Supporting Information

Palladium-mediated Functionalization of Heteroaromatic Cations. A Comparative Study on Quinolizinium Cations

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CONTENTS

Experimental section

General. Melting points were uncorrected. Infrared spectra were recorded on KBr pellets and spectral bands were reported in cm^{-1}. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 and 125 MHz) spectra were measured using DMSO-d_6, CD_3OH or acetone-d_6 as solvent, and chemical shifts are reported as δ values in ppm. Low-resolution mass spectra (MS) were obtained as CI (CH_4) or at FAB (*m*-NBA) or ESI (Na) and high resolution mass spectra (HRMS) were recorded with *m*-NBA and 35 KeV (Cs Iodide). LiCl, CuI, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd_2(dba)_3$, P(*o*-Tol)$_3$ and (2-Biphenyl)di-*tert*-butylphosphine were commercially available. The stannanes: tributylvinylstannane,

tributylphenylethynylstannane, tributylphenylstannane, tributyl-2-furanylstannane, tributyl-2-thiophenyl-stannane and 1-*N*-Methyl-2-(tributylstannyl)-1*H*-pyrrole, were used as received from the supplier. 2-Tributylstannyl-pyridine,[1] and 4-tributylstannyl-1-trityl-1*H*-pyrazole[2] were obtained by previously described methods. DMF was distilled over activated molecular sieves.

General Procedures for Substituted Quinolizinum Salts 23-26.

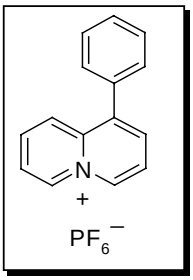
Method A. A flame-dried two-necked flask was charged under argon with the corresponding bromoquinolizinium salts **4-7** (50 mg, 0.173 mmol) in dry DMF (2 mL). Then 10 mol% CuI (3 mg, 0.0173 mmol), 5 mol% $Pd(PPh_3)_4$ (10 mg, 0.0086 mmol) and the corresponding stannane (0.225 mmol) were slowly added. After stirring at room temperature (15-20 h) or heating at 60-80 ºC as indicated, the solution was filtered through a small pad of Celite and washed with methanol. The solution was concentrated and the solid isolated by filtration. Some coupling products obtained from bromoquinoliziniums **4** and **5** were isolated as picrates (TNP) by treatment of the crude bromide with a slight excess of sodium picrate in refluxing ethanol for 1 h. Other derivatives were isolated as hexafluorophosphates by treatment with ammonium hexafluorophosphate in water followed by purification by column chromatography on silica gel, using CH_2Cl_2/MeOH (9.5:0.5) as the eluent. For the coupling products obtained from 3- and 4-bromoquinolizinium salts, after washing with methanol, the solvent was removed and the residue was triturated with ether and EtOAc. Purification of the crude product by column chromatography on silica gel (reverse phase) using

[1] Lee, A. S.-Y.; Dai, W.-C. *Tetrahedron* **1997**, *53*, 859.

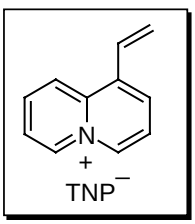
[2] Elguero, J.; Jaramillo, C.; Pardo, C. *Synthesis* **1997**, 563.

H_2O/AcOH (100:0.5) as the eluent yielded the coupling products **25** and **26**, which were isolated as bromides.

Method B: A dried two-necked flask was charged under argon with the corresponding quinolizinium salt (100 mg, 0.333 mmol) in dry DMF (5 mL). $Pd_2(dba)_3$ (5 mol%, 15.1 mg, 0.0165 mmol), P(*o*-Tol)$_3$ (5 mol%, 5 mg, 0.0165 mmol) and the corresponding stannane (1.3 eq, 0.429 mmol)) were slowly added. The mixture was stirred at room temperature or heating at 80 ºC, filtered through a small pad of Celite and washed with methanol. The solvent was removed and the residue was triturated with EtOAc. Purification of the crude product by column chromatography on silica gel (reverse phase) using water as the eluent yielded the product, which was isolated as the bromide.

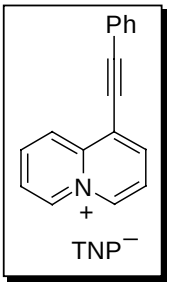


1-Phenylquinolizinium Hexafluorophosphate (23a): Following method A, from **4** and tributylphenylstannane, (0.225 mmol, 83 mg) after heating at 80 ºC for 31 h, 20 mg (34%) of **23a** were isolated as brown needles; mp 208-210 ºC; IR (KBr) ν_{max} 3111, 2924, 1637, 1407, 835 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 9.52 (d, 1H, *J* = 6.6 Hz); 9.46 (d, 1H, *J* = 6.6 Hz); 8.49-8.39 (m, 3H); 8.29-8.22 (m, 2H); 7.65 (s, 5H); ^{13}C NMR (125 MHz, acetone-d_6) δ 140.7, 138.4, 138.0, 137.2, 137.1, 135.8, 135.7, 130.6, 130.5, 130.1, 126.4, 124.9, 124.4. MS (ESI$^+$) *m/z* 206 (M$^+$). Anal. Calcd for $C_{14}H_{12}NPF_6$: C, 51.30; H, 3.44; N, 3.99. Found: C, 51.92; H, 3.51; N, 4.01.

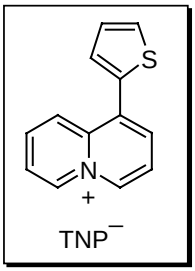


1-Vinylquinolizinium Picrate (23b). Following the method A, from **4** (50 mg, 0.173 mmol) and tributylvinylstannane (0.225 mmol, 0.065 mL), after stirring 20 h at rt, gave 36 mg (55%) of **23b** as yellow

powder; mp 180-182 ºC (EtOH); IR (KBr) ν_{max} 3441, 3081, 1634, 1561, 1338, 1280 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.37-9.28 (m, 2H), 8.76 (d, 1H, *J* = 9.3 Hz), 8.56-8.52 (m, 3H), 8.42-8.34 (m, 1H), 8.14-8.07 (m, 2H), 7.53 (dd, 1H, *J* = 16.9, 11.3 Hz), 6.20 (d, 1H, *J* = 17.3 Hz), 5.83 (d, 1H, *J* = 10.9 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.3, 160.4, 141.4, 137.2, 136.7, 136.0, 132.8, 126.5, 124.8, 123.8, 123.3, 123.2, 123.1, 122.9. Anal. Calcd for $C_{17}H_{12}N_4O_7$: C, 53.13; H, 3.15; N, 14.58. Found: C, 52.98; H, 3.42; N, 14.43.

