

Supporting Information

The Synthesis of Carbazoles: Light-Promoted Tandem Coupling of Nitroarenes with Grignard Reagents

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1. General information

Unless otherwise specified, commercially available reagents were used without further purification. Toluene and THF (tetrahydrofuran) were refluxed over Na/benzophenone and distilled under argon atmosphere. EtO₂ (Diethyl ether) were refluxed over CaH₂ and distilled under argon atmosphere. All reactions were carried out under an argon atmosphere unless otherwise noted. Column chromatography was performed on silica gel 200-300 Mesh with eluent (PE = petroleum ether, EA = ethyl acetate, DCM = dichloromethane). Reactions were monitored by thin-layer chromatography (TLC) and visualization on TLC was achieved by UV light, iodine or phosphomolybdic acid.

NMR spectra were recorded on Bruker-400 MHz NMR spectrometer (400 MHz for ¹H; 100 MHz for ¹³C). ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) (0.00 ppm) or at the signal of a residual protonated solvent: CDCl₃ (7.26 ppm) or DMSO-*d*₆ (2.50 ppm). ¹³C NMR chemical shifts were determined relative to CDCl₃ (77.16 ppm) or DMSO-*d*₆ (39.52 ppm). The coupling constants (*J*) were given in Hertz (Hz). The following abbreviations were used to explain NMR peak multiplicities: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). Gas chromatography (GC) analysis was carried out on a SHIMADZU GC with a HP-5 MS column.

The general reactions were carried with the assembled photoreactor (Figure S1). Each of lamp include: 9 W purple LED (390-395 nm, 3 LED lamp beads in series), plastic fan, electric driver (XC-8W600-OS). The optical power up to 200 ± 10 mw at 1 cm axis distance detected by Thorlabs' Optical Power Meter (PM100D, S120VC). The LED beads were purchased from Zhuhai UV Optoelectronics Co., Ltd. (TH-UV395T3WL-3535-60). We don't use band pass filters, and the specific wavelengths (390-395 nm) refer only to the max of irradiation. Furthermore, for all light sources, it only refers to the maximum value of the illumination.

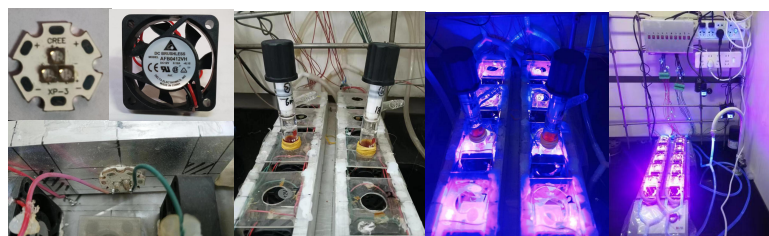
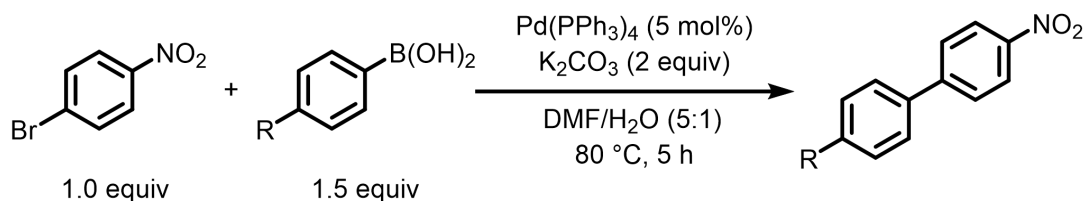


Figure S1. Pictures of assembled photoreactor.

(Notes: The thermal radiation of the LEDs allows the temperature of the THF reaction mixture to reach around 70 °C without an external heating unite.)

2. General procedure for the synthesis of substrates

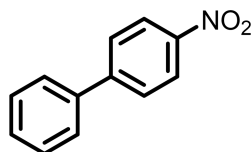
2.1. General procedure for the synthesis of nitroarenes¹



In an oven-dried 10 mL Schlenk flask, arylboronic acid (1.5 mmol), K_2CO_3 (276.4mg 2.0 mmol), and $\text{Pd(PPh}_3)_4$ (57.7 mg, 0.05 mmol) were dissolved in DMF and H_2O (DMF : H_2O = 5:1, 4.0 mL). 1-bromo-4-nitrobenzene (202.0 mg, 1.0 mmol) was then added, and the resulting mixture was heated to 80 °C for 5 hours under Ar atmosphere. The reaction mixture was poured into water and then the product was extracted with EtOAc (3 times), dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 5:1~3:1) to give the corresponding nitroarenes.

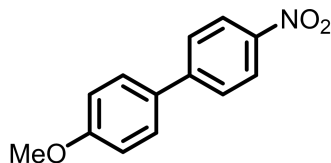
Analysis data of nitroarenes:

4-Nitro-1,1'-biphenyl (S1)



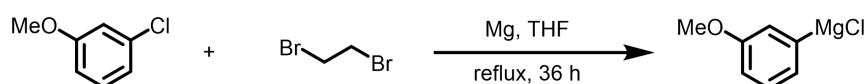
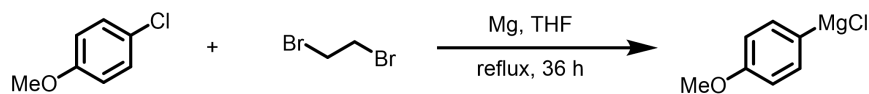
A white solid (159.4 mg, 80% yield), (PE/EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 7.54 – 7.42 (m, 3H). The obtained spectrum matched that reported in the literature.²

4-Methoxy-4'-nitro-1,1'-biphenyl (S2)



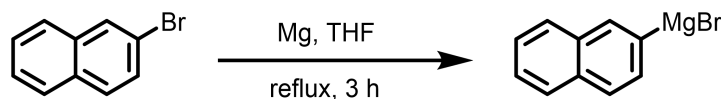
A yellowish solid (194.8 mg, 85% yield), (PE/EA = 3:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). The obtained spectrum matched that reported in the literature.³

2.2. General procedure for the synthesis of Grignard Reagent



(4-Methoxyphenyl)magnesium chloride (S3) and (3-methoxyphenyl)magnesium chloride (S4)⁴

In an oven-dried 50 mL Schlenk flask equipped with a stir bar, under Ar atmosphere, was added magnesium turnings that had been activated (16.0 mmol, 1.6 equiv). The flask containing the Mg was heated at 100 °C while flushing with Ar for 1 hour before cooling to room temperature. Once cool, dry degassed THF (20.0 mL) was added and the mixture was stirred while adding degassed 1,2-dibromoethane (~10 drops). 1-chloro-4-methoxybenzene or 1-chloro-3-methoxybenzene was then added dropwise over ~2 minutes (10 mmol, 1.0 equiv.). The mixture darkened slightly and was stirred while heating to reflux for 36 hours. Determining the concentration of Grignard reagents by the combined use of menthol and 1,10-phenanthroline in dry tetrahydrofuran solution⁵.

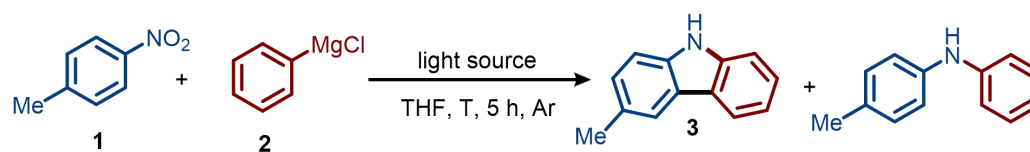


Naphthalen-2-ylmagnesium bromide (S5)⁶:

Magnesium powder (267.3 mg, 11 mmol) was added to a 50 mL round-bottom flask containing 15 mL anhydrous tetrahydrofuran (THF) and an iodine under argon pressure. A 2-bromonaphthalene solution of (2.0707 g, 10 mmol) in 5 mL anhydrous THF was dropped into the suspension of magnesium. After initiated the reaction, the dropping rate of 2-bromonaphthalene solution was adjusted to maintain the reaction system reflux. After the dropwise addition, heated the system continued to reflux for 2 more hours. Determining the concentration of Grignard reagents by the combined use of menthol and 1,10-phenanthroline in dry tetrahydrofuran solution⁵.

3. Tables of the optimization of reaction conditions

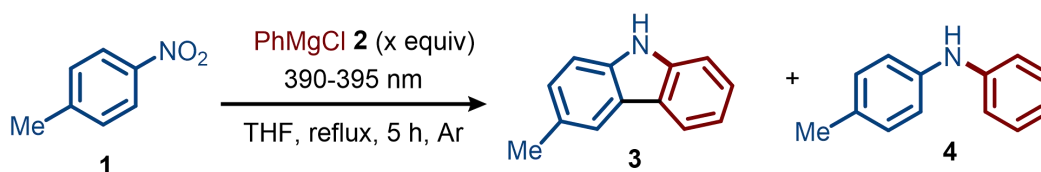
Table S1. The screening of light source^a



Entry	light source	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	390-395 nm, reflux	74	N.D.
2	390-395 nm, 40 °C	45	28
3	365-370 nm	63	N.D.
4	blue	N.D.	95
5	white	trace	trace
6	orange	trace	trace
7	red	trace	trace
8	no light, reflux	N.D	88

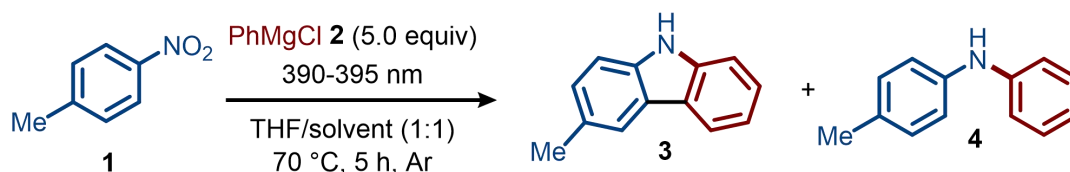
^aStandard conditions: 1 (0.5 mmol), 2 (2.5 mmol, 5.0 equiv), THF (2 mL), T, 5 h. ^bYields determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. N.D. = not detected.

Table S2. The screening of amount of Grignard reagent.^a



Entry	2 (x equiv)	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	1.0	N.D	30
2	1.5	N.D.	47
3	2.0	N.D.	58
4	2.5	N.D	68
5	3.0	5	61
6	3.5	22	45
7	4.0	45	20
8	4.5	57	9
9	5.0	74	N.D.
10	5.5	63	10
11	6.0	51	23
12	6.5	28	45

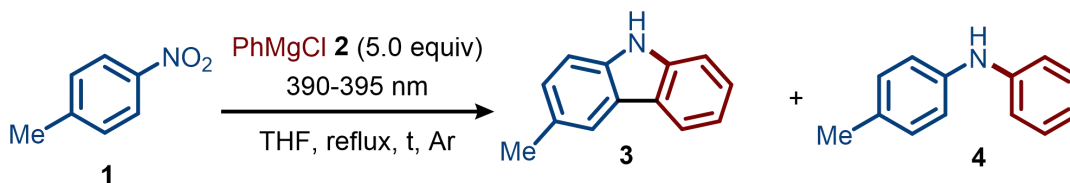
^aStandard conditions: 1 (0.5 mmol), 2 (x equiv), THF (2 mL), reflux, 5 h. ^bYields determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. N.D. = not detected.

Table S3. The screening of solvents.^a

Entry	solvent	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	THF (reflux)	74	N.D.
2	2-MeTHF	71	N.D.
3	dioxane	29	38
4	Et ₂ O (reflux)	9	76
5	DME	70	N.D.
6	toluene	70	N.D.

^aStandard conditions: **1** (0.5 mmol), **2** (5.0 equiv), THF/solvent (1:1, 2mL), 70 °C, 5 h, Ar.

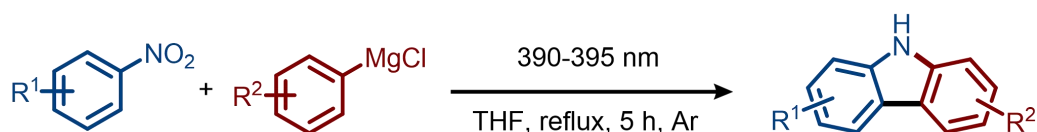
^bYields determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. N.D. = not detected.

Table S4. The screening of reaction time.^a

Entry	t (h)	Yield of 3 (%) ^b	Yield of 4 (%) ^b
1	1	12	60
2	2	27	56
3	3	52	21
4	4	65	7
5	5	74	N.D.
6	6	72	N.D.
7	7	74	N.D.
8	8	75	N.D.
9	9	74	N.D.
10	10	69	N.D.

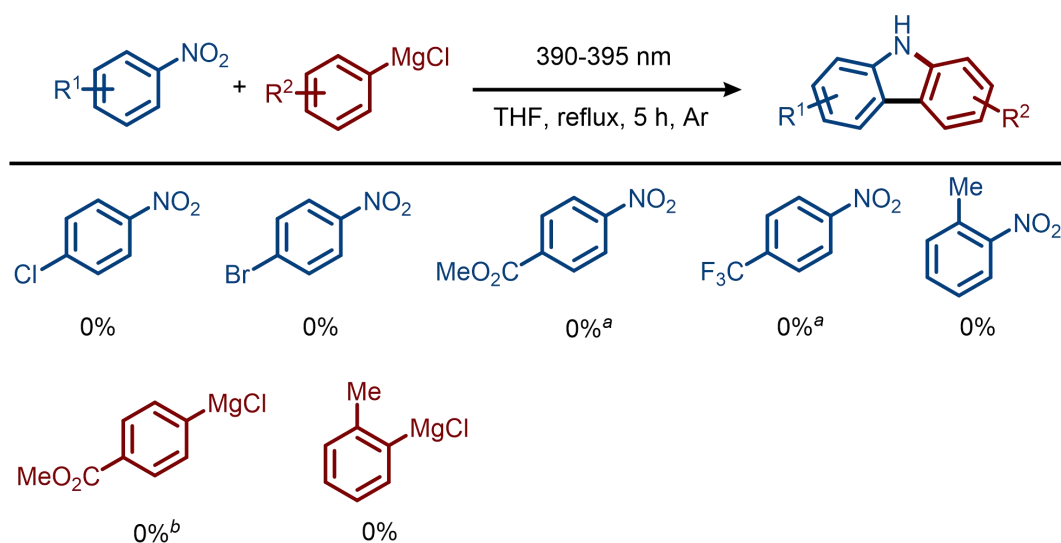
^aStandard conditions: **1** (0.5 mmol), **2** (5.0 equiv), THF (2.0 mL), reflux, t. ^bYields determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. N.D. = not detected.

4. Procedure for the synthesis of carbazoles



To a dry Schlenk flask equipped with a stir bar was added nitroarenes (0.5 mmol), then was evacuated and backfilled with Ar for 3 times, and THF (0.80 mL) was added. The Grignard reagent (2.0 M in THF solution) (1.3 mL, 2.5 mmol) was slowly added to a solution of the nitrobenzene in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, the 30 mL saturated NH₄Cl aqueous solution was added and the resulting mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by flash chromatography to afford carbazoles.

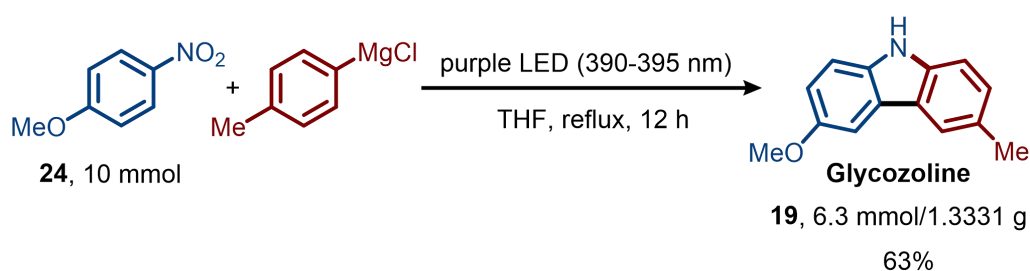
Table S5. Selected unsuccessful substrates.



Reaction condition: nitroarenes (0.5 mmol), Aryl Grignard reagents (5.0 equiv, 2.5 mmol), THF (2 mL), purple LEDs (390-395 nm), reflux, Ar, 5 h. ^aAdd TMEDA. ⁷ ^dThe preparation method of (4-(methoxycarbonyl)phenyl)magnesium chloride: to a solution of BDMAEE (250 μL, 1.3 mmol) in THF (1.0 mL) was added isopropyl magnesium chloride (0.6 mL, 1.2 mmol, 2 M solution in THF) at 15 °C. The mixture was stirred at this temperature for 20 min. methyl 4-iodobenzoate (327.6 mg, 1.25 mmol) in THF (1.0 mL) was added. After the resulting mixture was stirred at rt for 10 min. ⁸

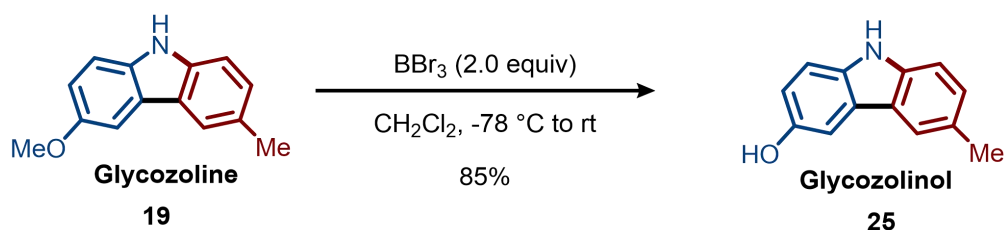
These substrates nitroarenes could not obtain carbazoles, but only the corresponding diarylamines with 80-90% yield.

5. Synthesis of glycozoline (19) in gram scale

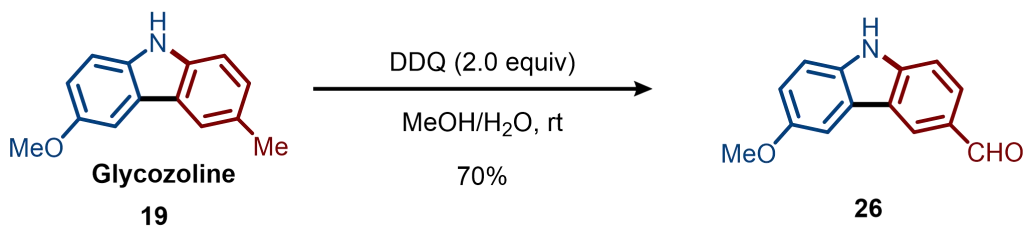


To a dry 100 mL Schlenk flask equipped with a stir bar was added 1-methoxy-4-nitrobenzene (10 mmol), then was evacuated and backfilled with Ar for 3 times, and THF (15.0 mL) was added. The Grignard reagent (2.0 M in THF solution) (25.0 mL, 50.0 mmol) was slowly added to a solution of the 1-methoxy-4-nitrobenzene in THF at 0 °C. The reaction mixture was then irradiated with four 9 W 390-395 nm LEDs lamp at reflux for 12 h. After cooling to room temperature, the 50 mL saturated NH_4Cl aqueous solution was added and the resulting mixture was extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The crude product was purified by flash chromatography to afford glycozoline **19**.

6. Derivations of glycozoline (19)



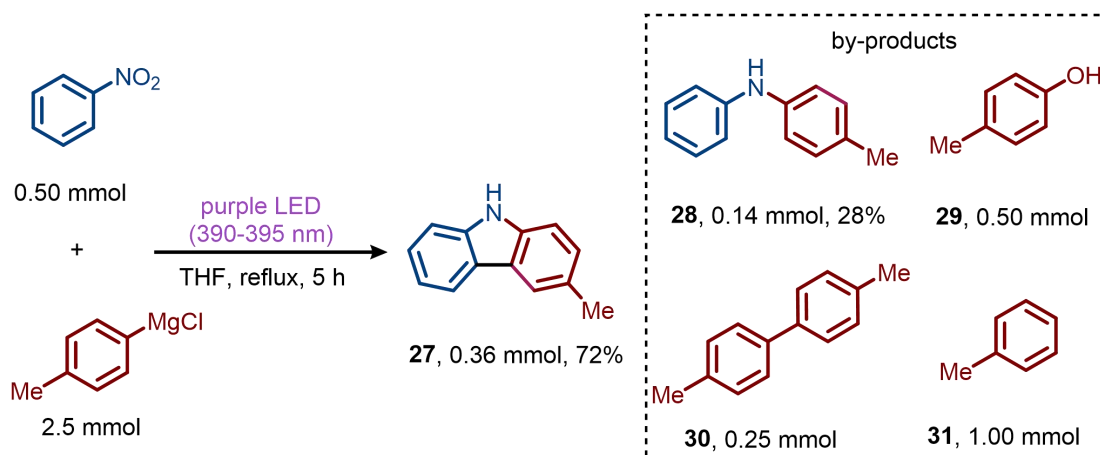
Glycozoline **19** (105.6 mg, 0.5 mmol) was dissolved in DCM (5.0 mL). After cooling to -78 °C, a solution of boron tribromide (1M in dichloromethane, 1.0 mL, 1 mmol) was added over a period of 11 min and the solution was allowed to warm to room temperature. The reaction mixture was stirred for 4 h at room temperature. The mixture was subsequently quenched with methanol (1 mL) under cooling, transferred to a separation funnel with ethyl acetate, and washed several times with water and brine. After extraction of the aqueous layer with ethyl acetate, the combined organic layers were dried over sodium sulfate, the solvent was evaporated, and the crude product was purified by chromatography on silica gel (PE/Acetone 3:1) to provide **25** (83.8 mg, 85% yield) as a white solid.⁹



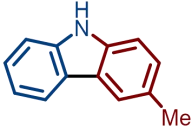
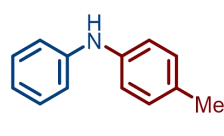
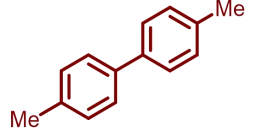
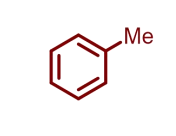
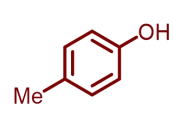
DDQ (249.7 mg, 1.1 mmol) was added in portions to a solution of Glycozoline **19** (105.6 mg, 0.5 mmol) in a mixture of methanol (5.0 mL), THF (1.5 mL), and water (0.5 mL). The reaction mixture was stirred for 1.5 h at room temperature, diluted with 10% NaOH and extracted several times with diethyl ether. The combined organic layers were washed with brine and dried over sodium sulfate. Removal of the solvent and flash chromatography of the crude product on silica gel (PE/EA 4:1) provided **26** (78.8 mg, 70% yield) as a white solid.⁹

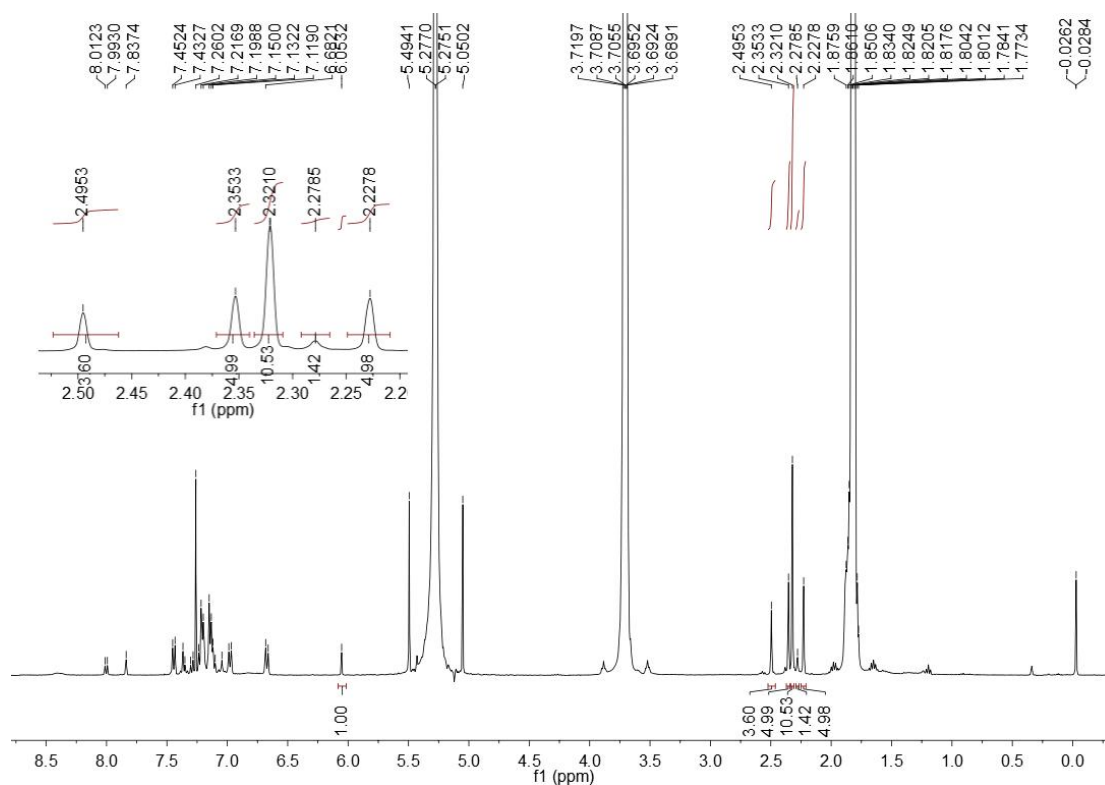
7. Mechanistic Investigations

7.1. The by-products in the synthesis of carbazoles.

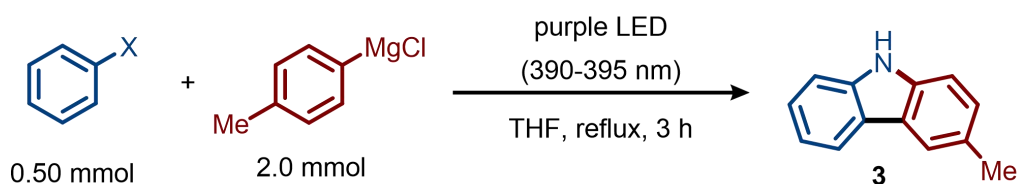


To a dry Schlenk flask equipped with a stir bar was evacuated and backfilled with Ar for 3 times, then was added nitrobenzene (61.5 mg, 0.5 mmol), and THF (1.3 mL) was added. The *p*-tolylmagnesium chloride (2.0 M in THF solution) (1.3 mL, 2.5 mmol) was slowly added to a solution of the nitrobenzene in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, the 30 mL saturated NH₄Cl aqueous solution and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, as internal standard) were added, then the resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine (30.0 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Yields determined by ¹H NMR.

