

Supplementary Information for:
**Effect of *Ortho*-Biphenyl Substitution on the Excited State Dynamics of
Multi-Carbazole TADF Molecule**

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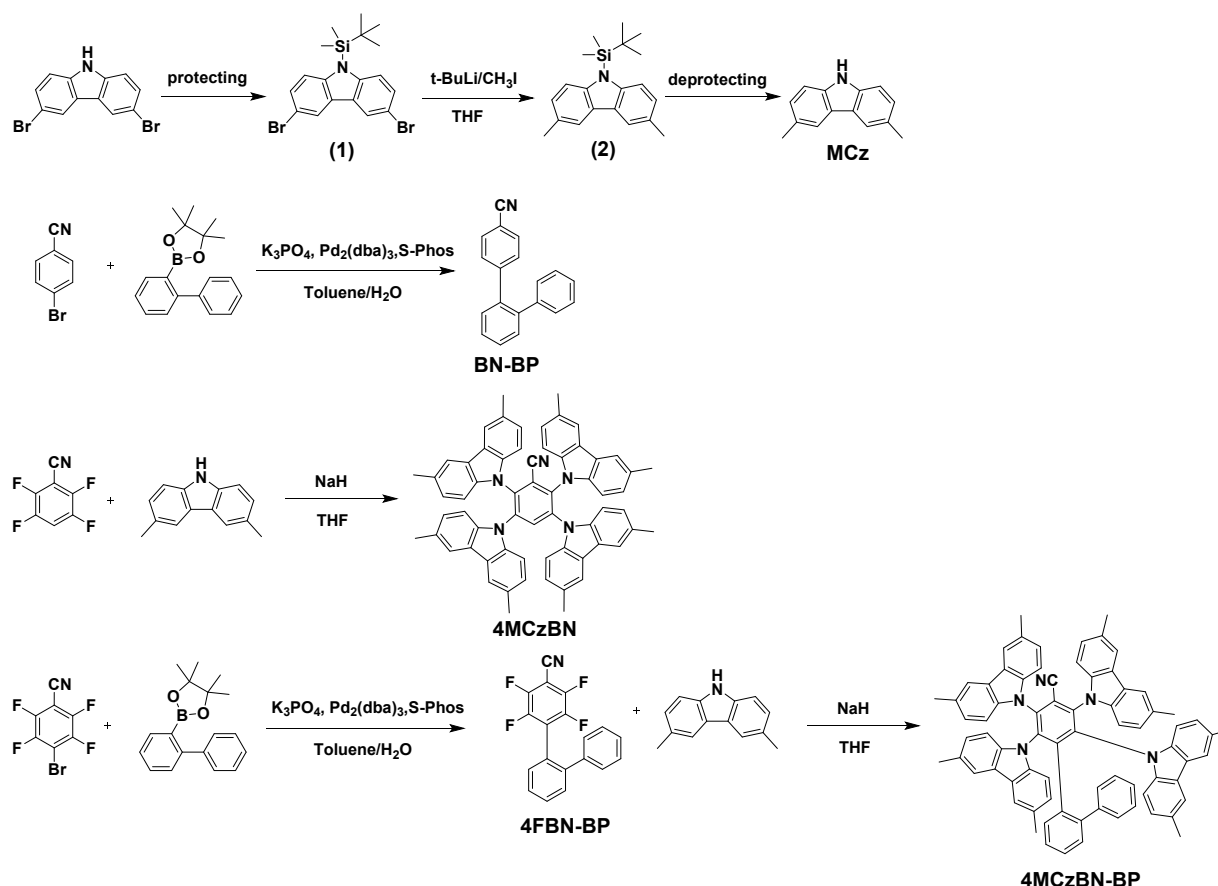
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1. Synthesis of the molecules



Scheme 1. Synthesis of BN-BP, 4mCzBN and 4mCzBN-BP.

Materials. All starting materials were commercially available from Aldrich, Alfa Aesar and TCI and were used without further purification. All solvents were purified prior to use and were purified by passage under a nitrogen atmosphere.

Characterization. ^1H NMR spectra were recorded using a Bruker 300 MHz spectrometer and ^{13}C NMR spectra were recorded using a Bruker DRX 500 MHz spectrometer. High resolution mass analysis was measured using a Joel JMS-700. Thermal analysis was performed using a TA 2050 TGA thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Differential scanning calorimeter (DSC) was conducted under nitrogen atmosphere using a TA instrument 2100 DSC. The samples were heated at $10\text{ }^\circ\text{C}/\text{min}$ from $10\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$. Cyclic voltammetry (CV) was performed at a room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in DMF under nitrogen gas at a scan rate of 50 mV/s . A Pt wire was used as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Synthesis of 3,6-dibromo-9-(tert-butyl(dimethyl)silyl)-9H-carbazole (1).

NaH (60% dispersion in mineral oil, 2.95 g, 73.83 mmol) was slowly added to a solution of 3,6-dibromo-9H-carbazole (20 g, 61.53 mmol) in THF (250 mL) at cooled to $0\text{ }^\circ\text{C}$. After stirring for 30 min, tert-butyl(dimethyl)silyl chloride (11.13 g, 73.83 mmol) was added in one portion, and reaction mixture was stirred at room temperature under nitrogen atmosphere for 3 h. Phases were separated by adding dichloromethane and water to the reaction mixture, and the aqueous layer was extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous MgSO_4 and removed in vacuo. The crude material recrystallized from DCM/hexane to afford the white solid. (20.1 g, 74% yield). ^1H NMR (300 MHz, CDCl_3): $\delta = 8.01$ (t, 2H), 7.35 (d, 4H), 0.91 (s,

9H), 0.63 (s, 6H). ¹³C NMR (500MHz, CDCl₃): δ= 144.26, 128.86, 127.31, 122.94, 115.75, 113.07, 26.65, 20.73, -1.10. ESI-MS *m/z* calcd for C₁₈H₂₁Br₂NSi ([M]⁺) 436.9810, found: 436.9811.

Synthesis of 9-(tert-butyldimethylsilyl)-3,6-dimethyl-9H-carbazole (2).

To a solution of **1** (20 g, 45.53 mmol) in freshly distilled THF, *n*-BuLi (107.13 mL, 1.7 M in hexane, 182.12 mmol) was slowly added at -78 °C. After stirring for 3 h at 0 °C, 14.2 mL of methyl iodide (227.65 mmol) was added at -78 °C. The suspension was warmed to room temperature and was stirred overnight. After adding 1 M HCl to the reaction mixture, phases were separated and the organic layer was washed with 1 M HCl and distilled water, then dried over anhydrous MgSO₄, and removed in vacuo. The crude material was recrystallized from DCM/hexane to afford the white solid. (12.5 g, 88% yield). ¹H NMR (300 MHz, CDCl₃): δ = 7.84 (s, 2H), 7.48 (d, 2H), 7.19-7.16 (dd, 2H), 2.52 (s, 6H), 1.05 (s, 9H), 0.74 (s, 6H). ¹³C NMR (500MHz, CDCl₃): δ= 143.68, 128.78, 126.74, 126.58, 126.52, 125.25, 119.98, 119.92, 119.51, 114.20, 113.91, 113.84, 26.81, 21.39, 20.82, -1.15. ESI-MS *m/z* calcd for C₂₀H₂₇NSi ([M]⁺) 309.1913, found: 309.1913.

Synthesis of 3,6-dimethyl-9H-carbazole (mCz).

Compound **2** (12 g, 38.76 mmol) was dissolved in toluene (70 mL), and TBAF (1.0 M THF solution, 58.14 mL) was added. The solution was stirred under nitrogen atmosphere for 30 min. After adding NH₄Cl (aq) to the reaction mixture, phases were separated and the aqueous layer was extracted with toluene. The combined organic layers were dried over anhydrous MgSO₄ and removed in vacuo. The crude material was recrystallized from DCM/hexane to afford the white solid (mCz). (6.9 g, 91% yield). ¹H NMR (300 MHz, DMSO-*d*₆): δ = 10.93 (s, 1H), 7.84 (s, 2H), 7.34(d, 2H), 7.19-7.15 (dd, 2H), 2.45 (s, 6H). ¹³C NMR (500MHz, CDCl₃): δ= 138.24, 128.67, 127.17, 123.59, 120.37, 110.42, 21.63. ESI-MS *m/z* calcd for C₁₄H₁₃N ([M]⁺) 195.1048, found: 195.1044.

Synthesis of [1,1':2',1''-terphenyl]-4-carbonitrile (BN-BP).

A Schlenk flask was charged with 4-bromobenzonitrile (1 g, 5.49 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.84 g, 6.59 mmol), 2-dicyclohexyl phosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.33 g, 0.82 mmol) and K₃PO₄ (3.49 g, 16.48 mmol) was dissolved in toluene/H₂O (5:1) and degassed with nitrogen for 30 min. After adding Pd₂(dba)₃ (0.15 g, 0.16 mmol), the mixture was heated to 90 °C under nitrogen atmosphere for 12 h. After cooling down to room temperature, dichloromethane and water was added to the reaction mixture. The phases were separated, and the aqueous layer was extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous MgSO₄ and removed in vacuo. The crude material was isolated by silica gel column chromatography using DCM/*n*-hexane (1:6) as eluent to afford a white solid (BN-p-BP). (1.09 g, 77% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.56-7.46 (m, 6H), 7.30-7.26 (m, 5H), 7.16-7.13 (m, 2H). ¹³C NMR (500MHz, CDCl₃): δ=146.66, 140.87, 138.82, 131.91, 131.06, 130.74, 130.44, 130.01, 128.78, 128.37, 127.97, 127.16, 119.16, 110.44. ESI-MS *m/z* calcd for C₁₄H₁₃N ([M]⁺) 255.1048, found: 255.1045.

Synthesis of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)benzonitrile (4mCzBN).

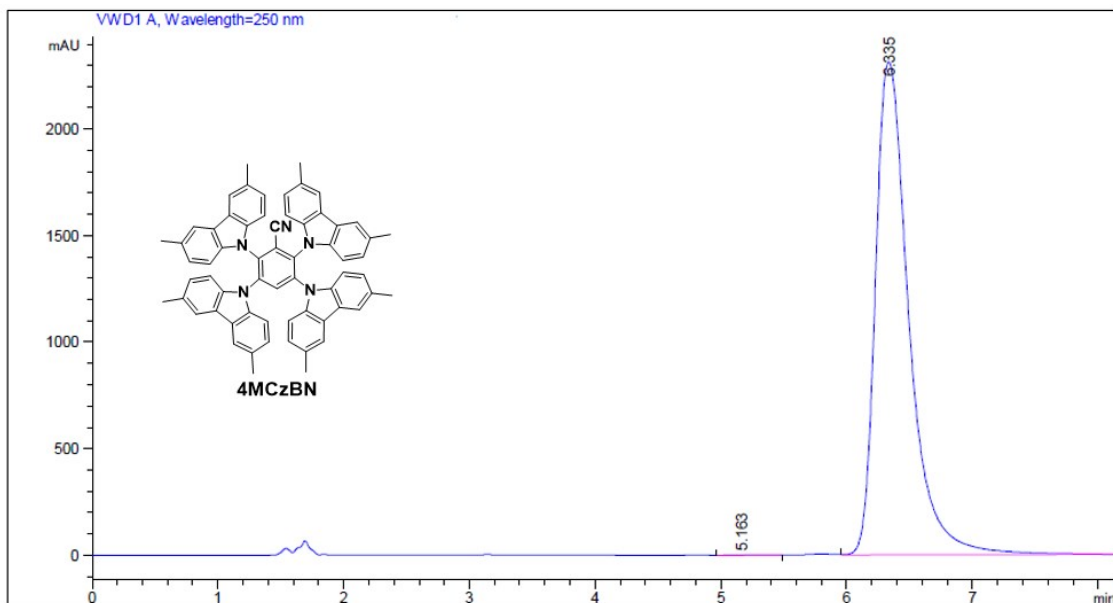
NaH (60% dispersion in mineral oil, 0.8 g, 19.99 mmol) was slowly added to a solution of 3,6-dimethyl-9H-carbazole (2.78 g, 14.27 mmol) in THF (50 mL) at 0 °C. After stirring for 30 min, 2,3,5,6-tetrafluorobenzonitrile (0.5 g, 2.85 mmol) was added in one portion and reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. The excess NaH of reaction mixture was quenched with water and washed with water for three times. The crude material was isolated by silica gel column chromatography using chloroform/*n*-hexane (1:1) as eluent to give a yellow solid (4mCzBN). (2.1 g, 83% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.29 (s, 1H), 7.71-7.66 (d, 8H), 7.36-7.30 (t, 8H), 7.16-7.04(dd, 8H), 2.46-2.43 (d, 24H). ¹³C NMR (500MHz, CDCl₃): δ= 138.51, 137.98, 137.24, 136.67, 130.48, 130.30, 127.13, 1243.65, 124.43, 120.62, 120.43, 118.05, 1130.12, 109.80, 109.34, 21.54, 21.47. HRMS (FAB) [M]⁺ calcd for C₆₃H₄₉N₅, 875.3988 (m/z); Found, 875.3986.

