Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

Temporary (P=O) Directing Group Enabled Carbazole Ortho Arylation via Palladium Catalysis

Zhi-Chao Qi,† Qin-Xin Lou,† Yuan Niu† and Shang-Dong Yang*†‡

†State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.

‡State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China.

Table of Contents

1. General Information ---------- S3

2. General Procedures for the Synthesis of Substrates ---------- S4

3. Screening of reaction conditions ---------- S4-7

4. General Procedures for the Synthesis of Arylation Products ---------- S5

5. Scope of hypervalent iodine for arylation and carbazole - P source ---------- S5-9

6. Gram-Scale Experiment and Derivatization ---------- S11-12

7. Investigation of the Reaction Mechanism ---------- S12-16

8. Characterization Data of Substrate ---------- S16-20

9. Characterization Data of New Product ---------- S20-26

10. X-ray Crystallographic Data ---------- S26-27

11. Reference ---------- S28

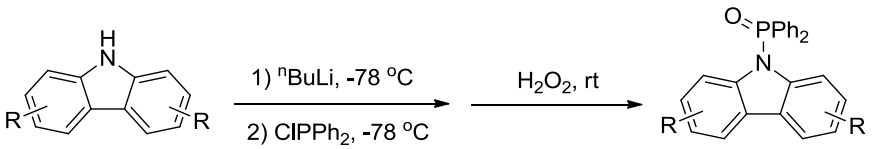
12. Copies of NMR Spectra ---------- S28-82

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H , 101 MHz for ^{13}C 162 MHz for ^{31}P and 376 MHz for ^{19}F) and Mercury plus 300 BB spectrometer (300 MHz for ^{1}H , 75 MHz for ^{13}C and 282 MHz for ^{19}F)in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P NMR spectra and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, J, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. Low resolution mass spectroscopic (LRMS) and mass spectra were measured using Bruker micro TOF-Q II mass spectrometer and Thermo Scientific DS Ⅱ mass spectrometer. X-ray diffraction experiments were performed on a SuperNova, Dual, Cu at zero, Eos diffractometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. The pH value was examined by universal indicator paper from Shangai SSS Reagent Co., LTD. Melting points (m.p.) were determined on Jingsong X-4B melting point apparatus. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). All carbazole derivatives were synthesized according to references 1-10. All diaryliodonium salts are known substrates, which were prepared according to reference 11.

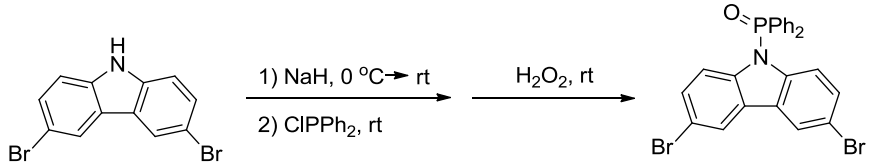
2. General Procedures for the Synthesis of Substrates

2.1 Method A (General procedure for 1-1g, 1i-1n)



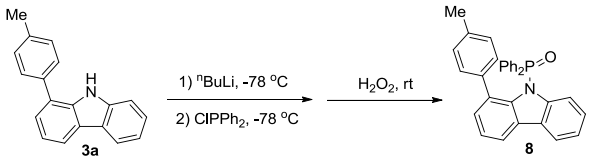
Carbazole (10 mmol) was dissolved in 20 mL of anhydrous THF under nitrogen and was cooled to -78 ℃ in a dry ice/acetone bath. n-Butyl lithium (5 mL, 12.0 mmol, 2.4 M in hexane) was then added dropwise to give a bright yellow solution that was thickened to form a slurry. After reaction for 1 h at -78 ℃, dichlorophenylphosphine (2.3 mL, 13.0 mmol) was added into. The mixture was stirred at -78 ℃ for 1 h and then at room temperature overnight. The reaction was quenched with water (10 mL), and extracted with dichloromethane (3×30 mL). The organic layers were collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL). Hydrogen peroxide (30%, 20 mL) was added into, and the reaction mixture was stirred overnight. The reaction was washed with saturated $NaHSO_3$ solution and extracted with dichloromethane (3×30 mL). The organic layer was dried with anhydrous Na_2SO_4 and purified by column chromatography on silica gel (n-Hexane:EtOAc =1:1) to give the product.

2.2 Method B (General procedure for 1h)



3,6-dibromo-9H-carbazole (10 mmol) was dissolved in 20 mL of anhydrous THF under nitrogen and was cooled to 0 ℃. NaH (1.2 equiv, 60% dispersion in mineral oil) was added portion wise at the same temperature under constant nitrogen pressure. After that it was allowed to warm to rt, and stirred at the same condition for 2 hours. Subsequently, dichlorophenylphosphine was added into. The mixture was stirred at room temperature overnight. The reaction was quenched with water (10 mL), and extracted with dichloromethane (3×30 mL). The organic layers were collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL). Hydrogen peroxide (30%, 20 mL) was added into, and the reaction mixture was stirred overnight. The reaction was washed with saturated $NaHSO_3$ solution and extracted with dichloromethane (3×30 mL). The organic layer was dried with anhydrous Na_2SO_4 and purified by column chromatography on silica gel (n-Hexane:EtOAc =1:1) to give the 1h.

2.3 Synthesis of intermediate product 8



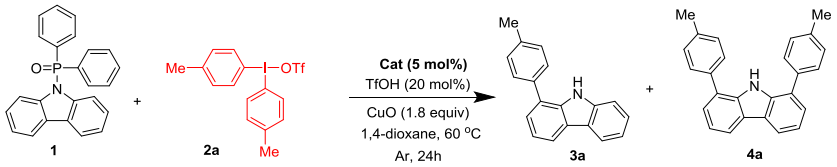
1-(p-tolyl)-9H-carbazole (3 mmol) was dissolved in 5 mL of anhydrous THF under nitrogen and was cooled to -78 ℃ in a dry ice/acetone bath. n-Butyl lithium (1.5 mL, 3.6 mmol, 2.4 M in hexane) was then added dropwise to give a bright yellow solution that was thickened to form a slurry. After reaction for 1 h at -78 ℃, dichlorophenylphosphine (0.7 mL, 3.9 mmol) was added into. The mixture was stirred at -78 ℃ for 1 h and then at room temperature overnight. The reaction was quenched with water (10 mL), and extracted with dichloromethane (3×30 mL). The organic layers were collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL). Hydrogen peroxide (30%, 20 mL) was added into, and the reaction mixture was stirred overnight. The reaction was washed with saturated $NaHSO_3$ solution and extracted with dichloromethane (3×30 mL). The organic layer was dried with anhydrous Na_2SO_4 and purified by column chromatography on silica gel (n-Hexane:EtOAc =1:1) to give the product.

2.4 Synthesis of asymmetric diaryliodonium salts and other symmetric diaryliodonium

Asymmetric diaryliodonium salts were synthesized according to corresponding literatures[11].

3. Screening of reaction conditions

Table S1. Catalyst screening [a]

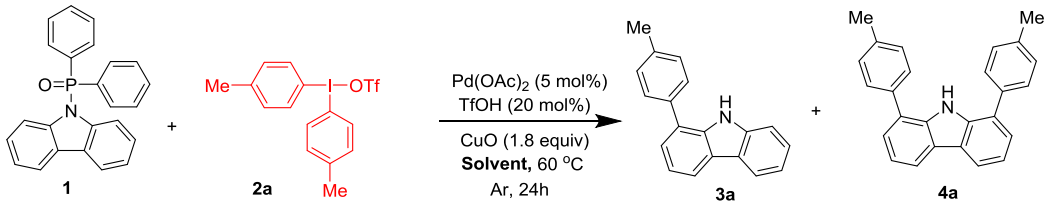


Entry	Cat.	Yield (3a) [b]	3a:4a [c]
1	$Pd(OAc)_2$	62%	12:1
2	$Pd(TFA)_2$	54%	>20:1
3	$Pd(acac)_2$	42%	>20:1
4	$Pd(PPh_3)_2Cl_2$	N.R.	-
5	$Pd_2(dba)_3$	N.R.	-
6	$Pd(dppf)Cl_2$	N.R.	-
7	$Pd(NO_3)_2$	N.R.	-
8	-	N.R.	-
9	Cp^*IrCl_2	N.R.	-
10	Cp^*RhCl_2	N.R.	-
11	$Ni(OTf)_2$	N.R.	-
12	$Fe(OTf)_2$	N.R.	-
13	$Co(acac)_2$	N.R.	-

[a] Reaction conditions:**1** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), cat (5 mol%), TfOH (20 mol%), CuO (1.8 equiv)

in 1,4-dioxane (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR.

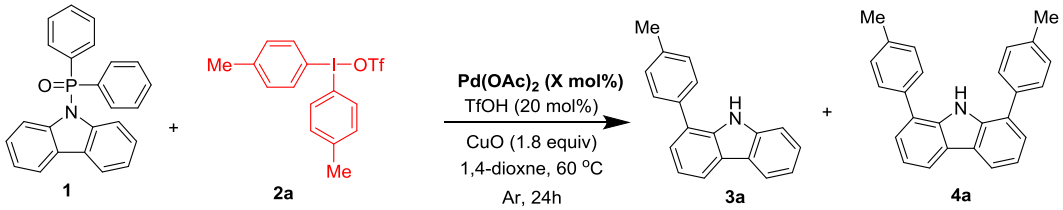
Table S2. Solvent screening [a]



Entry	Solvent	Yield (3a) [b]	3a:4a [c]
1	DCE	52%	13:1
2	Toluene	48%	>20:1
3	CH_3CN	N.R.	-
4	DME	N.R.	-
5	THF	N.R.	-
6	DMF	N.R.	-
7	CF_3CH_2OH	N.R.	-

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (5 mol%), TfOH (20 mol%), CuO (1.8 equiv) in solvent (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR.

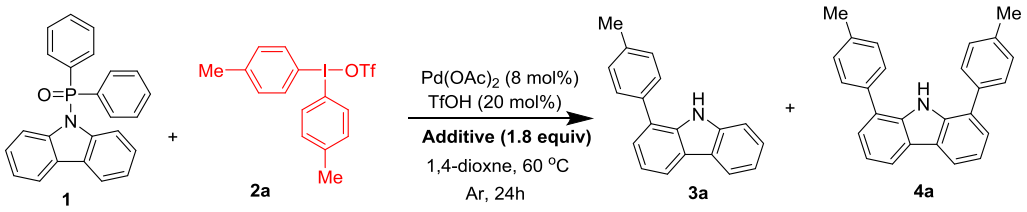
Table S3. The amount of $Pd(OAc)_2$ screening [a]



Entry	X mol%	Yield (3a) [b]	3a:4a [c]
1	2	48%	>20:1
2	8	72%	8:1
3	10	70%	8:1
4	15	66%	10:1
5	20	68%	10:1

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (X mol%), TfOH (20 mol%), CuO (1.8 equiv) in 1,4-dioxane (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR.

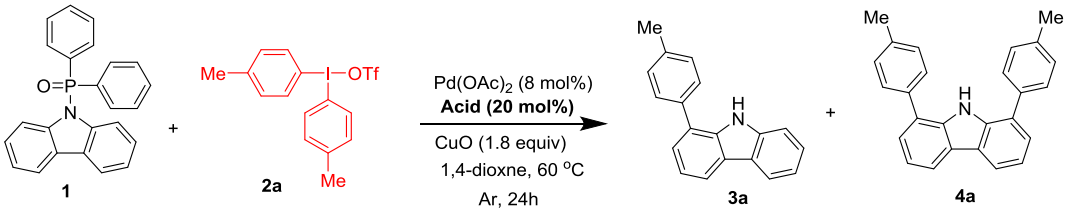
Table S4. Additive screening [a]



Entry	Additive	Yield (3a) [b]	3a:4a [c]
1	$Cu(OTf)_2$	62%	13:1
2	CuCl	N.R.	7:1
3	$Cu(OAc)_2$	N.R.	8:1
4	Cu_2O	N.R.	10:1
5	$Cu(TFA)_2$	N.R.	5:1
6	CuI	44%	18:1
7	Ag_2O	N.R.	4:1
8	oxone	30%	>20:1

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (8 mol%), TfOH (20 mol%), Additive (1.8 equiv) in 1,4-dioxane (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR.

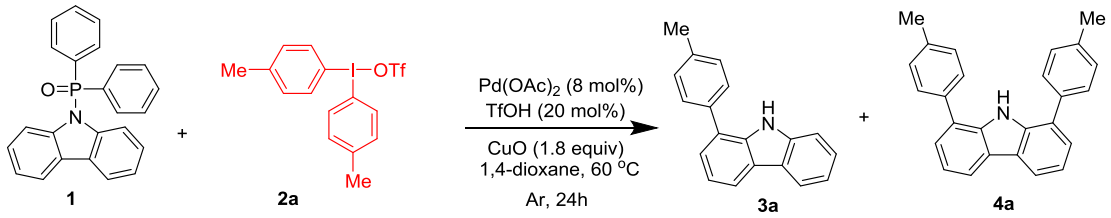
Table S5. Acid screening [a]



Entry	Acid	Yield (3a) [b]	3a:4a [c]
1	PivOH	32%	15:1
2	AcOH	68%	10:1
3	1-AdCOOH	66%	10:1
4	CF_3COOH	trace	-
5	TMBA [d]	60%	12:1
6	TfOH	72%	8:1

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (8 mol%), Acid (20 mol%), CuO (1.8 equiv) in 1,4-dioxane (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR. d TMBA = 2, 4, 6 – trimethylbenzoic acid

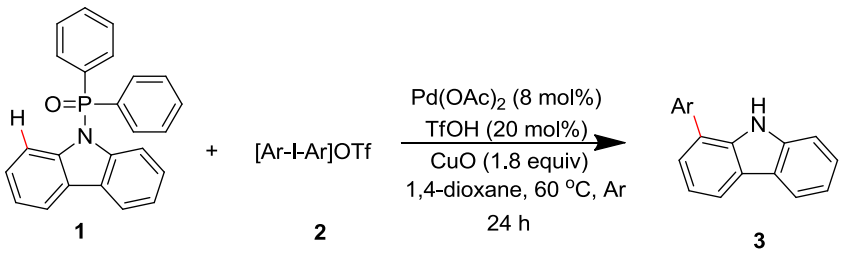
Table S6. Selection of reactant ratio [a].



Entry	1:2a	Yield (3a) [b]	3a:4a [c]
1	1:1	40%	>20:1
2	1:1.3	76%	7:1
3	1:1.5	72%	6:1
4	1:1.6	72%	5:1
5	**1:1.7**	**83%**	**5:1**
6	1:1.8	74%	4.5:1
7	1:1.9	76%	4:1
8	1:2	72%	4:1

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (X mmol,), $Pd(OAc)_2$ (8 mol%), TfOH (20 mol%), CuO (1.8 equiv) in 1,4-dioxane (0.05M) for 24h at 60 °C under Ar. [b] Isolated yield of only 3a. [c] Ratio of **3a**, **4a** was determined using ^{1}HNMR.

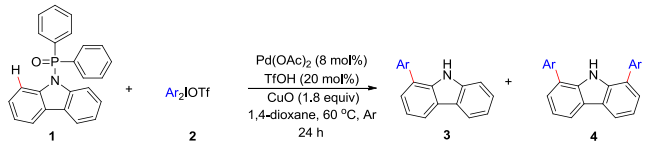
4. General Procedures for the Synthesis of Arylation Products

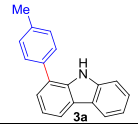
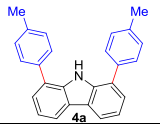
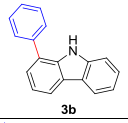
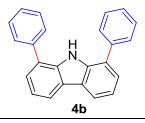
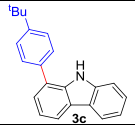
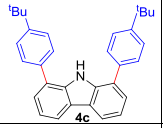
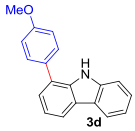
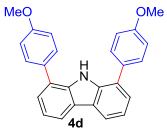
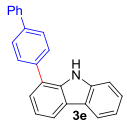
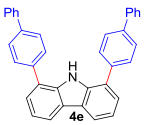
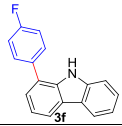
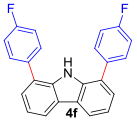
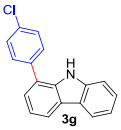
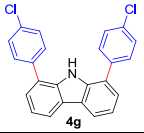
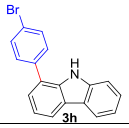
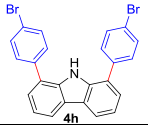
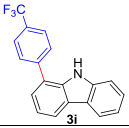
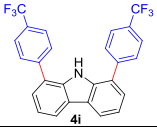
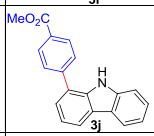
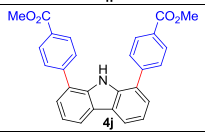
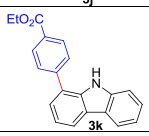
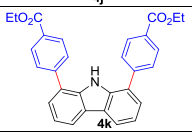
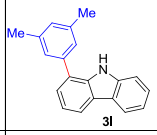
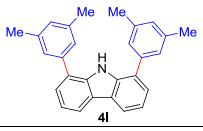
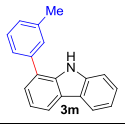
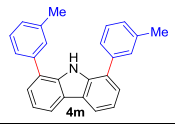


In a Schlenk-tube containing a magnetic stir bar, palladium(II) acetate (8 mol%), copper(II) oxide (0.18 mmol), diaryliodonium salts **2** (0.17 mmol) and (9H-carbazol-9-yl)diphenylphosphine oxide **1** (0.1 mmol) were added. Trifluoromethanesulfonic acid (1.8 u L, 0.02 mmol) in dried 1,4-dioxane (2 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC. The solution was then cooled to rt, and the solvent was removed under vaccum directly. The crude product was purified by silica gel column chromatography (Petroleum ether / Ethyl acetate) to afford pure product.

5. Scope of hypervalent iodine for arylation and carbazole - P source

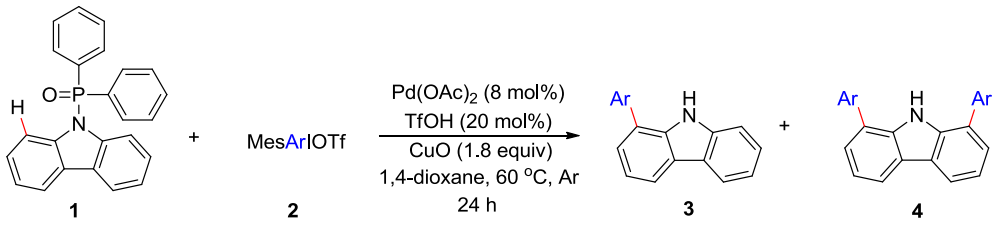
Table S1: Scope of symmetric diaryliodonium salts

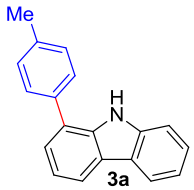
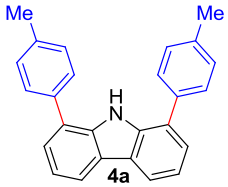
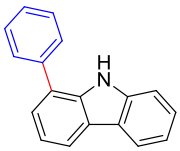
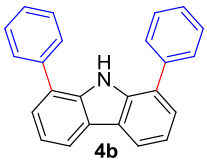
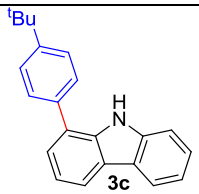
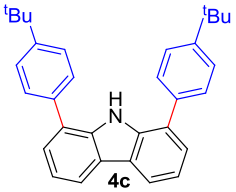
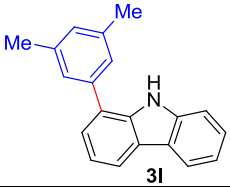
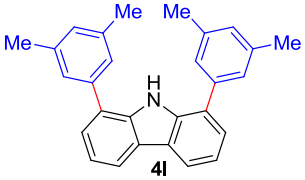
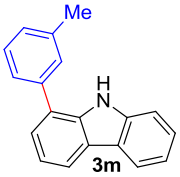
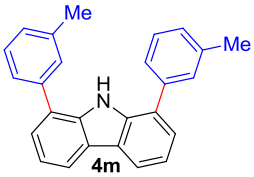


Entry	Monoarylation product **3**	Diarylation product **4**	Total Yield [b]	Ratio of **3:4** [c]
1			99%	5:1
2			75%	18:1
3			77%	6:1
4			78%	2.3:1
5			86%	8:1
6			56%	>20:1
7			35%	>20:1
8			31%	>20:1
9			48%	>20:1
10			43%	>20:1
11			34%	>20:1
12			69%	11:1
13			88%	8:1

[a] Reaction condition 1a (0.1 mmol), 2 (0.17 mmol), $Pd(OAc)_2$ (8 mol%), TfOH (20 mol%), and CuO (1.8 mmol) in 2 mL of 1,4-dioxane at 60 °C for 24 h. [b] Total yield of 3 and 4. [c] ratio of 3,4 was determined using ^1H NMR.

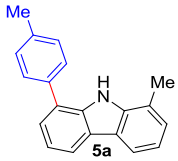
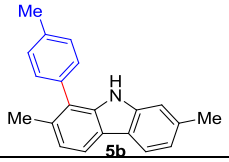
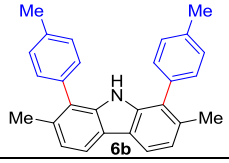
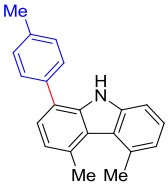
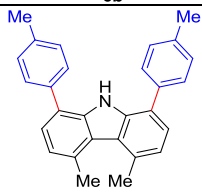
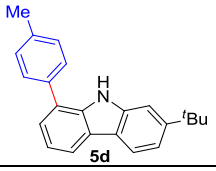
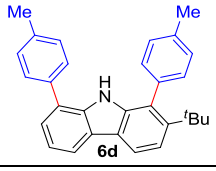
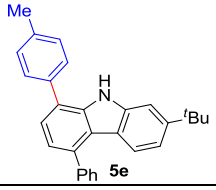
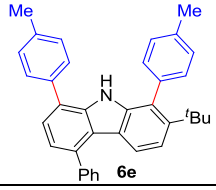
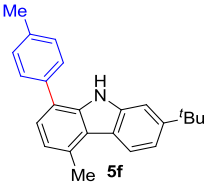
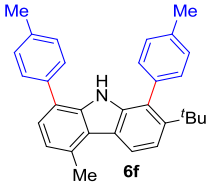
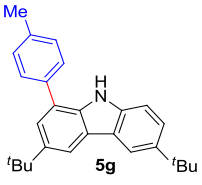
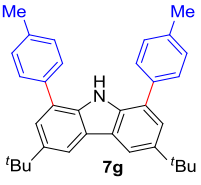
Table S2: Scope of asymmetric diaryliodonium salts

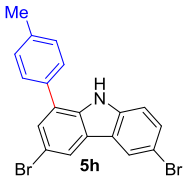
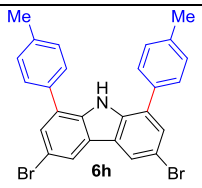
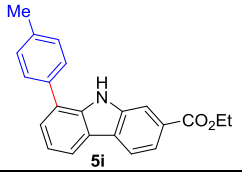
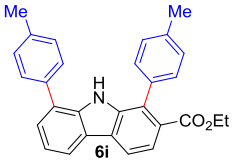
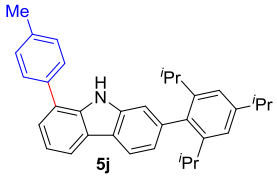
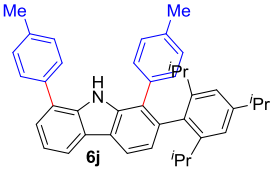
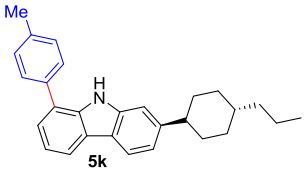
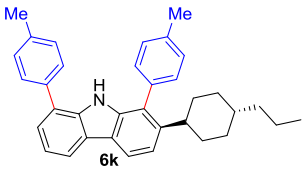
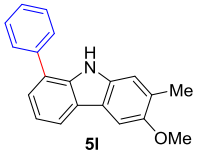
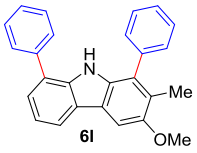
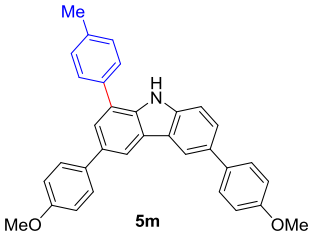
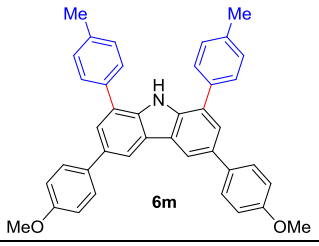
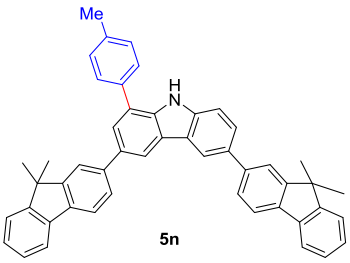
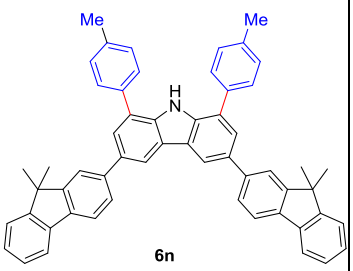


Entry	Monoarylation product **3**	Diarylation product **4**	Total Yield [b]	Ratio of **3:4** [c]
1	 **3a**	 **4a**	98%	4:1
2	 **3b**	 **4b**	51%	>20:1
3	 **3c**	 **4c**	94%	5:1
4	 **3l**	 **4l**	82%	10:1
5	 **3m**	 **4m**	70%	12:1

[a] Reaction condition **1a** (0.1 mmol), **2** (0.17 mmol), $Pd(OAc)_2$ (8 mol%), TfOH (20 mol%), and CuO (1.8 mmol) in 2 mL of 1,4-dioxane at 60 °C for 24 h. [b] Toatal yield of **3** and **4**. [c] ratio of **3**,**4** was determined using ^1H NMR.

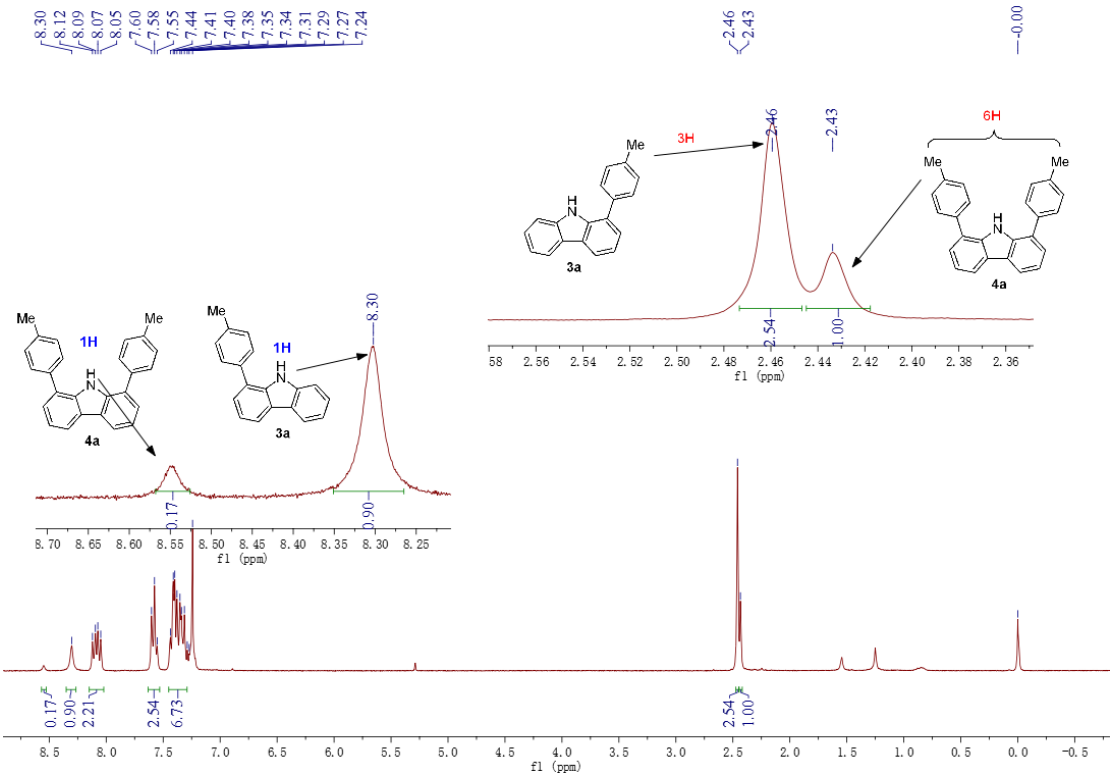
Table S3: Scope of carbazole – P source

Entry	Monoarylation product **5**	Diarylation product **6**	Total Yield [b]	Ratio of **5:6** [c]
1	 **5a**		56%	>20:1
2	 **5b**	 **6b**	50%	>20:1
3	 **5c**	 **6c**	68%	>20:1
4	 **5d**	 **6d**	90%	>20:1
5	 **5e**	 **6e**	81%	>20:1
6	 **5f**	 **6f**	92%	>20:1
7	 **5g**	 **7g**	90%	>20:1

Entry	Monoarylation product **5**	Diarylation product **6**	Total Yield [b]	Ratio of **5:6** [c]
8	 **5h**	 **6h**	38%	>20:1
9	 **5i**	 **6i**	45%	>20:1
10	 **5j**	 **6j**	80%	>20:1
11	 **5k**	 **6k**	96%	>20:1
12[d]	 **5l**	 **6l**	30%	>20:1
13	 **5m**	 **6m**	62%	>20:1
14	 **5n**	 **6n**	42%	>20:1

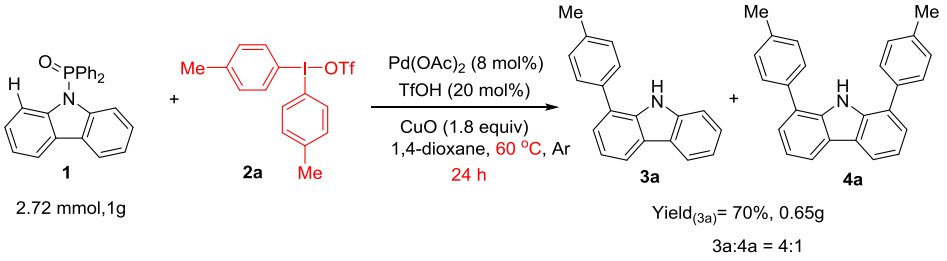
[a] Reaction condition **1a-1n** (0.1 mmol), **2** (0.17 mmol), $Pd(OAc)_2$ (8 mol%), TfOH (20 mol%), and CuO (1.8 mmol) in 2 mL of 1,4-dioxane at 60 °C for 24 h. [b] Isolated yield of **6** and **7.** [c] ratio of **6**,**7** was determined using ^1H NMR. [d] using Ph_2IOTf.

S4:[1]H NMR determining of the ratio of 3a and 4a.



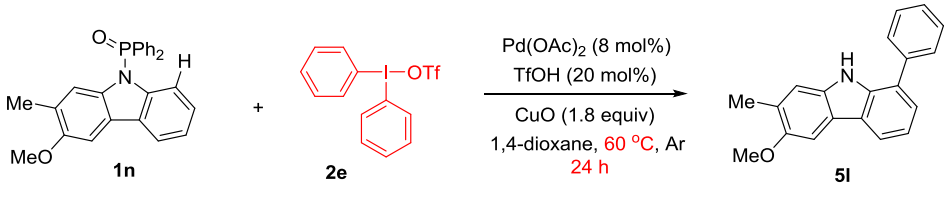
6. Gram-Scale Experiment and Derivatization

6.1 Gram-Scale Experiment



In a 100 mL Schlenk-tube containing a magnetic stir bar**,** palladium(II) acetate (8 mol %), copper(II) oxide (1.8 equiv), diaryliodonium salts **2a** (4.62 mmol) and (9H-carbazol-9-yl)diphenylphosphine oxide **1** (2.72 mmol) were added. Trifluoromethanesulfonic acid (20 mol%) in dried 1,4-dioxane (54 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC. The solution was then cooled to rt, and the solvent was removed under vaccum directly. The crude product was purified by silica gel column chromatography (Petroleum ether / Ethyl acetate = 50:1) to afford pure product 3a (0.65g,70%).

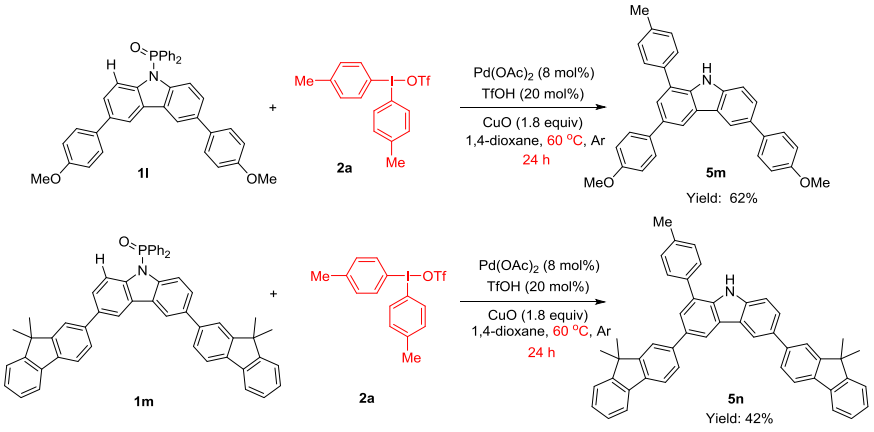
6.2Synthesis of Hyellazole analogue



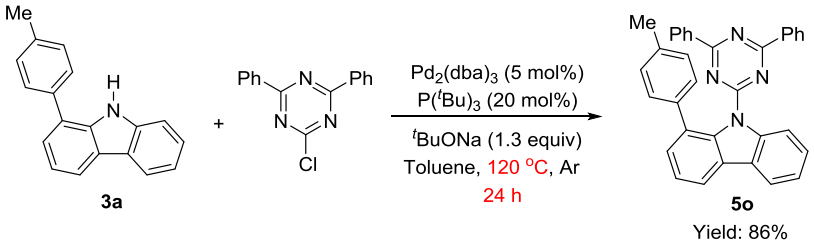
In a Schlenk-tube containing a magnetic stir bar, palladium(II) acetate (8 mol %), copper(II) oxide (0.18 mmol), diaryliodonium salts **2e** (0.17 mmol) and (3-methoxy-2-methyl-9H-carbazol-9-yl)diphenylphosphine oxide **1n** (0.1mmol) were added. Trifluoromethanesulfonic acid (0.02 mmol) in dried 1,4-dioxane (2 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 24 h as monitored by TLC. The solution was then cooled to rt, and the solvent was removed under vaccum directly. The crude product was purified by silica gel column chromatography (Petroleum ether / Ethyl acetate = 8:1) to afford pure product 5l (30%).

6.3 Modification of carbazole-based poly(aryl ethers) and carbazole fluorescent oligomers

Synthesis of 5m and 5n was followed General procedure for the synthesis of arylation product.



6.4 Synthesis of potential materials for organic light-emitting diodes



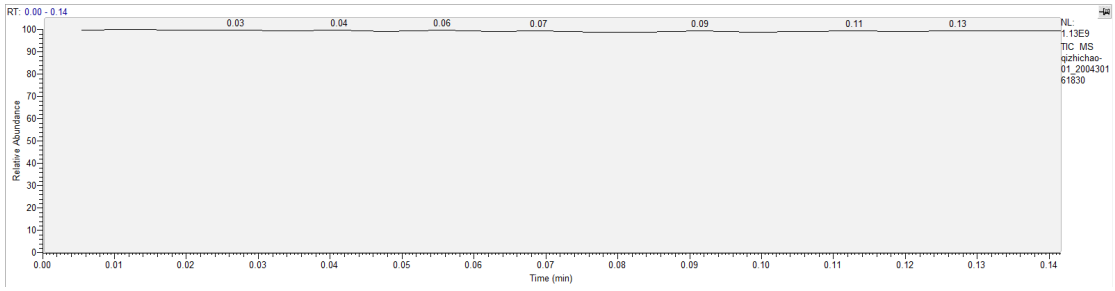
3a (0.257 g, 1 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (0.347g, 1.3 mmol), ^{t}BuONa(0.192g, 2 mmol), P(t-bu)$_3$ (0.2 mmol) and $Pd_2(dba)_3$ (0.046g, 0.05mmol) were dissolved in toluene (20 mL) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using DCM/n-hexane. The product was obtained as white solid (86%).

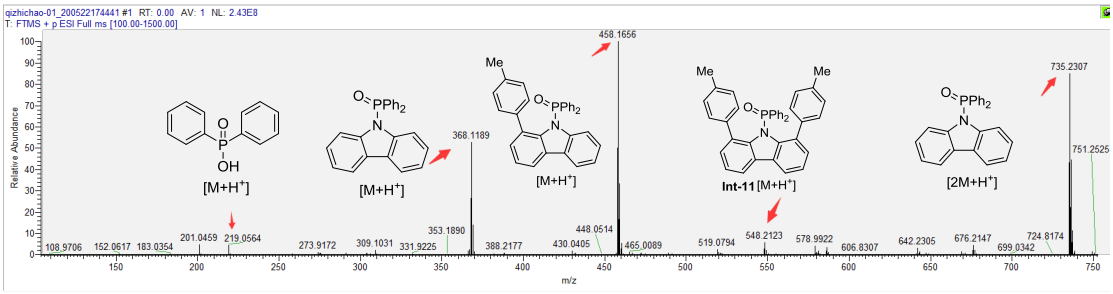
7. Investigation of the Reaction Mechanism

7.1. Analytical data of ESI-MS

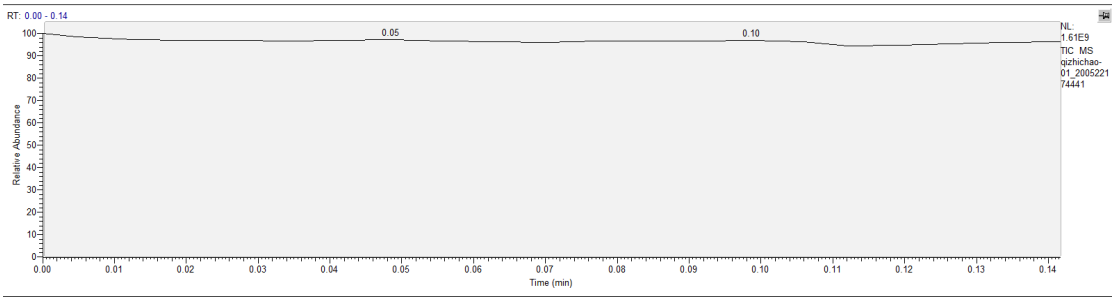
In a Schlenk-tube containing a magnetic stir bar, palladium(II) acetate (1.6mg, 8 mol %), copper(II) oxide (14.4mg, 0.18 mmol), diaryliodonium salts **2a** (77.8mg, 0.17 mmol) and (9H-carbazol-9-yl)diphenylphosphine oxide **1** (39.5mg, 0.1mmol) were added. Trifluoromethanesulfonic acid (1.8 u L,0.02 mmol) in dried 1,4-dioxane (2 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 10 min, 2 h and 24 h. The reaction was cooled to room temperature and diluted with CH_3CN (1/100) prior to the injection into the mass spectrometer.

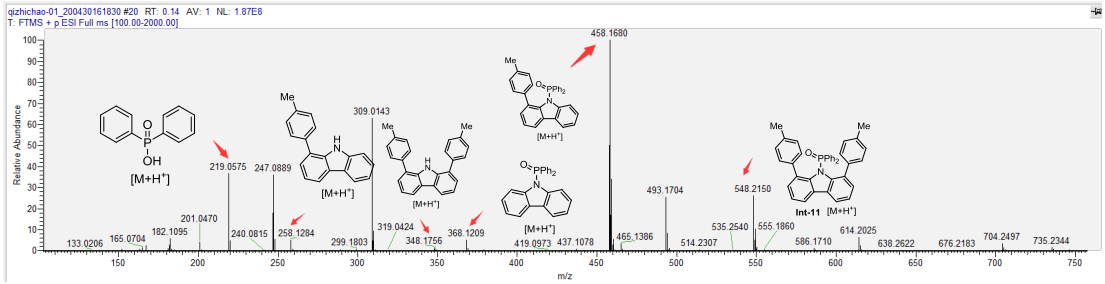
1.Reaction time is 10 min



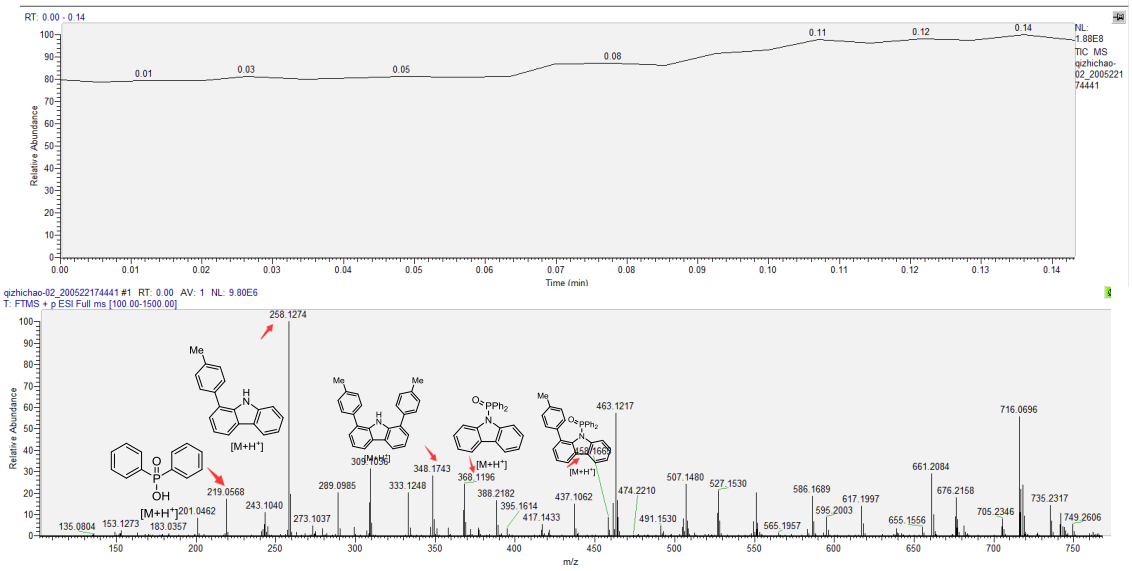


2. Reaction time is 2 h

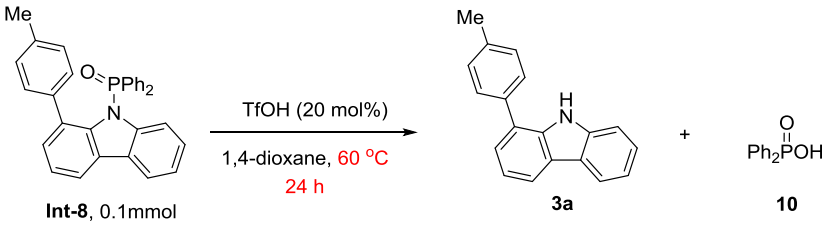




3.Reaction time is 24 h

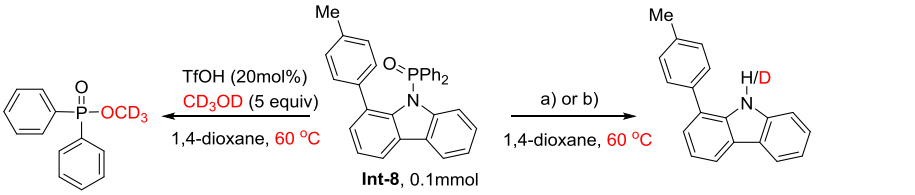


7.2. Control experiment



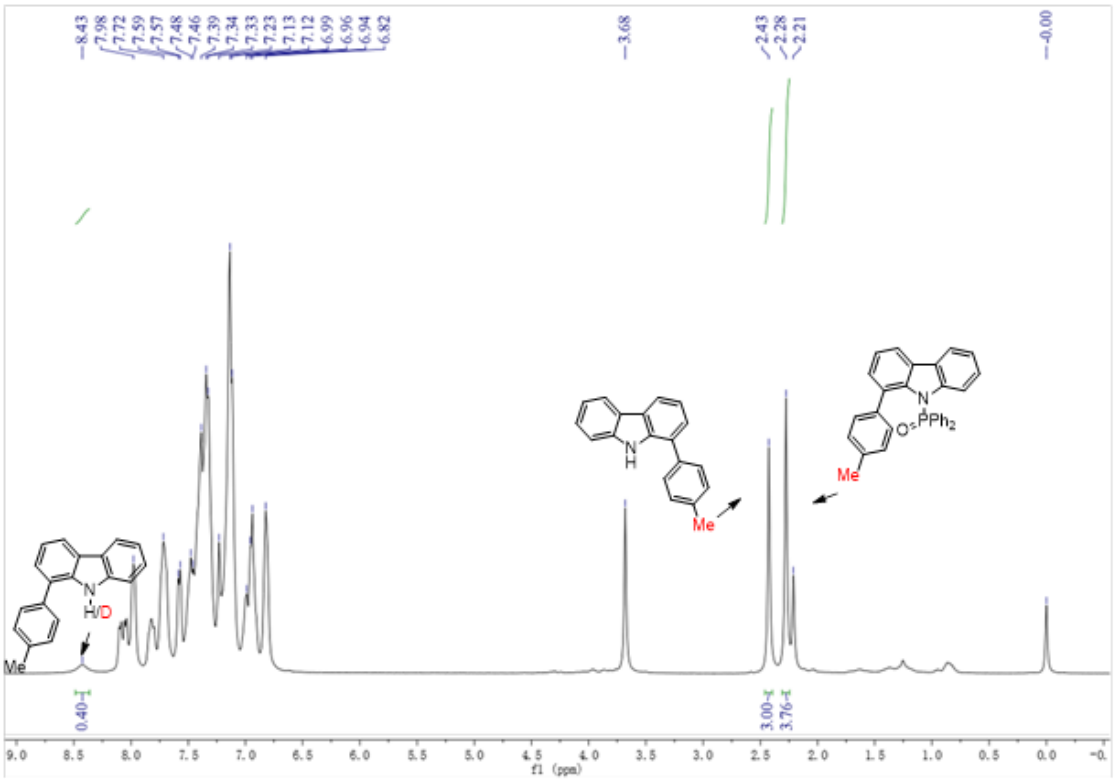
In a Schlenk-tube containing a magnetic stir bar, diphenyl(1-(p-tolyl)-9H-carbazol-9-yl)phosphine oxide (0.1mmol) was added. Trifluoromethanesulfonic acid (1.8 u L, 0.02 mmol) in dried 1,4-dioxane (2 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 24 h. The reaction was cooled to room temperature and the solvent was removed under vaccum directly. The crude product was purified by silica gel column chromatography (Petroleum ether / Ethyl acetate = 50:1) to afford pure product 3a (Yield: 89%) and obtain pure product 10 (Yield: 65%, PE : MeOH = 10:1).

Deuterium experiments

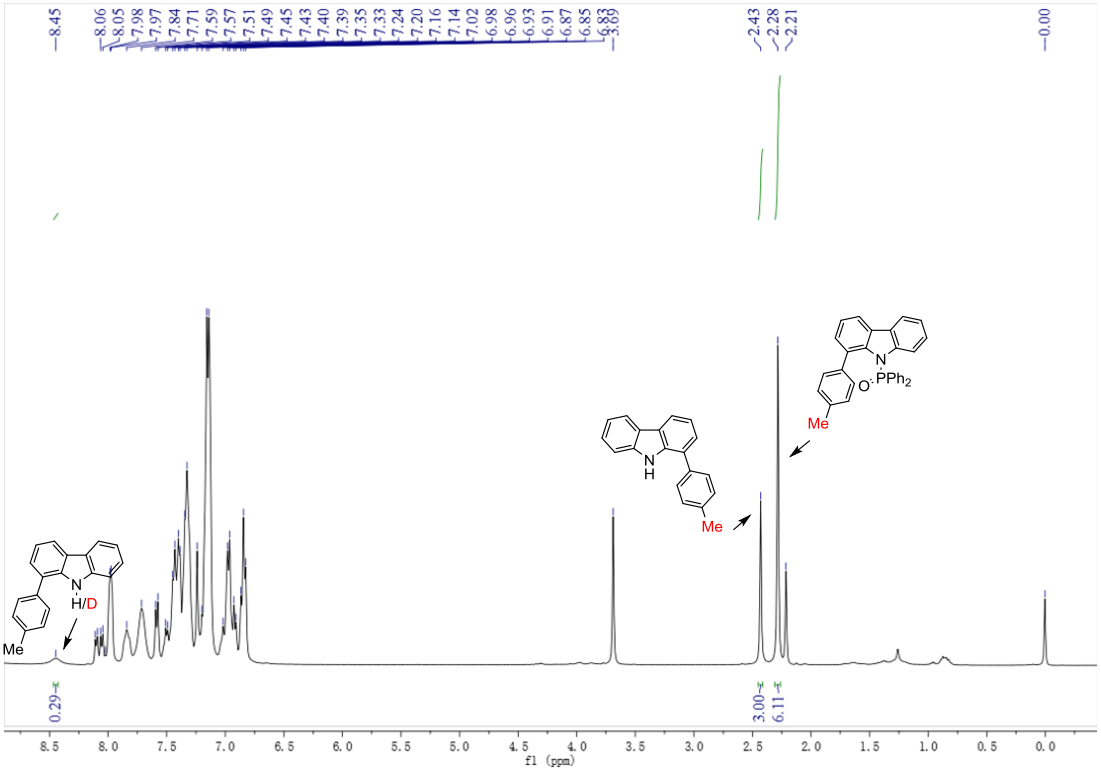


In a Schlenk-tube containing a magnetic stir bar, diphenyl(1-(p-tolyl)-9H-carbazol-9-yl)phosphine oxide (0.1 mmol) was added. (a) TfOH and D_2O, (b) TfOD and D_2O, (c) TfOH and CD_3OD in dried 1,4-dioxane (2 mL) was added to the reaction mixture. The reaction mixture was stirred at 60 °C under Ar for 24 h. After the reaction was complete, the reaction mixture was concentrated in vacuo, and deuterium incorporation ratio was determined by ^1H NMR spectroscopy using $CDCl_3$ as a solvent. 64% and 70% deuteration on the N-position of 3a was observed. When CD_3OD was used in the reaction, 100% deuteration of methyl diphenylphosphinate was observed.

