Electronic Supporting Information

Donnor-(π- bridge)-Azinium as D-π-A^+ one-dimensional and D-π-A^+-π-D multidimensional V-shaped chromophores

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1. Experimental procedures and characterization data for all new compounds reported

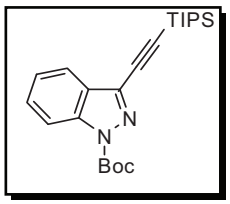
1a. General information

Melting points were uncorrected. Infrared spectra were recorded on KBr pellets and spectral bands were reported in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded at 200 MHz and 300 MHz respectively. Chemical shifts were reported as δ values (ppm). Mass spectra (MS) were obtained as (ESI^+). CuI, $PdCl(PPh_3)_2$, LiCl, were purchased from Aldrich. The acetylenes heterocycle of pyrazole and indazole were prepared using the classical catalytic procedures of Sonogashira coupling. 2-Triisopropylsilanyl ethynyl phenyl carbamic acid *tert*-butyl ester,[1] 1-triisopropylsilanyl-3-trimethylsilanylethynyl-1*H*-pyrrole,[2] 1-(toluene-4sulfonyl)-3-trimethylsilanylethynyl-1*H*-indole[3] were obtained by previously described methods. DMF and Et_3N were distilled over activated molecular sieves.

1b. Synthesis of heteroaryl ethynyl derivatives by Sonogashira protocol

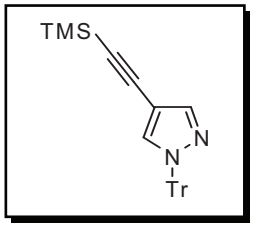
General Procedure

A flame-dried flask was charged under argon with the corresponding halo-heteroaryl-derivative (3 mmol), 10 mol% CuI (0.3 mmol, 0.05 g) and 5 mol % $PdCl(PPh_3)_2$ (0.15 mmol, 0.1 g) in dry THF (10 mL). Then, the corresponding silil acetylene (15 mmol) and Et_3N (17 mmol, 2.36 mL) were added. After being stirring at room temperature for 4 h, the solution was filtered through a small pad of celite and washed with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel in hexane/etil acetate (9.5:0.5) as eluent.



3-[(Triisopropylsillanyl)-ethynyl]-indazole-1-carboxylic acid tert-butyl ester

Following the general procedure, (1.11g, 93%) were obtained as a yellow oil. IR (KBr): υ_{max} (cm^{-1}) 2062, 1740; ^1H NMR (200 MHz, CD_3OD) δ (ppm) 8.21 (d, 1H, J = 8.4 Hz), 7.79 (d, 1H, J = 8.1 Hz), 7.68 (td, 1H, J = 1.1, 8.4 Hz), 7.47 (t, 1H, J = 6.9 Hz), 1.76 (s, 9H), 1.25 (s, 21H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 139.5, 129.1, 127.2, 123.8, 120.4, 114.5, 99.1, 96.1, 94.5, 85.9, 85.1, 27.9, 18.2, 10.8; MS (ESI^+) *m/z* (relative intensity) 398 (M^+, 100); Anal. Calcd for $C_{23}H_{34}N_2O_2Si$: C, 69.30; H, 8.6; N, 7.03. Found: C, 69.6; H, 8.03; N, 7.3.



4-Trimethylsilanylethynyl-1-trityl-1H-pyrazole

Following the general procedure, (1.15g, 95 %) were obtained as a yellow solid: mp 155-157 ºC; IR (KBr): υ_{max} (cm^{-1}) 2164, 1596, 845; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.73 (s, 1H), 7.52 (s, 1H), 7.29 (t, 10H, J = 2.56 Hz), 7.09 (m, 5H), 0.18 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 142.6, 142.5, 135.7, 130.0, 127.8, 127.8, 101.9, 96.5, 95.0, 0.03; MS (ESI^+) *m/z* (relative intensity) 406 (M^+, 100); Anal. Calcd for $C_{27}H_{26}N_2Si$: C, 79.76; H, 6.45; N, 6.89. Found: C, 79.89; H, 6.76; N, 6.76.

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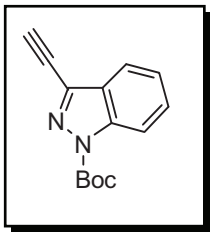
[1] Costa, M.; Della Ca, N.; Gabriele, B.; Massera C.; Salerno, G.; Solían, M. *J. Org. Chem.* **2004**, *69*, 2469-2477.

[2] Alvarez, A.; Guzmán, A.; Ruiz, A.; Velarde E. *J. Org. Chem.* **1992**, *57*, 1653-1656.

[3] Tanaka, K.; Kobayashi, T.; Mori, H.; Katsumura, S. *J. Org. Chem.* **2004**, *69*, 5906-5925.

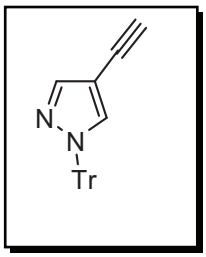
Desilylation of triisopropyl- and trimethyl- silyl group

To a solution of the corresponding heteroaryl ethynyl derivative (2.3 mmol) in THF (10 mL) and MeOH (10 mL), Bu_4NF (3.5 mmol) was added. The mixture was stirred at room temparature for 2 h. The reaction was quenched by dilution with water, and the mixture was extrated with CH_2Cl_2, and the extract was dried over $MgSO_4$. And the solvent was removed in vacuo. Finally the residue was purified by flash chromatography to give the corresponding product.



3-Ethynyl-indazole-1-carboxylic acid tert-butyl ester

Brown solid (0.6555 g, 97%): mp 106-108 ºC; IR (KBr): υ_{max} (cm^{-1}) 3226, 2114, 1749; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.2 (d, 1H, *J* = 8.4 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.68 (td, 1H, *J* = 1.1; 7.3 Hz), 7.49 (t, 1H, *J* = 6.9 Hz,4.21 (s, 1H), 1.75 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 139.7, 133.8, 129.3, 126.8, 124.1, 120.4, 114.7, 85.4, 83.4, 79.1, 28.1, 17.8; MS (ESI^+) *m/z* (relative intensity) 242 (M^+, 100); Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.41; H, 5.56; N, 11.82.



4-Ethynyl-1-trityl-1H-pyrazole

Yellow solid (0.946, 98%): mp 194-196 ºC; IR (KBr): υ_{max} (cm^{-1}) 2165; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 7.74 (s, 1H), 7.53 (s, 1H), 7.3 (t, 10H, *J* = 3.3 Hz), 7.1 (m, 5H), 2.97 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 142.6, 142.5, 135.9, 130.1, 127.9, 127.8, 79.1, 78.2, 75.4, 29.7; MS (ESI^+) *m/z* (relative intensity) 334 (M^+, 100); Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.43; H, 5.38; N, 8.20.

1c. General Procedure for the Synthesis of D-π-A Pyridinium Salts

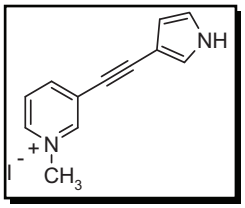
Method A

A flame-dried flask was charged under argon with 1 equiv. of bromopyridinium iodide or hexaflourophosphate, 10 mol % CuI (0.0667 mmol, 0.0127 g) and 5 mol % $PdCl_2(PPh_3)_2$ (0.0333 mmol, 0.0234 g) in dry DMF (10 mL). 1.2 equiv. of the corresponding acetylene heterocycle (0.7551 mmol) and 1.5 equiv. of Et_3N (0.9438 mmol, 0.1315 mL) were added. The mixture was heated at 65 ºC for 4 h and the solution was filtered through a small pad of celite and washed with methanol. The solution was concentrated, treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the solid was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5) as eluent.

Method B

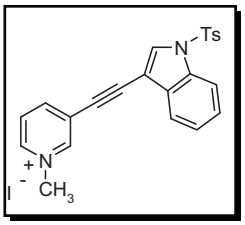
A flame-dried flask was charged under argon with 1 equiv. of bromopyridinium iodide (0.2 g, 0.6292mmol), 10 mol % CuI (0.0667 mmol, 0.0127 g), 5 mol % $PdCl_2(PPh_3)_2$ (0.0333 mmol, 0.0234 g), and 10 mol % LiCl (0.0667 mmol, 0.0026 g), in dry DMF (10 mL) were added. 1.2 equiv. of the corresponding acetylene heterocycle (0.7551 mmol) and 1.5 equiv. of Et_3N (0.9438 mmol, 0.1315 mL) were added. The mixture was stirred for 20 h at room temperature and the solution was filtered through a small pad of celite and washed with methanol. The solution was concentrated, treated with saturated

aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the solid was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5) as eluent.



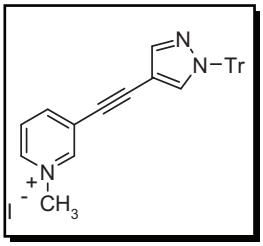
1-Methyl -3-(1H-pyrrol-3-ylethynyl) pyridinium iodide (4a)

Following the general procedure B, from **1a** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), afforded 0.1351 g, (63 %) of **4a** as a brown solid: mp 133 ºC; IR (KBr): υ_{max} (cm^{-1}) 3444, 3131, 2208, 1637; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.66 (d, 2H, *J* = 6.7 Hz), 7.9 (d, 2H, *J* = 6.7 Hz), 7.36 (t, 1H, *J* = 1.4 Hz), 6.85 (dd, 1H, *J* = 0.7, 2.0 Hz), 6.44 (dd, 1H, *J* = 1.2, 1.4 Hz), 4.89 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 145.7, 144.6, 132.9, 129.7, 127.5, 124.6, 120.5, 118.3, 112.9, 106.8, 47.8; MS (ESI^+) *m/z* (relative intensity) 341 (M^+, 100); Anal. Calcd for $C_{12}H_{11}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.57; H, 6.20; N, 15.23.



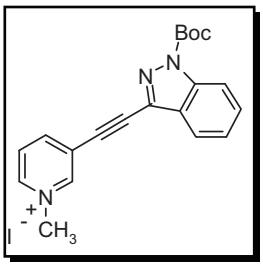
1-Methyl-3-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium iodide (4b)

Following the general procedure B, from **1a** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.2231 g), gave 0.1489 g, (61 %) of **4b** brown solid: mp 208 ºC; IR (KBr) : υ_{max} (cm^{-1}) 3505, 2231, 1378; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.84 (d, 2H, *J* = 6.7 Hz), 8.34 (s, 1H), 8.14 (d, 2H, *J* = 6.9 Hz), 8.03 (t, 2H, *J* = 8.6 Hz), 7.94 (d, 2H; *J* = 8.4 Hz), 7.8 (d, 1H; *J* = 0.9 Hz), 7.7-7.58 (m, 4H), 4.4 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 147.3, 146.3, 134.8, 133.7, 133.0, 132.6, 132.5, 131.2, 129.7, 129.6, 129.5, 128.1, 127.0, 126.6, 125.4, 121.2, 114.6, 90.57, 48.8, 47.6, 21.4; MS (ESI^+) *m/z* (relative intensity) 388 (M^+, 100); Anal. Calcd for $C_{23}H_{20}N_2O_2S$: C, 71.1; H, 5.1; N, 7.2. Found: C, 71.01; H, 5.21; N, 7.18.



1-Methyl -3-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium iodide (4c)

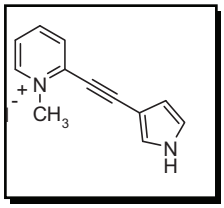
Following the general procedure A, from **1a** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), afforded 0.1812 g (48 %) of **4c** as a yellow solid: mp 246-247 ºC; IR (KBr): υ_{max} (cm^{-1}) 2231, 1443; ^{1}H NMR (200 MHz, DMSO-d6) δ (ppm) 9.23 (s, 1H), 8.9 (d, 1H, *J* = 6.2 Hz), 8.59 (d, 1H; *J* = 8.0 Hz), 8.11 (t, 1H, *J* = 8.4 Hz), 8.01 (m, 9H), 7.38 (m, 6H), 7.38 (m, 9H, *J* = 2.5 Hz), 7.06 (m, 6H, *J* = 3.6 Hz), 4.28 (s, 3H); ^{13}C NMR (300 MHz, acetone-d6) δ (ppm) 148.2, 147.1, 143.5, 142.8, 137.3, 130.9, 129.0, 128.8, 125.7, 100.9, 84.1, 80.4, 73.4, 61.9, 45.3, 41.0; MS (ESI^+) *m/z* (relative intensity) 426 (M^+, 100); Anal. Calcd for $C_{30}H_{24}N_3$: C, 83.94; H, 6.59; N, 9.47. Found: C, 83.67; H, 6.61; N, 9.31.



1-Methyl -3-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium iodide (4d)

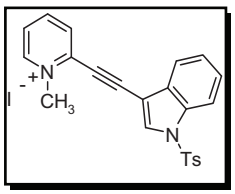
Following the general procedure A, from **1a** and 3-Ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), afforded 0.1705 g, (57 %) of **4d** as a brown solid: mp 134 ºC; IR (KBr): υ_{max} (cm^{-1}) 3419, 2230, 1742; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.45 (s, 1H), 9.01 (d, 1H, *J* = 6.2 Hz), 8.88 (d, 1H, *J* = 8.1 Hz), 8.25 (d, 1H, *J* = 8.4 Hz), 8.19 (dd, 1H, *J* = 6.2

Hz), 8.03 (d, 1H, *J* = 7.7 Hz), 7.74 (t, 1H, *J* = 7.3 Hz), 7.55 (t, 1H, *J* = 6.9 Hz), 4.51 (s, 3H), 1.78 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 209.1, 149.6, 148.4, 146.6, 141.1, 133.7, 131.3, 129.2, 127.7, 126.2, 124.5, 121.4, 115.9, 88.1, 87.7, 87.5, 48.4, 28.2; MS (ESI^+) *m/z* (relative intensity) 253 (M^+, 100); Anal. Calcd for $C_{20}H_{20}N_3O_2$: C, 71.77; H, 7.17; N, 11.96. Found: C, 71.96; H, 7.77; N, 11.17.



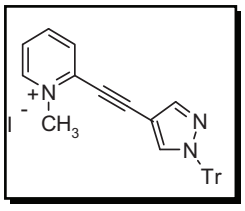
1-Methyl -2-(1H-pyrrol-3-ylethynyl) pyridinium iodide (5a)

Following the general procedure B, from **2** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), gave 0.0381 g, (26 %) of **5a** as an orange dark oil: IR (KBr): υ_{max} (cm^{-1}) 3434, 2206, 1619; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.88 (d, 1H; *J* = 7.2 Hz), 8.45 (t, 1H, *J* = 6.8 Hz), 8.13 (d, 1H, *J* = 8.0 Hz), 7.87 (t, 1H, *J* = 6.2 Hz), 7.5 (t, 1H, *J* = 1.6 Hz), 6.89 (dd, 1H, *J* = 0.9, 2.0 Hz), 6.53 (dd, 1H, *J* = 1.4, 2.9 Hz), 4.46 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 147.1, 145.2, 141.1, 131.5, 128.2, 125.7, 120.9, 113.0, 109.5, 101.3, 81.6, 47.86; MS (ESI^+) *m/z* (relative intensity) 341 (M^+, 100); Anal. Calcd for $C_{12}H_{11}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.13; H, 6.67; N, 15.32.



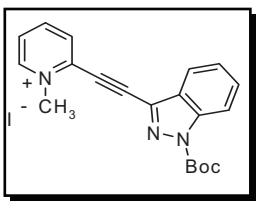
1-Methyl -2-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium iodide (5b)

Following the general procedure B, from **2** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.2231 g), afforded 0.2387 g, (70%) of **5b** as a yellow solid: mp 192 ºC. IR (KBr): υ_{max} (cm^{-1}) 3500, 2220, 1378; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.02 (d, 1H, *J* = 6.7 Hz), 8.58 (t, 1H, *J* = 7.1 Hz), 8.5 (s, 1H), 8.37 (d, 1H, *J* = 7.7 Hz), 8.09 (d, 1H, *J* = 7.8 Hz), 8.03 (t, 1H, *J* = 6.2 Hz), 7.97 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 7.5 Hz), 7.54-7.47 (m, 2H), 7.44 (t, 3H, *J* = 8.4 Hz), 4.59 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 148.0, 147.9, 145.9, 135.6, 135.5, 135.1, 132.7, 131.4, 130.8, 128.4, 127.4, 125.8, 121.3, 115.0, 102.3, 101.1, 85.2, 48.1, 47.9, 21.5; MS (ESI^+) *m/z* (relative intensity) 388 (M^+, 100); Anal. Calcd for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 71.29; H, 5.36; N, 7.59.



