

Supporting Information

Redox-Neutral Decarboxylative Photocyclization of Anthranilic Acids

Huawen Huang,* Kun Deng and Guo-Jun Deng*

Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China.
E-mail: hwhuang@xtu.edu.cn; gjdeng@xtu.edu.cn

List of Contents

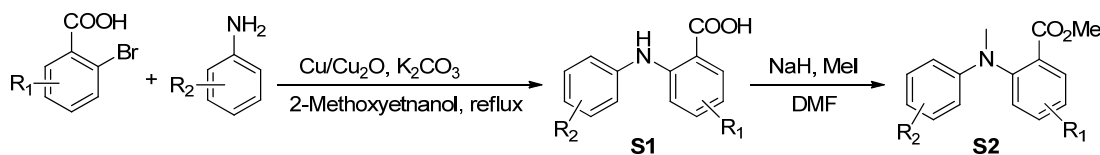
1. General information	S2
2. General synthesis procedure for preparation of starting materials	S2
3. General procedure for the synthesis of carbazoles	S4
4. Optimizing reaction conditions	S5
5. Mechanistic experiments	S6
6. Characterization data of products	S11
7. References	S23
8. Copies of ^1H and ^{13}C , ^{19}F NMR spectra of all products	S24

1. General information

The reactions via general procedure were carried out under an atmosphere of air. Column chromatography was performed using silica gel (200-300 mesh). ^1H NMR and ^{13}C , ^{19}F NMR spectra were recorded on Bruker-AV (400 and 100 MHz, and 376 MHz respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). The structures of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C , ^{19}F NMR data with those of literature. UV-Vis absorption was measured using Hitachi UH5300. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected.

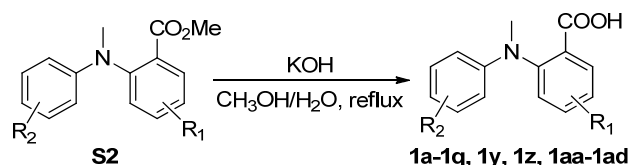
2. General synthesis procedure for preparation of starting materials

General synthesis procedure for preparation of starting materials **1a~1q**, **1y**, **1z**, **1aa~1ad** ^[1a]



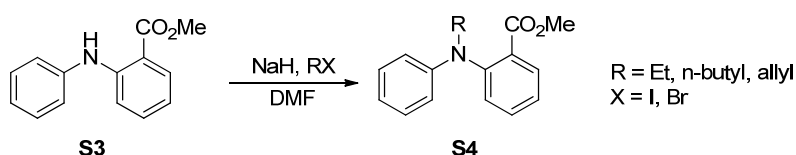
A mixture of substituted 2-bromobenzoic acid (8 mmol), substituted aniline (7.56 mmol), K_2CO_3 (1.04 g, 7.56 mmol), Cu (25.6 mg, 0.4 mmol), and Cu_2O (28.61 mg, 0.2 mmol) in 2-methoxyethanol (10 mL) was heated at $130\text{ }^\circ\text{C}$ under nitrogen for 24 h. The reaction mixture was diluted with H_2O (30 mL) and filtered through celite. The pH of the solution was adjusted to $\text{pH} = 3$ using 10% aqueous citric acid solution. The crude product was obtained. Then, 100 mL 5% Na_2CO_3 was used to dissolve the crude product and the filtrate was extracted by acidification with hydrochloric acid to obtain **S1**.

To a solution of **S1** (5 mmol) in dry DMF (30 mL) was added NaH (240 mg, 10 mmol). The suspension was stirred for 2 h, followed by the addition of MeI (15 mmol, 0.93 mL). The resulting mixture was stirred at room temperature until TLC indicated the total consumption of **S1**. The reaction mixture was poured into water and extracted with EtOAc . The organic layer was separated, washed with water and brine, and then dried over anhydrous MgSO_4 . The solvent was evaporated, and the residue was purified through column chromatography on silica gel ($\text{PE}:\text{EA} = 20:1$) to afford desired ester **S2**.

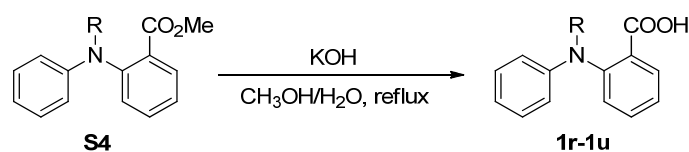


To a stirred of **S2** (5 mmol) in CH₃OH/H₂O (2:1, 15 mL) was added KOH (561 mg, 10 mmol). The resulting mixture was heated reflux 12 h. After being cooled to temperature, the reaction mixture was diluted H₂O (10 mL). And CH₃OH was evaporated. The pH of the solution was adjusted to pH = 3 using 10% aqueous citric acid solution. Extractive workup with EtOAc and purification by column chromatography obtained **1a~1q, 1y, 1z, 1aa-1ad**.

General synthesis procedure for preparation of starting materials **1r-1u** ^[1a]

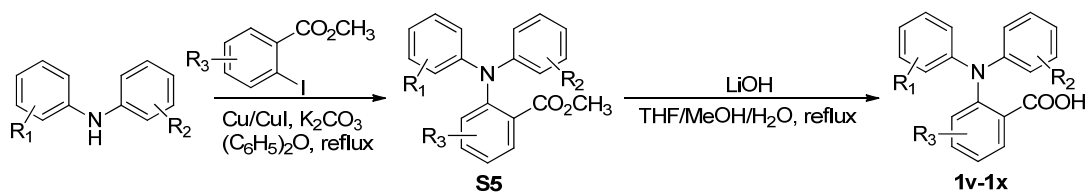


To a solution of **S3** (1.21 g, 5 mmol) in dry DMF (30 mL) was added NaH (240 mg, 10 mmol). The suspension was stirred for 2 h, followed by the addition of RX (15 mmol). The resulting mixture was stirred at room temperature until TLC indicated the total consumption of **S3**. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was separated, washed with water and brine, and then dried over anhydrous MgSO₄. The solvent was evaporated, and the residue was purified through column chromatography on silica gel (PE:EA=20:1) to afford desired ester **S4**.



To a stirred of **S4** (5 mmol) in CH₃OH/H₂O (2:1, 15 mL) was added KOH (561 mg, 10 mmol). The resulting mixture was heated reflux 12 h. After being cooled to temperature, The reaction mixture was diluted H₂O (10 mL). And CH₃OH was evaporated. The pH of the solution was adjusted to pH = 3 using 10% aqueous citric acid solution. Extractive workup with EtOAc and purification by column chromatography obtained **1r-1u**.

General synthesis procedure for preparation of starting materials **1v-1x** ^[1b]

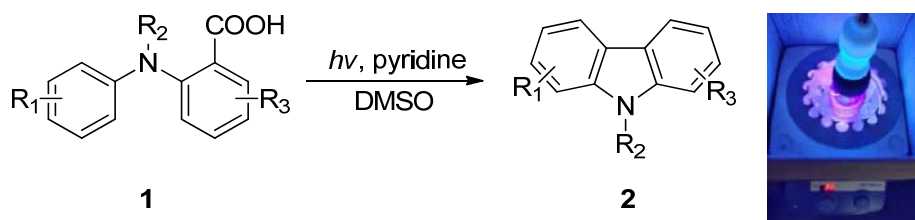


A mixture of substituted diphenylamine (5 mmol), substituted methyl 2-iodobenzoate (5 mmol), K₂CO₃ (1.73 g, 12.5 mmol), Cu (64mg, 1 mmol) and CuI (381 mg, 2 mmol) in diphenylether (5 mL) was heated at 190 °C under argon for 48 h. After cooling to room temperature, the reaction mixture was diluted with CH₂Cl₂. The residue was purified by column chromatography on silica gel (PE: EA= 20:1) to afford **S5** as yellow solid.

To a stirred solution of **S5** (1.5 mmol) in THF/MeOH/H₂O (1:1:1, 12 mL) was added lithium hydroxide hydrate (359 mg, 15 mmol). The resulting mixture was heated to 70 °C for 16 h. After being cooled to temperature, the reaction mixture was diluted with H₂O (8 mL) and the pH of the solution was adjusted to pH = 3 using 10% aqueous citric acid solution. Extractive workup with EtOAc and purification by column chromatography (PE:EA=9:1) afforded **1v-1x**.

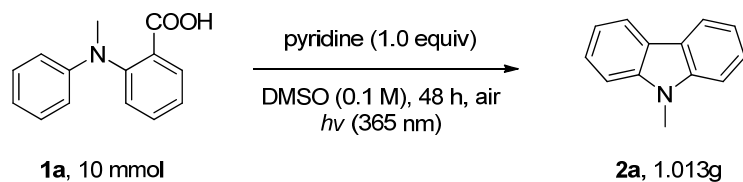
3. General procedure for the synthesis of carbazoles

To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added acids **1** (0.2 mmol), pyridine (0.2 mmol, 1 equiv), DMSO (2 mL). Thereafter, the test tube was filled with a cap and transferred to a UV-light photoreactor (365 nm, 36 W) under air, where it was irradiated for 48 h. Then the reaction was quenched with brine (5 mL), extracted with ethyl acetate (5 x 3 mL), the combined organic layer was dried over anhydrous magnesium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether/ethyl acetate, 100:1) to afford the product **2**.

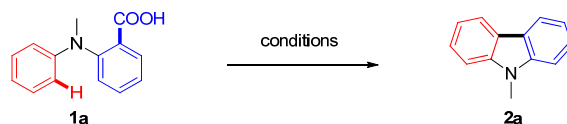


Gram scale reaction: A 150 mL round bottom flask was charged with **1a** (10 mmol, 2.270g), pyridine (10 mmol, 0.80 ml), DMSO (75 mL). The resulting mixture was stirred under air for 48 h under irradiation with 2 x 36 W UV-light. Then the reaction was quenched with brine, extracted with ethyl acetate, the combined organic layer was dried over anhydrous magnesium sulfate,

concentrated in vacuo, and purified by column chromatography (petroleum ether/ethyl acetate, 100:1) to afford the product **2a** (1.013 g, 56%).



4. Optimizing reaction conditions



Entry	PC	Light source	Base	Solvent	Yield (%) ^b
1	[Ir]PF ₆	Blue LEDs	pyridine	DMSO	46
2	4CzIPN	Blue LEDs	pyridine	DMSO	trace
3	Rose Bengal	Blue LEDs	pyridine	DMSO	ND
4 ^c	[Ir]PF ₆	Blue LEDs	pyridine	DMSO	trace
5 ^d	[Ir]PF ₆	Blue LEDs	pyridine	DMSO	40
6 ^e	[Ir]PF ₆	Blue LEDs	pyridine	DMSO	50 (46)
7	[Ir]PF ₆	Blue LEDs	KHCO ₃	DMSO	46
8	[Ir]PF ₆	Blue LEDs	NaHCO ₃	DMSO	28
9	-	UV light	pyridine	DMSO	68 (65)
10	-	UV light	pyridine	acetone	45
11	-	UV light	pyridine	H ₂ O	ND
12	-	UV light	pyridine	MeCN	51
13	-	UV light	pyridine	1,4-dioxane	51
14	-	UV light	pyridine	MeOH	ND
15	-	UV light	pyridine	EtOAc	60 (58)
16	-	UV light	DBU	DMSO	39
17	-	UV light	Et ₃ N	DMSO	37
18	-	UV light	2,6-lutidine	DMSO	48
19	-	UV light	DIPEA	DMSO	34
20	-	UV light	NaHCO ₃	DMSO	37
21	-	UV light	Cs ₂ CO ₃	DMSO	45
22	-	UV light		DMSO	30
23 ^c	-	UV light	pyridine	DMSO	35
24 ^d	-	UV light	pyridine	DMSO	65
25 ^f	-	In dark	pyridine	DMSO	ND

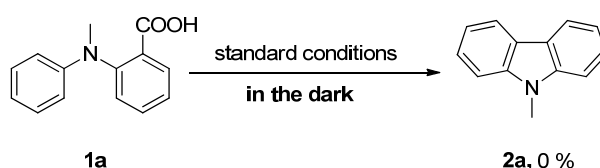
26^g - UV light pyridine DMSO 55

^a Reaction conditions: **1a** (0.2 mmol), photocatalyst (PC, 2.0 mol%) base (1.0 equiv), DMSO (2 mL), 36 W blue LED (405 nm) or 36 W UV light (365 nm), air, 48 h. [Ir]PF₆ = Ir(dF-CF₃ppy)₂(dtbbpy)PF₆. ^b Yields were determined by GC analysis using dodecane as the internal standard. Isolated yields were given in parentheses. ^c Under O₂ atmosphere. ^d Under N₂ atmosphere. ^e Pyridine (1.5 equiv). ^f No light. ^g Pyridine (0.5 equiv).

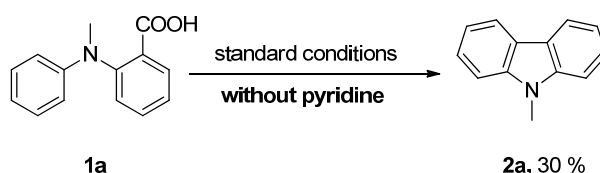
5. Mechanistic experiments

5.1 Control experiments

(1) When the reaction was performed, under the standard conditions, in a dark environment, no target product was detected.

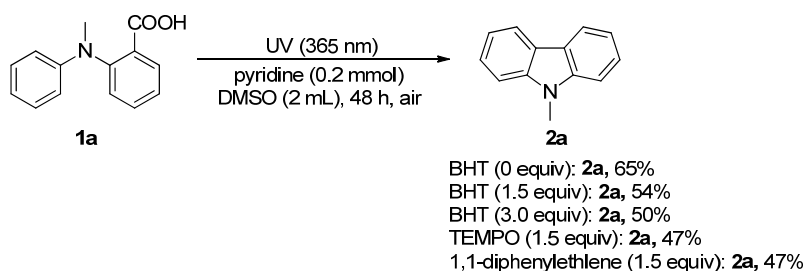


(2) In the absence of pyridine, the target product was detected, and the isolated yield was determined to be 30%.

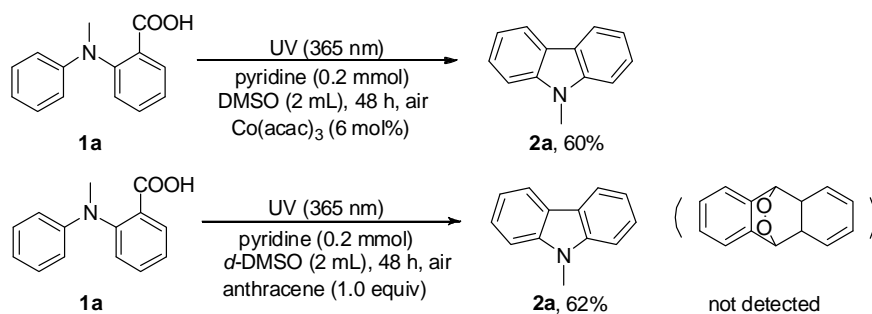


5.2 Radical-trapping experiments

When the radical scavenger BHT, TEMPO, or 1,1-diphenylethylene was added under the standard conditions, The reaction yield did not decrease significantly. No radical trapping products were detected.



We used Co(acac)₃ and anthracene to show if oxygen plays role in the reaction. When Co(acac)₃ was added under standard reaction conditions, the reaction yield did not decrease. When anthracene was added, the reaction yield did not decrease significantly. 9,10-dihydro-9,10-epidioxyanthracene was not detected. [2]



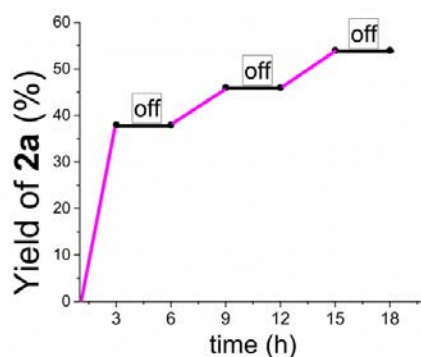
5.3 Detection of “HCOOH” by silver mirror reaction

After completion under standard reaction conditions, the reaction solution was dropped into the test tube containing the newly prepared silver ammonia solution. The test tube was placed in warm water at 35 °C for 5-10 minutes, and the generation of the silver mirror was observed.



5.4 Light on/of experiments

Following the general procedure, six reactions were set up in parallel. Sequentially, the reactions were stopped and quenched after the indicated reaction times. The yield was determined by ^1H NMR with CH_2Br_2 as internal standard.

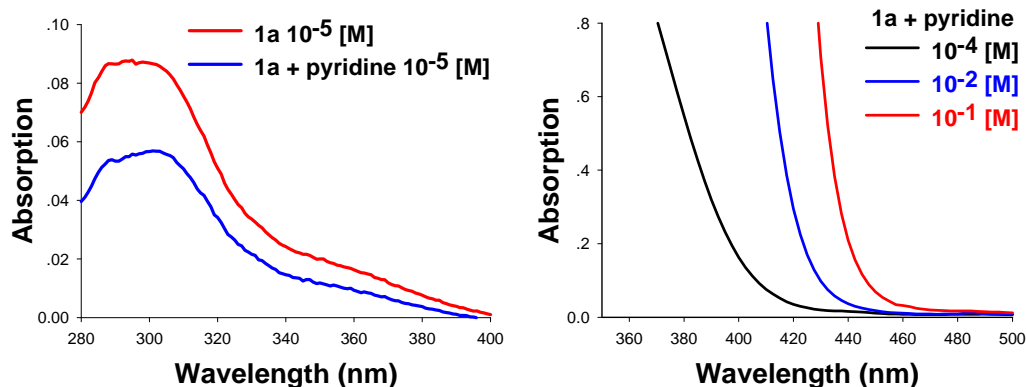


5.5 UV-Vis absorption

Formulation solution: 2-(methyl(phenyl)amino)benzoic acid (**1a**, 5.7 mg) and pyridine (2 μL) were dissolved in DMSO in a 25 mL volumetric flask to set the concentration is 10^{-3} M. This

solution was then diluted to a volume of 1.0 mL cuvette by adding DMSO to prepare 10^{-5} M solution. The 10^{-4} M, 10^{-2} M, and 10^{-1} M solutions were obtained following the above steps.^[3]

Experimental procedure: The above-mentioned solutions of different concentrations were added to the colorimetric dish, and the UV-Vis absorption curve was measured between 500nm-250nm.

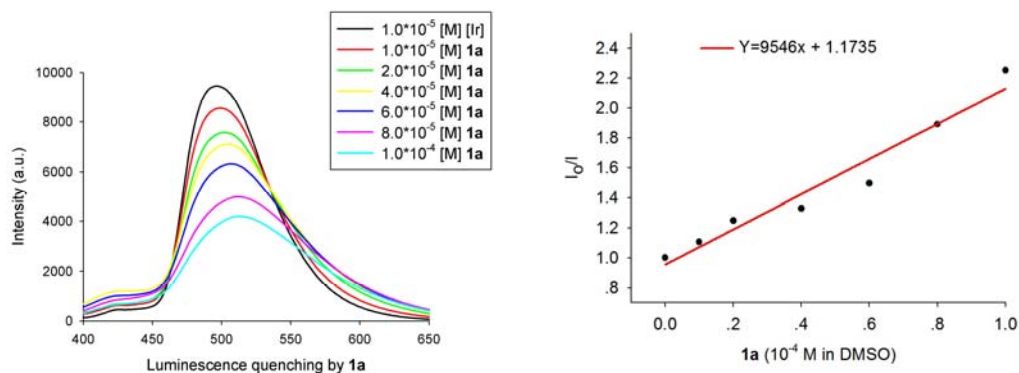


5.6 Stern-Volmer Quenching of **1a** to $\text{Ir}(\text{dF-CF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$

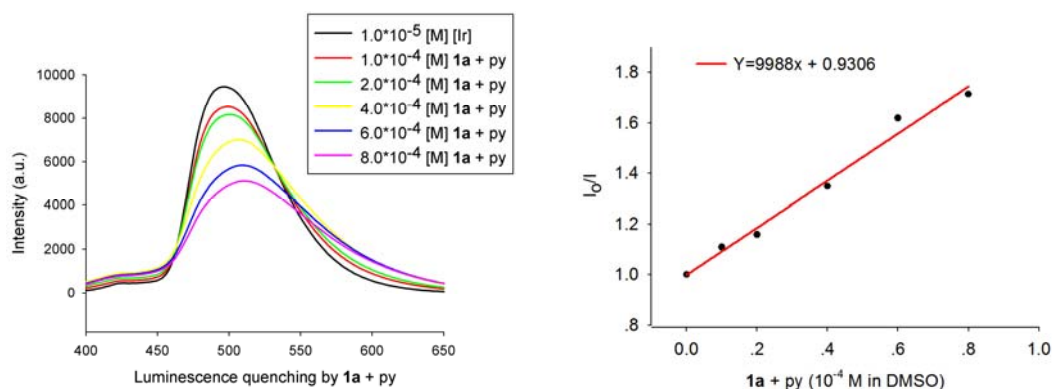
Formulation solution: 2-(methyl(phenyl)amino)benzoic acid (**1a**, 56.7 mg) and pyridine (20 μL) were dissolved in DMSO in a 25 mL volumetric flask to set the concentration is 10^{-2} M. $\text{Ir}(\text{dF-CF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (2 mg) was dissolved in DMSO in a 25 mL volumetric flask to set the concentration is 10^{-3} M.

Experimental procedure: The 10^{-3} M $\text{Ir}(\text{dF-CF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ solution was then diluted to a volume of 1.0 mL cuvette by adding DMSO to prepare 10^{-5} M solution. Fluorescence emission spectra were recorded. Fluorescence emission spectra of 1.0 μL , 2.0 μL , 4.0 μL , 6.0 μL , 8.0 μL , 10.0 μL **1a** fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern-Volmer relationship in turn.

(a) $\text{Ir}(\text{dF-CF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ quenched by **1a** in DMSO

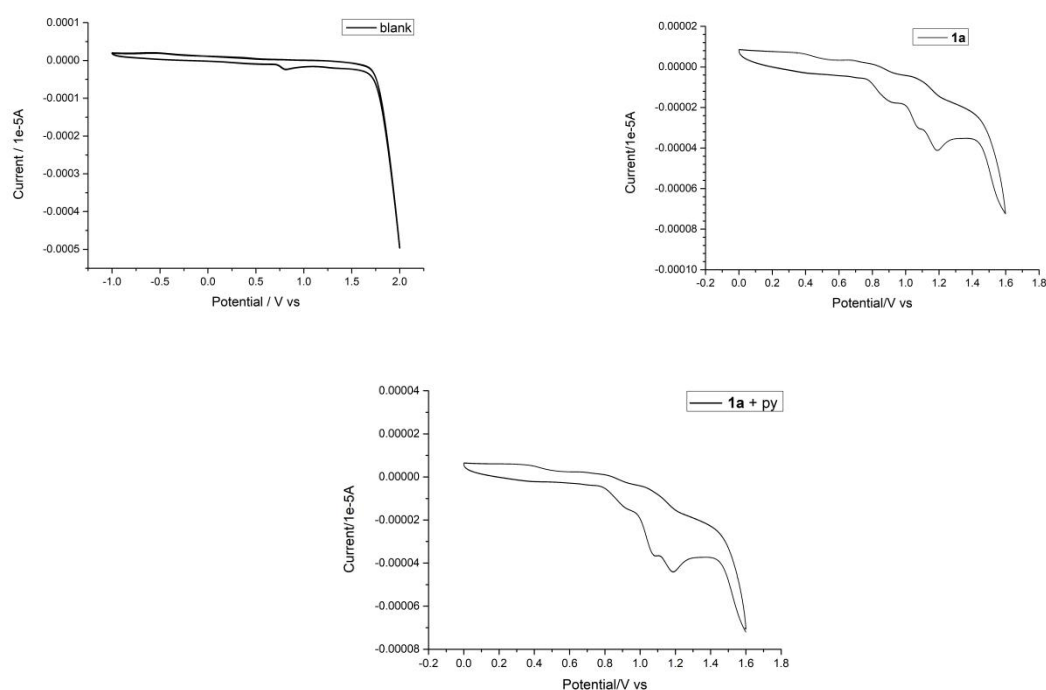


(b) Ir(dF-CF₃ppy)₂(dtbbpy)PF₆ quenched by **1a** + pyridine in DMSO



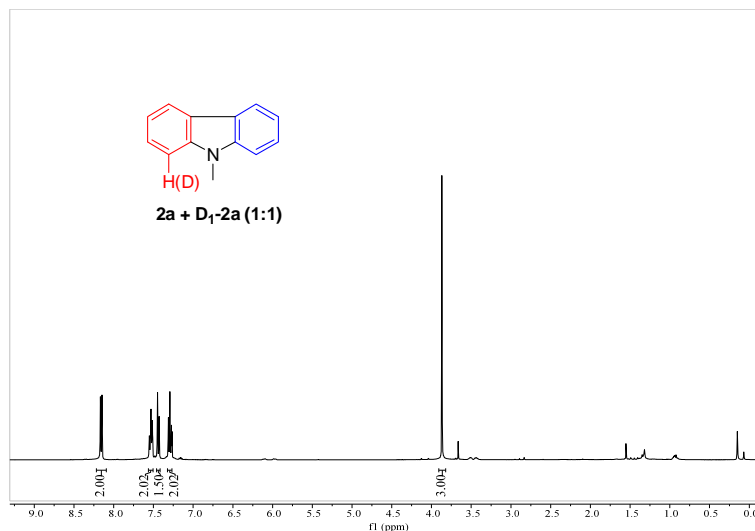
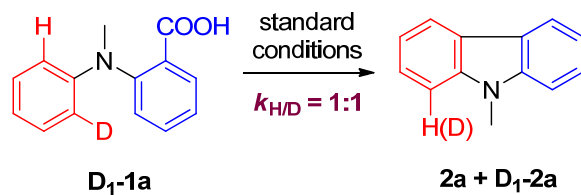
5.7 Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI604E potentiostat at room temperature in DMF. *n*-BuNBF₄ (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 100 mV · s⁻¹.