(a) ^{1}H NMR (TfOH + D_2O)

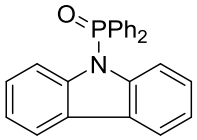


(b) ^{1}H NMR (TfOD + D_2O)



8. Characterization Data of Substrates

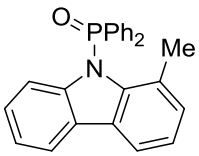
(9H-carbazol-9-yl)diphenylphosphine oxide (1)



1

According to the literature[3]

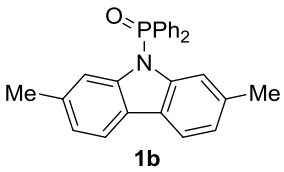
(1-methyl-9H-carbazol-9-yl)diphenylphosphine oxide (1a)



1a

According to the method A**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1a as white solid (m.p.=154-157 °C, 81% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 12.8, 8.1 Hz, 4H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.39 (dt, *J* = 10.5, 5.3 Hz, 4H), 7.24 (dd, *J* = 8.6, 6.4 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.86 (dd, *J* = 8.2, 7.4 Hz, 1H), 6.43 – 6.36 (m, 1H), 2.45 (d, *J* = 1.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.62 (s), 142.40 (s), 133.22 (s), 132.55 (s), 132.28 (d, *J* = 10.3 Hz), 131.96 (s), 130.16 (s), 128.74 (d, *J* = 13.5 Hz), 128.11 (d, *J* = 4.3 Hz), 127.46 (d, *J* = 5.3 Hz), 126.60 (s), 125.05 (s), 123.04 (s), 121.99 (s), 119.67 (s), 117.22 (s), 116.23 (s), 22.41 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.31 (s) ppm. **GRMS** Calculated for $C_{25}H_{20}NOP$, $[M+H]^+$:382.1355, found: 382.1196.

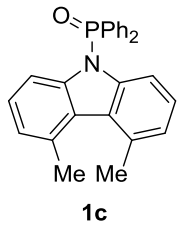
(2,7-dimethyl-9H-carbazol-9-yl)diphenylphosphine oxide (1b)



1b

According to the method A**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1b as white solid (m.p.=190-192 °C, 76% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.82 (s, 1H), 7.76 – 7.69 (m, 4H), 7.61 (d, *J* = 1.6 Hz, 2H), 7.48 (dt, *J* = 7.5, 3.8 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.01 (s, 2H), 2.26 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.11 (d, *J* = 3.6 Hz), 135.86 (s), 133.05 (d, *J* = 2.9 Hz), 132.21 (d, *J* = 10.9 Hz), 131.73 (s), 130.48 (s), 129.02 (d, *J* = 13.4 Hz), 124.19 (d, *J* = 5.8 Hz), 123.21 (s), 119.17 (s), 115.29 (s), 22.10 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.25 (s). **GRMS** Calculated for $C_{26}H_{22}NOP$, $[M+H]^+$:396.1512, found: 396.1085**.**

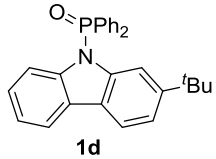
(4,5-dimethyl-9H-carbazol-9-yl)diphenylphosphine oxide (1c)



1c

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1c as grey solid (m.p.=180-183 °C, 78% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 13.1, 8.2 Hz, 4H), 7.59 (td, *J* = 7.4, 1.4 Hz, 2H), 7.46 (td, *J* = 7.6, 3.5 Hz, 5H), 7.37 (dd, *J* = 6.9, 2.3 Hz, 2H), 7.07 – 7.04 (m, 3H), 2.94 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.55 (d, *J* = 3.4 Hz), 132.96 (d, *J* = 2.9 Hz), 132.04 (d, *J* = 10.8 Hz), 131.86 (s), 130.62 (s), 129.00 (d, *J* = 13.5 Hz), 126.09 (d, *J* = 5.3 Hz), 125.55 (d, *J* = 19.5 Hz), 112.83 (s), 26.31 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.67 (s) ppm. **GRMS** Calculated for $C_{26}H_{22}NOP$, $[M+H]^+$:396.1512, found: 396.1129.

(2-(tert-butyl)-9H-carbazol-9-yl)diphenylphosphine oxide (1d)

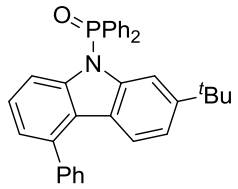


1d

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1d as white solid (m.p.=210-212 °C, 86% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 13.0, 8.0 Hz, 4H), 7.67 – 7.57 (m, 3H), 7.49 (dt, *J* = 7.4, 3.7 Hz, 4H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 9.4, 8.1 Hz, 2H), 7.00 (s, 1H), 1.11 (d, *J* = 0.9 Hz, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.71 (s), 142.18 (s), 141.70 (s), 133.03 (d, *J* = 2.9 Hz), 132.17 (d, *J* = 10.8 Hz), 131.88 (s), 130.63

(s), 129.05 (d, *J* = 13.4 Hz), 126.31 (s), 125.94 (s), 124.15 (d, *J* = 5.9 Hz), 121.92 (s), 119.55 (s), 119.28 (s), 115.51 (s), 111.74 (s), 35.05 (s), 31.45 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.27 (s) ppm. **GRMS** Calculated for $C_{28}H_{26}NOP$, $[M+H]^+$:424.1825, found: 424.1365.

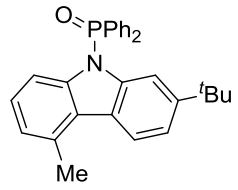
(2-(tert-butyl)-5-phenyl-9H-carbazol-9-yl)diphenylphosphine oxide (1e)



1e

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1e as pale yellow solid (m.p.=142-144 °C, 82% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 8.6, 5.8, 4.4 Hz, 5H), 7.65 – 7.59 (m, 2H), 7.56 – 7.47 (m, 9H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.02 – 6.99 (m, 2H), 1.03 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.30 (s), 142.48 (d, *J* = 3.8 Hz), 141.90 (s), 141.00 (s), 137.10 (s), 133.05 (d, *J* = 2.9 Hz), 132.16 (d, *J* = 10.8 Hz), 131.91 (s), 130.65 (s), 129.19 (d, *J* = 8.6 Hz), 129.01 (s), 128.44 (s), 127.59 (s), 125.49 (s), 123.78 (dd, *J* = 9.8, 5.6 Hz), 123.52 (s), 121.55 (s), 119.04 (s), 114.47 (s), 111.52 (s), 34.89 (s), 31.31 (s) ppm.**^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.58 (s) ppm. **GRMS** Calculated for $C_{34}H_{30}NOP$, $[M+H]^+$:500.2138, found: 500.1738.

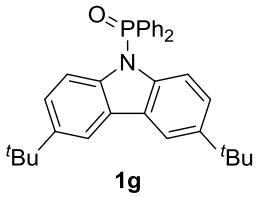
(2-(tert-butyl)-5-methyl-9H-carbazol-9-yl)diphenylphosphine oxide (1f)



1f

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1f as white solid (m.p.=128-132 °C, 72% yield).**^{1}H NMR** (400 MHz, CDCl3) δ 8.06 (d, J = 8.4 Hz, 1H), 7.76 (dd, J = 13.0, 7.8 Hz, 4H), 7.58 (ddd, J = 12.9, 9.5, 5.7 Hz, 3H), 7.47 (td, J = 7.6, 3.5 Hz, 4H), 7.32 (d, J = 8.4 Hz, 1H), 7.11 (dd, J = 10.0, 5.1 Hz, 2H), 7.03 (d, J = 7.3 Hz, 1H), 2.82 (s, 3H), 1.15 – 1.09 (m, 9H) ppm. **^{13}C NMR** (101 MHz, CDCl3) δ 148.88 (s), 142.27 (d, J = 3.9 Hz), 141.79 (s), 132.98 (d, J = 2.9 Hz), 132.59 (s), 132.15 (d, J = 10.8 Hz), 132.00 (s), 130.75 (s), 129.03 (d, J = 13.4 Hz), 125.58 (s), 124.88 (d, J = 5.8 Hz), 124.67 (d, J = 5.8 Hz), 123.62 (s), 121.85 (s), 119.37 (s), 113.07 (s), 111.71 (s), 34.95 (s), 31.43 (s), 21.04 (s) ppm. **^{31}P NMR** (162 MHz, CDCl3) δ 25.39 (s) ppm. **GRMS** Calculated for C29H28NOP, [M+H]+ :438.1981, found: 438.1526.

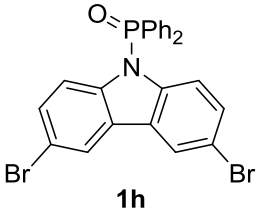
(3,6-di-tert-butyl-9H-carbazol-9-yl)diphenylphosphine oxide (1g)



1g

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1g as grey solid (m.p.=246-249 °C, 91% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.74 (dd, *J* = 13.0, 7.3 Hz, 4H), 7.61 (t, *J* = 7.0 Hz, 2H), 7.48 (td, *J* = 7.6, 3.3 Hz, 4H), 7.22 (dd, *J* = 8.8, 1.5 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 1.39 (s, 18H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.76 (s), 140.00 (d, *J* = 3.8 Hz), 132.98 (d, *J* = 2.9 Hz), 132.19 (d, *J* = 10.9 Hz), 131.83 (s), 130.58 (s), 128.98 (d, *J* = 13.4 Hz), 126.44 (d, *J* = 5.9 Hz), 123.98 (s), 115.84 (s), 114.31 (s), 34.63 (s), 31.79 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.58 (s) ppm. **GRMS** Calculated for $C_{32}H_{34}NOP$, $[M+H]^+$:480.2451, found: 480.1992.

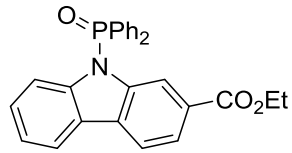
(3,6-dibromo-9H-carbazol-9-yl)diphenylphosphine oxide (1h)



1h

According to the method B**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1h as white solid (m.p.=203-205 °C, 60% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.70 (dd, *J* = 13.2, 7.6 Hz, 4H), 7.63 (dd, *J* = 7.9, 7.1 Hz, 2H), 7.49 (td, *J* = 7.7, 3.5 Hz, 4H), 7.30 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.76 (d, *J* = 3.5 Hz), 133.59 (d, *J* = 2.9 Hz), 132.01 (d, *J* = 11.0 Hz), 130.75 (s), 129.84 (s), 129.50 (s), 129.29 (d, *J* = 13.6 Hz), 127.13 (d, *J* = 5.6 Hz), 122.94 (s), 116.57 (s), 115.53 (s) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.93 (s) ppm. **GRMS** Calculated for $C_{32}H_{34}NOP$, $[M+H]^+$:523.9409, found: 523.9407.

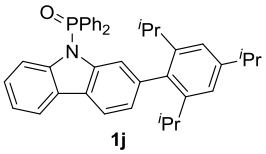
ethyl 9-(diphenylphosphoryl)-9H-carbazole-2-carboxylate (1i)



1i

According to the GP2-method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1 v/v) afforded 1i as pale yellow solid (m.p.=143-147 °C, 76% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.65 (d, *J* = 9.7 Hz, 4H), 7.55 – 7.47 (m, 4H), 7.31 (dd, *J* = 5.9, 3.1 Hz, 2H), 4.27 (d, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.60 (s), 143.16 (d, *J* = 3.6 Hz), 140.93 (d, *J* = 3.4 Hz), 133.43 (d, *J* = 2.9 Hz), 132.15 (d, *J* = 11.0 Hz), 131.02 (s), 130.29 (d, *J* = 5.6 Hz), 129.77 (s), 129.20 (d, *J* = 13.6 Hz), 128.15 (s), 127.73 (s), 125.49 (d, *J* = 5.5 Hz), 123.28 (s), 122.42 (s), 120.61 (s), 119.61 (s), 116.07 (s), 115.68 (s), 60.88 (s), 14.40 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.45 (s) ppm. **GRMS** Calculated for $C_{27}H_{22}NO_3P$, $[M+H]^+$:440.1410, found: 440.0885.

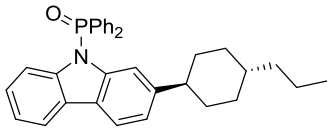
diphenyl(2-(2,4,6-triisopropylphenyl)-9H-carbazol-9-yl)phosphine oxide (1j)



1j

According to the method A**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1 v/v) afforded 1j as white solid (m.p.=236-240 °C, 65% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 6.9 Hz, 2H), 7.72 (dd, *J* = 13.0, 7.2 Hz, 4H), 7.55 (dd, *J* = 7.5, 6.3 Hz, 2H), 7.47 – 7.39 (m, 5H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.13 (s, 1H), 7.08 (s, 1H), 6.96 (s, 2H), 2.96 – 2.84 (m, 1H), 2.43 – 2.33 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 6H), 0.99 (d, *J* = 6.9 Hz, 6H), 0.84 (d, *J* = 6.9 Hz, 6H) ppm . **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.75 (s), 146.46 (s), 142.29 (d, *J* = 3.4 Hz), 141.38 (s), 139.14 (s), 137.10 (s), 133.03 (d, *J* = 2.9 Hz), 132.06 (d, *J* = 10.9 Hz), 131.55 (s), 130.30 (s), 126.36 (d, *J* = 8.5 Hz), 124.95 (d, *J* = 5.8 Hz), 124.23 (s), 122.07 (s), 120.28 (s), 119.70 (s), 119.23 (s), 116.41 (s), 115.22 (s), 34.24 (s), 30.17 (s), 24.22 (s), 24.15 (s), 24.09 (s) ppm.**^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.33 (s) ppm. **GRMS** Calculated for $C_{39}H_{40}NOP$, $[M+H]^+$:570.2920, found: 570.2398.

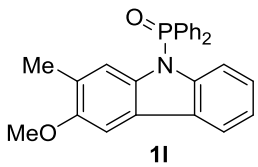
diphenyl(2-((1s,4r)-4-propylcyclohexyl)-9H-carbazol-9-yl)phosphine oxide (1k)



1k

According to the method A**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1k as white solid (m.p.=170-172 °C, 72% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.74 (dd, *J* = 13.0, 7.2 Hz, 4H), 7.63 – 7.56 (m, 2H), 7.47 (td, *J* = 7.6, 3.5 Hz, 4H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.18 – 7.08 (m, 2H), 6.98 (s, 1H), 2.38 (tt, *J* = 11.9, 3.0 Hz, 1H), 1.75 (dd, *J* = 23.9, 12.6 Hz, 4H), 1.33 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.24 – 1.12 (m, 5H), 0.96 (d, *J* = 12.8 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.62 (s), 142.08 (d, *J* = 3.4 Hz), 141.82 (d, *J* = 3.8 Hz), 133.01 (d, *J* = 2.9 Hz), 132.20 (d, *J* = 10.8 Hz), 131.82 (s), 130.56 (s), 129.03 (d, *J* = 13.5 Hz), 126.55 (d, *J* = 5.8 Hz), 125.78 (s), 124.50 (d, *J* = 5.8 Hz), 121.86 (s), 121.37 (s), 119.51 (d, *J* = 7.3 Hz), 115.18 (s), 113.04 (s), 44.98 (s), 39.69 (s), 37.02 (s), 34.43 (s), 33.54 (s), 20.06 (s), 14.43 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.74 (s) ppm. **GRMS** Calculated for $C_{33}H_{34}NOP$, $[M+H]^+$:492.2451, found: 492.2211.

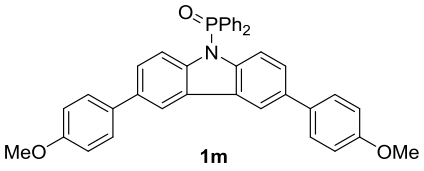
(3-methoxy-2-methyl-9H-carbazol-9-yl)diphenylphosphine oxide (1l)



1l

According to the method A**,** purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1 v/v) afforded 1l as pale yellow solid (m.p.=152-154 °C, 51% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.71 (dd, *J* = 13.0, 7.6 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.45 (td, *J* = 7.5, 3.3 Hz, 4H), 7.38 (s, 1H), 7.20 (dd, *J* = 14.5, 7.5 Hz, 2H), 7.10 (dd, *J* = 11.4, 4.0 Hz, 1H), 7.06 (s, 1H), 3.89 (s, 3H), 2.15 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.00 (s), 141.74 (d, *J* = 3.6 Hz), 135.94 (d, *J* = 3.6 Hz), 133.12 (d, *J* = 2.8 Hz), 132.39 – 132.00 (m), 131.64 (s), 130.38 (s), 129.06 (d, *J* = 13.5 Hz), 126.87 (d, *J* = 6.0 Hz), 126.50 (s), 125.63 (s), 124.83 (d, *J* = 5.9 Hz), 121.67 (s), 119.44 (s), 116.82 (s), 114.98 (s), 100.21 (s), 55.70 (s), 17.43 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.20 (s) ppm. **GRMS** Calculated for $C_{26}H_{22}NO_2P$, $[M+H]^+$:412.1461, found: 412.1033.

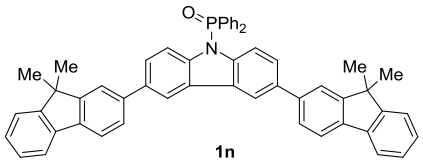
(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)diphenylphosphine oxide (1m)



1m

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1 v/v) afforded 1m as pink solid (m.p.=237-239 °C, 62% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.83 – 7.74 (m, 4H), 7.61 (dd, *J* = 16.7, 8.1 Hz, 6H), 7.51 (td, *J* = 7.6, 3.4 Hz, 4H), 7.41 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 4H), 3.86 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.95 (s), 141.23 (s), 135.04 (s), 133.82 (s), 132.16 (d, *J* = 10.9 Hz), 131.50 (s), 130.25 (s), 129.12 (d, *J* = 13.5 Hz), 128.24 (s), 127.12 (s), 125.56 (s), 117.79 (s), 115.20 (s), 114.25 (s), 55.38 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.32 (s) ppm. **GRMS** Calculated for $C_{38}H_{30}NO_3P$, $[M+H]^+$:580.2036, found: 580.1647.

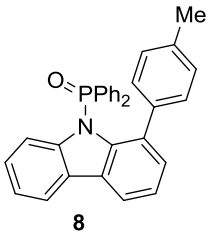
(3,6-bis(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-9-yl)diphenylphosphine oxide (1n)



1n

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 3/1 to 2/1 v/v) afforded 1n as pale yellow solid (m.p.=164-167 °C, 48% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 7.87 – 7.77 (m, 6H), 7.77 – 7.71 (m, 4H), 7.65 (t, *J* = 7.7 Hz, 4H), 7.53 (s, 6H), 7.42 (dd, *J* = 18.8, 7.7 Hz, 4H), 7.37 – 7.28 (m, 4H), 1.55 (s, 12H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.38 (s), 153.89 (s), 141.62 (d, *J* = 3.5 Hz), 140.45 (s), 138.95 (s), 138.22 (s), 135.94 (s), 133.33 (s), 132.22 (d, *J* = 10.9 Hz), 131.50 (s), 130.25 (s), 129.19 (d, *J* = 13.4 Hz), 127.34 – 126.97 (m), 126.37 (s), 126.10 (s), 122.65 (s), 121.55 (s), 120.35 (s), 120.07 (s), 118.40 (s), 115.34 (s), 47.02 (s), 27.33 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.39 (s) ppm. **GRMS** Calculated for $C_{54}H_{42}NOP$, $[M+H]^+$:752.3077, found: 752.3072.

diphenyl(1-(p-tolyl)-9H-carbazol-9-yl)phosphine oxide (8)



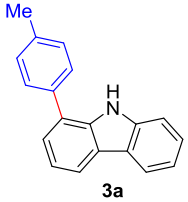
8

According to the method A, purification via silica gel column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1 v/v) afforded 8 as white solid (m.p.=216-219 °C, 80% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (td, *J* = 7.3, 1.3 Hz, 2H), 7.23 – 7.11 (m, 10H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.85 (m, 4H), 2.31 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.10 (d, *J* = 3.2 Hz), 140.45 (s), 137.65 (s), 136.14 (s), 133.15 (s), 131.93 (d, *J* = 9.5 Hz), 131.49 (d, *J* = 2.6 Hz), 131.34 (d, *J* = 9.9 Hz), 129.47 (s), 129.02 (s), 128.70 (d, *J* = 4.4 Hz), 128.38 – 128.11 (m), 127.17 (d, *J* = 4.9 Hz), 125.36 (s), 123.46 (s), 122.37 (s), 119.73 (s), 118.59 (s), 117.22 (d, *J* = 1.9 Hz), 21.21 (s) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.69 (s) ppm. GRMS Calculated for $C_{31}H_{24}NOP$, $[M+H]^+$:458.1668, found: 458.1249.

9. Characterization Data of Products

9.1 Characterization Data of Arylation Products.

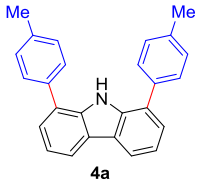
1-(p-tolyl)-9H-carbazole (3a)



3a

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3a as white solid (m.p.=129-131 °C, 83% or 78% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (brs, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.07 – 8.03 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.36 (t, *J* = 5.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.21 (m, 1H), 2.45 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.48 (s), 137.37 (s), 137.34 (s), 136.12 (s), 129.97 (s), 128.26 (s), 125.92 (s), 125.66 (s), 125.00 (s), 123.63 (s), 123.54 (s), 120.42 (s), 119.91 (s), 119.52 (s), 119.23 (s), 110.67 (s), 21.28 (s) ppm. **HRMS** Calculated for $C_{19}H_{15}N$, $[M+H]^+$:258.1277, found: 258.1277.

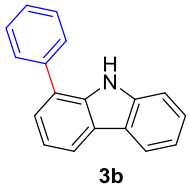
1,8-di-p-tolyl-9H-carbazole (4a)



4a

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 4a as white solid (m.p.=174-177 °C).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.43 (dd, *J* = 7.4, 1.1 Hz, 2H), 7.35 – 7.30 (m, 6H), 2.44 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.31 (s), 137.20 (s), 136.07 (s), 130.00 (s), 127.99 (s), 125.81 (s), 125.00 (s), 123.97 (s), 120.05 (s), 119.38 (s), 21.25 (s) ppm. **HRMS** Calculated for $C_{26}H_{21}N$, $[M+H]^+$:348.1747, found: 348.1747.

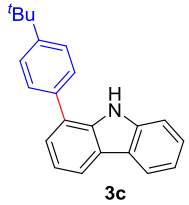
1-phenyl-9H-carbazole (3b)



3b

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3b as white solid (m.p.=110-115 °C, 71% or 51% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (brs, 1H), 8.13 – 8.06 (m, 2H), 7.72 – 7.67 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.22 (m, 1H) ppm. **^{13}C NMR** (101MHz, $CDCl_3$) δ 139.46 (s), 139.06 (s), 137.25 (s), 129.26 (s), 128.38 (s), 127.56 (s), 125.96 (s), 125.74 (s), 125.04 (s), 123.69 (s), 123.54 (s), 120.47 (s), 119.91 (s), 119.55 (s), 119.48 (s), 110.67 (s) ppm. **HRMS** Calculated for $C_{18}H_{13}N$, $[M+H]^+$:244.1121, found: 244.1121.

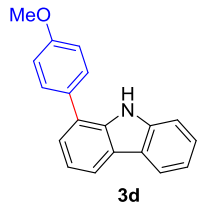
1-(4-(tert-butyl)phenyl)-9H-carbazole (3c)



3c

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3c as white solid (m.p.=126-128 °C, 78% or 66% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.42 (ddd, *J* = 5.7, 5.1, 2.0 Hz, 3H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 1.41 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.55 (s), 139.47 (s), 137.37 (s), 136.10 (s), 128.04 (s), 126.22 (s), 125.91 (s), 125.69 (s), 124.99 (s), 123.62 (s), 123.59 (s), 120.48 (s), 119.90 (s), 119.49 (s), 119.26 (s), 110.67 (s), 34.72 (s), 31.44 (s) ppm. **HRMS** Calculated for $C_{22}H_{21}N$, $[M+H]^+$:300.1747, found: 300.1746.

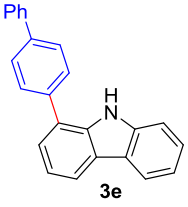
1-(4-methoxyphenyl)-9H-carbazole (3d)



3d

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 3d as white solid (m.p.=124-127 °C, 54% or 62%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (brs, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (dt, *J* = 7.7, 3.4 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$) δ 159.16 (s), 139.49 (s), 137.40 (s), 131.43 (s), 129.49 (s), 125.92 (s), 125.61 (s), 124.82 (s), 123.64 (s), 120.50 (s), 119.94 (s), 119.53 (s), 119.09 (s), 114.71 (s), 110.70 (s), 55.46 (s) ppm. **HRMS** Calculated for $C_{19}H_{15}NO$, $[M+H]^+$:274.1226, found: 274.1224.

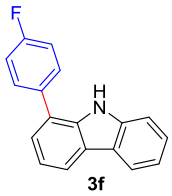
1-([1,1'-biphenyl]-4-yl)-9H-carbazole (3e)



3e

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1 to 20/1 v/v) afforded 3e as yellow solid (m.p.=181-184 °C, 54% or 62%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (brs, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 4H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 3H), 7.43 (d, *J* = 3.7 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.26 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.65 (s), 140.46 (s), 139.52 (s), 138.03 (s), 137.32 (s), 128.94 (s), 128.77 (s), 127.99 (s), 127.54 (s), 127.12 (s), 126.01 (s), 125.71 (s), 124.64 (s), 123.80 (s), 123.59 (s), 120.50 (s), 119.99 (s), 119.62 (s), 119.59 (s), 110.73 (s) ppm. **HRMS** Calculated for $C_{24}H_{17}N$, $[M+H]^+$:320.1434, found: 320.1433.

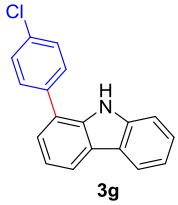
1-(4-fluorophenyl)-9H-carbazole (3f)



3f

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/ to 20/1 v/v) afforded 3f as white solid (m.p.=140-142 °C, 56%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (brs, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.39 (ddd, *J* = 8.2, 5.7, 0.9 Hz, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.21 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.58 (d, J = 245.4Hz), 139.51 (s), 137.26 (s), 135.07 (d, J = 3.3 Hz), 130.05 (d, J = 8.0 Hz), 126.08 (s), 125.81(s), 124.13 (s), 123.91(s), 123.62 (s), 120.52 (s), 120.01 (s), 119.97 (s), 119.71 (s), 116.32 (d, J = 22.0 Hz), 110.74 (s) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.53 (s) ppm. **HRMS** Calculated for $C_{18}H_{12}NF$, $[M+H]^+$:262.1027, found: 262.1025.

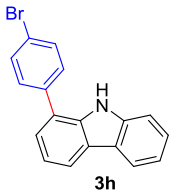
1-(4-chlorophenyl)-9H-carbazole (3g)



3g

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3g as pale yellow solid (m.p.=110-113 °C, 40%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (brs, 1H), 8.13 – 8.07 (m, 2H), 7.65 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H), 7.44 – 7.38 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.48 (s), 137.50 (s), 137.11 (s), 133.54 (s), 129.68 (s), 129.47 (s), 126.13 (s), 125.66 (s), 123.88 (s), 123.80 (s), 123.50 (s), 120.52 (s), 119.99 (s), 119.84 (s), 119.74 (s), 110.74 (s) ppm. **HRMS** Calculated for $C_{18}H_{12}ClN$, $[M+H]^+$:278.0731, found: 278.0730.

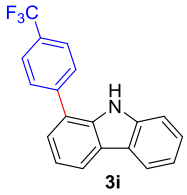
1-(4-bromophenyl)-9H-carbazole (3h)



3h

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3h as white solid (m.p.=122-124 °C, 31%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (brs, 1H), 8.08 (t, *J* = 8.3 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.22 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.49 (s), 137.98 (s), 137.06 (s), 132.43 (s), 130.02 (s), 126.15 (s), 125.61 (s), 123.91 (s), 123.80 (s), 123.50 (s), 121.64 (s), 120.52 (s), 120.01 (s), 119.89 (s), 119.76 (s), 110.76 (s) ppm. **HRMS** Calculated for $C_{18}H_{12}NBr$, $[M+H]^+$:322.0226, found: 322.0227.

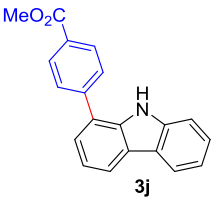
1-(4-(trifluoromethyl)phenyl)-9H-carbazole (3i)



3i

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 3i as white solid (m.p.=123-126 °C, 48%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (brs, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.82 – 7.76 (m, 4H), 7.44 – 7.37 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 (ddd, *J* = 8.0, 6.4, 1.8 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.81 (s), 139.55 (s), 137.09 (s), 129.63 (q, *J* = 32.5 Hz), 128.73 (s), 126.44 – 126.18 (m), 125.89 (s), 124.10 (s), 123.51 (d, *J* = 5.9 Hz), 120.61 (s), 120.42 (s), 120.13 (s), 119.94 (s), 110.88 (s).ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.39 (s) ppm. **HRMS** Calculated for $C_{19}H_{12}NF_3$, $[M+H]^+$:312.0995, found: 312.0994.

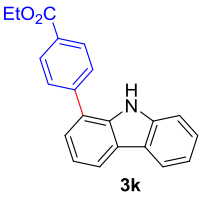
methyl 4-(9H-carbazol-1-yl)benzoate (3j)



3j

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 3j as white solid (m.p.=107-110 °C, 43%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 8.12 (t, *J* = 6.5 Hz, 2H), 7.80 – 7.75 (m, 2H), 7.48 – 7.42 (m, 3H), 7.34 (dd, *J* = 9.6, 5.5 Hz, 1H), 7.27 (dt, *J* = 5.9, 3.0 Hz, 1H), 3.97 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.89 (s), 143.83 (s), 139.53 (s), 137.07 (s), 130.58 (s), 128.31 (s), 126.20 (s), 125.80 (s), 124.04 (s), 123.87 (s), 123.44 (s), 120.51 (s), 120.29 (s), 120.02 (s), 119.80 (s), 110.80 (s), 52.27 (s) ppm. **HRMS** Calculated for $C_{20}H_{15}NO_2$, $[M+H]^+$:302.1176, found: 302.1175.

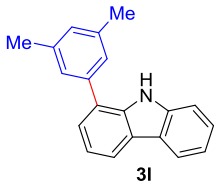
ethyl 4-(9H-carbazol-1-yl)benzoate (3k)



3k

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 3k as white solid (m.p.=97-100 °C, 39%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 8.22 (d, *J* = 8.2 Hz, 2H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 10.2, 5.6 Hz, 3H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 4.47 – 4.40 (m, 2H),1.44 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.43 (s), 143.70 (s), 139.52 (s), 137.08 (s), 130.53 (s), 129.51 (s), 128.27 (s), 126.19 (s), 125.79 (s), 124.00 (s), 123.92 (s), 123.42 (s), 120.51 (s), 120.26 (s), 120.00 (s), 119.78 (s), 61.15 (s), 14.41 (s) ppm. **HRMS** Calculated for $C_{21}H_{17}NO_2$, $[M+H]^+$:316.1332, found: 316.1331.

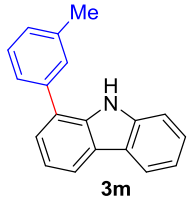
1-(3,5-dimethylphenyl)-9H-carbazole (3l)



3l

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3l as brown solid (m.p.=120-122 °C, 74% or 63% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (brs, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.33 – 7.27 (m, 3H), 7.26 – 7.22 (m, 1H), 7.08 (s, 1H), 2.43 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.43 (s), 139.01 (s), 138.89 (s), 137.32 (s), 129.26 (s), 126.19 (s), 125.89 (s), 125.73 (s), 125.31 (s), 123.60 (s), 123.58 (s), 120.48 (s), 119.85 (s), 119.49 (s), 119.31 (s), 110.68 (s), 21.54 (s) ppm. **HRMS** Calculated for $C_{20}H_{17}N$, $[M+H]^+$:272.1434, found: 272.1433.

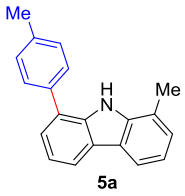
1-(m-tolyl)-9H-carbazole (3m)



3m

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1 v/v) afforded 3m as white solid (m.p.=80-83 °C, 83% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (brs, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.39 (m, 2H), 7.35 – 7.28 (m, 4H), 7.25 (ddd, *J* = 4.0, 3.1, 1.9 Hz, 3H), 2.48 (s, 3H) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$) δ 139.47 (s), 139.05 (s), 139.02 (s), 137.32 (s), 129.16 (s), 128.35 (s), 125.94 (s), 125.75 (s), 125.42 (s), 125.20 (s), 123.66 (s), 123.60 (s), 120.49 (s), 119.90 (s), 119.54 (s), 119.41 (s), 110.69 (s), 21.65 (s) ppm. **HRMS** Calculated for $C_{19}H_{15}N$, $[M+H]^+$:258.1277, found: 258.1276.

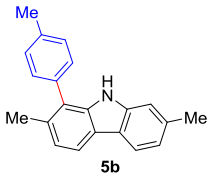
1-methyl-8-(p-tolyl)-9H-carbazole (5a)



5a

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1 to 20/1 v/v) afforded 5a as white solid (m.p.=119-121 °C, 56%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (brs, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.40 (dd, *J* = 9.1, 7.9 Hz, 3H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.14 (m, 1H), 2.52 (s, 3H), 2.47 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.85 (s), 137.36 (s), 137.17 (s), 136.29 (s), 130.05 (s), 128.22 (s), 126.52 (s), 125.63 (s), 125.12 (s), 124.20 (s), 123.12 (s), 119.97 (s), 119.83 (s), 119.70 (s), 119.43 (s), 118.07 (s), 21.30 (s), 16.93 (s) ppm. **HRMS** Calculated for $C_{20}H_{17}N$, $[M+H]^+$:272.1434, found:272.1432.

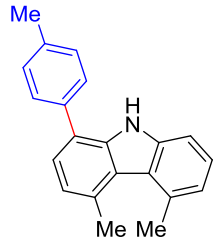
2,7-dimethyl-1-(p-tolyl)-9H-carbazole (5b)



5b

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5b as yellow solid (m.p.=137-140 °C, 50%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.66 (s, 1H), 7.38 – 7.31 (m, 4H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 2.48 (d, *J* = 3.3 Hz, 6H), 2.34 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.87 (s), 138.85 (s), 137.19 (s), 135.41 (s), 134.59 (s), 132.56 (s), 129.73 (s), 129.69 (s), 124.24 (s), 121.83 (s), 121.41 (s), 121.13 (s), 120.81 (s), 119.83 (s), 118.61 (s), 110.65 (s), 22.07 (s), 21.36 (s), 20.11 (s) ppm. **HRMS** Calculated for $C_{21}H_{19}N$, $[M+H]^+$:286.1590, found: 286.1590.

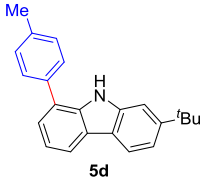
4,5-dimethyl-1-(p-tolyl)-9H-carbazole (5c)



5c

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5c as pale yellow solid (m.p.=120-123 °C, 68%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 6.8 Hz, 1H), 3.04 (d, *J* = 5.9 Hz, 6H), 2.46 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.11 (s), 137.83 (s), 137.20 (s), 136.17 (s), 132.38 (s), 131.30 (s), 129.95 (s), 128.54 (s), 125.58 (s), 125.41 (s), 123.08 (s), 123.02 (s), 122.83 (s), 108.58 (s), 26.16 (s), 25.97 (s), 21.26 (s) ppm. **HRMS** Calculated for $C_{21}H_{19}N$, $[M+H]^+$:286.1590, found: 286.1589.

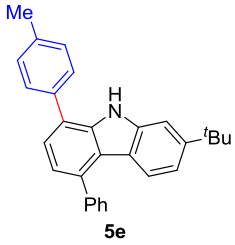
7-(tert-butyl)-1-(p-tolyl)-9H-carbazole (5d)



5d

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5d as white solid (m.p.=110-113 °C, 90%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (brs, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.26 (m, 6H), 2.45 (s, 3H), 1.40 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.66 (s), 139.77 (s), 137.54 (s), 137.26 (s), 136.27 (s), 129.95 (s), 128.26 (s), 125.14 (s), 124.89 (s), 123.66 (s), 121.17 (s), 119.95 (s), 119.76 (s), 119.08 (s), 117.61 (s), 107.25 (s), 35.17 (s), 31.81 (s), 21.32 (s) ppm. **HRMS** Calculated for $C_{23}H_{23}N$, $[M+H]^+$:314.1903, found: 314.1902.

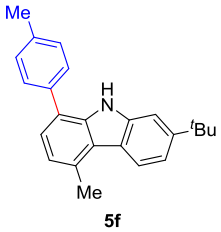
7-(tert-butyl)-4-phenyl-1-(p-tolyl)-9H-carbazole (5e)



5e

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5e as yellow solid (m.p.=117-120 °C, 92%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 7.68 – 7.65 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.42 (dd, *J* = 8.0, 4.1 Hz, 2H), 7.38 (dd, *J* = 8.2, 4.6 Hz, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 8.5, 1.6 Hz, 1H), 2.46 (s, 3H), 1.35 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.47 (s), 141.33 (s), 140.07 (s), 137.83 (s), 137.31 (s), 136.45 (s), 136.10 (s), 129.99 (s), 129.34 (s), 128.38 (s), 127.45 (s), 124.98 (s), 123.89 (s), 121.94 (s), 121.29 (s), 121.06 (s), 120.85 (s), 117.22 (s), 107.05 (s), 35.02 (s), 31.68 (s), 21.31 (s) ppm. **HRMS** Calculated for $C_{29}H_{27}N$, $[M+H]^+$:390.2216, found: 390.2215.

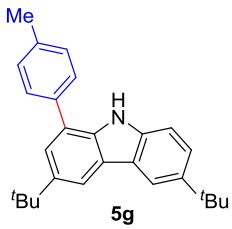
7-(tert-butyl)-4-methyl-1-(p-tolyl)-9H-carbazole (5f)



5f

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5f as white solid (m.p.=100-102 °C, 92%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (brs, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 1.3 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 2.89 (s, 3H), 2.44 (s, 3H), 1.41 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.98 (s), 139.78 (s), 137.45 (s), 137.02 (s), 136.38 (s), 132.13 (s), 129.93 (s), 128.32 (s), 125.00 (s), 122.33 (d, *J* = 47.4 Hz), 122.09 (s), 121.82 (s), 121.18 (s), 117.50 (s), 107.09 (s), 35.07 (s), 31.79 (s), 21.30 (s), 20.68 (s) ppm. **HRMS** Calculated for $C_{24}H_{25}N$, $[M+H]^+$:328.2060, found: 328.2059.

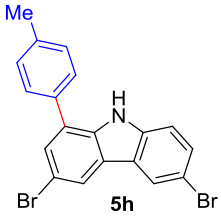
3,6-di-tert-butyl-1-(p-tolyl)-9H-carbazole (5g)



5g

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5g as white solid (m.p.=124-127 °C, 90%yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 – 8.08 (m, 2H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 2.45 (s, 3H), 1.48 (s, 9H), 1.45 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.77 (s), 142.32 (s), 138.04 (s), 137.15 (s), 136.76 (s), 135.94 (s), 129.89 (s), 128.29 (s), 124.56 – 124.28 (m), 123.69 (s), 123.65 (s), 123.58 (s), 123.54 (s), 116.35 (s), 115.27 (s), 110.07 (s), 34.82 (s), 34.75 (s), 32.13 (s), 32.08 (s), 21.28 (s) ppm. **HRMS** Calculated for $C_{27}H_{31}N$, $[M+H]^+$:370.2529, found: 370.2528.

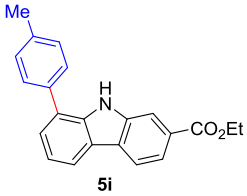
3,6-dibromo-1-(p-tolyl)-9H-carbazole (5h)



5h

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1 v/v) afforded 5h as white solid (m.p.=145-148 °C, 45%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (brs, 1H), 8.13 (s, 1H), 8.07 (s, 1H), 7.50 (dd, *J* = 11.5, 3.6 Hz, 4H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 2.45 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.27 (s), 138.22 (s), 136.42 (s), 134.36 (s), 130.16 (s), 129.34 (s), 128.76 (s), 128.10 (s), 126.93 (s), 124.35 (s), 124.20 (s), 123.38 (s), 121.93 (s), 113.06 – 112.98 (m), 112.67 (s), 112.33 (s), 21.31 (s) ppm. **HRMS** Calculated for $C_{19}H_{13}NBr_2$, $[M+H]^+$:413.9488, found:413.9482.

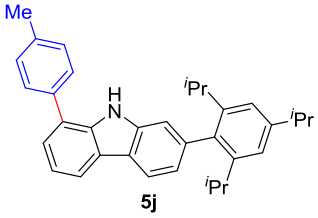
ethyl 8-(p-tolyl)-9H-carbazole-2-carboxylate (5i)



5i

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 v/v) afforded 5i as white solid (m.p.=122-125 °C, 52%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (brs, 1H), 8.17 – 8.07 (m, 3H), 7.97 – 7.93 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.48 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.35 (dd, *J* = 15.1, 7.6 Hz, 3H), 4.41 (d, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.25 (s) 138.81 (s), 138.67 (s), 137.63 (s), 135.67 (s), 130.06 (s), 128.18 (s), 127.73 (s), 127.26 (s), 126.87 (s), 125.43 (s), 122.90 (s), 120.74 (s), 120.40 (s), 120.03 (s), 119.96 (s), 112.56 (s), 60.96 (s), 21.28 (s), 14.43 (s) ppm. **HRMS** Calculated for $C_{22}H_{19}NO_2$, $[M+H]^+$:330.1489, found: 330.1487.

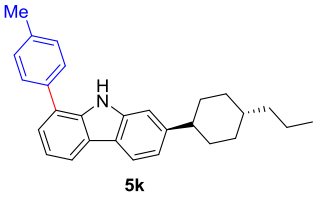
1-(p-tolyl)-7-(2,4,6-triisopropylphenyl)-9H-carbazole (5j)



5j

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 v/v) afforded 5j as yellow solid (m.p.=170-178 °C, 80%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (brs, 1H), 8.09 (dd, *J* = 14.7, 7.8 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.41 (s, 1H), 7.38 – 7.29 (m, 3H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 5.8 Hz, 3H), 2.98 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.68 (dt, *J* = 6.8, 5.5 Hz, 1H), 2.45 (s, 3H), 1.33 (dd, *J* = 6.9, 1.2 Hz, 6H), 1.08 (dd, *J* = 8.3, 2.9 Hz, 12H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.82 (s), 146.81 (s), 139.43 (s), 138.94 (s), 137.64 (s), 137.53 (s), 137.37 (s), 136.18 (s), 130.00 (s), 128.31 (s), 125.55 (s), 125.17 (s), 123.59 (s), 122.41 – 122.17 (m), 121.95 (s), 120.53 (s), 120.07 (s), 119.86 (s), 119.15 (s), 111.71 (s), 34.32 (s), 30.35 (s), 24.39 (s), 24.33 (s), 24.17 (s), 21.31 (s) ppm. **HRMS** Calculated for $C_{34}H_{37}N$, $[M+H]^+$:460.2999, found: 460.2997.

7-((1r,4s)-4-propylcyclohexyl)-1-(p-tolyl)-9H-carbazole (5k)

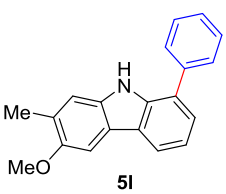


5k

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 v/v) afforded 5k as white solid (m.p.=118-120 °C, 96%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (brs, 1H), 7.99 (dd, *J* = 7.8, 3.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 12.0, 4.6 Hz, 3H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (s, 1H), 7.11 (dd, *J* = 8.1, 1.3 Hz, 1H), 2.60 (ddd, *J* = 12.1, 7.7, 3.3 Hz, 1H), 2.45 (s, 3H), 2.01 – 1.84 (m, 4H), 1.53 (qd, *J* = 12.8, 3.1 Hz, 2H), 1.40 – 1.31 (m, 3H), 1.25 – 1.19 (m, 2H), 1.08 (qd, *J* = 12.9, 3.2 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.47 (s), 139.92 (s), 137.41 (s), 137.23 (s), 136.28 (s), 129.91 (s), 128.24 (s), 125.10 (s), 124.87 (s), 123.78 (s), 121.69 (s), 120.14 (s), 119.74 (s), 119.19 (s), 118.97 (s), 108.44 (s), 45.21 (s), 39.79 (s), 37.16 (s), 34.83 (s), 33.73 (s), 21.27 (s), 20.09 (s), 14.46 (s) ppm. **HRMS** Calculated for $C_{28}H_{31}N$, $[M+H]^+$:382.2529, found: 382.2528.

9.2 Characterization Data of Derivatizations

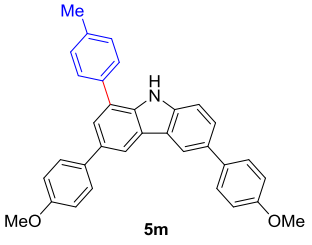
6-methoxy-7-methyl-1-phenyl-9H-carbazole (5l)



5l

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 to 8/1 v/v) afforded 5l as white solid (m.p.=133-136 °C, 30%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (brs, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.49 (s, 1H), 7.45 – 7.36 (m, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 3.96 (s, 3H), 2.38 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.61 (s), 139.29 (s), 137.53 (s), 134.15 (s), 129.22 (s), 128.39 (s), 127.47 (s), 126.65 (s), 125.06 (s), 125.01 (s), 124.05 (s), 121.63 (s), 119.42 (s), 118.99 (s), 112.41 (s), 101.08 (s), 56.00 (s), 17.38 (s) ppm. **HRMS** Calculated for $C_{20}H_{17}NO$, $[M+H]^+$:288.1383, found: 288.1382.

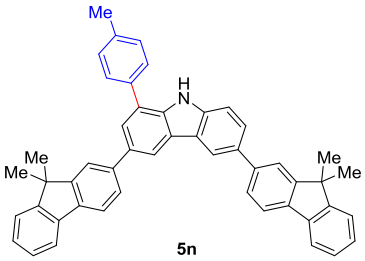
3,6-bis(4-methoxyphenyl)-1-(p-tolyl)-9H-carbazole (5m)



5m

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1 v/v) afforded 5m as yellow solid (m.p.=107-110 °C, 62%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 3.0 Hz, 2H), 8.25 (s, 1H), 7.70 – 7.61 (m, 8H), 7.41 (dd, *J* = 21.1, 8.1 Hz, 3H), 7.02 (d, *J* = 8.6 Hz, 4H), 3.88 (s, 6H), 2.48 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.73 (s), 158.67 (s), 139.11 (s), 137.52 (s), 137.03 (s), 136.05 (s), 134.74 (s), 134.70 (s), 133.32 (s), 132.84 (s), 130.04 (s), 128.37 (s), 128.30 (s), 125.39 (s), 125.32 (s), 125.16 (s), 124.41 (s), 124.31 (s), 118.53 (s), 117.36 (s), 114.29 (s), 110.99 (s), 55.42 (s), 21.32 (s) ppm. **HRMS** Calculated for $C_{33}H_{27}NO_2$, $[M+H]^+$:470.2115, found: 470.2110.

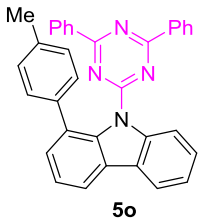
3,6-bis(9,9-dimethyl-9H-fluoren-2-yl)-1-(p-tolyl)-9H-carbazole (5n)



5n

Purification via silica gel column chromatography (petroleum ether/ dichloromethane = 5/1 to 3/1 v/v) afforded 5n as grey solid (m.p.= 160-163 °C, 42%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.41 (s, 1H), 8.36 (s, 1H), 7.85 – 7.66 (m, 12H), 7.49 (dd, *J* = 15.3, 7.6 Hz, 3H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.30 (m, 4H), 2.49 (s, 3H), 1.59 (d, *J* = 2.1 Hz, 12H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.32 (s), 153.30 (s), 152.84 (s), 152.83 (s), 140.23 (s), 140.20 (s), 138.36 (s), 138.36 (s), 138.04 (s), 138.04 (s), 136.80 (s), 136.72 (s), 136.60 (s), 136.30 (s), 134.93 (s), 133.10 (s), 132.61 (s), 129.03 (s), 127.30 (s), 126.03 (s), 125.98 (s), 125.38 (s), 125.32 (s), 124.81 (s), 124.55 (s), 124.41 (s), 123.41 (s), 123.34 (s), 121.57 (s), 120.59 (s), 120.50 (s), 119.28 (s), 119.27 (s), 118.95 (s), 118.03 (s), 116.85 (s), 110.01 (s), 45.96 (d, *J* = 1.6 Hz), 26.30 (s), 20.27 (s) ppm. **HRMS** Calculated for $C_{49}H_{39}N$, $[M+H]^+$:642.3155, found: 642.3147.

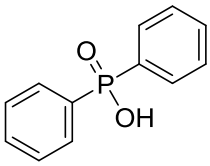
9-(4,6-diphenyl-1,3,5-triazin-2-yl)-1-(p-tolyl)-9H-carbazole (5o)



5o

Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1 v/v) afforded 50 as pale yellow solid (m.p.=170-172 °C, 86%yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (t, *J* = 8.6 Hz, 5H), 8.13 – 8.05 (m, 2H), 7.59 – 7.45 (m, 9H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 6.7 Hz, 2H), 6.53 (d, *J* = 7.9 Hz, 2H), 1.94 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.90 (s), 164.73 (s), 140.76 (s), 138.17 (s), 136.86 (s), 136.21 (s), 135.61 (s), 132.71 (s), 130.20 (s), 129.30 (s), 128.94 (s), 128.84 (s), 128.45 (s), 127.77 (s), 127.18 (s), 127.10 (s), 126.03 (s), 123.27 (s), 122.90 (s), 120.22 (s), 118.89 (s), 113.65 (s), 20.97 (s) ppm. **HRMS** Calculated for $C_{34}H_{24}N_4$, $[M+H]^+$:489.2074, found: 489.2071.

