Electronic Supplementary Information (ESI)

Synthesis of Charged Bis-heteroaryl Donor-Acceptor (D-A$^+$) NLO-phores Coupling (π-deficient–π-excessive) Heteroaromatic Rings

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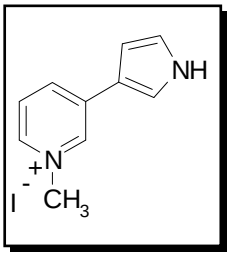
General information. Melting points were uncorrected. Infrared spectra were recorded on KBr pellets and spectral bands were reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 MHz and 300 MHz respectively. Chemical shifts were reported as δ values (ppm). Mass spectra (MS) were obtained as (ESI^{+}). CuI, $PdCl(PPh_3)_2$, $Pd(PPh_3)_4$, $Pd_2(dba)_3$, were purchased from Aldrich. The stannanes 4-Tributylstannanyl-1-trityl-1H-pyrazole[1], 3-tributylstannanyl -1-Triisopropyl- 1H-Pyrrole[2], (2-tributylstannanyl-phenyl)- carbamic acid tert-butyl ester[3], 3-tributylstannanyl-indazol-1-carbamic acid tert-butyl ester[4], 3-tributylstannanyl-1-terbutyldimethylsilyl-indole[5] were prepared according to literature procedures. DMF was distille over activated molecular sieves were obtained by previously described methods.

General Procedure for the Synthesis of D-A^{+} Pyridinium Salts.

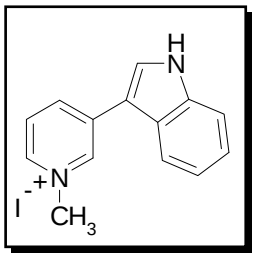
A flame-dried flask was charged under argon with 1 equiv. of bromopiridinium iodine (0.2 g, 0.667 mmol) or hexafluorophosphate (0.2 g, 0.629 mmol); 5 mol % $Pd(PPh_3)_4$ ***Method A*** or 5 mol % $Pd_2(dba)_3$ and 5 mol % P(*o*-Tol)$_3$ ***Method B*** in dry DMF (10 mL). Then, the 2.1 equiv. of the corresponding stannanyl heterocycle was added. After stirring at 65º C temperature for 15-20 h, the solution was filtered through a small pad of celite and washed with methanol. The solution was concentrated and the solid were purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9:1) as eluent, to give **4**, **5** and **6**.

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



Following the general procedure B, 0.0250 g (13 %) were obtained as a brown dust: mp 142-144 ºC; IR (KBr) 3445; 3031; 1488; 664cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) 9.27 (s, 1H); 8.72 (d, 1H, *J*=8.1); 8.60 (d, 1H, *J*=6.2); 7.98 (t, 1H, *J*=6.2); 7.73-7.71 (m, 1H); 7.04-7.01 (m, 1H); 6.90-6.88 (m, 1H); 4.46 (s, 3H); ^{13}C NMR (75 MHz, acetone) δ 142.2; 141.6; 139.9; 137.6; 128.4; 127.5; 126.3; 120.5; 109.6; 48.8. MS (ES^{+}) *m/z* (relative intensity) 159 (M^{+}, 100). Anal. Calcd for $C_{10}H_{11}N_2I$: C 41.96; H: 3.85; N: 9.79. Found: C, 41.93; H, 3.90; N, 9.80.

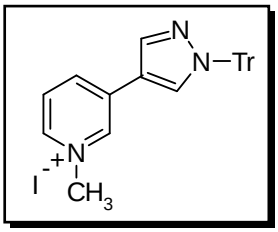
1-Methyl-3-(1H-indol-3-yl)pyridinium iodide (4b).



Following the general procedure A, 0.114 g (51 %) were obtained as a brown solid: mp 290 ºC; IR (KBr) 3416, 3178.76 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) : 9.24 (s, 1H); 8.88 (d, 1H, *J*=8.4); 8.67 (d, 1H, *J*=5.9); 8.04 (t, 1H, *J*=4.7); 8.0 (s, 1H); 7.58-7.54 (m, 2H); 7.33-7.28 (m, 2H); 4.5 (s, 3H). ^{13}C NMR (75 MHz, CD_3OD) 142.9; 141.7; 138.8; 128.9; 127.5; 125.5; 124.0; 122.4; 119.5; 113.4; 110.3; MS (ES^{+}) *m/z* (relative intensity) 209 (M^{+}, 100). Anal. Calcd for $C_{14}H_{13}N_2I$: C 50.02; H 3.87; N 8.33. Found: C 49.94; H 3.90; N 8.33.

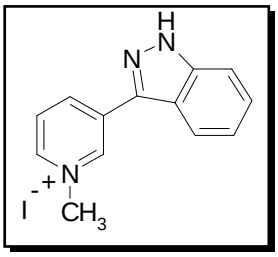
[1] Elguero, J.; Jaramillo, C.; Pardo, C. *Synthesis* **1997**, 563.
[2] Álvarez, A.; Guzmán, A.; Ruiz, A.; Velarde, E. *J. Org. Chem*. **1992**, *57*, 1653.
[3] Iwao, M.; Takehara, H.; Furkawa, S.; Watanabe, M.; *Heterocycles*, **1993**, *36*, 1483.
[4] Arnautu, A.; Collot, V.; Calvo, J.; Alayrac, C.; Witulski, B.; Rault, S.; *Tetrahedron Lett.* **2002**, *43*, 2695.
[5] a)Amat, M.; Hadida, S.; Sathyanarayana, S.; Bosch, J. *J. Org. Chem*. **1994**, *59*, 10. b) Amat, M.; Hadida, S.; Pshenichnyi, G. ; Bosch, J. *Tetrahedron Lett.* **1994**, *35*, 793.

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



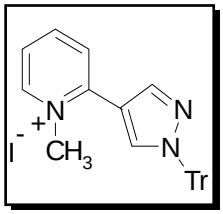
Following the general procedure A, 0.187 g (53 %) were obtained as a brown solid: mp 246 ºC; IR (KBr) 3419,3055, 1631,1373 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) 9.25 (s, 1H); 8.74-8.69 (m, 2H); 8.27 (s, 2H); 8.01 (t, 1H, *J*=6.2); 7.41-7.38 (m, 9H); 7.24-7-19 (m, 6H); 4.41 (s, 3H); ^{13}C NMR (75 MHz, acetone) δ 143.7; 143.1; 141.4; 138.5; 134.6; 132.4; 130.9; 128.8; 128.8; 128.7; 115.9; 73.0; 61.7; 49.1. MS (ES^+) *m/z* (relative intensity) 402 (M^+, 100). Anal. Calcd for $C_{28}H_{24}N_3I$: C 63.52; H 4.54; N 7.94. Found: C 62.93; H 3.71; N 7.25.

1-Methyl-3-(1H-indazol-3-yl)pyridinium iodide (4d).



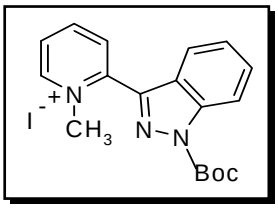
Following the general procedure A, gave 0.0742 g (33 %) of brown solid: mp 158-160 ºC; IR (KBr) 3133, 1633, 1588, 1172 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) : 9.54 (s, 1H); 9.19 (d, 1H, *J*=8.0); 8.90 (d, 1H, *J*=5.8); 8.28-8.19 (m, 2H); 7.71 (d, 1H, *J*=8.4); 7.55 (t, 1H, *J*=8.0); 7.40 (t, 1H, *J*=7.5); 4.58 (s, 3H). ^{13}C NMR (75 MHz, CD_3OD) 146.1; 132.7; 131.5; 131.3; 128.2; 127.7; 127.5; 127.1; 124.8; MS (ES^+) *m/z* (relative intensity) 210 (M^+, 100). Anal. Calcd for $C_{13}H_{12}N_3I$: C 46.29; H 3.56; N 12.46. Found: C 46.21; H 3.44; N: 11.65.