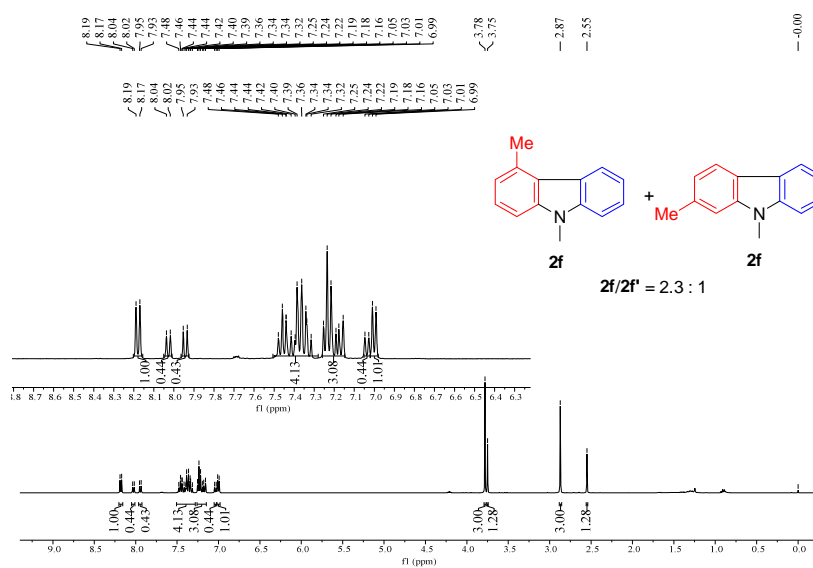
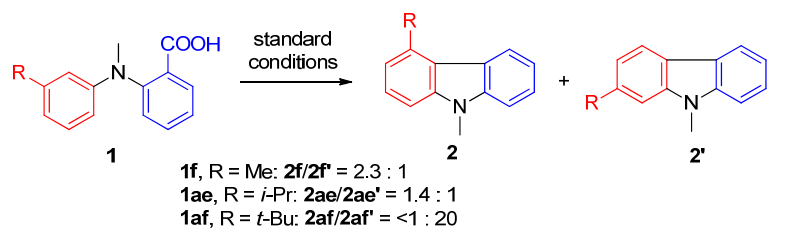


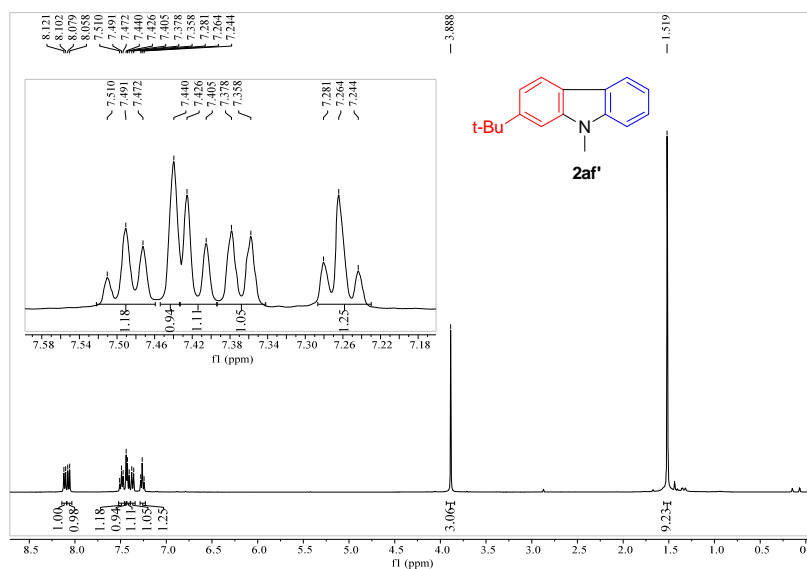
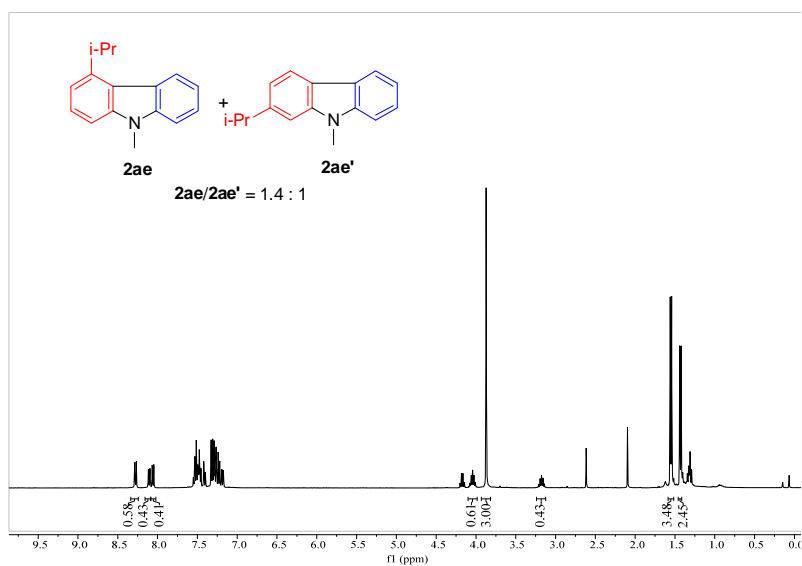
5.8 KIE experiment

D1-1a as the raw material was subjected to reaction under standard conditions. The result indicates that the KIE was $k_{H/D} = 1.0$.

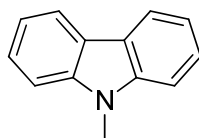


5.9 Steric hindrance effect of the meta-aniline





6. Characterization data of products

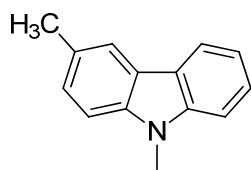


9-Methyl-9H-carbazole (2a) ^[4]

The general procedure was followed using 2-(methyl(phenyl)amino)benzoic acid (**1a**, 0.2 mmol, 45.4 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2a** (23.5 mg, 65%) as a white solid, mp: 85-87 $^{\circ}$ C.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.22 (t, J = 7.5 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 125.6, 122.7,

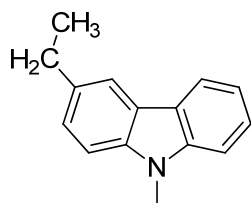
120.3, 118.8, 108.4, 28.9.



3,9-Dimethyl-9H-carbazole (**2b**)^[4]

The general procedure was followed using 2-(methyl(p-tolyl)amino)benzoic acid (**1b**, 0.2 mmol, 48.2 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2b** (22.2 mg, 57%) as a white solid, mp: 86-88 °C.

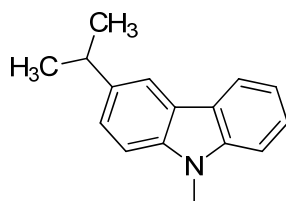
¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.7 Hz, 1H), 7.88 (s, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 (s, 2H), 7.20 (d, J = 7.0 Hz, 1H), 3.78 (s, 3H), 2.53 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 141.2, 139.3, 128.0, 126.9, 125.4, 122.8, 122.5, 120.2, 120.2, 118.5, 108.3, 108.1, 29.0, 21.4.



3-Ethyl-9-methyl-9H-carbazole (**2c**)^[5]

The general procedure was followed using 2-((4-ethylphenyl)(methyl)amino)benzoic acid (**1c**, 0.2 mmol, 51.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2c** (20.9 mg, 50%) as a white solid, mp: 86-88 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.7 Hz, 1H), 7.91 (s, 1H), 7.47–7.42 (m, 1H), 7.37–7.30 (m, 3H), 7.21–7.19 (m, 1H), 3.79 (s, 3H), 2.83 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.4, 134.8, 125.9, 125.4, 122.8, 122.6, 120.2, 119.0, 118.5, 108.3, 108.2, 29.0, 28.9, 16.6.

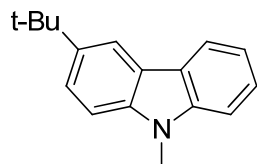


3-Isopropyl-9-methyl-9H-carbazole (**2d**)

The general procedure was followed using 2-((4-isopropylphenyl)(methyl)amino)benzoic acid (**1d**, 0.2 mmol, 53.8 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on

silica gel (PE/EA: 100/1) yielded **2d** (22.3 mg, 50%) as a white solid, mp: 90-92 °C.

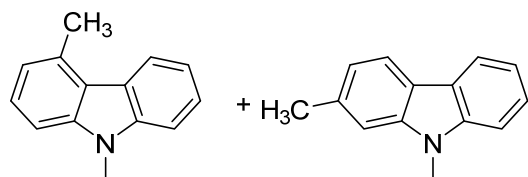
¹H NMR (400 MHz, CDCl₃) δ 8.11–8.06 (m, 1H), 7.95 (s, 1H), 7.45–7.42 (m, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.31 (s, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 3.78 (s, 3H), 3.10 (m, *J* = 6.8, 3.3 Hz, 1H), 1.37 (m, *J* = 6.9, 3.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.6, 139.5, 129.4, 125.4, 124.6, 122.7, 122.7, 120.2, 118.5, 117.5, 108.3, 108.2, 34.2, 29.0, 24.8.



3-(*tert*-Butyl)-9-methyl-9H-carbazole (**2e**)

The general procedure was followed using 2-((4-(*tert*-butyl)phenyl)(methyl)amino)benzoic acid (**1e**, 0.2 mmol, 56.8 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2e** (21.3 mg, 45%) as a colorless oil.

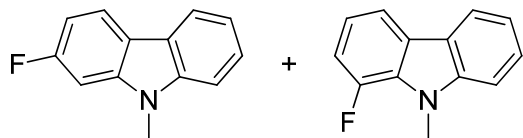
¹H NMR (400 MHz, CDCl₃) δ 8.12–8.08 (m, 2H), 7.55 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.46–7.42 (m, 1H), 7.34 (dd, *J* = 13.5, 8.4 Hz, 2H), 7.21 (d, *J* = 1.4 Hz, 1H), 3.80 (s, 3H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 141.3, 139.1, 125.4, 123.6, 122.9, 122.4, 120.1, 118.5, 116.4, 108.3, 107.9, 34.6, 32.0, 29.0.



1,9-Dimethyl-9H-carbazole (**2f**)^[6] + 2,9-Dimethyl-9H-carbazole (**2f'**)^[4]

The general procedure was followed using 2-(methyl(*m*-tolyl)amino)benzoic acid (**1**, 0.2 mmol, 48.2 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2f** + **2f'** (31.2 mg, 80%, **2f** + **2f'**: 2.3/1) as a colorless oil.

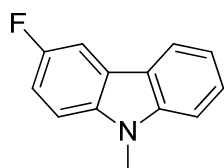
¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 0.43H), 7.94 (d, *J* = 7.9 Hz, 0.43H), 7.51–7.28 (m, 4.2H), 7.25–7.16 (m, 2.4H), 7.04 (d, *J* = 7.9 Hz, 0.43H), 7.00 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 1.28H), 2.87 (s, 3H), 2.55 (s, 1.28H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 140.9, 140.8, 135.8, 133.3, 125.4, 125.0, 124.9, 123.3, 122.8, 122.5, 121.2, 120.4, 120.3, 120.0, 119.9, 118.7, 118.6, 108.6, 108.3, 108.1, 105.9, 28.9, 28.9, 22.2, 20.8.



2-Fluoro-9-methyl-9H-carbazole (2g) ^[4] + **1-Fluoro-9-methyl-9H-carbazole (2g')**

The general procedure was followed using 2-((3-fluorophenyl)(methyl)amino)benzoic acid (**1g**, 0.2 mmol, 49.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2g** + **2g'** (25.0 mg, 63%, **2g** + **2g'**: 1/1) as a colorless oil.

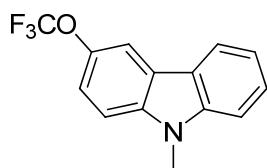
¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 7.7 Hz, 1H), 7.97 (m, J = 8.4, 5.5 Hz, 1H), 7.48 (m, J = 16.8, 9.0 Hz, 2H), 7.37 (m, J = 7.4 Hz, 3H), 7.28–7.21 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.05–7.02 (m, 1H), 6.97–6.87 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.1 (d, J = 240 Hz), 158.6 (d, J = 250 Hz), 143.2 (d, J = 11 Hz), 141.7 (d, J = 10 Hz), 141.4, 140.5, 126.2 (d, J = 9 Hz), 125.8, 125.2, 122.9 (d, J = 3 Hz), 122.4, 121.1 (d, J = 11 Hz), 120.2, 119.9, 119.5, 119.3, 119.1, 111.0 (d, J = 2 Hz), 108.4, 108.3, 106.8 (d, J = 24 Hz), 104.7 (d, J = 19 Hz), 104.3 (d, J = 3 Hz), 95.4 (d, J = 26 Hz), 29.4, 29.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.2, -119.4.



3-Fluoro-9-methyl-9H-carbazole (2h) ^[4]

The general procedure was followed using 2-((4-fluorophenyl)(methyl)amino)benzoic acid (**1h**, 0.2 mmol, 49.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2h** (24.6 mg, 62%) as a white solid, mp: 68–70 °C.

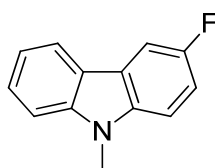
¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 7.8 Hz, 1H), 7.74 (dd, J = 8.3, 1.7 Hz, 1H), 7.51–7.47 (m, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.29 (dd, J = 8.8, 4.2 Hz, 1H), 7.24–7.18 (m, 2H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2 (d, J = 234 Hz), 141.7, 137.3, 126.2, 123.5 (d, J = 9 Hz), 122.3 (d, J = 5 Hz), 120.5, 118.8, 113.3 (d, J = 2.5 Hz), 108.9 (d, J = 11 Hz), 108.7, 106.0 (d, J = 24 Hz), 29.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -125.4.



9-Methyl-3-(trifluoromethoxy)-9H-carbazole (2i)

The general procedure was followed using 2-(methyl(4-(trifluoromethoxy)phenyl)amino)benzoic acid (**1i**, 0.2 mmol, 62.2 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2i** (35.5 mg, 67%) as a colorless oil.

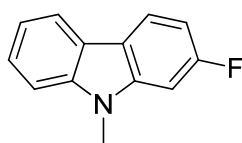
^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.8$ Hz, 1H), 7.92 (s, 1H), 7.50 (m, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.32 (s, 2H), 7.26–7.22 (m, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.1, 141.7, 139.1, 126.5, 122.9, 122.1, 121.0 (q, $J = 256$ Hz), 120.5, 119.3, 119.2, 113.2, 108.8, 108.8, 29.1. ^{19}F NMR (376 MHz, CDCl_3) δ -58.2.



3-Fluoro-9-methyl-9H-carbazole (**2j**)^[4]

The general procedure was followed using 5-fluoro-2-(methyl(phenyl)amino)benzoic acid (**1j**, 0.2 mmol, 49.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2j** (8.7 mg, 22%) as a white solid, mp: 68-70 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.8$ Hz, 1H), 7.74 (dd, $J = 8.3, 1.7$ Hz, 1H), 7.51–7.47 (m, 1H), 7.38 (d, $J = 8.2$ Hz, 1H), 7.29 (dd, $J = 8.8, 4.2$ Hz, 1H), 7.24–7.18 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.2 (d, $J = 234$ Hz), 141.7, 137.3, 126.2, 123.5 (d, $J = 9$ Hz), 122.3 (d, $J = 5$ Hz), 120.5, 118.8, 113.3 (d, $J = 2.5$ Hz), 108.9 (d, $J = 11$ Hz), 108.7, 106.0 (d, $J = 24$ Hz), 29.2. ^{19}F NMR (376 MHz, CDCl_3) δ -125.4.

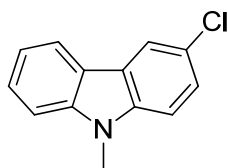


2-Fluoro-9-methyl-9H-carbazole (**2k**)^[4]

The general procedure was followed using 4-fluoro-2-(methyl(phenyl)amino)benzoic acid (**1k**, 0.2 mmol, 49.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2k** (16.2 mg, 41%) as a white solid, mp: 65-68 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.07–7.93 (m, 2H), 7.46 (m, $J = 7.6, 7.2$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.96 (q, $J = 8.2$ Hz, 1H), 3.79 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.1 (d, $J = 240$ Hz), 141.7 (d, $J = 13$ Hz), 141.4 (d, $J = 1$ Hz), 125.2, 122.4, 121.1 (d, $J = 11$ Hz), 119.9, 119.3, 119.1, 108.4, 106.9 (d, $J = 24$ Hz), 95.

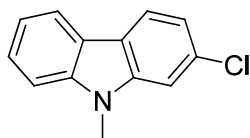
4 (d, $J = 24$ Hz), 29.2. ^{19}F NMR (376 MHz, CDCl_3) δ -115.2.



3-Chloro-9-methyl-9H-carbazole (2l) ^[4]

The general procedure was followed using 5-chloro-2-(methyl(phenyl)amino)benzoic acid (**1l**, 0.2 mmol, 52.2 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2l** (19.8 mg, 46%) as a colorless oil.

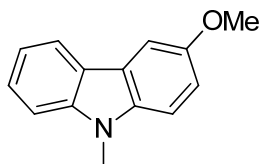
^1H NMR (400 MHz, CDCl_3) δ 8.10–7.96 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.43–7.35 (m, 2H), 7.29 (d, $J = 8.6$ Hz, 1H), 7.24–7.21 (m, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 139.2, 126.3, 125.7, 124.3, 123.8, 121.8, 120.5, 119.9, 119.2, 109.4, 108.7, 29.2.



2-Chloro-9-methyl-9H-carbazole (2m) ^[4]

The general procedure was followed using 4-chloro-2-(methyl(phenyl)amino)benzoic acid (**1m**, 0.2 mmol, 52.2 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2m** (30.24mg, 70%) as a white solid, mp: 72-74 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 7.8$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 1H), 7.53–7.48 (m, 1H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.29–7.26 (m, 1H), 7.21 (dd, $J = 8.3, 1.6$ Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 141.2, 131.4, 125.9, 122.2, 121.3, 121.0, 120.2, 119.3, 119.3, 108.6, 29.1.

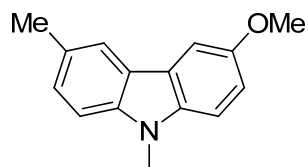


3-Methoxy-9-methyl-9H-carbazole (2n) ^[4]

The general procedure was followed using 5-methoxy-2-(methyl(phenyl)amino)benzoic acid (**1n**, 0.2 mmol, 51.4 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2n** (16.0 mg, 38%) as a white solid, mp: 94-95 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.8$ Hz, 1H), 7.57 (s, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 1H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.13–7.08 (m, 1H), 3.92 (s,

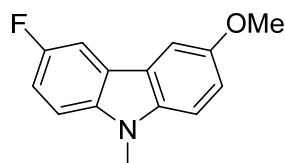
3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 141.4, 135.9, 125.6, 122.1, 122.5, 120.2, 118.6, 114.7, 109.1, 108.5, 103.2, 56.1, 29.1.



3-Methoxy-6,9-dimethyl-9H-carbazole (**2o**)^[4]

The general procedure was followed using 5-methoxy-2-(methyl(p-tolyl)amino)benzoic acid (**1o**, 0.2 mmol, 54.2 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2o** (27.0 mg, 60%) as a white solid, mp: 97-99 $^\circ\text{C}$.

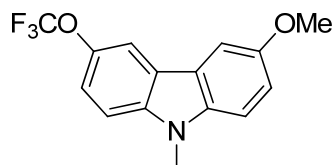
^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 1H), 7.75 (s, 1H), 7.18 (s, 2H), 6.77 (d, $J = 3.2$ Hz, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 142.5, 139.3, 128.1, 125.5, 122.9, 120.8, 119.4, 116.4, 107.8, 106.9, 92.6, 55.5, 28.9, 21.4.



3-Fluoro-6-methoxy-9-methyl-9H-carbazole (**2p**)

The general procedure was followed using 2-((4-fluorophenyl)(methyl)amino)-5-methoxybenzoic acid (**1p**, 0.2 mmol, 55.0 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2p** (28.8 mg, 63%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.9$ Hz, 1H), 7.48 (s, 1H), 7.27 (d, $J = 8.6$ Hz, 2H), 7.14 (m, $J = 8.9$ Hz, 2H), 3.92 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.9 (d, $J = 233$ Hz), 153.4, 137.8, 136.9, 122.7 (d, $J = 10$ Hz), 122.4, 115.6, 113.3 (d, $J = 25$ Hz), 109.4, 108.9 (d, $J = 9$ Hz), 105.8 (d, $J = 23$ Hz), 103.1, 56.1, 29.3. ^{19}F NMR (376 MHz, CDCl_3) δ -125.9.

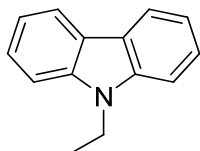


3-Methoxy-9-methyl-6-(trifluoromethoxy)-9H-carbazole (**2q**)

The general procedure was followed using 5-methoxy-2-(methyl(4-(trifluoromethoxy)phenyl)amino)benzoic acid (**1q**, 0.2 mmol, 68.2mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2q** (40.7 mg, 69%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.50 (d, $J = 2.4$ Hz, 1H), 7.30-7.28 (m, 2H), 7.25 (d, J

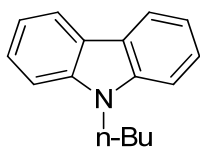
= 9.7 Hz, 1H), 7.14 (dd, $J = 8.9, 2.5$ Hz, 1H), 3.92 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.7, 141.7, 139.6, 136.7, 122.6, 122.4, 120.8 (q, $J = 254$ Hz), 119.3, 115.9, 113.1, 109.6, 108.9, 102.9, 56.0, 29.3. ^{19}F NMR (376 MHz, CDCl_3) δ -58.1.



9-Ethyl-9H-carbazole (**2r**)^[4]

The general procedure was followed using 2-(ethyl(phenyl)amino)benzoic acid (**1r**, 0.2 mmol, 48.2 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2r** (28.0 mg, 72%) as a white solid, mp: 57-59 $^\circ\text{C}$.

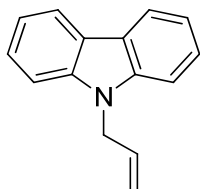
^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 7.7$ Hz, 2H), 7.48–7.42 (m, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.22 (t, $J = 7.3$ Hz, 2H), 4.35 (q, $J = 7.2$ Hz, 2H), 1.41 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.9, 125.6, 122.9, 120.4, 118.7, 108.4, 37.4, 13.8.



9-Butyl-9H-carbazole (**2s**)^[4]

The general procedure was followed using 2-(butyl(phenyl)amino)benzoic acid (**1s**, 0.2 mmol, 53.8 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2s** (30.3 mg, 68%) as a white solid, mp: 56-58 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 7.7$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.22 (t, $J = 7.3$ Hz, 2H), 4.29 (t, $J = 7.1$ Hz, 2H), 1.84 (p, $J = 7.3$ Hz, 2H), 1.39 (q, $J = 7.5$ Hz, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 125.5, 122.7, 120.3, 118.6, 108.6, 42.8, 31.1, 20.6, 13.9.

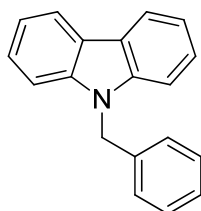


9-Allyl-9H-carbazole (**2t**)^[7]

The general procedure was followed using 2-(allyl(phenyl)amino)benzoic acid (**1t**, 0.2 mmol, 50.6 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA:

100/1) yielded **2t** (17.8 mg, 43%) as a colorless oil.

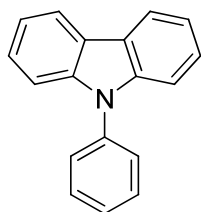
^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.7$ Hz, 2H), 7.51–7.46 (m, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 6.02 (ddd, $J = 21.9, 10.1, 4.9$ Hz, 1H), 5.21–5.16 (m, 1H), 5.10–5.03 (m, 1H), 4.97–4.90 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 132.3, 125.7, 122.9, 120.3, 119.0, 116.8, 108.7, 45.2.



9-Benzyl-9H-carbazole (**2u**)^[7]

The general procedure was followed using 2-(benzyl(phenyl)amino)benzoic acid (**1u**, 0.2 mmol, 60.6 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2u** (34.9 mg, 68%) as a white solid, mp: 102-104 $^\circ\text{C}$.

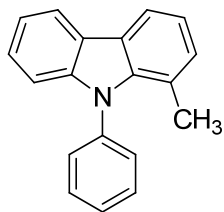
^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.24 (h, $J = 4.5$ Hz, 6H), 7.16–7.11 (m, 2H), 5.52 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 137.2, 128.8, 127.4, 126.4, 125.8, 122.9, 120.4, 119.2, 108.9, 46.5.



9-Phenyl-9H-carbazole (**2v**)^[8]

The general procedure was followed using 2-(diphenylamino)benzoic acid (**1v**, 0.2 mmol, 57.8 mg), pyridine (0.2 mmol, 16 μL). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2v** (34.9 mg, 72%) as a white solid, mp: 109-111 $^\circ\text{C}$.

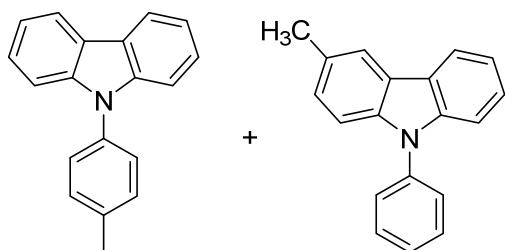
^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.5$ Hz, 2H), 7.57 (q, $J = 7.7$ Hz, 4H), 7.47–7.38 (m, 5H), 7.28 (ddd, $J = 7.9, 5.5, 3.1$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 137.6, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.7.



Methyl-9-phenyl-9H-carbazole (2w) ^[9]

The general procedure was followed using 2-(diphenylamino)-3-methylbenzoic acid (**1w**, 0.2 mmol, 60.6 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2w** (33.4 mg, 65%) as a colorless oil.

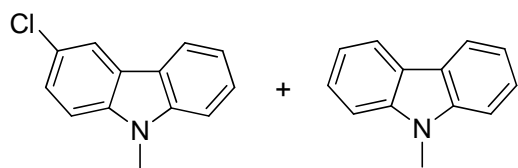
¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 7.7 Hz, 1H), 7.94 (s, 1H), 7.61–7.53 (m, 4H), 7.46–7.36 (m, 3H), 7.31 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 2.55 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 139.1, 137.9, 129.8, 129.4, 129.2, 127.3, 127.2, 126.9, 125.7, 123.4, 123.2, 120.2, 119.7, 109.7, 109.4, 21.4.



9-(p-Tolyl)-9H-carbazole (2x') ^[6] + **3-Methyl-9-phenyl-9H-carbazole (2x)**

The general procedure was followed using 2-(phenyl(*p*-tolyl)amino)benzoic acid (**1x**, 0.2 mmol, 60.6 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2x'** + **2x** (30.3 mg, 59%, **2x'**/**2x**: 1/1) as a white solid, mp: 101-103 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.18–8.16 (m, 2H), 8.14–8.12 (m, 1H), 7.97 (s, 1H), 7.60–7.54 (m, 4H), 7.49–7.41 (m, 12H), 7.29–7.21 (m, 4H), 2.54 (s, 3H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 139.1, 137.9, 137.3, 134.9, 130.4, 129.8, 129.2, 127.2, 126.9, 125.8, 125.7, 123.4, 123.2, 120.2, 120.2, 119.7, 119.6, 109.7, 109.7, 109.4, 21.4, 21.2.

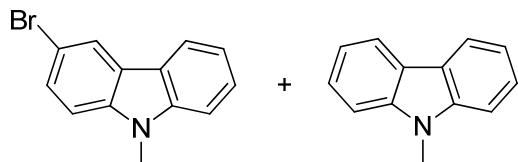


3-Chloro-9-methyl-9H-carbazole (2z) + **2a** ^[4]

The general procedure was followed using 2-((4-chlorophenyl)(methyl)amino)benzoic acid (**1**, 0.2

mmol, 52.4 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2z** + **2a** (24.2 mg, 58%, **2z/2a**: 4/1) as a colorless oil.

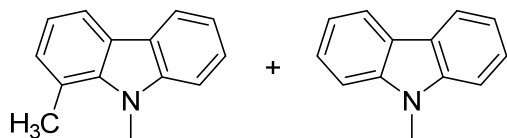
^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.7$ Hz, 0.5H), 8.06–7.99 (m, 2H), 7.50–7.45 (m, 1.5H), 7.42–7.36 (m, 2.5H), 7.29–7.22 (m, 2.5H), 3.84 (s, 0.75H), 3.81 (s, 3.00H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 140.9, 139.3, 126.4, 125.7, 125.6, 124.1, 123.8, 122.7, 121.8, 120.5, 120.3, 119.9, 119.2, 118.8, 109.4, 108.7, 108.4, 29.2, 29.0.



3-Bromo-9-methyl-9H-carbazole (2aa) + 2a ^[4]

The general procedure was followed using 2-((4-bromophenyl)(methyl)amino)benzoic acid (**1aa**, 0.2 mmol, 61.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2aa** + **2a** (29.7 mg, 62%, **2aa/2a**: 3.3/1) as a colorless oil.

