Supplementary Information

Electrochemical Dehydrogenative Cyclization/Aromatization of Aniline-Tethered Alkylidenecyclopropanes: Facile Access to Benzo[*c*]carbazole Frameworks

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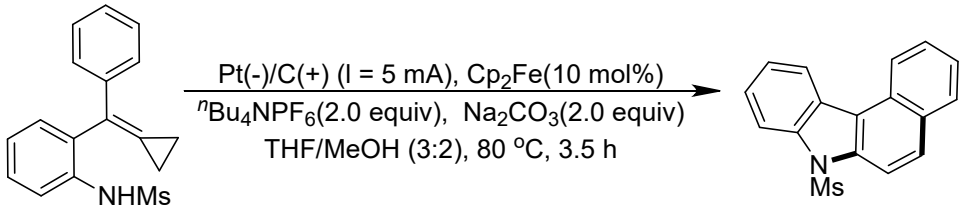
(A) Typical Experimental Procedure

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on an NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is graphite rod (Φ6 mm×80 mm) and cathode electrode is platinum electrodes (1.0×1.0 cm^2).

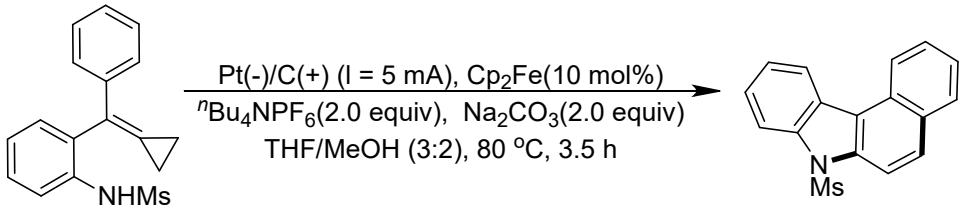
(b) General procedures for electrochemical dehydrogenative cyclization /aromatization of aniline-tethered Alkylidenecyclopropanes



To an undivided three-necked bottle (10 mL) were added **1a**[1] [2]. (0.2 mmol), Na_2CO_3 (2.0 equiv), $^{n}Bu_4NPF_6$ (2.0 equiv), Cp_2Fe (10 mol%), THF (4.5 mL) and MeOH (3 mL). The bottle was equipped with platinum electrodes (1.0×1.0 cm^2) as cathode and graphite rod electrode as anode under air or argon. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at 80 °C for 3.5 h until complete consumption of **1a** as monitored by TLC. After the reaction was finished, the solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered

and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **2a**.

(c) Screening of optimal reaction conditions



Entry	Variation from the Standard Conditions	Yield [%][j]
1	none	83
2	no catalyst	trace
3	no base	8
4	no electric current	0
5	3 mA	45[c]
6	7 mA	70[d]
7	$^{n}Bu_4NBF_4$ instead of $^{n}Bu_4NPF_6$	62
8	$^{n}Bu_4NBr$ instead of $^{n}Bu4NPF_6$	66
9	$LiClO_4$ instead of $^{n}Bu_4NPF_6$	70
10	$NaHCO_3$ instead Na_2CO_3	41
11	K_2CO_3 instead Na_2CO_3	50
12	Na_2HPO_4 instead Na_2CO_3	58
13	RVC as anode	40
14	Ni plate as cathode	trace
15	Zn plate as cathode	trace
16	MeCN as solvent	0
17	DMF as solvent	0
18	THF : MeOH = 4 : 1	67
19	THF : MeOH = 2 : 1	55
20	THF as solvent	0
21	MeOH as solvent	40
22	under air atmosphere	82

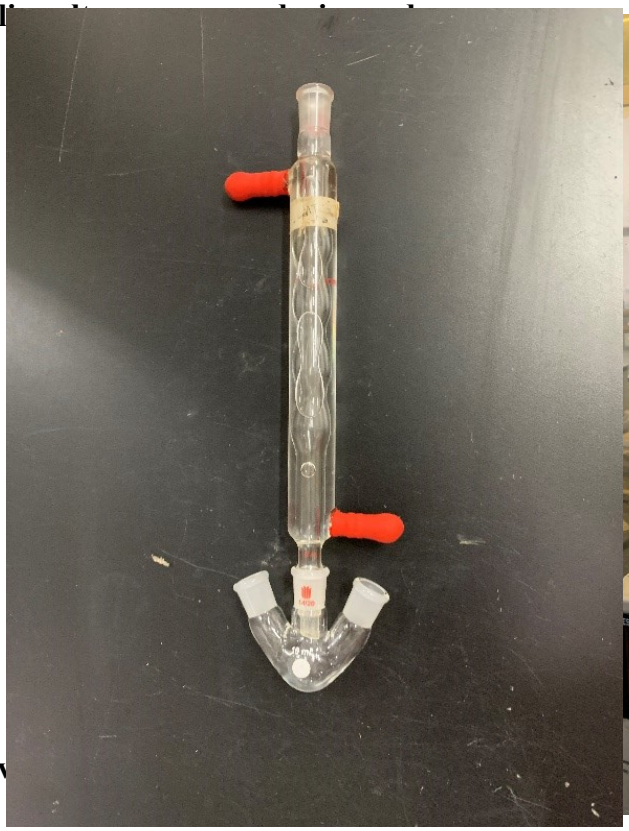
[a] Standard reaction conditions: graphite rod (Φ 6 mm) anode, platinum plate (1.0×1.0 cm^2) cathode, constant current (I = 5 mA), **1a** (0.2 mmol), Cp_2Fe (10 mol%), $^{n}Bu_4NPF_6$ (0.4 mmol), Na_2CO_3 (0.4 mmol), THF (4.5 mL), MeOH (3 mL), 80 °C, and 3.5 h. [b] Yield of isolated product. [c] Reaction time = 5 h. [d] Reaction time = 2.5 h.

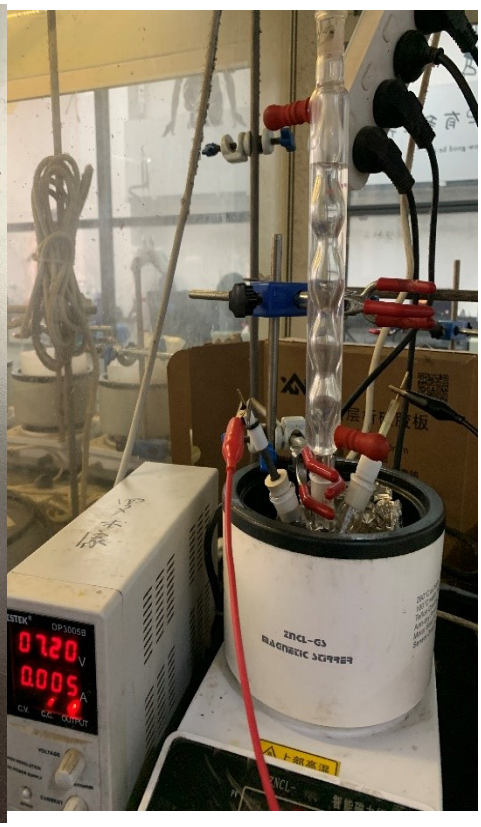
(d) Gram-scale synthesis of 7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2a):

In an oven-dried undivided three-necked bottle (50 mL) equipped with a stir bar, alkene 1a (1.0 g, 3.3 mmol), $^{n}Bu_4NPF_6$ (387 mg 1 mmol,), Cp_2Fe (40 mg), Na_2CO_3(70 mg). MeOH (9.0 mL) and THF (13.5 mL) were combined and added. Then the bottle was equipped with graphite electrode as anode and platinum plate as cathode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA for 18 h. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography (petroleum/ethyl acetate = 20:1) on silica gel to afford the desired product 2a (0.72 g, 72% yield).

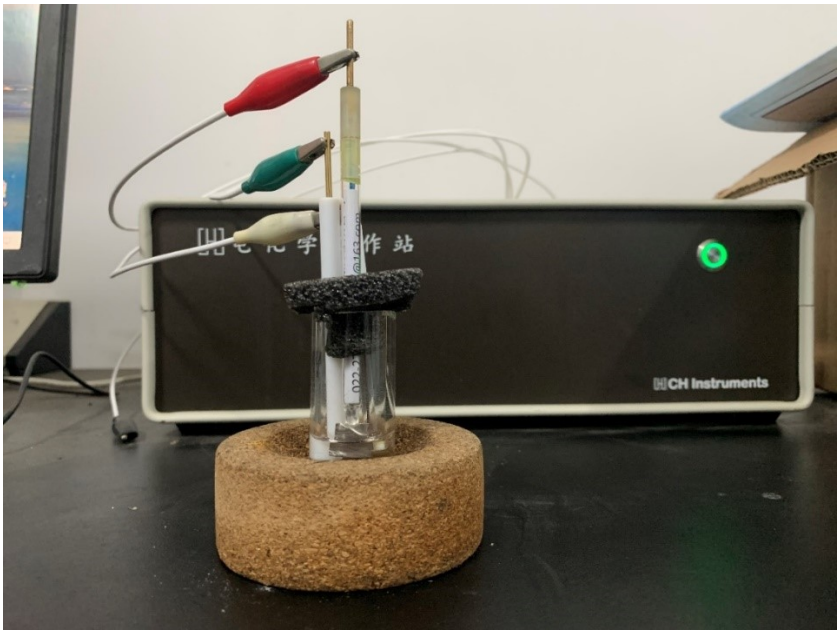
(e) Experimental device

(f) Cycli





Cyclic v



(g) Cyclic Voltammetry (CV) Experiment

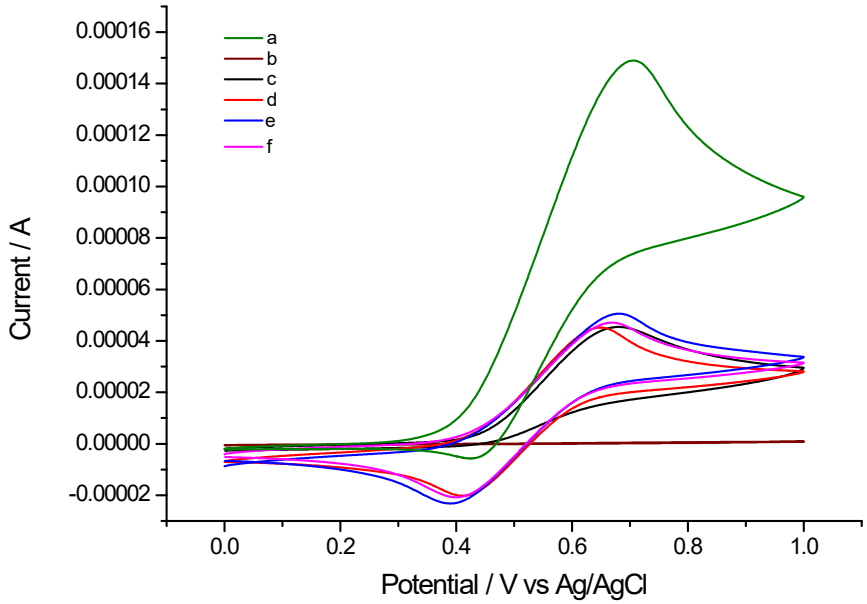
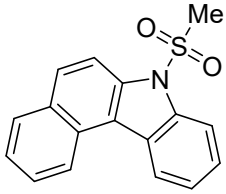


Figure S1. Cyclic voltammogram curves(0-1V). Using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. a) 1a (14mM). b) 1a (14mM) + NaOMe (14 mM). c) Cp_2Fe (3 mM). d) Cp_2Fe (3 mM) + 1a (14 mM). e) Cp_2Fe (3 mM) + 1a (14 mM) + Na_2CO_3. (28 mM) f): Cp_2Fe (3 mM) + 1a (14 mM) + NaOMe (14 mM)

The oxidation potential of reagent 1 was very high ($E_{p/2}$>1.5V) but decreased to 0.54 V in the presence of the base NaOMe (curve b). The oxidation potential of ferrocene was 0.53 V in the mixed solvent of THF/MeOH (3:2).

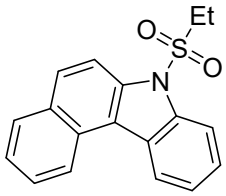
(B) Analytical data

7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2a):



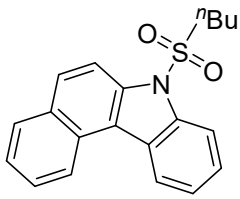
97.9 mg, 83% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$). δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 6.5 Hz, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 8.32 (t, *J* = 4.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.55 (m, 3H), 2.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.4, 131.0, 129.2, 128.8, 128.8, 127.5, 126.9, 126.4, 125.0, 124.5, 123.5, 122.3, 119.6, 114.9, 114.3, 39.3. HRMS *m/z* (ESI) Calcd. for $C_{17}H_{17}N_2O_2S$ requires $[M+H]^+$: 296.0740, found:296.0750.

7-(ethylsulfonyl)-7H-benzo[*c*]carbazole (2b):



98.8 mg, 80% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$). δ 8.79 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J* = 6.5 Hz, 1H), 8.42 (d, *J* = 10.0 Hz, 1H), 8.34 (d, *J* = 7.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.73 (t, *J* = 8.5 Hz, 1H), 7.59 – 7.52 (m, 3H), 3.30 (q, *J* = 8.0 Hz, 2H), 1.12 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 137.0, 130.9, 129.2, 128.8, 128.7, 127.5, 126.5, 126.2, 124.9, 124.2, 123.5, 122.3, 119.0, 114.7, 114.3, 48.1, 7.8. HRMS *m/z* (ESI) calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 310.0896, found:310.0883.

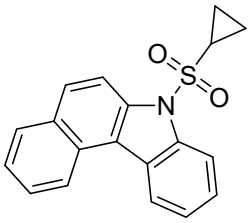
7-(butylsulfonyl)-7H-benzo[*c*]carbazole (2c):



102.4mg, 76% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 5.5 Hz, 1H), 8.41 (d, *J* = 9.0 Hz, 1H), 8.32(s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* =

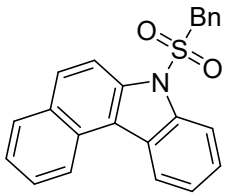
9.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.54 (m, 3H), 3.21 (t, *J* = 7.5 Hz, 2H), 1.58 (t, *J* = 8.0 Hz, 2H), 1.24 (t, *J* = 8.0 Hz, 2H), 0.72 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 136.8, 130.9, 129.2 128.8, 128.7, 127.4, 126.5, 126.2, 124.9, 124.2, 123.6, 122.3, 119.1, 114.7, 114.3, 53.0, 24.7, 21.2, 13.2.; HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 338.1209, found:228.1202.

7-(cyclopropylsulfonyl)-7H-benzo[*c*]carbazole (2d):



115.6 mg, 90% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 7.0 Hz, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 3H), 2.61 – 2.51 (q, J = 3.5Hz, 1H), 1.31 (d, *J* = 5.0 Hz, 2H), 0.80 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 136.8, 130.9, 129.1, 128.8, 128.6, 127.4, 126.8, 126.1, 124.8, 124.1, 123.5, 122.2, 119.4, 115.0, 114.5, 30.6, 5.3.; HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 322.0896, found: 322.0890.

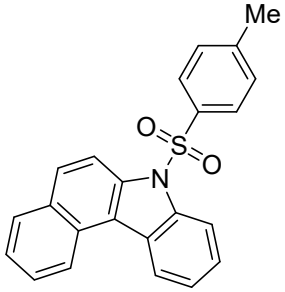
7-(benzylsulfonyl)-7H-benzo[*c*]carbazole (2e):



106.1 mg, 71% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.16 – 8.11 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.5 Hz, 2H), 4.47 (s, 2H).

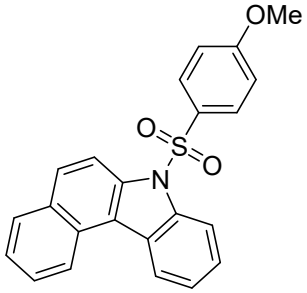
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 137.2, 130.8, 130.5, 129.1, 129.1, 128.7, 128.4, 128.4, 127.3, 126.3, 126.2, 126.0, 124.8, 124.0, 123.5, 122.0, 118.7, 114.6, 114.1, 59.2. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1053, found: 372.1060.

7-tosyl-7H-benzo[*c*]carbazole (2f):



106.5 mg, 72% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 9.0 Hz, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 3H), 7.54 - 7.47 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.1, 136.6, 135.0, 131.0, 129.6, 129.1, 128.8, 128.6, 127.3, 127.1, 126.4, 126.1, 124.8, 124.3, 123.5, 122.1, 119.8, 115.4, 114.9, 77.3, 77.0, 76.8 21.4. HRMS m/z (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1053, found: 372.1053.

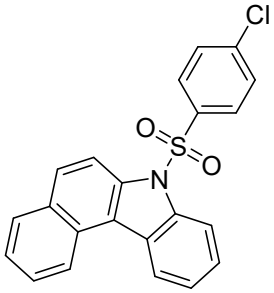
7-((4-methoxyphenyl)sulfonyl)-7H-benzo[*c*]carbazole (2g):



103.7 mg, 67% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$); δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.60 (d, *J* = 9.5 Hz, 1H), 8.51 (d, *J* = 8.5Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.94 (d, *J* = 9.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 138.2, 136.6, 131.0, 129.5, 129.09, 128.8, 128.6, 128.5, 127.3, 127.1, 126.1, 124.8, 124.2, 123.5,

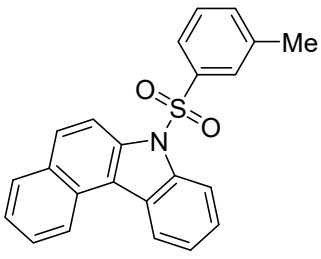
122.1, 119.8, 115.4, 115.0, 114.2, 55.4. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_3S$ $[M+H]^+$ 388.1002, found: 388.1011.

7-((4-chlorophenyl)sulfonyl)-7H-benzo[*c*]carbazole (2h):



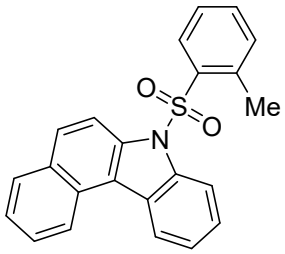
70.3 mg, 45% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.56 (d, *J* = 9.5 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 9.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 3H), 7.57-7.51 (m, 3H), 7.22 (d, *J* = 8.5 Hz, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 140.5, 138.0 136.3, 136.0, 131.1, 129.4, 129.1, 128.8, 128.7, 127.7, 127.5, 127.3, 126.4, 125.1, 124.7, 123.5, 122.3, 120.2, 115.4, 114.8. HRMS *m/z* (ESI) calcd for $C_{22}H_{14}ClNO_2S$ $[M+H]^+$ 392.0507, found: 392.0508.

7-(m-tolylsulfonyl)-7H-benzo[*c*]carbazole (2i):



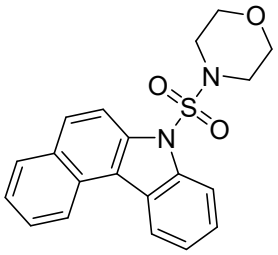
93.5mg, 63% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 – 8.68 (m, 1H), 8.60 (dd, *J* = 8.9, 4.5 Hz, 1H), 8.49 (ddd, *J* = 16.4, 8.3, 4.5 Hz, 2H), 7.97 (ddd, *J* = 25.1, 9.5, 5.0 Hz, 2H), 7.69 – 7.48 (m, 6H), 7.20 – 7.14 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 138.1, 137.9, 136.5, 134.7, 131.0, 129.1, 128.9, 128.8, 128.6, 127.3, 127.0, 126.7, 126.2, 124.9, 124.3, 123.5, 123.5, 122.1, 119.8, 115.3, 114.9, 21.3. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1053, found: 372.1053.

7-(o-tolylsulfonyl)-7H-benzo[*c*]carbazole (2j)



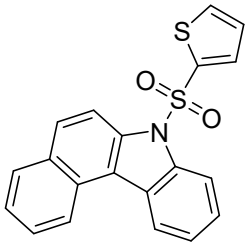
103.8 mg, 70% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.5, 5.0 Hz, 1H), 8.53 (t, *J* = 7.0 Hz, 1H), 8.34 (dd, *J* = 9.0, 5.0 Hz, 1H), 8.25 (t, *J* = 6.5 Hz, 1H), 7.97 (t, *J* = 6.5 Hz, 1H), 7.86 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.75 - 7.69 (m, 2H), 7.55 – 7.44 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.16 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.1, 138.0, 136.9, 133.5, 132.9, 130.7, 129.1, 128.8, 128.7, 128.4, 127.3, 126.2, 126.1, 126.0, 124.8, 123.9, 123.5, 122.2, 118.7, 115.0, 114.6, 20.4. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1053, found: 372.1055.

4-((7H-benzo[*c*]carbazol-7-yl)sulfonyl)morpholine (2k):



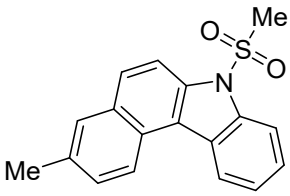
87.8 mg, 60% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.5 Hz, 1H), 8.56 (d, *J* = 7.0 Hz, 1H), 8.40 (d, *J* = 9.5 Hz, 1H), 8.33 (d, *J* = 7.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 9.5 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 2H), 3.47 (d, *J* = 5.7 Hz, 4H), 3.12 (d, *J* = 5.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 136.9, 130.7, 129.1, 128.8, 128.4, 127.5, 126.2 126.0, 124.8, 123.9, 123.5, 122.2, 118.7, 115.3, 114.9, 65.8, 47.0. HRMS m/z (ESI) calcd for $C_{20}H_{18}N_2O_3S$ $[M+H]^+$ 367.1111, found: 367.1109.

7-(thiophen-2-ylsulfonyl)-7H-benzo[*c*]carbazole (2l):



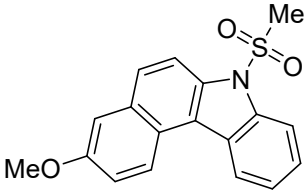
69.7 mg, 48% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.48 (t, *J* = 7.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.69 (s, 1H), 7.57 – 7.51 (m, 4H), 7.34 (d, *J* = 5.0 Hz, 1H), 6.82 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.4, 136.4, 133.0, 132.5, 131.2, 129.2, 128.7, 128.7, 127.5, 127.35, 127.2, 126.3, 125.0, 124.7, 123.6, 122.2, 120.3, 115.7, 115.1. HRMS *m/z* (ESI) calcd for $C_{20}H_{18}N_2O_3S$ $[M+H]^+$ 364.0460, found: 364.0467.

3-methyl-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2m):



68.0 mg, 55% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.5 Hz, 1H), 8.51 (d, *J* = 6.5 Hz, 1H), 8.35 -8.30 (m, 2H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (s, 1H), 7.53 (m, 3H), 2.97 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.0, 134.6, 131.3, 129.6, 128.3, 128.3, 127.0, 126.8, 126.3, 124.4, 123.3, 122.3, 119.6, 114.9, 114.26, 39.2, 21.5. HRMS *m/z* (ESI) calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 310.0896, found: 310.0903.

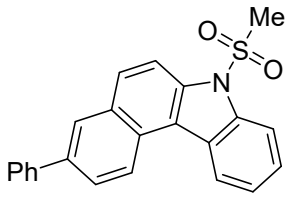
3-methoxy-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2n):



55.9 mg, 43% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 9.0 Hz, 1H), 8.50 (d, *J* = 6.5 Hz, 1H), 8.37 (d, *J* = 9.0 Hz, 1H), 8.37 (t, *J* = 5.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.53 (s, 2H), 7.39 (d, *J* = 9.5 Hz, 1H), 7.34 (s, 1H), 3.97 (s, 3H), 2.98 (s,

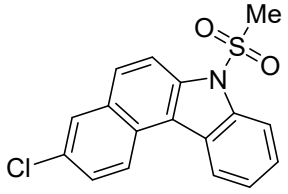
3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 138.1, 135.2, 132.5, 127.7, 126.9, 126.4, 124.9, 124.5, 123.8, 122.2, 120.0, 119.6, 115.0, 114.8, 107.7, 55.4, 39.0. HRMS *m/z* (ESI) calcd for $C_{18}H_{16}NO_3S$ $[M+H]^+$ 326.0845, found: 326.0846.

7-(methylsulfonyl)-3-phenyl-7H-benzo[*c*]carbazole (2o):



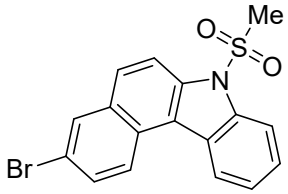
96.5 mg, 65% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 6.5 Hz, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.31 (s, 1H), 8.17 (s, 1H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.53 – 7.49 (m, 4H), 7.40 (d, *J* = 7.5 Hz, 1H), 2.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 138.1, 137.6, 136.4, 131.4, 129.1, 128.9, 127.8, 127.5, 127.3, 126.9, 126.8, 126.4, 124.5, 124.0, 122.3, 119.5, 114.9, 114.6, 39.3. HRMS *m/z* (ESI) calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1053, found: 372.1060.

3-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2p):



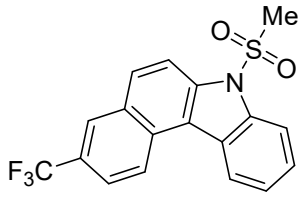
101.3 mg, 77% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.5 Hz, 1H), 8.49 (d, *J* = 6.5 Hz, 1H), 8.43 (d, *J* = 6.0 Hz, 1H), 8.33 (d, *J* = 5.0 Hz, 1H), 7.99 (d, *J* = 3.5 Hz, 1H), 7.8-5 (d, *J* = 4.5 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.56 (d, *J* = 5.0 Hz, 2H), 3.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.4, 131.8, 130.6, 128.1, 127.9, 127.8, 127.0, 126.8, 126.4, 125.1, 124.6, 122.2, 119.6, 115.4, 114.9, 39.5 HRMS *m/z* (ESI) calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 330.0350, found: 330.0343.

