Frustrated Lewis pair-catalyzed double hydroarylation of alkynes with *N*-substituted pyrroles

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Supporting Information

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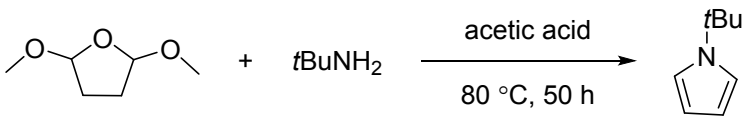
General information

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 were purchased from Alfa Aesar. Deuterated solvents (C_6D_6, toluene-d_8) were purchased from Cambridge Isotope Laboratories, Inc. and distilled from CaH_2 or sodium-benzophenone prior to use. All other deuterated solvents ($CDCl_3$, CD_3CN) were purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Phenylacetylene, 4-ethynyltoluene, 4-*tert*-butylphenylacetylene, 1-trifluoromethyl-2-ethynylbenzene, 1-trifluoromethyl-3-ethynylbenzene, 1-trifluoromethyl-4-ethynylbenzene, 1-octyne, 1-decyne and cyclopropylacetylene were obtained from Sigma Aldrich. 1-Bromo-4-ethynylbenzene,1-chloro-4-ethynylbenzene and 1,4-diethynylbenzene were obtained from TCI Chemical. Pyrrole, 1-methylpyrrole, N-*tert*-butylamine, 2,5-dimethoxytetrahydrofurran and triisopropylsilyl chloride were purchased from Sigma Aldrich. 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.

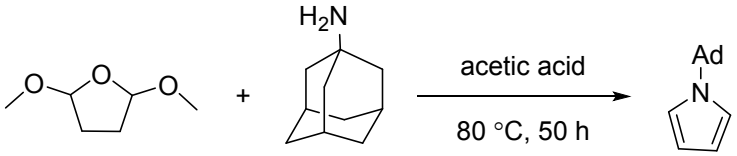
All NMR spectra were collected at 298 K on Agilent VnmrS 400, Agilent VnmrS 500 or Bruker 400 spectrometers in 5 mm diameter NMR tubes. ^1H chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 7.26 ppm; CD_3CN, δ = 1.94 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (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. $^{13}C\{^1H\}$ chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm; CD_3CN, δ = 118.26, 1.32 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 (DART: JEOL AccuTOF).

Preparation of N-*tert*-butylpyrrole



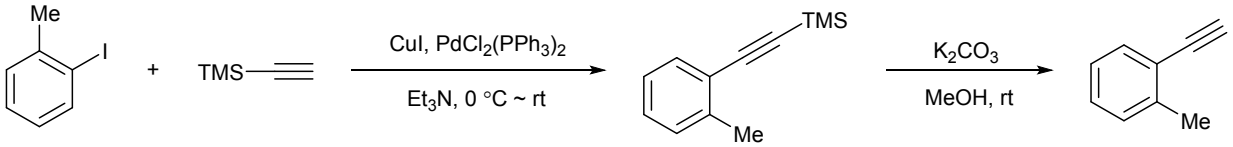
N-*tert*-Butylpyrrole was synthesized according to the following literature procedure.[1] Under a nitrogen atmosphere, a 300 mL two-necked round-bottomed flask was charged with *tert*-butylamine (14.7 g, 200 mmol), acetic acid (45.0 mL) and 2,5-dimethoxytetrahydrofuran (13.2 g, 100 mmol). After stirring at 80 °C for 50 h, the reaction mixture was diluted with Et_2O (100 mL). The resulting solution was washed with a 2N NaOH aqueous solution (50 mL x 3), H_2O (50 mL) and brine (50 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by vacuum distillation (78 °C/80 hPa) provided *N*-*tert*-butylpyrrole (8.3 g, 67% yield) as a colorless oil.

Preparation of N-(1-adamantyl)-1*H*-pyrrole



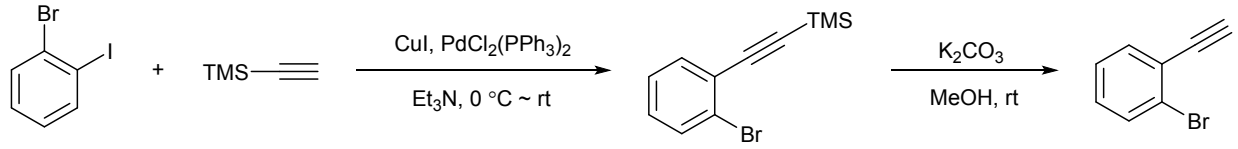
N-(1-adamantyl)-1*H*-pyrrole was synthesized according to the following modified literature procedure.[2] Under a nitrogen atmosphere, a 100 mL two-necked round-bottomed flask was charged with amantadine (1.59 g, 5 mmol), acetic acid (5.0 mL) and 2,5-dimethoxytetrahydrofuran (0.33 g, 2.5 mmol). After stirring at 80 °C for 50 h, the reaction mixture was diluted with Et_2O (5 mL) and ethyl acetate (10 mL). The resulting solution was washed with a 2N NaOH aqueous solution (10 mL x 3), H_2O (10 mL) and brine (50 mL), and then dried over anhydrous sodium sulfate. The residue was purified by flash chromatography (hexane) on silica gel to afford the product *N*-(1-adamantyl)-1*H*-pyrrole as a white solid.

Preparation of 1-ethynyl-2-methylbenzene[3]



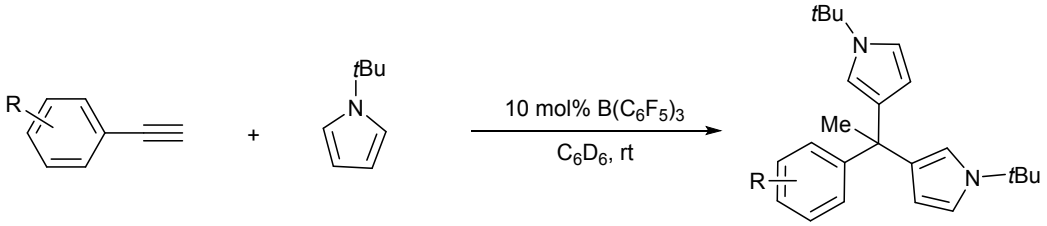
To a stirred mixture of 2-iodotoluene (2.92 mL, 22.9 mmol), $PdCl_2(PPh_3)_2$ (782 mg, 1.17 mmol) and CuI (436 mg, 2.29 mmol) in NEt_3 (20 mL), trimethylsilylacetylene (3.59 mL, 25.4 mmol) was added dropwise at 0 °C. Then, the reaction mixture was stirred at room temperature overnight. Upon completion, the mixture was filtered through a pad of celite. The filtrate was concentrated under vacuo. The residue was purified by flash chromatography on silica gel using hexane as eluent afforded the product as yellow oil. Then, to a stirred solution of trimethyl(o-tolylethynyl)silane (4.00 g, 21.2 mmol) in MeOH (10 mL) at room temperature was added K_2CO_3 (1.46 g, 10.6 mmol). The reaction was stirred overnight. On completion, the reaction was quenched with water (50 mL) and extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using hexane as eluent to afford the product as colourless oil. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.51 (d, J = 7.2 Hz, 1H), 6.96 - 6.81 (m, 3H), 2.92 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ: 140.90, 132.88, 129.73, 128.91, 125.88, 122.62, 82.83, 81.58, 20.64.

Preparation of1-bromo-2-ethynylbenzene[4]



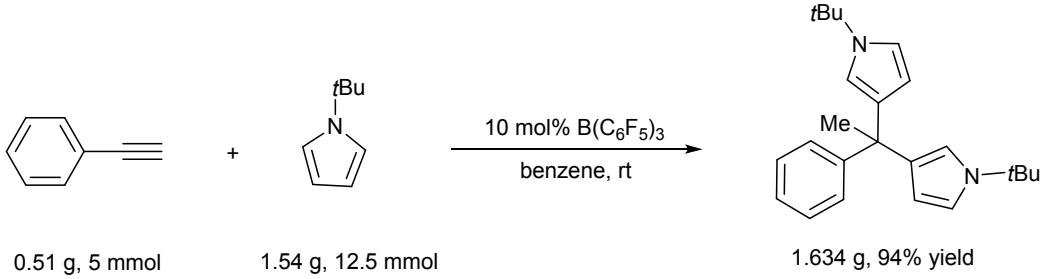
The $Pd(PPh_3)_2Cl_2$ (522 mg, 0.74 mmol, 2 mol%) and CuI (142 mg, 0.74 mmol, 2 mol%) were added to a solution of 2-bromoiodobenzene (10.515 g, 37.17 mmol) in Et_2NH (120 mL). After 10 min a solution of trimethylsilylacetylene (6.4 mL, 55.8 mmol, 1.5 eq) in Et_2NH (3.6 mL) was added dropwise and the reaction mixture was stirred for 18 h. Upon completion, the mixture was filtered through a pad of celite, concentrated and purified by flash chromatography (hexane) to give the product as a light-yellow oil. Then, (2-bromophenylethynyl)trimethylsilane (1.621 g, 6.40 mmol) and K_2CO_3 (0.885 g, 6.40 mmol, 1 eq) were stirred in MeOH (10 mL) for 2 h. The reaction was filtered, concentrated and purified by flash chromatography (hexane) to give the product as a light-yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.24 – 7.19 (m, 1 H), 6.62 (td, *J* = 7.6, 1.2, 1H), 7.29 (td, *J* = 7.6, 1.6, 1H), 2.93 (s, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: 134.23, 132.71, 129.95, 127.03, 126.03, 124.93, 82.56, 82.14.

Standard preparation for catalytic operations



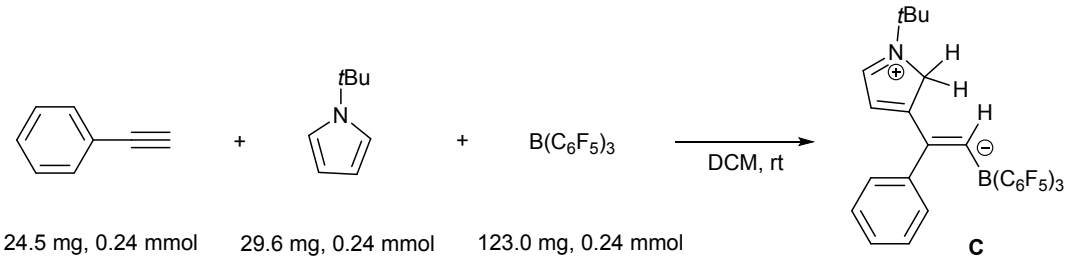
In an inert atmosphere glovebox, the mixture of alkynes (0.10 mmol) with the pyrroles (0.25 mmol) in 0.3 mL C_6D_6 was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 10 mol%) in 0.2 mL C_6D_6. The reaction mixture was stirred for the specified time at room temperature and monitored by ^1H NMR spectroscopy. The residue was purified by flash chromatography on silica gel to afford the product dipyrroalkanes.

Typical procedure for gram-scale version of double hydroarylation



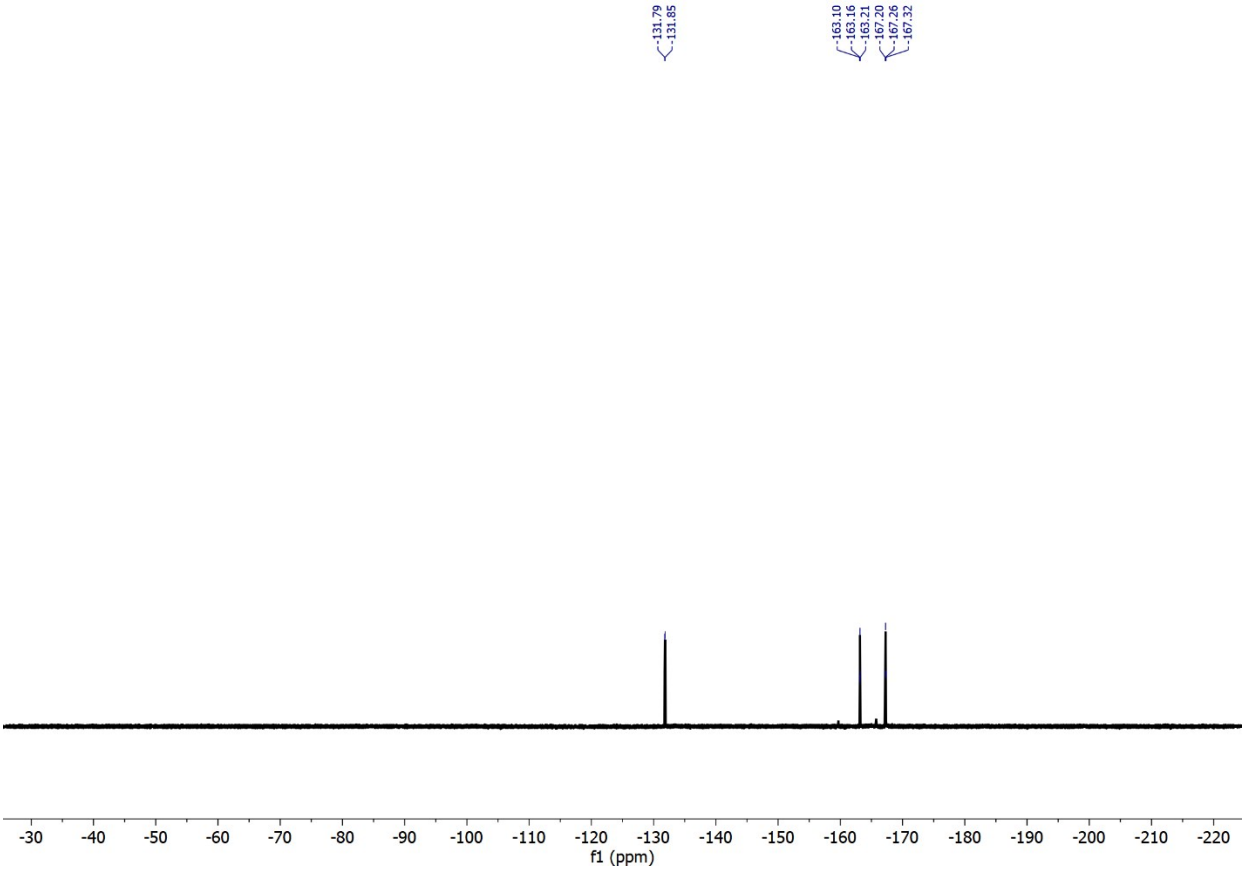
In an inert atmosphere glovebox, a flask (100 mL) was charged with phenylacetylene (**1a**, 0.51 g, 5.0 mmol). Then, 1-(*tert*-butyl)-1*H*-pyrrole (1.54 g, 12.5 mmol) and benzene (15 mL) were added. Finally, a solution of $B(C_6F_5)_3$ (0.255 g, 10 mol%) in 10 mL benzene was added to the mixture under stirring. The reaction mixture was stirred at room temperature for 12 h. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product as a white solid (1.634 g, 94% yield).

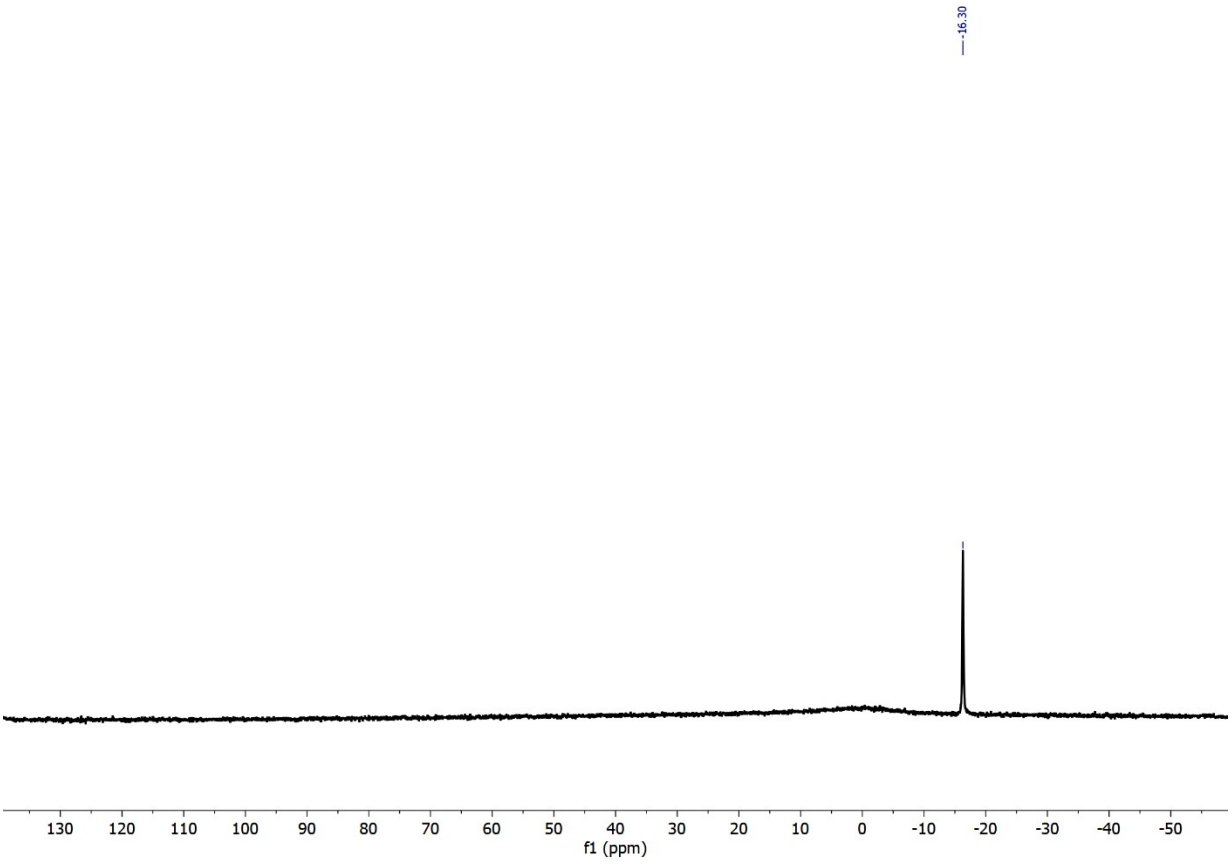
Preparation of the zwitterionic species C (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$))



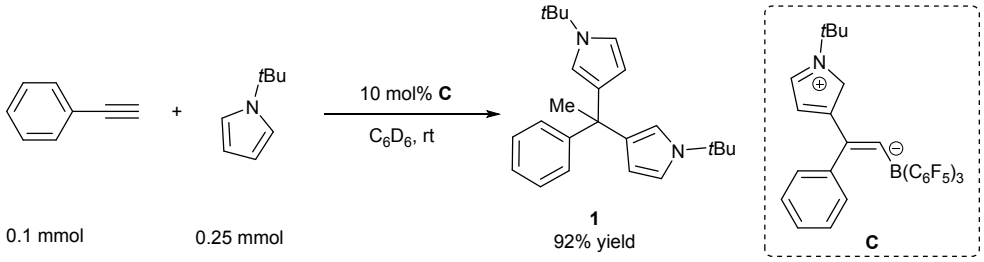
24.5 mg, 0.24 mmol 29.6 mg, 0.24 mmol 123.0 mg, 0.24 mmol **C**

According to the literature,[3] in an inert atmosphere glovebox, a solution of $B(C_6F_5)_3$ (123mg, 0.24 mmol) in 0.5 mL dichloromethane was cooled to −35 °C in a freezer. A solution of 1-(*tert*-butyl)-1*H*-pyrrole (29.6 mg, 0.24 mmol) in cold pentane (1.5 mL) was added in one portion followed by the dropwise addition of a solution of phenylacetylene (24.5 mg, 0.24 mmol) in cold pentane (1.5 mL). The solution was initially colorless and became more yellow over the course of the addition. After the phenylacetylene solution had been added, pentane (5 mL) was added in one portion to precipitate a yellow-white microcrystalline solid of the zwitterionic species **C** (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)). ^{19}F NMR (377 MHz, CH_2Cl_2) δ: -131.8 (d, 6F, $^3J_{F\text{-}F}$ =22 Hz, *o*-C_6F_5), -163.2 (t, 3F,$^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -167.3 (t, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *m*-C_6F_5). ^{11}B NMR (128 MHz, CH_2Cl_2) δ: -16.3 (s).



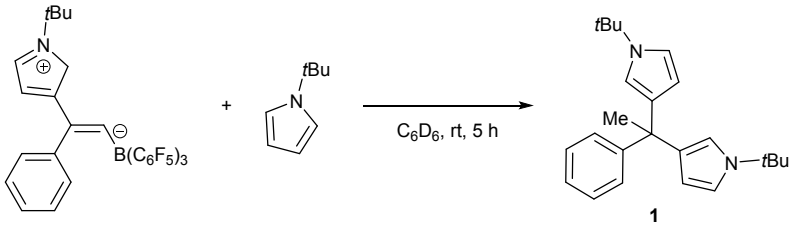


Zwitterionic species C (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)) catalyzed double hydroarylation



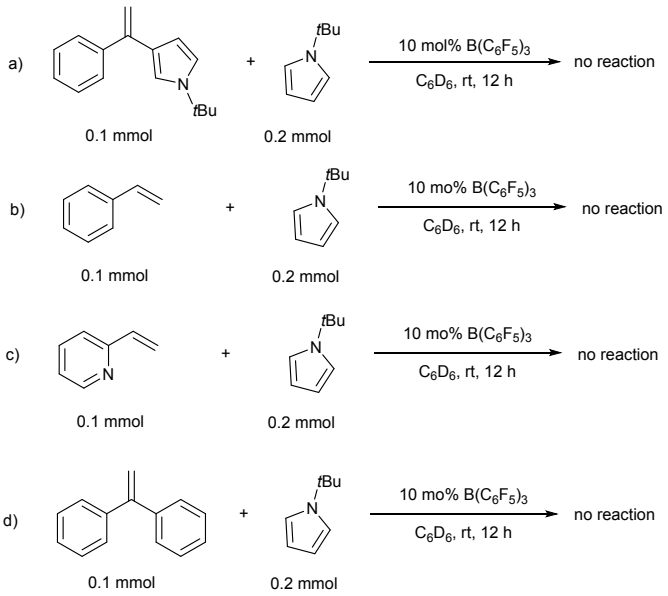
In an inert atmosphere glovebox, the mixture of phenylacetylene (0.10 mmol, 10.2 mg) with 1-(*tert*-butyl)-1*H*-pyrrole (0.25 mmol, 30.7 mg) in 0.3 mL C_6D_6 was added to a solution of zwitterionic species **C** (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)) (7.3 mg, 10 mol%) in 0.2 mL C_6D_6. The reaction mixture was stirred for the specified time at room temperature and monitored by ^{1}H NMR spectroscopy. The residue was purified by flash chromatography on silica gel to afford the product dipyrroalkanes (32.0 mg, 92% yield).

Zwitterionic species C (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)) reacted with *N-tert*-butylpyrrole double



In an inert atmosphere glovebox, the solution of 1-(*tert*-butyl)-1*H*-pyrrole (0.10 mmol, 12.3 mg) in 0.3 mL C_6D_6 was added to a solution of zwitterionic species **C** (*t*BuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)) (0.05 mmol, 36.9 mg) in 0.2 mL C_6D_6. The reaction mixture was stirred for 5 h at room temperature and monitored by ^{1}H NMR spectroscopy. The residue was purified by flash chromatography on silica gel to afford the product dipyrroalkanes (15.3 mg, 88% yield).

Control experiments



NMR spectra of these reactions

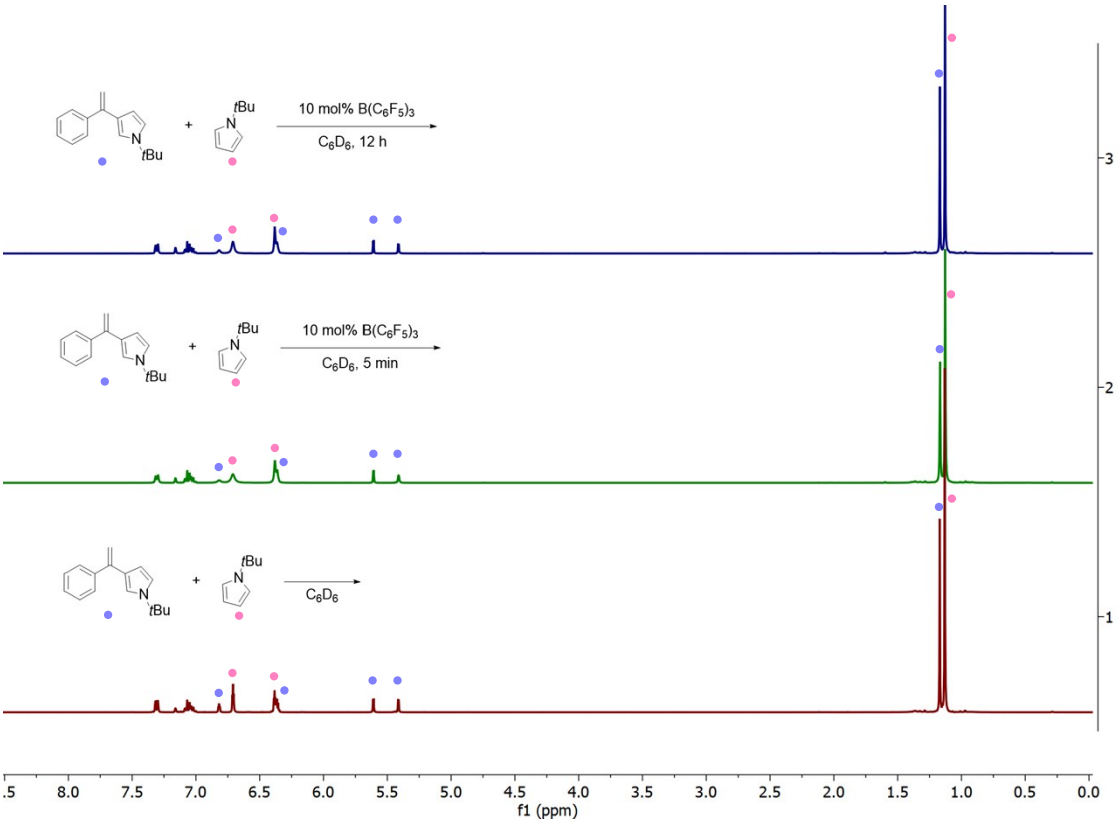


Figure S1. Hydroarylation of mono-hydroarylated product **1a** with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

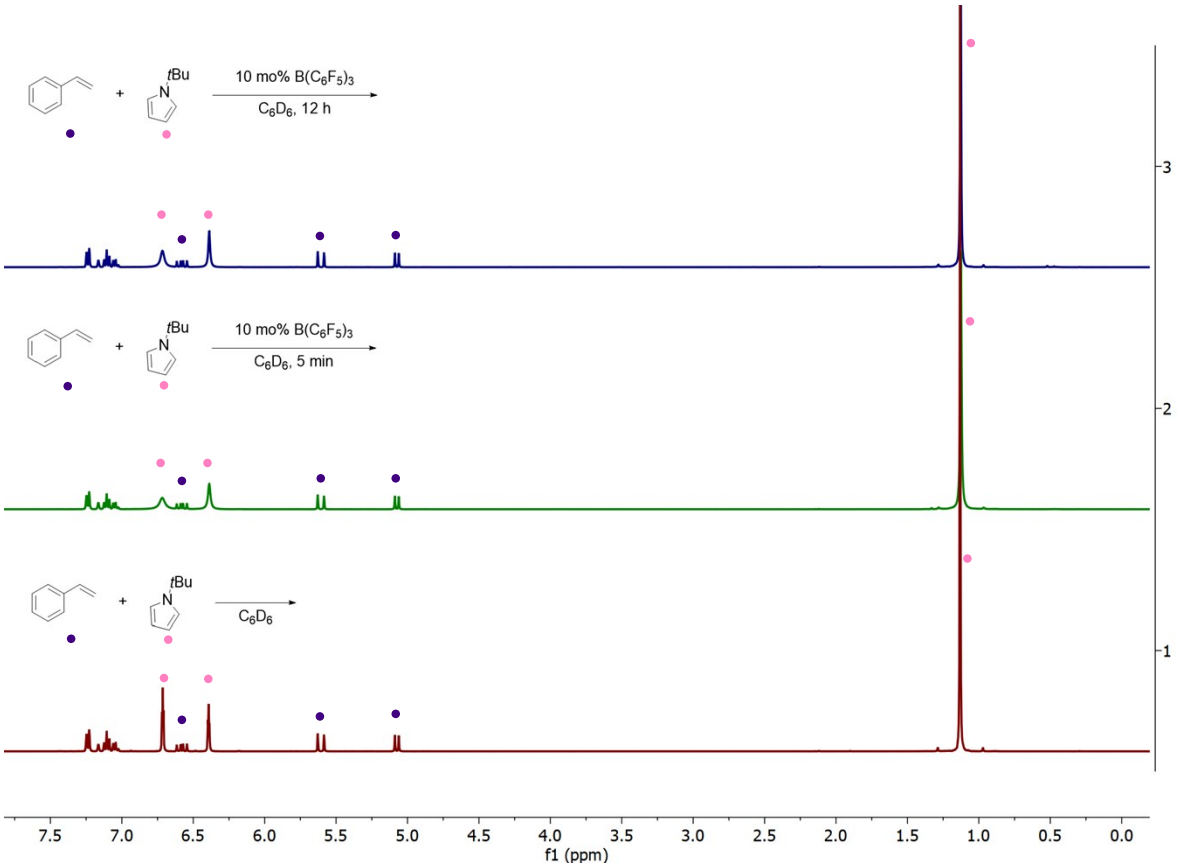


Figure S2. Hydroarylation of styrene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

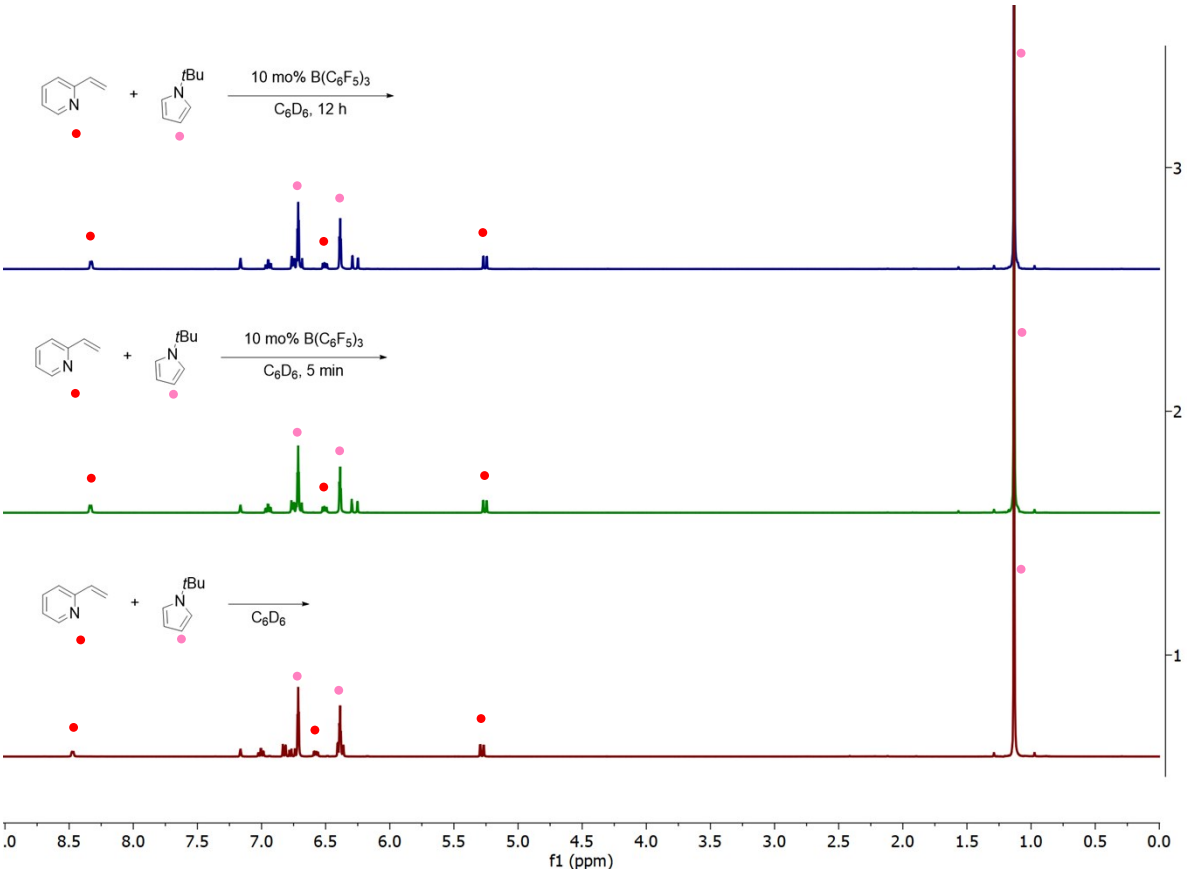


Figure S3. Hydroarylation of 2-vinylpyridine with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

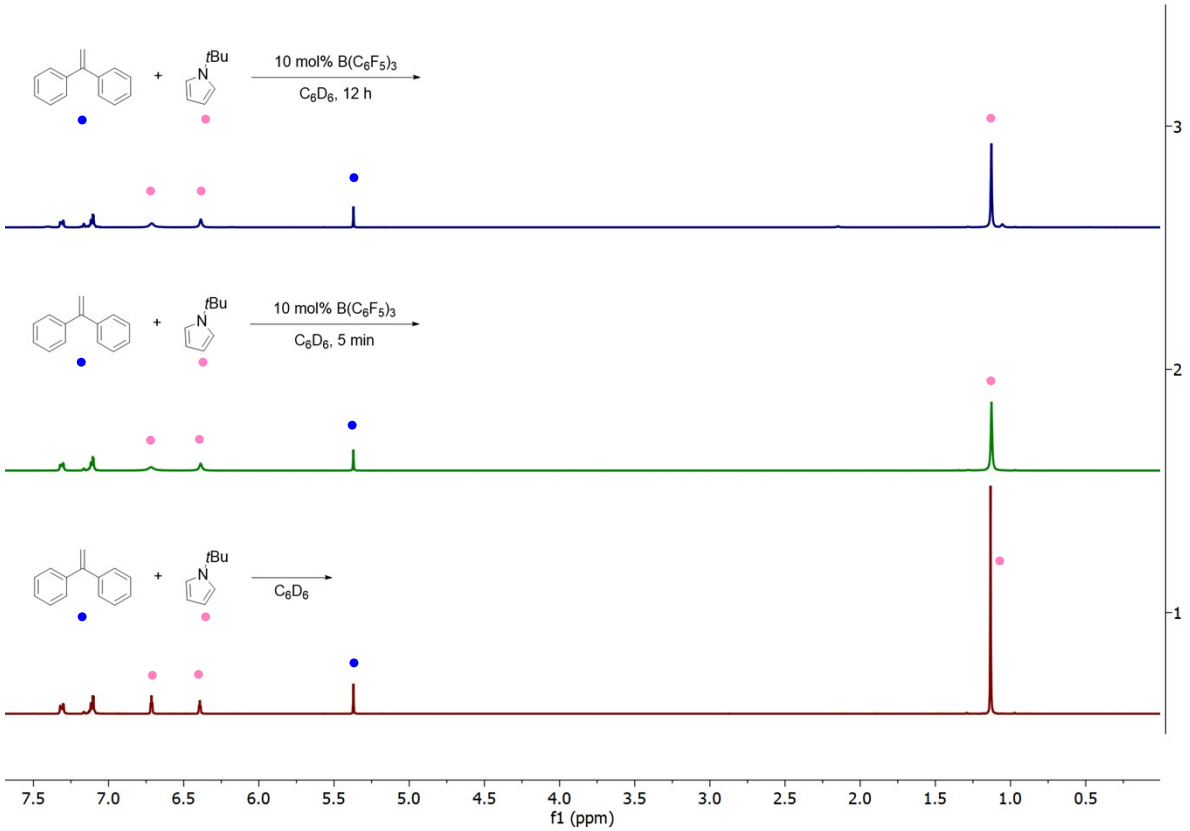
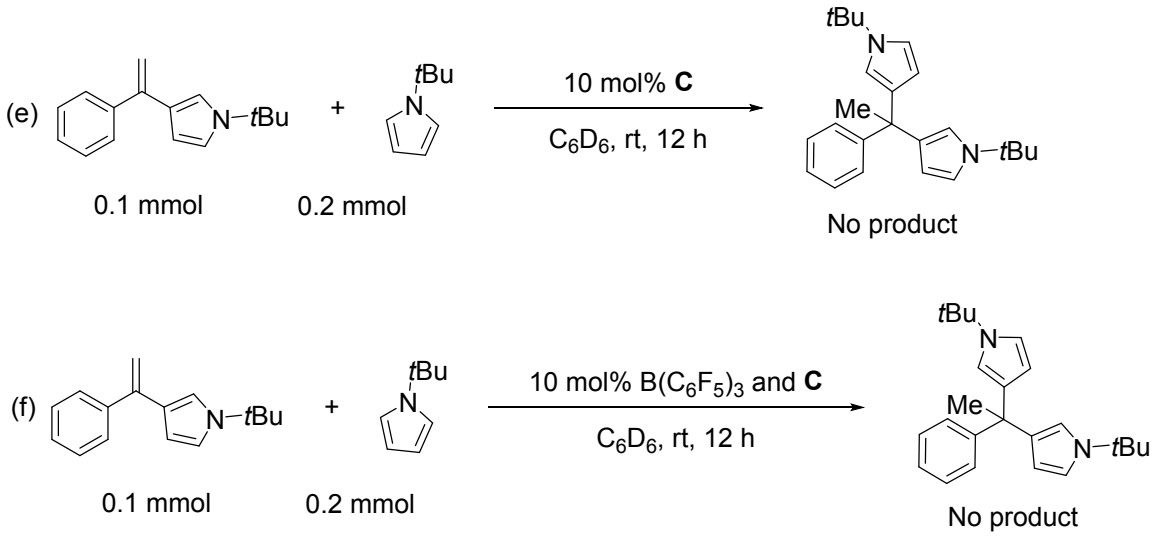


Figure S4. Hydroarylation of 1,1-diphenylethylene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.