Synthesis of 2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (4FBN-BP).

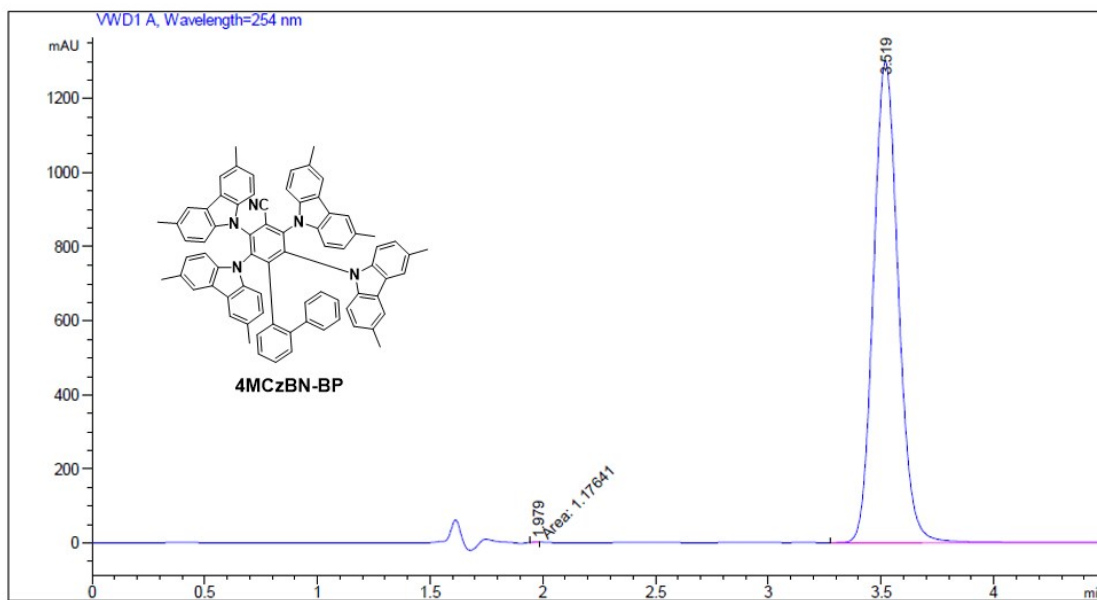
A Schlenk flask was charged with 4-bromo-2,3,5,6-tetrafluorobenzonitrile (1 g, 3.93 mmol), 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.32 g, 4.72 mmol), 2-dicyclohexyl phosphino-2',6'-dimethoxybiphenyl (S-Phos) (0.24 g, 0.59 mmol) and K_3PO_4 (2.5 g, 11.81 mmol) was dissolved in toluene/ H_2O (5:1) and degassed with nitrogen for 30 min. After adding $Pd_2(dba)_3$ (0.11 g, 0.12 mmol), the mixture was heated to 90 °C under nitrogen atmosphere for 12 h. After cooling down to room temperature, dichloromethane and water was added to the reaction mixture. The phases were separated and the aqueous layer was extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and removed in vacuo. The crude material was isolated by silica gel column chromatography using DCM/n-hexane (1:6) as eluent to give a white solid (4FBN-BP). (0.78 g, 77% yield). 1H NMR (300 MHz, CD_2Cl_2): δ = 7.69-7.63 (m, 1H), 7.59-7.53 (m, 2H), 7.42-7.39 (d, 1H), 7.33-7.31 (m, 3H), 7.18-7.15 (m, 2H). ^{13}C NMR (500MHz, $CDCl_3$): 148.78, 148.55, 145.54, 145.31, 145.08, 142.78, 142.23, 142.07, 139.82, 130.58, 130.55, 130.45, 128.47, 128.39, 127.87, 127.64, 124.38, 107.56, 93.20. ESI-MS m/z calcd for $C_{19}H_9F_4N$ ($[M]^+$) 327.0671, found: 327.0673.

Synthesis of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)-[1,1':2',1''-terphenyl]-4-carbonitrile (4mCzBN-BP).

NaH (60% dispersion in mineral oil, 0.42 g, 10.64 mmol) was slowly added to a solution of 3,6-dimethyl-9H-carbazole (1.92 g, 9.84 mmol) in THF (50 mL) at 0 °C. After stirring for 30 min, 2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (0.5 g, 1.52 mmol) was added in one portion and reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. The excess NaH of reaction mixture was quenched with water and washed with water three times. The crude material was isolated by silica gel column chromatography using chloroform/n-hexane (1:1) as eluent to give a yellow solid (4mCzBN-BP). (1.62 g, 80% yield). 1H NMR (300 MHz, CD_2Cl_2): δ = 7.62 (s, 2H), 7.53 (d, 4H), 7.43-7.40 (d, 2H), 7.34-7.30 (m, 5H), 7.25-7.20 (m, 4H), 7.11-7.08 (m, 4H), 6.91-6.88 (d, 2H), 6.84-6.76 (m, 5H), 6.42-6.36 (m, 1H), 6.32-6.28 (d, 2H), 6.23-6.21 (d, 2H), 2.49 (s, 6H), 2.43 (s, 6H), 2.34 (s, 6H), 2.21 (s, 6H). ^{13}C NMR (500MHz, $CDCl_3$): 149.97, 141.71, 140.56, 139.28, 139.22, 138.80, 138.18, 138.07, 131.07, 130.91, 130.30, 130.12, 129.80, 129.65, 129.20, 129.04, 128.82, 128.65, 127.54, 126.73, 126.31, 126.25, 126.15, 124.57, 124.36, 124.20, 123.22, 120.34, 120.01, 119.90, 118.86, 117.92, 112.82, 110.49, 110.34, 110.12, 110.02, 21.55, 21.47, 21.41, 21.24. HRMS (FAB) $[M+H]^+$ calcd for $C_{75}H_{57}N_5$, 1027.4614 (m/z); Found, 1028.4706.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.163	BB	0.2292	6.21236	3.83002e-1	0.0145
2	6.335	VBA	0.2799	4.28105e4	2313.58301	99.9855



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.979	MM	0.0505	1.17641	3.88037e-1	0.0118
2	3.519	BBA	0.1194	9966.38965	1300.05554	99.9882

Figure 1. HPLC data of 4mCzBN and 4mCzBN-BP.

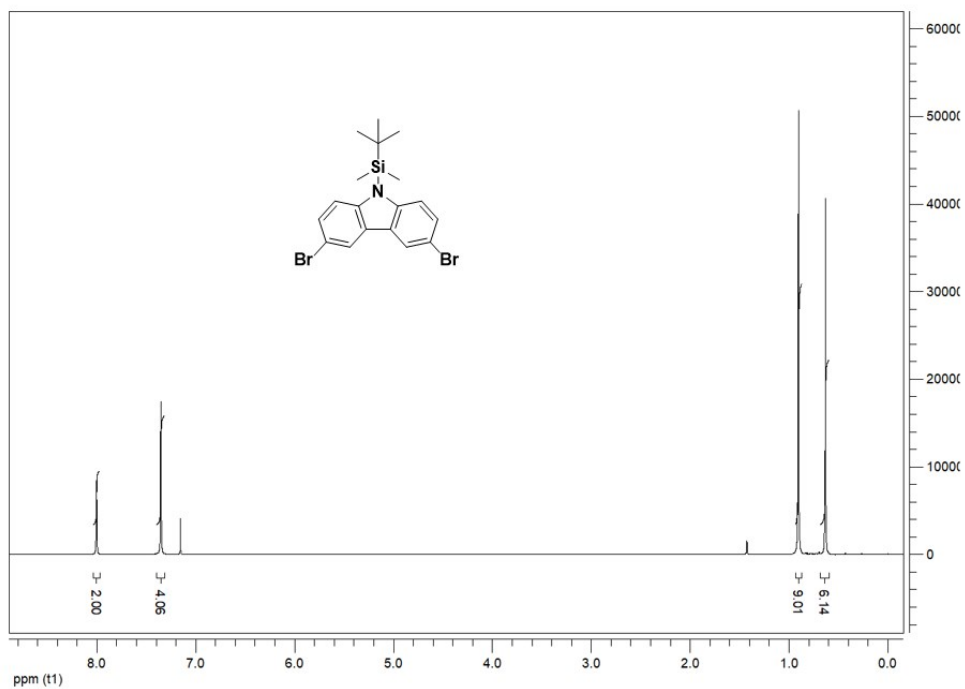


Figure 2. ^1H NMR spectrum of 3,6-dibromo-9-(tert-butyldimethylsilyl)-9H-carbazole.

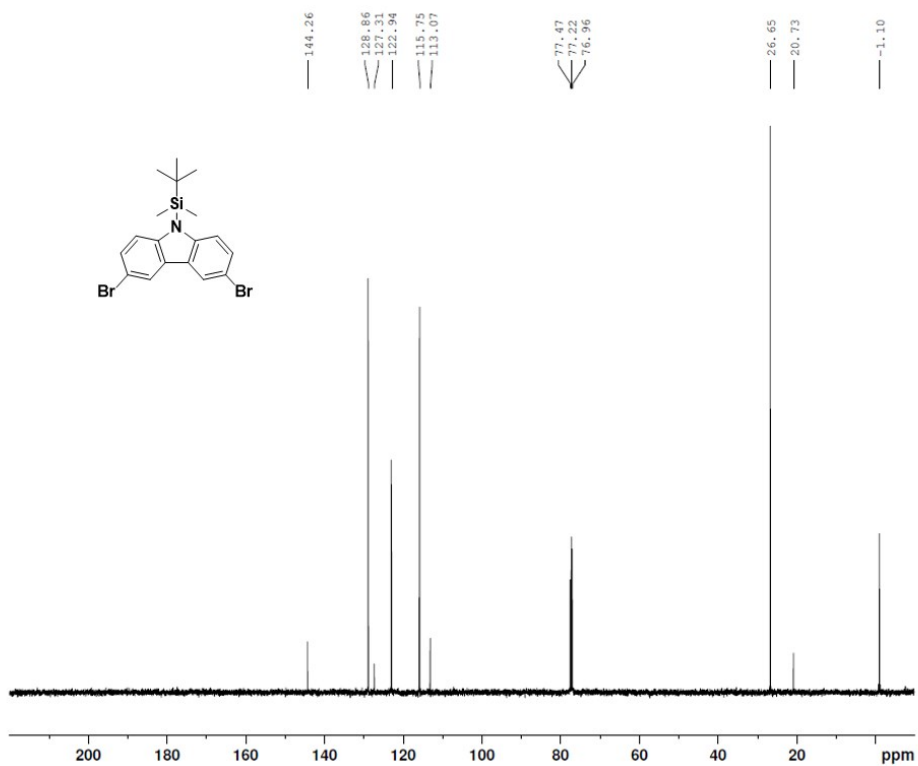


Figure 3. ^{13}C NMR spectrum of 3,6-dibromo-9-(tert-butyldimethylsilyl)-9H-carbazole.

