

## Supporting Information

### Synthesis of Indoles and Carbazoles from Lignin Model Compound $\alpha$ -Hydroxyacetophenones

Zhiyan Chen,<sup>a</sup> Wenbo Huang,<sup>a</sup> Liqi Yi,<sup>a</sup> Xiaohan Dong,<sup>a</sup> Keyan Sheng,<sup>b</sup> Minghao Li,<sup>a</sup> Rongxian Bai,<sup>a,e</sup>  
A. Yu. Sidorenko,<sup>f</sup> Jiang Huang,<sup>a,b\*</sup> Yanlong Gu<sup>a,c,d\*</sup>

<sup>a</sup>Huazhong University of Science and Technology, 1037 Luoyu road, Hongshan District, Wuhan 430074, China

<sup>b</sup>State Key Laboratory of Advanced Electromagnetic Engineering and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

<sup>c</sup>The Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi, Xinjiang 832003, China

<sup>d</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou 730000, China

<sup>e</sup>Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, China

<sup>f</sup>Institute of Chemistry of New Materials of National Academy of Sciences of Belarus, Skaryna str, 36, 220141 Minsk, Belarus

Corresponding authors: J. Huang ([jhuang@hust.edu.cn](mailto:jhuang@hust.edu.cn)); Y. Gu ([klgyl@hust.edu.cn](mailto:klgyl@hust.edu.cn))

### Table of contents

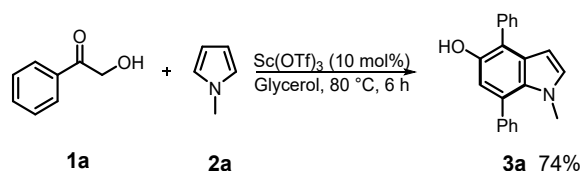
<b>1. General information</b> .....	S2-S2
<b>2. Experimental section</b> .....	S3-S6
<b>3. Condition optimization</b> .....	S7-S11
<b>4. Crystal data</b> .....	S12-S15
<b>5. Mechanism study and Kinetic data</b> .....	S16-S18
<b>6. Recovery experiments</b> .....	S19-S19
<b>7. Characterization data of all new compounds</b> .....	S20-S44
<b>8. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra</b> .....	S45-S108
<b>9. References</b> .....	S109-S109

## 1. General information

The chemical compositions of samples were characterized by FT-IR spectra using KBr (EQUINOX55, Bruker Compass) in the wavenumber range of 4000–400  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of organic compounds were recorded on Bruker AV-400 or Bruker AV-600 spectrometer. Chemical shifts are expressed in ppm relative to tetramethylsilane in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$ . ICP-MS data were recorded on a PerkinElmer ELAN DRC-e spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruker Compass Data Analysis 4.0. The data of liquid chromatography mass spectrometry (LC-MS) were obtained on Bruker UltiMate 3000-microTOFII. High performance liquid chromatography (HPLC) was tested on Thermo Scientific Ultimate 3000. All reagents and solvents were purchased from available commercial suppliers and used without further purification unless other noted.

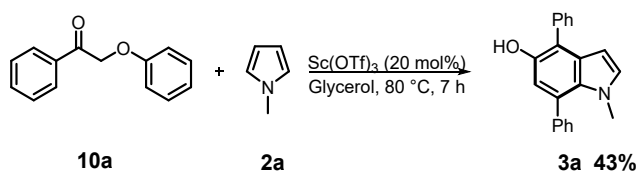
## 2. Experimental Section

### 2.1 Synthesis of 3a



#### Scheme S1. Synthesis of indole derivative **3a**.

In a glass tube, 2-hydroxyacetophenone **1a** (0.6 mmol) was mixed with 1-methylpyrrole **2a** (0.4 mmol) in 1 mL glycerol, and then Sc(OTf)<sub>3</sub> (24.6 mg, 10 mol%) was added. The tube reactor equipped with triangular magnetic stirrer was then sealed to react at 80 °C for 6 h. After that, the reaction mixture was extracted with a mixture of ethyl acetate and heptane (5 mL × 3). The product **3a** was isolated from combined organic phase by column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 (v/v)). The product of **3a** was obtained in 74% (88.5 mg) yield.



#### Scheme S2. Synthesis of indole derivative **3a**.

In a glass tube, 2-phenoxyacetophenone **10a** (0.6 mmol) was mixed with 1-methylpyrrole **2a** (0.4 mmol) in 1 mL glycerol, and then, Sc(OTf)<sub>3</sub> (49.2 mg, 20 mol%) was added. The tube reactor equipped with triangular magnetic stirrer was then sealed to react at 80 °C for 7 h. After reaction, the reaction mixture was extracted with a mixture of ethyl acetate and heptane (5 mL × 3). After reaction, the amount of **3a** was analyzed by HPLC, and the mixed solution was diluted with a suitable ratio of mobile phase, then filtered and analyzed by HPLC. The HPLC instrument was equipped with a UV detector and a C18 column (250 mm × 4.6 mm); the flow phase was CH<sub>3</sub>OH/H<sub>2</sub>O (9/1, v/v) and the flow rate was 1 mL/min. The column temperature was 30 °C and the wavelength of UV detector for product analysis was set at

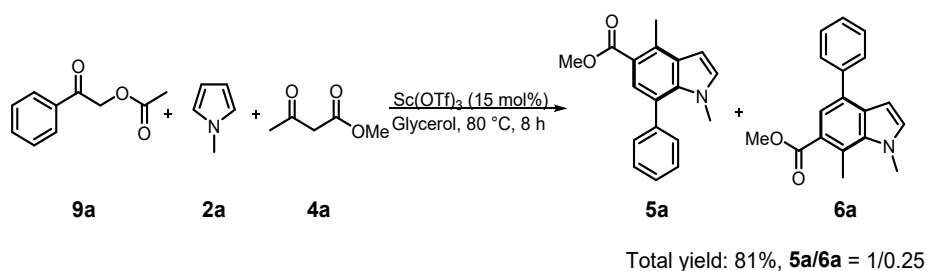
290 nm. The compound of **3a** was obtained in 43% (51.4 mg) yield.

## 2.2 Synthesis of **5a** and **6a**



### Scheme S3. Synthesis of indole derivative **5a** and **6a**.

In a glass tube, 2-hydroxyacetophenone **1a** (0.4 mmol) was mixed with 1-methylpyrrole **2a** (0.8 mmol) and methyl acetoacetate **4a** (0.8 mmol) in 1 mL glycerol, and then the catalyst Sc(OTf)<sub>3</sub> (19.7 mg, 10 mol%) was added. The tube reactor equipped with triangular magnetic stirrer was then sealed to react at 80 °C for 8 h. The solution was extracted with a mixture of ethyl acetate and heptane, and the reaction was detected by TLC. After the completion of the reaction, the product **5a** and **6a** was isolated respectively by column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 (v/v)). The mixture of **5a** and **6a** was obtained in 83% yield (92.6 mg), and the molar ratio of **5a/6a** is ca. 1/0.66.

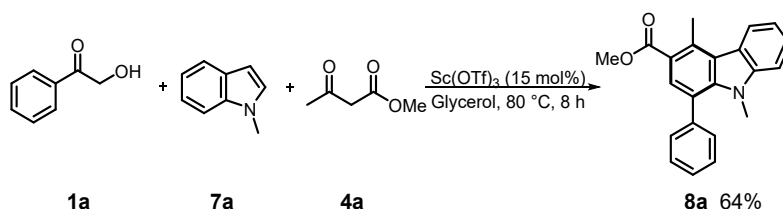


### Scheme S4. Synthesis of indole derivative **5a** and **6a**.

In a glass tube, acetate of 2-hydroxyacetophenone **9a** (0.4 mmol) was mixed with 1-methyl-pyrrole **2a** (0.8 mmol) and methyl acetoacetate **4a** (0.8 mmol) in 1 mL glycerol, and then the catalyst Sc(OTf)<sub>3</sub> (29.5 mg, 15 mol%) was added. The tube reactor equipped with triangular magnetic stirrer was then sealed to react at 80 °C for 8 h. The solution was extracted with a mixture of ethyl acetate and heptane, and the reaction was detected by TLC. After the completion of the reaction, the product **5a** and **6a** was isolated respectively by column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 (v/v)). The mixture

of **5a** and **6a** was obtained in 81% yield (90.4 mg), and the molar ratio of **5a/6a** is ca. 1/0.25.

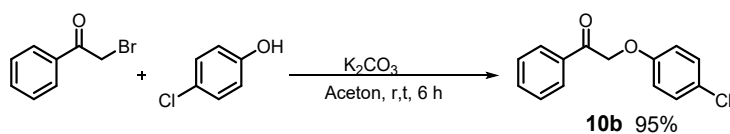
### 2.3 Synthesis of **8a**



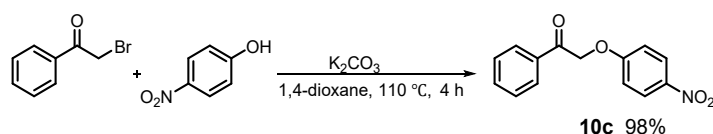
#### Scheme S5. Synthesis of indole derivative **8a**.

In a glass tube, 2-hydroxyacetophenone **1a** (0.4 mmol) was mixed with methyl acetoacetate **4a** (0.8 mmol) in 1 mL glycerol, and the 1-methyl-indole **7a** (0.6 mmol) was added dropwise to the solution over 30 minutes after the catalyst  $\text{Sc}(\text{OTf})_3$  (29.5 mg, 15 mol%) was performed. The tube reactor equipped with triangular magnetic stirrer was then sealed to react at 60 °C for 8 h. The solution was extracted with a mixture of ethyl acetate and heptane, and the reaction was detected by TLC. After the completion of the reaction, the product **8a** was isolated by column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 (v/v)). Compound **8a** was obtained in 64% yield (84.3 mg).

### 2.4 Synthesis of **10b** and **10c**



#### Scheme S6. Synthesis of 2-phenoxyacetophenone derivative **10b**.<sup>1</sup>

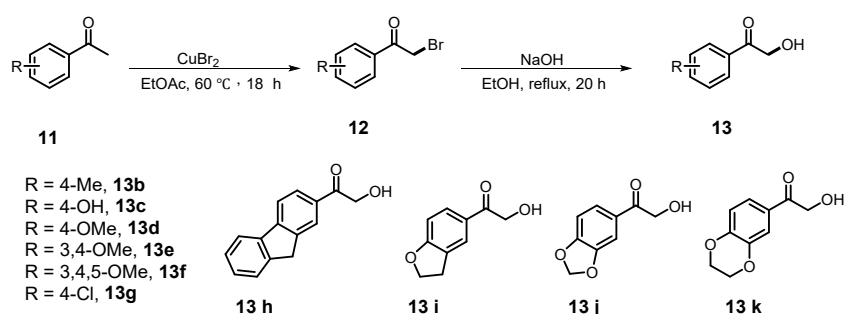


#### Scheme S7. Synthesis of 2-phenoxyacetophenone derivative **10c**.<sup>2</sup>

In a 250 ml round bottom flask equipped with a reflux condenser, 4-chlorophenol (33 mmol) was mixed with  $\text{K}_2\text{CO}_3$  (45.6 mmol) in acetone (30 mL). Then, 2-bromoacetophenone (30 mmol) was added

dropwise to the solution over 30 minutes at room temperature. After 6 h of stirring, the filtration operation was started and the volatile components were removed by evaporation under reduced pressure. The desired product **10b** was obtained by silica gel column chromatography using a mixture of ethyl acetate and petroleum ether as the eluting solvent (the ratio of ethyl acetate/petroleum ether is 1/50). Changing the substrate and solvent, and following the similar steps to obtain the desired product **10c**.

### 2.5 Synthesis of $\alpha$ -hydroxyacetophenone derivatives **13b-k**

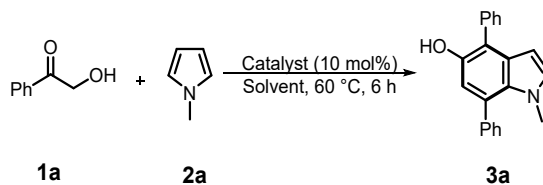


**Scheme S8.** Synthesis of  $\alpha$ -hydroxyacetophenone derivatives **13b-k**.<sup>3-4</sup>

1) In a 250 ml round bottom flask equipped with a reflux condenser, the acetophenone compound **11** (20 mmol) was mixed copper bromide (24 mmol) in EtOAc (100 mL). The reactor equipped with magnetic stirrer was then sealed to react at 60 °C for 18 h. Upon completion, the mixture was extracted with ethyl acetate (20 mL  $\times$  3). The organic layers were filtered and concentrated by rotary evaporation. The product was purified by preparative TLC (eluting solution: petroleum ether/ethyl acetate = 20/1 (v/v)), to obtain 2-bromoacetophenone derivative. Similar compounds were prepared following the standard procedure.

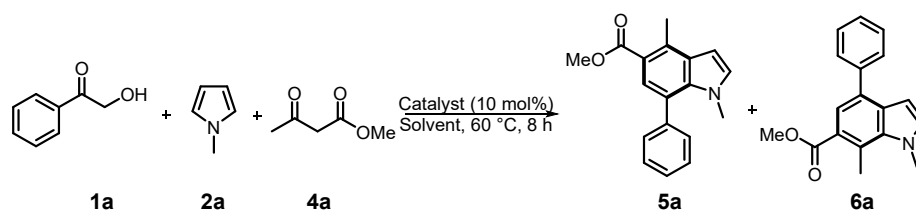
2) In a 250 ml round bottom flask with a reflux condenser, 2-bromoacetophenone compound **12** (10 mmol) was mixed with NaOH (16 mmol) in 50 ml EtOH, and refluxed for 20 h in an oil bath. Upon completion, the mixture was diluted with water (50 mL) and extracted with ethyl acetate (20 mL  $\times$  3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by preparative TLC (eluting solution: petroleum ether/ethyl acetate = 20/1 (v/v)), to obtain target product. Similar compounds were prepared following the standard procedure.

### 3. Condition optimization

**Table S1** Optimization of the reaction of lignin model compound and **2a**.<sup>a</sup>

Entry <sup>a</sup>	Catalyst	Solvent	Yield (%) <sup>c</sup>
1	ScCl <sub>3</sub>	EtOH	20
2 <sup>b</sup>	ScCl <sub>3</sub>	EtOH	16
3 <sup>c</sup>	ScCl <sub>3</sub>	EtOH	23
4 <sup>d</sup>	ScCl <sub>3</sub>	EtOH	21
5	Sc(OTf) <sub>3</sub>	EtOH	46
6 <sup>b</sup>	Sc(OTf) <sub>3</sub>	EtOH	33
7 <sup>c</sup>	Sc(OTf) <sub>3</sub>	EtOH	46
8 <sup>d</sup>	Sc(OTf) <sub>3</sub>	EtOH	51
9	Sc(OTf) <sub>3</sub>	Glycerol	45
10 <sup>b</sup>	Sc(OTf) <sub>3</sub>	Glycerol	37
11 <sup>c</sup>	Sc(OTf) <sub>3</sub>	Glycerol	50
12 <sup>d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	54

<sup>a</sup> Reaction conditions: **1a** (0.6 mmol), **2a** (0.3 mmol), catalyst (10 mol%), solvent (1.0 mL), 60 °C, 6 h, N.R. = no reaction; <sup>b</sup> **1a/2a** is 1/1; <sup>c</sup> **1a/2a** is 3/1; <sup>d</sup> **1a/2a** is 3/2; <sup>e</sup>: Isolated yield.

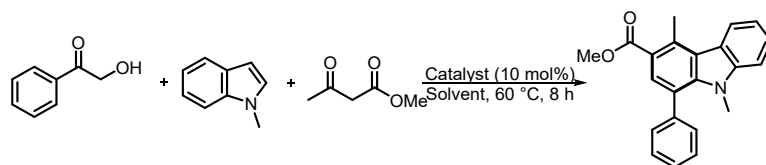
**Table S2** Optimization of the three-component reaction of **1a**, **2a** and 1,3-dicarbonyl compound.<sup>a</sup>

Entry <sup>a</sup>	Catalyst	Solvent	Yield ( <b>5a</b> and <b>6a</b> , %) <sup>f</sup>
1	—	EtOH	N.R.
2	MnCl <sub>2</sub>	EtOH	N.R.
3	ZrCl <sub>4</sub>	EtOH	15
4	AlCl <sub>3</sub>	EtOH	<10
5	ScCl <sub>3</sub>	EtOH	28(35 <sup>b</sup> )
6	<i>p</i> -TSA	EtOH	N.R.
7	TfOH	EtOH	<10
8	Fe(OTf) <sub>3</sub>	EtOH	N.R.
9	Sc(OTf) <sub>3</sub>	EtOH	56
10	Al(OTf) <sub>3</sub>	EtOH	<10
11	Sc(OTf) <sub>3</sub>	1,4-Dioxane	49
12	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> OH	52
13	Sc(OTf) <sub>3</sub>	Glycerol	60
14	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> CN	45
15	Sc(OTf) <sub>3</sub>	Toluene	39
16 <sup>b</sup>	Sc(OTf) <sub>3</sub>	Glycerol	83(79 <sup>c</sup> )
17 <sup>d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	82
18 <sup>b, d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	79
19 <sup>b, e</sup>	Sc(OTf) <sub>3</sub>	Glycerol	59

<sup>a</sup>Reaction condition: **1a** (0.4 mmol), **2a** (0.8 mmol), **4a** (0.8 mmol), catalyst (10 mol%), solvent (1.0 mL), 60 °C, 8 h, N.R. = no reaction; <sup>b</sup>: 80 °C; <sup>c</sup>: 100 °C; <sup>d</sup>: catalyst (15 mol%); <sup>e</sup> **1a/2a/4a** is 1/2/1, <sup>f</sup>: Isolated yield.



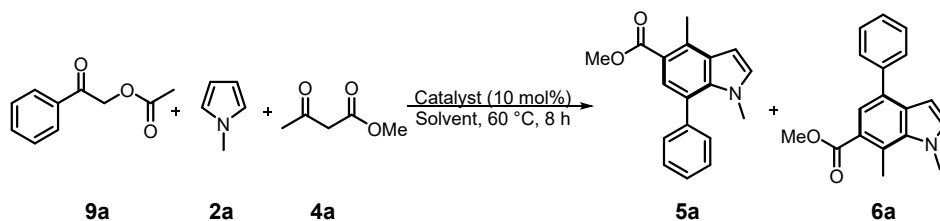
**Table S3** Optimization of the three-component reaction of **1a**, **4a** and 1-methyl-1*H*-indole.<sup>a</sup>



Entry <sup>a</sup>	<b>1a</b> Catalyst	<b>7a</b>	<b>4a</b> Solvent	<b>8a</b> Yield (%) <sup>f</sup>
1	—		EtOH	N.R.
2	MnCl <sub>2</sub>		EtOH	N.R.
3	ZrCl <sub>4</sub>		EtOH	21
4	AlCl <sub>3</sub>		EtOH	13
5	ScCl <sub>3</sub>		EtOH	24
6	<i>p</i> -TSA		EtOH	N.R.
7	TfOH		EtOH	<10
8	Fe(OTf) <sub>3</sub>		EtOH	N.R.
9	Sc(OTf) <sub>3</sub>		EtOH	39
10	Al(OTf) <sub>3</sub>		EtOH	<10
11	Sc(OTf) <sub>3</sub>		1,4-Dioxane	36
12	Sc(OTf) <sub>3</sub>		CH <sub>3</sub> OH	41
13	Sc(OTf) <sub>3</sub>		Glycerol	47
14	Sc(OTf) <sub>3</sub>		CH <sub>3</sub> CN	28
15	Sc(OTf) <sub>3</sub>		Toluene	19
16 <sup>b</sup>	Sc(OTf) <sub>3</sub>		Glycerol	54(49 <sup>c</sup> )
17 <sup>d</sup>	Sc(OTf) <sub>3</sub>		Glycerol	49
18 <sup>b, d</sup>	Sc(OTf) <sub>3</sub>		Glycerol	64
19 <sup>b, d, e</sup>	Sc(OTf) <sub>3</sub>		Glycerol	60

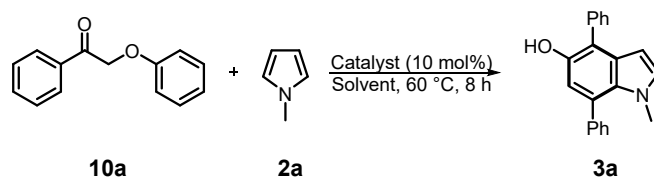
<sup>a</sup>Reaction condition: **1a** (0.4 mmol), **4a** (0.8 mmol), **7a** (0.6 mmol), catalyst (10 mol%), solvent (1.0 mL), 60 °C, 8 h, N.R. = no reaction; <sup>b</sup>: 80 °C; <sup>c</sup>: 100 °C; <sup>d</sup>: catalyst (15 mol%); <sup>e</sup> **1a/4a/7a** is 1/2/2, <sup>f</sup>: Isolated yield.

**Table S4** Optimization of the three-component reaction of **2a**, **4a** and lignin model compound derivative.<sup>a</sup>



Entry <sup>a</sup>	Catalyst	Solvent	Yield ( <b>5a</b> and <b>6a</b> , %) <sup>f</sup>
1	—	EtOH	N.R.
2	MnCl <sub>2</sub> , AlCl <sub>3</sub>	EtOH	N.R.
3	ZrCl <sub>4</sub>	EtOH	13
4	ScCl <sub>3</sub>	EtOH	27(38 <sup>b</sup> )
5	<i>p</i> -TSA	EtOH	N.R.
6	TfOH	EtOH	N.R.
7	Fe(OTf) <sub>3</sub>	EtOH	N.R.
8	Sc(OTf) <sub>3</sub>	EtOH	55
9	Sc(OTf) <sub>3</sub>	1,4-Dioxane	47
10	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> OH	56
11	Sc(OTf) <sub>3</sub>	Glycerol	62
12	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> CN	26
13	Sc(OTf) <sub>3</sub>	Toluene	33
14 <sup>b</sup>	Sc(OTf) <sub>3</sub>	Glycerol	78(74 <sup>c</sup> )
15 <sup>d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	79
16 <sup>b, d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	81
17 <sup>b, e</sup>	Sc(OTf) <sub>3</sub>	Glycerol	72

<sup>a</sup>Reaction condition: **9a** (0.4 mmol), **2a** (0.8 mmol), **4a** (0.8 mmol), catalyst (10 mol%), solvent (1.0 mL), 60 °C, 8 h, N.R. = no reaction; <sup>b</sup>: 80 °C; <sup>c</sup>: 100 °C; <sup>d</sup>: catalyst (15 mol%); <sup>e</sup> **9a/2a/4a** is 1/2/1, <sup>f</sup>: Isolated yield.

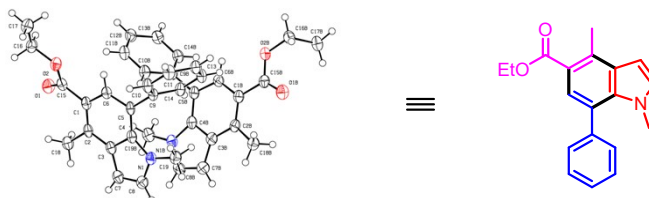
**Table S5** Optimization of the three-component reaction of lignin model compound derivative and **2a**.<sup>a</sup>

Entry <sup>a</sup>	Catalyst	Solvent	Yield (%) <sup>f</sup>
1	—	EtOH	N.R.
2	MnCl <sub>2</sub> , ZrCl <sub>4</sub> , AlCl <sub>3</sub>	EtOH	N.R.
3	ScCl <sub>3</sub>	EtOH	<10 (11 <sup>b</sup> )
4	<i>p</i> -TSA	EtOH	N.R.
5	TfOH	EtOH	N.R.
6	Fe(OTf) <sub>3</sub>	EtOH	N.R.
7	Sc(OTf) <sub>3</sub>	EtOH	17
8	Al(OTf) <sub>3</sub>	EtOH	N.R.
9	Sc(OTf) <sub>3</sub>	1,4-Dioxane	<10
10	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> OH	19
11	Sc(OTf) <sub>3</sub>	Glycerol	21
12	Sc(OTf) <sub>3</sub>	CH <sub>3</sub> CN	<10
13	Sc(OTf) <sub>3</sub>	Toluene	N.R.
14 <sup>b</sup>	Sc(OTf) <sub>3</sub>	Glycerol	37 (34 <sup>e</sup> )
15 <sup>d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	39
16 <sup>b, d</sup>	Sc(OTf) <sub>3</sub>	Glycerol	43
17 <sup>b, e</sup>	Sc(OTf) <sub>3</sub>	Glycerol	31

<sup>a</sup>Reaction condition: **10a** (0.6 mmol), **2a** (0.4 mmol), catalyst (10 mol%), solvent (1.0 mL), 60 °C, 8 h, N.R. = no reaction; <sup>b</sup>: 80 °C; <sup>c</sup>: 100 °C; <sup>d</sup>: catalyst (20 mol%); <sup>e</sup> **10a/2a** is 2/1 <sup>f</sup>: product analysis was determined by HPLC analysis.

#### 4. Crystal data

**5s**



**Table S6** Crystal data and structure refinement for **5s**.

Empirical formula	C <sub>19</sub> H <sub>19</sub> NO <sub>2</sub>
Formula weight	293.35
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.9813(6)
b/Å	11.4019(10)
c/Å	17.8408(8)
α/°	92.730(5)
β/°	90.852(5)
γ/°	108.525(7)
Volume/Å <sup>3</sup>	1536.9(2)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.268
μ/mm <sup>-1</sup>	0.651
F(000)	624.0
Crystal size/mm <sup>3</sup>	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	4.962 to 148.146
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 13, -11 ≤ l ≤ 21
Data/restraints/parameters	6028/0/403
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0753, wR <sub>2</sub> = 0.1509
Final R indexes [all data]	R <sub>1</sub> = 0.0935, wR <sub>2</sub> = 0.2178

It is worth noting that **5s** shows the structure of a bi-molecular sample. Crystal Data for Compound **5s**: CCDC 2131808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

6s

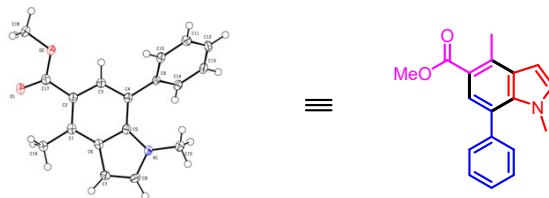


**Table S7** Crystal data and structure refinement for **6s**.

Empirical formula	C <sub>19</sub> H <sub>19</sub> NO <sub>2</sub>
Formula weight	293.35
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	12.6474(9)
b/Å	7.3679(5)
c/Å	17.5437(13)
α/°	90
β/°	110.655(9)
γ/°	90
Volume/Å <sup>3</sup>	1529.7(2)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.274
μ/mm <sup>-1</sup>	0.654
F(000)	624.0
Crystal size/mm <sup>3</sup>	0.12 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.512 to 147.002
Index ranges	-15 ≤ h ≤ 14, -6 ≤ k ≤ 8, -18 ≤ l ≤ 21
Data/restraints/parameters	2986/0/202
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0474, wR <sub>2</sub> = 0.1173
Final R indexes [all data]	R <sub>1</sub> = 0.0589, wR <sub>2</sub> = 0.1276

Crystal Data for Compound **6s**: CCDC 2131809 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

5a

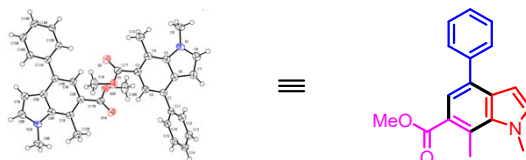


**Table S8** Crystal data and structure refinement for **5a**.

Empirical formula	C <sub>18</sub> H <sub>17</sub> NO <sub>2</sub>
Formula weight	279.32
Temperature/K	293.75(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.2100(4)
b/Å	9.4039(6)
c/Å	10.1909(8)
α/°	111.938(7)
β/°	99.562(5)
γ/°	97.455(5)
Volume/Å <sup>3</sup>	703.68(9)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.318
μ/mm <sup>-1</sup>	0.086
F(000)	296.0
Crystal size/mm <sup>3</sup>	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.432 to 49.988
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12
Data/restraints/parameters	2474/0/193
Final R indexes [I > 2σ (I)]	R <sub>1</sub> = 0.0407, wR <sub>2</sub> = 0.1009
Final R indexes [all data]	R <sub>1</sub> = 0.0469, wR <sub>2</sub> = 0.1065

Crystal Data for Compound **5a**: CCDC 2131810 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

**6a**



**Table S9** Crystal data and structure refinement for **6a**.

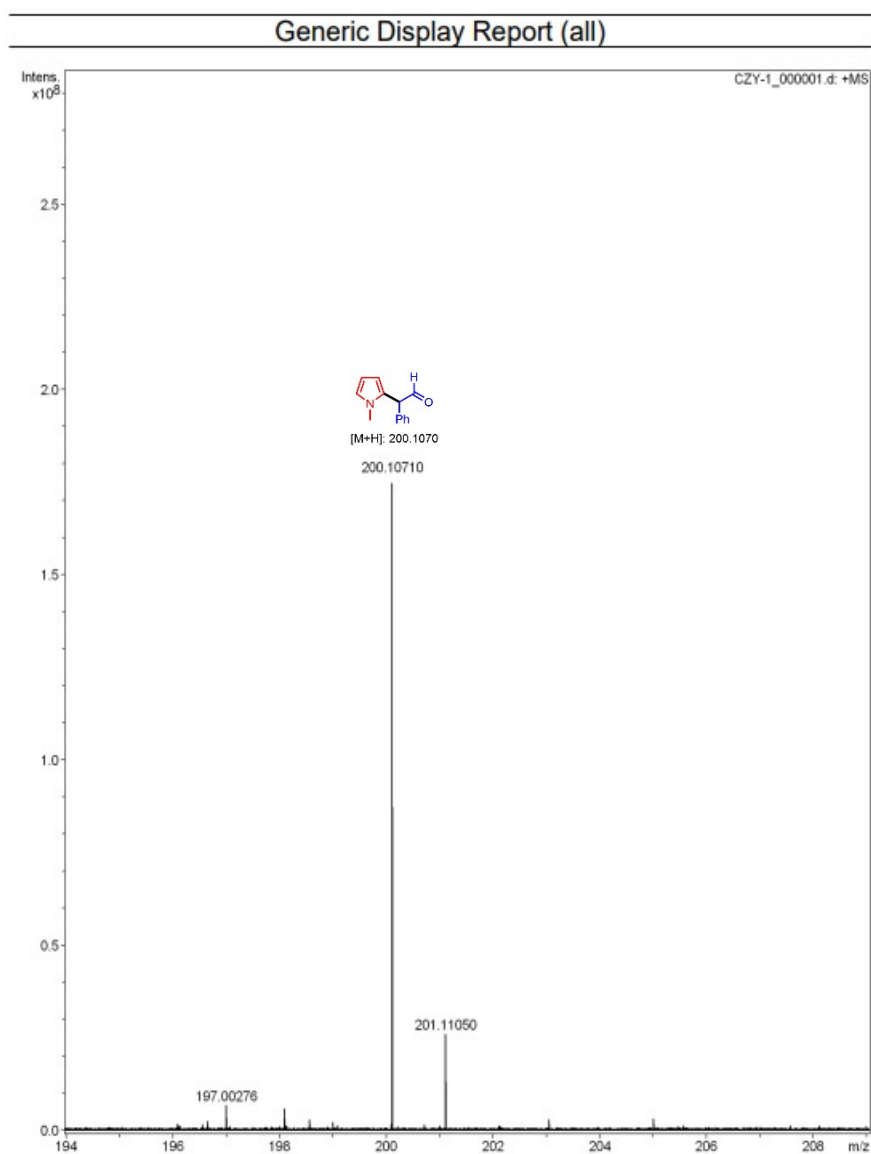
Empirical formula	C <sub>18</sub> H <sub>17</sub> NO <sub>2</sub>
Formula weight	279.32
Temperature/K	293.75(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	11.7113(6)
b/Å	9.8511(5)
c/Å	25.2850(14)
α/°	90
β/°	97.144(5)
γ/°	90
Volume/Å <sup>3</sup>	2894.5(3)
Z	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.282
μ/mm <sup>-1</sup>	0.084
F(000)	1184.0
Crystal size/mm <sup>3</sup>	0.14 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.042 to 49.998
Index ranges	-13 ≤ h ≤ 13, -11 ≤ k ≤ 9, -30 ≤ l ≤ 29
Data/restraints/parameters	5094/0/385
Final R indexes [I >= 2σ(I)]	R <sub>1</sub> = 0.0479, wR <sub>2</sub> = 0.1163
Final R indexes [all data]	R <sub>1</sub> = 0.0595, wR <sub>2</sub> = 0.1250

It is worth noting that **6a** shows the structure of a bi-molecular sample. Crystal Data for Compound **6a**: CCDC 2131811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

## 5. Mechanism study and Kinetic data

### 5.1 The key intermediates detected by HRMS for the synthesis of 3a

The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. The mixture of **1a** (0.6 mmol), **2a** (0.4 mmol) and Sc(OTf)<sub>3</sub> (0.04 mmol, 10 mol%) in glycerol (2.0 mL) was stirred at 80 °C for 1 h. After the completion of the reaction, the mixture cooled to room temperature, and the resulting mixture was extracted with ethyl acetate and heptane, and then the crude mixture was detected by HRMS (ESI, m/z: calcd for C<sub>13</sub>H<sub>14</sub>NO<sup>+</sup>, [M + H]<sup>+</sup> 200.1070, found 200.1071).

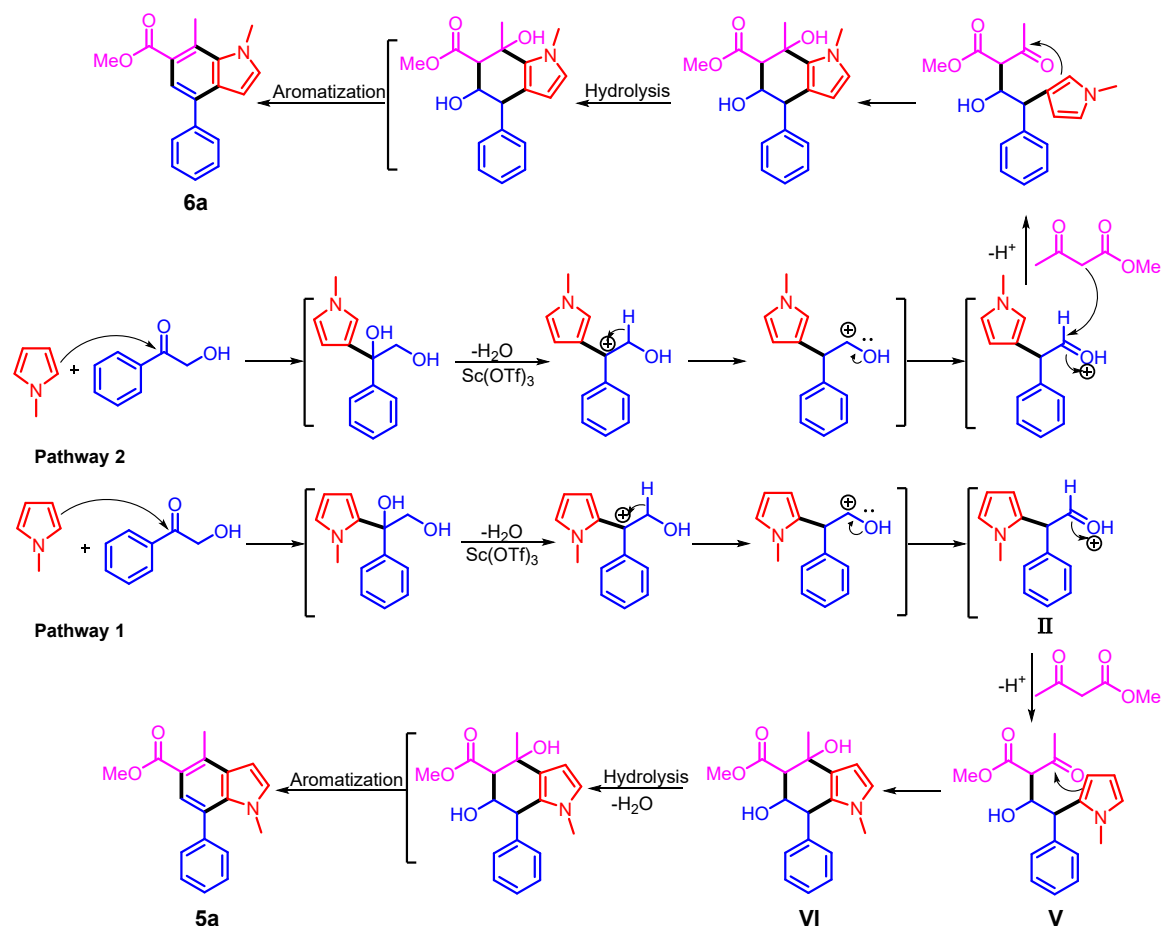


**Figure S1.** The



key intermediates detected by HRMS after 1 h of the reaction.

## 5.2 Proposed mechanism for the formation of 5a and 6a

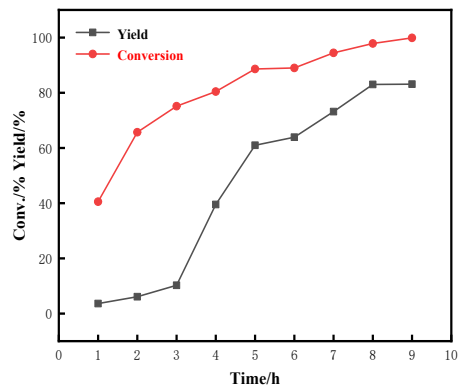
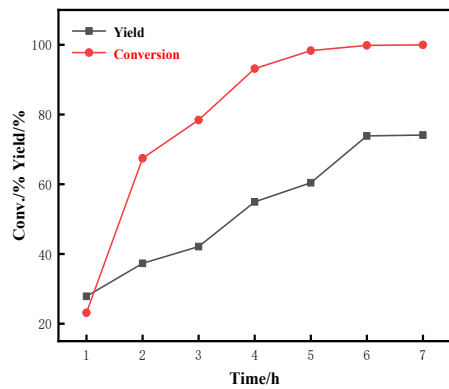


**Figure S2** Plausible mechanism for the formation of **5a** and **6a**

On the basis of the experiments, we provided the mechanism for the formation of **5a** and **6a**. The results were described in **Figure S1**. With respect to the pathway 1: given that we have described the reaction process of **1a** and **2a** to form the intermediate **II**, (as you can see the details in **Scheme 2**) and we will not repeat it here. The intermediate **II** presumably undergoes the attack of the 1,3-dicarbonyl compounds which can be activated under the standard conditions to generate the pivotal intermediate **V**. Subsequently, the carbonyl group of the 1,3-dicarbonyl compounds was attacked by the C3 position of pyrrole to give the intermediate **VI**. It should be noted that formation of six-membered ring transition state helps stabilize intermediate product, thereby promoting the formation of intermediate **VI**. Finally, after a series of chemical reactions, including hydrolysis, dehydration and aromatization, the promising product of **5a** is finally formed. As for the pathway 2, the prime principle and mechanism is similar to the pathway 1, however, the differences between them are mainly the order of the event which reacted

with pyrrole. In pathway 1, the reactivity of pyrrole at the C2 position is superior to C3 position, but opposite in pathway 2.<sup>3-5</sup>

### 5.3 Kinetic data

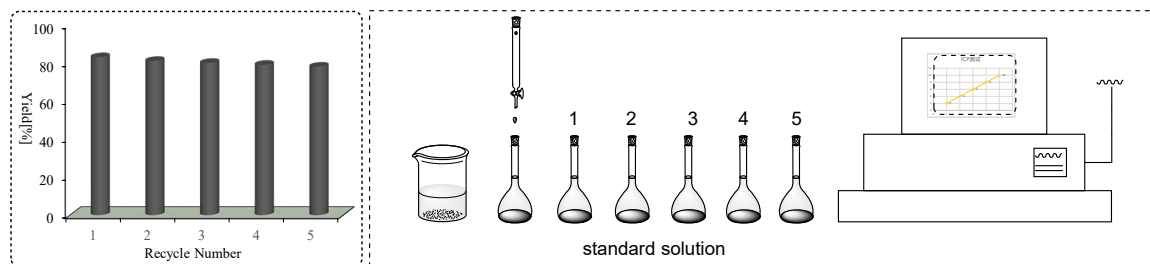


**Figure S3** Kinetic analysis (a) Based on the conversion of **1a** and yields of **3a**

(b) Based on the conversion of **1a** and yields of **5a** and **6a**

On the basis of the results obtained, we found that the yield of the two-component reaction increased at a gentle rate over time, while the yield of the three-component reaction increased substantially, which may be due to the stronger competitiveness of 1,3-dicarbonyl compound compared with **1a**, resulting in the formation of more products. Within 2 h, the conversion rate of **1a** was higher in both the two-component and three-component reactions, while the overall conversion rate of the two-component reaction **1a** changed significantly compared with the three-component reaction, which was mainly due to the reaction generate 1 molecule of product, requiring 2 molecules of **1a**.

## 6. Recovery experiments information



**Figure S4**

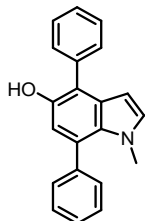
**Figure S5**

We also conducted repeated experiments on the recovery of glycerol and  $\text{Sc}(\text{OTf})_3$ . Indeed, as for the recovery of  $\text{Sc}(\text{OTf})_3$  and glycerol, the main experiments include two aspects, the first was the reuse of glycerol containing  $\text{Sc}(\text{OTf})_3$ , and the second is the recovery of Sc content.

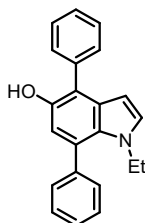
Details as follow: I) first, a small amount of ethyl acetate was added to the reaction system under the standard condition, and the reaction product was detected by TLC. Next, the reacted solution (glycerol containing  $\text{Sc}(\text{OTf})_3$ ) was washed with ethyl acetate and heptane and stand for a few minutes. The supernatant was removed for purification operation, and a small amount of ethyl acetate was added to the remaining part again. The cycle operation was carried out until the products were completely extracted and TCL analysis showed no products in the upper organic ethyl acetate phase. After removing the volatile components under reduced pressure, the starting materials are added into the glycerol phase for the next round of reaction. The results show that the combination of  $\text{Sc}(\text{OTf})_3$  and glycerol can be used continuously for many times.

II) The results in **Figure S4** show that the catalyst can be reused more than 5 times and displayed high catalytic performance throughout the repetitive process. As you can found that, after 5 runs, the yield of the product can be obtained in 78%. At the same time, the ICP test procedure was shown in **Figure S5**. The ICP result shows that the recovery rate of catalyst can reach 95%. The detailed operation steps are as follows: 1) dilute the standard solution (100 ug/mL) of scandium, prepare solutions with different concentration gradients in different 50 mL volumetric flask (2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm). 2) Put the reacted sample into a beaker, then, add slowly  $\text{HNO}_3$  about 5 mL. After 30 minutes, place the beaker on an electric heating device to heat and digest the sample. Keeping the temperature at 70 °C, and holding this state for about 30 minutes. After the temperature of the sample returns to room temperature, remove the black solid impurities with filter membrane, and then dilute the solution to a 50 mL volumetric flask for testing. 3) Test the sample and obtain a standard curve, then calculate the metal content in the solution. Ultimately, the conclusion we got through theoretical calculations is that, in this special system, the recoverability of the catalyst can reach 95%.

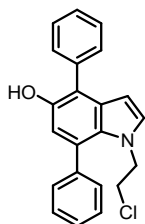
## 7. Characterization data of all new compounds



**1-Methyl-4,7-diphenyl-1H-indol-5-ol (3a):** yellow oil, yield 74%, 88.5 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.61 (d,  $J$  = 6.6 Hz, 2H), 7.55 (t,  $J$  = 7.6 Hz, 2H), 7.49 (dd,  $J$  = 7.8, 1.8 Hz, 2H), 7.46 – 7.40 (m, 4H), 6.93 (d,  $J$  = 3.1 Hz, 1H), 6.80 (s, 1H), 6.28 (d,  $J$  = 3.1 Hz, 1H), 4.96 (s, 1H), 3.29 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.1, 139.8, 135.6, 131.8, 130.1, 130.0, 129.6, 129.3, 127.7, 127.4, 117.1, 114.0, 99.9, 36.8 ppm; IR (KBr)  $\nu$  = 3549, 3449, 3056, 3025, 2923, 2852, 1600, 1508, 1482, 1327, 1169, 1088, 1016, 913, 866, 757, 702  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}^+$ ,  $[\text{M} + \text{H}]^+$  300.1383, found 300.1381.

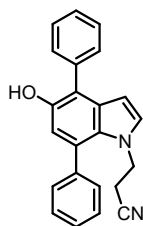


**1-Ethyl-4,7-diphenyl-1H-indol-5-ol (3b):** yellow oil, yield 76%, 95.2 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.61 (d,  $J$  = 6.5 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.43 (d,  $J$  = 7.4 Hz, 4H), 7.03 (d,  $J$  = 3.2 Hz, 1H), 6.78 (s, 1H), 6.31 (d,  $J$  = 3.2 Hz, 1H), 4.96 (s, 1H), 3.68 (q,  $J$  = 7.1 Hz, 2H), 0.98 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.1, 140.2, 135.6, 130.2, 129.9, 129.6, 129.3, 127.9, 127.7, 127.4, 117.2, 114.1, 100.6, 42.9, 16.0 ppm; IR (KBr)  $\nu$  = 3545, 3056, 3024, 2918, 1599, 1508, 1481, 1402, 1376, 1327, 1274, 1168, 1088, 1016, 910, 866, 758, 730, 702  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}^+$ ,  $[\text{M} + \text{H}]^+$  314.1539, found 314.1538.

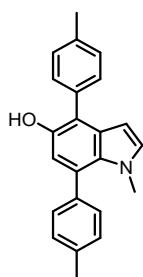


**1-(2-Chloroethyl)-4,7-diphenyl-1H-indol-5-ol (3c):** yellow oil, yield 61%, 84.7 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.61 – 7.52 (m, 2H), 7.47 – 7.41 (m, 6H), 7.04 (d,  $J$  = 3.2 Hz, 1H), 6.79 (s, 1H), 6.31 (d,  $J$  = 3.2 Hz, 1H), 5.01 (s, 1H), 3.97 (t,  $J$  = 6.6 Hz, 2H), 3.22 ppm (t,  $J$  = 6.6

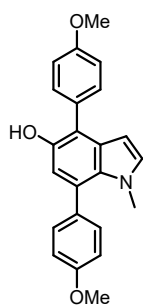
Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.5, 139.5, 135.3, 131.4, 130.1, 129.5, 129.4, 128.3, 127.9, 127.0, 117.6, 114.3, 101.0, 49.7, 42.9 ppm; IR (KBr)  $\nu$  = 3546, 3102, 2957, 2924, 2852, 1724, 1598, 1480, 1444, 1359, 1293, 1167, 1132, 1076, 1031, 912, 865, 758, 728, 702  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{19}\text{ClNO}^+$ ,  $[\text{M} + \text{H}]^+$  348.1150, found 348.1147.



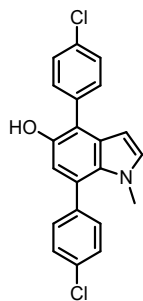
**3-(5-Hydroxy-4,7-diphenyl-1H-indol-1-yl)propanenitrile (3d)**: white solid, yield 55%, 74.4 mg, m.p.: 105–107 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.56 (dt,  $J$  = 15.2, 7.2 Hz, 4H), 7.49 – 7.41 (m, 6H), 7.04 (d,  $J$  = 3.2 Hz, 1H), 6.79 (s, 1H), 6.31 (d,  $J$  = 3.2 Hz, 1H), 5.02 (s, 1H), 3.97 (t,  $J$  = 6.6 Hz, 2H), 3.22 ppm (t,  $J$  = 6.6 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.5, 139.5, 135.3, 131.4, 130.1, 129.5, 129.4, 128.3, 127.9, 127.8, 127.0, 117.6, 114.3, 101.0, 49.7, 42.9 ppm; IR (KBr)  $\nu$  = 3422, 3057, 3025, 2960, 2252, 1713, 1588, 1481, 1364, 1347, 1288, 1225, 1073, 1031, 913, 866, 760, 731, 704  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}^+$ ,  $[\text{M} + \text{H}]^+$  339.1492, found 339.1491.



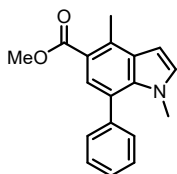
**1-Methyl-4,7-di-p-tolyl-1H-indol-5-ol (3e)**: white solid, yield 58%, 75.9 mg, m.p.: 114–118 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.53 – 7.45 (m, 3H), 7.39 – 7.33 (m, 5H), 6.92 (d,  $J$  = 3.1 Hz, 1H), 6.78 (s, 1H), 6.27 (d,  $J$  = 3.0 Hz, 1H), 4.97 (s, 1H), 3.30 (s, 3H), 2.44 (d,  $J$  = 5.2 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.2, 137.4, 137.0, 136.9, 131.6, 130.0, 129.9, 129.8, 129.2, 128.4, 114.0, 99.9, 36.8, 21.3 ppm; IR (KBr)  $\nu$  = 3553, 3022, 2921, 2855, 2246, 1701, 1587, 1490, 1406, 1373, 1324, 1266, 1222, 1167, 1068, 1023, 817, 731  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}^+$ ,  $[\text{M} + \text{H}]^+$  328.1696, found 328.1696.



**4,7-Bis(4-methoxyphenyl)-1-methyl-1H-indol-5-ol (3f):** colorless oil, yield 53%, 76.1 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.52 (d,  $J$  = 8.6 Hz, 2H), 7.40 (d,  $J$  = 8.5 Hz, 2H), 7.09 (d,  $J$  = 8.6 Hz, 2H), 6.97 (d,  $J$  = 8.6 Hz, 2H), 6.92 (d,  $J$  = 3.1 Hz, 1H), 6.77 (s, 1H), 6.26 (d,  $J$  = 3.1 Hz, 1H), 4.93 (s, 1H), 3.89 (d,  $J$  = 4.3 Hz, 6H), 3.31 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 159.1, 159.0, 145.2, 131.6, 131.3, 131.0, 127.5, 126.8, 116.6, 114.8, 114.0, 113.1, 99.9, 55.3, 36.8 ppm; IR (KBr)  $\nu$  = 3451, 2953, 2931, 2836, 1609, 1531, 1492, 1464, 1373, 1324, 1285, 1245, 1089, 1034, 912, 832, 741  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}_3^+$ ,  $[\text{M} + \text{H}]^+$  360.1594, found 360.1594.



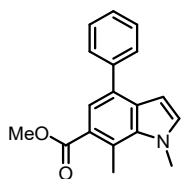
**4,7-Bis(4-chlorophenyl)-1-methyl-1H-indol-5-ol (3g):** colorless oil, yield 41%, 60.2 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.53 (s, 4H), 7.42 (s, 4H), 6.95 (d,  $J$  = 3.1 Hz, 1H), 6.74 (s, 1H), 6.25 (d,  $J$  = 3.2 Hz, 1H), 4.80 (s, 1H), 3.31 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 145.1, 138.1, 133.9, 133.6, 133.5, 132.2, 131.5, 131.2, 129.5, 128.0, 114.1, 99.9, 37.0 ppm; IR (KBr)  $\nu$  = 3449, 2922, 1907, 1732, 1589, 1485, 1405, 1374, 1297, 1223, 1168, 1092, 1014, 911, 871, 828, 729  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{NO}^+$ ,  $[\text{M} + \text{H}]^+$  368.0603, found 368.0604.



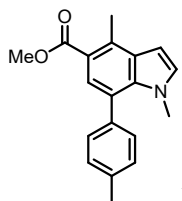
**Methyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5a):** white solid, yield 50%, 55.8 mg, m.p.: 99–101 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (s, 1H), 7.39 (s, 5H), 6.97



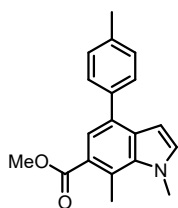
(d,  $J = 3.2$  Hz, 1H), 6.69 (d,  $J = 3.2$  Hz, 1H), 3.86 (s, 3H), 3.28 (s, 3H), 2.87 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.9, 139.7, 135.2, 134.0, 131.3, 130.7, 130.2, 127.8, 127.4, 126.6, 124.2, 119.7, 101.7, 51.6, 36.8, 17.1$  ppm; IR (KBr)  $\nu = 2949, 2927, 2855, 1711, 1577, 1438, 1341, 1233, 1165, 1053, 768, 705, 648$   $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  280.1332, found 280.1332.



**Methyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6a)**: white solid, yield 33%, 36.8 mg, m.p.: 95–97 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.68 - 7.58$  (m, 3H), 7.46 (t,  $J = 7.7$  Hz, 2H), 7.36 (t,  $J = 7.4$  Hz, 1H), 7.08 (d,  $J = 3.2$  Hz, 1H), 6.58 (d,  $J = 3.2$  Hz, 1H), 4.13 (s, 3H), 3.91 (s, 3H), 3.02 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.6, 140.5, 136.3, 134.2, 131.9, 130.4, 128.8, 128.5, 127.0, 124.7, 123.6, 121.6, 100.6, 51.9, 38.3, 15.9$ ; IR (KBr)  $\nu = 2950, 2927, 1712, 1607, 1435, 1302, 1237, 1198, 1056, 764, 703$   $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  280.1332, found 280.1332.

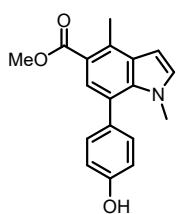


**Methyl 1,4-dimethyl-7-(p-tolyl)-1H-indole-5-carboxylate (5b)**: white solid; yield 68%, 79.7 mg, m.p.: 133–135 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.66$  (s, 1H), 7.29 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 7.7$  Hz, 2H), 6.97 (d,  $J = 3.2$  Hz, 1H), 6.68 (d,  $J = 3.2$  Hz, 1H), 3.85 (s, 3H), 3.30 (s, 3H), 2.87 (s, 3H), 2.41 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.9, 137.1, 136.7, 135.3, 133.8, 131.2, 130.6, 130.0, 128.5, 126.7, 124.1, 119.6, 101.6, 51.5, 36.8, 21.3, 17.1$  ppm; IR (KBr)  $\nu = 2949, 2924, 1712, 1577, 1435, 1341, 1234, 1164, 1053, 822, 736, 720$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ : 294.1489  $[\text{M} + \text{H}]^+$ ; found: 294.1489.



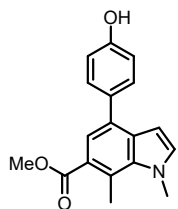
**Methyl 1,7-dimethyl-4-(p-tolyl)-1H-indole-6-carboxylate (6b):** white solid; yield

15%, 17.6 mg, m.p.: 120–122 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.59 (s, 1H), 7.54 (d,  $J$  = 8.0 Hz, 2H), 7.28 (s, 1H), 7.26 (d,  $J$  = 3.4 Hz, 1H), 7.08 (d,  $J$  = 3.2 Hz, 1H), 6.59 (d,  $J$  = 3.2 Hz, 1H), 4.14 (s, 3H), 3.91 (s, 3H), 3.02 (s, 3H), 2.42 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 137.6, 136.7, 136.3, 134.1, 131.9, 130.4, 129.2, 128.6, 124.7, 123.3, 121.4, 100.6, 51.9, 38.3, 21.2, 15.9 ppm; IR (KBr)  $\nu$  = 2954, 2925, 2854, 1713, 1607, 1515, 1458, 1377, 1339, 1238, 1196, 1057, 822, 733. HRMS (APCI, TOF):  $m/z$ : calcd for C<sub>19</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup>: 294.1489 [M + H]<sup>+</sup>; found: 294.1489.



**Methyl 7-(4-hydroxyphenyl)-1,4-dimethyl-1H-indole-5-carboxylate (5c):** white solid,

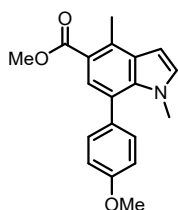
yield 54%, 63.7 mg, m.p.: 166–168 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.64 (s, 1H), 7.26 (d,  $J$  = 2.9 Hz, 1H), 7.24 (s, 1H), 6.99 (d,  $J$  = 3.3 Hz, 1H), 6.89 (d,  $J$  = 8.5 Hz, 2H), 6.69 (d,  $J$  = 3.2 Hz, 1H), 5.75 (s, 1H), 3.89 (s, 3H), 3.33 (s, 3H), 2.86 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.4, 155.3, 135.5, 133.7, 131.8, 131.3, 131.2, 130.6, 126.8, 123.9, 119.6, 114.7, 101.6, 51.7, 36.8, 17.1 ppm; IR (KBr)  $\nu$  = 3386, 2974, 2950, 1709, 1611, 1591, 1510, 1436, 1342, 1255, 1234, 1167, 1051, 837, 719; HRMS (APCI, TOF):  $m/z$ : calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>3</sub><sup>+</sup>: 296.1281 [M + H]<sup>+</sup>; found: 296.1281.



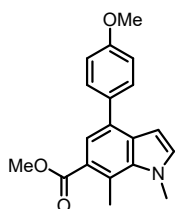
**Methyl 4-(4-hydroxyphenyl)-1,7-dimethyl-1H-indole-6-carboxylate (6c):** white solid,

yield 11%, 13.0 mg, m.p.: 173–175 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.55 (s, 1H), 7.51 (d,  $J$  = 8.5 Hz, 2H), 7.08 (d,  $J$  = 3.1 Hz, 1H), 6.93 (d,  $J$  = 8.5 Hz, 2H), 6.56 (d,  $J$  = 3.1 Hz, 1H), 5.14 (s, 1H), 4.14 (s, 3H), 3.92 (s, 3H), 3.01 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.8,

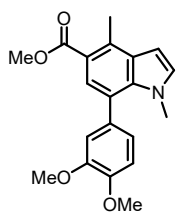
154.9, 136.3, 134.1, 133.1, 131.6, 130.4, 130.0, 124.7, 123.1, 121.2, 115.4, 100.6, 51.9, 38.3, 15.9 ppm;  
IR (KBr)  $\nu$  = 3380, 2950, 2925, 2852, 1709, 1687, 1611, 1515, 1434, 1341, 1240, 1198, 1054, 836, 731.  
HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{18}H_{18}NO_3^+$ : 296.1281 [M + H]<sup>+</sup>; found: 296.1281.



**Methyl 7-(4-methoxyphenyl)-1,4-dimethyl-1H-indole-5-carboxylate (5d)**: white solid; yield 57%, 70.4 mg, m.p.: 124–126 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.64 (s, 1H), 7.32 (d,  $J$  = 8.6 Hz, 2H), 6.99 (d,  $J$  = 3.2 Hz, 1H), 6.95 (d,  $J$  = 8.6 Hz, 2H), 6.68 (d,  $J$  = 3.2 Hz, 1H), 3.87 (d,  $J$  = 1.8 Hz, 6H), 3.32 (s, 3H), 2.86 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.9, 159.0, 135.4, 133.7, 131.9, 131.2, 130.6, 126.8, 123.8, 119.6, 113.2, 101.6, 55.3, 51.5, 36.8, 17.0 ppm; IR (KBr)  $\nu$  = 2994, 2949, 2837, 1711, 1601, 1508, 1436, 1341, 1284, 1248, 1165, 1053, 1033, 833, 726. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{19}H_{20}NO_3^+$ : 310.1438 [M + H]<sup>+</sup>; found: 310.1437.

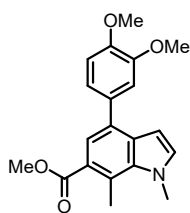


**Methyl 4-(4-methoxyphenyl)-1,7-dimethyl-1H-indole-6-carboxylate (6d)**: white solid; yield 10%, 12.4 mg, m.p.: 70–72 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.57 (d,  $J$  = 8.5 Hz, 3H), 7.08 (d,  $J$  = 3.2 Hz, 1H), 7.00 (d,  $J$  = 8.7 Hz, 2H), 6.57 (d,  $J$  = 3.1 Hz, 1H), 4.14 (s, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 3.01 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 158.8, 136.3, 134.0, 133.0, 131.6, 130.4, 129.8, 124.7, 123.1, 121.3, 113.9, 100.6, 55.4, 51.9, 38.3, 15.9 ppm; IR (KBr)  $\nu$  = 2992, 2950, 2837, 1712, 1610, 1514, 1436, 1339, 1284, 1245, 1179, 1033, 835, 787, 734. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{19}H_{20}NO_3^+$ : 310.1438 [M + H]<sup>+</sup>; found: 310.1437.



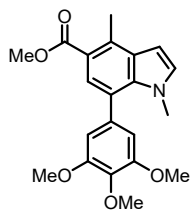
**Methyl 7-(3,4-dimethoxyphenyl)-1,4-dimethyl-1H-indole-5-carboxylate (5e)**: white

solid, yield 58%, 78.7 mg, m.p.: 123–125 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.69 (s, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 7.01 – 6.93 (m, 3H), 6.72 (d, *J* = 3.2 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 6H), 3.38 (s, 3H), 2.89 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 148.4, 148.2, 135.3, 133.9, 132.2, 131.2, 130.6, 126.6, 123.9, 122.5, 119.6, 113.5, 110.5, 101.6, 56.0, 51.5, 36.6, 17.0 ppm; IR (KBr)  $\nu$  = 2953, 2926, 2853, 1711, 1585, 1511, 1462, 1438, 1342, 1253, 1240, 1137, 1020, 762, 723. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>4</sub><sup>+</sup>: 340.1543 [M + H]<sup>+</sup>; found: 340.1544.