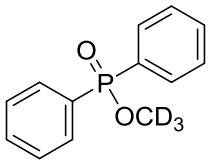
diphenylphosphinic acid (10)



10

Purification via silica gel column chromatography (dichloromethane/ Methanol = 10/1 v/v) afforded 10 as white solid (65% yield). **^{1}H NMR** (400 MHz, CD_3OD): δ 5.07 (s, 1H), 7.35-7.38 (m, 6H), 7.77-7.84 (m, 4H) ppm. **^{13}C NMR** (151 MHz, CD_3OD): δ 127.49 (d, *J* = 12.1 Hz,), 129.65 (d, *J* = 2.2 Hz,), 130.91 (d, *J* = 9.4 Hz), 139.41 (d, *J* = 131.7 Hz) ppm. **^{31}P NMR** (162 MHz, CD_3OD): δ 20.63 ppm. Spectral data is in good agreement with literature data.[12]

methyl-d3 diphenylphosphinate



Purification via silica gel column chromatography (dichloromethane/ Methanol = 10/1 v/v) afforded as colorless oil (20% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (m, 4H), 7.49 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.26 (d, *J* = 2.7 Hz), 131.69 (d, *J* = 10.1 Hz), 130.34 (d, J=136.8 Hz), 128.60 (d, *J* = 13.1 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.23 ppm. **GRMS** Calculated for $C_{13}H_{10}D_3O_2P$, $[M+H]^+$: 236.0914, found: 236.0249.

10. X-ray Crystallographic Data

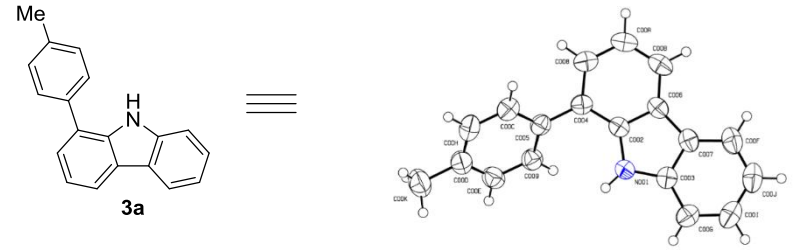


Figure S1. The structure of **3a**

Table S2. Crystal data and structure refinement for **3a**

Identification code	3a
Empirical formula	$C_{19}H_{15}N$
Formula weight	257.32
Temperature/K	293 K
Crystal system	orthorhombic
Space group	Aea2
a/Å	16.7467(4)
b/Å	21.6002(5)
c/Å	7.8088(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2824.69(12)
Z	8
ρcalcg/cm^3	1.210
μ/mm^{-1}	0.536
F(000)	1088.0
Crystal size/mm^3	0.18 x 0.15 x 0.12
Radiation	Cu K$^{\alpha}$ (λ = 1.54184)
2Θ range for data collection/°	8.186 to 133.14
Index ranges	-19 ≤ h ≤ 15, -25 ≤ k ≤ 18, -9 ≤ l ≤ 8
Reflections collected	2980
Independent reflections	1857 [R_{int} = 0.0175, R_{sigma} = 0.0248]
Data/restraints/parameters	1857/1/182
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.0979
Final R indexes [all data]	R_1 = 0.0397, wR_2 = 0.1007
Largest diff. peak/hole / e Å-3	0.14/-0.24
Flack parameter	0.6(7)

Single crystals of $C_{19}H_{15}N$ [yuanzhichao_0430] were collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Figure S1 and Table S2. CCDC 2014884 contains the supplementary crystallographic data for yuanzhichao_0430. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif

11. Reference

[1] Gao, H.; Xu, Q. L.; Yousufuddin, Xu, M.; Ess, D. H.; Kurti, L.Rapid Synthesis of Fused N-Heterocycles by Transition-Metal-Free Electrophilic Amination of Arene C-H Bonds. *Angew. Chem. Int. Ed.* **2014**, *53*, 2701-2705.

[2] Freeman, A. W.; Urvoy, M.; Criswell, M. E. Triphenylphosphine-Mediated Reductive Cyclization of 2-Nitrobiphenyls: A Practical and Convenient Synthesis of Carbazoles. *J. Org. Chem.* **2005**, *70*, 5014-5019.

[3] Tao, Y.; Xiao, J.; Zheng, C.; Zhang, Z.; Yan, M.; Chen, R.; Zhou, X.; Li, H.; An, Z.; Wang, Z; Xu, H.; Huang, W. Dynamically Adaptive Characteristics of Resonance Variation for Selectively Enhancing Electrical Performance of Organic Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 10491-10495.

[4] Cui, L. S.; Nomura, H.; Geng, Y.; Kim, J. U.; Nakanotani, H.; Adachi,C. Controlling Singlet–Triplet Energy Splitting for Deep‐Blue Thermally Activated Delayed Fluorescence Emitters. *Angew. Chem. Int. Ed.* **2017**, *56*, 1571-1575.

[5] Moonsin, P.; Prachumrak, N.; Rattanawan, R.; Keawin, T.; Jungsuttiwong, S.; Sudyoadsuk, T.; Promarak, V. Carbazole dendronised triphenylamines as solution processed high T_g amorphous hole-transporting materials for organic electroluminescent devices. *Chem. Comm.* **2012**, *48*, 3382-3384.

[6] Bag, P. P.; Wang, D.; Chen, Z.; Cao, R. Outstanding drug loading capacity by water stable microporous MOF: a potential drug carrier. *Chem. Commun.* **2016**, *52*, 3669-3672.

[7] Gu, Q. S.; Yang, D. Enantioselective Synthesis of (+)‐Mitomycin K by a Palladium‐Catalyzed Oxidative Tandem Cyclization. *Angew. Chem. Int. Ed.* **2017**, *56*, 5886-5889.

[8] Morrison, M. D.; Hanthorn, J. J.; Pratt, D. A. Synthesis of Pyrrolnitrin and Related Halogenated Phenylpyrroles. *Org. Lett*. **2009**, *11*, 1051-1054.

[9] Bahamonde, A.; Murphy, J. J.; Savarese, M.; Bremond, E.; Cavalli, A.; Melchiorre, P. Studies on the Enantioselective Iminium Ion Trapping of Radicals Triggered by an Electron-Relay Mechanism. *J. Am. Chem. Soc.* **2017**, *139*, 4559-4567.

[10] Wang, H.-Y.; Liu, F.; Xie, L.-H.; Tang, C.; Peng, B.; Huang, W.; Wei, W. *J.* Topological Arrangement of Fluorenyl-Substituted Carbazole Triads and Starbursts: Synthesis and Optoelectronic Properties. *Phy. Chem. C.* **2011**, *115*, 6961-6967.

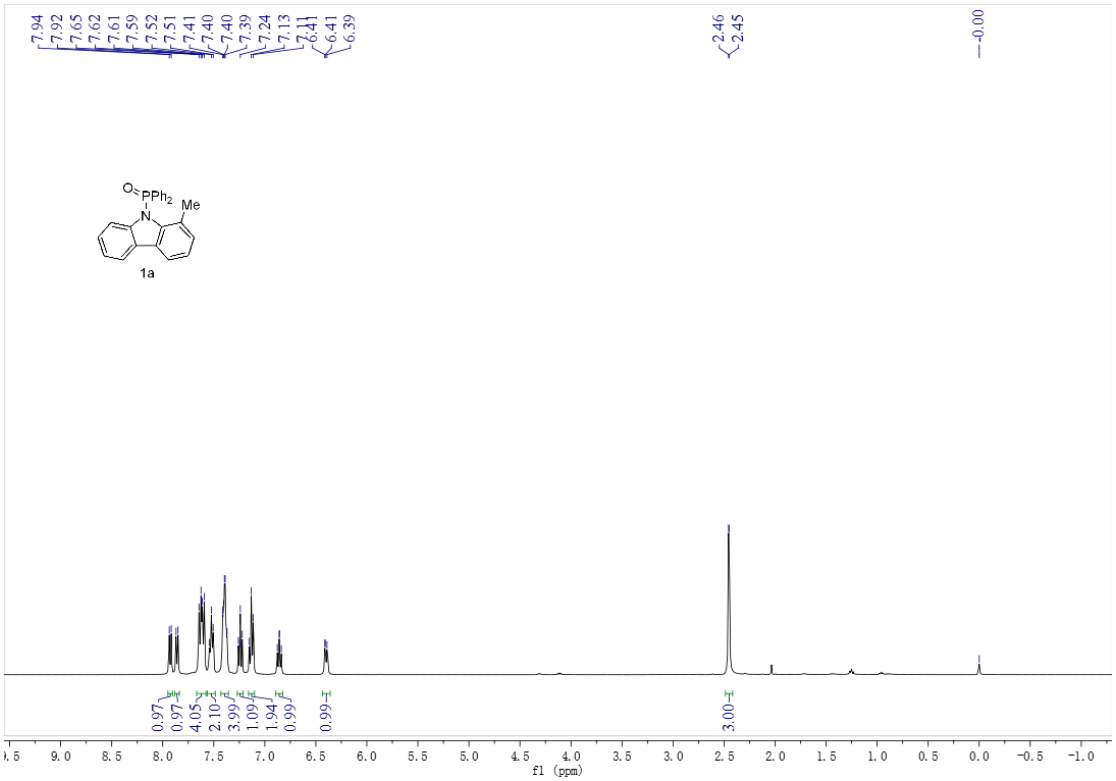
[11] Bigot, A.; Williamson, A. E.; Gaunt, M. J. Enantioselective α-Arylation of *N*-Acyloxazolidinones with Copper(II)-bisoxazoline Catalysts and Diaryliodonium Salts. *J. Am. Chem. Soc.* **2011**, *133*, 13778-13781.

[12] Li, B.-J.; Simard, R. D.; Beauchemin, A. M. *o*-Phthalaldehyde catalyzed hydrolysis of organophosphinic amides and other P(═O)–NH containing compounds. *Chem. Commun.* **2017**, *53*, 8667-8670.

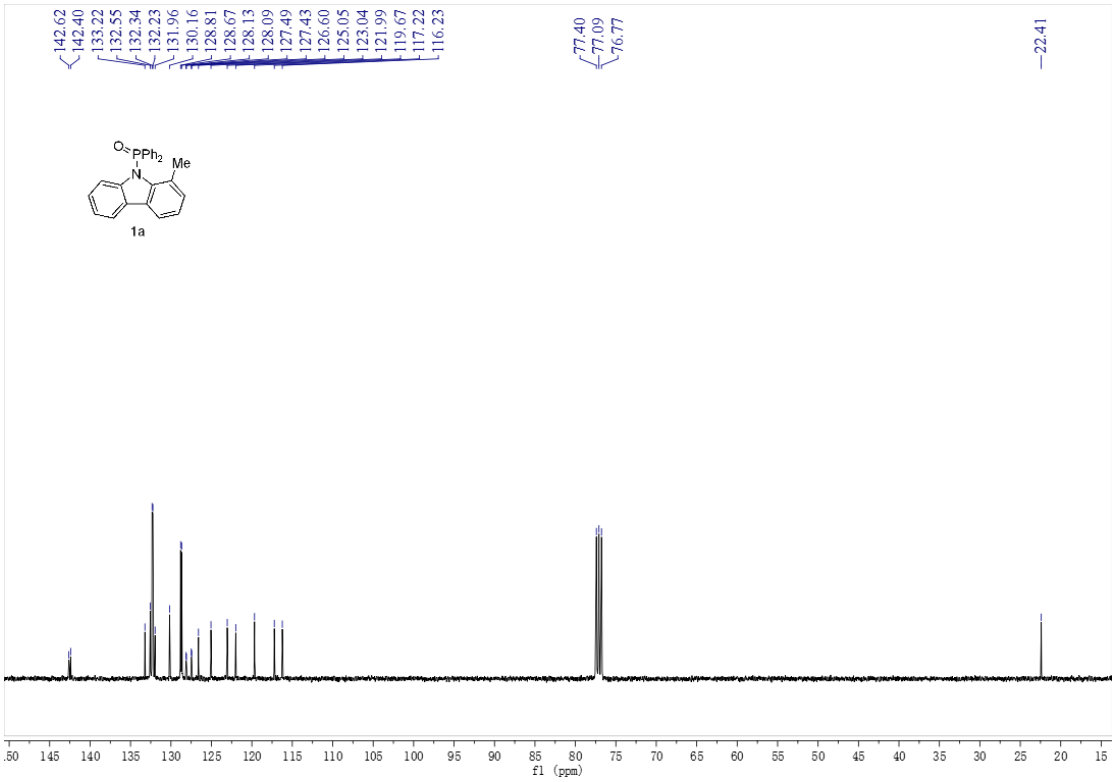
12. Copies of NMR Spectra

12.1 Copies of NMR Spectra of Substrates

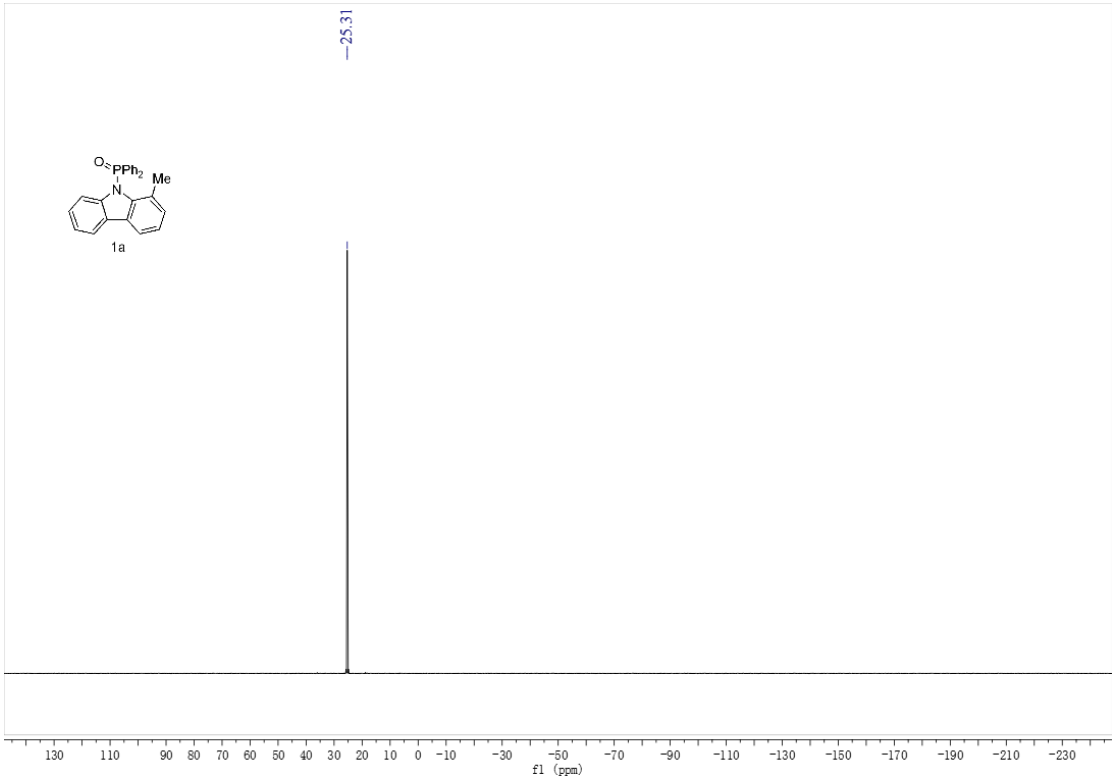
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1a



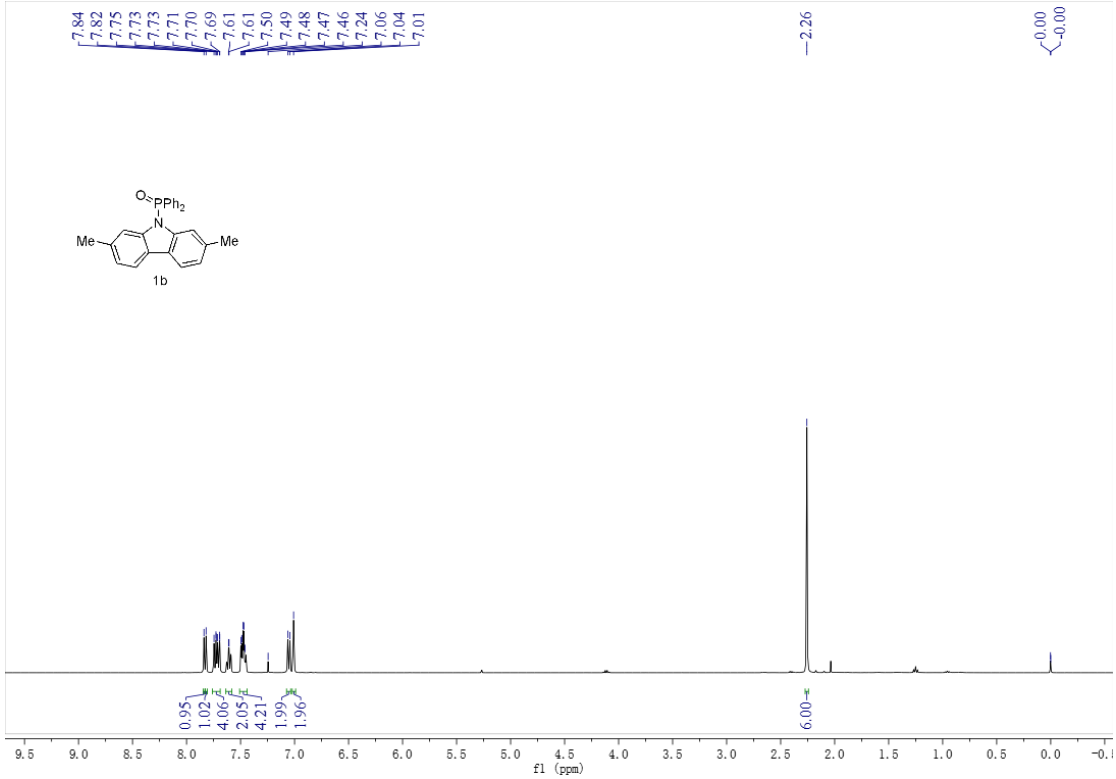
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1a



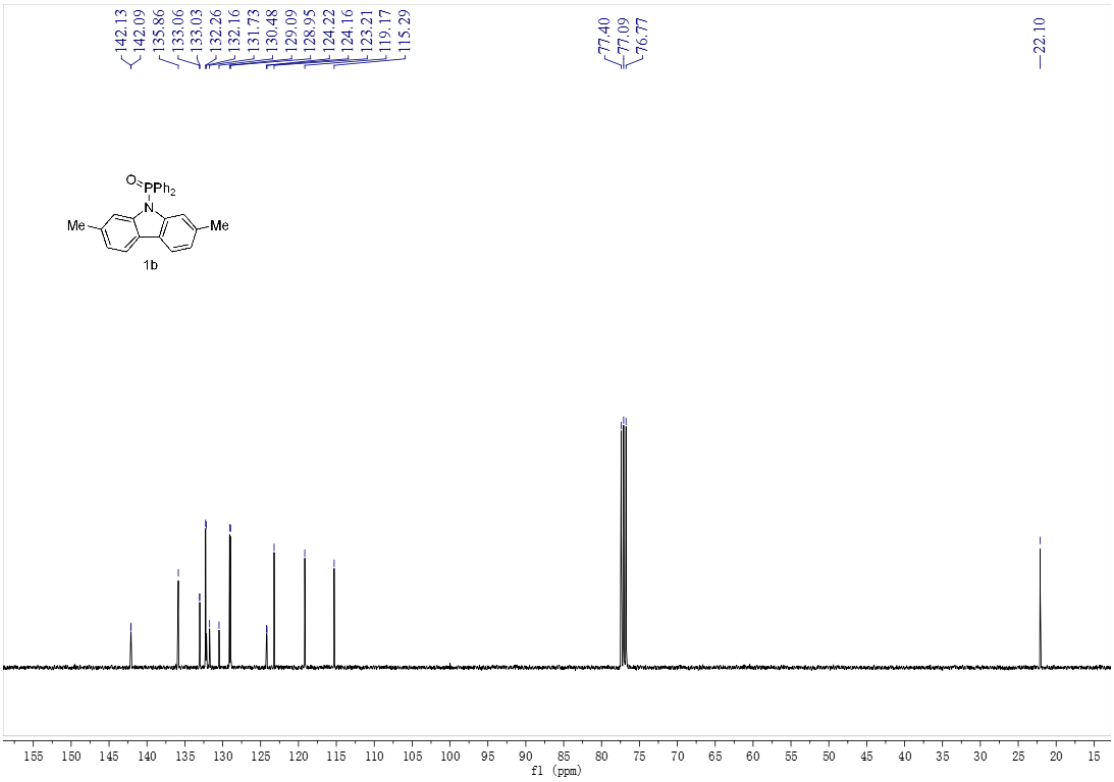
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1a



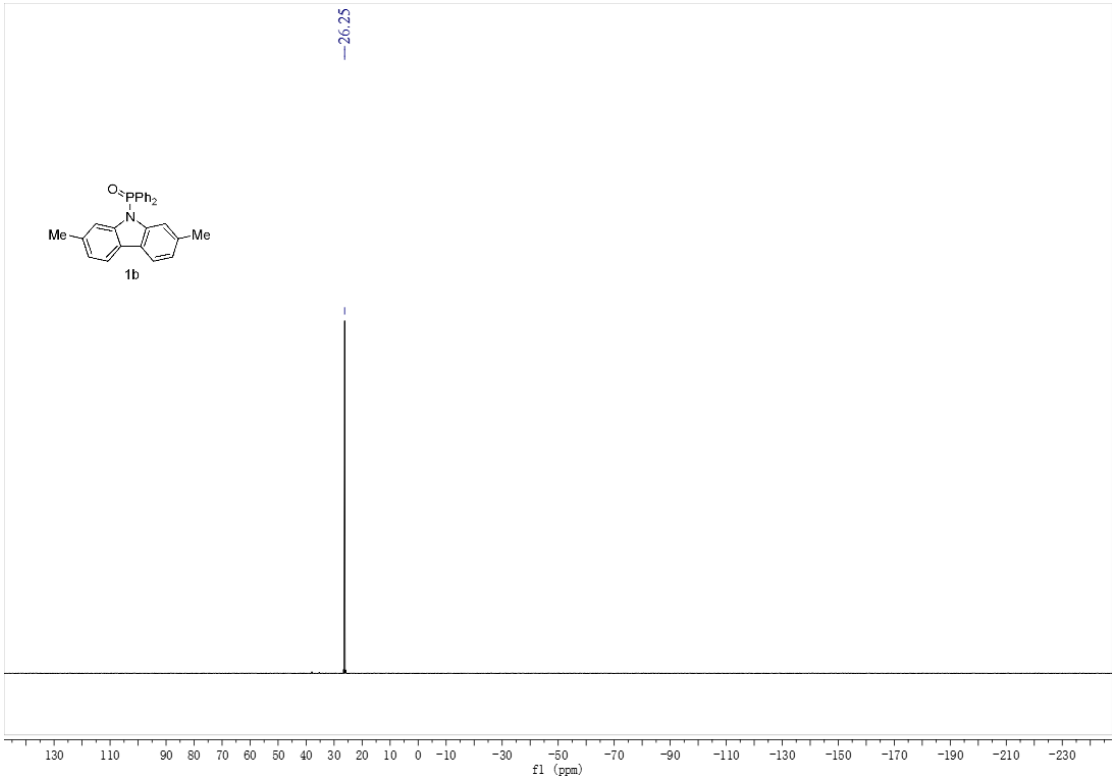
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1b



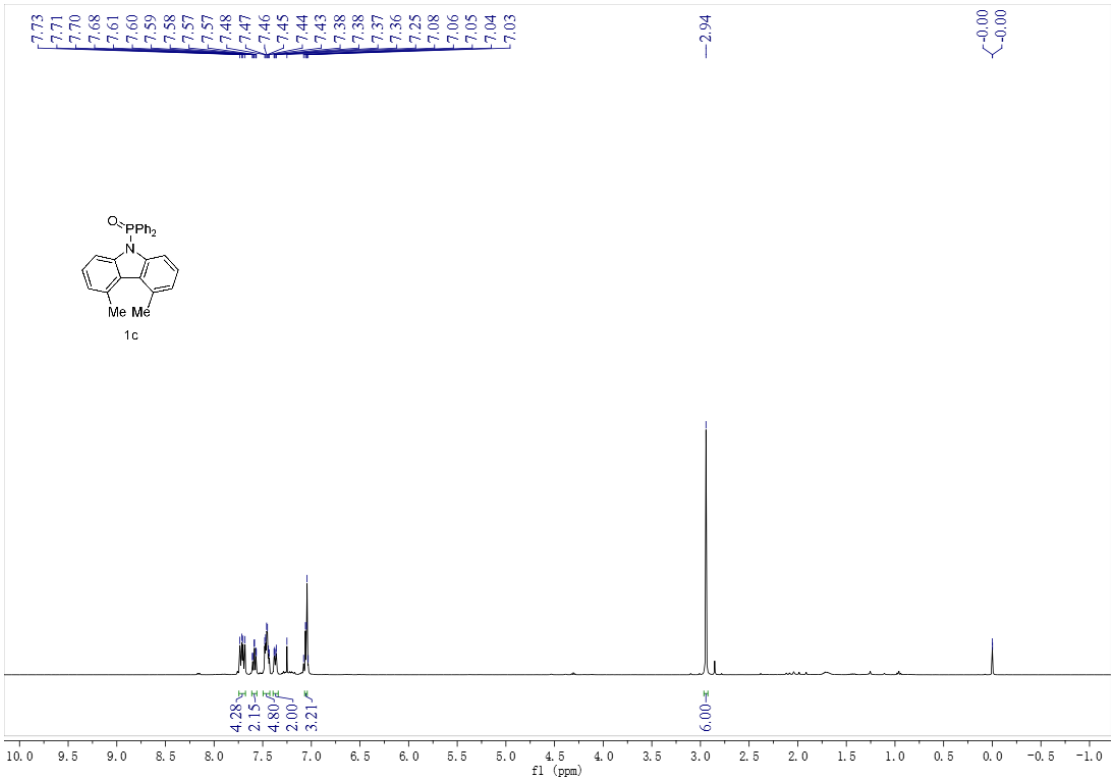
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1b



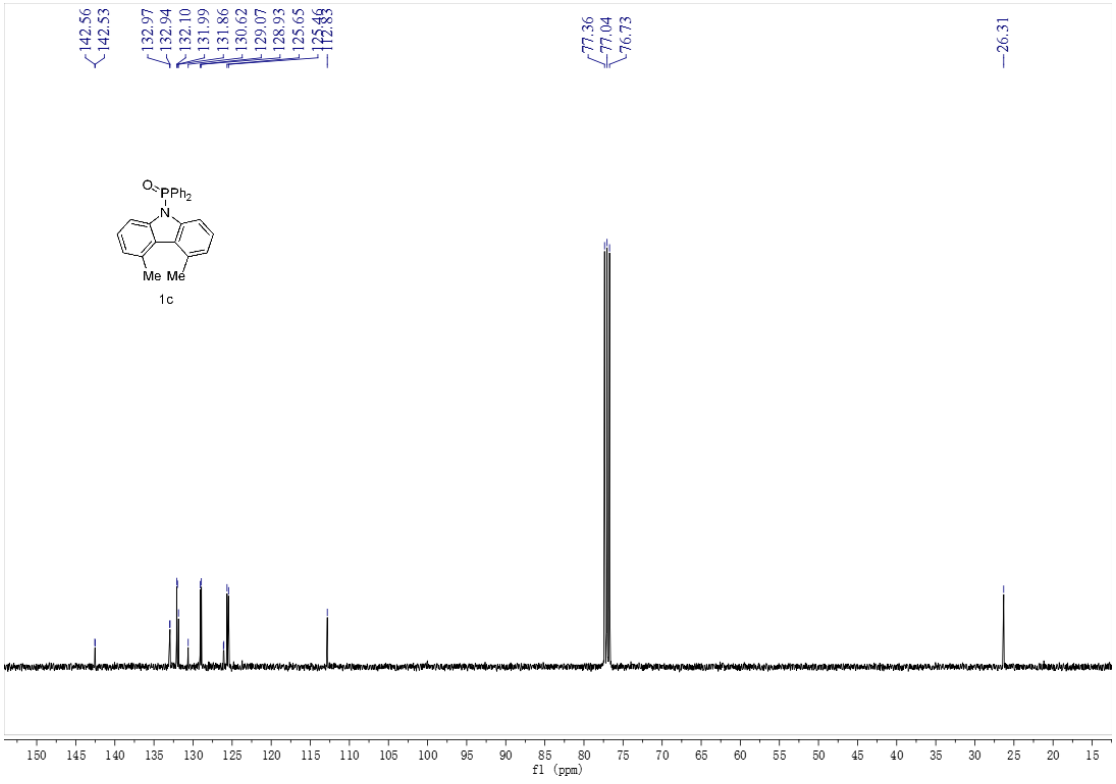
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1b



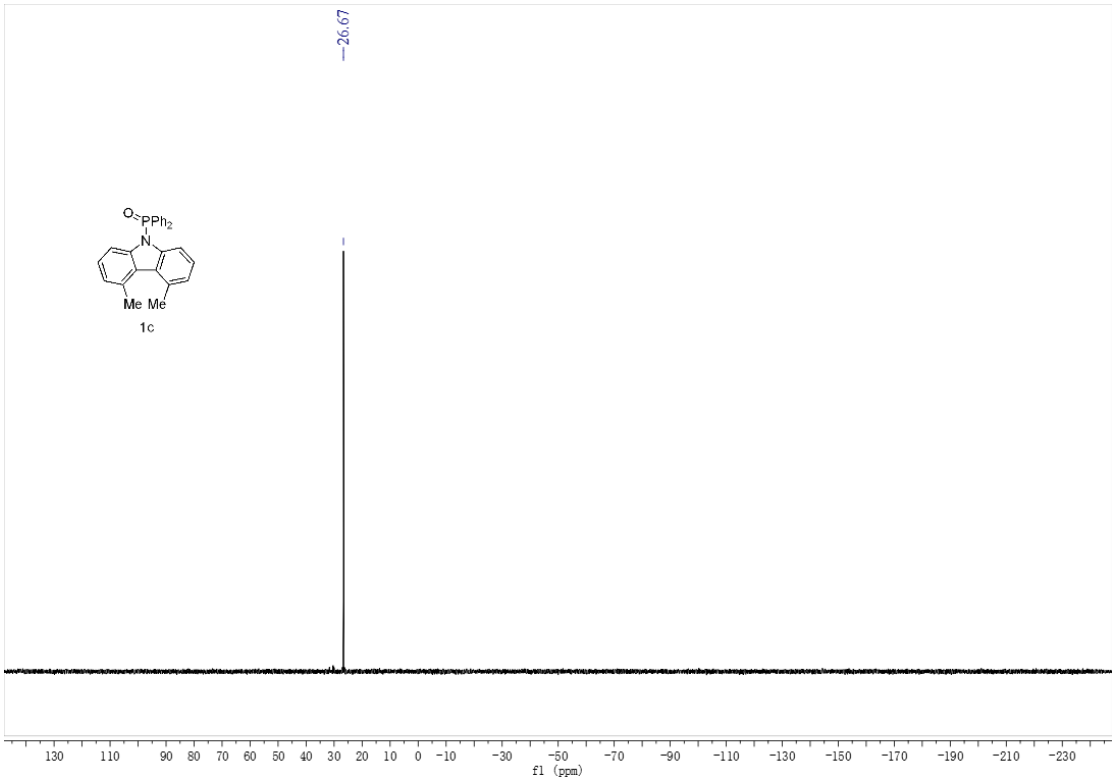
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1c



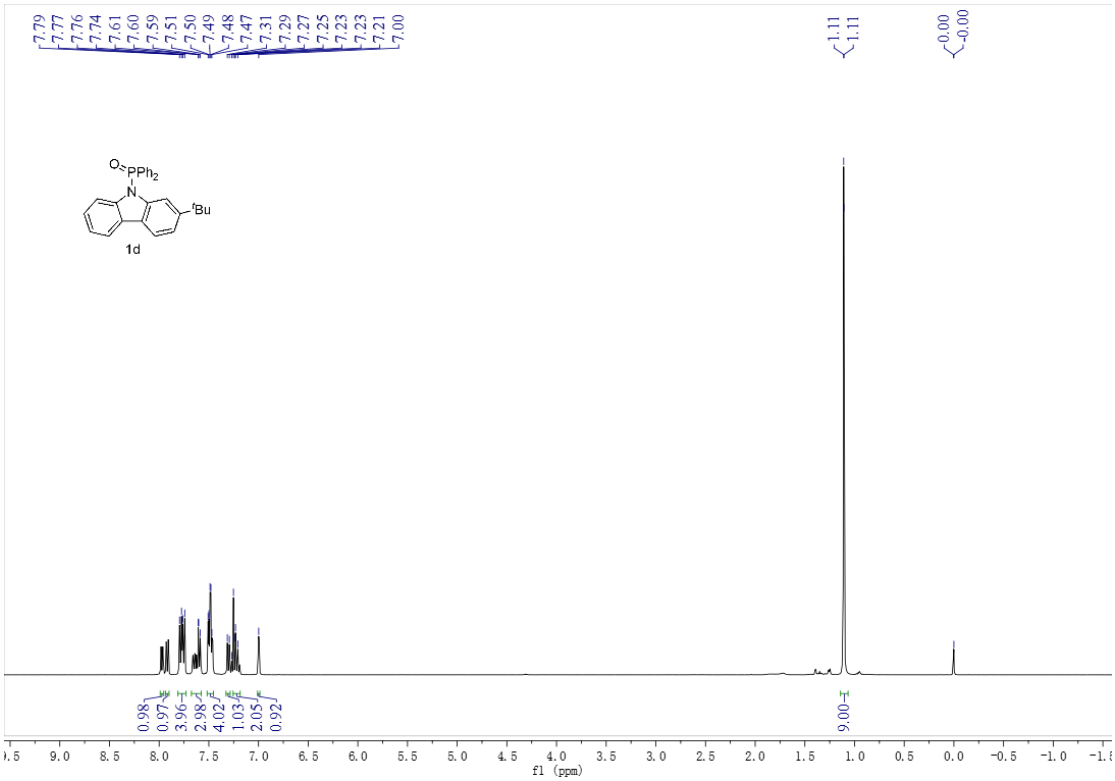
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1c



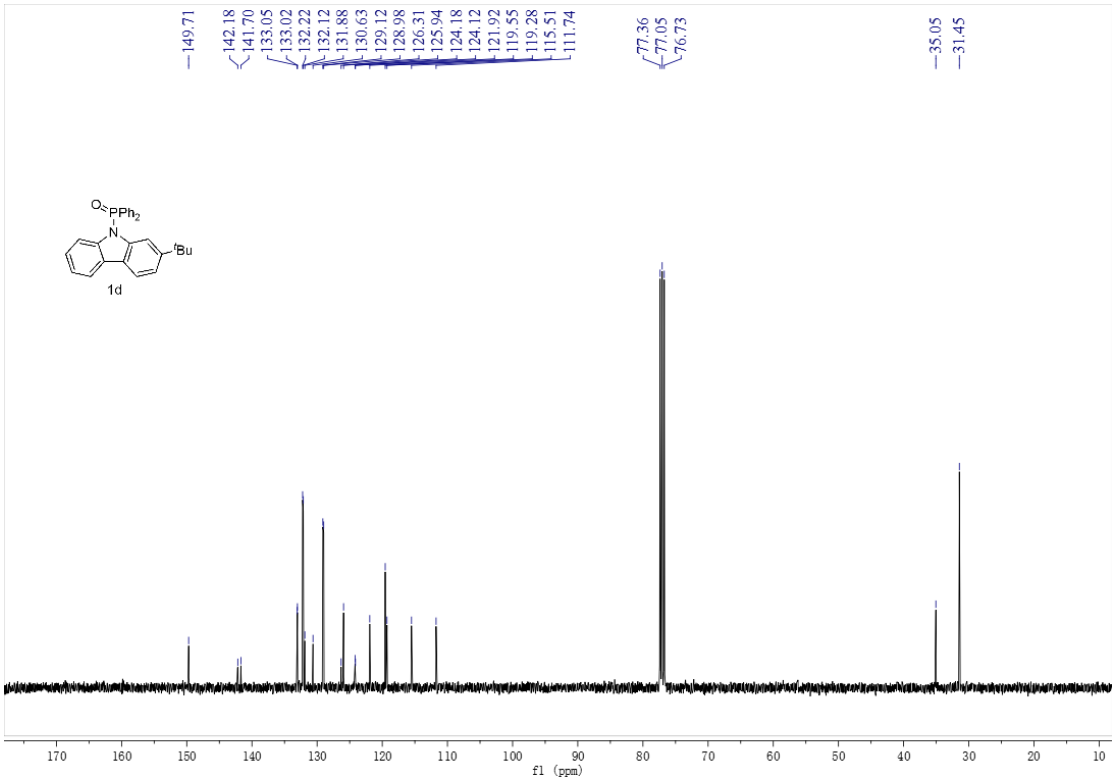
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1c



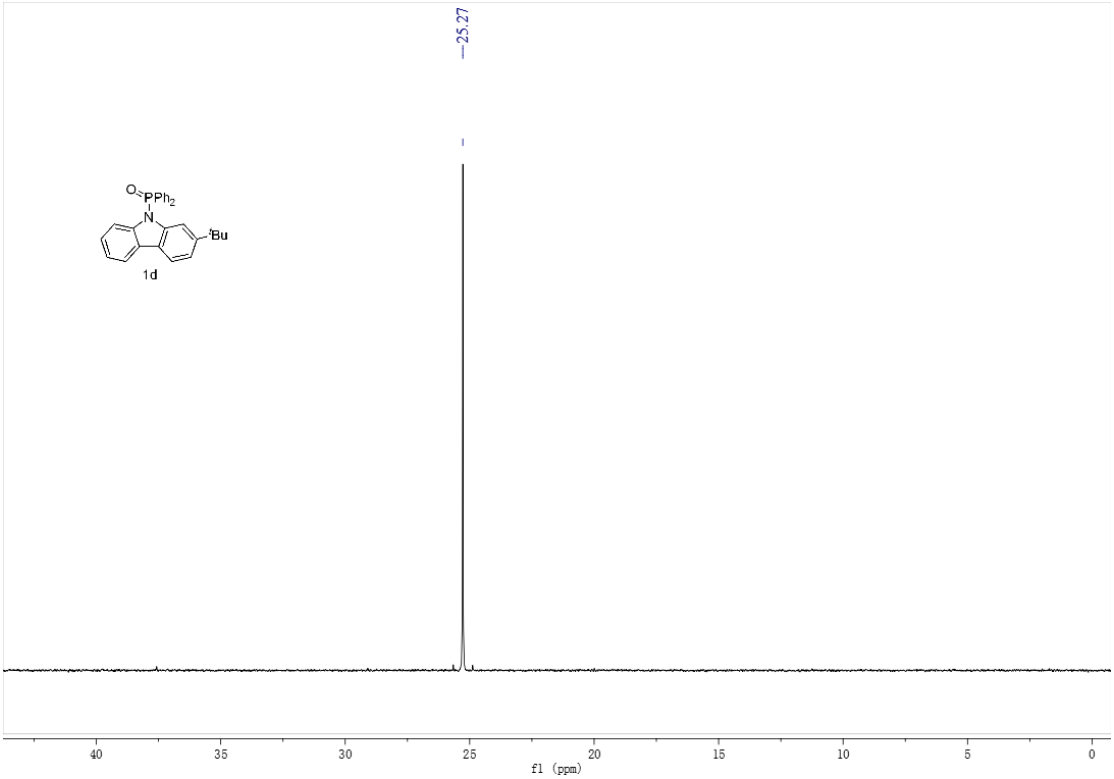
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1d



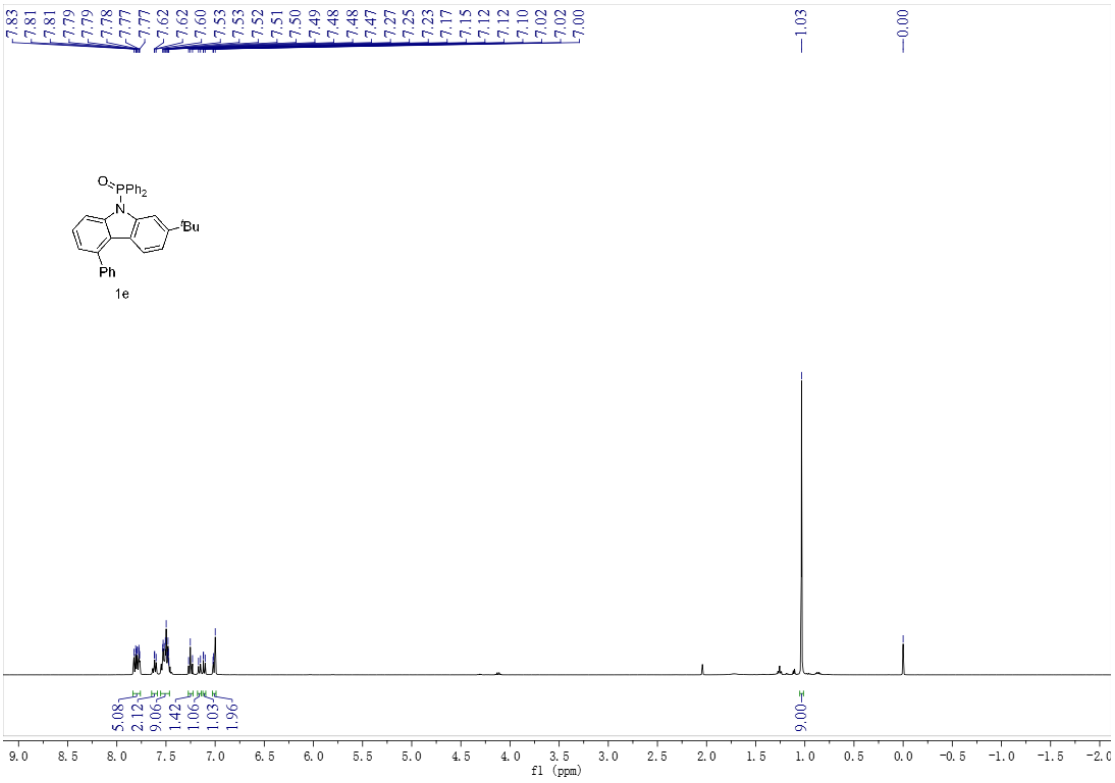
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1d



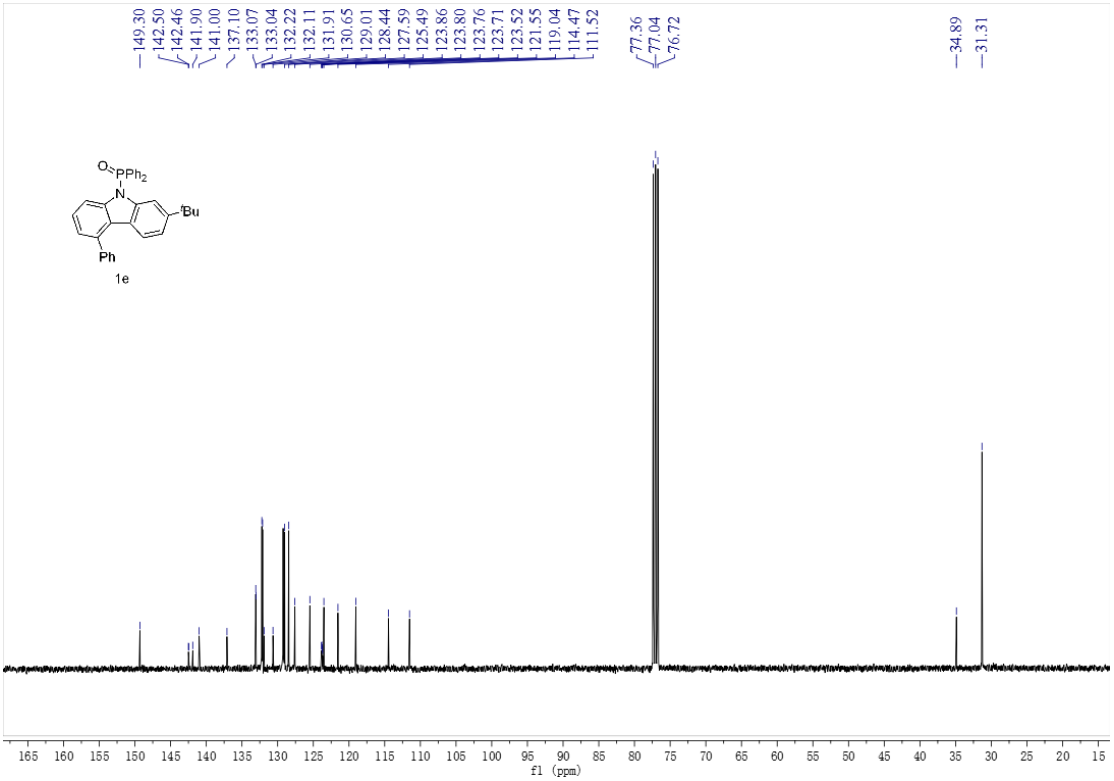
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1d



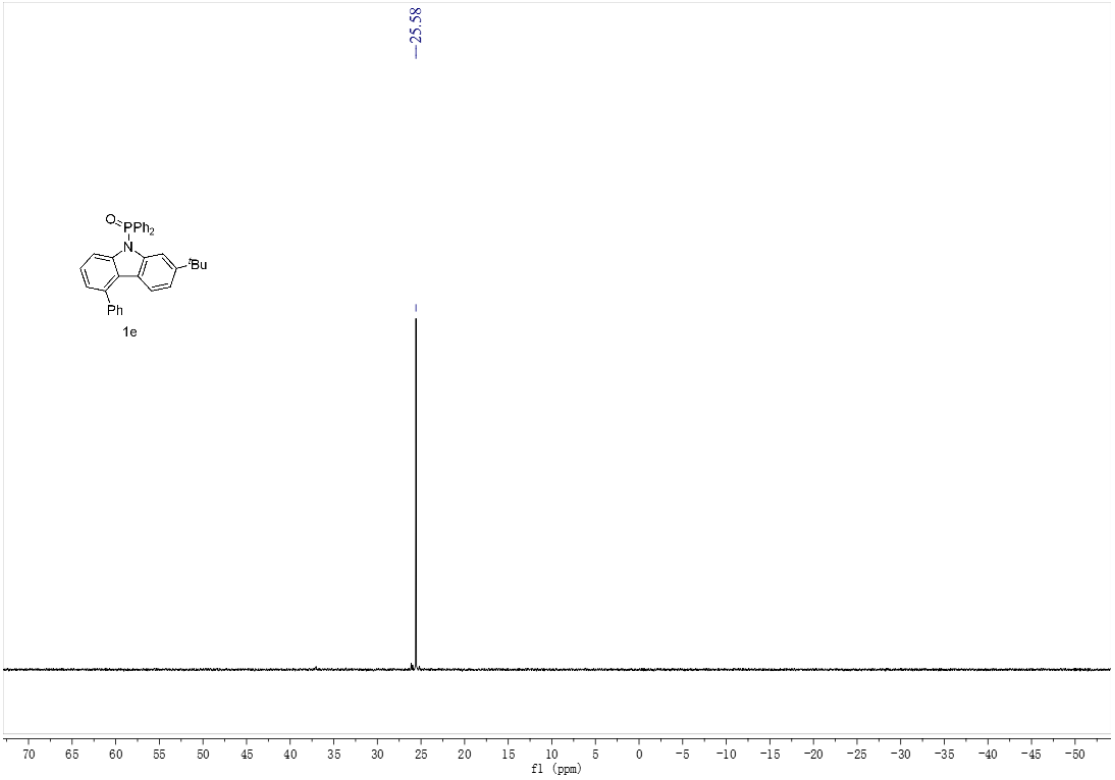
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1e



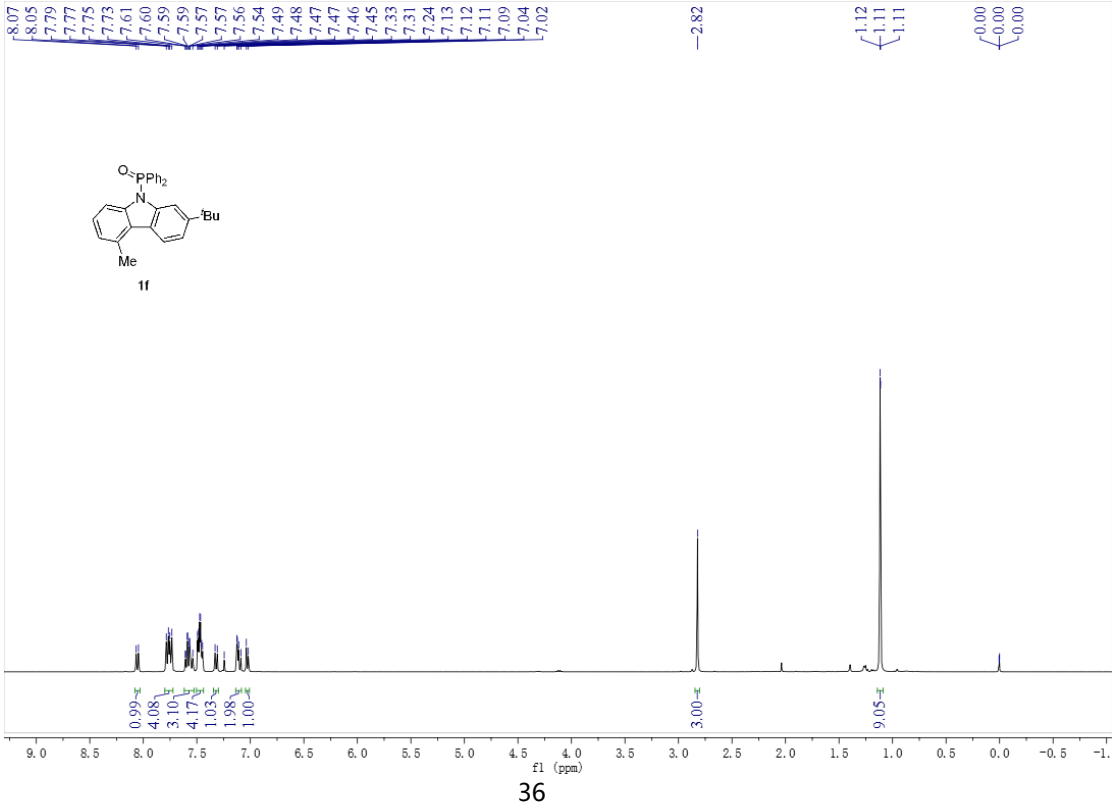
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1e