				
$\delta = 2.4953$ ppm 0.36 mmol	$\delta = 2.2785$ ppm 0.14 mmol	$\delta = 2.3533$ ppm 0.25 mmol	$\delta = 2.3210$ ppm 1.00 mmol	$\delta = 2.2278$ ppm 0.50 mmol



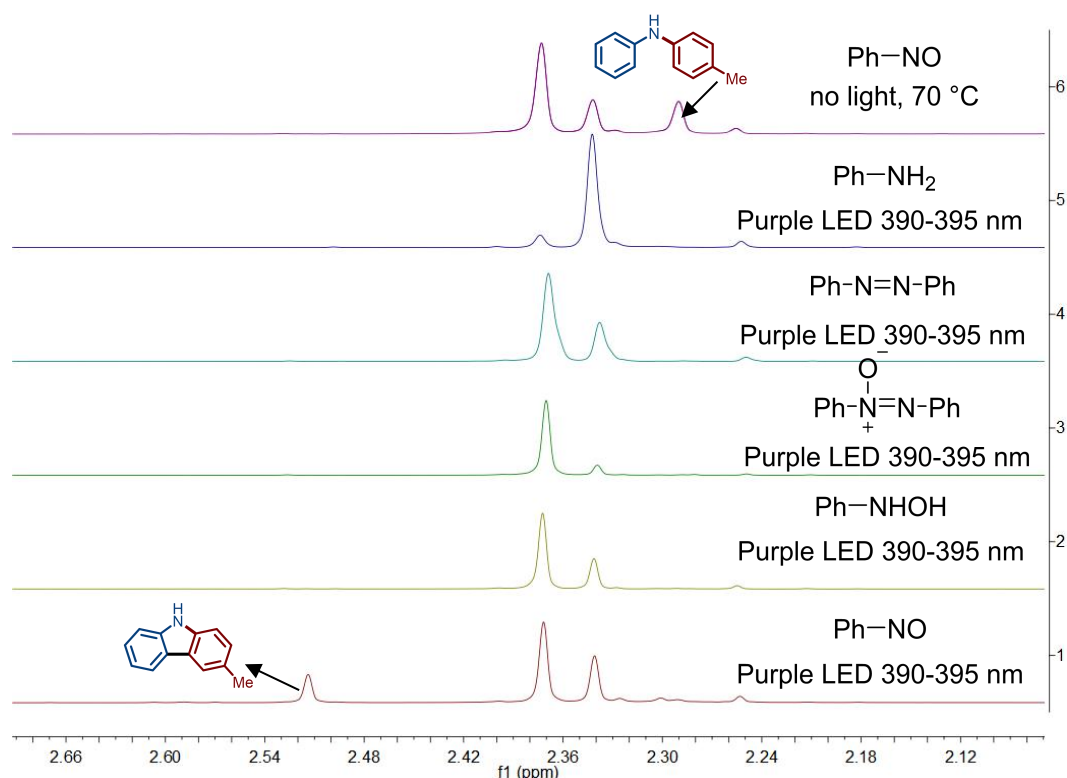
7.2. The search for possible intermediates.



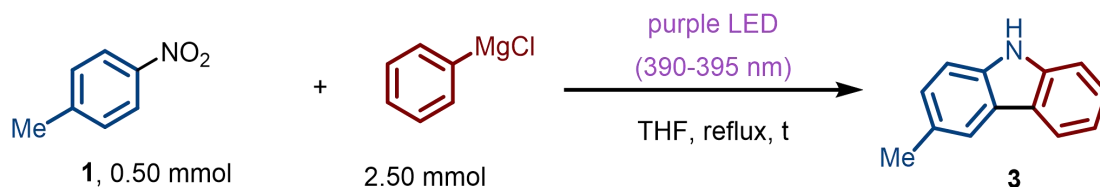
- | | |
|---|-----|
| (a) Ph-NO | 60% |
| (b) Ph-NHOH | 0% |
| (c) Ph-N ⁺ (Ph)=O ⁻ | 0% |
| (d) Ph-N=N-Ph | 0% |
| (e) Ph-NH ₂ | 0% |

To five dry Schlenk flask equipped with a stir bar was added five potential intermediates (0.5 mmol) respectively, then was evacuated and backfilled with Ar for 3

times, and THF (1.3 mL) was added. The *p*-tolylmagnesium chloride (2.0 M in THF solution) (1.0 mL, 2.0 mmol) was slowly added to a solution of the five potential intermediates in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, the 30 mL saturated NH₄Cl aqueous solution and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, as internal standard) were added, then the resulting mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Yields determined by ¹H NMR. Notably only nitrosoarene could afford the desired carbazole **3** (60%) or (0%) in light or no light conditions. The results are like those observed when nitrobenzene was used, implicating the nitrosoarene as a possible intermediate in the photochemical reaction.

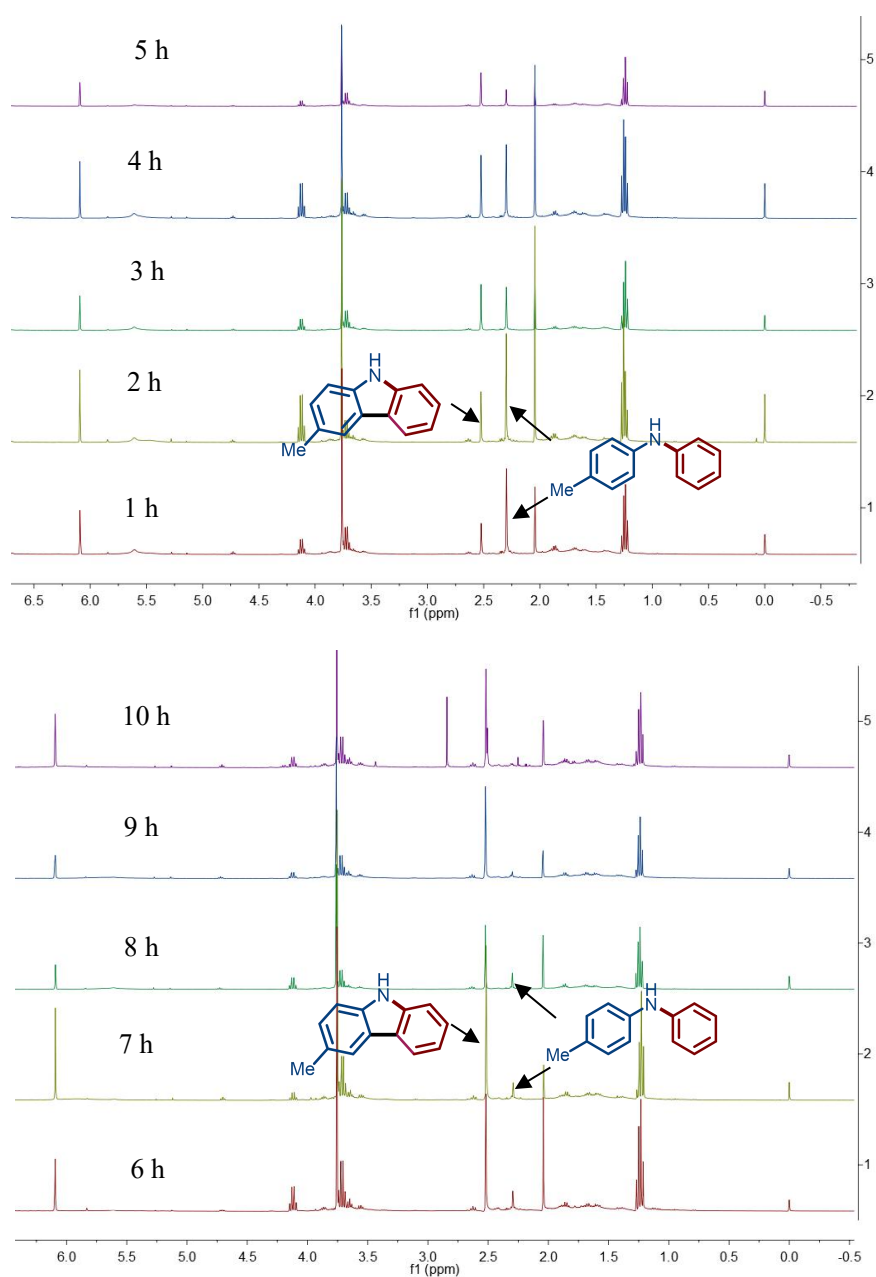
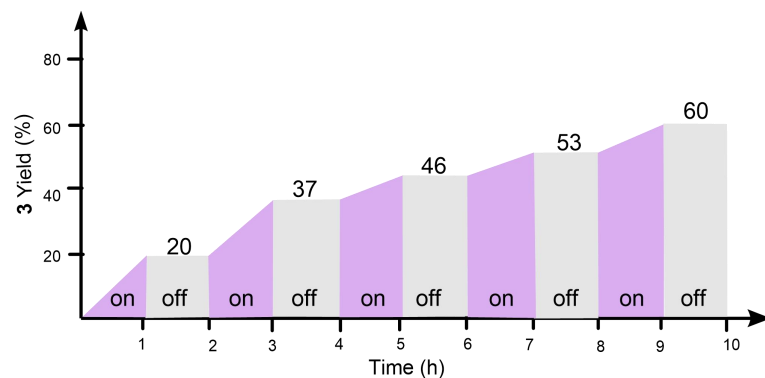


7.3. The light on/off experiment.



Ten parallel reactions are performed simultaneously under the same conditions. After being irradiated for 1 h, The first reaction was quenched with saturated NH₄Cl aqueous solution, then an internal standard 1,3,5-trimethoxybenzene was added, and then extracted. The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo, and yields determined by ¹H NMR. Then other reaction

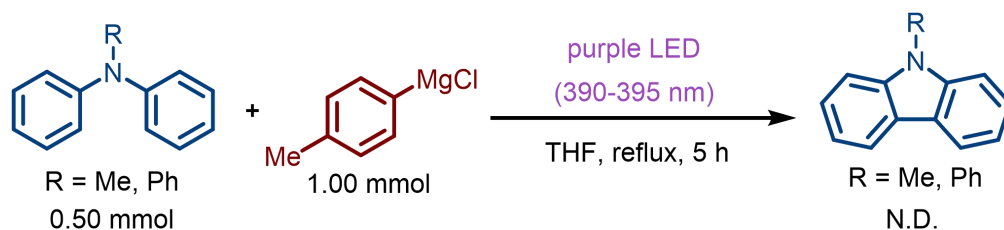
mixtures were stirred for 1 h with light-off. All of the following yields were analyzed in the identical way after a 1 h light on or off.



The experiments demonstrated that light plays a crucial role in the synthesis of

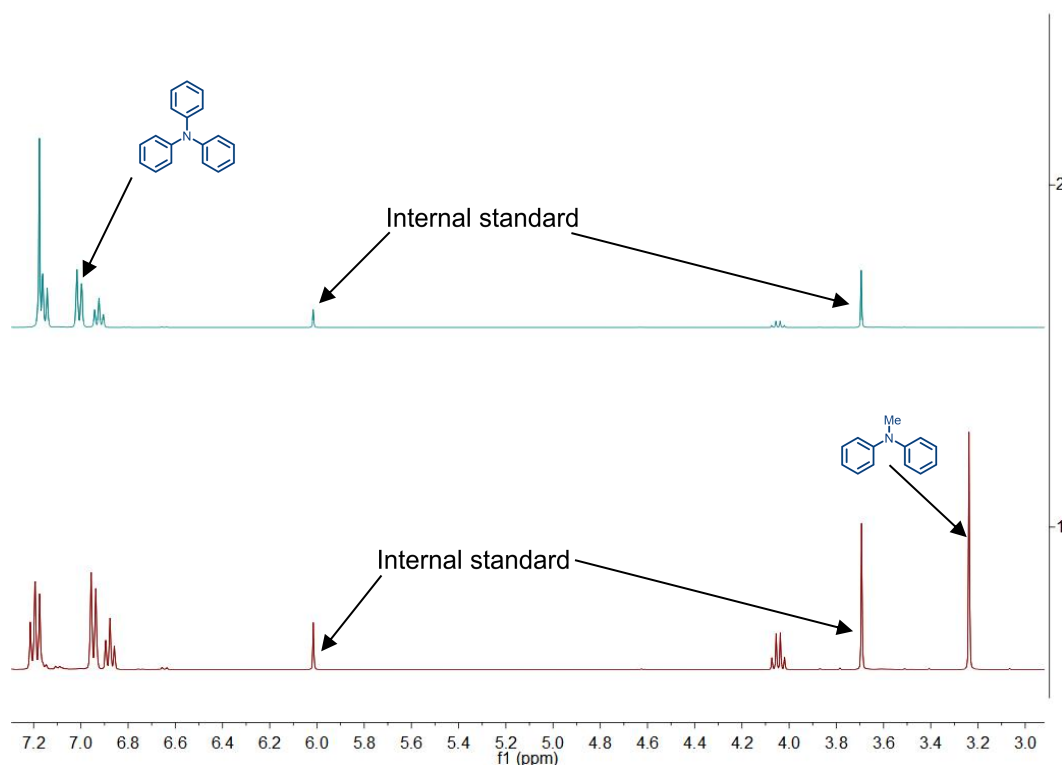
carbazole and requires continuous illumination.

7.4. The effect of NH of diarylamine for the construction of carbazole.

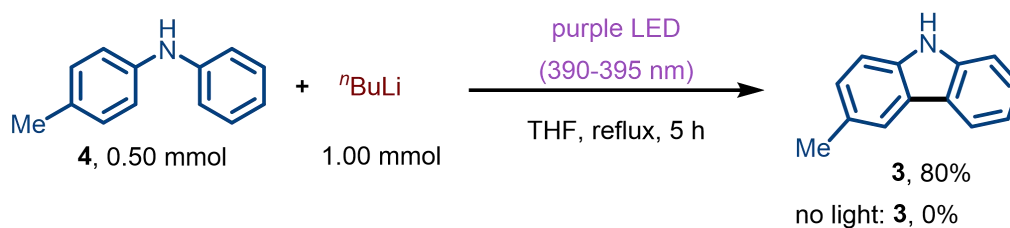


To a dry Schlenk flask equipped with a stir bar was added *N*-methyl-*N*-phenylaniline or triphenylamine (0.5 mmol), then was evacuated and backfilled with Ar for 3 times, and THF (1.5 mL) was added. The *p*-tolylmagnesium chloride (2.0 M in THF solution) (0.5 mL, 1 mmol) was slowly added to a mixed solution in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, the 30 mL saturated NH₄Cl aqueous solution and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, as internal standard) were added, then the resulting mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Yields determined by ¹H NMR.

The result of the experiment was that no corresponding carbazole products were observed, and materials were all recovered, suggesting that NH of diarylamine is crucial for the successful construction of carbazole.

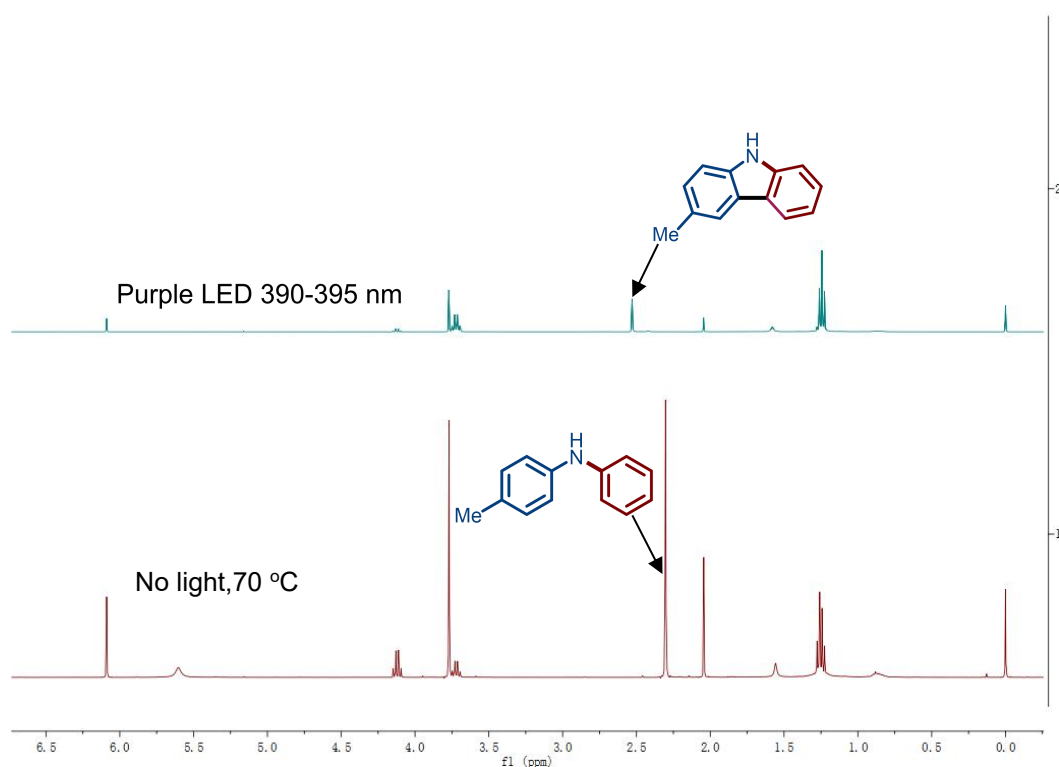


7.5. The effect of ⁿBuLi to the construction of carbazole.

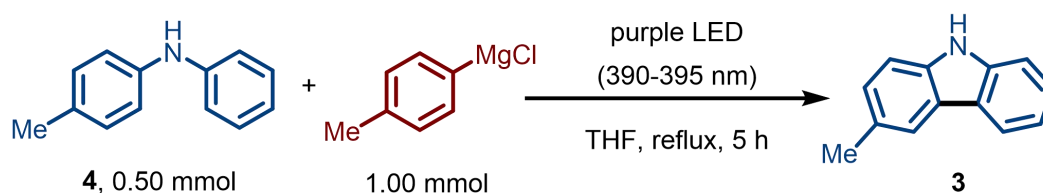


To a dry Schlenk flask equipped with a stir bar was added 4-methyl-*N*-phenylaniline **4** (91.6 mg, 0.5 mmol), then was evacuated and backfilled with Ar for 3 times, and THF (1.5 mL) was added. The $n\text{BuLi}$ (2.0 M in THF solution) (0.5 mL, 1 mmol) was slowly added to a solution of the nitrobenzene in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, the 30 mL saturated NH_4Cl aqueous solution and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, as internal standard) were added, then the resulting mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4 , and concentrated in vacuo. Yields determined by ^1H NMR.

The same results were obtained when $n\text{BuLi}$ was substituted for aryl Grignard reagent in light or no light, indicating that aryl Grignard reagent participated as a base in the reaction.



7.6. The experiment for releasing hydrogen.



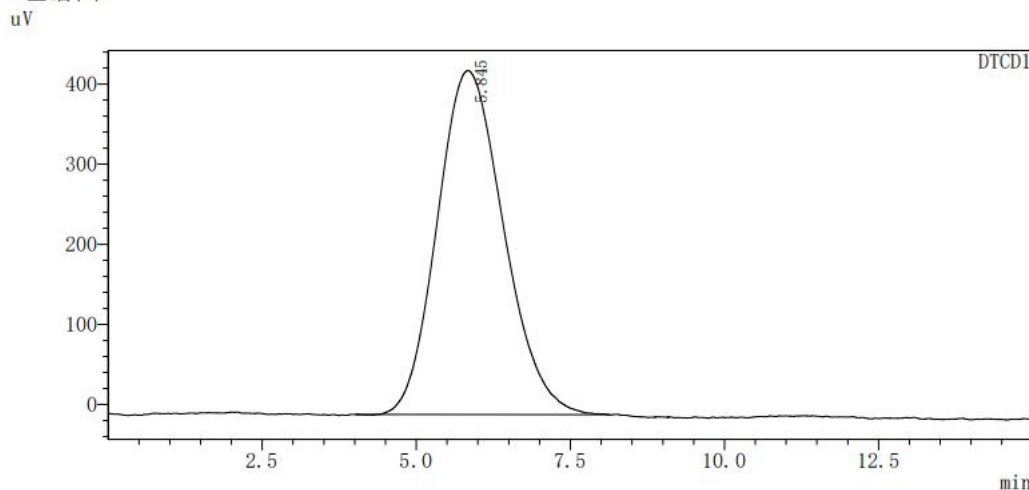
To a dry Schlenk flask equipped with a stir bar was added 4-methyl-*N*-phenylaniline **4** (91.6 mg, 0.5 mmol), then was evacuated and backfilled with Ar for 3 times, and THF (1.5 mL) was added. The *p*-tolylmagnesium chloride (2.0 M in THF solution) (0.5 mL, 1 mmol) was slowly added to a solution of the nitrobenzene in THF at 0 °C. The reaction mixture was then irradiated with two 9 W 390-395 nm LEDs lamp at reflux for 5 h. After cooling to room temperature, we detected the gas in the upper layer of the tube with GC.

分析报告

<样品信息>

样品名 : YC-H2-1
 样品ID :
 数据文件名 : H2-1.gcd
 方法文件名 : wangxuewei-h2-70oc-20 mins.gcm
 批处理文件名 :
 样品瓶号 : 1 样品类型 : 未知
 进样体积 : 1 uL
 分析日期 : 2023/3/18 22:57:35 分析者 : System Administrator
 处理日期 : 2023/3/18 23:12:39 处理者 : System Administrator

<色谱图>



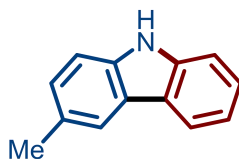
<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.845	32233	430	100.000		M	
总计		32233	430				

GC detected the hydrogen in the upper layer of the tube

8. Analytic data of compounds

3-Methyl-9H-carbazole (3)

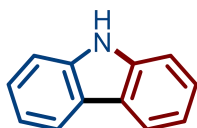


The product **3** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (61.6 mg, 68% yield). The obtained spectrum matched that reported in the literature.¹⁰

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.09 (br s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.23 – 7.17 (m, 1H), 7.15 – 7.08 (m, 1H), 2.46 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 140.1, 138.1, 127.3, 127.0, 125.5, 122.7, 122.4, 120.2, 120.0, 118.4, 111.0, 110.8, 21.2 ppm.

9H-carbazole (5)

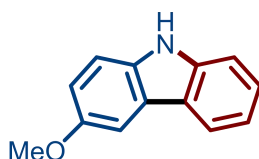


The product **5** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (50.2 mg, 60% yield). The obtained spectrum matched that reported in the literature.¹⁰

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.25 (br s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 139.9, 125.7, 122.5, 120.3, 118.7, 111.1 ppm.

3-Methoxy-9H-carbazole (6)

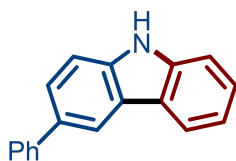


The product **6** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (54.2 mg, 55% yield). The obtained spectrum matched that reported in the literature.¹¹

¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.90 (br s, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.15 (m, 1H), 7.08 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.94 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 154.1, 140.4, 134.5, 125.9, 123.9, 123.5, 120.4, 119.2, 115.2, 111.4, 110.9, 103.4, 56.2 ppm.

3-Phenyl-9H-carbazole (7)

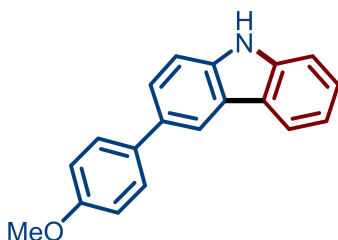


The product **7** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (54.7 mg, 45% yield). The obtained spectrum matched that reported in the literature.¹¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.33 (br s, 1H), 8.45 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.71 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.43 – 7.38 (m, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 141.3, 140.2, 139.3, 131.0, 128.8, 126.7, 126.3, 125.7, 124.6, 123.1, 122.6, 120.4, 118.6, 118.3, 111.3, 111.1. ppm.

3-(4-Methoxyphenyl)-9H-carbazole (8)

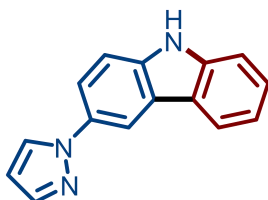


The product **8** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (72.4 mg, 53% yield). The obtained spectrum matched that reported in the literature.¹²

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.27 (s, 1H), 8.36 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.59 (m, 3H), 7.51 (dd, *J* = 14.4, 8.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.80 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 158.2, 140.2, 138.9, 133.8, 130.8, 127.7, 125.6, 124.3, 123.0, 122.6, 120.4, 118.5, 117.7, 114.3, 111.2, 111.0, 55.1 ppm.

