Electronic Supplementary Material (ESI) for ChemComm.

Catalytic hydroaminations of alkynes: A facile protocol to vinyl-carbazole derivatives via a frustrated Lewis pair mechanism

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Supporting Information

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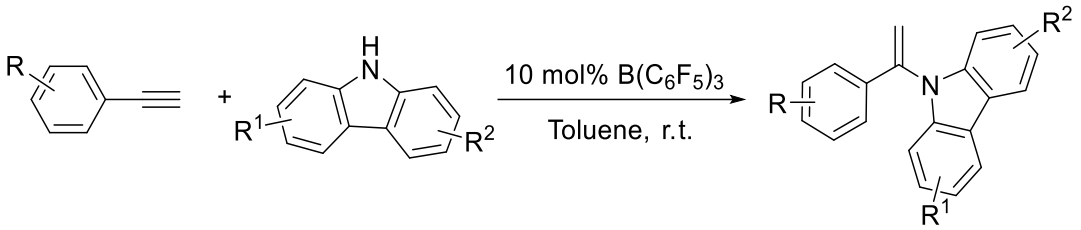
General information

All preparative procedures were performed in an inert atmosphere of dry, deoxygenated (O_2 < 0.5 ppm) nitrogen, using glovebox techniques or standard Schlenk techniques unless otherwise specified. Solvents were stored over activated 4Å molecular sieves following drying procedures. Benzene was purchased from Alfa Aesar. Deuterated solvents (C_6D_6, $CDCl_3$, toluene-d_8) were purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Phenylacetylene was purchased from Alfa Aesar. 1-Ethynyl-2-methylbenzene, 1-ehynyl-4-methylbenzene, 1-ethynyl-4-methoxybenzene, 1-ethyl-4-ethynylbenzene, 1-(*tert*-butyl)-4-ethynylbenzene, 1-ethynyl-2-fluorobenzene, 1-ethynyl-3-fluorobenzene, 1-bromo-4-ethynylbenzene, 1-trifluoromethyl-4-ethynylbenzene 1,4-diethynylbenzene 1,3-diethynylbenzene and 1,3,5-triethynylbenzene were obtained from Adamas-beta. 1-ehynyl-3-methylbenzene, 1-ethynyl-4-fluorobenzene, 1-chloro-4-ethynylbenzene, ethynylcyclopropane were purchased from TCI Chemical. Carbazole, 3,6-diphenyl-9*H*-carbazole, 3,6-dimethyl-9*H*-carbazole were purchased from Adamas-beta. 3,6-Dimethoxy-9*H*-carbazole, 3-phenyl-9*H*-carbazole, 2-phenyl-9*H*-carbazole were obtained from Ark. 3-Bromo-9*H*-carbazole, 3,6-di-*tert*-butyl-9*H*-carbazole were purchased from Innochem. All the carbazole derivatives were purified by flash chromatography on silica gel. Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F254 aluminum plates or EMD basic Aluminium Oxide 60 F254 plastic plates. Silicycle Silia-P Flash Silica Gel was used for all column chromatography.

All NMR spectra were collected at 298 K on Bruker 500 spectrometers in 5 mm diameter NMR tubes. ^{1}H chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 7.26 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets), coupling constants (Hz), integration and assignment. ^{13}C{^{1}H} chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm). ^{19}F NMR spectra were measured at 376 MHz and $CFCl_3$ (-63.2 ppm) was used as an external standard. Departmental facilities were used for mass spectrometry (FTMS ESI)

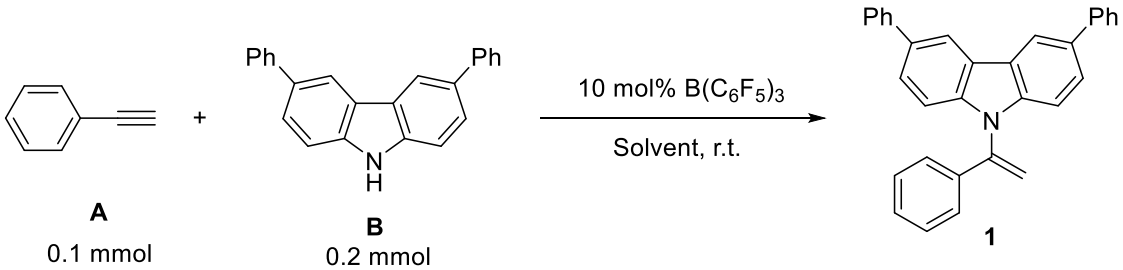
Standard preparation for catalytic operations



In an inert atmosphere glovebox, a 10 mL vial was charged with carbazoles (0.2 mmol). A solution of $B(C_6F_5)_3$ (5.1 mg, 10 mol%) in 1.5 mL toluene was added, and the mixture was stirred at room temperature for 0.5 h. Then, alkynes (0.1 mmol) in 0.5 mL toluene were added under stirring. The reaction mixture was stirred at room temperature for 48 h. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 100/1~20/1) on silica gel to afford the desired carbazolated products.

Extra optimization of the reaction conditions

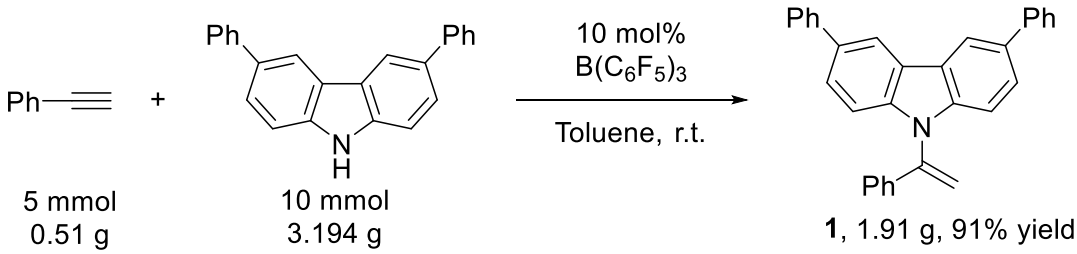
Table S1 Optimization of reaction conditions[a]



Entry	Solvent	Time (h)	Yield (%)(**1** [b])
1	THF	48	0
2	Et_2O	48	11
3	DCM	48	45
4	$CDCl_3$	48	85
5	C_6H_6	48	95
6	Toluene	48	97
7	Toluene	36	93
8	Toluene	24	85

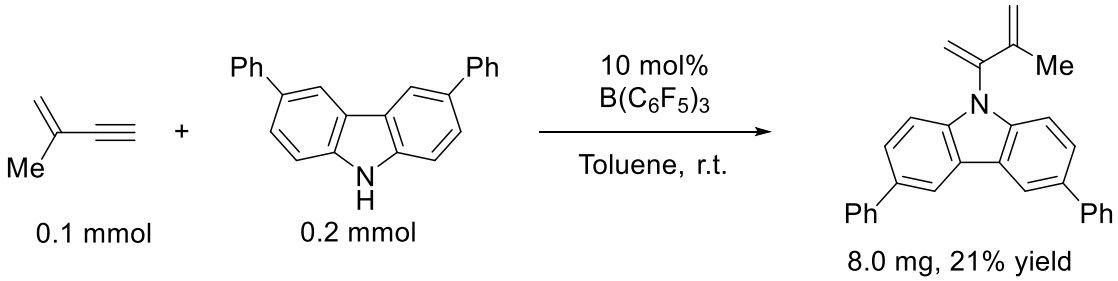
[a] All reactions were performed with phenylacetylene (**A**) (0.1 mmol), 3,6-diphenyl-9H-carbazole (**B**) (0.2 mmol), and $B(C_6F_5)_3$ (10 mol%, 5.1 mg) in solvent (2.0 mL) at room temperature for specified time. [b] Isolated yield.

Procedure for the gram-scale version of carbazolation reaction of phenylacetylene

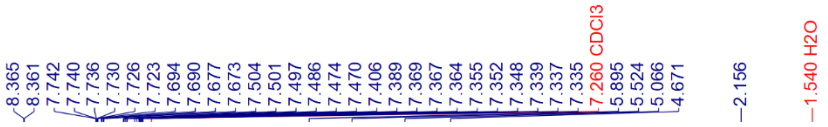


In an inert atmosphere glovebox, a flask (200 mL) was charged with 3,6-diphenyl-9*H*-carbazole (3.194 g, 10 mmol). Then, a solution of $B(C_6F_5)_3$ (0.255 g, 10 mol%, 0.5 mmol) in 75 mL toluene was added, and the mixture was stirred at room temperature for 0.5 h. Finally, a solution of phenylacetylene (0.51 g, 5.0 mmol) in 25 mL toluene was added the mixture under stirring. The reaction mixture was stirred at room temperature for 48 h. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 50/1) on silica gel to afford product **1** as a white solid (1.91 g, 91% yield).

Procedure for carbazolation reaction of 2-methyl-1-buten-3-yne with 3,6-diphenyl-9*H*-carbazole



In an inert atmosphere glovebox, a 10 mL vial was charged with 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). A solution of $B(C_6F_5)_3$ (5.1 mg, 10 mol%) in 1.5 mL toluene was added, and the mixture was stirred at room temperature for 0.5 h. Then, 2-methyl-1-buten-3-yne (6.6 mg, 0.1 mmol) in 0.5 mL toluene were added under stirring. The reaction mixture was stirred at room temperature for 48 h. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 50/1) on silica gel to afford the desired carbazolated product as a white solid (8.0 mg, 21% yield). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.36 (d, *J* = 2.0 Hz, 2H), 7.75 – 7.72 (m, 4H), 7.68 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.51 – 7.47 (m, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.33 (m, 2H), 5.90 (s, 1H), 5.52 (s, 1H), 5.07 (s, 1H), 4.67 (s, 1H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 143.89, 142.02, 141.04, 138.11, 133.16, 128.75, 127.31, 126.50, 125.55, 123.56, 118.73, 116.65, 115.20, 110.59, 19.89. DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.75, 127.31, 126.50, 125.55, 118.73, 116.65, 115.20, 110.60, 19.89.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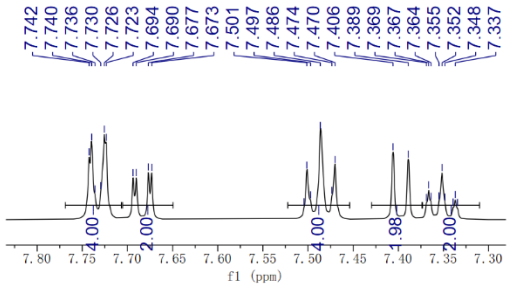
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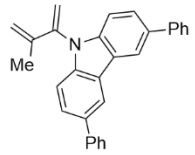
f1 (ppm)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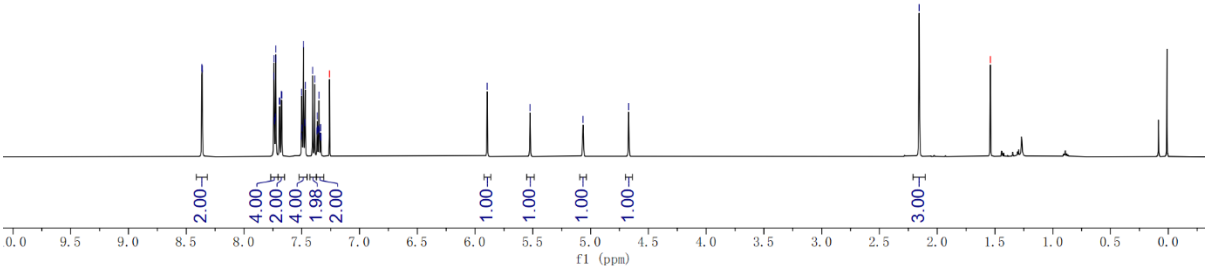
N
Ph
Ph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f1 (ppm)


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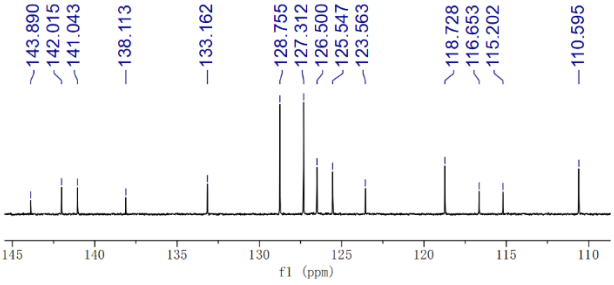
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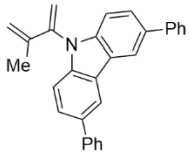
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N
Ph
Ph

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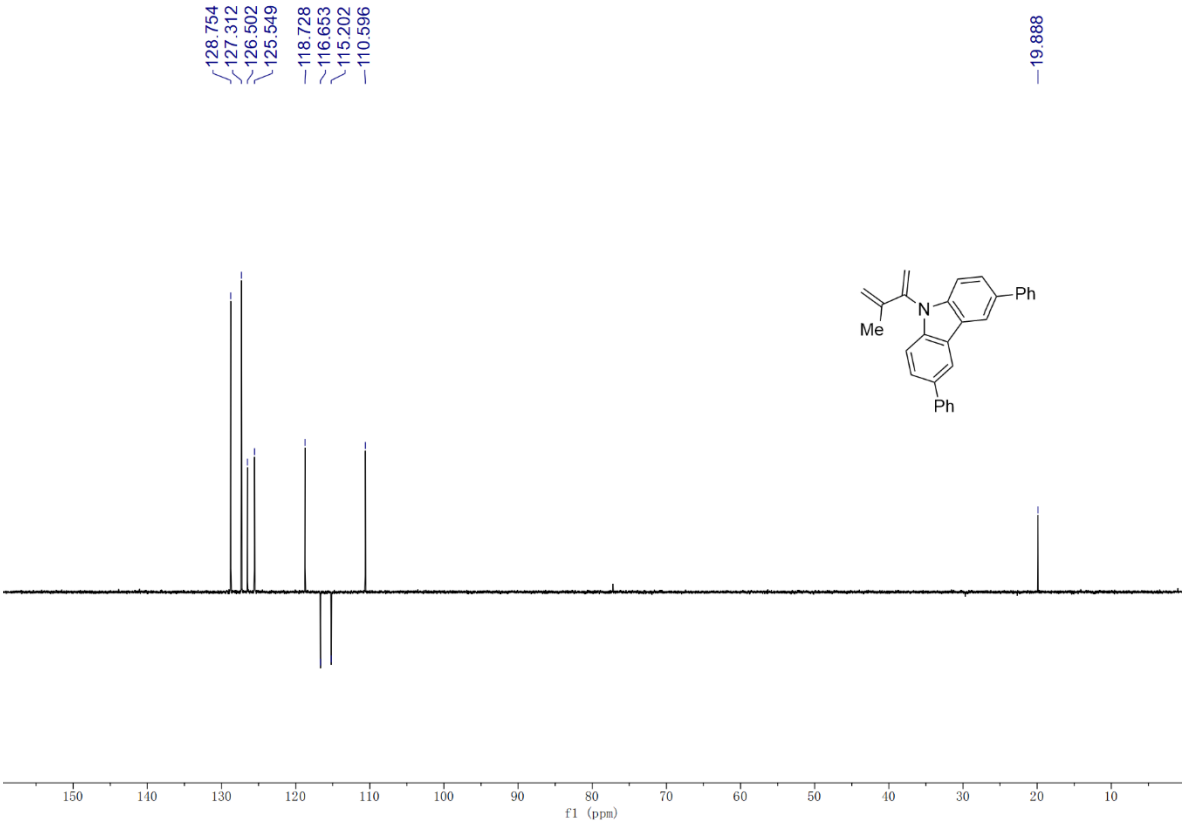
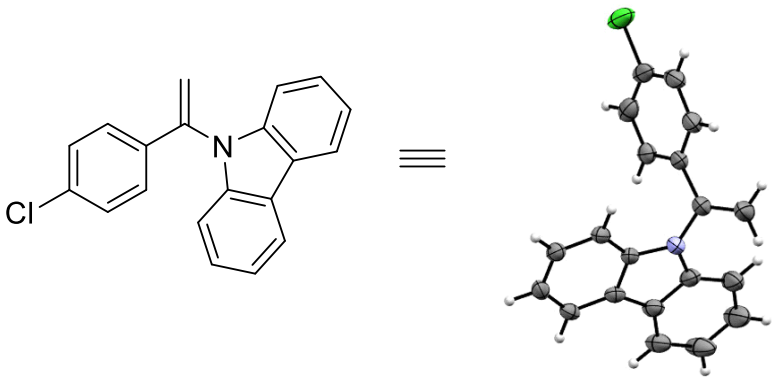


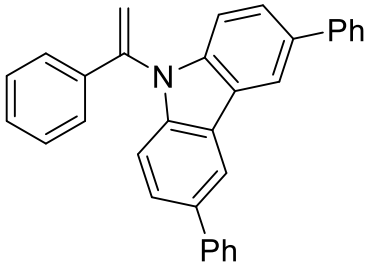
Single crystal X-ray crystallography

X-ray crystallographic data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources at 161 K. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS and SHELXL[1] within OLEX2.[2]



Characterization data

Preparation of 3,6-diphenyl-9-(1-phenylvinyl)-9*H*-carbazole (1)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of phenylacetylene (10.2 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **1** as a white solid (40.9 mg, 97% yield).

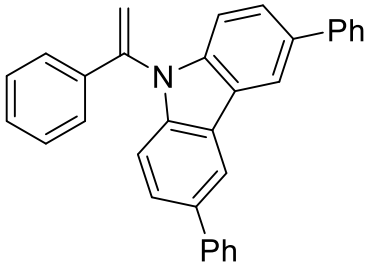
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.43 (d, *J* = 2.0 Hz, 2H), 7.77 – 7.74 (m, 4H), 7.65 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.53 – 7.49 (m, 4H), 7.41 – 7.33 (m, 9H), 6.13 (s, 1H), 5.67 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 142.66, 141.86, 140.73, 136.21, 133.49, 129.18, 128.80, 128.76, 127.29, 126.57, 126.27, 125.59, 124.05, 118.72, 112.83, 111.24.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.18, 128.80, 128.76, 127.29, 126.57, 126.27, 125.59, 118.72, 112.83, 111.24.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{24}N^+$, ($[M+H]^+$): 422.1903; Found: 422.1895.

Gram-scale of 3,6-diphenyl-9-(1-phenylvinyl)-9*H*-carbazole (1)

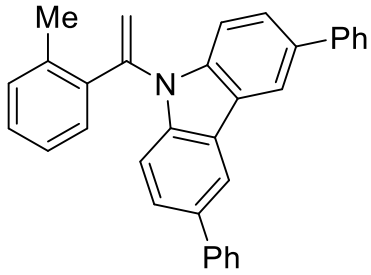


^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.42 (d, *J* = 1.5 Hz, 2H), 7.77 – 7.74 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.52 – 7.49 (m, 4H), 7.41 – 7.32 (m, 9H), 6.13 (s, 1H), 5.67 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 142.67, 141.86, 140.73, 136.22, 133.49, 129.19, 128.80, 128.76, 127.29, 126.57, 126.28, 125.59, 124.05, 118.73, 112.83, 111.24.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.19, 128.80, 128.76, 127.29, 126.57, 126.28, 125.59, 118.73, 112.83, 111.24.

Preparation of 3,6-diphenyl-9-(1-(*o*-tolyl)vinyl)-9*H*-carbazole (2)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1-ethynyl-2-methylbenzene (11.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **2** as a white solid (38.1 mg, 88% yield).

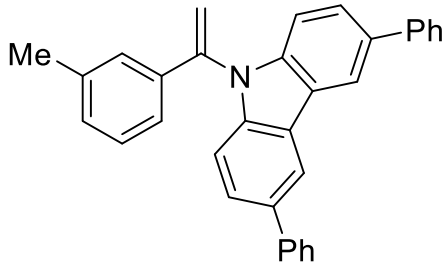
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.38 (d, *J* = 2.0 Hz, 2H), 7.75 – 7.72 (m, 4H), 7.62 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.51 – 7.47 (m, 4H), 7.39 – 7.32 (m, 6H), 7.16 – 7.13 (m, 1H), 5.78 (s, 1H), 5.73 (s, 1H), 1.87 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 143.50, 141.73, 140.01, 137.17, 136.51, 133.52, 131.04, 129.82, 129.04, 128.75, 127.22, 126.59, 126.34, 125.52, 124.28, 118.60, 112.98, 111.49, 20.00.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 131.04, 129.81, 129.04, 128.75, 127.22, 126.58, 126.34, 125.52, 118.60, 112.98, 111.49, 20.00.

HRMS (ESI, *m/z*): Calcd. for $C_{33}H_{26}N^+$, ($[M+H]^+$): 436.2060; Found: 436.2055.

Preparation of 3,6-diphenyl-9-(1-(*m*-tolyl)vinyl)-9*H*-carbazole (3)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1-ehynyl-3-methylbenzene (11.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **3** as a white solid (36.6 mg, 84% yield).

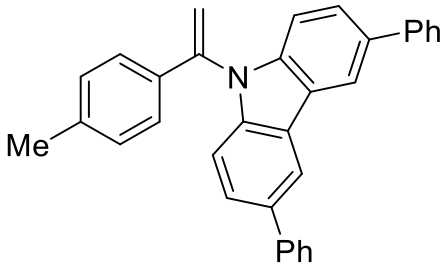
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.43 (d, *J* = 2.0 Hz, 2H), 7.78 – 7.74 (m, 4H), 7.65 (dd, *J* = 8.5 Hz, 1.5 Hz, 2H), 7.53 – 7.49 (m, 4H), 7.40 – 7.34 (m, 4H), 7.26 – 7.20 (m, 3H), 7.14 – 7.11 (m, 1H), 6.10 (s, 1H), 5.64 (s, 1H), 2.34 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 142.83, 141.89, 140.78, 138.49, 136.29, 133.42, 130.03, 128.77, 128.70, 127.29, 126.81, 126.56, 125.57, 124.04, 123.52, 118.69, 112.63, 111.29, 21.44.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 130.03, 128.77, 128.70, 127.29, 126.81, 126.57, 125.58, 123.52, 118.70, 112.63, 111.29, 21.44.

HRMS (ESI, *m/z*): Calcd. for $C_{33}H_{26}N^+$, ($[M+H]^+$): 436.2060; Found: 436.2055.

Preparation of 3,6-diphenyl-9-(1-(*p*-tolyl)vinyl)-9*H*-carbazole (4)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1-ehynyl-4-methylbenzene (11.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **4** as a white solid (42.1 mg, 97% yield).

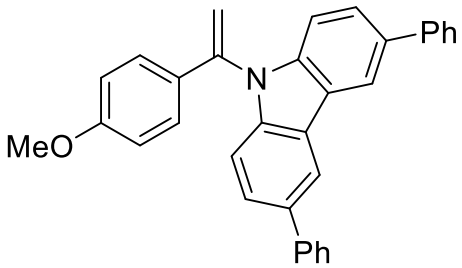
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.41 (d, *J* = 2.0 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.52 – 7.48 (m, 4H), 7.39 – 7.32 (m, 4H), 7.25 – 7.22 (m, 2H), 7.16 – 7.13 (m, 2H), 6.07 (s, 1H), 5.60 (s, 1H), 2.38 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 142.58, 141.90, 140.77, 139.25, 133.40, 133.37, 129.50, 128.75, 127.29, 126.55, 126.18, 125.55, 124.00, 118.69, 111.91, 111.28, 21.25.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.50, 128.75, 127.29, 126.55, 126.18, 125.56, 118.69, 111.91, 111.28, 21.25.

HRMS (ESI, *m/z*): Calcd. for $C_{33}H_{26}N^+$, ($[M+H]^+$): 436.2060; Found: 436.2052.

Preparation of 9-(1-(4-methoxyphenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (5)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hours. Then, a solution of 1-ethynyl-4-methoxybenzene (13.2 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **5** as a white solid (41.6 mg, 92% yield).

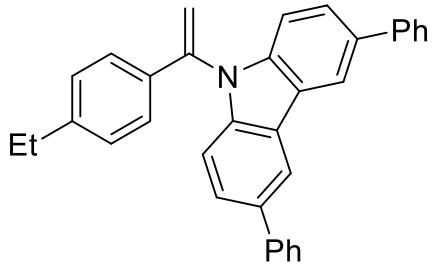
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.32 (d, *J* = 2.0 Hz, 2H), 7.67 – 7.64 (m, 4H), 7.54 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.30 – 7.23 (m, 4H), 7.18 – 7.15 (m, 2H), 6.78– 6.74 (m, 2H), 5.90 (s, 1H), 5.44 (s, 1H), 3.71 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 160.37, 142.17, 141.88, 140.76, 133.39, 128.75, 128.67, 127.64, 127.28, 126.55, 125.54, 124.00, 118.68, 114.12, 111.32, 110.78, 55.26.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.75, 127.64, 127.27, 126.55, 125.54, 118.68, 114.12, 111.32, 110.78, 55.26.

HRMS (ESI, *m/z*): Calcd. for $C_{33}H_{26}NO^+$, ($[M+H]^+$): 452.2009; Found: 452.2004.

Preparation of 9-(1-(4-ethylphenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (6)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1-ethyl-4-ethynylbenzene (13.0 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **6** as a white solid (42.4 mg, 94% yield).

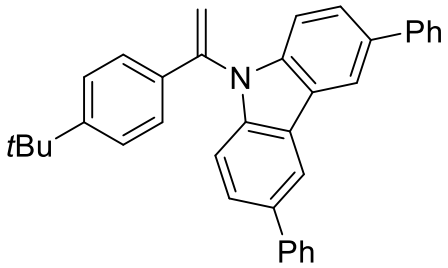
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.41 (d, *J* = 1.5 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.52 – 7.48 (m, 4H), 7.39 – 7.32 (m, 4H), 7.27 – 7.24 (m, 2H), 7.18 – 7.15 (m, 2H), 6.09 (s, 1H), 5.60 (s, 1H), 2.67 (q, *J* = 15.0 Hz, 7.5 Hz, 2H), .1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 145.56, 142.60, 141.91, 140.79, 133.58, 133.39, 128.75, 128.29, 127.29, 126.54, 126.23, 125.56, 124.00, 118.69, 112.03, 111.27, 28.59, 15.33.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.75, 128.29, 127.29, 126.54, 126.24, 125.56, 118.69, 112.03, 111.27, 28.59, 15.33.

HRMS (ESI, *m/z*): Calcd. for $C_{34}H_{28}N^+$, ($[M+H]^+$): 450.2216; Found: 450.2208.

Preparation of 9-(1-(4-(*tert*-butyl)phenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (7)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1-(*tert*-butyl)-4-ethynylbenzene (15.8 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **7** as a white solid (45.9 mg, 96% yield).

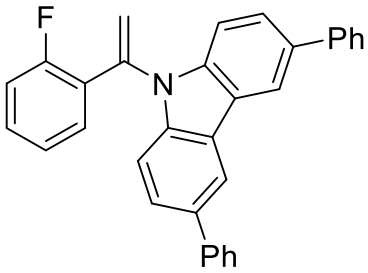
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.44 (d, *J* = 2.0 Hz, 2H), 7.78 – 7.75 (m, 4H), 7.65 (dd, *J* = 8.5 Hz, 1.5 Hz, 2H), 7.54 – 7.49 (m, 4H), 7.41 – 7.35 (m, 6H), 7.29 – 7.26 (m, 2H), 6.11 (s, 1H), 5.62 (s, 1H), 1.35 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 152.40, 142.46, 141.91, 140.83, 133.37, 133.21, 128.75, 127.28, 126.53, 125.90, 125.71, 125.57, 123.98, 118.69, 112.28, 111.25, 34.66, 31.20.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.75, 127.28, 126.53, 125.90, 125.71, 125.56, 118.69, 112.27, 111.25, 31.20.

HRMS (ESI, *m/z*): Calcd. for $C_{36}H_{32}N^+$, ($[M+H]^+$): 478.2529; Found: 478.2523.

Preparation of 9-(1-(2-fluorophenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (8)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 2-fluorophenylacetylene (12.0 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **8** as a white solid (41.6 mg, 95% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.41 (d, *J* = 2.0 Hz, 2H), 7.77 – 7.73 (m, 4H), 7.66 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.53 – 7.48 (m, 4H), 7.40 – 7.35 (m, 4H), 7.35 – 7.31 (m, 1H), 7.20 – 7.15 (m, 1H), 7.05 – 6.98 (m, 2H), 6.27 (d, *J* = 1.0 Hz, 1H), 5.92 (d, *J* = 1.5 Hz, 1H).

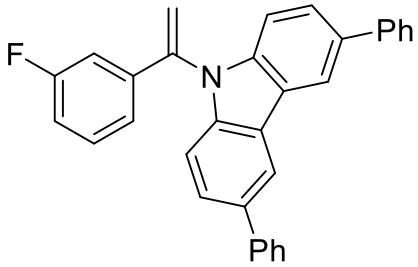
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 160.60 (d, *J* = 252.2 Hz, 1C), 141.83, 140.51, 136.82 (d, *J* = 2.1 Hz, 1C), 133.58, 130.47 (d, *J* = 8.7 Hz, 1C), 129.37 (d, *J* = 2.4 Hz, 1C), 128.76, 127.28, 126.58, 125.67, 124.44 (d, *J* = 3.7 Hz, 1C), 124.08 (d, *J* = 11.1 Hz, 1C), 124.01, 118.78, 118.0 (d, *J* = 8.3 Hz, 1C), 116.40 (d, *J* = 22.6 Hz, 1C), 110.81.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 130.47 (d, *J* = 8.7 Hz, 1C), 129.37 (d, *J* = 2.4 Hz, 1C), 128.76, 127.28, 126.58, 125.67, 124.44 (d, *J* = 3.7 Hz, 1C), 118.77, 118.0 (d, *J* = 8.3 Hz, 1C), 116.40 (d, *J* = 22.6 Hz, 1C), 110.81.

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) δ: -114.55.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{22}FNNa^+$, ($[M+Na]^+$): 462.1628; Found: 462.1622.

Preparation of 9-(1-(3-fluorophenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (9)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 3-fluorophenylacetylene (12.0 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **9** as a white solid (40.1 mg, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.42 (d, *J* = 2.0 Hz, 2H), 7.77 – 7.74 (m, 4H), 7.66 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.54 – 7.49 (m, 4H), 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 3H), 7.11 – 7.07 (m, 3H), 6.14 (s, 1H), 5.71 (s, 1H).

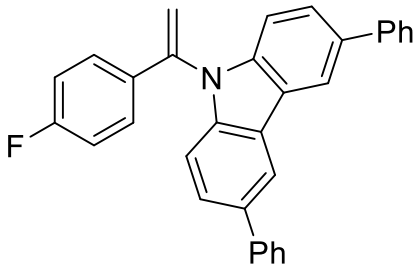
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 163.11 (d, *J* = 247.2 Hz, 1C), 141.77, 141.66 (d, *J* = 26.5 Hz, 1C), 140.56, 138.62 (d, *J* = 7.4 Hz, 1C), 133.71, 130.39 (d, *J* = 8.3 Hz, 1C), 128.78, 127.30, 126.63, 125.69, 124.12, 121.98 (d, *J* = 2.9 Hz, 1C), 118.81, 116.15 (d, *J* = 21.3 Hz, 1C), 113.99, 113.24 (d, *J* = 22.8 Hz, 1C), 111.07.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 130.39 (d, *J* = 8.3 Hz, 1C), 128.78, 127.30, 126.63, 125.69, 121.98 (d, *J* = 2.9 Hz, 1C), 118.81, 116.15 (d, *J* = 21.3 Hz, 1C), 113.99, 113.24 (d, *J* = 22.8 Hz, 1C), 111.07.

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) δ: -112.23.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{23}FN^+$, ($[M+H]^+$): 440.1809; Found: 440.1803.

Preparation of 9-(1-(4-fluorophenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (10)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-fluorophenylacetylene (12.0 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **10** as a white solid (43.5 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.41 (d, *J* = 2.0 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.52 – 7.48 (m, 4H), 7.39 – 7.32 (m, 2H), 7.25 – 7.22 (m, 4H), 7.16 – 7.13 (m, 2H), 6.05 (s, 1H), 5.64 (s, 1H).

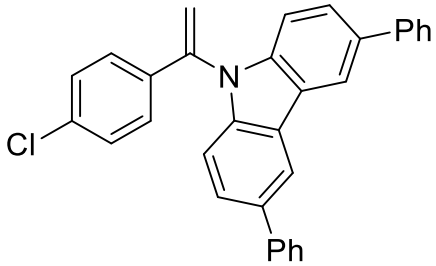
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 163.28 (d, *J* = 249.7 Hz, 1C), 141.78, 141.71, 140.57, 133.64, 132.36 (d, *J* = 3.3 Hz, 1C), 128.78, 128.15 (d, *J* = 8.3 Hz, 2C), 127.29, 126.63, 125.64, 124.10, 118.78, 115.84 (d, *J* = 21.8 Hz, 2C), 112.51, 111.18.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.78, 128.15 (d, *J* = 8.3 Hz, 2C), 127.29, 126.63, 125.64, 118.78, 115.84 (d, *J* = 21.8 Hz, 2C), 112.51, 111.18.

^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ: -111.81.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{23}FN^+$, ([M+H]$^+$): 440.1809; Found: 440.1801.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (11)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **11** as a white solid (45.0 mg, 99% yield).

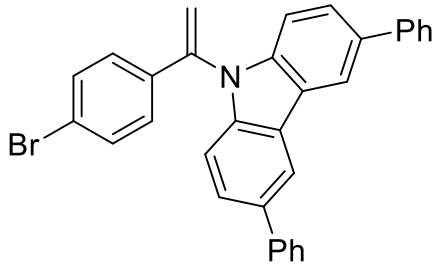
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.39 (d, *J* = 1.5 Hz, 2H), 7.74 – 7.71 (m, 4H), 7.63 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.38 – 7.34 (m, 2H), 7.33 – 7.23 (m, 6H), 6.10 (s, 1H), 5.67 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.77, 141.70, 140.53, 135.13, 134.71, 133.71, 129.07, 128.79, 127.61, 127.30, 126.65, 125.68, 124.12, 118.81, 113.24, 111.14.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.07, 128.79, 127.61, 127.30, 126.65, 125.68, 118.80, 113.24, 111.14.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{23}Cl^{34.9689}N^+$, ([M+H]$^+$): 456.1514; Found: 456.1507; $C_{32}H_{23}Cl^{35.4500}N^+$, ([M+H]$^+$): 457.1547; Found: 457.1541.

Preparation of 9-(1-(4-bromophenyl)vinyl)-3,6-diphenyl-9*H*-carbazole (12)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-bromophenylacetylene (18.1 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **12** as a white solid (49.4 mg, 98% yield).

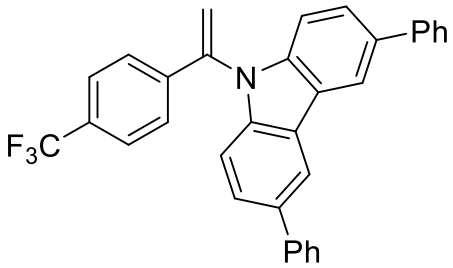
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.41 (d, *J* = 1.5 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 1.5 Hz, 2H), 7.52 – 7.45 (m, 6H), 7.40 – 7.36 (m, 2H), 7.30 (s, 1H), 7.29 (s, 1H), 7.21 – 7.17 (m, 2H), 6.10 (s, 1H), 5.68 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.74, 140.51, 135.16, 133.71, 132.01, 128.78, 127.86, 127.28, 126.64, 125.67, 124.11, 123.36, 118.80, 113.31, 111.13.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 132.01, 128.78, 127.86, 127.28, 126.64, 125.67, 118.80, 113.31, 111.13.

HRMS (ESI, *m/z*): Calcd. for $C_{32}H_{22}Br^{79.9183}NNa^+$, ([M+Na]$^+$): 522.0828; Found: 522.0828; $C_{32}H_{22}Br^{80.9163}NNa^+$, ([M+Na]$^+$): 524.0807; Found: 524.0804.

Preparation of 3,6-diphenyl-9-(1-(4-(trifluoromethyl)phenyl)vinyl)-9*H*-carbazole (13)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-trifluoromethylphenylacetylene (17.0 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **13** as a white solid (36.1 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.42 (d, *J* = 2.0 Hz, 2H), 7.76 – 7.72 (m, 4H), 7.64 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.48 (m, 4H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.40– 7.36 (m, 2H), 7.29 (s, 1H), 7.27 (s, 1H), 6.21 (s, 1H), 5.79 (s, 1H).

