Supplementary Material (ESI) for Chemical Communications

Enyne Ring-closing Metathesis on Heteroaromatic Cations

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Supplementary Information

(13 pages)

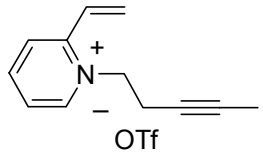
General experimental details. Melting points were uncorrected. Infrared spectra were recorded on NaCl pellets and spectral bands were reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 / 300 MHz and 50 /75 MHz respectively. Chemical shifts were reported as δ values (ppm). The mass spectra (MS) were obtained as (ESI^{+}). Ruthenium's catalyst **9**, **10** and **11**, 2-vinyl-pyridine and alcohols were purchased from Aldrich. 2-Alkynylpyridines **13a–e** were prepared according to literature procedures: 2-(prop-1-ynyl)-pyridine (**13a)**: Miwa, K.; Aoyama, T.; Shioiri, T. *Synlett* **1994**, 107-108; 2-[4-(*tert*-butyl-dimethyl-silanyloxy)-but-1-ynyl]-pyridine (**13b**): Lautens, M.; Yoshida, M. *J. Org. Chem*. **2003**, *68*, 762-769; 2-(4-methoxy-phenyl-ethynyl)-pyridine (**13c**): Kim, D.-K.; Kim, J; Park, H.-J. *Bioorg. Med. Chem. Lett*. **2004**, *14*, 2401-2405; 2-(4-trifluoromethyl-phenyl-ethynyl)-pyridine (**13d**): Kerwin, S. M.; David, W. M. U.S. Pat. Appl. Publ. (**2002**), 59 pp., Cont.-in-part of U.S. 6,297,284; 2-(thiophen-2-yl-ethynyl)-pyridine (**13e**): Neenan, T. X.; Driessen, W. L.; de Graaff, R. A. G.; van der Plas, J. L.; Reedijk, J. *Inorg. Chim. Acta* **1998**, *267*, 193-199.

Synthesis of enynes 5. General procedure.

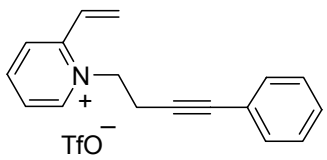
To a solution of the alkynyl alcohol (2.6 mmol) in dry CCl_4 (2 mL) under an argon atmosphere was added dry pyridine (0.205 g, 2.6 mmol) and the mixture was stirred for 5–10 min under argon. The mixture was added dropwise (5–10 min) to a cooled solution (–10 ºC) of triflic anhydride (0.733 g, 2.6 mmol) in dry CCl_4 (3 mL). The resulting solid was filtered off through Na_2SO_4 and the solution was added by cannula to a solution of 2-vinyl-pyridine (2 mmol) in dry CCl_4 (2 mL). The mixture was stirred at room temperature for 24 h. Removal of the solvent in vacuo afforded compounds **5** as oils or solids. The oils were purified by flash

chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5) and the solids by precipitation and washing with Et_2O.

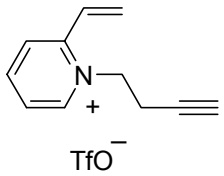
1-(Pent-3-ynyl)-2-vinyl-pyridinium triflate (5a). Following the general procedure, from 2-vinyl-pyridine (0.210 g, 2 mmol) and pent-3-ynyl triflate (0.560 g, 2.6 mmol), chromatography gave 495 mg (77%) of **5a** as a pale-yellow oil. IR (NaCl) 3087, 2280, 1621, 1510, 1430, 1230, 1161, 1030, 785 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 9.05 (dd, 1H, *J* = 0.9, 6.2 Hz), 8.69 (td, 1H, *J* = 0.9, 7.9 Hz), 8.45 (d, 1H, *J* = 8.0 Hz), 8.16 (td, 1H, *J* = 1.3, 7.7 Hz), 7.50 (dd, 1H, *J* = 11.2, 16.8 Hz), 6.55 (d, 1H, *J* = 17.0 Hz), 6.20 (d, 1H, *J* = 11.3 Hz), 4.99 (t, 2H, *J* = 6.6 Hz), 2.91 (tc, 2H, *J* = 2.4, 6.4 Hz), 1.67 (t, 3H, *J* = 2.5 Hz). ^{13}C NMR (50 MHz, acetone-d_6) δ 153.1, 146.7, 130.3, 127.9, 127.3, 127.0, 125.1, 121.4 (c, *J* = 322.5 Hz), 81.1, 73.5, 57.4, 20.6, 2.9. MS (ES^+) *m/z* (relative intensity) 172 (M^+, 100). Anal. Calcd for $C_{13}H_{14}F_3NO_3S$: C, 48.59; H, 4.39; N, 4.36; S, 9.98. Found: C, 48.24; H, 4.52; N, 4.11; S, 10.17.



