A Unified Approach to Quinolizinium Cations and Related Systems by Ring-closing Metathesis

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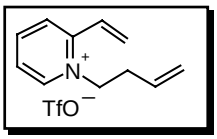
Supporting Information

(10 pages)

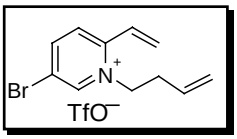
General experimental details. Melting points were uncorrected. Infrared spectra were recorded on NaCl pellets and spectral bands were reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 / 300 MHz and 50 /75 MHz respectively. Chemical shifts were reported as δ values (ppm). The mass spectra (MS) were obtained as (ESI^{+}). Ruthenium's catalyst **1** and **2,** 2-vinylpyridine and alcohols were purchased from Aldrich.

General procedure for the preparation of salts 4.

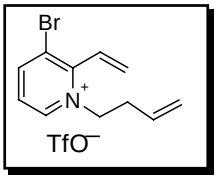
A solution of the corresponding alcohol (2.6 mmol) and dry pyridine (0.205 g, 2.6 mmol) in dry CCl_4 (2 mL) was stirred at room temperature for 5-10 min under argon. Then the mixture was added dropwise (5-10 min) over a cooled solution (-10ºC) of triflic anhydride (0.733 g, 6 mmol) in dry CCl_4 (3 mL). The white solid formed was filtered off trough sodium sulphate, the solution was added via cannula to a solution of the vinyl derivative (2 mmol) in dry CCl_4 (2 mL) and the reaction mixture stirred for 24 h at room temperature. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: CH_2Cl_2 /MeOH 9.5:0.5) or by washing with Et_2O (**4b, 4d, 4i** and **4j**).



1-(3'-Butenyl)-2-vinylpyridinium triflate (4a). Following the general procedure, the reaction of 2-vinylpyridine (0.21 g, 2 mmol) and 3-butenyl triflate (0.53 g, 2.6 mmol), afforded 0.507 g (82%) of **4a** as a pale-yellow oil: IR (NaCl) 3087, 1621, 1257, 1512, 1161, 1030, 785 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, 1H, *J* = 6.2 Hz), 8.39 (t, 1H, *J* = 7.9 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 7.90 (t, 1H, *J* = 6.4 Hz), 7.13 (dd, 1H, *J* = 11.3, 17.0 Hz); 6.28 (dd, 1H, *J* = 1.3, 17.0 Hz), 6.13 (dd, 1H, *J* = 1.1, 11.2 Hz), 5.84-5.71 (m, 1H); 5.06 (d, 1H, *J* = 10.2 Hz); 4.94 (dd, 1H, *J* = 1.3, 17.0 Hz); 4.79 (t, 2H, *J* = 6.9 Hz); 2.65 (dd, 2H, *J* = 6.9, 14.1 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 153.2, 146.6, 133.2, 130.5, 128.3, 127.6, 127.3, 119.7, 58.2, 34.7. MS (ESI^+) m/z 160 (M^+). Anal. Calcd. for $C_{12}H_{14}NSO_3F_3$: C, 46.60; H, 4.56; N, 4.53; S, 10.37. Found: C, 46.52; H, 4.79; N, 4.44; S, 10.41;

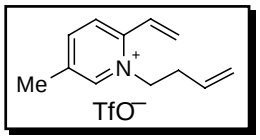


5-Bromo-1-(3'-butenyl)-2-vinylpyridinium triflate (4b). Following the general procedure, the reaction of 5-bromo-2-vinylpyridine (0.368 g, 2 mol) and 3-butenyl triflate (0.53 g, 2.6 mol) afforded 0.318 g (41%) of **4b** as a white powder: mp 258-260ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3065, 1618, 1508, 1256, 1165, 1030, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, 1H, *J* = 1.8 Hz), 8.45 (dd, 1H, *J* = 1.8, 8.8 Hz), 7.99 (d, 1H, *J* = 8.6 Hz), 7.10 (dd, 1H, *J* = 11.3, 17.0 Hz); 6.35 (d, 1H, *J* = 17.0 Hz), 6.17 (d, 1H, *J* = 11.3 Hz), 5.82-5.71 (m, 1H); 5.10 (d, 1H, *J* = 10.6 Hz); 4.96 (d, 1H, *J* = 15.9 Hz); 4.80 (t, 2H, *J* = 6.9 Hz); 2.65 (dd, 2H, *J* = 6.9, 14.1 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 151.3, 148.9, 147.3, 133.1, 131.4, 128.4, 127.6, 121.4, 119.9, 58.8, 34.6. MS (ESI^+) m/z 238 (M^+), 240 (M+2) Anal. Calcd. for $C_{12}H_{13}NBrSO_3F_3$: C, 37.13; H, 3.38; N, 3.61; S, 8.26. Found: C, 36.90; H, 3.45; N, 3.74; S, 8.16.