3-bromo-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2q):



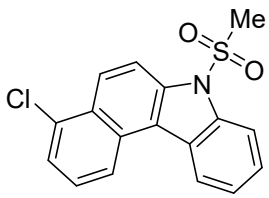
116.0 mg, 78% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.0 Hz, 1H), 8.45 (d, *J* = 7.0 Hz, 1H), 8.40 (d, *J* = 9.5 Hz, 1H), 8.31 (d, *J* = 7.5 Hz, 1H), 8.13 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 3.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.4, 132.2, 131.1, 130.6, 127.7, 127.2, 126.7, 126.3, 125.1, 124.6, 122.2, 119.6, 118.7, 115.3, 114.9, 39.6. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}BrNO_2S$ $[M+H]^+$ 373.9845, found: 373.9842.

7-(methylsulfonyl)-3-(trifluoromethyl)-7H-benzo[*c*]carbazole (2r):



123.4 mg, 85% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.5 Hz, 1H), 8.47 – 8.44 (m, 4.0 Hz, 2H), 8.31 (t, *J* = 3.5 Hz, 1H), 8.26 (s, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.56 – 7.54 (m, 2H), 3.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.4, 130.1, 129.7, 129.2, 126.9, 126.8, 126.7, 126.6, 126.6, 126.1, 125.4, 124.7, 124.4, 123.2, 123.0, 123.0, 122.9, 122.2, 119.3, 115.5, 114.8, 39.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.02; HRMS *m/z* (ESI) calcd for $C_{18}H_{13}F_3NO_2S$ $[M+H]^+$ 364.0614, found: 364.0615.

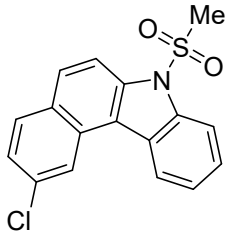
4-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2s):



69.7 mg, 53% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.48 (dd, *J* = 9.0, 3.5 Hz, 2H), 8.41 (d, *J* = 9.5 Hz, 1H), 8.33 – 8.31 (m, 1H), 7.65 – 7.53 (m, 4H), 3.02

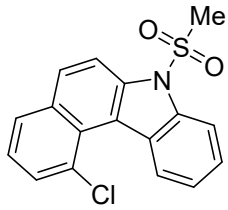
(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.8, 133.2, 130.1, 128.3, 127.3, 126.8, 126.4, 125.5, 125.1, 124.6, 122.6, 122.4, 119.7, 115.2, 114.9, 39.6. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}ClNO_2S$ $[M+H]^+$ 330.0350, found: 330.0349.

2-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2s'):

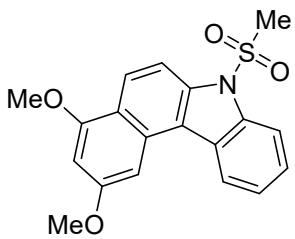


30.2 mg, 23% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.50 – 8.49 (m, 1H), 8.41 (dd, *J* = 9.0, 3.5 Hz, 1H), 8.34 (d, *J* = 6.0 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.58 – 7.51 (m, 3H), 3.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.0, 133.6, 130.6, 129.4, 129.2, 128.5, 126.7, 126.4, 125.9, 124.7, 122.8, 122.1, 118.9, 114.9, 114.5, 39.6. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}ClNO_2S$ $[M+H]^+$ 330.0350, found: 330.0344.

1-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2t):



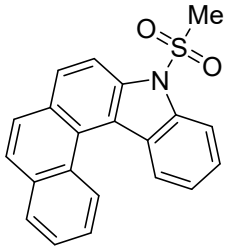
67.1 mg, 51% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 9.5 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.51 – 7,47 (m, 3H), 3.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.0, 133.3, 129.9, 129.2, 129.1, 128.2, 127.9, 127.0, 126.3, 126.3, 125.3, 123.1, 119.4, 115.1, 114.0, 39.6. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}ClNO_2S$ $[M+H]^+$ 330.0350, found:330.0344.**2,4-dimethoxy-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2u):**



68.1 mg, 48% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.5 Hz, 1H), 8.31 (t, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 9.5 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 9.5 Hz, 1H) 6.58 (s,

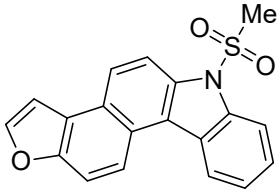
1H), 4.04 (d, *J* = 23.0 Hz, 6H), 3.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 157.4, 138.0, 137.7, 130.6, 127.2, 126.0, 124.3, 122.8, 121.8, 118.6, 118.6, 114.8, 110.6, 96.52, 95.1, 55.7 55.7, 39.1. HRMS *m/z* (ESI) calcd for $C_{19}H_{18}NO_4S$ $[M+H]^+$ 356.0951, found: 356.0944.

9-(methylsulfonyl)-9H-naphtho[2,1-*c*]carbazole (2v):



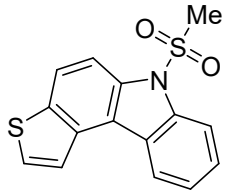
100.7 mg, 73% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 9.5 Hz, 1H), 8.68 – 8.66 (m, 2H), 8.54 (d, *J* = 7.0 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.30 (t, *J* = 5.0 Hz, 1H), 7.92 (t, *J* = 8.6 Hz, 2H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.51 (m, 2H), 2.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.0, 131.0, 130.6, 128.6, 127.5, 127.2, 127.1, 126.9, 126.7, 126.3, 124.4, 122.9, 122.8, 122.7, 122.0, 120.8, 114.8, 113.7, 39.1. HRMS *m/z* (ESI) calcd for $C_{21}H_{16}NO_2S$ $[M+H]^+$ 346.0896, found: 346.0905.

6-(methylsulfonyl)-6H-benzofuro[4,5-*c*]carbazole (2w):



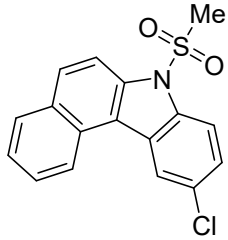
93.8 mg, 70% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 9.0 Hz, 1H), 8.60 (t, *J* = 3.5 Hz, 1H), 8.51 (d, *J* = 9.0 Hz, 1H), 8.36 – 8.34 (m, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.83 (s, 1H), 7.57 – 7.55 (m, 2H), 7.34 (s, 1H), 3.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 144.9, 138.2, 135.8, 127.0, 126.6, 125.5, 125.4, 124.5, 124.0, 122.5, 120.8, 120.3, 115.0, 114.5, 113.5, 105.8, 39.1. HRMS *m/z* (ESI) calcd for $C_{19}H_{14}NO_3S$ $[M+H]^+$ 336.0689, found: 336.0688.

6-(methylsulfonyl)-6H-thieno[2,3-*c*]carbazole (2x):



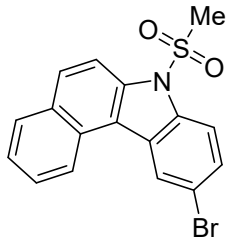
110.8 mg, 92% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.19 (m, 3H), 7.97 – 7.94 (m, 2H), 7.72 (d, *J* = 5.5 Hz, 1H), 7.50 – 7.47 (m, 2H), 2.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 136.7, 135.8, 133.0, 129.1, 126.9, 126.1, 124.4, 121.5, 121.5, 121.2, 120.1, 114.7, 111.6, 38.7. HRMS *m/z* (ESI) calcd for $C_{15}H_{12}NO_2S_2$ $[M+H]^+$ 302.0304, found: 302.0291.

10-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2y):



98.7 mg, 75% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.5 Hz, 1H), 8.46 (s, 1H), 8.34 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 9.5 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 3.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 136.3, 131.0, 130.2, 129.7, 129.3, 128.6, 128.1, 127.9, 126.3, 125.3, 123.2, 122.0, 118.6, 115.8, 114.1, 39.5. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}ClNO_2S$ $[M+H]^+$ 330.0350, found: 330.0347.

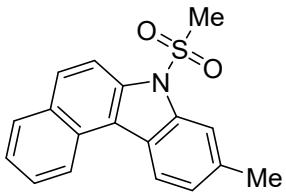
10-bromo-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2z):



107.4 mg, 72% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 6.5 Hz, 2H), 8.35 (d, *J* = 9.0 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 10.5 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.63 – 7.57 (m, 2H), 3.01 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 136.7, 131.0, 129.71, 129.3, 129.1, 128.6, 127.9, 125.3, 125.0,

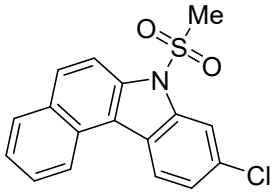
123.2, 118.5, 117.9, 116.2, 114.0, 39.5 HRMS *m/z* (ESI) calcd for $C_{17}H_{13}BrNO_2S$ $[M+H]^+$ 373.9845, found:373.9842.

9-methyl-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2aa):



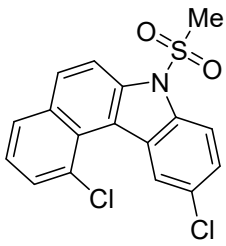
89.0 mg, 72% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.5 Hz, 1H), 8.39 (t, *J* = 9.0 Hz, 2H), 8.13 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 2.99 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 136.8, 136.3, 131.1, 129.1, 128.6, 128.2, 127.3, 125.8, 124.9, 124.6, 123.6, 121.9, 119.81, 115.1, 114.4, 39.2, 22.1. HRMS *m/z* (ESI) calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 310.0896, found: 310.0905.

9-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2ab):



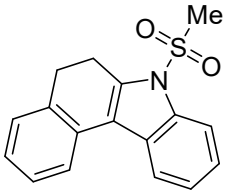
101.3 mg, 77% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 9.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 9.5 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 3.04 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 136.7, 132.2, 131.0, 129.3, 129.2, 128.5 127.7, 125.3, 125.2, 124.9, 123.3, 122.9, 118.9, 115.0, 114.0, 39.7. HRMS *m/z* (ESI) calcd for $C_{17}H_{13}ClNO_2S$ $[M+H]^+$ 330.0350, found: 330.342.

1,10-dichloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2ac):



84.0 mg, 58% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.41 (d, *J* = 9.0 Hz, 1H), 8.22 (d, *J* = 9.5 Hz, 1H), 7.90 (t, *J* = 10.0 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.44 (m, 2H), 3.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 136.2, 133.3, 130.2, 130.0, 129.0, 128.9, 128.3, 127.5, 127.4, 126.8, 126.2, 125.5, 118.3, 114.9, 114.89, 39.7. HRMS *m/z* (ESI) calcd for $C_{17}H_{12}Cl_2NO_2S$ $[M+H]^+$ 363.9960, found: 363.9958.

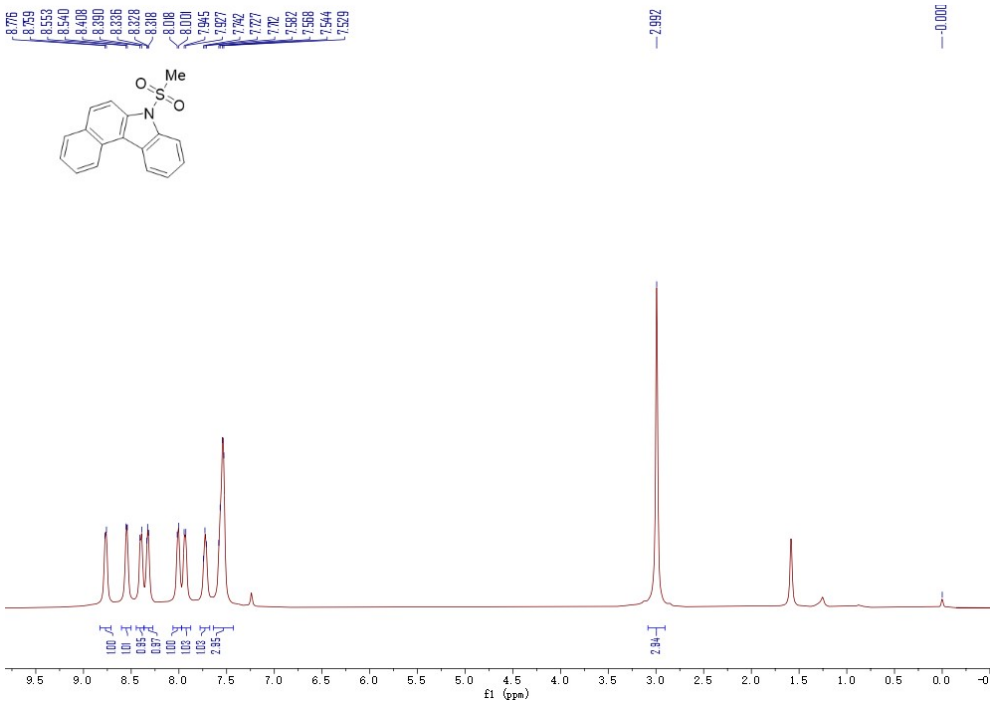
7-(methylsulfonyl)-6,7-dihydro-5H-benzo[*c*]carbazole (Intermediate E):



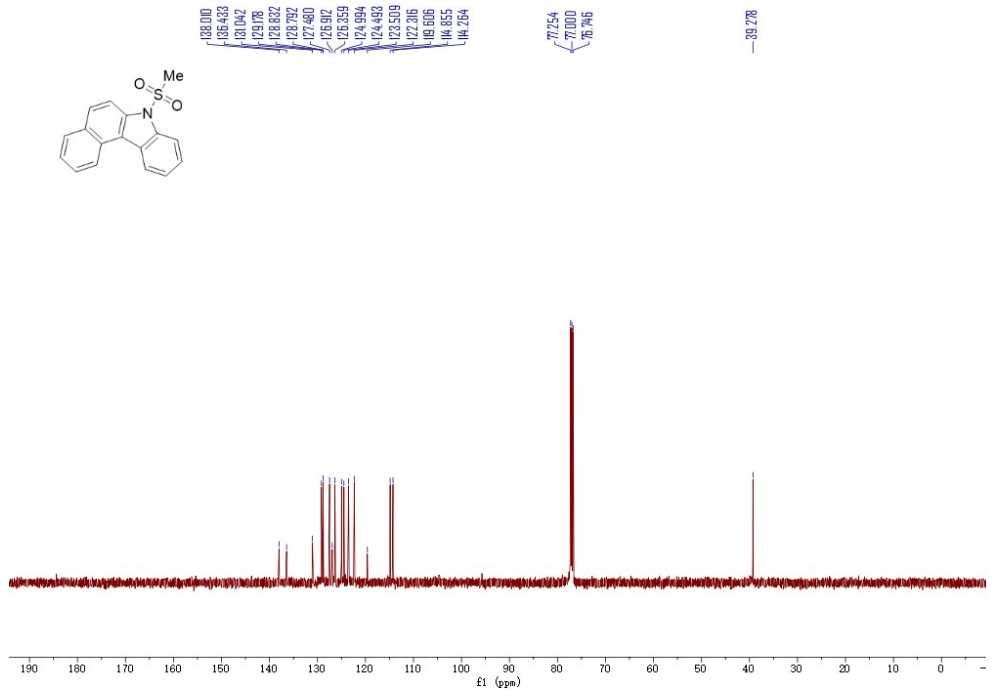
white solid;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.38 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 3.30 (t, *J* = 8.0 Hz, 2H), 3.08 (d, *J* = 7.0 Hz, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 137.0, 134.5, 131.4, 128.0, 127.3, 127.0, 126.5, 124.4, 124.3, 123.3, 120.2, 117.9, 114.4, 40.8, 29.3, 22.3.

(C) Spectra（NMR Spectra)

7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2a):

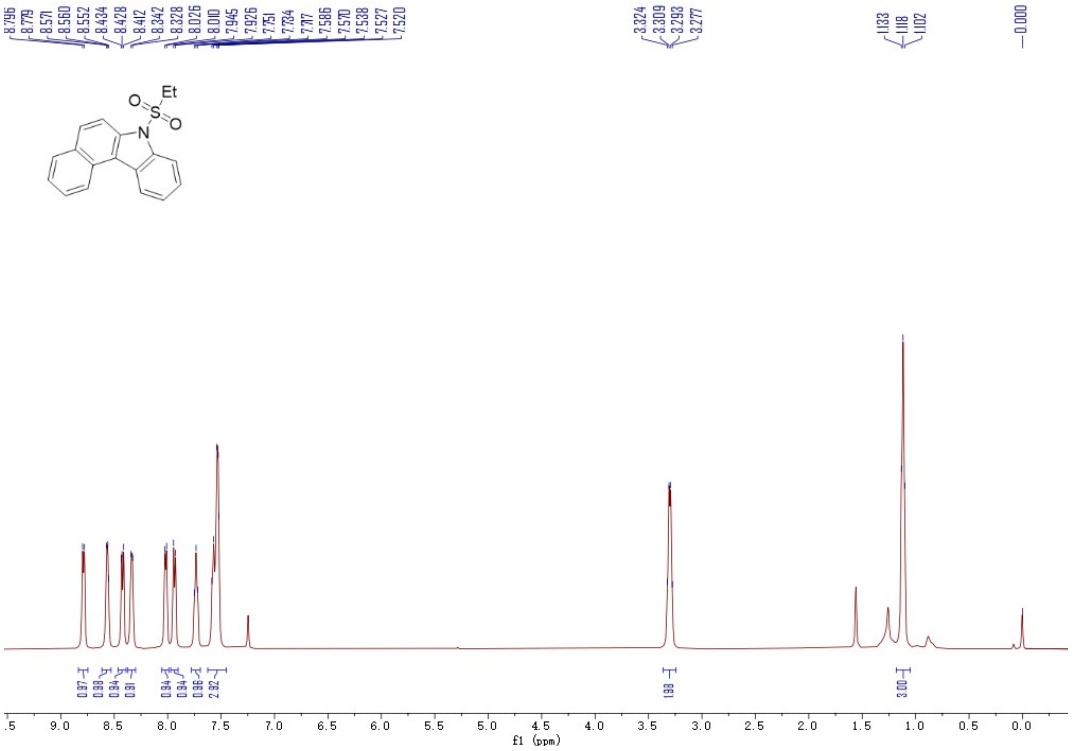


^{1}H NMR (500 MHz, $CDCl_3$)

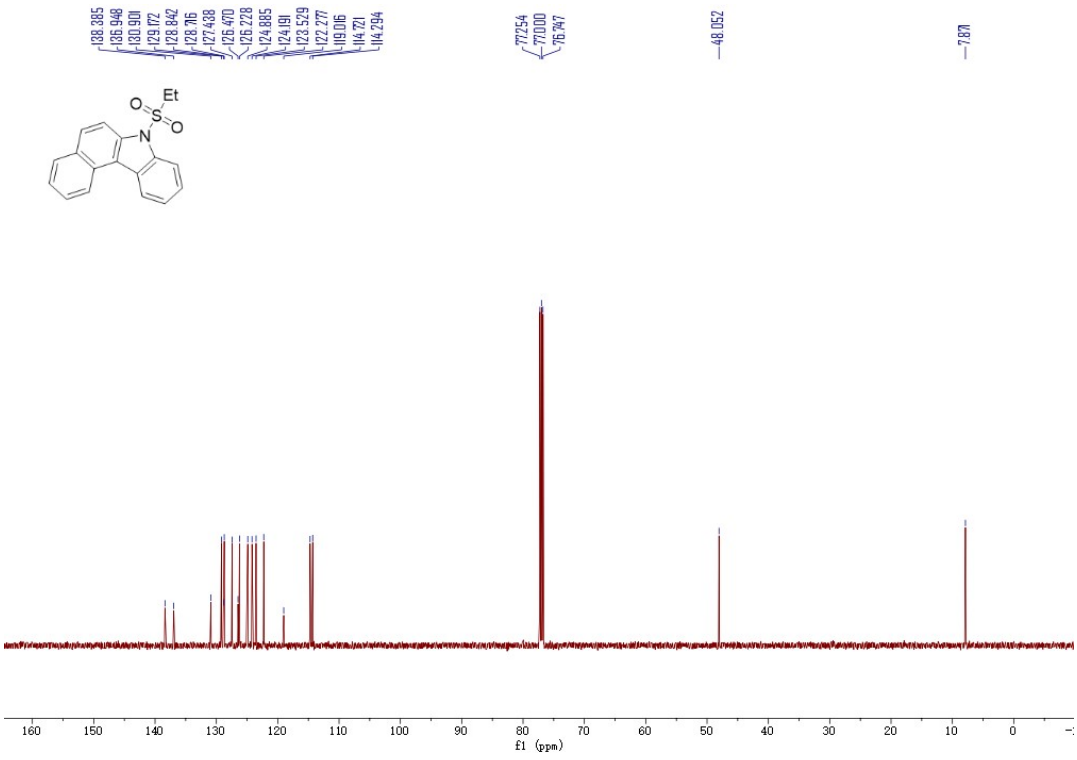


^{13}C NMR (125 MHz, $CDCl_3$)

7-(ethylsulfonyl)-7H-benzo[*c*]carbazole (2b):

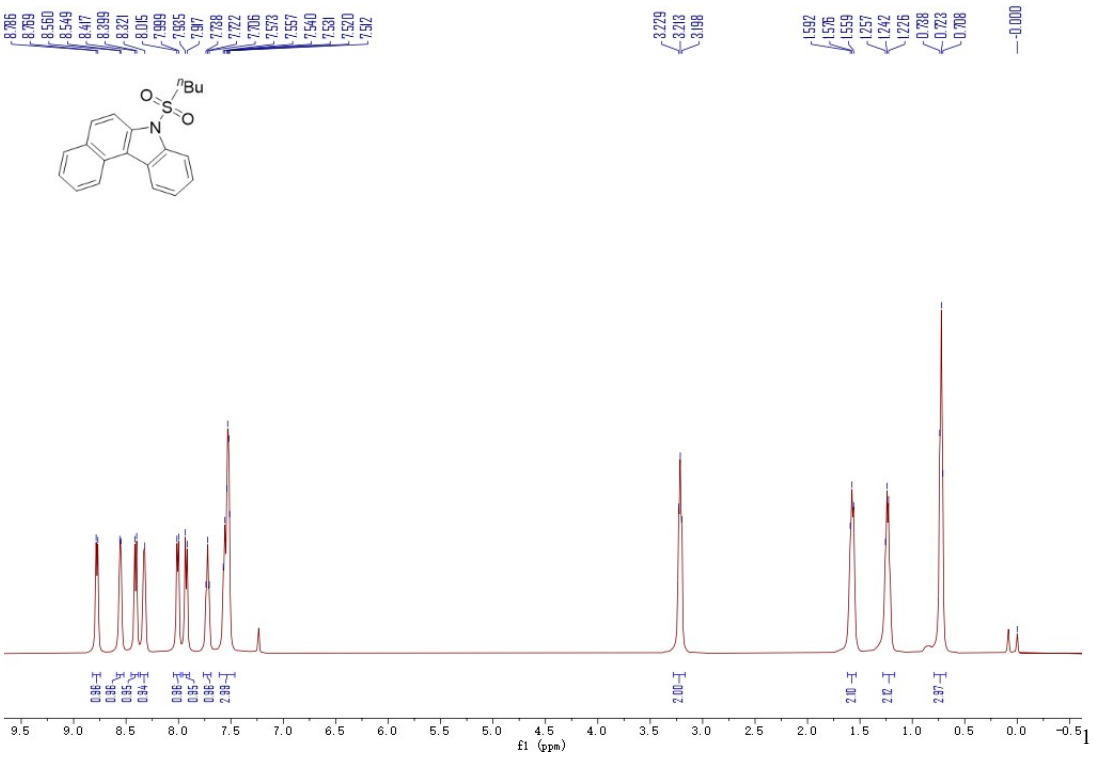


^{1}H NMR (500 MHz, $CDCl_3$)

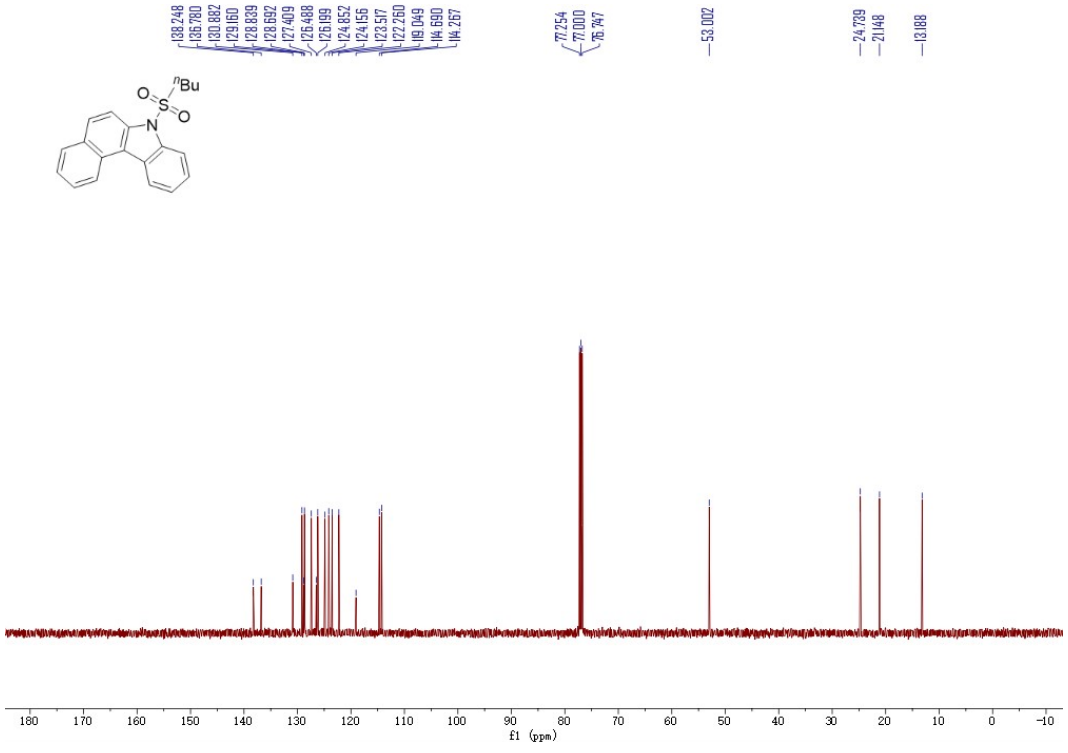


^{13}C NMR (125 MHz, $CDCl_3$)

7-(butylsulfonyl)-7H-benzo[*c*]carbazole (2c):