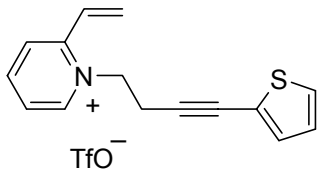
1-(4-Phenyl-but-3-ynyl)-2-vinyl-piridinium triflate (5b). Following the general procedure, from 2-vinyl-pyridine (0.210 g, 2 mmol) and 4-phenyl-but-3-ynyl triflate (0.722 g, 2.6 mmol), chromatography gave 490 mg (64%) of **5b** as a yellow oil: IR (NaCl) 3085, 2318, 1621, 1573, 1511, 1491, 1259, 1155, 1029, 759 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 9.22 (dd, 1H, *J* = 0.9, 6.2 Hz), 8.72 (td, 1H, *J* = 0.9, 7.7 Hz), 8.49 (d, 1H, *J* = 7.1 Hz), 8.21 (td, 1H, *J* = 1.5, 7.7 Hz), 7.59 (dd, 1H, *J* = 11.3, 17.0 Hz), 7.35-7.30 (m, 5H), 6.57 (d, 1H, *J* = 17.0 Hz), 6.23 (d, 1H, *J* = 11.3 Hz), 5.17 (t, 2H, *J* = 6.6 Hz), 3.30 (t, 2H, *J* = 6.4 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 146.6, 146.3, 131.3, 130.3, 128.8, 128.7, 127.6, 127.1, 126.8, 122.5, 122.2, 121.6 (c, *J* = 321.1 Hz), 83.8, 72.7, 56.7, 20.7. MS (ES^+) *m/z* (relative intensity) 234 (M^+). Anal. Calcd. for $C_{18}H_{16}F_3NO_3S$: C, 56.39; H, 4.21; N, 3.65; S, 8.36. Found: C, 56.54; H, 3.95; N, 3.87; S, 8.41.



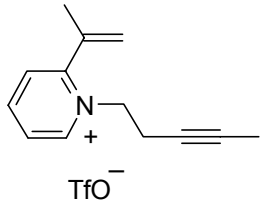
1-(But-3-ynyl)-2-vinyl-pyridinium triflate (5c). Following the general procedure, from 2-vinyl-pyridine (0.210 g, 2 mmol) and but-3-ynyl triflate (0.525 g, 2.6 mmol), chromatography gave 307 mg (50%) of **5c** as a colorless oil. IR (NaCl) 3261, 2949, 1626, 1511, 1454, 1258, 1167, 1030, 782 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.13 (d, 1H, *J* = 6.4 Hz), 8.72 (t, 1H, *J* = 8.0 Hz), 8.47 (d, 1H, *J* = 8.2 Hz), 8.18 (t, 1H, *J* = 7.5 Hz), 7.53 (dd, 1H, *J* = 11.3, 16.8 Hz), 6.56 (d, 1H, *J* = 17.0 Hz), 6.23 (d, 1H, *J* = 11.3 Hz), 5.07 (t, 2H, *J* = 6.6 Hz), 3.05 (td, 2H, *J* = 2.7, 6.8 Hz), 2.83 (s, 1H) . ^{13}C NMR (75 MHz, acetone-d_6) δ 146.9, 146.7, 130.8, 127.9, 127.5, 127.2, 123.5, 121.4 (c, *J* = 321.8 Hz), 74.4, 72.9, 56.9, 20.0. MS (ES^+) *m/z* (relative intensity) 158 (M^+, 100). Anal. Calcd. for $C_{12}H_{12}F_3NO_3S$: C, 46.90; H, 3.94; N, 4.56; S, 10.43. Found: C, 46.77; H, 4.08; N, 4.66; S, 10.78.



1-[4-(Thiophen-2-yl)-but-3-ynyl)]-2-vinyl-pyridinium triflate (5d). Following the general procedure, from 2-vinyl-pyridine (0.21 g, 2 mmol) and 4-(thiophen-2-yl)-but-3-ynyl triflate (0.738 g, 2.6 mmol), chromatography gave 396 mg (51%) of **5d** as a yellow oil. IR (NaCl) 2924, 1621, 1573, 1510, 1426, 1258, 1158, 1029, 783 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.17 (d, 1H, *J* = 6.2 Hz), 8.70 (t, 1H, *J* = 8.0 Hz), 8.48 (d, 1H, *J* = 8.0 Hz), 8.17 (t, 1H, *J* = 7.3 Hz), 7.57 (dd, 1H, *J* = 11.3, 17.0 Hz), 7.45 (dd, 1H, *J* = 0.9, 5.3Hz), 7.15 (d, 1H, *J* = 3.7 Hz), 7.00 (dd, 1H, *J* = 3.7, 5.1 Hz), 6.56 (d, 1H, *J* = 17.0 Hz), 6.21 (d, 1H, *J* = 11.3 Hz), 5.15 (t, 2H, *J* = 6.4 Hz), 3.30 (t, 2H, *J* = 6.5 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 153.2, 146.6, 146.3, 132.4, 130.3, 127.8, 127.6, 127.4, 127.1, 126.9, 122.3, 121.6 (c, *J* = 320.4 Hz), 87.9, 77.9, 56.4, 21.0. MS (ES^+) *m/z* (relative intensity) 240 (M^+, 100), 241 (M + 1, 19). Anal. Calcd. for $C_{16}H_{14}F_3NO_3S$: C, 49.35; H, 3.62; N, 3.60; S, 16.47. Found: C, 49.29; H, 3.86; N, 3.48; S, 16.59.



2-(1-Methyl-vinyl)-1-pent-3-ynyl-pyridinium triflate (5e). Following de general procedure, from 2-(1-methyl-vinyl)-pyridine (0.238 g, 2 mmol) and pent-3-ynyl triflate (0.561 g, 2.6 mmol), chromatography gave 477 mg (71%) of **5e** as a colorless oil: IR (NaCl) 2924, 2237, 1623, 1508, 1440, 1263, 1157, 1031, 786 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 9.20 (d, 1H, *J* = 6.4 Hz), 8.72 (td, 1H, *J* = 1.3, 7.8 Hz), 8.22 (td, 1H, *J* = 1.5, 7.6 Hz), 8.12 (d, 1H, *J* = 7.9 Hz), 5.87 (d, 1H, *J* = 0.6 Hz), 5.61 (d, 1H, *J* = 0.6 Hz), 4.88 (t, 2H, *J* = 6.6 Hz), 2.99-2.93 (m, 2H), 2.31 (s, 3H), 1.69 (t, 3H, *J* = 2.6 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 158.3, 147.1, 146.3, 137.7, 129.6, 127.5, 124.3, 122.2 (c, *J* = 323.7 Hz), 80.9, 73.6, 57.3, 23.1, 21.5, 2.8. MS (ES^+) *m/z* (relative intensity) 186 (M^+, 100), 187 (M + 1, 56). Anal. Calcd. for $C_{14}H_{16}F_3NO_3S$: C, 50.14; H, 4.81; N, 4.18; S, 9.56. Found: C, 50.43; H, 4.61; N, 4.20; S, 9.65.