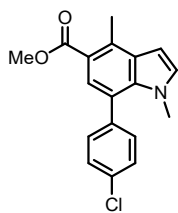
**Methyl 4-(3,4-dimethoxyphenyl)-1,7-dimethyl-1H-indole-6-carboxylate (6e):**

yellow oil, yield 20%, 27.1 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.59 (s, 1H), 7.21 (dd, *J* = 10.6, 2.6 Hz, 2H), 7.12 (d, *J* = 3.2 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.61 (d, *J* = 3.1 Hz, 1H), 4.18 (s, 3H), 3.38 (s, 3H), 3.99 – 3.93 (m, 9H), 3.04 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 148.4, 148.1, 135.3, 133.9, 132.2, 131.2, 130.5, 126.6, 123.8, 122.5, 119.6, 113.5, 110.4, 101.6, 56.0, 51.5, 36.6, 17.0 ppm; IR (KBr)  $\nu$  = 2950, 2837, 1711, 1593, 1515, 1461, 1437, 1341, 1259, 1239, 1193, 1167, 1140, 1112, 1027, 787, 730; HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>4</sub><sup>+</sup>: 340.1543 [M + H]<sup>+</sup>; found: 340.1544.

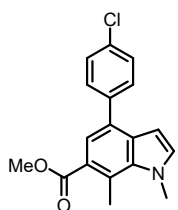


**Methyl 1,4-dimethyl-7-(3,4,5-trimethoxyphenyl)-1H-indole-5-carboxylate (5f):**

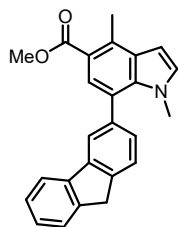
yellow oil, yield 53%, 70.2 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.68 (s, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.72 (d, *J* = 3.2 Hz, 1H), 6.63 (s, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 3.86 (s, 6H), 3.39 (s, 3H), 2.87 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 152.6, 137.4, 135.1, 135.0, 134.1, 131.2, 130.6, 126.2, 124.0, 119.6, 107.5, 101.7, 61.1, 56.2, 51.6, 36.5, 17.0 ppm; IR (KBr)  $\nu$  = 2945, 2836, 1711, 1583, 1503, 1463, 1412, 1354, 1237, 1197, 1127, 1007, 913, 744. HRMS (APCI, TOF): *m/z*: calcd for C<sub>21</sub>H<sub>24</sub>NO<sub>5</sub><sup>+</sup>: 370.1649 [M + H]<sup>+</sup>; found: 370.1647.



**Methyl 7-(4-chlorophenyl)-1,4-dimethyl-1H-indole-5-carboxylate (5g):** white solid; yield 45%, 56.3 mg, m.p.: 117–119 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.63 (s, 1H), 7.40 (d,  $J$  = 8.5 Hz, 2H), 7.35 (d,  $J$  = 8.5 Hz, 2H), 7.00 (d,  $J$  = 3.2 Hz, 1H), 6.70 (d,  $J$  = 3.2 Hz, 1H), 3.87 (s, 3H), 3.32 (s, 3H), 2.87 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.7, 138.2, 135.0, 134.3, 133.5, 131.4, 131.3, 130.8, 128.0, 126.6, 122.7, 119.8, 101.8, 51.6, 36.9, 17.1 ppm; IR (KBr)  $\nu$  = 2948, 1713, 1586, 1525, 1485, 1435, 1341, 1235, 1165, 1089, 1053, 1015, 829, 776, 735. HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{17}\text{ClNO}_2^+$ : 314.0942 [M + H] $^+$ ; found: 314.0943.

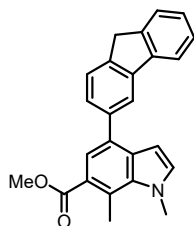


**Methyl 4-(4-chlorophenyl)-1,7-dimethyl-1H-indole-6-carboxylate (6g):** white solid; yield 19%, 23.8 mg, m.p.: 122–124 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.59 – 7.55 (m, 3H), 7.43 (d,  $J$  = 8.4 Hz, 2H), 7.11 (d,  $J$  = 3.2 Hz, 1H), 6.53 (d,  $J$  = 3.2 Hz, 1H), 4.15 (s, 3H), 3.92 (s, 3H), 3.02 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.5, 139.0, 136.3, 134.4, 132.9, 130.6, 130.2, 130.0, 128.6, 124.8, 124.0, 121.5, 100.3, 51.9, 38.4, 15.9 ppm; IR (KBr)  $\nu$  = 2988, 2950, 1713, 1516, 1487, 1434, 1340, 1304, 1240, 1197, 1116, 1013, 908, 832, 787, 734, 674. HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{17}\text{ClNO}_2^+$ : 314.0942 [M + H] $^+$ ; found: 314.0943.



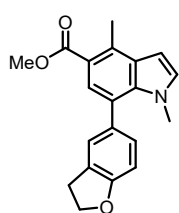
**Methyl 7-(9H-fluoren-3-yl)-1,4-dimethyl-1H-indole-5-carboxylate (5h):** white solid, yield 44%, 64.6 mg, m.p.: 153–155 °C;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.87 (t,  $J$  = 7.4 Hz, 2H), 7.77 (s, 1H), 7.62 (d,  $J$  = 15.1 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 7.05 (d,  $J$  = 3.2 Hz, 1H), 6.76 (d,  $J$  = 3.3 Hz, 1H), 4.00 (s, 2H), 3.92 (s, 3H), 3.38 (s, 3H), 2.93 ppm (s, 3H);  $^{13}\text{C}$

NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.9, 143.4, 142.9, 141.4, 140.9, 138.1, 135.3, 133.9, 131.2, 130.7, 128.9, 126.9, 126.9, 126.8, 126.6, 125.1, 124.4, 120.0, 119.7, 119.1, 101.7, 51.6, 37.0, 36.9, 17.1 ppm; IR (KBr)  $\nu$  = 2948, 2258, 1709, 1570, 1431, 1399, 1338, 1237, 1189, 1164, 1049, 916, 845, 771, 726; HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{25}H_{22}NO_2^+$ : 368.1645 [M + H]<sup>+</sup>; found: 368.1646.



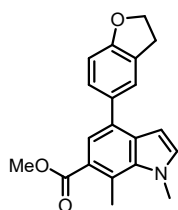
**Methyl 4-(9H-fluoren-3-yl)-1,7-dimethyl-1H-indole-6-carboxylate (6h):** white

solid, yield 23%, 33.8 mg, m.p.: 138–140 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.87 (d,  $J$  = 7.9 Hz, 1H), 7.83 (d,  $J$  = 8.2 Hz, 2H), 7.67 (d,  $J$  = 4.4 Hz, 2H), 7.57 (d,  $J$  = 7.5 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 1H), 7.32 (t,  $J$  = 6.8 Hz, 1H), 7.11 (d,  $J$  = 3.1 Hz, 1H), 6.64 (d,  $J$  = 3.2 Hz, 1H), 4.17 (s, 3H), 3.98 (s, 2H), 3.93 (s, 3H), 3.04 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.9, 143.4, 142.9, 141.4, 140.9, 138.1, 135.3, 133.9, 131.2, 130.7, 128.9, 126.9, 126.9, 126.8, 126.6, 125.1, 124.4, 120.0, 119.7, 119.1, 101.7, 51.6, 37.0, 36.9, 17.1 ppm; IR (KBr)  $\nu$  = 2925, 2854, 1710, 1611, 1436, 1377, 1320, 1215, 1155, 1093, 1034, 738, 711; HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{25}H_{22}NO_2^+$ : 368.1645 [M + H]<sup>+</sup>; found: 368.1646.



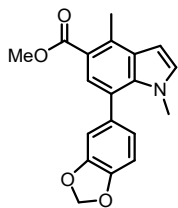
**Methyl 7-(2,3-dihydrobenzofuran-5-yl)-1,4-dimethyl-1H-indole-5-carboxylate**

**(5i):** colorless oil, yield 50%, 64.2 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.64 (s, 1H), 7.24 (d,  $J$  = 7.8 Hz, 1H), 7.13 (d,  $J$  = 8.2 Hz, 1H), 6.99 (d,  $J$  = 3.2 Hz, 1H), 6.82 (d,  $J$  = 8.1 Hz, 1H), 6.69 (d,  $J$  = 3.2 Hz, 1H), 4.64 (t,  $J$  = 8.7 Hz, 2H), 3.87 (s, 3H), 3.36 (s, 3H), 3.26 (t,  $J$  = 8.7 Hz, 2H), 2.86 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 159.4, 136.3, 134.0, 133.0, 132.1, 130.5, 128.6, 127.2, 125.3, 121.3, 118.5, 109.2, 106.9, 100.7, 71.4, 51.9, 38.3, 29.8, 15.9 ppm; IR (KBr)  $\nu$  = 2949, 1711, 1611, 1575, 1488, 1436, 1342, 1241, 1165, 1098, 1053, 983, 824, 738; HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{20}H_{20}NO_3^+$ : 322.1438 [M + H]<sup>+</sup>; found: 322.1438.



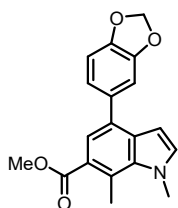
**Methyl 4-(2,3-dihydrobenzofuran-5-yl)-1,7-dimethyl-1H-indole-6-carboxylate**

**(6i):** yellow oil, yield 21%, 27.0 mg;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.57 (s, 1H), 7.49 (s, 1H), 7.42 (ddt,  $J$  = 8.2, 1.8, 0.8 Hz, 1H), 7.10 (d,  $J$  = 3.2 Hz, 1H), 6.90 (d,  $J$  = 8.2 Hz, 1H), 6.60 (d,  $J$  = 3.1 Hz, 1H), 4.66 (t,  $J$  = 8.6 Hz, 2H), 4.17 (s, 3H), 3.94 (s, 3H), 3.31 (t,  $J$  = 8.1 Hz, 2H), 3.04 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.9, 159.6, 135.5, 133.6, 131.8, 131.1, 130.6, 129.9, 126.8, 126.6, 126.6, 124.2, 119.6, 108.4, 101.6, 71.4, 51.5, 36.8, 29.8, 17.0 ppm; IR (KBr)  $\nu$  = 2950, 2855, 1711, 1611, 1575, 1488, 1435, 1341, 1238, 1196, 1147, 1053, 983, 825, 787, 733; HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_3^+$ : 322.1438 [M + H] $^+$ ; found: 322.1438.



**Methyl 7-(benzo[d][1,3]dioxol-5-yl)-1,4-dimethyl-1H-indole-5-carboxylate (5j):**

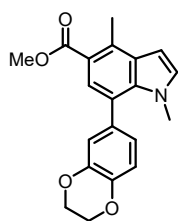
white solid, yield 48%, 62.0 mg, m.p.: 149–151 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (d,  $J$  = 3.5 Hz, 1H), 7.03 (d,  $J$  = 3.3 Hz, 1H), 6.91 (d,  $J$  = 13.0 Hz, 3H), 6.72 (d,  $J$  = 3.2 Hz, 1H), 6.06 (s, 2H), 3.91 (s, 3H), 3.42 (s, 3H), 2.89 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 147.1, 147.0, 135.2, 134.0, 133.3, 131.2, 130.6, 126.7, 123.6, 123.5, 119.6, 110.7, 107.7, 101.6, 101.2, 51.5, 36.7, 17.0 ppm; IR (KBr)  $\nu$  = 2949, 2903, 1711, 1576, 1485, 1439, 1344, 1319, 1243, 1200, 1164, 1095, 1039, 935, 736; HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{NO}_4^+$ : 324.1230 [M + H] $^+$ ; found: 324.1229.



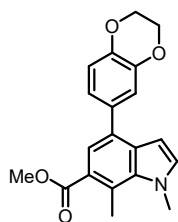
**Methyl 4-(benzo[d][1,3]dioxol-5-yl)-1,7-dimethyl-1H-indole-6-carboxylate (6j):**

white solid, yield 28%, 36.2 mg, m.p.: 112–114 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.58

(s, 1H), 7.17 – 7.09 (m, 3H), 6.94 (d,  $J = 7.9$  Hz, 1H), 6.60 (d,  $J = 3.1$  Hz, 1H), 6.04 (s, 2H), 4.16 (s, 3H), 3.94 (s, 3H), 3.03 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.6, 140.5, 136.3, 134.2, 131.9, 130.4, 128.8, 128.5, 127.0, 124.7, 123.6, 121.6, 100.6, 51.9, 38.3, 15.9$  ppm; IR (KBr)  $\nu = 2949, 1712, 1599, 1516, 1488, 1434, 1378, 1342, 1302, 1239, 1196, 1115, 1057, 786, 737, 703$ ; HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{NO}_4^+$ : 324.1230  $[\text{M} + \text{H}]^+$ ; found: 324.1229.

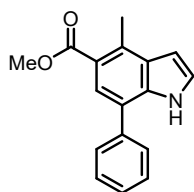


**Methyl 7-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1,4-dimethyl-1H-indole-5-carboxylate (5k)**: white solid, yield 49%, 66.1 mg, m.p.: 122–124 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.64$  (s, 1H), 7.00 (d,  $J = 3.2$  Hz, 1H), 6.95 – 6.85 (m, 3H), 6.68 (d,  $J = 3.2$  Hz, 1H), 4.31 (s, 4H), 3.87 (s, 3H), 3.39 (s, 3H), 2.86 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.8, 143.0, 142.8, 135.2, 133.9, 132.9, 131.2, 130.6, 126.7, 123.5, 123.4, 119.6, 116.5, 101.6, 64.4, 51.5, 36.8, 17.0$  ppm; IR (KBr)  $\nu = 2980, 2947, 2878, 1711, 1581, 1504, 1435, 1341, 1282, 1250, 1223, 1191, 1164, 1067, 821, 780, 736$ ; HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_4^+$ : 338.1387  $[\text{M} + \text{H}]^+$ ; found: 338.1389.

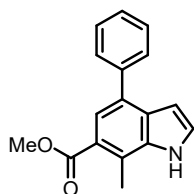


**Methyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1,7-dimethyl-1H-indole-6-carboxylate (6k)**: white solid, yield 25%, 33.7 mg, m.p.: 118–120 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.56$  (s, 1H), 7.18 – 7.11 (m, 2H), 7.08 (d,  $J = 3.2$  Hz, 1H), 6.95 (d,  $J = 8.3$  Hz, 1H), 6.61 (d,  $J = 3.1$  Hz, 1H), 4.31 (s, 4H), 4.14 (s, 3H), 3.90 (s, 3H), 3.01 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.6, 143.4, 142.8, 136.3, 134.1, 131.3, 130.3, 124.6, 123.3, 121.9, 121.3, 117.5, 117.2, 100.6, 64.5, 51.8, 38.3, 15.9$  ppm; IR (KBr)  $\nu = 2980, 2949, 1712, 1583, 1511, 1435, 1341, 1284, 1240, 1168, 1068, 890, 787, 735$ ; HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_4^+$ : 338.1387  $[\text{M} + \text{H}]^+$ ; found: 338.1389.

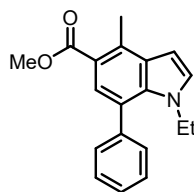




**Methyl 4-methyl-7-phenyl-1H-indole-5-carboxylate (5l):** yellow oil, yield 49%, 51.9 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 8.60 (s, 1H), 7.86 (s, 1H), 7.60 (d,  $J$  = 6.7 Hz, 2H), 7.49 ((t,  $J$  = 7.6 Hz, 2H), 7.39 (t,  $J$  = 7.4 Hz, 1H), 7.23 (t,  $J$  = 3.0 Hz, 1H), 6.80 – 6.74 (m, 1H), 3.89 (s, 3H), 2.88 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.0, 138.4, 135.0, 134.1, 129.4, 129.2, 128.2, 127.6, 124.7, 124.6, 123.0, 121.1, 103.4, 51.6, 17.4 ppm; IR (KBr)  $\nu$  = 3359, 3026, 2949, 1699, 1591, 1436, 1345, 1319, 1250, 1160, 1052, 883, 762, 732, 704  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{16}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  266.1176, found 266.1176.

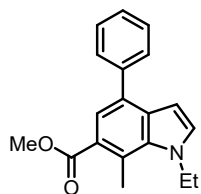


**Methyl 7-methyl-4-phenyl-1H-indole-6-carboxylate (6l):** yellow oil, yield 20%, 21.2 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 8.57 (s, 1H), 7.86 (s, 1H), 7.62 (d,  $J$  = 6.9 Hz, 2H), 7.50 ((t,  $J$  = 7.7 Hz, 2H), 7.40 (t,  $J$  = 7.4 Hz, 1H), 7.25 (t,  $J$  = 3.0 Hz, 1H), 6.80 – 6.75 (m, 1H), 3.90 (s, 3H), 2.89 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.0, 138.4, 135.0, 134.1, 129.4, 129.2, 128.2, 127.6, 124.7, 124.6, 123.0, 121.1, 103.4, 51.6, 17.4 ppm; IR (KBr)  $\nu$  = 3359, 3028, 2945, 1700, 1591, 1436, 1345, 1325, 1255, 1160, 1052, 874, 762, 733, 704  $\text{cm}^{-1}$ . HRMS (APCI, TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{16}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  266.1176, found 266.1176.

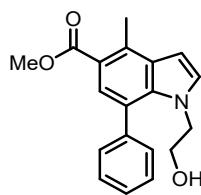


**Methyl 1-ethyl-4-methyl-7-phenyl-1H-indole-5-carboxylate (5m):** white solid; yield 52%, 60.9 mg, m.p.: 112–114 °C;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.69 (d,  $J$  = 8.3 Hz, 2H), 7.66 (s, 1H), 7.51 (t,  $J$  = 7.6 Hz, 2H), 7.42 – 7.39 (m, 1H), 7.23 (d,  $J$  = 3.2 Hz, 1H), 6.68 (d,  $J$  = 3.2 Hz, 1H), 4.52 (q,  $J$  = 7.2 Hz, 2H), 3.96 (s, 3H), 3.02 (s, 3H), 1.50 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.8, 140.6, 135.4, 132.6, 132.0, 130.6, 128.9, 128.5, 127.0, 125.0, 123.0, 121.5, 101.3, 52.0, 44.7, 17.8, 15.9 ppm; IR (KBr)  $\nu$  = 3055, 2998, 2977, 2948, 1707, 1569, 1524,

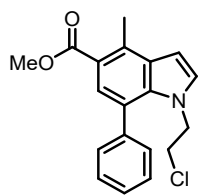
1483, 1430, 1343, 1323, 1229, 1204, 1161, 1054, 773, 739, 709  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ : 294.1489  $[\text{M} + \text{H}]^+$ ; found: 294.1487.



**Methyl 1-ethyl-4-methyl-7-phenyl-1H-indole-5-carboxylate (6m)**: white solid; yield 29%, 34.0 mg, m.p.: 102–104 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 – 7.60 (m, 3H), 7.46 (t,  $J$  = 7.5 Hz, 2H), 7.36 (t,  $J$  = 7.3 Hz, 1H), 7.18 (d,  $J$  = 3.2 Hz, 1H), 6.63 (d,  $J$  = 3.2 Hz, 1H), 4.47 (q,  $J$  = 7.2 Hz, 2H), 3.91 (s, 3H), 2.97 (s, 3H), 1.46 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 140.6, 135.4, 132.6, 132.0, 130.6, 128.9, 128.5, 127.0, 125.0, 123.0, 121.5, 101.3, 51.9, 44.6, 17.8, 15.8 ppm; IR (KBr)  $\nu$  = 3057, 2978, 2948, 1712, 1602, 1515, 1435, 1343, 1313, 1253, 1226, 1117, 1058, 787, 737, 703  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ : 294.1489  $[\text{M} + \text{H}]^+$ ; found: 294.1487.

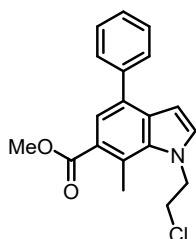


**Methyl 1-(2-hydroxyethyl)-4-methyl-7-phenyl-1H-indole-5-carboxylate (5n)**: yellow oil, yield 54%, 59.0 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.65 – 7.59 (m, 3H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.24 (d,  $J$  = 3.3 Hz, 1H), 6.64 (d,  $J$  = 3.2 Hz, 1H), 4.58 (t,  $J$  = 5.4 Hz, 2H), 3.94 (t,  $J$  = 5.4 Hz, 2H), 3.90 (s, 3H), 2.91 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 140.4, 135.5, 133.9, 132.2, 130.8, 128.8, 128.5, 127.1, 125.4, 122.8, 121.7, 101.4, 63.2, 52.0, 51.6, 16.3 ppm; IR (KBr)  $\nu$  = 3450, 2980, 2950, 2253, 1739, 1712, 1436, 1334, 1224, 1145, 1090, 1054, 913, 773, 734, 706  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_3^+$ : 310.1438  $[\text{M} + \text{H}]^+$ ; found: 310.1438.

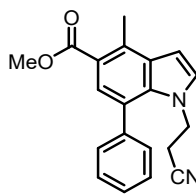


**Methyl 1-(2-chloroethyl)-4-methyl-7-phenyl-1H-indole-5-carboxylate (5o)**: yellow oil, yield 37%, 48.4 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (s, 1H), 7.42 (d,  $J$  = 3.9 Hz,

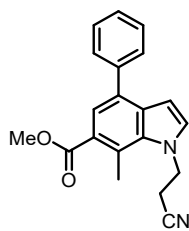
5H), 7.11 (d,  $J = 3.2$  Hz, 1H), 6.74 (d,  $J = 3.4$  Hz, 1H), 3.99 (t,  $J = 6.5$  Hz, 2H), 3.86 (s, 3H), 3.21 (t,  $J = 6.5$  Hz, 2H), 2.88 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.7, 139.3, 134.1, 134.1, 131.2, 130.9, 129.8, 128.3, 127.9, 127.1, 123.8, 120.3, 102.5, 51.6, 49.6, 42.9, 17.1$  ppm; IR (KBr)  $\nu = 3058, 2950, 2253, 1711, 1573, 1527, 1482, 1438, 1337, 1236, 1207, 1055, 770, 720$   $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{19}\text{ClNO}_2^+$ : 328.1099 [M + H] $^+$ ; found: 328.1097.



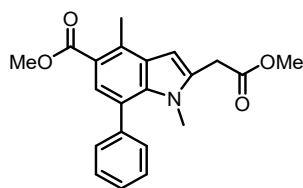
**Methyl 1-(2-chloroethyl)-7-methyl-4-phenyl-1H-indole-6-carboxylate (60)**: yield yellow oil, yield 34%, 44.5 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.63$  (d,  $J = 8.0$  Hz, 3H), 7.47 (t,  $J = 7.7$  Hz, 2H), 7.37 (t,  $J = 7.4$  Hz, 1H), 7.22 (d,  $J = 3.3$  Hz, 1H), 6.66 (d,  $J = 3.3$  Hz, 1H), 4.74 (t,  $J = 6.8$  Hz, 2H), 3.92 (s, 3H), 3.79 (t,  $J = 6.8$  Hz, 2H), 2.93 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.6, 140.2, 135.2, 133.6, 132.3, 130.9, 128.9, 128.5, 127.2, 125.7, 122.3, 122.1, 102.0, 52.1, 51.1, 43.5, 16.0$  ppm; IR (KBr)  $\nu = 2952, 2903, 1713, 1601, 1518, 1435, 1346, 1242, 1197, 1068, 912, 788, 740, 704$   $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{19}\text{ClNO}_2^+$ : 328.1099 [M + H] $^+$ ; found: 328.1097.



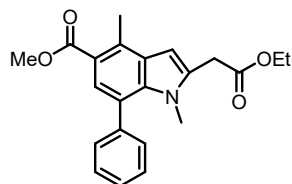
**Methyl 1-(2-cyanoethyl)-4-methyl-7-phenyl-1H-indole-5-carboxylate (5p)**: white solid, yield 35%, 44.5 mg, m.p.: 98–100 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.68$  (s, 1H), 7.44 (dt,  $J = 7.7, 4.5$  Hz, 5H), 7.13 (d,  $J = 3.4$  Hz, 1H), 6.78 (d,  $J = 3.4$  Hz, 1H), 4.00 (t,  $J = 6.8$  Hz, 2H), 3.87 (s, 3H), 2.86 (s, 3H), 2.21 ppm (t,  $J = 6.8$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.6, 139.1, 134.3, 133.8, 131.4, 130.0, 129.7, 128.5, 128.2, 127.3, 123.6, 120.7, 116.8, 103.5, 51.7, 43.9, 19.3, 17.0$  ppm; IR (KBr)  $\nu = 3058, 2952, 2251, 1710, 1573, 1528, 1437, 1337, 1237, 1193, 1160, 1053, 900, 770, 710$   $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_2^+$ : 319.1441 [M + H] $^+$ ; found: 319.1441.



**Methyl 1-(2-cyanoethyl)-7-methyl-4-phenyl-1H-indole-6-carboxylate (6p)**: white solid, yield 34%, 43.3 mg, m.p.: 123–125 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 – 7.60 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 3.3 Hz, 1H), 6.70 (d, *J* = 3.3 Hz, 1H), 4.75 (t, *J* = 6.9 Hz, 2H), 3.93 (s, 3H), 2.93 (s, 3H), 2.81 (t, *J* = 6.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.4, 140.0, 135.0, 132.9, 131.2, 128.8, 128.6, 127.3, 126.0, 122.5, 122.0, 116.7, 108.8, 103.1, 52.1, 45.3, 20.8, 15.9 ppm; IR (KBr)  $\nu$  = 2953, 2251, 1712, 1520, 1437, 1364, 1325, 1245, 1073, 912, 788, 740, 704 cm<sup>-1</sup>. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>: 319.1441 [M + H]<sup>+</sup>; found: 319.1441.

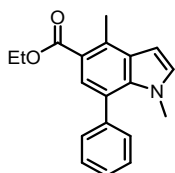


**Methyl 2-(2-methoxy-2-oxoethyl)-1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5q)**: yellow oil, yield 49%, 68.8 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.65 (s, 1H), 7.41 (s, 4H), 6.66 (s, 1H), 3.86 (s, 3H), 3.79 (s, 2H), 3.71 (s, 3H), 3.21 (s, 3H), 2.21 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 170.2, 168.8, 139.8, 136.2, 134.1, 133.4, 130.1, 129.4, 127.9, 127.4, 127.0, 123.9, 119.7, 103.0, 52.4, 51.5, 33.3, 17.0 ppm; IR (KBr)  $\nu$  = 2991, 2951, 1741, 1711, 1577, 1436, 1332, 1237, 1199, 1139, 1054, 1015, 770, 705 cm<sup>-1</sup>. HRMS (APCI, TOF): *m/z*: calcd for C<sub>21</sub>H<sub>22</sub>NO<sub>4</sub><sup>+</sup>: 352.1543 [M + H]<sup>+</sup>; found: 352.1543.

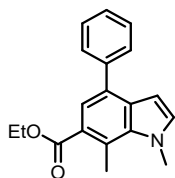


**Methyl 2-(2-methoxy-2-oxoethyl)-1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (5r)**: yellow oil, yield 54%, 78.8 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.65 (s, 1H), 7.41 (s, 5H), 6.66 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 2H), 3.21 (s, 3H), 2.84 (s, 3H), 1.26 ppm (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.8, 168.8, 139.9,

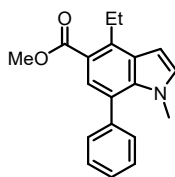
136.2, 134.3, 133.3, 130.1, 129.5, 127.9, 127.3, 126.9, 123.9, 119.7, 102.9, 61.4, 51.5, 33.6, 33.3, 17.0, 14.2 ppm; IR (KBr)  $\nu$  = 2952, 2253, 1741, 1711, 1610, 1548, 1436, 1347, 1233, 1173, 1108, 1059, 912, 737, 704  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{24}\text{NO}_4^+$ : 366.1700  $[\text{M} + \text{H}]^+$ ; found: 366.1700.



**Ethyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5s)**: yellow oil, yield 58%, 69.0 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.66 (s, 1H), 7.42 (s, 5H), 7.00 (s, 1H), 6.70 (s, 1H), 4.35 (q,  $J$  = 7.1 Hz, 2H), 3.30 (s, 3H), 2.87 (s, 3H), 1.38 ppm (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.5, 139.7, 135.1, 133.8, 131.2, 130.6, 130.2, 127.8, 127.4, 126.5, 124.1, 120.1, 101.6, 60.4, 36.8, 17.1, 14.5 ppm; IR (KBr)  $\nu$  = 2980, 2950, 1707, 1576, 1525, 1445, 1340, 1328, 1231, 1167, 1052, 768, 706  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  294.1489, found: 294.1488.

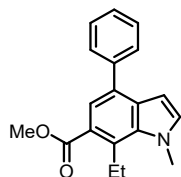


**Ethyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6s)**: yellow oil, yield 24%, 28.6 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (d,  $J$  = 8.0 Hz, 2H), 7.62 (s, 1H), 7.50 (t,  $J$  = 7.6 Hz, 2H), 7.40 (t,  $J$  = 7.3 Hz, 1H), 7.11 (d,  $J$  = 3.2 Hz, 1H), 6.61 (d,  $J$  = 3.1 Hz, 1H), 4.41 (q,  $J$  = 7.1 Hz, 2H), 4.17 (s, 3H), 3.05 (s, 3H), 1.43 ppm (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.3, 140.6, 136.3, 134.1, 131.9, 130.3, 128.8, 128.5, 127.0, 125.3, 123.3, 121.5, 100.5, 60.7, 38.3, 16.0, 14.4 ppm; IR (KBr)  $\nu$  = 2979, 2929, 1707, 1515, 1449, 1367, 1338, 1236, 1192, 1056, 762, 702  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  294.1489, found: 294.1488.

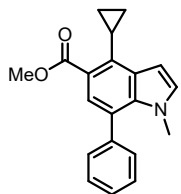


**Methyl 4-ethyl-1-methyl-7-phenyl-1H-indole-5-carboxylate (5t)**: white solid, yield 42%, 49.2 mg, m.p.: 72–74 °C;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.74 (s, 1H), 7.51 – 7.44 (m, 5H), 7.05 (d,  $J$  = 3.3 Hz, 1H), 6.78 (d,  $J$  = 3.3 Hz, 1H), 3.95 (s, 3H), 3.44 (q,  $J$  = 7.5, 7.0 Hz, 2H),

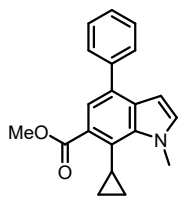
3.36 (s, 3H), 1.46 ppm (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.6, 140.2, 139.7, 135.4, 131.3, 130.2, 129.8, 127.8, 127.4, 126.8, 124.3, 119.0, 101.3, 51.6, 36.8, 24.1, 15.5$  ppm; IR (KBr)  $\nu = 2974, 2950, 2873, 1711, 1575, 1465, 1435, 1345, 1232, 1164, 1092, 1077, 730, 704$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  294.1489, found: 294.1489.



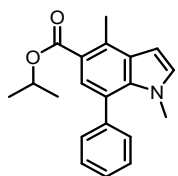
**Methyl 7-ethyl-1-methyl-4-phenyl-1H-indole-6-carboxylate (6t)**: white solid, yield 37%, 43.4 mg, m.p.: 60–62 °C;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.69 - 7.63$  (m, 3H), 7.50 (t,  $J = 7.7$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.14 (d,  $J = 3.2$  Hz, 1H), 6.65 (d,  $J = 3.2$  Hz, 1H), 4.17 (s, 3H), 3.95 (s, 3H), 3.49 (q,  $J = 7.4$  Hz, 2H), 1.47 ppm (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.4, 140.6, 135.1, 134.4, 132.0, 131.0, 130.1, 128.9, 128.5, 127.0, 123.9, 121.9, 100.7, 51.9, 37.8, 21.3, 17.3$  ppm; IR (KBr)  $\nu = 2950, 2872, 1713, 1601, 1516, 1433, 1342, 1237, 1193, 1117, 762, 737, 703$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  294.1489, found: 294.1489.



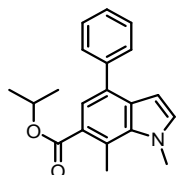
**Methyl 4-cyclopropyl-1-methyl-7-phenyl-1H-indole-5-carboxylate (5u)**: yellow solid, yield 51%, 62.2 mg, m.p.: 87–89 °C;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.43$  (d,  $J = 2.1$  Hz, 1H), 7.39 (s, 5H), 6.98 (d,  $J = 3.2$  Hz, 1H), 6.87 (d,  $J = 3.3$  Hz, 1H), 3.90 (d,  $J = 1.6$  Hz, 3H), 3.28 (s, 3H), 2.46 (td,  $J = 6.1, 2.7$  Hz, 1H), 1.07 (d,  $J = 8.8$  Hz, 2H), 0.70 ppm (d,  $J = 5.7$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.7, 139.6, 136.2, 135.1, 131.3, 130.8, 130.1, 127.7, 127.4, 125.6, 124.8, 123.4, 102.1, 51.8, 36.8, 13.1, 7.2$  ppm; IR (KBr)  $\nu = 3080, 2999, 2948, 2250, 1602, 1718, 1571, 1434, 1336, 1247, 1158, 1141, 1089, 1027, 736, 706$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_2^+$ : 306.1489  $[\text{M} + \text{H}]^+$ ; found: 306.1487.



**Methyl 7-cyclopropyl-1-methyl-4-phenyl-1H-indole-6-carboxylate (6u):** yellow solid, yield 25%, 30.5 mg, m.p.: 86–88 °C; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.49 (s, 1H), 7.46 – 7.42 (m, 5H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 3.96 (s, 3H), 3.33 (s, 3H), 2.52 (tt, *J* = 8.7, 5.7 Hz, 1H), 1.15 – 1.11 (m, 2H), 0.77 – 0.74 ppm (m, 2H); <sup>13</sup>C NMR (151 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.7, 139.6, 136.2, 135.1, 131.3, 130.8, 130.1, 127.8, 127.4, 125.6, 124.8, 123.4, 102.1, 51.9, 36.8, 13.2, 7.2 ppm; IR (KBr)  $\nu$  = 3080, 3000, 2948, 1719, 1571, 1434, 1336, 1247, 1158, 1141, 1089, 1026, 737, 706. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup>: 306.1489 [M + H]<sup>+</sup>; found: 306.1487.

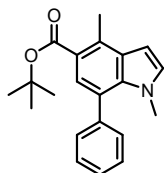


**Isopropyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5v):** yellow oil, yield 48%, 58.9 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (s, 1H), 7.47 (s, 5H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.73 (d, *J* = 3.2 Hz, 1H), 5.30 (hept, *J* = 6.2 Hz, 1H), 3.33 (s, 3H), 2.91 (s, 3H), 1.40 ppm (d, *J* = 6.2 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.1, 139.8, 135.0, 133.4, 131.2, 130.6, 130.3, 127.8, 127.4, 126.4, 124.0, 120.6, 101.5, 67.6, 36.8, 22.1, 17.1 ppm; IR (KBr)  $\nu$  = 3057, 2979, 2935, 1704, 1577, 1467, 1447, 1375, 1351, 1250, 1232, 1168, 1109, 1043, 892, 725 cm<sup>-1</sup>. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub><sup>+</sup>, [M + H]<sup>+</sup> 308.1645, found: 308.1646.

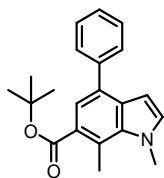


**Isopropyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6v):** yellow oil, yield 24%, 29.5 mg; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.73 – 7.61 (m, 2H), 7.57 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.60 (d, *J* = 3.1 Hz, 1H), 5.31 (hept, *J* = 6.3 Hz, 1H), 4.17 (s, 3H), 3.03 (s, 3H), 1.42 ppm (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.9, 140.6, 136.3, 134.0, 131.9, 130.2, 128.8, 128.5, 127.0, 125.9, 122.9, 121.3, 100.5,

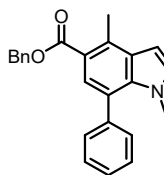
68.1, 38.3, 22.1, 16.0 ppm; IR (KBr)  $\nu$  = 3058, 2978, 2930, 1705, 1601, 1515, 1453, 1376, 1302, 1240, 1194, 1106, 1054, 1029, 786, 703  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  308.1645, found: 308.1646.



**Tert-butyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5w)**: yellow solid, yield 38%, 48.8 mg, m.p.: 89–91 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.56 (s, 1H), 7.42 (s, 5H), 6.98 (d,  $J$  = 3.3 Hz, 1H), 6.67 (d,  $J$  = 3.2 Hz, 1H), 3.29 (s, 3H), 2.83 (s, 3H), 1.60 ppm (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.2, 139.9, 134.9, 132.7, 131.1, 130.6, 130.3, 127.8, 127.3, 126.4, 124.0, 122.0, 101.5, 80.4, 36.8, 28.5, 17.1 ppm; IR (KBr)  $\nu$  = 3057, 2976, 2929, 1704, 1577, 1472, 1449, 1367, 1341, 1252, 1155, 1092, 1050, 766, 705  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{24}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  322.1802, found: 322.1802.



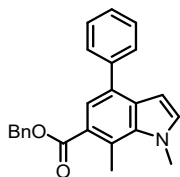
**Tert-butyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6w)**: yellow oil, yield 21%, 27.1 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.64 (d,  $J$  = 7.0 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.06 (d,  $J$  = 3.2 Hz, 1H), 6.56 (d,  $J$  = 3.2 Hz, 1H), 4.13 (s, 3H), 2.98 (s, 3H), 1.62 ppm (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.0, 140.7, 136.2, 133.8, 131.9, 129.9, 128.8, 128.5, 127.4, 127.0, 122.1, 121.2, 100.5, 80.9, 38.2, 28.4, 16.0 ppm; IR (KBr)  $\nu$  = 3058, 2976, 2930, 1601, 1704, 1516, 1472, 1368, 1344, 1301, 1250, 1162, 1116, 1056, 909, 702  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{24}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  322.1802, found: 322.1802.



**Benzyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5x)**: yellow oil, yield 57%, 81.0 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.70 (s, 1H), 7.46 – 7.29 (m, 10H), 6.98 (d,  $J$  = 3.2 Hz, 1H), 6.69 (d,  $J$  = 3.2 Hz, 1H), 5.35 (s, 2H), 3.27 (s, 3H), 2.88 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,

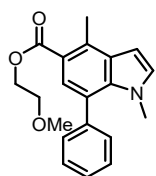


Chloroform-*d*, 25 °C)  $\delta$  = 168.2, 139.6, 136.7, 135.2, 134.2, 131.3, 130.7, 130.2, 128.5, 128.2, 128.0, 127.8, 127.4, 126.5, 124.2, 119.6, 101.7, 66.2, 36.8, 17.2 ppm; IR (KBr)  $\nu$  = 3031, 2948, 1708, 1576, 1525, 1447, 1375, 1341, 1328, 1230, 1162, 1046, 727, 702. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{24}H_{22}NO_2^+$ ,  $[M + H]^+$  356.1645, found: 356.1645.



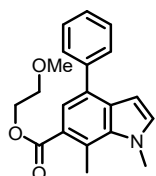
**Benzyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6x)**: yellow oil; yield 24%,

34.0 mg;  $^1H$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 – 7.60 (m, 3H), 7.45 (t,  $J$  = 7.5 Hz, 4H), 7.40 – 7.29 (m, 4H), 7.08 (d,  $J$  = 3.2 Hz, 1H), 6.57 (d,  $J$  = 3.2 Hz, 1H), 5.38 (s, 2H), 4.12 (s, 3H), 3.01 ppm (s, 3H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.0, 140.5, 136.4, 136.3, 134.2, 132.0, 130.5, 128.8, 128.6, 128.5, 128.1, 128.1, 127.0, 124.7, 123.7, 121.6, 100.6, 66.5, 38.3, 16.0 ppm. IR (KBr)  $\nu$  = 3032, 2928, 2851, 1709, 1599, 1515, 1489, 1453, 1378, 1340, 1232, 1188, 1113, 736, 700. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{24}H_{22}NO_2^+$ ,  $[M + H]^+$  356.1645, found: 356.1643.



**2-Methoxyethyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5y)**: yellow oil, yield

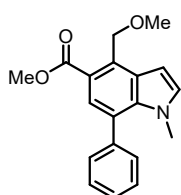
60%, 77.5 mg;  $^1H$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.73 (s, 1H), 7.45 (s, 5H), 7.03 (d,  $J$  = 3.3 Hz, 1H), 6.74 (d,  $J$  = 3.2 Hz, 1H), 4.52 – 4.46 (m, 2H), 3.79 – 3.73 (m, 2H), 3.44 (s, 3H), 3.33 (s, 3H), 2.92 ppm (s, 3H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.4, 139.7, 135.2, 134.0, 131.2, 130.6, 130.2, 127.8, 127.4, 126.6, 124.1, 119.6, 101.6, 70.8, 63.4, 59.0, 36.8, 17.1 ppm; IR (KBr)  $\nu$  = 3007, 2934, 2841, 2739, 1736, 1687, 1601, 1578, 1512, 1462, 1315, 1261, 1161, 1027, 833, 599  $cm^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{20}H_{22}NO_3^+$ ,  $[M + H]^+$  324.1594, found: 324.1594.



**2-Methoxyethyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6y)**: yellow oil, yield

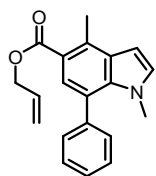
18%, 23.3 mg;  $^1H$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.70 – 7.63 (m, 3H), 7.49 (t,  $J$  = 7.5 Hz,

2H), 7.39 (t,  $J = 7.4$  Hz, 1H), 7.11 (d,  $J = 3.2$  Hz, 1H), 6.61 (d,  $J = 3.1$  Hz, 1H), 4.53 – 4.49 (m, 2H), 4.17 (s, 3H), 3.78 – 3.75 (m, 2H), 3.45 (s, 3H), 3.05 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 169.2, 140.5, 136.3, 134.2, 131.9, 130.5, 128.8, 128.5, 127.0, 124.8, 123.6, 121.6, 100.6, 70.6, 63.8, 59.0, 38.3, 16.0$  ppm; IR (KBr)  $\nu = 3057, 2928, 1709, 1600, 1515, 1450, 1377, 1340, 1301, 1236, 1191, 1114, 1058, 907, 786, 703$   $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_3^+$ ,  $[\text{M} + \text{H}]^+$  324.1594, found: 324.1594.



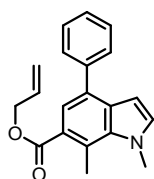
**Methyl 4-(methoxymethyl)-1-methyl-7-phenyl-1H-indole-5-carboxylate (5z):**

yellow oil, yield 64%, 79.1 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.66$  (s, 1H), 7.45 (s, 5H), 7.07 (d,  $J = 3.3$  Hz, 1H), 6.88 (d,  $J = 3.2$  Hz, 1H), 5.22 (s, 2H), 3.92 (s, 3H), 3.49 (s, 3H), 3.33 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.6, 139.4, 135.7, 132.0, 131.8, 130.5, 130.1, 127.8, 127.6, 126.3, 126.1, 120.7, 101.9, 69.2, 58.4, 51.8, 36.8$  ppm; IR (KBr)  $\nu = 2985, 2949, 2901, 1715, 1581, 1435, 1397, 1340, 1236, 1198, 1163, 1092, 1042, 955, 910, 733, 705$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{20}\text{NO}_3^+$ : 310.1438  $[\text{M} + \text{H}]^+$ ; found: 310.1438.

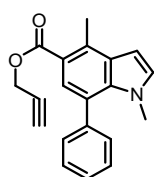


**Allyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5aa):**

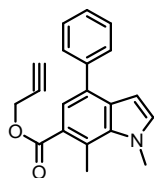
yellow oil, yield 51%, 62.2 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta = 7.70$  (s, 1H), 7.40 (s, 5H), 6.98 (d,  $J = 3.3$  Hz, 1H), 6.69 (d,  $J = 3.2$  Hz, 1H), 6.04 (ddt,  $J = 16.1, 10.8, 5.6$  Hz, 1H), 5.40 (d,  $J = 1.5$  Hz, 1H), 5.23 (dd,  $J = 10.4, 1.4$  Hz, 1H), 4.80 (d,  $J = 5.6$  Hz, 2H), 3.28 (s, 3H), 2.88 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta = 168.8, 140.5, 136.3, 134.2, 132.6, 132.0, 130.5, 128.8, 128.5, 127.1, 124.7, 123.7, 121.6, 118.1, 100.6, 65.4, 38.3, 16.0$  ppm; IR (KBr)  $\nu = 3058, 2981, 2946, 1710, 1576, 1444, 1357, 1326, 1230, 1163, 1093, 1046, 769, 706$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_2^+$ ,  $[\text{M} + \text{H}]^+$  306.1489, found: 306.1489.



**Allyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6aa):** yellow oil; yield 32%, 39.1 mg; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.64 (d, *J* = 3.6 Hz, 3H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.13 – 6.00 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.86 – 4.80 (m, 2H), 4.12 (s, 3H), 3.02 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 140.5, 136.3, 134.2, 132.6, 131.9, 130.5, 128.8, 128.5, 127.1, 124.7, 123.7, 121.6, 118.1, 100.6, 65.4, 38.3, 16.0 ppm; IR (KBr)  $\nu$  = 3058, 2932, 1710, 1599, 1515, 1448, 1338, 1234, 1189, 1114, 1055, 1007, 786, 703. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup>, [M + H]<sup>+</sup> 306.1489, found: 306.1489.

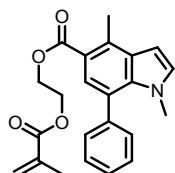


**Prop-2-yn-1-yl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5ab):** yellow solid, yield 56%, 67.9 mg, m.p.: 88–90 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.69 (d, *J* = 15.8 Hz, 1H), 7.40 (s, 5H), 6.99 (d, *J* = 3.3 Hz, 1H), 6.70 (t, *J* = 2.9 Hz, 1H), 4.89 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 2H), 3.3 (s, 3H), 2.87 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 167.3, 139.5, 135.4, 134.7, 131.3, 130.7, 130.2, 127.8, 127.4, 126.7, 124.2, 118.7, 101.7, 78.4, 74.5, 51.8, 36.8, 17.1 ppm; IR (KBr)  $\nu$  = 3291, 3058, 2947, 1715, 1576, 1444, 1366, 1340, 1230, 1200, 1160, 1092, 1048, 920, 769, 727, 706. HRMS (APCI, TOF): *m/z*: calcd for C<sub>20</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup>, [M + H]<sup>+</sup> 304.1332, found: 304.1330.



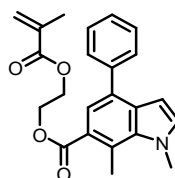
**Prop-2-yn-1-yl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6ab):** white solid, yield 20%, 24.2 mg, m.p.: 1102–104 °C; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.66 – 7.61 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 ((t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 4.92 (d, *J* = 2.5 Hz, 2H), 4.13 (s, 3H), 3.91 (s, 1H), 3.03 ppm (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.1, 140.4, 136.3, 134.5, 132.0, 130.8, 128.8, 128.5, 127.1, 124.2, 123.6, 121.7, 100.6, 78.2,

74.7, 52.1, 38.4, 15.9 ppm; IR (KBr)  $\nu$  = 3529, 3056, 3025, 2950, 1712, 1599, 1508, 1481, 1402, 1375, 1327, 1274, 1222, 1169, 1088, 1016, 911, 866, 730, 703. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{20}H_{18}NO_2^+$ ,  $[M + H]^+$  304.1332, found: 304.1330.



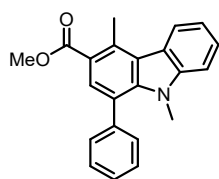
**2-(Methacryloyloxy)ethyl 1,4-dimethyl-7-phenyl-1H-indole-5-carboxylate (5ac):**

colorless oil, yield 38%, 57.5 mg;  $^1H$  NMR (600 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 (s, 1H), 7.39 (s, 5H), 6.98 (d,  $J$  = 3.2 Hz, 1H), 6.68 (d,  $J$  = 3.2 Hz, 1H), 6.10 (s, 1H), 5.52 (s, 1H), 4.56 – 4.53 (m, 2H), 4.47 (dd,  $J$  = 5.9, 3.8 Hz, 2H), 3.28 (s, 3H), 2.86 (s, 3H), 1.90 ppm (s, 3H);  $^{13}C$  NMR (151 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.1, 167.2, 139.6, 136.0, 135.3, 134.1, 131.4, 130.7, 130.2, 127.8, 127.5, 126.7, 126.1, 124.2, 119.4, 101.7, 62.7, 62.1, 36.9, 18.3, 17.20 ppm; IR (KBr)  $\nu$  = 3057, 2954, 1888, 1717, 1636, 1576, 1447, 1368, 1341, 1323, 1232, 1158, 1092, 1068, 943, 768. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{23}H_{24}NO_4^+$ ,  $[M + H]^+$  378.1700, found: 378.1700.



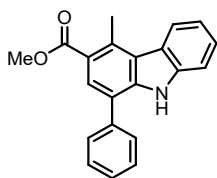
**2-(Methacryloyloxy)ethyl 1,7-dimethyl-4-phenyl-1H-indole-6-carboxylate (6ac):**

colorless oil, yield 35%, 52.9 mg;  $^1H$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 7.67 – 7.59 (m, 3H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.10 (d,  $J$  = 3.2 Hz, 1H), 6.59 (d,  $J$  = 3.1 Hz, 1H), 6.15 (s, 1H), 5.57 (s, 1H), 4.60 – 4.55 (m, 2H), 4.52 – 4.48 (m, 2H), 4.14 (s, 3H), 3.02 (s, 3H), 1.94 ppm (s, 3H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.8, 167.2, 140.4, 136.3, 136.0, 134.3, 132.0, 130.6, 128.8, 128.5, 127.1, 126.1, 124.4, 123.7, 121.7, 100.6, 62.6, 62.4, 38.3, 18.3, 15.9 ppm; IR (KBr)  $\nu$  = 2956, 1718, 1637, 1601, 1515, 1451, 1377, 1341, 1236, 1165, 1114, 1064, 786, 703. HRMS (APCI, TOF):  $m/z$ : calcd for  $C_{23}H_{24}NO_4^+$ ,  $[M + H]^+$  378.1700, found: 378.1700.

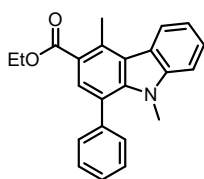


**Methyl 4,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (8a):** colorless oil,

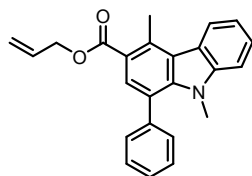
yield 64%, 84.3 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 8.06 (d,  $J$  = 7.8 Hz, 1H), 7.92 (d,  $J$  = 8.2 Hz, 1H), 7.64 (d,  $J$  = 8.1 Hz, 1H), 7.50 (t,  $J$  = 7.1 Hz, 1H), 7.48 – 7.33 (m, 2H), 7.33 – 7.14 (m, 4H), 4.12 (s, 3H), 3.94 (s, 3H), 3.01 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.5, 143.3, 140.6, 134.3, 129.7, 129.0, 128.6, 126.8, 126.4, 126.2, 122.8, 122.2, 121.2, 120.6, 119.5, 117.4, 109.1, 52.1, 33.6, 17.0 ppm; IR (KBr)  $\nu$  = 2949, 1711, 1696, 1620, 1575, 1512, 1459, 1435, 1384, 1338, 1320, 1295, 1241, 1222, 1201, 1154, 1116, 1064, 912, 788, 774, 748, 734  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}_2^+$ : 330.1489 [M + H] $^+$ ; found: 330.1489.



**Methyl 4-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (8b):** yellow oil, yield 41%, 51.8 mg;  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C)  $\delta$  = 11.49 (s, 1H), 8.16 (d,  $J$  = 7.9 Hz, 1H), 7.58 – 7.55 (m, 4H), 7.41 – 7.35 (m, 5H), 3.87 (s, 3H), 2.80 ppm (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>, 25 °C)  $\delta$  = 168.6, 141.4, 139.9, 133.6, 130.7, 129.7, 128.8, 127.5, 126.5, 125.7, 123.6, 123.2, 123.0, 121.9, 120.6, 119.5, 111.7, 52.2, 20.5 ppm; IR (KBr)  $\nu$  = 3379, 2967, 2874, 1696, 1620, 1574, 1514, 1459, 1436, 1383, 1342, 1229, 1233, 1203, 1154, 1119, 1059, 912, 746  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2^+$ : 316.1332 [M + H] $^+$ ; found: 316.1332.



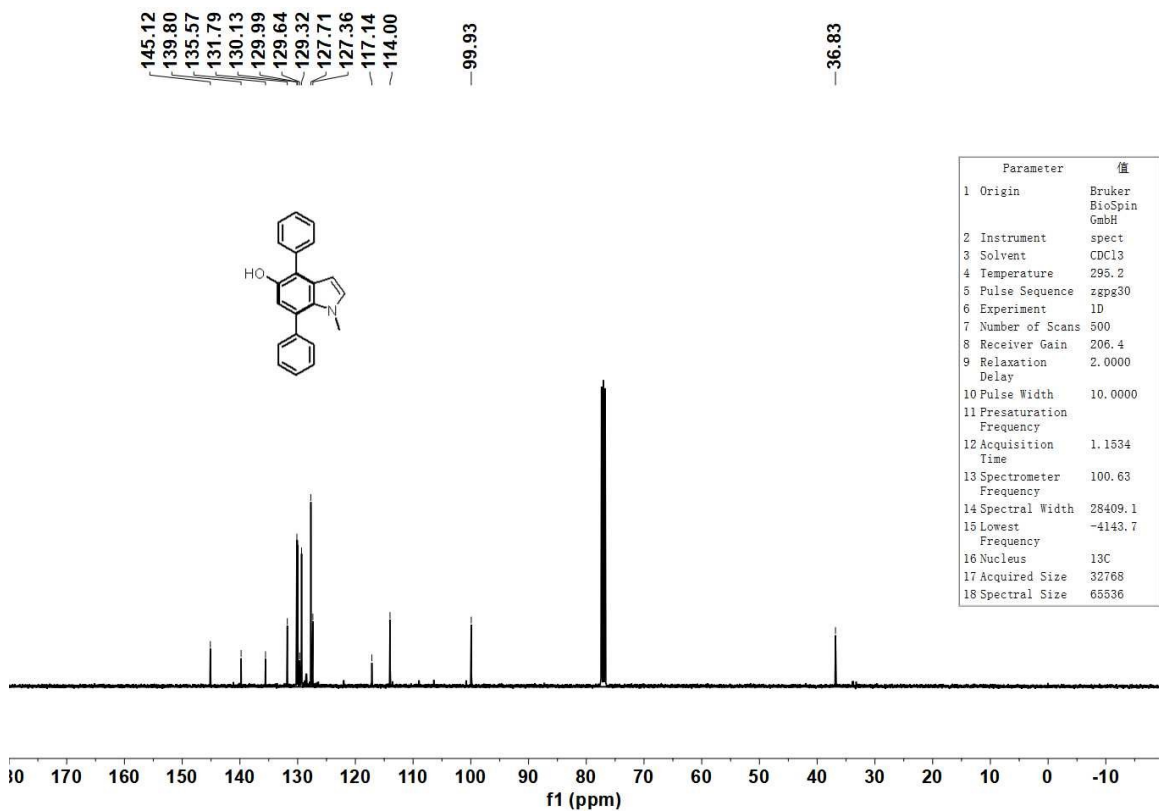
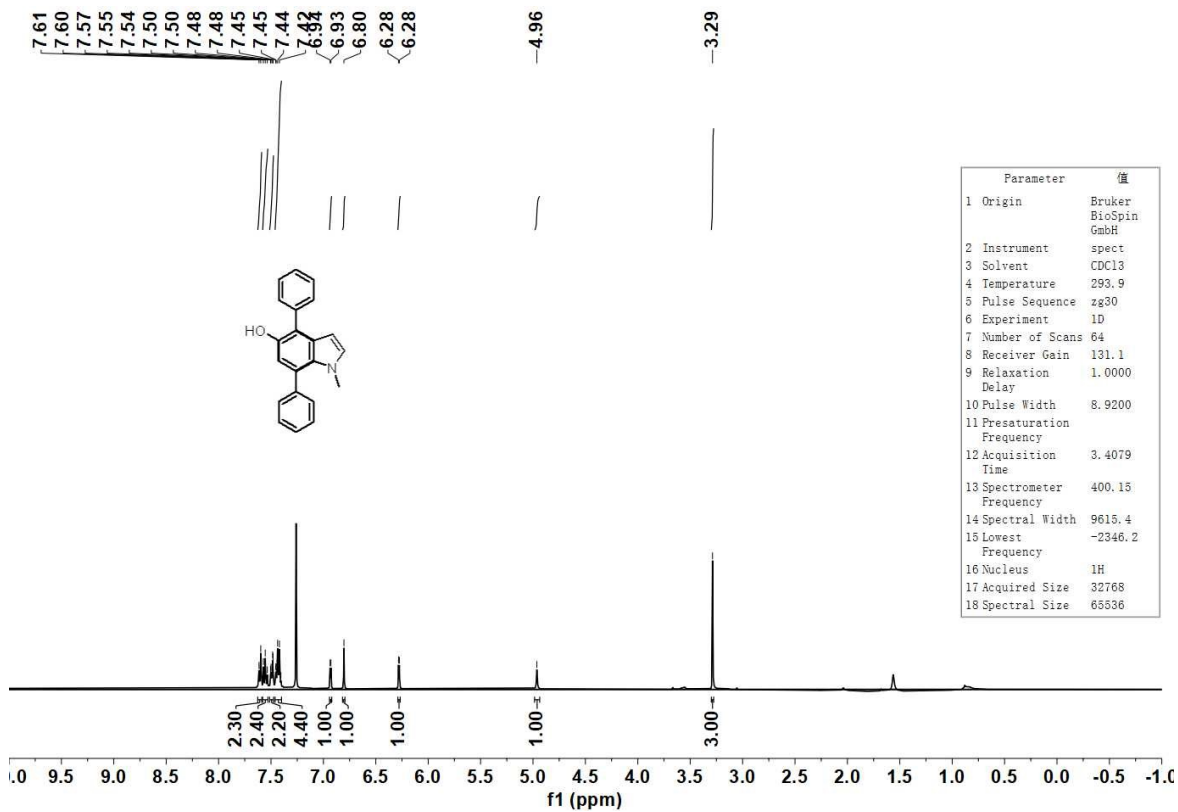
**Ethyl 4, 9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (8c):** yellow oil, yield 52%, 71.3 mg;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 8.05 (d,  $J$  = 7.8 Hz, 1H), 7.91 (d,  $J$  = 8.1 Hz, 1H), 7.63 (d,  $J$  = 8.3 Hz, 1H), 7.49 (t,  $J$  = 7.7 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.26 (dt,  $J$  = 21.9, 8.0 Hz, 4H), 4.14 (q,  $J$  = 7.2 Hz, 2H), 4.10 (s, 3H), 3.00 (s, 3H), 1.43 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 169.2, 143.3, 140.6, 134.3, 129.7, 129.5, 128.6, 126.7, 126.5, 126.1, 122.5, 122.3, 121.2, 120.6, 119.4, 117.4, 109.1, 61.0, 33.6, 17.0, 14.4 ppm; IR (KBr)  $\nu$  = 2980, 2937, 1692, 1620, 1576, 1513, 1459, 1386, 1367, 1321, 1295, 1240, 1221, 1196, 1062, 912, 872, 774, 747  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$ : 344.1645 [M + H] $^+$ ; found: 344.1645.



