Transition-metal free synthesis of N-Aryl carbazoles and their extended analogs

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Instrumental Parameters

All chemicals and solvents were purchased in reagent grade from commercial suppliers (Acros®, Sigma-Aldrich® or Fluka®, Fluorochem®, Merck®, ChemPur®) and used as received, unless otherwise specified. Solvents in HPLC grade were purchased from VWR® and Sigma-Aldrich® .

Flash column chromatography was performed on a Interchim PuriFlash XS420 using flash grade silica gel from (Machery-Nagel 60 M (40–63 mm, deactivated)).

NMR spectra were recorded on a Bruker Avance 400 at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), Bruker Avance 300 operating at 300 MHz (^{1}H NMR), a Bruker Avance Neo 500, operating at 500 MHz (^{1}H NMR) at 120 °C. The signals were referenced to residual solvent peaks (in parts per million (ppm) ^{1}H: $CDCl_3$, 7.27 ppm; CD_2Cl_2, 5.32 ppm; $C_2D_2Cl_4$, 6.00 ppm. ^{13}C: $CDCl_3$, 77.0 ppm; $C_2D_2Cl_4$, 73.8 ppm; CD_2Cl_2, 53.84 ppm;). Coupling constants were assigned as observed. The obtained spectra were evaluated with the program MestReNova.

(MA)LDI-MS spectra were recorded on a Shimadzu Biotech AXIMA Confidence MALDI-TOF.

High resolution APPI spectra were recorded on a Bruker ESI TOF maXis 4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2.

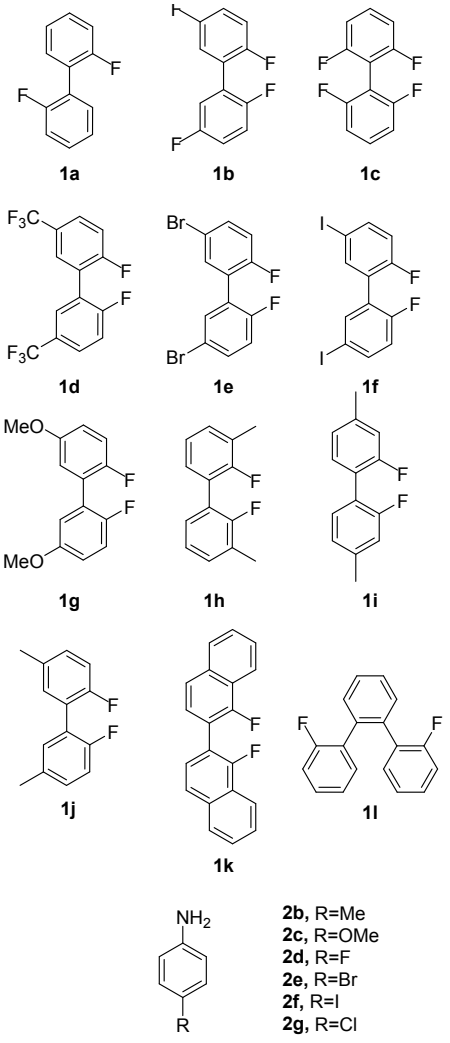
Melting points (MP) were obtained on Buchi B-540

Experimental.

General Procedure.

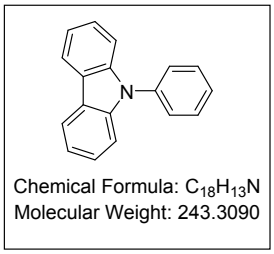
A glass tube for microwave reactor was charged with fluoroarene (0.1 mmol of difluorooligophenylene or 0,5 mmol of tetrafluorooligophenylene or 0.33 mmol of hexafluorooligophenylene), NaH (6 equiv.) and DMSO (1 ml). The tube was bubbled with argon for 1 minute and corresponding aniline (2 equiv.) was added. The tube was put in microwave reactor and stirred for 3 h at 80 °C. The temperature should not exceed 80ºC, otherwise decomposition of DMSO starts, which causes side reactions. After cooling to room temperature, the mixture was purified via column chromatography using hexane-hexane:EtOAc (10:1) as an eluent. The organic solvent was evaporated under the reduced pressure yielding the product.

Precursors were synthesized according to previously published procedure[1].



Scheme S1. Precursors.

9-phenyl-9H-carbazole (3a).



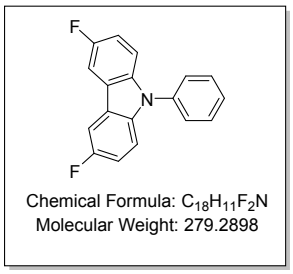
The compound was obtained according to the general procedure using 2,2'-difluoro -1,1'-biphenyl (19 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 21 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 7.7, 0.9 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.40 – 7.26 (m, 5H), 7.25 – 7.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 137.7, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.7.

The spectroscopic data were consistent with previously reported[2].

3,6-difluoro-9-phenyl-9H-carbazole (3b).



The compound was obtained according to the general procedure using 2,2',5,5'-tetrafluoro-1,1'-biphenyl (23 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 21 mg (75%). Mp. 65-67 °C.

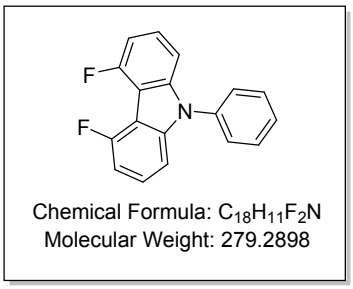
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.7, 2.5 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.53 (dt, *J* = 3.9, 2.2 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.32 (dd, *J* = 9.0, 4.2 Hz, 2H), 7.17 (td, *J* = 9.0, 2.5 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.74 (tdd, *J* = 8.9, 4.3, 1.5 Hz,2F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 (d, *J* = 236.9 Hz), 138.1 137.4, 130.0, 127.7, 127.0, 123.3 (dd, *J* = 9.5, 4.2 Hz), 114.4 (d, *J* = 25.5 Hz), 110.8 (d, *J* = 9.0 Hz), 106.0 (d, *J* = 24.0 Hz).

HRMS (m/z): $[M]^+$ calcd. for $C_{18}H_{11}F_2N$, 279.0855; found, 279.0863

4,5-difluoro-9-phenyl-9H-carbazole (3c).



Chemical Formula: $C_{18}H_{11}F_2N$
Molecular Weight: 279.2898

The compound was obtained according to the general procedure using 2,2',6,6'-tetrafluoro-1,1'-biphenyl (23 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 13 mg (46%). Mp. 60-62 °C.

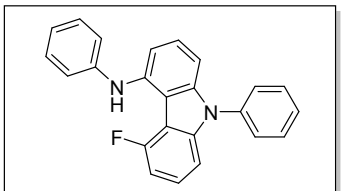
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 – 7.60 (m, 2H), 7.59 – 7.50 (m, 3H), 7.43 – 7.34 (m, 2H), 7.14 (dd, *J* = 8.3, 0.5 Hz, 2H), 7.01 (ddd, *J* = 8.0, 5.6, 0.7 Hz, 2H).

^{19}F NMR (376 MHz, CD_2Cl_2) δ -113.08 (ddd, *J* = 7.7, 4.8, 2.5 Hz, 2F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.7 (dd, *J* = 260.5, 10.4 Hz), 143.6 (t, *J* = 5.0 Hz), 137.4, 130.5, 128.8, 127.8, 127.7 (t, *J* = 4.5 Hz), 109.3 (dd, *J* = 11.5, 8.1 Hz), 106.8 (dd, *J* = 12.5, 8.3 Hz), 106.2 (t, *J* = 1.5 Hz).

HRMS (m/z): $[M]^+$ calcd. for $C_{18}H_{11}F_2N$, 279.0855; found, 279.0870

5-fluoro-N,9-diphenyl-9H-carbazol-4-amine (3c').



Chemical Formula: $C_{24}H_{17}FN_2$
Molecular Weight: 352.4124

The compound was obtained according to the general procedure using 2,2',6,6'-tetrafluoro-1,1'-biphenyl (23 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown oil. Yield 5 mg (14%).

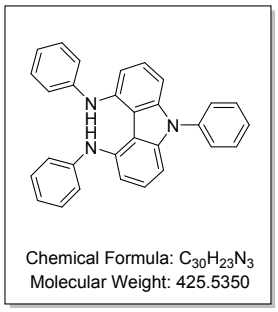
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.53 – 7.49 (m, 3H), 7.40 – 7.33 (m, 4H), 7.33 – 7.24 (m, 2H), 7.19 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.07 – 6.92 (m, 2H), 6.79 (dd, *J* = 8.0, 0.8 Hz, 1H), 2.73 (d, *J* = 9.7 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.81 (dd, *J* = 12.8, 5.4 Hz, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (d, *J* = 240.7 Hz), 142.9, 142.6, 139.1, 137.3, 123.0, 129.3, 128.2, 127.9, 127.5, 125.7 (d, *J* = 9.9 Hz), 121.9, 119.7, 106.1 – 105.8 (m), 101.2.

HRMS (m/z): $[M]^+$ calcd. for $C_{24}H_{17}FN_2$, 352.1371; found, 352.1388

N^4,N^5,9-triphenyl-9H-carbazole-4,5-diamine (3c'').



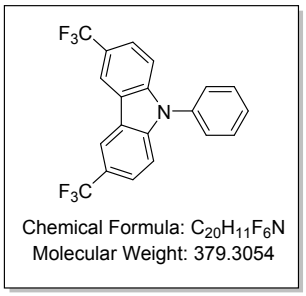
The compound was obtained according to the general procedure using 2,2',6,6'-tetrafluoro-1,1'-biphenyl (23 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown semi-solid. Yield 6 mg (13%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 9.6, 3.4 Hz, 4H), 7.54 – 7.41 (m, 1H), 7.22 – 7.17 (m, 6H), 7.12 – 7.09 (m, 4H), 7.00 (t, *J* = 7.3 Hz, 4H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 13.9 Hz, 1H), 5.11 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 144.1, 142.1, 138.0, 129.8, 129.2, 127.5, 127.1, 125.6, 123.7, 123.6, 115.8, 109.9, 102.2.

HRMS (m/z): $[M]^+$ calcd. for $C_{30}H_{23}N_3$, 425.1887; found, 425.1897.

9-phenyl-3,6-bis(trifluoromethyl)-9H-carbazole (3d).



The compound was obtained according to the general procedure using 2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (32 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 14 mg (37%). Mp. 150-152 °C.

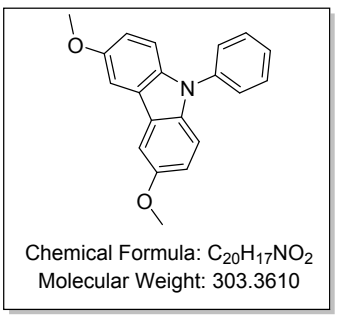
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.44 (m, 2H), 7.71 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.68 (dt, *J* = 10.0, 1.9 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -60.48 (s, 6F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1 , 136.3, 130.3, 128.7, 127.2, 124.9 (q, *J* =216 Hz), 123.7 (q, *J* = 3.5 Hz), 123.1 (q, *J* = 32.4 Hz), 122.5, 118.3 (q, *J* = 4.1 Hz).

HRMS (m/z): $[M]^+$ calcd. for $C_{20}H_{11}F_6N$, 379.0791; found, 379.0805

3,6-dimethoxy-9-phenyl-9H-carbazole (3g).



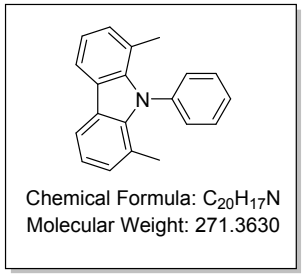
The compound was obtained according to the general procedure using 2,2'-difluoro-5,5'-dimethoxy-1,1'-biphenyl (25 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 8 mg (27%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 6H), 7.48 – 7.39 (m, 1H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 2H), 3.96 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 138.2, 136.3, 129.8, 126.9, 126.7, 123.6, 115.2, 110.7, 102.9, 56.1.

The spectroscopic data were consistent with previously reported[3]

1,8-dimethyl-9-phenyl-9H-carbazole (3h).

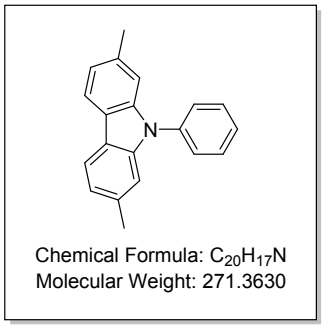


The compound was obtained according to the general procedure using 2,2'-difluoro-3,3'-dimethyl-1,1'-biphenyl (22 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 7 mg (26%). Mp. 71-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.52 (dd, *J* = 9.9, 5.1 Hz, 3H), 7.48 – 7.41 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 1.90 (s, 6H).

HRMS (m/z): $[M]^+$ calcd. for $C_{20}H_{17}N$, 271.1356; found, 271.1378

2,7-dimethyl-9-phenyl-9H-carbazole (3i).



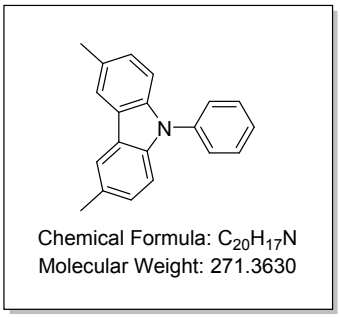
The compound was obtained according to the general procedure using 2,2'-difluoro-4,4'-dimethyl-1,1'-biphenyl (22 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 14 mg (50%). Mp. 80-83 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.57 – 7.52 (m, 2H), 7.51 – 7.42 (m, 1H), 7.16 (s, 2H), 7.11 – 7.05 (m, 2H), 2.48 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 137.9, 135.5, 129.8, 127.3, 121.3, 121.1, 119.6, 109.8, 22.1.

HRMS (m/z): $[M]^+$ calcd. for $C_{20}H_{17}N$, 271.1356; found, 271.1362

3,6-dimethyl-9-phenyl-9H-carbazole (3j).



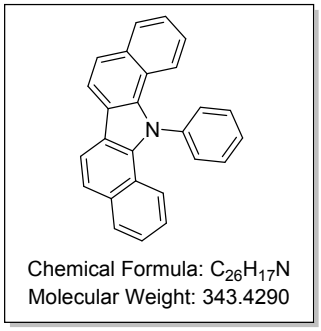
The compound was obtained according to the general procedure using 2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl (22 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 6 mg (22%). Mp. 55-57 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.64 – 7.52 (m, 4H), 7.49 – 7.40 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 8.5, 1.4 Hz, 2H), 2.55 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 138.2, 129.7, 129.0, 127.0, 127.0, 126.9, 123.4, 120.1, 109.4, 21.4.

HRMS (m/z): $[M]^+$ calcd. for $C_{20}H_{17}N$, 271.1356; found, 271.1373

13-phenyl-13H-dibenzo[a,i]carbazole (3k).



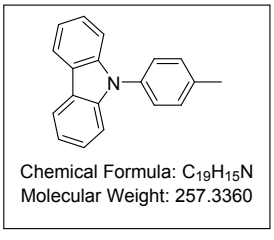
The compound was obtained according to the general procedure using 1,1'-difluoro-2,2'-binaphthalene (29 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 29 mg (85%). Mp. 141-143 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.86 – 7.69 (m, 3H), 7.41 (ddd, *J* = 8.1, 6.6, 1.4 Hz, 1H), 7.29 – 7.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 134.7, 133.1, 130.6, 130.3, 130.0, 129.3, 125.1, 124.3, 122.6, 121.8, 121.4, 119.7, 118.6.

HRMS (m/z): $[M]^+$ calcd. for $C_{26}H_{17}N$, 343.1356; found, 343.1377.

9-(p-tolyl)-9H-carbazole (3l).



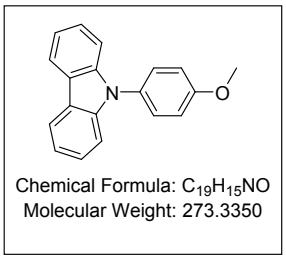
The compound was obtained according to the general procedure using 2,2'-difluoro -1,1'-biphenyl (19 mg), 60% NaH in mineral oil (24 mg) and 4-methylaniline (22 mg). White solid. Yield 14 mg (54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.36 (m, 6H), 7.31 – 7.26 (m, 2H), 2.50 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 137.4, 135.0, 130.4, 127.0, 125.8, 123.2, 120.2, 119.7, 109.8, 21.2.

The spectroscopic data were consistent with previously reported[2]

9-(4-methoxyphenyl)-9H-carbazole (3m).



Chemical Formula: $C_{19}H_{15}NO$
Molecular Weight: 273.3350

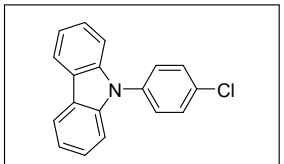
The compound was obtained according to the general procedure using 2,2'-difluoro -1,1'-biphenyl (19 mg), 60% NaH in mineral oil (24 mg) and 4-methoxylaniline (25 mg). White solid. Yield 13 mg (48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.07 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.33 (dd, *J* = 8.2, 0.8 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.16 – 7.07 (m, 2H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 141.4, 130.3, 128.6, 125.8, 123.1, 120.2, 119.6, 115.1, 109.7, 55.6.

The spectroscopic data were consistent with previously reported[3]

9-(4-chlorophenyl)-9H-carbazole (3q).



Chemical Formula: $C_{18}H_{12}ClN$
Molecular Weight: 277.7510

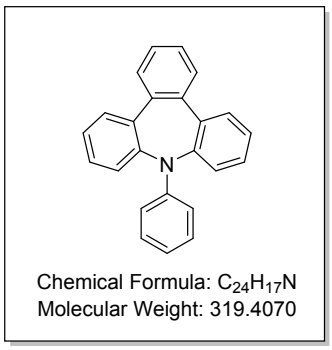
The compound was obtained according to the general procedure using 2,2'-difluoro -1,1'-biphenyl (19 mg), 60% NaH in mineral oil (24 mg) and 4-chlorolaniline (27 mg). White solid. Yield 7.5 mg (27%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.34 (m, 2H), 7.30 (ddd, *J* = 7.9, 6.9, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 136.3, 133.0, 130.1, 128.4, 126.1, 123.5, 120.4, 120.2, 109.5.

The spectroscopic data were consistent with previously reported[4].

9-phenyl-9H-tribenzo[b,d,f]azepine (3r).



Chemical Formula: $C_{24}H_{17}N$
Molecular Weight: 319.4070

The compound was obtained according to the general procedure using 2,2"-difluoro-1,1':2',1"-terphenyl (27 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). White solid. Yield 13 mg (41%).