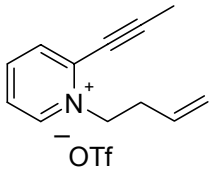


Synthesis of enynes 7. General procedure.

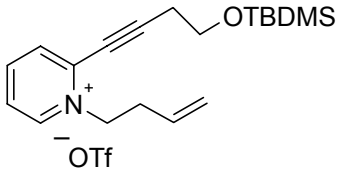
To a solution of 3-butenyl alcohol (2.6 mmol) in dry CCl_4 (2 mL) under an argon atmosphere was added pyridine (0.205 g, 2.6 mmol) and the mixture was stirred for 5–10 min under argon. The mixture was added dropwise (5–10 min) to a cooled solution (–10 ºC) of triflic anhydride (0.733 g, 2.6 mmol) in dry CCl_4 (3 mL). The resulting solid was filtered off through Na_2SO_4, the solution was added by cannula to a solution of the corresponding 2-alkynyl pyridine **13a**–**e** (2 mmol) in dry CCl_4 (2 mL) and the mixture was stirred at room temperature for 24 h. Removal of the solvent in vacuo afforded an oil, which was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5).

1-(But-3-enyl)-2-(prop-1-ynyl)-pyridinium triflate (7a). Following the general procedure, from 2-(prop-1-ynyl)-pyridine (0.234 g, 2 mmol) and but-3-enyl triflate (0.530 g, 2.6 mmol), chromatography gave 321 mg (50%) of **7a** as a yellow oil. IR (NaCl) 3084, 2232, 1619, 1510, 1463, 1259, 1154, 1030, 779 cm^{-1}. ^1H NMR (300MHz, acetone-d_6) δ 9.11 (d, 1H, *J* = 6.0 Hz), 8.63 (td, 1H, *J* = 1.3, 8.0 Hz), 8.23 (d, 1H, *J* = 7.9 Hz), 8.12 (td, 1H, *J* = 1.1, 7.5 Hz), 6.02-5.88 (m, 1H), 5.07-5.02 (m, 2H), 4.99 (t, 2H, *J* = 6.9 Hz), 2.85 (dd, 2H, *J* = 6.9, 14.1 Hz), 2.38

(s, 3H).^{13}C NMR (75 MHz, acetone-d_6) δ 147.0, 145.9, 133.3, 132.8, 127.2, 121.9 (c, *J* = 323.2 Hz), 119.4, 107.7, 71.6, 58.9, 34.8, 4.6. MS (ES^+) *m/z* (relative intensity) 172 (M^+, 100). Anal. Calcd for $C_{13}H_{14}F_3NO_3S$: C, 48.59; H, 4.39; N, 4.36; S, 9.98. Found: C, 48.64; H, 4.74; N, 4.56; S, 10.07.

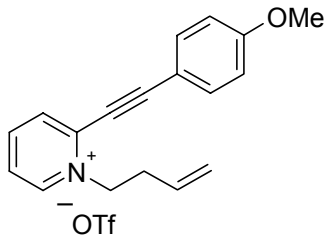


1-(But-3-enyl)-2-[4-(*tert*-butyl-dimethyl-silanyloxy)-but-1-ynyl]-pyridinium triflate (7b). Following the general procedure, from 2-[4-(*tert*-butyl-dimethyl-silanyloxy)-but-1-ynyl]-pyridine (0.522 g, 2 mmol) and but-3-enyl triflate (0.530 g, 2.6 mmol), chromatography gave 753 mg (81%) of **7b** as a pale-pink oil. IR (NaCl) 2930, 2858, 2233, 1619, 1510, 1260, 1159, 1105, 1031, 779 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) 9.14 (d, 1H, *J* = 6.2 Hz), 8.67 (td, 1H, *J* = 1.3, 7.9 Hz), 8.26 (d, 1H, *J* = 8.0 Hz), 8.16 (t, 1H, *J* = 7.7 Hz), 6.07-5.89 (m, 1H), 5.09-5.06 (m, 2H), 5.03 (t, 2H, *J* = 6.9 Hz), 4.00 (t, 2H, *J* = 6.2 Hz), 2.98 (t, 2H, *J* = 6.2 Hz), 2.88 (dd, 2H, *J* = 6.9, 14.1 Hz), 0.91 (s, 9H), 0.16 (s, 6H).^{13}C NMR (75 MHz, acetona-d_6) δ 147.3, 146.2, 133.3, 132.9, 127.5, 122.2 (c, *J* = 320.3 Hz), 119.6, 109.8, 109.4, 73.2, 60.1, 35.0, 26.0, 24.8, 18.6, 8.1, -5.3. MS (ES^+) *m/z* (relative intensity) 316 (M^+, 100), 317 (M + 1, 42). Anal. Calcd for $C_{20}H_{30}F_3NO_4SSi$: C, 51.59; H, 6.49; N, 3.01; S, 6.89. Found: C, 51.41; H, 6.55; N, 3.15; S, 6.98.

