

Supporting Information

Sustainable production of carbazole-based BioALEgens from lignin major motifs

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Table of Contents

1. General.....	2
2. Experimental methods.....	3
3. The photophysical property of carbazoles.....	4
4. Copies of NMR spectra and analytical data.....	5

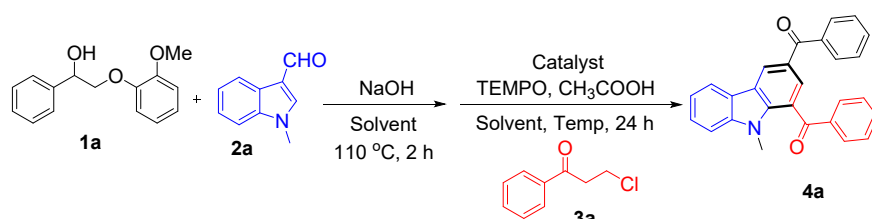
1. General

The chemicals were obtained commercially and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or solvent peak. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. Column chromatographic purifications were performed on SDZF silica gel 160. The carbazole derivatives were purified by column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane, 25:1:5) to afford pure products. The UV-visible absorption spectra of all the compounds are collected with a Shimadzu UV2450 spectrometer. Liquid products were quantified using a high-performance liquid chromatograph (HPLC, Prominence-i LC2030) equipped with a UV-vis Detector ($\lambda=280$ nm) and a C8 column (C8-3, $5\mu\text{m}$ 4.6×150 mm). A mixed solution composed of acetonitrile and H_2O with a ration of 80:20 (v/v) was used as a mobile phase and the flow rate was 1.0 mL min^{-1} . Photoluminescence spectra are recorded on a Fluoromax-4 spectrofluorometer (Horiba) for different water fraction (f_w).

2. Experimental methods

The experimental procedure for the synthesis of carbazole derivatives: lignin β -O-4 model compound (0.2 mmol), 1-methyl-1H-indole-3-carbaldehyde (0.1 mmol), NaOH (0.8 mmol) and 2 mL of toluene were added into the pressure tube with stirring at 110 °C for 2 h under air, and the reactions were paralleled in three groups. After the reaction, the reaction cooled to room temperature, and 126 μ L acetic acid was added into the reaction with stirring at room temperature for 30 min. Subsequently, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (20 mol%), TEMPO (0.2 mmol), and 3-chloro-1-phenylpropan-1-one (0.1 mmol) was added to reaction solution and stirred at 160 °C for 24 h. After cooling to room temperature, CH_2Cl_2 (10 mL) and H_2O was added into the reaction and the solution was filtered. The collected filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether /EtOAc = 10:1) to afford carbazole products.

Table S1. Screening of reaction parameters.^[a]



Entry	Solvent	The ratio 1a:2a:3a	4a Yield ^[b]
1	Touene	1.5:1:1	15
2	Toluene	1:1:1	14
3	Toluene	2:1:1	70
4	--	2:1:1	1.8

^[a]Reaction conditions: lignin β -O-4 model compound **1** (0.x mmol), substrate **2a** (0.1 mmol), substrate **3a** (0.1 mmol), NaOH (0.8 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (20 mol%), CH_3COOH (126 μ L), TEMPO (0.2 mmol) in toluene (2 mL) at 160 °C; ^[b]the yields are determined by HPLC using external standard method.

3. The photophysical property of carbazoles

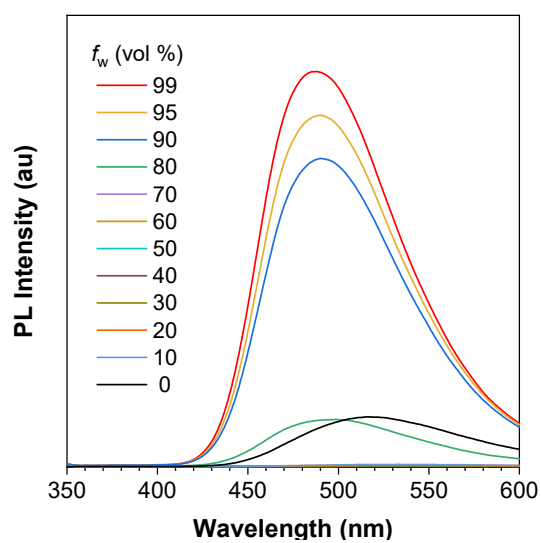


Fig. S1. PL spectra of **4j** in ACN/H₂O mixtures with different f_w . λ_{ex} : 309 nm, concentration: 20 μM .

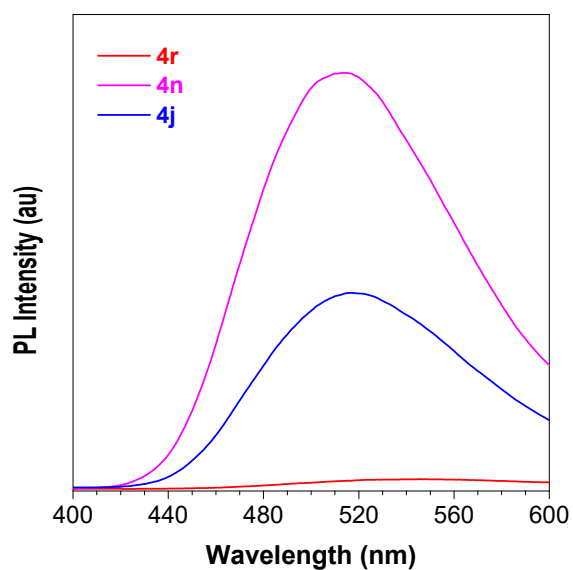
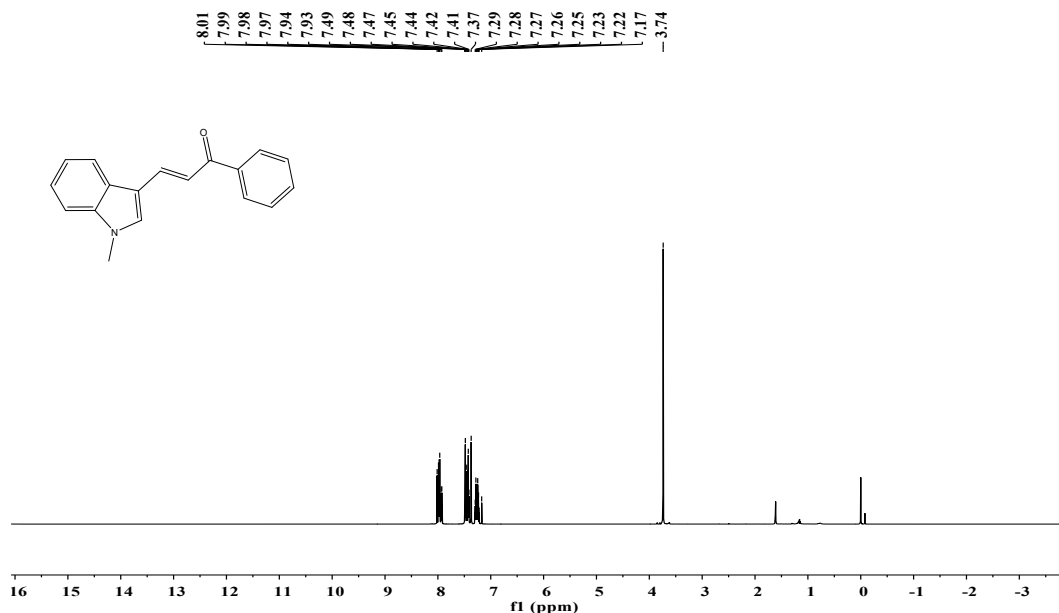


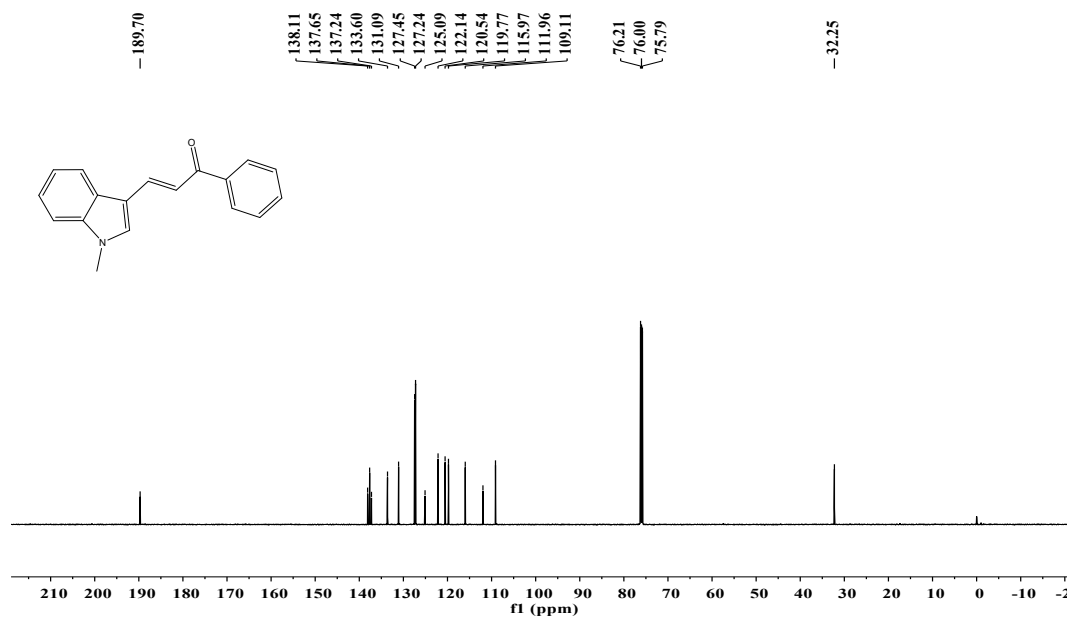
Fig. S2. PL spectra of **4r**, **4n**, and **4j** in pure acetonitrile (ACN) solution. Concentration: 20 μM . (**4r**: λ_{ex} : 311 nm, **4n**: λ_{ex} : 304 nm, **4j**: λ_{ex} : 309 nm).

4. Copies of NMR spectra and analytical data

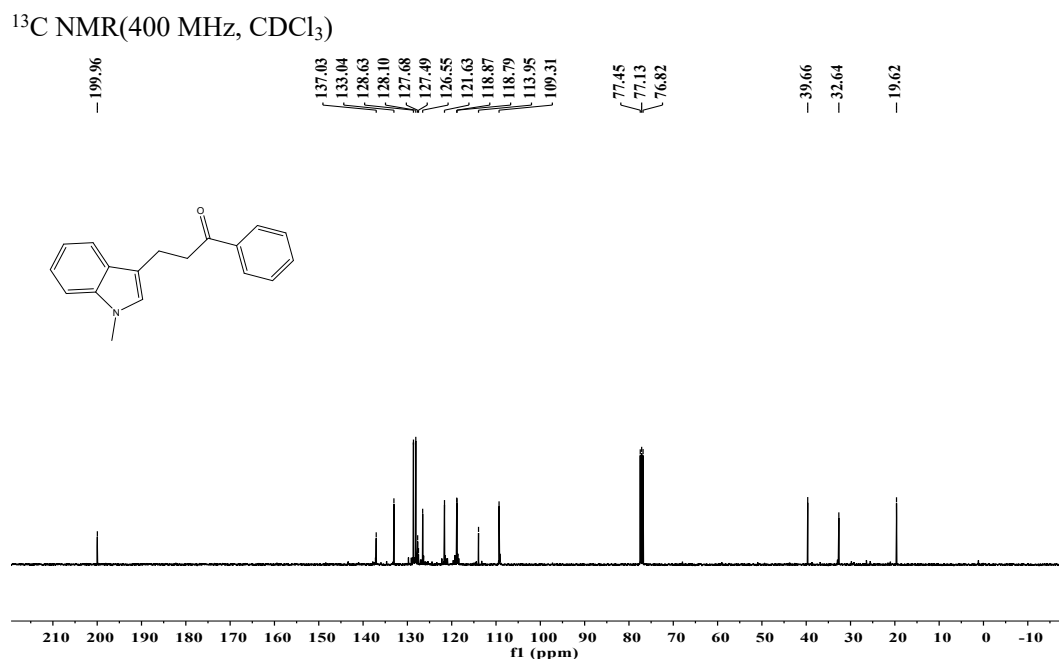
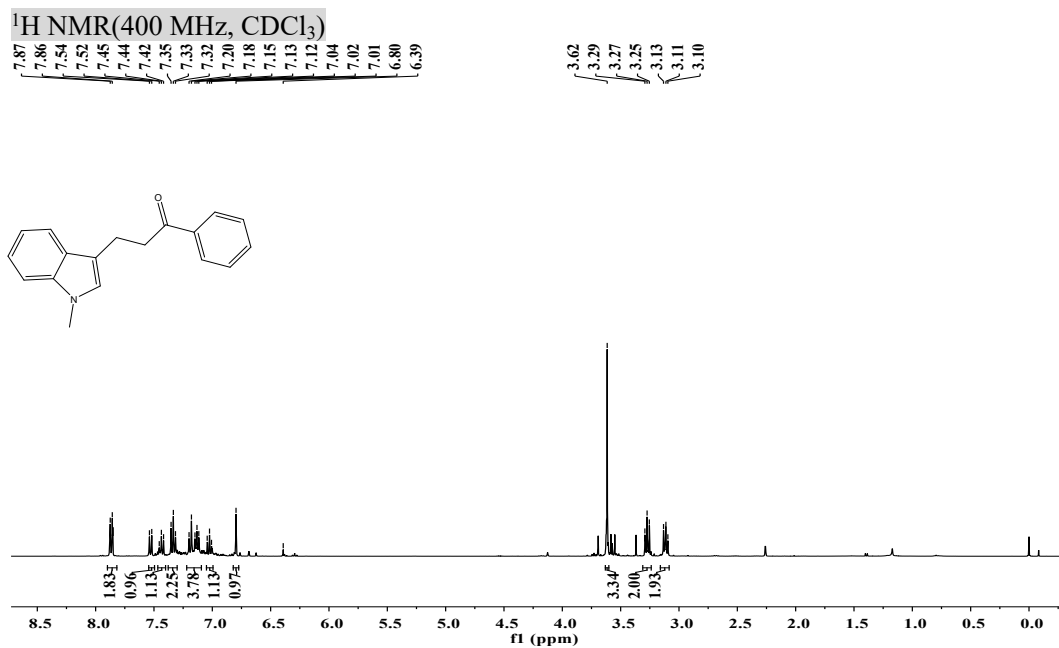
^1H NMR(600 MHz, CDCl_3)



^{13}C NMR(600 MHz, CDCl_3)

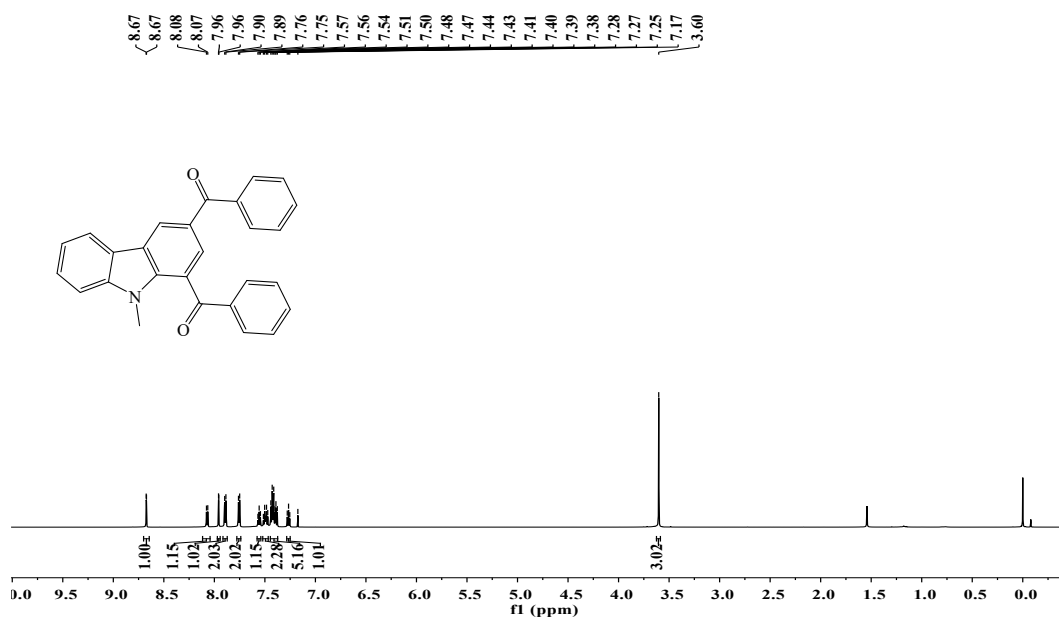


(E)-3-(1-methyl-1H-indol-3-yl)-1-phenylprop-2-en-1-one (7): yellow solid. ^1H NMR (600 MHz, Chloroform-d) δ 8.03-7.95 (m, 3H), 7.93 (d, $J = 7.1$ Hz, 1H), 7.54-7.40 (m, 4H), 7.37 (s, 1H), 7.31-7.20 (m, 3H), 3.74 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-d) δ 189.70(C=O), 138.11, 137.65, 137.24, 133.60, 131.09, 127.45, 127.24, 125.09, 122.14, 120.54, 119.77, 115.97, 111.96, 109.11, 32.25.

