Facile and Practical Synthesis of *β*-Carbolinium Salts and *γ*-Carbolinium Salts via Rhodium-Catalyzed Three-Component Reactions

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Supporting Information

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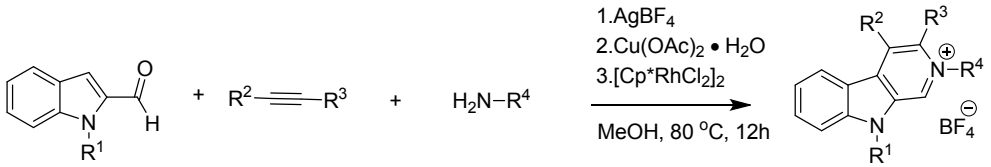
General Information

The ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR were recorded with Bruker 400 MHz spectrometer instruments in DMSO or $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated DMSO (δ = 2.50 and 39.52) or nondeuterated $CDCl_3$ (δ = 7.26 and 77.70) as internal standards. The chemical shifts (δ) of ^{31}P NMR were measured in ppm, referenced to the ^{31}P signal of PPh_3 (δ = -5.65) as an external standard. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource. Indolyl aldehydes **1a** [1], **1b**[1], **1c**[2], **1e**[3, 1], **7f**[4] and alkynes **2b**[5], **2c**[6] were synthesized according to the literature. Other Indolyl aldehydes and Alkynes were commercially available.

Synthesis of *β*-carbolinium salts 4

General Procedure A

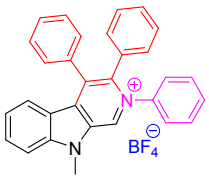


1 **2** **3** **4**

A sealed tube contained $[RhCp^*Cl_2]_2$ (0.8 mol %, 0.00251 mmol), $AgBF_4$ (0.628 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.628 mmol) was evacuate and purged with nitrogen gas three times. Then, **1** (0.314 mmol), **2** (0.377 mmol) and **3** (0.628 mmol) in MeOH (5.0 mL) were added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 80°C for 12 h. When the reaction was completed, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a Celite pad and the

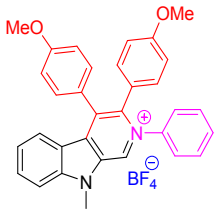
Celite pad was washed several times with CH_2Cl_2 (5 mL). The combined filtrate was concentrated in vacuo and the residue was purified by column chromatography on neutral Al_2O_3 using DCM: MeOH (30:1) as eluent to afford the desired pure product **4**.

9-Methyl-2,3,4-triphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4a)**



Green solid (146 mg, 93%); M.p.: 161-163 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.04 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.45 (dd, *J* = 11.9, 6.5 Hz, 8H), 7.37 – 7.29 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 3H), 6.86 (d, *J* = 8.1 Hz, 1H), 4.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.93, 143.66, 143.11, 135.29, 134.93, 133.81, 132.82, 131.96, 130.44, 130.37, 129.70, 129.49, 129.37, 129.34, 127.84, 127.80, 124.01, 122.38, 119.47, 112.19, 31.05. ^{19}F NMR (376 MHz, DMSO) δ -148.37 (s). HRMS (ESI): calcd for $C_{30}H_{23}N_2^+$ $[M\text{-}BF_4]^+$: 411.1856, found 411.1853. IR (neat): *v* = 553, 701, 767, 1056 ($\nu_{B\text{-}F}$)[7], 1137, 1339, 1381, 1430, 1470, 1495, 1602, 1633, 3055, 3412 cm^{-1}.

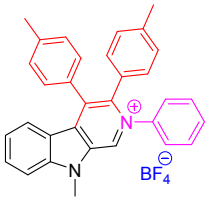
3,4-Bis(4-methoxyphenyl)-9-methyl-2-phenyl-9H-pyrido[3,4-b]indol-2-ium tetra-fluoroborate **(4b)**



Green solid (166.5 mg, 95%); M.p.: 144-145 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.93 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.92–7.83 (m, 1H), 7.65 (d, *J* = 5.9 Hz, 2H), 7.50 (d, *J* = 6.4 Hz, 3H), 7.30 (m, *J* = 16.5, 8.0 Hz, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.03 (m, *J* = 24.1, 8.2 Hz, 3H), 6.68 (d, *J* = 8.4 Hz, 2H), 4.24 (s, 3H), 3.81 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 159.32, 159.04, 145.50, 143.51, 143.16, 134.78, 132.94, 132.36, 130.61, 132.94, 130.61, 129.94, 129.62, 129.14, 127.27, 123.77,

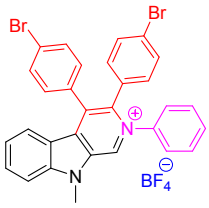
123.73, 121.99, 119.21, 114.38, 112.94, 111.63, 55.21, 55.03, 30.53. HRMS (ESI): calcd for $C_{32}H_{27}N_2O_2^+$ [M-BF_4]$^+$: 471.2067, found 471.2069. IR (neat): ν = 548, 698, 754, 779, 839, 1057 (ν_{B-F}), 1179, 1251, 1292, 1336, 1383, 1432, 1469, 1498, 1608, 1634, 2838, 2936, 3096, 3425 cm^{-1}.

9-Methyl-2-phenyl-3,4-di-p-tolyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4c)**



Green solid (150.3 mg, 91%). M.p.: 158-160 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.95 (s, 1H), 8.02 – 7.80 (m, 2H), 7.67 – 7.39 (m, 6H), 7.36 – 7.12 (m, 8H), 6.91 (d, J = 6.0 Hz, 3H), 4.23 (s, 3H), 2.35 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.90, 144.77, 143.31, 138.64, 135.18, 134.02, 132.80, 132.22,132.00, 131.77, 130.42, 130.24, 129.98, 129.53, 129.10, 128.53, 127.71, 124.09, 122.40, 119.53, 112.09, 30.96, 21.43, 21.20. HRMS (ESI): calcd for $C_{32}H_{27}N_2^+$[M-BF_4]$^+$: 439.2169, found 439.2166. IR (neat): ν = 530, 697, 751, 818, 1057 (ν_{B-F}), 1163, 1276, 1336, 1383, 1429, 1471, 1497, 1605, 1634, 3060, 3426 cm^{-1}.

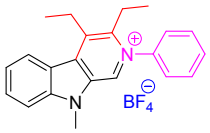
(3,4-bis(4-bromophenyl)-9-methyl-2-phenyl-9H-pyrido[3,4-b]indol-2-ium tetra-fluoroborate **(4d)**



Green solid (149.9 mg, 73%). M.p.: 175-177 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.07 (dd, J = 5.6, 2.3 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.71 (dd, J = 8.7, 7.3 Hz, 4H), 7.50 (d, J = 5.5 Hz, 3H), 7.43 – 7.28 (m, 7H), 6.95 (d, J = 8.2 Hz, 1H), 4.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.94, 143.40, 141.83, 135.31, 133.99, 133.00, 132.56, 132.54, 131.93, 131.69, 131.61, 131.22, 131.02, 130.69,

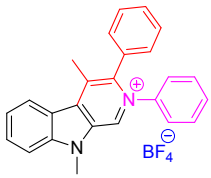
129.64, 127.73, 123.90, 123.21, 123.03, 122.73, 119.26, 112.32, 31.13. HRMS (ESI): calcd for $C_{30}H_{21}Br_2N_2^+[M\text{-}BF_4]^+$: 567.0066, found 567.0068. IR (neat): ν = 755, 1056 ($\nu_{B\text{-}F}$), 1276, 1336, 1390, 1429, 1469, 1495, 1593, 1632, 2338, 2364, 3096, 3421 cm^{-1}.

3,4-Diethyl-9-methyl-2-phenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4e)**



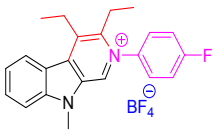
Green solid (101 mg, 80%). M.p.: 181-183 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.63 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.04 – 7.90 (m, 2H), 7.85 (dd, *J* = 6.9, 2.8 Hz, 2H), 7.81 – 7.75 (m, 3H), 7.58 (dd, *J* = 11.1, 4.0 Hz, 1H), 4.10 (s, 3H), 3.48 (q, *J* = 7.3 Hz, 2H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.46 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.61, 144.81, 142.97, 135.13, 134.71, 132.37, 131.96, 131.35, 130.30, 129.43, 127.07, 125.61, 122.71, 118.85, 111.91, 30.76, 22.92, 22.80, 14.43, 13.94. HRMS (ESI): calcd for $C_{22}H_{23}N_2^+$ $[M\text{-}BF_4]^+$: 315.1856, found 315.1859. IR (neat): ν = 698, 771, 1056 ($\nu_{B\text{-}F}$), 1271, 1333, 1382, 1503, 1600, 1633, 2937, 3398 cm^{-1}.

4,9-Dimethyl-2,3-diphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4f)**



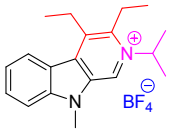
Green solid (109.6 mg, 80%). M.p.: 140-142 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.87 (s, 1H), 8.57 (d, *J* = 4.9 Hz, 1H), 8.07–7.94 (m, 2H), 7.65–7.55 (m, 3H), 7.46–7.35 (m, 8H), 4.21 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.20, 143.33, 142.57, 134.52, 132.07, 131.78, 131.79, 131.57, 131.06, 129.96, 129.74, 128.71, 128.37, 127.32, 127.32, 125.34, 122.28, 119.63, 111.55, 30.57, 17.51. HRMS (ESI): calcd for $C_{25}H_{21}N_2^+$ $[M\text{-}BF_4]^+$: 349.1699, found 349.1695. IR (neat): ν = 549, 703, 772, 1056 ($\nu_{B\text{-}F}$), 1158, 1340, 1378, 1426, 1474, 1493, 1601, 1634, 3055, 3415 cm^{-1}.

3,4-Diethyl-2-(4-fluorophenyl)-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetra-fluoroborate **(4g)**



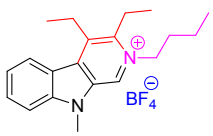
Green solid (149 mg, 92%). M.p.: 147-148 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.55 (s, 2H), 8.49 (s, 1H), 7.92 (s, 4H), 7.62 (s, 3H), 4.06 (s, 3H), 2.71 (d, *J* = 156.1 Hz, 4H), 1.44 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 162.78 (d, *J* = 246 Hz), 145.99, 145.15, 144.61, 138.72, 134.66, 134.22, 134.14, 131.91, 131.85,131.62, 131.58, 129.25, 129.11, 129.03, 125.10, 122.31, 122.22, 122.11, 118.36, 116.80, 116.56, 111.32, 30.12, 22.39, 22.24, 13.78, 13.35. HRMS (ESI): calcd for $C_{22}H_{22}FN_2^+$ $[M\text{-}BF_4]^+$: 333.1762, found 333.1763. IR (neat): *v* = 548, 701, 755, 784, 847, 1058 (ν $_{B\text{-}F}$), 1159, 1224, 1336, 1384, 1428, 1470, 1505, 1633, 3061, 3425 cm^{-1}.

3,4-Diethyl-2-isopropyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4h)**



Yellow solid (115.6 mg, 100%). M.p.: 158-160 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.73 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.89–7.70 (m, 2H), 7.46–7.35 (m, 1H), 5.47–5.34 (m, 1H), 4.16 (s, 3H), 3.39–3.24 (m, 4H), 1.81 (d, *J* = 6.5 Hz, 6H), 1.34 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 144.78, 143.38, 135.40, 134.76, 131.32, 130.38, 124.66, 124.45, 121.77, 118.30, 111.05, 58.17, 30.57, 23.31, 22.88, 21.21, 20.33, 14.29, 13.40. HRMS (ESI): calcd for $C_{19}H_{25}N_2^+$ $[M\text{-}BF_4]^+$: 281.2012, found 281.2016. IR (neat): *v* = 755, 1056 (ν $_{B\text{-}F}$), 1098, 1185, 1332, 1382, 1473, 1504, 1606, 1638, 2935, 2970, 3449 cm^{-1}.

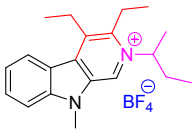
2-Butyl-3,4-diethyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4i)**



Yellow solid (120 mg, 100%). M.p.: 168-170 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.81 (s, 1H), 8.34 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.76 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 4.73 (s, 2H), 4.06 (s, 3H), 3.35 (d, *J* = 7.3 Hz, 2H), 3.21 (d, *J* = 7.3 Hz, 2H), 1.96 (s, 2H), 1.49 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.39 – 1.28 (m, 6H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR

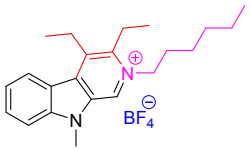
(100 MHz, DMSO) δ 145.12, 143.89, 135.54, 135.32, 131.81, 130.95, 128.62, 125.21, 122.29, 118.83, 111.58, 58.29, 34.25, 30.63, 22.91, 21.41, 19.70, 14.68, 14.01, 13.95. HRMS (ESI): calcd for $C_{20}H_{27}N_2^+$ $[M\text{-}BF_4]^+$: 295.2169, found 295.2170. IR (neat): ν = 755, 1059 ($\nu_{B\text{-}F}$), 1338, 1385, 1436, 1475, 1506, 1607, 1641, 2872, 2960, 3427 cm^{-1}.

2-(Sec-butyl)-3,4-diethyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4j)**



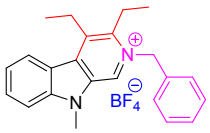
Yellow solid (120 mg, 100%). M.p.: 108-110 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.63 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.83 (m, 2H), 7.53 (dd, *J* = 10.9, 4.0 Hz, 1H), 5.20 (dd, *J* = 13.7, 6.8 Hz, 1H), 4.19 (s, 3H), 3.43 (d, *J* = 7.6 Hz, 2H), 3.32 (dd, *J* = 14.8, 7.3 Hz, 2H), 2.34 – 2.16 (m, 2H), 1.79 (d, *J* = 6.5 Hz, 3H), 1.38 (dt, *J* = 20.4, 7.4 Hz, 6H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.45, 144.39, 136.04, 135.35, 131.99, 131.01, 125.32, 124.66, 122.37, 118.88, 111.68, 63.74, 30.97, 30.23, 23.36, 22.09, 21.64, 14.69, 13.87, 10.73. HRMS (ESI): calcd for $C_{20}H_{27}N_2^+$ $[M\text{-}BF_4]^+$: 295.2169, found 295.2168. IR (neat): ν = 760, 1056 ($\nu_{B\text{-}F}$), 1342, 1387, 1440, 1469, 1503, 1614, 2880, 2954, 3440 cm^{-1}.

3,4-Diethyl-2-hexyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4k)**



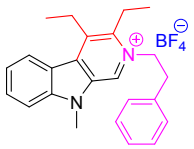
Yellow solid (128.8 mg, 100%). M.p.: 135-137 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.74 (m, 2H), 7.50 – 7.35 (m, 1H), 4.81 – 4.72 (m, 2H), 4.07 (s, 3H), 3.33 (q, *J* = 7.4 Hz, 2H), 3.20 (q, *J* = 7.3 Hz, 2H), 2.02 – 1.90 (m, 2H), 1.52 – 1.40 (m, 2H), 1.32 (ddd, *J* = 9.2, 6.8, 3.3 Hz, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.05, 143.77, 135.44, 135.28, 131.73, 130.84, 128.84, 125.11, 122.23, 118.79, 111.56, 58.32, 32.32, 31.23, 30.77, 25.94, 22.89, 22.45, 21.41, 14.70, 14.32, 13.93. HRMS (ESI): calcd for $C_{22}H_{31}N_2^+$ $[M\text{-}BF_4]^+$: 323.2482, found 323.2481. IR (neat): ν = 758, 1057 ($\nu_{B\text{-}F}$), 1193, 1337, 1384, 1477, 1505, 1605, 1639, 2859, 2929, 2958, 3425 cm^{-1}.

2-Benzyl-3,4-diethyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4l)**



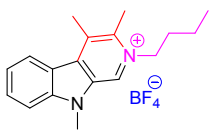
Green solid (130.7 mg, 100%). M.p.: 210-212 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.06 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.98–7.85 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (m, *J* = 14.3, 7.0 Hz, 3H), 7.24 (d, *J* = 7.1 Hz, 2H), 6.15 (s, 2H), 4.11 (s, 3H), 3.39 (m, 2H), 3.12 (m, *J* = 14.7, 7.2 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.06, 143.99, 135.93, 135.40, 135.12, 131.72, 131.11, 129.53, 129.18, 128.51, 126.55, 125.05, 122.11, 118.53, 111.37, 61.32, 30.37, 22.40, 21.37, 13.87, 13.59. HRMS (ESI): calcd for $C_{23}H_{25}N_2^+$ [[M-BF_4]$^+$: 329.2012, found 329.2015. IR (neat): *v* = 703, 737, 762, 1059 (ν $_{B-F}$), 1165, 1188, 1284, 1337, 1379, 1454, 1478, 1505, 1606, 1641, 2939, 3421 cm^{-1}.

3,4-Diethyl-9-methyl-2-phenethyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4m)**



Yellow solid (135 mg, 100%). M.p.: 190-192ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.86 (s, 1H), 8.40 (t, *J* = 7.1 Hz, 1H), 7.96–7.83 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.27 (s, 5H), 4.98 (t, *J* = 7.5 Hz, 2H), 4.06 (s, 3H), 3.34 (m, 4H), 3.07 (q, *J* = 7.3 Hz, 2H), 1.31 (dt, *J* = 21.4, 7.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 144.91, 143.77, 136.57, 135.03, 134.91, 131.58, 130.72, 129.20, 128.64, 128.34, 127.13, 124.95, 122.00, 118.56, 111.32, 58.60, 37.35, 30.28, 22.52, 20.94, 14.13, 13.55. HRMS (ESI): calcd for $C_{24}H_{27}N_2^+$ [M-BF_4]$^+$: 343.2169, found 343.2170. IR (neat): *v* = 699, 740, 1059 (ν $_{B-F}$), 1164, 1195, 1269, 1339, 1387, 1478, 1505, 1605, 1643, 2936, 2969, 3423 cm^{-1}.

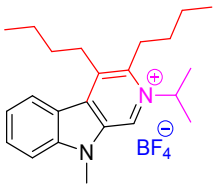
2-Butyl-3,4,9-trimethyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4n)**



Yellow solid (112 mg, 100%). M.p.: 162-164 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.83

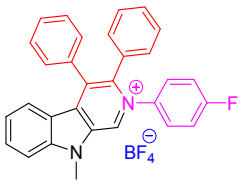
(s, 1H), 8.48 (d, J = 8.1 Hz, 1H), 7.94–7.78 (m, 2H), 7.46 (t, J = 7.2 Hz, 1H), 4.86–4.70 (m, 2H), 4.05 (s, 3H), 2.93 (s, 3H), 2.83 (s, 3H), 1.90 (dt, J = 15.3, 7.7 Hz, 2H), 1.44 (dt, J = 14.7, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 145.05, 140.13, 134.87, 131.70, 131.19, 130.38, 127.85, 125.50, 121.93, 119.61, 111.38, 59.00, 32.71, 30.62, 19.60, 16.96, 15.71, 13.99. HRMS (ESI): calcd for $C_{18}H_{23}N_2^+$ [M-BF_4]$^+$: 267.1856, found 267.1854. IR (neat): v = 755, 1052 ($\nu_{B\text{-}F}$), 1113, 1334, 1396, 1477, 1505, 1607, 1642, 2867, 2940, 3406 cm^{-1}.

3,4-Dibutyl-2-isopropyl-9-methyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4o)**



Yellow solid (122.6 mg, 92%). M.p.: 154-156 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.62 (d, J = 7.1 Hz, 1H), 8.30 (t, J = 7.1 Hz, 1H), 8.01–7.80 (m, 2H), 7.58–7.42 (m, 1H), 5.76 (d, J = 7.2 Hz, 2H), 5.37 (d, J = 6.5 Hz, 1H), 4.17 (d, J = 7.1 Hz, 3 H), 3.35 (d, J = 21.4 Hz, 2H), 1.78 (d, J = 6.3 Hz, 6H), 1.69–1.47 (m, 8H), 1.05–0.94 (m, 6H). ^{13}C NMR (100 MHz, DMSO) δ 144.98, 142.42, 135.48, 133.82, 131.53, 130.68, 124.64, 124.38, 122.01, 118.59, 111.32, 58.33, 55.05, 31.67, 30.92, 30.51, 29.41, 27.62, 23.38, 22.44, 22.20, 13.86, 13.68. HRMS (ESI): calcd for $C_{23}H_{33}N_2^+$ [M-BF_4]$^+$: 337.2638, found 337.2637. IR (neat): v = 750, 1059 ($\nu_{B\text{-}F}$), 1333, 1383, 1471, 1504, 1607, 1639, 2867, 2930, 2959, 3423 cm^{-1}.

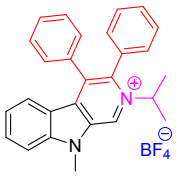
2-(4-Fluorophenyl)-9-methyl-3,4-diphenyl-9H-pyrido[3,4-b]indol-2-ium tetra-fluoroborate **(4p)**



Green solid (150.7 mg, 93%). M.p.: 147-148 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.88 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 2.6 Hz, 2H), 7.51 – 7.23 (m, 10H), 7.14 (s, 3H), 6.89 (d, J = 8.0 Hz, 1H), 4.27 (s, 3H). ^{13}C NMR

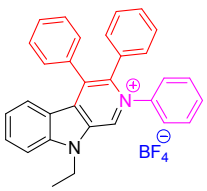
(100 MHz, DMSO) δ 162.07 (d, J = 246 Hz), 145.49, 142.79, 139.44, 134.76, 134.29, 133.29, 132.44, 131.60, 131.38, 130.03, 129.76, 129.66, 129.13, 128.92, 128.87, 127.46, 123.54, 121.98, 118.95, 116.02, 115.78, 111.68, 30.50. HRMS (ESI): calcd for $C_{30}H_{22}FN_2^+$ $[M\text{-}BF_4]^+$: 429.1762, found 429.1764. IR (neat): v = 548, 701, 755, 784, 847, 1058 ($\nu_{B\text{-}F}$), 1159, 1224, 1336, 1384, 1428, 1470, 1505, 1633, 3061, 3425 cm^{-1}.

2-Isopropyl-9-methyl-3,4-diphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4q)**



Yellow solid (145.8 mg, 100%). M.p.: 138-140 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.11 (s, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 4.3 Hz, 2H), 7.47 – 7.30 (m, 8H), 7.18 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 4.82 – 4.69 (m, 1H), 4.36 (s, 3H), 1.75 (d, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 145.67, 142.24, 136.47, 135.23, 134.12, 132.44, 132.10, 131.17, 130.60, 130.20, 129.52, 129.15, 128.97, 125.56, 123.78, 122.07, 119.39, 111.95, 60.91, 31.31, 23.10, 20.80. HRMS (ESI): calcd for $C_{27}H_{25}FN_2^+$ $[M\text{-}BF_4]^+$: 377.2012, found 377.2011. IR (neat): v = 705, 756, 1059 ($\nu_{B\text{-}F}$), 1335, 1381, 1438, 1469, 1502, 1606, 1633, 2975, 3421 cm^{-1}.