3-(1H-pyrazol-1-yl)-9H-carbazole (9)



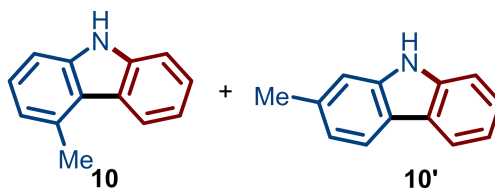
The product **9** was purified with silica gel chromatography (PE/DCM/EA = 10:3:1) as a white solid (66.5 mg, 57% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.39 (br s, 1H), 8.70 – 8.34 (m, 2H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.96 – 7.83 (m, 1H), 7.80 – 7.66 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.68 – 6.39 (m, 1H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 140.6, 140.1, 138.1, 132.5, 127.7, 126.1, 122.6, 122.4, 120.5, 118.7, 117.6, 111.4, 111.2, 110.6, 107.2 ppm.

HRMS (ESI) (*m/z*): calcd. for C₁₅H₁₂N₃ [M+H]⁺ : 234.1026, found: 234.1022.

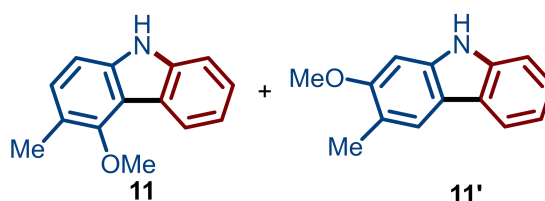
4-methyl-9*H*-carbazole (**10**) and 2-methyl-9*H*-carbazole (**10'**)



The 3.6:1 mixture of product **10** and **10'** were purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (61.6 mg, 68% yield). (Obtained as a 3.6:1 mixture of isomers, resulting in a double set of signals.) The obtained spectrum matched that reported in the literature.¹³

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.09 – 7.99 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (br s, 1H), 7.43 (d, *J* = 4.0 Hz, 2H), 7.38 (d, *J* = 3.6 Hz, 2H), 7.36 – 7.17 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 2.89 (s, 3H), 2.52 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 140.1, 139.6, 136.1, 133.5, 125.8, 125.4, 125.3, 124.1, 123.6, 122.7, 122.1, 121.1, 121.1, 120.1, 119.5, 119.5, 110.9, 110.6, 110.5, 108.3, 22.2, 20.9 ppm.



4-Methoxy-3-methyl-9*H*-carbazole (**11**)

The product **11** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (41.2 mg, 39% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.21 (br s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.10 (m, 3H), 3.90 (s, 3H), 2.37 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.0, 140.1, 139.6, 128.6, 125.1, 121.9, 120.6, 119.0, 118.7, 115.4, 110.7, 106.8, 59.4, 14.9 ppm.

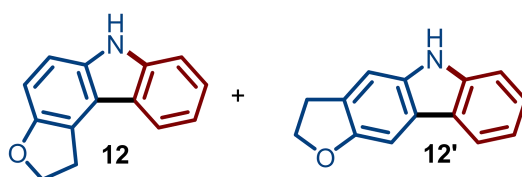
HRMS (ESI) (*m/z*): calcd. for C₁₄H₁₄NO [M+H]⁺ : 212.1070, found: 212.1075.

2-Methoxy-3-methyl-9H-carbazole (11')

The product **11'** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (29.6 mg, 28% yield). The obtained spectrum matched that reported in the literature.¹⁴

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.00 (br s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.81 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.96 (s, 1H), 3.87 (s, 3H), 2.28 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 156.7, 139.5, 139.4, 123.7, 122.6, 121.1, 119.0, 118.3, 117.3, 115.2, 110.5, 92.7, 55.3, 16.6. ppm.



1,6-Dihydro-2H-furo[2,3-c]carbazole (12)

The product **12** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (37.7 mg, 36% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.05 (br s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 4.65 (t, *J* = 8.8 Hz, 2H), 3.59 (t, *J* = 8.8 Hz, 2H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.2, 140.7, 135.0, 125.5, 121.7, 121.2, 119.4, 118.1, 117.8, 110.8, 109.2, 107.5, 70.8, 29.0 ppm.

HRMS (ESI) (*m/z*): calcd. for C₁₄H₁₂NO [*M*+*H*]⁺: 210.0913, found: 210.0917.

3,5-Dihydro-2H-furo[3,2-b]carbazole (12')

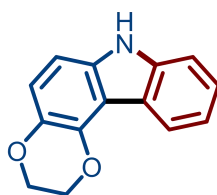
The product **12'** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (29.3 mg, 28% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.96 (br s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.33 (s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 4.54 (t, *J* = 8.4 Hz, 2H), 3.30 (t, *J* = 8.4 Hz, 2H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.5, 140.2, 135.0, 126.8, 124.7, 122.5, 121.6, 119.9, 117.7, 110.8, 107.3, 98.8, 70.8, 29.8 ppm.

HRMS (ESI) (*m/z*): calcd. for C₁₄H₁₂NO [*M*+*H*]⁺: 210.0913, found: 210.0917.

2,3-Dihydro-7H-[1,4]dioxino[2,3-c]carbazole (13)



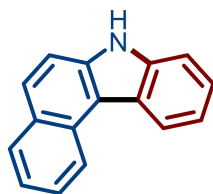
The product **13** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (68.7 mg, 61% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.73 (br s, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.12 (m, 2H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 4.50 – 4.37 (m, 2H), 4.35 – 4.24 (m, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 139.7, 139.1, 136.4, 135.5, 125.3, 123.0, 122.4, 119.3, 116.1, 112.9, 110.2, 103.0, 65.1, 64.4 ppm.

HRMS (ESI) (*m/z*): calcd. for C₁₄H₁₂NO₂ [M+H]⁺: 226.0863, found: 226.0871.

7H-benzo[*c*]carbazole (14)

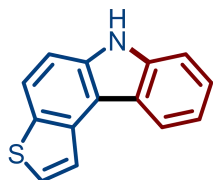


The product **14** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (68.4 mg, 63% yield). The obtained spectrum matched that reported in the literature.¹⁴

¹H NMR (400 MHz, CDCl₃) δ 8.80 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.36 (br s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.66 – 7.35 (m, 5H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 138.6, 137.2, 130.1, 129.3, 127.6, 127.0, 124.5, 124.1, 123.4, 123.2, 122.2, 120.4, 115.6, 112.7, 111.3 ppm.

6H-thieno[2,3-*c*]carbazole (15)



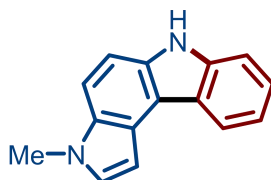
The product **15** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (61.4 mg, 55% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.55 (br s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 5.2 Hz, 1H), 8.10 – 7.84 (m, 1H), 7.69 – 7.51 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO- d_6) δ 138.8, 137.2, 133.1, 131.0, 128.2, 124.7, 121.8, 121.8, 121.1, 119.8, 118.9, 115.6, 111.2, 109.7 ppm.

HRMS (APCI) (m/z): calcd. for $\text{C}_{14}\text{H}_{10}\text{NS}$ $[\text{M}+\text{H}]^+$: 224.0528, found: 224.0527.

3-Methyl-3,6-dihydropyrrolo[2,3-c]carbazole (16)



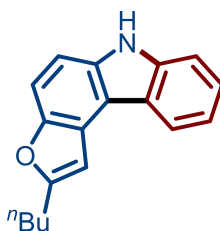
The product **16** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (58.4 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 7.8$ Hz, 1H), 7.92 (br s, 1H), 7.42 – 7.33 (m, 3H), 7.31 – 7.25 (m, 1H), 7.22 (d, $J = 8.6$ Hz, 1H), 7.17 (d, $J = 2.6$ Hz, 1H), 7.00 (d, $J = 2.6$ Hz, 1H), 3.83 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 134.4, 132.0, 128.7, 124.3, 123.9, 121.9, 121.4, 119.2, 114.6, 110.6, 108.5, 106.0, 99.2, 33.4 ppm.

HRMS (ESI) (m/z): calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_2$ $[\text{M}+\text{H}]^+$: 221.1073, found: 221.1078.

2-Butyl-6H-furo[2,3-c]carbazole (17)



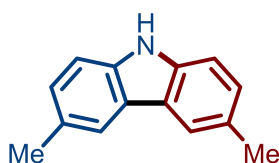
The product **17** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (79.0 mg, 60% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 7.8$ Hz, 1H), 8.09 (br s, 1H), 7.51 (d, $J = 8.6$ Hz, 1H), 7.48 – 7.36 (m, 2H), 7.33 – 7.20 (m, 2H), 6.93 (s, 1H), 2.89 (t, $J = 7.4$ Hz, 2H), 1.97 – 1.72 (m, 2H), 1.58 – 1.40 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.5, 150.0, 139.6, 135.8, 125.1, 123.5, 122.2, 121.3, 119.4, 114.8, 110.8, 109.3, 106.0, 101.0, 30.2, 28.6, 22.5, 14.0.

HRMS (ESI) (m/z): calcd. for $\text{C}_{18}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 264.1383, found: 264.1389.

3,6-Dimethyl-9H-carbazole (18)

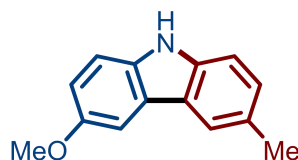


The product **18** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (66.4 mg, 68% yield). The obtained spectrum matched that reported in the literature.¹⁵

¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 2.52 (s, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 138.2, 128.6, 127.1, 123.6, 120.3, 110.4, 21.6 ppm.

3-Methoxy-6-methyl-9H-carbazole (**19**)

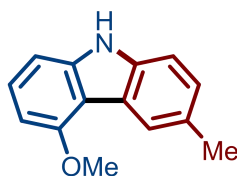


The product **19** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (73.9 mg, 70% yield). The obtained spectrum matched that reported in the literature.¹⁶

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.85 (br s, 1H), 7.87 (s, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.83 (s, 3H), 2.45 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆) δ 152.8, 138.7, 134.8, 126.7, 126.5, 122.6, 122.5, 119.9, 114.5, 111.5, 110.7, 102.9, 55.6, 21.1 ppm.

5-Methoxy-3-methyl-9H-carbazole (**20**)

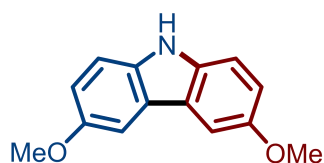


The product **20** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (59.1 mg, 56% yield). The obtained spectrum matched that reported in the literature.¹⁷

¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.94 (br s, 1H), 7.37 – 7.25 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.09 (s, 3H), 2.54 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 156.4, 141.4, 137.0, 129.0, 126.6, 126.3, 123.1, 123.0, 112.6, 109.7, 103.7, 100.3, 55.6, 21.6 ppm.

3,6-Dimethoxy-9H-carbazole (21)

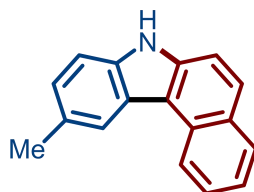


The product **21** was purified with silica gel chromatography (PE/DCM/EA = 20:4:1) as a white solid (68.2 mg, 60% yield). The obtained spectrum matched that reported in the literature.¹⁶

¹H NMR (400 MHz, CDCl₃) δ 7.75 (br s, 1H), 7.49 (d, *J* = 2.0 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.03 (dd, *J* = 8.6, 2.4 Hz, 2H), 3.91 (s, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 153.8, 135.4, 123.8, 115.4, 111.7, 103.1, 56.2 ppm.

10-Methyl-7H-benzo[*c*]carbazole (22)

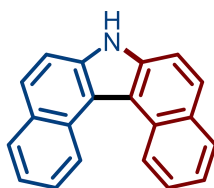


The product **22** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (64.7mg, 56% yield). The obtained spectrum matched that reported in the literature.¹⁴

¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, *J* = 8.4 Hz, 1H), 8.37 (s, 1H), 8.29 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.54 – 7.39 (m, 2H), 7.34 – 7.23 (m, 1H), 2.65 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 137.5, 136.9, 130.2, 129.7, 129.3, 129.3, 127.3, 126.9, 125.9, 124.4, 123.4, 130.0, 122.1, 115.4, 112.8, 110.9, 22.0 ppm.

7H-dibenzo[*c,g*]carbazole (23)

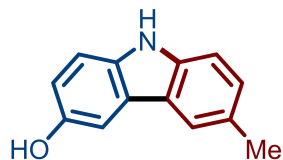


The product **23** was purified with silica gel chromatography (PE/DCM/EA = 20:2:1) as a white solid (73.5 mg, 55% yield) The obtained spectrum matched that reported in the literature.¹⁸

¹H NMR (400 MHz, CDCl₃) δ 9.28 (d, *J* = 8.4 Hz, 2H), 8.38 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 136.2, 130.1, 129.3, 129.3, 126.9, 125.6, 125.3, 123.4, 117.7, 112.7 ppm.

6-Methyl-9H-carbazol-3-ol (**25**)

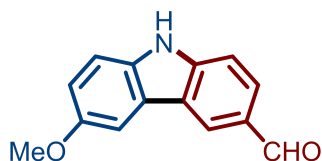


The product **25** was purified with silica gel chromatography (PE/ Acetone = 3:1) as a white solid (83.8 mg, 85% yield). The obtained spectrum matched that reported in the literature.¹⁹

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.72 (br s, 1H), 8.89 (br s, 1H), 7.76 (s, 1H), 7.37 (s, 1H), 7.32 – 7.21 (m, 2H), 7.13 (d, J = 8.2 Hz, 1H), 6.92 – 6.82 (m, 1H), 2.43 (s, 3H) ppm.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 150.2, 138.7, 134.1, 126.5, 126.2, 122.9, 122.4, 119.8, 114.8, 111.2, 110.5, 104.7, 21.0 ppm.

6-Methoxy-9H-carbazole-3-carbaldehyde (**26**)



The product **26** was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (78.8 mg, 70% yield).

^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 8.59 – 8.53 (m, 1H), 8.46 (br s, 1H), 7.95 (dd, J = 8.6, 1.6 Hz, 1H), 7.59 (d, J = 2.4 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.12 (dd, J = 8.8, 2.4 Hz, 1H), 3.94 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 154.9, 144.1, 134.8, 128.9, 127.3, 124.3, 123.9, 123.7, 116.4, 112.1, 111.2, 103.4, 56.1 ppm.

HRMS (ESI) (m/z): calcd. for $\text{C}_{14}\text{H}_{12}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 226.0863, found: 226.0867.

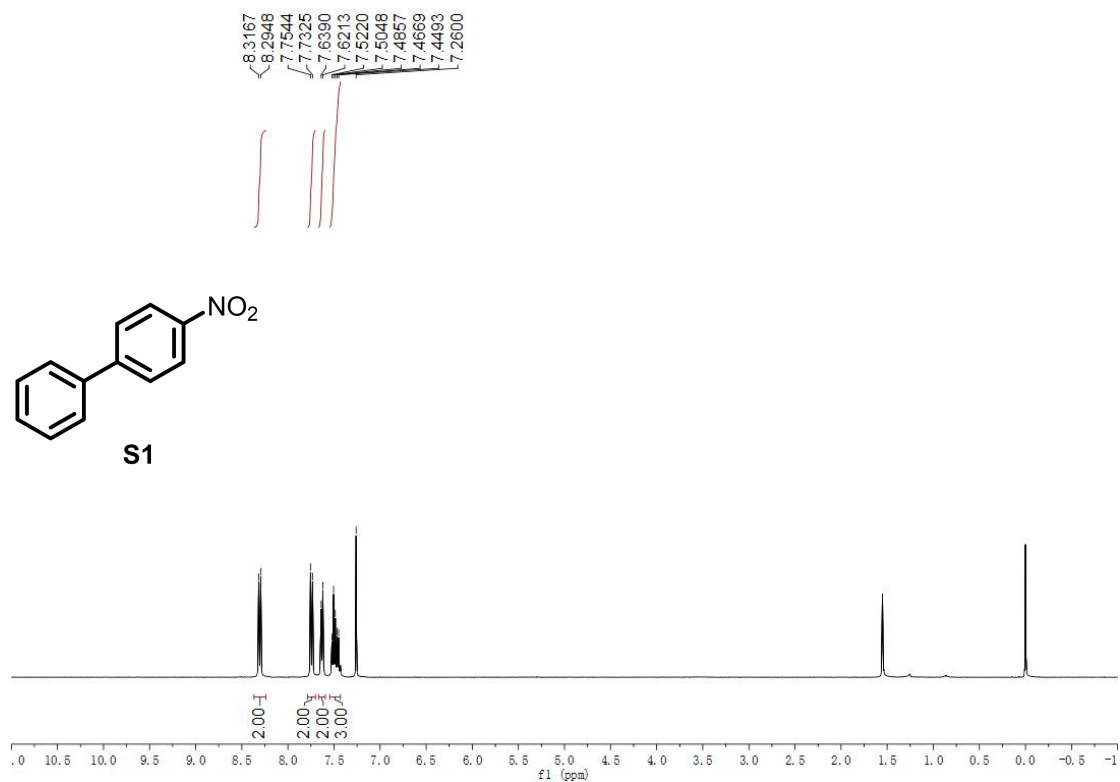
9. References

- 1 H. Gao, Q.-L. Xu, M. Yousufuddin, D. H. Ess and L. Kürti, 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 J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, Highly Active Palladium Catalysts for Suzuki Coupling Reactions, *J. Am. Chem. Soc.*, 1999, **121**, 9550-9561.
- 3 S. Karanjit, M. Kashihara, A. Nakayama, L. K. Shrestha, K. Ariga and K. Namba, Highly active and reusable hydrotalcite-supported Pd(0) catalyst for Suzuki coupling reactions of aryl bromides and chlorides, *Tetrahedron*, 2018, **74**, 948–954.
- 4 E. D. Entz, J. E. A. Russell, L. V. Hooker and S. R. Neufeldt, Small Phosphine Ligands Enable Selective Oxidative Addition of Ar–O over Ar–Cl Bonds at Nickel(0), *J. Am. Chem. Soc.*, 2020, **142**, 15454-15463.
- 5 H. S. Lin and L. A. Paquette, A Convenient Method for Determining the Concentration of Grignard Reagents, *Synthetic Communications*, 1994, **24**, 2503-2506.
- 6 F. Yu, P. Li, B. Wang and K. Han, Reversible Near-Infrared Fluorescent Probe Introducing Tellurium to Mimetic Glutathione Peroxidase for Monitoring the Redox Cycles between Peroxynitrite and Glutathione in Vivo, *J. Am. Chem. Soc.*, 2013, **135**, 7674-7680.
- 7 T. Hatakeyama, Y. Yoshimoto, S. K. Ghorai and M. Nakamura, Transition-Metal-Free Electrophilic Amination between Aryl Grignard Reagents and N-Chloroamines, *Org. Lett.*, 2010, **12**, 1516–1519.
- 8 X.-J. Wang, X. Sun, L. Zhang, Y. Xu, D. Krishnamurthy and C. H. Senanayake, Noncryogenic I/Br–Mg Exchange of Aromatic Halides Bearing Sensitive Functional Groups Using *i*-PrMgCl–Bis[2-(*N,N*-dimethylamino)ethyl] Ether Complexes, *Org. Lett.*, 2006, **8**, 305–307.
- 9 R. Hesse, K. K. Gruner, O. Kataeva, A. W. Schmidt and H.-J. Knölker, Efficient Construction of Pyrano[3,2-*a*]carbazoles: Application to a Biomimetic Total Synthesis of Cyclized Monoterpenoid Pyrano[3,2-*a*]carbazole Alkaloids, *Chem. Eur. J.*, 2013, **19**, 14098–14111.
- 10 L. Yang, Y. Zhang, X. Zou, H. Lu and G. Li, Visible-light-promoted intramolecular C–H amination in aqueous solution: synthesis of carbazoles, *Green Chem.* 2018, **20**, 1362–1366.
- 11 B. J. Stokes, B. Jovanović, H. Dong, K. J. Richert, R. D. Riell and T. G. Driver, Rh₂(II)-Catalyzed Synthesis of Carbazoles from Biaryl Azides, *J. Org. Chem.*, 2009, **74**, 3225–3228.
- 12 H. F. Grantham and M. C. Kimber, Dimeric Cyclobutane Formation Under

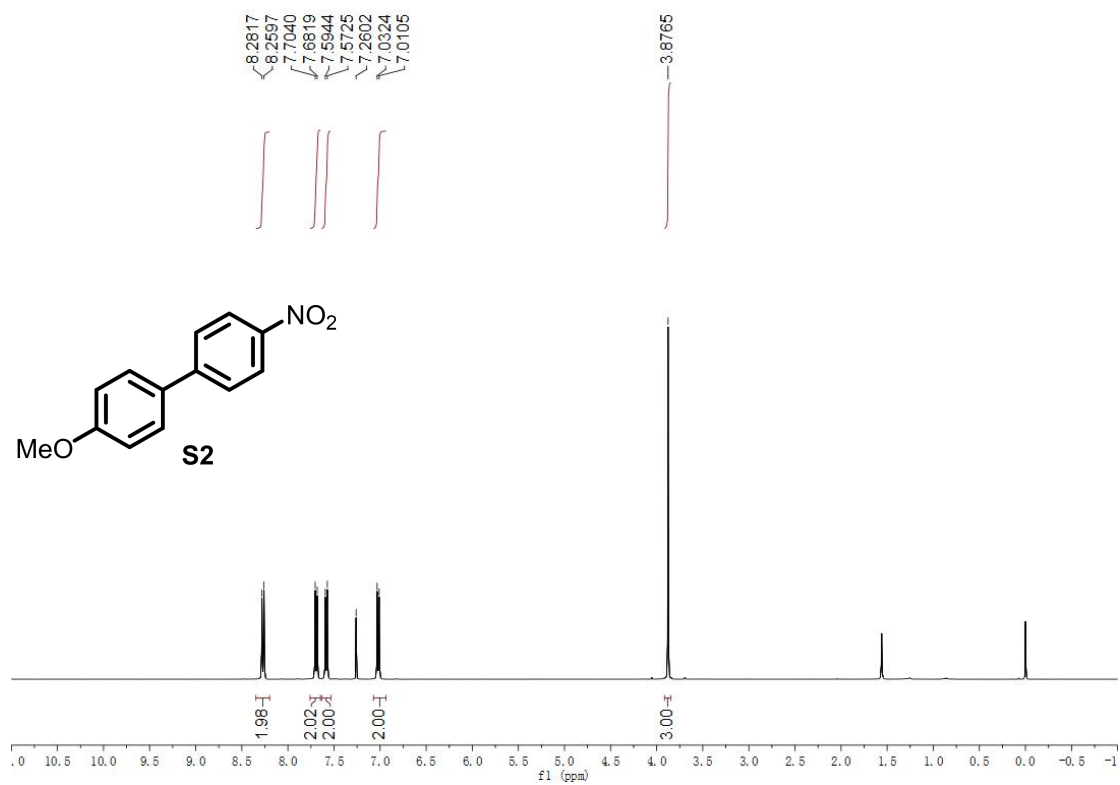
- Continuous Flow Conditions Using Organophotoredox-Catalysed [2+2] Cycloaddition, *ChemPhotoChem*, 2022, **6**, e202100273.
- 13 S. Chakrabarty, I. Chatterjee, L. Tebben, A. Studer, Reactions of Arynes with Nitrosoarenes—An Approach to Substituted Carbazoles, *Angew. Chem. Int. Ed.*, 2013, **52**, 2968–2971.
 - 14 D.-Y. Goo and S. K. Woo, One-pot synthesis of carbazoles via tandem C–C cross-coupling and reductive amination, *Org. Biomol. Chem.*, 2016, **14**, 122–130.
 - 15 M.-L. Louillat, A. Biafora, F. Legros and F. W. Patureau, Ruthenium-Catalyzed Cross-Dehydrogenative ortho-N-Carbazolation of Diarylamines: Versatile Access to Unsymmetrical Diamines, *Angew. Chem. Int. Ed.*, 2014, **53**, 3505–3509.
 - 16 G. Chakraborti, S. Paladhi, T. Mandal and J. Dash, “On Water” Promoted Ullmann-Type C–N Bond-Forming Reactions: Application to Carbazole Alkaloids by Selective N-Arylation of Aminophenols, *J. Org. Chem.*, 2018, **83**, 7347–7359.
 - 17 T. Akiyama, Y. Wada, M. Yamada, Y. Shio, T. Honma, S. Shimoda, K. Tsuruta, Y. Tamenori, H. Haneoka, T. Suzuki, K. Harada, H. Tsurugi, K. Mashima, J.-Y. Hasegawa, Y. Sato and M. Arisawa, Self-Assembled Multilayer Iron(0) Nanoparticle Catalyst for Ligand-Free Carbon–Carbon/Carbon–Nitrogen Bond-Forming Reactions, *Org. Lett.*, 2020, **22**, 7244–7249.
 - 18 C. K. Rank, A. W. Jones, T. Wall, P. D. Martino-Fumo, S. Schröck, M. Gerhards and F. W. Patureau, An intermolecular C–H oxidizing strategy to access highly fused carbazole skeletons from simple naphthylamines, *Chem. Commun.*, 2019, **55**, 13749–13752.
 - 19 G. Karan, S. Sahu and M. S. Maji, A one-pot “back-to-front” approach for the synthesis of benzene ring substituted indoles using allylboronic acids, *Chem. Commun.*, 2021, **57**, 5274–5277.