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



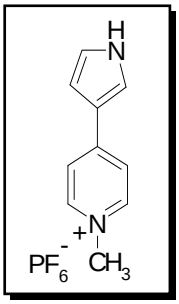
Procedure A, orange solid (0.120 g, 34 %): mp 249-250 ºC; IR (KBr) 3428, 2920, 1625,1382 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) : 8.89 (d, 1H, *J*=6.2); 8.48 (t, 1H, *J*=7.5); 8.24 (s, 1H); 8.21 (s, 1H); 8.17 (d, 1H, *J*= 8.4); 7.92 (t, 1H, *J*=7.0), 7.43-7.40 (m, 9H) ; 7.27-7.22 (m, 6H) ; 4.36 (s, 3H); ^{13}C NMR (75 MHz, DMSO) : 145.6; 143.8; 141.4; 139.7; 134.5; 129.0; 128.3; 127.4; 124.4; 111.9; 78.6; 46.7. MS (ES^+) *m/z* (relative intensity) 402 (M^+, 100). Anal. Calcd for $C_{28}H_{24}N_3I$: C, 63.41; H, 4.71; N, 7.93. Found: C 63.43; H 4.74; N 7.95.

1-Methyl-2-(1-tert-Butoxycarbonyl-1H-indazol-3-yl)pyridinium iodide (5d).



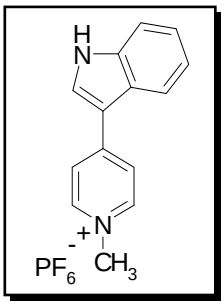
Procedure A, orange oil (0.0903 g, 31 %); IR (KBr) 3133, 1633, 1588, 1172 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) : 9.10 (d, 1H, *J*=6.2); 8.65 (t, 1H, *J*=8.1); 8.10 (t, 2H, *J*=6.2); 8.00 (d, 1H, *J*=7.7); 7.83 (d, 1H, *J*=7.7); 7.67 (t, 2H, *J*=7.9); 4.91 (s, 3H); 1.57 (s, 9H). ^{13}C NMR (75 MHz, CD_3OD): 152.0; 145.0; 143.8; 135.7; 135.0; 131.2; 129.5; 129.2; 128.2; 122.0; 116.6; 114.7; 111.7; 72.0, 49.0; 45.5. MS (ES^+) *m/z* (relative intensity) 310 (M^+, 100). Anal. Calcd for $C_{18}H_{20}N_3O_2I$: C 49.44; H 4.58; N 9.61. Found: C 49.2; H 4.44; N 9.65.

1-Methyl-4-(1H-pyrrol-3-yl)pyridinium hexafluorophosphate (6a).



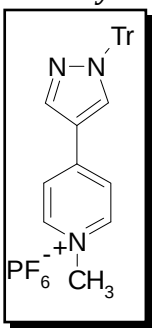
Procedure B, brown solid (0.188 g , 98 %): mp 106-108 ºC; IR (KBr) 3420, 3199, 1638 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) 8.52 (d, 2H, *J*=6.9); 8.07 (d, 2H, *J*=6.9); 7.84 (s,1H); 7.00-6.98 (m, 1H); 6.85-6.82 (m, 1H), 4.23 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 145.2; 128.2; 125.7; 122.9; 121.9; 109.6; 108.2; 47.7. MS (ES^+) *m/z* (relative intensity) 159 (M^+, 100). Anal. Calcd for $C_{10}H_{11}N_2PF_6$: C 69.08; H 3.62; N 9.21. Found: C 69.24; H 3.50; N 9.33.

1-Methyl-4-(1H-indol-3-yl)pyridinium hexafluorophosphate (6b).



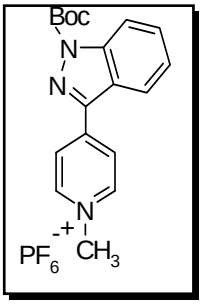
Procedure A, brown solid (0.174 g , 78 %): mp 222 ºC; IR (KBr) 3414; 1644; 836 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) : 8.56 (d, 2H, *J*=7.3); 8.38 (s, 1H); 8.30 (d, 2H, *J*=6.9); 8.16-8.12 (m, 1H); 7.61-7.57 (m, 1H), 7.40-7.34 (m, 2H); 4.26 (s, 3H). ^{13}C NMR (75 MHz, CD_3OD) 145.1; 132.4; 124.6; 123.6; 122.5; 121.5; 120.5; 113.9; 47.7. MS (ES^+) *m/z* (relative intensity) 209 (M^+, 100). Anal. Calcd for $C_{14}H_{13}N_2PF_6$: C 47.46; H 3.67; N 7.91. Found: C 47.33; H 3.52; N 8.02

1-Methyl-4-(1-trityl-1H-pyrazol-4-yl)pyridinium hexafluoro phosphate (6c).



Procedure A, yellow solid (0.313 g, 91 %): mp 204-206 ºC; IR (KBr) 3431, 3134, 1640, 1385 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) 8.65 (d, 2H, *J*=6.6); 8.43 (s, 1H); 8.42 (s, 1H); 8.18 (d, 2H, *J*=6.7); 7.41-7.39 (m, 9H) 7.23-7.20 (m, 6H); 4.30 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 147.1; 144.5; 141.6; 138.9; 133.3; 129.1; 127.6; 127.5; 127.4; 121.6; 116.4; 78.7; 46.1. MS (ES^+) *m/z* (relative intensity) 402 (M^+, 100). Anal. Calcd for $C_{28}H_{24}N_3$ PF_6: C 61.43; H 4.39; N 7.68. Found: C, 61.05; H, 3.95; N, 6.85.

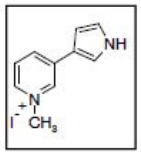
1-Methyl-4-(1-tert-Butoxycarbonyl-1H-indazol-3-yl)pyridinium hexafluorophosphate (6d).

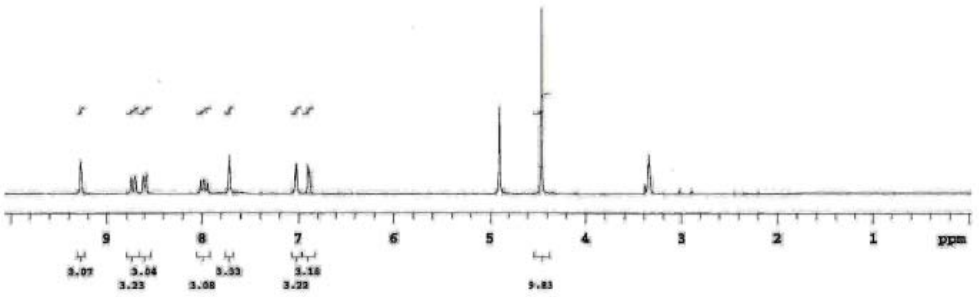


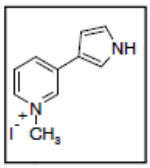
Procedure A, orange solid (0.258 g, 90 %): mp 119-121 ºC; IR (KBr) 3413, 1644, 1265, 834 cm^{-1}; ^{1}H NMR (200 MHz, acetone): 9.10 (d, 2H, *J*=6.3); 8.73 (d, 2H, *J*=6.3); 8.38 (d, 1H, *J*=8.4); 8.25 (d, 1H, *J*=7.4); 7.78 (t , 1H, *J*=8.5); 7.60 (t, 1H, *J*=7.3); 4.41 (s, 3H); 1.70 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD):147.3; 145.6; 142.4; 140.2; 129.5; 124.9; 124.5; 122.3; 120.7; 114.3; 85.6; 47.2. MS (ES^+) *m/z* (relative intensity) 310 (M^+, 100). Anal. Calcd for $C_{18}H_{20}N_3O_2$ PF_6: C 47.47; H 4.40; N 9.23. Found: C 47.63; H 4.23; N 9.10.