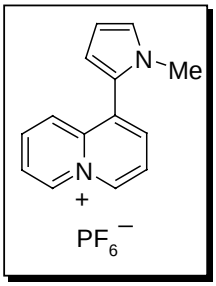


1-Phenylethynylquinolizinium Picrate (23c). Following the method A, from **4** and tributylphenylethynylstannane (0.225 mmol, 0.083 mL) after stirring 15 h, gave 46 mg (58%) of **23c** as yellow needles; mp 242-243 ºC (MeOH); IR (KBr) ν_{max} 3085, 2218, 1633, 1555, 1363, 1308, 1070, 783 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.44 (d, 1H, *J* = 6.4 Hz), 9.35 (d, 1H, *J* = 6.8 Hz), 8.91 (d, 1H, *J* = 8.9 Hz), 8.61 (d, 1H, *J* = 7.5 Hz), 8.56 (s, 2H), 8.51 (t, 1H, *J* = 7.8 Hz), 8.21 (t, 1H, *J* = 7.2 Hz), 8.12 (t, 1H, *J* = 7.2 Hz), 7.83-7.79 (m, 2H), 7.55-7.52 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.7, 138.9, 138.2, 137.0, 132.2, 132.1, 132.0, 130.6, 129.2, 125.5, 125.4, 125.3, 125.2, 124.6, 123.3, 120.6, 120.4, 99.5, 82.2. MS (FAB, *m*-NBA) *m/z* (relative intensity) 230 (100, (M^+-TNP)), 154 (21); HRMS calcd for $C_{17}H_{12}N$: 230.0970, found 230.0973.

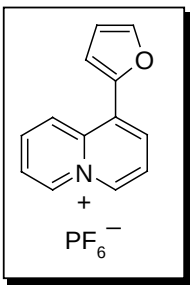


1-(2-Thiophenyl)quinolizinium Picrate (23d). Following the method A, from **4** and tributyl-2-thiophenylstannane (0.225 mmol, 0.088 mL), after stirring at rt for 16 h, 45 mg (60%) of **23d** were obtained as yellow prisms; mp 160-161 ºC (MeOH); IR (KBr) ν_{max}

3089, 1612, 1337, 1165, 805 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.45 (d, 1H, *J* = 6.6 Hz), 9.36 (d, 1H, *J* = 6.2 Hz), 8.58 (m, 3H), 8.41-8.35 (m, 2H), 8.14 (m, 2H), 7.94 (d, 1H, *J* = 5.0 Hz); 7,54 (d, 1H, *J* = 3.5 Hz); 7,35 (dd, 1H, *J* = 5.1, 3.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 137.9, 137.7, 137.5, 136.8, 136.6, 130.4, 129.8, 128.4, 126.9, 125.1, 124.8, 124.1, 123.9, 123.7, 122.9. Anal. Calcd for $C_{19}H_{12}SN_4O_7$: C, 51.82; H, 2.75; N, 12.72. Found: C, 51.51; H, 3.01; N, 12.92.

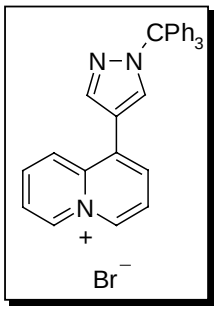


1-(2-*N*-Methylpyrrolyl)quinolizinium Bromide (23e): Following the method A, from **4** and tributyl-2-*N*-methylpyrrolylstannane (0.225 mmol, 83 mg) after heating at 80 ºC for 3.5 h, 47 mg (77%) of **23e** were obtained as yellow dust; mp 172-174ºC; IR (KBr) ν_{max} 3121, 1642, 1395, 835 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.48(d, 1H, *J* = 6.8Hz); 9.41 (d, 1H, *J* = 6.7 Hz); 8.51-8.38 (m, 3H); 8.26-8.23 (m, 2H); 7.08 (t, 1H, *J* = 2.3 Hz); 6.43 (dd, 1H, *J* = 1.8, 3.8 Hz); 6.31 (dd, 1H, *J* = 2.6, 3.6 Hz); 3.59 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 144.4, 139.1, 138.6, 138.4, 137.1, 132.4, 126.8, 126.8, 126.2, 125.1, 124.3, 113.7, 109.4, 34.8. MS (ESI^+) *m/z* 209 (M^+). Anal. Calcd for $C_{14}H_{13}N_2PF_6$: C, 47.47; H, 3.70; N, 7.91. Found: C, 47.34; H, 4.02; N, 7.47.

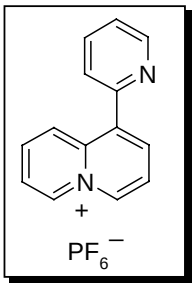


1-(2-Furanyl)quinolizinium Hexafluorophosphate (23f). Following the method A, from **4** and tributyl-2-furanylstannane (0.225 mmol, 0.073 mL), after heating at 60ºC for 3.5 h, 31 mg (53%) de **23f** were obtained as a yellow dust; mp 190-191ºC; IR (KBr) ν_{max} 3123, 1637, 1463, 834 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.50 (d, 1H, *J*= 6.8 Hz); 9.39 (d, 1H, *J* = 6.8 Hz); 9.10 (d, 1H, *J* = 9.1 Hz); 8.66 (d, 1H, *J* = 7.7 Hz); 8.57

(td, 1H, *J* = 1.1, 8.6 Hz); 8.25 (dd, 2H, *J* = 7.3, 14.5 Hz); 8.01 (s, 1H); 7.33 (d, 1H, *J* = 3.5 Hz); 6.83 (dd,1H, *J* = 1.6, 3.5 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 148.0, 146.5, 141.1, 138.7, 137.1, 135.8, 132.5, 129.1, 126.0, 125.1, 124.2, 114.5, 113.2; MS (ESI$^+$) *m/z* 196 (M^+). Anal. Calcd for $C_{13}H_{10}ONPF_6$. C, 45.75; H, 2.93; N, 4.10; O, 4.69. Found: C, 45.97; H, 3.19; N,4.24.