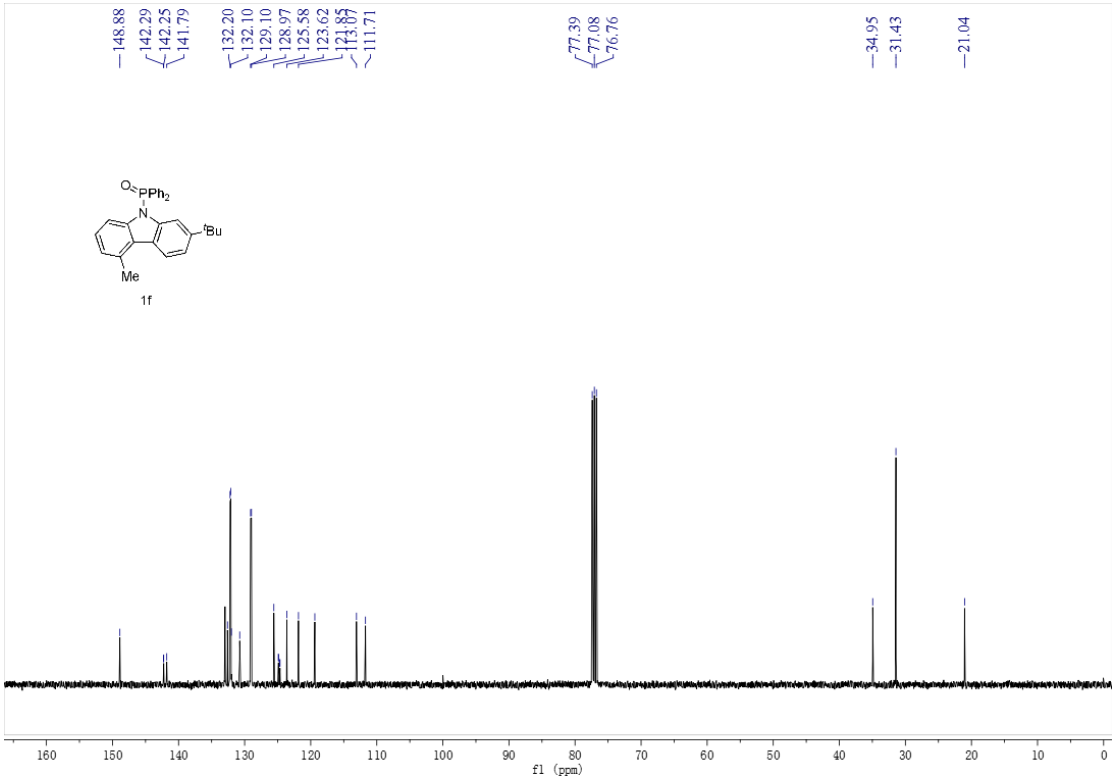
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1e



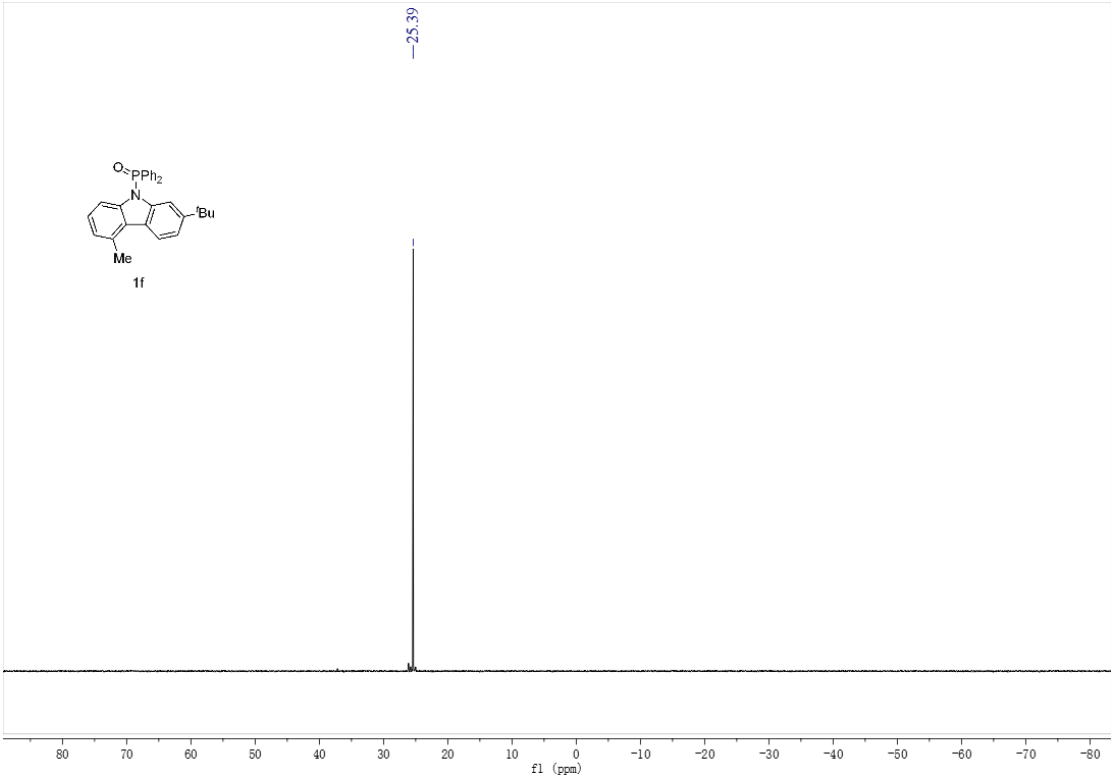
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1f



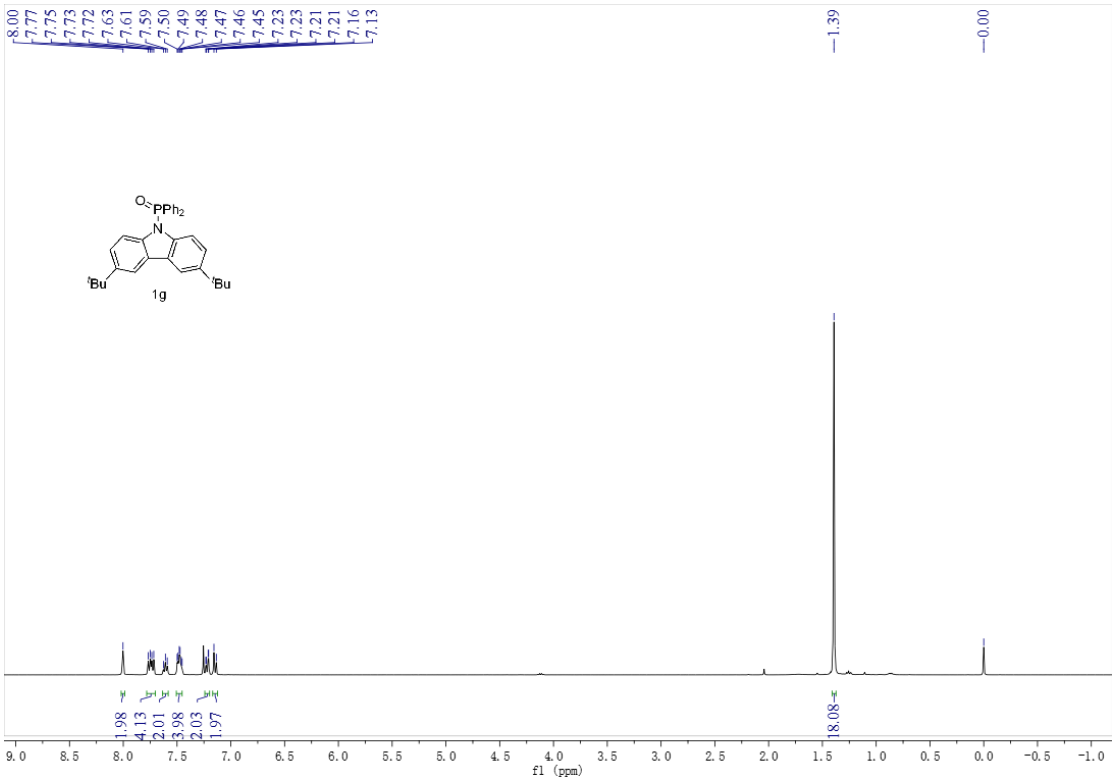
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1f



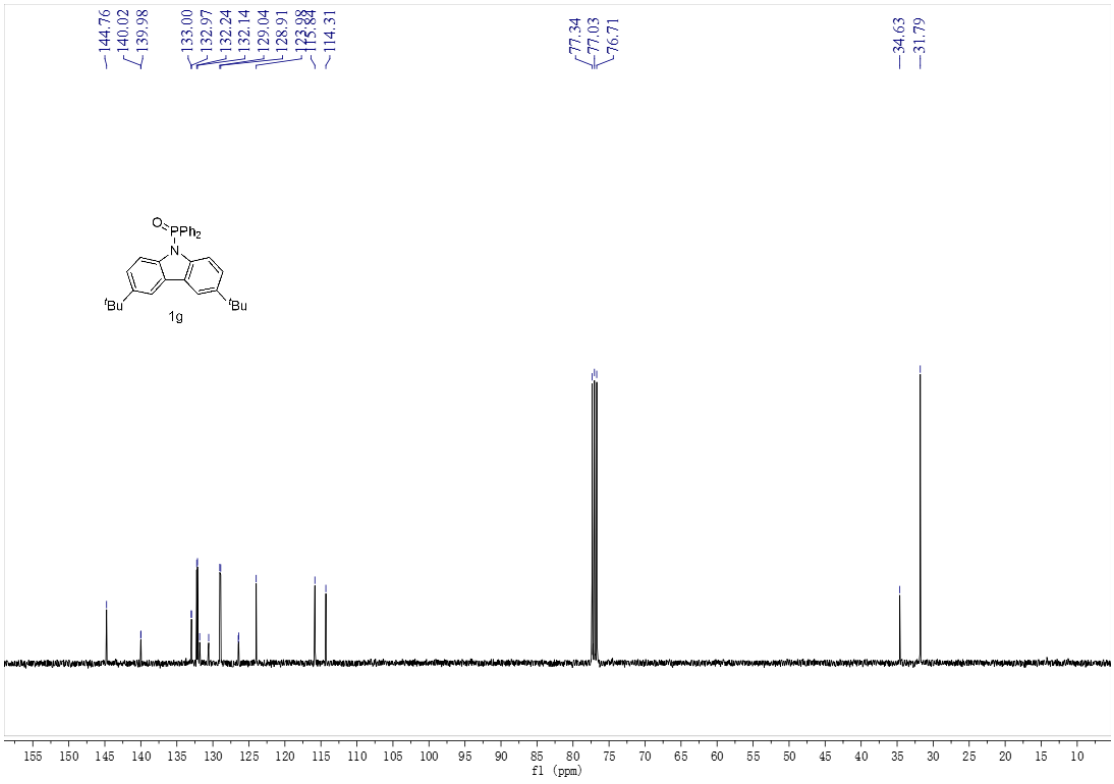
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1f



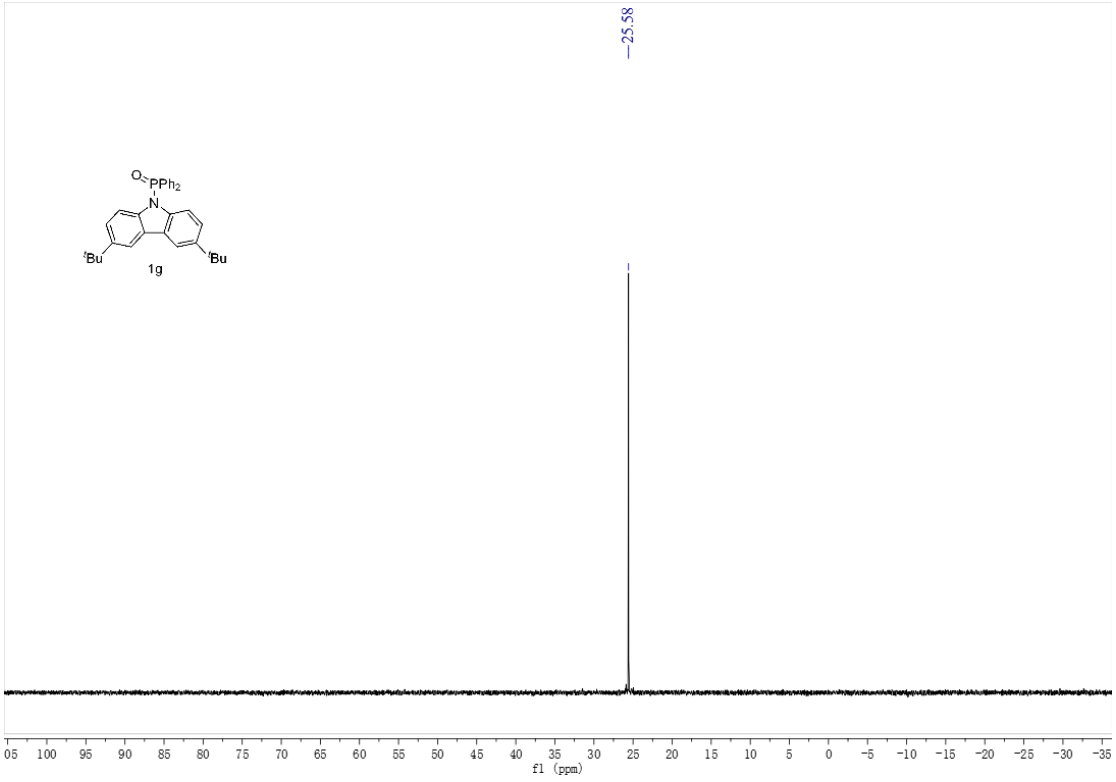
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1g



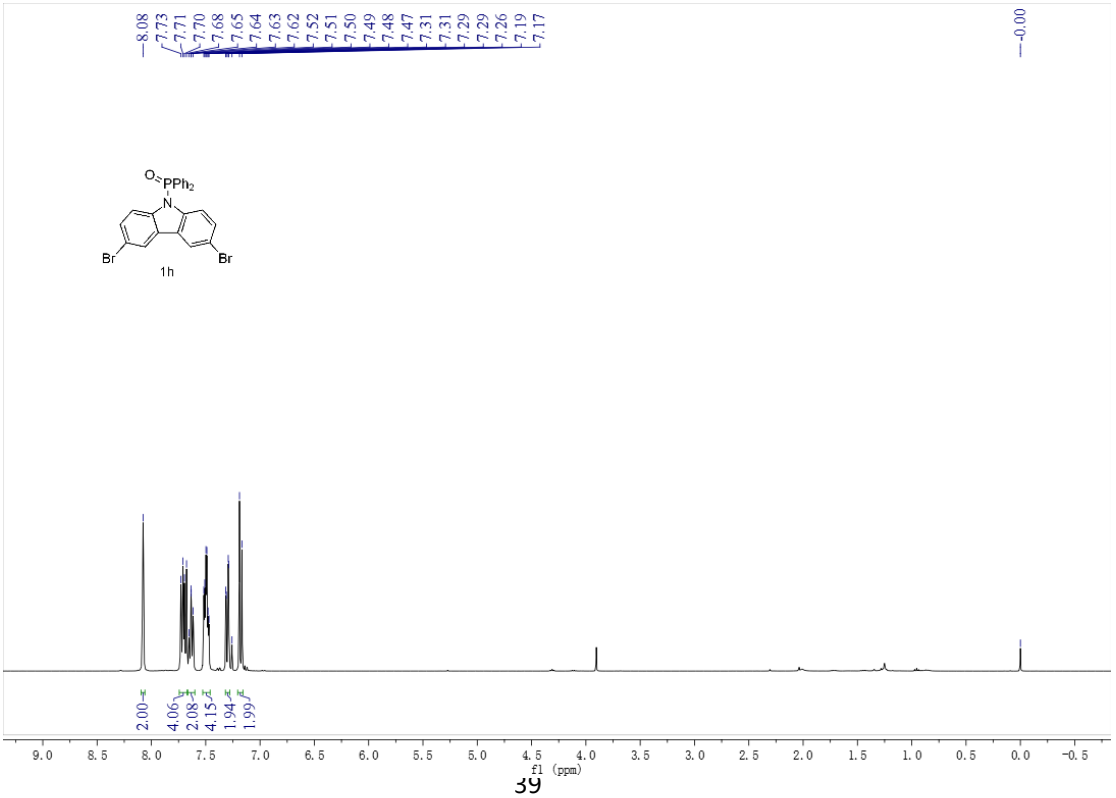
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1g



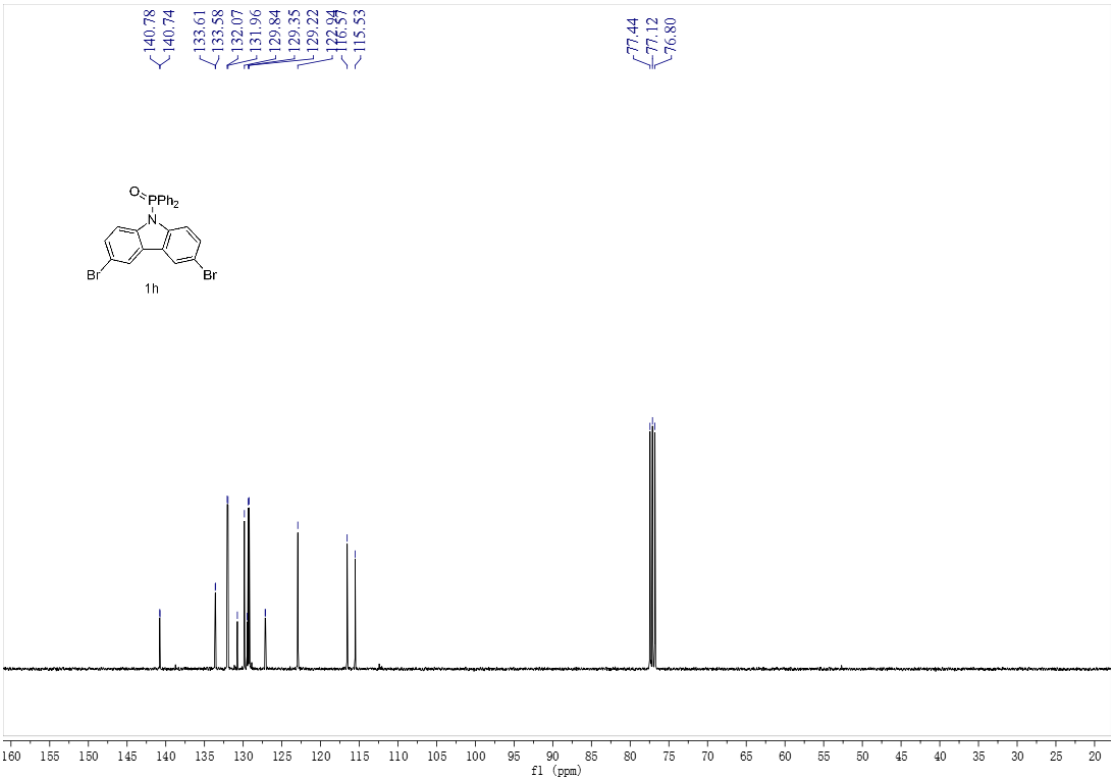
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1g



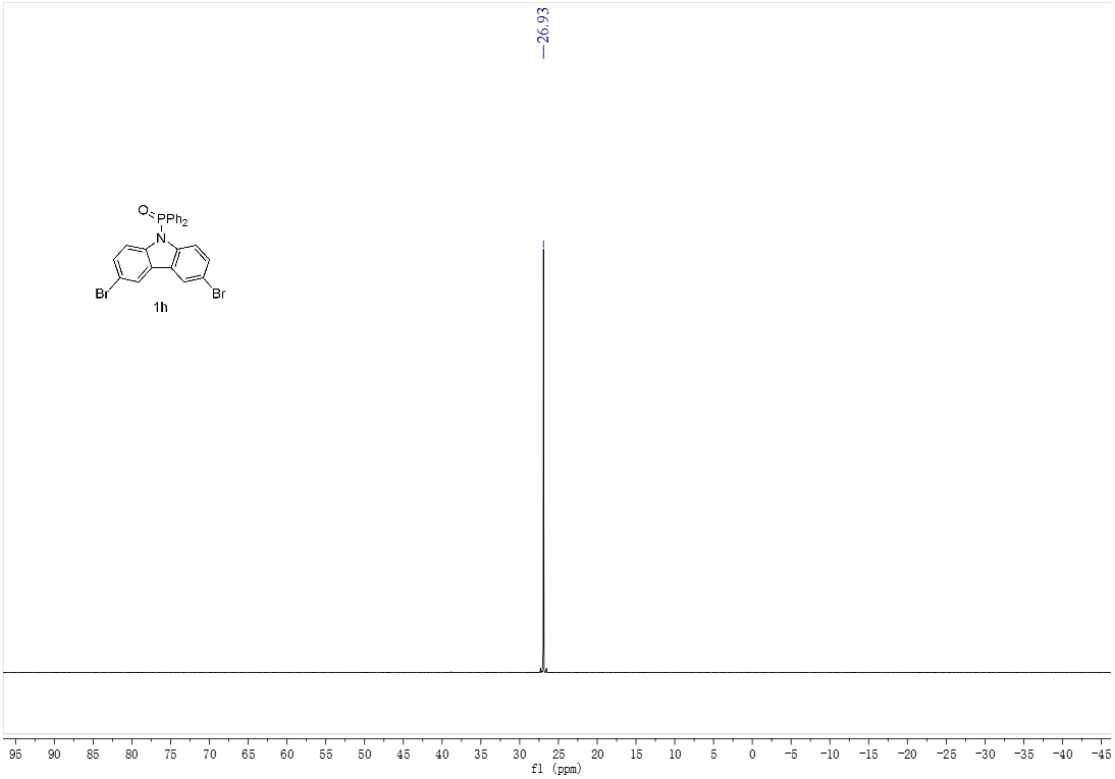
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1h



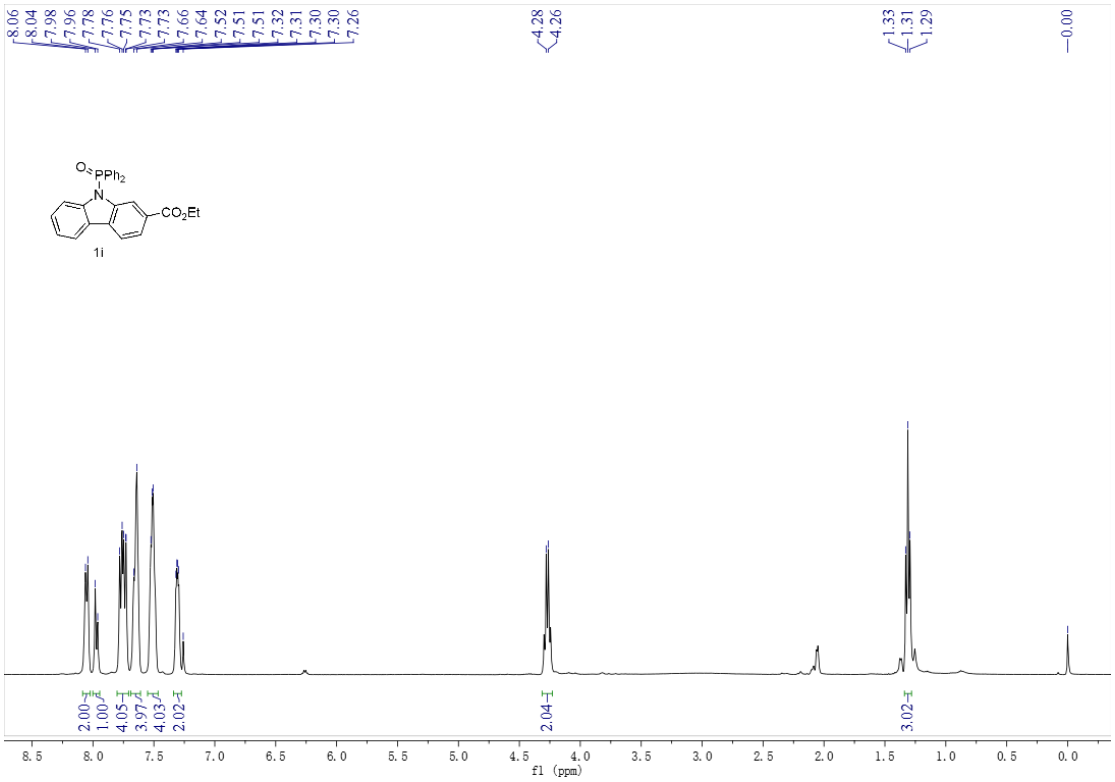
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1h



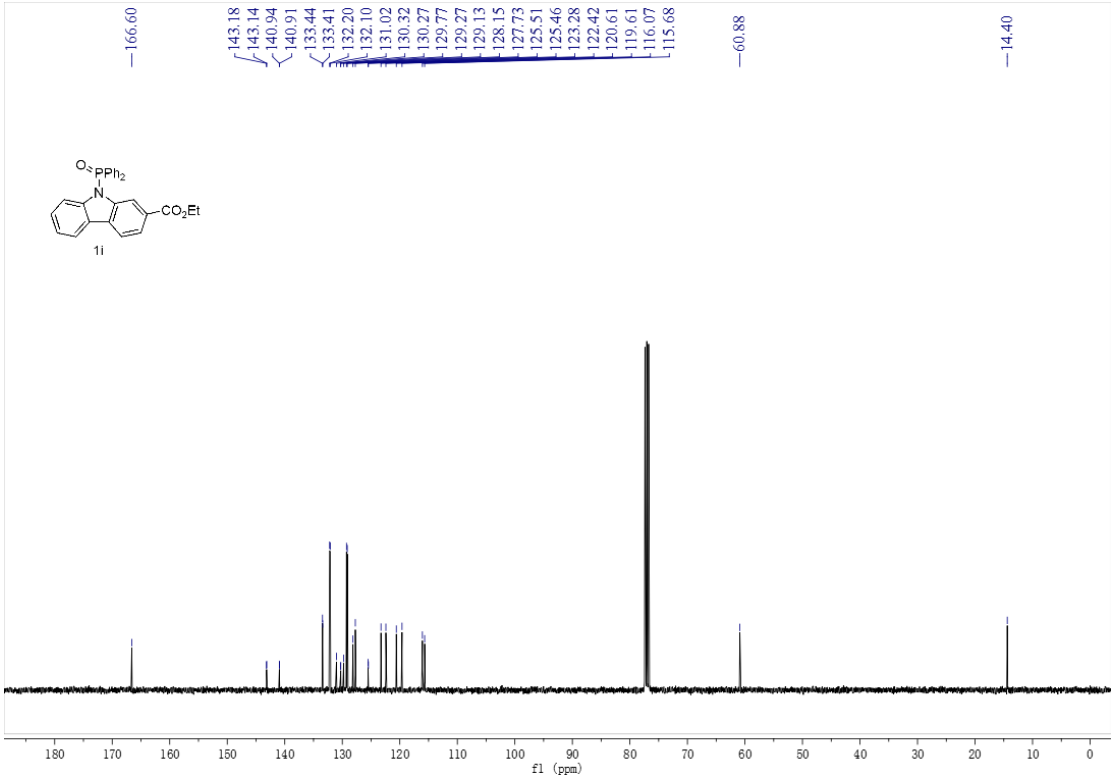
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1h



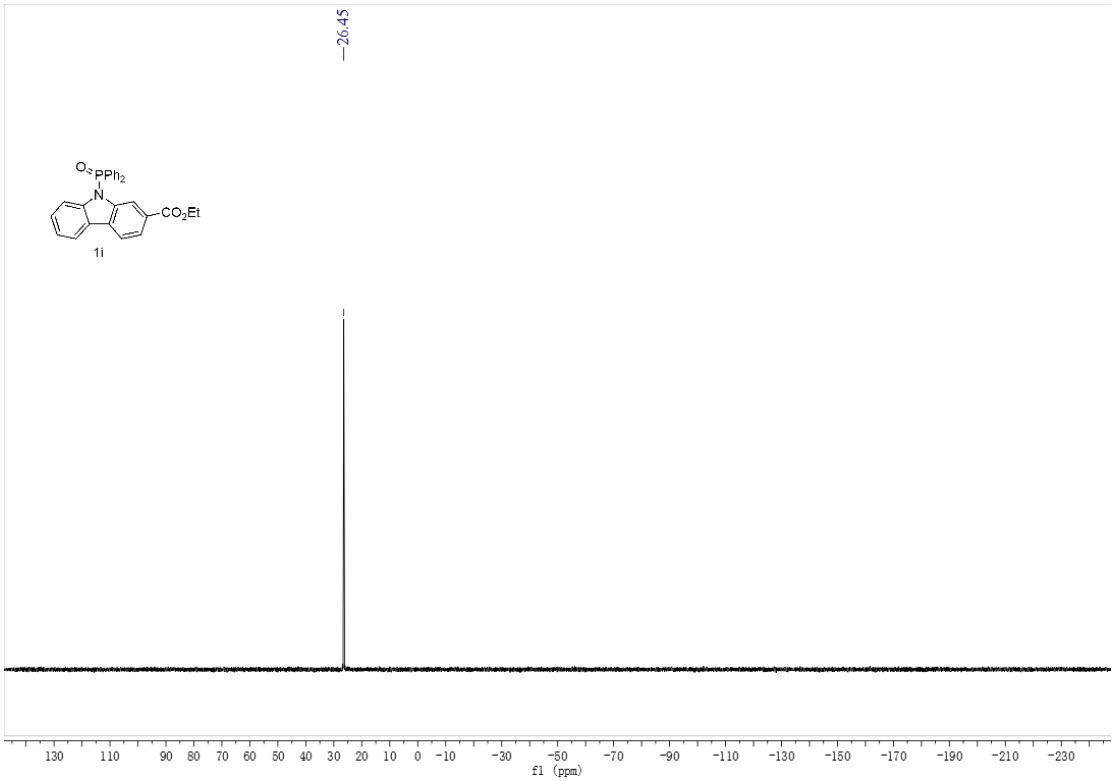
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1i



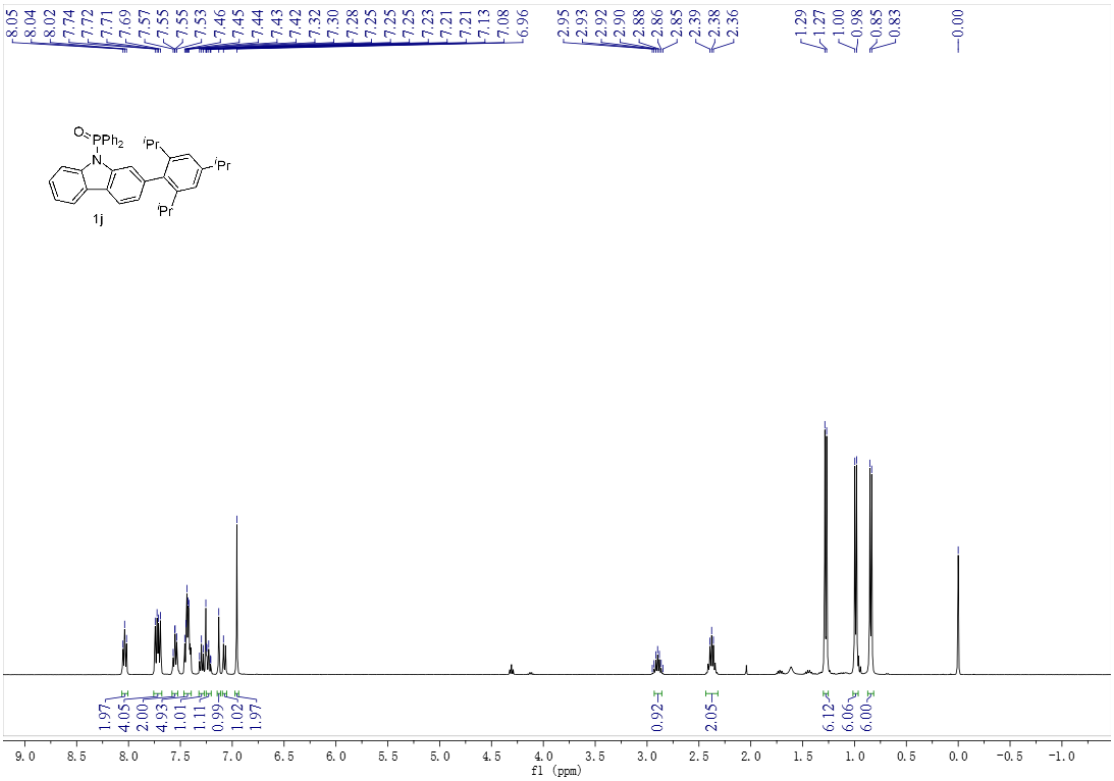
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1i



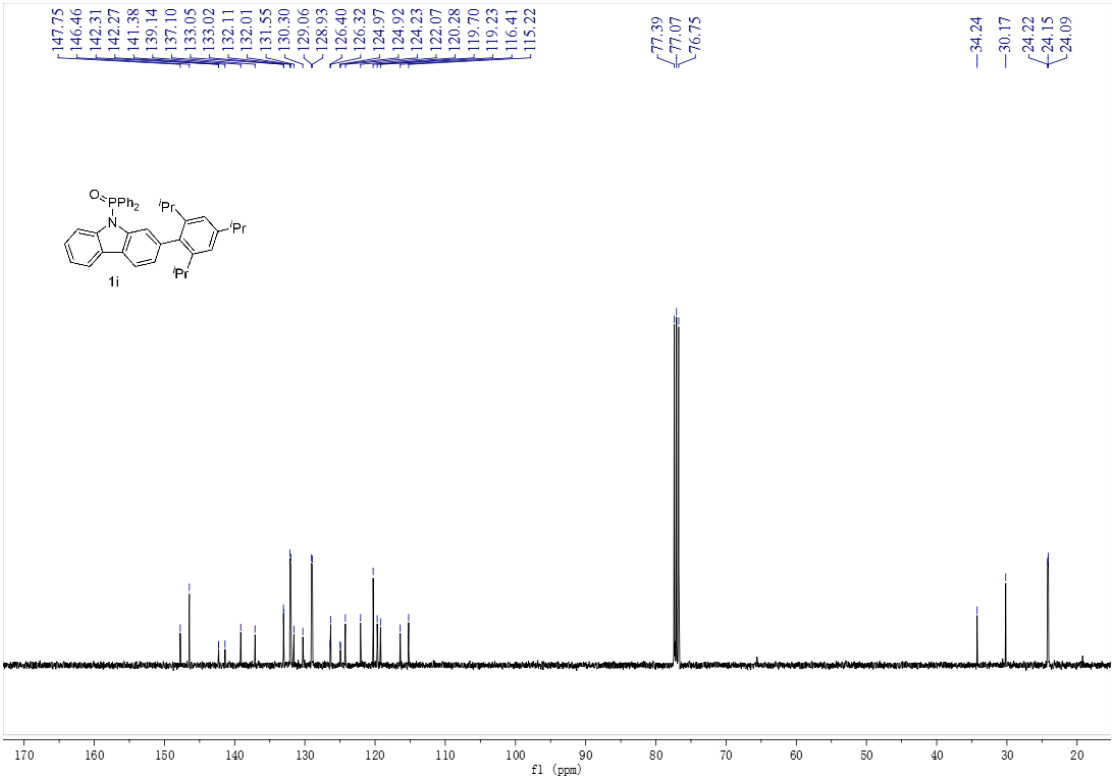
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1i



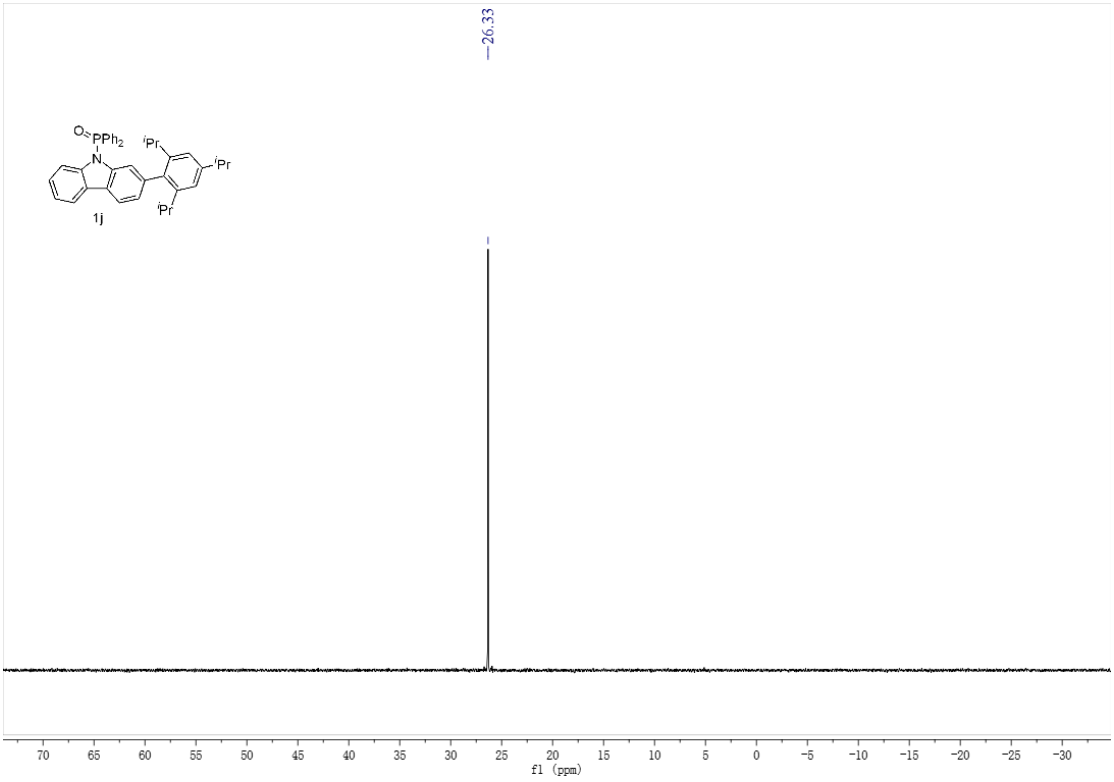
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1j



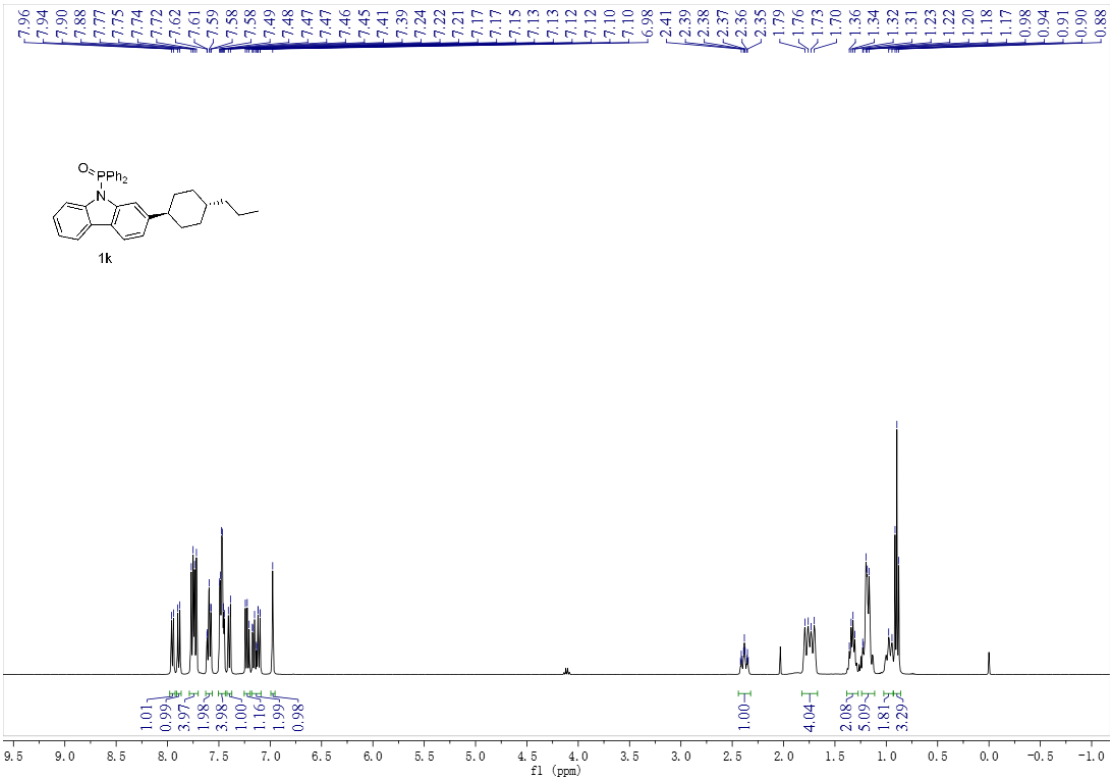
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1j



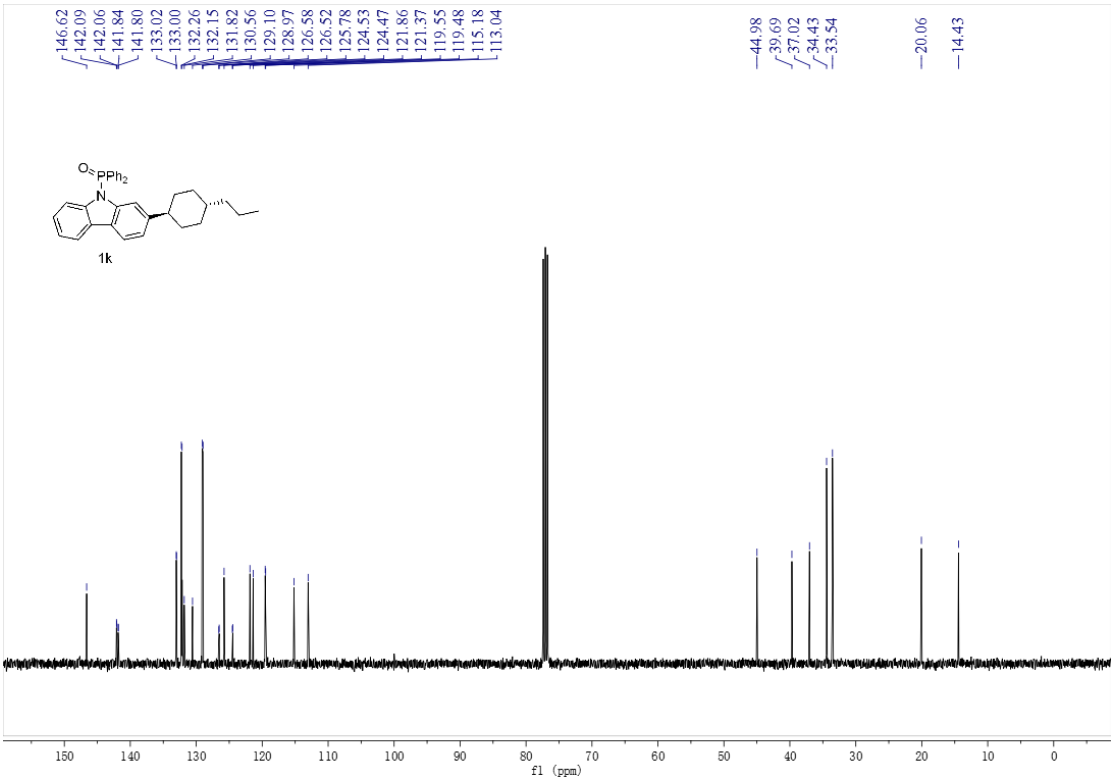
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1j



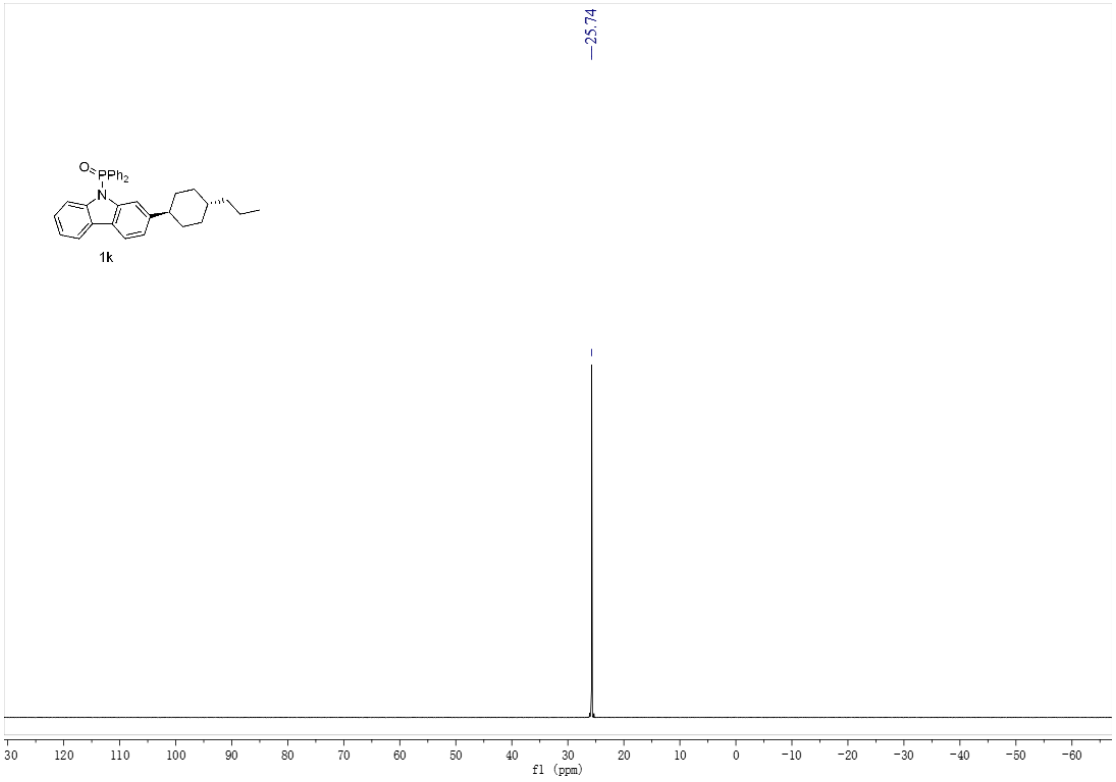
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1k



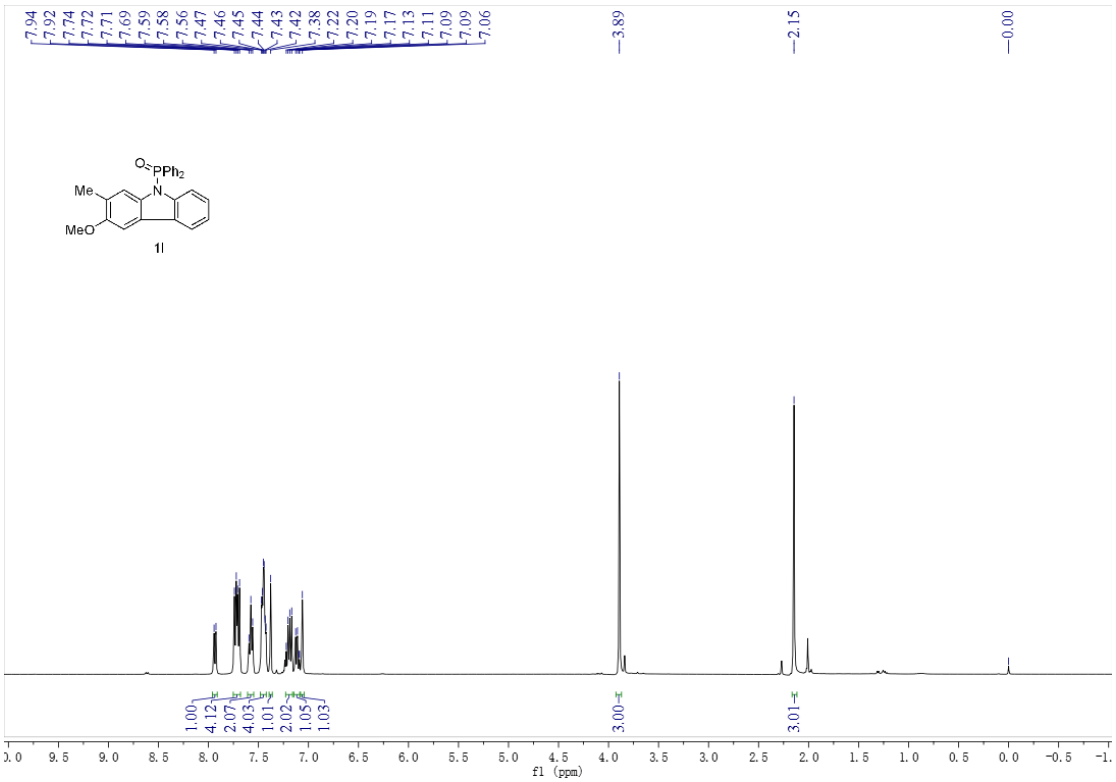
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1k