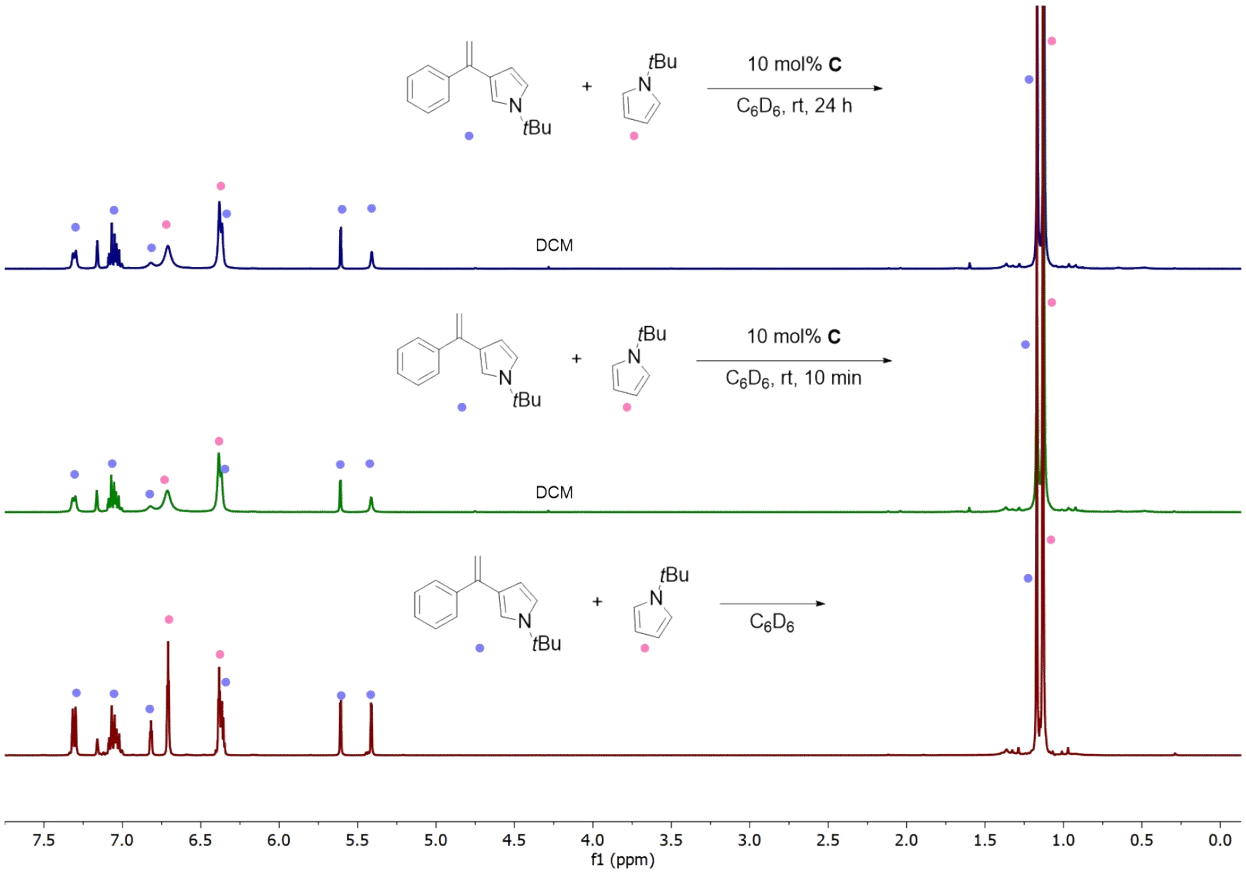


Figure S5. Hydroarylation of mono-hydroarylated product **1a** with *N*-*t*-butylpyrrole using 10 mol% **C** in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

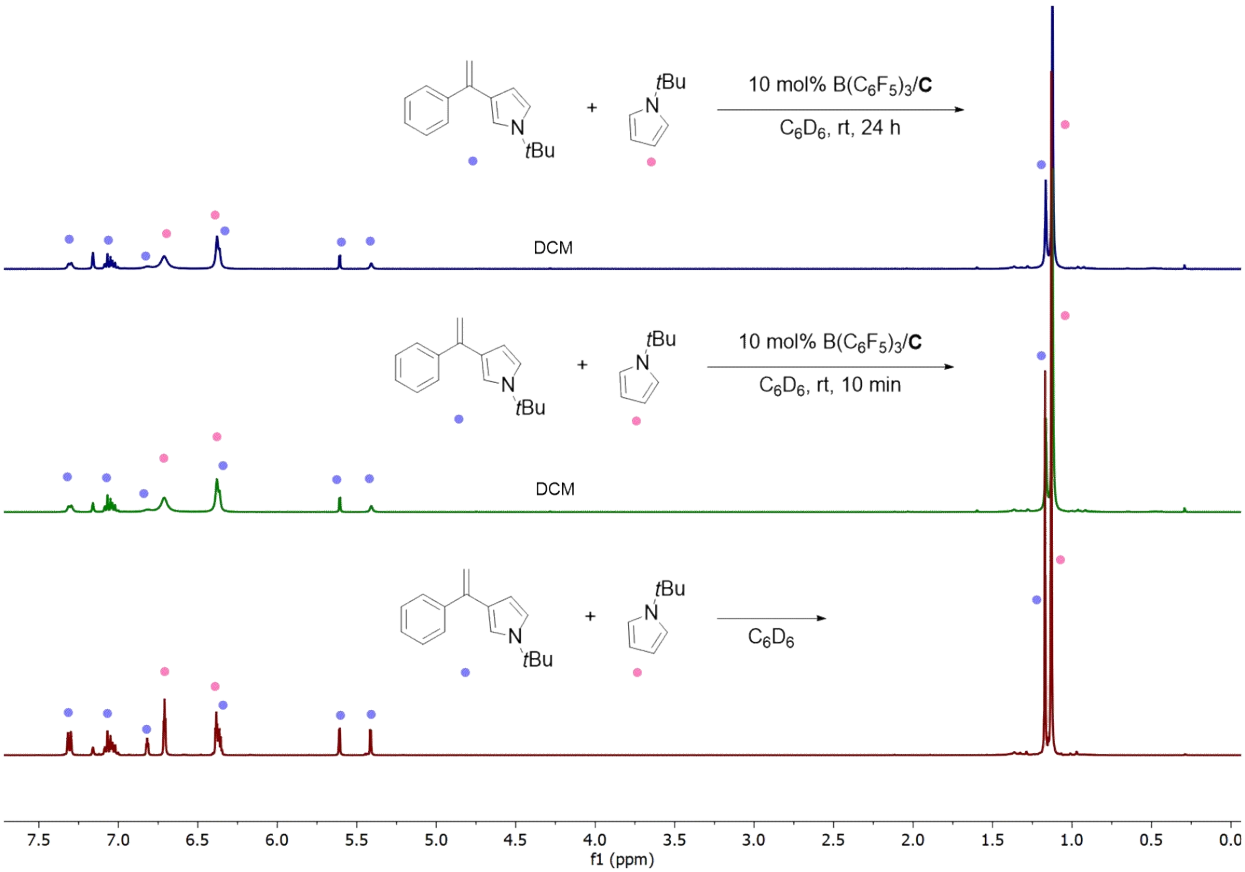
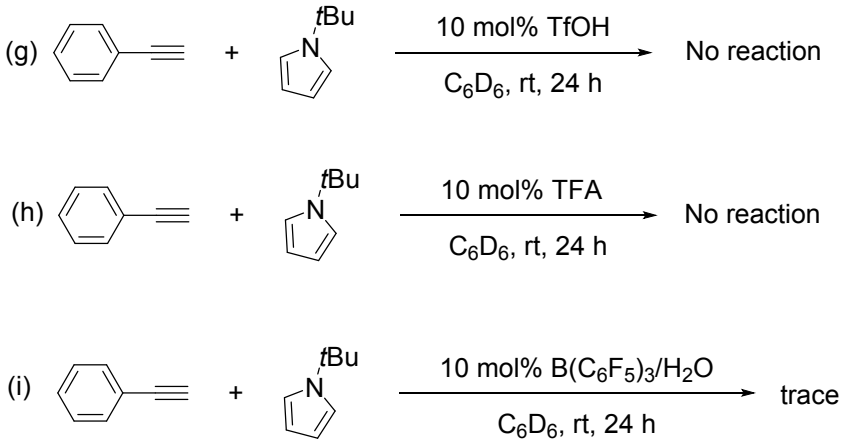


Figure S6. Hydroarylation of mono-hydroarylated product **1a** with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ and **C** in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.



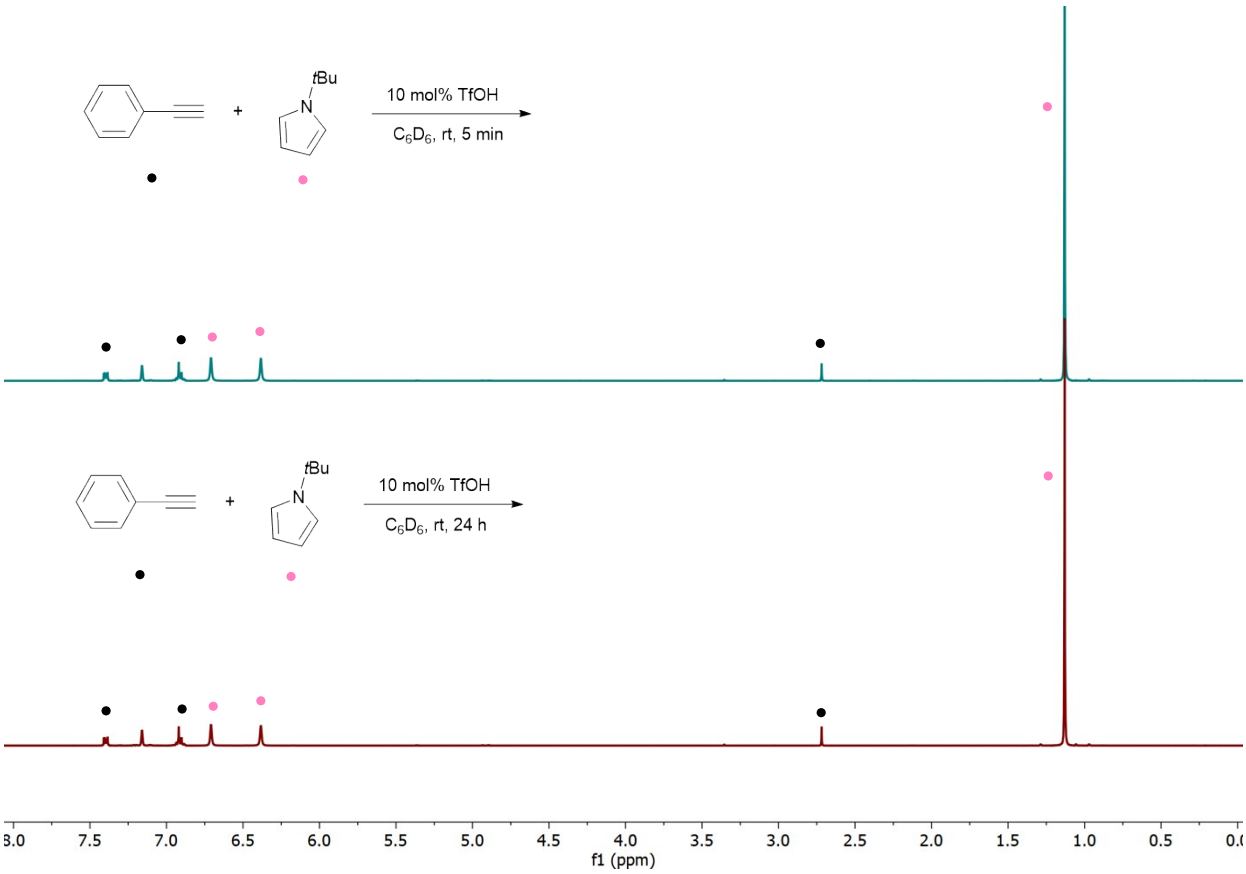


Figure S7. Hydroarylation of phenylacetylene with *N*-*t*-butylpyrrole using 10 mol% TfOH in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

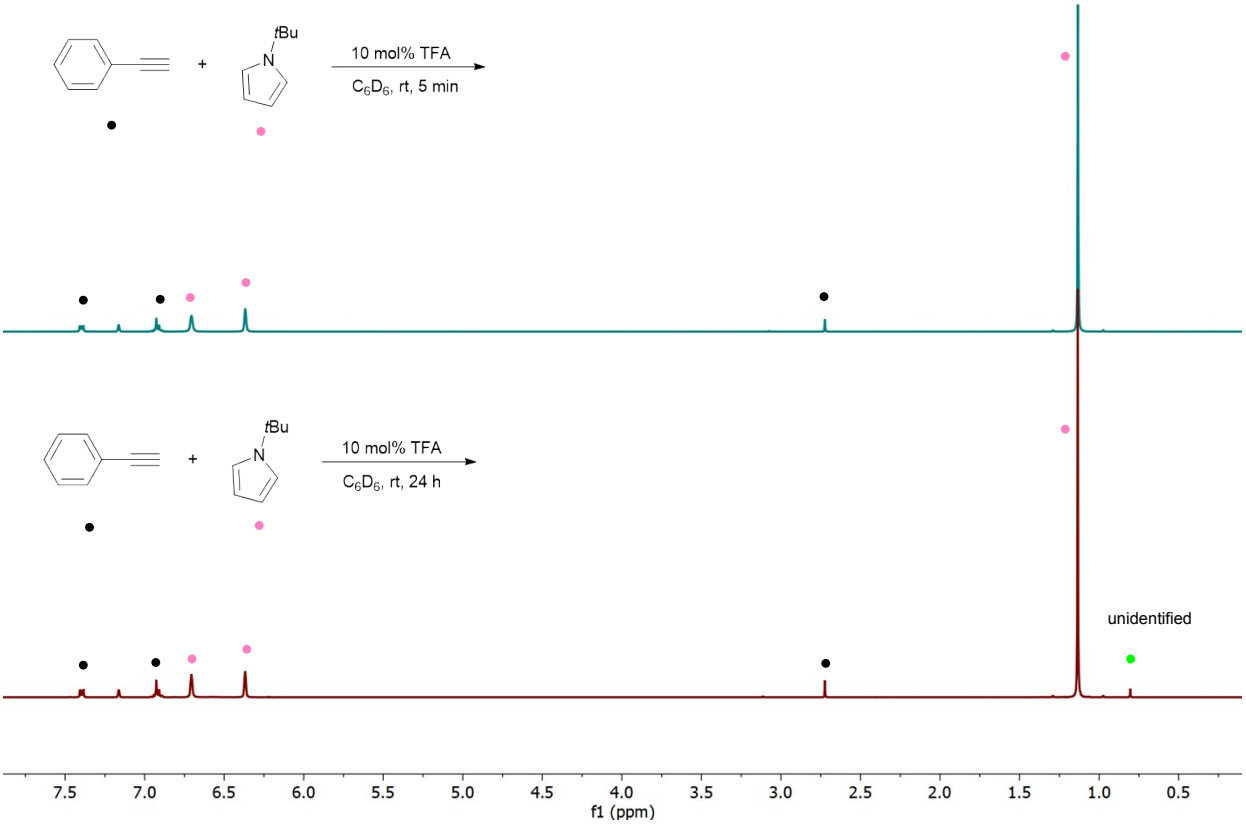


Figure S8. Hydroarylation of phenylacetylene with *N*-*t*-butylpyrrole using 10 mol% TFA in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

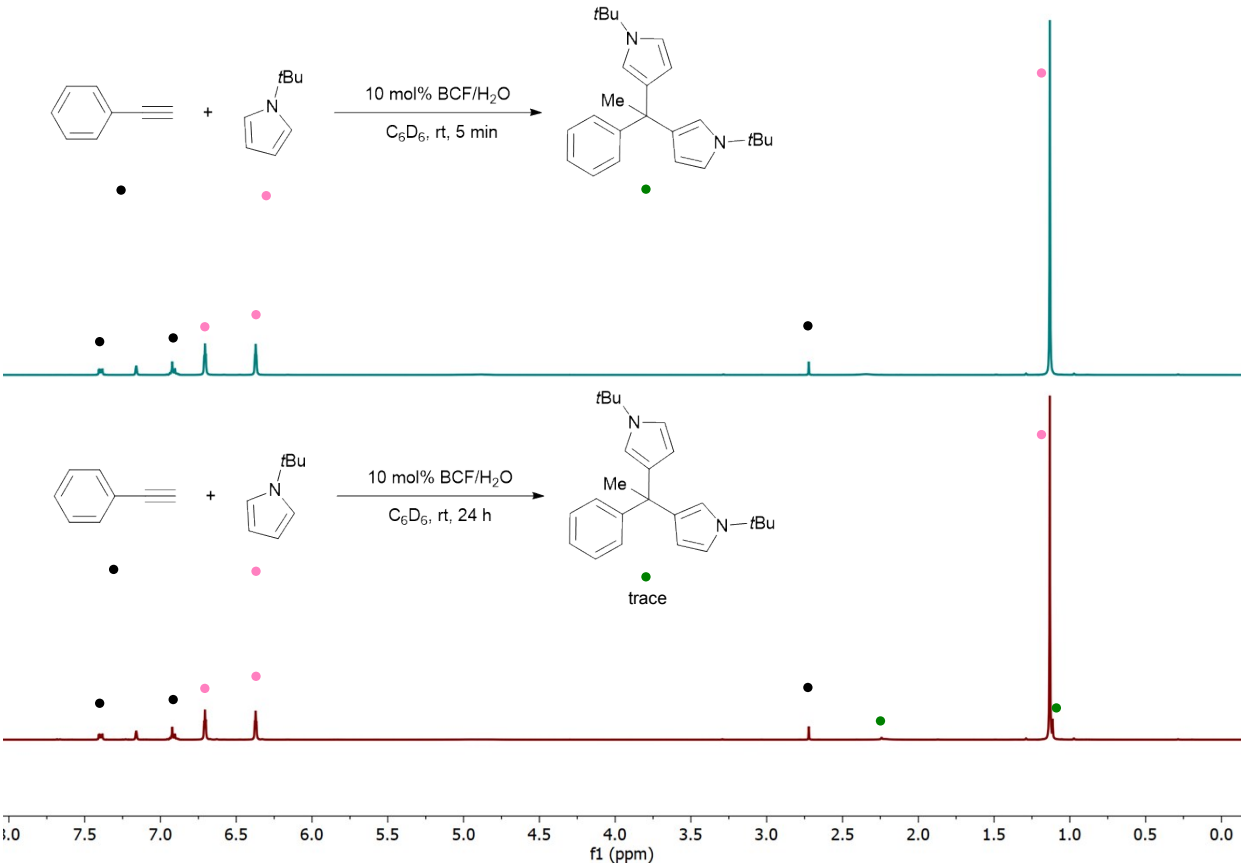


Figure S9. Hydroarylation of phenylacetylene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ and H_2O in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

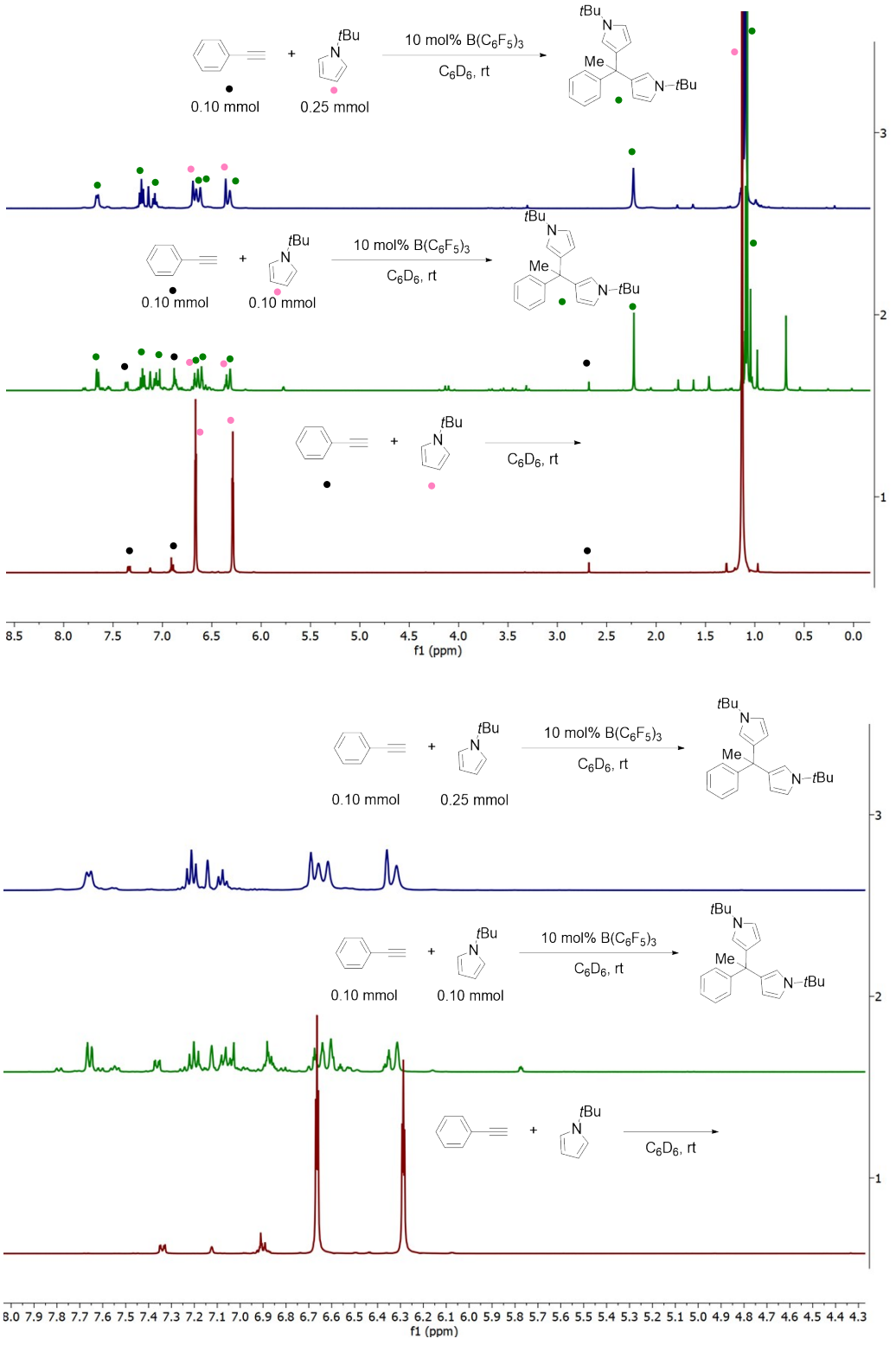


Figure S10. Hydroarylation of different ratio of phenylacetylene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

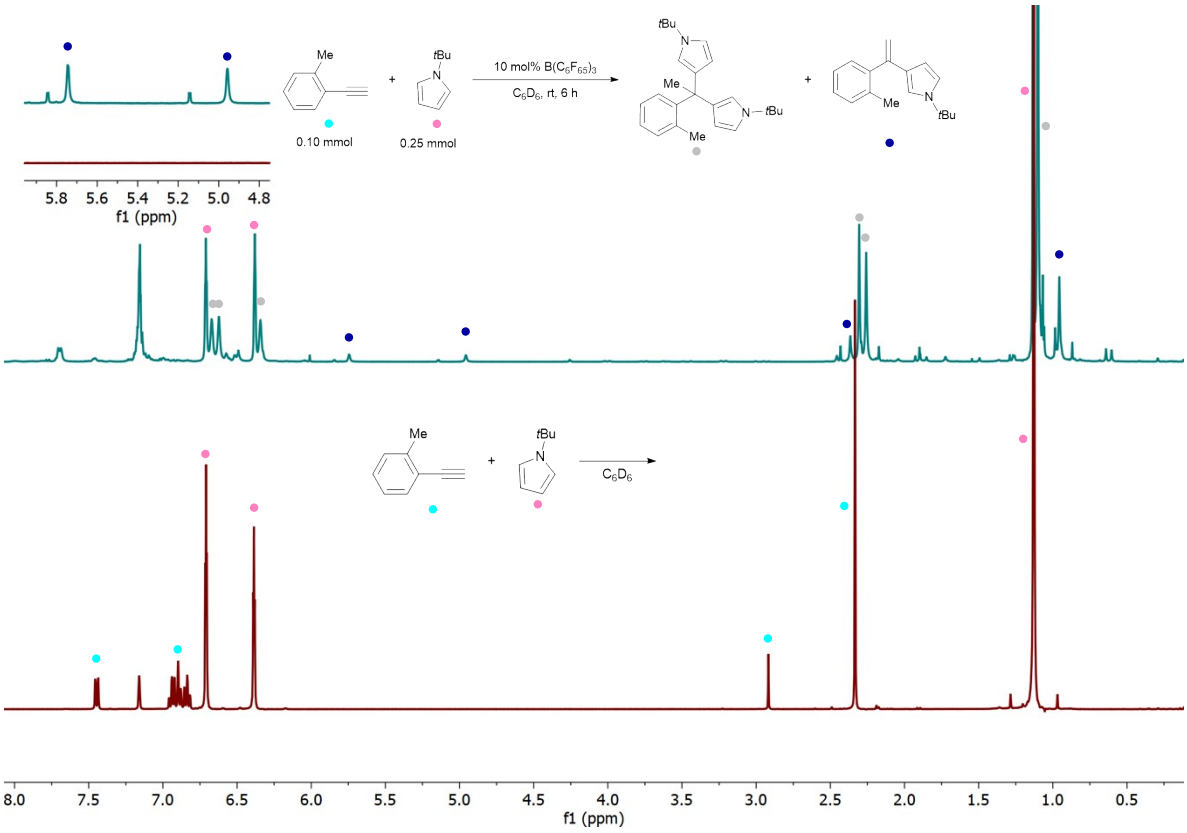


Figure S11. Hydroarylation of 1-ethynyl-2-methylbenzene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

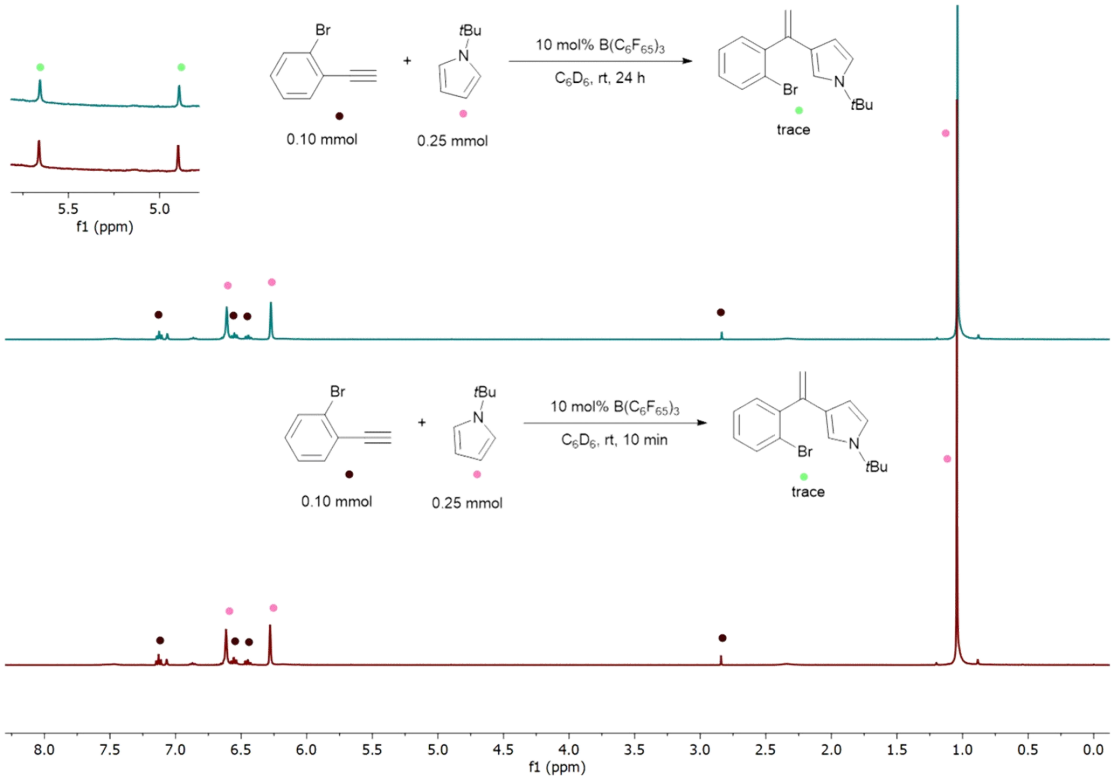
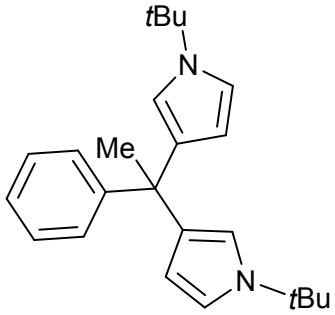


Figure S12. Hydroarylation of 1-ethynyl-2-bromobenzene with *N*-*t*-butylpyrrole using 10 mol% $B(C_6F_5)_3$ in C_6D_6, as monitored by ^1H NMR (400 MHz) spectroscopy.