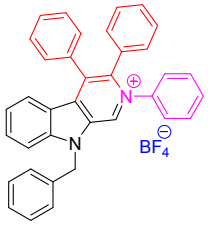
9-Ethyl-2,3,4-triphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4r)**



Green solid (149.61 mg, 93%). M.p.: 140-142 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.07 (s, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.90–7.82 (m, 1H), 7.69 (d, J = 5.3 Hz, 2H), 7.44 (d, J = 14.2 Hz, 9H), 7.26 (dd, J = 20.0, 12.5 Hz, 3H), 7.09 (s, 2H), 6.88 (d, J = 7.8 Hz, 1H), 4.85 (d, J = 6.4 Hz, 2H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ

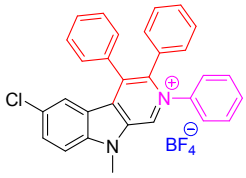
144.48, 143.23, 142.82, 134.47, 133.91, 133.51, 132.48, 131.69, 131.52, 131.49, 129.99, 129.70, 129.24, 129.04, 128.94, 127.42, 123.82, 122.00, 119.24, 111.72, 38.69, 14.25. HRMS (ESI): calcd for $C_{31}H_{25}N_2^+$ $[M\text{-}BF_4]^+$: 425.2012, found 425.2014. IR (neat): ν = 701, 764, 1058 ($\nu_{B\text{-}F}$), 1269, 1336, 1387, 1456, 1494, 1631, 2364, 3423 cm^{-1}.

9-Benzyl-2,3,4-triphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4s)**



Green solid (171.35 mg, 95%). M.p.: 143-145 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.68 (d, J = 6.3 Hz, 2H), 7.48–7.30 (m, 15H), 7.24 (t, J = 7.6 Hz, 1H), 7.11–7.08 (m, 3H), 6.88 (d, J = 8.2 Hz, 1H), 6.11 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 144.85, 143.37, 143.23, 136.33, 134.81, 134.42, 133.64, 132.56, 131.92, 131.49, 131.47, 130.03, 129.65, 129.26, 129.08, 129.01, 128.96, 128.90, 128.01, 127.43, 127.33, 127.26, 123.81, 122.25, 119.42, 112.25. HRMS (ESI): calcd for $C_{36}H_{27}N_2^+$ $[M\text{-}BF_4]^+$: 487.2169, found 487.2170. IR (neat): ν = 548, 701, 753, 1057 ($\nu_{B\text{-}F}$), 1179, 1336, 1386, 1449, 1494, 1601, 1630, 3059, 3423 cm^{-1}.

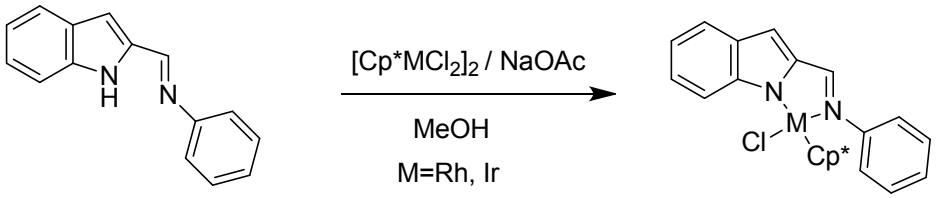
6-Chloro-9-methyl-2,3,4-triphenyl-9H-pyrido[3,4-b]indol-2-ium tetrafluoroborate **(4u)**



Green solid (135.50 mg, 81%). M.p.: 147-148 ºC. ^{1}H NMR (400 MHz, DMSO) δδ 10.22 – 10.02 (m, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.91 (s, 1H), 7.71 (s, 2H), 7.52 – 7.40 (m, 8H), 7.35 (s, 3H), 7.10 (d, J = 2.4 Hz, 3H), 6.70 (d, J = 1.5 Hz, 1H), 4.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 144.33, 143.55, 143.37, 135.70, 134.52, 134.12, 132.62, 131.92, 131.75, 131.70, 131.23, 130.99, 130.51, 129.57, 129.48, 129.43, 127.87, 127.72, 126.49, 122.82, 120.35, 114.25, 100.00, 31.40. HRMS (ESI): calcd

for $C_{36}H_{27}N_2^+$ $[M\text{-}BF_4]^+$: 445.1466, found 445.1467. IR (neat): ν = 550, 703, 766, 1057 ($\nu_{B\text{-}F}$), 1135, 1434, 1472, 1497, 1602, 1633, 3059, 3413 cm^{-1}.

Circle metallization reaction for the synthesis of 6



5 **6**

a: Rh
b: Ir

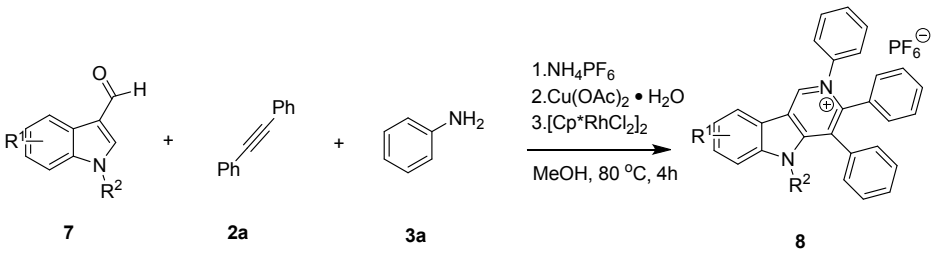
A mixture of $[Cp^*MCl_2]_2$ (0.5 equiv), **5** (1.0 equiv), and sodium acetate (2.0 equiv) in methanol (10 mL) was stirred for 30 min at room temperature. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of petrol ether/ethyl acetate as the eluent. The products were recrystallized from CH_2Cl_2 at room temperature to afford **6** as red crystals.

6a (M=Rh): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.13–7.08 (m, 1H), 7.03 (s, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 1.52 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.78, 154.77, 147.54, 147.14, 129.30, 129.25, 127.06, 123.76, 123.39, 123.09, 115.81, 115.58, 111.15, 87.91, 9.23.

6b (M=Ir): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.18–7.12 (m, 1H), 7.10 (s, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 1.50 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.85, 151.10, 146.35, 146.05, 131.09, 129.15, 127.28, 124.35, 123.48, 123.22, 118.36, 115.12, 111.01, 86.70, 9.22.

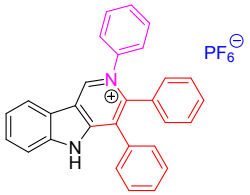
Synthesis of γ -carbolinium salts 8

General Procedure B



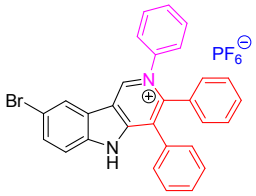
A sealed tube contained $[RhCp^*Cl_2]_2$ (0.6 mol %, 0.00206 mmol), NH_4PF_6 (0.688 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.688 mmol) was evacuate and purged with nitrogen gas three times. Then, **1a** (0.344 mmol), **2a** (0.413 mmol) and **3a** (0.688 mmol) in MeOH (5.0 mL) were added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 80°C for 4 h. When the reaction was completed, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a Celite pad and the Celite pad was washed several times with CH_2Cl_2 (5 mL). The combined filtrate was concentrated in vacuo and the residue was purified by column chromatography on neutral Al_2O_3 using DCM/MeOH (30:1) as eluent to afford the desired pure product **8**.

2,3,4-Triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate **(8a)**



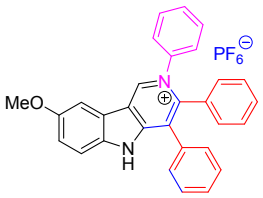
Green solid (177 mg, 95%). M.p.: 216-218 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.79 (s, 1H), 8.41 (d, J = 7.7 Hz, 1H), 7.68 – 6.98 (m, 17H), 6.59 (d, J = 53.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 154.32, 152.81, 144.36, 143.66, 137.01, 134.06, 133.31, 131.79, 129.63, 129.44, 128.89, 128.80, 128.36, 127.82, 127.69, 124.52, 123.27, 121.96, 121.49, 121.28, 118.69. ^{31}P NMR (162 MHz, DMSO) δ -143.03 (sep, J_{F-P} = 711.18 Hz; PF_6). ^{19}F NMR (376 MHz, DMSO) δ -70.14 (d, J_{F-P} = 711.26 Hz; PF_6). HRMS (ESI): calcd for $C_{29}H_{21}N_2^+$ $[M\text{-}PF_6]^+$: 397.1699, found 397.1696. IR (neat): ν = 557, 698, 760, 790, 841, 1030, 1113, 1230, 1357, 1397, 1436, 1489, 1595, 1635, 3059, 3421 cm^{-1}.

8-Bromo-2,3,4-triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate **(8b)**



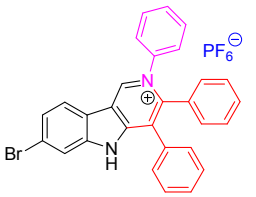
Green solid (156 mg, 73%). M.p.: 174-176 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.75 (s, 1H), 8.62 (s, 1H), 7.70–6.87 (m, 18H). ^{13}C NMR (101 MHz, DMSO) δ 153.85, 151.37, 143.81, 143.21, 137.17, 133.93, 132.85, 131.38, 130.31, 130.03, 129.09, 128.94, 128.31, 128.16, 127.78, 127.39, 127.23, 125.01, 124.48, 124.04, 120.05, 119.64, 112.62. ^{31}P NMR (162 MHz, DMSO) δ -143.11 (sep, J_{F-P} = 711.34 Hz; PF_6). HRMS (ESI): calcd for $C_{29}H_{20}BrN_2^+$ [M-PF_6]$^+$: 475.0804, found 475.0805. IR (neat): ν = 556, 698, 760, 842, 1224, 1303, 1445, 1488, 1590, 1637, 3060, 3420 cm^{-1}.

8-Methoxy-2,3,4-triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate **(8c)**



Green solid (126 mg, 64%). M.p.: 182-184 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.73 (s, 1H), 8.02 (s, 1H), 7.72 – 6.91 (m, 17H), 6.60 (d, J = 51.4 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 154.91, 153.97, 147.42, 143.71, 143.47, 137.10, 134.18, 133.36, 131.81, 130.63, 129.52, 129.42, 128.84, 128.71, 128.29, 127.77, 127.66, 124.51, 123.85, 121.37, 119.29, 117.45, 104.04, 55.93. ^{31}P NMR (162 MHz, DMSO) δ -142.93 (sep, J_{F-P} = 711.50 Hz; PF_6). HRMS (ESI): calcd for $C_{30}H_{23}N_2O^+$ [M-PF_6]$^+$: 427.1804, found 427.1802. IR (neat): ν = 558, 698, 754, 841, 1028, 1153, 1217, 1261, 1298, 1387, 1436, 1491, 1592, 1635, 2957, 3059, 3421 cm^{-1}.

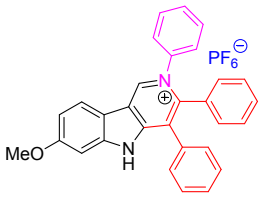
7-Bromo-2,3,4-triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate (**8d**)



Green solid (118 mg, 55%). M.p.: 174-176 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.74 (s, 1H), 8.34 (d, J = 8.3 Hz, 1H), 7.77 (s, 1H), 7.55 (d, J = 6.4 Hz, 2H), 7.48–7.19 (m,

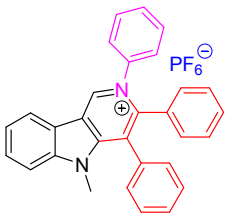
12H), 7.07–7.03 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ 159.34, 154.95, 143.54, 142.01, 135.46, 135.32, 133.54, 131.70, 130.92, 128.83, 128.72, 128.02, 127.50, 127.20, 126.89, 124.58, 123.17, 122.83, 121.98, 121.00, 120.50, 119.98. ^{31}P NMR (162 MHz, DMSO) δ -143.11 (sep, J_{F-P} = 711.83 Hz; PF_6). HRMS (ESI): calcd for $C_{29}H_{20}BrN_2^+$ [M-PF_6]$^+$: 475.0804, found 475.0803. IR (neat): *v*=556, 697, 760, 801, 843, 902, 1047, 1075, 1123, 1168, 1214, 1244, 1296, 1331, 1355, 1401, 1429, 1490, 1519, 1588, 1636, 2851, 2921, 3058, 3419 cm^{-1}.

7-Methoxy-2,3,4-triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate **(8e)**



Green solid (134 mg, 68%). M.p.: 162-164 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.62 (s, 1H), 8.28 (s, 1H), 7.70 – 6.53 (m, 19H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 159.80, 154.33, 143.27, 134.76, 133.87, 132.95, 131.34, 130.33, 129.01, 128.91, 128.37, 128.18, 127.81, 127.32, 127.16, 123.53, 122.19, 121.10, 116.10, 110.70, 100.76, 55.36. ^{31}P NMR (162 MHz, DMSO) δ -143.05 (sep, J_{F-P} = 711.83 Hz; PF_6). HRMS (ESI): calcd for $C_{30}H_{23}N_2O^+$ [M-PF_6]$^+$: 427.1805, found 427.1803. IR (neat): *v* = 699, 843, 1115, 1153, 1434, 1458, 1615, 3423 cm^{-1}.

5-Methyl-2,3,4-triphenyl-5H-pyrido[4,3-b]indol-2-ium hexafluorophosphate **(8f)**



Green solid (176 mg, 92%). M.p.: M.p.: 223-225 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.28 (d, *J* = 3.5 Hz, 1H), 8.62 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.0 Hz, 3H), 7.47 – 7.40 (m, 5H), 7.39 – 7.34 (m, 3H), 7.26 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.09 – 7.03 (m, 3H), 3.38 (s, 3H). ^{13}C NMR (100 MHz,

DMSO) δ 149.27, 144.70, 143.92, 143.16, 139.16, 132.86, 132.12, 131.54. 131.45, 130.38, 130.24, 129.55, 129.39, 129.29, 128.56, 127.96, 127.70, 124.19, 123.24, 122.63, 120.50, 119.92, 112.33, 32.67. IR (neat): ν = 699, 843, 1115, 1153, 1434, 1458, 1615, 3423 cm^{-1}. ^{31}P NMR (162 MHz, DMSO) δ -143.08 (sep, J_{F-P} = 711.02 Hz; PF_6). HRMS (ESI): calcd for $C_{30}H_{23}N_2^+$ $[M-PF_6]^+$: 411.1856, found 411.1851. IR (neat): ν = 557, 700, 765, 789, 840, 1082, 1139, 1246, 1367, 1414, 1451, 1495, 1560, 1599, 1637, 3057, 3419 cm^{-1}.

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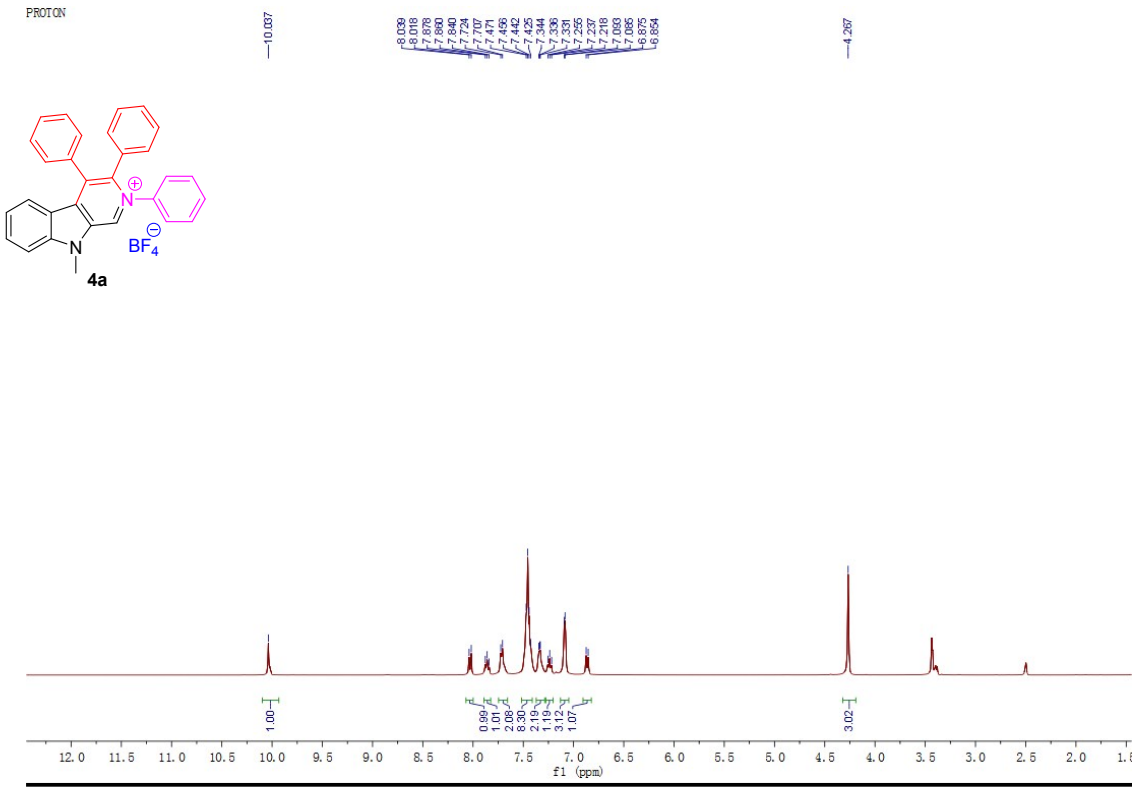
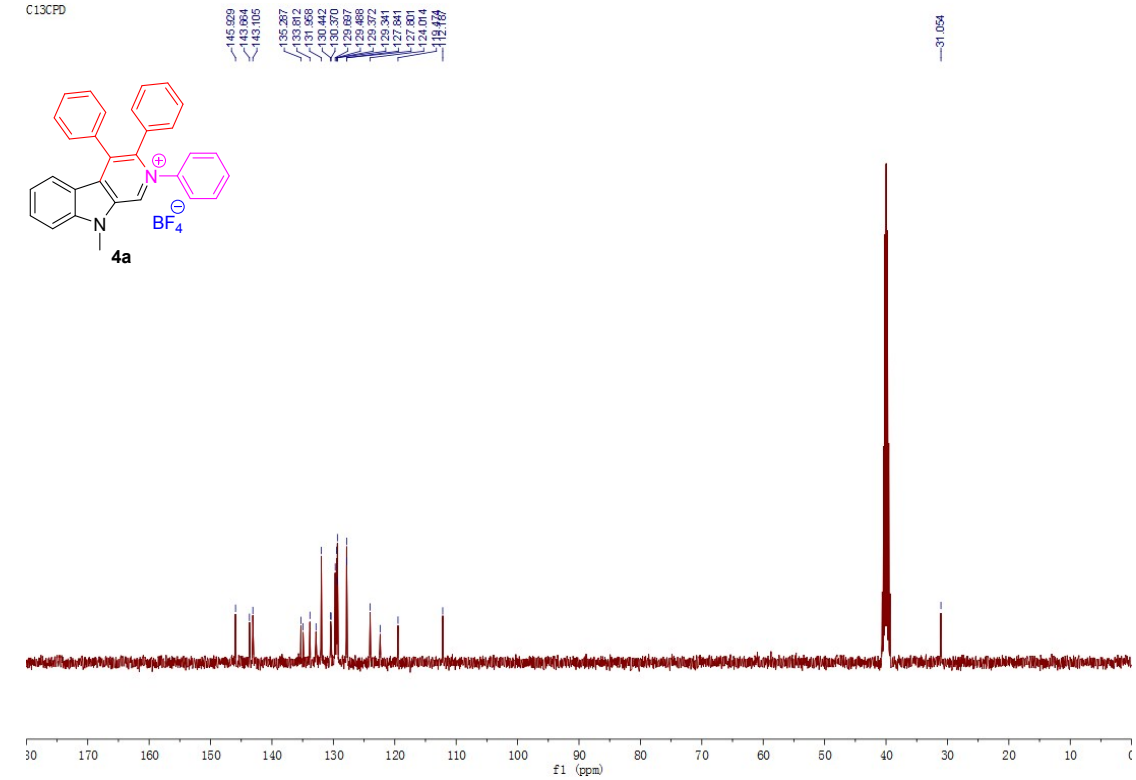
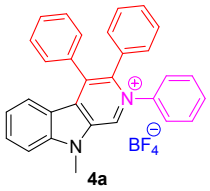
NMR Spectra


PROTON
10.037
8.039
8.018
7.878
7.860
7.840
7.724
7.707
7.471
7.456
7.442
7.425
7.344
7.336
7.331
7.255
7.237
7.218
7.093
7.085
6.875
6.854
4.267
BF4
4a
1.00
0.99
1.01
2.08
8.30
2.19
1.19
3.12
1.07
3.02
f1 (ppm)

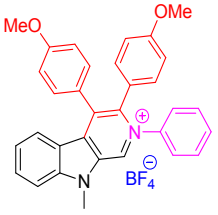

C13CPD
145.929
143.864
143.105
135.287
133.812
131.958
130.442
130.370
129.687
129.466
129.372
129.341
127.841
127.801
124.014
31.054
BF4
4a
f1 (ppm)

