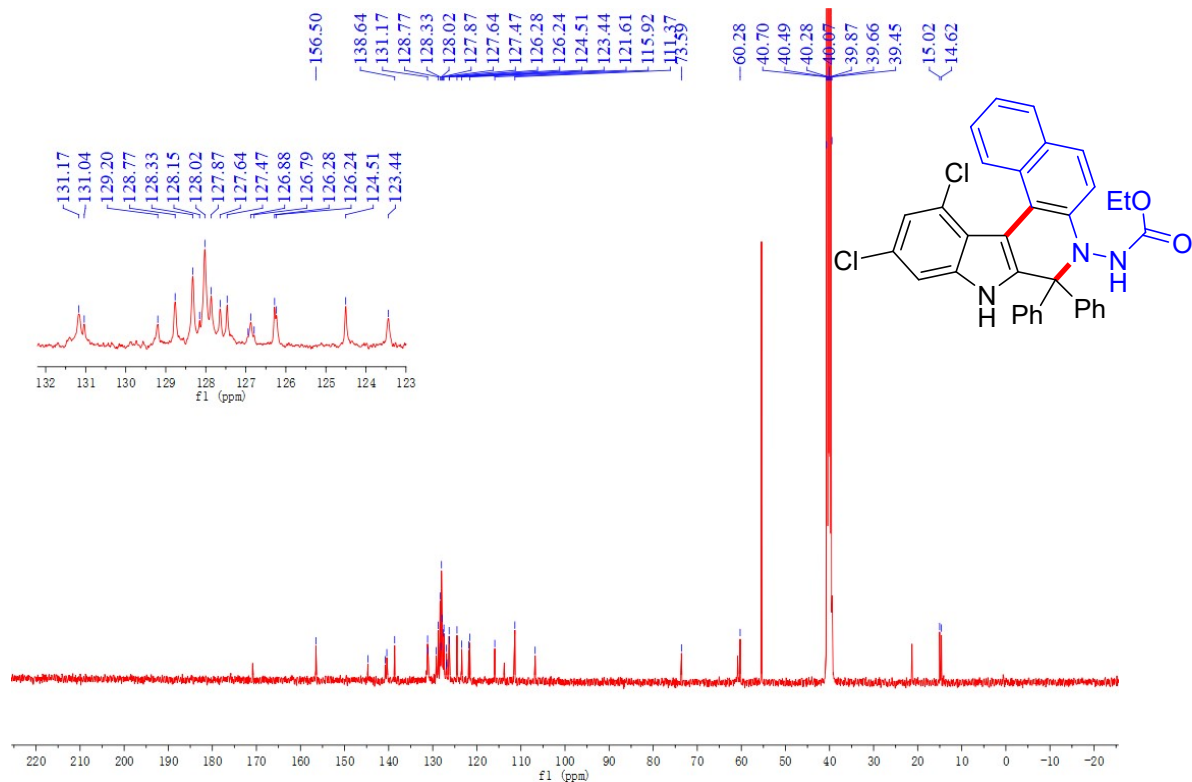
<sup>13</sup>C NMR spectrum of **4u** (DMSO-*d*<sub>6</sub>)



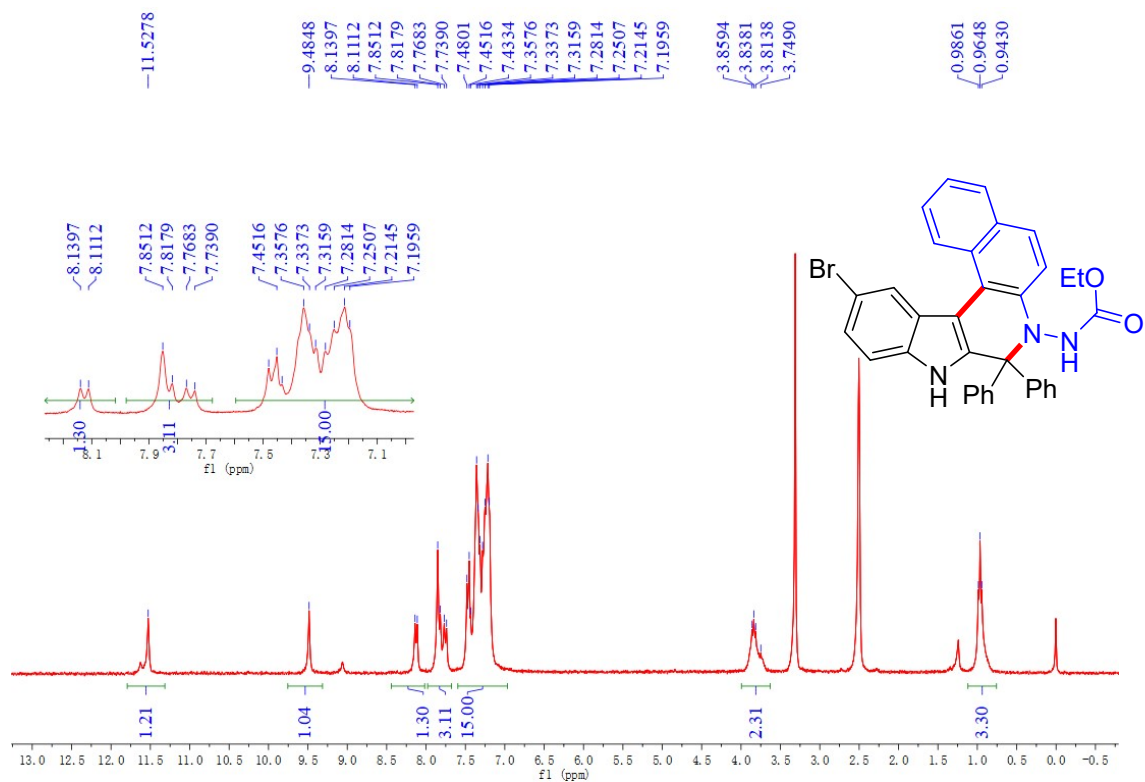
<sup>1</sup>H NMR spectrum of **4v** (DMSO-*d*<sub>6</sub>)