10. Copies of ^1H and ^{13}C NMR spectra of compounds

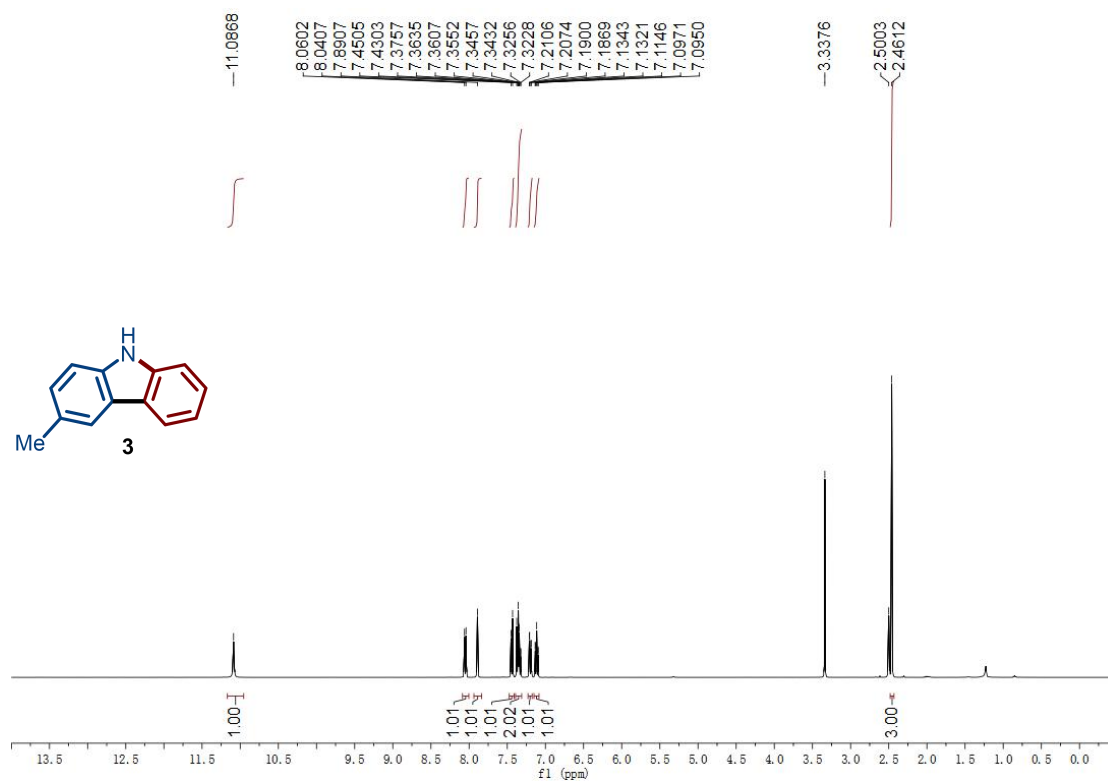
^1H NMR (400 MHz, CDCl_3) of 4-Nitro-1,1'-biphenyl (S1)



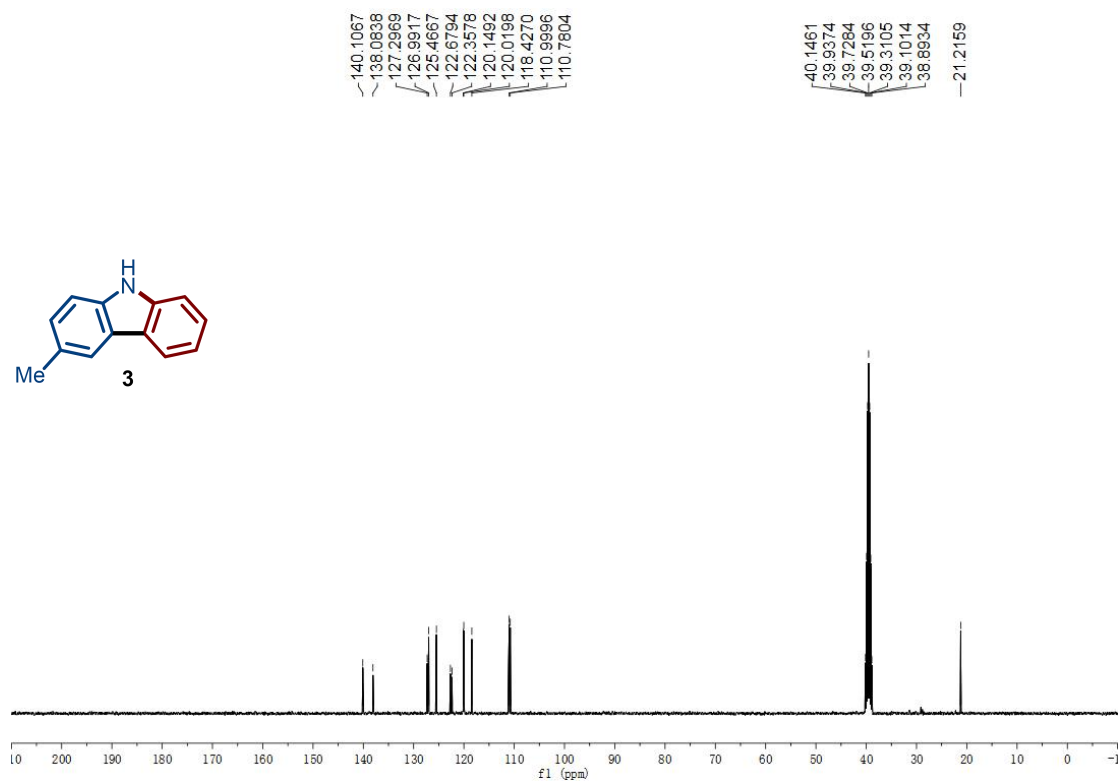
^1H NMR (400 MHz, CDCl_3) of 4-Methoxy-4'-nitro-1,1'-biphenyl (S2)



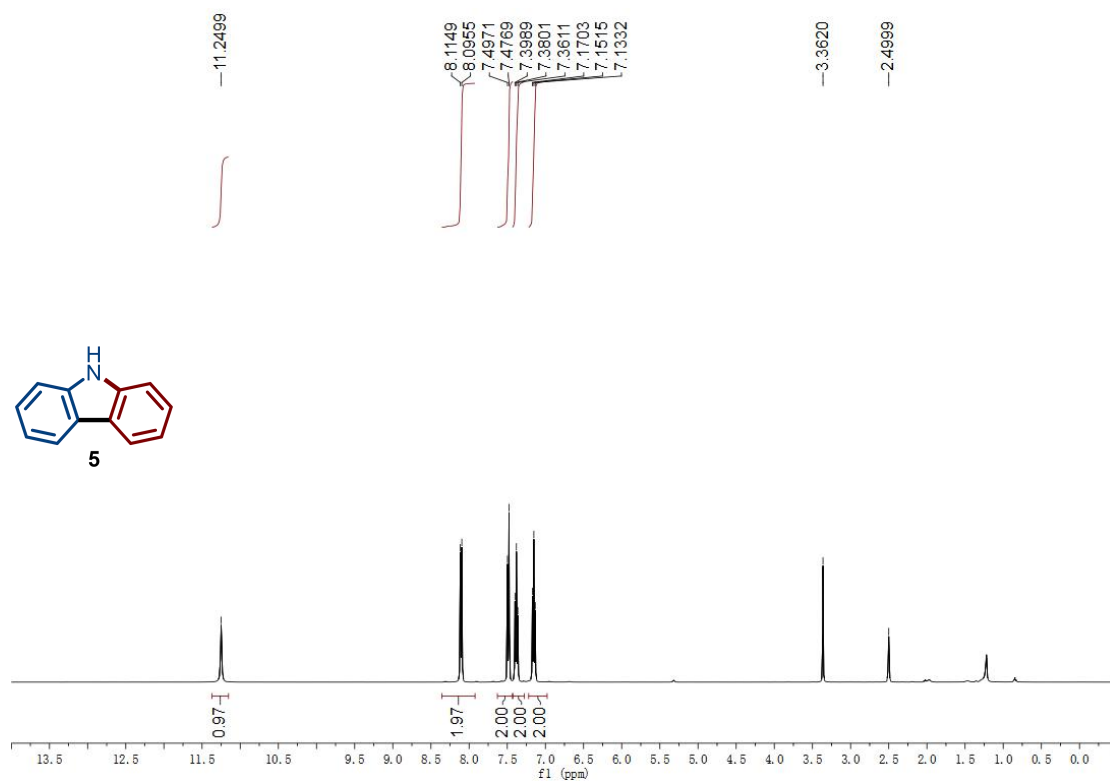
¹H NMR (400 MHz, DMSO-*d*₆) of 3-Methyl-9*H*-carbazole (3)



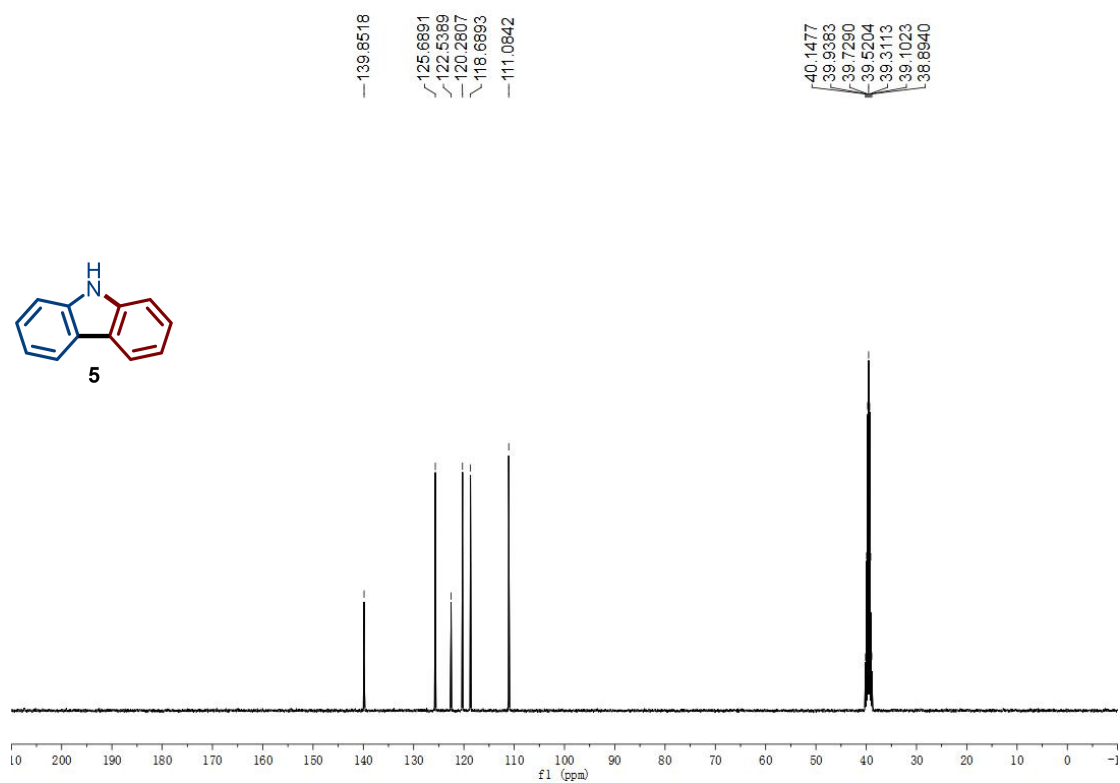
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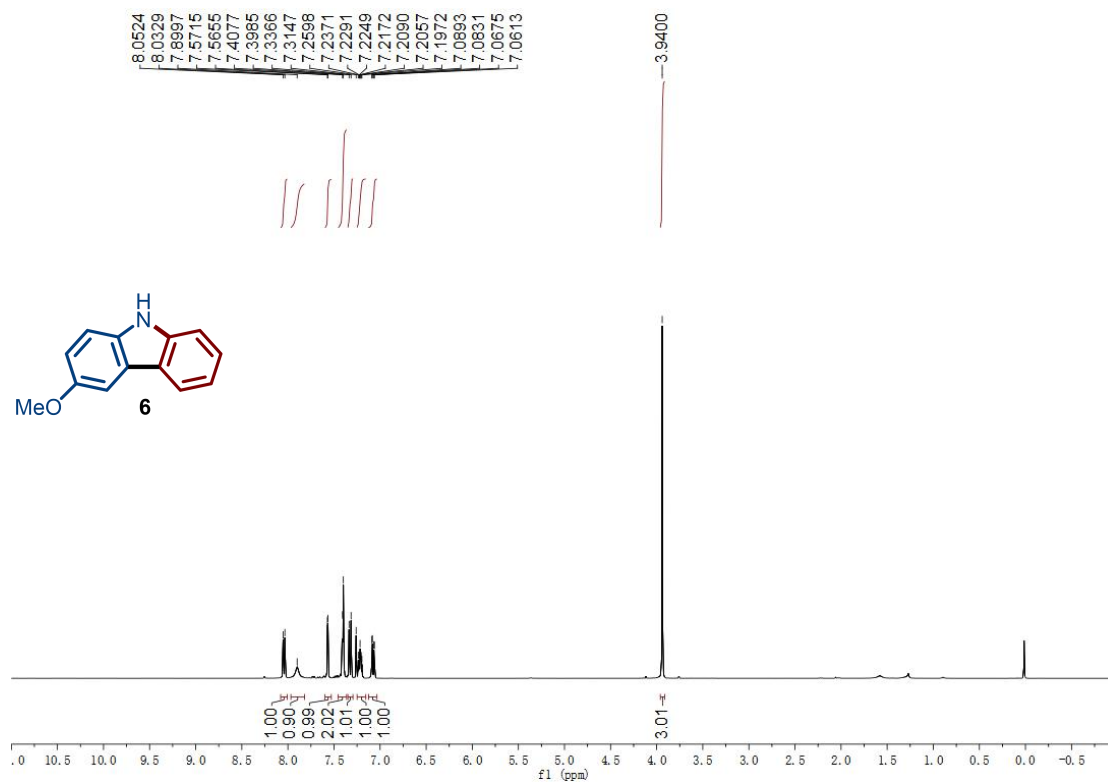
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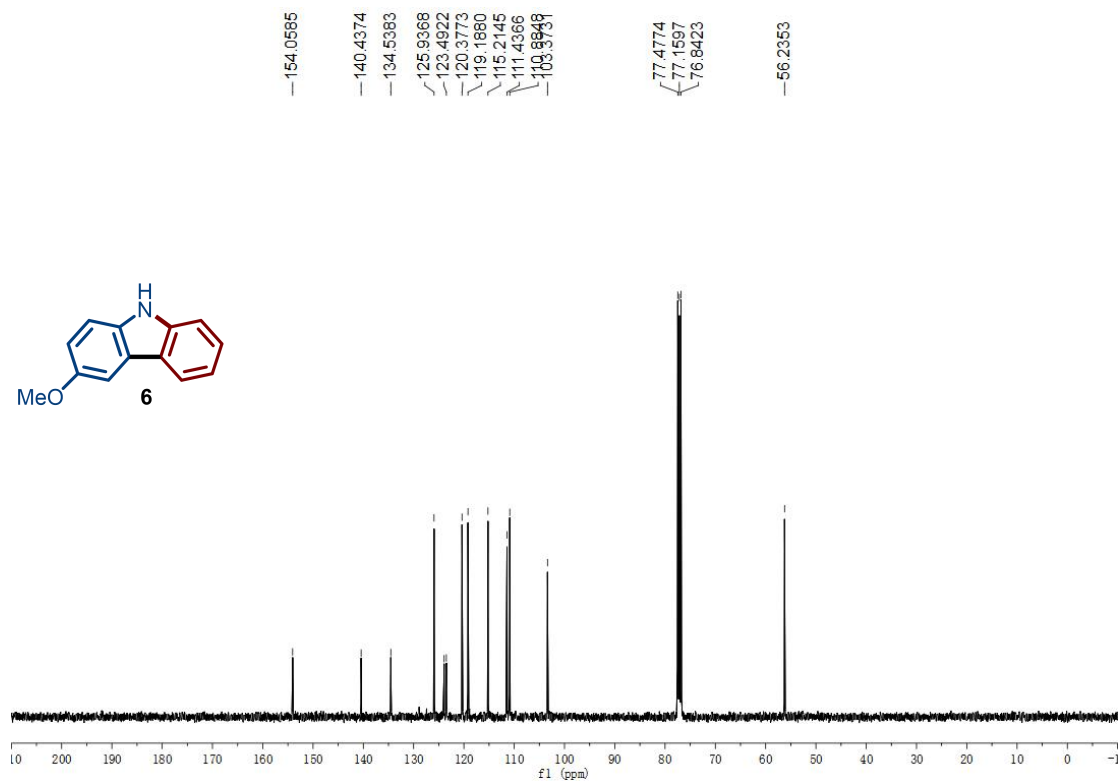
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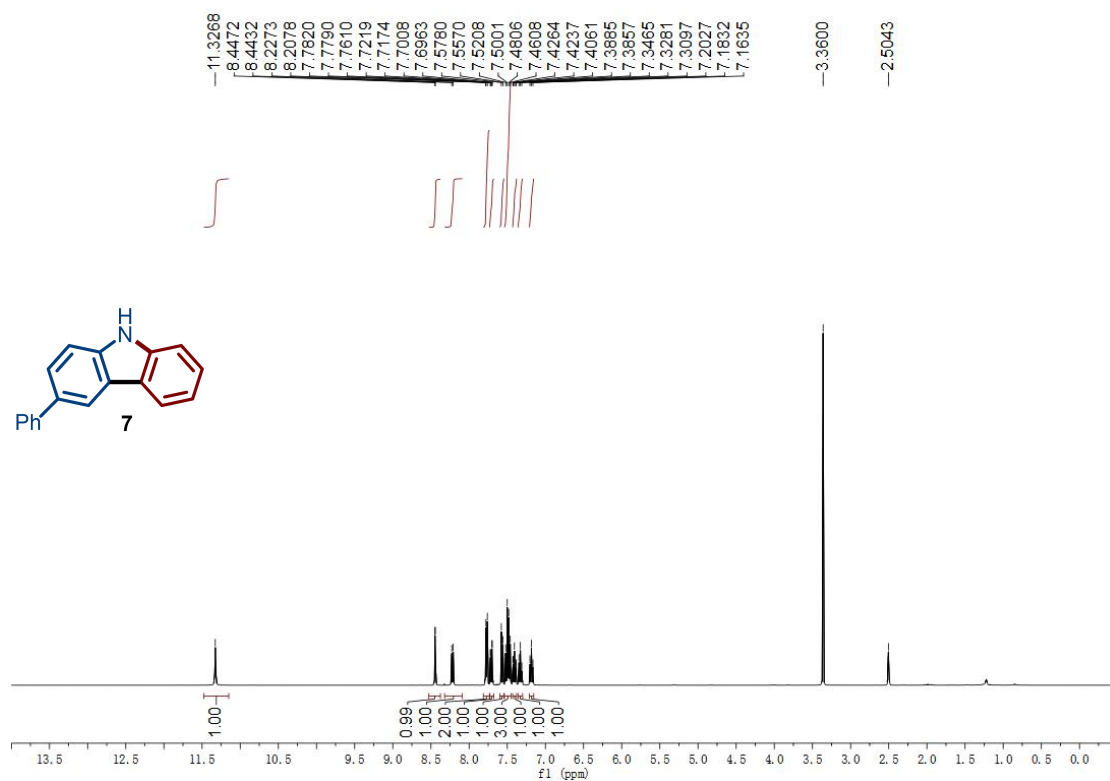
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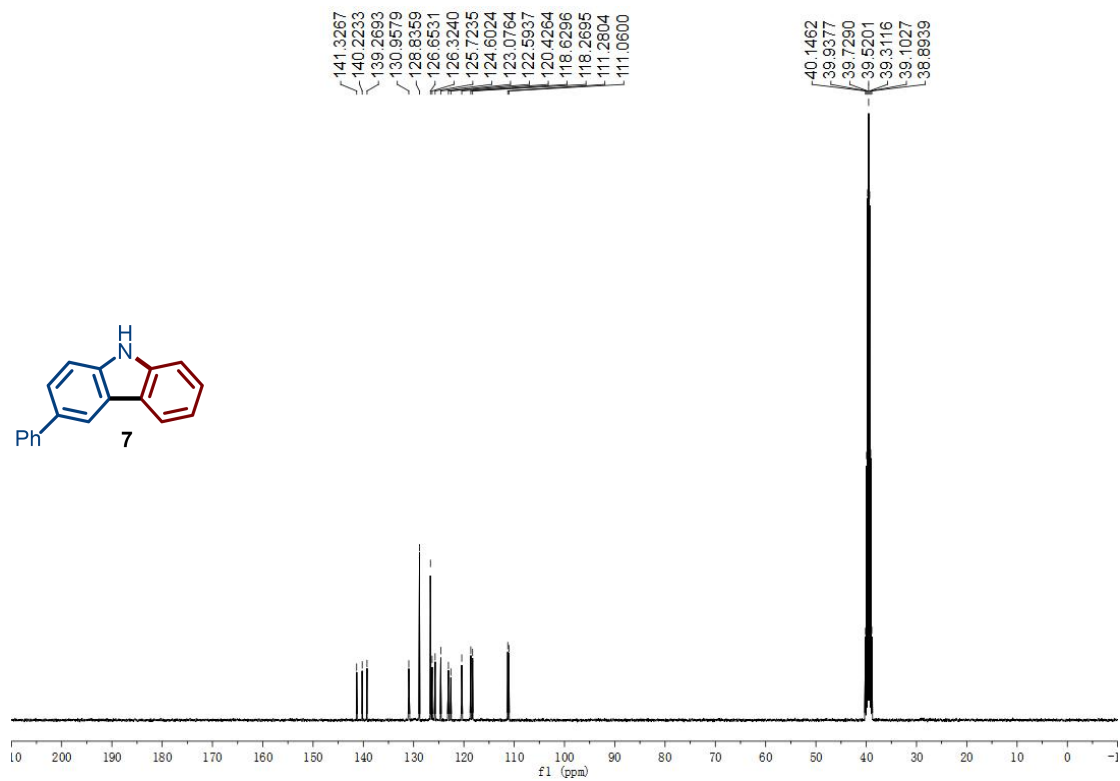
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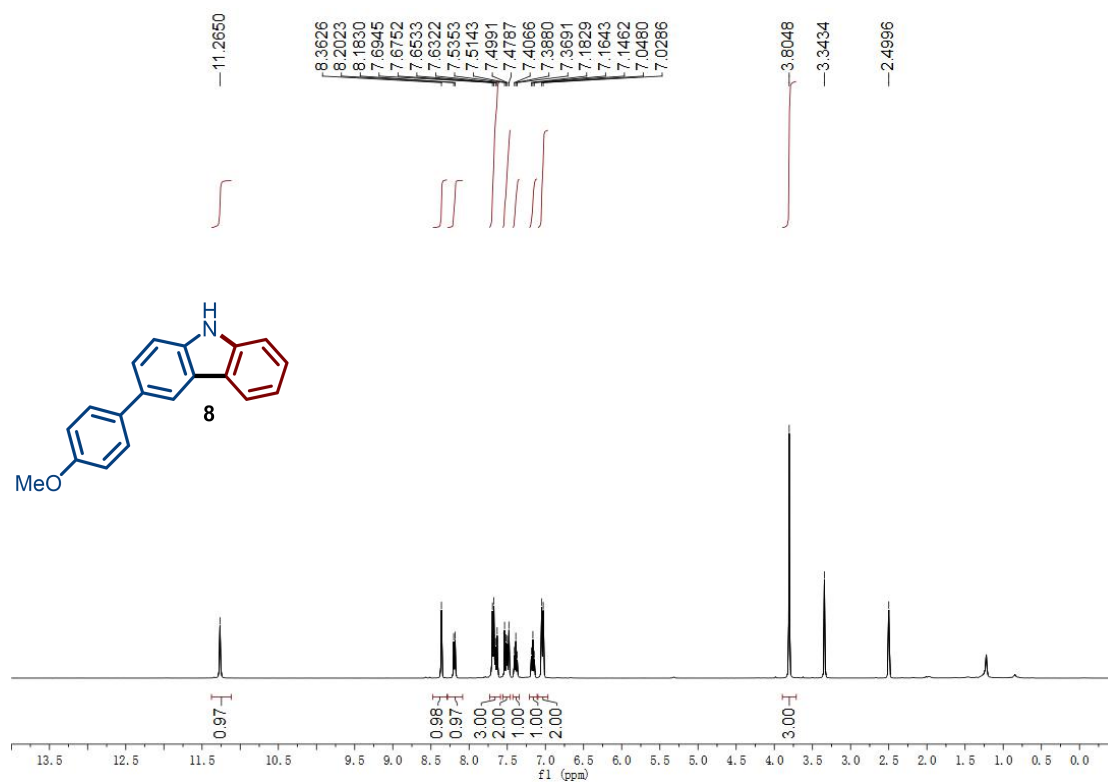
¹H NMR (400 MHz, DMSO-*d*₆) of 3-Phenyl-9*H*-carbazole (7)