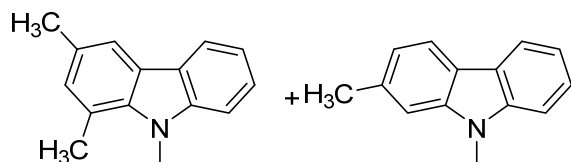
^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 1.8$ Hz, 1H), 8.12 (d, $J = 7.7$ Hz, 0.6H), 8.05 (d, $J = 7.8$ Hz, 1H), 7.58–7.48 (m, 2.6H), 7.45–7.39 (m, 1.6H), 7.28–7.24 (m, 2.6H), 3.86 (s, 0.9H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 140.9, 139.6, 128.3, 126.4, 125.7, 124.5, 123.0, 122.7, 121.8, 120.5, 120.3, 119.3, 118.8, 111.7, 109.9, 108.7, 108.4, 29.2, 29.0.



1,9-Dimethyl-9H-carbazole (2ab) ^[6] + **2a** ^[4]

The general procedure was followed using 2-(methyl(o-tolyl)amino)benzoic acid (**1ab**, 0.2 mmol, 48.2 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2ab** + **2a** (18.9 mg, 32%, **2ab/2a**: 6/1) as a colorless oil.

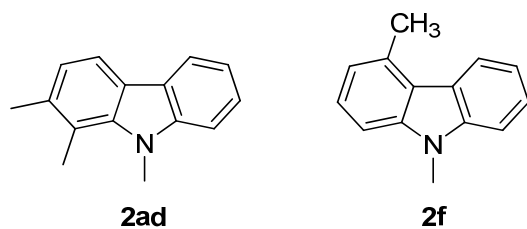
^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 0.33H), 8.06 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.49–7.35 (m, 2.6H), 7.23–7.15 (m, 2.3H), 7.10 (t, $J = 7.4$ Hz, 1H), 4.12 (s, 3H), 3.85 (s, 0.5H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 139.7, 128.8, 125.6, 125.5, 123.5, 122.9, 120.3, 120.3, 119.9, 119.0, 118.8, 118.2, 108.5, 108.4, 32.3, 20.4.



1,3,9-Trimethyl-9H-carbazole (2ac) + 2,9-Dimethyl-9H-carbazole (2f') ^[4]

The general procedure was followed using 2-((2,4-dimethylphenyl)(methyl)amino)benzoic acid (**1ac**, 0.2 mmol, 51.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2ac** + **2f'** (17.2 mg, 42%, **2ac/2f'**: 3/1) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 7.7 Hz, 0.33H), 8.02 (d, J = 7.7 Hz, 1H), 7.89 (s, 0.33H), 7.73 (s, 1H), 7.48–7.40 (m, 1.33H), 7.36–7.30 (m, 1.33H), 7.29 (s, 0.66H), 7.21–7.16 (m, 1.33H), 7.00 (s, 1H), 4.07 (s, 3H), 3.81 (s, 1H), 2.81 (s, 3H), 2.54 (s, 1H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 137.9, 130.3, 128.2, 126.9, 125.4, 125.3, 123.7, 122.7, 120.2, 120.2, 112.0, 119.9, 118.5, 118.5, 118.0, 108.4, 108.3, 108.1, 32.2, 29.1, 21.4, 21.0, 20.2.



4,9-Dimethyl-9H-carbazole (2f) ^[6]

The general procedure was followed using 2-((2,3-dimethylphenyl)(methyl)amino)benzoic acid (**1ad**, 0.2 mmol, 51.0 mg), pyridine (0.2 mmol, 16 μ L). Purification by column chromatography on silica gel (PE/EA: 100/1) yielded **2ad**+**2f** (19.8 mg, 51%, **2ad/2f**: 1/25) as a white solid, mp: 86–88 °C.

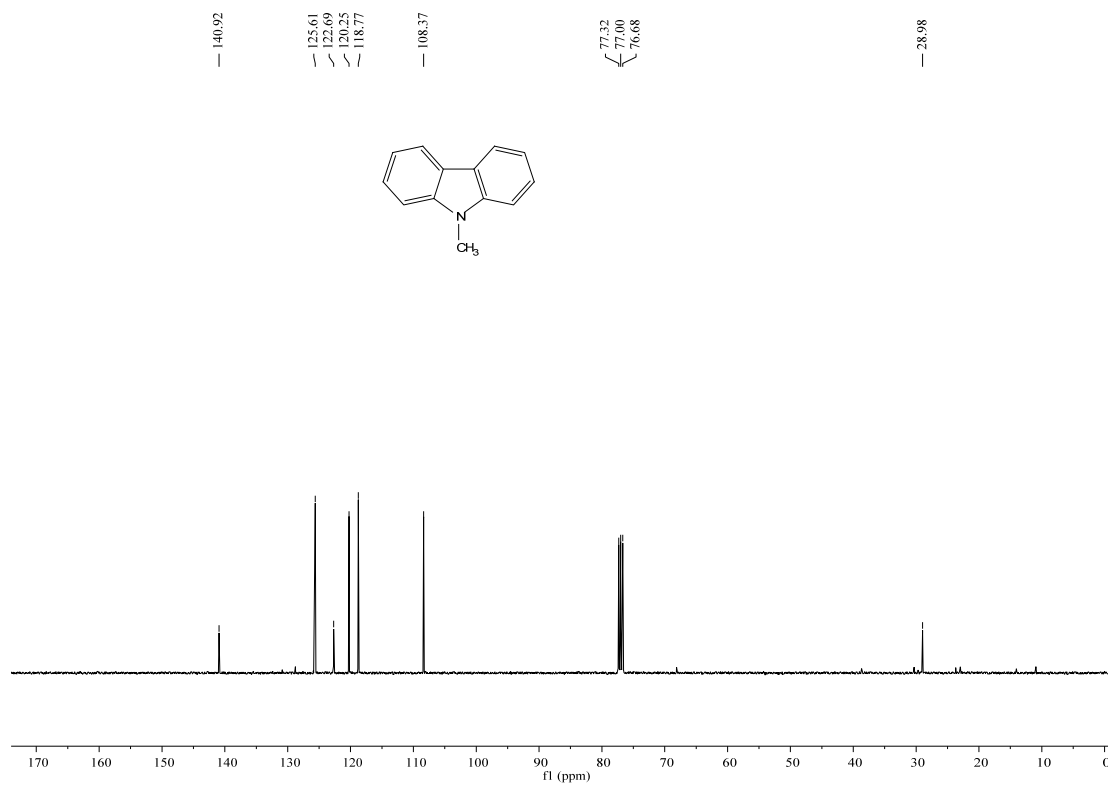
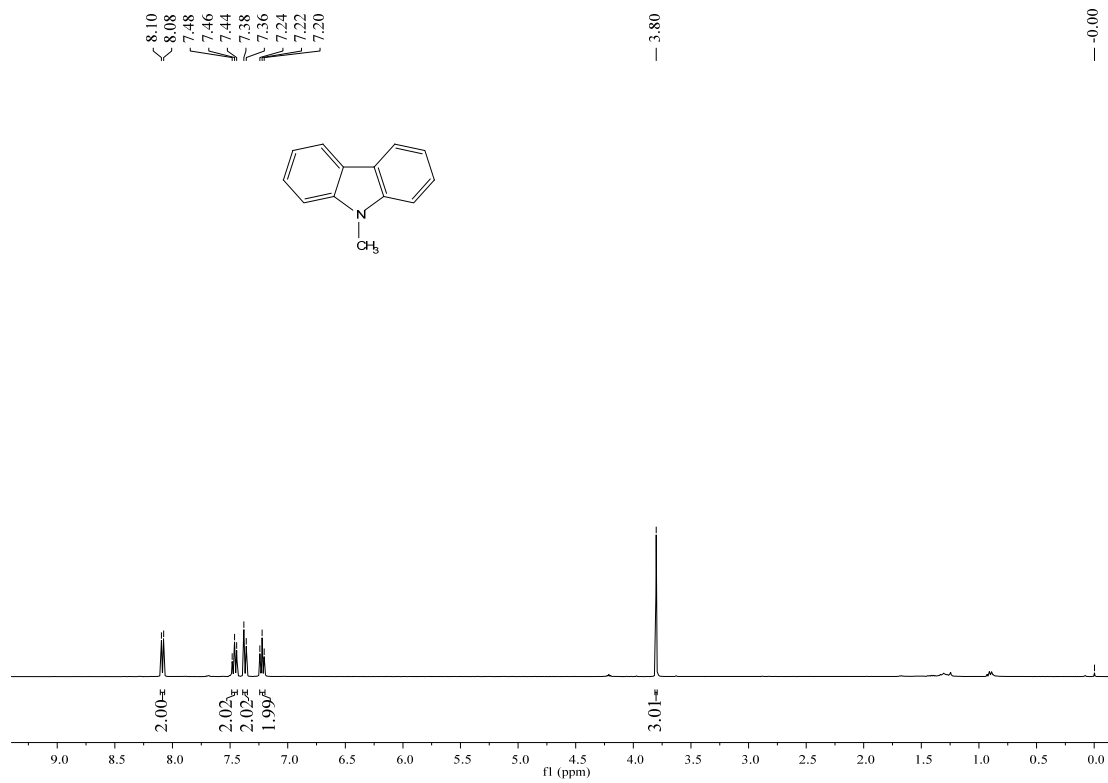
¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.39 (dd, J = 15.7, 7.9 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.2 Hz, 1H), 3.83 (s, 3H), 2.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.9, 133.4, 125.4, 124.9, 123.4, 122.5, 121.2, 120.4, 118.7, 108.1, 105.97, 29.0, 20.8.

7. References

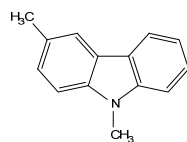
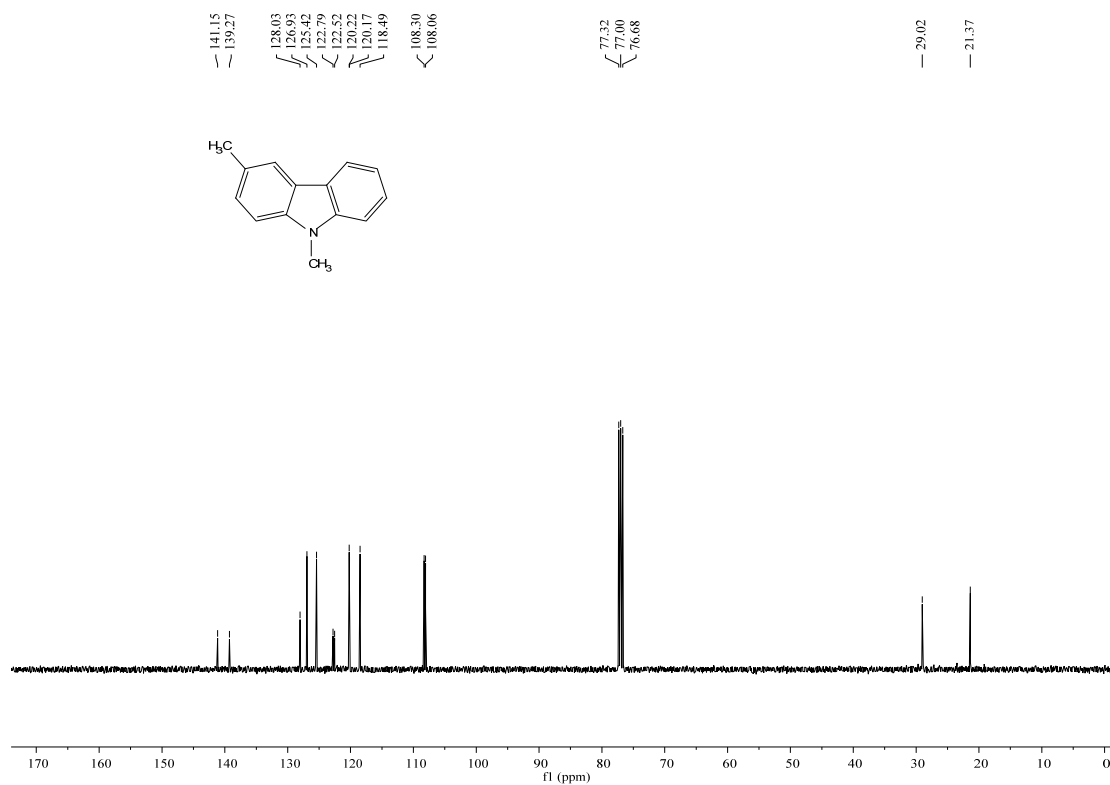
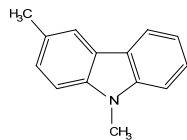
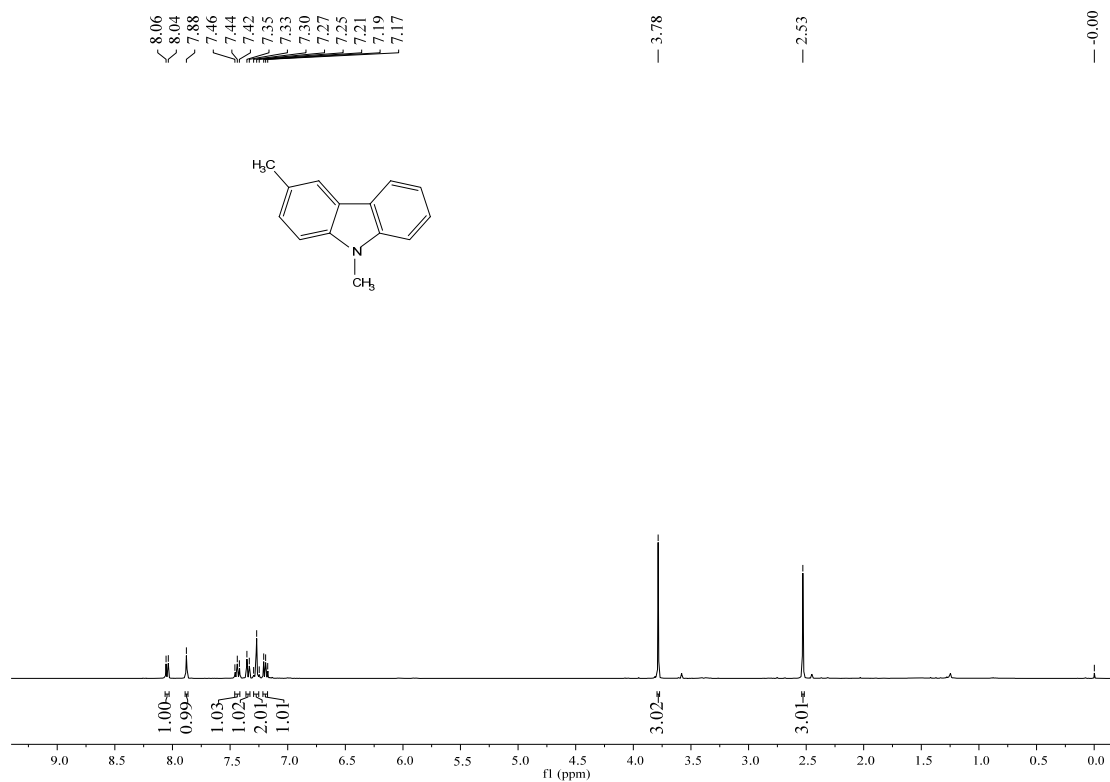
- [1]. a. Z.-S Zheng, K. Zhao, *J. Org. Chem.* **2014**, *79*, 7451. b. X. Yu, B. Zhong, *Angew. Chem. Int. Ed.* **2018**, *57*, 7997.
- [2]. M. Marin, M.-A. Miranda, *Org. Lett.* **2012**, *14*, 1788.
- [3]. S. Pusch, T. Opatz, *Org. Lett.* **2016**, *18*, 3043.
- [4]. Z.-Y. Hu, X.-X. Guo, *Org. Lett.* **2019**, *21*, 989.
- [5]. Majumdar, Roy, *Can. J. Chem.* **2005**, *83*, 63.
- [6]. Y.-L. Gu, X. Wang, *Org. Lett.* **2018**, *20*, 4285.
- [7]. James A. Jordan-Hore, Matthew J. Gaunt. *J. Am. Chem. Soc.* **2008**, *130*, 16184.
- [8]. S.-P. Collette, S.-K. Collins, *Org. Lett.* **2016**, *18*, 4994.
- [9]. W.-J. Yoo, K. Shu, *Org. Lett.* **2015**, *17*, 3640.

8. Copies of ^1H , ^{13}C , and ^{19}F NMR spectra of all products

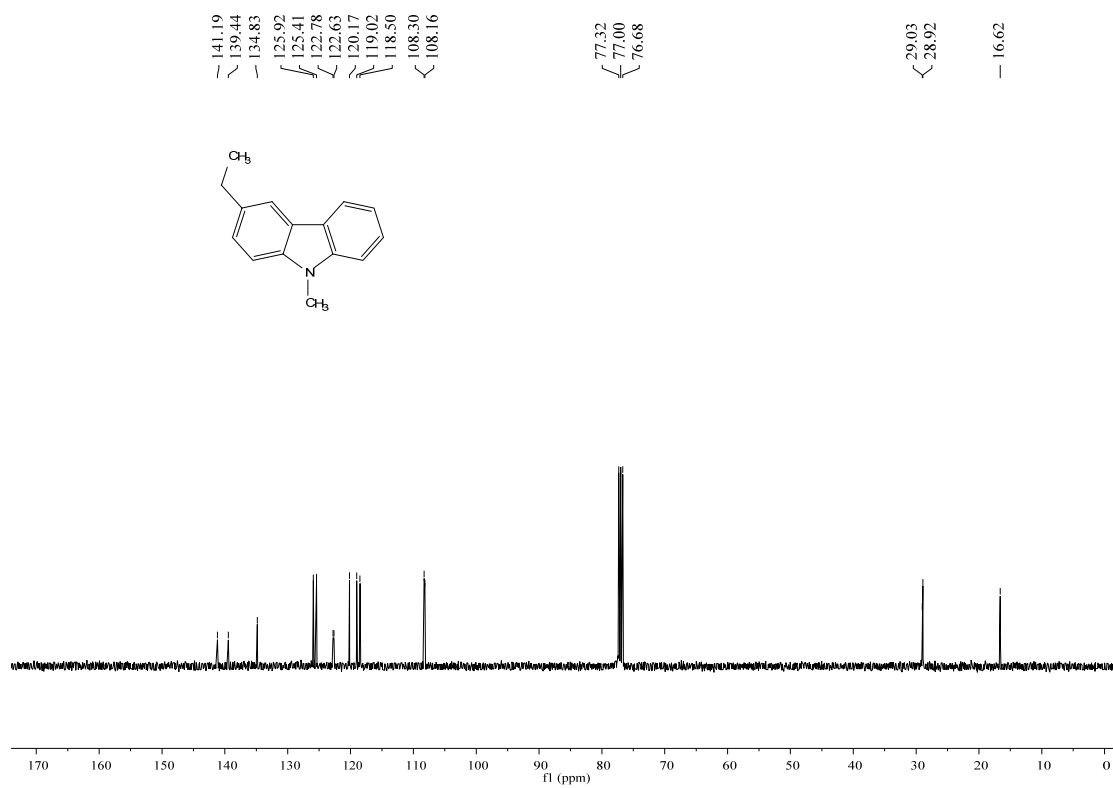
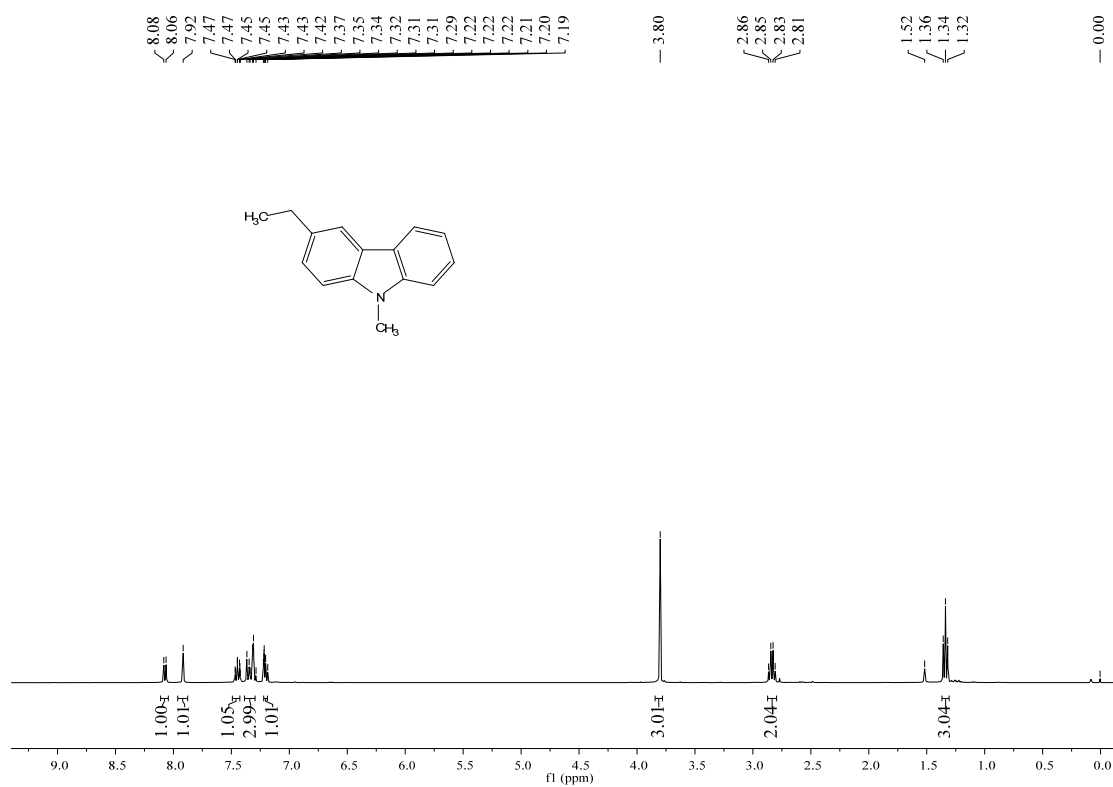
^1H and ^{13}C NMR spectra of 2a



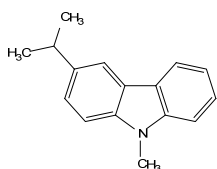
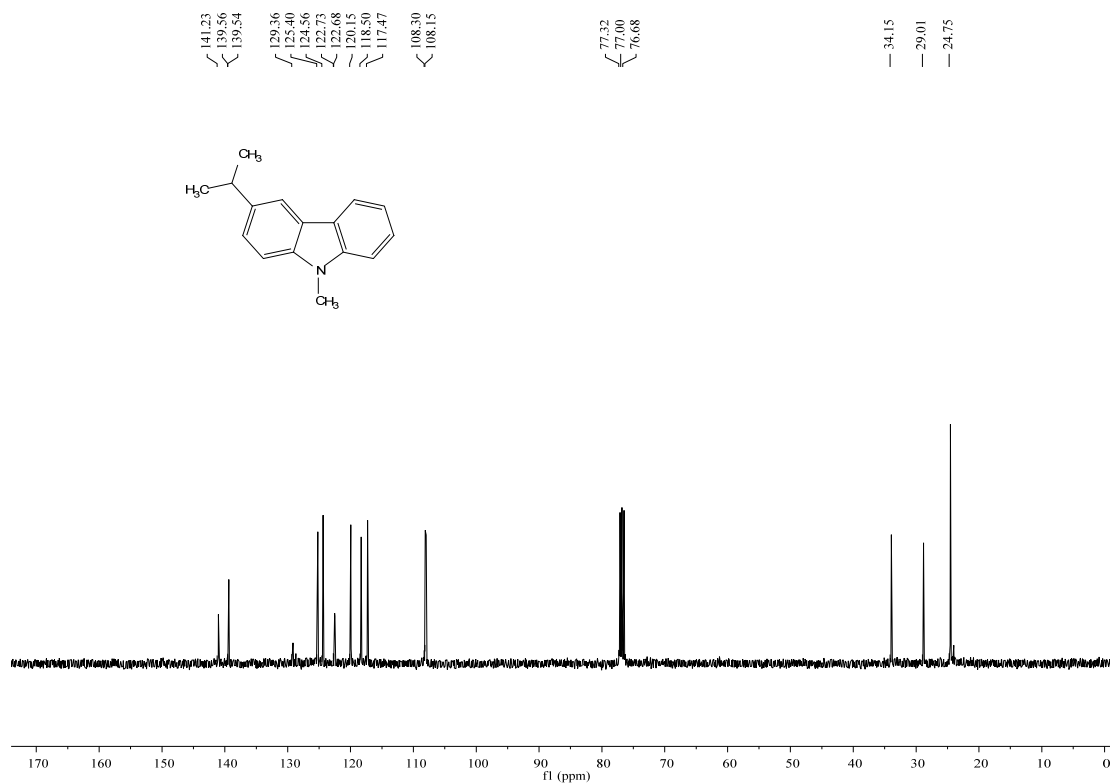
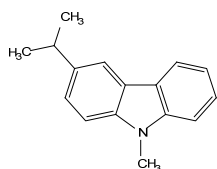
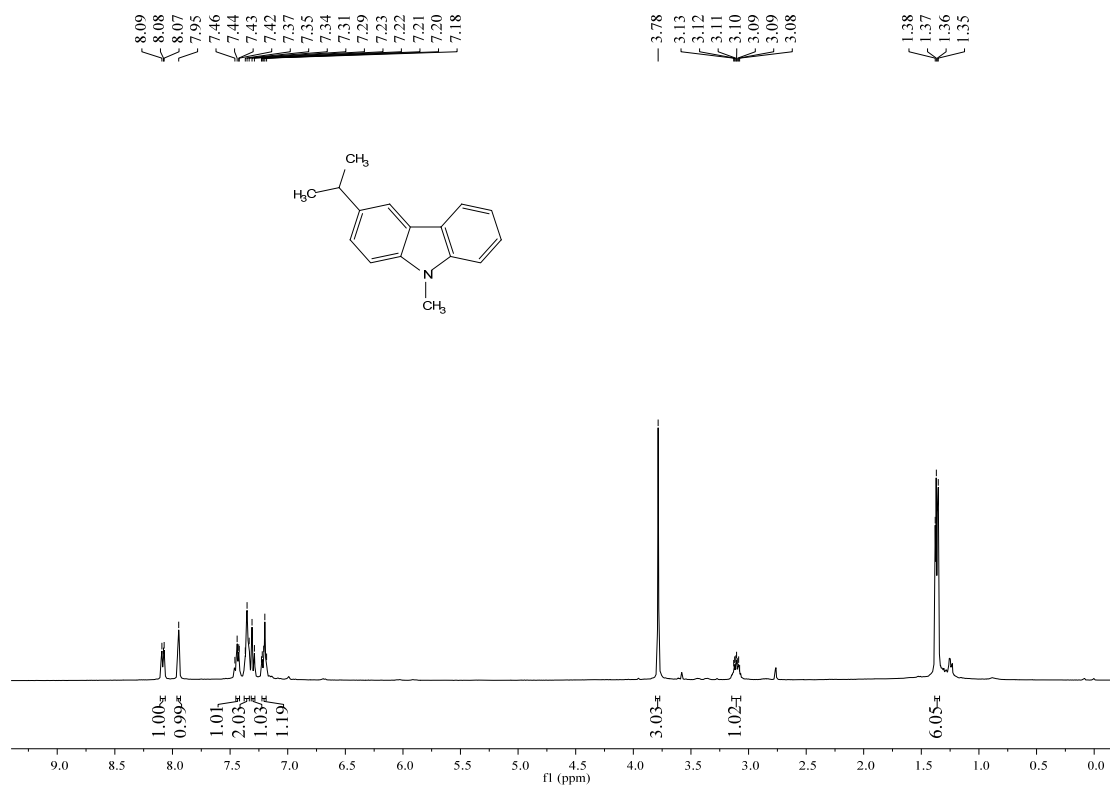
¹H and ¹³C NMR spectra of 2b



