Supporting Information

Palladium(II)-catalyzed norbornene derivatives-mediated *ortho*-C−H silylation: access to divergent silicon-containing carbazoles

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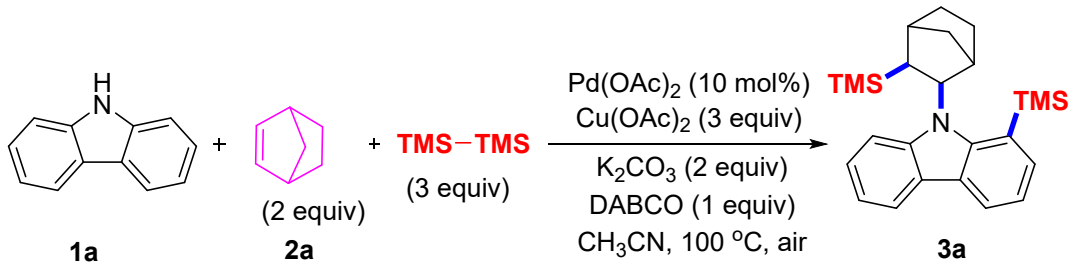
1) General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) at room temperature, unless otherwise noted. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) or DMSO-d_6 (δ = 2.50 for ^{1}H-NMR, δ = 39.60 for ^{13}C-NMR) as an internal reference. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC systemcoupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all starting materials were commercially available and were used without further purification.

2) Typical experimental procedures

A) Synthesis of 1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole **(3a)**

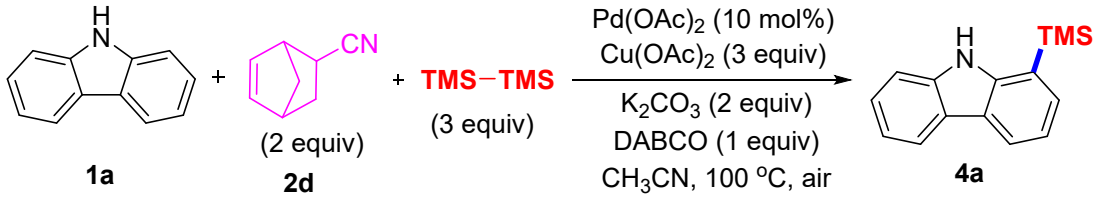


Scheme 4

The stirred mixture of carbazole (0.5 mmol, 84 mg), Hexamethyldisilane (3.0 equiv, 219 mg), Norbornene (**2a**) (2.0 equiv, 94 mg), $Pd(OAc)_2$ (10 mol %, 11.3 mg), $Cu(OAc)_2$ (3.0 equiv, 279 mg), and K_2CO_3 (2.0 equiv, 138 mg), DABCO (1.0 equiv,

56 mg) in CH_3CN (5 mL) at 100 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether unless otherwise noted) to provide the desired products **3a** as a pale yellow oil (154 mg, 76% yield).

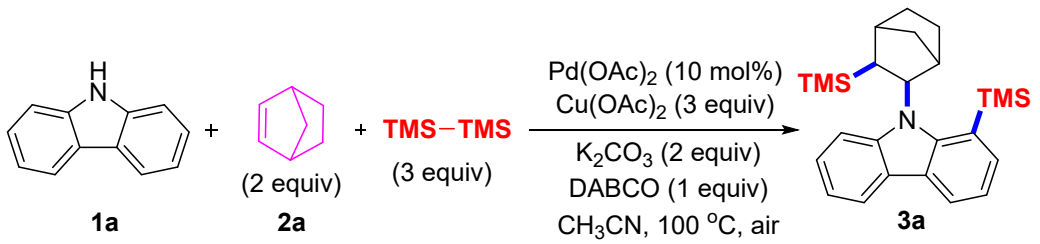
B) Synthesis of 1-(trimethylsilyl)-9*H*-carbazole **(4a)**



Scheme 5

The stirred mixture of carbazole (0.5 mmol, 84 mg), Hexamethyldisilane (3.0 equiv, 219 mg), 2-carbonitrile-norbornene (**2d**) (2.0 equiv, 119 mg), $Pd(OAc)_2$ (10 mol %, 11.3 mg), $Cu(OAc)_2$ (3.0 equiv, 279 mg), and K_2CO_3 (2.0 equiv, 138 mg), DABCO (1.0 equiv, 56 mg) in CH_3CN (5 mL) at 100 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=100:1 unless otherwise noted) to provide the desired products **4a** as a pale yellow oil (86 mg, 72% yield).

Table S1. Screening of optimal reaction conditions[a]



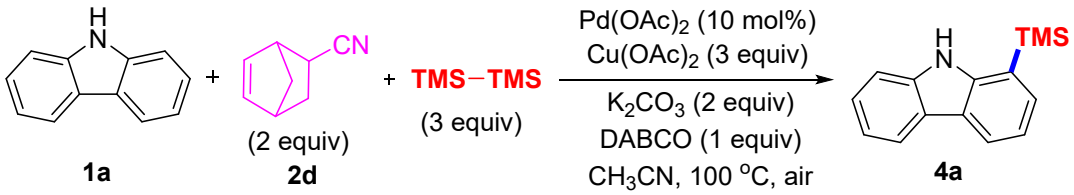
Entry	Catalyst	Oxidant	Base	Solvent	Yield/%[b]
1	$Pd(dba)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	0
2	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	59

3	$PdCl_2(PPh_3)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	25
4	$Pd(PPh_3)_4$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	0
5	$PdCl_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	28
6	$Pd(CF_3COO)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	31
7	/	$Cu(OAc)_2$	K_2CO_3	CH_3CN	0
8	$Pd(OAc)_2$	/	K_2CO_3	CH_3CN	0
9	$Pd(OAc)_2$	AgOAc	K_2CO_3	CH_3CN	trace
10	$Pd(OAc)_2$	Ag_2CO_3	K_2CO_3	CH_3CN	trace
11	$Pd(OAc)_2$	$Cu(OAc)_2$	K_3PO_4	CH_3CN	24
12	$Pd(OAc)_2$	$Cu(OAc)_2$	Cs_2CO_3	CH_3CN	trace
13	$Pd(OAc)_2$	$Cu(OAc)_2$	Na_2CO_3	CH_3CN	trace
14	$Pd(OAc)_2$	$Cu(OAc)_2$	KOH	CH_3CN	trace
15	$Pd(OAc)_2$	$Cu(OAc)_2$	KO^tBu	CH_3CN	trace
16	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	DMF	32
17	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	DMA	0
18	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	THF	0
19	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	Dioxane	0
20	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	Toluene	0
21	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	DMSO	0
22	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	NMP	0
23[c]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	0
24[d]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	37
25[e]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	76
26[f]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	73
27[e, g]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	69
38[e, h]	$Pd(OAc)_2$	$Cu(OAc)_2$	K_2CO_3	CH_3CN	62

[a] Conditions: carbazole (0.5 mmol), Norbornene (2.0 equiv), TMS-TMS (3 equiv), $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (3 equiv), K_2CO_3 (2 equiv), DABCO (1 equiv), and CH_3CN (5 mL) at 100 °C under air for 24 h. [b] Isolated yields. [c] AcOH (50 mol %). [d] $AgBF_4$ (20 mol %). [e] DABCO (1 equiv). [f] DABCO (triethylenediamine) (2 equiv). DMF (1 mL). [g] 110 °C instead of 100 °C. [h] 90 °C instead of 100 °C. trace <

10.

Table S2. Screening of optimal reaction conditions[a]



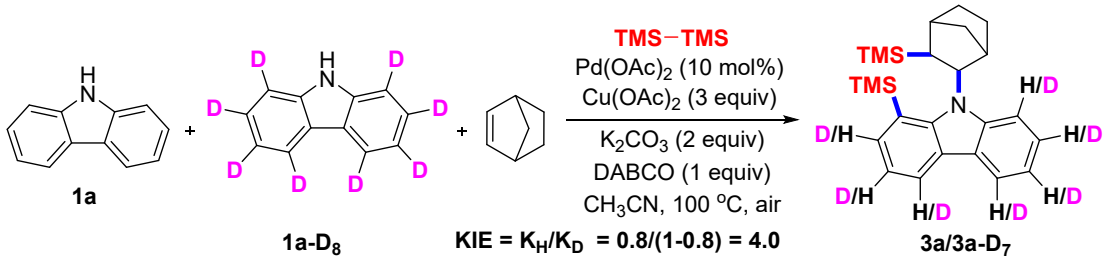
Entry	variation from the standard conditions	Yield/%[b]
1	none	72
2	under O_2 atmosphere	26
3	under N_2 atmosphere	65
4	without $Pd(OAc)_2$	0
5	$Pd_2(dba)_3$ instead of $Pd(OAc)_2$	0
6	$Pd(PPh_3)_4$ instead of $Pd(OAc)_2$	0
7	$PdCl_2$ instead of $Pd(OAc)_2$	34
8	$Pd(PPh_3)_2Cl_2$ instead of $Pd(OAc)_2$	46
12	$CuCl_2$ instead of $Cu(OAc)_2$	0
13	BQ instead of $Cu(OAc)_2$	0
14	$K_2S_2O_8$ instead of $Cu(OAc)_2$	0
15	K_3PO_4 instead of K_2CO_3	39
16	Cs_2CO_3 instead of K_2CO_3	trace
17	^{t}BuOK instead of K_2CO_3	trace
18	KOAc instead of K_2CO_3	trace
19	DMF instead of MeCN	27
20	Dioxane or Toluene instead of MeCN	0
21	without DABCO	54
22	at 110 °C	65
23	at 90 °C	56

[a] Conditions: carbazole (0.5 mmol, 1.0 equiv), 2-carbonitrile-norbornene (1.0 mmol, 2 equiv), hexamethyldisilane (1.5 mmol, 3 equiv), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$

(3 equiv), DABCO (1 equiv), K_2CO_3 (2 equiv), and MeCN (5 mL) at 100 °C for 24 h under air atmosphere. [b]Isolated yield. trace < 10.

3) Control experiment

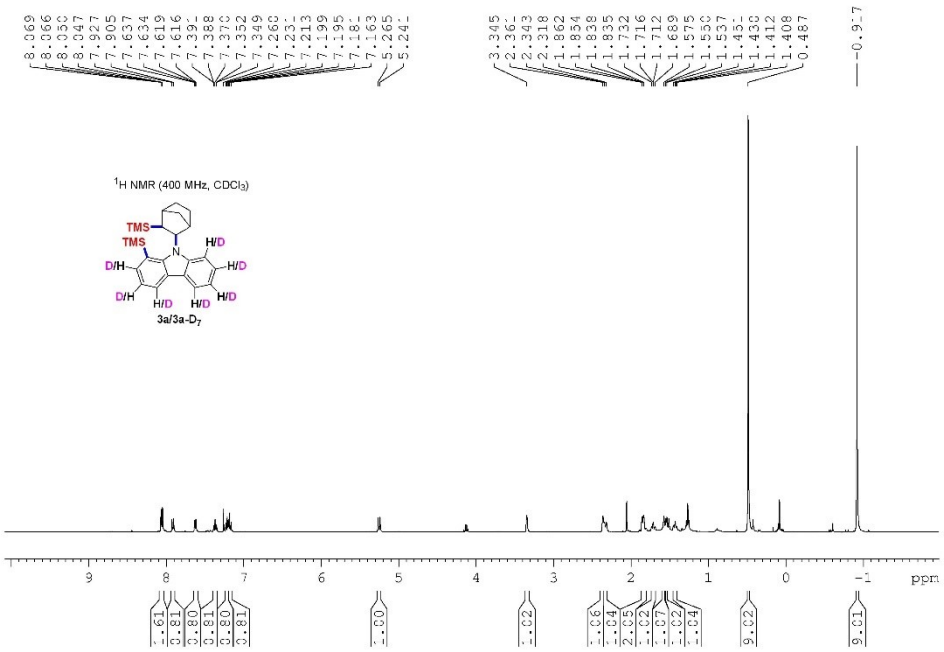
a) Intermolecular competetion experiment in the presence of norbornene



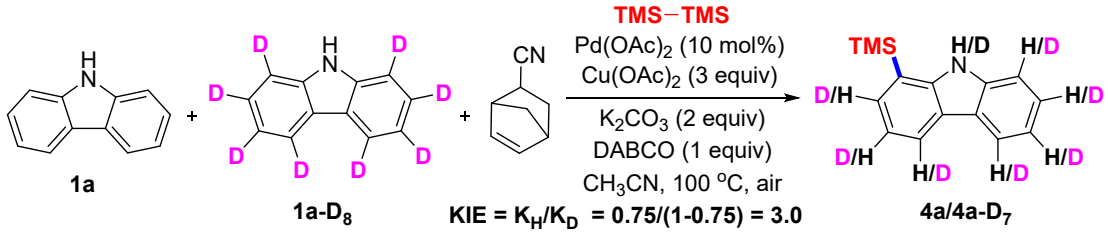
Scheme 6

To a 25 mL schlenk tube equipped with magnetic bar was added carbazole (**1a**, 42 mg, 0.25 mmol, 0.5 equiv), carbazole-$\mathbf{D_8}$ (**1a-D_8**, 46 mg, 0.25 mmol, 0.5 equiv), Hexamethyldisilane (219 mg, 1.5 mmol, 3.0 equiv), Norbornene (94 mg, 1 mmol, 2.0 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 10 mol %), $Cu(OAc)_2$ (279 mg, 1.5 mmol, 3.0 equiv), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in CH_3CN (5 mL). The reaction mixture was placed in a pre-heated oil bath (100 ℃) and stirred for 4 h. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel with PE as the eluent to afford product (36 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 7.48 Hz, 0.97 Hz, 1.6H), 7.91 (d, J = 8.58 Hz, 0.8H), 7.62 (dd, J = 7.20 Hz, 1.11 Hz, 0.8H), 7.39-7.35 (m, 0.8H), 7.23-7.20 (m, 0.8H), 7.20-7.16 (m, 0.8H), 5.25 (d, J = 9.69 Hz, 1H), 3.34 (s, 1H), 2.36 (s, 1H), 2.33 (d, J = 9.97 Hz, 1H), 1.86-1.84 (m, 2H), 1.73-1.69 (m, 1H), 1.57 (s, 1H), 1.54 (d, J = 5.12 Hz, 1H), 1.45-1.41 (m, 1H), 0.49 (s, 9H), -0.92 (s, 9H).



b) Intermolecular competetion experiment in the presence of 2-carbonitrile-norbornene

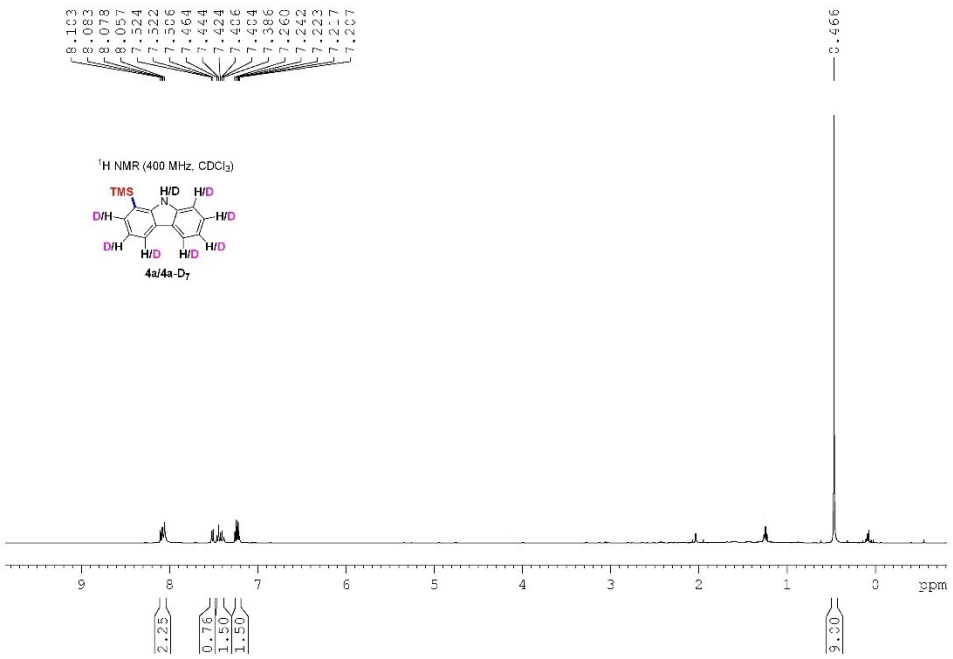


Scheme 7

To a 25 mL schlenk tube equipped with magnetic bar was added carbazole (**1a**, 42 mg, 0.25 mmol, 0.5 equiv), carbazole-**D$_8$** (**1a-D$_8$**, 46 mg, 0.25 mmol, 0.5 equiv), Hexamethyldisilane (219 mg, 1.5 mmol, 3.0 equiv), 2-carbonitrile-norbornene (**2d**) (119 mg, 1 mmol, 2.0 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 10 mol %), $Cu(OAc)_2$ (279 mg, 1.5 mmol, 3.0 equiv), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in CH_3CN (5 mL). The reaction mixture was placed in a pre-heated oil bath (100 °C) and stirred for 4 h. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel with PE: EA (100:1) as

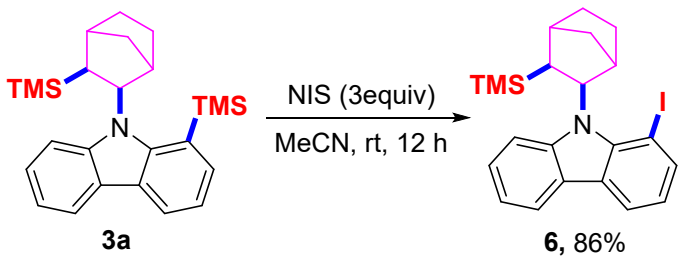
the eluent to afford product (32 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.06 (m, 2.25H), 7.52-7.51 (m, 0.75H), 7.46-7.39 (m, 1.50H), 7.24-7.21 (m, 1.50H), 0.47 (s, 9H).



4) Procedure for transformation experiment

a) Synthesis of 1-iodo-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole **(6)** [1]

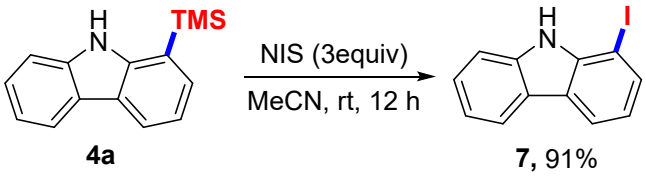


Scheme 8

The stirred mixture of 1-(trimethylsilyl)-9-((2*R*,3*S*)-3-

(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole **3a** (0.5 mmol), NIS (*N*-Iodosuccinimide) (3.0 equiv) were dissolved in CH_3CN (5 ml). The reaction mixture was stired for 12 h at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=100:1 unless otherwise noted) to provide the desired products **6** as a red oil (197 mg, 86% yield).

b) Synthesis of 1-iodo-9*H*-carbazole **(7)** [1]

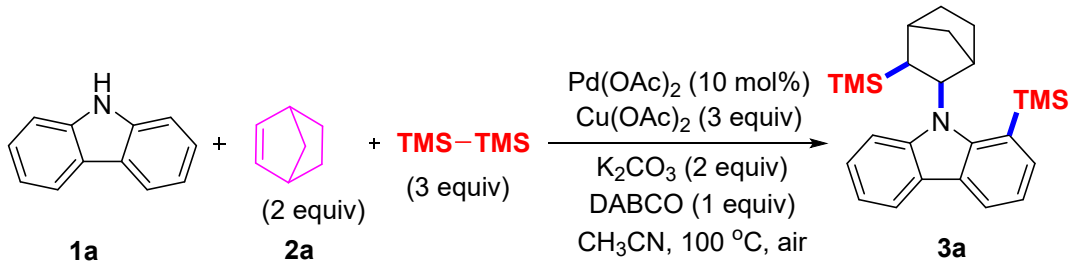


Scheme 9

The stirred mixture of 1-(trimethylsilyl)-9*H*-carbazole **4a** (0.5 mmol), NIS (*N*-Iodosuccinimide) (3.0 equiv) were dissolved in CH_3CN (5 ml). The reaction mixture was stired for 12 h at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=100:1 unless otherwise noted) to provide the desired products **7** as a red oil (127 mg, 91% yield).

5) Larger-scale experiment

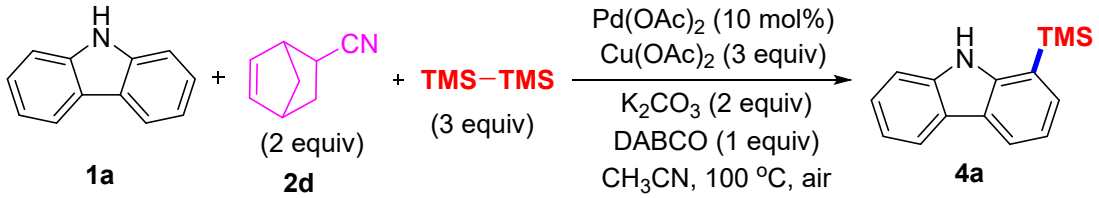
A) Synthesis of 1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole **(3a)**



Scheme 10

The stirred mixture of carbazole (5.0 mmol, 840 mg), Hexamethyldisilane (3.0 equiv, 2190 mg), Norbornene (**2a**) (2.0 equiv, 940 mg), $Pd(OAc)_2$ (10 mol %, 113 mg), $Cu(OAc)_2$ (3.0 equiv, 2790 mg), and K_2CO_3 (2.0 equiv, 1380 mg), DABCO (1.0 equiv, 560 mg) in CH_3CN (50 mL) at 100 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether unless otherwise noted) to provide the desired products **3a** as a pale yellow oil (1420 mg, 70% yield).

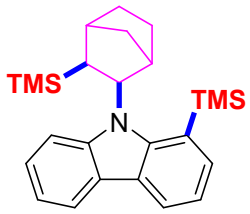
B) Synthesis of 1-(trimethylsilyl)-9*H*-carbazole **(4a)**



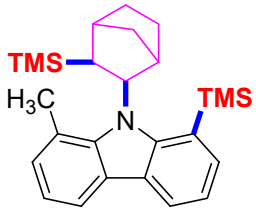
Scheme 11

The stirred mixture of carbazole (1.0 mmol, 840 mg), Hexamethyldisilane (3.0 equiv, 2190 mg), 2-carbonitrile-norbornene (**2d**) (2.0 equiv, 1190 mg), $Pd(OAc)_2$ (10 mol %, 113 mg), $Cu(OAc)_2$ (3.0 equiv, 2790 mg), and K_2CO_3 (2.0 equiv, 1380 mg), DABCO (1.0 equiv, 560 mg) in CH_3CN (50 mL) at 100 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=100:1 unless otherwise noted) to provide the desired products **4a** as a pale yellow oil (775 mg, 65% yield).

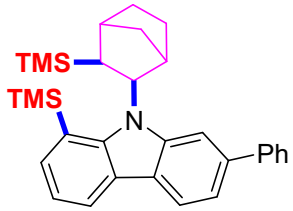
6) Characterization data



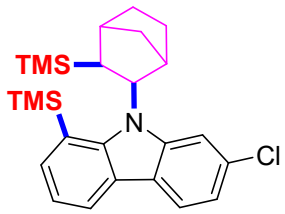
1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3a): pale yellow oil, isolated yield 76% (154 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.62 Hz, 1.12 Hz, 2H), 8.01 (d, *J* = 8.49 Hz, 1H), 7.72 (dd, *J* = 7.26 Hz, 1.22 Hz, 1H), 7.47 (td, *J* = 7.08 Hz, 1.18 Hz, 1H), 7.35-7.28 (m, 2H), 5.35 (d, *J* = 9.77 Hz, 1H), 3.44 (s, 1H), 2.46-2.42 (m, 2H), 1.96-1.94 (m, 2H), 1.84-1.79 (m, 1H), 1.67-1.64 (m, 2H), 1.55-1.51 (m, 1H), 0.59 (s, 9H), -0.81 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.0, 134.3, 128.1, 124.8, 123.6, 121.0, 120.6, 119.5, 119.1, 118.7, 113.9, 65.2, 44.9, 41.6, 39.5, 38.7, 31.8, 30.4, 1.4, -1.5. HRMS (ESI) m/z calcd for $C_{25}H_{36}NSi_2$+ $(M+H)^+$ 406.2381, found 406.2384.



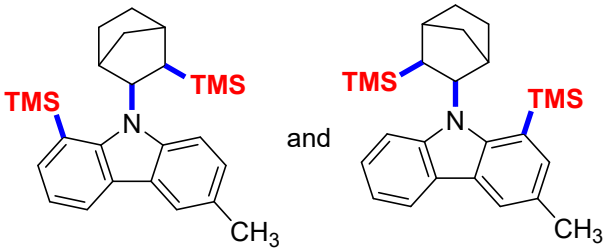
1-methyl-8-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3b): pale yellow oil, isolated yield 47% (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.91 (d, *J* = 7.80 Hz, 2H), 7.36 (d, *J* = 7.80 Hz, 1H), 7.23 (d, *J* = 7.22 Hz, 1H), 7.14 (t, *J* = 7.51 Hz, 1H), 3.66 (d, *J* = 10.68 Hz, 1H), 2.94 (s, 1H), 2.57 (s, 4H), 2.26 (d, *J* = 9.82 Hz, 1H), 1.94-1.90 (m, 1H), 1.77-1.74 (m, 1H), 1.65 (d, *J* = 9.53 Hz, 2H), 1.54-1.51 (m, 2H), 0.42 (s, 9H), -0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.2, 137.2, 132.7, 126.4, 126.2, 126.1, 122.3, 119.4, 119.3, 118.0, 50.7, 44.7, 40.6, 39.6, 38.9, 33.6, 31.7, 16.7, 2.0, -1.0. HRMS (ESI) m/z calcd for $C_{26}H_{38}NSi_2$+ $(M+H)^+$ 420.2537, found 420.2540.