1-Methyl -2-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium iodide (5c)

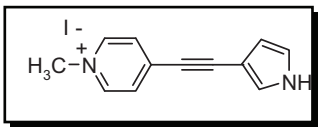
Following the general procedure A, from **2** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), gave 0.08 g, (45 %) of **5c** as a brown solid: mp 233 ºC. IR (KBr): υ_{max} (cm^{-1}) 2215, 1615, 1443; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.93 (d, 1H, *J* = 5.8 Hz), 8.51 (t, 1H, *J* = 8.1 Hz), 8.21 (d, 1H, *J* = 7.8 Hz), 8.08 (s, 2H), 7.96 (t, 1H, *J* = 6.2 Hz), 7.41 (t, 9H, *J* = 3.6 Hz), 7.18 (m, 6H), 4.45 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 146.3, 144.0, 142.4, 141.4, 137.4, 137.0, 130.2, 129.1, 127.6, 125.5, 116.5, 98.8, 98.4, 81.8, 78.7, 46.6; MS (ESI^+) *m/z* (relative intensity) 426 (M^+, 100); Anal. Calcd for $C_{30}H_{24}N_3$: C, 83.94; H, 6.59; N, 9.47. Found: C, 83.47; H, 6.94; N, 9.59.



1-Methyl -2-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium iodide (5d)

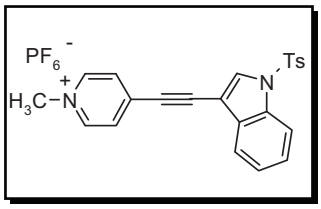
Following the general procedure A, from **2** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), gave 0.1705 g, (53 %) of **5d** as an orange solid: mp 185 ºC; IR (KBr): υ_{max} (cm^{-1}) 3418, 2350, 1628; ^{1}H NMR (200 MHz,

CD_3OD) δ (ppm) 9.18 (d, 1H, *J* = 6.6 Hz), 8.79 (t, 1H, *J* = 6.6 Hz), 8.38 (d, 1H, *J* = 8.1 Hz), 8.19 (t, 1H, *J* = 7.7 Hz), 7.94 (d,1 H, *J* = 8.1 Hz), 7.73 (td, 2H, *J* = 1.1, 7.3 Hz), 7.6 (td, 1H, *J* = 1.8, 4.4 Hz), 4.44 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 209.0, 148.3, 148.3, 146.5, 141.1, 136.0, 130.3, 126.9, 126.7, 125.5, 125.1, 120.8, 111.4, 100.2, 95.6, 46.8, 17.8, 11.2; MS (ESI^+) *m/z* (relative intensity) 253 (M^+, 100); Anal. Calcd for $C_{20}H_{20}N_3O_2$: C, 71.17; H, 7.17; N, 11.96. Found: C, 71.96; H, 7.27; N, 11.34.



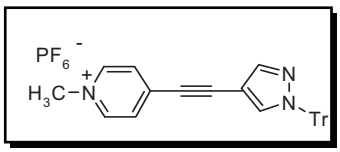
1-Methyl -4-(1H-pyrrol-3-ylethynyl) pyridinium hexafluoro phosphate (6a)

Following the general procedure B, from **3** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), gave 0.0379 g, (32 %) of **6a** as a brown solid: mp 133 ºC; IR (KBr): υ_{max} (cm^{-1}) 3444, 3131, 2208, 1637; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.66 (d, 2H, *J* = 6.7 Hz), 7.9 (d, 2H, *J* = 6.7 Hz), 7.36 (t, 1H, *J* = 1.4 Hz), 6.85 (dd, 1H, *J* = 0.7, 2.0 Hz), 6.44 (dd, 1H, *J* = 1.3, 1.4 Hz), 4.89 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 145.7, 144.6, 132.9, 129.7, 127.5, 124.6, 120.5, 118.3, 112.9, 106.8, 47.8; MS (ESI^+) *m/z* (relative intensity) 341 (M^+, 100); Anal. Calcd for $C_{12}H_{11}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.57; H, 6.20; N, 15.33.



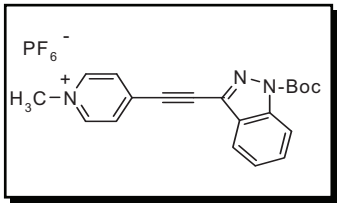
1-Methyl-4-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium hexafluoro phosphate (6b)

Following the general procedure B, from **3** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.0.2231 g), gave 0.1692 g, (50 %) of **6b** as a brown solid: mp 208 ºC; IR (KBr): υ_{max} (cm^{-1}) 3564, 2238, 1384. ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.84 (d, 2H, *J* = 6.7 Hz), 8.34 (s, 1H), 8.14 (d, 2H, *J* = 6.9 Hz), 8.03 (t, 2H, *J* = 8.6 Hz), 7.94 (d, 2H; *J* = 8.4 Hz), 7.8 (d, 1H; *J* = 0.9 Hz), 7.7-7.58 (m, 4H), 4.4 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 147.3, 146.3, 134.8, 133.7, 133.0, 132.6, 132.5, 131.2, 129.7, 129.6, 129.5, 128.1, 127.0, 126.6, 125.4, 121.2, 114.6, 90.5, 48.8, 47.6, 21.4; MS (ESI^+) *m/z* (relative intensity) 388 (M^+, 100); Anal. Calcd for $C_{23}H_{20}N_2O_2S$: C, 71.1; H, 5.1; N, 7.2. Found: C, 71.34; H, 5.27; N, 7.43.



1-Methyl-4-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium hexafluorophosphate (6c)

Following the general procedure A, from **3** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), afforded 0.2485 g, (77 %) of **6c** as an orange solid: mp 249-251 ºC; IR (KBr): υ_{max} (cm^{-1}) 2215, 1637, 1447; ^{1}H NMR (200 MHz, DMSO-d6) δ (ppm) 8.89 (d, 2H, *J* = 6.7 Hz), 8.09(d, 2H, *J* = 7.1 Hz), 7.93 (s, 1H), 7.39 (m, 10H), 7.06 (m, 6H), 4.25 (s, 3H); ^{13}C NMR (300 MHz, acetone-d6) δ (ppm) 146.2, 143.3, 141.2, 138.3, 130.8, 129.3, 128.9, 128.7, 100.7, 97.8, 80.0, 73.3, 48.7; MS (ESI^+) *m/z* (relative intensity) 426 (M^+, 100); Anal. Calcd for $C_{30}H_{24}N_3$: C, 83.94; H, 6.59; N, 9.47. Found: C, 83.59; H, 6.78; N, 9.74.

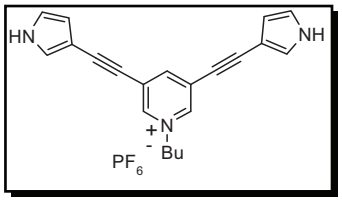


1-Methyl-4-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (6d)

Following the general procedure A, from **3** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), gave 0.2066 g, (69 %) of **6d** as a black solid: mp 144 ºC; IR (KBr): υ_{max} (cm^{-1}) 3418, 2207, 1636; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.02 (d, 2H, *J* = 6.6 Hz), 8.37 (d, 2H, *J* = 6.9 Hz), 8.28 (d, 1H, *J* = 8.4 Hz), 8.06 (d, 1H, *J* = 8.1 Hz), 7.75 (t, 1H, *J* = 7.3 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 4.47 (s, 3H), 1.78 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 209.1, 145.5, 143.0, 140.6, 139.8, 129.0, 127.6, 125.1, 122.9, 119.6, 117.1, 110.9, 95.5, 88.7, 69.4, 47.0, 29.9; MS (ESI^+) *m/z* (relative intensity) 253 (M^+, 100).; Anal. Calcd for $C_{20}H_{20}N_3O_2$: C, 71.9; H, 7.95; N, 11.43. Found: C, 71.95; H, 7.43; N, 11.83.

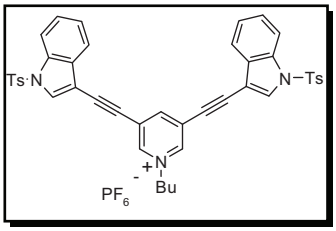
1d. General Procedure for the Synthesis of D-π-A- π-D Pyridinium Salts
Method C

A flame-dried flask was charged under argon with 1 equiv. of the corresponding 3,5-dibromo-N-butylpyridinium hexafluoro -phosphate salt (0.3 g, 0.6834 mmol), 10 mol % CuI (0.013 g, 0.0683 mmol), 5 mol % $PdCl(PPh_3)_2$ (0.0239 g, 0.0341 mmol) in dry THF (10 mL) were added. The corresponding acetylene heterocycle (2.4 equiv., 1.6401 mmol) and Et_3N (3 equiv., 2.0502 mmol, 0.2815 mL) were added. The mixture was stirred at room temperature for 1 h and the solution was filtered through a small pad of celite and washed with methanol. The solution was concentrated, the solvent was evaporated under reduced pressure, and the solid was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (9.5:0.5) as eluent.



1-Butyl -3,5-(1H-pyrrol-3-ethynyl) pyridinium hexafluoro phosphate (7a)

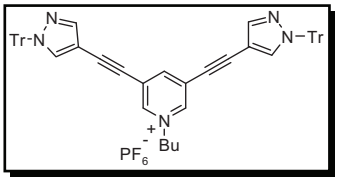
Following the general procedure C, **1b** and 3-Ethynyl-1-triisopropylsilanyl-1H-pyrrole (1.6401 mmol, 0.4074 g), gave 0.1714 g, (55 %) of **7a** as a brown solid: mp descomposed at 210 ºC; IR (KBr): υ_{max} (cm^{-1}) 3444, 2965, 2215; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.15 (d, 2H, *J* = 1.4 Hz), 8.54 (s, 1H), 7.32 (dd, 2H, *J* = 1.2, 1.4 Hz), 6.91 (dd, 2H, *J* = 2.0, 2.5 Hz), 6.35 (t, 2H, *J* = 2.5 Hz), 4.84 (t, 2H; *J* = 7.5 Hz), 2.22-2.20 (m, 2H, *J* = 8.0 Hz), 1.53-1.5 (m, 2H), 0.99 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR (300 MHz, CD_3OD) δ (ppm) 145.7, 143.1, 126.1, 124.8, 119.4, 111.3, 101.5, 96.2, 80.8, 62.4, 32.9, 19.1, 12.8; MS (ESI^+) *m/z* (relative intensity) 314 (M^+, 100); Anal. Calcd for $C_{18}H_{14}N_3$: C 79.39; H, 5.18; N, 15.43. Found: C, 79.43; H, 5.39; N, 15.36.



1-Butyl-3,5-[1-(toluene-4-sulfonyl)-3-ethynylindole] pyridinium hexafluoro phosphate (7b)

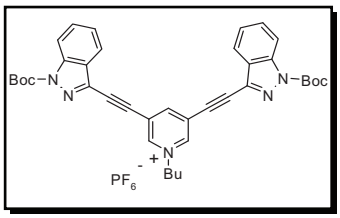
Following the general procedure C, from **1b** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (1.6401 mmol, 0.4846 g), afforded 0.4778 g, (83 %) of **7b** as a brown solid: mp 177 ºC. IR (KBr) υ_{max} (cm^{-1}) 2220; 1373; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.45 (d, 2H, *J* = 1.5 Hz), 9.02 (s, 1H), 8.21 (s, 2H), 8.09 (d, 2H, *J* = 8.2 Hz), 7.99 (d, 4H; *J* = 8.5 Hz), 7.79 (d, 2H; *J* = 6.9 Hz), 7.54-7.37 (m, 9H), 4.92 (t, 2H, *J* = 7.6 Hz), 2.37 (s, 6H), 2.20-2.06 (m, 2H), 1.53-1.48 (m, 2H), 1.0 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (300 MHz, CD_3OD) δ (ppm) 148.4, 147.3, 146.0, 135.2, 134.9, 132.4, 131.3, 130.8, 128.1, 127.1, 125.7, 125.3, 121.3, 114.7,

103.5, 90.6, 86.9, 63.7, 33.8, 21.5, 20.0, 13.7; MS (ESI^+) *m/z* (relative intensity) 722 (M^+, 100); Anal. Calcd for $C_{40}H_{30}N_3O_4S2$: C, 70.57; H, 4.44; N 6.17. Found: C, 70.54; H, 4.47; N, 6.23.



1-Butyl-3,5-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium hexafluorophosphate (7c)

Following the general procedure C, from **1b** and 4-ethynyl-1-trityl-1*H*-pyrazol (1.6401 mmol, 0.5711 g), gave 0.5317 g, (80 %) of **7c** as a brown solid: mp descomposes at 230ºC; IR (KBr): υ_{max} (cm^{-1}) 2223, 1618; ^1H NMR (200 MHz, DMSO-d_6) δ (ppm) 9.2 (s, 2H), 8.6 (s, 1H), 7.8 (s, 2H), 7.7 (s, 2H), 7.41-7.38 (m, 15H), 7.17- 7.14 (m, 10H), 7.3-7.28 (m, 5H), 4.8 (t, 2H, *J* = 3.6 Hz), 4.28 (s, 3H); ^{13}C NMR (300 MHz, acetone-d_6) δ (ppm) 147.9, 146.8, 144.4, 142.6, 141.9, 136.5, 131.8, 130.0, 128.1, 127.9, 127.8, 127.5, 126.7, 125.1, 99.9, 90.4, 83.1, 79.5, 62.6, 19.1, 12.7; MS (ESI^+) *m/z* (relative intensity) 801 (M^+, 100); Anal. Calcd for $C_{57}H_{46}N_5$: C, 85.16; H, 6.28; N, 8.56. Found: C, 85.43; H, 6.56; N, 8.16.



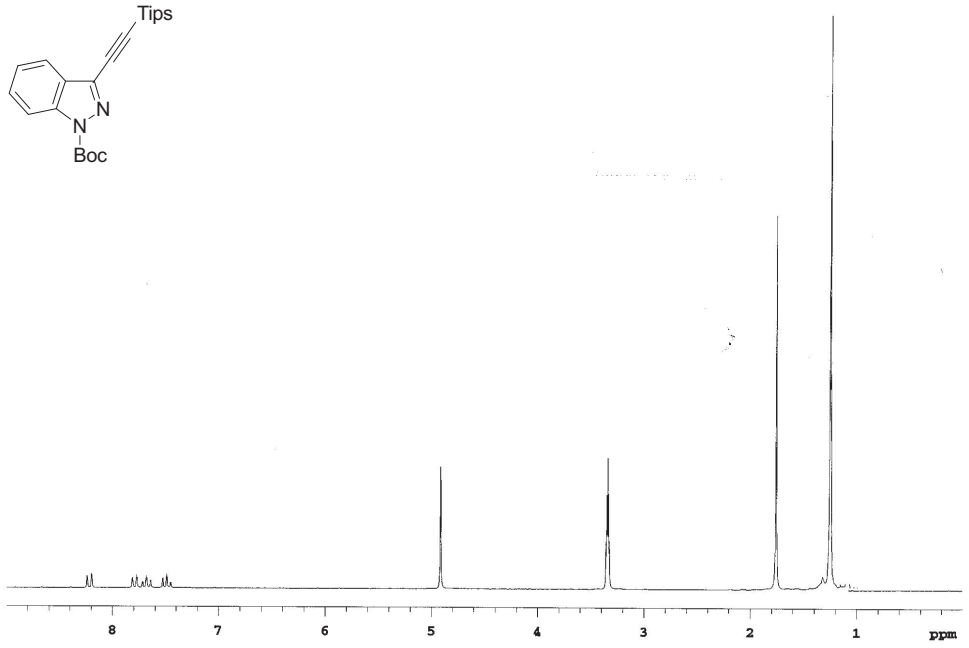
1-Butyl-3,5-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (7d)

Following the general procedure C, from **1b** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (1.6401 mmol, 0.3772 g), gave 0.2315 g, (55 %) of **7d** as a black solid: mp: descompose at 240ºC; IR (KBr): υ_{max} (cm^{-1}) 2229; 1744; 1382; ^1H-NMR (200 MHz, acetone-d_6) δ (ppm) 9.69 (d, 2H, *J* = 1.2 Hz), 9.37 (s, 1H), 8.27 (d, 2H, *J* = 8.5 Hz), 8.03 (d, 2H, *J* = 7.9 Hz), 7.73 (t, 2H, *J* = 6.9 Hz), 7.52 (t, 2H, *J* = 7.3 Hz), 4.9 (t, 2H, *J* = 7.6 Hz), 2.23-2.20 (m, 2H), 1.53-1.48 (m, 2H, *J* = 7.3 Hz), 1.02 (t, 3H, *J* = 7.6 Hz); ^{13}C-NMR (300 MHz, CD_3OD) δ (ppm) 150.0, 149.1, 147.8, 140.8, 132.8, 130.8, 127.5, 125.8, 124.7, 121.1, 115.8, 88.6, 87.4, 86.5, 64.0, 33.7, 28.2, 20.1, 13.7; MS (ESI^+) m/z (relative intensity) 616 (M^+, 100); Anal. Calcd for $C_{34}H_{32}N_5O_4$: C, 71.06; H, 5.61; N, 12.19. Found: C, 71.12; H, 5.51; N, 12.13.