Characterization data

Preparation of 3,3'-(1-phenylethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (1)



To a solution of phenylacetylene (10.2 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **1** as a white solid (32.0 mg, 92% yield).

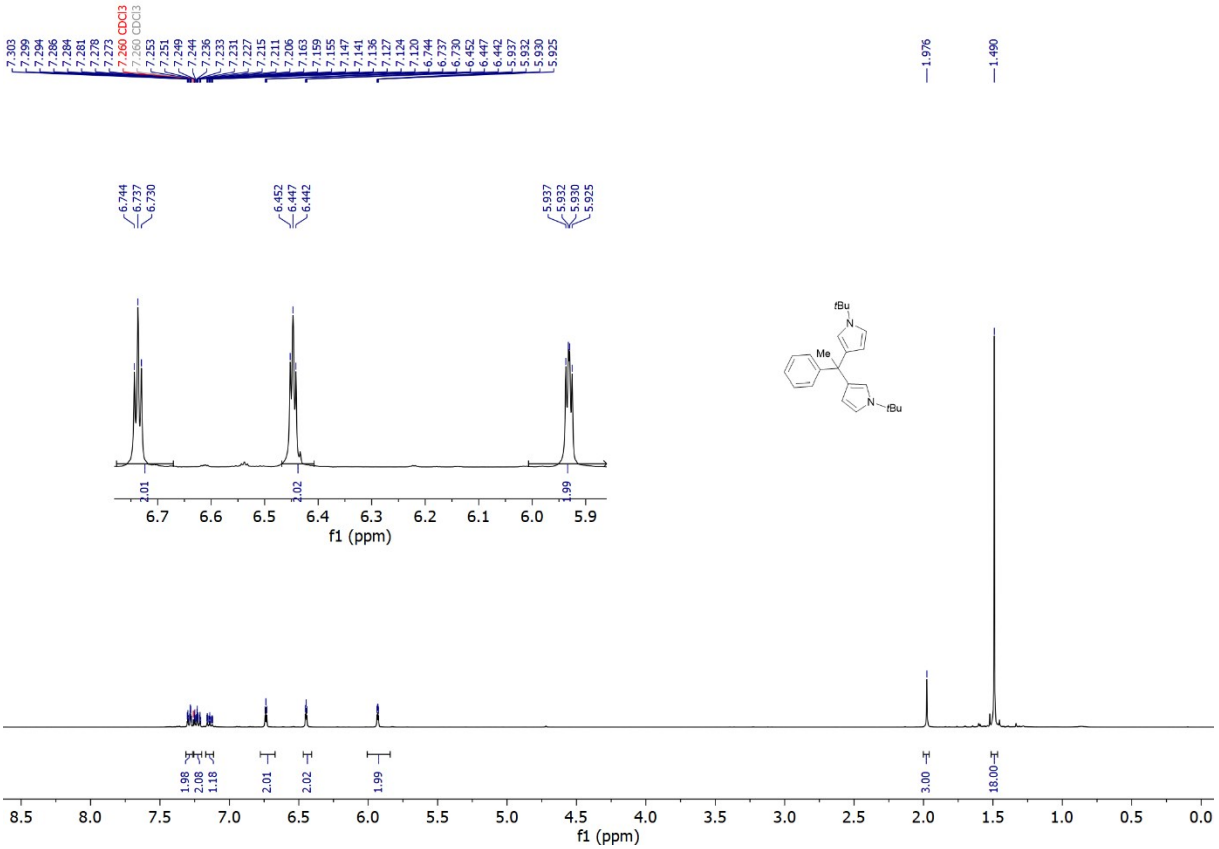
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 7.16 – 7.12 (m, 1H), 6.74 (t, *J* = 2.8 Hz, 2H), 6.45 (t, *J* = 2.0 Hz, 2H), 6.45 (dd, *J* = 2.8, 2.0 Hz, 2H), 1.98 (s, 3H), 1.49 (s, 18H).

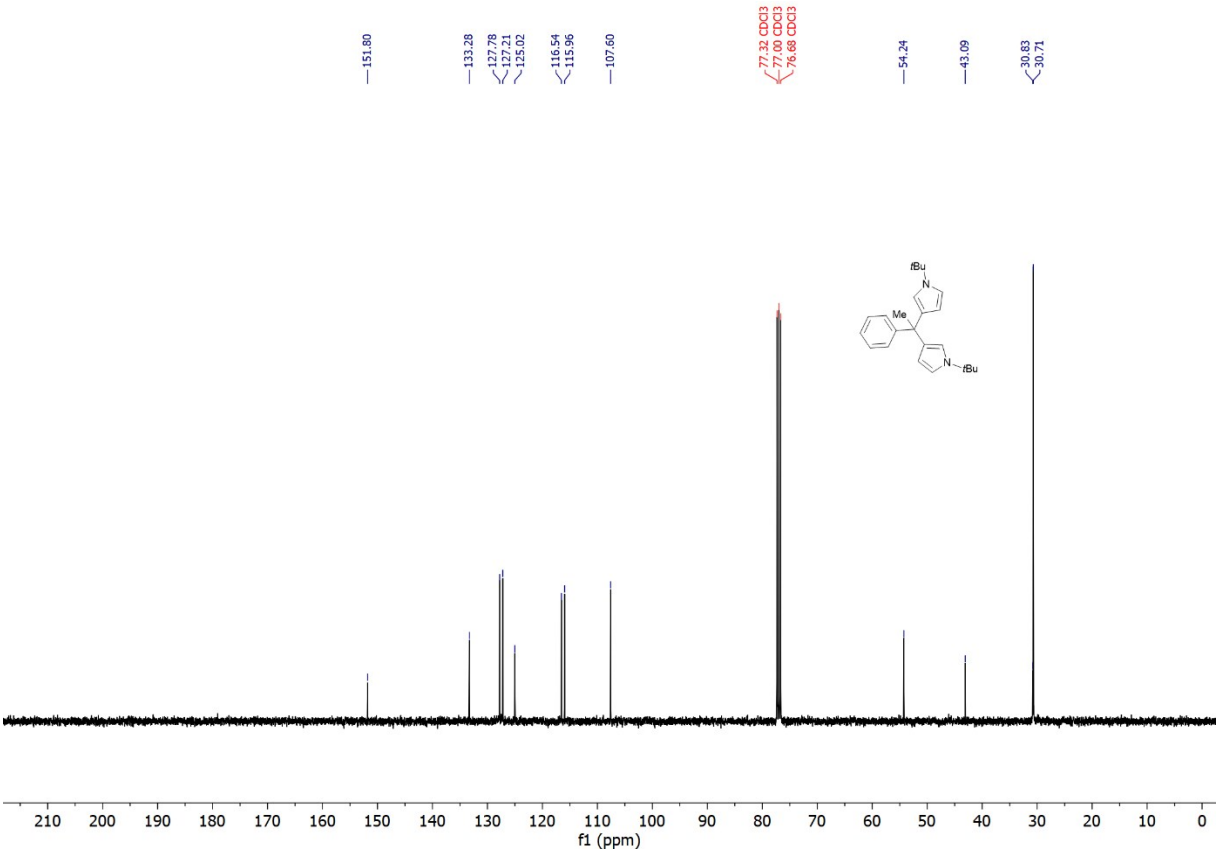
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), δ: 151.80, 133.28, 127.78, 127.21, 125.02, 116.54, 115.96, 107.60, 54.24, 43.09, 30.83, 30.71.

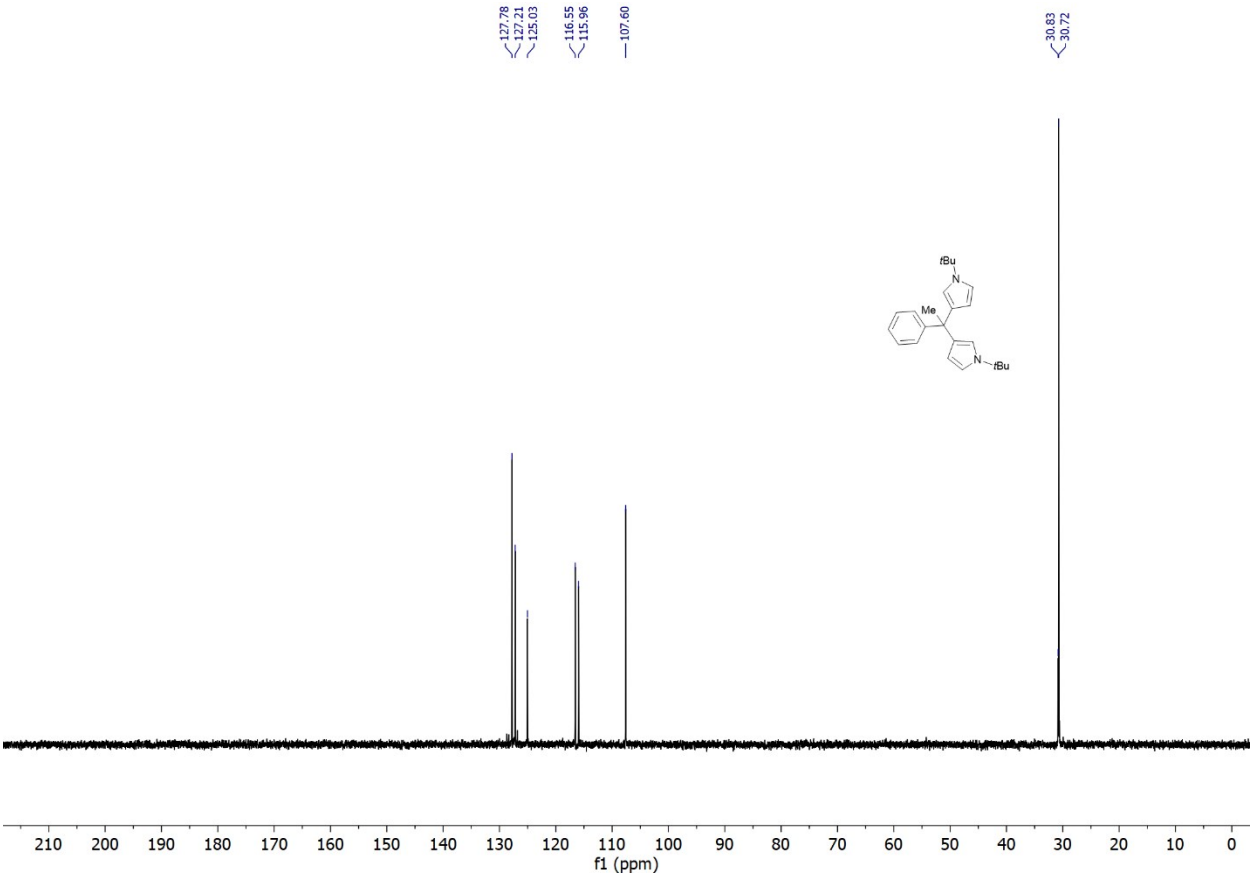
DEPT^{135} NMR (100 MHz, $CDCl_3$) δ: 127.78, 127.21, 125.03, 116.55, 115.96, 107.60, 30.83, 30.72.

MS (DART Ionization, *m/z*): 349.3 ([M+H]$^+$).

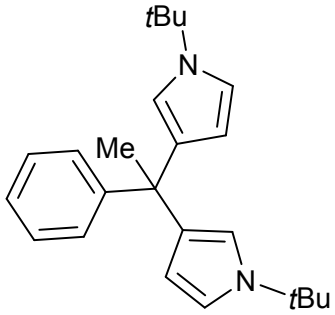
HRMS (DART Ionization, *m/z*): Calcd. for $C_{24}H_{33}N_2^+$, ([M+H]$^+$): 349.26437; Found: 349.26520.


7.303
7.299
7.294
7.286
7.284
7.281
7.278
7.273
7.260 CDCl3
7.253
7.251
7.249
7.244
7.236
7.233
7.231
7.227
7.215
7.211
7.206
7.163
7.159
7.155
7.147
7.141
7.136
7.127
7.124
7.120
6.744
6.737
6.730
6.452
6.447
6.442
5.937
5.932
5.930
5.925
1.976
1.490
tBu
N
Me
N
tBu
2.01
2.02
1.99
f1 (ppm)
1.98
2.08
1.18
2.01
2.02
1.99
3.00
18.00
f1 (ppm)


151.80
133.28
127.78
127.21
125.02
116.54
115.96
107.60
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
54.24
43.09
30.83
30.71
tBu
N
Me
N
tBu
f1 (ppm)



Gram-scale of 3,3'-(1-phenylethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (1)

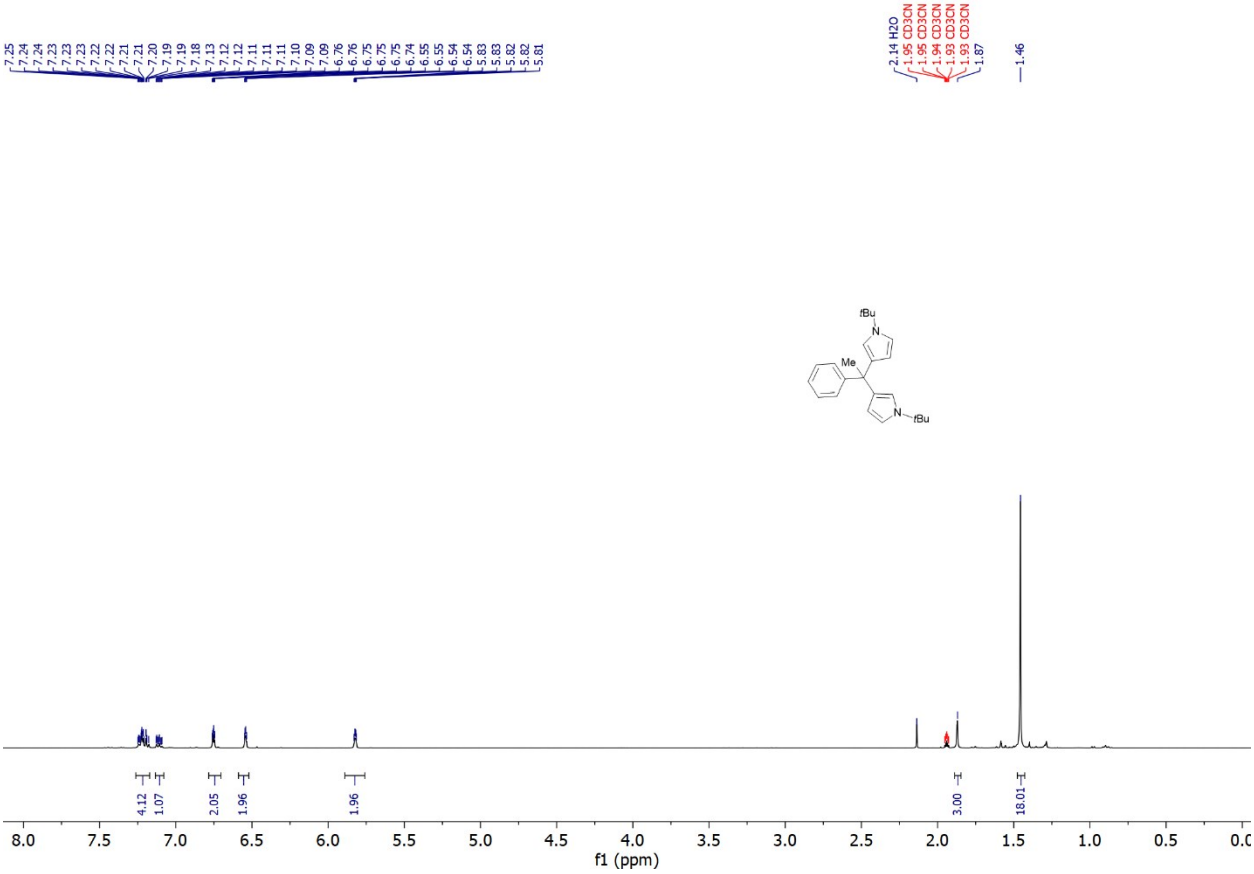


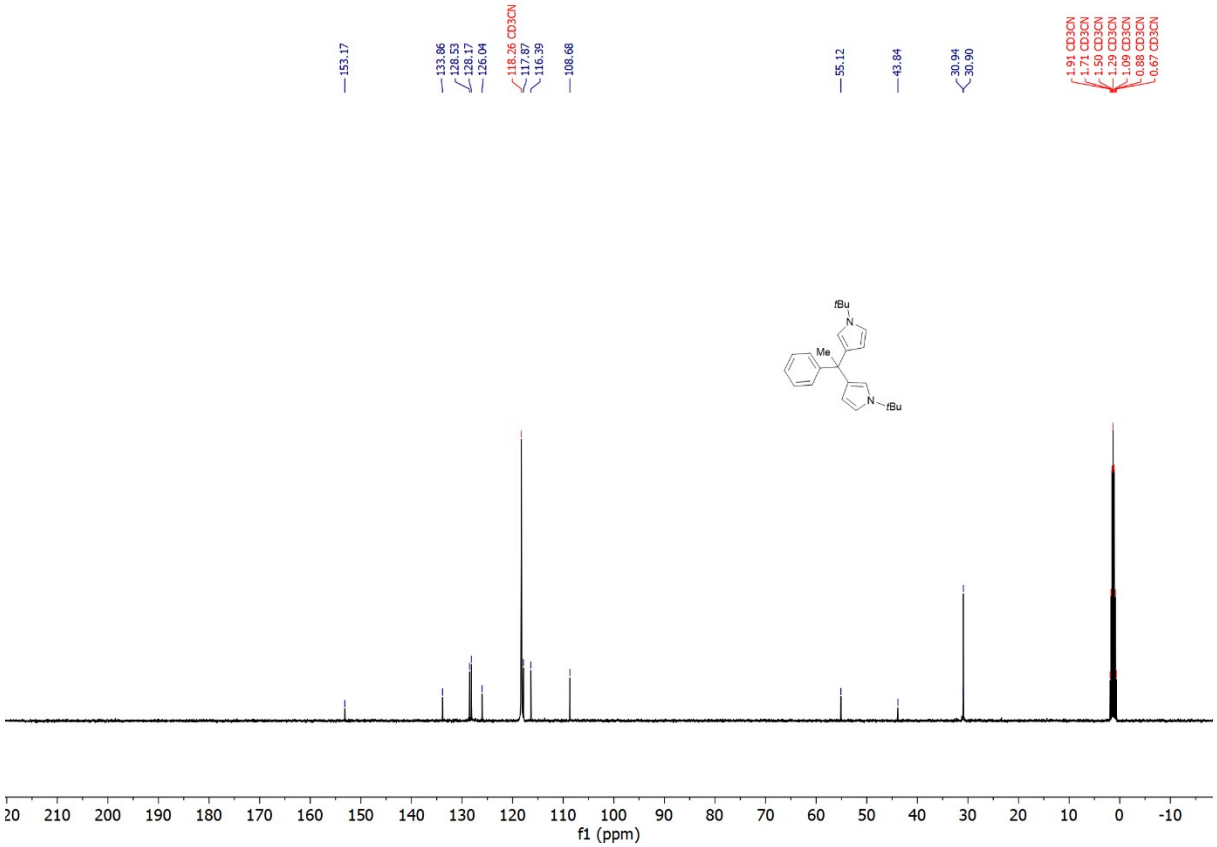
In an inert atmosphere glovebox, a flask (100 mL) was charged with phenylacetylene (0.51 g, 5.0 mmol). Then, 1-(*tert*-butyl)-1*H*-pyrrole (1.54 g, 12.5 mmol) and benzene (15 mL) were added. Finally, a solution of $B(C_6F_5)_3$ (0.255 g, 10 mol%) in 10 mL benzene was added to the mixture under stirring. The reaction mixture was stirred at room temperature for 12 h. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product as a white solid (1.634 g, 94% yield).

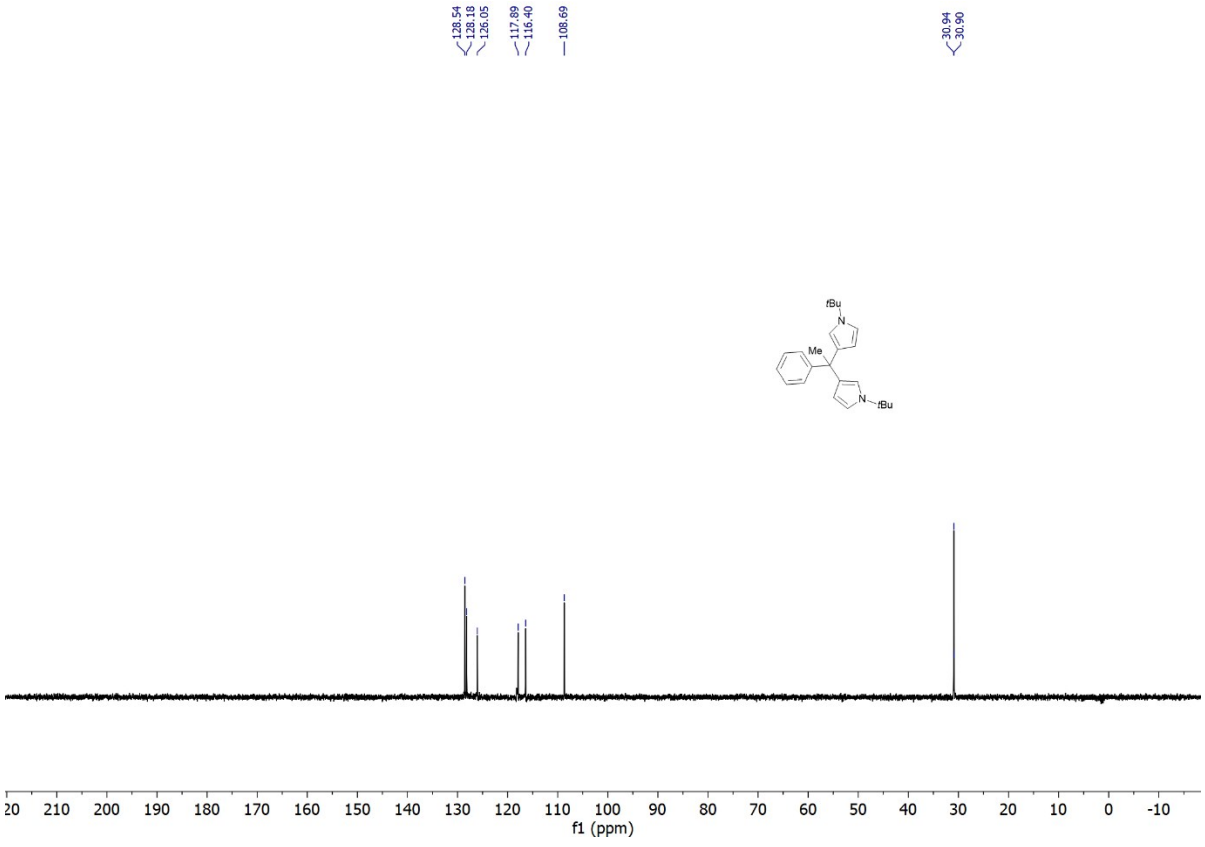
^{1}H NMR (400 MHz, CD_3CN), δ: 7.26 – 7.18 (m, 4H), 7.13 – 7.09 (m, 1H), 6.76 – 6.74 (m, 2H), 6.55 – 6.54 (m, 2H), 5.83 – 5.81 (m, 2H), 1.87 (s, 3H), 1.46 (s, 18H).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 153.17, 133.86, 128.53, 128.17, 126.04, 117.87, 116.39, 108.68, 55.12, 43.84, 30.94, 30.90.

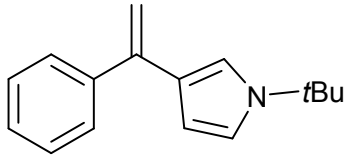
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 128.54, 128.18, 126.05, 117.89, 116.40, 108.69, 30.94, 30.90.




153.17
133.86
128.53
128.17
126.04
118.26 CD3CN
117.87
116.39
108.68
55.12
43.84
30.94
30.90
1.91 CD3CN
1.71 CD3CN
1.50 CD3CN
1.29 CD3CN
1.09 CD3CN
0.88 CD3CN
0.67 CD3CN
tBu
N
Me
N
tBu
f1 (ppm)


128.54
128.18
126.05
117.89
116.40
108.69
30.94
30.90
tBu
N
Me
N
tBu
f1 (ppm)

Preparation of 1-(*tert*-butyl)-3-(1-phenylvinyl)-1*H*-pyrrole (1a)



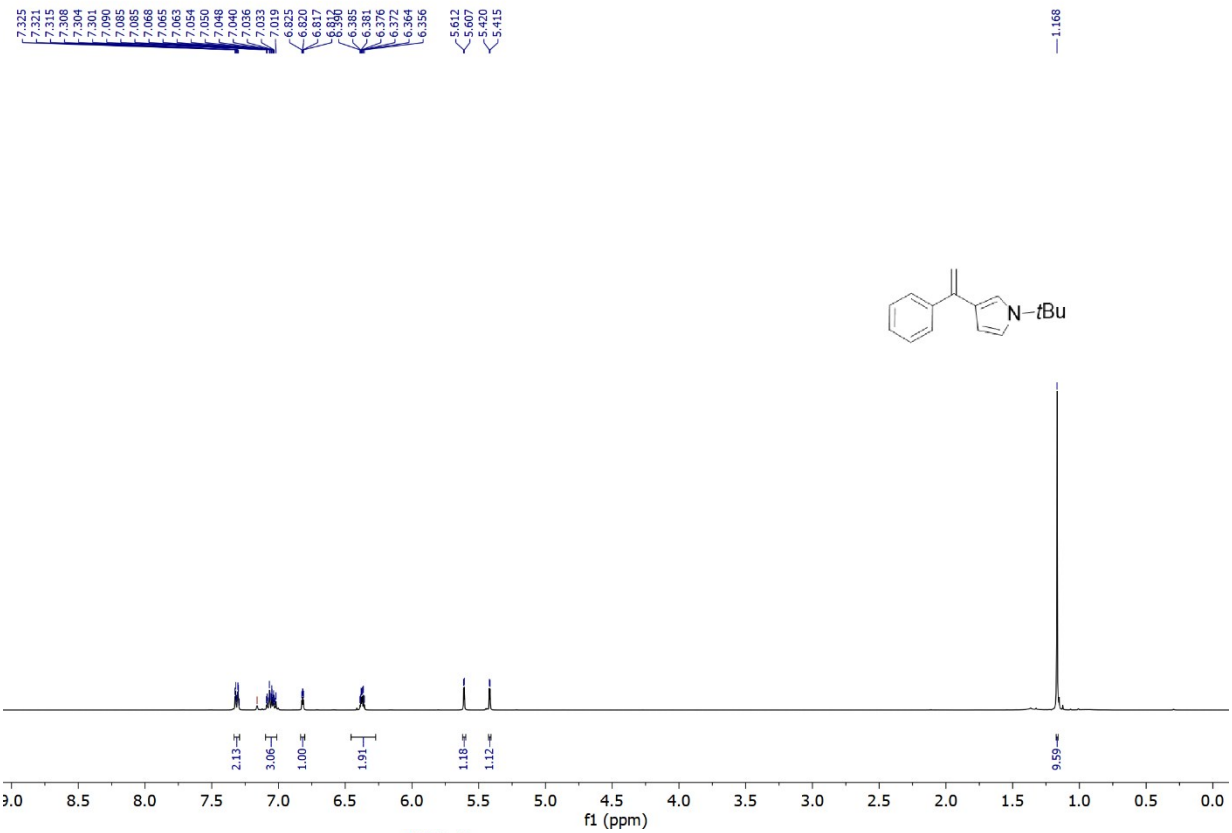
To a solution of phenylacetylene (10.2 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $InCl_3$ (2.2 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was stirred after 12 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/DCM= 10/1) on silica gel to afford the product **1a** as a colorless oil (7.2 mg, 32% yield).

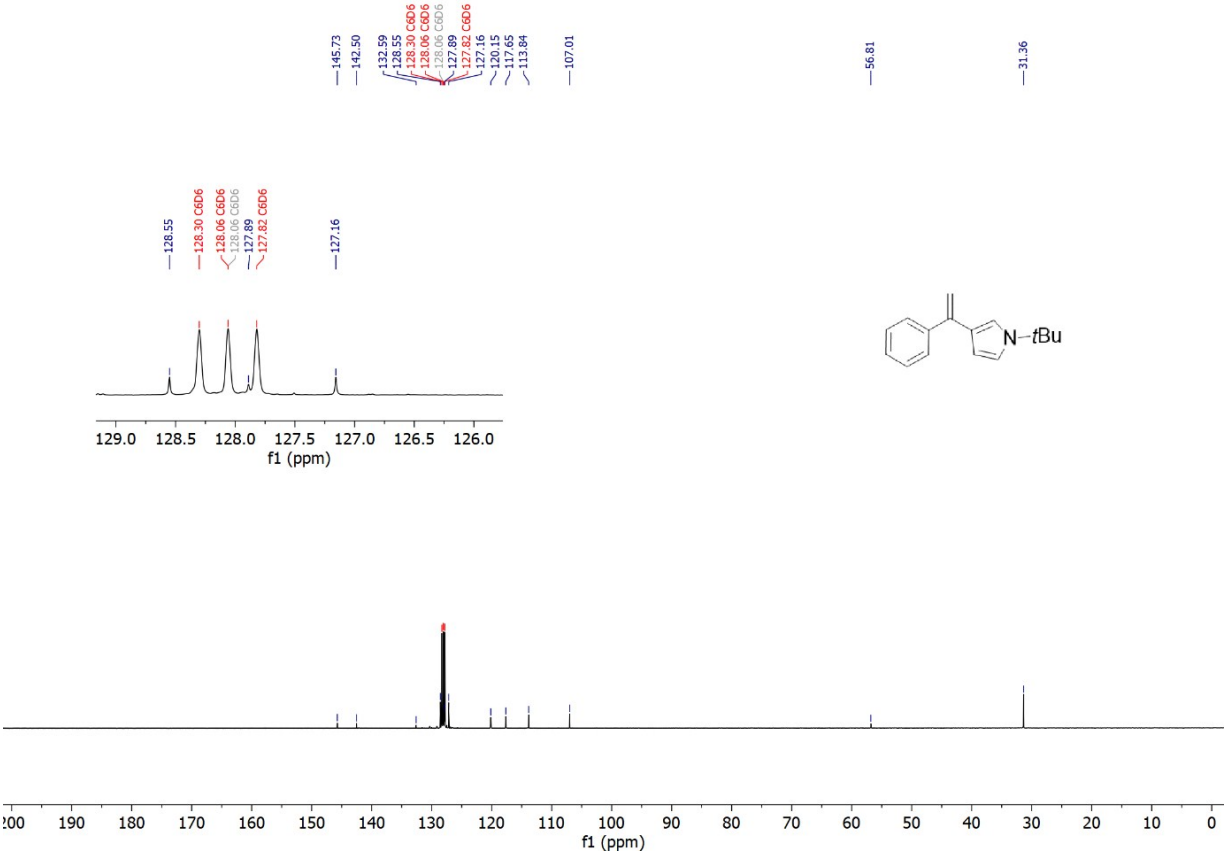
^{1}H NMR (400 MHz, C_6D_6), δ: 7.33 – 7.30 (m, 2H), 7.07 – 7.20 (m, 3H), 6.82 (dd, *J* = 2.8, 2.0 Hz, 1H), 6.40 – 6.35 (m, 2H), 5.61 (d, *J* = 2.0 Hz, 1H), 5.42 (d, *J* = 2.0 Hz, 1H), 1.17 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6), δ: 145.73, 142.50, 132.59, 128.55, 127.89, 127.16, 120.15, 117.65, 113.84, 107.01, 56.81, 31.36.

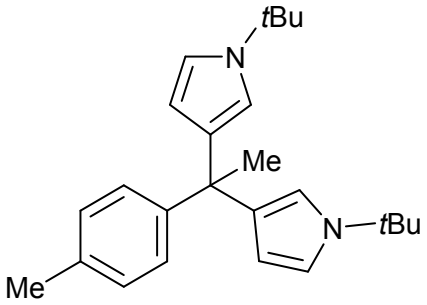
MS (DART Ionization, *m/z*): 226.16 ([M+H]$^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{16}H_{20}N^+$, ([M+H]$^+$): 226.15903; Found: 226.15910.


7.325
7.321
7.315
7.308
7.304
7.301
7.090
7.085
7.085
7.068
7.065
7.063
7.054
7.050
7.048
7.040
7.036
7.033
7.019
6.825
6.820
6.817
6.390
6.385
6.381
6.376
6.372
6.364
6.356
5.612
5.607
5.420
5.415
1.168
N–tBu
2.13
3.06
1.00
1.91
1.18
1.12
9.59
f1 (ppm)


145.73
142.50
132.59
128.55
128.30 C6D6
128.06 C6D6
128.06 C6D6
127.89
127.82 C6D6
127.16
120.15
117.65
113.84
107.01
56.81
31.36
128.55
128.30 C6D6
128.06 C6D6
128.06 C6D6
127.89
127.82 C6D6
127.16
N–tBu
f1 (ppm)

Preparation of 3,3'-(1-(*p*-tolyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (2)



To a solution of 4-ethynyltoluene (11.6 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **2** as a colourless oil (27.5 mg, 76% yield).