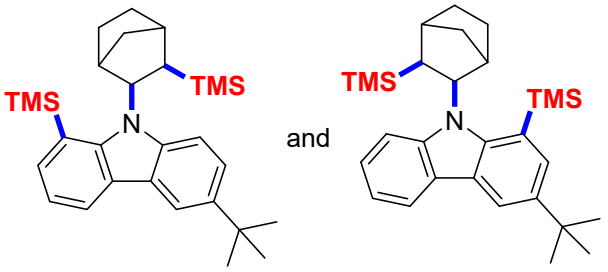
7-phenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3c): pale yellow oil, isolated yield 53% (62 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.10 (d, *J* = 8.06 Hz, 1H), 8.07 (dd, *J* = 7.59 Hz, 0.81 Hz, 1H), 7.70 (d, *J* = 7.36 Hz, 2H), 7.63 (dd, *J* = 7.13 Hz, 0.81 Hz, 1H), 7.51-7.45 (m, 3H), 7.20 (t, *J* = 7.36 Hz, 1H), 5.28 (d, *J* = 9.78 Hz, 1H), 3.39 (s, 1H), 2.49 (d, *J* = 9.44 Hz, 1H), 2.41 (s, 1H), 1.87-1.85 (m, 1H), 1.75-1.74 (m, 1H), 1.71-1.69 (m, 1H), 1.64 (d, *J* = 9.71 Hz, 1H), 1.57-1.55 (m, 1H), 1.47-1.45 (m, 1H), 0.50 (s, 9H), -0.87 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 142.7, 140.5, 138.2, 134.4, 128.8, 127.5, 126.8, 124.4, 123.5, 121.1, 120.7, 119.7, 118.9, 118.9, 112.7, 65.3, 45.0, 41.8, 39.6, 38.8, 31.8, 30.4, 1.4, -1.5. HRMS (ESI) m/z calcd for $C_{31}H_{40}NSi_2$+ $(M+H)^+$ 482.2694, found 482.2697.



7-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3d): pale yellow oil, isolated yield 49% (108 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.00 (d, *J* = 7.55 Hz, 1H), 7.94 (d, *J* = 8.24 Hz, 1H), 7.90 (d, *J* = 1.00 Hz, 1H), 7.63 (d, *J* = 6.70 Hz, 1H), 7.21-7.17 (m, 2H), 5.21 (d, *J* = 9.78 Hz, 1H), 3.28 (s, 1H), 2.38 (s, 1H), 2.26 (d, *J* = 9.94 Hz, 1H), 1.87-1.84 (m, 2H), 1.70-1.68 (m, 1H), 1.59 (d, *J* = 9.17 Hz, 2H), 1.52 (dd, *J* = 9.78 Hz, 1.69 Hz, 1H), 0.48 (s, 9H), -0.89 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 140.4, 134.6, 130.4, 123.7, 123.1, 121.0, 120.9, 120.2, 119.5, 119.2, 111.3, 65.2, 44.9, 41.5, 39.5, 38.7, 31.7, 30.3, 1.3, -1.5. HRMS (ESI) m/z calcd for $C_{25}H_{35}ClNSi_2$+ $(M+H)^+$ 440.1991, found 440.1994.

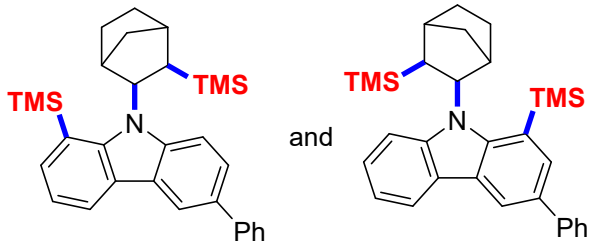


6-methyl-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3e) and 3-methyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3e'), (3e:3e' = 1:1): pale yellow oil, isolated yield 81% (170 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.57 Hz, 2H), 7.89 (d, *J* = 8.61 Hz, 1H), 7.86 (s, 2H), 7.80 (d, *J* = 8.61 Hz, 1H), 7.61 (dd, *J* = 7.23 Hz, 1.20 Hz, 1H), 7.44 (d, *J* = 1.38 Hz, 1H), 7.37-7.33 (m, 1H), 7.21-7.14 (m, 3H), 5.23 (dd, *J* = 9.47 Hz, 3.61 Hz, 2H), 3.33 (s, 2H), 2.52 (d, *J* = 5.34 Hz, 6H), 2.37-2.32 (m, 4H), 2.07 (s, 2H), 1.86-1.84 (m, 2H), 1.74-1.69 (m, 2H), 1.57-1.51 (m, 4H), 1.46-1.42 (m, 2H), 0.49 (s, 18H), -0.89 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 146.5, 140.2, 138.2, 135.6, 134.1, 128.4, 127.5, 126.2, 125.3, 125.0, 124.6, 123.8, 123.5, 121.0, 120.9, 120.4, 120.3, 119.5, 119.4, 118.9, 118.4, 113.8, 113.7, 65.2, 65.0, 44.9, 44.8, 41.6, 41.6, 39.4, 38.7, 31.8, 30.4, 30.3, 21.2, 21.0, 1.4, 1.4, -1.4, -1.5. HRMS (ESI) m/z calcd for $C_{26}H_{38}NSi_2^+$ $(M+H)^+$ 420.2537, found 420.2540.

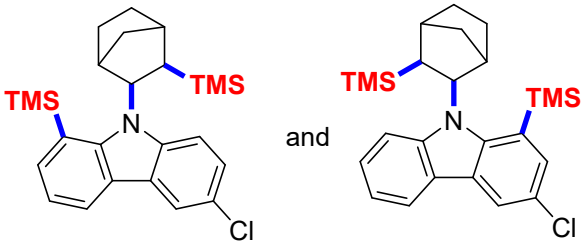


6-(tert-butyl)-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3f) and 3-(tert-butyl)-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3f'), (3f:3f' = 1:1): pale yellow oil, isolated yield 85% (196 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 4H), 7.89 (d, *J* = 8.48 Hz, 1H), 7.85 (d, *J* = 8.79 Hz, 1H), 7.71 (d, *J* = 1.88 Hz, 1H), 7.61 (d, *J* = 7.22 Hz, 1H), 7.45 (dd, *J* = 8.95 Hz, 1.23 Hz, 1H), 7.35 (t, *J* = 7.38 Hz,

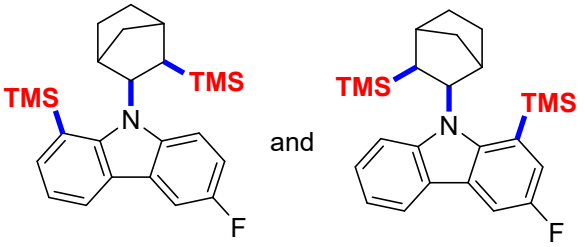
1H), 7.23-7.16 (m, 2H), 5.24 (d, *J* = 9.73 Hz, 2H), 3.34 (s, 2H), 2.37 (s, 2H), 2.33 (d, *J* = 9.89 Hz, 1H), 2.07 (s, 1H), 1.85 (d, *J* = 7.22 Hz, 4H), 1.74-1.70 (m, 2H), 1.55 (t, *J* = 11.30 Hz, 4H), 1.46 (s, 9H), 1.45 (s, 9H), 1.30-1.29 (m, 2H), 051 (s, 9H), 0.49 (s, 9H), -0.90 (s, 9H), -0.90 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.4, 142.2, 141.1, 140.4, 138.1, 133.9, 132.3, 125.4, 124.8, 124.5, 123.9, 123.2, 122.8, 120.8, 120.4, 119.8, 119.3, 118.8, 118.4, 117.0, 115.4, 113.8, 113.5, 65.2, 65.0, 45.0, 41.6, 41.6, 39.4, 38.7, 34.5, 34.5, 31.9, 31.8, 30.4, 30.3, 21.0, 1.4, 1.3, -1.5, -1.5. HRMS (ESI) m/z calcd for $C_{29}H_{44}NSi_2$+ $(M+H)^+$ 462.3007, found 462.3010.



6-phenyl-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3g) and 3-phenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3g'), (3g:3g' = 1:1): pale yellow oil, isolated yield 71% (171 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 5.51 Hz, 1.52 Hz, 1H), 8.18 (d, *J* = 7.61 Hz, 1H), 8.06-7.96 (m, 1H), 7.84-7.79 (m, 2H), 7.74-7.71 (m, 1H), 7.56 (t, *J* = 7.58 Hz, 2H), 7.48-7.39 (m, 2H), 7.33-7.28 (m, 1H), 5.34 (d, *J* = 9.65 Hz, 1H), 3.44 (s, 1H), 2.46-2.41 (m, 2H), 2.13 (s, 1H), 1.93 (d, *J* = 5.86 Hz, 1H),1.82-1.78 (m, 1H), 1.64-1.61 (m, 2H), 1.52 (t, *J* = 8.27 Hz, 1H), 0.59 (d, *J* = 13.09 Hz, 9H), -0.80 (d, *J* = 2.24 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.7, 142.1, 141.8, 140.5, 139.4, 134.5, 133.8, 132.2, 131.5, 128.7, 127.1, 127.1, 126.4, 126.3, 125.6, 125.2, 125.0, 124.2, 123.8, 121.0, 120.9, 120.8, 119.6, 119.3, 118.8, 117.8, 114.1, 114.0, 65.3, 65.2, 44.9, 44.9, 41.6, 39.5, 38.8, 38.8, 31.8, 30.4, 30.4, 1.4, 1.4, -1.4. HRMS (ESI) m/z calcd for $C_{31}H_{40}NSi_2$+ $(M+H)^+$ 482.2694, found 482.2697.

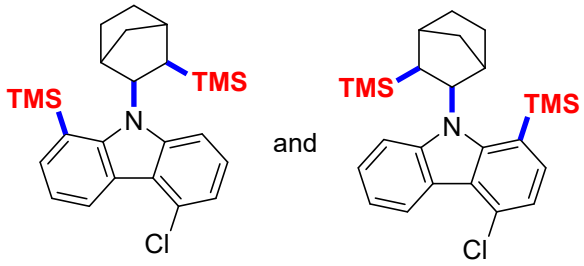


6-chloro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3h) and 3-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3h'), (3h:3h' = 2:1): pale yellow oil, isolated yield 74% (162 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.00 (m, 3H), 7.91 (d, *J* = 8.59 Hz, 1H), 7.83 (d, *J* = 9.09 Hz, 0.5H), 7.66-7.65 (m, 0.5H), 7.53 (d, *J* = 1.85 Hz, 1H), 7.40 (t, *J* = 7.41 Hz, 1H), 7.32 (dd, *J* = 8.92 Hz, 1.85 Hz, 0.5H), 7.24-7.17 (m, 1.5H), 5.25-5.18 (m, 1.5H), 3.33-3.29 (m, 1.5H), 2.38 (s, 1.5H), 2.31 (d, *J* = 9.60 Hz, 1H), 2.25 (d, *J* = 9.60 Hz, 0.5H), 1.86-1.84 (m, 2.5H), 1.71-1.69 (m, 1.5H), 1.58-1.55 (m, 2H), 1.52-1.50 (m, 1.5H), 1.45-1.42 (m, 1.5H), 0.50-0.49 (m, 13.5H), -0.88--0.89 (m, 13.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.3, 140.5, 138.2, 135.0, 133.7, 126.4, 125.5, 125.0, 124.7, 124.7, 124.5, 124.1, 123.0, 122.7, 121.2, 121.0, 120.3, 119.8, 119.5, 119.2, 119.1, 114.8, 114.1, 65.4, 65.2, 44.8, 44.8, 41.6, 41.5, 39.5, 39.4, 38.7, 31.7, 30.4, 30.3, 1.4, 1.2, -1.4, -1.4. HRMS (ESI) m/z calcd for $C_{25}H_{35}ClNSi_2$+ $(M+H)^+$ 440.1991, found 440.1994.



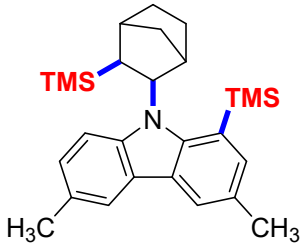
6-fluoro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3i) and 3-fluoro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3i'), (3i:3i' = 2:1): pale yellow oil, isolated yield 56% (118 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.95 Hz, 1.5H), 7.90 (d, *J* = 8.68 Hz, 1H), 7.83 (dd, *J* = 9.40 Hz, 4.34 Hz, 0.5H), 7.71-7.68 (m, 1H), 7.67-7.63 (m, 1H), 7.40-7.36 (m, 1H), 7.34 (dd, *J* = 10.19 Hz, 2.68 Hz, 1H), 7.22-7.19 (m, 1H), 7.17-7.15 (m, 0.5H), 7.11 (td, *J* = 9.07 Hz, 2.60 Hz, 0.5H), 5.23 (d, *J* = 9.74 Hz, 0.5H), 5.18 (d, *J* = 9.67 Hz, 1H), 3.33 (s, 1H), 3.29 (s, 0.5H),

2.36 (s, 1.5H), 2.30 (d, J = 9.89 Hz, 1H), 2.25 (d, J = 9.62 Hz, 0.5H), 2.05 (s, 1H), 1.86-1.83 (m, 2.5H), 1.71-1.69 (m, 1H), 1.57-1.54 (m, 2H), 1.51-1.48 (m, 1.5H), 1.44-1.42 (m, 1H), 0.49-0.48 (m, 13.5H), -0.90--0.91 (m, 13.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 158.0, 156.1, 155.6, 149.0, 144.4, 140.9, 136.4, 134.9, 125.9 (d, J = 9.65 Hz), 125.4, 124.6 (d, J = 3.79 Hz), 124.4 (d, J = 8.52 Hz), 123.2 (d, J = 3.79 Hz), 122.8 (d, J = 3.79 Hz), 121.4, 121.2 (d, J = 3.79 Hz), 121.0, 119.8, 119.1, 118.7, 114.6 (d, J = 8.26 Hz), 114.1, 112.4 (d, J = 24.77 Hz), 106.2 (d, J = 22.52 Hz), 105.0 (d, J = 23.27 Hz), 65.5, 65.2, 44.9, 44.8, 41.6, 41.6, 39.4, 39.4, 38.7, 31.8, 31.7, 30.4, 30.3, 1.3, 1.2, -1.4, -1.5. ^{19}F{^{1}H} NMR (400 MHz, $CDCl_3$) δ -124.85 (td, J = 8.43, 4.16 Hz), -124.12 (t, J = 9.68 Hz). HRMS (ESI) m/z calcd for $C_{25}H_{35}FNSi_2$+ $(M+H)^+$ 424.2287, found 424.2290.

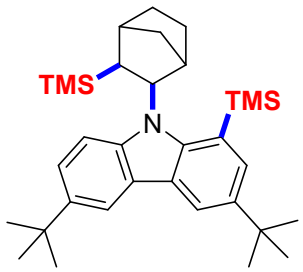


5-chloro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3j) and 4-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3j'), (3j:3j' = 2:1): pale yellow oil, isolated yield 45% (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73-8.70 (m, 1.5H), 7.95 (d, J = 8.55 Hz, 1H), 7.86 (d, J = 8.32 Hz, 0.5H), 7.67 (d, J = 7.22 Hz, 0.5H), 7.50 (d, J = 7.80 Hz, 1H), 7.42 (t, J = 8.27 Hz, 1H), 7.30-7.27 (m, 1H), 7.24 (d, J = 0.93 Hz, 0.5H), 7.21 (t, J = 7.69 Hz, 1H), 7.16 (d, J = 7.92 Hz, 1H), 5.26 (d, J = 9.90 Hz, 0.5H), 5.22 (d, J = 9.78 Hz, 1H), 3.35 (s, 1H), 3.33 (s, 0.5H), 2.36 (s, 1.5H), 2.30 (d, J = 10.02 Hz, 1H), 1.85-1.83 (m, 2.5H), 1.71-1.69 (m, 1H), 1.58-1.55 (m, 2.5H), 1.51 (s, 0.5H), 1.49-1.46 (m, 2H), 1.42-1.40 (m, 1H), 0.48 (s, 4.5H), 0.47 (s, 9H), -0.93--0.93 (m, 13.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.3, 141.4, 140.3, 134.8, 134.2, 130.2, 128.3, 125.3, 124.7, 124.2, 124.1, 123.0, 122.8, 121.8, 120.6, 120.4, 120.4, 119.8, 119.6, 119.0, 118.9, 113.7, 112.1, 65.7, 65.5, 44.8, 44.7, 41.6, 39.5, 38.8, 38.7, 31.7, 30.3, 1.3, 1.3, -1.5, -1.5. HRMS (ESI) m/z calcd for

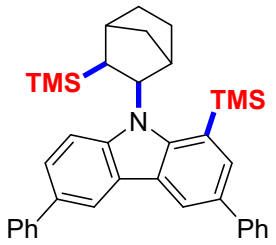
$C_{25}H_{35}ClNSi_2$+ $(M+H)^+$ 440.1991, found 440.1994.



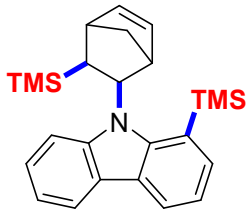
3,6-dimethyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3k): pale yellow oil, isolated yield 78% (169 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.76 (d, *J* = 8.55 Hz, 1H), 7.41 (d, *J* = 0.95 Hz, 1H), 7.16 (d, *J* = 8.79 Hz, 1H), 5.18 (d, *J* = 9.74 Hz, 1H), 3.29 (s, 1H), 2.53 (s, 1H), 2.50 (d, *J* = 5.46 Hz, 6H), 2.36-2.31 (m, 2H), 1.84-1.82 (m, 1H), 1.72-1.70 (m, 1H), 1.55-1.49 (m, 2H), 1.45-1.41 (m, 1H), 0.48 (s, 9H), -0.87 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 138.4, 135.4, 128.1, 127.2, 126.0, 125.1, 123.6, 120.9, 120.1, 119.4, 113.6, 65.0, 44.8, 41.6, 39.4, 38.7, 31.8, 30.4, 21.2, 1.4, -1.4. HRMS (ESI) m/z calcd for $C_{27}H_{40}NSi_2$+ $(M+H)^+$ 434.2694, found 434.2697.



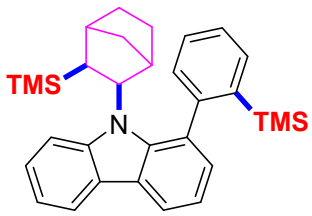
3,6-di-tert-butyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3k): pale yellow oil, isolated yield 91% (235 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 5.21 Hz, 2.00 Hz, 2H), 7.81 (d, *J* = 8.82 Hz, 1H), 7.68 (d, *J* = 2.00 Hz, 1H), 7.42 (dd, *J* = 8.82 Hz, 2.00 Hz, 1H), 5.21 (d, *J* = 9.62 Hz, 1H), 3.33 (s, 1H), 2.37-2.33 (m, 2H), 2.36-2.31 (m, 2H), 1.86-1.84 (m, 2H), 1.74-1.69 (m, 1H), 1.56-1.54 (m, 2H), 1.51 (d, *J* = 1.60 Hz, 1H), 1.47 (d, *J* = 4.01 Hz, 18H), 0.51 (s, 9H), -0.90 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 141.8, 140.8, 138.5, 132.0, 125.1, 123.5, 122.4, 119.7, 116.8, 115.2, 113.4, 65.1, 45.1, 41.6, 39.4, 38.7, 34.6, 34.5, 31.9 (d, *J* = 2.84 Hz), 30.4, 1.4, -1.5. HRMS (ESI) m/z calcd for $C_{33}H_{52}NSi_2$+ $(M+H)^+$ 518.3633, found 518.3637.



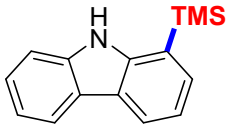
3,6-diphenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3m): pale yellow oil, isolated yield 54% (150 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 5.64 Hz, 1.76 Hz, 2H), 7.98 (d, *J* = 8.88 Hz, 1H), 7.90 (d, *J* = 1.94 Hz, 1H), 7.78-7.73 (m, 4H), 7.66 (dd, *J* = 8.70 Hz, 1.85 Hz, 1H), 7.48 (t, *J* = 7.49 Hz, 4H), 7.34 (t, *J* = 7.33 Hz, 2H), 5.28 (d, *J* = 9.72 Hz, 1H), 3.37 (s, 1H), 2.40-2.36 (m, 2H), 2.05 (s, 2H), 1.89-1.87 (m, 2H), 1.76-1.72 (m, 1H), 1.48-1.44 (m, 1H), 0.54 (s, 9H), -0.85 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 142.0, 141.7, 139.9, 134.0, 132.4, 131.7, 128.7, 127.1, 126.5, 126.4, 125.7, 124.3, 124.3, 121.2, 119.3, 117.8, 114.2, 65.3, 44.9, 41.6, 39.5, 38.8, 31.8, 30.4, 1.4, -1.3. HRMS (ESI) m/z calcd for $C_{37}H_{44}NSi_2$+ $(M+H)^+$ 558.3007, found 558.3010.



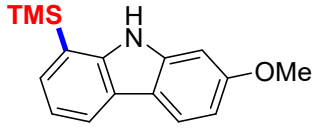
1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]hept-5-en-2-yl)-9*H*-carbazole (3n): pale yellow oil, isolated yield 60% (121 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.90 (d, *J* = 8.11 Hz, 1H), 7.71 (dd, *J* = 7.16 Hz, 1.05 Hz, 1H), 7.47-7.43 (m, 1H), 7.32 (d, *J* = 7.44 Hz, 1H), 7.30-7.28 (m, 1H), 6.56-6.54 (m, 1H), 6.42-6.40 (m, 1H), 5.27 (d, *J* = 9.30 Hz, 1H), 3.91 (s, 1H), 3.03 (s, 1H), 2.50 (d, *J* = 8.49 Hz, 1H), 2.00 (d, *J* = 8.36 Hz, 1H), 1.41 (dd, *J* = 9.30 Hz, 2.29 Hz, 1H), 0.50 (s, 9H), -0.78 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 139.9, 139.5, 135.7, 134.3, 125.3, 124.9, 123.6, 121.0, 120.8, 119.7, 119.2, 118.8, 113.5, 63.9, 49.0, 46.8, 43.4, 32.5, 1.3, -1.6. HRMS (ESI) m/z calcd for $C_{25}H_{34}NSi_2$+ $(M+H)^+$ 404.2224, found 404.2227.



9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-1-(2-(trimethylsilyl)phenyl)-9*H*-carbazole (3o): pale yellow oil, isolated yield 67% (161 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.06 Hz, 1H), 8.02 (d, *J* = 7.74 Hz, 1H), 7.60-7.58 (m, 1H), 7.51 (s, 1H), 7.44 (d, *J* = 7.42 Hz, 1H), 7.36 (t, *J* = 7.42 Hz, 1H), 7.30 (d, *J* = 7.74 Hz, 1H), 7.24-7.19 (m, 3H), 7.07-7.05 (m, 1H), 3.54 (d, *J* = 10.96 Hz, 1H), 2.00 (d, *J* = 3.55 Hz, 1H), 1.94 (s, 1H), 1.38 (s, 1H), 1.35 (s, 1H), 1.10 (s, 1H), 0.86 (d, *J* = 8.71 Hz, 2H), 0.65 (d, *J* = 10.00 Hz, 1H), 0.44 (s, 9H), 0.31 (d, *J* = 10.00 Hz, 1H), -0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 142.9, 139.3, 139.2, 135.8, 135.4, 134.8, 128.3, 126.7, 125.6, 125.4, 123.7, 122.3, 120.4, 119.3, 119.2, 118.9, 110.7, 54.6, 44.0, 40.0, 39.0, 38.6, 33.1, 32.4, 2.3, -2.2. HRMS (ESI) m/z calcd for $C_{31}H_{40}NSi_2$+ $(M+H)^+$ 482.2694, found 482.2697.

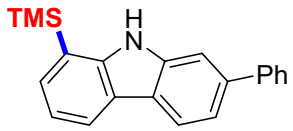


1-(trimethylsilyl)-9*H*-carbazole (4a): pale yellow oil, isolated yield 72% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.11 (m, 2H), 8.08 (s, 1H), 7.57 (d, *J* = 7.06 Hz, 1H), 7.51 (d, *J* = 8.07 Hz, 1H), 7.46 (t, *J* = 7.06 Hz, 1H), 7.31-7.28 (m, 2H), 0.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 139.3, 131.6, 125.7, 123.1, 122.1, 121.4, 120.2, 120.2, 119.4, 119.3, 110.5, -0.5. HRMS (ESI) m/z calcd for $C_{15}H_{18}NSi$+ $(M+H)^+$ 240.1203, found 240.1206.

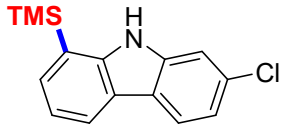


7-methoxy-1-(trimethylsilyl)-9*H*-carbazole (4b): pale yellow oil, isolated yield 75% (101 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.75 Hz, 1H), 8.03 (s, 1H), 7.99 (d, *J* = 8.68 Hz, 1H), 7.50 (dd, *J* = 7.08 Hz, 0.93 Hz, 1H), 7.31-7.28 (m, 1H), 7.02 (d,

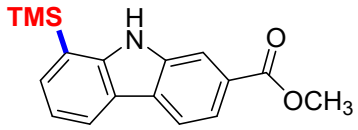
J = 2.14 Hz, 1H), 6.91 (dd, *J* = 8.55 Hz, 2.27 Hz, 1H), 3.96 (s, 3H), 0.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.7, 140.6, 130.2, 122.3, 121.0, 120.5, 119.9, 119.4, 117.0, 108.3, 94.6, 55.6, -0.5. HRMS (ESI) m/z calcd for $C_{16}H_{20}NOSi^+$ $(M+H)^+$ 270.1309, found 270.1312.



7-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4c): pale yellow oil, isolated yield 66% (104 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.03 Hz, 3H), 7.64-7.61 (m, 3H), 7.46-7.44 (m, 1H), 7.42-7.37 (m, 3H), 7.29 (d, *J* = 7.34 Hz, 1H), 7.20-7.15 (m, 1H), 0.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.9, 139.9, 139.1, 131.6, 128.7, 127.4, 127.0, 122.4, 121.9, 121.4, 120.5, 120.2, 119.5, 119.2, 109.1, -0.5. HRMS (ESI) m/z calcd for $C_{21}H_{22}NSi^+$ $(M+H)^+$ 316.1516, found 316.1519.