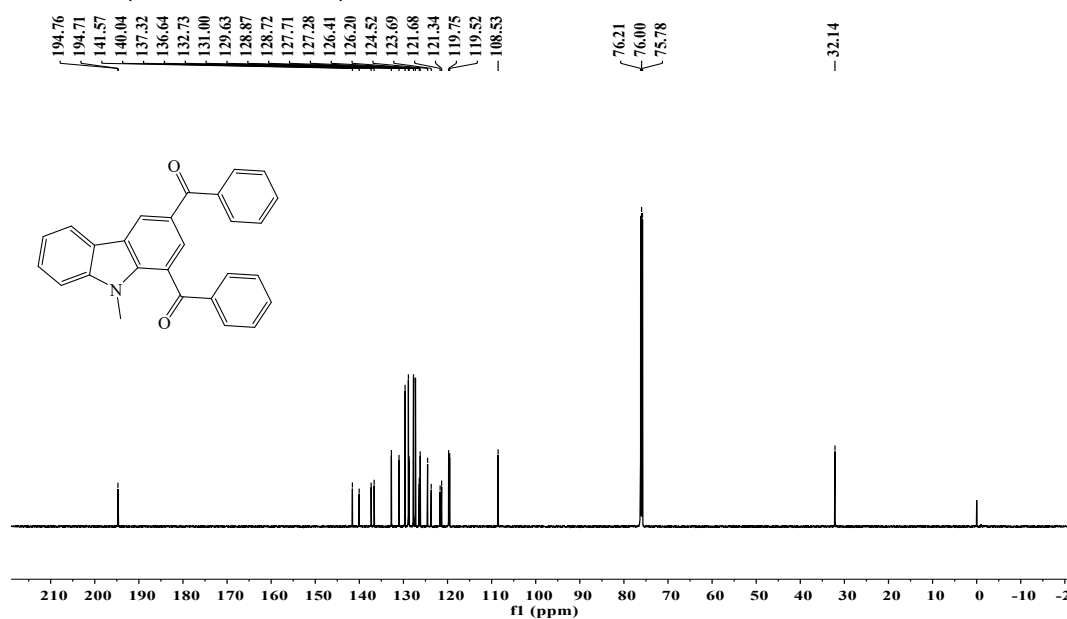


3-(1-methyl-1H-indol-3-yl)-1-phenylpropan-1-one (8): yellow liquid. ¹H NMR (400 MHz, Chloroform-d) δ 7.87 (d, J = 7.0 Hz, 2H), 7.53 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.22 – 7.09 (m, 4H), 7.05 – 6.99 (m, 1H), 6.80 (s, 1H), 3.62 (s, 3H), 3.27 (t, J = 7.6 Hz, 2H), 3.16 – 3.08 (m, 2H). ¹³C NMR (400 MHz, Chloroform-d) δ 199.96(C=O), 137.03, 133.04, 128.63, 128.10, 127.68, 127.49, 126.55, 121.63, 118.87, 118.79, 113.95, 109.31, 39.66, 32.64, 19.62.

¹H NMR(600 MHz, CDCl₃)

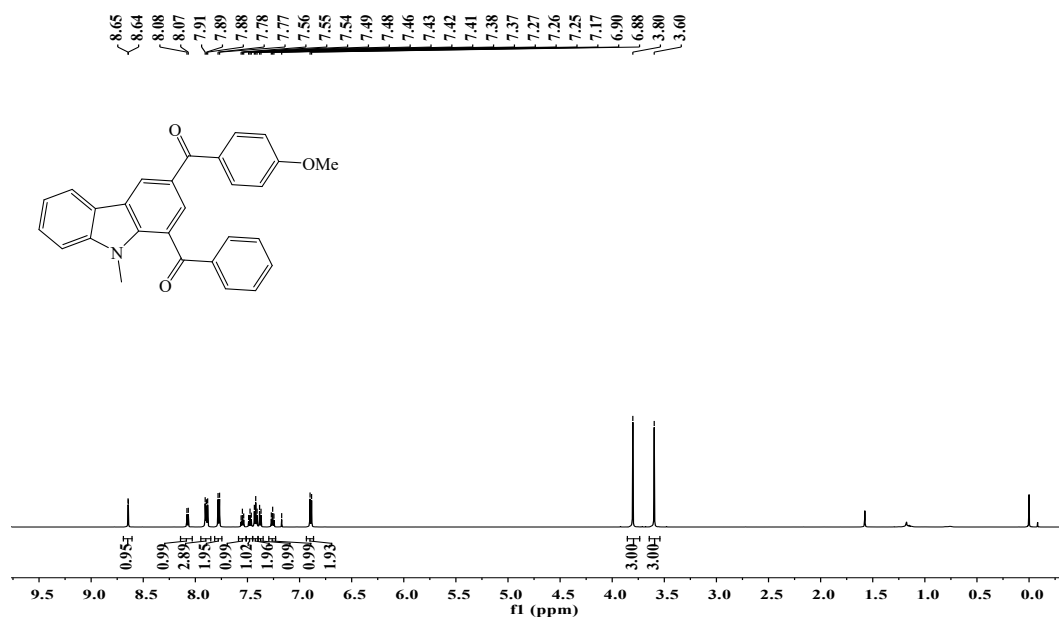


¹³C NMR(600 MHz, CDCl₃)

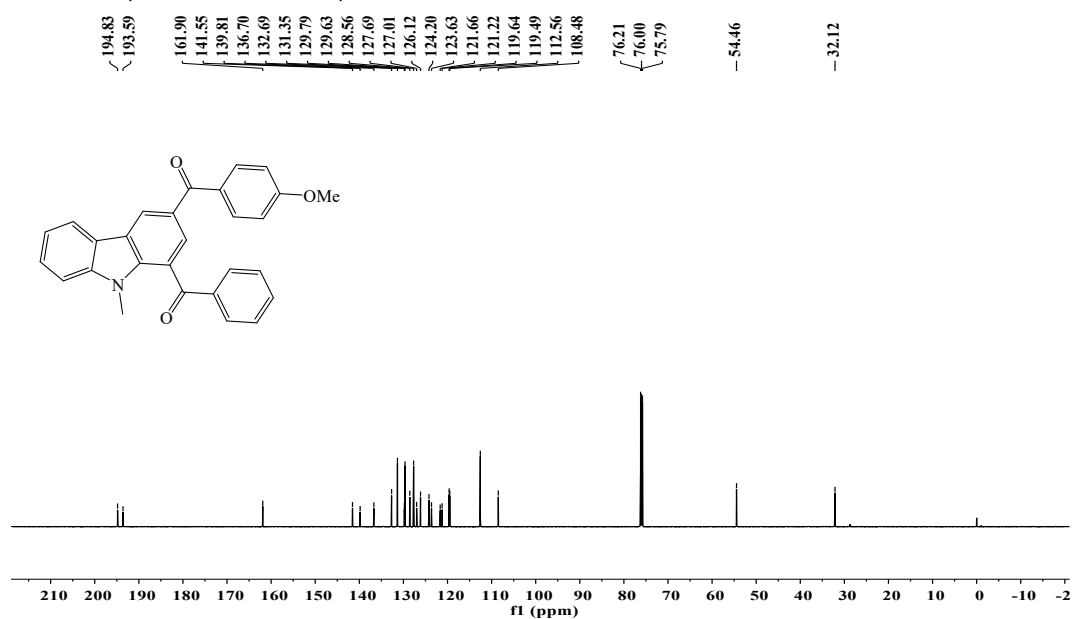


(9-methyl-9H-carbazole-1,3-diyl)bis(phenylmethanone) (4a): pale yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 8.67 (d, *J* = 1.6 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.52-7.47 (m, 2H), 7.45-7.37 (m, 5H), 7.27 (t, *J* = 7.5 Hz, 1H), 3.60 (s, 3H). ¹³C NMR (600 MHz, CDCl₃) δ 194.76, 194.71 (Cq each, C=O), 141.57, 140.04, 137.32, 136.64, 132.73, 131.00, 129.63, 128.87, 128.72, 127.71, 127.28, 126.41, 126.20, 124.52, 123.69, 121.68, 121.34, 119.75, 119.52, 108.53, 32.14.

¹H NMR(600 MHz, CDCl₃)

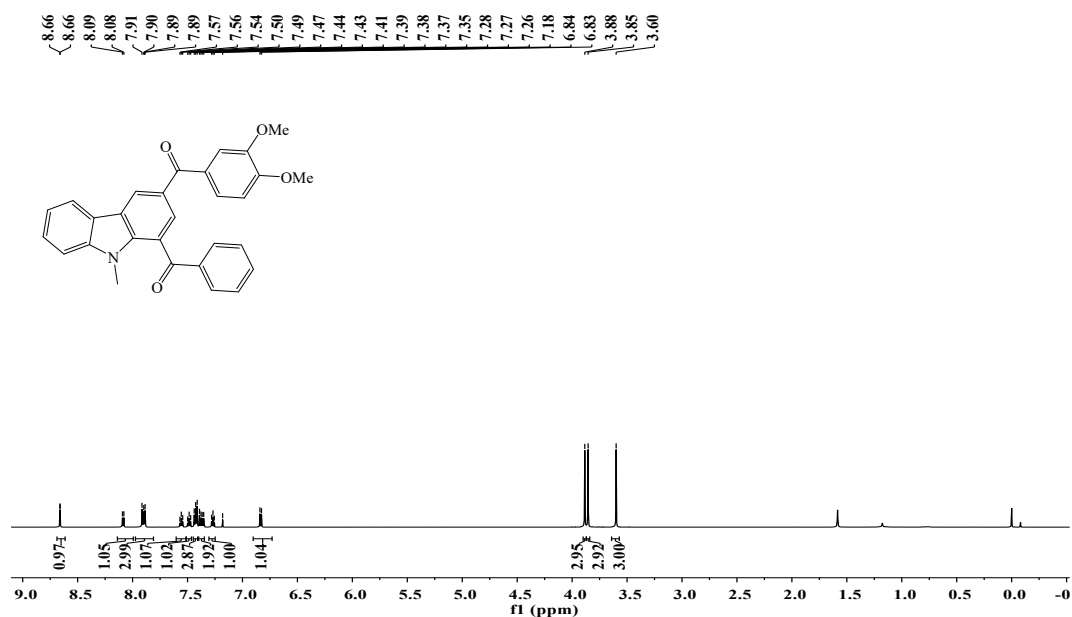


¹³C NMR(600 MHz, CDCl₃)

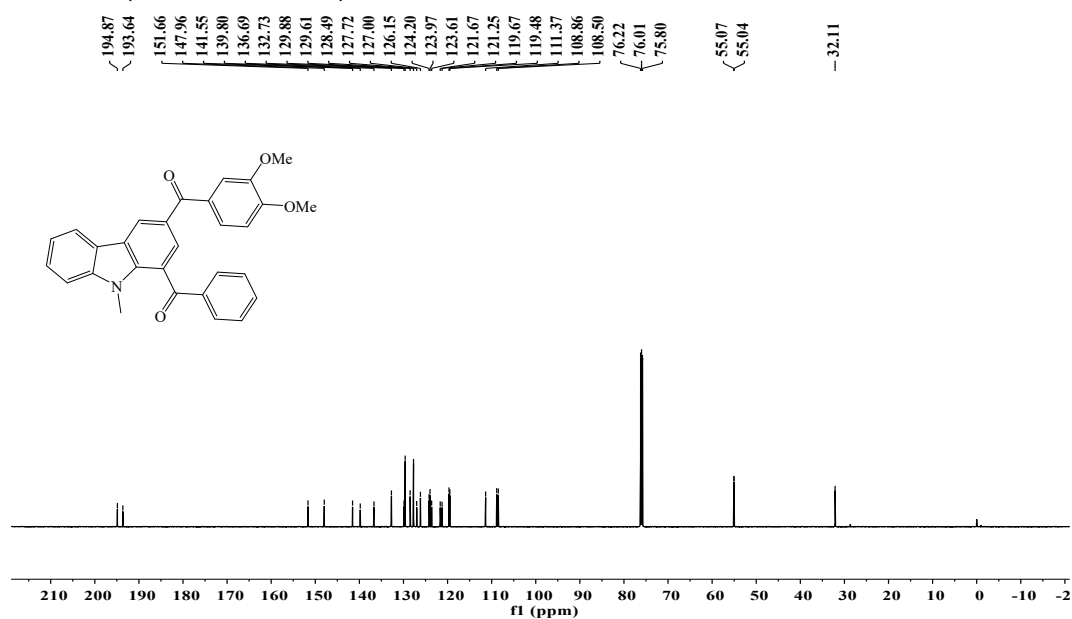


(1-benzoyl-9-methyl-9H-carbazol-3-yl)(4-methoxyphenyl)methanone (4b): yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 1.5 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.95-7.85 (m, 3H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.83, 193.59 (Cq each, C=O), 161.90, 141.55, 139.81, 136.70, 132.69, 131.35, 129.79, 129.63, 128.56, 127.69, 127.01, 126.12, 124.20, 123.63, 121.66, 121.22, 119.64, 119.49, 112.56, 108.48, 54.46, 32.12.

¹H NMR(600 MHz, CDCl₃)

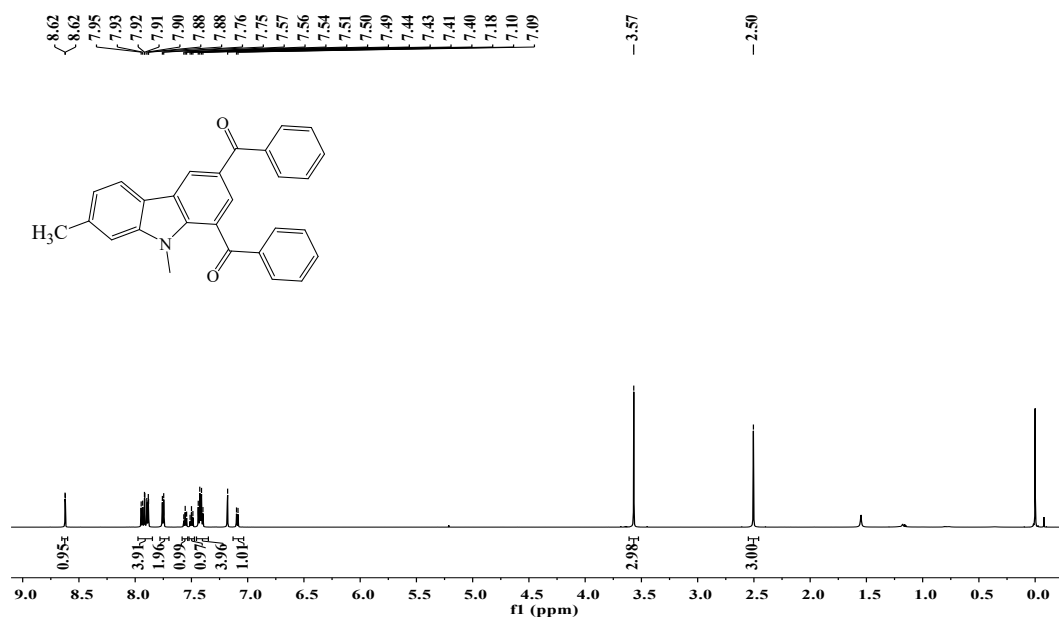


¹³C NMR(600 MHz, CDCl₃)

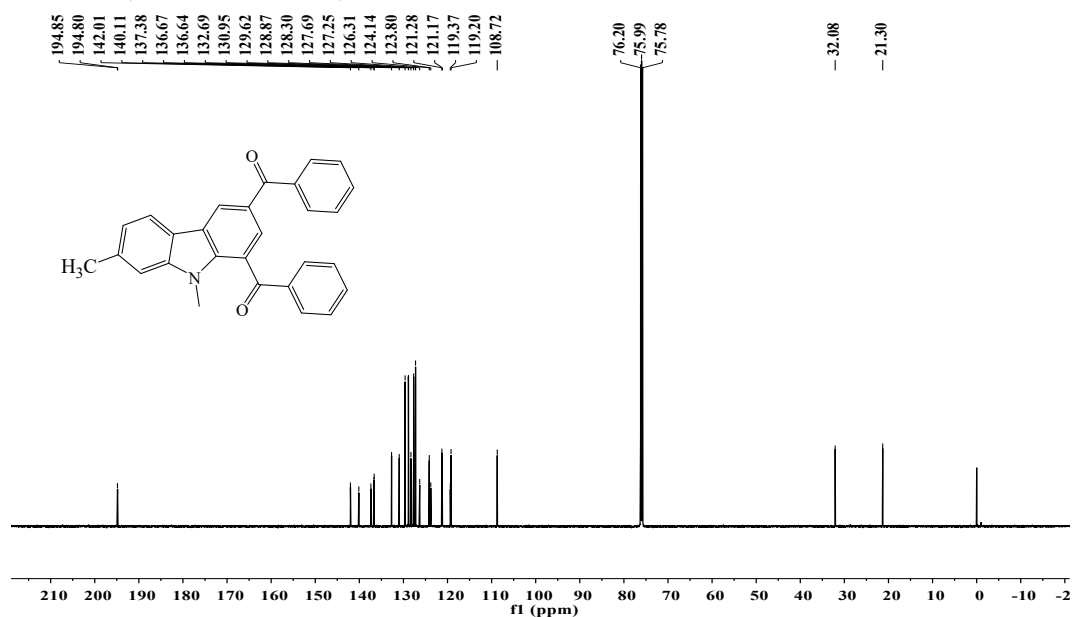


(1-benzoyl-9-methyl-9H-carbazol-3-yl)(3,4-dimethoxyphenyl)methanone (4c): white solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 1.6 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.97-7.81 (m, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.45-7.41 (m, 3H), 7.37 (dd, *J* = 14.8, 8.3 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.88 and 3.85(s each, 3:3H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.87, 193.64 (Cq each, C=O), 151.66, 147.96, 141.55, 139.80, 136.69, 132.73, 129.88, 129.61, 128.49, 127.72, 127.00, 126.15, 124.20, 123.97, 123.61, 121.67, 121.25, 119.67, 119.48, 111.37, 108.86, 108.50, 55.07, 55.04, 32.11.