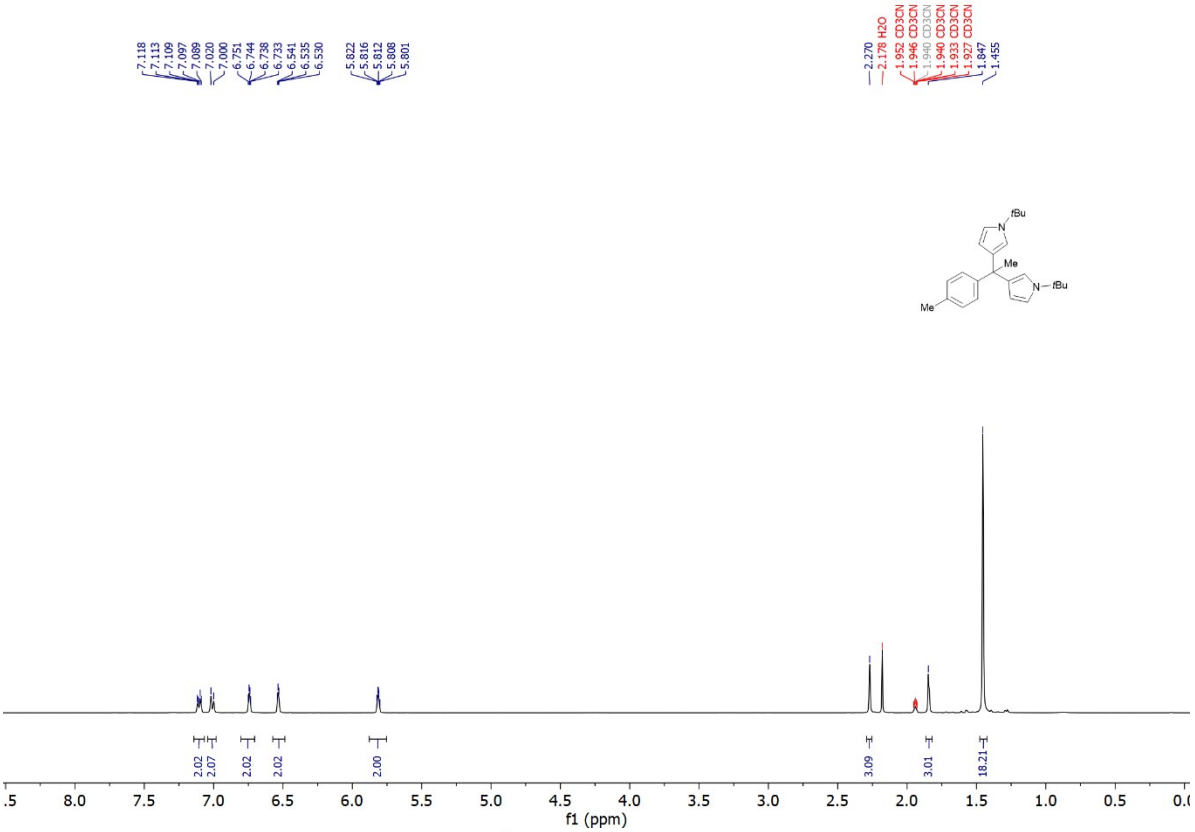
^{1}H NMR (400 MHz, CD_3CN), δ: 7.12 – 7.00 (m, 2H), 7.01 (d, *J* = 3.6, 2H), 6.74 (t, *J* = 2.4 Hz, 2H), 6.54 (t, *J* = 2.4 Hz, 2H), 5.83 – 5.80 (m, 2H), 2.27 (s, 3H), 1.85 (s, 3H), 1.46 (s, 18H).

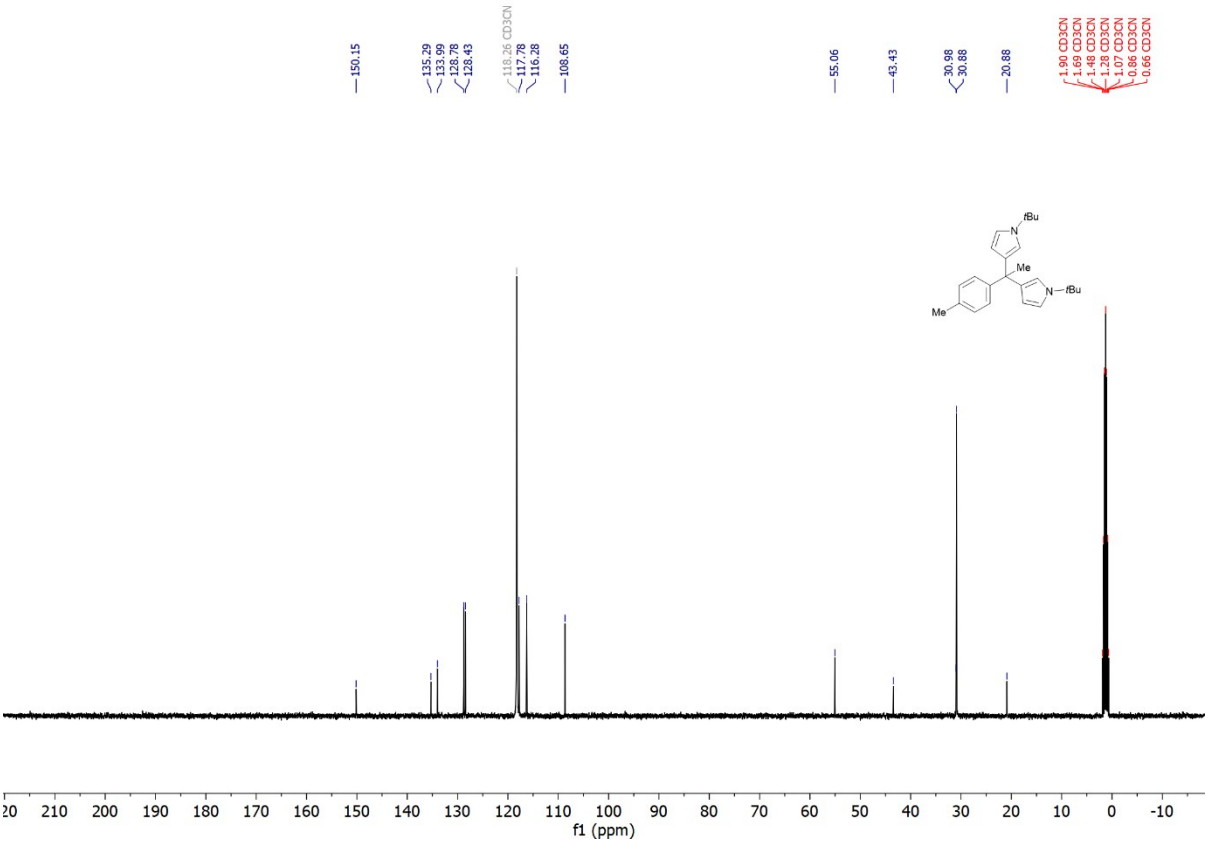
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 150.15, 135.29, 133.99, 128.78, 128.43, 117.78, 116.28, 108.65, 55.06, 43.43, 30.98, 30.88, 20.88.

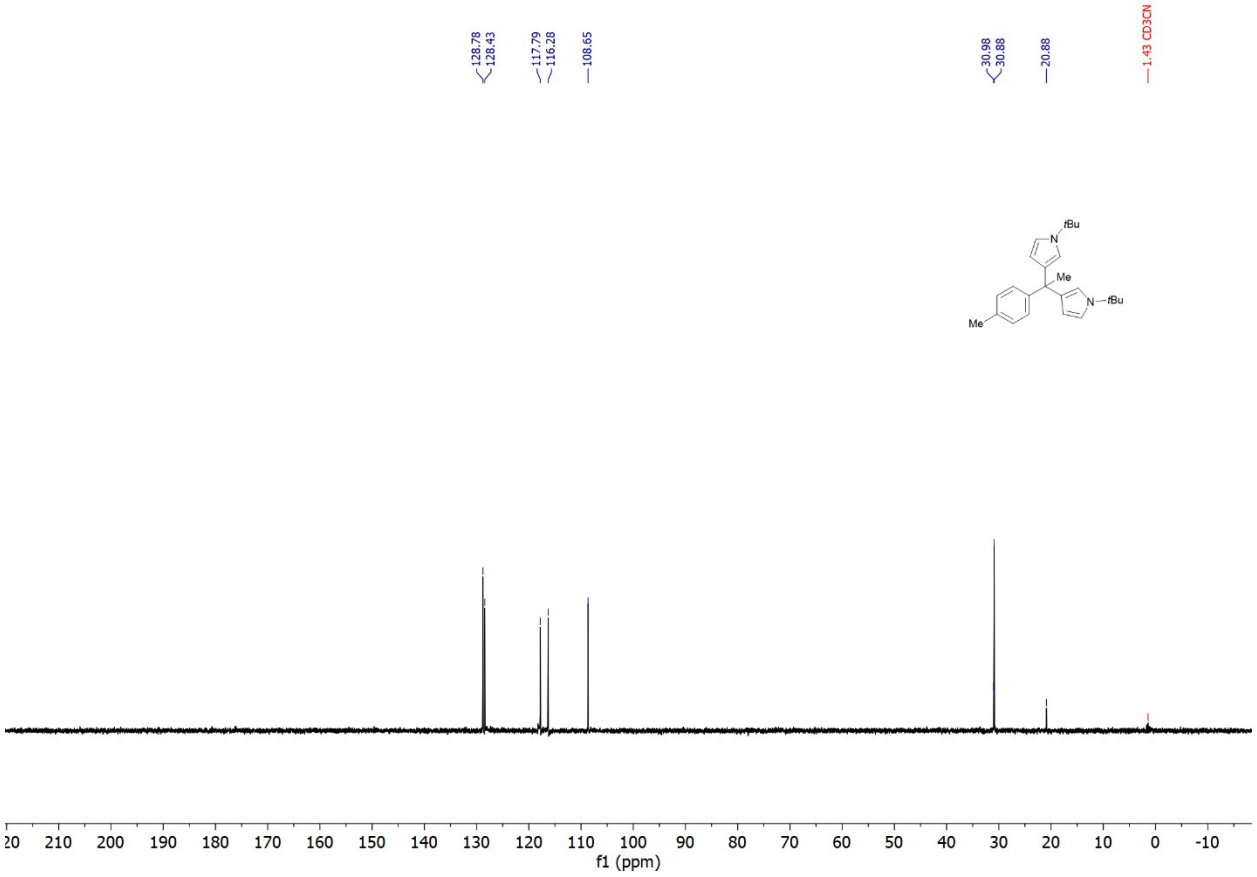
DEPT^{135} NMR (100 MHz, CD3CN) δ: 128.78, 128.43, 117.79, 116.28, 108.65, 30.98, 30.88, 20.88.

MS (DART Ionization, *m/z*): 363.3 ([M+H]$^+$).

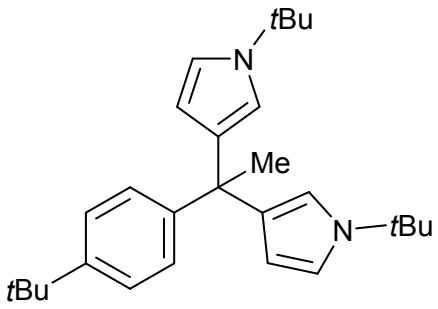
HRMS (DART Ionization, *m/z*): Calcd. for $C_{25}H_{35}N_2^+$, ([M+H]$^+$): 363.28002; Found: 363.27968.


7.118
7.113
7.109
7.097
7.089
7.020
7.000
6.751
6.744
6.738
6.733
6.541
6.535
6.530
5.822
5.816
5.812
5.808
5.801
2.270
2.178 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.940 CD3CN
1.933 CD3CN
1.927 CD3CN
1.847
1.455
tBu
Me
N
tBu
Me
2.02
2.07
2.02
2.02
2.00
3.09
3.01
18.21
f1 (ppm)


150.15
135.29
133.99
128.78
128.43
118.26 CD3CN
117.78
116.28
108.65
55.06
43.43
30.98
30.88
20.88
1.90 CD3CN
1.69 CD3CN
1.48 CD3CN
1.28 CD3CN
1.07 CD3CN
0.86 CD3CN
0.66 CD3CN
tBu
Me
N
tBu
Me
f1 (ppm)


128.78
128.43
117.79
116.28
108.65
30.98
30.88
20.88
1.43 CD3CN
tBu
N
Me
N
tBu
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Preparation of 3,3'-(1-(4-(*tert*-butyl)phenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (3)



To a solution of 4-*tert*-butylphenylacetylene (15.8 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **3** as a white solid (35.0 mg, 86% yield).

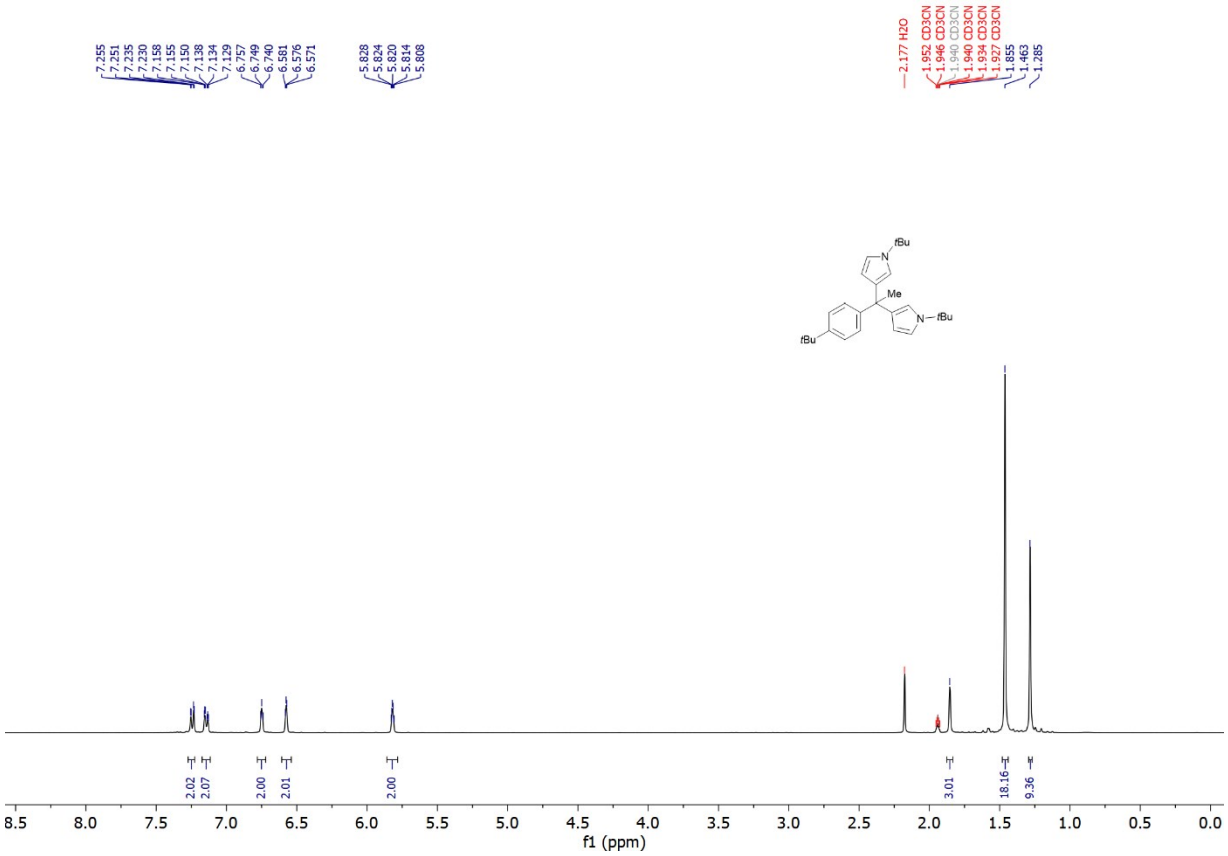
^{1}H NMR (400 MHz, CD_3CN), δ: 7.26 – 7.23 (m, 2H), 7.16 – 7.12 (m, 2H), 6.76 (t, *J* = 3.2 Hz, 2H), 6.54 (t, *J* = 2.0 Hz, 2H), 5.83 – 5.80 (m, 2H), 1.86 (s, 3H), 1.46 (s, 18H), 1.29 (s, 9H).

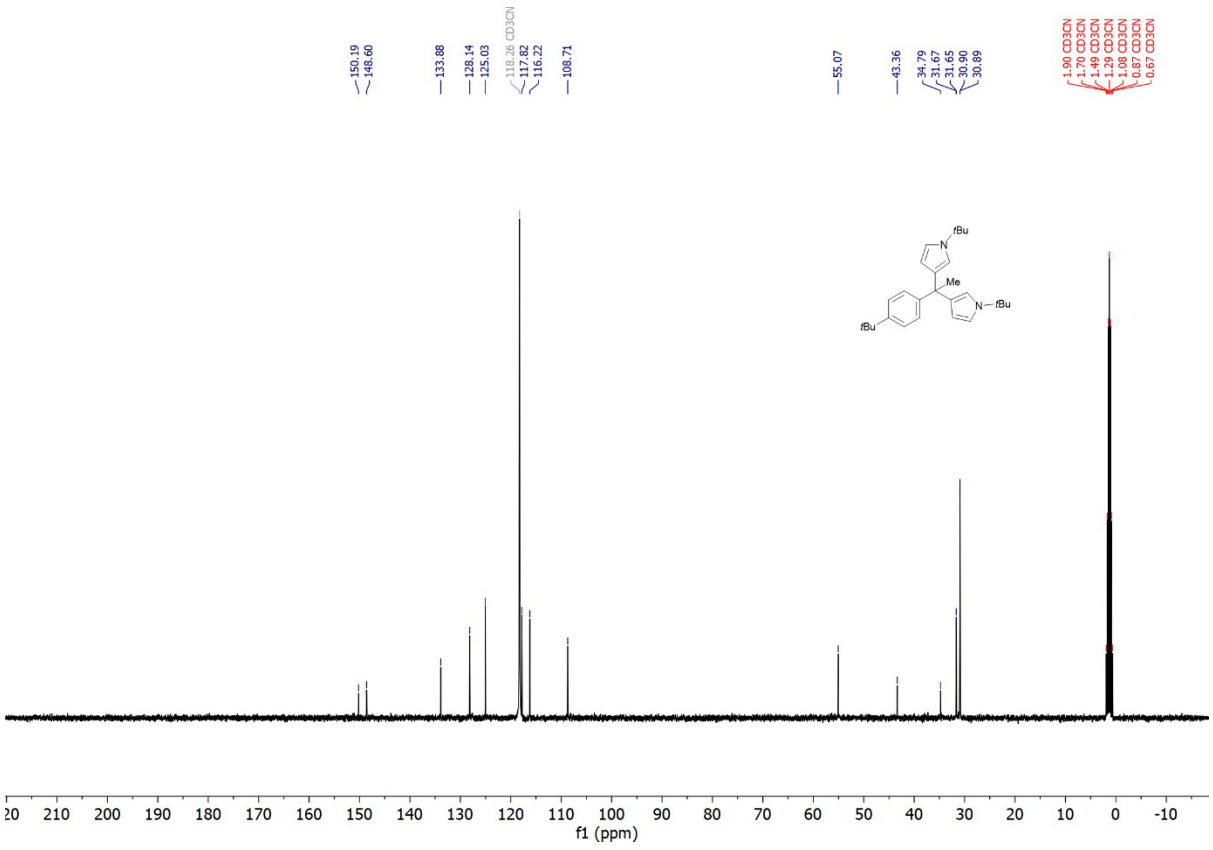
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 150.19, 148.60, 133.88, 128.14, 125.03, 117.82, 116.22, 108.71, 55.07, 43.36, 34.79, 31.67, 31.65, 30.90, 30.89.

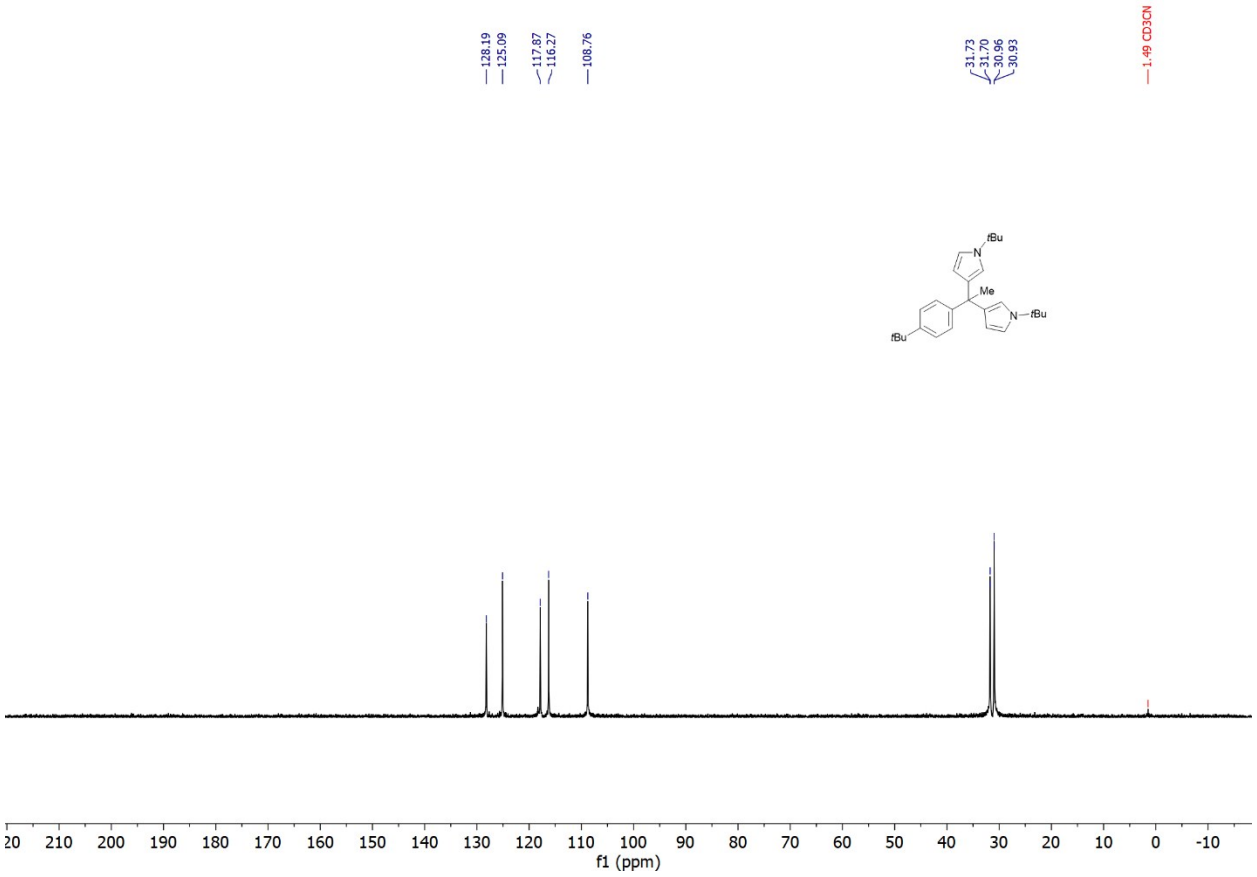
DEPT^{135} NMR (100 MHz, CD3CN) δ: 128.19, 125.09, 117.87, 116.27, 108.76, 31.73, 31.70, 30.96, 30.93.

MS (DART Ionization, *m/z*): 405.3 ([M+H]$^+$).

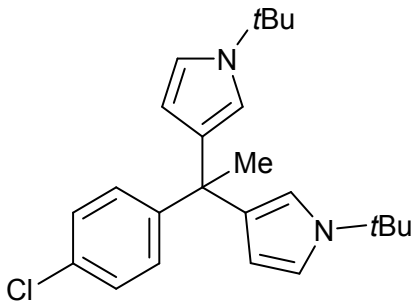
HRMS (DART Ionization, *m/z*): Calcd. for $C_{28}H_{41}N_2^+$, ([M+H]$^+$): 405.32697; Found: 405.32614.


7.255
7.251
7.235
7.230
7.158
7.155
7.150
7.138
7.134
7.129
6.757
6.749
6.740
6.581
6.576
6.571
5.628
5.624
5.620
5.814
5.808
2.177 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.940 CD3CN
1.934 CD3CN
1.927 CD3CN
1.855
1.463
1.285
tBu
N
Me
N
tBu
tBu
2.02
2.07
2.00
2.01
2.00
3.01
18.16
9.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.19
148.60
133.88
128.14
125.03
118.26 CD3CN
117.82
116.22
108.71
55.07
43.36
34.79
31.67
31.65
30.90
30.89
1.90 CD3CN
1.70 CD3CN
1.49 CD3CN
1.29 CD3CN
1.08 CD3CN
0.87 CD3CN
0.67 CD3CN
tBu
N
Me
N
tBu
tBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


128.19
125.09
117.87
116.27
108.76
31.73
31.70
30.96
30.93
1.49 CD3CN
tBu
N
Me
N
tBu
tBu
f1 (ppm)

Preparation of 3,3'-(1-(4-chlorophenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (4)



To a solution of 1-chloro-4-ethynylbenzene (13.6 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **4** as a white solid (34.0 mg, 89% yield).

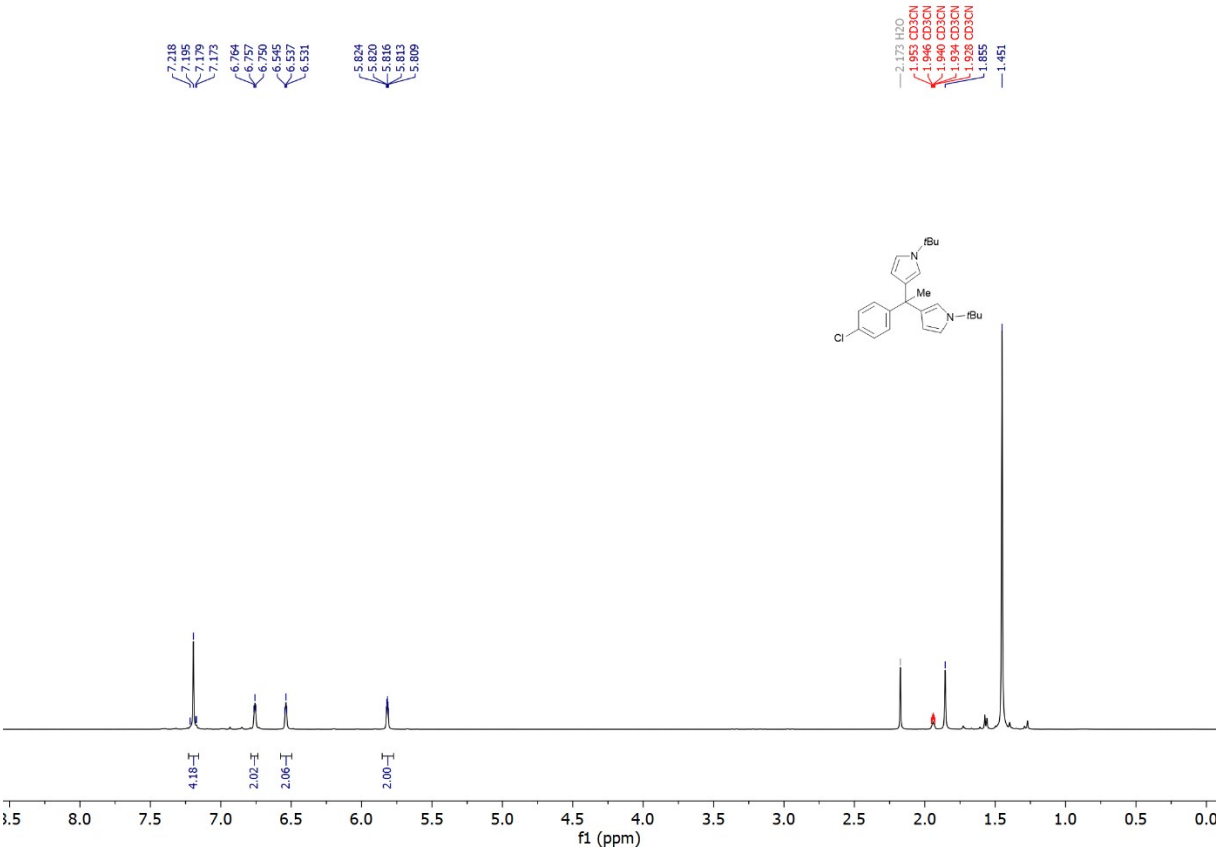
^{1}H NMR (400 MHz, CD_3CN), δ: 7.21 – 7.17 (m, 4H), 6.76 (t, *J* = 2.8 Hz, 2H), 6.54 (t, *J* = 2.4 Hz, 2H), 5.84 – 5.80 (m, 2H), 1.86 (s, 3H), 1.45 (s, 18H).

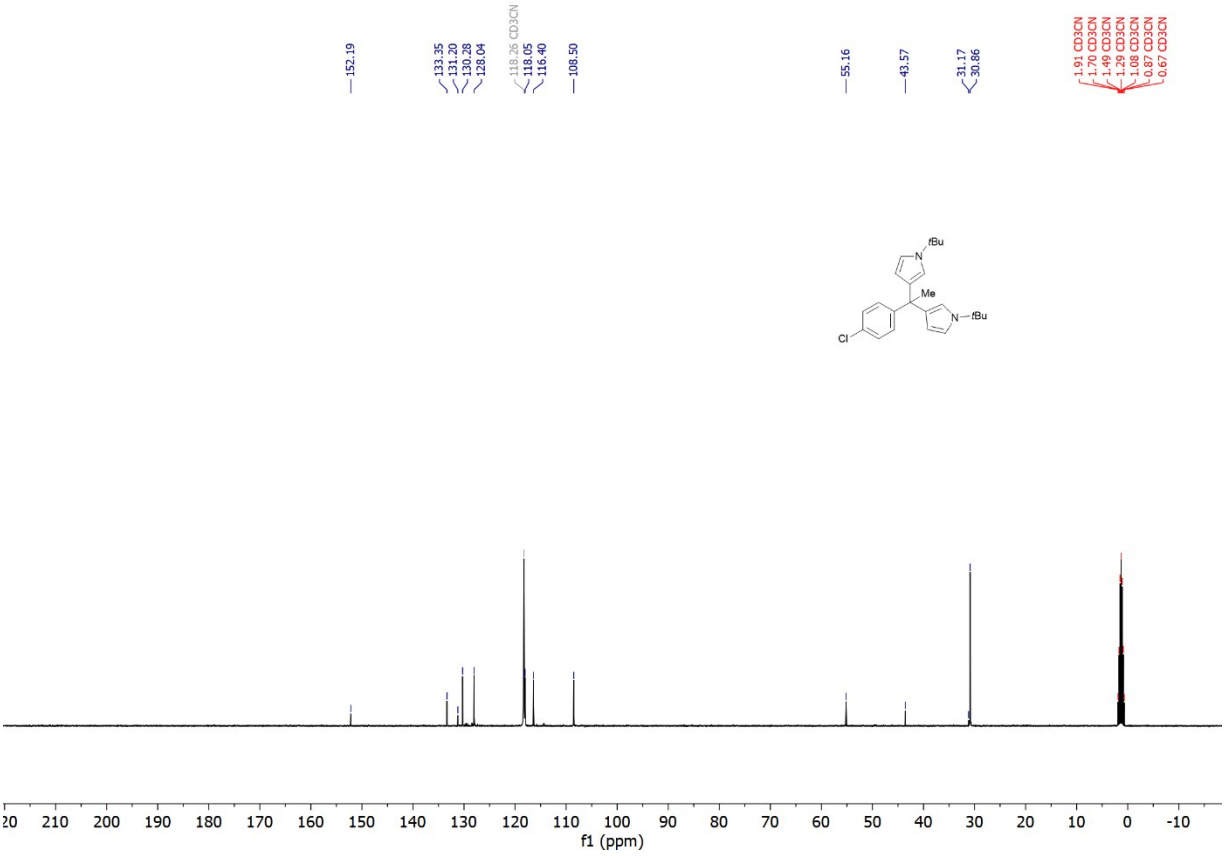
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 152.19, 133.35, 131.20, 130.28, 128.04, 118.05, 116.40, 108.50, 55.16, 43.57, 31.17, 30.86.