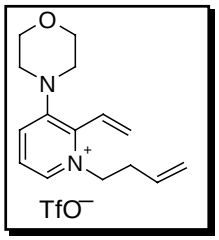


3-Bromo-1-(3'-butenyl)-2-vinylpyridinium triflate (4c). Following the general procedure, the reaction of 3-bromo-2-vinylpyridine (0.368 g, 2 mmol) and 3-butenyl triflate (0.530 g, 2.6 mmol) afforded 0.52 g (67%) of **4c** as a pale-yellow oil: IR (NaCl) 3084, 1463, 1261, 1156, 1030, 636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, 1H, *J* = 6.0 Hz), 8.57 (d, 1H, *J* = 8.2 Hz), 7.87 (dd, 1H, *J* = 6.2, 8.4 Hz), 6.78 (dd, 1H, *J* = 12.1, 17.9 Hz); 6.22 (d, 1H, *J* = 12.1 Hz), 6.03 (d, 1H, *J* = 17.5 Hz), 5.83-5.69 (m, 1H); 5.10

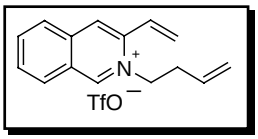
(d, 1H, *J* = 10.2 Hz); 5.00 (d, 1H, *J* = 17.2 Hz); 4.83 (t, 2H, *J* = 7.1 Hz); 2.64 (dd, 2H, *J* = 6.9, 14.1 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 153.9, 150.3, 146.3, 133.1, 131.0, 128.4, 127.8, 125.0, 119.7, 60.3, 34.6. MS (ESI$^+$) m/z 238 (M^+), 240 (M+2). Anal. Calcd. for $C_{12}H_{13}NBrSO_3F_3$: C, 37.13; H, 3.38; N, 3.61; S, 8.26. Found: C, 37.24; H, 3.61; N, 3.42; S, 8.05.



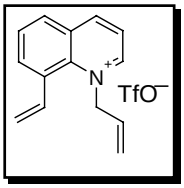
1-(3'-Butenyl)-5-methyl-2-vinylpyridinium triflate (4d). Following the general procedure, the reaction of 3-methyl-6-vinylpyridine (0.238 g, 2 mmol) and 3-butenyl triflate (0.53 g, 2.6 mmol) afforded 0.388 g (60%) of **4d** as a white powder: mp 60-62 ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3076, 1525, 1250, 1157, 1030, 850 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (s, 1H); 8.49 (d, 1H, *J* = 7.9 Hz); 8.32 (d, 1H, *J* = 8.4 Hz); 7.43 (dd, 1H, *J* = 11.2, 17.0 Hz); 6.49 (d, 1H, *J* = 17.0 Hz); 6.15 (d, 1H, *J* = 11.2 Hz); 5.99-5.85 (m, 1H); 5.09-5.03 (m, 2H); 4.90 (t, 2H, *J* = 7.1 Hz); 2.83-2.76 (m, 2H); 2.57 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 150.7, 147.2, 145.9, 138.9, 133.4, 129.6, 128.1, 126.9, 119.6, 58.2, 34.9, 17.9. MS (ESI$^+$) m/z 174 (M^+). Anal. Calcd. for $C_{13}H_{16}NSO_3F_3$: C, 48.29; H, 4.99; N, 4.33; S, 9.92. Found: C, 48.57; H, 4.61; N, 4.43; S, 9.71.