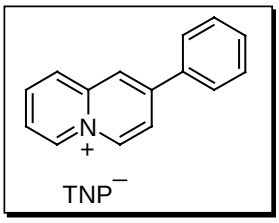


1-(1-Trityl-1*H*-4-pirazolyl)quinolizinium Bromide (23g). Following the method A, from **4** and 4-tributylstannyl-1-trityl-1*H*-pyrazole (0.225 mmol, 135 mg) after heating at 80 ºC for 16 h, 40 mg (45%) of **23g** were obtained as a red solid; mp 241-243 ºC (dec) ; IR (KBr) ν_{max} 3386, 3055, 1637, 1445, 702 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 9.34 (d, 1H, *J* = 8.9 Hz); 9.23 (d, 1H, *J* = 6.7 Hz); 8.63 (d, 1H, *J* = 8.9 Hz); 8.42-8.32 (m, 2H); 8.12-8.02 (m, 4H); 7.43-7.41 (m, 9H,), 7.1-7.28 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 141.2, 139.0, 138.9, 137.1, 136.9, 132.5, 131.0, 129.9, 128.2, 128.0, 124.1, 123.9, 123.4, 114.2, 79.8. MS (ESI$^+$) *m/z* 438 (M^+, 100); 439 (98.12); Anal. Calcd for $C_{31}H_{24}N_3Br$. C, 71.82; H, 4.67; N, 8.10. Found: C, 71.61; H, 4.86; N, 7.70.

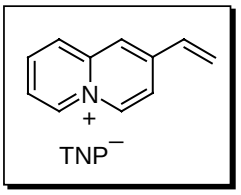


1-(2-Pyridinyl)quinolizinium Hexafluorophosphate (23h). From **4** and tributyl-2-pyridinylstannane (0.225 mmol, 83 mg), after heating at 80 ºC for 24h, 31 mg (51%) of **23h** were obtained as a brown solid; mp 189-191 ºC; IR (KBr) 3110, 1638, 1406, 834 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 9.54 (t, 2H, *J* = 8.0 Hz); 8.88 (d, 2H, *J* = 7.5 Hz); 8.60 (dd, 1H, *J* = 1.1, 7.5 Hz); 8.50 (td, 1H, *J* = 1.3, 7.3 Hz); 8.34-8.25 (m, 2H); 8.14 (td, 1H, *J* = 1.8, 7.9 Hz); 7.93 (d, 1H, *J* = 7.9 Hz); 7.65 (ddd, 1H, *J* = 1.1, 4.8, 7.9Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.1, 154.5, 150.9, 138.9, 139.8, 138.7, 138.5,

138.1, 126.9, 126.4, 125.3, 125.2, 124.4. MS (ESI^+) *m/z* 207 (M^+). Anal. Calcd for $C_{14}H_{11}N_2PF_6$: C, 47.74; H, 3.15; N, 7.95.Found: C, 47.43; H, 3.02; N, 7.81.

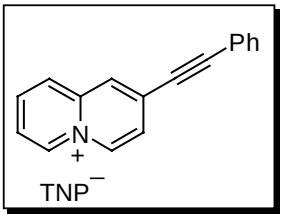


2-Phenylquinolizinium Picrate (24a). Following the method A, from **5** and tetraphenylstannane (0.225 mmol, 96.1 mg) or tributylphenylstannane, (0.225 mmol, 83 mg), after heating at 80 ºC h for 17 h, 45 mg (60%) of **24a** were obtained as yellow prisms; mp 174-175 ºC (MeOH) (Lit.[3] 168-170 ºC); IR (KBr) ν_{max} 3430, 3087, 1732, 1633, 1326, 1157, 747 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.38 (d, 1H, *J* = 7.5 Hz), 9.29 (d, 1H, *J* = 6.5 Hz), 8.99 (d, 1H, *J* = 2.0 Hz), 8.56 (s, 1H), 8.54 (dd, 1H, *J* = 7.0, 2.0 Hz), 8.51 (d, 1H, *J* = 8.5 Hz), 8.36 (td, 1H, *J* = 7.5, 1.0 Hz), 8.11-8.09 (m, 3H), 7.68-7.63 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.6, 142.9, 141.9, 137.1, 137.0, 136.4, 134.3, 131.3, 129.7; 127.7, 127.2, 125.2, 124.1, 123.3, 122.7, 121.6; MS (*m/z*) 207 (15), 194 (28), 79 (15). Anal. Calcd for $C_{21}H_{14}N_4O_7$:C, 58.07; H, 3.25; N, 12.90. Found: C, 57.92; H, 3.43; N, 13.04.

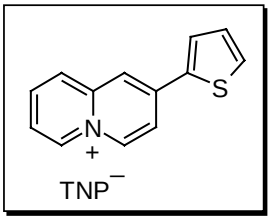


2-Vinylquinolizinium Picrate (24b). Following the method A, from **5** and tributylvinylstannane (0.225 mmol, 0.065 mL), after stirring 20 h at rt, 7 mg (10%) of **24b** were obtained as an unstable yellow dust; ^1H NMR (300 MHz, DMSO-d_6) δ 9.25 (dd, 2H, *J* = 7.7, 7.3 Hz), 8.56 (s, 2H), 8.51 (s, 1H), 8.43 (d, 1H, *J* = 8.8 Hz), 8.30 (t, 2H, *J* = 6.8 Hz), 7.03 (dd, 1H, *J* = 11.0, 17.5 Hz), 6.51 (d, 1H, *J* = 17.5 Hz), 5.91 (d, 1H, *J* = 11.0 Hz).