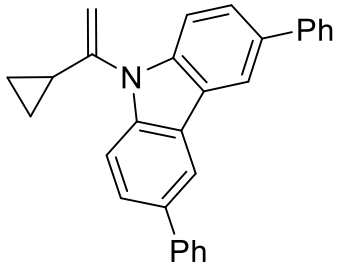
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.70, 141.57, 140.46, 139.68, 133.87, 131.08 (dd, $J_{C\text{-}F}$ = 65.4 Hz, 32.6 Hz), 128.80, 127.30, 126.64 (d, $J_{C\text{-}F}$ = 13.9 Hz, 1C), 125.86 (dd, $J_{C\text{-}F}$ = 7.6 Hz, 3.8 Hz, 2C), 125.77, 124.18, 123.90 (d, $J_{C\text{-}F}$ = 272.7 Hz, 1C), 118.87, 115.04, 111.02.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.80, 127.30, 126.64 (d, $J_{C\text{-}F}$ = 13.9 Hz, 1C), 125.86 (dd, $J_{C\text{-}F}$ = 7.6 Hz, 3.8 Hz, 2C), 125.77, 118.88, 115.04, 111.02.

^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ: -62.63.

HRMS (ESI, *m/z*): Calcd. for $C_{33}H_{22}F_3NNa^+$, ($[M+Na]^+$): 512.1597; Found: 512.1594.

Preparation of 9-(1-cyclopropylvinyl)-3,6-dimethyl-9*H*-carbazole (14)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (63.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of ethynylcyclopropane (6.6 mg, 0.10 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **14** as a colorless oil (11.2 mg, 29% yield).

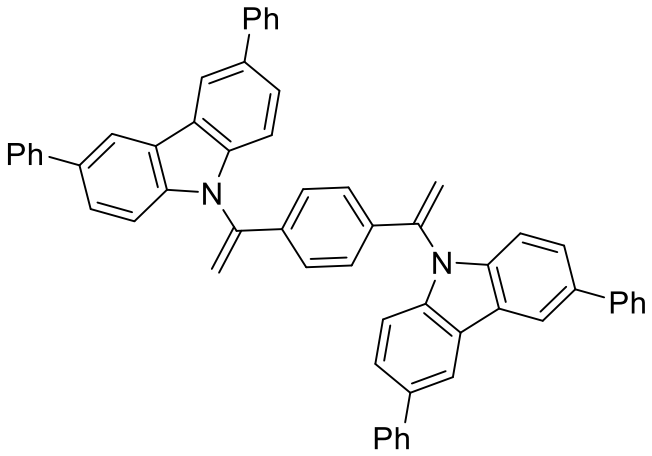
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.36 (d, *J* = 1.5 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.72 (dd, *J* = 8.5 Hz, 1.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.52 – 7.47 (m, 4H), 7.38 – 7.34 (m, 2H), 5.52 (s, 1H), 5.27(s, 1H), 1.90 – 1.8 4 (m, 1H), 0.91 – 0.86 (m, 2H), 0.73 – 0.69 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 145.90, 141.99, 140.81, 133.10, 128.76, 127.30, 126.51, 125.54, 123.70, 118.70, 110.87, 110.71, 15.39, 8.09.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.76, 127.29, 126.50, 125.53, 118.70, 110.86, 110.71, 15.39, 8.09.

HRMS (ESI, *m/z*): Calcd. for $C_{29}H_{23}NNa^+$, ([M+Na]$^+$): 408.1723; Found: 408.1718.

Preparation of 1,4-bis(1-(3,6-diphenyl-9*H*-carbazol-9-yl)vinyl)benzene (15)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (127.6 mg, 0.4 mmol). Toluene (2 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1,4-diethynylbenzene (12.6 mg, 0.1 mmol) in toluene (2 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate/DCM = 40/1/2) on silica gel to afford product **15** as a white solid (63.9 mg, 84% yield).

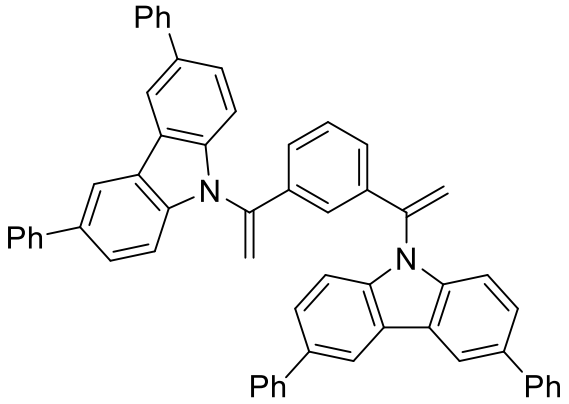
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.38 (s, 4H), 7.71 (d, *J* = 7.5 Hz, 8H), 7.62 (d, *J* = 8.5 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 8H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 4H), 7.24 (s, 4H), 6.09 (s, 2H), 5.65 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.99, 141.80, 140.59, 136.92, 133.62, 128.77, 127.29, 126.75, 126.60, 125.61, 124.06, 118.79, 113.53, 111.14.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.77, 127.29, 126.75, 126.60, 125.61, 118.79, 113.54, 111.14.

HRMS (ESI, *m/z*): Calcd. for $C_{58}H_{41}N_2^+$, ([M+H]$^+$): 765.3264; Found: 765.3260.

Preparation of 1,3-bis(1-(3,6-diphenyl-9*H*-carbazol-9-yl)vinyl)benzene (16)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (127.6 mg, 0.4 mmol). Toluene (2 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1,3-diethynylbenzene (12.6 mg, 0.1 mmol) in toluene (2 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 40/1) on silica gel to afford product **16** as a white solid (71.9 mg, 94% yield).

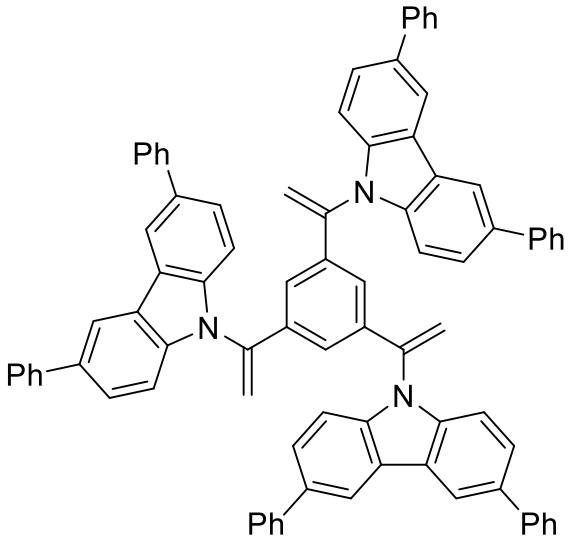
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.33(s, 4H), 7.71 (d, *J* = 7.5 Hz, 8H), 7.59 (dd, *J* = 8.5 Hz, 1.5 Hz, 4H), 7.50 (t, *J* = 7.5 Hz, 8H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.34 – 7.27 (m, 3H), 7.23 (d, *J* = 8.5 Hz, 4H), 7.15 (s, 1H), 5.99 (s, 2H), 5.62 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 142.08, 141.75, 140.50, 137.04, 133.43, 129.36, 128.79, 127.23, 127.00, 126.57, 125.45, 124.38, 124.00, 118.71, 113.43, 111.03.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.36, 128.79, 127.23, 127.00, 126.57, 125.45, 124.38, 118.71, 113.43, 111.03.

HRMS (ESI, *m/z*): Calcd. for $C_{58}H_{40}N_2Na^+$, ($[M+Na]^+$): 787.3084; Found: 787.3078.

Preparation of 1,3,5-tris(1-(3,6-diphenyl-9*H*-carbazol-9-yl)vinyl)benzene (17)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-diphenyl-9*H*-carbazole (191.4 mg, 0.6 mmol). Toluene (4.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 1,3,5-triethynylbenzene (15.0 mg, 0.1 mmol) in toluene (1.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 20/1) on silica gel to afford product **17** as a white solid (75.3 mg, 68% yield).

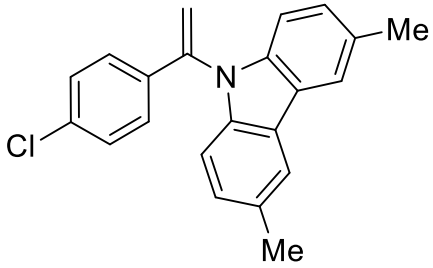
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.25 (s, 6H), 7.67 (d, *J* = 7.5 Hz, 12H), 7.54 (d, *J* = 8.5 Hz, 6H), 7.49 (t, *J* = 7.5 Hz, 12H), 7.40 (t, *J* = 7.5 Hz, 6H), 7.12 (d, *J* = 8.0 Hz, 9H), 5.87 (s, 3H), 5.57 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.63, 141.58, 140.28, 138.00, 133.37, 128.83, 127.17, 126.57, 125.33, 125.04, 123.97, 118.69, 113.97, 110.86.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.83, 127.17, 126.57, 125.33, 125.04, 118.69, 113.97, 110.86.

HRMS (ESI, *m/z*): Calcd. for $C_{84}H_{58}N_3^+$, ($[M+H]^+$): 1108.4625; Found: 1108.4616.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-3,6-dimethyl-9*H*-carbazole (18)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-dimethyl-9*H*-carbazole (39.0 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **18** as a white solid (31.5 mg, 95% yield).

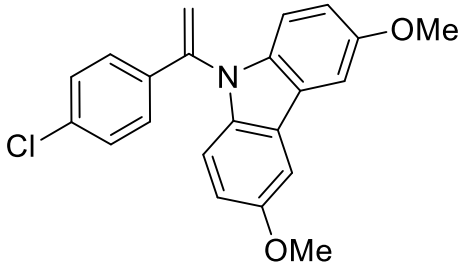
^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.90 (s, 2H), 7.326 (dd, *J* = 8.5 Hz, 1.5 Hz, 2H), 7.18 (td, *J* = 8.5 Hz, 1.5 Hz, 4H), 7.11 – 7.06 (m, 2H), 5.99 (s, 1H), 5.58 (s, 1H), 2.54 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.95, 139.10, 135.09, 134.83, 129.13, 128.90, 127.62, 127.04, 123.48, 120.10, 112.49, 110.46, 21.34.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.89, 127.62, 127.04, 120.10, 112.49, 110.46, 21.34.

HRMS (ESI, *m/z*): Calcd. for $C_{22}H_{19}Cl^{34.9689}N^+$, ($[M+H]^+$): 332.1201; Found: 332.1198; $C_{22}H_{19}Cl^{35.4500}N^+$, ($[M+H]^+$): 334.1171; Found: 334.1169.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-3,6-dimethoxy-9*H*-carbazole (19)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-dimethoxy-9*H*-carbazole (45.4 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford product **19** as a white solid (29.5 mg, 81% yield).

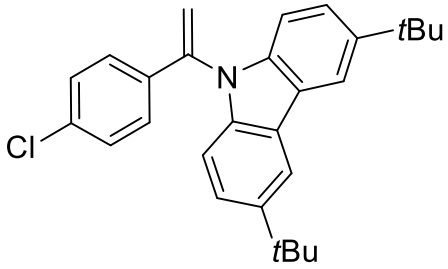
^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.54 (d, *J* = 2.5 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.15 (m, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.08 (dd, *J* = 8.5 Hz, 2.0 Hz, 2H), 5.94 (s, 1H), 5.55 (s, 1H), 3.94 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 153.99, 142.02, 136.06, 135.18, 134.90, 128.91, 128.88, 127.69, 123.74, 115.06, 112.07, 111.78, 102.85, 56.04.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.91, 127.69, 115.06, 112.07, 111.78, 102.85, 56.04.

HRMS (ESI, *m/z*): Calcd. for $C_{22}H_{19}Cl^{34.9689}NO_2^+$, ($[M+H]^+$): 364.1099; Found: 364.1094; $C_{22}H_{19}Cl^{35.4500}NO_2^+$, ($[M+H]^+$): 366.1069; Found: 366.1065.

Preparation of 3,6-di-*tert*-butyl-9-(1-(4-chlorophenyl)vinyl)-9*H*-carbazole (20)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3,6-di-*tert*-butyl-9*H*-carbazole (55.8 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **20** as a white solid (41.2 mg, 99% yield).

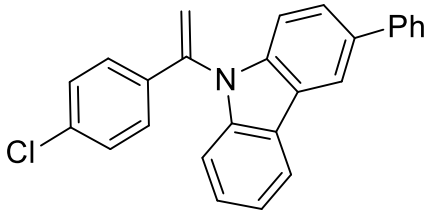
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.12 (d, *J* = 2.0 Hz, 2H), 7.40 (dd, *J* = 9.0 Hz, 2.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.24– 7.20 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.96 (s, 1H), 5.56 (s, 1H), 1.46 (s, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 142.81, 142.08, 139.06, 135.23, 134.82, 128.89, 127.74, 123.56, 123.43, 116.11, 112.21, 110.27, 34.69, 31.98.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.89, 127.74, 123.56, 116.11, 112.21, 110.27, 31.98.

HRMS (ESI, *m/z*): Calcd. for $C_{28}H_{31}Cl^{34.9689}N^+$, ($[M+H]^+$): 416.2140; Found: 416.2135; $C_{28}H_{31}Cl^{35.4500}N^+$, ($[M+H]^+$): 418.2110; Found: 418.2101.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-3-phenyl-9*H*-carbazole (21)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3-phenyl-9*H*-carbazole (48.6 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **21** as a white solid (35.1 mg, 92% yield).

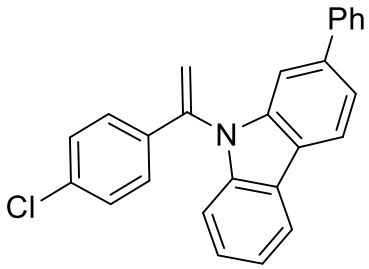
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.36 (d, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, 3.0 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.62 (dt, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 3H), 6.09 (s, 1H), 5.65 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.85, 141.68, 141.05, 140.09, 135.05, 134.76, 133.57, 129.01, 128.77, 127.57, 127.31, 126.60, 126.12, 125.50, 123.97, 123.57, 120.30, 120.14, 118.75, 113.26, 110.96, 110.90.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.01, 128.76, 127.57, 127.30, 126.60, 126.12, 125.50, 120.30, 120.14, 118.75, 113.26, 110.96, 110.90.

HRMS (ESI, *m/z*): Calcd. for $C_{26}H_{19}Cl^{34.9689}N^+$, ($[M+H]^+$): 380.1201; Found: 380.1194; $C_{26}H_{19}Cl^{35.4500}N^+$, ($[M+H]^+$): 382.1171; Found: 382.1162.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-2-phenyl-9*H*-carbazole (22)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 2-phenyl-9*H*-carbazole (48.6 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in

toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **22** as a white solid (25.9 mg, 68% yield).

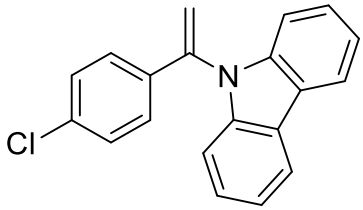
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.18 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.42 (m, 3H), 7.39 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 7.24 – 7.17 (m, 3H), 6.12 (s, 1H), 5.67 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.81, 141.63, 141.26, 141.06, 139.44, 135.04, 134.70, 129.02, 128.73, 127.51, 127.47, 127.10, 125.96, 123.21, 122.68, 120.50, 120.28, 120.13, 119.71, 113.68, 110.79, 109.08.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.02, 128.73, 127.51, 127.48, 127.09, 125.96, 120.50, 120.28, 120.13, 119.71, 113.68, 110.79, 109.08.

HRMS (ESI, *m/z*): Calcd. for $C_{26}H_{19}Cl^{34.9689}N^{+}$, ($[M+H]^{+}$): 380.1201; Found: 380.1194; $C_{26}H_{19}Cl^{35.4500}N^{+}$, ($[M+H]^{+}$): 382.1171; Found: 382.1163.

Preparation of 9-(1-(4-chlorophenyl)vinyl)-9*H*-carbazole (24)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and carbazole (33.4 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 48 hours at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **24** as a white solid (24.6 mg, 81% yield).

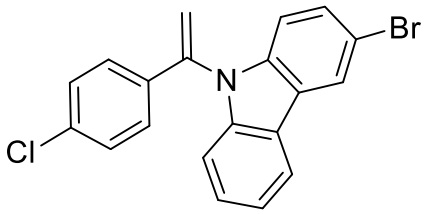
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.15 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.32 – 7.23 (m, 6H), 7.23 – 7.18 (m, 2H), 6.08 (s, 1H), 5.64 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.68, 140.58, 134.96, 134.82, 128.96, 127.53, 125.91, 123.44, 120.23, 119.97, 113.28, 110.72.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 128.96, 127.53, 125.91, 120.23, 119.97, 113.28, 110.72.

HRMS (ESI, *m/z*): Calcd. for $C_{20}H_{15}Cl^{34.9689}N^{+}$, ($[M+H]^{+}$): 304.0888; Found: 304.0881; $C_{20}H_{15}Cl^{35.4500}N^{+}$, ($[M+H]^{+}$): 306.0858; Found: 306.0852.

Preparation of 3-bromo-9-(1-(4-chlorophenyl)vinyl)-9*H*-carbazole (25)



A 16 mL vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) and 3-Bromo-9*H*-carbazole (49.2 mg, 0.2 mmol). Toluene (1.5 mL) was added, and the mixture was stirred at room temperature for 0.5 hour. Then, a solution of 4-chlorophenylacetylene (13.6 mg, 0.1 mmol) in toluene (0.5 mL) was added under stirring. The reaction was complete after 5 days at room temperature. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford product **25** as a white solid (23.0 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.22 (d, *J* = 2.0 Hz, 1H), 8.06 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H),7.42 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.29 – 7.24 (m, 3H),7.21 (dt, *J* = 8.5 Hz, 1.0 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.07 (d, J = 8.5 Hz, 1H), 6.07 (s, 1H), 5.59 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 141.40, 140.91, 139.23, 135.20, 134.44, 129.07, 128.64, 127.45, 126.69, 125.19, 123.02, 122.38, 120.44, 120.42, 113.58, 112.87, 112.20, 110.91.

DEPT^{135} NMR (126 MHz, $CDCl_3$), δ: 129.07, 128.64, 127.45, 126.69, 123.01, 120.43, 120.41, 113.58, 112.20, 110.91.

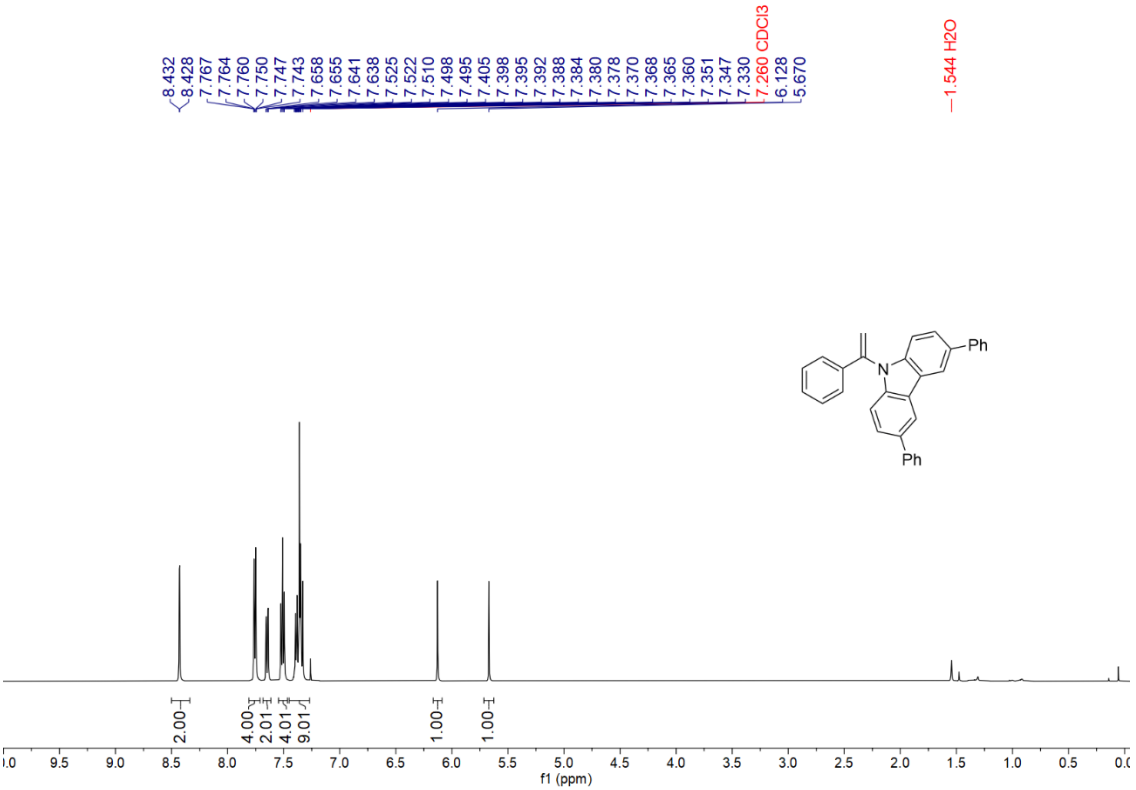
HRMS (ESI, *m/z*): Calcd. for $C_{20}H_{14}Cl^{34.9689}Br^{79.9183}N^+$, ($[M+H]^+$): 381.9993; Found: 381.9990; $C_{20}H_{14}Cl^{35.4500}Br^{80.9163}N^+$, ($[M+H]^+$): 383.9972; Found: 383.9966.

References

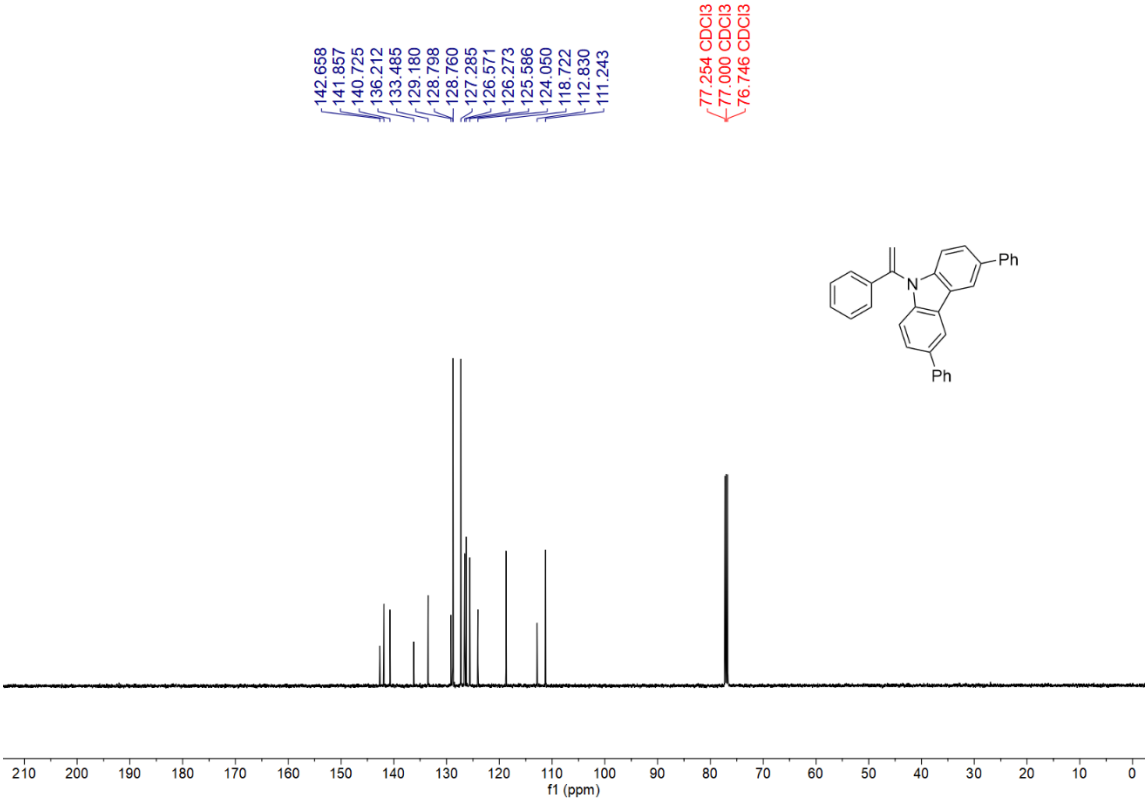
1 G. M. Sheldrick, *Acta Crystallographica Section A,* 2008, **64**, 112.
2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.,* 2009, **42**, 339.

NMR spectra of isolated compounds

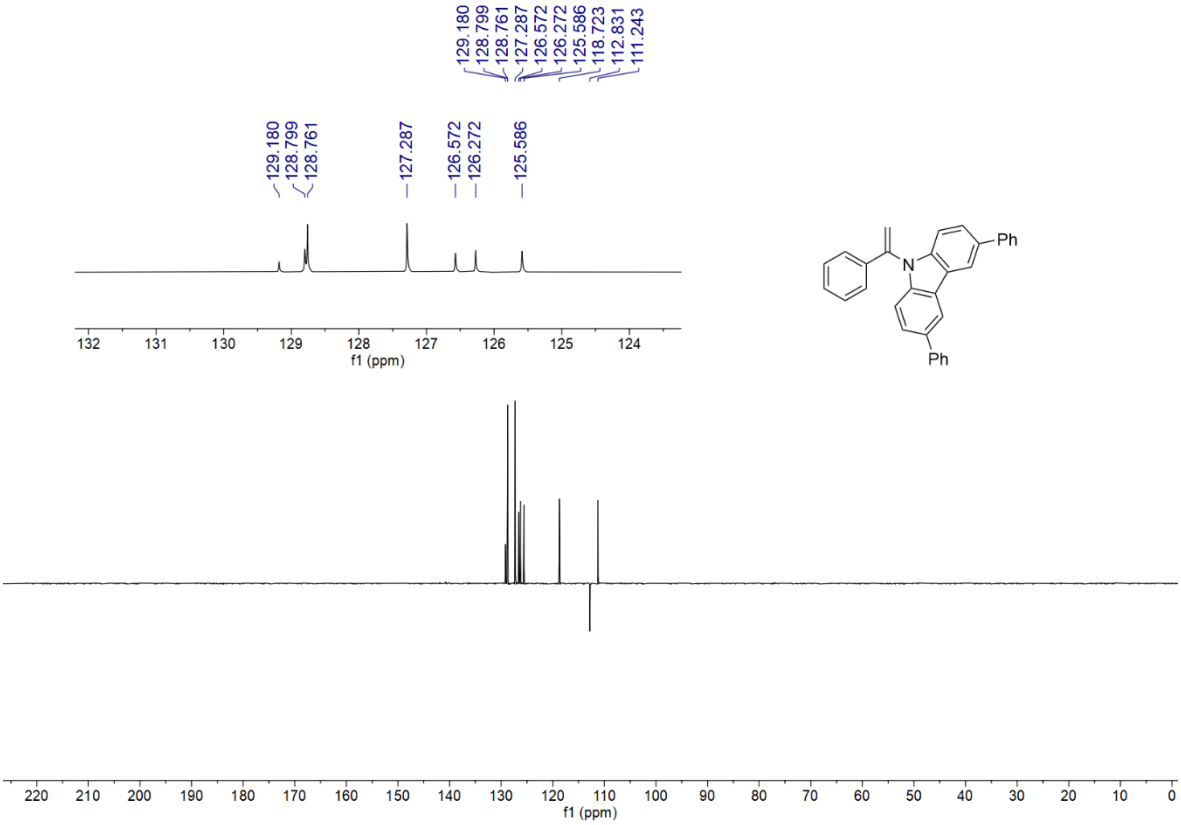
1 ^{1}H NMR (500 MHz, $CDCl_3$)



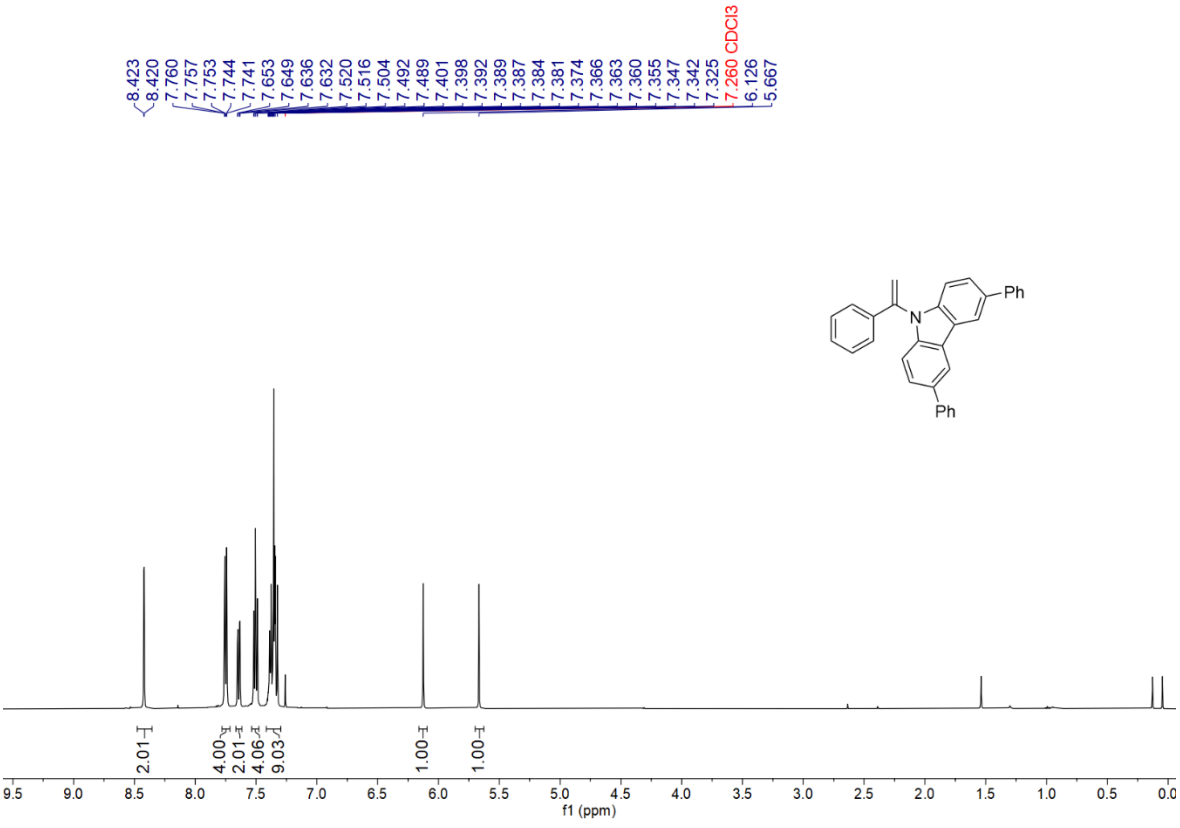
1 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



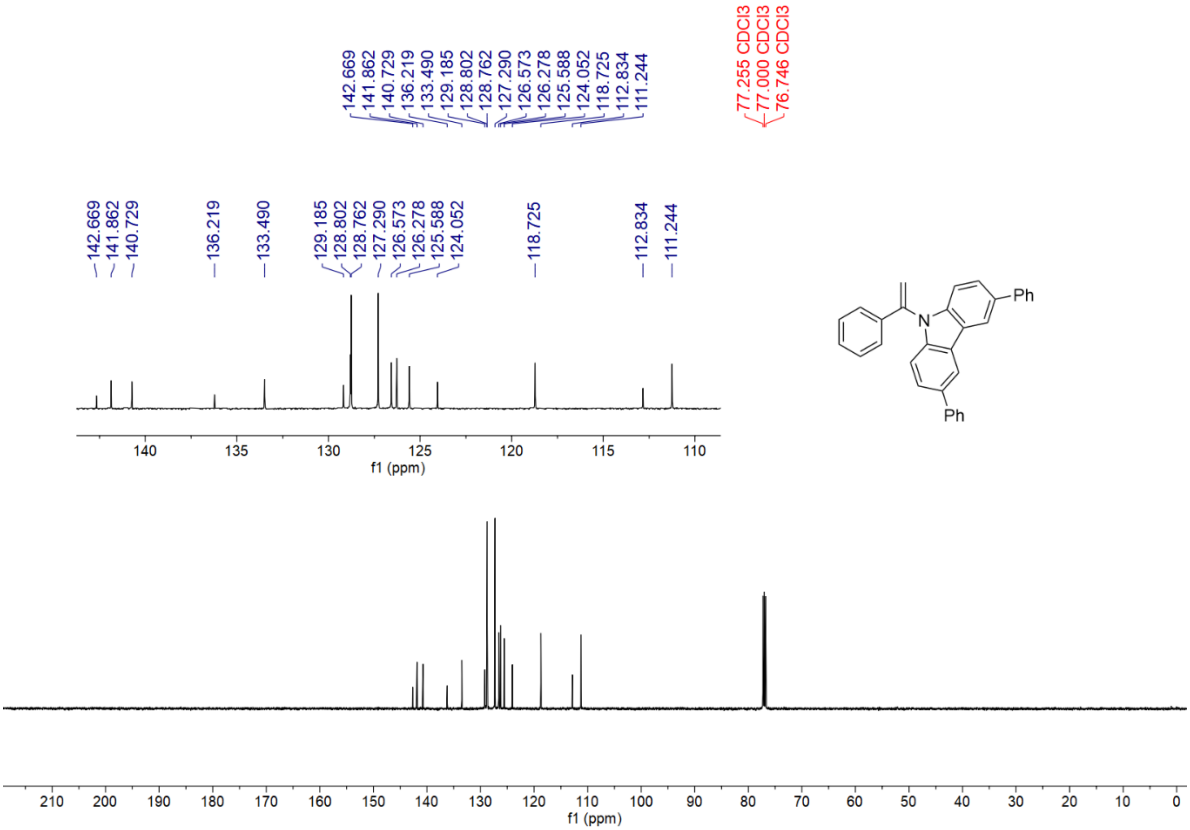
1 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



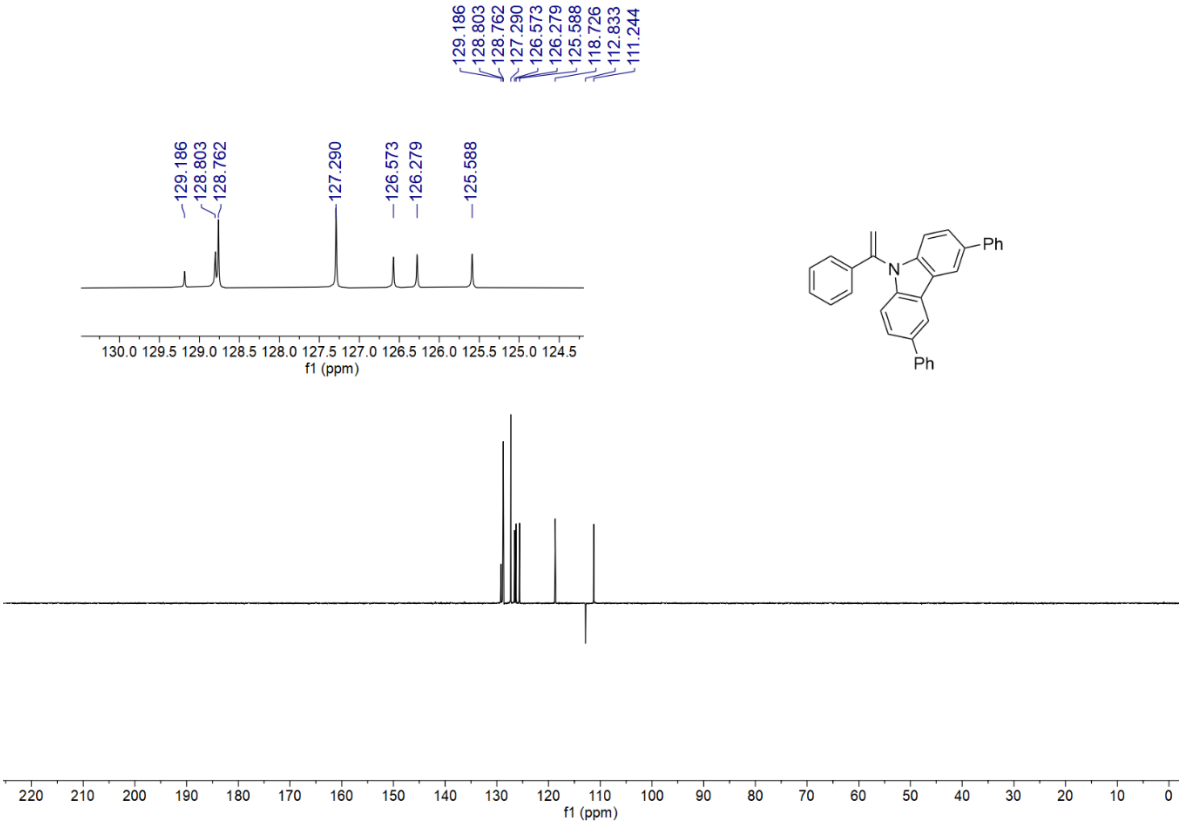
1 (Gram-scale) ^{1}H NMR (500 MHz, $CDCl_3$)