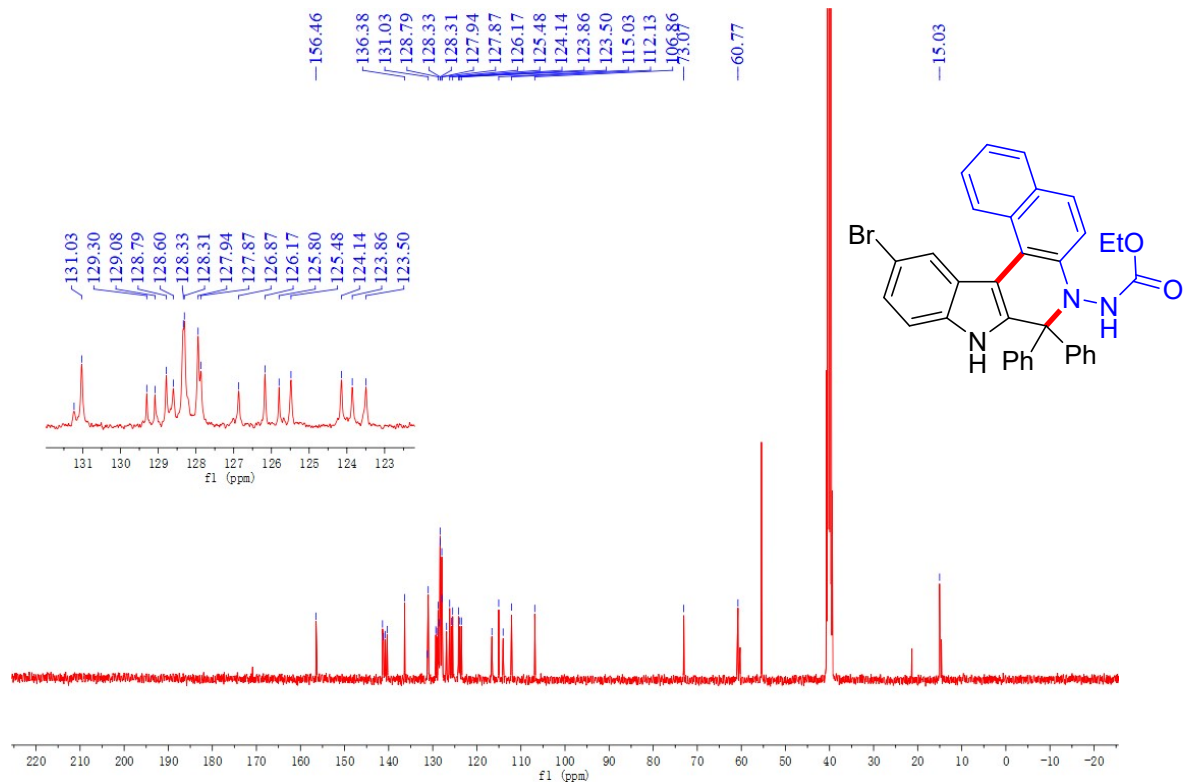
<sup>13</sup>C NMR spectrum of **4v** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4w** (DMSO-*d*<sub>6</sub>)

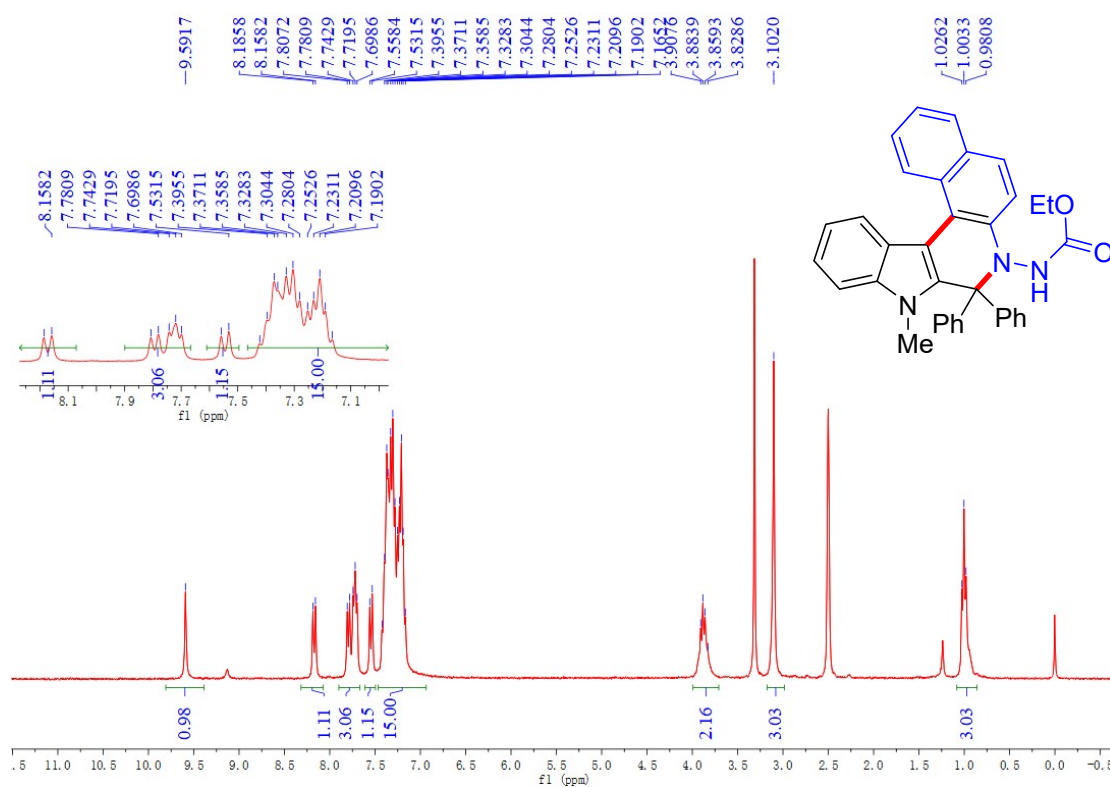


<sup>13</sup>C NMR spectrum of **4w** (DMSO-*d*<sub>6</sub>)