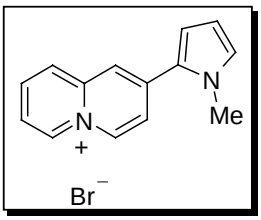
[3] Glover, E. E.; Jones, G. *J. Chem. Soc.* **1958**, 3021.



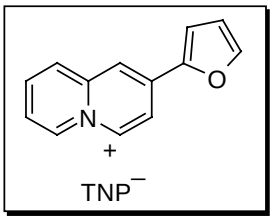
2-Phenylethynylquinolizinium Picrate (24c). Following the method A, from **5** and tributylphenylethynylstannane (0.225 mmol, 0.083 mL), after stirring 15 h, 72 mg (91%) of **24c** were obtained as brown needles; mp 186-188 ºC (MeOH); IR (KBr) ν_{max} 3415, 3080, 2202, 1635, 1559, 1362 cm^{-1}; ^{1}H NMR (300 MHz., DMSO-d_6): δ 9.32 (d, 2H, *J* = 7.0 Hz), 8.79 (s, 1H), 8.56 (s, 2H), 8.50 (d, 1H, *J* = 8.4 Hz), 8.41 (t, 1H, *J* = 8.0 Hz), 8.19 (d, 1H, *J* = 7.0 Hz), 8.11 (t, 1H, *J* = 6.4 Hz), 7.72-7.69 (m, 2H), 7.57-7.45 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.7, 160.9, 142.5, 142.0, 137.8, 137.3, 136.9, 132.2, 130.9, 130.1, 129.3, 129.0, 127.1, 125.3, 124.2, 99.1, 86.0; MS (*m/z*) 230 (9), 105 (21), 79 (9). Anal. Calcd for $C_{23}H_{14}N_4O_7$: C, 60.27; H, 3.08; N, 12.22. Found: C, 59.88; H, 3.21; N, 12.48.



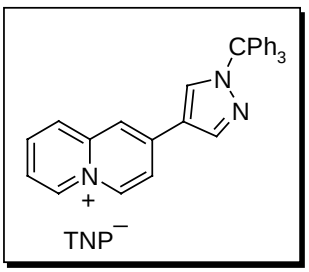
2-(2-Thiophenyl)quinolizinium Picrate (24d). Using the method A, from**5** and tributyl-2-thiophenylstannane (0.225 mmol, 0.088 mL), after stirring at rt for 18 h, 52 mg (68%) of **24d** were obtained as yellow needles; mp 222-224 ºC (MeOH); IR (KBr) ν_{max} 3078, 1635, 1551, 1417, 1315, 1270, 1078, 709 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.28 (d, 1H, *J* = 7.0 Hz), 9.20 (d, 1H, *J* = 7.0 Hz), 8.77 (s, 1H), 8.56 (s, 2H), 8.46 (d, 2H, *J* = 8.0 Hz), 8.30 (t, 1H, *J* = 7.7 Hz), 8.16 (d, 1H, *J* = 3.3 Hz), 8.03 (d, 1H, *J* = 4.7 Hz), 7.97 (t, 1H, *J* = 7.0 Hz), 7.37 (t, 1H, *J* = 4.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.9, 141.8, 140.5, 137.8, 136.9, 136.8, 133.5, 130.4, 129.7, 126.7, 125.0, 122.7, 119.9, 115.0. MS (FAB, m-NBA) *m/z* (relative intensity) 212 (100, (M^+-TNP)), 154 (20); HRMS calcd for $C_{13}H_{10}NS$: 212.0534, found 212.0538.



2-(2-*N*-Methylpyrrolyl)quinolizinium Bromide (24e): Following the method A, from **5** and tributyl-2-N-methylpyrrolylstannane (0.225 mmol, 83 mg) after stirring at r.t for 23 h, 42 mg (85%) of **24e** were obtained as yellow plates; mp 241-243ºC; IR (KBr) ν_{max} 3399, 3086, 1642, 1443, 768 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.04 (t, 2H, *J* = 7.0 Hz); 8.42-8.39 (m, 2H); 8.22-8.17 (m, 2H); 7.82 (td, 1H, *J* = 1.3, 7.0 Hz); 7.17 (t, 1H, *J* = 2.0 Hz); 7.05 (dd, 1H, *J* = 2.0, 4.0Hz); 6.34 (dd, 1H, *J* = 2.5, 4.0 Hz); 4.07 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 144.6, 141.3, 136.9, 136.8, 136.6, 132.8, 129.6, 127.7, 122.9, 122.7, 119.6, 117.6, 110.9, 37.3. MS (ESI^+) *m/z* 209 (M^+). Anal. Calcd for $C_{14}H_{13}N_2Br$: C, 58.15 ; H, 4.53; N, 9.69. Found: C, 58.30; H, 4.87; N, 9.25

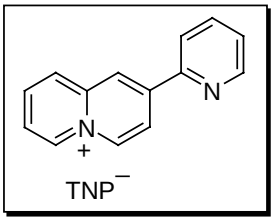


2-(2-Furanyl)quinolizinium Picrate (24f). Following the method A, from **5** and tributyl-2-furanylstannane (0.225 mmol, 0.073 mL), after stirring at rt for 18 h, 40 mg (55%) of **24f** were isolated as yellow needles; mp 208-209 ºC (EtOH); IR (KBr) ν_{max} 3415, 3077, 2369, 1632, 1551, 1419, 1314, 1273, 1151, 820 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.28 (d, 1H, *J* = 7.2 Hz), 9.20 (d, 1H, *J* = 6.7 Hz), 8.77 (d, 1H, *J* = 2.3 Hz), 8.56 (s, 2H), 8.47-8.45 (m, 2H), 8.30 (t, 1H, *J* = 7.5 Hz), 8.15 (dd, 1H, *J* = 3.6, 1.0 Hz), 8.03 (dd, 1H, *J* = 5.0, 1.0 Hz), 7.97 (dt, 1H, *J* = 7.0, 1.5 Hz), 7.37 (dd, 1H, *J* = 5.0, 3.9 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.5, 141.3, 140.0, 137.4; 136.5, 136.4, 135.9, 132.1, 130.0, 129.3, 126.3, 124.6; 122.2, 119.7, 119.4. Anal. Calcd for $C_{19}H_{12}N_4O_8$: C, 53.78; H, 2.85; N, 13.20. Found: C, 53.58; H, 2.87; N, 12.99.