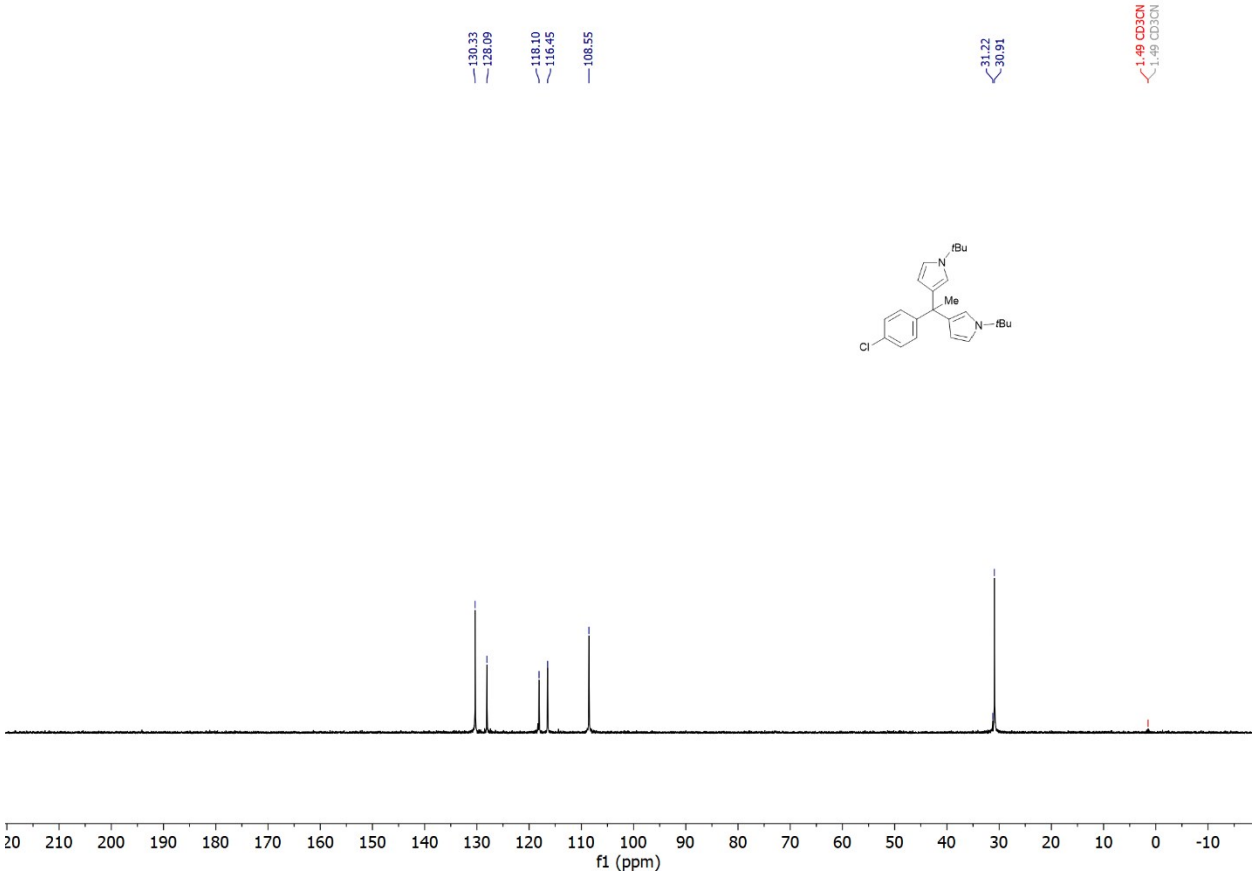
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 130.33, 128.09, 118.10, 116.45, 108.55, 31.22, 30.91.

MS (DART Ionization, *m/z*): 383.2 ([M+H]$^+$).

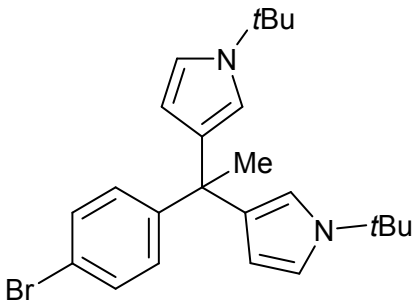
HRMS (DART Ionization, *m/z*): Calcd. for $C_{24}H_{32}ClN_2^+$, ([M+H]$^+$): 383.22540; Found: 383.22559.


7.218
7.195
7.179
7.173
6.764
6.757
6.750
6.545
6.537
6.531
5.824
5.820
5.816
5.813
5.809
2.173 H2O
1.953 CD3CN
1.946 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.855
1.451
tBu
N
Me
N
tBu
Cl
4.18
2.02
2.06
2.00
f1 (ppm)


152.19
133.35
131.20
130.28
128.04
118.26 CD3CN
118.05
116.40
108.50
55.16
43.57
31.17
30.86
1.91 CD3CN
1.70 CD3CN
1.49 CD3CN
1.29 CD3CN
1.08 CD3CN
0.87 CD3CN
0.67 CD3CN
tBu
N
Me
N
tBu
Cl
f1 (ppm)


130.33
128.09
118.10
116.45
108.55
31.22
30.91
1.49 CD3CN
1.49 CD3CN
tBu
N
Me
N
tBu
Cl
f1 (ppm)

Preparation of 3,3'-(1-(4-bromophenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (5)



To a solution of 1-bromo-4-ethynylbenzene (18.1 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **5** as a white solid (38.0 mg, 89% yield).

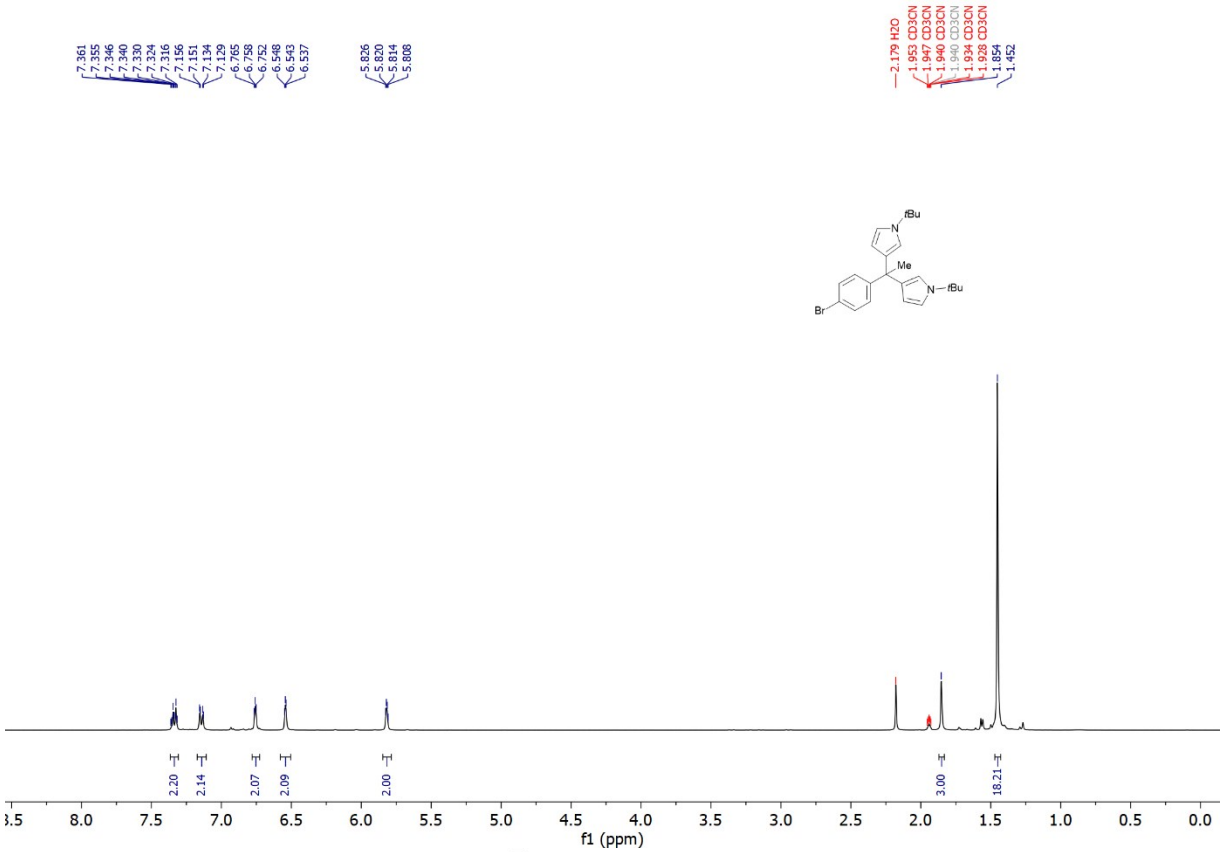
^{1}H NMR (400 MHz, CD_3CN), δ: 7.36 – 7.31 (m, 2H), 7.16 – 7.12 (m, 2H), 6.76 (t, *J* = 2.4 Hz, 2H), 6.54 (t, *J* = 2.0 Hz, 2H), 5.84 – 5.80 (m, 2H), 1.85 (s, 3H), 1.45 (s, 18H).

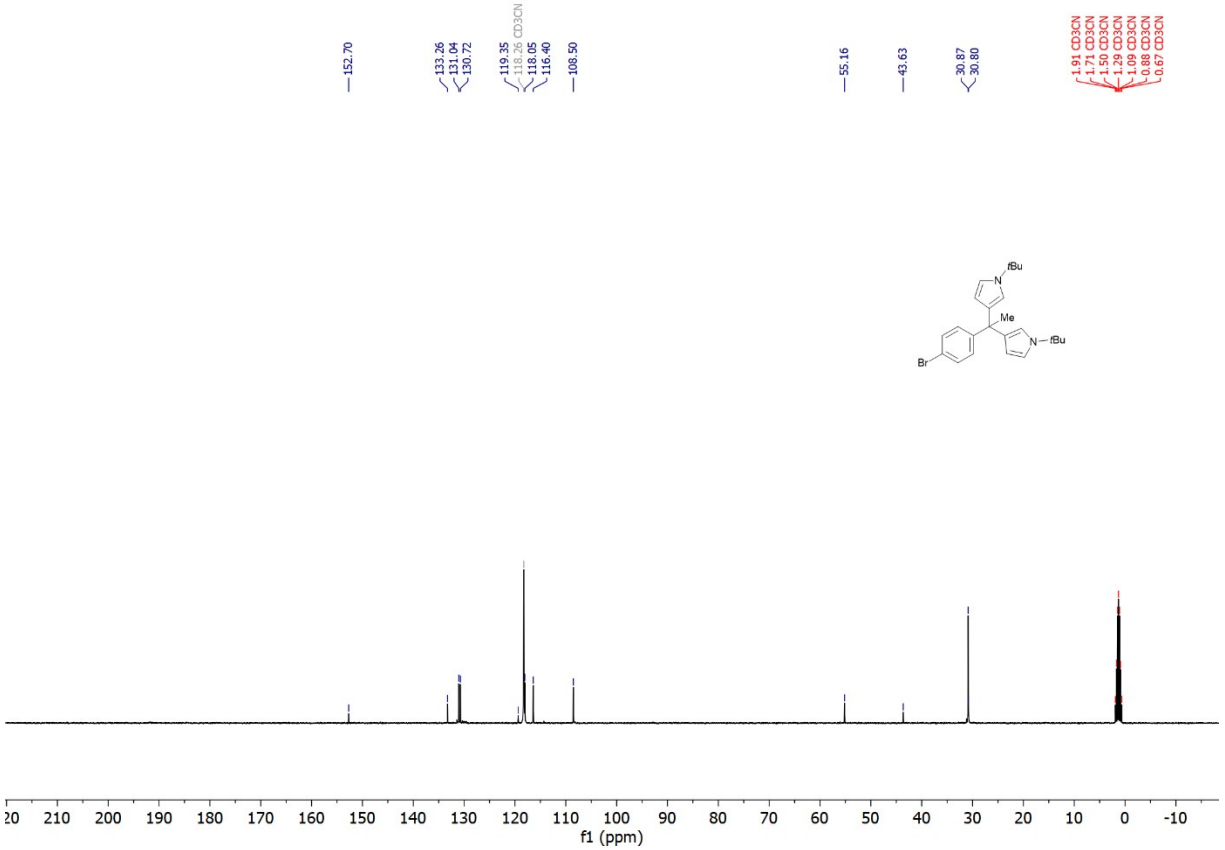
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 152.70, 133.26, 131.04, 130.72, 119.35, 118.05, 116.40, 108.50, 55.16, 43.63, 30.87, 30.80.

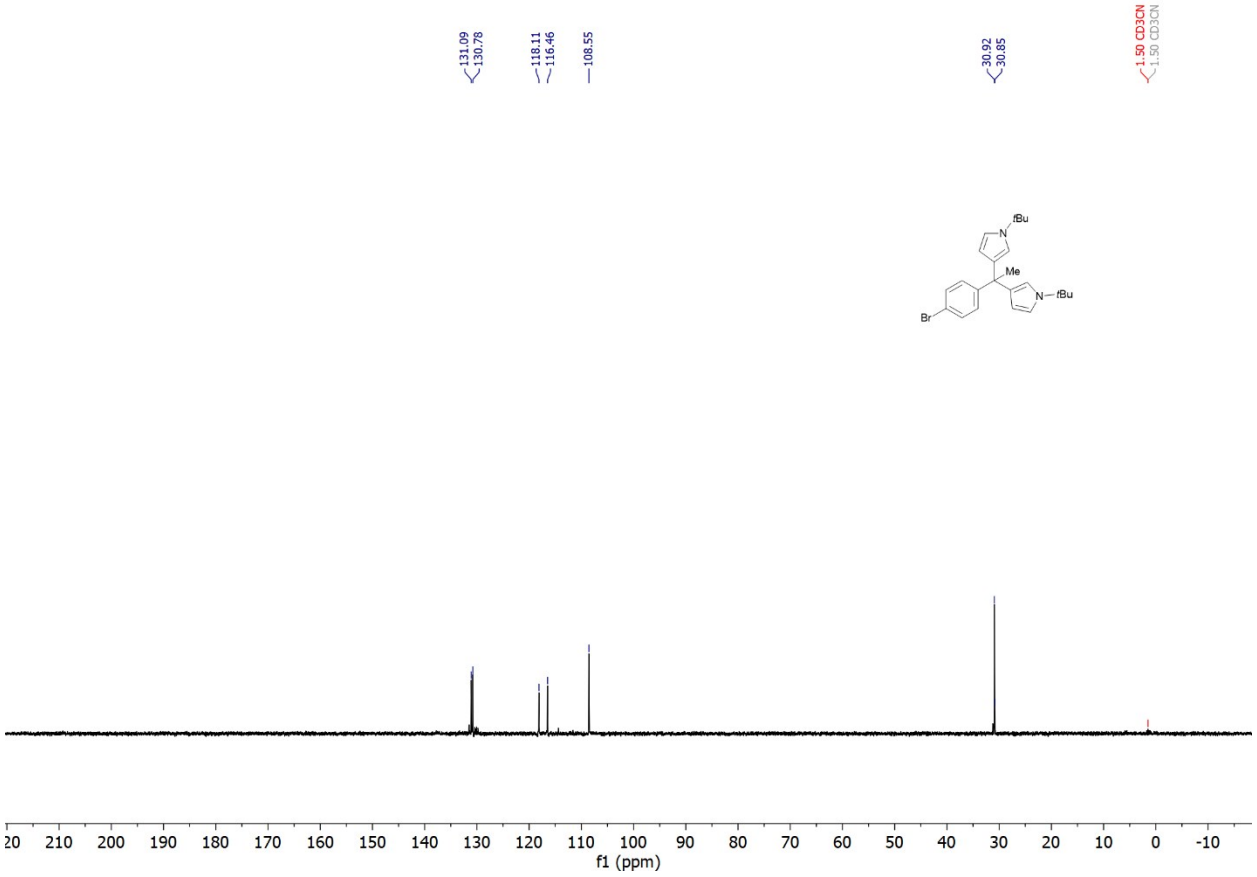
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 131.09, 130.78, 118.11, 116.46, 108.55, 30.92, 30.85.

MS (DART Ionization, *m/z*): 427.2 ([M+H]$^+$).

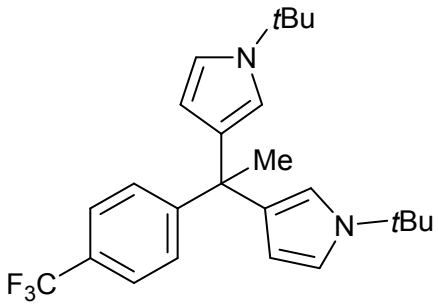
HRMS (DART Ionization, *m/z*): Calcd. for $C_{24}H_{32}BrN_2^+$, ([M+H]$^+$): 427.17489; Found: 427.17419.


7.361
7.355
7.346
7.340
7.330
7.324
7.316
7.156
7.151
7.134
7.129
6.765
6.758
6.752
6.546
6.543
6.537
5.826
5.820
5.814
5.808
2.179 H2O
1.953 CD3CN
1.947 CD3CN
1.940 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.854
1.452
fBu
Me
Br
2.20
2.14
2.07
2.09
2.00
3.00
18.21
f1 (ppm)


152.70
133.26
131.04
130.72
119.35
118.26 CD3CN
118.05
116.40
108.50
55.16
43.63
30.87
30.80
1.91 CD3CN
1.71 CD3CN
1.50 CD3CN
1.29 CD3CN
1.09 CD3CN
0.88 CD3CN
0.67 CD3CN
fBu
Me
Br
f1 (ppm)


131.09
130.78
118.11
116.46
108.55
30.92
30.85
1.50 CD3CN
1.50 CD3CN
tBu
N
Me
N
tBu
Br
f1 (ppm)

Preparation of 3,3'-(1-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (6)



To a solution of 1-trifluoromethyl-4-ethynylbenzene (18.1 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 6 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **6** as a white solid (37.0 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.51 (d, J =8.4 Hz, 2H), 7.39 (d, J =8.0 Hz, 2H), 6.77 (t, *J* = 2.8 Hz, 2H), 6.57 (t, *J* = 2.4 Hz, 2H), 6.45 (dd, *J* = 2.8, 2.0 Hz, 2H), 1.89 (s, 3H), 1.46 (s, 18H).

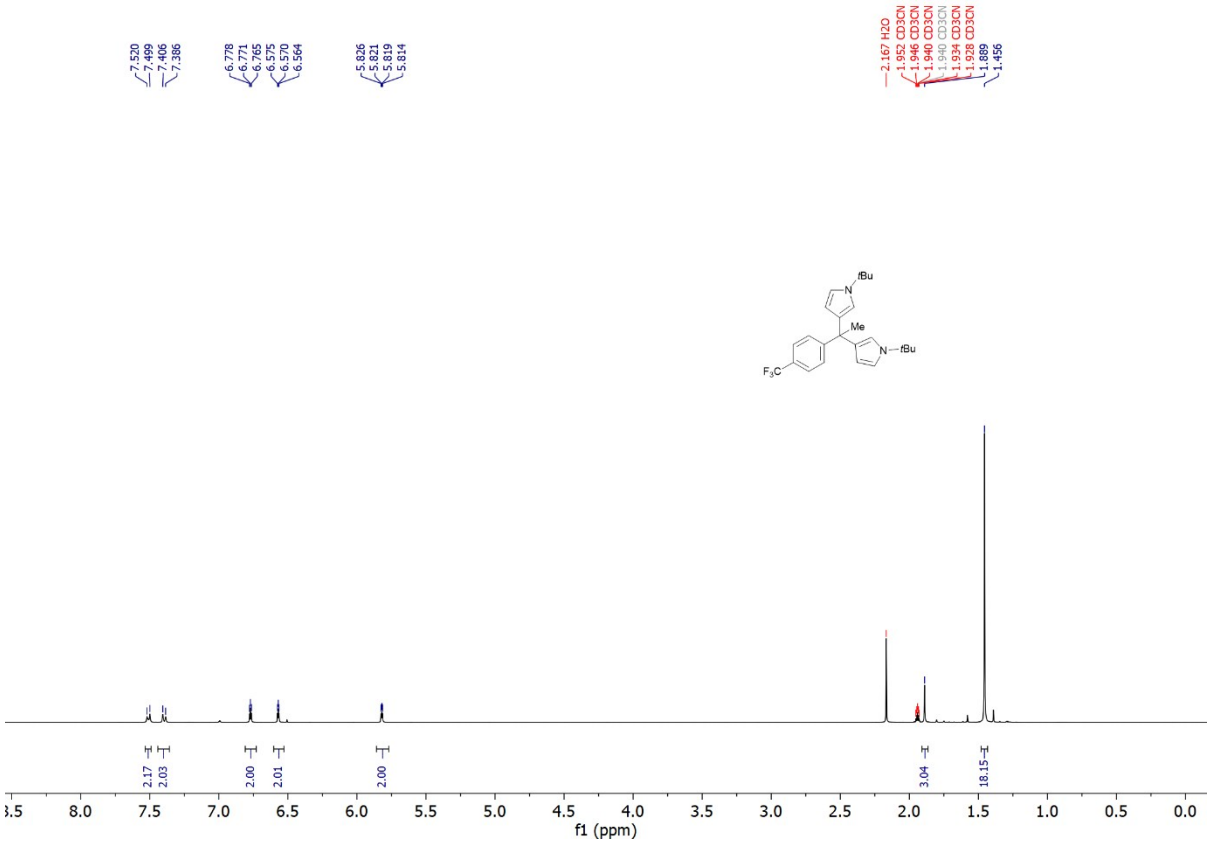
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 157.90 (d, *J* = 1.1 Hz, 2C), 132.96, 129.09, 128.53, 127.41, 125.04 (dd, *J* = 7.8, 4.0 Hz, 1C), 118.15, 116.47, 108.47, 55.21, 44.06, 30.83, 30.66.

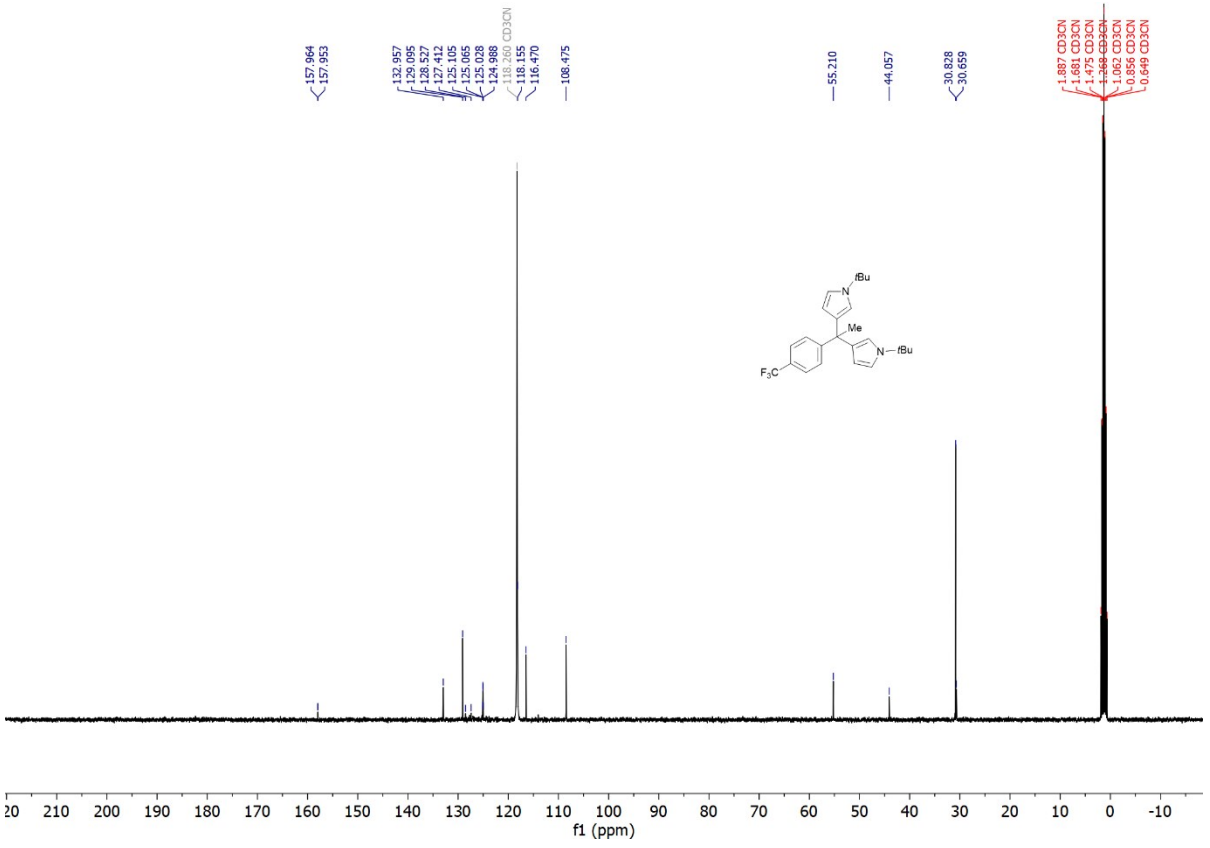
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 129.15, 125.11 (dd, *J* = 7.8, 4.0 Hz, 1C), 118.21, 116.52, 108.53, 30.88, 30.71.

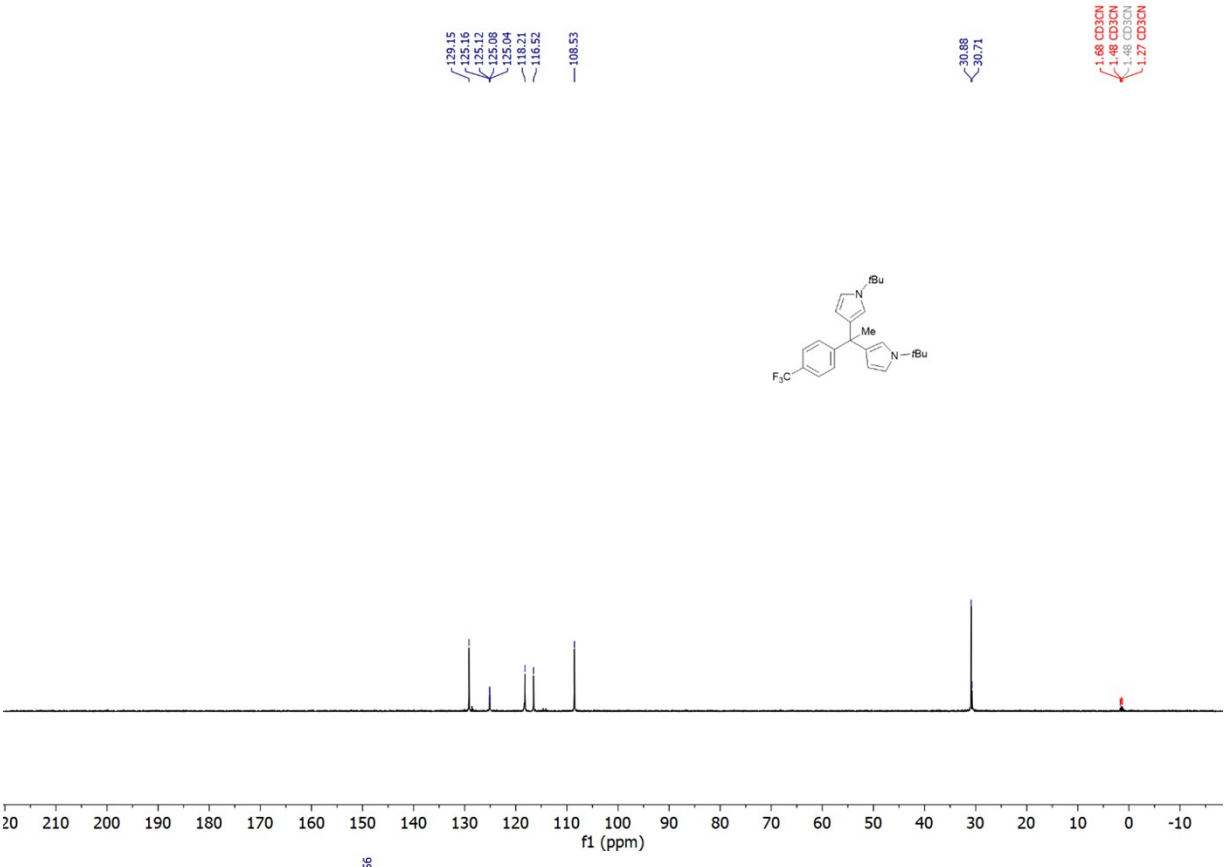
^{19}F{^{1}H} NMR (377 MHz, CD_3CN) δ: -62.56.

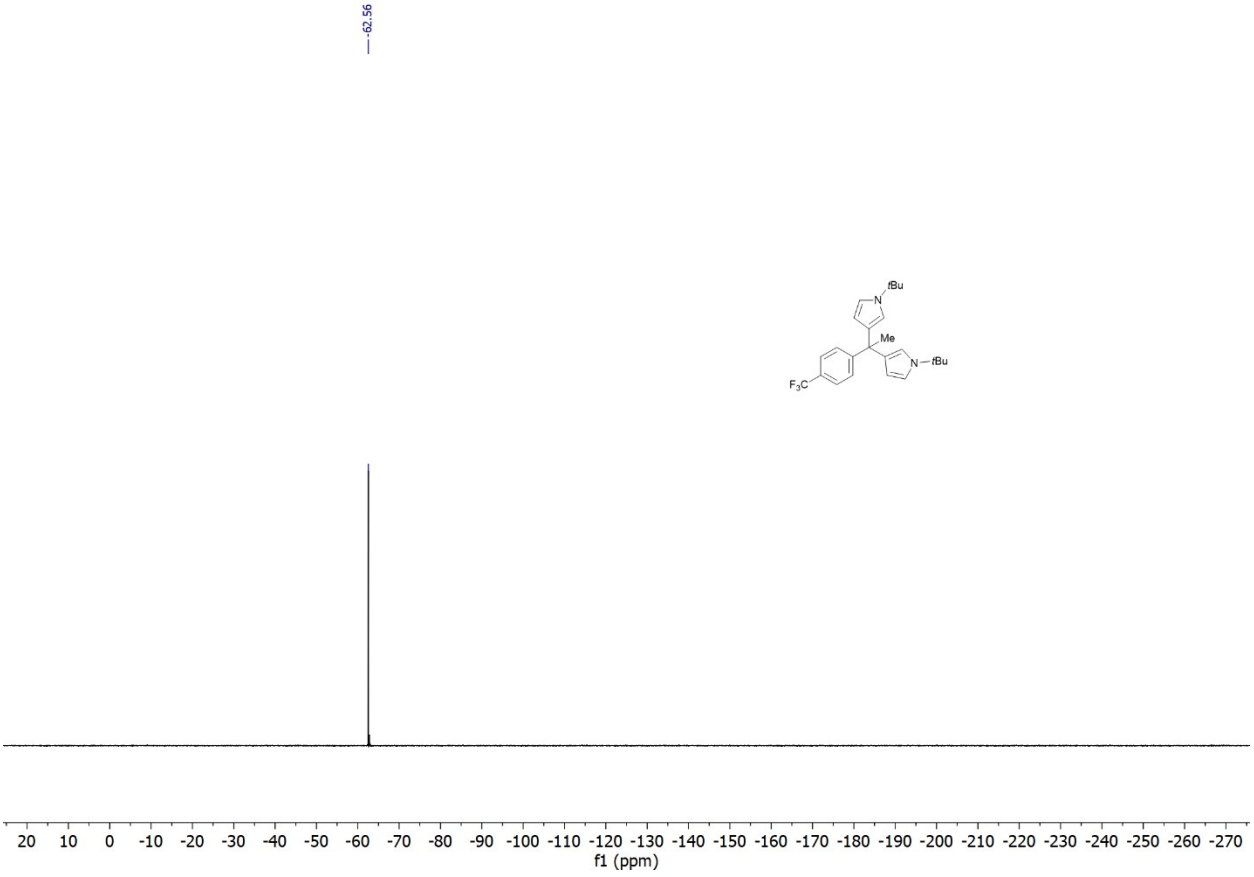
MS (DART Ionization, *m/z*): 417.2 ([M+H]$^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{25}H_{32}F_3N_2^+$, ([M+H]$^+$): 417.25176; Found: 417.25110.

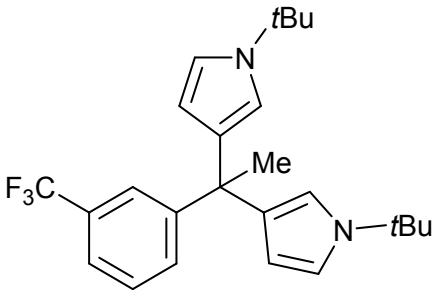

7.520
7.499
7.406
7.386
6.778
6.771
6.765
6.575
6.570
6.564
5.826
5.821
5.819
5.814
2.167 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.889
1.456
tBu
N
Me
N
tBu
F3C
2.17
2.03
2.00
2.01
2.00
3.04
18.15
f1 (ppm)


157.964
157.953
132.957
129.095
128.527
127.412
125.105
125.065
125.028
124.988
118.260 CD3CN
118.155
116.470
108.475
55.210
44.057
30.828
30.659
1.887 CD3CN
1.681 CD3CN
1.475 CD3CN
1.062 CD3CN
0.856 CD3CN
0.649 CD3CN
tBu
N
Me
N
tBu
F3C
f1 (ppm)


129.15
125.16
125.12
125.08
125.04
118.21
116.52
108.53
30.88
30.71
1.68 CD3CN
1.48 CD3CN
1.46 CD3CN
1.27 CD3CN
tBu
N
Me
N
tBu
F3C
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.56
tBu
N
Me
N
tBu
F3C
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

Preparation of 3,3'-(1-(3-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (7)



To a solution of 1-trifluoromethyl-3-ethynylbenzene (18.1 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 6 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **7** as a white solid (39.5 mg, 95% yield).

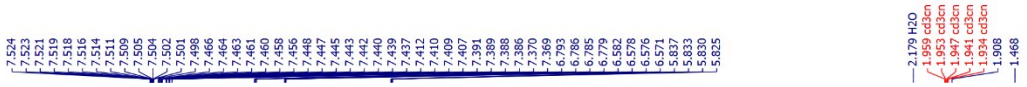
^{1}H NMR (400 MHz, CD_3CN), δ: 7.52 – 7.49 (m, 2H), 7.47 – 7.44 (m, 1H), 7.41 – 7.37 (m, 1H), 6.79 (dd, *J* = 2.8, 2.4 Hz, 2H), 6.58 (dd, *J* = 2.4, 1.6 Hz, 2H), 5.83 (dd, *J* = 2.8, 1.6 Hz, 2H), 1.91 (s, 3H), 1.47 (s, 18H).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 154.67, 133.03, 132.52, 132.50, 129.55, 128.99, 124.95 (dd, *J* = 8.0, 4.0 Hz, 1C), 122.88 (dd, *J* = 8.0, 4.0 Hz, 1C), 118.19, 116.54, 108.45, 55.23, 44.03, 30.84, 30.75.