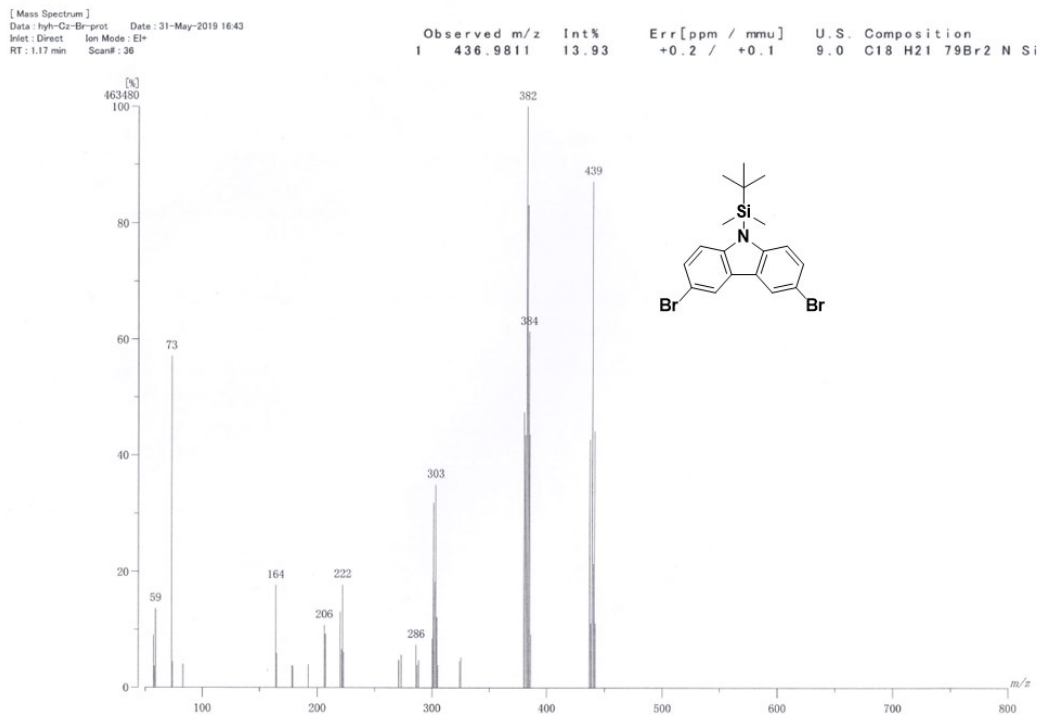


Figure 4. MASS spectrum of 3,6-dibromo-9-(tert-butyldimethylsilyl)-9H-carbazole.

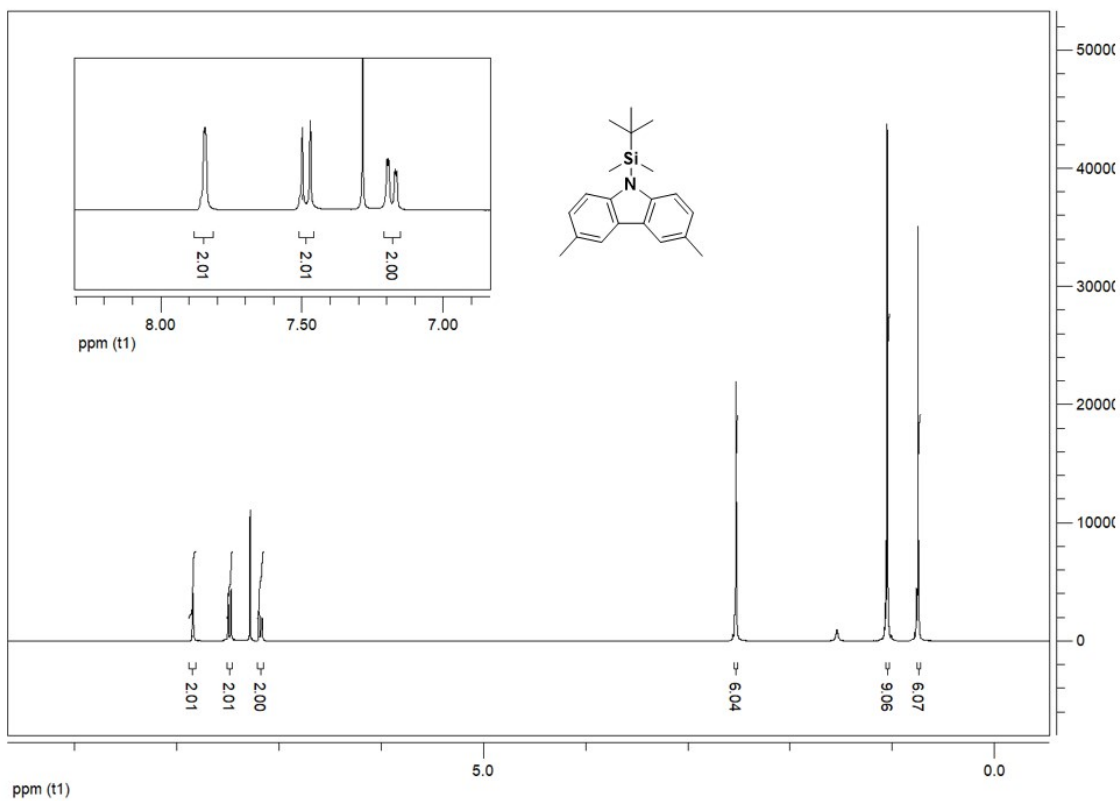


Figure 5. ¹H NMR spectrum of 9-(tert-butyldimethylsilyl)-3,6-dimethyl-9H-carbazole.

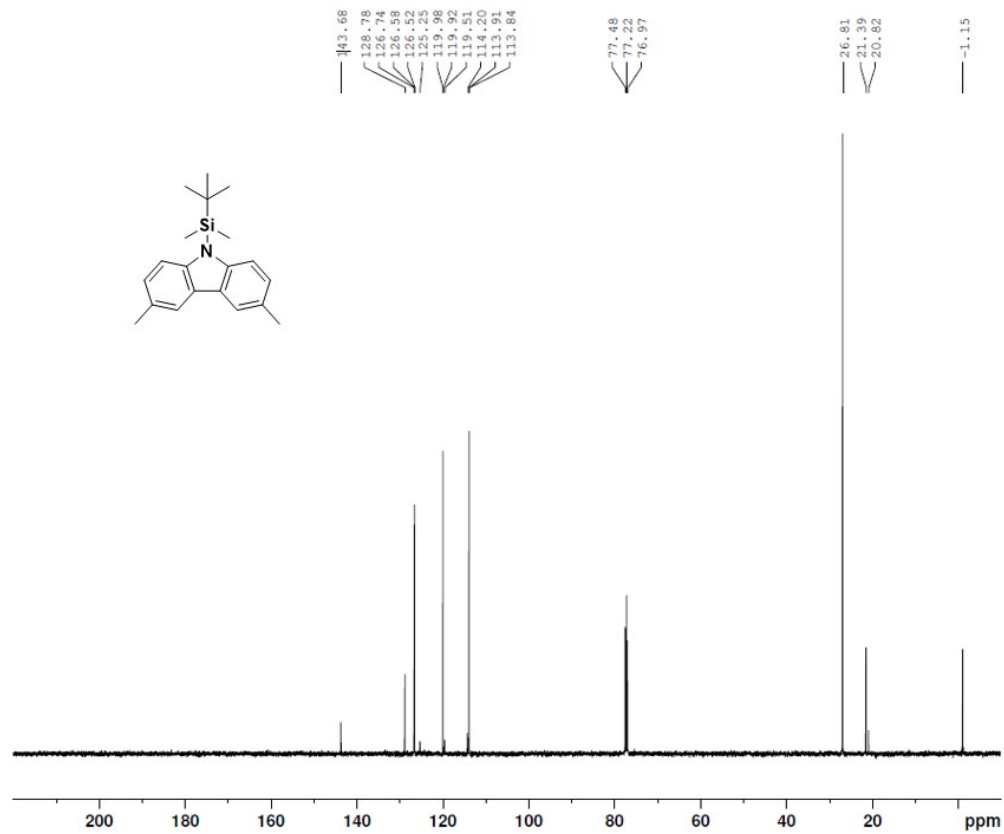


Figure 6. ¹³C NMR spectrum of 9-(tert-butyldimethylsilyl)-3,6-dimethyl-9H-carbazole.

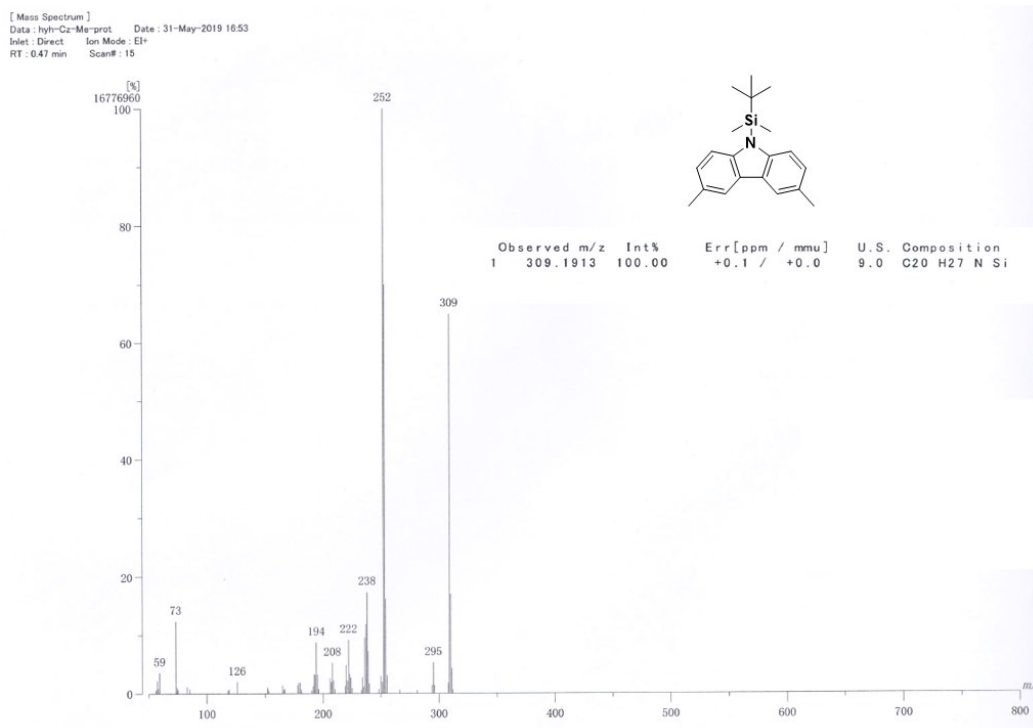


Figure 7. MASS spectrum of 9-(tert-butyldimethylsilyl)-3,6-dimethyl-9H-carbazole.