^1H NMR(600 MHz, CDCl_3)

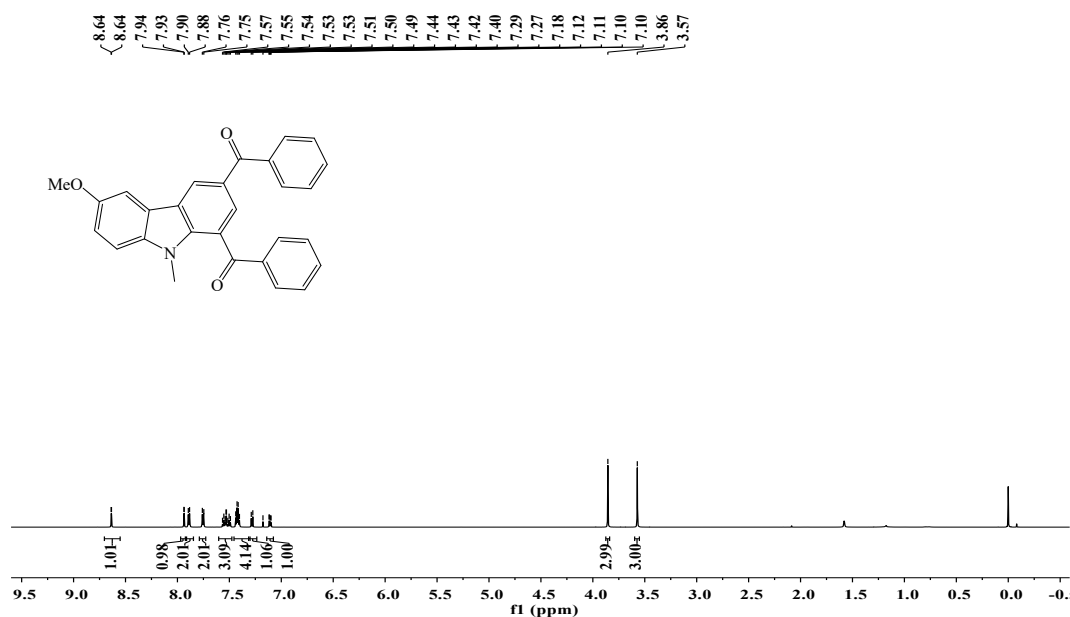


^{13}C NMR(600 MHz, CDCl_3)

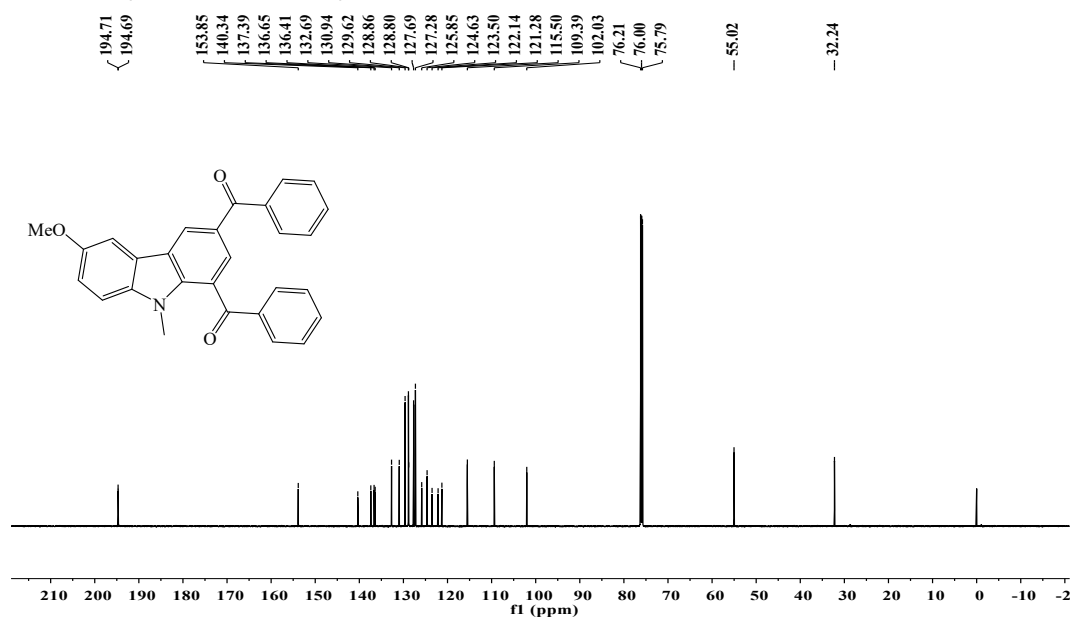


(7,9-dimethyl-9H-carbazole-1,3-diyl)bis(phenylmethanone) (4d): yellow solid. ^1H NMR (600 MHz, Chloroform-d) δ 8.62 (d, J = 1.6 Hz, 1H), 7.98-7.85 (m, 4H), 7.75 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.46-7.35 (m, 4H), 7.09 (d, J = 7.9 Hz, 1H), 3.57 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-d) δ 194.85, 194.80 (Cq each, C=O), 142.01, 140.11, 137.38, 136.67, 136.64, 132.69, 130.95, 129.62, 128.87, 128.30, 127.69, 127.25, 126.31, 124.14, 123.80, 121.28, 121.17, 119.37, 119.20, 108.72, 32.08, 21.30.

¹H NMR(600 MHz, CDCl₃)

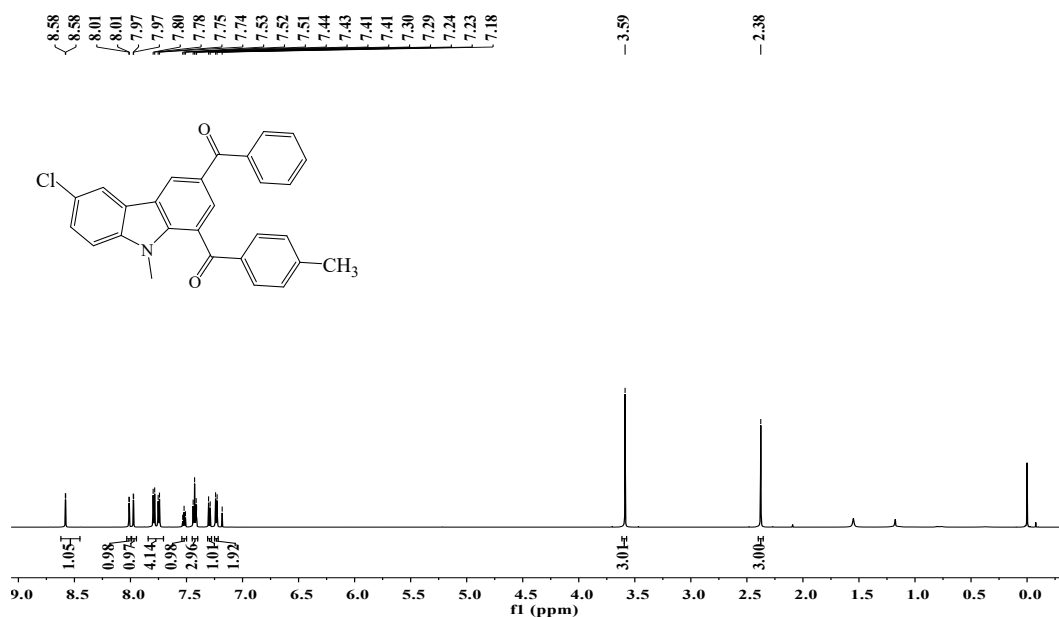


¹³C NMR(600 MHz, CDCl₃)

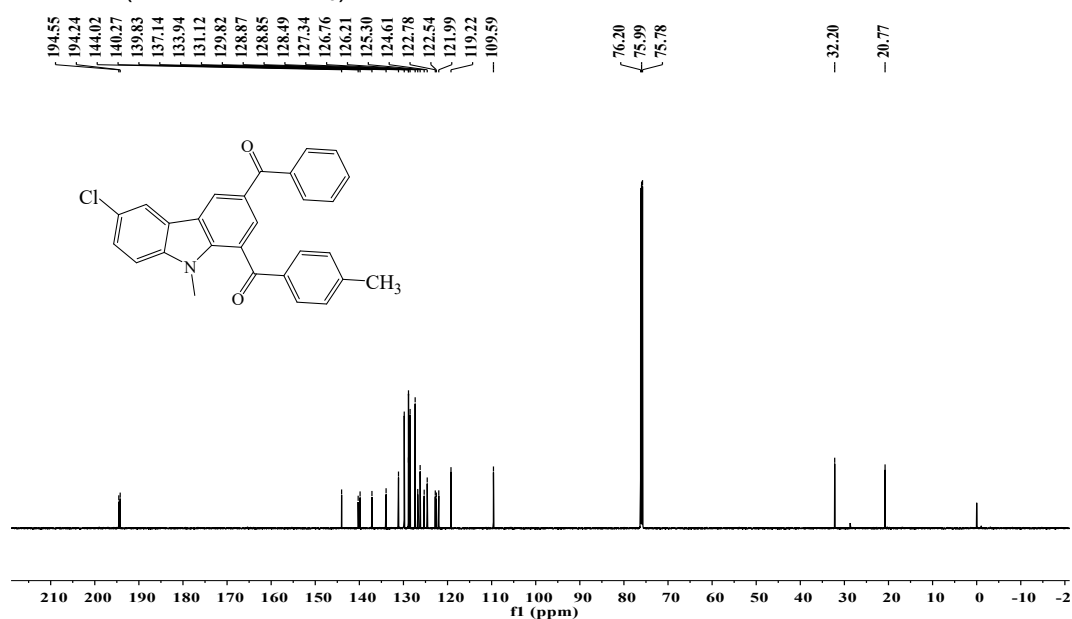


(6-methoxy-9-methyl-9H-carbazole-1,3-diyl)bis(phenylmethanone) (4e): yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 1.6 Hz, 1H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.60-7.48 (m, 3H), 7.42 (q, *J* = 7.6 Hz, 4H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.11 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.86 (s, 3H), 3.57 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.71, 194.69 (Cq each, C=O), 153.85, 140.34, 137.39, 136.65, 136.41, 132.69, 130.94, 129.62, 128.86, 128.80, 127.69, 127.28, 125.85, 124.63, 123.50, 122.14, 121.28, 115.50, 109.39, 102.03, 55.02, 32.24.

¹H NMR(600 MHz, CDCl₃)

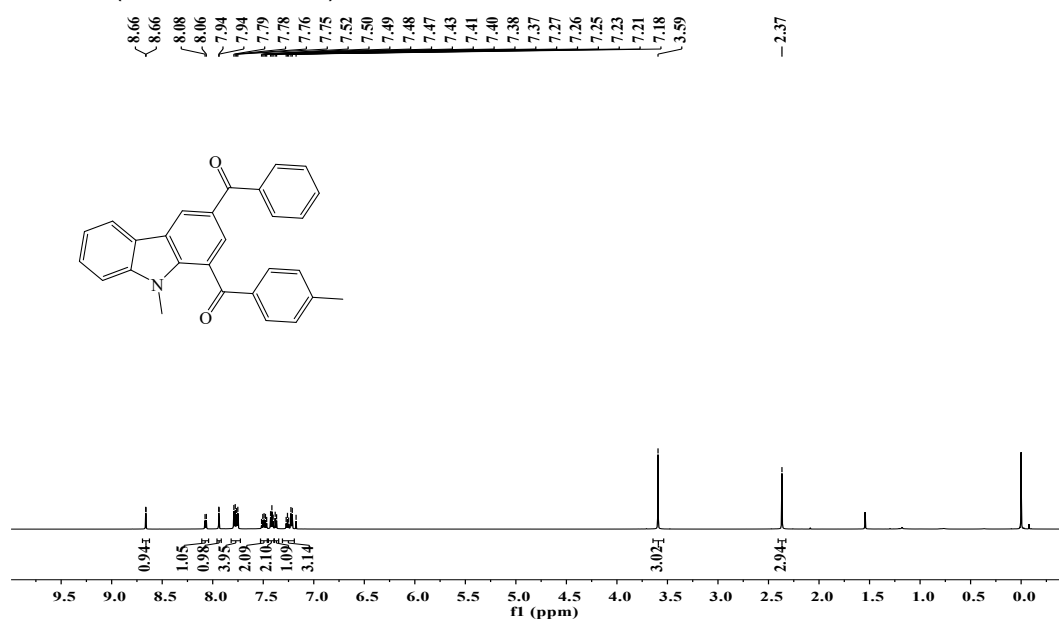


¹³C NMR(600 MHz, CDCl₃)

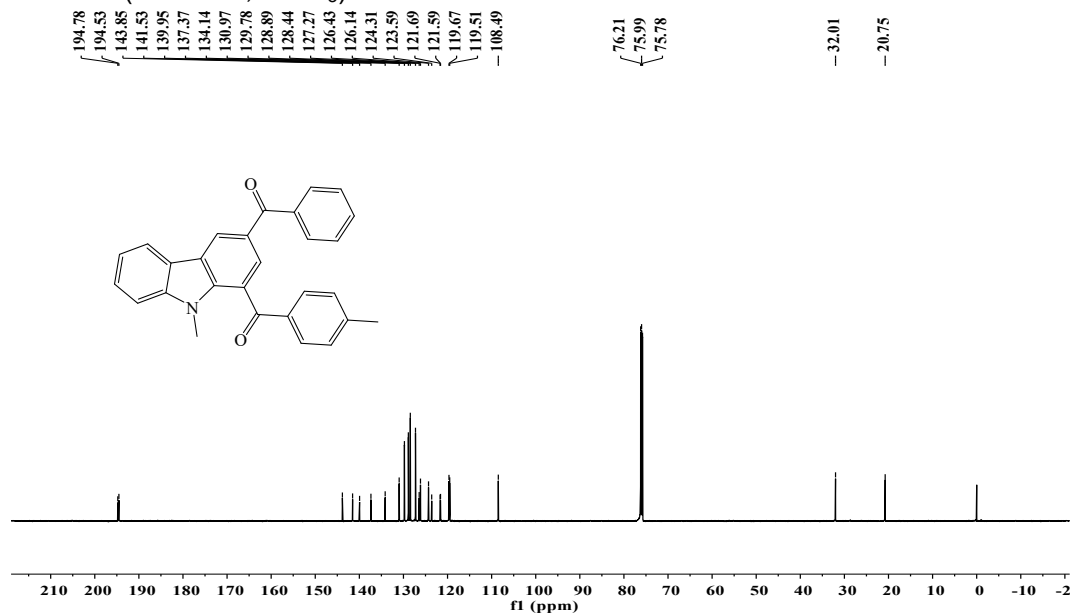


(3-benzoyl-6-chloro-9-methyl-9H-carbazol-1-yl)(p-tolyl)methanone (4f): yellow solid.
¹H NMR (600 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.77 (dd, *J* = 26.3, 7.6 Hz, 4H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45-7.40 (m, 3H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.59 (s, 3H), 2.38 (s, 3H).
¹³C NMR (600 MHz, Chloroform-*d*) δ 194.55, 194.24 (Cq each, C=O), 144.02, 140.27, 139.83, 137.14, 133.94, 131.12, 129.82, 128.87, 128.85, 128.49, 127.34, 126.76, 126.21, 125.30, 124.61, 122.78, 122.54, 121.99, 119.22, 109.59, 32.20, 20.77.

