

## Supporting Information for

### **Sequential annulation of bidentate diamines for the modular access to N-fused/helical/spiro-carbazole scaffolds**

Yi Xiao, Xiya Zhang, Yuqin Wang, Kaida Li, Guixia Wang, Xiangfei Kong, Jinghua Wang\*, and Shiqing Li\*

*Guangxi Key Laboratory of Electrochemical and Magneto-Chemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541006, P. R. China.*

*E-mail: [lisq@glut.edu.cn](mailto:lisq@glut.edu.cn)*

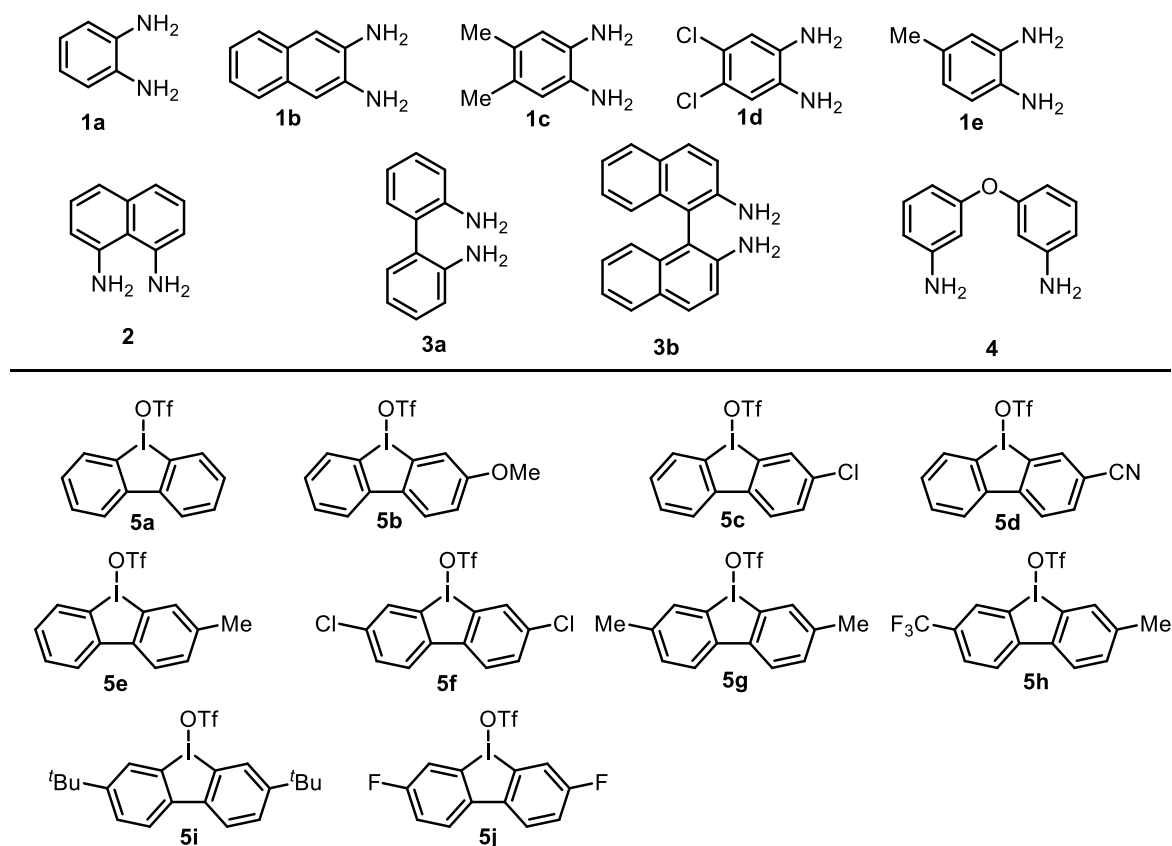
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## 1 General remarks

NMR spectra were obtained on a BRUKER Ascend 500. The  $^1\text{H}$  NMR (500 MHz) chemical shifts were measured relative to  $\text{CDCl}_3$  as the internal reference ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). All  $^{13}\text{C}$  NMR spectra were recorded with complete proton decoupling. The  $^{13}\text{C}$  NMR (125 MHz) chemical shifts were given using  $\text{CDCl}_3$  the internal standard ( $\text{CDCl}_3$ :  $\delta = 77.16$  ppm). High-resolution mass spectra (HRMS) were obtained with Waters G2-xs qtof at Nth Power Test Platform For Scientific Research. Fluorescence emission spectra were obtained using Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence and Hitachi F-7000 spectrometers. Melting points were determined with SGW<sup>®</sup> X-4 and are uncorrected. The single crystal diffraction XRD measurement was conducted by Bruker D8 VENTURE METALJET Ga-Target SC-XRD at Shiyanjia lab ([www.Shiyanjia.com](http://www.Shiyanjia.com)). Quantum yield (QY) measurement was conducted by Edinburgh FLS1000.

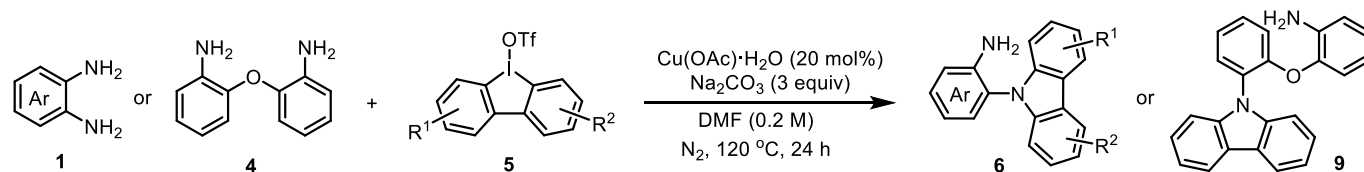
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu}(\text{OAc})_2$ ,  $\text{NEt}_3$ , 2,2'-bipyridine,  $\text{Na}_2\text{CO}_3$  and DMF were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd. TfOH and *m*-CPBA (purity of 75%) were purchased from Adamas-Beta Ltd.



All diamines **1-4** were commercially available. Cyclic diaryliodonium salts **5a-j** were known compounds and prepared according to the literature procedures.<sup>[1]</sup>

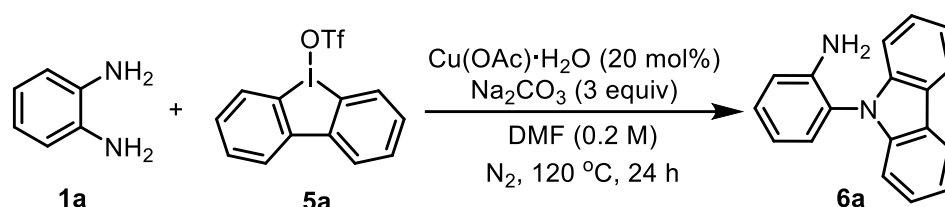
## 2 General procedure for the synthesis of *N*-aminoaryl carbazoles

### 2.1 General procedure A (GP A) for the synthesis of compounds **6** and **9**



The mixture of 1,2-diamine **1** or **4** (0.2 mmol), cyclic iodonium **5** (0.25 mmol, 1.25 equiv),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (8.0 mg, 20 mol%),  $\text{Na}_2\text{CO}_3$  (63.6 mg, 0.6 mmol, 3 equiv), and DMF (1 mL) was reacted at 120 °C for 24 h under  $\text{N}_2$  atmosphere. After reaction tube was cooled down, the mixture was directly passed through a flash chromatography, eluting with petroleum ether/EtOAc (100/1  $\rightarrow$  60/1, v/v) to afford products **6** and **9**.

**Table S1.** Optimization of the reaction conditions of **1a** and **5a**

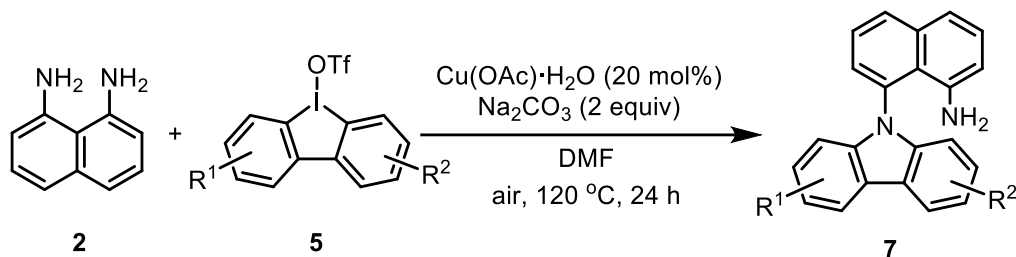


Entry	Catalyst (x mol%)	Base (y equiv)	Solvent	Yield (%)
1	$\text{Cu}(\text{OAc})_2$ (20)	$\text{Na}_2\text{CO}_3$ (3)	<i>i</i> -PrOH/( $\text{CH}_2\text{OH}$ ) <sub>2</sub> (9:1)	59
2	$\text{Cu}(\text{OAc})_2$ (10)	$\text{Na}_2\text{CO}_3$ (3)	<i>i</i> -PrOH/( $\text{CH}_2\text{OH}$ ) <sub>2</sub> (9:1)	41
3	$\text{Cu}(\text{OAc})_2$ (20)	$\text{NEt}_3$ (1)	DMF	75
4	$\text{Cu}(\text{OAc})_2$ (10)	$\text{Na}_2\text{CO}_3$ (3)	<i>i</i> -PrOH	Trace
5	$\text{Cu}(\text{OAc})_2$ (20)	$\text{Na}_2\text{CO}_3$ (3)	<i>i</i> -PrOH	53
6	$\text{Cu}(\text{OAc})_2$ (20)	$\text{Na}_2\text{CO}_3$ (3)	DMF	37
7	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{NEt}_3$ (1)	$\text{CH}_3\text{OH}$	39
8	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{NEt}_3$ (1)	$\text{CH}_3\text{CN}$	51
9	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{NEt}_3$ (1)	1,4-Dioxane	64
10	$\text{CuI}$ (20)	$\text{Na}_2\text{CO}_3$ (3)	DMF	65
11	$\text{CuBr}$ (20)	$\text{Na}_2\text{CO}_3$ (3)	DMF	80
12	$\text{CuCl}$ (20)	$\text{Na}_2\text{CO}_3$ (3)	DMF	72
13	$\text{Cu}(\text{OTf})_2$ (20)	$\text{Na}_2\text{CO}_3$ (3)	DMF	81
<b>14</b>	<b><math>\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}</math> (20)</b>	<b><math>\text{Na}_2\text{CO}_3</math> (3)</b>	<b>DMF</b>	<b>90</b>
15	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (10)	$\text{Na}_2\text{CO}_3$ (3)	DMF	68
16	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (10)	$\text{Na}_2\text{CO}_3$ (2)	DMF	76
17	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{Na}_2\text{CO}_3$ (1)	DMF	48
18	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{NEt}_3$ (1)	DMF	53
19	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	2,2'-bipy (0.1)/ $\text{NEt}_3$ (1)	DMF	Trace
20	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	2,2'-bipy (0.1)/ $\text{K}_2\text{CO}_3$ (1)	DMF	32
21	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	Xantphos/ $\text{Cs}_2\text{CO}_3$ (1)	DMF	ND
22	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{Cs}_2\text{CO}_3$ (1)	DMF	71
23	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	$\text{K}_3\text{PO}_4$ (3)	DMF	81

### Scale-up synthesis of 6a (1 mmol)

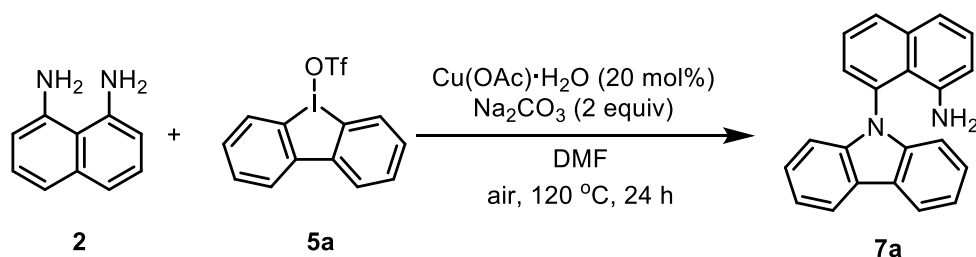
The mixture of **1a** (108 mg, 1.0 mmol), **5a** (534.9 mg, 1.25 mmol, 1.25 equiv), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (40 mg, 20 mol%), Na<sub>2</sub>CO<sub>3</sub> (318 mg, 3.0 mmol, 3 equiv), and DMF (5 mL) was reacted at 120 °C for 24 h under N<sub>2</sub> atmosphere. The reaction mixture was cooled down before concentrated under vacuum. The residue was purified by a silica gel (200–300 mesh) column, eluting with petroleum ether/EtOAc (100/1, v/v) to afford product **6a** as a white solid (136 mg, 75% yield).

### 2.2 General procedure B (GP B) for the synthesis of compounds 7



To a dry Schlenk tube was added naphthalene-1,8-diamine **2** (31.6 mg, 0.2 mmol), diaryliodonium **5** (0.25 mmol, 1.25 equiv), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (8.0 mg, 20 mol%), Na<sub>2</sub>CO<sub>3</sub> (42.4 mg, 0.4 mmol, 2 equiv), and DMF (1 mL), the mixture was reacted at 120 °C for 24 h under air. After reaction tube was completed, the mixture was directly passed through a flash chromatography [petroleum ether/EtOAc (100/1 → 60/1, v/v)] to afford products **7**.

**Table S2.** Optimization of reaction conditions of **2** and **5a**



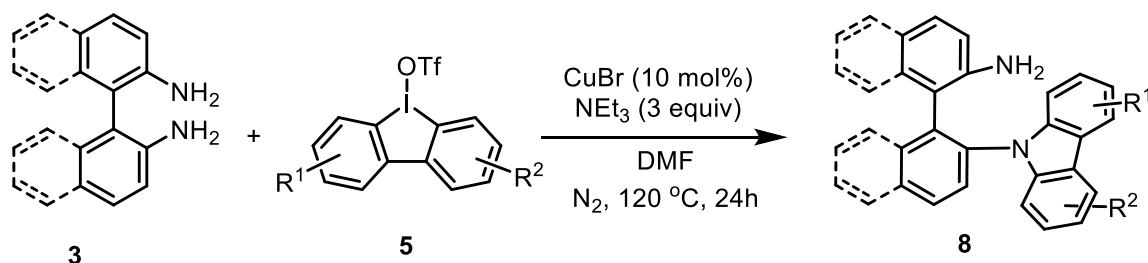
Entry	Catalyst (x mol%)	Base (y equiv)	Atmosphere	Yield (%)
1	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (20)	Na <sub>2</sub> CO <sub>3</sub> (3)	air	81%
2	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	Na <sub>2</sub> CO <sub>3</sub> (3)	air	87%
<b>3</b>	<b>Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (20)</b>	<b>Na<sub>2</sub>CO<sub>3</sub> (2)</b>	<b>air</b>	<b>96%</b>
4	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	Na <sub>2</sub> CO <sub>3</sub> (3)	N <sub>2</sub>	75%

### Scale-up synthesis of 7a (1 mmol)

The mixture of **2** (158 mg, 1.0 mmol), **5a** (534.9 mg, 1.25 mmol, 1.25 equiv), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (40 mg, 20 mol%), Na<sub>2</sub>CO<sub>3</sub> (212 mg, 2.0 mmol, 2 equiv), and DMF (5 mL) was reacted at 120 °C for 24 h under air. The

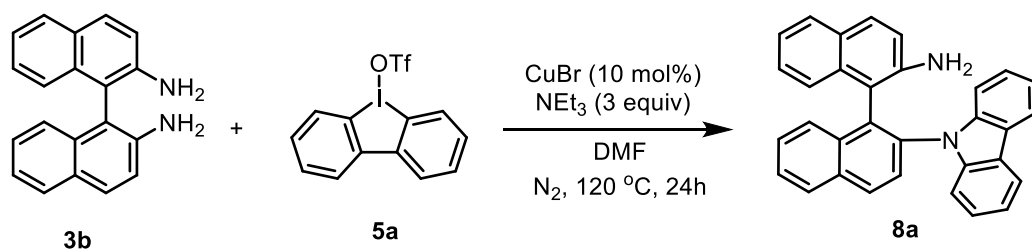
reaction mixture was cooled down before concentrated under vacuum. The residue was purified by a silica gel (200–300 mesh) column, eluting with petroleum ether/EtOAc (100/1, v/v) to afford product **7a** as a yellow solid (276 mg, 90% yield).

### 2.3 General procedure C (GP C) of for the synthesis of compounds **8**



The mixture of [1,1'-biaryl]-2,2'-diamine **3** (0.2 mmol), diaryliodonium **5** (0.25 mmol, 1.25 equiv), CuBr (2.8 mg, 10 mol%), NEt<sub>3</sub> (84 μL, 3 equiv), and DMF (1 mL) was reacted at 120 °C for 24 h under N<sub>2</sub>. After reaction tube was cooled down, the mixture was directly passed through a flash chromatography [petroleum ether/EtOAc (100/1 → 80/1, v/v)] to afford products **8**.

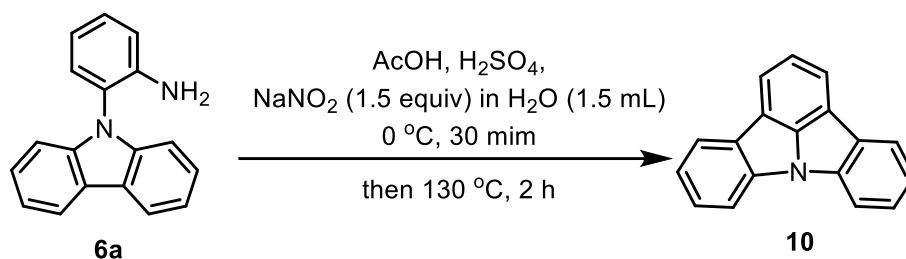
**Table S3.** Optimization of reaction conditions of **3b** and **5a**



Entry	Catalyst (x mol%)	Base (y equiv)	Yield (%)
1	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	NEt <sub>3</sub> (1)	18
2	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (20)	NEt <sub>3</sub> (1)	16
3	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (10)	NEt <sub>3</sub> (2)	12
4	Cu(OAc) <sub>2</sub> (20)	NEt <sub>3</sub> (3)	26
5	Cu(OAc) <sub>2</sub> (10)	NEt <sub>3</sub> (3)	21
<b>6</b>	<b>CuBr (10)</b>	<b>NEt<sub>3</sub> (3)</b>	<b>33</b>

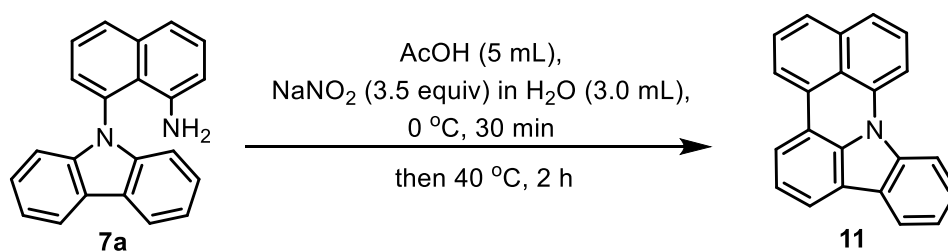
### 3 Procedures for diazotization/cyclization to access compounds 10–13

#### 3.1 Synthesis of ICz 10



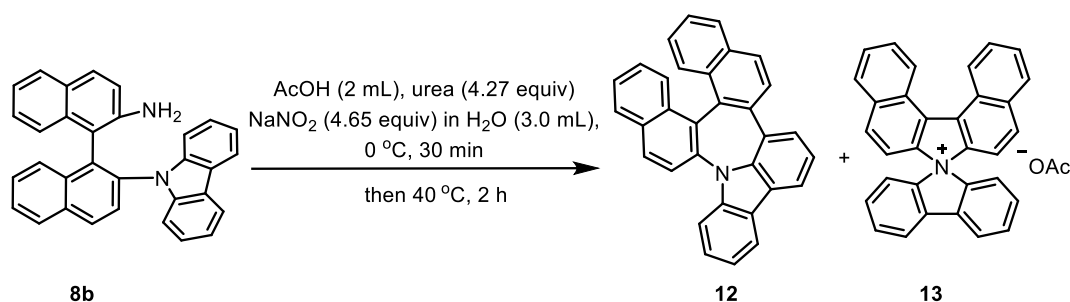
Compound **10** was synthesized according to the modified literature procedures.<sup>[21]</sup> To a solution of 9-(2-aminophenyl)-9H-carbazole **6a** (129.2 mg, 0.5 mmol) in acetic acid (1.3 mL) and sulfuric acid (130  $\mu$ L) mixture was added dropwise an aqueous solution of NaNO<sub>2</sub> (51.8 mg, 0.75 mmol, 1.5 equiv, in 1.5 mL water) at 0 °C. After 30 min, the mixture was heated to 130 °C for 2 h. The reaction mixture was cooled to room temperature and poured into water (10 mL), giving a large amount of precipitate. The precipitate was collected by filtration and washed with methanol to give the crude product, which was purified on a silica gel (200–300 mesh) column and eluted with petroleum ether/EtOAc (100/1, v/v) to obtain product **10** as a white solid (71.1 mg, 60% yield).

#### 3.2 Synthesis of compound 11



To a solution of **7a** (154.6 mg, 0.5 mmol) in acetic acid (5 mL) a was added dropwise an aqueous solution of NaNO<sub>2</sub> (120.8 mg, 1.75 mmol, 3.5 equiv, in 3.0 mL water). The temperature of the mixture was maintained below 0 °C for 30 min. After then, the reaction was stirred at 40 °C for 2 h. After being cooled down to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  30 mL). The combined organic phase was dried by Na<sub>2</sub>SO<sub>4</sub>, and filtered. After removing the volatile components from the filtrate, the crude product was purified on a silica gel (300–400 mesh) column and eluted with petroleum ether to obtain product **11** as a yellowish-green solid (80.1 mg, 55% yield).

### 3.3 Synthesis of compounds **12** and **13**



The operation was according to the modified literature procedures.<sup>[3]</sup> To a solution of **8b** (87.2 mg, 0.2 mmol) in acetic acid (2 mL) a was added dropwise an aqueous solution of NaNO<sub>2</sub> (64.2 mg, 0.93 mmol, 4.65 equiv, in 3 mL water). The temperature of the mixture was maintained below 0 °C for 30 minutes before adding urea (51.3 mg, 0.86 mmol, 4.27 equiv). Then heating the tube to 40 °C for 2 hours. After being cooled down to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic phase was dried by Na<sub>2</sub>SO<sub>4</sub>, and filtered. After removing the volatile components from the filtrate, the crude product was purified on a silica gel (200–300 mesh) column and eluted with petroleum ether/EtOAc (120/1, v/v) to obtain product **12** as a gray solid (35 mg, 42% yield); going on eluting with CH<sub>2</sub>Cl<sub>2</sub>/methanol (15/1, v/v), to obtain product **13** as a yellow solid (53.5 mg, 56% yield).

## 4 Photophysical properties

### 4.1 UV-vis absorption and fluorescence emission data

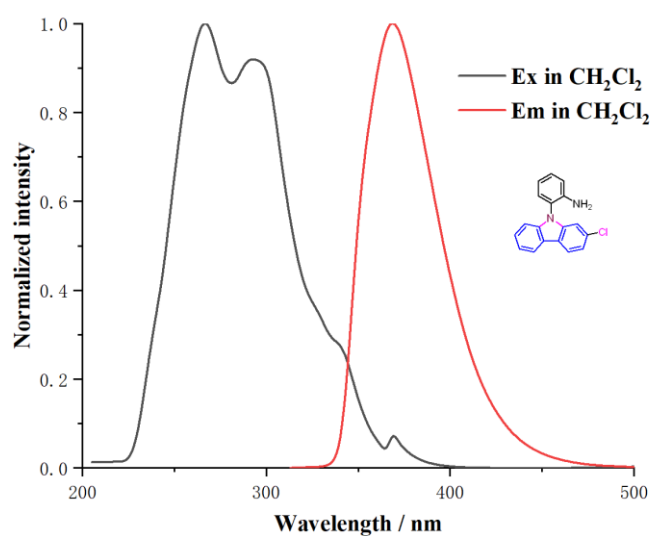
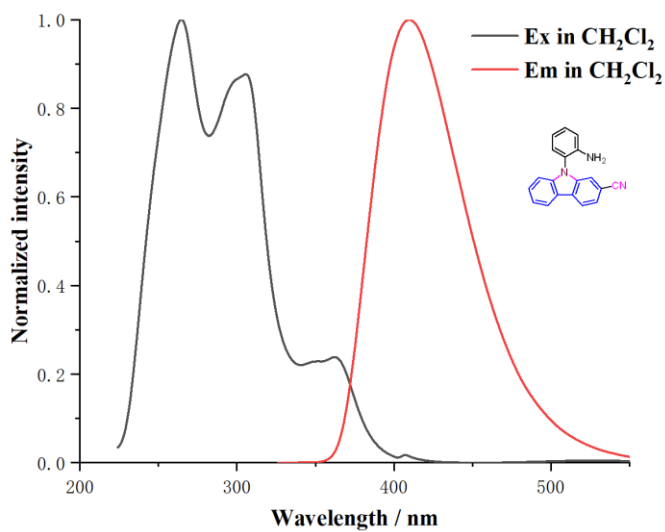
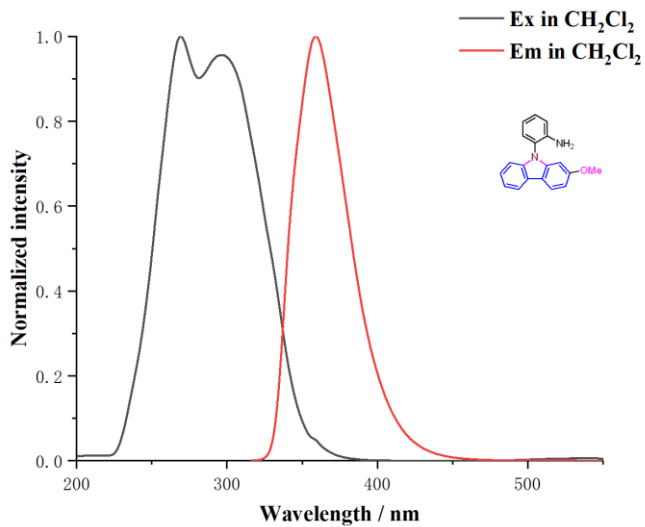
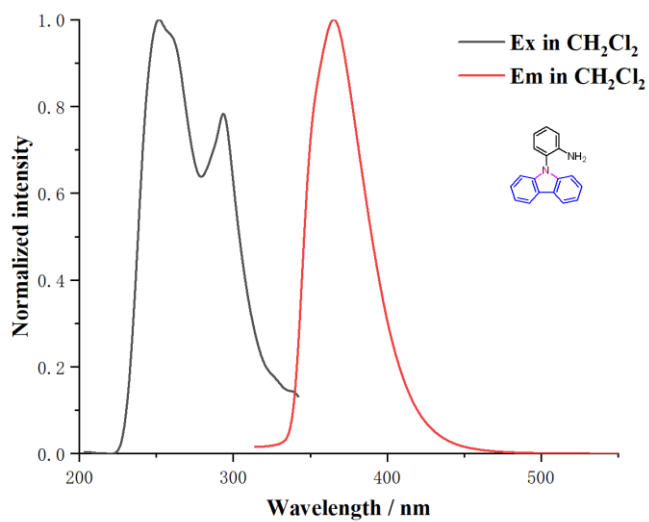
*Table S4.* Photophysical data in CH<sub>2</sub>Cl<sub>2</sub> (10 μM).

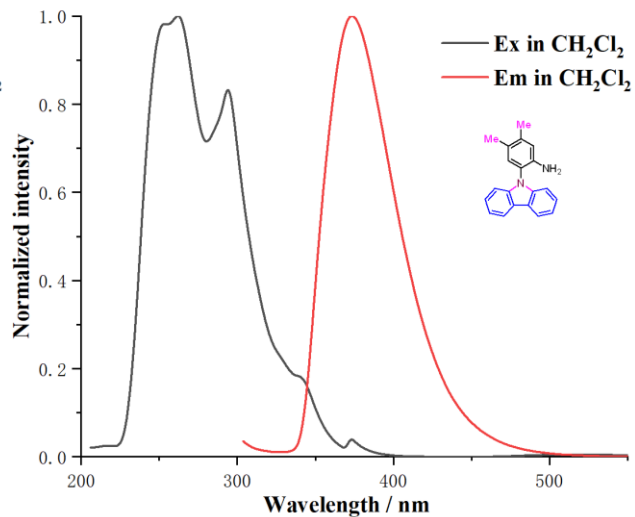
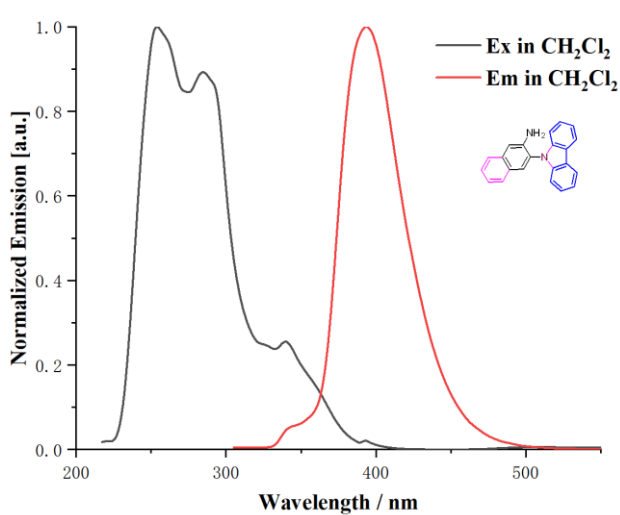
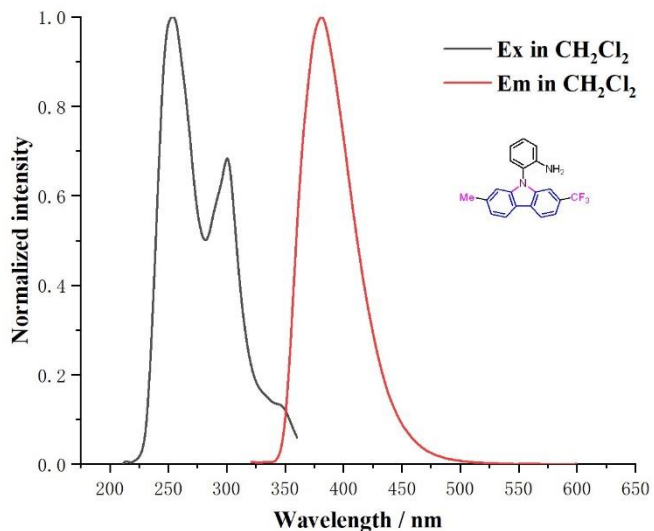
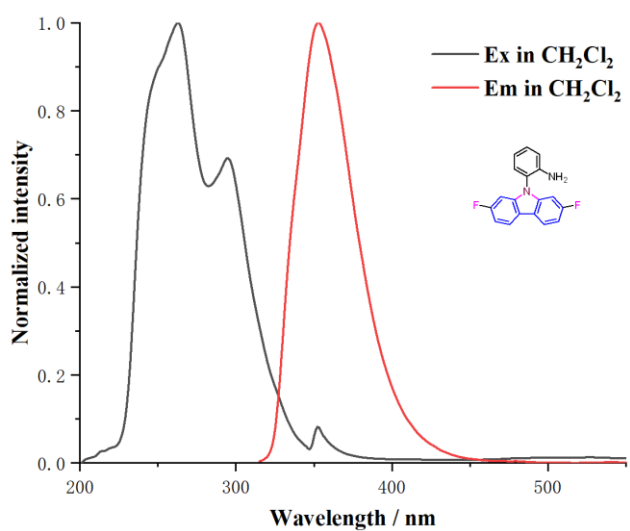
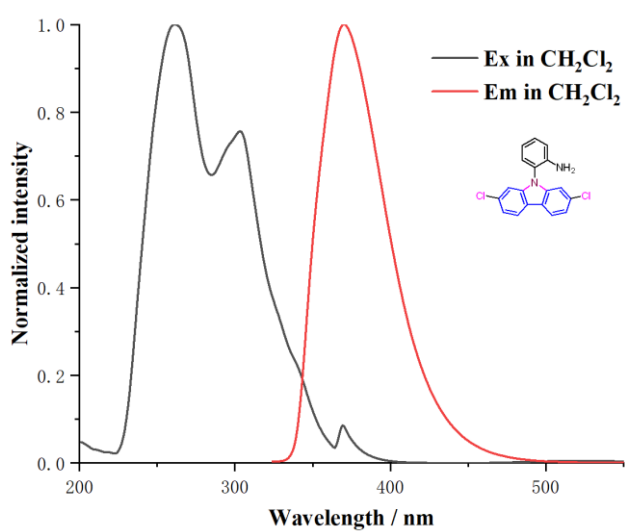
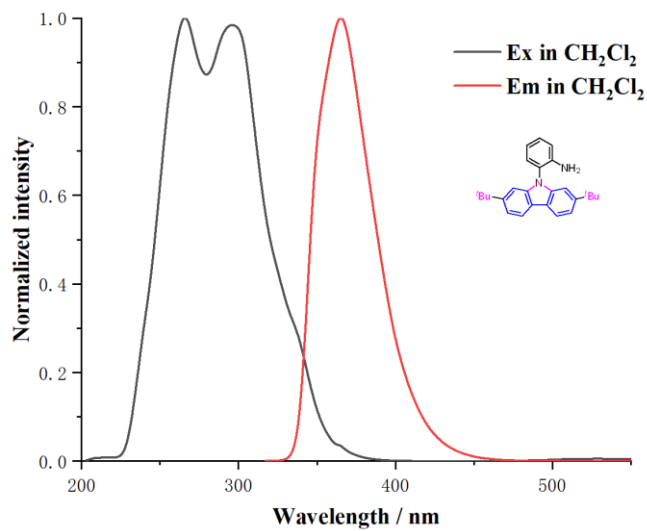
Compd.	$\lambda_{\text{max}}$ (Emission)	FWHM
<b>6a</b>	365 nm	45 nm
<b>6b</b>	359 nm	44 nm
<b>6c</b>	410 nm	68 nm
<b>6d</b>	369 nm	49 nm
<b>6e</b>	365 nm	41 nm
<b>6f</b>	369 nm	51 nm
<b>6g</b>	353 nm	43 nm
<b>6h</b>	381 nm	51 nm
<b>6i</b>	393 nm	48 nm
<b>6j</b>	373 nm	53 nm
<b>6k</b>	360 nm	55 nm
<b>7a</b>	424 nm	66 nm
<b>7b</b>	422 nm	65 nm
<b>7c</b>	423 nm	68 nm
<b>7d</b>	424 nm	66 nm
<b>7e</b>	424 nm	66 nm
<b>8a</b>	383 nm	76 nm