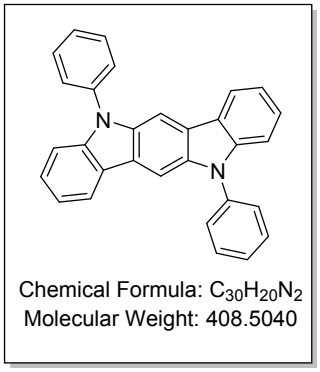
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.60 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.46

(td, *J* = 7.6, 1.7 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.01 – 6.92 (m, 2H), 6.62 – 6.57 (m, 1H), 6.57 – 6.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 146.0, 139.1, 137.6, 130.9, 129.4, 128.9, 128.7, 128.6, 127.7, 127.3, 117.4, 111.8.

The spectroscopic data were consistent with previously reported[5].

5,11-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (3s).



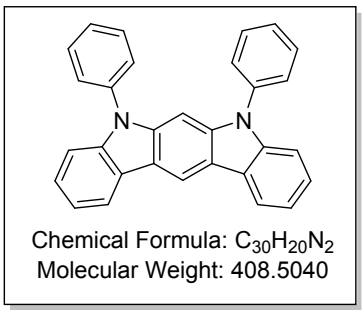
The compound was obtained according to the general procedure using 2,2',2",5'-tetrafluoro-1,1':4',1"-terphenyl (15 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 20 mg (98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 2H), 8.08 (s, 2H), 7.74 – 7.65 (m, 8H), 7.57 – 7.50 (m, 2H), 7.47 – 7.38 (m, 4H), 7.28 – 7.22 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.4, 137.1, 130.0, 127.3, 126.0, 123.5, 123.4, 120.3, 119.3, 109.5, 99.8.

The spectroscopic data were consistent with previously reported[6]

5,7-diphenyl-5,7-dihydroindolo[2,3-b]carbazole (3t).



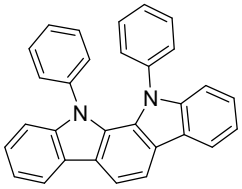
The compound was obtained according to the general procedure using 2,2",4',6'-tetrafluoro-1,1':3',1"-terphenyl (15 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 15 mg (74%). Mp. 160-162 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.26 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 4.3 Hz, 8H), 7.43 (td, *J* = 8.4, 4.0 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.25 (d, *J* = 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.4, 138.0, 129.9, 127.3, 127.1, 125.0, 123.9, 119.9, 119.6, 118.7, 111.4, 109.4, 89.1.

HRMS (m/z): $[M]^+$ calcd. for $C_{30}H_{20}N_2$, 408.1616; found, 408.1631.

11,12-diphenyl-11,12-dihydroindolo[2,3-a]carbazole (3u).



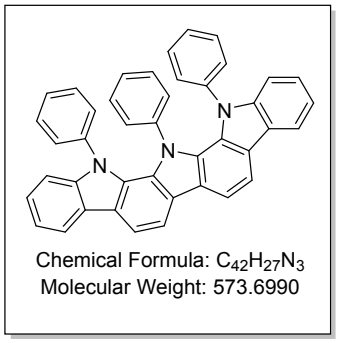
The compound was obtained according to the general procedure using 2,2',2",3'-tetrafluoro-1,1':4',1"-terphenyl (15 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 13 mg (63%). Mp. 184-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 2H), 8.12 (s, 2H), 7.35 – 7.25 (m, 6H), 7.15 – 7.05 (m, 6H), 6.82 – 6.75 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.3, 128.9, 128.1, 126.3, 126.0, 125.5, 125.4, 124.9, 121.0, 119.8, 113.6, 110.9.

HRMS (m/z): $[M]^+$ calcd. for $C_{30}H_{20}N_2$, 408.1621; found, 408.1639

13,14,15-triphenyl-14,15-dihydro-13H-pyrrolo[2,3-a:5,4-a']dicarbazole (3v).



The compound was obtained according to the general procedure using 2,2',2",2"',3',3"-hexafluoro-1,1':4',1":4",1"'-quaterphenyl (13 mg), 60% NaH in mineral oil (24 mg) and aniline (20 mg). Brown solid. Yield 20 mg (95%). Mp. 220-223 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 4H), 8.13 – 8.07 (m, 2H), 7.48 – 7.32 (m, 6H), 7.32 – 7.21 (m, 8H), 7.07 (dt, J = 8.8, 2.8 Hz, 4H), 6.78 (t, J = 6.8 Hz, 1H), 6.45 (t, J = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.8, 140.7, 135.3, 129.4, 129.2, 128.7, 127.9, 127.8, 126.9, 126.3, 126.0, 125.4, 125.2, 125.0, 120.9, 119.5, 115.4, 113.1, 110.7.

HRMS (m/z): $[M]^+$ calcd. for $C_{42}H_{27}N_3$, 573.2200; found, 573.2191

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2 W. J. Yoo, T. Tsukamoto and S. Kobayashi, *Org. Lett.*, 2015, **17**, 3640–3642.

3 A. W. Jones, M. L. Louillat-Habermeyer and F. W. Patureau, *Adv. Synth. Catal.*, 2015, **357**, 945–949.

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Spectral appendix (^{1}H, ^{13}C NMR).

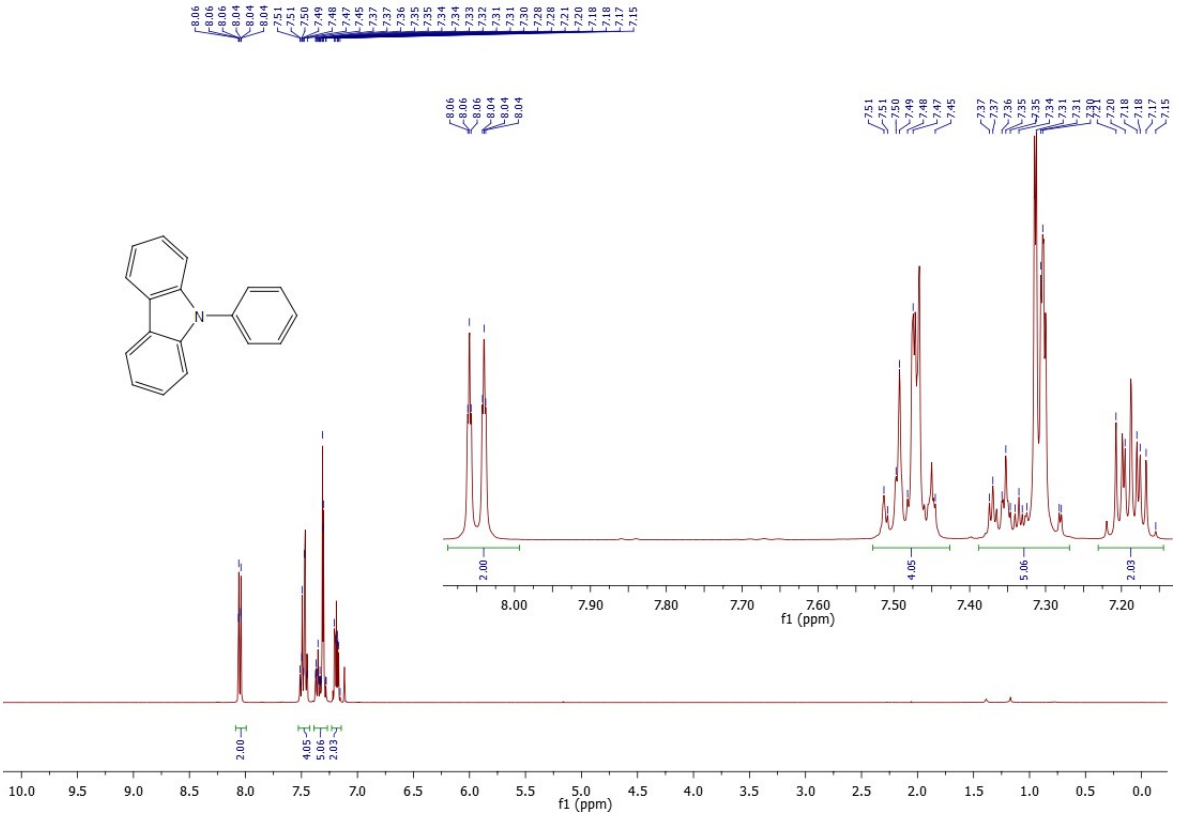

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-9H-carbazole.

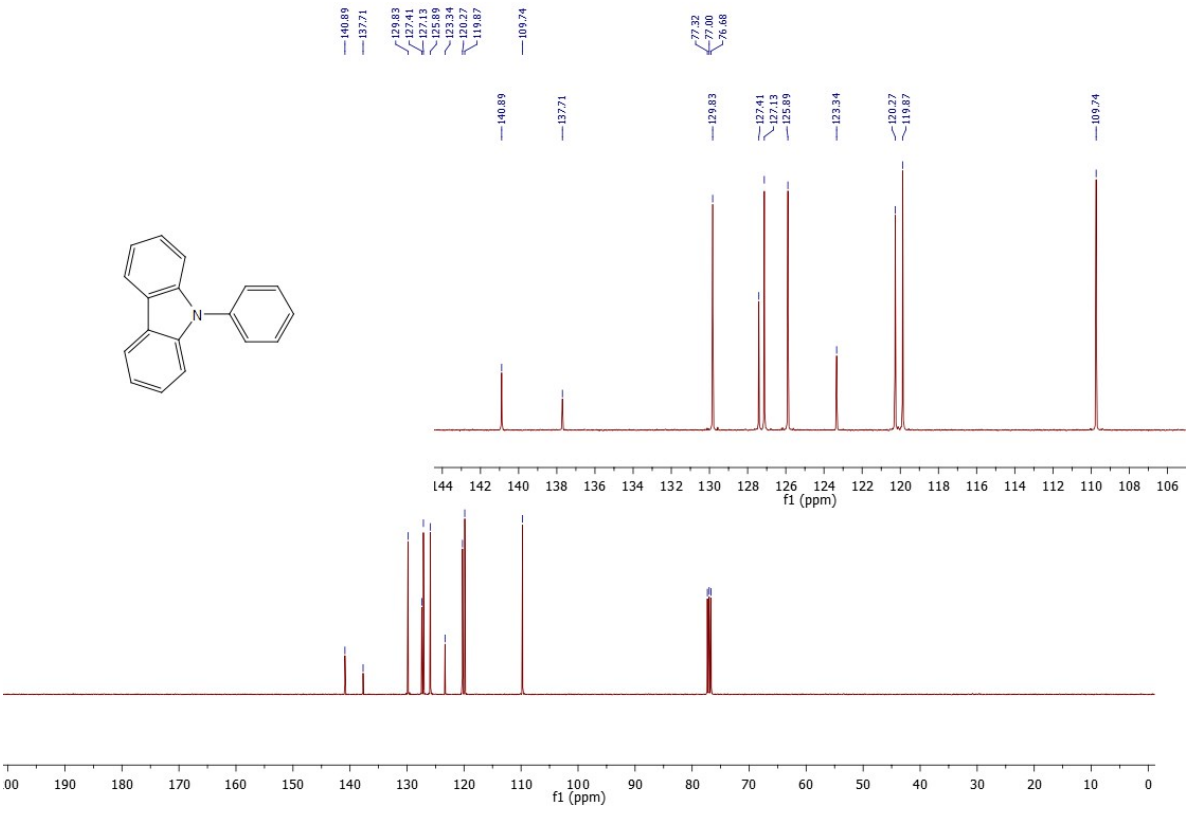

Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-9H-carbazole.

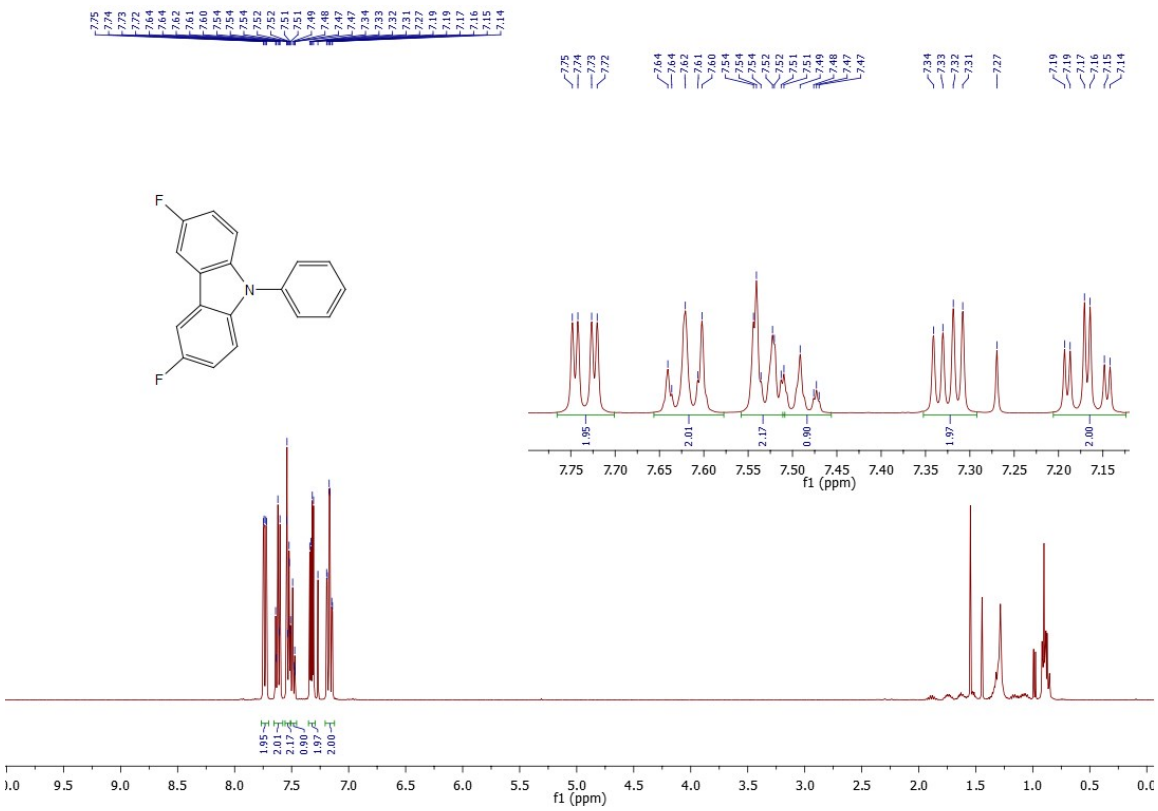

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 3,6-difluoro-9-phenyl-9H-carbazole.

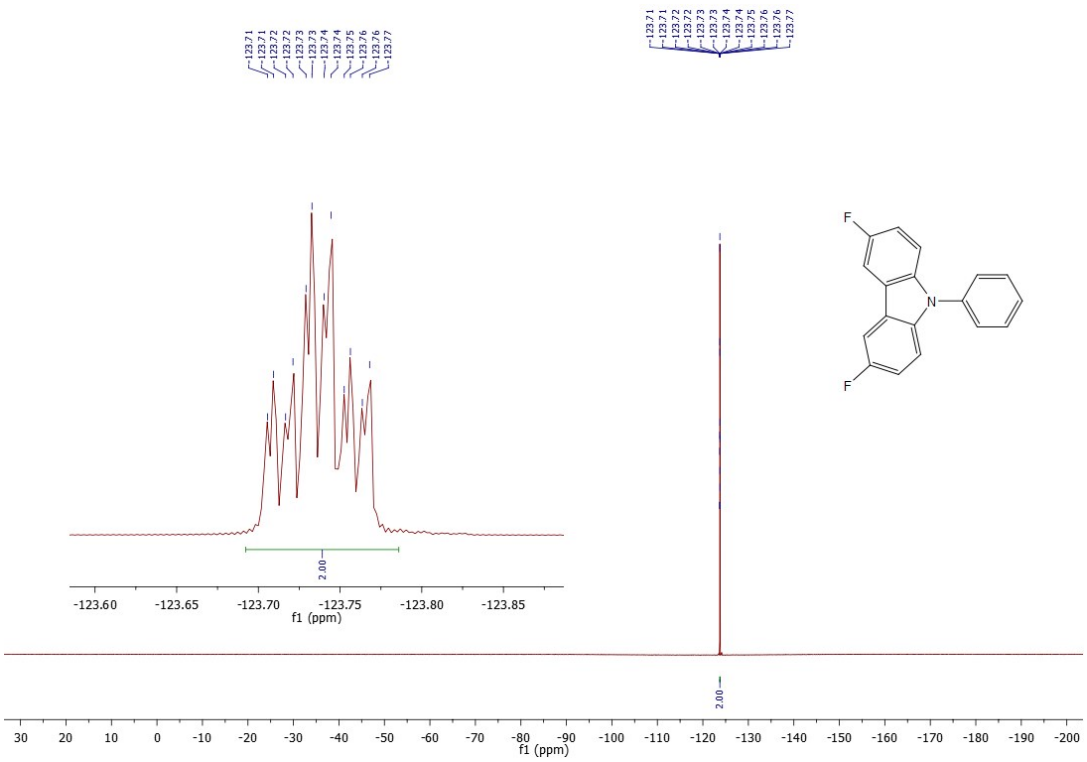

Figure S4. ^{19}F NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 3,6-difluoro-9-phenyl-9H-carbazole.