^1H NMR(600 MHz, CDCl_3)

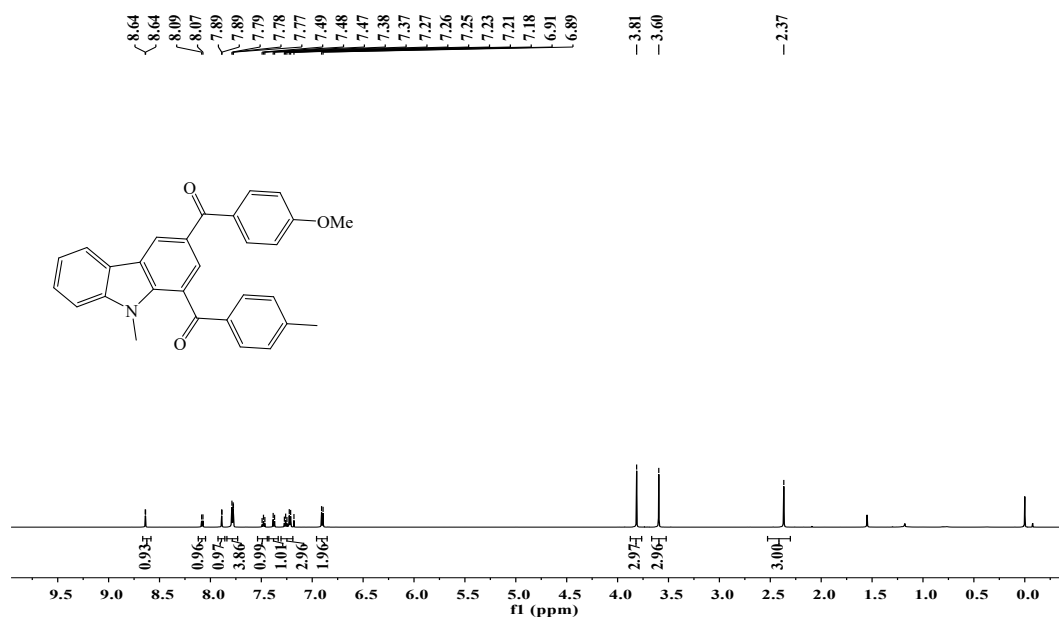


^{13}C NMR(600 MHz, CDCl_3)

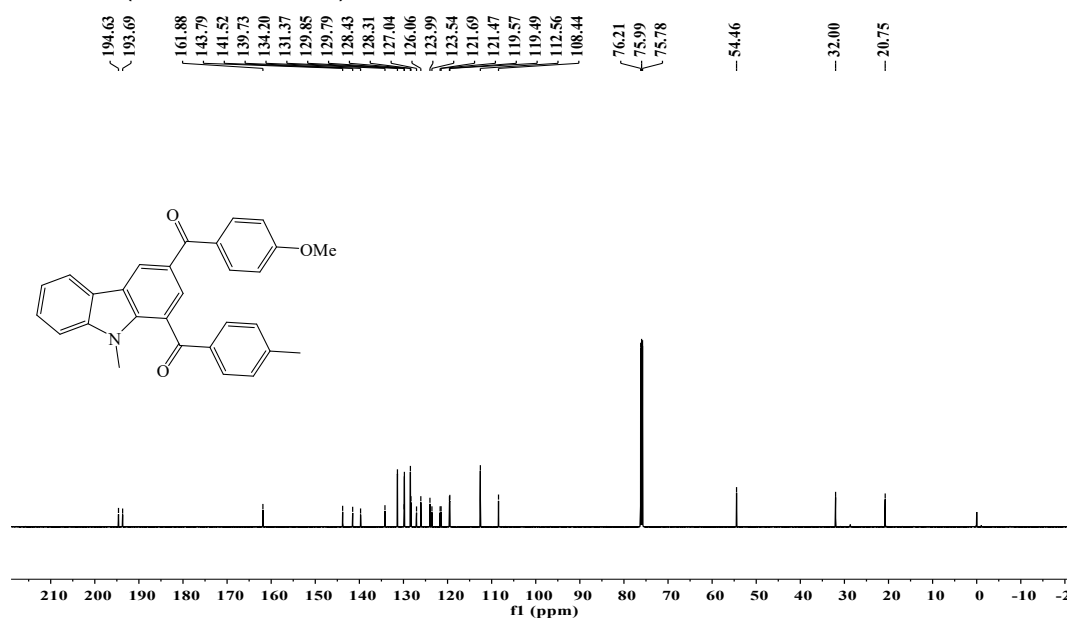


(3-benzoyl-9-methyl-9H-carbazol-1-yl)(p-tolyl)methanone (4g): yellow solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, J = 1.6 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 1.6 Hz, 1H), 7.77 (dd, J = 16.0, 7.6 Hz, 4H), 7.49 (dt, J = 15.4, 7.3 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 8.2 Hz, 1H), 7.31-7.19 (m, 3H), 3.59 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-*d*) δ 194.78, 194.53 (Cq each, C=O), 143.85, 141.53, 139.95, 137.37, 134.14, 130.97, 129.78, 128.89, 128.44, 127.27, 126.43, 126.14, 124.31, 123.59, 121.69, 121.59, 119.67, 119.51, 108.49, 32.01, 20.75.

¹H NMR(600 MHz, CDCl₃)

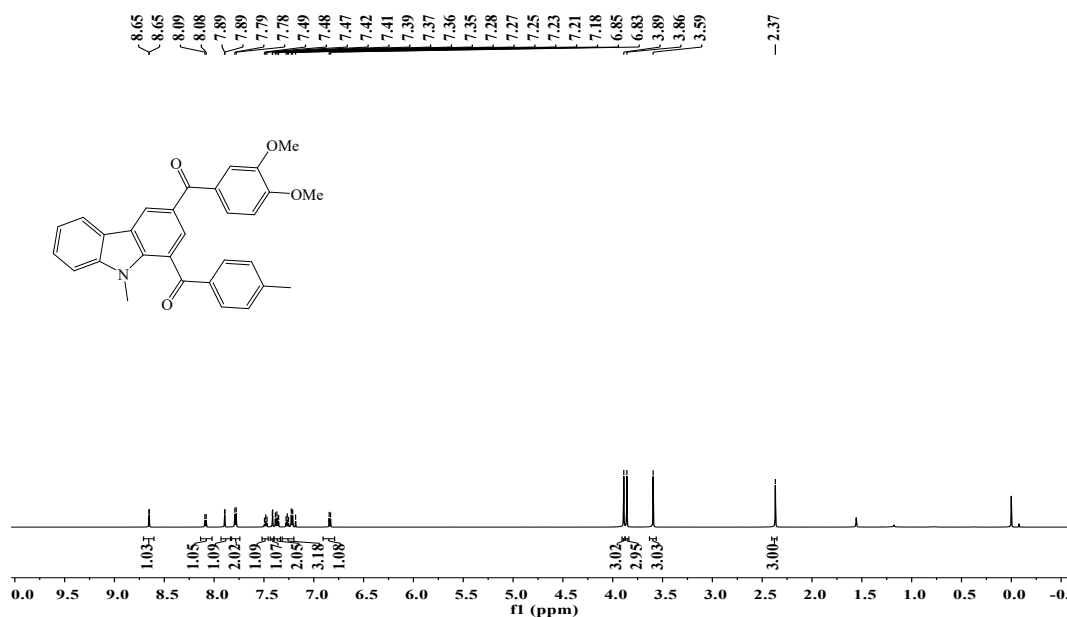


¹³C NMR(600 MHz, CDCl₃)

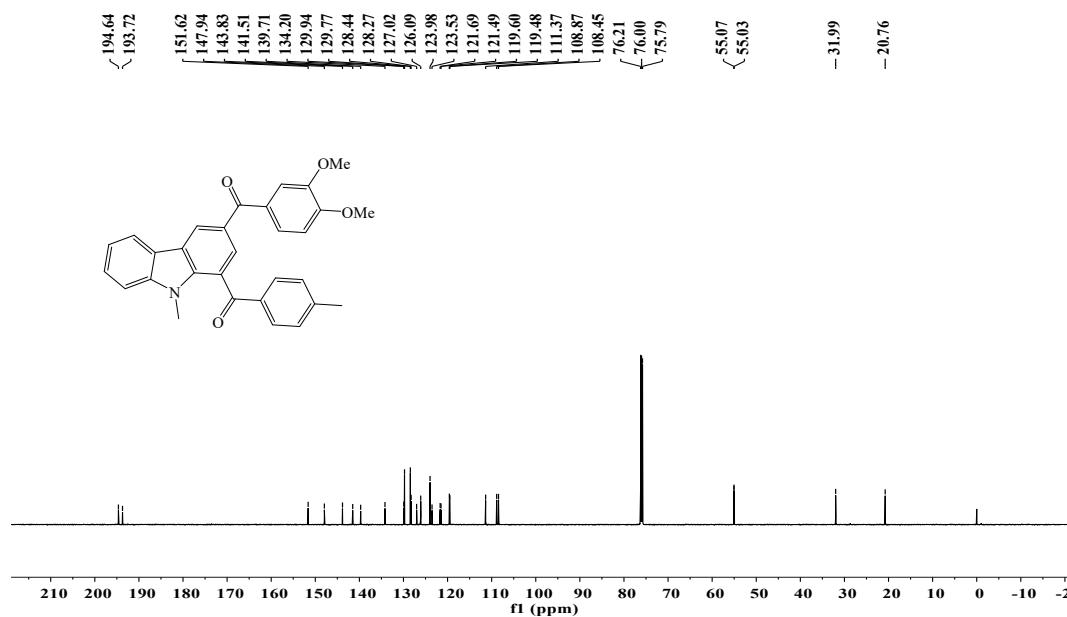


(3-(4-methoxybenzoyl)-9-methyl-9H-carbazol-1-yl)(p-tolyl)methanone (4h): yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.84-7.73 (m, 4H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31-7.19 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.60 (s, 3H), 2.37 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.63, 193.69 (Cq each, C=O), 161.88, 143.79, 141.52, 139.73, 134.20, 131.37, 129.85, 129.79, 128.43, 128.31, 127.04, 126.06, 123.99, 123.54, 121.69, 121.47, 119.57, 119.49, 112.56, 108.44, 54.46, 32.00, 20.75.

^1H NMR(600 MHz, CDCl_3)

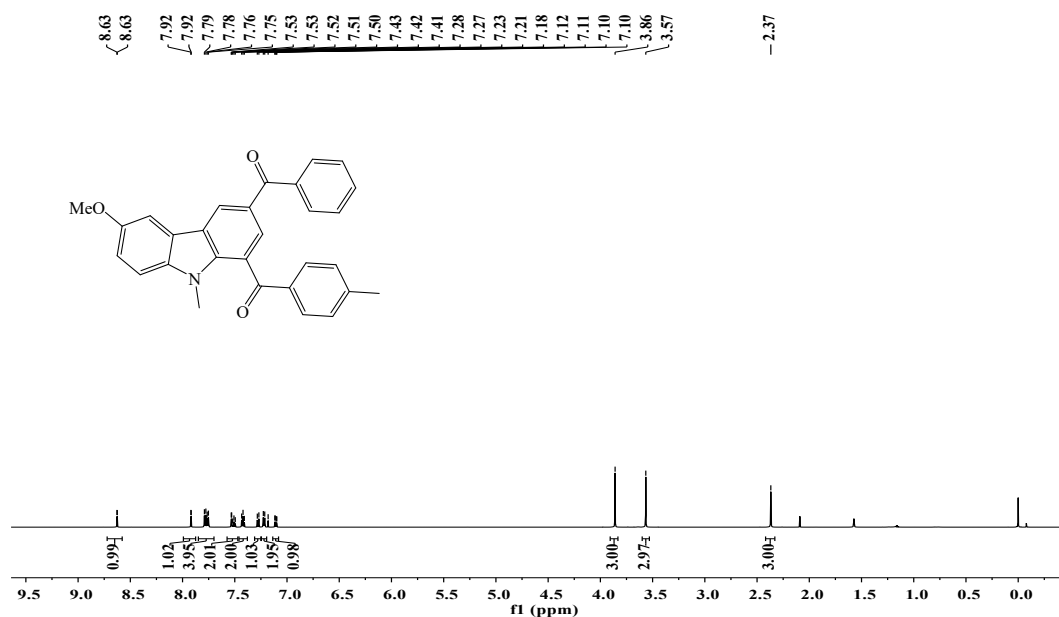


^{13}C NMR(600 MHz, CDCl_3)

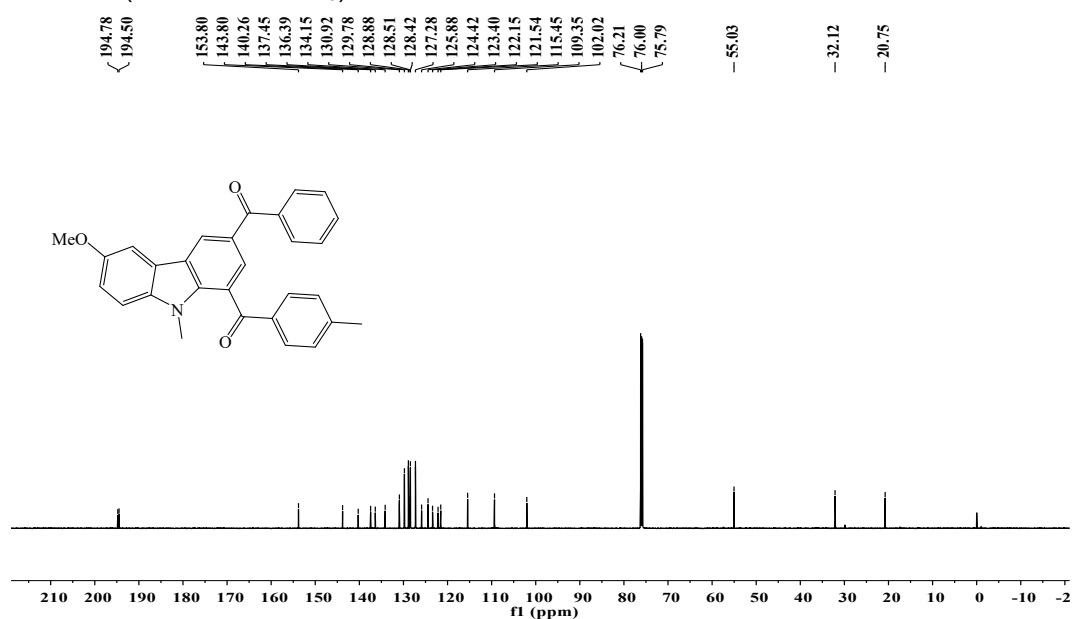


(3-(3,4-dimethoxybenzoyl)-9-methyl-9H-carbazol-1-yl)(p-tolyl)methanone (4i): white solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.65 (d, J = 1.7 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 1.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.40-7.33 (m, 2H), 7.32-7.20 (m, 3H), 6.84 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.59 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-*d*) δ 194.64, 193.72 (Cq each, C=O), 151.62, 147.94, 143.83, 141.51, 139.71, 134.20, 129.94, 129.77, 128.44, 128.27, 127.02, 126.09, 123.98, 123.53, 121.69, 121.49, 119.60, 119.48, 111.37, 108.87, 108.45, 55.07, 55.03, 31.99, 20.76.