F19CPD

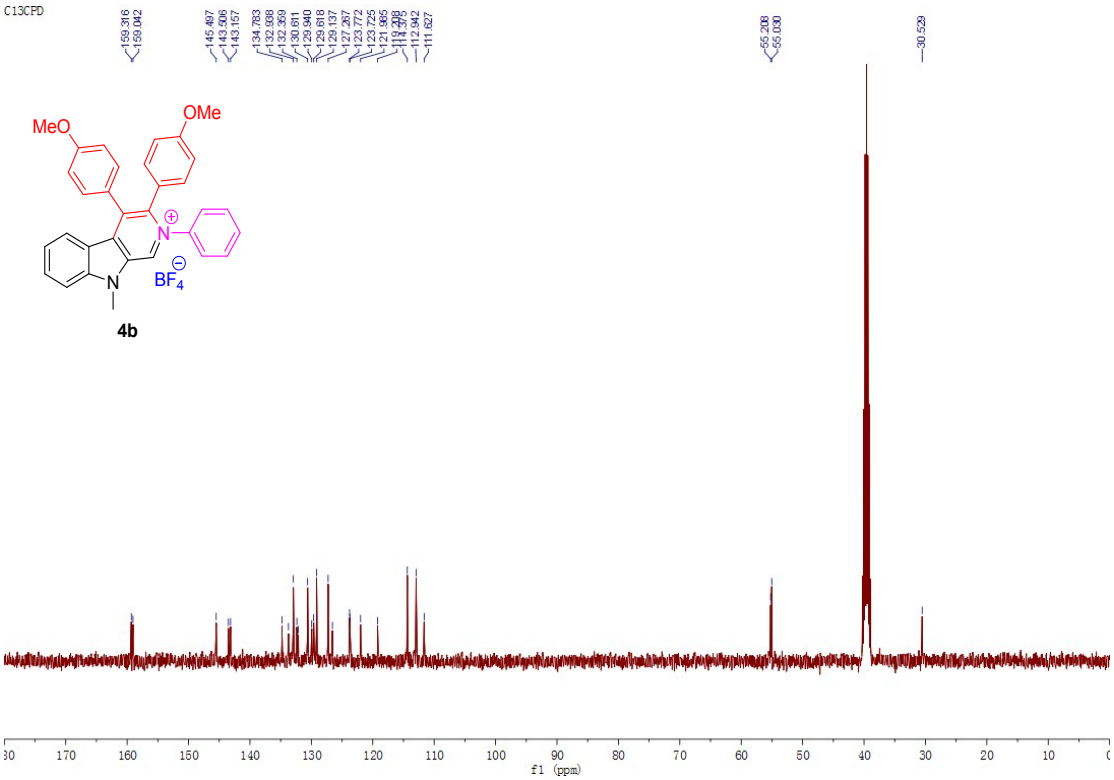


4a

PROTON



4b


C13CPD
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159.042
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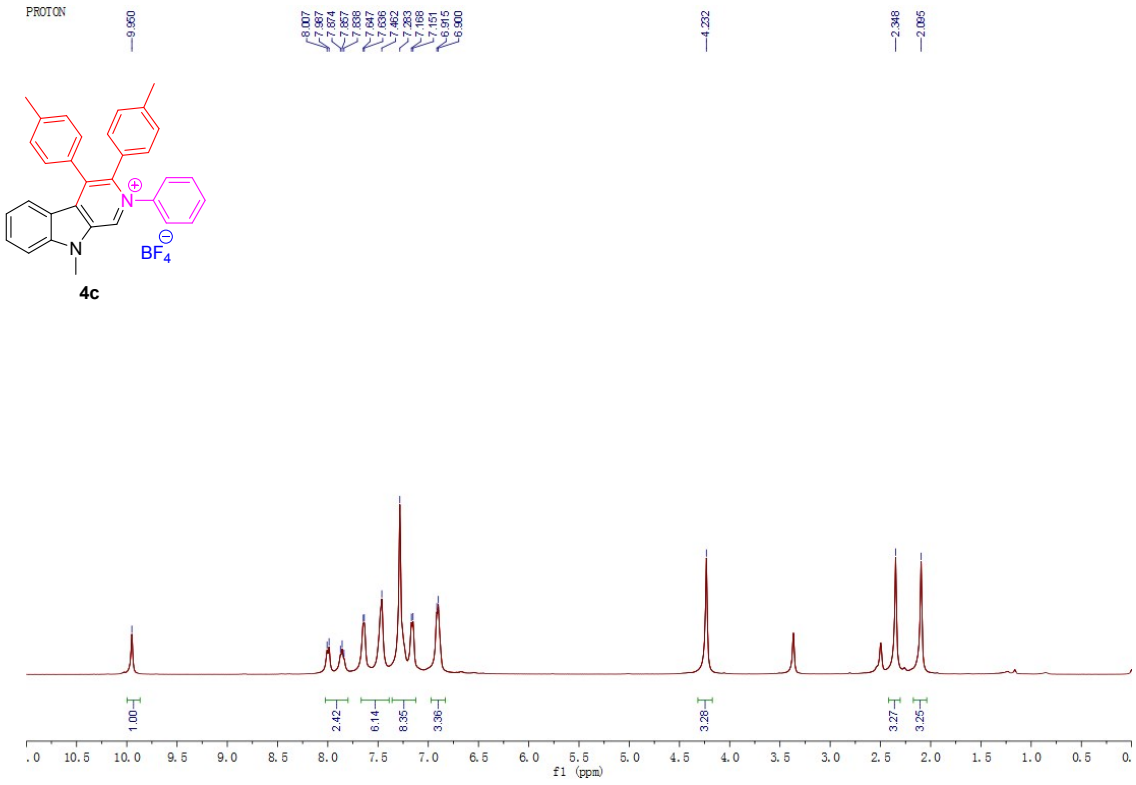
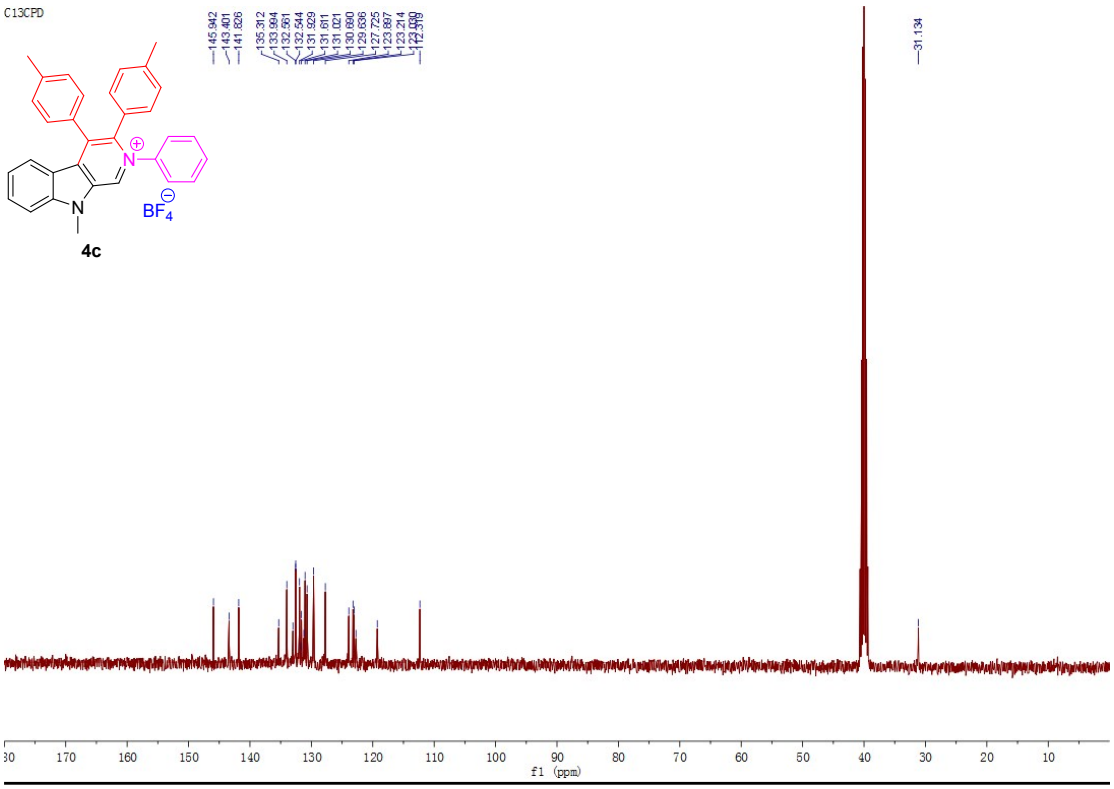
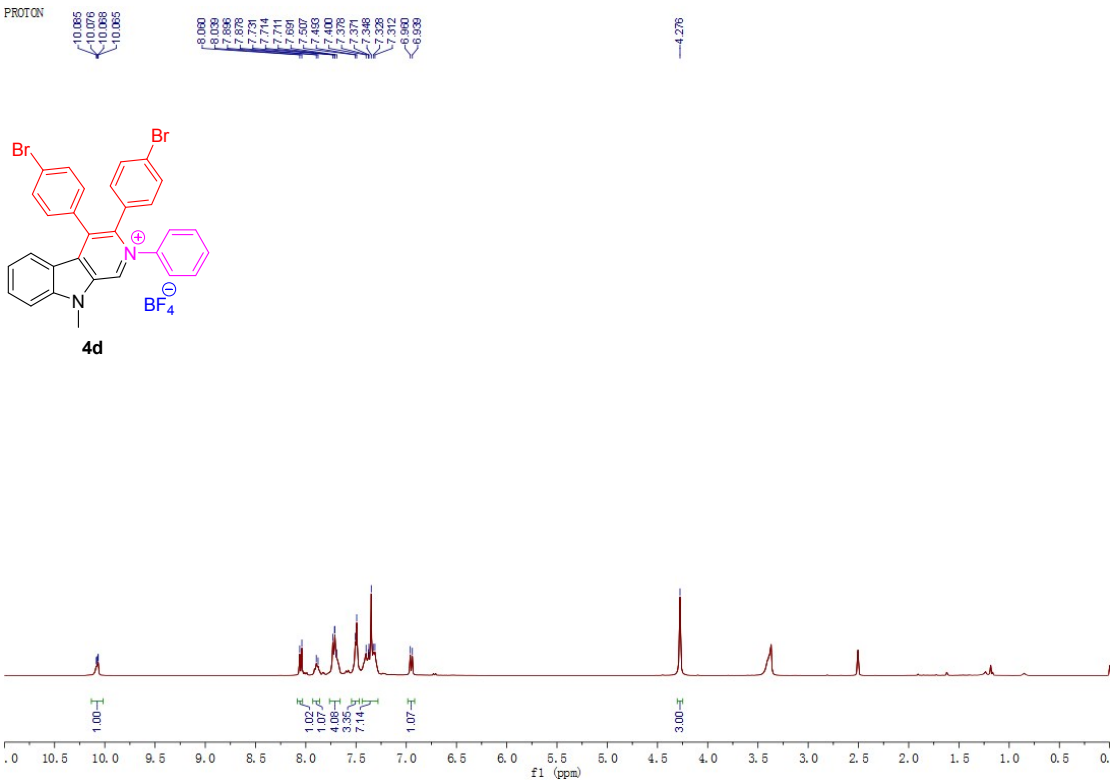
143.506
143.157
134.783
132.998
132.369
130.891
129.940
129.618
129.137
127.267
123.772
123.725
121.385
112.942
111.627
55.208
55.000
30.529
MeO
OMe
N
BF4
N
4b
f1 (ppm)

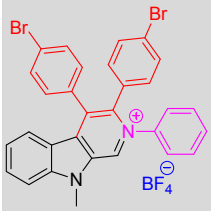

PROTON
9.950
9.007
7.877
7.874
7.867
7.838
7.647
7.636
7.462
7.283
7.168
7.151
6.915
6.900
4.232
2.348
2.095
N
BF4
N
4c
1.00
2.42
6.14
8.35
3.36
3.28
3.27
3.25
f1 (ppm)


C13CPD
145.942
145.401
141.826
135.312
133.994
132.661
132.544
131.929
131.651
131.101
130.990
129.636
127.725
123.897
123.214
31.134
f1 (ppm)

4c


PROTON
10.085
10.076
10.068
10.065
8.060
8.039
7.896
7.893
7.733
7.714
7.711
7.691
7.507
7.493
7.400
7.378
7.371
7.348
7.332
7.312
6.990
6.939
4.276
1.00
1.02
1.07
4.08
3.35
7.14
1.07
3.00
f1 (ppm)

4d

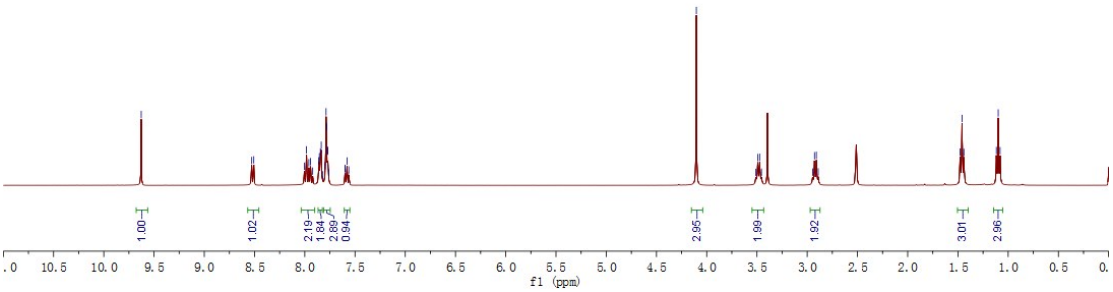

Br
Br
N
BF4
N

4d


PROTON
9.628
8.528
8.508
8.003
7.963
7.959
7.942
7.921
7.860
7.855
7.845
7.836
7.824
7.798
7.788
7.783
7.774
7.771
7.762
7.600
7.597
7.580
7.562
4.103
3.510
3.492
3.473
3.455
2.946
2.928
2.909
2.890
1.478
1.459
1.441
1.118
1.099
1.080

N
BF4
N

4e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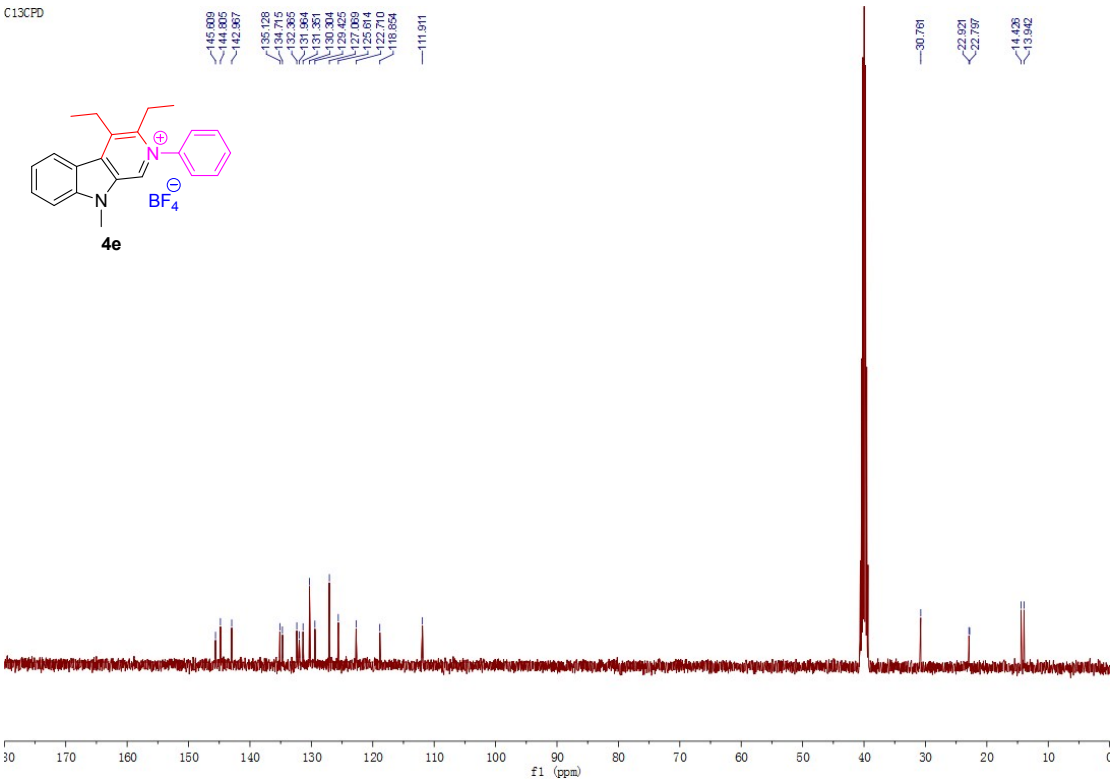
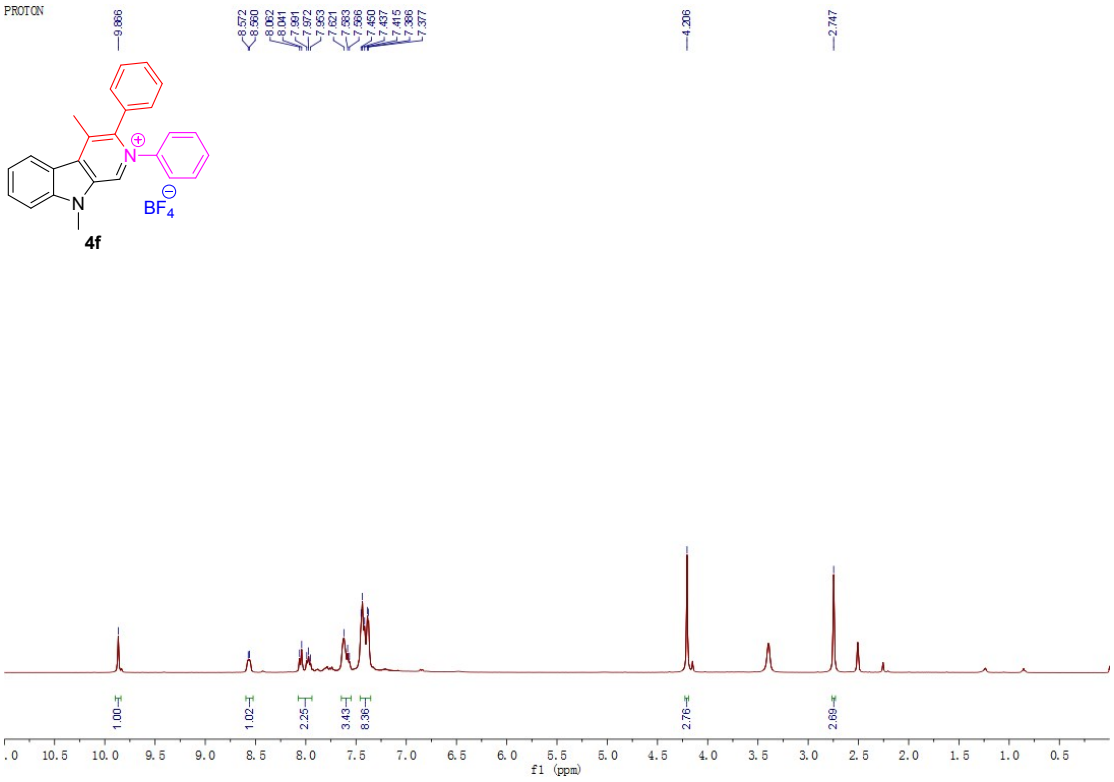
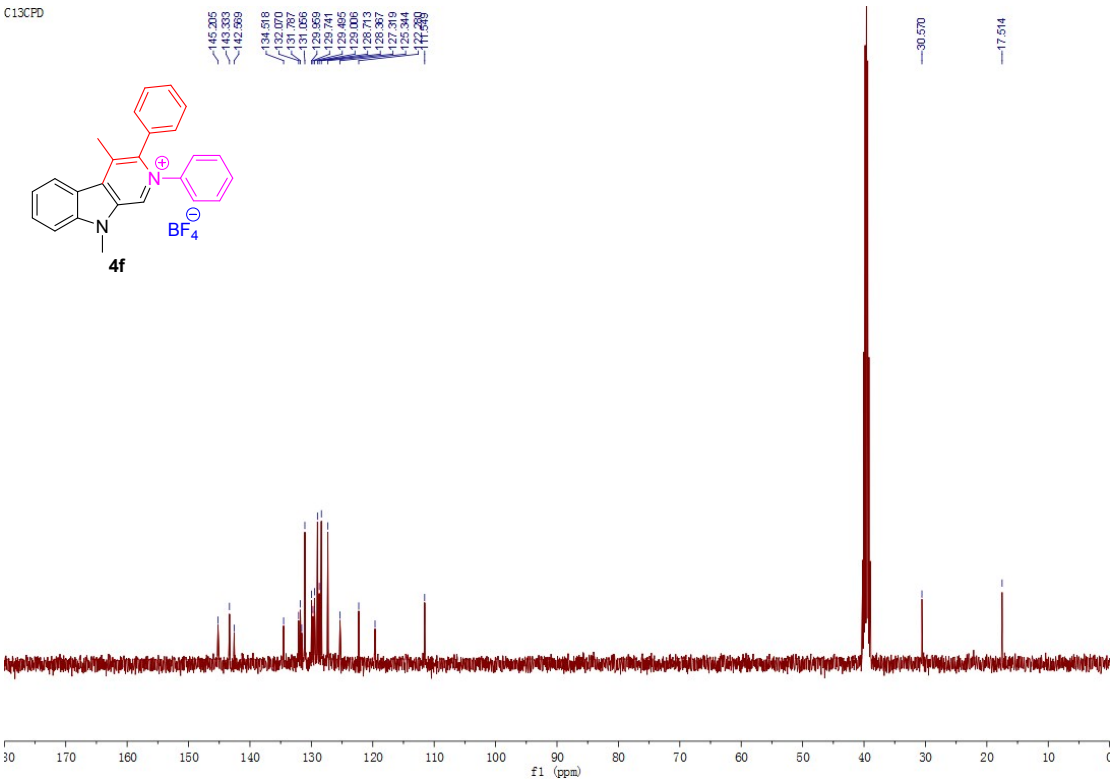
2.19
1.84
2.89
0.94
2.95
1.99
1.92
3.01
2.96
f1 (ppm)


C13CPD
145.609
144.805
142.967
135.128
134.715
132.365
131.964
131.351
130.304
129.425
127.069
125.814
122.710
118.654
111.911
30.761
22.921
22.797
14.426
13.942
BF4
4e
f1 (ppm)


PROTON
9.866
8.572
8.560
8.062
8.041
7.991
7.972
7.953
7.621
7.583
7.566
7.450
7.437
7.415
7.396
7.377
4.206
2.747
BF4
4f
1.00
1.02
2.25
3.43
8.36
2.76
2.69
f1 (ppm)