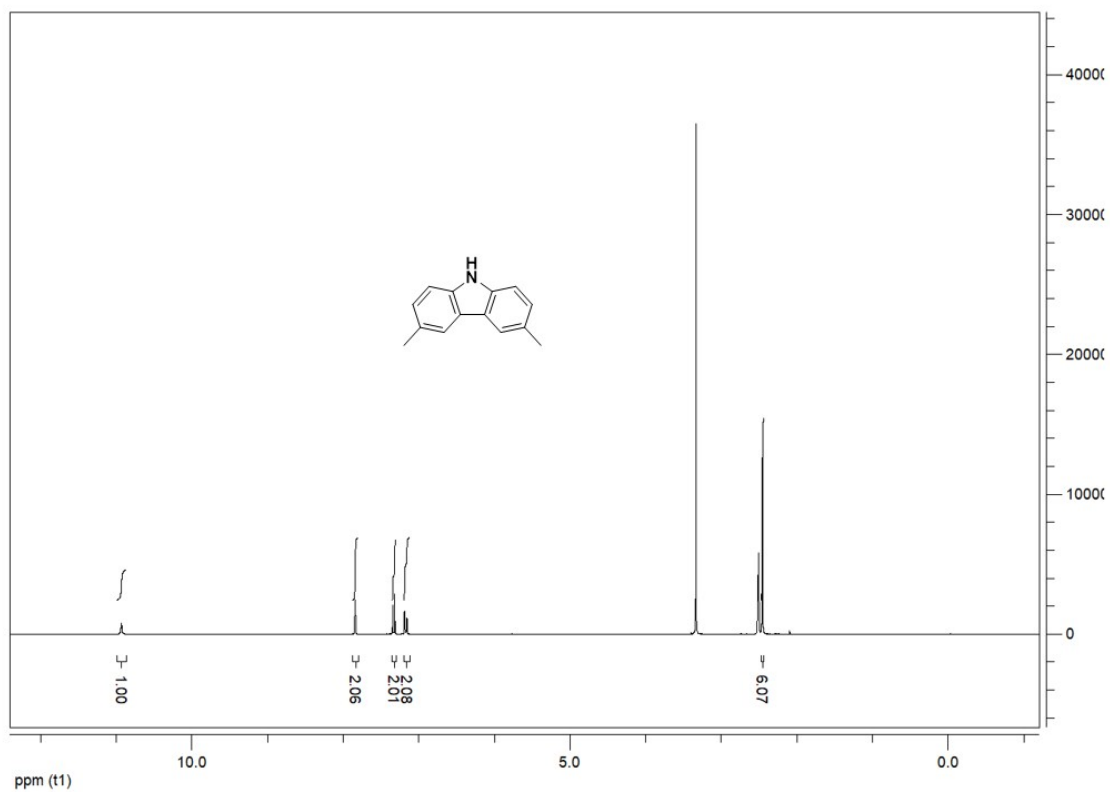


Figure 8. ¹H NMR spectrum of 3,6-dimethyl-9H-carbazole (mCz).

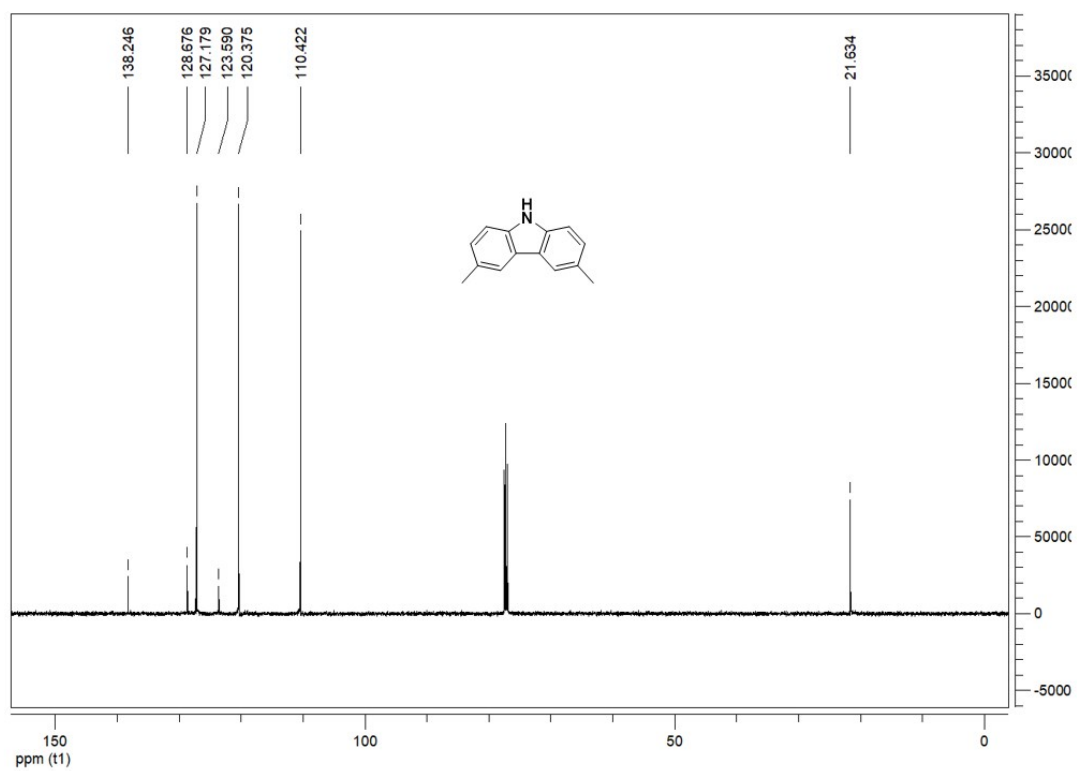


Figure 9. ¹³C NMR spectrum of 3,6-dimethyl-9H-carbazole (mCz).

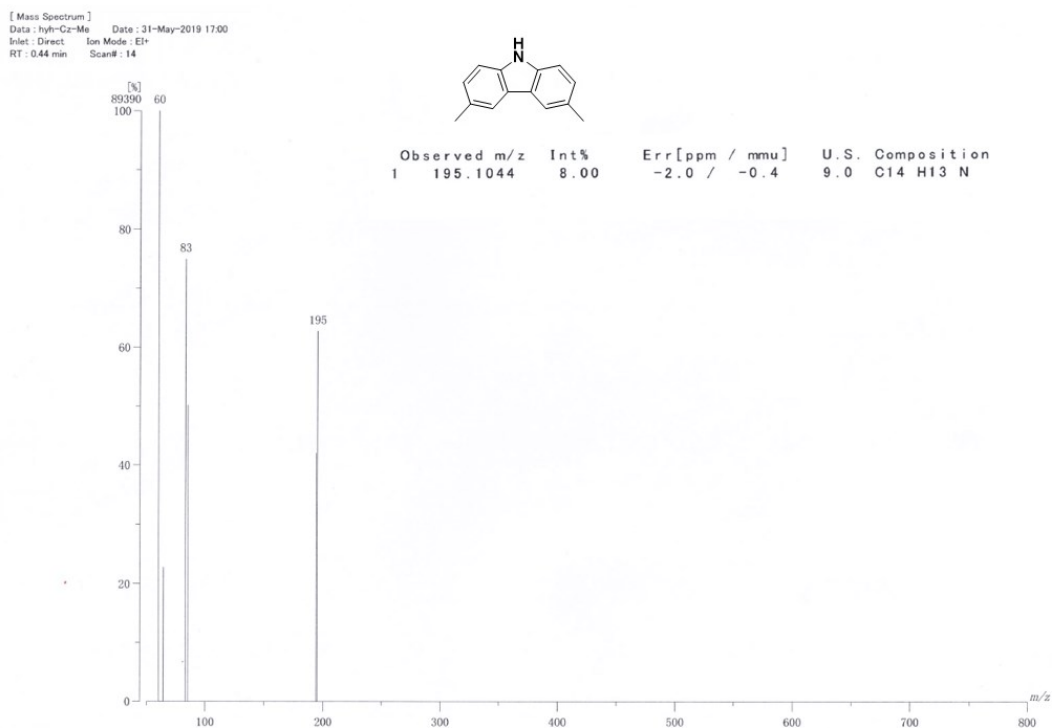


Figure 10. MASS spectrum of 3,6-dimethyl-9H-carbazole (mCz).

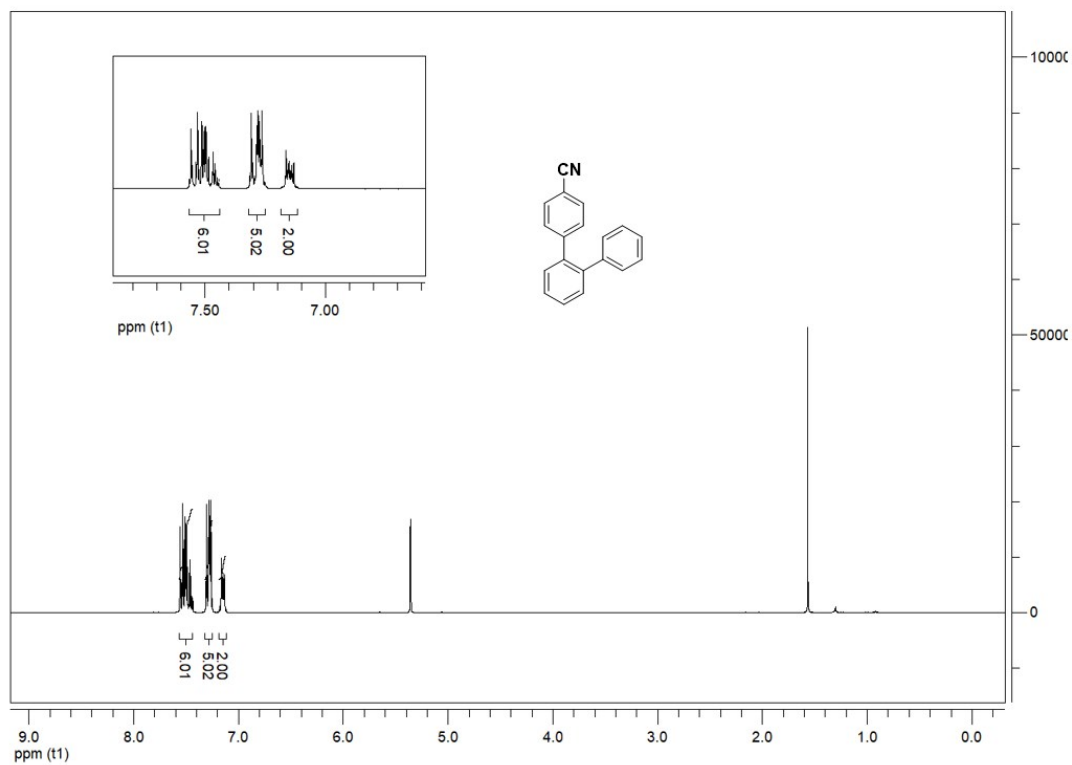


Figure 11. ¹H NMR spectrum of [1,1':2',1''-terphenyl]-4-carbonitrile (BN-BP).