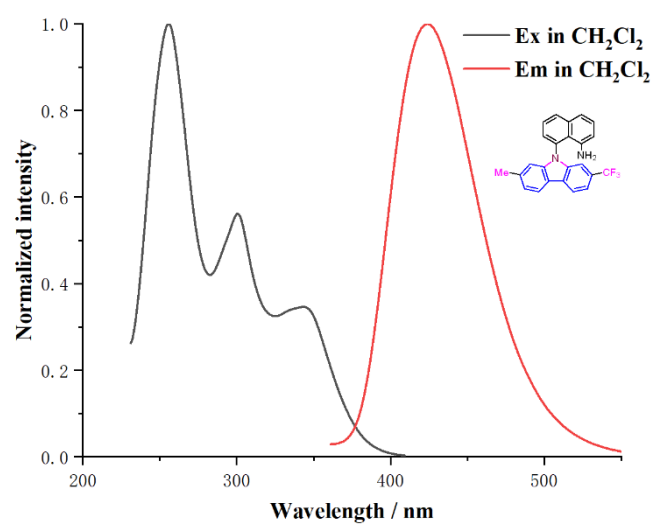
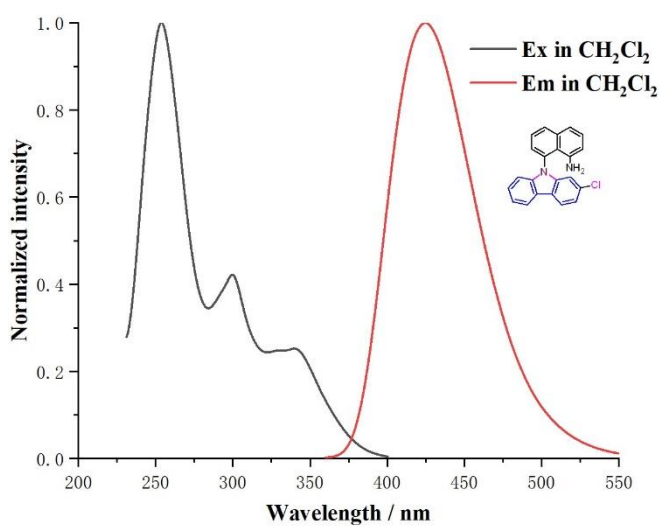
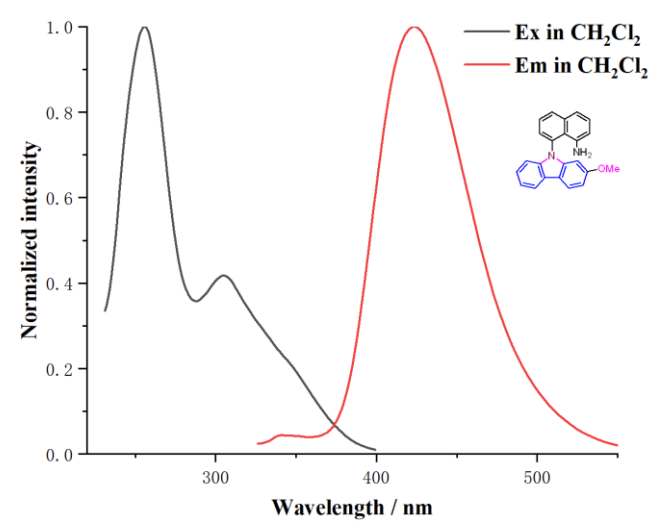
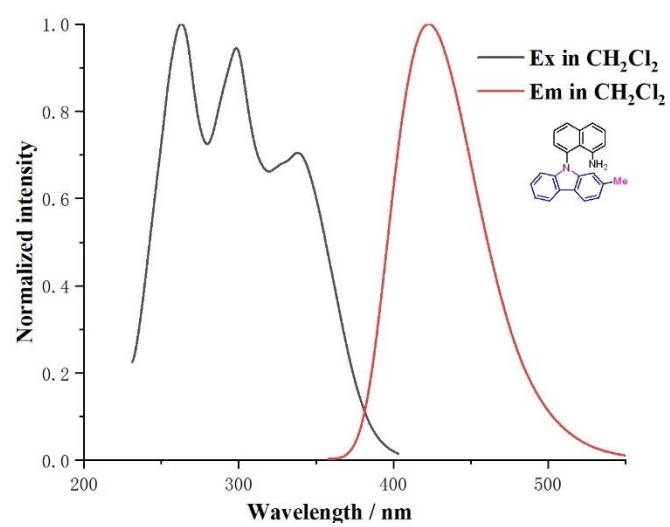
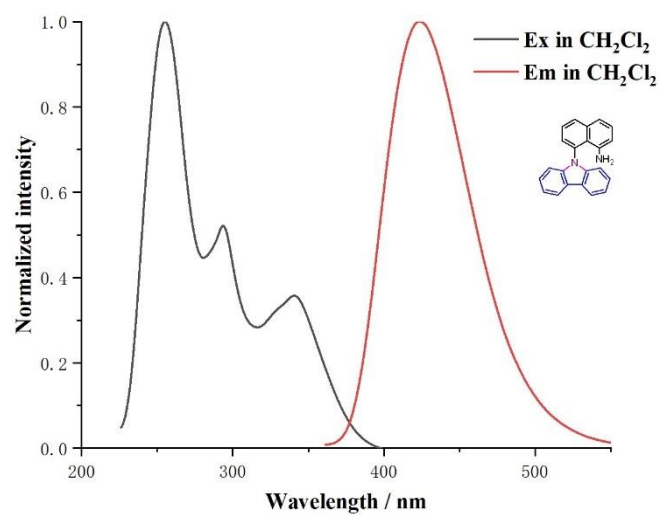
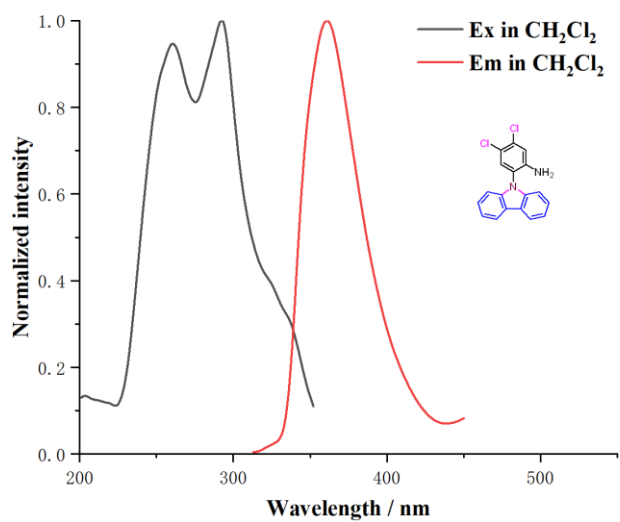


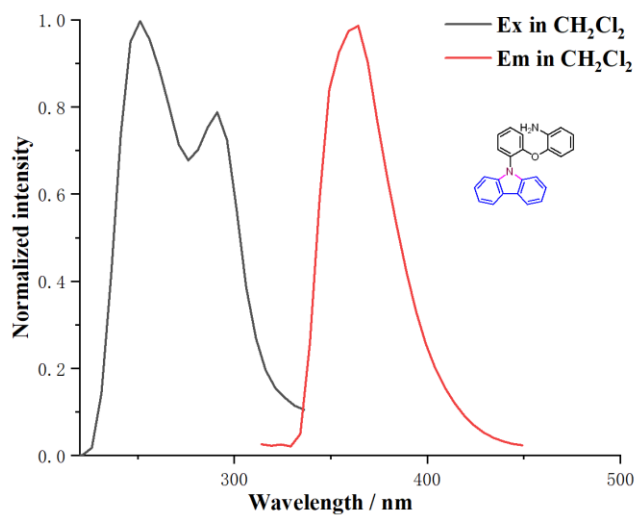
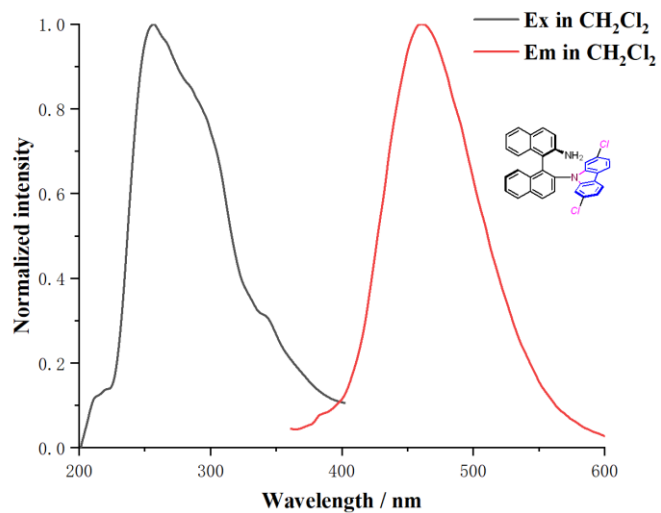
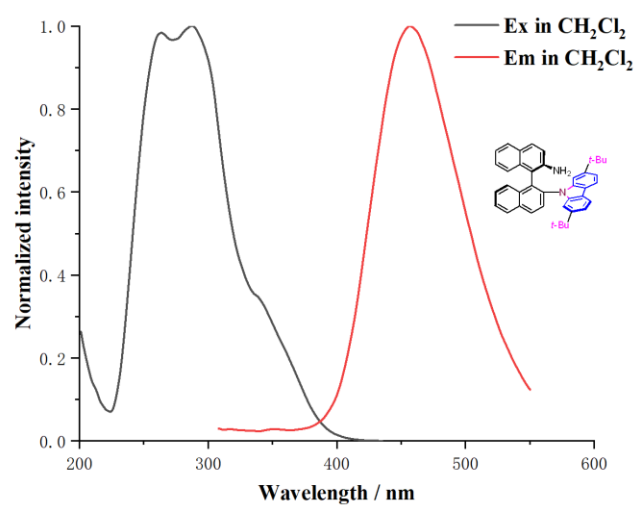
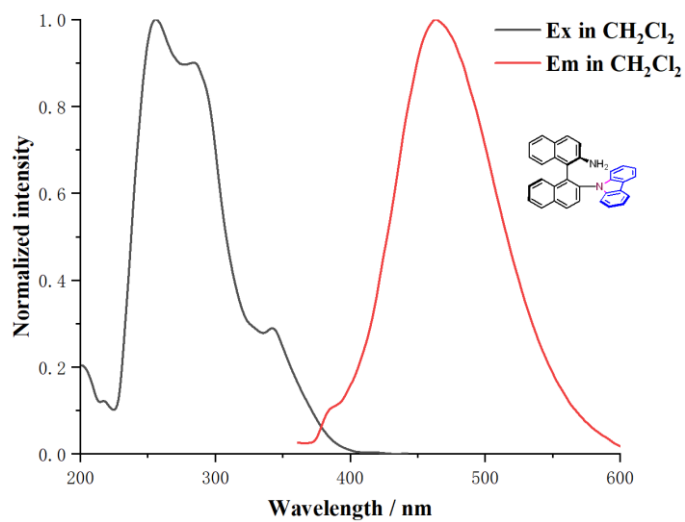
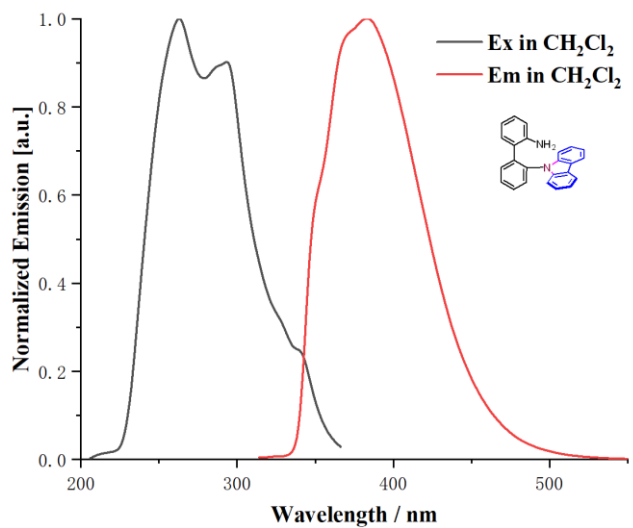
<b>8b</b>	463 nm	89 nm
<b>8c</b>	456 nm	81 nm
<b>8d</b>	461 nm	84 nm
<b>9</b>	364 nm	42 nm

## 4.2 Fluorescence spectra in DCM





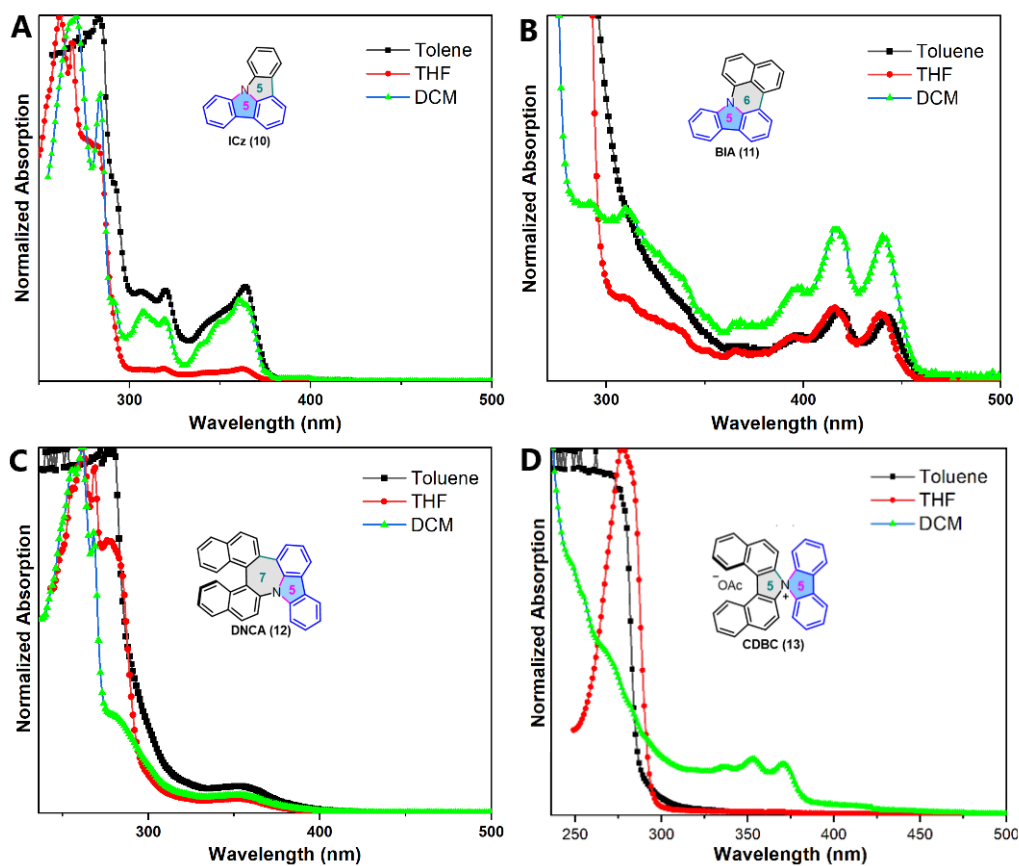




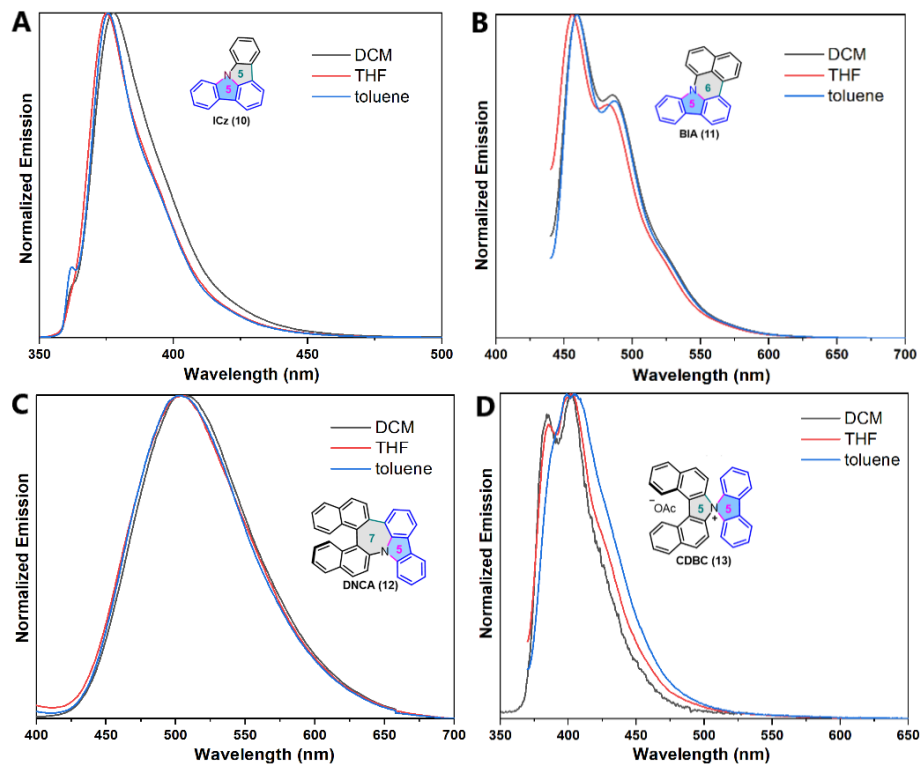
### 4.3 UV-vis absorption and emission spectra in different solvents

**Table S5.** Photophysical data in different solvents (10  $\mu$ M).

Compd.	Solvent	$\lambda_{\max}$ (absorption)	$\lambda_{\max}$ (Emission)	QY
10	DCM	360 nm	375 nm	0.36
10	THF	362 nm	379 nm	0.37
10	Toluene	364 nm	371 nm	0.36
11	DCM	441 nm	482 nm	0.61
11	THF	439 nm	481 nm	0.63
11	Toluene	443 nm	485 nm	0.45
12	DCM	354 nm	505 nm	0.05
12	THF	351 nm	503 nm	0.05
12	Toluene	353 nm	504 nm	0.09
13	DCM	371 nm	402 nm	0.05
13	THF	/(insoluble)	403 nm	0.06
13	Toluene	/(insoluble)	404 nm	0.02

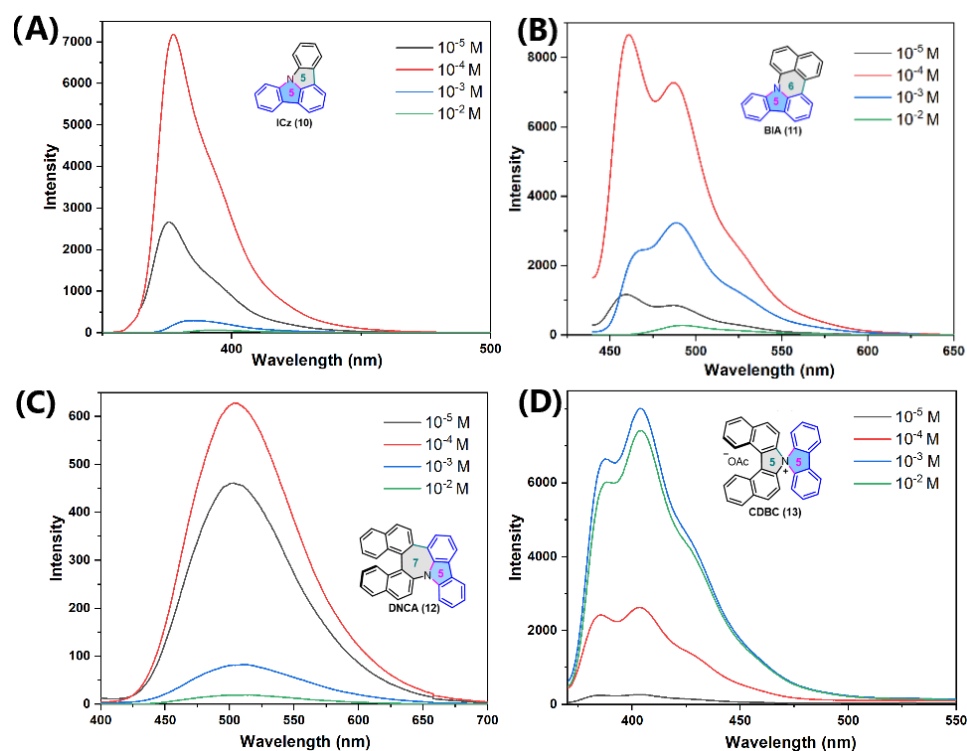


**Figure S1.** Normalized absorption spectra of compounds (A) 10, (B) 11, (C) 12, and (D) 13 in  $\text{CH}_2\text{Cl}_2$  (DCM), THF and toluene.



**Figure S2.** Normalized emission spectra of compounds (A) 10, (B) 11, (C) 12, and (D) 13 in  $\text{CH}_2\text{Cl}_2$  (DCM), THF and toluene.

#### 4.4 Fluorescence spectra at different concentrations



**Figure S3.** Emission spectra of compounds (A) 10, (B) 11, and (C) 12 in toluene and (D) 13 in DCM at different concentrations ( $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  M).

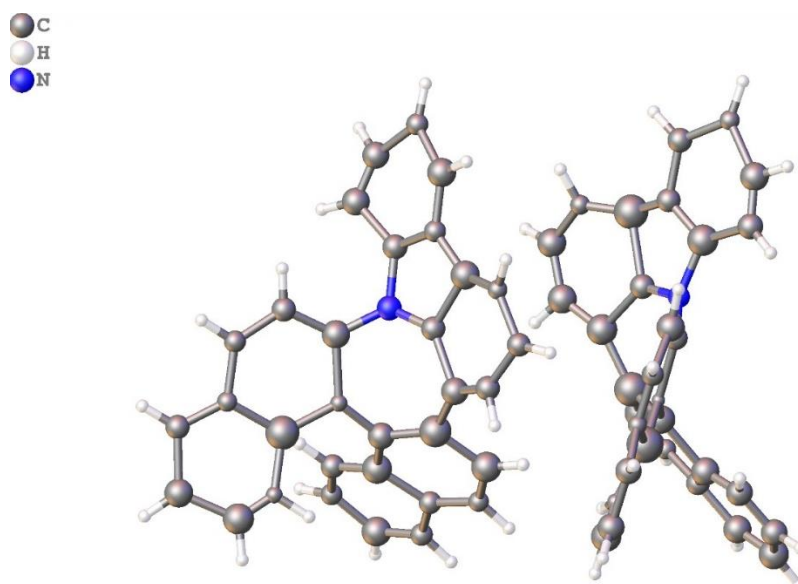
## 5 Computational Details

The theoretical calculations were performed via the Gaussian 16 suite of programs.<sup>[4]</sup> The structures of the studied molecules (denoted by A, B, C, and D) were fully optimized at the B3LYP-D3BJ/6-31G\* level of theory. The solvent effect was included in the calculations using the solvation model based on the density (SMD) model. The vibrational frequencies of the optimized structures were carried out at the same level. The structures were characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The molecular orbital levels of studied compounds were investigated via theoretical calculations, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The GaussView package<sup>[5]</sup> was used to plot the color-filled iso-surface graphs to visualize the molecular orbitals.

## 6 X-ray crystallographic analysis of compound 12

Crystallographic data for **12** have been deposited with the Cambridge Crystallographic Data Centre as deposition number 2300973. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

General crystal growing conditions of **12**: X-ray quality single crystal of **12** was grown from the co-solvent of DCM and hexane (1:4, v/v) at room temperature by slow evaporation for 3 days.



**Figure S4** ORTEP diagram of **12** (CCDC 2300973). Thermal ellipsoids are shown at the 50% probability level.

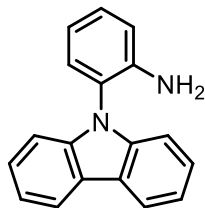
**Table S6 Crystal data and structure refinement for 230612ZH\_ZHCZ299138\_ZCS\_0m.**

Identification code	230612ZH_ZHCZ299138_ZCS_0m
Empirical formula	C32H19N
Formula weight	417.48
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pca21
a/Å	12.987(2)
b/Å	21.072(3)
c/Å	7.5399(9)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2063.4(5)
Z	4
$\rho$ calc/g/cm <sup>3</sup>	1.344
$\mu$ /mm <sup>-1</sup>	0.378
F(000)	872.0
Crystal size/mm <sup>3</sup>	0.3 × 0.2 × 0.1
Radiation	GaK $\alpha$ ( $\lambda$ = 1.34138)
2 $\Theta$ range for data collection/°	6.956 to 108.112
Index ranges	-15 ≤ h ≤ 15, -25 ≤ k ≤ 15, -9 ≤ l ≤ 7
Reflections collected	13080
Independent reflections	3005 [Rint = 0.0948, Rsigma = 0.0930]
Data/restraints/parameters	3005/4/250
Goodness-of-fit on F <sup>2</sup>	1.114
Final R indexes [ $I \geq 2\sigma(I)$ ]	R1 = 0.0892, wR2 = 0.2250
Final R indexes [all data]	R1 = 0.1514, wR2 = 0.2696
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.39
Flack parameter	-1.9(10)



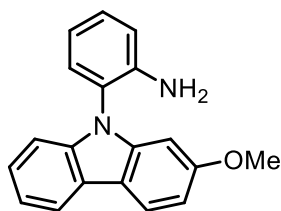
## 7 Experimental data for the described substances

### 2-(9*H*-carbazol-9-yl)aniline (6a)



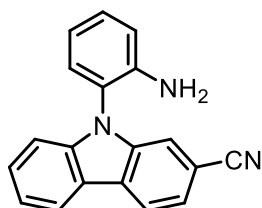
White solid (46.5 mg, 90% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 105–107 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.16 (d,  $J$  = 7.5 Hz, 2H), 7.42 (t,  $J$  = 7.5 Hz, 2H), 7.35–7.26 (m, 4H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 6.97 (d,  $J$  = 8.0 Hz, 1H), 6.92 (t,  $J$  = 7.5 Hz, 1H), 3.55 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 144.1, 140.7, 129.8, 129.7, 126.1, 123.5, 122.4, 120.5, 120.0, 119.0, 116.7, 110.3 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub> ([M + H]<sup>+</sup>) 259.1230, found 259.1229.

### 2-(2-methoxy-9*H*-carbazol-9-yl)aniline (6b)



Yellow solid (23.1 mg, 40% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 47–49 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.04 (d,  $J$  = 8.0 Hz, 1H), 8.01 (d,  $J$  = 8.5 Hz, 1H), 7.33 (t,  $J$  = 7.5 Hz, 2H), 7.27–7.24 (m, 2H, cover the solvent), 7.12 (d,  $J$  = 8.0 Hz, 1H), 6.97 (d,  $J$  = 8.0 Hz, 1H), 6.93–6.89 (m, 2H), 6.64 (s, 1H), 3.83 (s, 3H), 3.58 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 159.5, 144.2, 142.2, 140.8, 129.8, 124.8, 123.7, 122.4, 121.2, 120.1, 119.6, 119.0, 117.2, 116.7, 110.0, 108.8, 94.2. 55.8 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O ([M + H]<sup>+</sup>) 289.1335, found 289.1340.

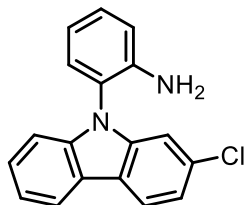
### 9-(2-aminophenyl)-9*H*-carbazole-2-carbonitrile (6c)



White solid (23.2 mg, 41% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 164–166 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.20 (t,  $J$  = 8.5 Hz, 2H), 7.55–

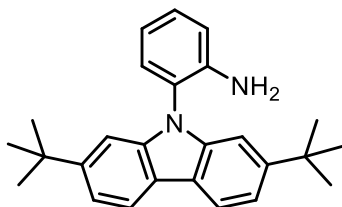
7.49 (m, 3H), 7.39–7.35 (m, 2H), 7.25–7.22 (m, 2H), 7.00 (d,  $J = 8.5$  Hz, 1H), 6.94 (t,  $J = 7.5$  Hz, 1H), 3.54 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 143.9, 142.0, 139.8, 130.5, 129.5, 128.2$  (2C), 126.9, 123.3, 122.4, 121.4, 121.2, 121.1, 120.1, 119.3, 117.0, 114.7, 110.9, 108.7 ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_3$  ( $[\text{M} + \text{H}]^+$ ) 284.1182, found 284.1183.

#### 2-(2-chloro-9H-carbazol-9-yl)aniline (6d)



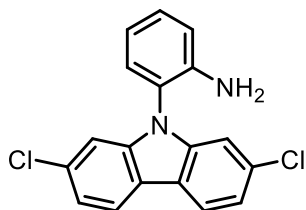
White solid (35.0 mg, 60% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 46–48 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.11$  (d,  $J = 7.5$  Hz, 1H), 8.04 (d,  $J = 8.0$  Hz, 1H), 7.42 (t,  $J = 7.8$  Hz, 1H), 7.36–7.29 (m, 2H), 7.25–7.23 (m, 2H), 7.18–7.16 (m, 2H), 6.97 (d,  $J = 8.0$  Hz, 1H), 6.92 (t,  $J = 7.5$  Hz, 1H), 3.55 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.0, 141.3, 141.1, 132.0, 130.1, 129.7, 126.5, 122.9, 122.0, 121.7, 121.3, 120.6, 120.5, 120.4, 119.1, 116.8, 110.5, 110.4$  ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{14}\text{ClN}_2$  ( $[\text{M} + \text{H}]^+$ ) 293.0840, found 293.0836.

#### 2-(2,7-di-*tert*-butyl-9H-carbazol-9-yl)aniline (6e)



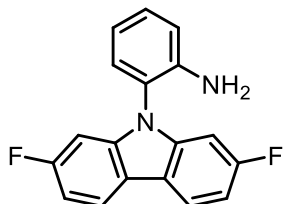
White solid (40.0 mg, 54% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 138–140 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.02$  (d,  $J = 8.5$  Hz, 2H), 7.34–7.28 (m, 4H), 7.13 (s, 2H), 6.99 (d,  $J = 8.0$  Hz, 1H), 6.94 (t,  $J = 7.5$  Hz, 1H), 3.59 (s, 2H), 1.37 (s, 18H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.4, 144.1$  (2C), 129.8, 129.4, 122.7, 121.1, 119.6, 118.9, 117.8, 116.7, 106.6, 35.3, 31.9 ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{26}\text{H}_{31}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ) 371.2482, found 371.2493.

### 2-(2,7-dichloro-9H-carbazol-9-yl)aniline (6f)



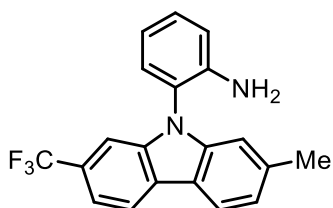
Red solid (57.4 mg, 88% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 93–95 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.98 (d,  $J$  = 7.0 Hz, 2H), 7.34 (t,  $J$  = 7.8 Hz, 1H), 7.25–7.24 (m, 2H), 7.19 (d,  $J$  = 8.0 Hz, 1H), 7.13 (s, 2H), 6.96 (d,  $J$  = 8 Hz, 1H), 6.91 (t,  $J$  = 7.5, 1H), 3.55 (s, 2H) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.9, 141.7, 132.3, 130.5, 129.5, 121.5, 121.3, 121.1, 121.0, 119.3, 116.9, 110.6 ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{Cl}_2$  ( $[\text{M} + \text{H}]^+$ ) 327.0450, found 327.0453.