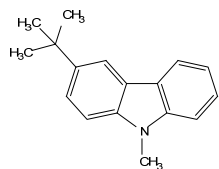
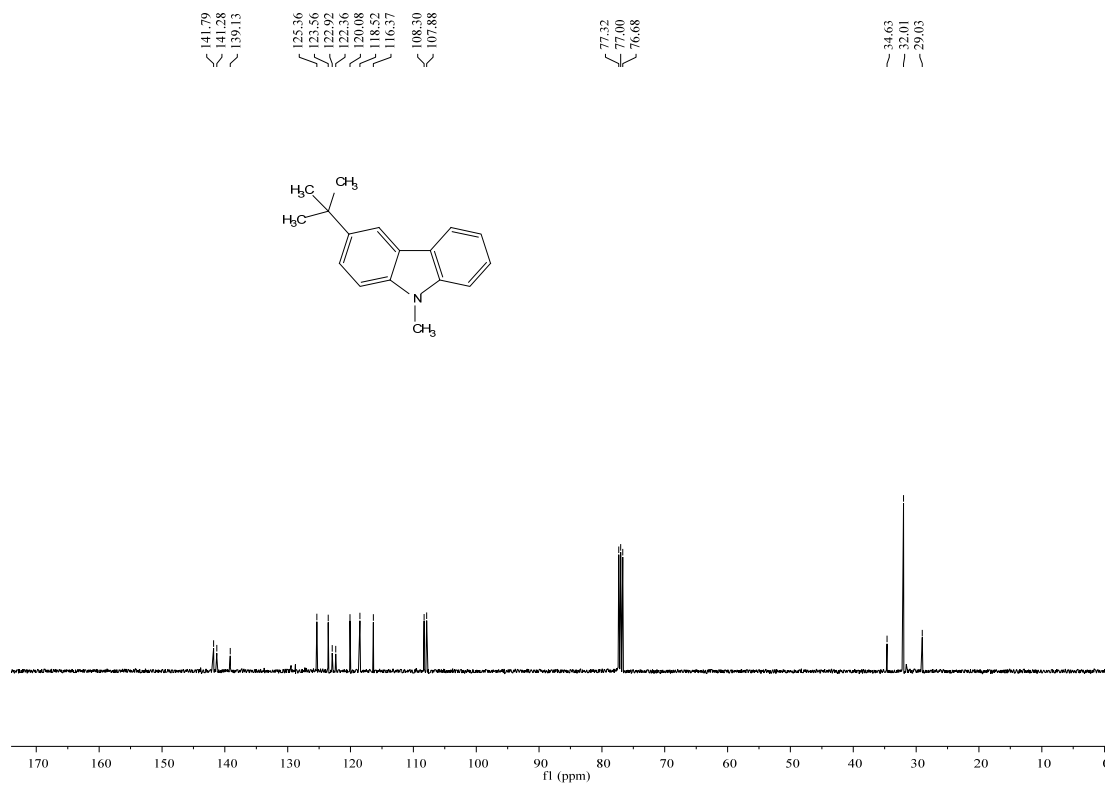
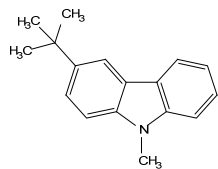
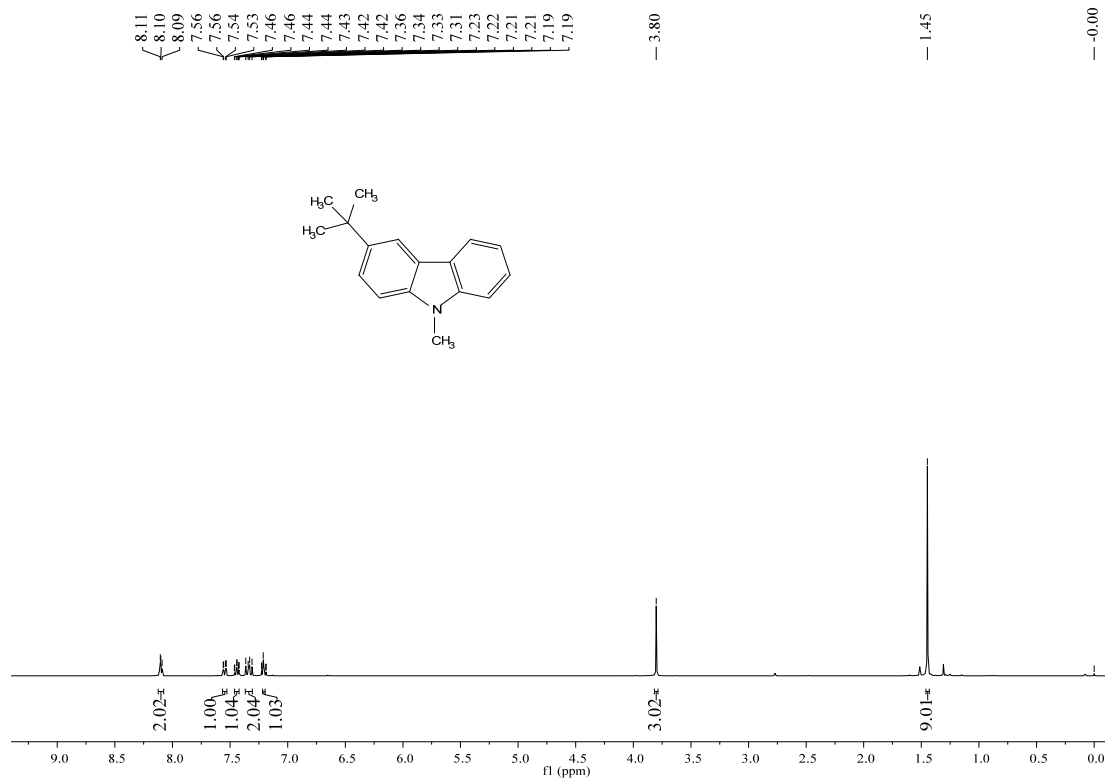
¹H and ¹³C NMR spectra of 2c



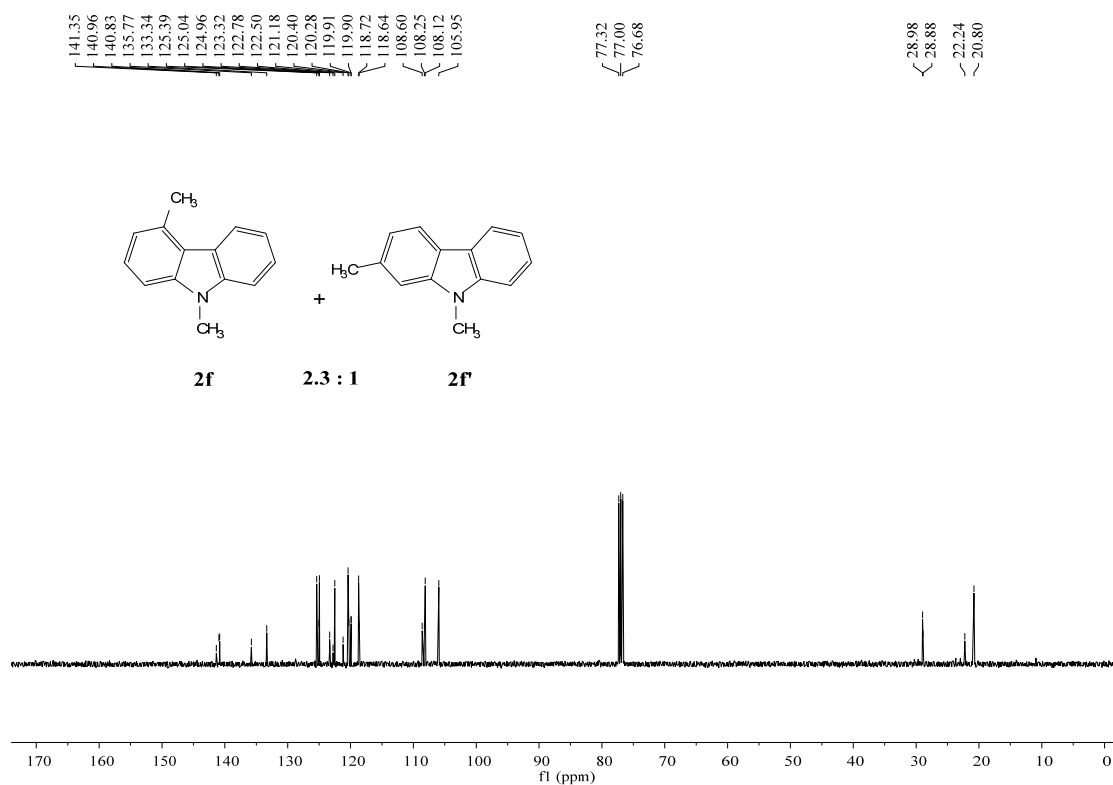
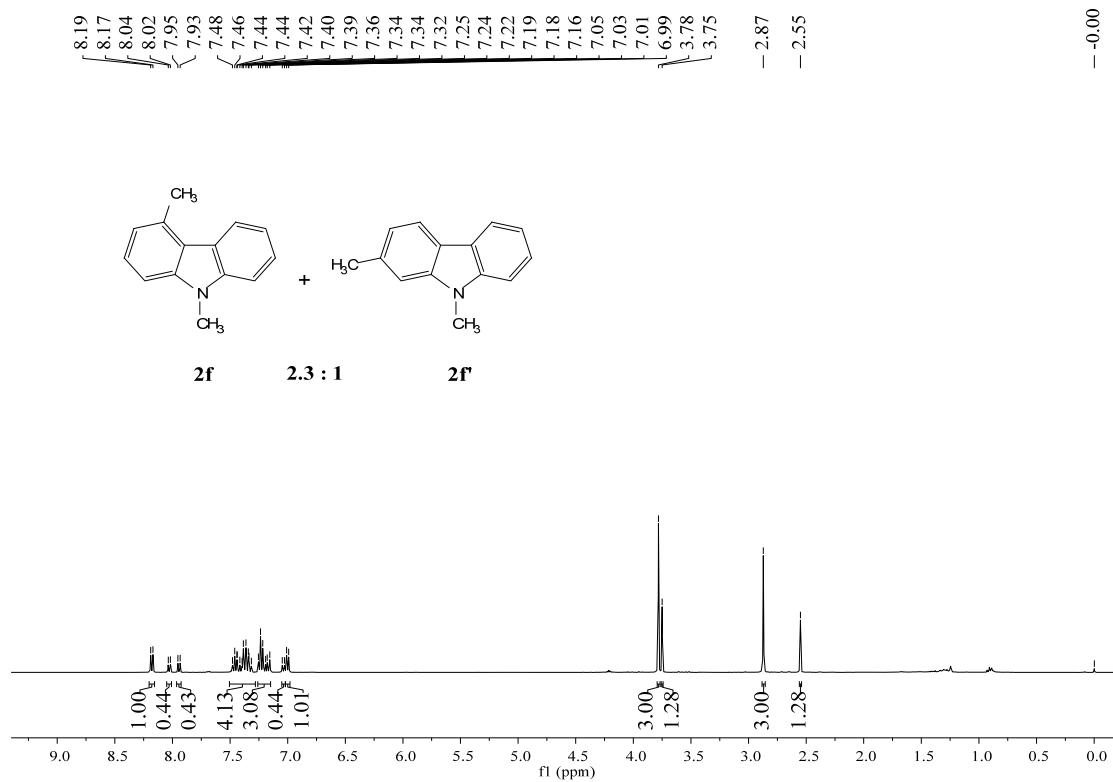
¹H and ¹³C NMR spectra of 2d



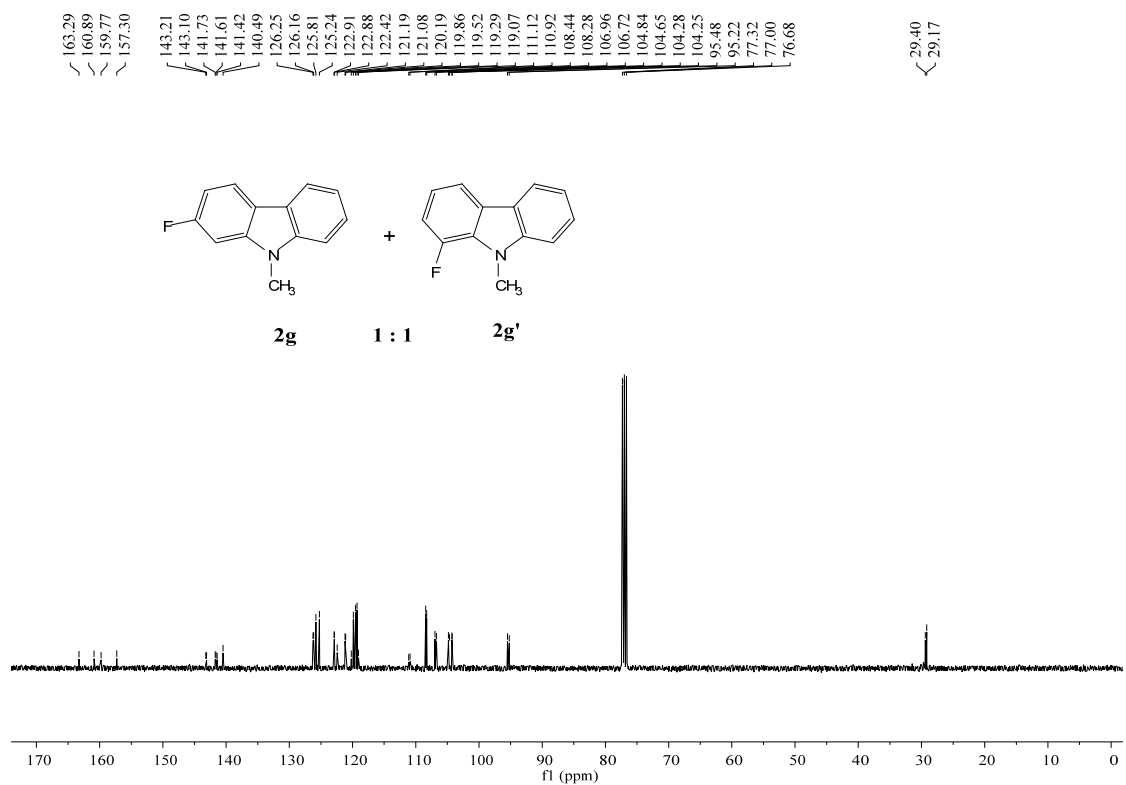
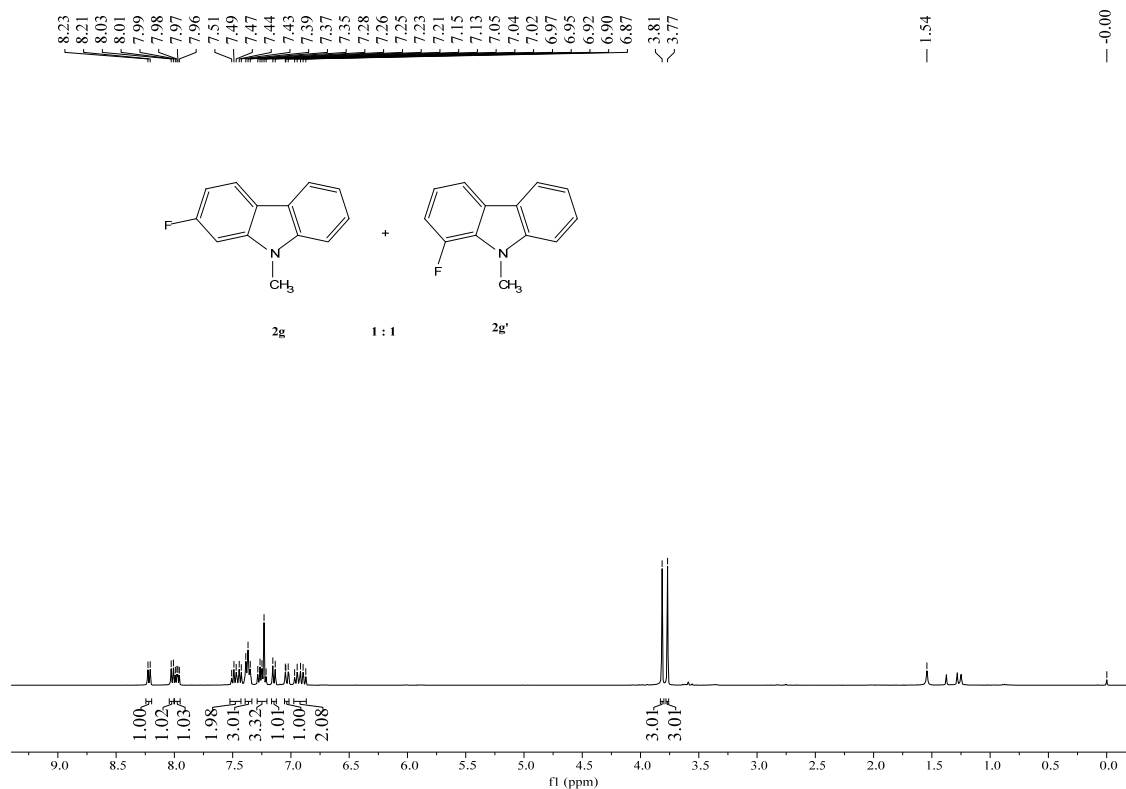
^1H and ^{13}C NMR spectra of 2e

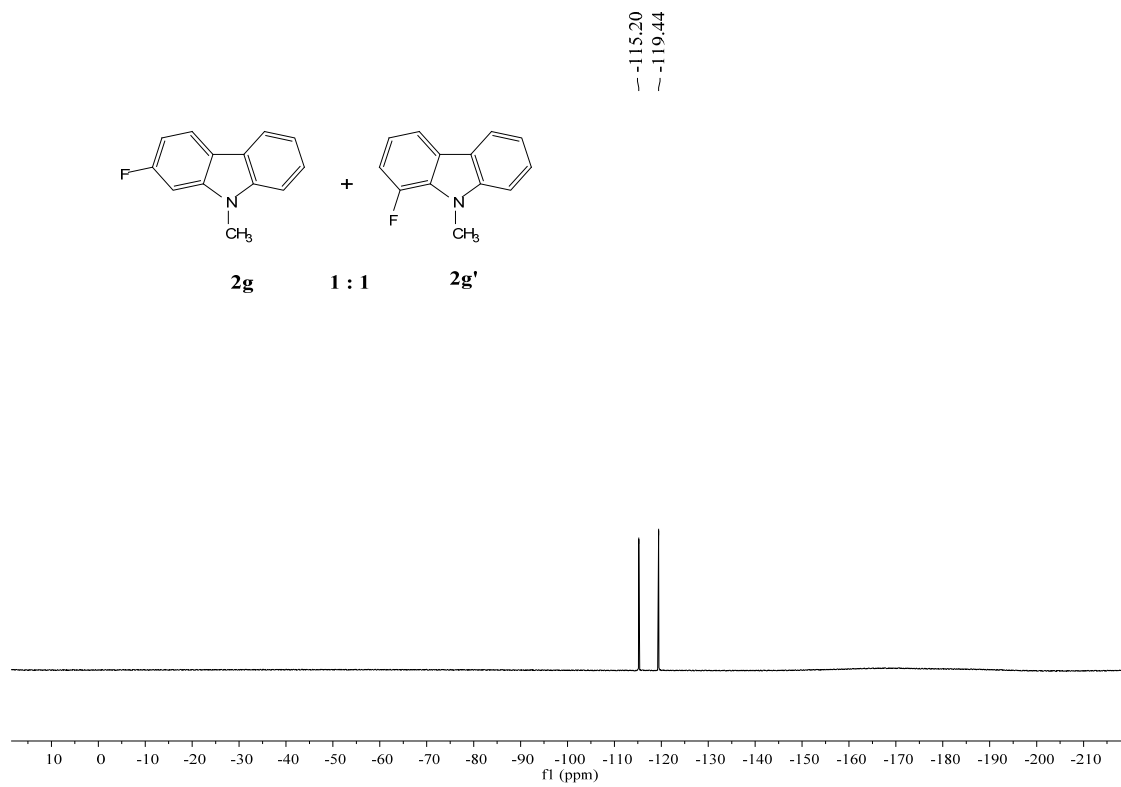


¹H and ¹³C NMR spectra of 2f+2f'

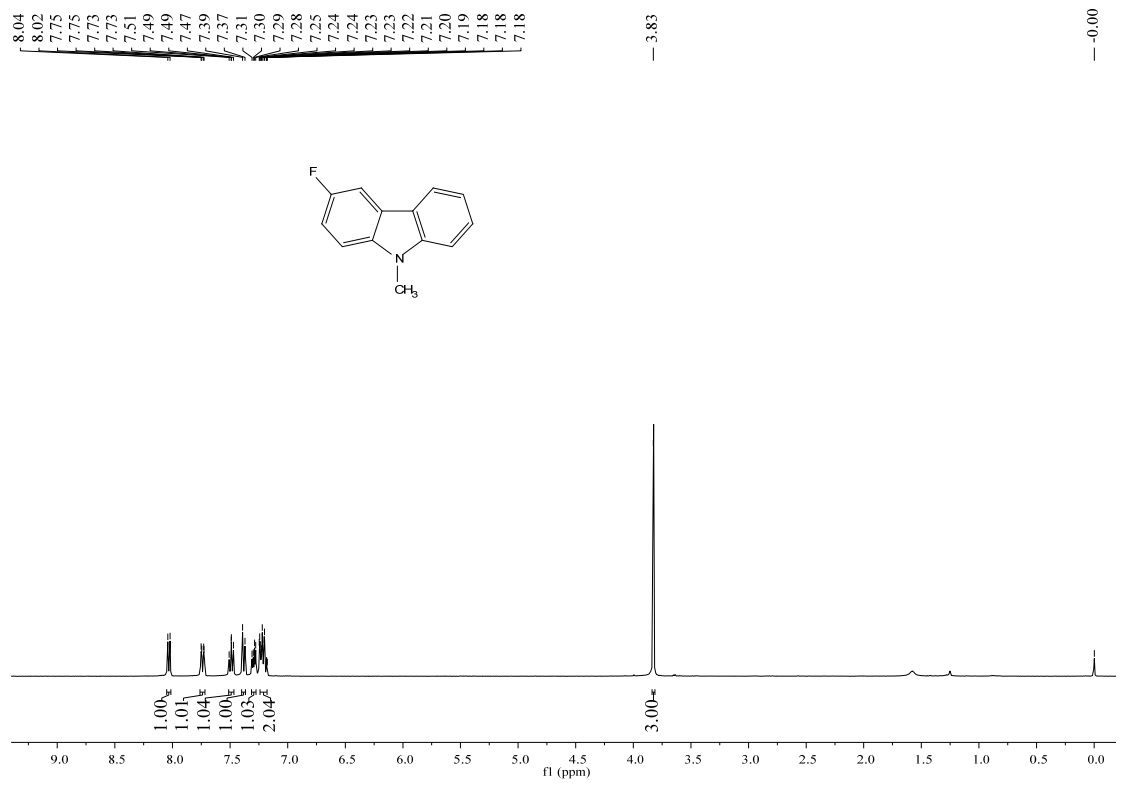


^1H and ^{13}C , ^{19}F NMR spectra of 2g+2g'





¹H and ¹³C, ¹⁹F NMR spectra of 2h or 2j



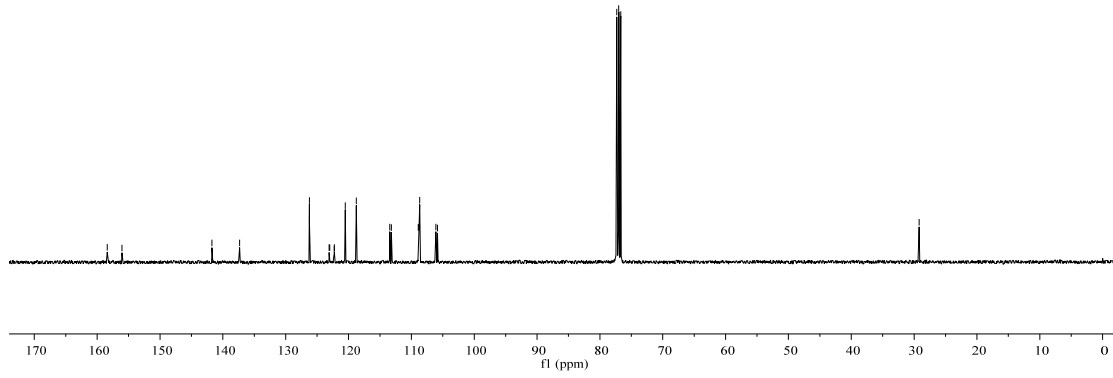
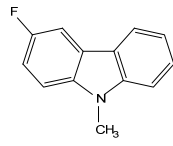
158.39
156.05

141.74
137.33

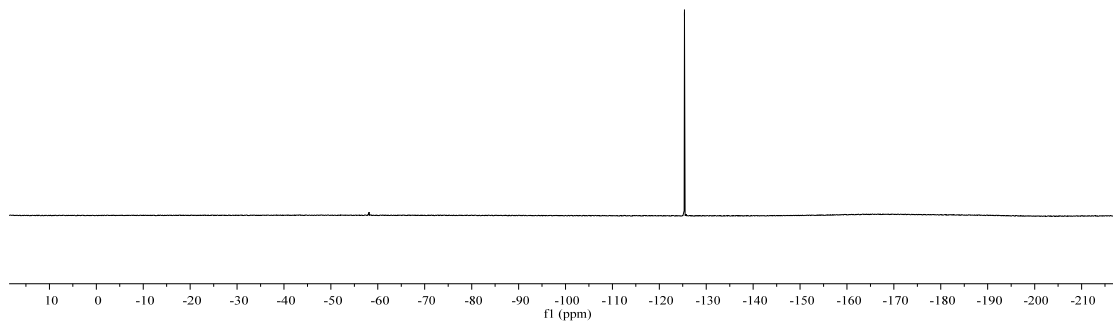
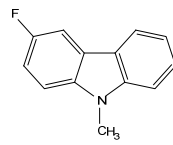
126.22
123.09
123.00
122.29
122.24
120.51
118.75
113.44
113.19
108.90
108.81
106.09
105.85