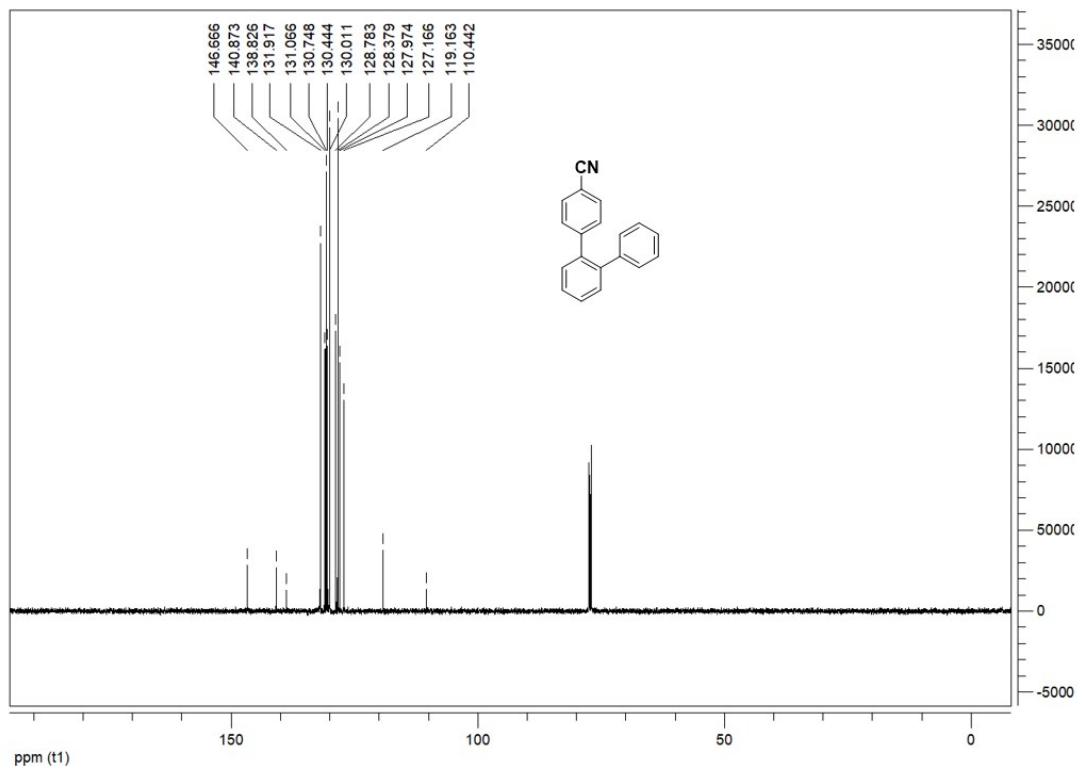


Figure 12. ^{13}C NMR spectrum of [1,1':2',1''-terphenyl]-4-carbonitrile (BN-BP).

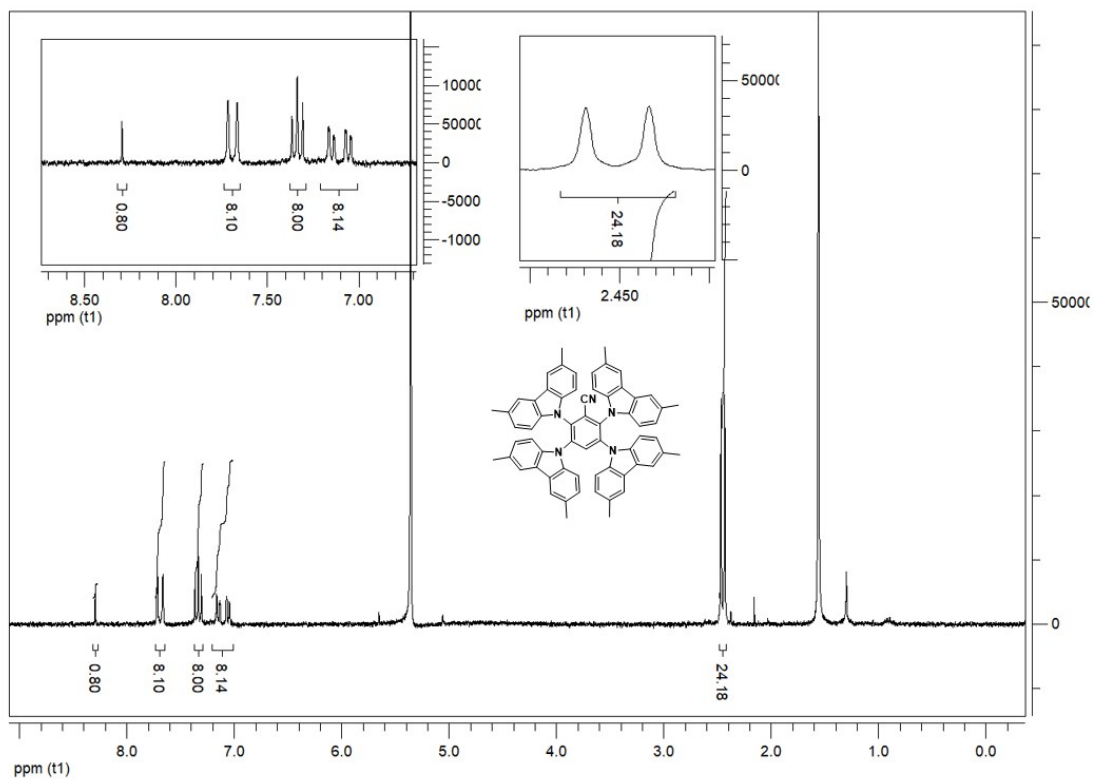


Figure 13. ^1H NMR spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)benzonitrile (4mCzBN).

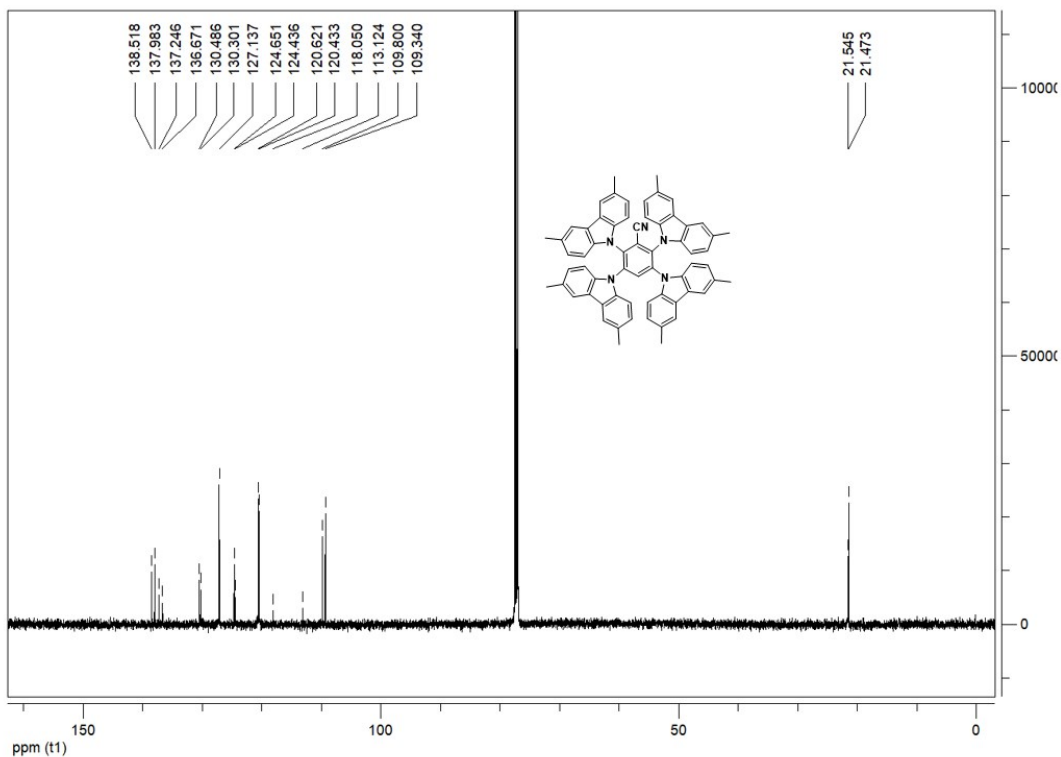


Figure 14. ^{13}C NMR spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)benzonitrile (4mCzBN).

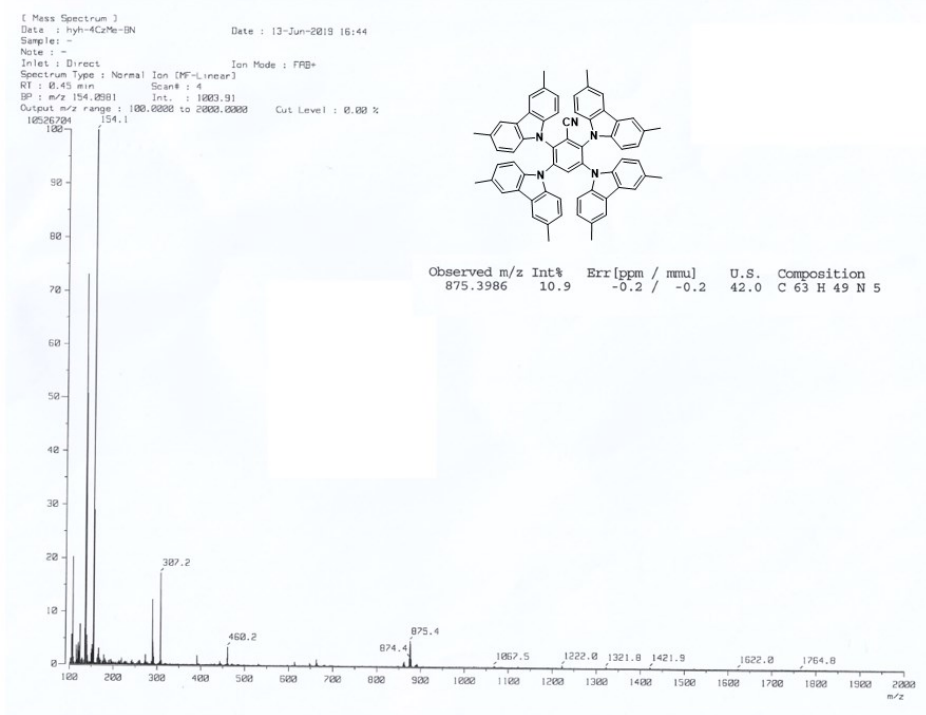


Figure 15. MASS spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)benzonitrile (4mCzBN).