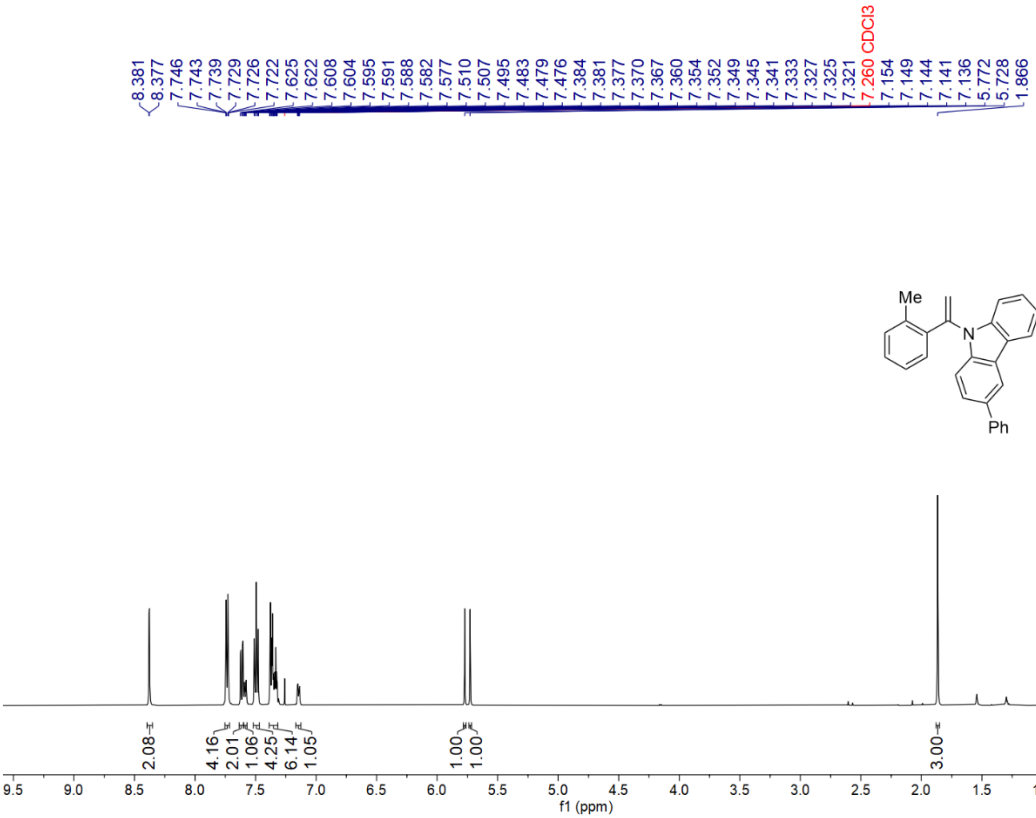
1 (Gram-scale) $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



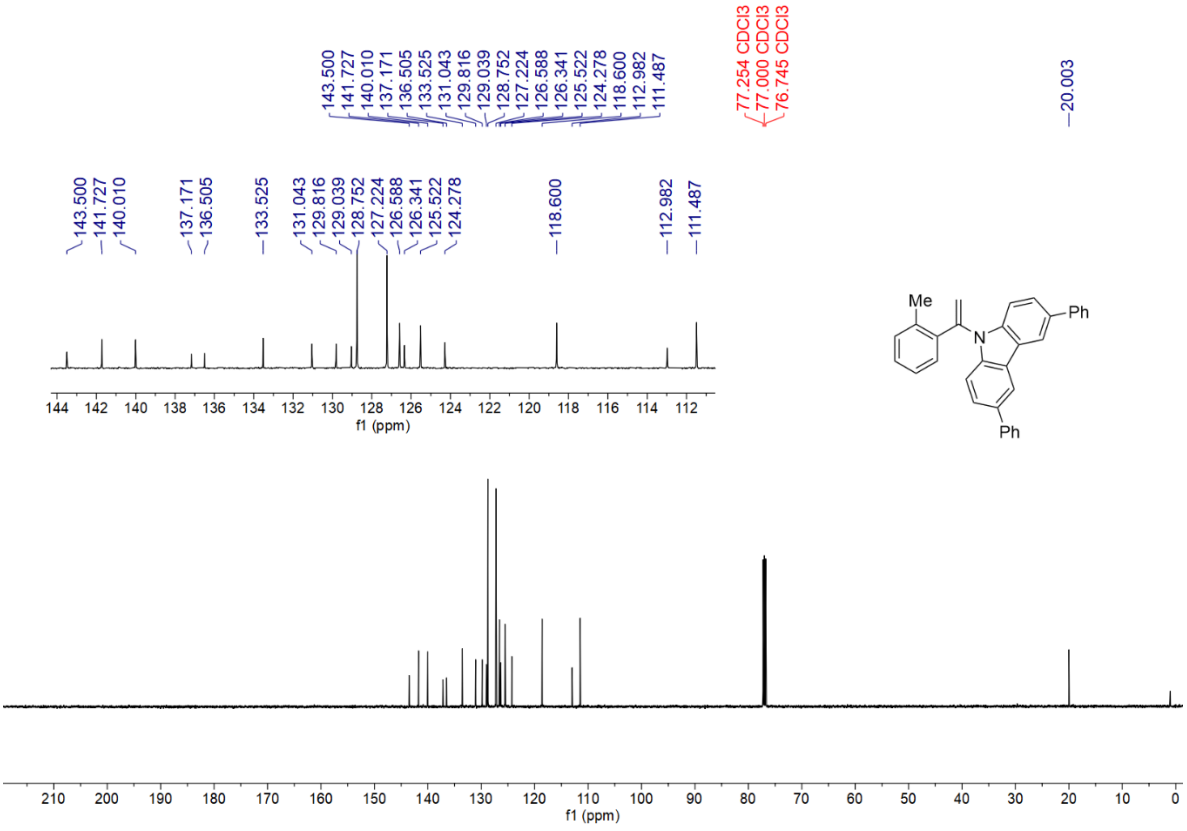
1 (Gram-scale) $DEPT^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



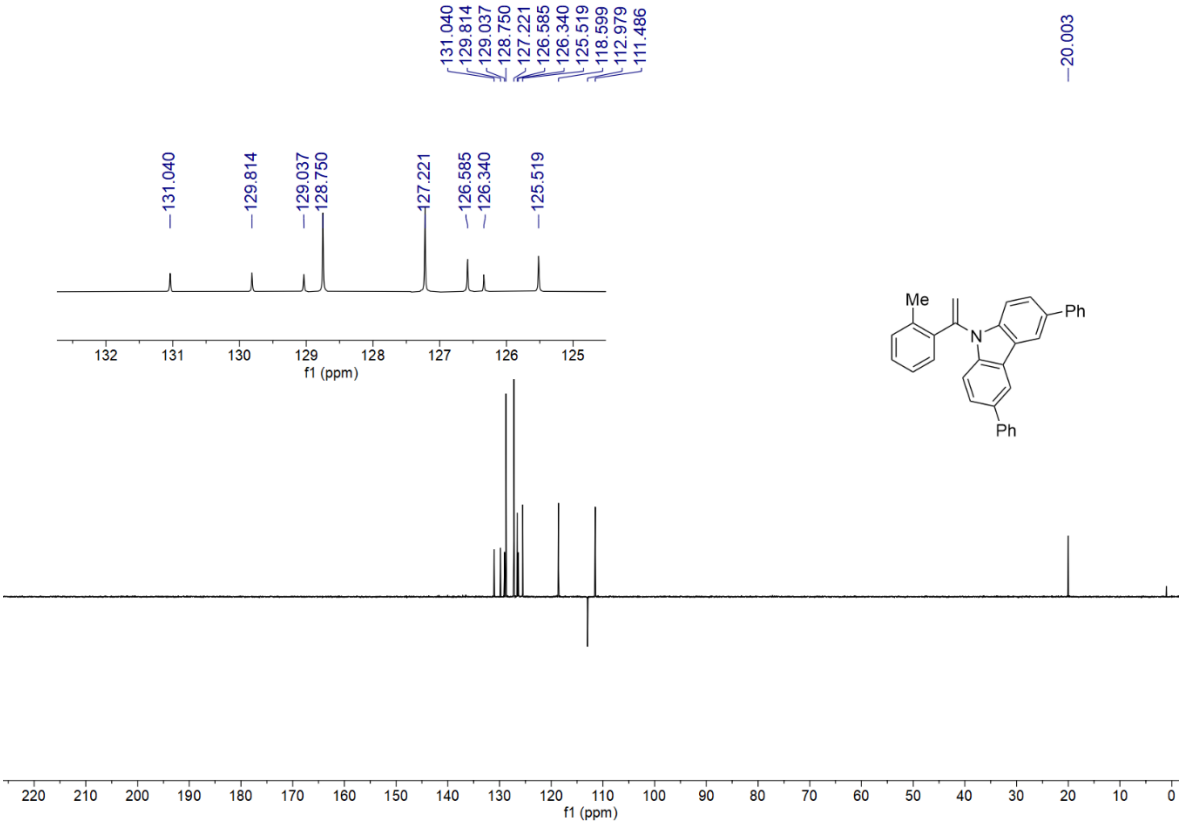
2 ^{1}H NMR (500 MHz, $CDCl_3$)



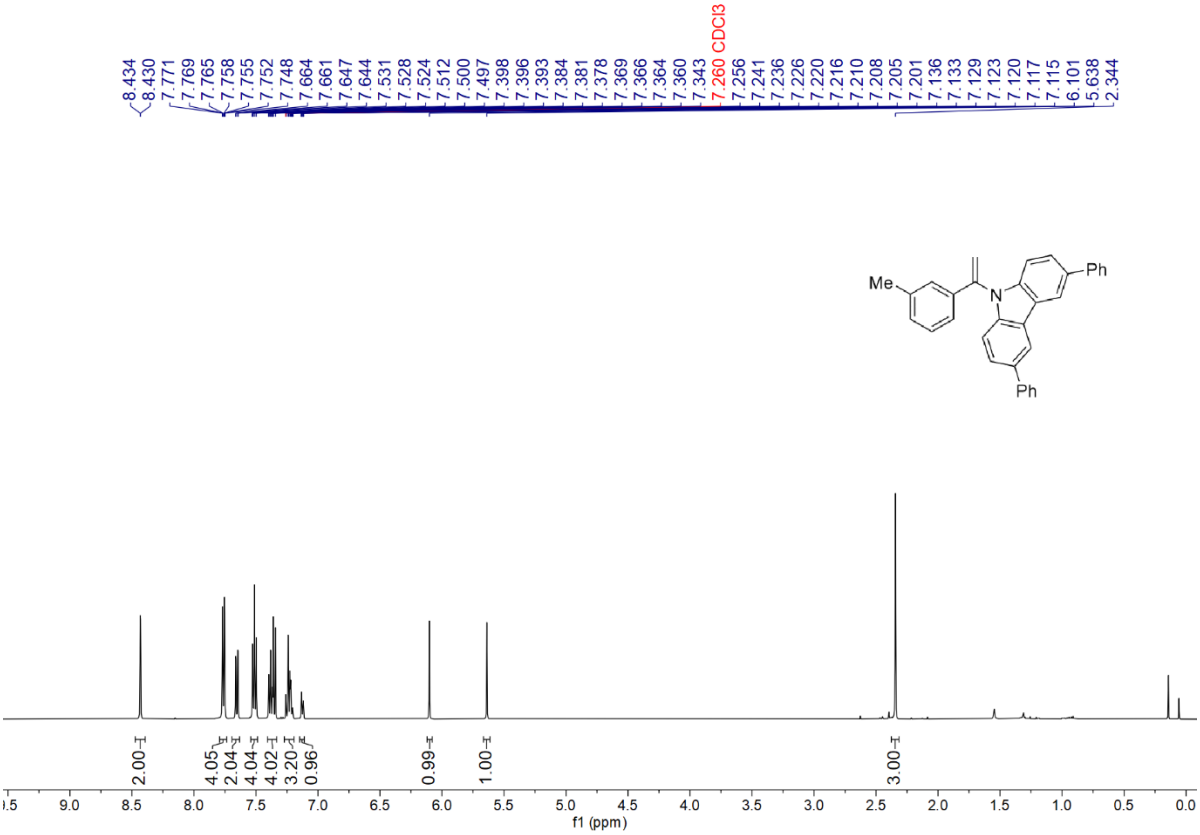
2 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



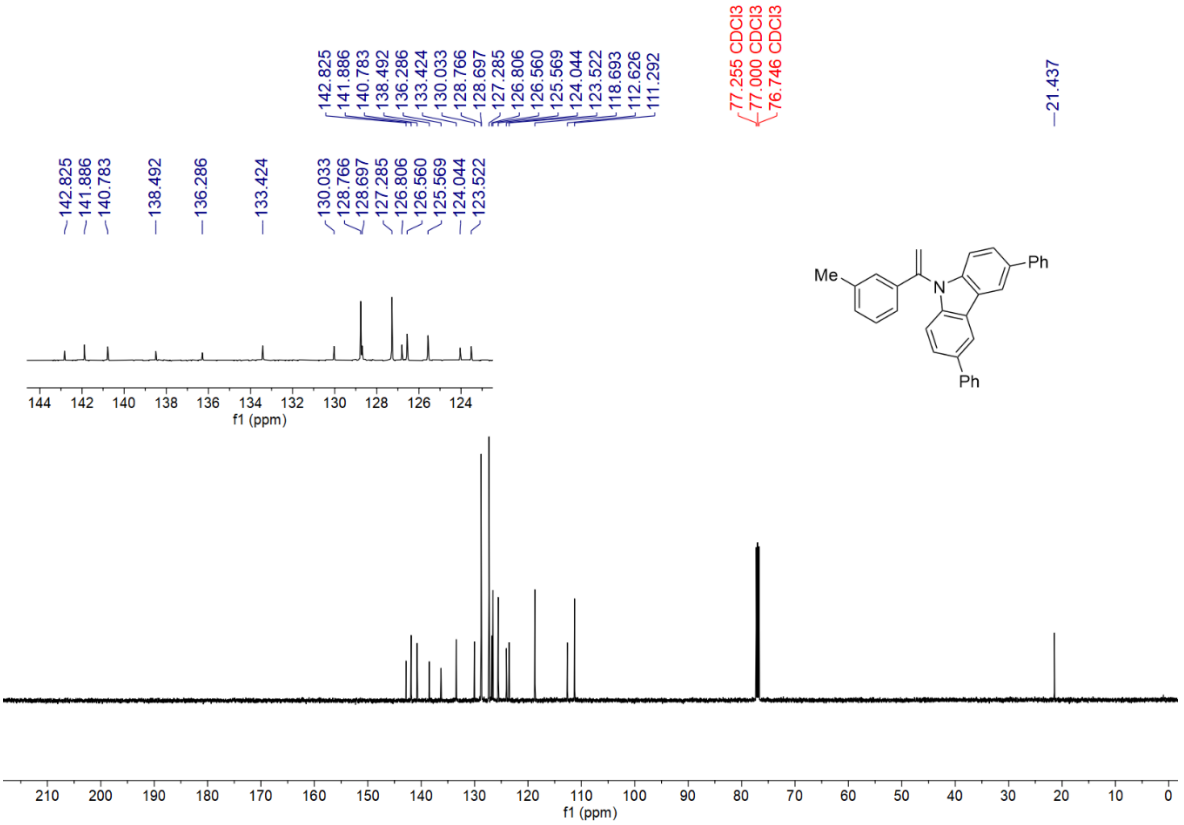
2 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



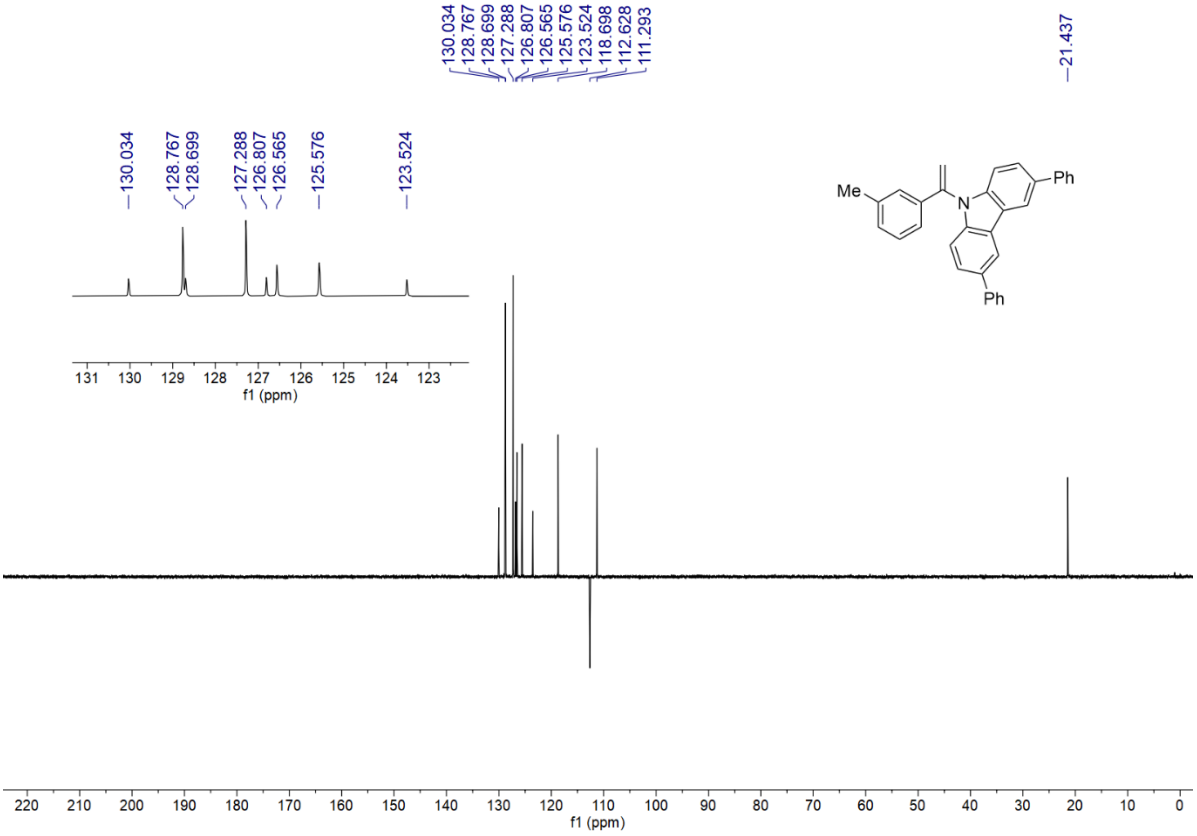
3 ^{1}H NMR (500 MHz, $CDCl_3$)



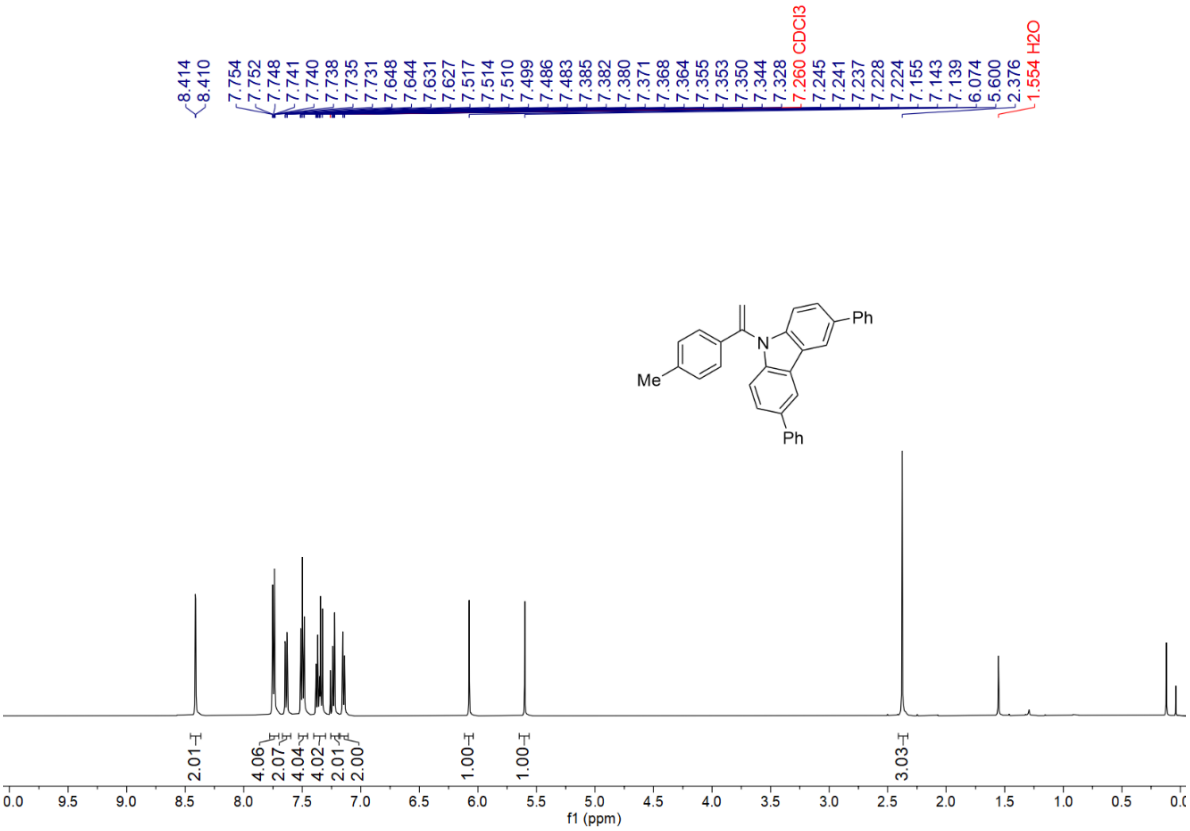
3 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



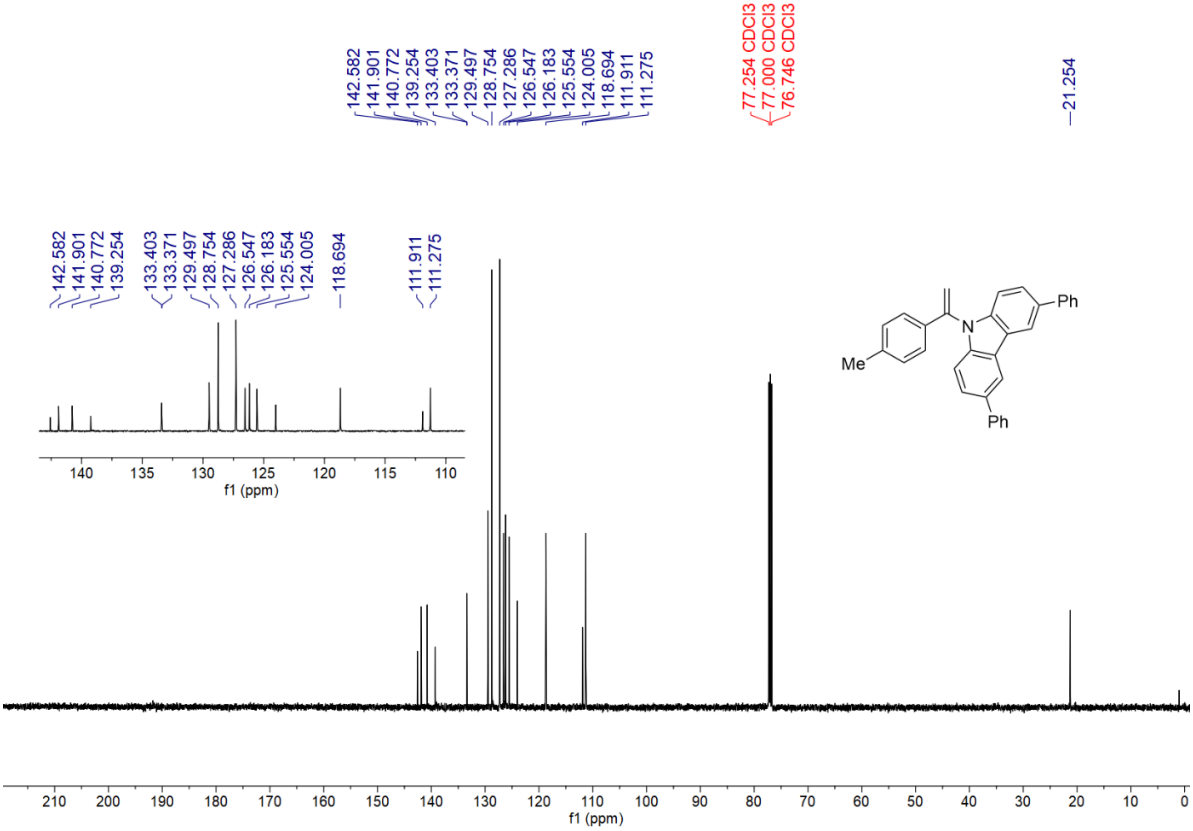
3 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



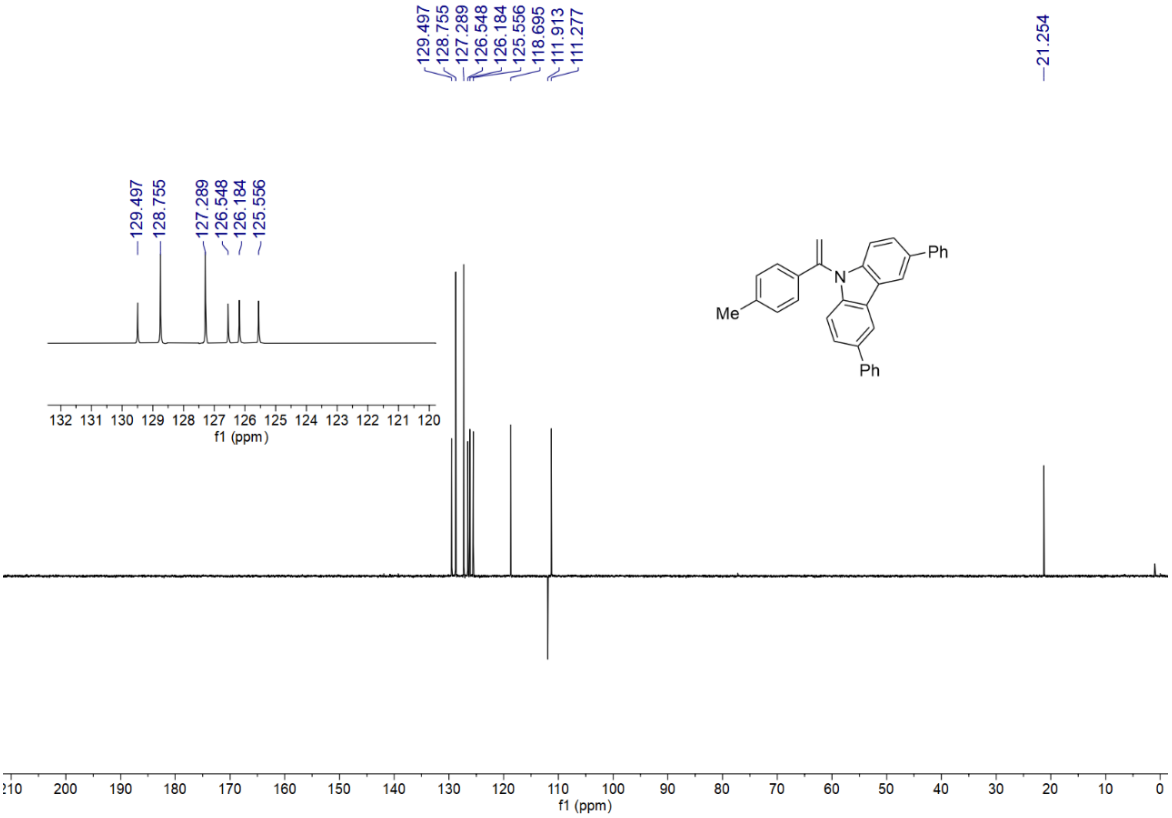
4 ^{1}H NMR (500 MHz, $CDCl_3$)



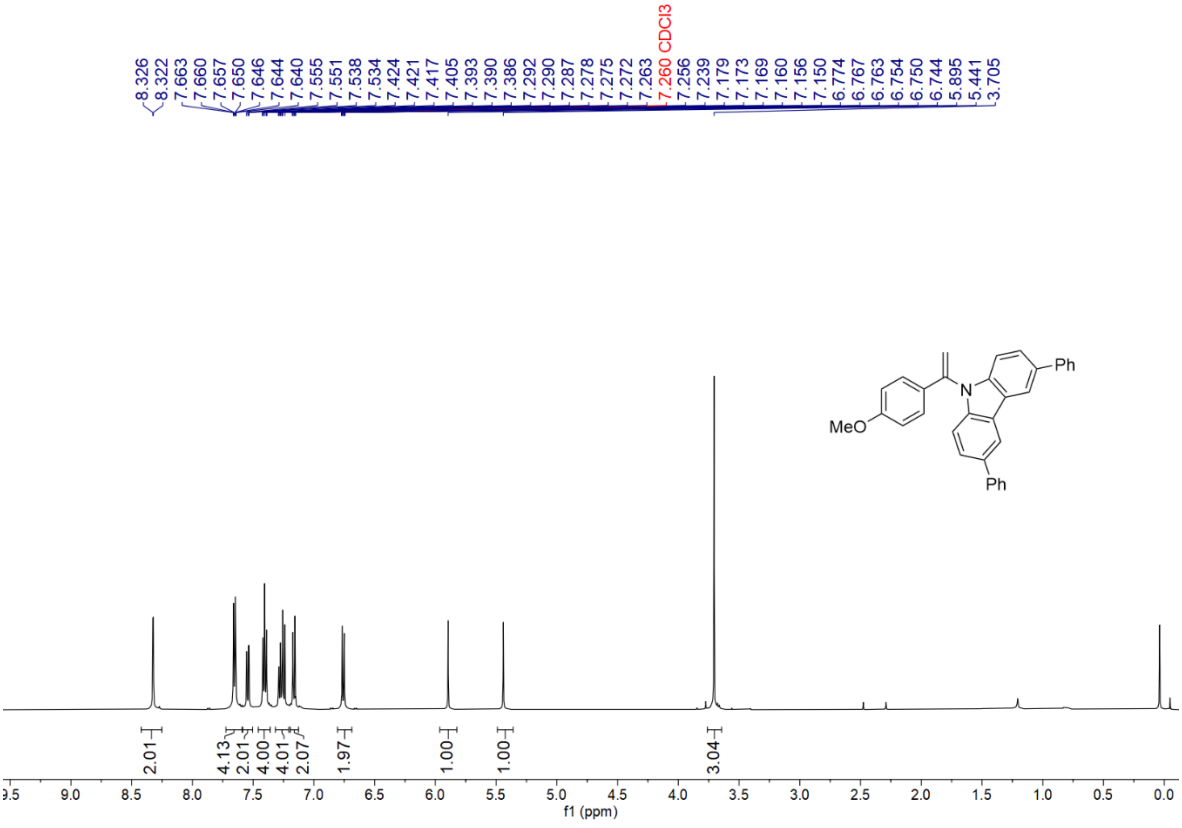
4 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



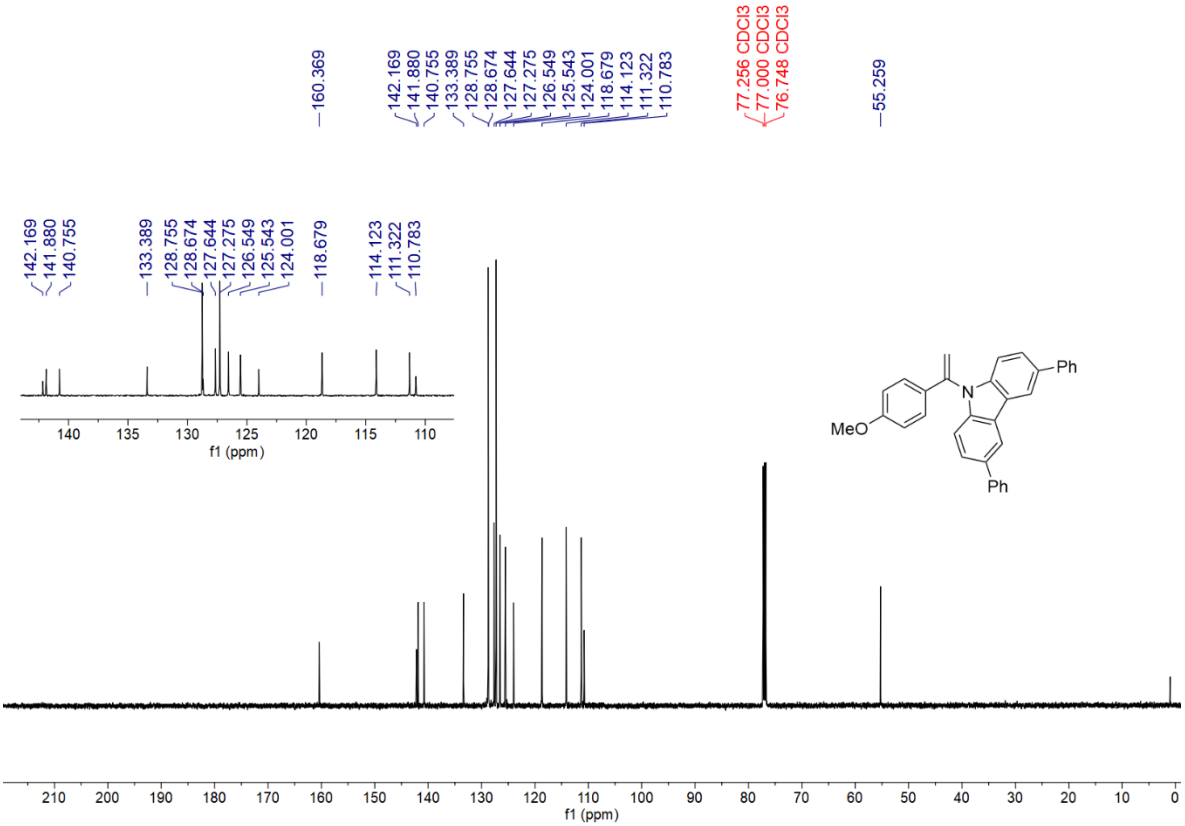
4 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



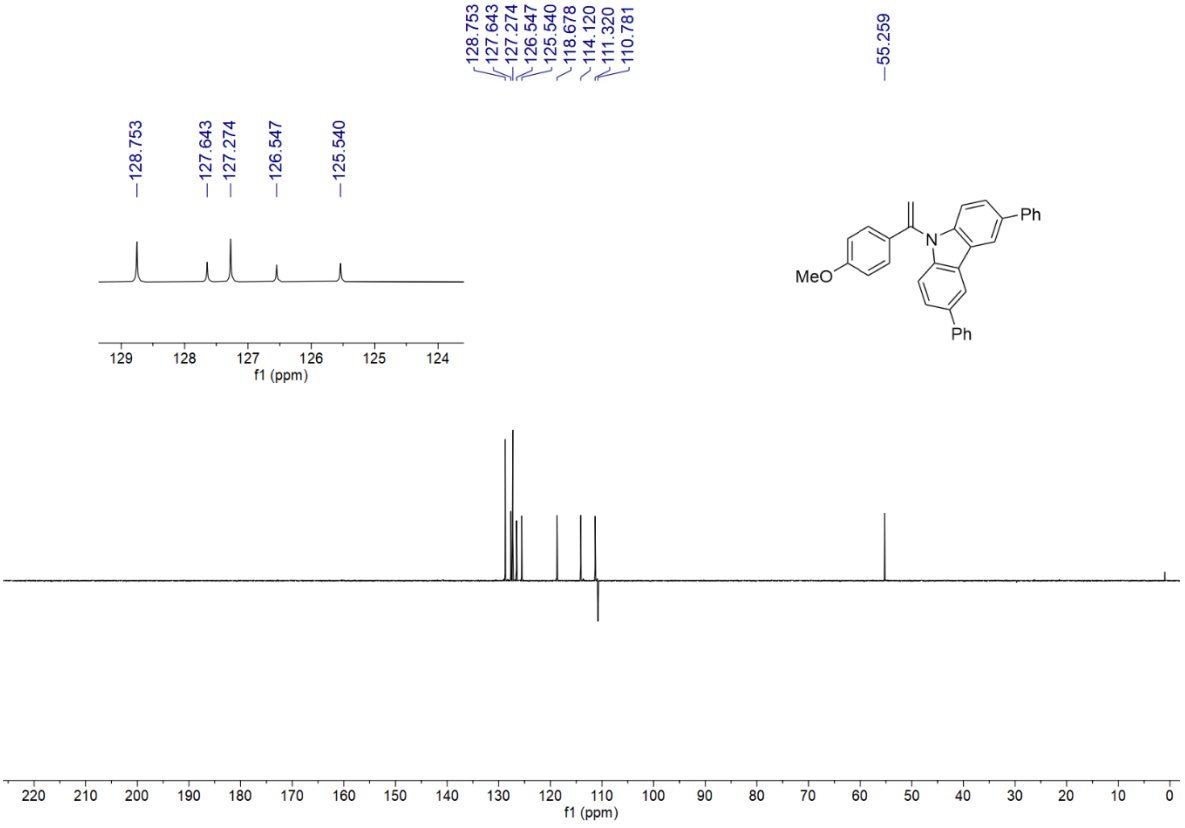
5 ^{1}H NMR (500 MHz, $CDCl_3$)