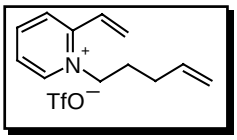
1-(3'-Butenyl)-3-morpholin-4-yl-2-vinylpyridinium triflate (4e). Following the general procedure, the reaction of 3-morpholin-4-yl-2-vinylpyridine (0.38 g, 2 mmol) and 3-butenyltriflate (0.53 g, 2.6 mmol) afforded 0.433 g (55%) of **4e** as a yellow oil: IR (NaCl) 2854, 1578, 1449, 1260, 1154, 1030, 755 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.65 (dd, 1H, *J* = 1.0, 6.1 Hz), 8.23 (dd, 1H, *J* = 1.0, 8.4 Hz), 7.96 (dd, 1H, *J* = 6.0, 8.4 Hz), 7.13 (dd, 1H, *J* = 12.0, 17.9 Hz); 6.29 (dd, 1H, *J* = 1.3, 17.9 Hz), 6.19 (dd, 1H, *J* = 1.0, 12.0 Hz), 6.00-5.79 (m, 1H); 5.13-5.10 (m, 1H); 5.04-5.02 (m, 1H); 4.81 (t, 2H, *J* = 7.2 Hz); 3.74 (t, 4H, *J* = 4.6 Hz); 3.18 (t, 4H, *J* = 4.8 Hz); 2.76 (dd, 2H, *J* = 7.2, 14.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.4, 146.5, 138.0, 134.1, 131.4, 128.2, 126.6, 125.8, 119.8, 66.2, 58.3, 50.9, 34.3. MS (ESI$^+$) m/z 245 (M^+). Anal. Calcd. for $C_{16}H_{21}N_2SO_4F_3$: C, 48.72; H, 5.37; N, 7.10; S, 8.13. Found: C, 48.54; H, 5.26; N, 7.01; S, 8.45.



1-(3'-Butenyl)-3-vinylisoquinolinium triflate (4f). Following the general procedure, the reaction of 3-vinylisoquinoline (0.31 g, 2 mmol) and 3-butenyl triflate (0.530 g, 2.6 mmol) afforded 0.395 g (55%) of **4f** as a yellow powder: mp 91-93ºC, IR (NaCl) 3049, 1643, 1403, 1257, 1156, 1029, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.64 (d, 1H, *J* = 8.4 Hz), 8.19 (s, 1H), 8.13-8.05 (m, 2H), 7.93 (t, 1H, *J* = 7.1 Hz); 7.09 (dd, 1H, *J* = 11.3, 17.0 Hz); 6.18 (d, 1H, *J* = 17.0 Hz), 6.00 (d, 1H, *J* = 11.2 Hz), 5.94-5.82 (m, 1H); 5.05 (d, 1H, *J* = 9.9 Hz); 4.99-4.89 (m, 3H); 2.74 (dd, 2H, *J* 6.9, 13.9 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 151.5, 144.1, 138.9, 137.7, 133.1, 131.6, 130.7, 128.3, 127.9, 127.5, 127.1, 124.9, 119.5, 58.2, 34.6. MS (ESI^+) m/z 210 (M^+). Anal. Calcd. for $C_{16}H_{16}NSO_3F_3$: C, 53.48; H, 4.49; N, 3.90; S, 8.92. Found: C, 53.61; H, 4.30; N, 4.02; S, 8.78.