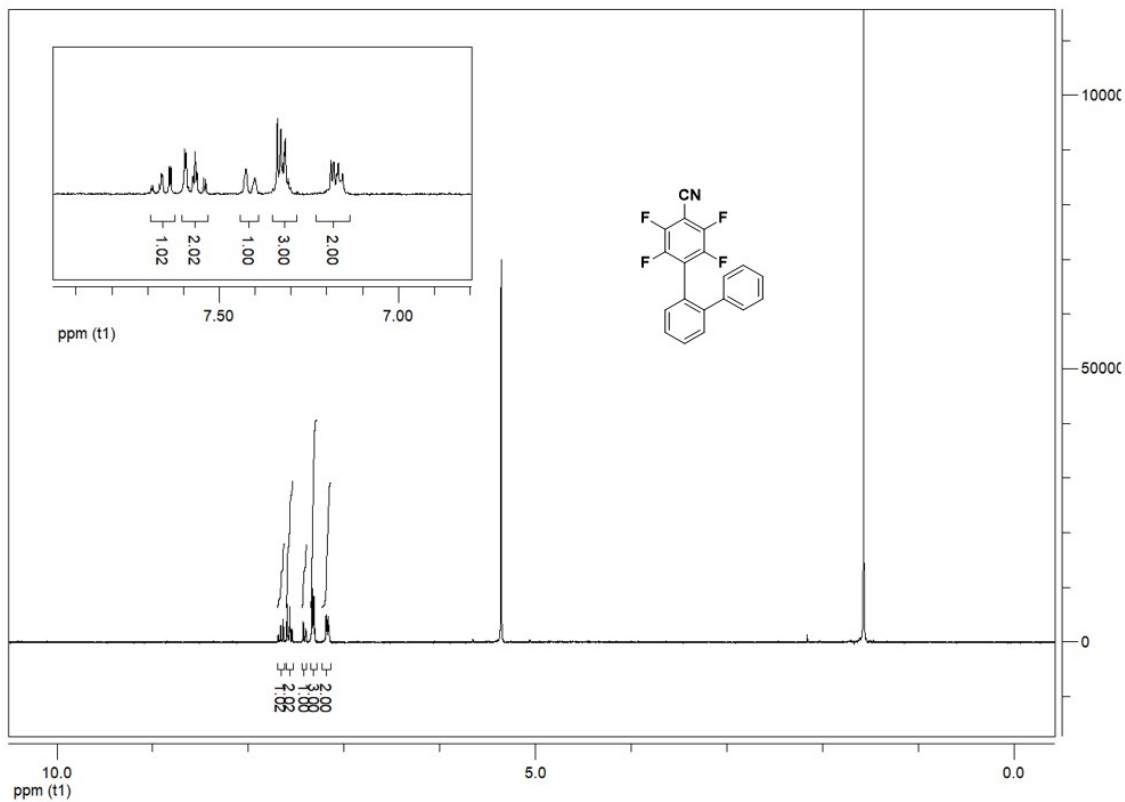


Figure 16. ¹H NMR spectrum of 2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (4FBN-BP).

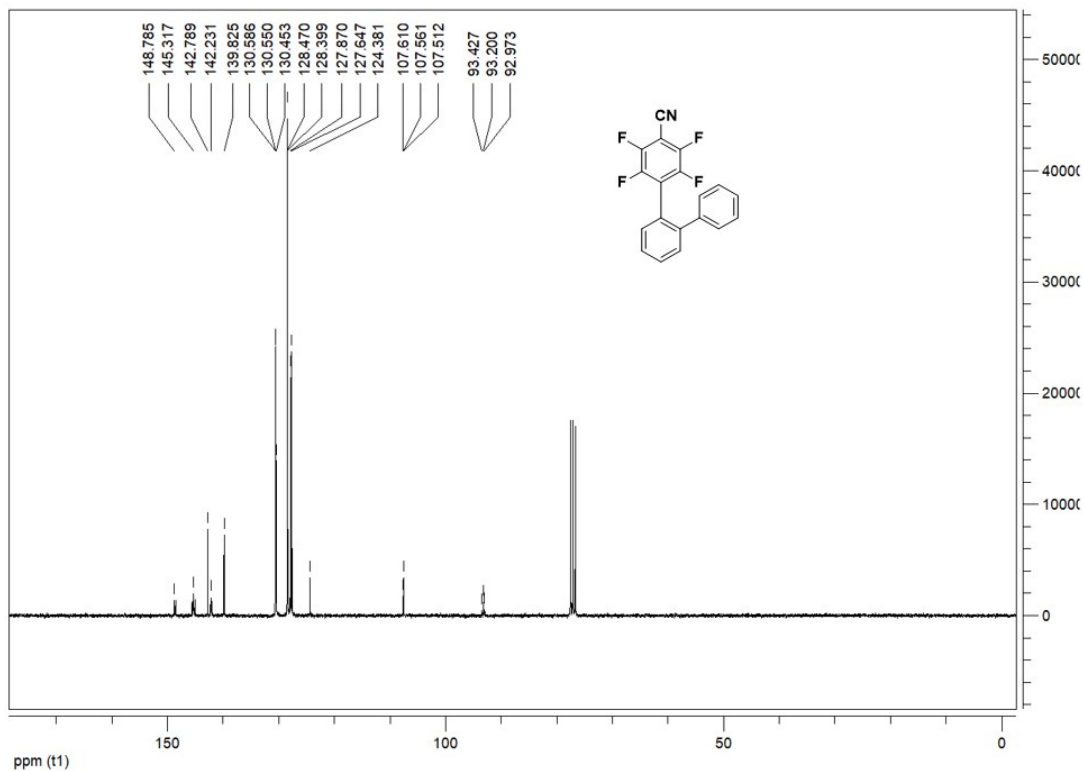


Figure 17. ¹³C NMR spectrum of 2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (4FBN-BP).

[Mass Spectrum]
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 Inlet : Direct Ion Mode : EI-
 RT : 0.07 min Scan# : 3

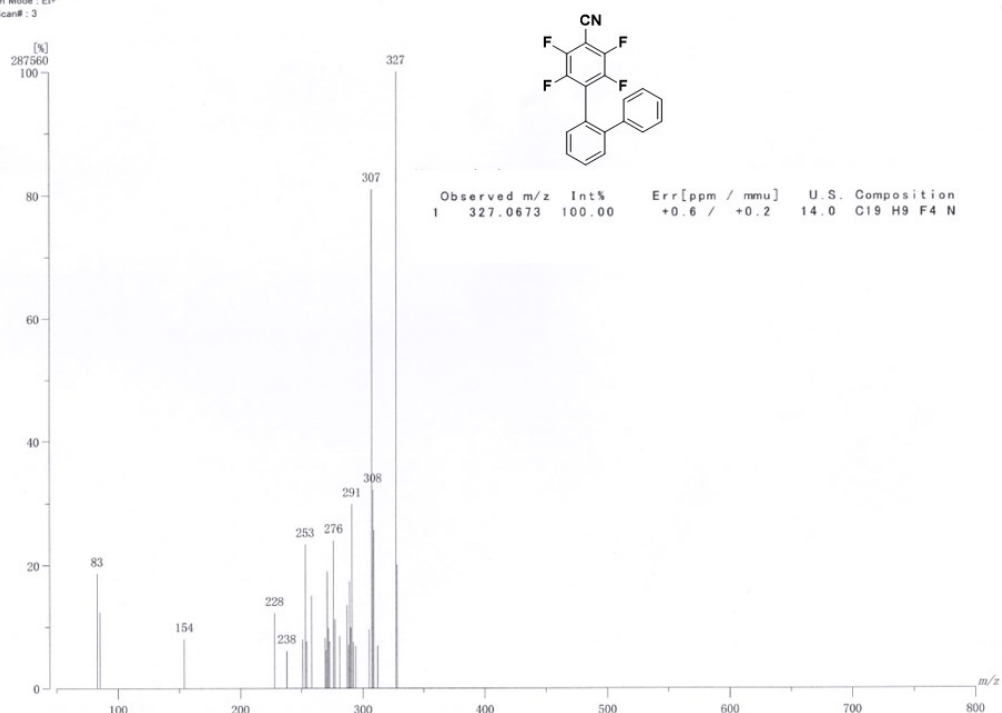


Figure 18. MASS spectrum of 2,3,5,6-tetrafluoro-[1,1':2',1''-terphenyl]-4-carbonitrile (4FBN-BP).

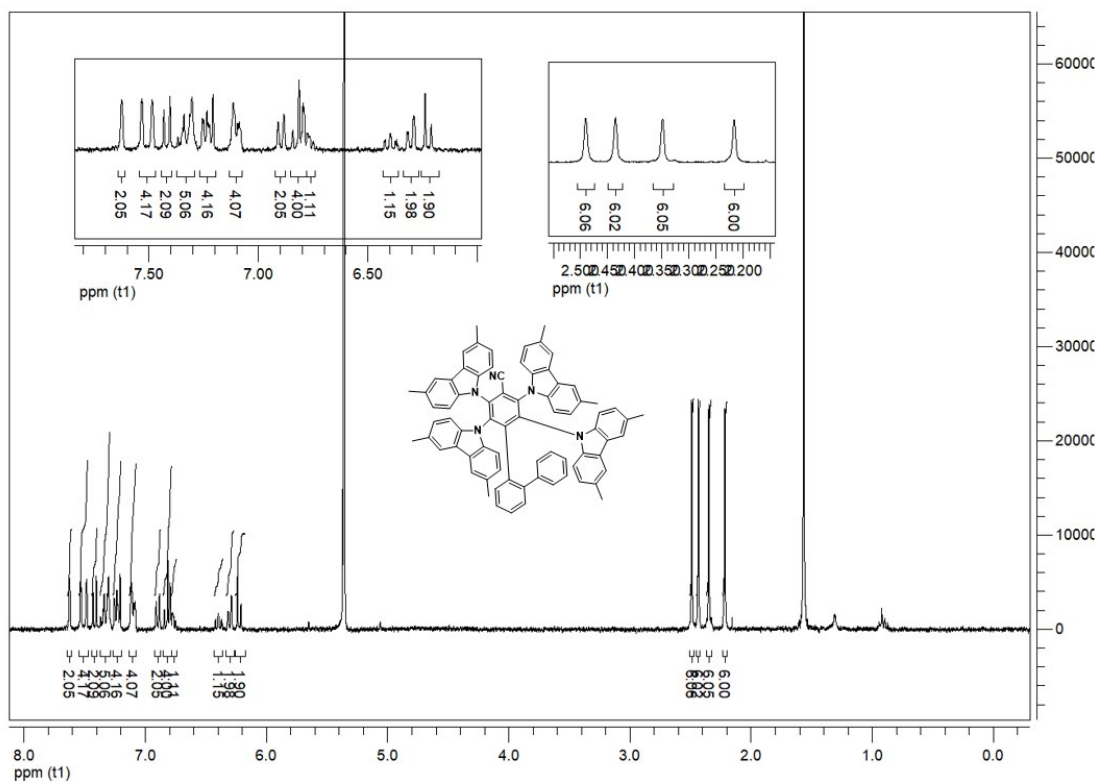


Figure 19. ¹H NMR spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)-[1,1':2',1''-terphenyl]-4-carbonitrile (4mCzBN-BP).

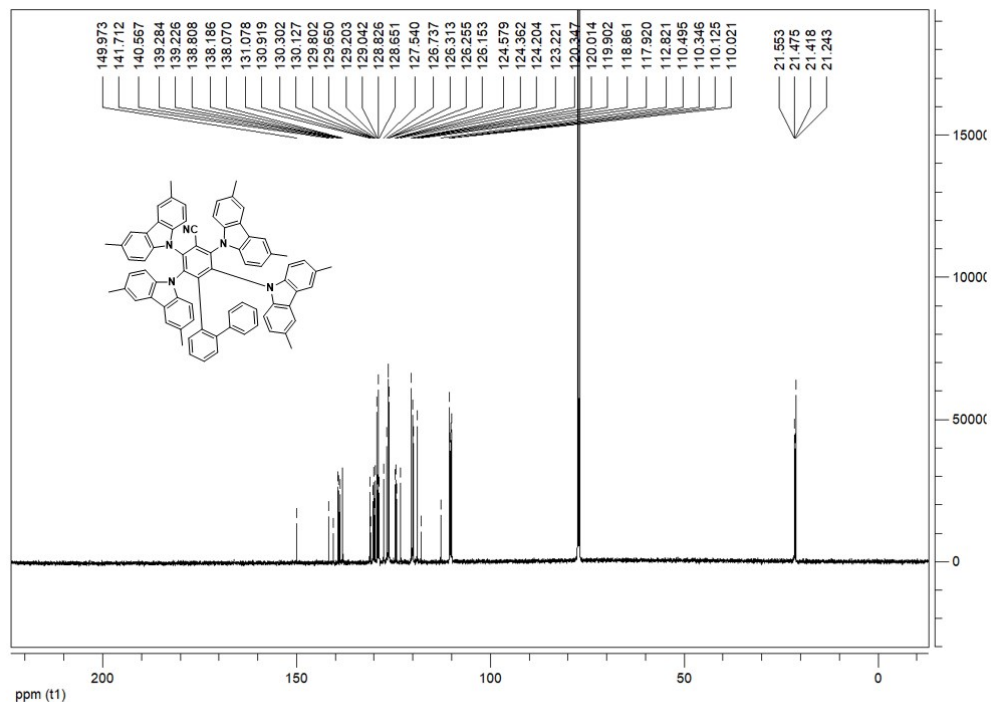


Figure 20. ^{13}C NMR spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)-[1,1':2',1''-terphenyl]-4-carbonitrile (4mCzBN-BP).