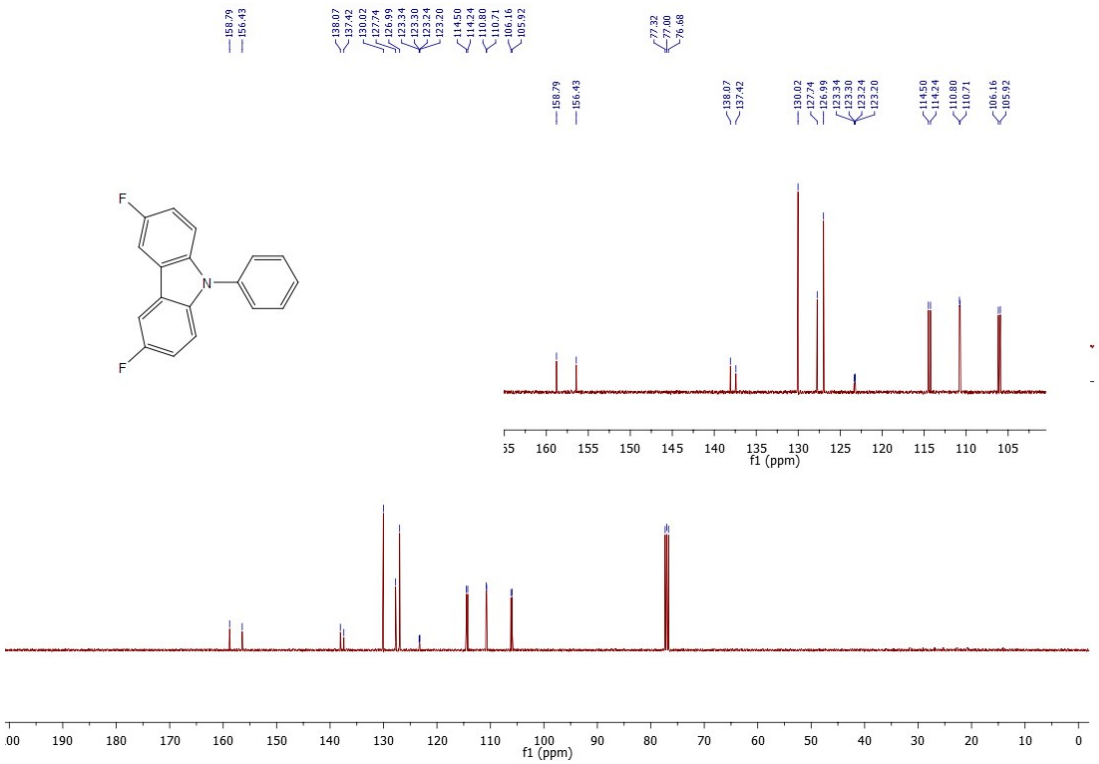

Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 3,6-difluoro-9-phenyl-9H-carbazole.

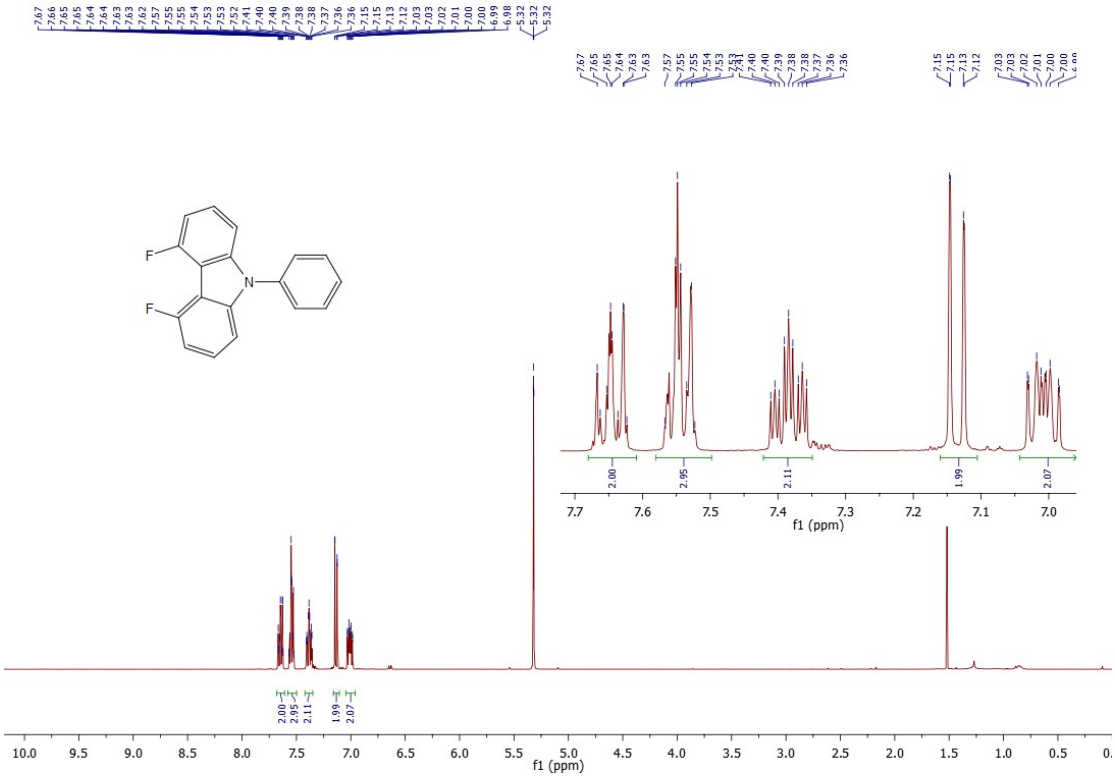

Figure S6. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K) spectrum of 4,5-difluoro-9-phenyl-9H-carbazole.

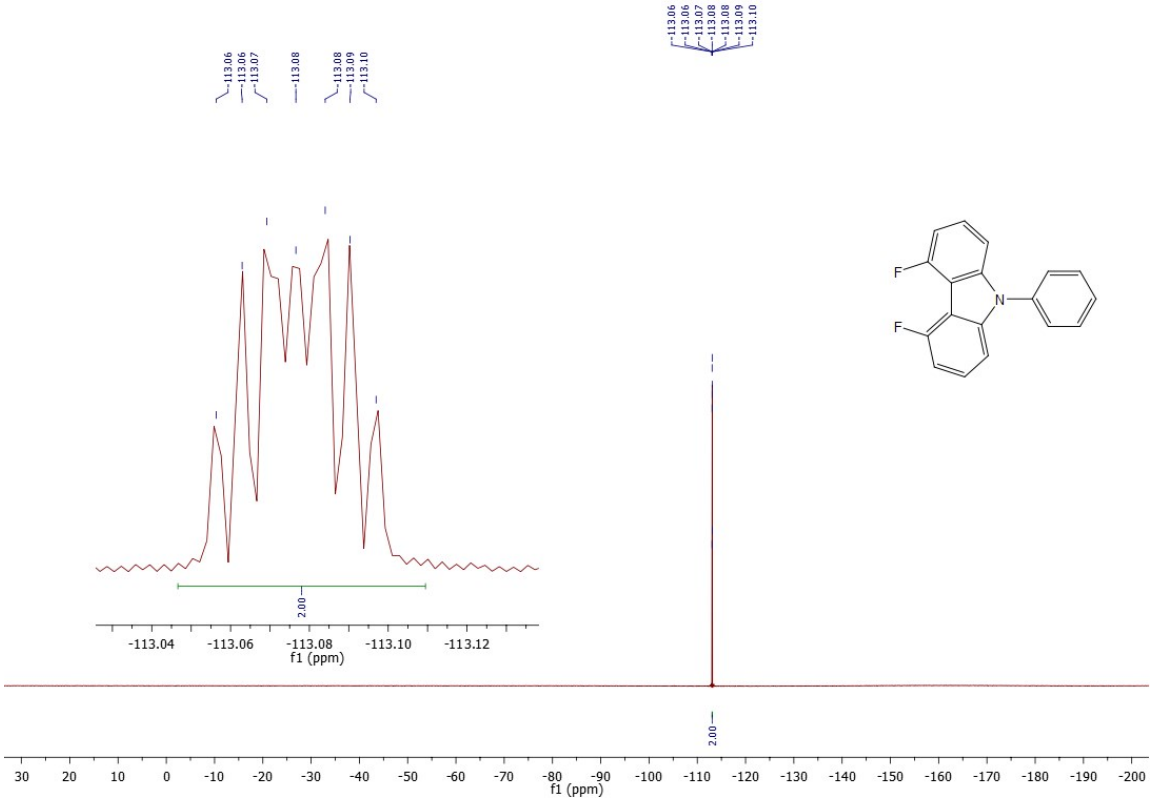

Figure S7. ^{19}F NMR (376 MHz, CD_2Cl_2, 293 K) spectrum of 4,5-difluoro-9-phenyl-9H-carbazole.

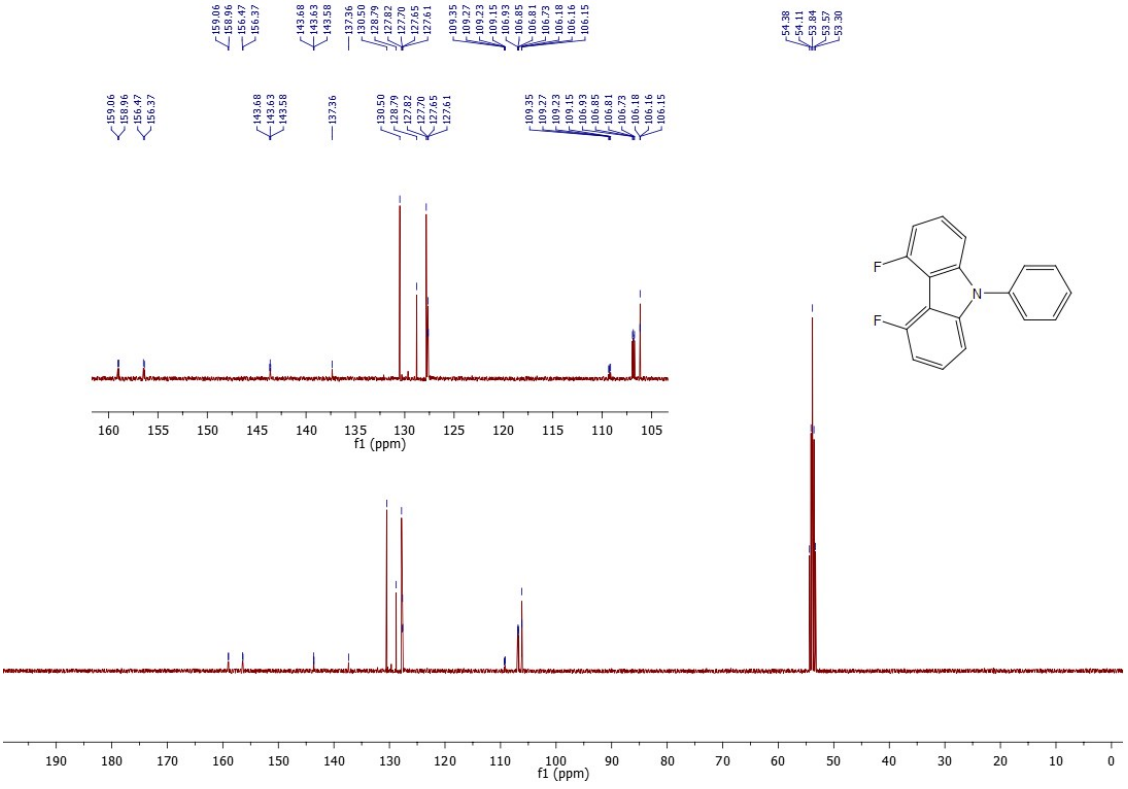

Figure S8. ^{13}C NMR (101 MHz, CD_2Cl_2, 293 K) spectrum of 4,5-difluoro-9-phenyl-9H-carbazole.

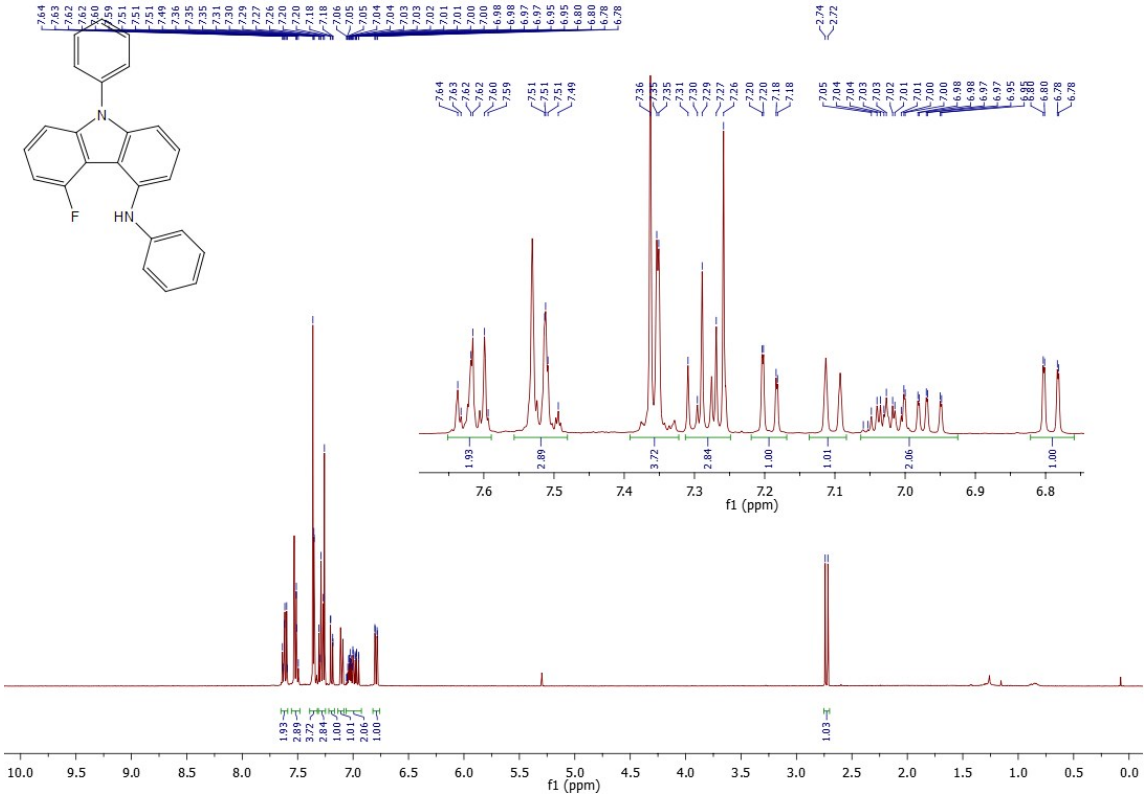

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 5-fluoro-N,9-diphenyl-9H-carbazol-4-amine.

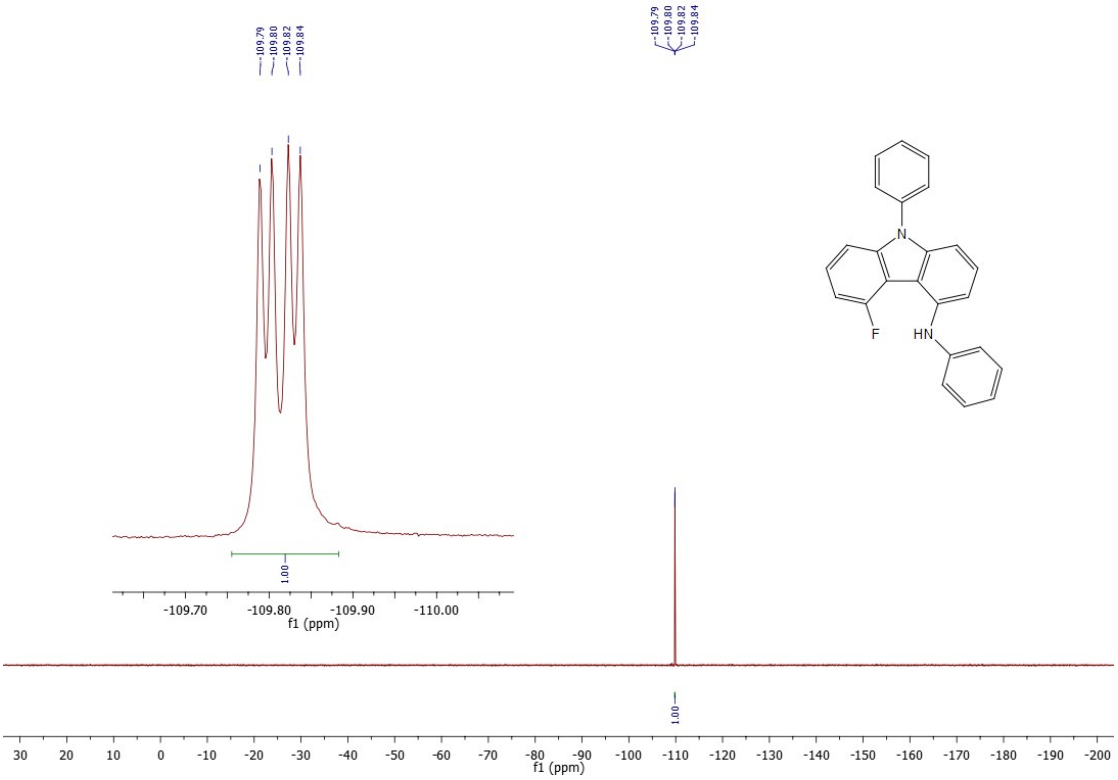

Figure S10. ^{19}F NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 5-fluoro-N,9-diphenyl-9H-carbazol-4-amine.

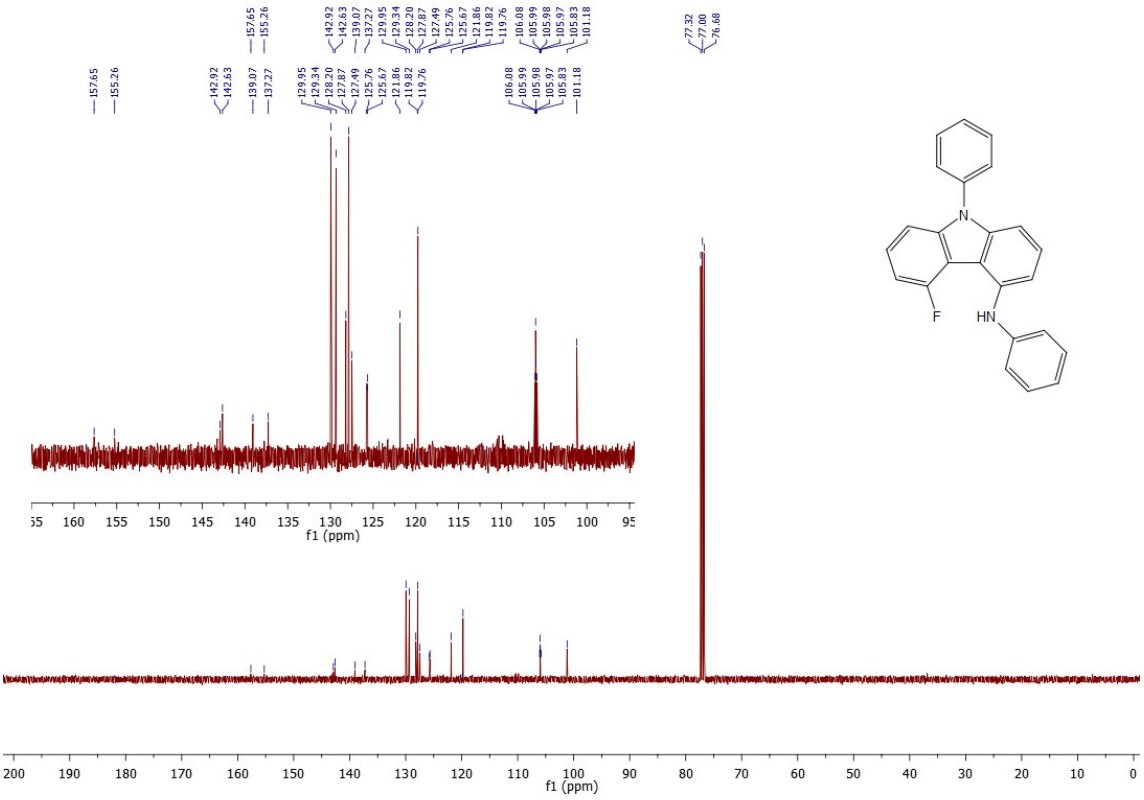

Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 5-fluoro-N,9-diphenyl-9H-carbazol-4-amine.