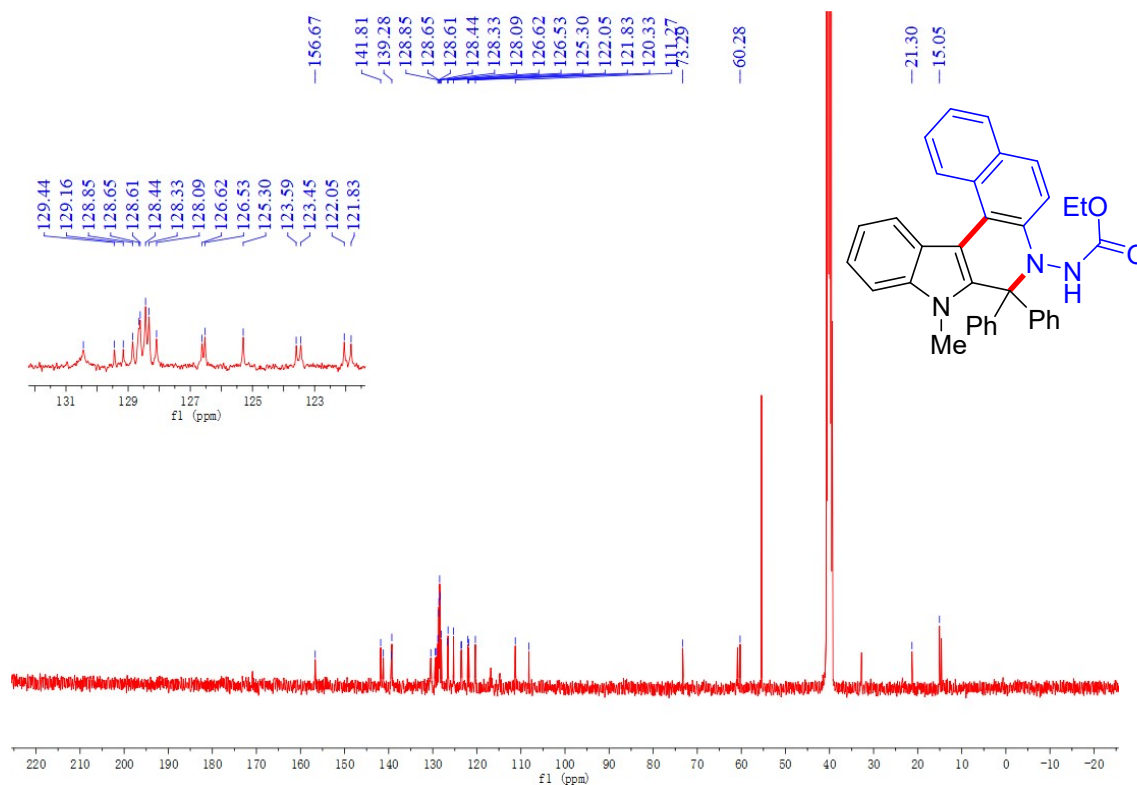




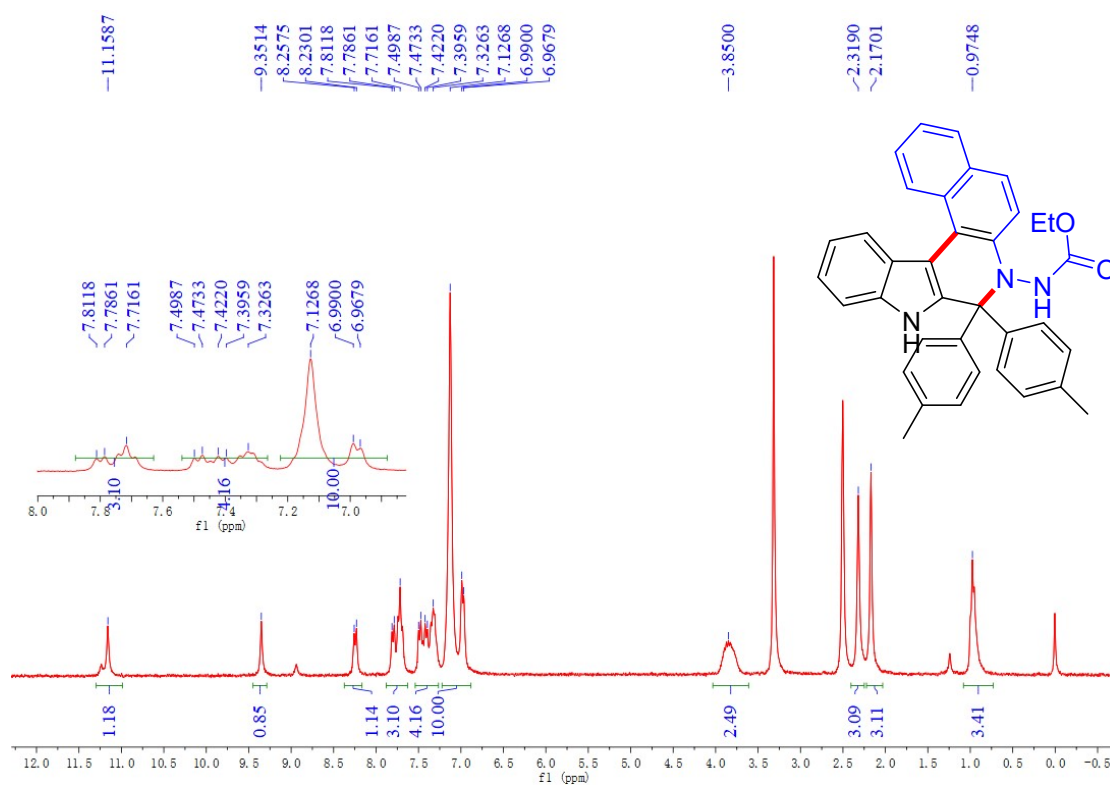
<sup>1</sup>H NMR spectrum of **4x** (DMSO-*d*<sub>6</sub>)