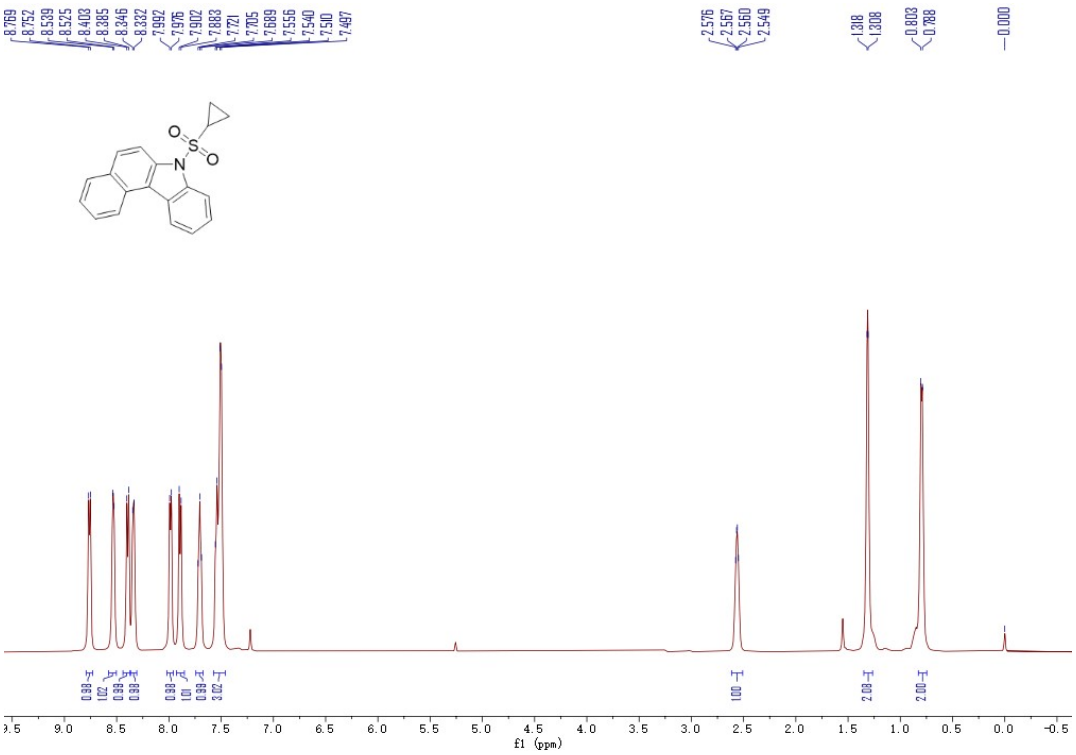


^{1}H NMR (500 MHz, $CDCl_3$)

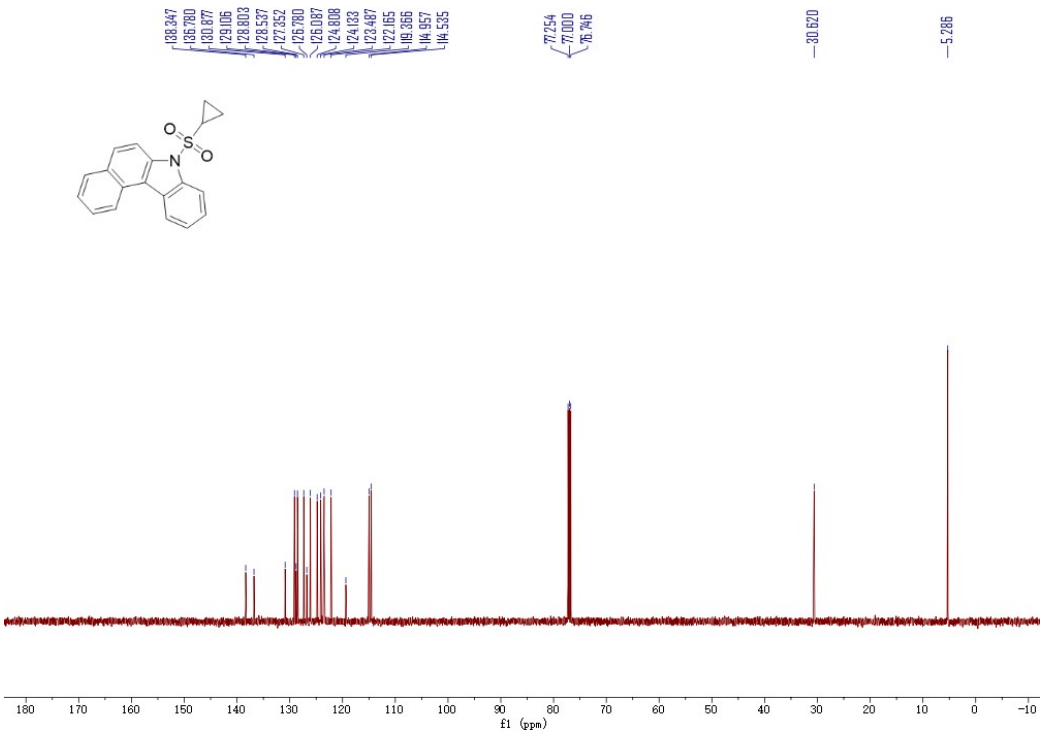


^{13}C NMR (125 MHz, $CDCl_3$)

7-(cyclopropylsulfonyl)-7H-benzo[*c*]carbazole (2d):

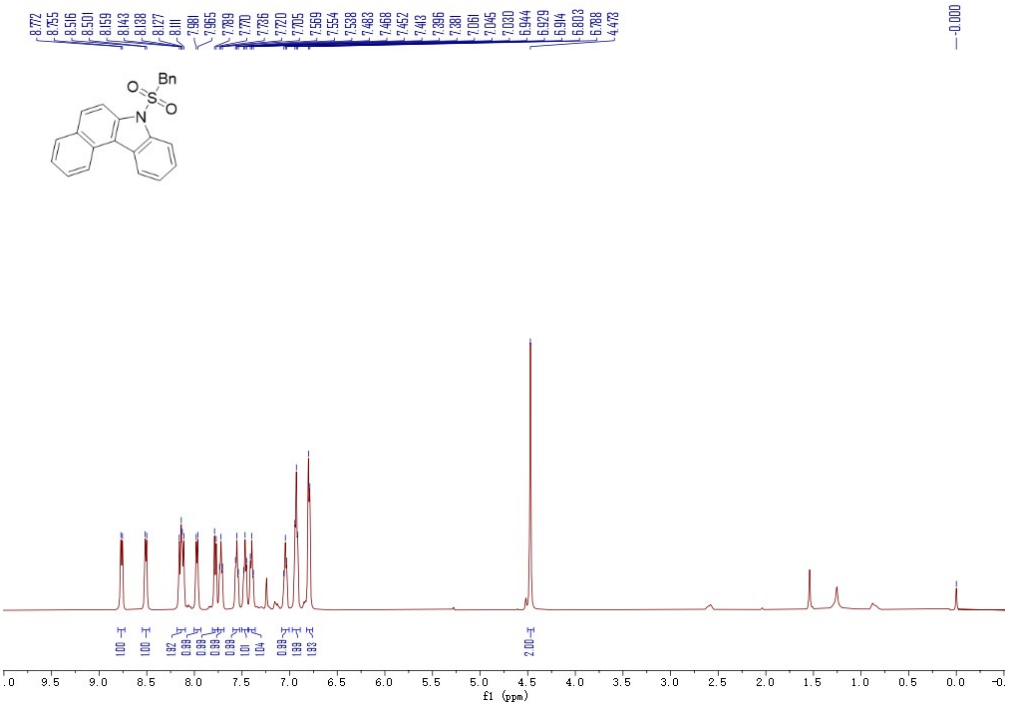


^{1}H NMR (500 MHz, $CDCl_3$)

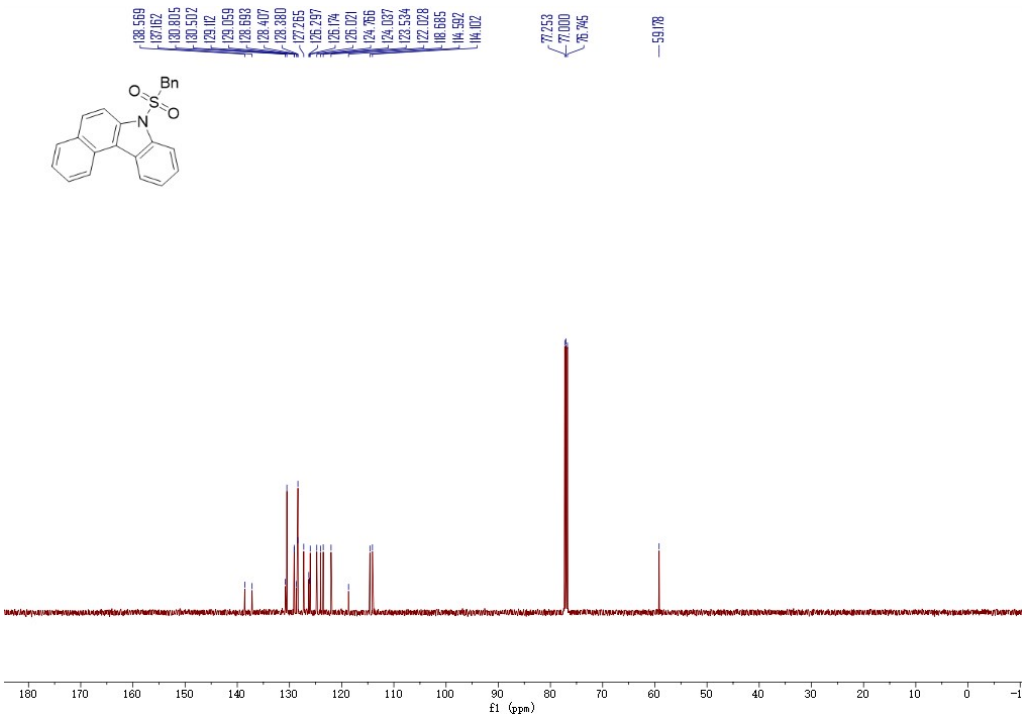


^{13}C NMR (125 MHz, $CDCl_3$)

7-(benzylsulfonyl)-7H-benzo[*c*]carbazole (2e):

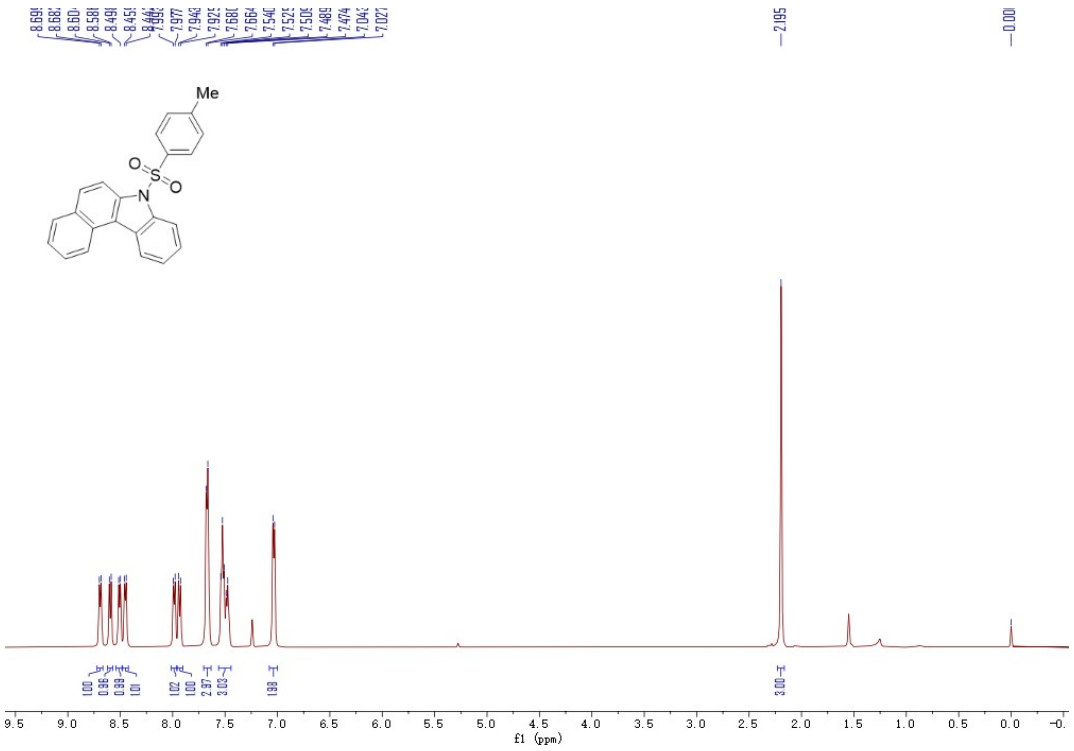


^{1}H NMR (500 MHz, $CDCl_3$)

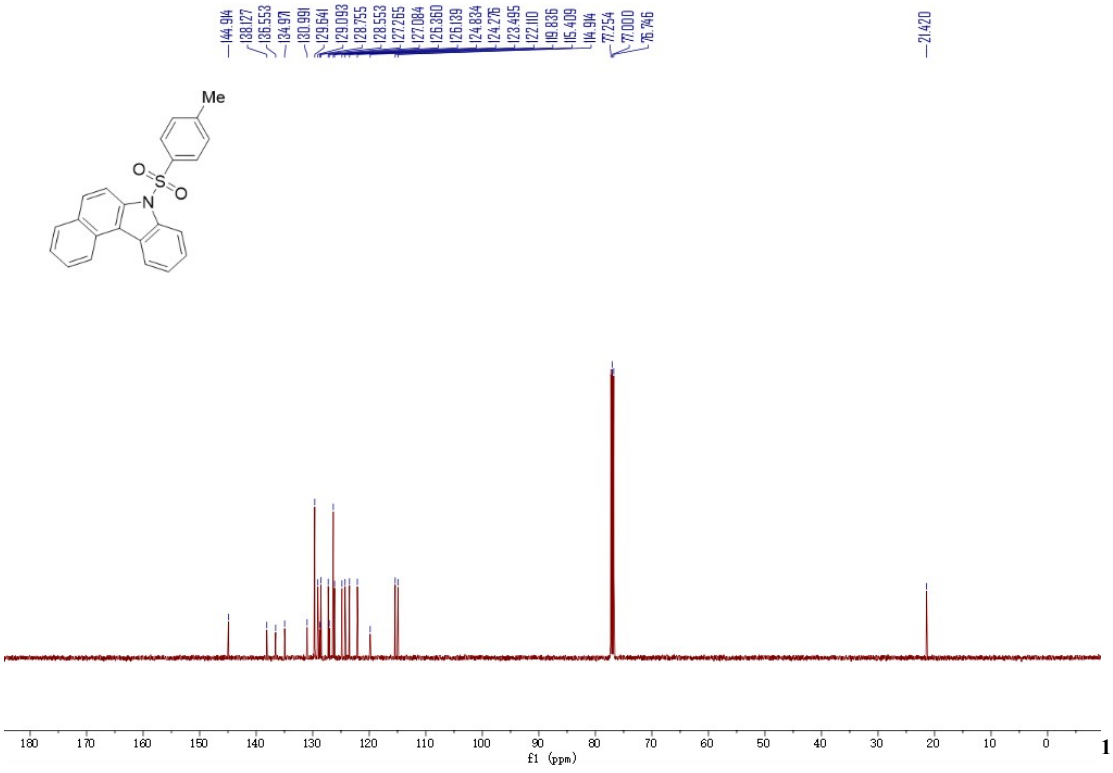


^{13}C NMR (125 MHz, $CDCl_3$)

7-tosyl-7H-benzo[*c*]carbazole (2f):

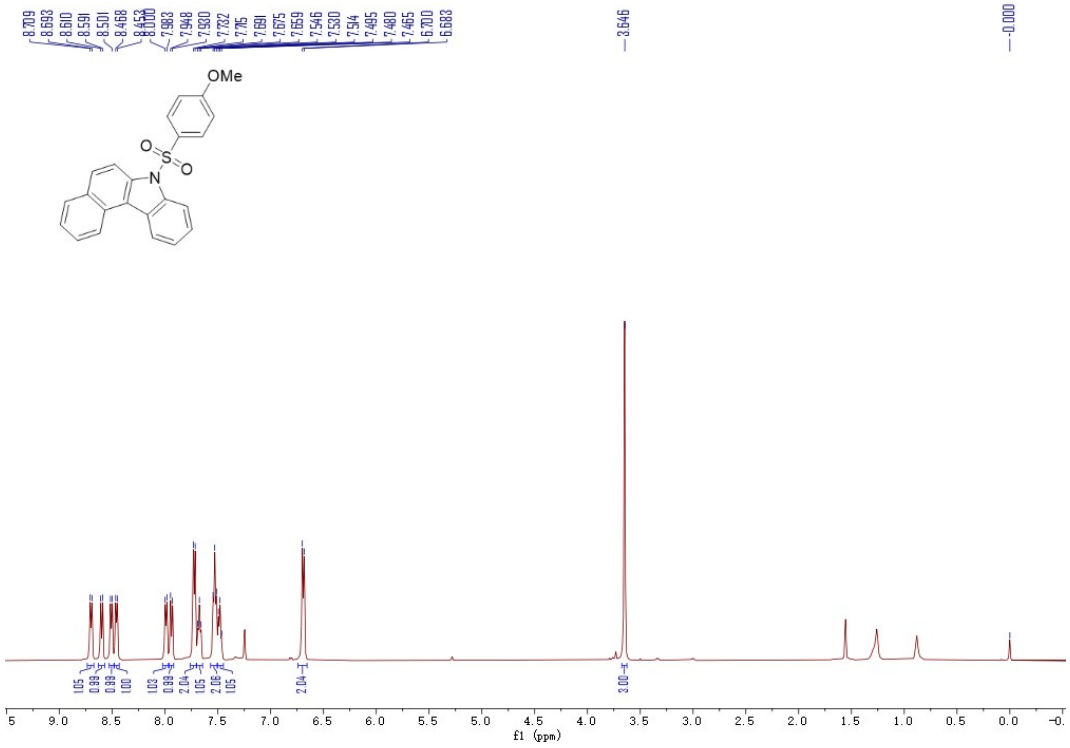


^{1}H NMR (500 MHz, $CDCl_3$)

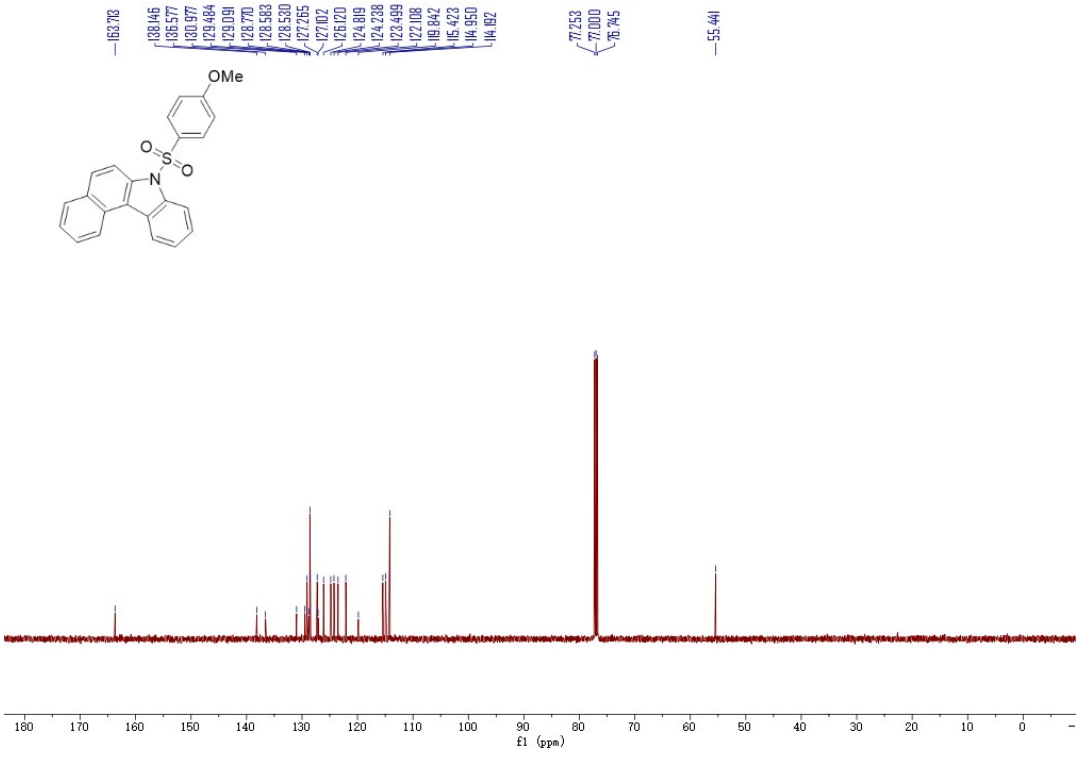


^{3}C NMR (125 MHz, $CDCl_3$)

7-((4-methoxyphenyl)sulfonyl)-7H-benzo[*c*]carbazole (2g):

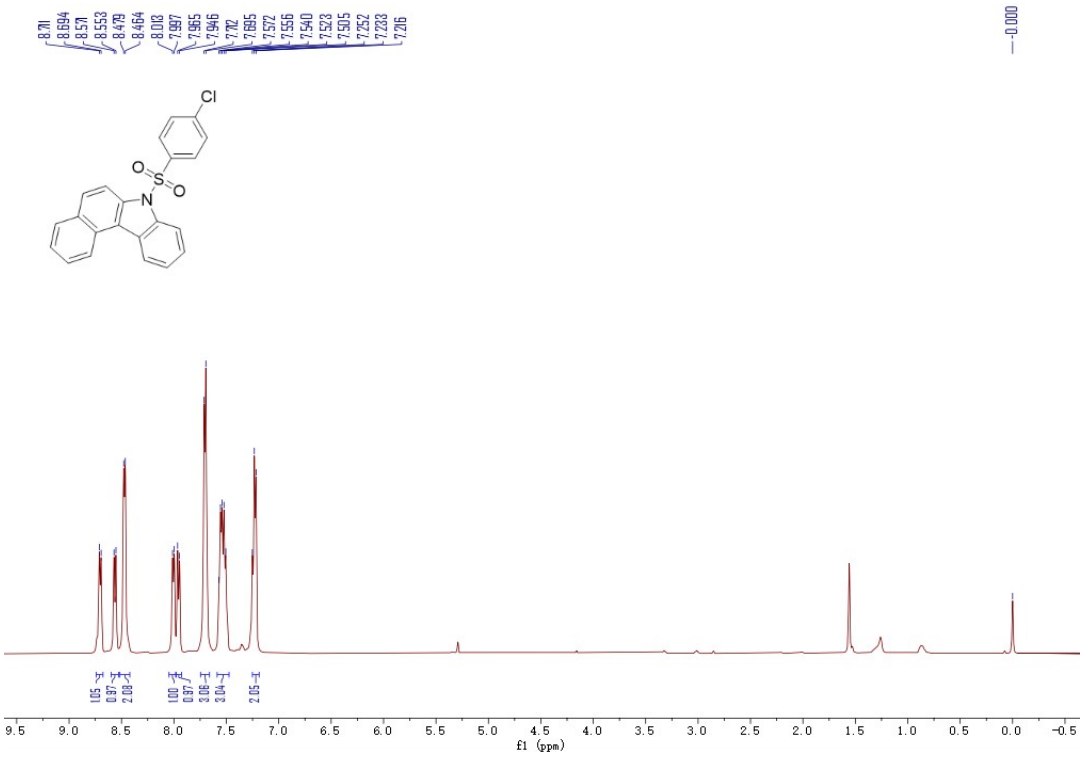


^{1}H NMR (500 MHz, $CDCl_3$)

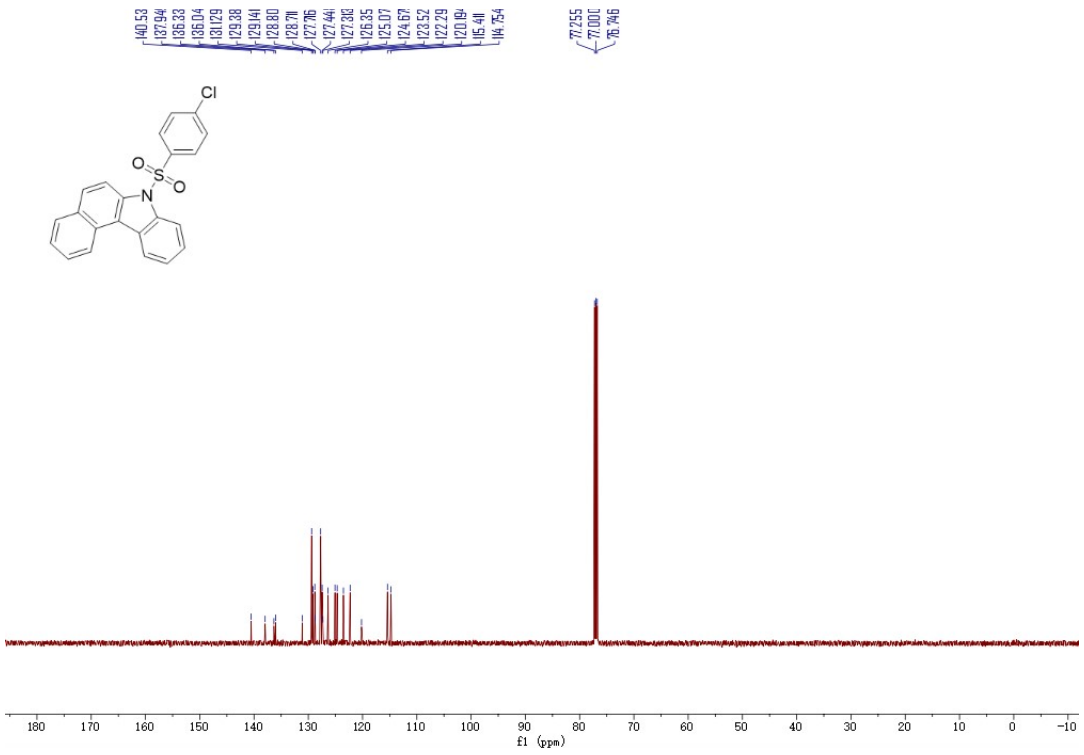


^{13}C NMR (125 MHz, $CDCl_3$)