77.32
77.00
76.68

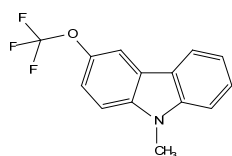
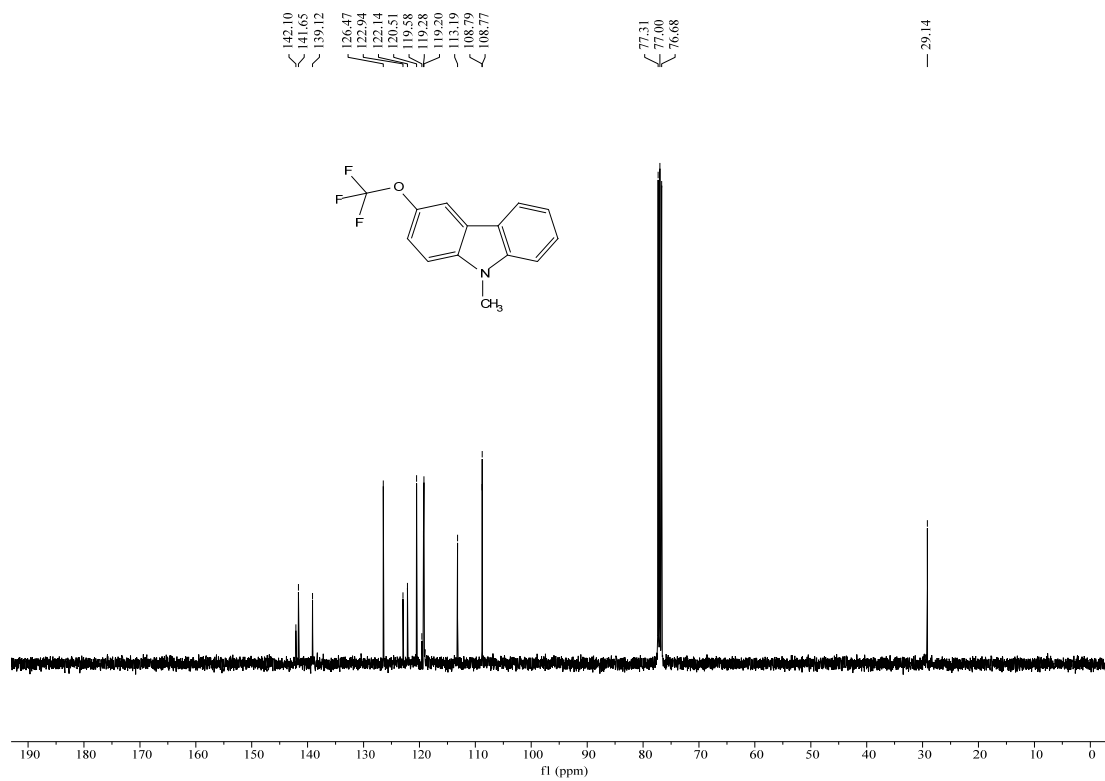
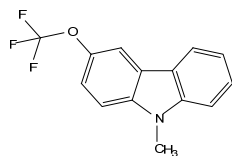
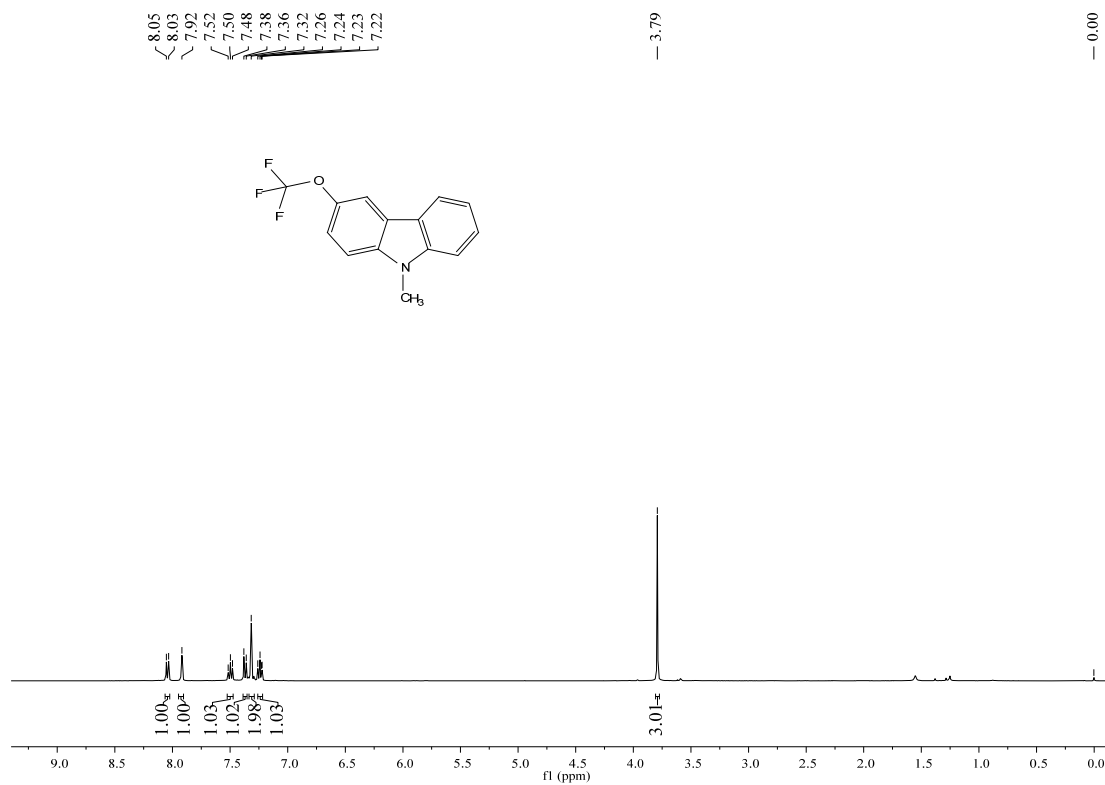
29.21

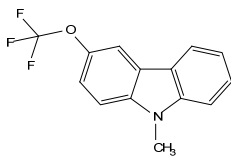
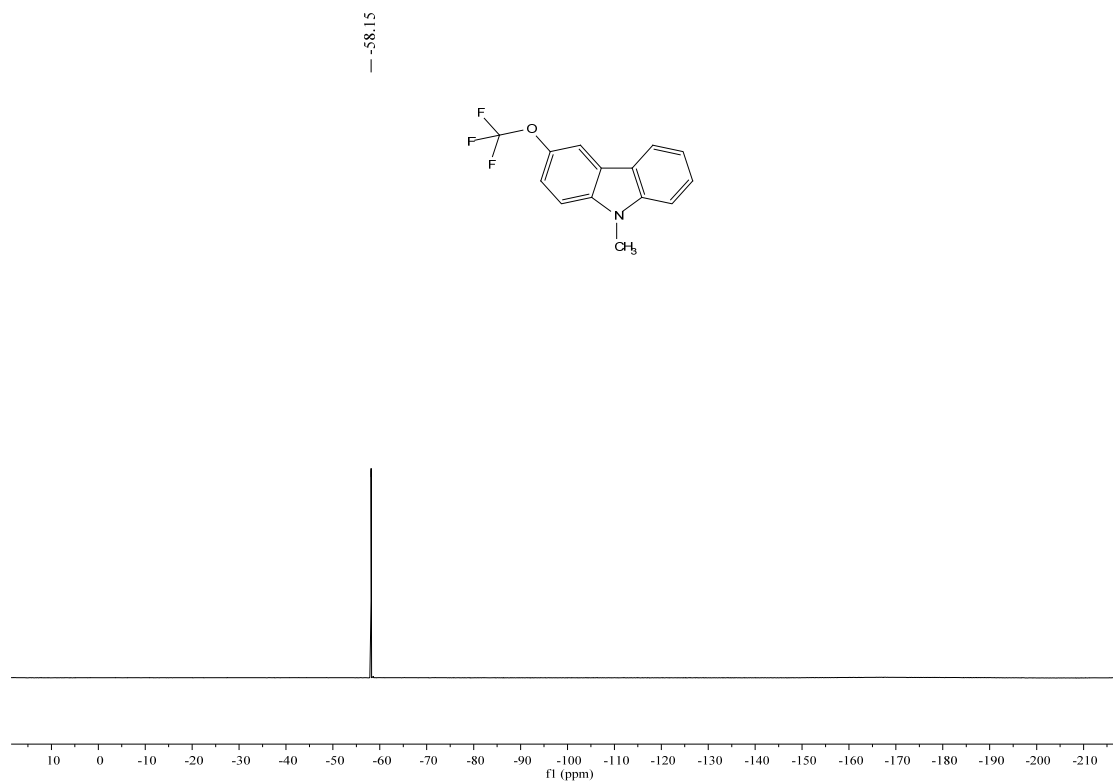


-125.37

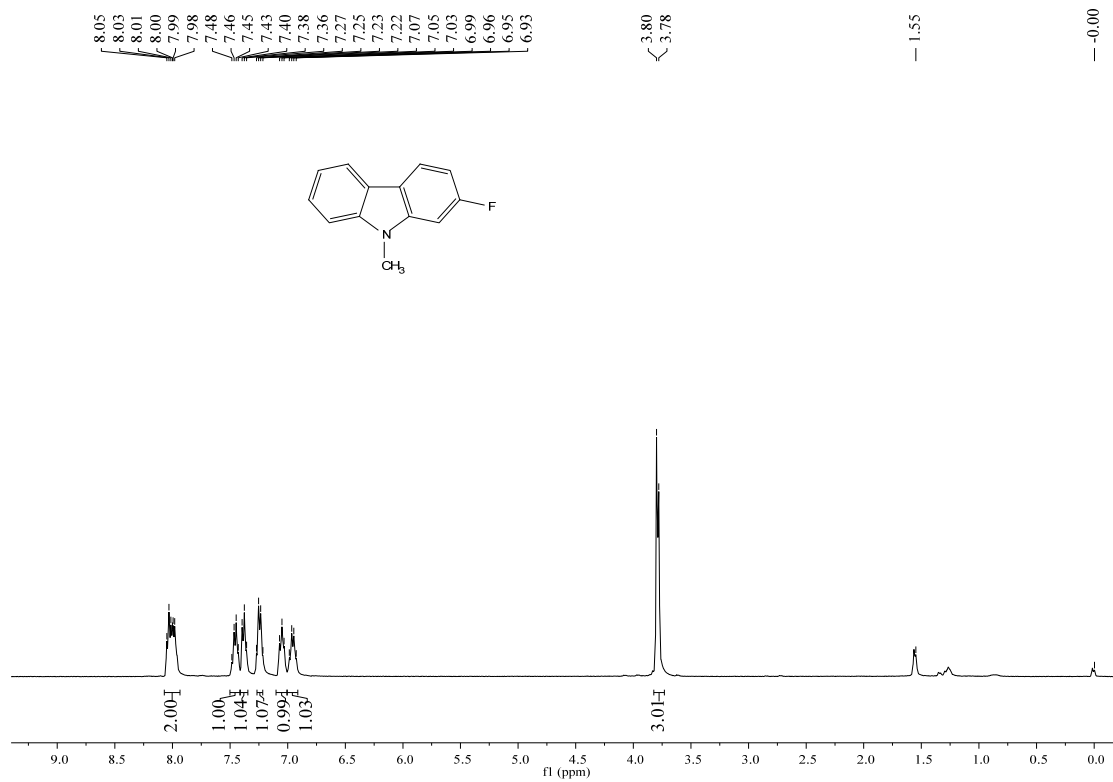


¹H and ¹³C, ¹⁹F NMR spectra of 2i





¹H and ¹³C, ¹⁹F NMR spectra of 2k

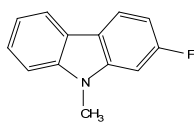


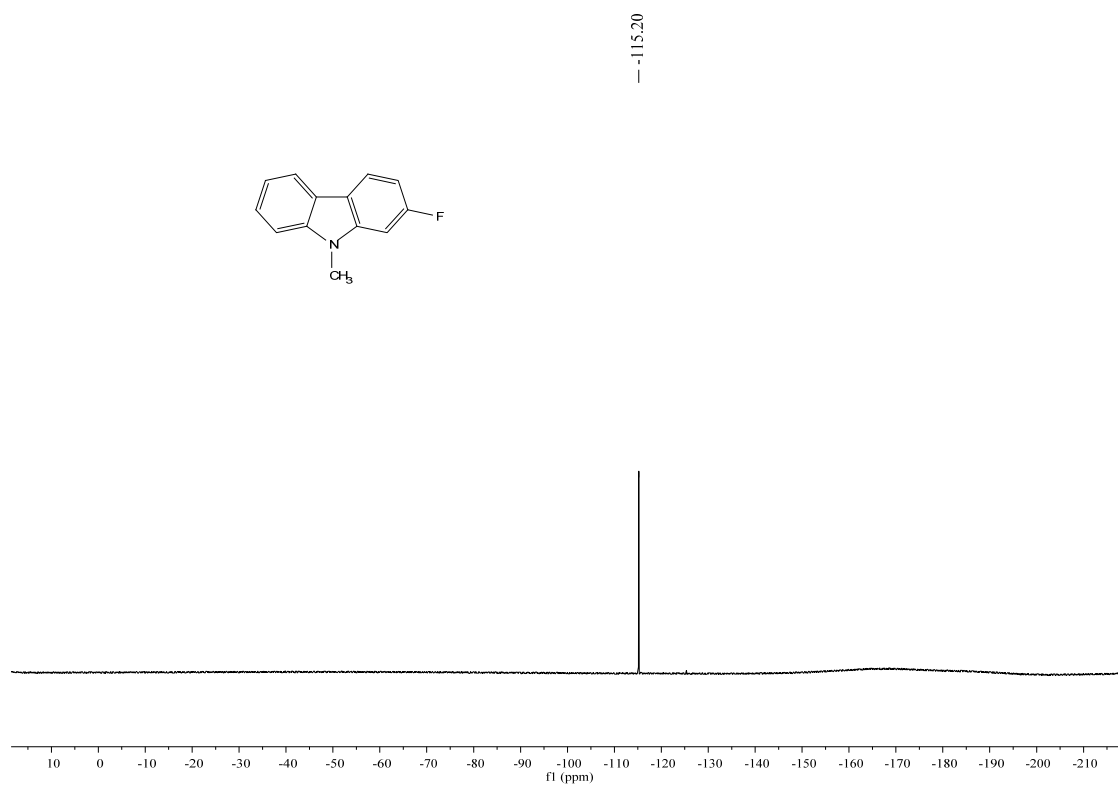
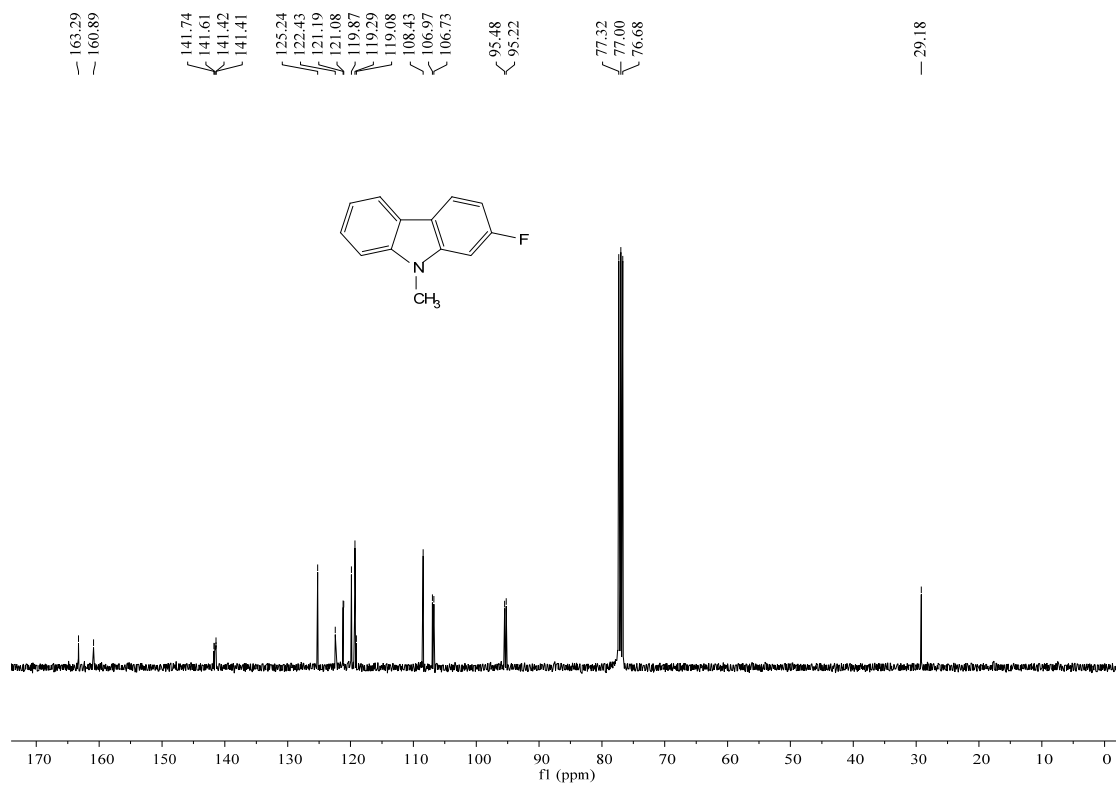
8.05
8.03
8.01
8.00
7.99
7.98
7.48
7.46
7.45
7.43
7.40
7.38
7.36
7.27
7.25
7.23
7.22
7.07
7.05
7.03
6.99
6.96
6.95
6.93

3.80
3.78

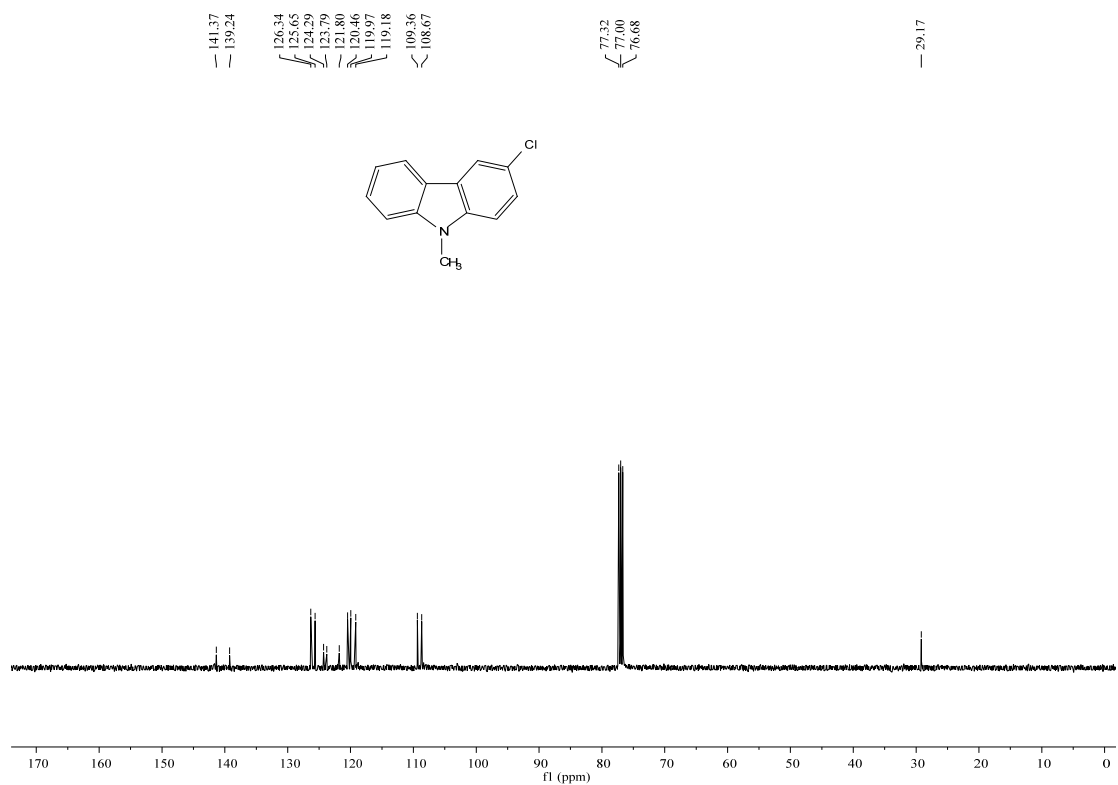
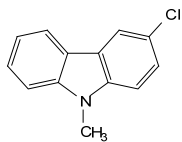
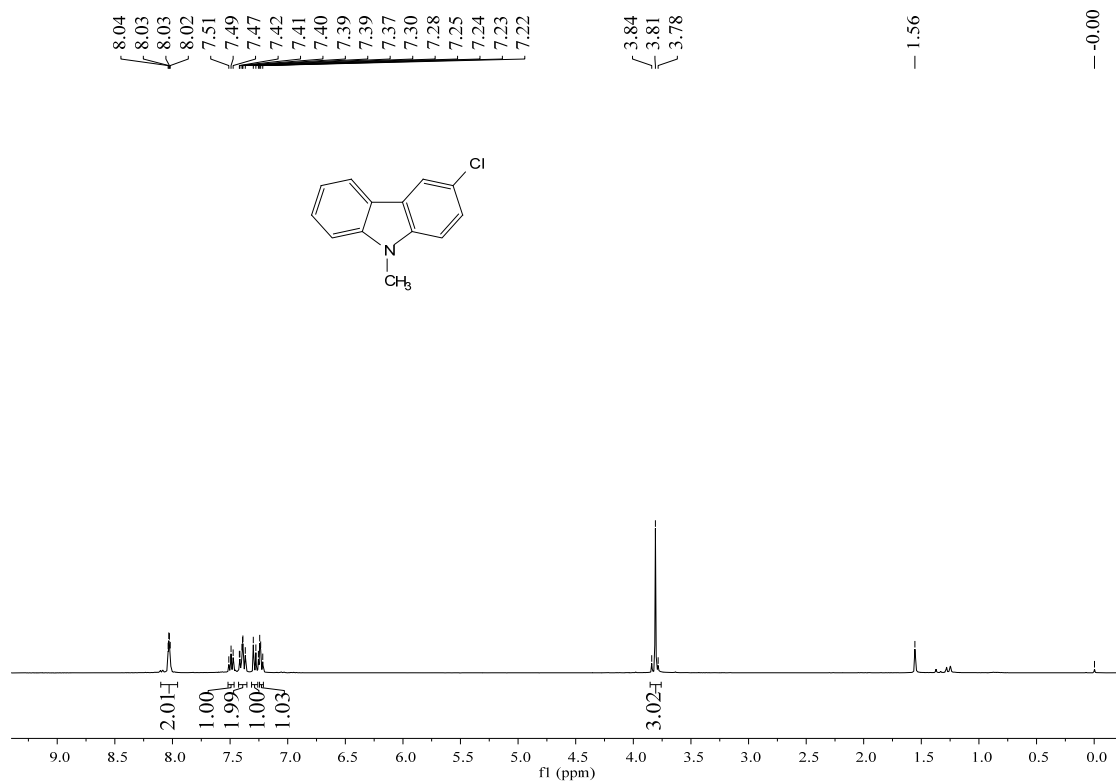
1.55

0.00

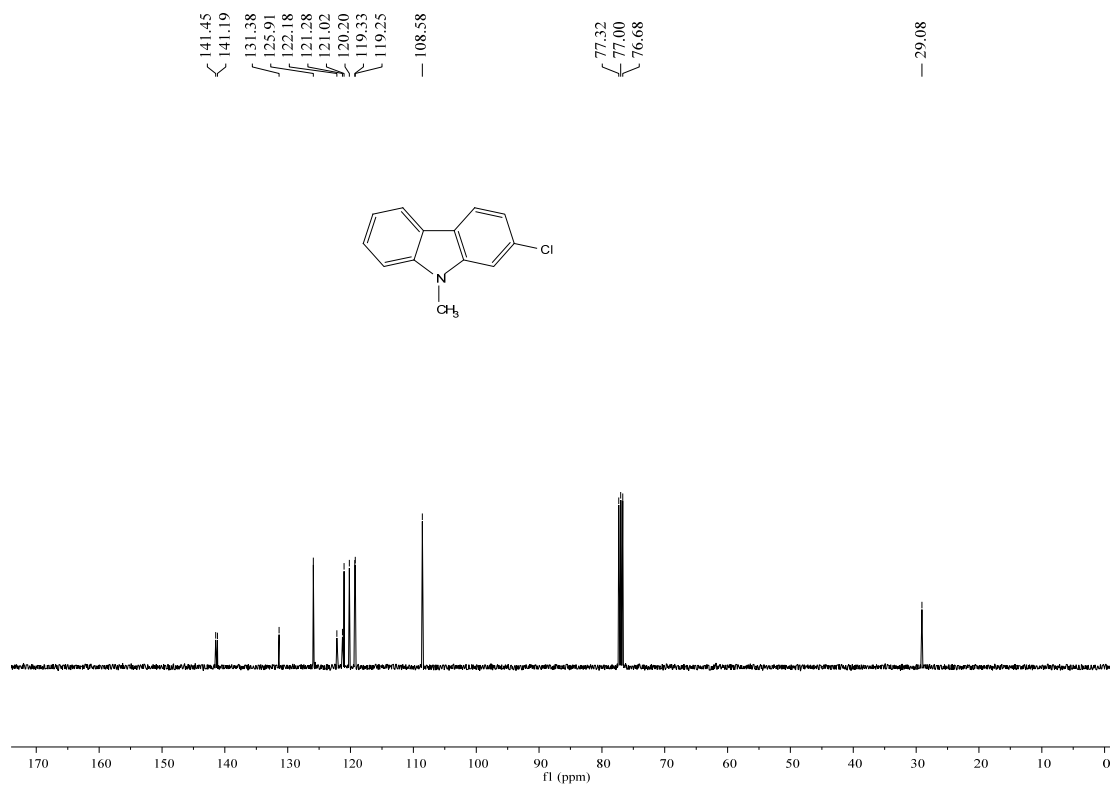
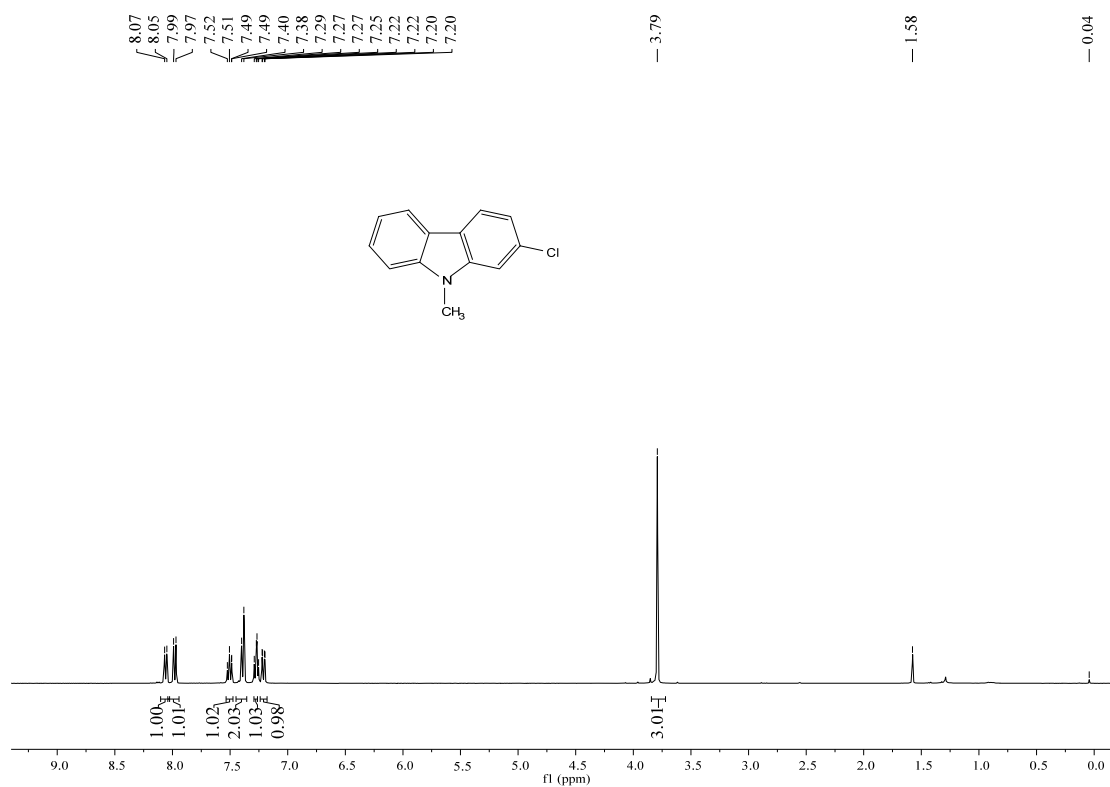