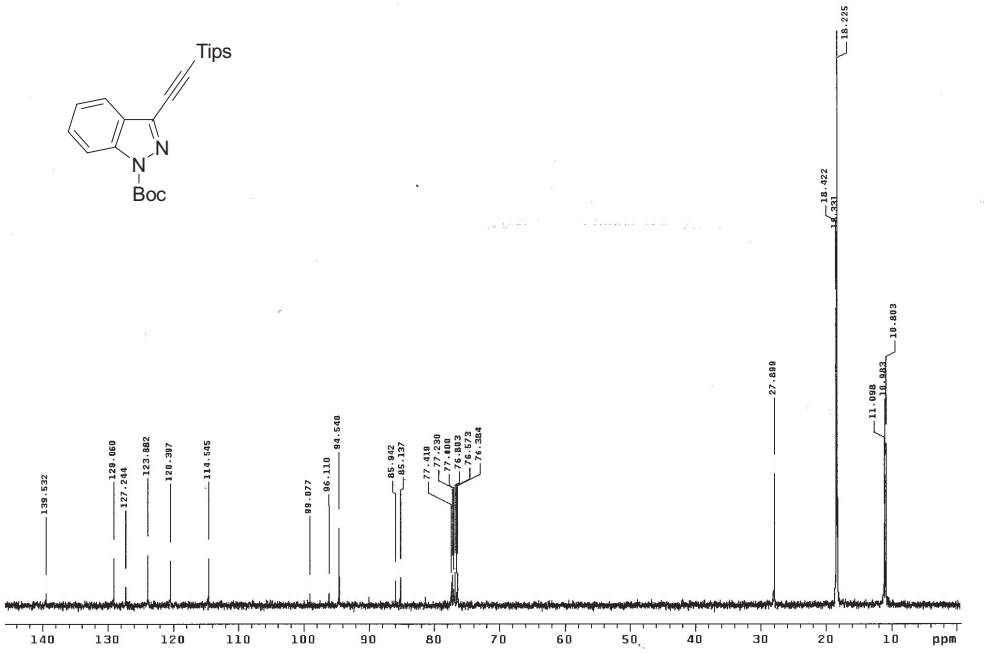
1e. Copies of ^{1}H and ^{13}C NMR for all new compounds reported

3-[(Triisopropylsilanyl)-ethynyl]-indazole-1-carboxylic acid tert-butyl ester

^{1}H NMR (200 MHz, CD_3OD) : 8.21 (d, 1H, J= 8.44); 7.79 (d, 1H, J= 8.07); 7.68 (td, 1H, J= 1.1, 8.4); 7.47 (t, 1H, J= 6.97); 1.76 (s, 9H); 1.25 (s, 21H).

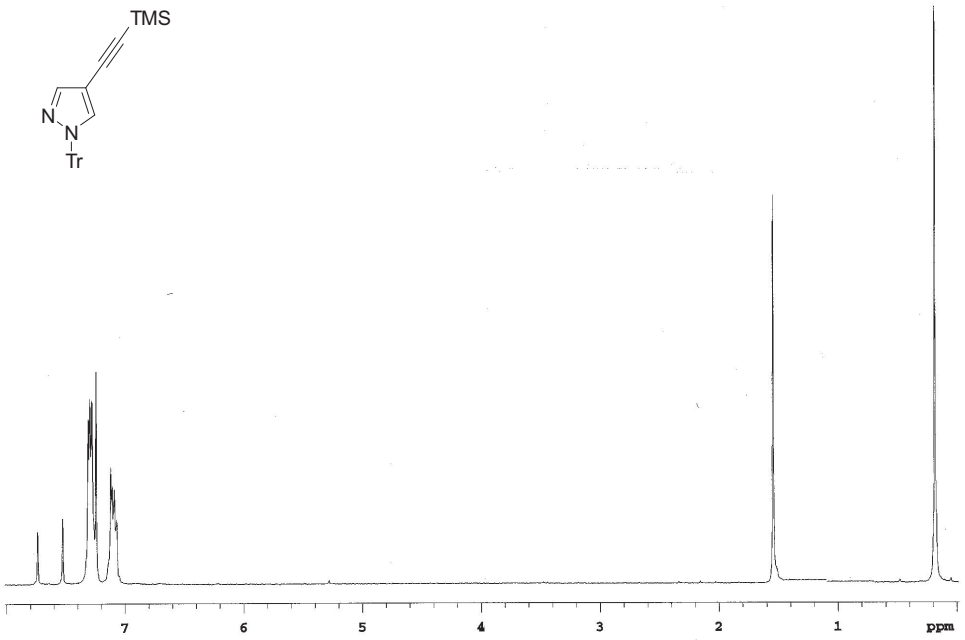


^{13}C NMR (300 MHz, $CDCl_3$) 139.53; 129.06; 127.24; 123.88; 120.39; 114.54; 99.07; 96.11; 94.54; 85.94; 85.13; 27.89; 18.22; 10.80.

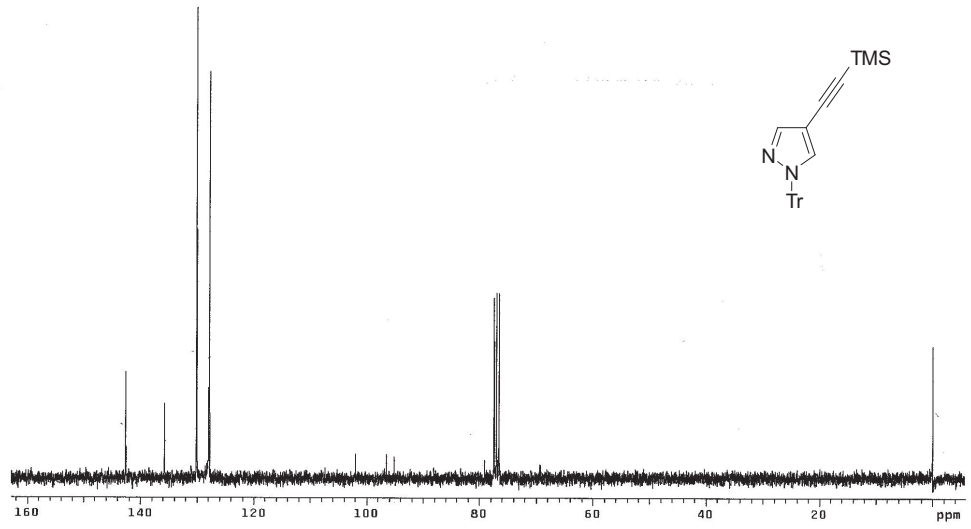


4-Trimethylsilanylethynyl-1-trityl-1H-pyrazole

^{1}H NMR (200 MHz, $CDCl_3$): 7.73 (s, 1H); 7.52 (s, 1H); 7.29 (t, 10H, J= 2.56); 7.09 (m, 5H); 0.18 (s, 9H).

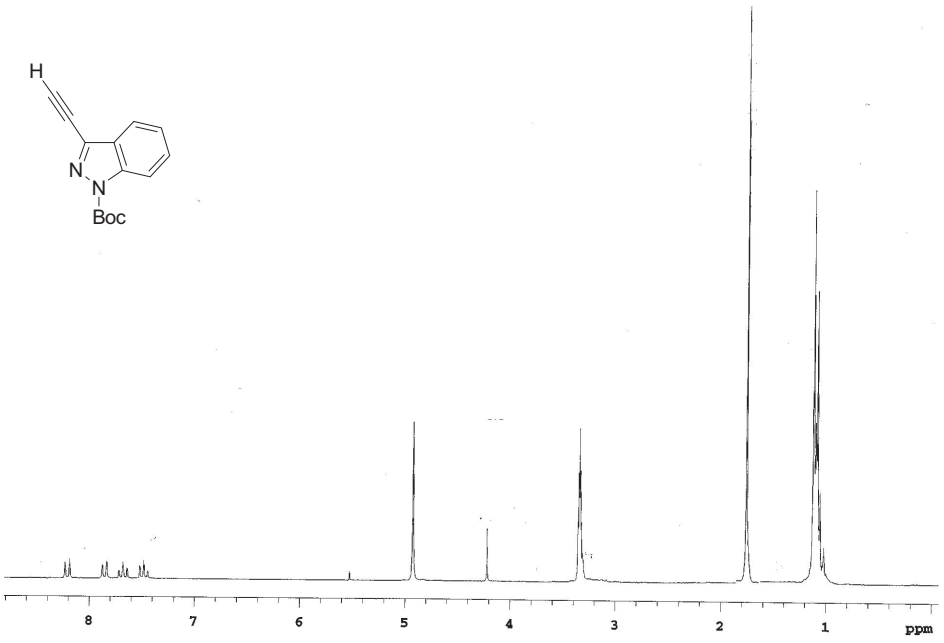


^{13}C NMR (300 MHz, $CDCl_3$) 142.63; 142.56; 135.71; 130.0; 127.87; 127.8; 101.96; 96.49; 95.0; 0.03

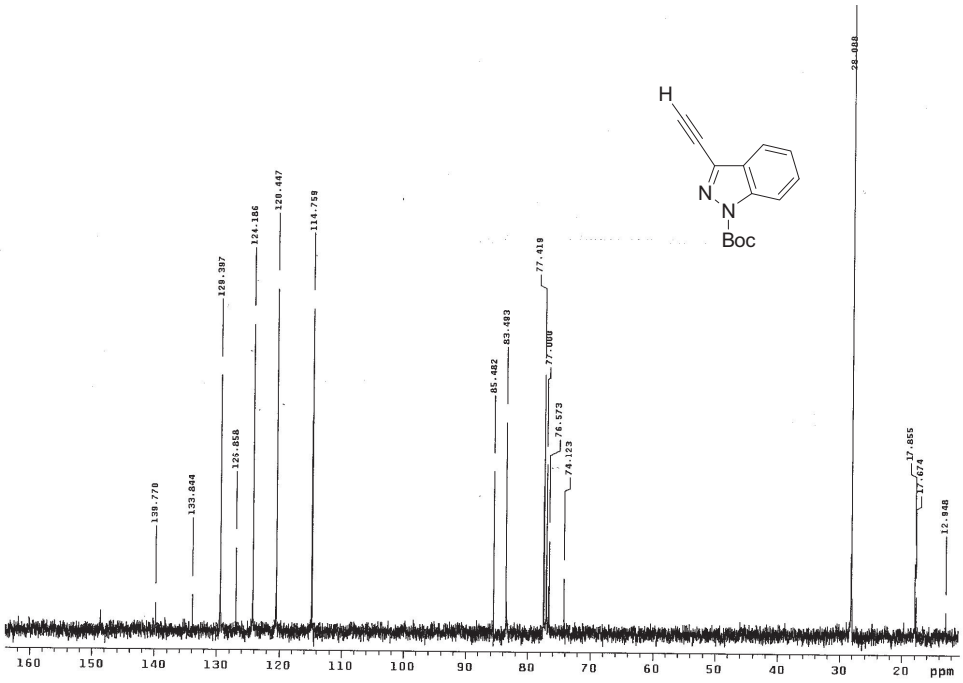


3-Ethynyl-indazole-1-carboxylic acid tert-butyl ester.

^{1}H NMR (200 MHz, CD_3OD) : 8.2 (d, 1H, J= 8.44); 7.85 (d, 1H, J= 8.07); 7.68 (td, 1H, J= 1.1; 7.34); 7.49 (t, 1H, J= 6.97); 4.21 (s, 1H); 1.75 (s,9H).

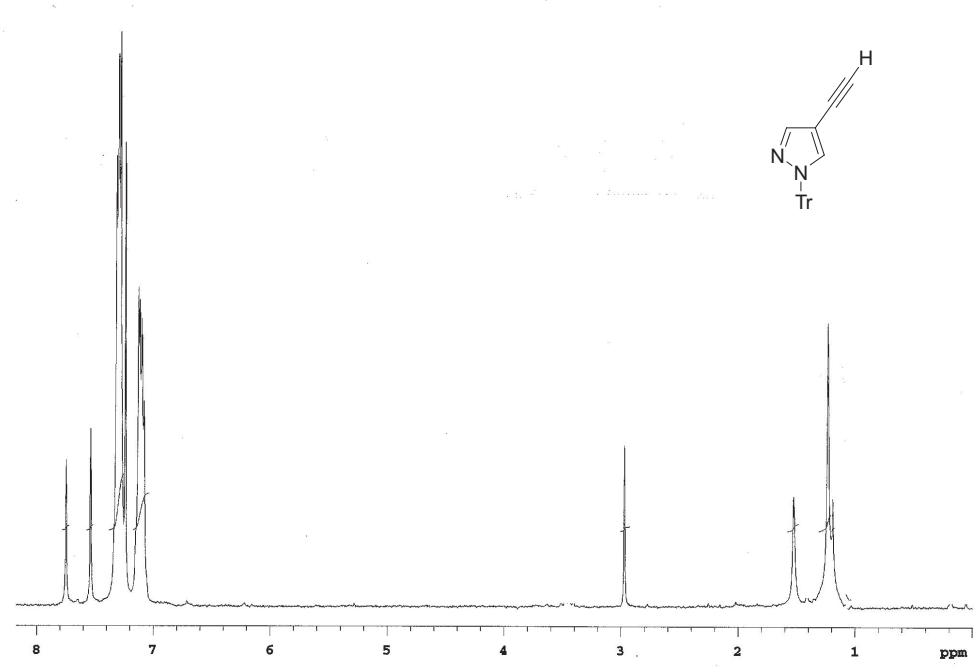


^{13}C NMR (300 MHz, $CDCl_3$) 139.7; 133.8; 129.3; 126.8; 124.1; 120.4; 114.7; 85.4; 83.4; 79.1; 28.08; 17.8.

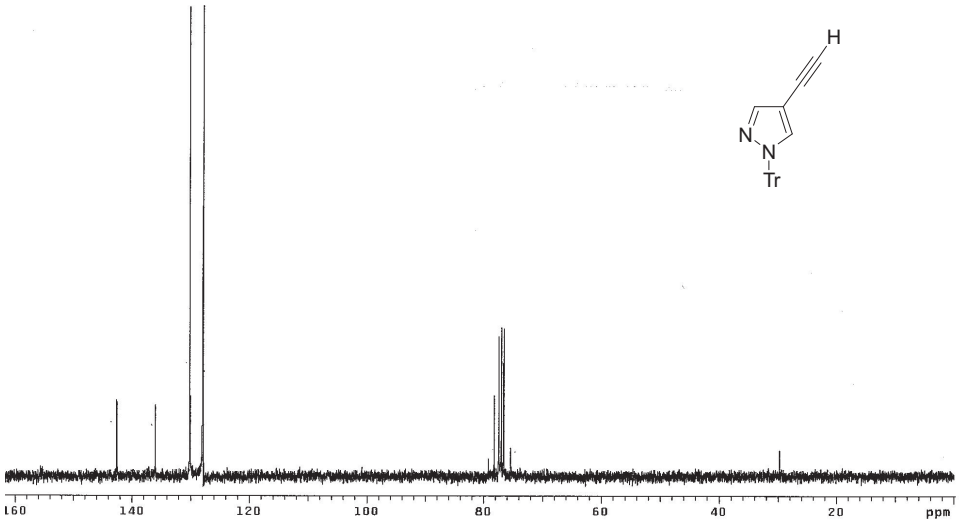


4-Ethynyl-1-trityl-1H-pyrazole.

^{1}H NMR (200 MHz, CD_3OD) : 7.74 (s, 1H); 7.53 (s, 1H); 7.3 (t, 10H, J= 3.3); 7.1 (m, 5H); 2.97 (s, 1H).

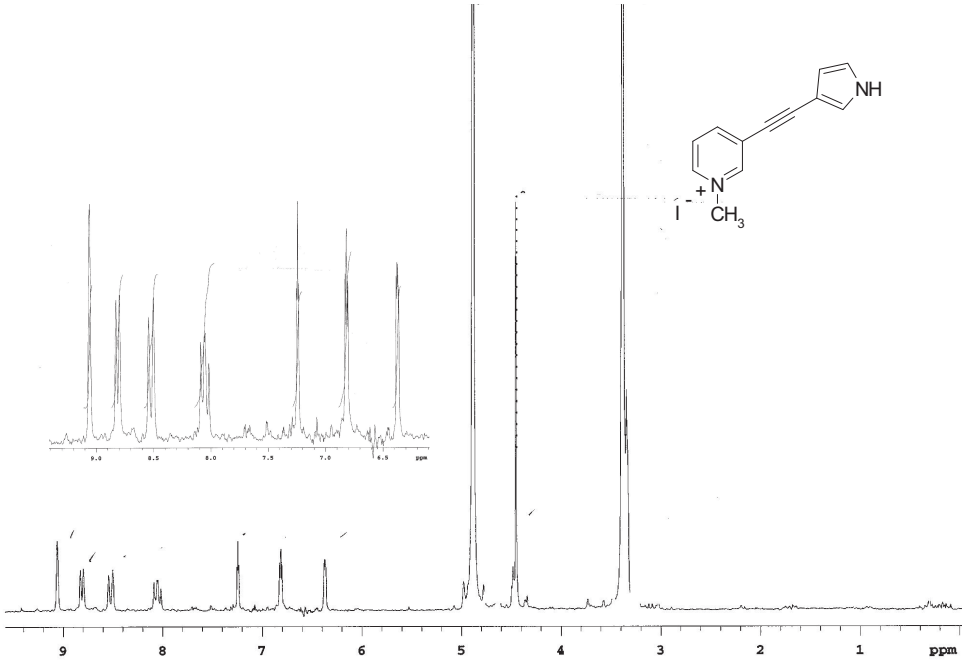


^{13}C NMR (300 MHz, $CDCl_3$) 142.58; 142.53; 135.95; 130.08; 127.92; 127.82; 79.15; 78.22; 75.39; 29.69.