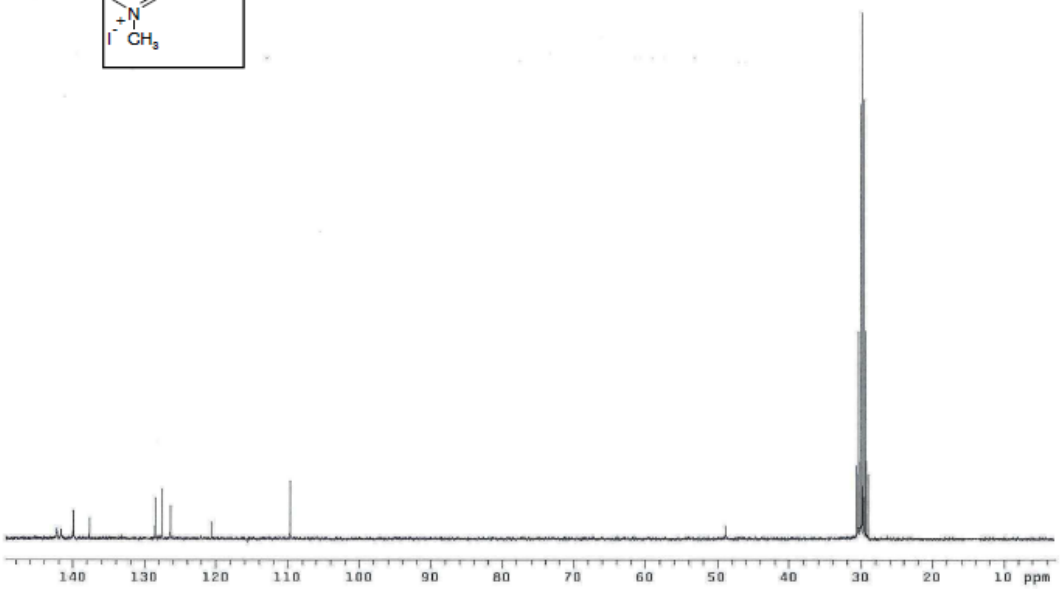
1c. Copies of ^{1}H and ^{13}C NMR for all new compounds reported

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



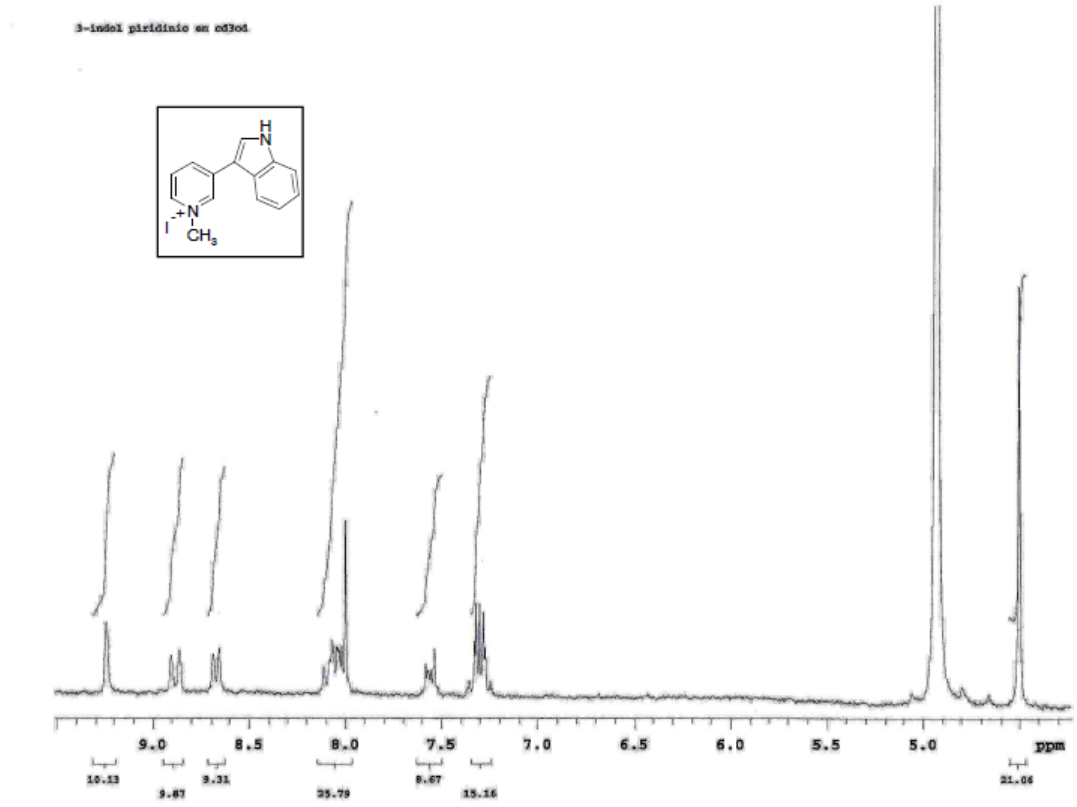






^{1}H NMR (200 MHz, CD_3OD) 9.27 (s, 1H); 8.72 (d, 1H, *J*=8.1); 8.60 (d, 1H, *J*=6.2); 7.98 (t, 1H, *J*=6.2); 7.73-7.71 (m, 1H); 7.04-7.01 (m, 1H); 6.90-6.88 (m, 1H); 4.46 (s, 3H);
^{13}C NMR (75 MHz, acetone) δ 142.2; 141.6; 139.9; 137.6; 128.4; 127.5; 126.3; 120.5; 109.6; 48.8.

1-Methyl-3-(1H-indol-3-yl)pyridinium iodide (4b)