7-((4-chlorophenyl)sulfonyl)-7H-benzo[*c*]carbazole (2h):

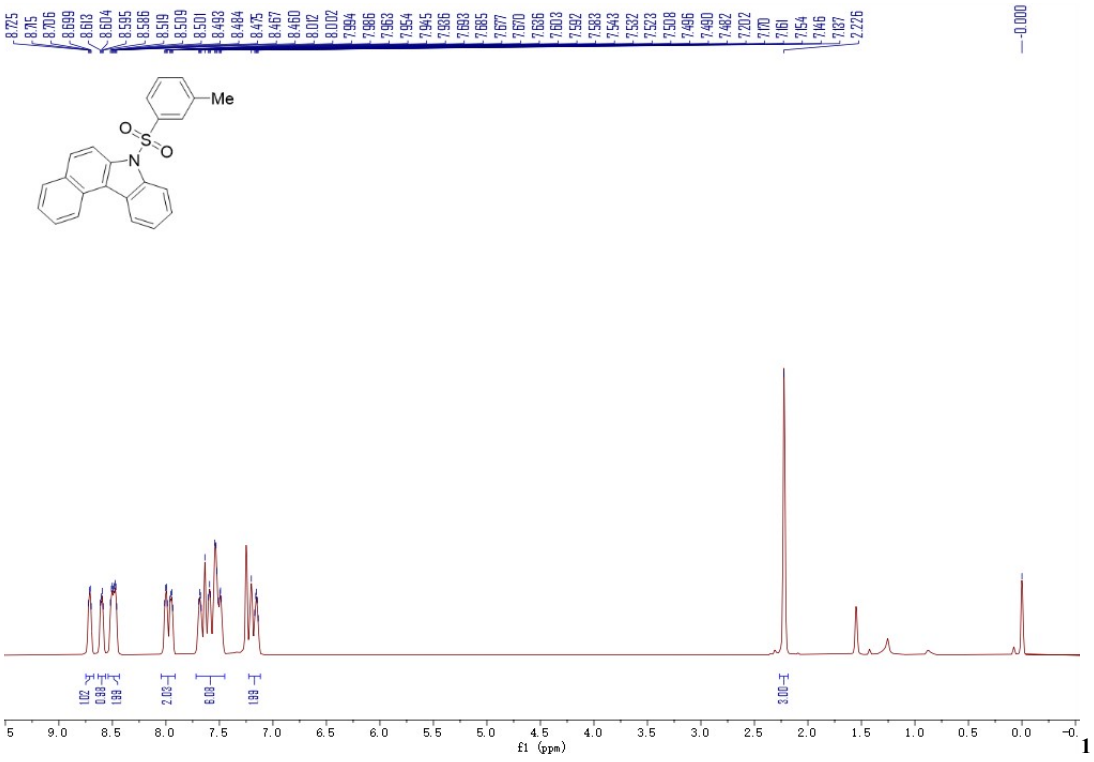


^{1}H NMR (500 MHz, $CDCl_3$)

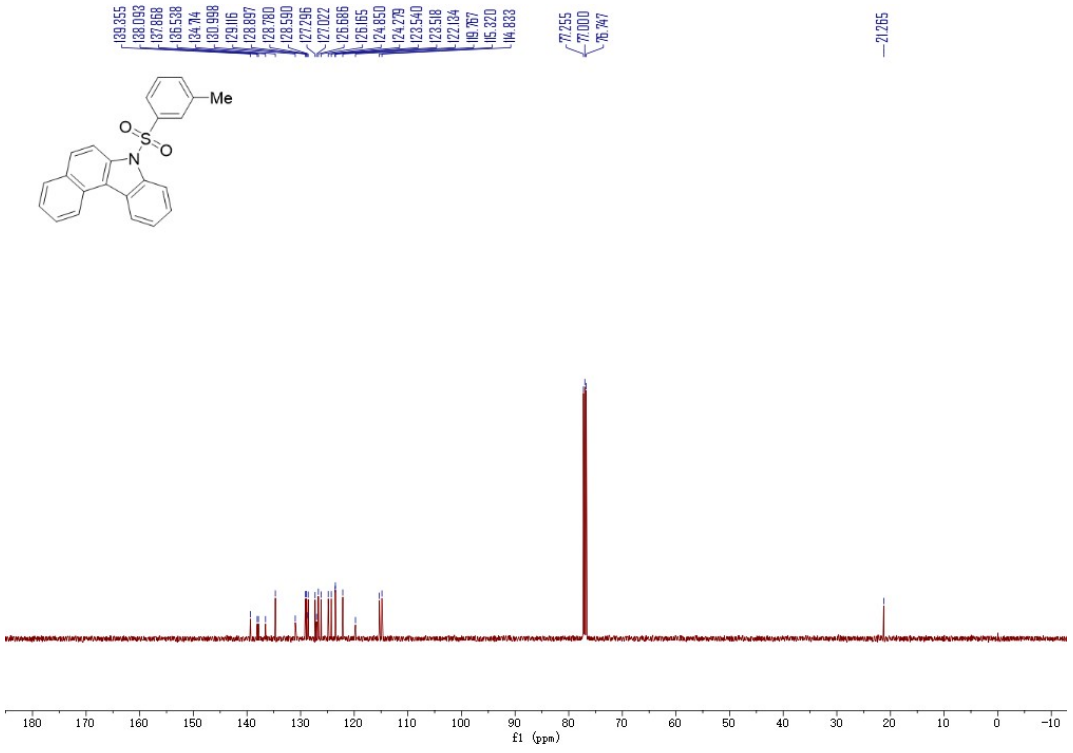


^{13}C NMR (125 MHz, $CDCl_3$)

7-(m-tolylsulfonyl)-7H-benzo[*c*]carbazole (2i):

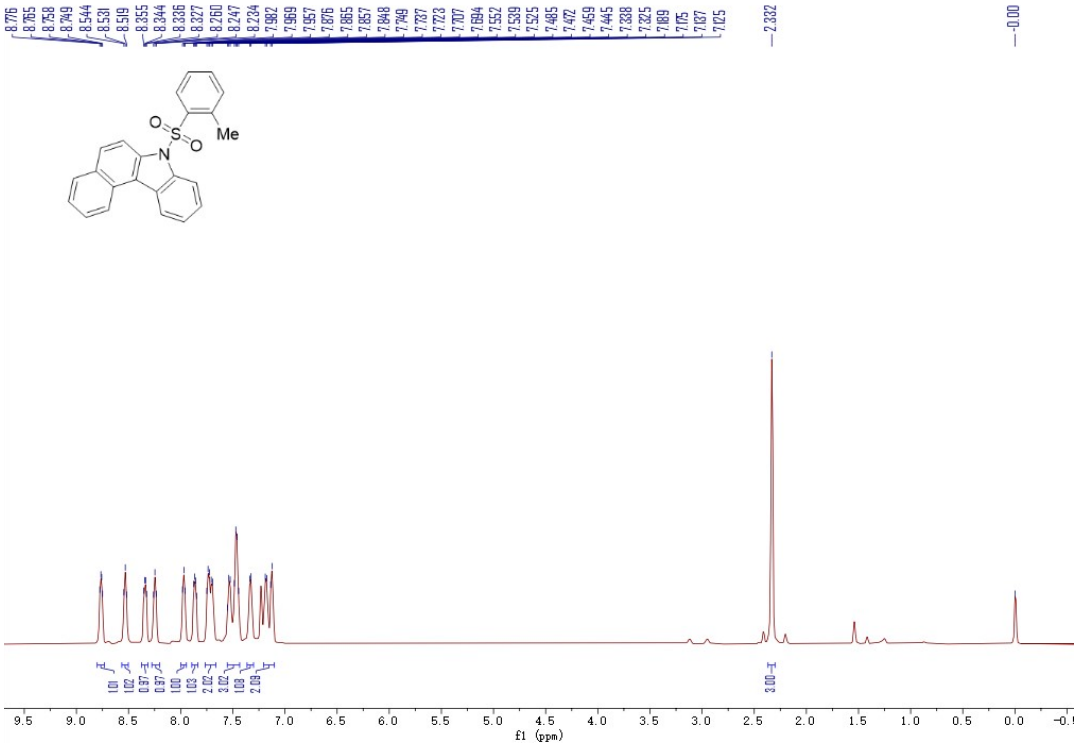


H NMR (500 MHz, $CDCl_3$)

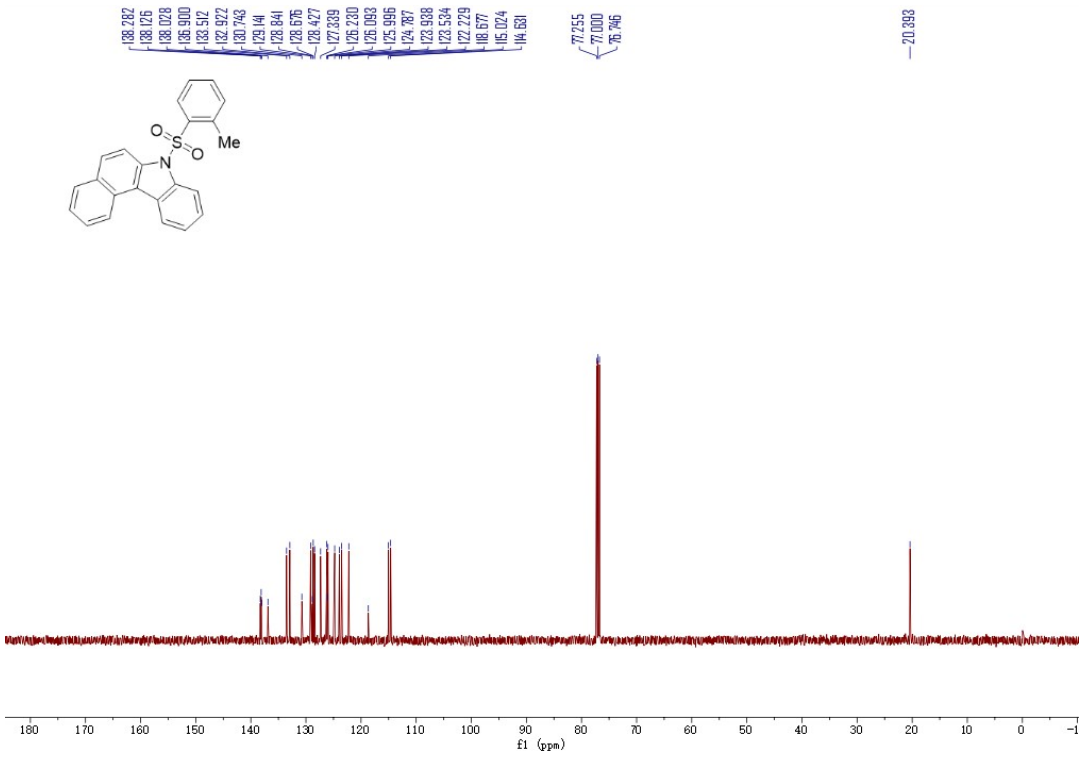


^{13}C NMR (125 MHz, $CDCl_3$)

7-(o-tolylsulfonyl)-7H-benzo[*c*]carbazole (2j)

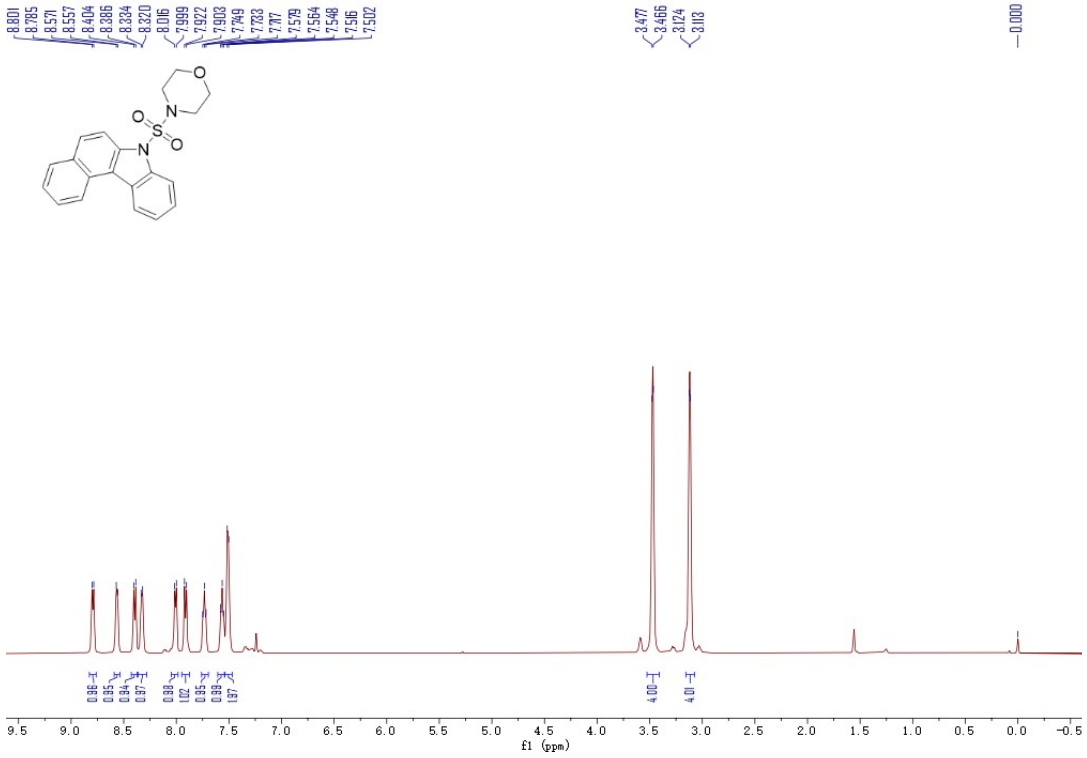


^{1}H NMR (500 MHz, $CDCl_3$)

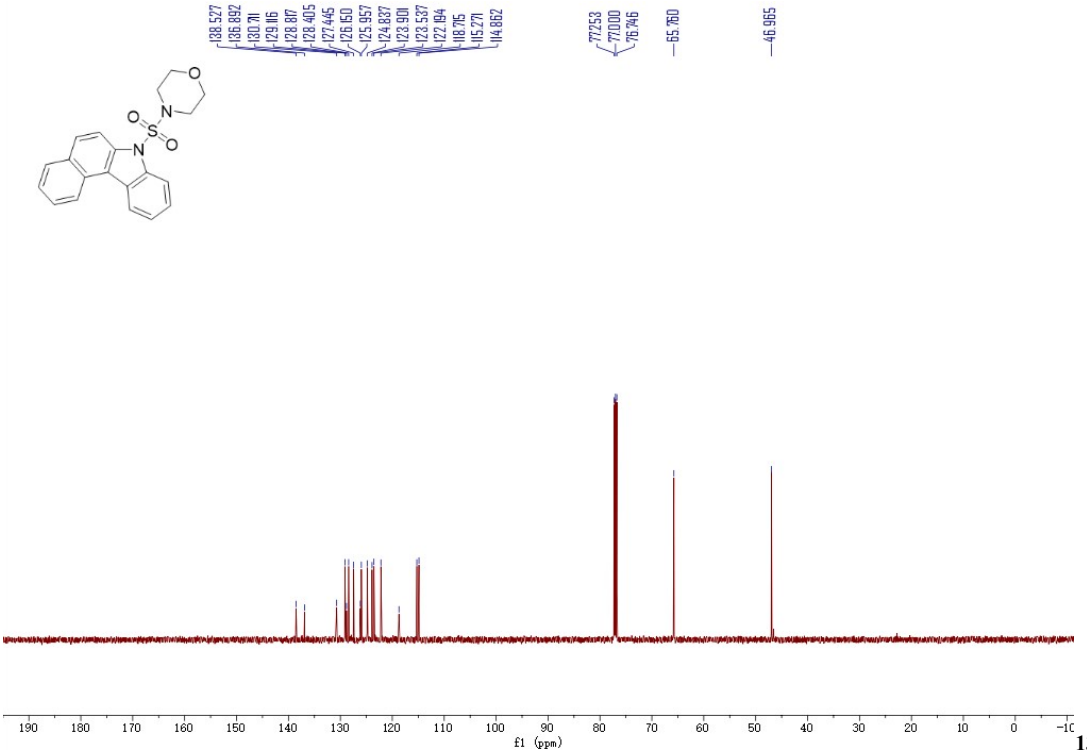


^{13}C NMR (125 MHz, $CDCl_3$)

4-((7H-benzo[*c*]carbazol-7-yl)sulfonyl)morpholine (2k):



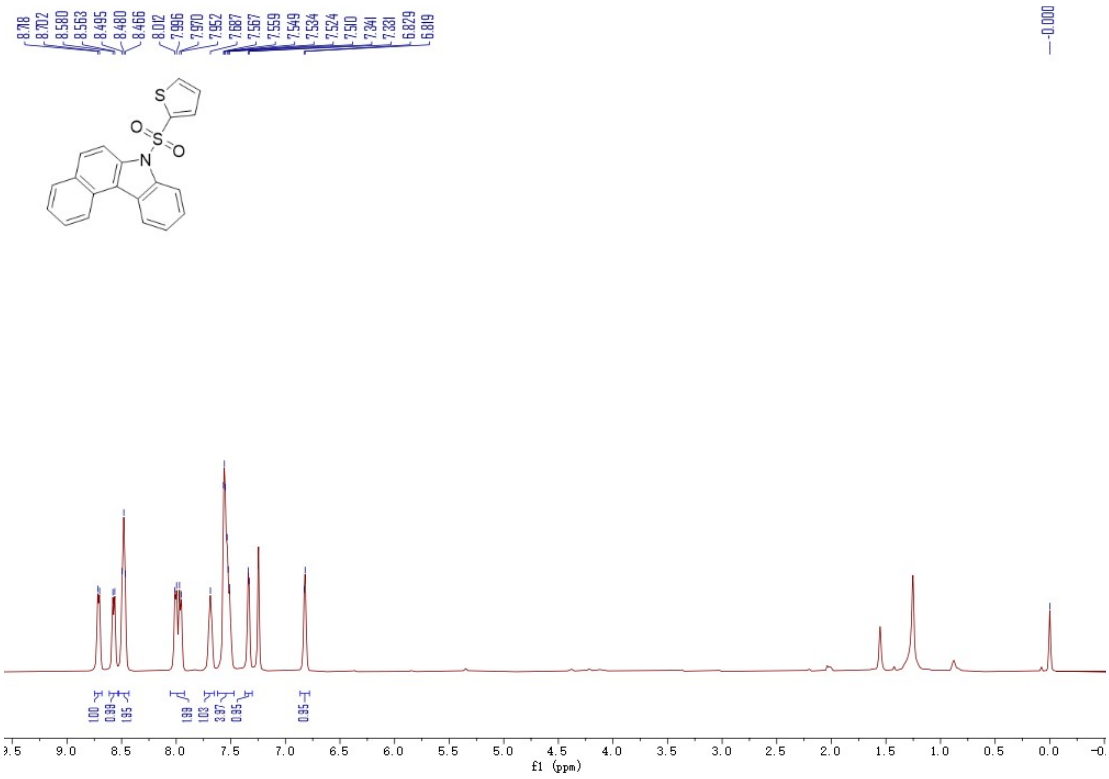
^{1}H NMR (500 MHz, $CDCl_3$)



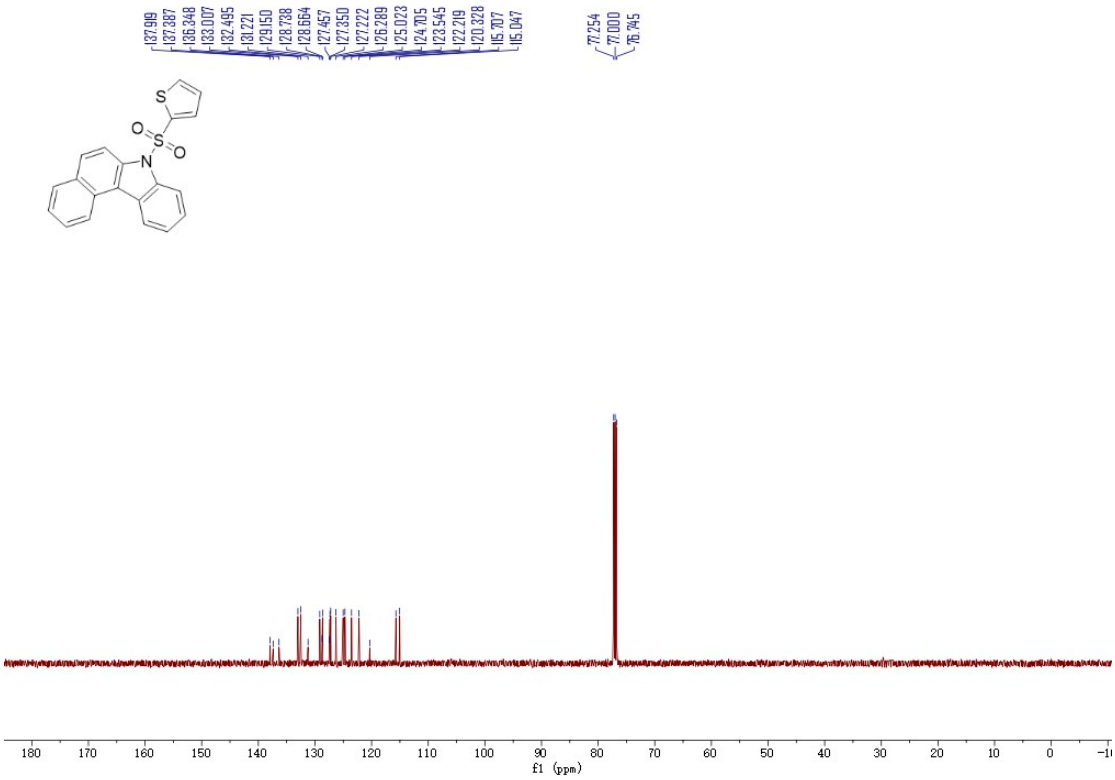
13

C NMR (125 MHz, $CDCl_3$)

7-(thiophen-2-ylsulfonyl)-7H-benzo[*c*]carbazole (2l):

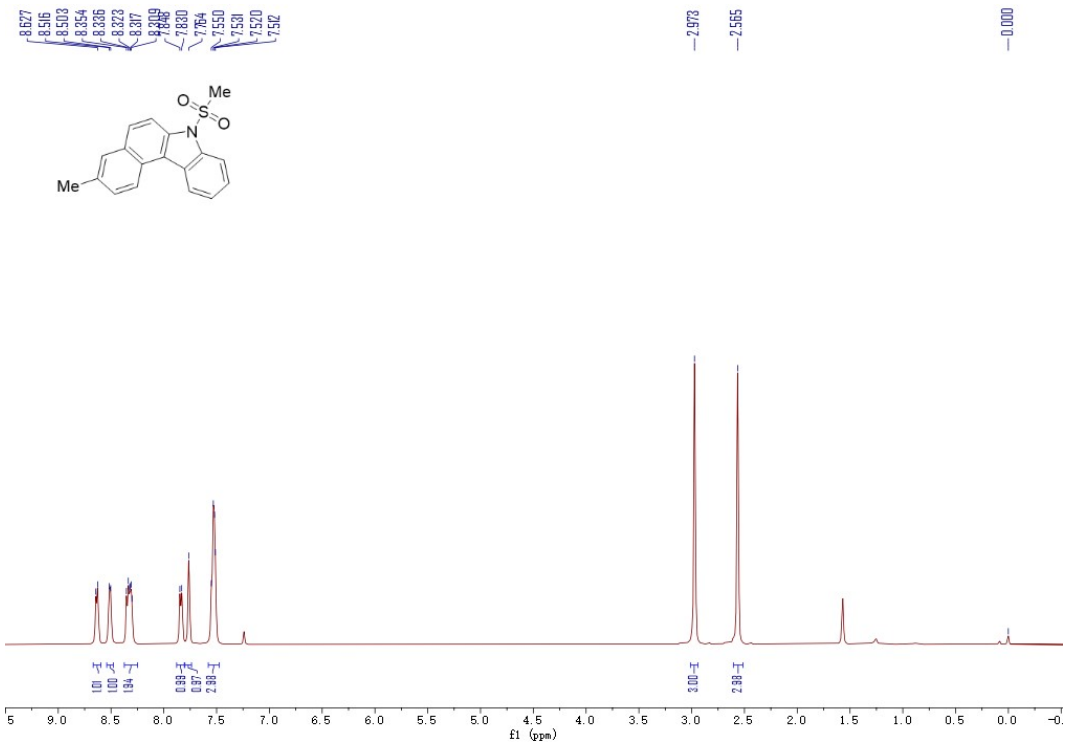


^{1}H NMR (500 MHz, $CDCl_3$)

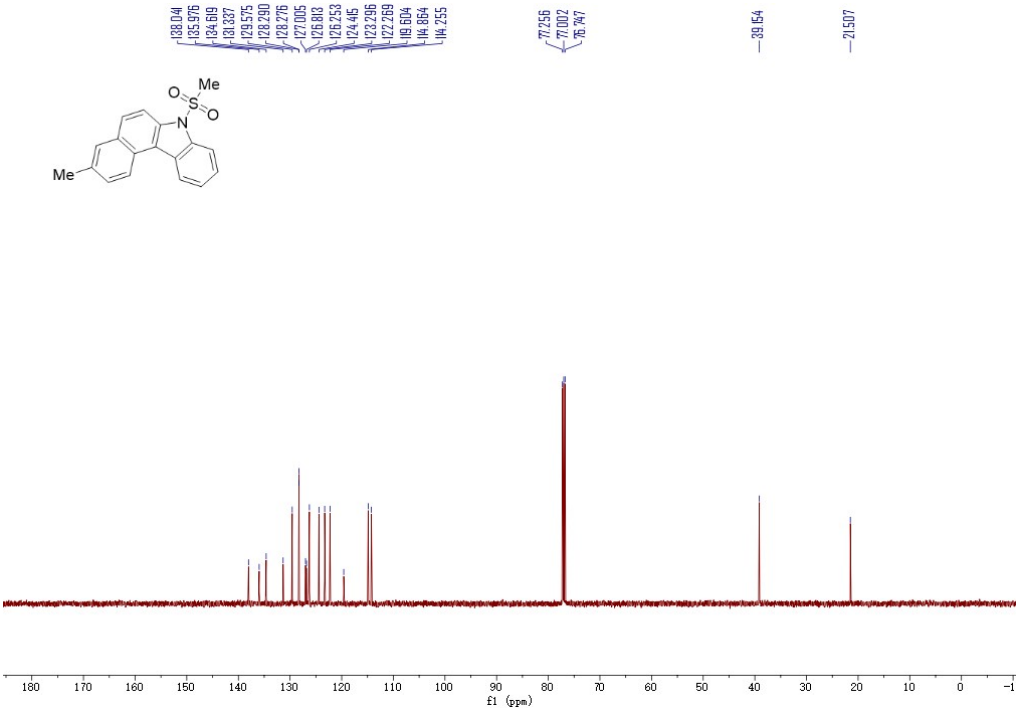


^{13}C NMR (125 MHz, $CDCl_3$)