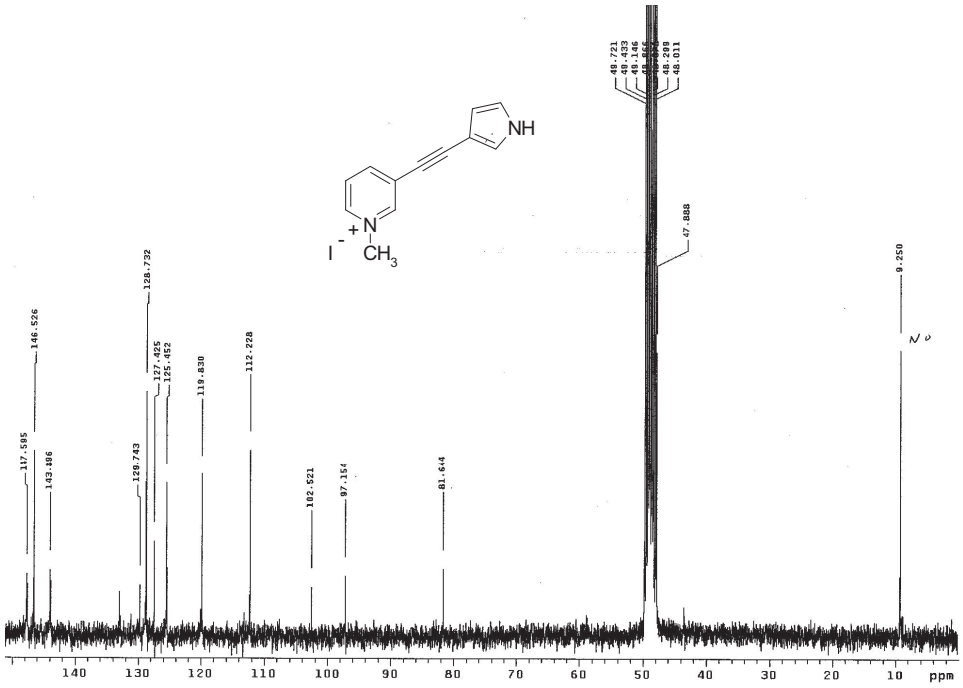


1-Methyl -3-(1H-pyrrol-3-ylethynyl) pyridinium iodide (4a)

^{1}H NMR (200 MHz, CD_3OD) 9.06 (s,1H); 8.81 (d,1H, *J*=5.8 Hz); 8.52 (d,1H, *J*=8.4 Hz); 8.04 (t,1H, J=6.2 Hz); 7.24 (t,1H, *J*=1.4 Hz); 6.81 (t,1H, *J*=1.8 Hz); 6.36 (dd, 1H, *J*=1.4, 1.4 Hz); 4.45 (s,3H)

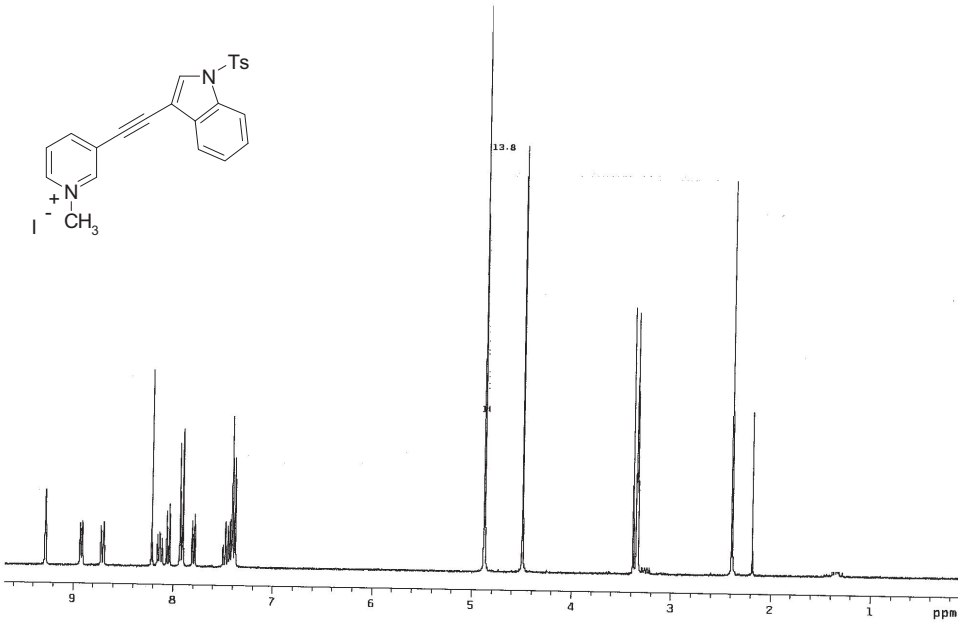


^{13}C NMR (300 MHz, CD_3OD) δ 147.59; 146.52; 143.9; 128.73; 127.42; 125.45; 119.83; 112.22; 102.52; 97.15; 81.64; 47.88.

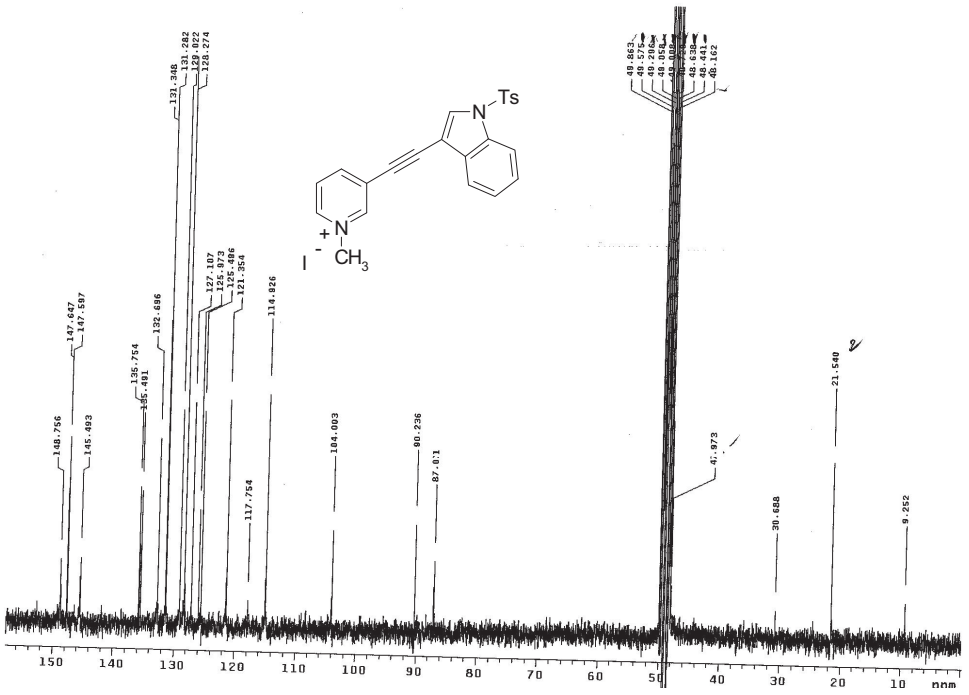


1-Methyl-3-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium Iodide (4b)

^{1}H NMR (200 MHz, CD_3OD) : 9.27 (s, 1H); 8.91 (d, 1H,*J*=5.8 Hz); 8.63 (d, 1H, *J*=8.1 Hz); 8.2 (s, 1H); 8.12-7.98 (m, 3H); 7.88 (d, 3H, *J*=8.4 Hz); 7.78 (d, 1H, *J*=6.6 Hz); 7.48-7.3 (m, 5H); 4.5 (s, 3H); 2.32 (s, 3H).

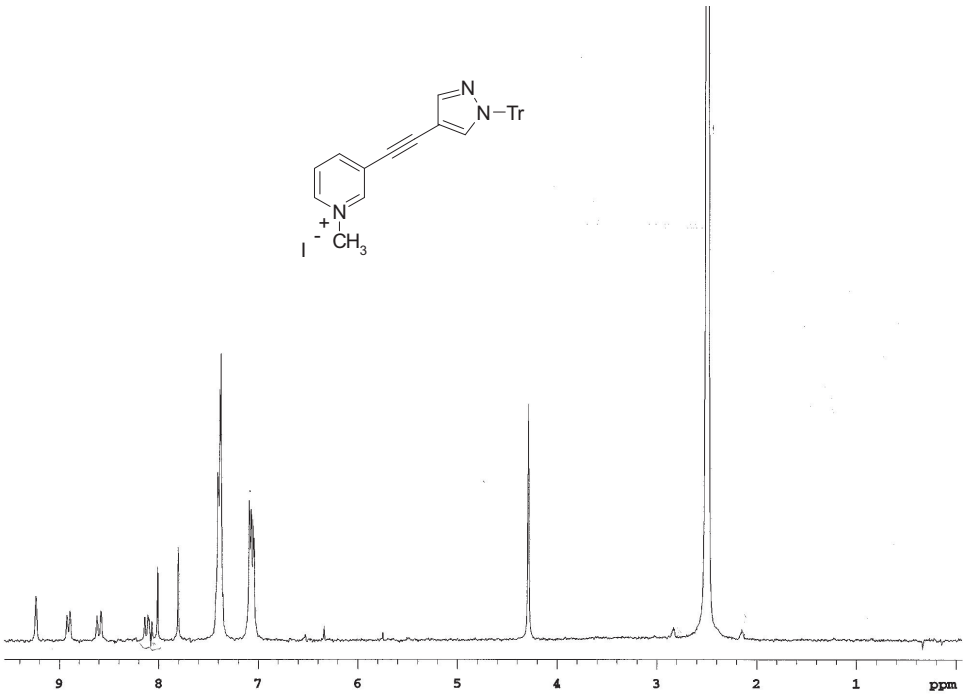


^{13}C NMR (300 MHz, CD_3OD) 148.75; 147.64; 147.59; 145.49; 135.75; 135.49; 132.69; 131.34; 129.02; 128.27; 127.1; 125.97; 125.49; 121.35; 117.75; 114.92; 104.0; 90.23; 87.07; 48.16; 47.97; 21.54.

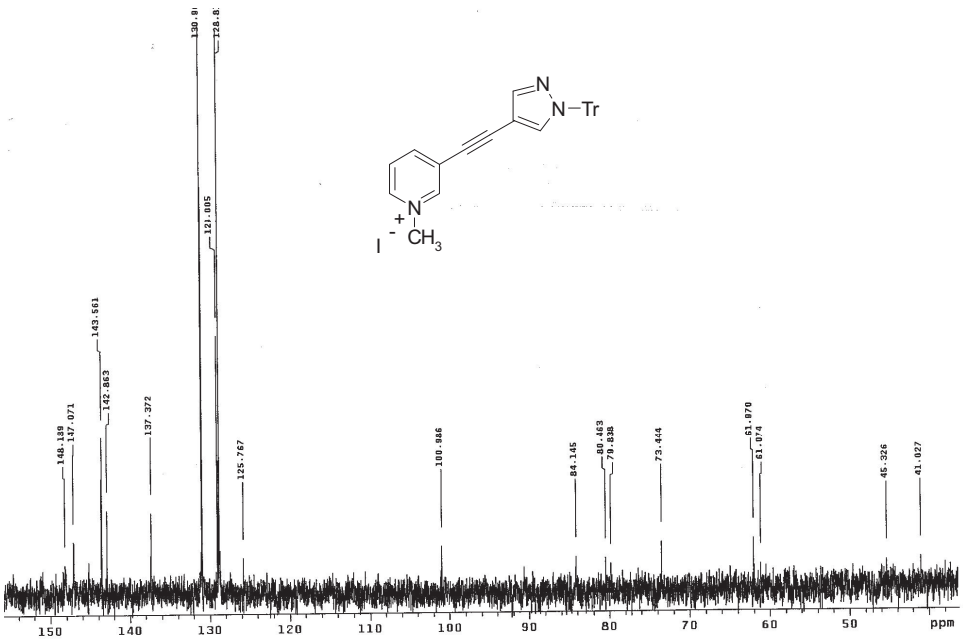


1-Methyl -3-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium Iodide (4c)

^{1}H NMR (200 MHz, DMSO-d6) 9.23 (s, 1H); 8.9 (d,1H, *J*=6.2 Hz); 8.59 (d, 1H; *J*= 8.1 Hz); 8.11 (t,1H, *J*=8.4 Hz); 8.01 (s); 7.38 (s); 7.38 (t,9H, *J*=2.5 Hz); 7.06 (c,6H, *J*=3.6 Hz); 4.28 (s,3H)

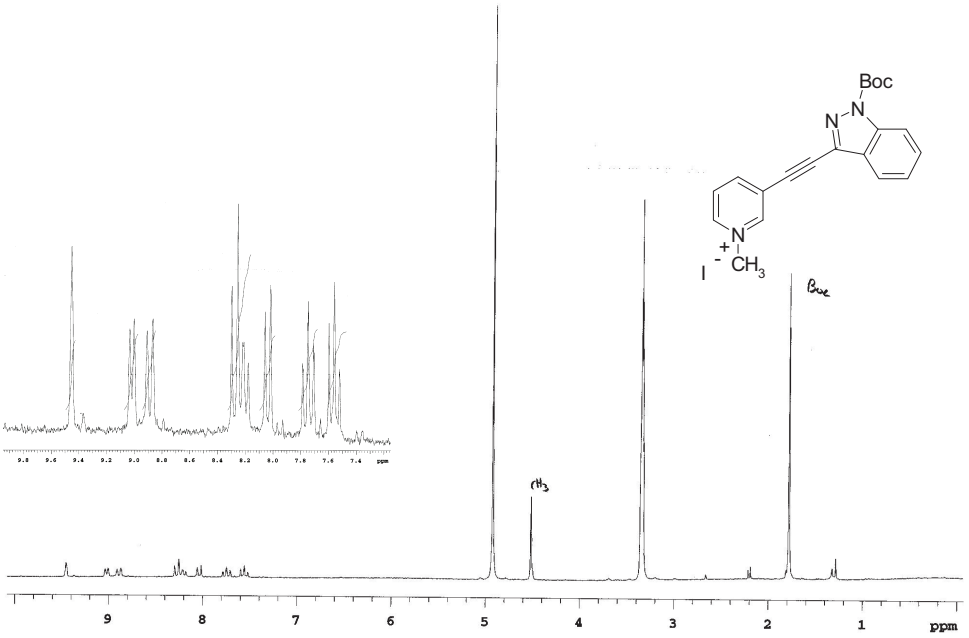


^{13}C NMR (300 MHz, acetone-d6) δ 148.18; 147.07; 143.56; 142.86; 137.37; 130.96; 129.0; 128.81; 125.76; 100.98; 84.14; 80.46; 73.44; 61.97; 45.32; 41.02

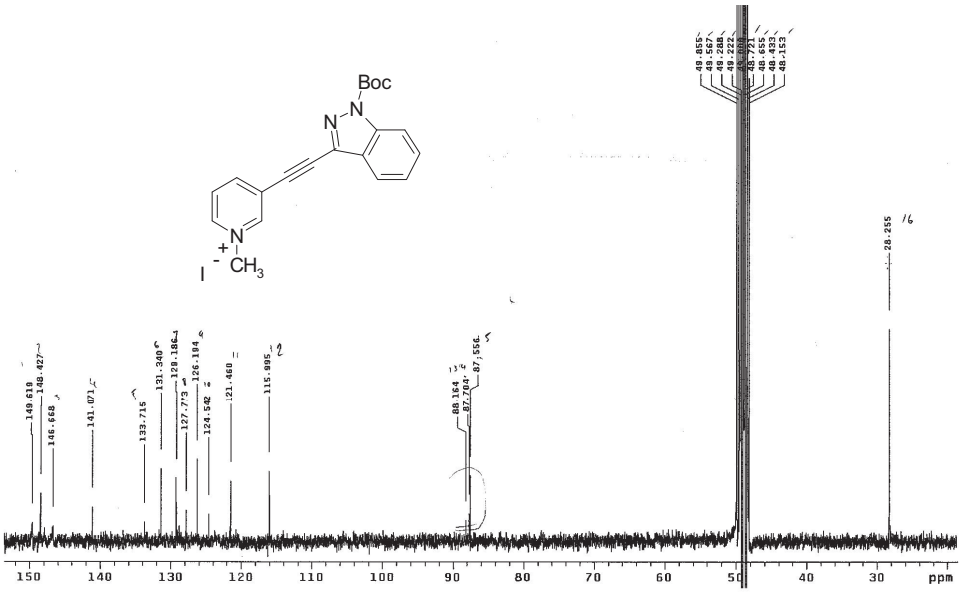


1-Methyl -3-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium iodide (4d)

^{1}H NMR (200 MHz, CD_3OD) : 9.45 (s,1H); 9.01 (d, 1H, *J*=6.2 Hz); 8.88 (d, 1H,*J*=8.1 Hz); 8.25 (d, 1H, *J*= 8.4 Hz); 8.19 (dd,1H, *J*=6.2 Hz); 8.03 (d, 1H, *J*=7.7 Hz); 7.74 (t, 1H, J=7.3 Hz); 7.55 (t,1H, J=6.9 Hz); 4.51 (s, 3H); 1.78 (s,9H).