### 2-(2,7-difluoro-9H-carbazol-9-yl)aniline (6g)



White solid (18.3 mg, 31% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 113–115 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.00–7.98 (m, 2H), 7.35 (t,  $J$  = 7.8 Hz, 1H), 7.22 (d,  $J$  = 8.0 Hz, 1H), 7.02 (t,  $J$  = 9.0 Hz, 2H), 6.97 (d,  $J$  = 8.5 Hz, 1H), 6.92 (t,  $J$  = 7.5 Hz, 1H), 6.85 (d,  $J$  = 9.5 Hz, 2H), 3.56 (s, 2H) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.1 (d,  $J_{\text{C-F}}$  = 240.9 Hz), 143.9, 142.1 (d,  $J_{\text{C-F}}$  = 12.9 Hz), 130.3, 129.4, 121.4, 121.0 (d,  $J_{\text{C-F}}$  = 10.3 Hz), 119.5, 119.2, 116.9, 108.6 (d,  $J_{\text{C-F}}$  = 24.0 Hz), 97.4 (d,  $J_{\text{C-F}}$  = 27.4 Hz) ppm.  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -115.2 ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_2\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ) 295.1041, found 295.1046.

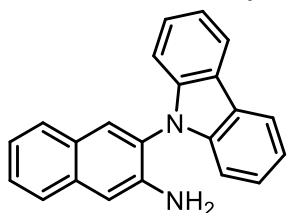
### 2-(2-methyl-7-(trifluoromethyl)-9H-carbazol-9-yl)aniline (6h)



White solid (36.7 mg, 54% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 123–125 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.16 (d,  $J$  = 8.0 Hz, 1H), 8.05

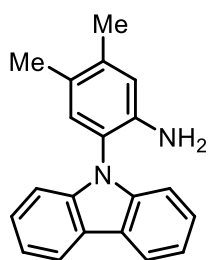
(d,  $J = 8.0$  Hz, 1H), 7.50 (d,  $J = 8.0$  Hz, 1H), 7.38–7.35 (m, 2H), 7.23 (d,  $J = 8.0$  Hz, 1H), 7.16 (d,  $J = 8.0$  Hz, 1H), 7.00–6.98 (m, 2H), 6.94 (t,  $J = 7.5$  Hz, 1H), 3.53 (s, 2H), 2.49 (s, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.1, 142.3, 140.0, 138.1, 130.2, 129.7, 127.5$  (q,  $J_{\text{C-F}} = 31.8$  Hz), 126.2, 125.0 (q,  $J_{\text{C-F}} = 270.5$  Hz), 122.3, 121.7, 120.8, 120.4, 120.3, 119.2, 116.9, 116.7 (q,  $J_{\text{C-F}} = 3.8$  Hz), 110.6, 107.5 (q,  $J_{\text{C-F}} = 4.3$  Hz), 22.3 ppm.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta = -60.7$  ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{16}\text{F}_3\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ) 341.1260, found 341.1270.

### 3-(9H-carbazol-9-yl)naphthalen-2-amine (6i)



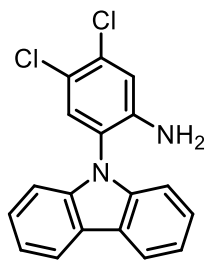
White solid (34.5 mg, 56% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 148–150 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.19$  (d,  $J = 8.0$  Hz, 2H), 7.83 (s, 1H), 7.75–7.71 (m, 2H), 7.48 (t,  $J = 7.5$  Hz, 1H), 7.42 (t,  $J = 7.8$  Hz, 2H), 7.33–7.29 (m, 4H), 7.21 (d,  $J = 8.0$  Hz, 2H), 3.72 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.3, 141.1, 135.0, 129.1, 128.0, 127.9, 127.3, 126.3, 125.8, 125.3, 123.6, 123.2, 120.6, 120.2, 110.4, 110.3$  ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ) 309.1387, found 309.1384.

### 2-(9H-carbazol-9-yl)-4,5-dimethylaniline (6j)



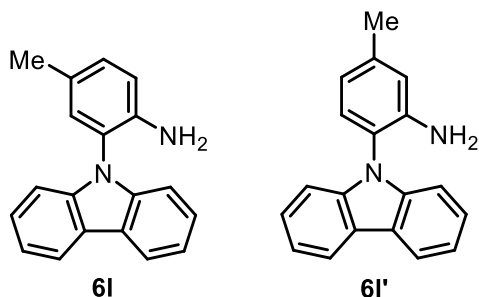
Yellow solid (20.0 mg, 35% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 40/1, v/v) M.p.: 51–53 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.14$  (d,  $J = 7.5$  Hz, 2H), 7.40 (t,  $J = 7.8$  Hz, 2H), 7.28–7.26 (m, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.02 (s, 1H), 6.81 (s, 1H), 2.99 (br s, 2H), 2.31 (s, 3H), 2.21 (s, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 141.0, 138.4, 130.2, 127.9, 126.1, 123.4, 120.5, 120.4, 119.9, 118.6, 110.3, 19.9, 19.0$  ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ) 287.1543, found 287.1542.

## 2-(9H-carbazol-9-yl)-4,5-dichloroaniline (6k)



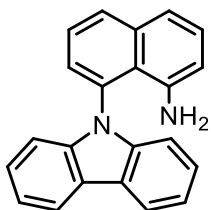
Red solid (33.3 mg, 51% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 87–89 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.14 (d,  $J$  = 7.5 Hz, 2H), 7.43 (t,  $J$  = 7.8 Hz, 2H), 7.36 (s, 1H), 7.31 (t,  $J$  = 7.5 Hz, 2H), 7.17 (d,  $J$  = 8.0 Hz, 2H), 7.07 (s, 1H), 3.67 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.8, 140.3, 133.4, 131.1, 126.4, 123.7, 121.9, 121.0, 120.6 (2C), 117.5, 110.1 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>18</sub>H<sub>13</sub>N<sub>2</sub>Cl<sub>2</sub> ([M + H]<sup>+</sup>) 327.0450, found 327.0451.

## 2-(9H-carbazol-9-yl)-4-methylaniline (6l) and 2-(9H-carbazol-9-yl)-5-methylaniline (6l')



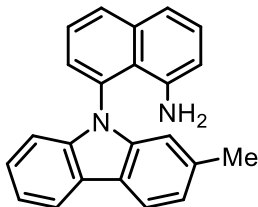
Red solid (27.7 mg, 51% yield, a mixture of 6l and 6l', their ratio is 3:2). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.12 (d,  $J$  = 7.5 Hz, 3.3H, major + minor), 7.37 (t,  $J$  = 7.8 Hz, 3.3H, major + minor), 7.25–7.22 (m, 3.3H, major + minor), 7.17–7.14 (m, 3.3H, major + minor), 7.10 (d,  $J$  = 8.0 Hz, 1.7H, major + minor), 7.04 (s, 0.7H, minor), 6.85 (d,  $J$  = 8.5 Hz, 0.7H, minor), 7.75 (s, 1H, major), 6.69 (d,  $J$  = 8.0 Hz, 1H, major), 3.67 (br s, 3.3H, major + minor), 2.37 (s, 3H, major), 2.27 (s, 2H, minor) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 146.0, 145.8, 144.7, 143.8, 141.9, 140.9, 130.4, 129.9, 129.5, 127.0, 126.3, 126.1, 123.4, 122.5, 120.4, 120.0, 119.9 (2C), 117.2, 110.3 (2C), 21.6, 20.5 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub> ([M + H]<sup>+</sup>) 273.1386, found 273.1393.

### 8-(9*H*-carbazol-9-yl)naphthalen-1-amine (7a)



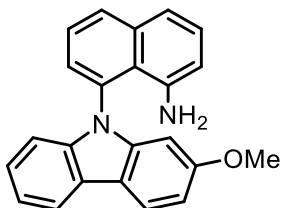
Yellow solid (59.2 mg, 96% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 135–137 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.19 (d,  $J$  = 8.0 Hz, 2H), 7.98 (d,  $J$  = 8.5 Hz, 1H), 7.52 (t,  $J$  = 7.8 Hz, 1H), 7.44–7.31 (m, 6H), 7.25 (d,  $J$  = 8.5 Hz, 1H), 7.07 (d,  $J$  = 8.5 Hz, 2H), 6.60 (d,  $J$  = 7.5 Hz, 1H), 3.60 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.0, 142.7, 137.3, 133.0, 130.5, 127.5, 127.3, 126.5, 125.9, 123.4, 121.3, 120.5, 120.4, 118.7, 112.0, 110.9 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>, ([M + H]<sup>+</sup>) 309.1386, found 309.1388.

### 8-(2-methyl-9*H*-carbazol-9-yl)naphthalen-1-amine (7b)



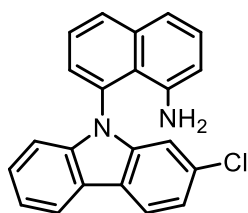
Yellow solid (36.1 mg, 52% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 89–91 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.13 (d,  $J$  = 7.5 Hz, 1H), 8.05 (d,  $J$  = 8.0 Hz, 1H), 7.98 (d,  $J$  = 8.5 Hz, 1H), 7.52 (t,  $J$  = 7.8 Hz, 1H), 7.43 (d,  $J$  = 8.0 Hz, 1H), 7.36–7.33 (m, 2H), 7.29 (t,  $J$  = 7.5 Hz, 1H), 7.23 (d,  $J$  = 7.0 Hz, 1H), 7.14 (d,  $J$  = 8.0 Hz, 1H), 7.01 (d,  $J$  = 8.0 Hz, 1H), 6.85 (s, 1H), 6.60 (d,  $J$  = 7.5 Hz, 1H), 3.62 (br s, 2H), 2.42 (s, 3H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.1, 143.0, 142.7, 137.2, 136.9, 133.1, 130.4, 127.5, 127.3, 126.0, 125.9, 123.5, 122.0, 121.3, 121.1, 120.4, 120.2 (2C), 118.7, 112.0, 110.9, 110.8, 22.2 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>, ([M + H]<sup>+</sup>) 323.1543, found 323.1554.

### 8-(2-methoxy-9*H*-carbazol-9-yl)naphthalen-1-amine (7c)



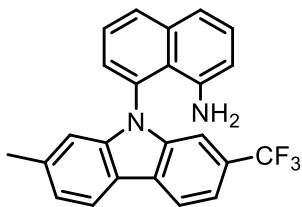
Yellow solid (43.9 mg, 65% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). 155–157 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.08–8.06 (m, 1H), 8.03 (d,  $J$  = 8.5 Hz, 1H), 7.97 (d,  $J$  = 8.5 Hz, 1H), 7.52 (t,  $J$  = 7.5 Hz, 1H), 7.42 (d,  $J$  = 8.0 Hz, 1H), 7.34 (t,  $J$  = 7.8 Hz, 1H), 7.29–7.28 (m, 2H), 7.24 (d,  $J$  = 7.0 Hz, 1H), 6.97 (d,  $J$  = 6.5 Hz, 1H), 6.92 (d,  $J$  = 9.0 Hz, 1H), 6.60 (d,  $J$  = 7.5 Hz, 1H), 6.51 (s, 1H), 3.74 (s, 3H), 3.49 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 159.7, 144.0, 143.0, 142.7, 137.3, 132.9, 130.5, 127.5, 127.4, 125.9, 125.2, 123.5, 121.3 (2C), 120.6, 119.6, 118.7, 117.1, 112.0, 110.7, 109.4, 94.7, 55.7 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O, ([M + H]<sup>+</sup>) 339.1492, found 339.1499.

#### 8-(2-chloro-9H-carbazol-9-yl)naphthalen-1-amine (7d)



Yellow solid (23.3 mg, 34% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 184–186 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.13 (d,  $J$  = 7.5 Hz, 1H), 8.07 (d,  $J$  = 8.5 Hz, 1H), 7.99 (d,  $J$  = 8.0 Hz, 1H), 7.52 (t,  $J$  = 7.8 Hz, 1H), 7.43 (d,  $J$  = 8.0 Hz, 1H), 7.40–7.28 (m, 4H), 7.23 (d,  $J$  = 7.5 Hz, 1H), 7.05–7.03 (m, 2H), 6.62 (d,  $J$  = 7.5 Hz, 1H), 3.53 (s, 2H) ppm. **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.2, 143.0, 142.7, 137.3, 132.3 (2C), 130.8, 127.5 (2C), 126.9, 125.9, 122.8, 122.0, 121.4, 121.1, 121.0, 120.9, 120.5, 119.0, 112.4, 111.1, 111.0 ppm. **HRMS (ESI)  $m/z$ :** calcd for C<sub>22</sub>H<sub>16</sub>ClN<sub>2</sub>, ([M + H]<sup>+</sup>) 343.0997, found 343.0999.

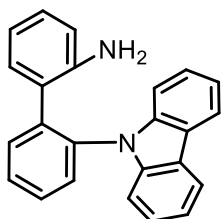
#### 8-(2-methyl-7-(trifluoromethyl)-9H-carbazol-9-yl)naphthalen-1-amine (7e)



Yellow solid (42.9 mg, 55% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 64–66 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.21 (d,  $J$  = 8.0 Hz, 1H), 8.09 (d,  $J$  = 8.0 Hz, 1H), 8.02 (d,  $J$  = 8.5 Hz, 1H), 7.57–7.53 (m, 2H), 7.46 (d,  $J$  = 8.5 Hz, 1H), 7.38 (t,  $J$  = 7.8 Hz, 1H), 7.28 (s, 1H), 7.23 (d,  $J$  = 7.0 Hz, 1H), 7.19 (d,  $J$  = 8.0 Hz, 1H), 6.86 (s, 1H), 6.63 (d,  $J$  = 7.5 Hz, 1H),

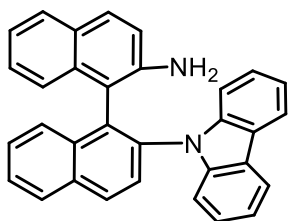
3.51 (s, 2H), 2.43 (s, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.2, 142.7, 141.8, 138.5, 137.3, 132.2, 131.0, 127.9 (q,  $J_{\text{C-F}}$  = 32.1 Hz), 127.6, 127.5, 126.1, 125.9, 122.8, 122.7 (q,  $J_{\text{C-F}}$  = 270.5 Hz), 120.7 (q,  $J_{\text{C-F}}$  = 46.4 Hz), 119.0, 117.1 (q,  $J_{\text{C-F}}$  = 3.8 Hz), 112.4, 111.2, 108.1 (q,  $J_{\text{C-F}}$  = 4.3 Hz), 22.3 ppm.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -60.8 ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_2$ , ( $[\text{M} + \text{H}]^+$ ) 391.1417, found 391.1420.

### 2'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-2-amine (8a)



White solid (33.4 mg, 50% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.02 (br s, 2H), 7.70 (d,  $J$  = 8.0 Hz, 1H), 7.61–7.56 (m, 3H), 7.34–7.14 (m, 6H, cover the solvent), 6.79 (t,  $J$  = 7.5 Hz, 1H), 6.67 (d,  $J$  = 8.0 Hz, 1H), 6.46 (d,  $J$  = 8.0 Hz, 1H), 6.29 (t,  $J$  = 7.5 Hz, 1H), 3.65 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.3, 138.6, 136.2, 132.3, 130.4, 129.8, 129.1, 128.9, 128.8, 125.8, 125.6, 123.7, 123.5, 123.3, 120.2, 119.6, 118.3, 115.7 ppm. The NMR data are consistent with the literature.<sup>[6]</sup>

### 2'-(9H-carbazol-9-yl)-[1,1'-binaphthalen]-2-amine (8b)

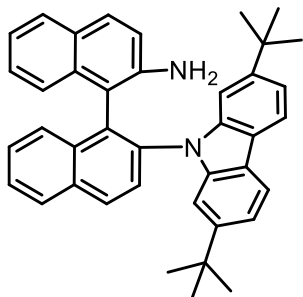


Yellow solid (41.7 mg, 48% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: >250 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17 (d,  $J$  = 9.0 Hz, 1H), 8.09 (d,  $J$  = 8.0 Hz, 1H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 7.85 (d,  $J$  = 7.5 Hz, 1H), 7.69 (d,  $J$  = 7.5 Hz, 1H), 7.64 (t,  $J$  = 7.5 Hz, 1H), 7.58 (d,  $J$  = 7.5 Hz, 1H), 7.47–7.43 (m, 2H), 7.40 (d,  $J$  = 8.5 Hz, 1H), 7.35 (d,  $J$  = 8.0 Hz, 1H), 7.24 (d,  $J$  = 8.0 Hz, 1H), 7.18–7.12 (m, 2H), 7.08 (d,  $J$  = 7.5 Hz, 1H), 7.04–6.96 (m, 4H), 6.71 (d,  $J$  = 9.0 Hz, 1H), 3.58 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 142.0, 141.6, 141.4, 135.8, 133.7, 133.6, 133.5, 133.4, 130.1, 129.5, 128.6, 128.1, 128.0, 127.9, 127.5, 127.1 (2C), 125.9, 125.3, 125.0, 124.8, 123.3, 123.1, 122.1,



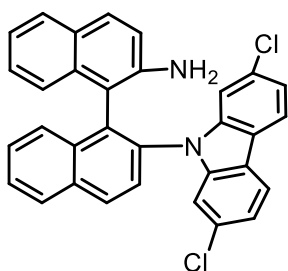
120.0, 119.7, 119.5 (2C), 118.2, 113.0, 111.0, 110.2 ppm. **HRMS (ESI)  $m/z$** : calcd for  $C_{32}H_{23}N_2$ , ( $[M + H]^+$ ) 435.1856, found 435.1864.

**2'-(2,7-di-*tert*-butyl-9*H*-carbazol-9-yl)-[1,1'-binaphthalen]-2-amine (8c)**



Yellow solid (56.8 mg, 52% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 90/1, v/v). M.p.: 225–227 °C.  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**:  $\delta$  = 8.17 (d,  $J$  = 8.5 Hz, 1H), 8.11 (d,  $J$  = 8.5 Hz, 1H), 7.78 (d,  $J$  = 8.0 Hz, 1H), 7.69 (d,  $J$  = 8.0 Hz, 1H), 7.65–7.62 (m, 2H), 7.54 (d,  $J$  = 8.5 Hz, 1H), 7.48–7.42 (m, 3H), 7.24 (s, 1H), 7.20 (d,  $J$  = 8.5 Hz, 1H), 7.17 (d,  $J$  = 8.5 Hz, 1H), 7.10 (d,  $J$  = 8.5 Hz, 1H), 7.03 (s, 1H), 6.98 (t,  $J$  = 7.5 Hz, 1H), 6.93 (t,  $J$  = 7.5 Hz, 1H), 6.75 (d,  $J$  = 8.5 Hz, 1H), 3.64 (s, 2H), 1.32 (s, 9H), 1.16 (s, 9H) ppm.  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**:  $\delta$  = 148.6, 148.5, 142.4, 142.3, 142.0, 136.2, 133.8, 133.6 (2C), 133.5, 130.1, 129.5, 128.7, 128.6, 128.0, 127.9, 127.4, 127.2, 127.0, 126.2, 124.9, 122.0, 121.1, 120.9, 119.1, 118.9, 118.3, 117.3, 117.2, 113.1, 107.2, 106.7, 35.3, 35.0, 31.9, 31.8 ppm. **HRMS (ESI)  $m/z$** : calcd for  $C_{40}H_{39}N_2$ , ( $[M + H]^+$ ) 547.3108, found 547.3118.

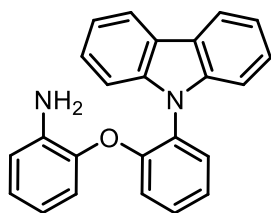
**2'-(2,7-dichloro-9*H*-carbazol-9-yl)-[1,1'-binaphthalen]-2-amine (8d)**



Yellow solid (45.2 mg, 45% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 158–160 °C  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**:  $\delta$  = 8.21 (d,  $J$  = 9.0 Hz, 1H), 8.11 (d,  $J$  = 8.0 Hz, 1H), 7.70–7.60 (m, 5H), 7.48 (t,  $J$  = 7.8 Hz, 1H), 7.43–7.39 (m, 3H), 7.16 (s, 1H), 7.04–6.91 (m, 5H), 6.79 (d,  $J$  = 9.0 Hz, 1H), 3.67 (s, 2H) ppm.  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**:  $\delta$  = 142.1, 142.0, 141.9, 134.4, 133.9, 133.6, 133.3, 133.0, 131.4, 131.2, 130.4, 129.7, 128.8, 127.9, 127.8 (2C), 127.5, 127.4, 126.9,

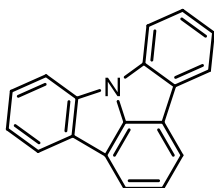
126.0, 124.4, 122.3, 121.0 (2C), 120.6, 120.4, 120.3, 118.0, 112.4, 111.1, 111.0 ppm. **HRMS (ESI)  $m/z$** : calcd for  $C_{32}H_{21}Cl_2N_2$ , ( $[M + H]^+$ ) 503.1076, found 503.1077.

**2-(2-(9H-carbazol-9-yl)phenoxy)aniline (9)**



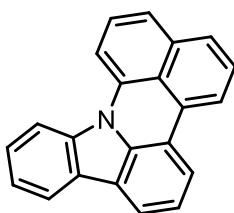
White solid (22.4 mg, 32% yield). Purification via a silica (100–200 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 165–167 °C.  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**:  $\delta$  = 8.12 (d,  $J$  = 8.0 Hz, 2H), 7.57 (d,  $J$  = 7.5 Hz, 1H), 7.46–7.39 (m, 3H), 7.30–7.25 (m, 5H), 7.13 (d,  $J$  = 8.0 Hz, 1H), 6.82–6.76 (m, 2H), 6.59–6.54 (m, 2H), 3.36 (s, 2H) ppm.  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**:  $\delta$  = 154.0, 142.6, 141.5, 138.4, 130.6, 129.8, 127.3, 125.9, 125.0, 123.7, 123.5, 120.5, 119.8, 119.6, 118.6, 118.2, 116.6, 110.0 ppm. **HRMS (ESI)  $m/z$** : calcd for  $C_{18}H_{13}F_2N_2$  ( $[M + H]^+$ ) 351.1492, found 351.1490.

**indolo[3,2,1- $jk$ ]carbazole (10)**



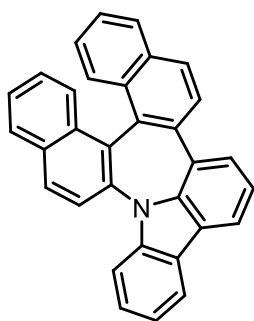
White solid (71.1 mg, 60% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v).  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**:  $\delta$  = 8.15 (d,  $J$  = 8.0 Hz, 2H), 8.06 (d,  $J$  = 7.5 Hz, 2H), 7.92 (d,  $J$  = 8.0 Hz, 2H), 7.61–7.55 (m, 3H), 7.37 (t,  $J$  = 7.8 Hz, 2H) ppm.  **$^{13}C$  NMR (125 MHz,  $CDCl_3$ )**:  $\delta$  = 143.9, 138.9, 130.2, 126.9, 123.3, 123.0, 121.9, 119.6, 118.6, 112.3 ppm. The NMR data are consistent with the literature.<sup>[2]</sup>

**benzo[ $kl$ ]indolo[3,2,1- $de$ ]acridine (11)**



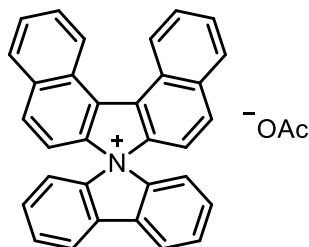
Yellowish-green solid (80.1 mg, 55% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). M.p.: 179–181 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.18 (d,  $J$  = 8.5 Hz, 1H), 8.10 (d,  $J$  = 8.0 Hz, 1H), 7.88–7.82 (m, 3H), 7.78 (d,  $J$  = 7.5 Hz, 1H), 7.58–7.55 (m, 2H), 7.57–7.56 (m, 2H), 7.39–7.35 (m, 2H), 7.30 (t,  $J$  = 7.5 Hz, 1H) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.5, 137.0, 136.9, 136.4, 129.3, 127.2, 127.0, 126.4, 126.0 (2C), 123.2, 122.9, 121.7, 121.3, 121.2, 120.8, 120.0, 119.1, 116.4, 113.5, 107.7 ppm. **HRMS (ESI)  $m/z$** : calcd for  $\text{C}_{22}\text{H}_{14}\text{N}$  ( $[\text{M} + \text{H}]^+$ ) 292.1121, found 292.1127.

**dinaphtho[2',1':4,5;1'',2'':6,7]azepino[3,2,1-*jk*]carbazole (12)**



Yellow solid (35.1 mg, 42% yield). Purification via a silica (200–300 mesh) gel column (petroleum ether/EtOAc = 120/1, v/v). M.p.: 227–229 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01 (d,  $J$  = 7.5 Hz, 1H), 7.97 (d,  $J$  = 8.5 Hz, 1H), 7.91 (t,  $J$  = 8.5 Hz, 2H), 7.87–7.31 (m, 2H), 7.78 (d,  $J$  = 8.0 Hz, 1H), 7.74 (d,  $J$  = 9.0 Hz, 1H), 7.64 (d,  $J$  = 9.0 Hz, 2H), 7.51 (t,  $J$  = 7.8 Hz, 1H), 7.46 (t,  $J$  = 7.5 Hz, 1H), 7.42–7.31 (m, 4H), 7.25–7.23 (m, 1H), 7.12 (t,  $J$  = 7.8 Hz, 1H), 6.97 (d,  $J$  = 9.0 Hz, 1H) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.7, 146.5, 143.0, 138.7, 134.6, 133.8, 132.6, 131.9, 129.3, 128.9, 128.7, 128.6, 128.3, 128.0 (2C), 127.8, 127.5, 127.1, 126.4, 126.3, 126.1 (2C), 125.2, 125.0, 124.6, 124.0, 123.0, 121.1, 119.1, 119.0, 117.4, ppm. **HRMS (ESI)  $m/z$** : calcd for  $\text{C}_{32}\text{H}_{20}\text{N}$ , ( $[\text{M} + \text{H}]^+$ ) 418.1590, found 418.1589.

**spiro[carbazole-9,7'-dibenzo[*c,g*]carbazol]-9-ium acetate (13)**



Yellow solid (53.1 mg, 56% yield). Purification via a silica (200–300 mesh) gel column ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  = 60/1  $\rightarrow$  15/1, v/v). M.p.: 162–168 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.04 (d,  $J$  = 8.5 Hz, 2H), 8.49 (d,  $J$

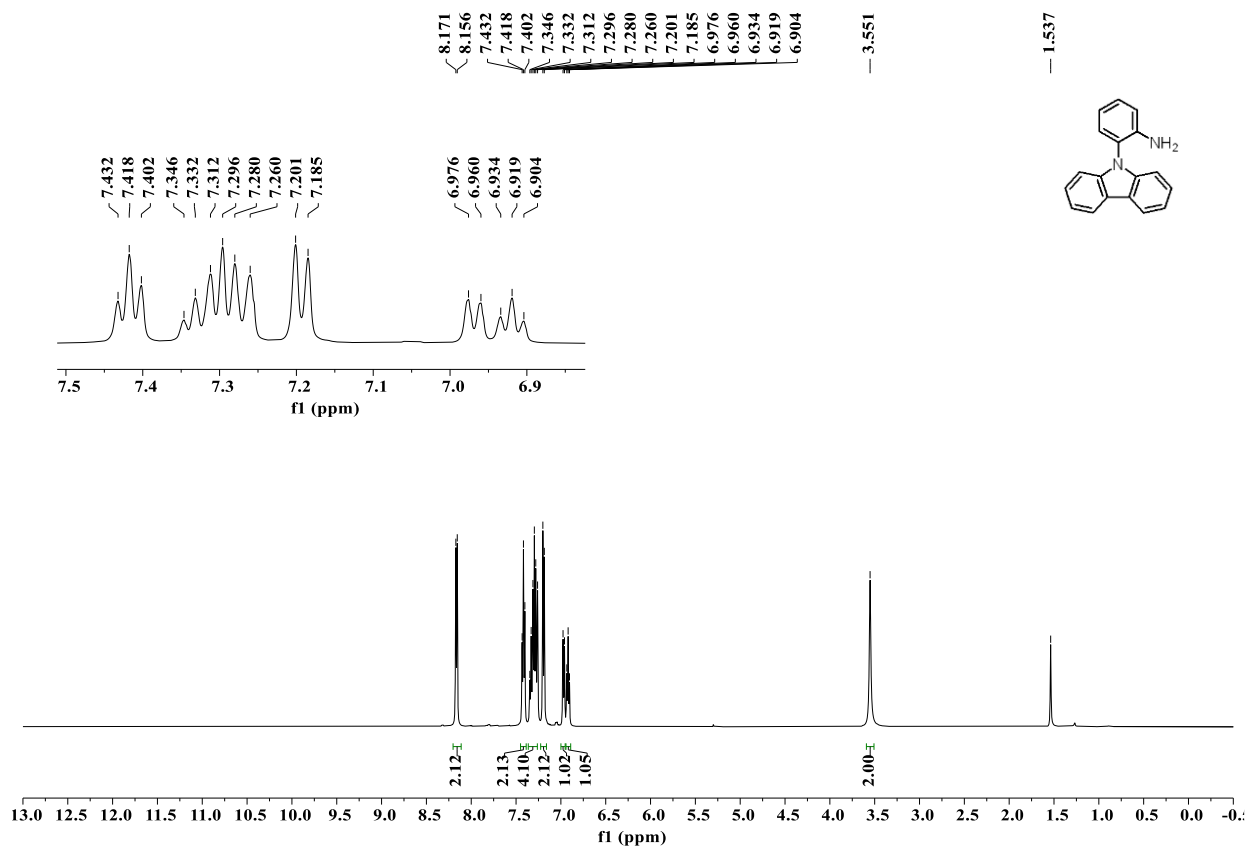
= 7.5 Hz, 2H), 8.12 (q,  $J = 8.2$  Hz, 4H), 7.96 (t,  $J = 7.8$  Hz, 2H), 7.85 (q,  $J = 8.5$  Hz, 4H), 7.46 (t,  $J = 7.8$  Hz, 2H), 7.08 (d,  $J = 9.5$  Hz, 2H), 6.89 (d,  $J = 8.5$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.2, 136.1, 134.0, 133.8, 132.5, 131.7, 130.3, 129.5, 129.0$  (2C), 128.0, 127.1, 124.8, 117.9, 114.3, ppm. HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{32}\text{H}_{20}\text{N}^+$ , ( $[\text{M} - \text{OAc}]^+$ ) 418.1591, found 418.1598.