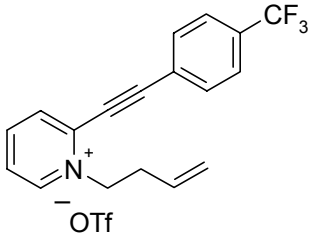


1-(But-3-enyl)-2-(4-methoxy-phenyl-ethynyl)-pyridinium triflate (7c). Following the general procedure, from 2-(4-methoxy-phenyl-ethynyl)-pyridine (0.418 g, 2 mmol) and but-3-enyl triflate (0.530 g, 2.6 mmol), **7c** (702 mg, 85%) was obtained as a yellow solid. Mp 94-96 ºC. IR (NaCl) 3074, 2190, 1603, 1569, 1519, 1271, 1161, 1030, 836, 799 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (d, 1H, *J* = 6.0 Hz), 8.40 (t, 1H, *J* = 7.9 Hz), 8.03 (d, 1H, *J* = 8.0 Hz), 7.92 (t, 1H, *J* = 6.4 Hz), 7.58 (d, 2H, *J* = 8.8 Hz), 6.96 (d, 2H, *J* = 8.8 Hz), 5.93-5.79 (m, 1H), 5.09 (d, 1H, *J* = 10.1 Hz), 5.01 (d, 1H, *J* = 18.7 Hz), 4.93 (t, 2H, *J* = 6.9 Hz), 3.86 (s, 3H),

2.81 (dd, 2H, *J* = 6.8, 13.7 Hz)**.** ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 147.1, 144.8, 137.8, 134.9, 131.7, 131.6, 126.5, 121.2 (c, *J* = 318.3 Hz), 120.5, 115.1, 110.7, 109.2, 79.6, 59.7, 55.9, 34.8**.** MS (ES^+) m/z (relative intensity) 264 (M^+, 100). Anal. Calcd. for $C_{19}H_{18}F_3NO_4S$: C, 55.20; H, 4.39; N, 3.39; S, 7.76. Found: C, 54.72; H, 4.43; N, 3.40; S, 7.73.

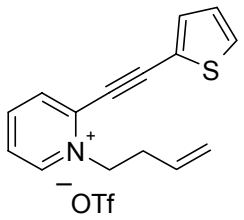


1-(But-3-enyl)-2-(4-trifluoromethyl-phenyl-ethynyl)-pyridinium triflate (7d). Following the general procedure, from 2-(4-trifluoromethyl-phenyl-ethynyl)-pyridine (0.494 g, 2 mmol) and but-3-enyl triflate (0.530 g, 2.6 mmol), **7d** (586 mg, 65%) was obtained as a white solid. Mp. 106-107 ºC. IR (NaCl) 3082, 2231, 1617, 1573, 1503, 1324, 1260, 1162, 1030, 846 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.26 (d, 1H, *J* = 6.2 Hz), 8.77 (td, 1H, *J* = 1.3, 7.9 Hz), 8.55 (d, 1H, *J* = 8.0 Hz), 8.28 (t, 1H, *J* = 7.7 Hz), 8.08 (d, 2H, *J* = 8.0 Hz), 7.93 (d, 2H, *J* = 8.2 Hz), 6.08-5.95 (m, 1H), 5.19 (t, 2H, *J* = 6.9 Hz), 5.13-5.07 (m, 2H), 3.00 (dd, 2H, *J* = 7.1, 14.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 145.0, 136.5, 133.3 (c, *J* = 32.7 Hz), 132.9, 132.2, 131.4, 127.6, 126.0 (c, *J* = 3.6 Hz), 123.3 (c, *J* = 269.6 Hz), 122.4, 120.5 (c, *J* = 318.1 Hz), 120.4, 104.6, 80.6, 59.9, 34.7. MS (ES^+) *m/z* (relative intensity) 302 (M^+, 100). Anal. Calcd. for $C_{19}H_{15}F_6NO_3S$: C, 50.56; H, 3.35; N, 3.10; S, 7.10. Found: C, 50.42; H, 3.15; N, 3.20; S, 7.05.

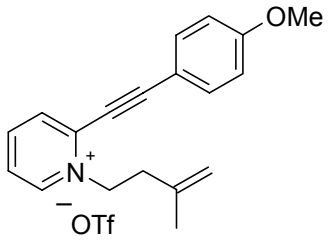


1-(But-3-enyl)-2-(thiophen-2-yl-ethynyl)-pyridinium triflate (7e). Following the general procedure, from 2-(thiophen-2-yl-ethynyl)-pyridine (0.370 g, 2 mmol) and but-3-enyl triflate (0.530 g, 2.6 mmol), chromatography gave 746 mg (96%) of **7e** as a green oil. IR (NaCl) 3084, 2204, 1617, 1572, 1497, 1263, 1159, 1030, 779 cm^{-1}.^{1}H NMR (300 MHz, acetone-d_6) δ 9.18 (d, 1H, *J* = 5.5 Hz), 8.68 (td, 1H, *J* = 1.3, 8.0 Hz), 8.41 (dd, 1H, *J* = 1.3, 8.2 Hz), 8.15

(ddd, 1H, *J* = 1.5, 6.4, 7.7 Hz), 7.95 (dd, 1H, *J* = 0.9, 4.9 Hz), 7.82 (dd, 1H, *J* = 1.0, 3.7 Hz), 7.28 (dd, 1H, *J* = 3.8, 5.1 Hz), 6.06-5.92 (m, 1H), 5.15-5.09 (m, 2H), 5.06 (t, 2H, *J* = 7.1 Hz), 2.93 (dd, 2H, J = 7.1, 14.1 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 147.2, 145.8, 137.9, 134.2, 133.2, 132.5, 129.1, 127.4, 121.9 (c, *J* = 319.6 Hz), 119.5, 118.9, 100.4, 84.3, 60.1, 34.8. MS (ES^+) *m/z* (relative intensity) 240 (M^+, 100), 241 (M + 1, 72). Anal. Calcd. for $C_{16}H_{14}F_3NO_3S_2$: C, 49.35; H, 3.62; N, 3.60; S, 16.47. Found: C, 49.29; H, 3.86; N, 3.48; S, 16.59.