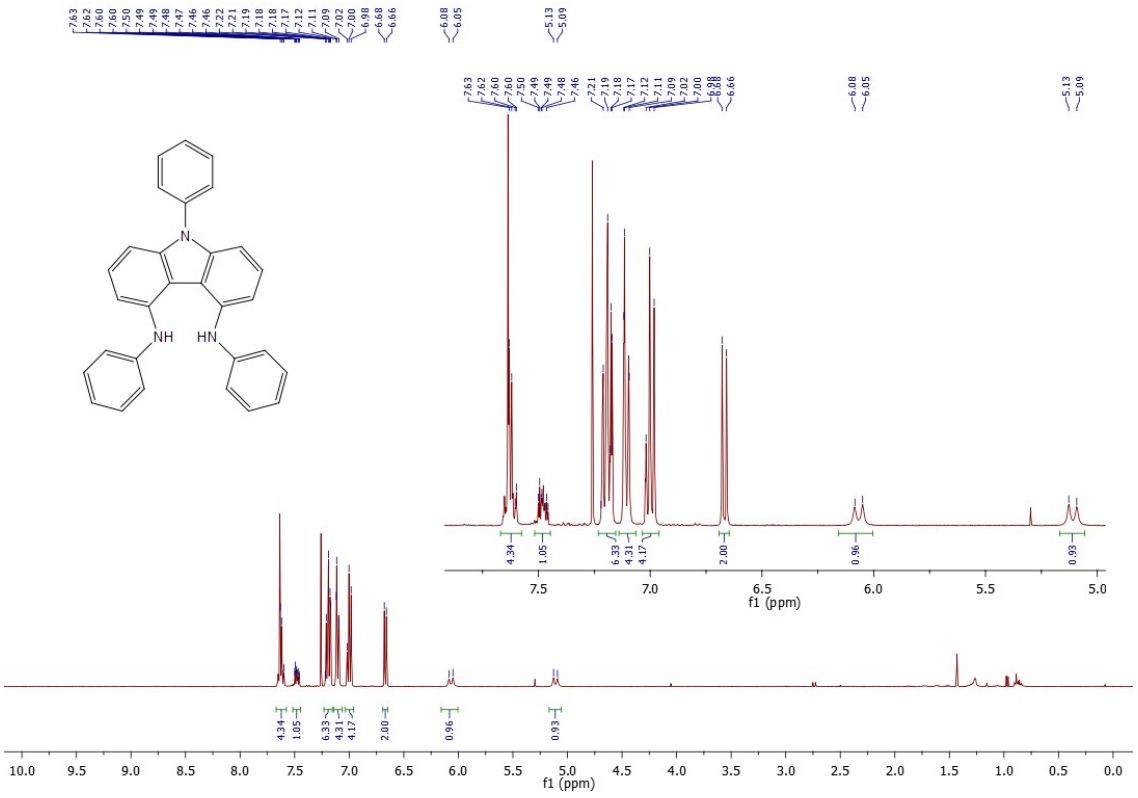

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of N^4,N^5,9-triphenyl-9H-carbazole-4,5-diamine.

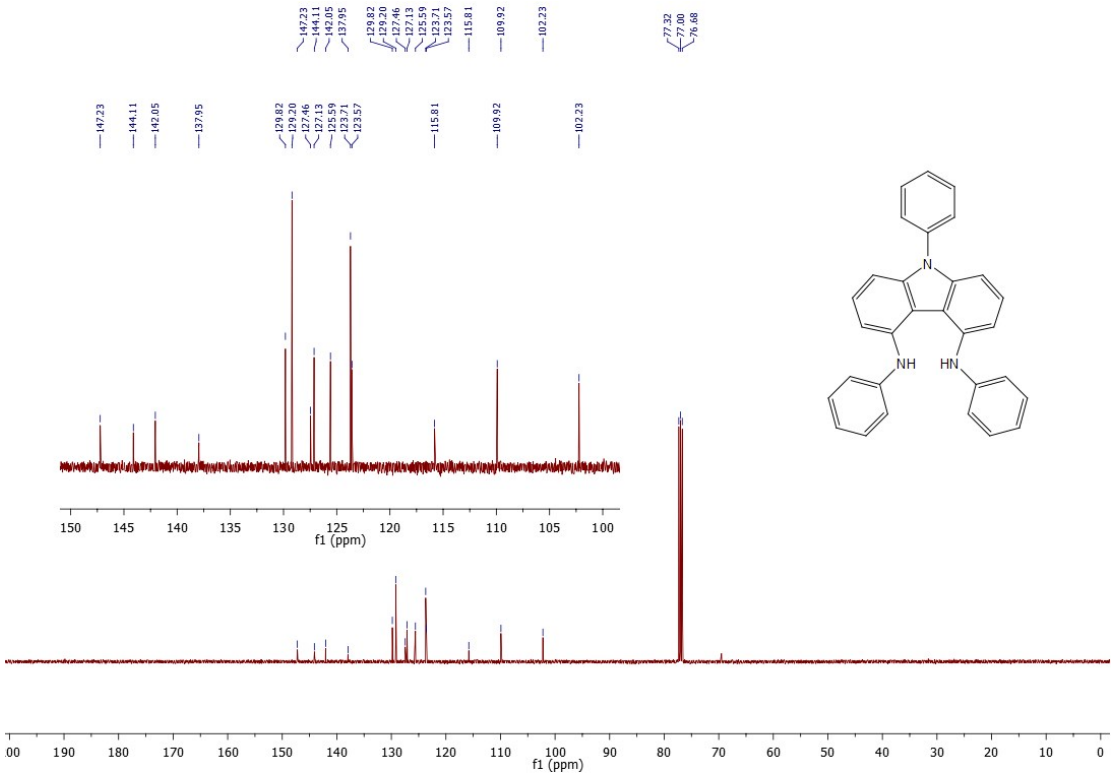

Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of N^4,N^5,9-triphenyl-9H-carbazole-4,5-diamine.

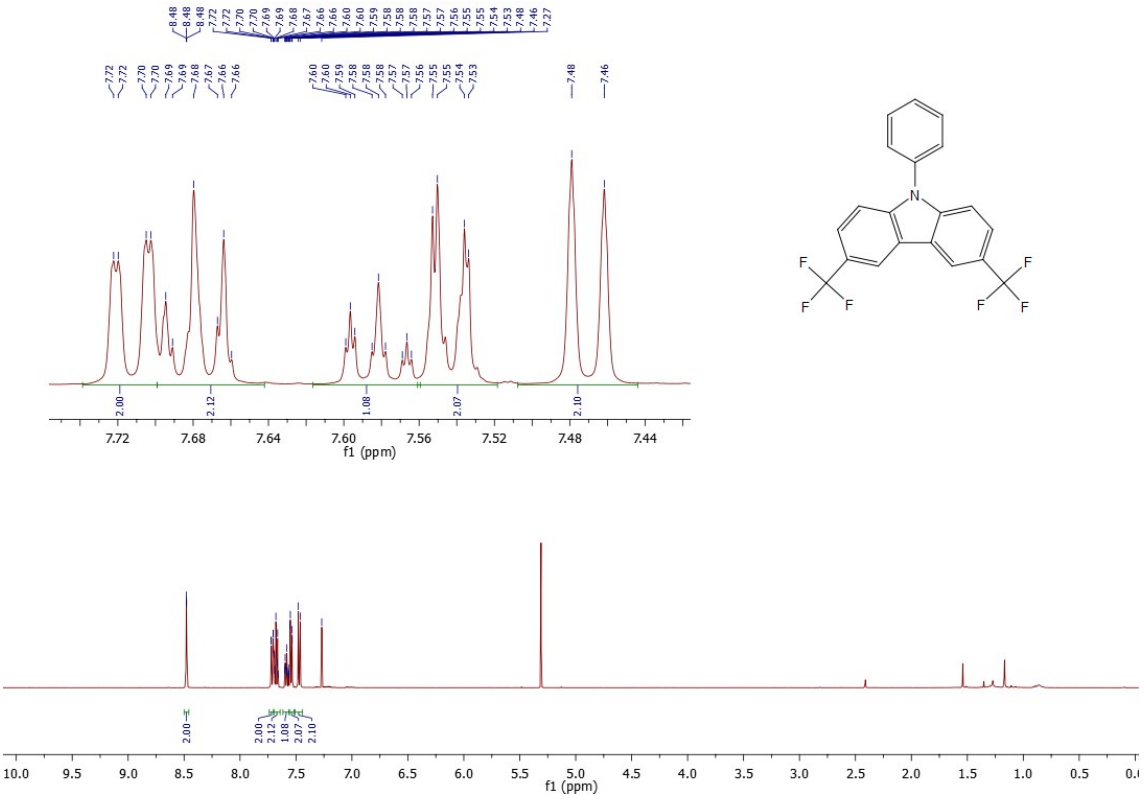

Figure S14. ^1H NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-3,6-bis(trifluoromethyl)-9H-carbazole.

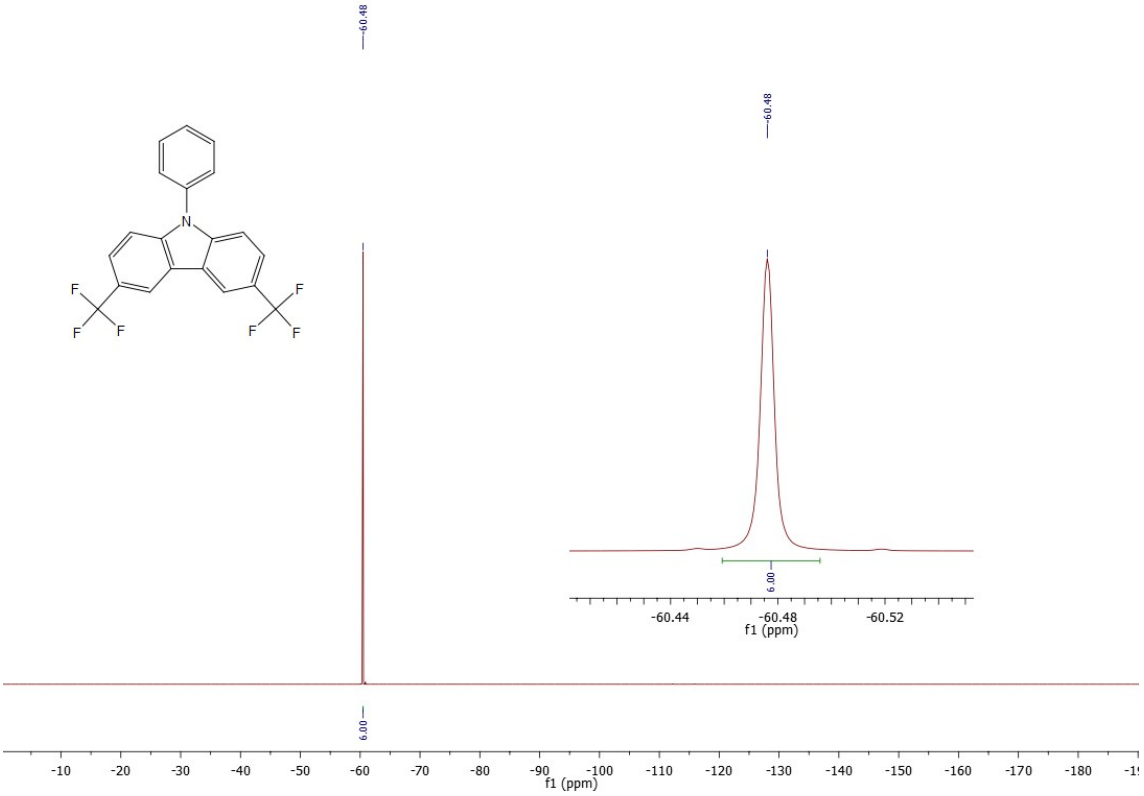

Figure S15. ^{19}F NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-3,6-bis(trifluoromethyl)-9H-carbazole.

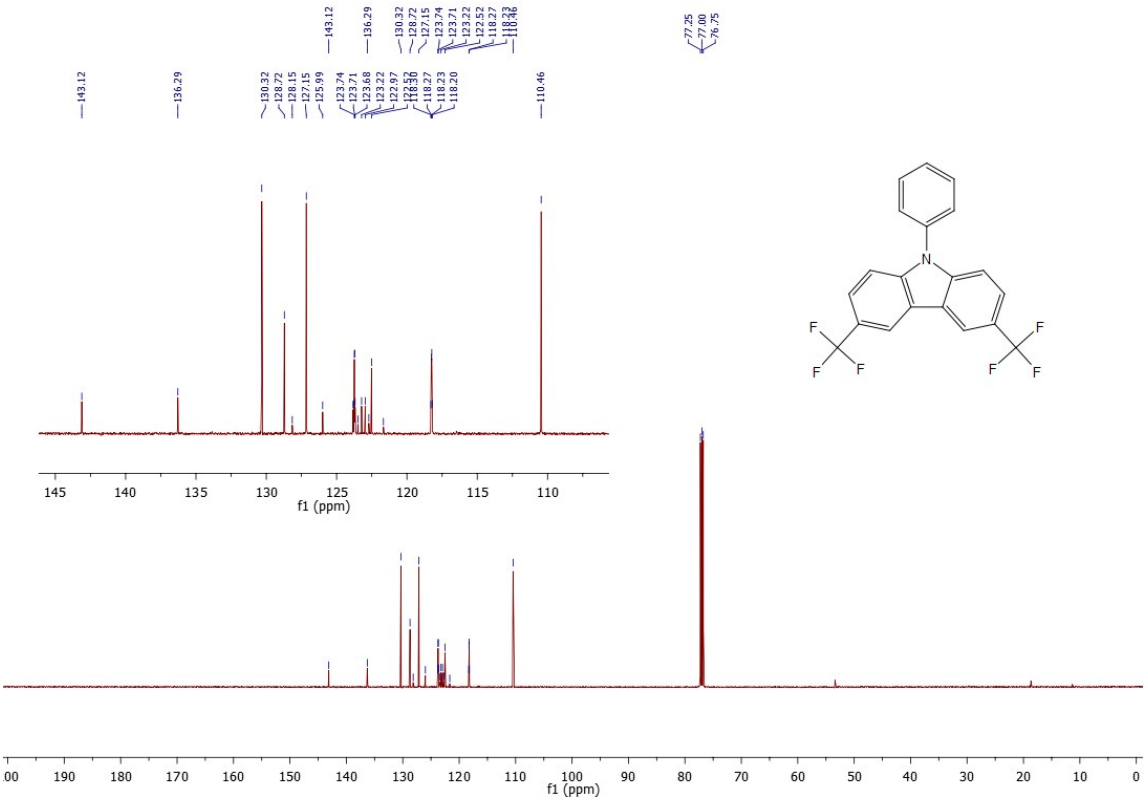

Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-3,6-bis(trifluoromethyl)-9H-carbazole.

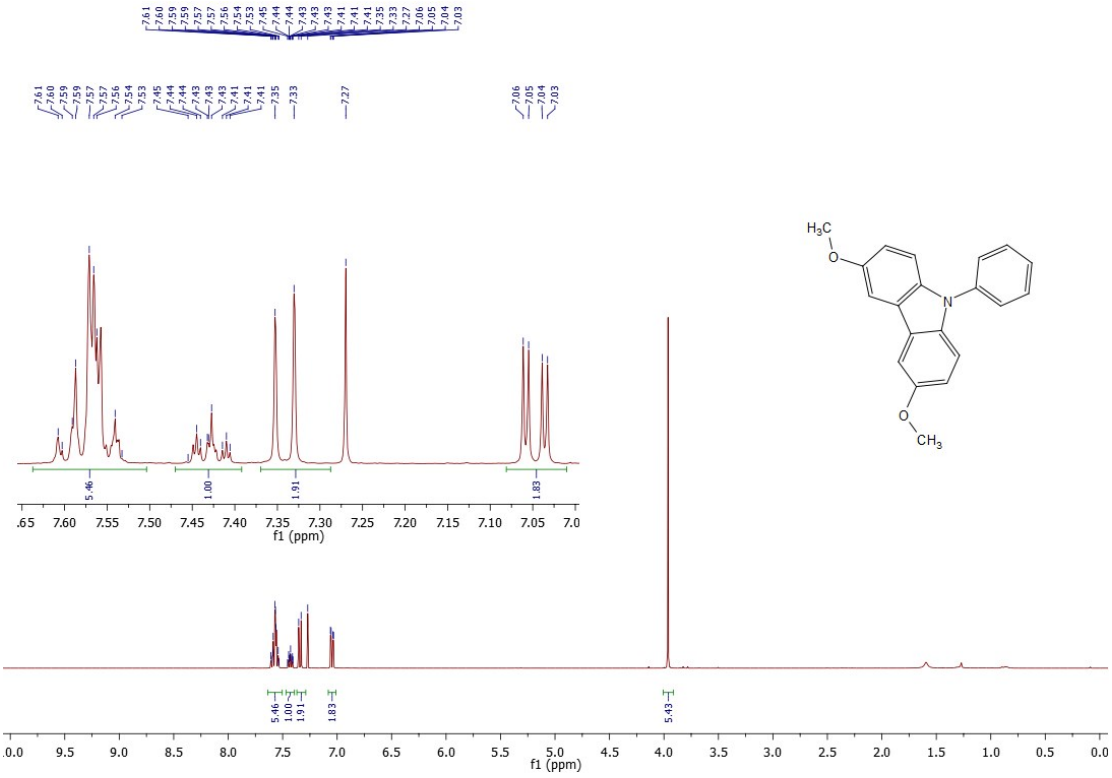

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 3,6-dimethoxy-9-phenyl-9H-carbazole.