^{19}F{^{1}H} NMR (377 MHz, CD_3CN) δ: -62.87.

MS (DART Ionization, *m/z*): 417.2 ($[M+H]^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{25}H_{32}F_3N_2^+$, ($[M+H]^+$): 417.25176; Found: 417.25245.


7.524
7.523
7.521
7.519
7.518
7.516
7.514
7.511
7.509
7.505
7.504
7.502
7.501
7.498
7.466
7.464
7.463
7.461
7.460
7.458
7.456
7.448
7.447
7.445
7.443
7.442
7.440
7.439
7.437
7.412
7.410
7.409
7.407
7.391
7.389
7.388
7.386
7.370
7.369
6.793
6.786
6.785
6.779
6.582
6.578
6.576
6.571
5.837
5.833
5.830
5.825
2.179 H2O
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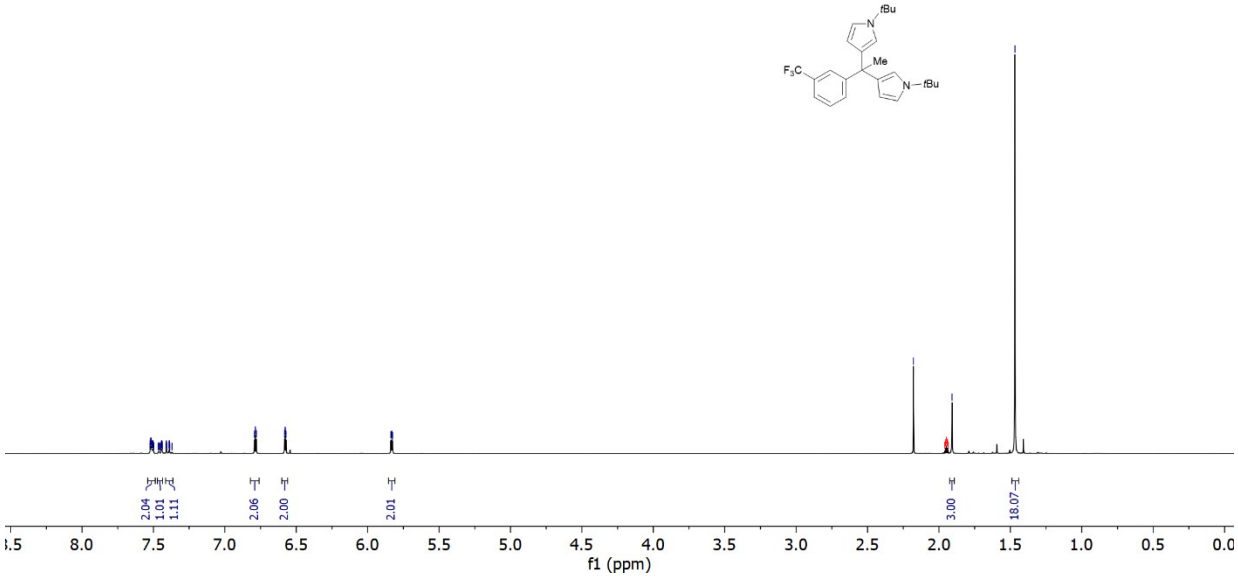
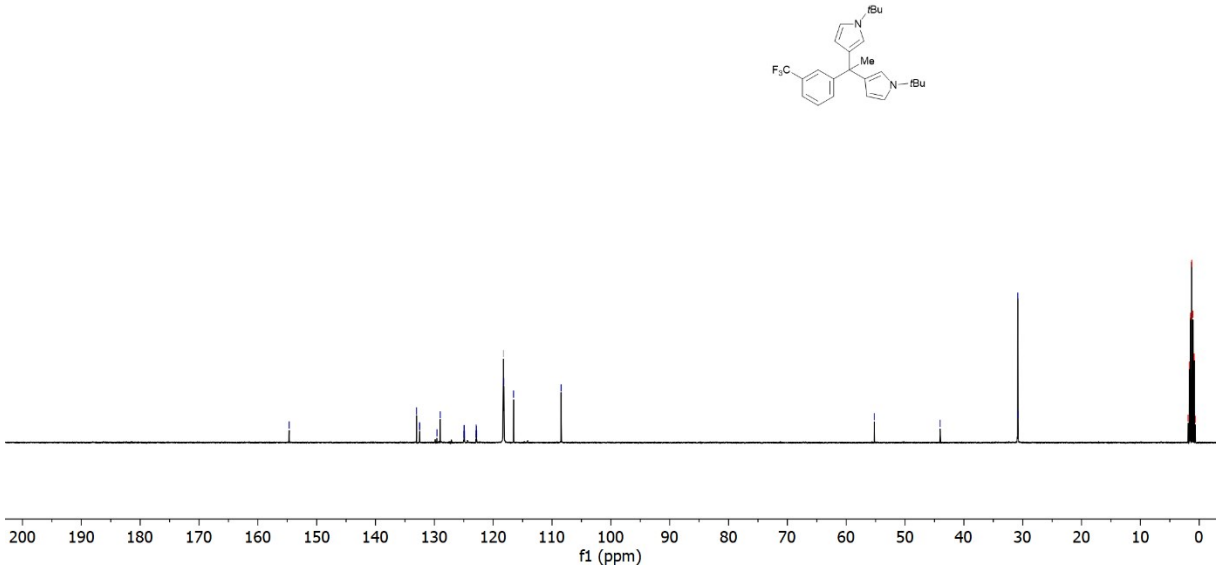
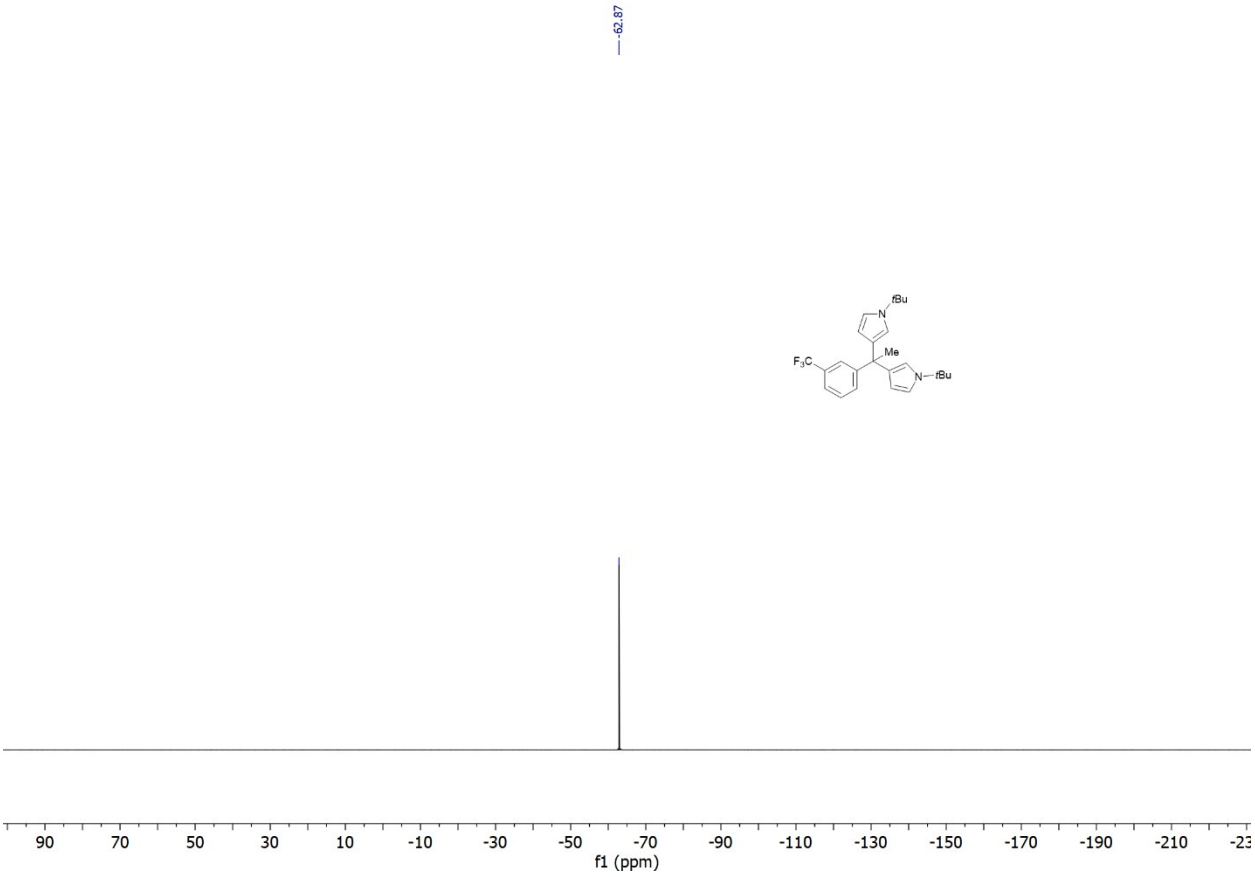
1.953 cd3cn
1.947 cd3cn
1.941 cd3cn
1.934 cd3cn
1.908
1.468

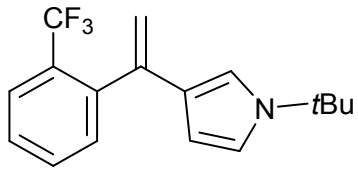

fBu
N
Me
F3C
N
fBu
2.04
1.01
1.11
2.06
2.00
2.01
3.00
18.07
f1 (ppm)


154.67
133.03
132.52
132.50
129.55
128.99
125.01
124.97
124.93
124.89
122.94
122.90
122.86
122.82
118.26 CD3CN
118.19
116.54
108.45
55.23
44.03
30.84
30.75
1.90 cd3cn
1.69 cd3cn
1.48 cd3cn
1.28 cd3cn
1.07 cd3cn
0.86 cd3cn
0.66 cd3cn


fBu
N
Me
F3C
N
fBu
f1 (ppm)


-62.87
tBu
N
Me
F3C
N
tBu
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Preparation of 3,3'-(1-(3-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (8)



To a solution of 1-trifluoromethyl-2-ethynylbenzene (18.1 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 12 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/diethyl ether = 20/1) on silica gel to afford the product **8** as a colorless oil (19.0 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 2.8 Hz, 2H), 6.41 (t, *J* = 2.0 Hz, 2H), 6.16 (dd, *J* = 2.8, 2.0 Hz, 2H), 5.56 (d, *J* = 1.2 Hz, 1H), 4.73 (s, 1H), 1.40 (s, 9H).

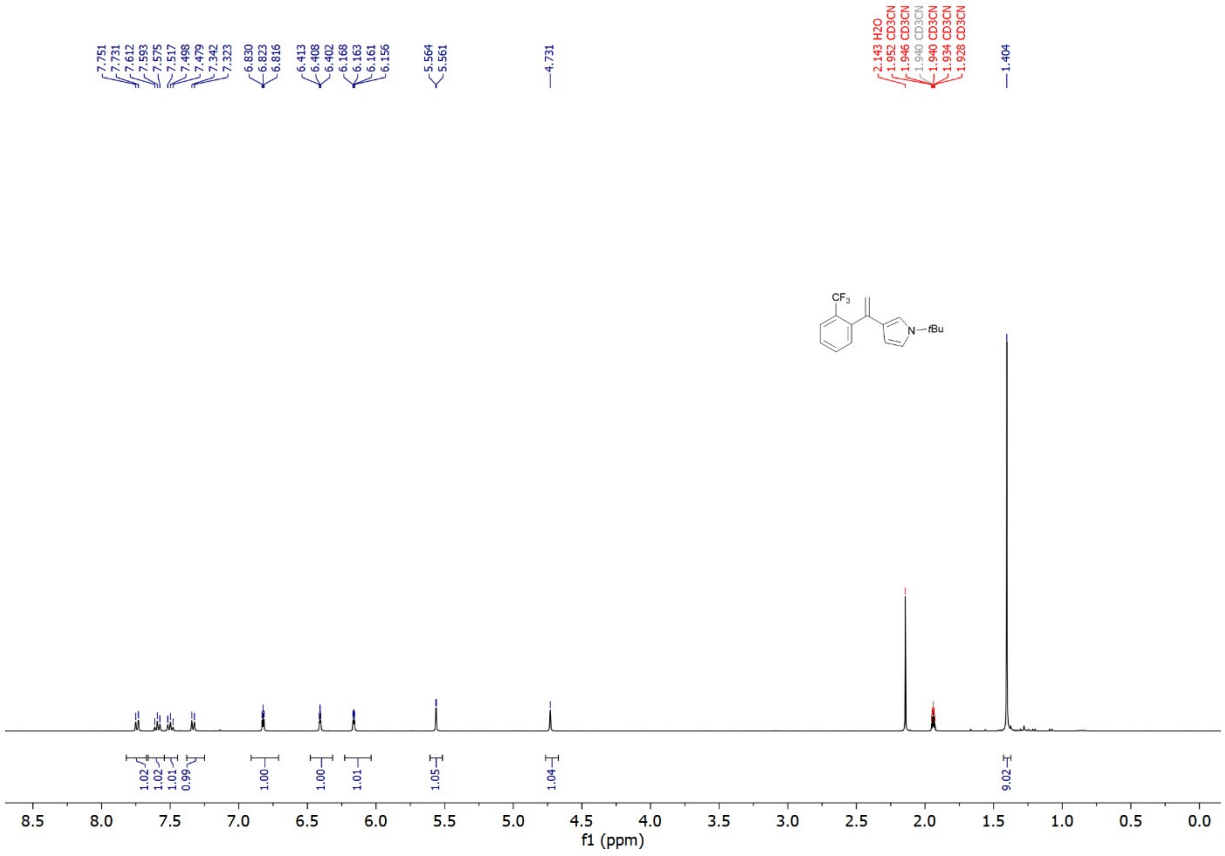
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 142.67, 142.44, 132.56, 132.53, 128.35, 126.95, 126.90, 125.80, 119.64, 118.02, 109.61, 106.24, 55.71, 30.64.

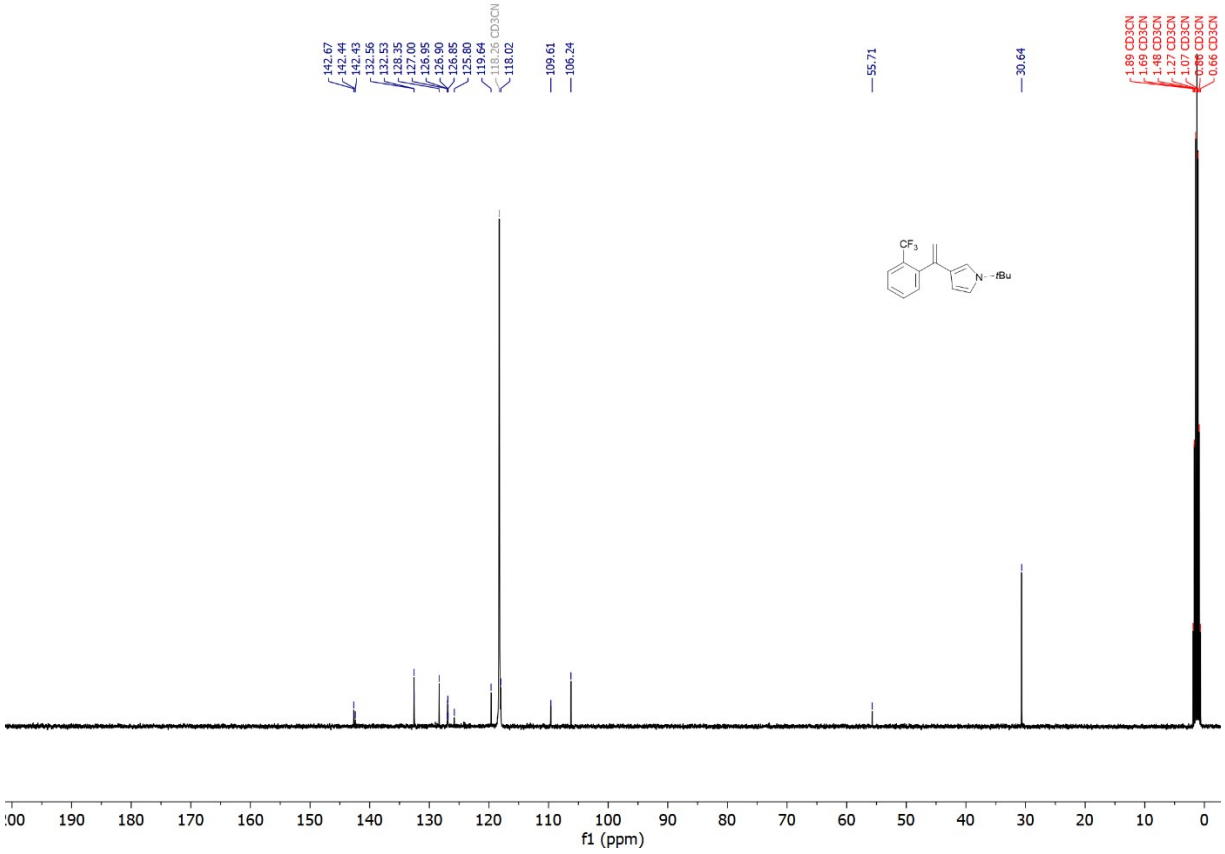
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 132.55, 132.53, 128.35, 126.95, 126.90, 119.64, 118.02, 106.24, 30.64.

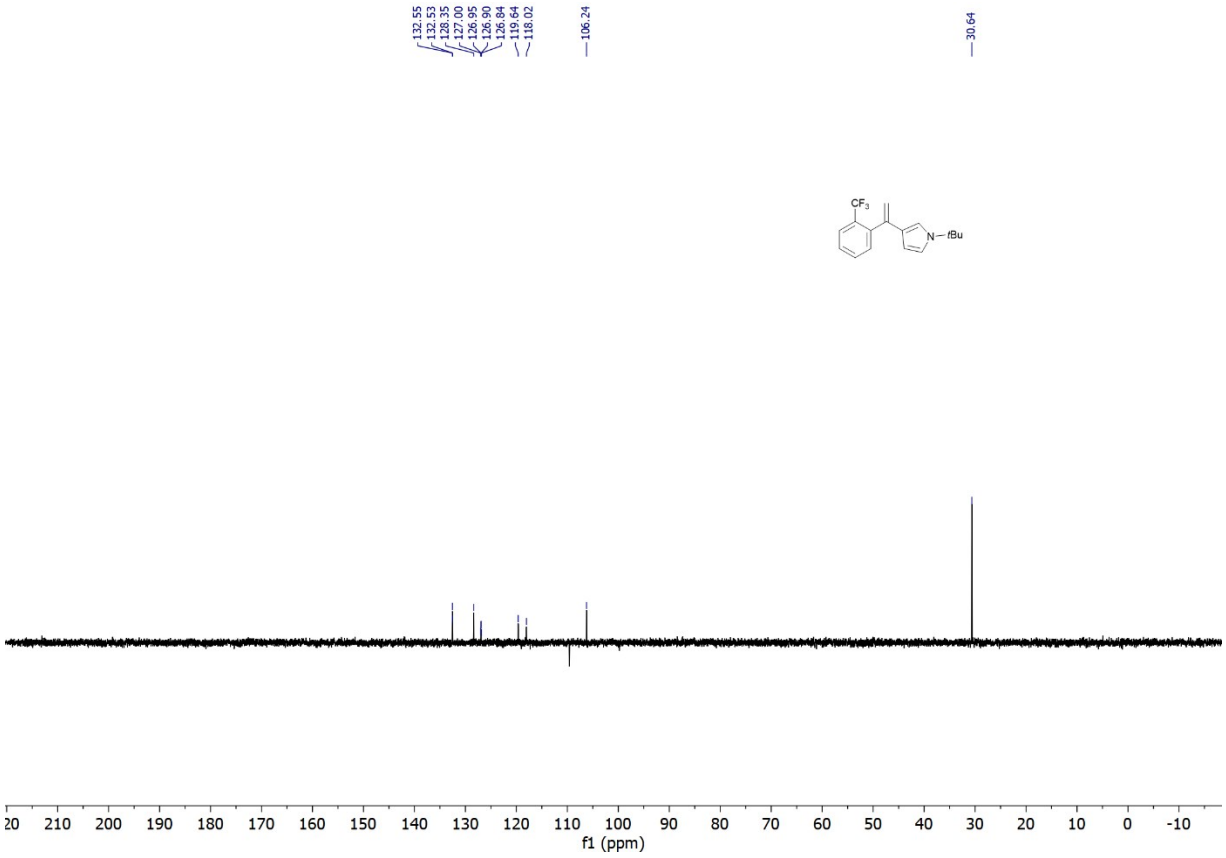
^{19}F{^{1}H} NMR (377 MHz, CD_3CN) δ: -58.08.

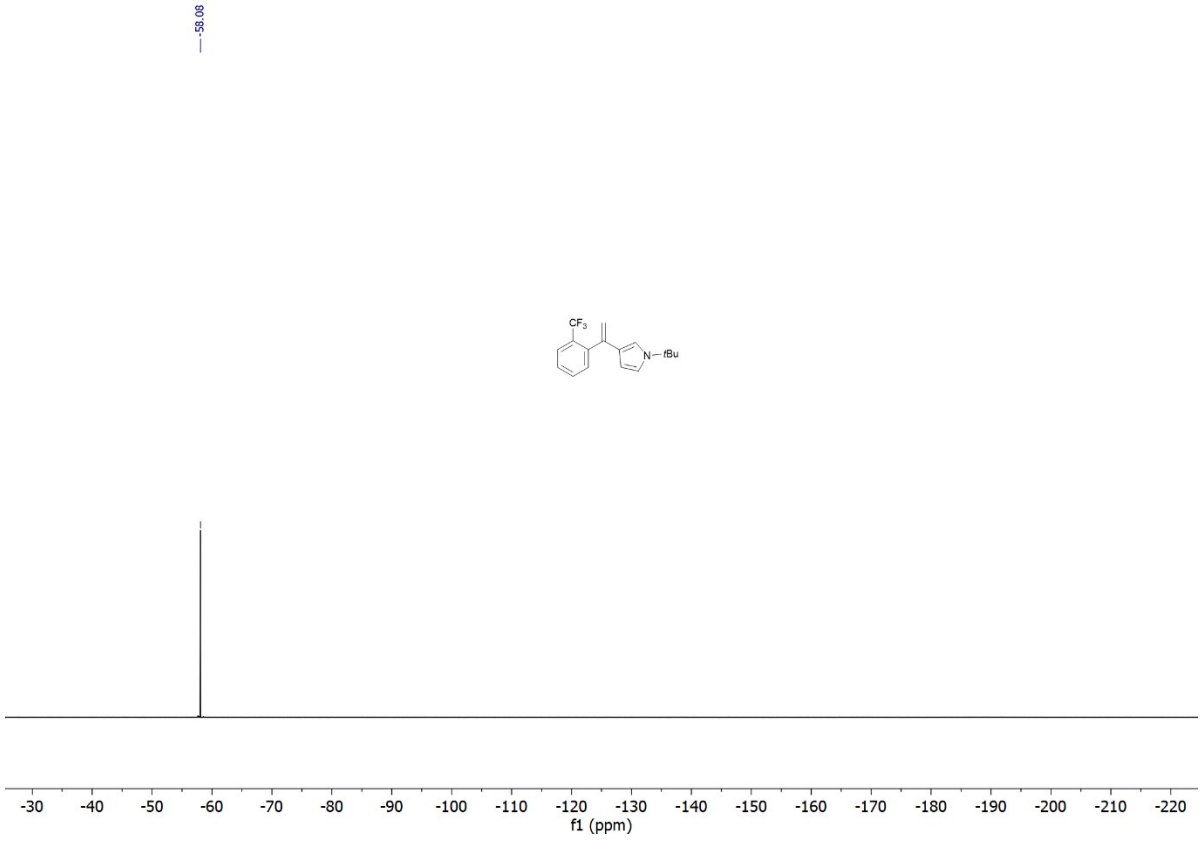
MS (DART Ionization, *m/z*): 294.1 ([M+H]$^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{17}H_{19}F_3N^+$, ([M+H]$^+$): 294.14696; Found: 294.14693.

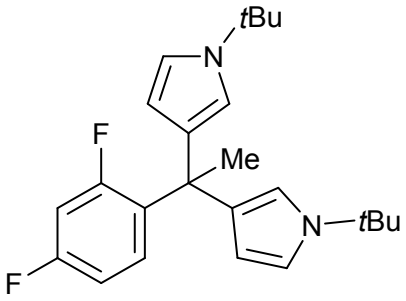

7.751
7.731
7.612
7.593
7.575
7.517
7.498
7.479
7.342
7.323
6.830
6.823
6.816
6.413
6.408
6.402
6.168
6.163
6.161
6.156
5.564
5.561
4.731
2.143 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.404
CF3
N
tBu
1.02
1.02
1.01
0.99
1.00
1.00
1.01
1.05
1.04
9.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.67
142.44
142.43
132.56
132.53
128.35
127.00
126.95
126.90
126.85
125.80
119.64
118.26 CD3CN
118.02
109.61
106.24
55.71
30.64
1.89 CD3CN
1.69 CD3CN
1.48 CD3CN
1.27 CD3CN
1.07 CD3CN
0.88 CD3CN
0.66 CD3CN
CF3
N
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


132.55
132.53
128.35
127.00
126.95
126.90
126.84
119.64
118.02
106.24
30.64
CF3
N
tBu
f1 (ppm)


-58.08
CF3
N
tBu
f1 (ppm)

Preparation of 3,3'-(1-(2,4-difluorophenyl)ethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (9)



To a solution of 1-ethynyl-2,4-difluorobenzene (13.8 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **9** as a white solid (30.8 mg, 80% yield).

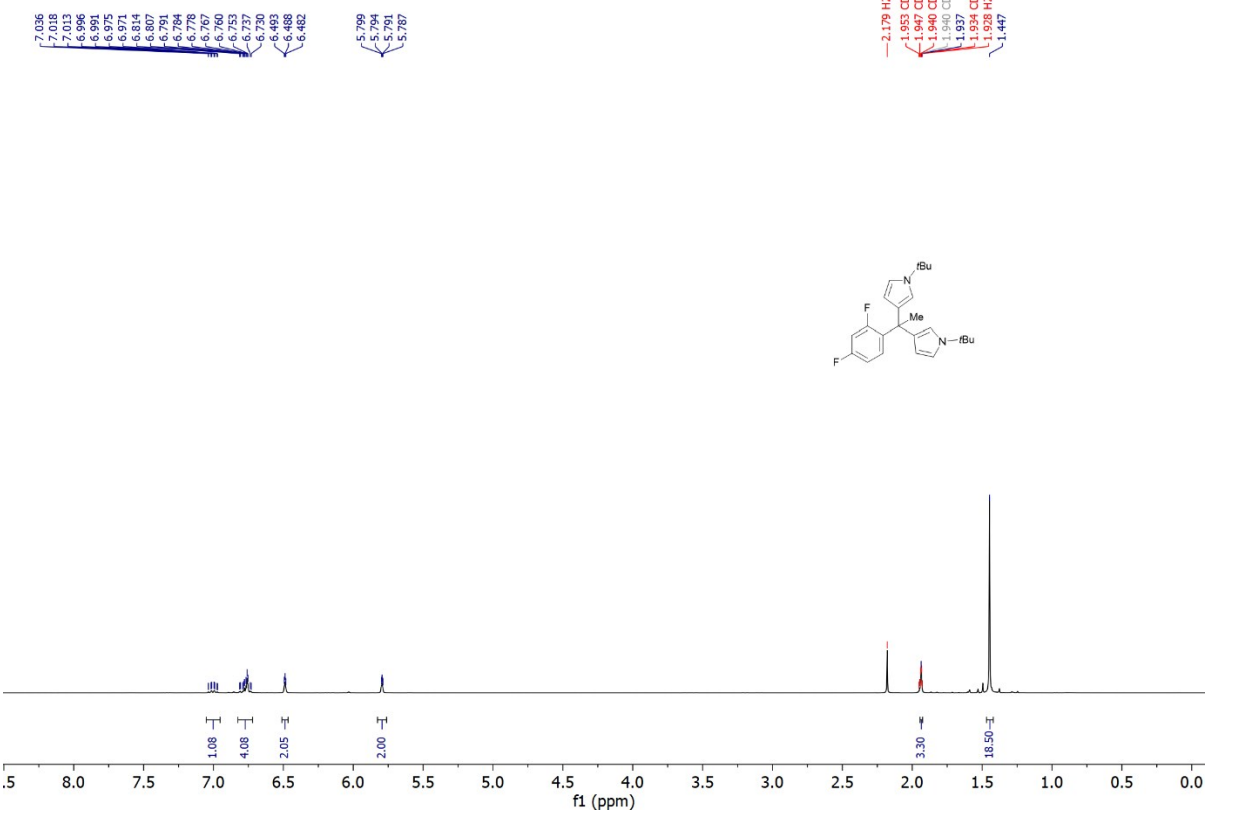
^{1}H NMR (400 MHz, CD_3CN), δ: 7.04 – 6.97 (m, 1H), 6.82 – 6.73 (m, 4H), 6.48 (t, *J* = 2.0 Hz, 2H), 5.79 (dd, *J* = 3.2, 2.0 Hz, 2H), 1.94 (s, 3H), 1.45 (s, 18H).

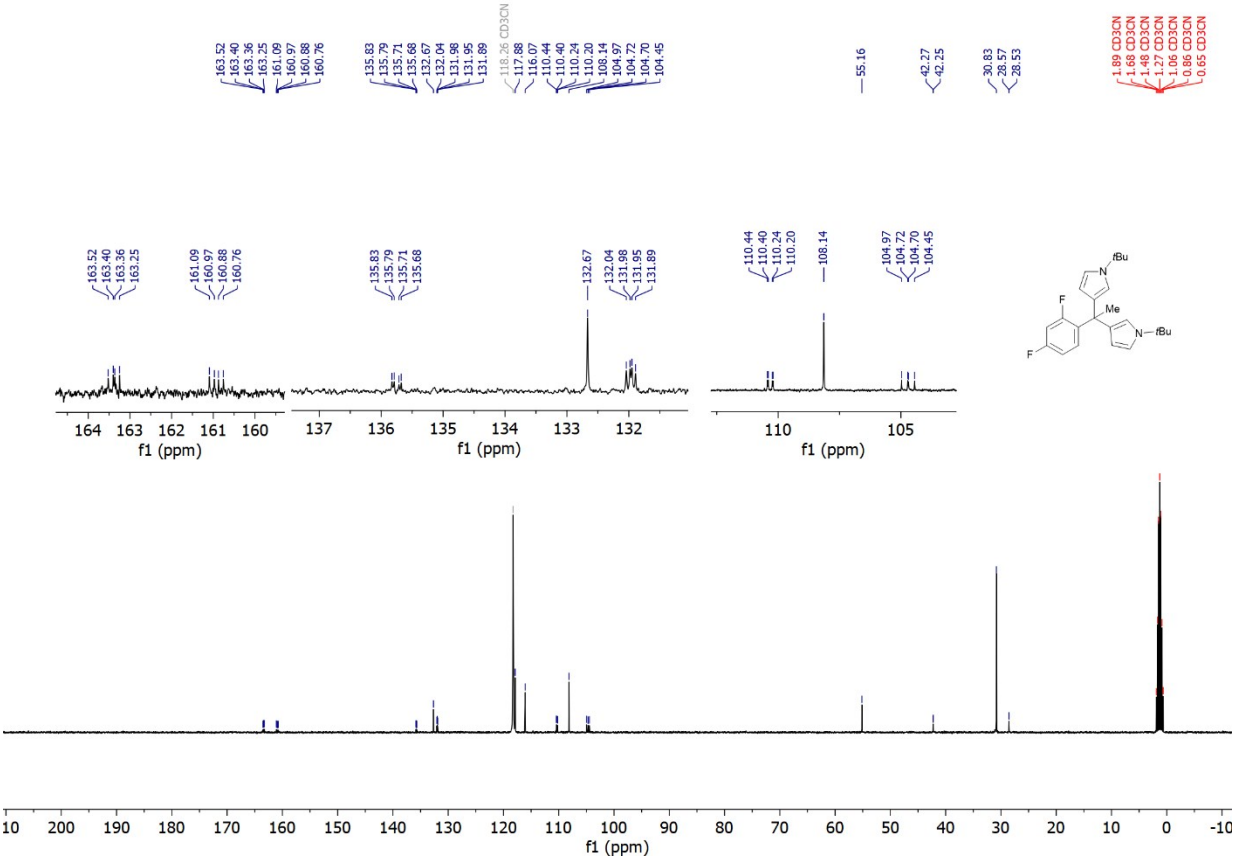
^{13}C{^{1}H} NMR (100 MHz, CD_3CN), δ: 163.52, 163.40, 163.36, 163.25, 161.09, 160.97, 160.88, 160.76, 135.83, 135.79, 135.71, 135.68, 132.67, 132.04, 131.98, 131.95, 131.89, 117.88, 116.07, 110.44, 110.40, 110.24, 110.20, 108.14, 104.97, 104.72, 104.70, 104.45, 55.16, 42.27, 42.25, 30.83, 28.57, 28.53.