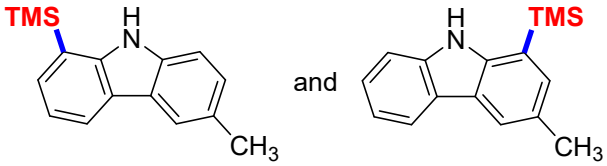


7-chloro-1-(trimethylsilyl)-9*H*-carbazole (4d): pale yellow oil, isolated yield 70% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.45 Hz, 2H), 7.93 (d, *J* = 8.62 Hz, 1H), 7.51 (dd, *J* = 7.07 Hz, 0.93 Hz, 1H), 7.44 (d, *J* = 1.73 Hz, 1H), 7.24-7.22 (m, 1H), 7.17 (dd, *J* = 8.26 Hz, 1.73 Hz, 1H), 0.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.7, 131.9, 131.3, 121.7, 121.6, 121.3, 121.0, 120.6, 120.0, 119.8, 110.7, -0.5. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClNSi^+$ $(M+H)^+$ 274.0813, found 274.0816.

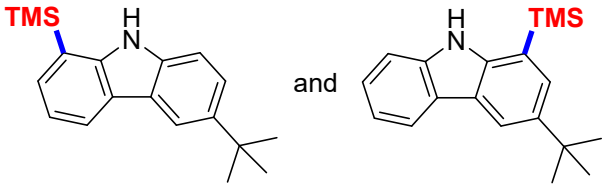


methyl 8-(trimethylsilyl)-9*H*-carbazole-2-carboxylate (4e): pale yellow oil, isolated yield 57% (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 8.14 (d, *J* = 7.86 Hz, 1H), 8.11 (d, *J* = 8.19 Hz, 1H), 7.94 (dd, *J* = 8.19 Hz, 1.31 Hz, 1H), 7.60-7.58 (m, 1H), 7.29 (t, *J* = 7.20 Hz, 1H), 3.97 (s, 3H), 0.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 144.9, 138.6, 133.0, 127.1, 126.9, 122.1, 121.4, 120.9, 120.7, 119.9, 119.8, 112.5, 52.1, -0.5. HRMS (ESI) m/z calcd for $C_{17}H_{20}NO_2Si^+$ $(M+H)^+$ 298.1258, found

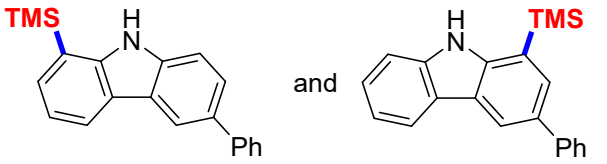
298.1261.



6-methyl-1-(trimethylsilyl)-9*H*-carbazole (4f) and 3-methyl-1-(trimethylsilyl)-9*H*-carbazole (4f'), (4f:4f' = 1:1): pale yellow oil, isolated yield 83% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 8.73 Hz, 2H), 8.02 (s, 2H), 7.95 (d, *J* = 11.96 Hz, 2H), 7.57 (dd, *J* = 7.11 Hz, 0.97 Hz, 1H), 7.52-7.46 (m, 2H), 7.44-7.40 (m, 2H), 7.31-7.28 (m, 3H), 2.60 (m, 6H), 0.54 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.0, 139.6, 137.5, 132.9, 131.4, 128.7, 128.3, 127.1, 125.5, 123.3, 123.0, 122.4, 122.0, 121.4, 121.3, 120.2, 120.1, 119.9, 119.2, 119.1, 110.5, 110.2, 21.4, -0.5, -0.5. HRMS (ESI) m/z calcd for $C_{16}H_{20}NSi^+$ $(M+H)^+$ 254.1360, found 254.1363.

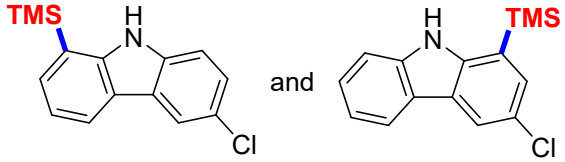


6-(*tert*-butyl)-1-(trimethylsilyl)-9*H*-carbazole (4g) and 3-(*tert*-butyl)-1-(trimethylsilyl)-9*H*-carbazole (4g'), (4g:4g' = 1:1): pale yellow oil, isolated yield 87% (128 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.09 (m, 4H), 7.96 (s, 2H), 7.60 (d, *J* = 1.70 Hz, 2H), 7.45-7.43 (m, 2H), 7.41-7.38 (m, 2H), 7.24-7.21 (m, 2H), 1.47 (s, 18H), 0.49 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.9, 141.8, 139.8, 137.4, 131.3, 129.4, 125.4, 123.7, 123.4, 122.8, 122.3, 121.9, 121.2, 120.1, 119.5, 119.2, 119.0, 117.6, 116.3, 110.5, 110.0, 34.7, 32.0, -0.4. HRMS (ESI) m/z calcd for $C_{19}H_{26}NSi^+$ $(M+H)^+$ 296.1829, found 296.1832.

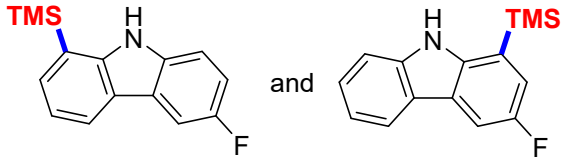


6-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4h) and 3-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4h'), (4h:4h' = 1:1): pale yellow oil, isolated yield 90% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.12 Hz, 2H), 8.21-8.15 (m, 4H), 7.81-7.72

(m, 6H), 7.60-7.58 (m, 2H), 7.55-7.52 (m, 4H), 7.50-7.47 (m, 2H), 7.42-7.37 (m, 2H), 7.34-7.29 (m, 2H), 0.56 (d, J = 11.07 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.2, 142.4, 142.1, 139.8, 138.8, 132.9, 132.7, 131.8, 131.2, 128.7, 127.4, 127.3, 126.4, 125.9, 125.3, 123.6, 123.2, 122.7, 122.2, 121.4, 120.5, 120.4, 120.3, 120.0, 119.6, 119.4, 118.7, 110.8, 110.7, -0.5, -0.5. HRMS (ESI) m/z calcd for $C_{21}H_{22}NSi^+$ $(M+H)^+$ 316.1516, found 316.1519.

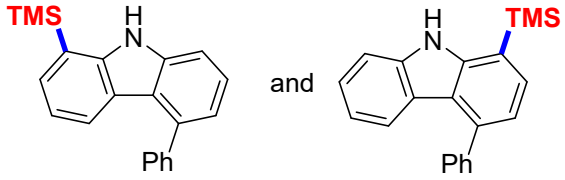


6-chloro-1-(trimethylsilyl)-9*H*-carbazole (4i) and 3-chloro-1-(trimethylsilyl)-9*H*-carbazole (4i'), (4i:4i' = 4:1): pale yellow oil, isolated yield 78% (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 3.25H), 8.05 (s, 0.5H), 7.61 (dd, J = 6.93 Hz, 0.88 Hz, 0.5H), 7.51-7.49 (m, 2H), 7.41 (d, J = 1.18 Hz, 1H), 7.33-7.30 (m, 1H), 7.30-7.28 (m, 0.5H), 0.54 (d, J = 1.47 Hz, 11.25H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.8, 139.8, 137.5, 132.3, 131.1, 126.4, 125.7, 125.1, 124.8, 124.3, 123.6, 122.4, 122.3, 121.5, 121.3, 120.8, 120.6, 120.4, 119.9, 119.8, 119.6, 111.5, 110.8, -0.5, -0.7. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClNSi^+$ $(M+H)^+$ 274.0813, found 274.0816.

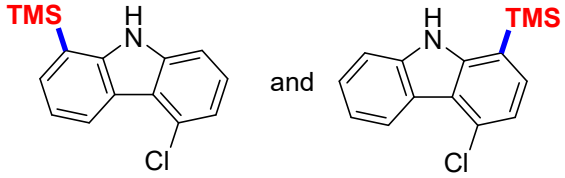


6-fluoro-1-(trimethylsilyl)-9*H*-carbazole (4j) and 3-fluoro-1-(trimethylsilyl)-9*H*-carbazole (4j'), (4j:4j' = 1:1): pale yellow oil, isolated yield 65% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 3H), 7.98 (s, 1H), 7.73 (d, J = 2.36 Hz, 1H), 7.71 (d, J = 2.36 Hz, 1H), 7.54 (d, J = 7.07 Hz, 1H), 7.47-7.45 (m, 1H), 7.43-7.41 (m, 1H), 7.37 (dd, J = 8.75 Hz, 4.21 Hz, 1H), 7.25-7.24 (m, 2H), 7.22-7.20 (m, 1H), 7.15 (td, J = 9.09 Hz, 2.52 Hz, 1H), 0.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J = 3.75 Hz), 156.3, 144.7, 140.3, 139.8, 135.6, 132.2, 126.3, 123.7 (d, J = 9.38 Hz), 123.1 (d, J = 7.51 Hz), 122.9 (d, J = 3.75 Hz), 122.1 (d, J = 5.63 Hz), 121.9 (d, J = 3.75 Hz), 121.6, 120.6, 120.5, 119.4, 119.3, 118.6 (d, J = 22.52 Hz), 113.5 (d, J = 24.39 Hz), 111.1 (d, J = 9.38 Hz), 110.8, 106.8 (d, J = 22.52 Hz), 105.8 (d, J = 24.39

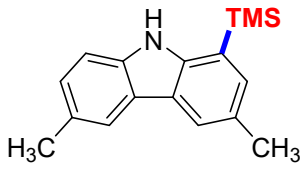
Hz), -0.5, -0.7. $^{19}F\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) δ -124.36 (td, *J* = 9.33, 4.37 Hz), -125.12 (t, *J* = 8.86 Hz). HRMS (ESI) m/z calcd for $C_{15}H_{17}FNSi^+$ $(M+H)^+$ 258.1109, found 258.1112.



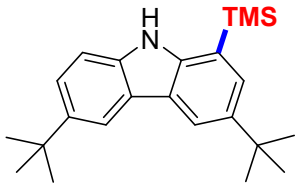
5-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4k) and 4-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4k'), (4k:4k' = 1:1): pale yellow oil, isolated yield 61% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.66-7.63 (m, 4H), 7.58 (d, *J* = 7.28 Hz, 1H), 7.56-7.56 (m, 1H), 7.54 (d, *J* = 2.01 Hz, 2H), 7.52-7.45 (m, 9H), 7.39-7.35 (m, 1H), 7.15 (d, *J* = 7.28 Hz, 1H), 7.12 (dd, *J* = 6.20 Hz, 2.32 Hz, 1H), 7.03-6.97 (m, 2H), 0.54 (s, 9H), 0.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.8, 141.3, 141.2, 139.6, 139.5, 138.8, 137.7, 131.4, 129.2, 129.1, 128.4, 127.5, 127.4, 125.5, 125.5, 123.5, 122.7, 122.5, 121.8, 121.1, 121.0, 120.5, 119.9, 119.6, 119.0, 118.9, 118.8, 110.3, 109.5, -0.4, -0.5. HRMS (ESI) m/z calcd for $C_{21}H_{22}NSi^+$ $(M+H)^+$ 316.1516, found 316.1519.



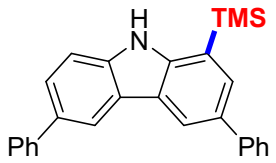
5-chloro-1-(trimethylsilyl)-9*H*-carbazole (4l) and 4-chloro-1-(trimethylsilyl)-9*H*-carbazole (4l'), (4l:4l' = 1:1): pale yellow oil, isolated yield 50% (68 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.92 Hz, 1H), 8.66 (d, *J* = 8.10 Hz, 1H), 8.18 (s, 2H), 7.63 (dd, *J* = 7.22 Hz, 1.06 Hz, 1H), 7.54-7.52 (m, 2H), 7.46 (d, *J* = 7.57 Hz, 1H), 7.44-7.41 (m, 1H), 7.39-7.37 (m, 1H), 7.36-7.32 (m, 2H), 7.30-7.27 (m, 2H), 0.54 (s, 9H), 0.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.6, 140.3, 139.3, 132.2, 131.9, 130.2, 128.7, 126.2, 126.0, 124.2, 123.2, 122.1, 121.2, 120.4, 120.3, 120.2, 120.0, 119.8, 119.8, 119.5, 118.5, 110.3, 108.9, -0.5, -0.5. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClNSi^+$ $(M+H)^+$ 274.0813, found 274.0816.



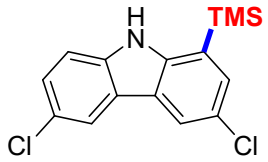
3,6-dimethyl-1-(trimethylsilyl)-9*H*-carbazole (4m): pale yellow oil, isolated yield 86% (115 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 3H), 7.38-7.36 (m, 2H), 7.27-7.25 (m, 1H), 2.57 (d, *J* = 2.57 Hz, 6H), 0.51 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.9, 132.7, 128.4, 128.0, 126.9, 123.1, 122.3, 121.3, 120.1, 119.8, 110.2, 21.4, -0.5. HRMS (ESI) m/z calcd for $C_{17}H_{22}NSi^+$ $(M+H)^+$ 268.1516, found 268.1519.



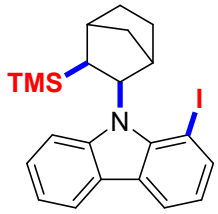
3,6-di-*tert*-butyl-1-(trimethylsilyl)-9*H*-carbazole (4n): pale yellow oil, isolated yield 93% (163 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.76 Hz, 1H), 8.13 (d, *J* = 1.41 Hz, 1H), 7.90 (s, 1H), 7.61 (d, *J* = 1.86 Hz, 1H), 7.51 (dd, *J* = 8.40 Hz, 1.82 Hz, 1H), 7.41 (d, *J* = 8.52 Hz, 1H), 1.52 (d, *J* = 4.66 Hz, 18H), 0.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.2, 141.6, 137.9, 129.0, 123.4, 123.1, 122.2, 119.3, 117.5, 116.1, 109.9, 34.7 (d, *J* = 1.85 Hz), 32.0 (d, *J* = 2.27 Hz), -0.5. HRMS (ESI) m/z calcd for $C_{23}H_{34}NSi^+$ $(M+H)^+$ 352.2355, found 352.2358.



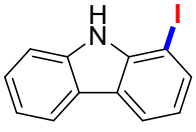
3,6-diphenyl-1-(trimethylsilyl)-9*H*-carbazole (4o): pale yellow oil, isolated yield 75% (147 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 2H), 8.17 (s, 1H), 7.81 (d, *J* = 1.70 Hz, 1H), 7.78-7.73 (m, 5H), 7.58 (d, *J* = 8.49 Hz, 1H), 7.55-7.50 (m, 4H), 7.41-7.37 (m, 2H), 0.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.3, 142.0, 139.2, 133.0, 132.8, 131.4, 128.7, 127.4, 127.2, 126.5, 125.5, 123.8, 122.8, 120.8, 120.0, 118.8, 110.9, -0.5. HRMS (ESI) m/z calcd for $C_{27}H_{26}NSi^+$ $(M+H)^+$ 392.1829, found 392.1832.



3,6-dichloro-1-(trimethylsilyl)-9*H*-carbazole (4p): pale yellow oil, isolated yield 62% (95 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (d, *J* = 2.26 Hz, 2H), 7.44 (d, *J* = 2.03 Hz, 1H), 7.38 (d, *J* = 0.95 Hz, 2H), 0.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 138.1, 131.9, 126.5, 125.6, 125.3, 123.5, 122.9, 122.7, 121.0, 120.1, 111.8, -0.7. HRMS (ESI) m/z calcd for $C_{17}H_{22}NSi^+$ $(M+H)^+$ 308.0424, found 308.0427.



1-iodo-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (6): pale yellow oil, isolated yield 86% (197 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 8.03 (d, *J* = 7.61 Hz, 1H), 7.96 (d, *J* = 8.59 Hz, 1H), 7.43 (t, *J* = 8.31 Hz, 1H), 7.23 (t, *J* = 7.47 Hz, 1H), 6.89 (t, *J* = 7.61 Hz, 1H), 6.04 (d, *J* = 10.35 Hz, 1H), 3.21 (d, *J* = 2.80 Hz, 1H), 2.53 (d, *J* = 2.68 Hz, 1H), 2.37 (d, *J* = 9.62 Hz, 1H), 2.07-2.04 (m, 1H), 1.93-1.87 (m, 1H), 1.76-1.71 (m, 1H), 1.65 (d, *J* = 9.74 Hz, 1H), 1.62-1.59 (m, 1H), 1.56-1.52 (m, 1H), -0.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.9, 139.5, 125.8, 125.7, 122.4, 120.6, 119.9, 119.5, 119.0, 113.0, 72.8, 62.5, 47.1, 40.7, 40.6, 39.2, 31.9, 31.4, -1.0. HRMS (ESI) m/z calcd for $C_{22}H_{27}INSi^+$ $(M+H)^+$ 460.0952, found 460.0955.



1-iodo-9*H*-carbazole (7): pale yellow oil, isolated yield 91% (133 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.06-8.03 (m, 2H), 7.77 (d, *J* = 7.48 Hz, 1H), 7.52-7.45 (m, 2H), 7.30-7.26 (m, 1H), 7.02 (t, *J* = 7.48 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.6, 134.1, 126.4, 123.9, 123.5, 121.0, 120.9, 120.1, 120.0, 111.0,

75.8. HRMS (ESI) m/z calcd for $C_{12}H_9IN+$ $(M+H)^+$ 293.9774, found 293.9777.

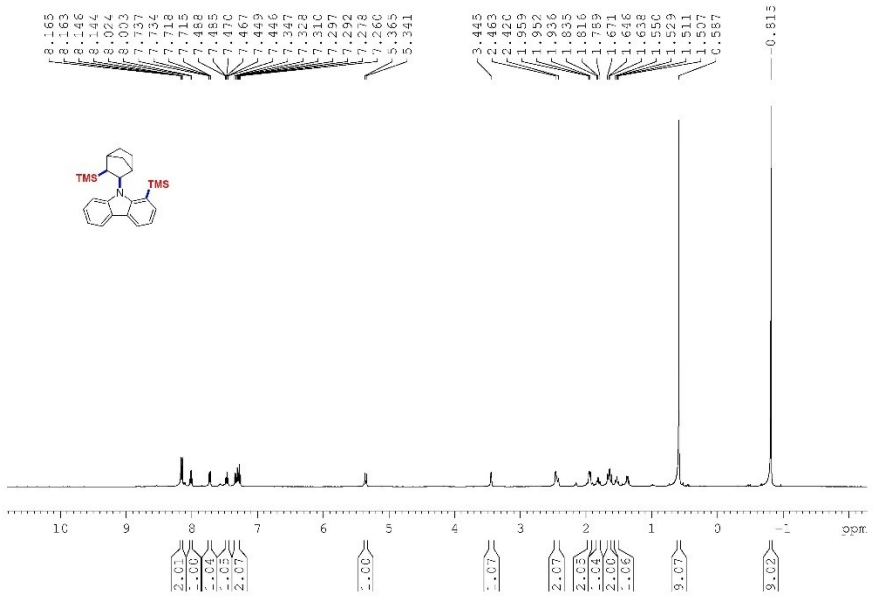
7) References

1. Li, W.; Yu, Y.; Zhang, X.; Zhang, C.; Chen, M.; Li, T. *J. Org. Chem.* **2023**, *88*, 14659–14669.

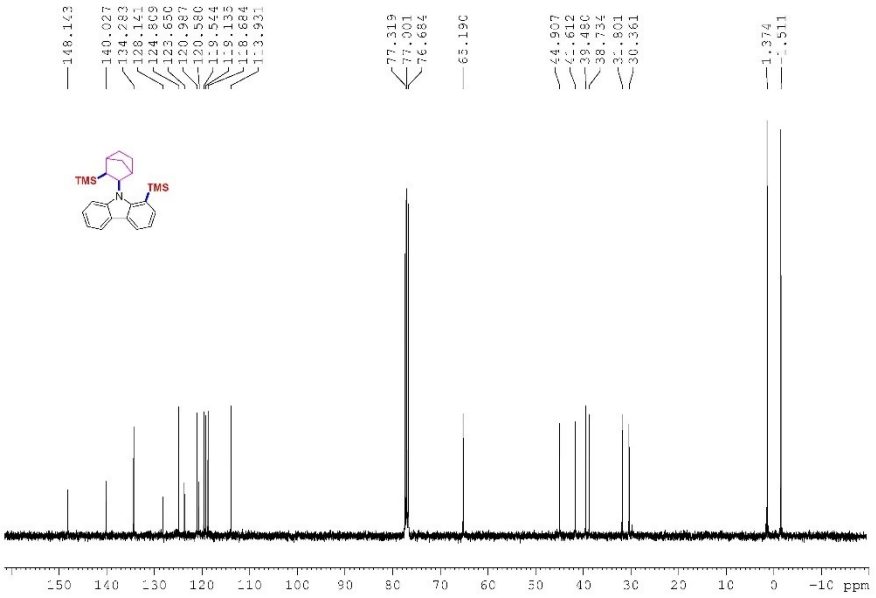
8) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds.

1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3a):

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



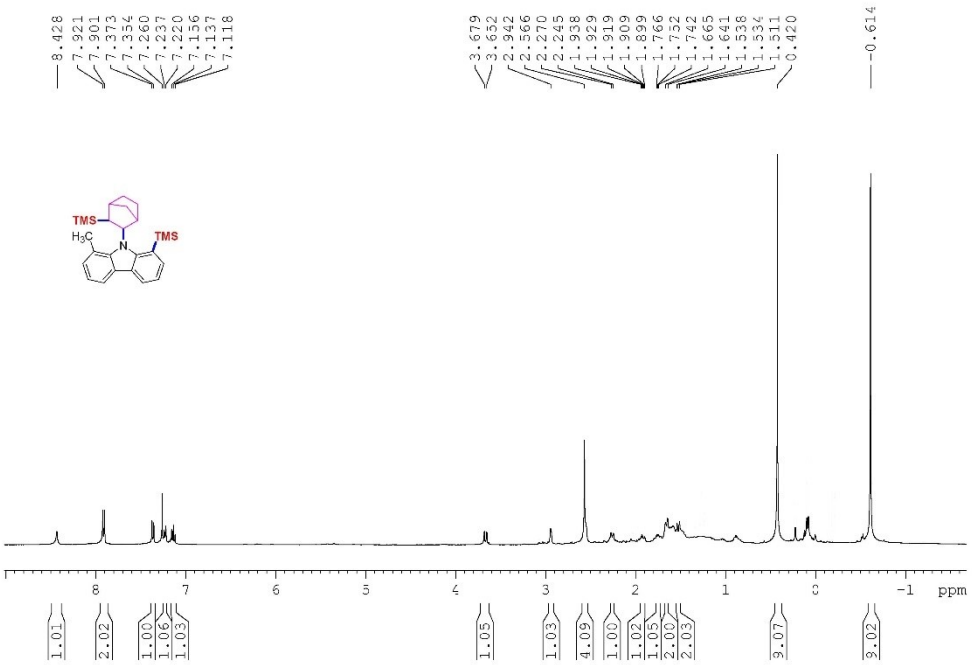
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



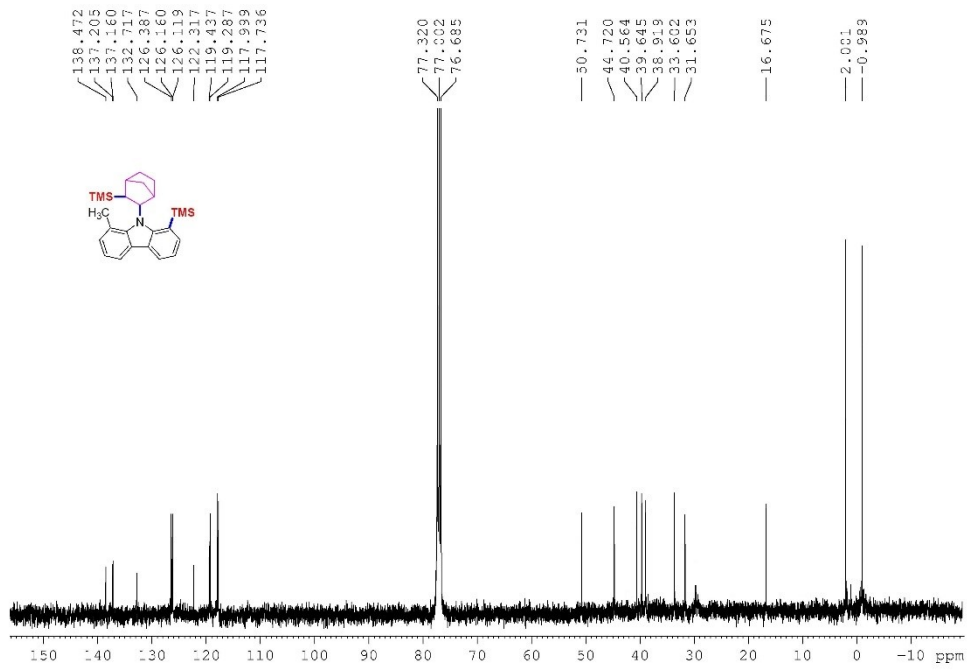
1-methyl-8-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-

yl)-9*H*-carbazole (3b):