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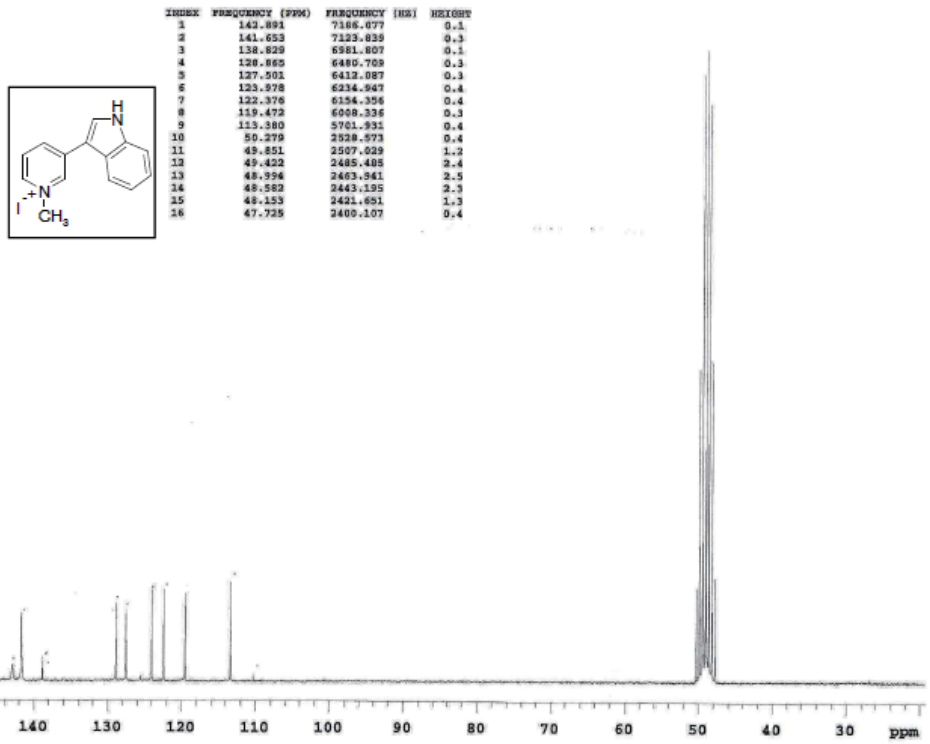
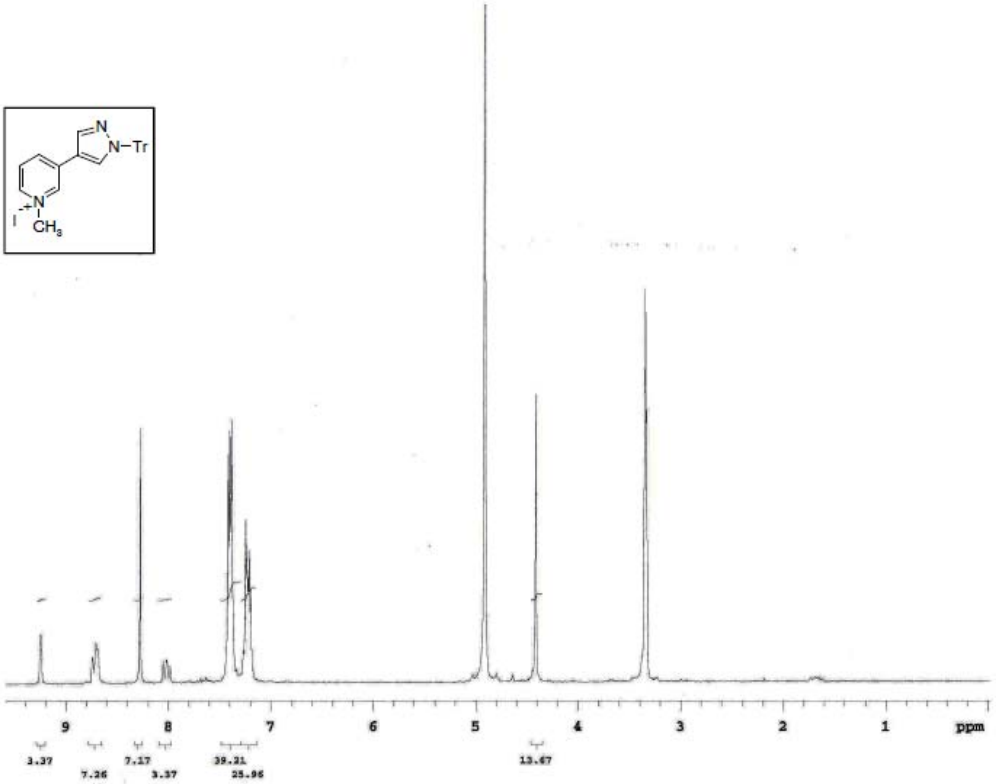
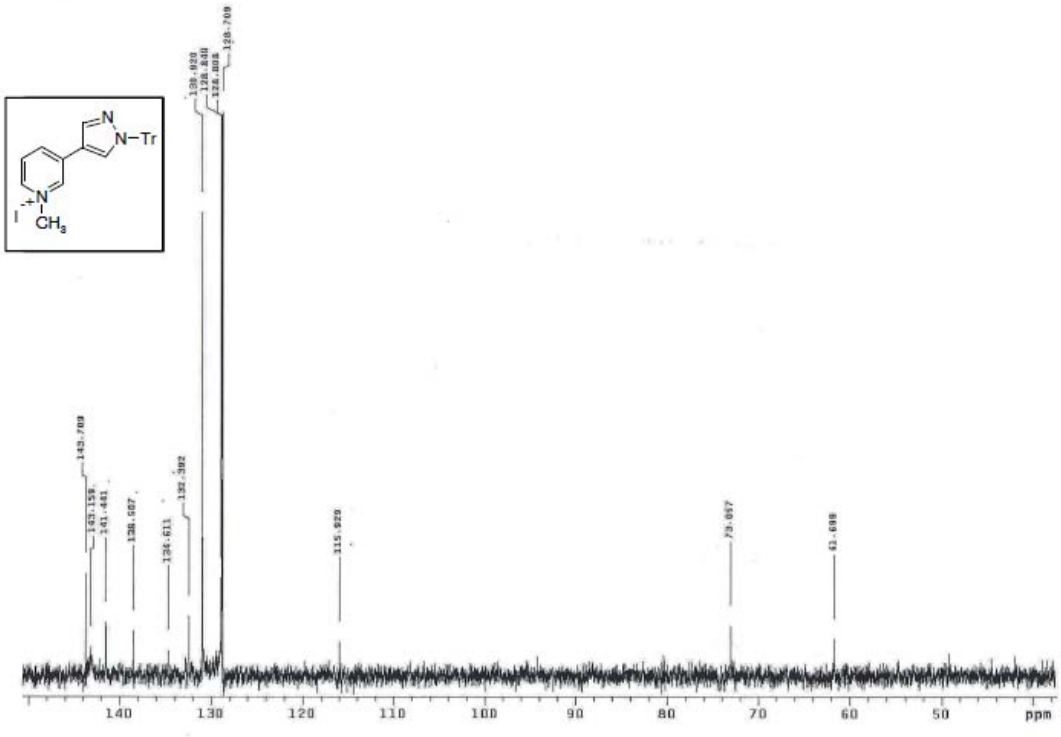


^{1}H NMR (200 MHz, CD_3OD) : 9.24 (s, 1H); 8.88 (d, 1H, *J*=8.4); 8.67 (d, 1H, *J*=5.9); 8.04 (t, 1H, *J*=4.7); 8.0 (s, 1H); 7.58-7.54 (m, 2H); 7.33-7.28 (m, 2H); 4.5 (s, 3H).
^{13}C NMR (75 MHz, CD_3OD) 142.9; 141.7; 138.8; 128.9; 127.5; 125.5; 124.0; 122.4; 119.5; 113.4; 110.3;

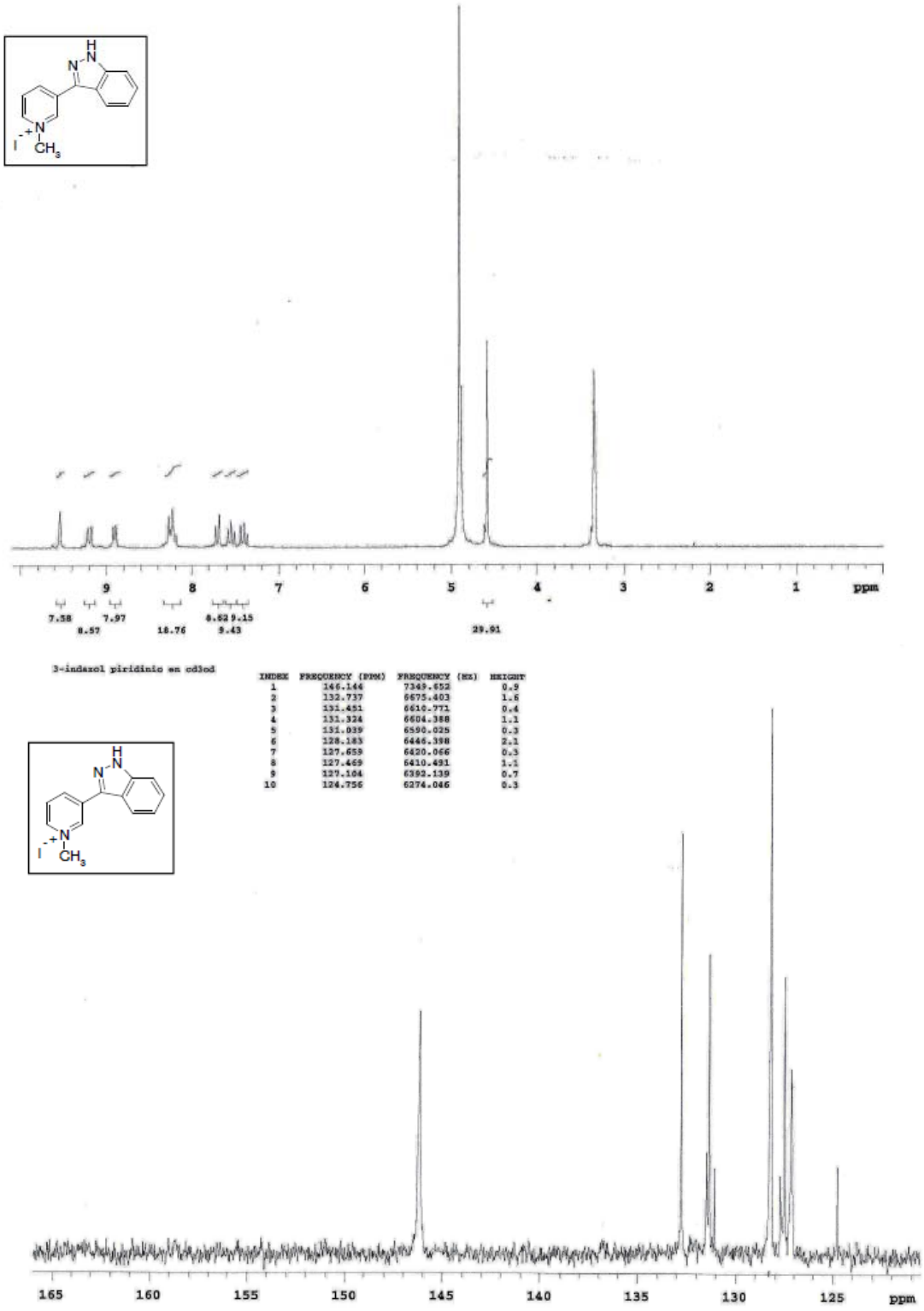
1-Methyl-3-(1-trityl-1H-pyrazol-4-yl)pyridinium iodide (4c)