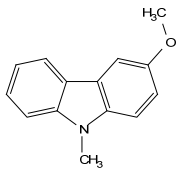
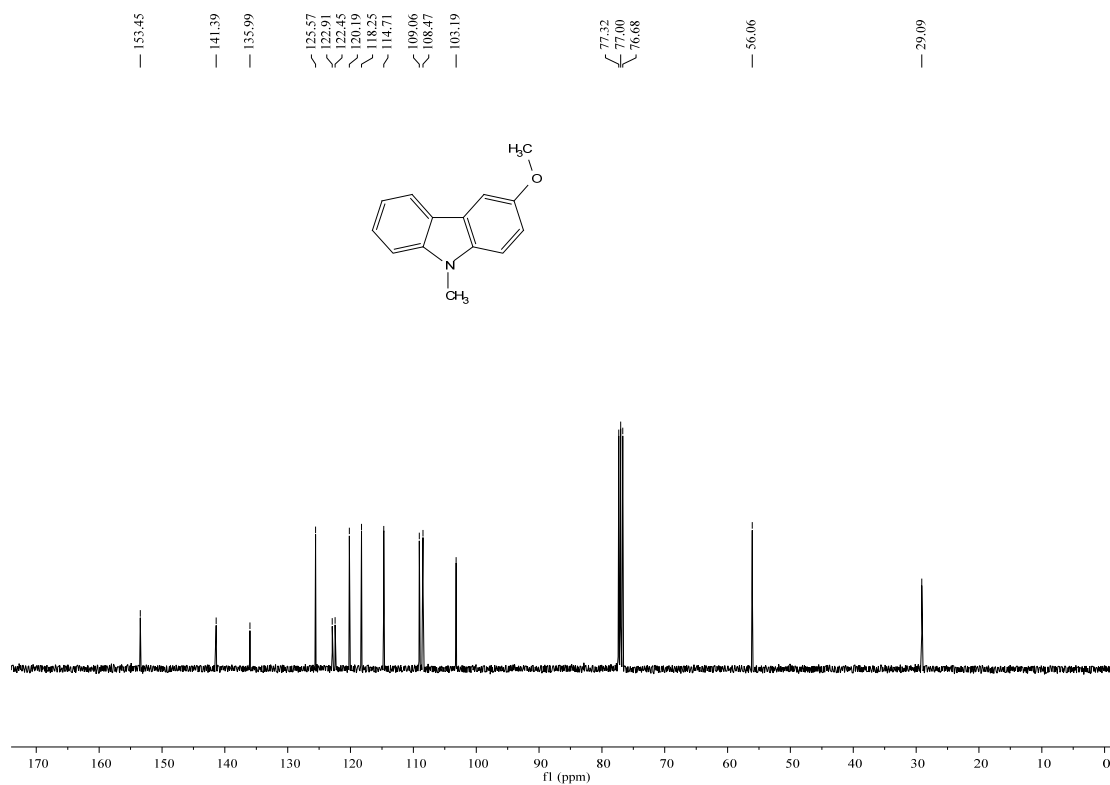
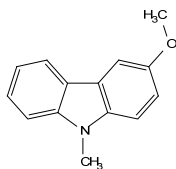
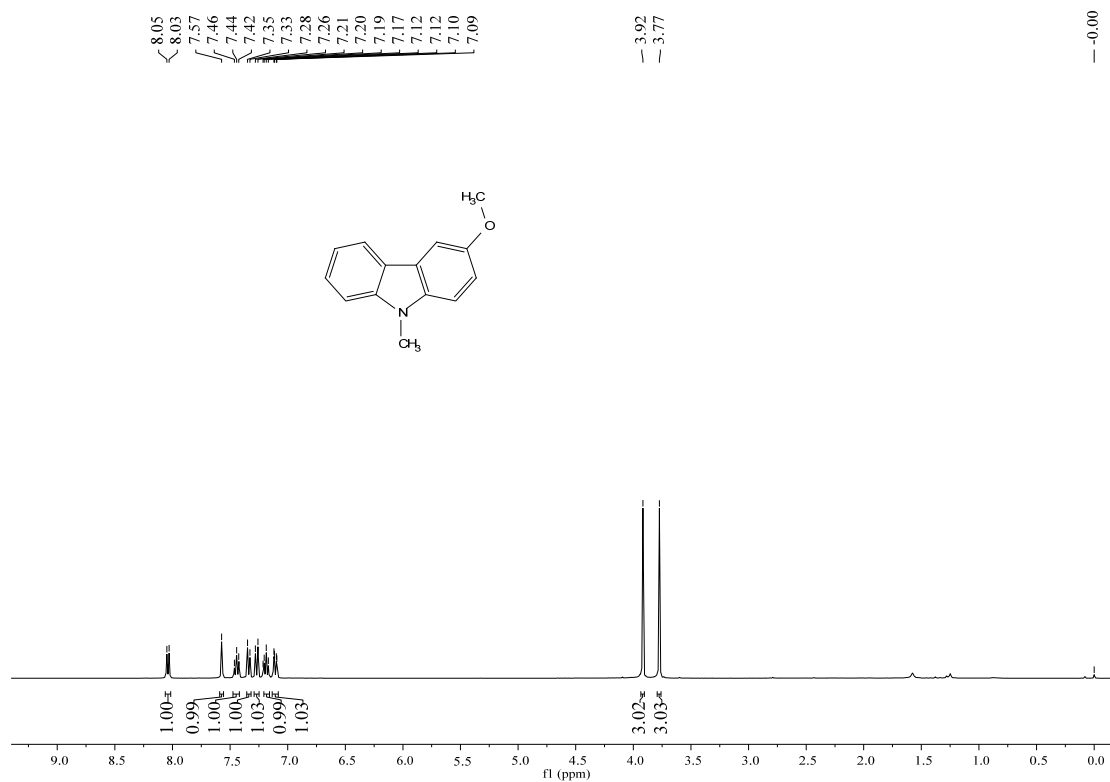
¹H and ¹³C NMR spectra of 2l



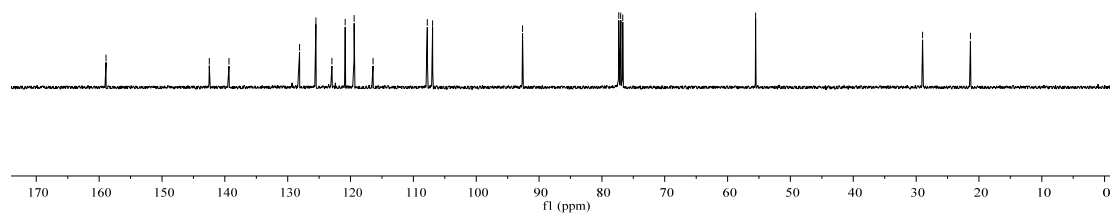
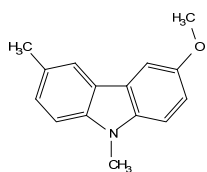
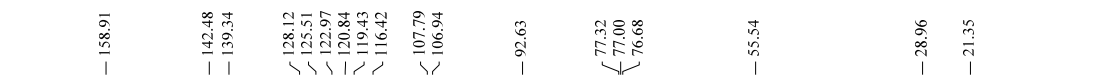
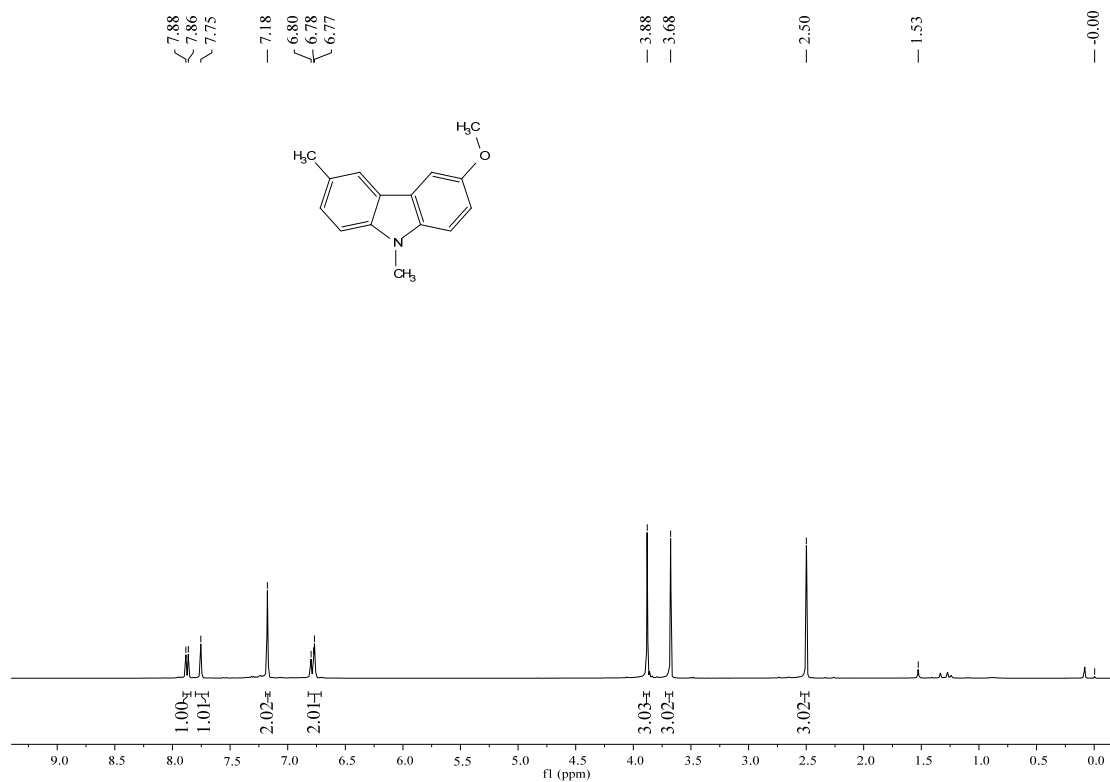
¹H and ¹³C NMR spectra of 2m



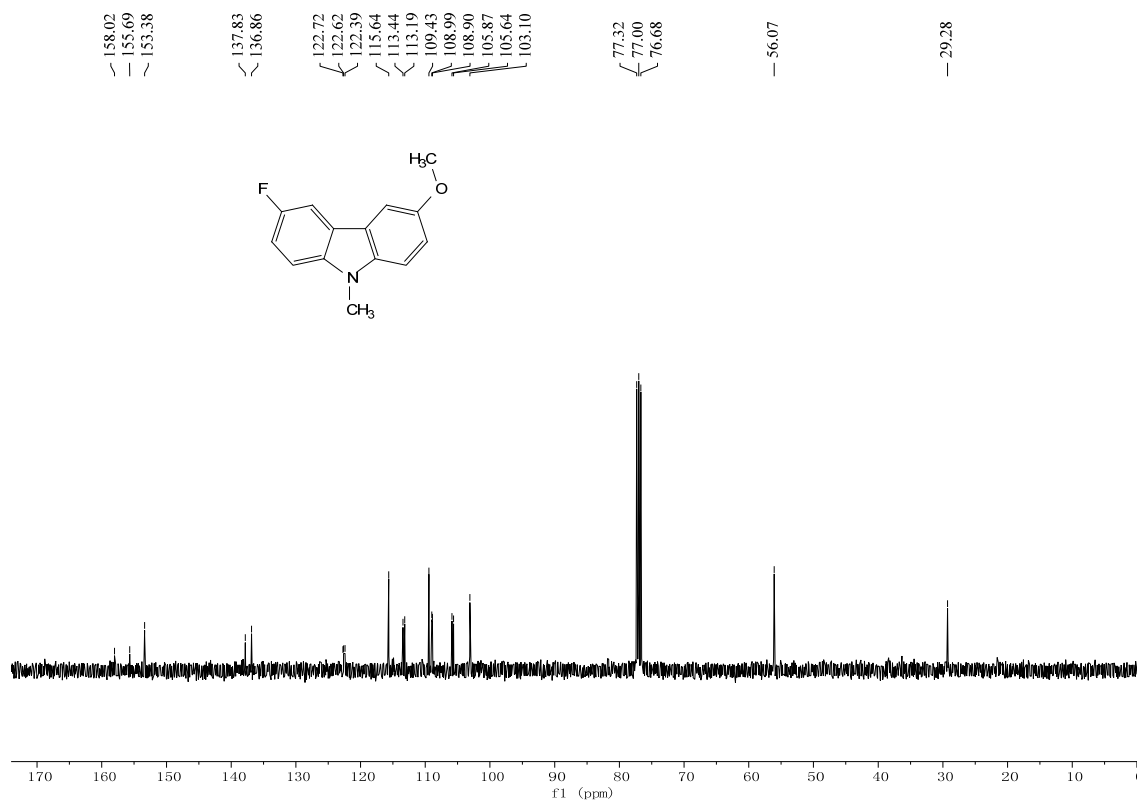
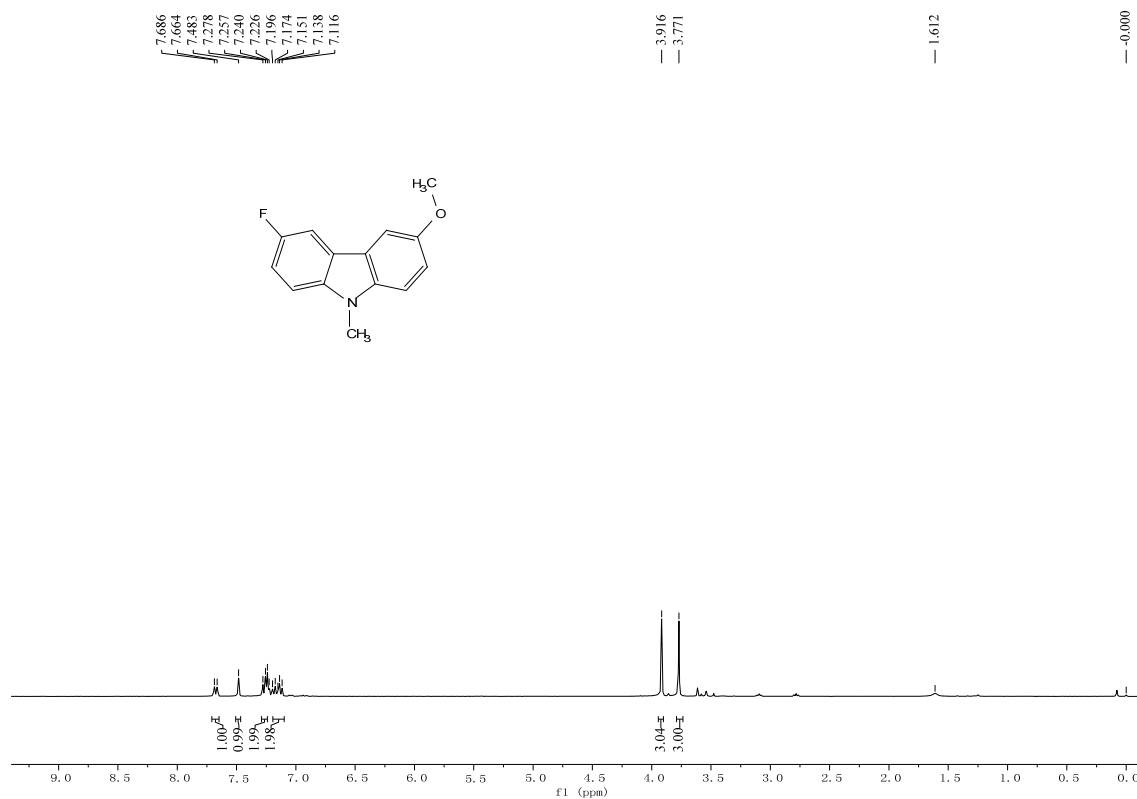
¹H and ¹³C NMR spectra of 2n

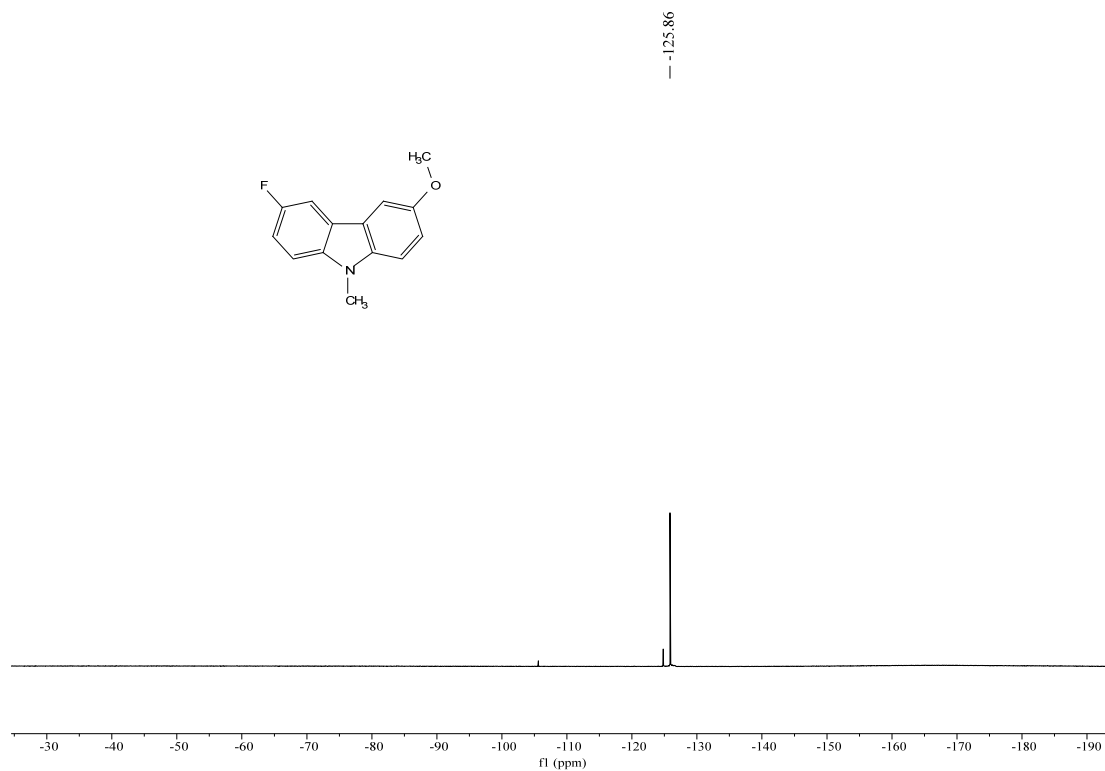


^1H and ^{13}C NMR spectra of 2o

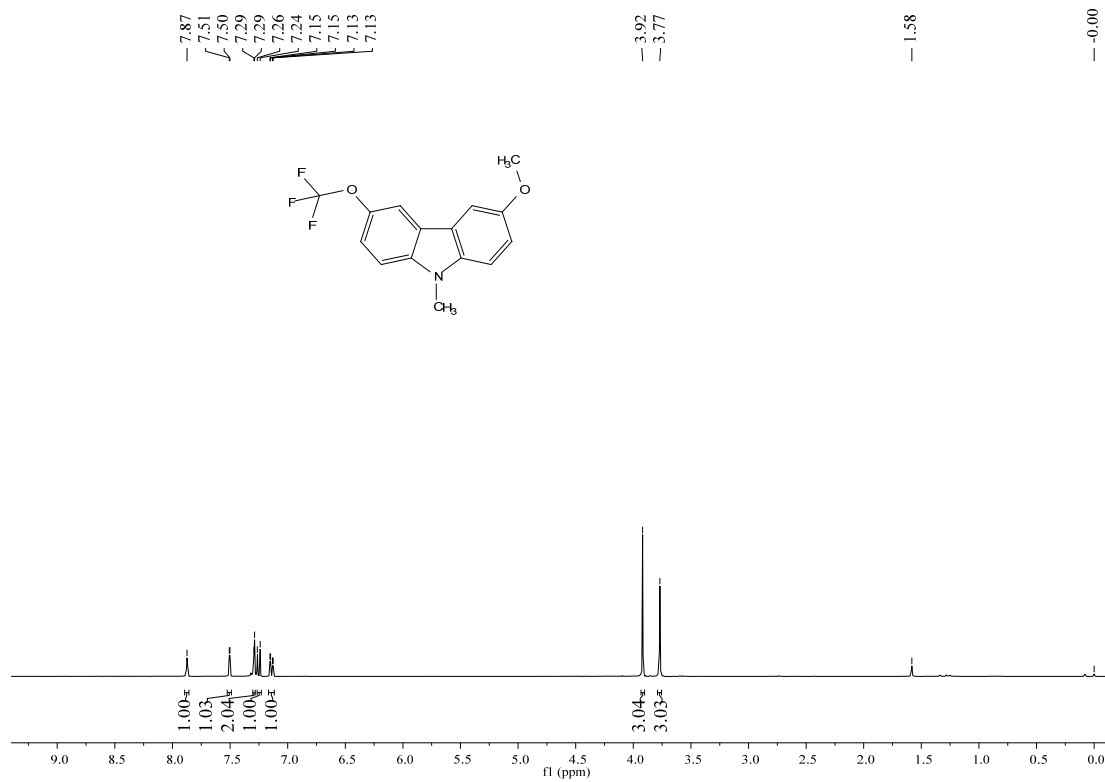


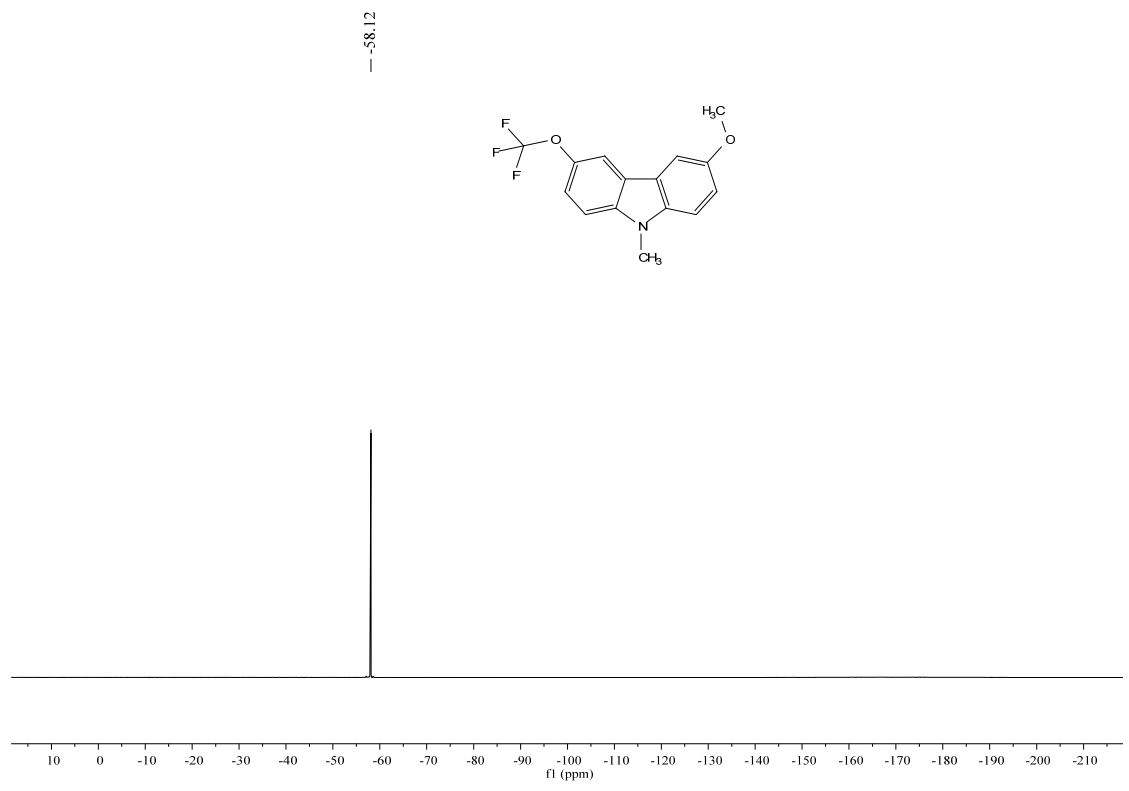
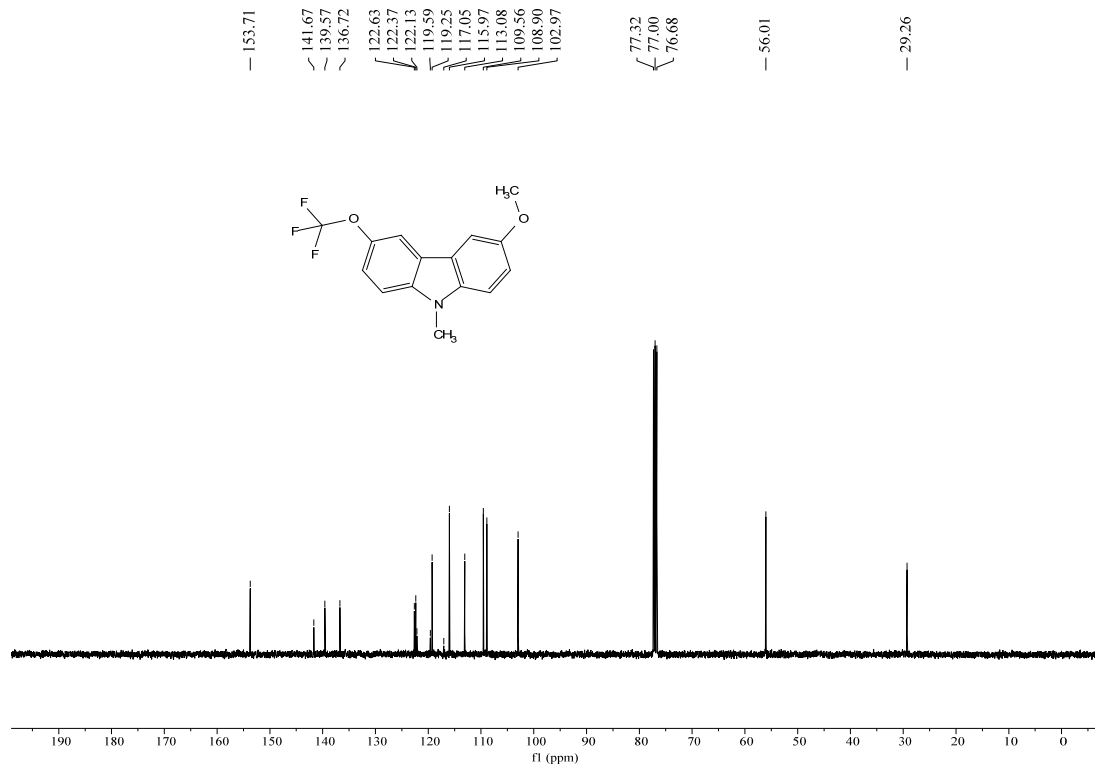
¹H and ¹³C, ¹⁹F NMR spectra of 2p