2-(4-Methoxy-phenyl-ethynyl)-1-(3-methyl-but-3-enyl)-pyridinium triflate (7f). Following the general procedure, from 2-(4-methoxy-phenyl-ethynyl)-pyridine (0.418 g, 2 mmol) and 3-methyl-but-3-enyl triflate (0.569 g, 2.6 mmol), **7f** (708 mg, 83%) was obtained as a yellow solid. Mp. 74-75 ºC. IR (NaCl) 3080, 2924, 2216, 1602, 1518, 1258, 1153, 1030, 838, 638 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.16 (d, 1H, *J* = 6.4 Hz), 8.69 (td, 1H, *J* = 1.3, 8.0 Hz), 8.42 (d, 1H, *J* = 8.0 Hz), 8.16 (t, 1H, *J* = 7.7 Hz), 7.77 (d, 2H, *J* = 8.8 Hz), 7.13 (d, 2H, *J* = 8.9 Hz), 5.14 (t, 2H, *J* = 7.1 Hz), 4.87 (s, 1H), 4.71 (s, 1H), 3.91 (s, 3H), 2.91 (t, 2H, *J* = 7.3 Hz), 1.91 (s, 3H).^{13}C NMR (75 MHz, acetone-d_6) δ 163.4, 146.9, 145.8, 141.2, 138.6, 135.4, 132.8, 127.2, 122.3 (c, *J* = 321.5 Hz), 115.7, 114.7, 111.5, 108.2, 80.2, 59.3, 55.9, 38.7, 22.2. MS (ES^+) *m/z* (relative intensity) 278 (M^+, 100). Anal. Calcd. for $C_{20}H_{20}F_3NO_4S$: C, 56.20; H, 4.72; N, 3.28; S, 7.50. Found: C, 56.32; H, 4.42; N, 3.12; S, 7.35.

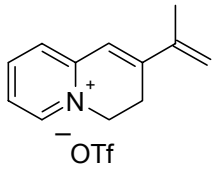


Ring closing metathesis of 5. General procedure for 2-vinyl-3,4-dihydroquinolizinium derivatives 4a–e.

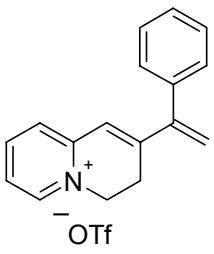
Ethylene was slowly bubbled through a solution of the enyne **5** (0.15 mmol) in dry $ClCH_2CH_2Cl$ (150 mL) and, after 10 min, 5% mmol of the Hoveyda–Grubbs' catalyst **11** was

added. The mixture was stirred and heated under reflux until TLC analysis showed completion of the reaction. Removal of the solvent in vacuo afforded a dark oil, which was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5).

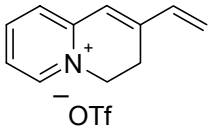
2-(1-Methyl-vinyl)-3,4-dihydroquinolizinium triflate (4a). The general procedure (2 h) afforded 39.9 mg (83%) of **4a** as a pale-brown solid. M.p. 80-81 ºC. IR (NaCl) 2925, 1634, 1565, 1508, 1458, 1257, 1159, 1030, 776 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 8.93 (d, 1H, *J* = 6.2 Hz), 8.54 (t, 1H, *J* = 7.9 Hz), 8.06 (d, 1H, *J* = 7.9 Hz), 7.92 (t, 1H, *J* = 7.3 Hz), 6.09 (s, 1H), 5.73 (s, 1H), 5.54 (s, 1H), 4.94 (t, 2H, *J* = 7.5 Hz), 3.17 (t, 2H, *J* = 7.7 Hz), 2.12 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 149.8, 146.2, 145.5, 141.1, 127.3, 125.5, 122.6, 122.1 (c, *J* = 319.6 Hz), 120.7, 117.3, 54.1, 23.9, 19.6. MS (ES^+) *m/z* (relative intensity) 172 (M^+, 100). Anal. Calcd. for $C_{13}H_{14}F_3NO_3S$: C, 48.59; H, 4.39; N, 4.36; S, 9.98. Found: C, 48.51; H, 4.46; N, 4.32; S, 10.05.