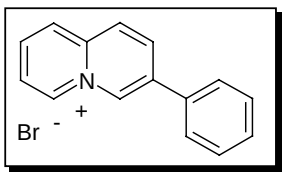


2-(1-Trityl-1*H*-4-pirazolyl)quinolizinium Picrate (24g). Following the method A, from **5** and 4-tributylstannyl-

1-trityl-1*H*-pyrazole (0.225 mmol, 131 mg), after stirring at rt for 19 h, 111 mg (96%) of **24g** were obtained as yellow needles; mp 230-231 ºC (EtOH); IR (KBr) ν_{max} 3430, 3064, 1644, 1551, 1154, 872 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.21 (d, 1H, *J* = 7.3 Hz), 9.12 (d, 1H, *J* = 7.3 Hz), 8.74 (s, 1H), 8.56 (s, 2H), 8.50 (s, 2H), 8.40 (d, 1H, *J* = 7.3 Hz), 8.23-8.21 (m, 2H), 7.95-7.75 (m, 1H), 7.38 (m, 9H), 7.12 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.9, 142.2, 140.2, 138.9, 137.0, 136.8, 136.4, 136.2, 132.9, 129.6, 128.0, 127.9, 126.3, 122.2, 120.9, 119.8, 78.3; MS (*m/z*) 243 (84), 183 (13), 165 (100). Anal. Calcd for $C_{37}H_{26}N_6O_7$: C, 66.66; H, 3.93; N, 12.61. Found: C, 66.53; H, 4.07; N, 12.72.

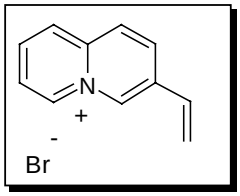


2-(2-Pyridinyl)quinolizinium Picrate (24h). Following the method A, from **5** and 2-tributylstannylpyridine (0.225 mmol, 83 mg), after stirring at rt for 16 h, 26 mg (35%) of **24h** were obtained as yellow plates; mp 217-219 ºC (EtOH); IR (KBr) ν_{max} 3075, 1637, 1363, 1316, 1268, 788 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.42 (d, 1H, *J* = 7.3 Hz), 9.35 (d, 1H, *J* = 6.5 Hz), 9.30 (s, 1H), 8.87 (d, 1H, *J* = 4.0 Hz), 8.79 (dd, 1H, *J* = 7.3, 2.0 Hz), 8.66 (d, 1H, *J* = 7.7 Hz), 8.56 (s, 2H), 8.43-8.37 (m, 2H), 8.16-8.08 (m, 2H), 7.64 (dd, 1H, *J* = 6.9, 4.8 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.5, 144.8, 144.7, 143.0, 141.9, 138.2, 137.2, 136.8, 127.7, 127.6, 125.9, 125.2, 123.9, 123.3, 122.6, 120.8; MS (*m/z*) 209 (50), 80 (61). Anal. Calcd for $C_{20}H_{13}N_5O_7$; C, 55.18; H, 3.01; N, 16.09. Found: C, 55.37; H, 3.02; N, 15.73.

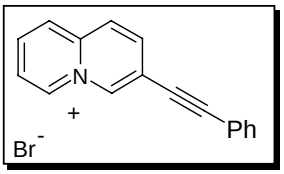


3-Phenylquinolizinium Bromide (25a). Following method A, from **6** and tributylphenylstannane, (0.225 mmol, 83 mg), after heating at 80 ºC for 24 h, 26 mg (53%) of **25a** were

isolated as brown needles; mp 205-207 ºC; IR (KBr) ν_{max} 3060, 3023, 1630, 774 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.64 (s, 1H); 9.33 (d, 1H, *J* = 6.8 Hz); 8.74 (dd, 1H, *J* = 1.6, 9.0 Hz); 8.58 (t, 2H, *J* = 9.3 Hz); 8.38 (t, 1H, *J* = 7.5 Hz); 8.10 (t, 1H, *J* = 7.3 Hz); 7.96 (dd, 2H, *J* = 1.6, 8.2 Hz); 7.69-7.62 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 138.6, 138.1, 138.0, 137.8, 137.4, 135.1, 132.7, 131.5, 130.9, 128.8, 128.4, 128.2, 125.4. MS (ESI^+) *m/z* 206 (M^+). Anal. Calcd for $C_{14}H_{12}NBr$: C, 58.74; H, 4.19; N, 4.89 Found: C, 58.37; H, 3.96; N, 5.01.

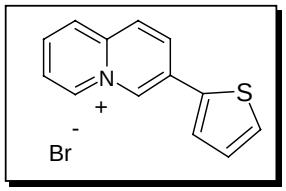


3-Vinylquinolizinium Bromide (25b). Following the method A, from **6** and tributylvinylstannane (0.225 mmol, 79 mg), after heating at 80 ºC for 24 h, 9 mg (22%) of **25b** were obtained as a brown oil; IR (KBr) ν_{max} 3068, 1634, 1150, 870 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.34 (s, 1H); 9.25 (d, 1H, *J* = 6.8 Hz); 8.63 (dd, 1H, *J* = 1.6, 9.1 Hz); 8.51 (t, 2H, *J* = 8.0 Hz); 8.36 (td, 1H, *J* = 1.1, 7.3 Hz); 8.07 (t, 1H, *J* = 6.9 Hz); 7.05 (dd, 1H, *J* = 11.0, 17.6 Hz); 6.39 (d, 1H, *J* = 17.6,Hz); 5.83 (d, 1H, *J* = 11.0 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 138.0, 137.9, 135.5, 135.4, 135.0, 131.5, 128.2, 128.1, 128.0, 125.4, 122.9. MS (ESI^+) *m/z* 156 (M^+). Anal. Calcd for $C_{11}H_{10}NBr$. C, 46.15; H, 4.24; N, 5.93. Found: C, 46.35; H, 4.12; N, 5.94.