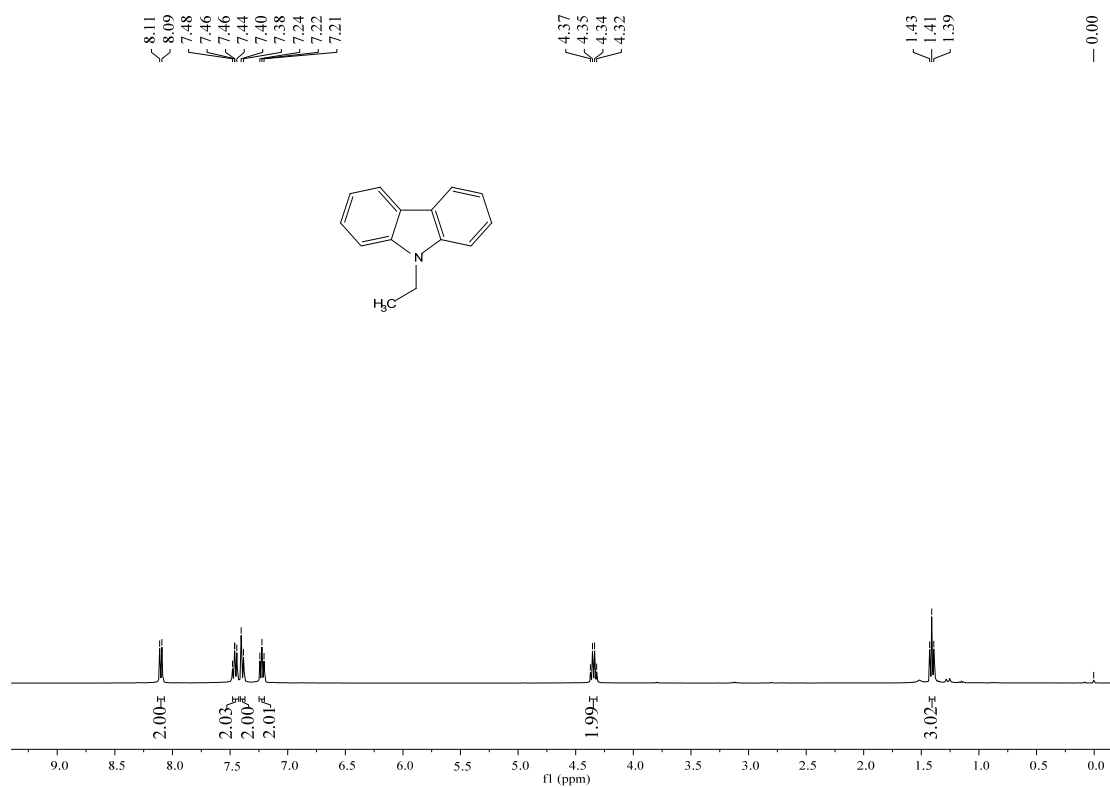


¹H and ¹³C, ¹⁹F NMR spectra of 2q

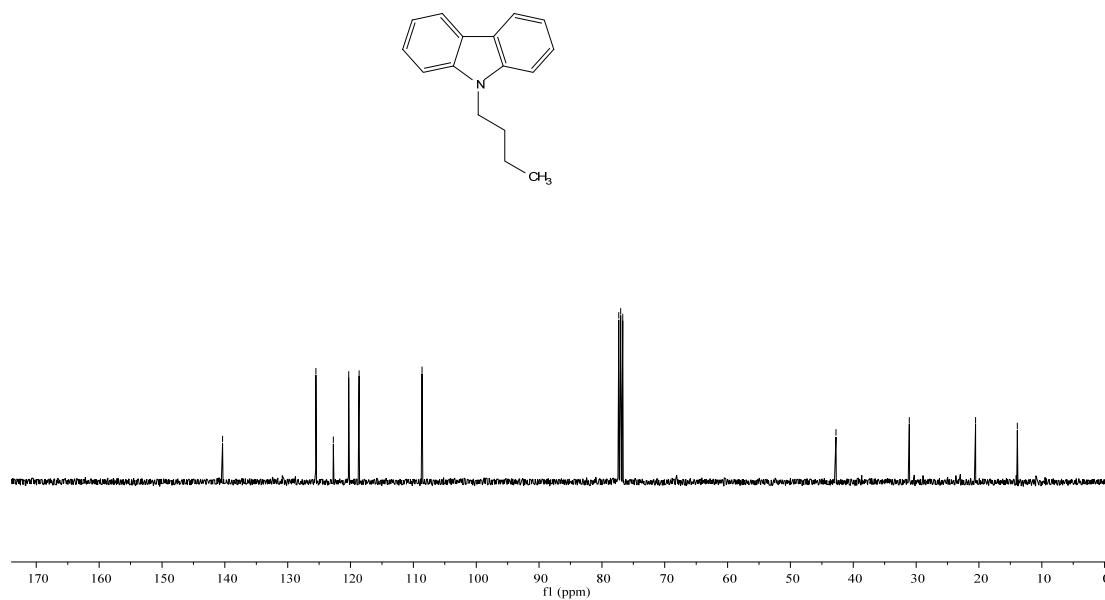
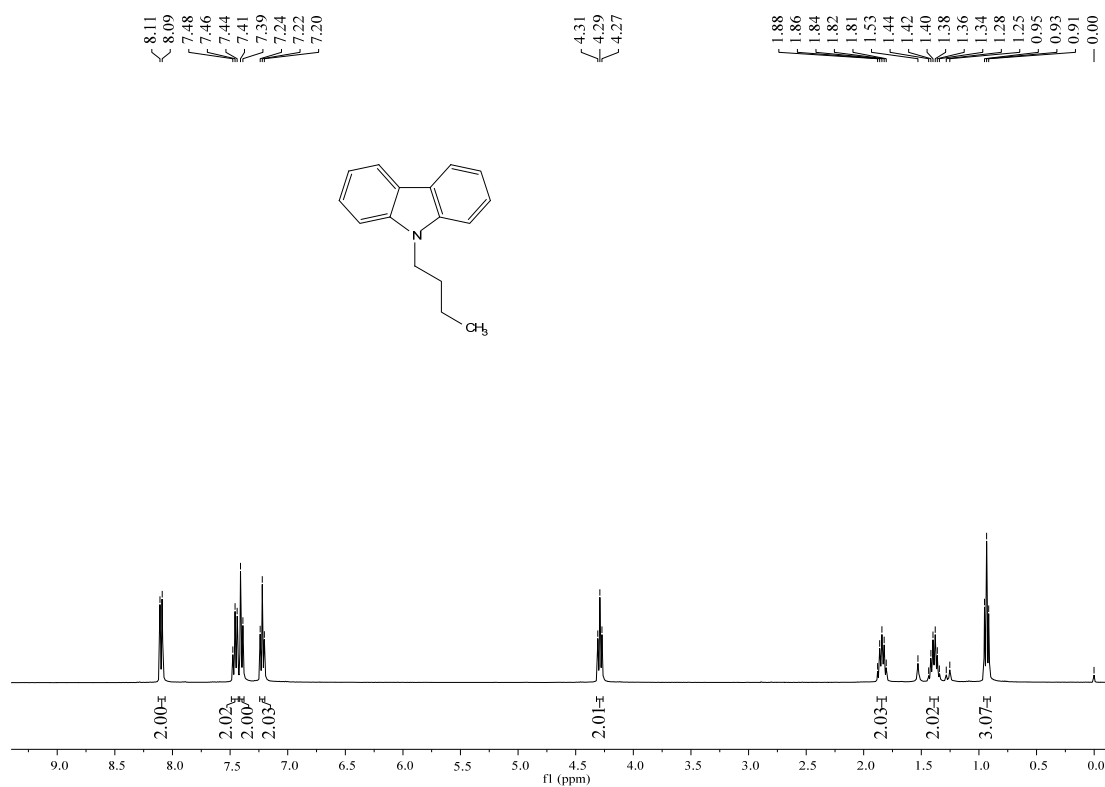




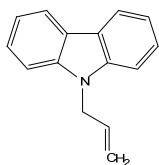
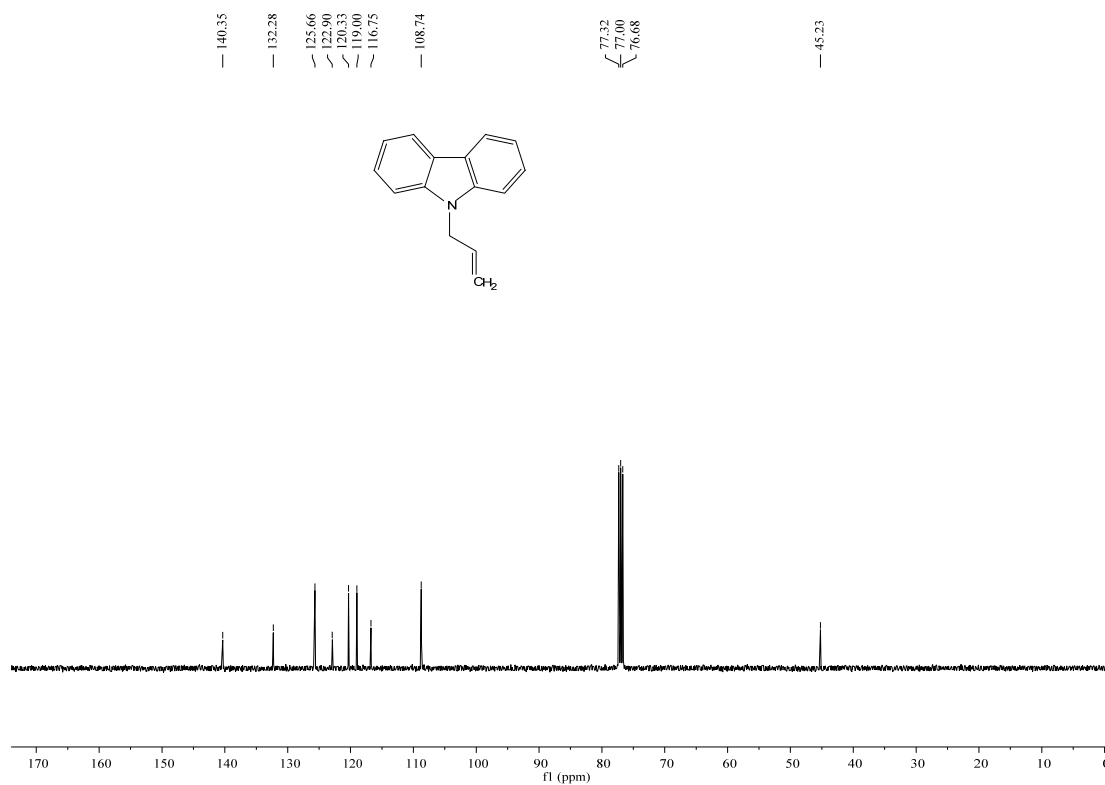
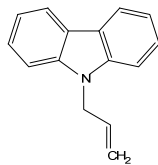
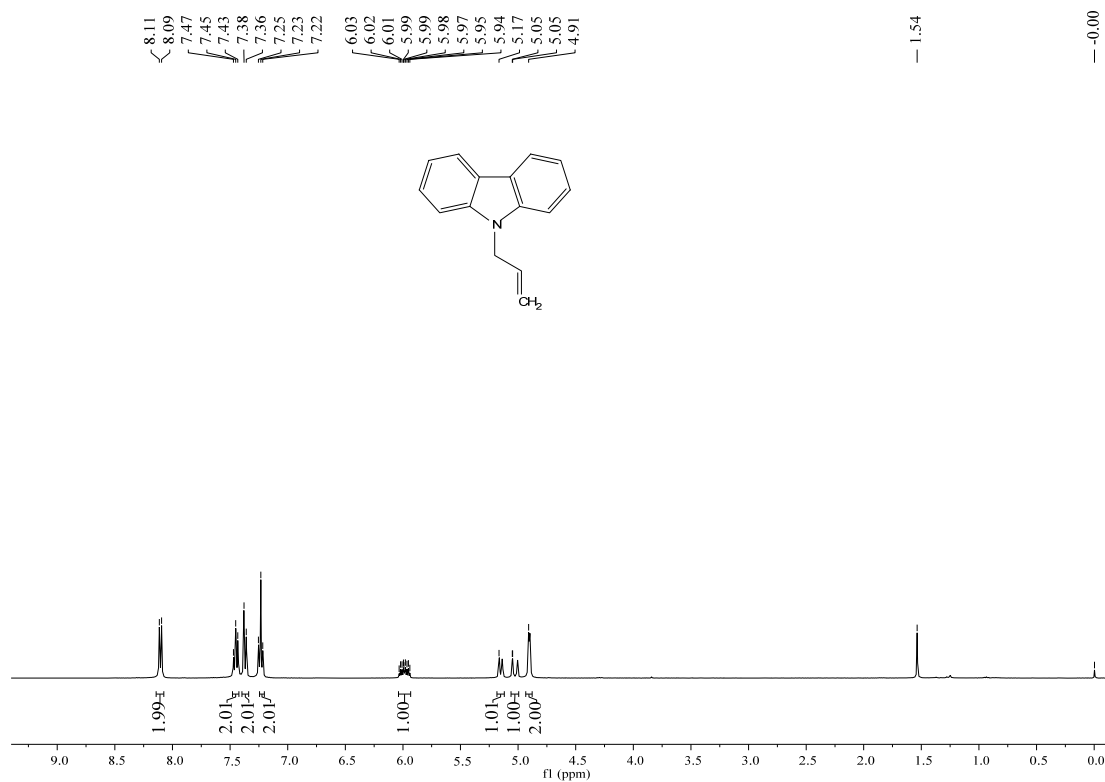
¹H and ¹³C NMR spectra of 2r



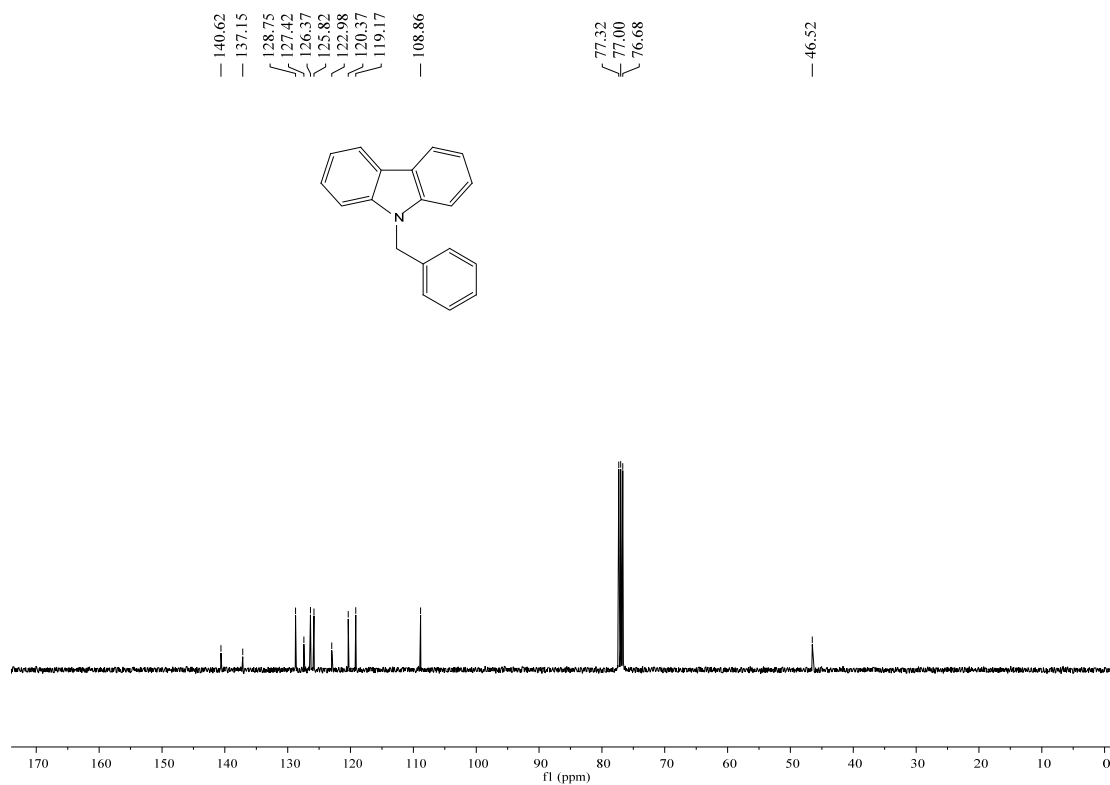
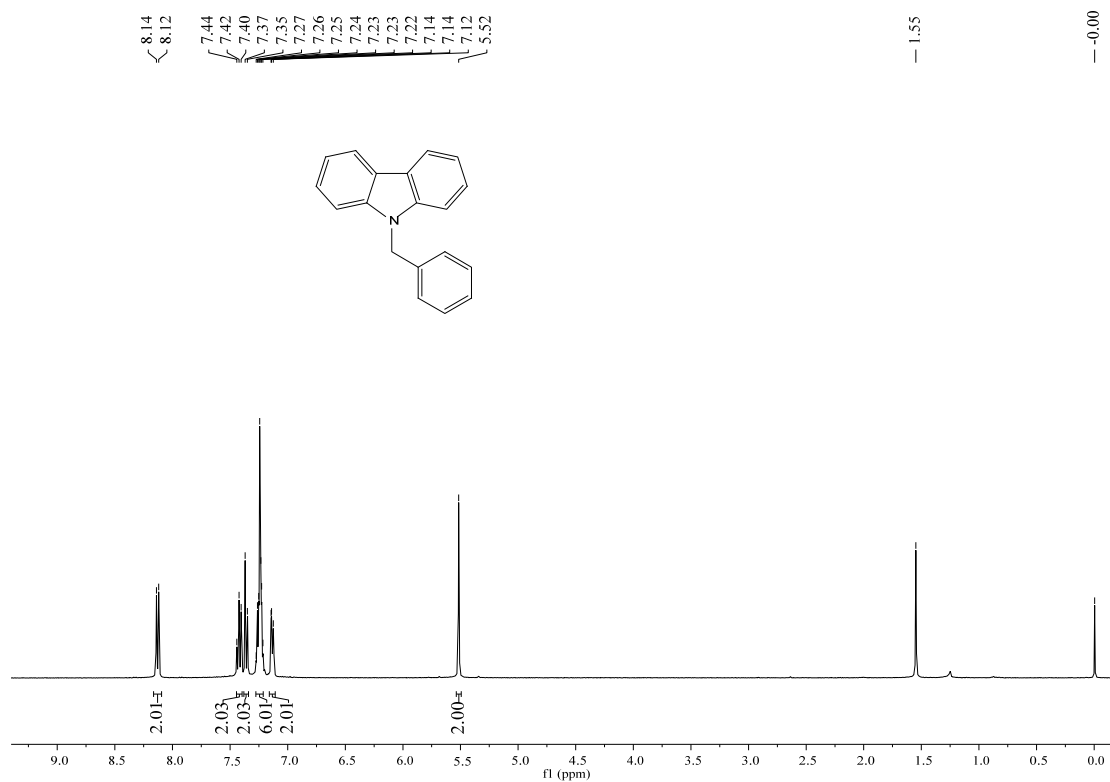
¹H and ¹³C NMR spectra of 2s



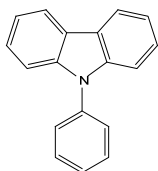
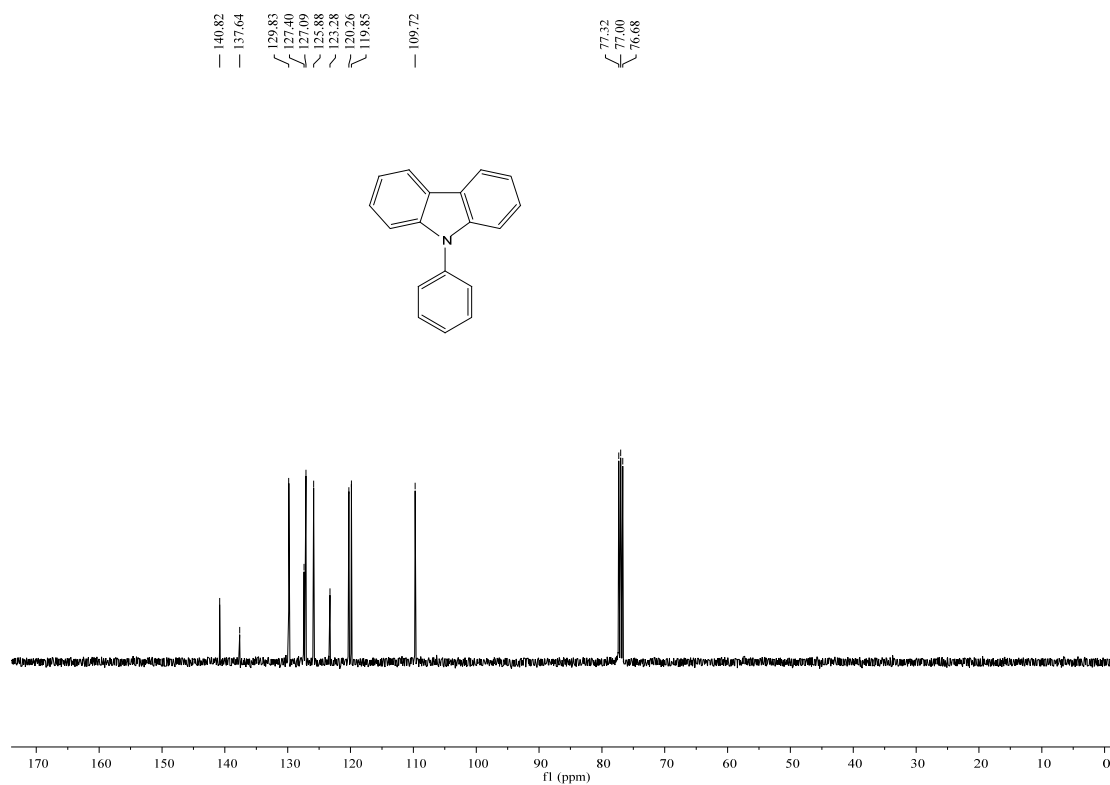
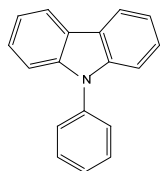
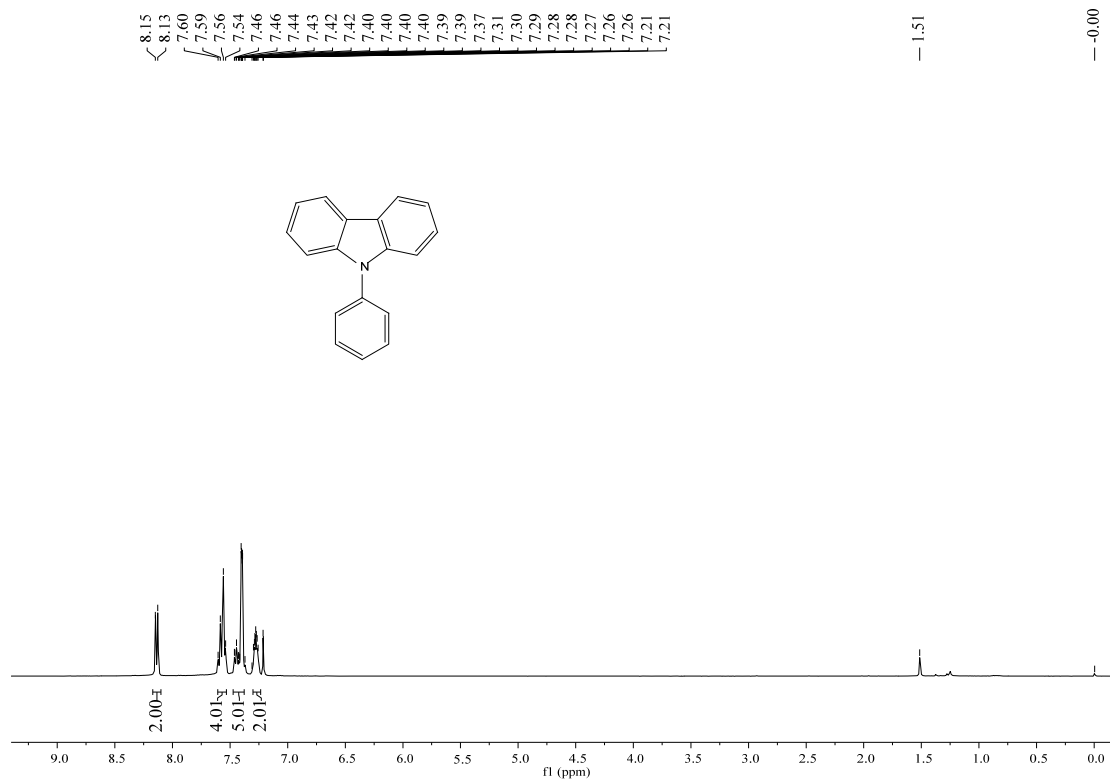
¹H and ¹³C NMR spectra of 2t



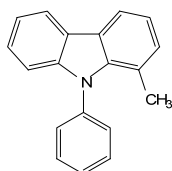
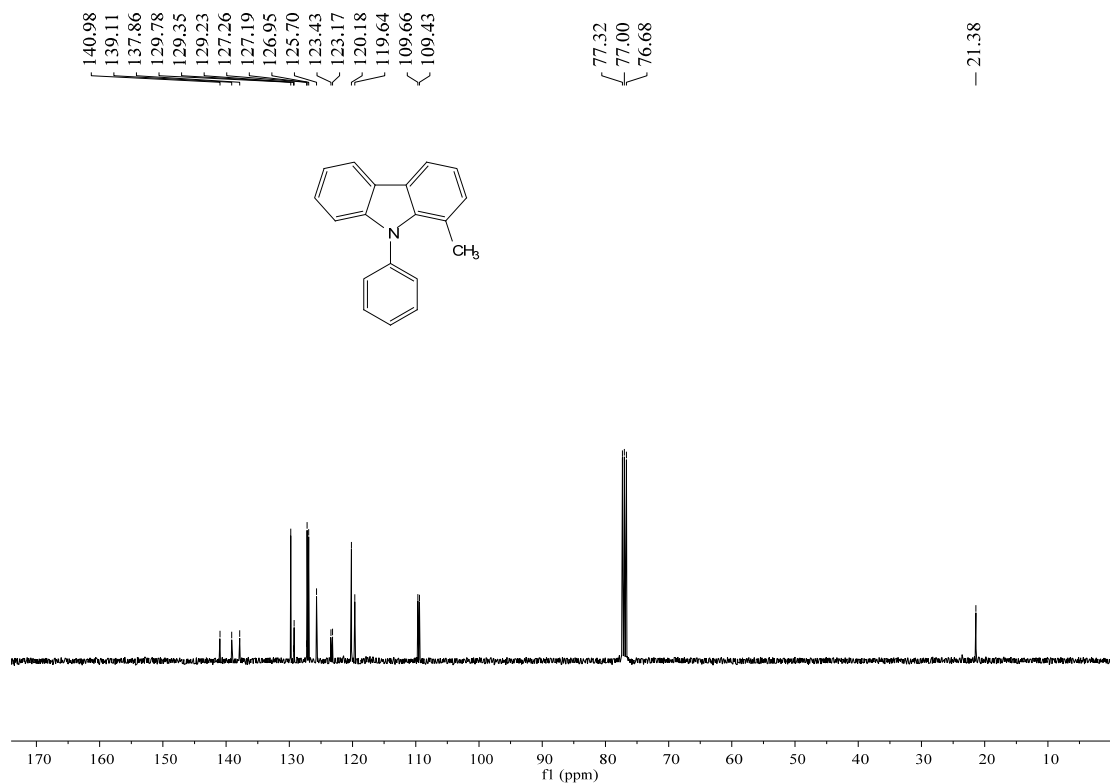
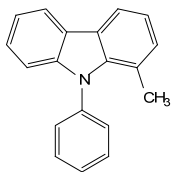
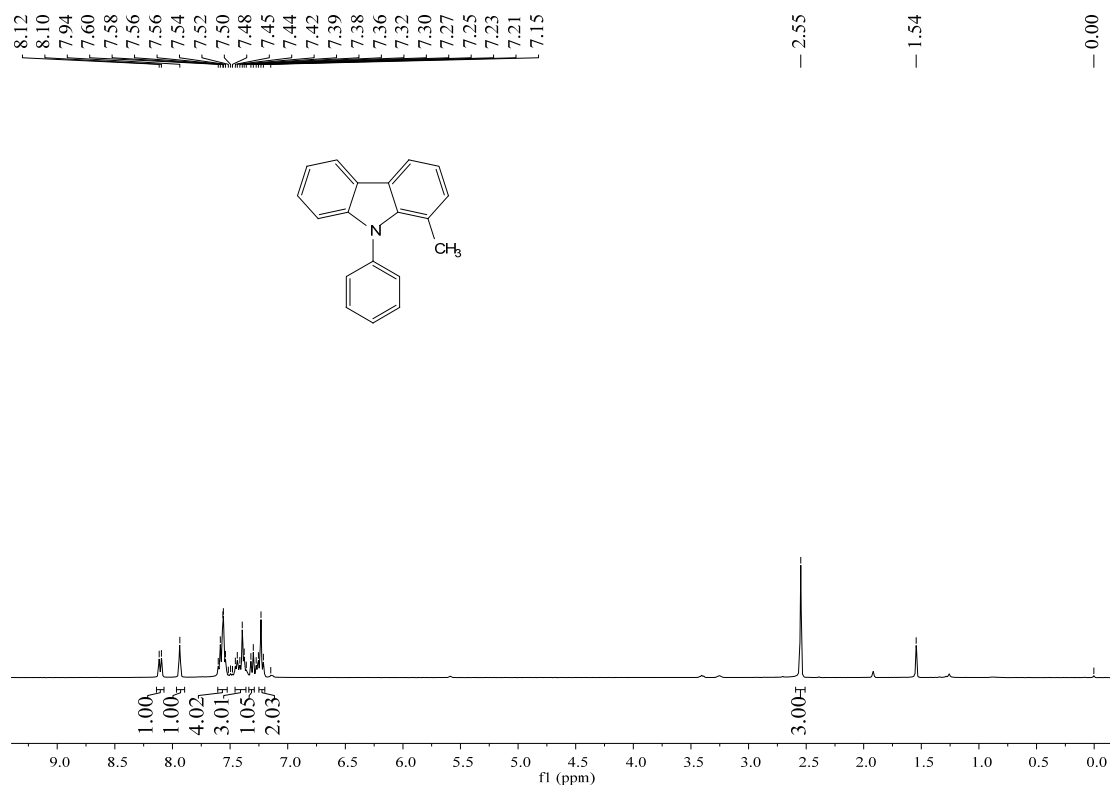
¹H and ¹³C NMR spectra of 2u