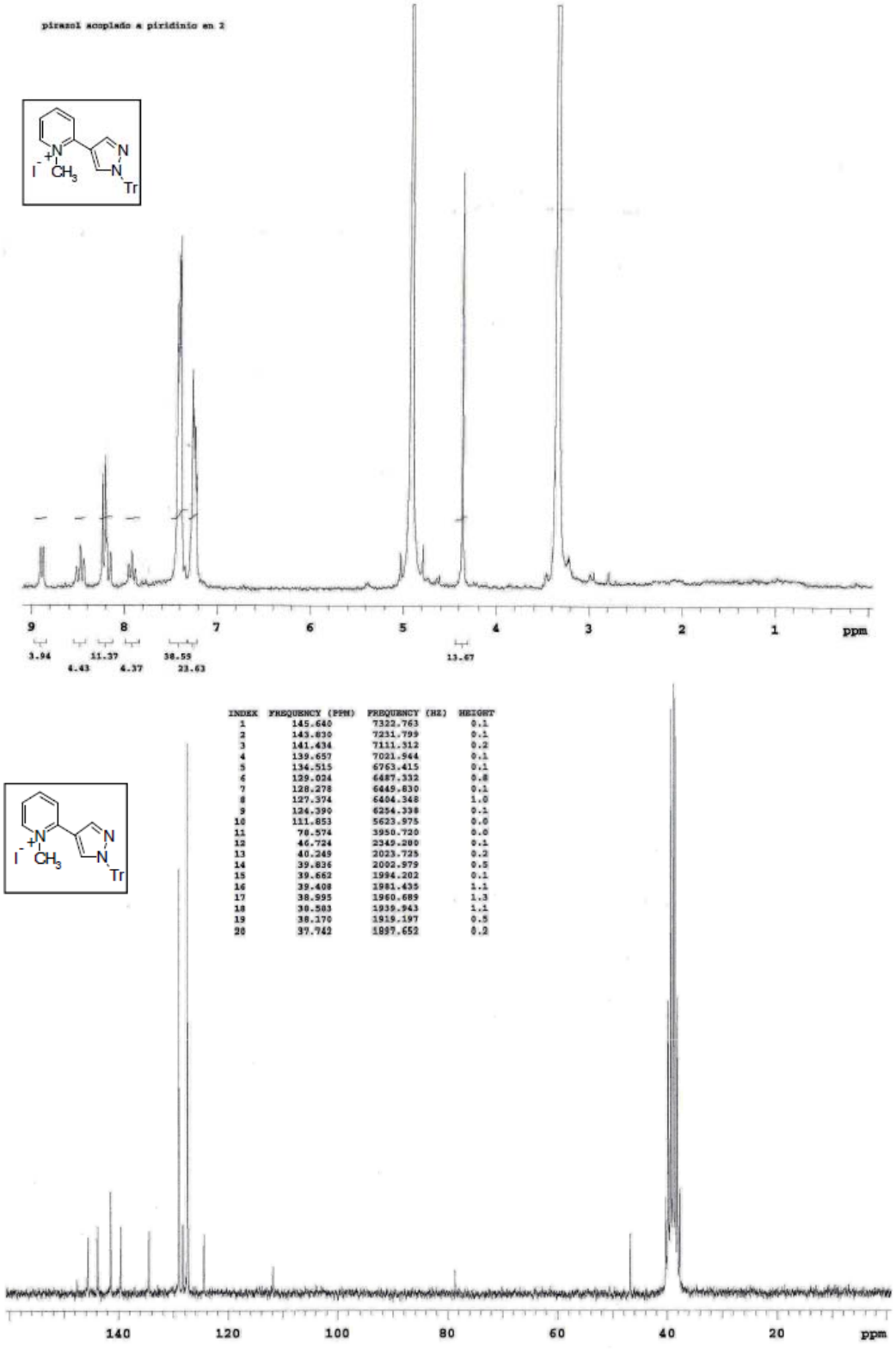
1H NMR (200 MHz, CD3OD) 9.25 (s, 1H); 8.74-8.69 (m, 2H); 8.27 (s, 2H); 8.01 (t, 1H, J=6.2); 7.41-7.38 (m, 9H); 7.24-7-19 (m, 6H); 4.41 (s, 3H);
13C NMR (75 MHz, acetone) δ 143.7; 143.1; 141.4; 138.5; 134.6; 132.4; 130.9; 128.8; 128.8; 128.7; 115.9; 73.0; 61.7; 49.1.

1-Methyl-3-(1H-indazol-3-yl)pyridinium iodide (4d)



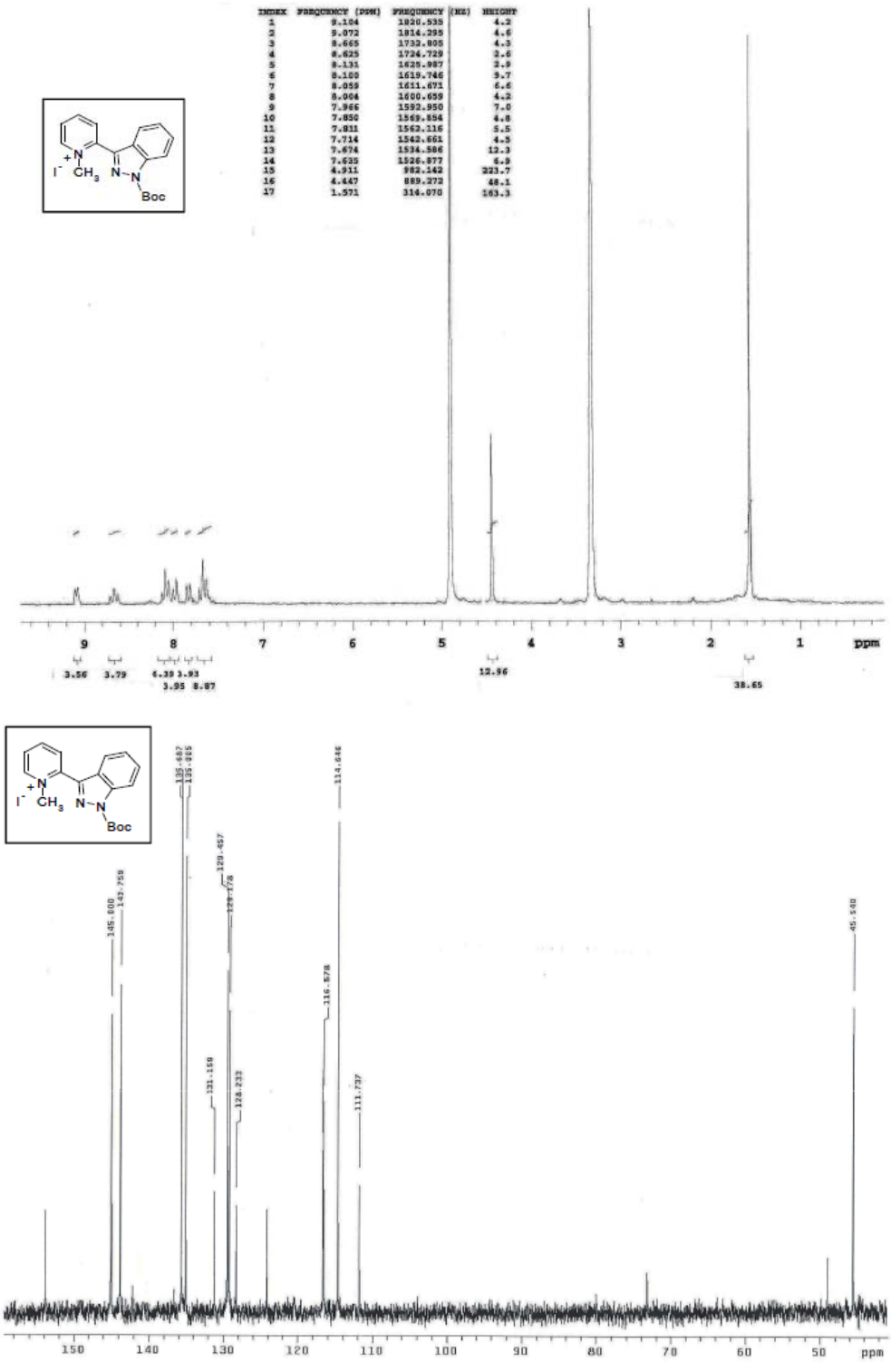
1H NMR (200 MHz, CD3OD) : 9.54 (s, 1H); 9.19 (d, 1H, J=8.0); 8.90 (d, 1H, J=5.8); 8.28-8.19 (m, 2H); 7.71 (d, 1H, J=8.4); 7.55 (t, 1H, J=8.0); 7.40 (t, 1H, J=7.5); 4.58 (s, 3H).
13C NMR (75 MHz, CD3OD) 146.1; 132.7; 131.5; 131.3; 128.2; 127.7; 127.5; 127.1; 124.8;