^1H NMR(600 MHz, CDCl_3)

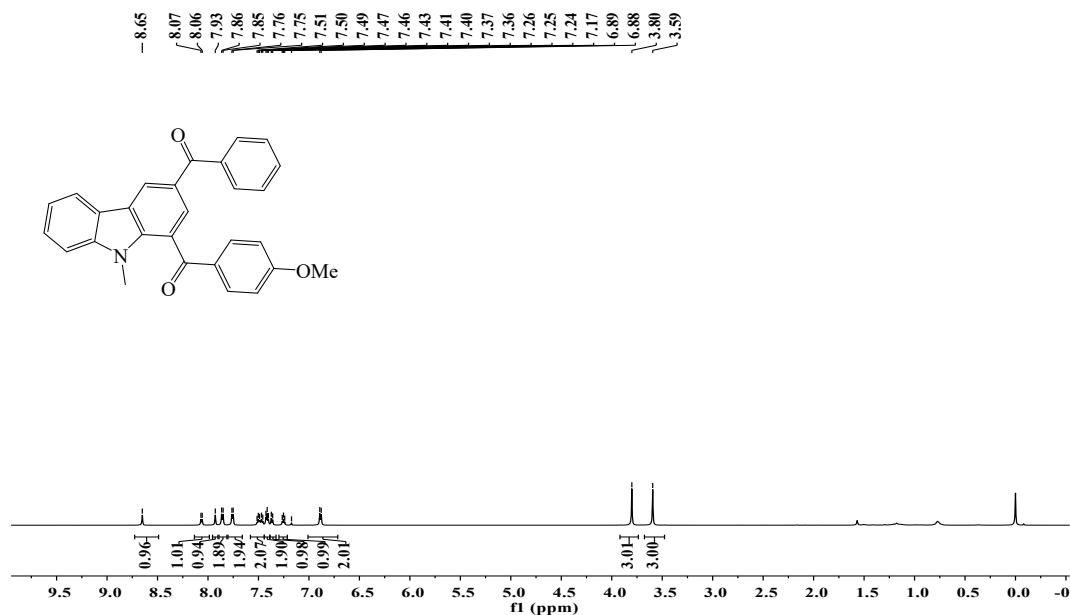


^{13}C NMR(600 MHz, CDCl_3)

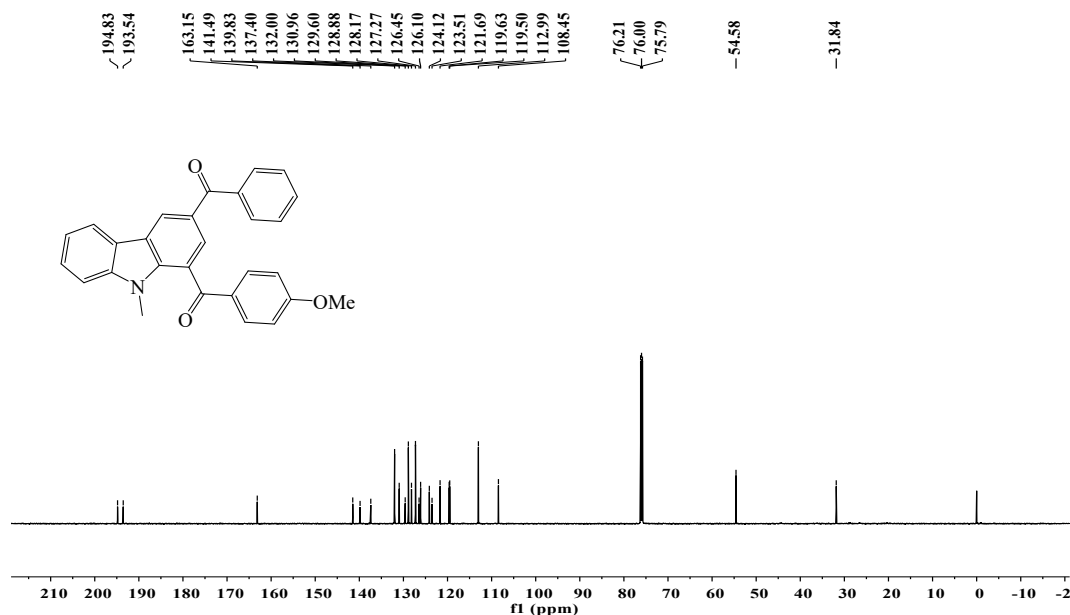


(3-benzoyl-6-methoxy-9-methyl-9H-carbazol-1-yl)(p-tolyl)methanone (4j): yellow solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, J = 1.7 Hz, 1H), 7.92 (d, J = 1.7 Hz, 1H), 7.77 (dd, J = 15.3, 7.6 Hz, 4H), 7.57-7.47 (m, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 8.9 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H), 3.57 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-*d*) δ 194.78, 194.50 (Cq each, C=O), 153.80, 143.80, 140.26, 137.45, 136.39, 134.15, 130.92, 129.78, 128.88, 128.51, 128.42, 127.28, 125.88, 124.42, 123.40, 122.15, 121.54, 115.45, 109.35, 102.02, 55.03, 32.12, 20.75.

^1H NMR(600 MHz, CDCl_3)

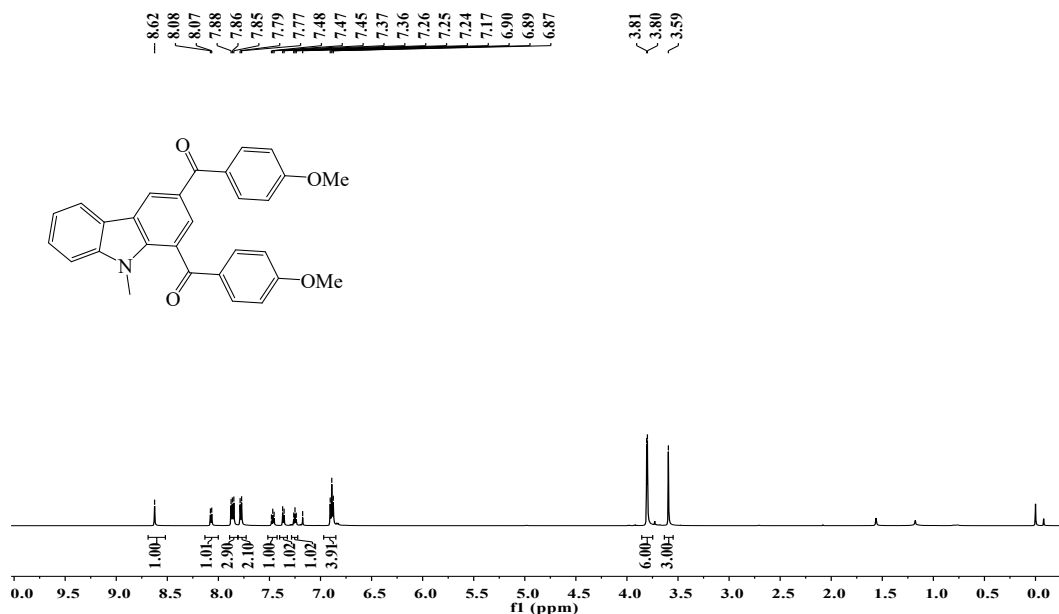


^{13}C NMR(600 MHz, CDCl_3)

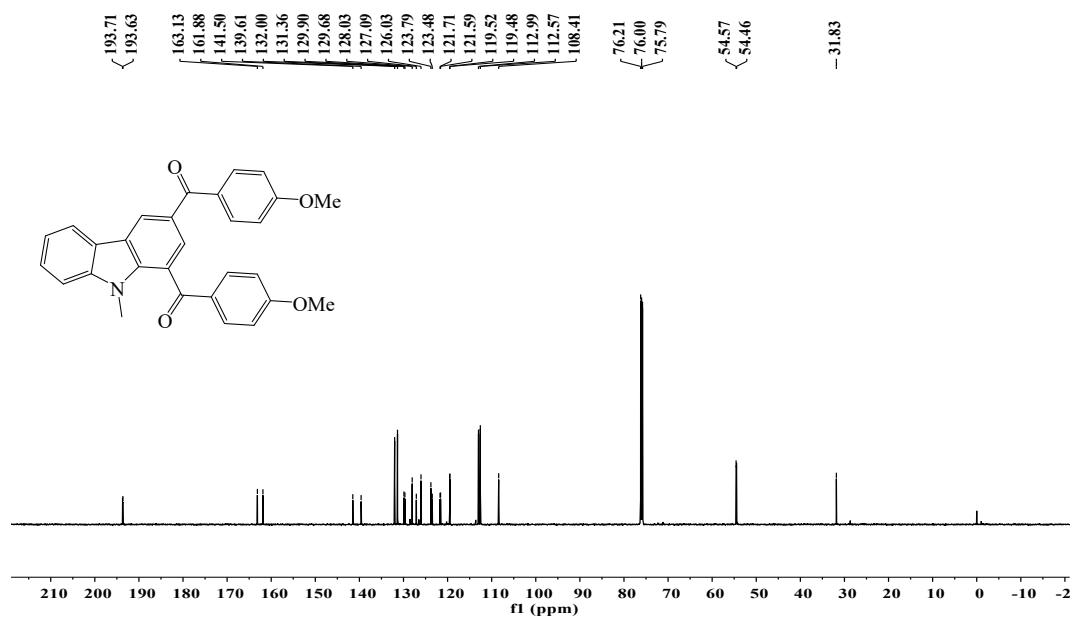


(3-benzoyl-9-methyl-9H-carbazol-1-yl)(4-methoxyphenyl)methanone (4k): yellow solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.93 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 7.4 Hz, 2H), 7.58-7.44 (m, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 8.1 Hz, 1H), 7.25 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-*d*) δ 194.83, 193.54 (Cq each, C=O), 163.15, 141.49, 139.83, 137.40, 132.00, 130.96, 129.60, 128.88, 128.17, 127.27, 126.45, 126.10, 124.12, 123.51, 121.69, 119.63, 119.50, 112.99, 108.45, 54.58, 31.84.

^1H NMR(600 MHz, CDCl_3)

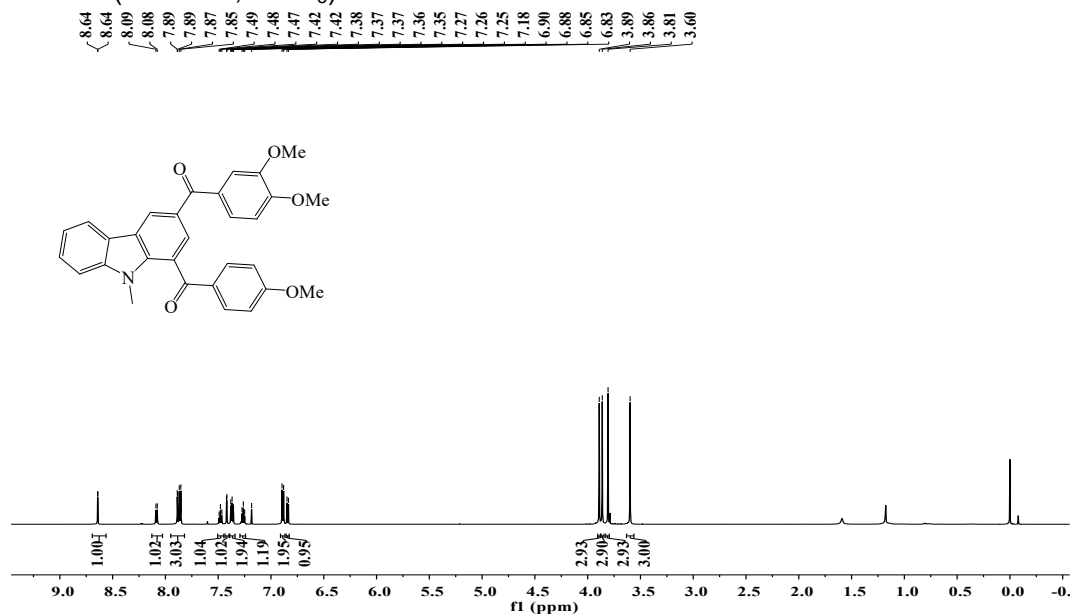


^{13}C NMR(600 MHz, CDCl_3)

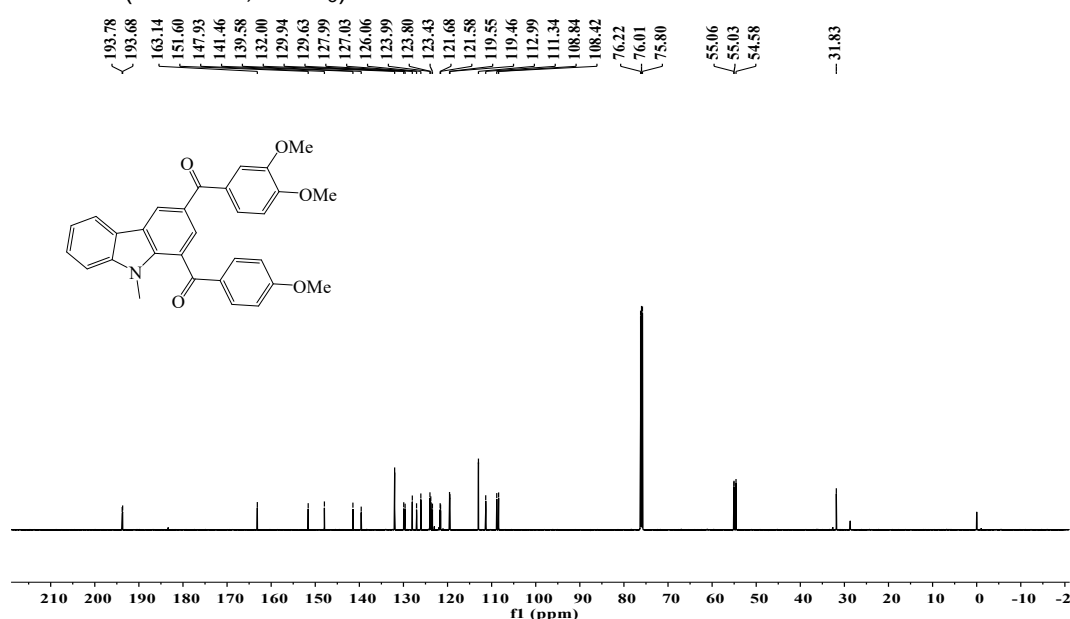


(9-methyl-9H-carbazole-1,3-diyl)bis((4-methoxyphenyl)methanone) (4l): yellow solid. ^1H NMR (600 MHz, Chloroform- d) δ 8.62 (s, 1H), 8.07 (d, $J = 7.7$ Hz, 1H), 7.89 – 7.81 (m, 3H), 7.78 (d, $J = 8.6$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 6.89 (t, $J = 9.0$ Hz, 4H), 3.81 and 3.80 (s each, 3H), 3.59 (s, 3H). ^{13}C NMR (600 MHz, Chloroform- d) δ 193.71, 193.63 (Cq each, C=O), 163.13, 161.88, 141.50, 139.61, 132.00, 131.36, 129.90, 129.68, 128.03, 127.09, 126.03, 123.79, 123.48, 121.71, 121.59, 119.52, 119.48, 112.99, 112.57, 108.41, 54.57, 54.46, 31.83.