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



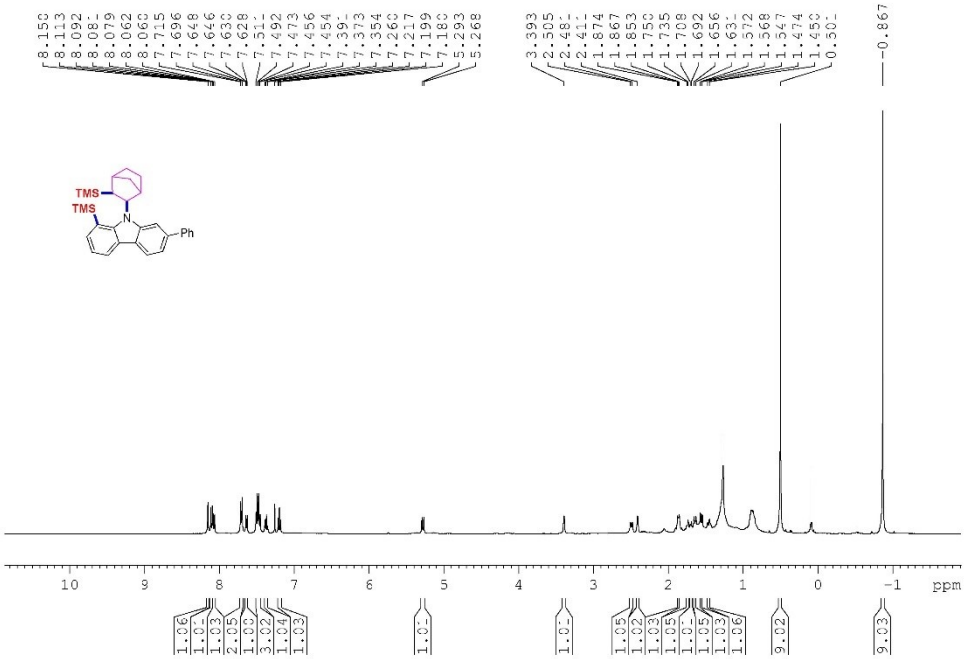
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



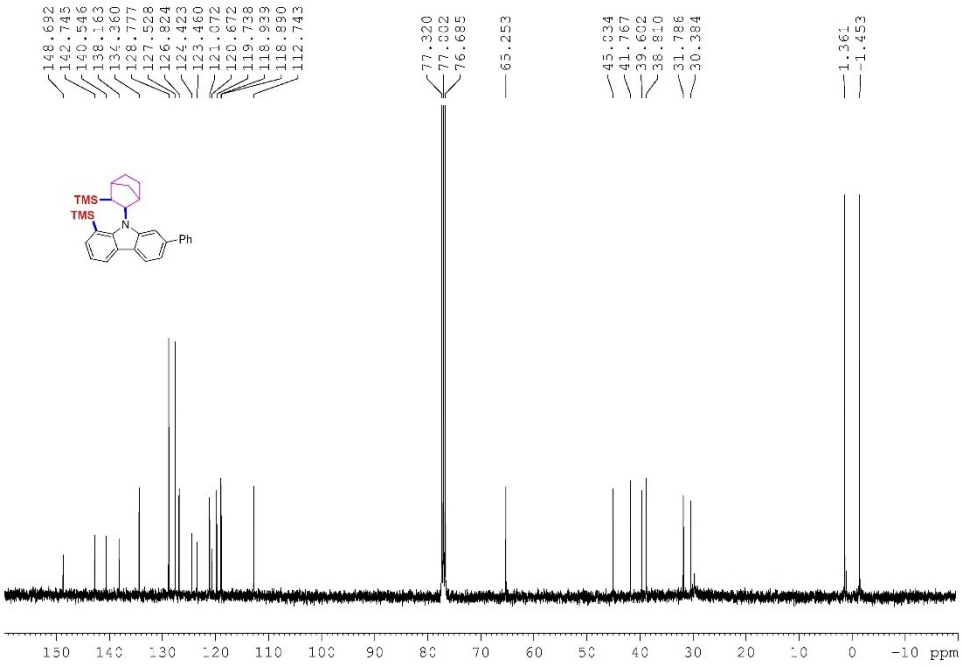
7-phenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-

yl)-9*H*-carbazole (3c):

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



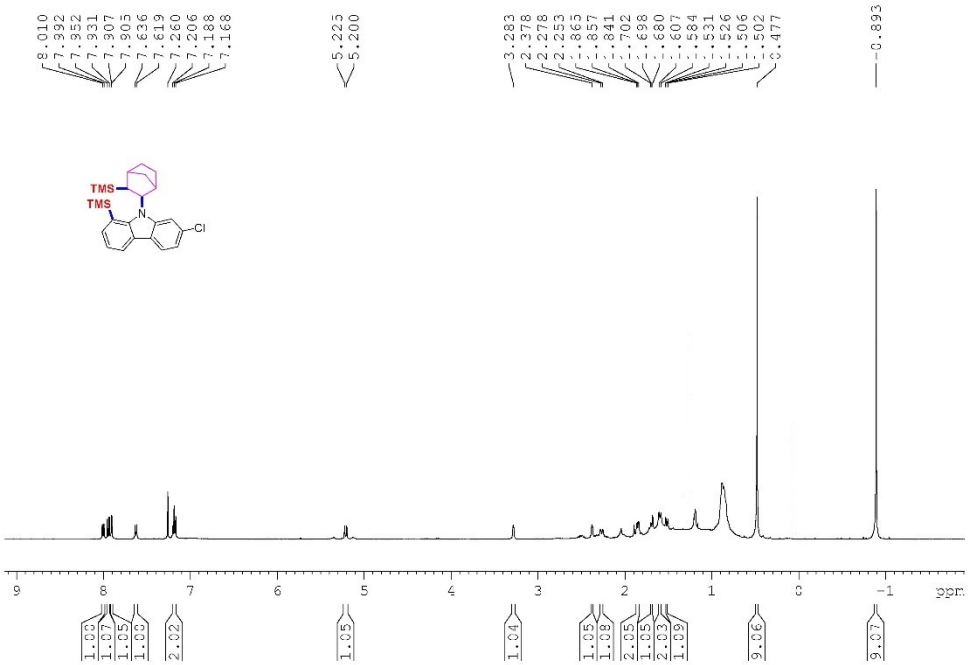
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



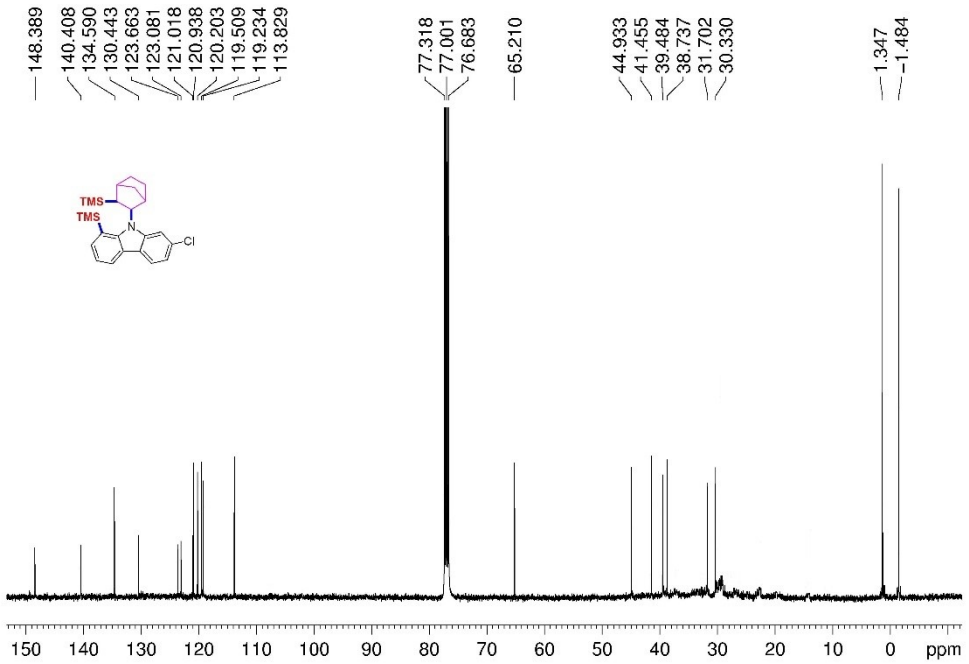
7-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-

9*H*-carbazole (3d):

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



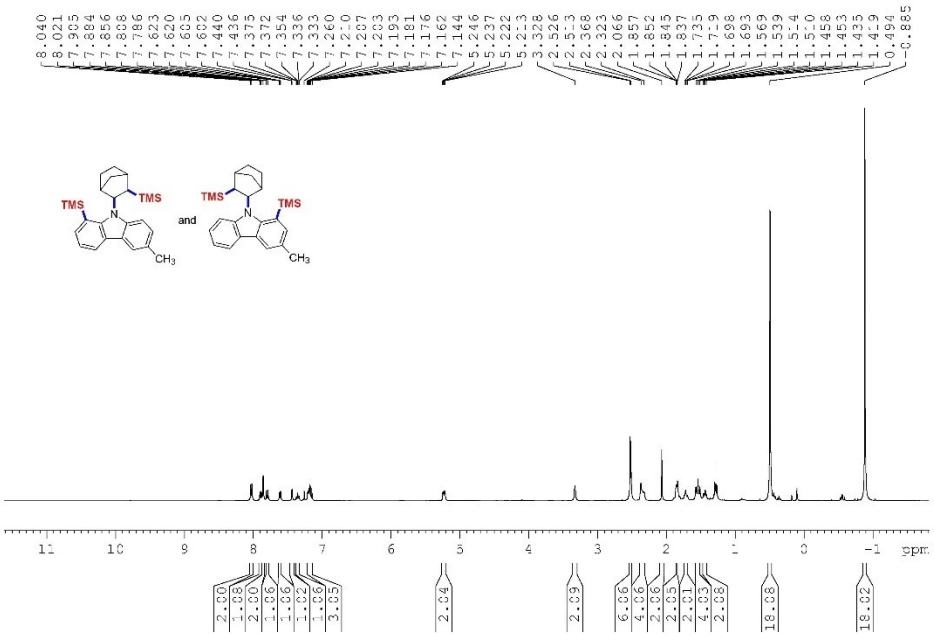
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



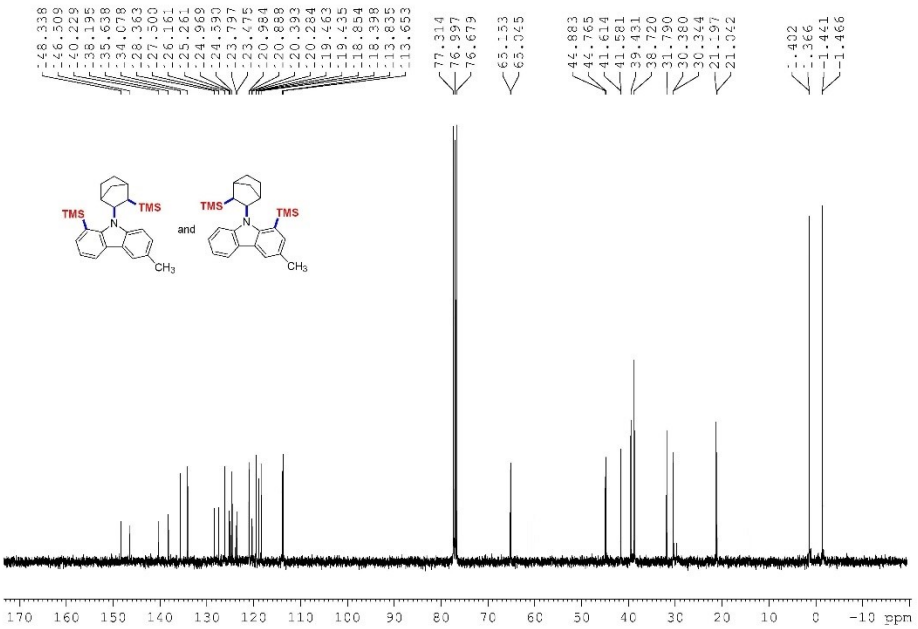
6-methyl-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-

yl)-9*H*-carbazole (3e) and 3-methyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3e'), (3e:3e' = 1:1):

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



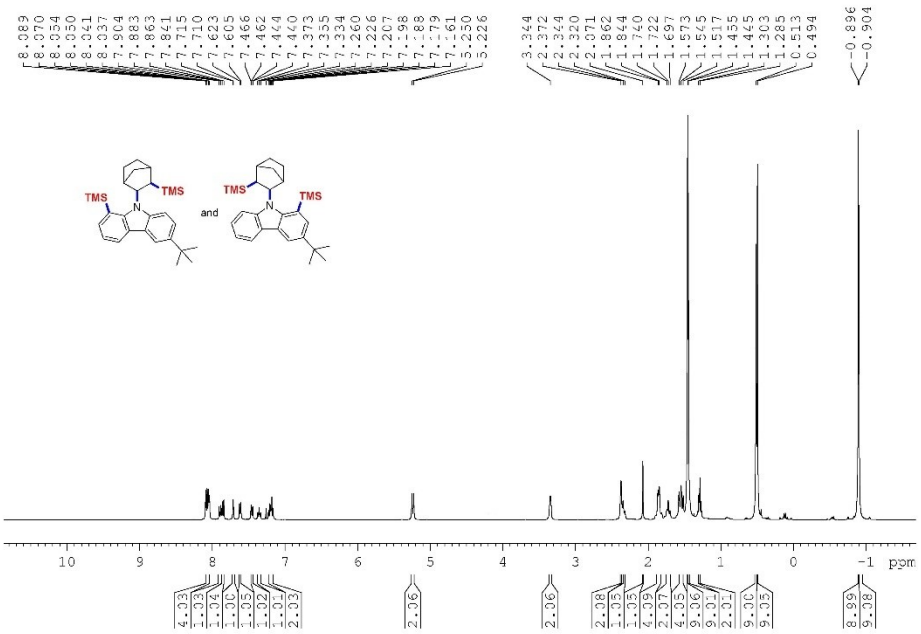
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



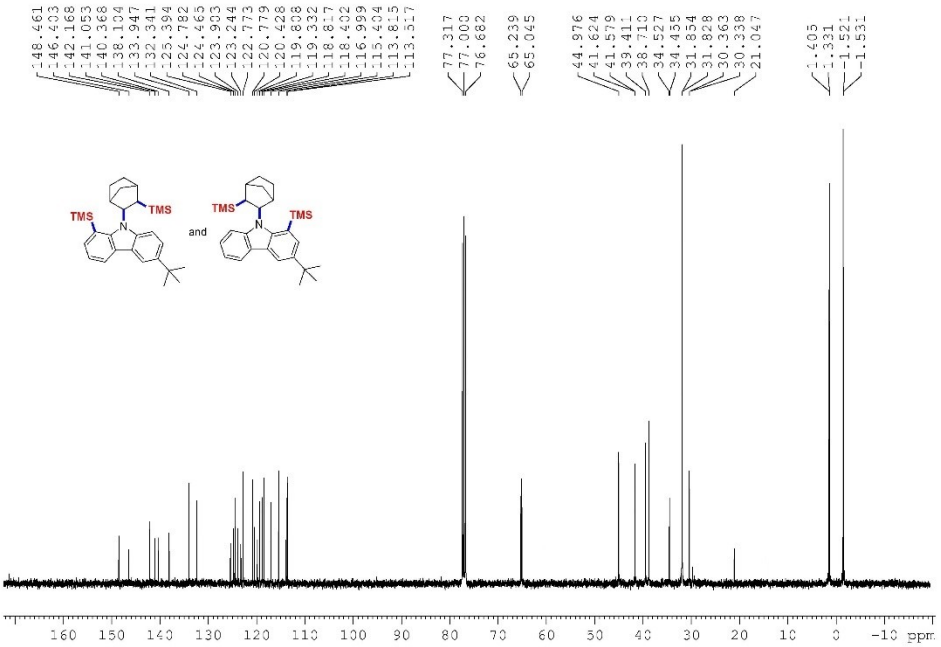
6-(*tert*-butyl)-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-

2-yl)-9*H*-carbazole (3f) and 3-(*tert*-butyl)-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3f'), (3f:3f' = 1:1):

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



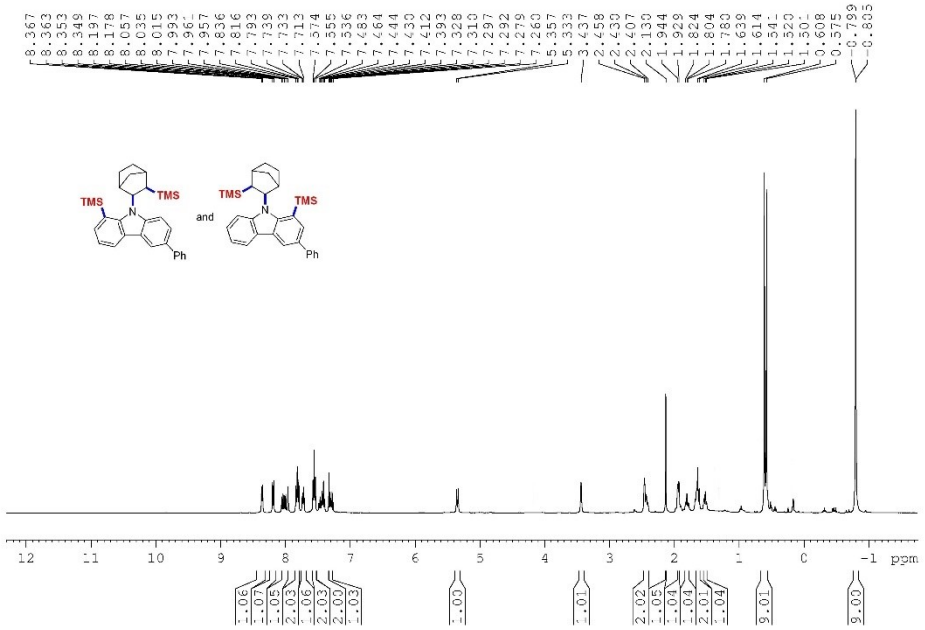
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



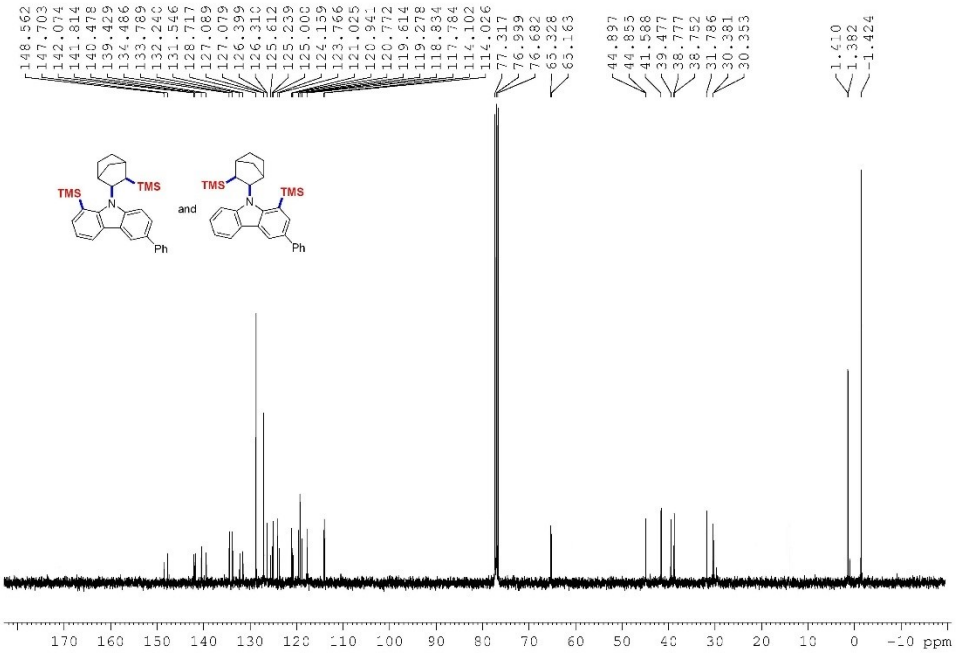
6-phenyl-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-

yl)-9*H*-carbazole (3g) and 3-phenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3g'), (3g:3g' = 1:1):

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



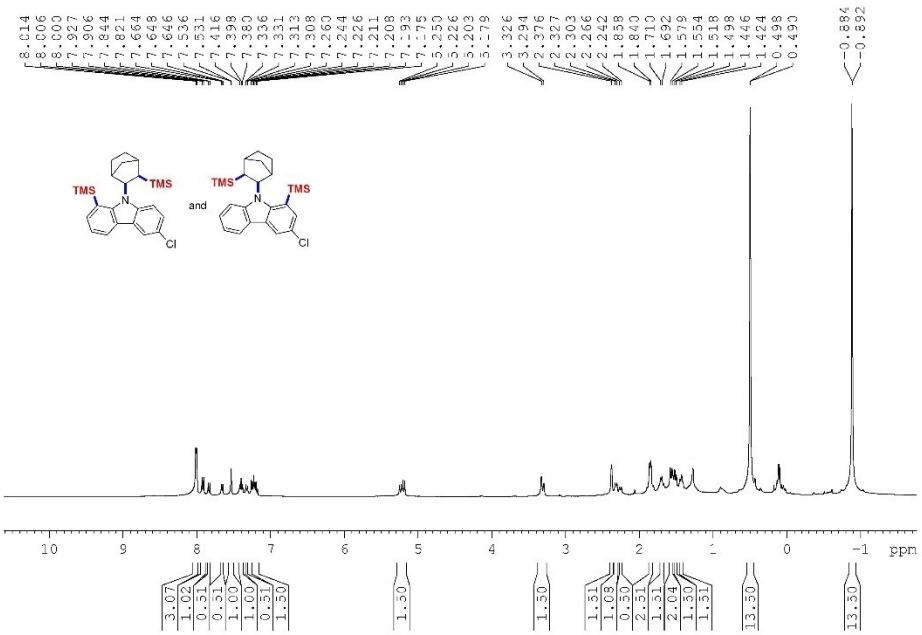
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



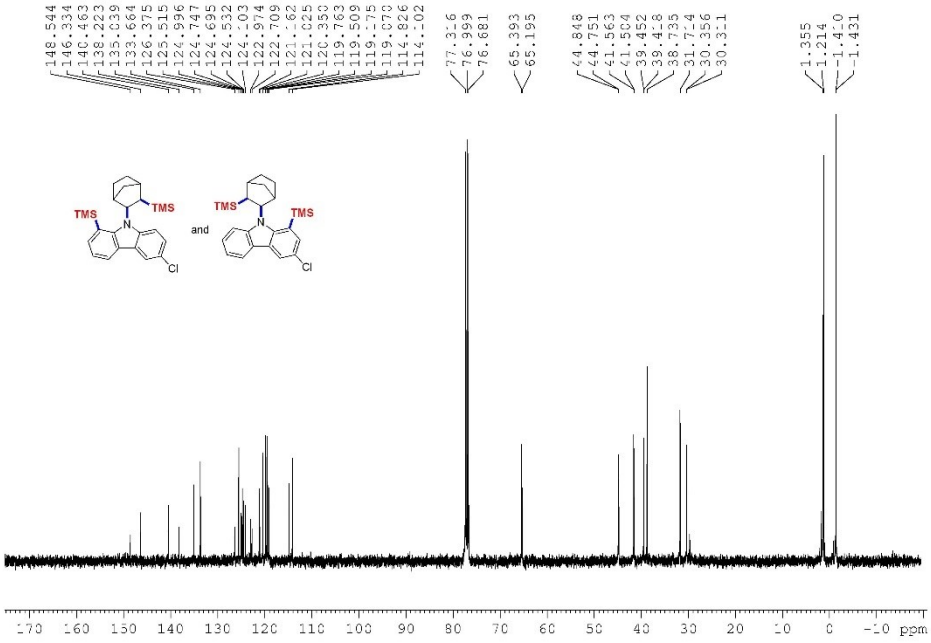
6-chloro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-

9*H*-carbazole (3h) and 3-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3h'), (3h:3h' = 2:1):

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



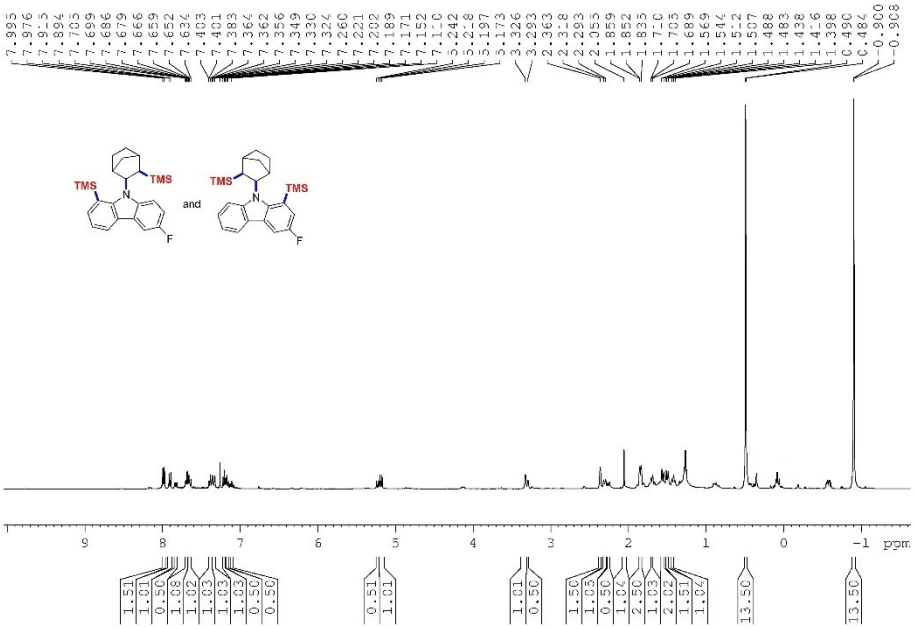
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