## 8 References

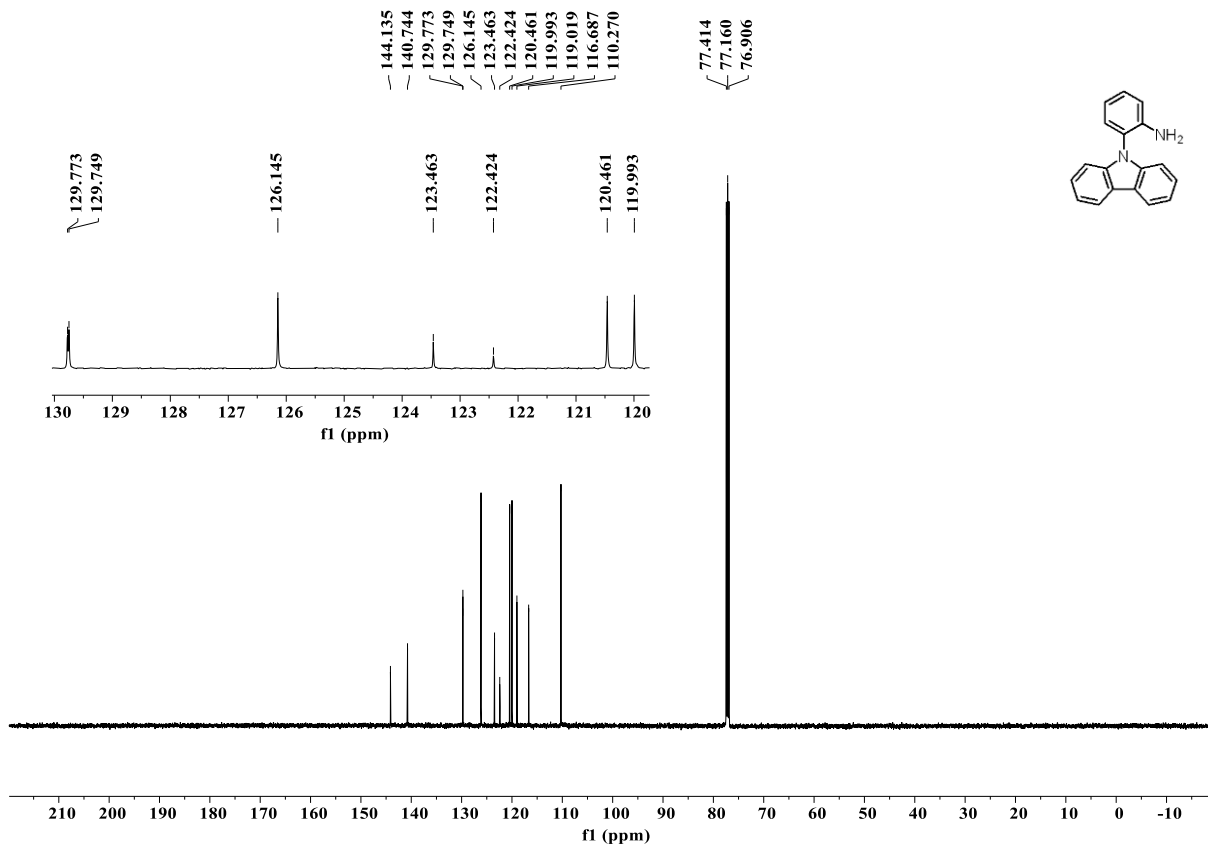
- [1] (a) Z. Liu, D. Zhu, B. Luo, N. Zhang, Q. Liu, Y. Hu, R. Pi, P. Huang and S. Wen, Mild Cu(I)-catalyzed cascade reaction of cyclic diaryliodoniums, sodium azide, and alkynes: Efficient synthesis of triazolophenanthridines, *Org. Lett.*, 2014, **16**, 5600–5603; (b) D. Zhu, Y. Wu, B. Wu, B. Luo, A. Ganesan, F.-H. Wu, R. Pi, P. Huang and S. Wen, Three-component Pd/Cu-catalyzed cascade reactions of cyclic iodoniums, alkynes, and boronic acids: An approach to methylenefluorenes, *Org. Lett.*, 2014, **16**, 2350–2353; (c) B. Wu and N. Yoshikai, Conversion of 2-iodobiaryls into 2,2'-diiodobiaryls via oxidation-iodination sequences: A versatile route to ladder-type heterofluorenes, *Angew. Chem., Int. Ed.*, 2015, **54**, 8736–8739.
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- [3] N. Gjineci, S. Aharonovich, D. R. Dekel and C. E. Diesendruck, Increasing the alkaline stability of *N,N*-diaryl carbazolium salts using substituent electronic effects. *ACS Appl. Mater. Interfaces*, 2020, **12**, 49617–49625.
- [4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian 16 Revision. A.03, Gaussian Inc., Wallingford, CT, 2016.
- [5] R.I. Dennington and T. Keith, J. Millam, GaussView, Version 6.0.16, Semichem. Inc, Shawnee Mission, KS, 2008
- [6] N. Gjineci, S. Aharonovich, S. Willdorf-Cohen, D. R. Dekel and C. E. Diesendruck, The reaction mechanism between tetraarylammonium salts and hydroxide, *Eur. J. Org. Chem.*, 2020, **21**, 3161–3168.

# 9 Copies of $^1\text{H}$ and $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra

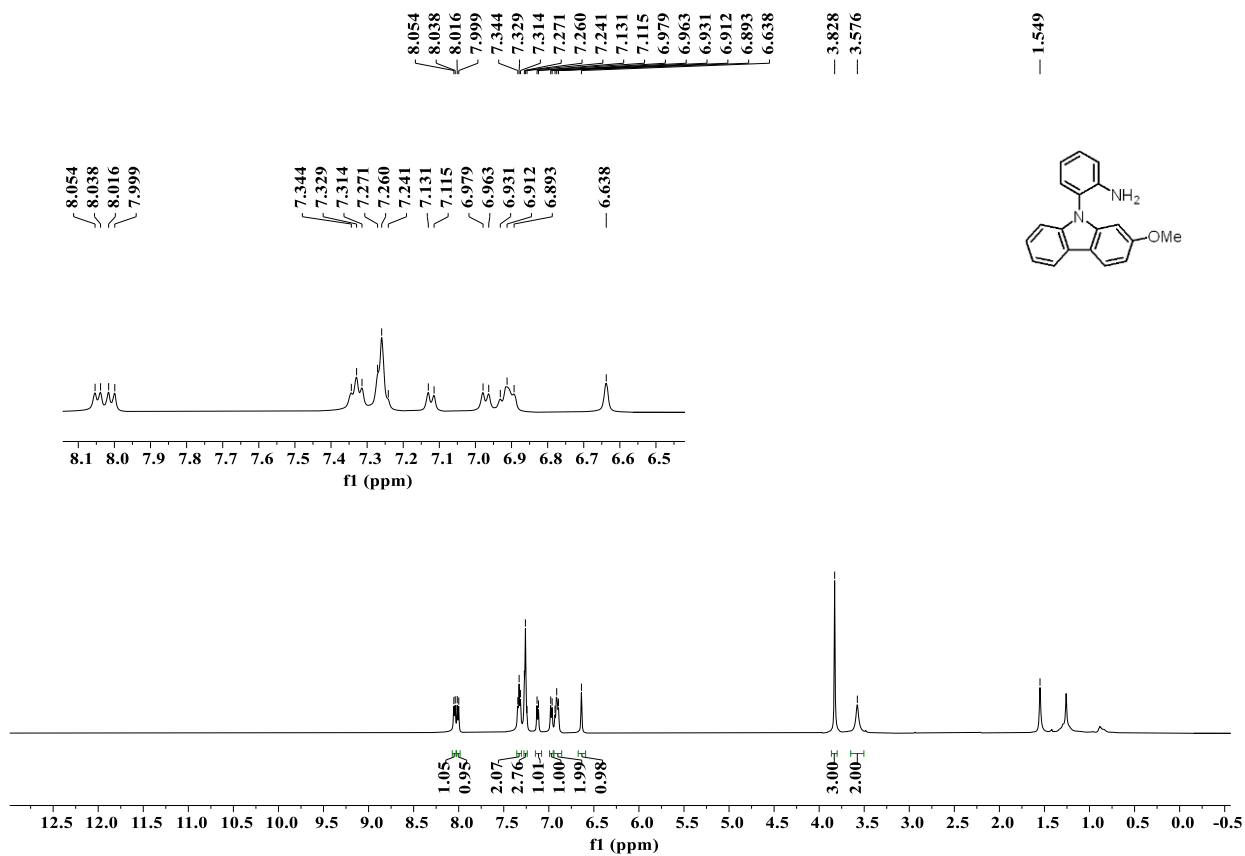
## $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ ) of **6a**



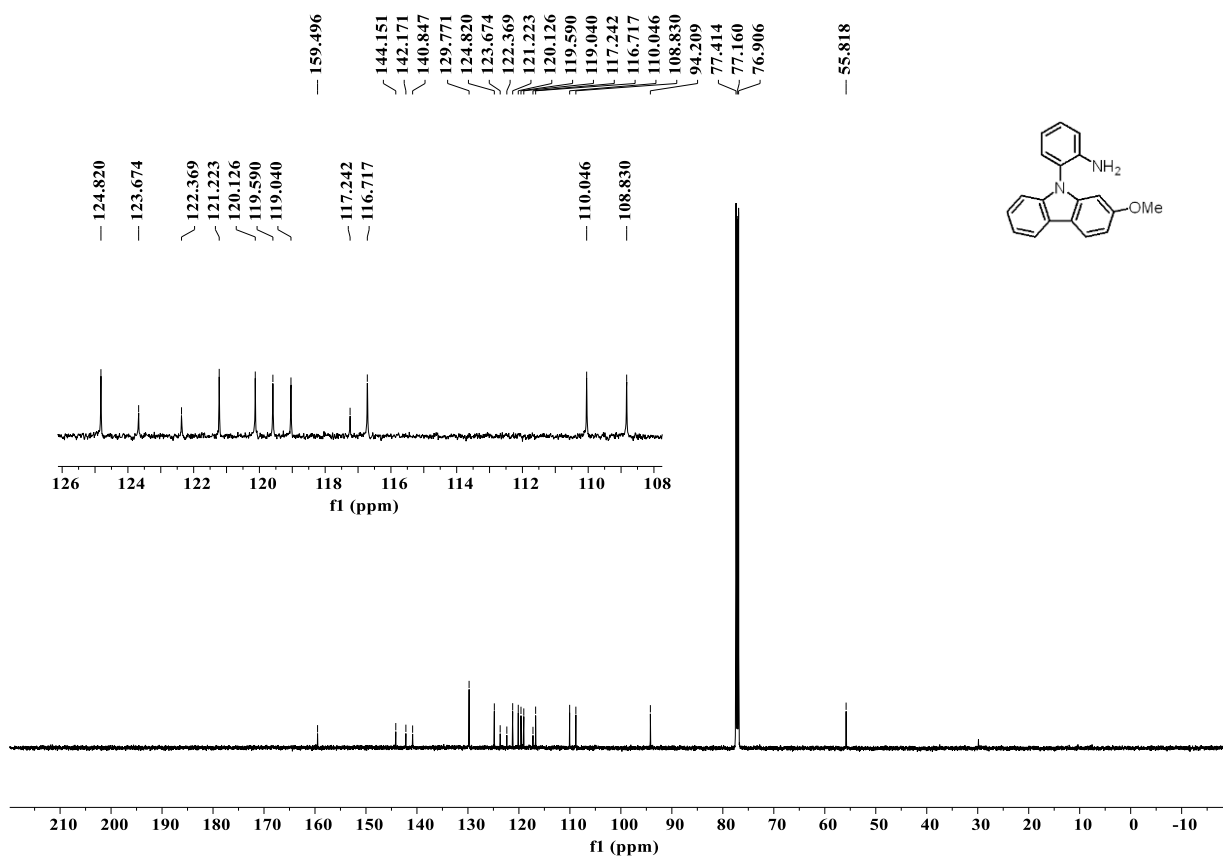
## $^{13}\text{C}$ NMR (125 MHz, $\text{CDCl}_3$ ) of **6a**



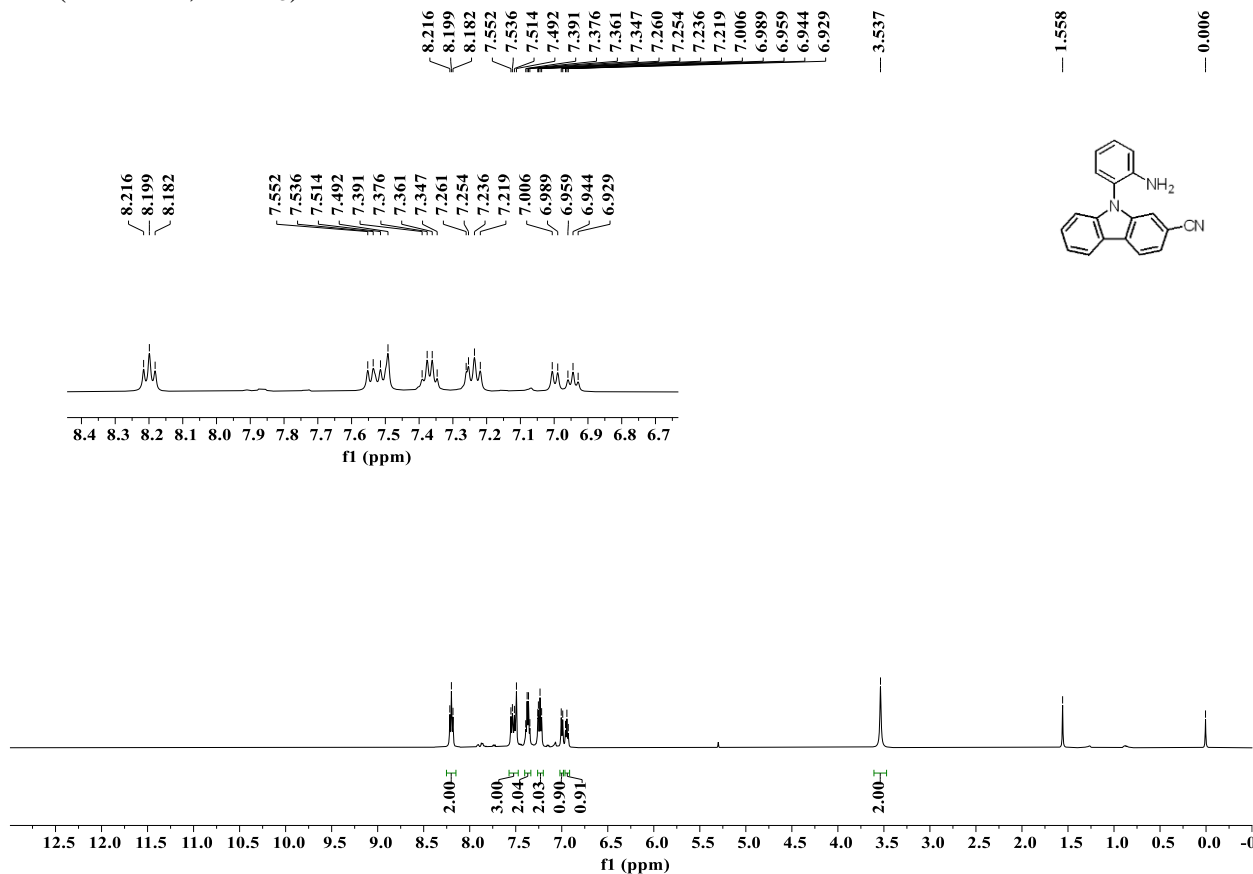
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **6b**



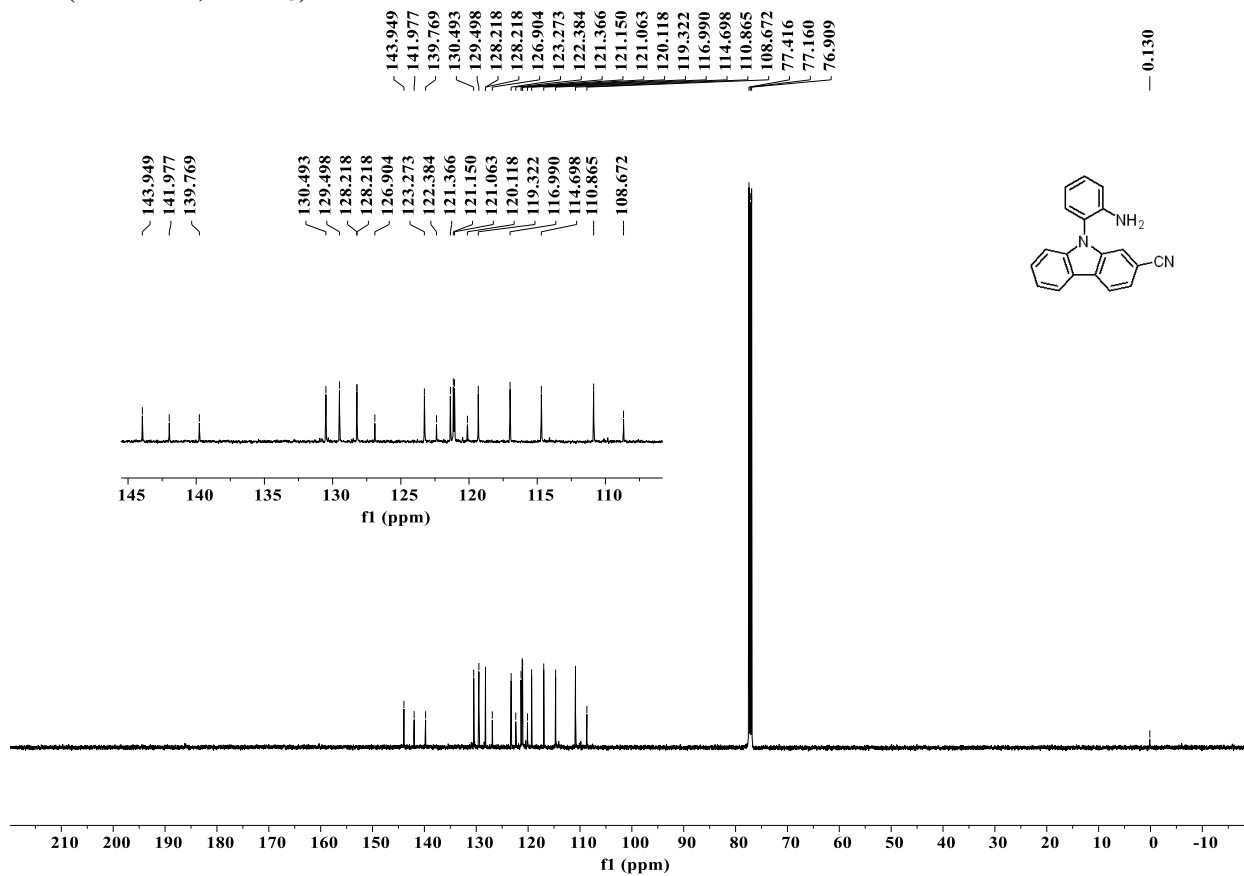
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **6b**



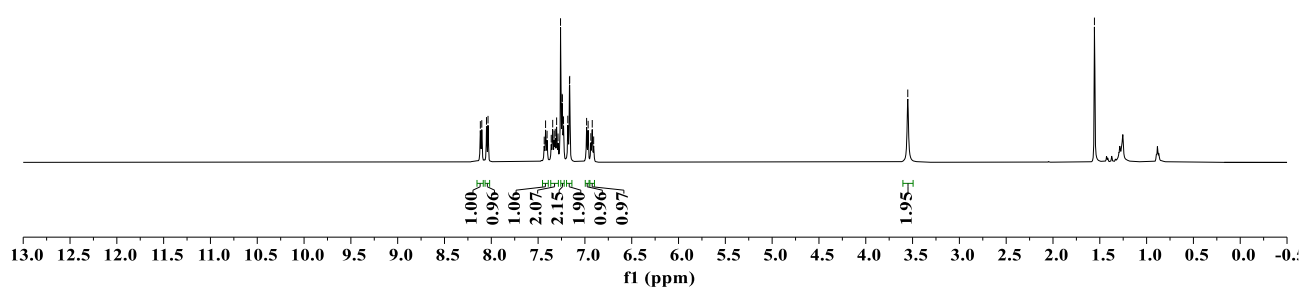
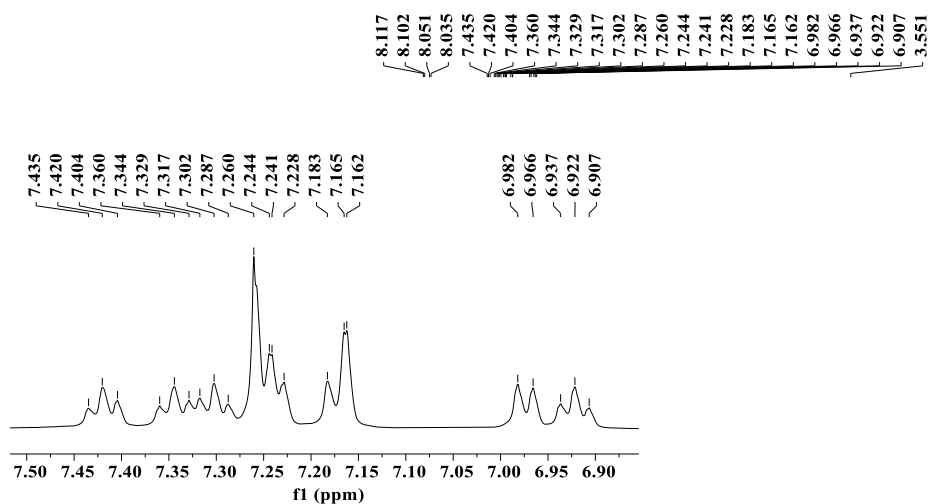
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of **6c**



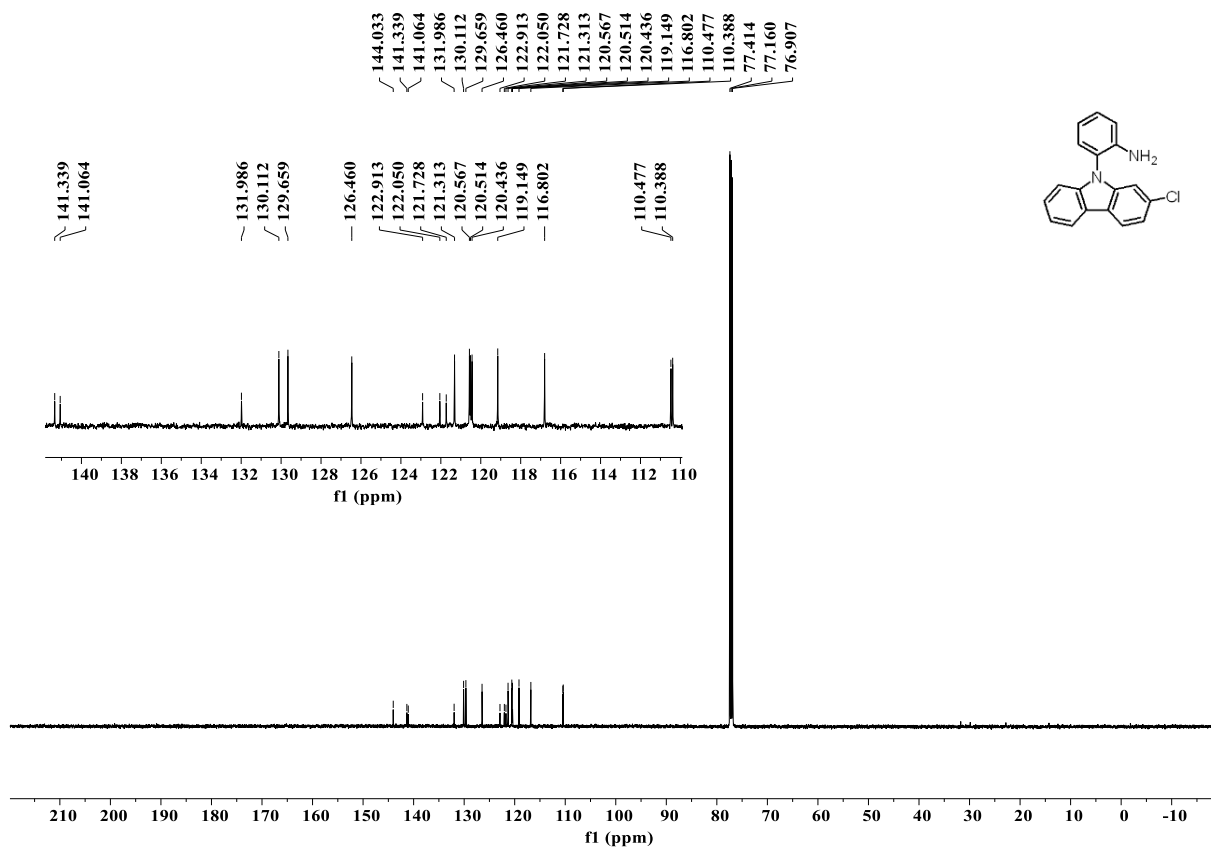
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$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of **6d**

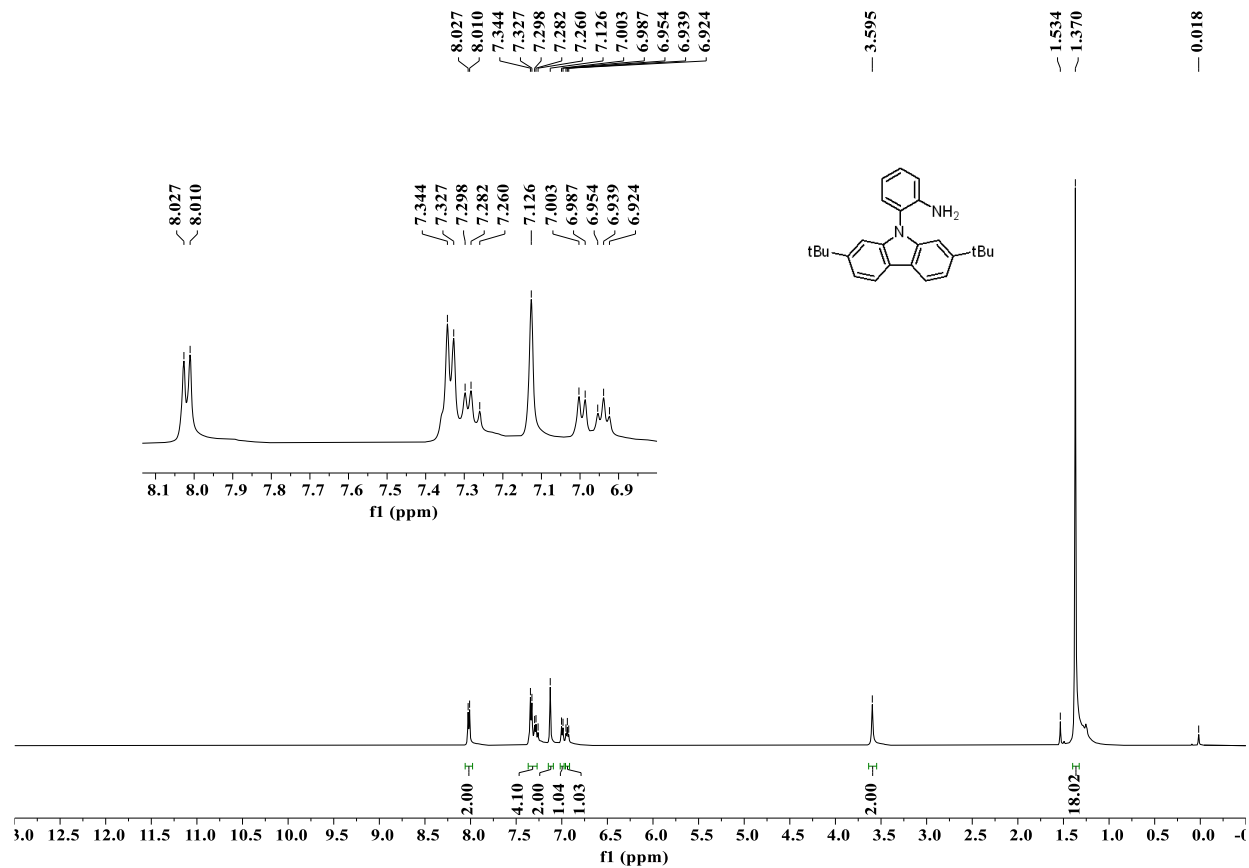


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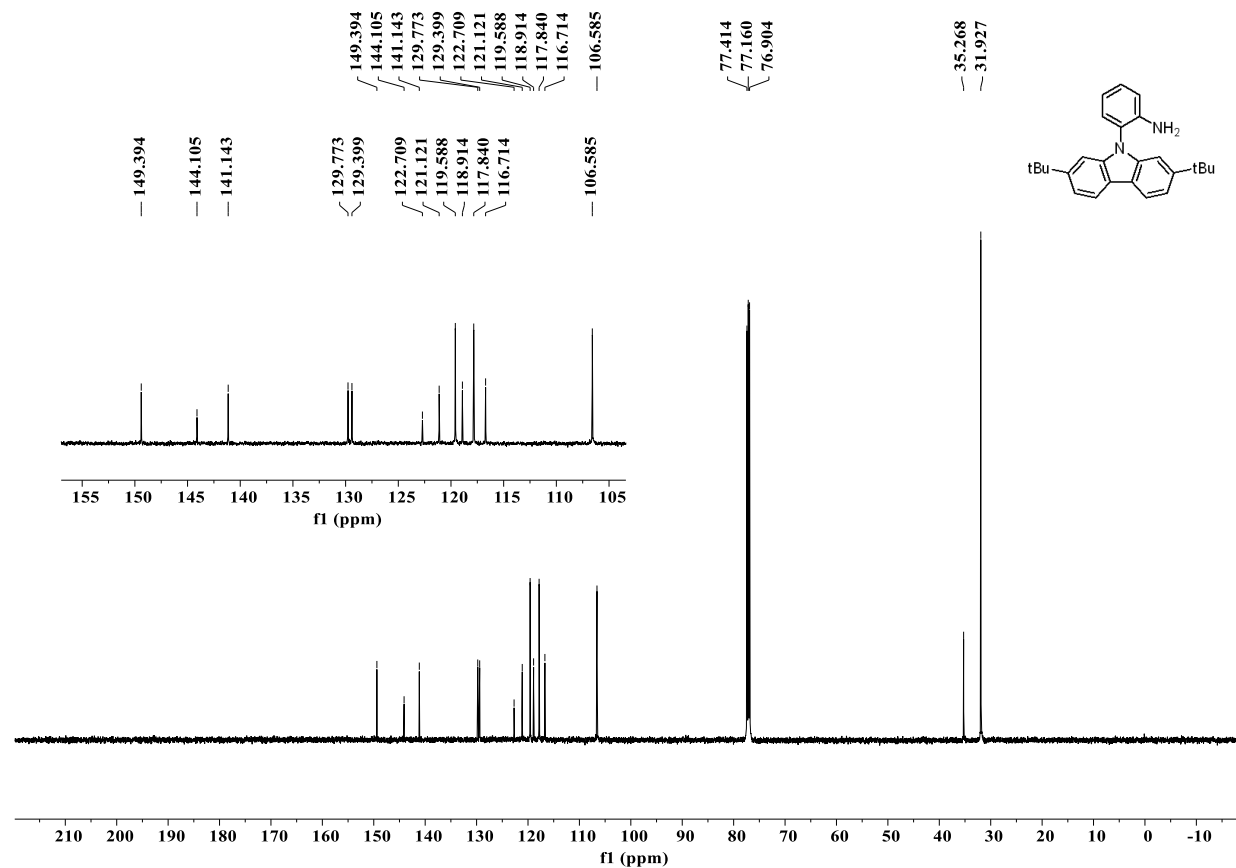




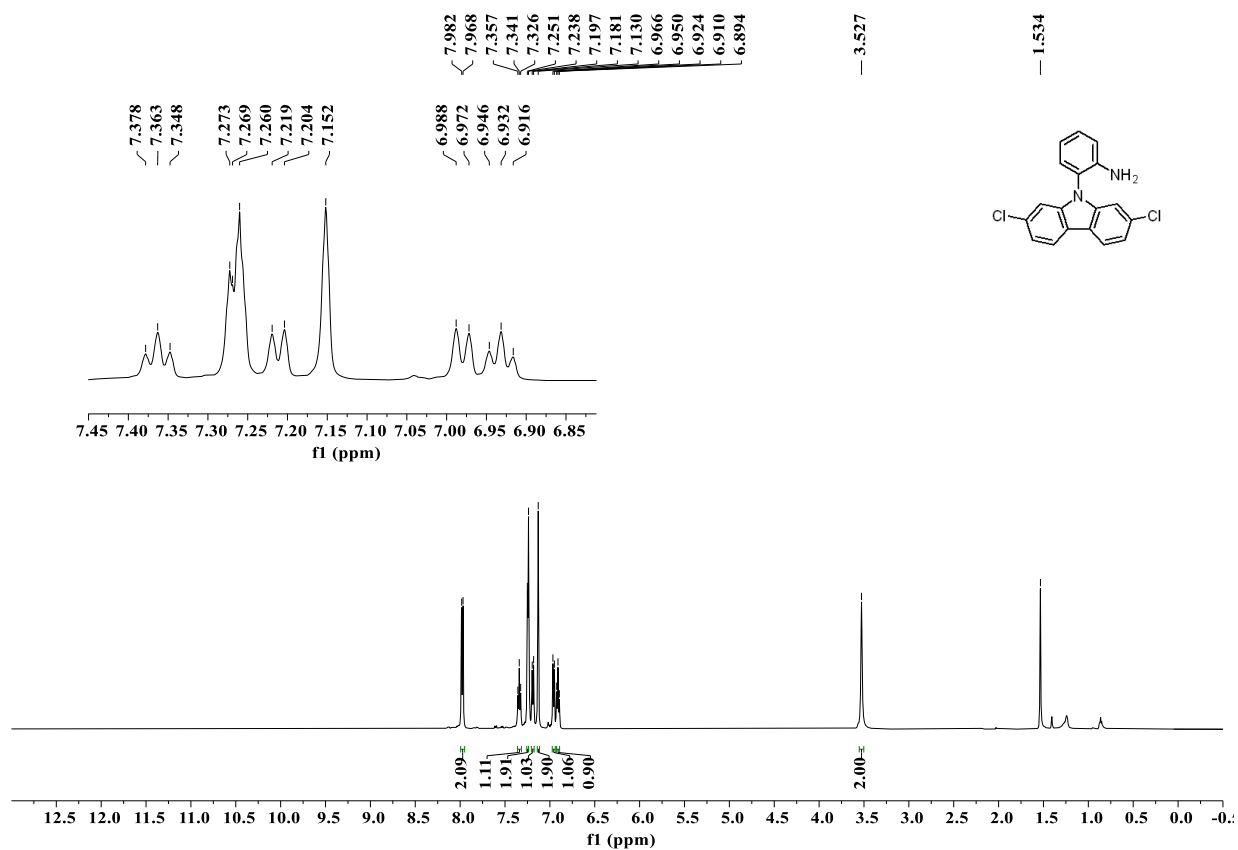
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of **6e**