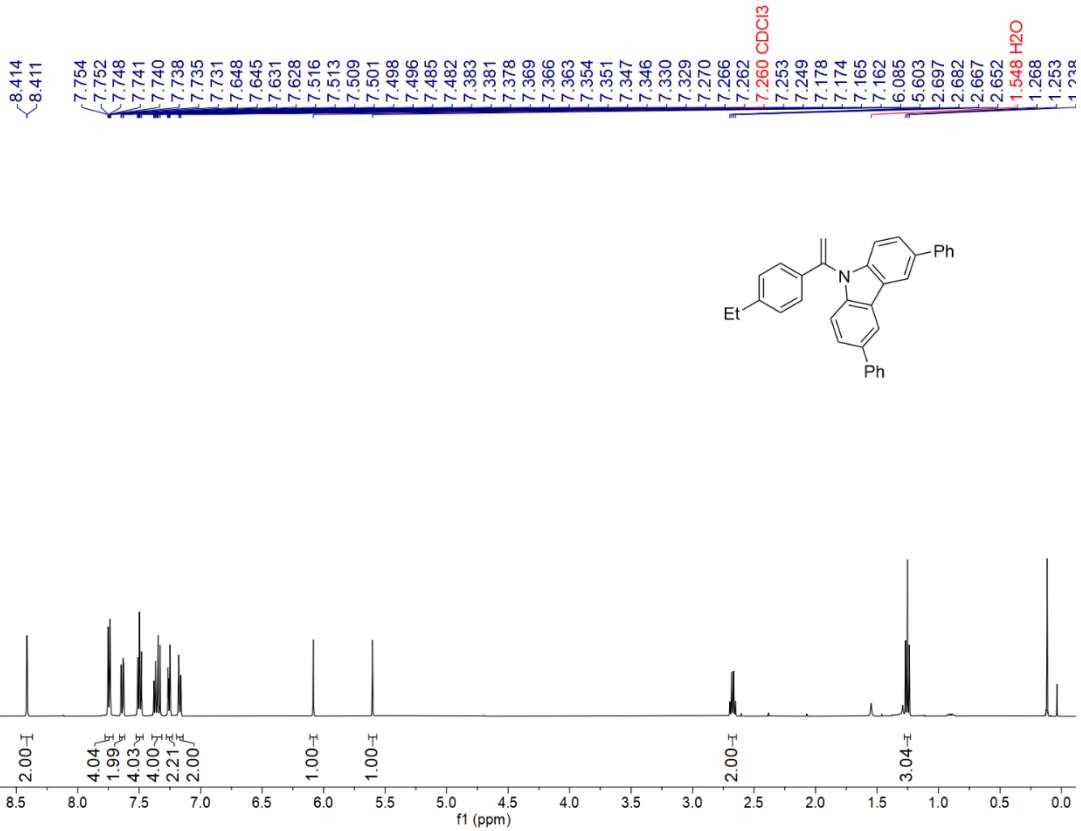
5 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



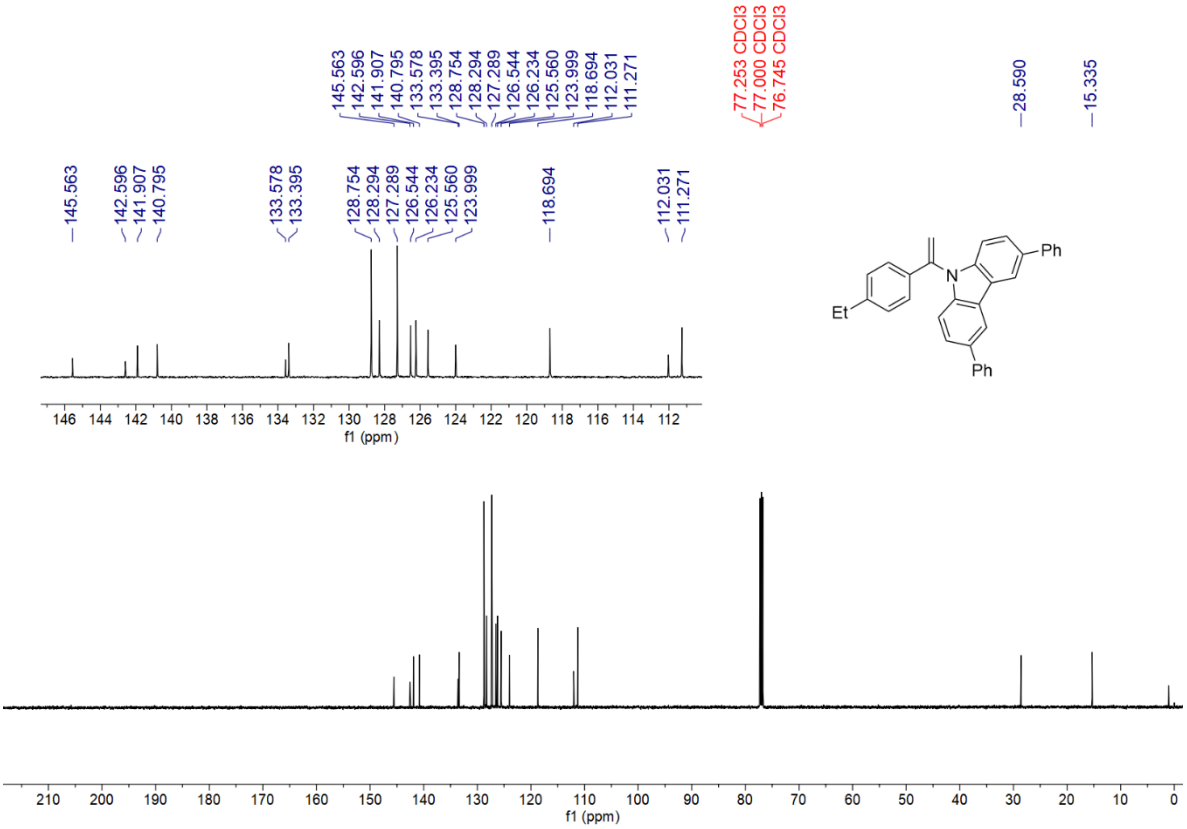
5 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



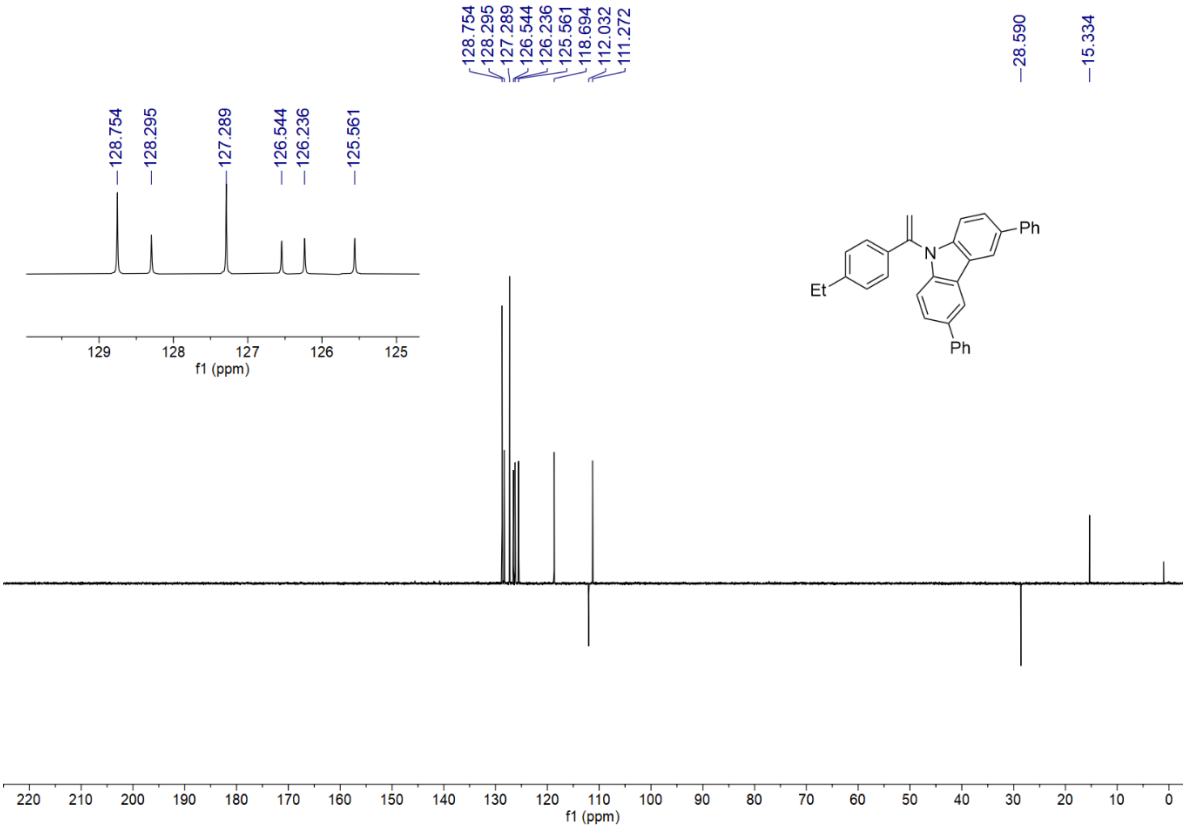
6 ^{1}H NMR (500 MHz, $CDCl_3$)



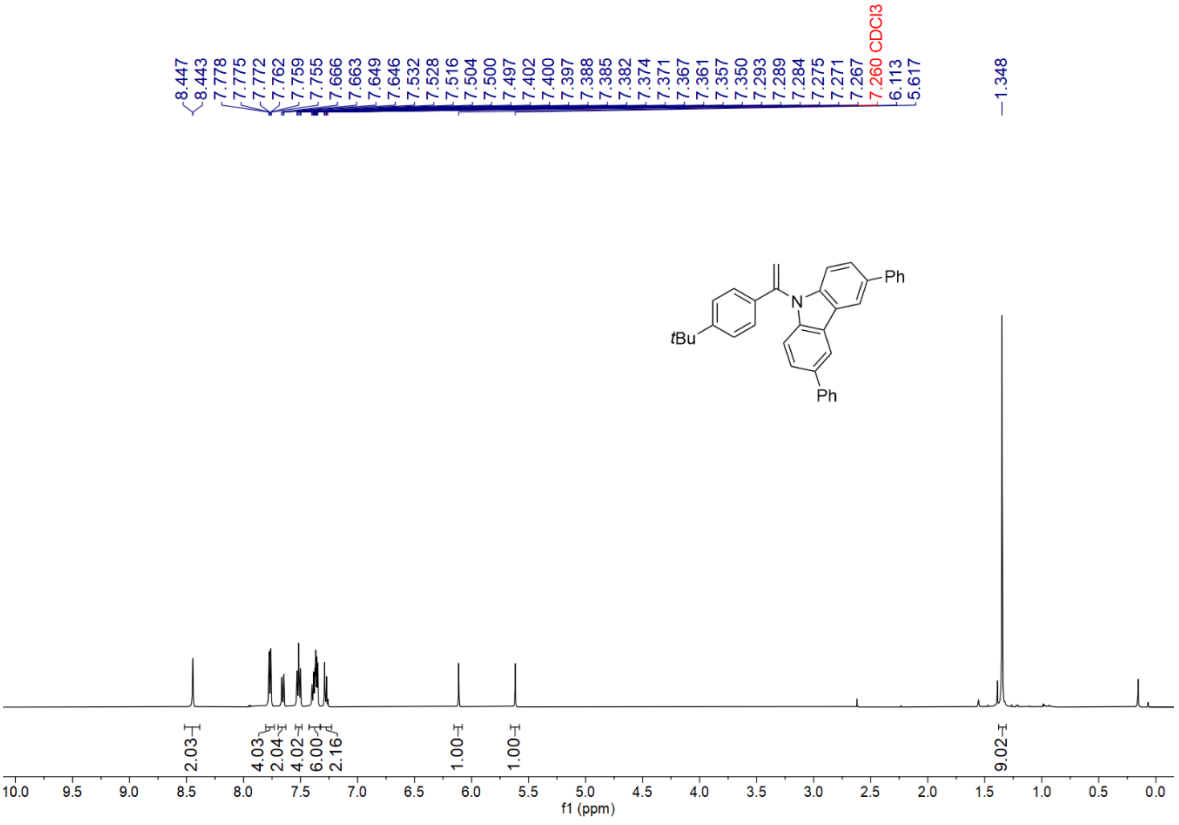
6 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



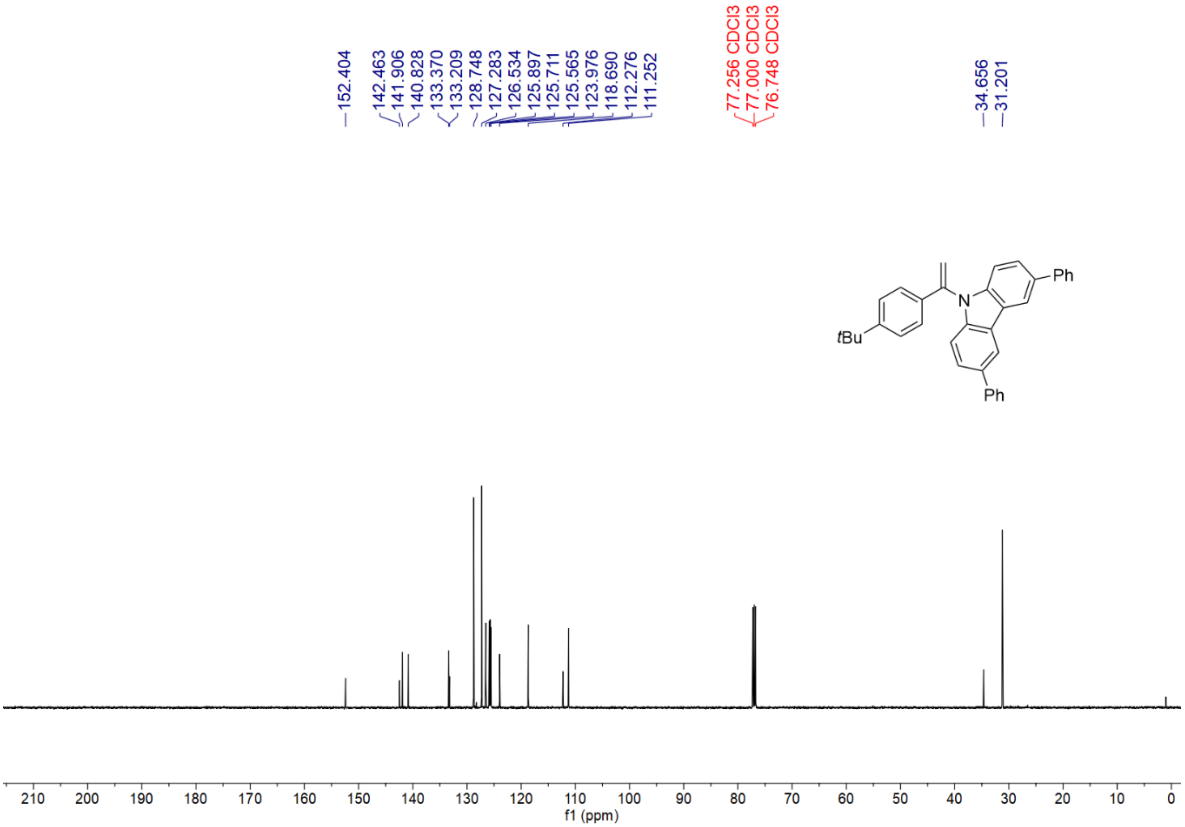
6 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



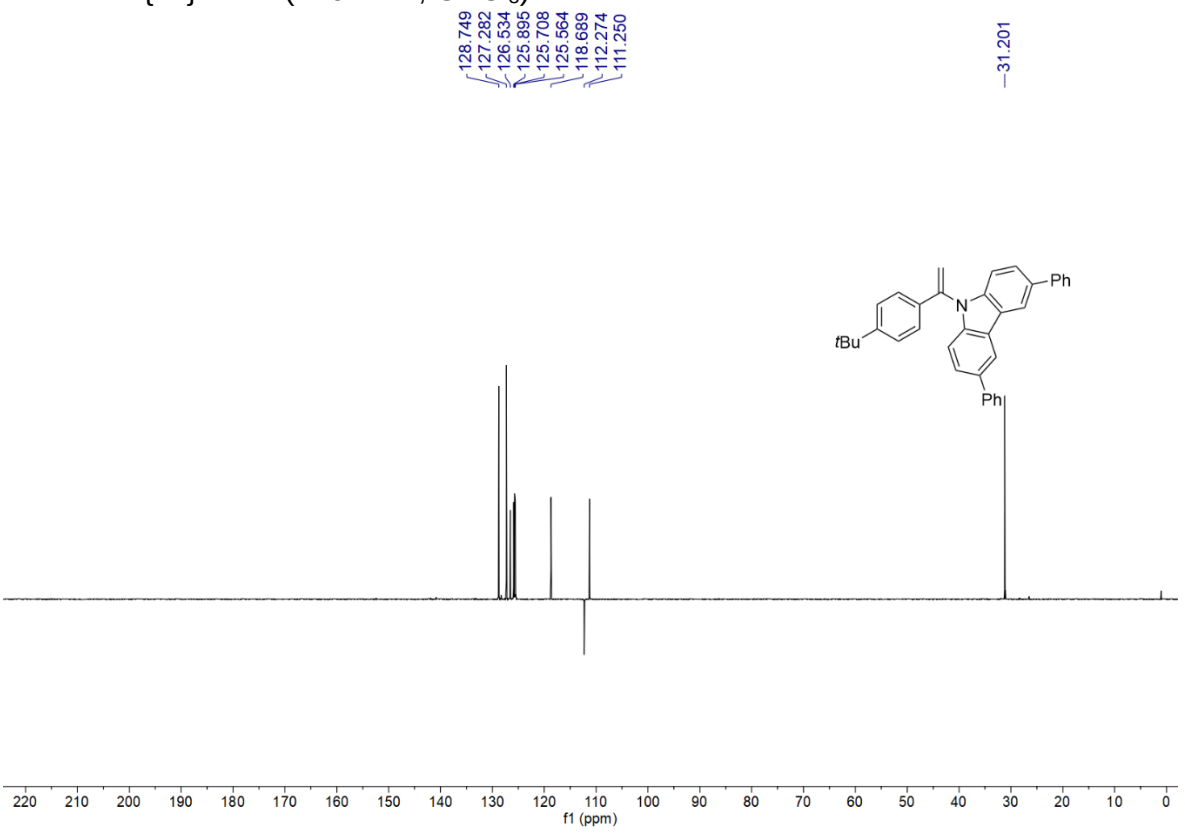
7 ^{1}H NMR (500 MHz, $CDCl_3$)



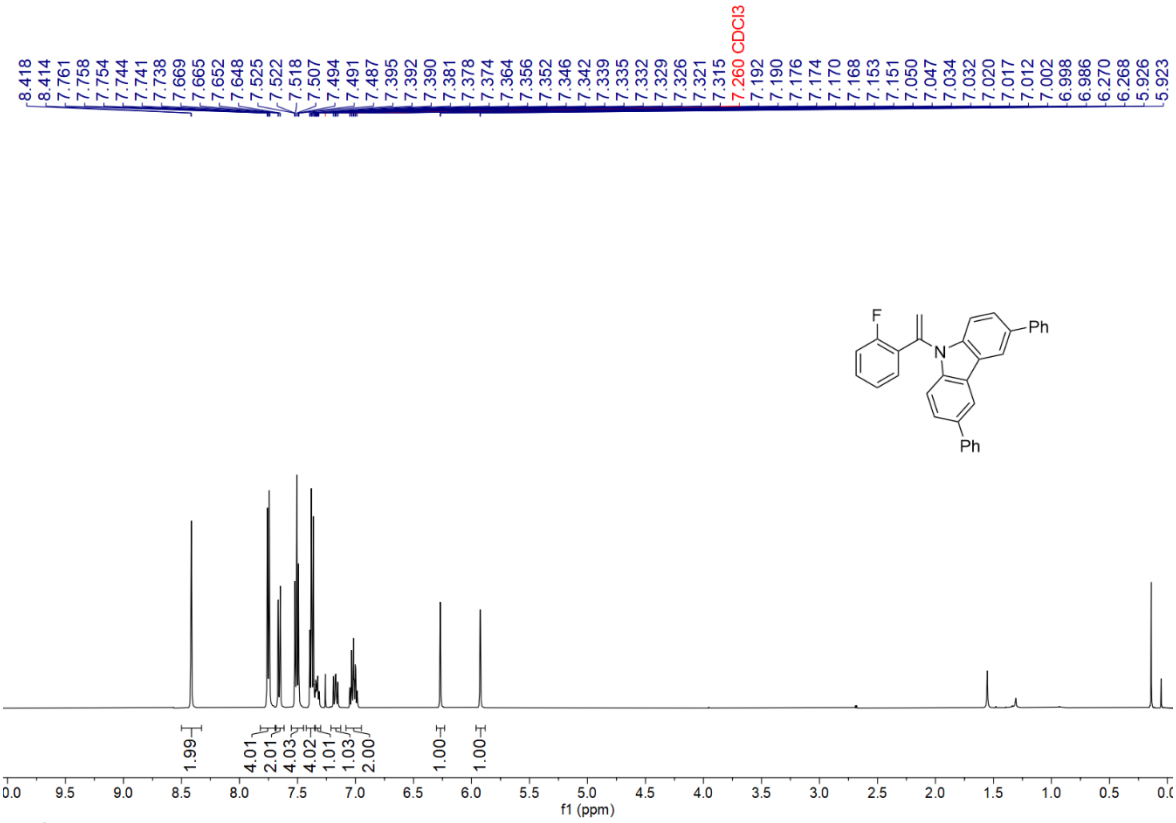
7 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



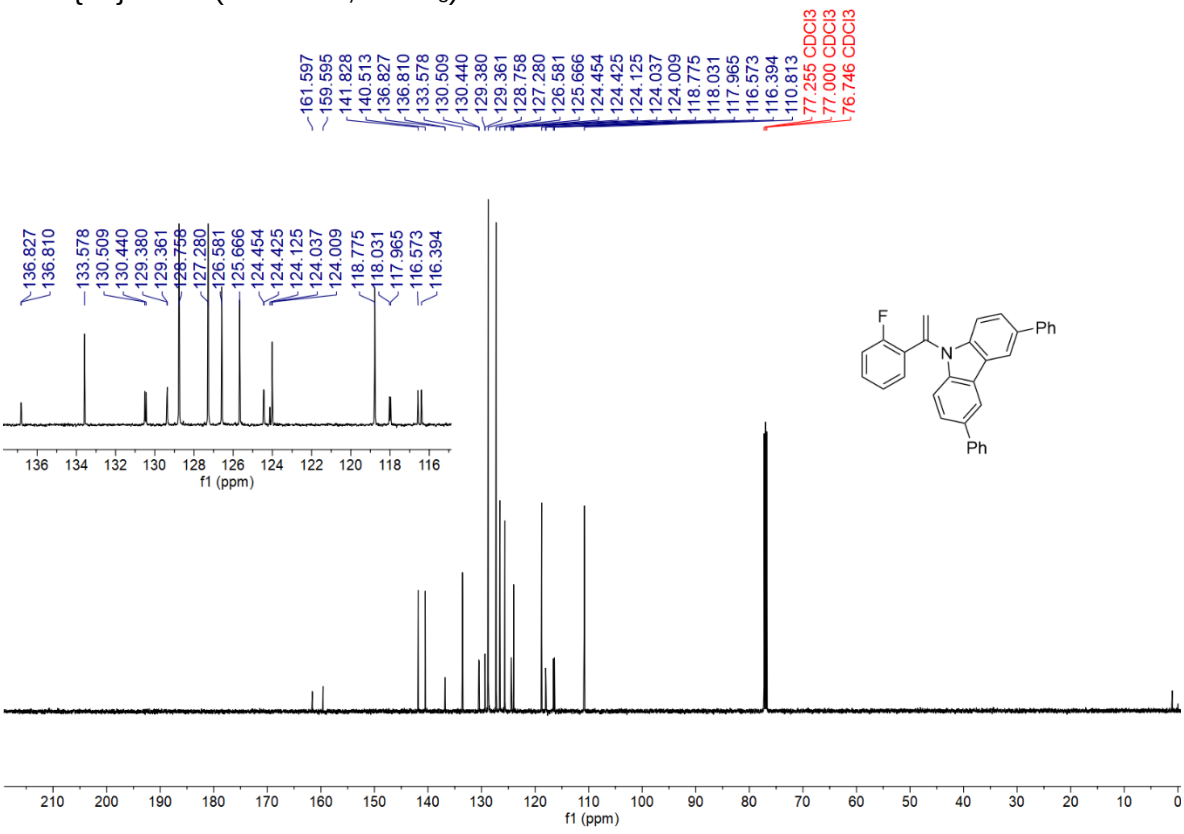
7 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



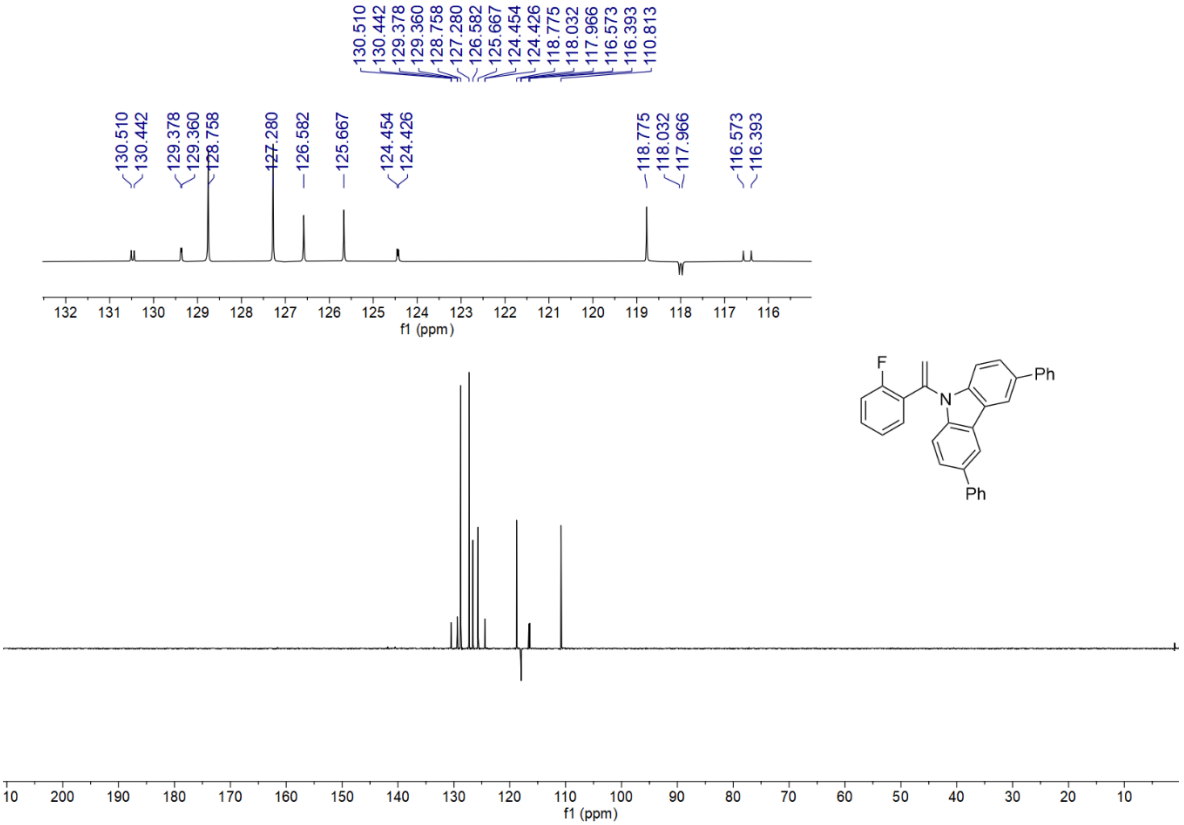
8 ^{1}H NMR (500 MHz, $CDCl_3$)



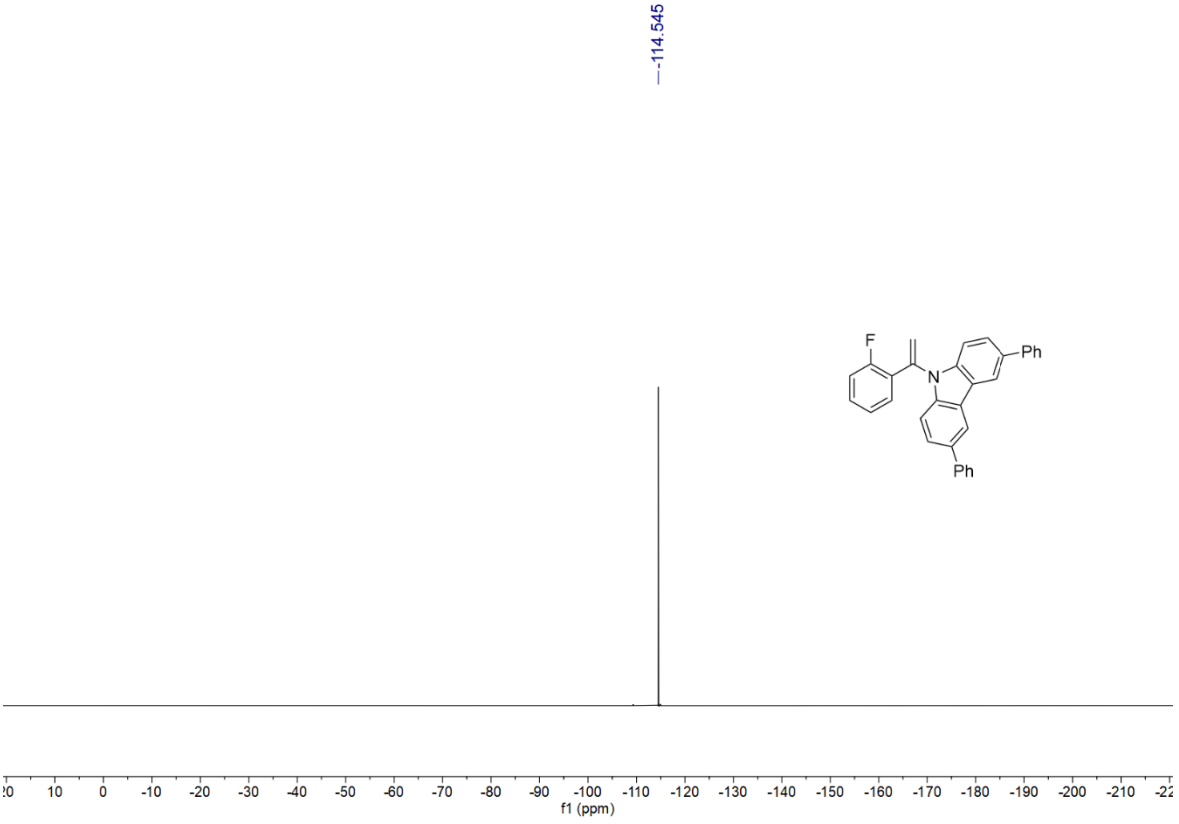
8 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



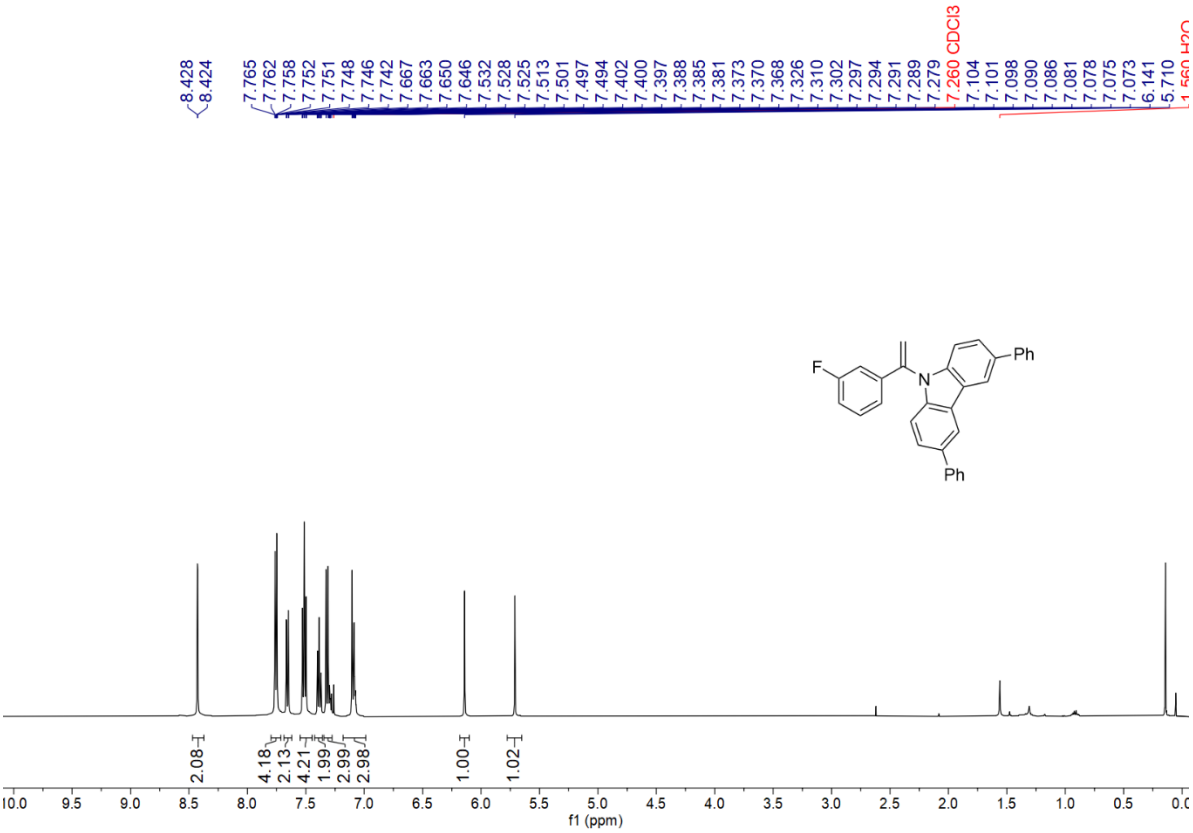
8 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