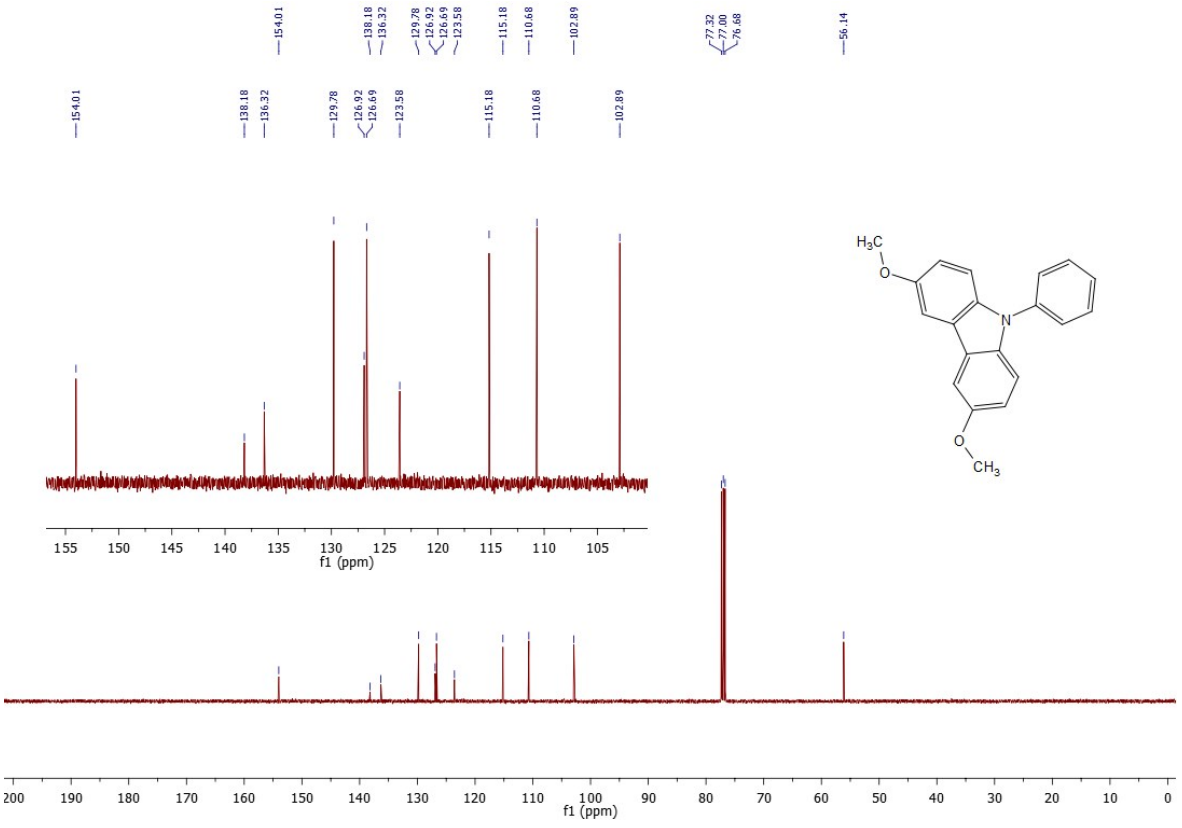

Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 3,6-dimethoxy-9-phenyl-9H-carbazole.

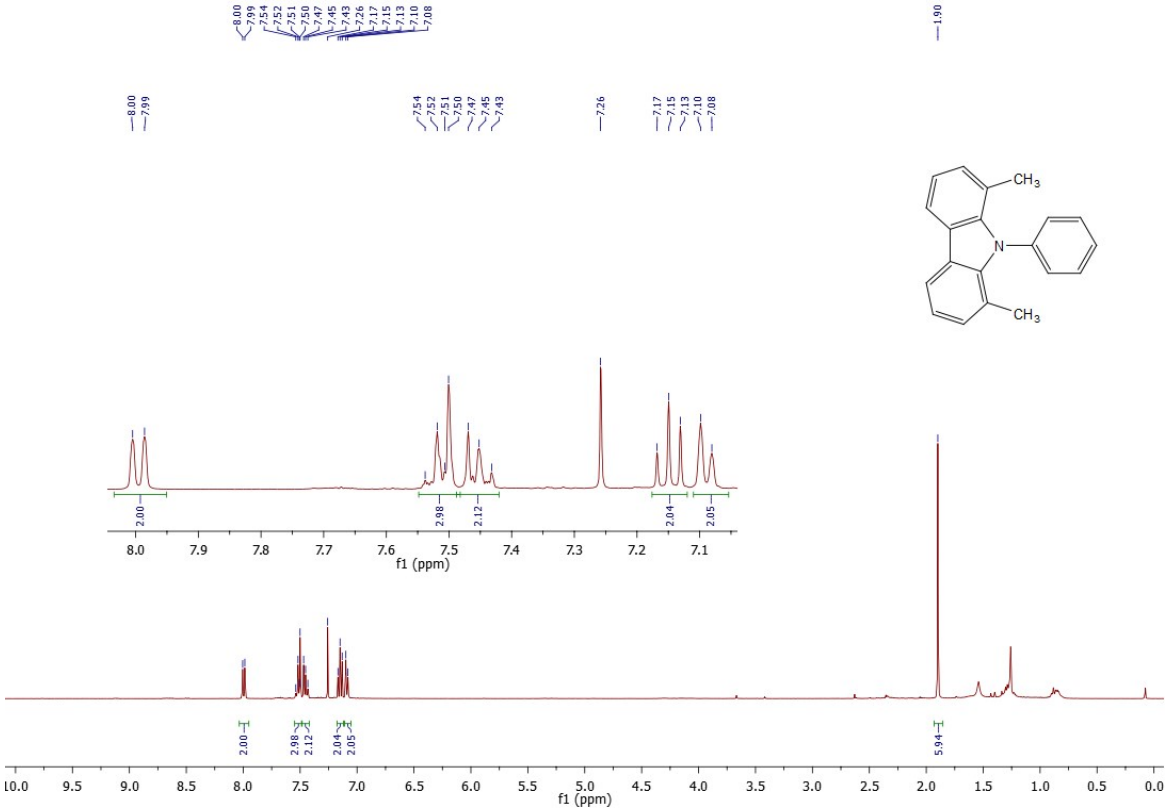

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 1,8-dimethyl-9-phenyl-9H-carbazole.

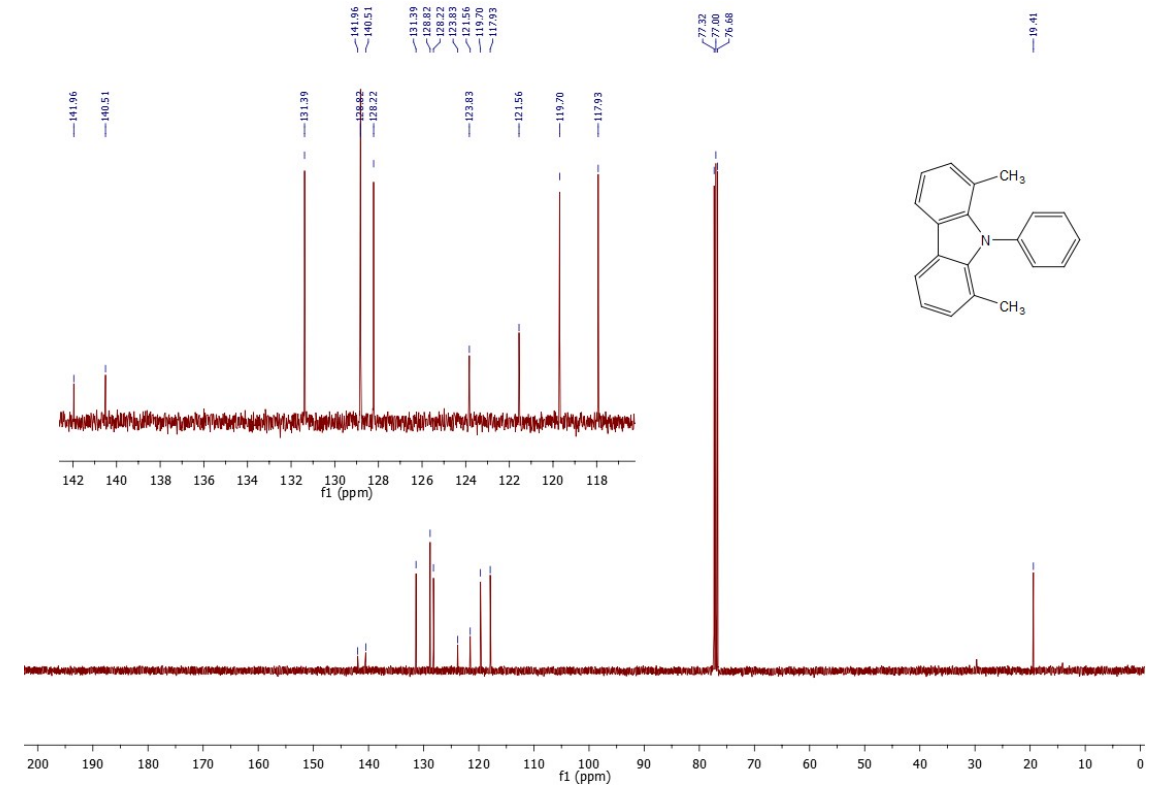

Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 1,8-dimethyl-9-phenyl-9H-carbazole.

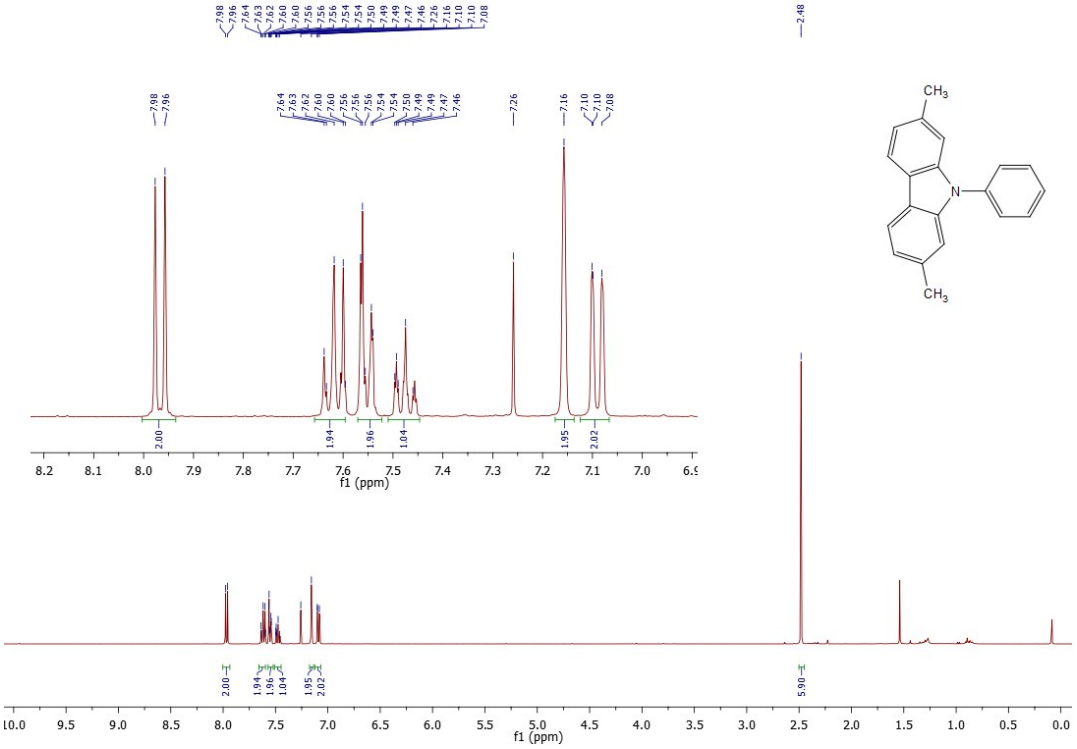

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2,7-dimethyl-9-phenyl-9H-carbazole.

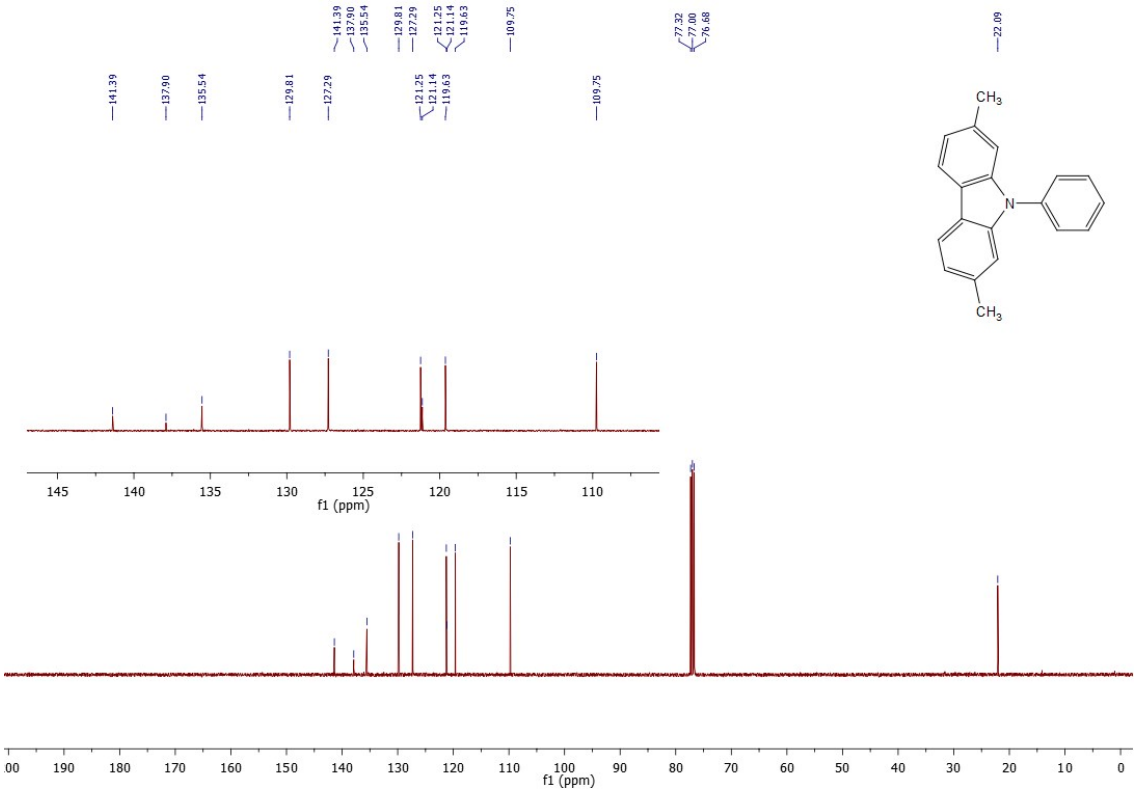

Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2,7-dimethyl-9-phenyl-9H-carbazole.

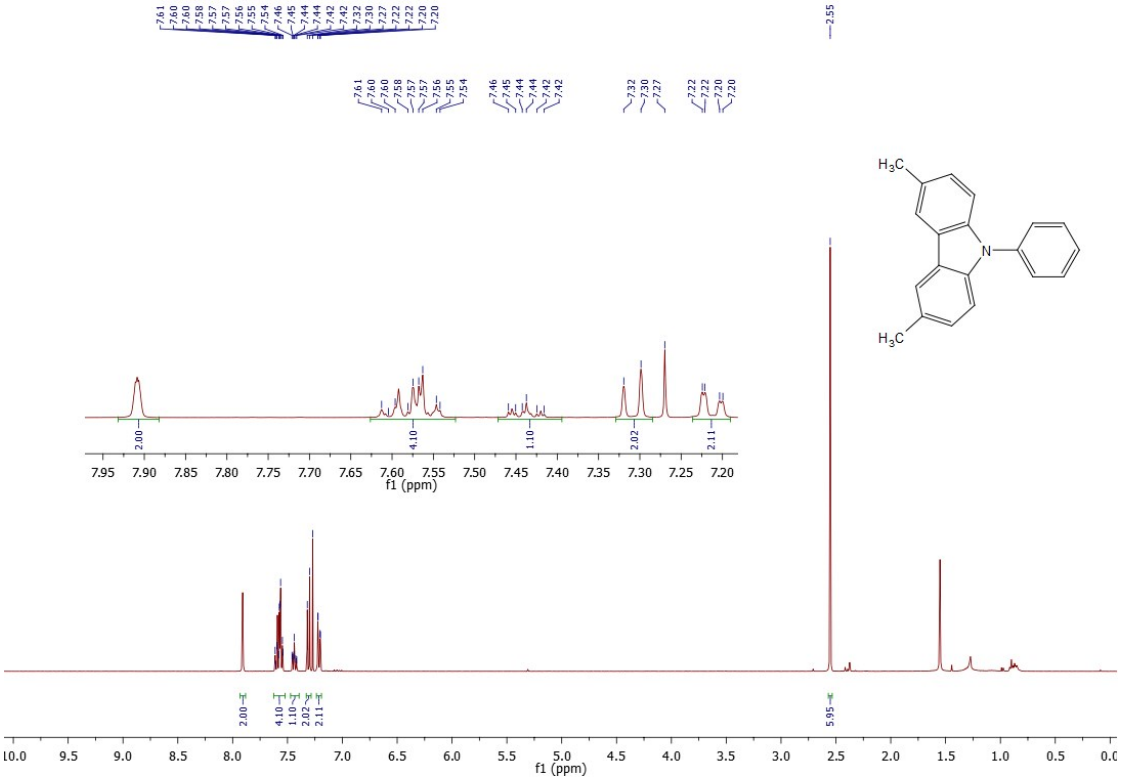

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 3,6-dimethyl-9-phenyl-9H-carbazole.