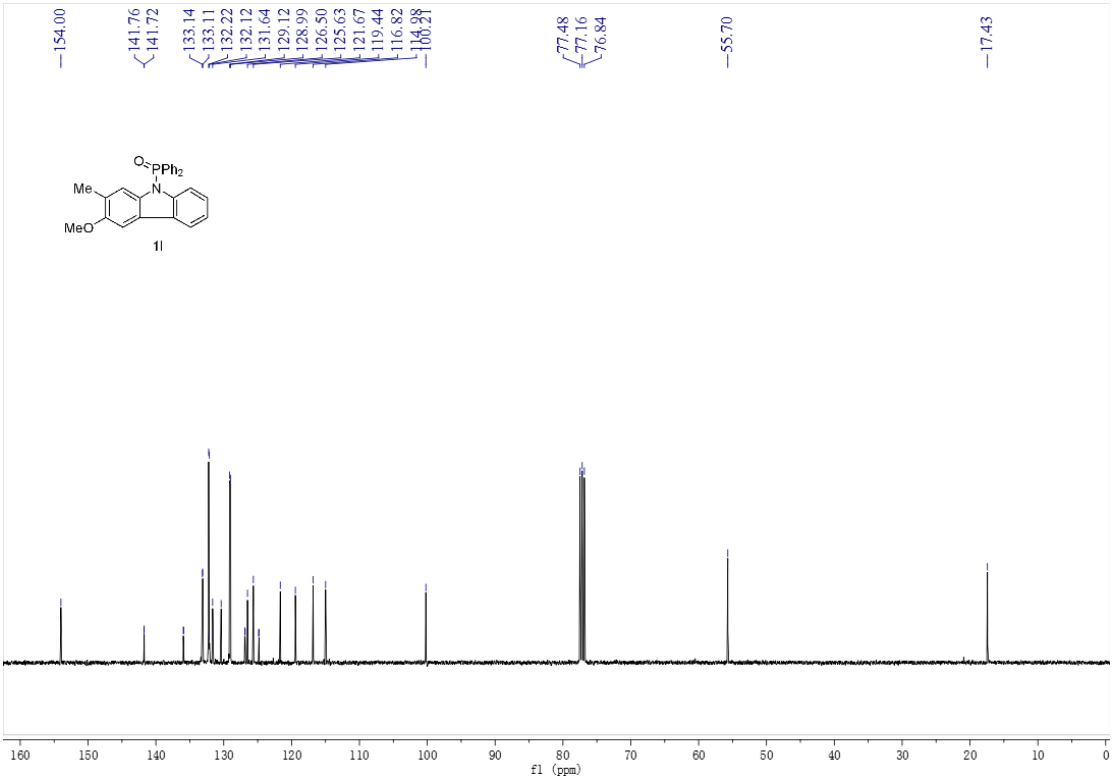
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1k



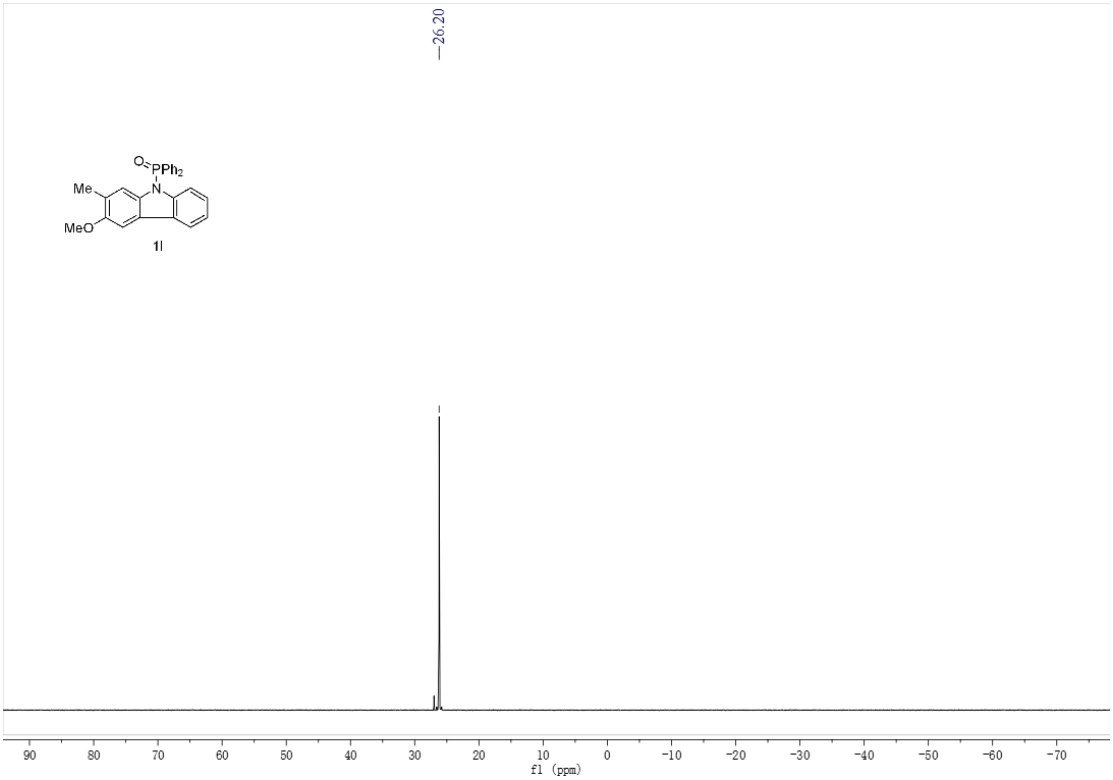
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1l



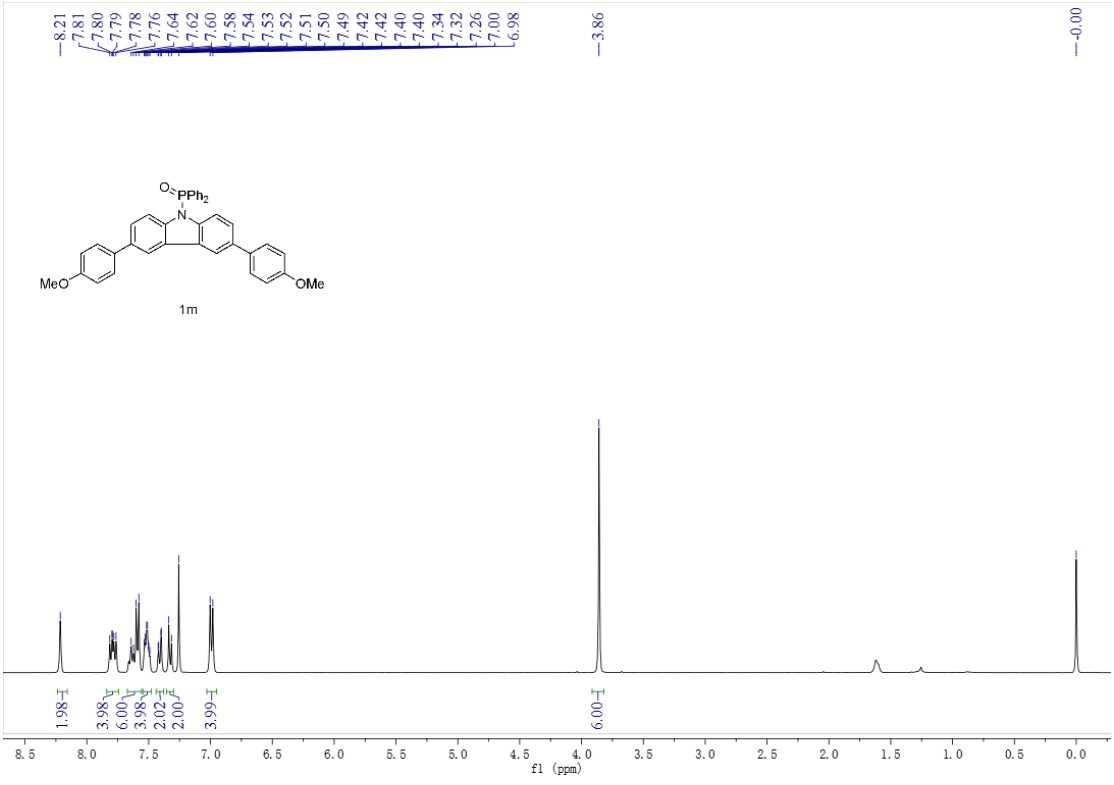
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1l



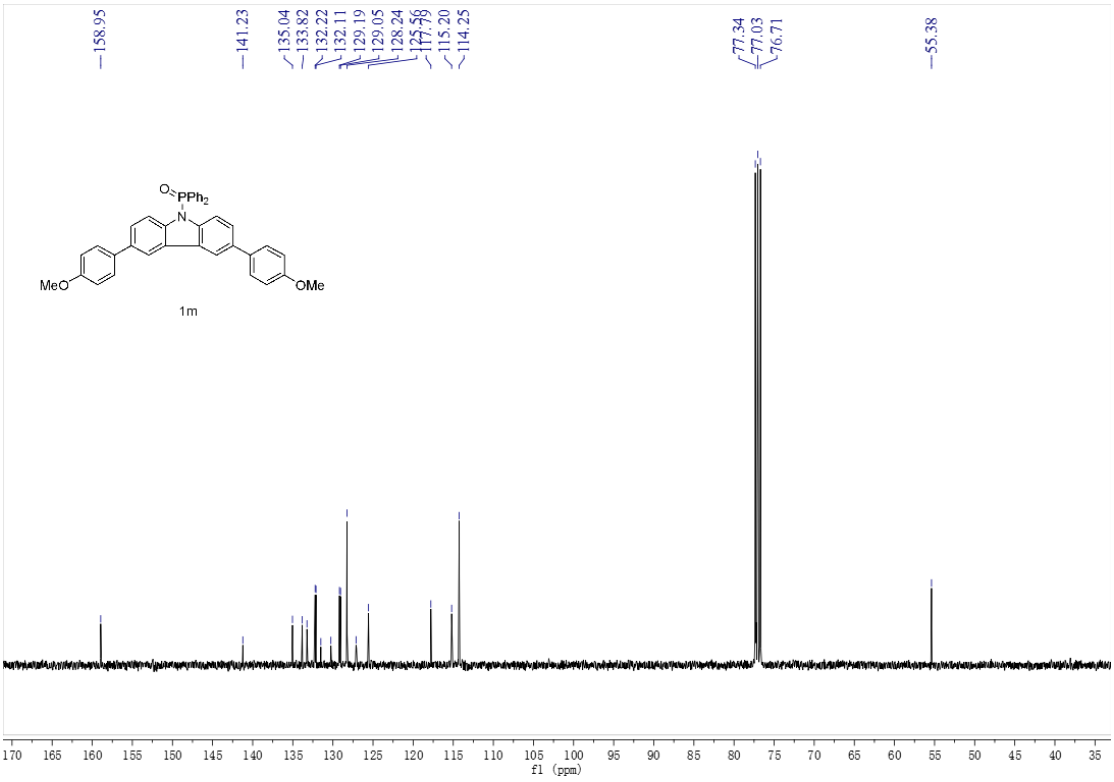
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1l



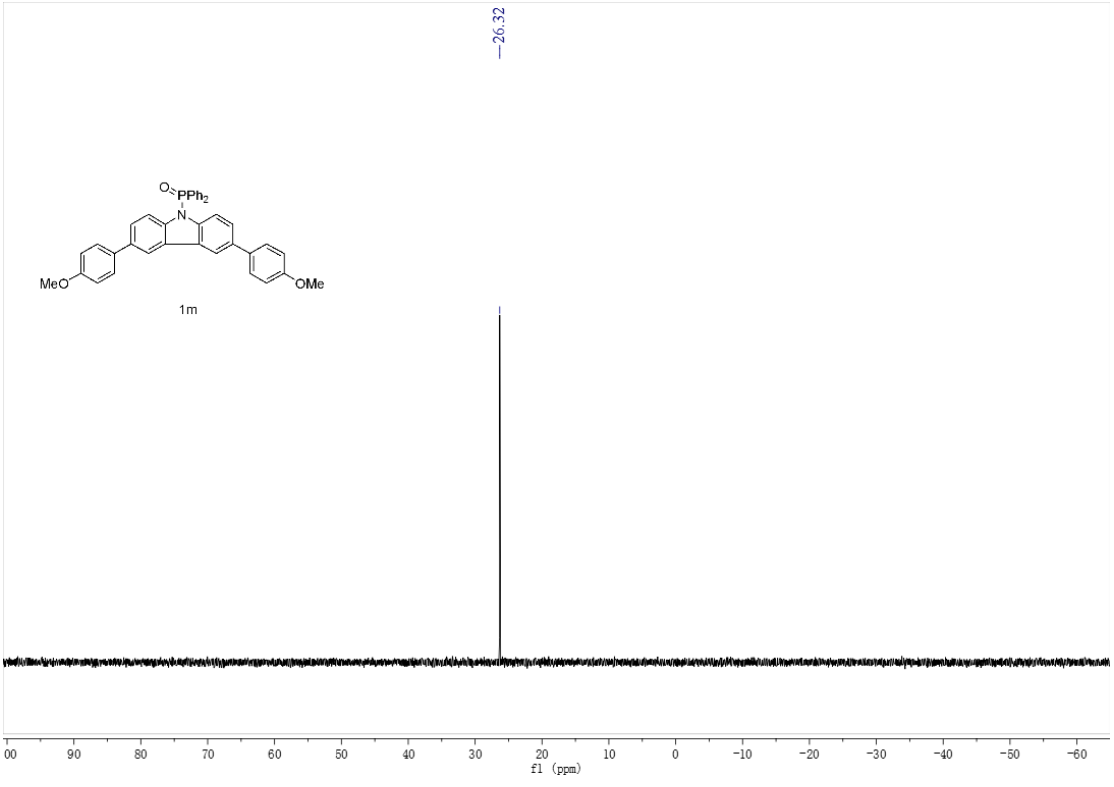
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1m



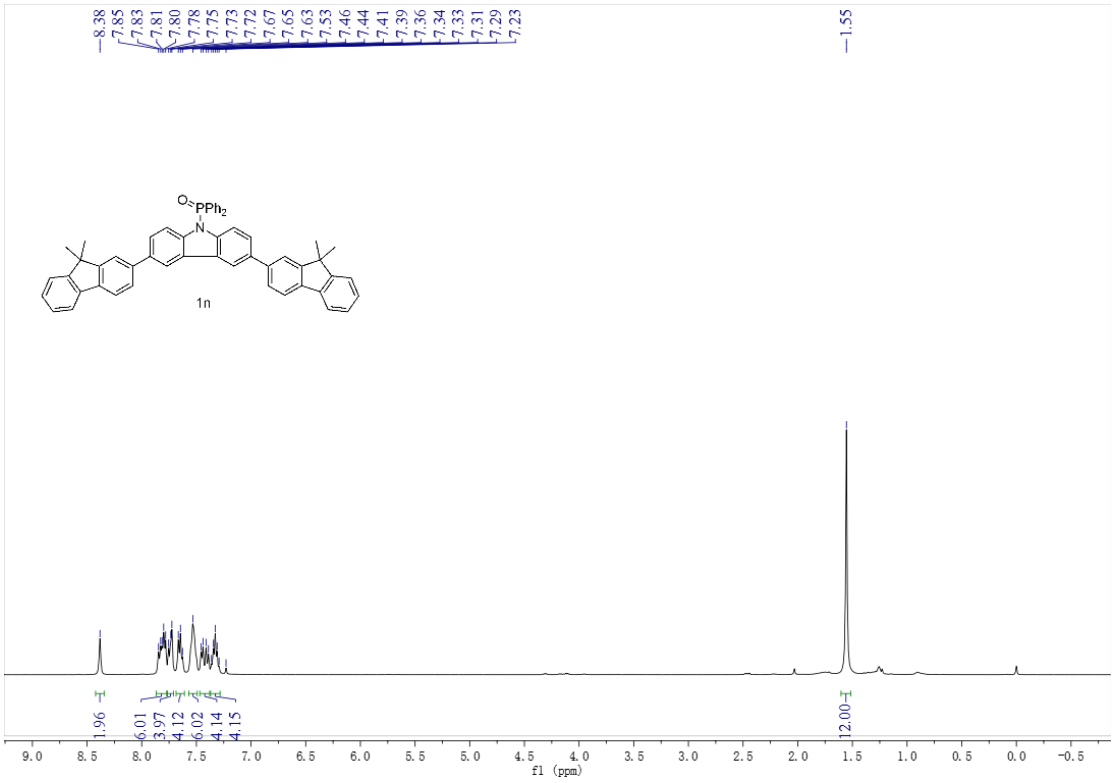
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1m



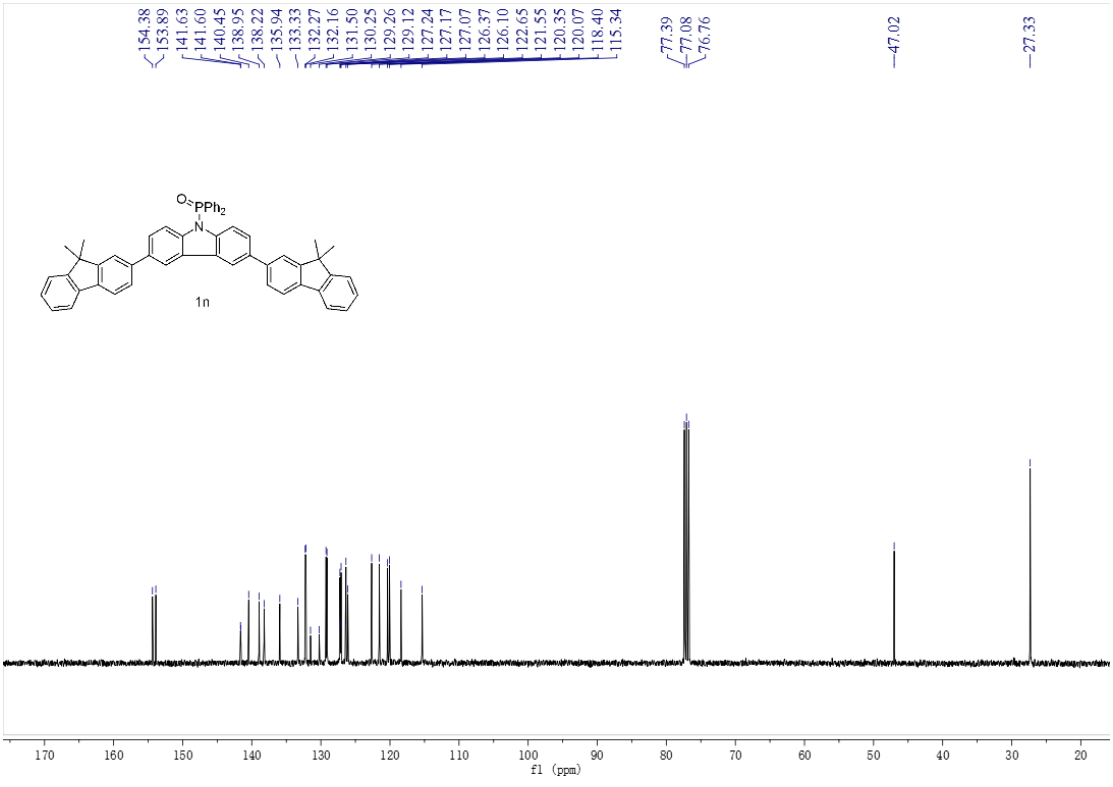
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1m



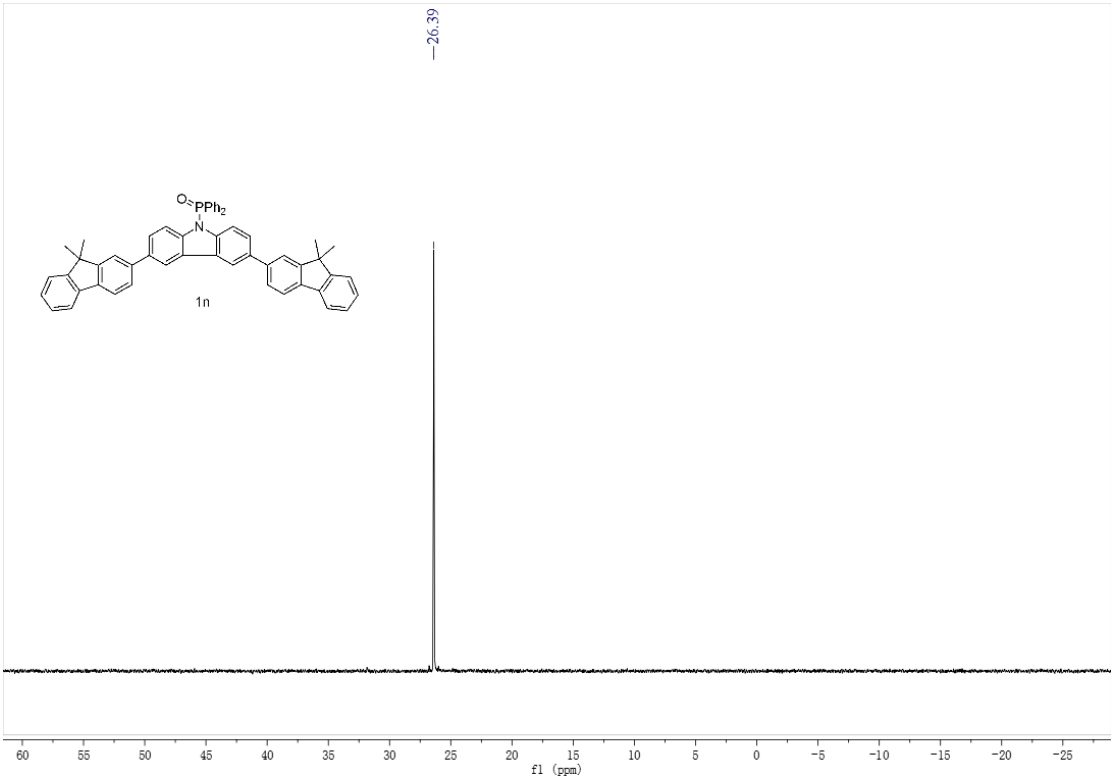
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1n



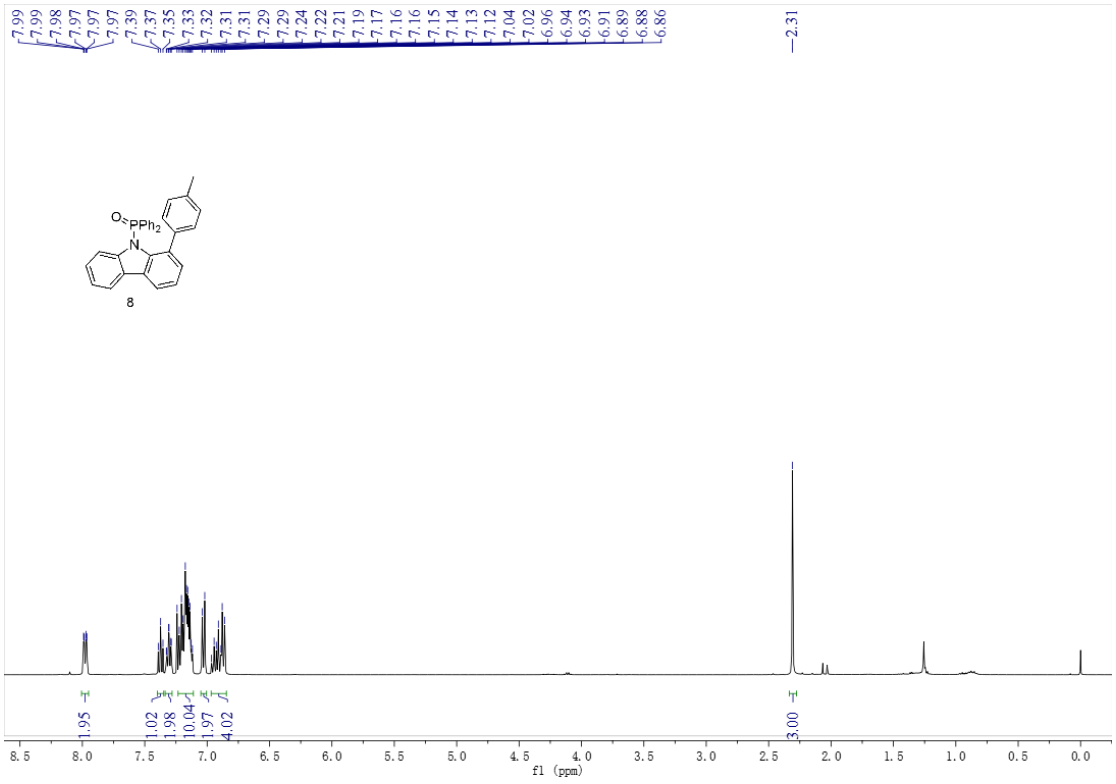
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 1n



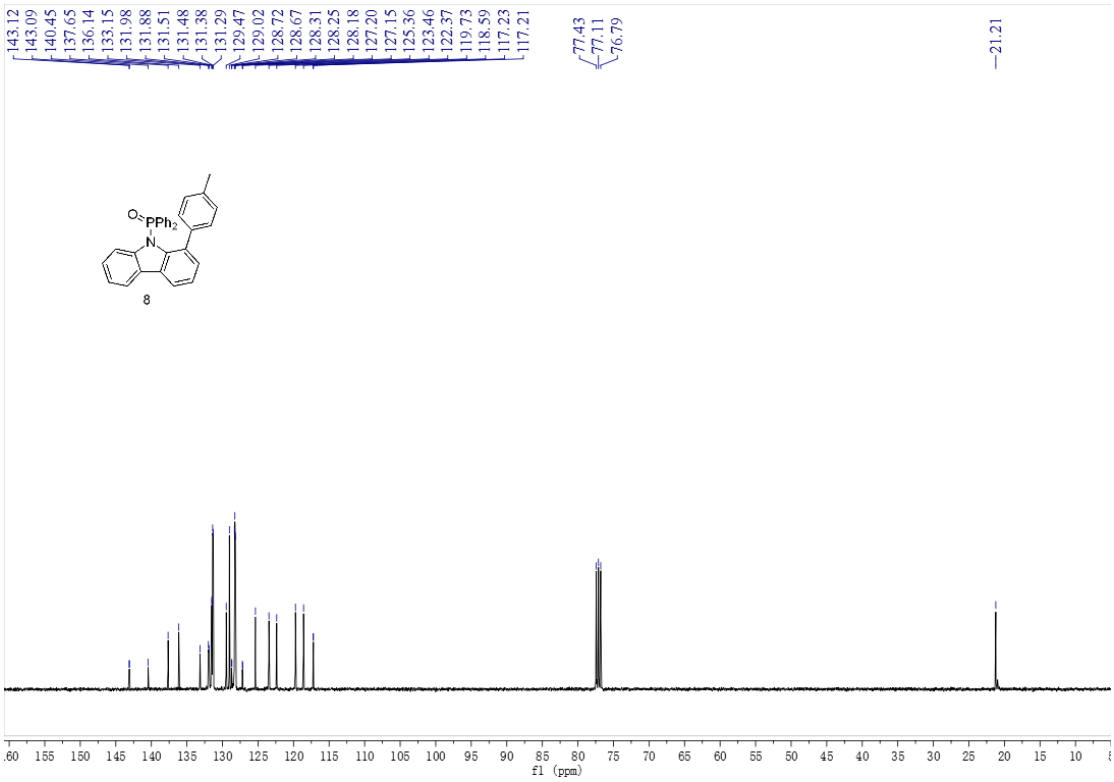
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 1n



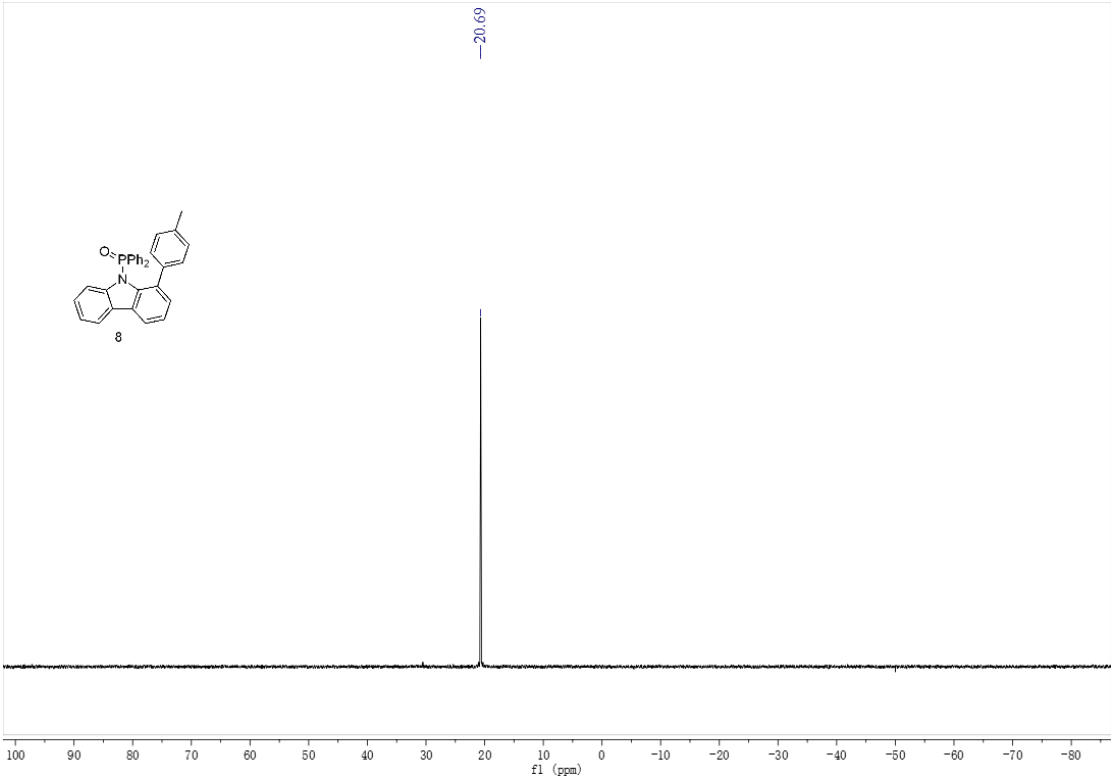
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 8



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 8

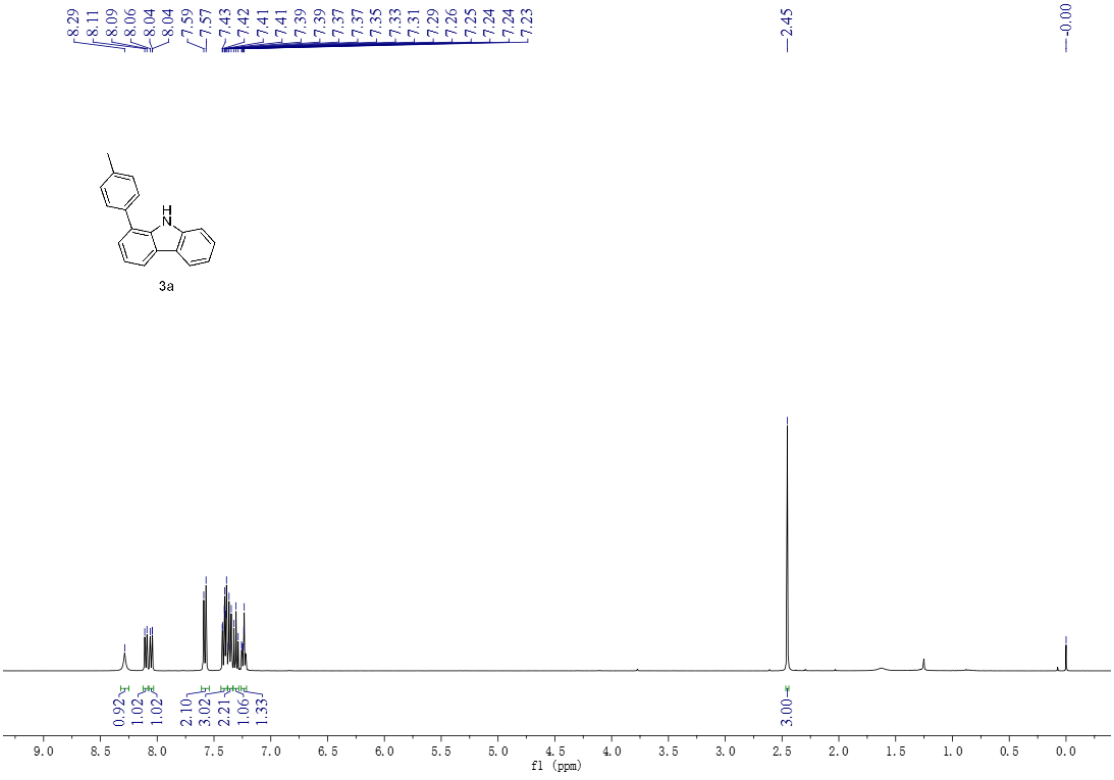


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 8

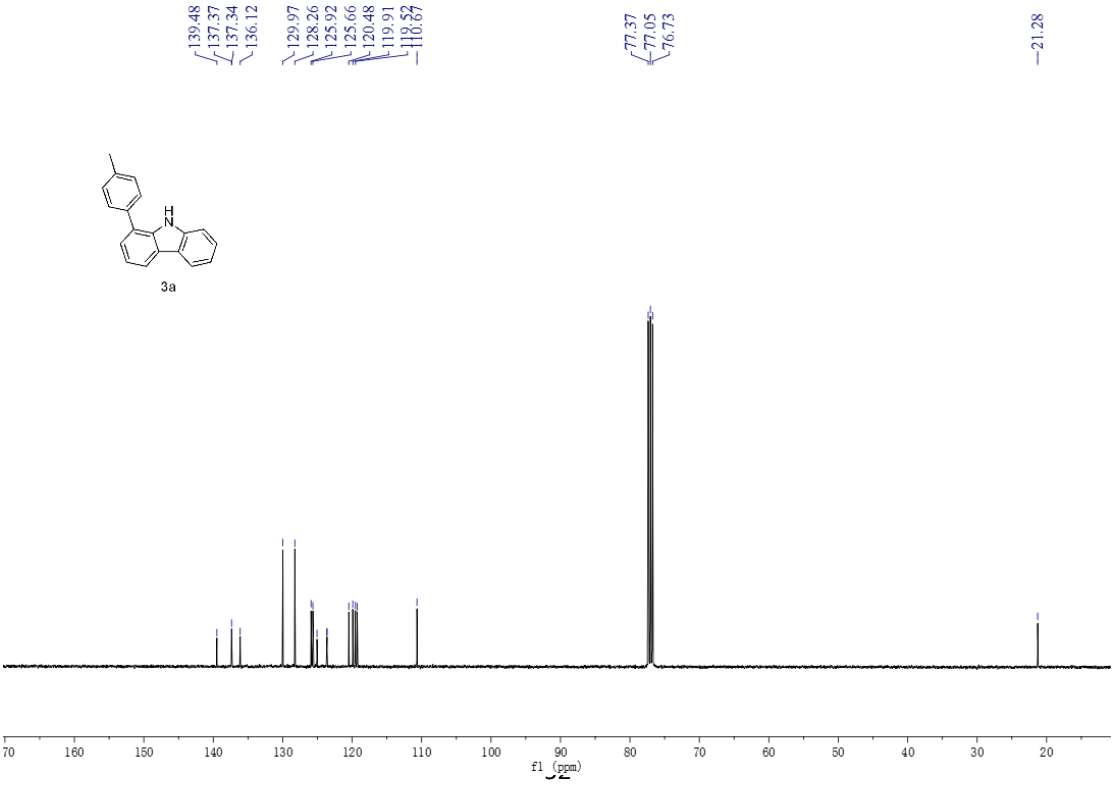


12.2 Copies of NMR Spectra of Products.

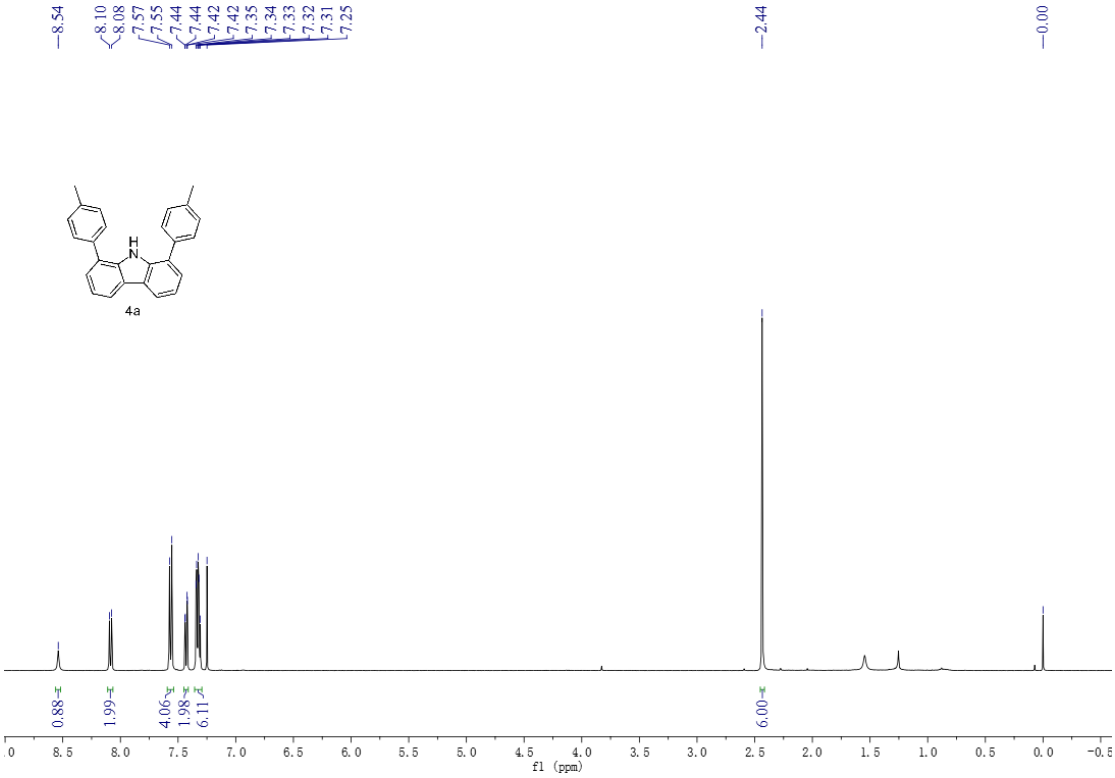
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



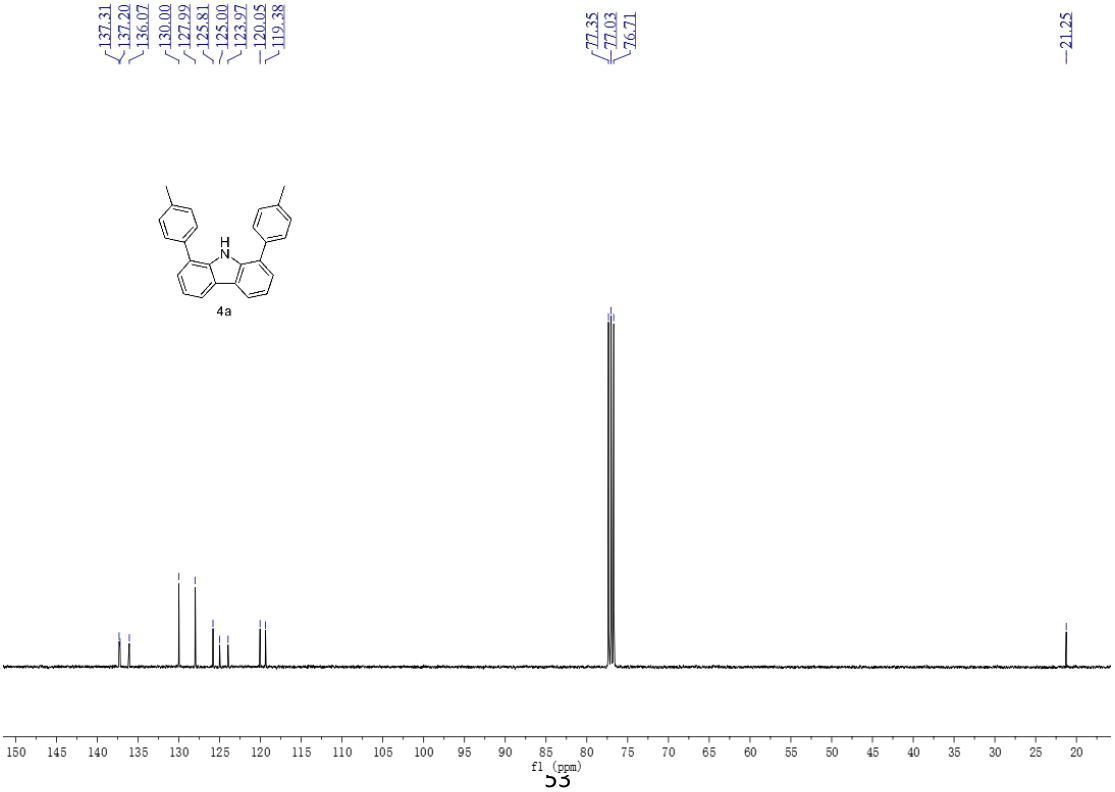
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3a



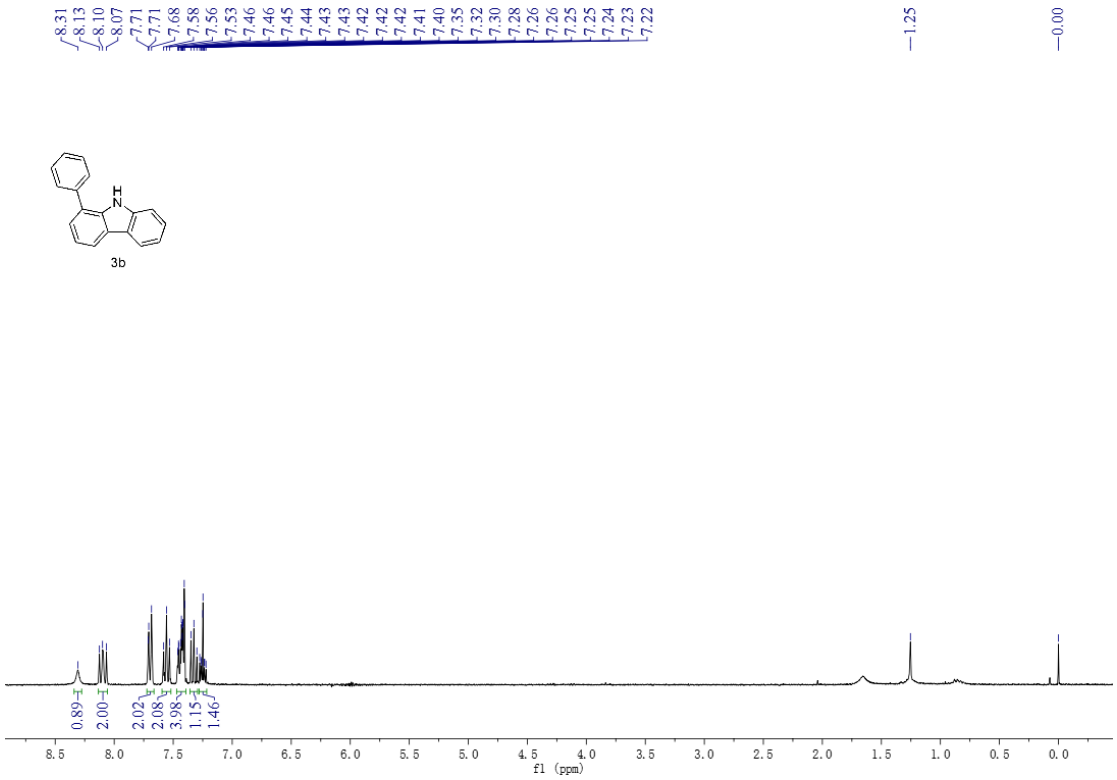
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4a



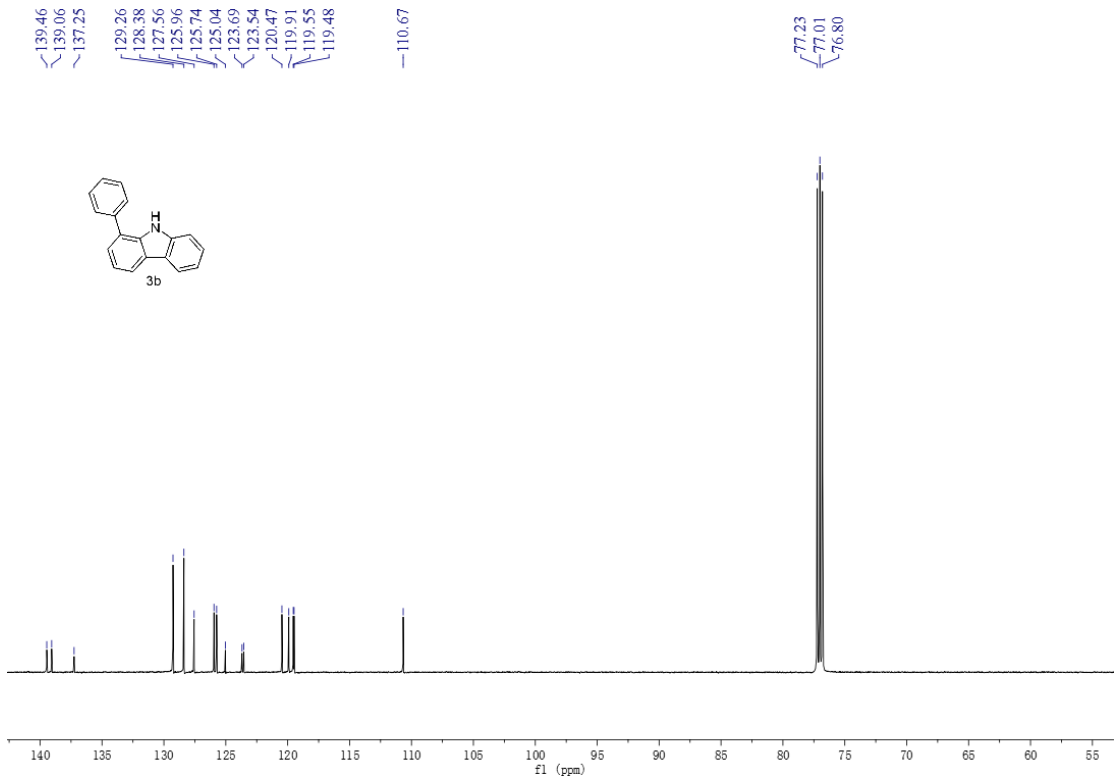
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4a



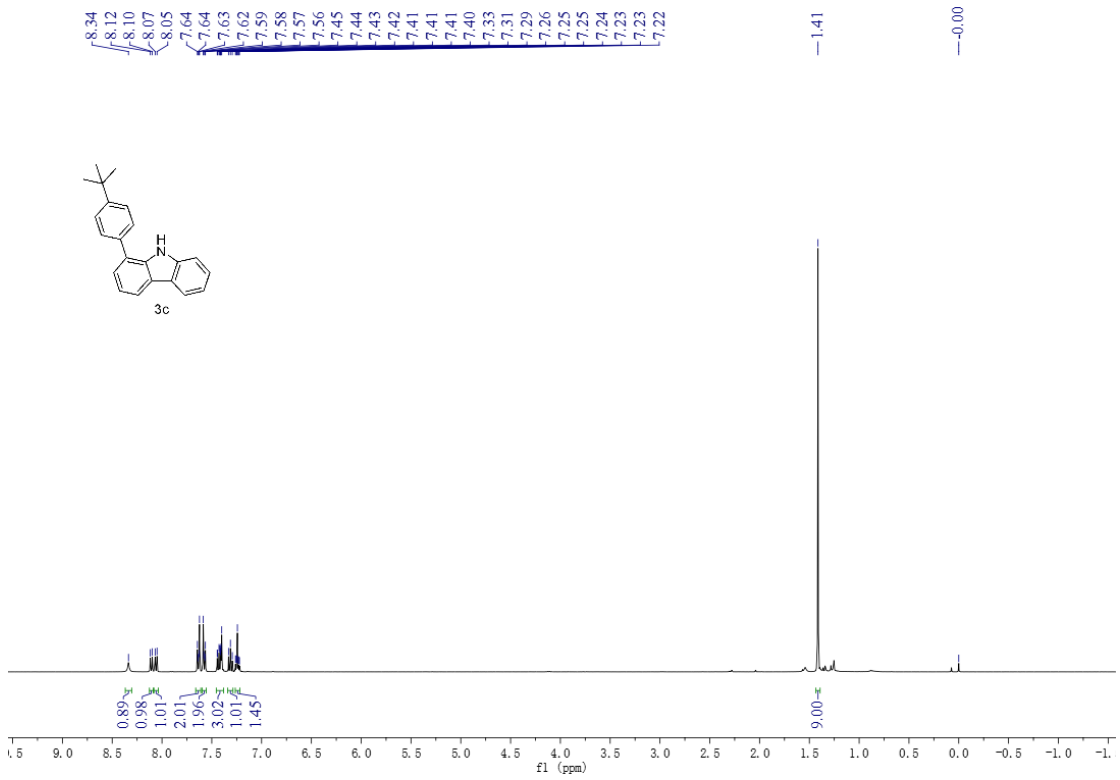
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b



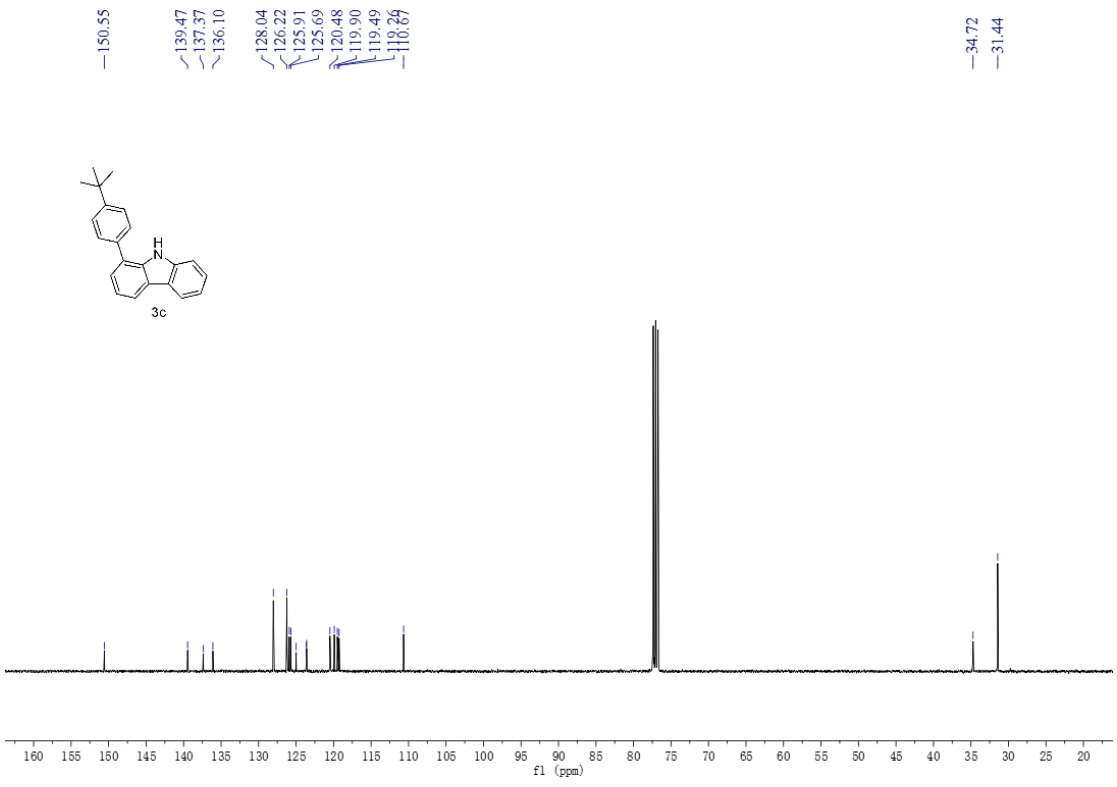
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3b