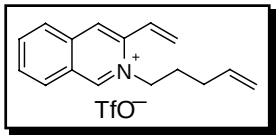


1-(2'-Propenyl)-8-vinylquinolinium triflate (4g). Following the general procedure, the reaction of 8-vinylquinoline (0.31 g, 2 mmol) and allyl triflate (0.494 g, 2.6 mmol) afforded 0.153 g (47%) of **4g** as a yellow oil: IR (NaCl) 3084, 1529, 1259, 1157, 1030, 768 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.50 (dd, 1H, *J* = 1.3, 5.8 Hz), 9.40 (dd, 1H, *J* = 1.3, 8.4 Hz), 8.48 (dd, 1H, *J* = 1.3, 8.2 Hz), 8.27 (dd, 1H, *J* = 6.0, 8.2 Hz), 8.16 (d, 1H, *J* = 7.3 Hz); 8.05 (t, 1H, *J* = 7.9 Hz); 7.63 (dd, 1H, *J* = 10.8, 17.0 Hz), 6,43-6.31 (m, 1H), 6.01-5.99 (m, 2H); 5.82 (dd, 1H, *J* = 0.9, 17.0 Hz); 5.71 (dd, 1H, *J* = 0.9, 10.8 Hz); 5.48 (dt, 1H, *J* = 1.5, 9.1 Hz); 5.16 (dt, 1H, *J* = 1.6, 17.3 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 152.5, 149.8, 139.2, 138.0, 136.6, 133.1, 132.6, 132.3, 131.9, 130.5, 122.9, 121.1, 120.2, 63,1. MS (ESI^+) m/z 196 (M^+). Anal. Calcd. for $C_{15}H_{14}NSO_3F_3$: C, 52.17; H, 4.09; N, 4.06; S, 9.28. Found: C, 52.30; H, 4.09; N, 4.27; S, 9.14.

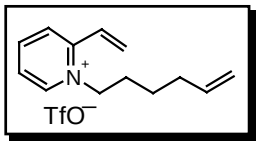


1-(4'-Pentenyl)-2-vinylpyridinium triflate (4h). Following the general procedure, the reaction of 2-vinylpyridine (0.21 g, 2.0 mmol) and 4-pentenyl triflate (0.567 g, 2. 6 mmol) afforded 0.452 g (70%) of **4h** as a pale-yellow oil: IR (NaCl) 3085, 1512, 1621, 1257, 1157, 1030, 787 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, 1H, *J*= 6.2 Hz), 8.43 (t, 1H, *J* = 7.9 Hz), 8.10 (d, 1H, *J* = 8.0 Hz), 7.90 (t, 1H, *J* = 7.5 Hz), 7.08 (dd, 1H, *J* = 11.3, 17.0 Hz); 6.32

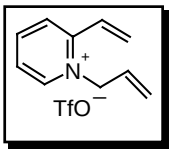
(d, 1H, *J* = 17.0 Hz), 6.11 (d, 1H, *J* = 11.3 Hz), 5.79-5.65 (m, 1H); 5.07-4.99 (m, 2H); 4.63 (t, 2H, *J* = 7.7 Hz); 2.19-2.12 (m, 2H); 2.02-1.86 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 153.5, 146.6, 146.5, 137.5, 130.5, 128.3, 127.8, 116.4, 59.0, 54.9, 30.7. MS (ESI$^+$) m/z 174 (M^+). Anal. Calcd. for $C_{13}H_{16}NSO_3F_3$: C, 48.29; H, 4.99; N, 4.33; S, 9.92. Found: C, 48.59; H, 5.17; N, 4.12; S, 10.11.



1-(4'-Pentenyl)-3-vinylisoquinolinium triflate (4i). Following the general procedure, the reaction of 3-vinylisoquinoline (0.31 g, 2 mmol) and 4-pentenyl triflate (0.567 g, 2.6 mmol) afforded 0.336 g (45%) of **4i** as a yellow powder: mp 104-105ºC. IR (NaCl) 3052, 1643, 1514, 1258, 1156, 1029, 768 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.69 (s, 1H); 8.53 (d, 1H, *J* = 8.4 Hz), 8.36 (d, 1H, *J* = 8.4 Hz), 8.24 (t, 1H, *J*= 6.9 Hz), 8.03 (t, 1H, *J* = 7.1 Hz); 7.45 (dd, 1H, *J* = 11.2, 17.0 Hz); 6.43 (d, 1H, *J* = 16.8 Hz), 6.02 (d, 1H, *J* = 11.2 Hz), 5.30-5.80 (m, 1H); 5.08 (d, 1H, *J* = 15.7 Hz); 5.01-4.96 (m, 3H); 2.31-2.16 (m, 4H); 2.17-2.06 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 151.5, 144.2, 139.1, 137.7, 137.5, 131.7, 130.8, 128.3, 127.9, 127.8, 126.9, 124.9, 116.1, 58.9, 30.6, 29.9. MS (ESI$^+$) m/z 224 (M^+). Anal. Calcd. for $C_{17}H_{18}NSO_3F_3$: C, 54.68; H, 4.86; N, 3.75; S, 8.59. Found: C, 54.32; H, 4.73; N, 3.88; S, 8.40.