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



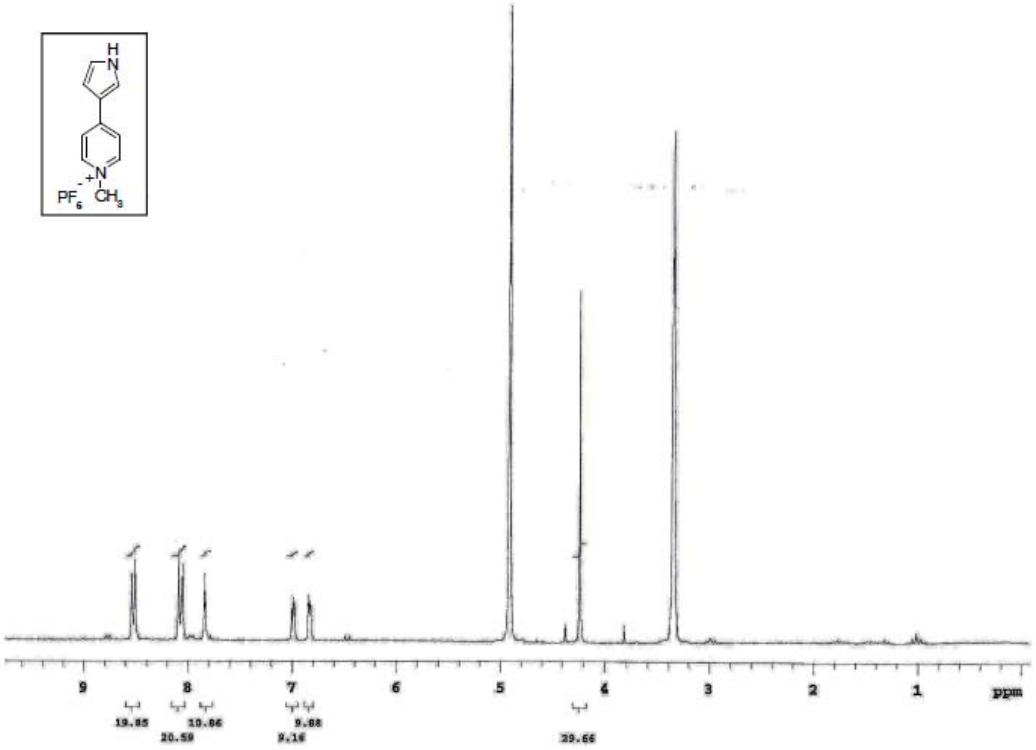
1H NMR (200 MHz, CD3OD) : 8.89 (d, 1H, J=6.2); 8.48 (t, 1H, J=7.5); 8.24 (s, 1H); 8.21 (s, 1H); 8.17 (d, 1H, J= 8.4); 7.92 (t, 1H, J=7.0), 7.43-7.40 (m, 9H) ; 7.27-7.22 (m, 6H) ; 4.36 (s, 3H);
13C NMR (75 MHz, DMSO) : 145.6; 143.8; 141.4; 139.7; 134.5; 129.0; 128.3; 127.4; 124.4; 111.9; 78.6; 46.7.

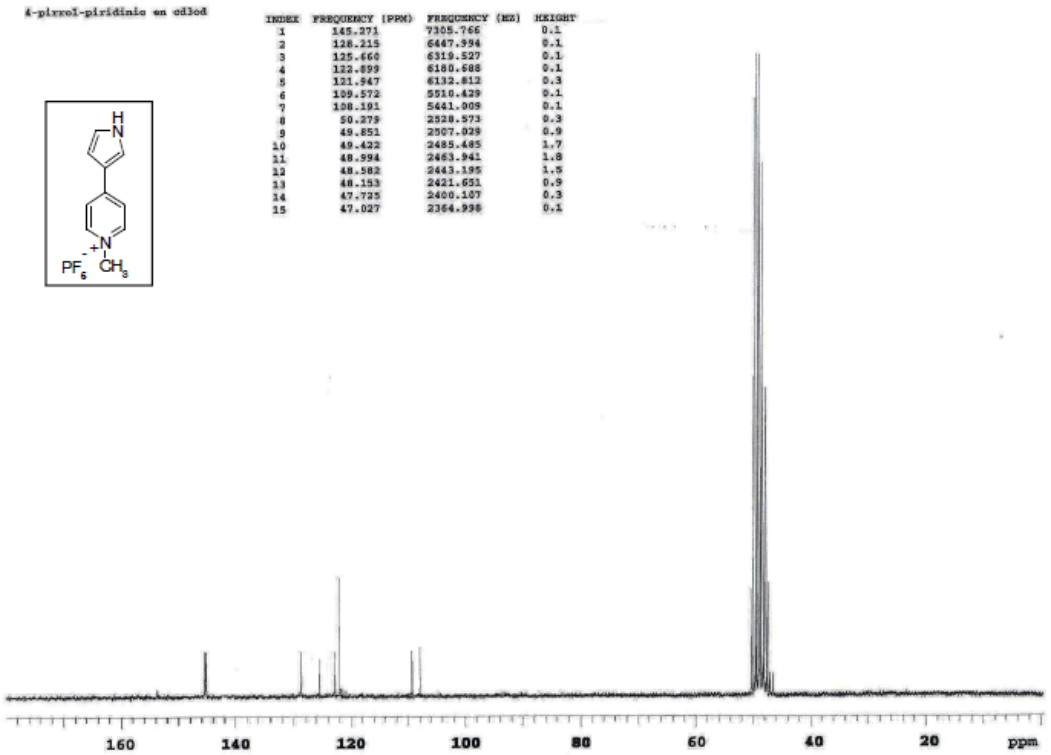
1-Methyl-2-(1-tert-Butoxycarbonyl-1H-indazol-3-yl)pyridinium iodide (5d)



^{1}H NMR (200 MHz, CD_3OD) : 9.10 (d, 1H, *J*=6.2); 8.65 (t, 1H, *J*=8.1); 8.10 (t, 2H, *J*=6.2); 8.00 (d, 1H, *J*=7.7); 7.83 (d, 1H, *J*=7.7); 7.67 (t, 2H, *J*=7.9); 4.91 (s, 3H); 1.57 (s, 9H).
^{13}C NMR (75 MHz, CD_3OD): 152.0; 145.0; 143.8; 135.7; 135.0; 131.2; 129.5; 129.2; 128.2; 122.0; 116.6; 114.7; 111.7; 72.0, 49.0; 45.5.