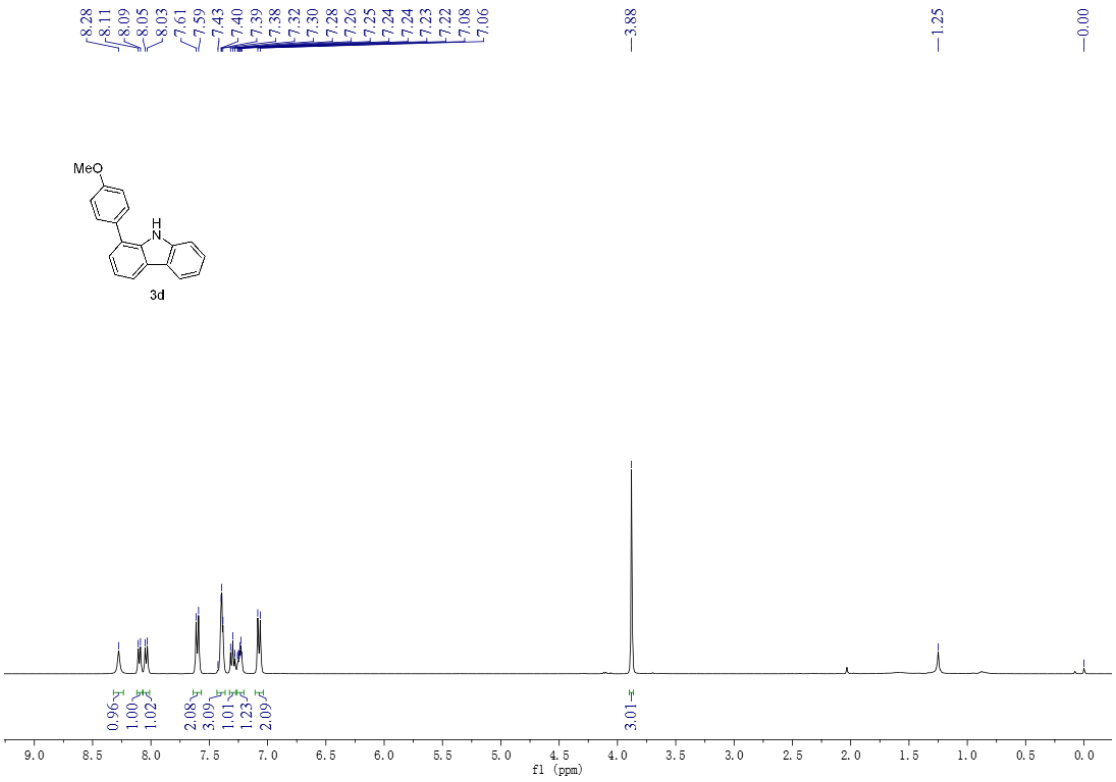
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c



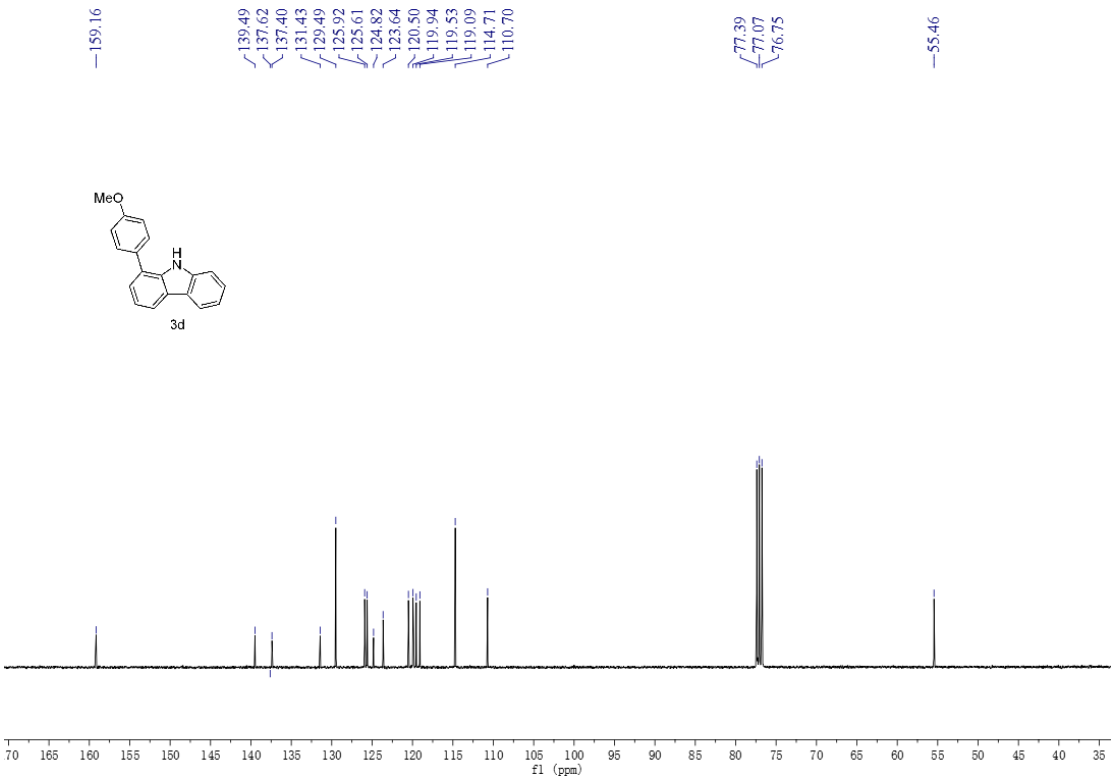
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3c



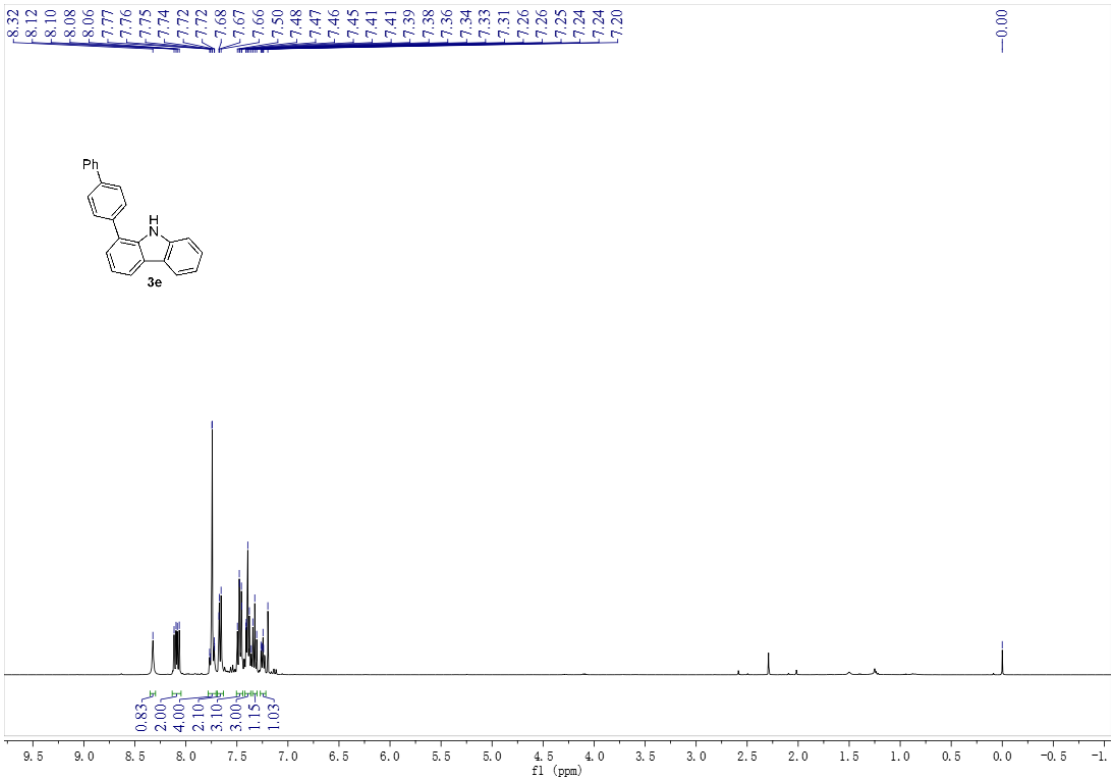
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3d



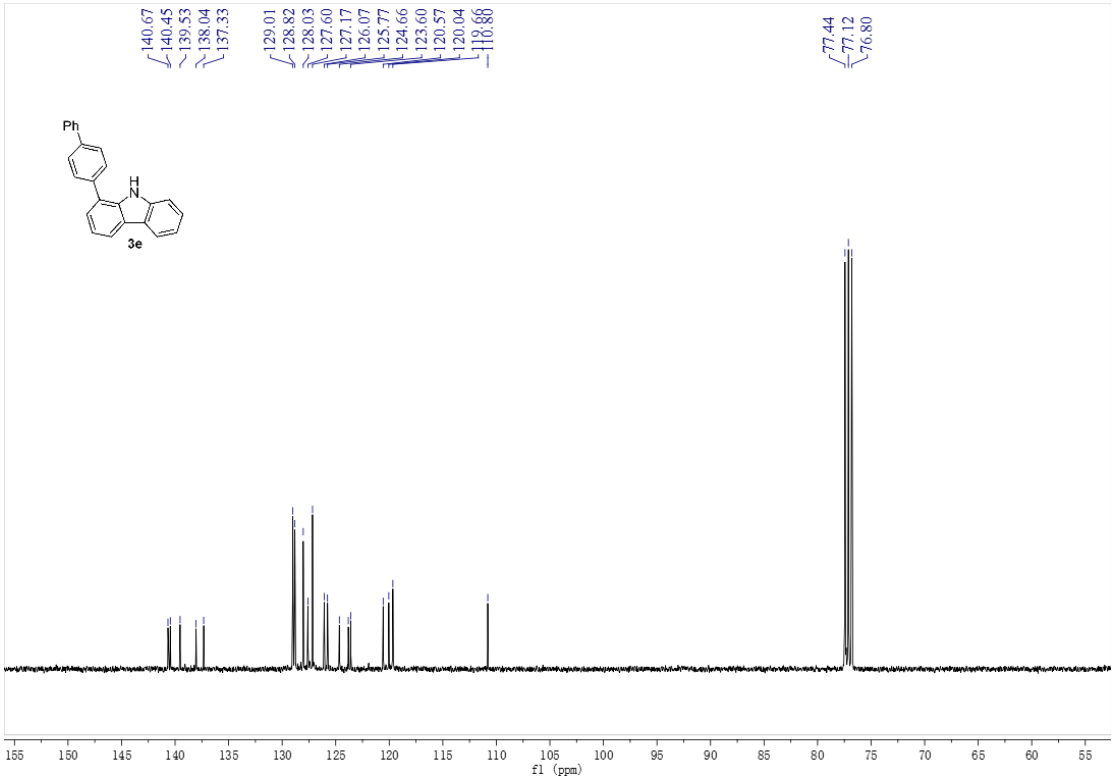
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3d



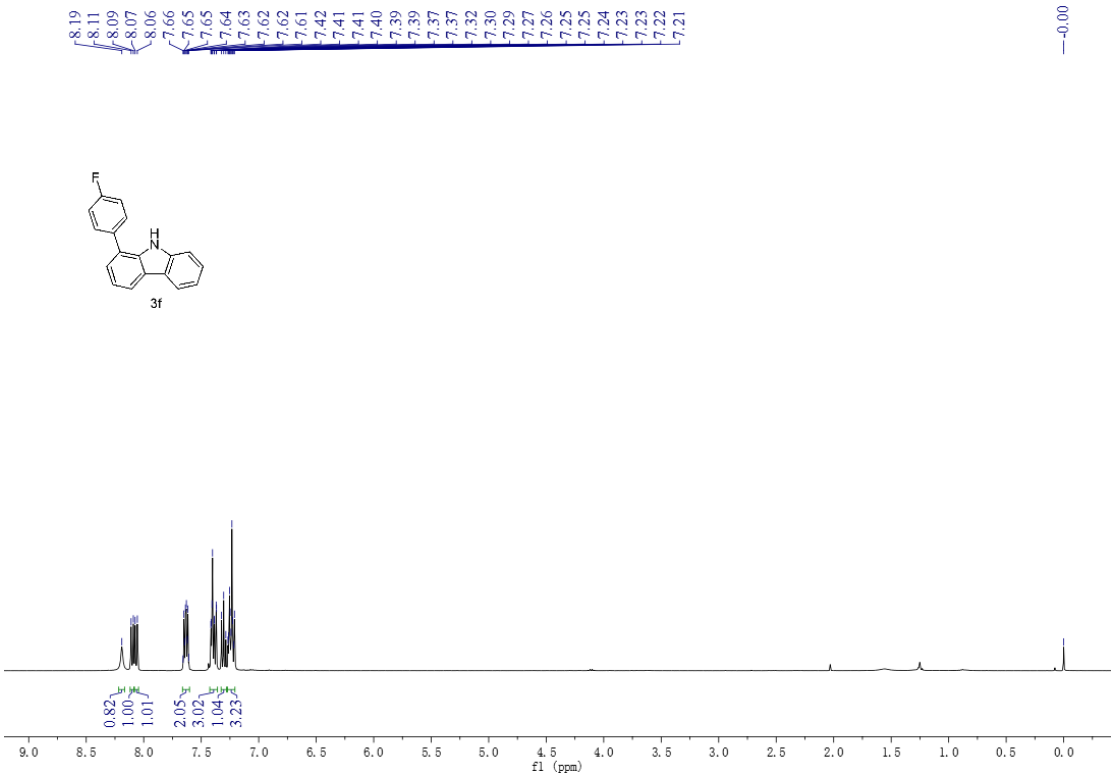
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e



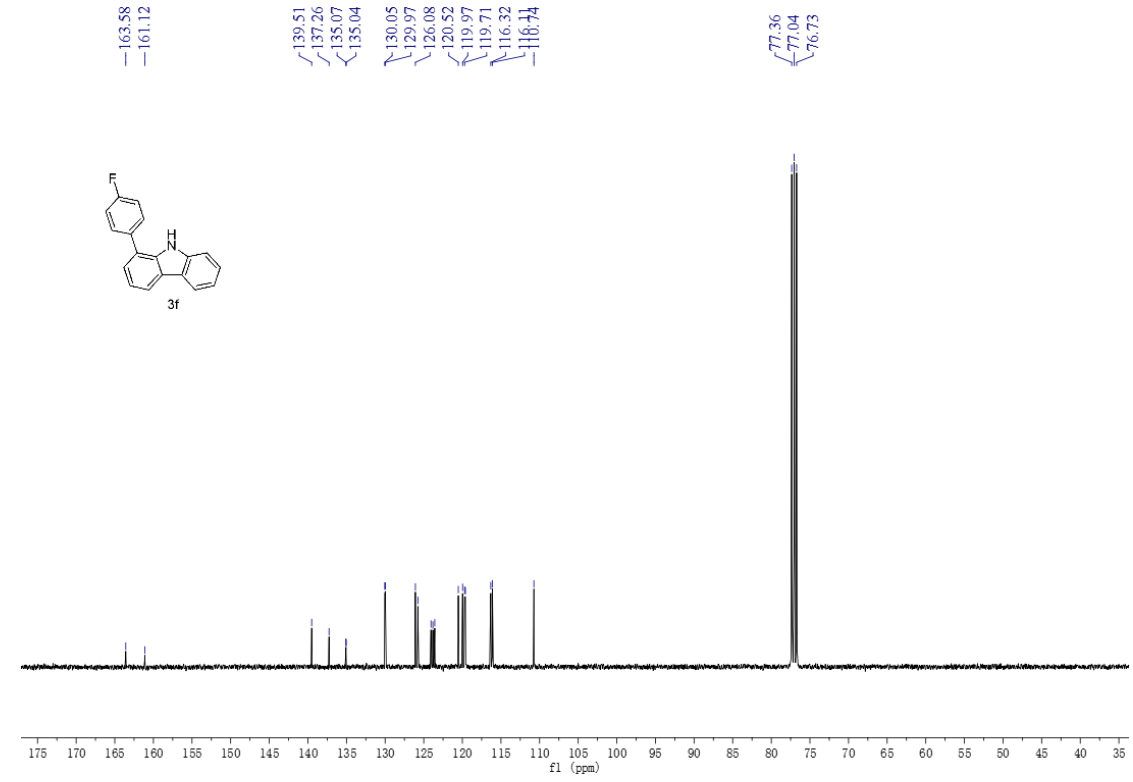
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3e



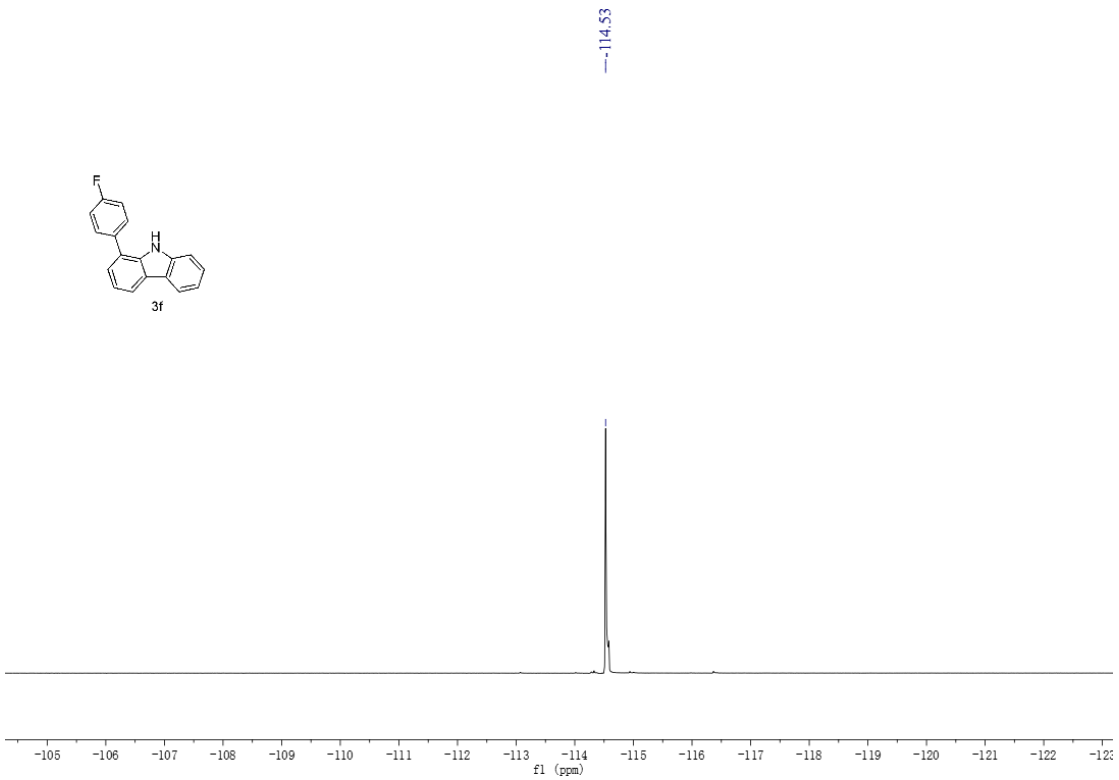
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f



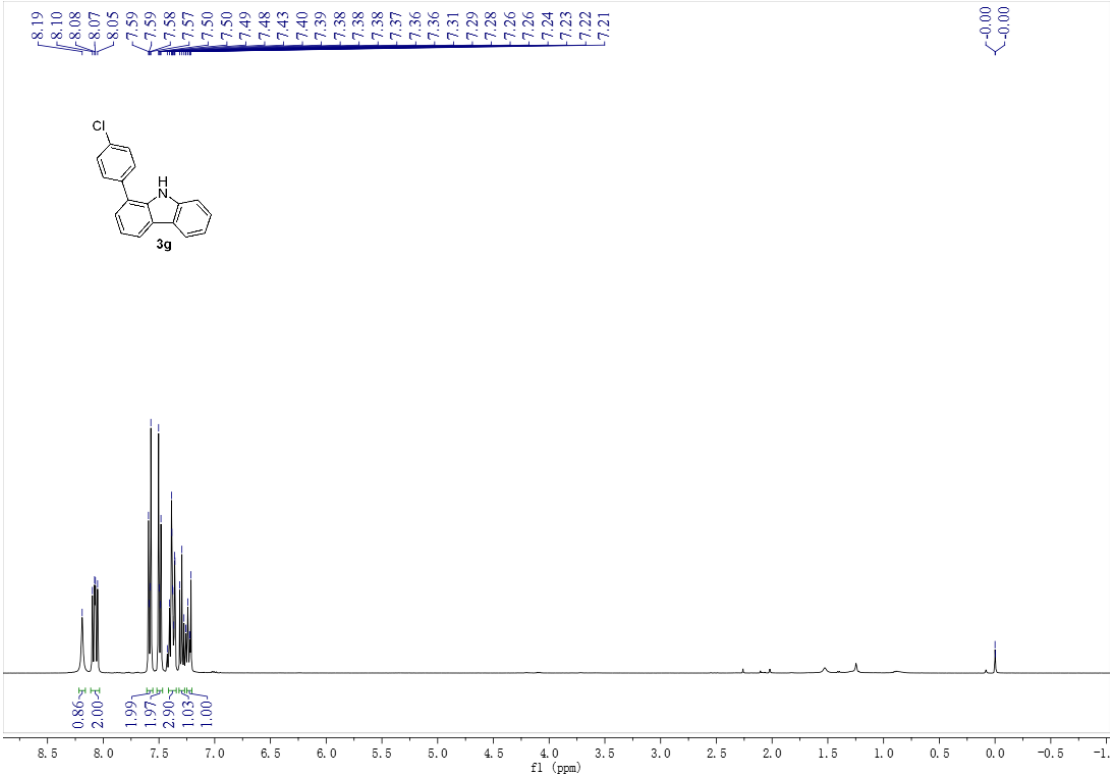
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3f



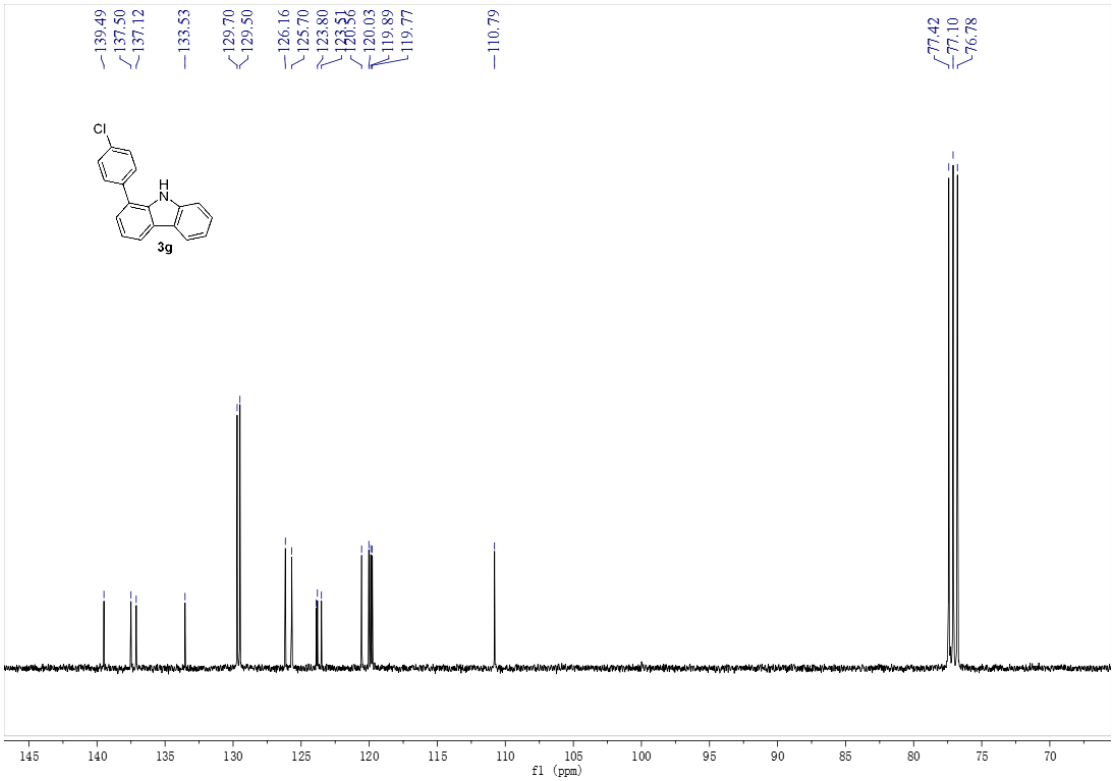
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3f



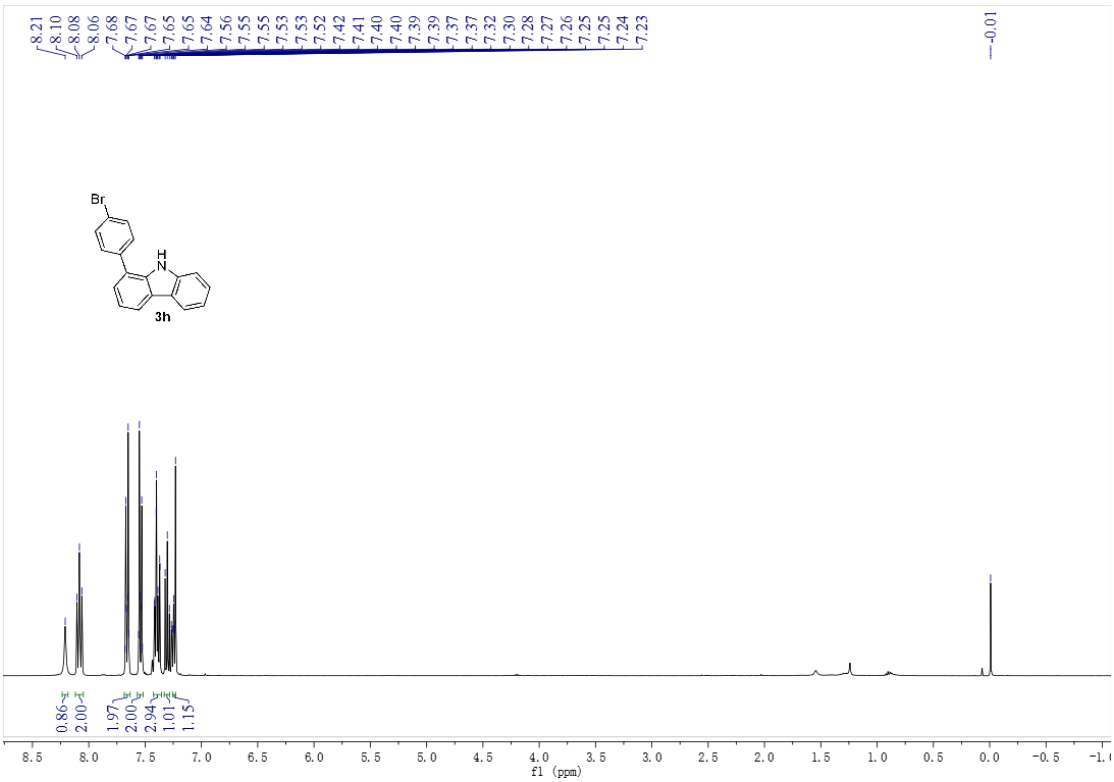
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g



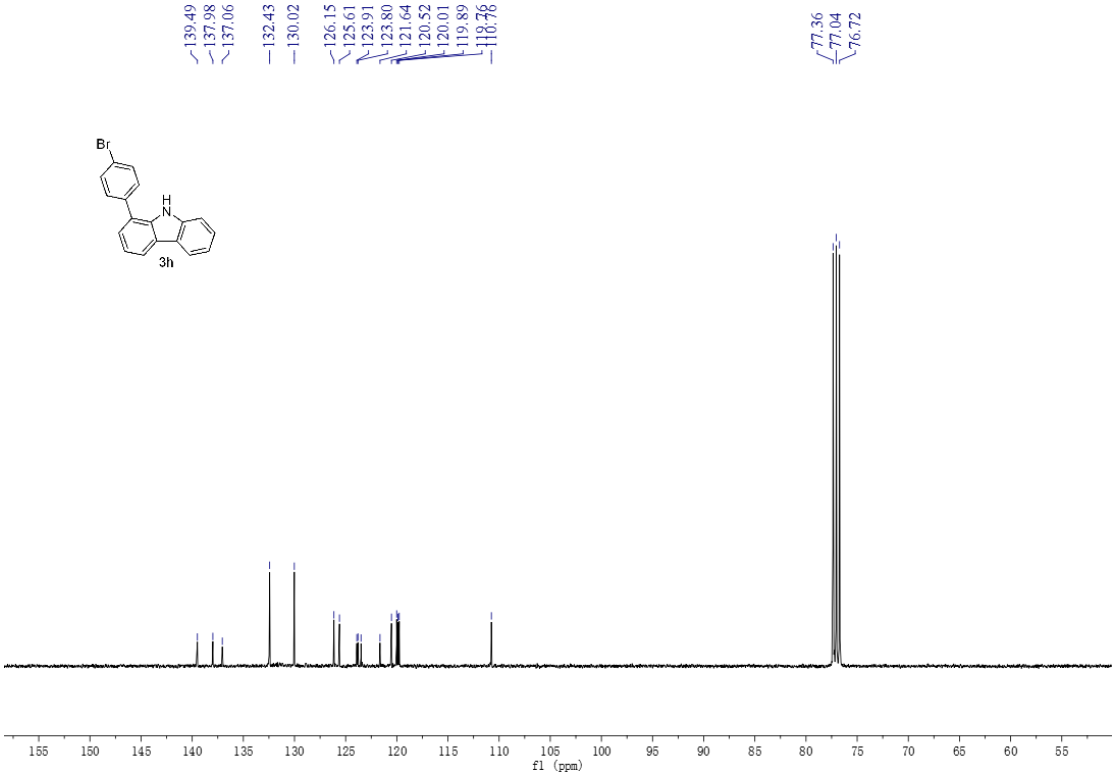
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3g



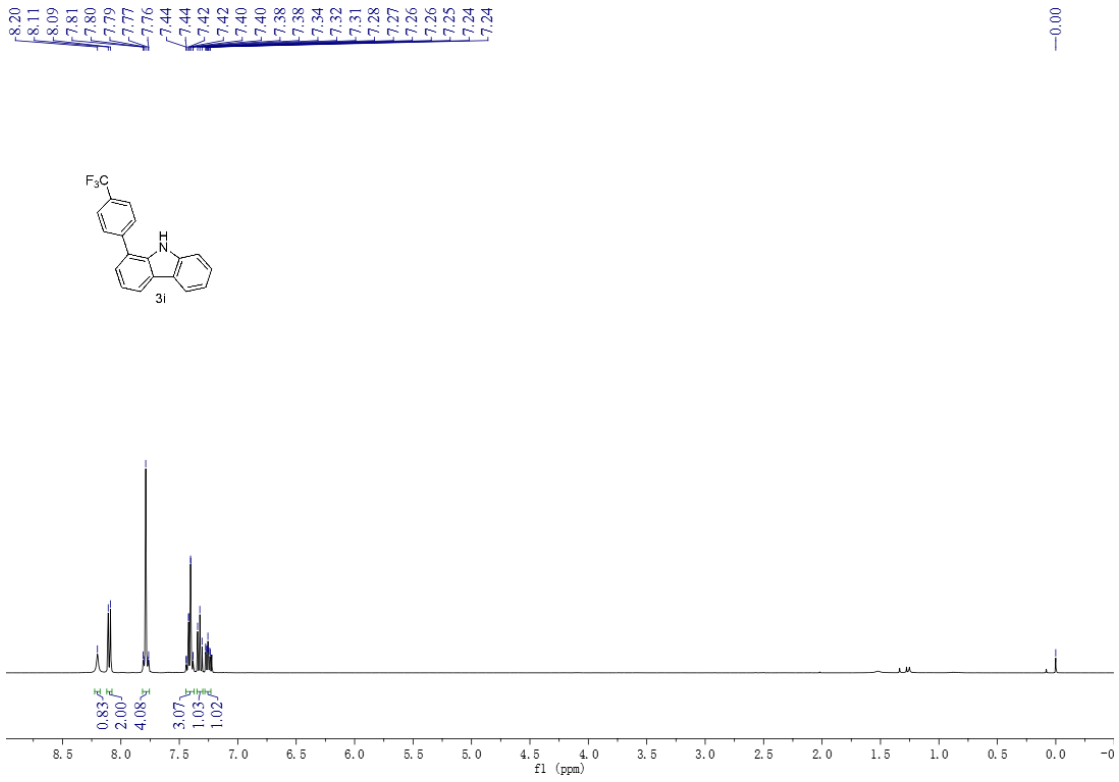
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



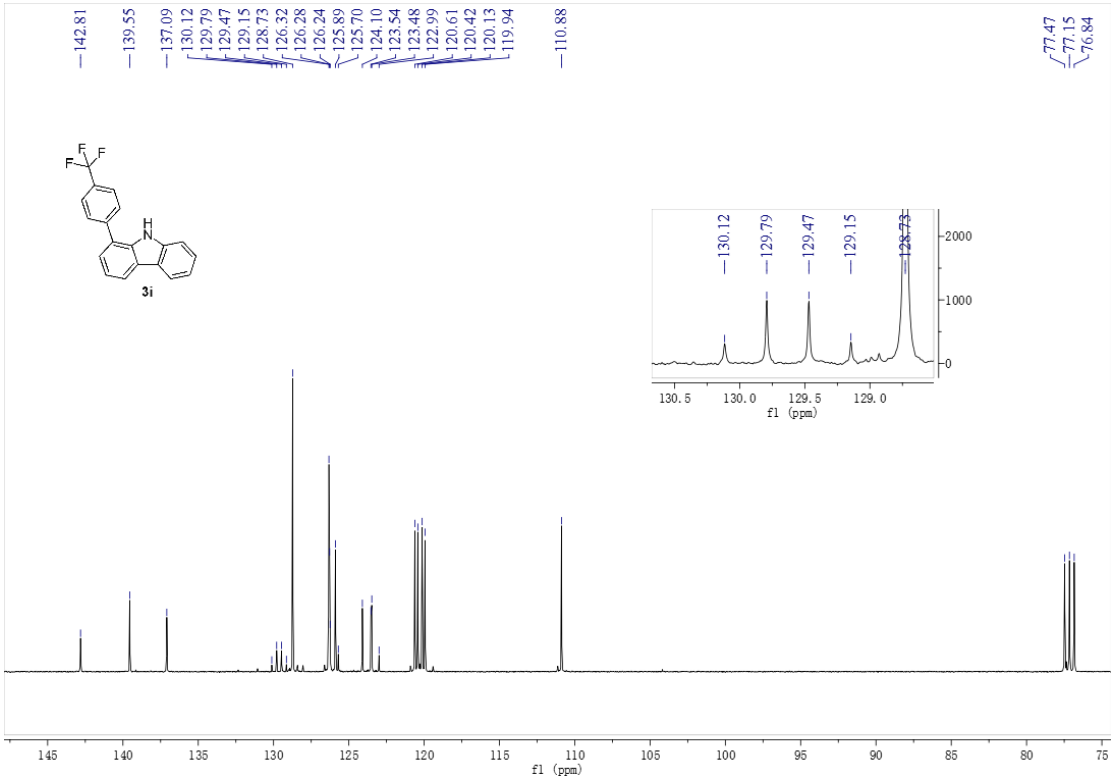
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3h



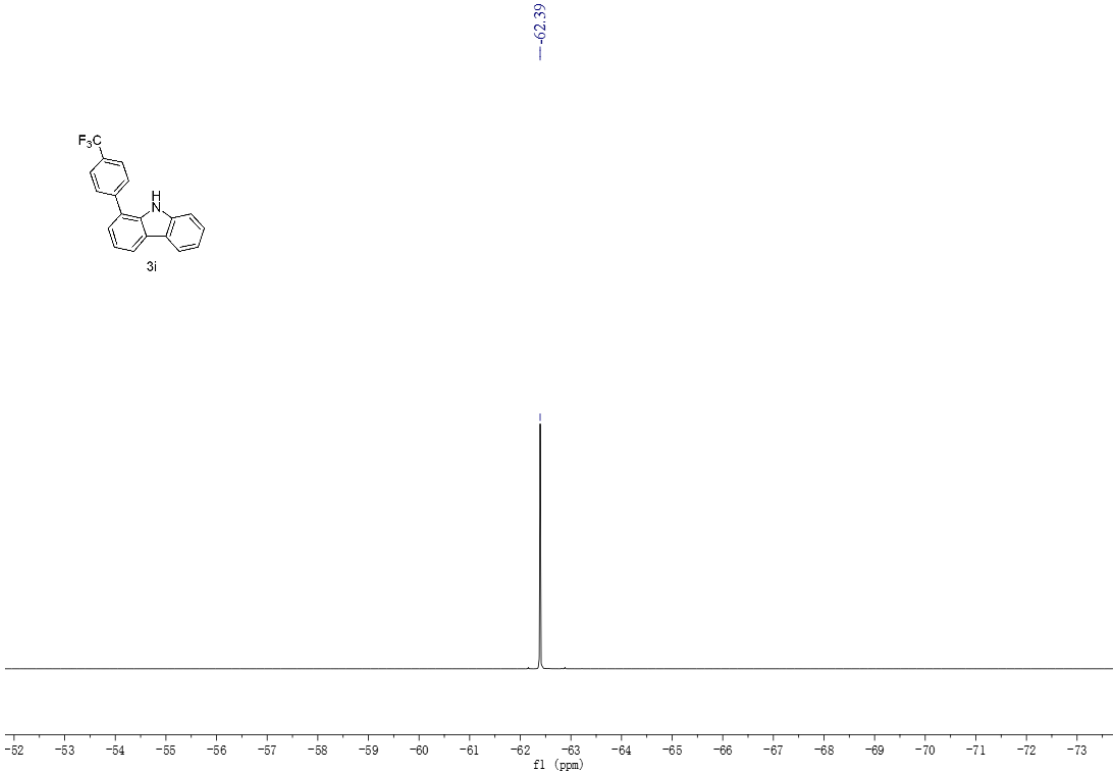
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i



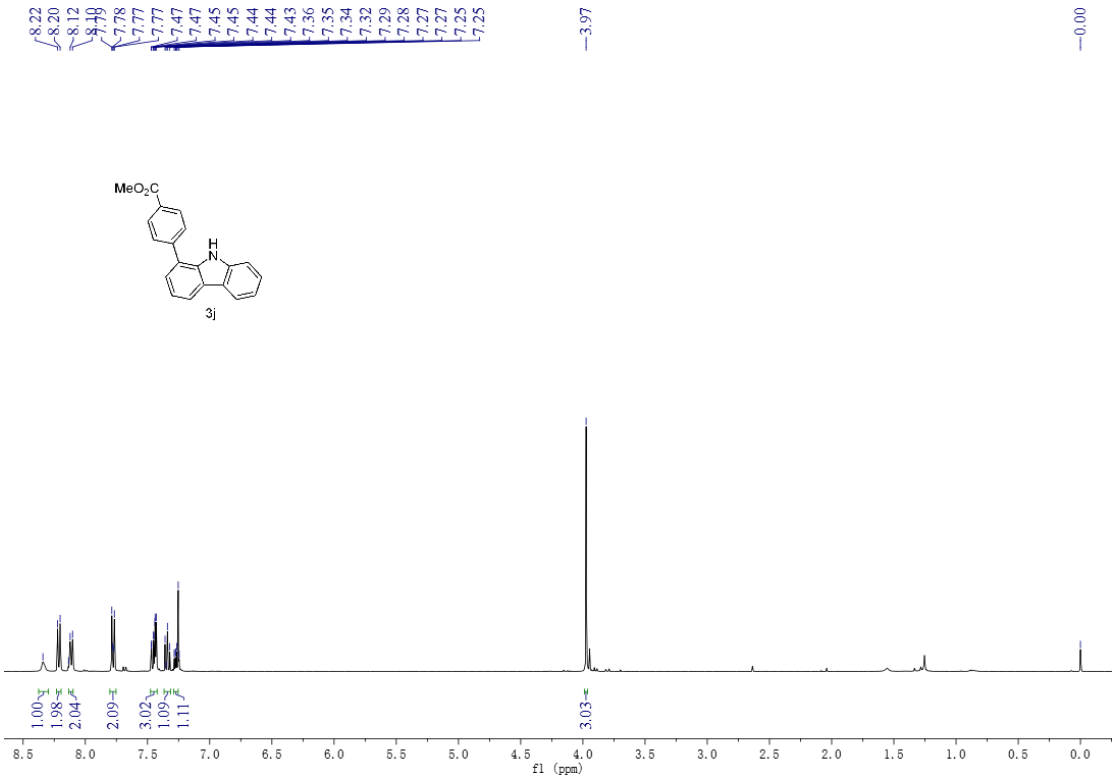
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3i



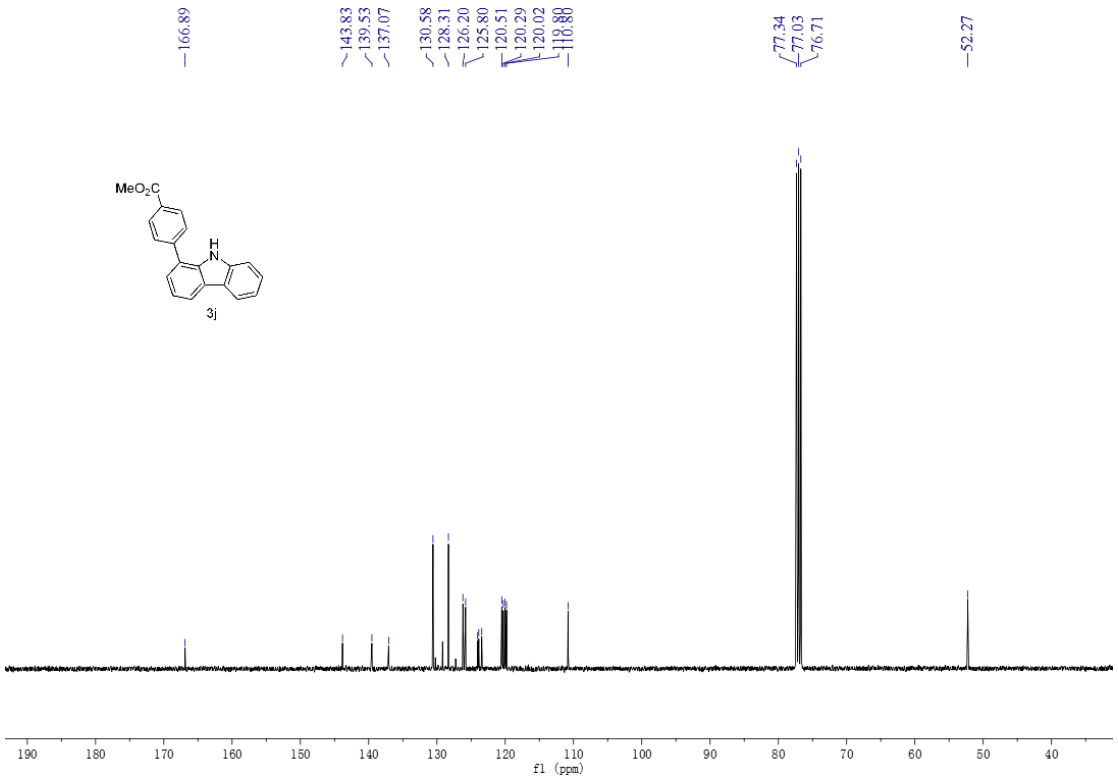
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3i



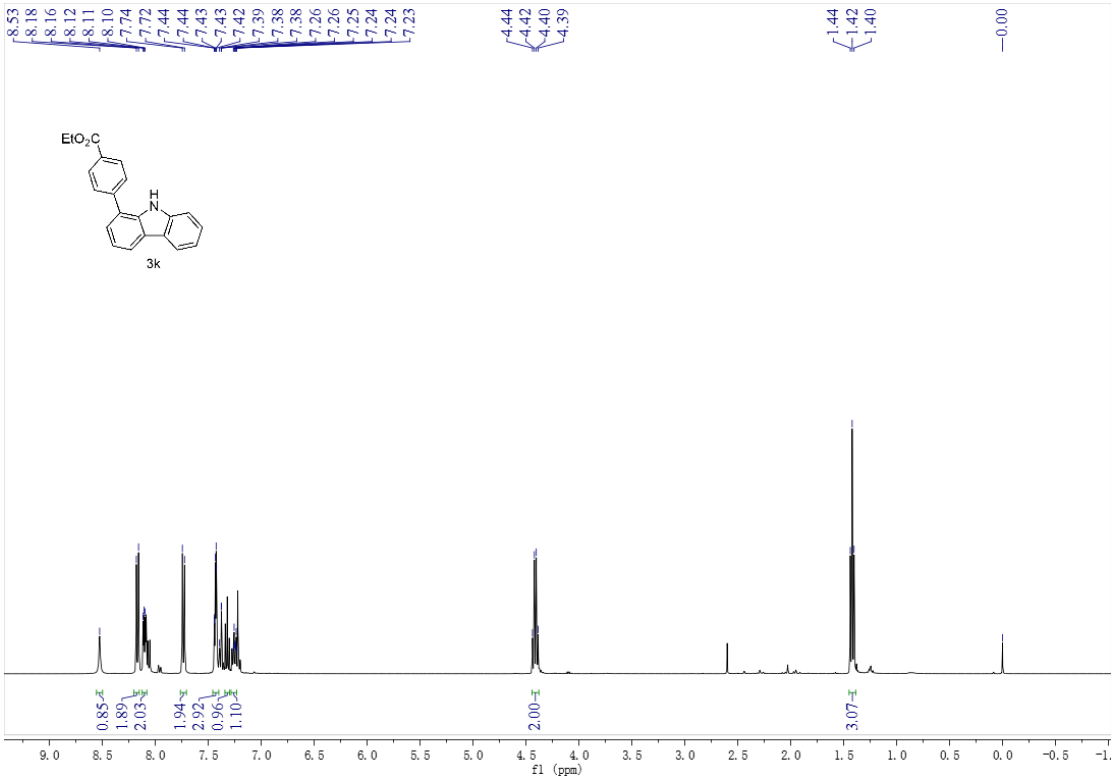
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j



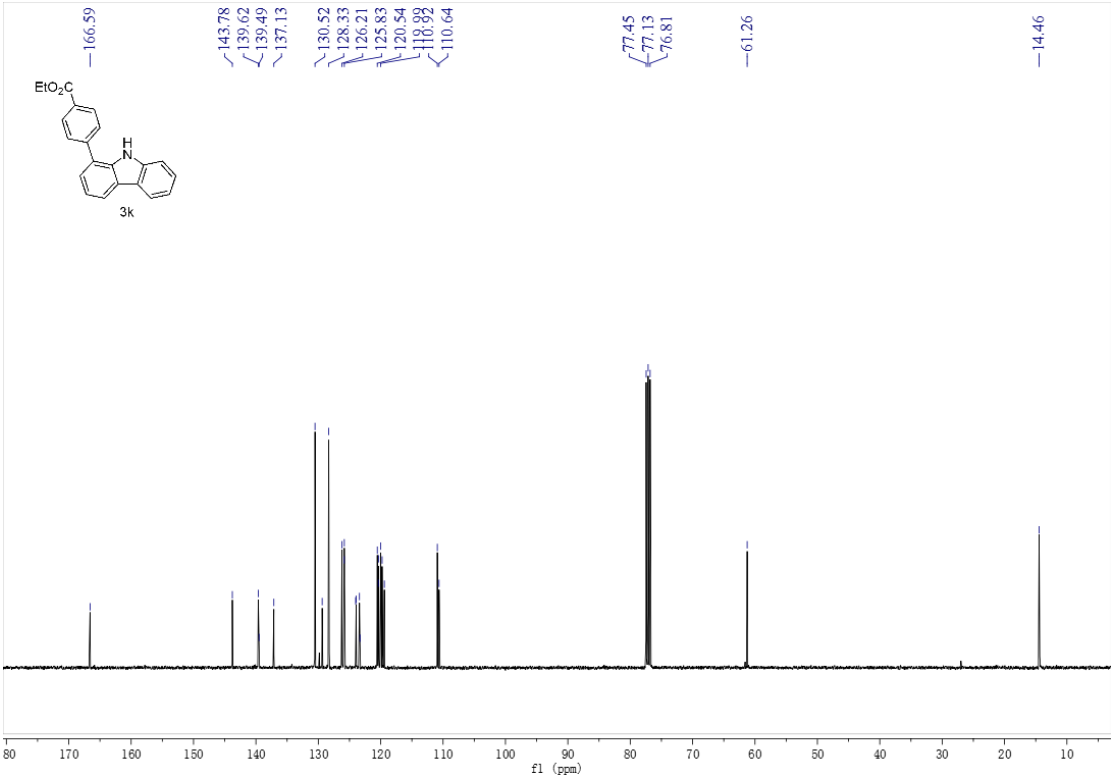
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3j