1-(5'-Hexenyl)-2-vinylpyridinium triflate (4j). Following the general procedure, the reaction of 2-vinylpyridine (0.21 g, 2 mmol) and 5-hexenyl triflate (0.603 g, 2.6 mmol) afforded 0.66 g (98%) of **4j** as a pale-yellow oil: IR (NaCl) 3084, 1622, 1511, 1257, 1158, 1029, 786 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (d, 1H, *J*= 6.1 Hz), 8.41 (t, 1H, *J* = 7.7 Hz), 8.03 (d, 1H, *J* = 7.9 Hz), 7.94 (td, 1H, *J* = 1.3, 7.7 Hz), 7.09 (dd, 1H, *J* = 11.3, 17.2 Hz); 6.29 (d, 1H, *J* = 17.0 Hz), 6.12 (d, 1H, *J* = 11.3 Hz), 5.82-5.62 (m, 1H); 5.05-4.95 (m, 2H); 4.68 (t, 2H, *J* = 7.9 Hz); 2.16-2.05 (m, 2H); 1.98-1.82 (m, 2H); 1.66-1.43 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 146.4, 146.3, 138.6, 130.3, 128.2, 127.6, 127.5, 115.4, 59.2, 33.6, 30.4, 25.8. MS (ESI$^+$) m/z 188 (M^+). Anal. Calcd. for $C_{14}H_{18}NSO_3F_3$: C, 49.84; H, 5.38; N, 4.15; S, 9.50. Found: C, 49.72; H, 5.17; N, 4.41; S, 9.73.

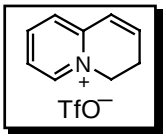


***N*-Allyl-2-vinylpyridinium triflate (4k)**. Following the general procedure, the reaction of 2-vinylpyridine (0.21 g, 2 mmol) and allyl triflate (0.494 g, 2.6 mmol) afforded 0.348 g (59%) of **4k** as a pale-yellow oil: IR (NaCl) 3090, 1621, 1508, 1258, 1158, 1029, 786 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.94 (dd, 1H, *J*= 1.0, 6.4 Hz), 8.45 (td, 1H, *J* = 1.0, 7.9 Hz), 8.06 (d, 1H, *J* = 6.9 Hz), 7.96 (td, 1H, *J* = 1.4, 7.7 Hz), 7.07 (dd, 1H, *J* = 11.3, 17.2 Hz); 6.28 (d, 1H, *J* = 17.0 Hz), 6.11 (d, 1H, *J* = 11.3 Hz), 6.11-5.94 (m, 1H); 5.46 (dt, 1H, *J* = 1.3, 10.2 Hz); 5.34-5.28 (m, 2H); 5.20 (dt, 1H, *J* = 1.5, 17.2 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 153.4, 146.8, 146.2, 131.2, 130.3, 128.0, 127.7, 127.4, 120.9, 60.8. MS (ESI^+) m/z 146 (M^+). Anal. Calcd. for $C_{11}H_{12}NSO_3F_3$: C, 44.74; H, 4.10; N, 4.74; S, 10.86. Found: C, 44.52; H, 4.20; N, 4.89; S, 10.63.

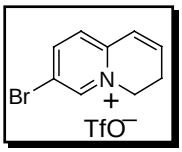
Ring-closing metathesis of salts 4. General procedure for cations 3a-g.

To a solution of the corresponding salt **4** (0.2 mmol) in dry CH_2Cl_2 (1.5 mL), ruthenium catalyst **1** (2 mol %) for **3a** or **2** (5 mol %) for **3b-g** in CH_2Cl_2 (1 mL) was added under argon atmosphere. The reaction mixture was stirred for 1-3 h at room temperature.

Then, the solvent was evaporated under reduced pressure and the residue purified by flash chromatography (eluent: CH_2Cl_2 /MeOH 9.3:0.7) or by washing with CH_2Cl_2:Et_2O (**3g**).