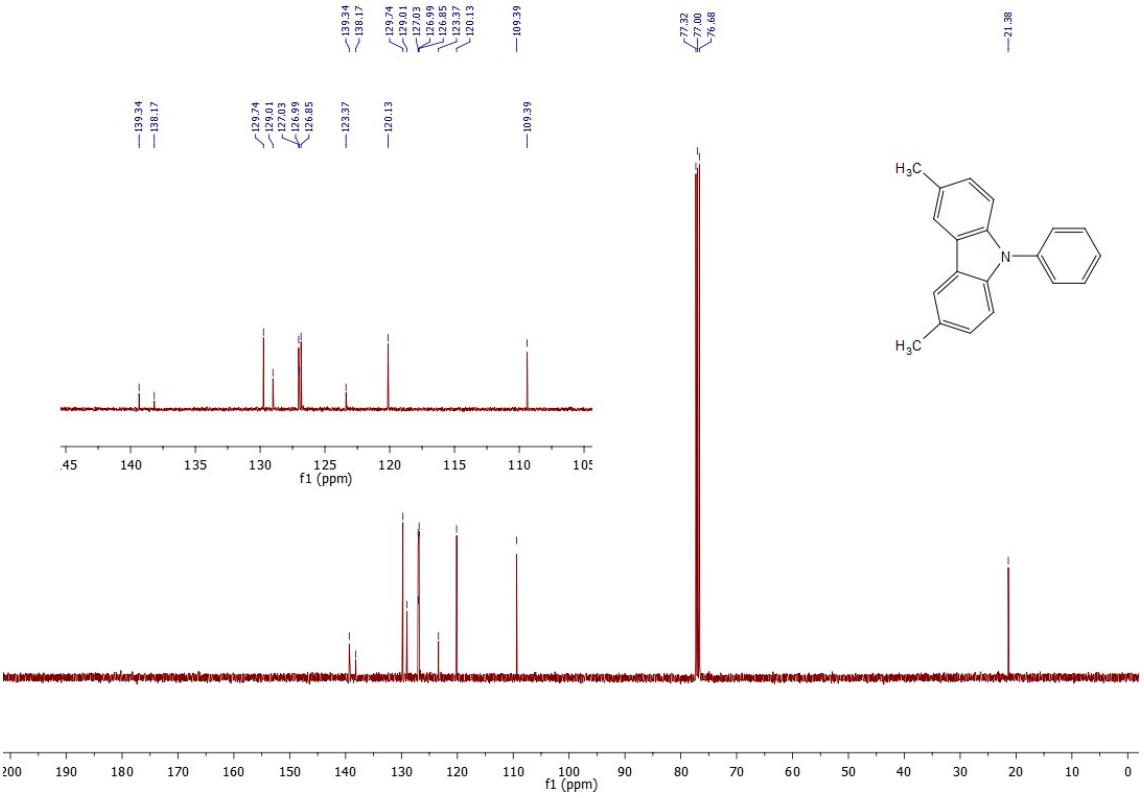

Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 3,6-dimethyl-9-phenyl-9H-carbazole.

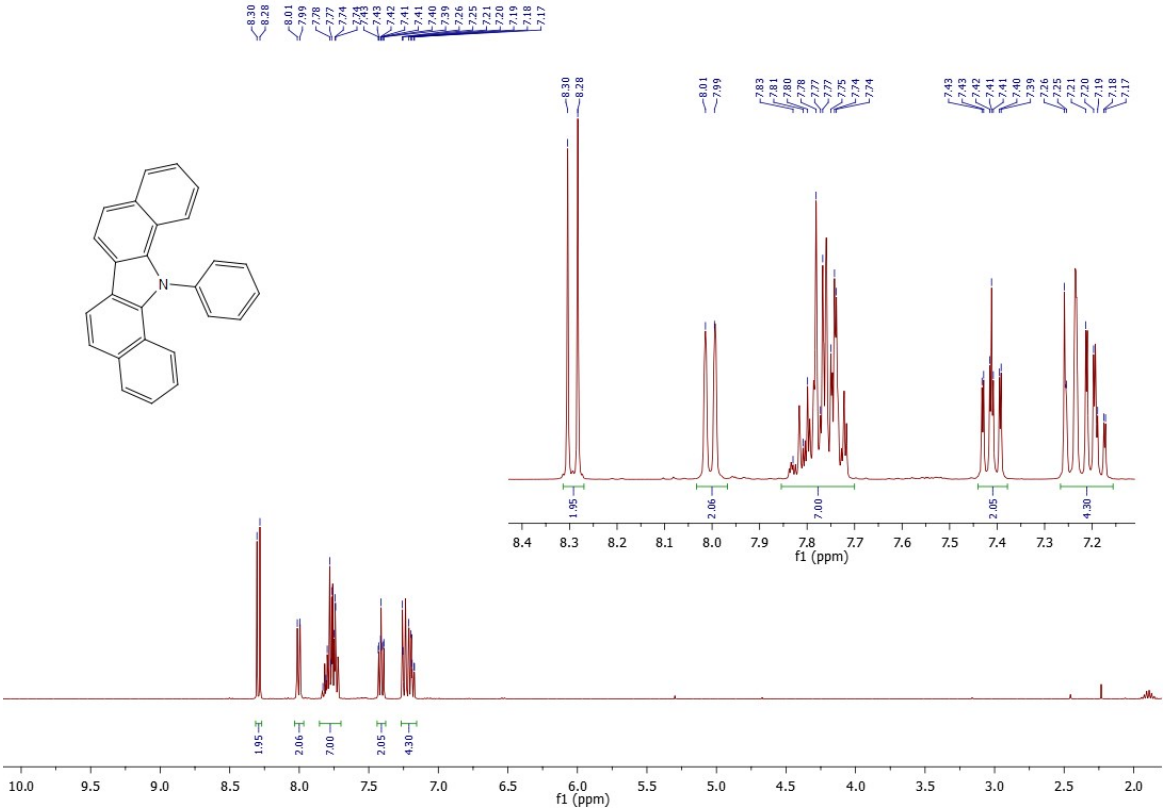

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 7-phenyl-7H-dibenzo[c,g] carbazole.

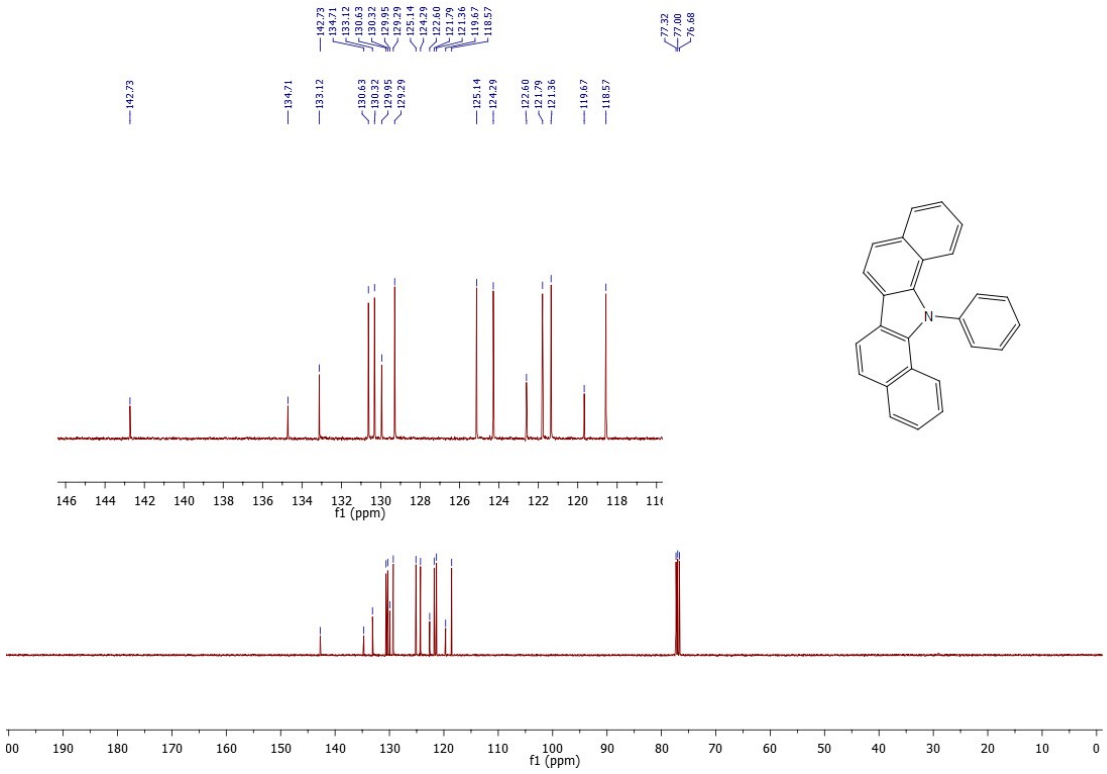

Figure S26. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 7-phenyl-7H-dibenzo[c,g] carbazole.

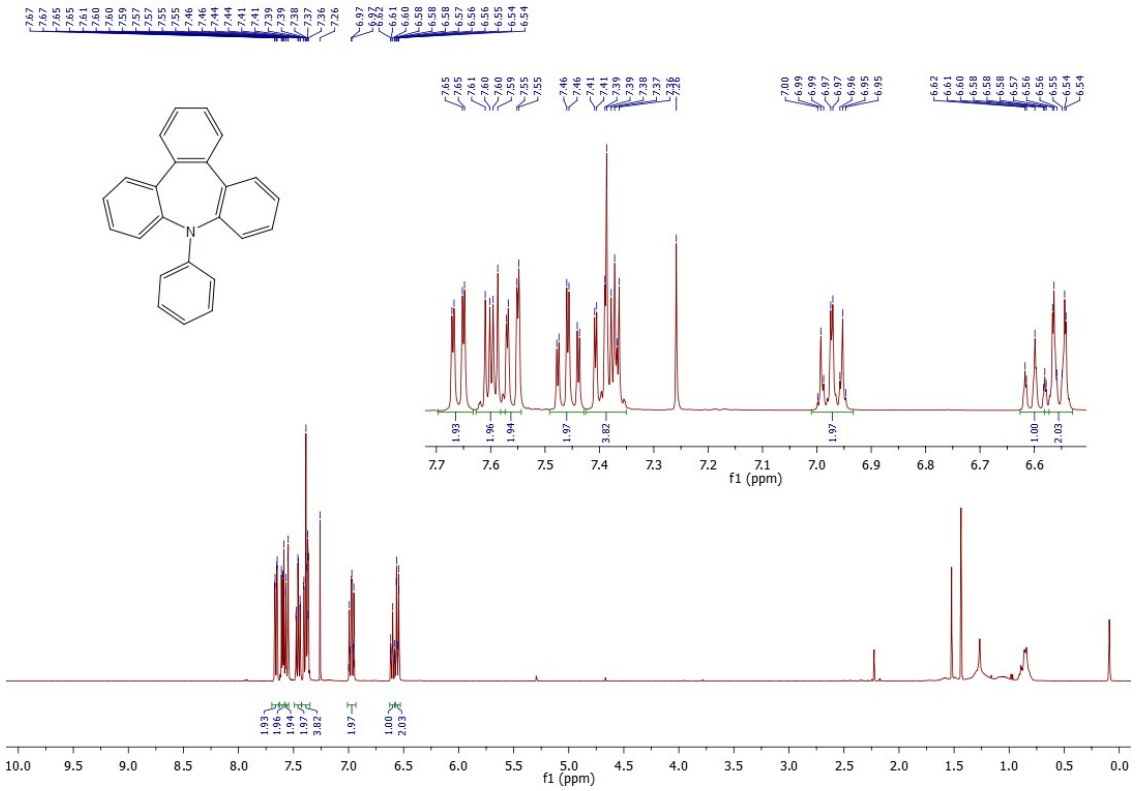

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-9H-tribenzo[b,d,f]azepine.

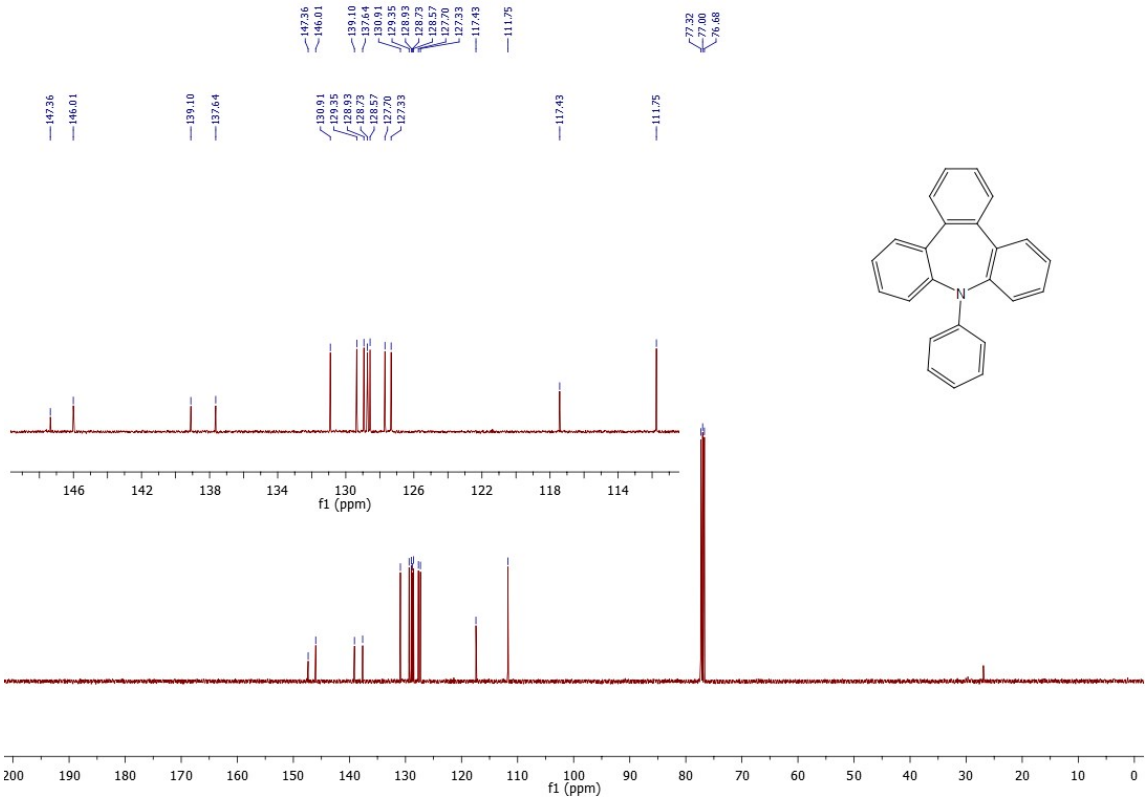

Figure S28. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9-phenyl-9H-tribenzo[b,d,f]azepine.

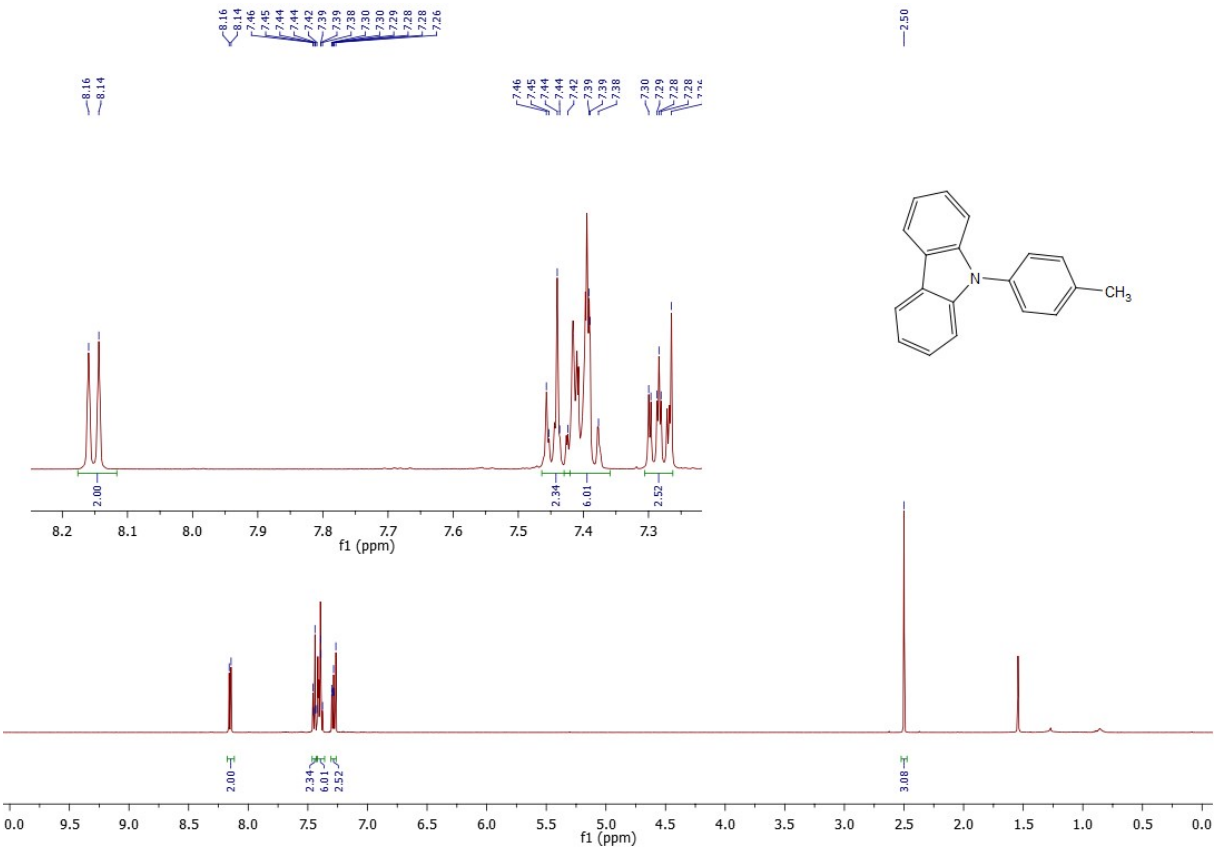

Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 9-(p-tolyl)-9H-carbazole.