C13CPD
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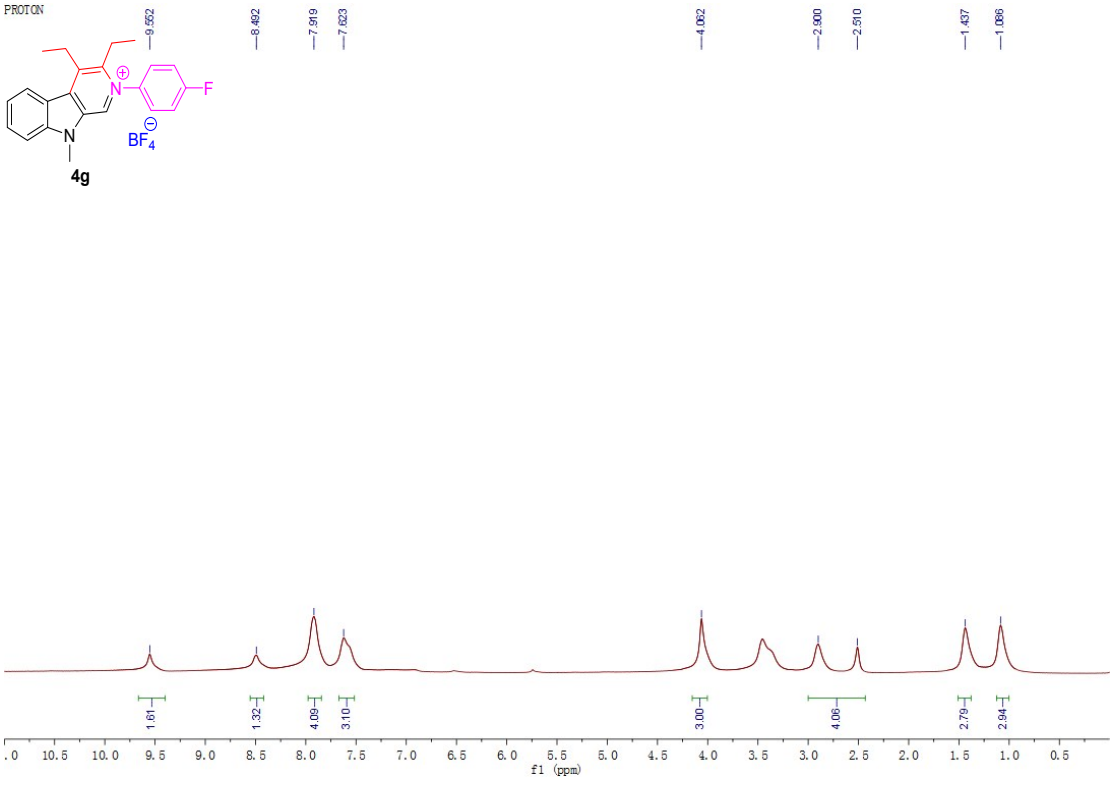
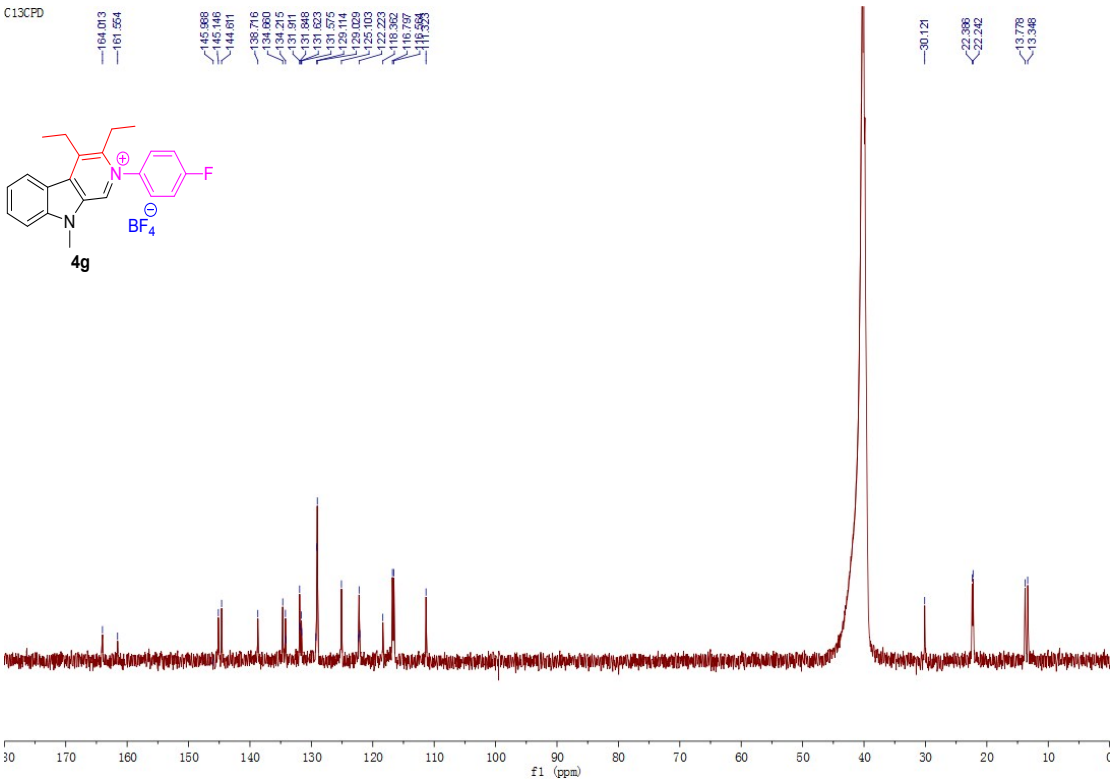
143.303
142.569
134.518
132.070
131.787
131.056
129.959
129.741
129.485
129.006
128.713
128.387
127.319
125.344
122.289
111.549
30.570
17.514
BF4
4f
f1 (ppm)


PROTON
9.562
8.482
7.919
7.623
4.062
2.900
2.510
1.437
1.066
F
BF4
4g
1.61
1.32
4.09
3.10
3.00
4.06
2.79
2.94
f1 (ppm)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161.564
145.968
145.146
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134.215
131.911
131.848
131.623
131.575
129.114
129.029
125.103
122.223
118.992
116.797
116.594
111.323
30.121
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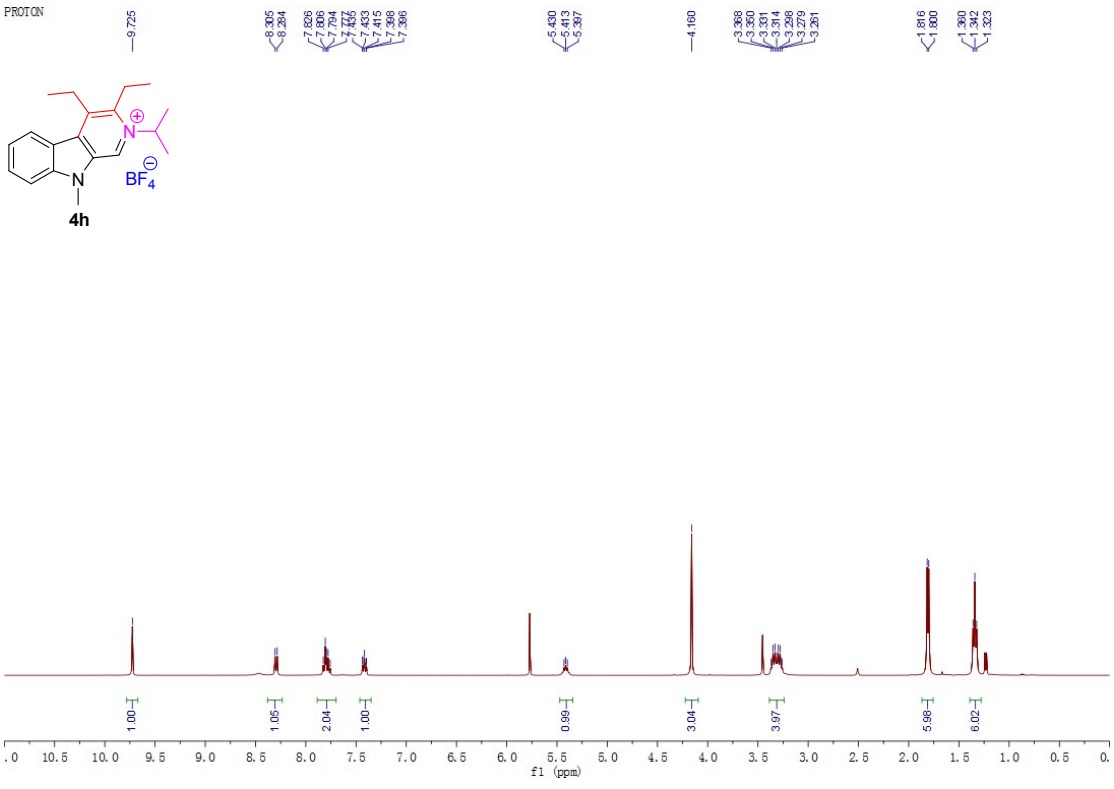
22.242
13.778
13.348
F
BF4
N
f1 (ppm)

4g


PROTON
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8.284
7.826
7.806
7.794
7.477
7.455
7.433
7.415
7.398
7.396
5.430
5.413
5.397
4.160
3.368
3.350
3.331
3.314
3.298
3.279
3.261
1.816
1.800
1.360
1.342
1.323
BF4
N
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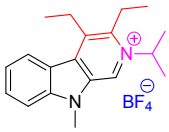
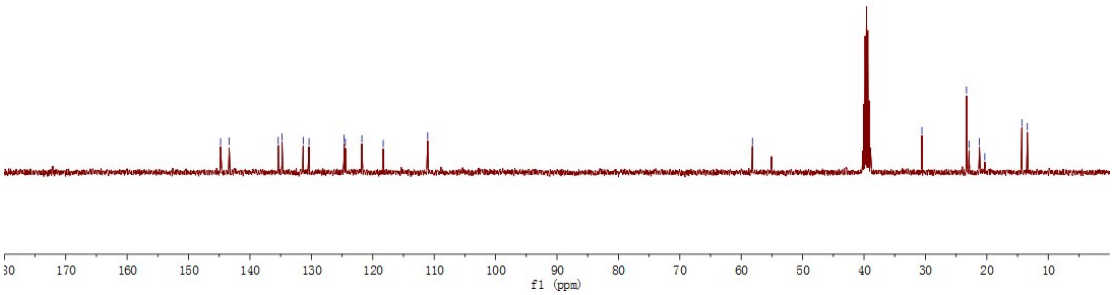
1.00
0.99
3.04
3.97
5.98
6.02
f1 (ppm)

4h

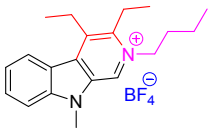
C13CPD



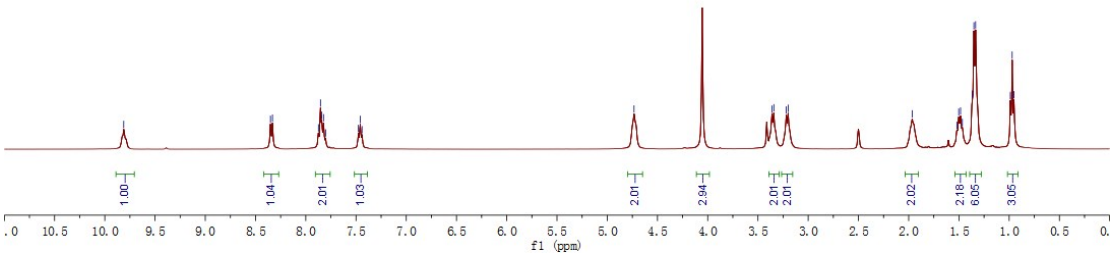
4h

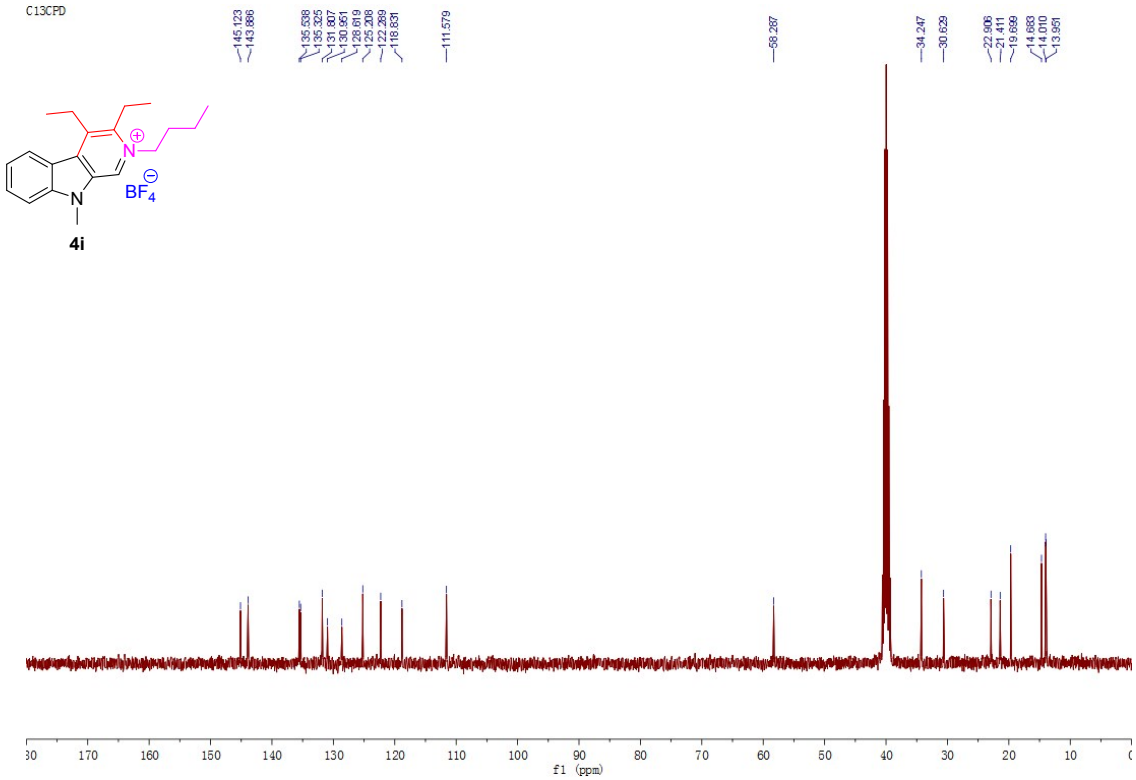


PROTON



4i

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135.255
131.907
130.951
128.619
125.208
122.289
118.831
111.579
58.287
34.247
30.629
22.906
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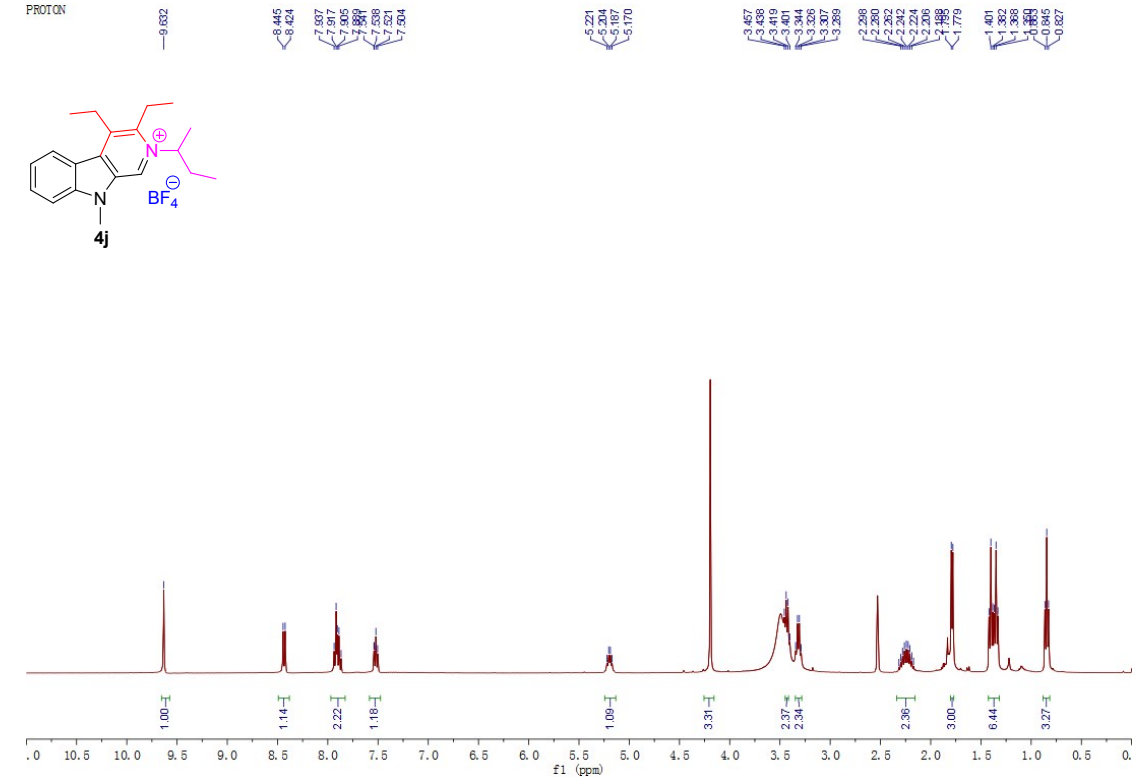
19.699
14.683
14.010
13.951
BF4
4i
f1 (ppm)


PROTON
9.632
8.445
8.424
7.997
7.977
7.905
7.538
7.521
7.504
5.221
5.204
5.187
5.170
3.457
3.438
3.419
3.401
3.344
3.326
3.307
3.289
2.298
2.280
2.262
2.242
2.224
2.206
1.779
1.401
1.382
1.368
0.845
0.827
BF4
4j
1.00
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2.22
1.18
1.09
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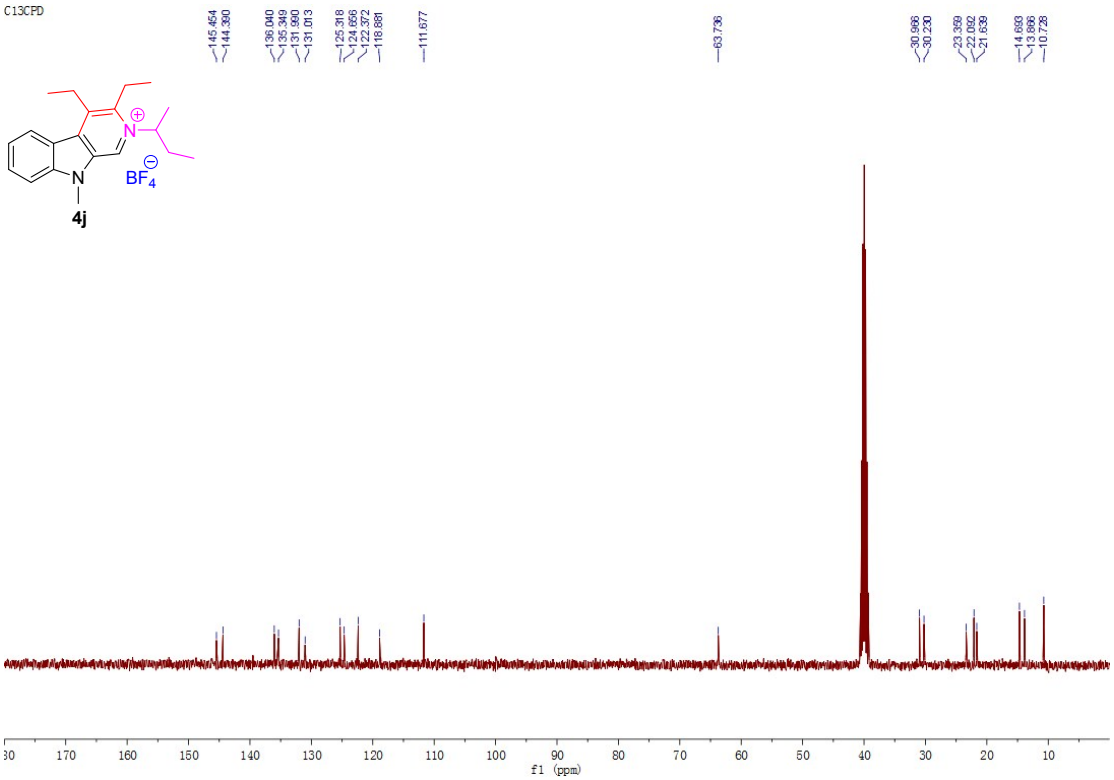
2.36
3.00
6.44
3.27
f1 (ppm)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131.360
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125.316
124.666
122.372
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13.866
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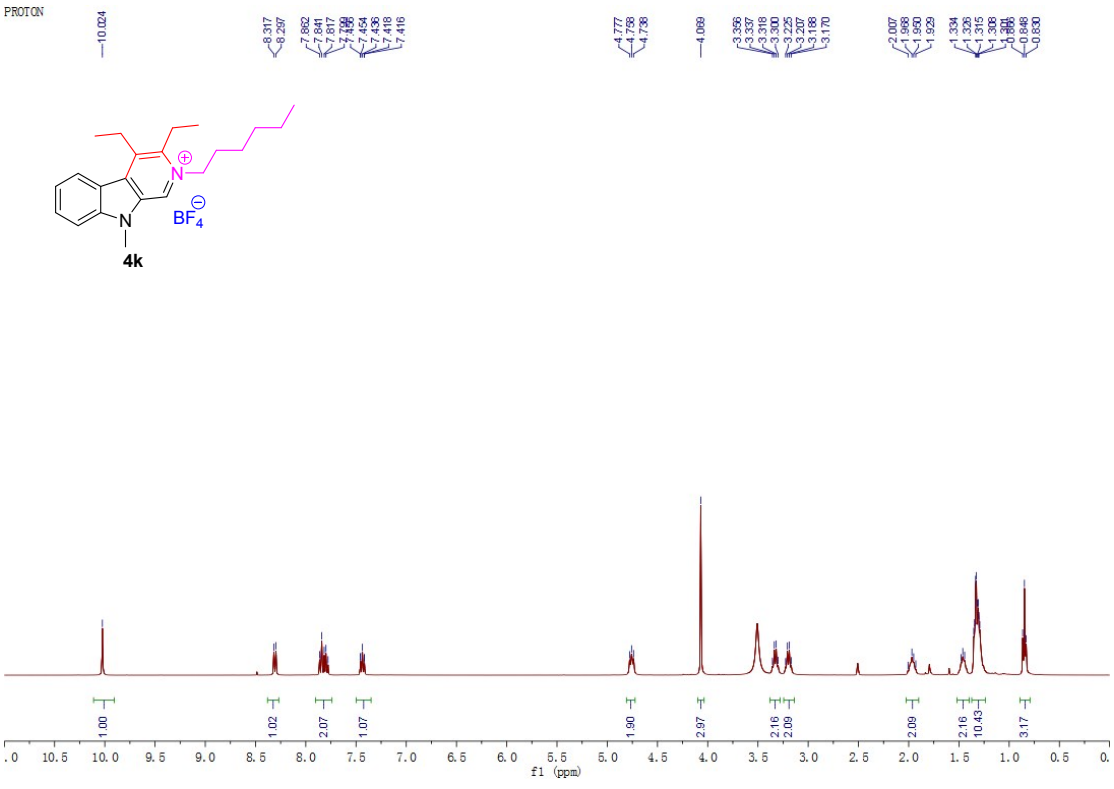
BF4
4j
f1 (ppm)


PROTON
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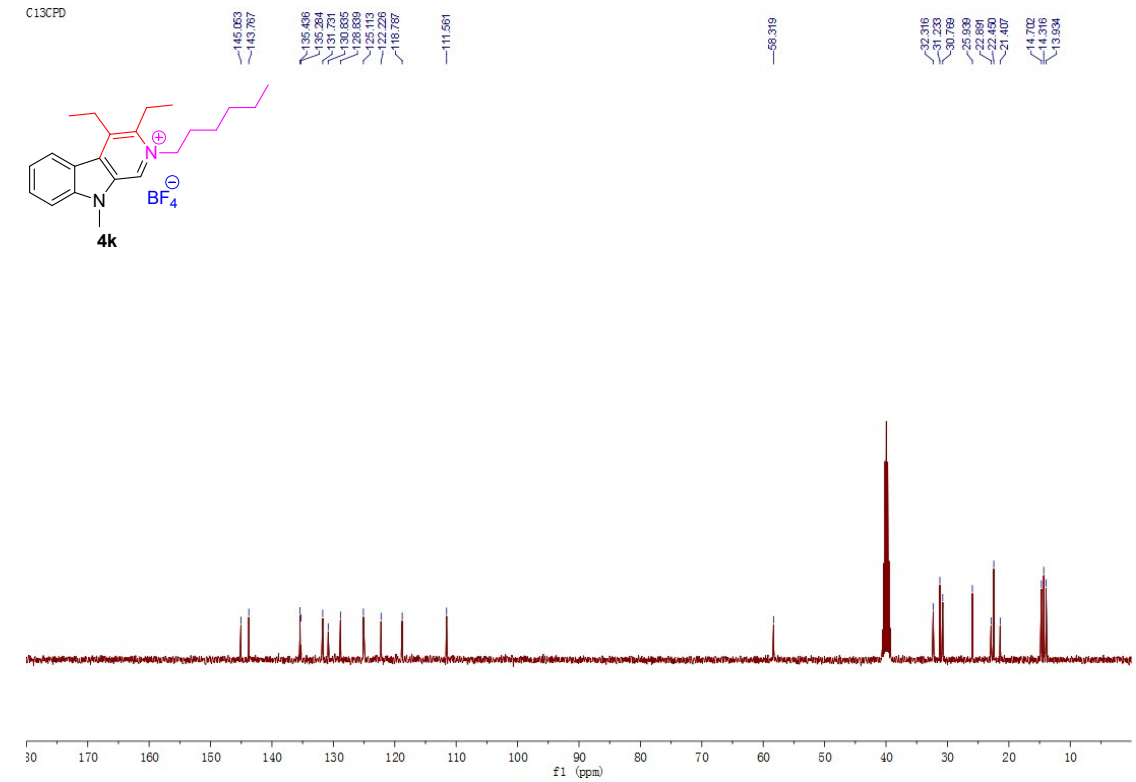
7.841
7.817
7.454
7.436
7.418
7.416
4.777
4.758
4.738
4.069
3.356
3.337
3.318
3.300
3.225
3.207
3.188
3.170
2.007
1.998
1.990
1.929
1.334
1.326
1.315
1.308
0.846
0.830
BF4
4k
1.00
1.02
2.07
1.07
1.90
2.97
2.16
2.09
2.09
2.16
10.43
3.17
f1 (ppm)