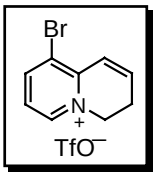


3,4-Dihydroquinolizinium triflate (3a). Following the general procedure, after stirring for 1.5 h, 46.8 mg (83%) of **3a** were obtained as a grey powder: mp 124-125 ºC (Acetone: Et_2O). IR (NaCl) 3086, 1646, 1507, 1263, 1150, 1031, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, 1H, *J* = 6.2 Hz); 8.33 (t, 1H, *J* = 7.8 Hz); 7.80 (t, 1H, *J* = 7.1 Hz); 7.65 (d, 1H, *J* = 7.9 Hz); 6.89-6.83 (m, 1H); 6.72 (d, 1H, *J* = 9.7 Hz); 4.81 (t, 2H, *J* = 7.7 Hz); 2.85 (dd, 2H, *J* = 7.7, 12.3 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 146.7, 146.1, 140.6, 126.6, 126.0, 122.1, 53.7, 22.9. MS (ESI^+) m/z 132 (M^+). Anal. Calcd. for $C_{10}H_{11}NSO_3F_3$: C, 42.71; H, 3.58; N, 4.98; S, 11.40. Found: C, 42.40; H, 3.76; N, 4.85; S, 11.34.

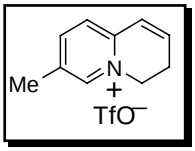


7-Bromo-3,4-dihydroquinolizinium triflate (3b). Following the general procedure, after stirring for 2 h, 72.0 mg (80%) of **3b** were

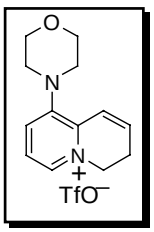
obtained as a grey solid: mp 65-67 ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3069, 1641, 1504, 1258, 1167, 1029, 857 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.22 (s, 1H); 8.75 (dd, 1H, *J* = 1.8, 8.6 Hz); 7.97 (d, 1H, *J* = 8.6 Hz); 7.09-6.98 (m, 2H); 4.94 (t, 2H, *J* = 7.9 Hz); 2.99-2.93 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 149.3, 147.7, 147.4, 141.7, 127.7, 122.2, 119.9, 54.5, 32.2. MS (ESI^+) m/z 210 (M^+), 212 (M+2). Anal. Calcd. for $C_{10}H_9NBrSO_3F_3$: C, 33.35; H, 2.52; N, 3.89. Found: C, 33.21; H, 2.42; N, 3.53.



9-Bromo-3,4-dihydroquinolizinium triflate (3c). Following the general procedure, after stirring for 1 h, 57.6 mg (80%) of **3c** were obtained as a pale-brown solid: mp 145-147ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3084, 1632, 1477, 1262, 1149, 1029, 784 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.03 (d, 1H, *J* = 5.8 Hz); 8.86 (d, 1H, *J* = 8.2 Hz); 7.94 (t, 1H, *J* = 8.1 Hz); 7.27-7.17 (m, 2H); 4.97 (t, 2H, *J* = 7.5 Hz); 3.02-2.85 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 150.1, 147.2, 146.2, 143.8, 126.3, 121.7, 121.2, 55.4, 22.8. MS (ESI^+) m/z 211 (M^+) 213 (M+2). Anal. Calcd. for $C_{10}H_9NBrSO_3F_3$: C, 33.35; H, 2.52; N, 3.89. Found: C, 33.12; H, 2.74; N, 3.51.

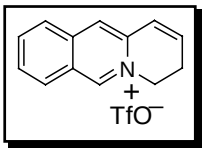


7-Methyl-3,4-dihydroquinolizinium triflate (3d). Following the general procedure, after stirring for 1 h, 48.4 mg (82%) of **3d** were obtained as a white powder: mp 94-96 ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3048, 1643, 1531, 1265, 1152, 1032, 863 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 8.80 (s, 1H); 8.40 (d, 1H, *J* = 8.2 Hz); 7.88 (d, 1H, *J* = 8.2 Hz); 6.96-6.87 (m, 2H); 4.83 (t, 2H, *J* = 7.9 Hz); 2.92-2.89 (m, 2H); 2.53 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 147.5, 145.9, 139.6, 137.5, 126.3, 122.2, 54.0, 23.2, 18.0. MS (ESI^+) m/z 146 (M^+). Anal. Calcd. for $C_{11}H_{12}NSO_3F_3$: C, 44.74; H, 4.10; N, 4.74; S, 10.86. Found: C, 44.56; H, 3.93; N, 4.48; S, 11.52.