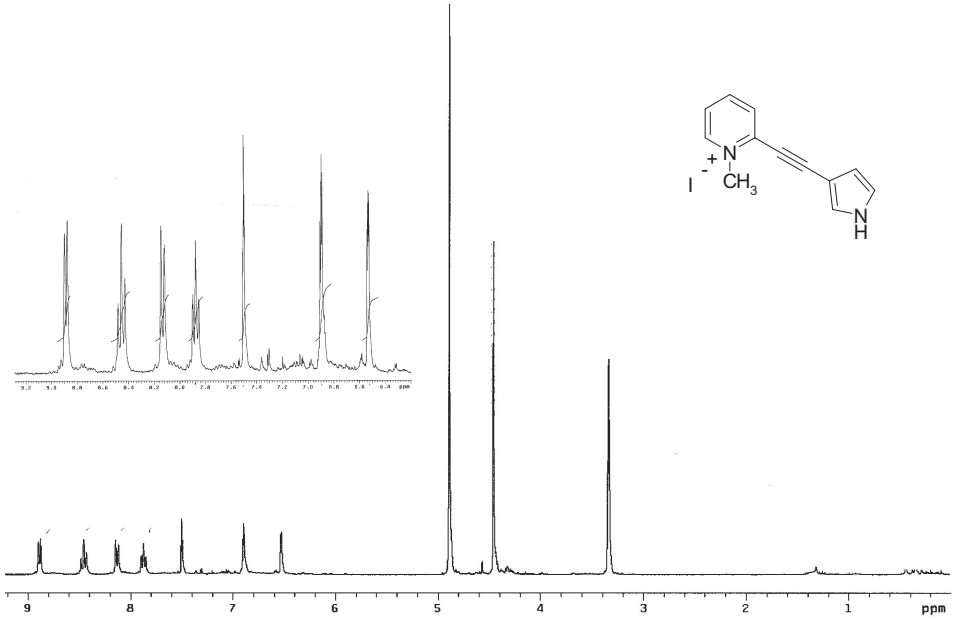


^{13}C NMR (300 MHz, CD_3OD) 209.11; 149.61; 148.42; 146.66; 141.07; 133.71; 131.34; 129.18; 127.77; 126.19; 124.54; 121.46; 115.99; 88.16; 87.7; 87.55; 48.43; 28.25.

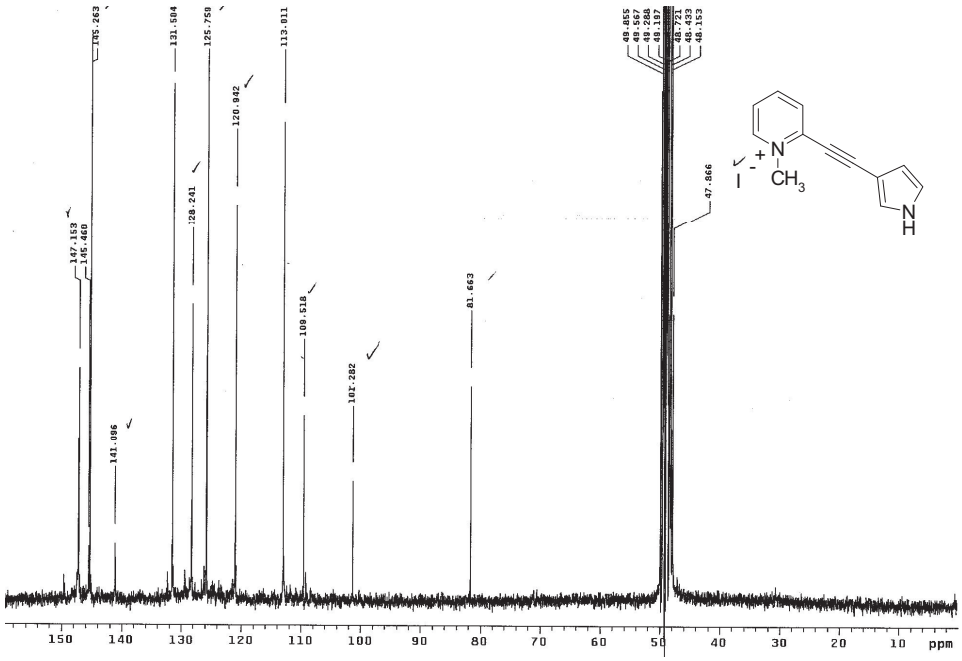


1-Methyl -2-(1H-pyrrol-3-ylethynyl) pyridinium iodide (5a)

; ^{1}H NMR (200 MHz, CD_3OD) 8.88 (d,1H; *J*= 7.2 Hz); 8.45 (t,1H, *J*=6.8 Hz); 8.13 (d,1H, *J*=8.0 Hz); 7.87 (t,1H, *J*=6.2 Hz); 7.5 (t,1H, *J*=1.6 Hz); 6.89 (dd,1H, *J*= 0.9 Hz, 2.0 Hz); 6.53 (dd, 1H,*J*=1.4, 1.4 Hz); 4.46 (s,3H)

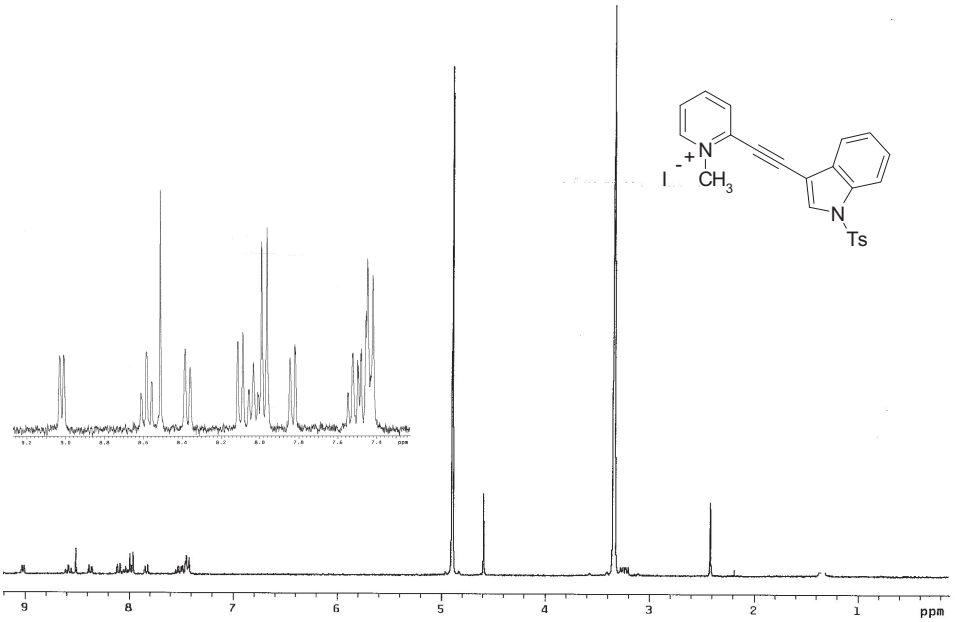


^{13}C NMR (300 MHz, CD_3OD) δ 147.15; 145.26; 141.09; 131.5; 128.24; 125.76; 120.94; 113.01; 109.51; 101.28; 81.66; 47.86.

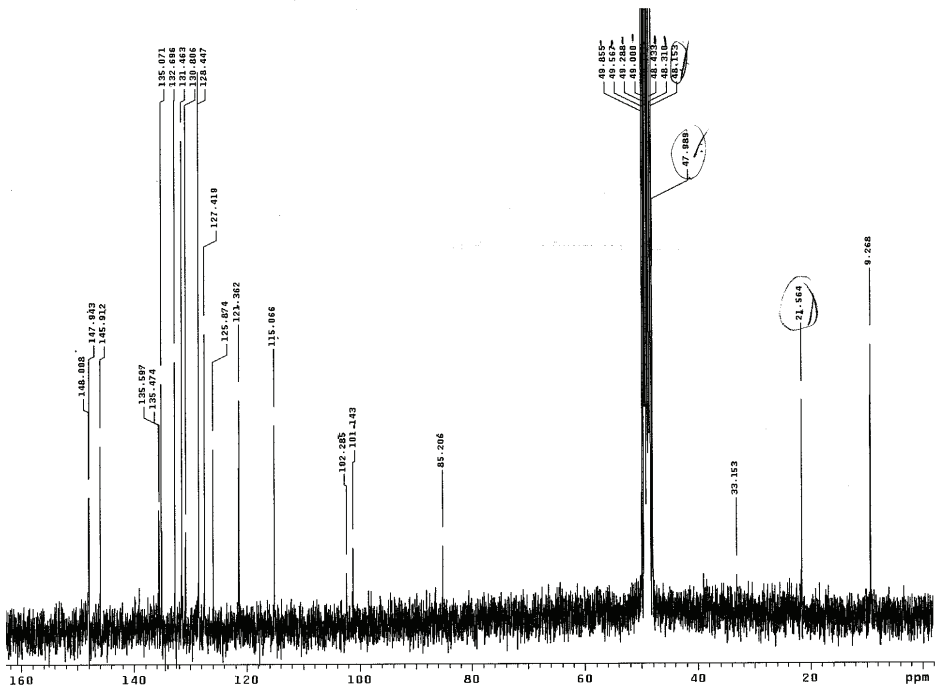


1-Methyl -2-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium iodide (5b)

^{1}H NMR (200 MHz, CD_3OD) : 9.02 (d, 1H, *J*= 6.7 Hz); 8.58 (t, 1H, *J*=7.1 Hz); 8.5 (s, 1H); 8.37 (d, 1H, *J*=7.7 Hz); 8.09 (d, 1H, *J*= 7.8 Hz); 8.03 (t, 1H, *J*= 6.2 Hz); 7.97 (d, 2H, *J*= 8.4 Hz); 7.83 (d, 1H, *J*=7.5 Hz); 7.54-7.47 (m, 2H); 7.44 (t, 3H, *J*=8.4 Hz) 4.59 (s, 3H); 2.41 (s, 3H).

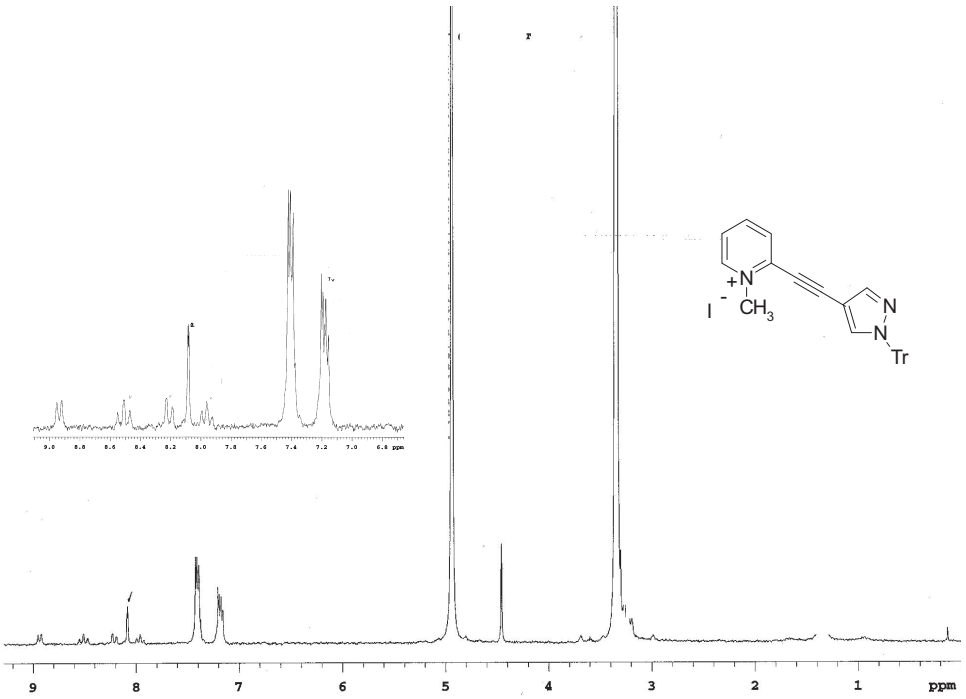


^{13}C NMR (300 MHz, CD_3OD) 148.0; 147.94; 145.91; 135.59; 135.47; 135.07; 132.69; 131.46; 130.8; 128.44; 127.41; 125.87; 121.36; 115.06; 102.28; 101.14; 85.2; 48.15; 47.98; 21.56.

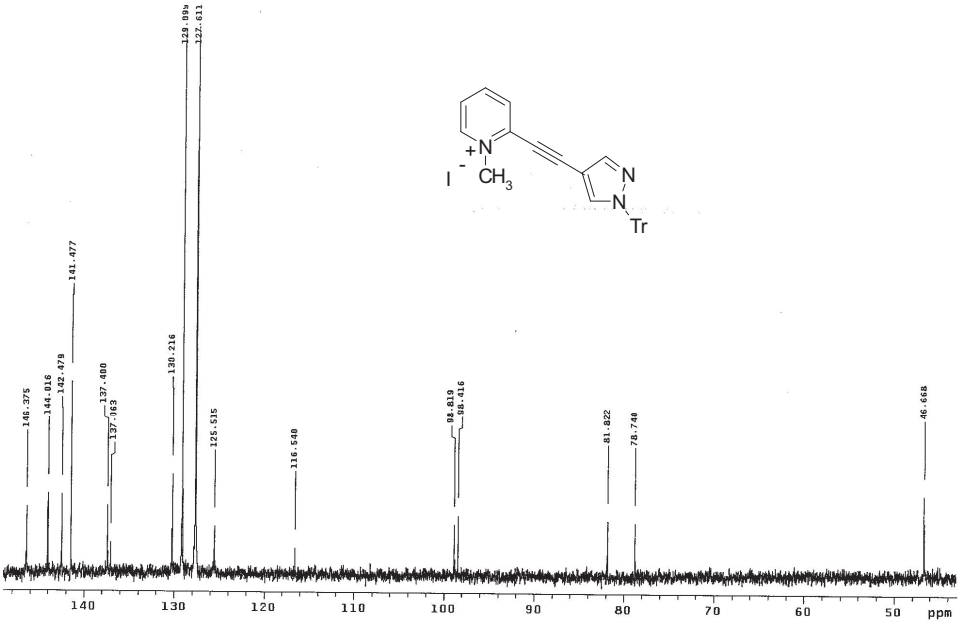


1-Methyl -2-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium iodide (5c)

^{1}H NMR (200 MHz, CD_3OD) : 8.93 (d, 1H, *J*=5.8 Hz); 8.51 (t, 1H, *J*=8.1 Hz); 8.21 (d, 1H, *J*=7.7 Hz); 8.08 (s, 2H); 7.96 (t, 1H, *J*=6.2 Hz), 7.41 (t, 9H, *J*=3.7 Hz) ; 7.18 (c, 6H, *J*=3.7 Hz) ; 4.45 (s, 3H);

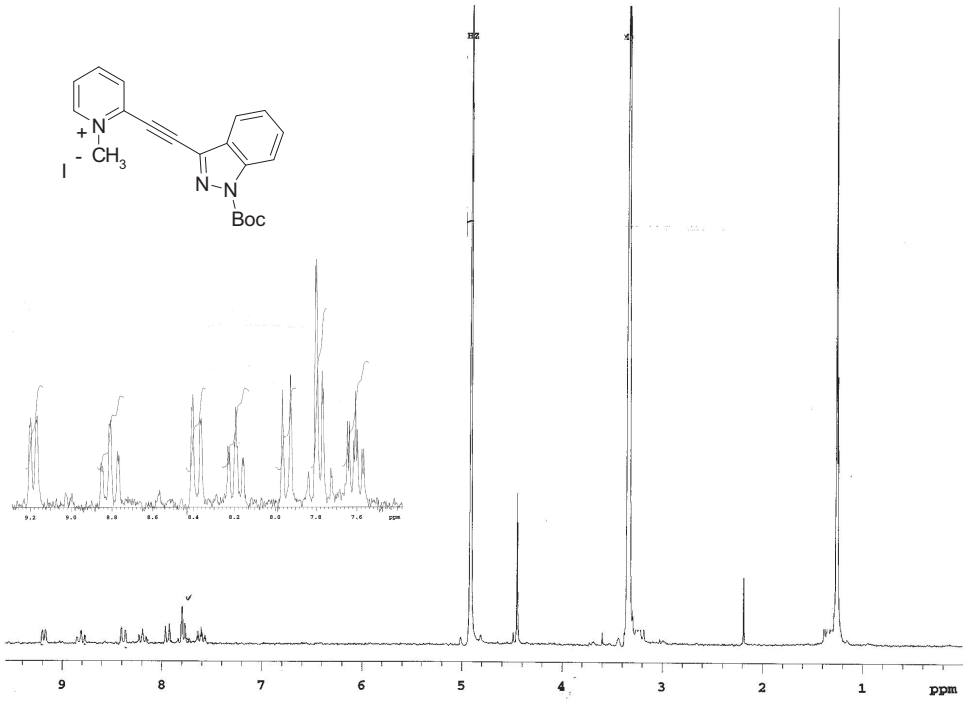


^{13}C NMR (300 MHz, CD_3OD) : 146.3; 144.01; 142.4; 141.4; 137.4; 137.0; 130.2; 129.1; 127.6; 125.5; 116.5; 98.8; 98.4; 81.8; 78.7; 46.6.