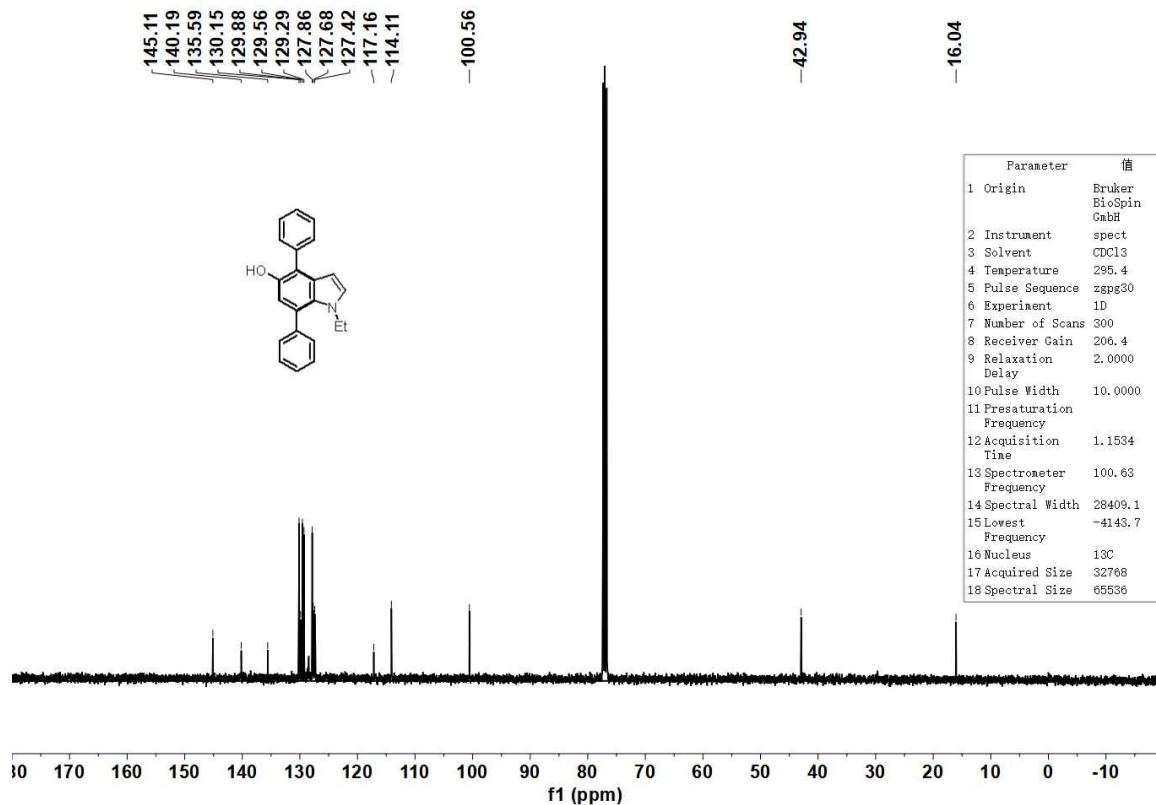
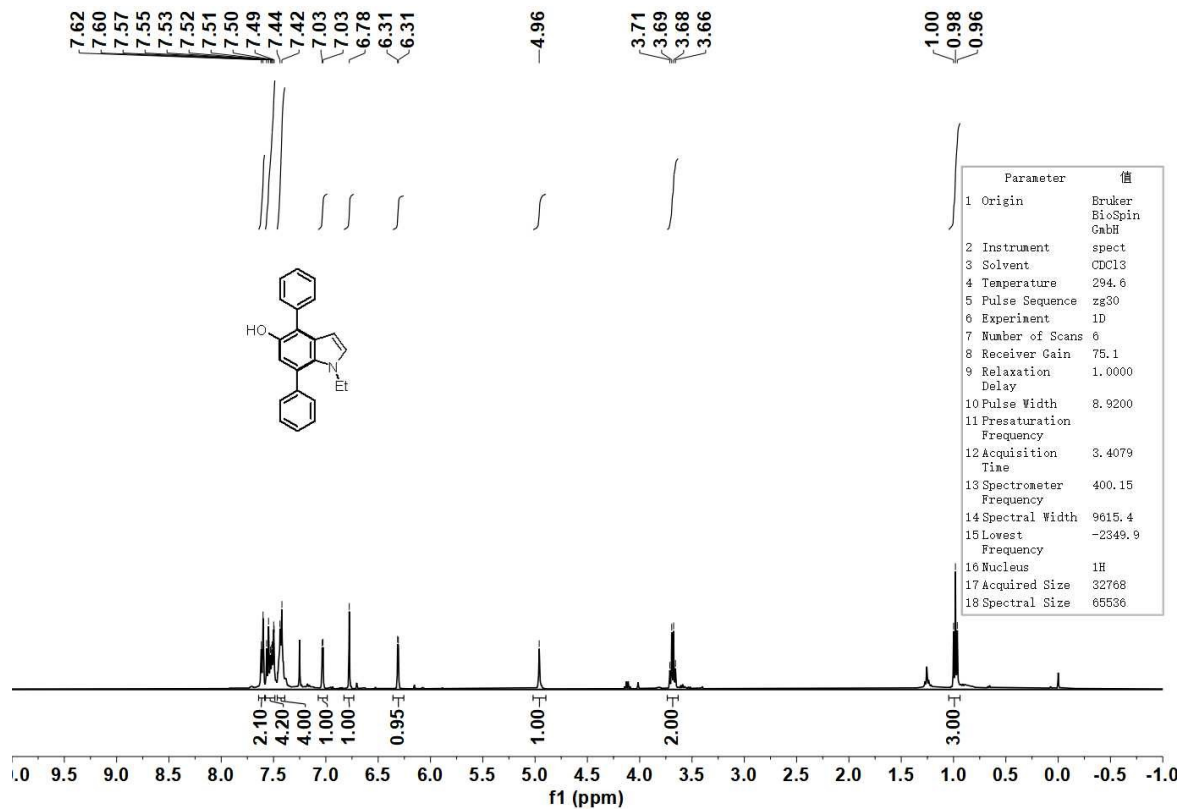
**Allyl 4, 9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (8d):** yellow oil, yield 57%, 80.9 mg;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 8.07 (d,  $J$  = 7.8 Hz, 1H), 7.92 (d,  $J$  = 8.2 Hz, 1H), 7.68 (d,  $J$  = 8.2 Hz, 1H), 7.67 – 7.42 (m, 2H), 7.42 – 7.27 (m, 2H), 7.27 – 7.05 (m, 3H), 6.14 – 6.04 (m, 1H), 5.45 (dd,  $J$  = 17.2, 1.6 Hz, 1H), 5.31 (dd,  $J$  = 10.4, 1.4 Hz, 1H), 4.86 (d,  $J$  = 5.7 Hz, 2H), 4.13 (s, 3H), 3.02 ppm (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*, 25 °C)  $\delta$  = 168.7, 143.3, 140.6, 132.4, 129.7, 129.0, 126.8, 126.3, 125.9, 122.9, 122.2, 121.3, 120.6, 119.5, 119.1, 118.3, 117.4, 109.1, 108.6, 65.6, 33.7, 17.0 ppm; IR (KBr)  $\nu$  = 2971, 2937, 1697, 1620, 1513, 1458, 1386, 1320, 1295, 1221, 1193, 1128, 1059, 992, 913, 774, 746  $\text{cm}^{-1}$ . HRMS (APCI, TOF):  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{22}\text{NO}_2^+$ : 356.1645  $[\text{M} + \text{H}]^+$ ; found: 356.1643.

## 8. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

3a

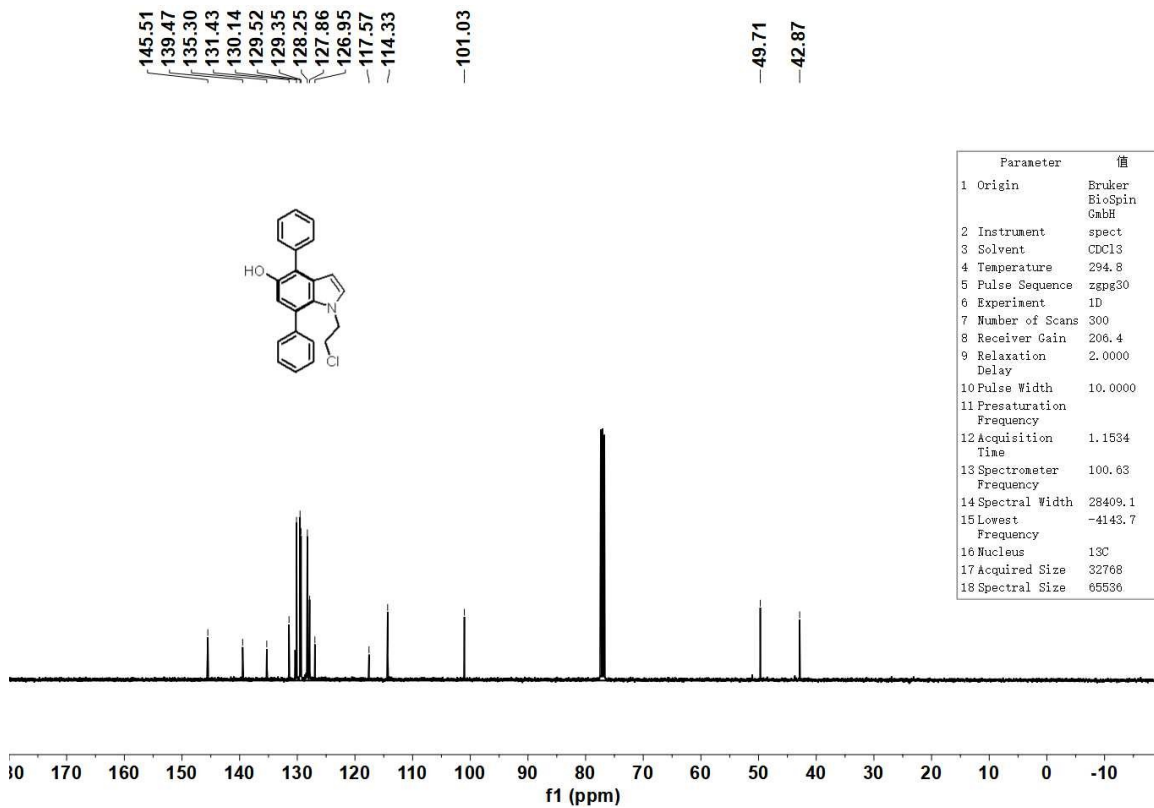
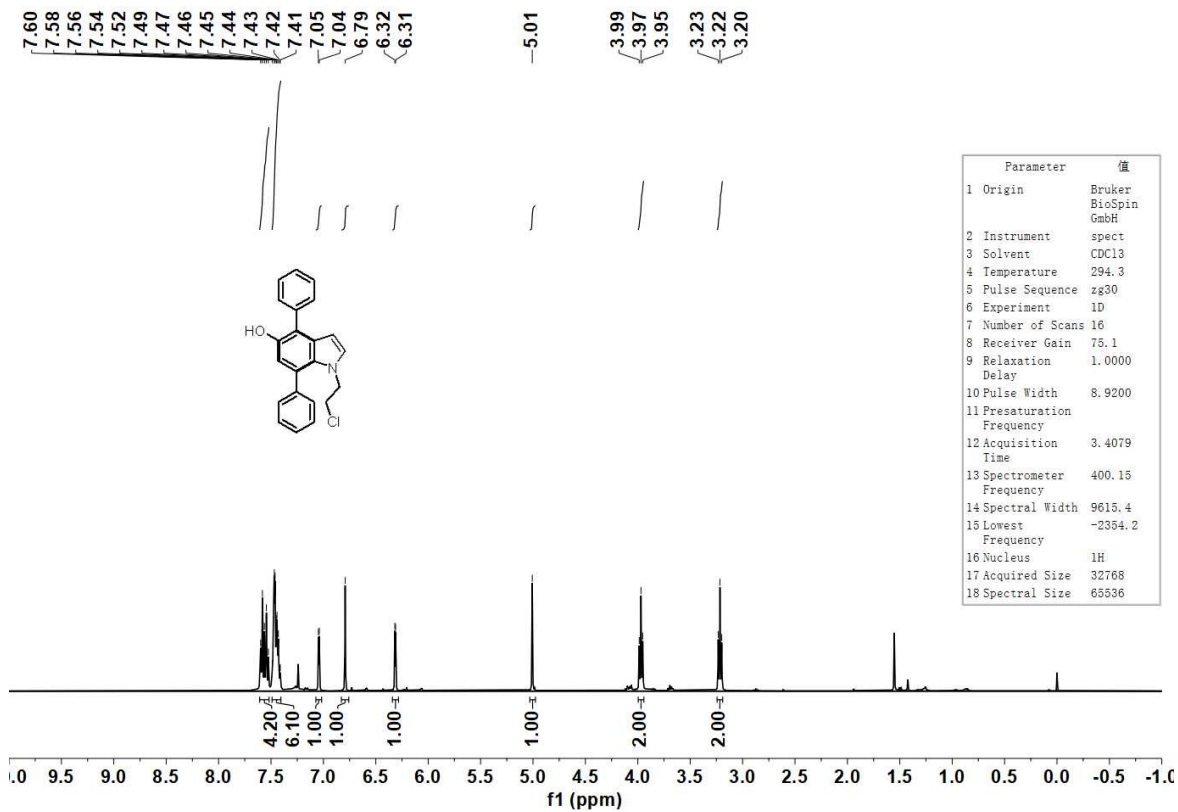


3b

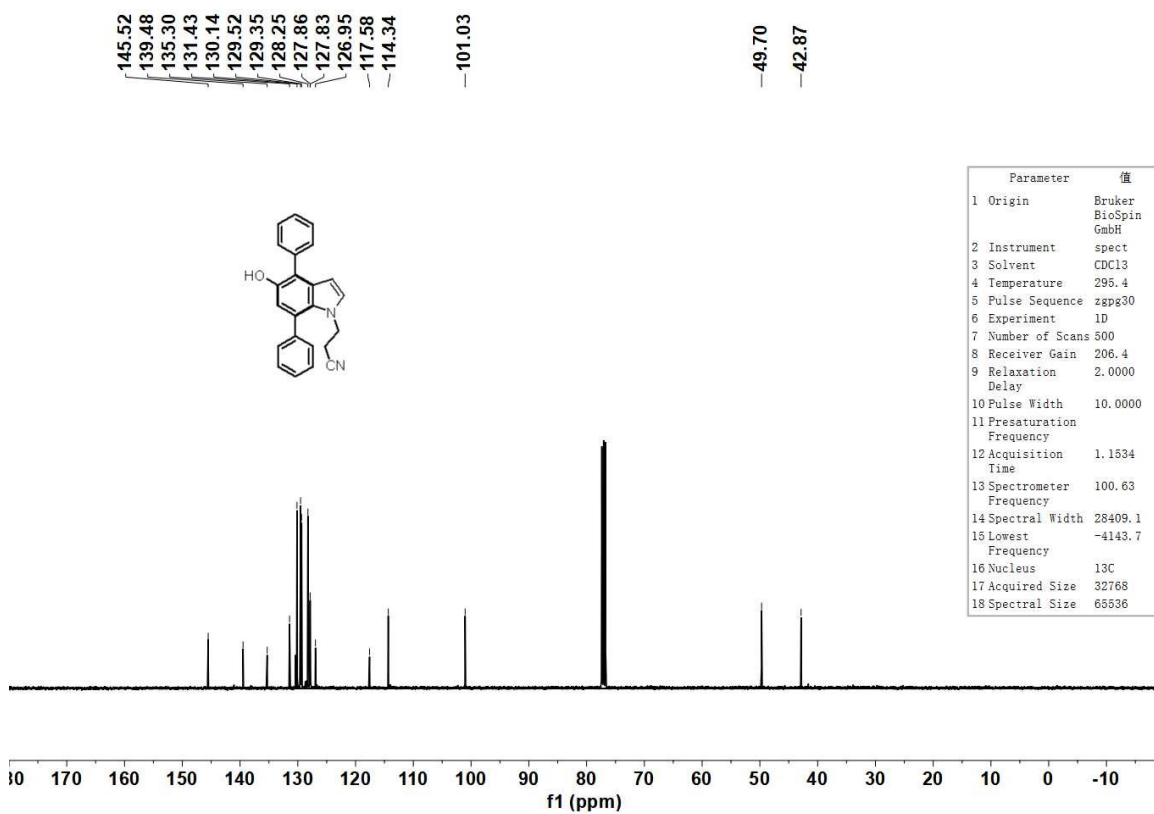
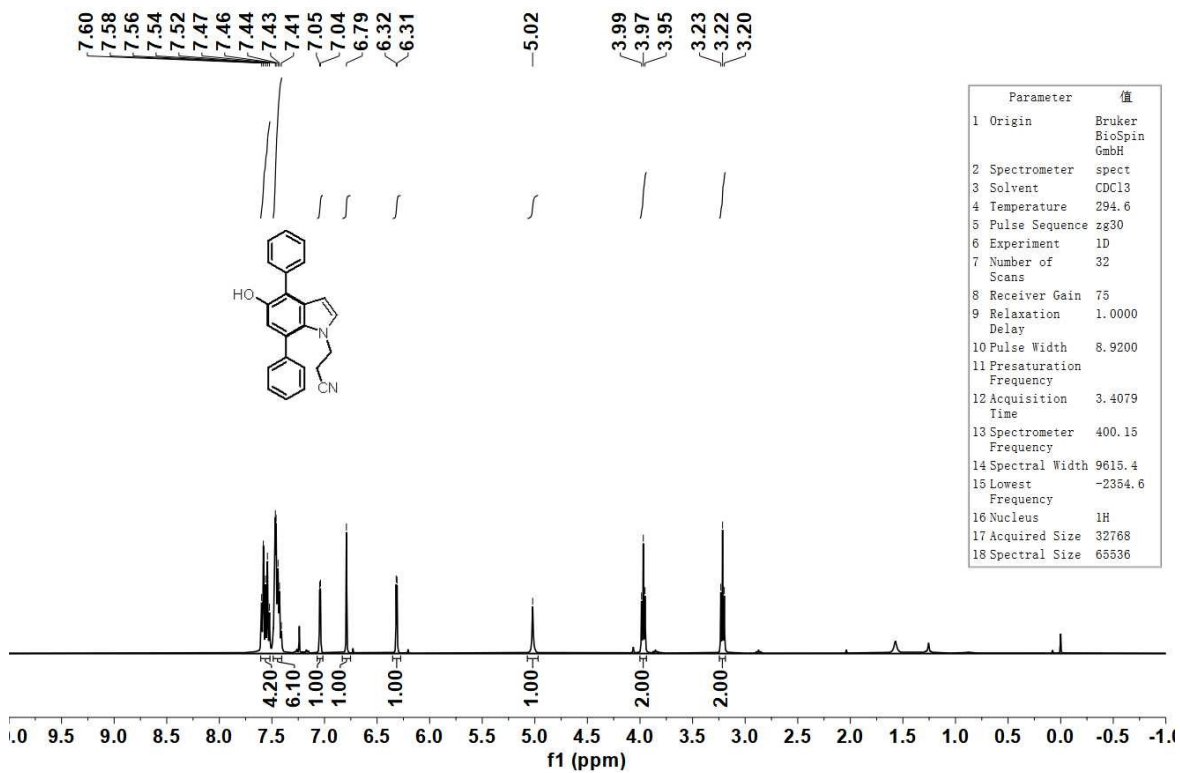




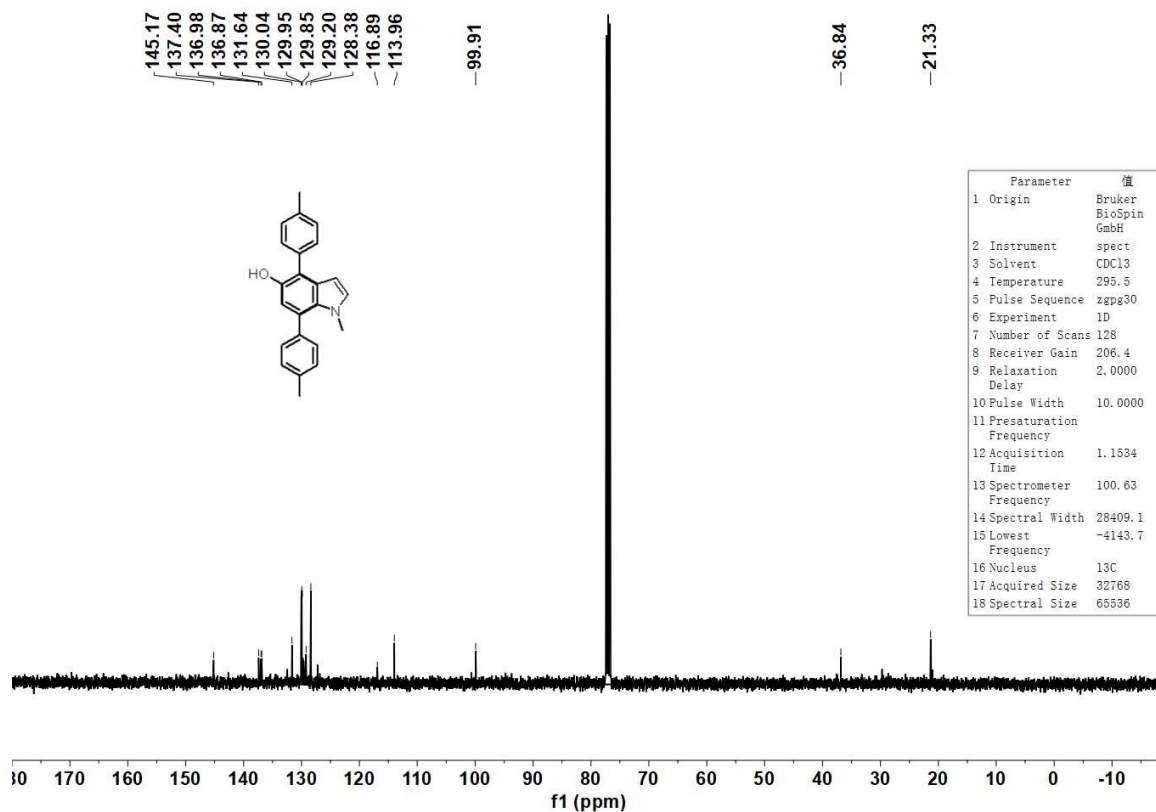
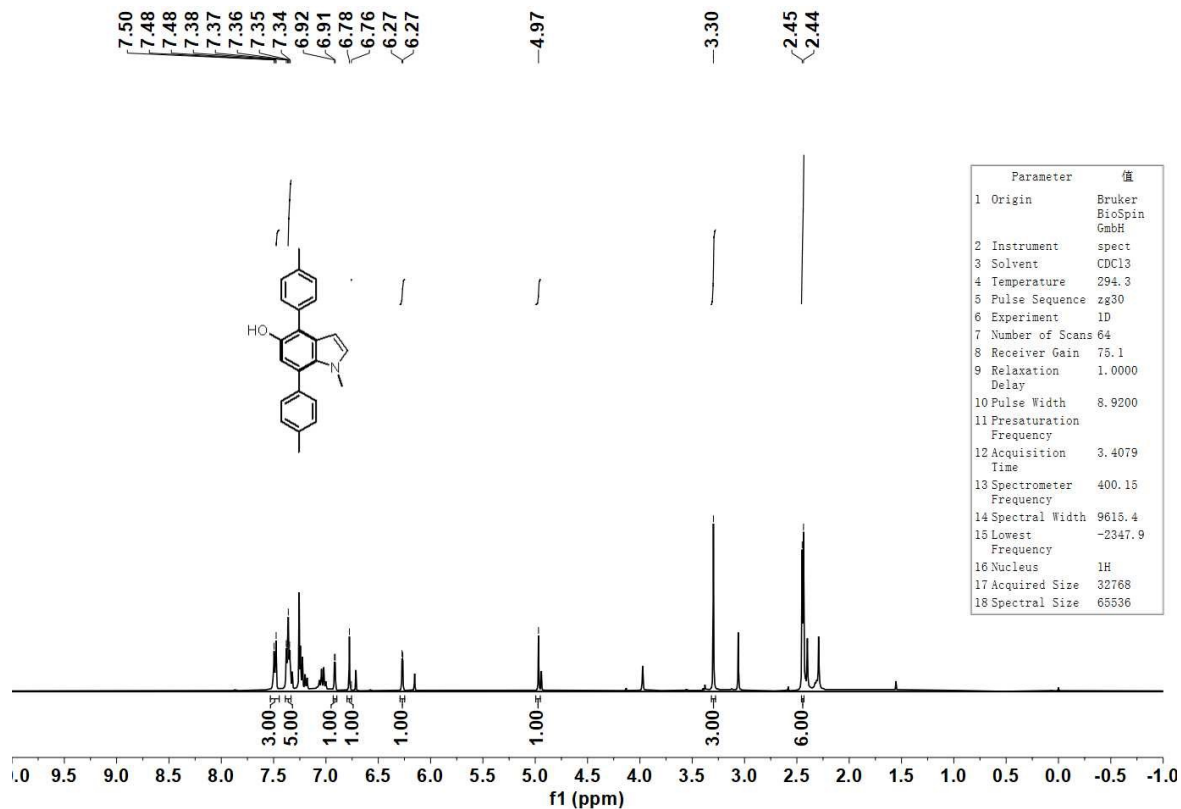
3c



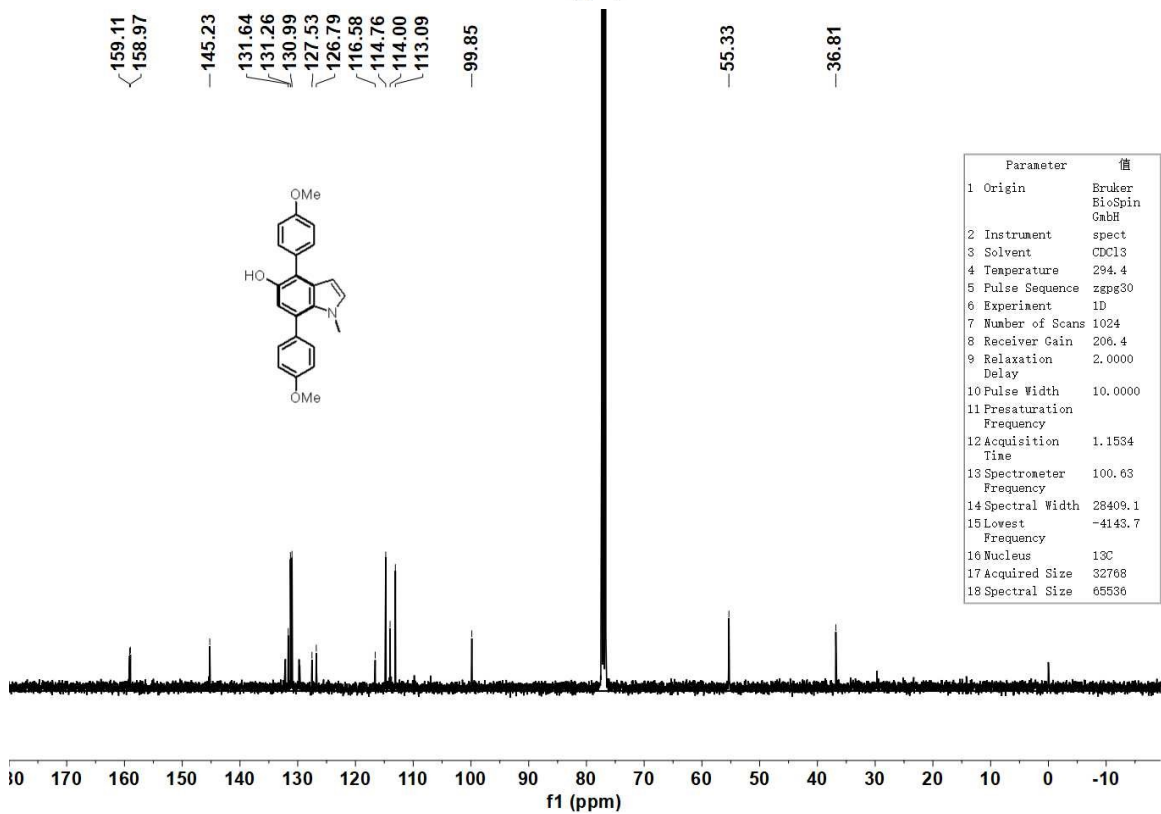
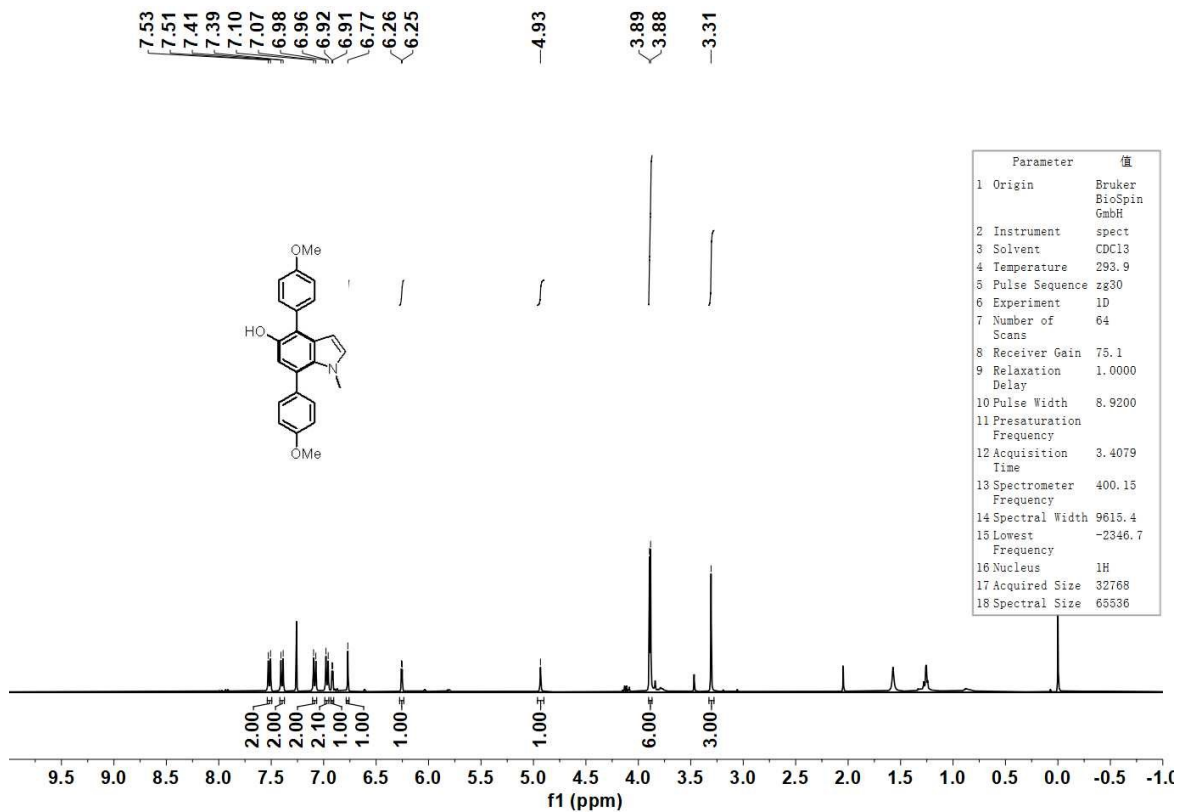
3d



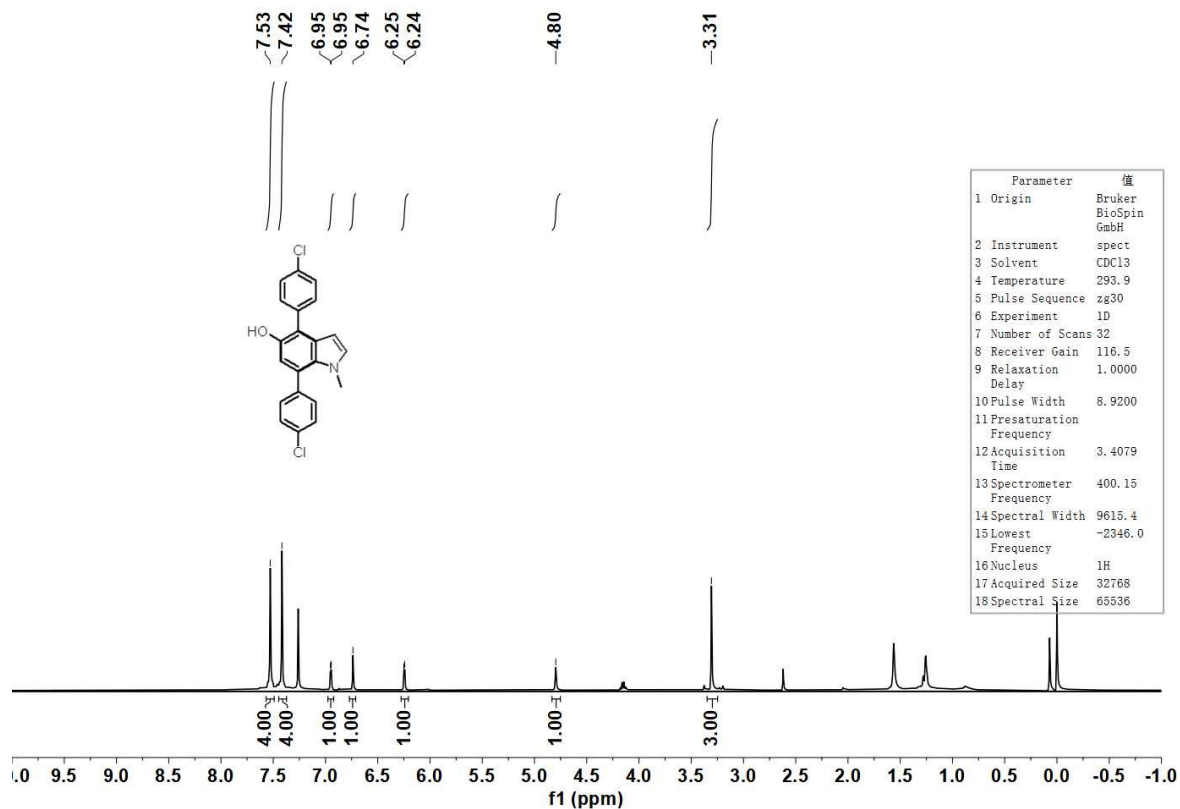
3e



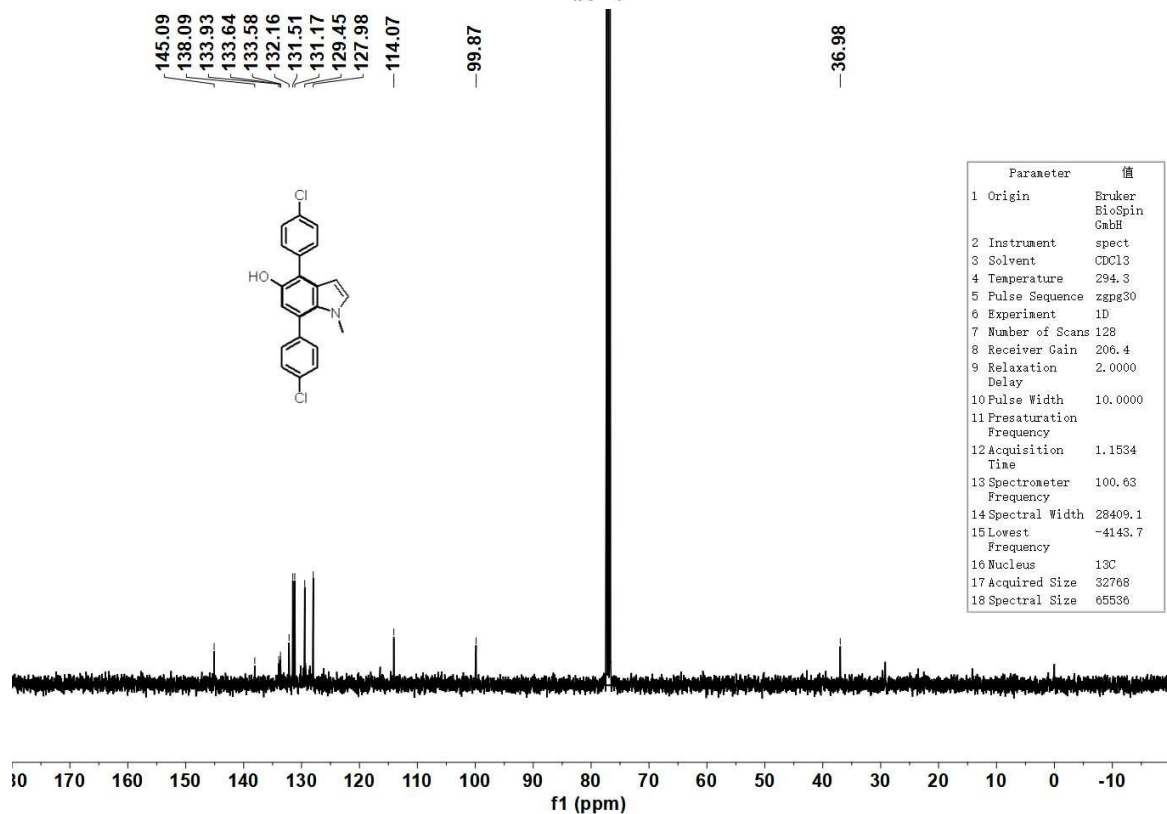
3f



3g

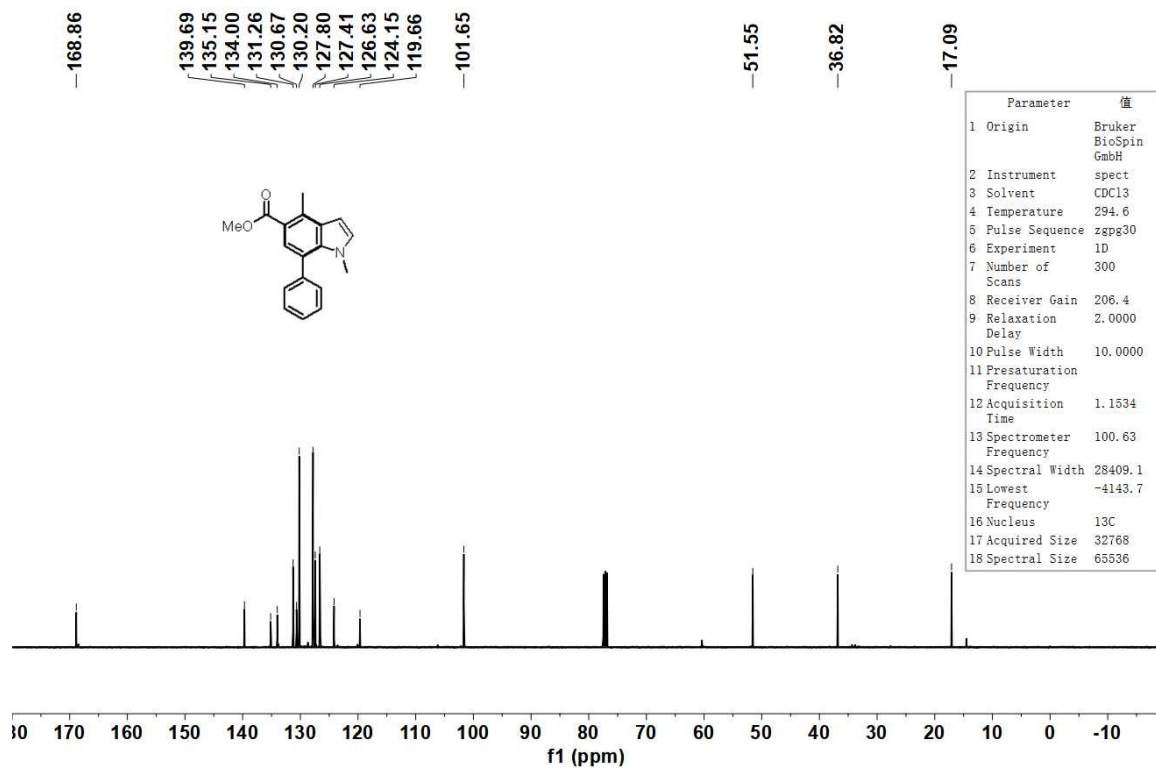
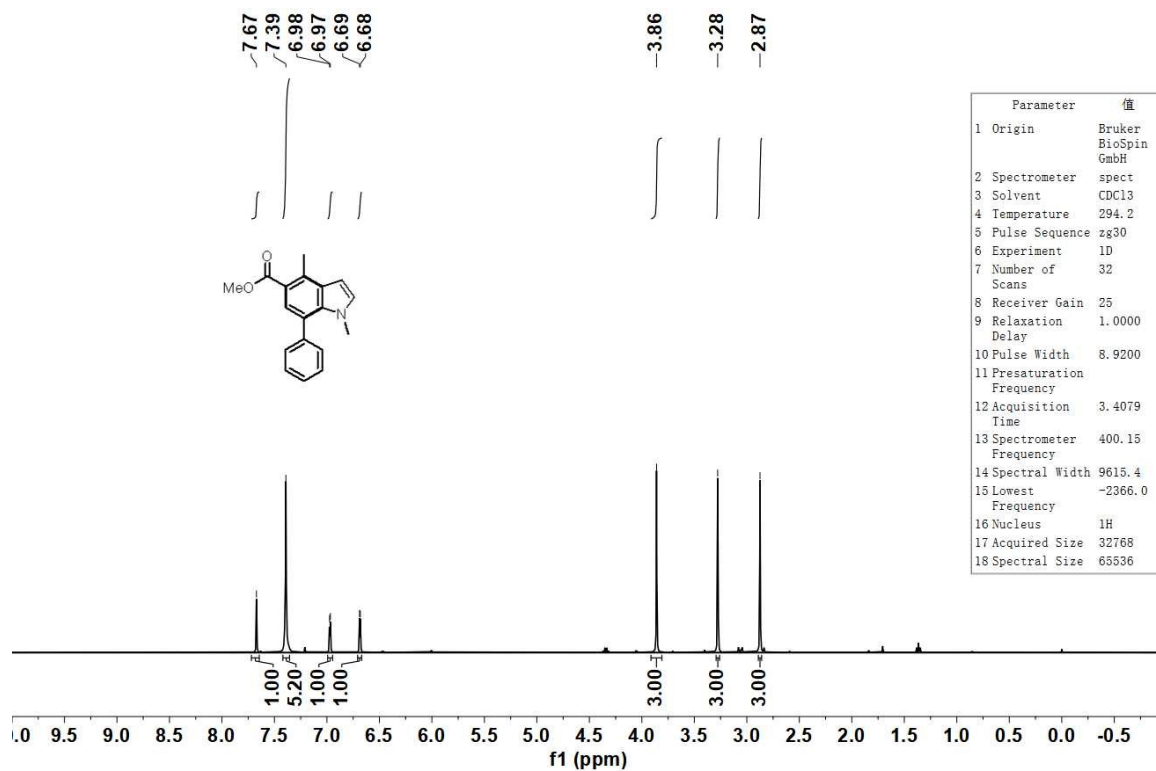


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	293.9
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	32
8 Receiver Gain	116.5
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2346.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

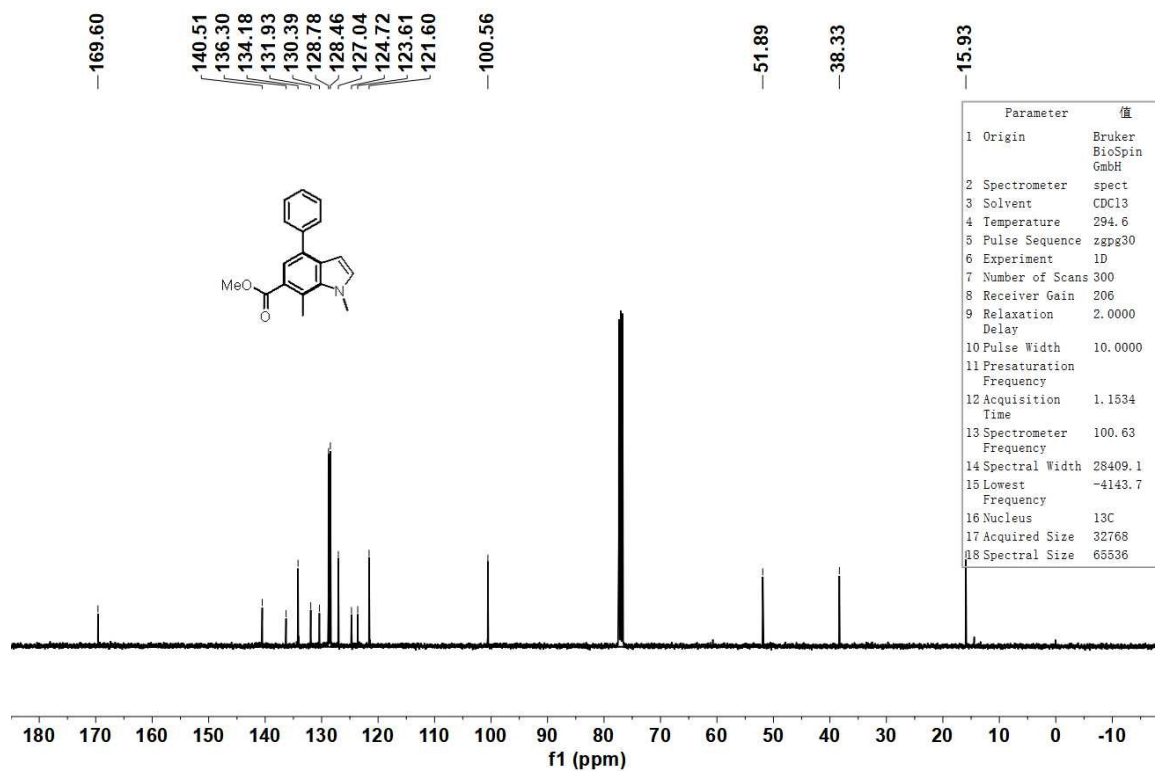
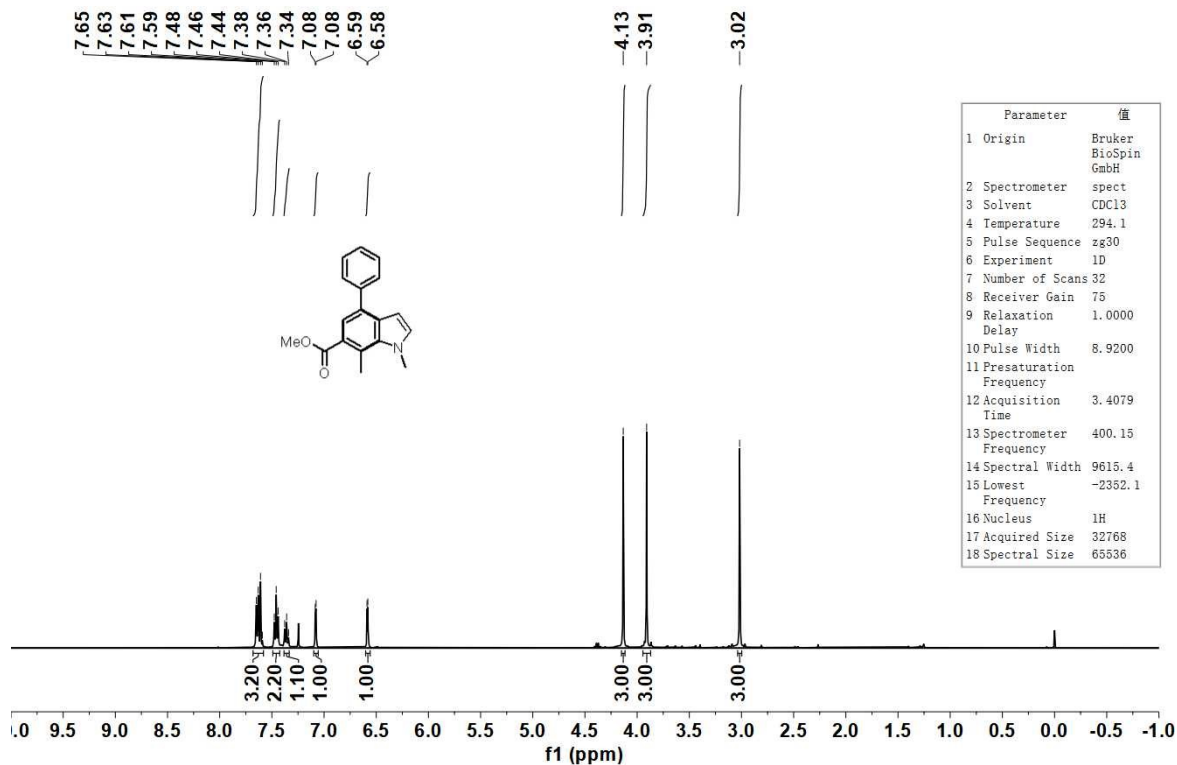


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	294.3
5 Pulse Sequence	zpgg30
6 Experiment	1D
7 Number of Scans	128
8 Receiver Gain	206.4
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

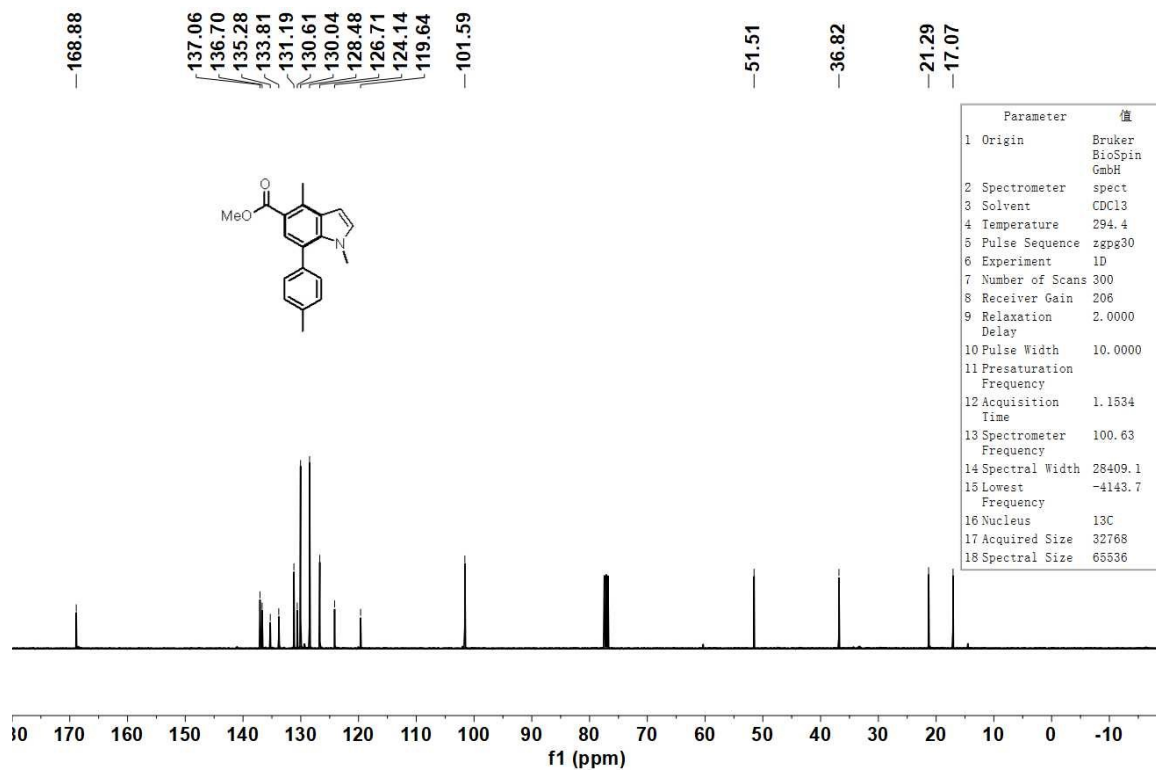
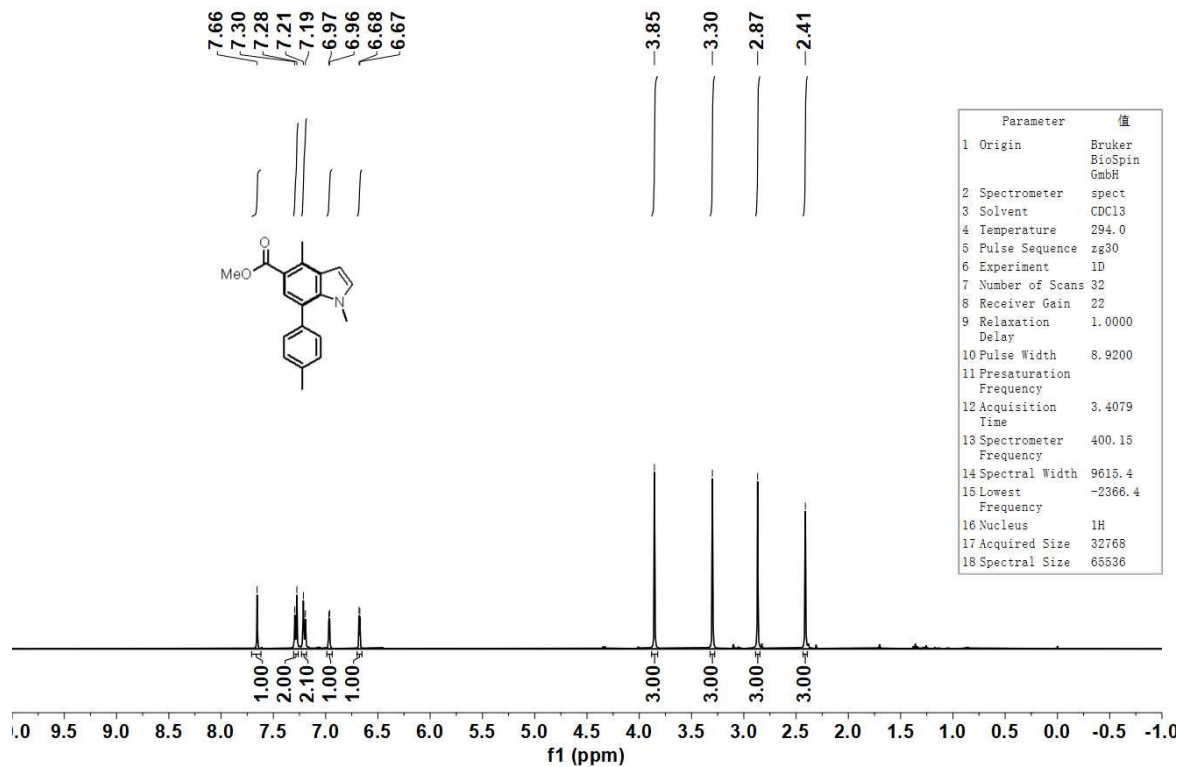
5a



6a

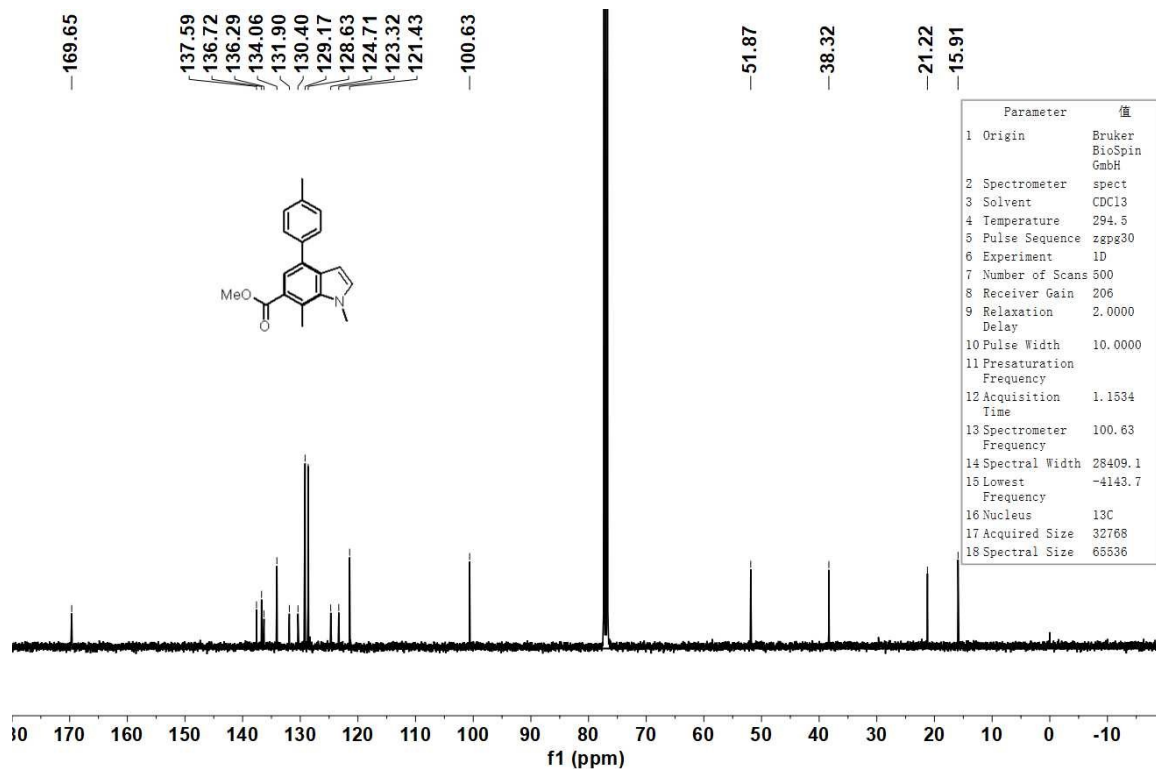
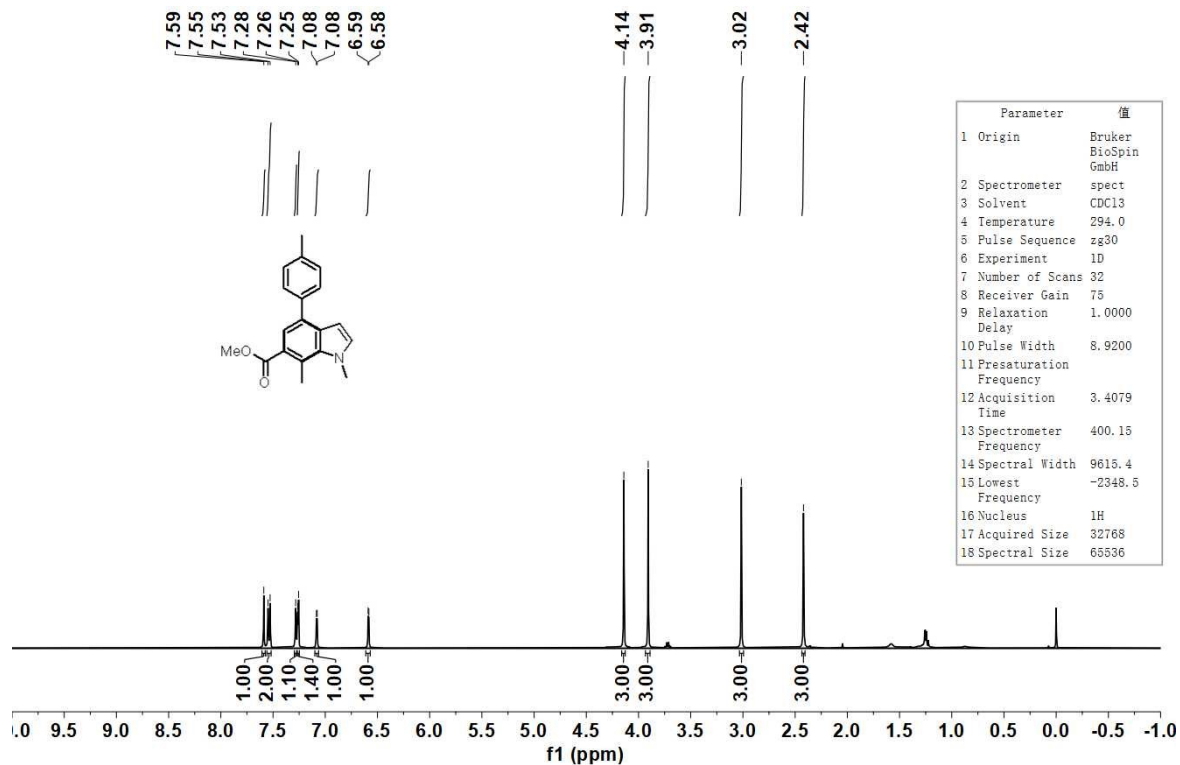