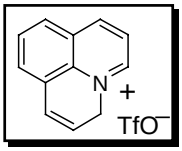


9-Morpholin-4-yl-3,4-dihydroquinolizinium triflate (3e). Following the general procedure, after stirring for 2 h, 62.2 mg (85%) of **3e** were obtained as a green oil: IR (NaCl) 3087, 1636, 1488, 1261, 1158, 1030,

786 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 8.58 (d, 1H, *J* = 6.0 Hz); 8.25 (d, 1H, *J* = 8.4 Hz); 7.89 (dd, 1H, *J* = 6.0, 8.4 Hz); 7.12-6.99 (m, 2H); 4.84 (t, 2H, *J* = 7.7 Hz); 3.85 (t, 4H, *J* = 4.6 Hz); 3.12 (t, 4H, *J* = 4.6 Hz); 2.93-2.86 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 148.8, 143.2, 139.2, 139.0, 135.4, 125.6, 118.9, 66.4, 53.9, 52.2, 22.1. MS (ESI^+) m/z 217 (M^+). Anal. Calcd. for $C_{14}H_{17}N_2SO_4F_3$: C, 45.90; H, 4.68; N, 7.65. Found: C, 45.71; H, 4.75; N, 7.42; 8.64.



3,4-Dihydropyrido[1,2-*b*]isoquinolinium triflate (3f). Following the general procedure, after stirring for 3 h, 49.6 mg (75%) of **3f** were obtained as a white powder: mp 105-107 ºC (CH_2Cl_2:Et_2O). IR (NaCl) 3053, 1652, 1428, 1261, 1155, 1029, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H); 8.51 (d, 1H, *J* = 8.2 Hz); 8.07-7.98 (m, 2H); 7.87-7.83 (m, 2H); 6.77 (d, 2H, *J* = 9.9 Hz); 6.70-6.63 (m, 2H); 5.00 (t, 2H, *J* = 7.1 Hz); 2.89-2.84 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 151.7, 139.4, 137.6, 135.8, 131.3, 131.2, 127.9, 127.2, 123.3, 123.2, 122.4, 55.0, 23.2. MS (ESI^+) m/z 182 (M^+). Anal. Calcd. for $C_{14}H_{12}NSO_3F_3$: C, 50.75; H, 3.65; N, 4.23; S, 9.68. Found: C, 50.65; H, 3.54; N, 4.18; S, 9.55.

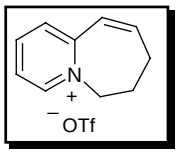


3*H*-Pyrido[3,2,1-*ij*]quinolinium triflate (3g). Following the general procedure, stirring for 1.5 h, 50.0 mg (79%) of **3g** were obtained as a brown solid: mp 171-173 ºC (Acetone: Et_2O). IR (NaCl) 1587, 1266, 1150, 1030, 844 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.42(d, 1H, *J* = 5.5 Hz); 9.20 (d, 1H, *J* = 8.2 Hz); 8.27-8.17 (m, 2H); 7.91-7.88 (m, 2H); 6.99 (d, 1H, *J* = 10.2 Hz); 6.47-6.44 (m, 1H); 6.07 (s, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 167.5, 149.1, 147.4, 131.7, 131.2, 130.9, 129.1, 126.5, 125.4, 123.7, 123.8, 56.9. MS (ESI^+) m/z 167 (M^+). Anal. Calcd. for $C_{12}H_8NSO_3F_3$: C, 49.21; H, 3.18; N, 4.41; S, 10.11. Found: C, 49.11; H, 3.49; N, 4.17; S, 10.27.

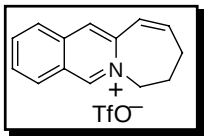
Ring-closing metathesis of salts 4. General procedure for cations 3h-j.