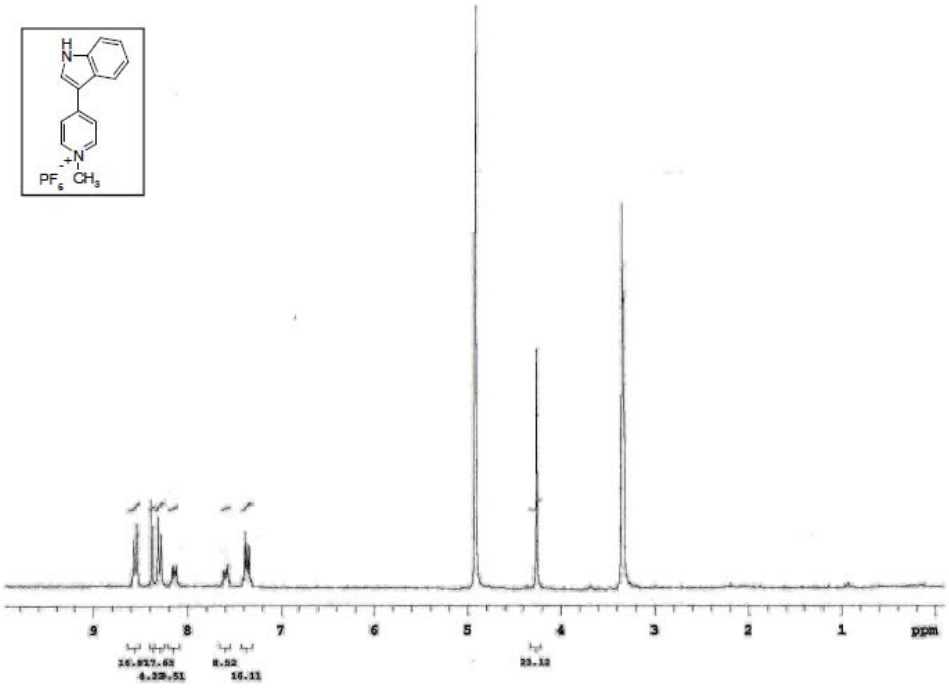
1-Methyl-4-(1H-pyrrol-3-yl)pyridinium hexafluorophosphate (6a)

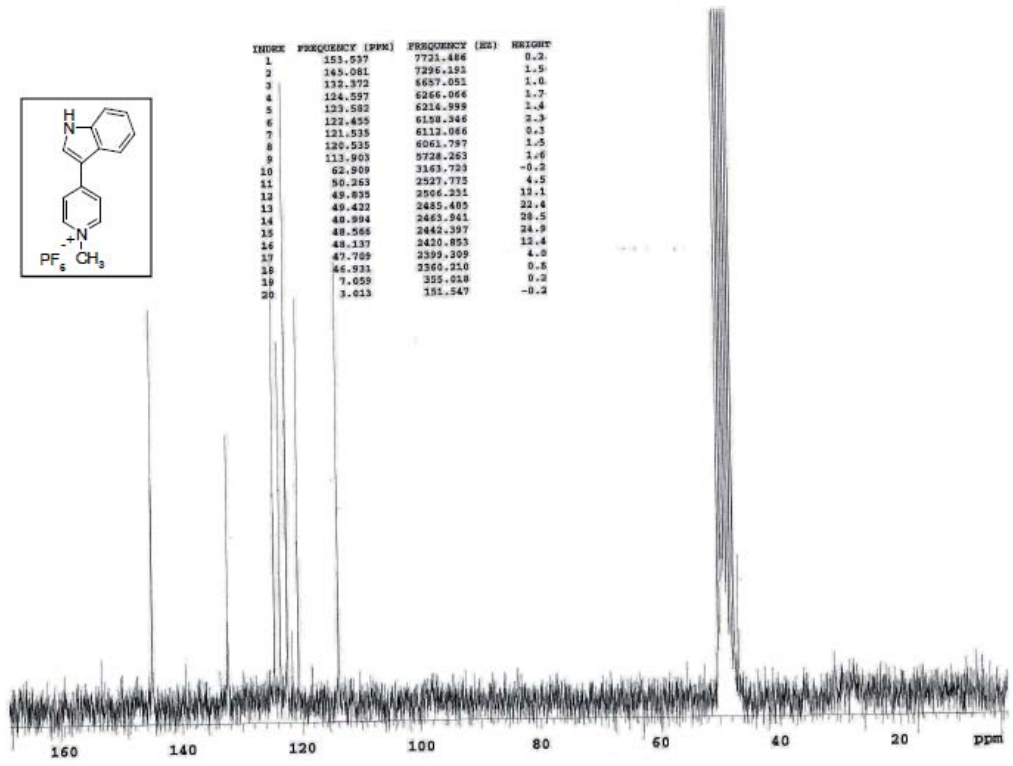




^{1}H NMR (200 MHz, CD_3OD) 8.52 (d, 2H, *J*=6.9); 8.07 (d, 2H, *J*=6.9); 7.84 (s,1H); 7.00-6.98 (m, 1H); 6.85-6.82 (m, 1H), 4.23 (s, 3H);
^{13}C NMR (75 MHz, CD_3OD) δ 145.2; 128.2; 125.7; 122.9; 121.9; 109.6; 108.2; 47.7.

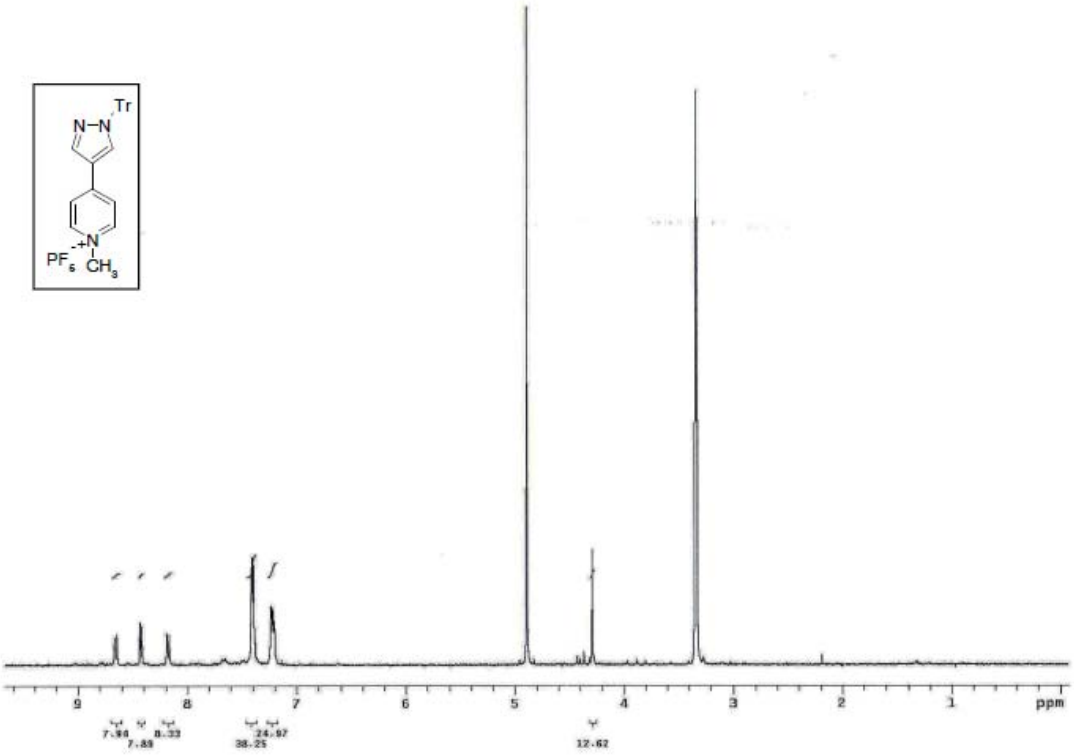
1-Methyl-4-(1H-indol-3-yl)pyridinium hexafluorophosphate (6b)