¹H NMR(600 MHz, CDCl₃)

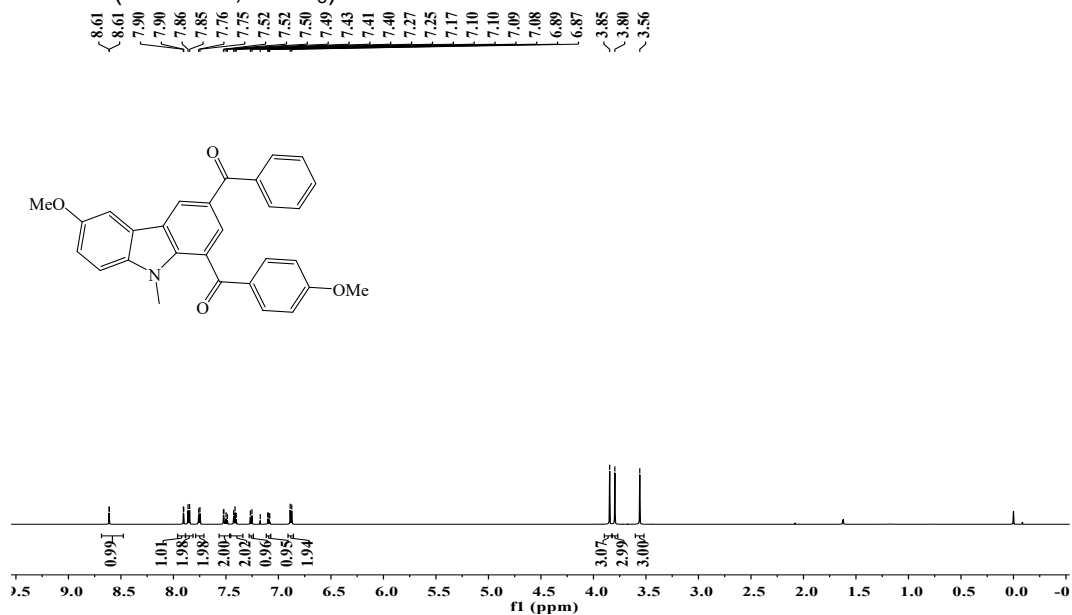


¹³C NMR(600 MHz, CDCl₃)

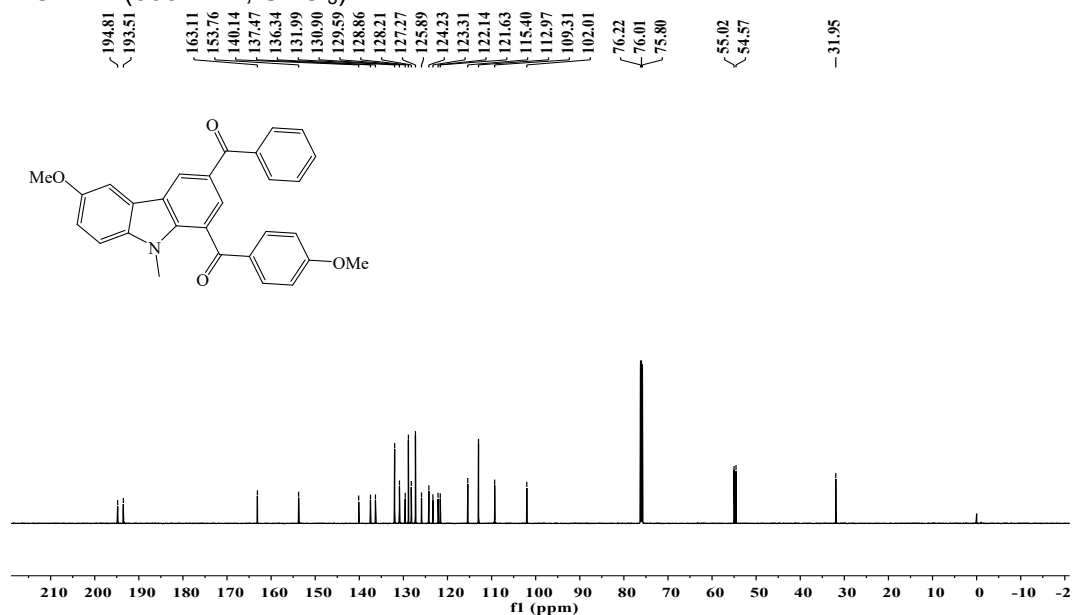


(3-(3,4-dimethoxybenzoyl)-9-methyl-9H-carbazol-1-yl)(4-methoxyphenyl)methanone (4m): white solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, J = 1.6 Hz, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.95-7.82 (m, 3H), 7.48 (t, J = 7.7 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H), 7.39-7.34 (m, 2H), 7.26 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 193.78, 193.68 (Cq each, C=O), 163.14, 151.60, 147.93, 141.46, 139.58, 132.00, 129.94, 129.63, 127.99, 127.03, 126.06, 123.99, 123.80, 123.43, 121.68, 121.58, 119.55, 119.46, 112.99, 111.34, 108.84, 108.42, 55.06, 55.03, 54.58, 31.83.

¹H NMR(600 MHz, CDCl₃)



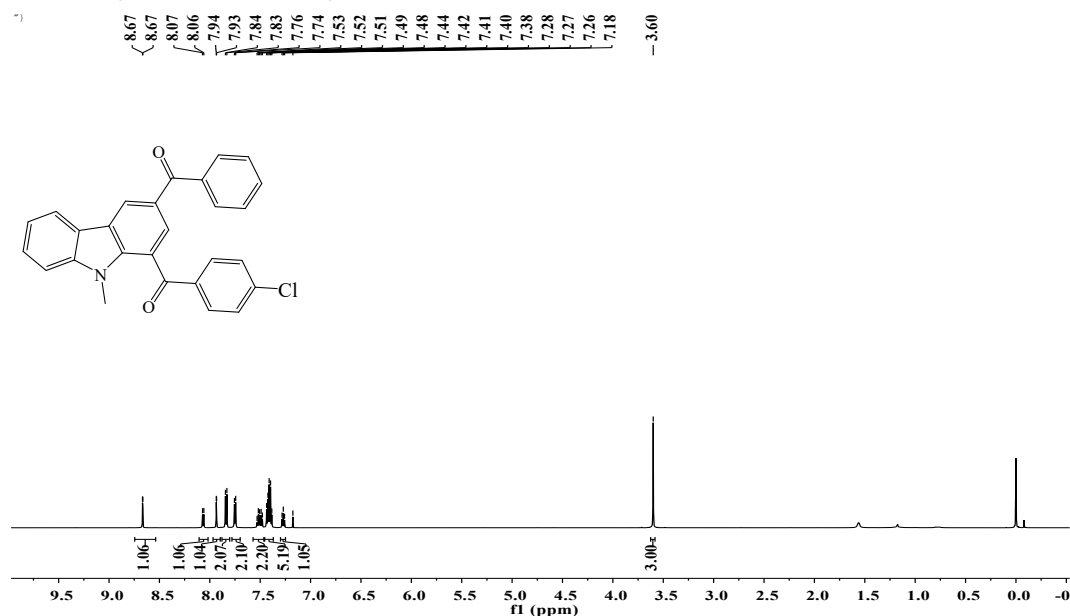
¹³C NMR(600 MHz, CDCl₃)



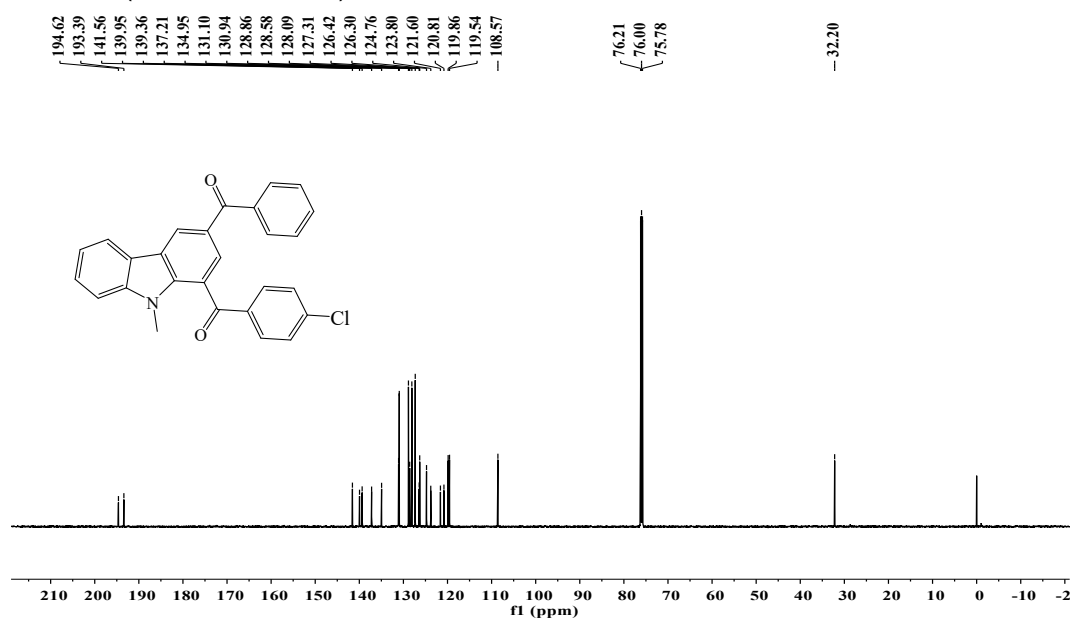
(3-benzoyl-6-methoxy-9-methyl-9H-carbazol-1-yl)(4-methoxyphenyl)methanone(4n):

yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.61 (d, J = 1.7 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.85 (d, J = 8.9 Hz, 2H), 7.75 (d, J = 7.0 Hz, 2H), 7.56-7.46 (m, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.26 (d, J = 8.9 Hz, 1H), 7.09 (dd, J = 8.8, 2.5 Hz, 1H), 6.88 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.56 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.81, 193.51, 163.11, 153.76, 140.14, 137.47, 136.34, 131.99, 130.90, 129.59, 128.86, 128.21, 127.27, 125.89, 124.23, 123.31, 122.14, 121.63, 115.40, 112.97, 109.31, 102.01, 55.02, 54.57, 31.95.

¹H NMR(600 MHz, CDCl₃)

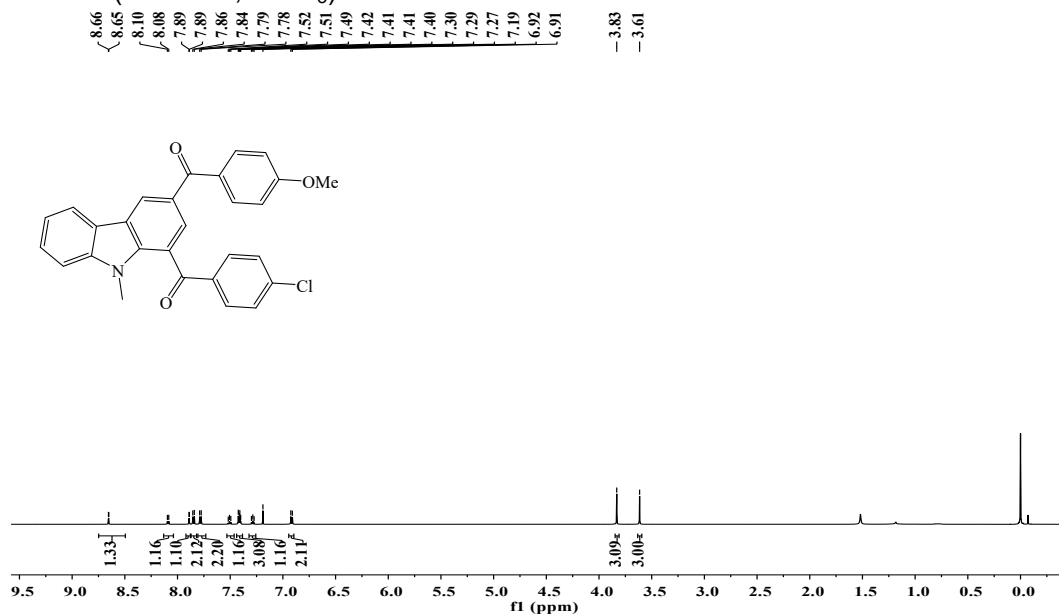


¹³C NMR(600 MHz, CDCl₃)

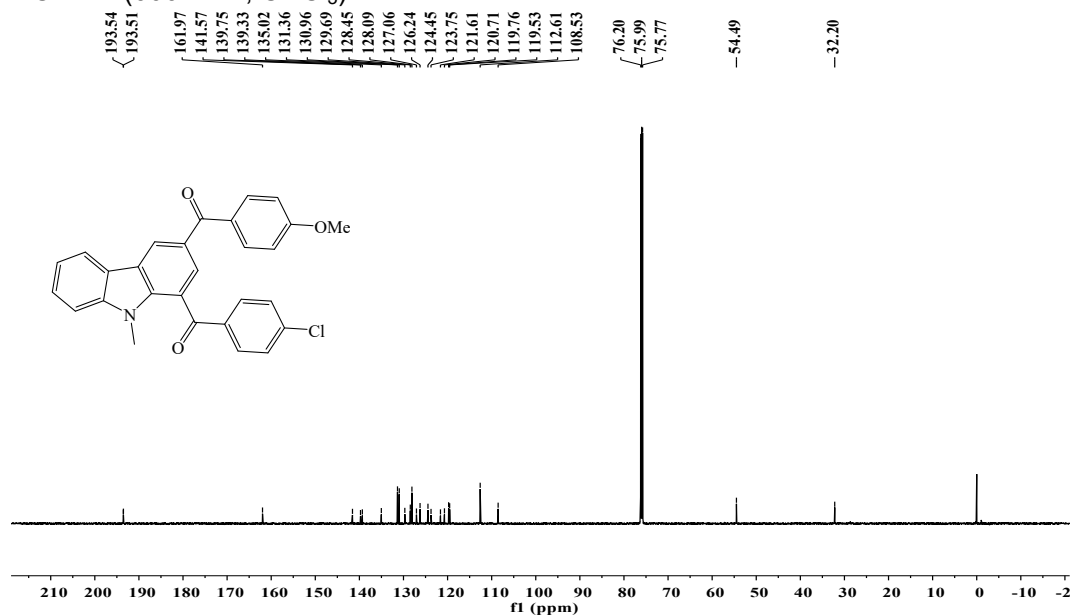


(3-benzoyl-9-methyl-9H-carbazol-1-yl)(4-chlorophenyl)methanone (4o): yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.67 (d, J = 1.6 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.93 (d, J = 1.6 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 7.1 Hz, 2H), 7.50 (dt, J = 16.2, 7.4 Hz, 2H), 7.41 (dt, J = 15.8, 7.6 Hz, 5H), 7.27 (t, J = 7.5 Hz, 1H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.62, 193.39 (Cq each, C=O), 141.56, 139.95, 139.36, 137.21, 134.95, 131.10, 130.94, 128.86, 128.58, 128.09, 127.31, 126.42, 126.30, 124.76, 123.80, 121.60, 120.81, 119.86, 119.54, 108.57, 32.20.

¹H NMR(600 MHz, CDCl₃)

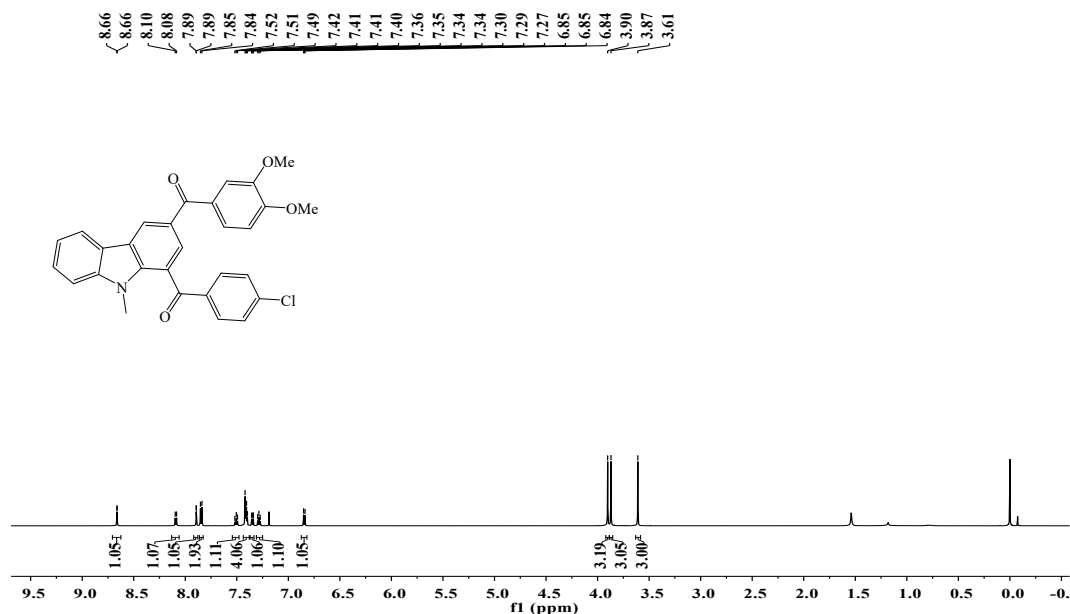


¹³C NMR(600 MHz, CDCl₃)

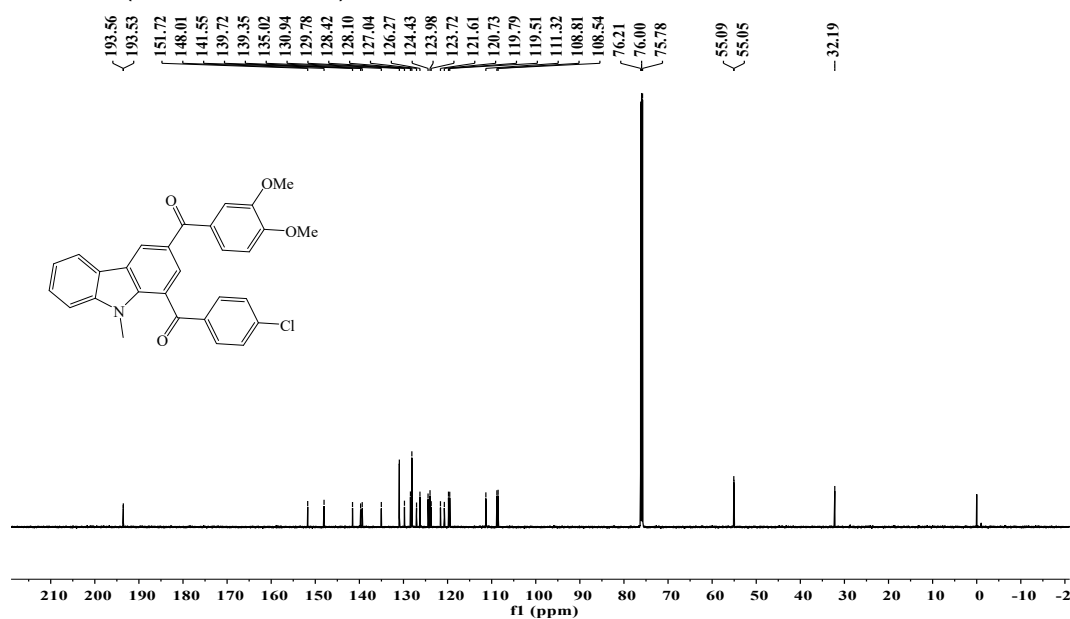


(1-(4-chlorobenzoyl)-9-methyl-9H-carbazol-3-yl)(4-methoxyphenyl)methanone (4p): yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.65 (d, J = 1.6 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.41 (dd, J = 8.4, 5.1 Hz, 3H), 7.29 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.61 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 193.54, 193.51 (Cq each, C=O), 161.97, 141.57, 139.75, 139.33, 135.02, 131.36, 130.96, 129.69, 128.45, 128.09, 127.06, 126.24, 124.45, 123.75, 121.61, 120.71, 119.76, 119.53, 112.61, 108.53, 54.49, 32.20.