3-methyl-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2m):

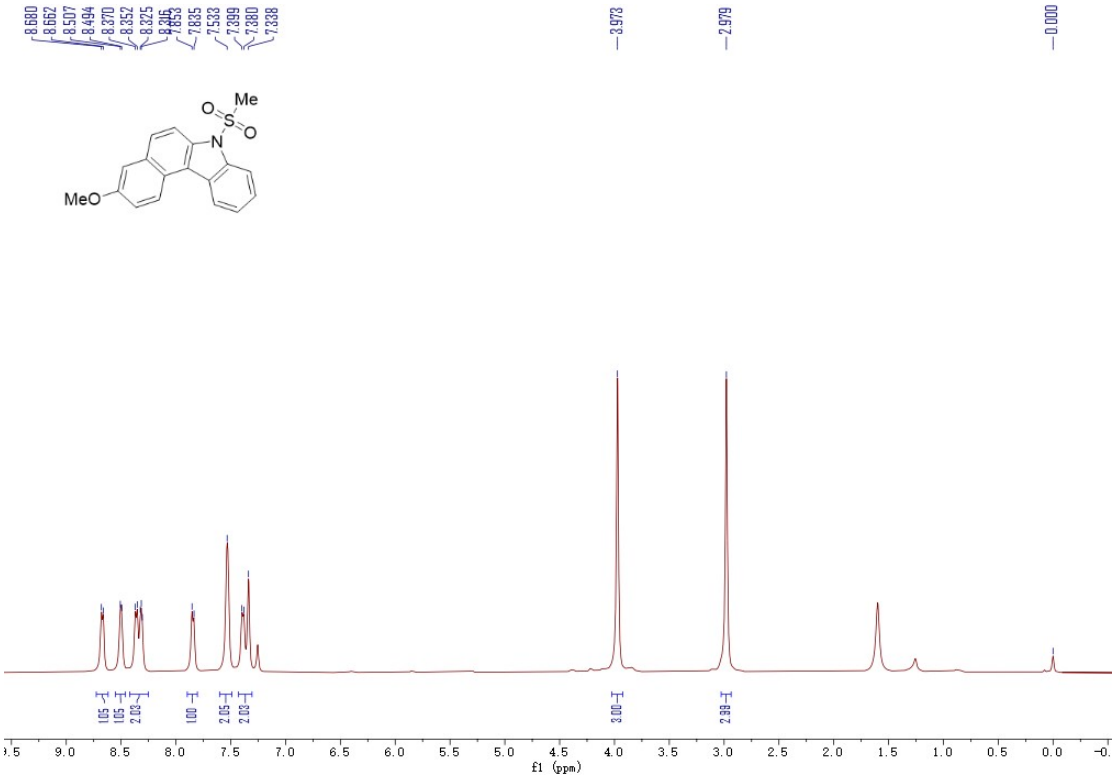


^{1}H NMR (500 MHz, $CDCl_3$)

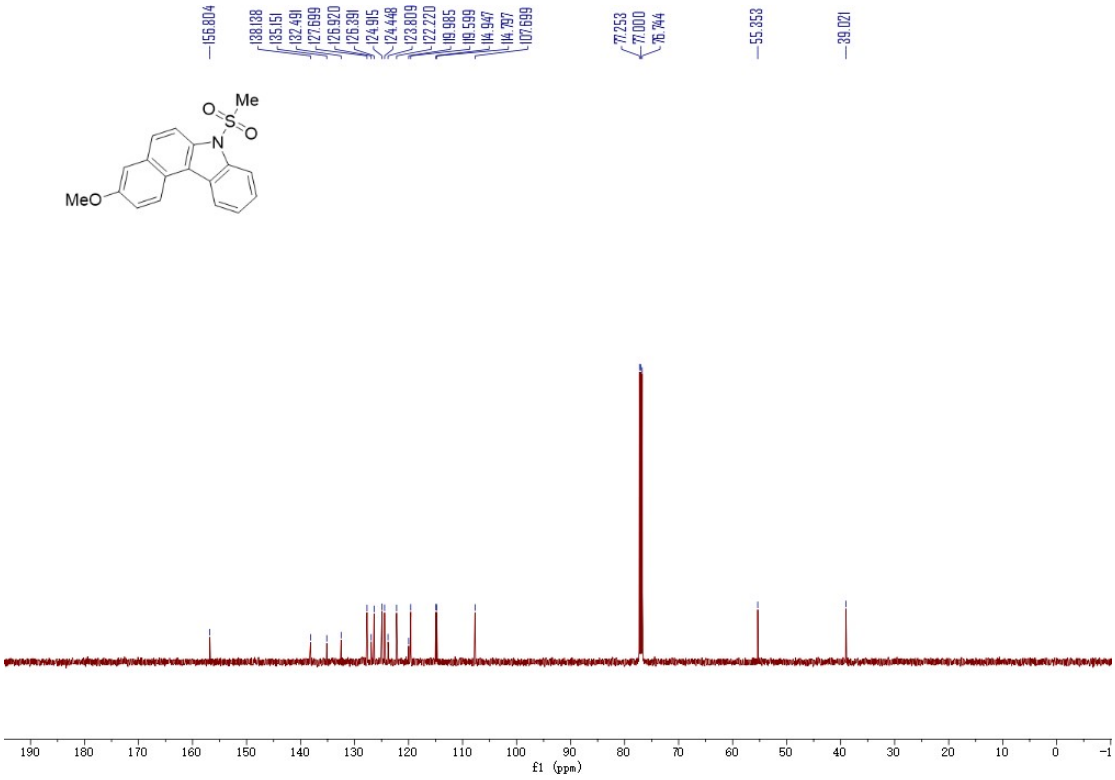


^{13}C NMR (125 MHz, $CDCl_3$)

3-methoxy-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2n):

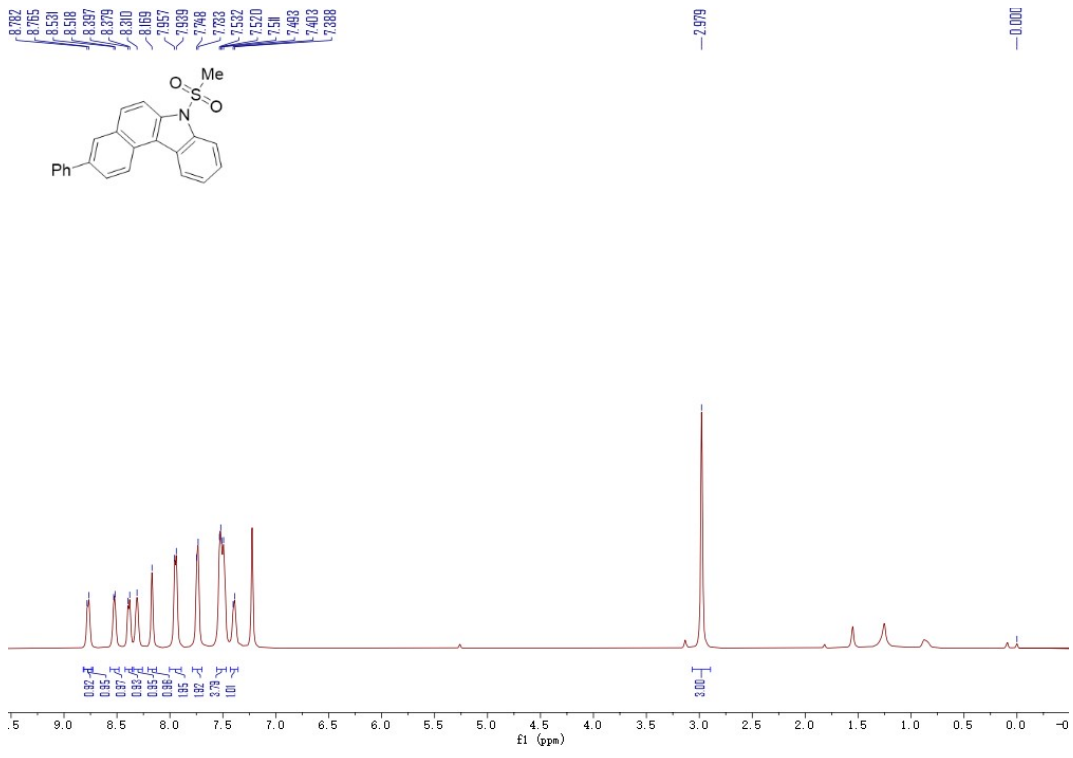


^{1}H NMR (500 MHz, $CDCl_3$)

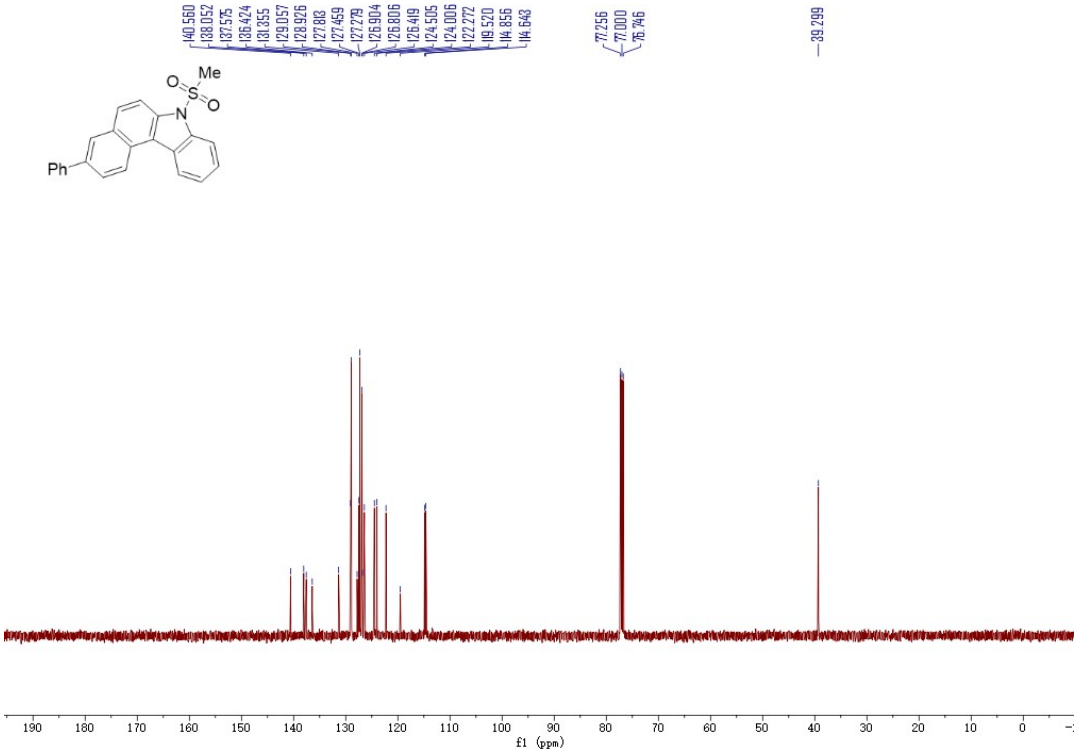


^{13}C NMR (125 MHz, $CDCl_3$)

7-(methylsulfonyl)-3-phenyl-7H-benzo[*c*]carbazole (2o)：

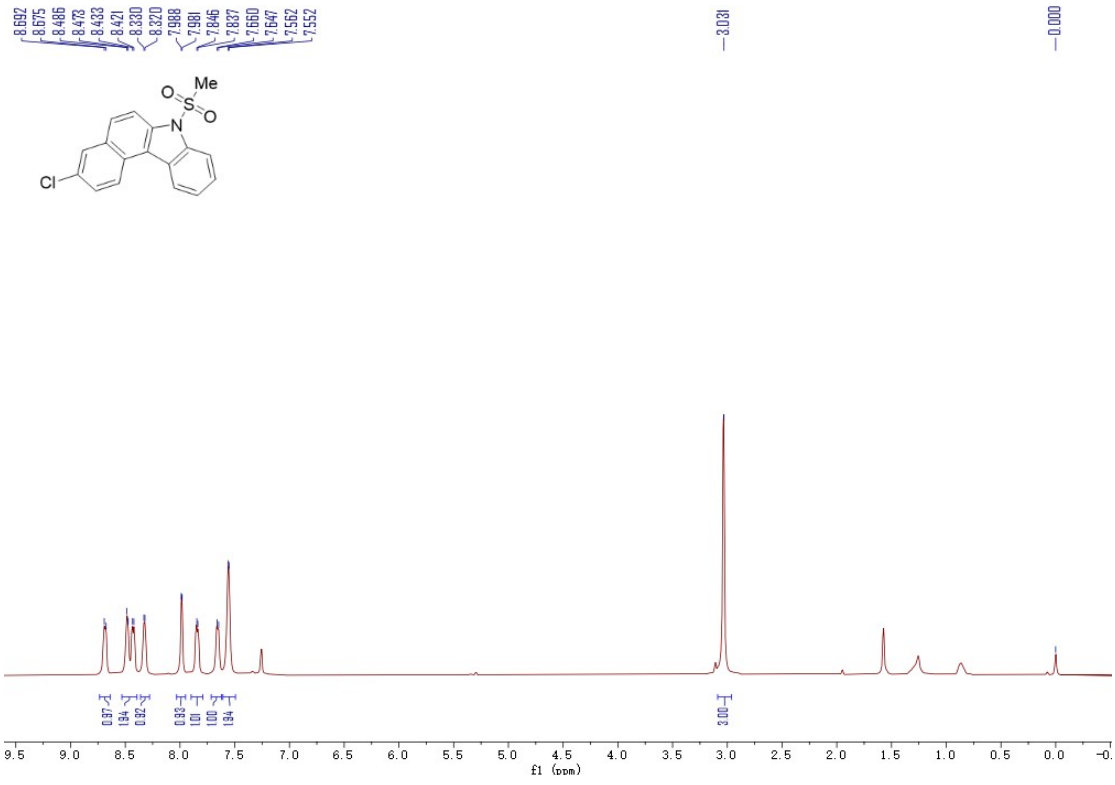


^{1}H NMR (500 MHz, $CDCl_3$)

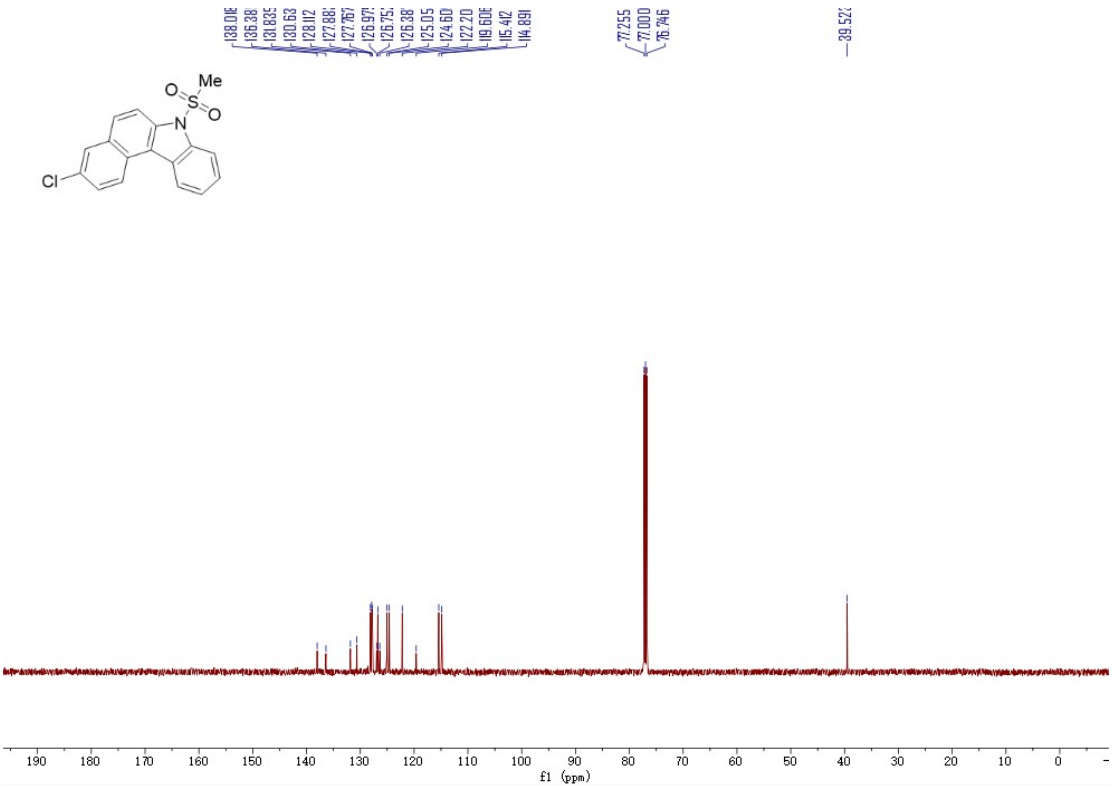


^{13}C NMR (125 MHz, $CDCl_3$)

3-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2p):

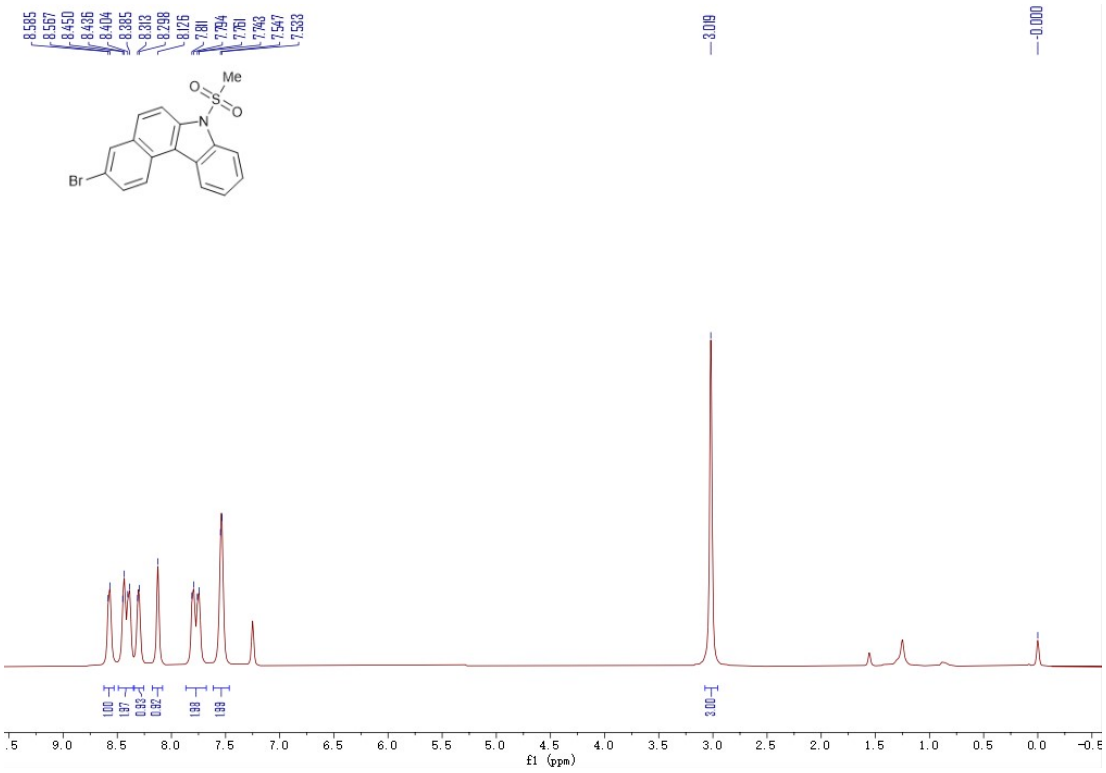


^{1}H NMR (500 MHz, $CDCl_3$)

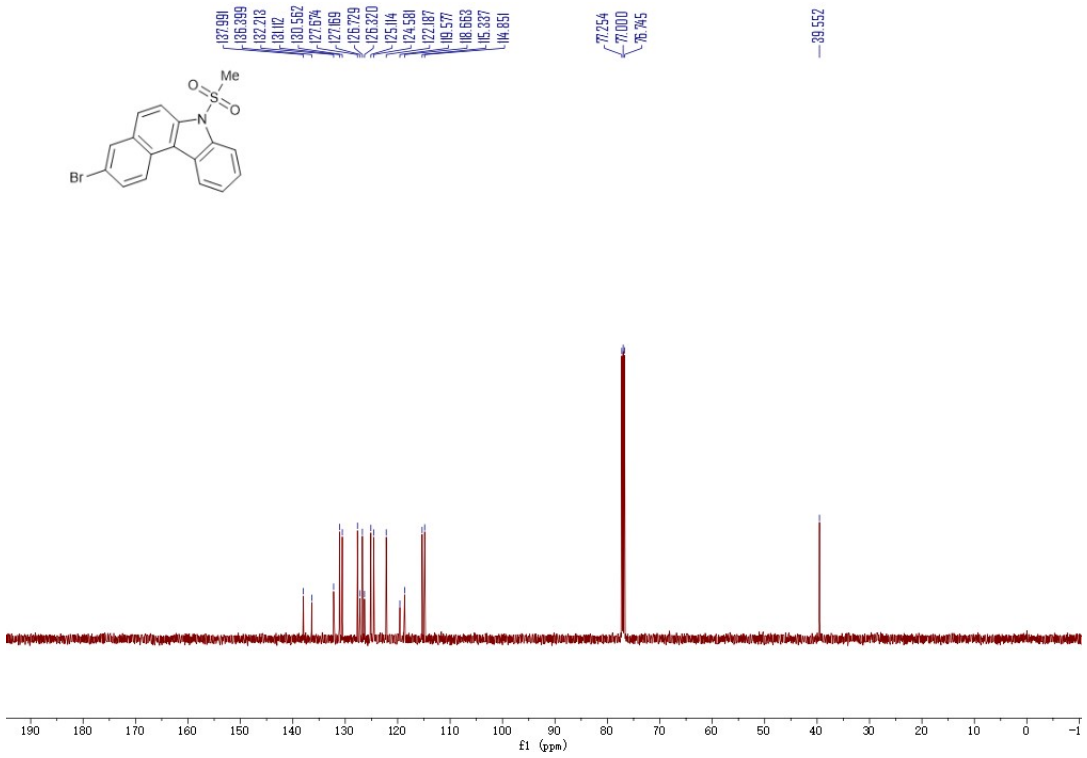


^{13}C NMR (125 MHz, $CDCl_3$)

3-bromo-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2q):

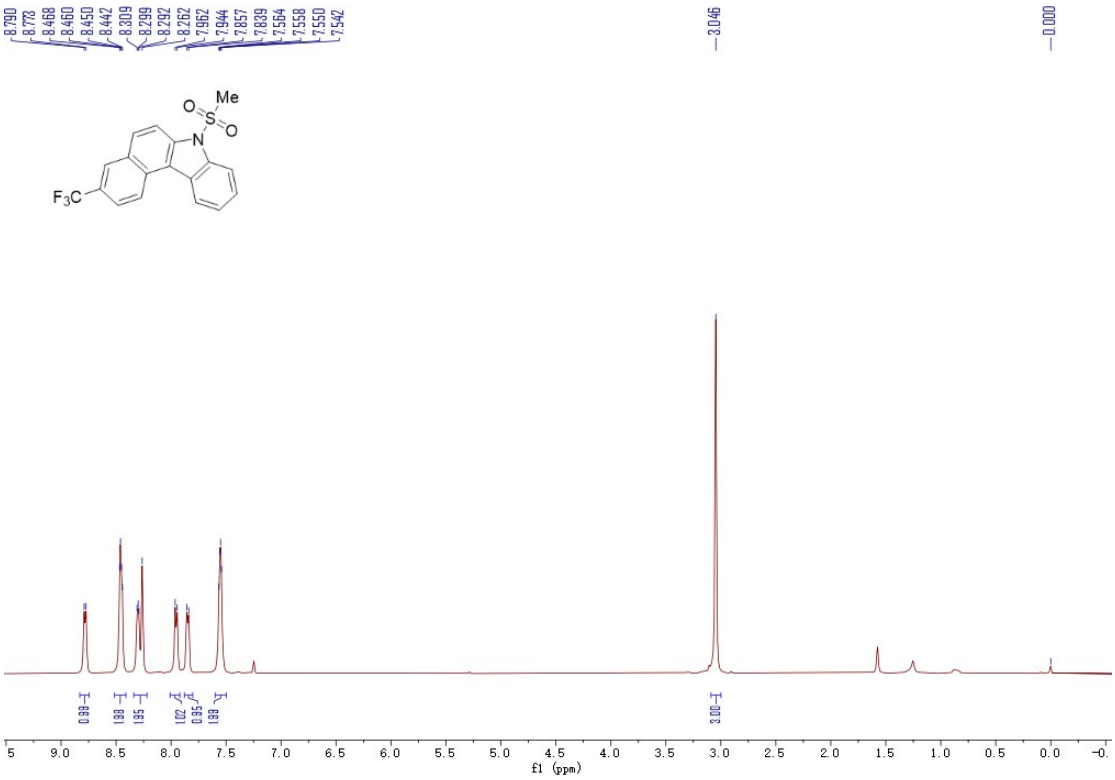


^{1}H NMR (500 MHz, $CDCl_3$)