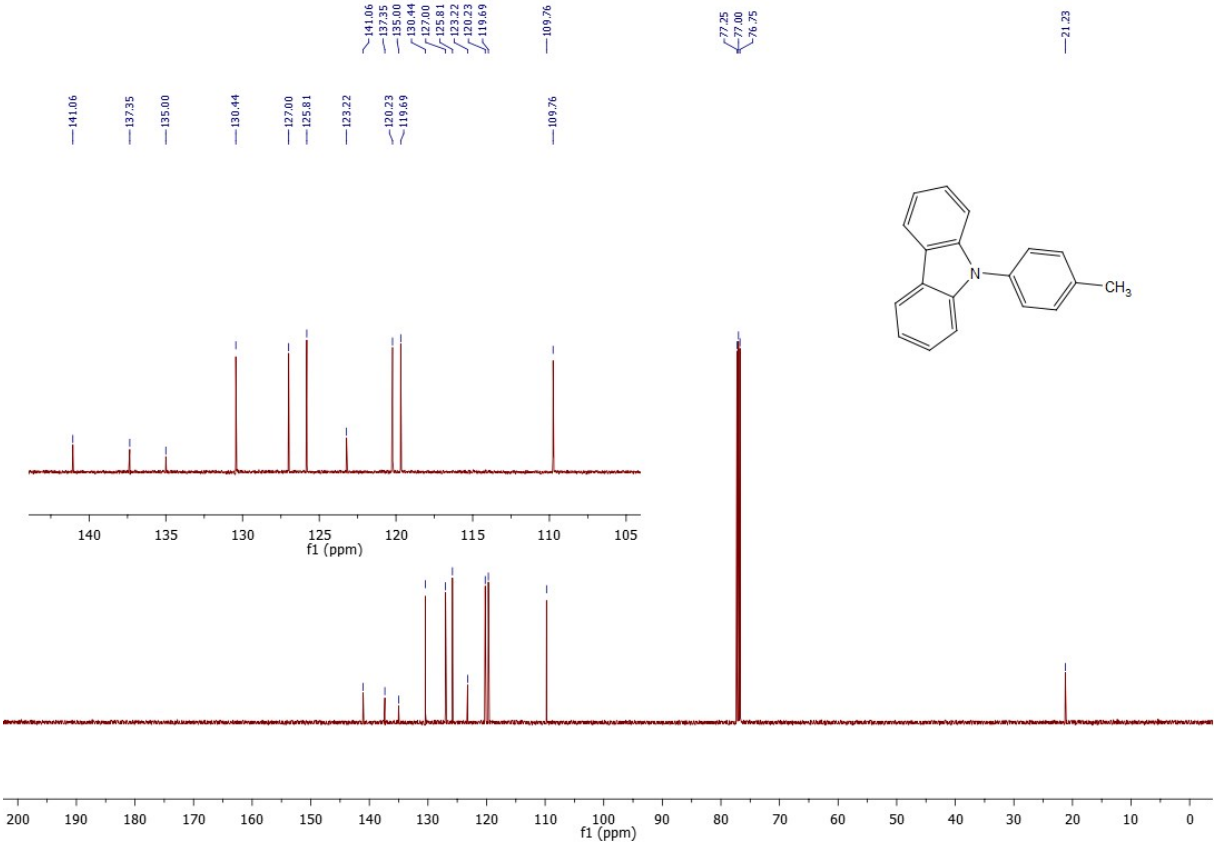

Figure S30. ^{13}C NMR (136 MHz, $CDCl_3$, 293 K) spectrum of 9-(p-tolyl)-9H-carbazole.

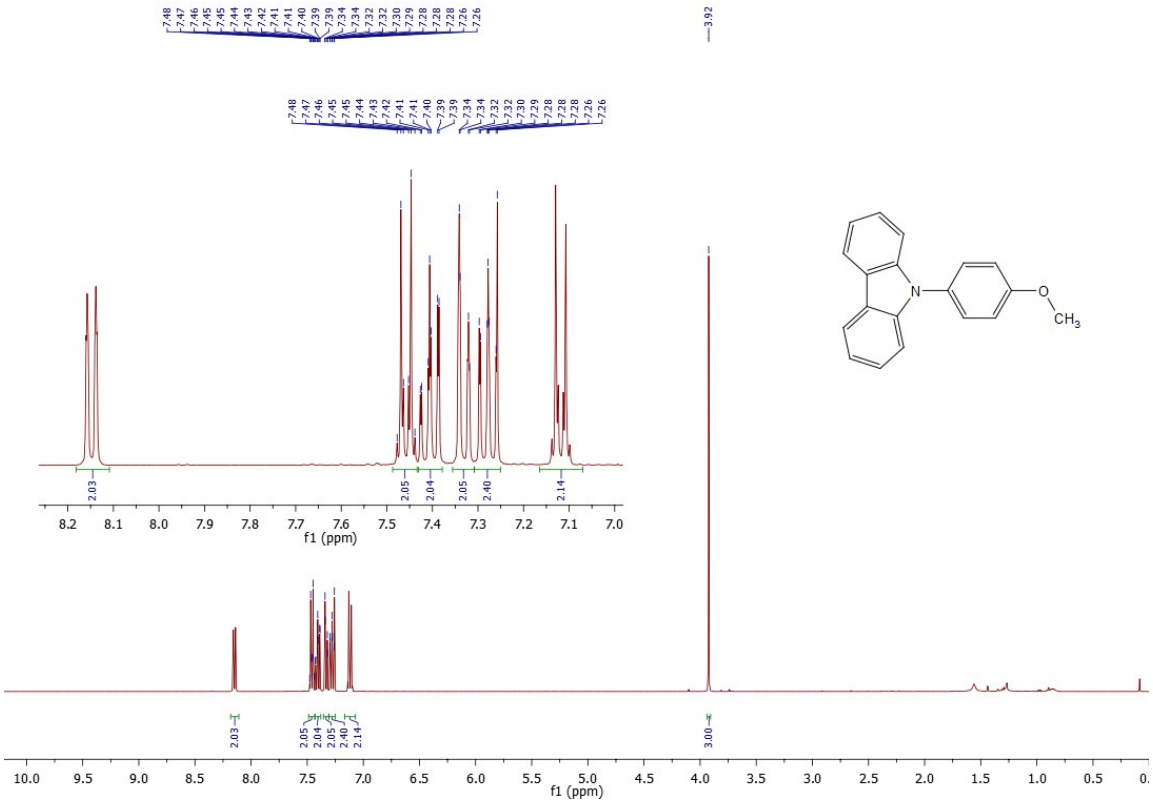

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9-(4-methoxyphenyl)-9H-carbazole.

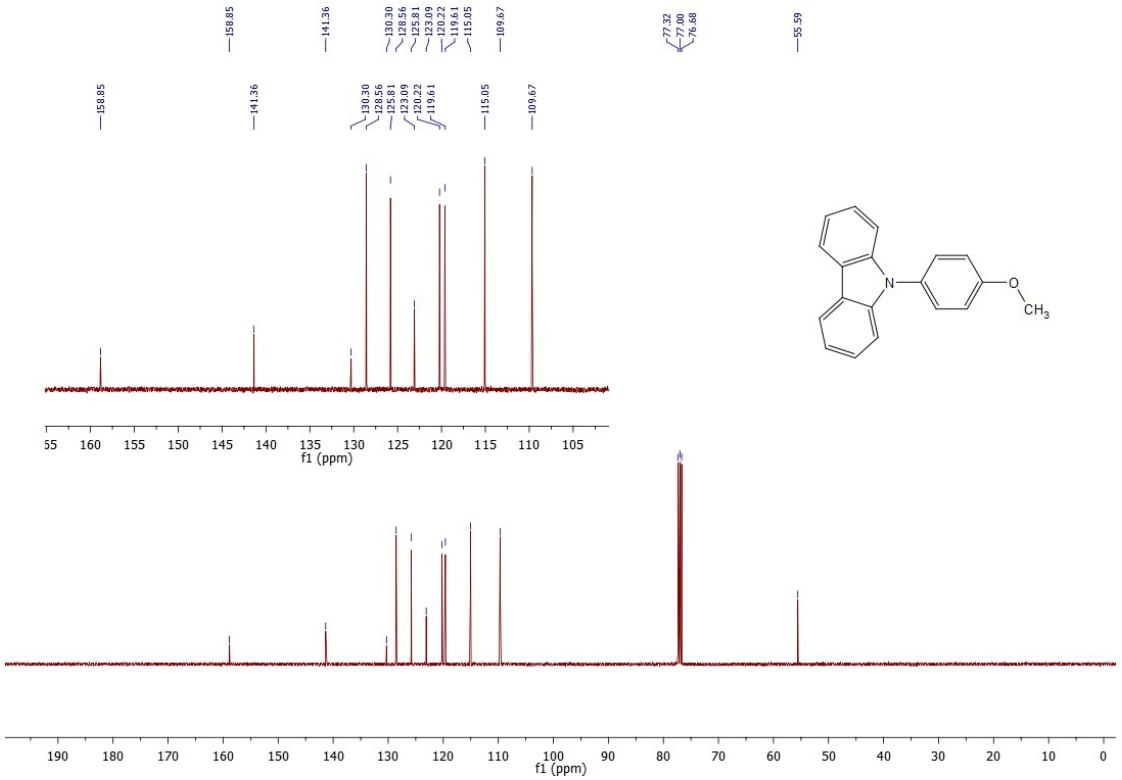

Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9-(4-methoxyphenyl)-9H-carbazole.

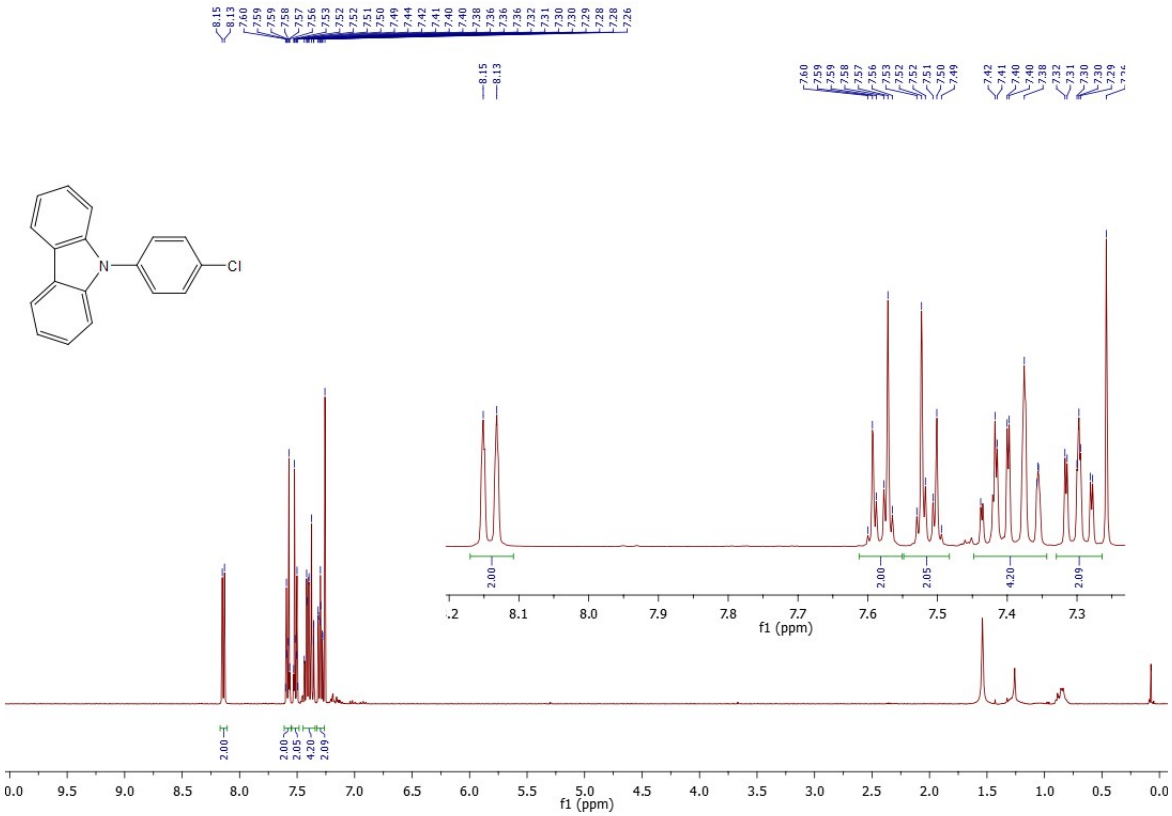

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9-(4-chlorophenyl)-9H-carbazole.

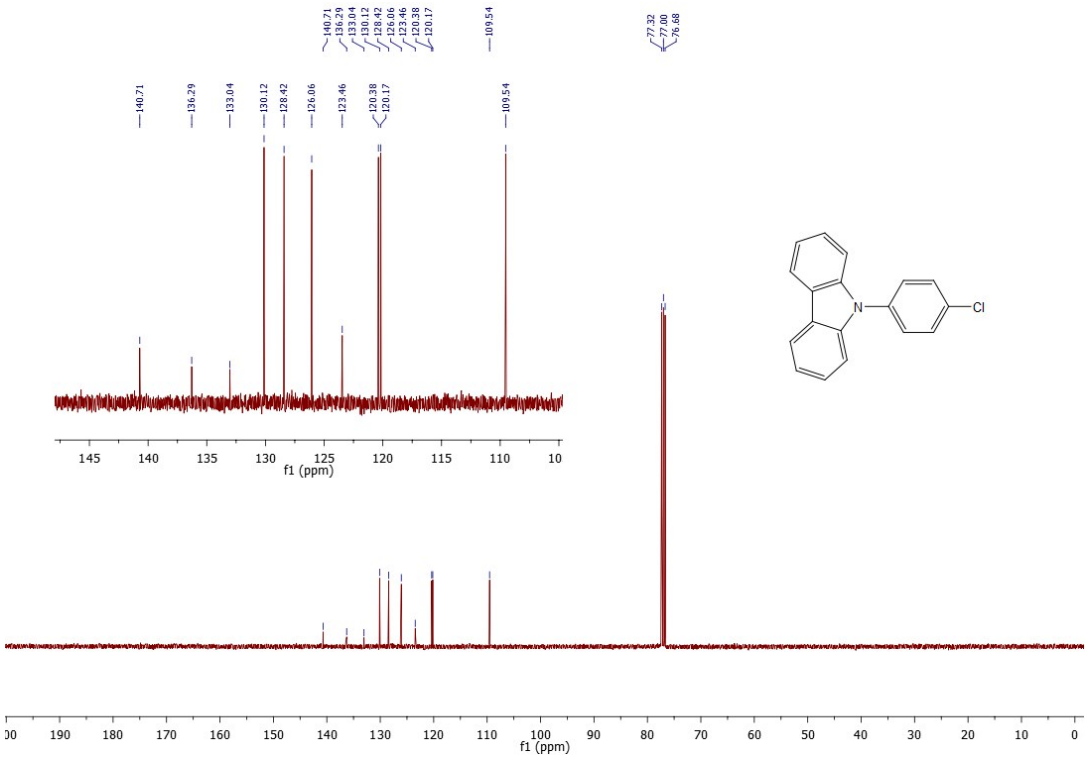

Figure S34. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9-(4-chlorophenyl)-9H-carbazole.

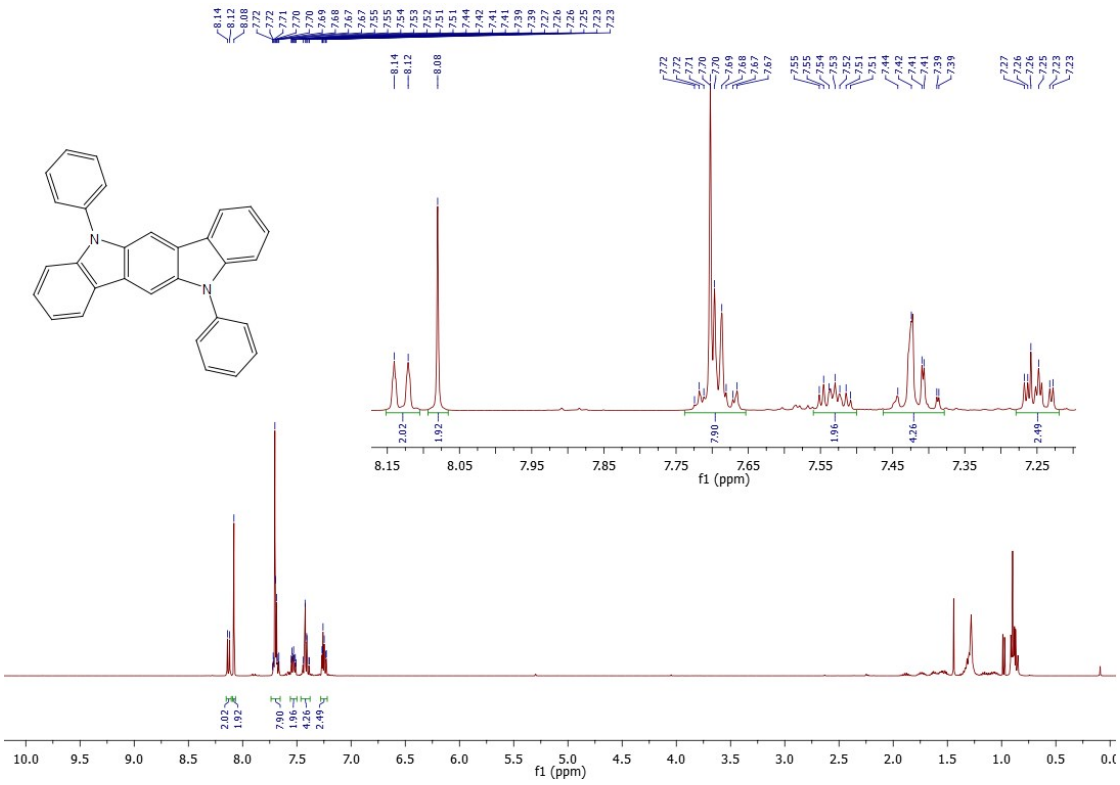

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 5,11-diphenyl-5,11-dihydroindolo[3,2-b]carbazole.

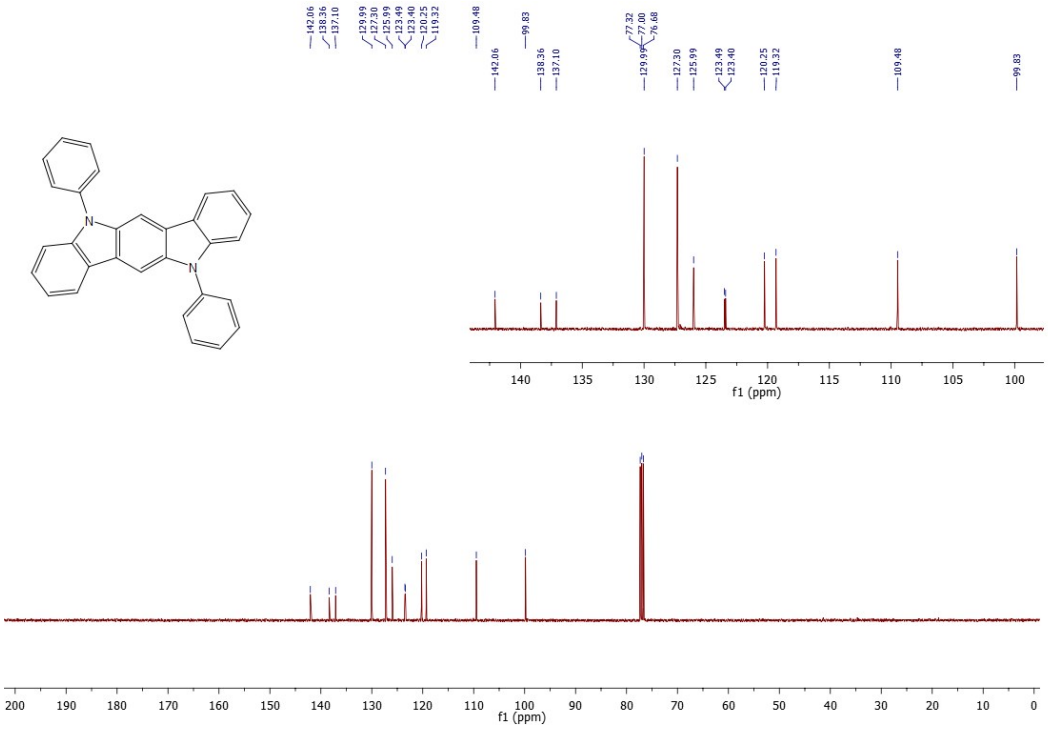

Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 5,11-diphenyl-5,11-dihydroindolo[3,2-b]carbazole.