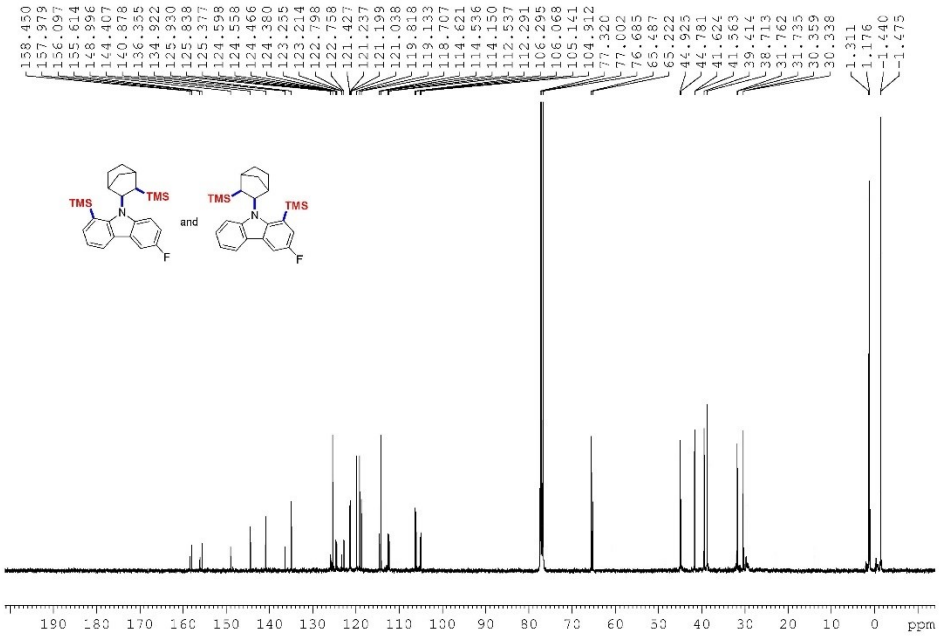
6-fluoro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-

9*H*-carbazole (3i) and 3-fluoro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3i'), (3i:3i' = 2:1):

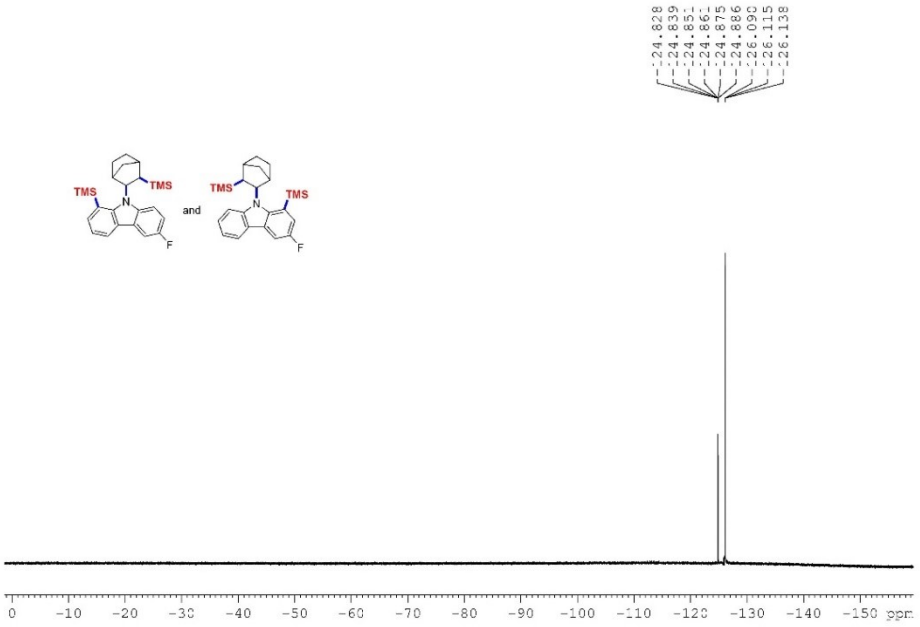
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

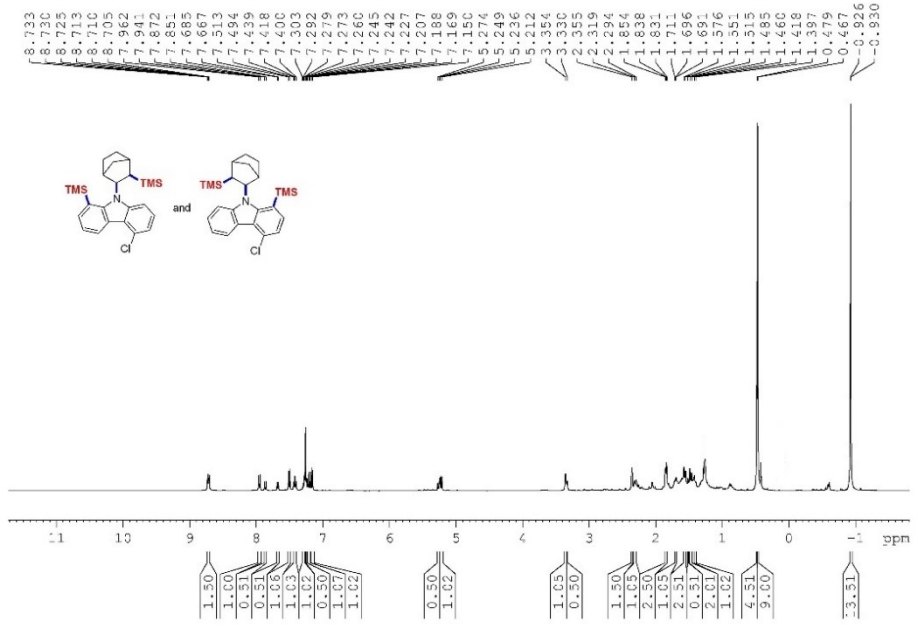


^{19}F{^{1}H} NMR (400 MHz, $CDCl_3$)

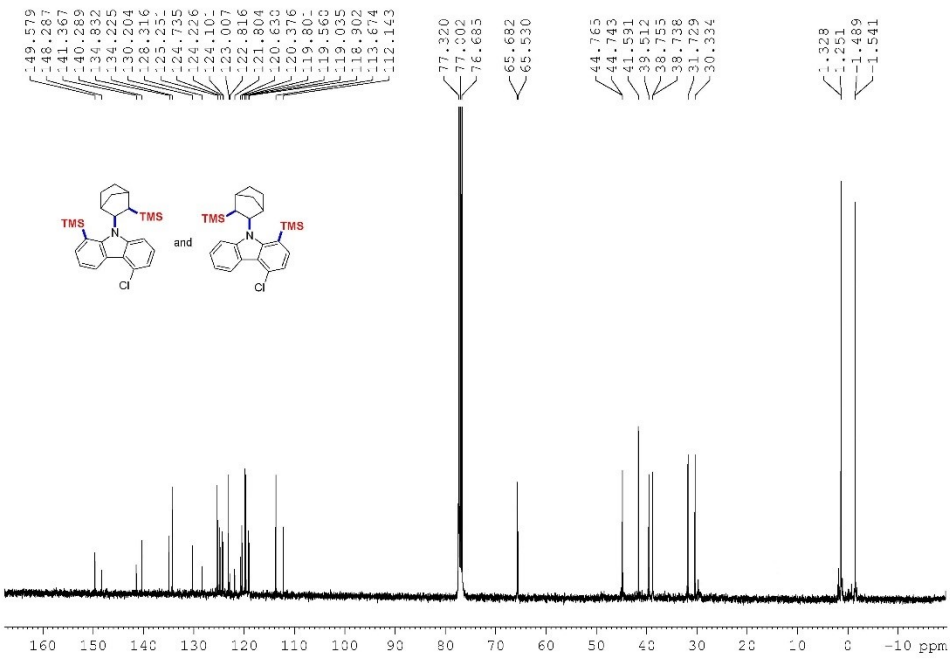


5-chloro-1-(trimethylsilyl)-9-((2*S*,3*R*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3j) and 4-chloro-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3j'), (3j:3j' = 2:1):

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

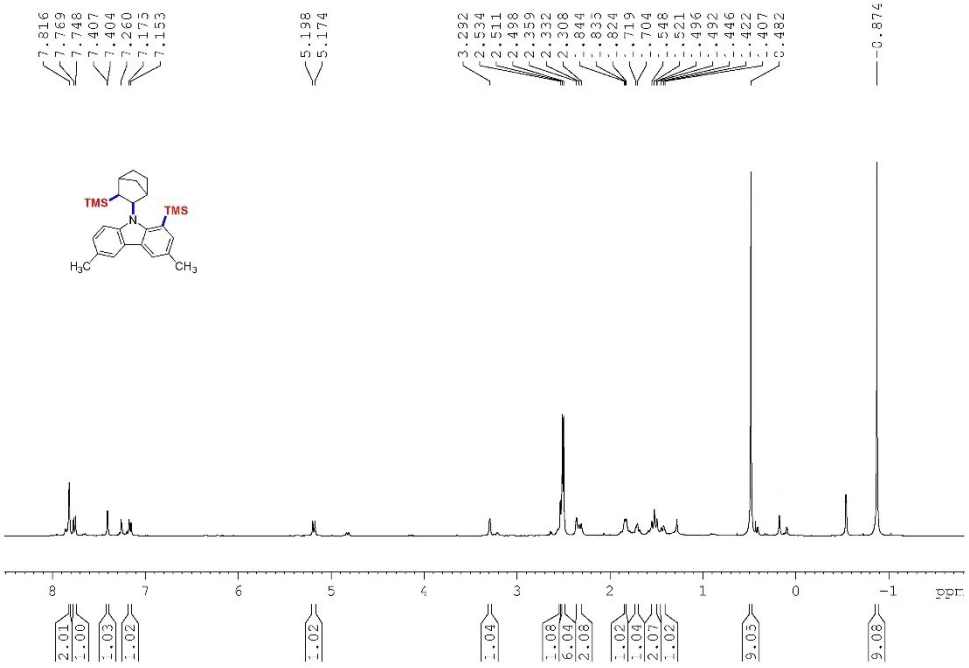


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

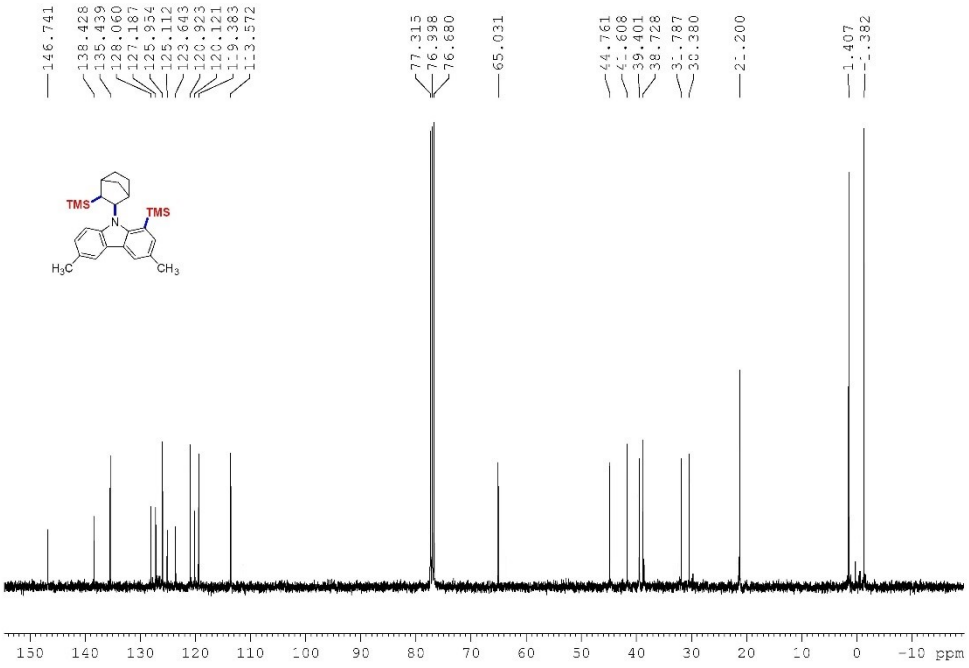


3,6-dimethyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3k):

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

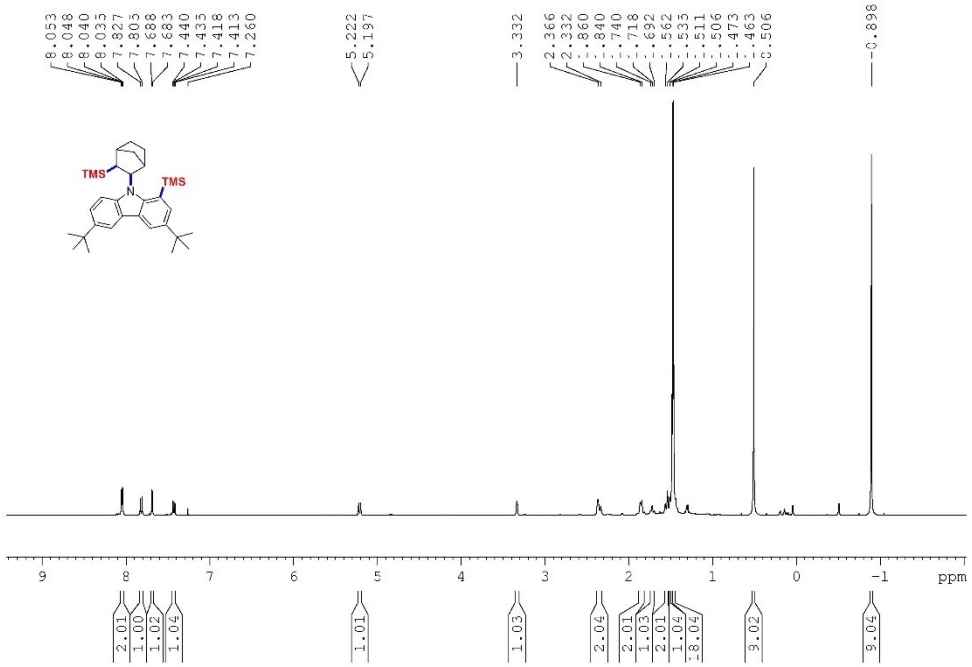


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

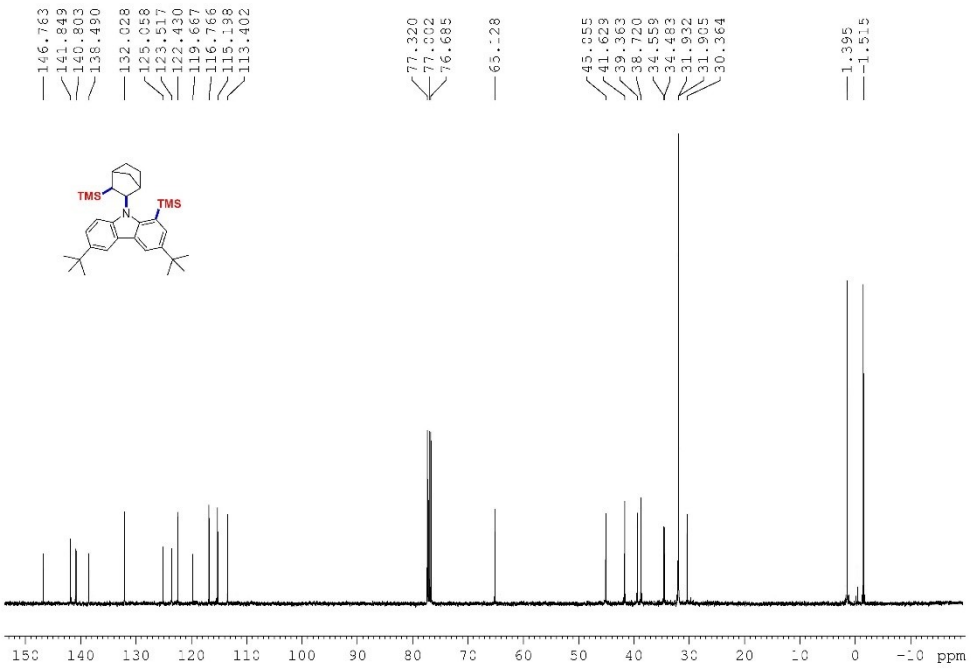


3,6-di-*tert*-butyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3k):

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

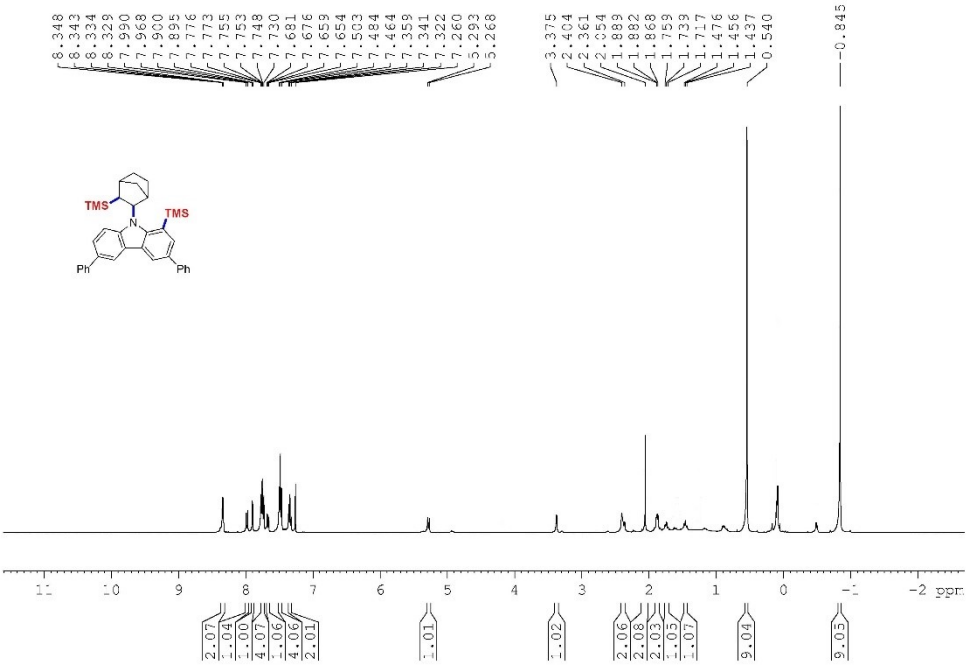


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

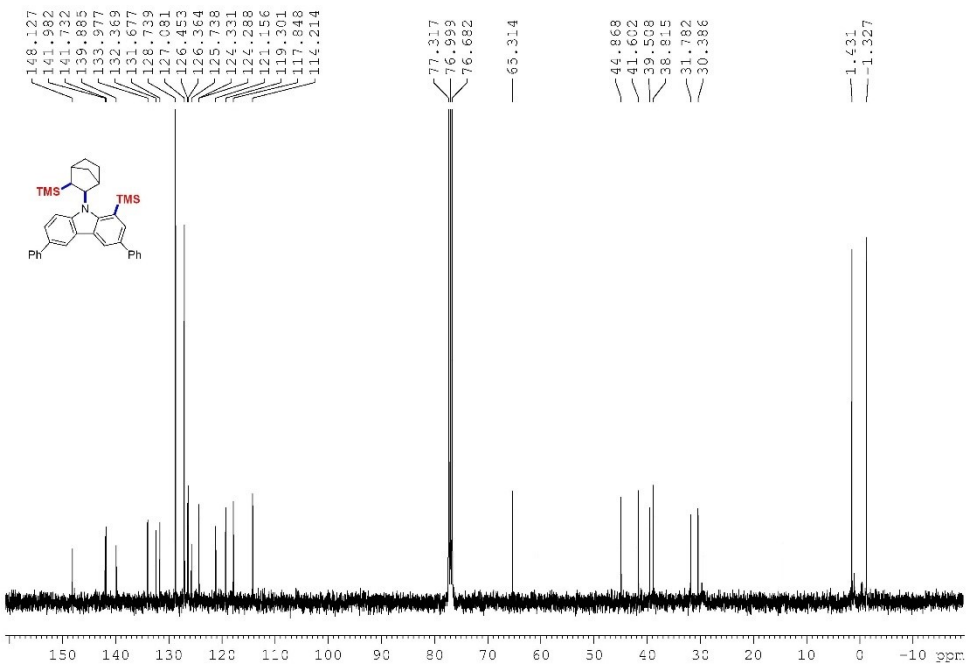


3,6-diphenyl-1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (3m):

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

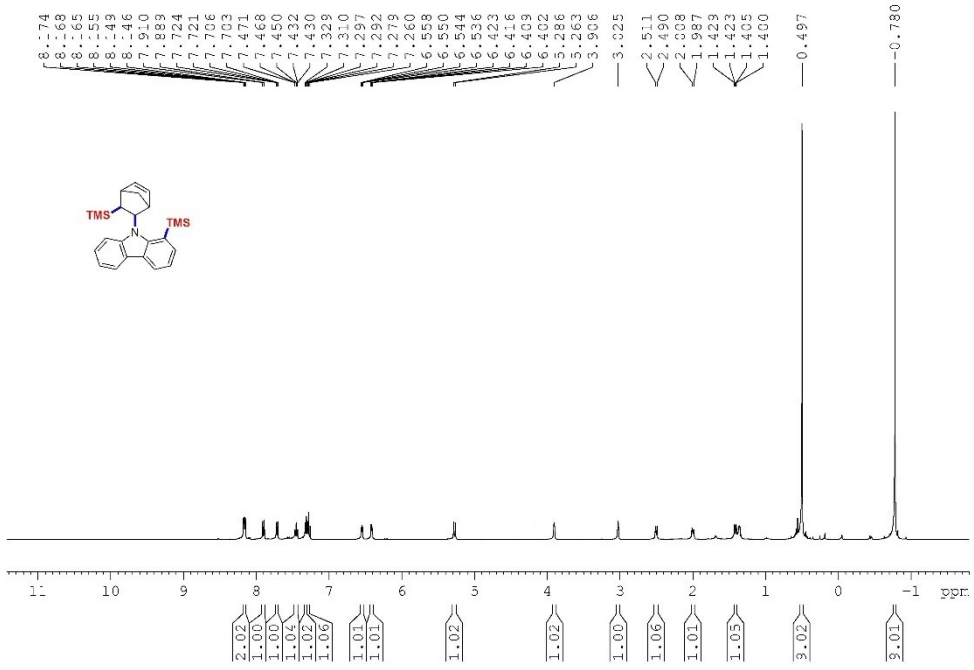


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

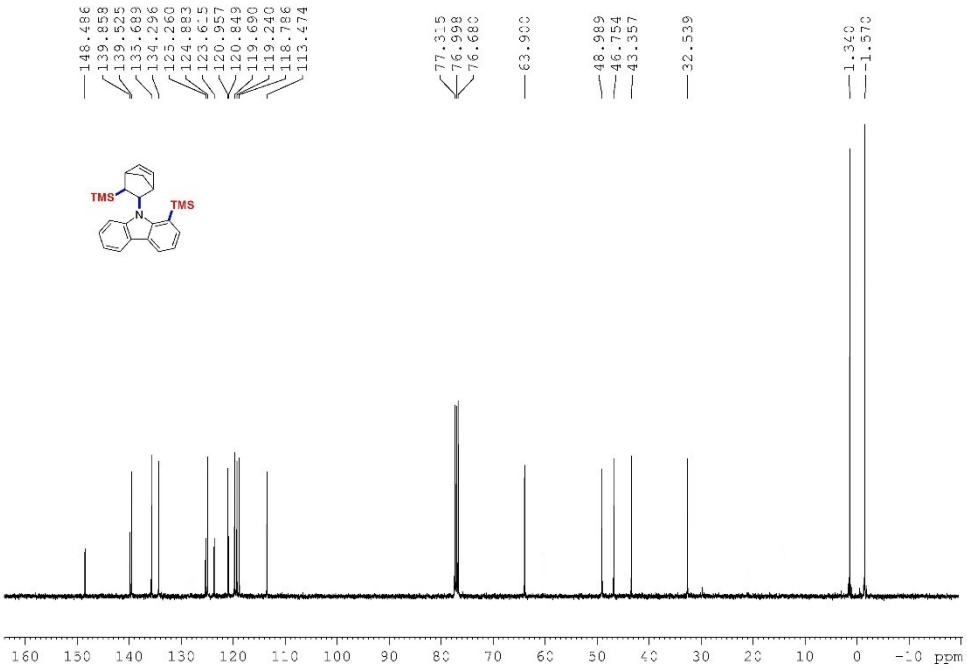


1-(trimethylsilyl)-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]hept-5-en-2-yl)-9*H*-carbazole (3n):

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

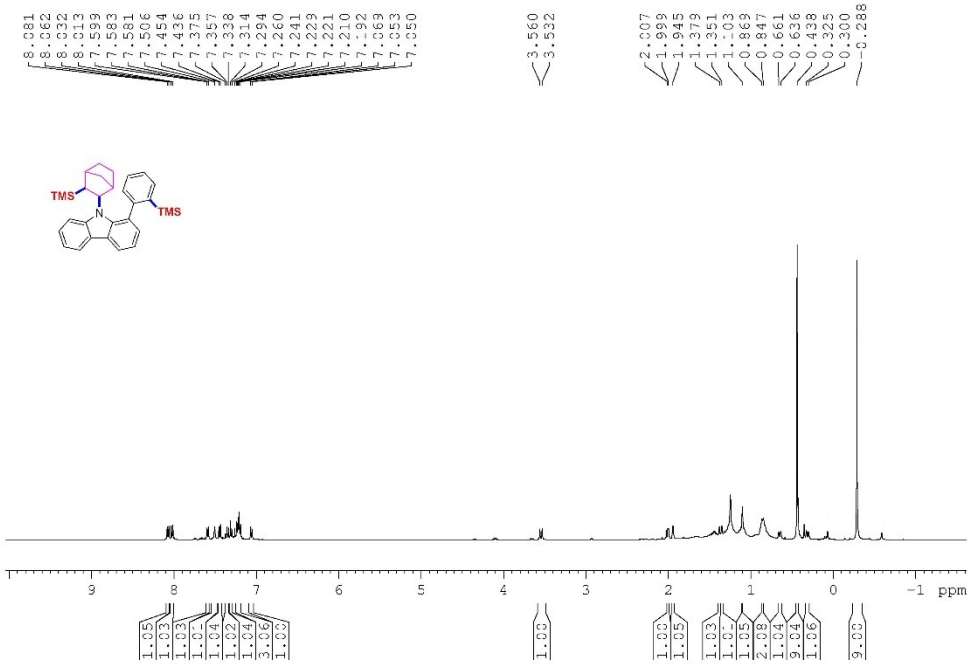


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

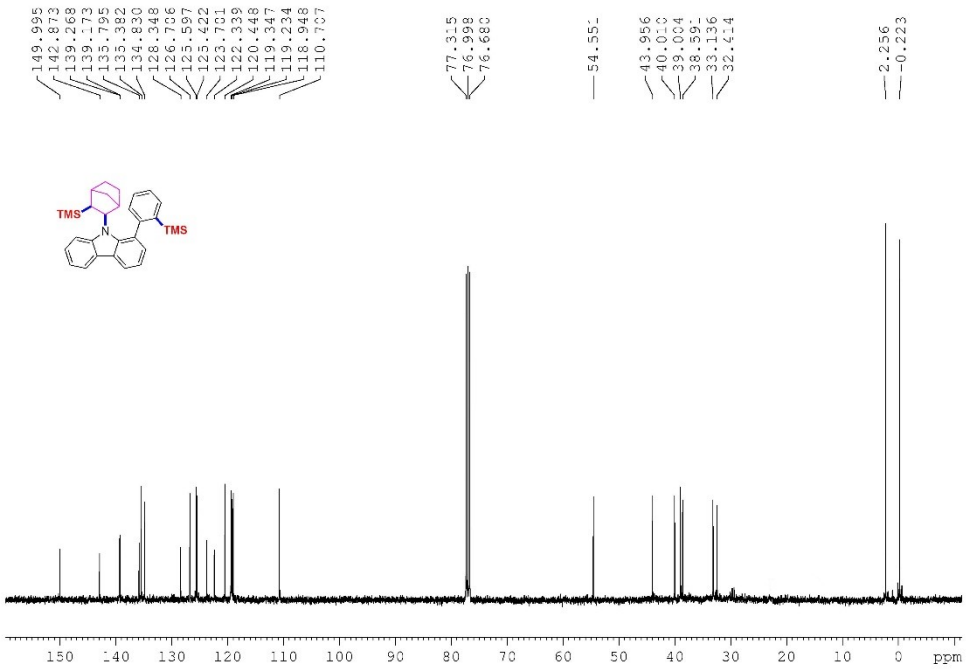


9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-1-(2-(trimethylsilyl)phenyl)-9*H*-carbazole (3o):