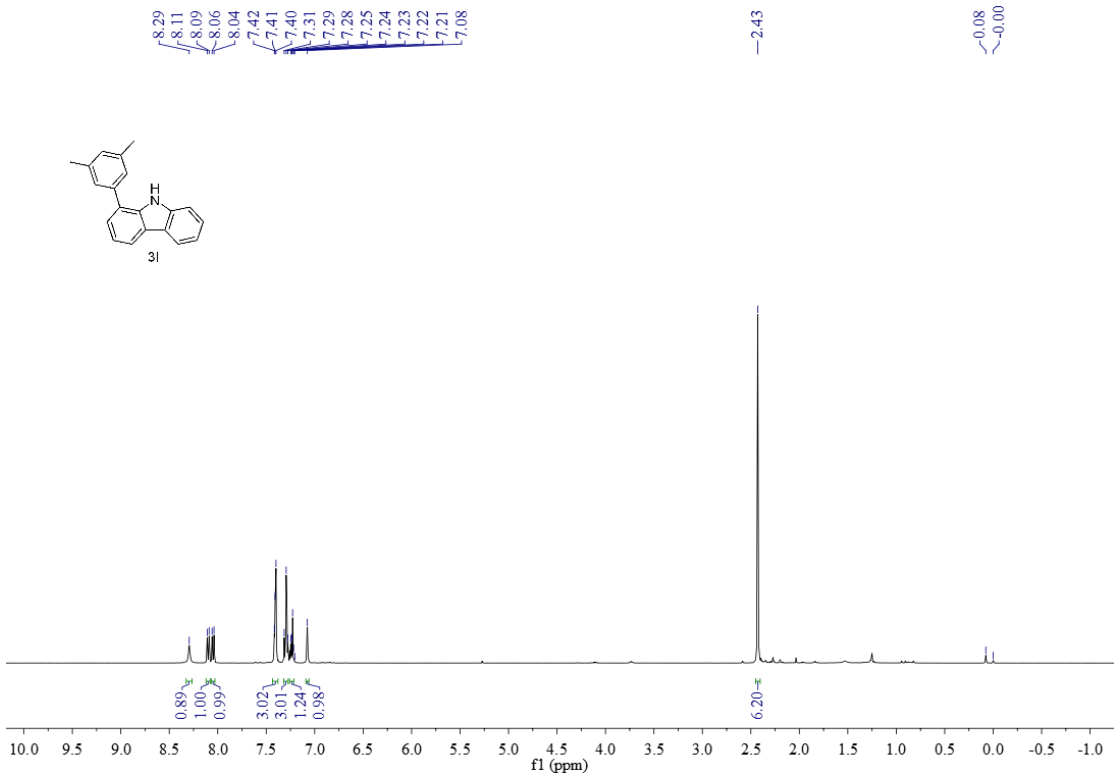
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3k



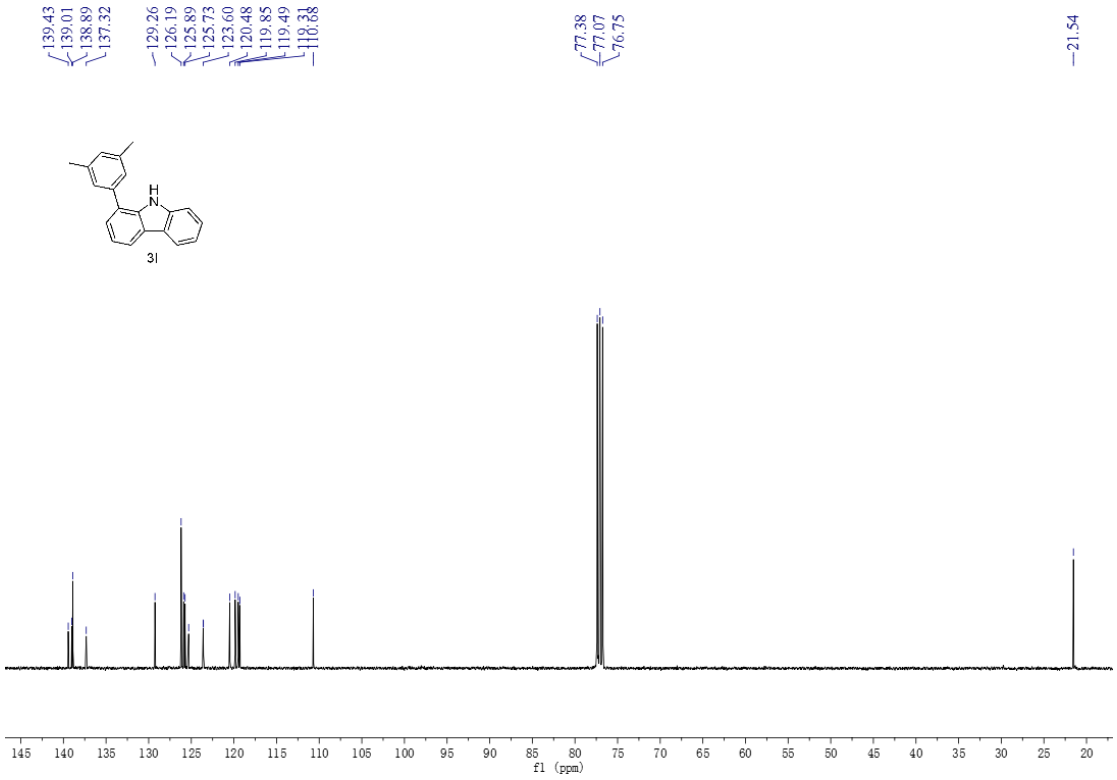
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3k



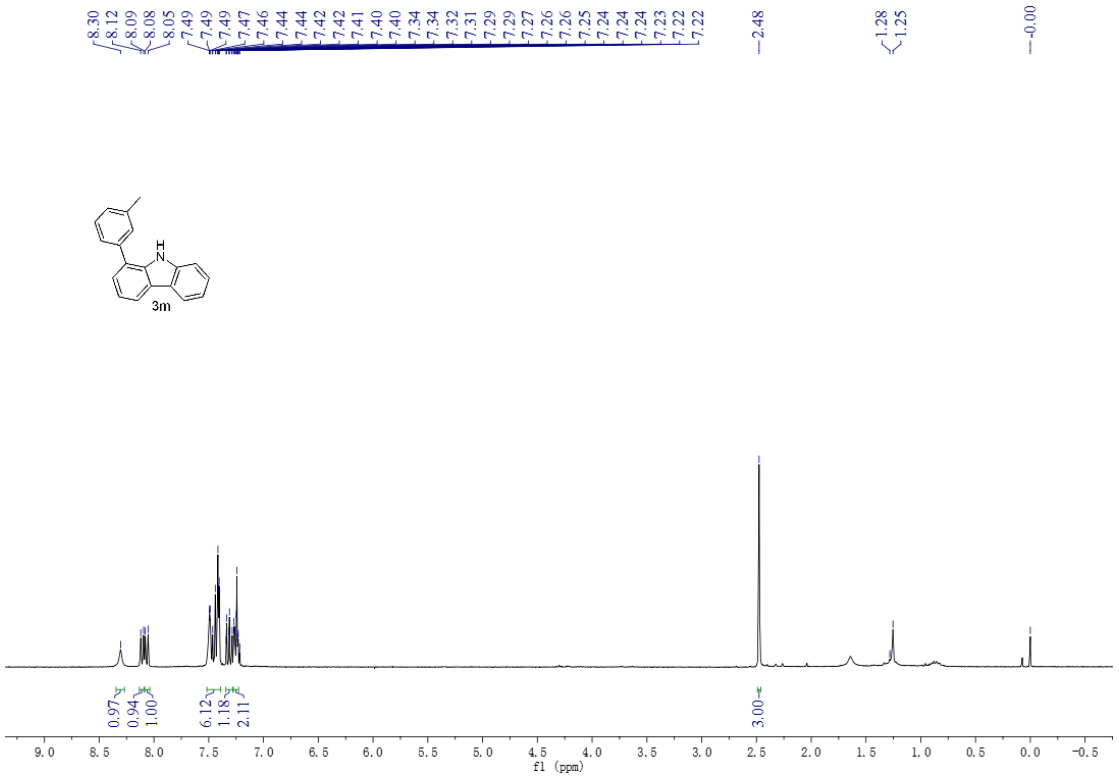
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l



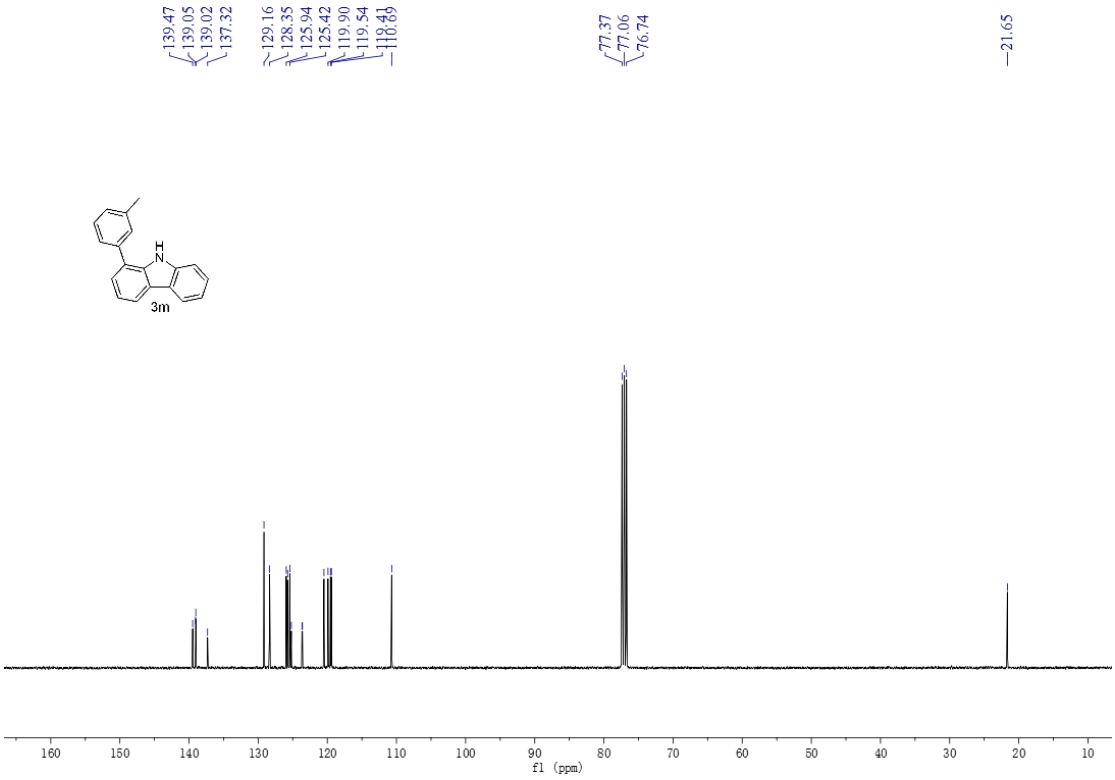
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3l



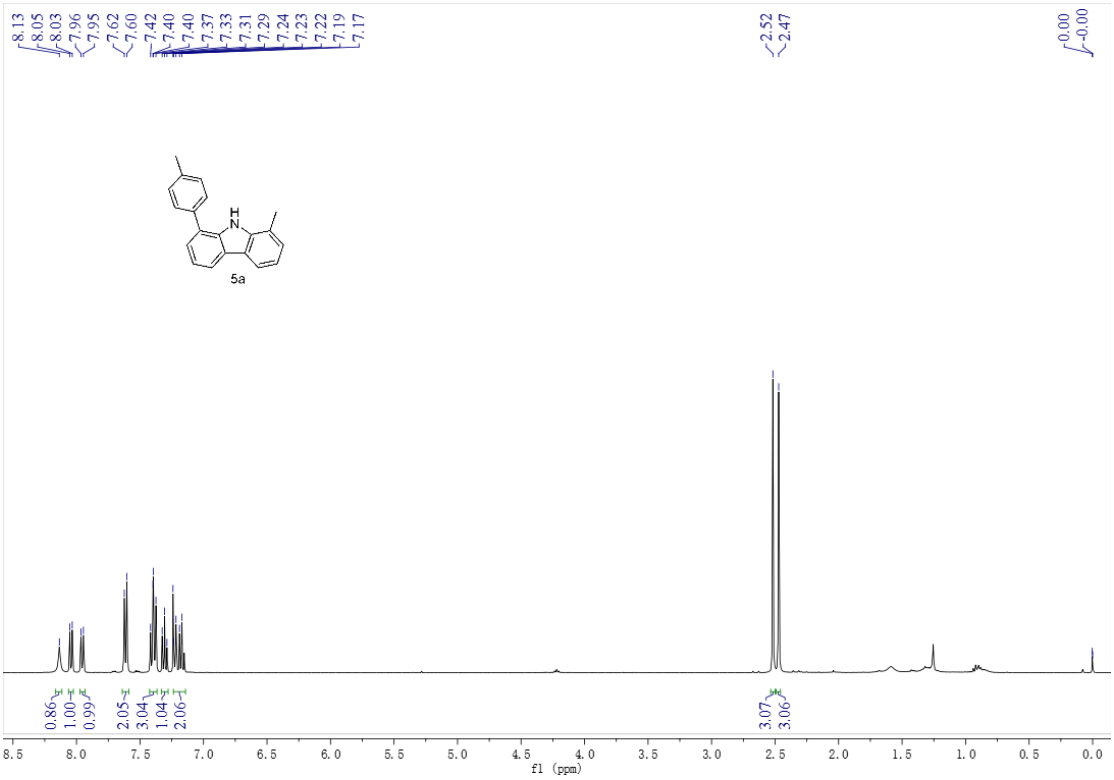
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3m



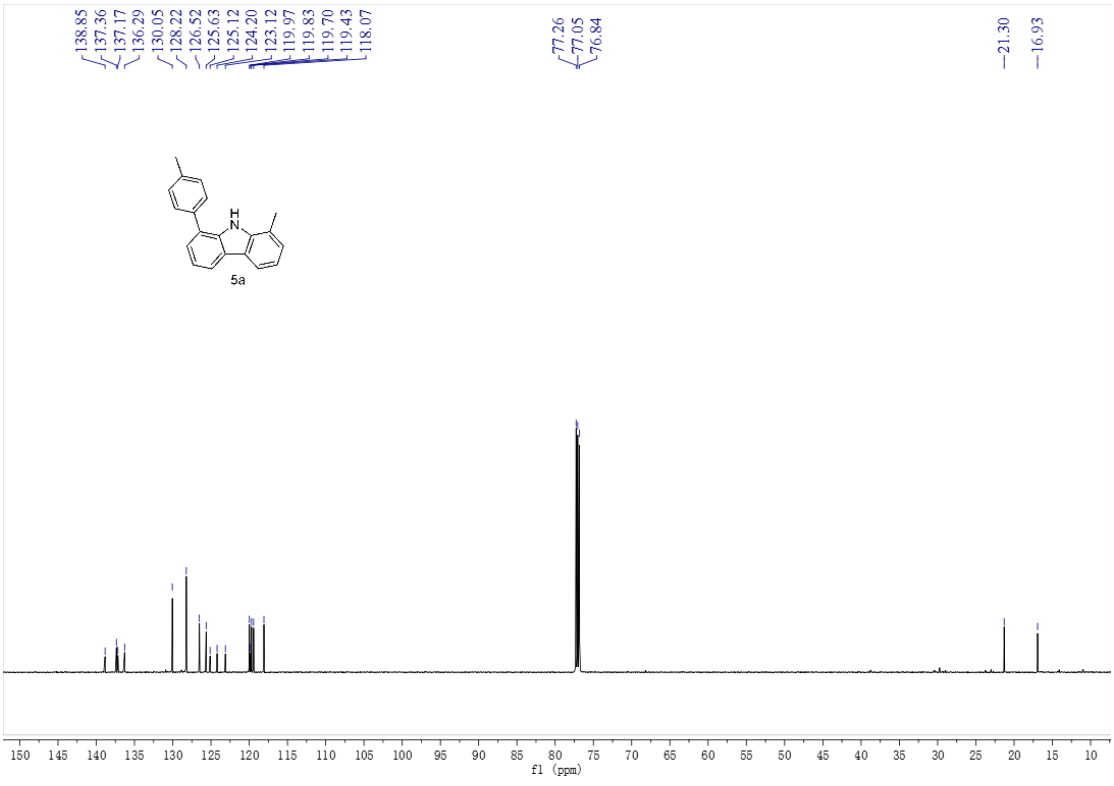
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3m



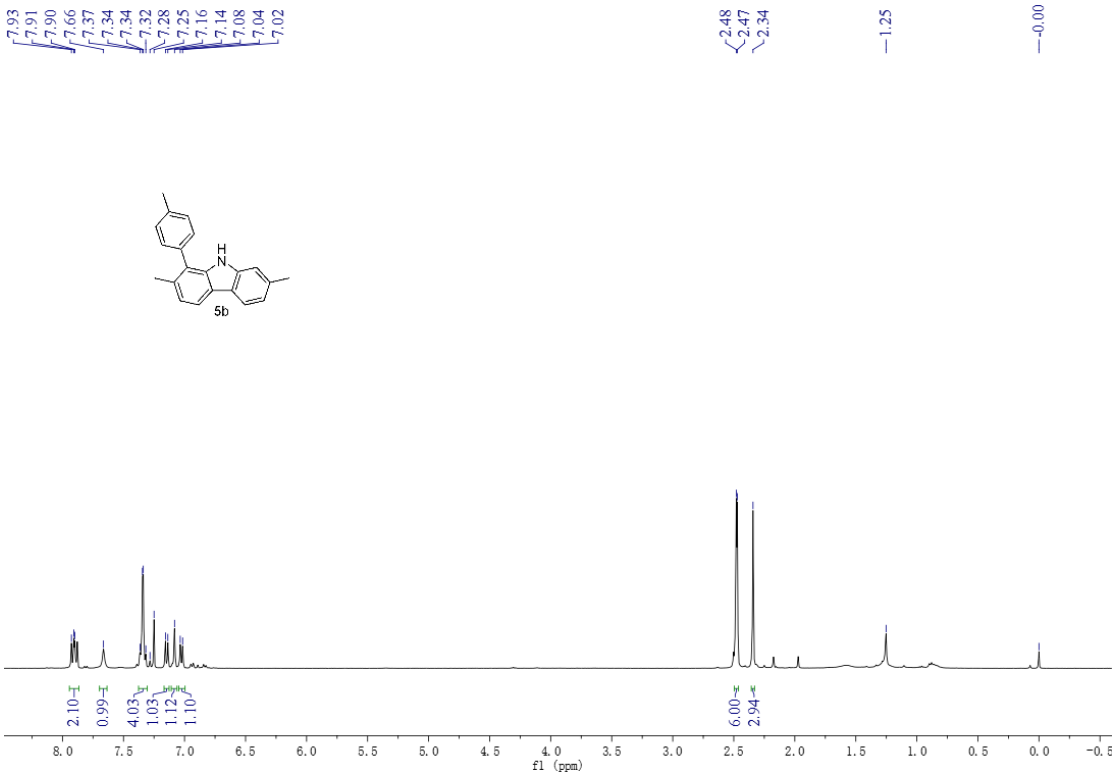
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5a



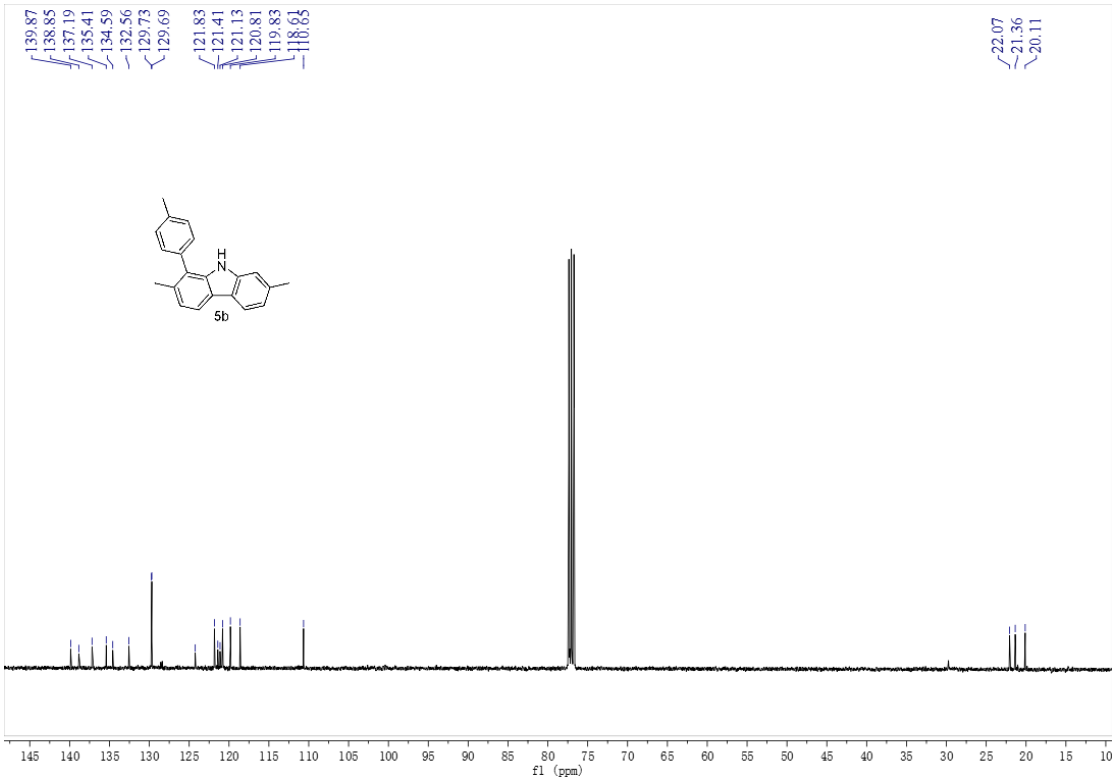
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5a



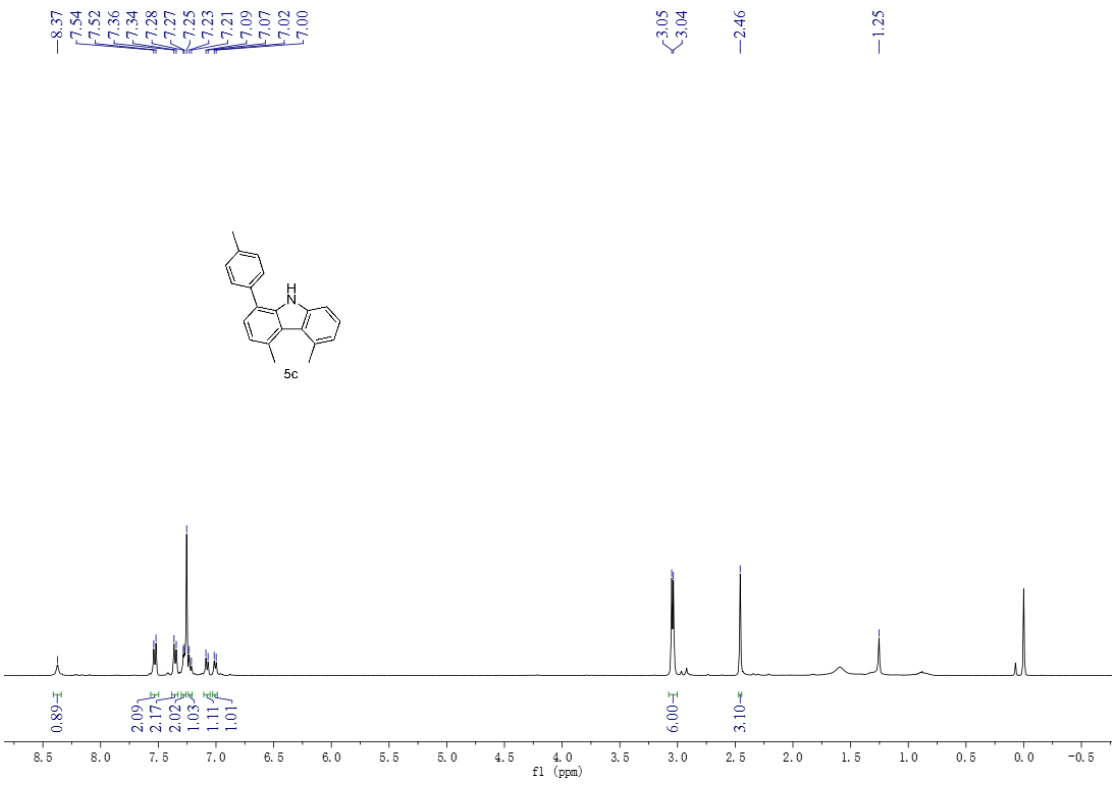
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5b



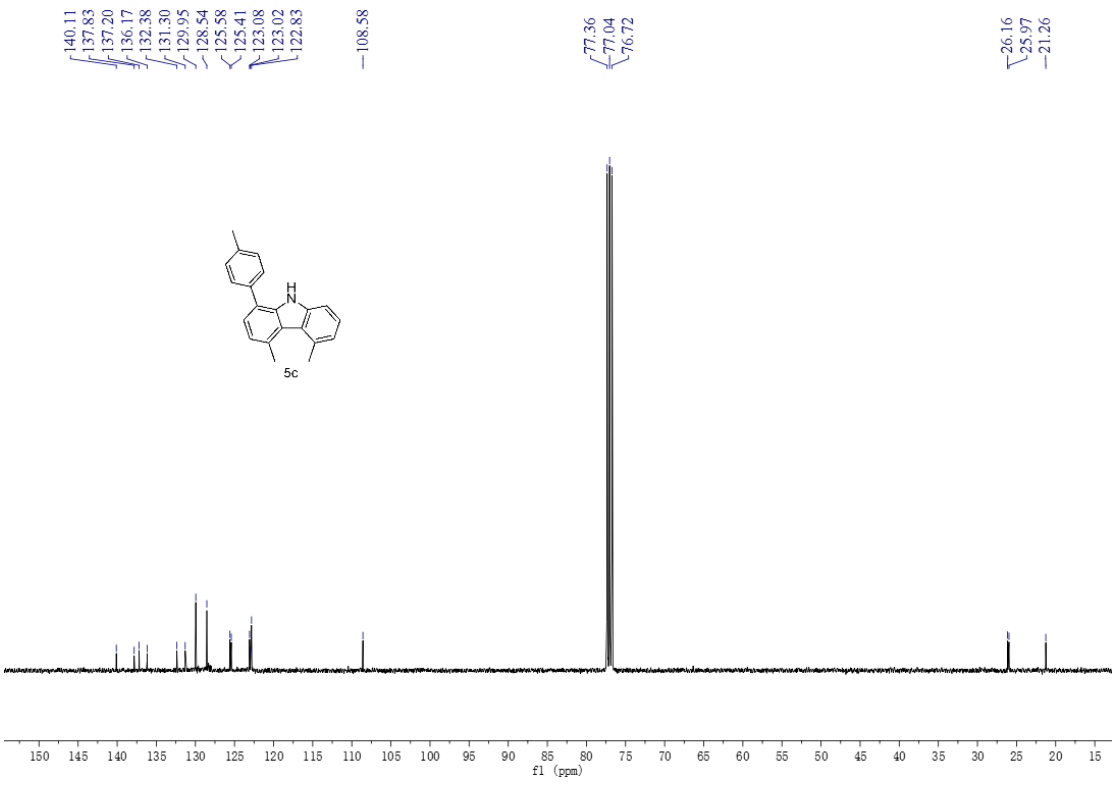
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5b



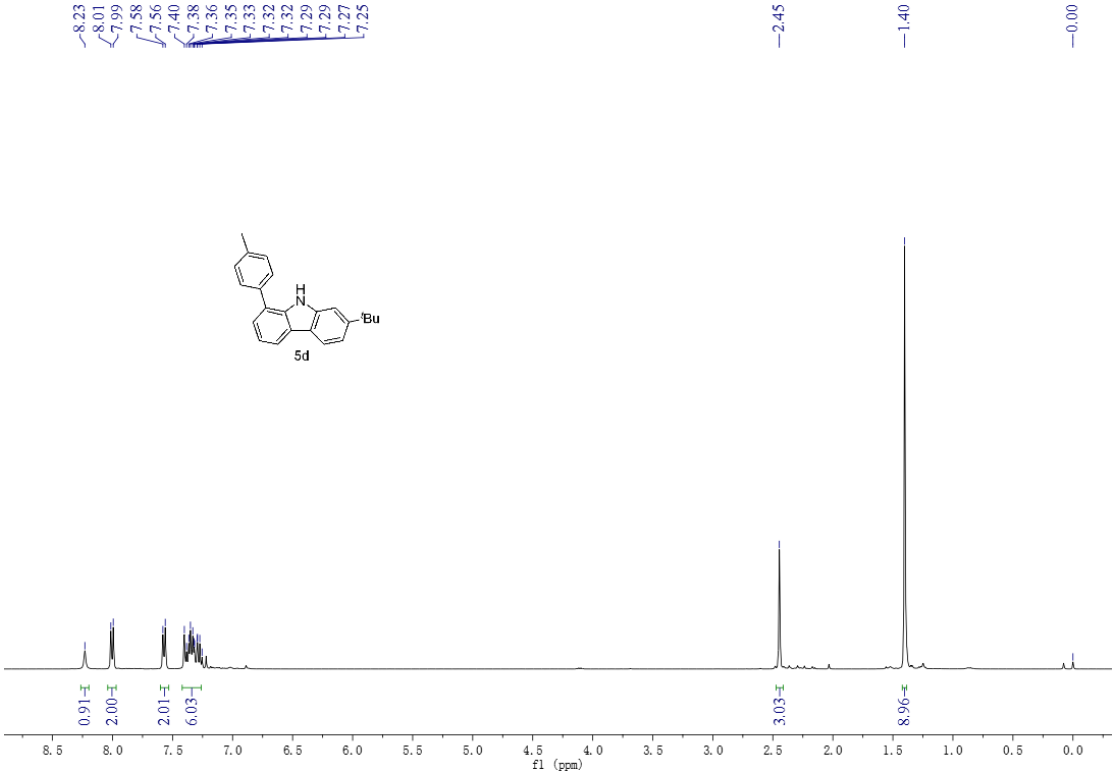
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5c



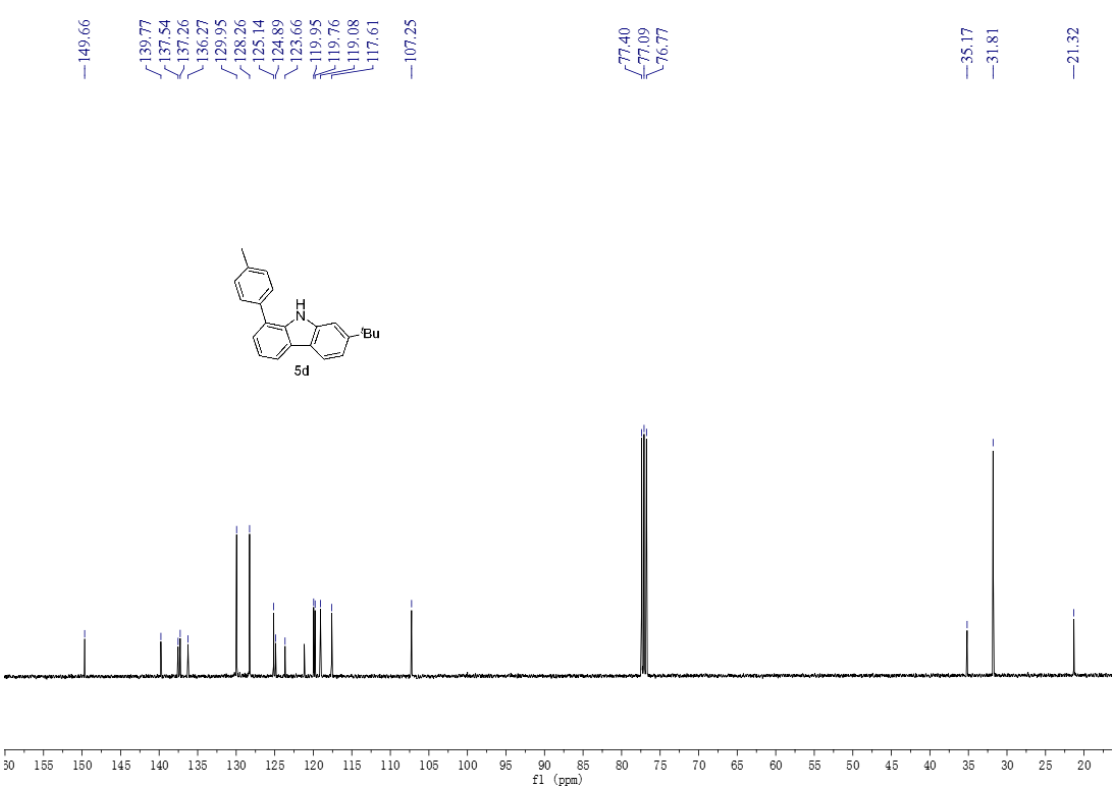
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5c



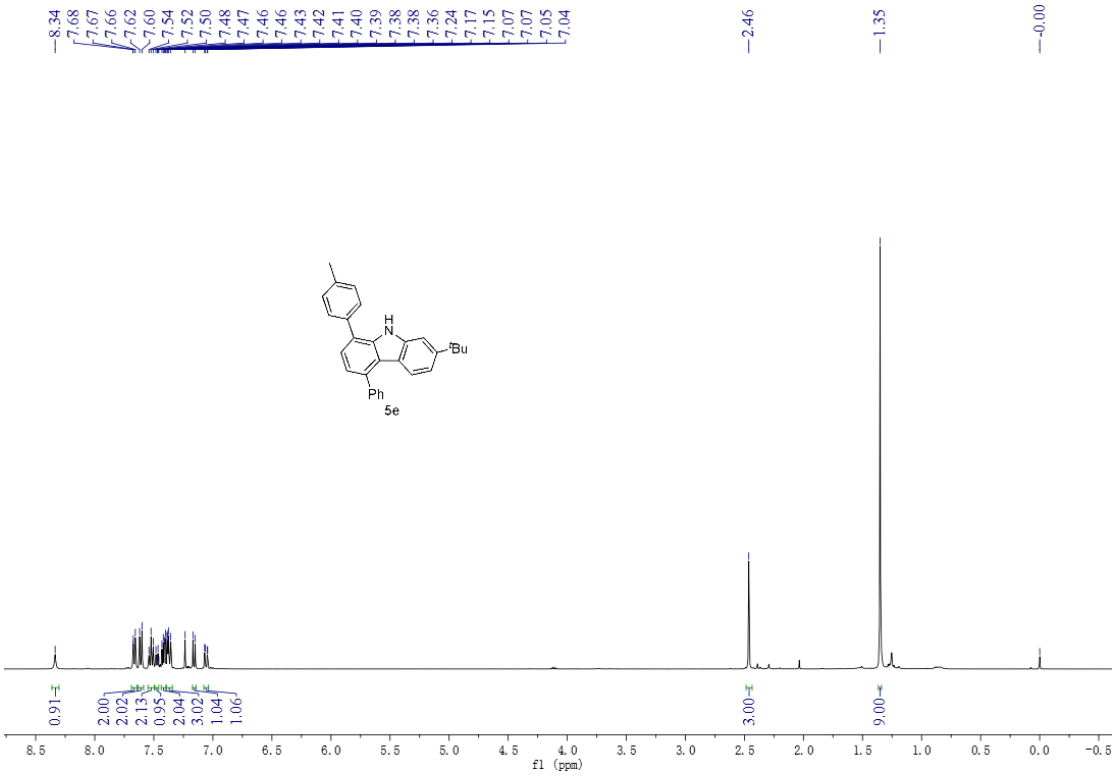
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5d



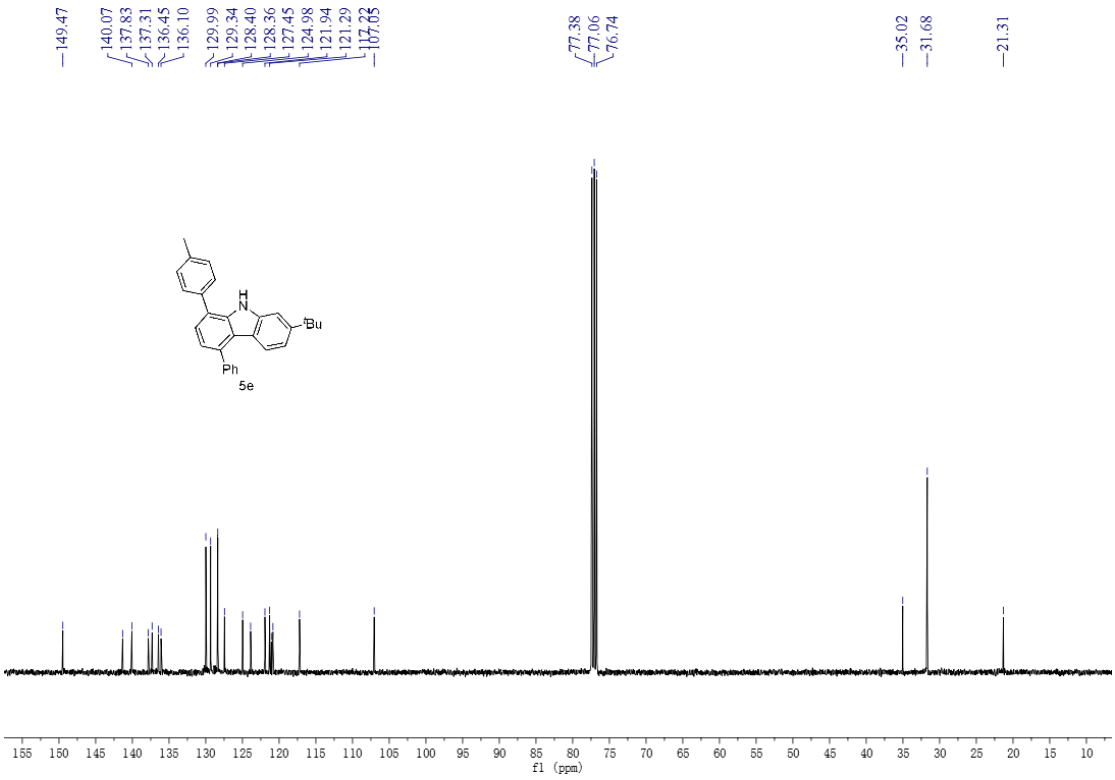
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5d



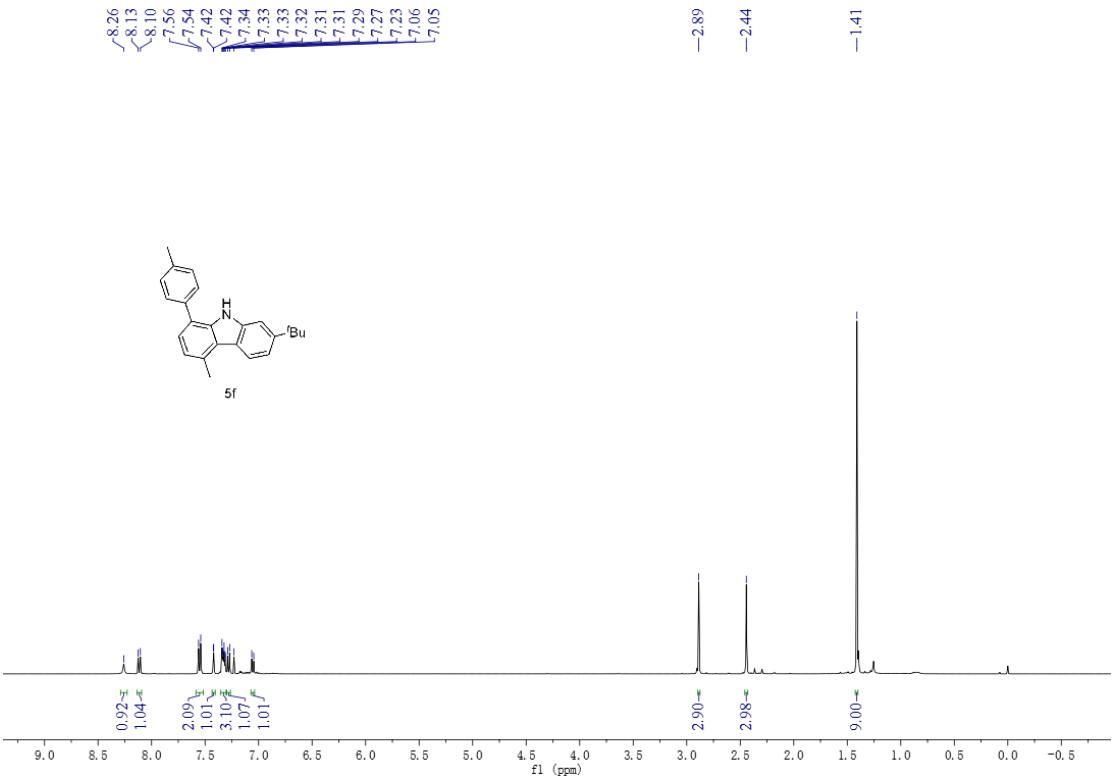
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5e



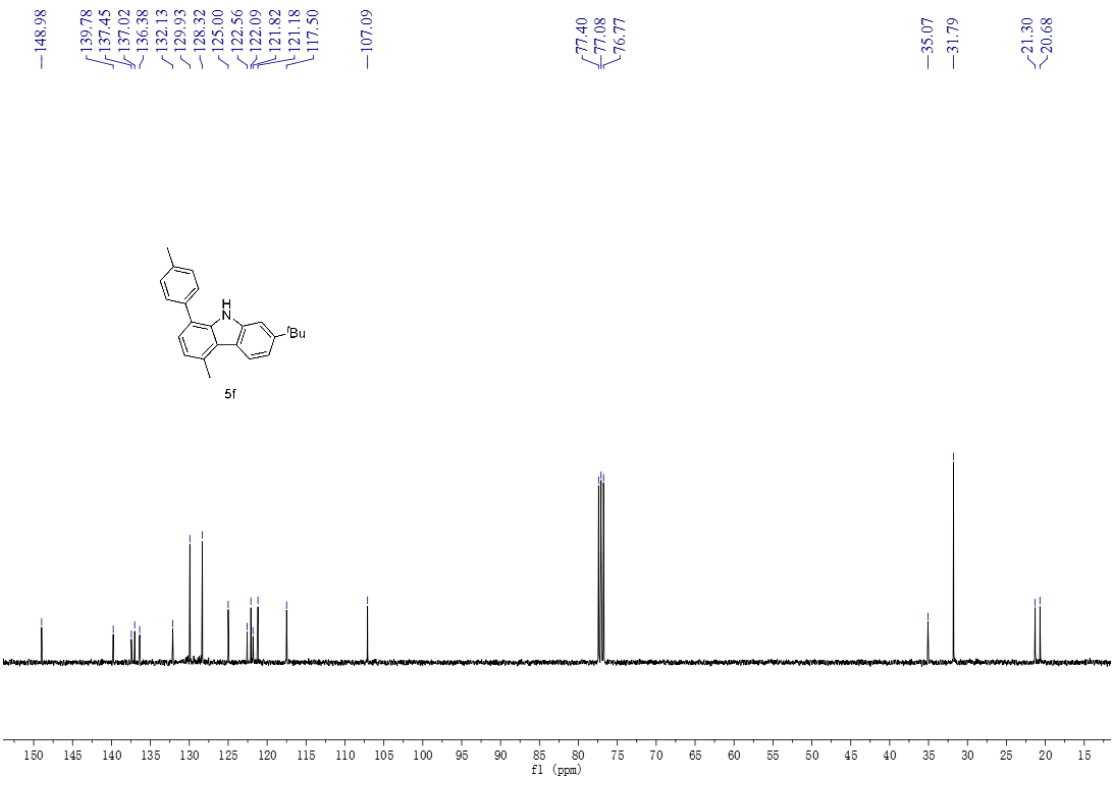
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5e



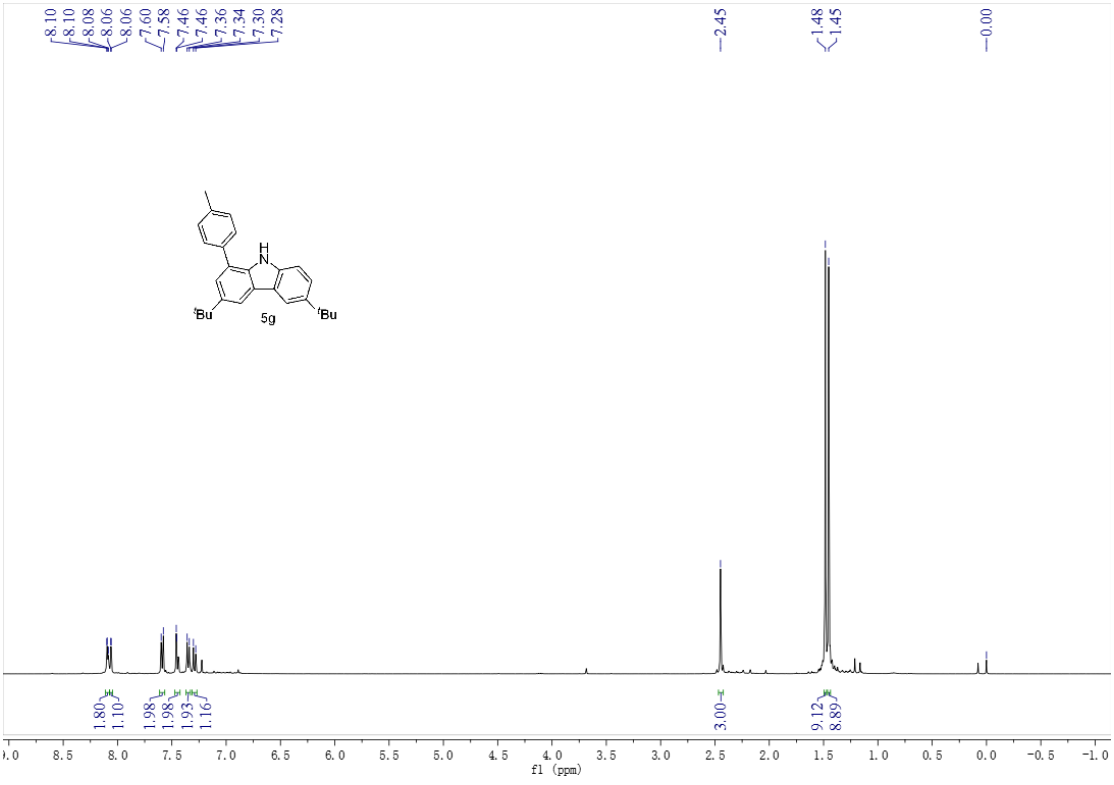
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5f



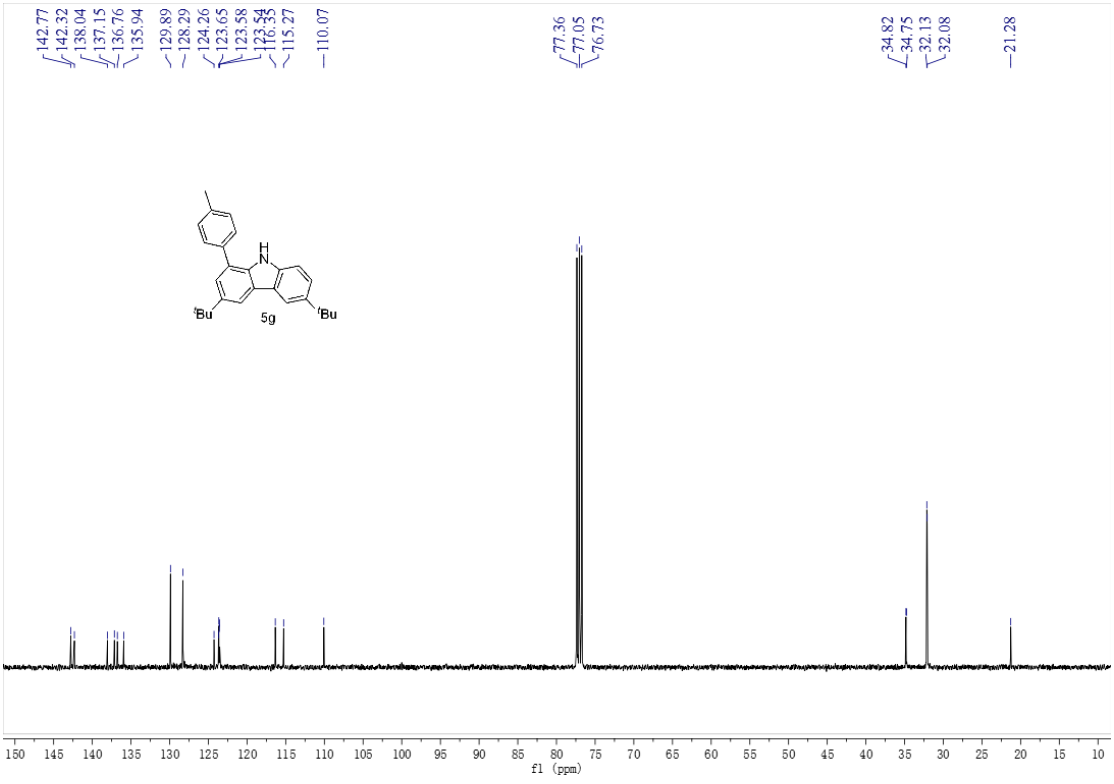
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5f