5b

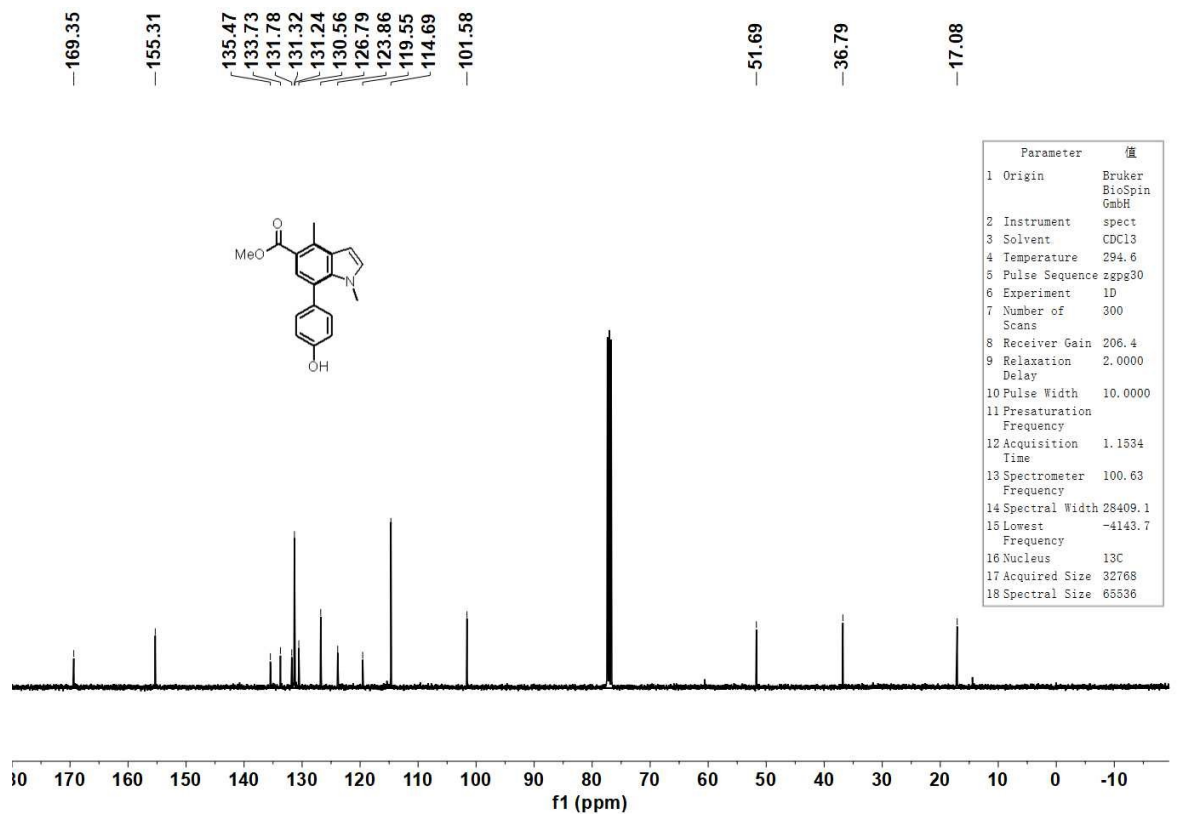
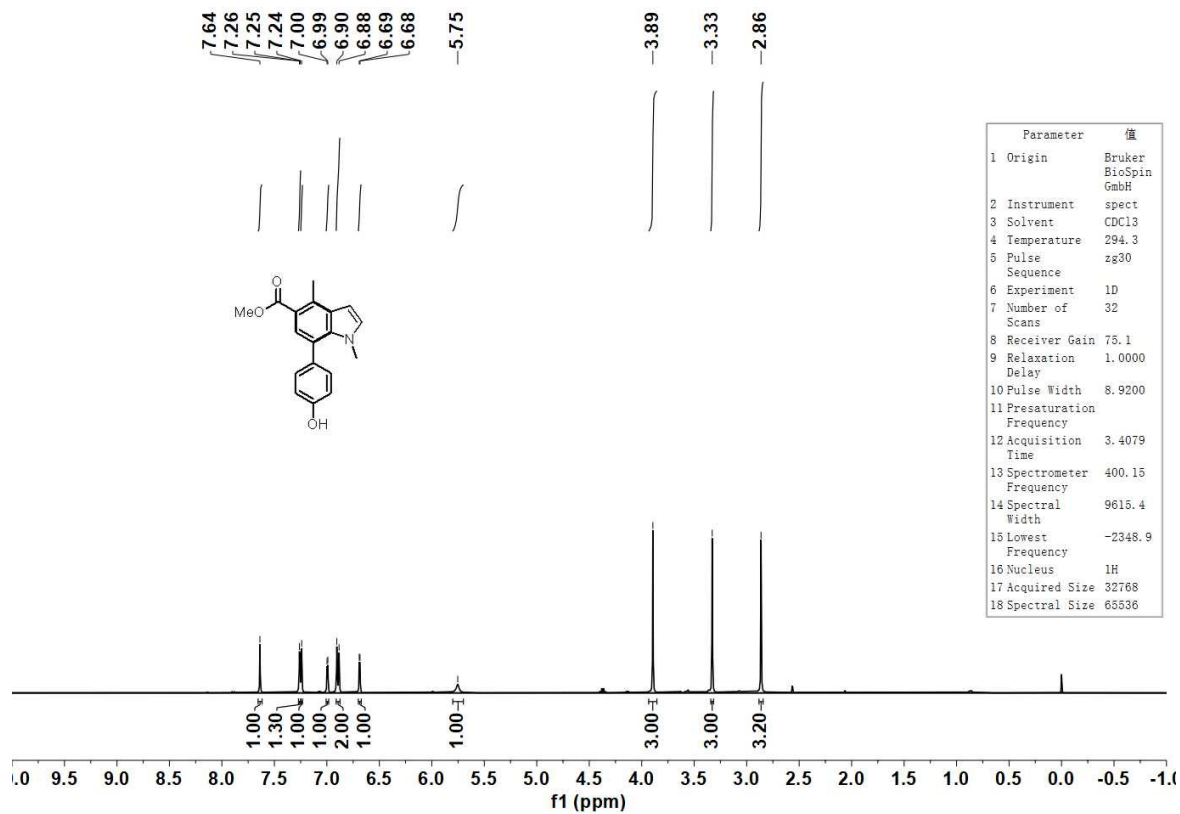




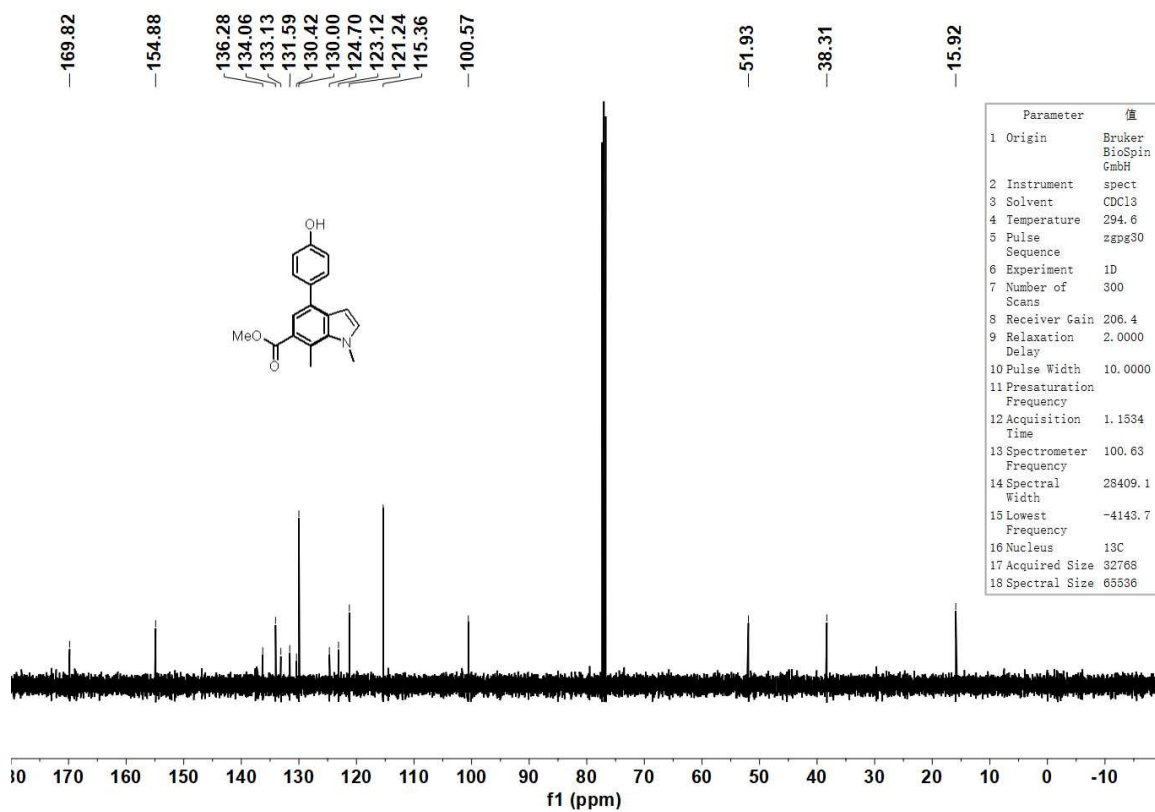
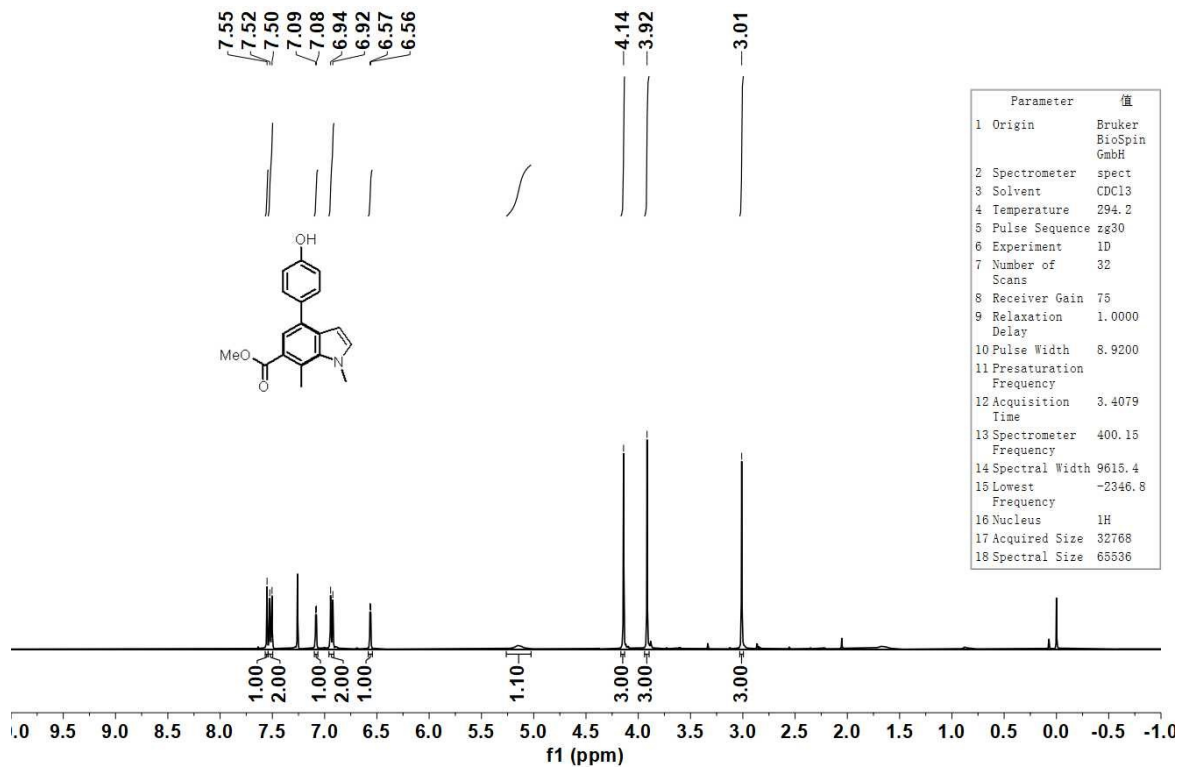
6b



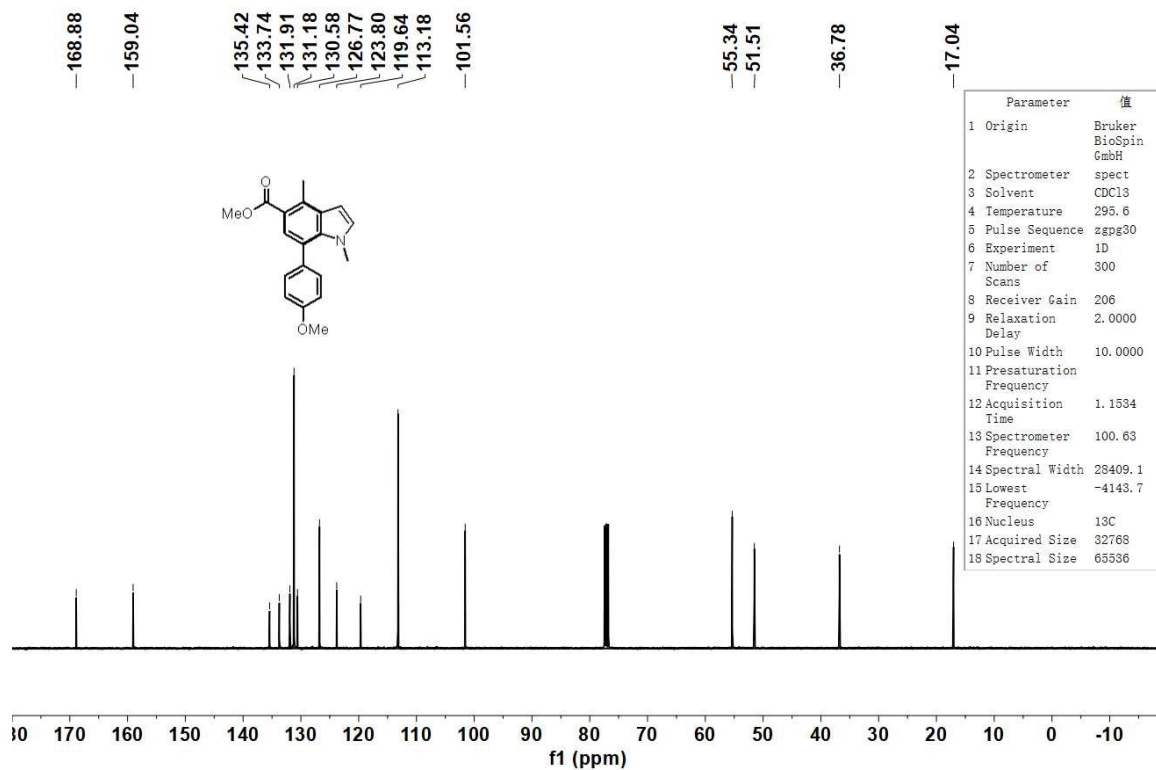
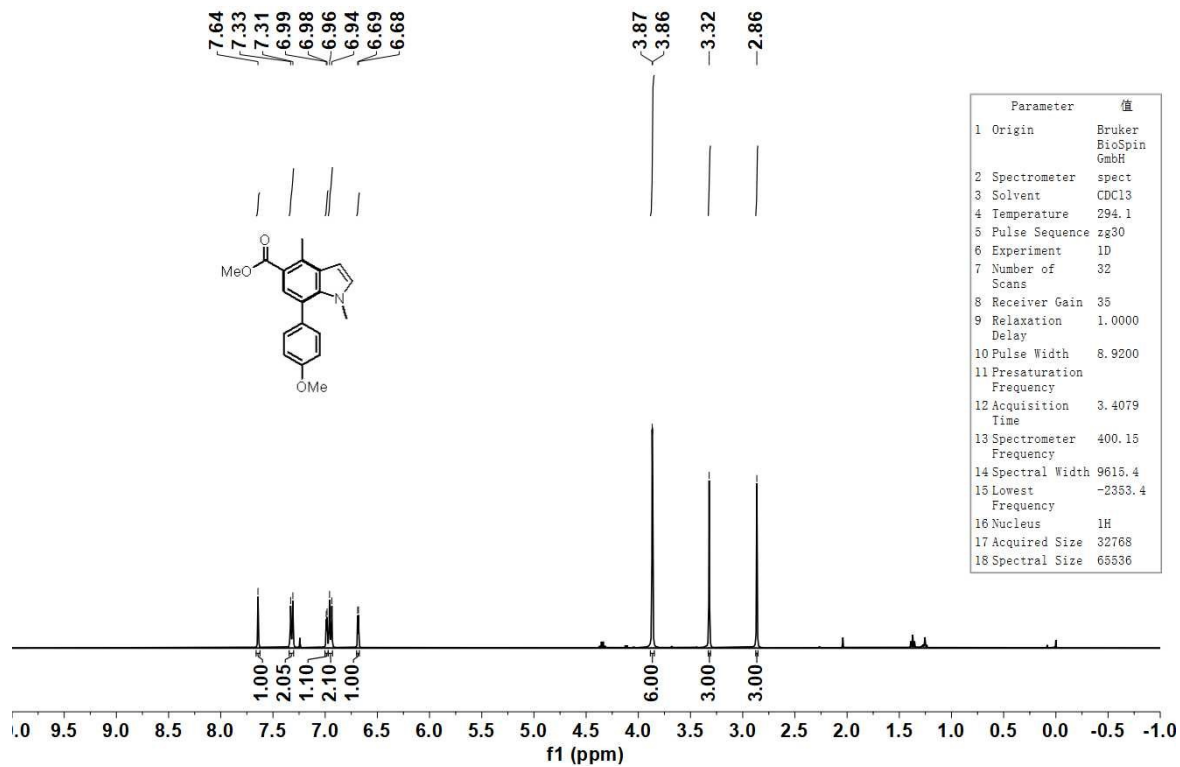
5c



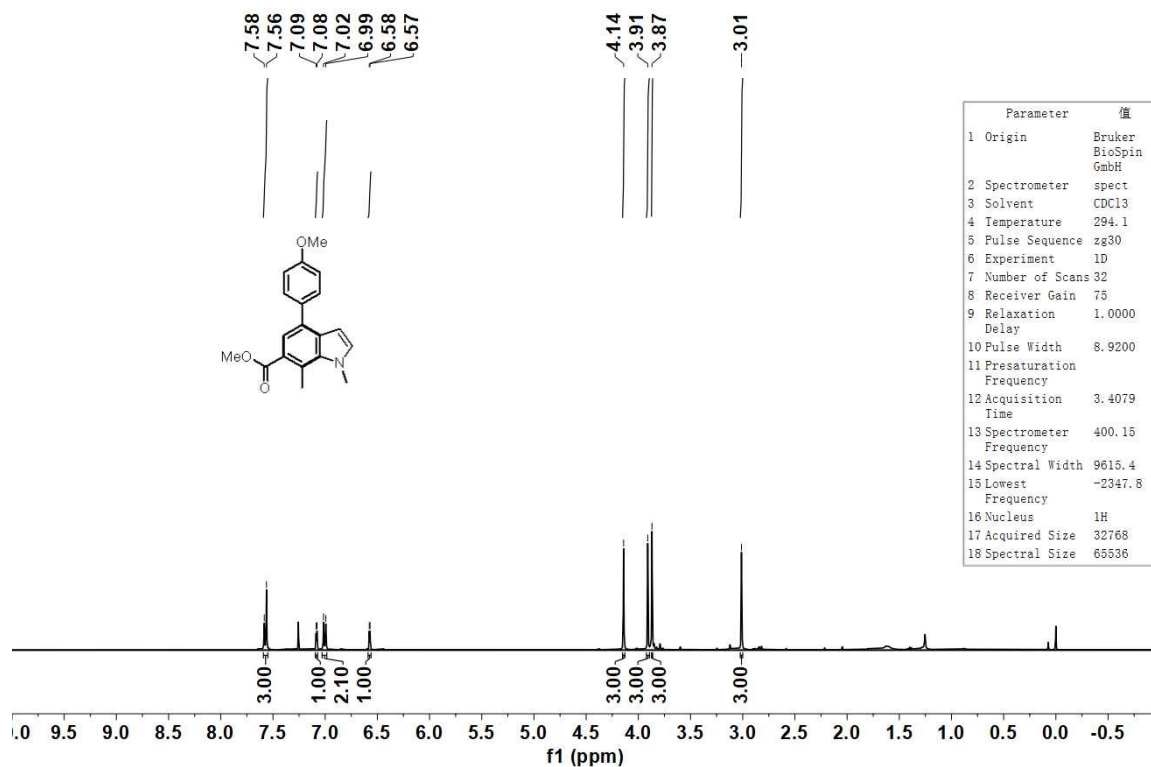
6c



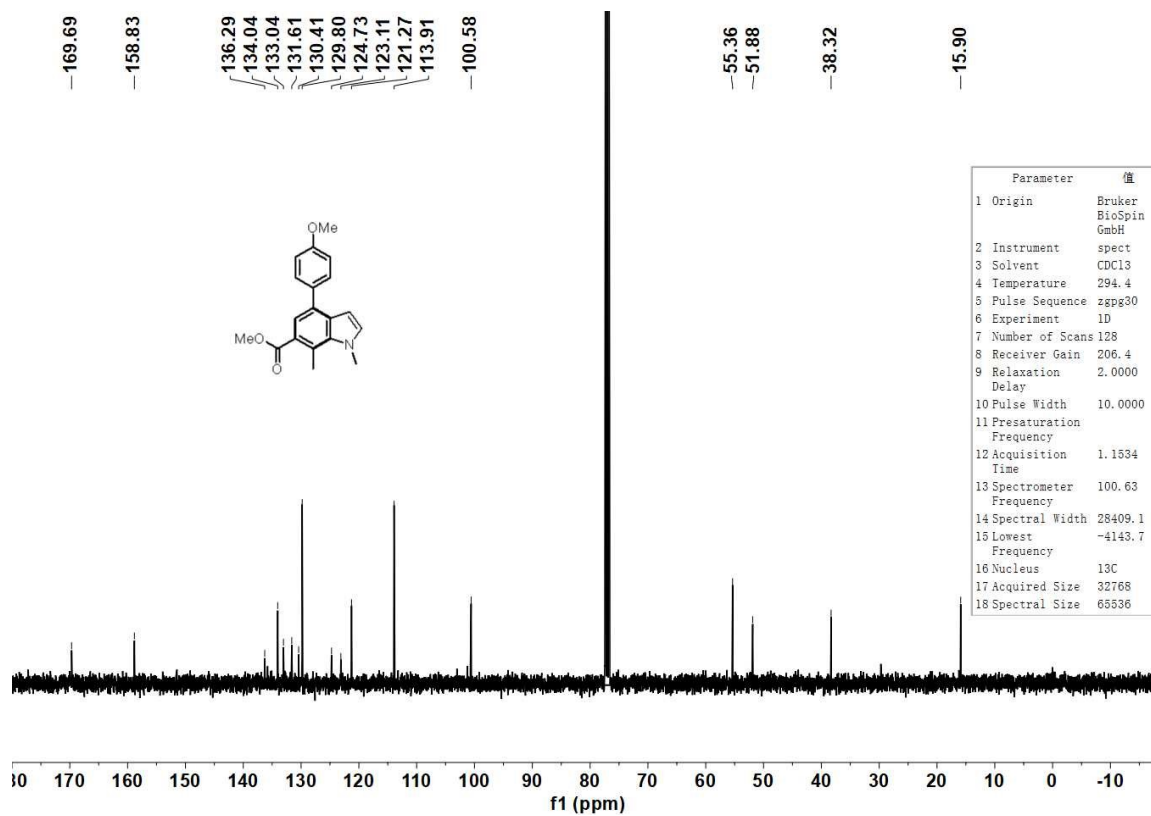
5d



6d

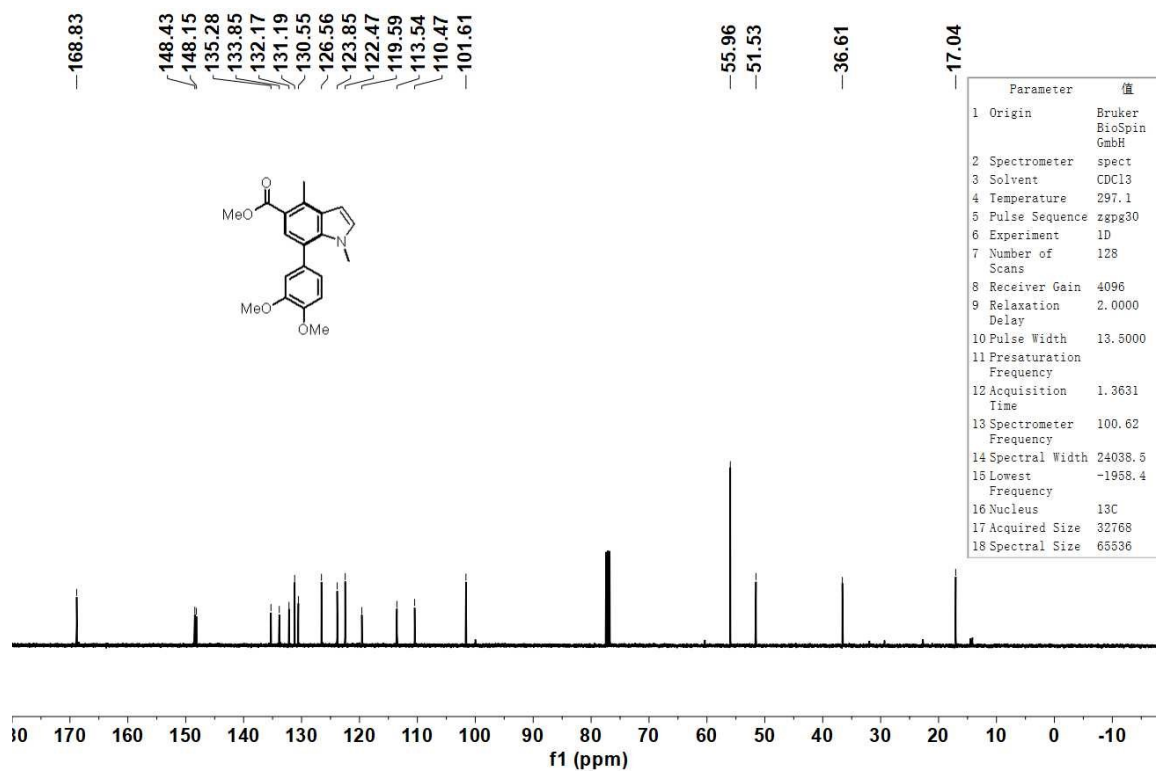
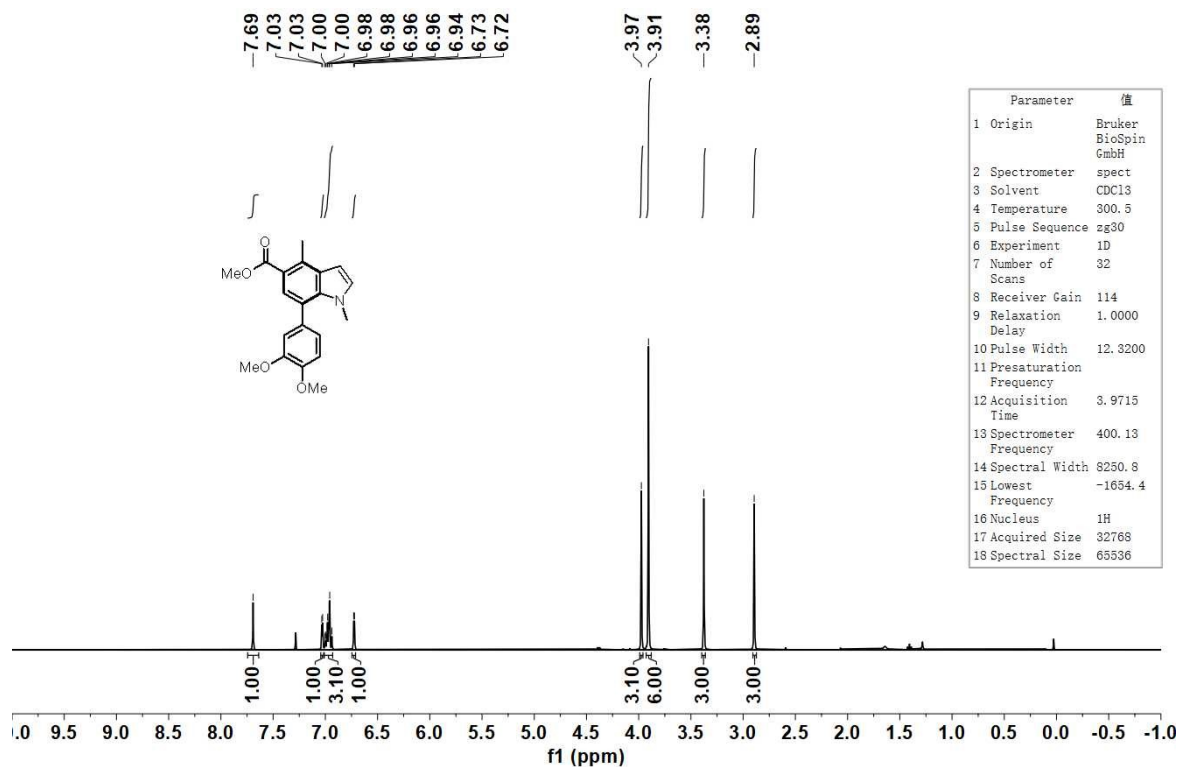


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	32
8 Receiver Gain	75
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2347.8
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

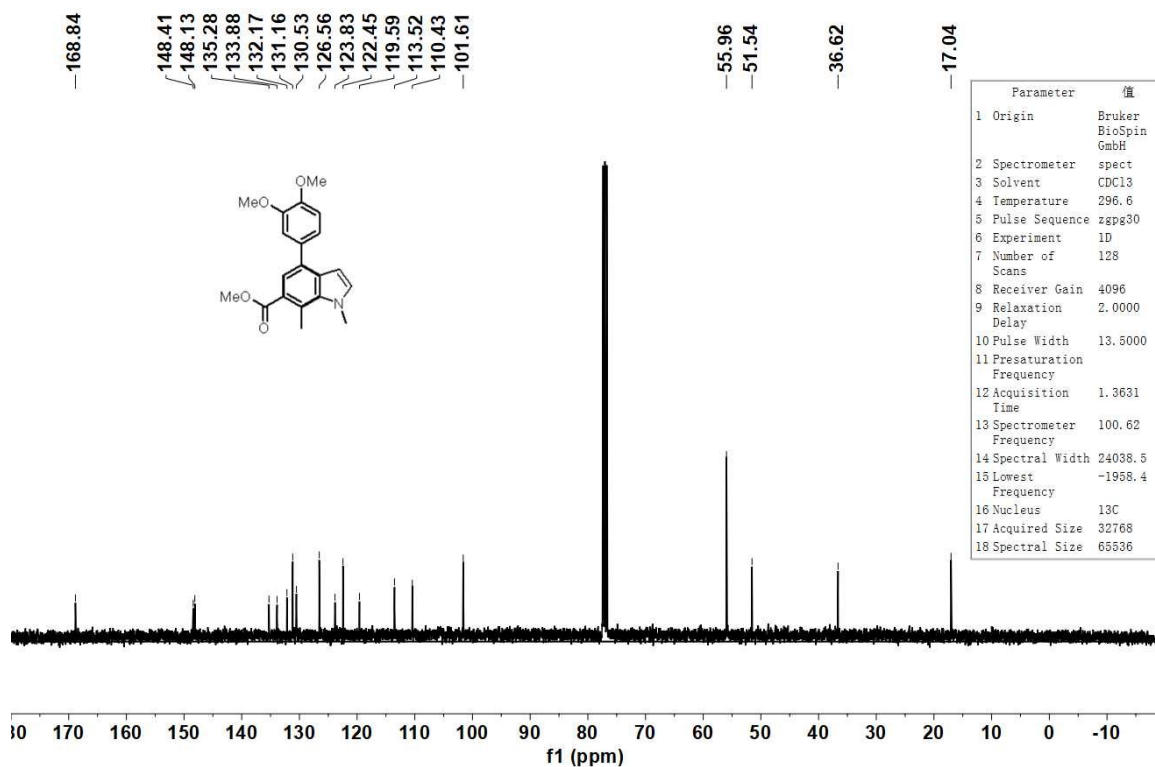
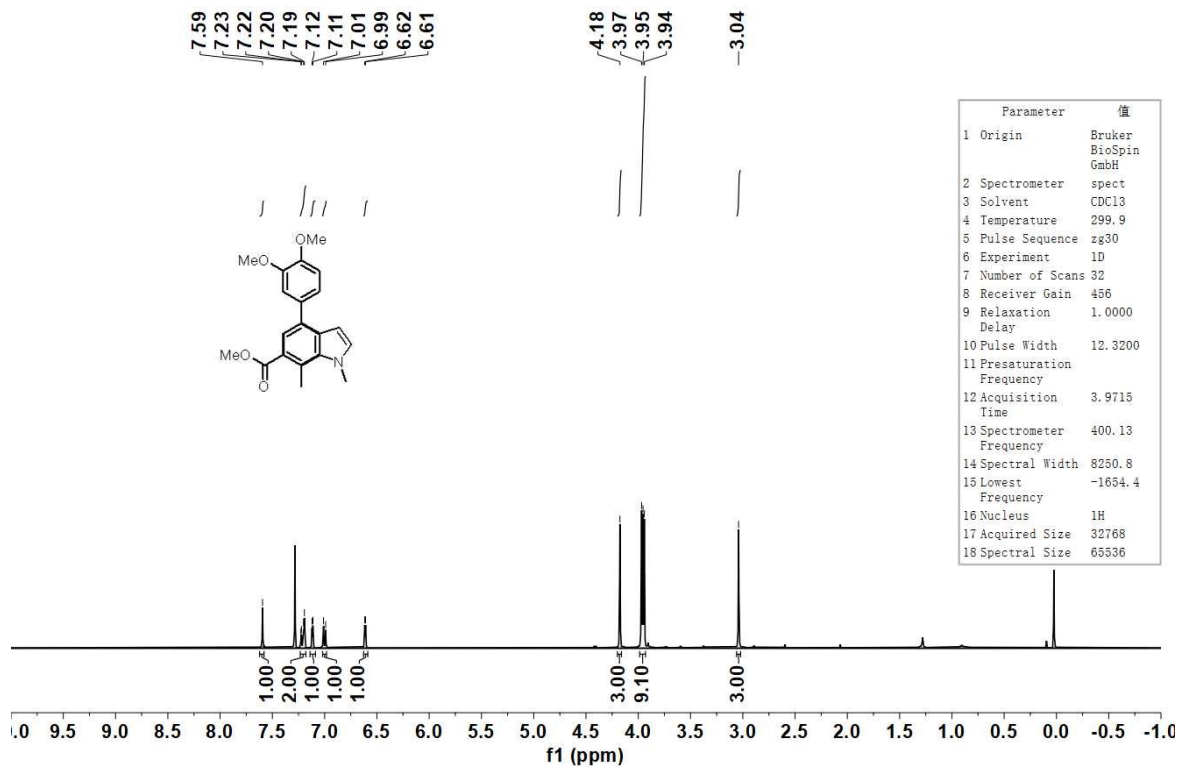


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	294.4
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Number of Scans	128
8 Receiver Gain	206.4
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

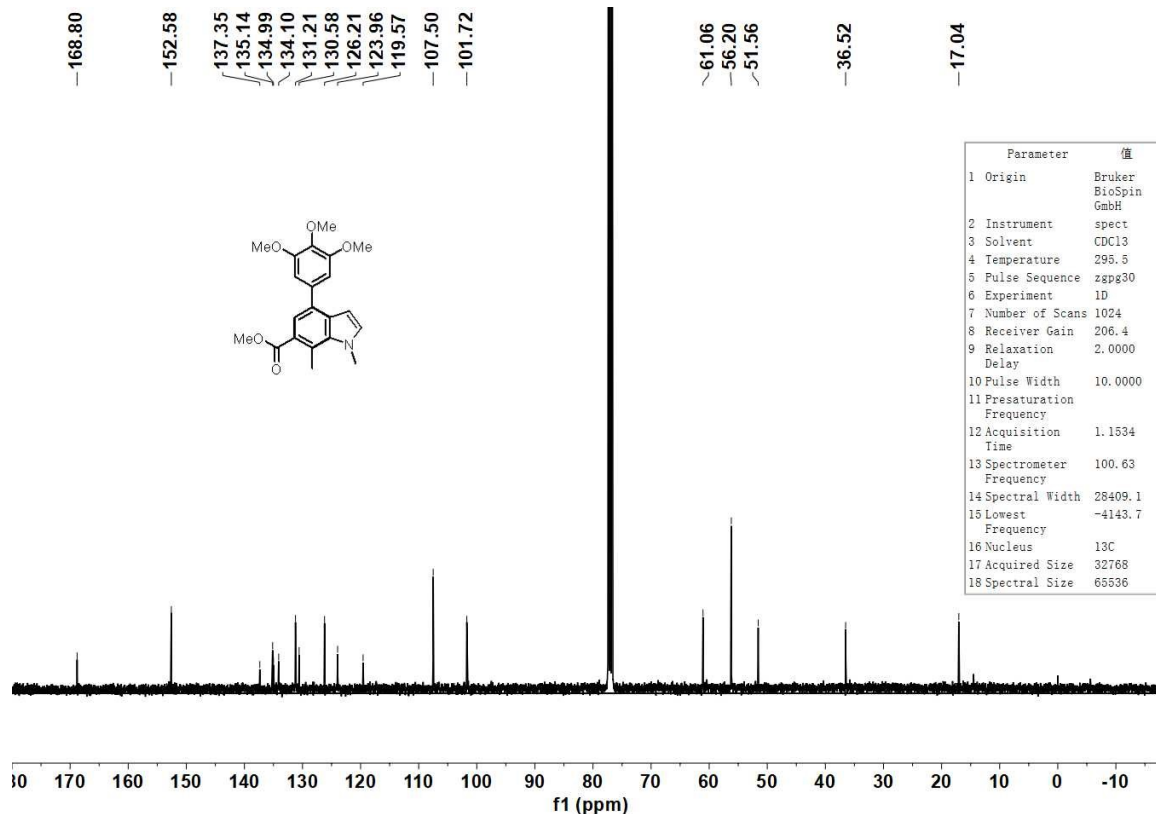
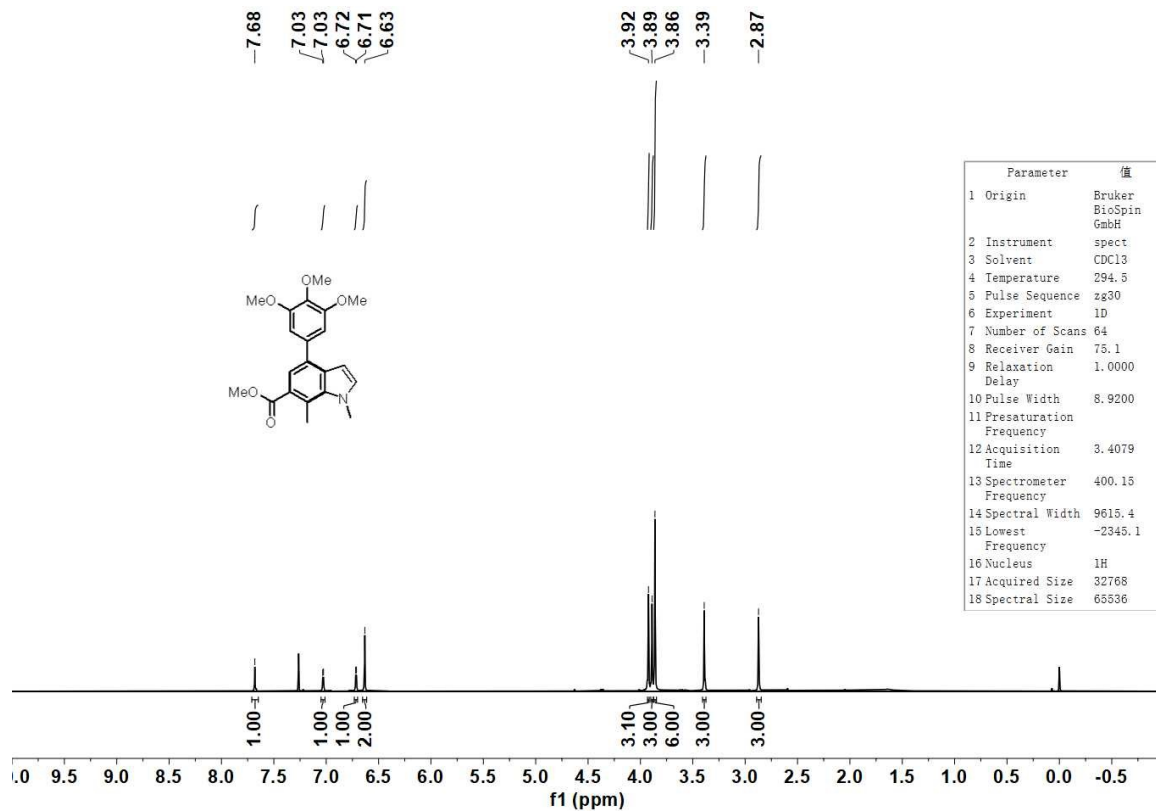
5e



6e

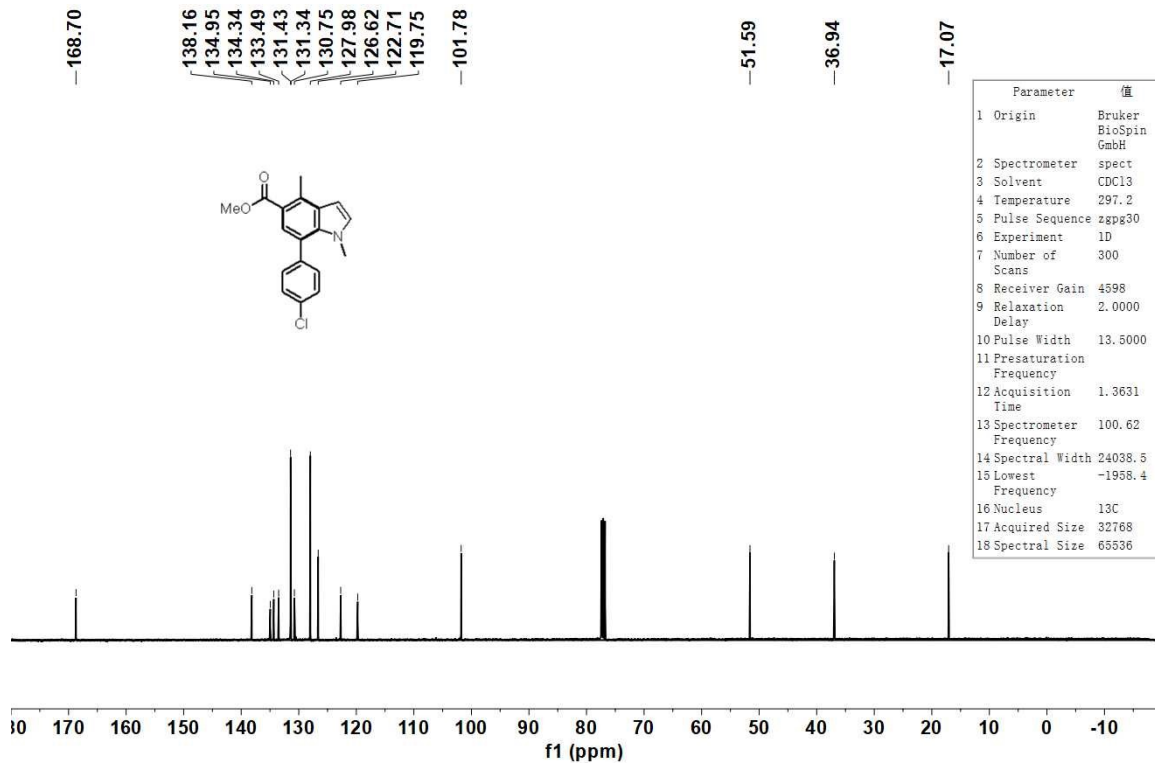
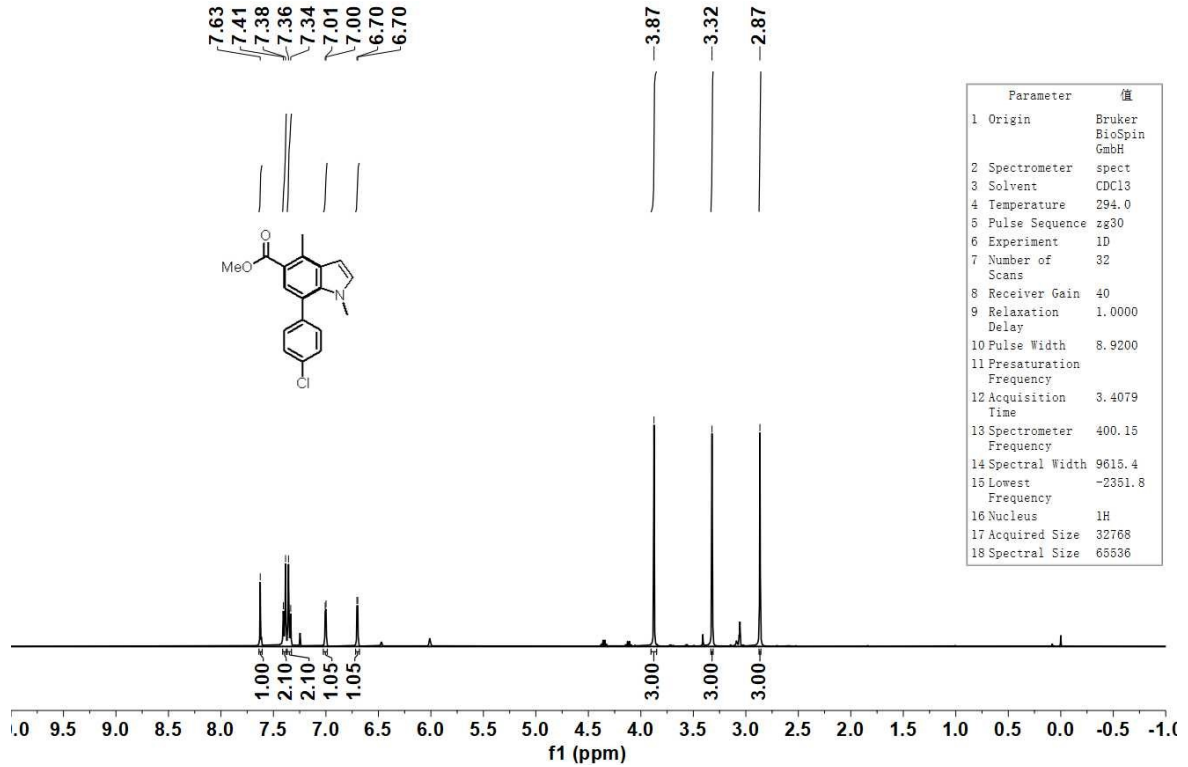


5f

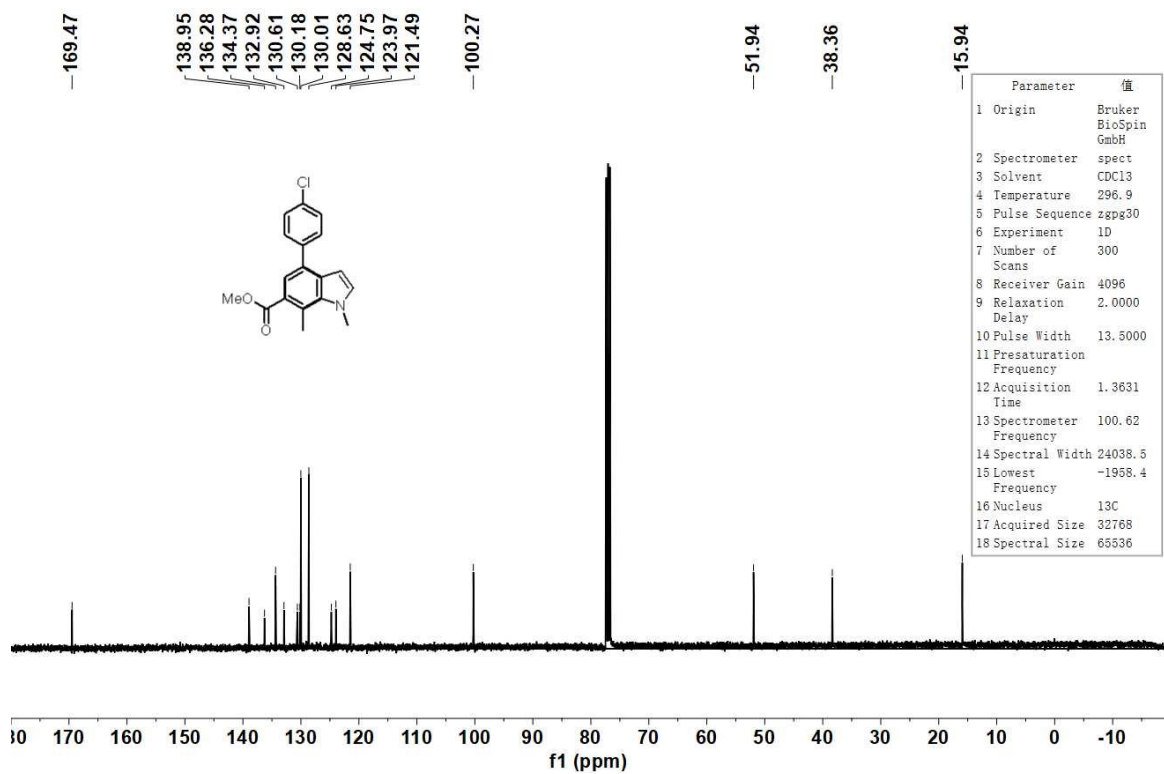
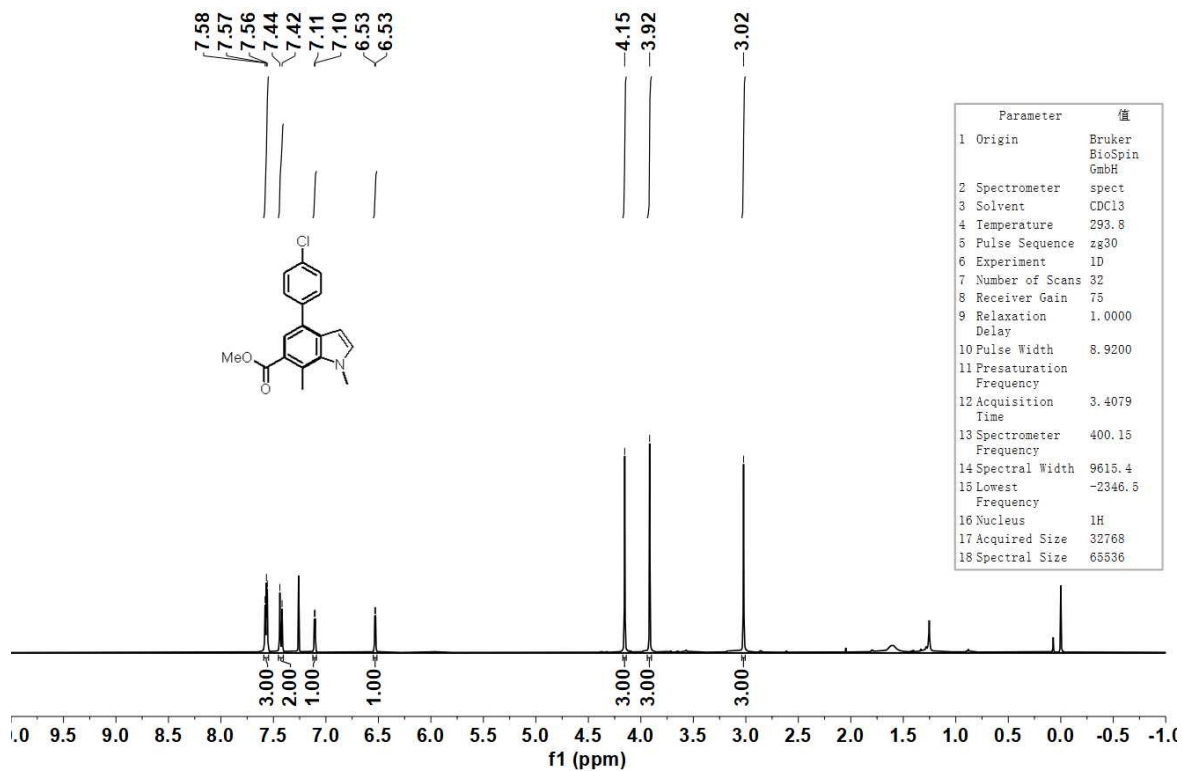




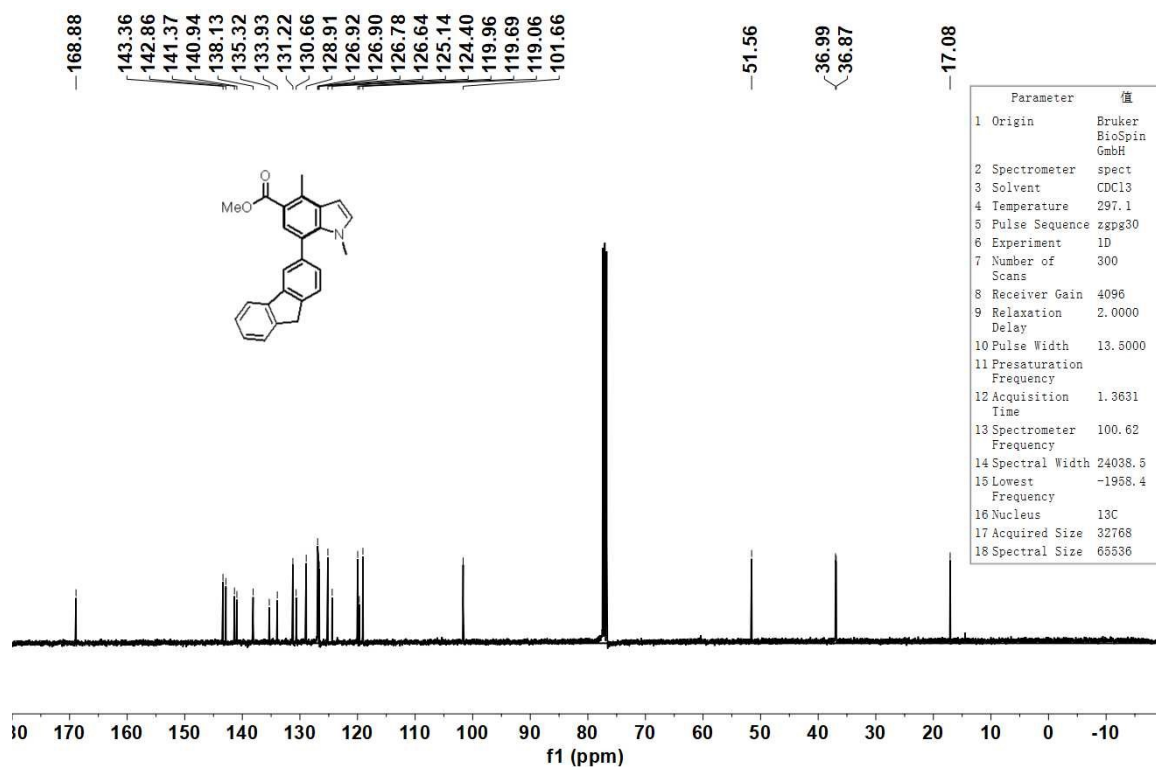
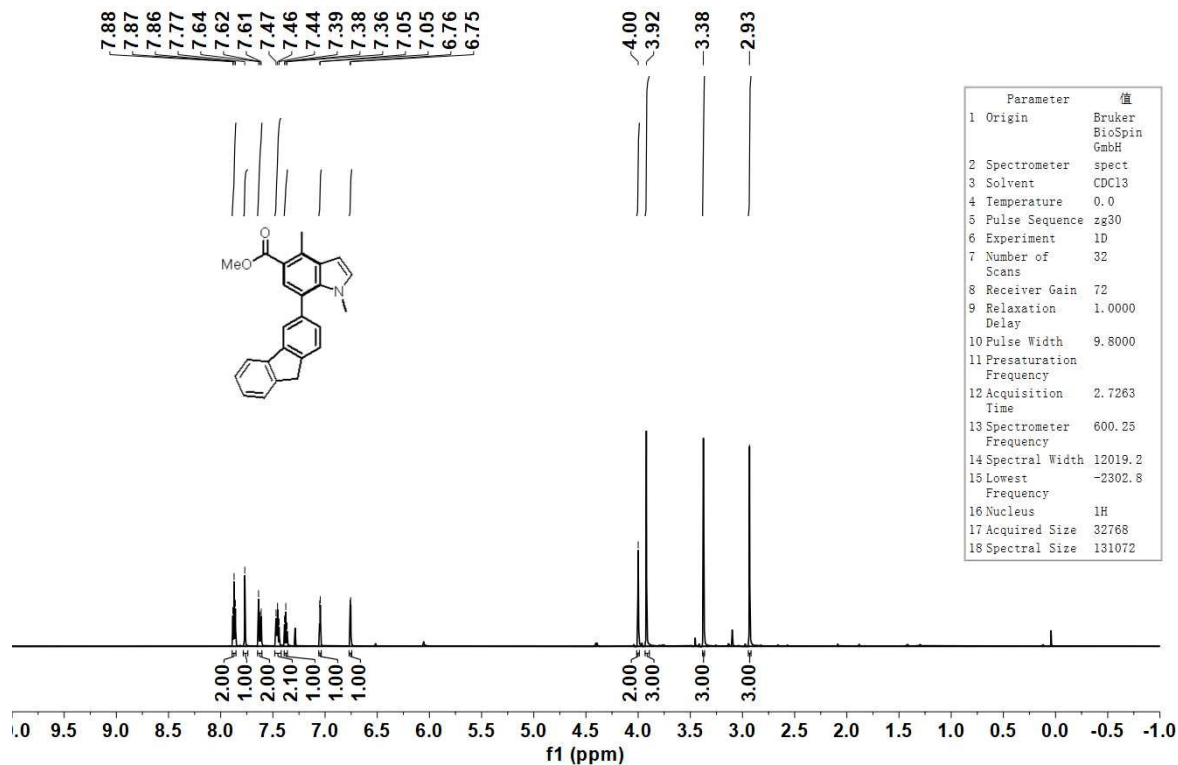
5g



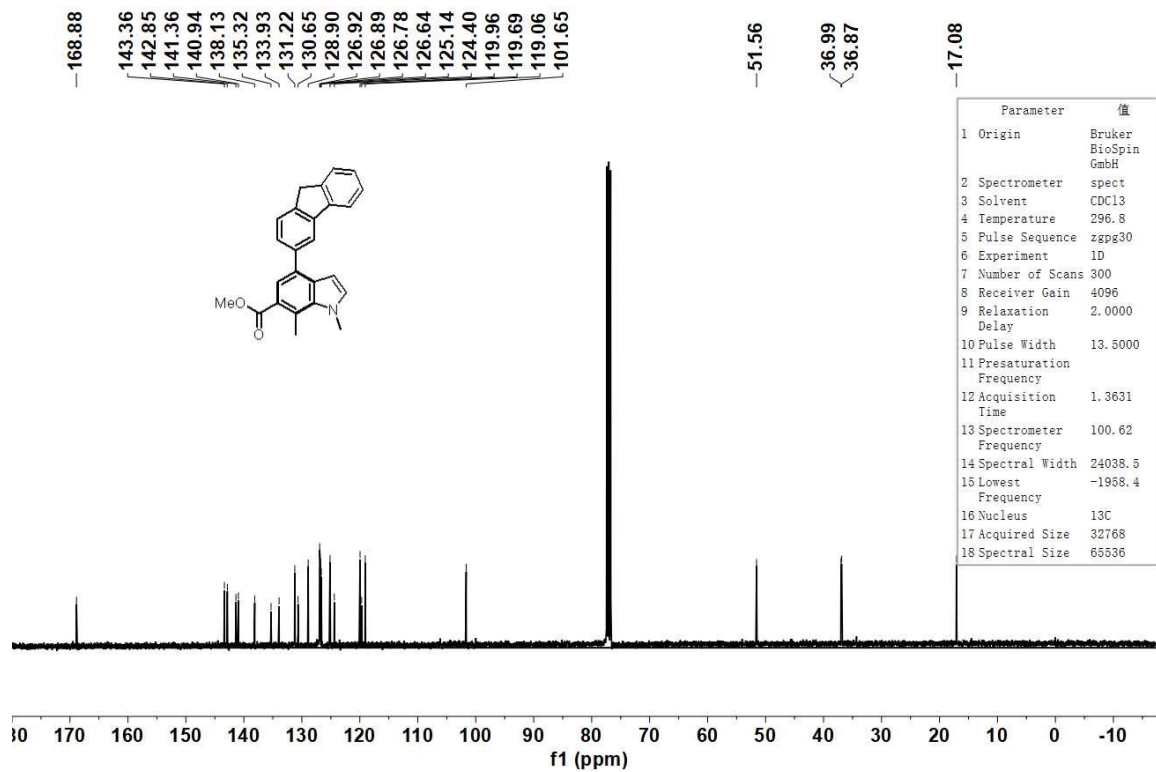
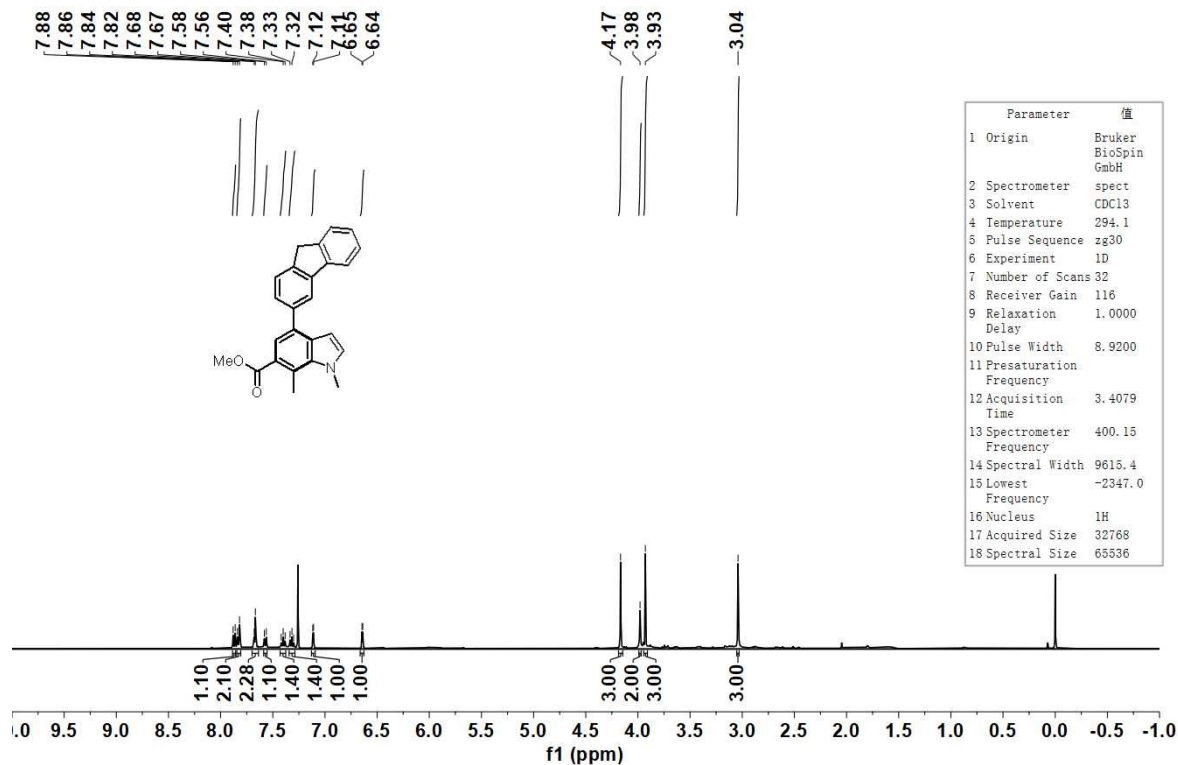
6g