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

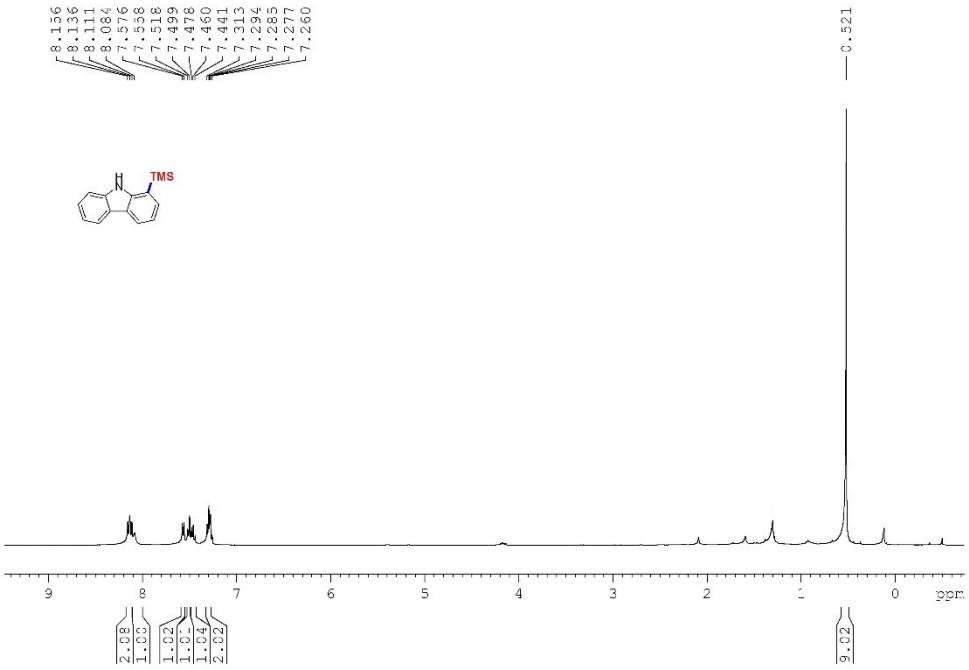


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

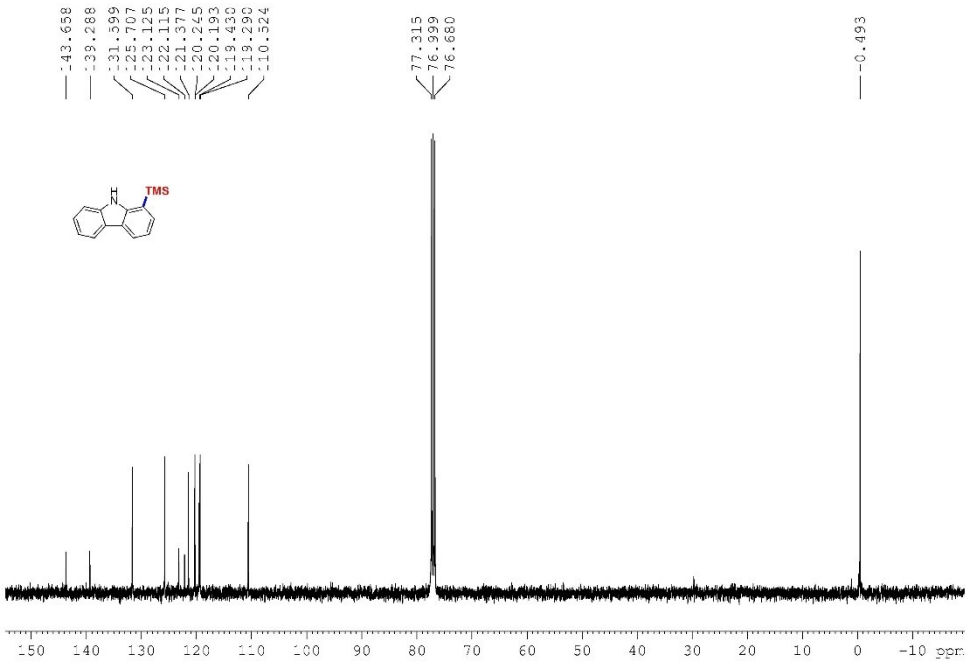


1-(trimethylsilyl)-9*H*-carbazole (4a):

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

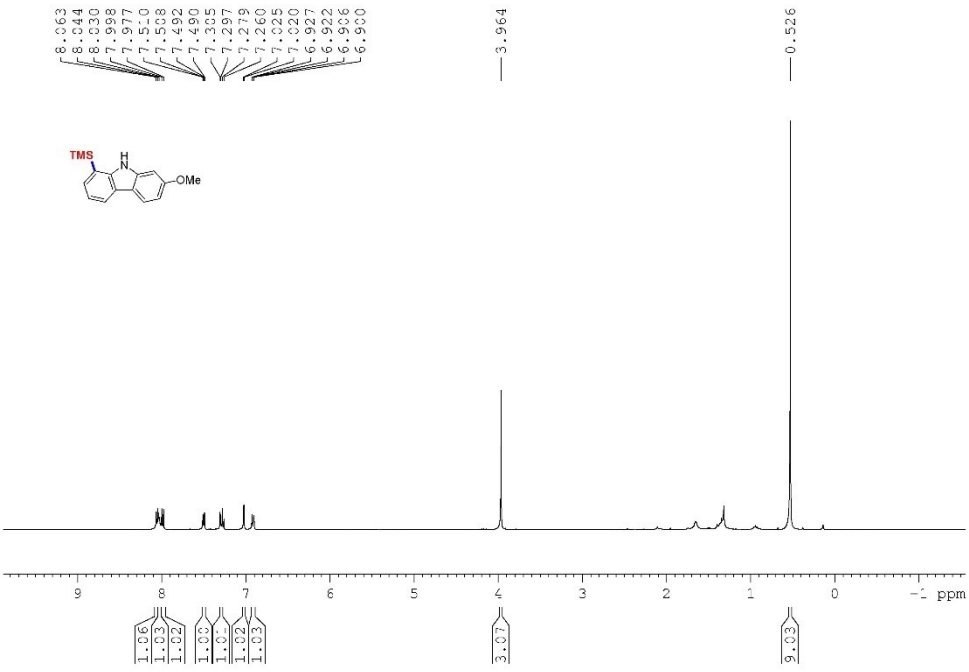


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

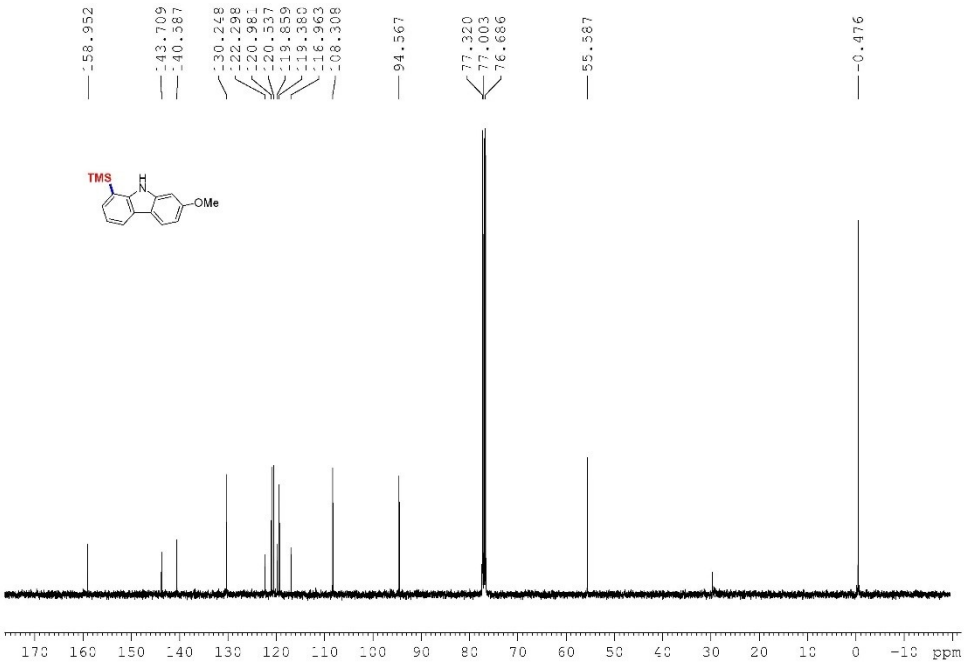


7-methoxy-1-(trimethylsilyl)-9*H*-carbazole (4b):

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

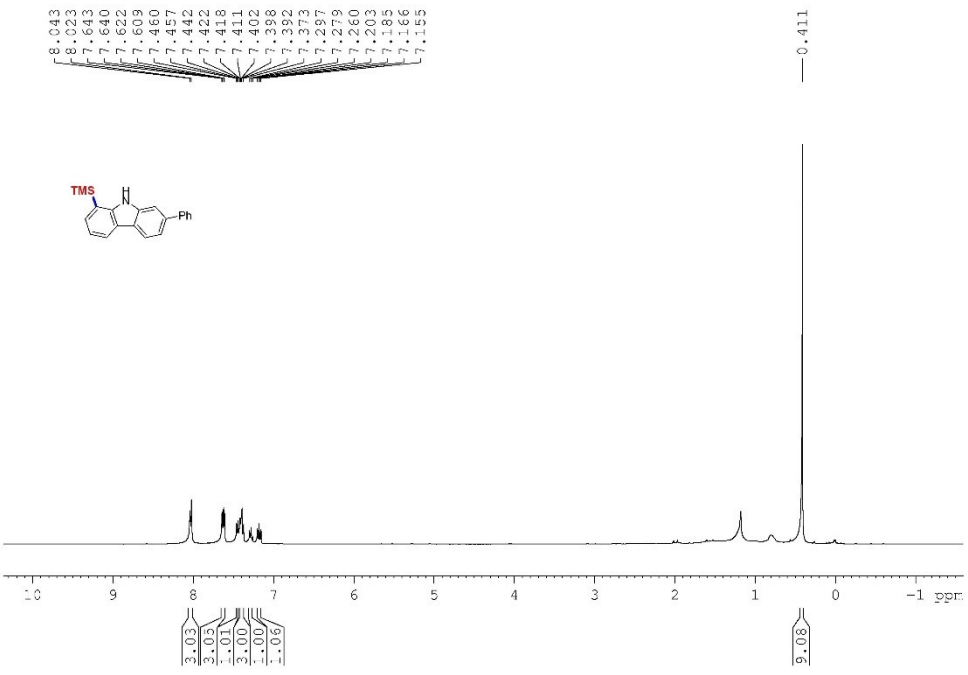


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

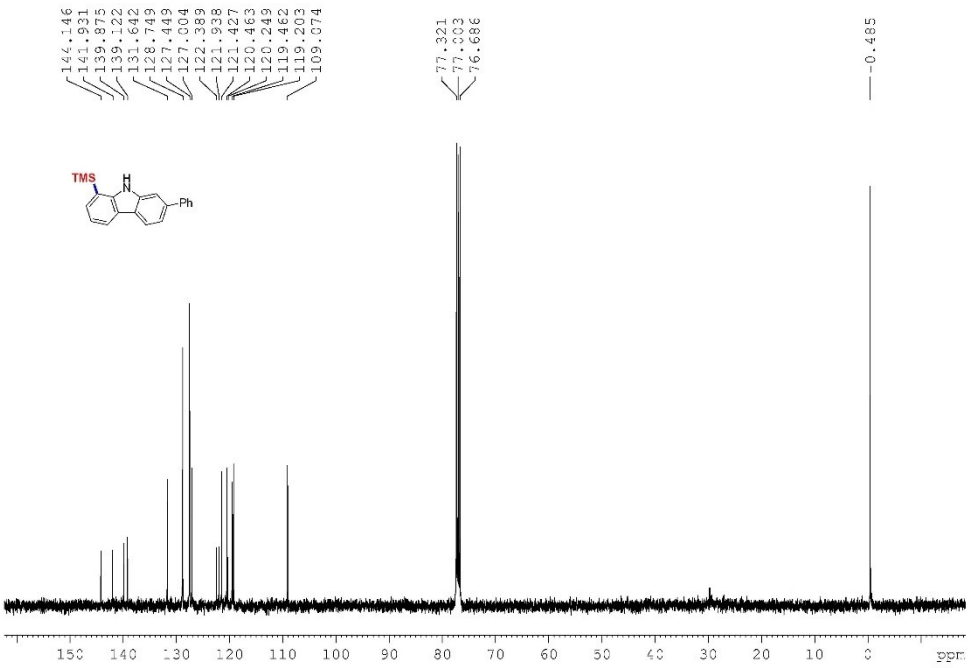


7-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4c):

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

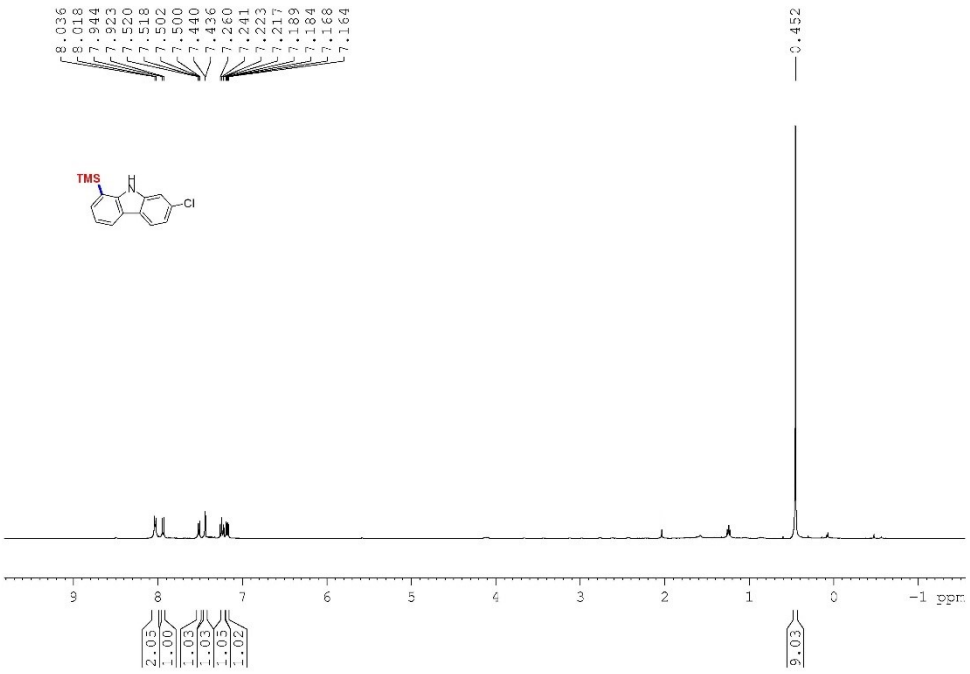


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

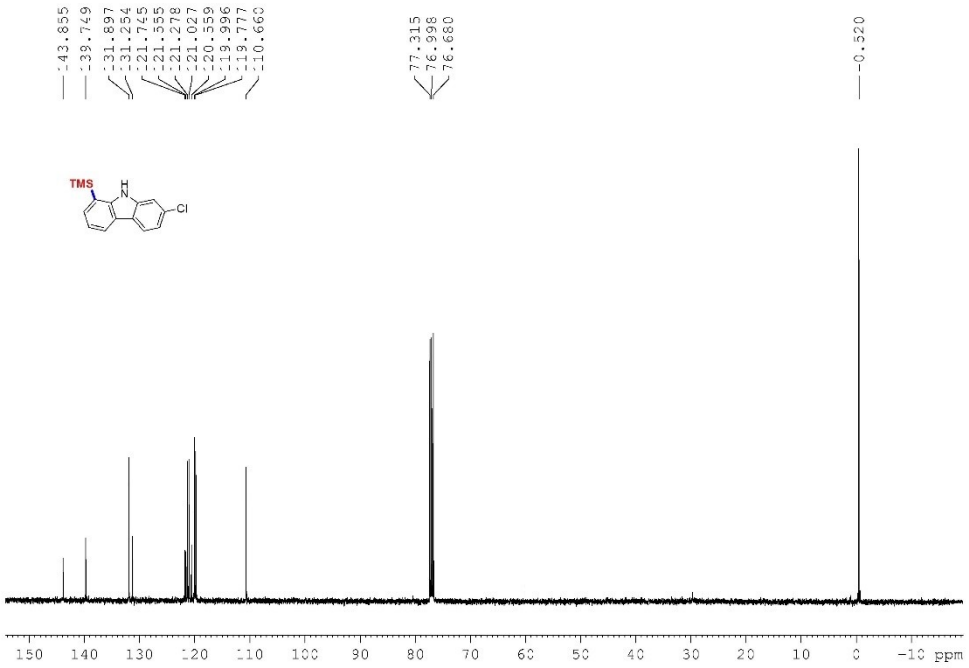


7-chloro-1-(trimethylsilyl)-9*H*-carbazole (4d):

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

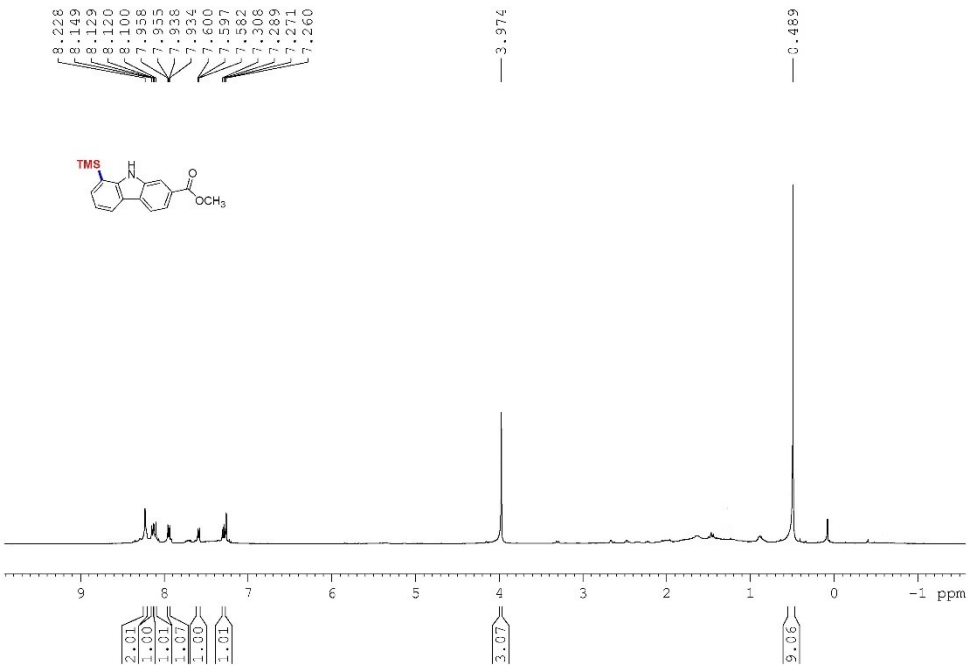


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

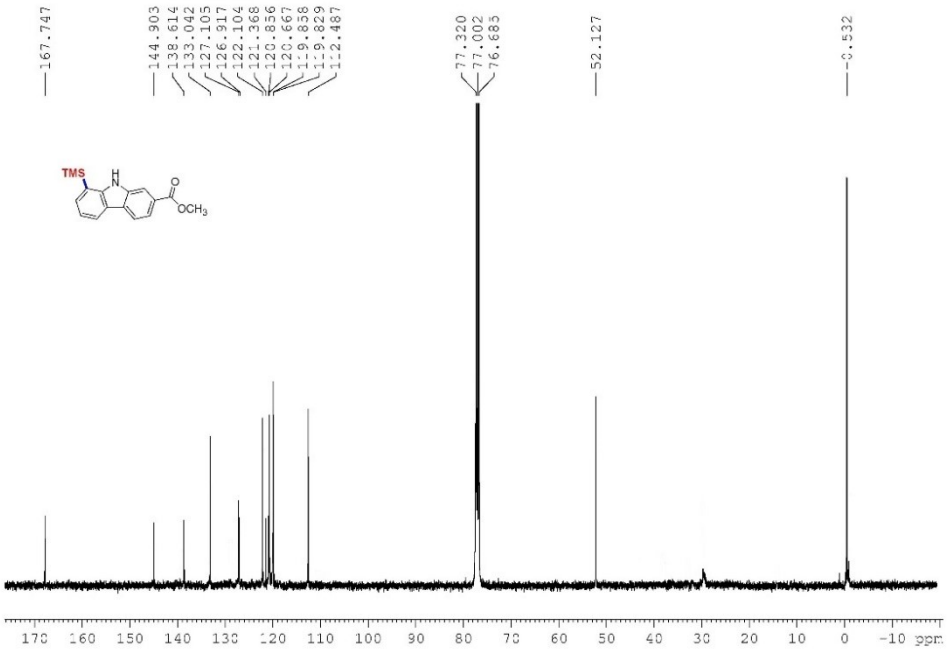


methyl 8-(trimethylsilyl)-9*H*-carbazole-2-carboxylate (4e):

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

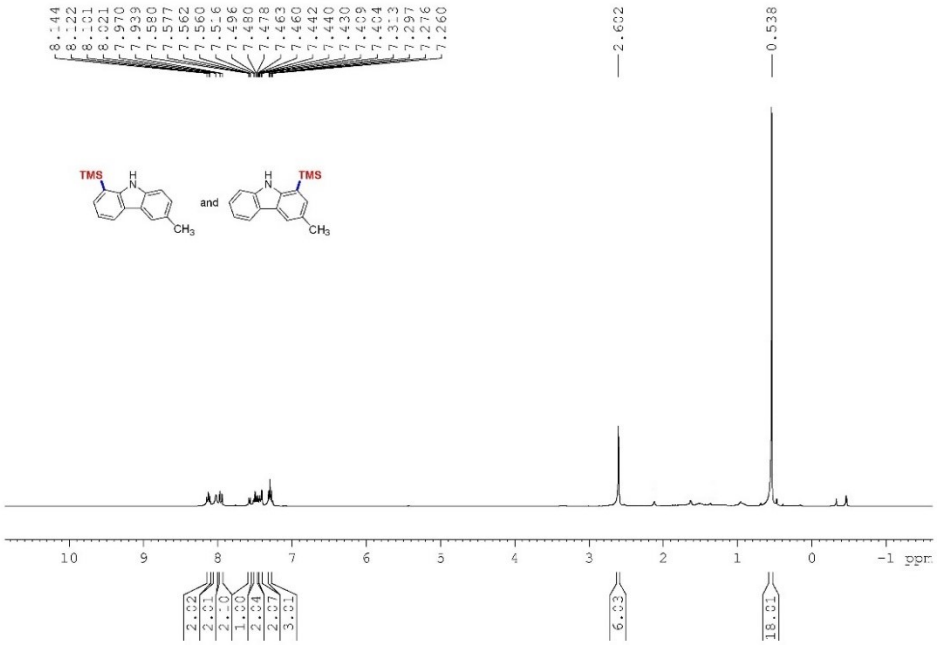


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

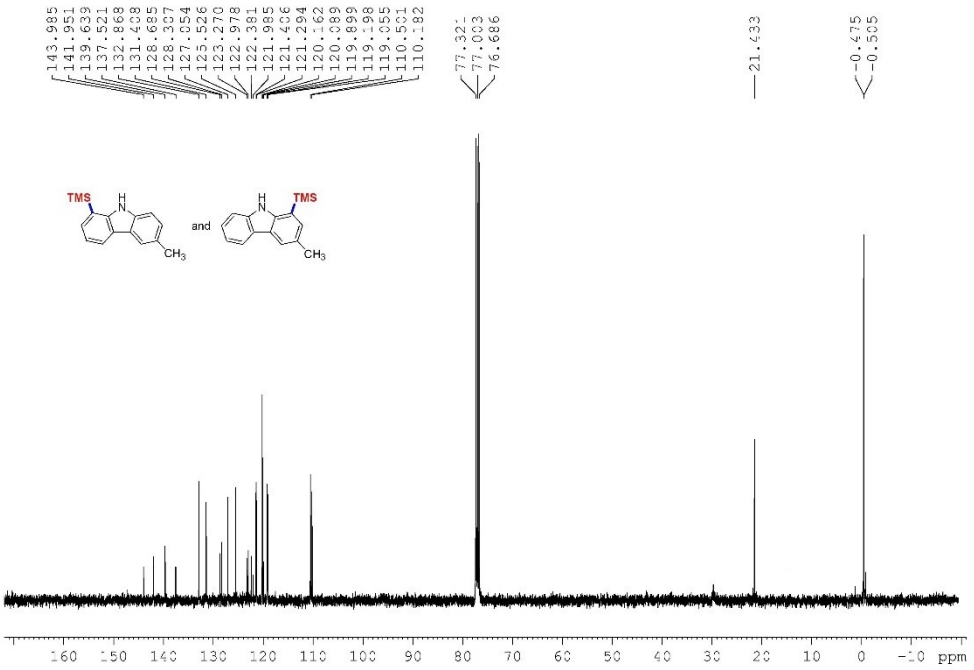


6-methyl-1-(trimethylsilyl)-9*H*-carbazole (4f) and 3-methyl-1-(trimethylsilyl)-9*H*-carbazole (4f'), (4f:4f' = 1:1):