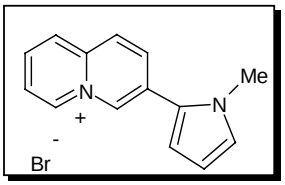


3-Phenylethynylquinolizinium Bromide (25c). Using the method A, from **6** and tributylphenylethynylstannane (0.225 mmol, 88 mg), after stirring at rt for 24 h, 18 mg (35%) of **25c** were isolated as a brown solid; mp 226-228 ºC; IR (KBr) ν_{max} 3028, 2219, 1629, 765 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.56 (s, 1H); 9.26 (d, 1H, *J* = 6.8 Hz); 8.55 (t, 2H, *J* = 7.8 Hz); 8.45-8.39 (m, 2H); 8.13 (t, 1H, *J* = 6.8 Hz);

7.71-7.68 (m, 2H); 7.54-7.47 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 134.5, 139.8, 139.5, 138.7, 139.6, 137.7, 133.1, 131.4, 129.9, 128.4, 128.3, 125.8, 122.3, 122.1, 89.0, 83.5. MS (ESI^+) *m/z* 230 (M^+). Anal. Calcd for $C_{17}H_{12}NBr$: C, 65.80; H, 3.87; N, 4.51. Found: C, 65.45; H, 4.02; N, 4.52.

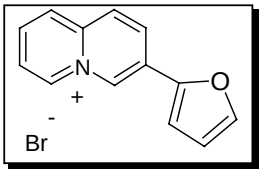


3-(2-Thiophenyl)quinolizinium Bromide (25d). Following the method A, from **6** and tributyl-2-thiophenylstannane (0.225 mmol, 84mg) after stirring at rt for 21 h, 16 mg (48%) of **25d** were obtained as yellow dust; mp d; IR (KBr) ν_{max} 3044, 1626, 1431, 831 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 9.63 (s, 1H); 9.28 (d, 1H, *J* = 6.9 Hz); 8.69 (dd, 1H, *J* = 1.8, 8.9 Hz); 8.51 (d, 2H, *J* = 9.2 Hz); 8.33 (t, 1H, *J* = 1.0, 3.8 Hz); 8.10 (t, 1H, *J* = 6.8 Hz); 7.91 (d, 1H, *J* = 3.8 Hz); 7.80 (dd, 1H, *J* = 1.0, 5.1 Hz); 7.33 (dd, 1H, *J* = 3.8, 4.9 Hz). ^{13}C NMR (75 MHz, CD_3OD) δ 143.4, 138.0, 137.9, 137.5, 136.1, 135.0, 132.9, 131.1, 130.6, 129.8, 128.8, 128.6, 125.9. MS (ESI^+) *m/z* 212 (M^+). Anal. Calcd for $C_{13}H_{10}NSBr$: C, 53.42; H, 3.42; N, 4.79; S, 10.96. Found: C, 53.39; H, 3.17; N, 4.99; S, 11.12.

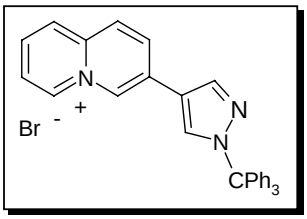


3-(2-*N*-Methylpyrrolyl)quinolizinium Bromide (25e). Following the method A, from **6** and tributyl-2-*N*-methylpyrrolylstannane (0.225 mmol, 83 mg) after heating at 80 ºC for 18 h, 29 mg (57%) of **25e** were isolated as yellow plates; mp 213-215ºC (dec); IR (KBr) ν_{max} 3025, 1626, 1424, 730 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 9.30-9.27 (m, 2H); 9.54-9.47 (m, 3H); 8.31 (t, 1H, *J* = 7.3 Hz); 8.05 (t, 1H, *J* = 6.9 Hz); 7.06 (s, 1H); 6.74 (dd, 1H, *J* = 1.6, 3.7 Hz); 6.31 (t, 1H, *J* = 3.8 Hz); 4.91 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 137.5, 137.3, 136.7, 133.0, 131.1, 129.4,

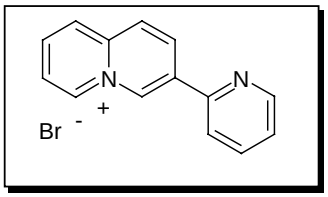
127.8, 127.6, 127.5, 125.0, 114.4, 110.1, 36.0. MS (ESI^+) *m/z* 209 (M^+). Anal. Calcd for $C_{14}H_{13}N_2Br$: C, 58.13 ; H, 4.49; N, 9.69. Found: C, 58.24; H, 4.34; N,9.65.



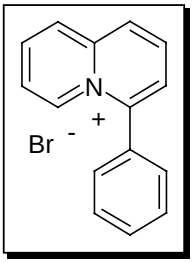
3-(2-Furanyl)quinolizinium Bromide (25f). Following the method A, from **6** and tributyl-2-furanylstannane (0.225 mmol, 80 mg) after heating at 80 ºC for 18 h, 27 mg (57%) of **25f** were obtained as a brown solid; mp 237-238 ºC; IR (KBr) ν_{max} 3027, 1636, 1409, 760 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 8.98 (s, 1H); 8.77 (d, 1H, *J* = 6.8 Hz); 8.16-8.05 (m, 3H); 7.99 (t, 1H, *J* = 7.5 Hz); 7.73 (td, 1H, *J* = 1.1, 6.9 Hz); 7.44 (d, 1H, *J* = 1.6 Hz); 6.88 (d, 1H, *J* = 3.5 Hz); 6.36 (dd, 1H, *J* = 1.6, 3.5 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 148.6, 147.1, 137.8, 137.5, 133.5, 131.2, 128.4, 128.2, 125.5, 114.0, 133.3. MS (ESI^+) *m/z* 196 (M^+). Anal. Calcd for $C_{13}H_{10}NOBr$: C, 56.52; H, 3.62; N, 5.07; O, 5.79. Found: C, 56.72; H, 5.16; O, 5.25.