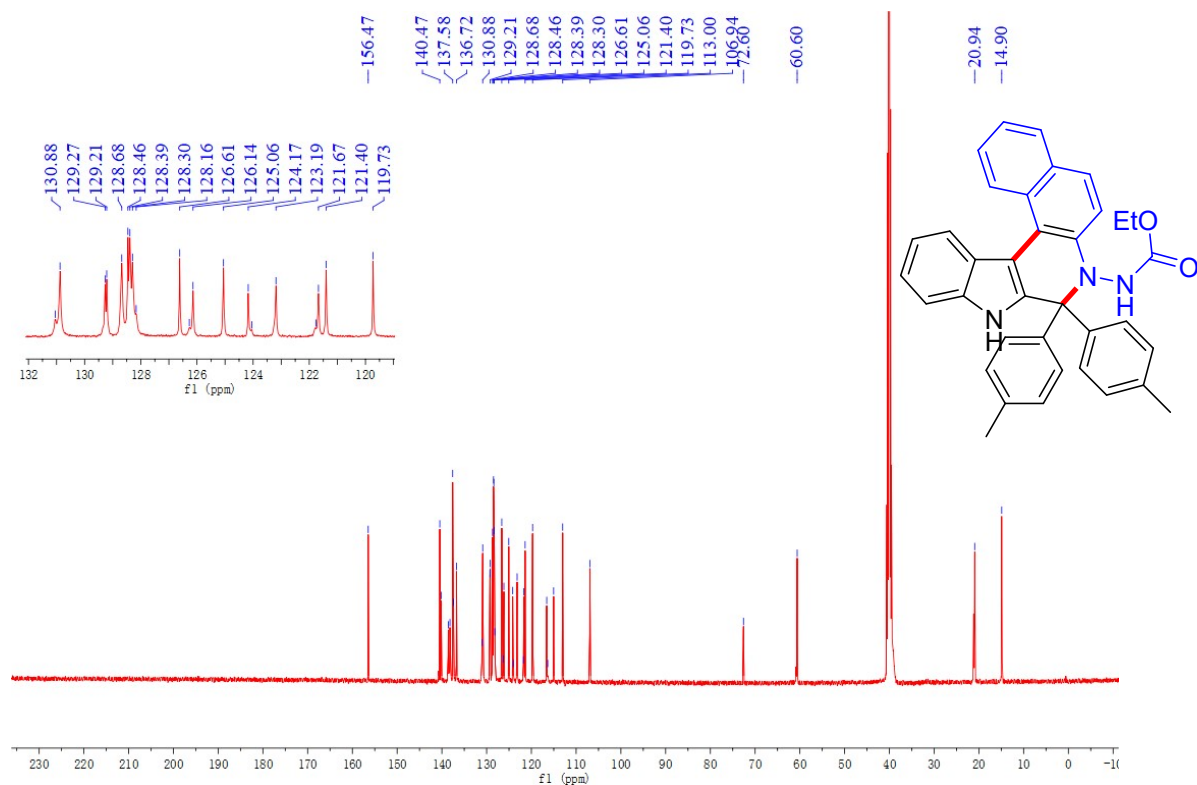
<sup>13</sup>C NMR spectrum of **4x** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **4y** (DMSO-*d*<sub>6</sub>)

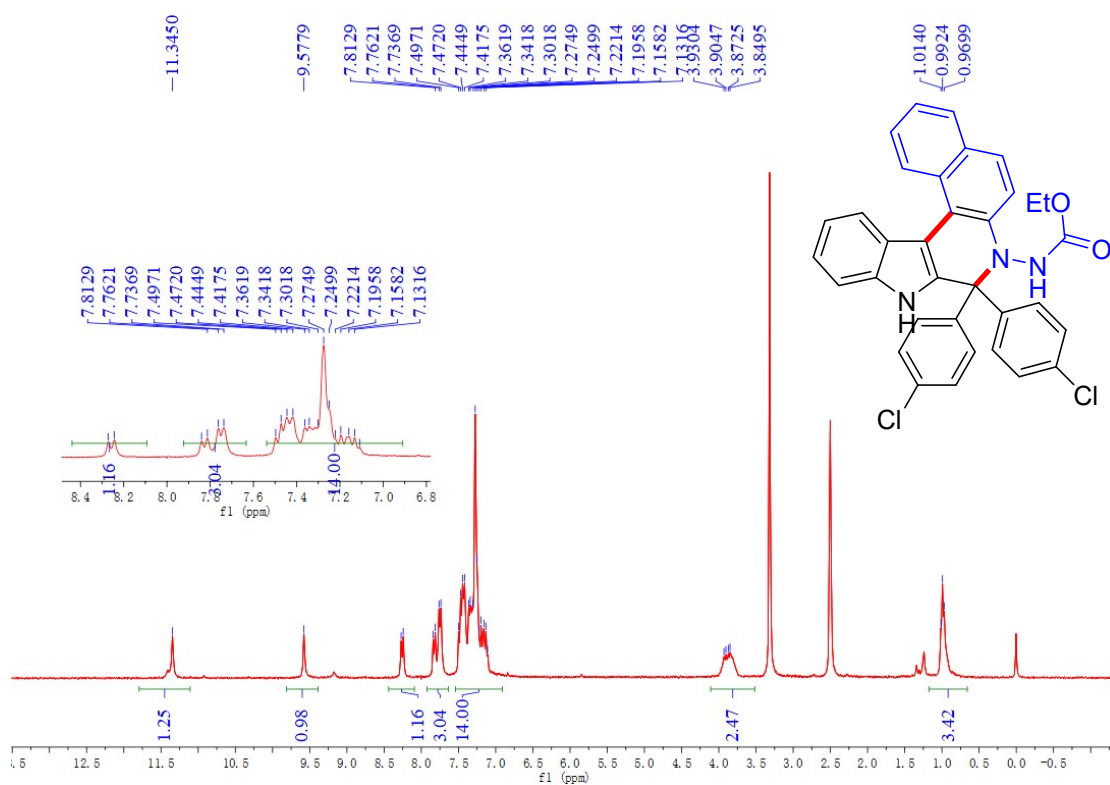


<sup>13</sup>C NMR spectrum of **4y** (DMSO-*d*<sub>6</sub>)