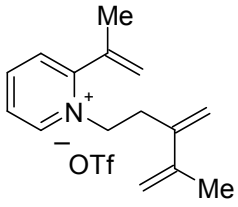
2-(1-Phenyl-vinyl)-3,4-dihydroquinolizinium triflate (4b). The general procedure (4 h) afforded 46.5 mg (81%) of **4b** as a yellow oil. IR (NaCl) 2924, 1630, 1567, 1508, 1445, 1258, 1163, 1030, 778 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 8.98 (d, 1H, *J* = 6.2 Hz), 8.52 (t, 1H, *J* = 8.0 Hz), 7.99 (d, 1H, *J* = 7.9 Hz), 7.95 (t, 1H, *J* = 6.2 Hz), 7.47-7.37 (m, 5H), 6.72 (s, 1H), 5.96 (s, 1H), 5.64 (s, 1H), 5.06 (t, 2H, *J* = 7.5 Hz), 3.28 (t, 2H, *J* = 7.6 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 150.4, 148.6, 146.5, 145.9, 139.8, 130.5, 129.6, 129.4, 129.2, 127.6, 125.9, 122.3 (c, *J* = 320.4 Hz), 121.0, 120.4, 54.4, 25.3. MS (ES^+) *m/z* (relative intensity) 234 (M^+, 100). Anal. Calcd. for $C_{18}H_{16}F_3NO_3S$: C, 56.39; H, 4.21; N, 3.65; S, 8.36. Found: C, 56.15; H, 4.39; N, 3.71; S, 8.54.



2-Vinyl-3,4-dihydroquinolizinium triflate (4c). The general procedure (20 h) afforded 17.5 mg (38%) of **4c** as a dark-yellow oil. IR (NaCl) 2925, 1637, 1568, 1508, 1258, 1166, 1030, 777 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 8.93 (d, 1H, *J* = 6.1 Hz), 8.53 (td, 1H, *J* = 1.5, 8.2 Hz), 7.99 (d, 1H, *J* = 8.0 Hz), 7.93 (t, 1H, *J* = 7.6 Hz), 6.99 (s, 1H), 6.79 (dd, 1H, *J* = 10.7, 17.4 Hz), 5.92 (d, 1H, *J* = 17.4 Hz), 5.68 (d, 1H, *J* = 10.7 Hz), 4.96 (t, 2H, *J* = 7.6 Hz), 3.13 (t, 2H, *J* = 7.6 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 148.5, 146.3, 145.7, 135.8, 127.0, 125.5, 124.0, 122.5, 121.9 (c, *J* = 319.3 Hz), 120.2, 54.0, 22.2. MS (ES^+) *m/z* (relative intensity) 158 (M^+, 100). Anal. Calcd. for $C_{12}H_{12}F_3NO_3S$: C, 46.90; H, 3.94; N, 4.56; S, 10.43. Found: C, 46.98; H, 3.65; N, 4.69; S, 10.68.

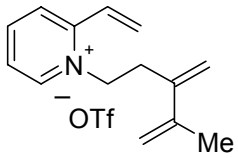


1-(4-Methyl-3-methylene-pent-4-enyl)-2-(1-methyl-vinyl)-pyridinium triflate (12b). The general procedure (24 h) afforded 29.9 mg (55%) of **12b** as a paled-yellow oil. IR (NaCl) 2925, 1623, 1465, 1261, 1159, 1031, 785. ^1H NMR (300 MHz, acetone-d_6) δ 9.09 (d, 1H, *J* = 6.3 Hz), 8.67 (td, 1H, *J* = 1.3, 7.9 Hz), 8.16 (dd, 1H, *J* = 1.3, 7.7 Hz), 8.08 (t, 1H, *J* = 7.9 Hz), 5.86 (d, 1H, *J* = 0.6 Hz), 5.61 (d, 1H, *J* = 0.6 Hz), 5.27 (s, 1H), 5.22 (s, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.87 (t, 2H, *J* = 7.2 Hz), 3.09 (t, 2H, *J* = 7.3 Hz), 2.28 (d, 3H, *J* = 1.0 Hz), 1.91 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 157.9, 146.8, 146.4, 143.1, 141.9, 137.7, 129.6, 127.6, 124.2, 122.0 (c, *J* = 319.9 Hz), 116.6, 114.4, 58.3, 35.4, 22.9, 20.7. MS (ES^+) *m/z* (relative intensity) 214 (M^+, 100), 215 (M + 1, 61). Anal. Calcd. for $C_{16}H_{20}F_3NO_3S$: C, 52.88; H, 5.55; N, 3.85; S, 8.82. Found: C, 52.65; H, 5.23; N, 4.01; S, 8.53.



1-(4-methyl-3-methylene-pent-4-enyl)-2-vinyl-pyridinium triflate (12a). Ethylene was slowly bubbled through a solution of the enyne **5a** (0.15 mmol) in dry Cl_2CH_2 (150 mL) and, after 10 min, 5% mmol of the Hoveyda-Grubbs' catalyst **11** was added. The mixture was stirred for 2.5 h. Removal of the solvent in vacuo afforded a dark oil, which was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5). **12a** was obtained (5.2 mg,

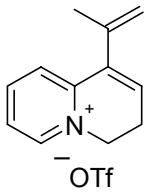
10%) as a yellow oil. IR (NaCl) 1620, 1451, 1260, 1155, 1030, 873. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.90 (d, 1H, *J* = 6.0 Hz), 8.66 (t, 1H, *J* = 8.0 Hz), 8.43 (d, 1H, *J* = 7.7 Hz), 8.11 (t, 1H, *J* = 6.8 Hz), 7.43 (dd, 1H, *J* = 11.3, 17.0 Hz), 6.55 (d, 1H, *J* = 17.0 Hz), 6.22 (d, 1H, *J* = 11.3 Hz), 5.26 (s, 1H), 5.16 (s, 1H), 5.12 (s, 1H), 5.01 (t, 2H, *J* = 6.9 Hz), 4.91 (s, 1H), 3.08 (t, 2H, *J* = 6.9 Hz), 1.89 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 146.1, 146.0, 141.6, 130.1, 127.6, 127.1, 126.9, 116.4, 114.1, 109.4, 58.0, 33.8, 20.3. EM (ES^+) *m/z* (relative intensity) 200 (M^+, 100). Anal. Calcd. for $C_{15}H_{18}F_3NO_3S$: C, 51.57; H, 5.19; N, 4.01; S, 9.18. Found: C, 51.23; H, 5.10; N, 4.32; S, 9.01.