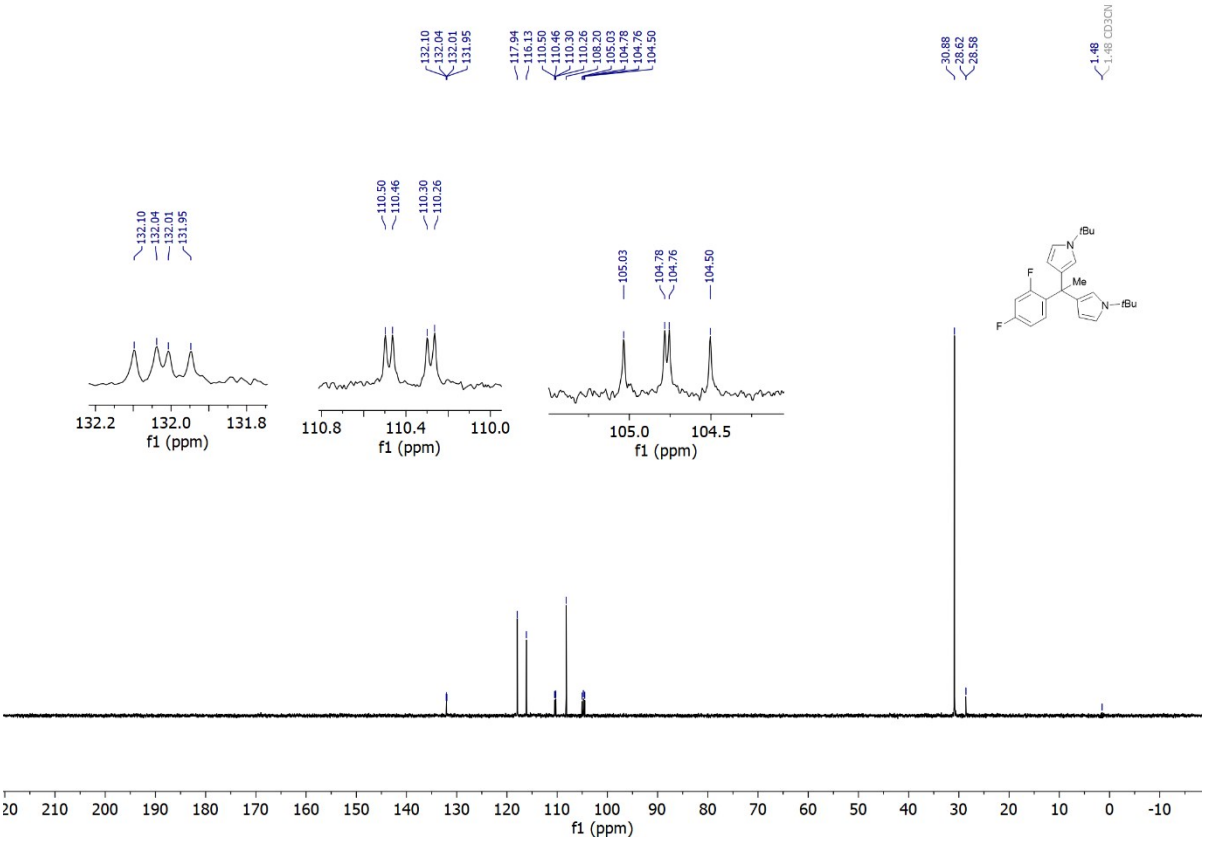
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 132.10, 132.04, 132.01, 131.95, 117.94, 116.13, 110.50, 110.46, 110.30, 110.26, 108.20, 105.03, 104.78, 104.76, 104.50, 30.88, 28.62, 28.58.

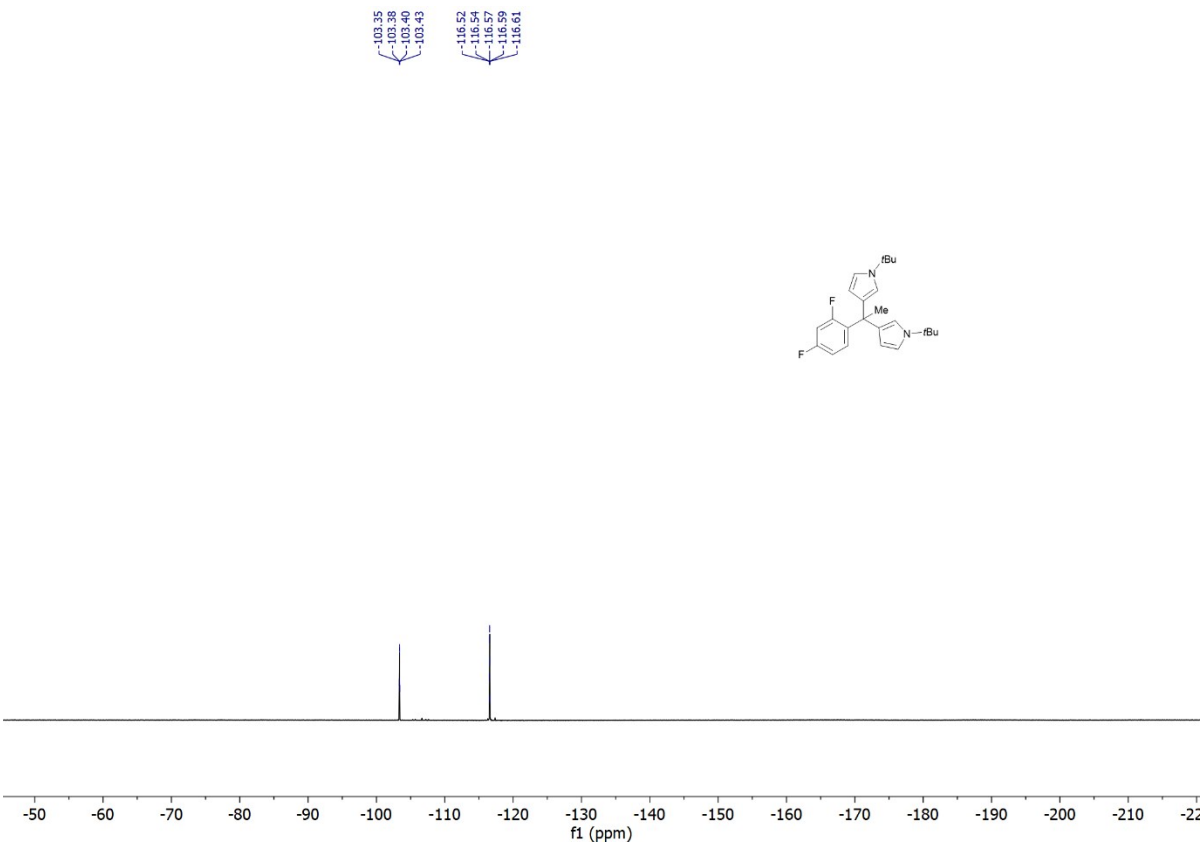
^{19}F{^{1}H} NMR (377 MHz, CD_3CN) δ: -103.39 (m, 1F), -116.57 (m, 1F).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{24}H_{31}F_2N_2^+$, ([M+H]$^+$): 385.24553; Found: 385.24577.

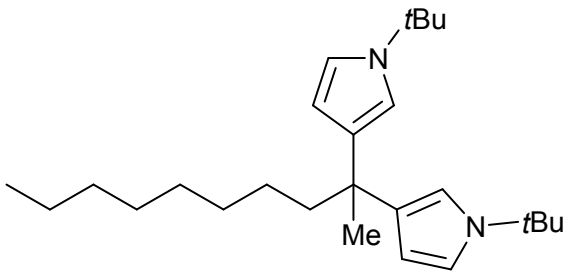

7.036
7.018
7.013
6.996
6.991
6.975
6.971
6.814
6.807
6.791
6.784
6.778
6.767
6.760
6.753
6.737
6.730
6.493
6.488
6.482
5.799
5.794
5.791
5.787
2.179 H2O
1.955 CD3CN
1.947 CD3CN
1.940 CD3CN
1.940 CD3CN
1.937
1.934 CD3CN
1.928 H2O
1.447
tBu
N
F
Me
N—tBu
F
1.08
4.08
2.05
2.00
3.30
18.50
f1 (ppm)


163.52
163.40
163.36
163.25
161.09
160.97
160.88
160.76
135.83
135.79
135.71
135.68
132.67
132.04
131.98
131.95
131.89
118.26 CD3CN
117.88
116.07
110.44
110.40
110.24
110.20
108.14
104.97
104.72
104.70
104.45
55.16
42.27
42.25
30.83
28.57
28.53
1.89 CD3CN
1.68 CD3CN
1.48 CD3CN
1.27 CD3CN
1.06 CD3CN
0.86 CD3CN
0.65 CD3CN
f1 (ppm)
tBu
N
F
Me
N—tBu
F


132.10
132.04
132.01
131.95
117.94
116.13
110.50
110.46
110.30
110.26
108.20
105.03
104.78
104.76
104.50
30.88
28.62
28.58
1.48
1.48 CD3CN
f1 (ppm)


-103.35
-103.38
-103.40
-103.43
-116.52
-116.54
-116.57
-116.59
-116.61
f1 (ppm)

Preparation of 3,3'-(decane-2,2-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (10)



Condition A: To a solution of 1-decyne (13.8 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 12 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product **10** as a colourless oil (13.1 mg, 34% yield).

Condition B: To a solution of 1-decyne (13.8 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 24 hours at 50 °C. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product **10** as a colourless oil (20.0 mg, 52% yield).

^{1}H NMR (500 MHz, CD_3CN), δ: 6.70 (t, *J* = 2.0 Hz, 2H), 6.60 (t, *J* = 2.0 Hz, 2H), 5.92 (dd, *J* = 2.4, 1.2 Hz, 2H), 1.83 – 1.79 (m, 2H), 1.47 (s, 18H), 1.46 (s, 3H), 1.32 – 1.26 (m, 12H), 0.89 (t, *J* = 5.6 Hz, 3H).

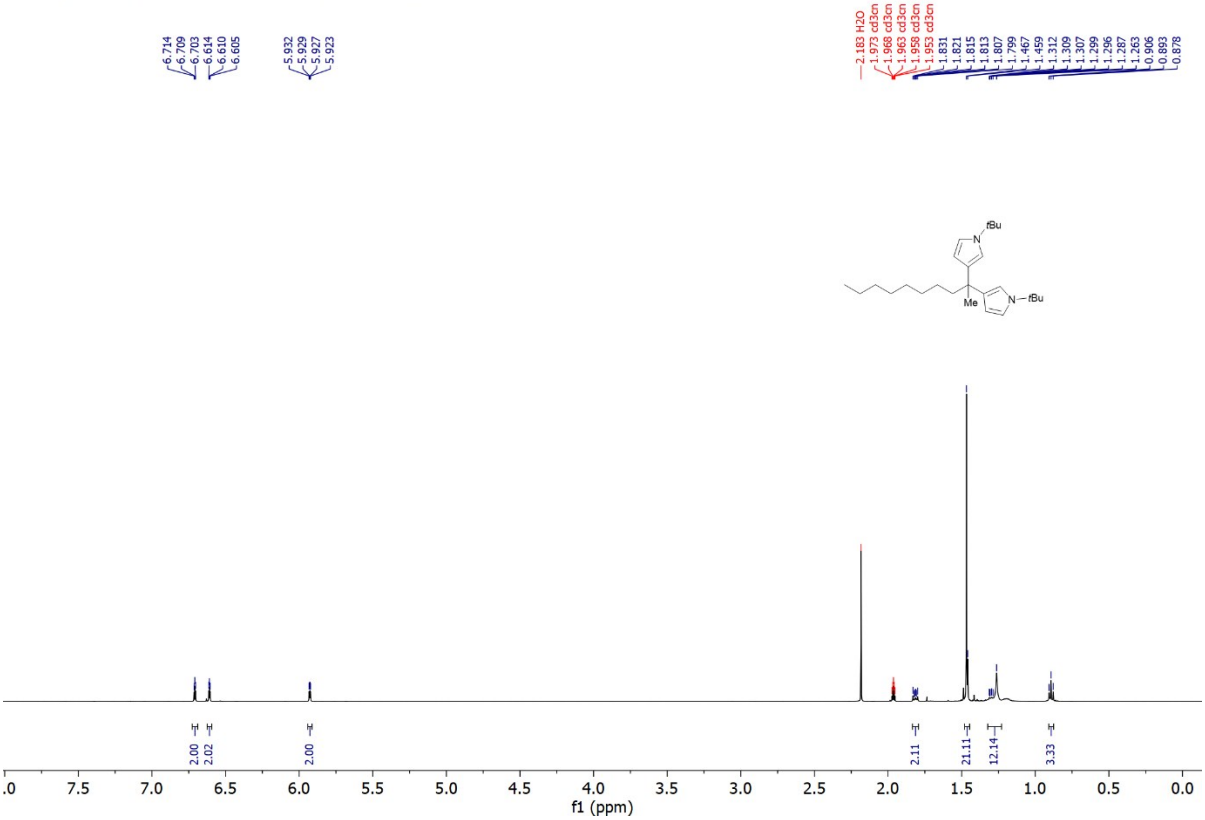
^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ: 134.59, 117.46, 114.86, 107.28, 54.94, 44.71, 37.97, 32.59, 31.09, 30.87, 30.32, 30.04, 27.63, 25.71, 23.36, 14.35.

DEPT^{135} NMR (100 MHz, CD_3CN) δ: 117.48, 114.86, 107.28, 44.71, 32.60, 31.10, 30.88, 30.34, 30.05, 27.62, 25.72, 23.37, 14.37.

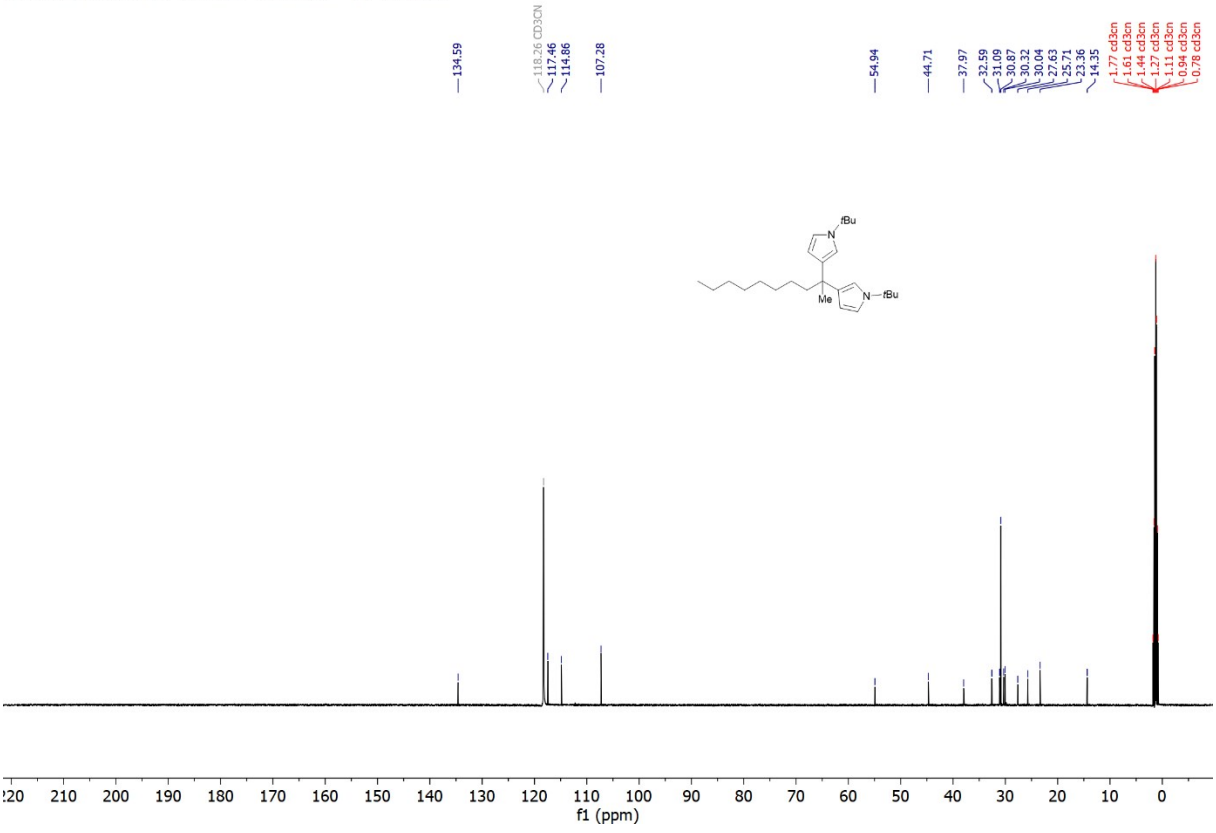
MS (DART Ionization, *m/z*): 385.4 ($[M+H]^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{26}H_{45}N_2^+$, ($[M+H]^+$): 385.35827; Found: 385.35772.

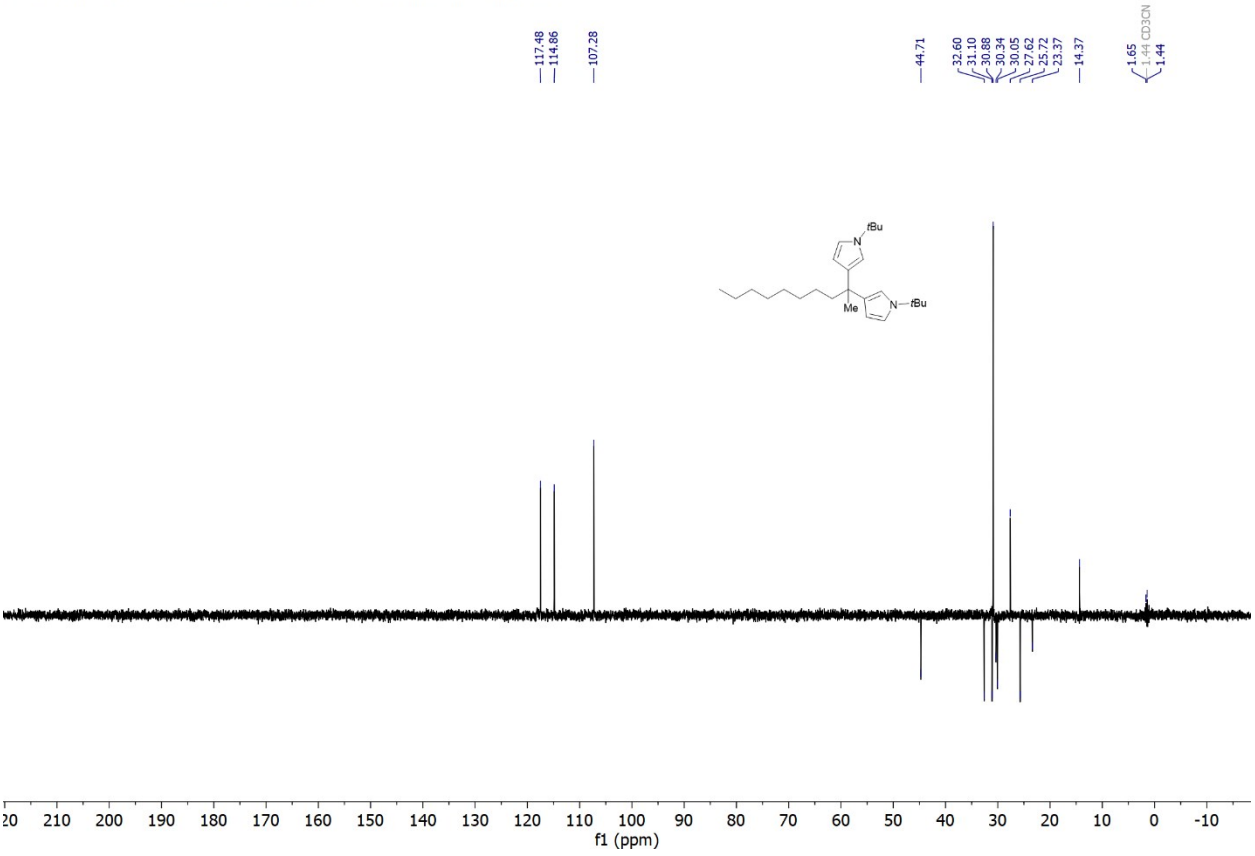
20190518_vnmrs_500_BCF-Oct-isolate-PROTON_01 — BCF-Oct-isolate —



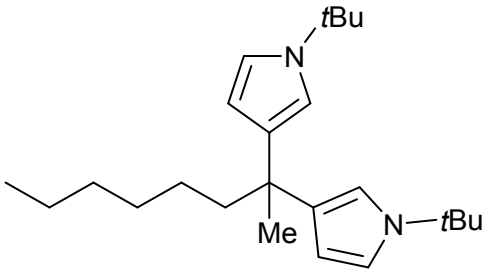
20190518_vnmrs_500_BCF-Oct-isolate-CARBON_01 — BCF-Oct-isolate —



20190521-jguo2-BCF-Oct-isolate.1.fid — bbo_DEPT135 CD3CN /home/data jguo2 186



Preparation of 3,3'-(octane-2,2-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (11)



Condition B: To a solution of 1-octyne (11.0 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 48 hours at 50 °C. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product **11** as a colourless oil (20.0 mg, 56% yield).

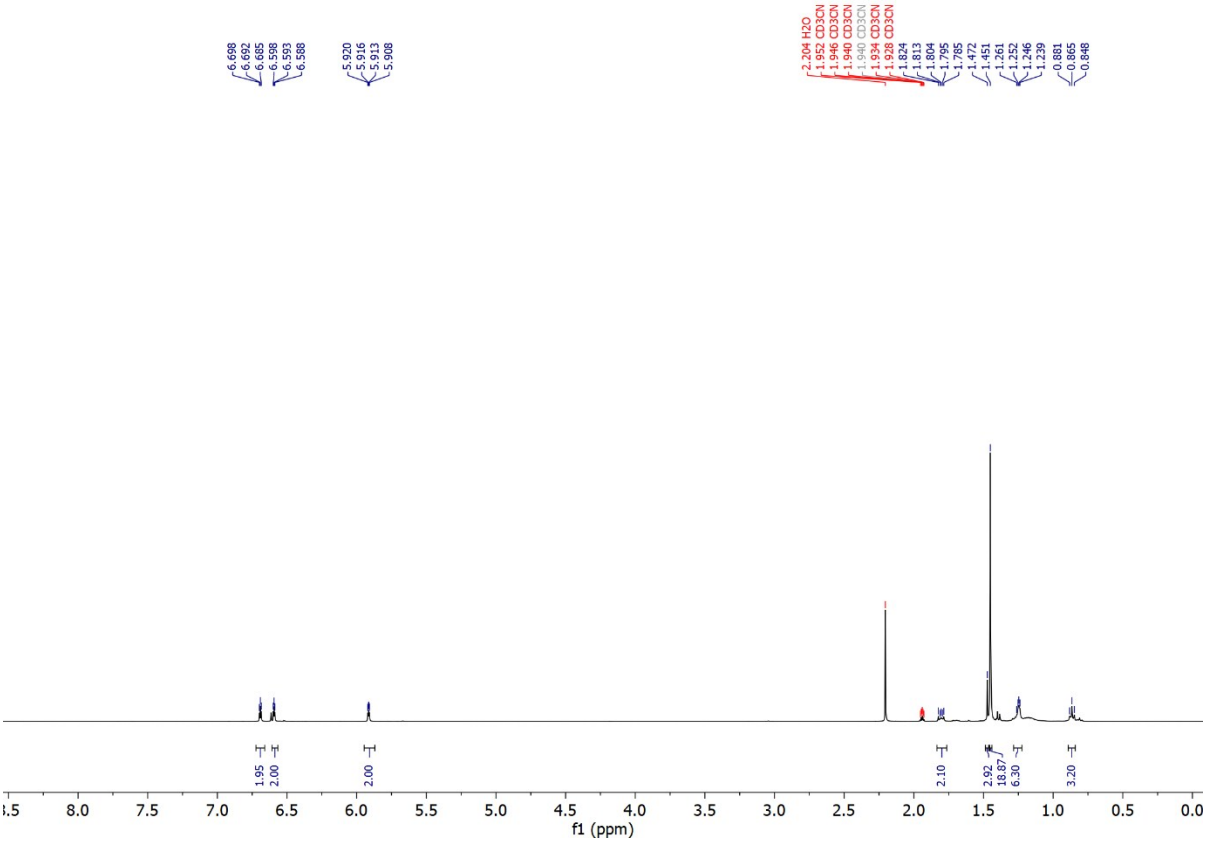
^{1}H NMR (400 MHz, CD_3CN), δ: 6.69 (t, *J* = 2.4 Hz, 2H), 6.60 (t, *J* = 2.0 Hz, 2H), 5.92 (dd, *J* = 2.8, 1.6 Hz, 2H), 1.83 – 1.78 (m, 2H), 1.47 (s, 3H), 1.45 (s, 18H), 1.26 – 1.23 (m, 6H), 0.86 (t, *J* = 6.4 Hz, 3H).

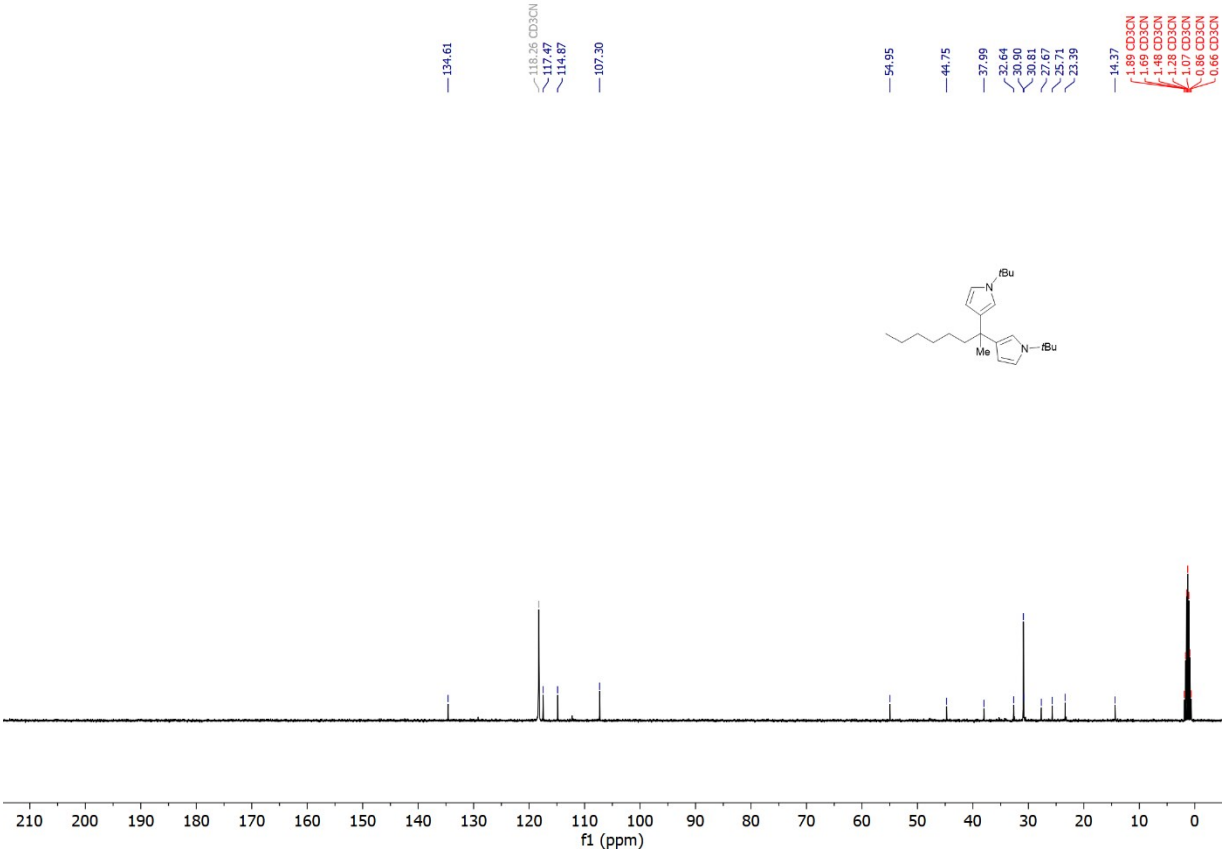
^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ: 134.61, 117.47, 114.87, 107.30, 54.95, 44.75, 37.99, 32.64, 30.90, 30.81, 27.67, 25.71, 23.39, 14.37.

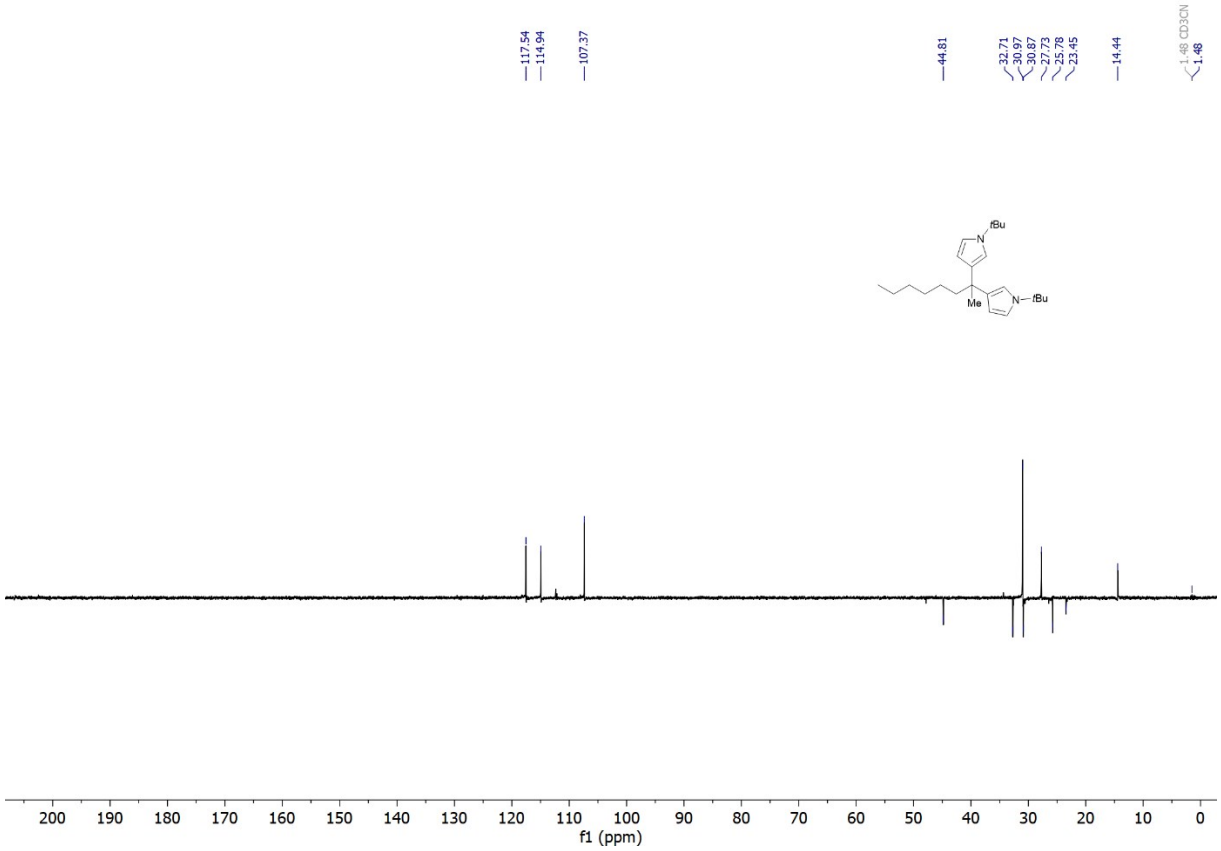
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 117.54, 114.94, 107.37, 44.81, 32.71, 30.97, 30.87, 27.73, 25.78, 23.45, 14.44.

MS (DART Ionization, *m/z*): 357.3 ([M+H]$^+$).

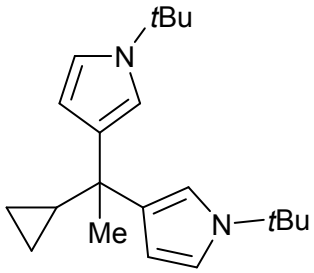
HRMS (DART Ionization, *m/z*): Calcd. for $C_{24}H_{41}N_2^+$, ([M+H]$^+$): 357.32697; Found: 357.32746.


6.698
6.692
6.685
6.598
6.593
6.588
5.920
5.916
5.913
5.908
2.204 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.824
1.813
1.804
1.795
1.785
1.472
1.451
1.261
1.252
1.246
1.239
0.881
0.865
0.848
1.95
2.00
2.00
2.10
2.92
18.87
6.30
3.20
f1 (ppm)


134.61
118.26 CD3CN
117.47
114.87
107.30
54.95
44.75
37.99
32.64
30.90
30.81
27.67
25.71
23.39
14.37
1.89 CD3CN
1.69 CD3CN
1.48 CD3CN
1.28 CD3CN
1.07 CD3CN
0.86 CD3CN
0.66 CD3CN
tBu
N
Me
tBu
f1 (ppm)


117.54
114.94
107.37
44.81
32.71
30.97
30.87
27.73
25.78
23.45
14.44
1.49 CD3CN
1.48
tBu
N
Me
N
tBu
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Preparation of 3,3'-(1-cyclopropylethane-1,1-diyl)bis(1-(*tert*-butyl)-1*H*-pyrrole) (12)



To a solution of cyclopropylacetylene (6.6 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (30.7 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 24 hours at 50 °C. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 12/1) on silica gel to afford the product **12** as a colourless oil (12.1 mg, 38% yield).