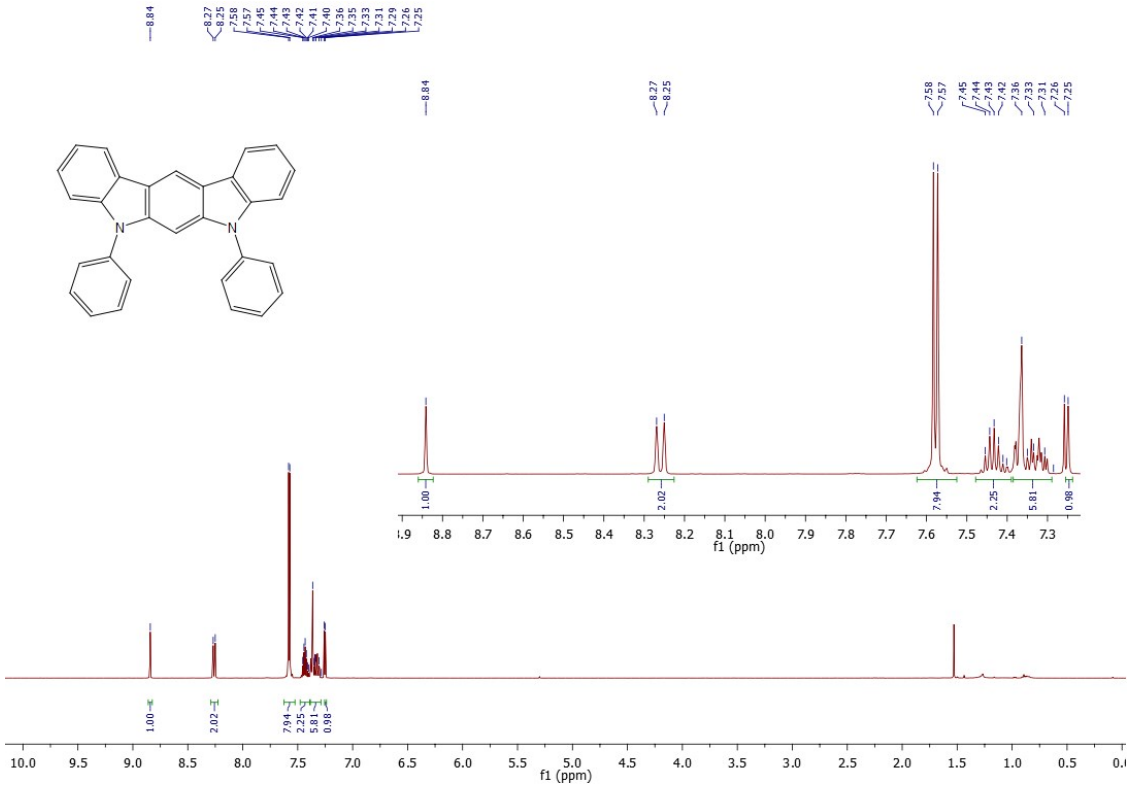

Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 5,7-diphenyl-5,7-dihydroindolo[2,3-b]carbazole.

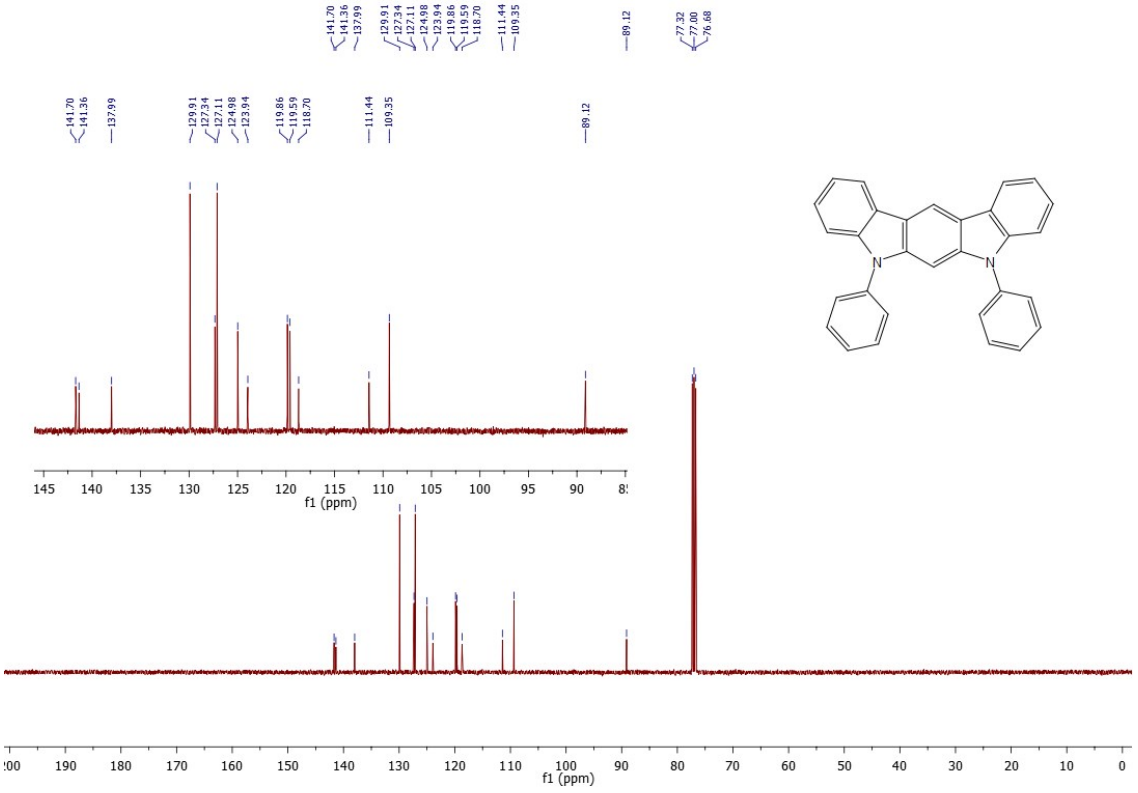

Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 5,7-diphenyl-5,7-dihydroindolo[2,3-b]carbazole.

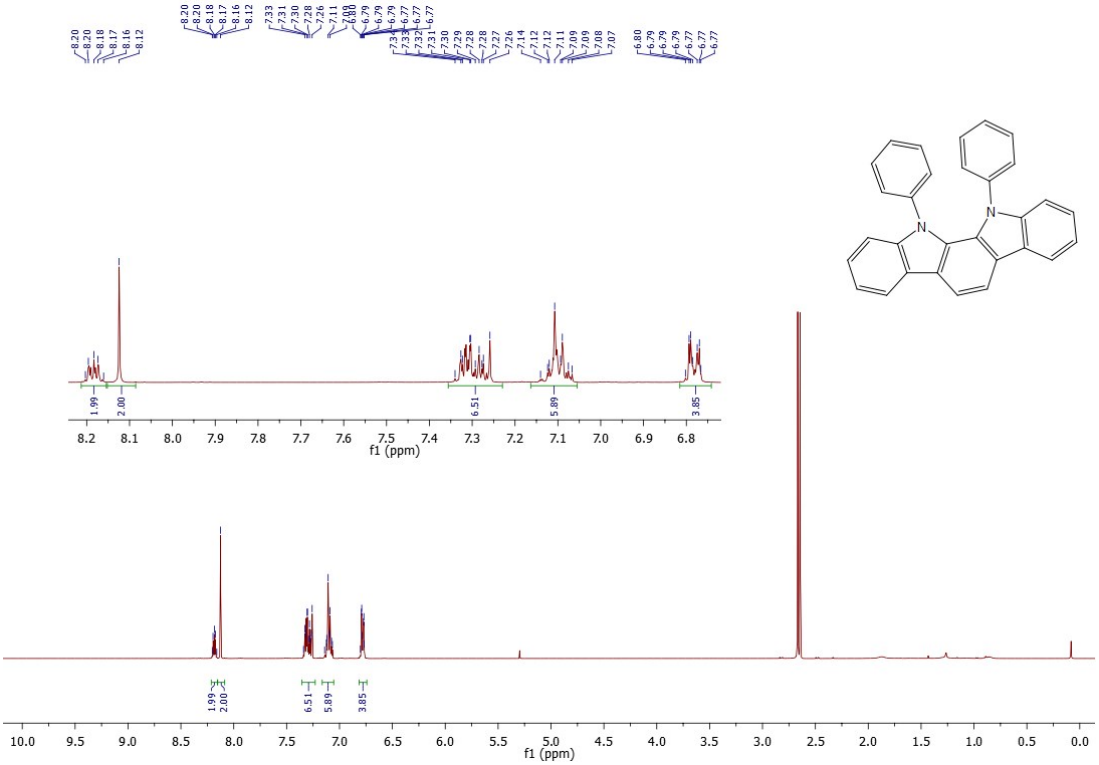

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 11,12-diphenyl-11,12-dihydroindolo[2,3-a]carbazole.

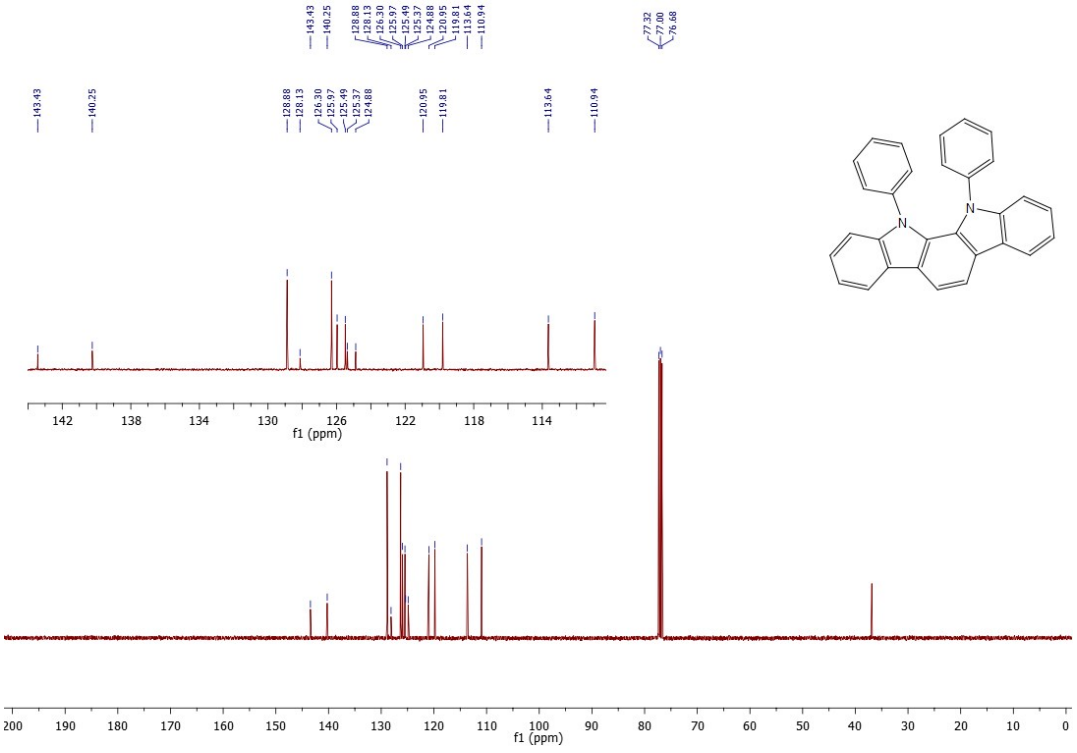

Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 11,12-diphenyl-11,12-dihydroindolo[2,3-a]carbazole.

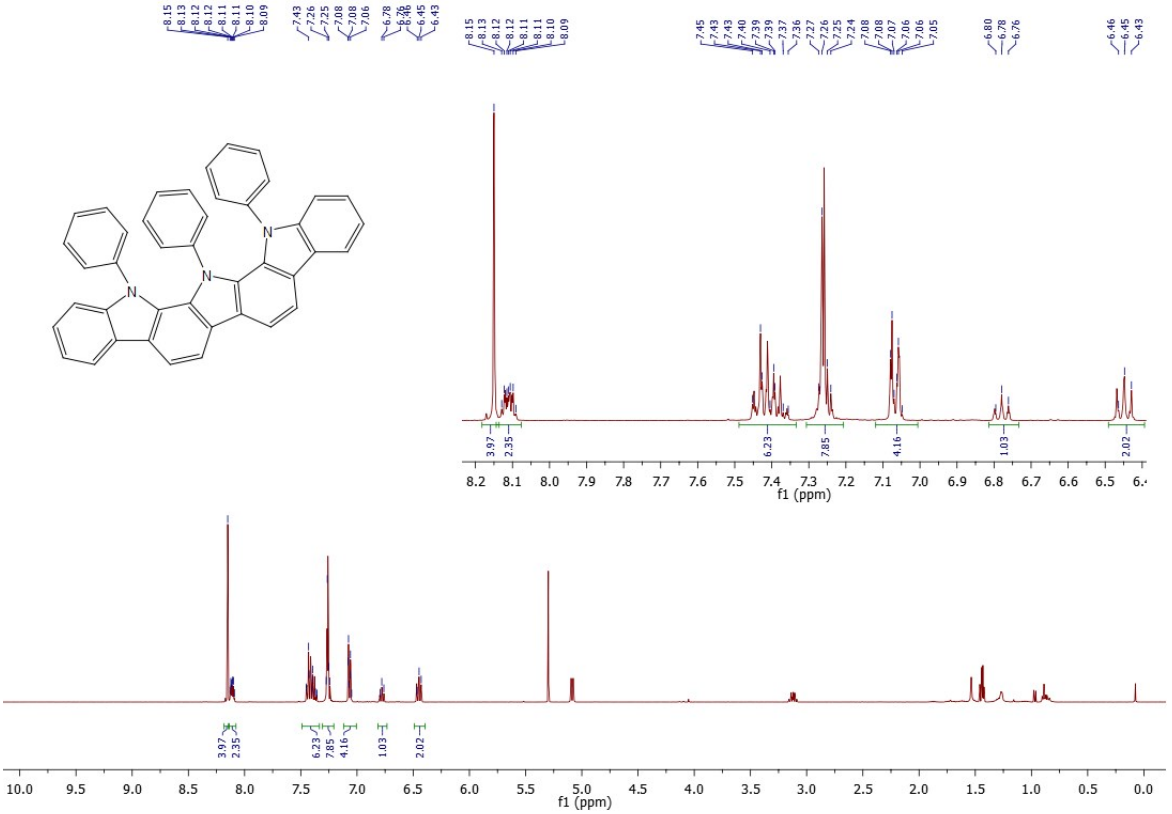

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 13,14,15-triphenyl-14,15-dihydro-13H-pyrrolo[2,3-a:5,4-a']dicarbazole.

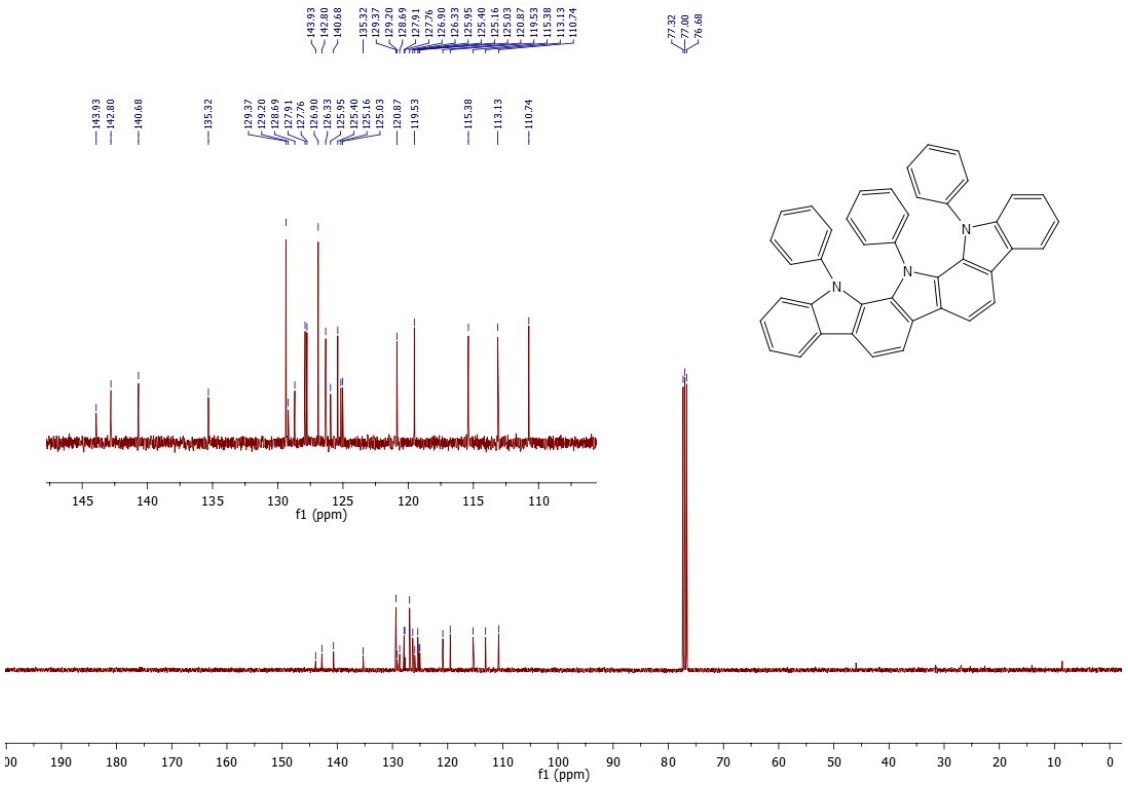

Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 13,14,15-triphenyl-14,15-dihydro-13H-pyrrolo[2,3-a:5,4-a']dicarbazole.