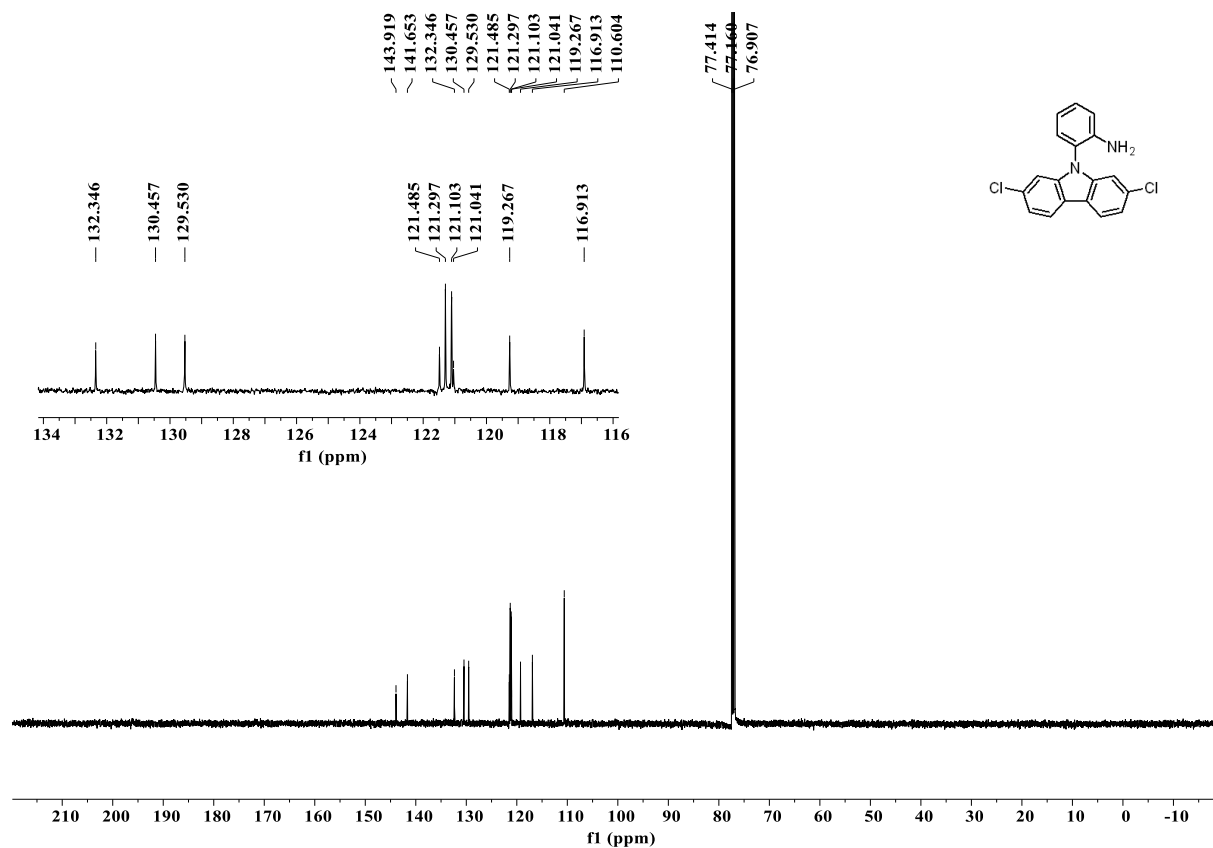
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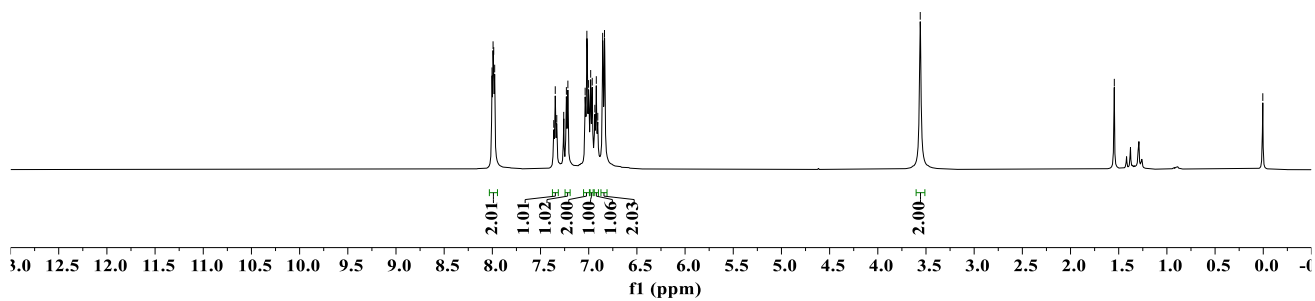
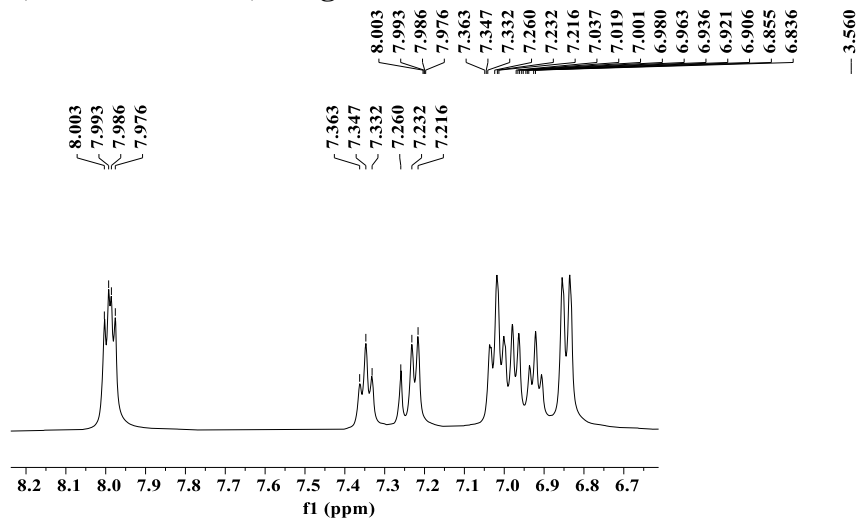
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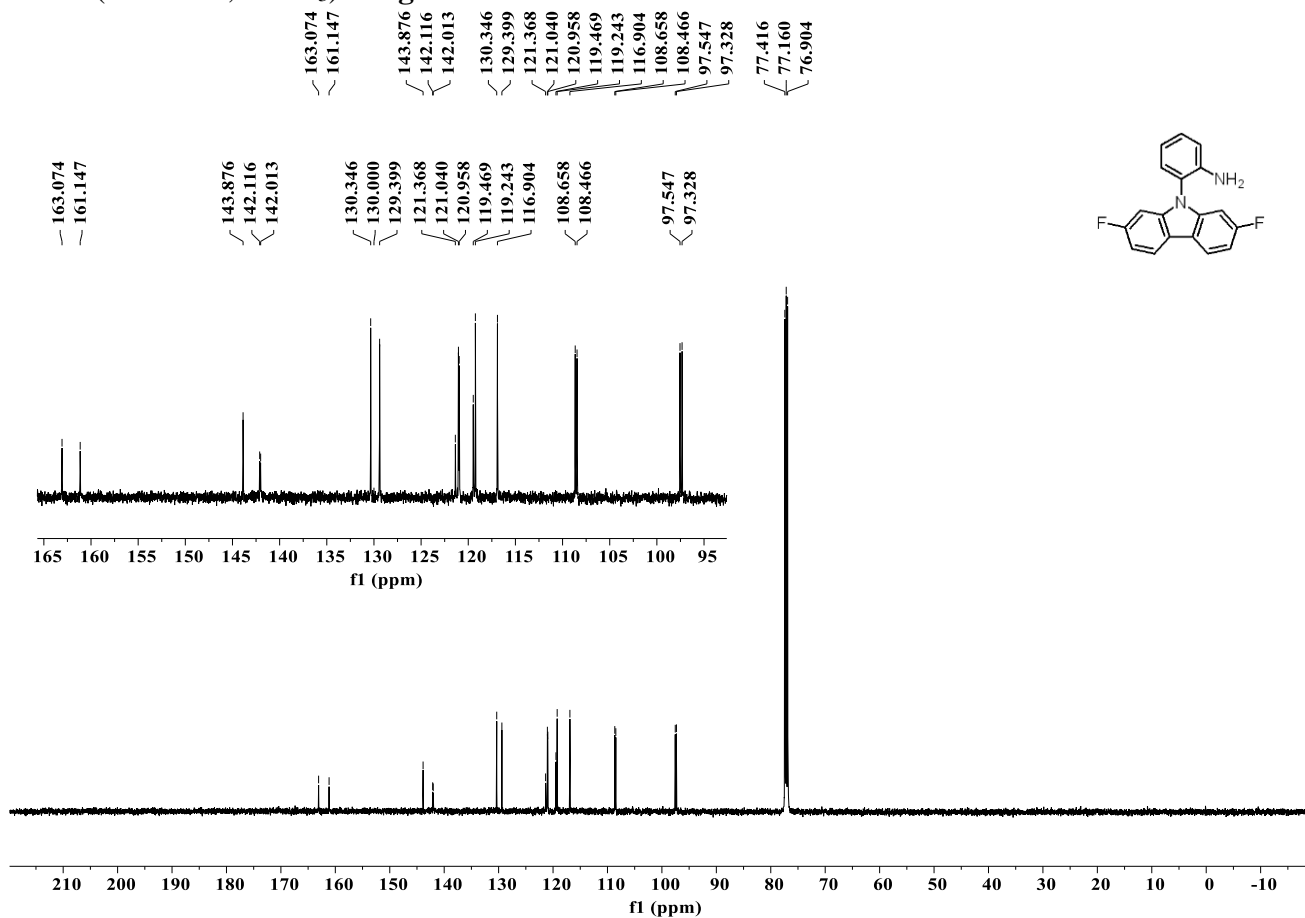
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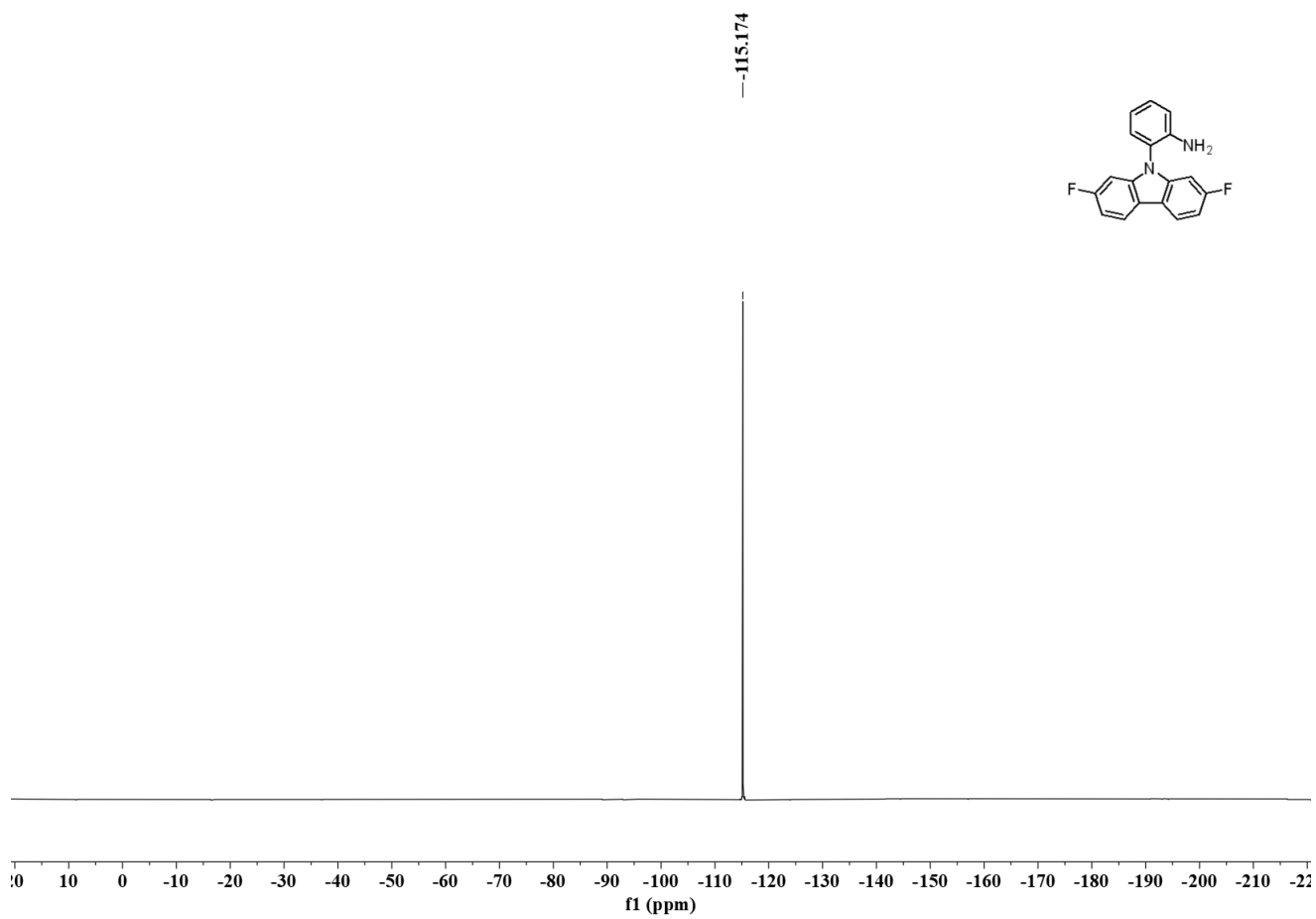
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of **6g**



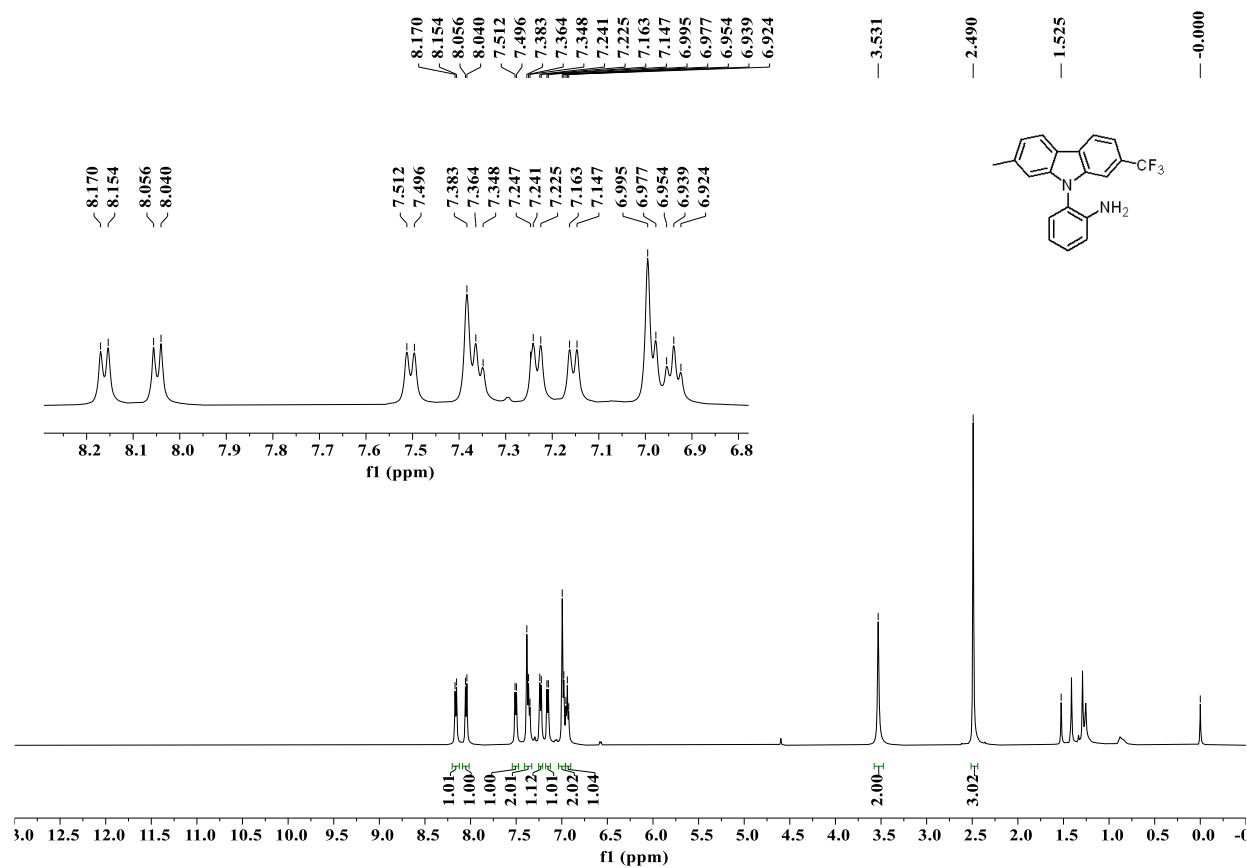
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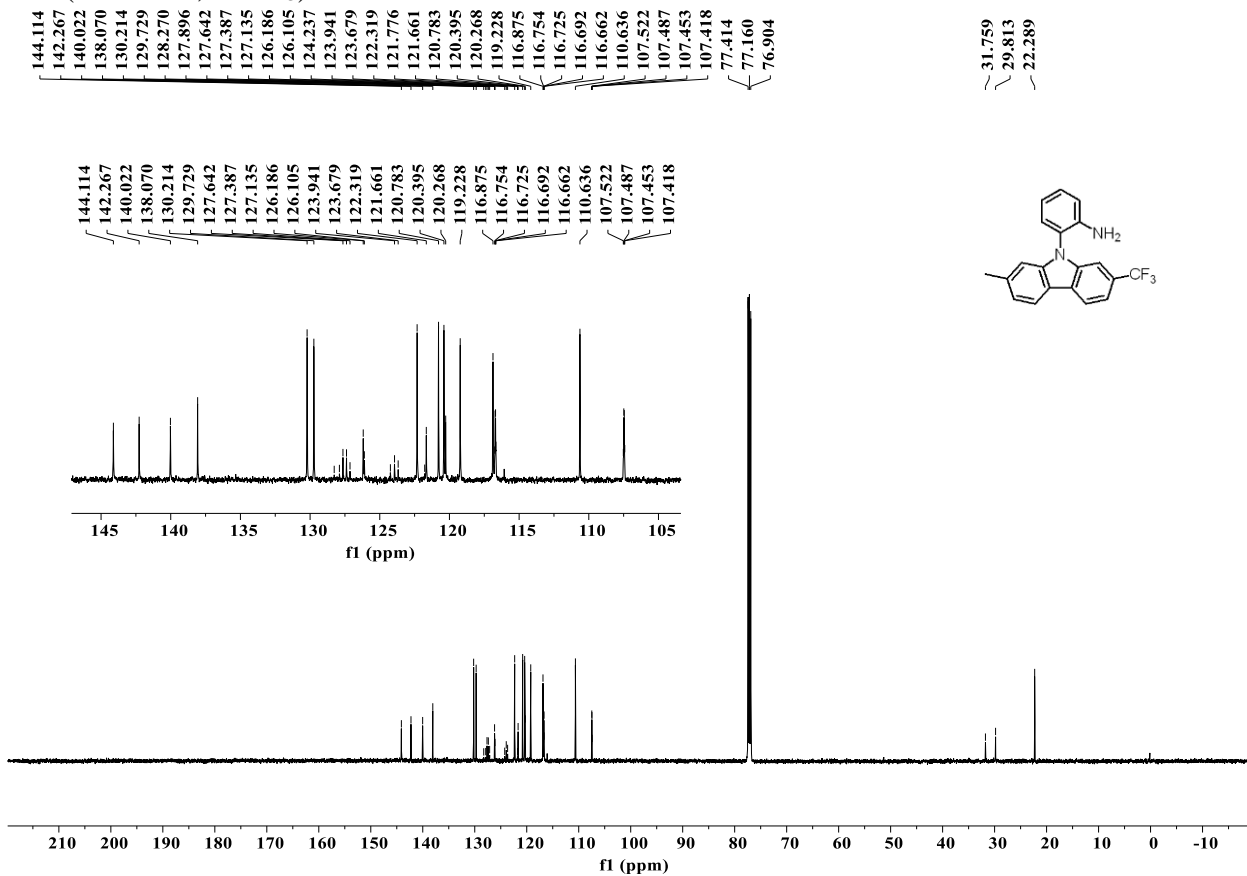
$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) of **6g**



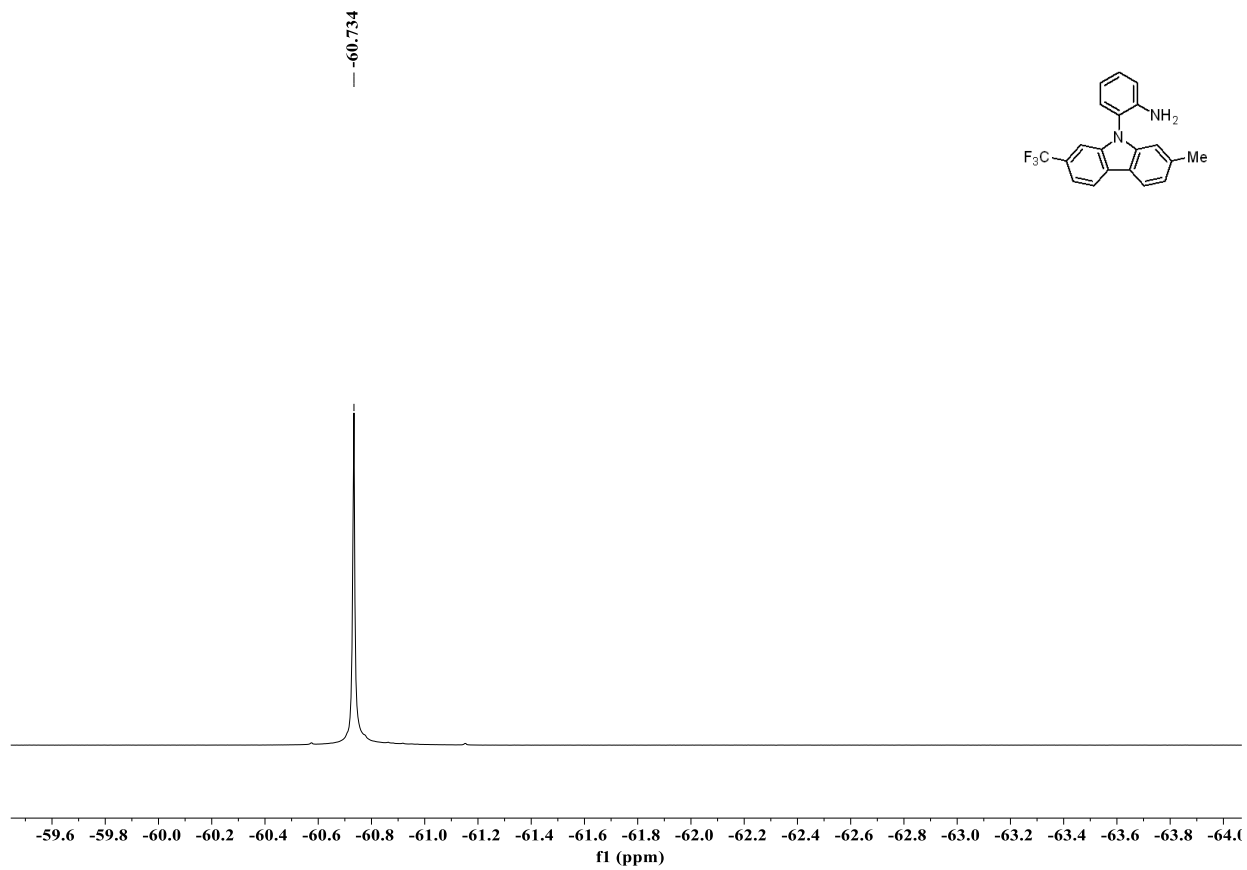
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **6h**



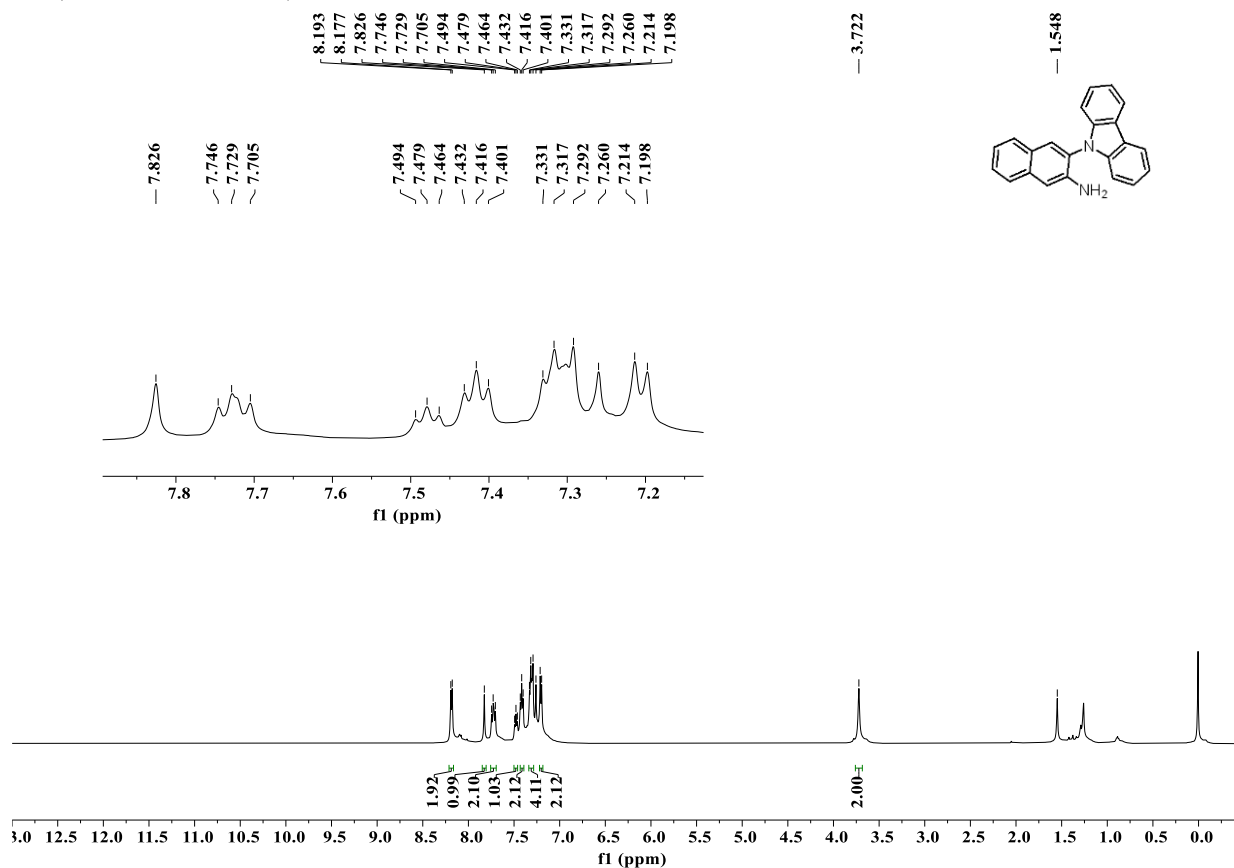
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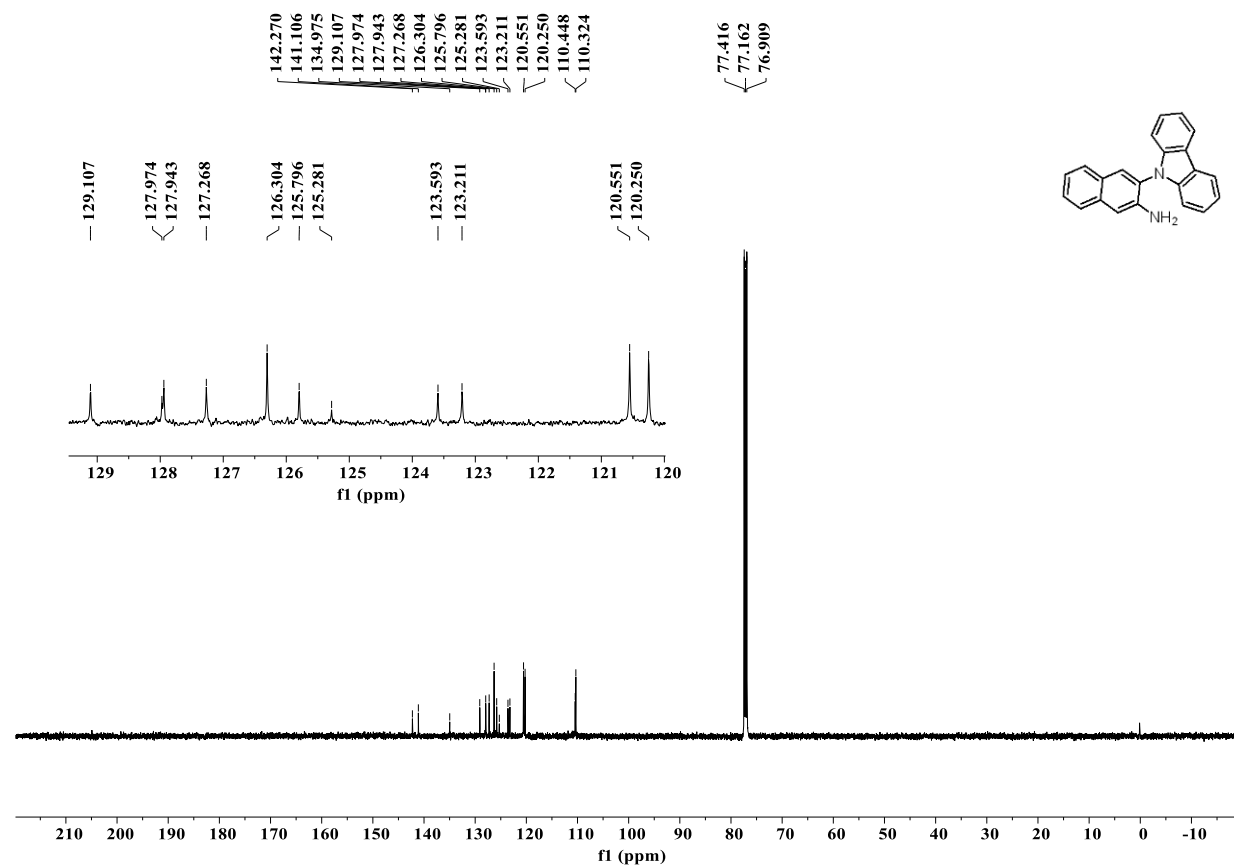
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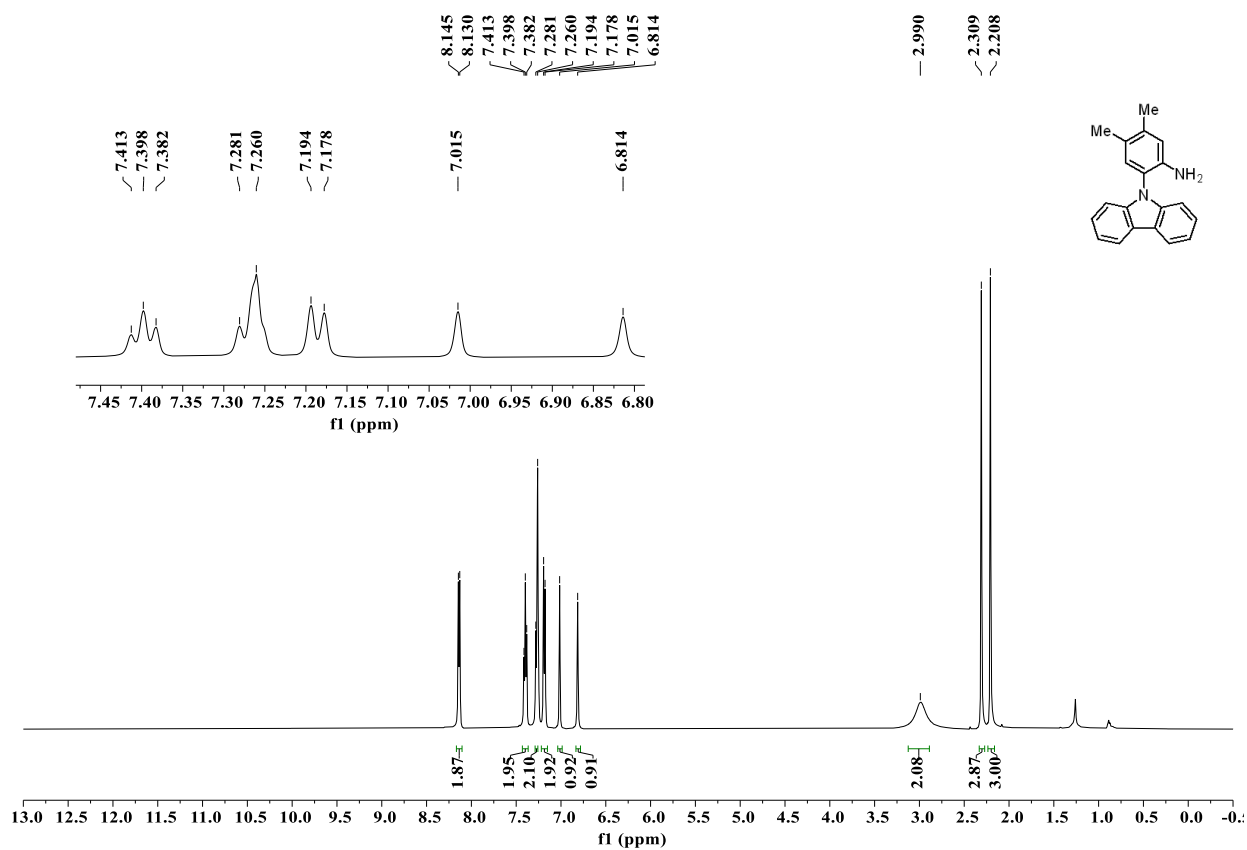
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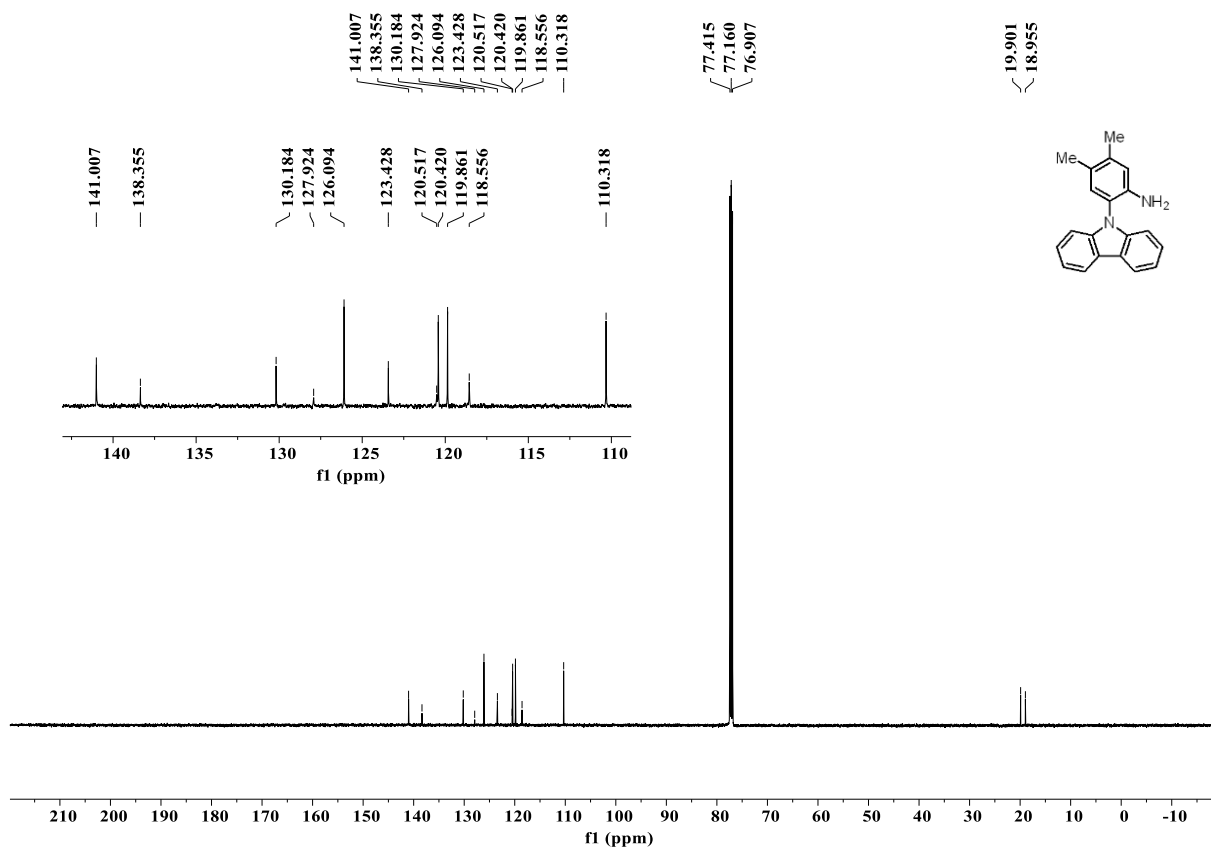
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **6i**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **6j**