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

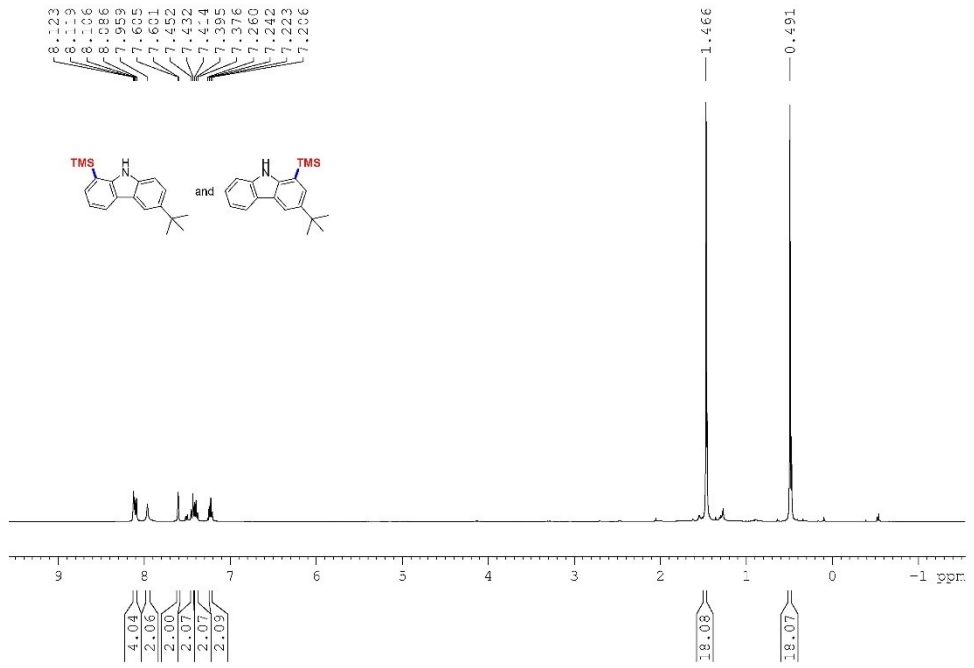


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

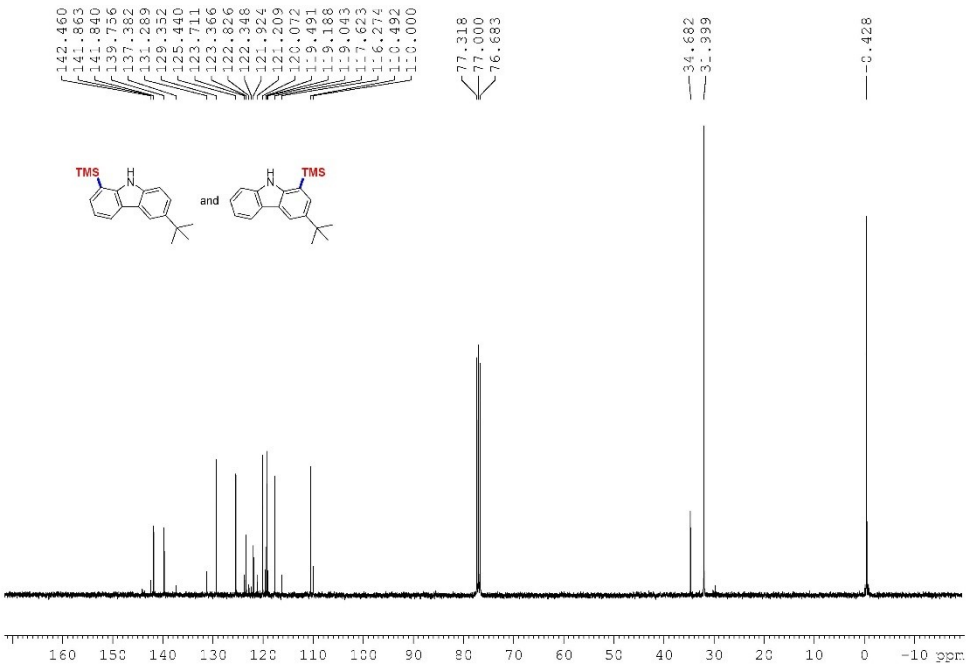


6-(*tert*-butyl)-1-(trimethylsilyl)-9*H*-carbazole (4g) and 3-(*tert*-butyl)-1-(trimethylsilyl)-9*H*-carbazole (4g'), (4g:4g' = 1:1):

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

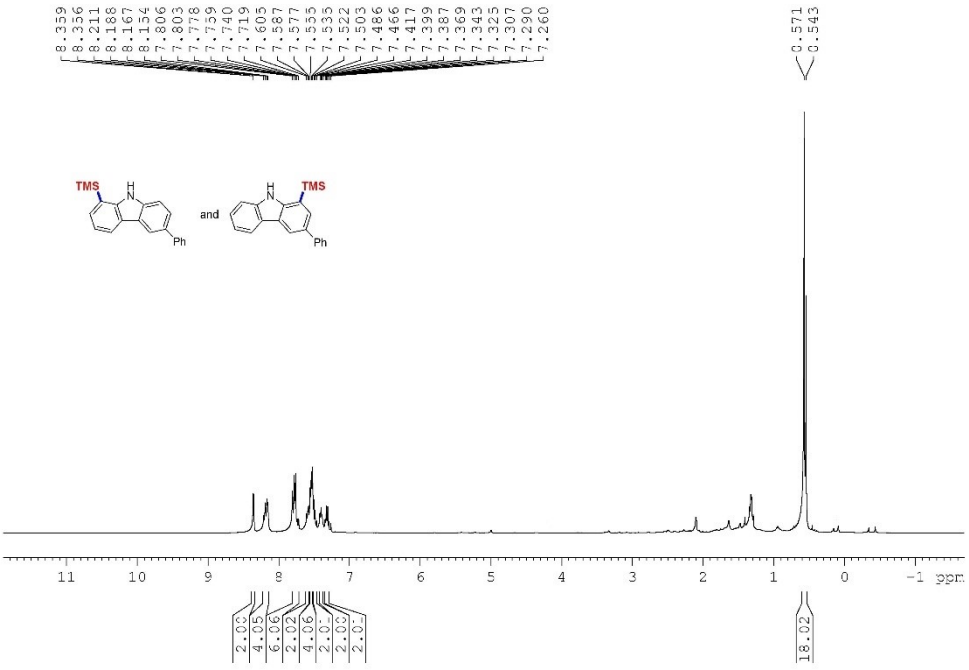


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

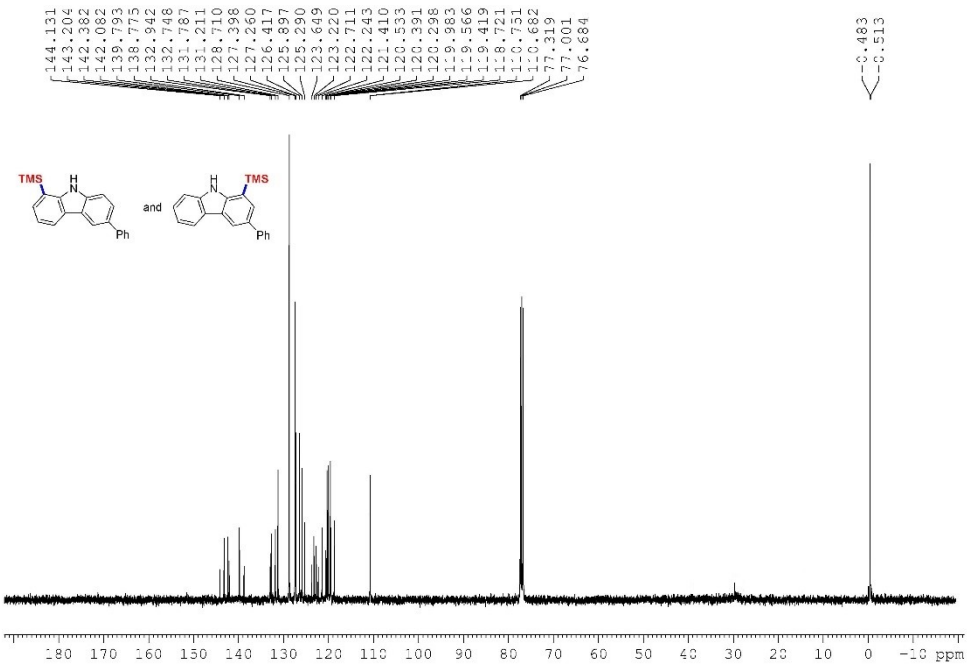


6-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4h) and 3-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4h'), (4h:4h' = 1:1):

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

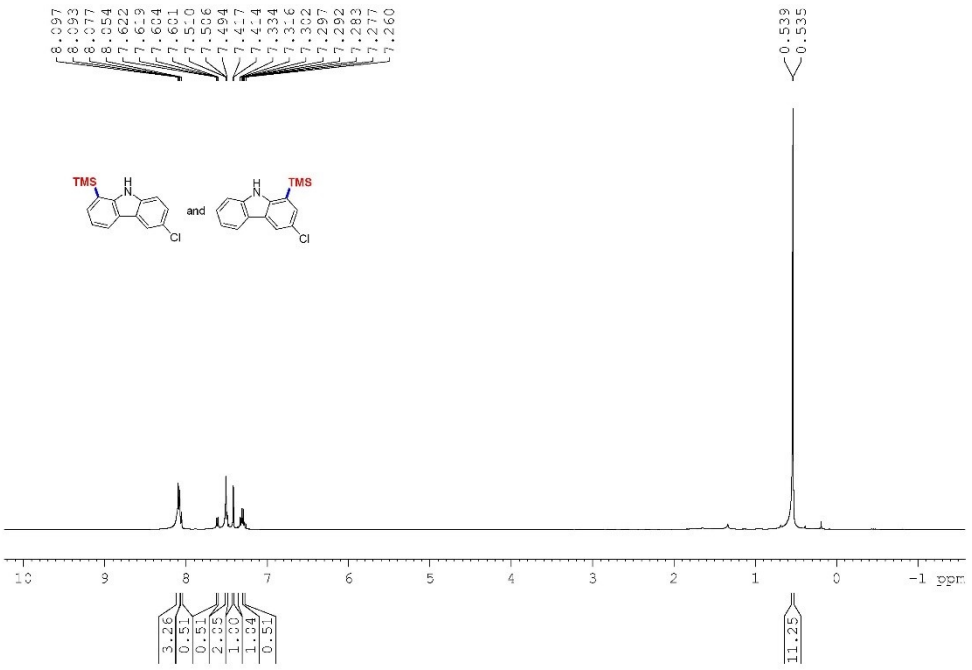


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

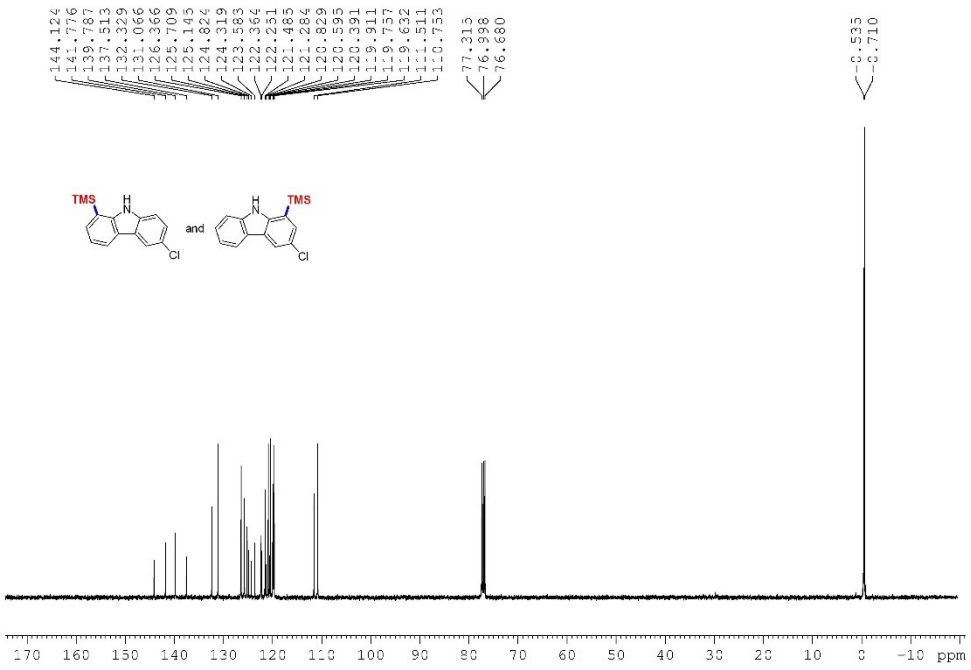


6-chloro-1-(trimethylsilyl)-9*H*-carbazole (4i) and 3-chloro-1-(trimethylsilyl)-9*H*-carbazole (4i'), (4i:4i' = 4:1):

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

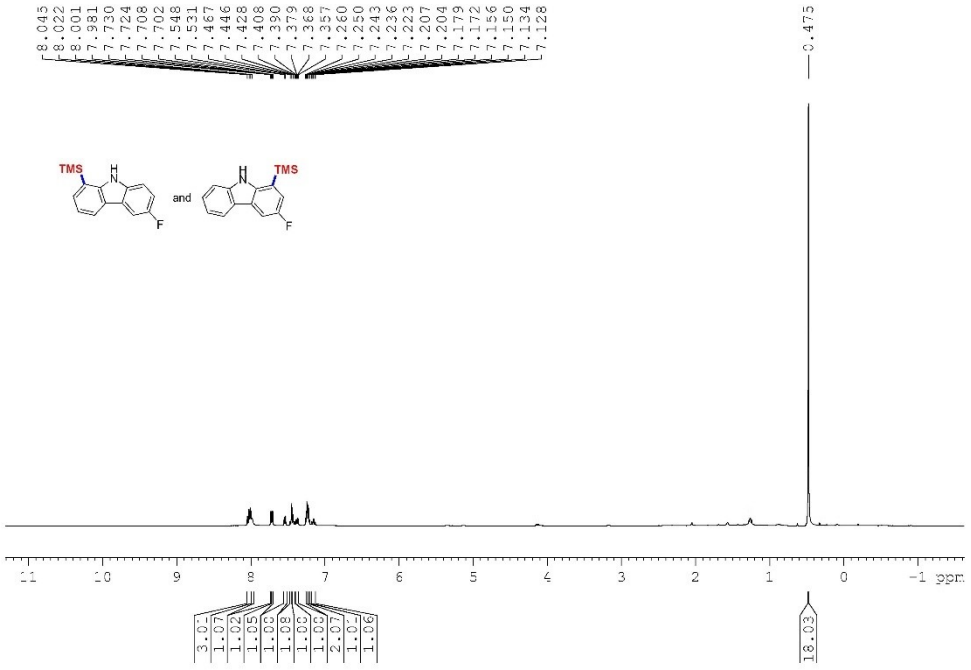


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

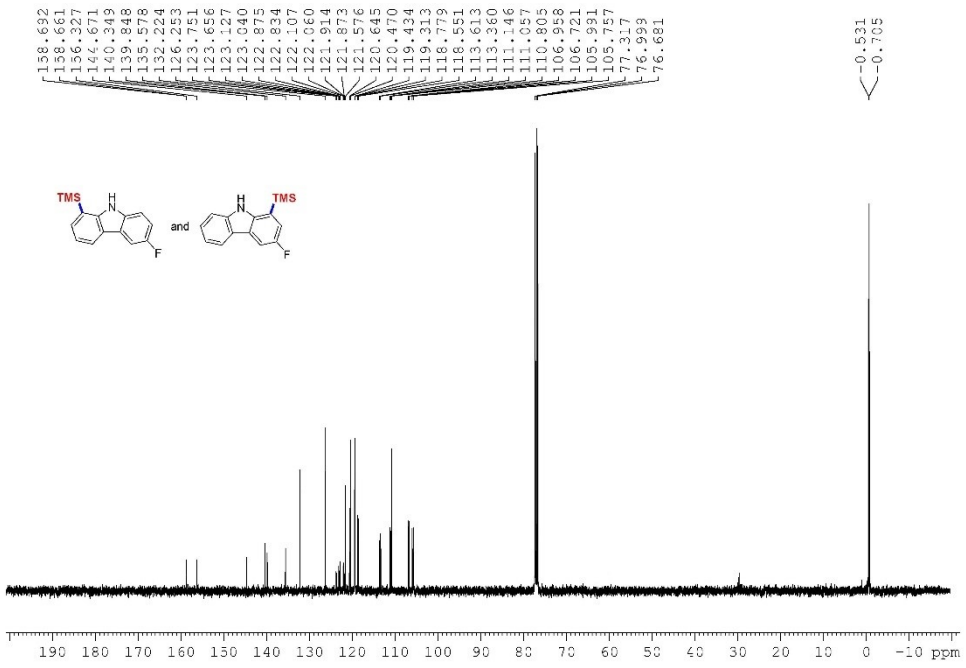


6-fluoro-1-(trimethylsilyl)-9*H*-carbazole (4j) and 3-fluoro-1-(trimethylsilyl)-9*H*-carbazole (4j'), (4j:4j' = 1:1):

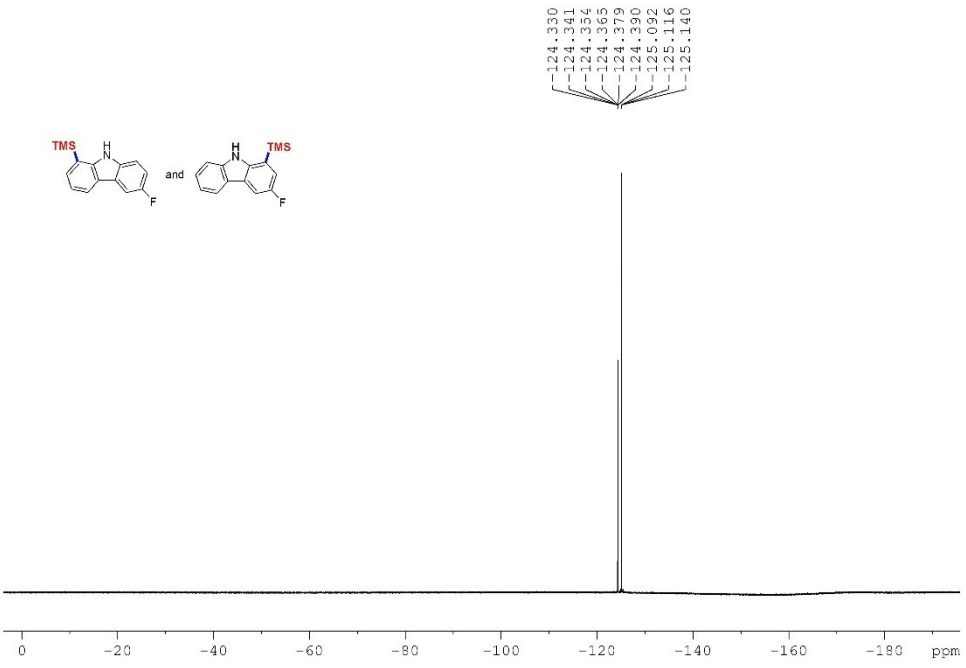
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



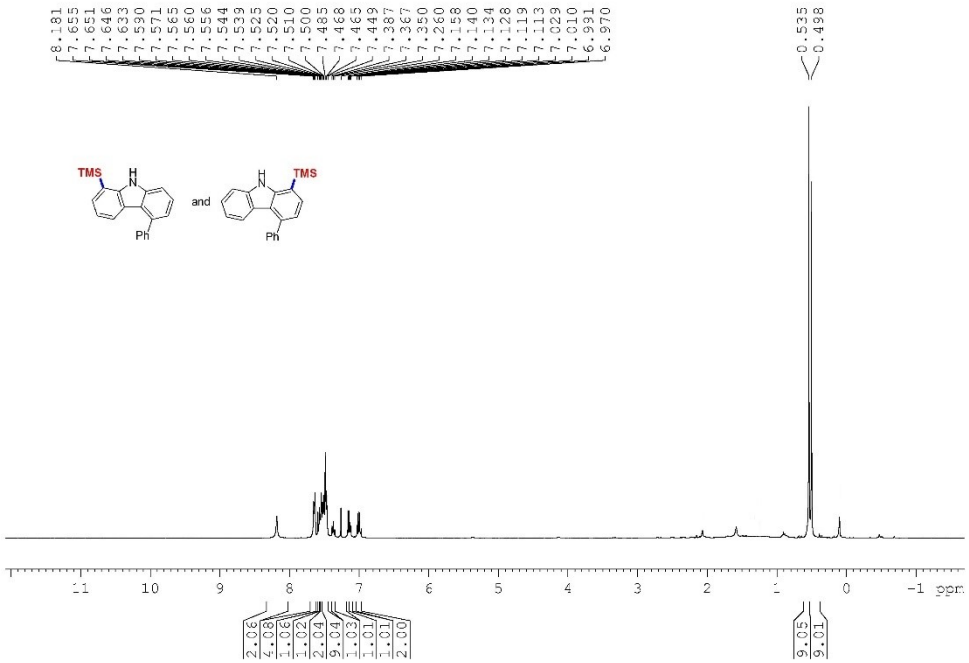
$^{19}F\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



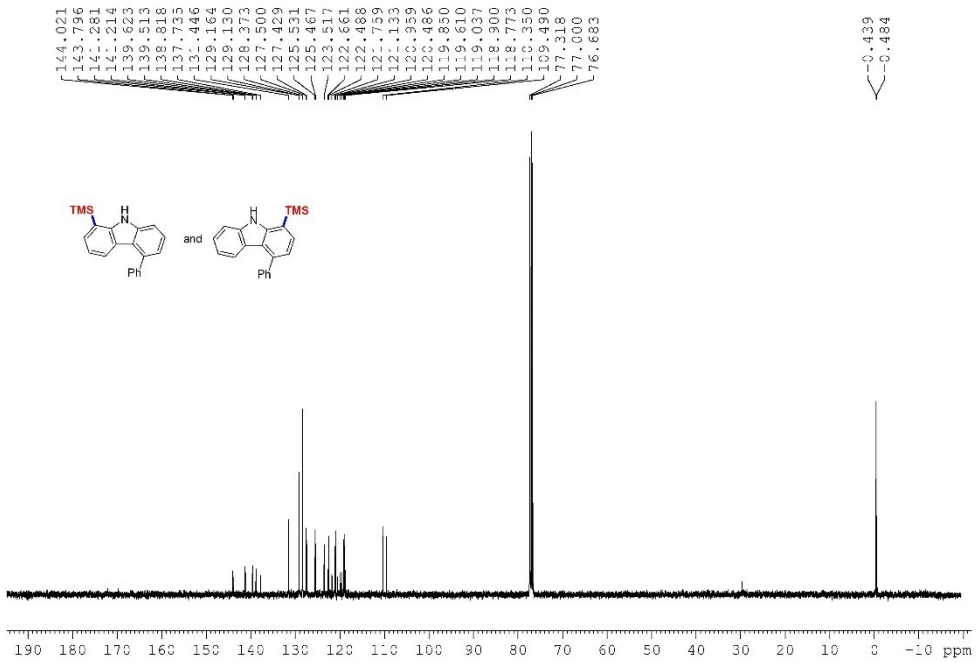
5-phenyl-1-(trimethylsilyl)-9*H*-carbazole (4k) and 4-phenyl-1-(trimethylsilyl)-

9*H*-carbazole (4k'), (4k:4k' = 1:1):

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



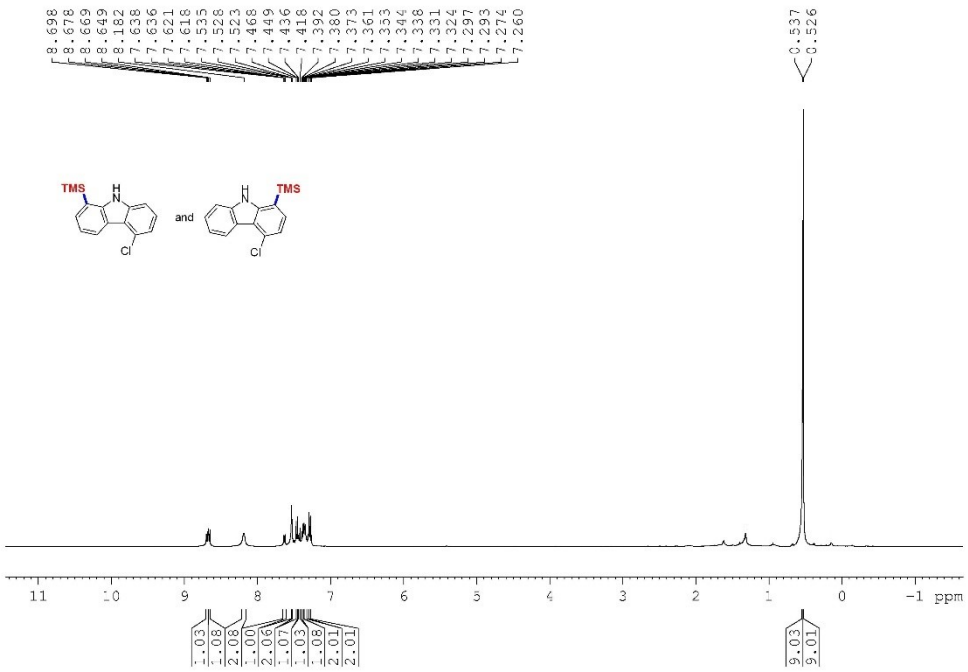
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