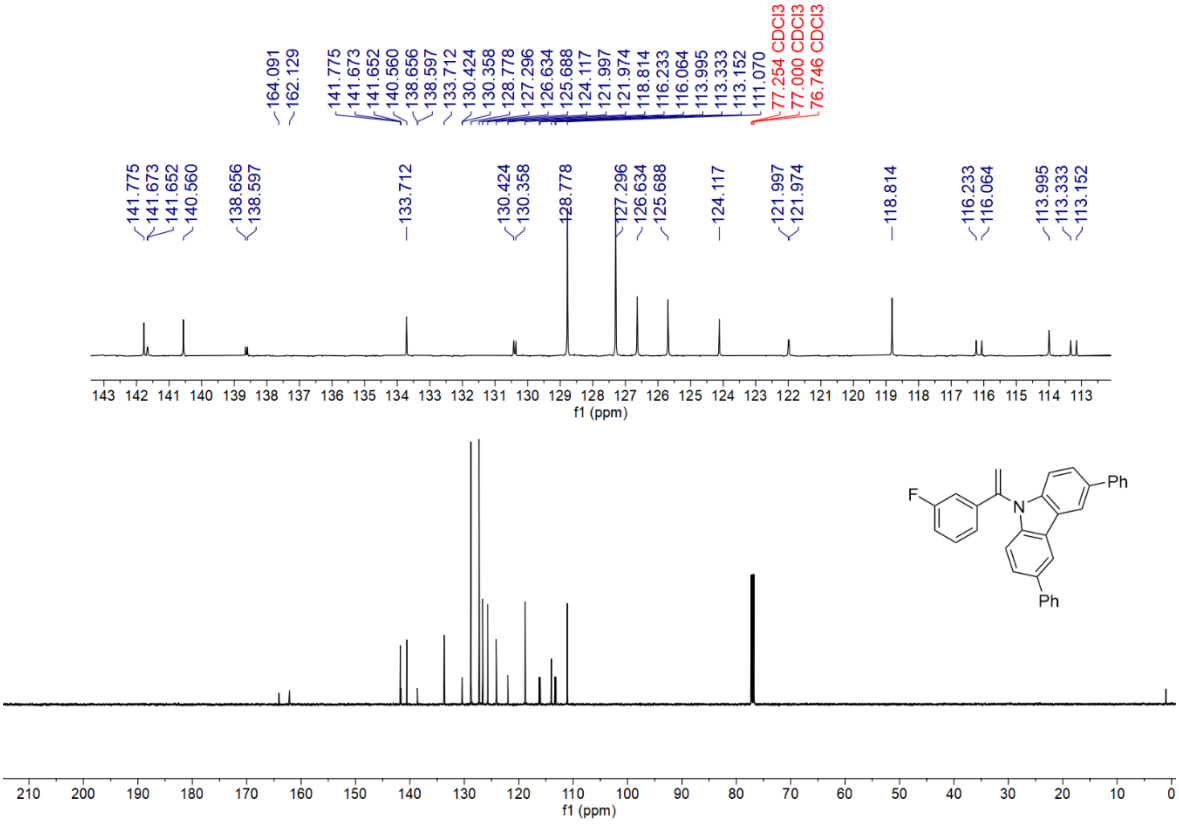
8 ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)



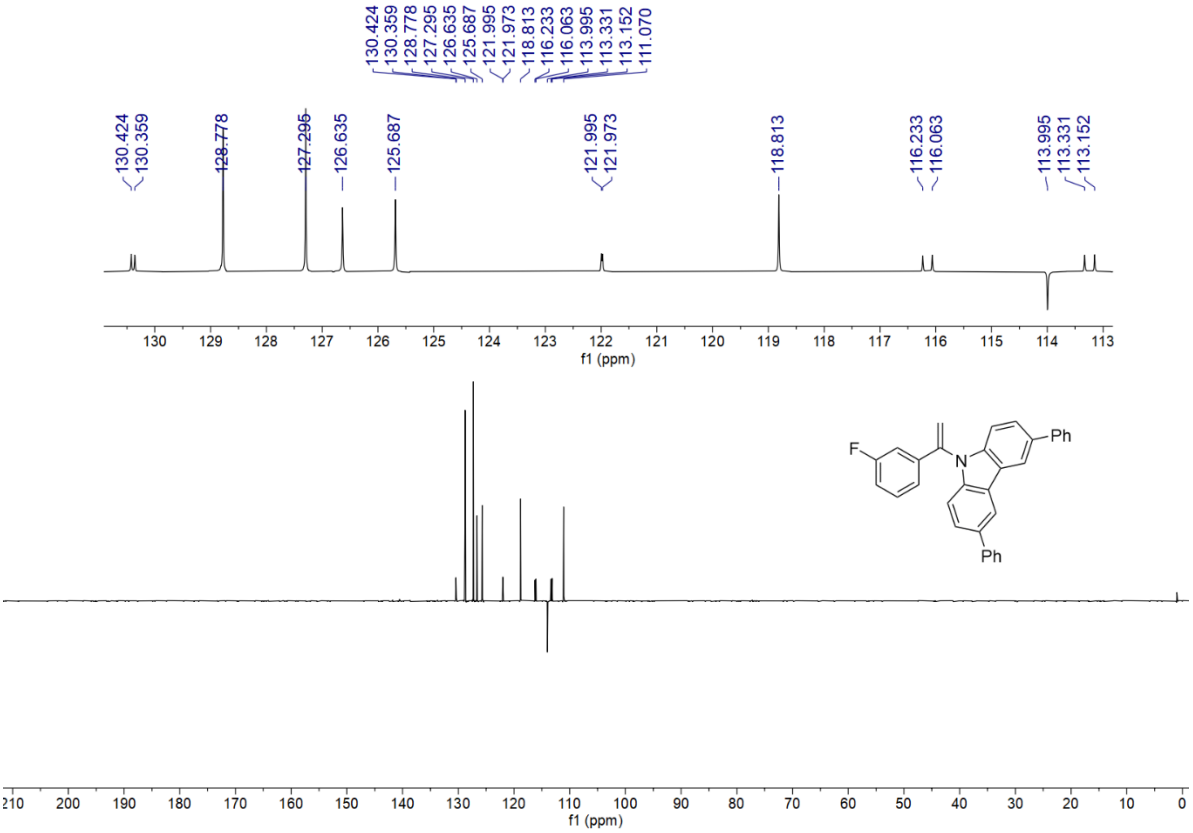
9 ^{1}H NMR (500 MHz, $CDCl_3$)



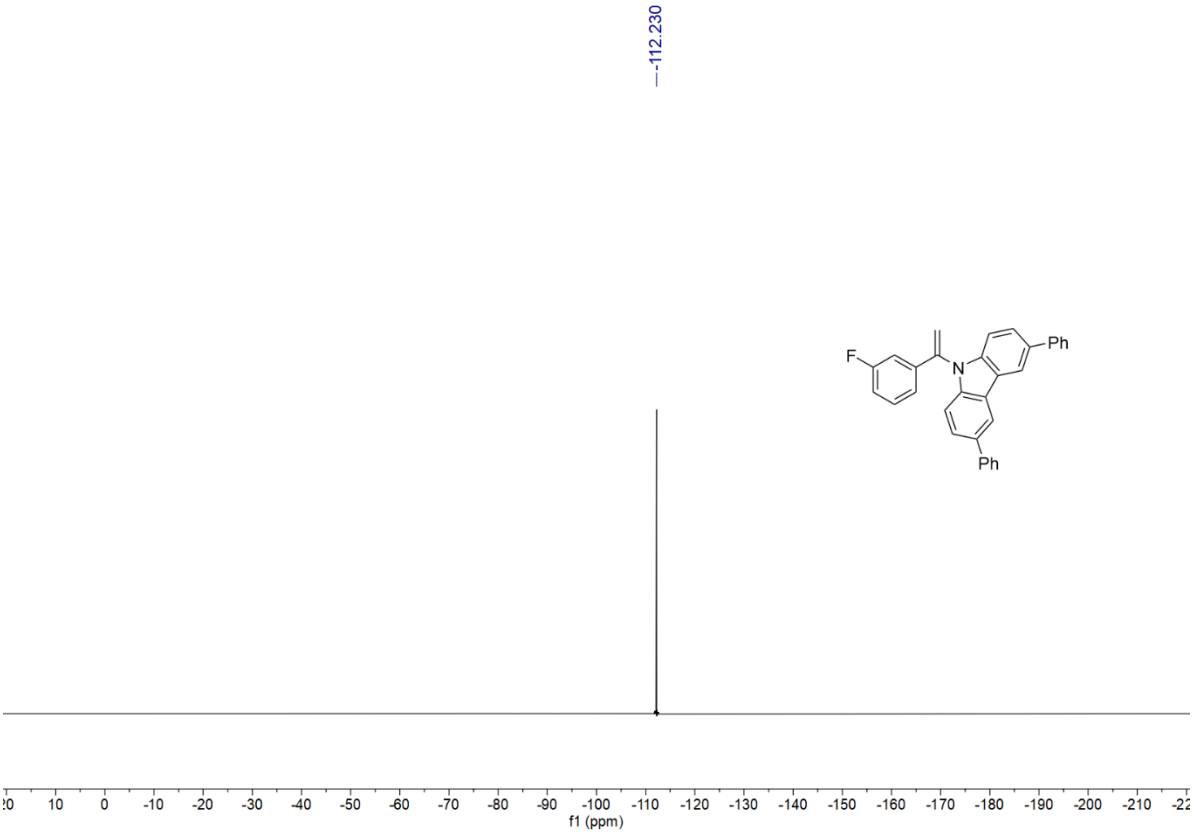
9 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



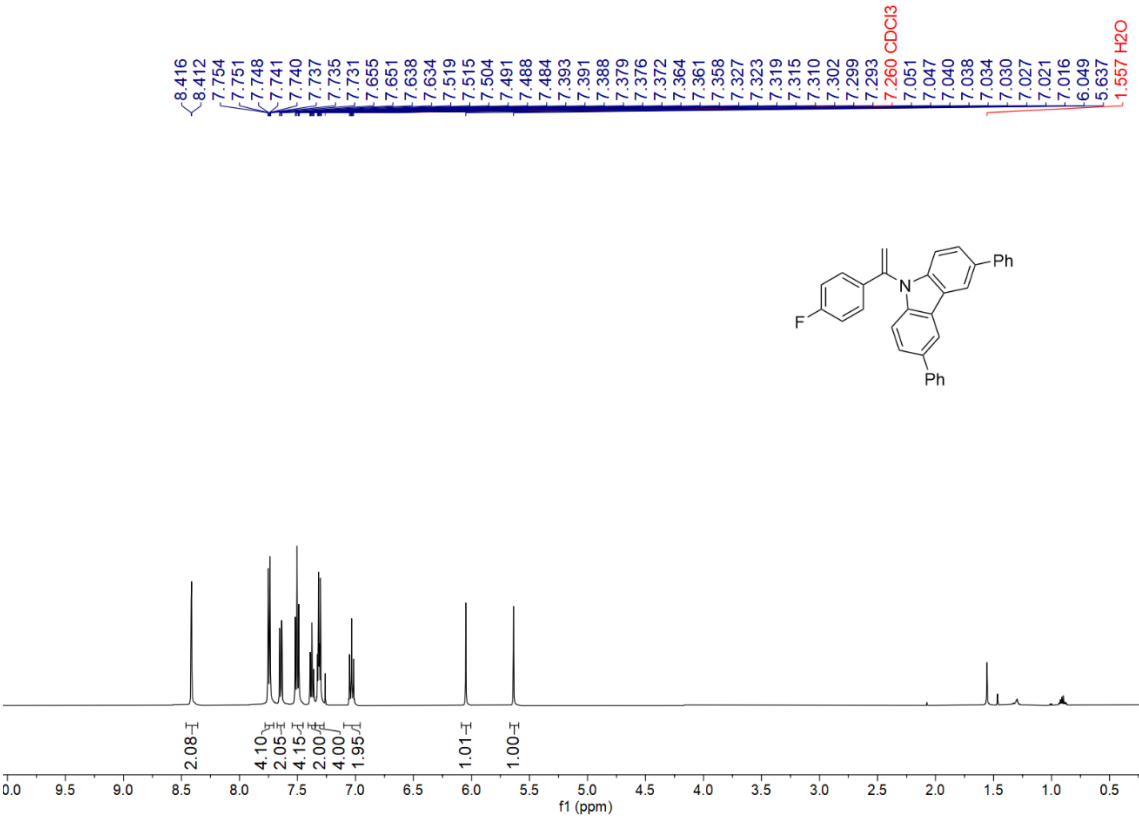
9 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



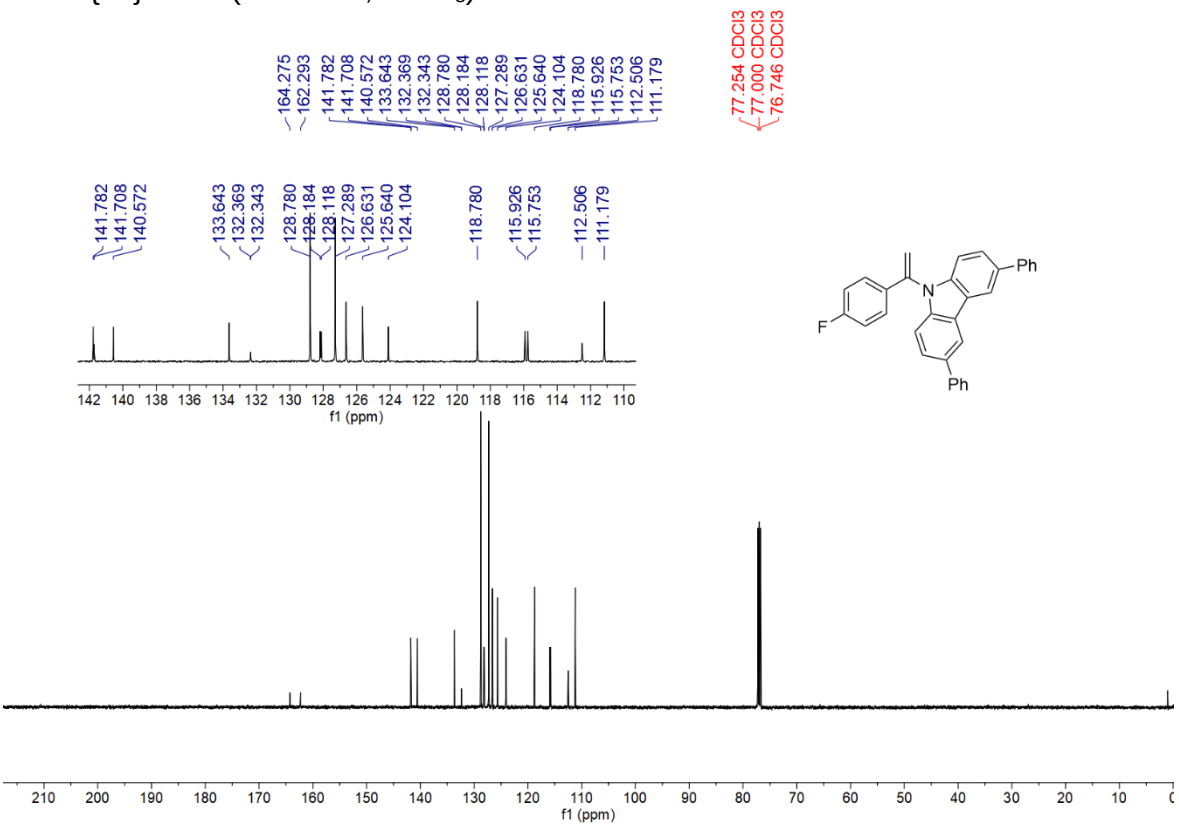
9 ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)



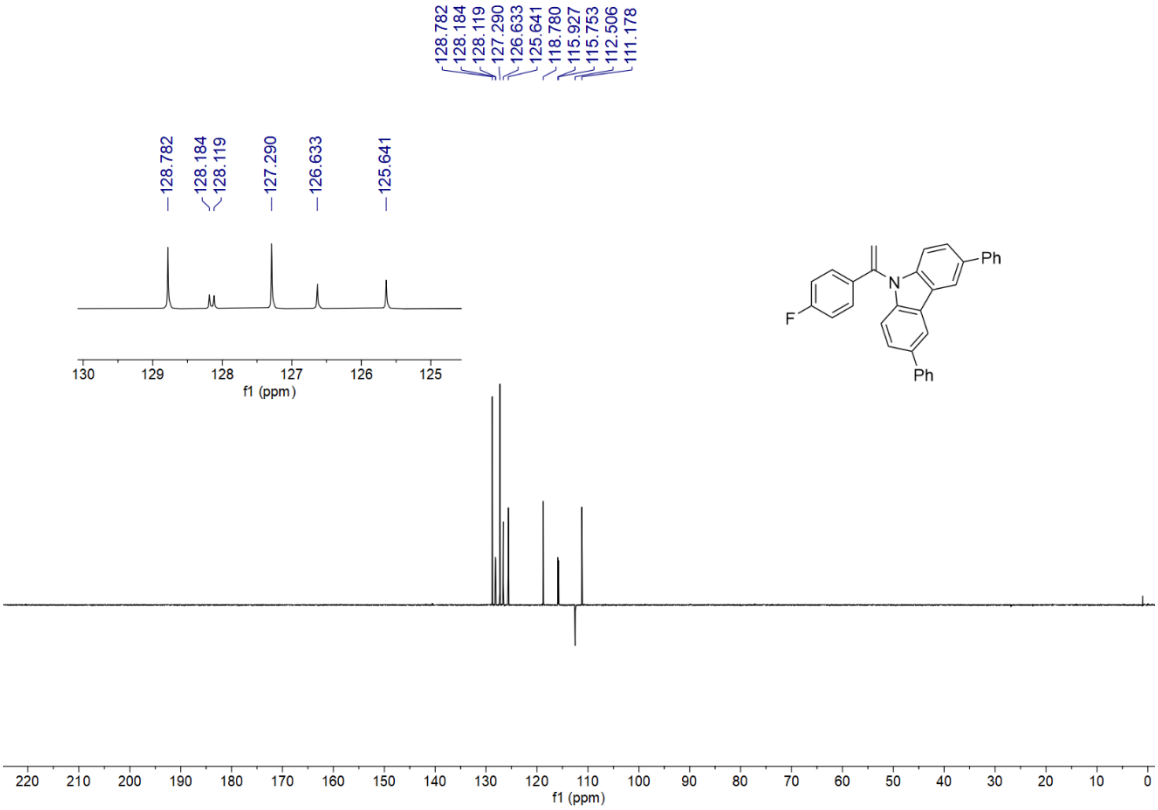
10 ^{1}H NMR (500 MHz, $CDCl_3$)



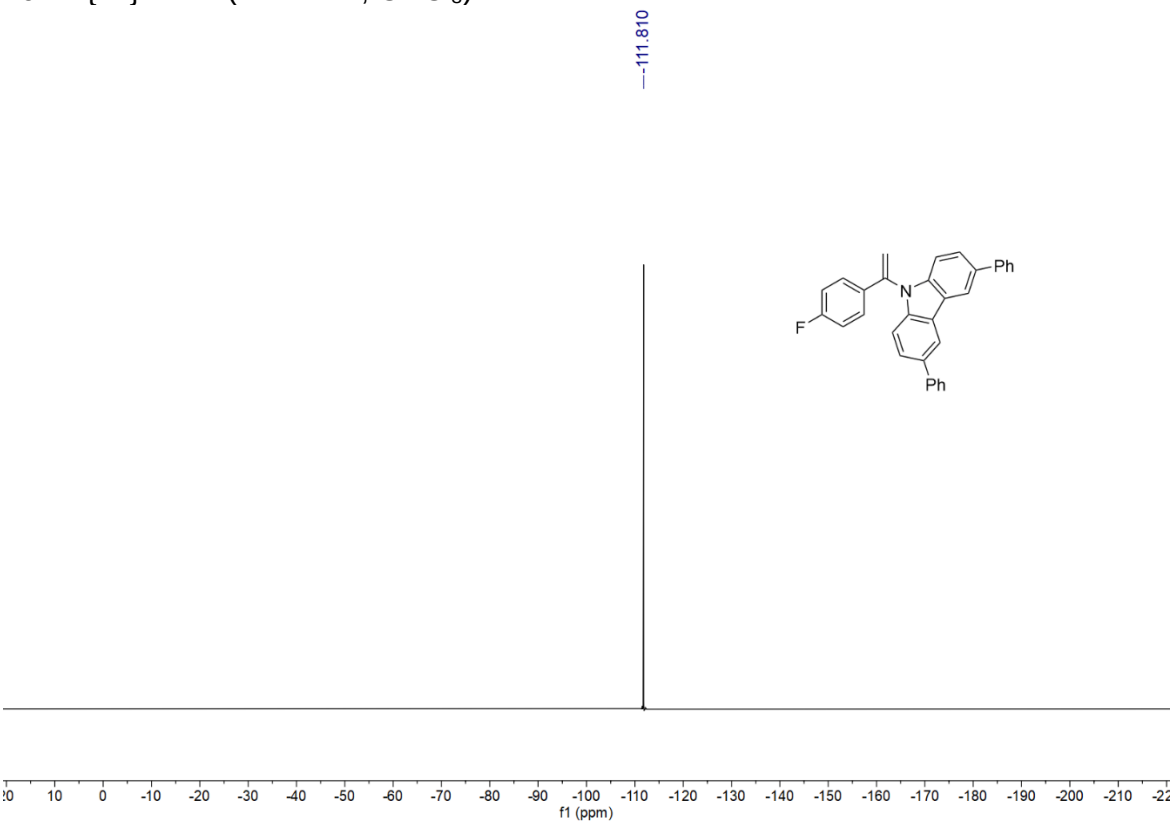
10 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



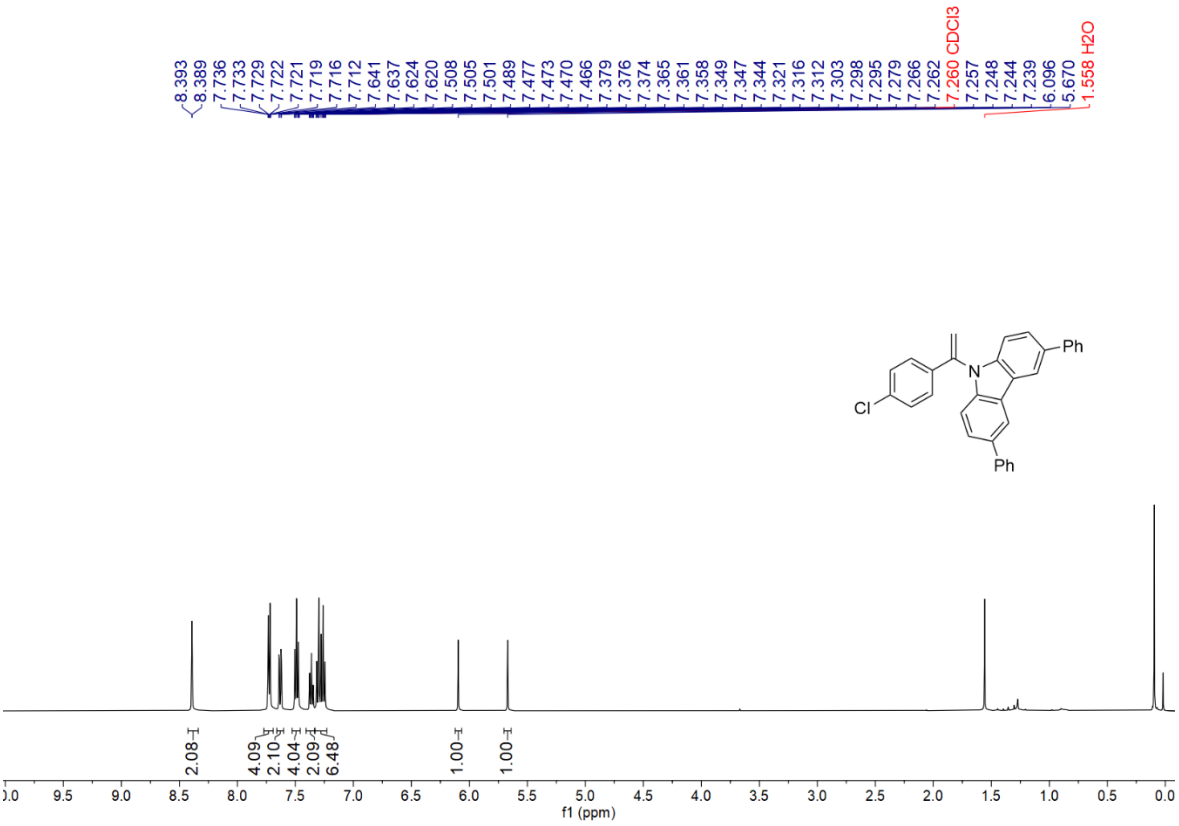
10 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



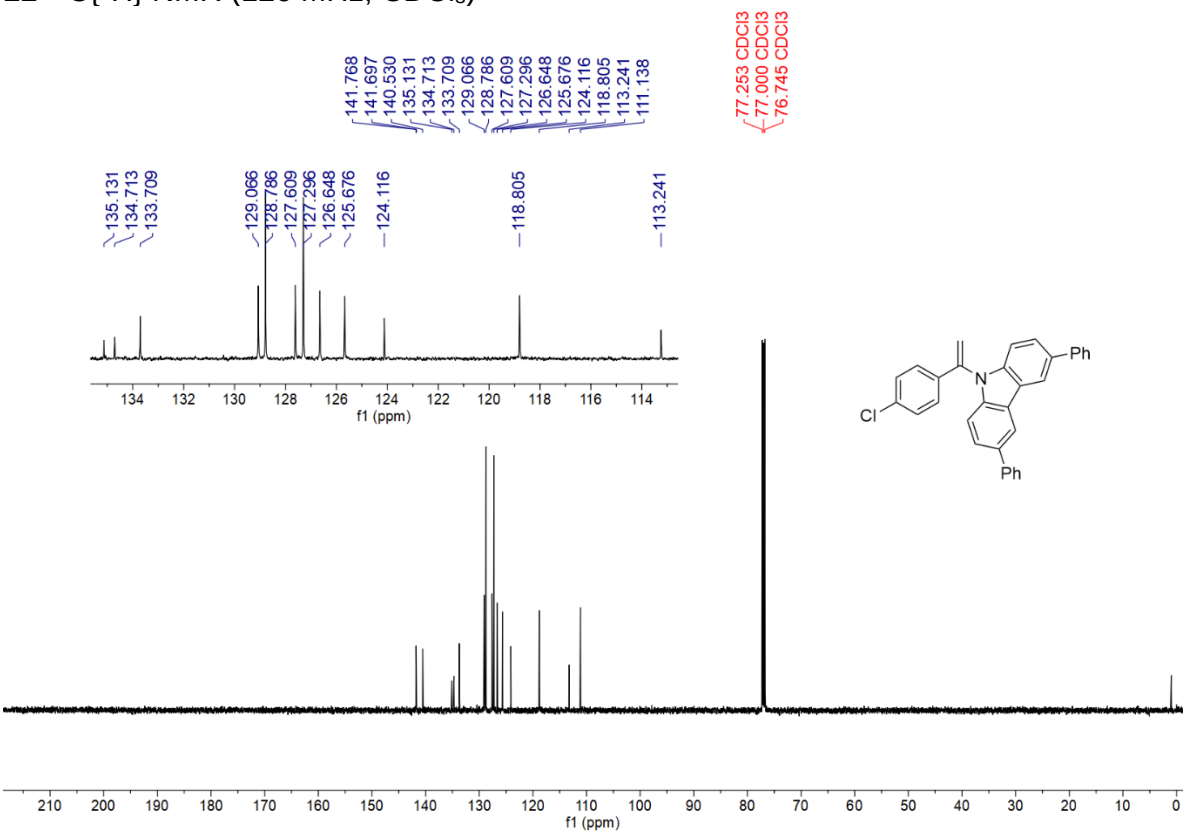
10 ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)



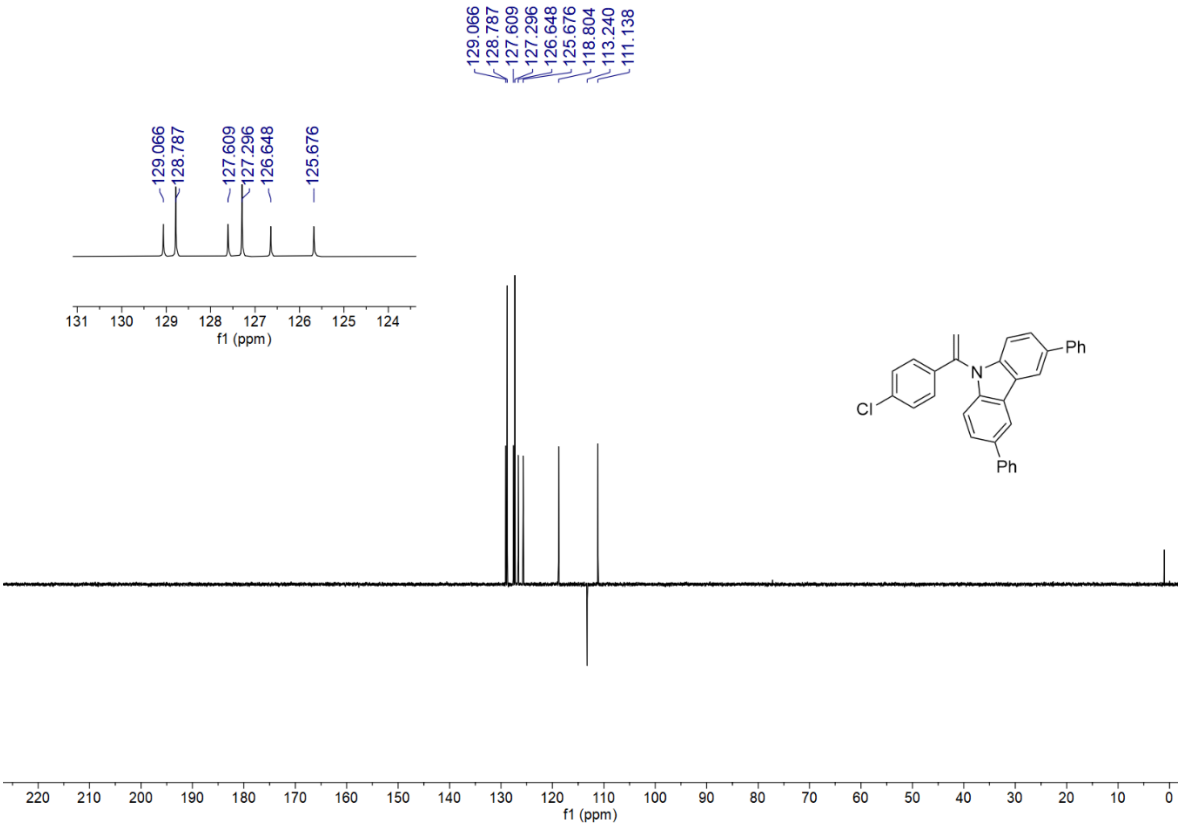
11 ^{1}H NMR (500 MHz, $CDCl_3$)



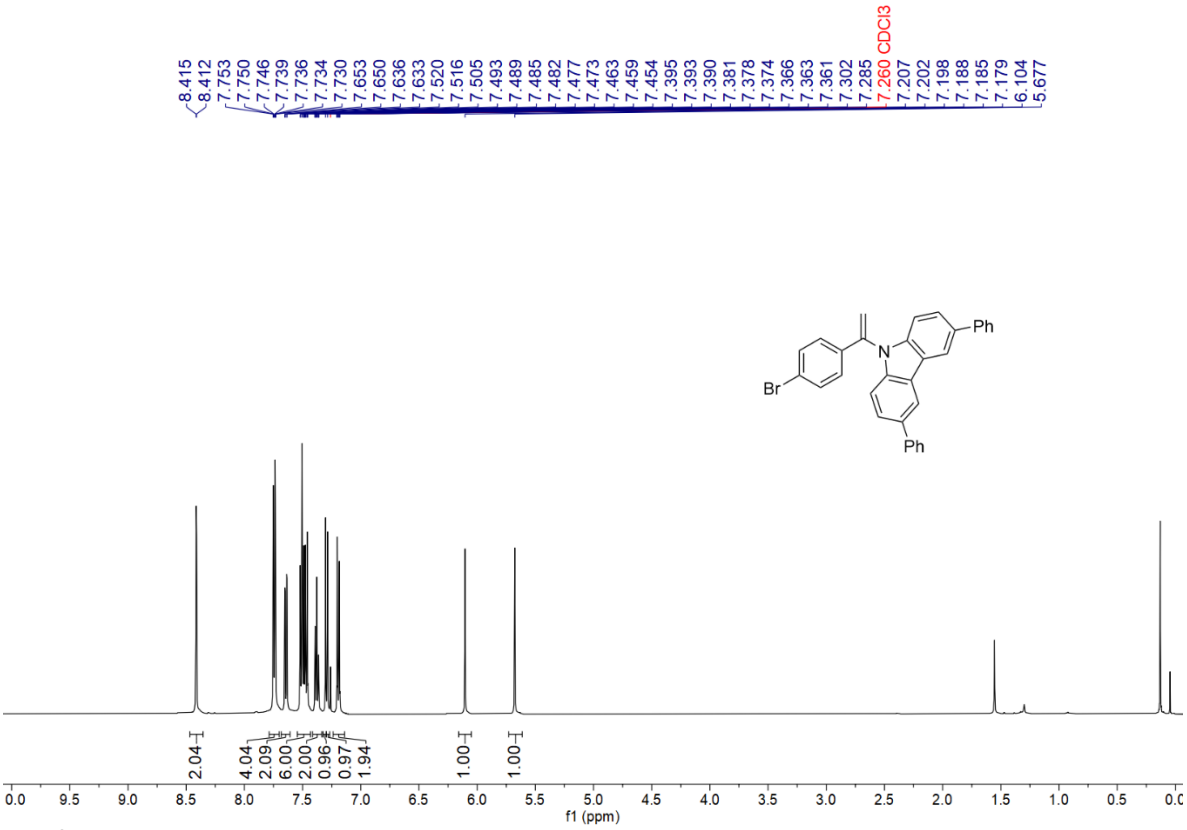
11 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



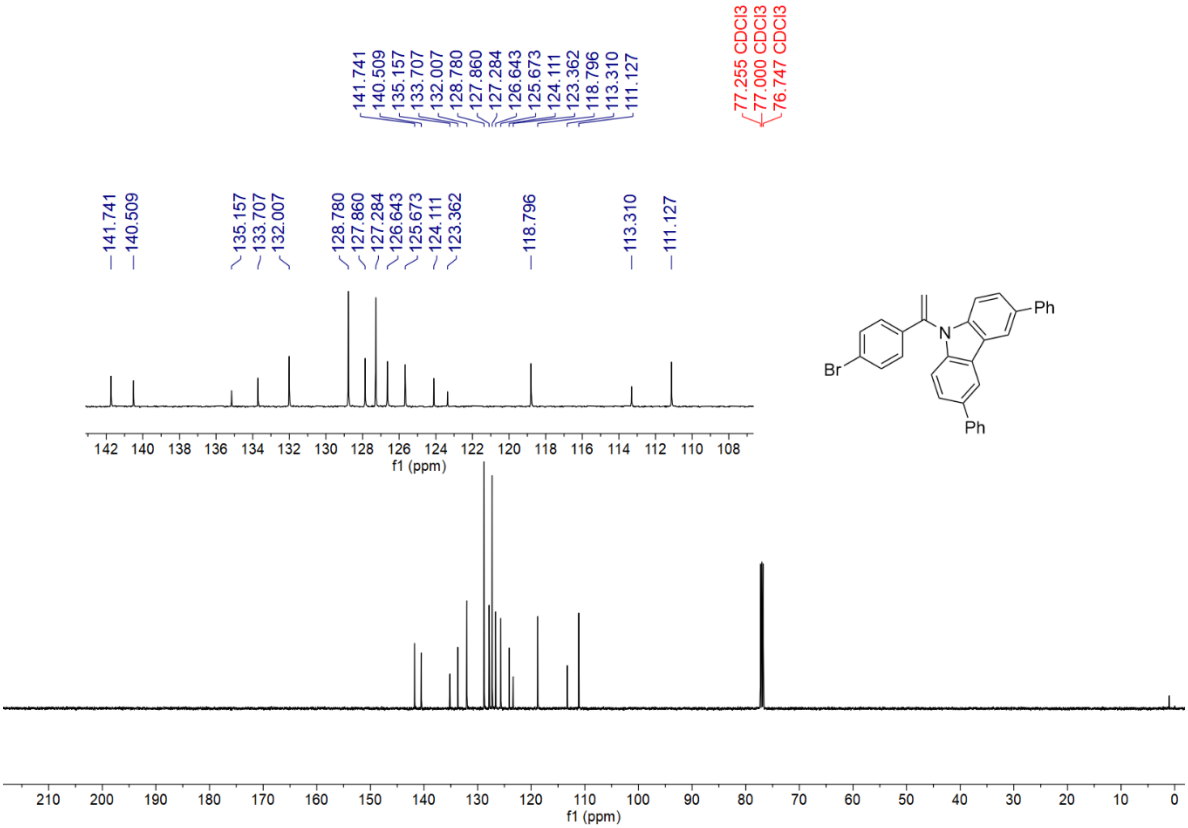
11 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