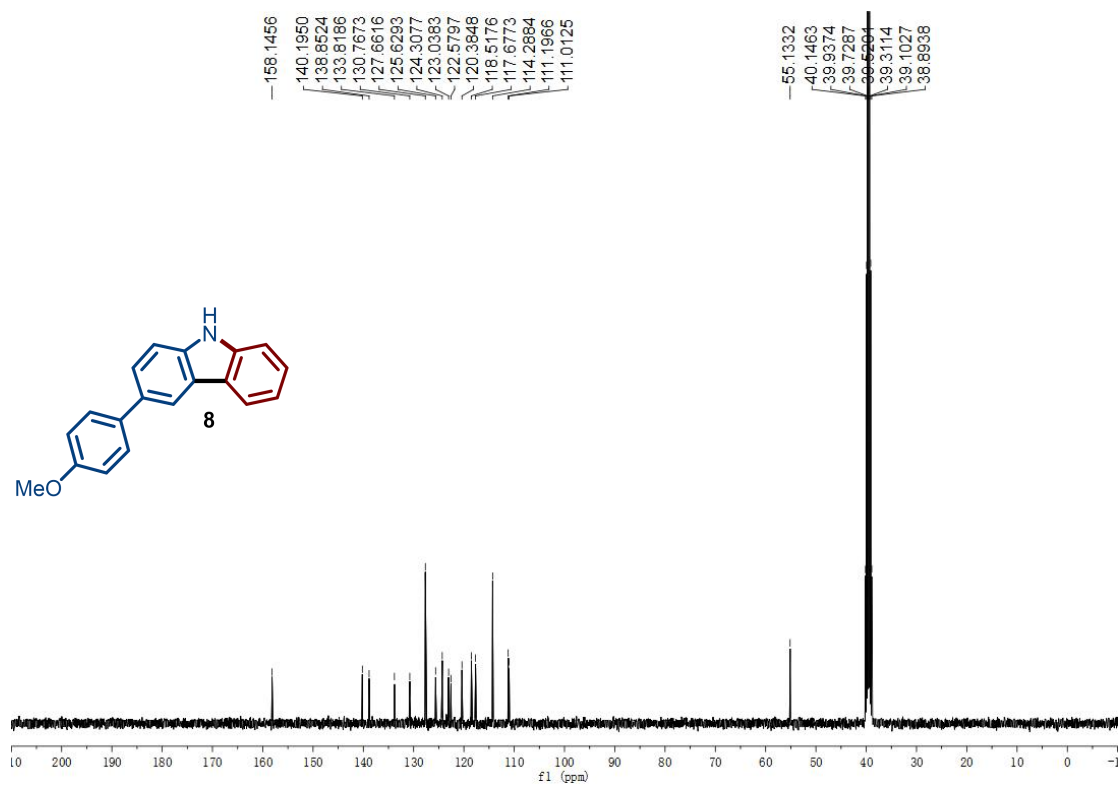
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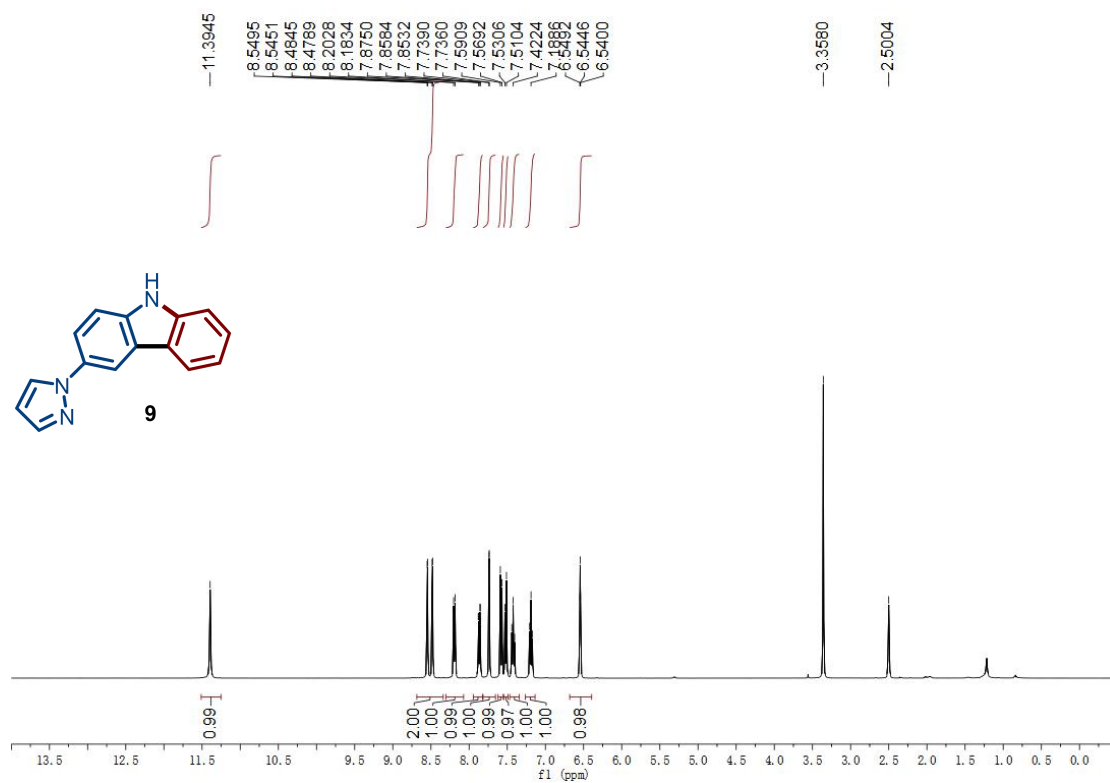
¹H NMR (400 MHz, DMSO-*d*₆) of 3-(4-Methoxyphenyl)-9*H*-carbazole (8)



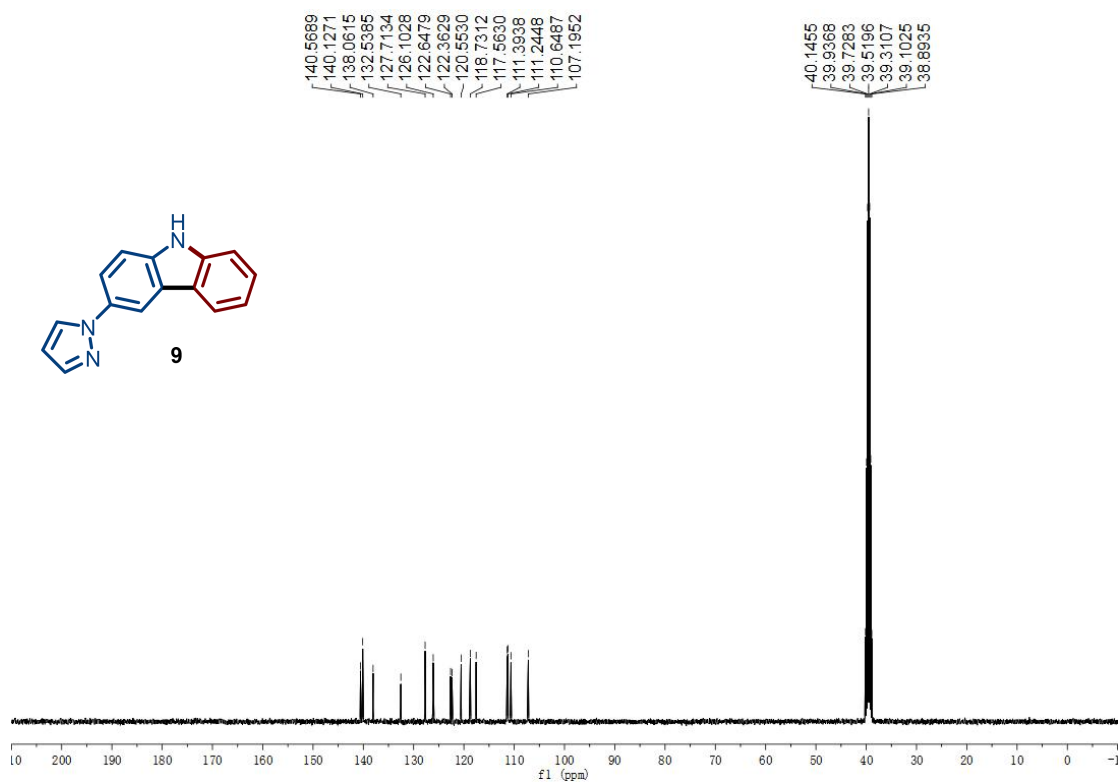
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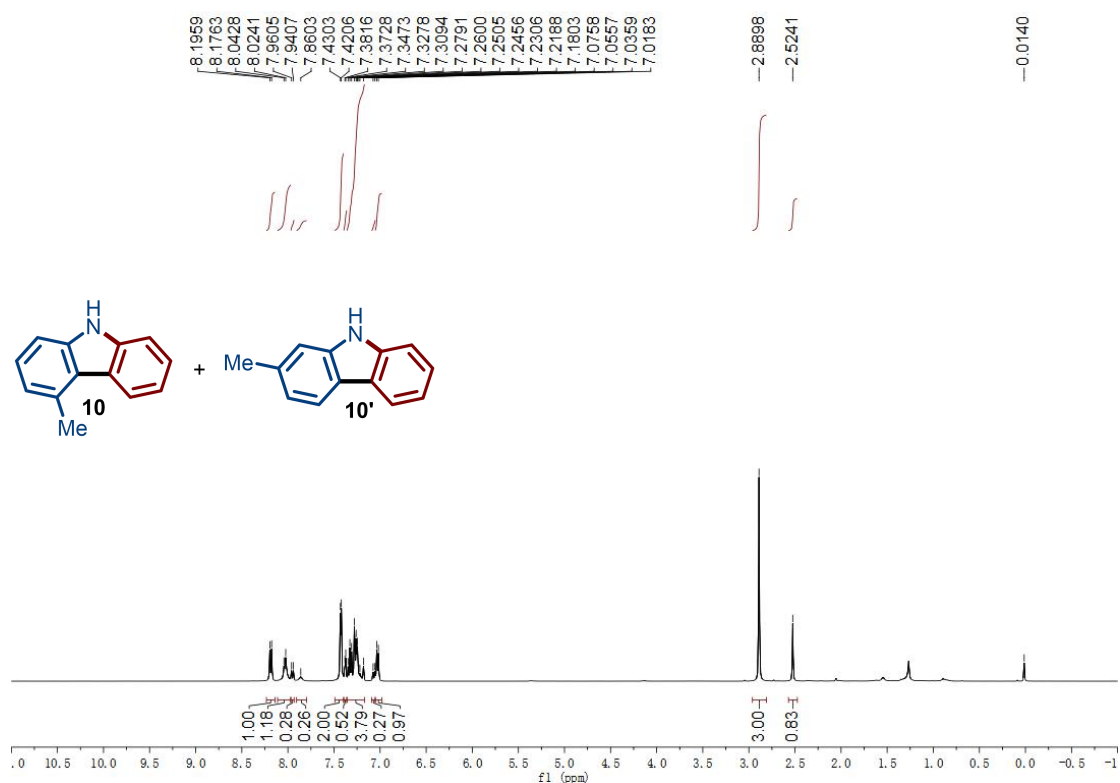
¹H NMR (400 MHz, DMSO-*d*₆) of 3-(1*H*-pyrazol-1-yl)-9*H*-carbazole (9)



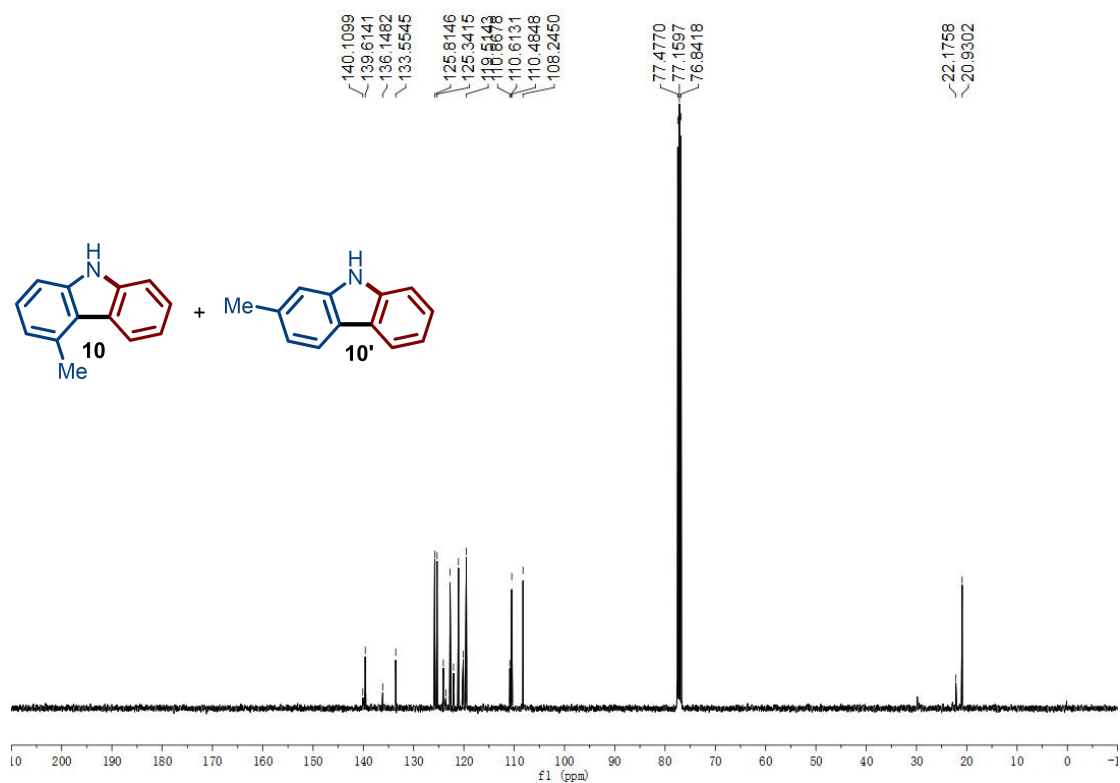
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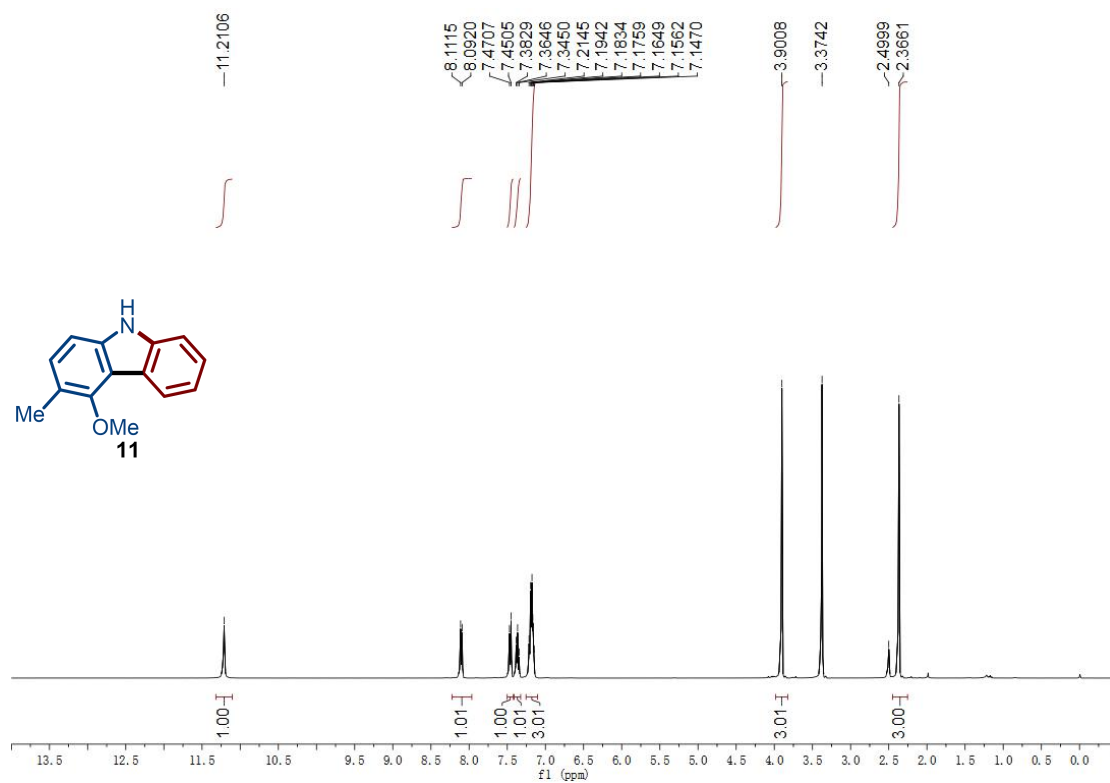
¹H NMR (400 MHz, CDCl₃) of 4-methyl-9H-carbazole (10) and 2-methyl-9H-carbazole (10')