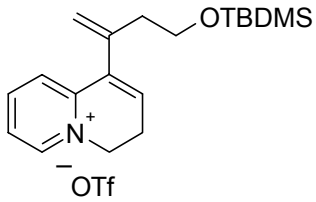
Ring closing metathesis of 7. General procedure for 1-vinyl-3,4-dihydroquinolizinium derivatives 6a–f.

Ethylene was slowly bubbled through a solution of the enyne **7** (0.2 mmol) in dry $ClCH_2CH_2Cl$ (20 mL) and, after 10 min, 5% mmol of the Hoveyda–Grubbs' catalyst **11** was added. The mixture was stirred and heated under reflux until TLC analysis indicated completion of the reaction. Removal of the solvent in vacuo afforded a dark oil, which was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5:0.5).

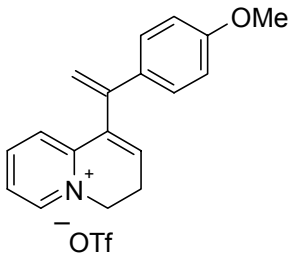
1-(1-Methyl-vinyl)-3,4-dihydroquinolizinium triflate (6a). The general procedure (4.5 h) afforded 55.2 mg (86%) of **6a** as a brown oil. IR (NaCl) 3090, 1636, 1509, 1441, 1262, 1160, 1030, 788 cm-^{1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (d, 1H, *J* = 6.0 Hz), 8.33 (td, 1H, *J* = 1.1, 7.9 Hz), 7.86 (t, 1H, *J* = 6.4 Hz), 7.76 (d, 1H, *J* = 8.0 Hz), 6.68 (t, 1H, *J* = 4.8 Hz), 5.35 (s, 1H), 5.16 (s, 1H), 4.82 (t, 2H, *J* = 7.4 Hz), 2.84 (td, 2H, *J* = 4.9, 7.3 Hz), 1.98 (s, 3H). ^{13}C NMR (50 MHz, acetone-d_6) δ 148.2, 146.7, 140.7, 136.6, 135.9, 126.2, 125.9, 125.2, 122.0 (c, *J* = 319.0 Hz), 118.6, 54.4, 22.8, 22.2. MS (ES^+) *m/z* (relative intensity) 172 (M^+, 100). Anal. Calcd. for $C_{13}H_{14}F_3NO_3S$: C, 48.59; H, 4.39; N, 4.36; S, 9.98. Found: C, 48.81; H, 4.45; N, 4.47; S, 10.12.



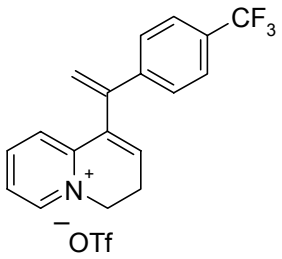
1-[3-(*tert*-Butyl-dimethyl-silanyloxy)-1-methylene-propyl]-3,4-dihydroquinolizinium triflate (6b). The general procedure (2 h) afforded 86.5 mg (93%) of **6b** as a grey solid. Mp 77-78 ºC. IR (NaCl) 3081, 2926, 1634, 1263, 1149, 1031, 774 cm-^{1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (d, 1H, *J* = 5.9 Hz), 8.26 (t, 1H, *J* = 7.7 Hz), 7.87 (d, 1H, *J* = 7.9 Hz), 7.84 (t, 1H, *J* = 6.4 Hz), 6.65 (t, 1H, *J* = 4.8 Hz), 5.39 (s, 1H), 5.23 (s, 1H), 4.83 (t, 2H, *J* = 7.3 Hz), 3.70 (t, 2H, *J* = 5.8 Hz), 2.85 (td, 2H, *J* = 5.1, 7.1 Hz), 2.44 (t, 2H, *J* = 6.0 Hz), 0.85 (s, 9H), 0.01 (s, 6H). ^{13}C NMR (75 MHz, CD_3OD) δ 149.8, 147.4, 147.0, 143.5, 137.3, 136.8, 126.9, 127.0, 122.0 (c, J = 320.2 Hz), 120.6, 62.5, 55.1, 40.2, 26.6, 23.6, 19.4, -4.9. MS (ES^{+}) *m/z* (relative intensity) 316 (M^{+}, 97), 317 (M + 1, 100). Anal. Calcd. for $C_{20}H_{30}F_3NO_4SSi$: C, 51.59; H, 6.49; N, 3.01; S, 6.89. Found: C, 51.74; H, 6.89; N, 3.36; S, 6.55.



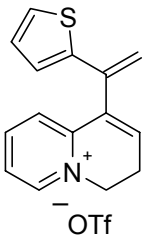
1-[1-(4-Methoxy-phenyl)-vinyl]-3,4-dihydroquinolizinium triflate (6c). The general procedure (8 h) afforded 74.3 mg (90%) of **6c** as a green solid. M.p. 114-116 ºC. IR (NaCl) 3092, 1605, 1511, 1258, 1158, 1030, 841 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.03 (d, 1H, *J* = 6.0 Hz), 8.44 (t, 1H, *J* = 7.5 Hz), 7.97 (t, 1H, *J* = 6.5 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.46 (d, 2H, *J* = 8.9 Hz), 7.05 (t, 1H, *J* = 4.8 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 5.85 (s, 1H), 5.49 (s, 1H), 5.08 (t, 2H, *J* = 7.5 Hz), 3.77 (s, 3H), 3.09 (td, 2H, *J* = 4.8, 7.3 Hz). ^{13}C NMR (50 MHz, acetone-d_6) δ 160.9, 158.3, 148.6, 146.6, 144.3, 139.6, 134.7, 130.7, 128.6, 126.2, 126.0, 122.1 (c, *J* = 319.5 Hz), 116.8, 114.7, 55.3, 54.5, 23.0. MS (ES^{+}) *m/z* (relative intensity) 264 (M^{+}, 100), 265 (M + 1, 83). Anal. Calcd. for $C_{19}H_{18}F_3NO_4S$: C 55.20; H, 4.39; N, 3.39; S, 7.76. Found: C, 55.01; H, 4.05; N, 3.28; S, 7.50.