C13CPD
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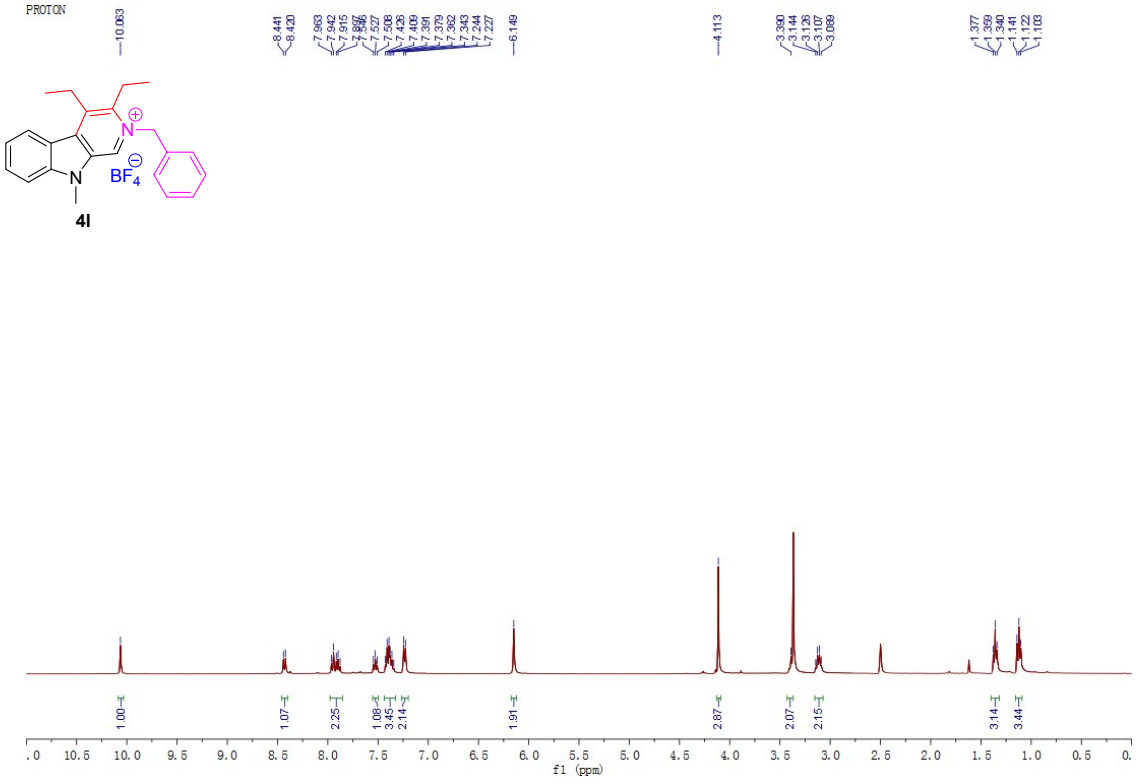
135.436
135.284
131.757
130.835
128.839
125.113
122.226
118.787
111.561
58.319
32.316
31.233
30.789
25.939
22.891
22.450
21.407
14.702
14.316
13.934
BF4
4k
f1 (ppm)


PROTON
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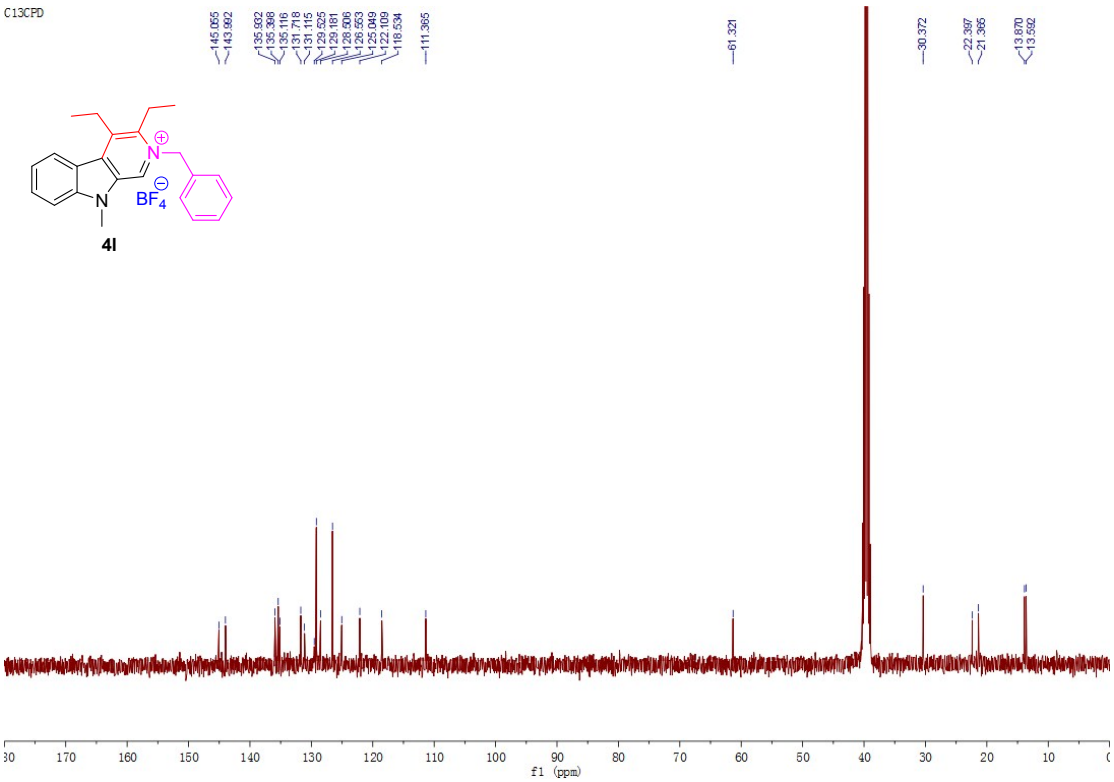
8.441
8.420
7.963
7.940
7.915
7.607
7.596
7.527
7.508
7.439
7.409
7.391
7.379
7.362
7.343
7.244
7.227
6.149
4.113
3.900
3.144
3.135
3.107
3.089
1.377
1.359
1.340
1.141
1.122
1.103
BF4
4l
1.00
1.07
2.25
1.08
3.45
2.14
1.91
2.87
2.07
2.15
3.14
3.44
f1 (ppm)


C13CPD
145.055
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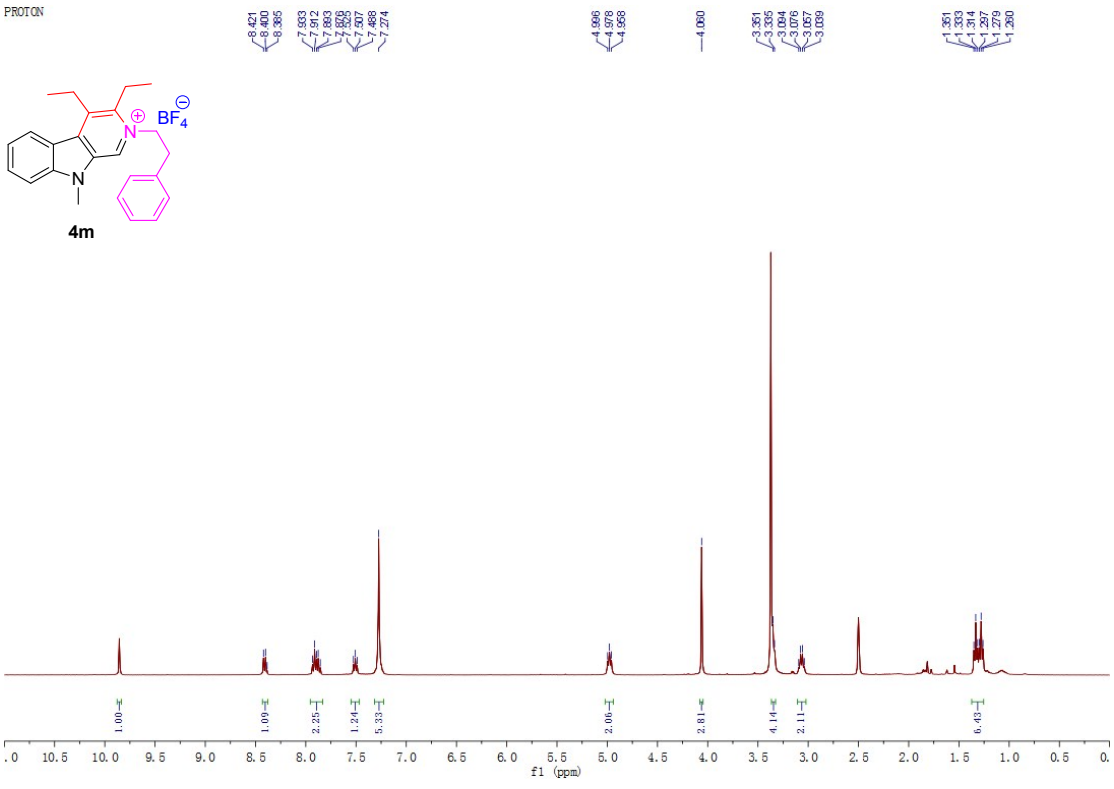
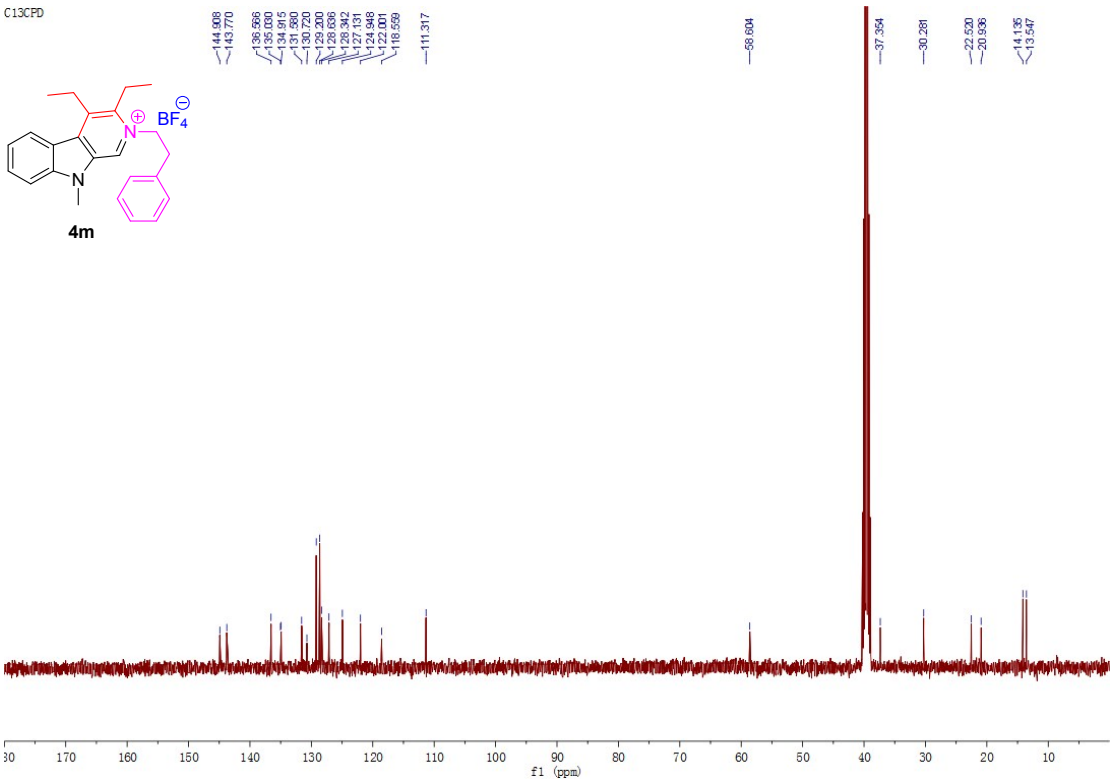
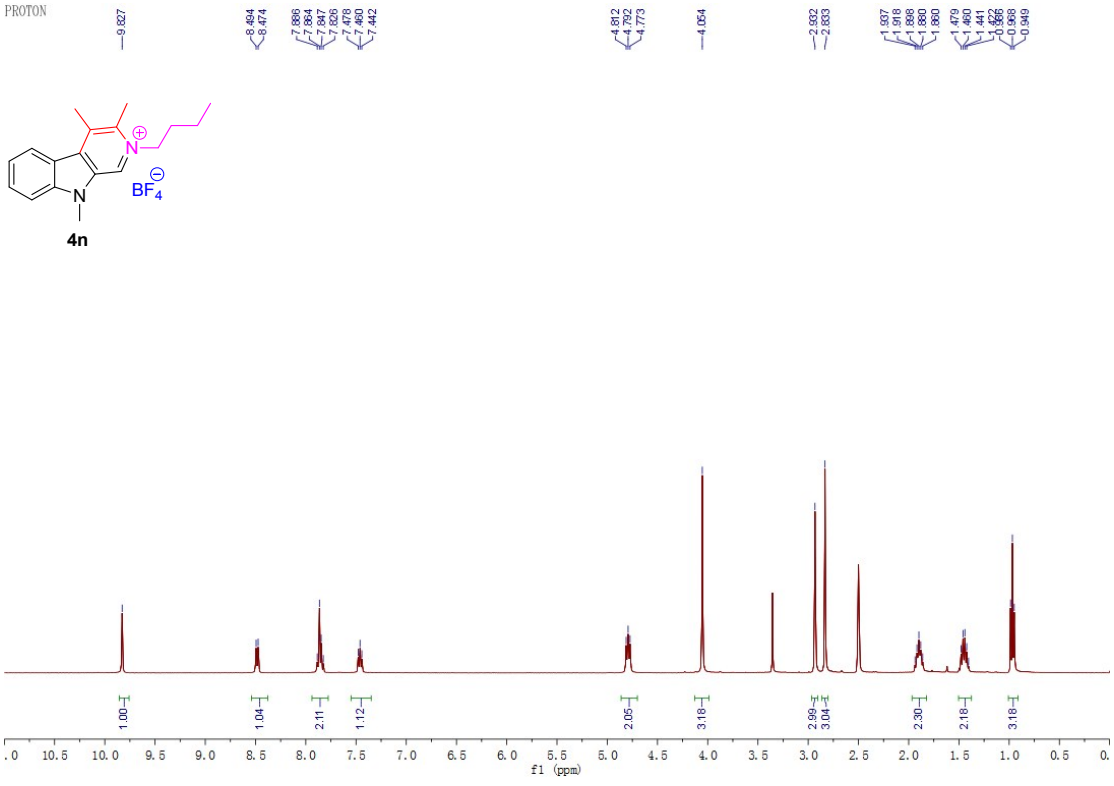
135.992
135.368
135.116
131.778
131.115
129.525
129.181
128.806
126.553
125.049
122.109
118.534
111.365
61.321
30.372
22.397
21.365
13.870
13.592
BF4
N
4l
f1 (ppm)

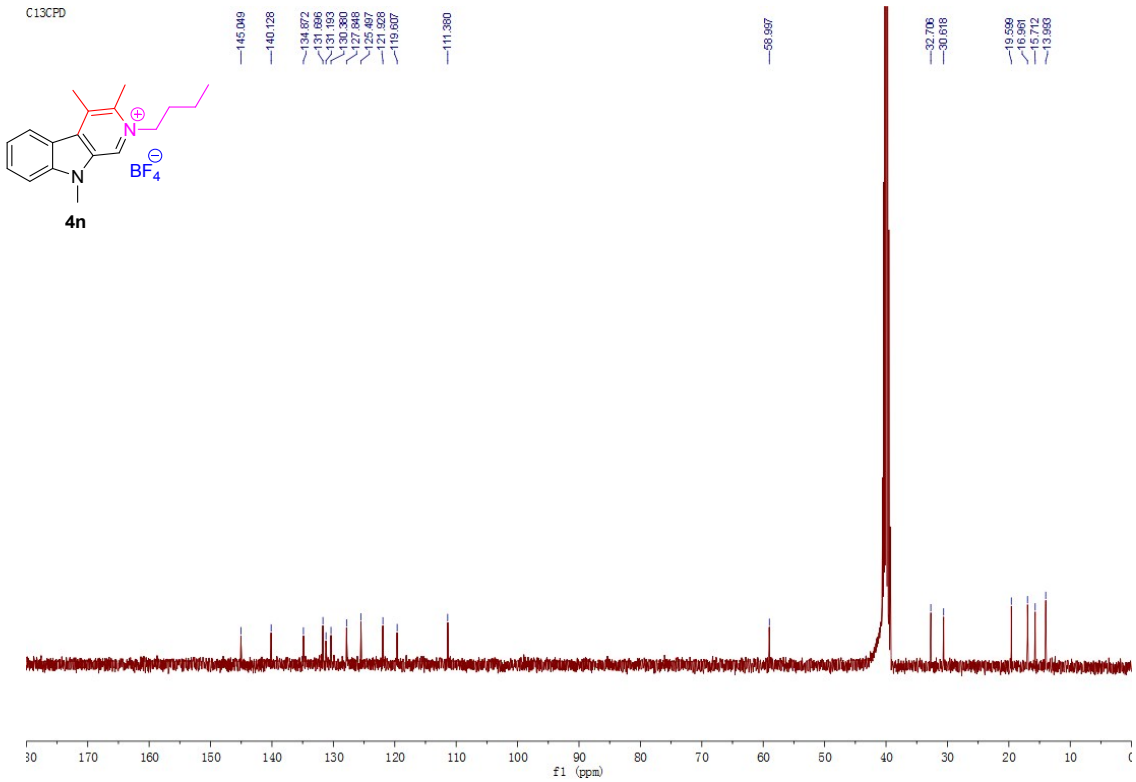

PROTON
8.421
8.400
8.385
7.933
7.912
7.883
7.528
7.507
7.488
7.274
4.996
4.978
4.958
4.060
3.351
3.335
3.094
3.076
3.057
3.039
1.351
1.333
1.314
1.297
1.279
1.260
BF4
N
4m
1.00
1.09
2.25
1.24
5.33
2.06
2.81
4.14
2.11
6.43
f1 (ppm)

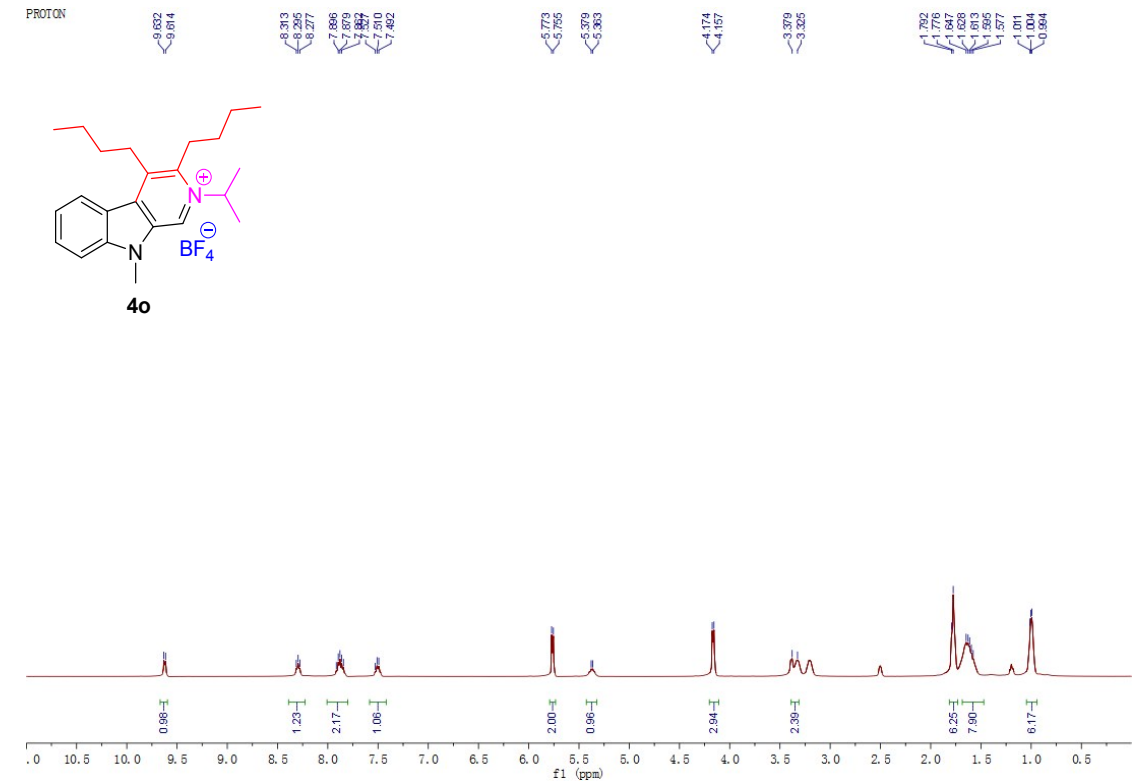

C13CPD
144.908
143.770
136.866
135.000
134.915
131.680
130.720
129.200
128.636
128.342
127.131
124.948
122.001
116.559
111.317
58.604
37.354
30.281
22.520
20.936
14.135
13.547
BF4
N
f1 (ppm)

4m

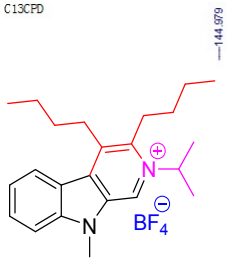

PROTON
9.827
8.494
8.474
7.886
7.864
7.847
7.826
7.478
7.460
7.442
4.812
4.792
4.773
4.054
2.932
2.833
1.997
1.918
1.898
1.880
1.860
1.479
1.460
1.441
1.422
0.988
0.968
0.949
BF4
N
1.00
1.04
2.11
1.12
2.05
3.18
2.99
3.04
2.30
2.18
3.18
f1 (ppm)