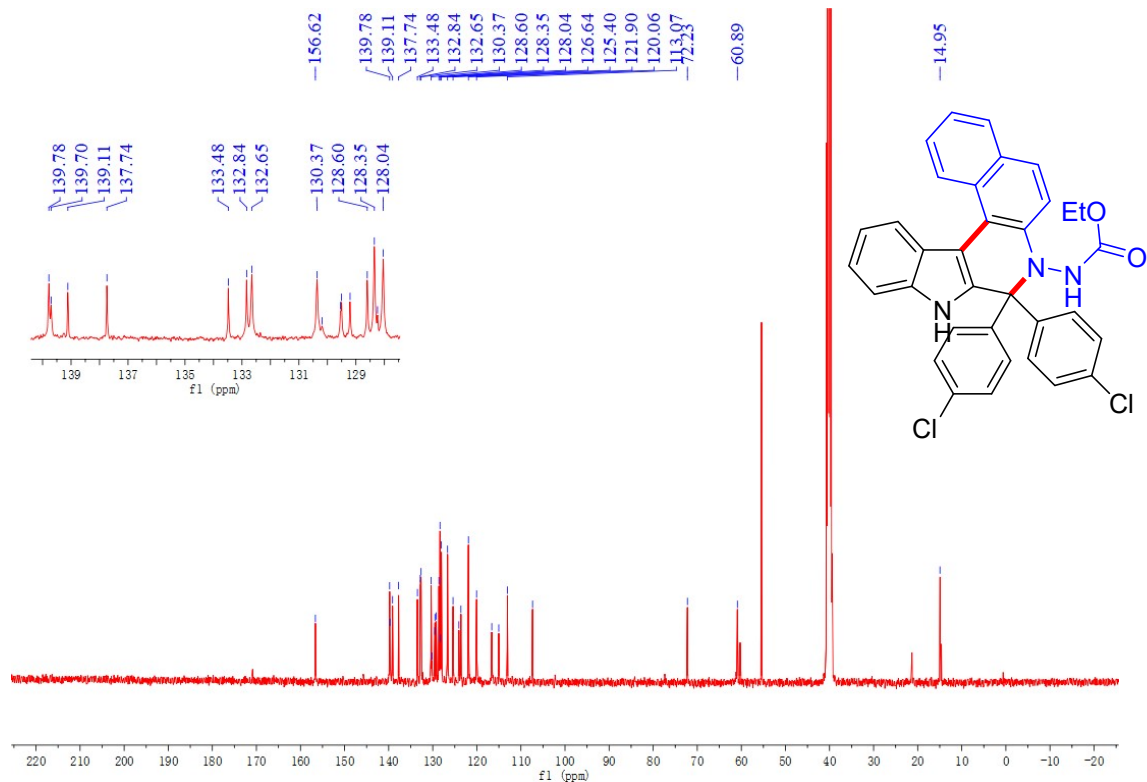




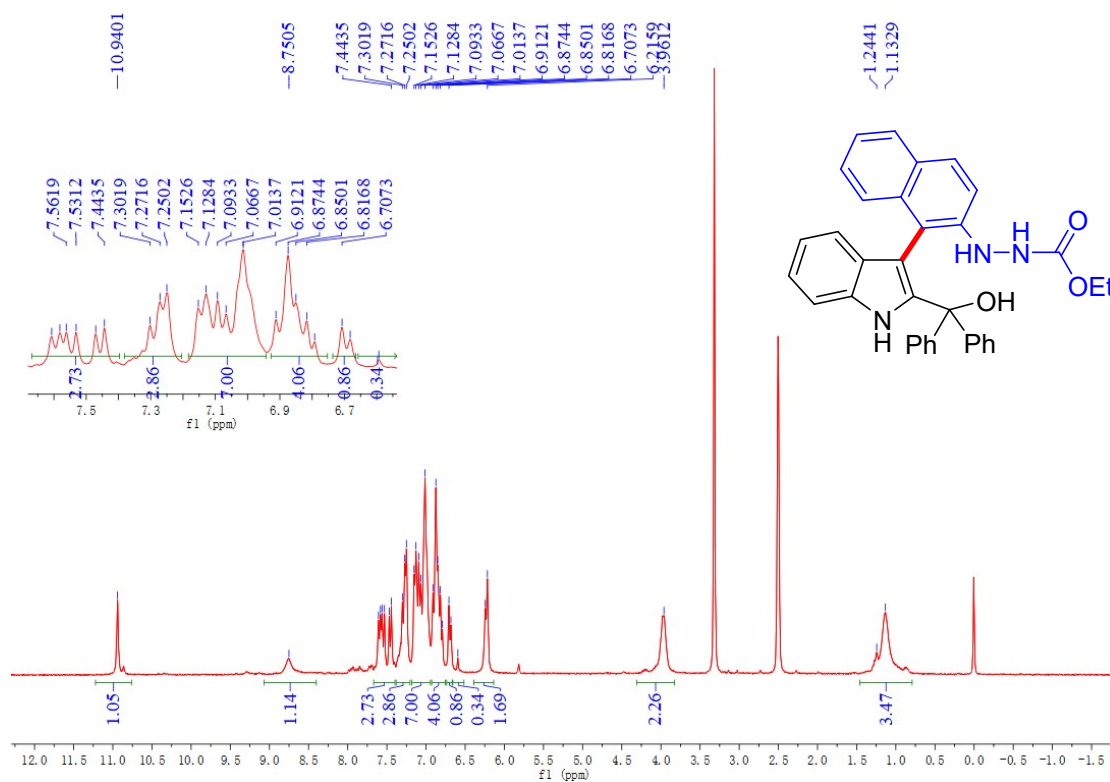
<sup>1</sup>H NMR spectrum of **4z** (DMSO-*d*<sub>6</sub>)