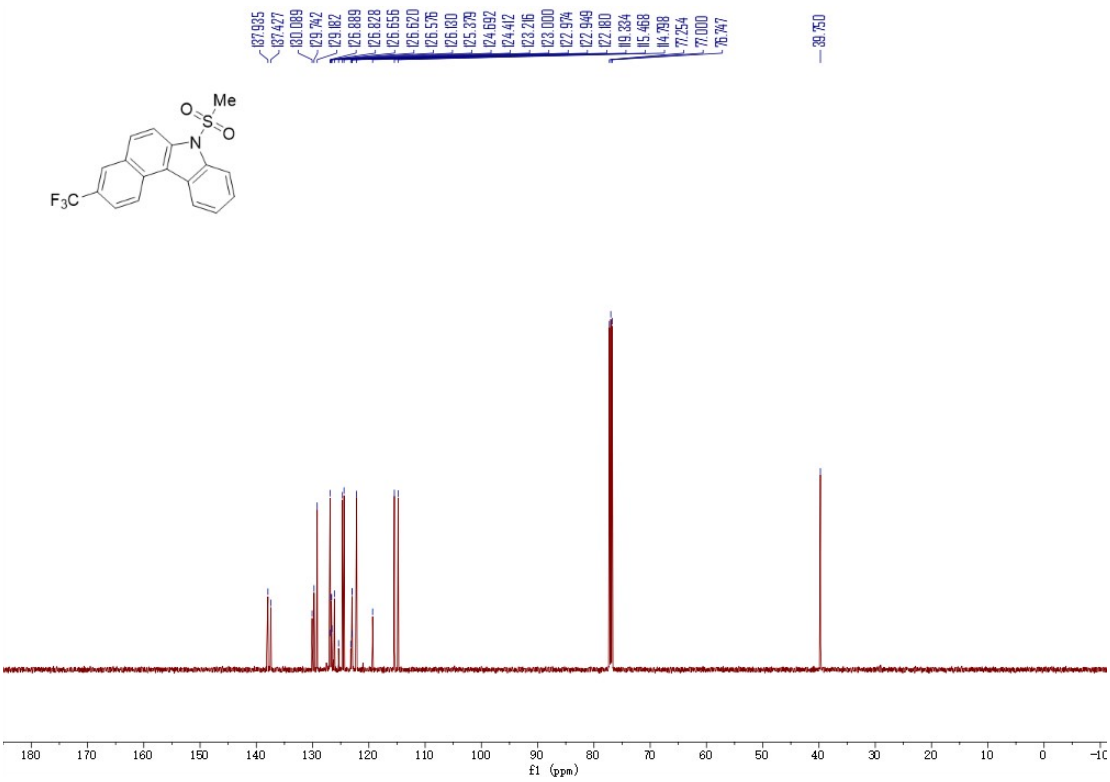


^{13}C NMR (125 MHz, $CDCl_3$)

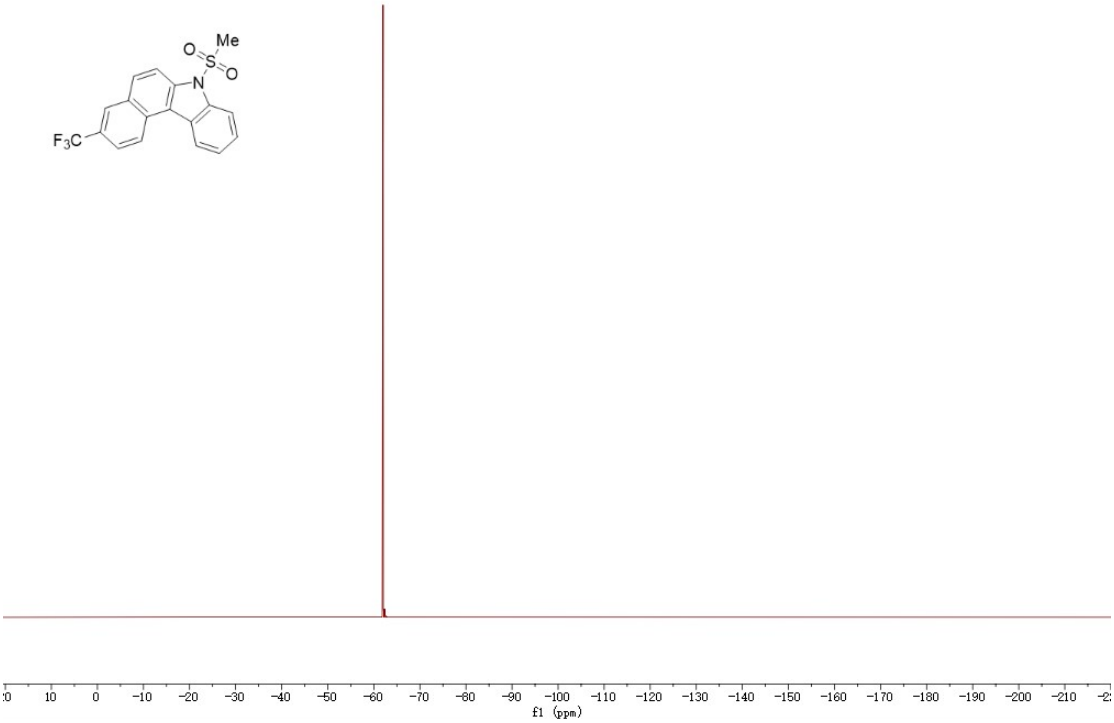
7-(methylsulfonyl)-3-(trifluoromethyl)-7H-benzo[*c*]carbazole (2r):



^{1}H NMR (500 MHz, $CDCl_3$)

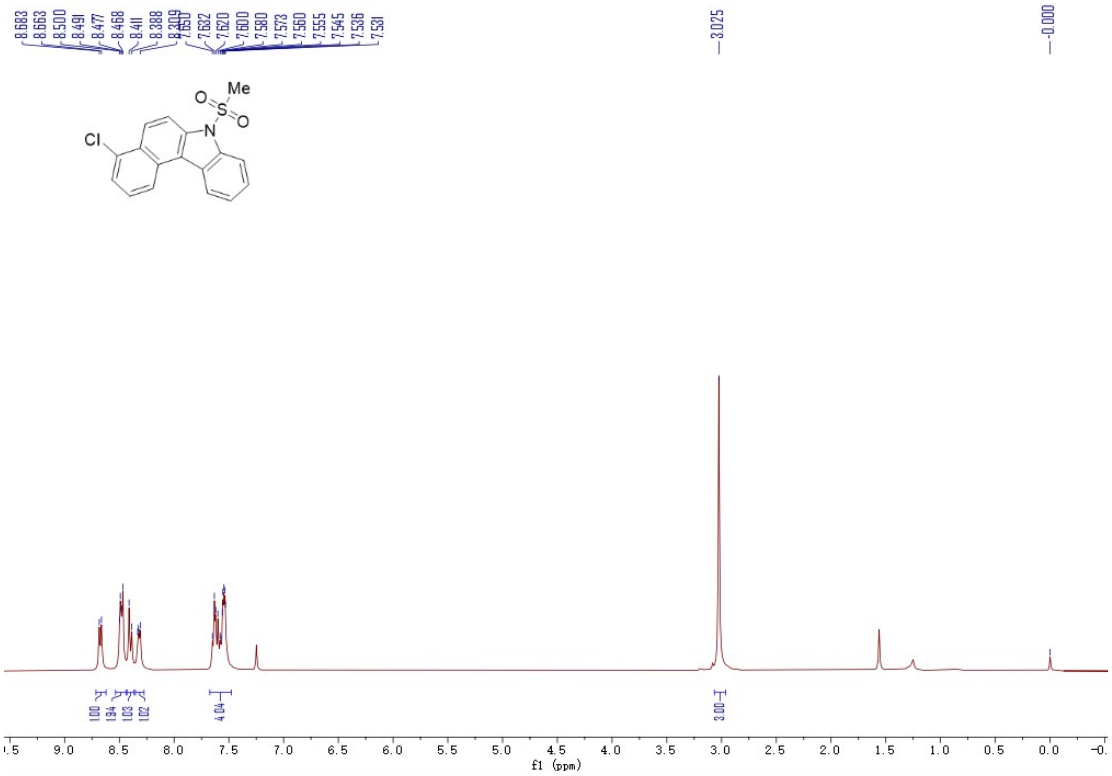


^{13}C NMR (125 MHz, $CDCl_3$)

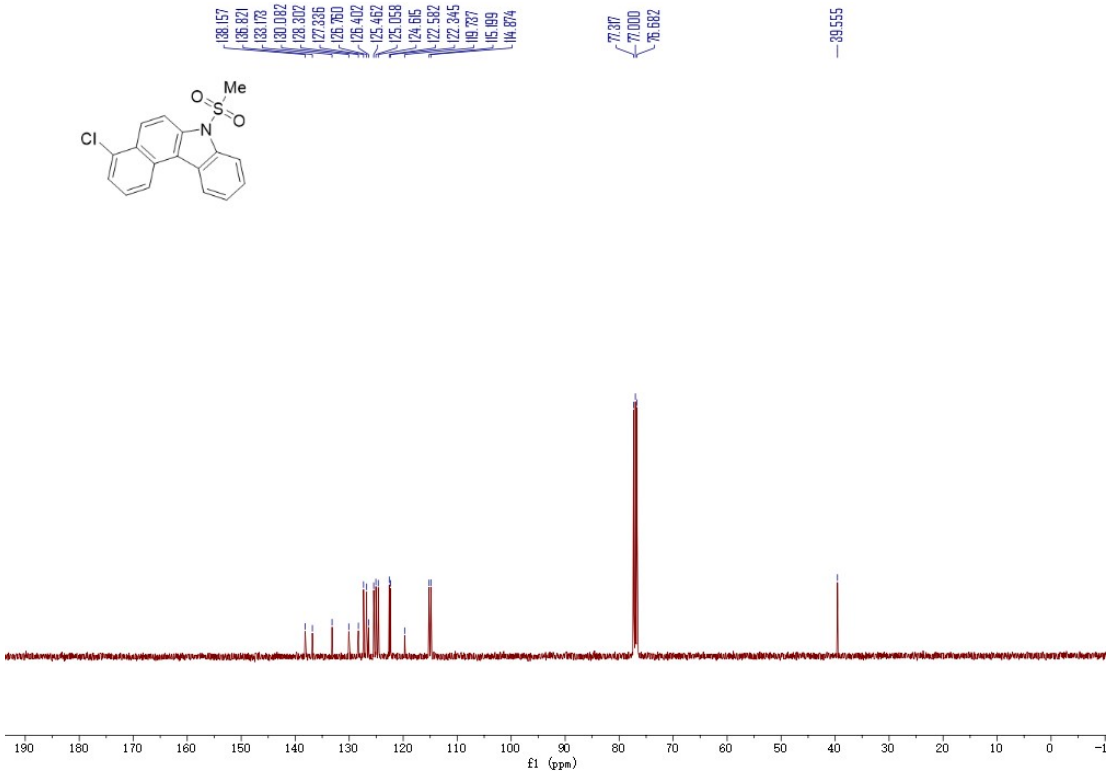


^{19}F NMR (471 MHz, $CDCl_3$)

4-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2s):

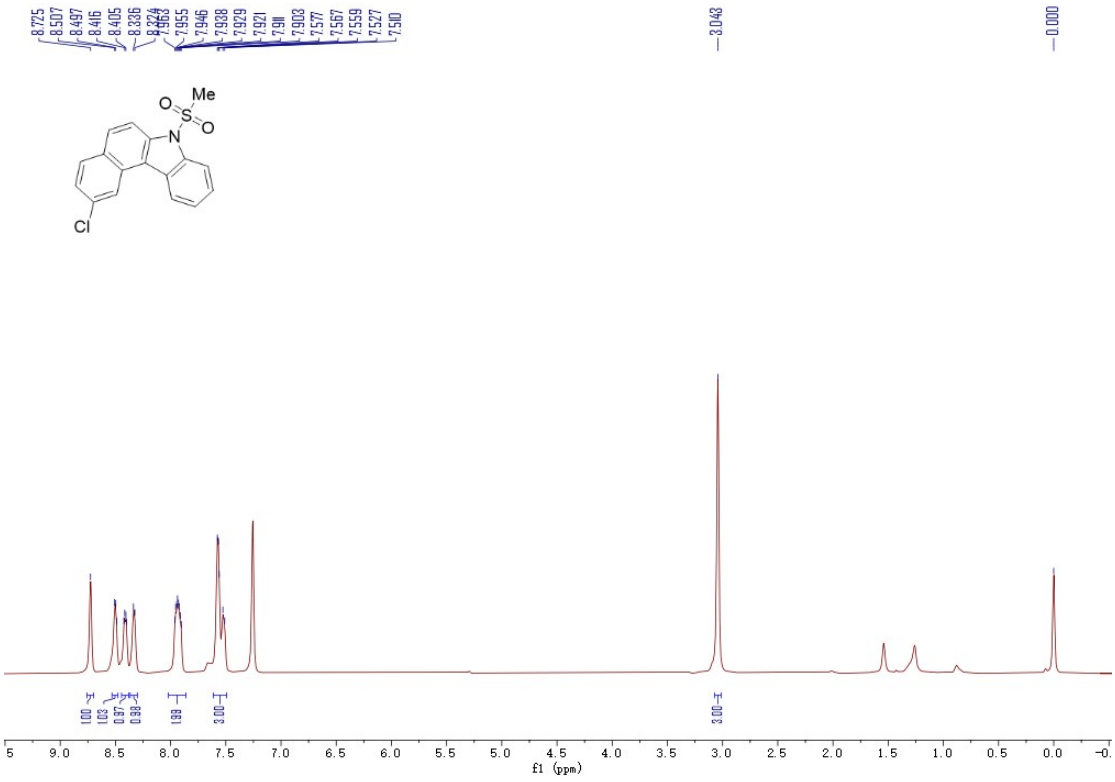


^{1}H NMR (400 MHz, $CDCl_3$)

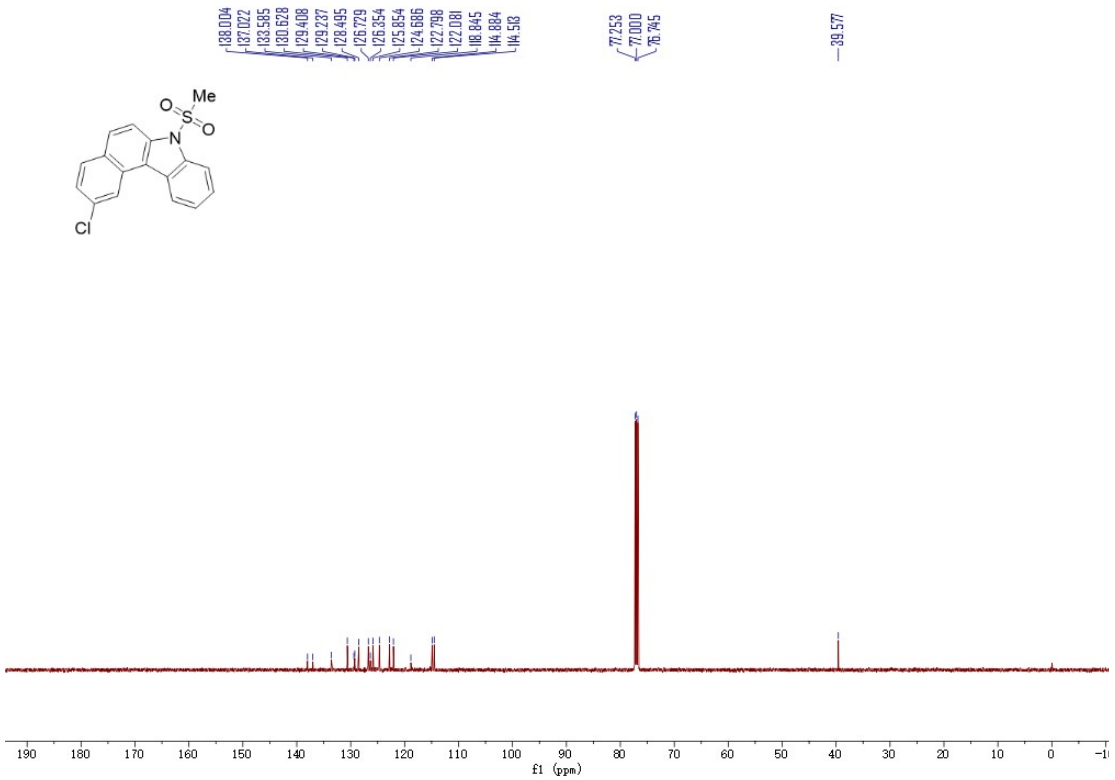


^{13}C NMR (100 MHz, $CDCl_3$)

2-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2s'):

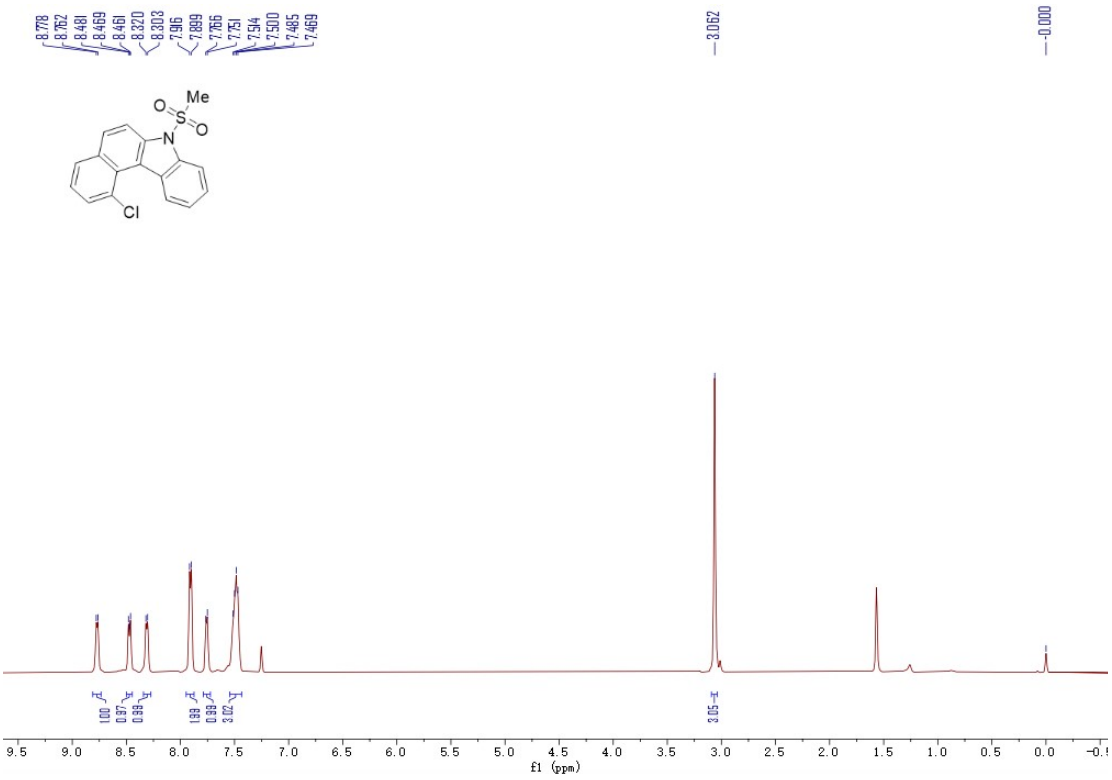


^{1}H NMR (500 MHz, $CDCl_3$)

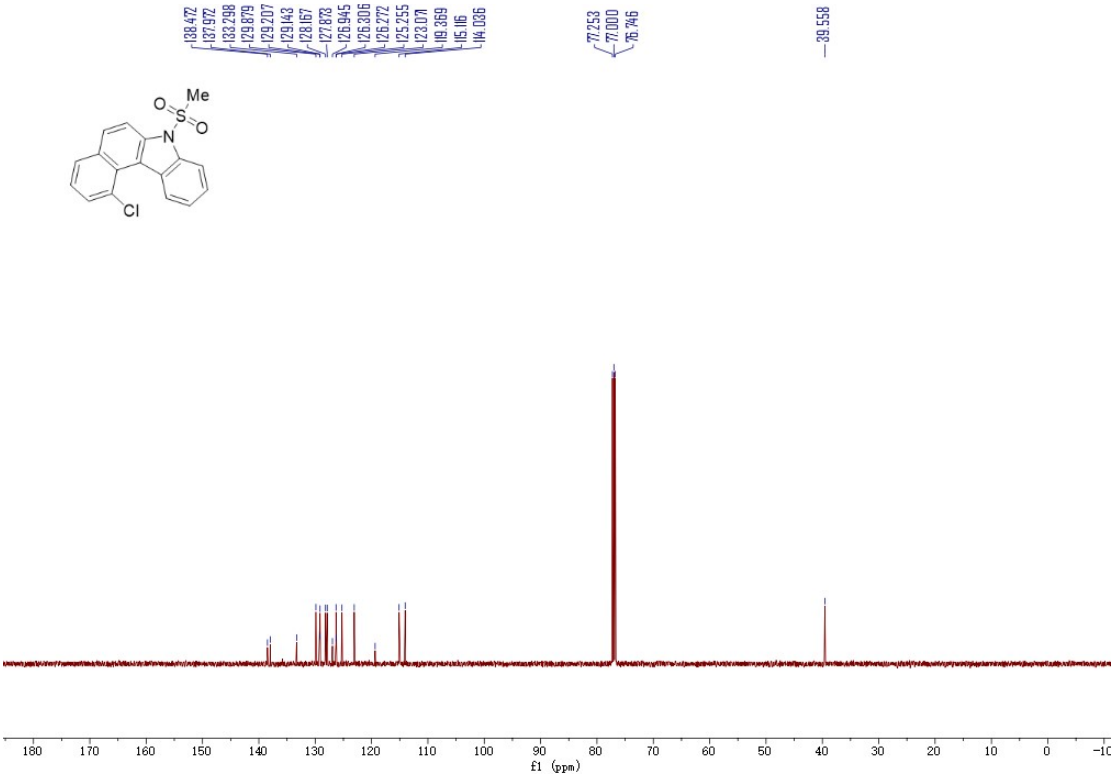


^{13}C NMR (125 MHz, $CDCl_3$)

1-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2t):

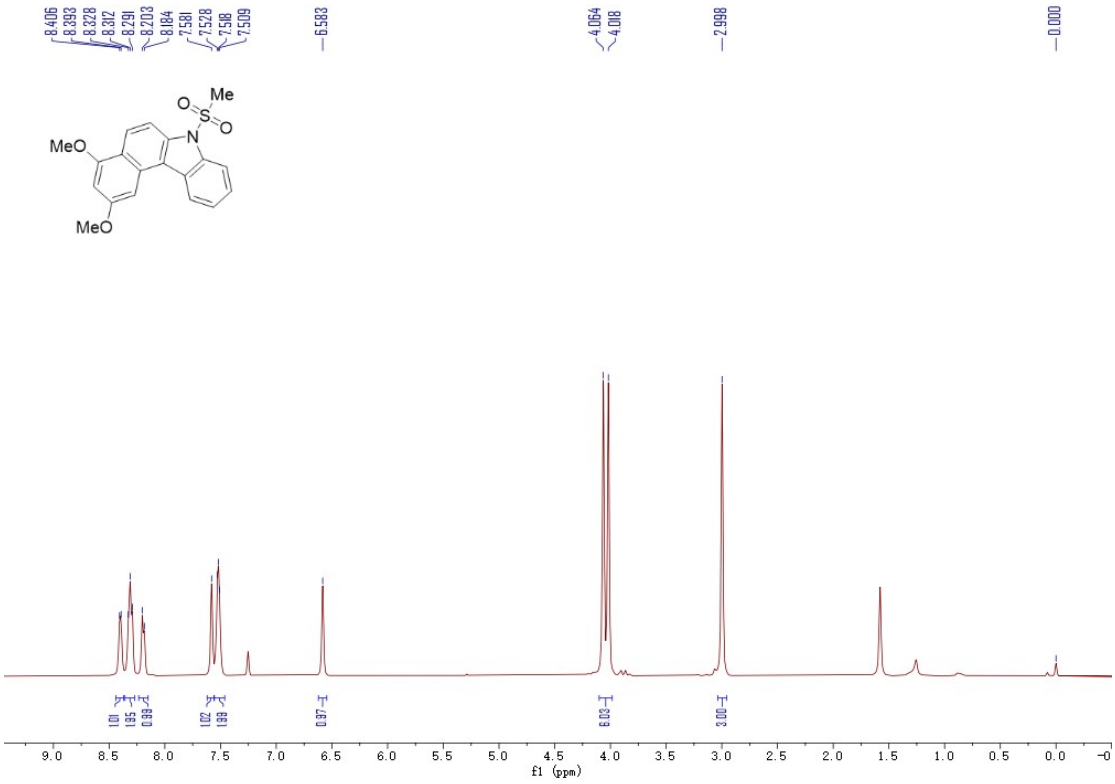


^{1}H NMR (500 MHz, $CDCl_3$)