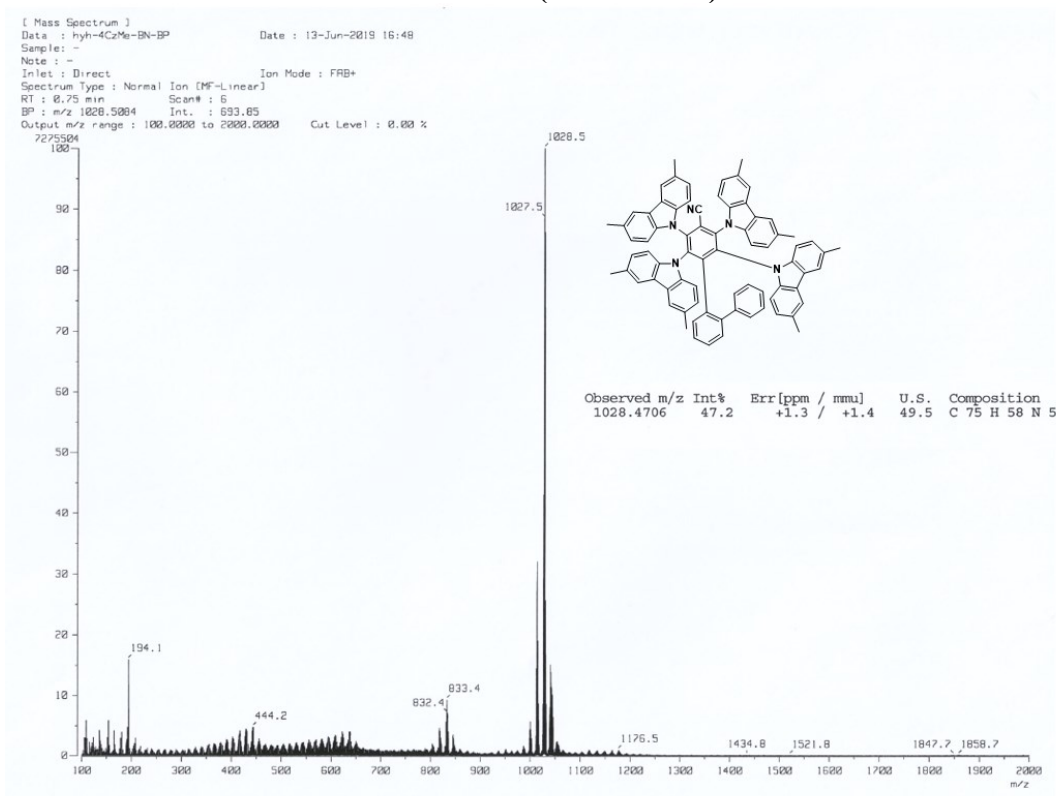


Figure 21. MASS spectrum of 2,3,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)-[1,1':2',1''-terphenyl]-4-carbonitrile (4mCzBN-BP).

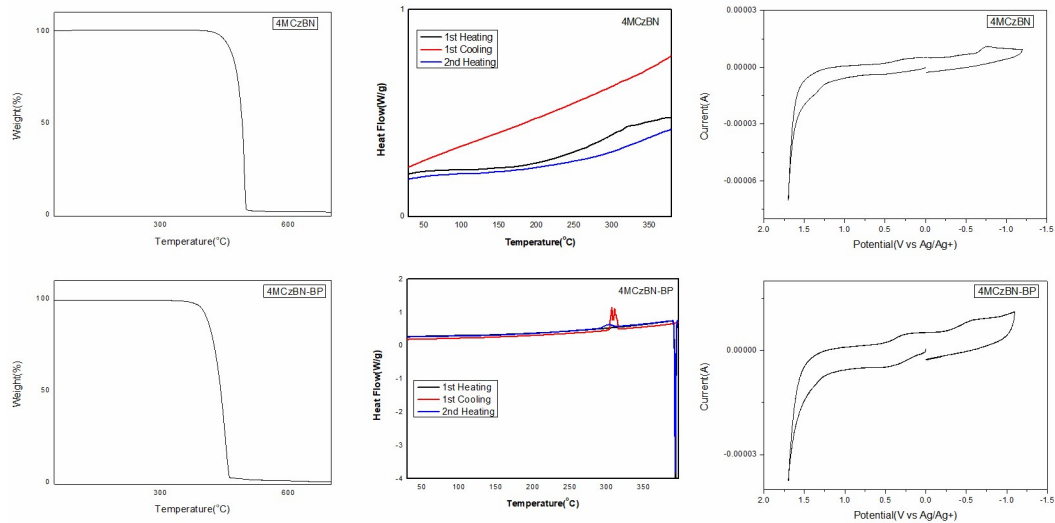


Figure 22. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC, and cyclic voltammetry results of 4mCzBN and 4mCzBN-BP.

2. Supplementary Figures

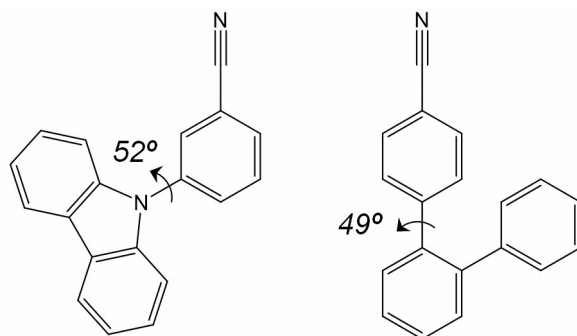


Figure S1. Dihedral angle of carbazole-benzonitrile and biphenyl-benzonitrile at ground state.

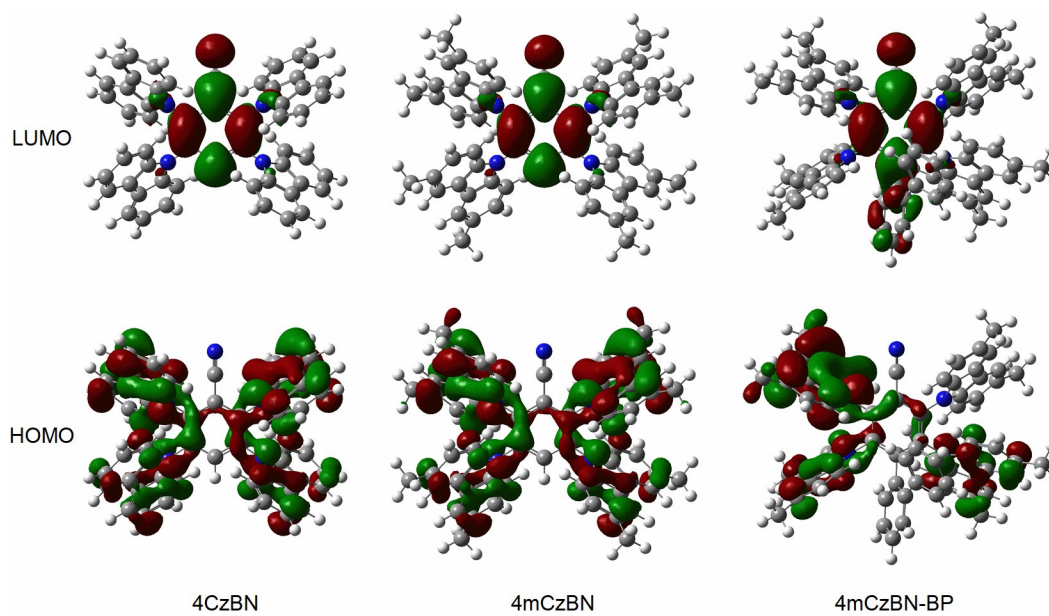


Figure S2. HOMO and LUMO of the TADF molecules.

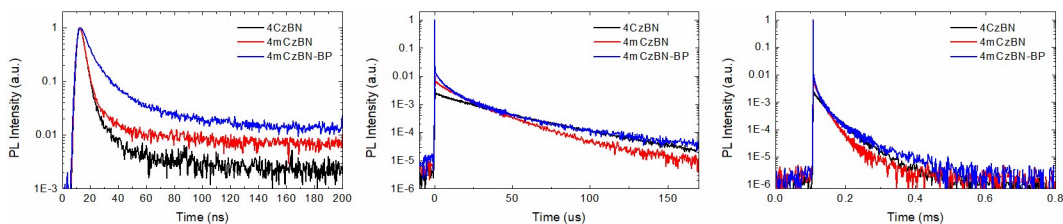


Figure S3. Transient decay curves of the TADF molecules in mCBP (10 wt%).

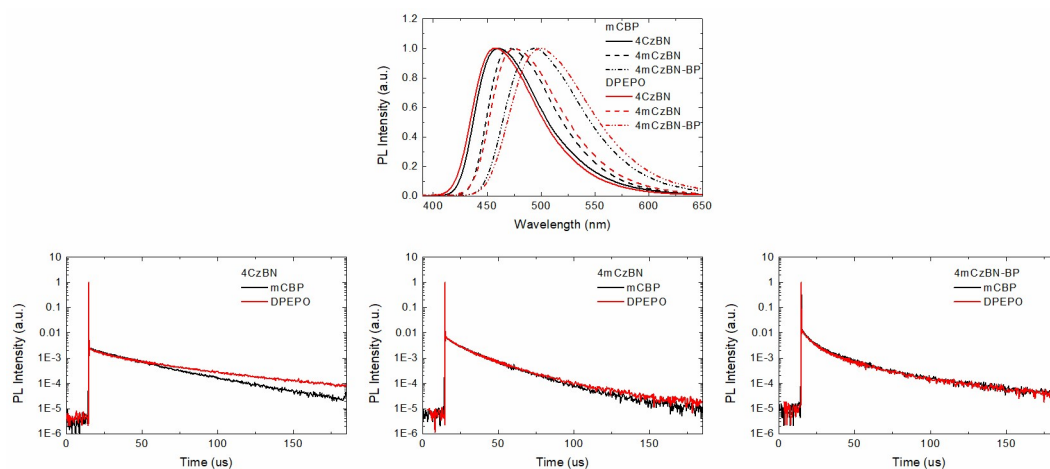


Figure S4. Transient decay curves of the TADF molecules in mCBP and DPEPO (10 wt%). Similar multiexponential decay was observed from TADF:DPEPO films. DPEPO host is not excited by the 337 nm laser and the T_1 of DPEPO is higher than 3.0 eV. DPEPO host do not participate in the excited state dynamics of the TADF-doped film. Therefore, the multiexponential decay is not caused by processes such as energy transfer from the host to the TADF dopant.