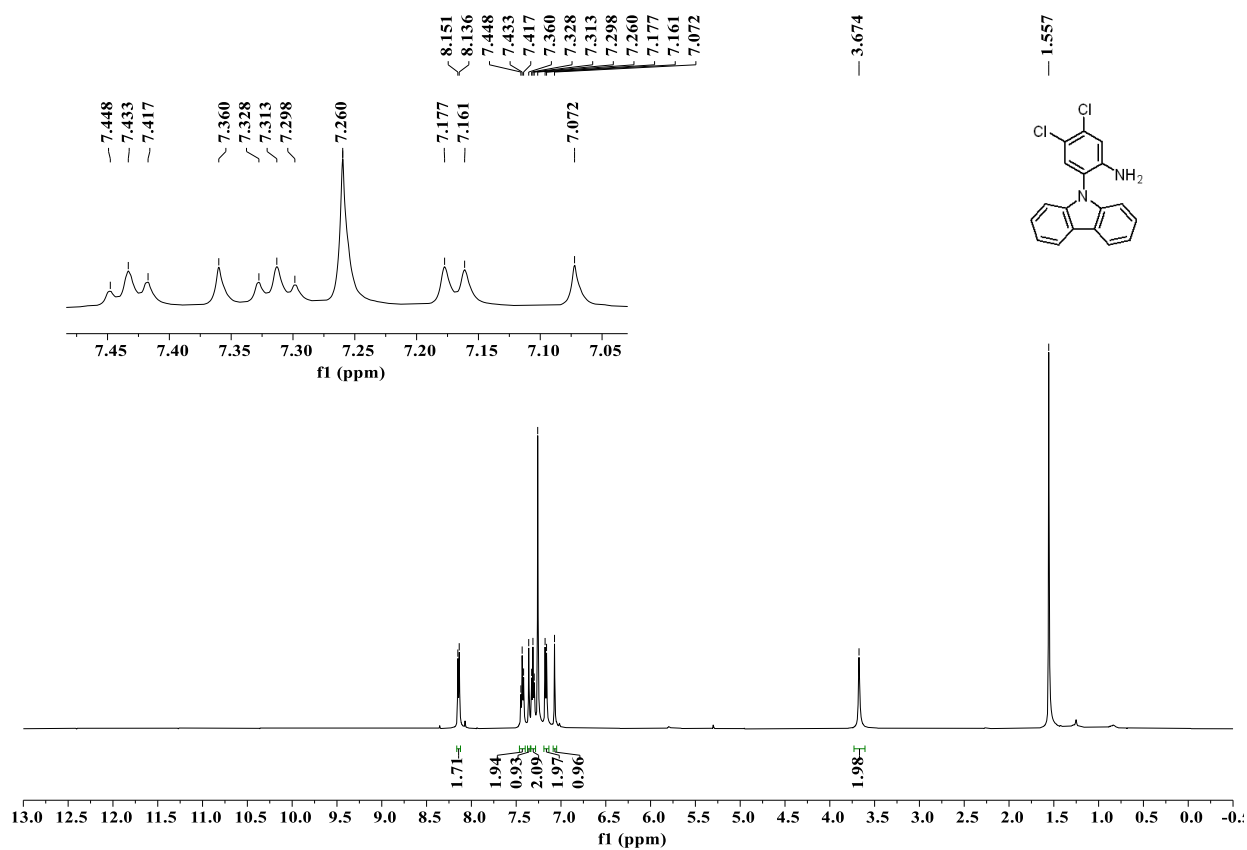


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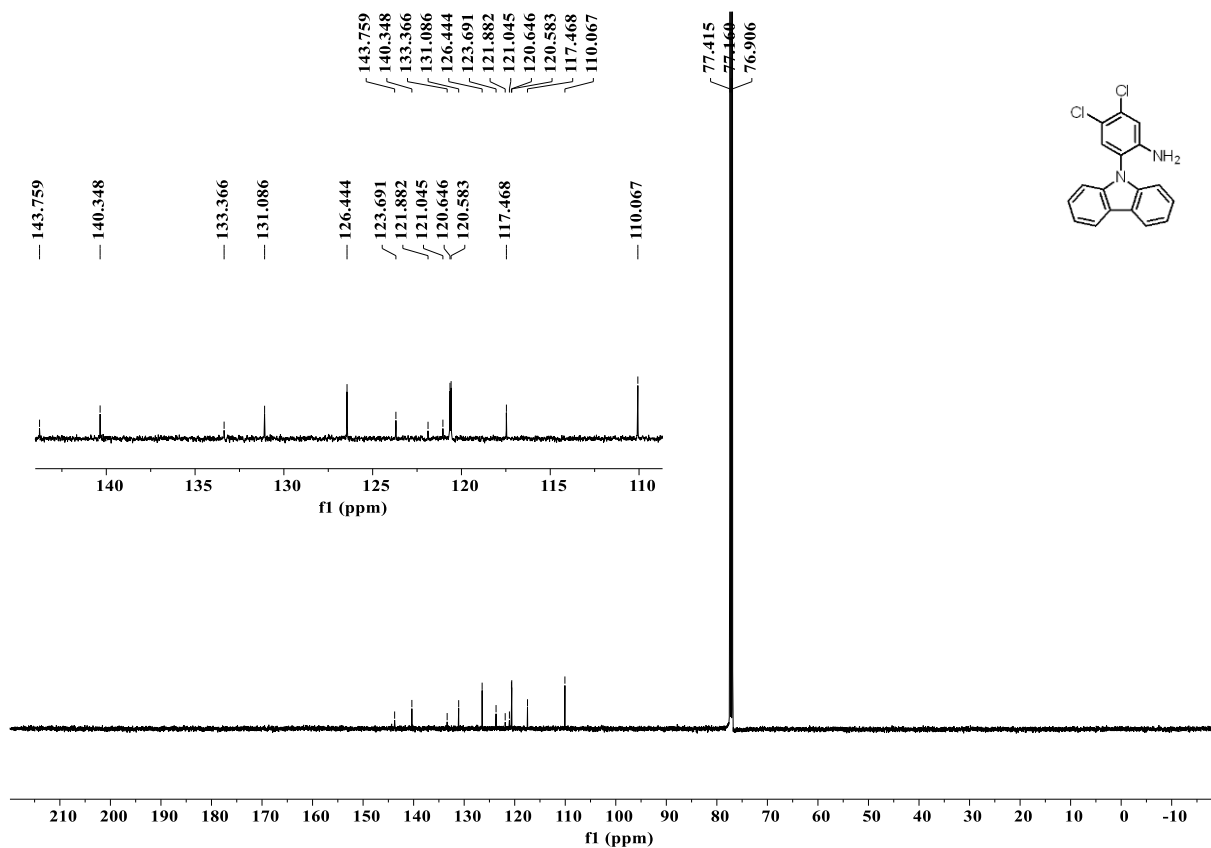




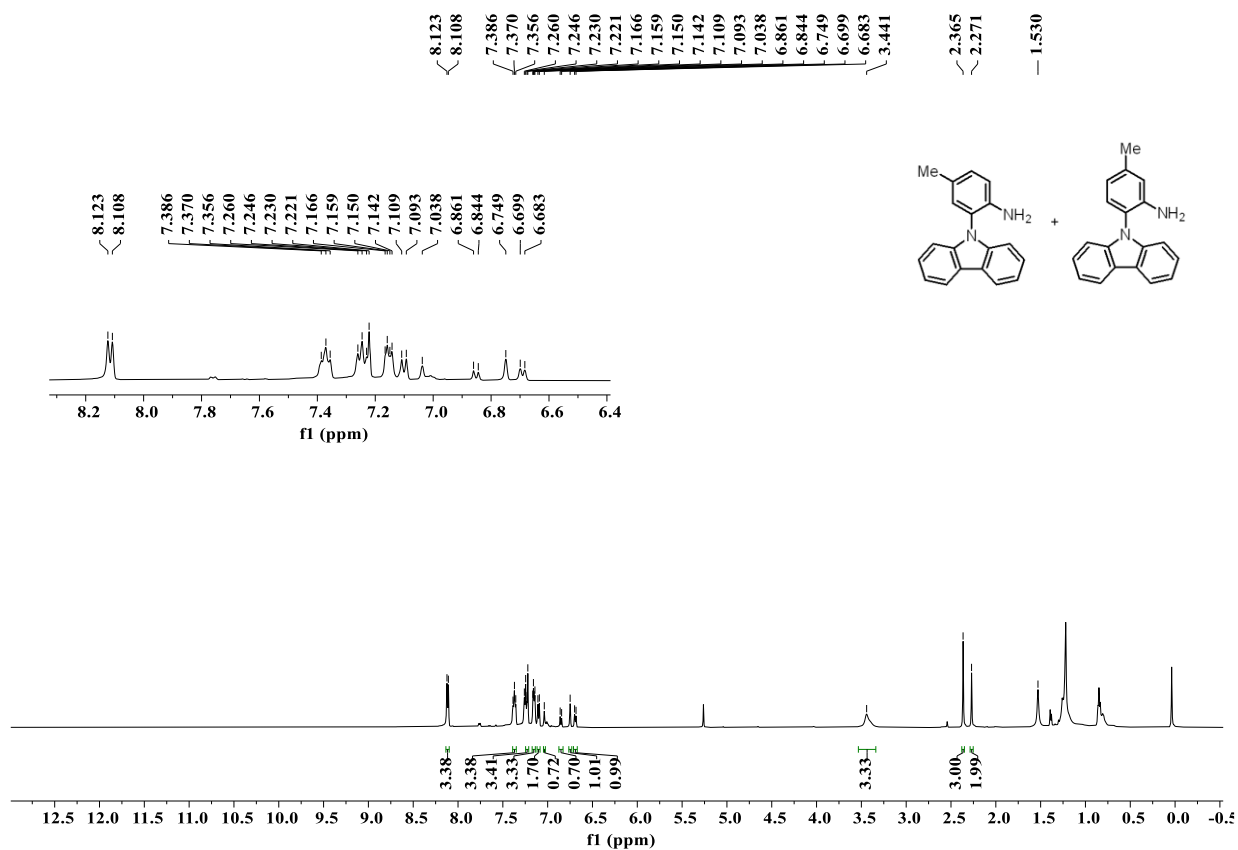
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **6k**



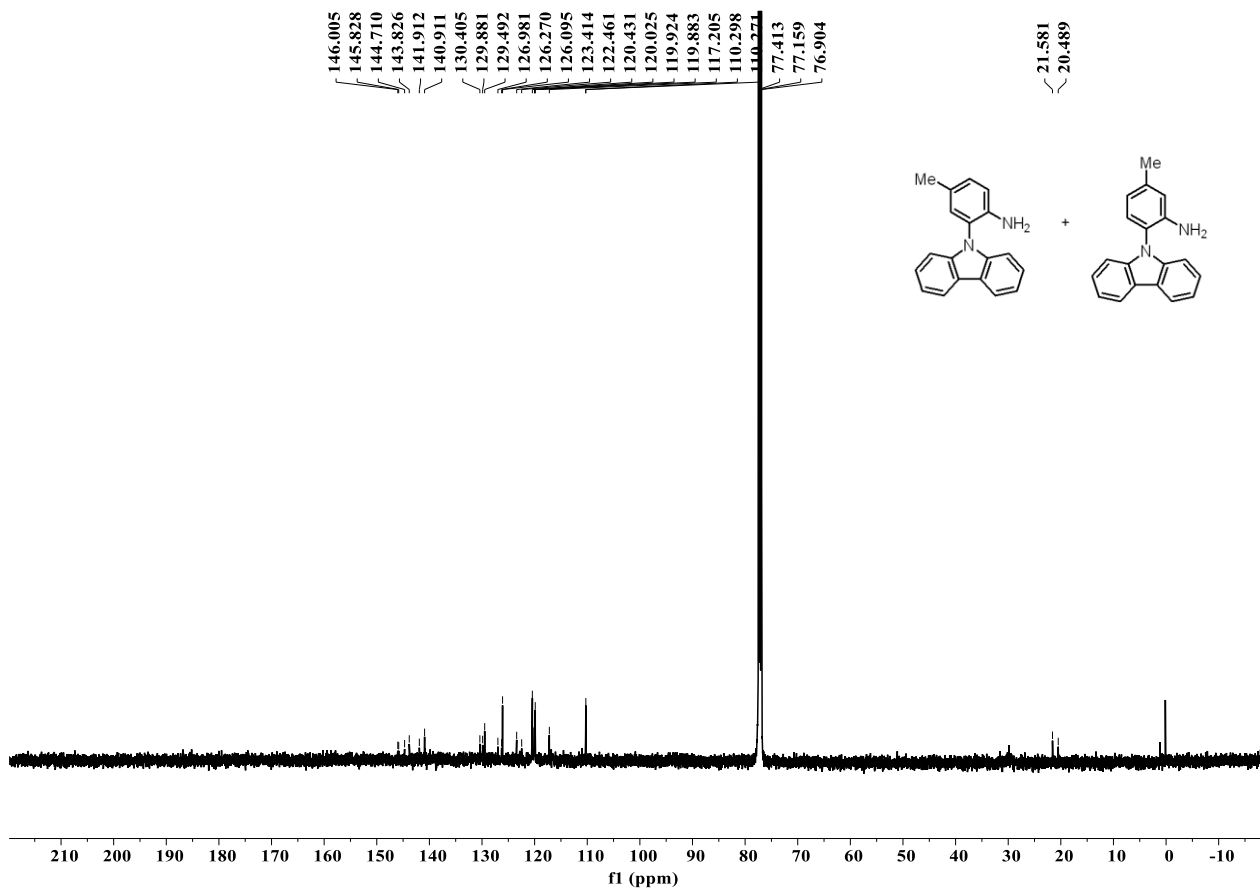
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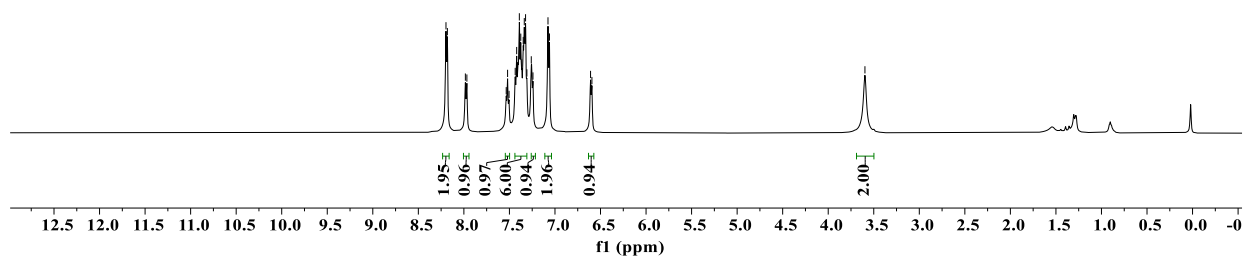
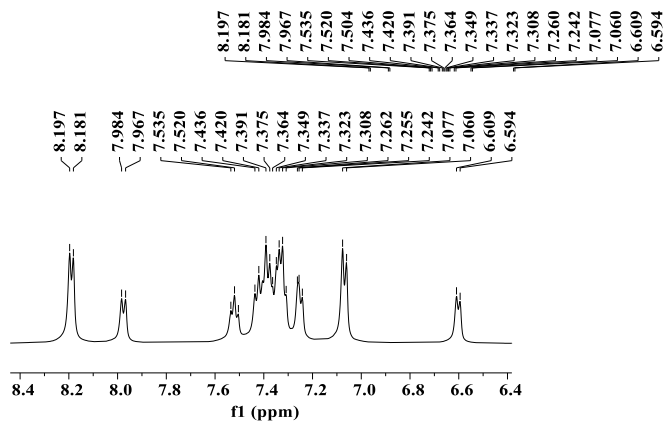
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **6I** and **6I'**



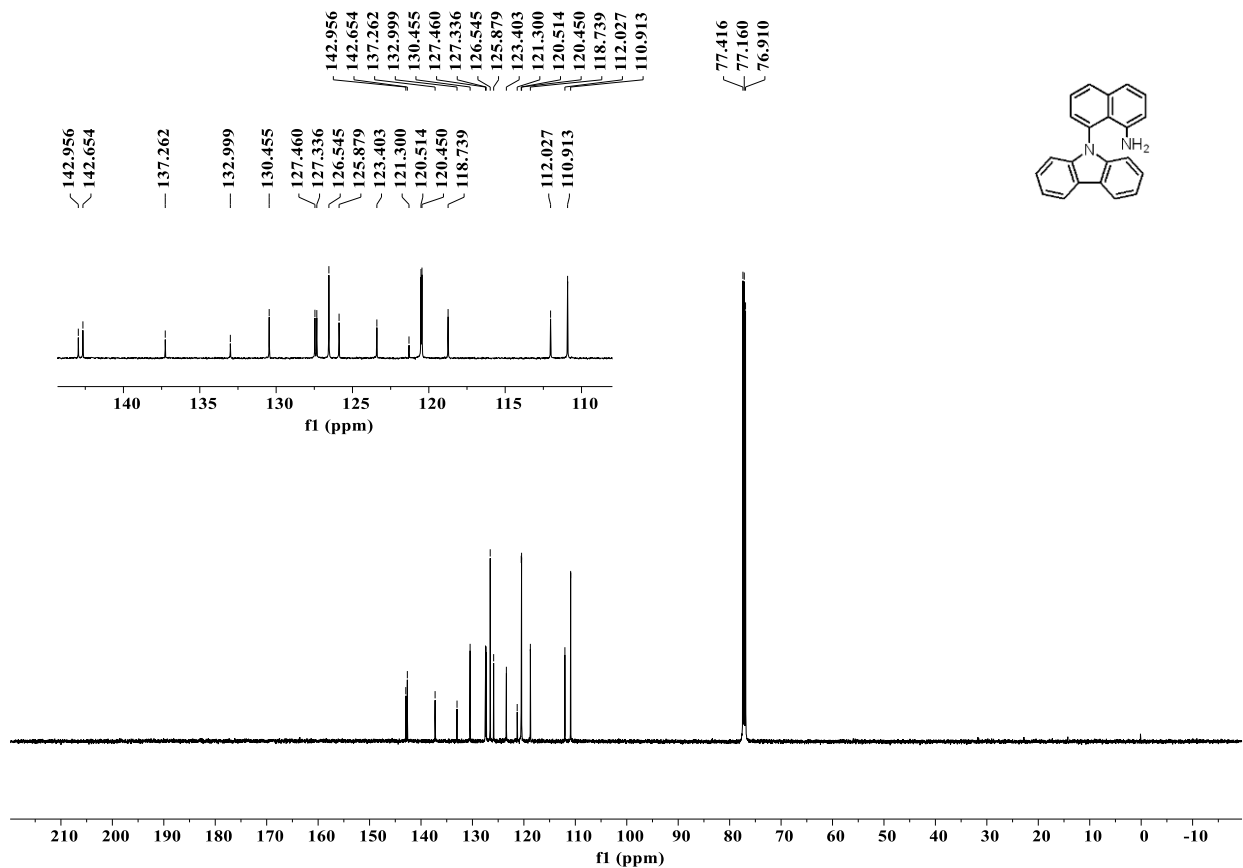
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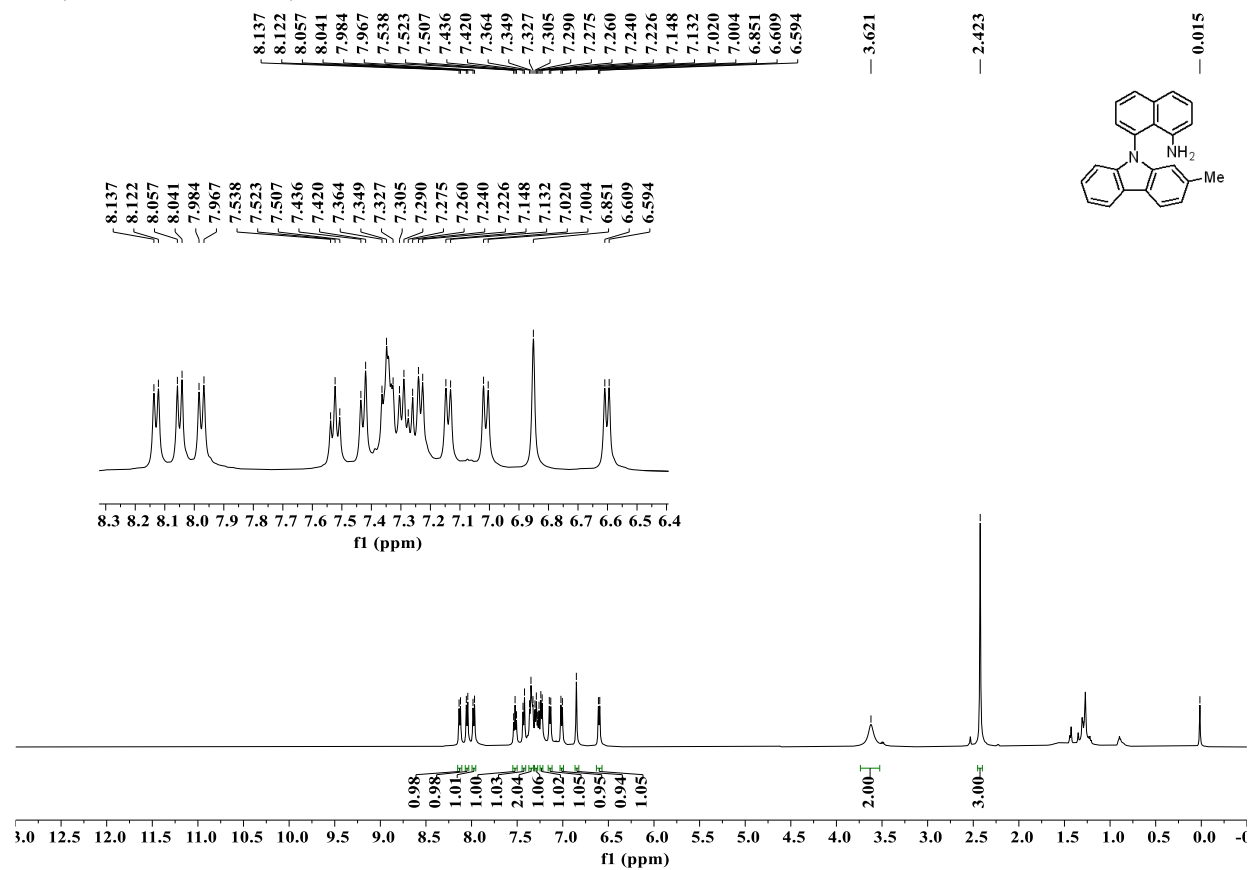
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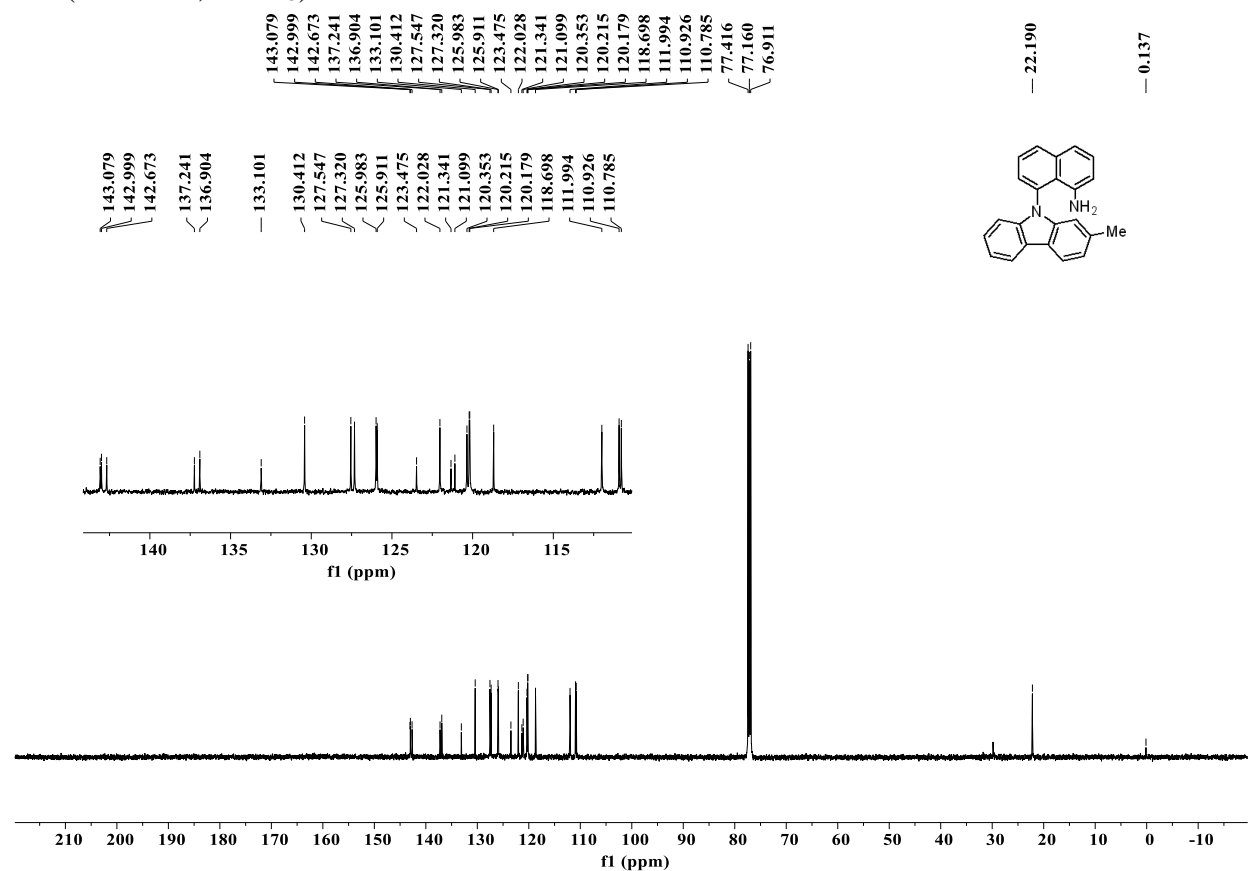
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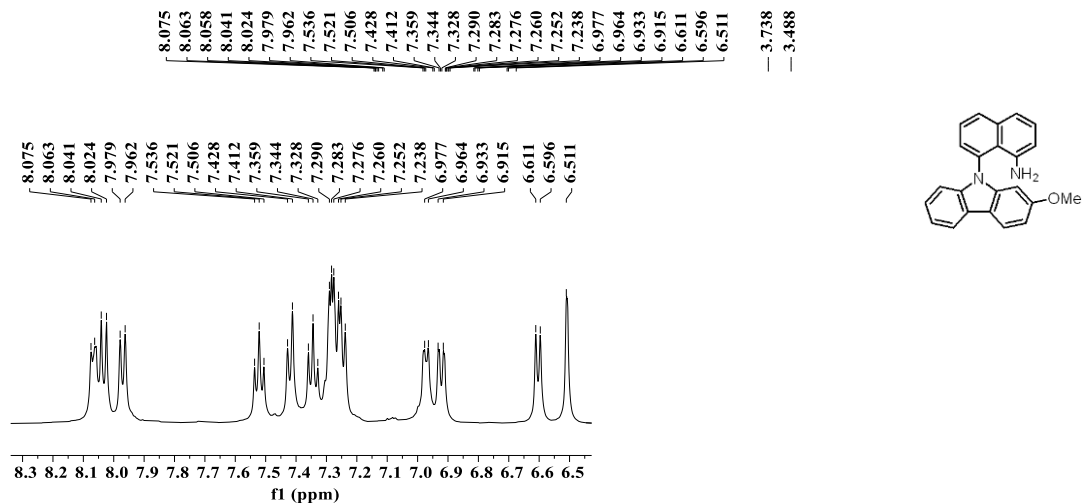
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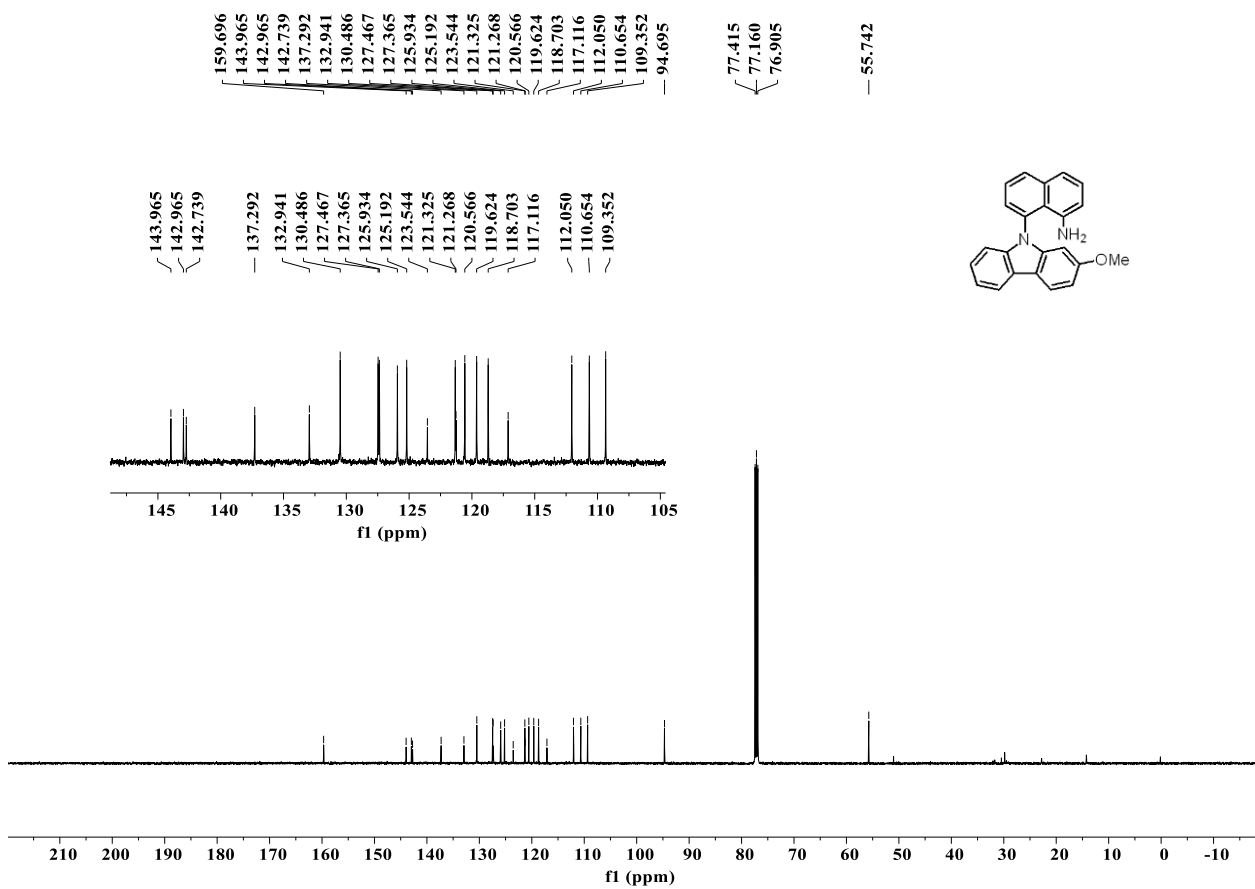
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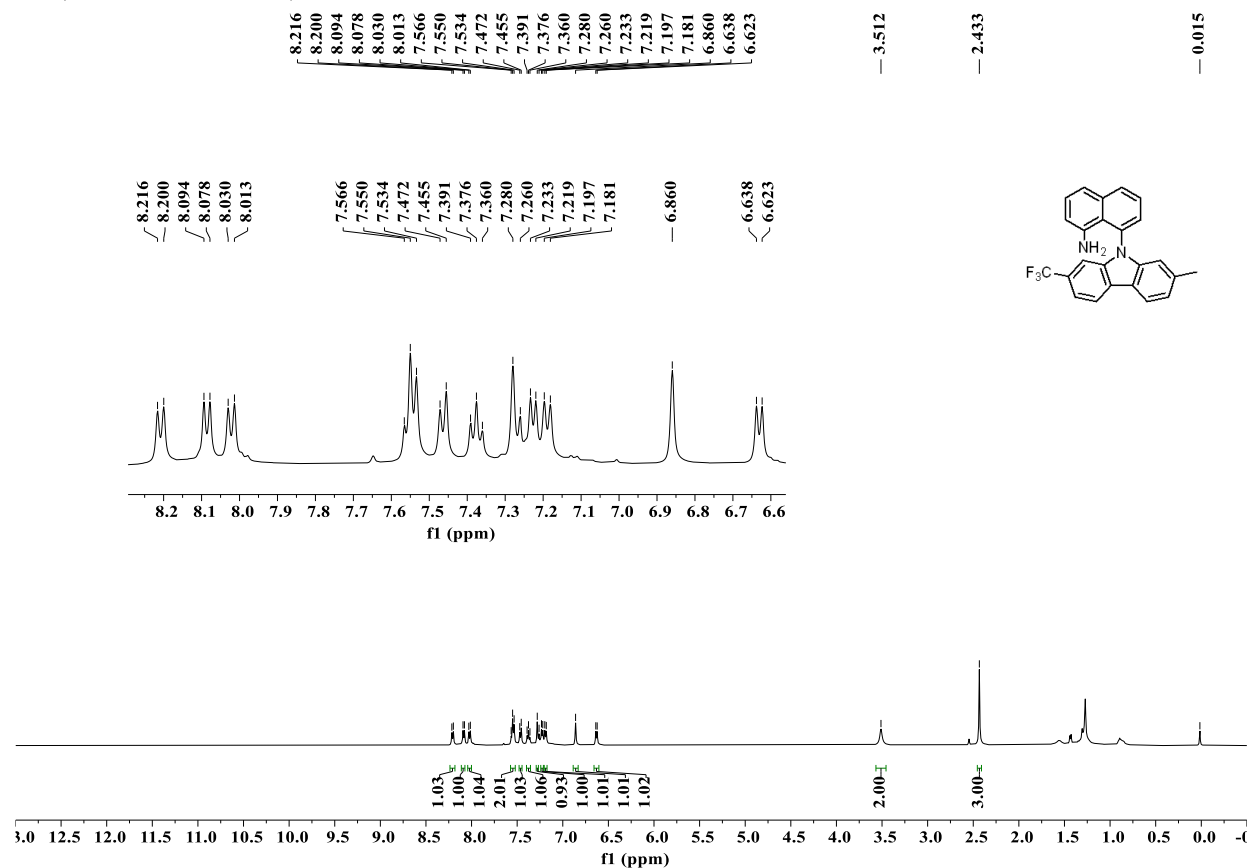