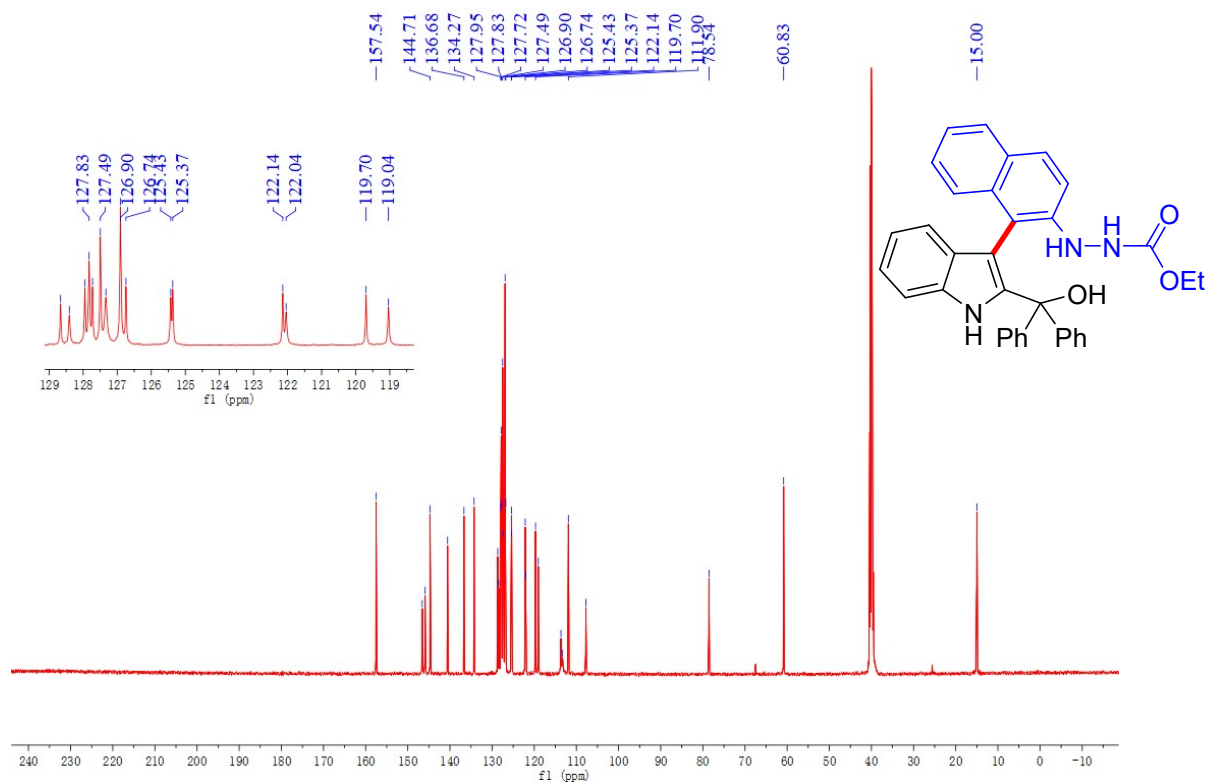
<sup>13</sup>C NMR spectrum of **4z** (DMSO-*d*<sub>6</sub>)



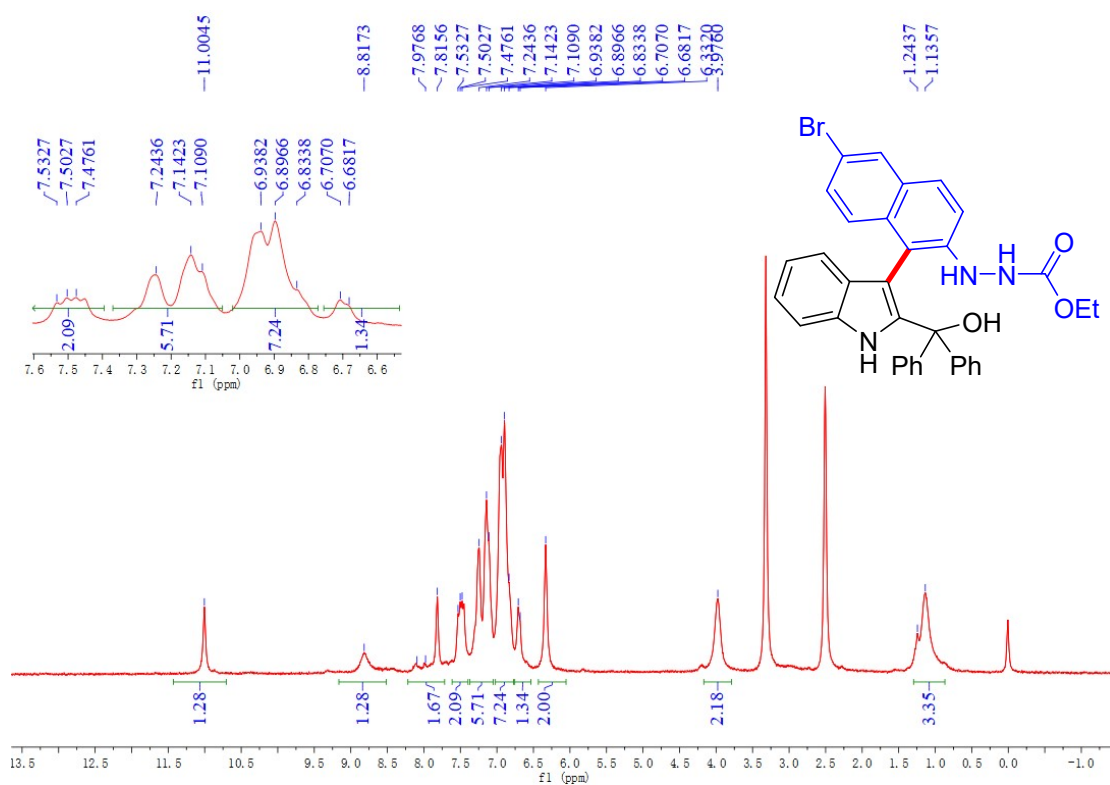
<sup>1</sup>H NMR spectrum of **5a** (DMSO-*d*<sub>6</sub>)