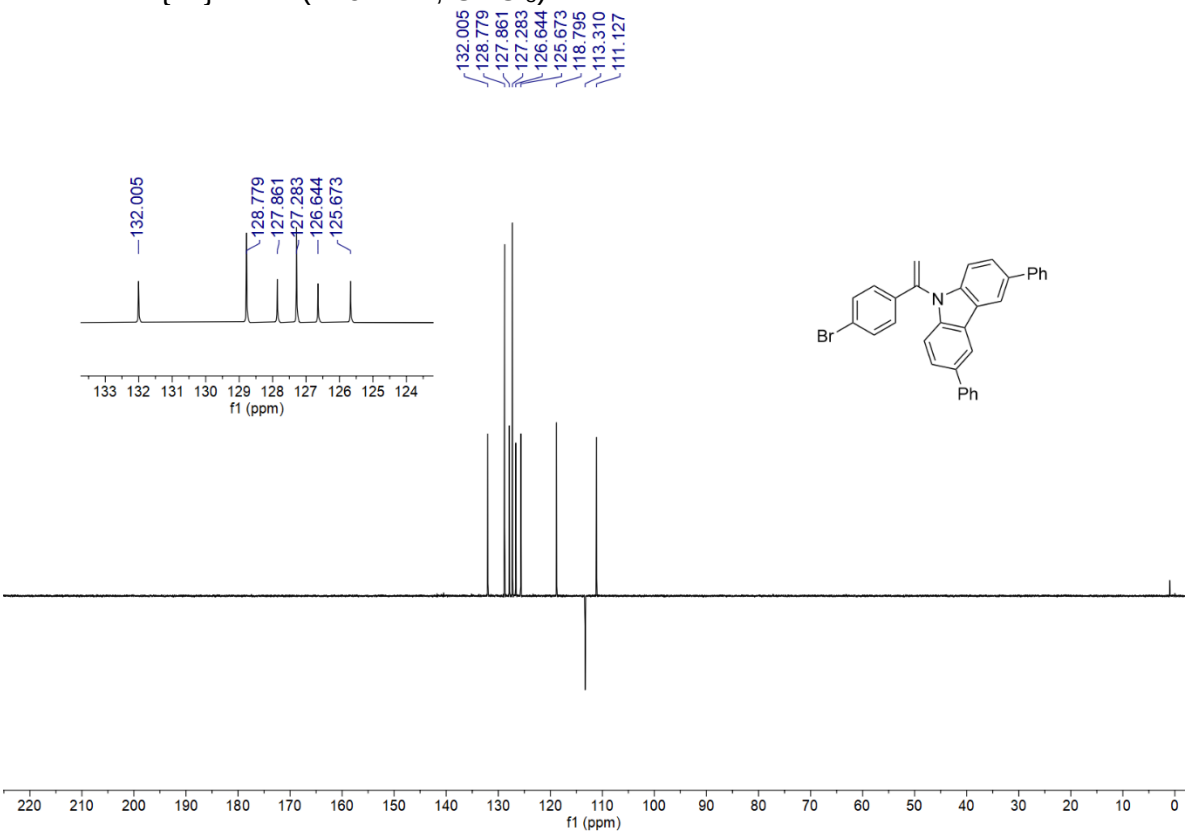
12 ^{1}H NMR (500 MHz, $CDCl_3$)



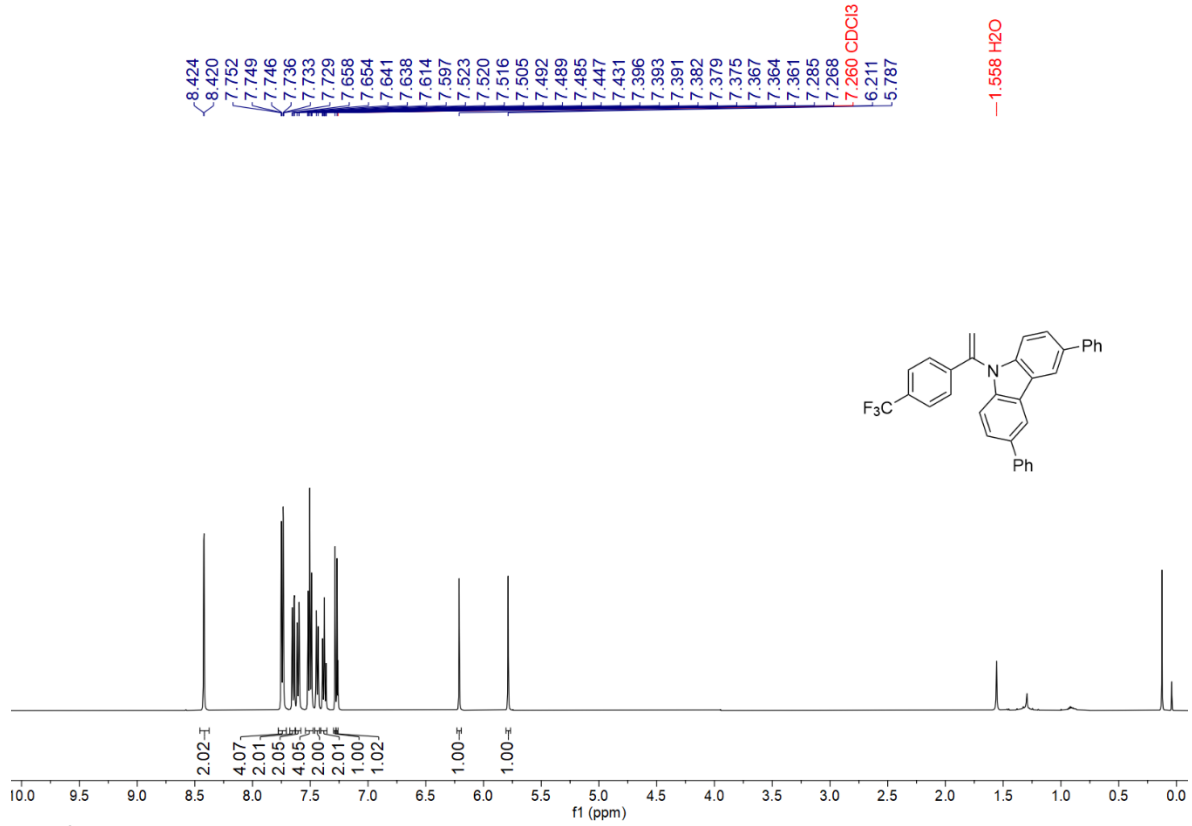
12 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



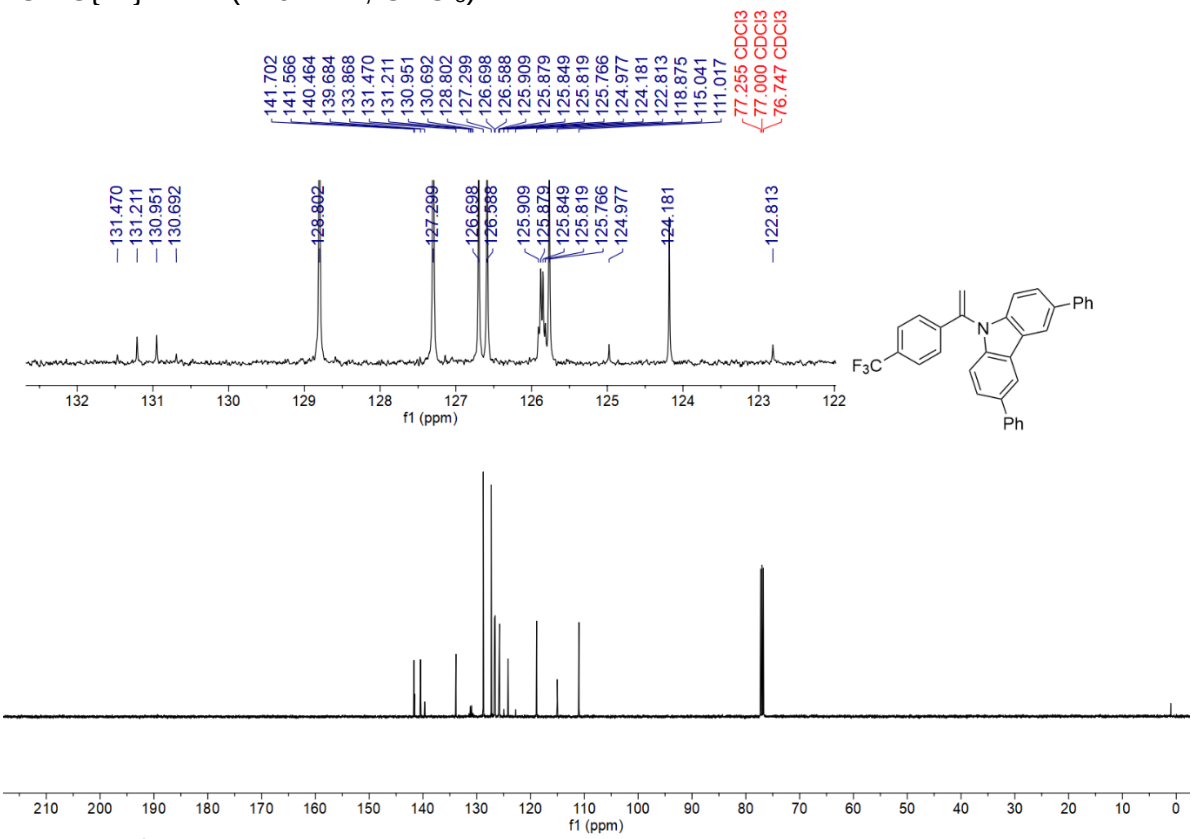
12 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



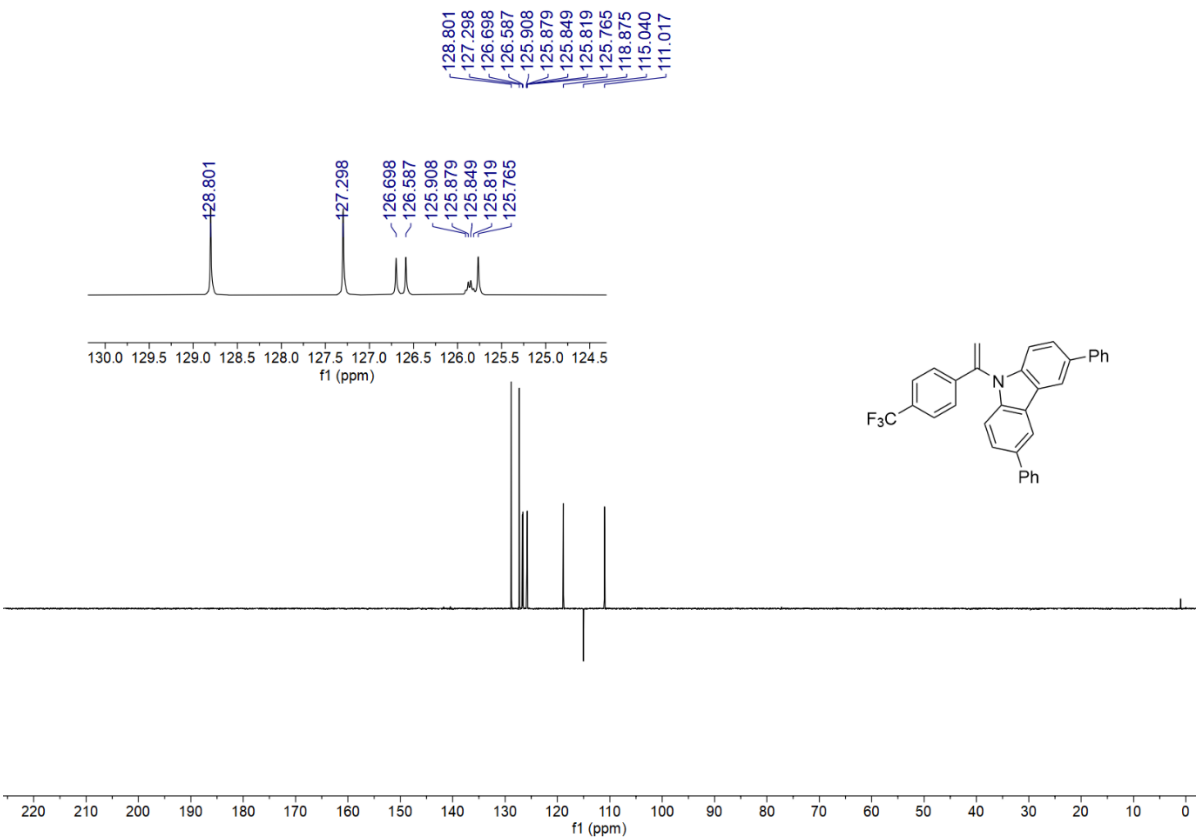
13 ^{1}H NMR (500 MHz, $CDCl_3$)



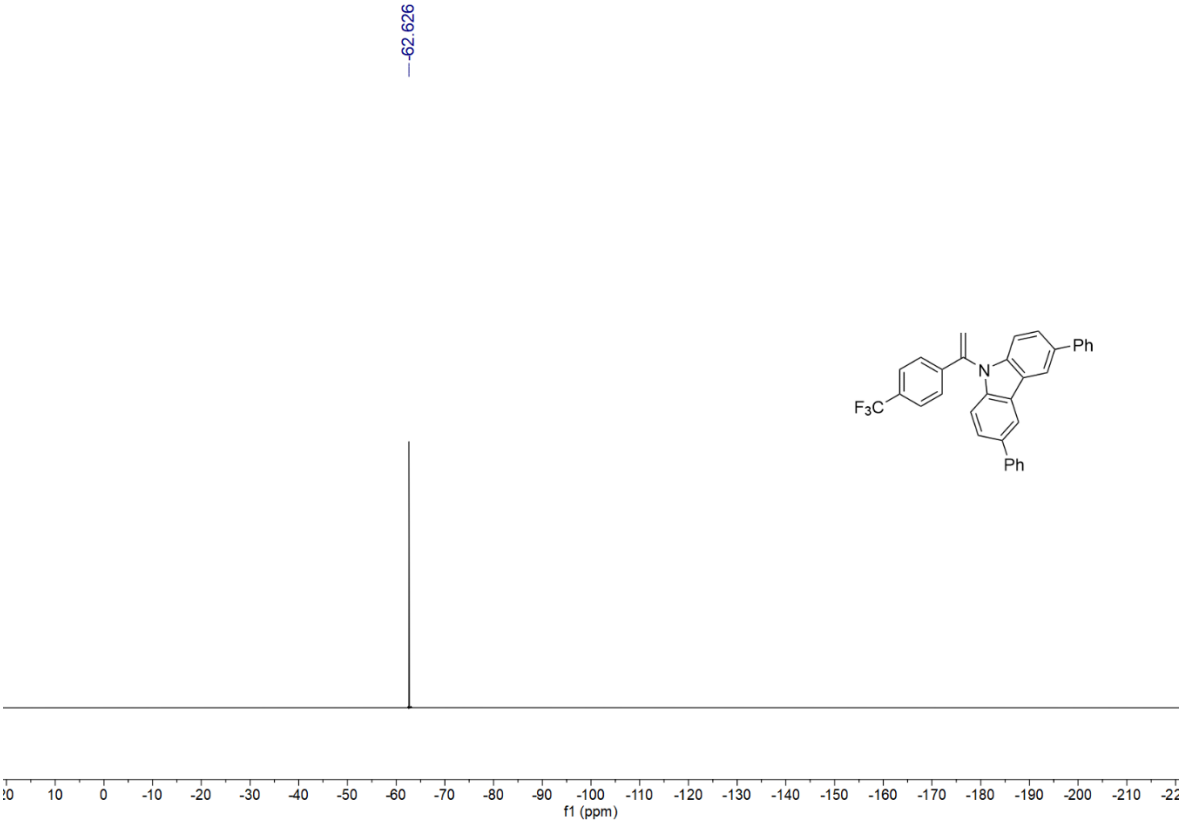
13 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



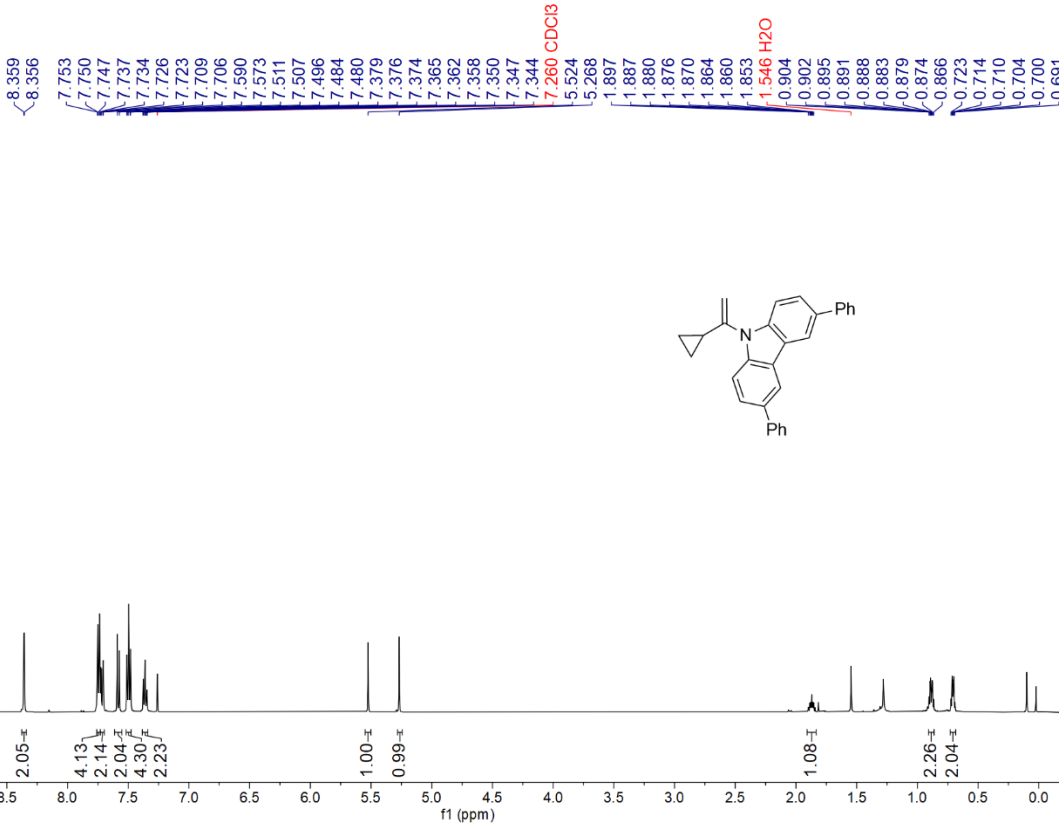
13 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



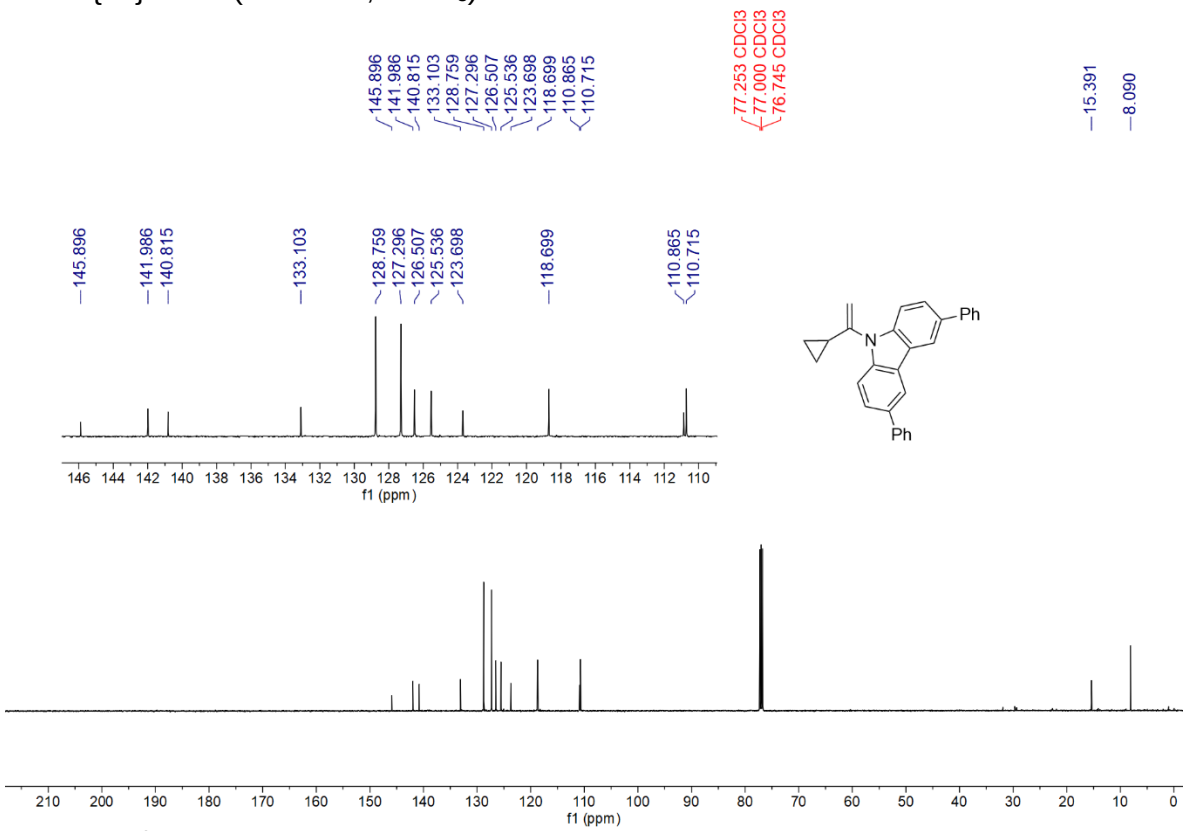
13 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



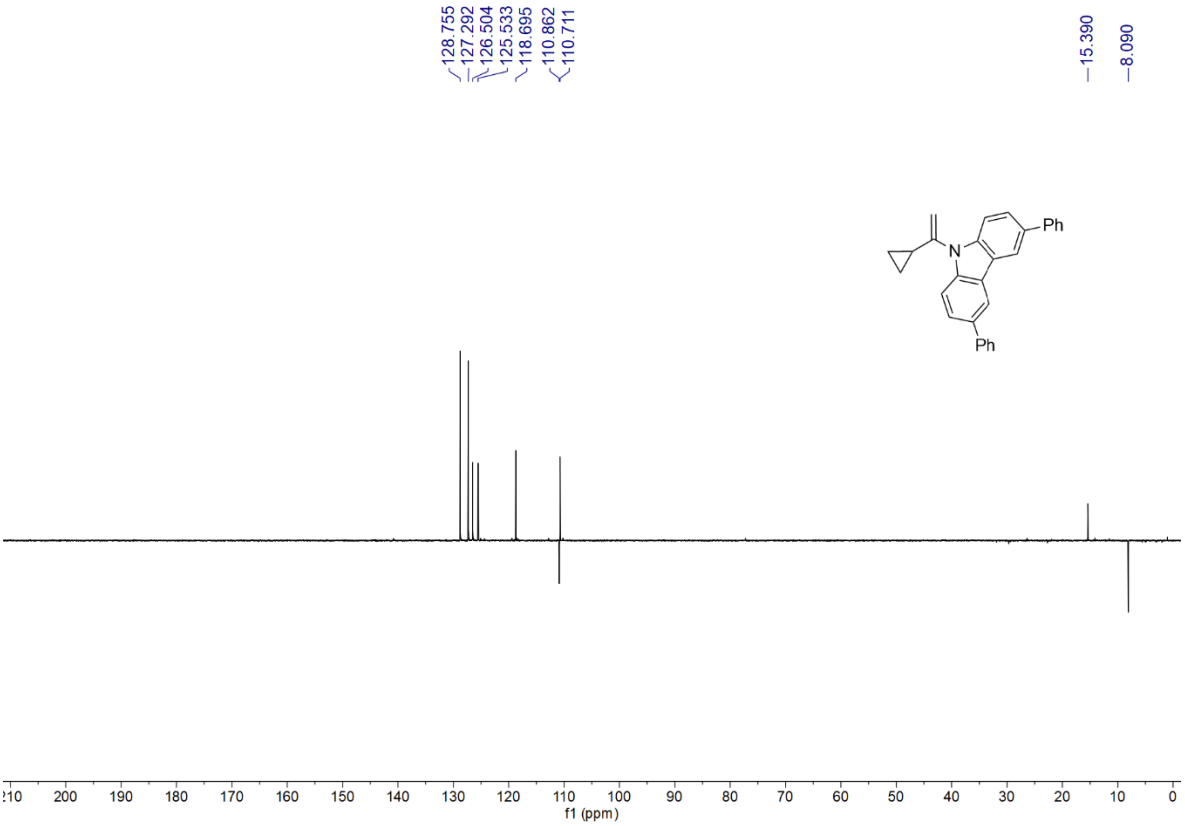
14 ^{1}H NMR (500 MHz, $CDCl_3$)



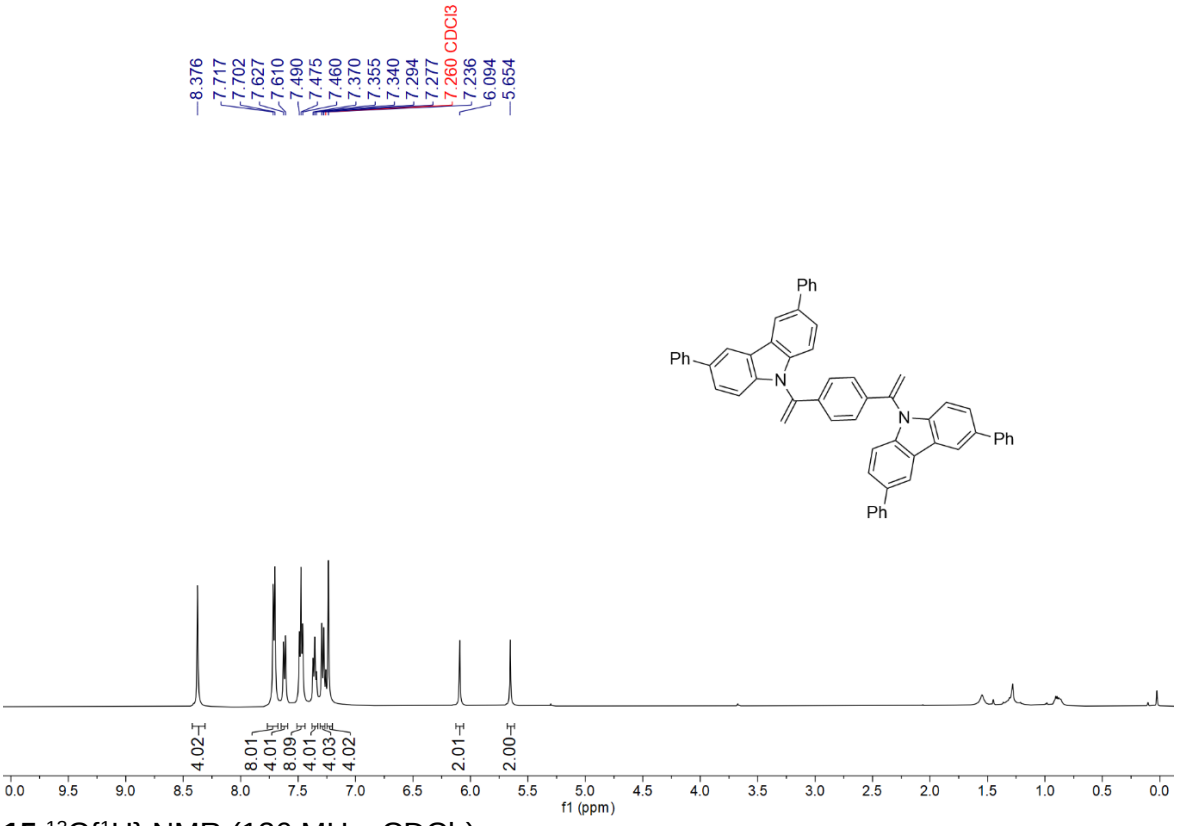
14 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



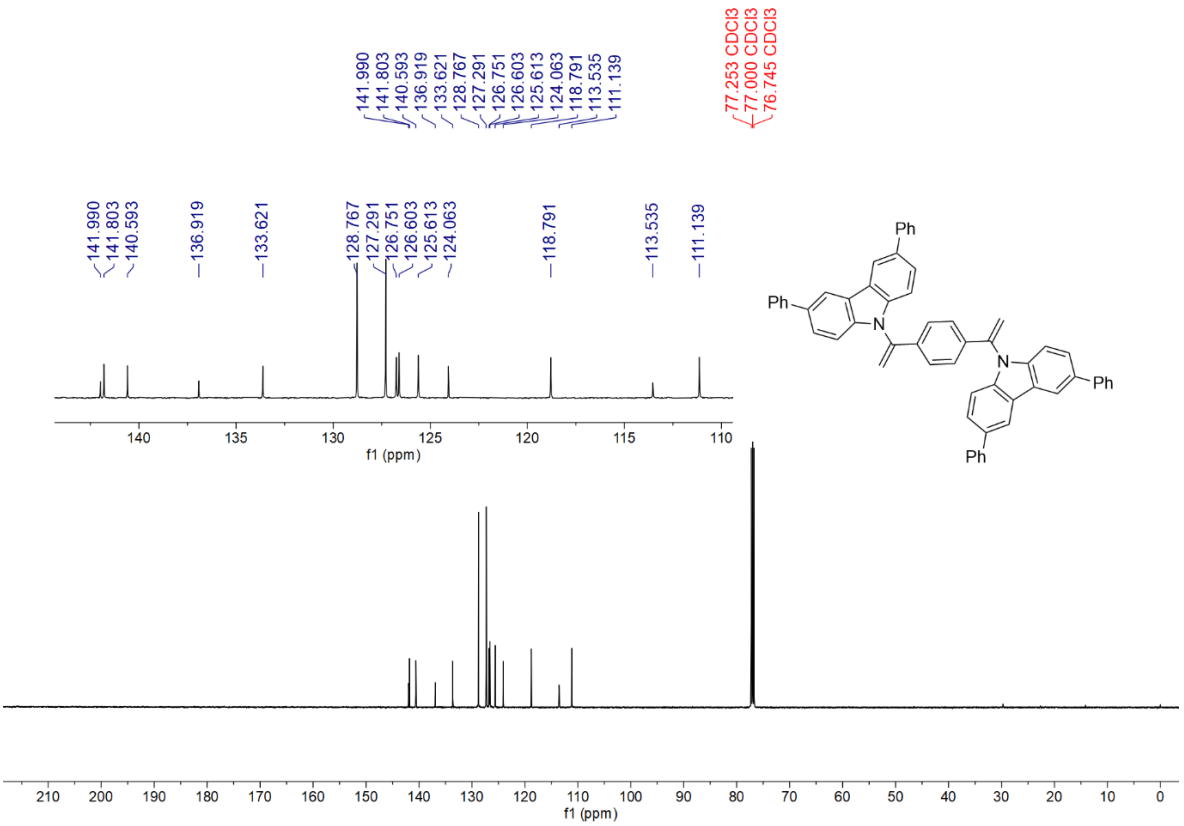
14 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



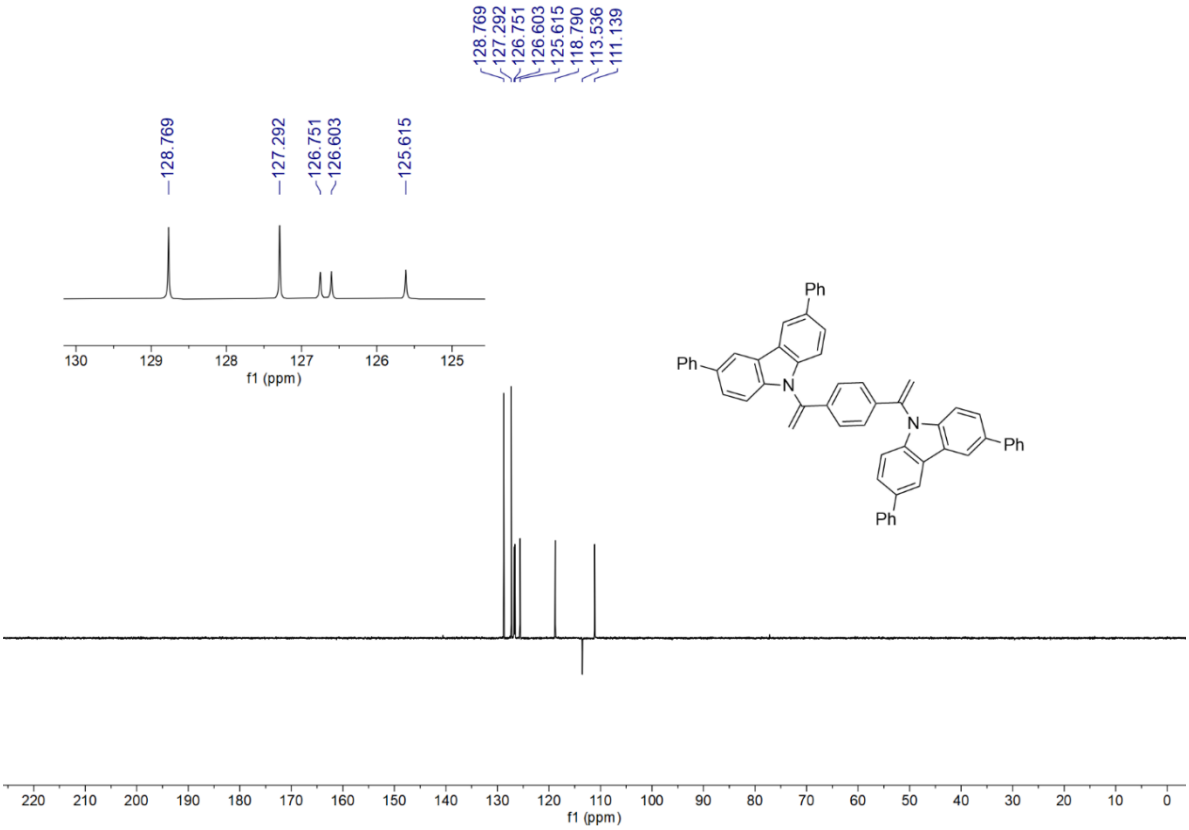
15 ^{1}H NMR (500 MHz, $CDCl_3$)



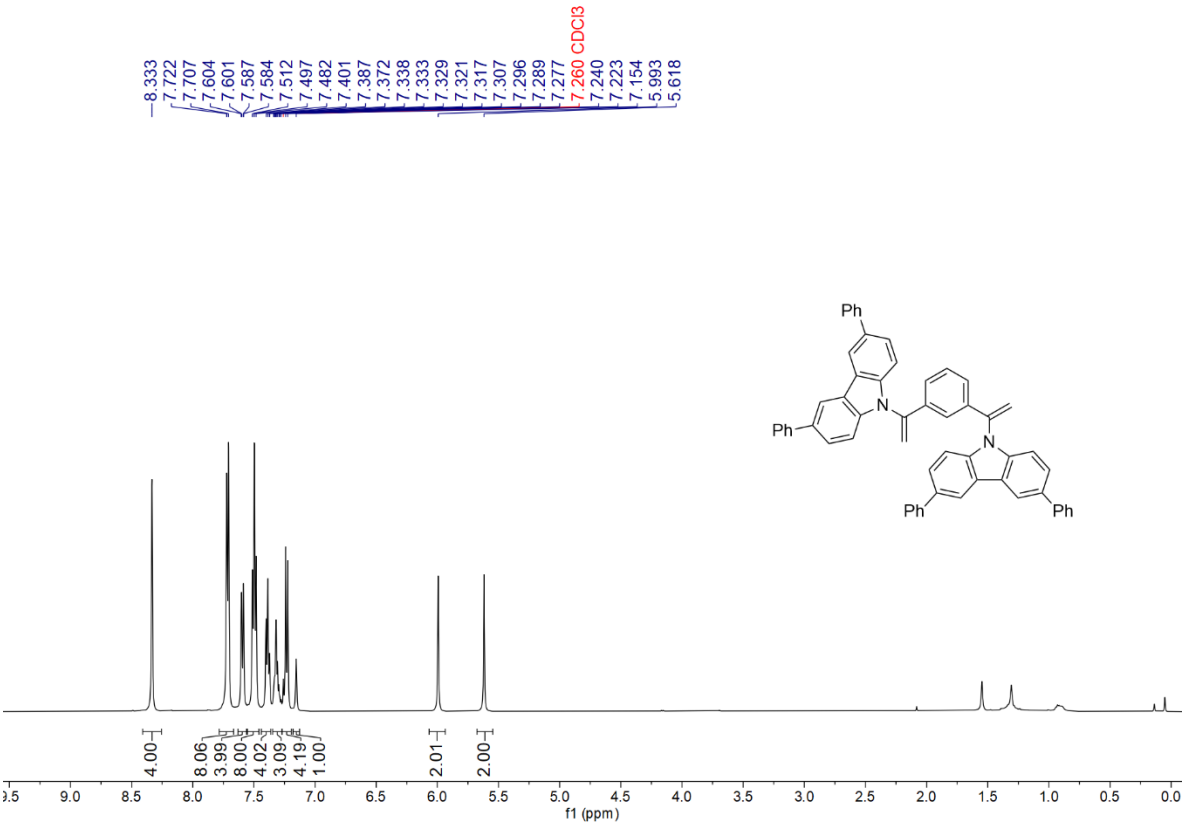
15 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