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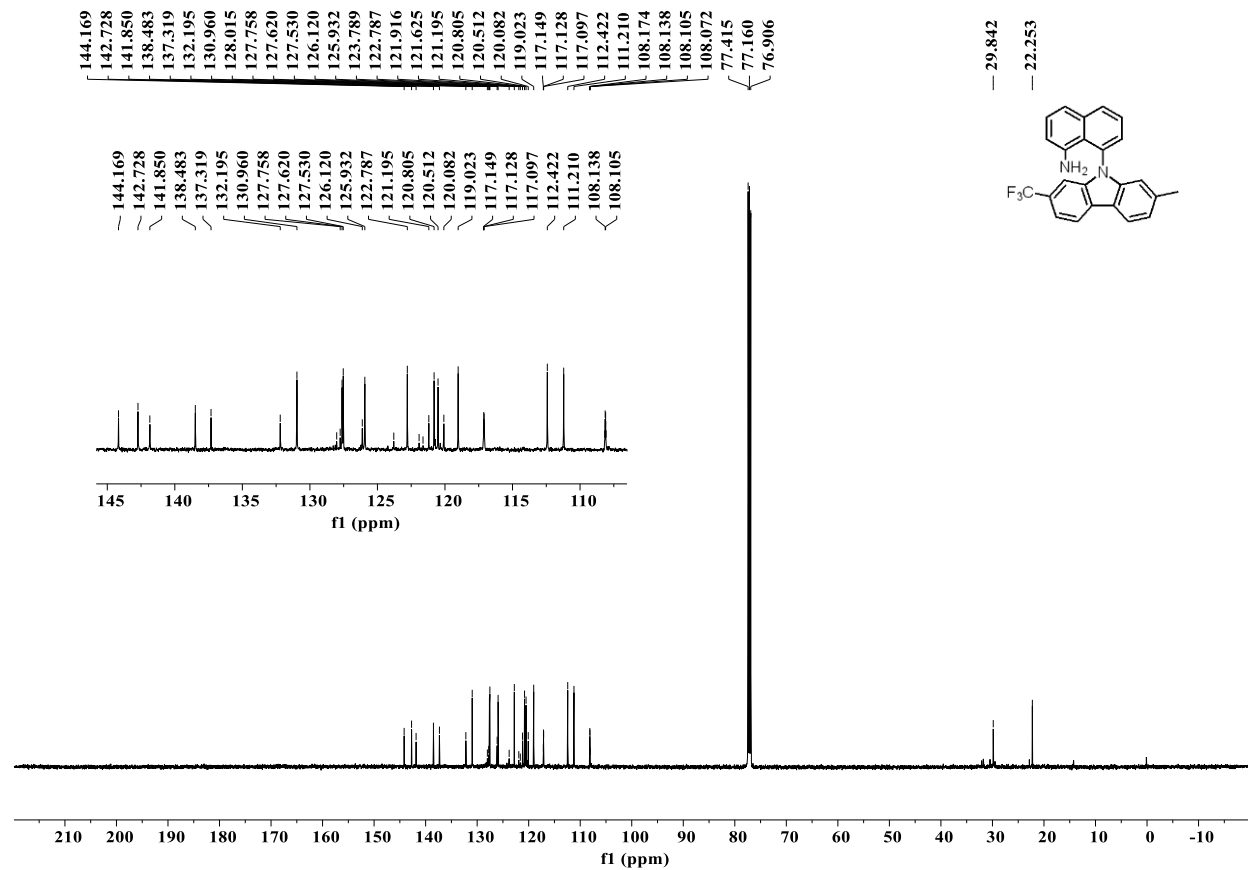




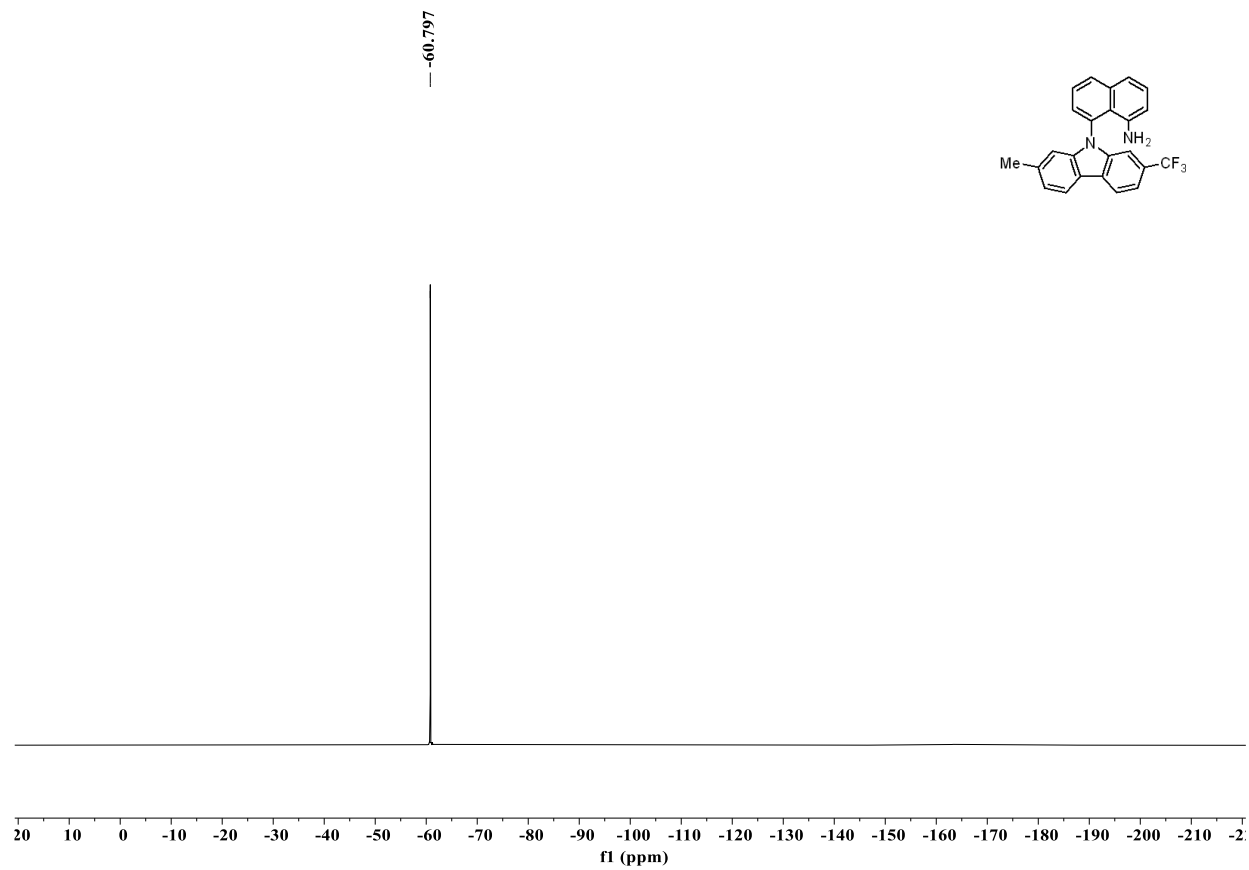
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **7e**



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **7e**

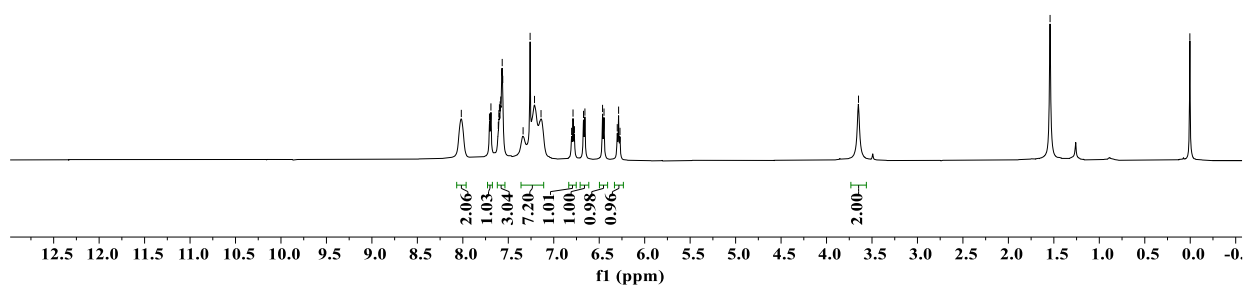
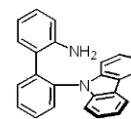
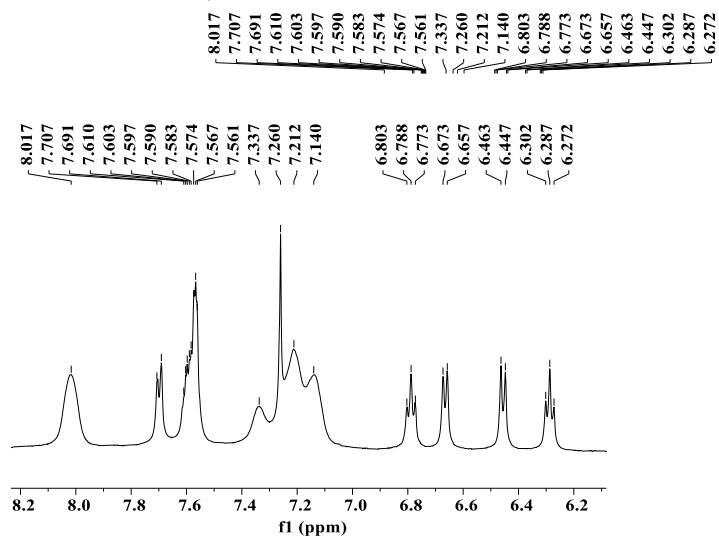


$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) of **7e**

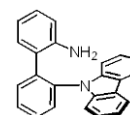
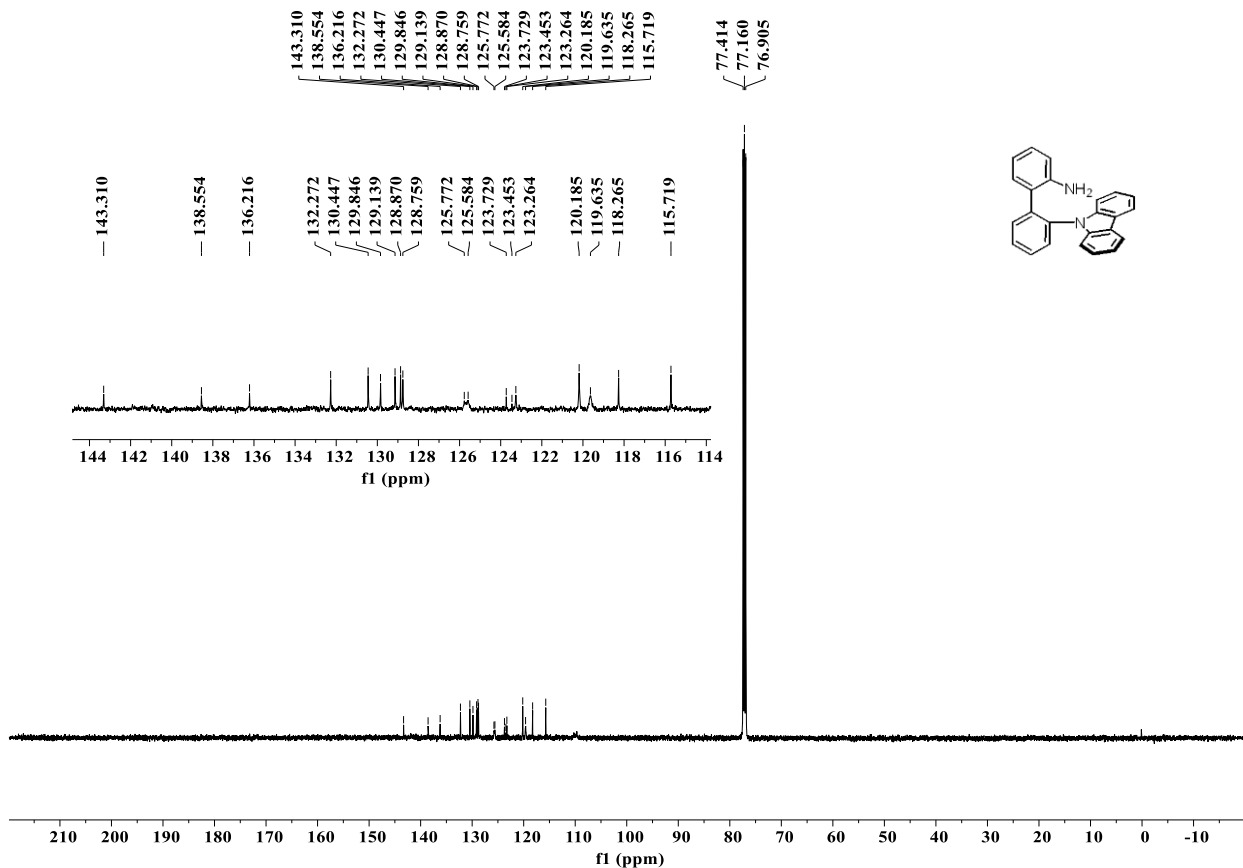




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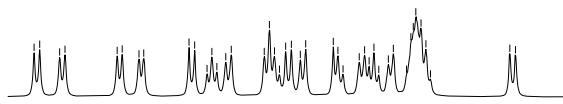
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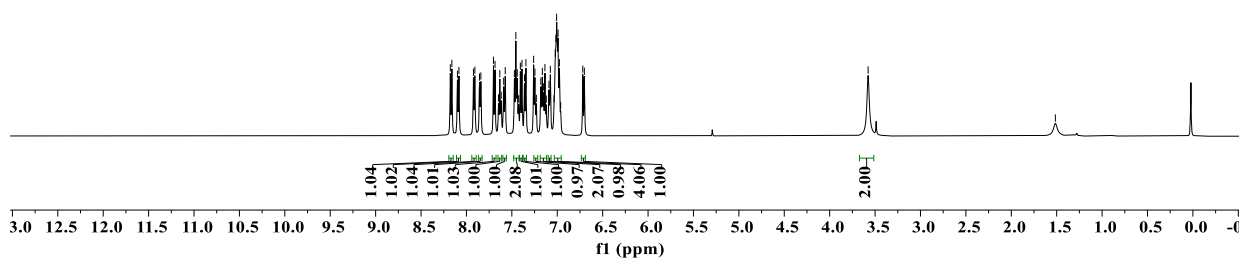
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8.178, 8.160, 8.083, 7.923, 7.907, 7.702, 7.685, 7.573, 7.472, 7.456, 7.440, 7.406, 7.389, 7.345, 7.246, 7.164, 7.136, 7.076, 7.022, 7.015, 7.007, 6.991, 6.976, 6.719, 6.701



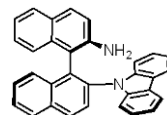
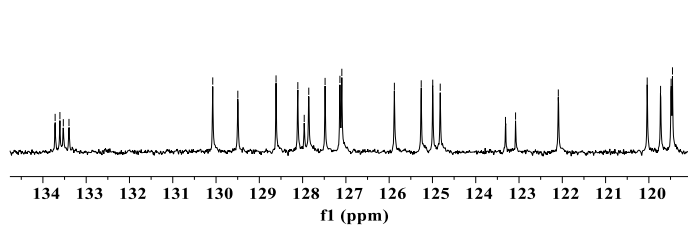
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<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **8b**

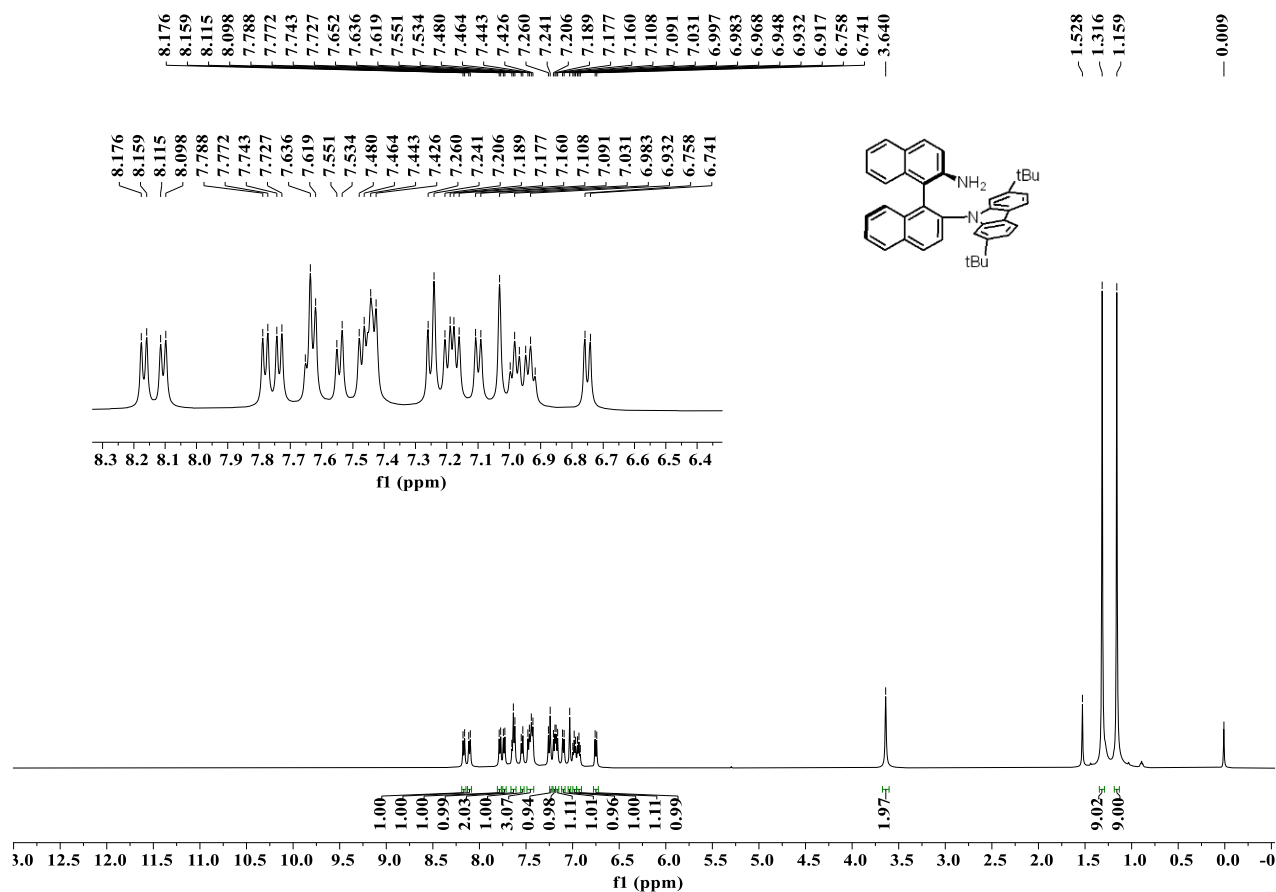
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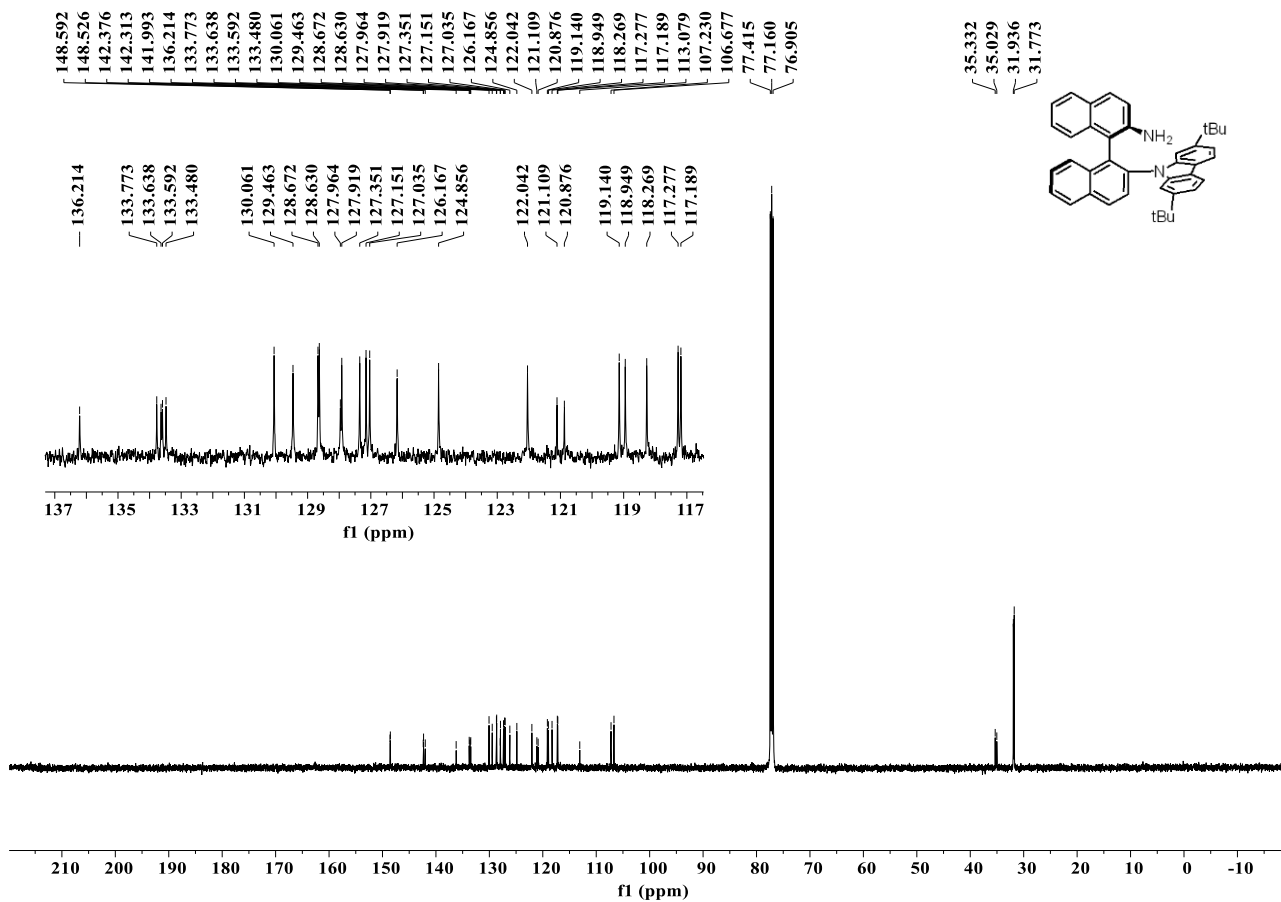


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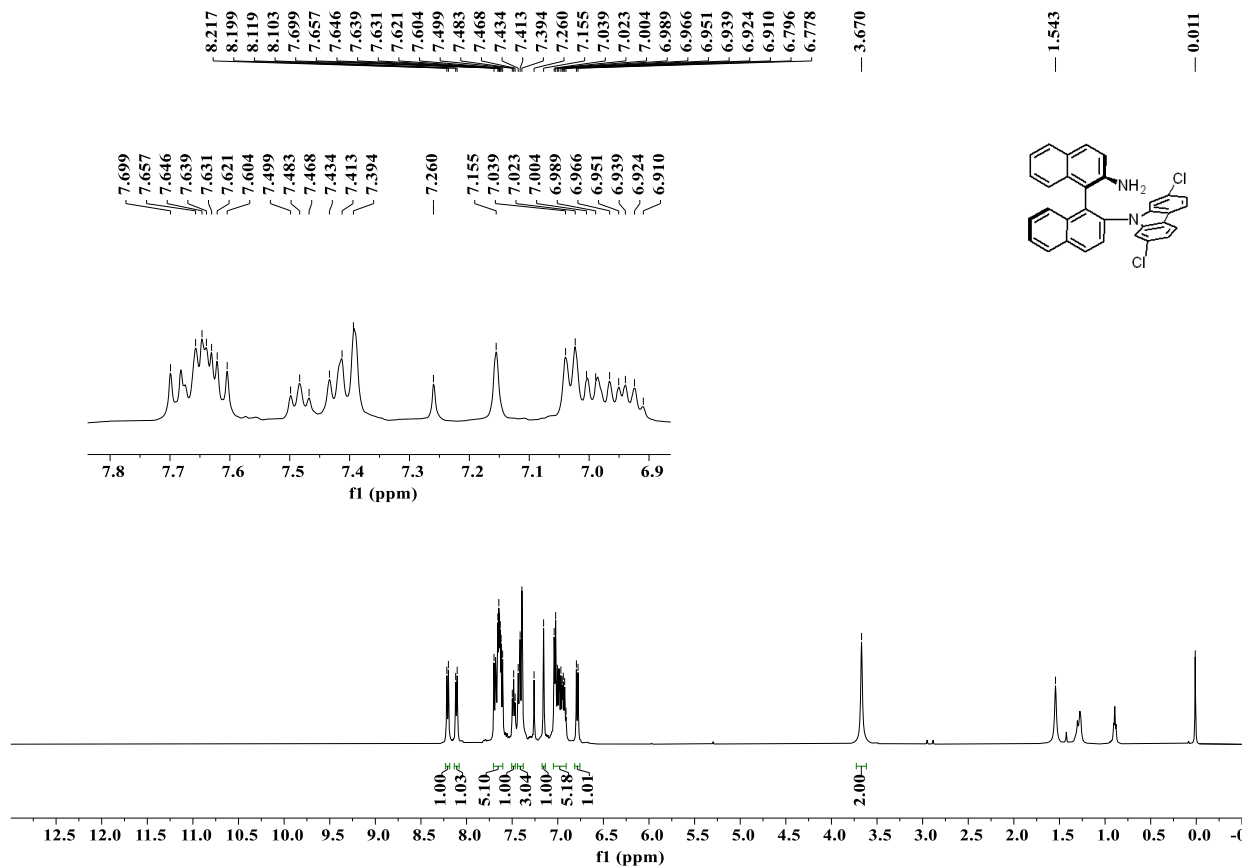
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **8c**