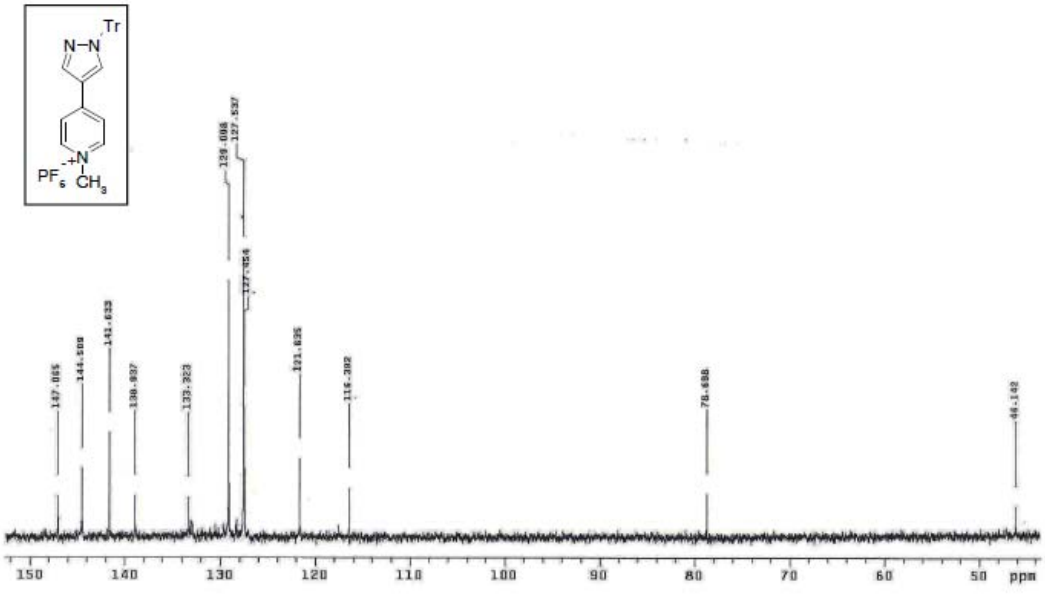




1H NMR (200 MHz, CD3OD) : 8.56 (d, 2H, J=7.3); 8.38 (s, 1H); 8.30 (d, 2H, J=6.9); 8.16-8.12 (m, 1H); 7.61-7.57 (m, 1H), 7.40-7.34 (m, 2H); 4.26 (s, 3H).
13C NMR (75 MHz, CD3OD) 145.1; 132.4; 124.6; 123.6; 122.5; 121.5; 120.5; 113.9; 47.7.

1-Methyl-4-(1-trityl-1H-pyrazol-4-yl)pyridinium hexafluoro phosphate (6c).

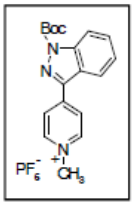




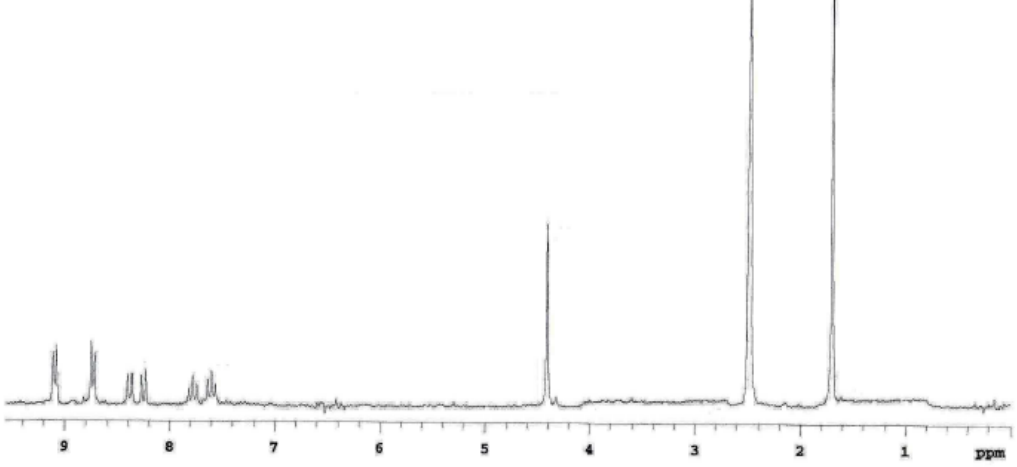
1H NMR (200 MHz, CD3OD) 8.65 (d, 2H, J=6.6); 8.43 (s, 1H); 8.42 (s, 1H); 8.18 (d, 2H, J=6.7); 7.41-7.39 (m, 9H) 7.23-7.20 (m, 6H); 4.30 (s, 3H);

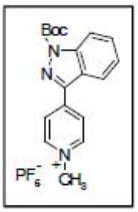
13C NMR (75 MHz, CD3OD) δ 147.1; 144.5; 141.6; 138.9; 133.3; 129.1; 127.6; 127.5; 127.4; 121.6; 116.4; 78.7; 46.1.

1-Methyl-4-(1-tert-Butoxycarbonyl-1H-indazol-3-yl)pyridinium hexafluorophosphate (6d)



INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	9.111	1821.977	40.6
2	9.078	1815.369	43.3
3	8.747	1749.296	42.2
4	8.714	1742.688	43.4
5	8.402	1680.287	46.4
6	8.369	1671.844	45.6
7	8.270	1653.857	46.0
8	8.228	1645.415	7.5
9	7.782	1556.216	6.2
10	7.740	1547.774	4.0
11	7.639	1527.585	5.3
12	7.600	1519.676	7.2
13	7.563	1512.535	4.0
14	4.410	881.904	43.1
15	2.490	497.946	111.9
16	1.701	340.105	144.3





INDEX	FREQUENCY (PPM)	FREQUENCY (HZ)	HEIGHT
1	147.267	7406.159	0.0
2	145.601	7322.377	0.1
3	142.428	7162.791	0.0
4	140.191	7050.283	0.1
5	129.481	6511.682	0.1
6	124.880	6280.283	0.1
7	124.451	6258.739	0.2
8	122.309	6151.012	0.0
9	120.675	6068.832	0.1
10	114.344	5750.459	0.1
11	85.642	4307.008	0.1
12	47.182	2372.831	0.1
13	43.866	2206.064	0.0
14	40.249	2024.137	0.1
15	40.090	2016.158	0.0
16	39.836	2003.391	0.4
17	39.678	1995.412	0.1
18	39.408	1981.847	0.9
19	39.248	1973.868	0.1
20	38.595	1941.101	1.0
21	38.837	1953.121	0.1
22	38.583	1940.355	0.9
23	38.194	1918.810	0.4
24	37.742	1898.064	0.1
25	27.143	1365.049	0.4

1H NMR (200 MHz, acetone): 9.10 (d, 2H, J=6.3); 8.73 (d, 2H, J=6.3); 8.38 (d, 1H, J=8.4); 8.25 (d, 1H, J=7.4); 7.78 (t , 1H, J=8.5); 7.60 (t, 1H, J=7.3); 4.41 (s, 3H); 1.70 (s, 9H);
13C NMR (75 MHz, CD3OD):147.3; 145.6; 142.4; 140.2; 129.5; 124.9; 124.5; 122.3; 120.7; 114.3; 85.6; 47.2.

2. Linear properties

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

General Information

The second-order noninear polarizability, or first hyperpolarizability, β, of the compounds was determined by Hyper-Rayleigh scattering (HRS).[6] 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.[7] 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.[8] From the 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.[9]

[6] 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.

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

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

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