To a solution of 5 mmol % ruthenium catalyst **2** (8.5mg, 0.01 mmol) in dry CH_2Cl_2 (35 mL) was added under argon a solution of the corresponding salt **4h-j** (0.2 mmol) in dry CH_2Cl_2 (5 mL, 0.005 M). After stirring for 1-2 h at room temperature (**3h,i**) or heating

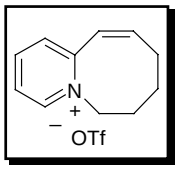
at 40 ºC (**3j**), the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: CH_2Cl_2 /MeOH 9.3:0.7) (**3j**) or by washing with CH_2Cl_2/Et_2O (**3h** and **3i**).



7,8-Dihydro-6*H*-pyrido[1,2-*a*]azepinylium triflate (3h). Following the general procedure, after stirring for 1.5 h, 51.9 mg (88%) of **3h** were obtained as grey solid: mp 97-98 ºC (CH_2Cl_2: Et_2O). IR (NaCl) 3094, 1647, 1460, 1259, 1147, 1031, 801 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.00 (d,1H, *J* = 6.2 Hz); 8.57 (td, 1H, *J* = 1.3, 8.9 Hz); 8.12 (d, 1H, *J* = 8.0 Hz); 7.97 (t, 1H, *J* = 6.6 Hz); 6.93-6.81 (m, 2H); 4.89 (t, 2H, *J* = 4.6 Hz); 2.80-2.75 (m, 2H); 2.47-2.39 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 148.5, 146.3, 146.0, 139.5, 131.6, 126.4, 122.7, 62.4, 32.6, 28.0. MS (ESI^+) m/z 146 (M^+). Anal. Calcd. for $C_{11}H_{12}NSO_3F_3$: C, 44.74; H, 4.10; N, 4.74; S, 10.86. Found: C, 44.66; H, 3.97; N, 4.38; S, 10.74.



8,9-Dihydro-7*H*-azepino[1,2-*b*]isoquinolinium triflate (3i). Following the general procedure, after stirring for 2 h, 64.8 mg (94%) of **3i** were obtained as a pale-brown powder: mp 156-158 ºC (CH_2Cl_2: Et2O). IR (NaCl) 3039, 1652, 1523, 1260, 1154, 1030, 754 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 10.03 (s, 1H); 8.52-8.47 (m, 2H); 8.30-8.17 (m, 2H); 8.05 (td, 1H, *J* = 1.3, 7.9 Hz); 6.66-6.55 (m, 1H); 5.05 (t, 2H, *J* = 4.6 Hz); 2.78-2.70 (m, 2H); 2.54-2.43 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ 151.3, 143.6, 142.3, 139.7, 138.2, 132.2, 131.1, 128.9, 128.3, 127.7, 122.8, 62.6, 31.8, 27.8. MS (ESI^+) m/z 196 (M^+). Anal. Calcd. for $C_{15}H_{14}NSO_3F_3$: C, 52.17; H, 4.09; N, 4.06; S, 9.28. Found: C, 51.99; H, 4.14; N, 4.19; S, 9.34.



6,7,8,9-Tetrahydropyrido[1,2-*a*]azocinylium triflate (3j). Following the general procedure, after stirring for 1 h at 40ºC, 33.4 mg (54%) of **3j** were obtained as a white solid: 85-86ºC (CH_2Cl_2: Et_2O). IR (NaCl) 2928, 1649, 1465, 1263, 1031, 638 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 9.08 (d, 1H, *J* = 6.0 Hz); 8.62 (t, 1H, *J* = 7.7 Hz); 8.14-8.09 (m, 2H); 6.73-6.67 (m, 2H); 4.92 (t, 2H, *J* = 5.7 Hz); 2.60-2.55 (m, 2H); 2.22-2.17 (m, 2H); 1.59-1.51 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ 147.3, 145.6, 145.5, 129.9, 127.6, 119.6, 58.5, 32.0, 29.4, 20.0. MS

(ESI$^+$) m/z 160 (M^+). Anal. Calcd. for $C_{12}H_{14}NSO_3F_3$: C, 46.60; H, 4.56; N, 4.53; S, 10.37. Found: C, 46.78; H, 4.25; N, 4.43; S, 10.65.