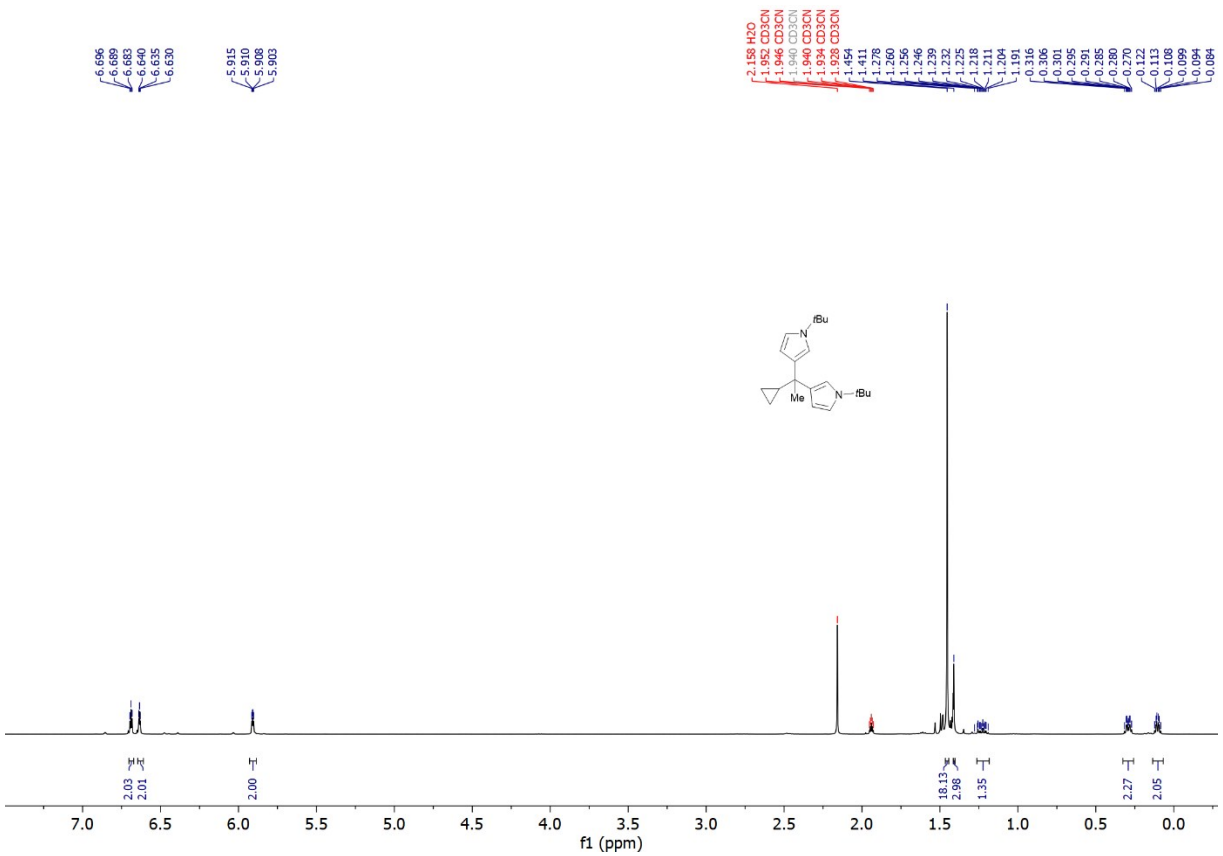
^{1}H NMR (400 MHz, CD_3CN), δ: 6.69 (t, *J* = 2.4 Hz, 2H), 6.60 (t, *J* = 2.0 Hz, 2H), 5.92 (dd, *J* = 2.8, 2.0 Hz, 2H), 1.45 (s,18 H), 1.41 (s, 3H), 1.28 – 1.19 (m, 1H), 0.32 – 0.27 (m, 2H), 0.12 – 0.08 (m, 2H).

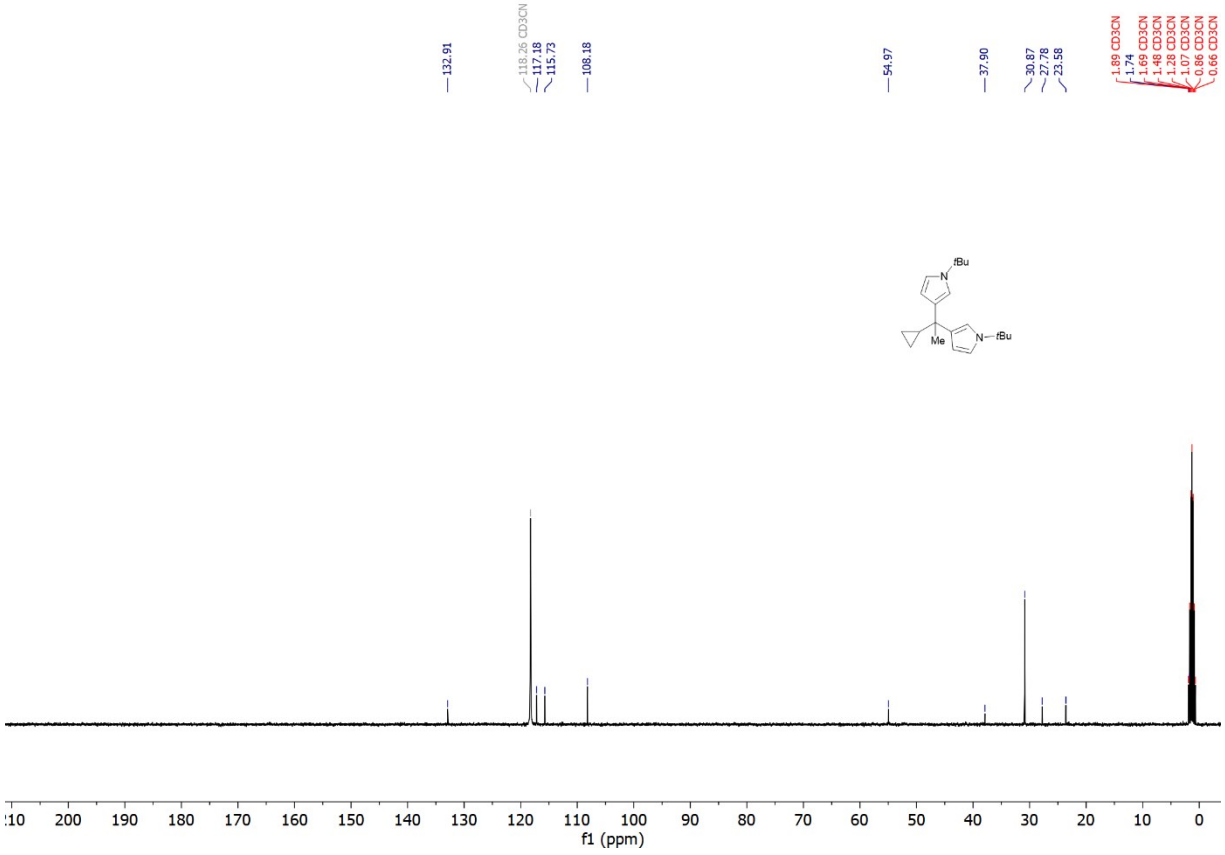
^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ: 132.91, 117.18, 115.73, 108.18, 54.97, 37.90, 30.87, 27.78, 23.58, 1.74.

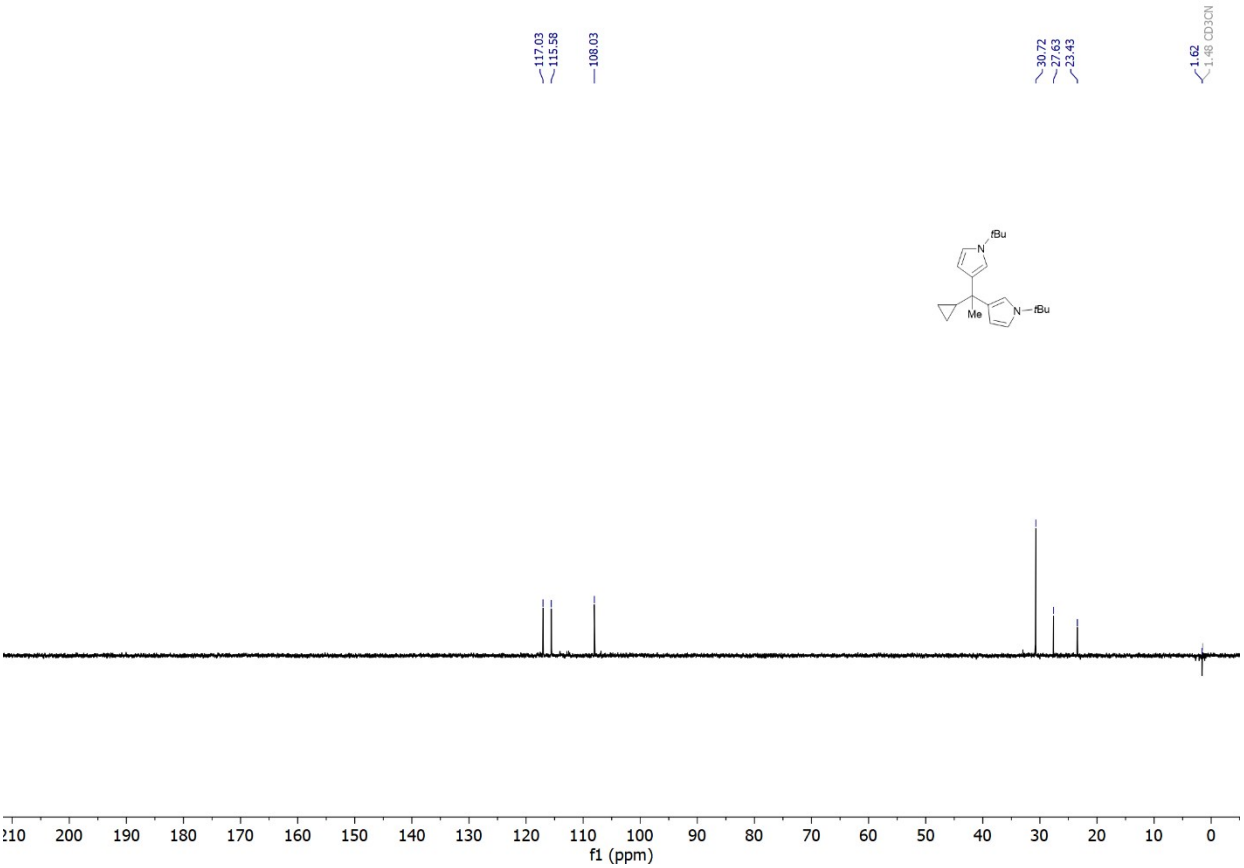
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 117.03, 115.58, 108.03, 30.72, 27.63, 23.43, 1.62.

MS (DART Ionization, *m/z*): 313.3 ($[M+H]^+$).

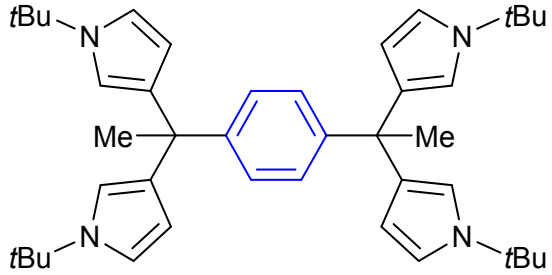
HRMS (DART Ionization, *m/z*): Calcd. for $C_{21}H_{33}N_2^+$, ($[M+H]^+$): 313.26437; Found: 313.26367.


6.696
6.689
6.683
6.640
6.635
6.630
5.915
5.910
5.908
5.903
2.158 H2O
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.934 CD3CN
1.454
1.411
1.278
1.260
1.256
1.246
1.239
1.232
1.225
1.218
1.211
1.204
1.191
0.316
0.306
0.301
0.295
0.291
0.285
0.280
0.270
0.122
0.113
0.108
0.099
0.094
0.084
tBu
N
Me
N
tBu
2.03
2.01
2.00
18.13
2.98
1.35
2.27
2.05
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


132.91
118.26 CD3CN
117.18
115.73
108.18
54.97
37.90
30.87
27.78
23.58
1.89 CD3CN
1.74
1.69 CD3CN
1.48 CD3CN
1.28 CD3CN
1.07 CD3CN
0.86 CD3CN
0.66 CD3CN
tBu
N
Me
N
tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Preparation of 1,4-bis(1,1-bis(1-(*tert*-butyl)-1*H*-pyrrol-3-yl)ethyl)benzene (13)



To a solution of 1,4-diethynylbenzene (12.6 mg, 0.1 mmol) and 1-(*tert*-butyl)-1*H*-pyrrole (61.4 mg, 0.5 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 12 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **13** as a white solid (33.0 mg, 53% yield).

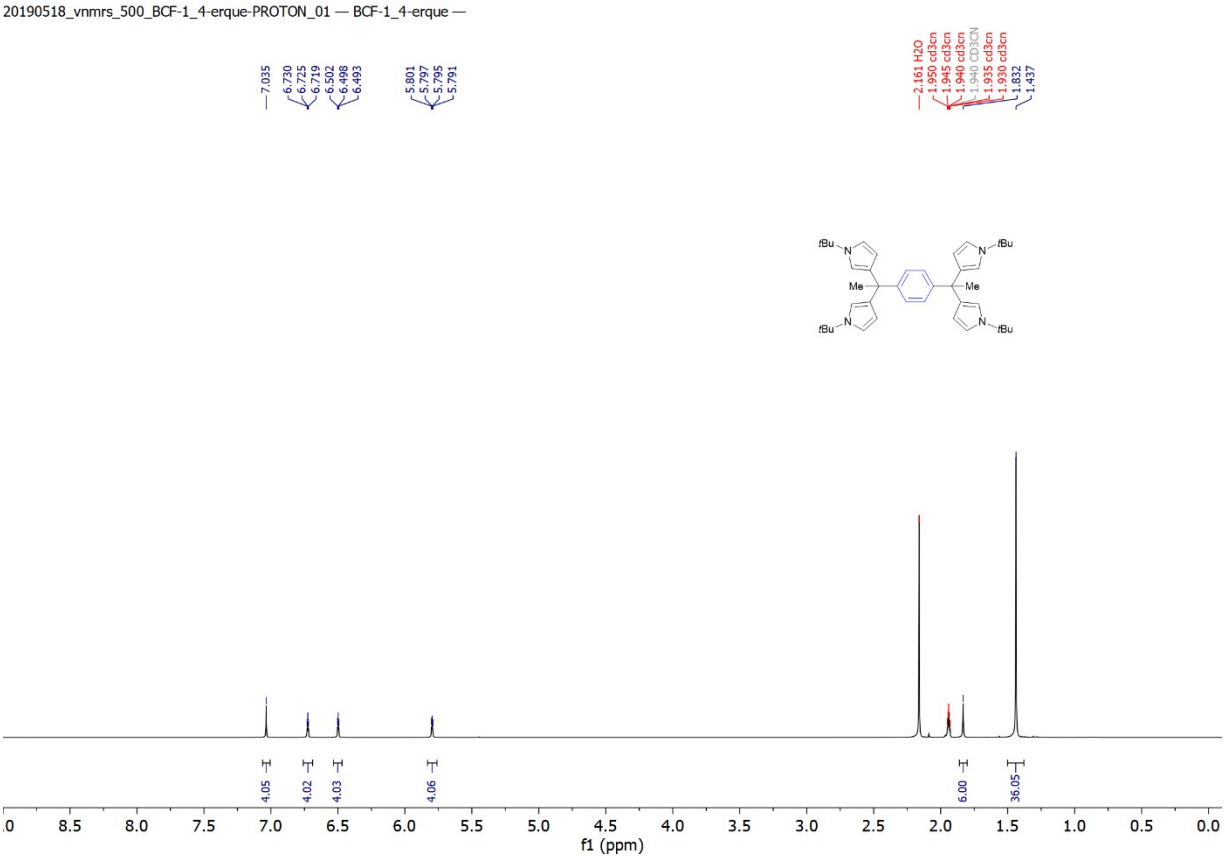
^{1}H NMR (500 MHz, CD_3CN), δ: 7.3 (s, 4H), 6.72 (t, *J* = 2.0 Hz, 4H), 6.49 (t, *J* = 2.0 Hz, 4H), 5.79 (dd, *J* = 2.4, 2.0 Hz, 4H), 1.83 (s, 6H), 1.44 (s, 36H).

^{13}C{^{1}H} NMR (126 MHz, CD_3CN), 149.57, 134.07, 127.30, 117.71, 116.31, 108.62, 55.03, 43.29, 30.84, 30.79.

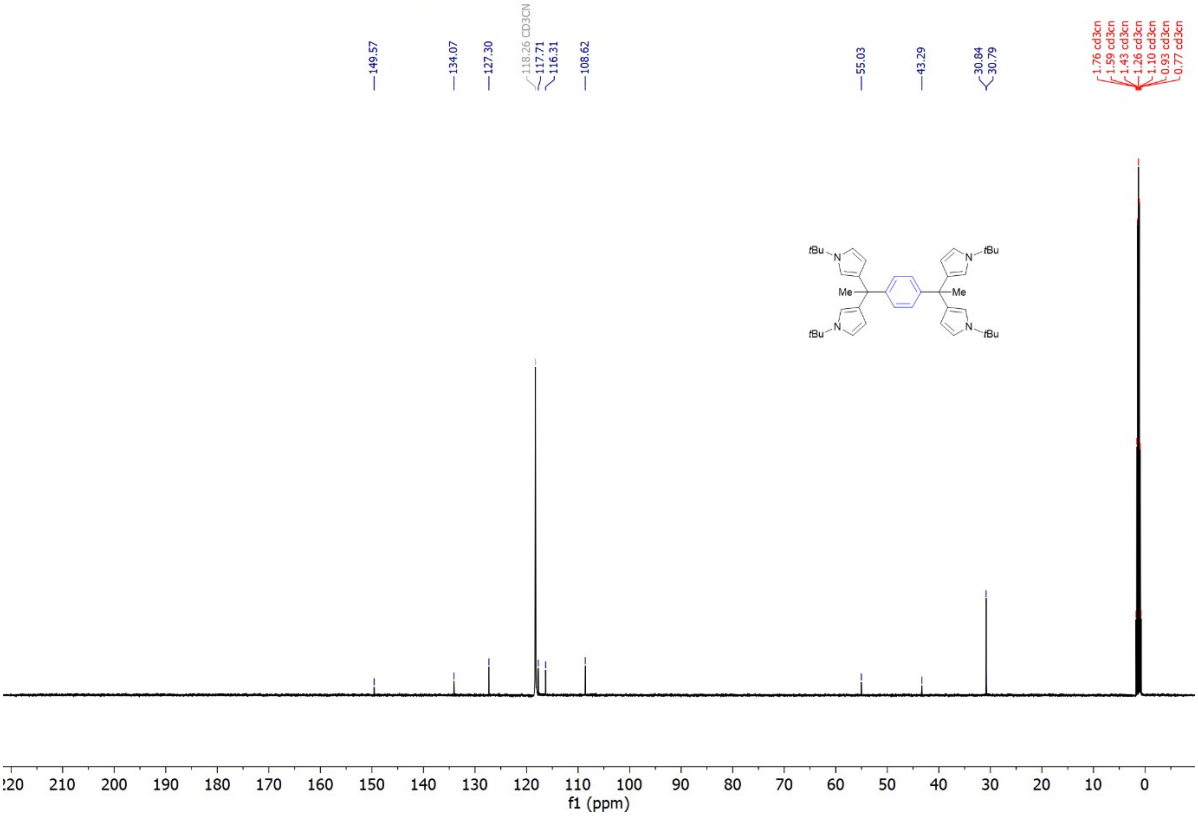
DEPT^{135} NMR (100 MHz, CD_3CN) δ: 127.26, 117.68, 116.26, 108.57, 30.80, 30.75.

MS (DART Ionization, *m/z*): 619.5 ([M+H]$^+$).

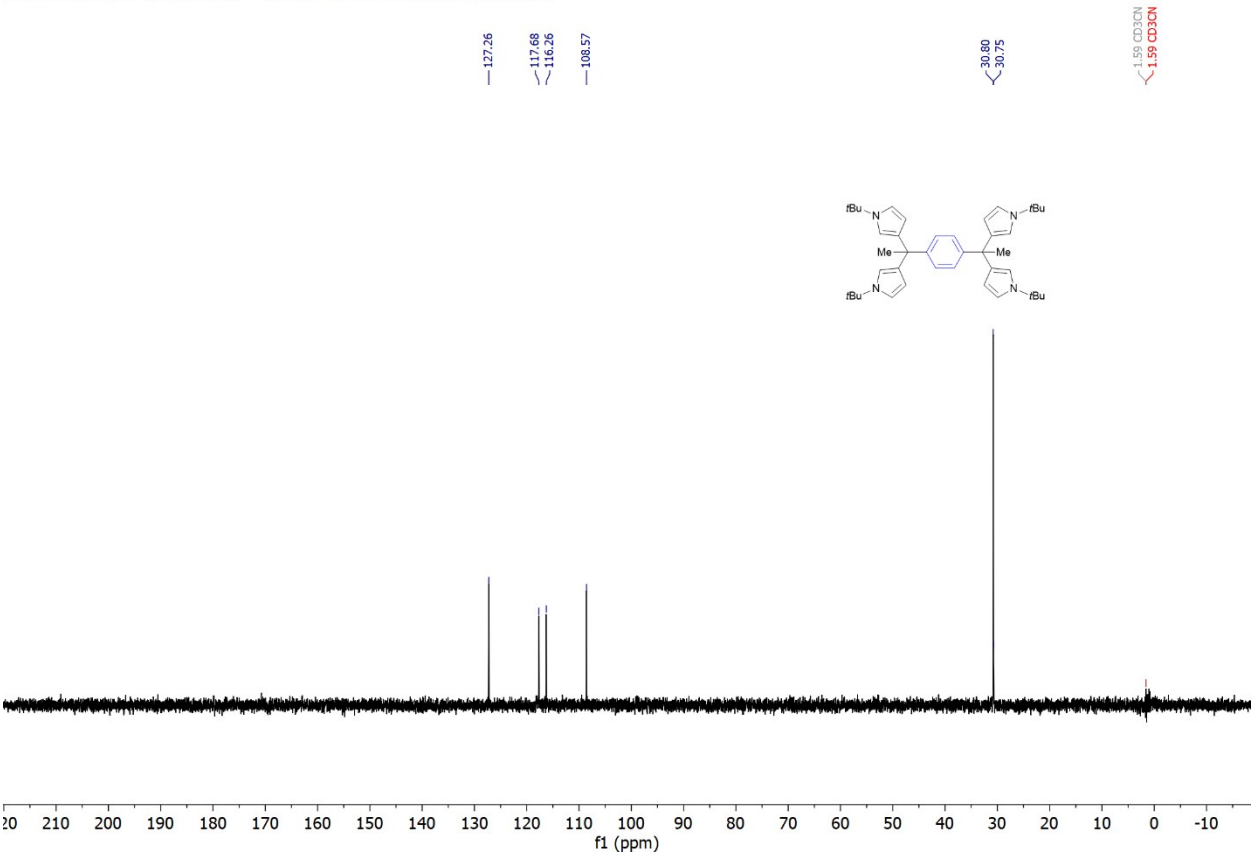
HRMS (DART Ionization, *m/z*): Calcd. for $C_{42}H_{59}N_4^+$, ([M+H]$^+$): 619.47397; Found: 619.47473.



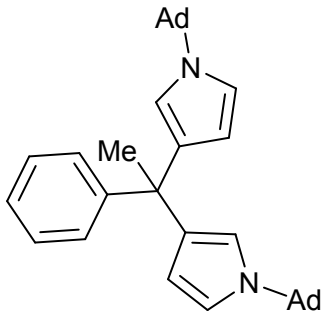
20190518_vnmrs_500_BCF-1_4-erque-CARBON_01 — BCF-1_4-erque —



20190518-jguo2-BCF-1,4-erque.1.fid — bbo_DEPT135 CD3CN /home/data jguo2 134



Preparation of 3,3'-(1-phenylethane-1,1-diyl)bis(1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1*H*-pyrrole) (14)



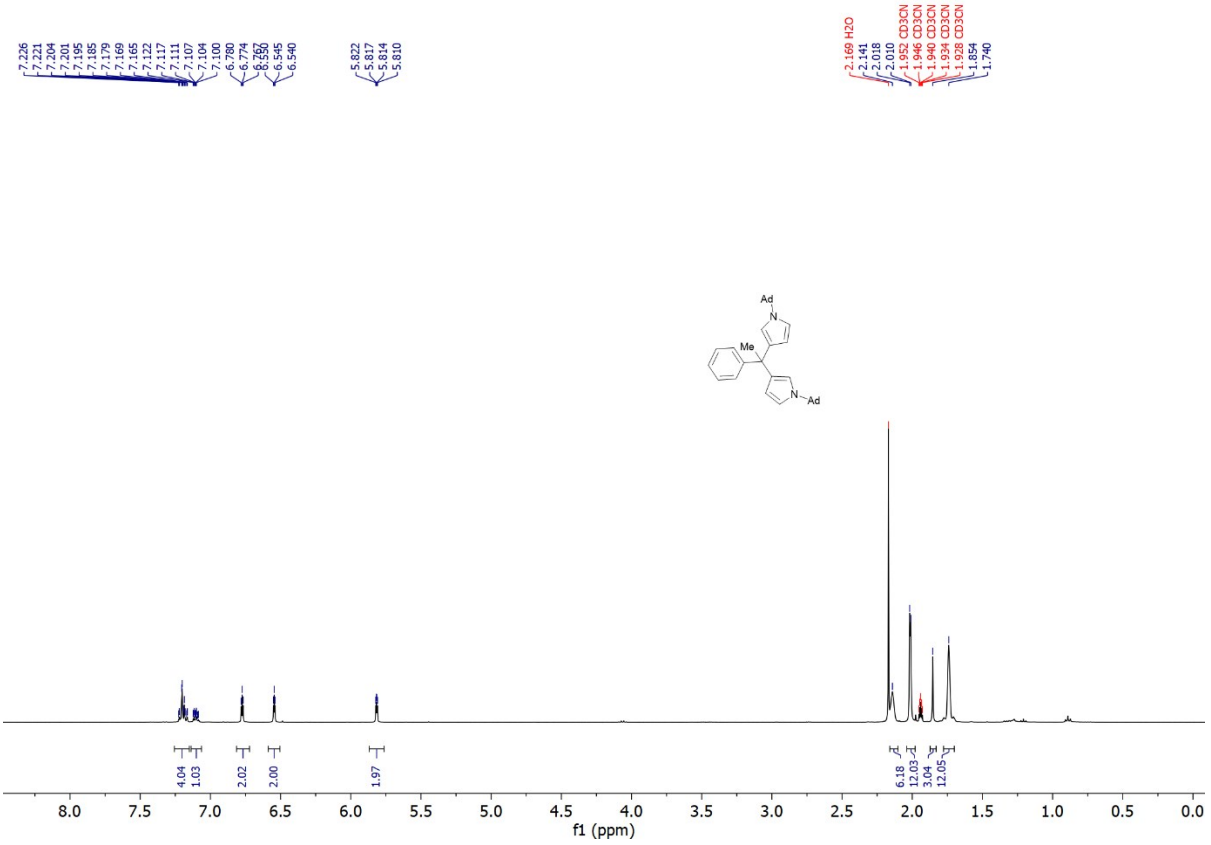
To a solution of phenylacetylene (10.2 mg, 0.1 mmol) and 1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1*H*-pyrrole (50.3 mg, 0.25 mmol) in C_6D_6 (0.3 mL) was added to a solution of $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 10 mol%) in C_6D_6 (0.2 mL). The reaction was complete after 5 hours at room temperature. The residue was purified by flash chromatography (eluent: hexane/ethyl acetate = 8/1) on silica gel to afford the product **14** as a white solid (42.8 mg, 85% yield).

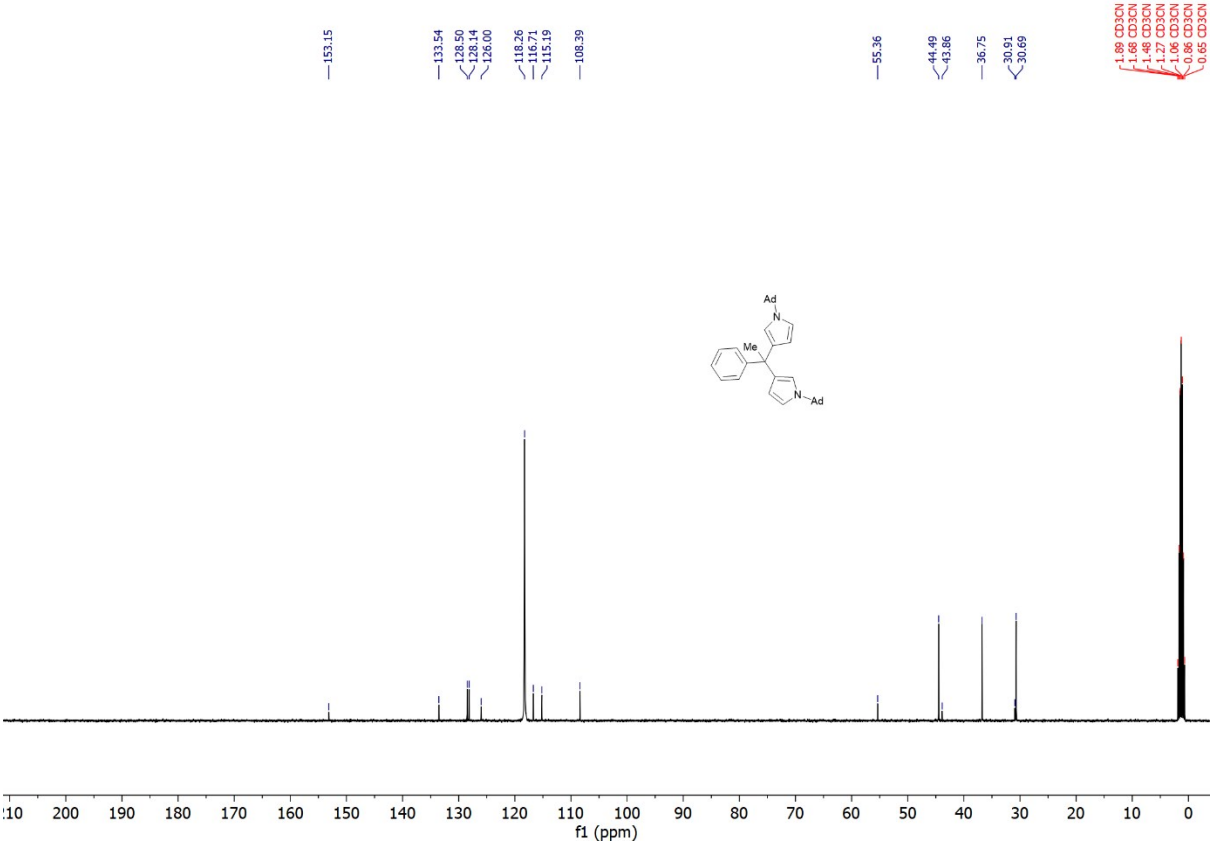
^{1}H NMR (400 MHz, CD_3CN), δ: 7.23 – 7.16 (m, 4H), 7.12 – 7.08 (m, 1H), 6.77 (t, *J* = 2.4 Hz, 2H), 6.54 (t, *J* = 2.0 Hz, 2H), 5.92 (dd, *J* = 2.8, 2.0 Hz, 2H), 2.14 (s,6 H), 2.01 (d, *J* = 3.2 Hz, 12H), 1.85 (s, 3H), 1.74 (s, 12H).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ: 153.15, 133.54, 128.50, 128.14, 126.00, 116.71, 115.19, 108.39, 55.36, 44.49, 43.86, 36.75, 30.91, 30.69.

MS (DART Ionization, *m/z*): 505.36 ($[M+H]^+$).

HRMS (DART Ionization, *m/z*): Calcd. for $C_{36}H_{45}N_2^+$, ($[M+H]^+$): 505.36773; Found: 505.35716.


7.226
7.221
7.204
7.201
7.195
7.185
7.179
7.169
7.165
7.122
7.117
7.111
7.107
7.104
7.100
6.780
6.774
6.767
6.550
6.545
6.540
5.822
5.817
5.814
5.810
2.169 H2O
2.141
2.018
2.010
1.952 CD3CN
1.946 CD3CN
1.940 CD3CN
1.934 CD3CN
1.928 CD3CN
1.854
1.740
Ad
Me
Ad
4.04
1.03
2.02
2.00
1.97
6.18
12.03
3.04
12.05
f1 (ppm)


153.15
133.54
128.50
128.14
126.00
118.26
116.71
115.19
108.39
55.36
44.49
43.86
36.75
30.91
30.69
1.89 CD3CN
1.68 CD3CN
1.48 CD3CN
1.27 CD3CN
1.06 CD3CN
0.86 CD3CN
0.65 CD3CN
Ad
Me
Ad
f1 (ppm)

Single crystal X-ray crystallography

X-ray crystallographic data were collected on a Bruker Apex2 X-ray diffractometer at 150±2 K using a graphite monochromator with MoK(α) radiation (λ = 0.71073 Å) and the Bruker APEX3 software[4] package. Suitable crystals were selected and mounted in Paratone-N oil on a MiTeGen cryoloop, then placed in the cold (N_2) stream of the diffractometer. Unit cell parameters were determined from consecutive scans at different orientations. The data were integrated using the SAINT software package[5] and a multi-scan absorption correction was applied using SADABS.[6] All structures were solved and refined by intrinsic phasing in the SHELXTL suite of programs using XT and refinement by full-matrix least-squares on F2 using XL.[7-8] All non-hydrogen atoms were subjected to anisotropic refinement and carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors (Uiso(H) = 1.2Ueq(C)).

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