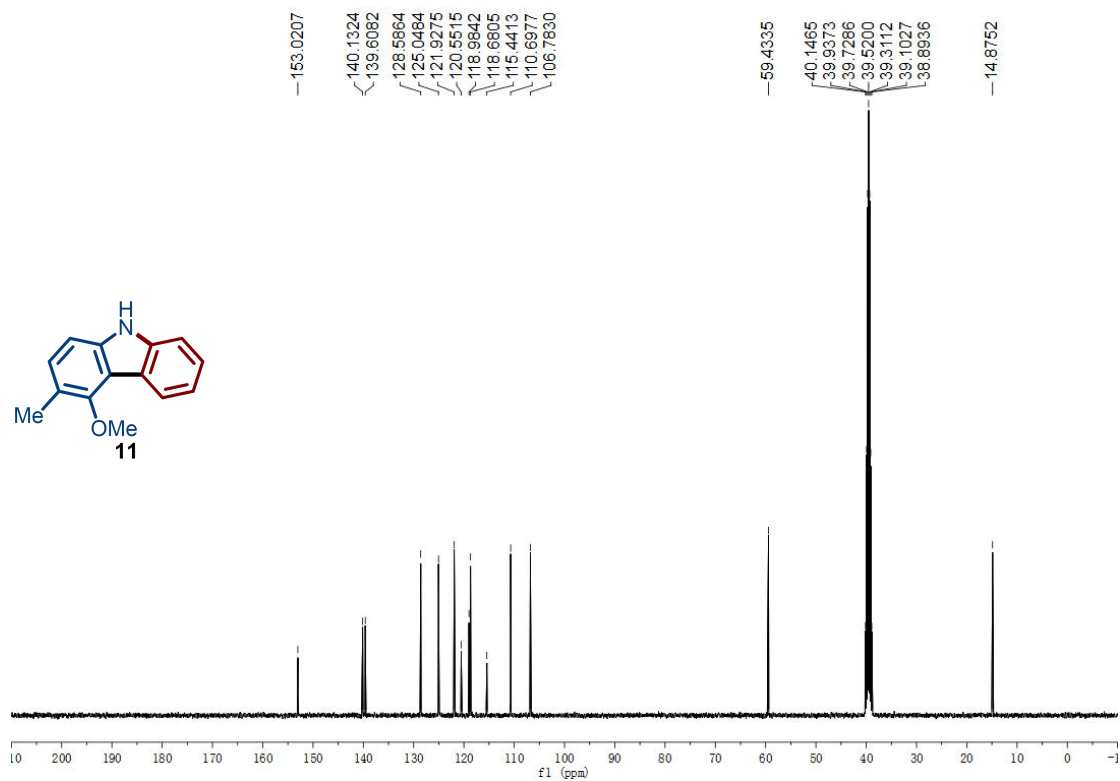
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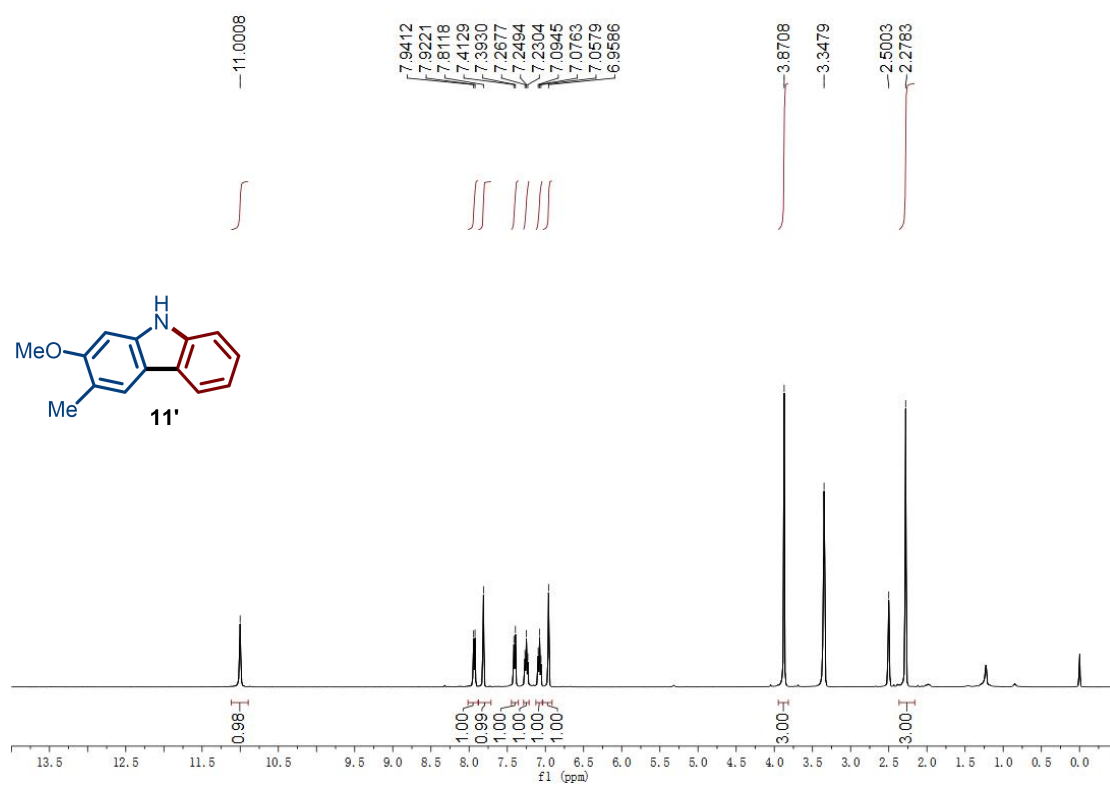
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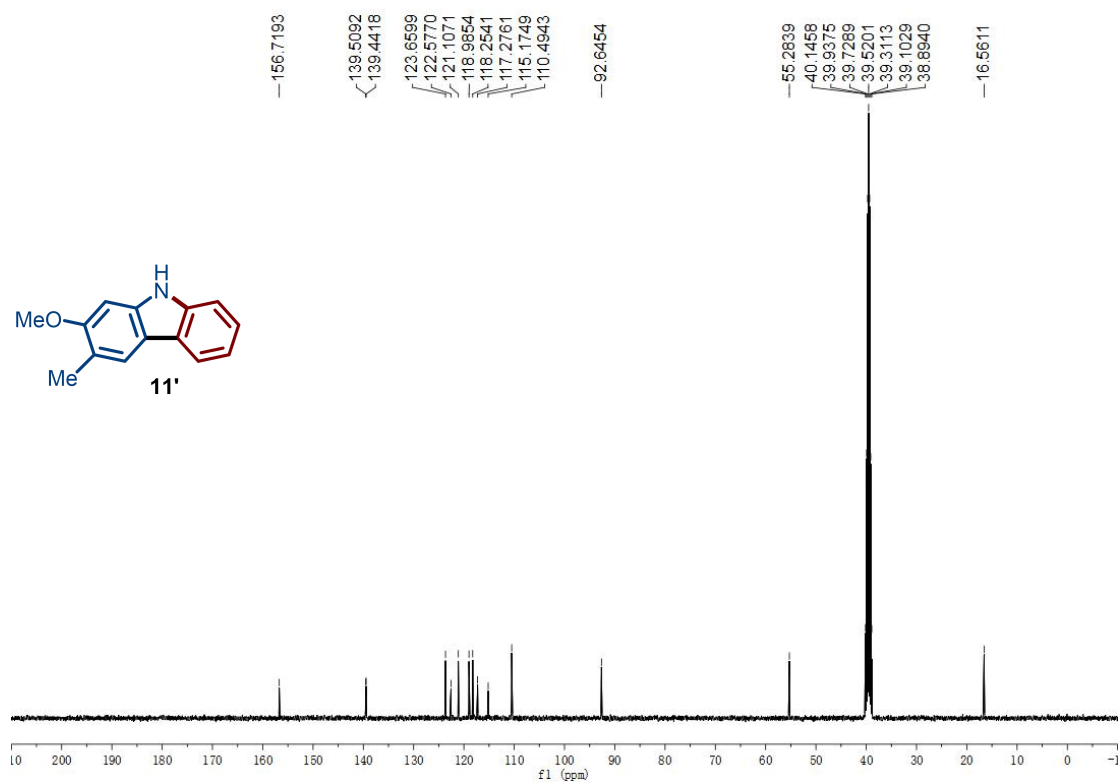
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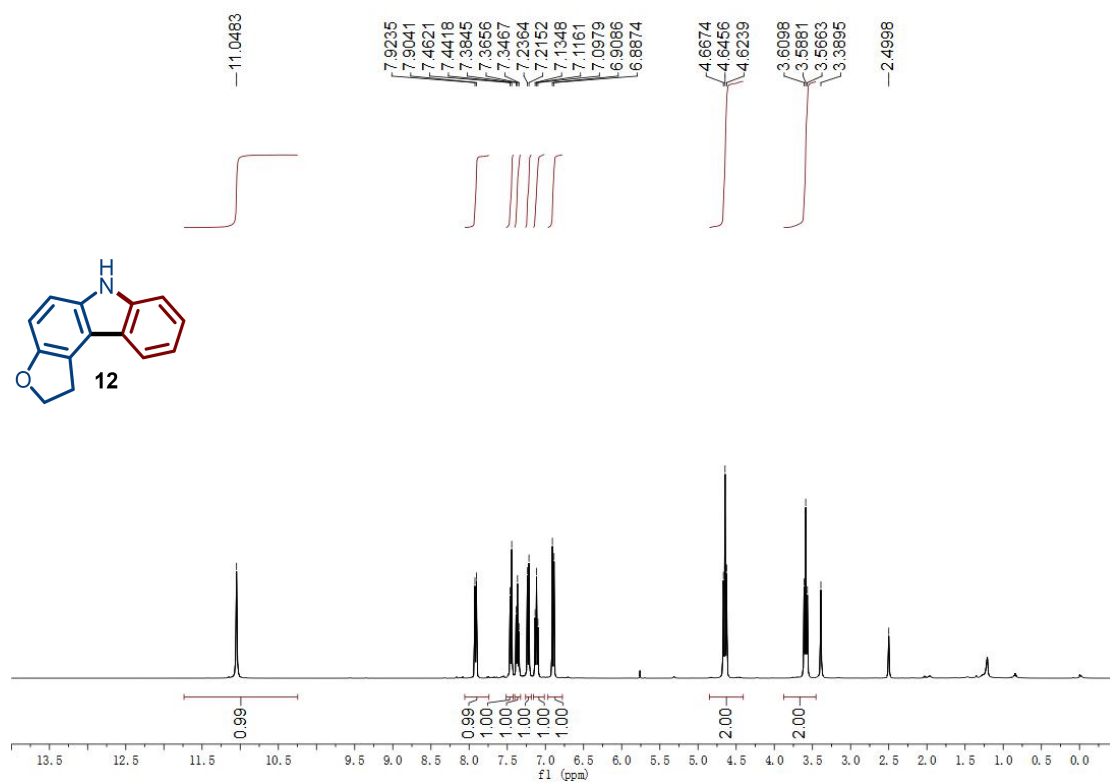
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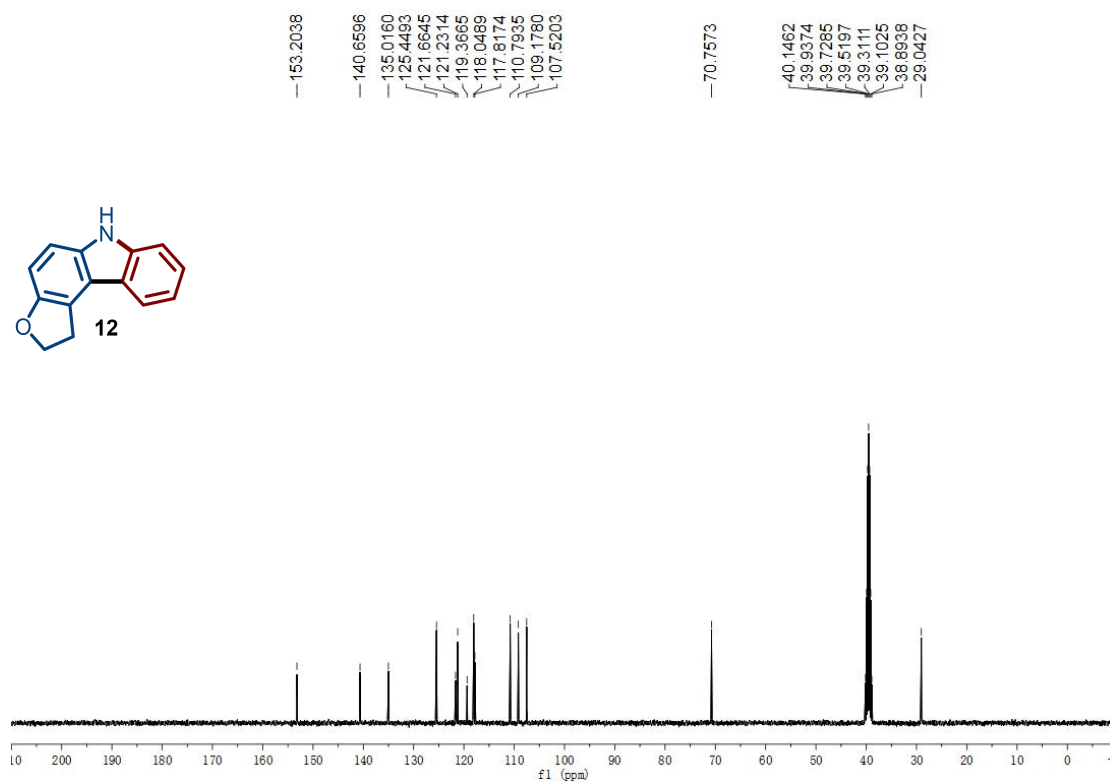
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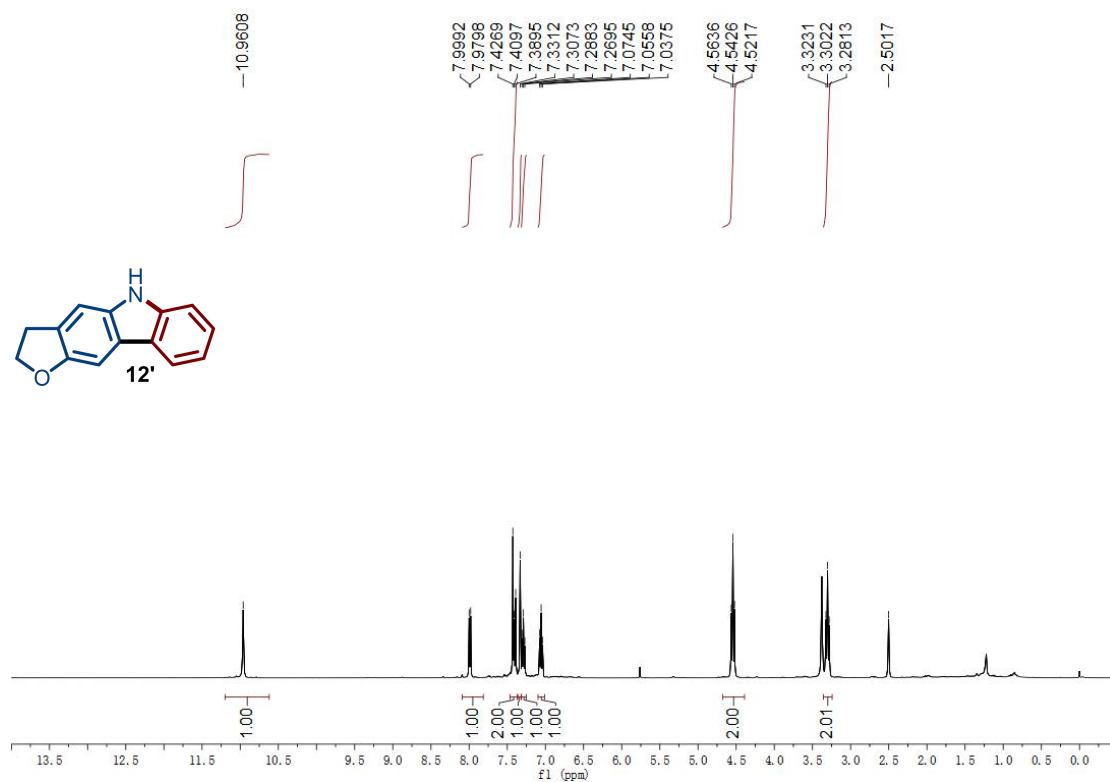
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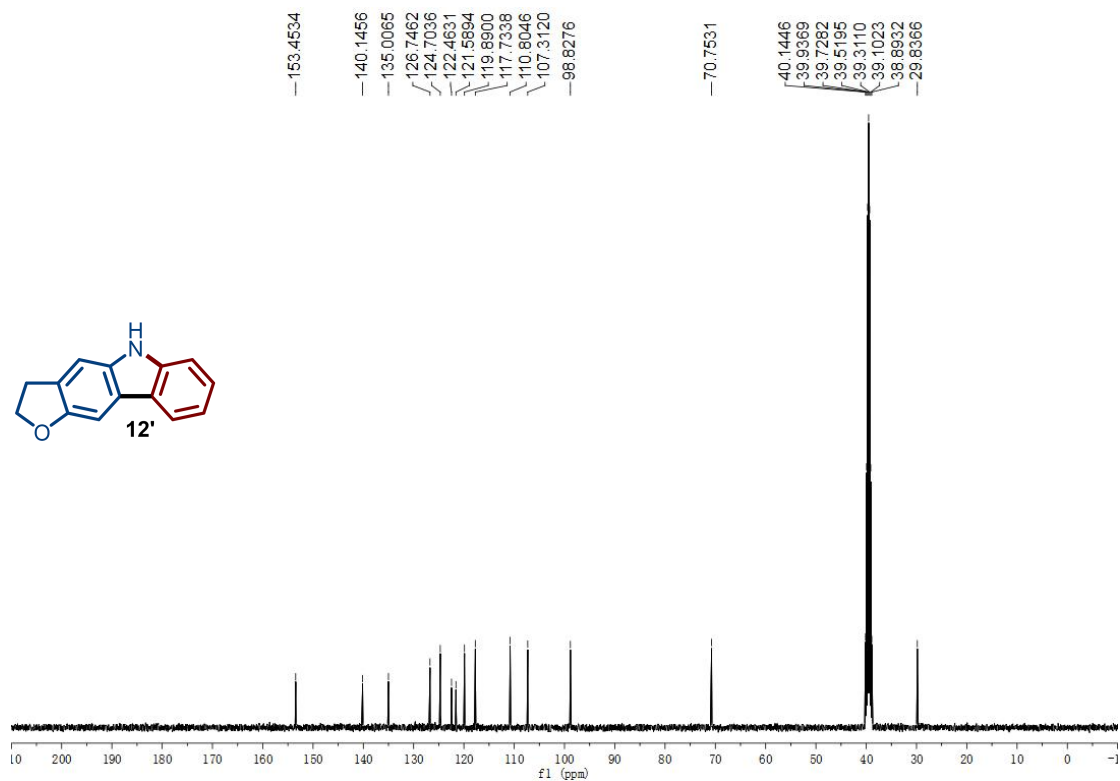
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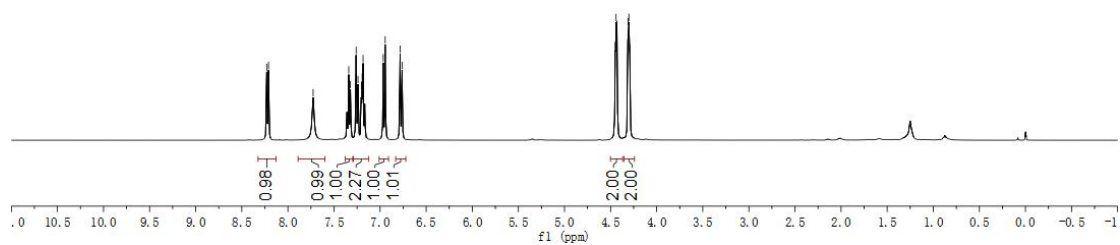
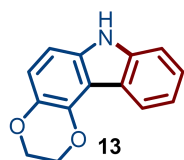
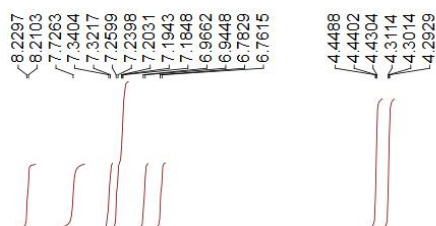
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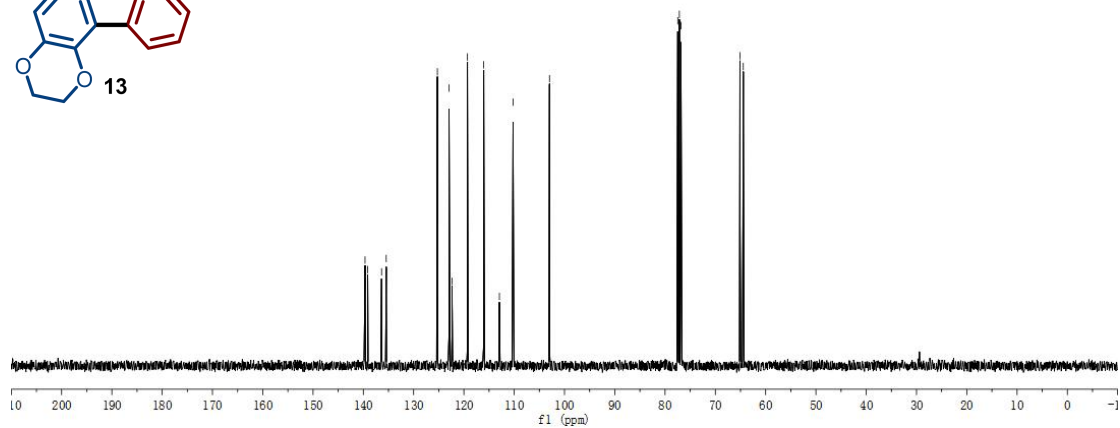
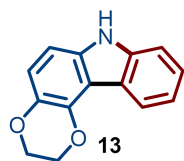
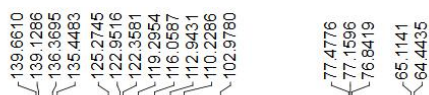
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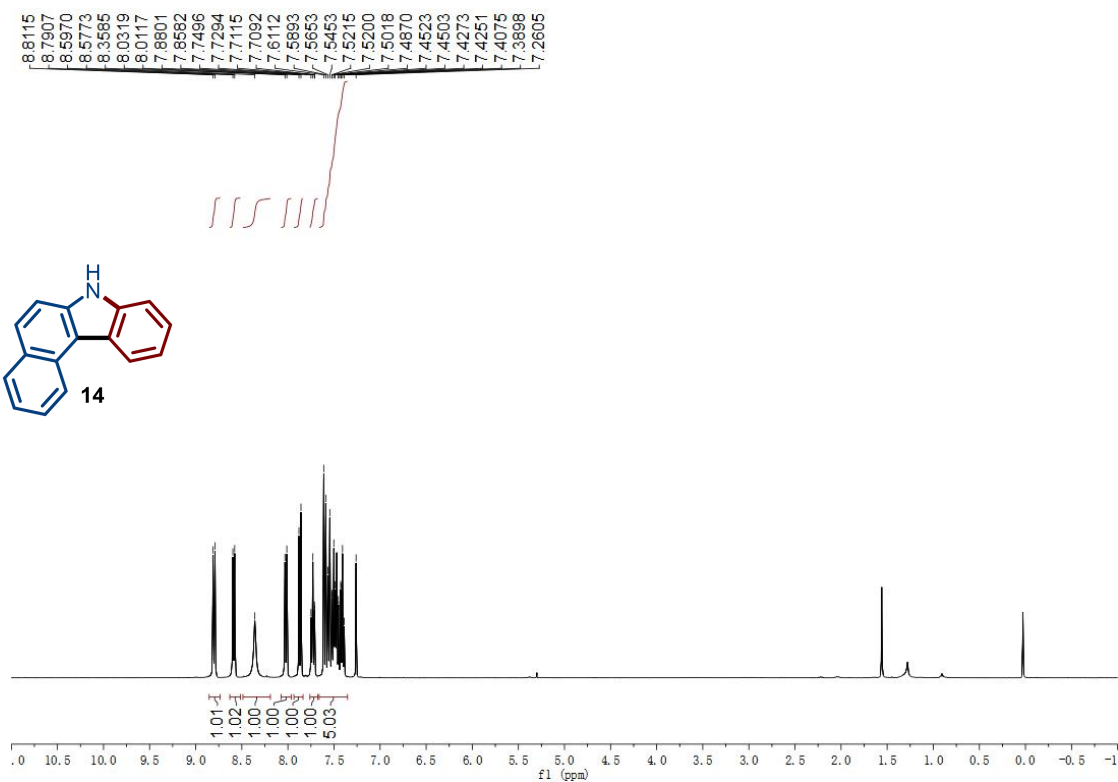
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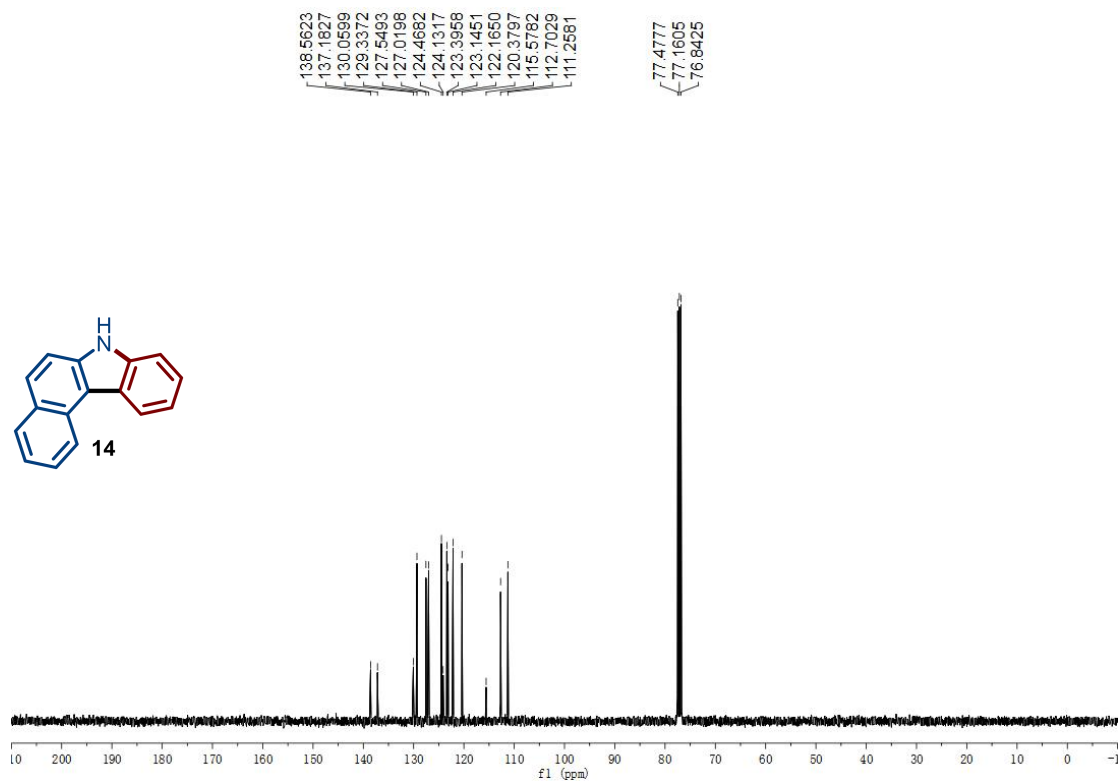
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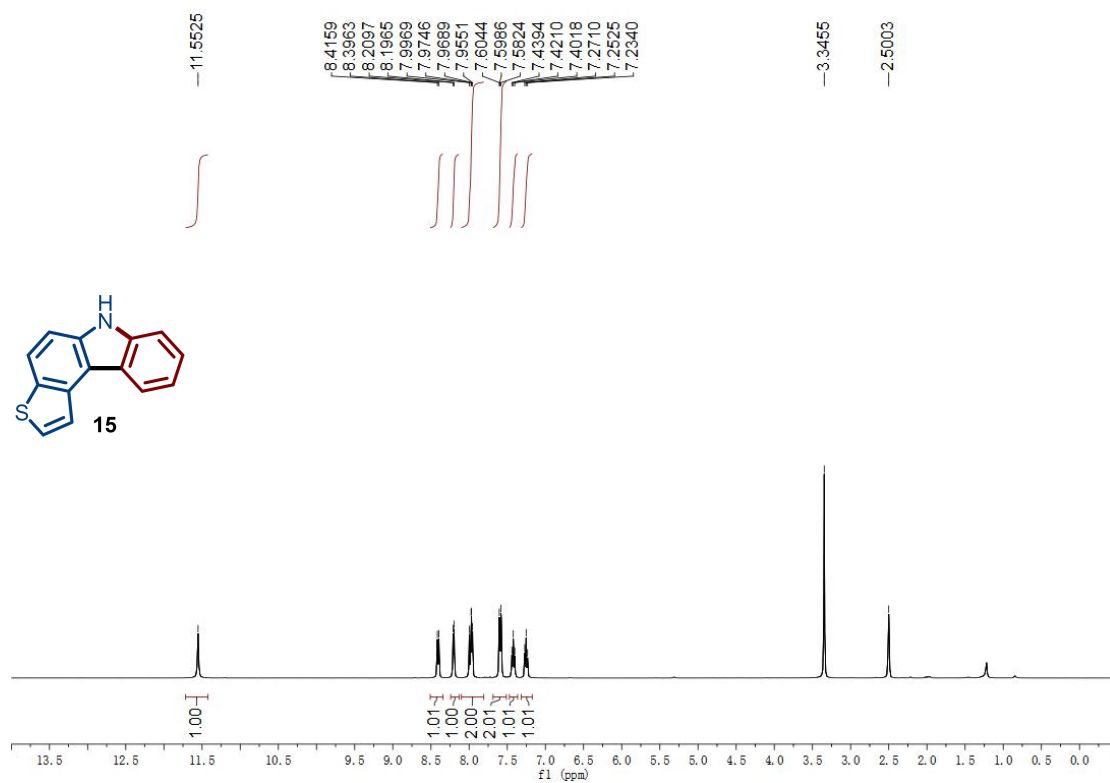
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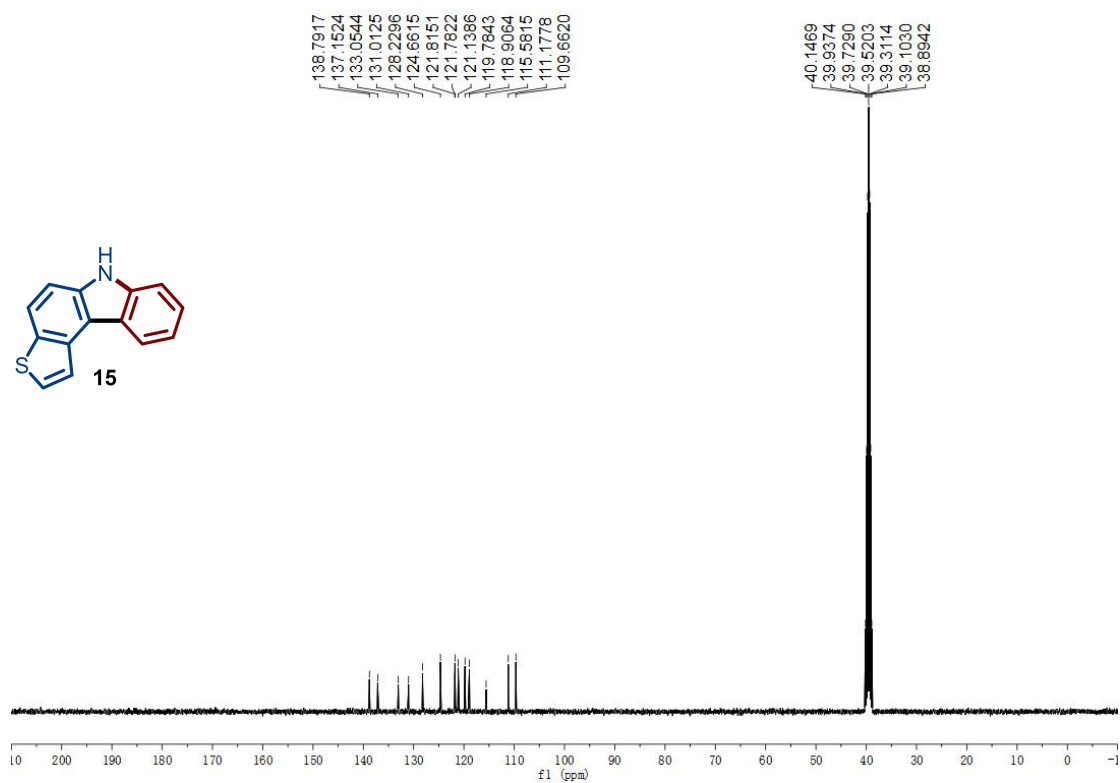
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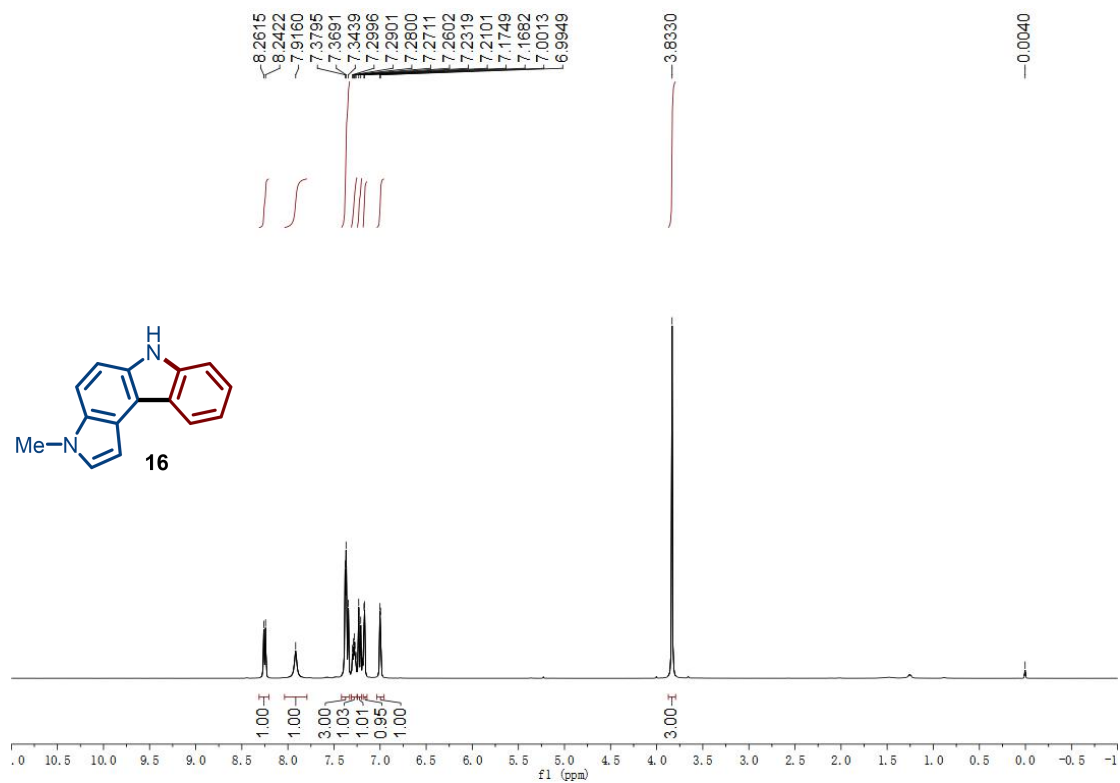
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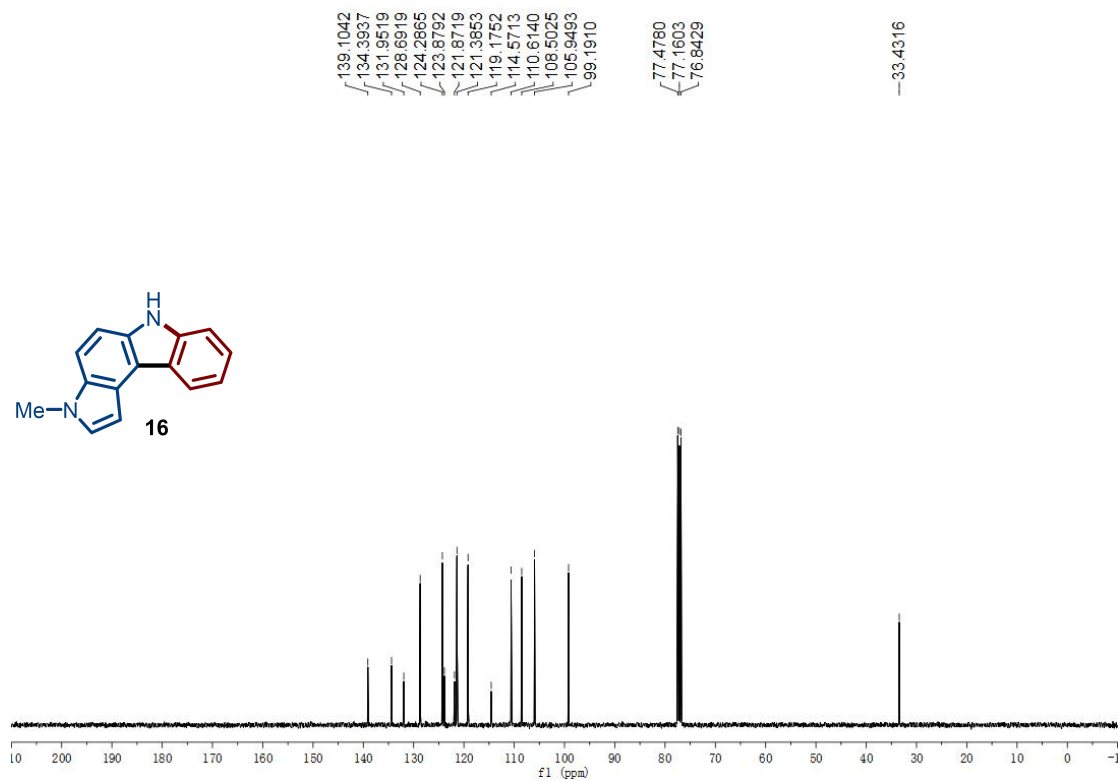
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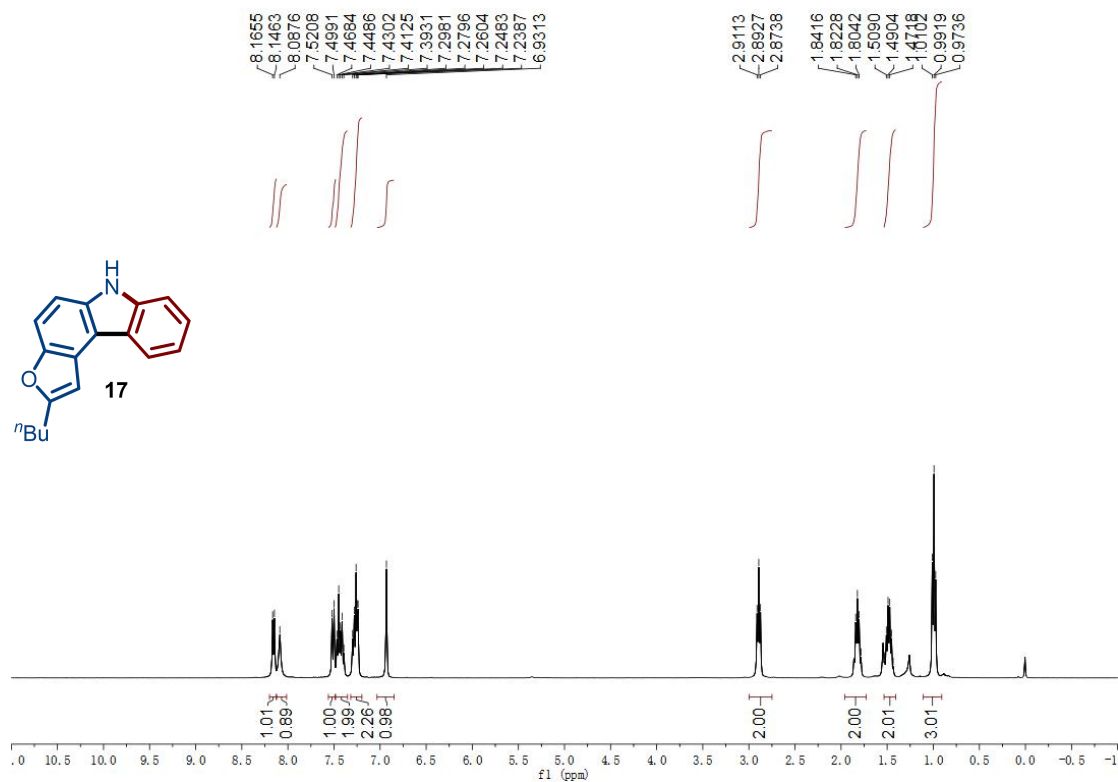
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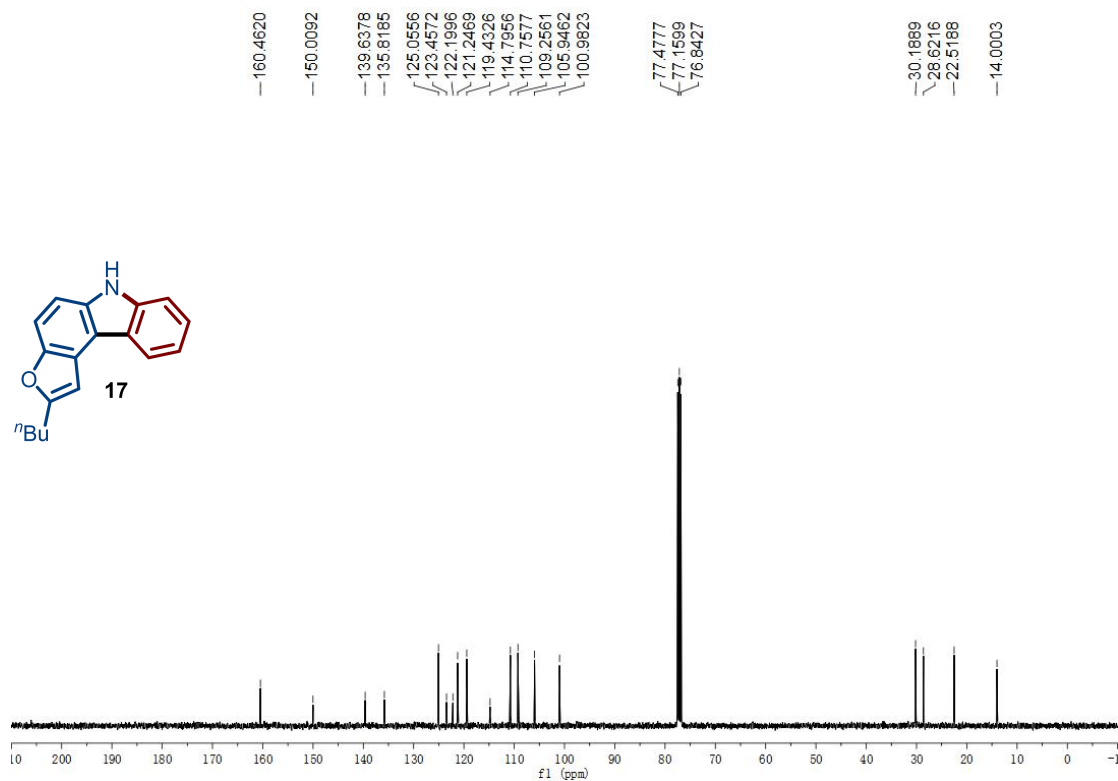
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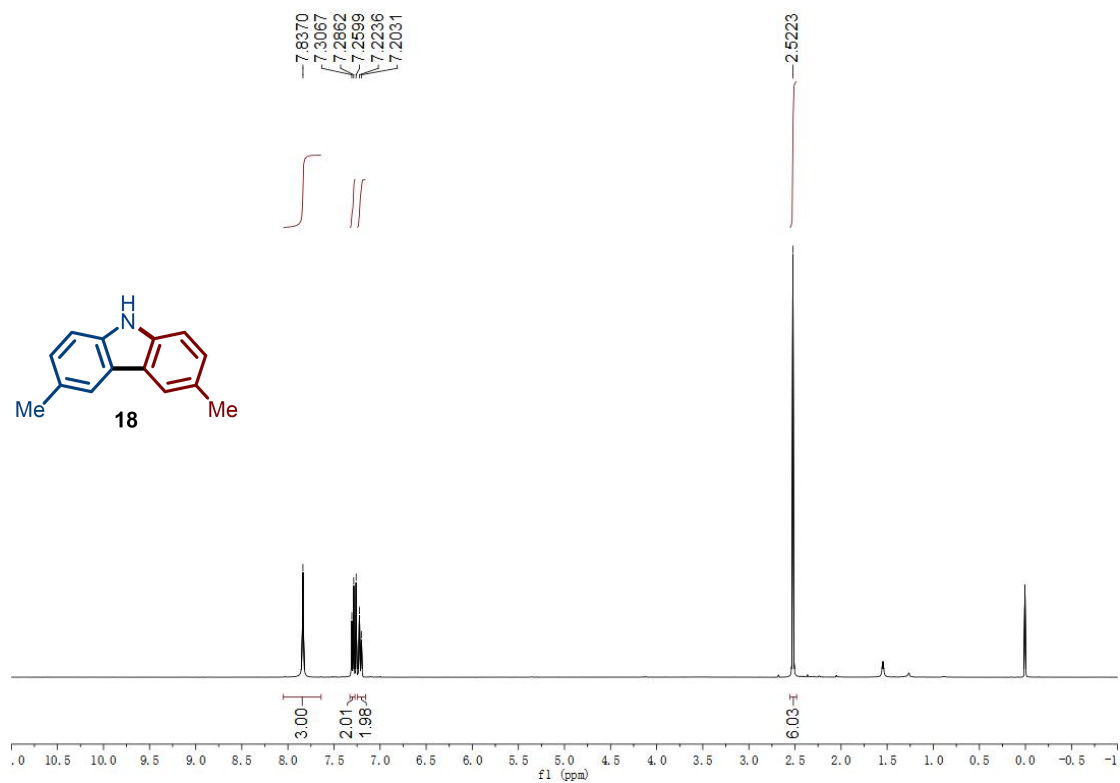
¹H NMR (400 MHz, CDCl₃) of 2-Butyl-6H-furo[2,3-c]carbazole (17)