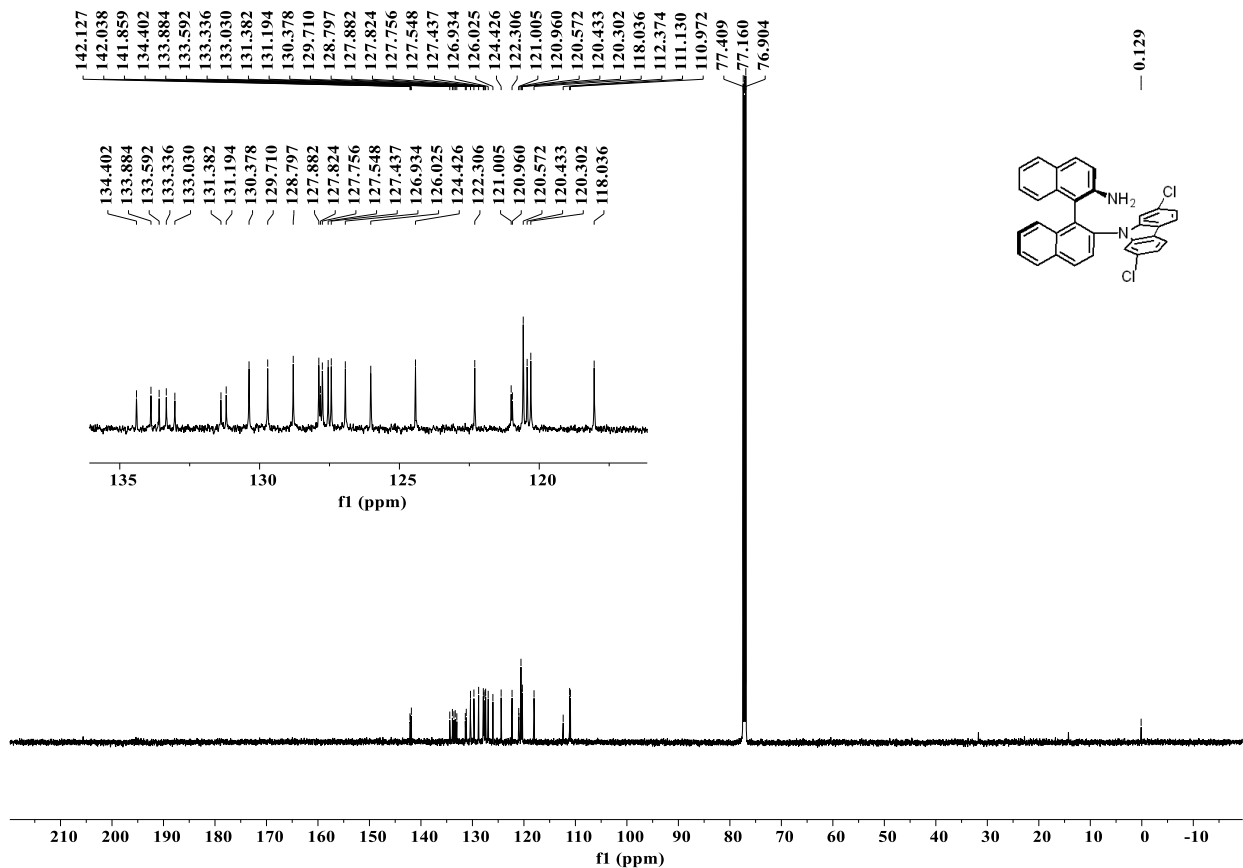
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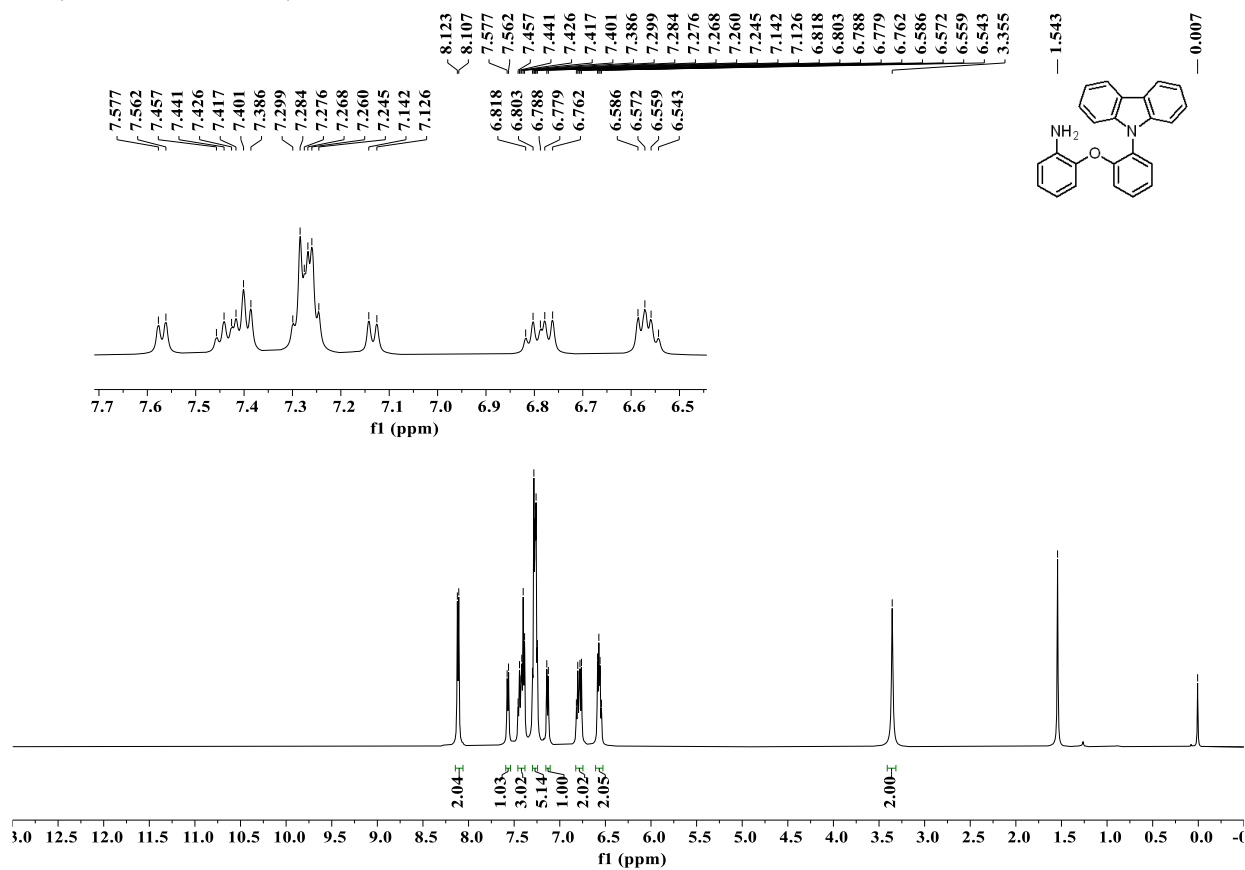
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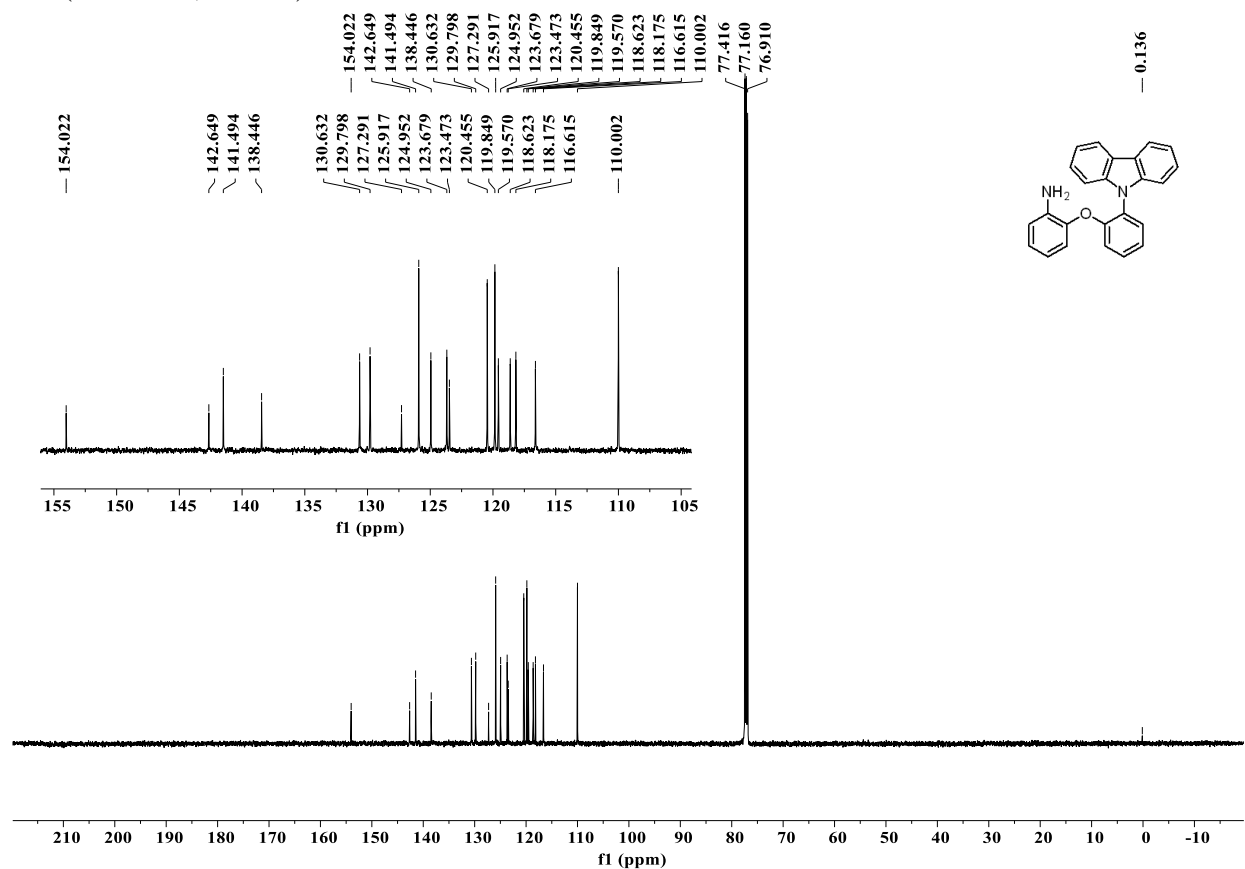
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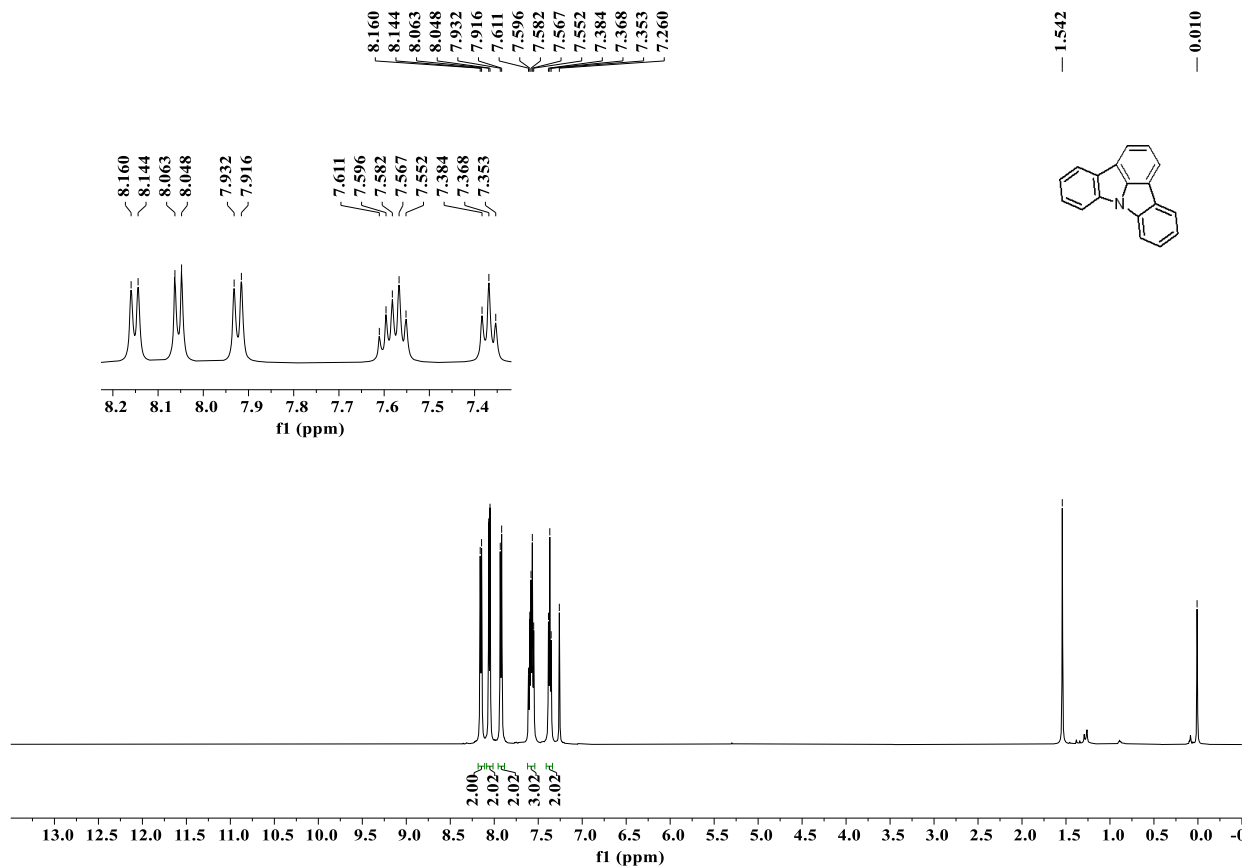
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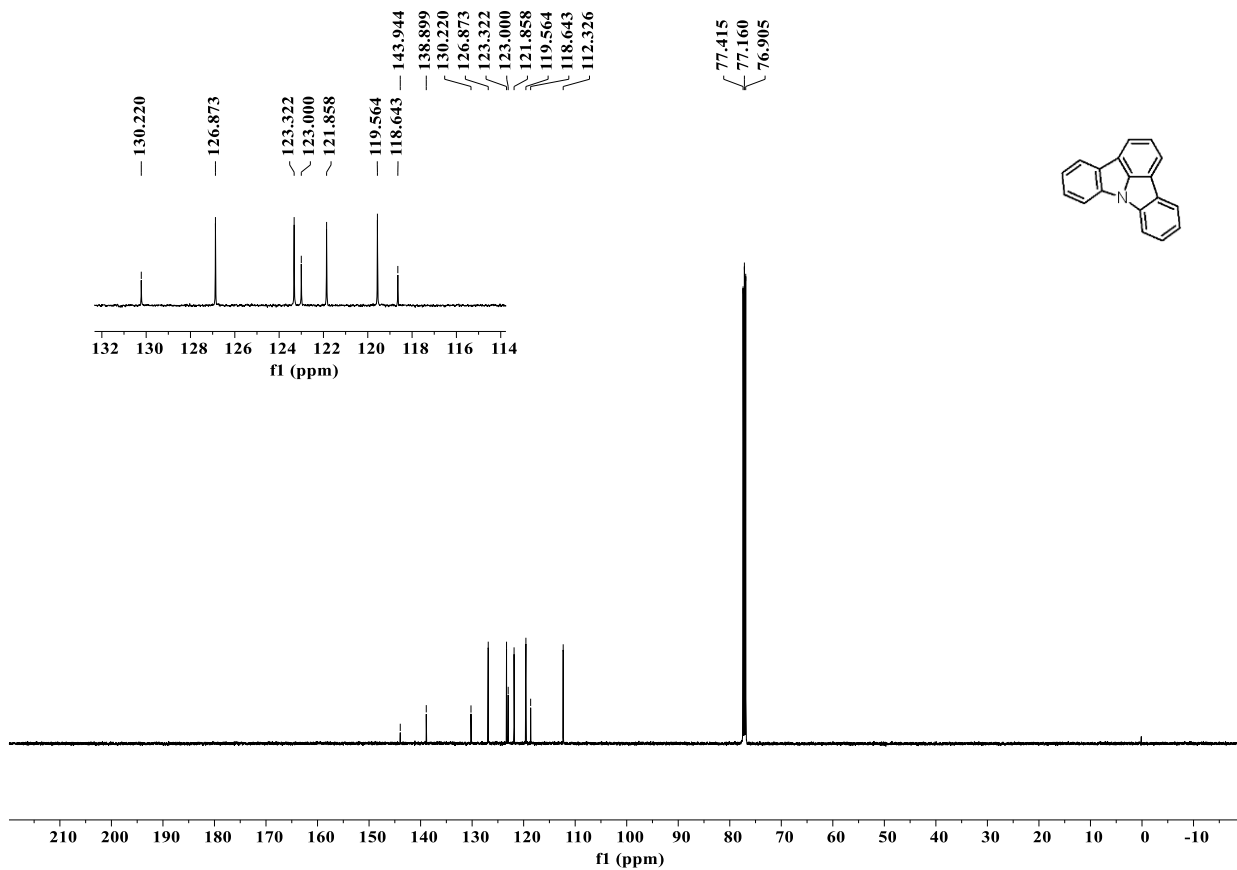
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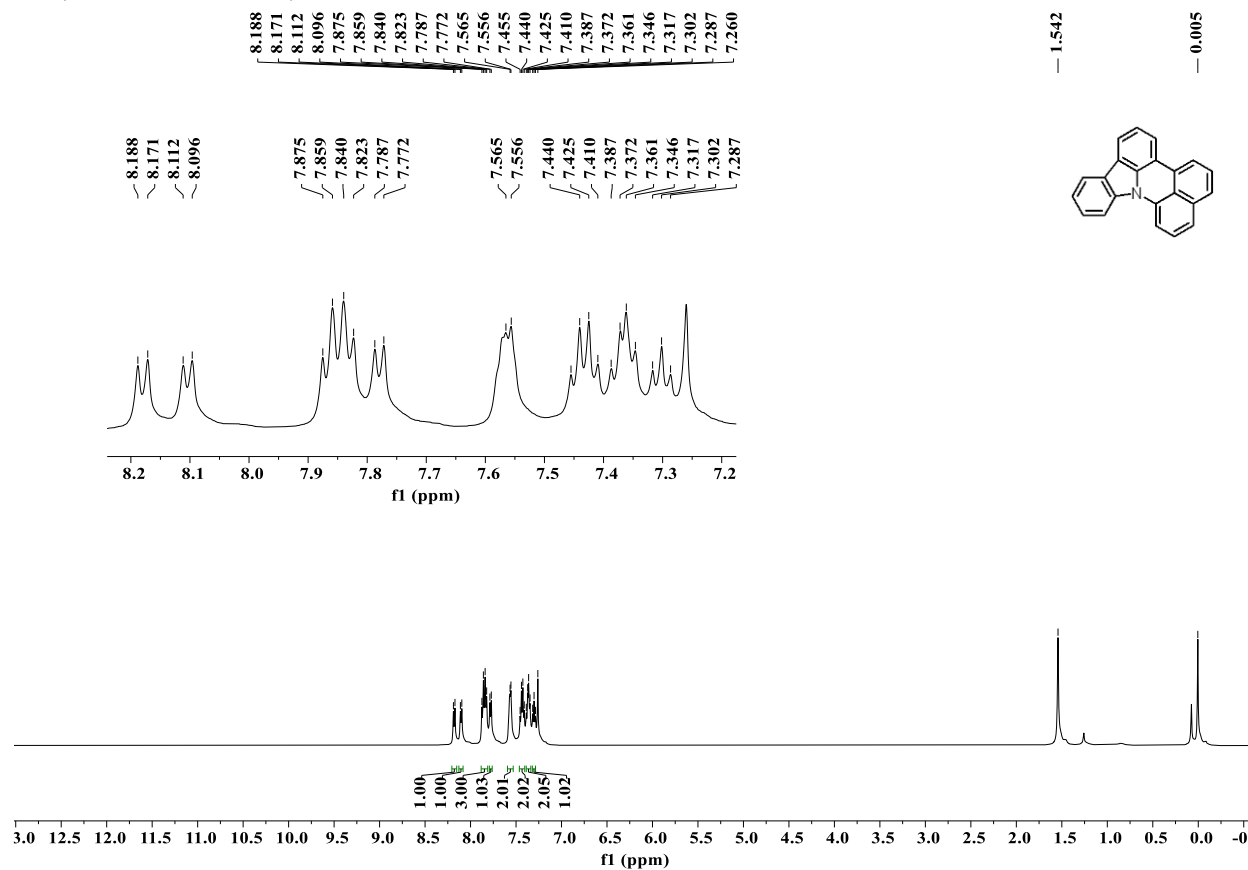
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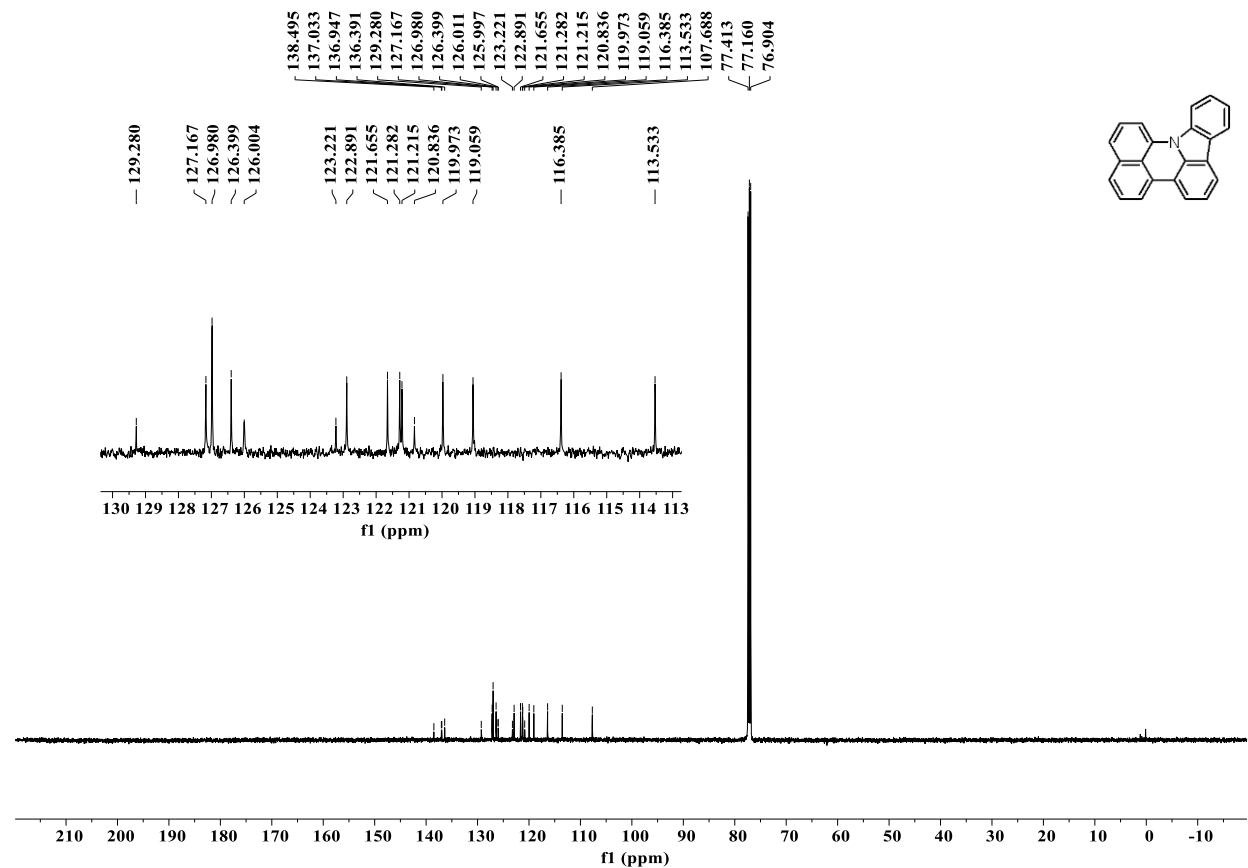
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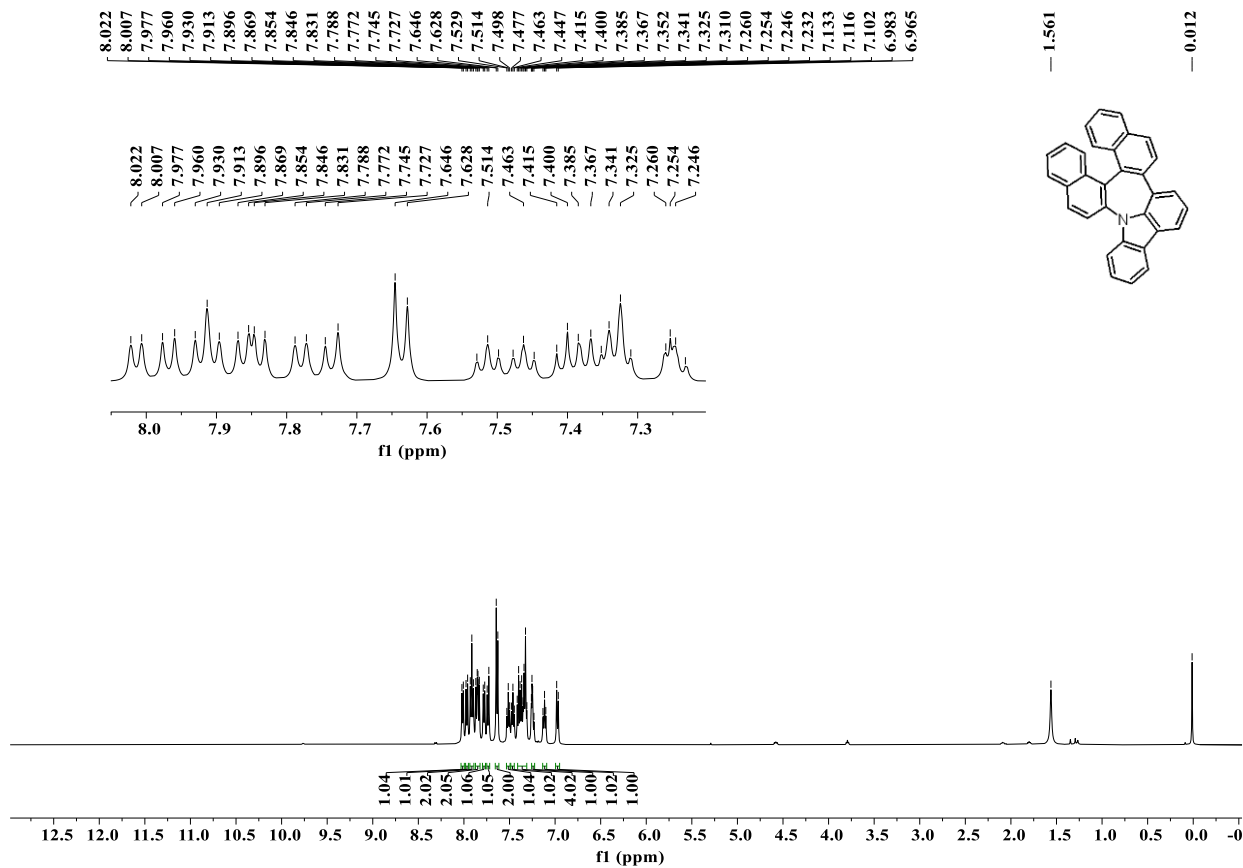
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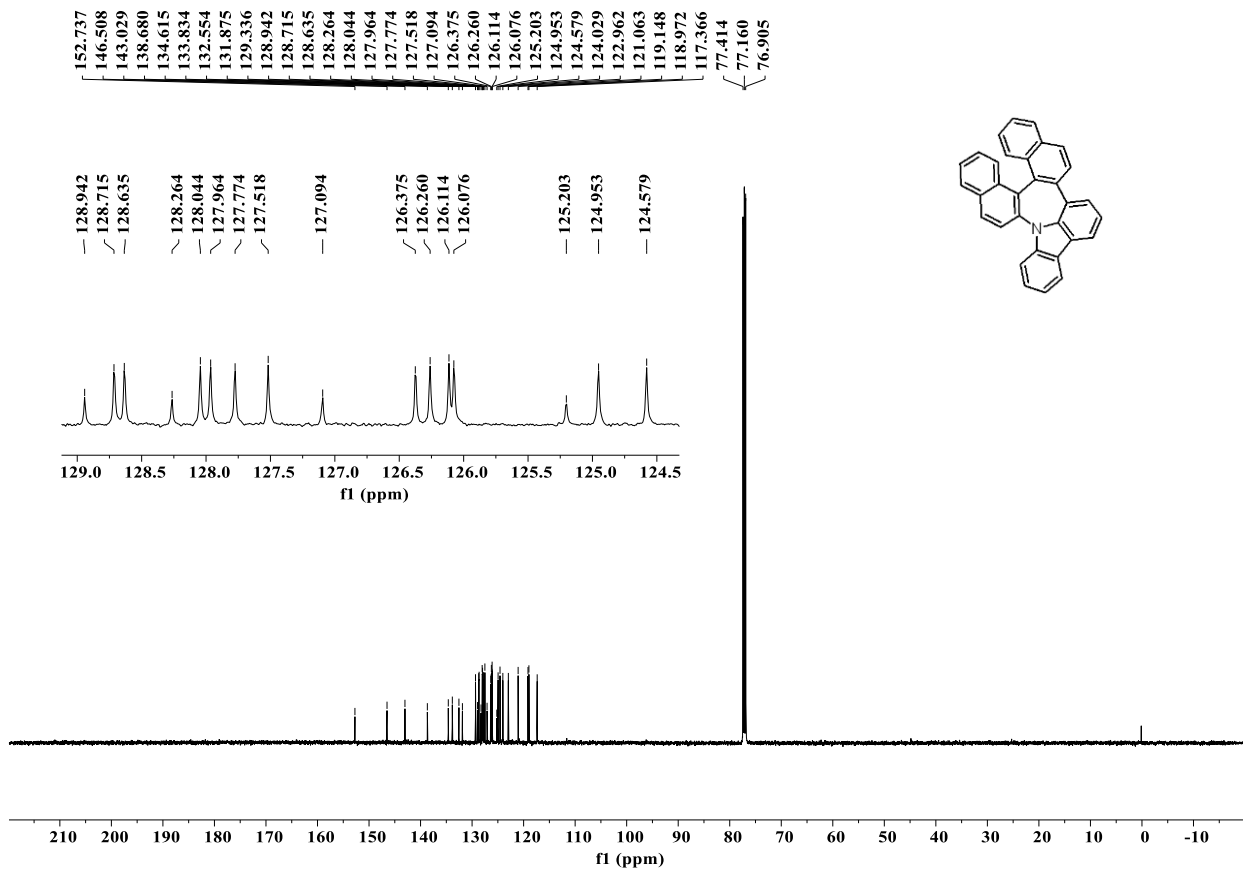
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<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **12**

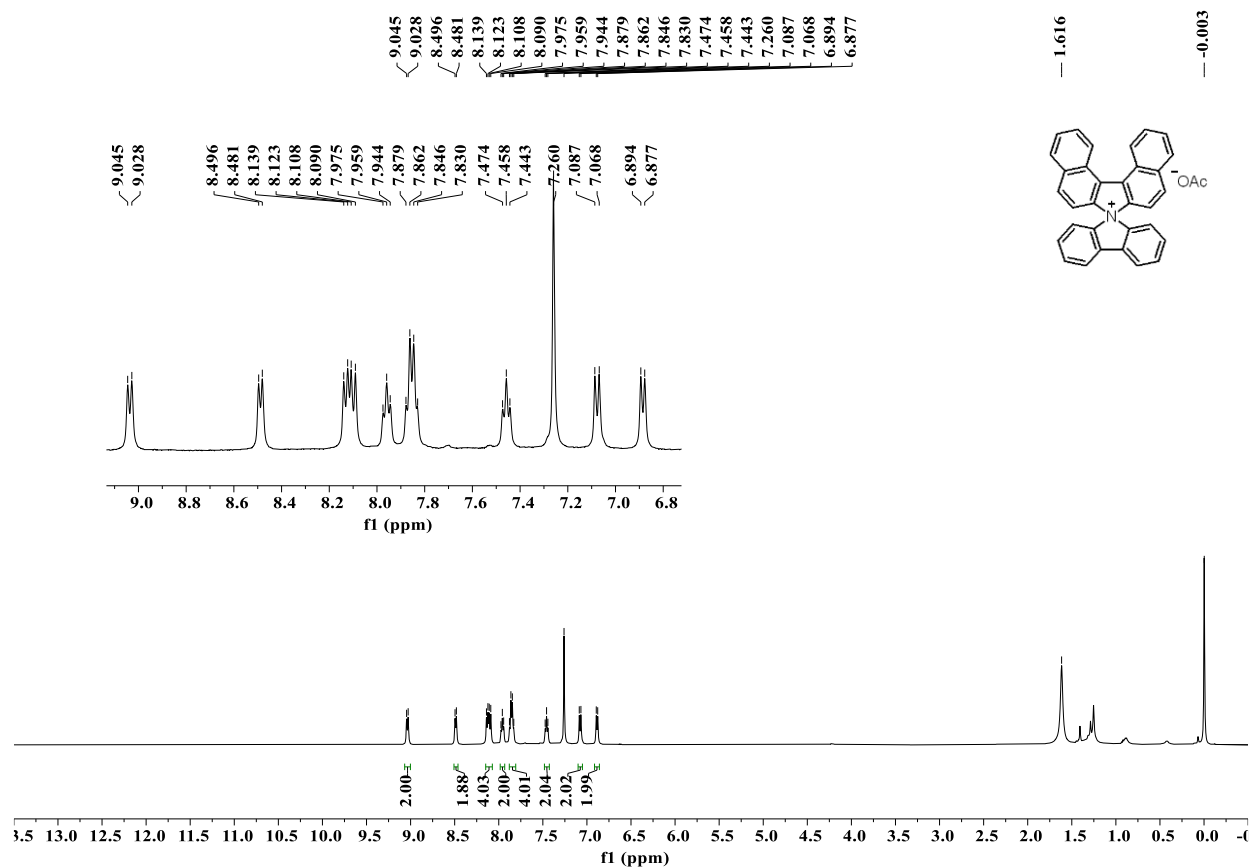


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **12**





<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of **13**



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of **13**