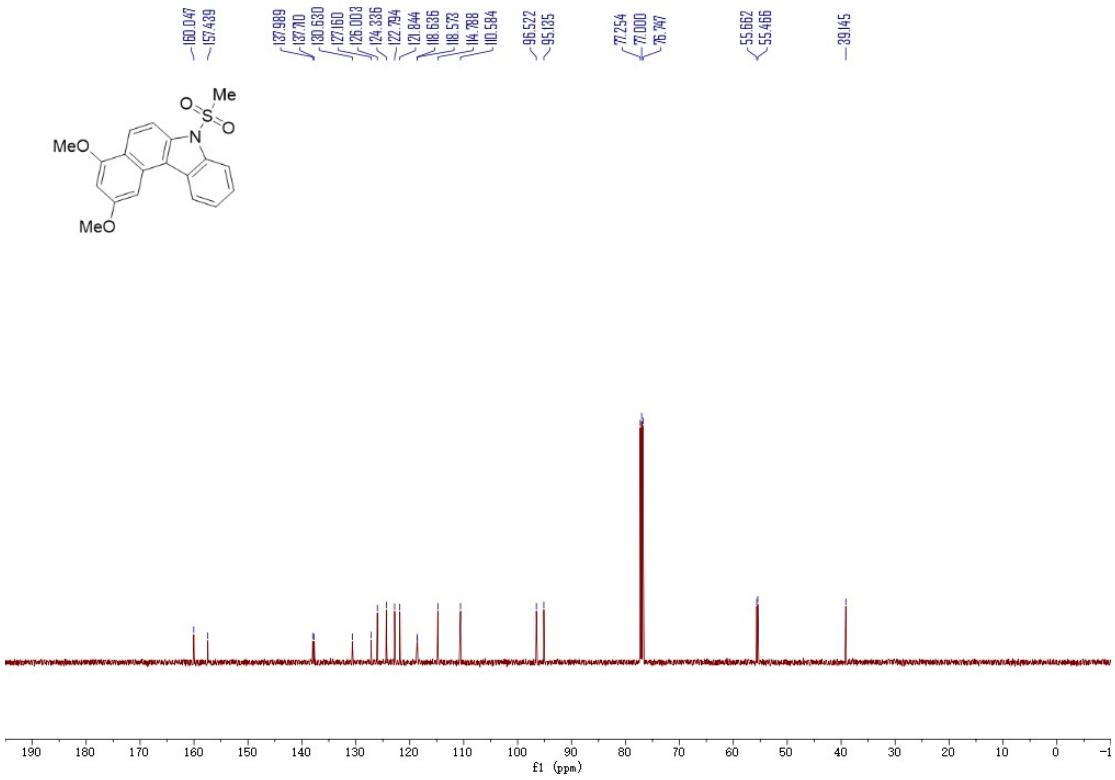


^{13}C NMR (125 MHz, $CDCl_3$)

2,4-dimethoxy-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2u):

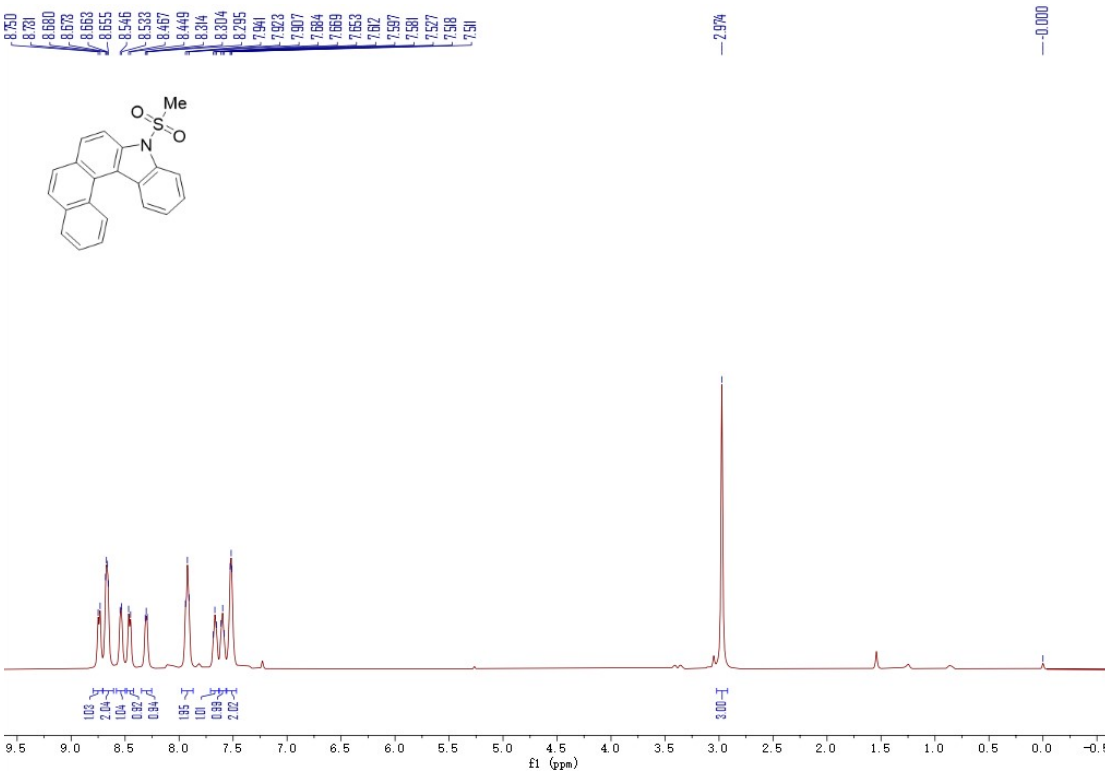


^{1}H NMR (500 MHz, $CDCl_3$)

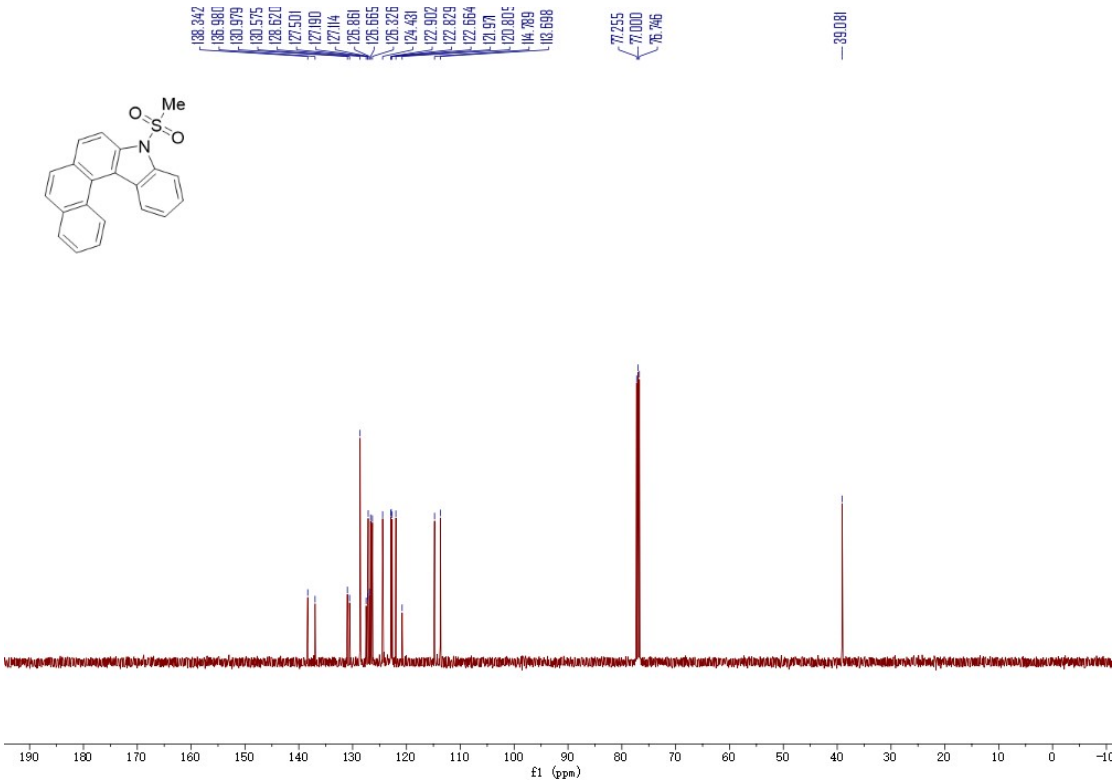


^{13}C NMR (125 MHz, $CDCl_3$)

9-(methylsulfonyl)-9H-naphtho[2,1-*c*]carbazole (2v):

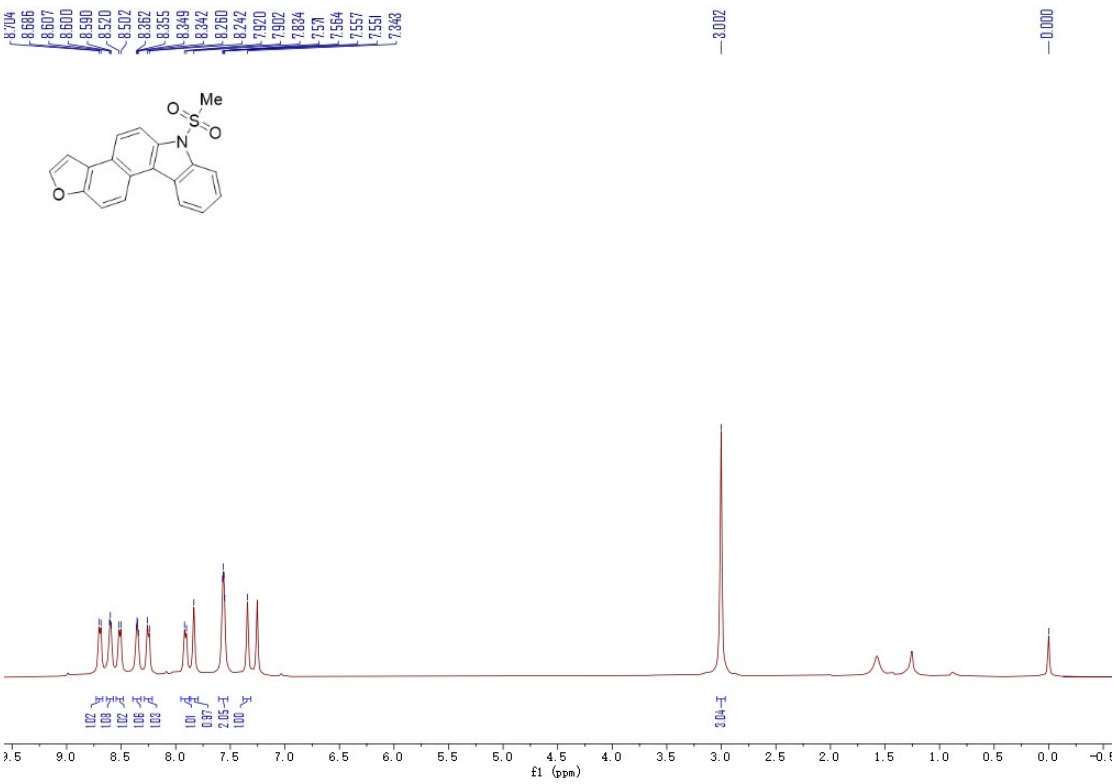


^{1}H NMR (500 MHz, $CDCl_3$)

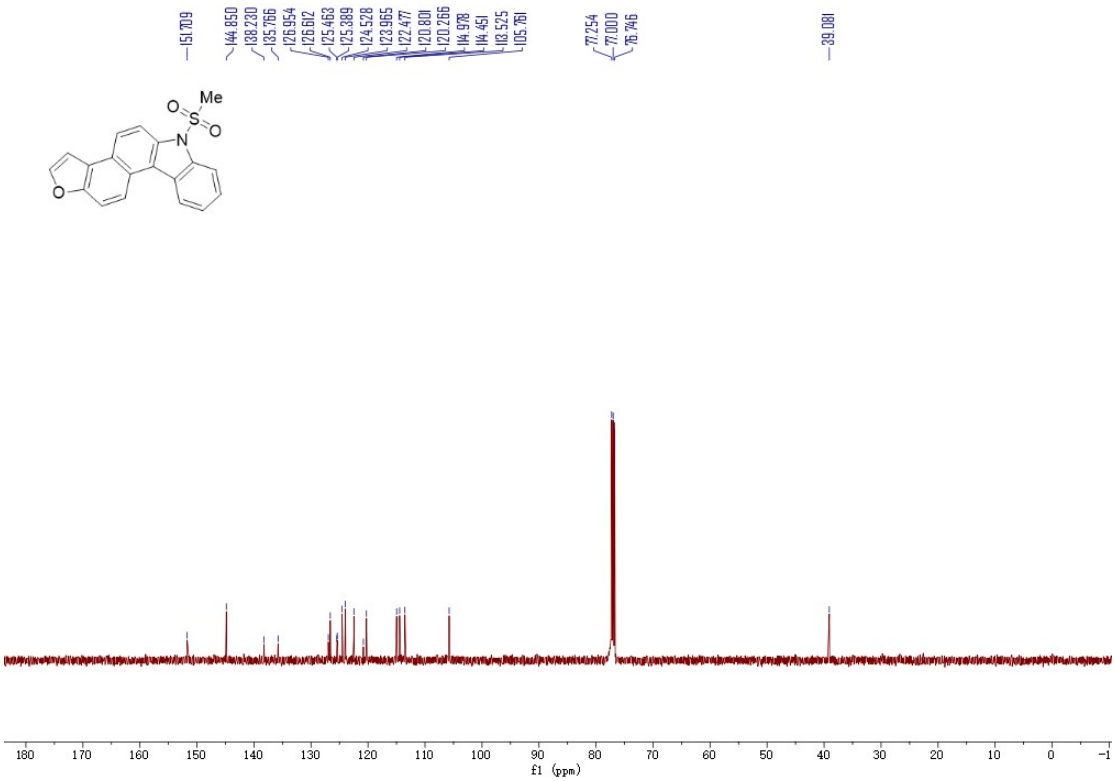


^{13}C NMR (125 MHz, $CDCl_3$)

6-(methylsulfonyl)-6H-benzofuro[4,5-*c*]carbazole (2w):

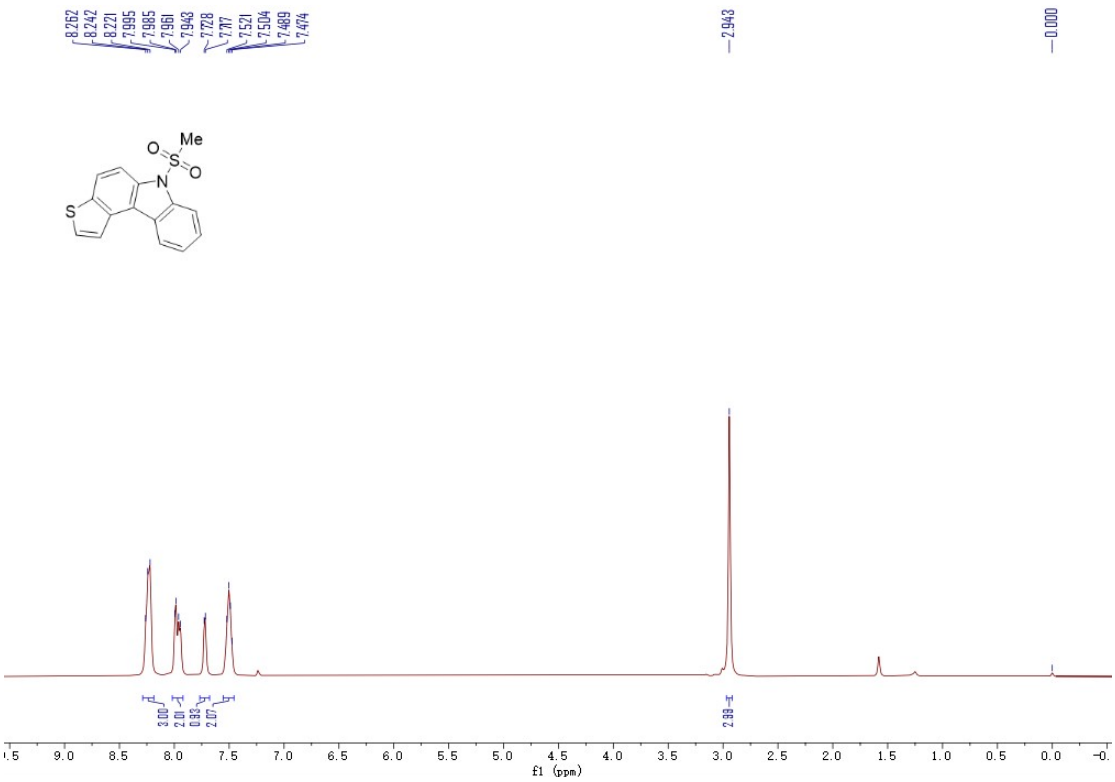


^{1}H NMR (500 MHz, $CDCl_3$)

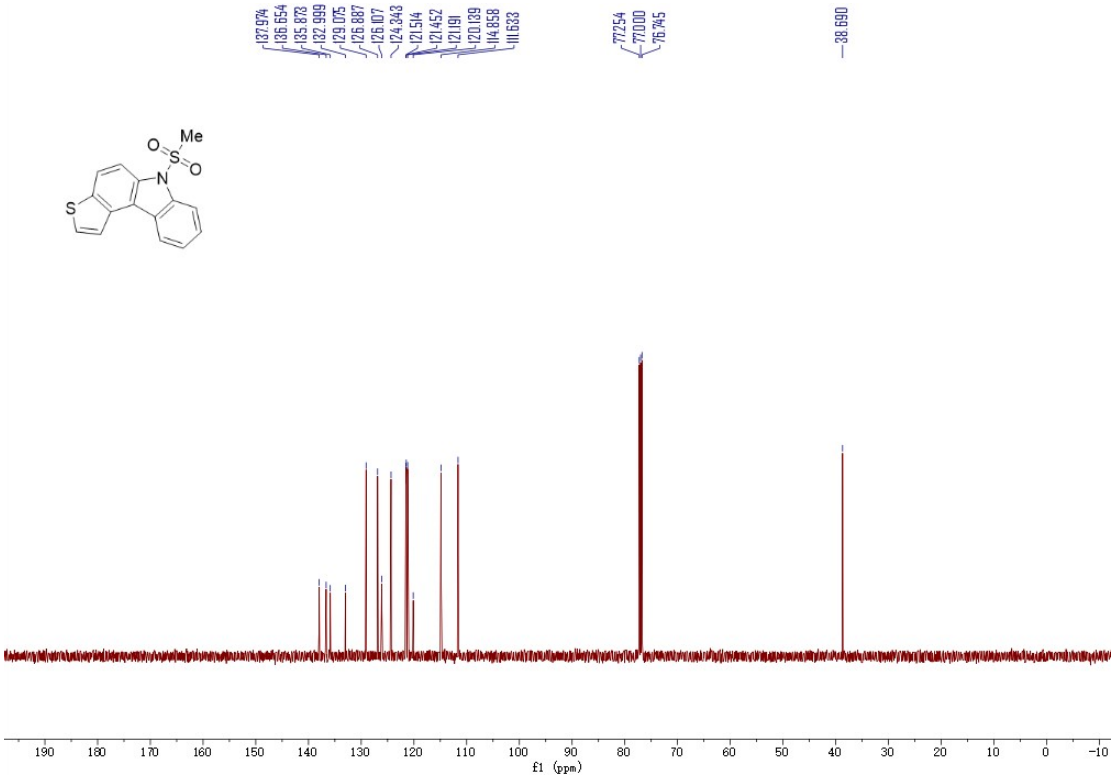


^{13}C NMR (125 MHz, $CDCl_3$)

6-(methylsulfonyl)-6H-thieno[2,3-*c*]carbazole (2x):

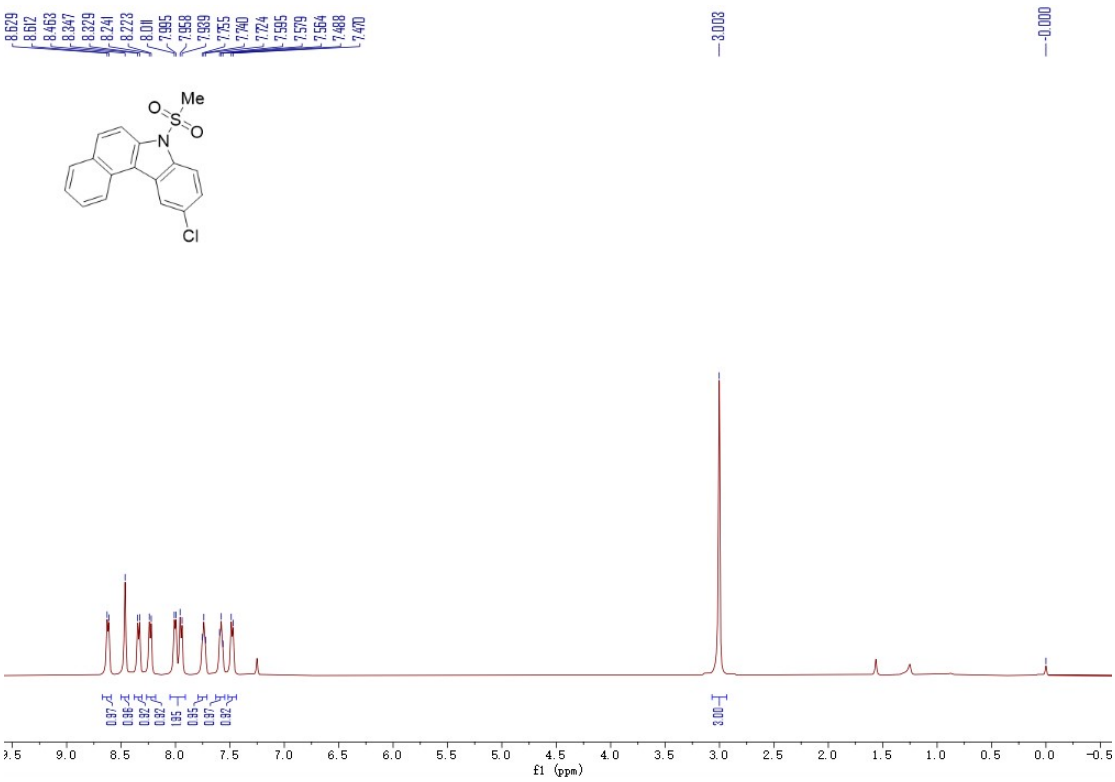


^{1}H NMR (500 MHz, $CDCl_3$)

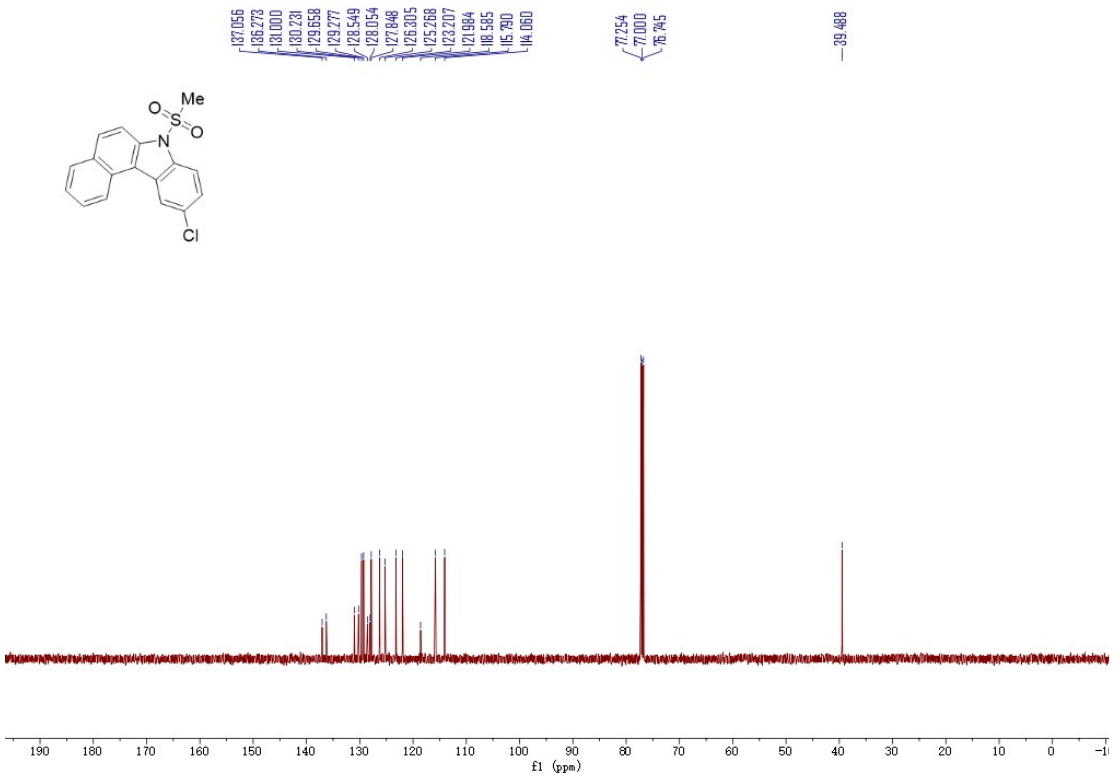


^{13}C NMR (125 MHz, $CDCl_3$)

10-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2y):

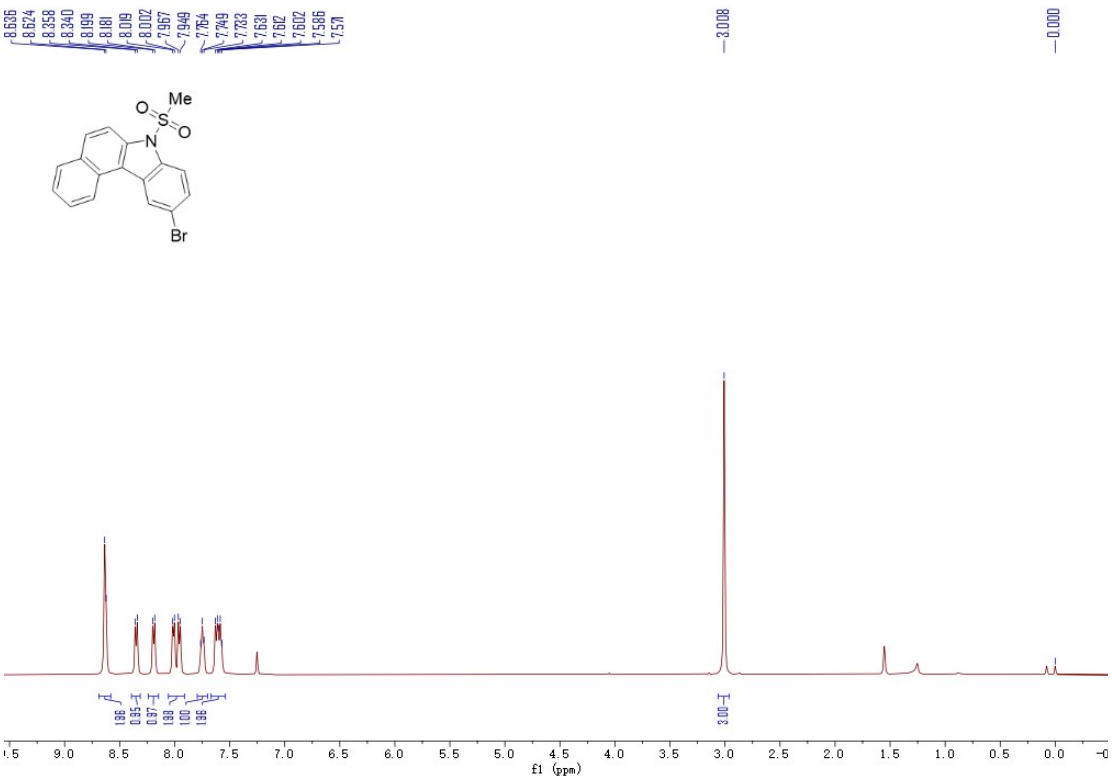


^{1}H NMR (500 MHz, $CDCl_3$)