¹H NMR(600 MHz, CDCl₃)



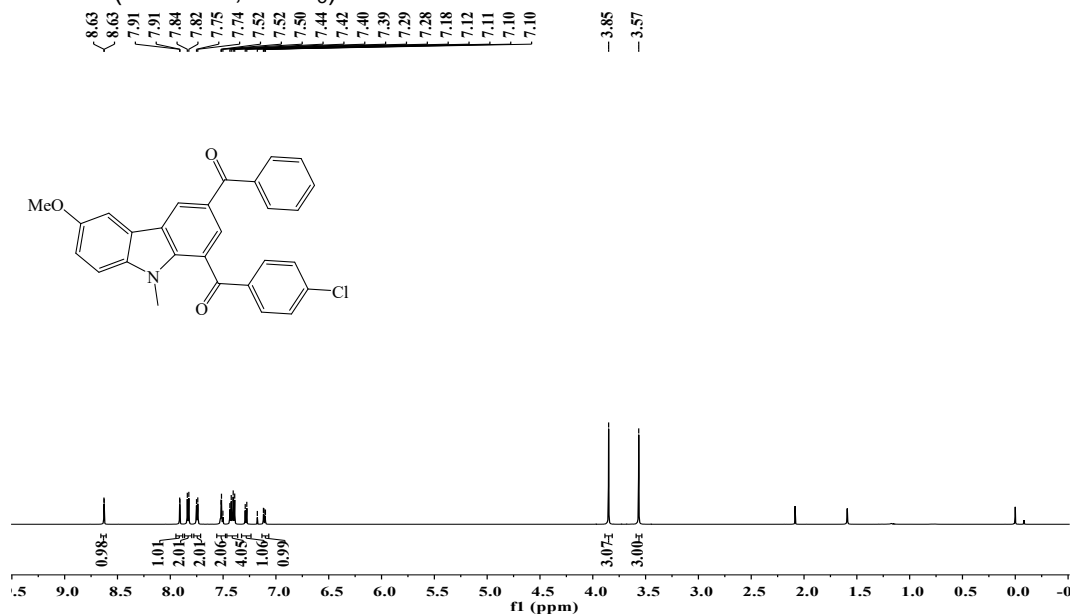
¹³C NMR(600 MHz, CDCl₃)



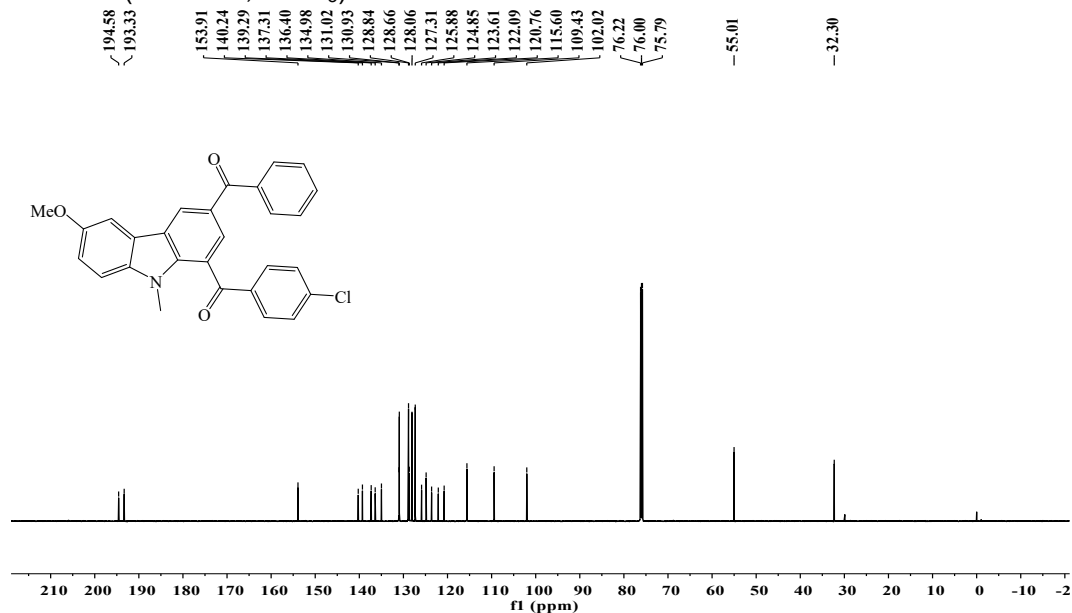
(1-(4-chlorobenzoyl)-9-methyl-9H-carbazol-3-yl)(3,4-dimethoxyphenyl)methanone

(4q): pale yellow. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 1.5 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.4, 5.0 Hz, 4H), 7.35 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.61 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 193.56, 193.53 (Cq each, C=O), 151.72, 148.01, 141.55, 139.72, 139.35, 135.02, 130.94, 129.78, 128.42, 128.10, 127.04, 126.27, 124.43, 123.98, 123.72, 121.61, 120.73, 119.79, 119.51, 111.32, 108.81, 108.54, 55.09, 55.05, 32.19.

¹H NMR(600 MHz, CDCl₃)



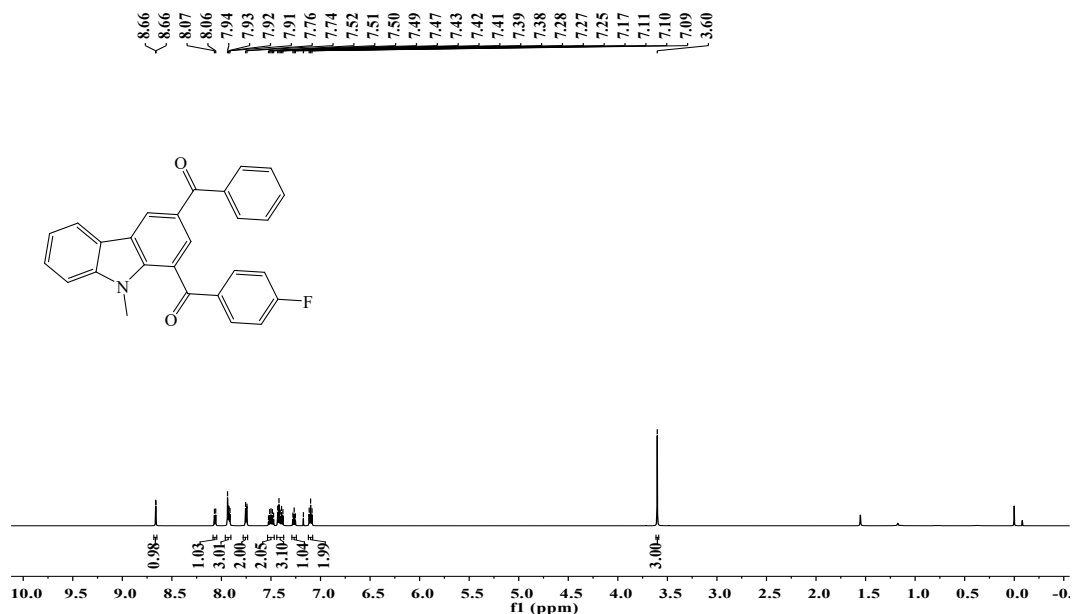
¹³C NMR(600 MHz, CDCl₃)



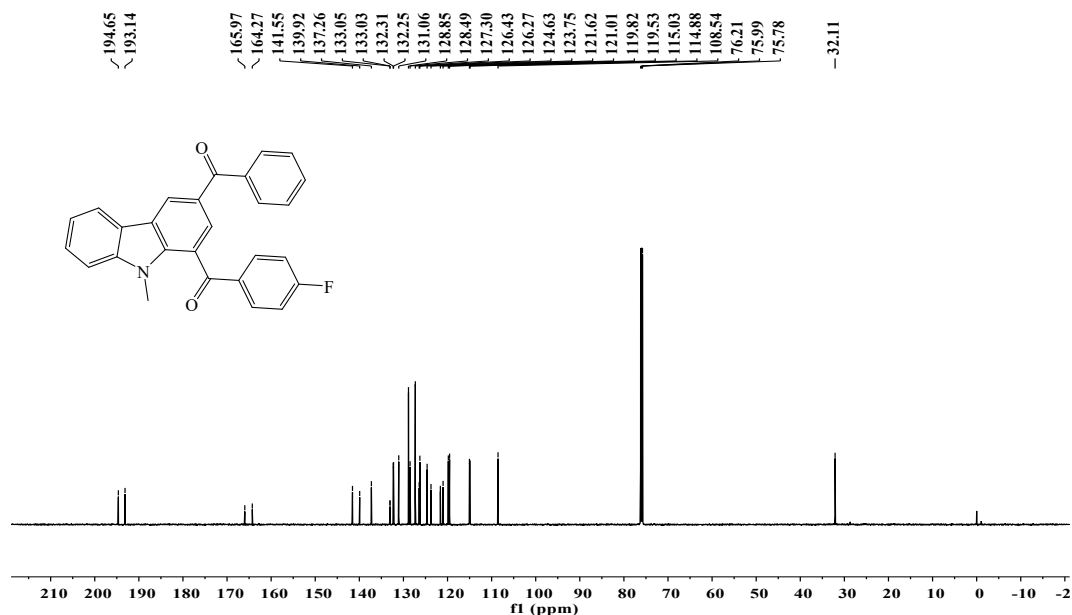
(3-benzoyl-6-methoxy-9-methyl-9H-carbazol-1-yl)(4-chlorophenyl)methanone(4r):

yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 7.1 Hz, 2H), 7.56-7.48 (m, 2H), 7.41 (dd, *J* = 19.3, 8.1 Hz, 4H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.11 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.85 (s, 3H), 3.57 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.58, 193.33 (Cq each, C=O), 153.91, 140.24, 139.29, 137.31, 136.40, 134.98, 131.02, 130.93, 128.84, 128.66, 128.06, 127.31, 125.88, 124.85, 123.61, 122.09, 120.76, 115.60, 109.43, 102.02, 55.01, 32.30.

¹H NMR(600 MHz, CDCl₃)



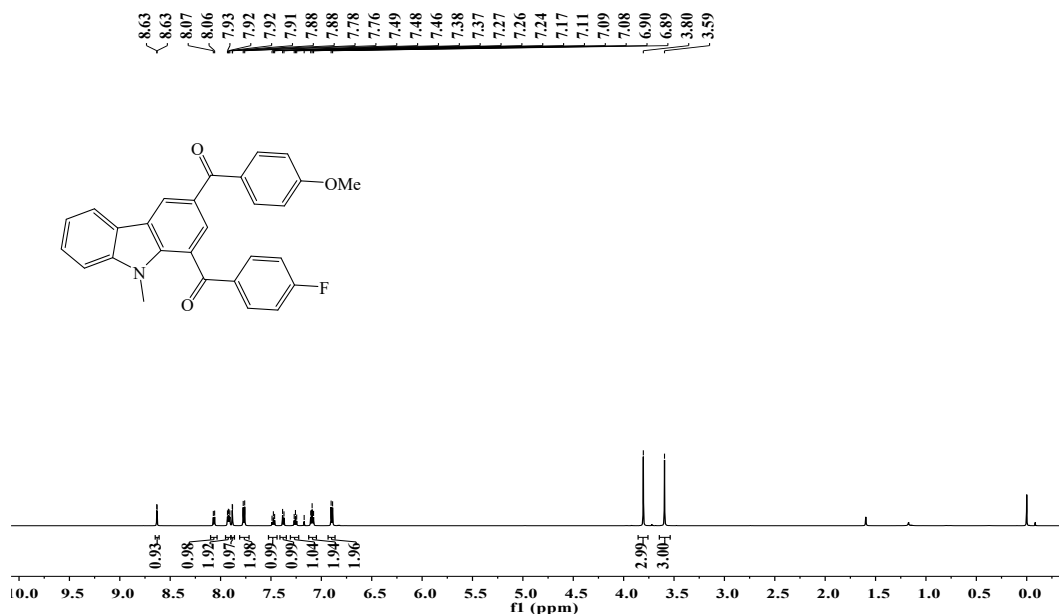
¹³C NMR(600 MHz, CDCl₃)



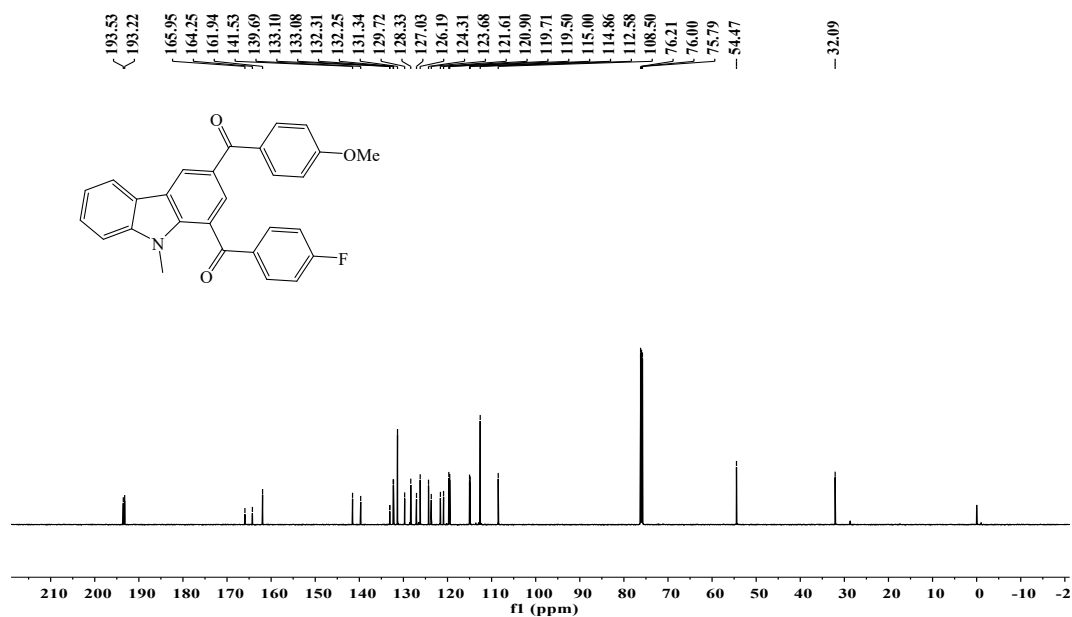
(3-benzoyl-9-methyl-9H-carbazol-1-yl)(4-fluorophenyl)methanone (4s): yellow solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, J = 1.6 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.96-7.90 (m, 3H), 7.75 (d, J = 8.3 Hz, 2H), 7.50 (dt, J = 15.6, 7.3 Hz, 2H), 7.44-7.37 (m, 3H), 7.27 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.65, 193.14 (Cq each, C=O), 165.97, 164.27, 141.55, 139.92, 137.26, 133.05, 133.03, 132.31, 132.25, 131.06, 128.85, 128.49, 127.30, 126.43, 126.27, 124.63, 123.75, 121.62, 121.01, 119.82, 119.53, 115.03, 114.88, 108.54, 76.21, 75.99, 75.78, 32.11.