4n

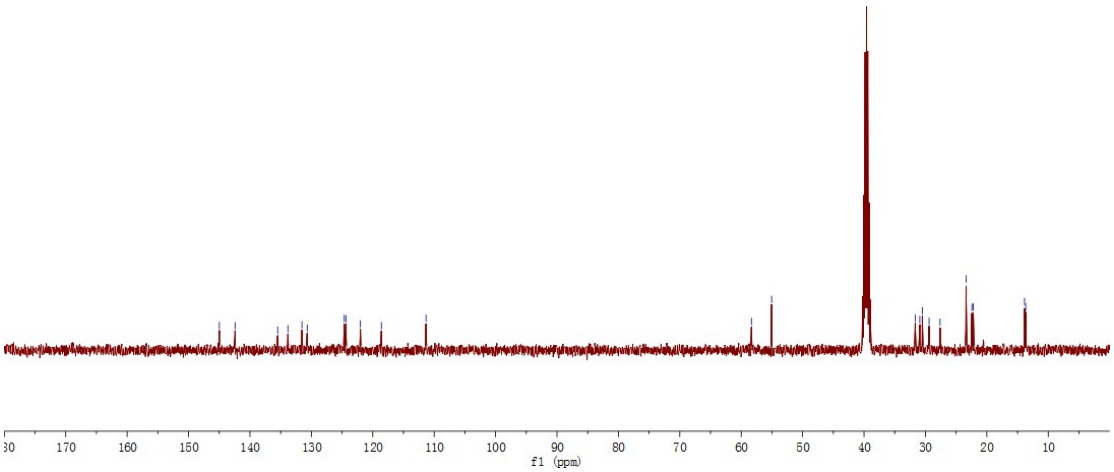

C13CPD
145.049
140.128
134.672
131.865
131.193
130.380
127.848
125.497
121.928
119.607
111.380
58.997
32.706
30.618
19.539
16.961
15.712
13.993
BF4
4n
f1 (ppm)


PROTON
9.632
9.614
8.313
8.295
8.277
7.886
7.879
7.873
7.867
7.510
7.492
5.773
5.755
5.379
5.363
4.174
4.157
3.379
3.325
1.792
1.776
1.647
1.628
1.613
1.595
1.577
1.011
1.004
0.984
BF4
4o
0.98
1.23
2.17
1.06
2.00
0.96
2.94
2.39
6.25
7.90
6.17
f1 (ppm)

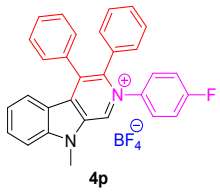
C13CPD



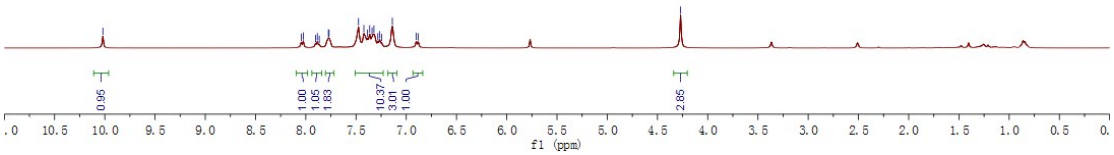
4o

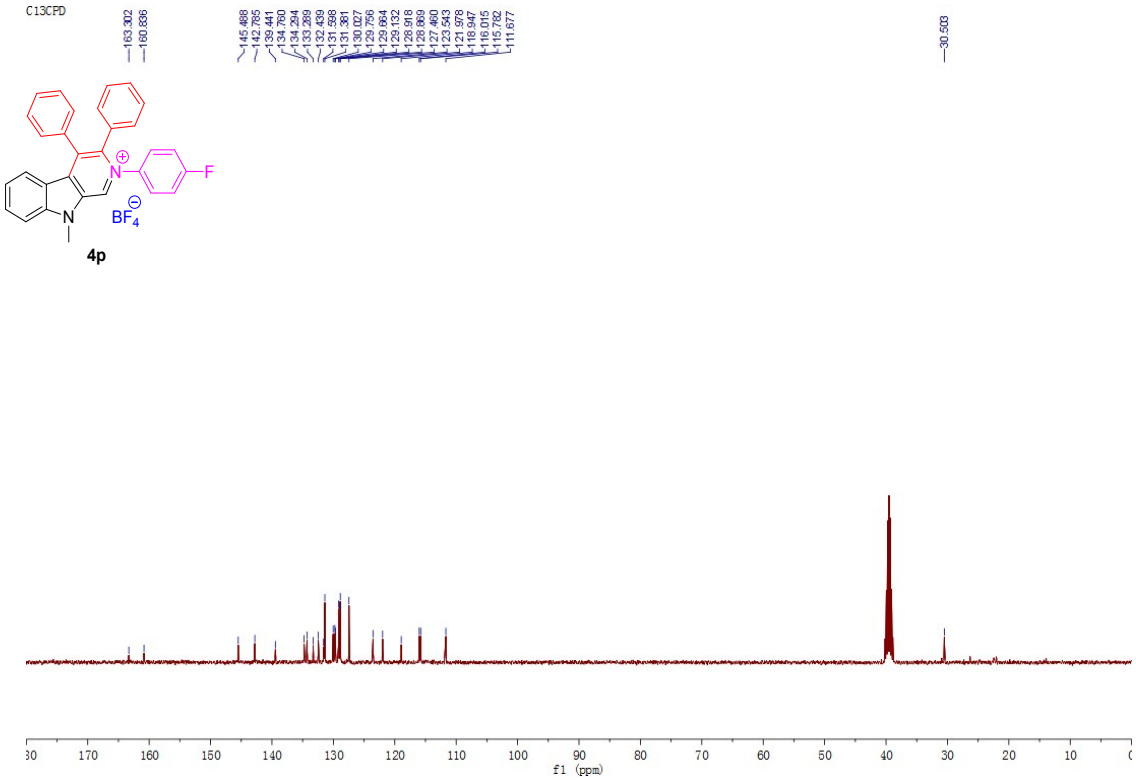


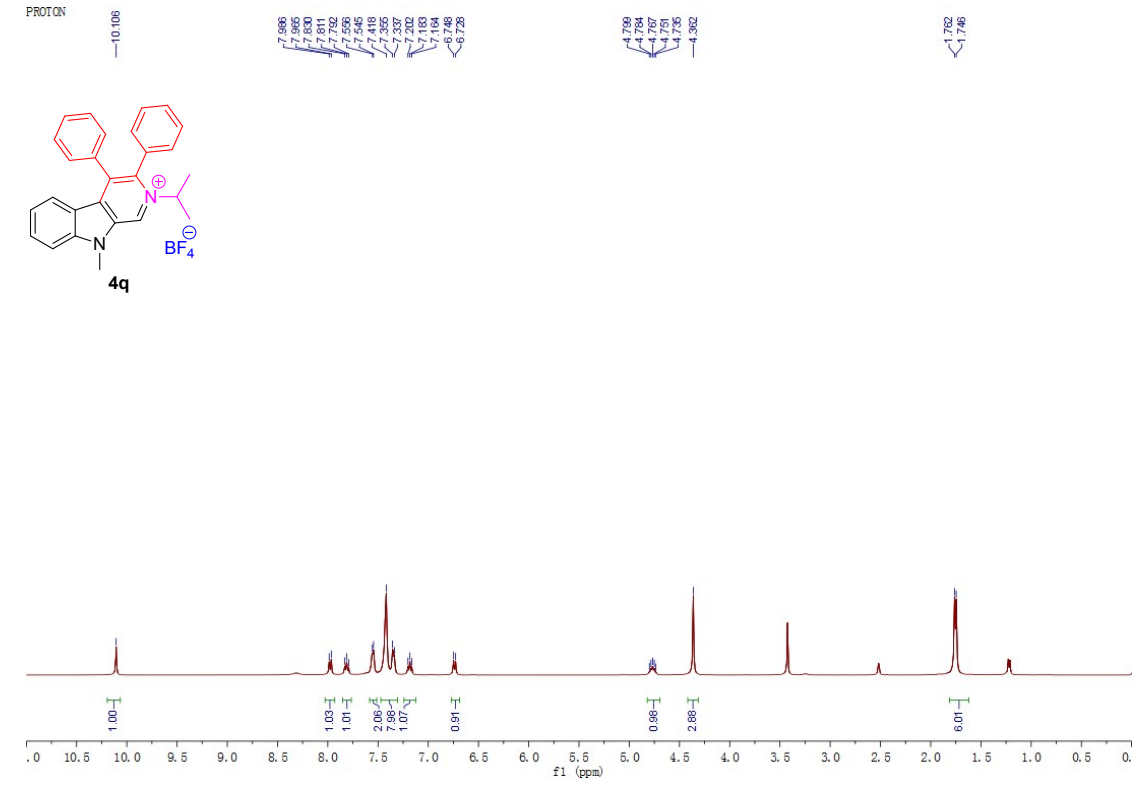
PROTON



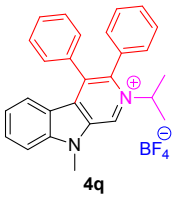
4p



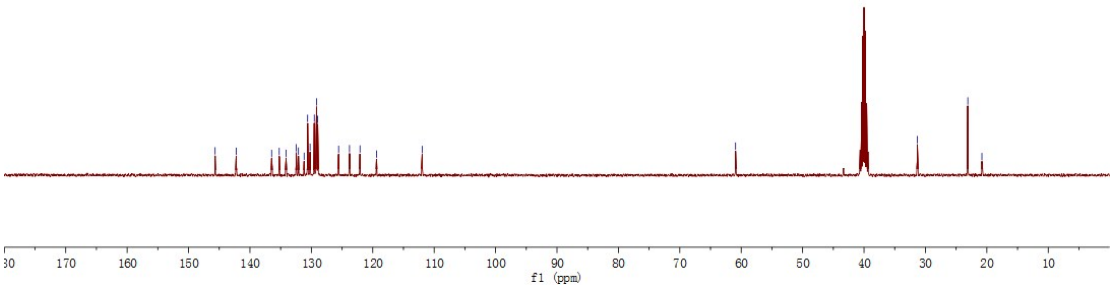

C13CPD
163.302
160.836
145.488
142.785
139.441
134.760
134.294
133.289
132.439
131.998
131.381
130.027
129.756
129.664
129.132
128.918
128.869
127.460
123.543
121.978
118.947
116.015
115.782
111.677
30.503
F
BF4
4p
f1 (ppm)


PROTON
10.106
7.996
7.965
7.830
7.811
7.792
7.656
7.645
7.418
7.355
7.337
7.202
7.183
7.164
6.748
6.728
4.799
4.784
4.767
4.751
4.735
4.362
1.762
1.746
BF4
4q
1.00
1.03
1.01
2.06
7.98
1.07
0.91
0.98
2.88
6.01
f1 (ppm)