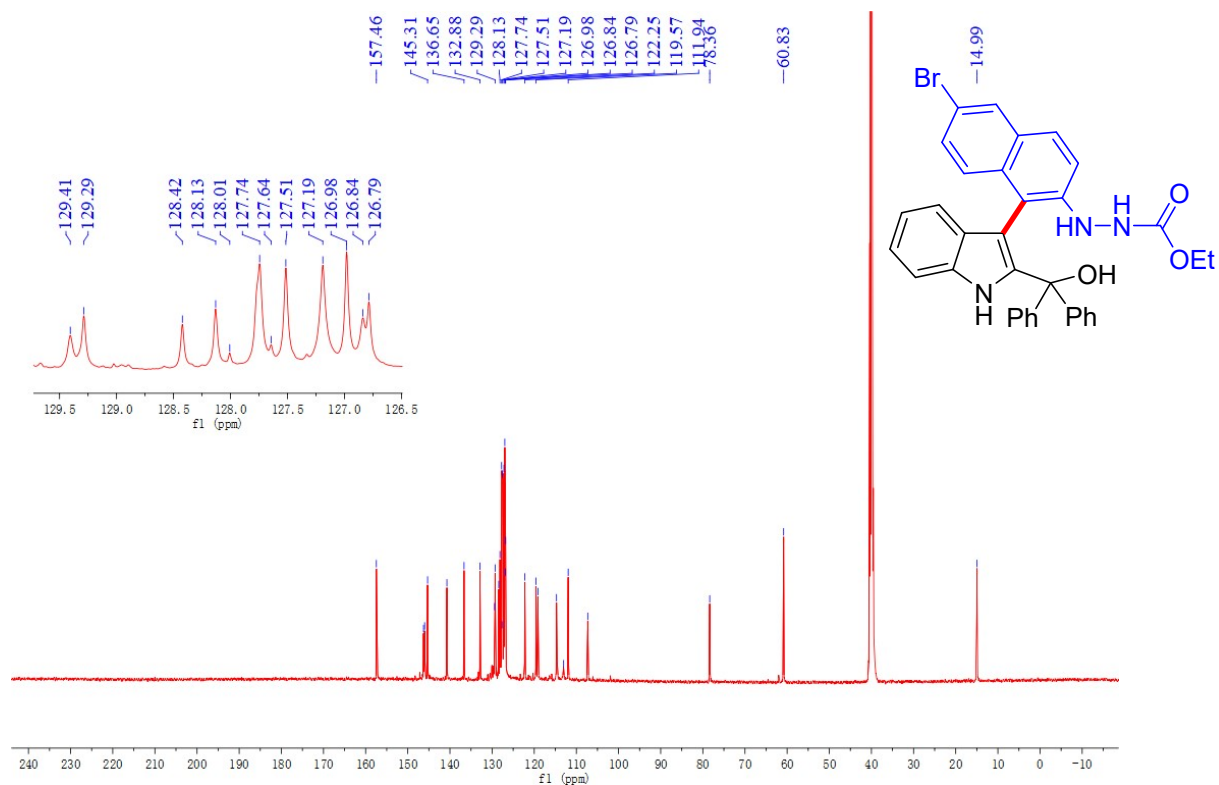
<sup>13</sup>C NMR spectrum of **5a** (DMSO-*d*<sub>6</sub>)



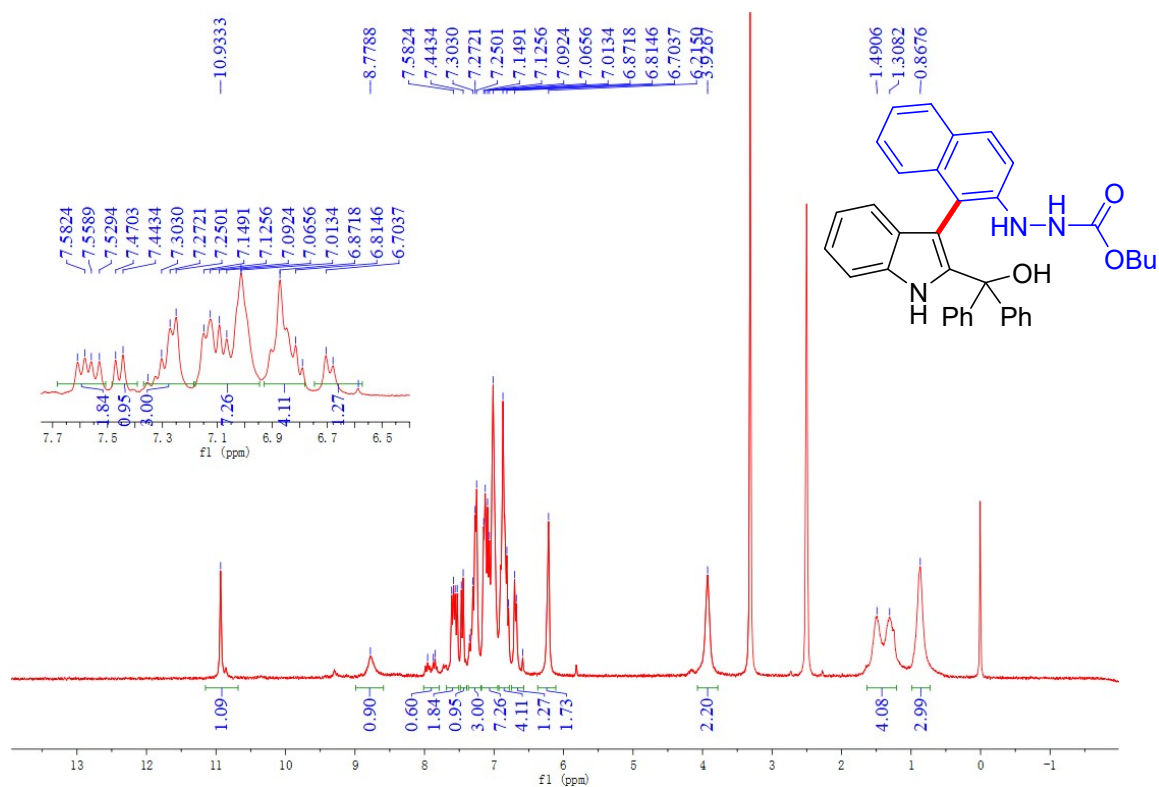
<sup>1</sup>H NMR spectrum of **5b** (DMSO-*d*<sub>6</sub>)