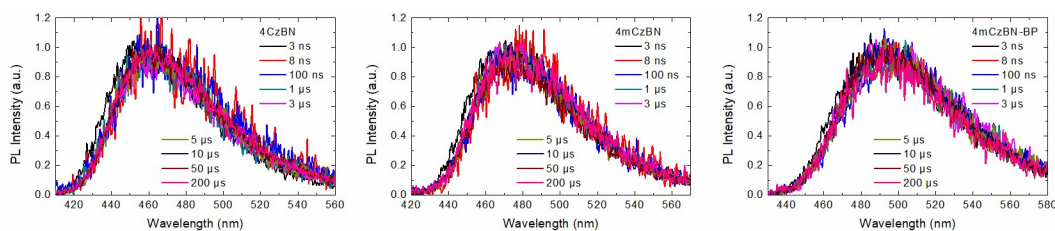


Figure S5. Time resolved spectra of the TADF molecules in mCBP (10 wt%).

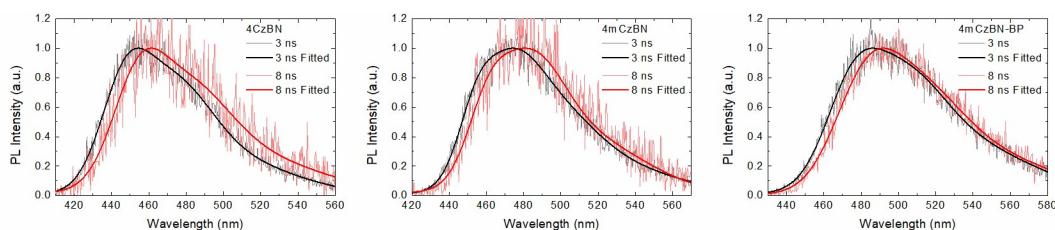


Figure S6. Time resolved spectra of TADF molecules in mCBP with fitted gaussian curves.

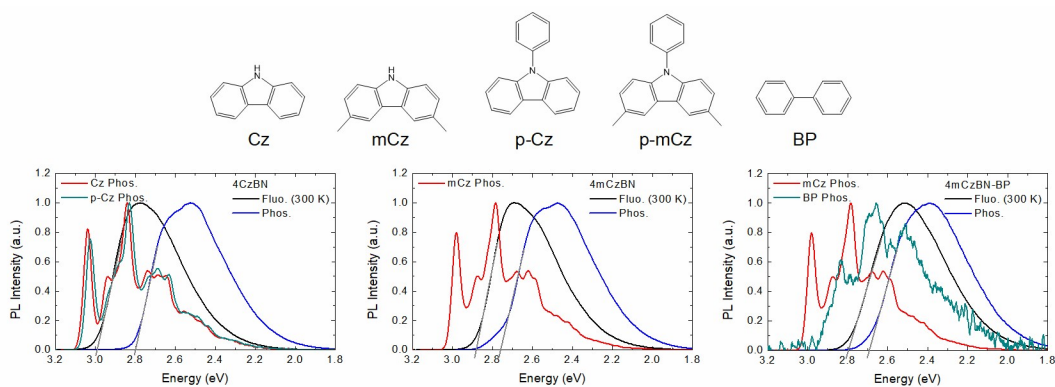
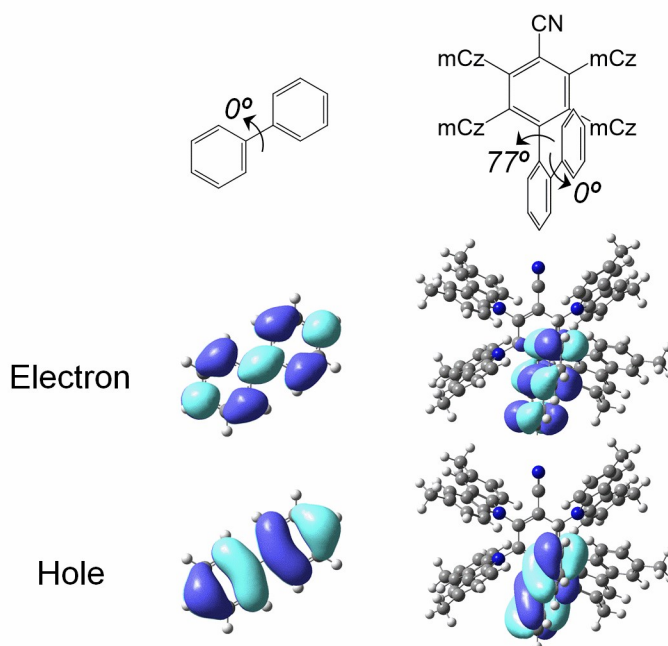


Figure S7. Phosphorescence spectra at 77 K (10^{-5} M toluene). Note that the phosphorescence spectra of p-Cz and p-mCz are redshifted for 0.01 eV from that of Cz and mCz respectively, with almost same vibronic peak configurations.



	Biphenyl (BP)	4mCzBN-BP
DFT, M06HF	2.8654 eV	2.8398 eV
Phos. at 77 K, 0-0 Peak	2.836 eV	-
Estimated $T_{1,BP}$	-	2.811 eV

Figure S8 NTOs and triplet energies localized at the biphenyl and estimation of $T_{1,BP}$ in 4mCzBN-BP. The M06-HF functional was used for the geometry optimization (Fig. 6) and single point calculation. $T_{1,BP} = 2.8398 \times 2.836 / 2.8654 = 2.811$ eV.

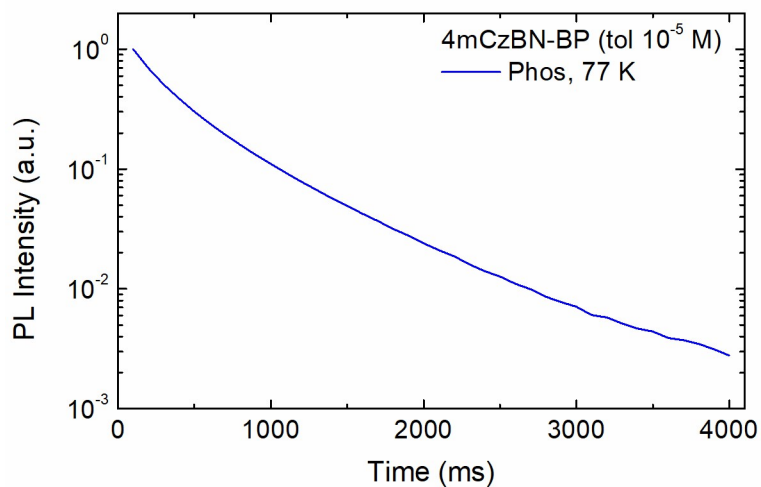


Figure S9. Phosphorescence decay curve of 4mCzBN-BP.

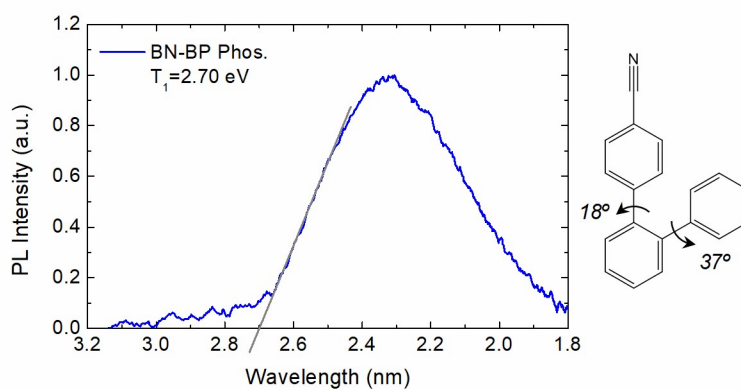


Figure S10. Phosphorescence of BN-BP and optimized T_1 geometry. This state cannot be formed in 4mCzBN-BP due to the steric hindrance among the donors and the biphenyl.

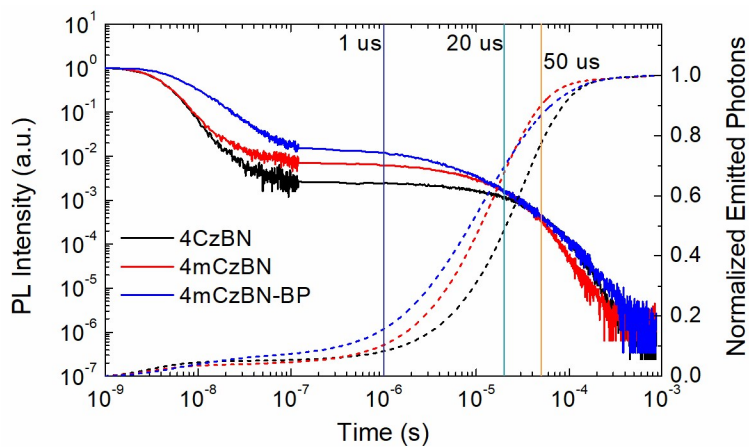


Figure S11. PL decay and normalized emitted photons curves.

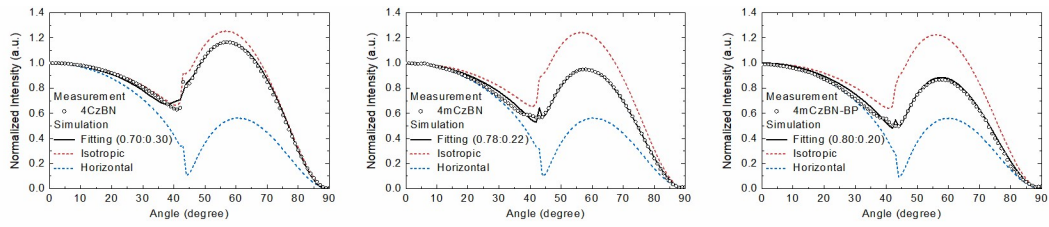


Figure S12. Angle dependent PL fitting of the TADF molecules (10 wt% in mCBP).

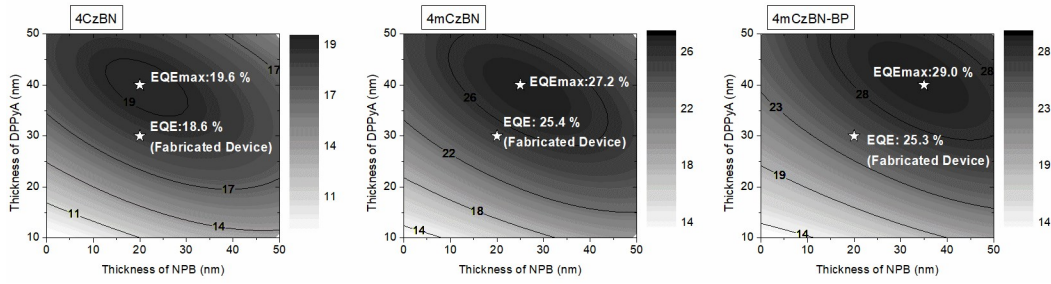


Figure S13. EQE optical simulation.

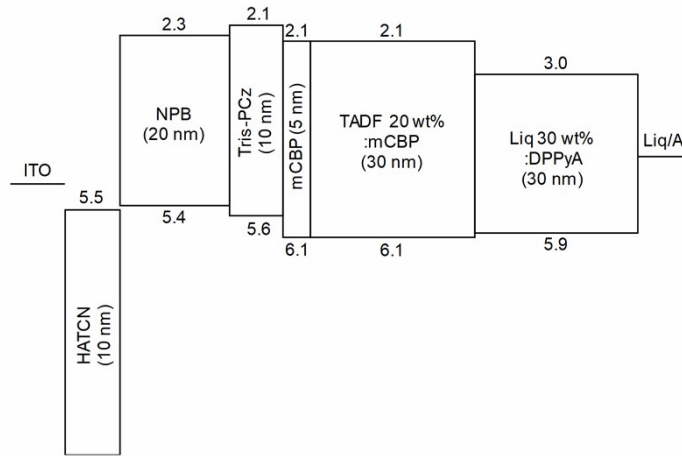


Figure S14. Device structure.