^1H NMR(600 MHz, CDCl_3)



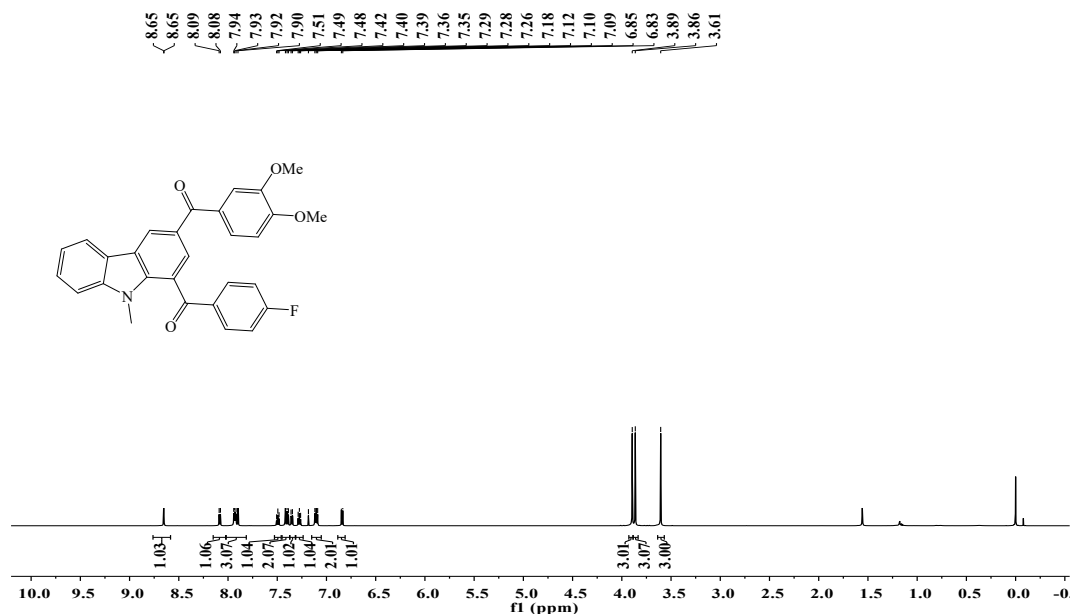
^{13}C NMR(600 MHz, CDCl_3)



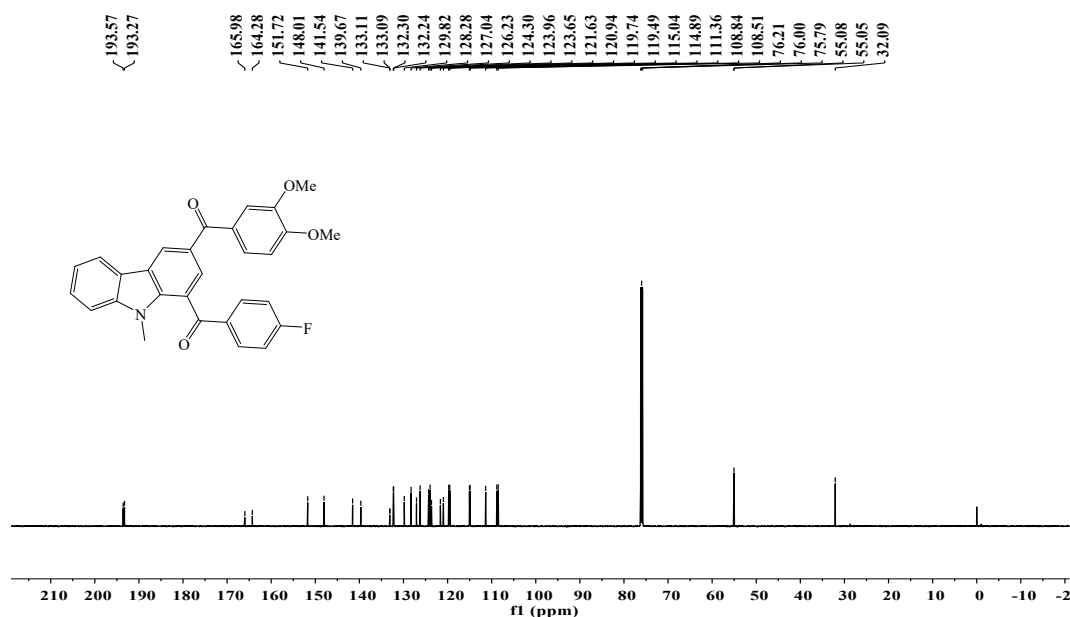
(1-(4-fluorobenzoyl)-9-methyl-9H-carbazol-3-yl)(4-methoxyphenyl)methanone

(4t) : yellow solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, J = 1.5 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.92 (dd, J = 8.7, 5.4 Hz, 2H), 7.88 (d, J = 1.5 Hz, 1H), 7.77 (d, J = 8.7 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 8.5 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (600 MHz, Chloroform-*d*) δ 193.53, 193.22 (Cq each, C=O), 165.95, 164.25, 161.94, 141.53, 139.69, 133.10, 133.08, 132.31, 132.25, 131.34, 129.72, 128.33, 127.03, 126.19, 124.31, 123.68, 121.61, 120.90, 119.71, 119.50, 115.00, 114.86, 112.58, 108.50, 54.47, 32.09.

¹H NMR(600 MHz, CDCl₃)



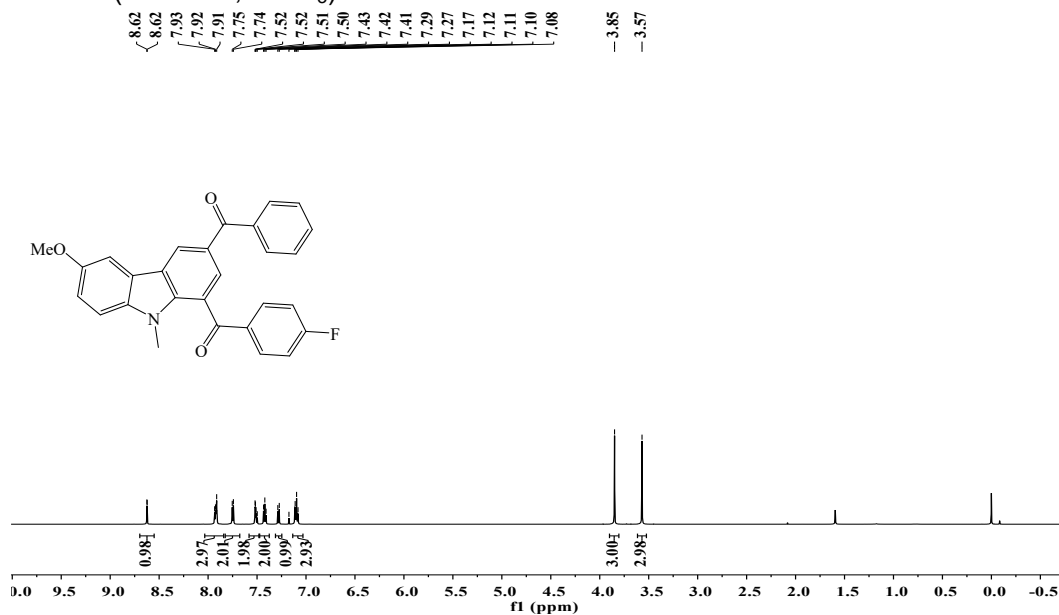
¹³C NMR(600 MHz, CDCl₃)



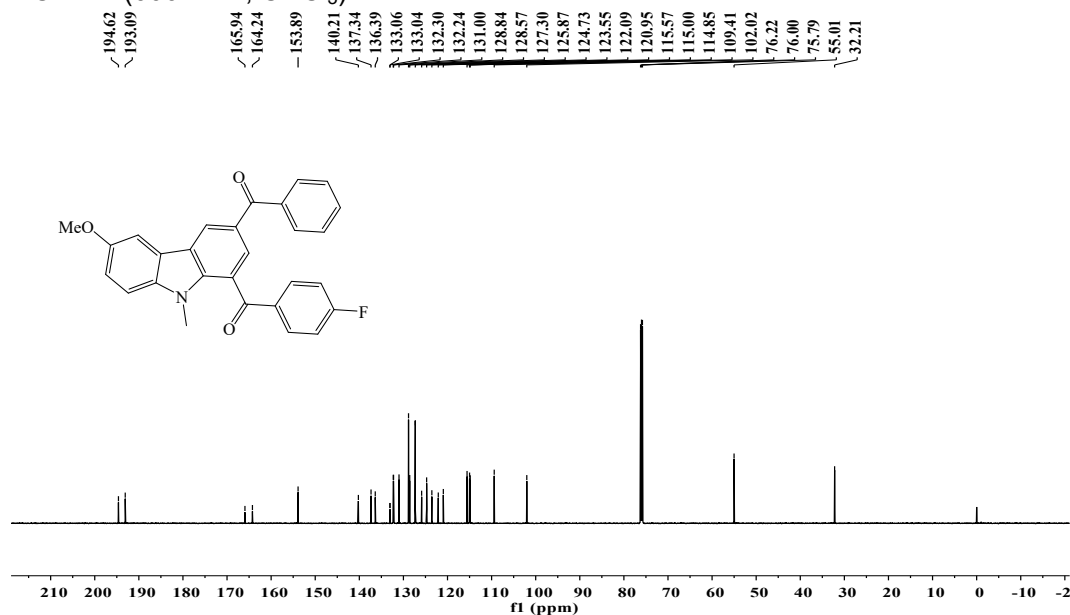
(3-(3,4-dimethoxybenzoyl)-9-methyl-9H-carbazol-1-yl)(4-fluorophenyl)methanone

(4u): white solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 1.5 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 8.02-7.81 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.45-7.37 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.61 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 193.57, 193.27 (Cq each, C=O), 165.98, 164.28, 151.72, 148.01, 141.54, 139.67, 133.11, 133.09, 132.30, 132.24, 129.82, 128.28, 127.04, 126.23, 124.30, 123.96, 123.65, 121.63, 120.94, 119.74, 119.49, 115.04, 114.89, 111.36, 108.84, 108.51, 55.08, 55.05, 32.09.

¹H NMR(600 MHz, CDCl₃)



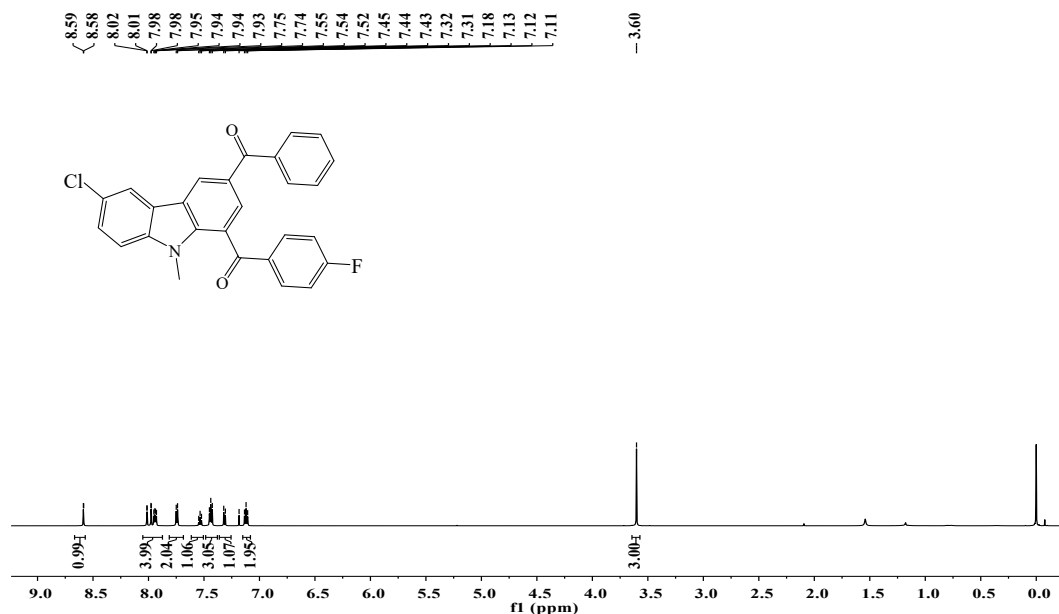
¹³C NMR(600 MHz, CDCl₃)



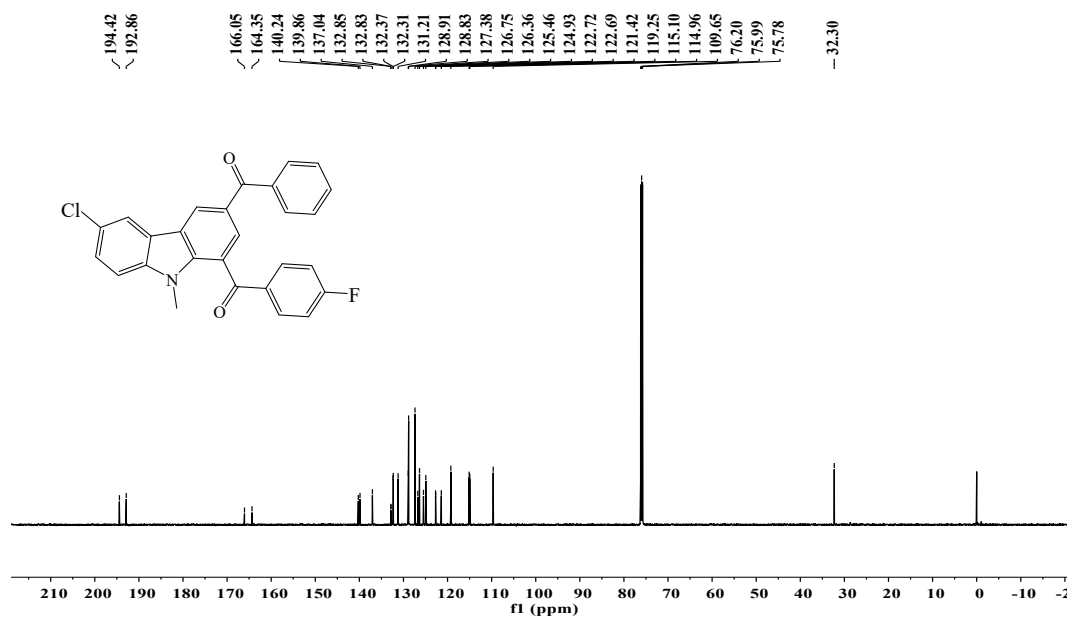
(3-benzoyl-6-methoxy-9-methyl-9H-carbazol-1-yl)(4-fluorophenyl)methanone (4v):

yellow solid. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.03-7.84 (m, 3H), 7.75 (d, *J* = 7.1 Hz, 2H), 7.58-7.48 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.14-7.03 (m, 3H), 3.85 (s, 3H), 3.57 (s, 3H). ¹³C NMR (600 MHz, Chloroform-*d*) δ 194.62, 193.09 (Cq each, C=O), 165.94, 164.24, 153.89, 140.21, 137.34, 136.39, 133.06, 133.04, 132.30, 132.24, 131.00, 128.84, 128.57, 127.30, 125.87, 124.73, 123.55, 122.09, 120.95, 115.57, 115.00, 114.85, 109.41, 102.02, 76.22, 76.00, 75.79, 55.01, 32.21.

¹H NMR(600 MHz, CDCl₃)



¹³C NMR(600 MHz, CDCl₃)



(3-benzoyl-6-chloro-9-methyl-9H-carbazol-1-yl)(4-fluorophenyl)methanone (4w): yellow solid. ¹H NMR (600 MHz, Chloroform-d) δ 8.59 (d, J = 1.6 Hz, 1H), 8.05-7.87 (m, 4H), 7.74 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.48-7.38 (m, 3H), 7.31 (d, J = 8.7 Hz, 1H), 7.12 (t, J = 8.5 Hz, 2H), 3.60 (s, 3H). ¹³C NMR (600 MHz, Chloroform-d) δ 194.42, 192.86 (Cq each, C=O), 166.05, 164.35, 140.24, 139.86, 137.04, 132.85, 132.83, 132.37, 132.31, 131.21, 128.91, 128.83, 127.38, 126.75, 126.36, 125.46, 124.93, 122.72, 122.69, 121.42, 119.25, 115.10, 114.96, 109.65, 32.30.