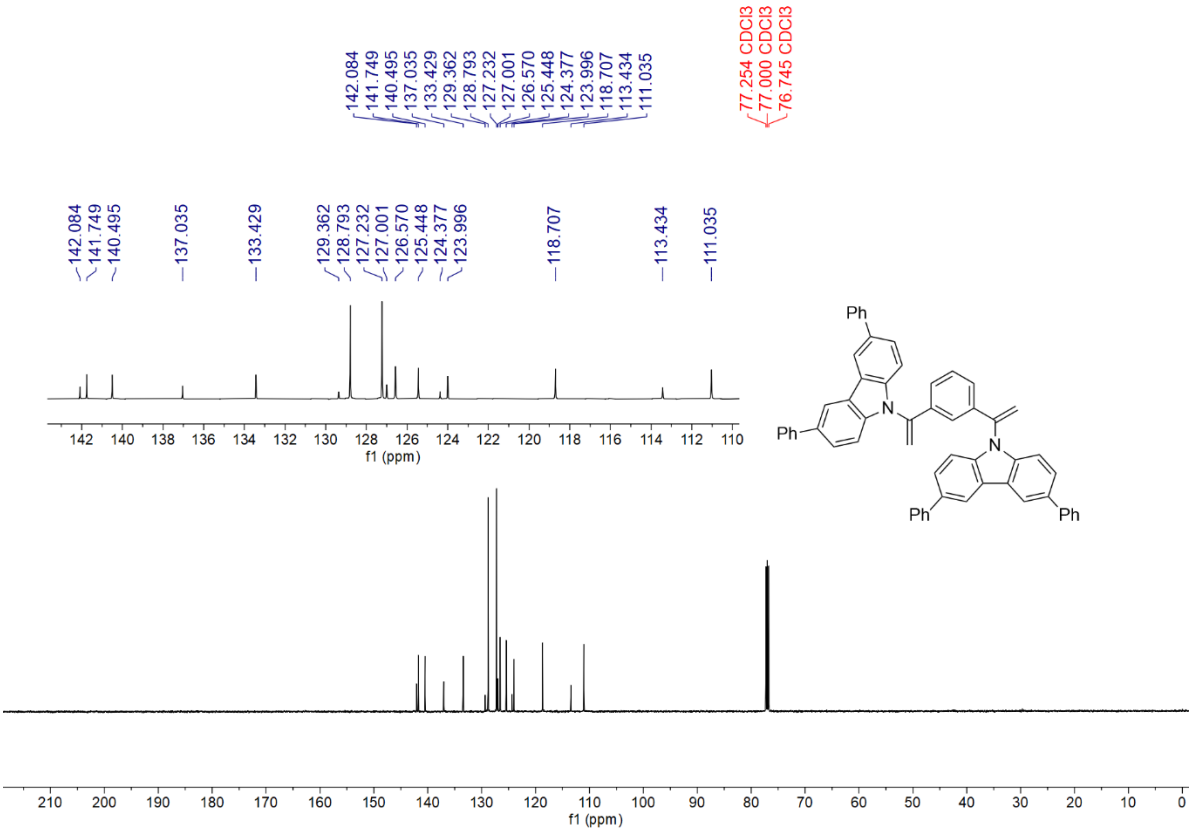
15 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



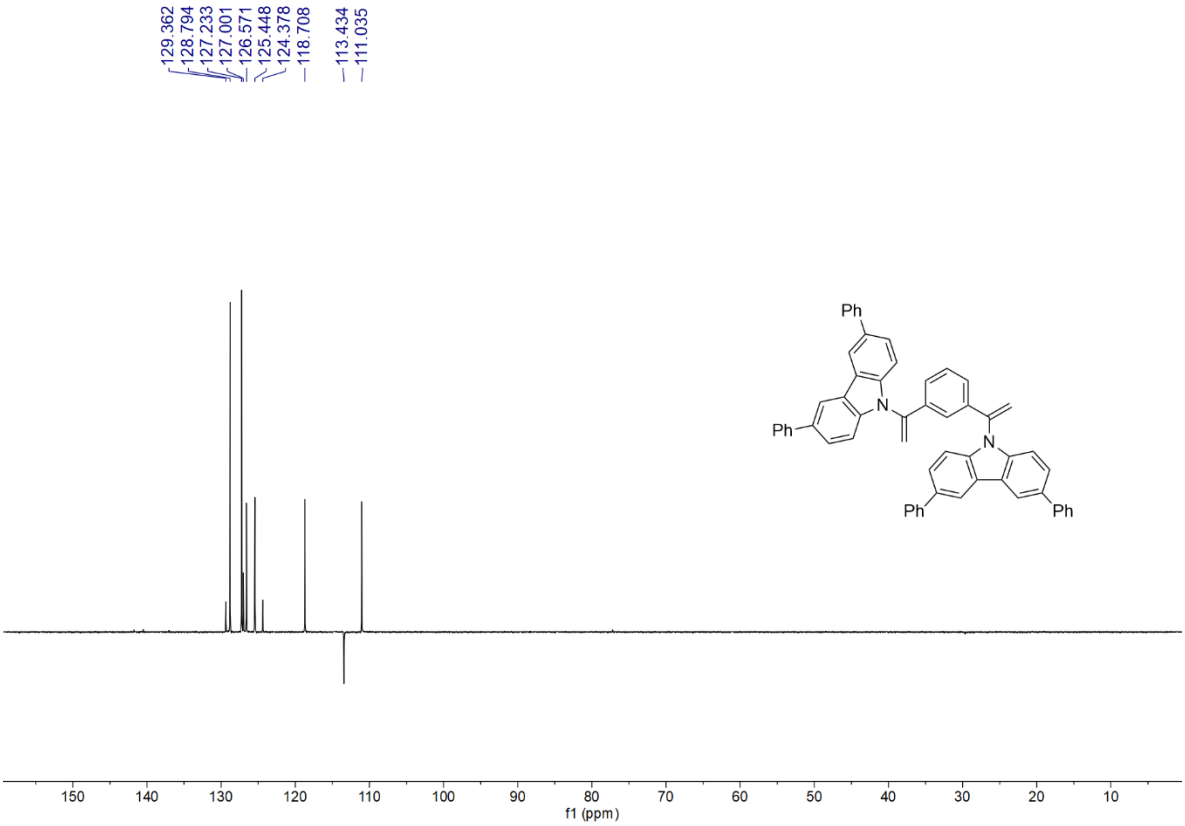
16 ^{1}H NMR (500 MHz, $CDCl_3$)



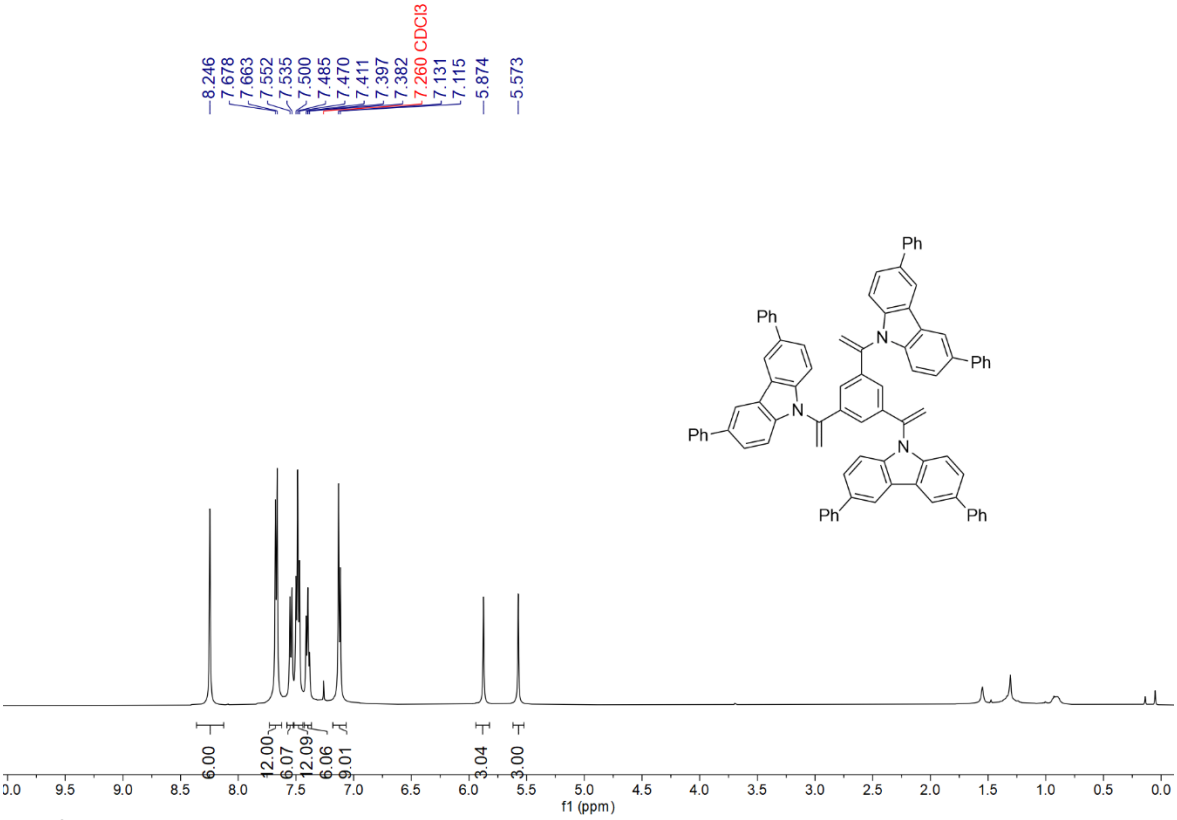
16 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



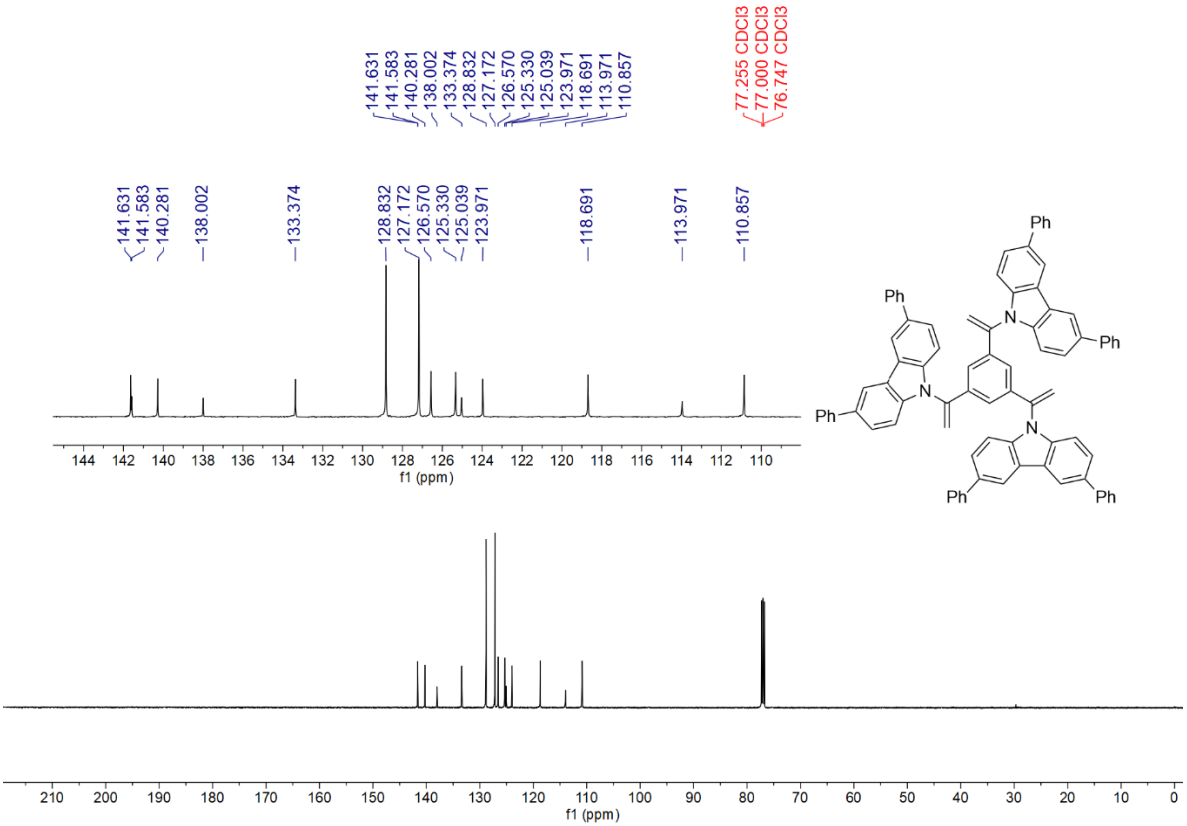
16 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



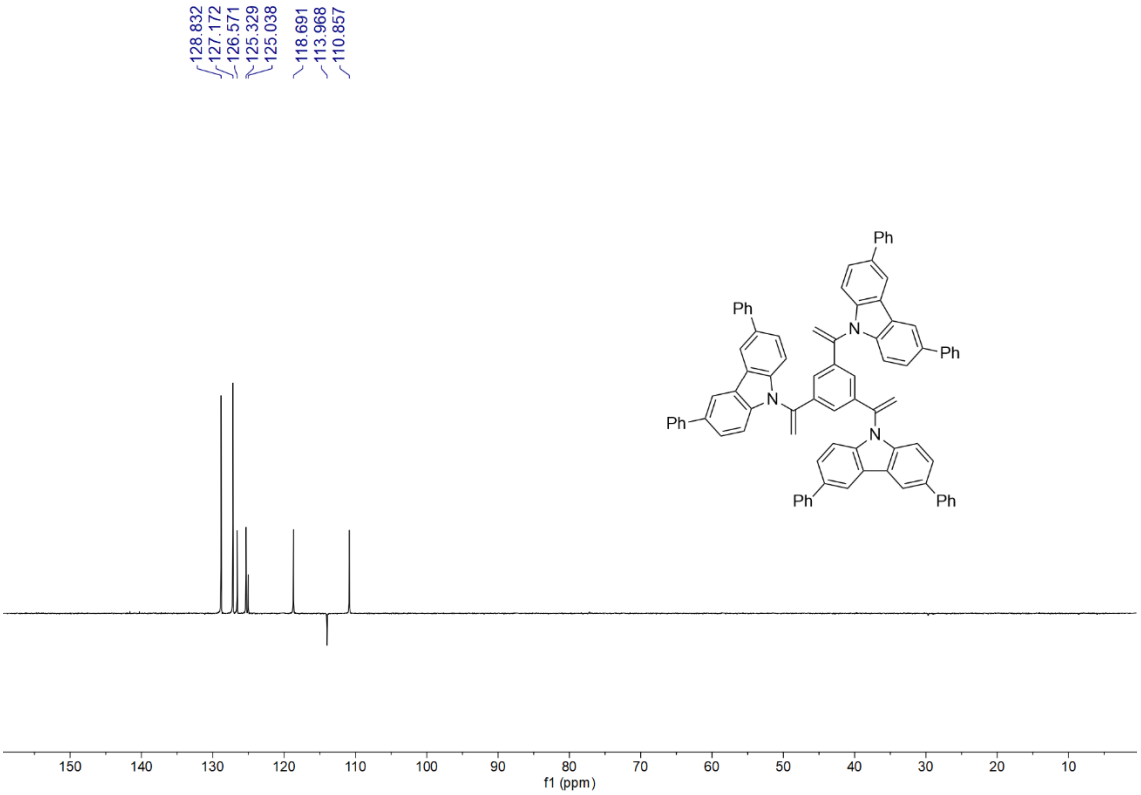
17 ^{1}H NMR (500 MHz, $CDCl_3$)



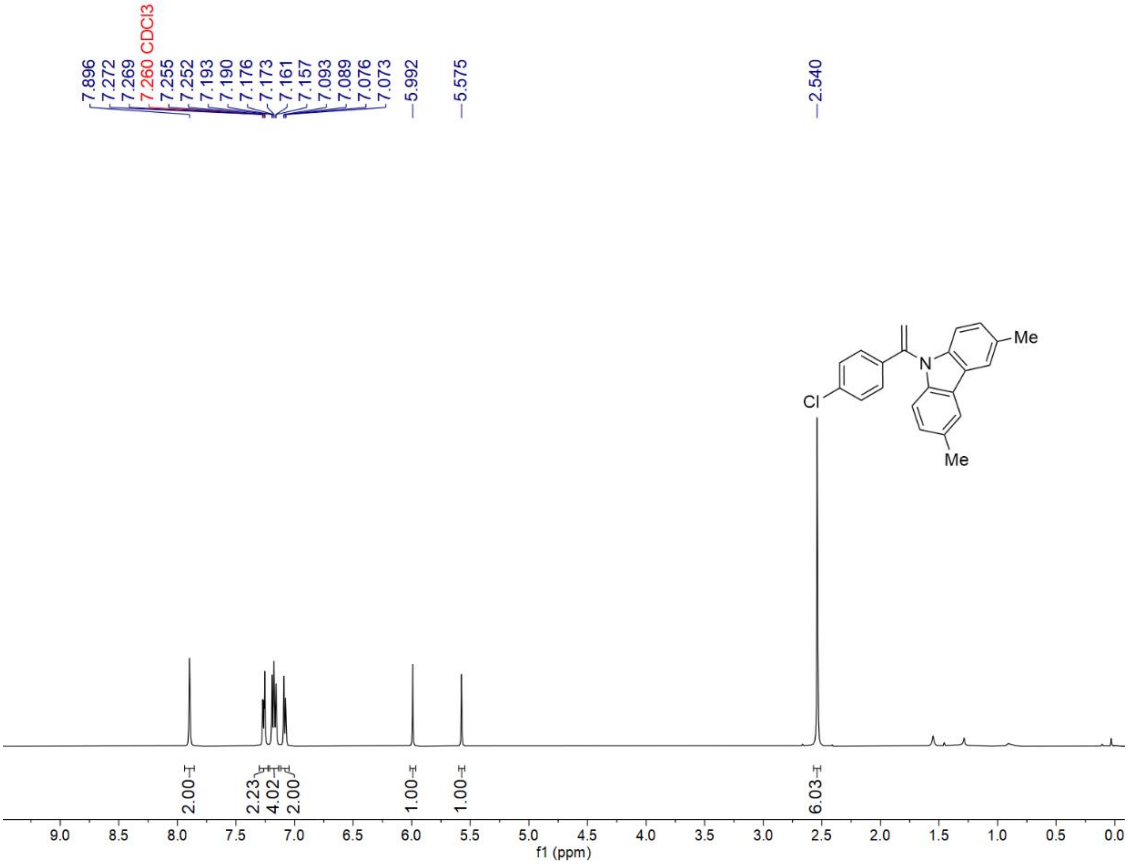
17 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



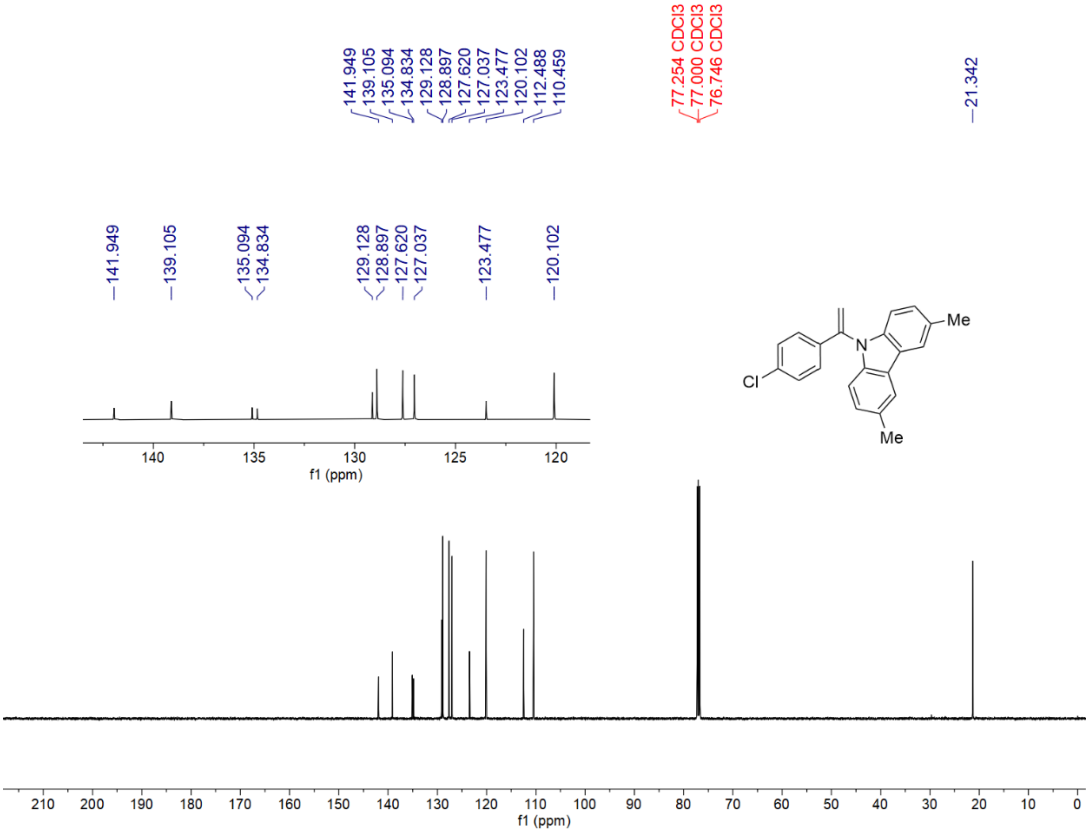
17 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



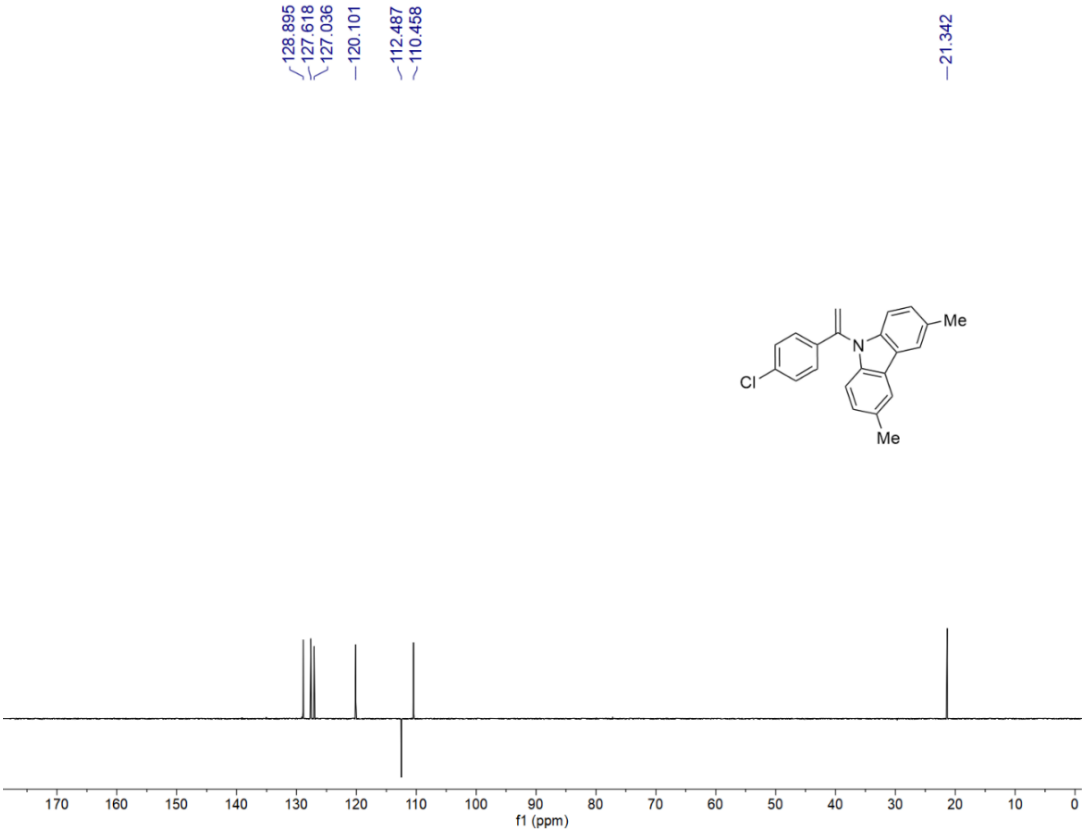
18 ^{1}H NMR (500 MHz, $CDCl_3$)



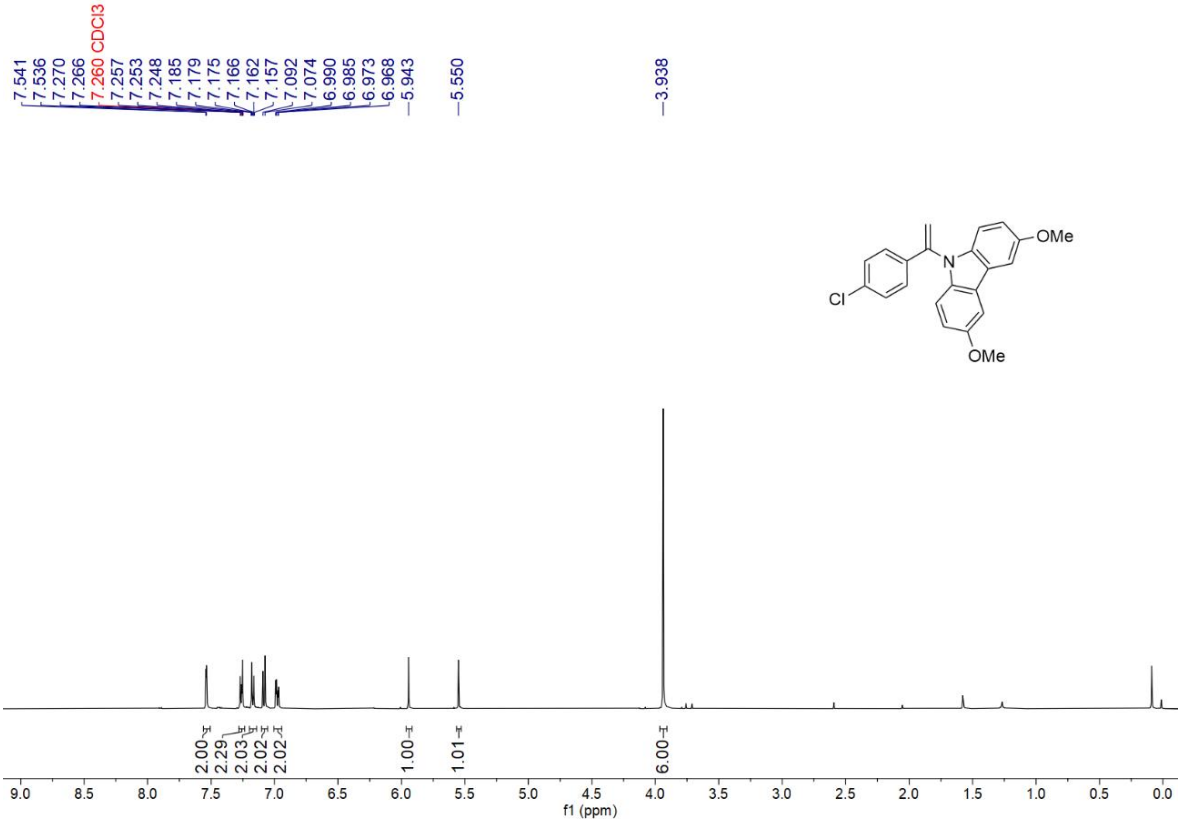
18 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



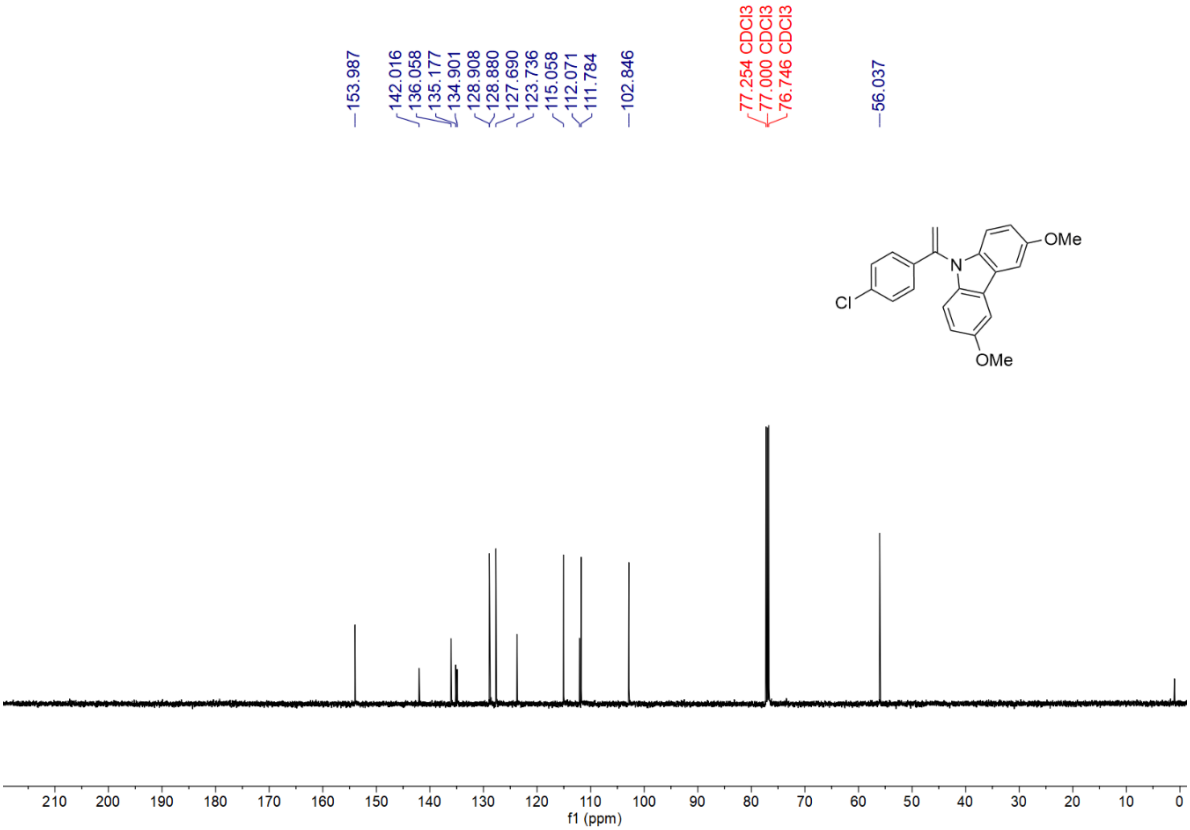
18 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



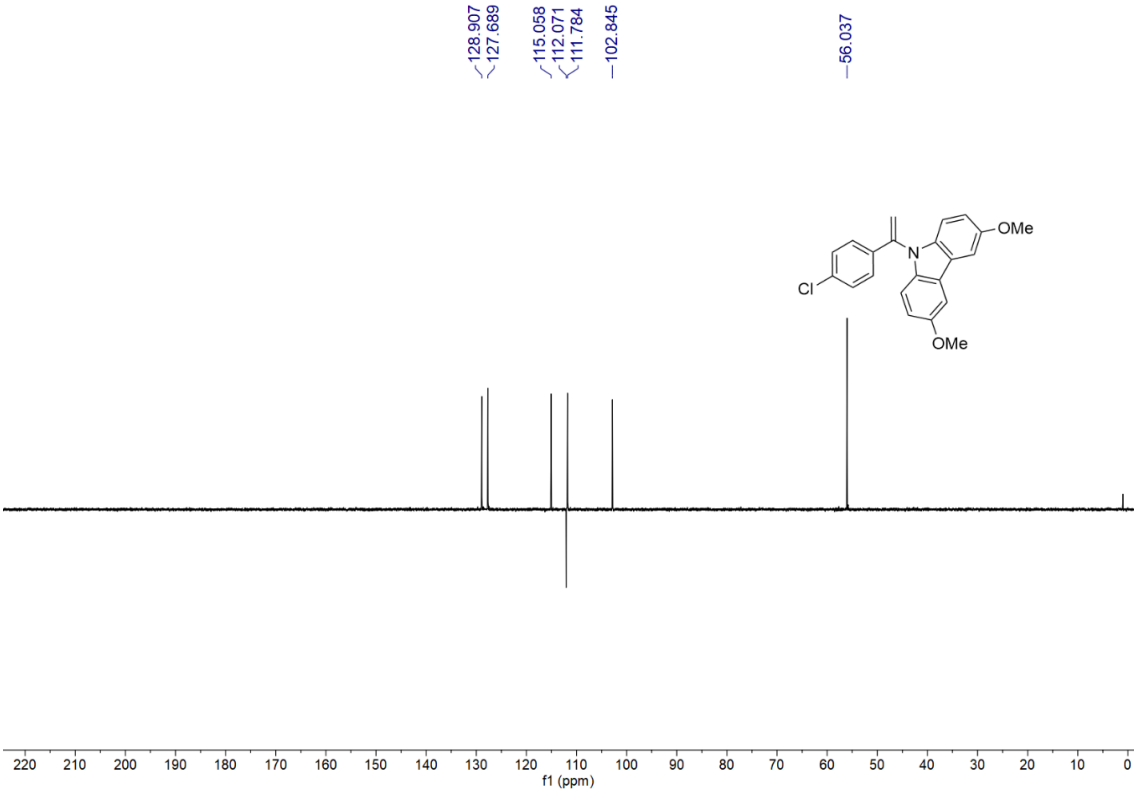
19 ^{1}H NMR (500 MHz, $CDCl_3$)



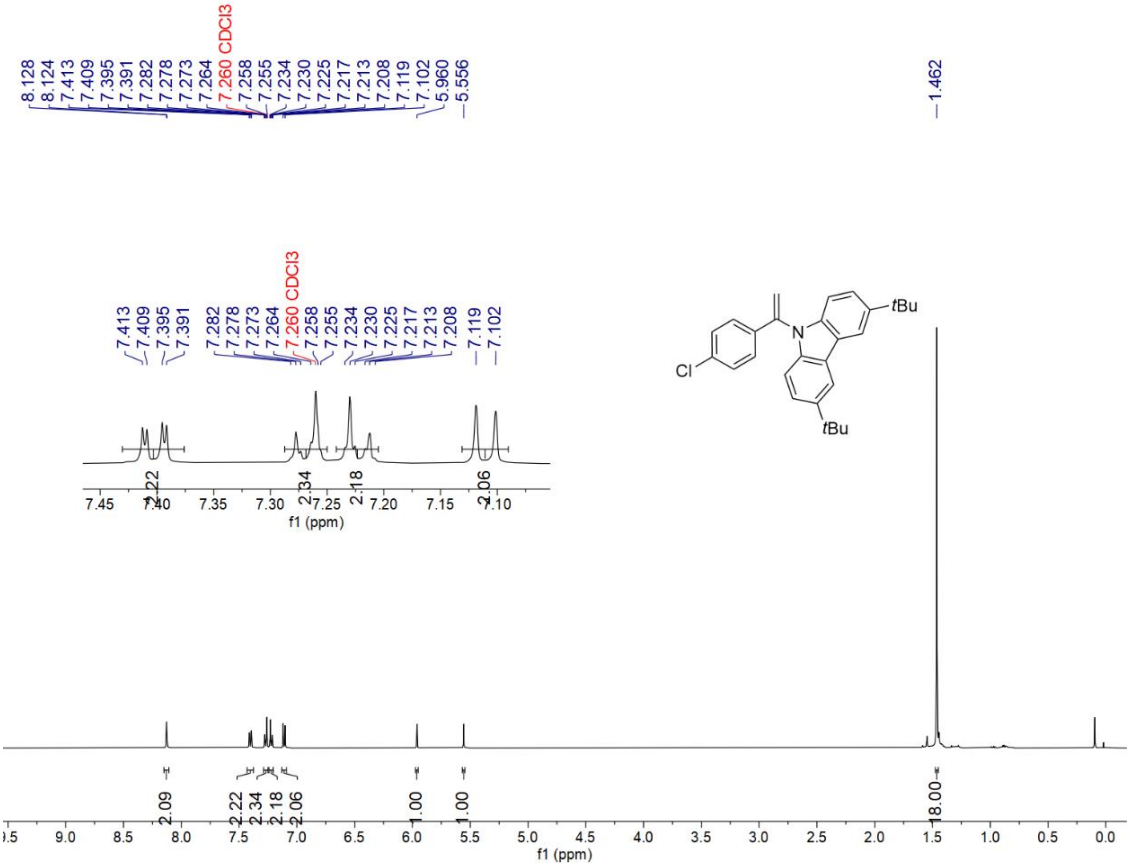
19 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