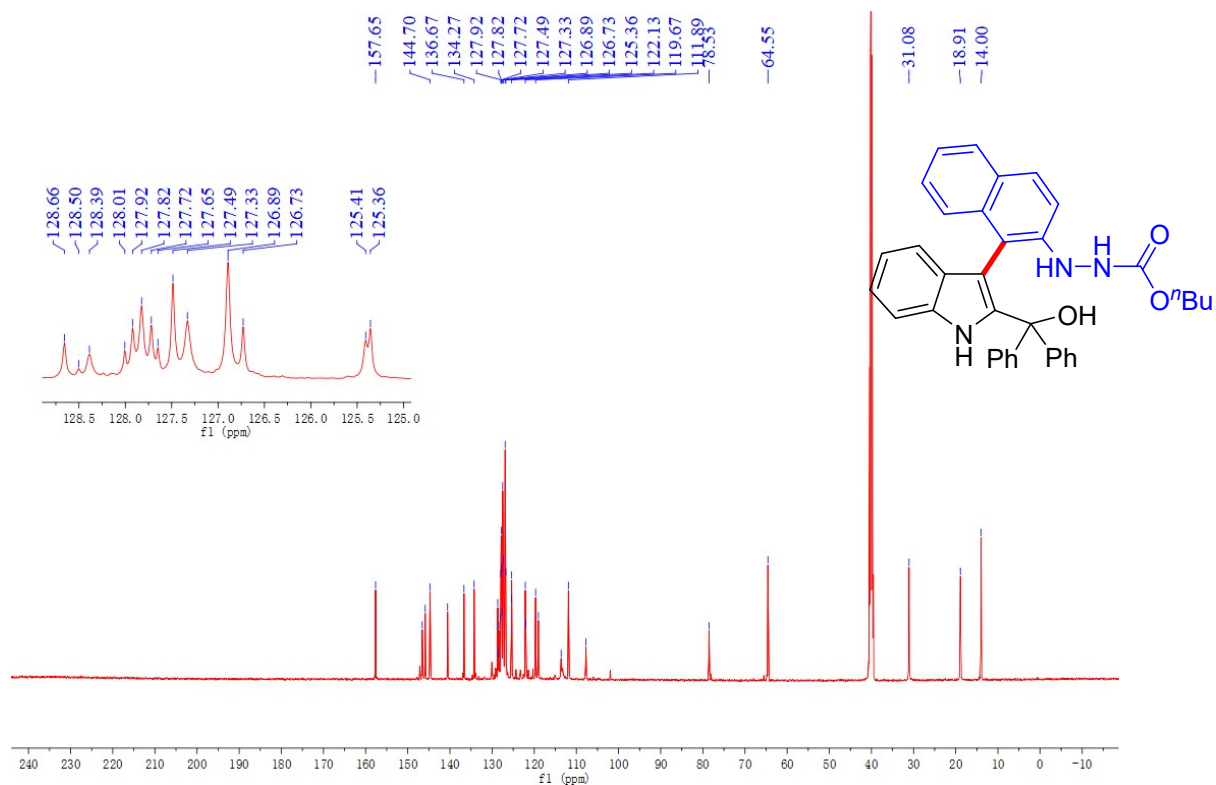
<sup>13</sup>C NMR spectrum of **5b** (DMSO-*d*<sub>6</sub>)



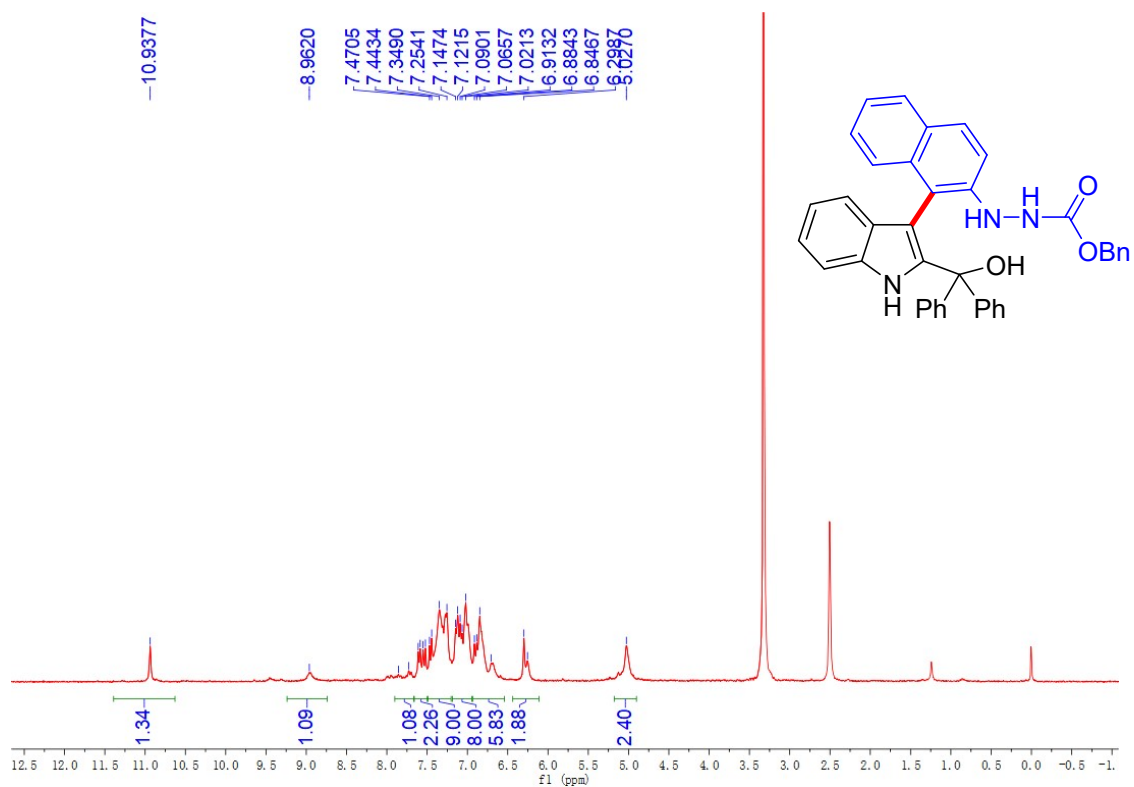
<sup>1</sup>H NMR spectrum of **5c** (DMSO-*d*<sub>6</sub>)



<sup>13</sup>C NMR spectrum of **5c** (DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR spectrum of **5d** (DMSO-*d*<sub>6</sub>)



<sup>13</sup>C NMR spectrum of **5d** (DMSO-*d*<sub>6</sub>)