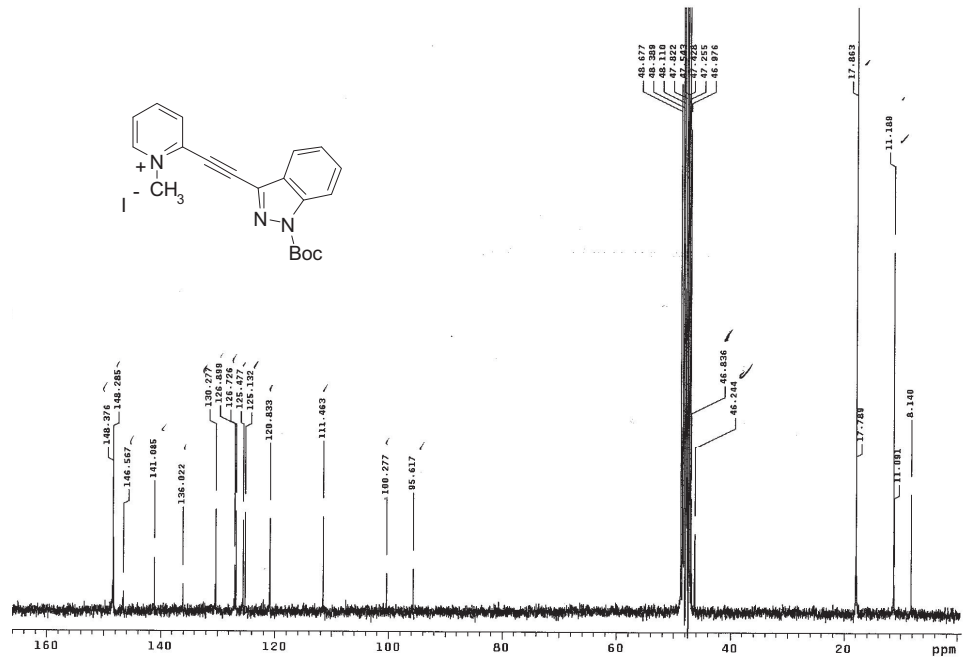


1-Methyl -2-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium iodide (5d)

; ^{1}H NMR (200 MHz, CD_3OD) : 9.18 (d, 1H, *J*=6.6 Hz); 8.79 (t, 1H, *J*=6.6 Hz); 8.38 (d, 1H, *J*=8.1 Hz); 8.19 (t, 1H, *J*=7.7 Hz); 7.94 (d,1H, *J*= 8.1 Hz); 7.73 (td, 2H, *J*= 1.1, 7.3 Hz); 7.6 (td, 1H, *J*= 1.8, 4.4 Hz); 4.44 (s, 3H); 1.25 (s,9H).

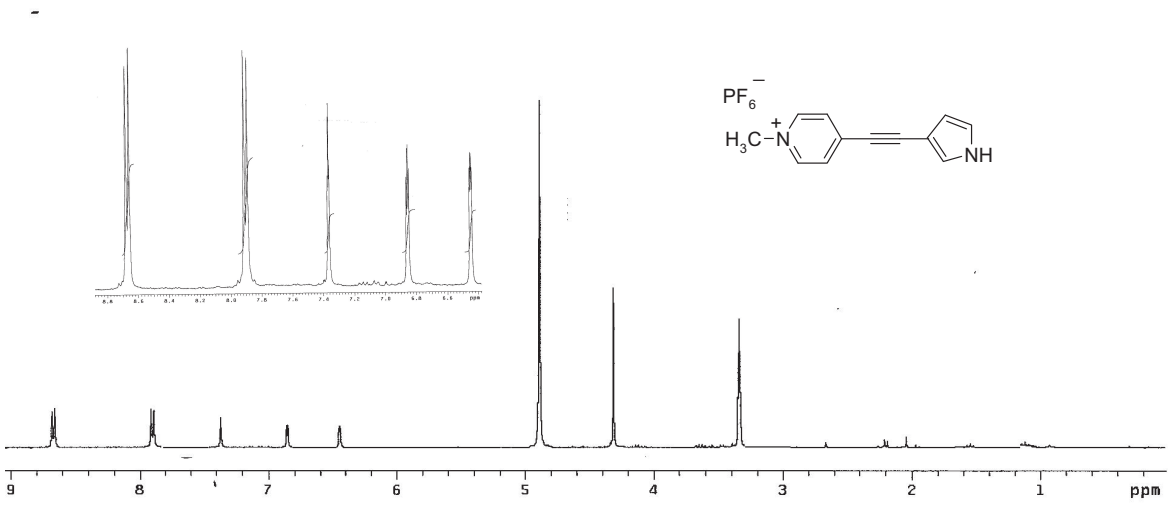


^{13}C NMR (300 MHz, CD_3OD): 209; 148.37;148.28; 146.56; 141.08; 136.02; 130.27; 126.9; 126.72; 125.47; 125.13; 120.83; 111.46; 100.27; 95.61; 46.83; 17.86; 11.18.

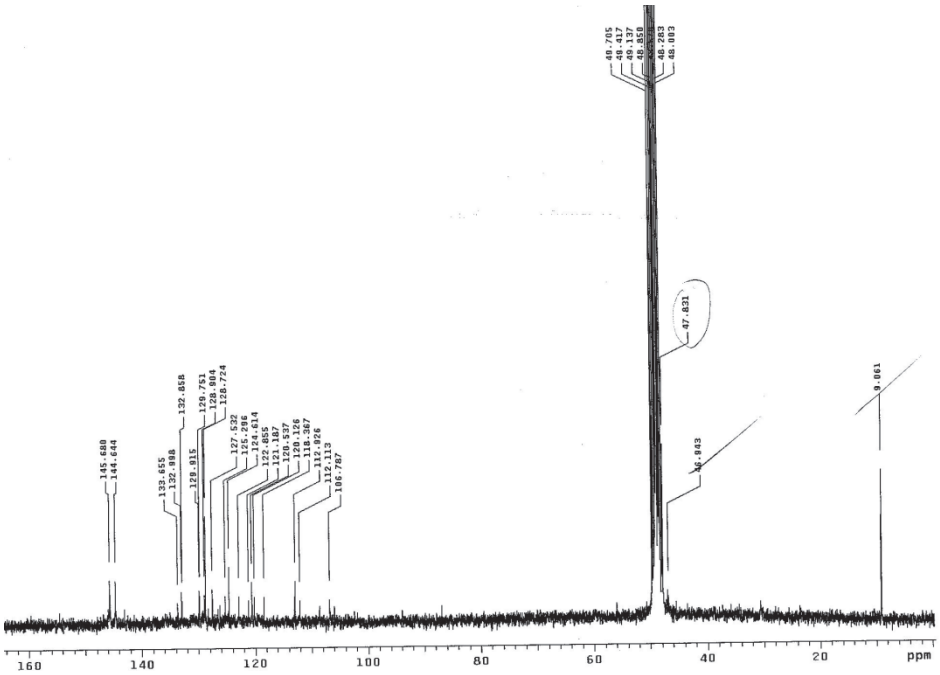


1-Methyl -4-(1H-pyrrol-3-ylethynyl) pyridinium hexafluoro phosphate (6a)

^{1}H NMR (200 MHz, CD_3OD) 8.66 (d,2H, *J*=6.7 Hz); 7.9 (d,2H, *J*=6.7 Hz); 7.36 (t,1H, *J*=1.4 Hz); 6.85 (dd,1H, *J*=2.0, 0.7 Hz); 6.44 (dd,1H, *J*=1.2, 1.4 Hz), 4.89 (s, 3H)

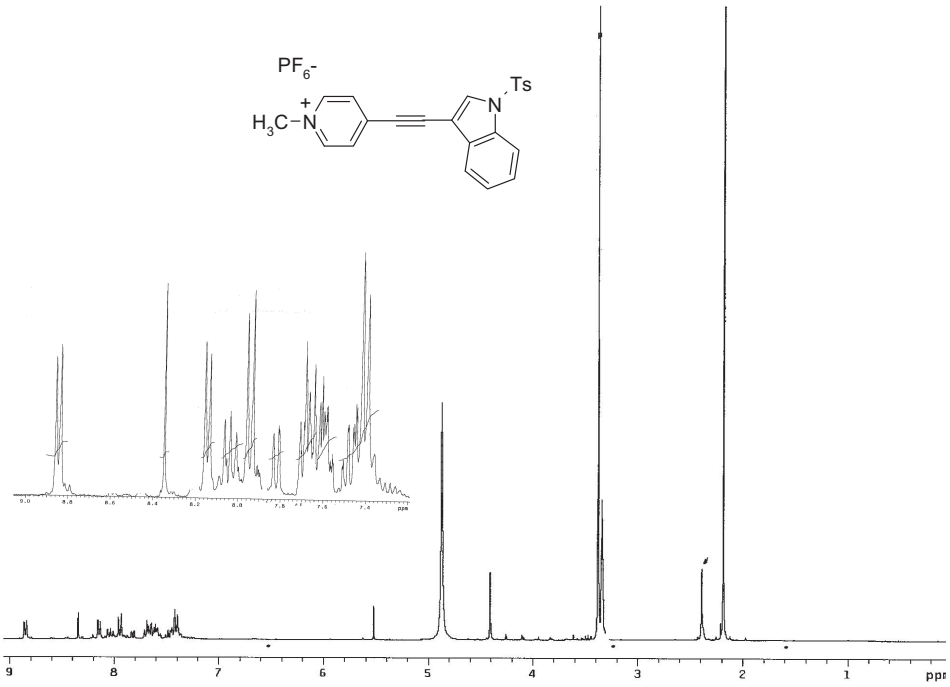


^{13}C NMR (300 MHz, CD_3OD) δ 145.68; 144.64; 132.99; 129.72; 127.53; 124.61; 120.53; 118.36; 112.92; 106.78; 47.83.

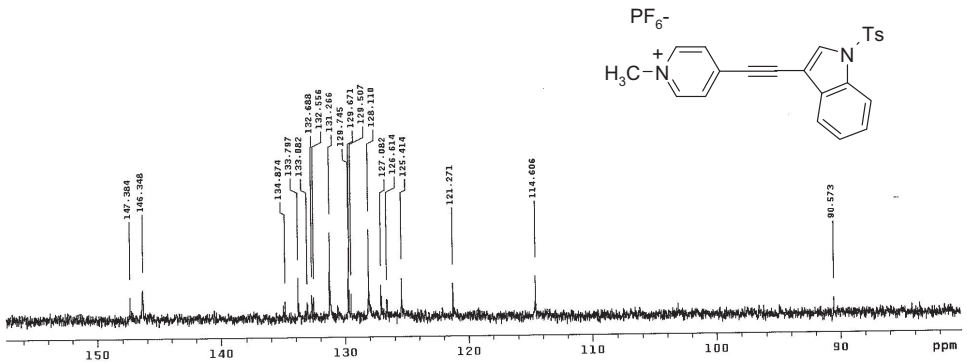


1-Methyl-4-[1-(toluene-4-sulfonyl)-1H-indol-3-ylethynyl] pyridinium hexafluoro phosphate (6b)

^{1}H NMR (200 MHz, CD_3OD) : 8.84 (d, 2H, *J*=6.7 Hz); 8.34 (s, 1H); 8.14 (d, 2H, *J*=6.95 Hz); 8.03 (t, 2H, *J*= 8.6 Hz); 7.94 (d, 2H; *J*= 8.4 Hz), 7.8 (d, 1H; *J*= 0.9 Hz); 7.7-7.58 (m, 4H); 4.4 (s, 3H); 2.38 (s,3H).

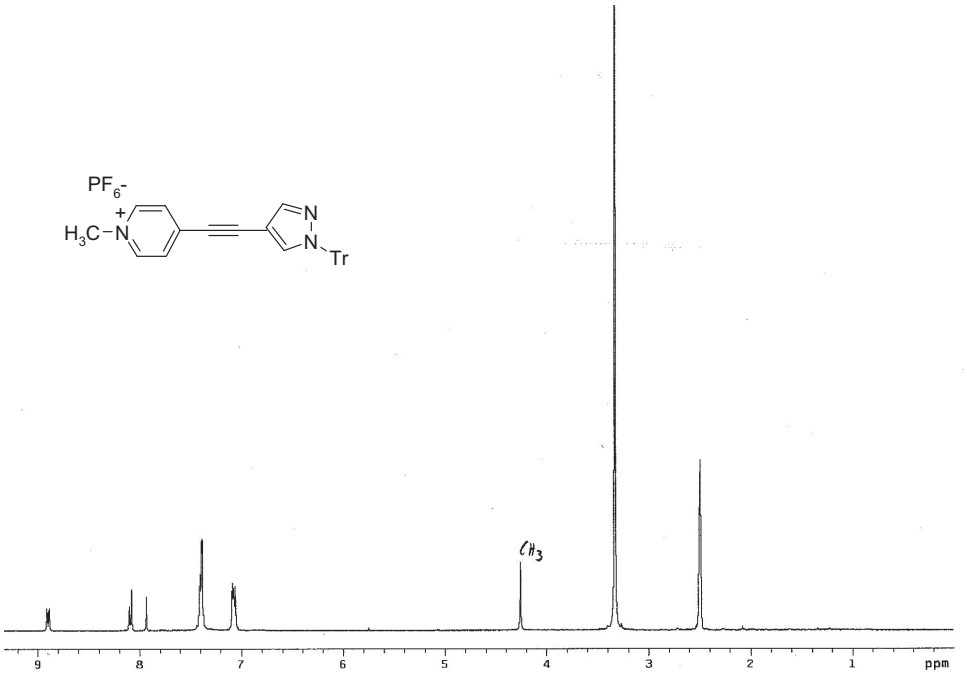


^{13}C NMR (300 MHz, CD_3OD) 147.3; 146.3; 134.8; 133.7; 133.0; 132.6; 132.5; 131.2; 129.7; 129.6; 129.5; 128.1; 127.0; 126.6; 125.4; 121.2; 114.6; 90.57; 48.8; 47.6; 21.4.