¹H and ¹³C NMR spectra of 2v



¹H and ¹³C NMR spectra of 2w



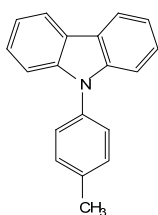
¹H and ¹³C NMR spectra of 2x+2x'

8.18
8.16
8.14
8.12
7.97
7.63
7.61
7.60
7.59
7.57
7.48
7.47
7.45
7.43
7.41
7.39
7.35
7.33
7.32
7.30
7.28
7.27
7.24

2.58
2.51

1.57

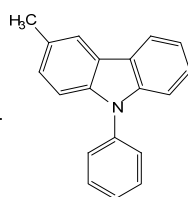
0.03



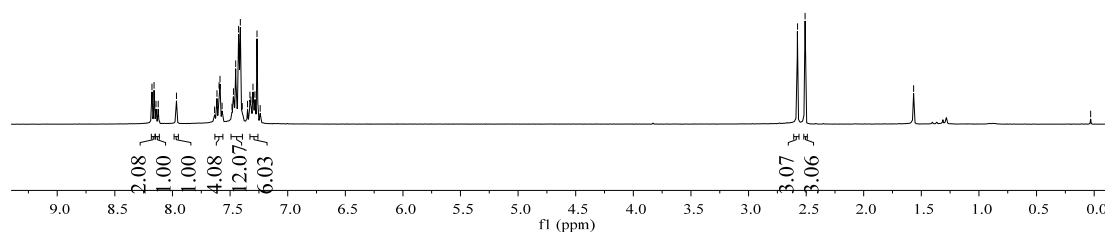
2x'

+

1 : 1



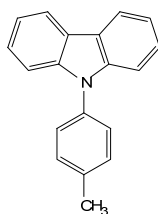
2x



140.99
137.33
134.93
130.43
129.78
129.24
127.19
126.96
125.80
125.70
123.43
123.18
120.22
120.18
119.67
109.74
109.67
109.43

77.32
77.00
76.68

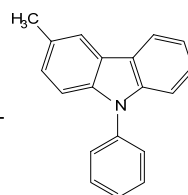
21.39
21.22



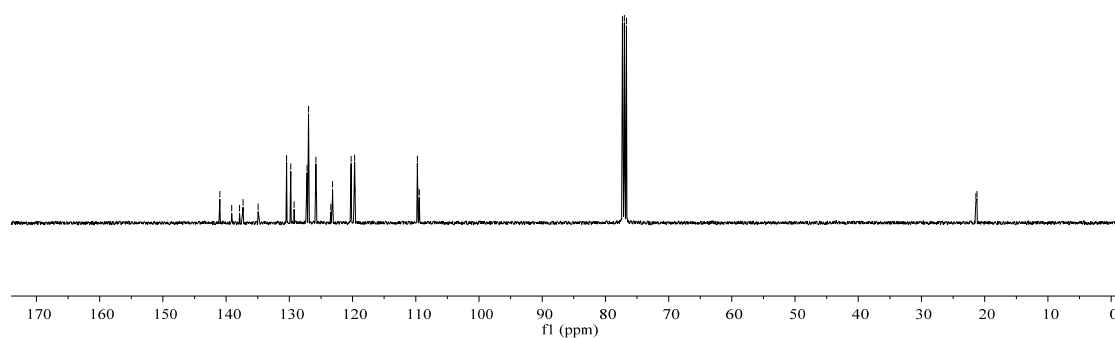
2x'

+

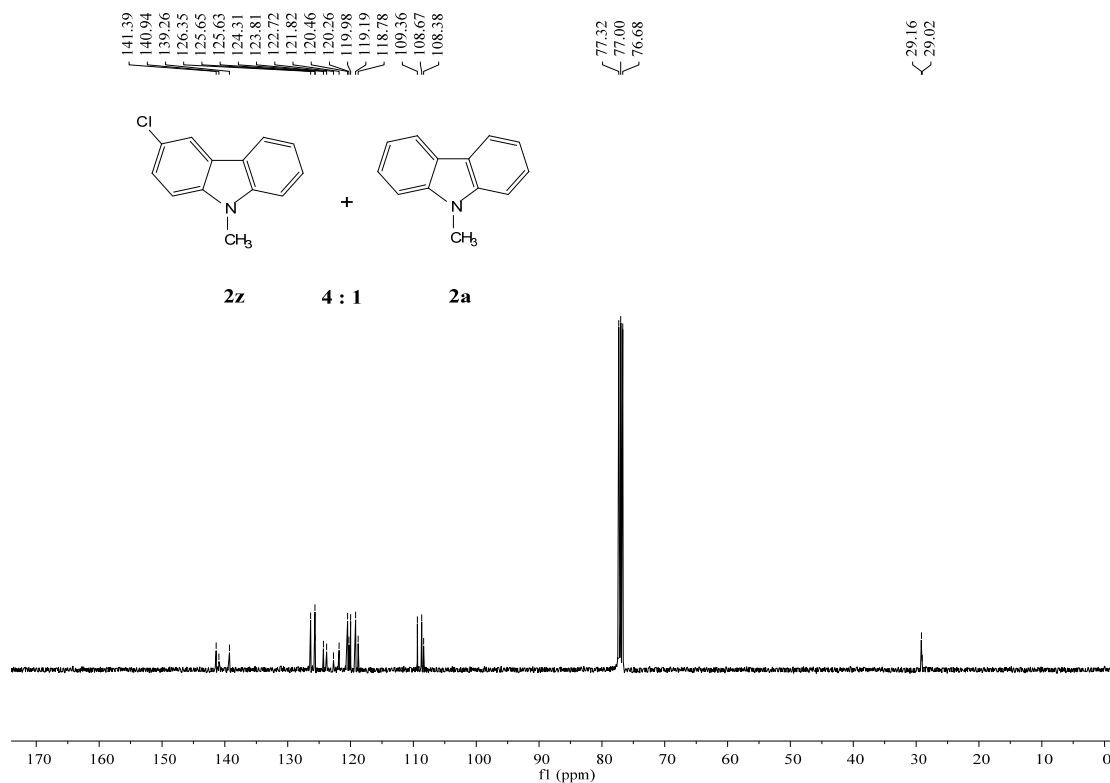
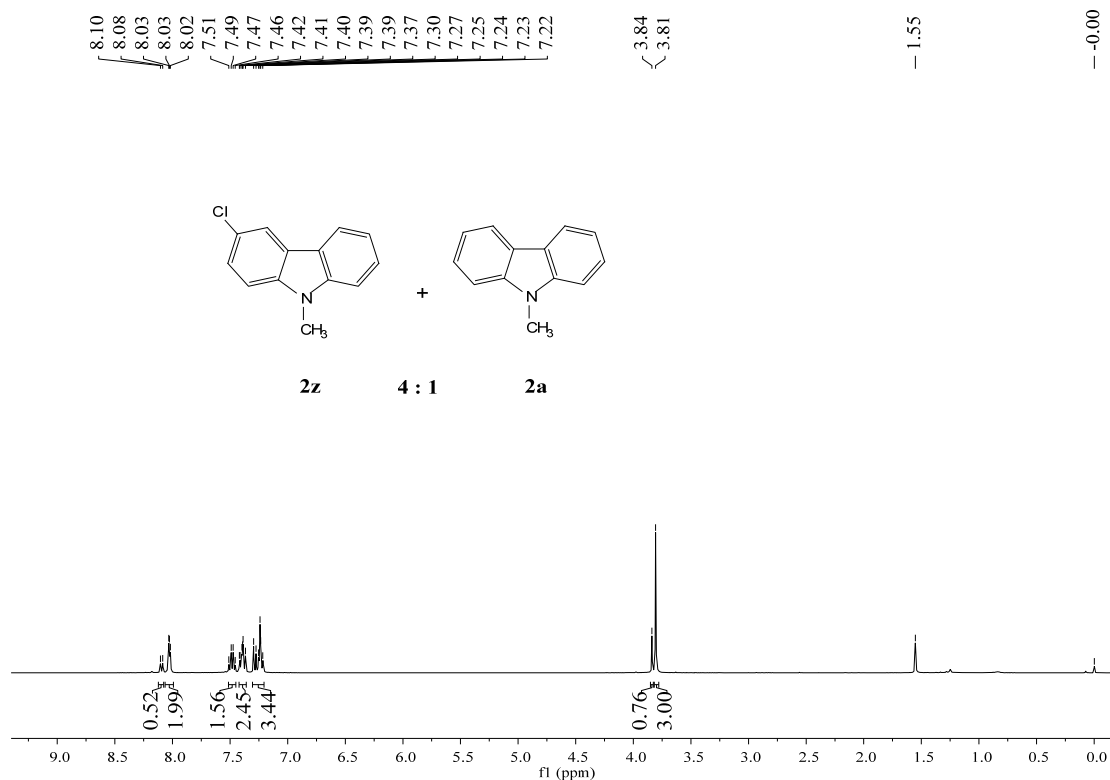
1 : 1



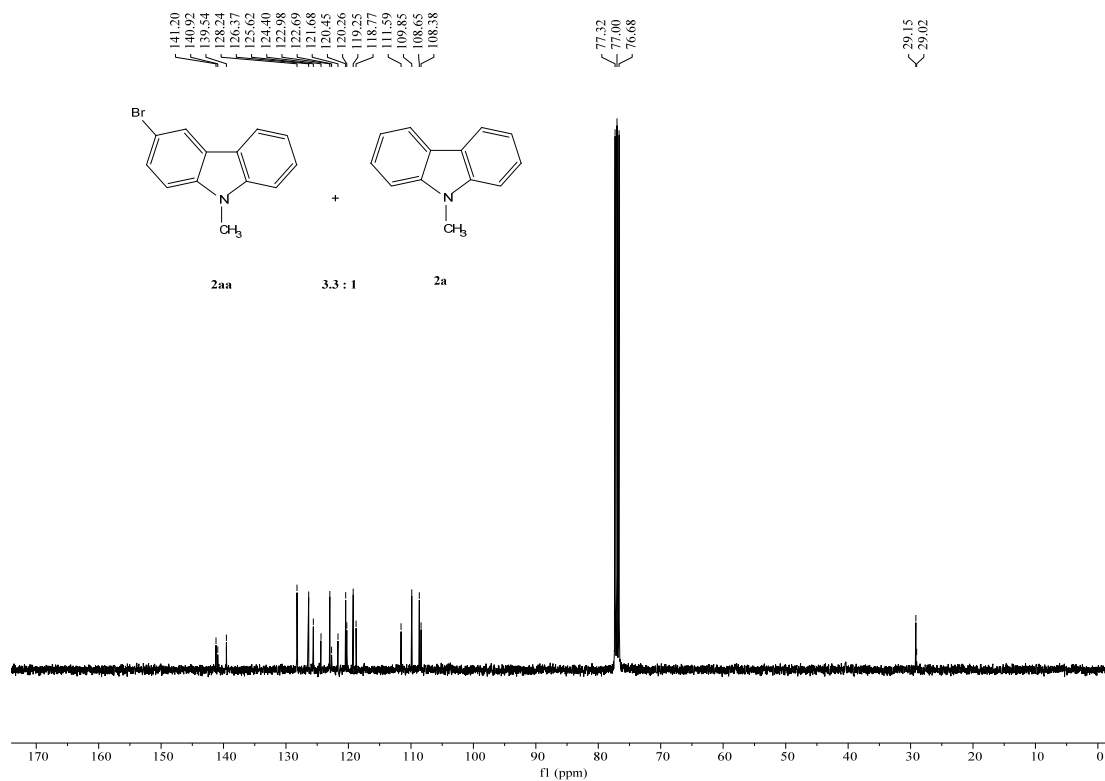
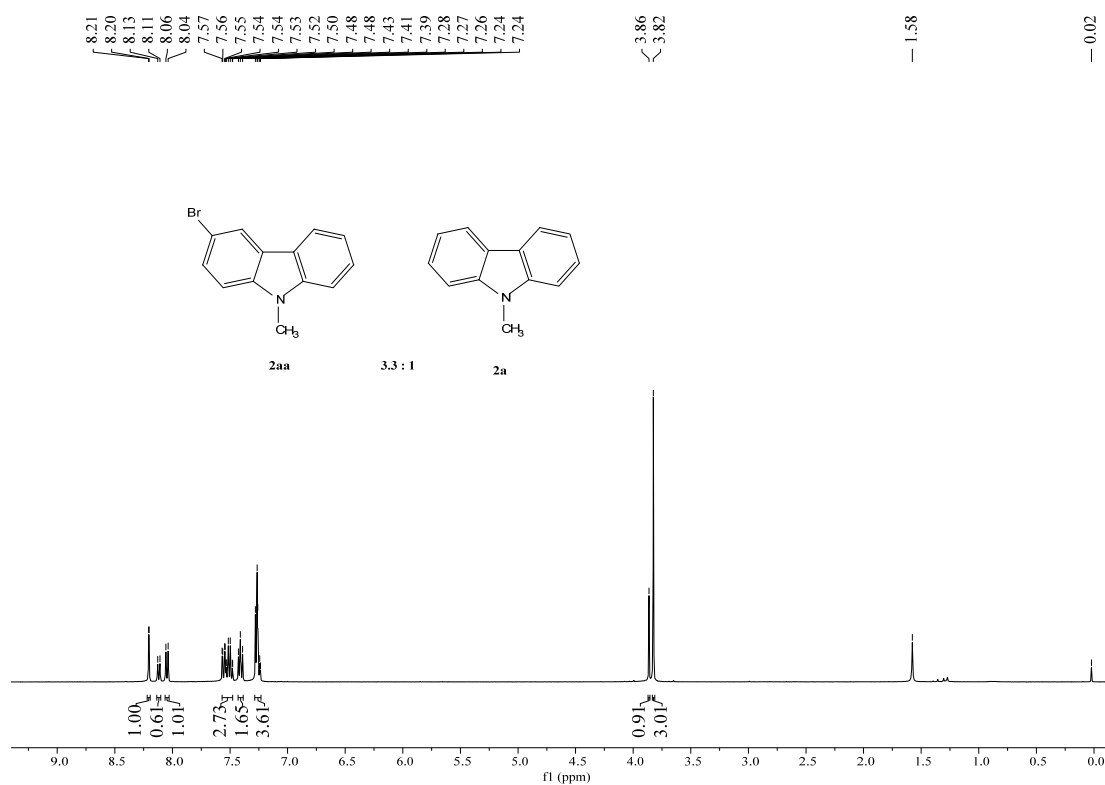
2x



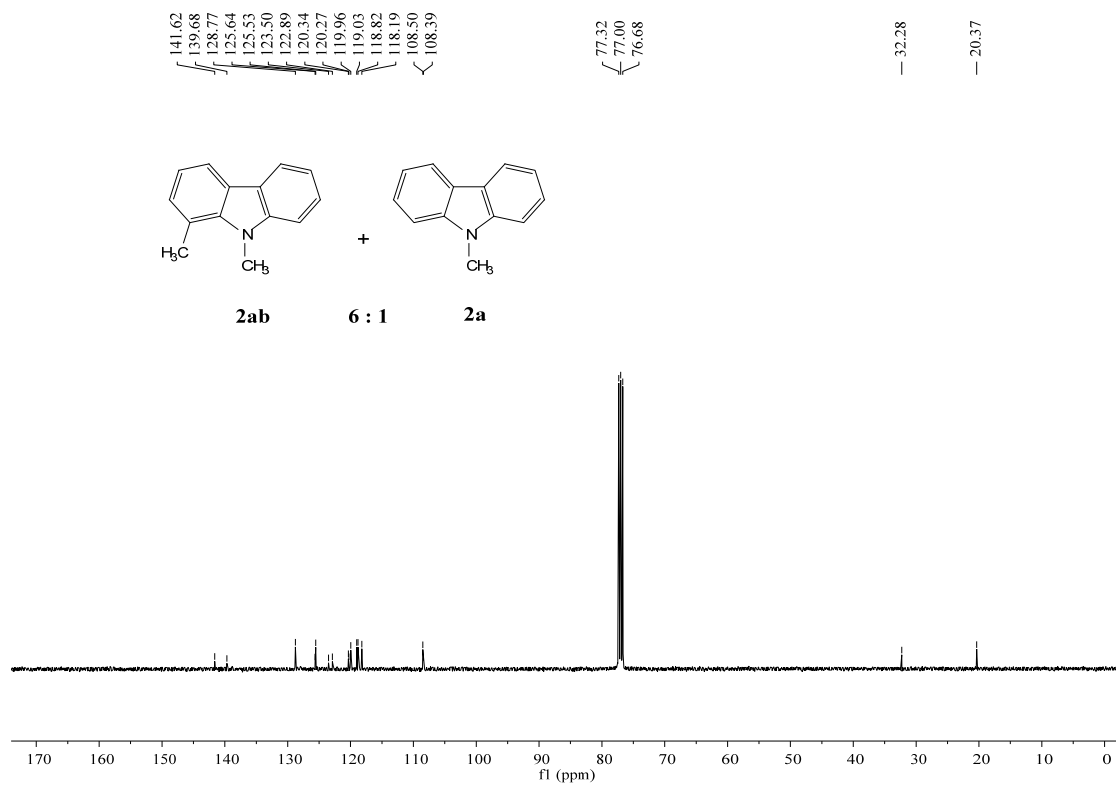
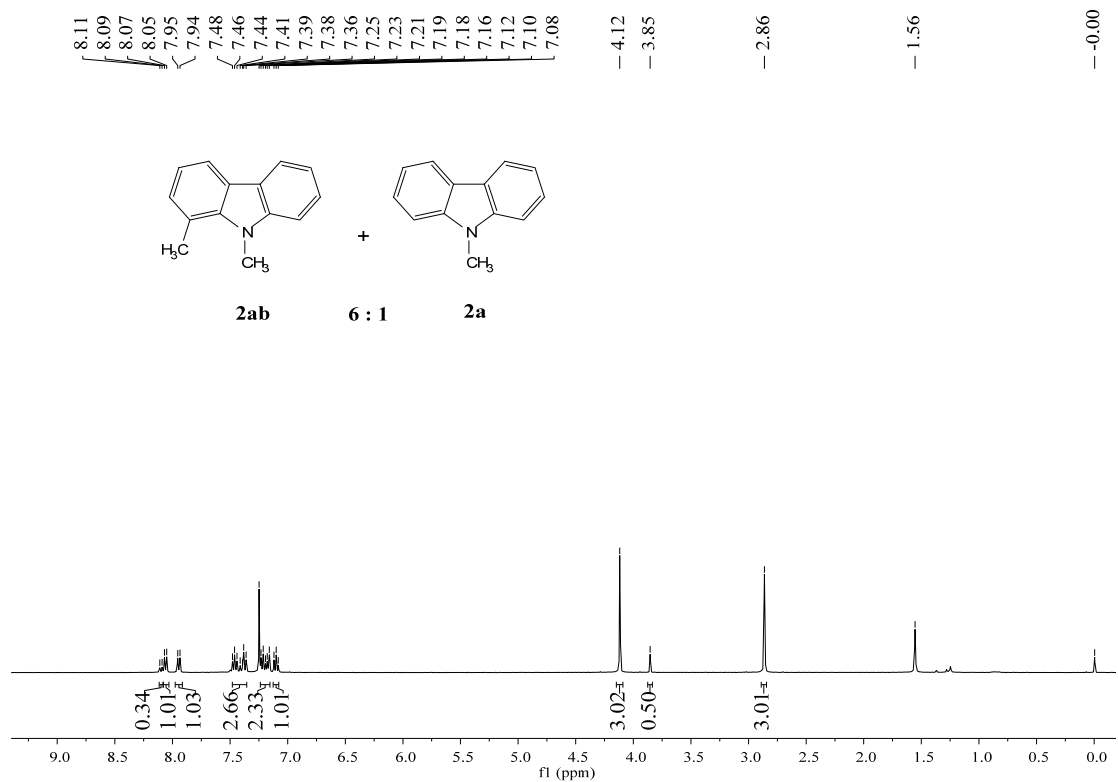
¹H and ¹³C NMR spectra of 2z+2a



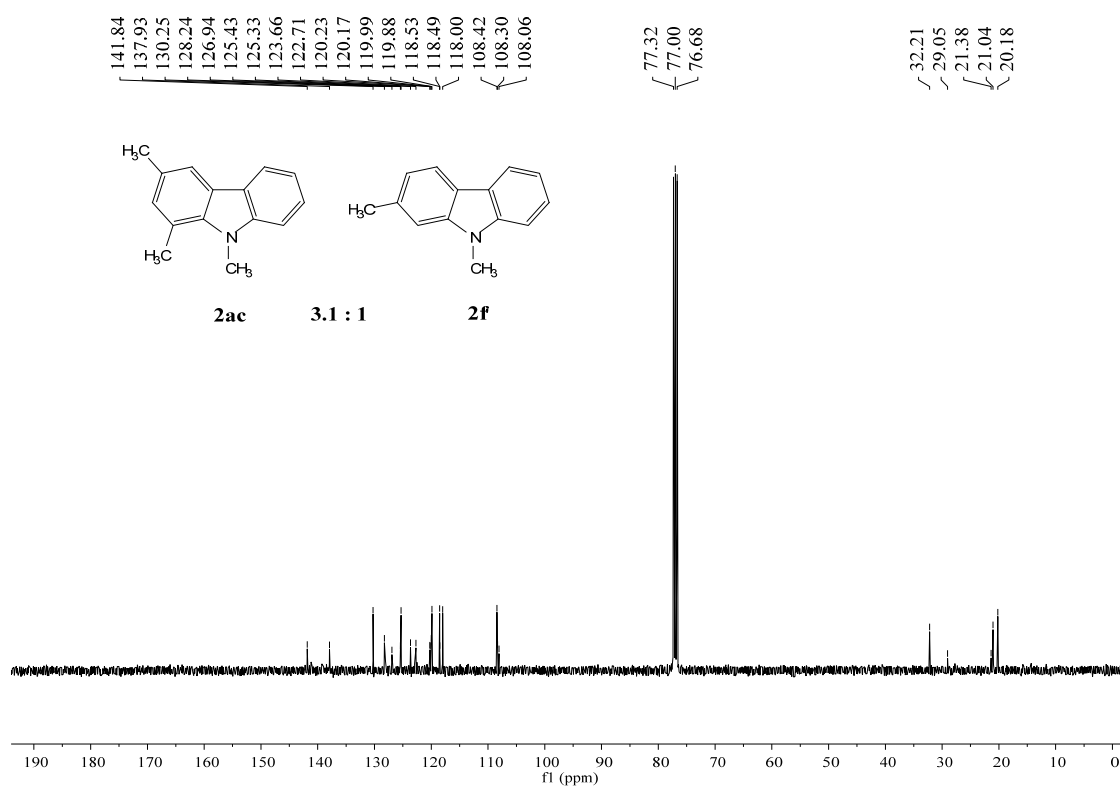
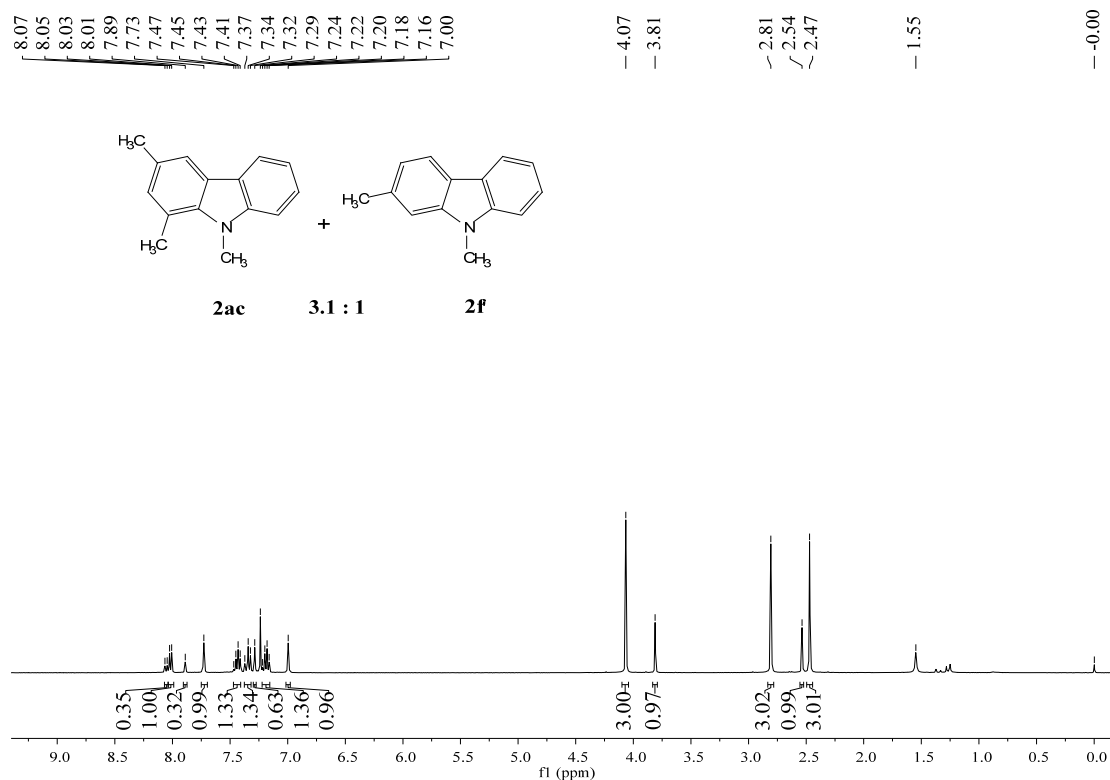
¹H and ¹³C NMR spectra of 2aa+2a



¹H and ¹³C NMR spectra of 2ab + 2a



¹H and ¹³C NMR spectra of 2ac+2f



¹H and ¹³C NMR spectra of 2ad+2f (1:25)