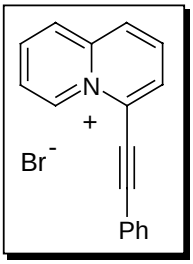
3-(1-Trityl-1*H*-4-pirazolyl)quinolizinium Bromide (25g) Following the method A, from **6** and 4-tributylstannyl-1-trityl-1*H*-pyrazole (0.225 mmol, 135 mg), after heating at 80 ºC for 18 h, 64 mg (71%) of **25g** were obtained as a brown solid; mp 278-280 ºC; IR (KBr) ν_{max} 3057, 2359, 1562, 1444, 701 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.55 (s, 1H); 9.12 (d, 1H, *J* = 6.4 Hz); 8.60 (d, 1H, *J* = 9.3 Hz); 8.45 (d, 2H, *J* = 6.6 Hz); 8.34-8.25 (m, 3H); 8.02 (t, 1H, *J* = 6.7 Hz), 7.41-7.39 (m, 9H); 7.25-7.23 (m, 6H); ^{13}C NMR (75 MHz, CD_3OD) δ 143.5, 143.4, 138.6, 136.9, 136.6, 135.8, 132.5, 132.4, 132.3, 130.9, 130.8, 128.9, 128.7, 128.0, 127.9, 125.0, 117.4. MS (ESI^+) *m/z* 438 (M^+). Anal. Calcd for $C_{31}H_{24}N_3Br$. C, 71.82; H, 4.67; N, 8.10. Found: C, 72.03; H, 4.42; N, 7.86.



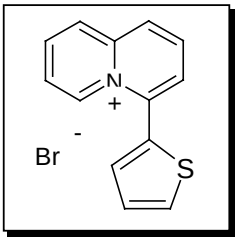
3-(2-Pyridinyl)quinolizinium Bromide (25h). Following the method A, from **6** and tributyl-2-pyridinylstannane (0.225 mmol, 83 mg), after heating at 80 ºC for 18h, 29 mg (58%) of **25h** were obtained as a brown solid; mp 229-231 ºC; IR (KBr) ν_{max} 3018, 1586, 1440, 799 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 10.03 (s, 1H); 9.40 (d, 1H, *J* = 6.9 Hz); 9.08 (d, 1H, *J* = 9.0 Hz); 8.87 (d, 1H, *J* = 4.0 Hz); 8.61 (dd, 2H, *J* = 9.0, 14.6 Hz); 8.42 (t, 1H, *J* = 7.2 Hz); 8.28 (d, 1H, *J* = 8.1 Hz); 8.15-8.05 (m, 2H): 7.63-7.57 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 151.8, 151.7, 144.3, 139.5, 139.3, 138.5, 138.4, 136.7, 136.2, 128.4, 128.3, 126.4, 125.5, 123.1. MS (ESI^+) *m/z* 207 (M^+). Anal. Calcd for $C_{14}H_{11}N_2Br$: C, 58.54; H, 3.83; N, 9.75.Found: C, 58.43; H, 4.10; N, 9.65.



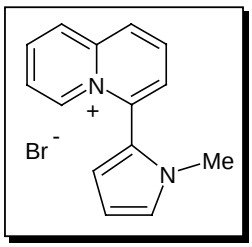
4-Phenylquinolizinium Bromide (26a): Following the method A, from **7** and tributylphenylstannane (0.225 mmol, 82 mg), after heating at 80 ºC for 20 h, 5 mg (10%) of **26a** were obtained as a yellow oil; IR (KBr) ν_{max} 3378, 1573, 1402, 817 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 9.06 (d, 1H, *J* = 2.4 Hz); 8.63 (t, 2H, *J* = 9.3 Hz); 8.48-8.37 (m, 2H); 8.04-7.94 (m, 2H); 7.79-7.76 (m, 5H); ^{13}C NMR (75 MHz, CD_3OD) δ 147.7, 145.3, 137.5, 137.3, 134.4, 132.6, 132.3, 130.8, 130.4, 128.9, 127.0, 124.9. MS (ESI^+) *m/z* 206 (M^+). Anal. Calcd for $C_{14}H_{12}NBr$: C, 58.74; H, 4.19; N, 4.89. Found: C, 59.01; H, 4.08; N, 4.75.



4-Phenylethynylquinolizinium Bromide (26c). Following the method A, from **7** and tributylphenyethynylstannane (0.225 mmol, 88 mg), after stirring at rt for 22 h, 30 mg (55%) of **26c** were obtained as a brown solid; mp 221-223 ºC; IR (KBr) ν_{max} 3041, 2218, 2202, 1614 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) δ 9.89 (d, 1H, *J* = 6.9 Hz) 8.65-8.31 (m, 5H); 8.23 (t, 1H, *J* = 6.9 Hz); 7.86 (dd, 2H, *J* = 3.6, 7.7 Hz); 7.60-7.54 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 145.0, 138.7, 136.9, 135.8, 133.7, 133.4, 132.4, 130.1, 129.5, 128.4, 126.1, 121.0, 106.9, 79.8. MS (ESI^+) *m/z* 230 (M^+). Calcd for $C_{17}H_{12}NBr$: C, 65.80; H, 3.87; N, 4.51. Found: C, 65.71; H, 3.65; N, 4.74.