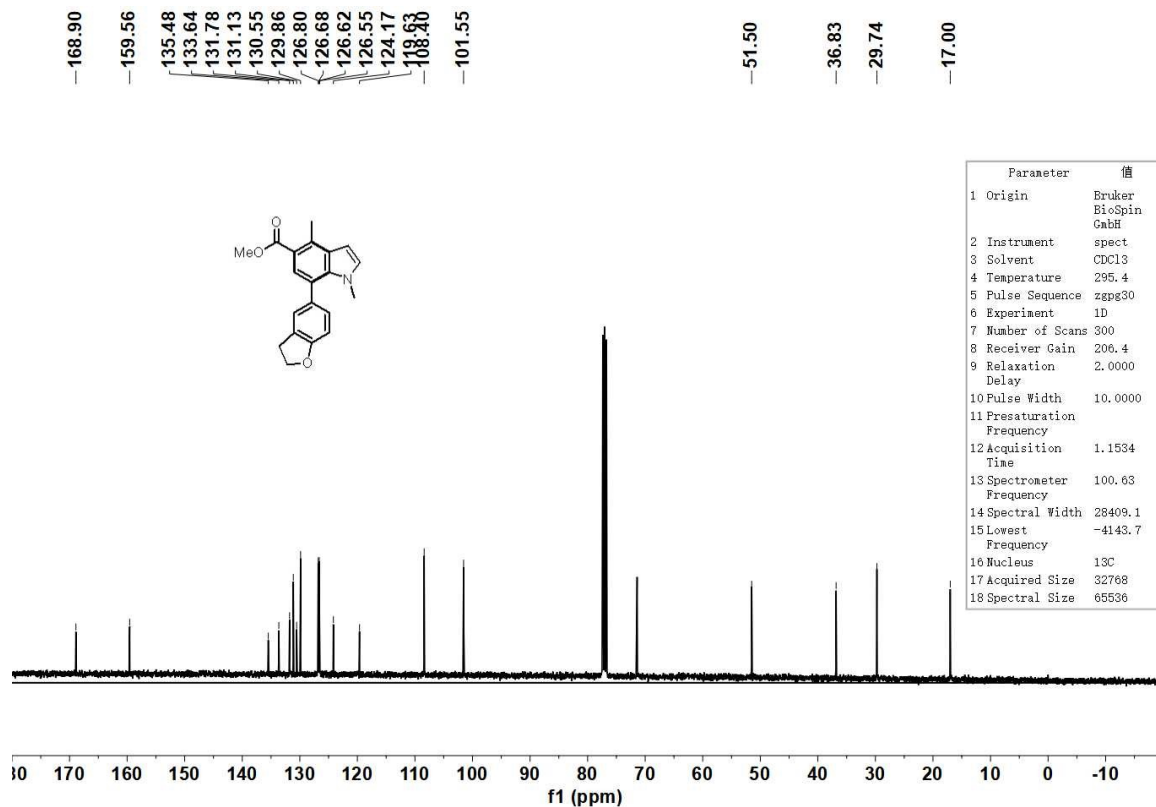
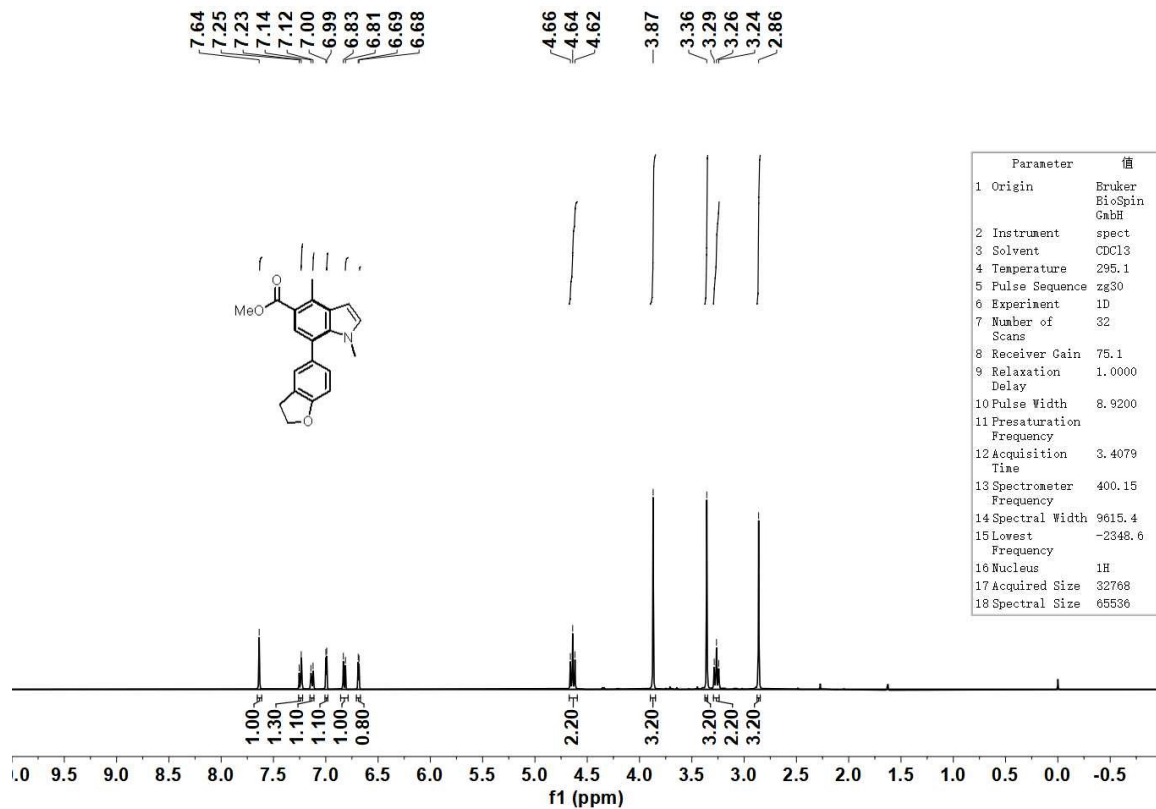
5h



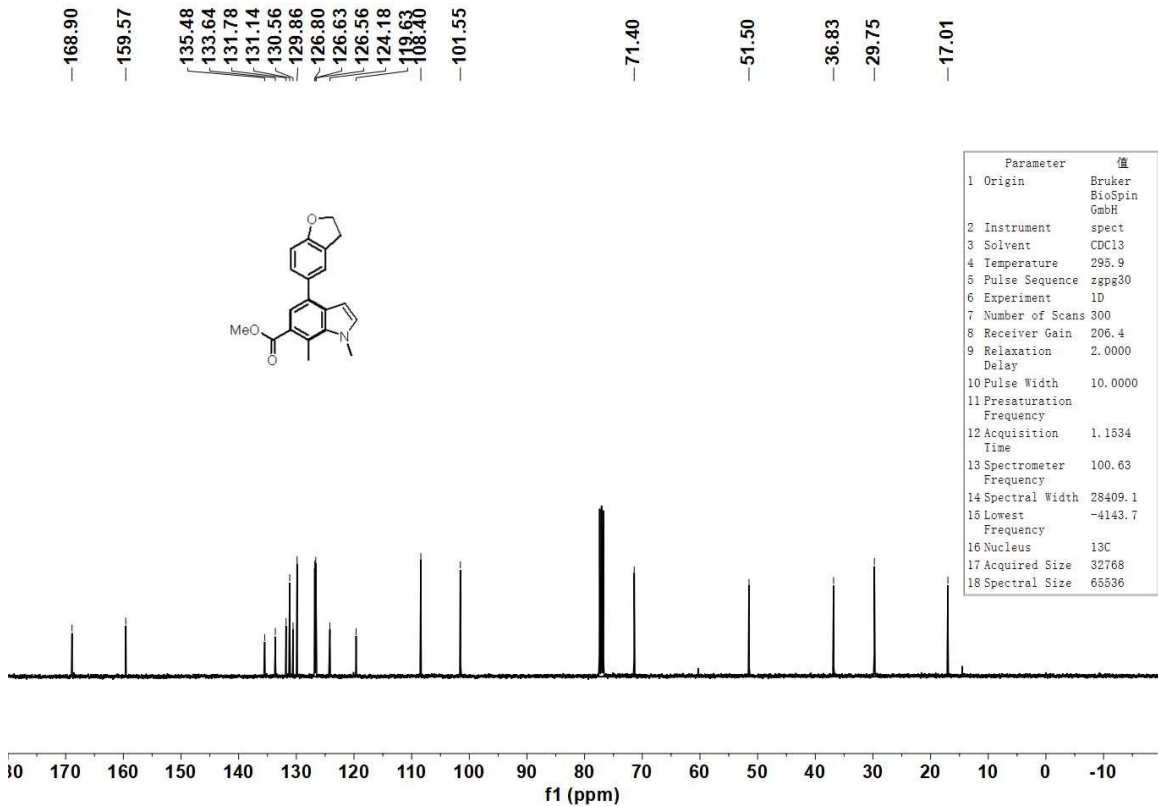
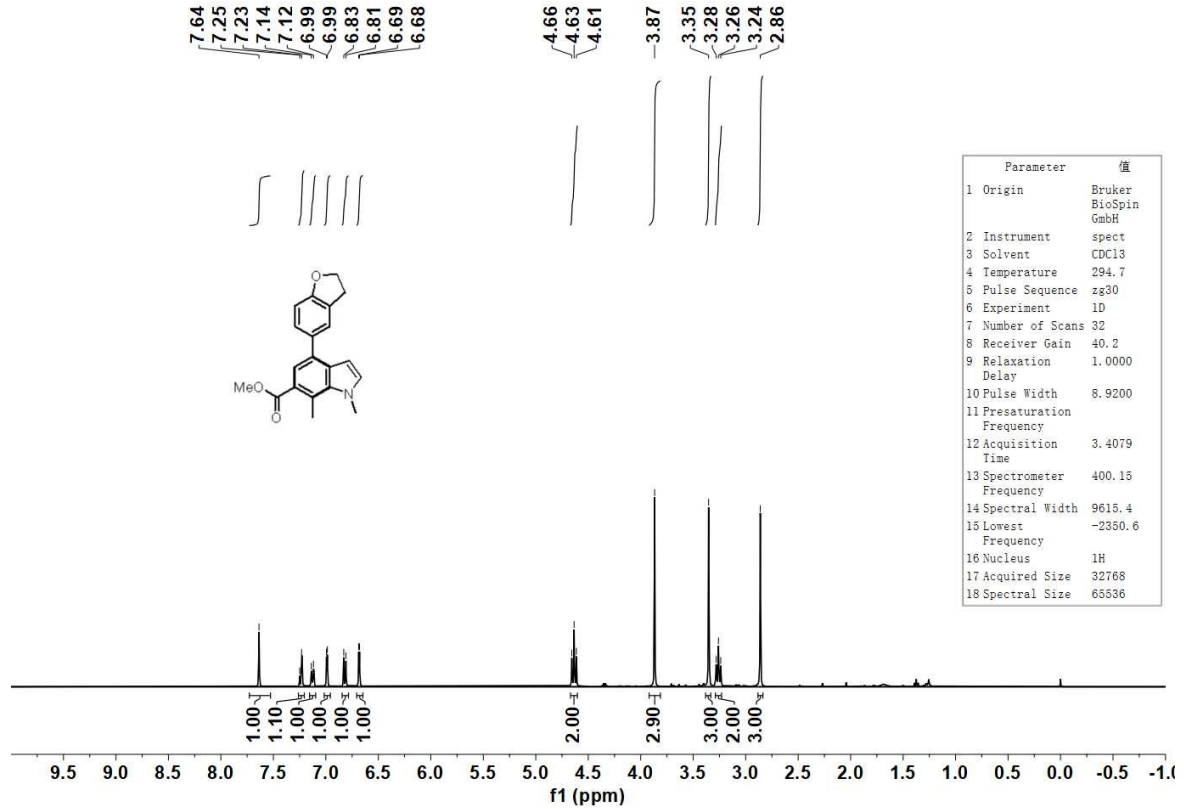
6h



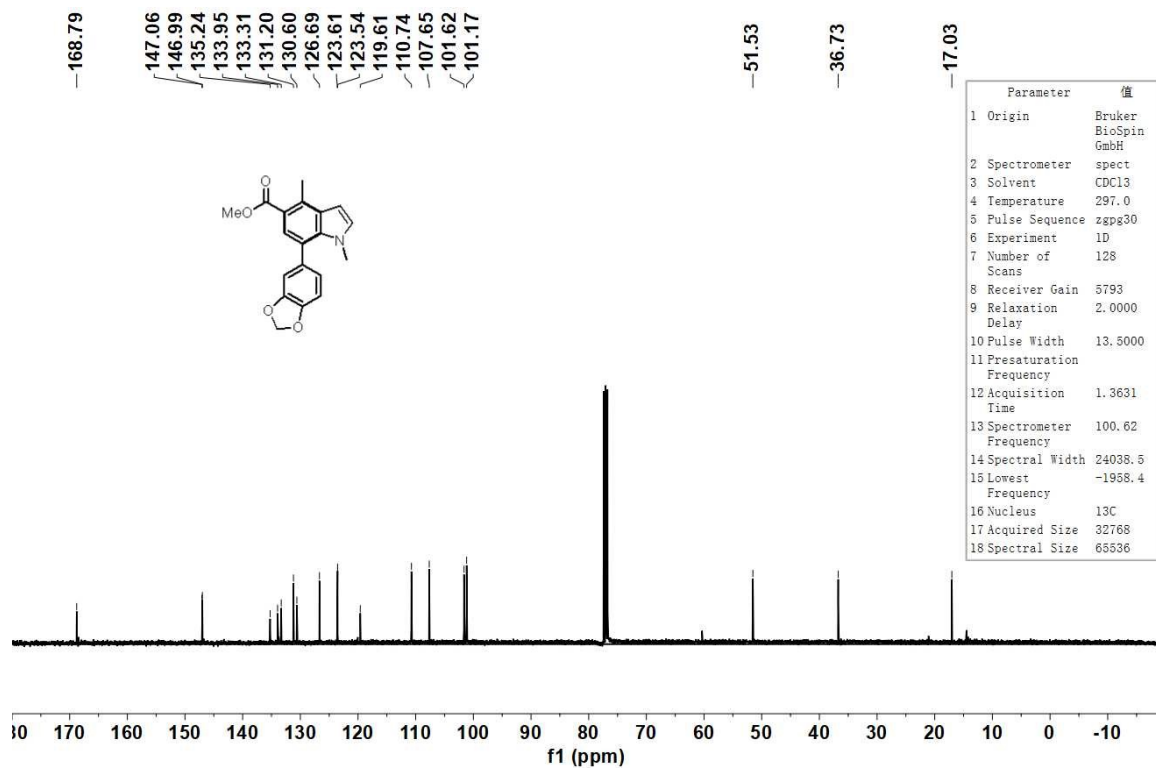
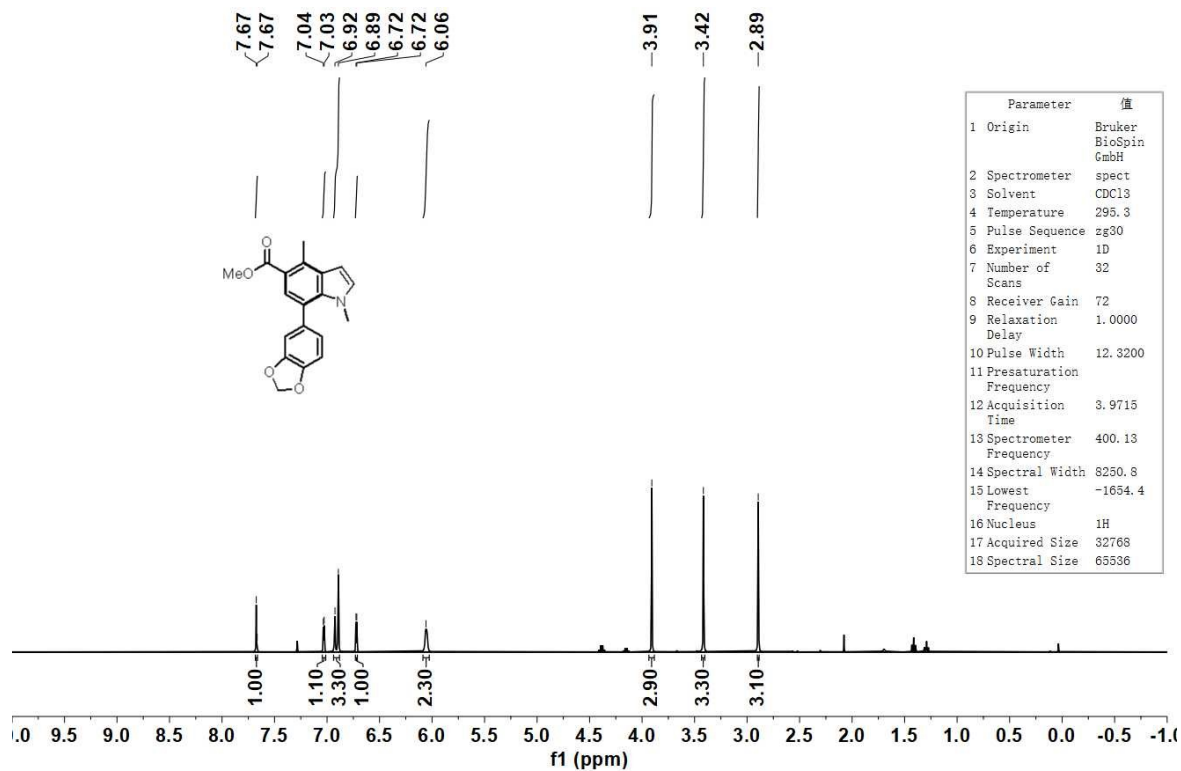
5i



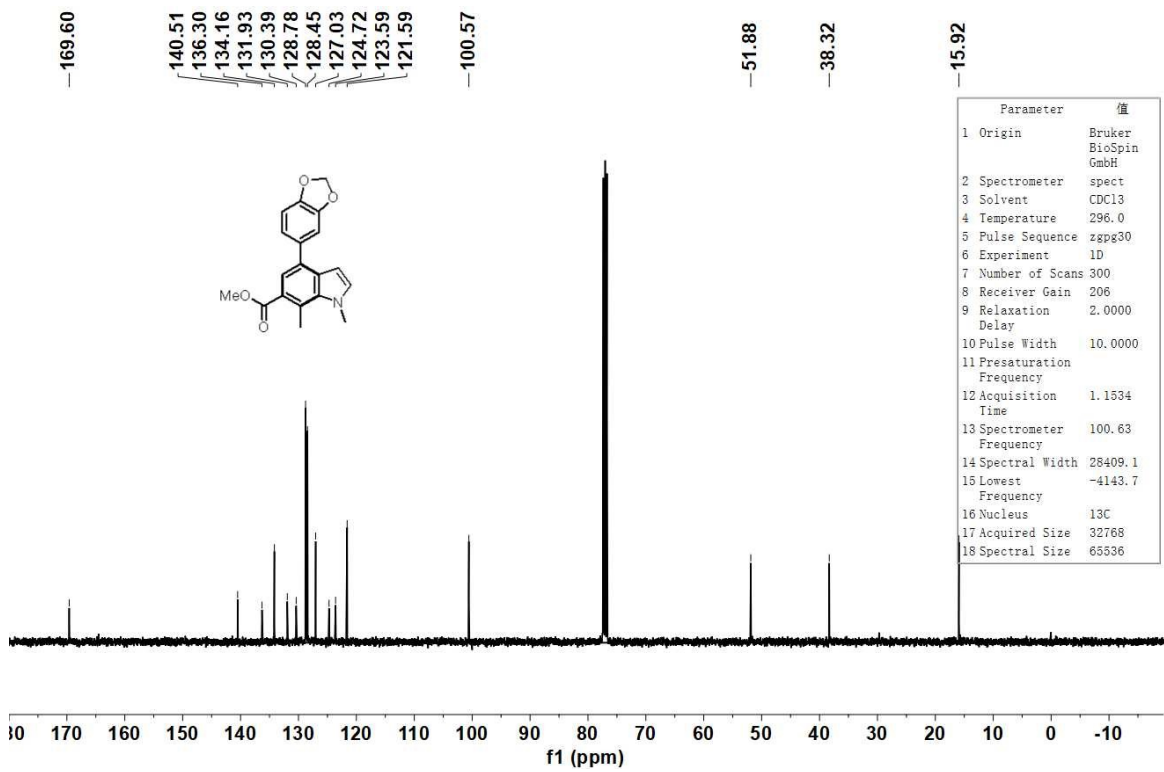
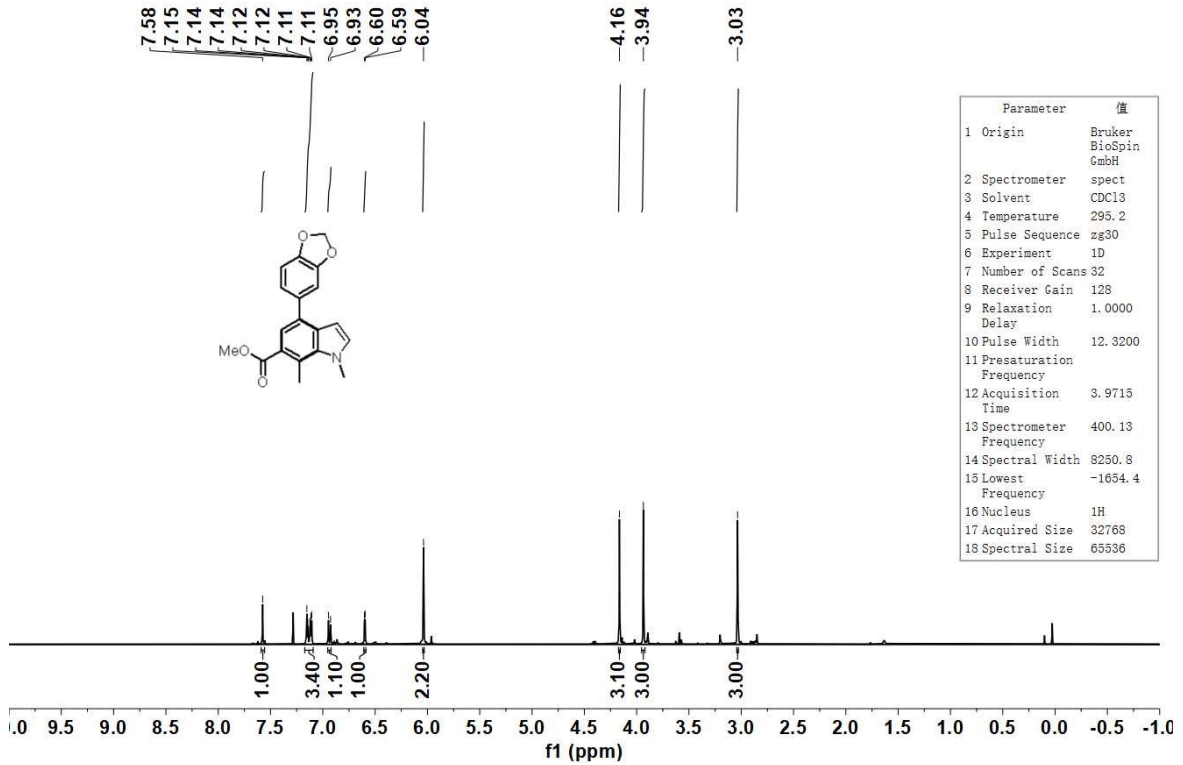
6i



5j

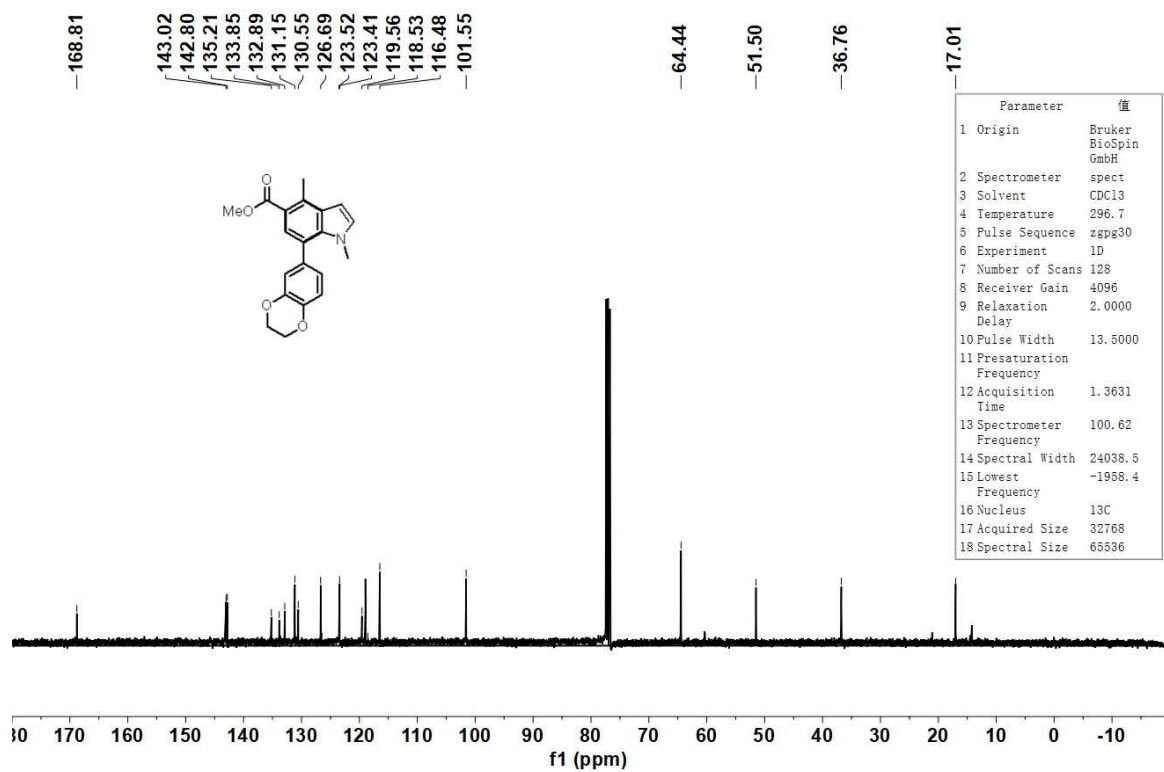
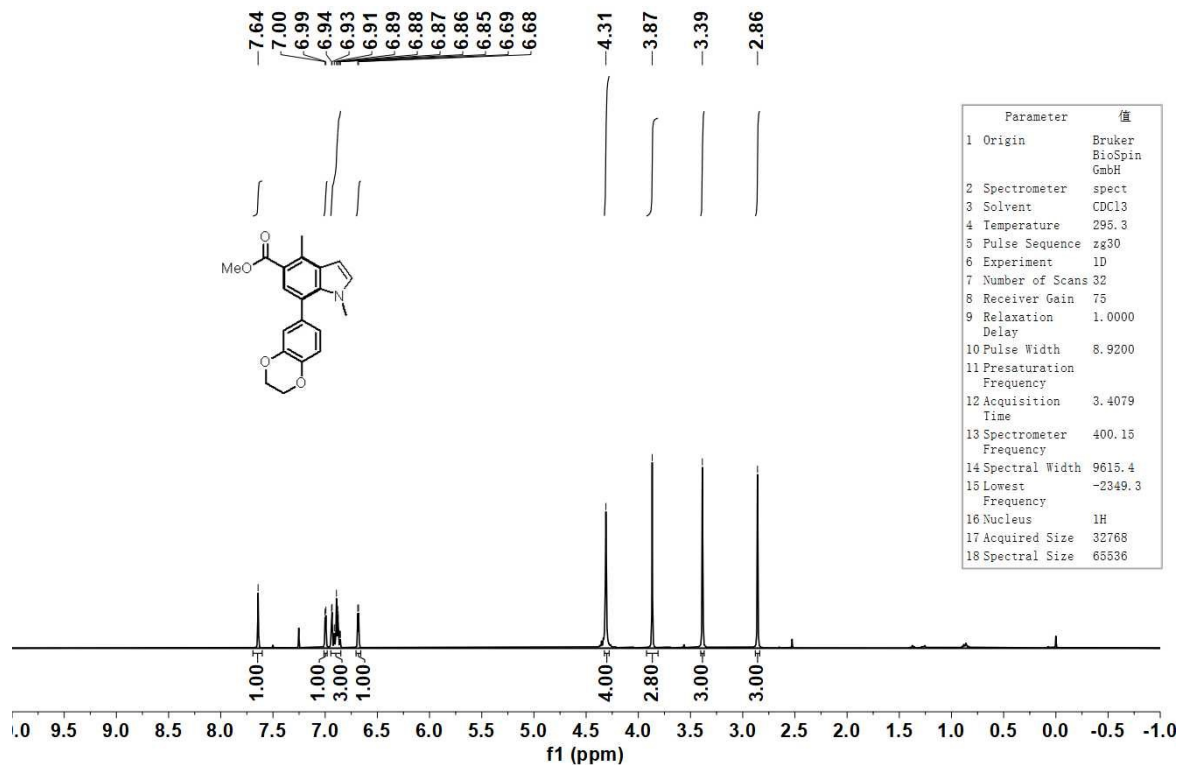


6j

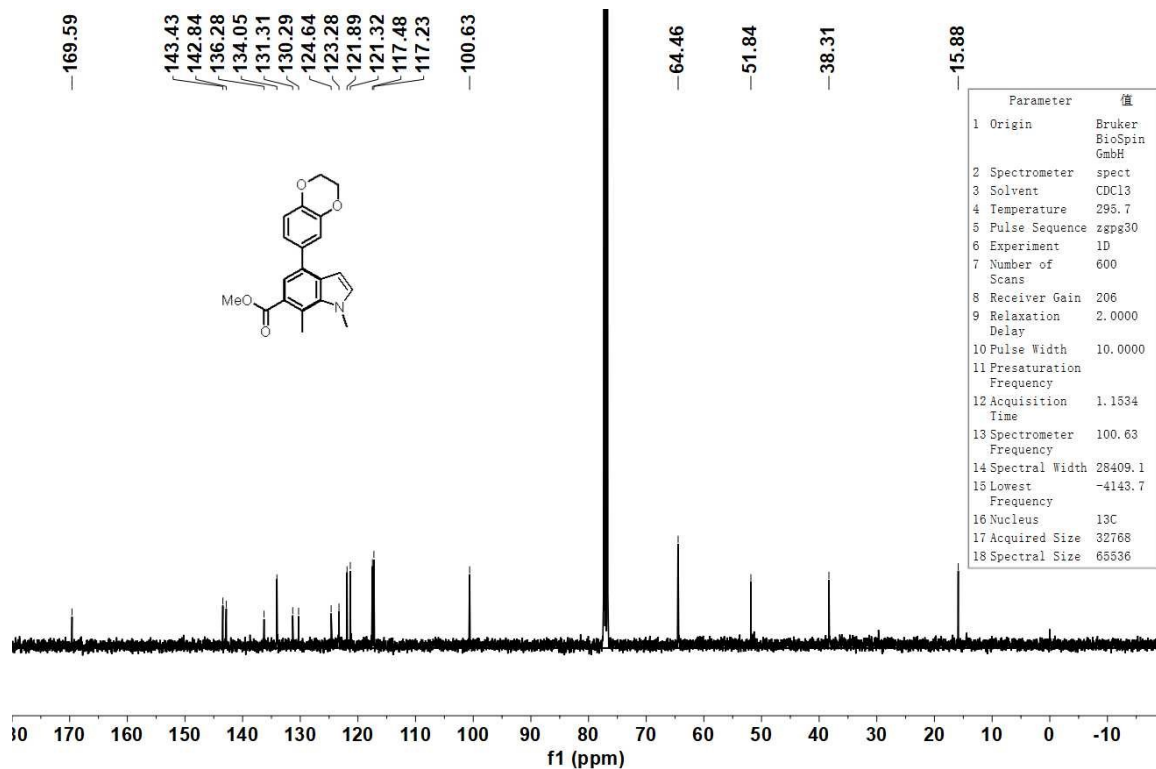
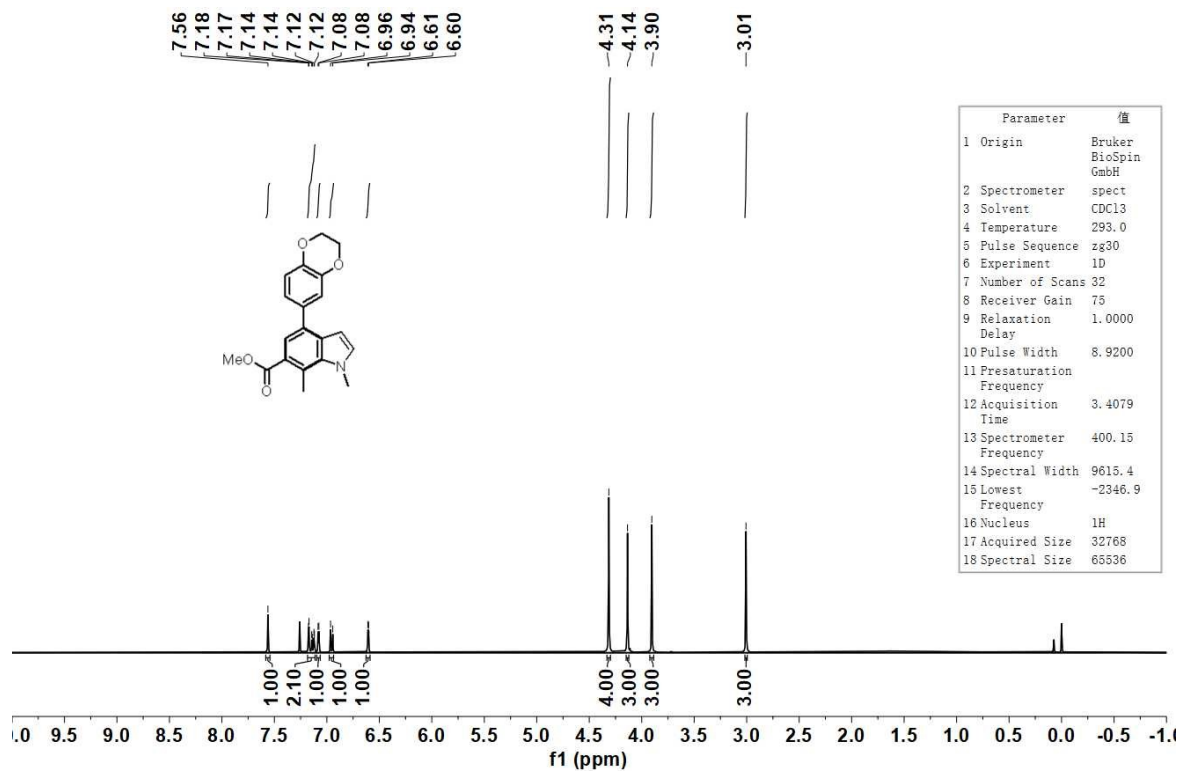




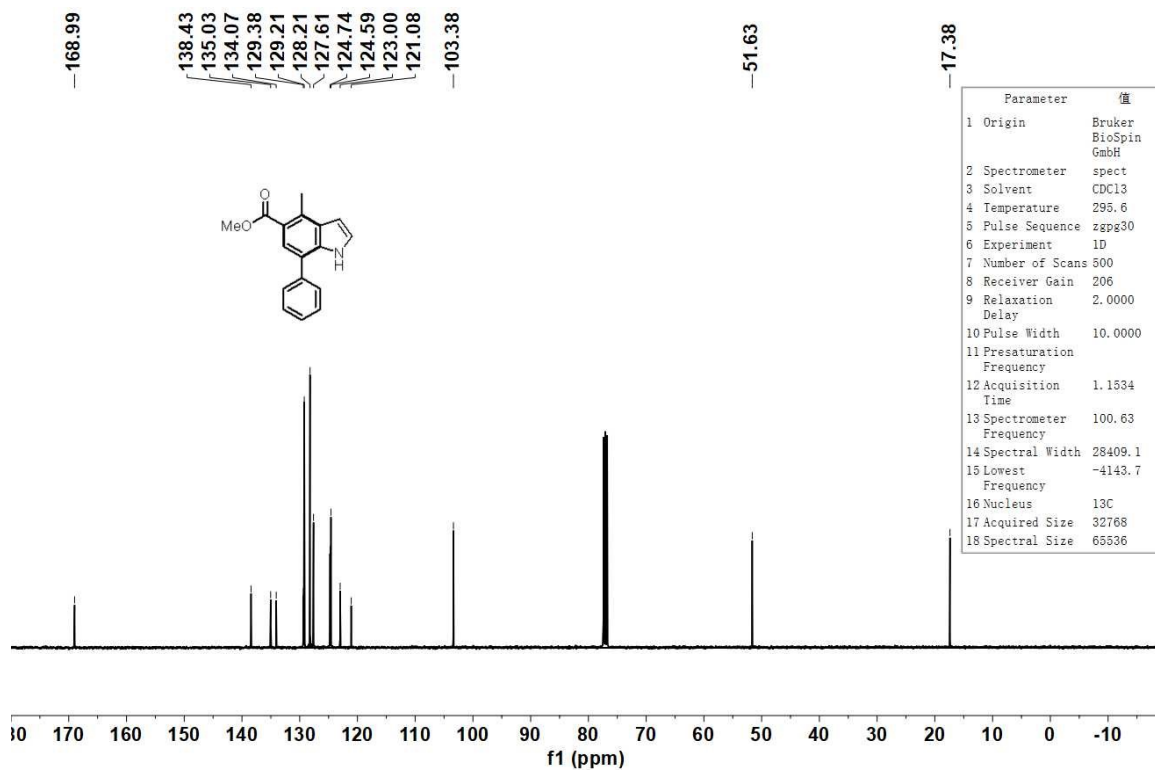
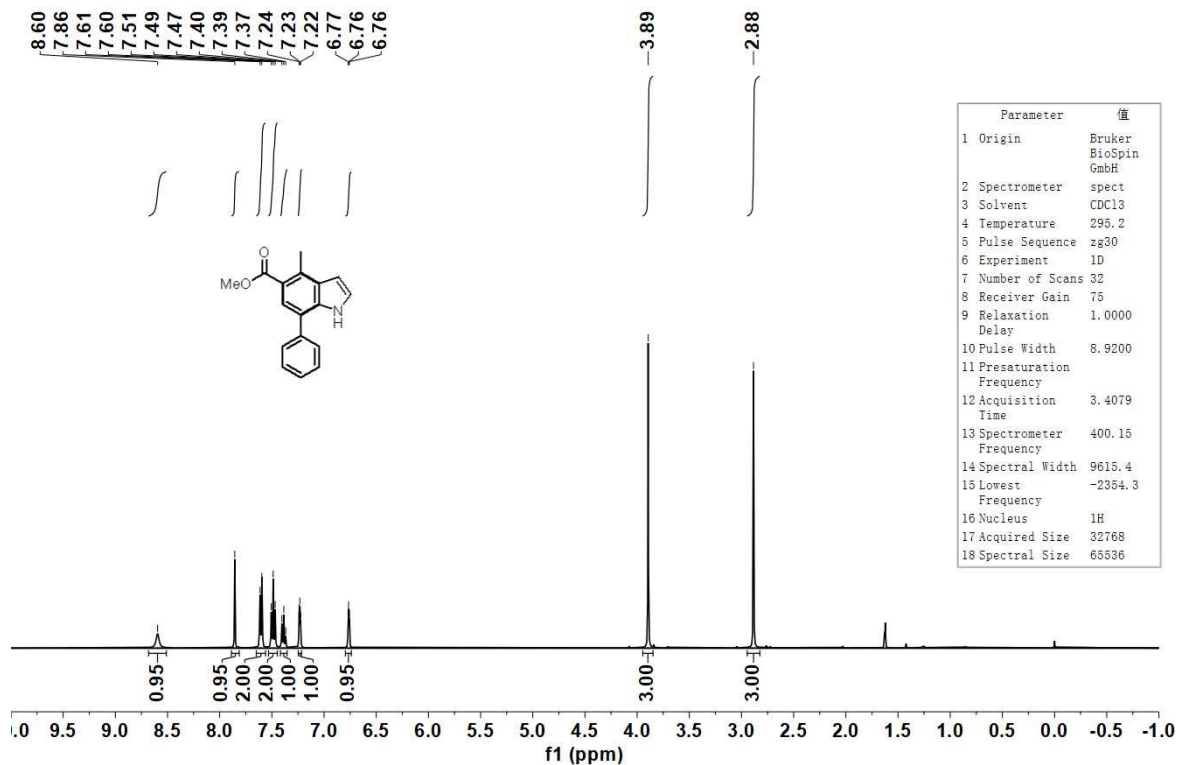
5k



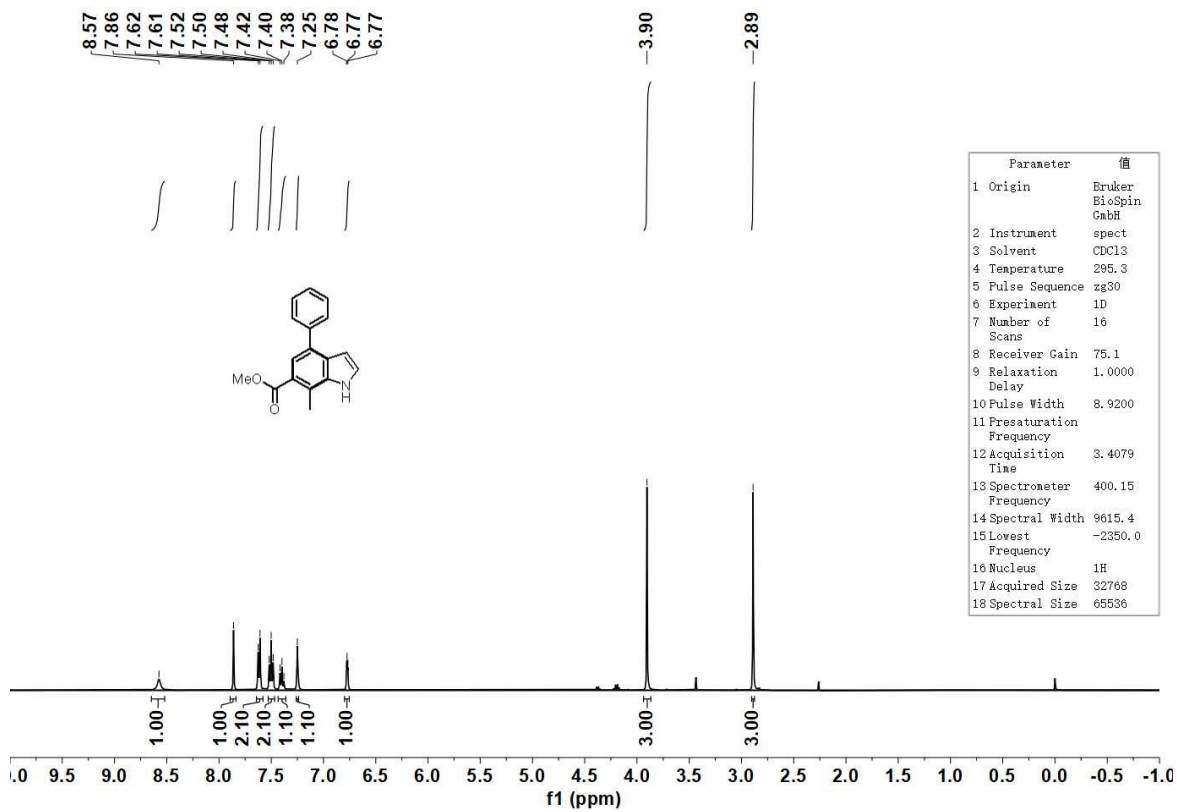
6k



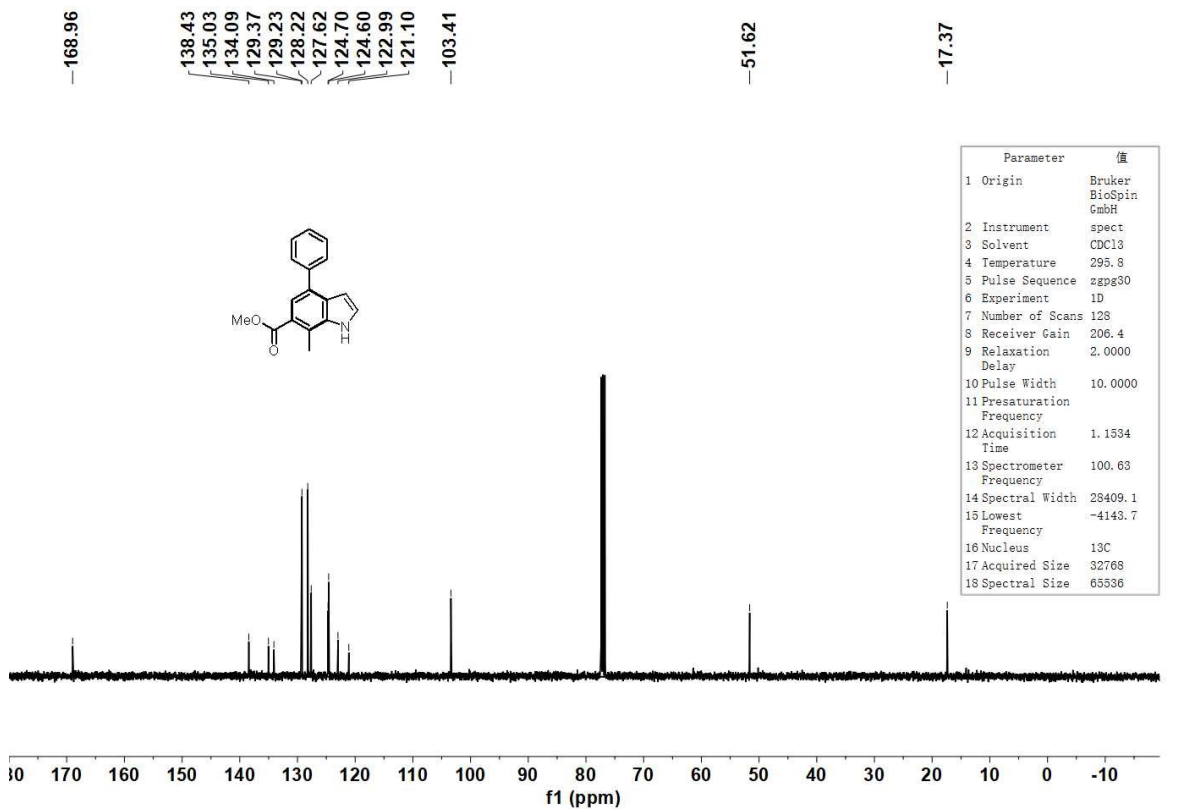
51



61

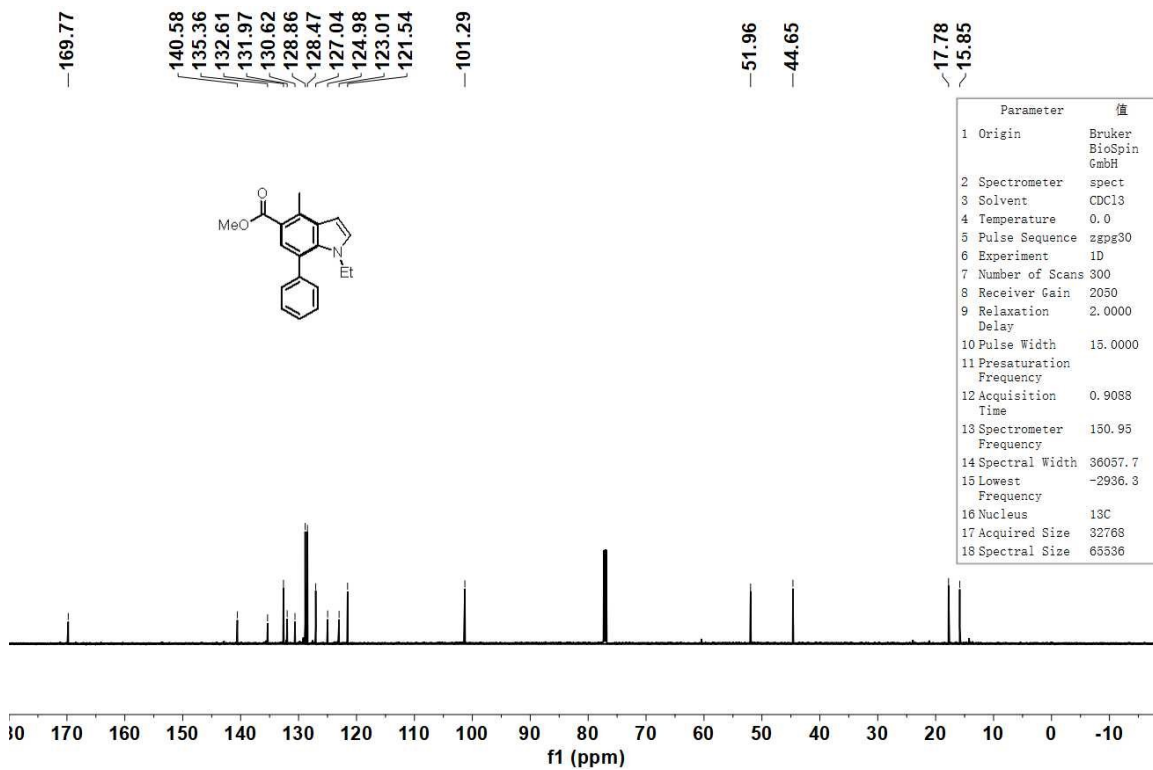
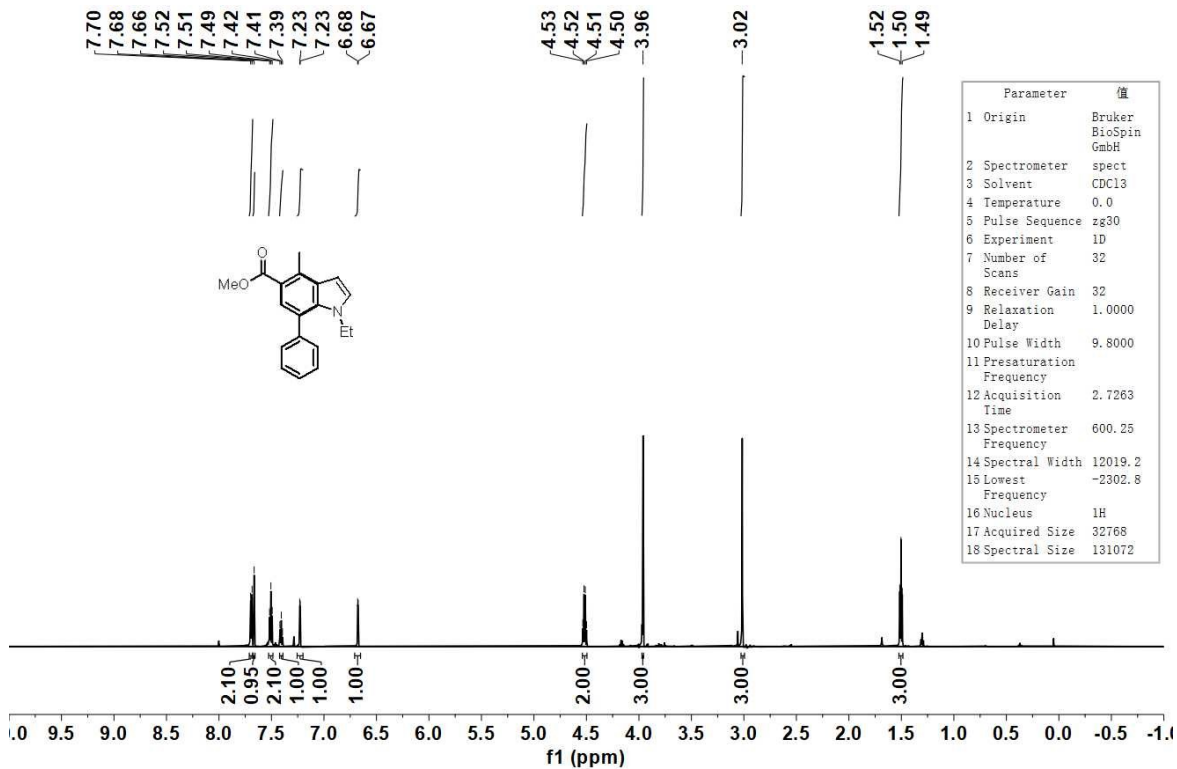


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	295.3
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	75.1
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2350.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

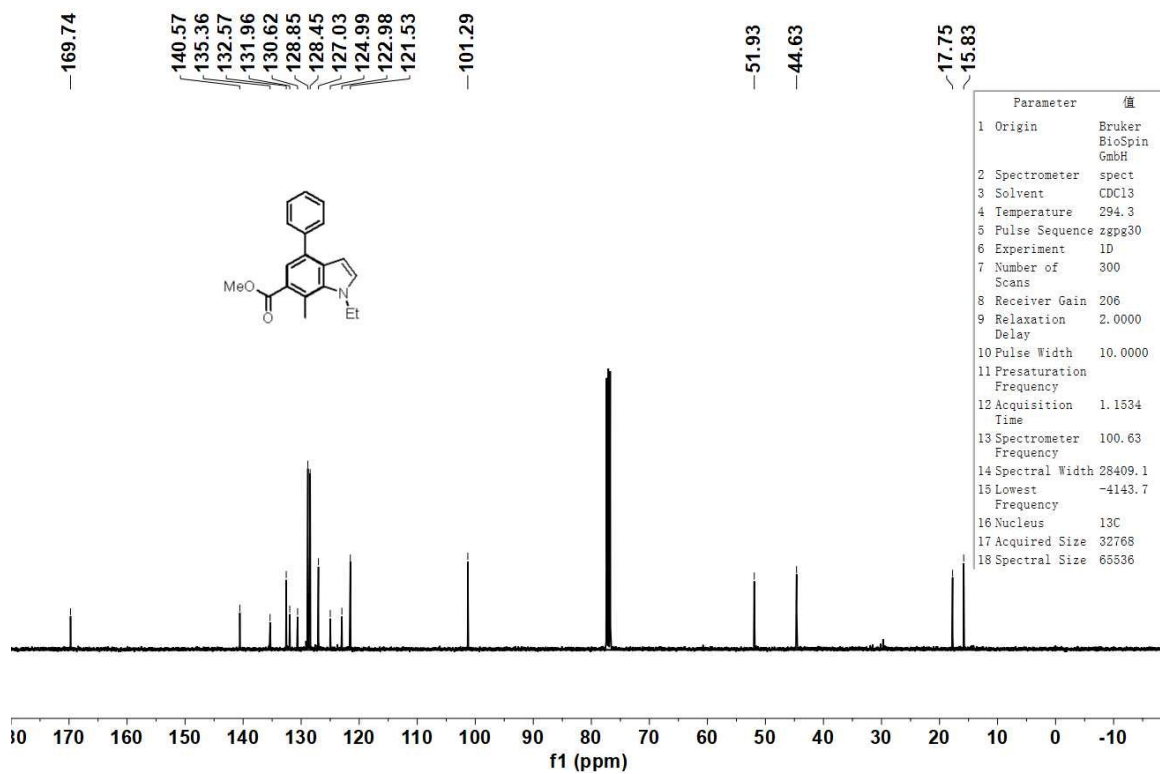
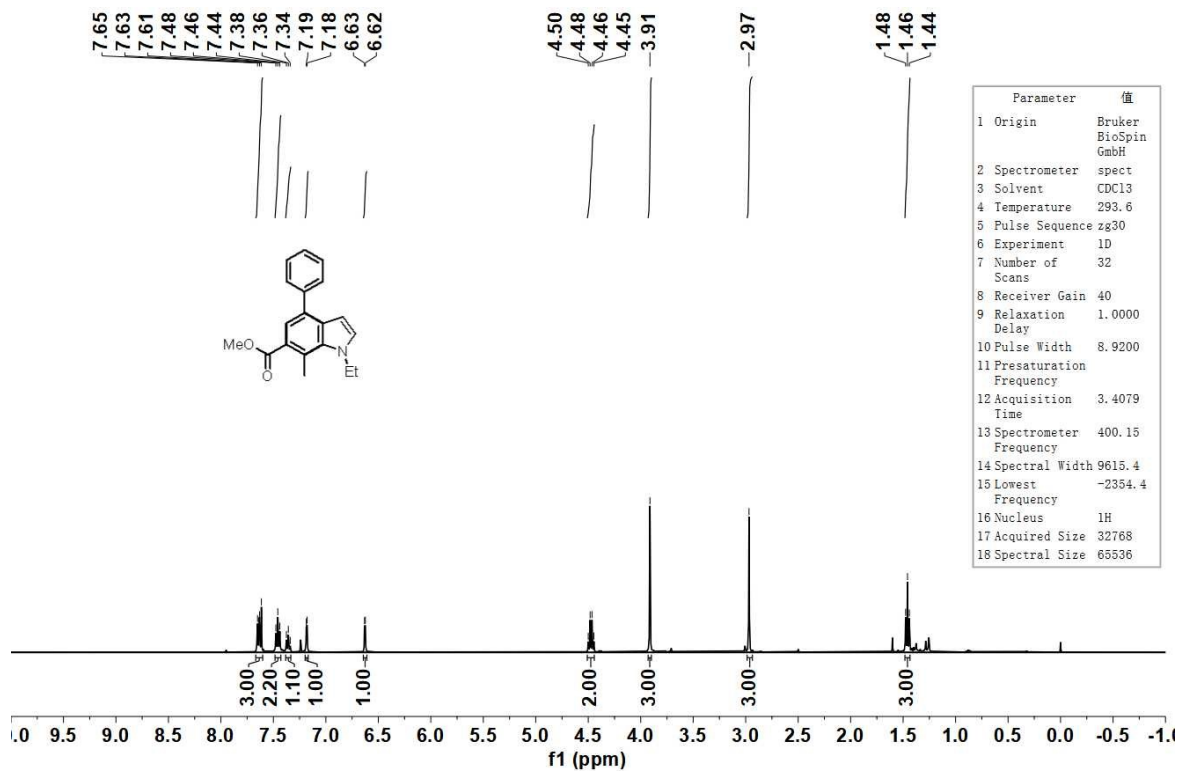


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	295.8
5 Pulse Sequence	zpg30
6 Experiment	1D
7 Number of Scans	128
8 Receiver Gain	206.4
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

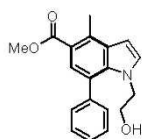
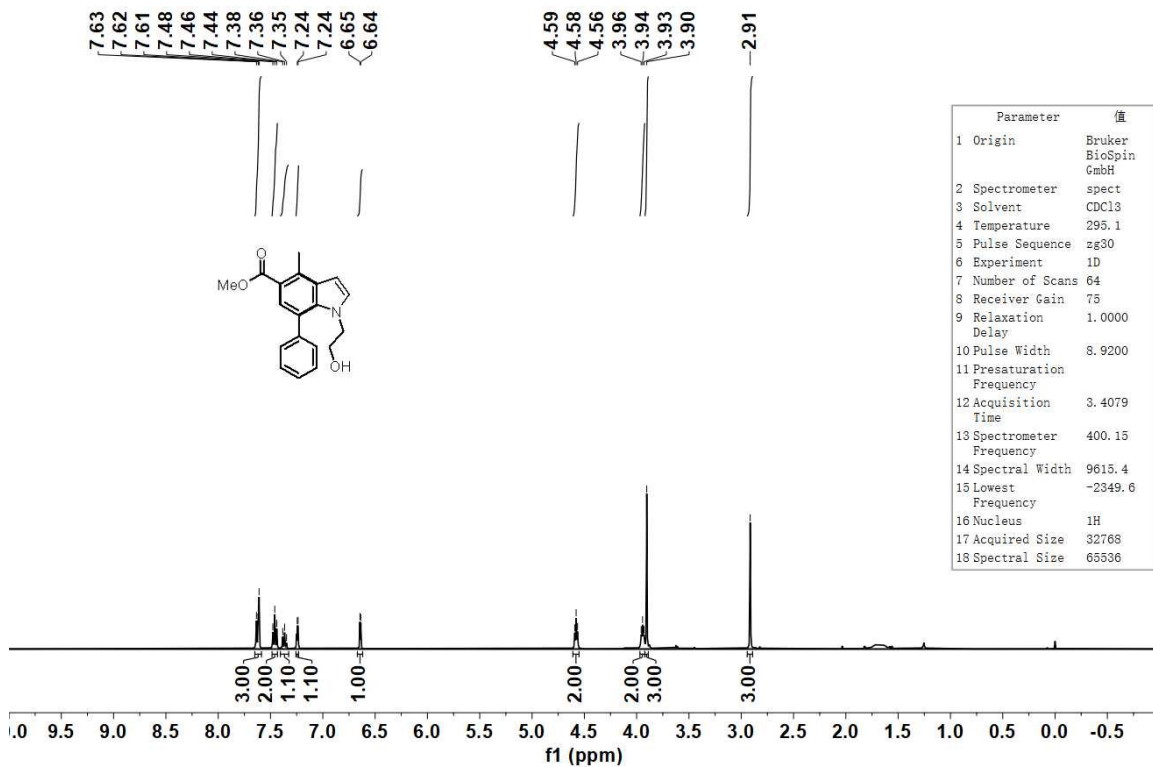
5m