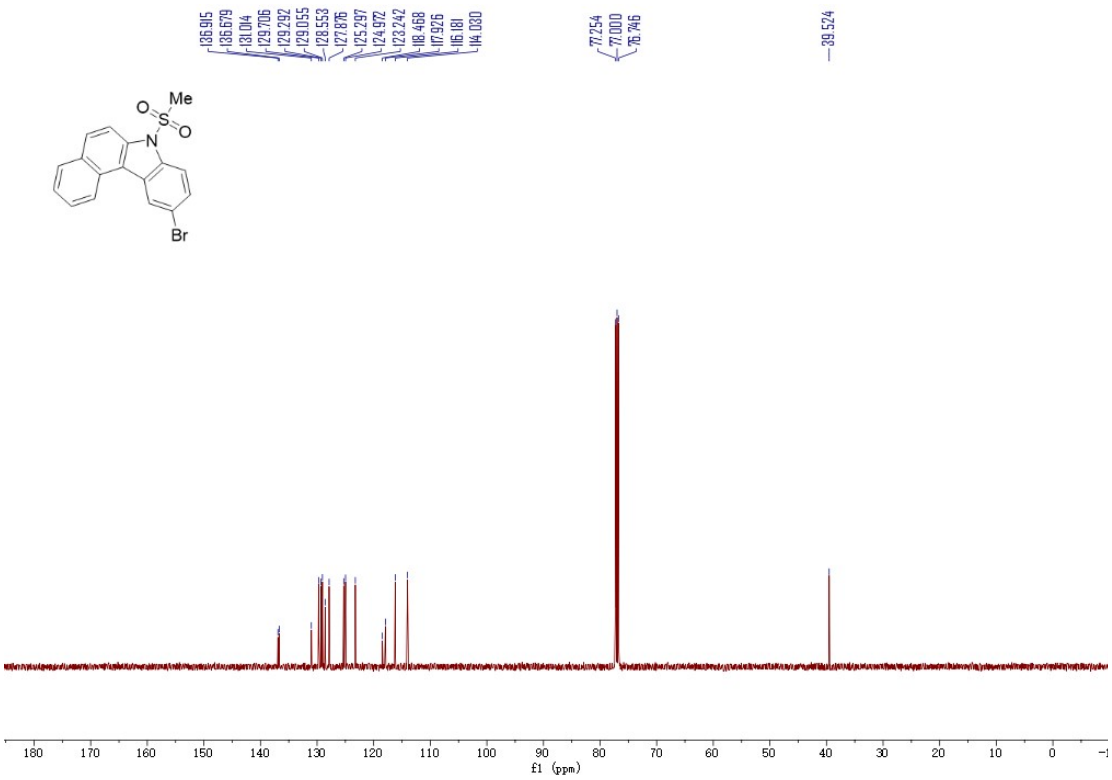


^{13}C NMR (125 MHz, $CDCl_3$)

10-bromo-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2z):

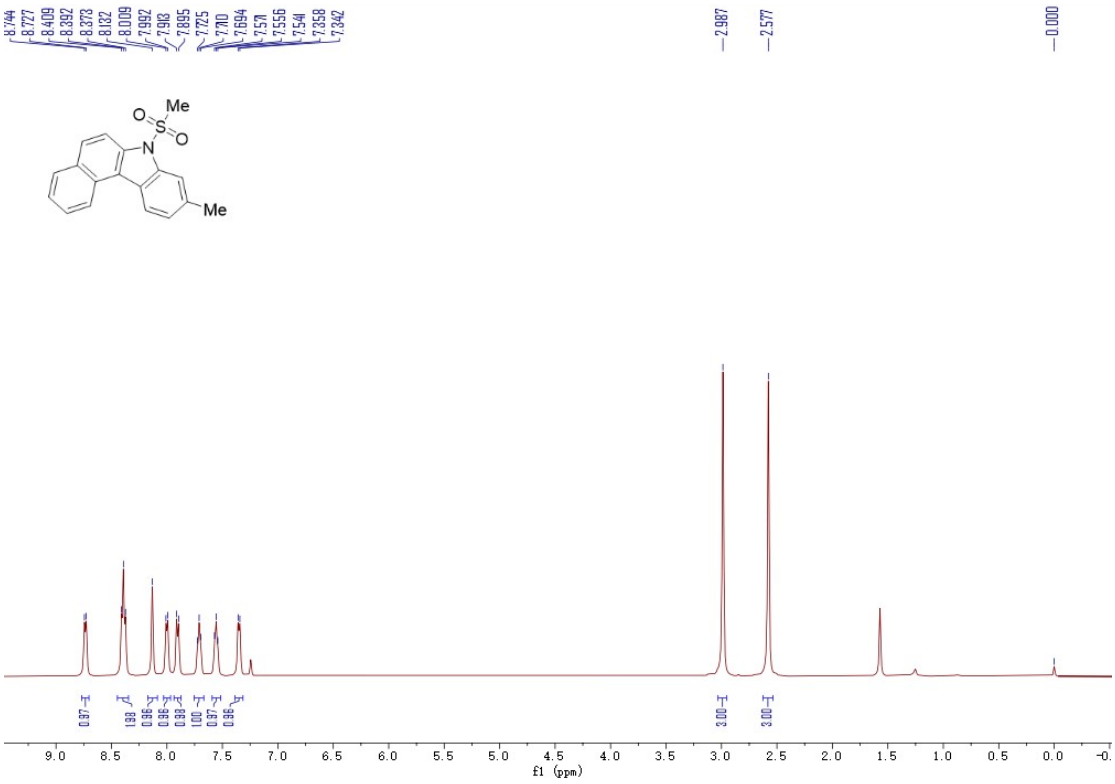


^{1}H NMR (500 MHz, $CDCl_3$)

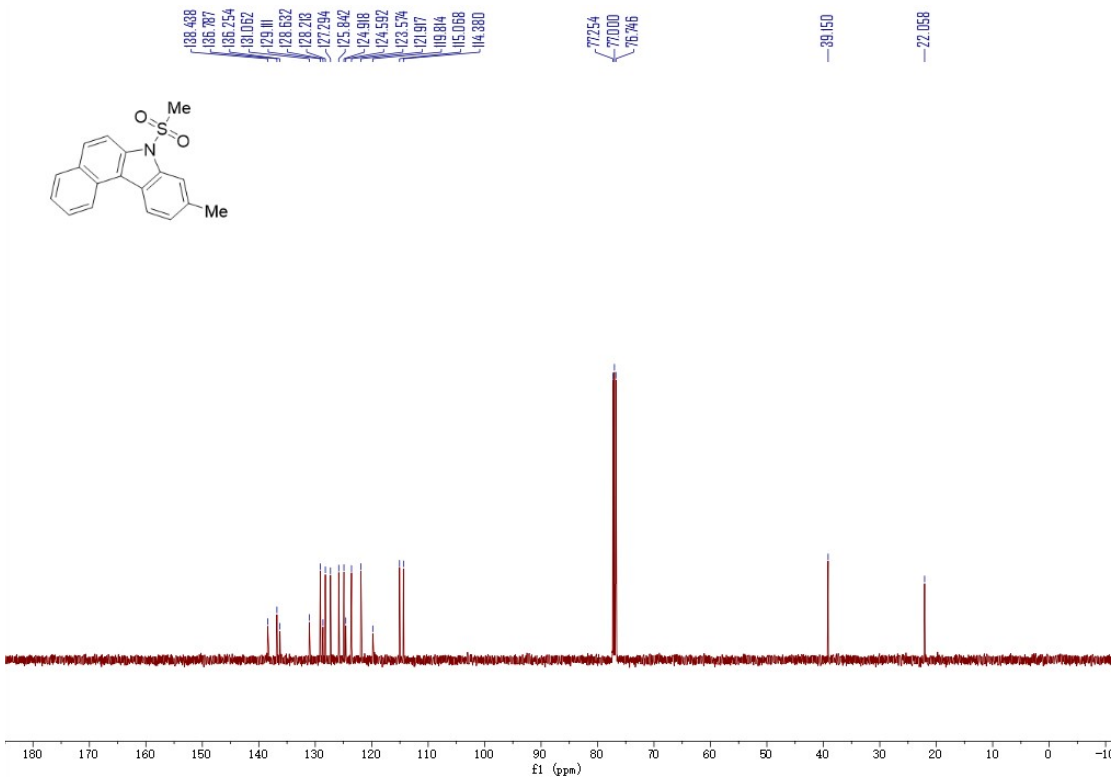


^{13}C NMR (125 MHz, $CDCl_3$)

9-methyl-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2aa):

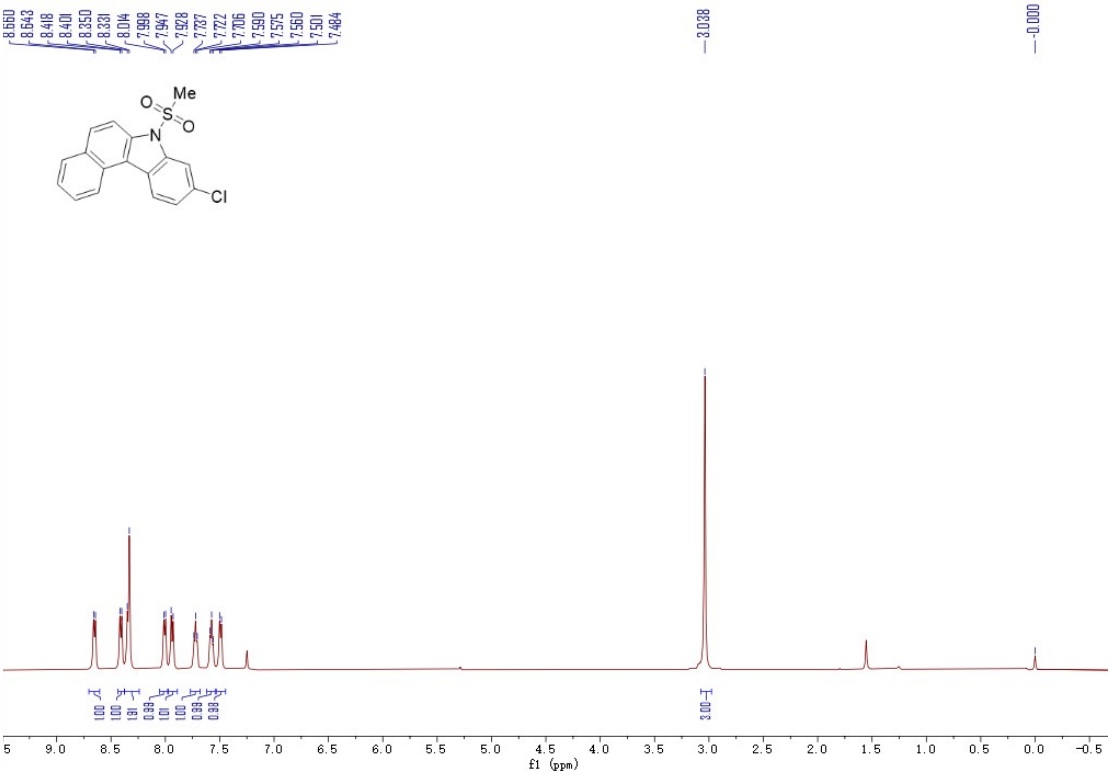


^{1}H NMR (500 MHz, $CDCl_3$)

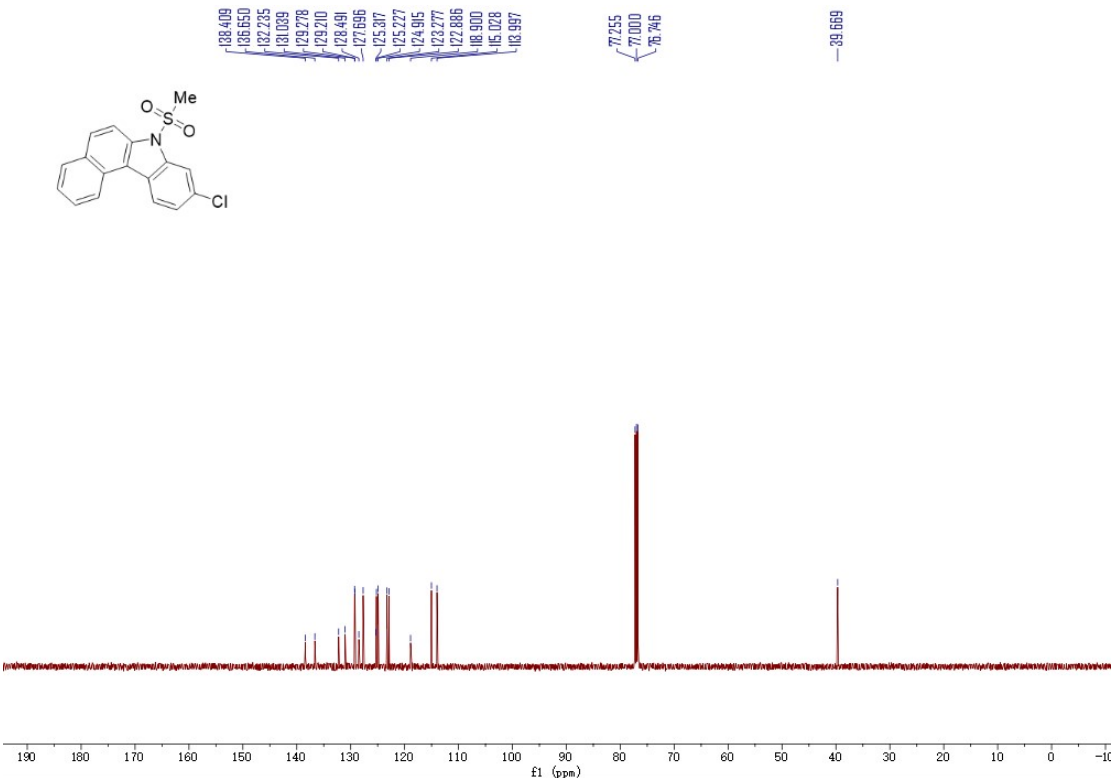


^{13}C NMR (125 MHz, $CDCl_3$)

9-chloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2ab):

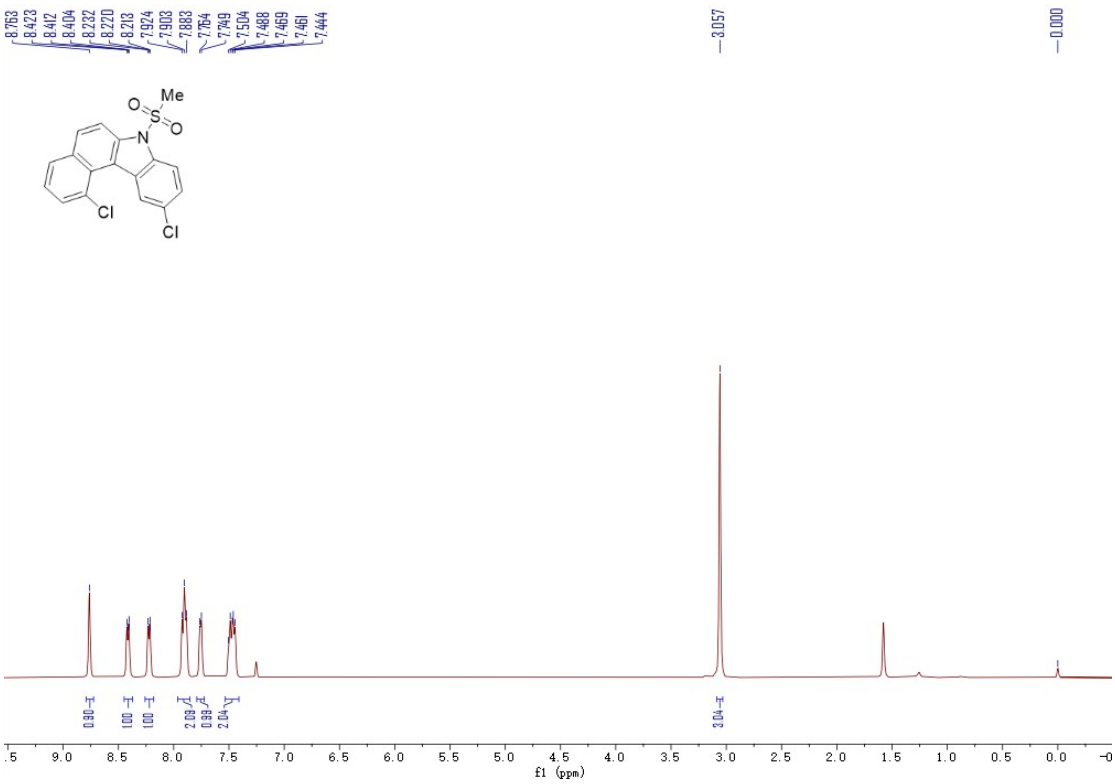


^{1}H NMR (500 MHz, $CDCl_3$)

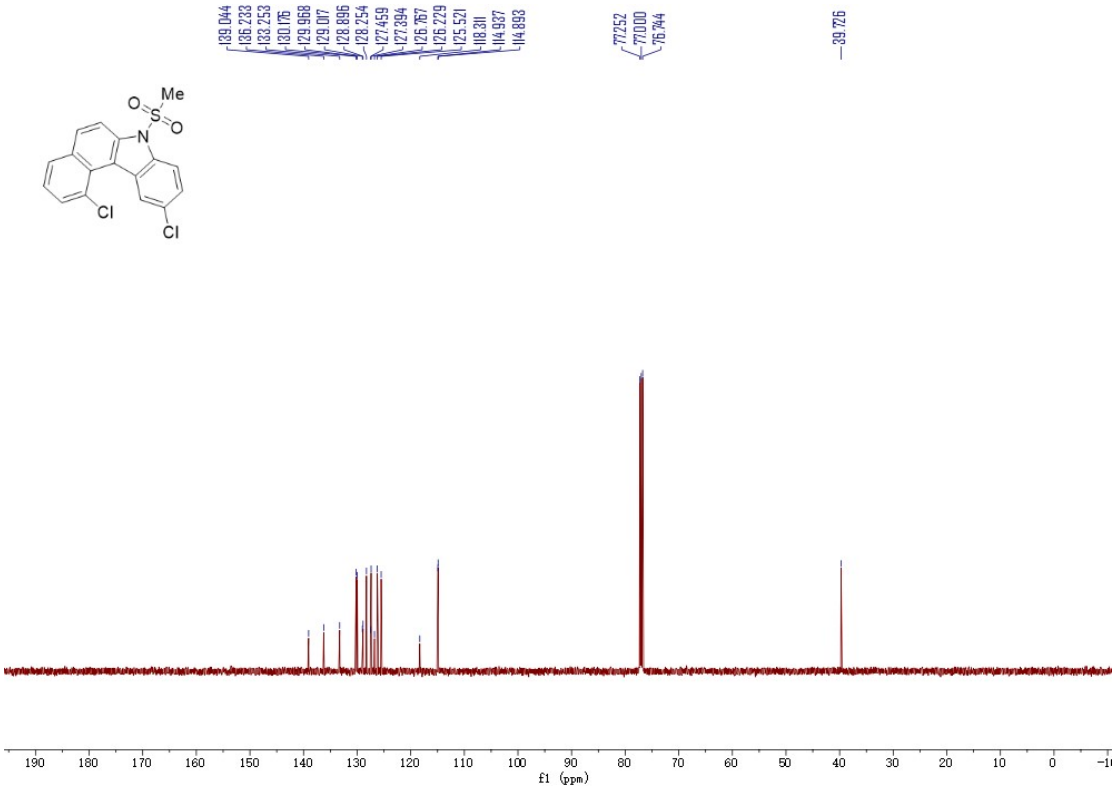


^{13}C NMR (125 MHz, $CDCl_3$)

1,10-dichloro-7-(methylsulfonyl)-7H-benzo[*c*]carbazole (2ac):

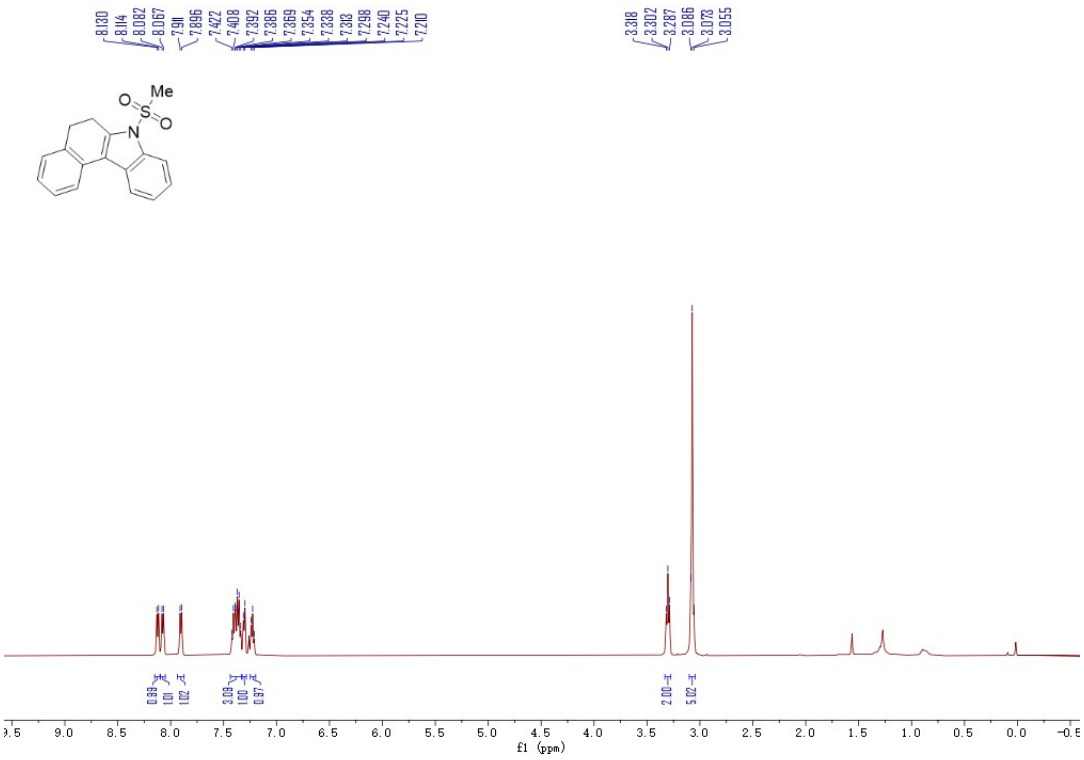


^{1}H NMR (500 MHz, $CDCl_3$)

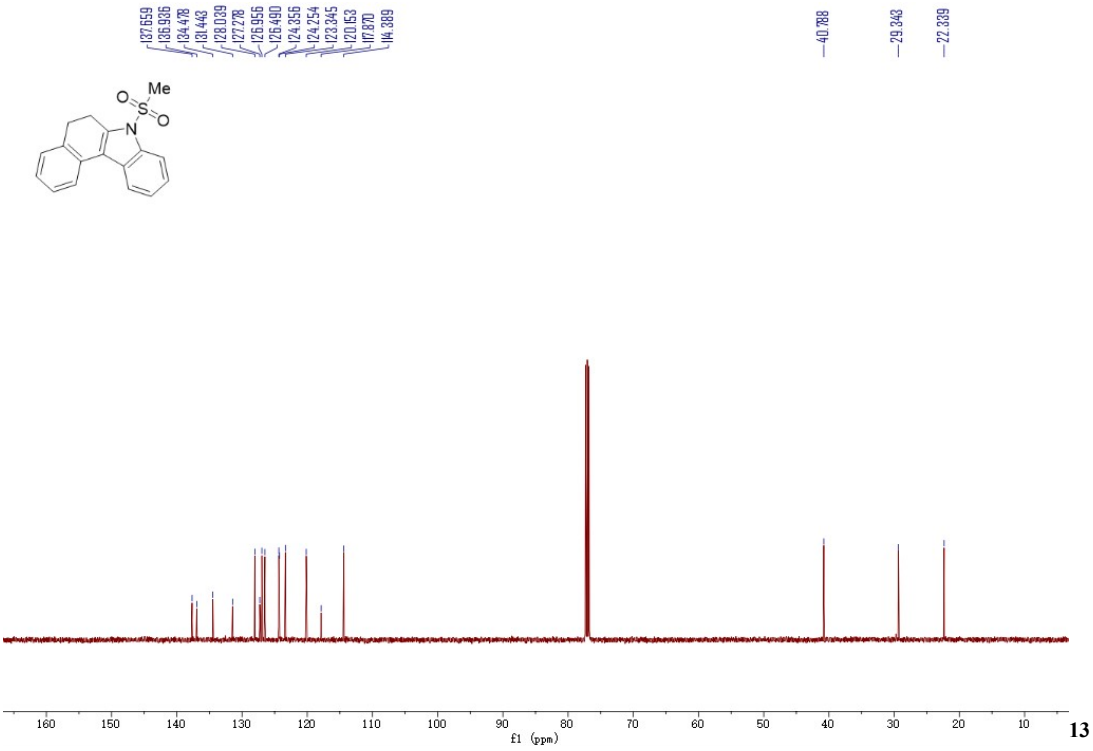


^{13}C NMR (125 MHz, $CDCl_3$)

7-(methylsulfonyl)-6,7-dihydro-5H-benzo[*c*]carbazole (Intermediate E):



^{1}H NMR (500 MHz, $CDCl_3$)



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C NMR (125 MHz, $CDCl_3$)

(D) Reference

[1] J. A. Stafford, J. E. McMurry, *Tetrahedron Lett*., 1988, **29**, 2531-2534.

[2] X. Fan, L.-Z. Yu, Y. Yu and M. Shi, *Org. Lett.,* 2017, **19**, 4476-4479.