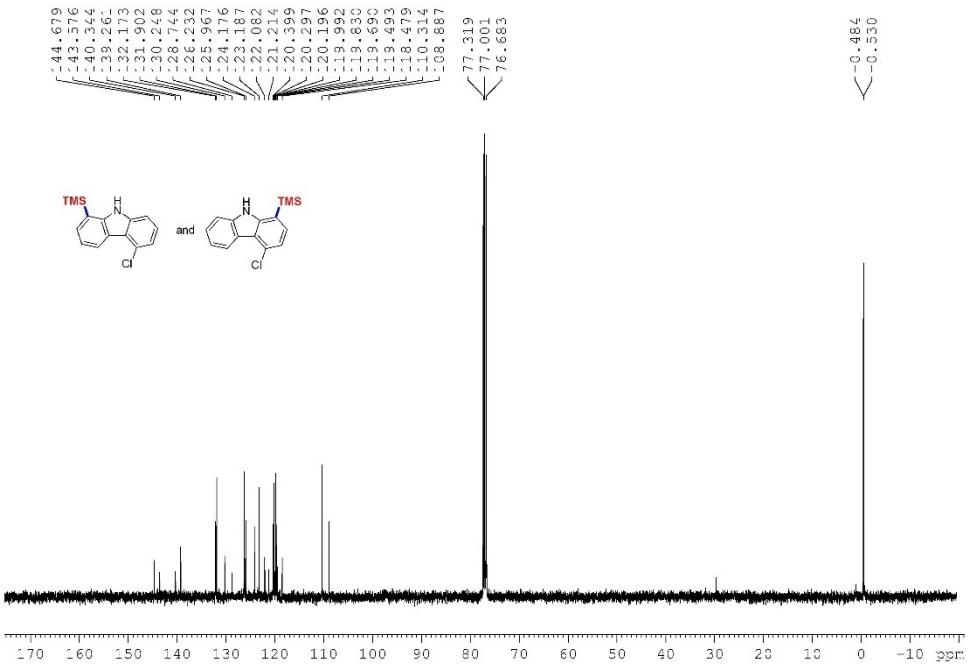
5-chloro-1-(trimethylsilyl)-9*H*-carbazole (4l) and 4-chloro-1-(trimethylsilyl)-9*H*-

carbazole (4l'), (4l:4l' = 1:1):

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

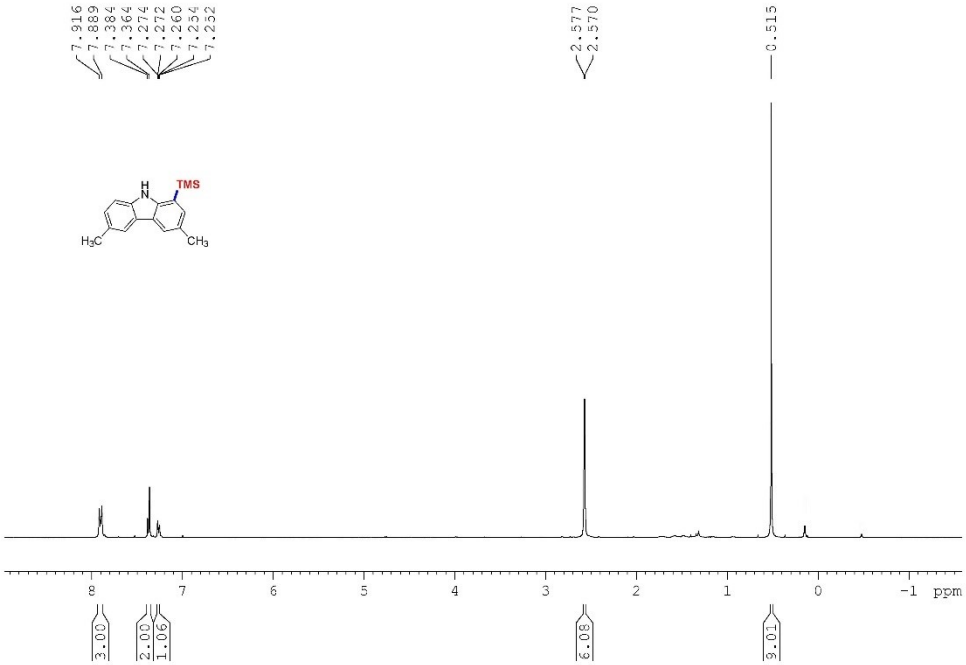


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

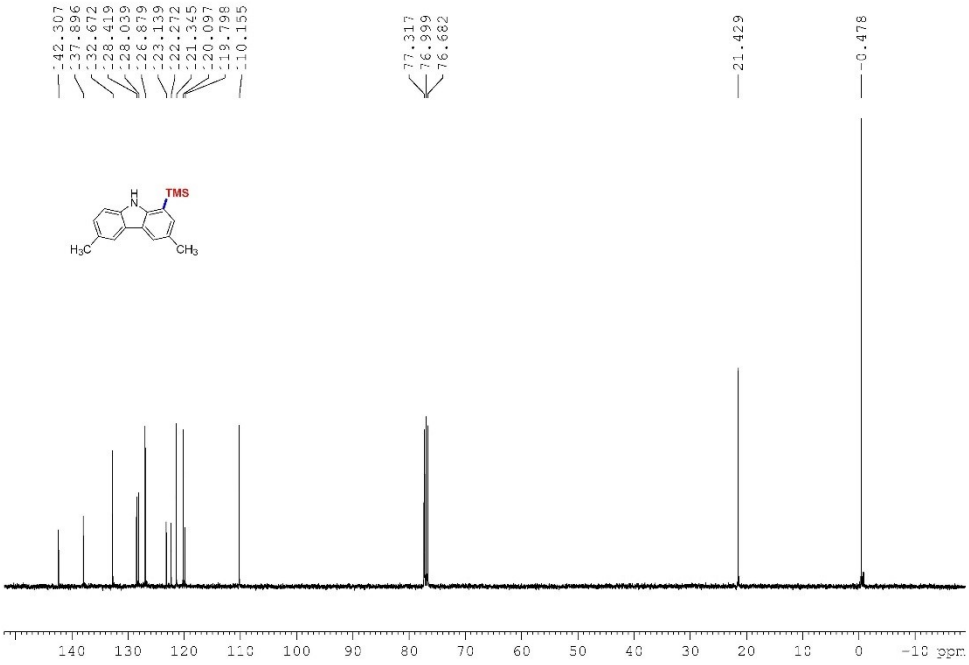


3,6-dimethyl-1-(trimethylsilyl)-9*H*-carbazole (4m):

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

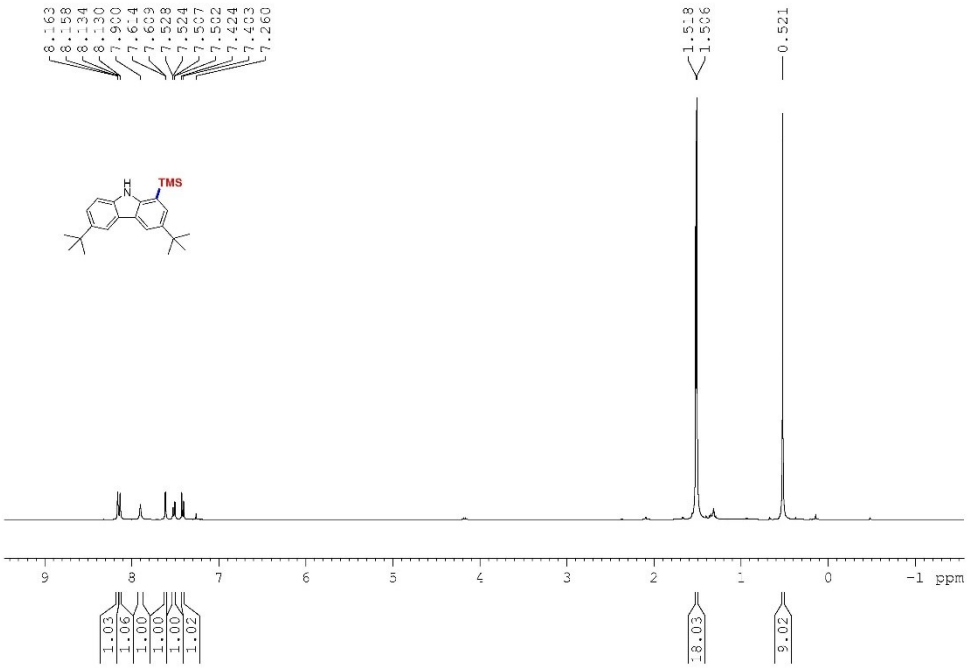


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

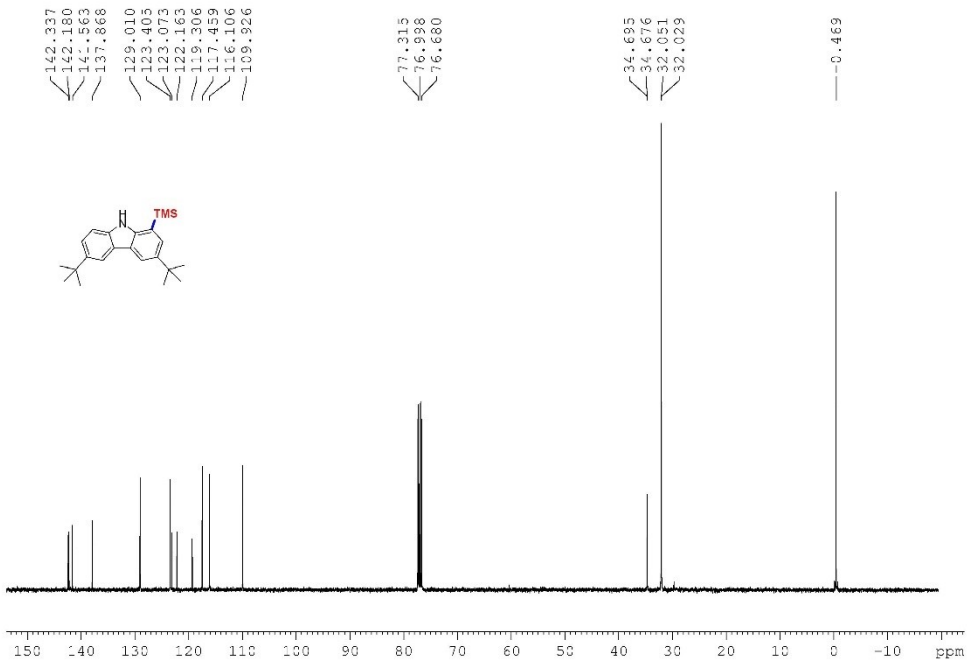


3,6-di-*tert*-butyl-1-(trimethylsilyl)-9*H*-carbazole (4n):

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

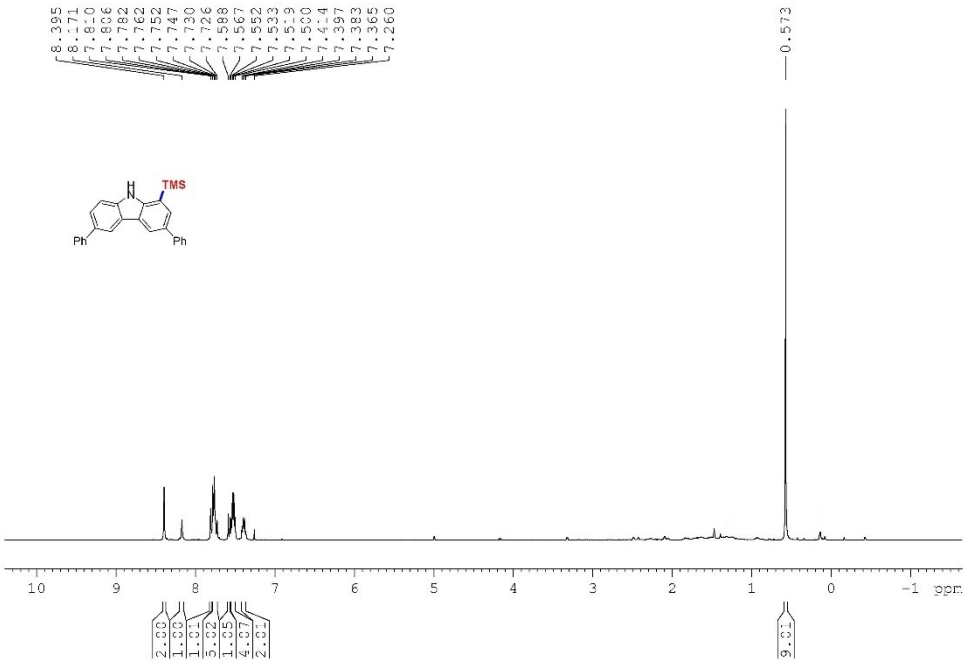


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

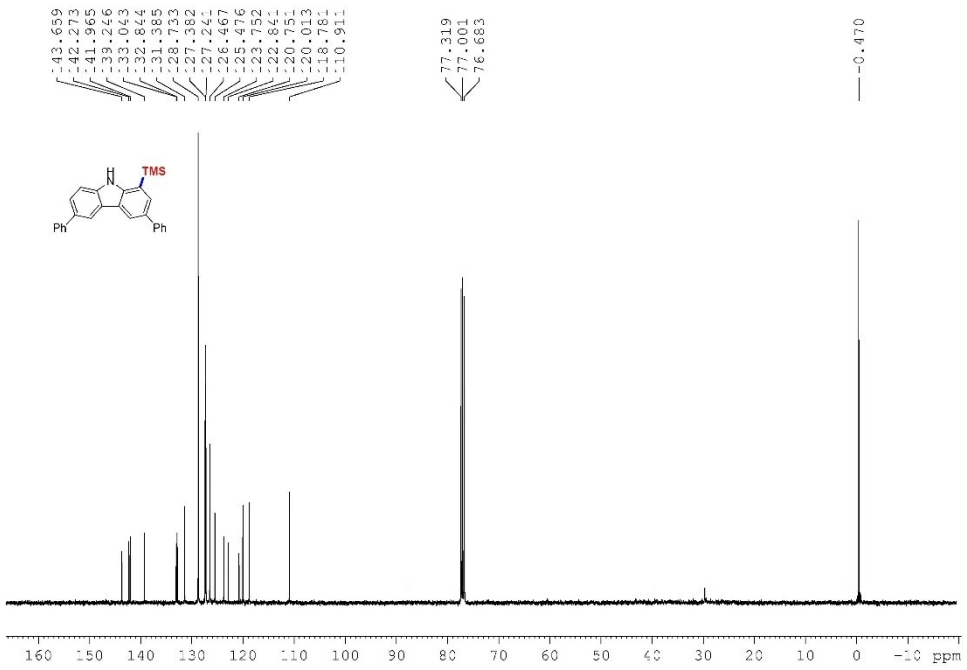


3,6-diphenyl-1-(trimethylsilyl)-9*H*-carbazole (4o):

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

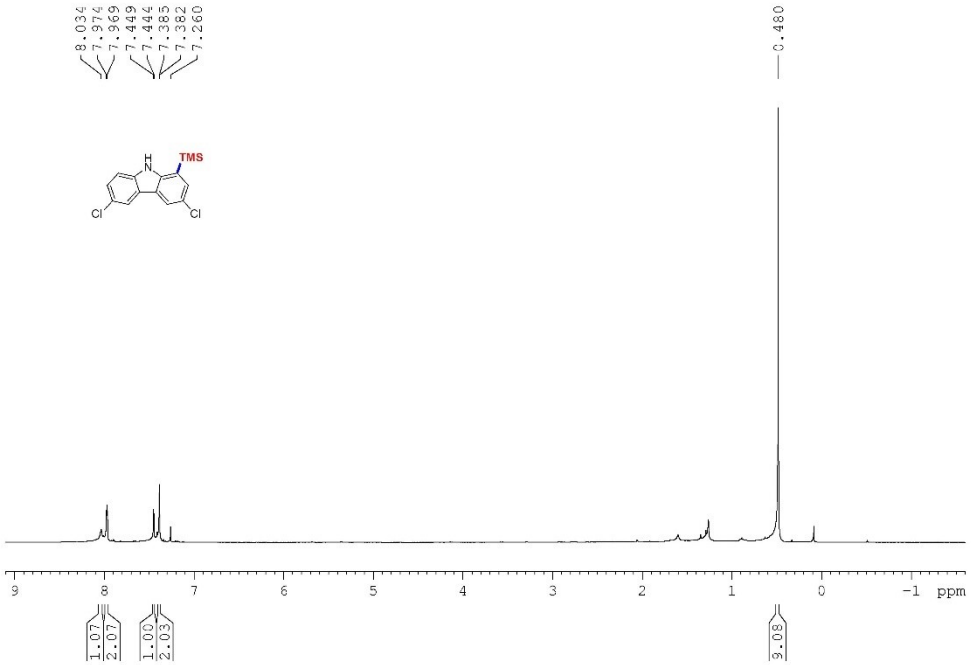


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

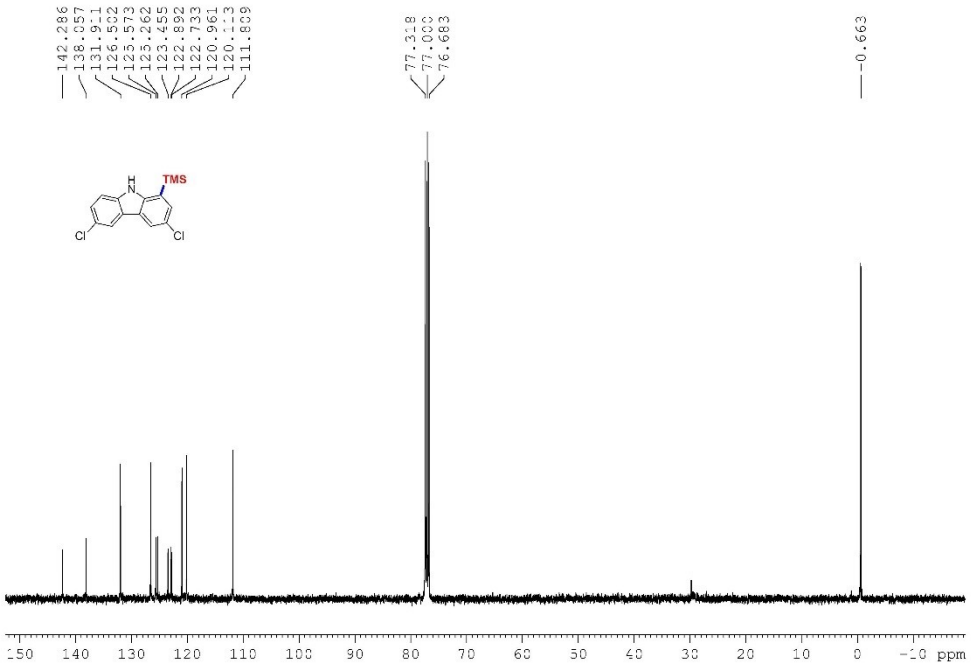


3,6-dichloro-1-(trimethylsilyl)-9*H*-carbazole (4p):

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

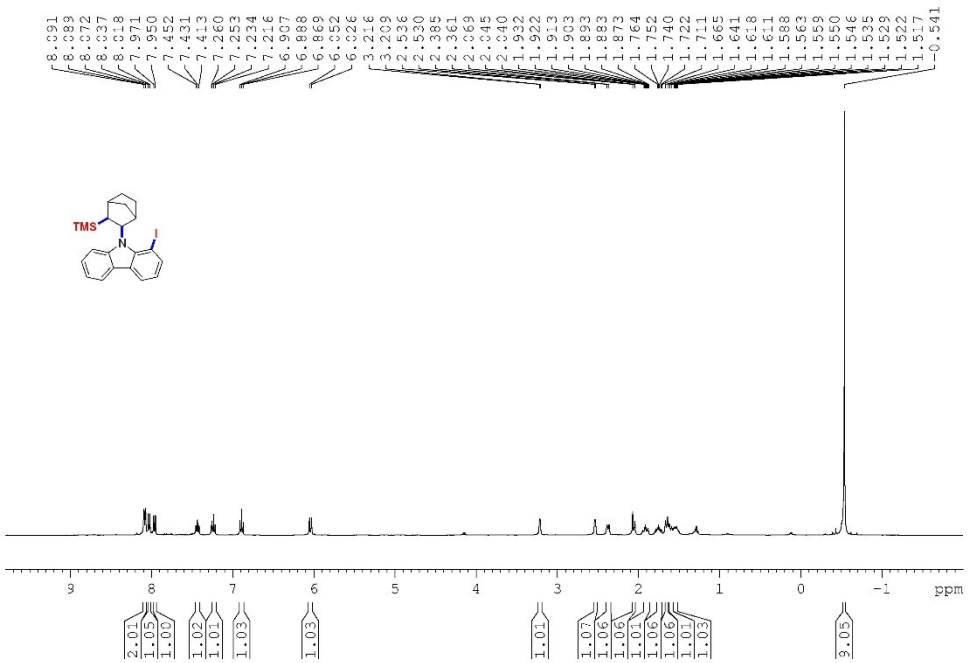


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

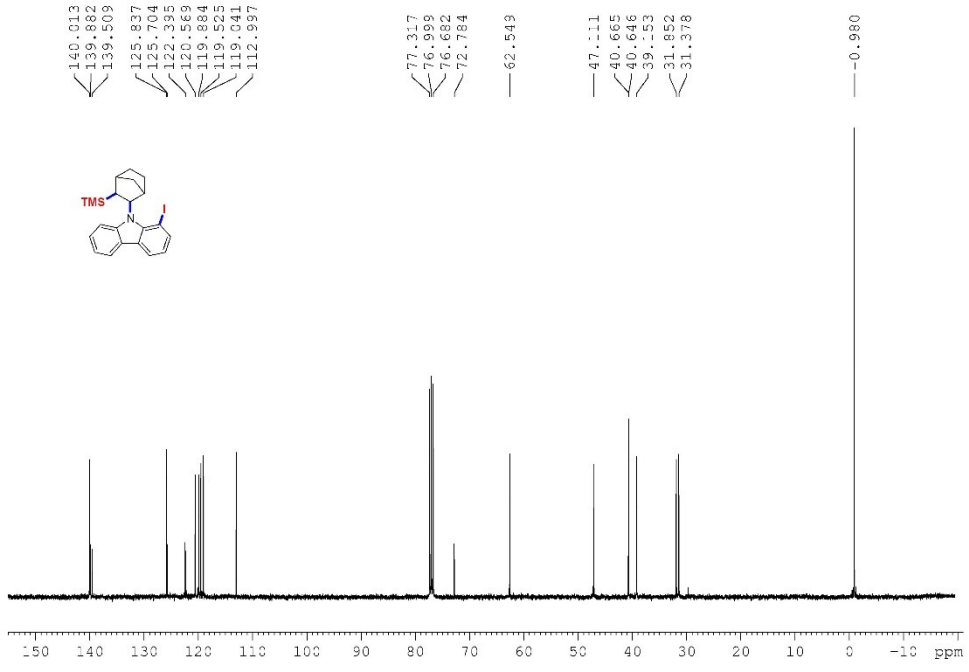


1-iodo-9-((2*R*,3*S*)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)-9*H*-carbazole (6):

^{1}H NMR (400 MHz, CDCl3)

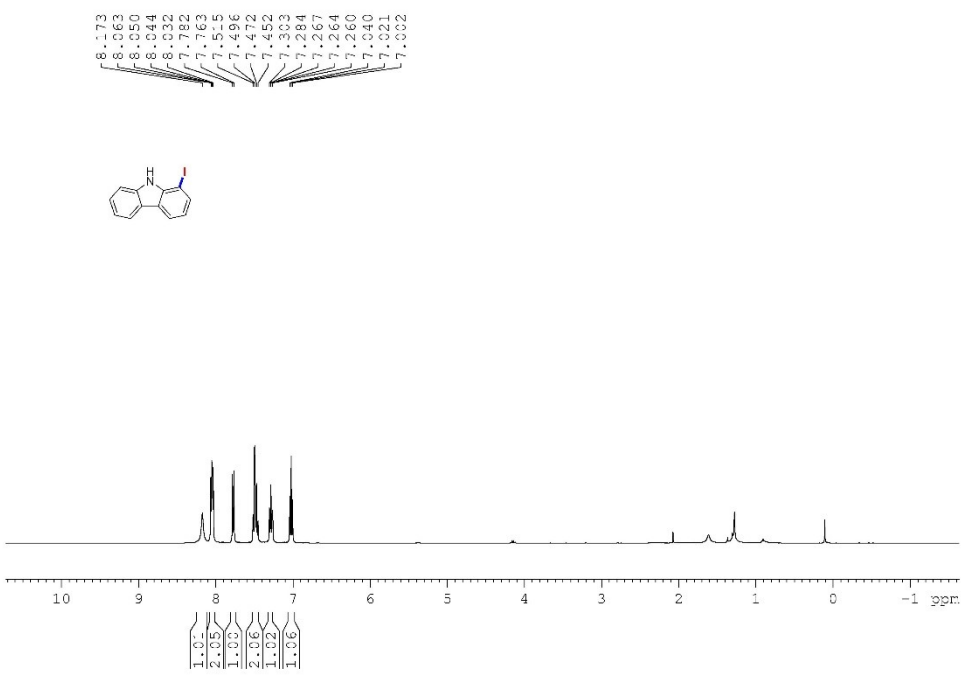


^{13}C{1H} NMR (100 MHz, CDCl3)



1-iodo-9*H*-carbazole (7):

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



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)