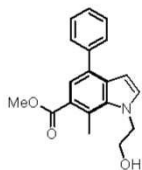
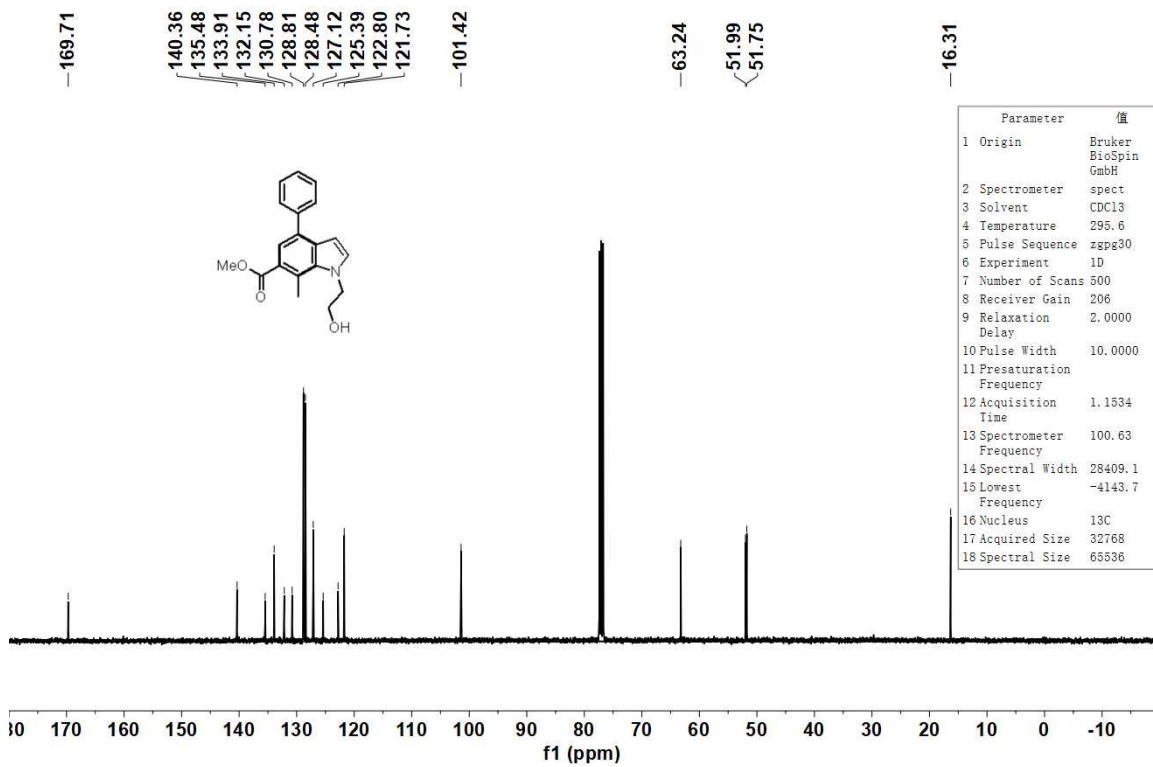
6m



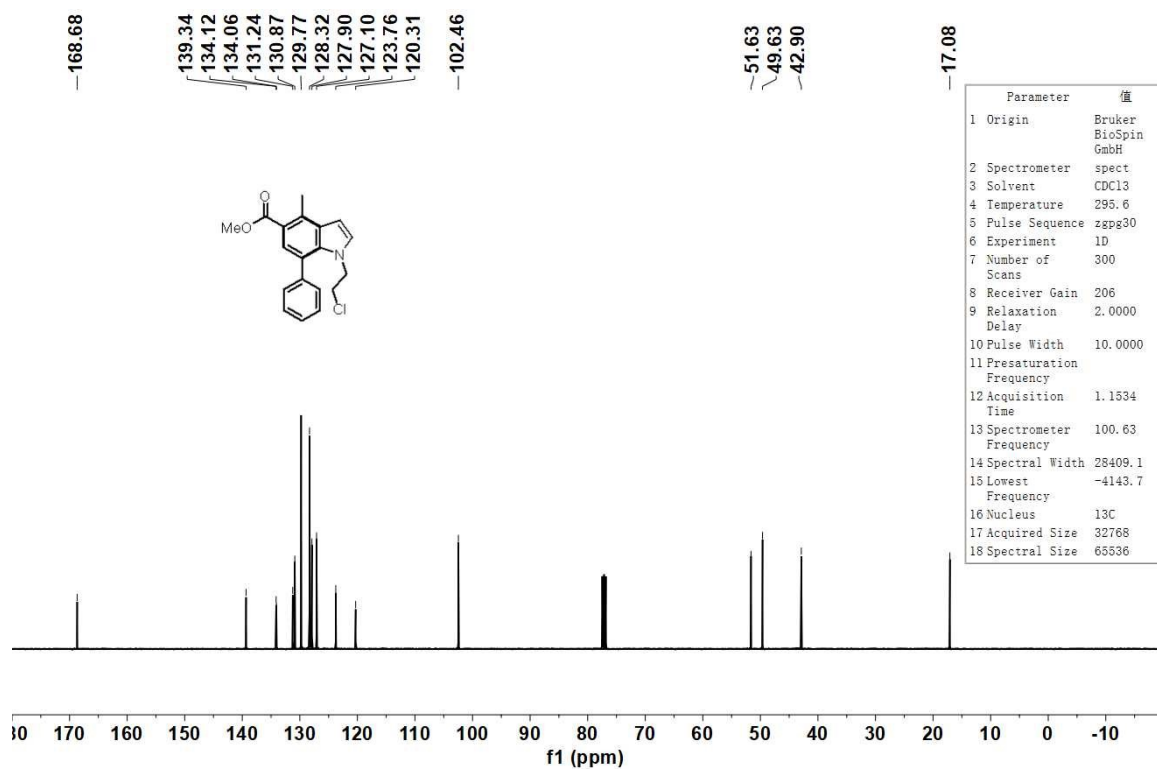
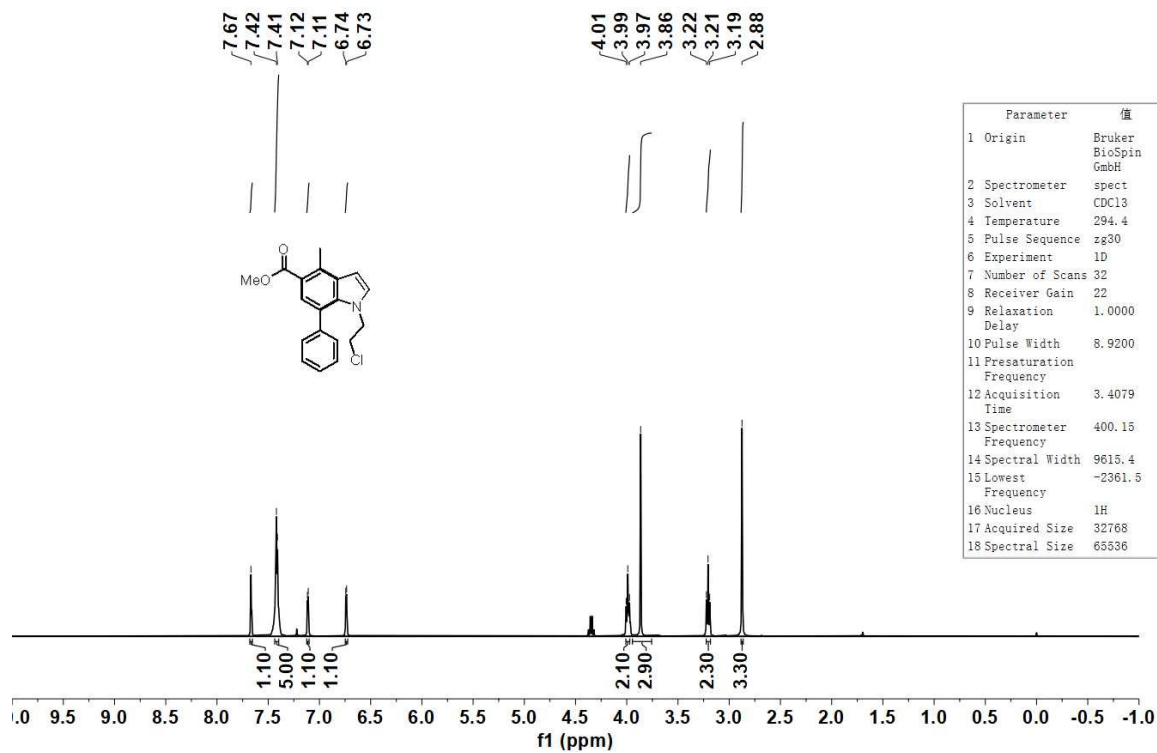
5n



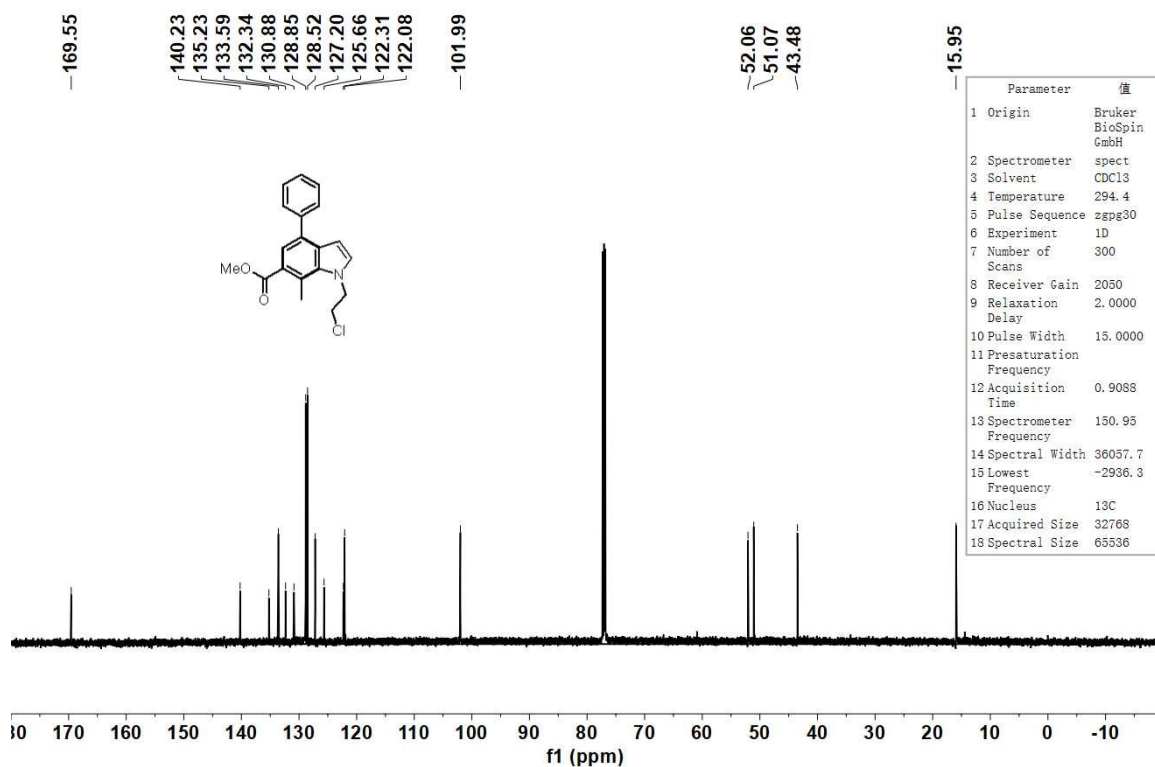
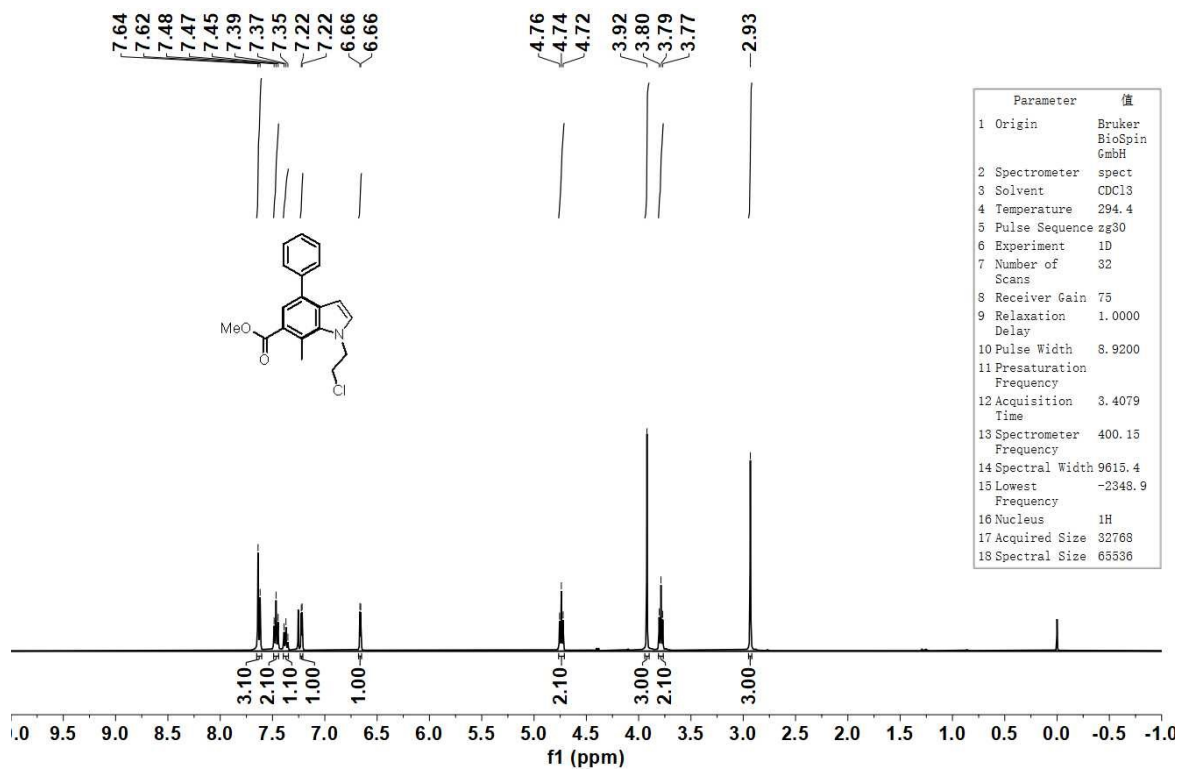
Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	295.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	64
8 Receiver Gain	75
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2349.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536



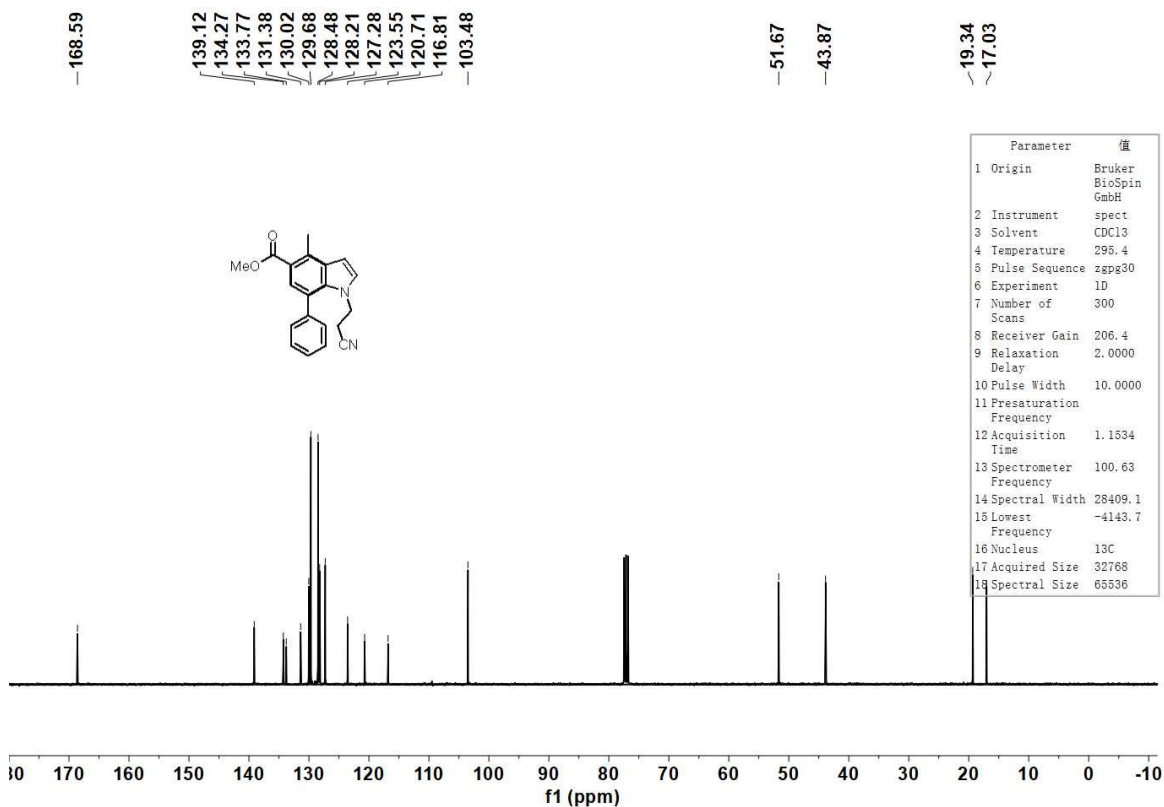
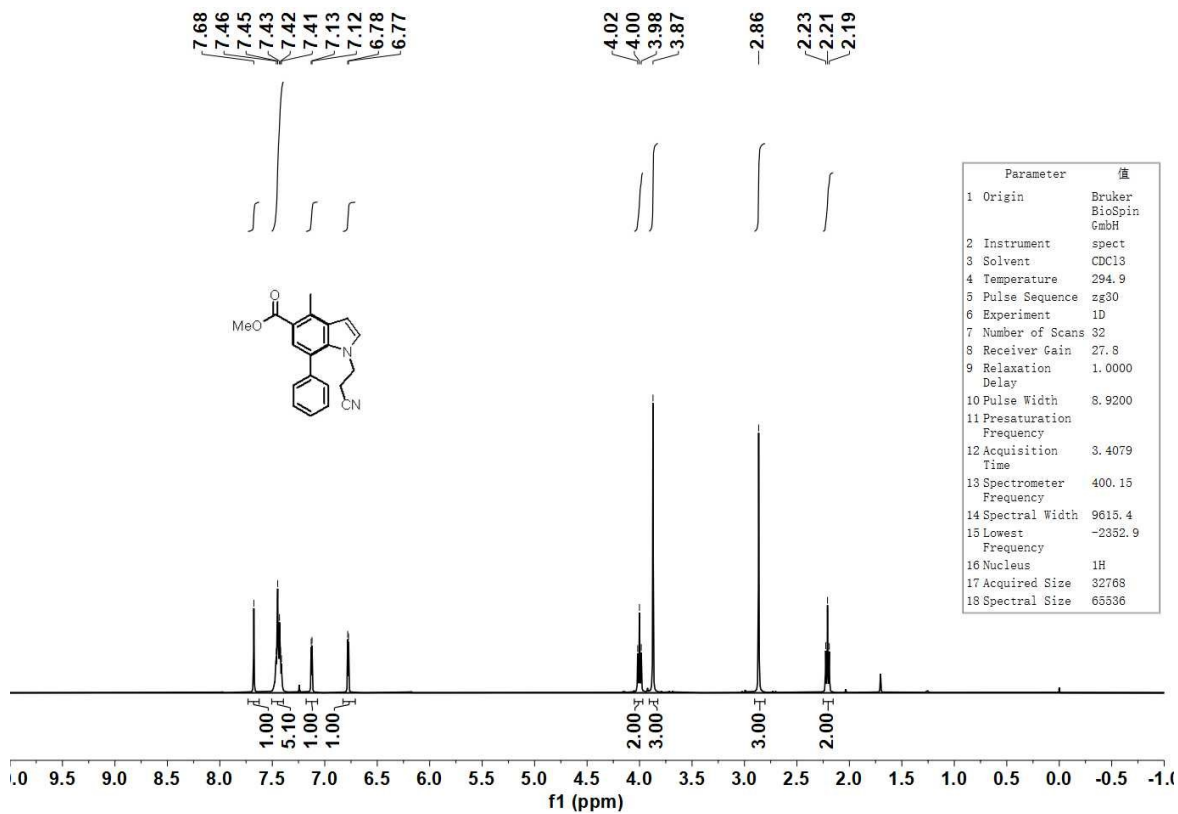
Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	295.6
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Number of Scans	500
8 Receiver Gain	206
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536



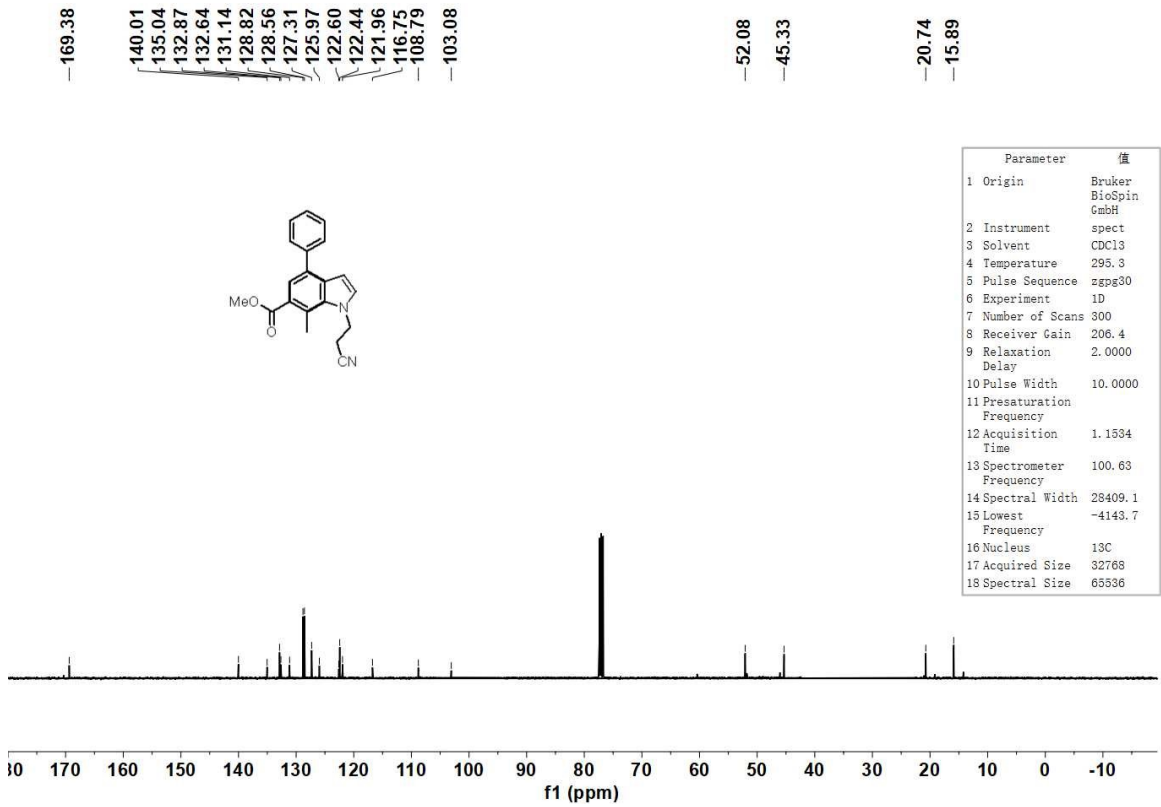
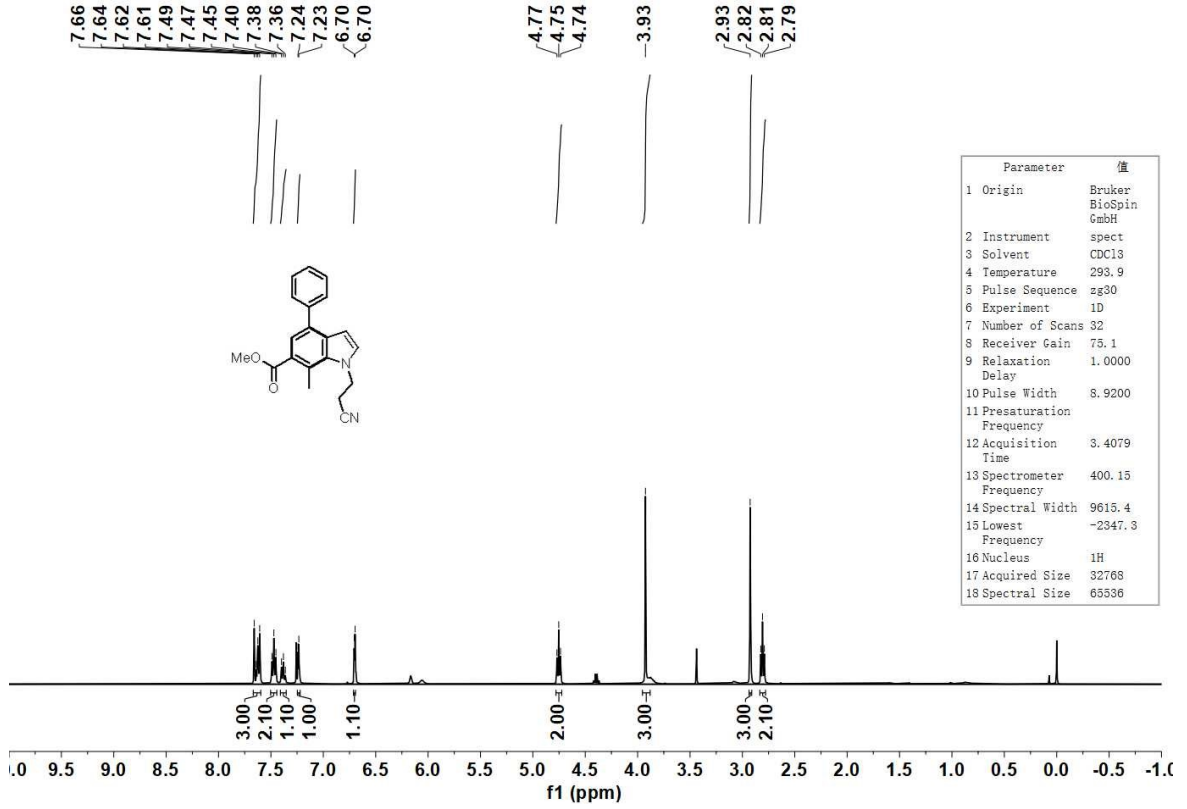




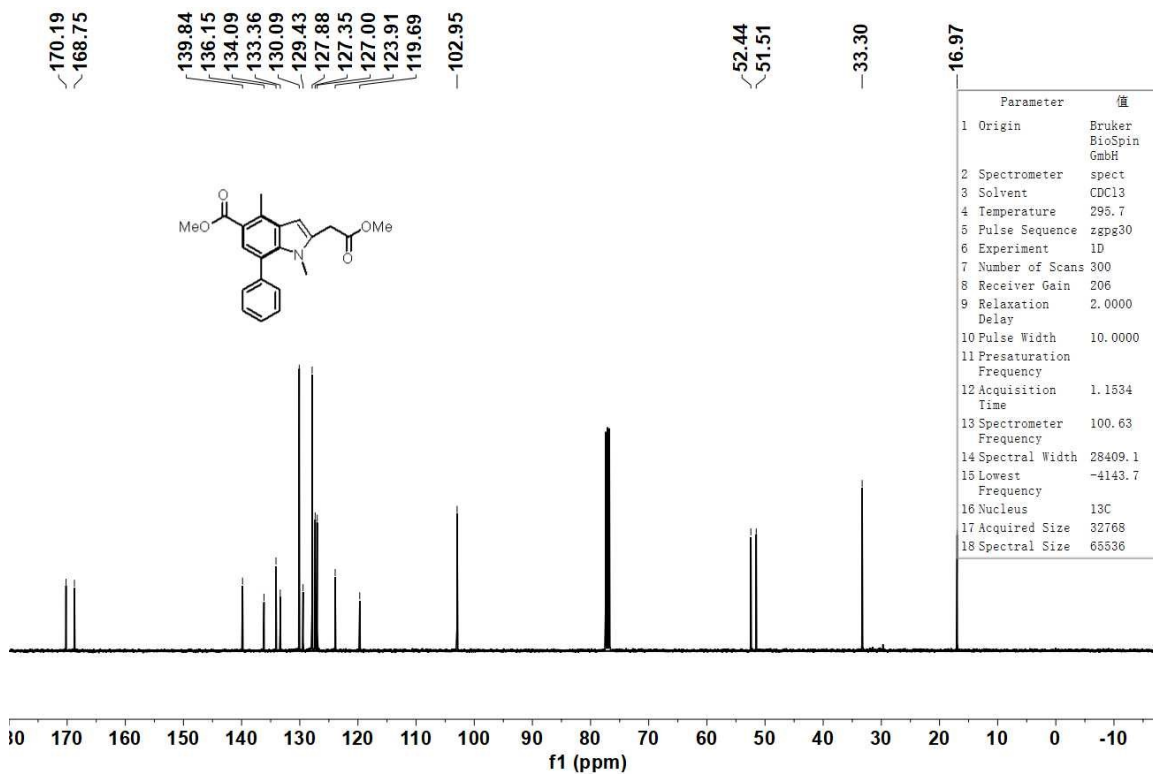
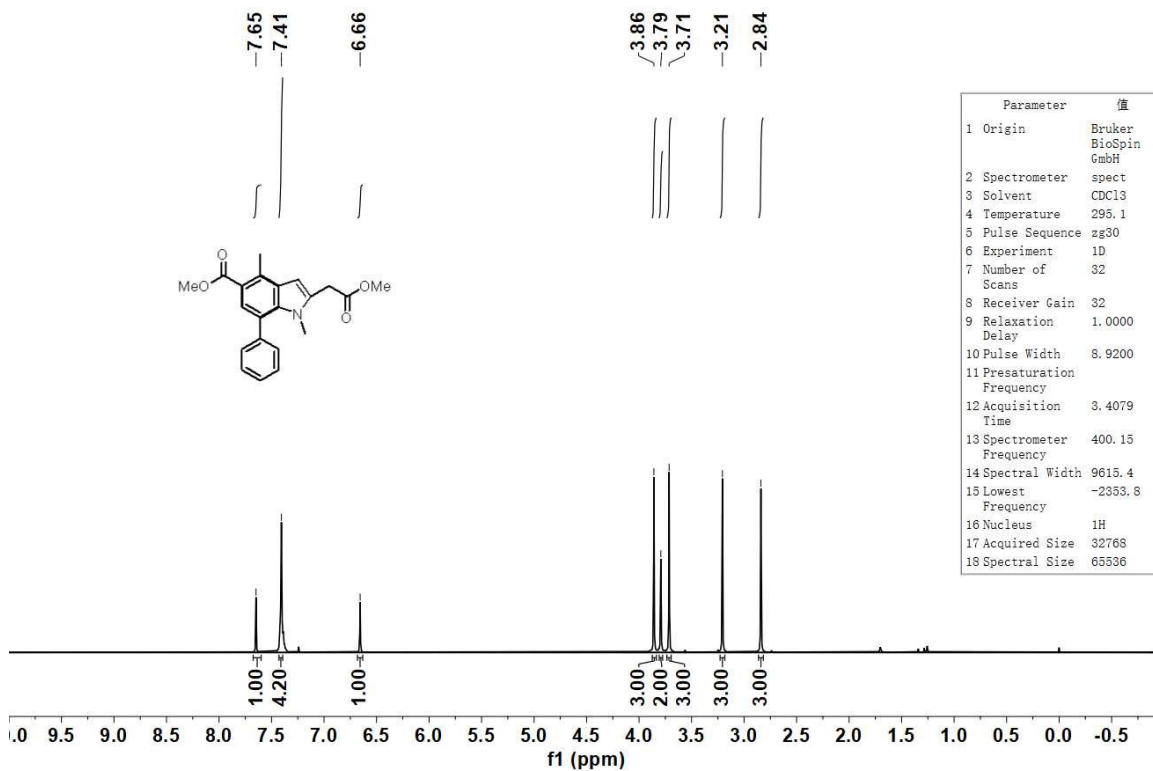
5p



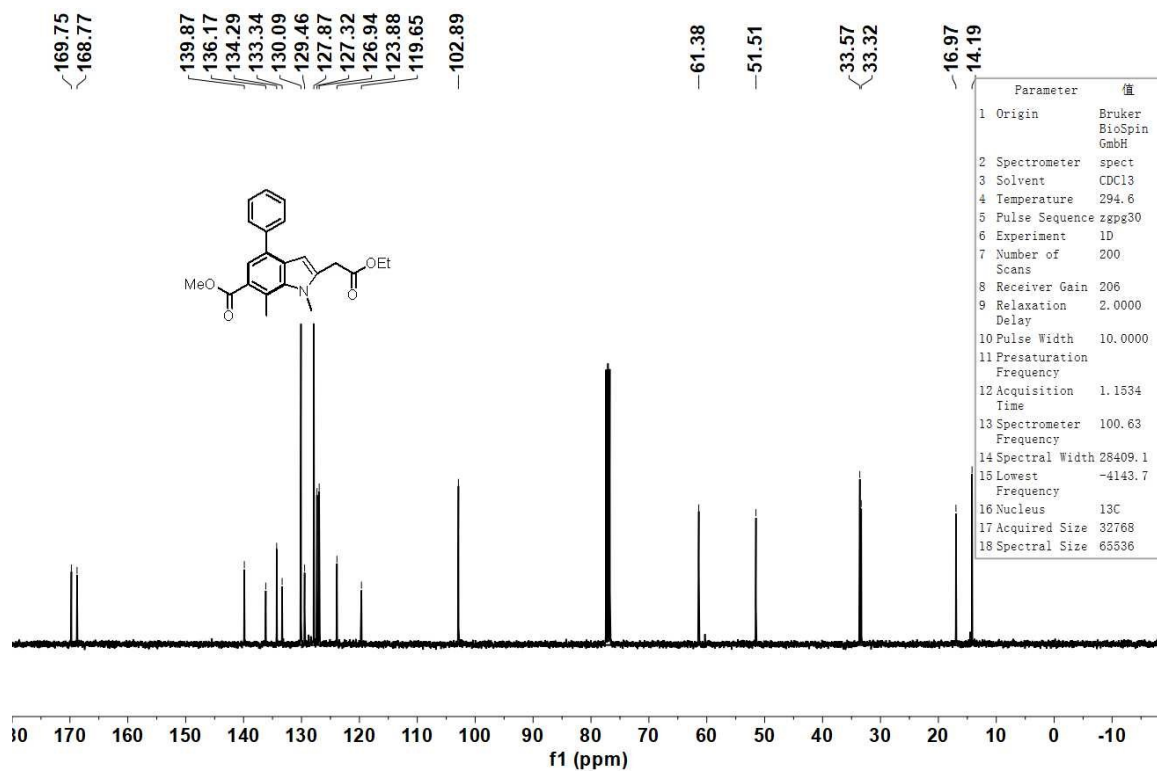
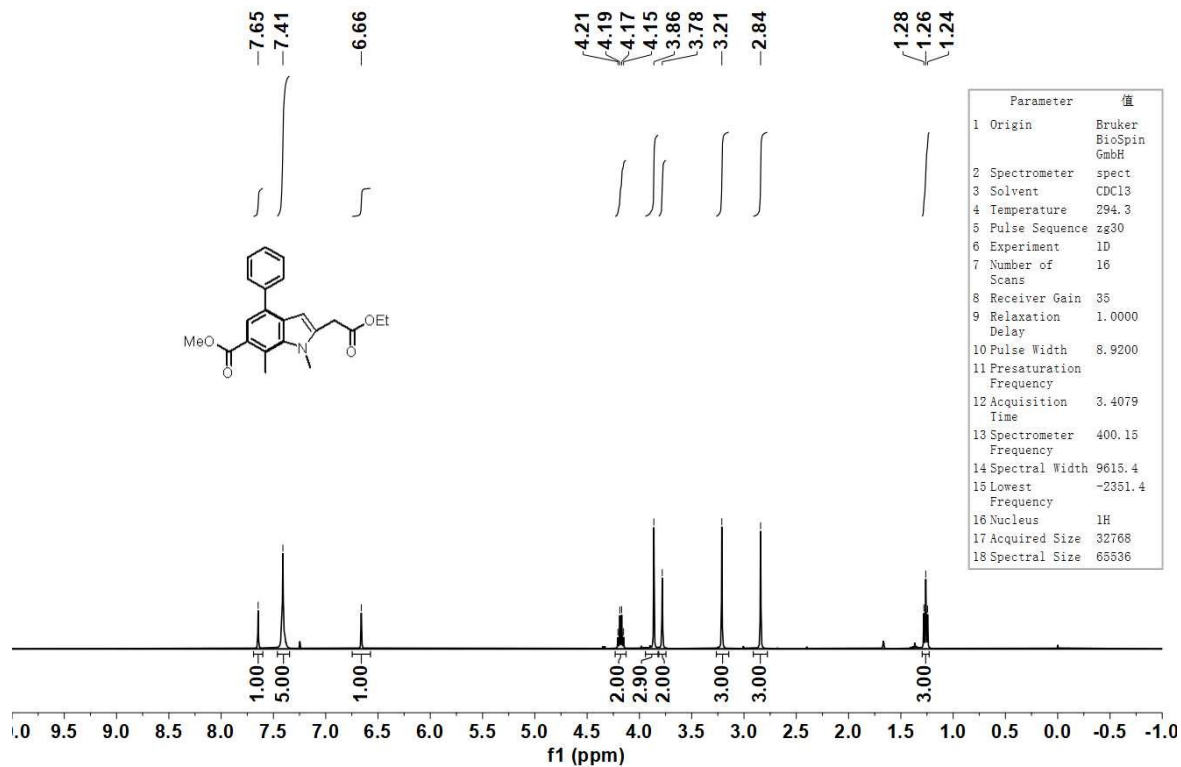
6p



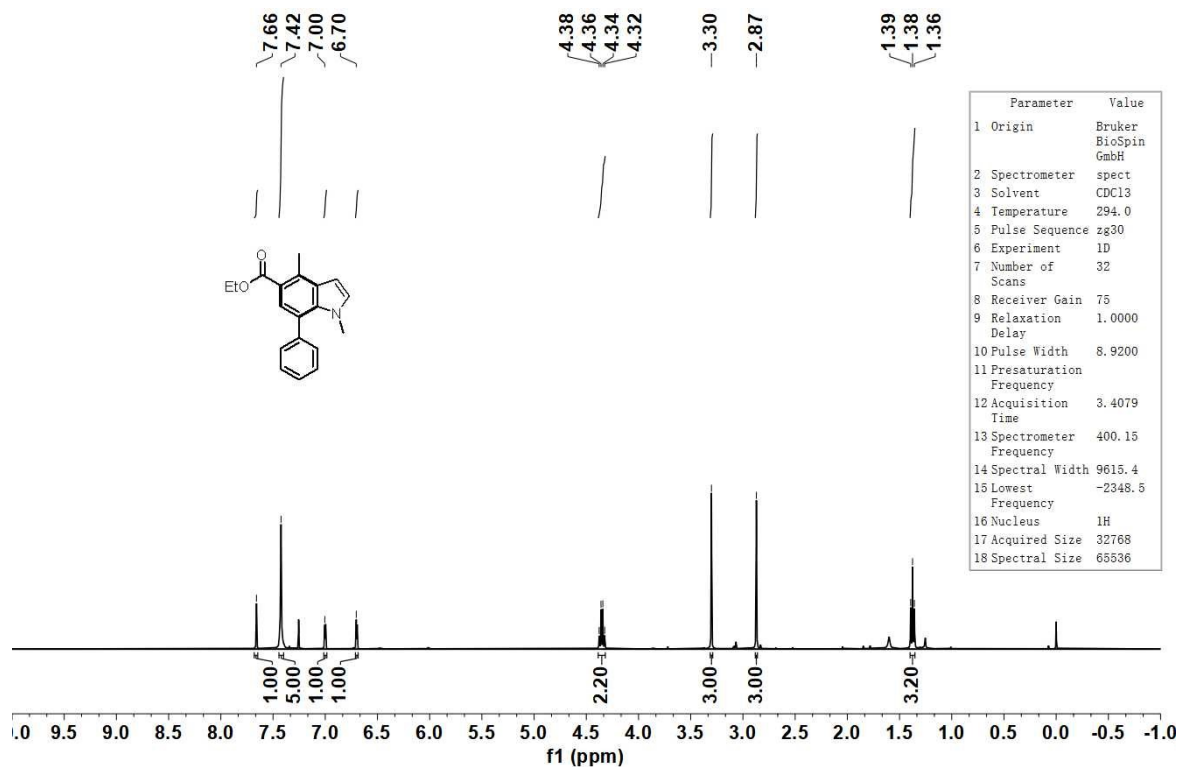
5q



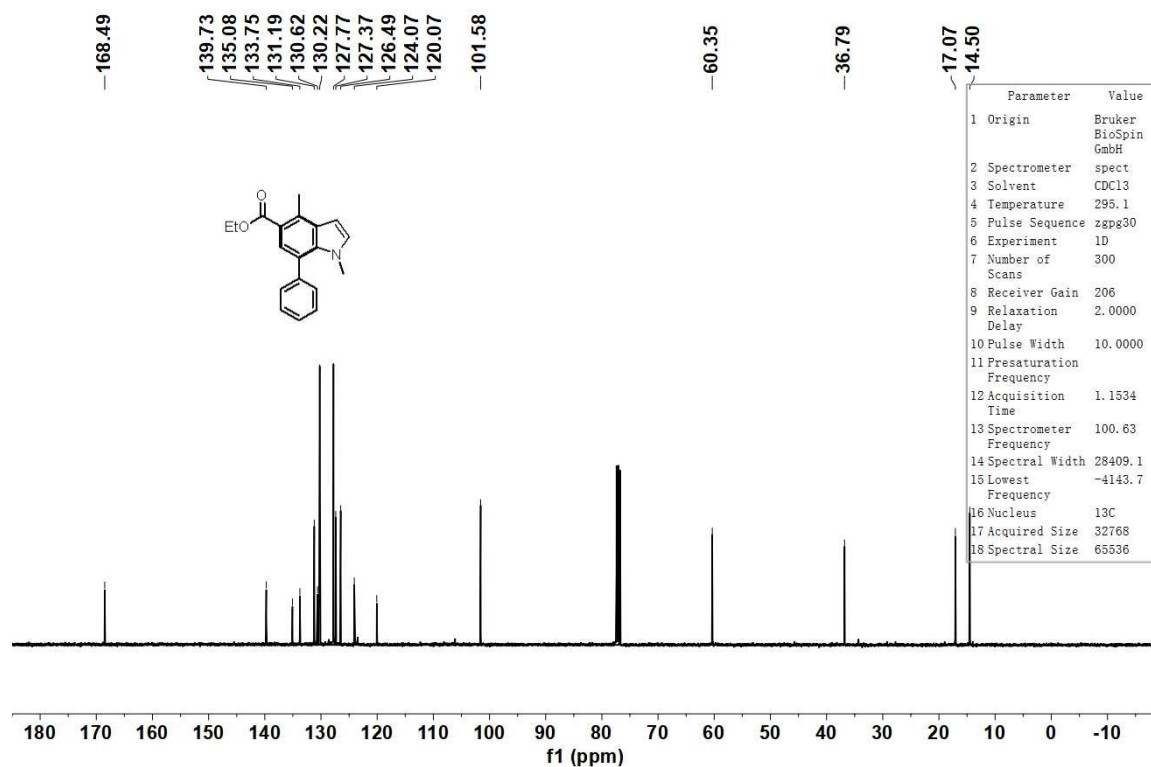
5r



5s

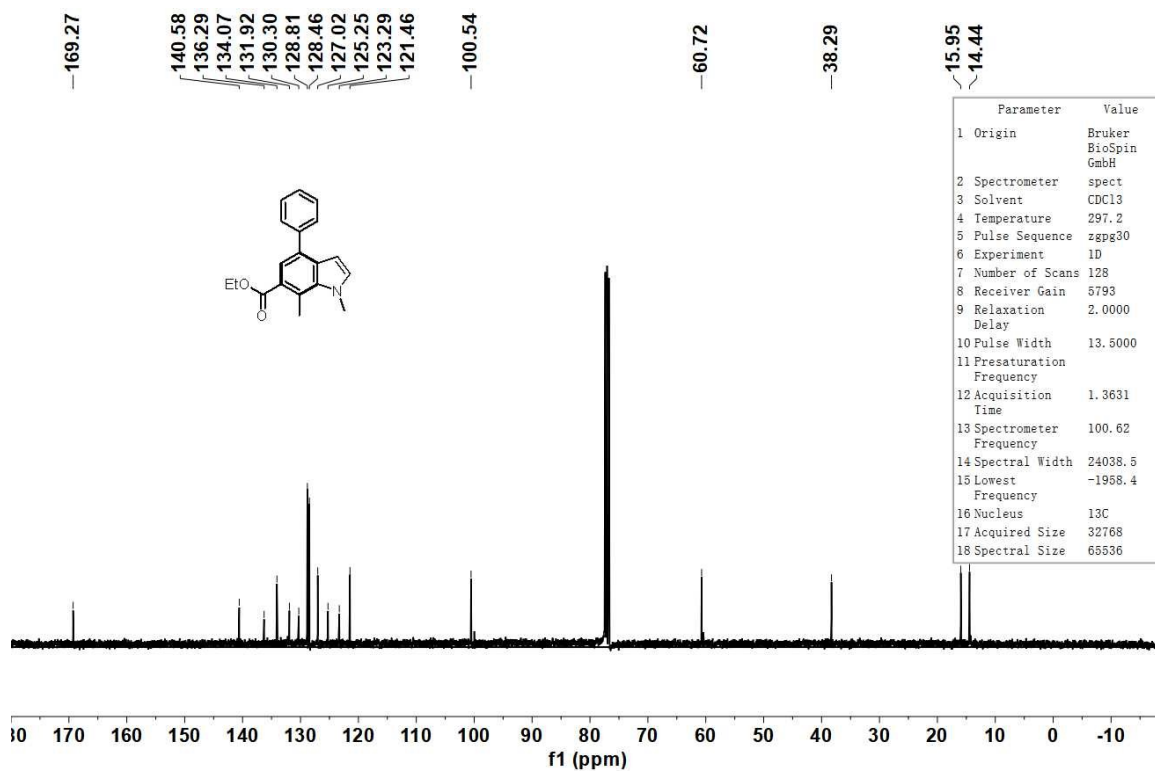
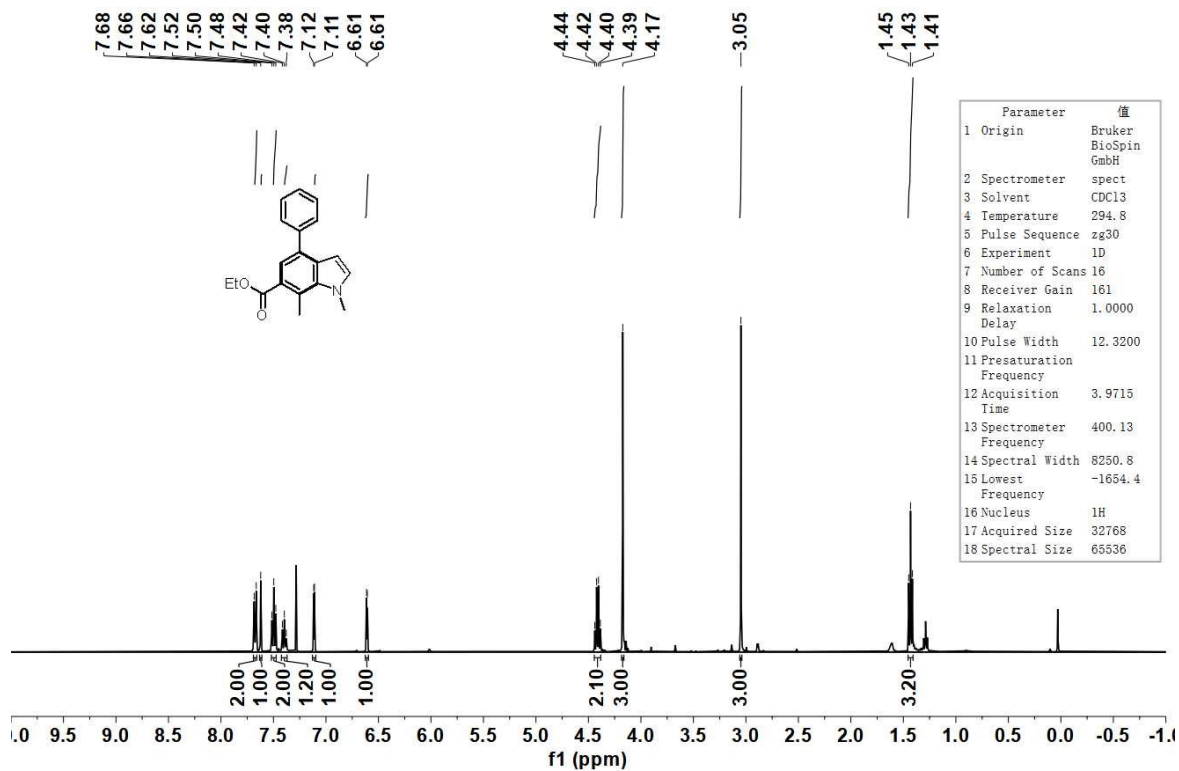


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	32
8 Receiver Gain	75
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2348.5
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

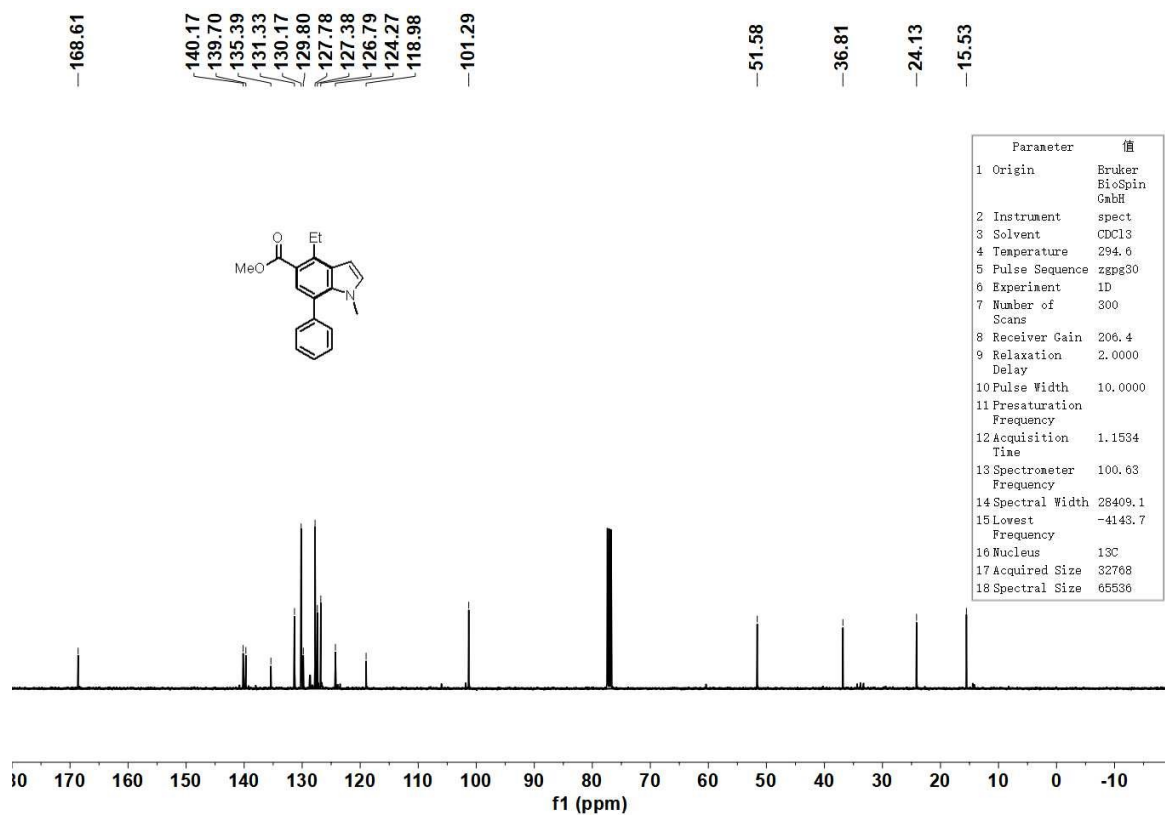
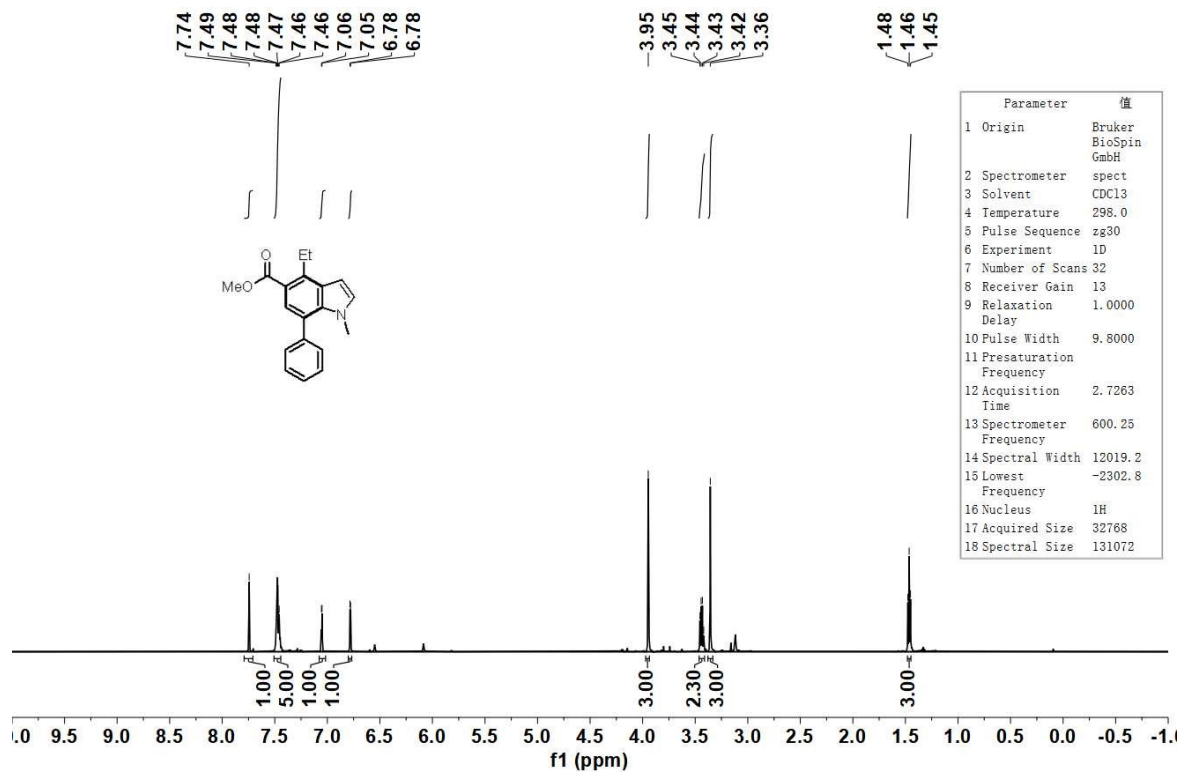


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	295.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Number of Scans	300
8 Receiver Gain	206
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

6s

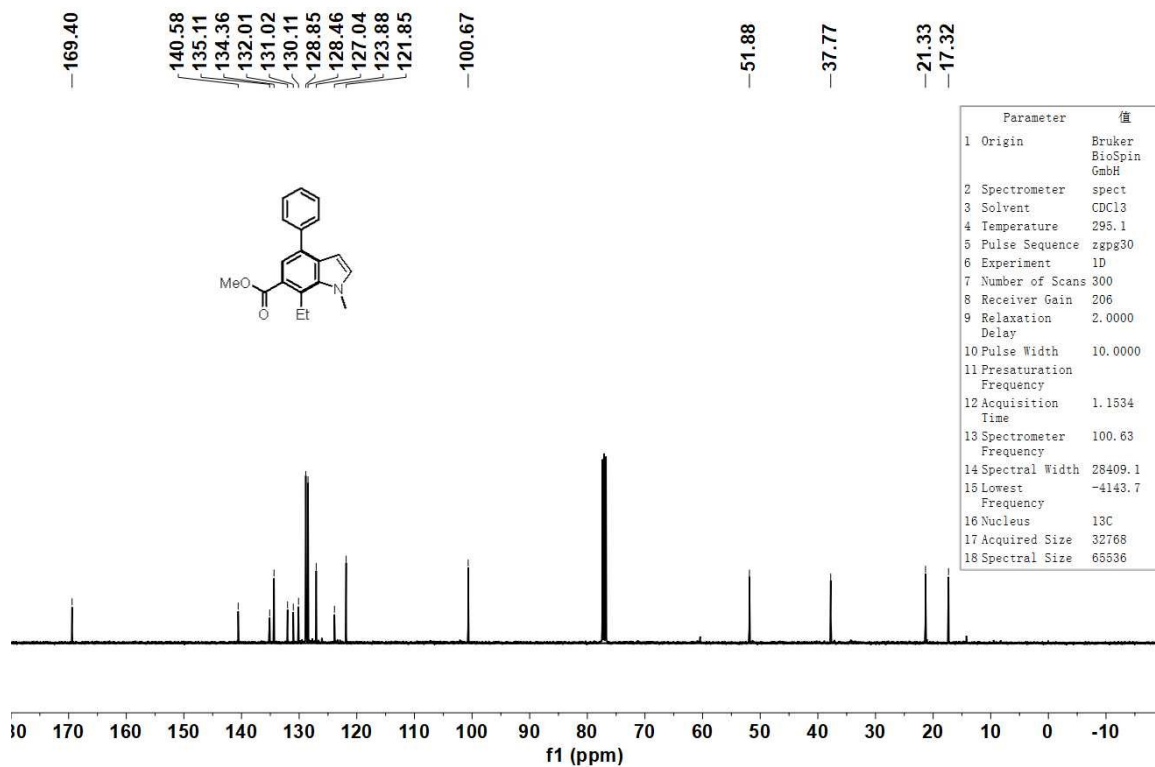
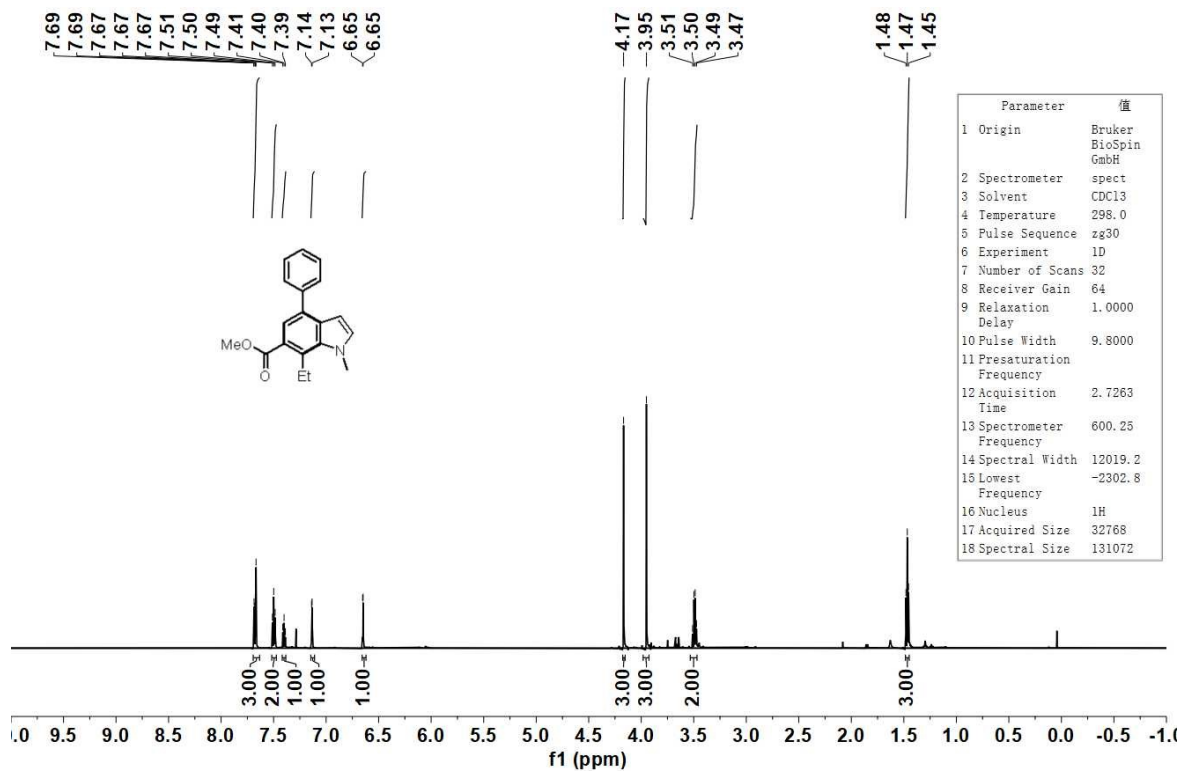