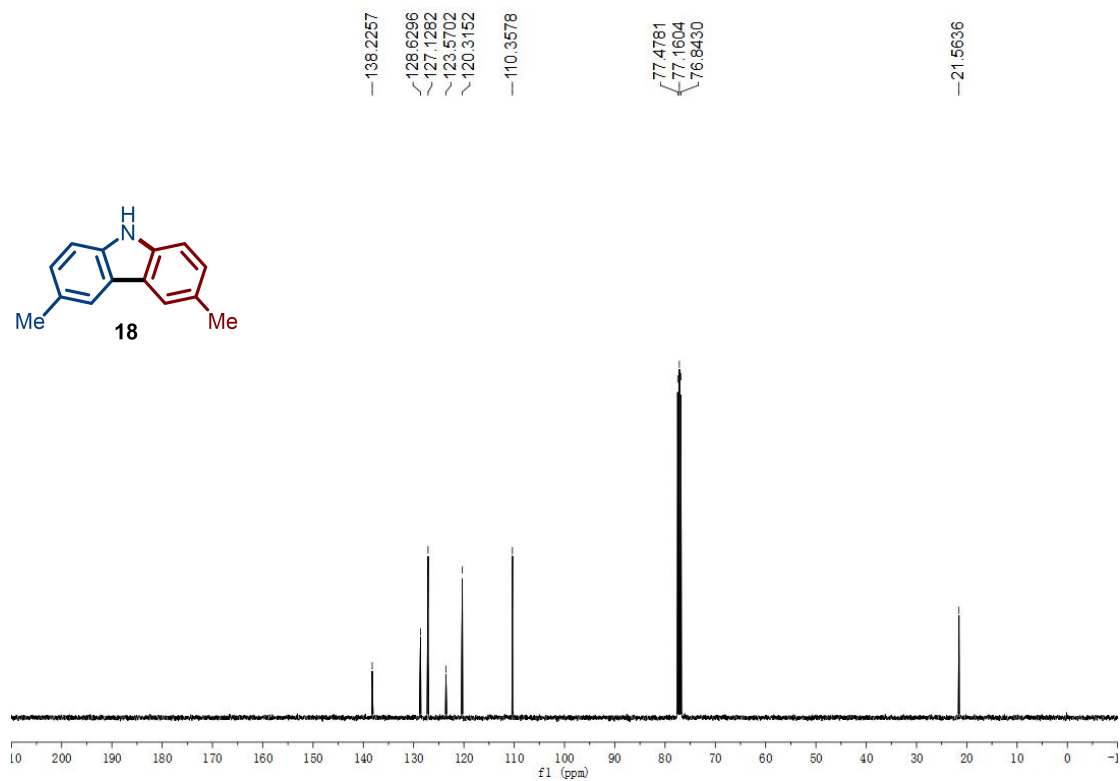
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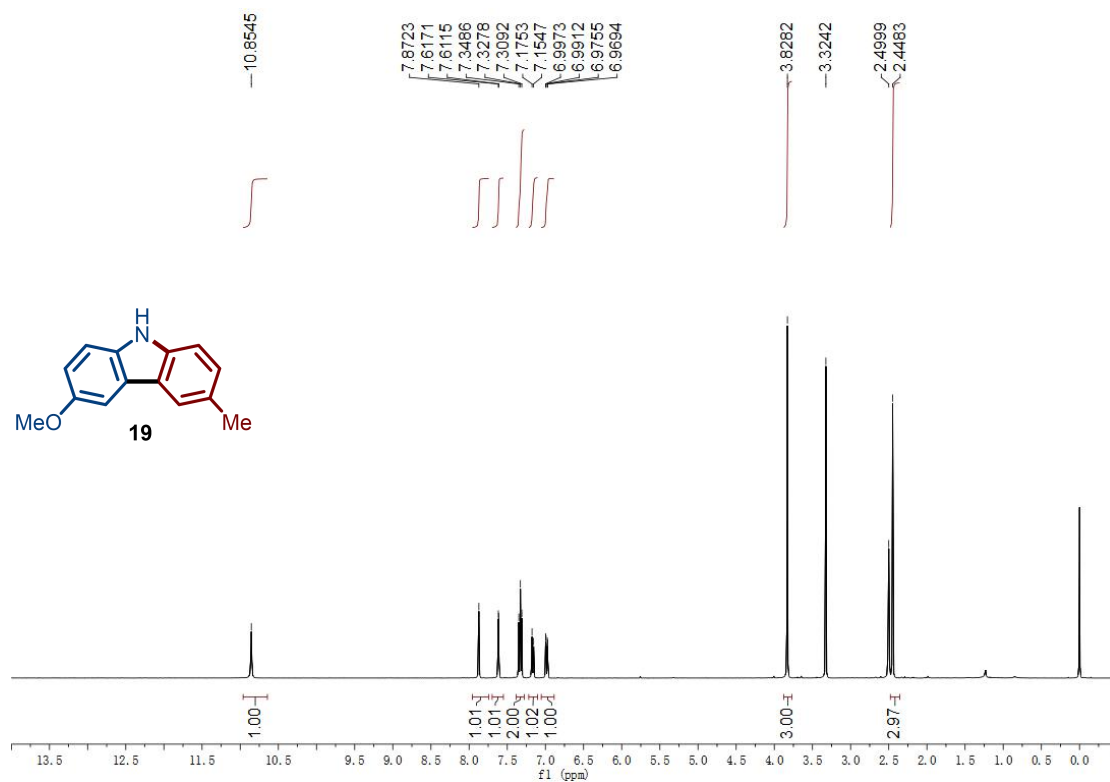
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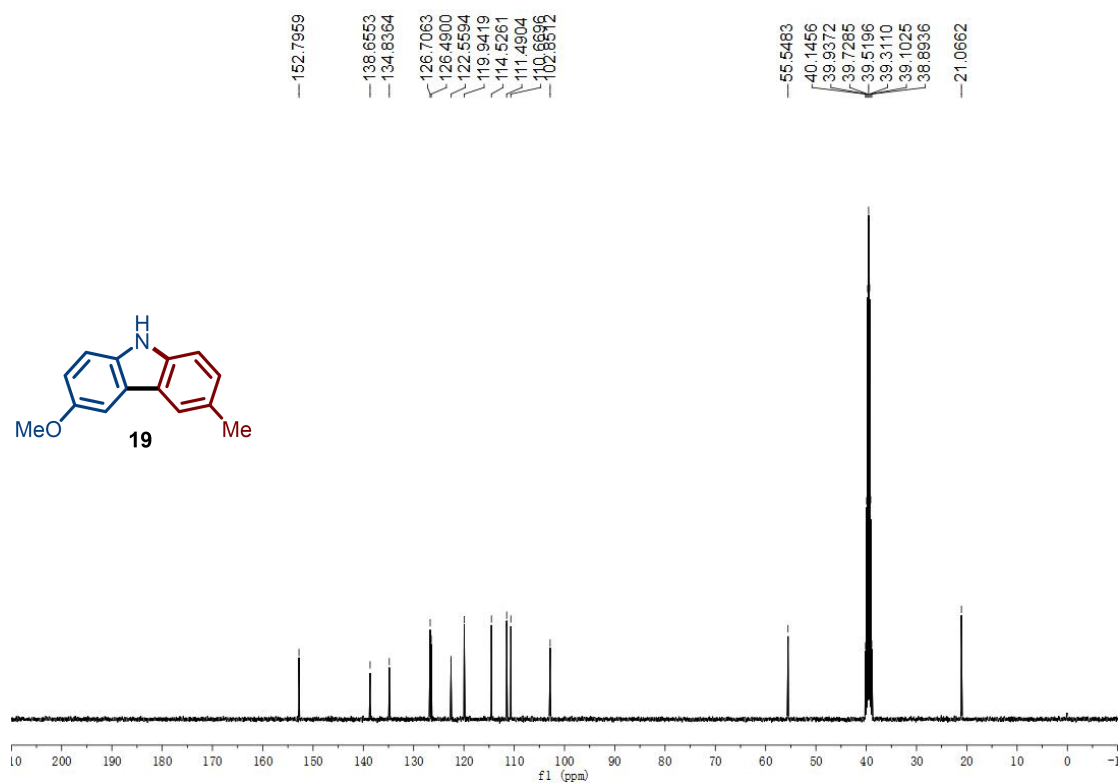
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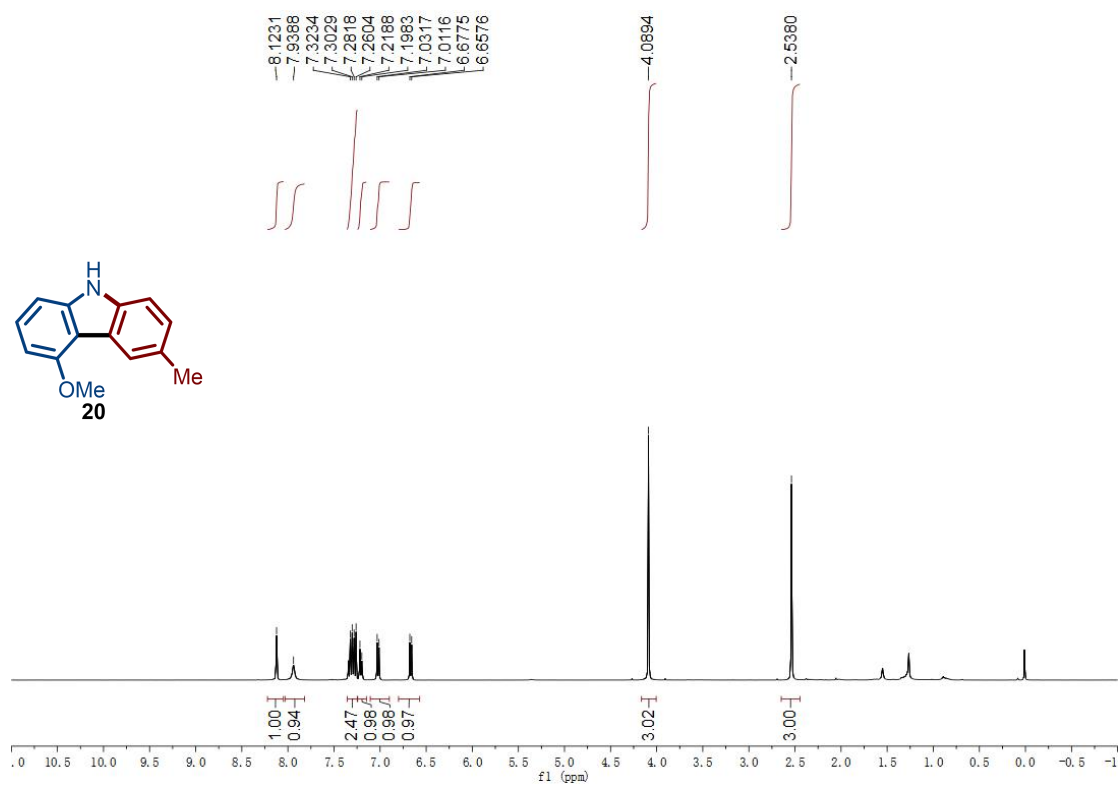
¹H NMR (400 MHz, DMSO-*d*₆) of 3-Methoxy-6-methyl-9*H*-carbazole (19)



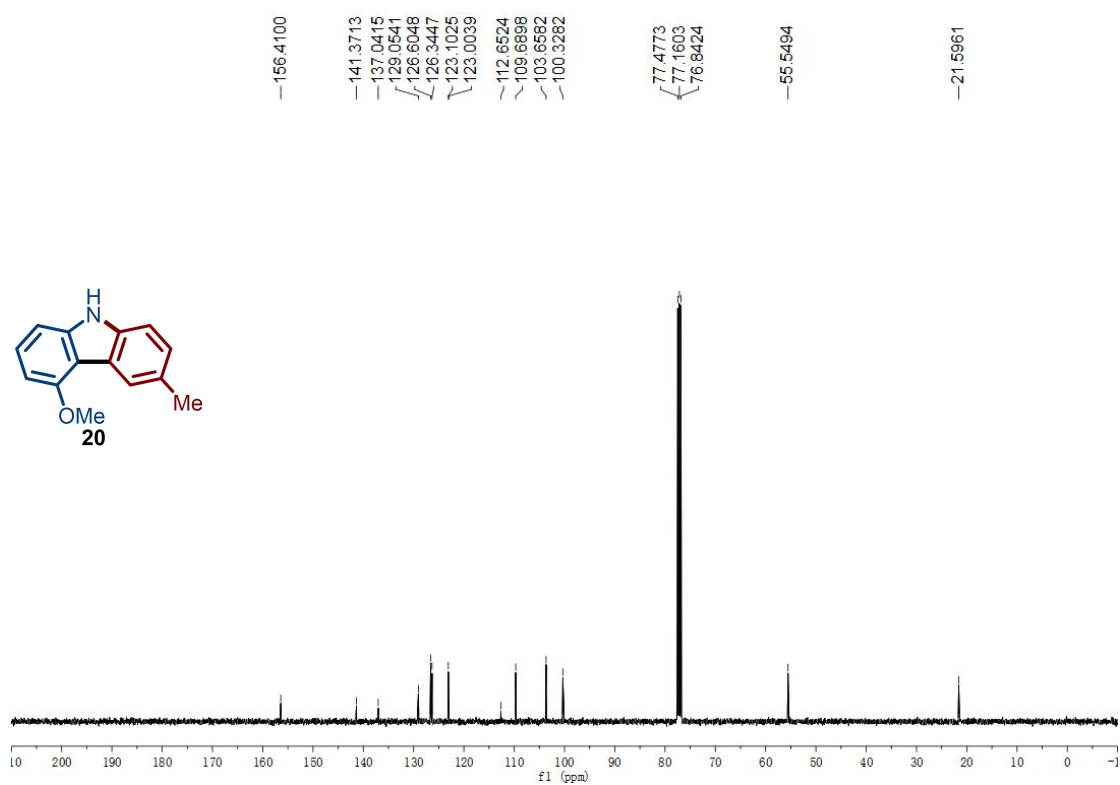
¹³C NMR (100 MHz, DMSO-*d*₆) of 3-Methoxy-6-methyl-9*H*-carbazole (19)