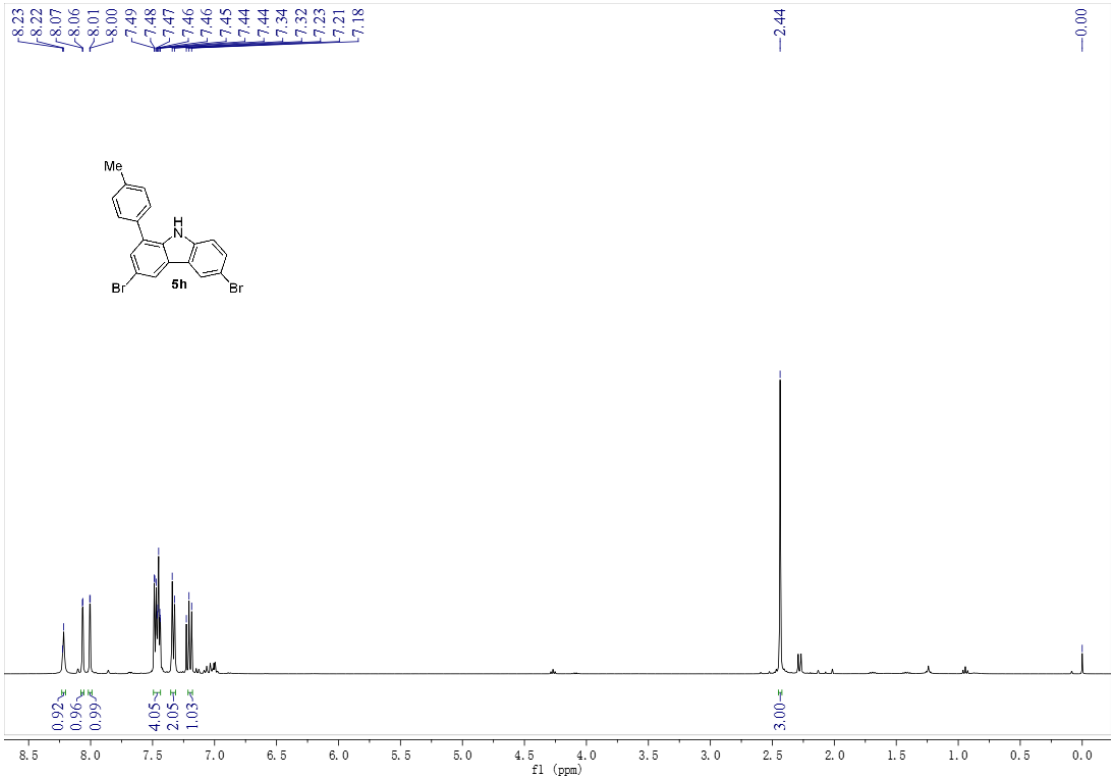
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5g



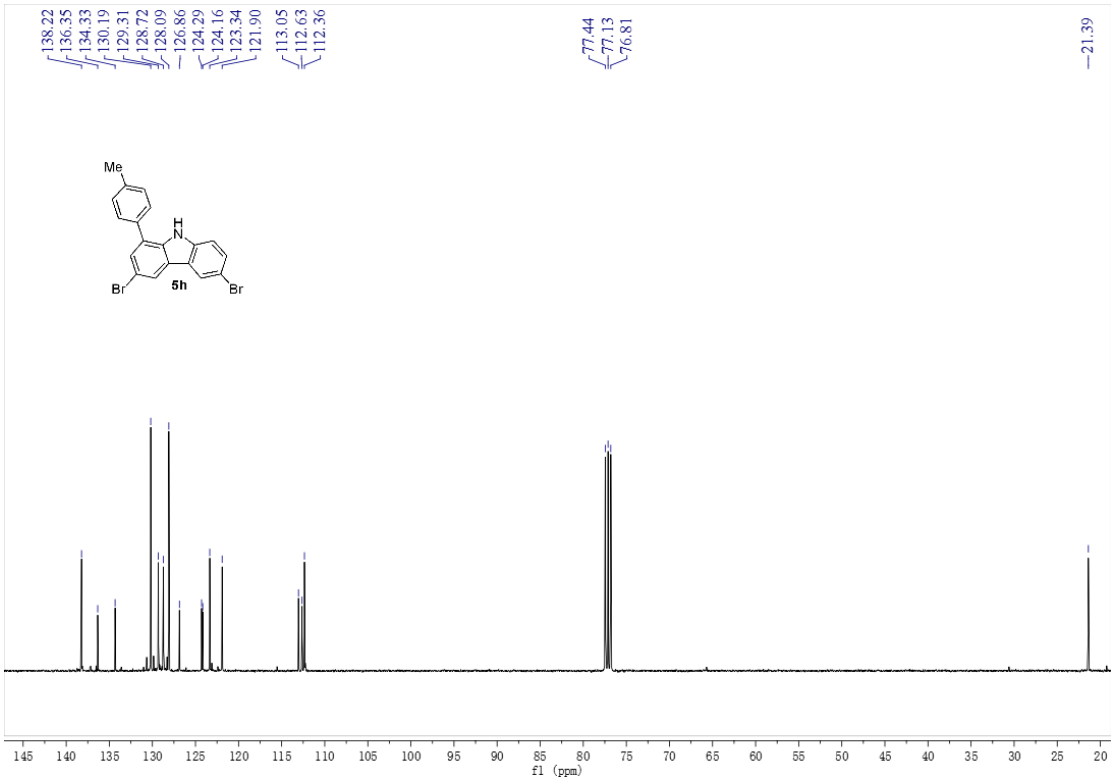
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5g



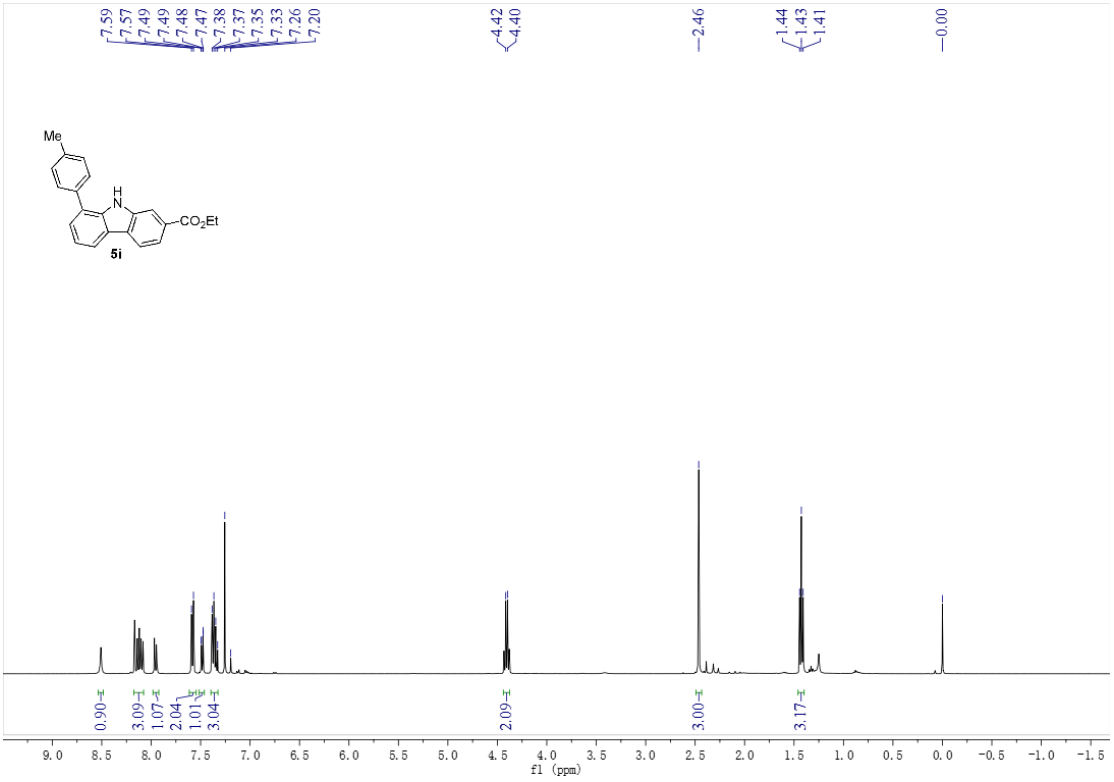
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5h



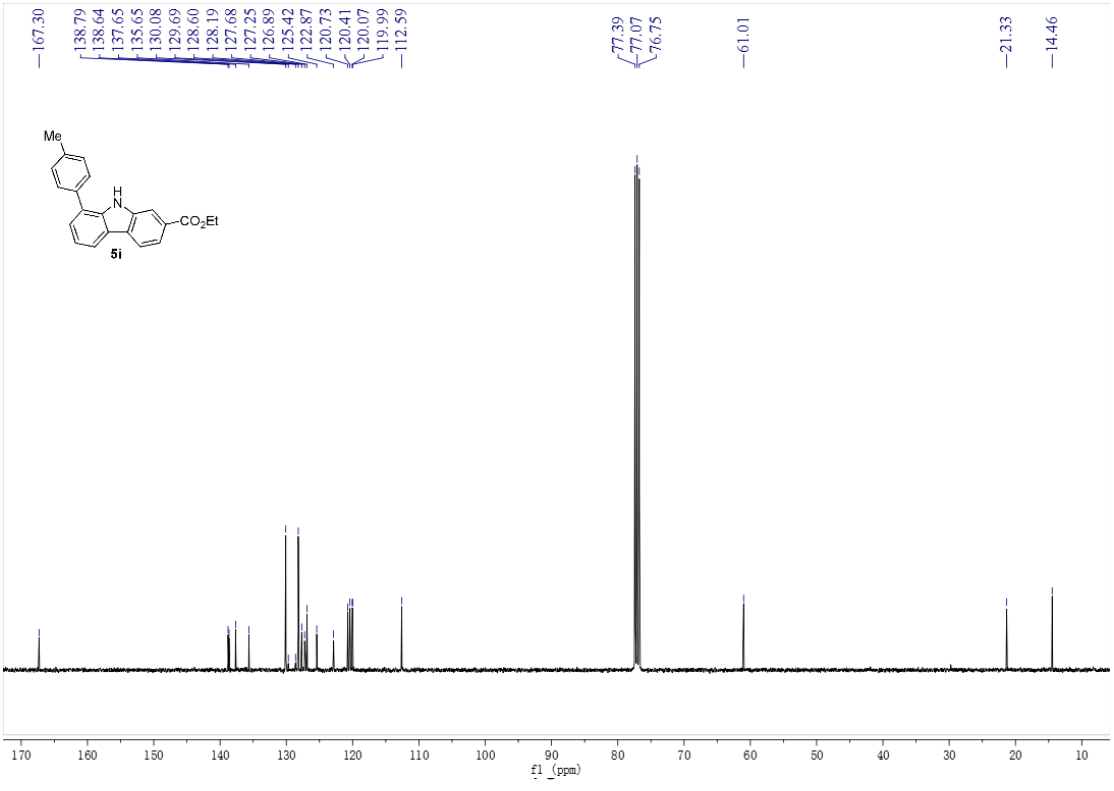
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5h



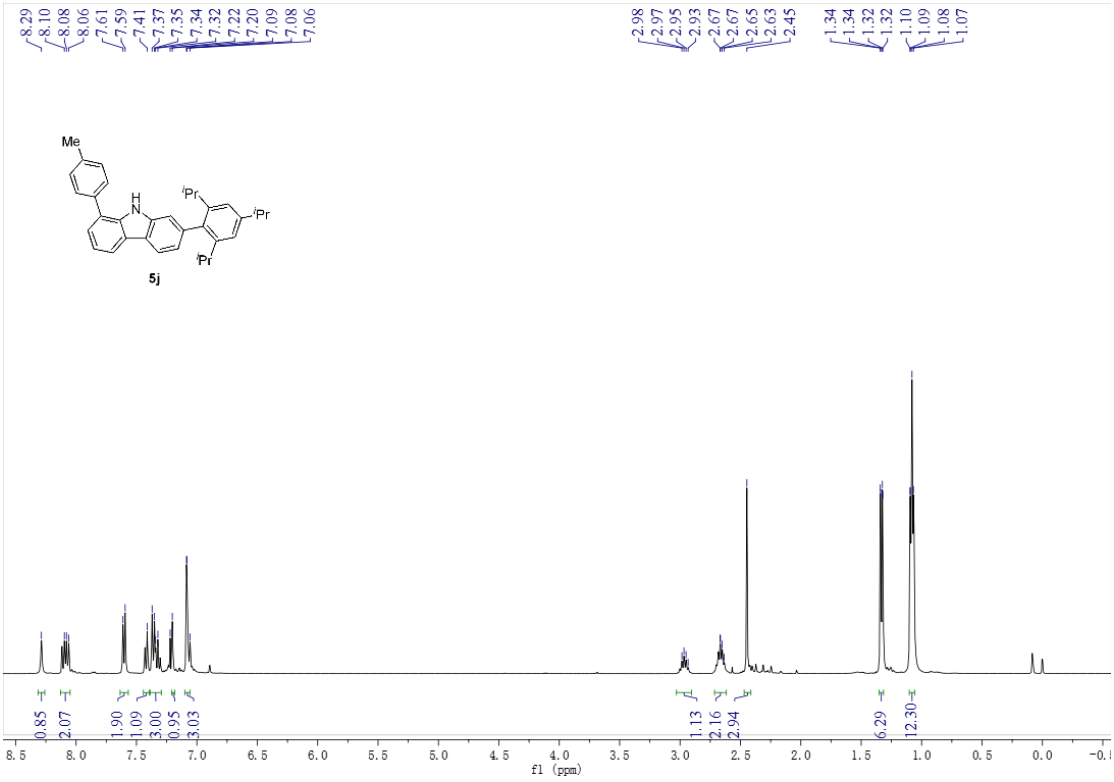
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5i



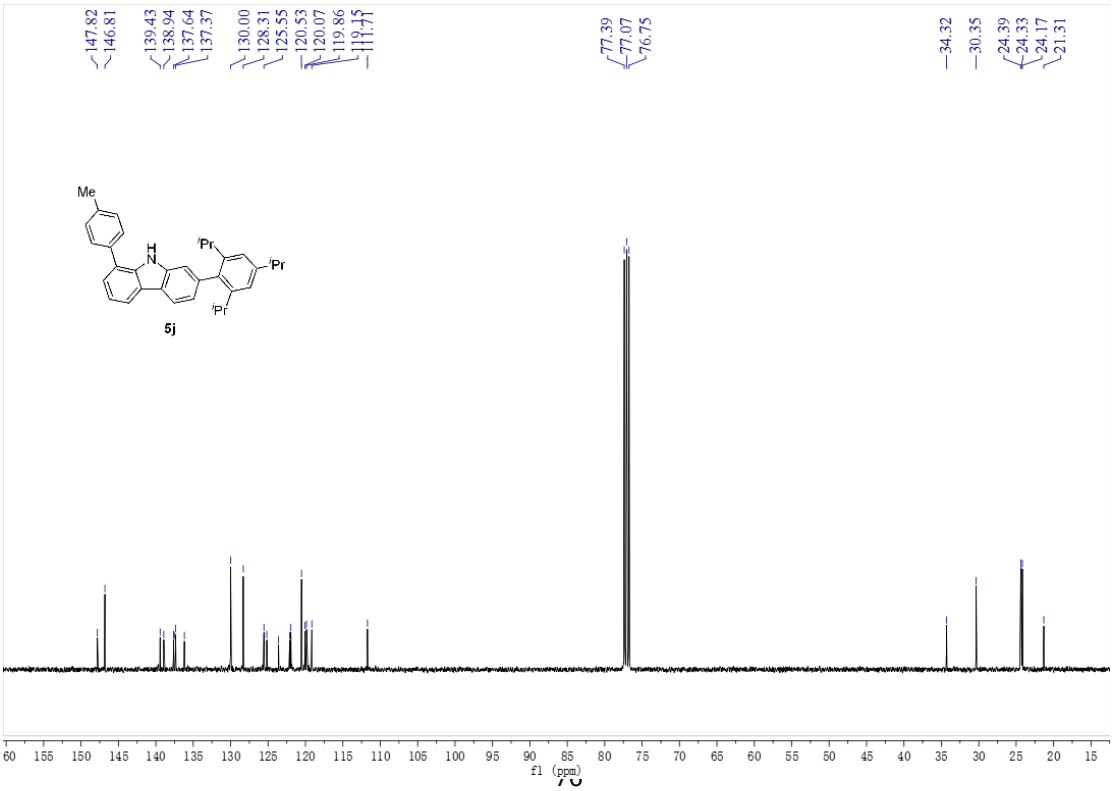
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5i



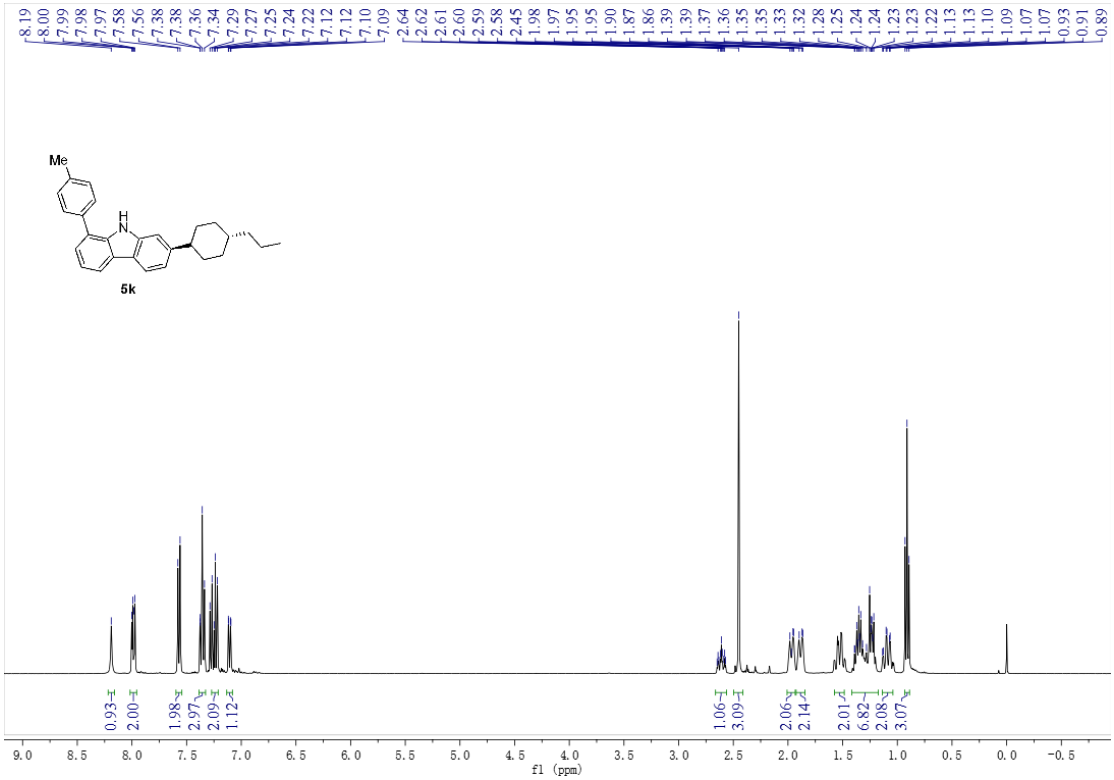
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5j



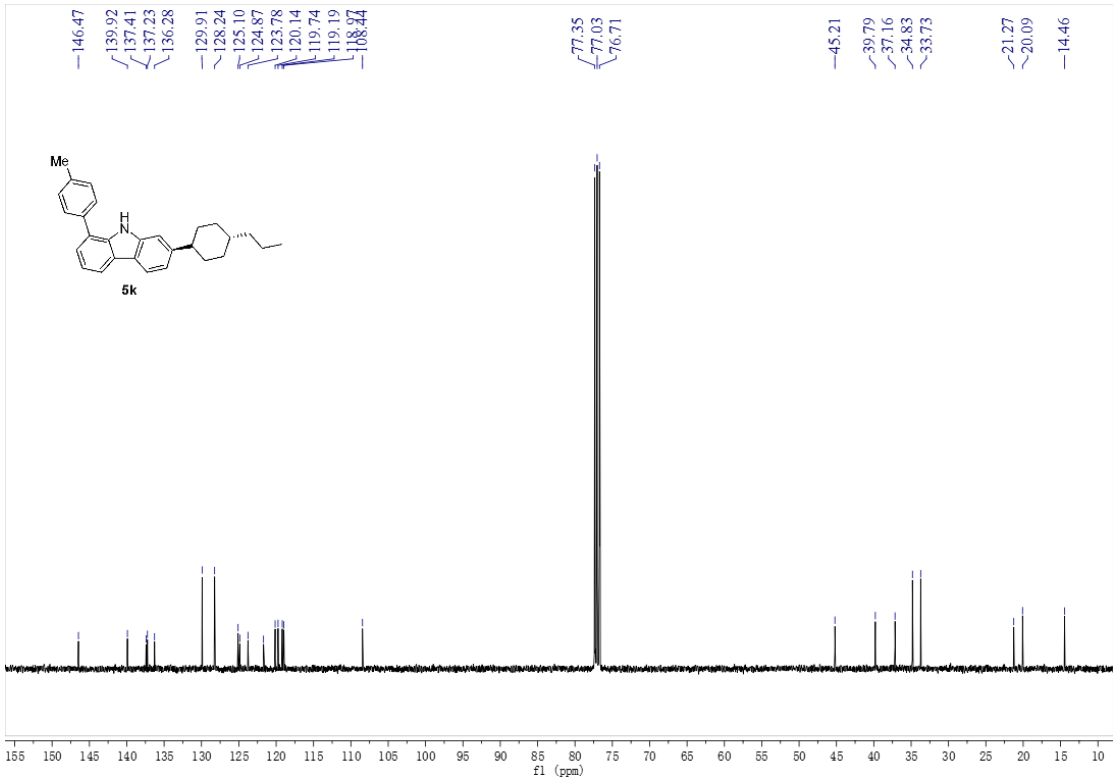
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5j



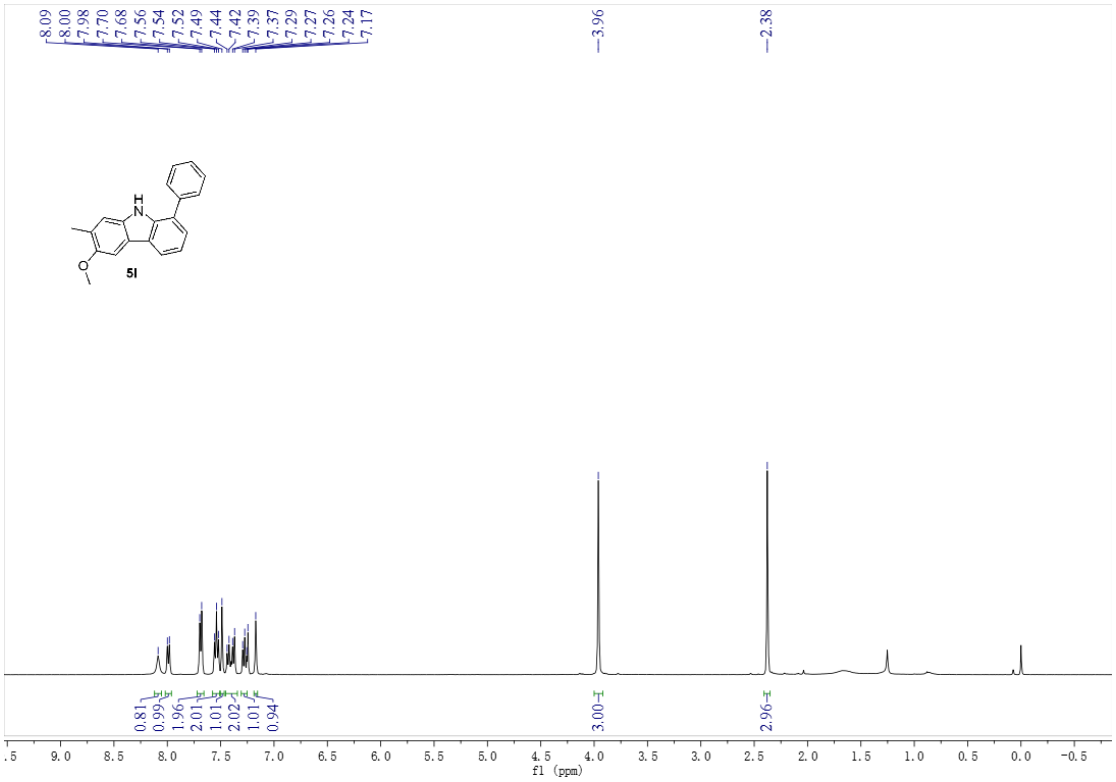
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5k



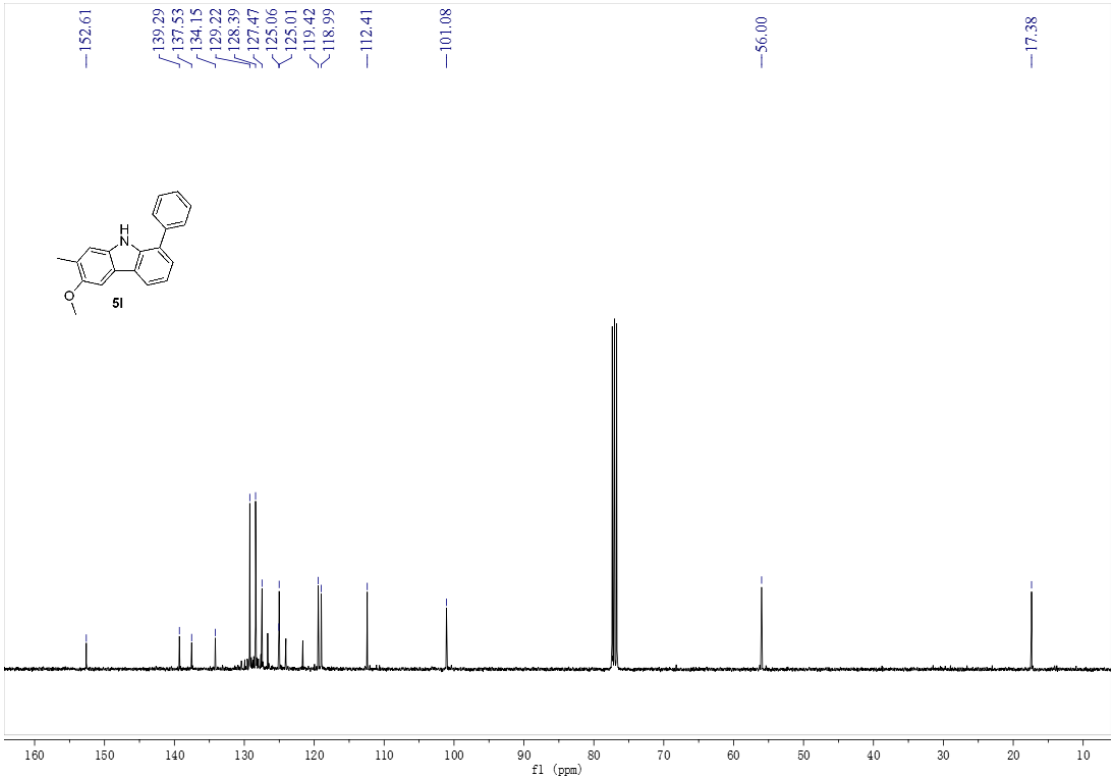
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5k



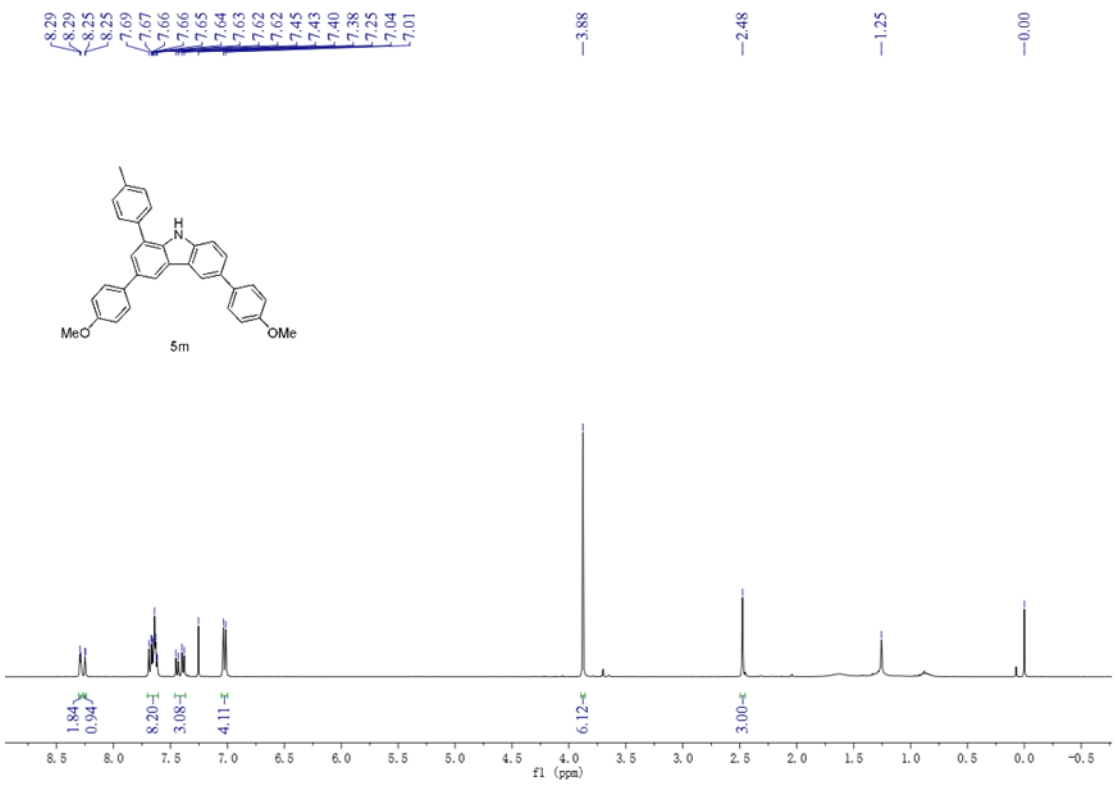
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5l



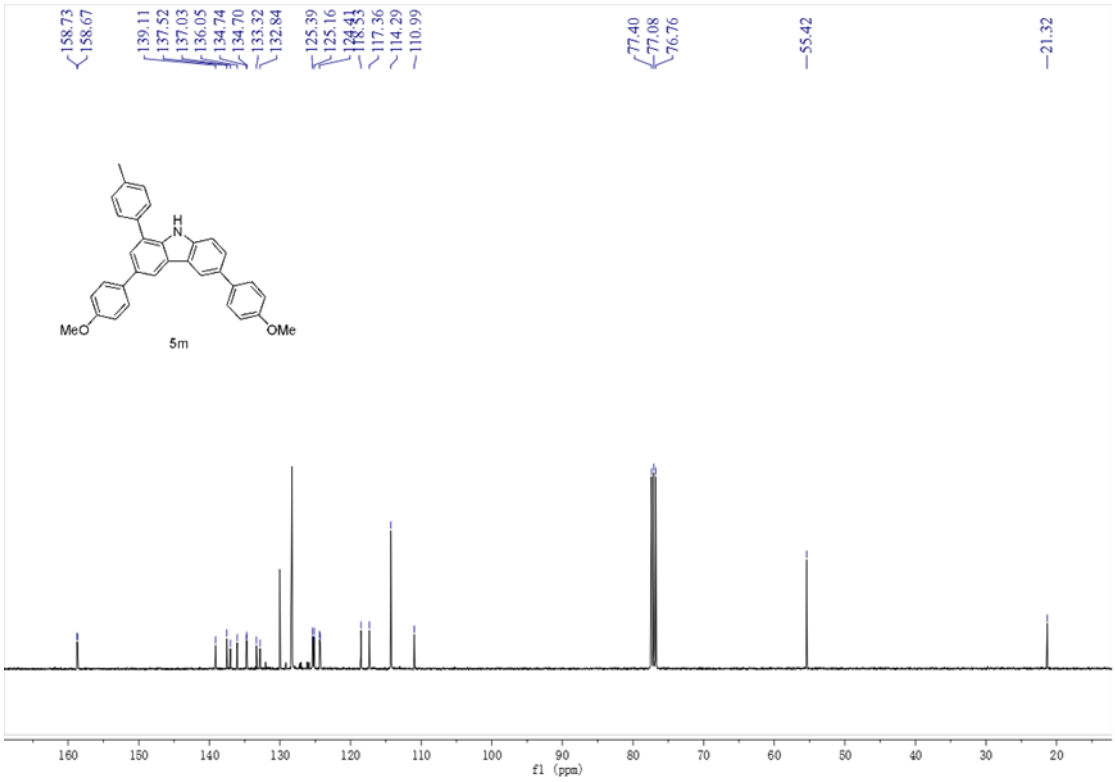
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5l



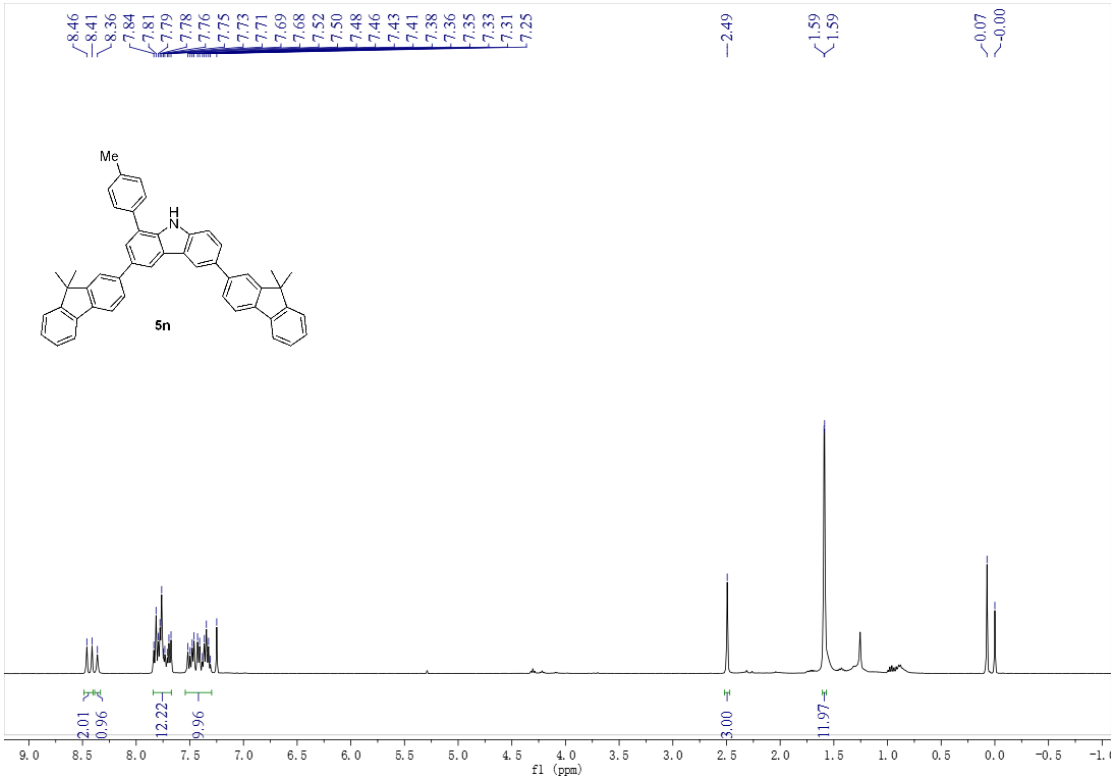
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5m



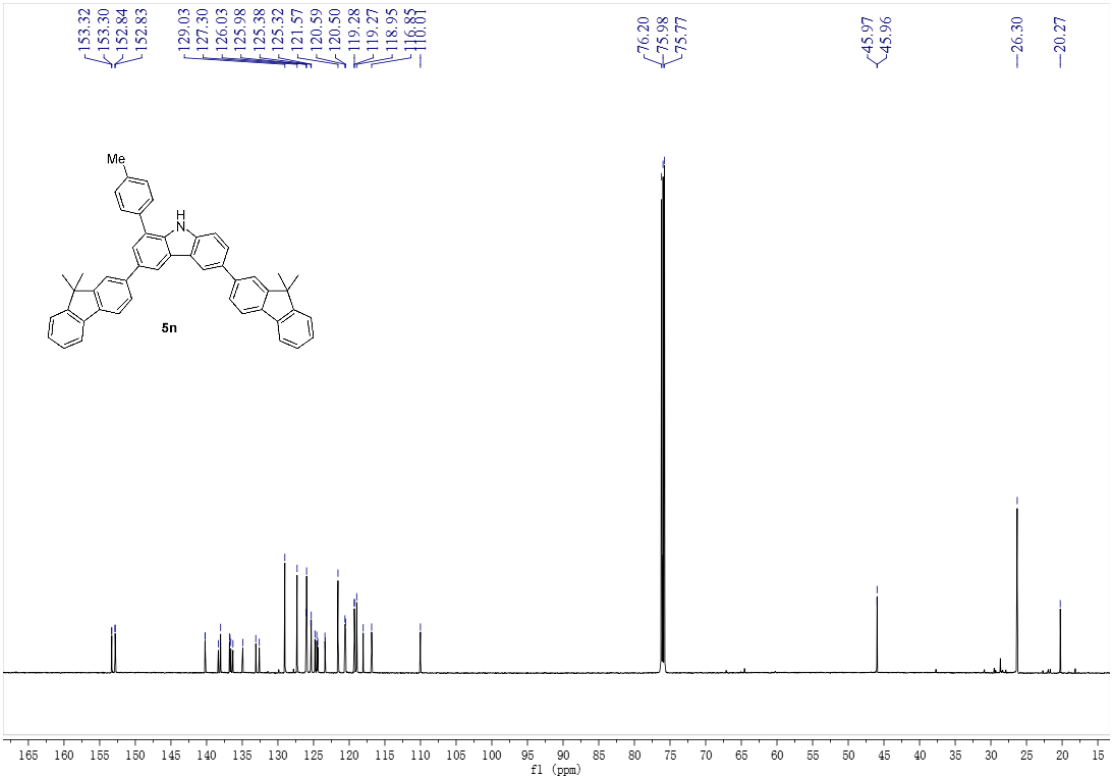
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5m



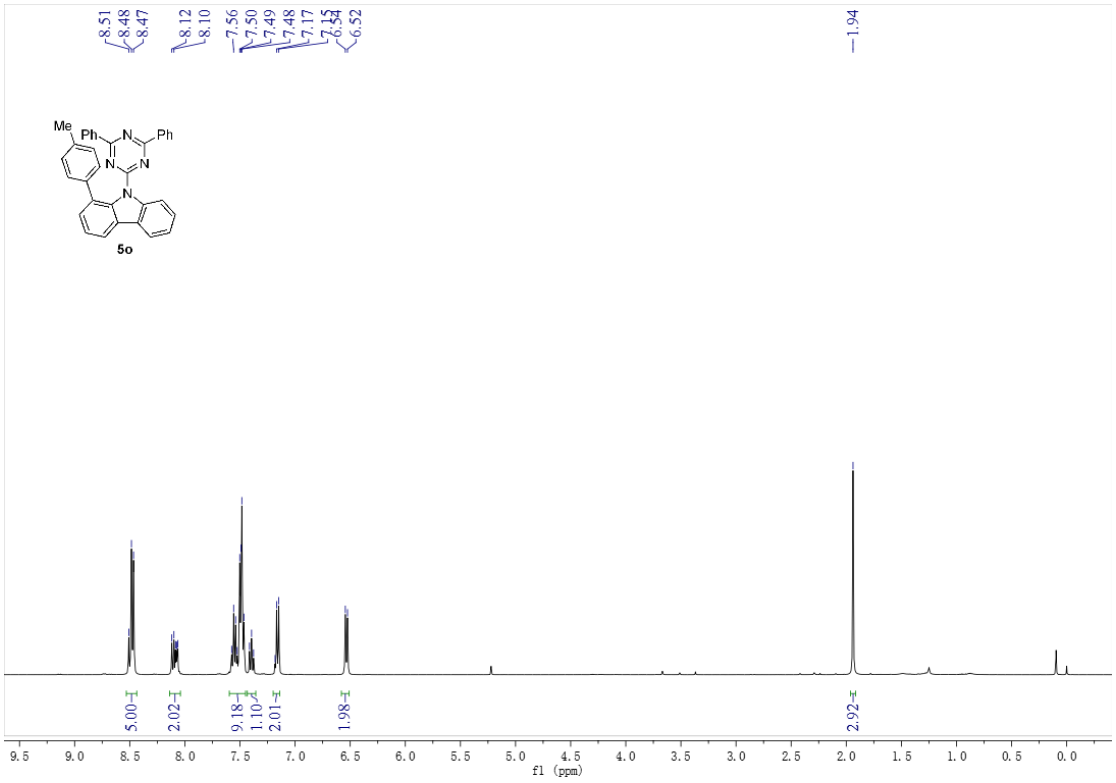
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5n



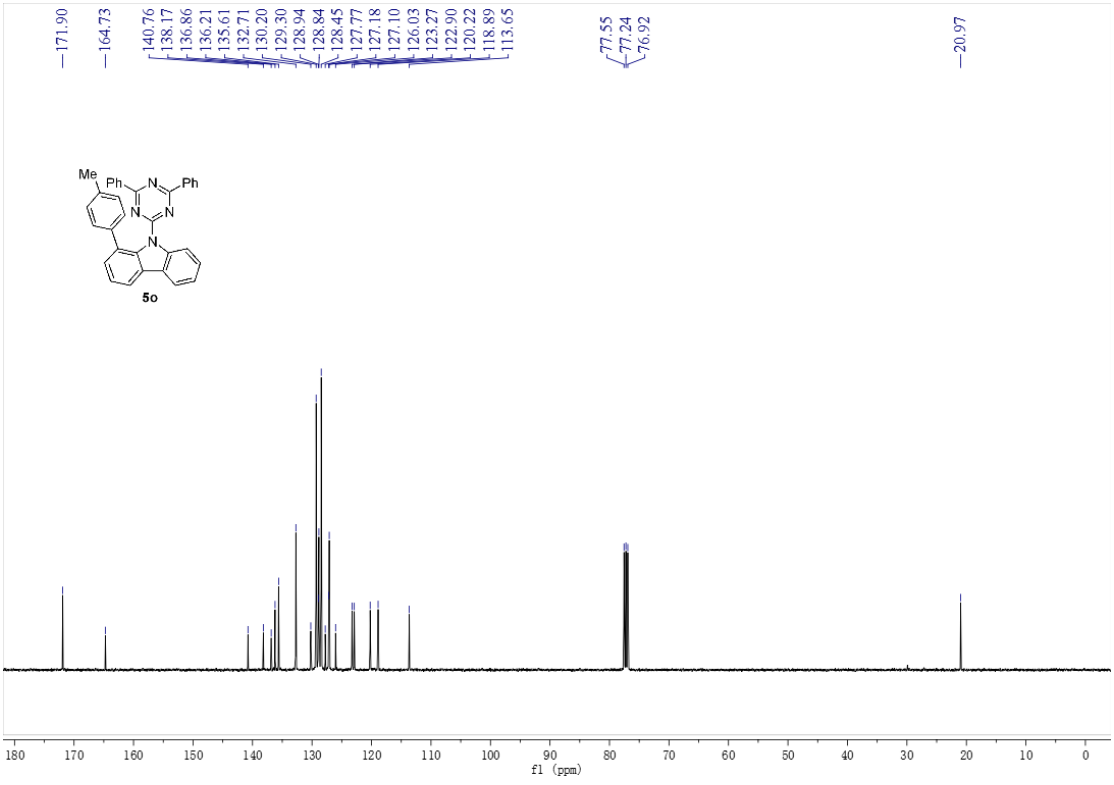
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5n



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

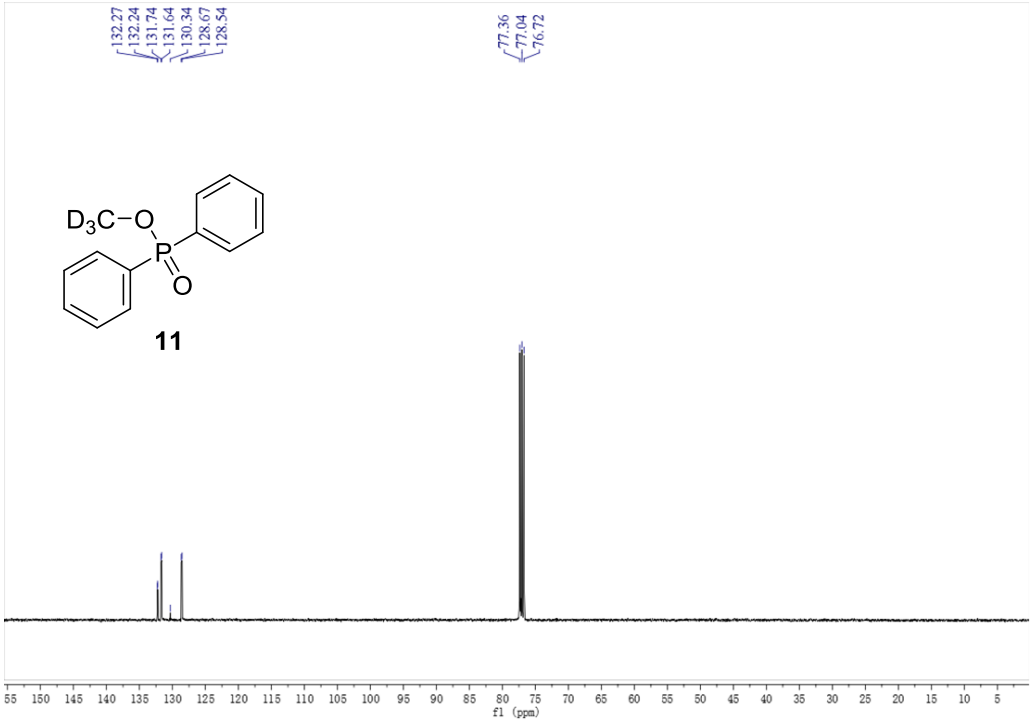


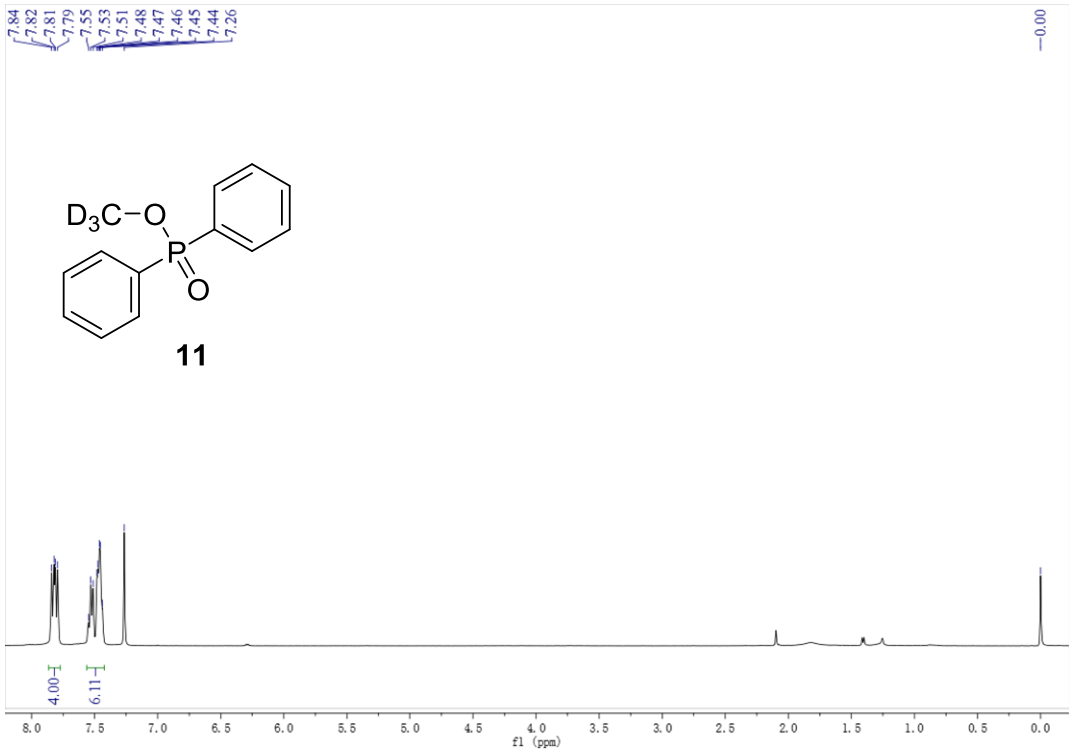
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5o



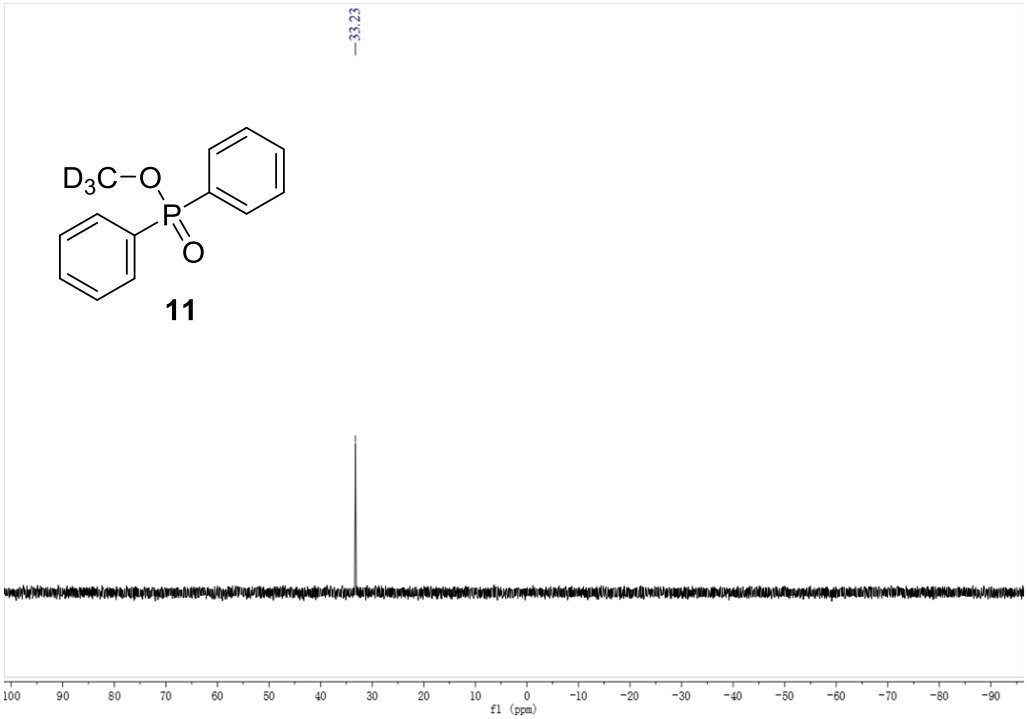
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 11

^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 11





^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 11


33.23
D3C−O
P
O
11
100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)