5t

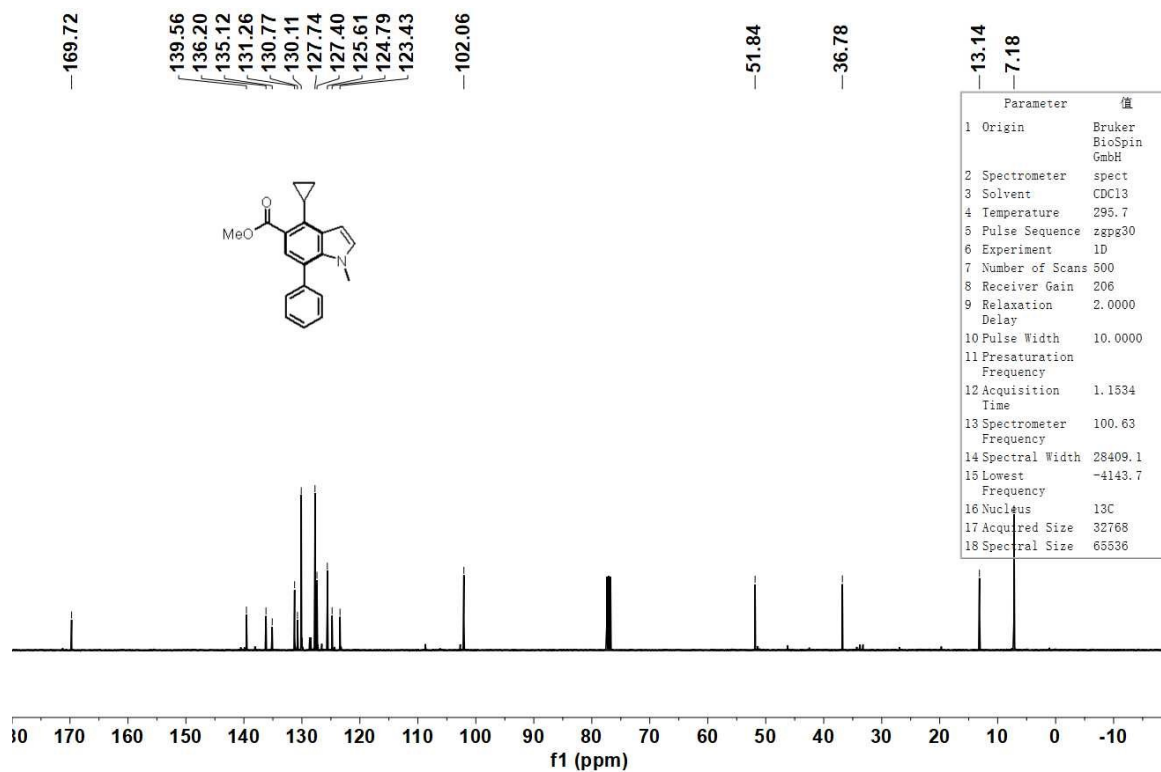
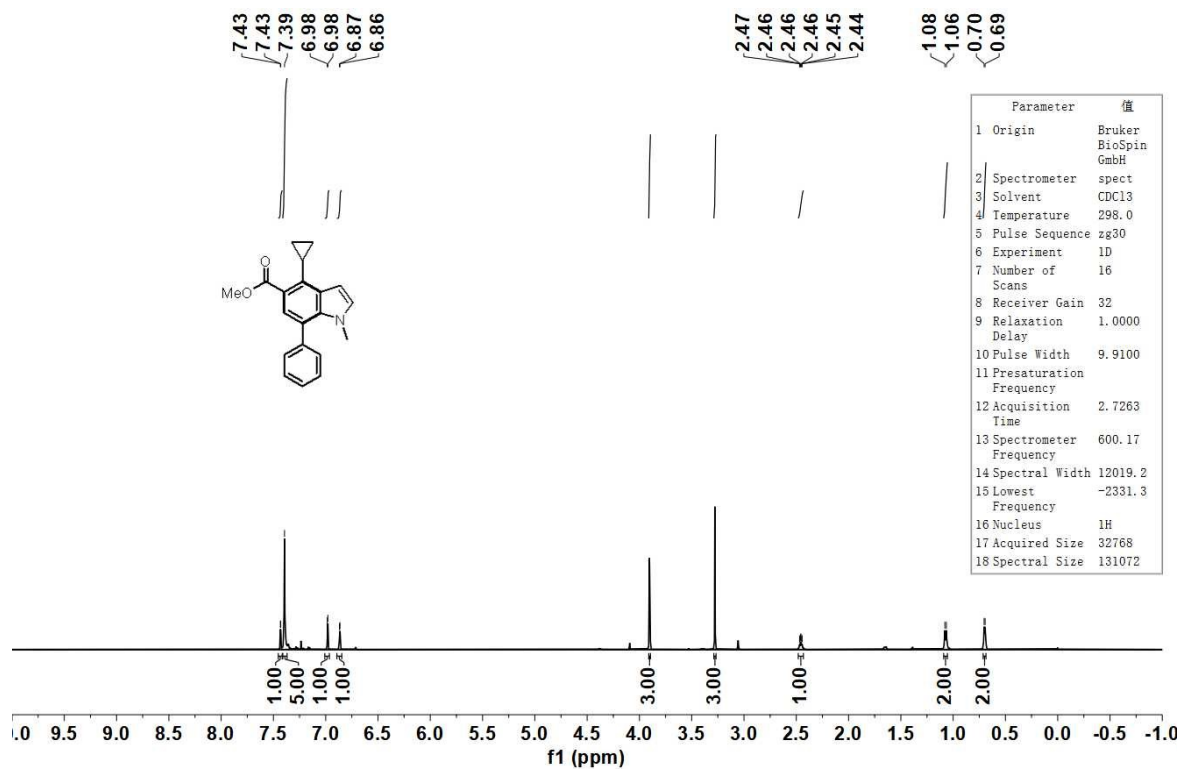




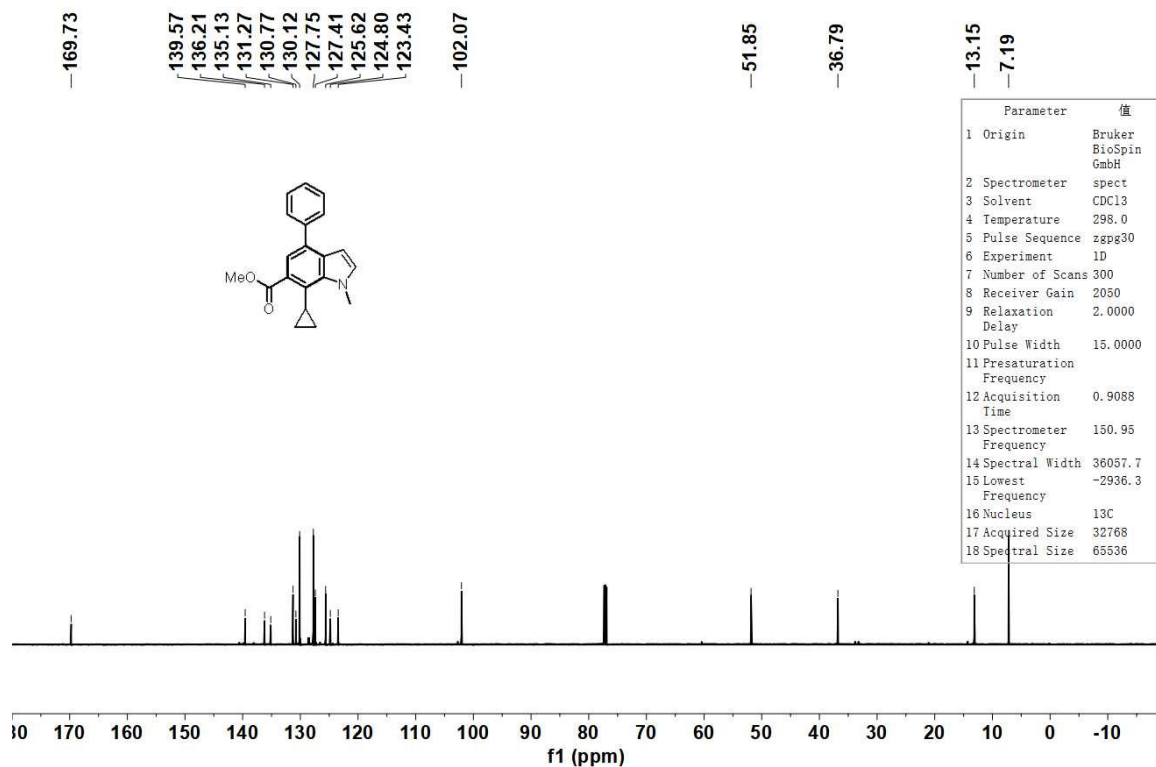
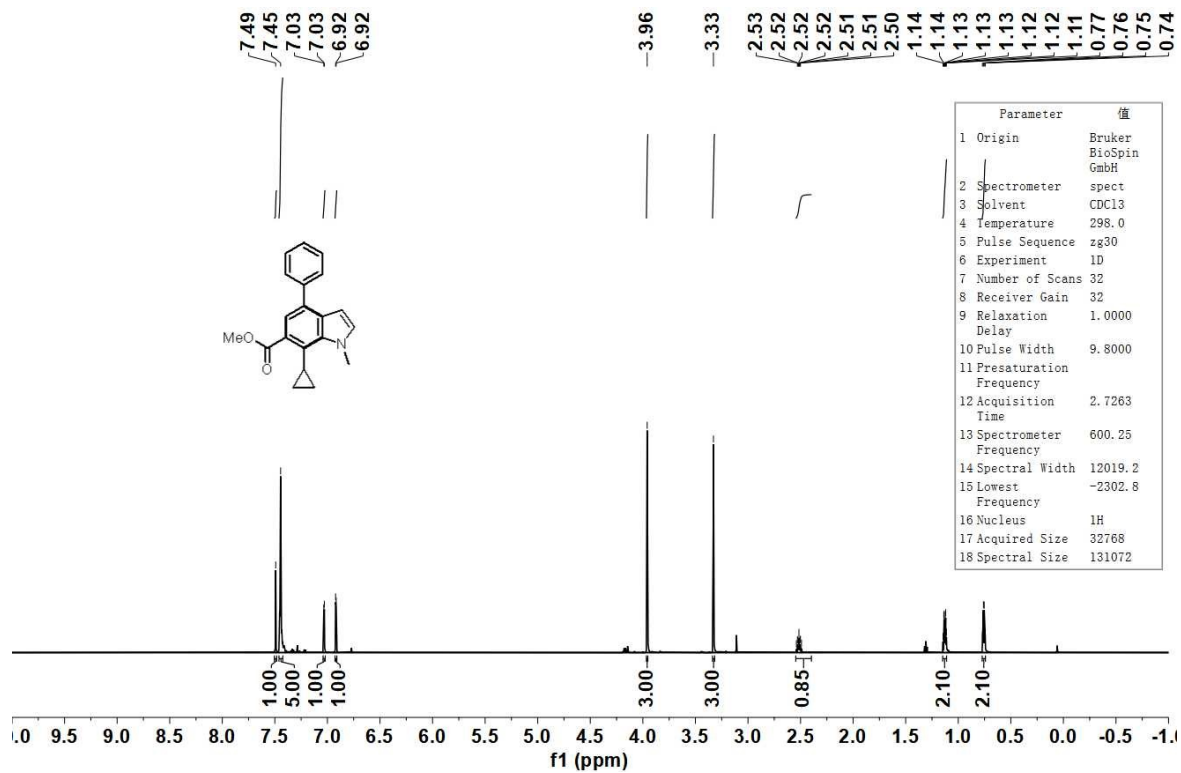
6t



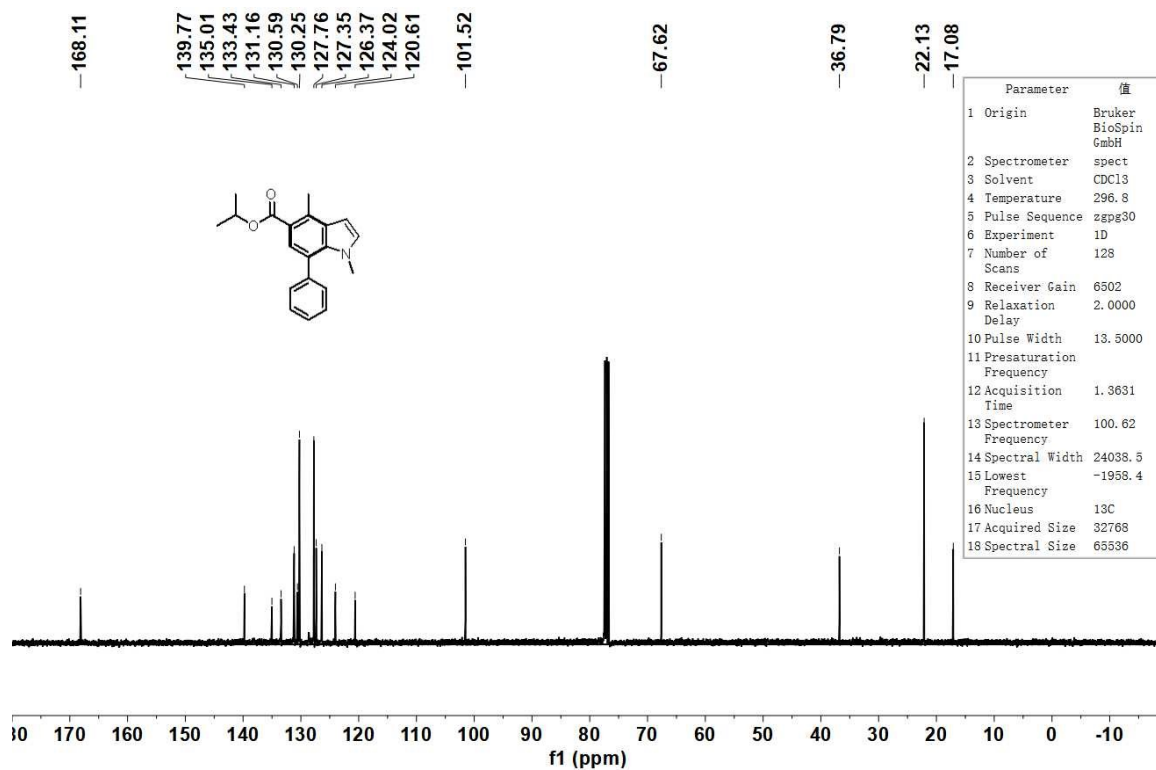
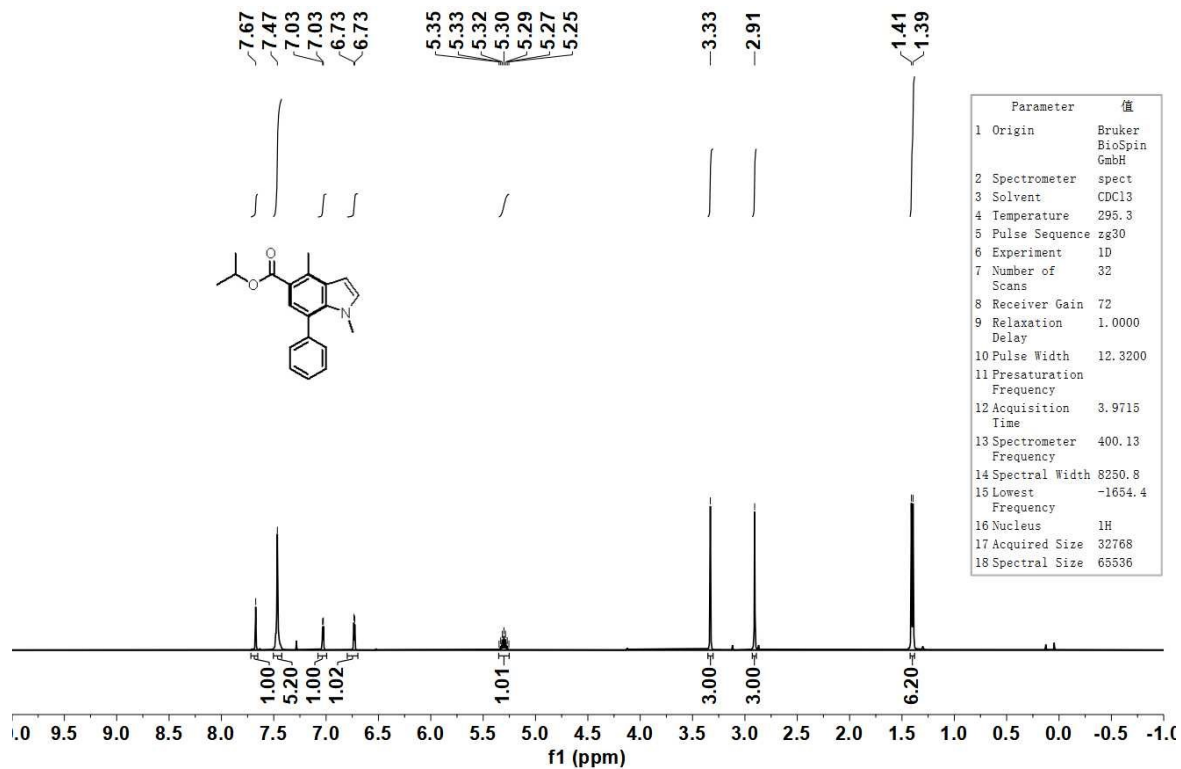
5u



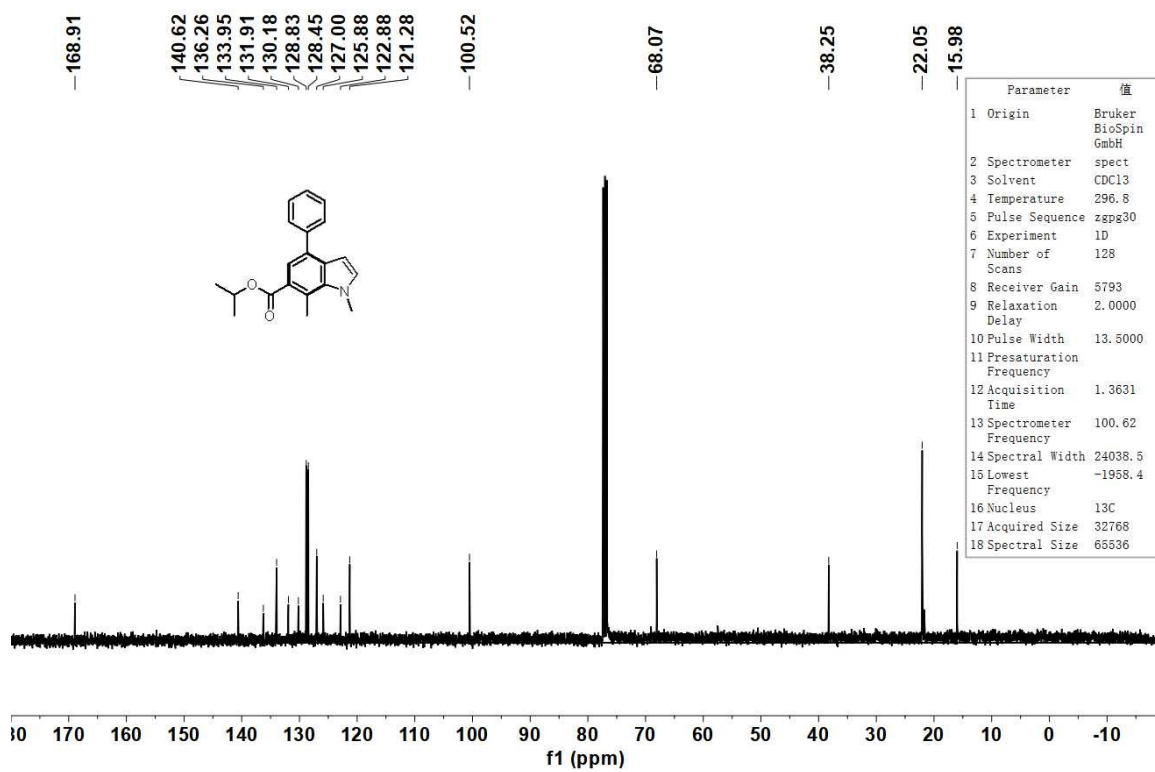
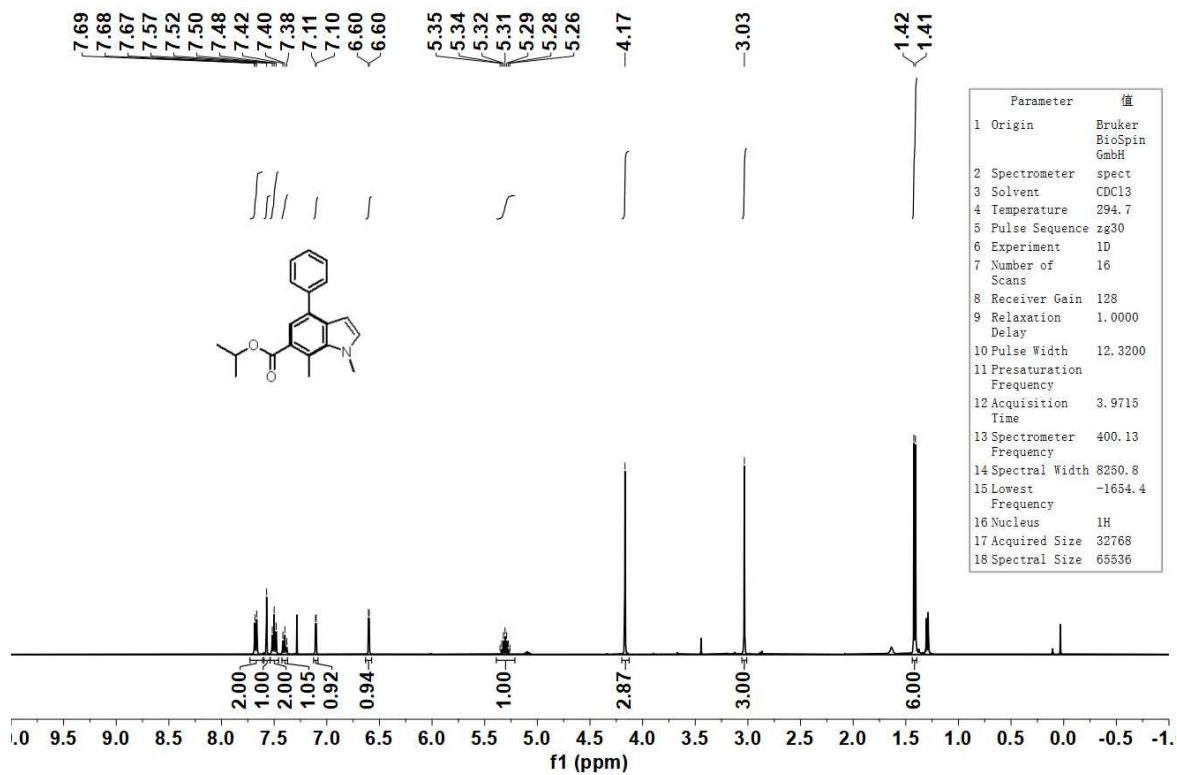
6u



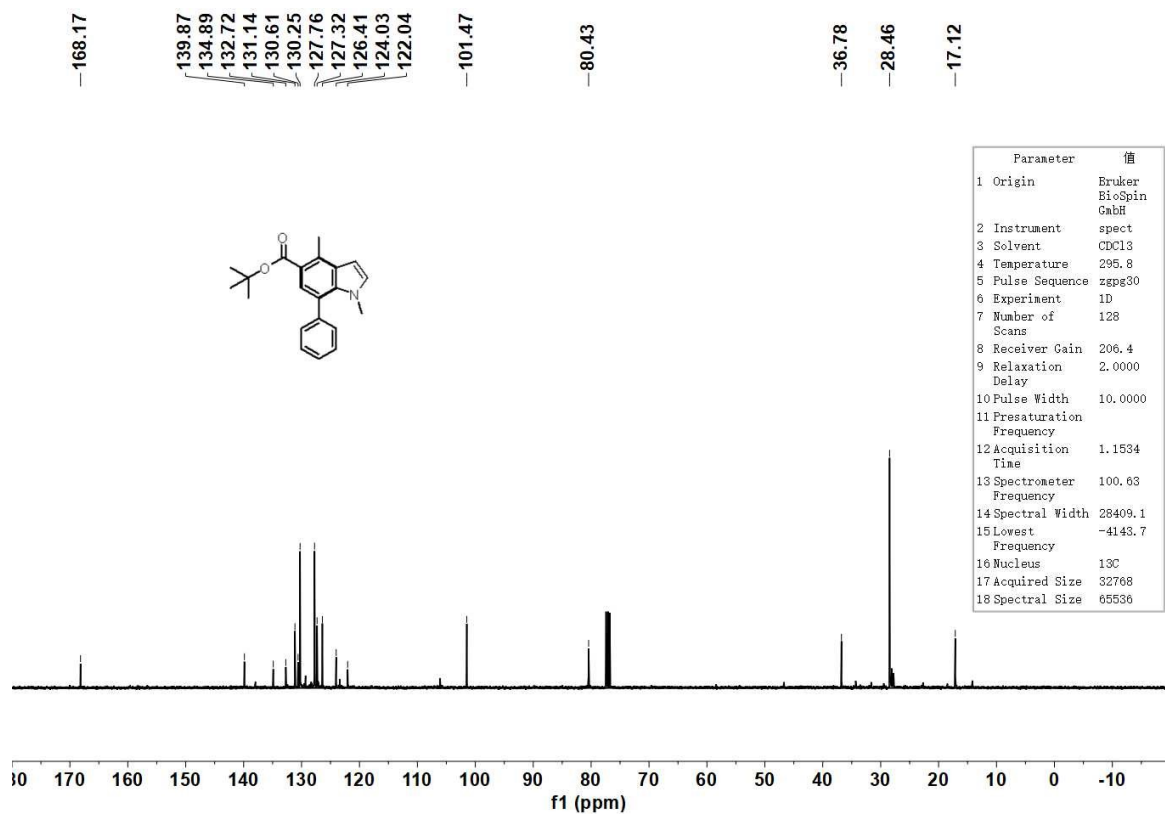
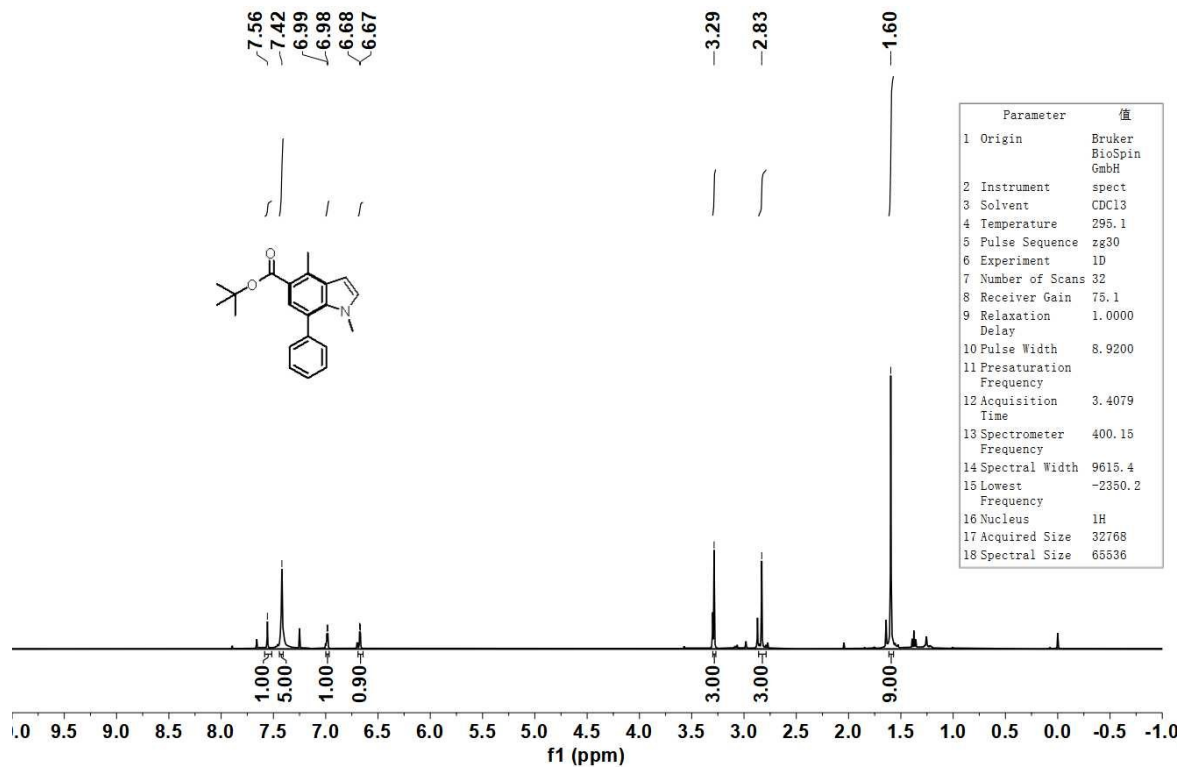
5v



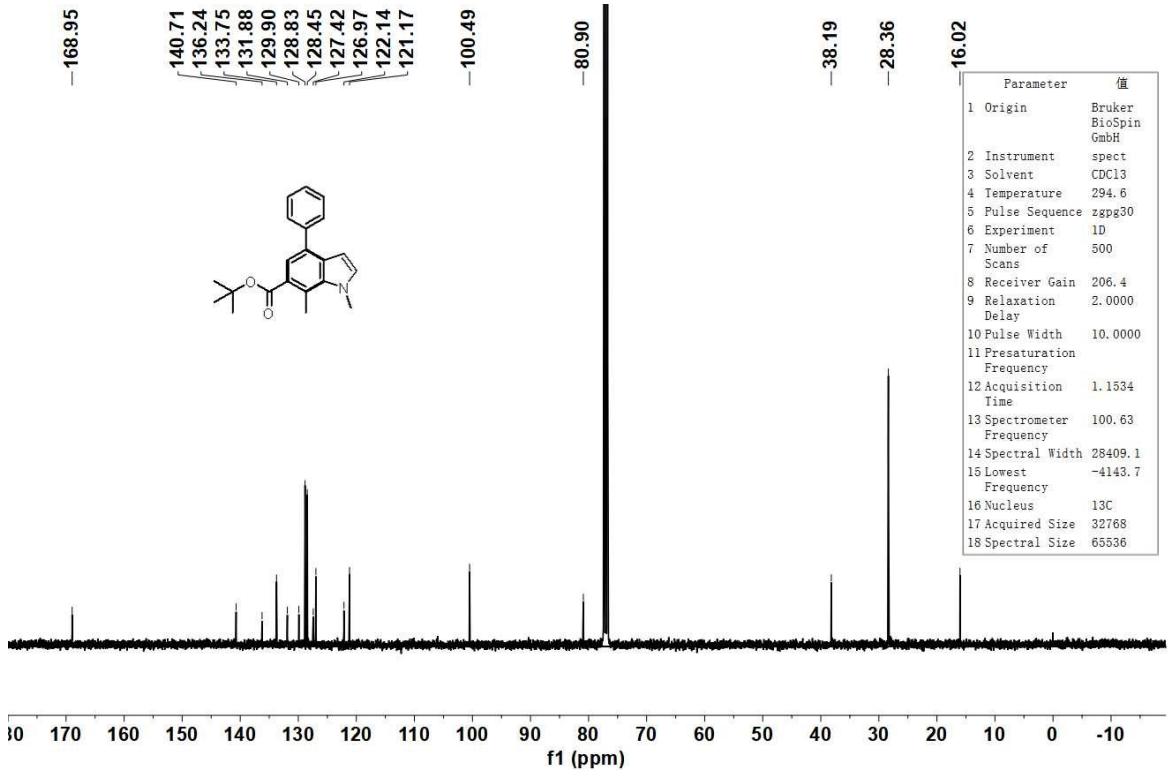
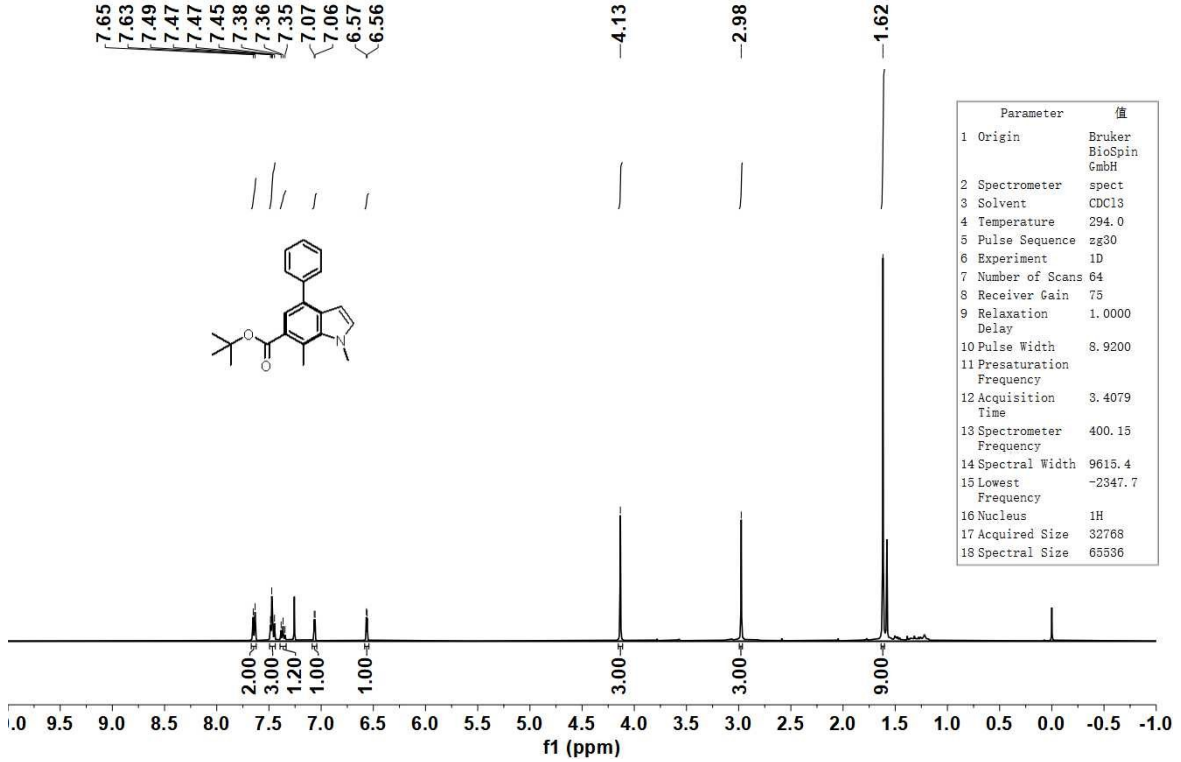
6v



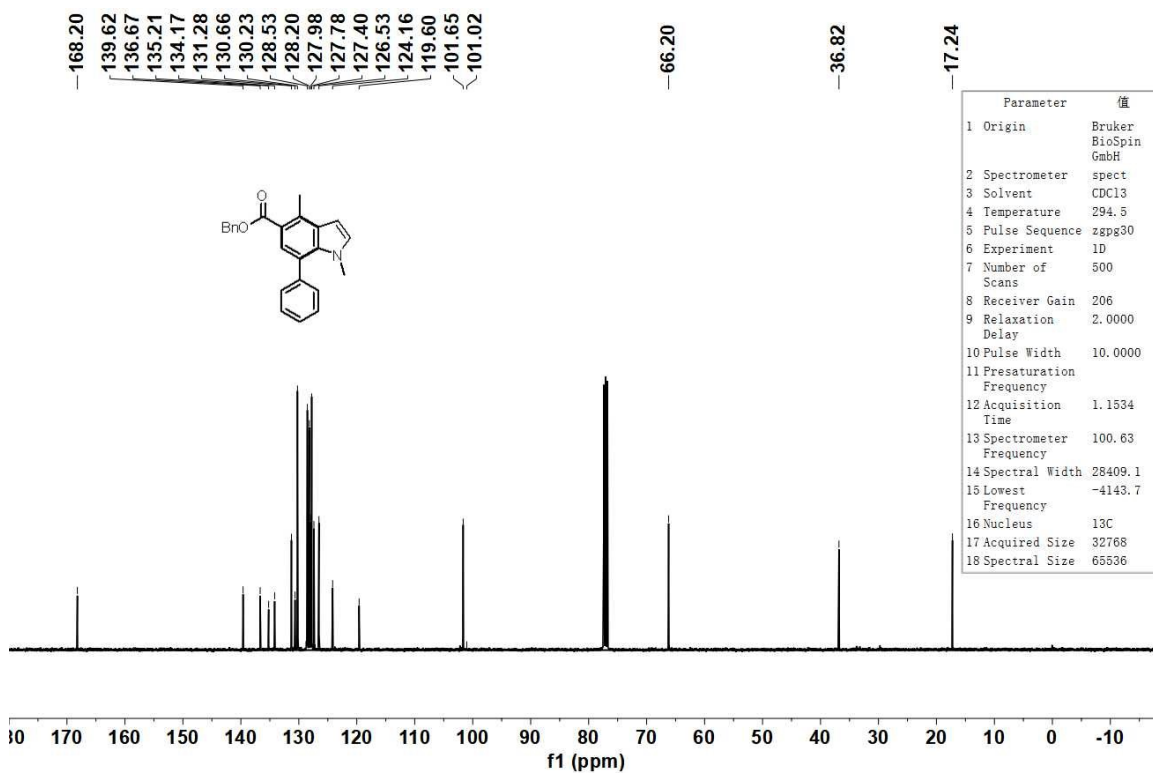
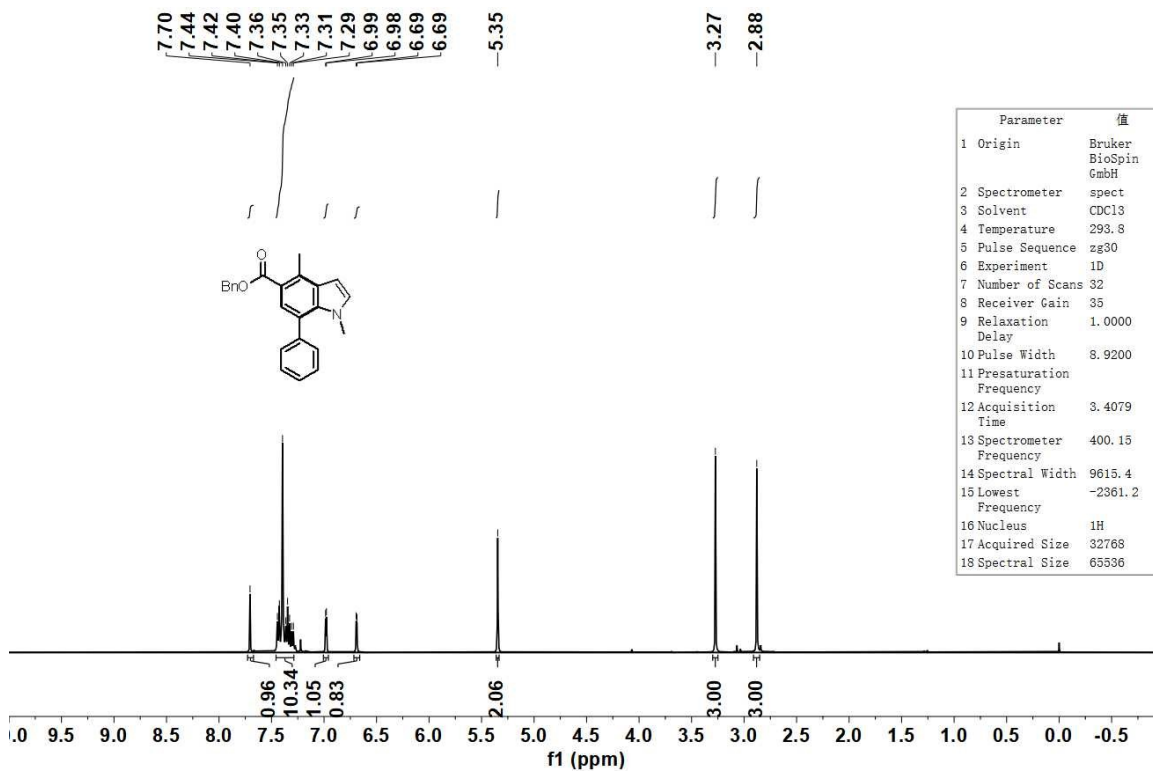
5w



6w

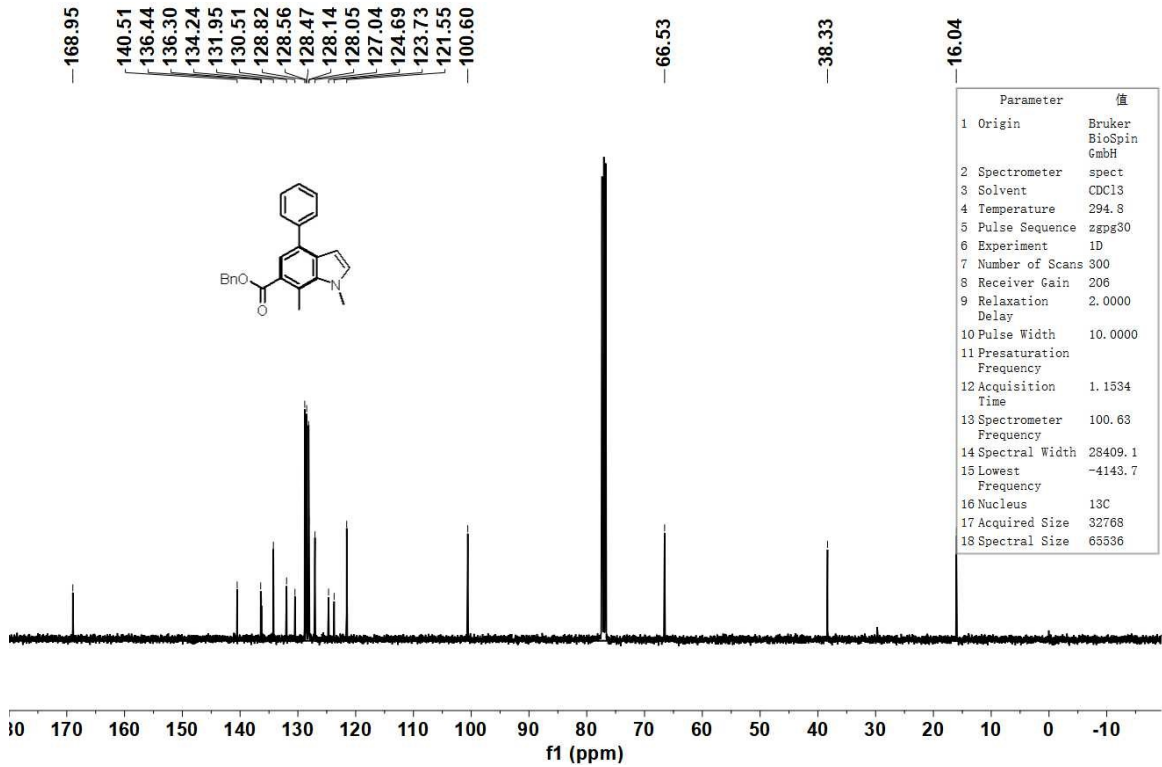
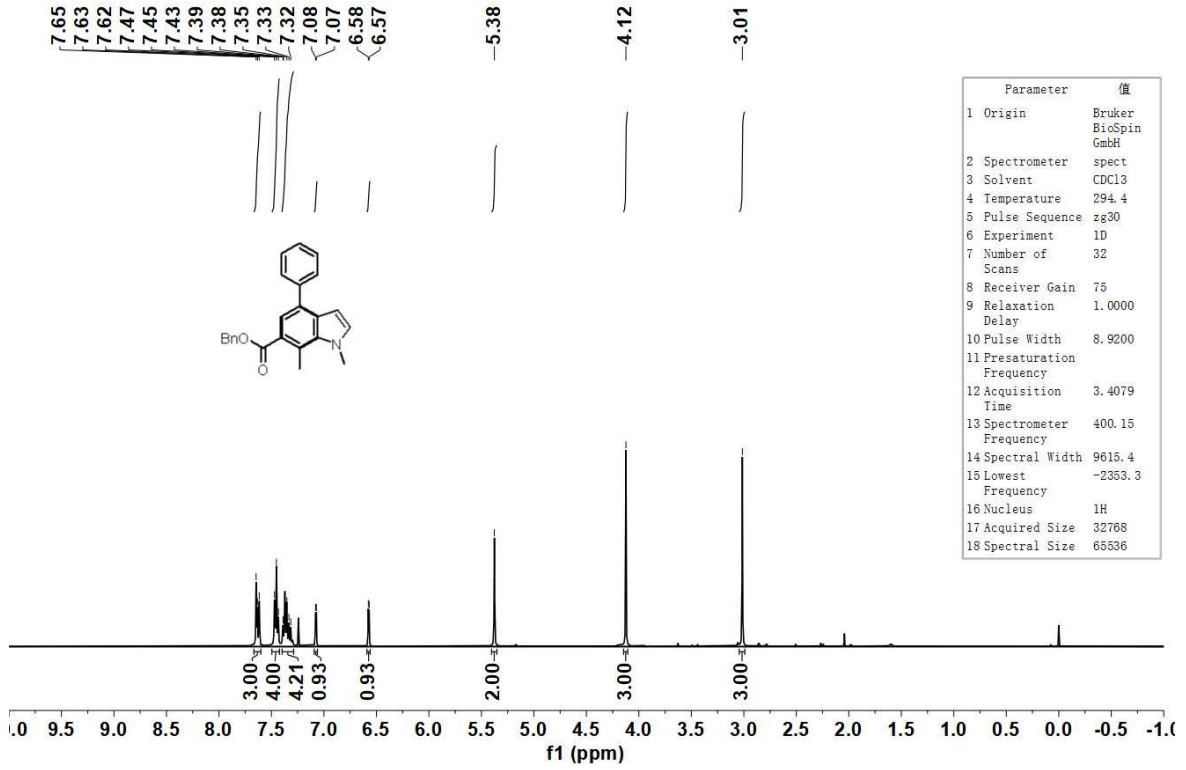


5x

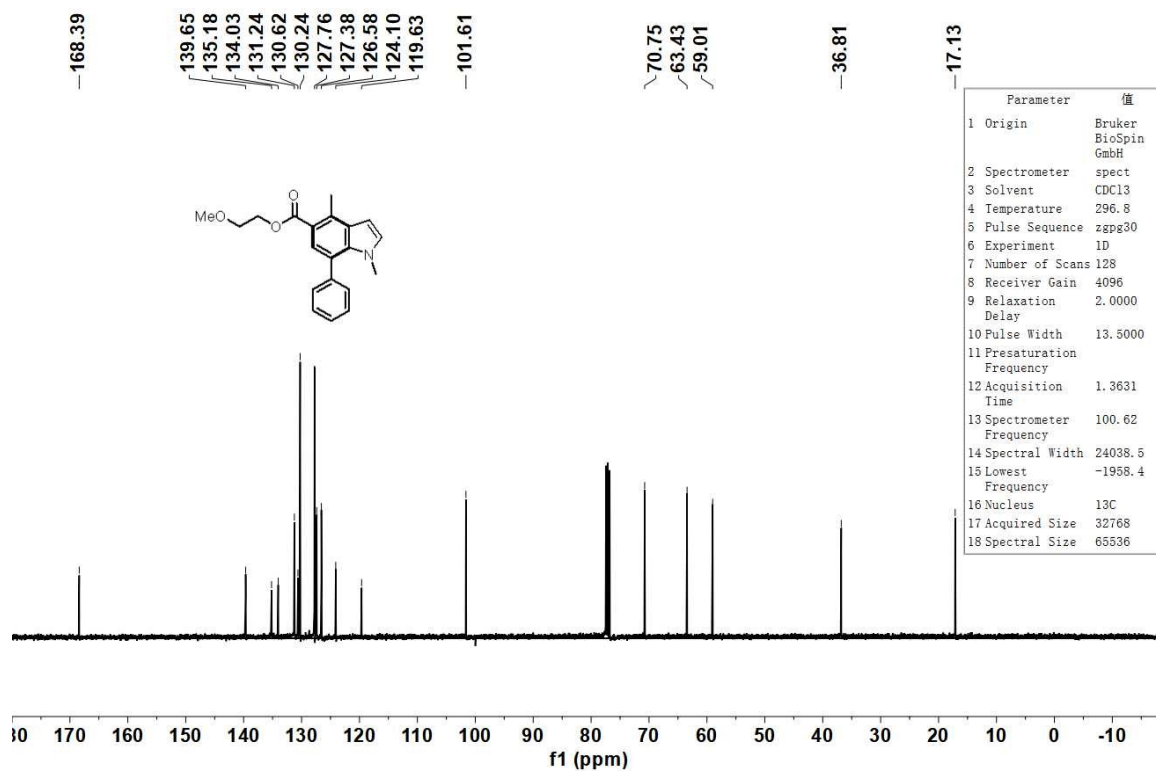
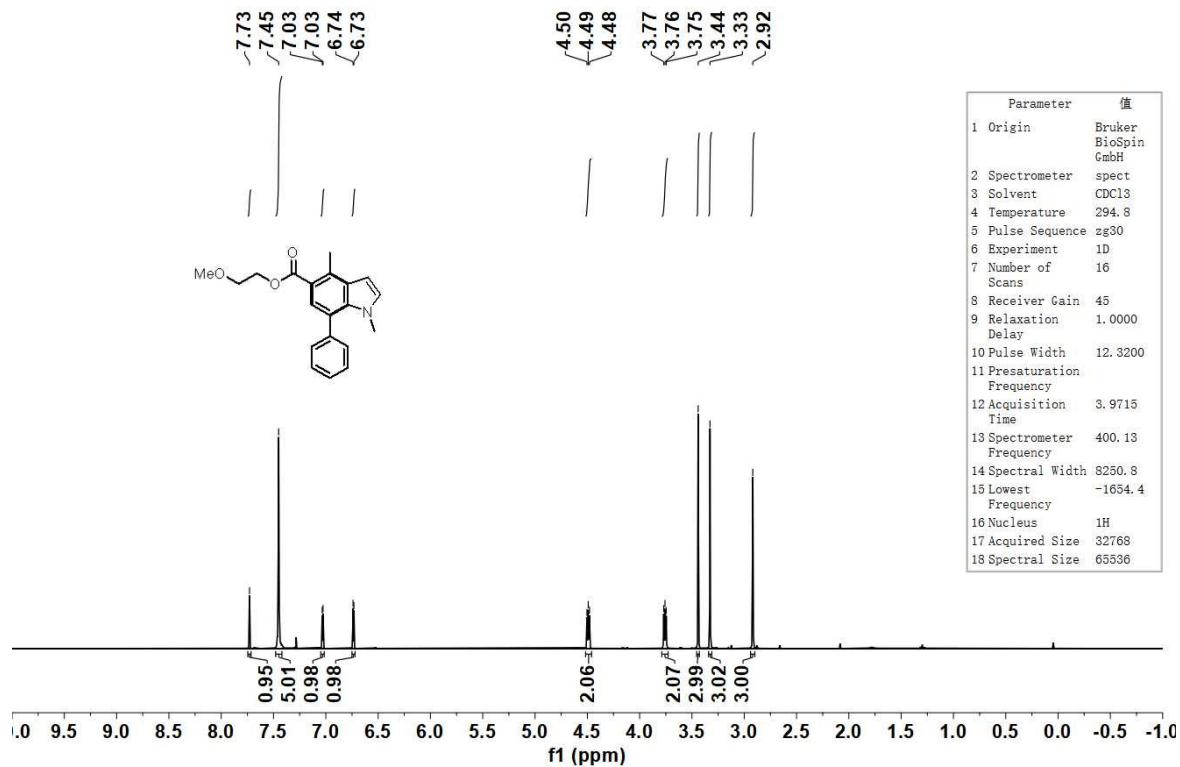




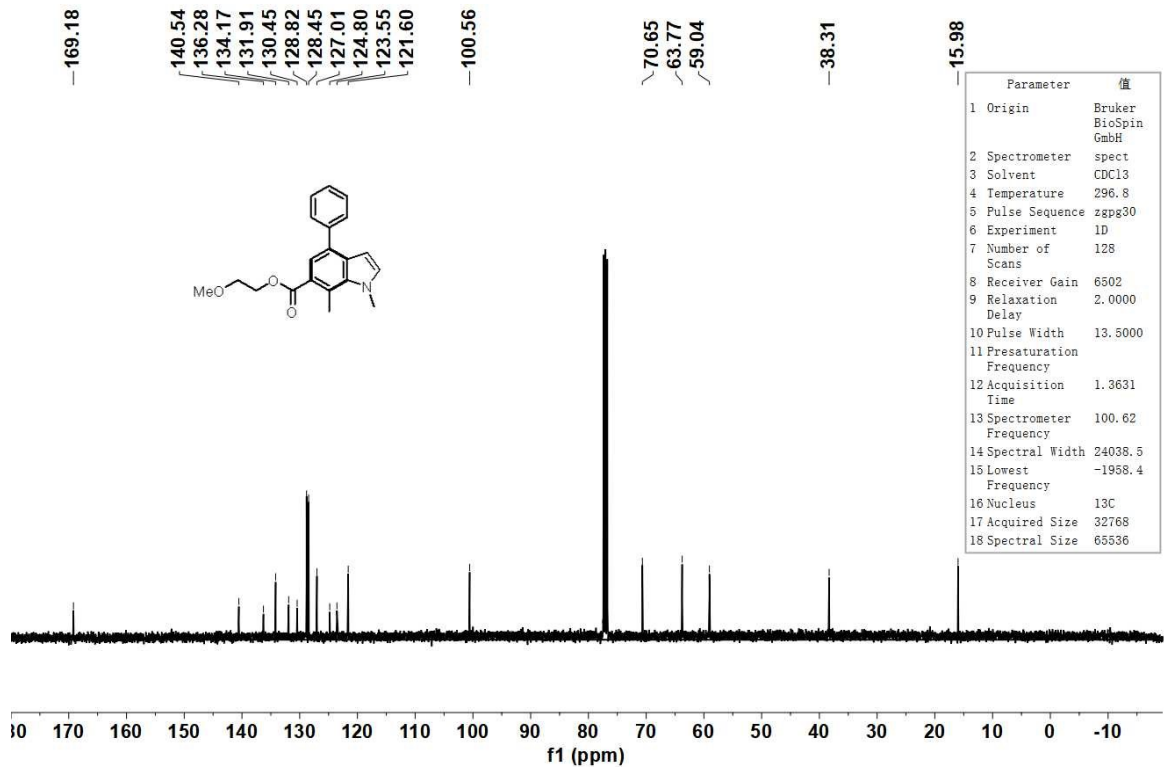
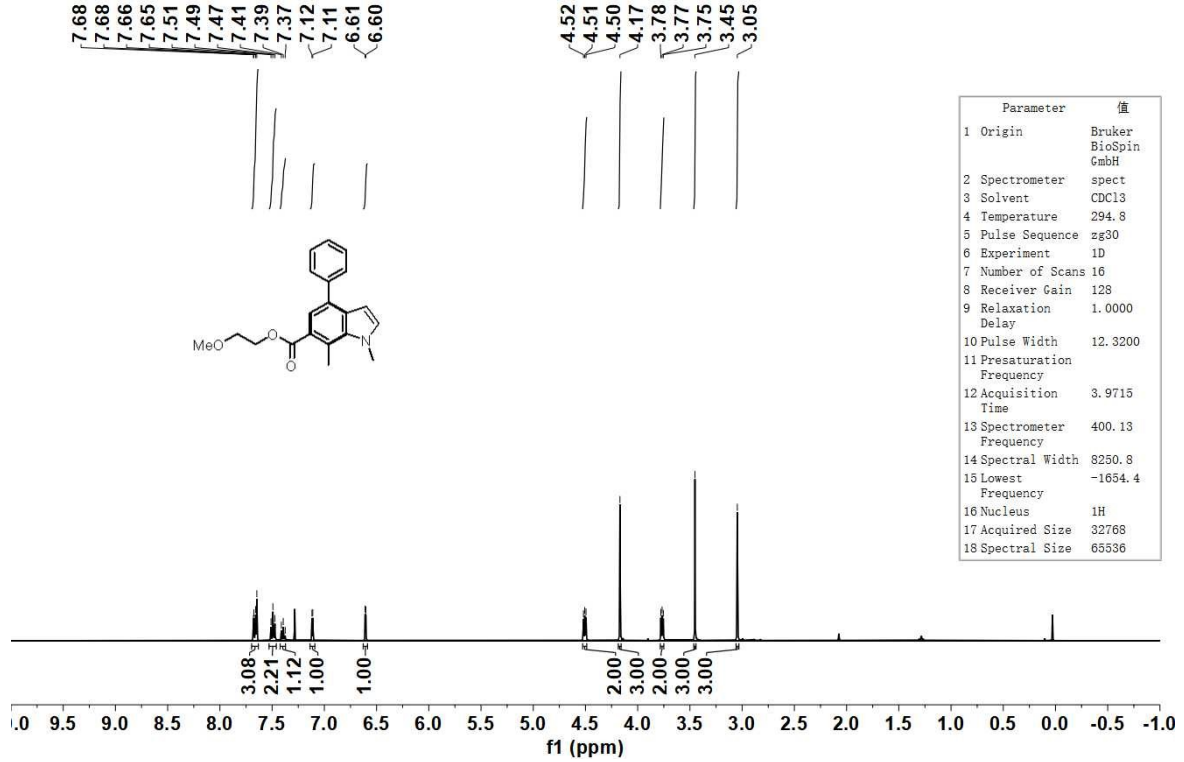
6x



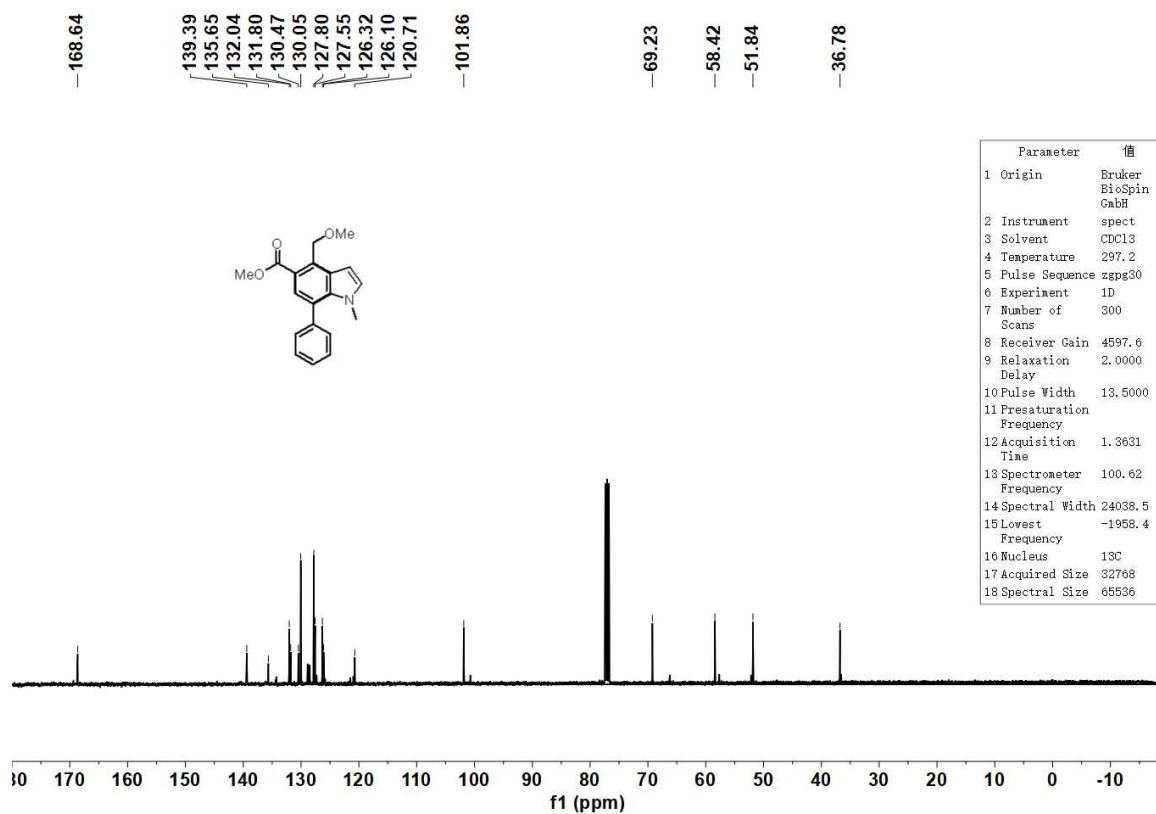
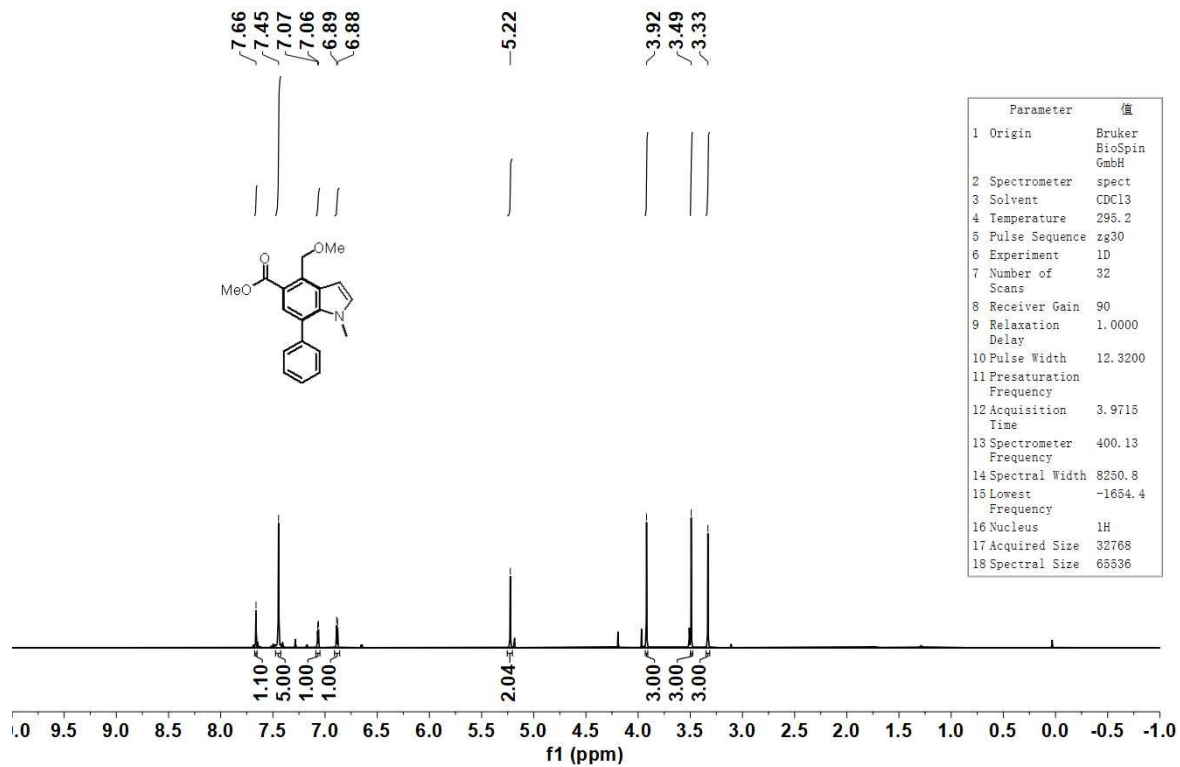
5y