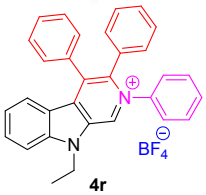
C13CPD



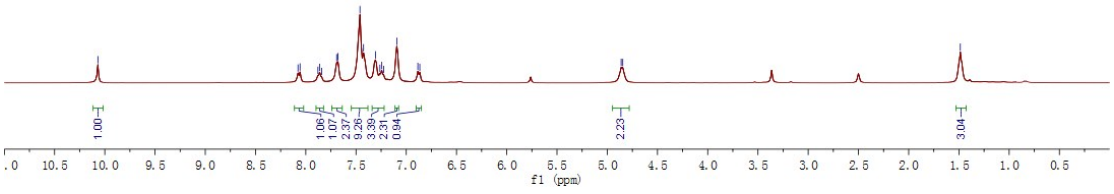
4q

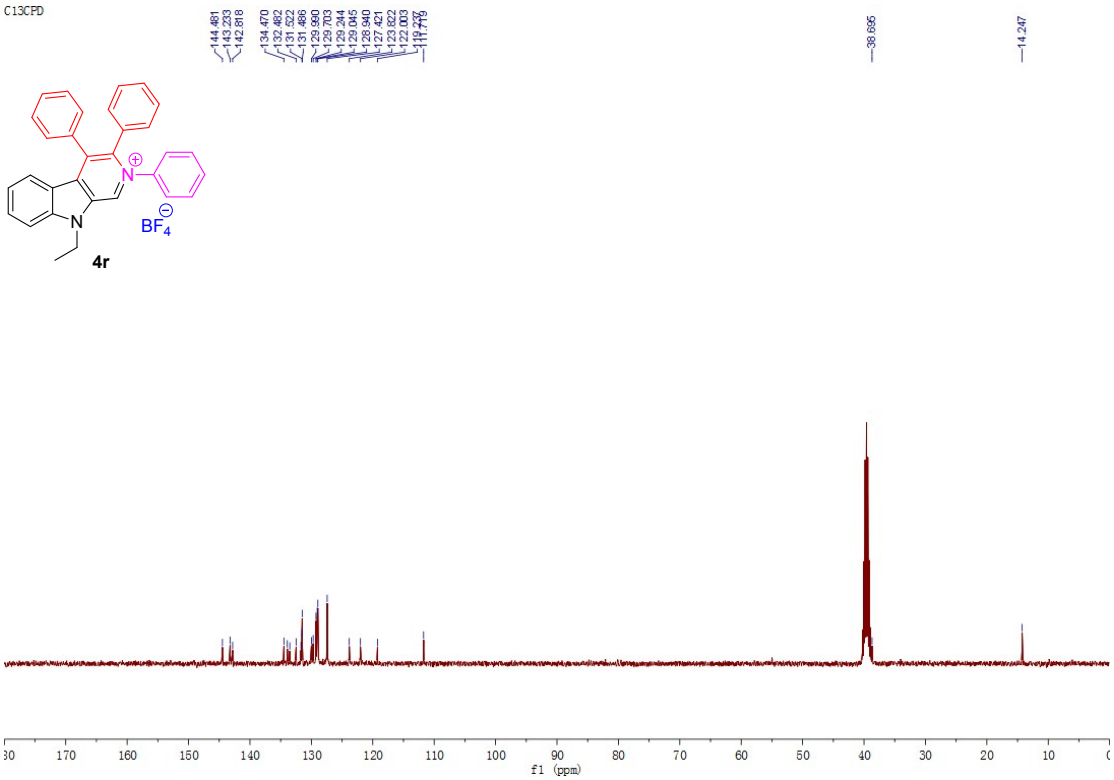


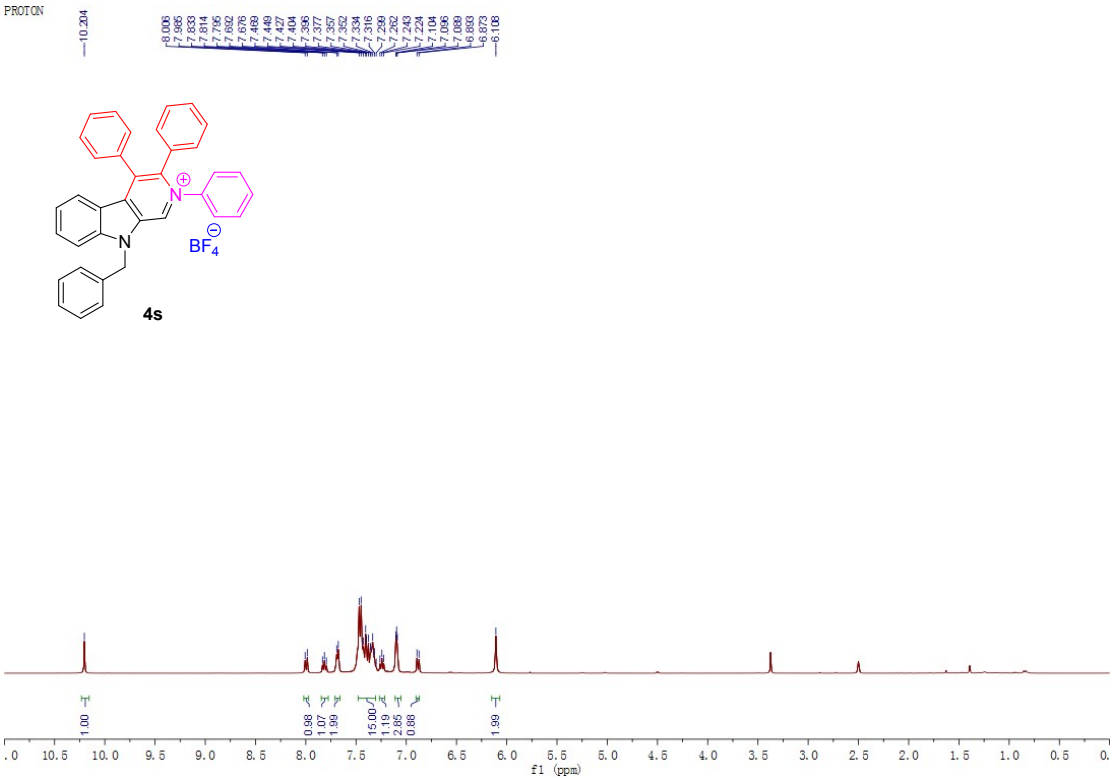
PROTON

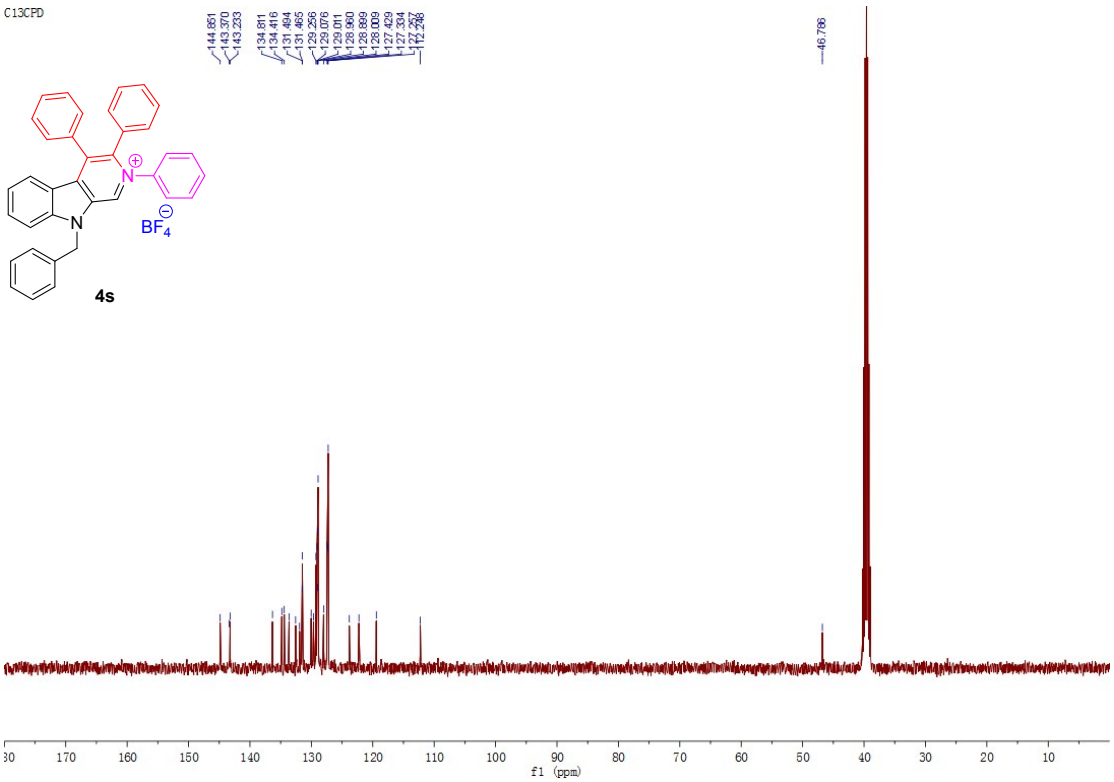


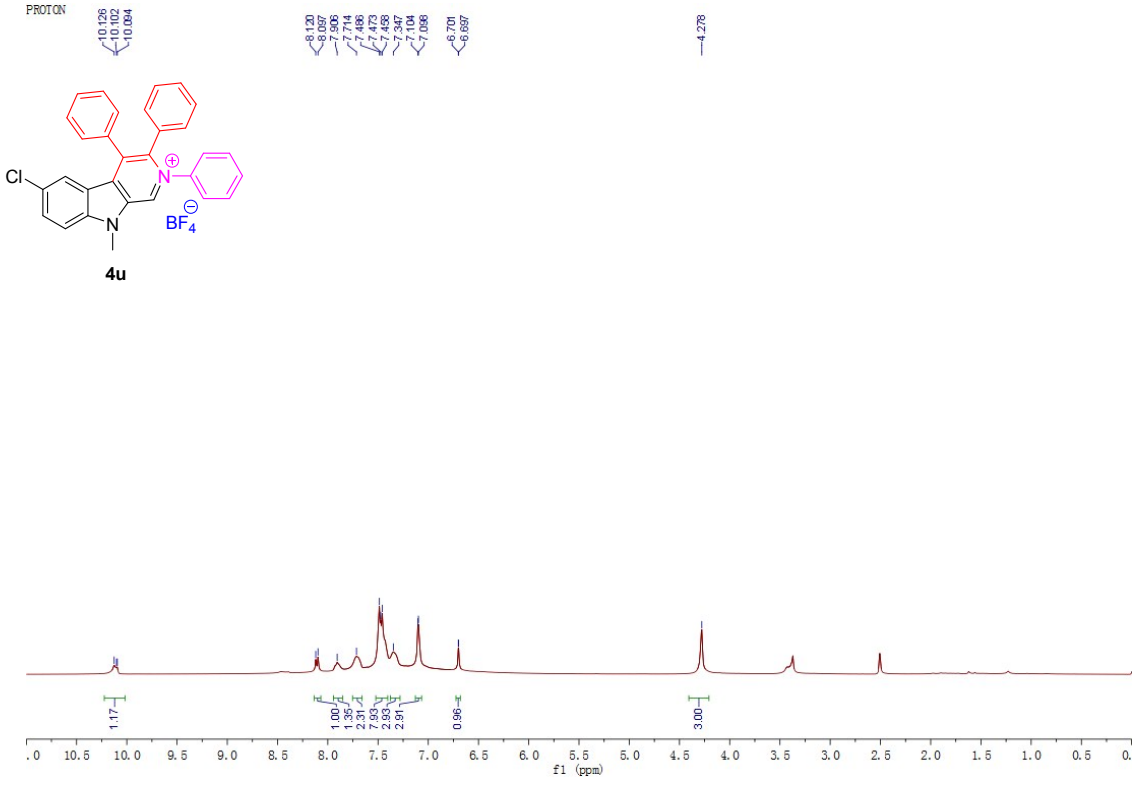
4r

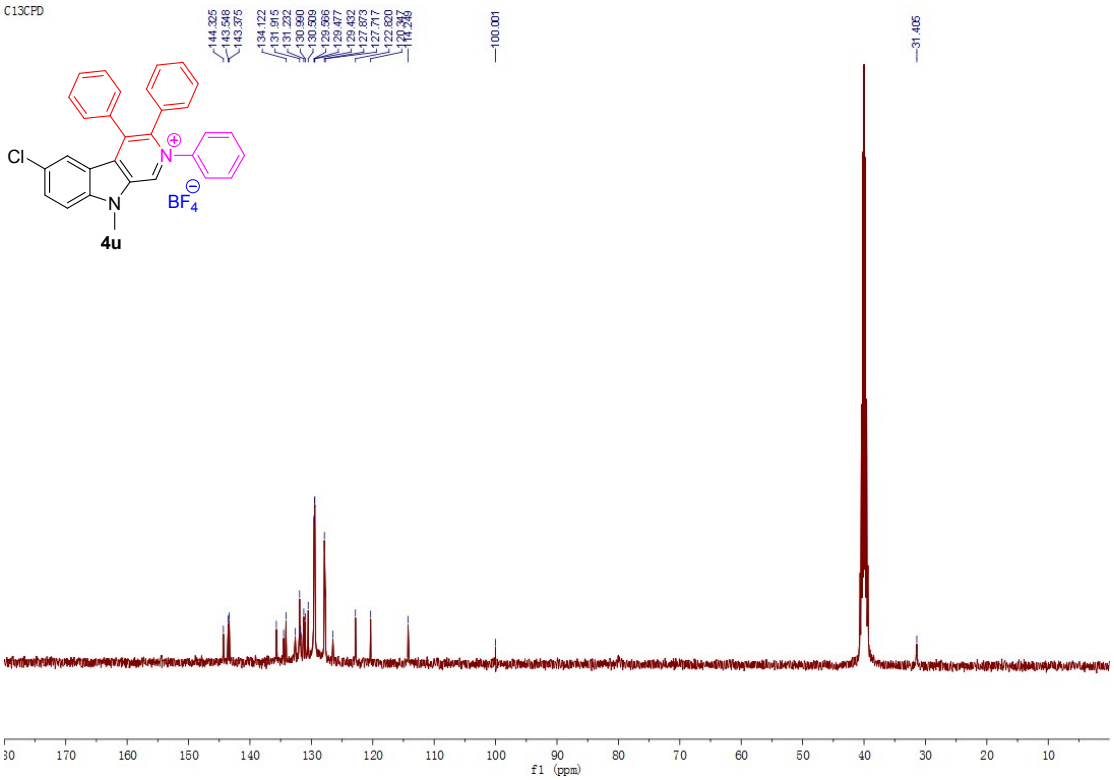


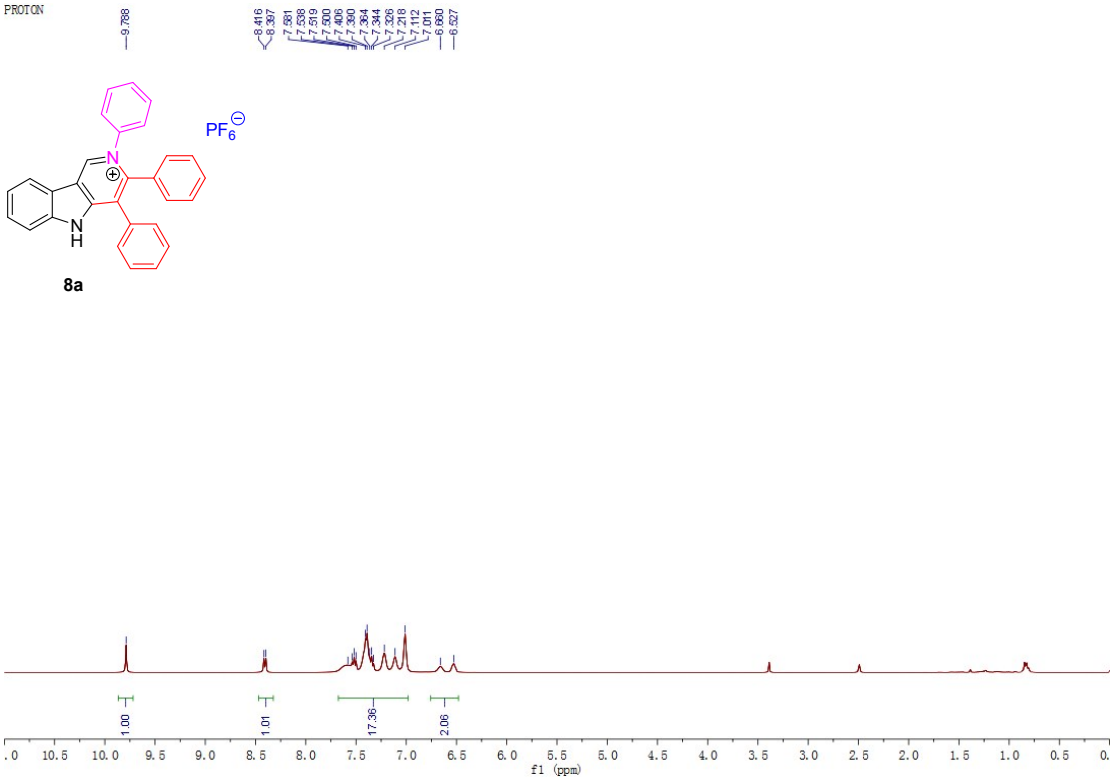

C13CPD
144.481
143.233
142.818
134.470
132.462
131.522
131.486
129.990
129.703
129.244
129.045
128.940
127.491
123.822
122.003
111.719
38.695
14.247
BF4
4r
f1 (ppm)

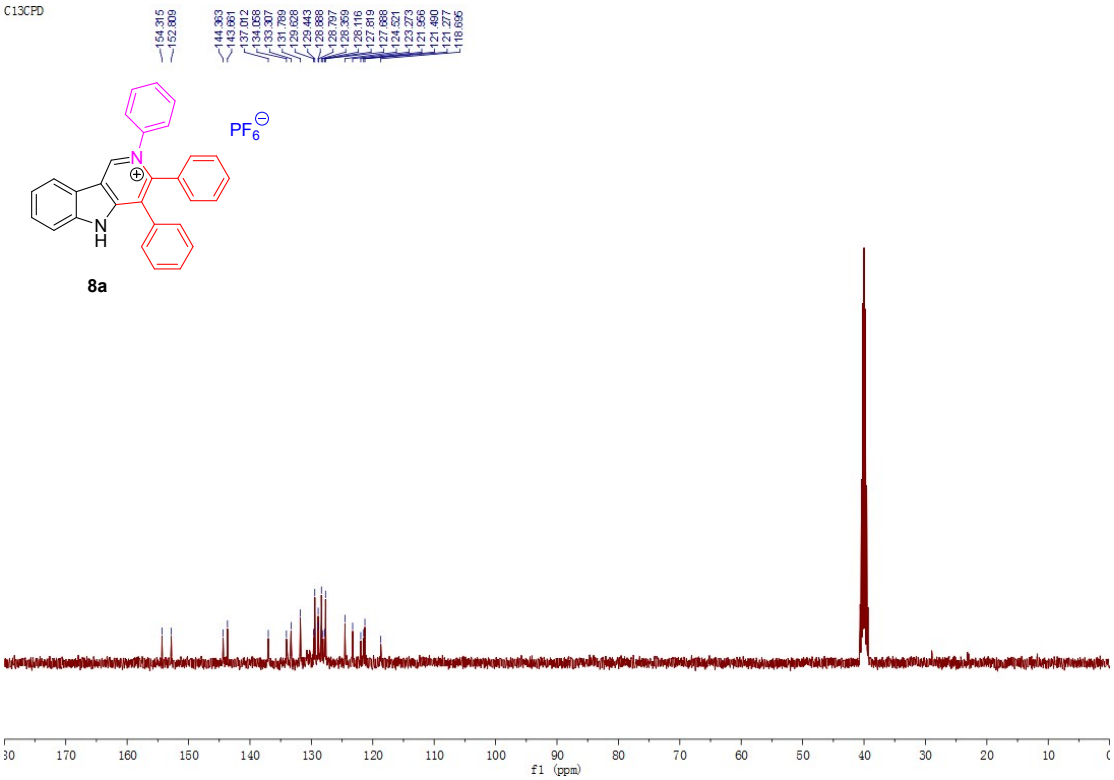

PROTON
10.204
8.006
7.985
7.833
7.814
7.795
7.692
7.676
7.469
7.446
7.427
7.404
7.396
7.377
7.357
7.352
7.334
7.316
7.289
7.262
7.243
7.224
7.104
7.096
7.089
6.893
6.873
6.108
BF4
4s
1.00
0.98
1.07
1.99
15.00
1.19
2.85
0.88
1.99
f1 (ppm)

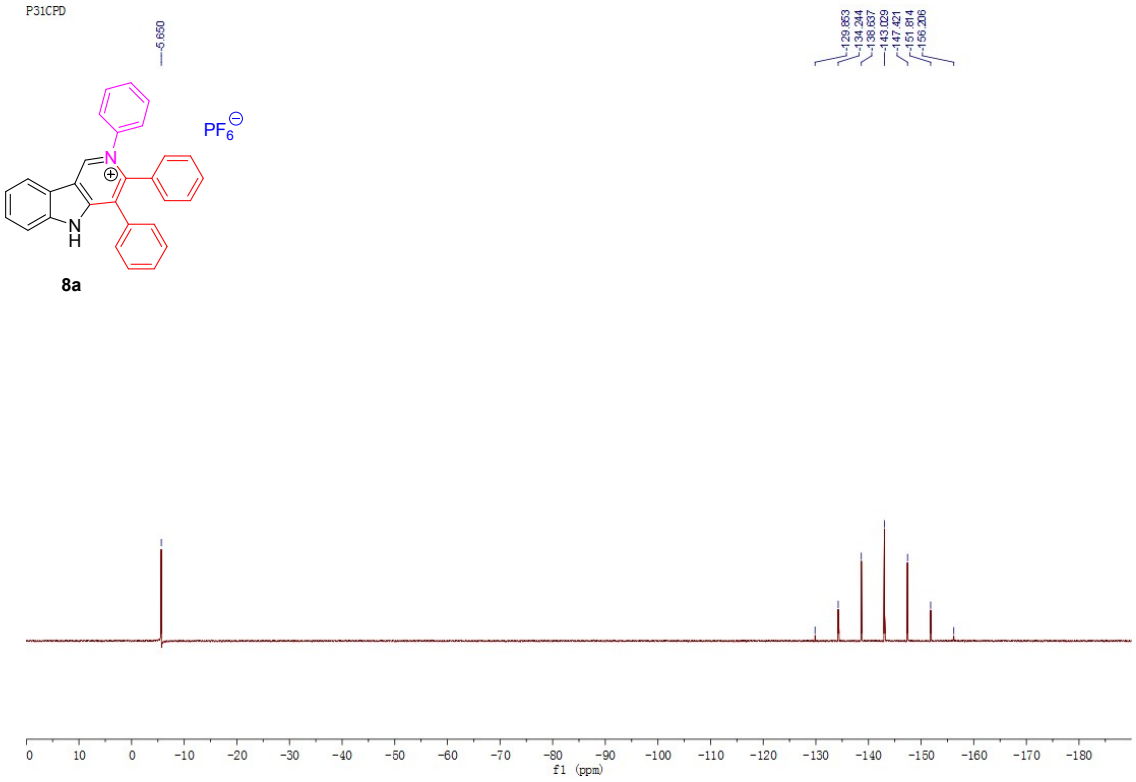

C13CPD
144.951
143.370
143.233
134.811
134.416
131.494
131.465
129.256
129.076
129.071
128.960
128.889
128.009
127.429
127.334
122.267
122.236
46.786
BF4
4s
f1 (ppm)


PROTON
10.126
10.102
10.094
8.120
8.097
7.906
7.714
7.486
7.473
7.458
7.347
7.104
7.098
6.701
6.697
4.278
Cl
BF4
4u
1.17
1.00
1.35
2.31
2.83
2.91
0.96
3.00
f1 (ppm)

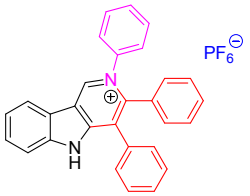

C13CPD
144.305
143.648
143.375
134.122
131.915
131.232
130.990
130.309
129.996
129.477
129.457
127.873
127.717
122.820
120.347
114.248
100.001
31.405
Cl
N
BF4
N
4u
f1 (ppm)


PROTON
9.788
8.416
8.397
7.581
7.538
7.519
7.500
7.406
7.380
7.364
7.344
7.326
7.218
7.112
7.011
6.660
6.627
PF6
N
H
8a
1.00
1.01
17.36
2.06
f1 (ppm)


C13CPD
154.315
152.809
144.363
143.661
137.012
134.168
133.307
131.769
129.628
129.443
128.886
128.797
128.359
128.116
127.819
127.668
124.521
123.273
121.496
121.277
118.695
PF6
N
H
8a
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

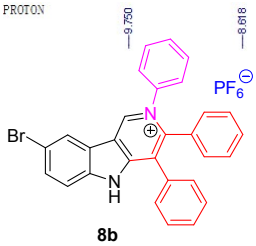

P31CPD
-5.650
129.853
134.244
138.637
143.029
147.421
151.814
156.206
PF6
N
H
8a
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

F19CPD

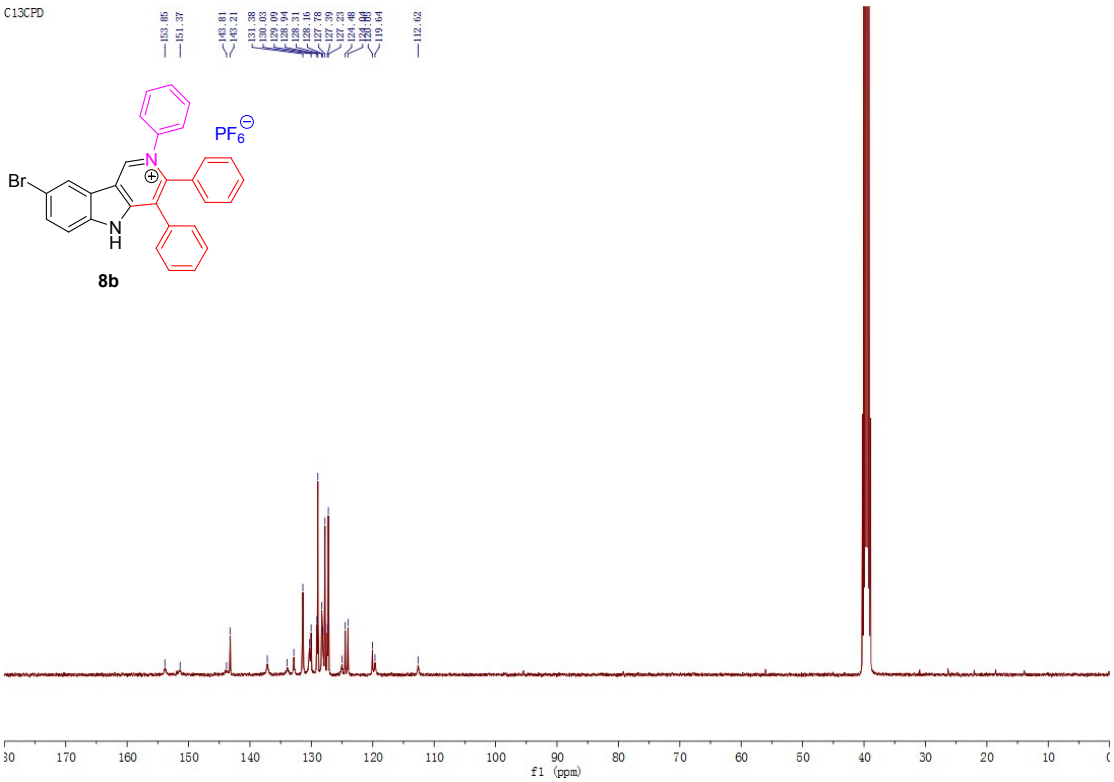


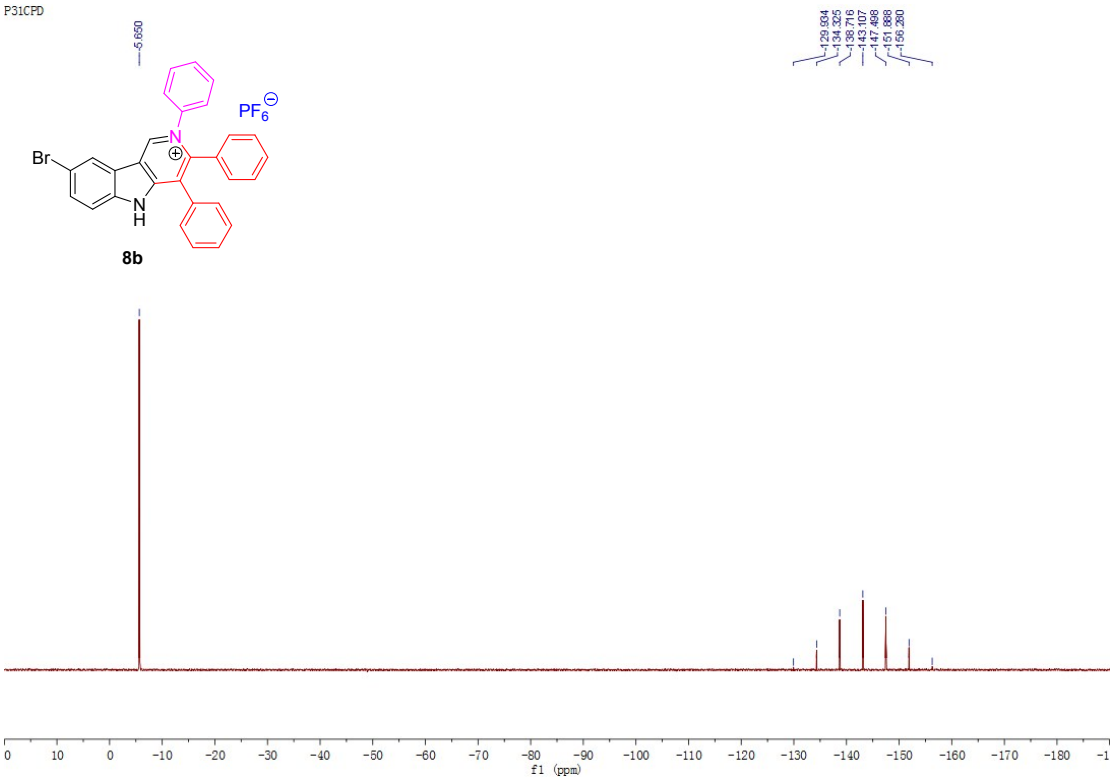
8a

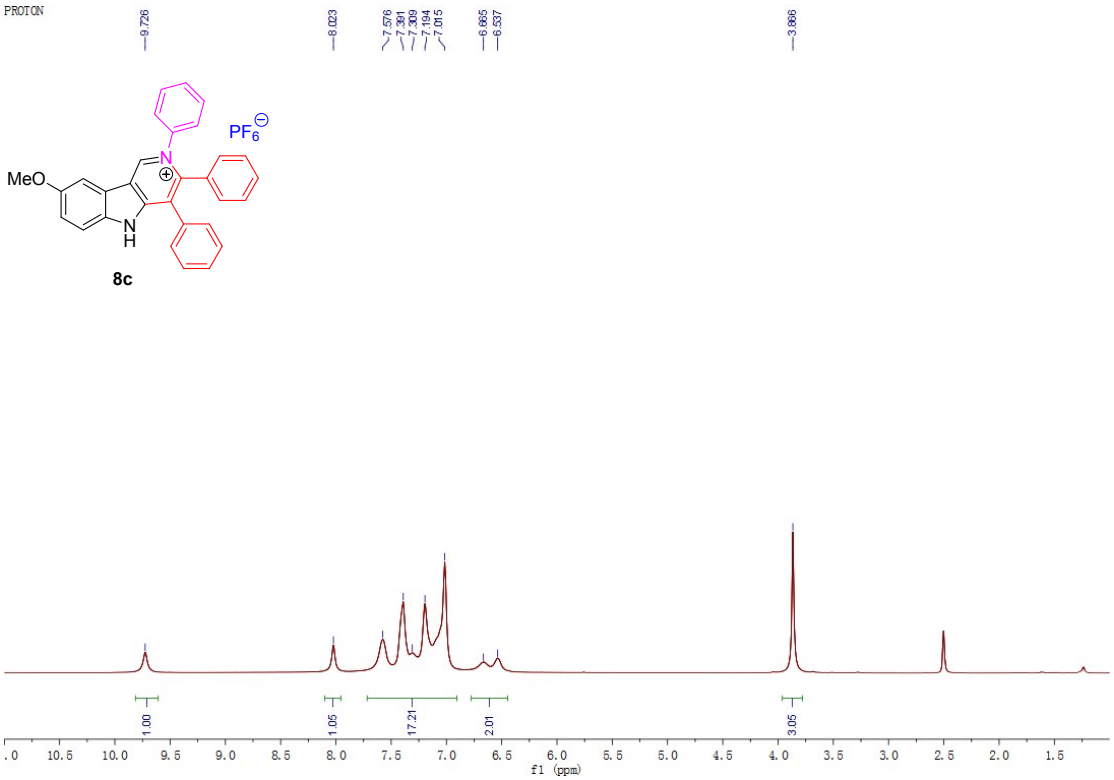
PROTON



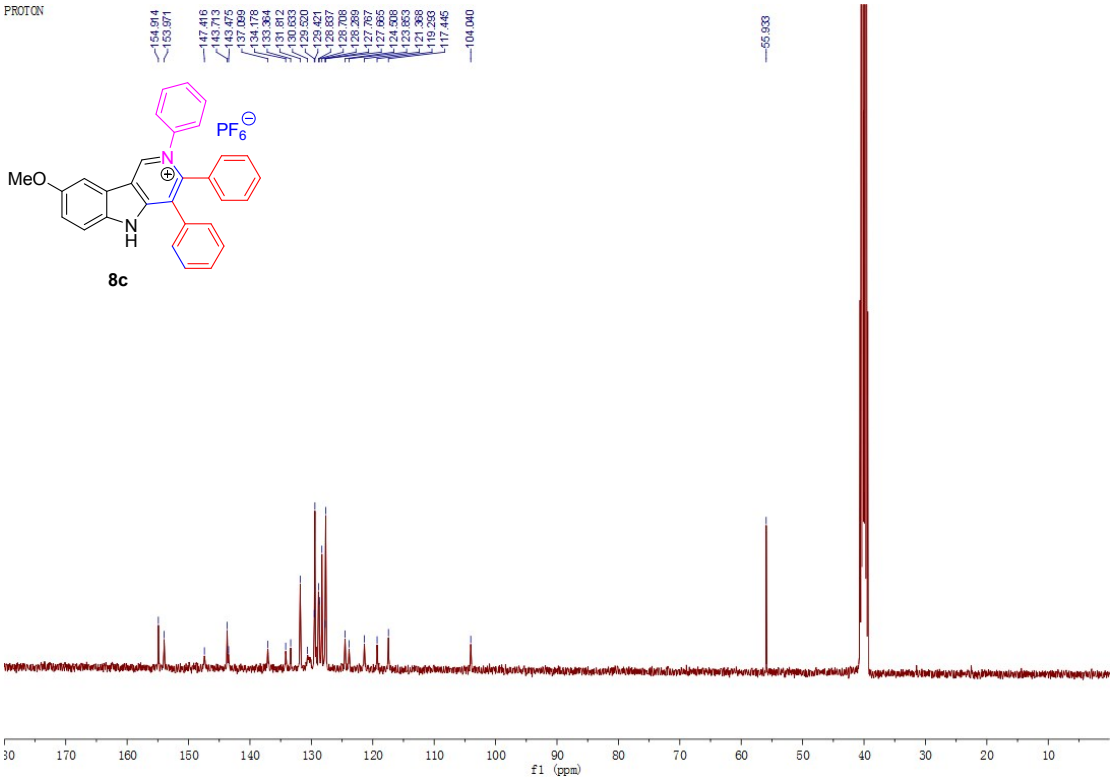
8b


C13CPD
153.85
151.37
143.81
143.21
131.38
130.03
129.09
128.94
128.31
128.16
127.78
127.39
127.23
124.00
119.64
112.62
PF6
Br
N
H
8b
f1 (ppm)