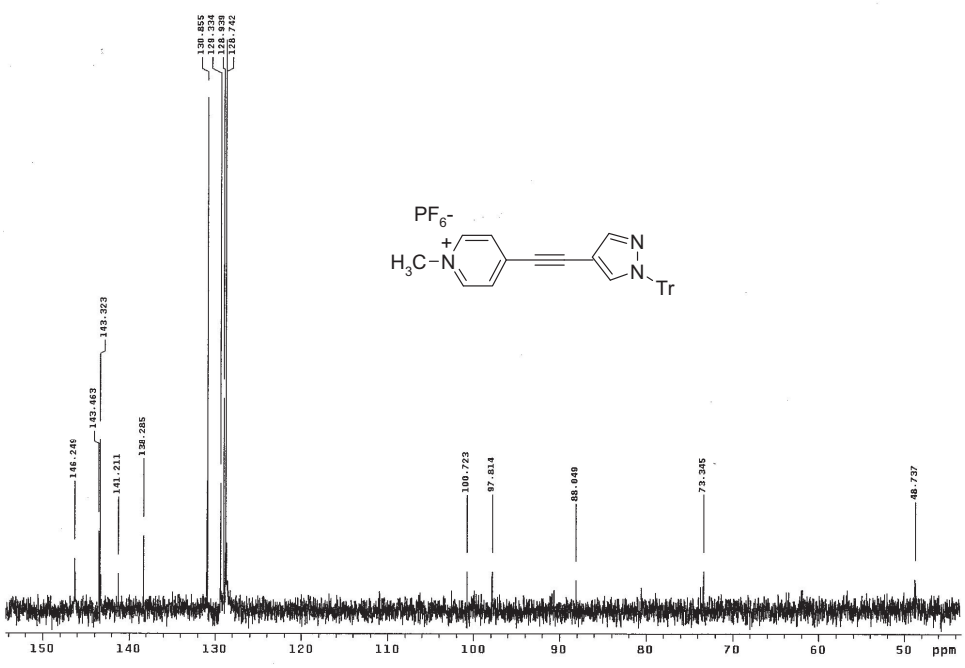


1-Methyl-4-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium hexafluorophosphate (6c)

; ^{1}H NMR (200 MHz, DMSO-d6) 8.89 (d,2H, *J*=6.7 Hz); 8.091(d,2H, *J*=7.1 Hz); 7.93 (s); 7.39 (c, 10H, *J*=3.6 Hz); 7.06 (c, 6H, *J*=3.4 Hz); 4.25 (s, 3H)

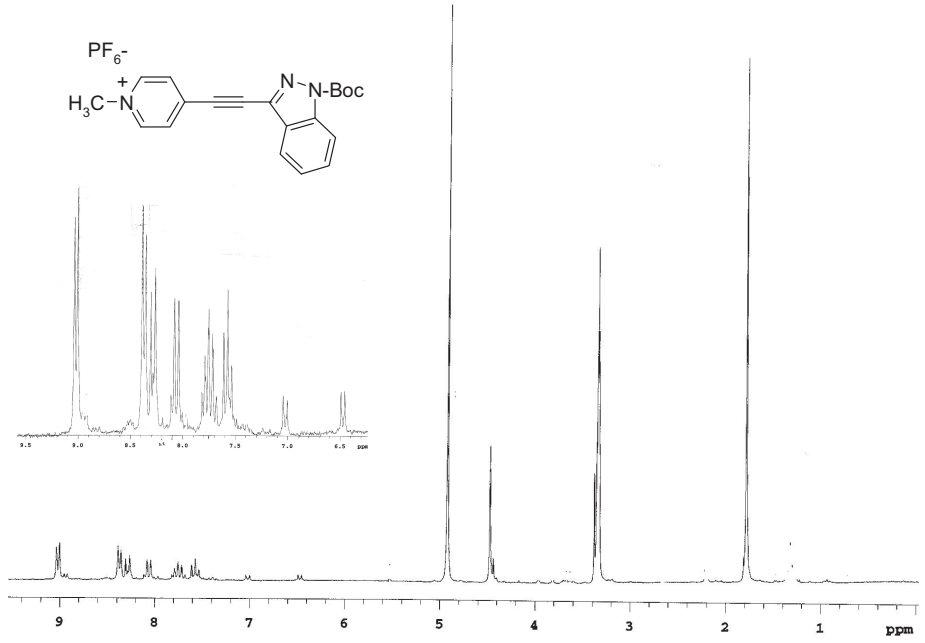


^{13}C NMR (300 MHz, acetone-d6) δ 146.25; 143.32; 141.21; 138.28; 130.85; 129.33; 128.93; 128.74; 100.72; 97.81; 80.04; 73.34; 48.73.

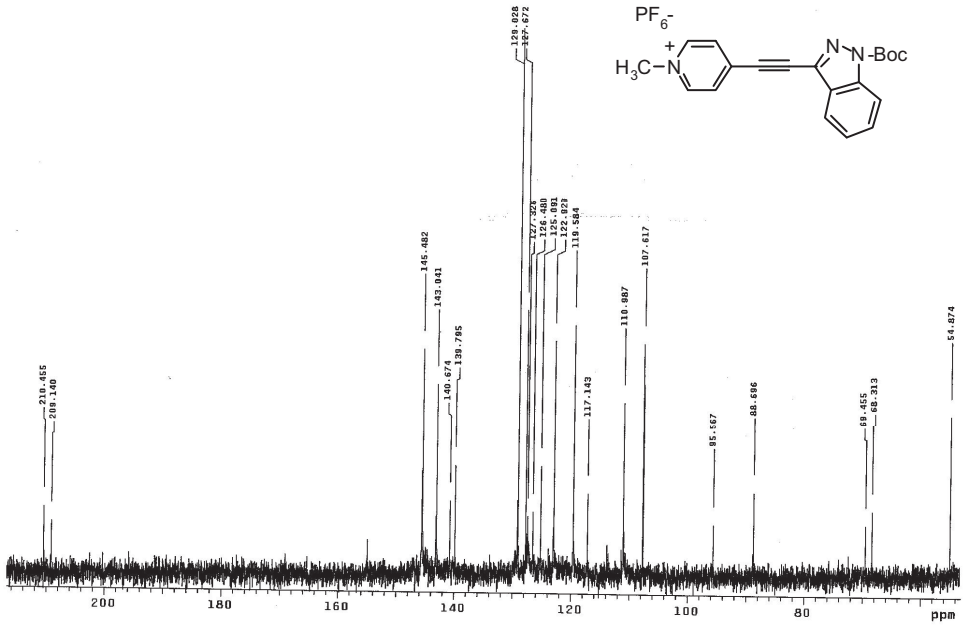


1-Methyl-4-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (6d)

^{1}H NMR (200 MHz, CD_3OD): 9.02 (d, 2H, *J*=6.6 Hz); 8.37 (d,2H, *J*=6.9 Hz); 8.28 (d, 1H, *J*=8.4 Hz); 8.06 (d, 1H, *J*=8.1 Hz); 7.75 (t,1H, *J*=7.3 Hz); 7.57 (t, 1H, *J*=7.3 Hz); 4.47 (s, 3H); 1.78 (s,9H)

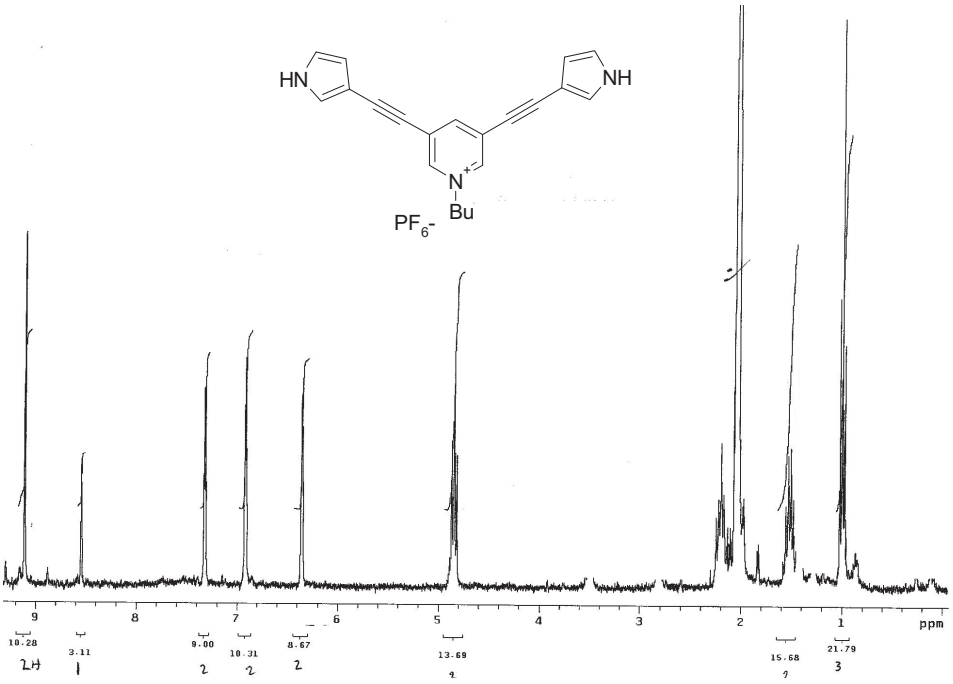


^{13}C NMR (300 MHz, CD_3OD): 209.11; 145.48; 143.04; 140.67; 139.79; 129.02; 127.67; 125.09; 122.92; 119.58; 117.14; 110.98; 95.56; 88.69; 69.45; 47.0; 29.98.

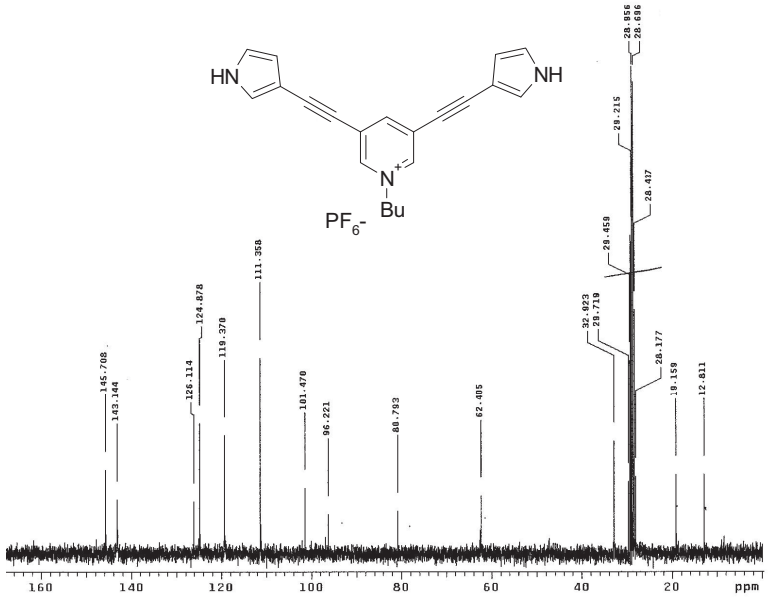


1-Butyl -3,5-(1H-pyrrol-3-ethynyl) pyridinium hexafluorophosphate (7a)

^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.15 (d,2H, *J*= 1.4 Hz); 8.54 (s,1H); 7.32 (dd, 2H, *J*=1.2, 1.4 Hz); 6.91 (dd,2H, *J*= 2.0, 2.5 Hz); 6.35 (t,2H, *J*= 2.5 Hz), 4.84 (t, 2H; *J*= 7.5 Hz); 2.22 (q, 2H, *J*= 8.0 Hz); 1.53 (sex, 2h, *J*= 7.3 Hz); 0.99 (t, 3H, *J*= 7.3 Hz);

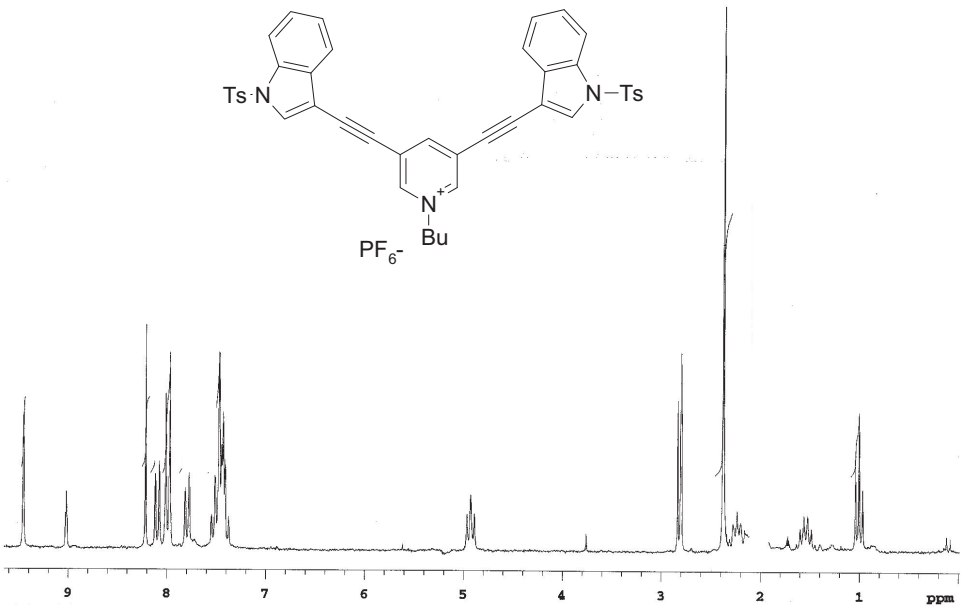


^{13}C-NMR (300 MHz, CD_3OD) δ (ppm) 145.7; 143.14; 126.11; 124.87; 119.37; 111.35; 101.47; 96.22; 80.79; 62.4; 32.92; 19.15; 12.81.

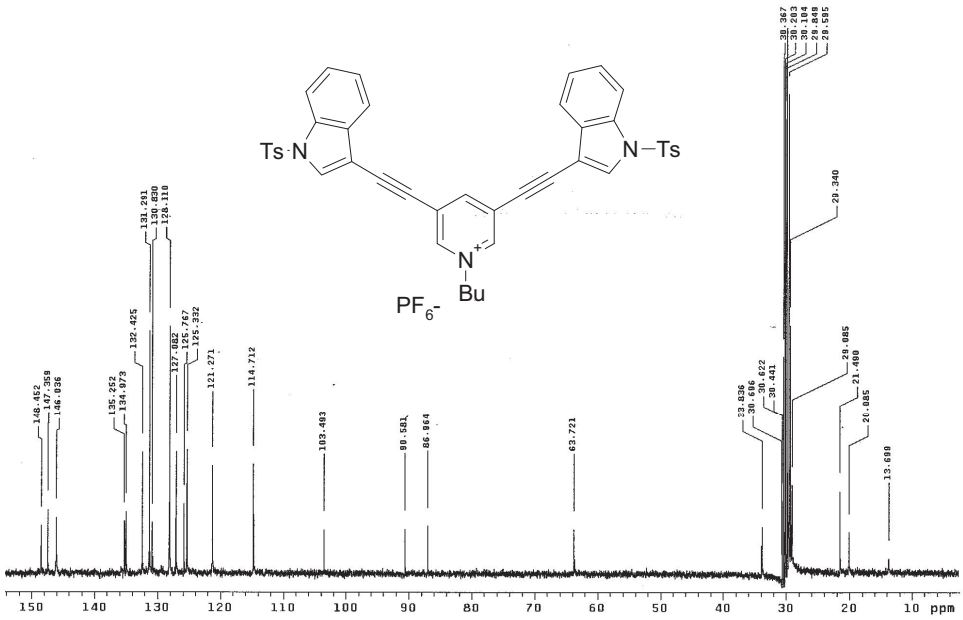


1-Butyl-3,5-[1-(toluene-4-sulfonyl)-3-ethynylindole] pyridinium Hexafluoro phosphate (7b)

^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.45 (d, 2H, *J*= 1.5 Hz); 9.02 (s, 1H); 8.21 (s, 2H); 8.09 (d, 2H, *J*= 8.2 Hz); 7.99 (d, 4H; *J*= 8.5 Hz), 7.79 (d, 2H; *J*= 6.9 Hz); 7.54-7.37 (m, 9H); 4.92 (t, 2H, *J*= 7.6 Hz); 2.37 (s,6H); 2.22 (dd, 2H, *J*= 8.05 Hz); 1.53 (td, 2H, *J*= 7.3 Hz); 1.0 (t, 3H, *J*=7.6 Hz).

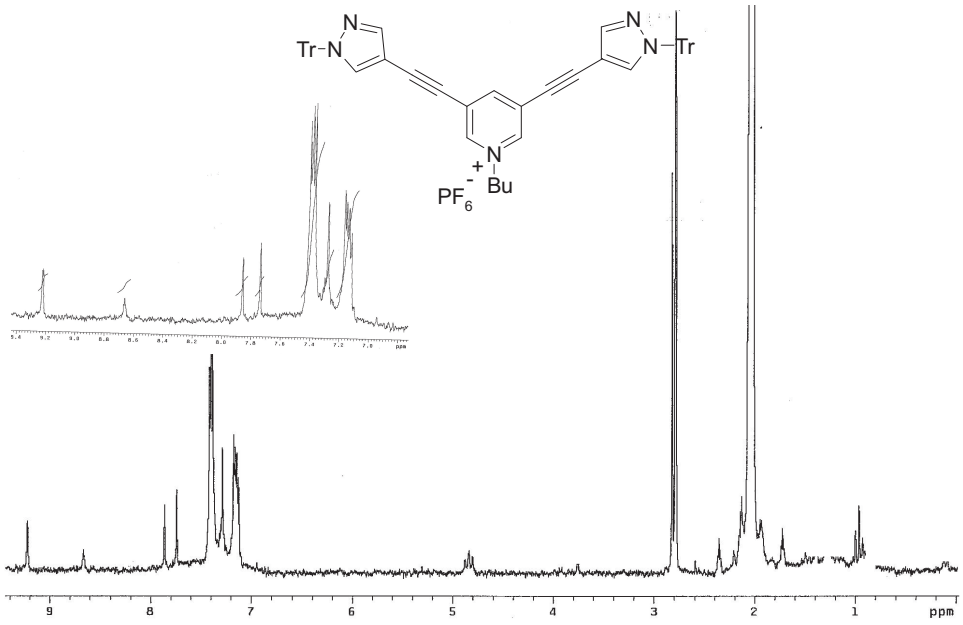


^{13}C-NMR (300 MHz, CD_3OD) 148.45; 147.35; 146.03; 135.25; 134.97; 132.42; 131.29; 130.83; 128.11; 127.08; 125.76; 125.33; 121.27; 114.71; 103.49; 90.58; 86.96; 63.72; 33.83; 21.49; 20.08; 13.69.