1-[1-(4-Trifluoromethyl-phenyl)-vinyl]-3,4-dihydroquinolizinium triflate (6d). The general procedure (24 h) afforded 78.4 mg (87%) of **6d** as a brown oil. IR (NaCl) 3093, 1617, 1573, 1510, 1327, 1259, 1163, 1119, 1031, 852 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$) δ 9.02 (d, 1H, *J* = 6.0 Hz), 8.42 (td, 1H, *J* = 1.1, 8.0 Hz), 7.95 (td, 1H, *J* = 1.1, 7.5 Hz), 7.81 (d, 2H, *J* = 8.0 Hz), 7.66 (d, 2H, *J* = 8.2 Hz), 7.65 (d, 1H, *J* = 8.4 Hz), 7.11(t, 1H, *J* = 4.9 Hz), 6.13 (s, 1H), 5.79 (s, 1H), 5.07 (t, 2H, *J* = 7.5 Hz), 2.84 (td, 2H, *J* = 4.9, 7.5 Hz). ^{13}C NMR (50 MHz, acetone-d_6) δ 147.9, 146.7, 146.6, 143.4, 142.2, 140.5, 133.7, 130.2 (c, *J* = 32.2 Hz), 127.9, 126.3, 126.1 (c, *J* = 3.7 Hz), 125.7, 124.7 (c, *J* = 269.7 Hz), 121.8 (c, *J* = 319.6 Hz), 121.5, 54.2, 22.9. (ES^+) *m/z* (relative intensity) 302 (M^+, 100). Anal. Calcd. for $C_{19}H_{15}F_6NO_3S$: C, 50.56; H, 3.35; N, 3.10; S, 7.10. Found: C, 50.34; H, 3.59; N, 3.50; S, 6.98.



1-[1-(Thiophen-2-yl)-vinyl]-3,4-dihydroquinolizinium triflate (6e). The general procedure (7 h) afforded 73.1 mg (94%) of **6e** as a brown solid. Mp 94-96 ºC. IR (KBr) 3092, 1639, 1509, 1431, 1261, 1160, 1030, 790 cm^{-1}.^1H NMR (300 MHz, acetone-d_6) δ 9.05 (d, 1H, *J* = 6.0 Hz), 8.50 (td, 1H, *J* = 1.3, 8.0 Hz), 7.99 (td, 1H, *J* = 1.3, 7.5 Hz), 7.75 (d, 1H, *J* = 8.0 Hz), 7.45 (dd, 1H, *J* = 0.9, 5.1 Hz), 7.09-7.06 (m, 2H), 6.96 (dd, 1H, *J* = 3.7, 5.1 Hz), 5.88 (s, 1H), 5.45 (s, 1H), 5.07 (t, 2H, *J* = 7.5 Hz), 3.09 (ddd, 2H, *J* = 4.8, 7.5, 12.4 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ 148.4, 146.8, 142.5, 139.9, 138.6, 133.9, 128.6, 127.6, 127.3, 126.4, 125.7, 122.0 (c, *J* = 320.0 Hz), 117.2, 54.4, 23.0. MS (ES^+) *m/z* (relative intensity) 240 (M^+, 100), 241 (M + 1, 86). Anal. Calcd. for $C_{16}H_{14}F_3NO_3S$: C, 49.35; H, 3.62; N, 3.60; S, 16.47. Found: C,49.24; H, 3.42; N, 3.29; S, 16.28



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1-[1-(4-Methoxy-phenyl)-vinyl]-2-methyl-3,4-dihydroquinolizinium triflate (6f). The general procedure (24 h) afforded 16.2 mg (19%) of **6f** as a green oil. IR (NaCl) 2924, 1604, 1509, 1253, 1166, 1030, 840, 638 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6) δ 8.92 (d, 1H, *J* = 6.0 Hz), 8.40 (t, 1H, *J* = 8.0 Hz), 7.88 (t, 1H, *J* = 6.4 Hz), 7.67 (d, 1H, *J* = 8.6 Hz), 7.51 (d, 2H, *J* = 8.9 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 6.14 (s, 1H), 5.32 (s, 1H), 5.04 (t, 2H, *J* = 7.5 Hz), 3.78 (s, 3H), 3.10 (t, 2H, *J* = 7.7 Hz), 2.14 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 161.0, 149.9, 146.4, 145.8, 141.8, 130.4, 130.3, 128.7, 127.9, 125.3, 125.0, 122.2 (c, *J* = 320.2 Hz), 117.4, 114.9, 73.1, 55.4, 54.0, 21.6. MS (ES^+) *m/z* (relative intensity) 278 (M^+, 100). Anal. Calcd. for $C_{20}H_{20}F_3NO_4S$: C, 56.20; H, 4.72; N, 3.28; S, 7.50. Found: C, 56.41; H, 4.85; N, 3.29; S, 7.28.