P31CPD
-5.650
129.934
134.325
138.716
143.107
147.498
151.888
156.280
PF6
Br
N
H
8b
f1 (ppm)

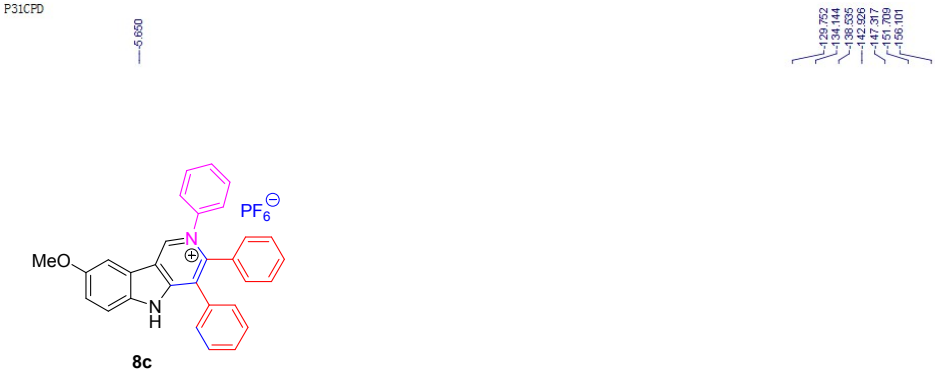

PROTON
9.726
8.023
7.576
7.391
7.309
7.194
7.015
6.665
6.537
3.866
MeO
N
H
$PF_6^{\ominus}$
1.00
1.05
17.21
2.01
3.05
f1 (ppm)

8c

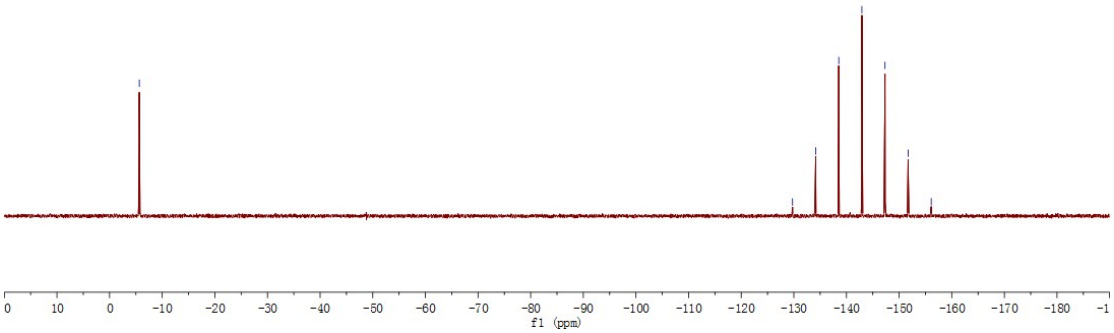

PROTON
154.914
153.971
147.416
143.713
143.475
137.099
134.178
133.364
131.812
130.033
129.520
129.421
128.837
128.708
128.289
127.767
127.665
124.569
123.853
121.368
119.239
117.445
104.040
55.933
MeO
N
H
$PF_6^{\ominus}$
f1 (ppm)

8c

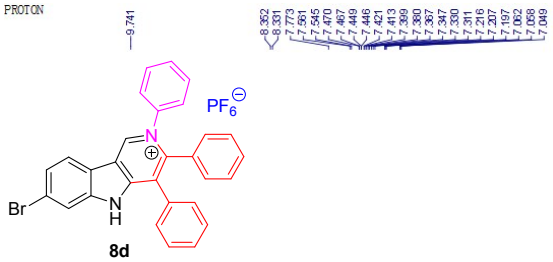
P31CPD



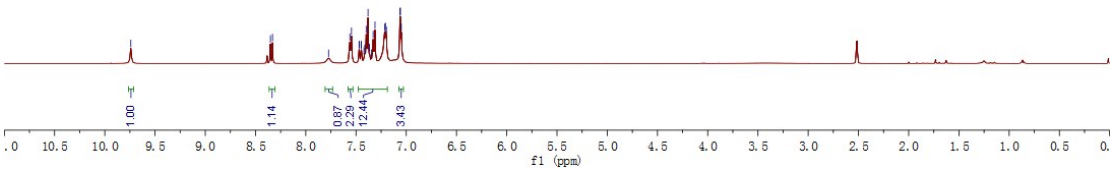
8c

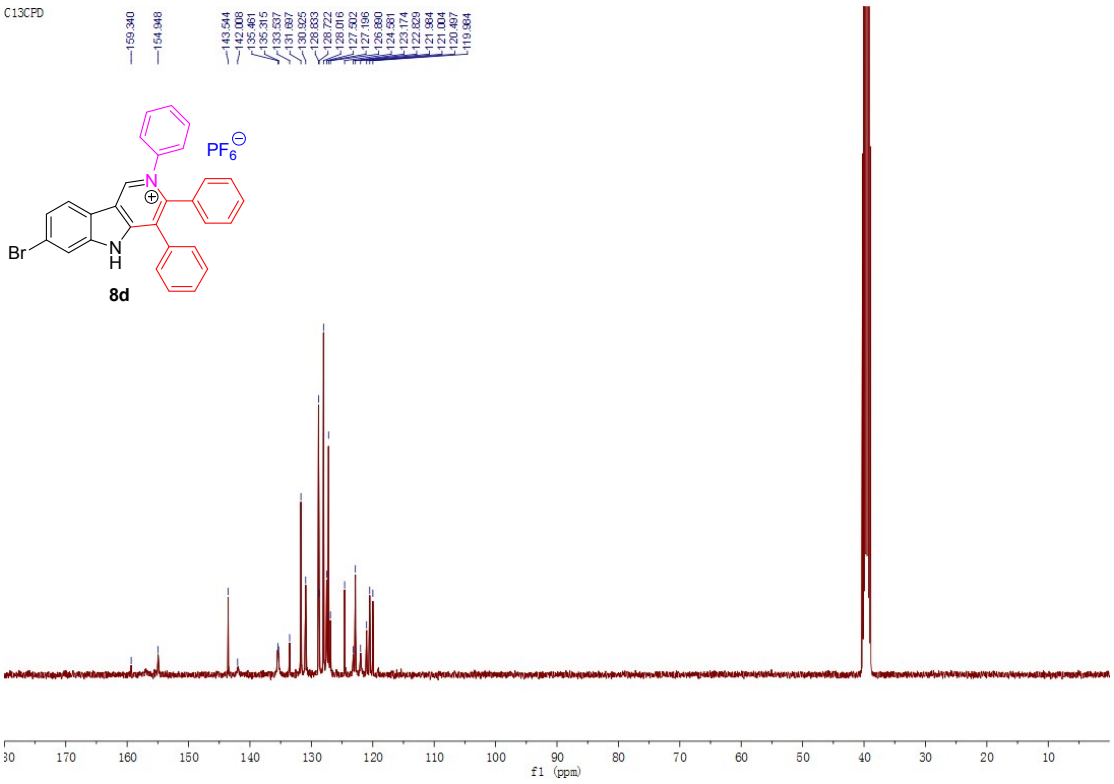


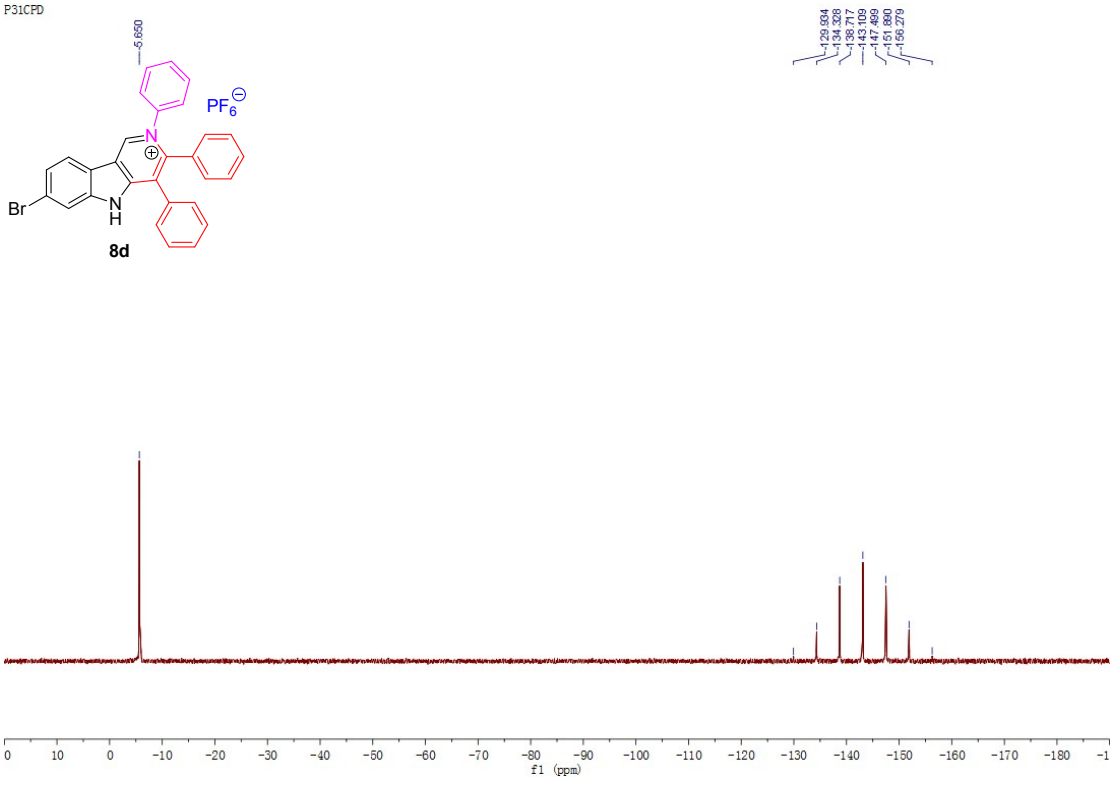
PROTON

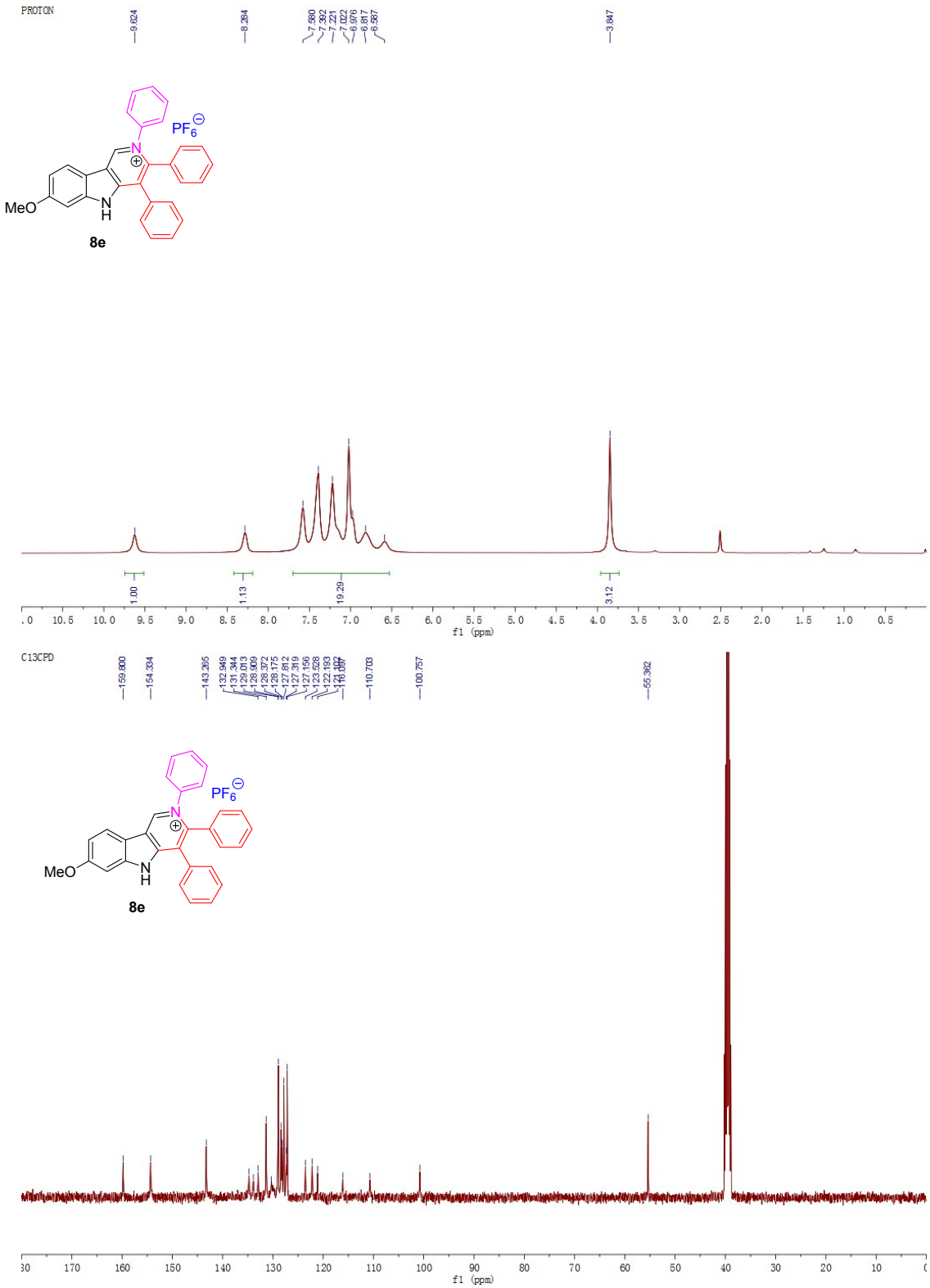


8d

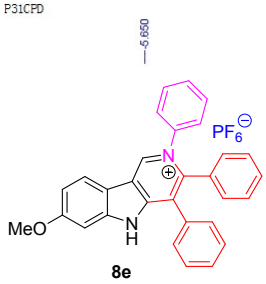



C13CPD
159.340
154.948
143.544
142.008
135.461
135.315
133.537
131.897
130.925
128.833
128.722
128.016
127.392
127.196
126.880
124.391
123.174
122.829
121.384
121.004
120.497
119.864
PF6
Br
N
H
8d
f1 (ppm)

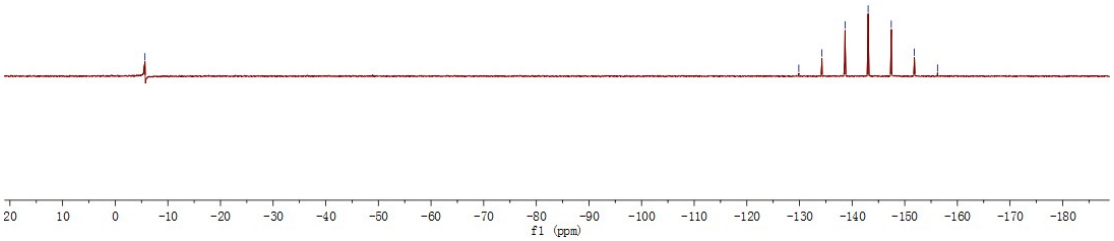

P31CPD
-5.650
129.934
134.328
138.717
143.109
147.469
151.860
156.279
PF6
Br
N
H
8d
f1 (ppm)


PROTON
9.624
8.284
7.580
7.392
7.221
7.022
6.976
6.617
6.387
3.847
PF6
N
MeO
N
H
8e
1.00
1.13
19.29
3.12
f1 (ppm)
C13CPD
159.800
154.334
143.265
132.949
131.344
129.013
128.909
128.372
128.175
127.812
127.319
127.156
123.528
122.193
121.107
116.087
110.703
100.757
55.362
PF6
N
MeO
N
H
8e
f1 (ppm)

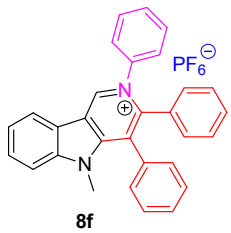
P31CPD



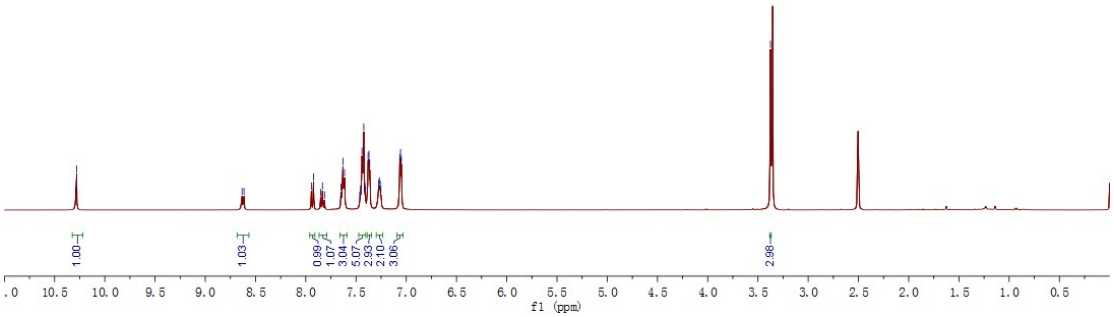
8e

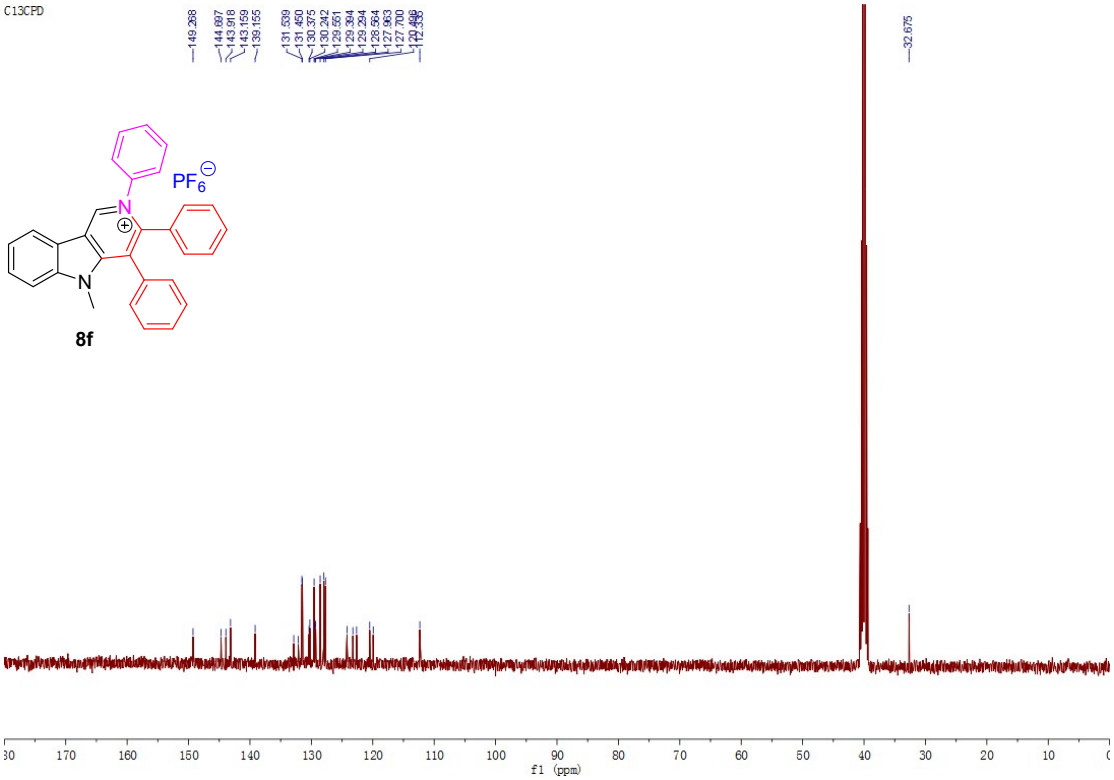


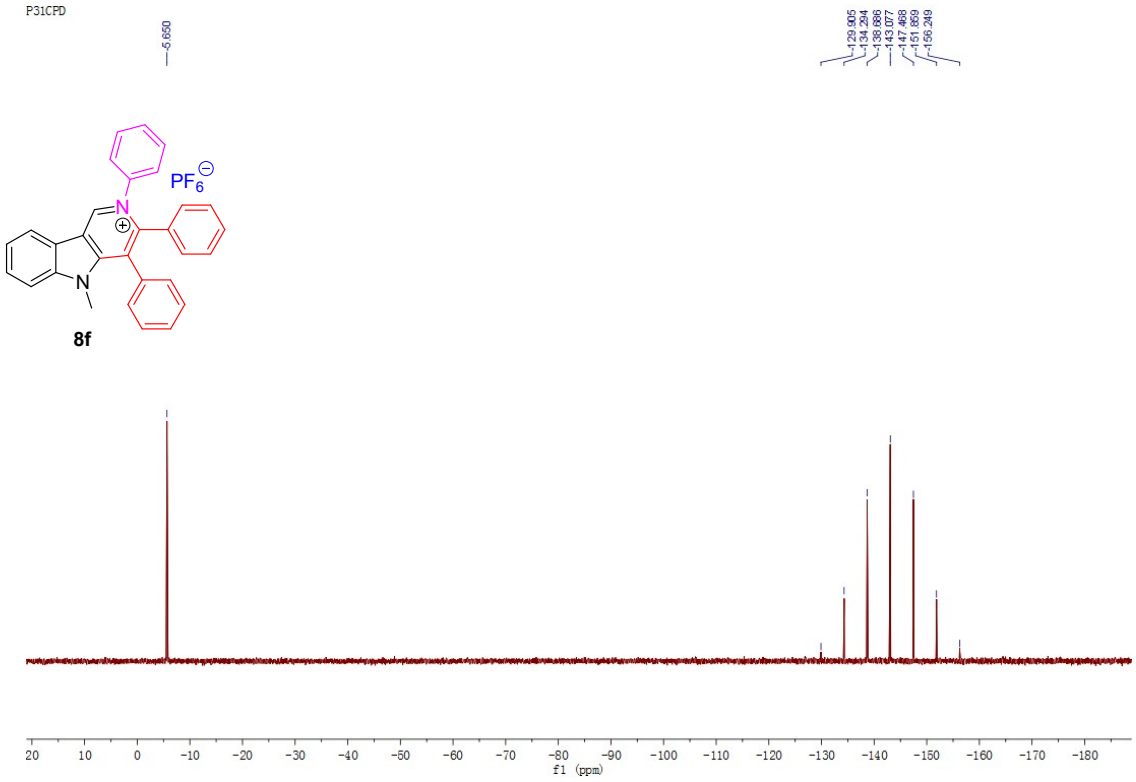
PROTON



8f




C13CPD
149.268
144.697
143.918
143.159
139.155
131.539
131.450
130.375
130.242
129.451
129.394
129.294
128.564
127.963
127.700
32.675
PF6
N
N
8f
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


P31CPD
-5.660
129.905
134.264
138.896
143.077
147.468
151.859
156.249
PF6
N
N
8f
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)