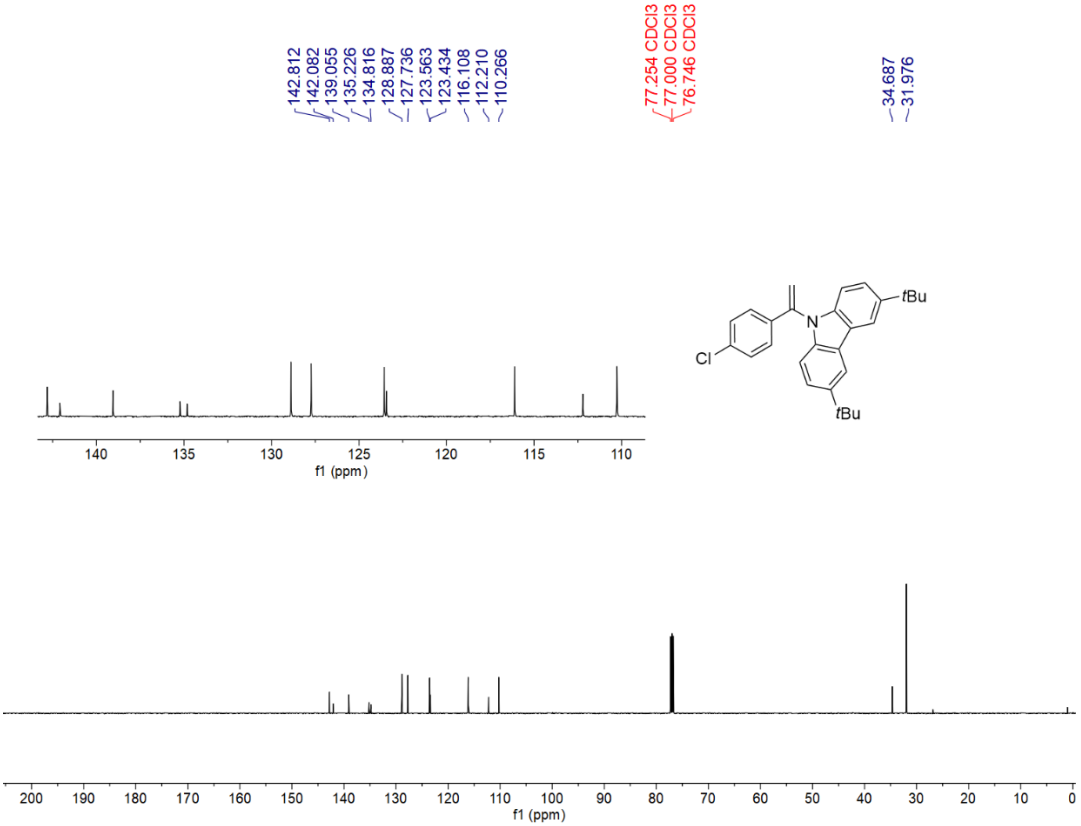
19 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



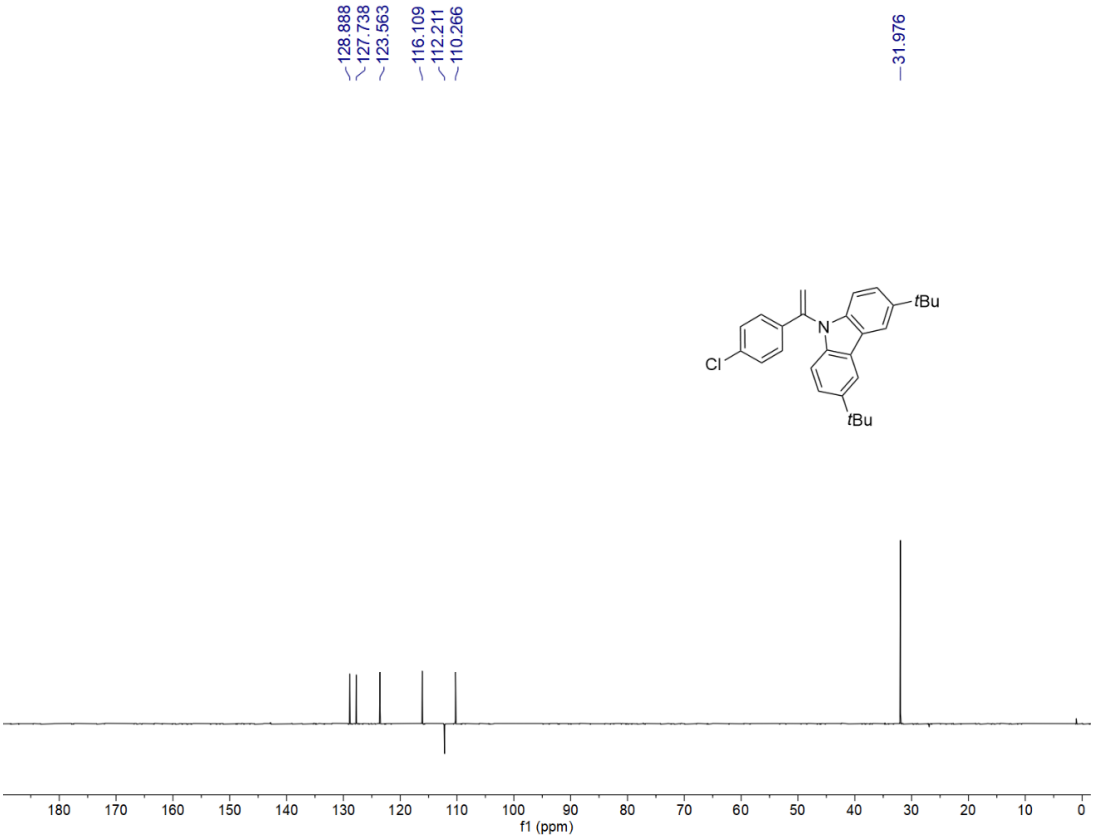
20 ^{1}H NMR (500 MHz, $CDCl_3$)



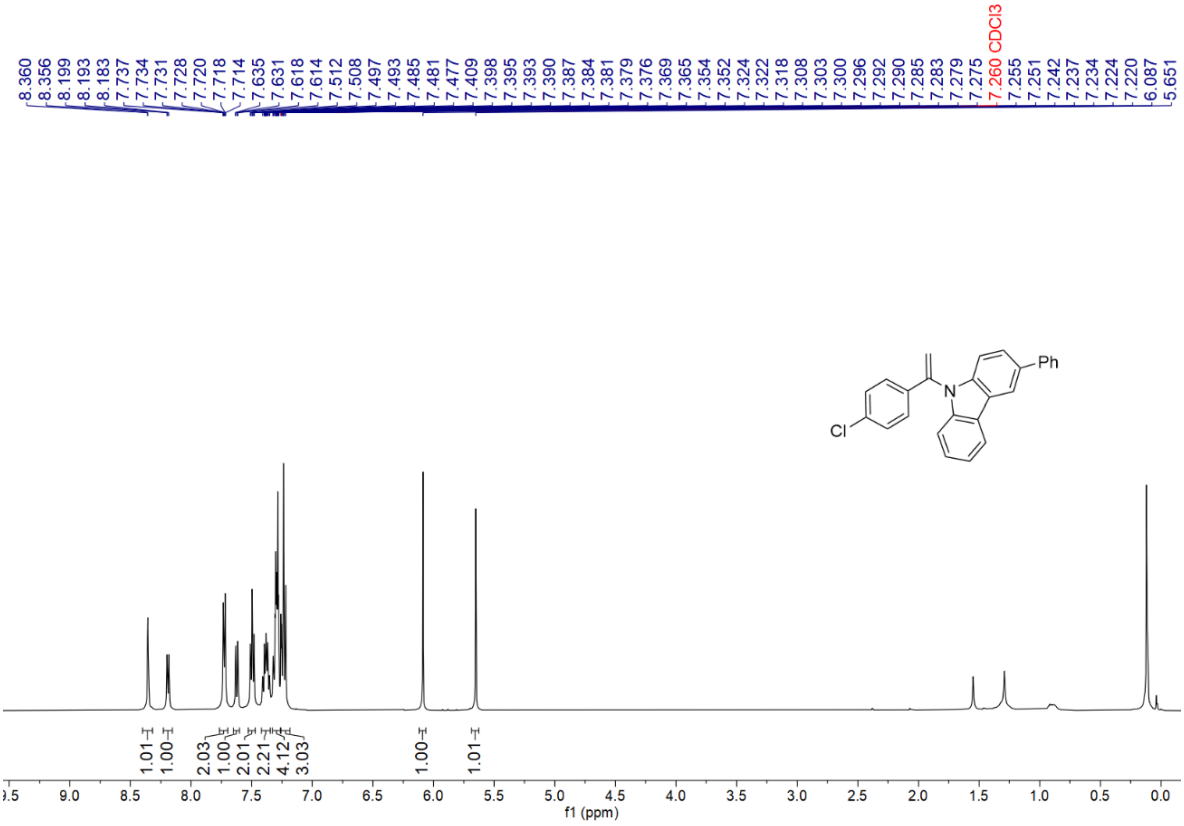
20 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



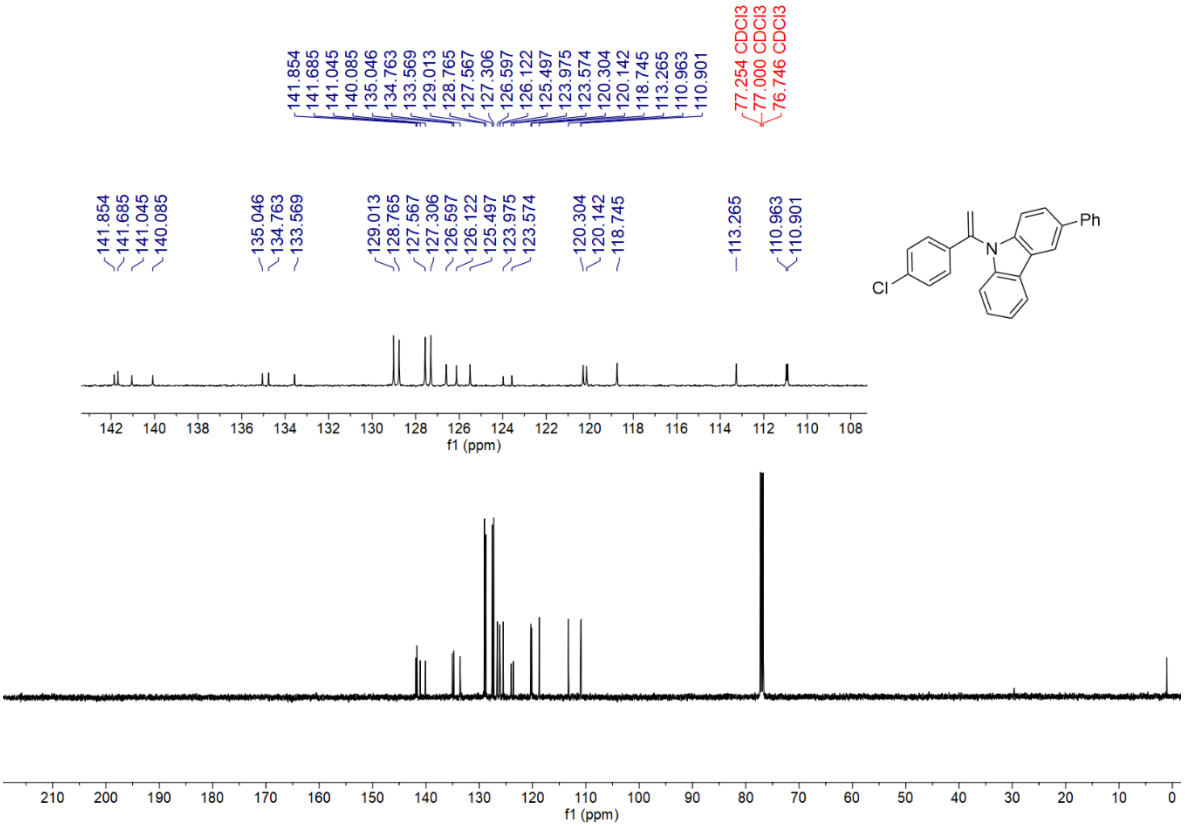
20 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



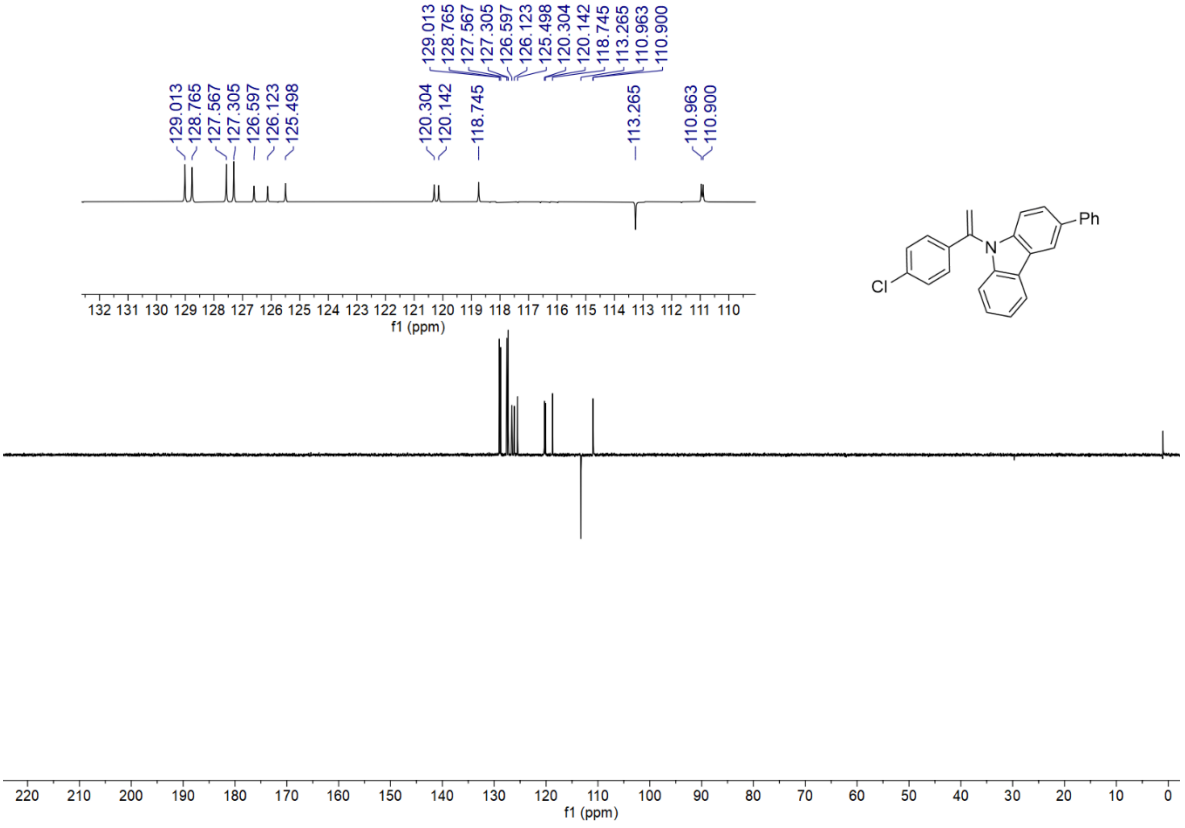
21 ^{1}H NMR (500 MHz, $CDCl_3$)



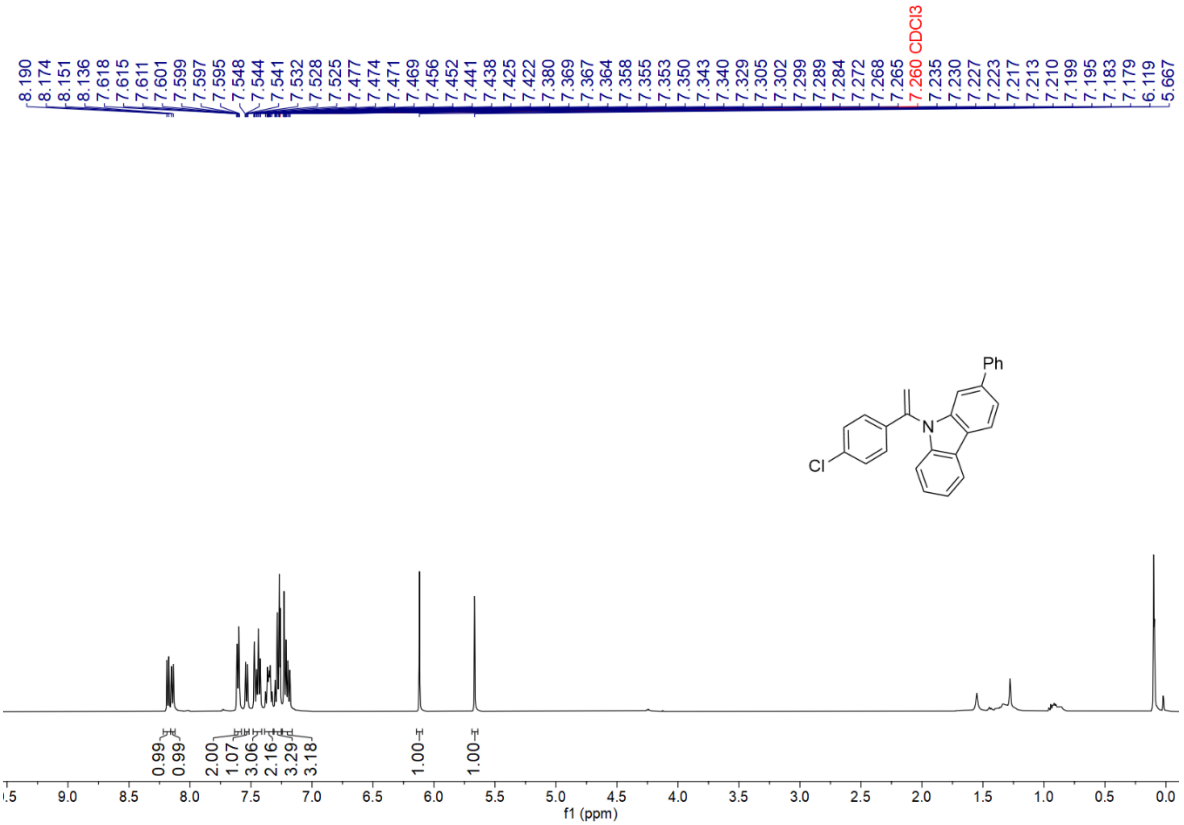
21 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



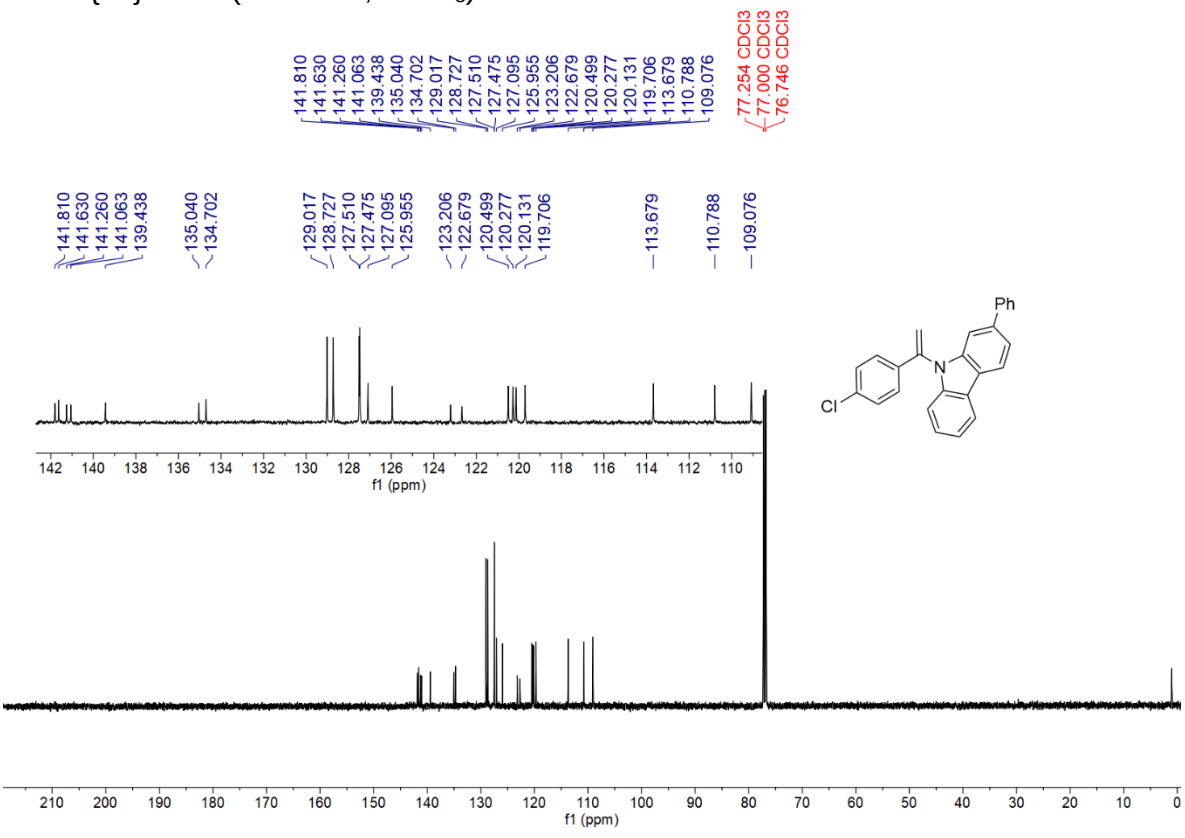
21 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



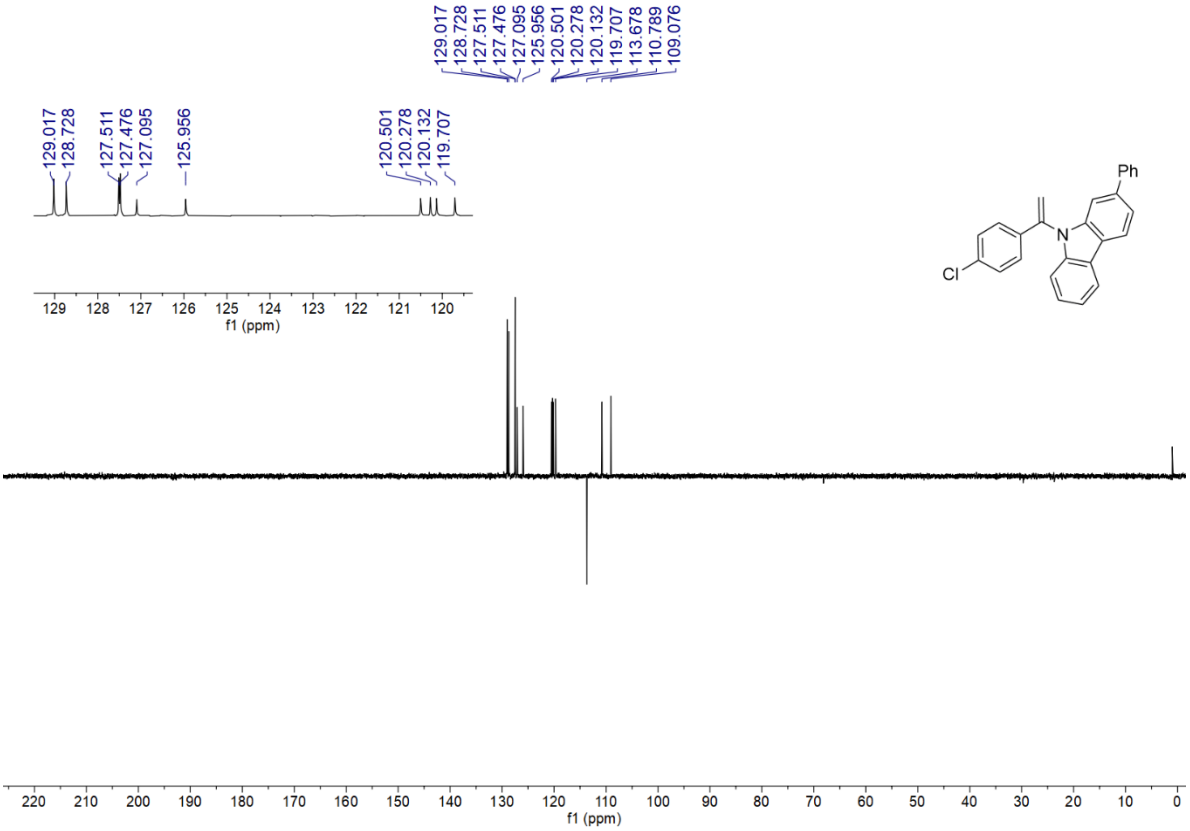
22 ^{1}H NMR (500 MHz, $CDCl_3$)



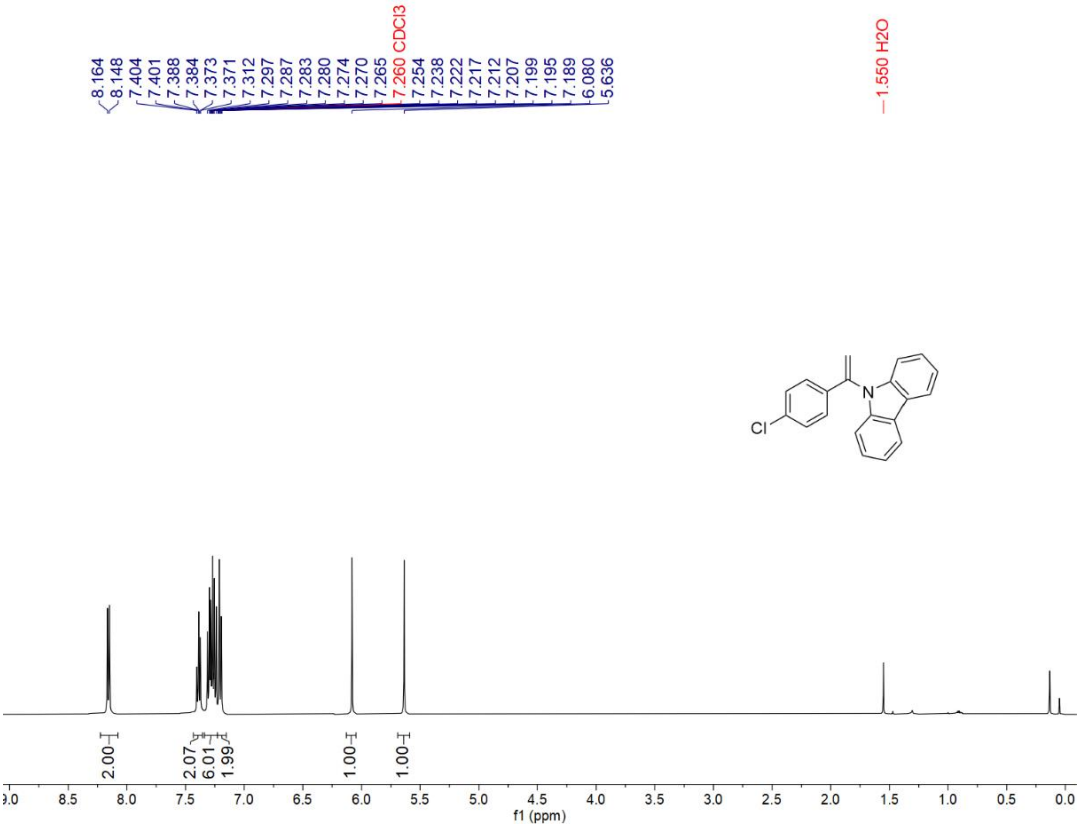
22 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



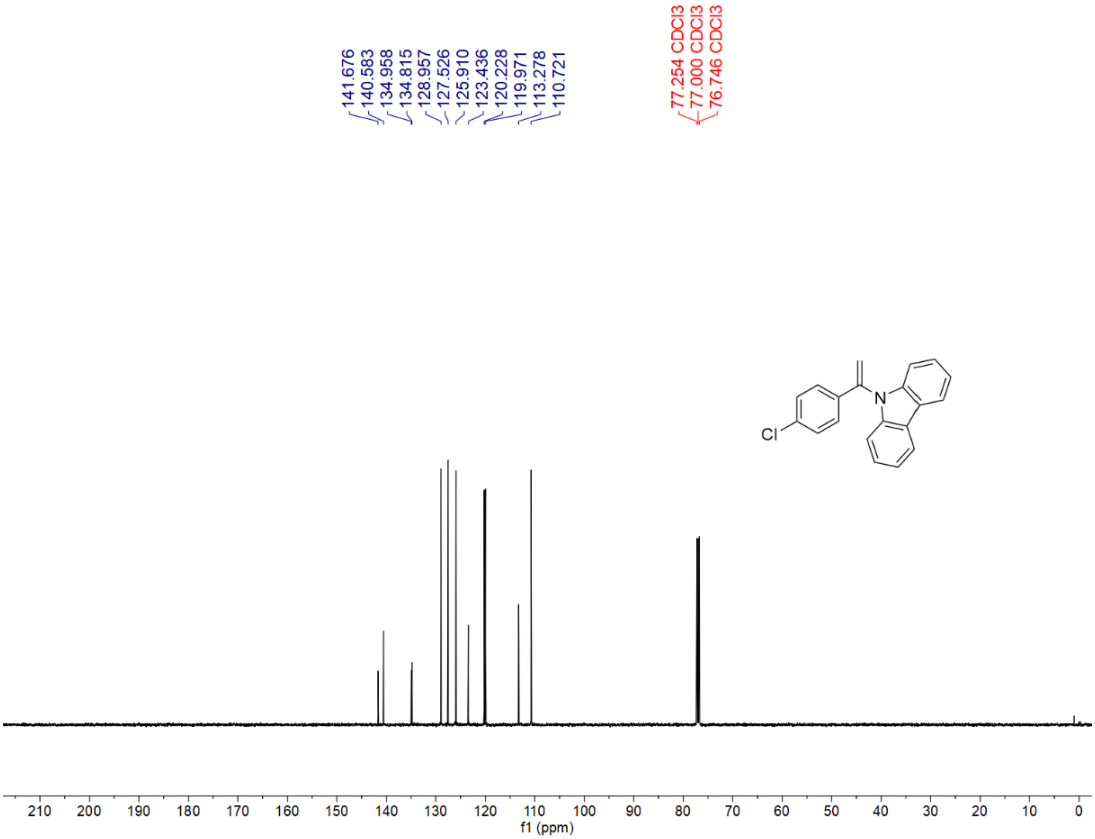
22 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)



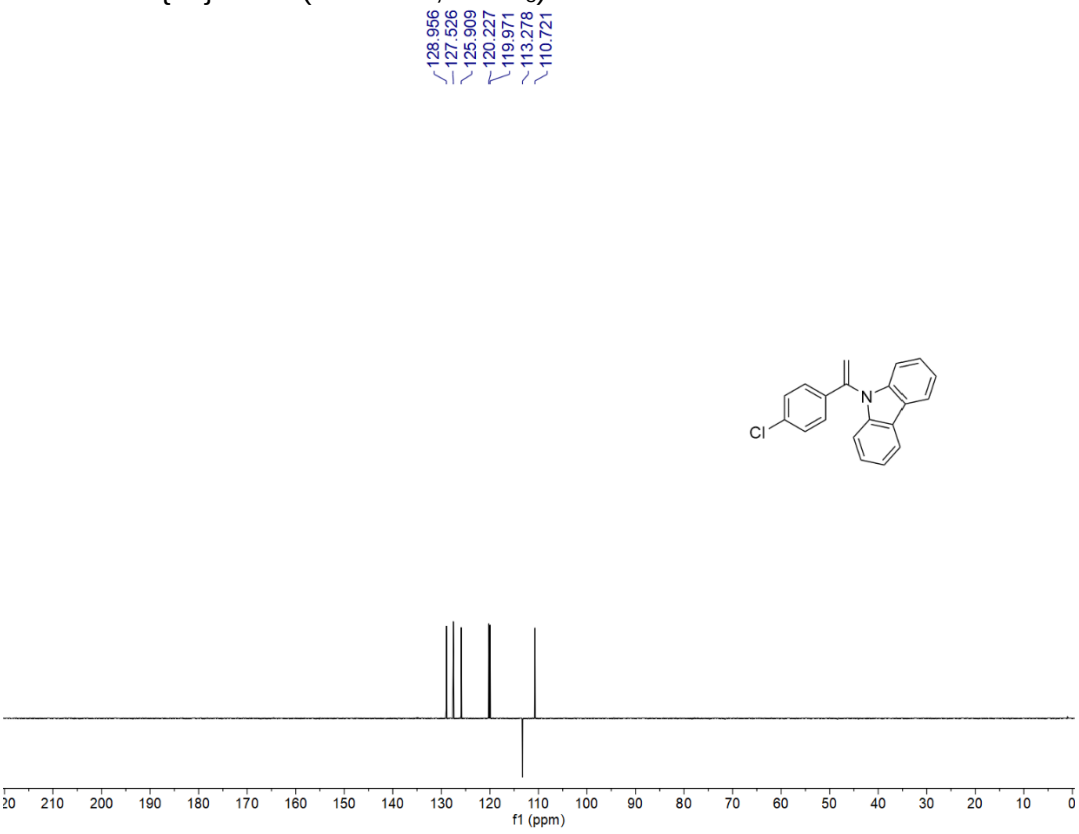
24 ^{1}H NMR (500 MHz, $CDCl_3$)



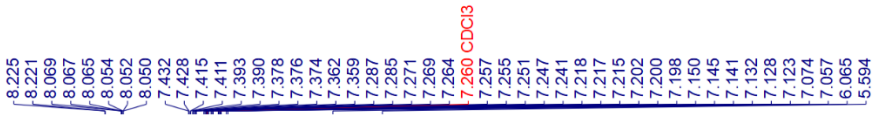
24 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

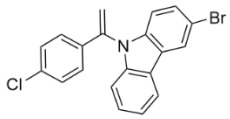


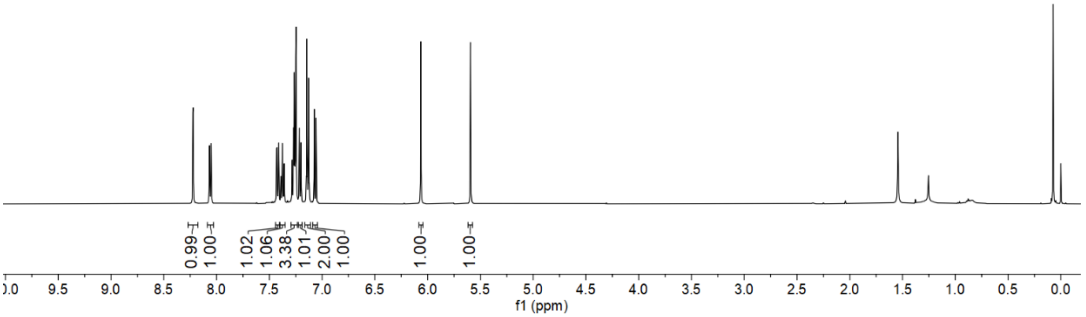
24 DEPT$^{135}\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



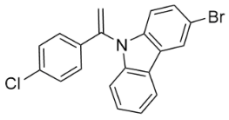
25 ^{1}H NMR (500 MHz, $CDCl_3$)







25 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



25 DEPT^{135}{^{1}H} NMR (126 MHz, $CDCl_3$)