

Supporting Material

General. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. – ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker AM 400 spectrometer in deuterated chloroform unless otherwise stated, with tetramethylsilane as internal standard. – Mass spectra were recorded on a Finnigan MAT 312 (70 eV) or a VG Autospec spectrometer at room temperature unless otherwise stated. – Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30 - 60 μm). – Analytical TLC was carried out on aluminium-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck). – CH_2Cl_2 (DCM) was distilled over CaH_2 before use. Methyl *t*-butyl ether (MTBE) and light petroleum (PE, bp 40-60 $^\circ\text{C}$) were distilled before use.

4+3 cycloaddition, Method A. To a solution of furan component (1.0 eq) and silyl enol ether (1.0 eq) in DCM (0.005 M solution) was added TMSOTf (0.1 eq) at -95°C . After 5 min sat. aq. NaHCO_3 solution was added and the mixture was allowed to reach room temperature. The aqueous layer was extracted with DCM (3 $\times$), the combined organic phase was dried (MgSO_4) and concentrated. The crude product was purified by column chromatography (silica gel, PE/MTBE). **Method B.** To a solution of furan component (1.0 eq) in DCM (0.005 M solution) was added TMSOTf (0.1 eq) at -95°C . A solution of acetal component (1.2 eq) in DCM (25 ml/mmol) was then added slowly. Work up after 5 min as described for method A.

(1S,2R,5S)-2-[(1R)-Phenylethoxy]-6-bromo-8-oxabicyclo[3.2.1]oct-6-en-3-one 7 A and **(1R,2R,5S)-2-[(1R)-phenylethoxy]-6-bromo-8-oxabicyclo[3.2.1]oct-6-en-3-one 7 C.** 3-Bromofuran (445 mg, 3.03 mmol) and silyl enol ether **1a** were allowed to react according to the general procedure (method A) to afford **7 A** (389 mg, 40%) and **7 C** (39 mg, 4%). Data for **7 A**, crystalline solid, mp 56-58 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} = +85.4^\circ$ ($c = 1$, CHCl_3). IR ν 3028, 2980, 2929, 2864, 1716, 1601, 1491, 1449, 1397, 1330, 1298, 1285, 1209, 1171, 1139, 1097, 1072, 1052, 975, 925, 888, 855, 843, 805, 760 cm^{-1} ; ^1H NMR δ 7.39-7.27 (m, 5 H, Ar), 6.42 (d, $J = 2.0$ Hz, 1 H, H7), 4.85 (q, $J = 6.5$ Hz, 1 H, H-8), 4.74 (dd, $J = 4.4$, 1.4 Hz, 1 H, H5), 4.64 (dd, $J = 5.0$, 2.0 Hz, 1 H, H1), 3.87 (d, $J = 5.0$ Hz, 1 H, H2), 2.64 (dd, $J = 16.0$, 4.4 Hz, 1 H, H4_{ax}), 2.58 (dd, $J = 16.0$, 1.4 Hz, 1 H, H4_{eq}), 1.49 (d, $J = 6.5$ Hz, 3 H, H-9); ^{13}C NMR δ 204.56 (4 $^\circ$, C3), 142.98 (4 $^\circ$, Ar), 130.69 (3 $^\circ$, C7), 128.65, 128.02, 126.35 (3 $^\circ$, Ar), 124.72 (4 $^\circ$, C6), 81.43, 81.19, 80.99, 79.47 (3 $^\circ$, C1, C2, C5, C8), 44.08 (2 $^\circ$, C4), 24.03 (1 $^\circ$, C9); MS m/z 324 (2), 322 (2), 220 (97), 218 (100), 177 (18), 175 (20), 161 (13), 159 (12), 149 (27), 148 (43), 147 (25), 146 (45), 139 (12), 121 (10); HRMS calcd. for $\text{C}_{15}\text{H}_{15}\text{BrO}_3$ 322.0205, found 322.0197. Data for **7 C**, yellowish oil, $[\alpha]_{\text{D}}^{20} = +69.8^\circ$ ($c = 1$, CHCl_3). IR (CHCl_3) ν 2978, 2958, 2935, 2912, 2876, 1729, 1454, 1375, 1325, 1304, 1281, 1237, 1146, 1110, 1079, 1016, 974, 914, 829, 818 cm^{-1} ; ^1H NMR δ 7.38-7.25 (m, 5 H, Ar), 6.36 (d, $J = 2.0$ Hz, 1 H, H6), 4.87 (ddd, $J = 4.9$, 2.0, 1.0 Hz, 1 H, H5), 4.82 (q, $J = 6.4$ Hz, 1 H, H8), 4.54 (d, $J = 5.1$ Hz, 1 H, H1), 3.99 (d, $J = 5.1$ Hz, 1 H, H2), 2.71 (dd, $J = 15.7$, 4.9 Hz, 1 H, H4_{ax}), 2.42 (d, $J = 15.7$ Hz, 1 H, H4_{eq}), 1.51 (d, $J = 6.4$ Hz, 3 H, H9); ^{13}C NMR δ 204.57 (4 $^\circ$, C3), 143.05 (4 $^\circ$, Ar), 133.13 (3 $^\circ$, C6), 128.58, 127.95, 126.51 (3 $^\circ$, Ar), 122.67 (4 $^\circ$, C7), 82.89, 82.61, 79.66, 79.31 (3 $^\circ$, C1, C2, C5, C8), 45.70 (2 $^\circ$, C4), 23.69 (1 $^\circ$, C9); MS m/z 324 (1), 322 (1), 295 (1), 293 (1), 220 (12), 218 (13), 148 (6), 146 (6), 106 (10), 105 (100), 103 (32), 79 (5), 77 (9), 75 (27).