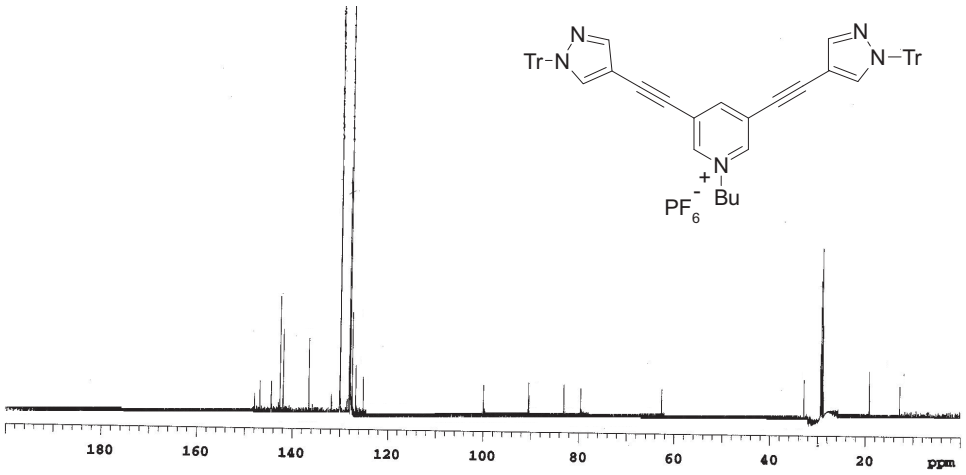


1-Butyl-3,5-(1-trityl-1H-pyrazol-4-ylethynyl) pyridinium hexafluorophosphate (7c)

^{1}H NMR (200 MHz, DMSO-d6) 9.2 (s, 2H); 8.6 (s,1H); 7.8 (s, 2H); 7.7 (s, 2H); 7.41-7.38 (m, 15H); 7.17- 7.14 (m, 10H); 7.3-7.28 (m, 5H); 4.8 (t, 2H, *J*=3.6 Hz); 4.28 (s,3H);

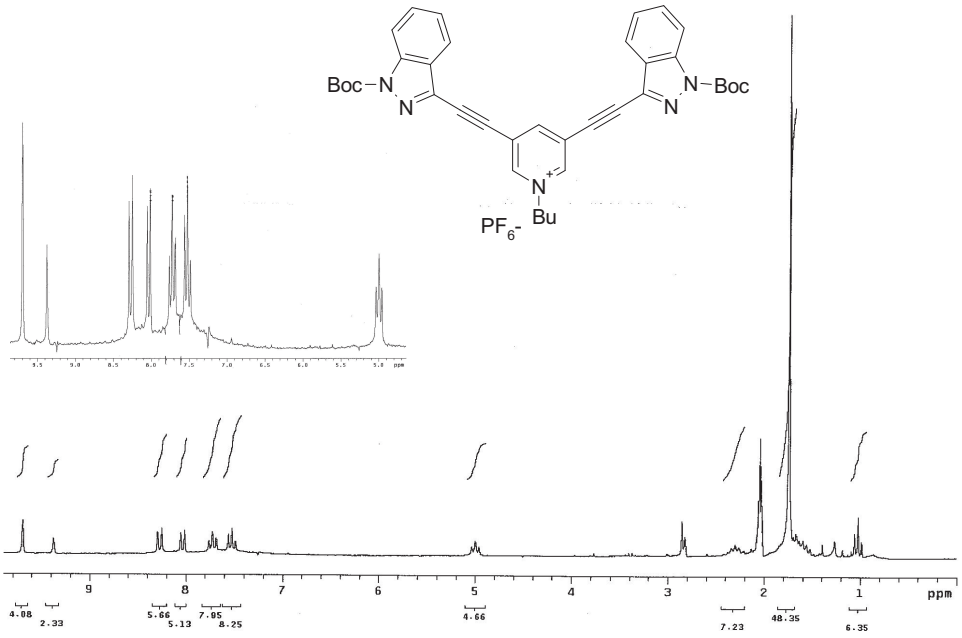


^{13}C NMR (300 MHz, acetone-d6) δ 147.89; 146.78; 144.43; 142.57; 141.93; 136.52; 131.79; 130.01; 128.09; 127.99; 127.88; 127.48; 126.72; 125.17; 99.95; 90.46; 83.11; 79.56; 62.62; 19.12; 12.77.

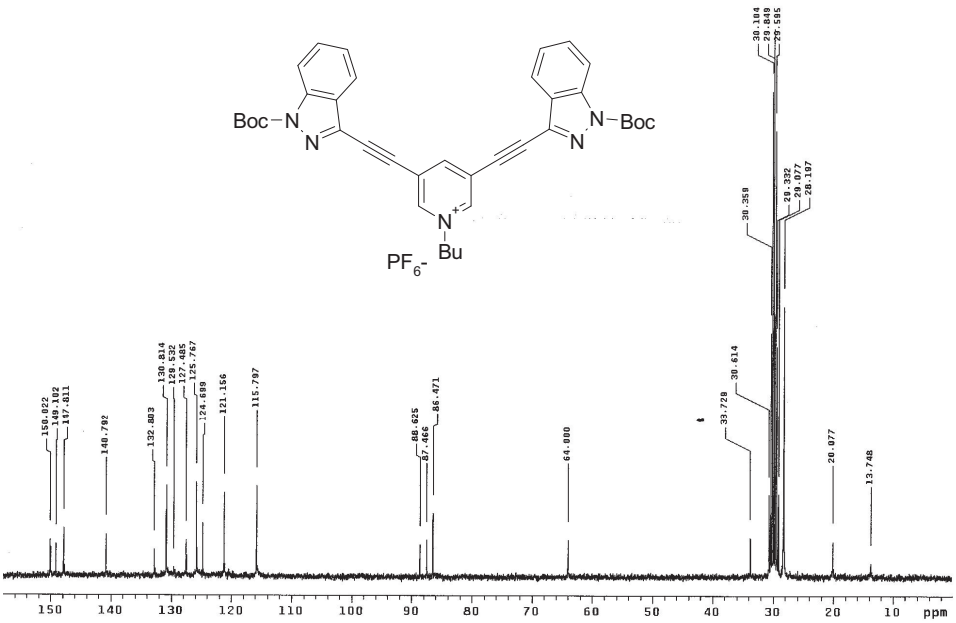


1-Butyl-3,5-(1-tert-butoxycarbonyl-1H-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (7d)

^{1}H-NMR (200 MHz, acetone-D6) δ (ppm) 9.69 (d, 2H, *J*=1.27 Hz); 9.37 (s,1H); 8.27 (d, 2H, *J*=8.57 Hz); 8.03 (d, 2H, *J*=7.93 Hz); 7.73 (t,2H, *J*=6.9 Hz); 7.52 (t, 2H, *J*=7.3 Hz); 4.9 (t, 2H, *J*= 7.6 Hz); 2.23 (dd, 2H, *J*= 8.05); 1.53 (td, 2H, *J*=7.3 Hz); 1.02 (t, 3H, *J*= 7.6 Hz);



^{13}C-NMR (300 MHz, CD_3OD) δ (ppm) 150.02, 149.1; 147.81; 140.79; 132.8; 130.81; 127.48; 125.76; 124.69; 121.15; 115.79; 88.62; 87.46; 86.47; 64.0; 33.72; 28.19; 20.07; 13.74



2. Linear properties

2a. General information

Absorption Spectra were recorded in a UV-Vis Perkin-Elmer L35 Spectrophotometer in the 200-1000 nm range. Steady-state fluorescence measurements were performed by using an SLM 8100 AMINCO spectrofluorimeter equipped with polarizers and a double (single) concave grating monochromator in the excitation (emission) path and a cooled photomultiplier. Slit widths were set at 8 nm for excitation and emission and polarizers at the magic angle. Fluorescence decay measurements were performed on a time-correlated single-photon-counting FL900 Edinburgh Instruments Spectrometer. The thyratron-gated lamp (nF900) was filled with H_2. Concave gratings monochromators were used at the excitation and emission. Photons were detected by a red sensitive cooled photomultiplier. The data acquisition was carried out by using 1024 channels of the multichannel analyzer with a time window width of 125 ns. A total of 10000-5000 counts in the peak channel were taken for each measurement. Instrumental response functions were regularly achieved by measuring the scattering of a Ludox solution and the quality of the fit was judged by the reduced χ^2 criterion, the inspection of the weighted residuals per channel and the autocorrelation function of the weighted residuals. Decay intensity profiles were fitted to a sum of exponential decay functions as

$$I(t) = \sum_{i=1}^{n} B_i e^{-t/\tau_i} \qquad (1)$$

by the iterative reconvolution method. The average lifetime of a multiple-exponential decay function was then defined as

$$\langle \tau \rangle = \frac{\sum_{1}^{n} B_i \tau_i^2}{\sum_{1}^{n} B_i \tau_i} \qquad (2)$$

where B_i is the pre-exponential factor of the component with a lifetime τ_i of the multi-exponential function intensity decay.

3. Non-linear properties

3a. General Information

The second-order noninear polarizability, or first hyperpolarizability, β, of the compounds was determined by Hyper-Rayleigh scattering (HRS).[4] This is the only available experimental technique that can measure directly the molecular second-order nonlinear response of ionic species in solution.

The HRS measurements were performed at room temperature in methanol, with crystal violet as the reference molecule and with high-frequency demodulation of the the multiphoton fluorescence contribution.[5] The HRS signal was analyzed towards a single major dipolar hypepolarizability tensor element β_{zzz} along the molecular z-axis. The dynamic, on resonantly-enhanced, $\beta_{zzz,800}$ value obtained at 800nm was reduced to the static, or off-resonance $\beta_{zzz.0}$ value by applying the classical two-level model.[6] From the

[4] Ref. 6 in text. K.Clays and A. Peersons, *Phys. Rev. Lett*. **1991**, *66*, 2980-2983. (b) K.Clays and A. Peersons, *Rev, Sci. Instrum.* **1992**, 63, 3285- 3289.

[5] Olbrechts, G.; Strobbe, R.; Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1998**, *69* , 2233-2241.

[6] Oudar, J. L.; Chemla, D. S. ; *J. Chem. Phys*. **1997**, 66, 2664.

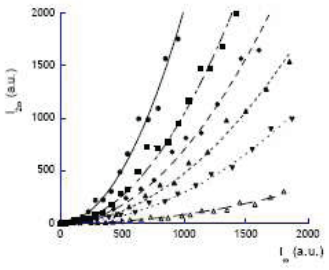
fitting of the apparent $\beta_{zzz,800}$ as a function of modulation frequency, a fluorescence lifetime could be obtained, as well as the accurate fluorescence-free hyperpolarizability value.[7]

3b. Experimental datas HRS Compounds 7

According to the theory of hyper-Rayleigh scattering (HRS) following equations 1, 2 and 3, for a typical experiment a clear linear dependence of the HRS response QC is observed as function of concentration (eq. 1 and 2) and the ratio of the slopes is directly proportional to the ratio of their orientational averaged hyperpolarisabilities squared (eq. 3). In this study, only in the case of **7d** a good quality measurement a linear fitting was obtained.

$$\mathbf{I_{2\omega} = G\,(N_s\,[\beta^2_{HRS}]_s + N_x\,[\beta^2_{HRS}]_x)\,I^2_{\omega}} \qquad \textit{eq. 1}$$

G includes all constants and local field factors, and is treated as a calibration constant.
$\mathbf{I_{2\omega}}$ represents the HRS intensity,
$\mathbf{I_{\omega}}$ the intensity of the input light
N the chromophores concentration and the orientational averaged hyperpolarisability squared.
The subscripts **s** and **x** refer to solvent and chromophore.



For a typical HRS experiment, the quadratic dependence of $I_{2\omega}$ on I_{ω} for a dilution series is determined (Fig. 1). From a quadratic fit $y = a\,x^2$, the product of the G factor and the factor between brackets is determined and is called the quadratic coefficient (Q.C).
The quadratic coefficient is equal to:

$$\mathbf{QC = G\,(N_s\,[\beta^2_{HRS}]_s + N_x\,[\beta^2_{HRS}]_x)} \qquad \textit{eq. 2}$$

Figure 1*: The intensity of the scattered light $I_{2\omega}$ versus the intensity of the fundamental beam I_{ω} for a dilution series.*

The quadratic coefficient is a linear function of the chromophores concentration (N_x), which is demonstrated in Fig. 1 and is fitted to the equation below:

Q.C.=intercept+slopeN

In a example of a good fitting: a linear dependence of the HRS response QC is observed as a function of concentration.

Y-axis: the Q.C. of the HRS signal is plotted,
X-axis: the concentration.
$I_{2\omega} = G\,(N_s\,[\beta^2_{HRS}]_s + N_x\,[\beta^2_{HRS}]_x)\,I^2_{\omega}$ ***eq. 1***

[7] Clays, K.; Wostyn, K.; Binnemans, K.; Persoons, A. *Rev. Sci. Instrum.* **2001**, *72* 3215-3220 .

$QC = G\,(N_s\,[\beta^2_{HRS}]_s + N_x\,[\beta^2_{HRS}]_x)$ *eq. 2*

Figure 2a represents the data as obtained for a sample randomly chosen from all the measured samples, while in figure 2b the reference sample is plotted.

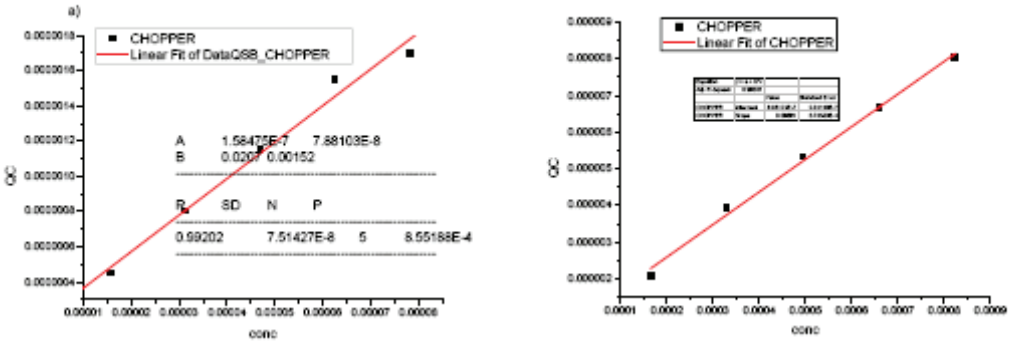


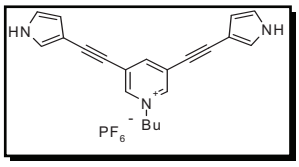
***Fig. 2**: 2a and 2b*

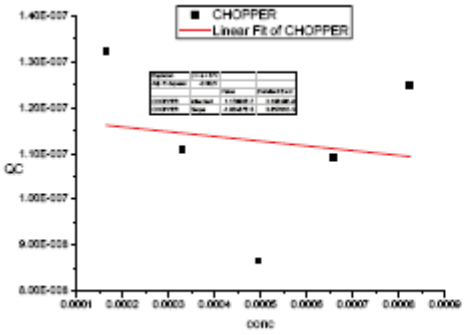
For the external reference method, the quadratic dependence of $I_{2\omega}$ on I_{ω} is measured for the dilution series of a reference (in this case, crystal violet (CV)) as well as for the chromophore of unknown hyperpolarisability. Both results are plotted as a function of chromophore concentration. The ratio of the slopes is directly proportional to the ratio of their orientational averaged hyperpolarisabilities squared.

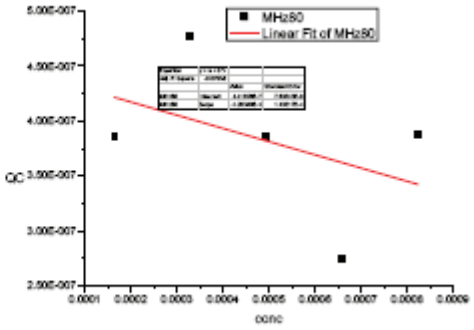
$$\frac{\mathbf{Slope_{CV}}}{\mathbf{Slope_{chromophore}}} = \frac{\mathbf{[\beta^2_{HRS}]_{CV}}}{\mathbf{[\beta^2_{HRS}]\ chromophore}} \qquad \textit{eq.3}$$

CV:crystal violet

The plotted graphic obtained from **7a** are indicade in ***Fig. 3***







The plotted graphic obtained from **7b,** are indicated in ***Fig.4***