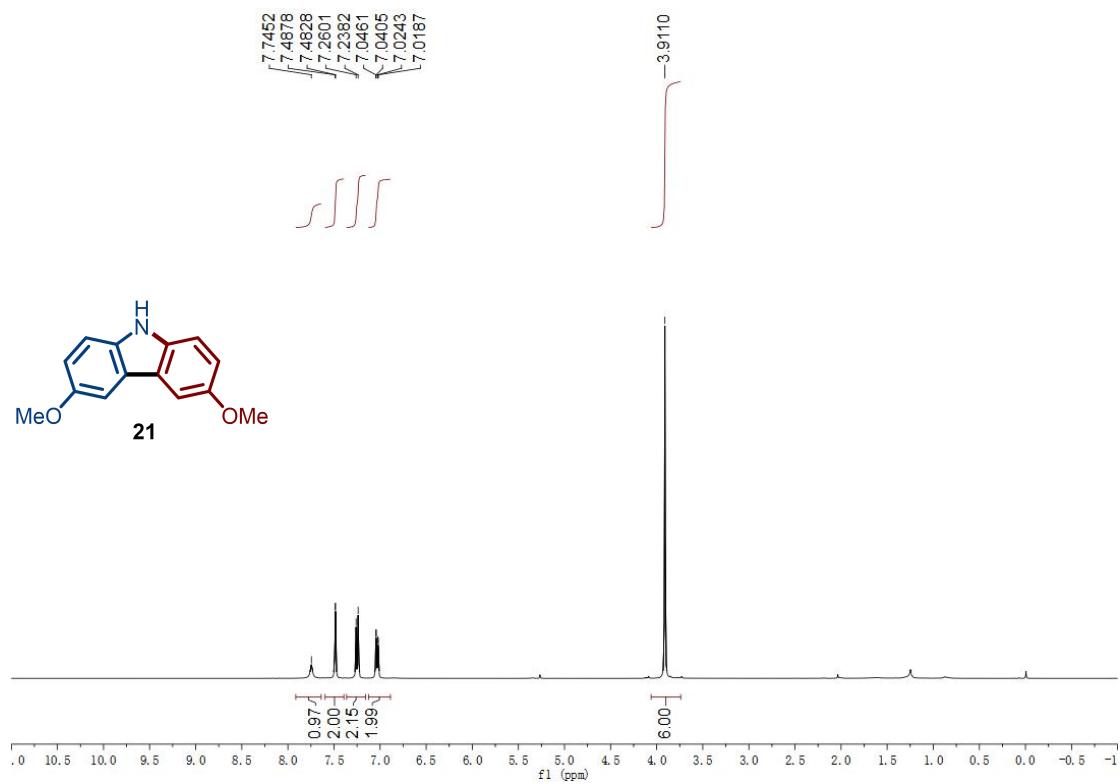
¹H NMR (400 MHz, CDCl₃) of 5-Methoxy-3-methyl-9H-carbazole (20)



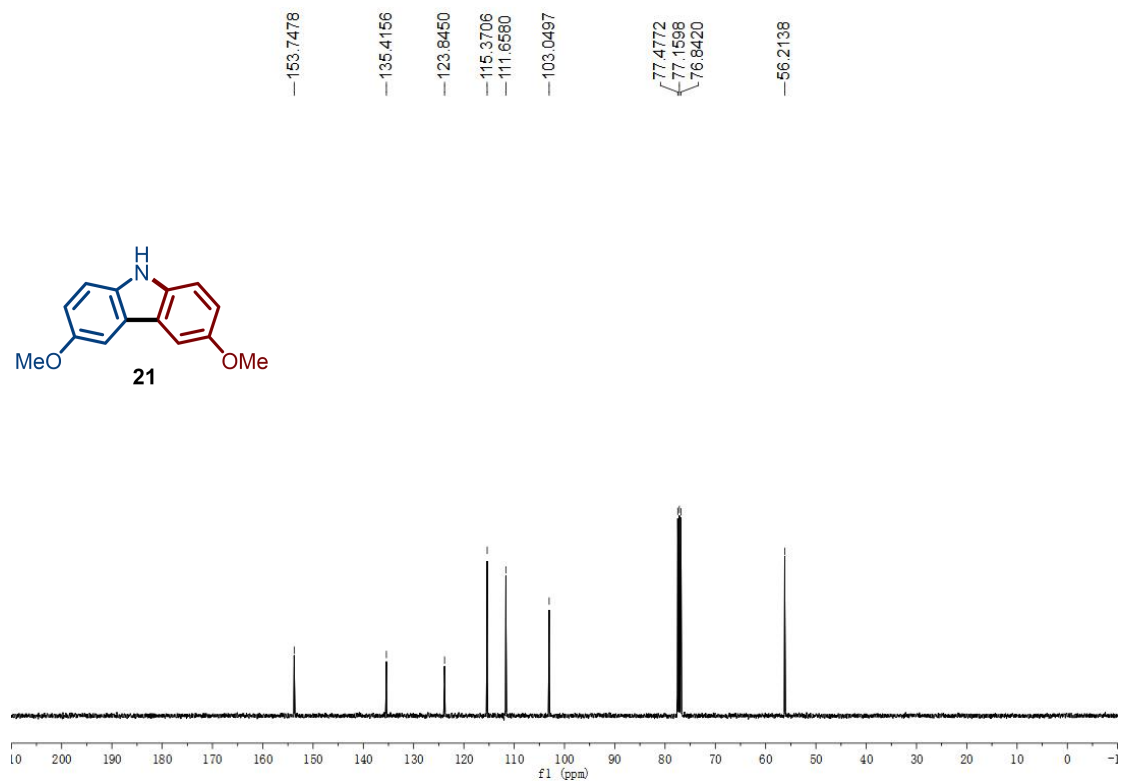
¹³C NMR (100 MHz, CDCl₃) of 5-Methoxy-3-methyl-9H-carbazole (20)



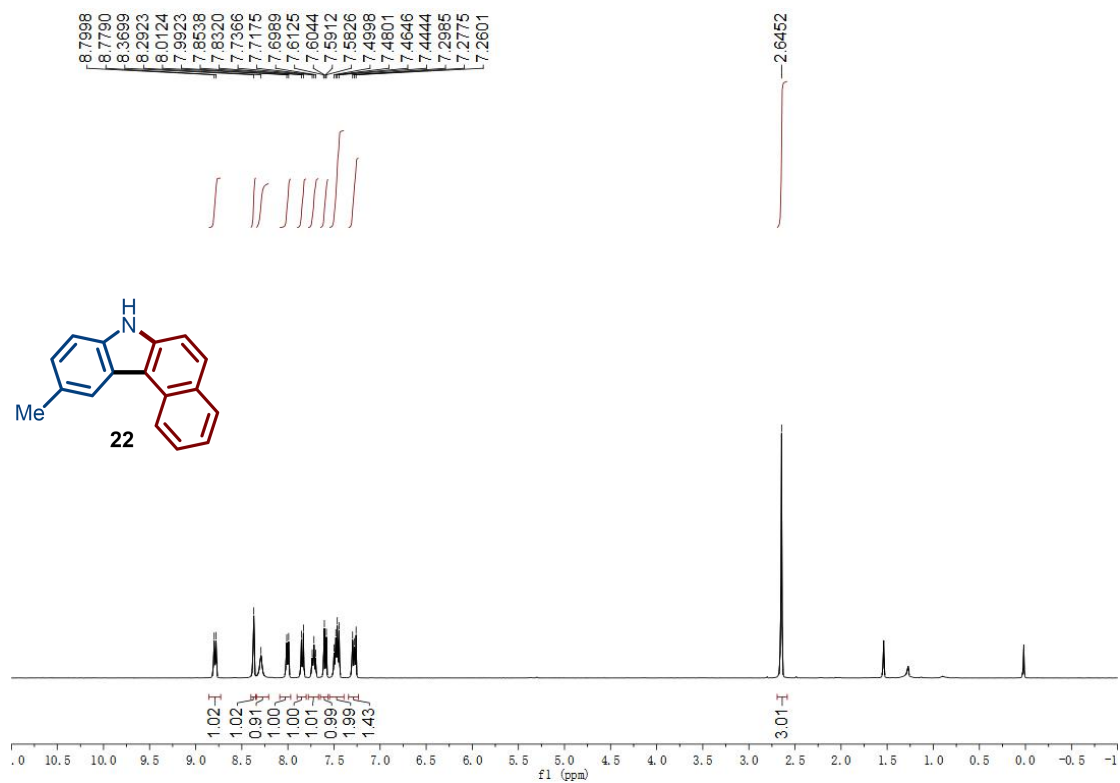
¹H NMR (400 MHz, CDCl₃) of 3,6-Dimethoxy-9H-carbazole (21)



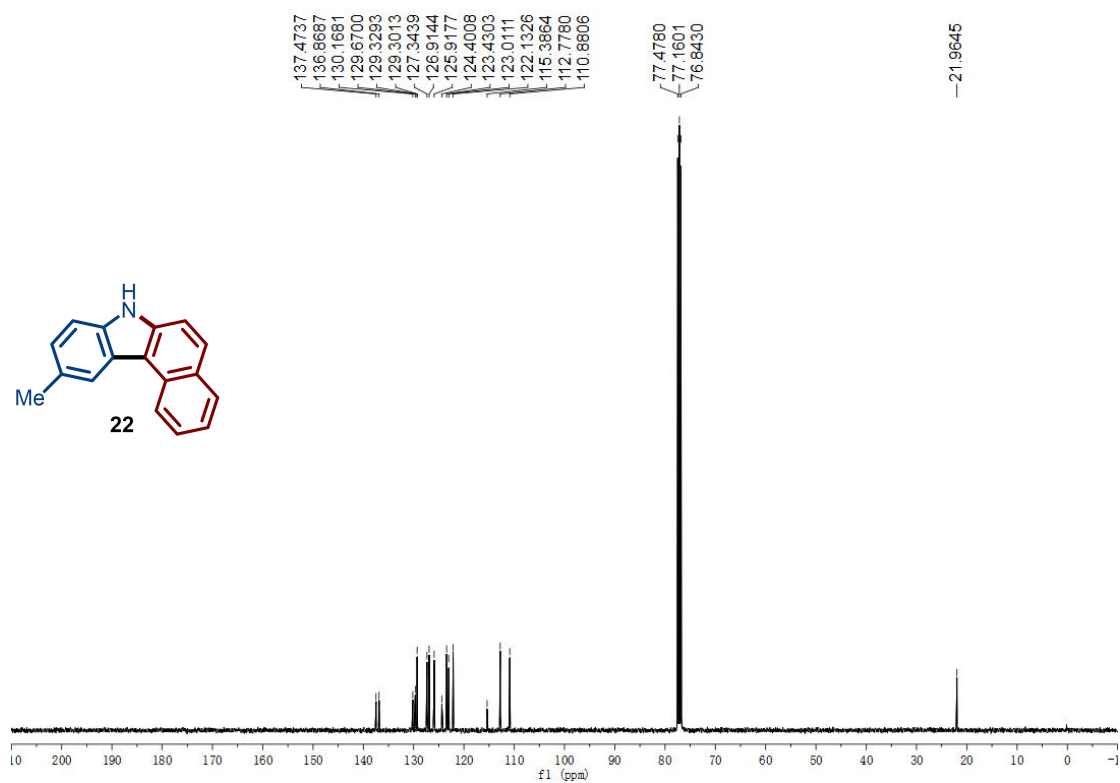
¹³C NMR (100 MHz, CDCl₃) of 3,6-Dimethoxy-9H-carbazole (21)



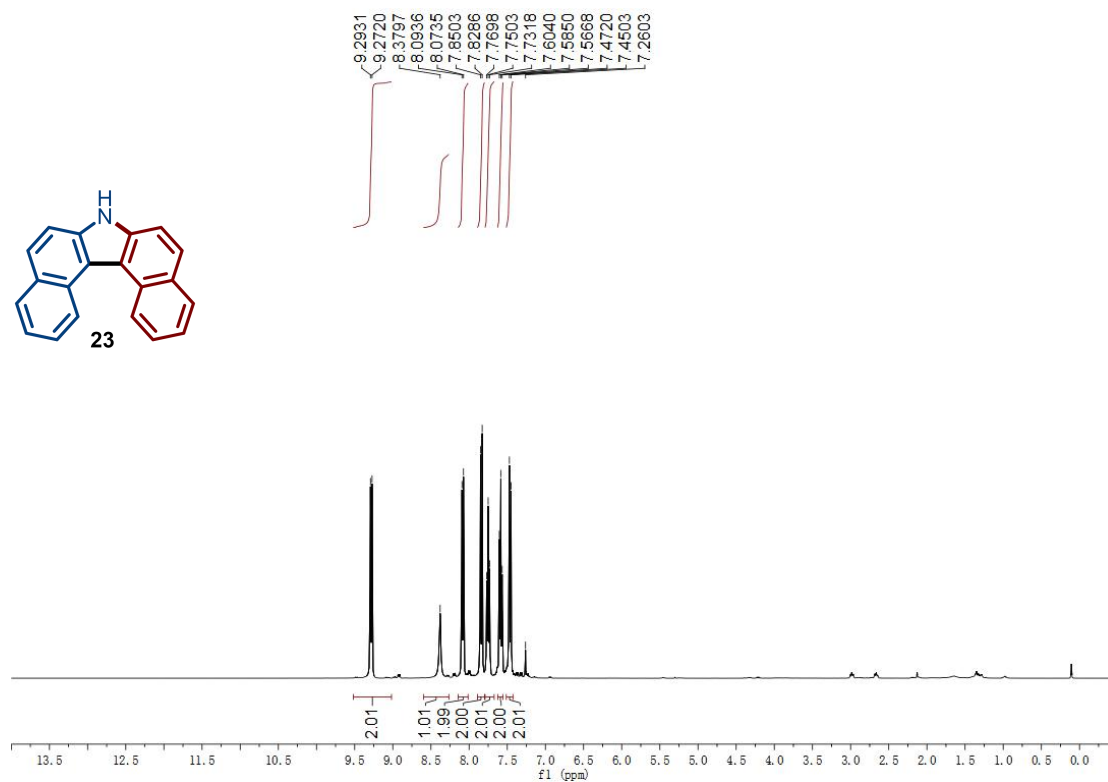
¹H NMR (400 MHz, CDCl₃) of 10-Methyl-7H-benzo[*c*]carbazole (22)



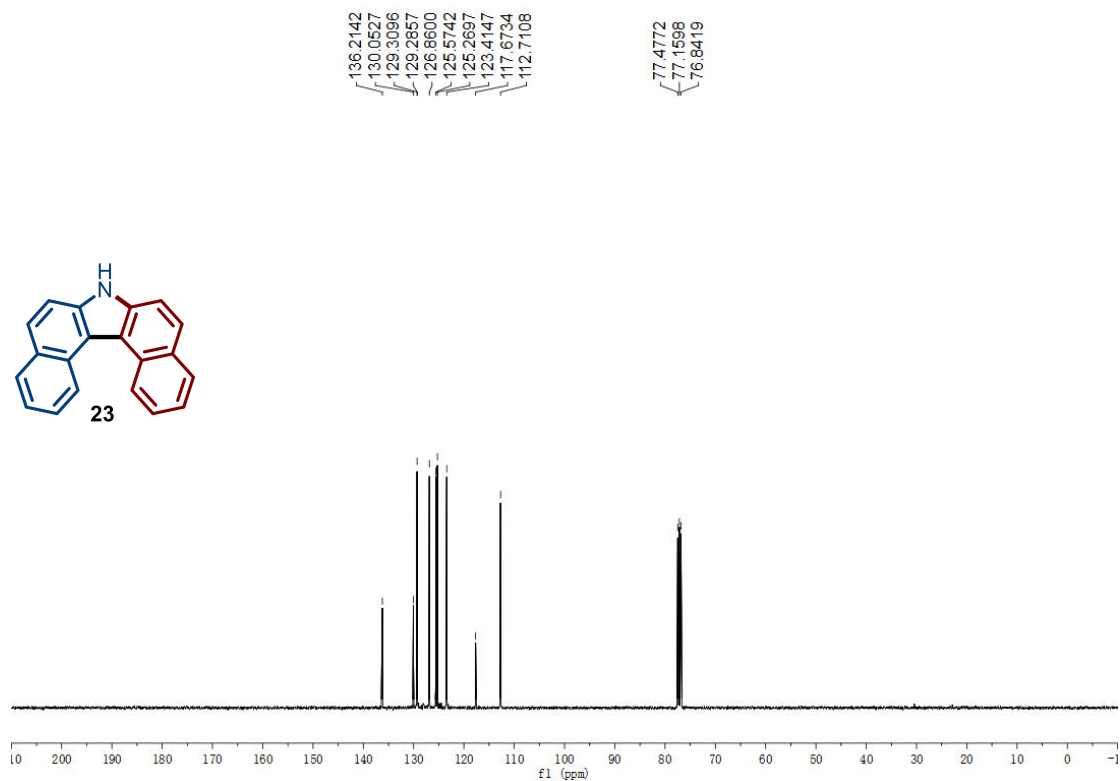
¹³C NMR (100 MHz, CDCl₃) of 10-Methyl-7H-benzo[*c*]carbazole (22)



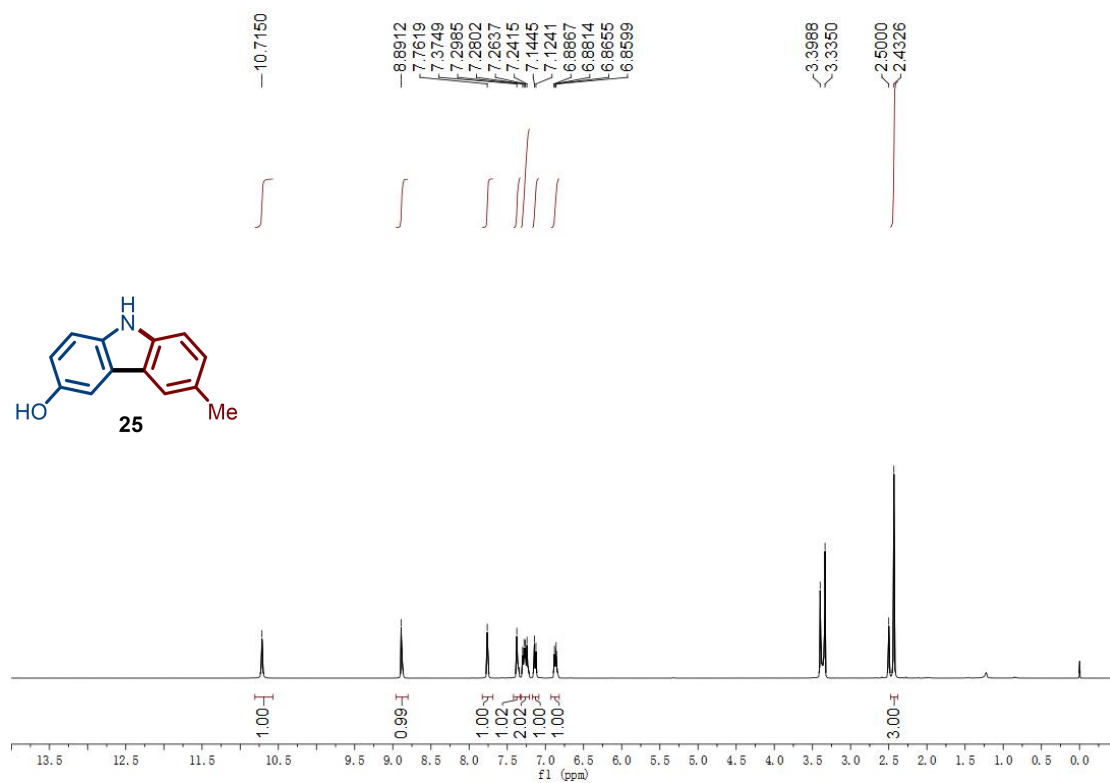
¹H NMR (400 MHz, CDCl₃) of 7H-dibenzo[*c,g*]carbazole (23)



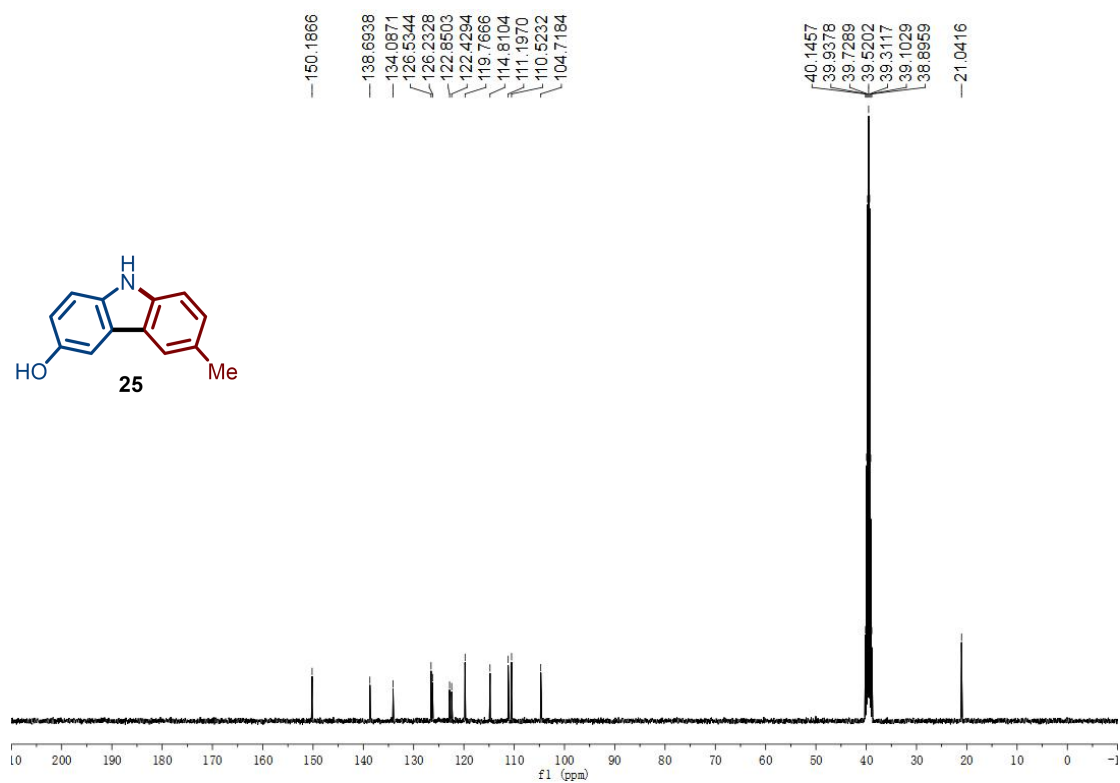
¹³C NMR (100 MHz, CDCl₃) of 7H-dibenzo[*c,g*]carbazole (23)



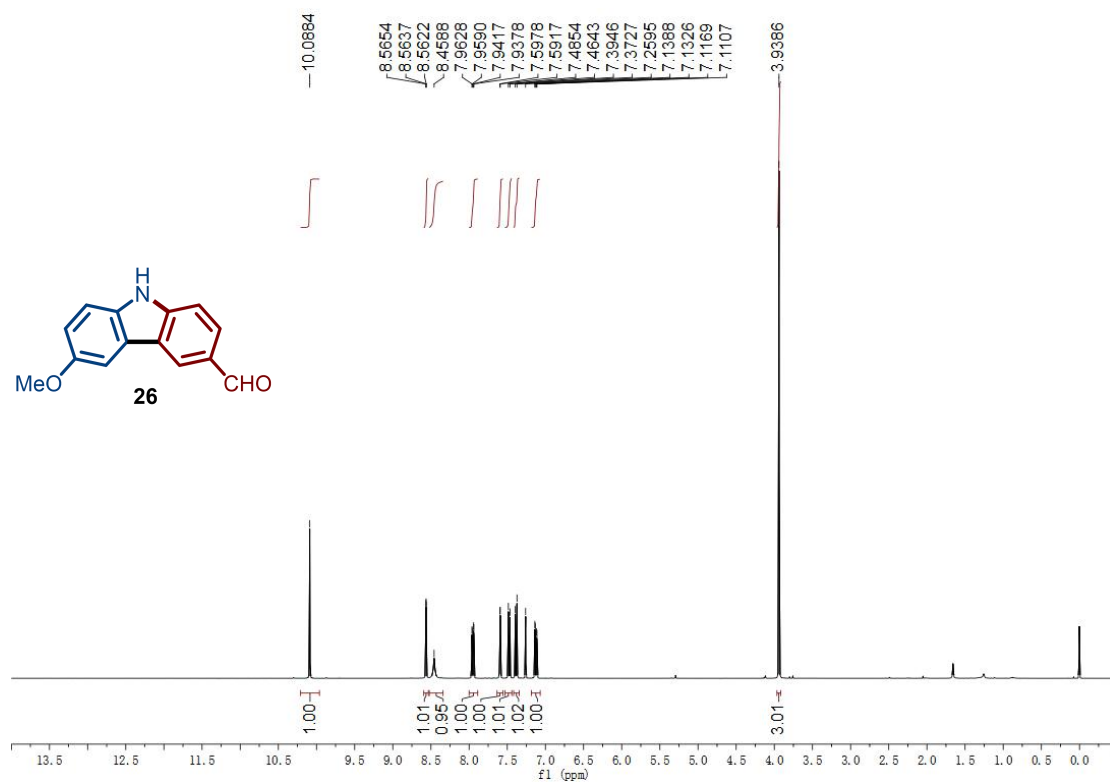
¹H NMR (400 MHz, DMSO-*d*₆) of 6-Methyl-9H-carbazol-3-ol (25)



¹³C NMR (100 MHz, DMSO-*d*₆) of 6-Methyl-9H-carbazol-3-ol (25)



¹H NMR (400 MHz, CDCl₃) of 6-Methoxy-9H-carbazole-3-carbaldehyde (26)



¹³C NMR (100 MHz, CDCl₃) of 6-Methoxy-9H-carbazole-3-carbaldehyde (26)