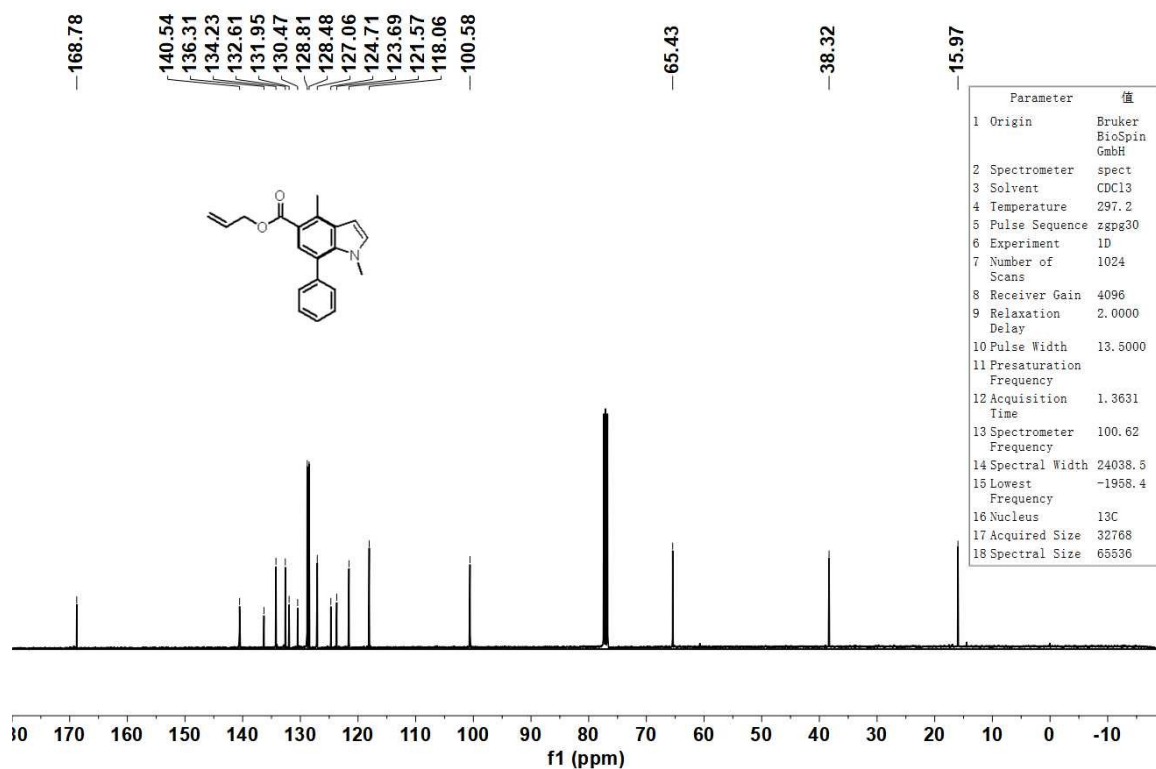
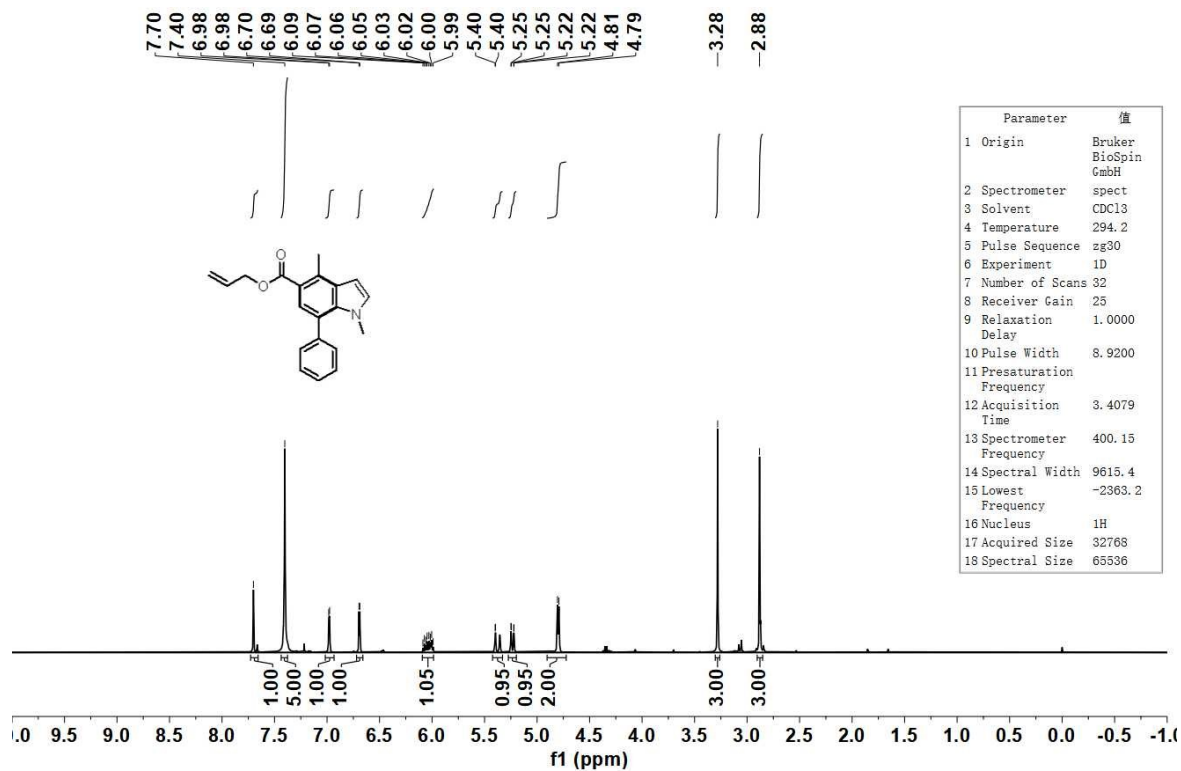
6y



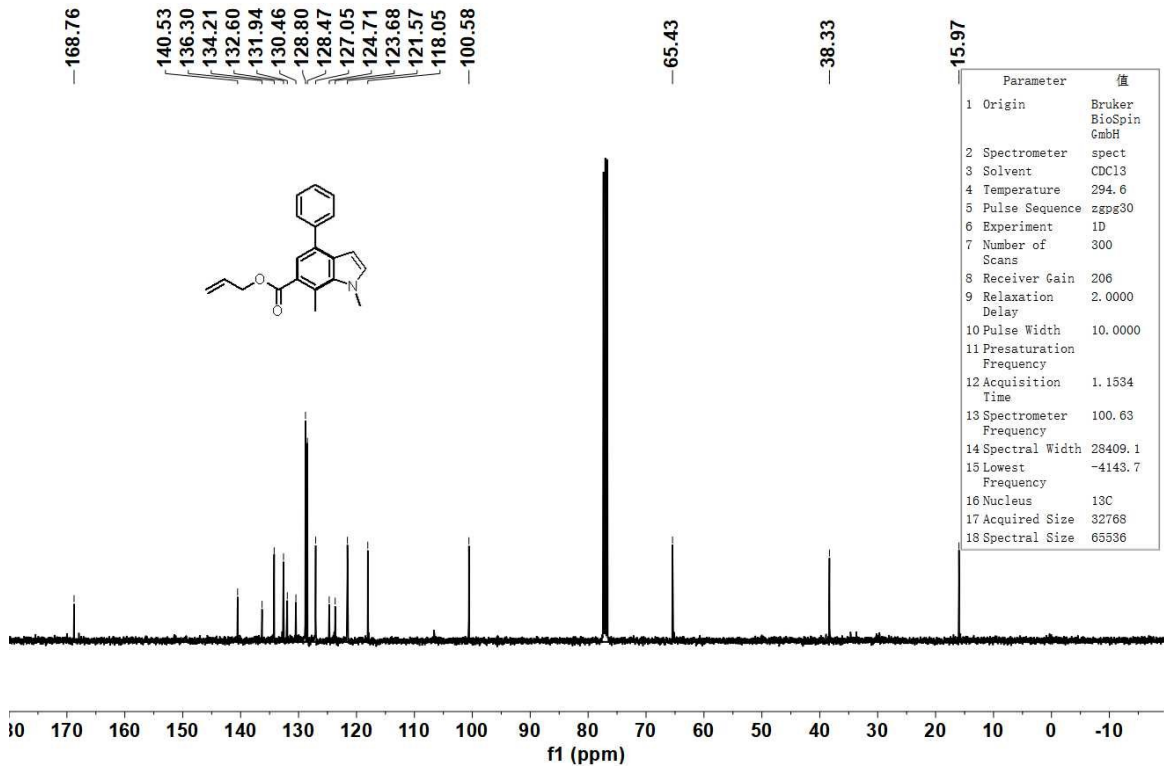
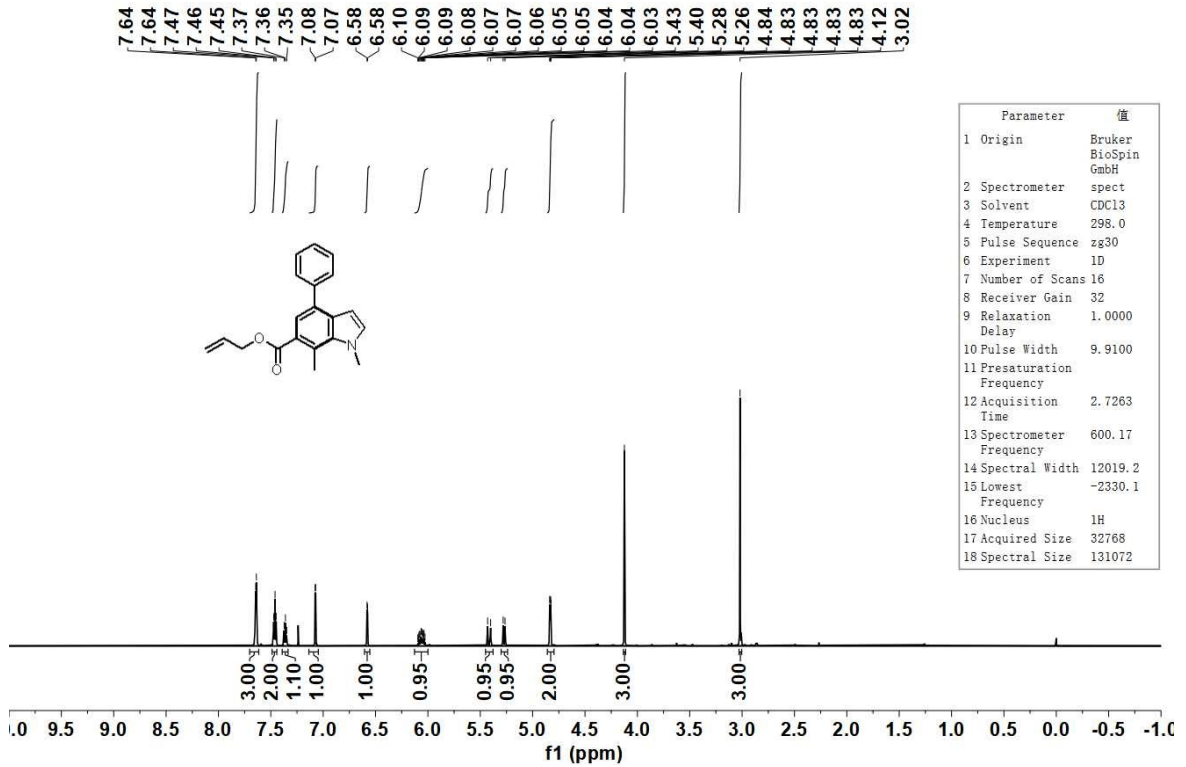
5z



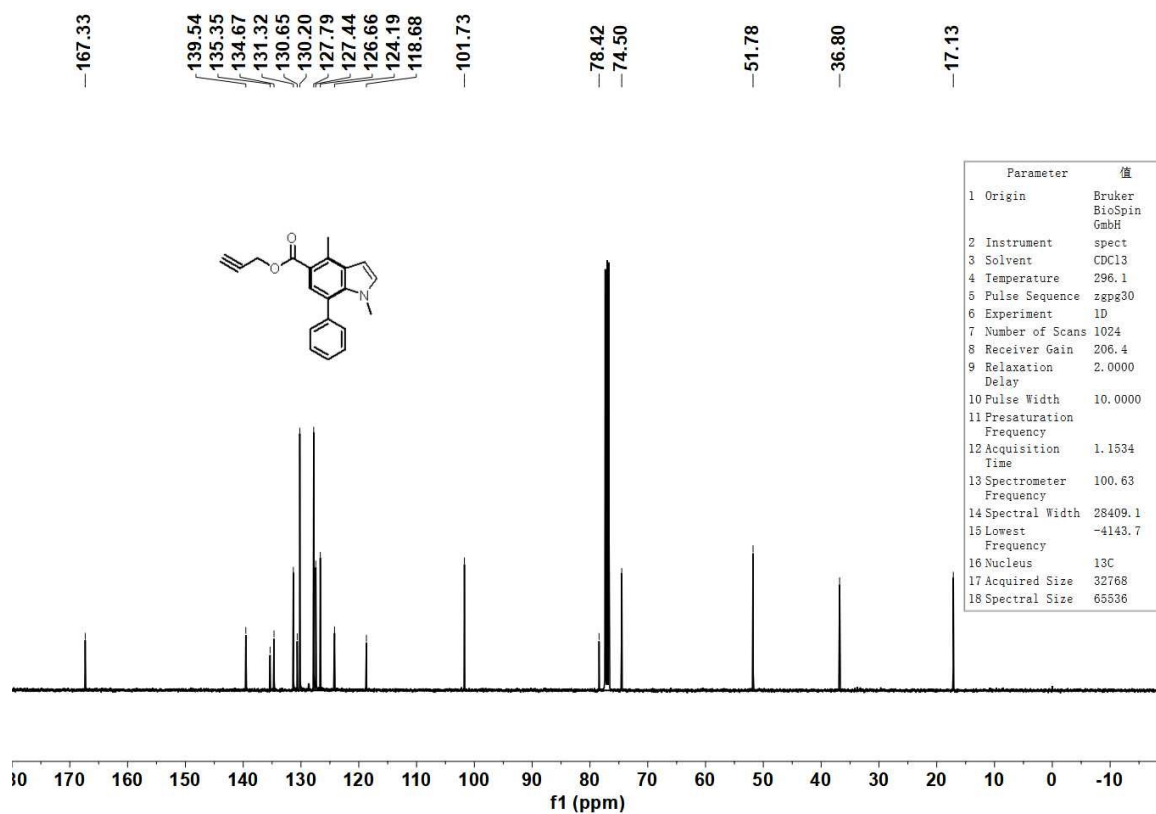
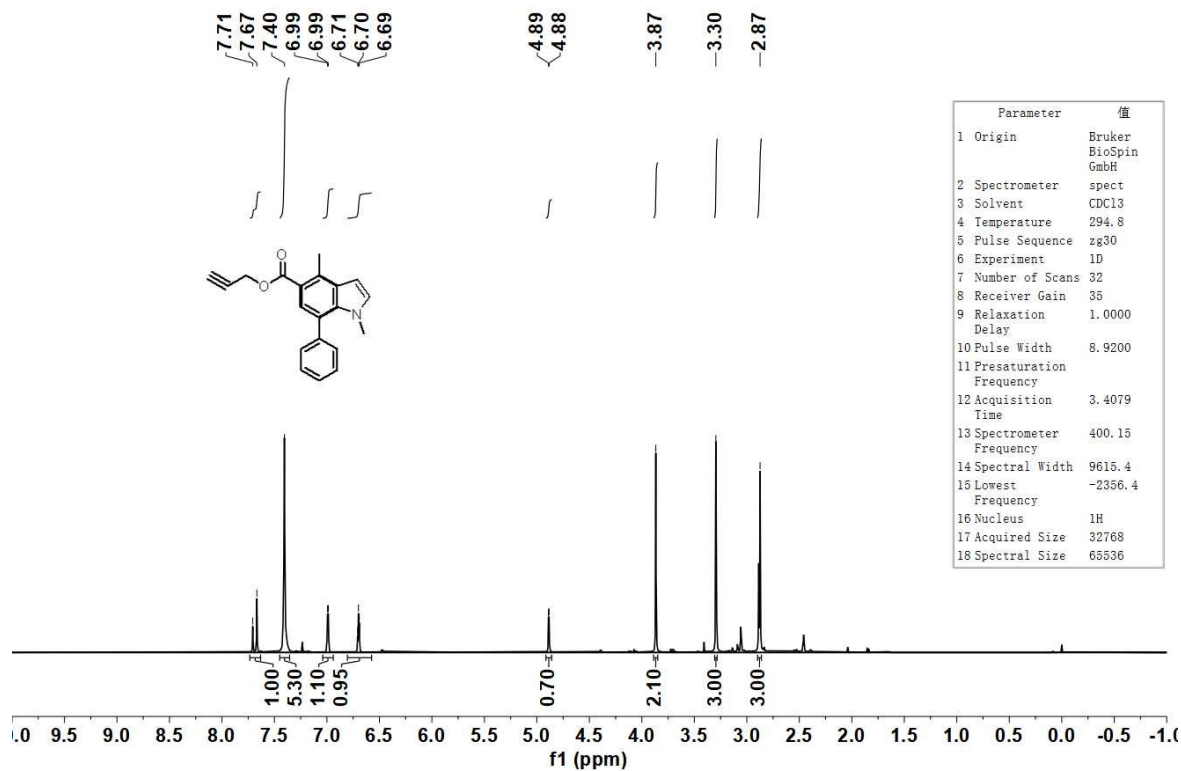
5aa



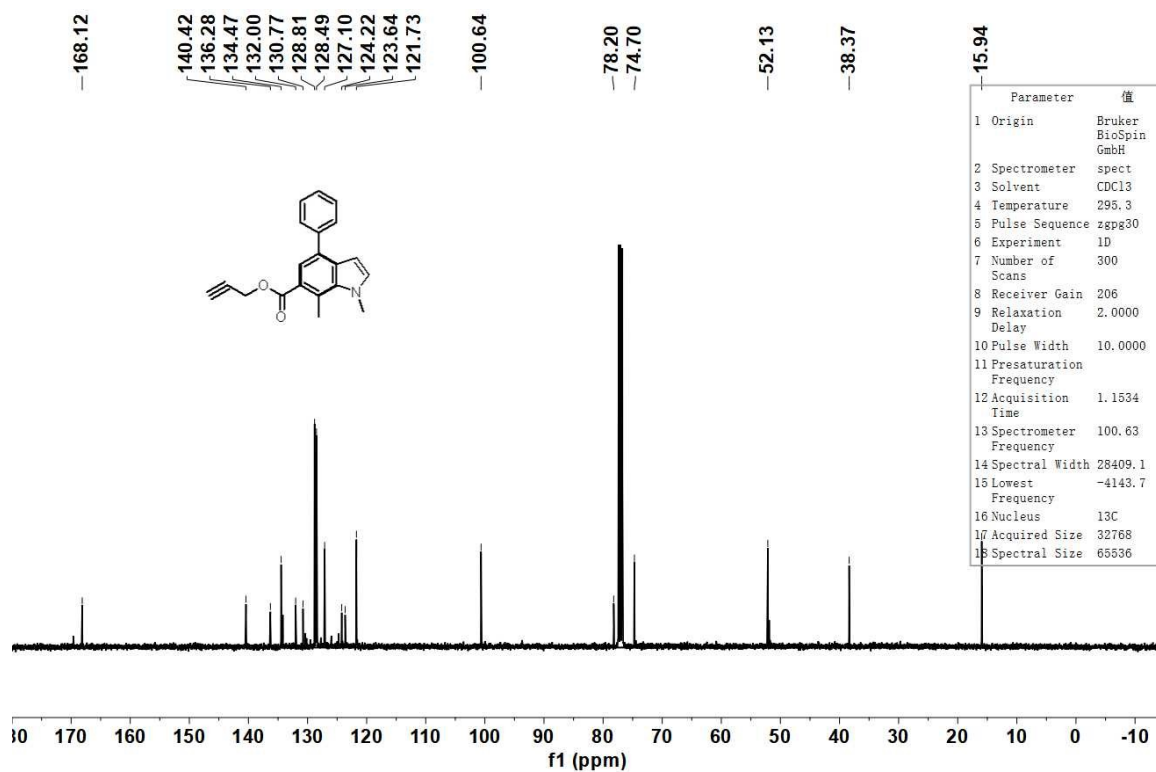
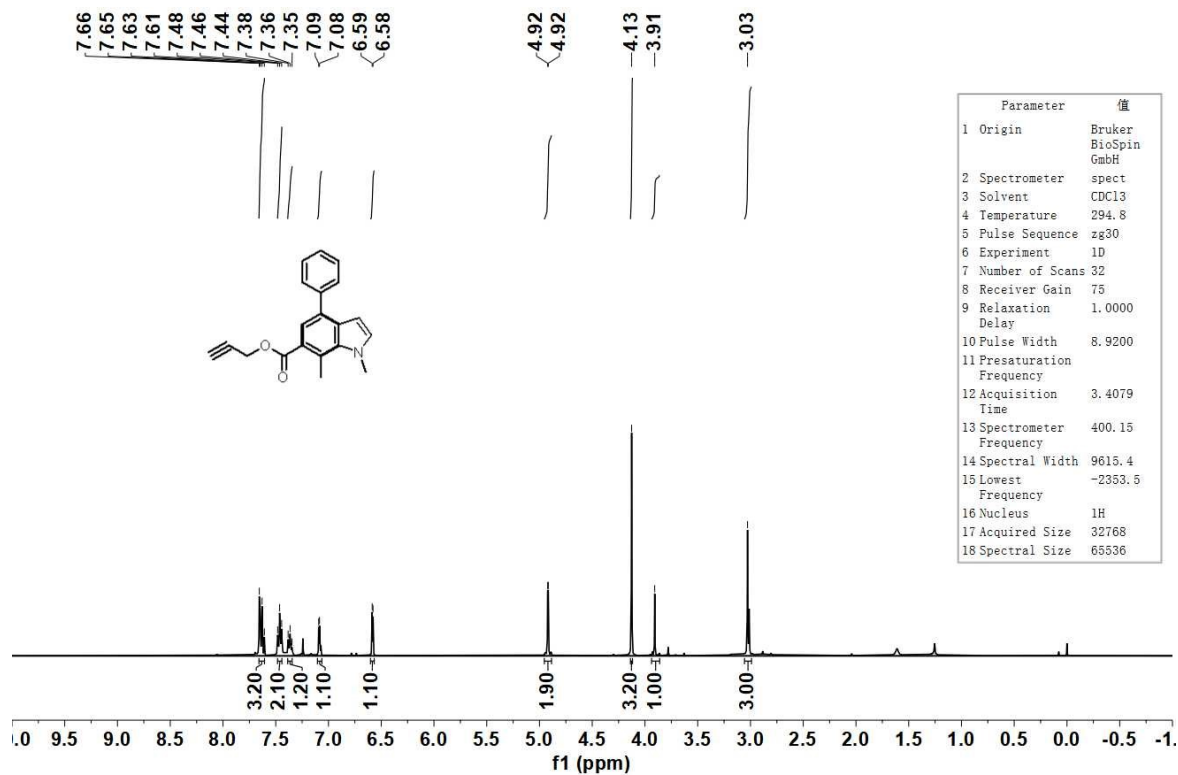
6aa



5ab

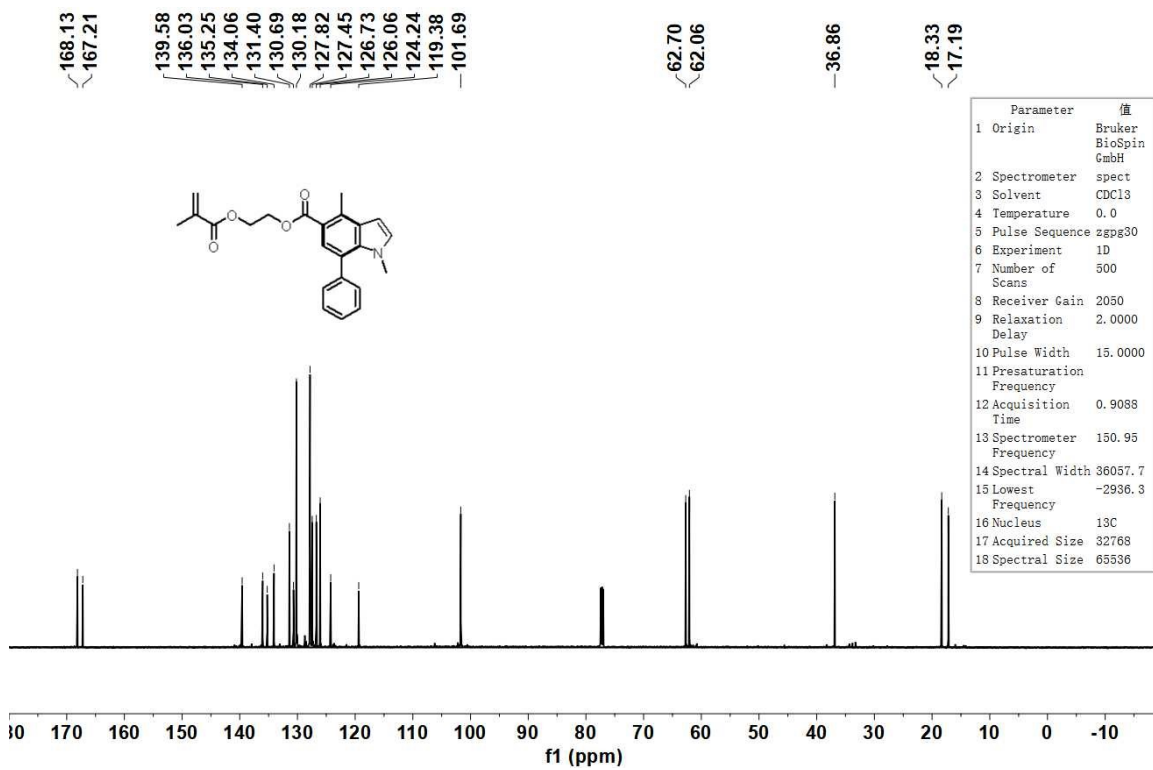
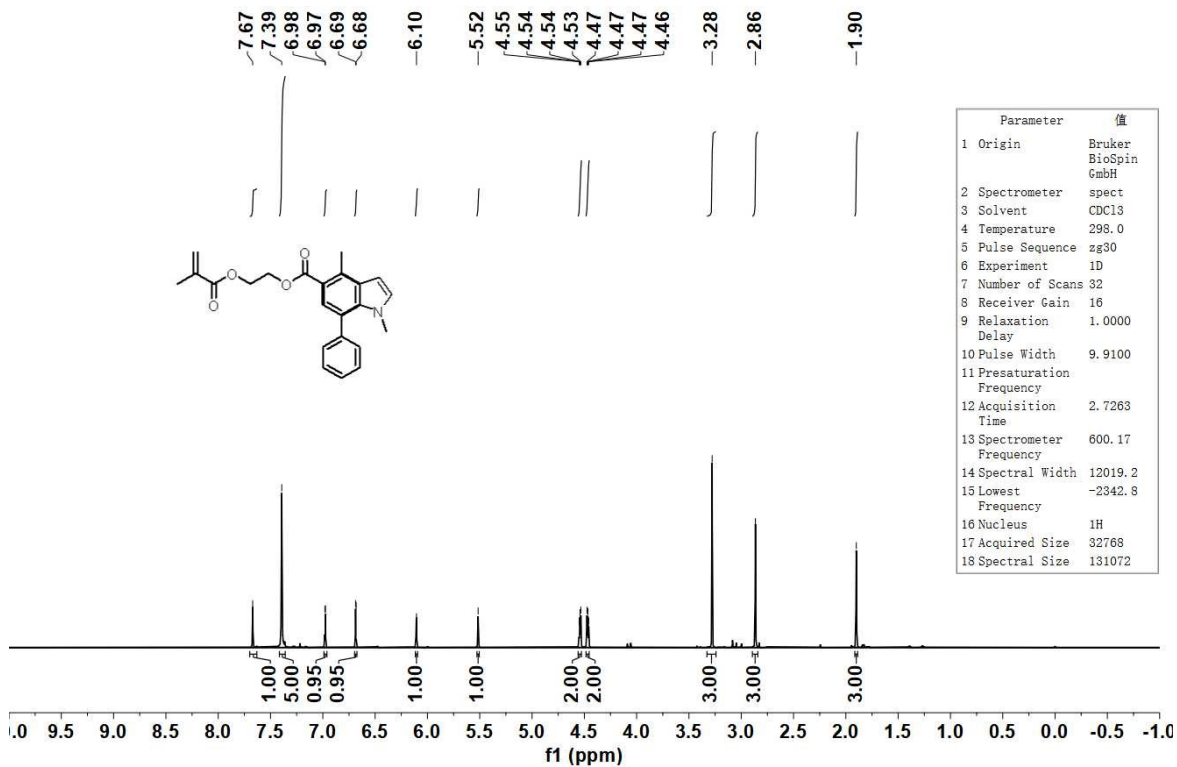


6ab

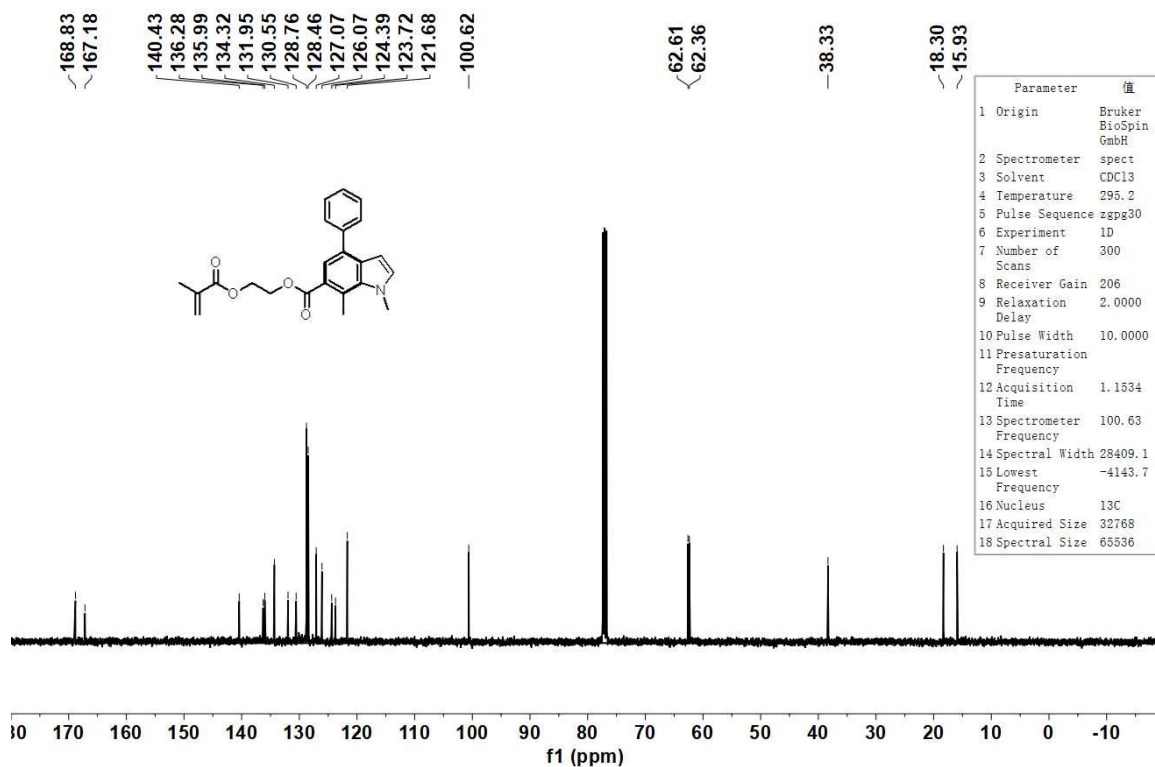
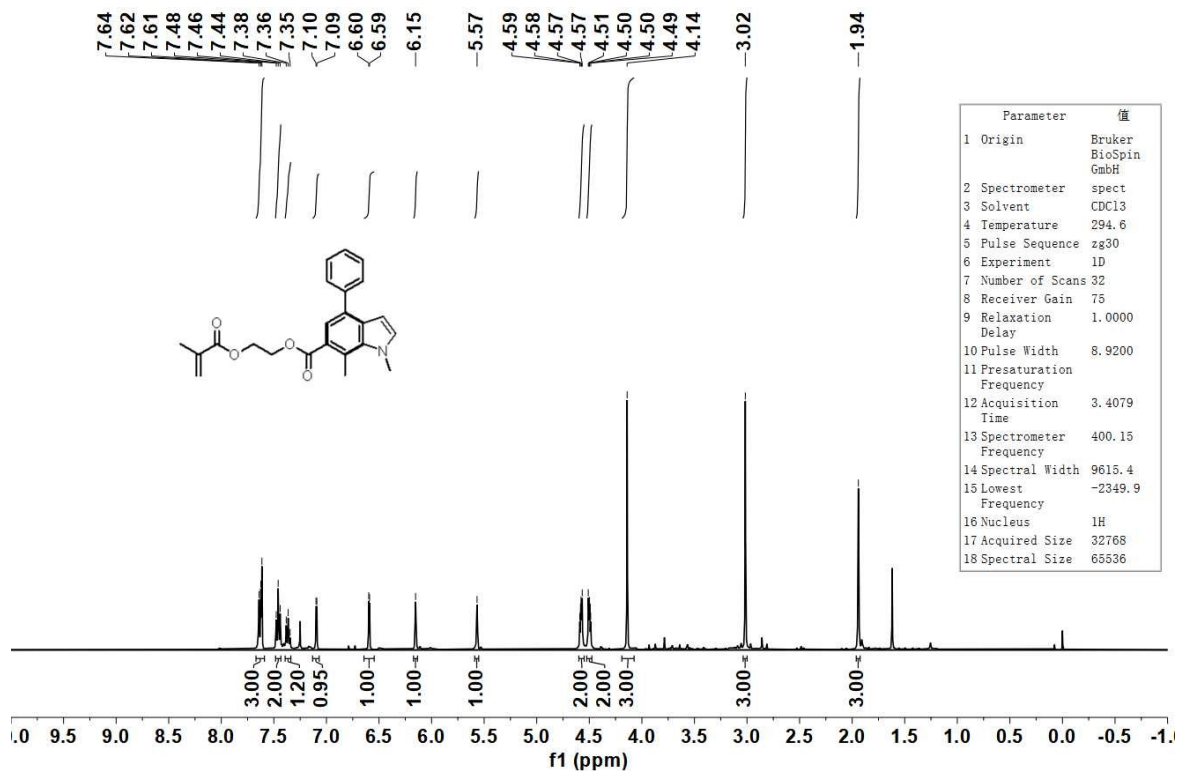




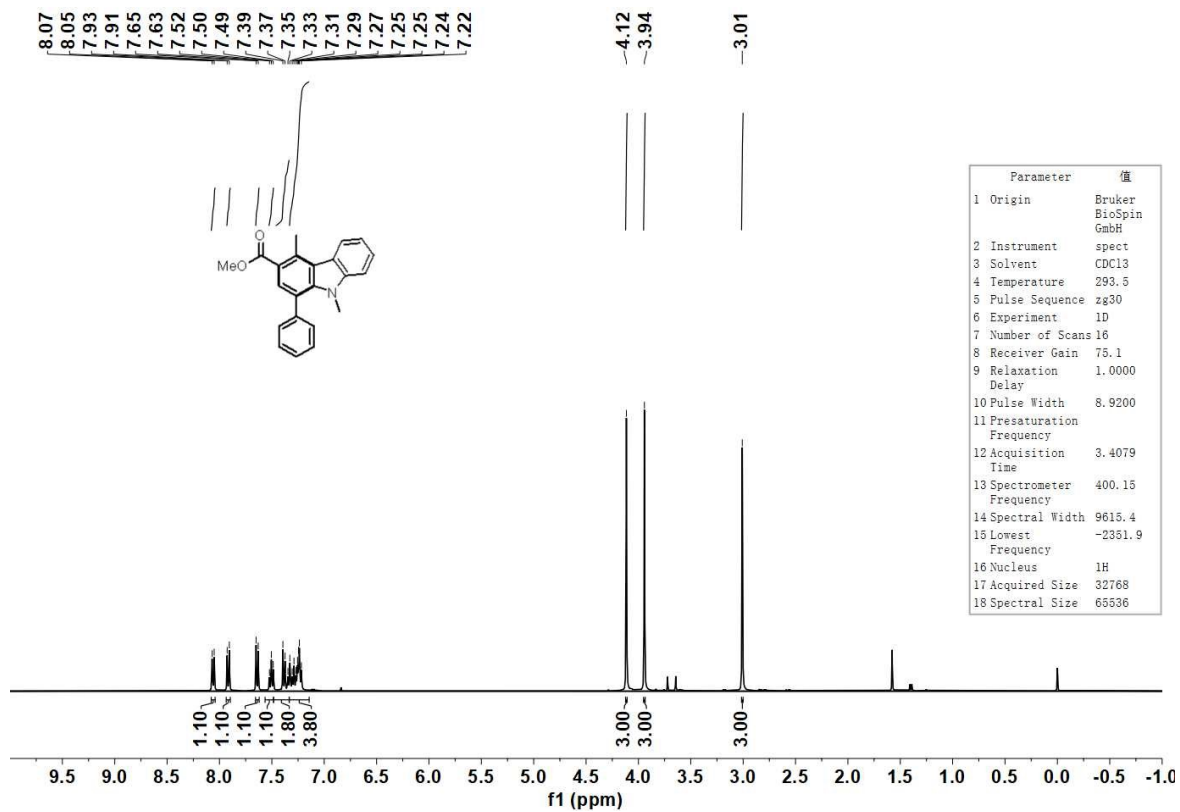
5ac



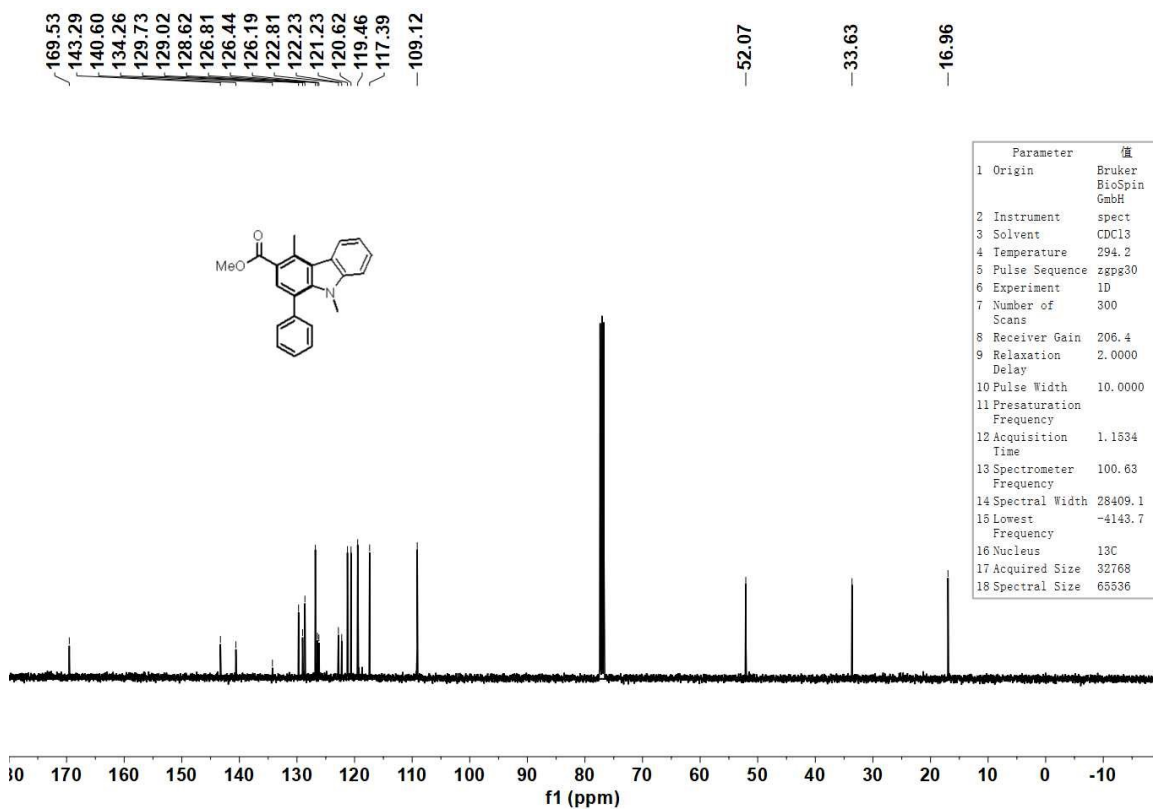
6ac



8a

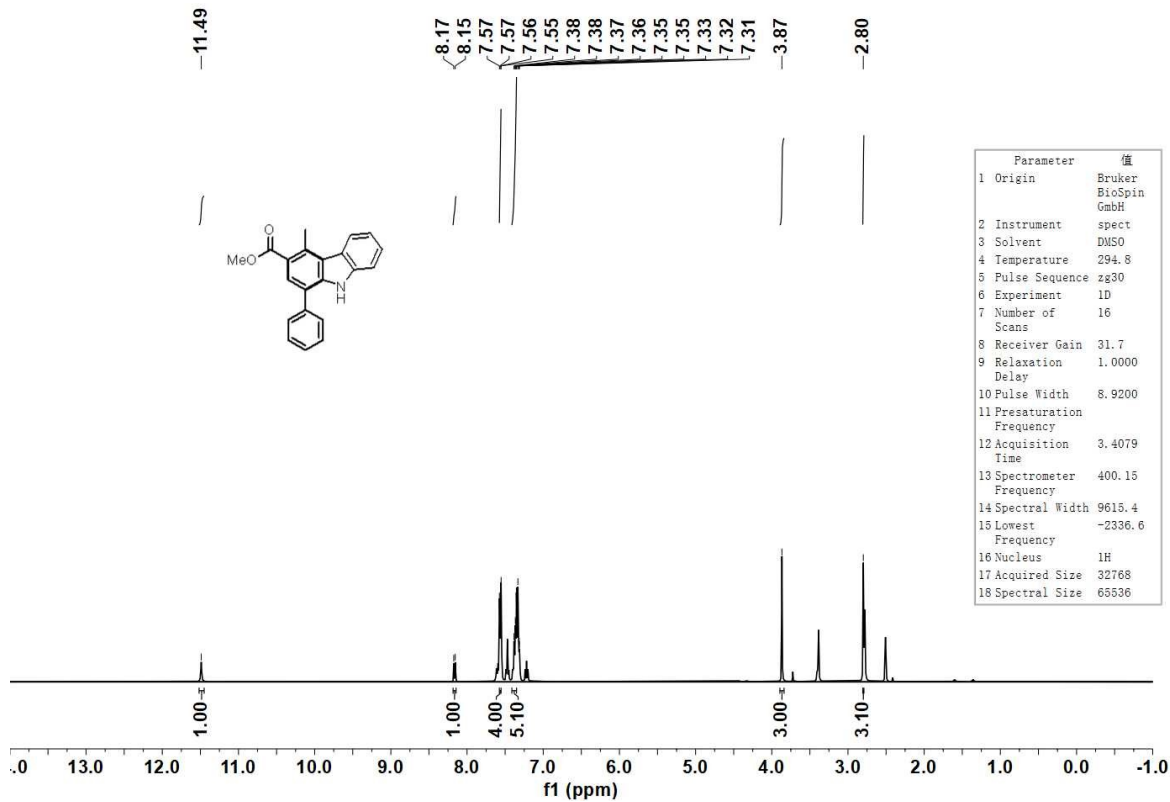


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	293.5
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	75.1
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2331.9
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

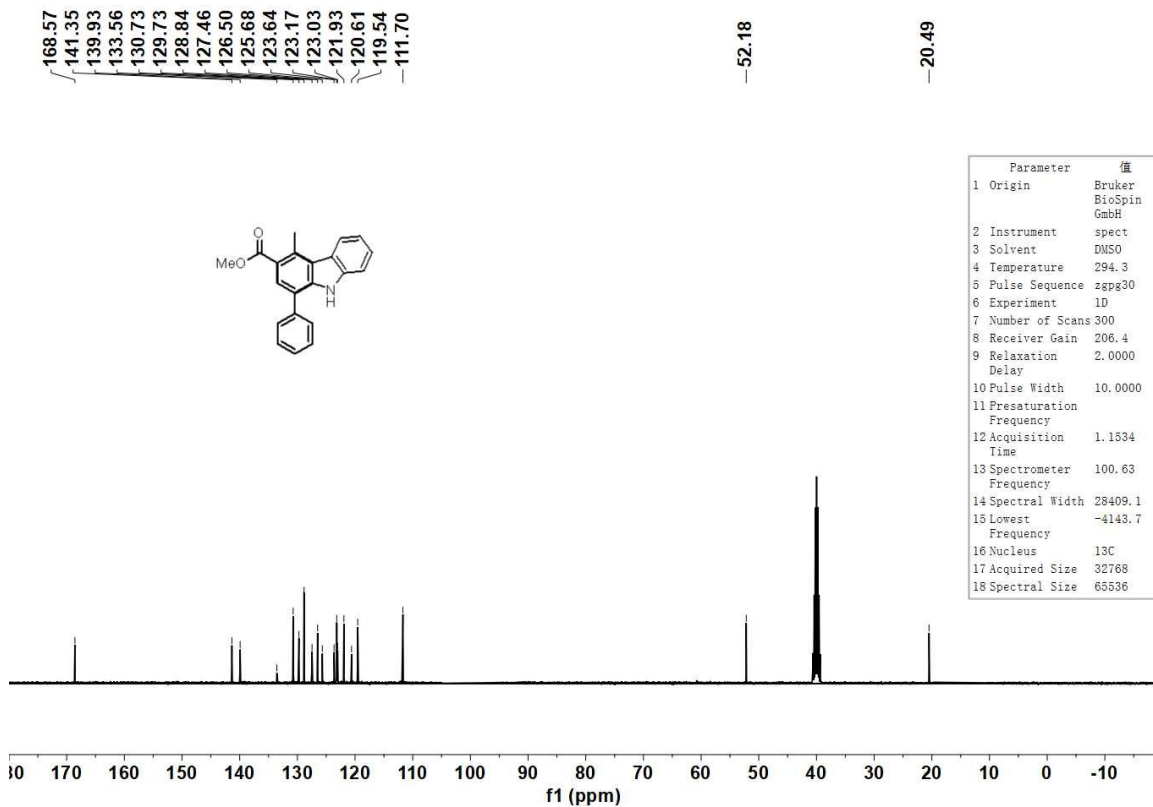


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	294.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Number of Scans	300
8 Receiver Gain	206.4
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

8b

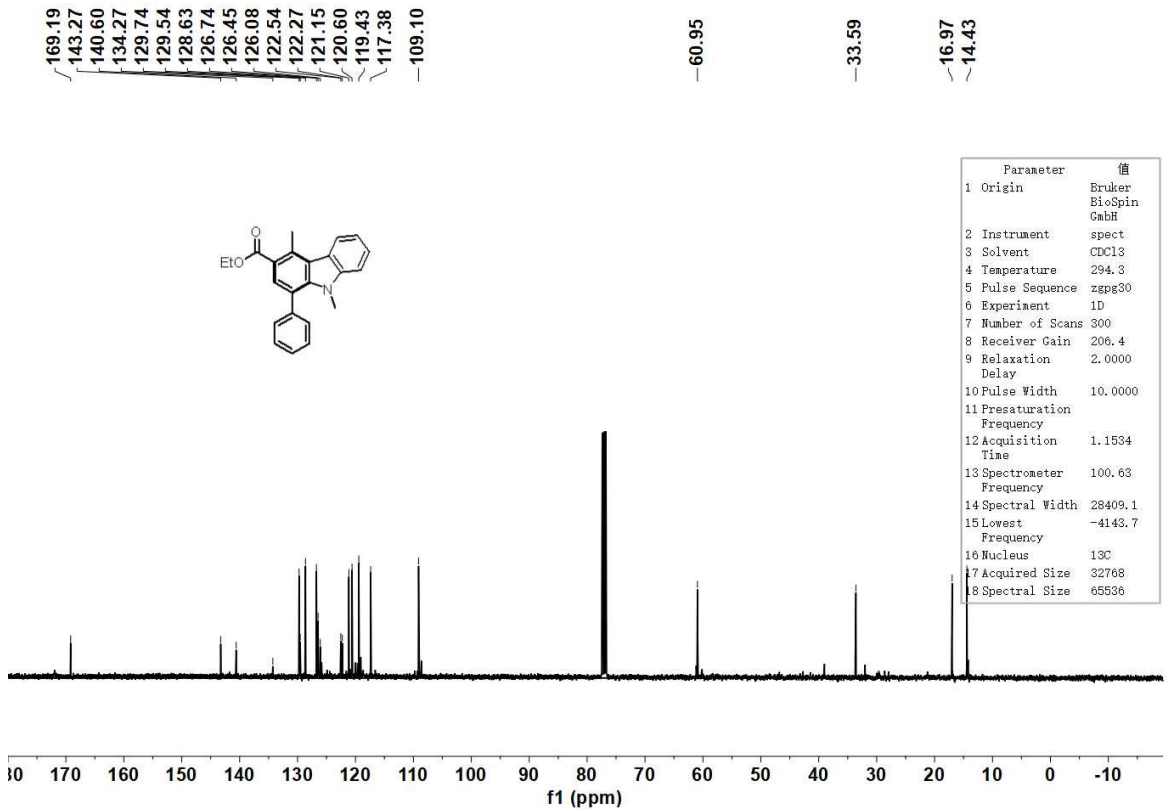
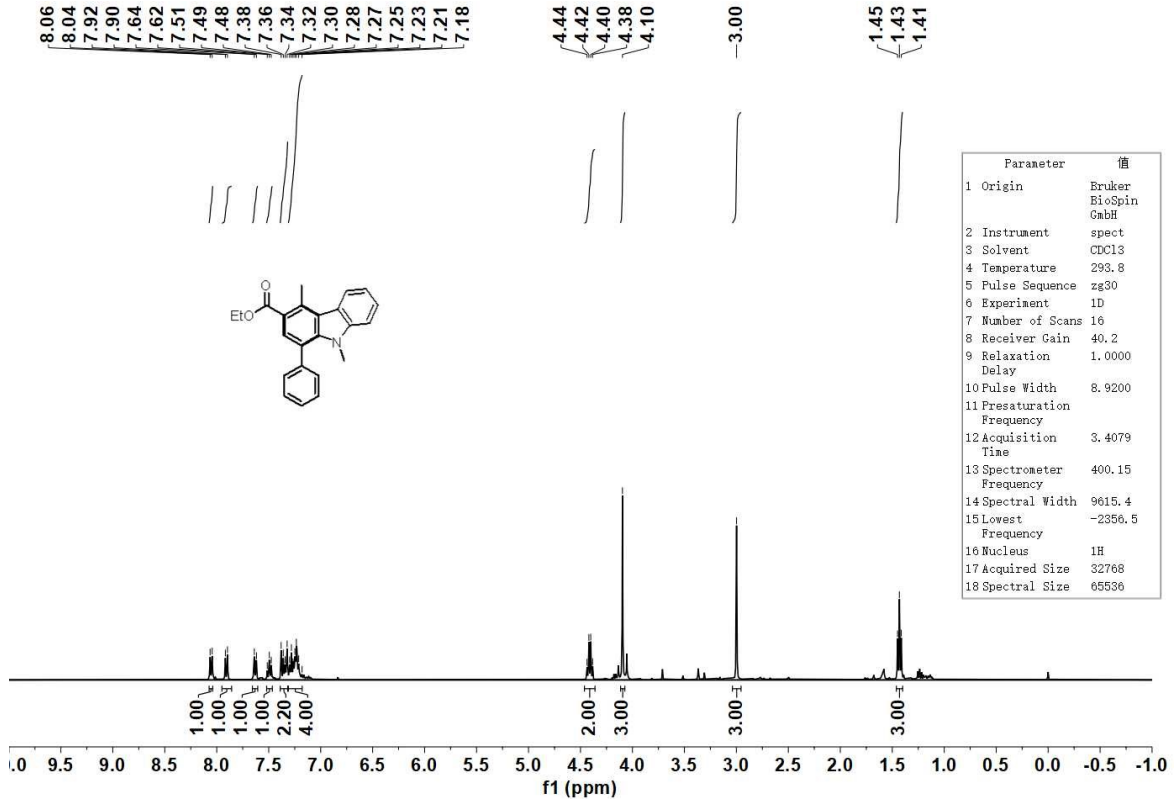


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	DMSO
4 Temperature	294.8
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	31.7
9 Relaxation Delay	1.0000
10 Pulse Width	8.9200
11 Presaturation Frequency	
12 Acquisition Time	3.4079
13 Spectrometer Frequency	400.15
14 Spectral Width	9615.4
15 Lowest Frequency	-2336.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536

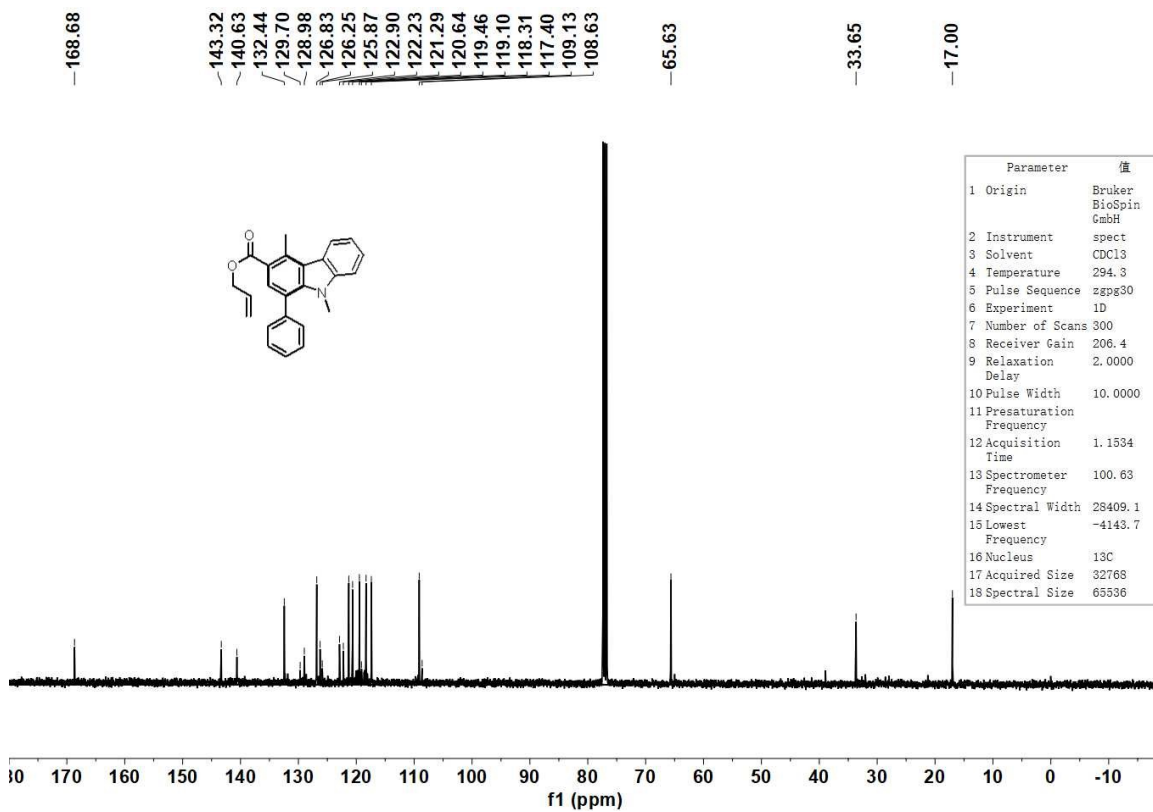
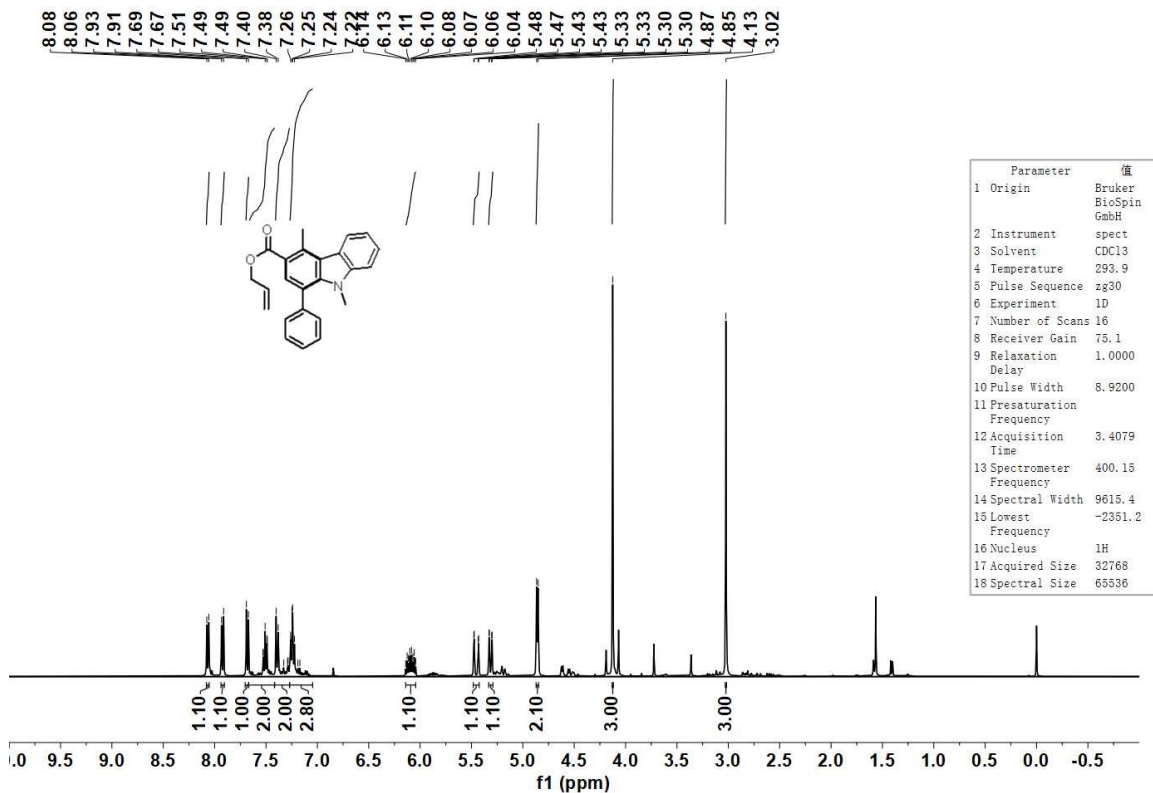


Parameter	值
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	DMSO
4 Temperature	294.3
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Number of Scans	300
8 Receiver Gain	206.4
9 Relaxation Delay	2.0000
10 Pulse Width	10.0000
11 Presaturation Frequency	
12 Acquisition Time	1.1534
13 Spectrometer Frequency	100.63
14 Spectral Width	28409.1
15 Lowest Frequency	-4143.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536

8c



8d



## 9. References

1. M.-M. Chen, M. Zhang, F. Xie and X.-T. Wang, *Monatsh. Chem. Chem. Mon.*, 2014, **146**, 663.
2. Y. Guo, Y. Wang, H. Xue, S. Cao and Y. Zhao, *Tetrahedron*, 2019, **75**, 1481.
3. R. Aeluri, M. Alla, S. Polepalli and N. Jain, *Eur. J. Med. Chem.*, 2015, **100**, 18.
4. R. Zhu, B. Wang, M. Cui, J. Deng, X. Li, Y. Ma and Y. Fu, *Green Chem.*, 2016, **18**, 2029.
5. S. Kundu, A. Banerjee and M. S. Maji, *J. Org. Chem.*, 2019, **84**, 16003.
6. Y. Gu, W. Huang, S. Chen and X. Wang, *Org. Lett.*, 2018, **20**, 4285.
7. J. Yang, F. Mei, S. Fu and Y. Gu, *Green Chem.*, 2018, **20**, 1367.