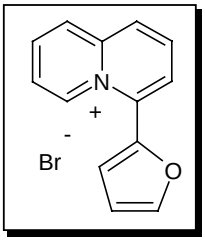


4-(2-Thiophenyl)quinolizinium Bromide (26d): Following procedure B, from **7** and tributyl-2-thiophenylstannane (0.449 mmol, 167 mg), after stirring at rt for 22 h, 86 mg (85%) of **26d** were isolated as a brown solid; mp 161-163ºC; IR (KBr) ν_{max} 3112, 2952, 1618, 1455, 808 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 9.34 (d, 1H, *J* = 7.1Hz); 8.65 (t, 2H, *J* = 8.8 Hz); 8.43(dd, 2H, *J* = 6.4, 14.1 Hz); 8.15 (d, 1H, *J* = 4.1 Hz); 8.07-8.02(m, 2H); 7.72(dd, 1H, *J* = 1.1, 3.7 Hz); 7.45(dd, 1H, *J* = 3.7, 5.1 Hz). ^{13}C NMR (75 MHz, CD_3OD) δ 145.8,141.4, 138.3, 137.2, 134.8, 133.6, 132.6, 131.9, 129.7, 129.4, 128.9, 125.5. MS (ESI^+) *m/z* 212 (M^+). Calcd for $C_{13}H_{10}NSBr$: C, 53.42; H, 3.42; N, 4.79; S, 10.96. Found: C, 53.26; H, 3.65; N, 4.52; S, 10.75.

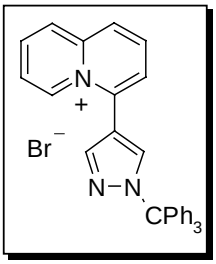


4-(2-*N*-Methylpyrrolyl)-*N*-methylquinolizinium Bromide (26e). Following the method A, from **7** and tributyl-2-*N*-methylpyrrolylstannane (0.225 mmol, 83 mg), after stirring 23 h

at rt, 35 mg of **26e** (70%) were obtained as a brown-reddish oil; IR (KBr) ν_{max} 3052, 1625, 1460, 813 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.04 (d, 1H, *J* = 7.1 Hz); 8.63 (dd, 2H, *J* = 8.6, 12.8 Hz); 8.46-8.339 (m, 2H); 8.11-8.02 (m, 2H); 7.20 (t, 1H, *J* = 1.8 Hz); 6.69 (dd, 1H, *J*= 1.6, 3.8 Hz); 6.45 (dd, 1H, *J* = 2.7, 3.7 Hz); 3.57 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 145.9, 140.0, 138.1, 137.3, 134.6, 129.5, 129.2, 128.6, 128.4, 125.7, 123.0, 115.6, 110.6, 34.9. MS (ESI^+) *m/z* 209 (M^+). Anal. Calcd for $C_{14}H_{13}N_2Br$: C, 58.13; H, 4.49; N, 9.69. Found: C, 58.24; H, 4.37; N, 9.40.

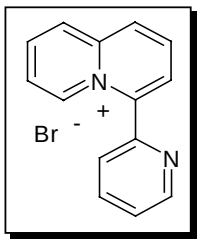


4-(2-Furanyl)quinolizinium Bromide (26f). Following method A, from **7** and tributyl-2-furanylstannane (0.225 mmol, 83 mg), after stirring 21 h at rt, 24 mg (51%) of **26f** were obtained as a brown solid; mp 241-242ºC; IR (KBr) ν_{max} 3052, 1625, 1488, 766 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 9.51 (d, 1H, *J* = 7.2 Hz); 8.65-8.54 (m, 2H); 8.46-8.37 (m, 2H) ; 8.27 (dd, 1H, *J* = 7.4, 1.5 Hz); 8.13-8.04 (m, 2H); 7.44 (d, 1H, *J* =3.6Hz); 6.89 (dd, 1H, *J* =3.6, 1.8 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.7, 143.0, 136.5, 135.6, 135.1, 133.3, 127.7, 126.9, 125.1, 124.1, 116.5, 112.3; MS (ESI^+) *m/z* 196 (M^+); Anal. Calcd for $C_{13}H_{10}NOBr$: C, 56.52; H, 3.62; N, 5.07; O, 5.79. Found: C, 56.72; H, 3.41; N, 5.20; O, 5.58.



4-(1-Trityl-1*H*-4-pirazolyl)quinolizinium Bromide (26g). Following the method B, from **7** and 4-tributylstannyl-1-trityl-1*H*-pyrazole (135 mg, 0.225 mmol), after heating at 80 ºC for 18 h, 10 mg (13%) of **26g** were isolated as a brown solid; mp 232-233ºC; IR (KBr) ν_{max} 3423. 3049, 1620, 702 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.62 (d, 1H, *J* = 7.1 Hz); 8.79 (d, 1H, *J* = 8.6 Hz); 8.73 (d, 1H, *J* = 8.4 Hz); 8.50-844 (m, 2H);

8.20-8.11 (m, 4H); 7.41-7.39 (m, 9H), 7.28-7.25 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 142.0, 139.1, 138.9, 136.7, 136.6, 134.2, 131.8, 130.1, 129.9, 128.4, 128.3, 128.2, 126.9, 124.8, 111.1, 80.3. MS (ESI^+) *m/z* 438 (M^+), . Anal. Calcd for $C_{31}H_{24}N_3Br$. C, 71.82; H, 4.67; N, 8.10. Found: C, 72.01; H, 4.86; N, 7.71.



4-(2-Pyridinyl)quinolizinium Bromide (26h). Following method A, from **7** and 2-tributylstannylpyridine (0.225mmol, 83mg), after stirring 18 h at rt, 41 mg (83%) of **26h** were isolated as a brown solid; mp 230-232 ºC; IR (KBr) ν_{max} 3030, 1643, 1627, 799 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.26 (d, 2H, *J* = 7.2 Hz); 8.89 (d, 1H, *J* = 4.1 Hz); 8.73 (d, 2H, *J* =8.7Hz); 8.48 (dd, 2H, *J* = 7.7, 15.9 Hz); 8.26-8.20 (m, 2H); 8.04-7.94 (m, 2H); 7.75 (dd, 1H, *J* = 4.9, 7.4 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 149.7, 149.5, 142.9, 142.7, 138.3, 136.7, 135.8, 133.5, 127.4, 127.3, 126.1, 125.8, 125.3, 123.6; MS (ESI^+) *m/z* 207 (M^+). Anal. Calcd for $C_{14}H_{11}N_2Br$: C, 58.54; H, 3.83; N, 9.75. Found: C, 58.37; H, 3.94; N, 9.62.