(1S,2R,5S)-4-Methyl-2-[(1R)-phenylethoxy]-6-tributylstannyl-8-oxabicyclo[3.2.1]oct-6-en-3-one 8 A. 3-Tributylstannylfuran (103 mg, 0.289 mmol) and silyl enol ether **1c** were allowed to react according to the general procedure (method B) to afford **8 A** (81 mg, 51%) as colourless oil, $[\alpha]_{\text{D}}^{25} = +73.2^\circ$ ($c = 1$, CHCl_3). IR (film) ν 3084, 3060, 3028, 2956, 2928, 2872, 2852, 1724, 1452, 1376, 1116, 1080, 940, 700 cm^{-1} ; ^1H NMR δ 7.38-7.24 (m, 5 H, Ar), 6.48 (d, $J = 1.7$ Hz, 1 H, H7), 4.87 (d, $J = 4.7$ Hz, 1 H, H5), 4.79 (q, $J = 6.4$ Hz, 1 H, H9), 4.68 (dd, $J = 5.1$, 1.7 Hz, 1 H, H1), 3.93 (dd, $J = 5.1$, 0.7 Hz, 1 H, H2), 2.73 (ddq, $J = 7.1$, 4.7, 0.7 Hz, 1 H, H4), 1.48 (d, $J = 6.4$ Hz, 3 H, H10), 1.52-1.24, 0.95 (m, 18 H, Bu-CH₂), 0.94 (d, $J = 7.0$ Hz, 3 H, H8) 0.90 (t, $J = 7.3$ Hz, 9 H, Bu-CH₃); ^{13}C -NMR δ 206.86 (4 $^\circ$, C3), 147.04 (4 $^\circ$, C6), 143.62 (4 $^\circ$, Ar), 143.29 (3 $^\circ$, C7), 128.56, 127.75, 126.37 (3 $^\circ$, Ar), 88.46, 82.46, 81.17, 78.74 (3 $^\circ$, C1, C2, C5, C9), 50.49 (3 $^\circ$, C4), 28.90, 27.38 (2 $^\circ$, Bu-CH₂), 24.25 (1 $^\circ$, C10), 13.64 (1 $^\circ$, Bu-CH₃), 10.34 (2 $^\circ$, Bu-CH₂), 10.29 (1 $^\circ$, C8); MS m/z 491 (2), 405 (2), 387 (2), 319 (15), 301 (20), 289 (12), 235 (7), 179 (10), 137 (2), 121 (4), 105 (100), 91 (2), 79 (5); HRMS calcd. for $\text{C}_{24}\text{H}_{36}\text{O}_3\text{Sn}$ 491.1608, found 491.1607.

(1S,2R,5S)-2-[(1R)-Phenylethoxy]-6-triethylsilyl-8-oxabicyclo[3.2.1]oct-6-en-3-one 9 A and **(1R,2R,5S)-2-[(1R)-Phenylethoxy]-7-triethylsilyl-8-oxabicyclo[3.2.1]oct-6-en-3-one 9 C.** 3-Triethylsilylfuran (56 mg, 0.311 mmol) and silyl enol ether **1a** were allowed to react according to the general procedure (method B) to afford **9 A** (42 mg, 38%) and **9 C** (30 mg, 27%). Data for **9 A**, colourless oil, $[\alpha]_{\text{D}}^{25} = +74.2^\circ$ ($c = 1$, CHCl_3). IR (CHCl_3) ν 3060, 3028, 2952, 2908, 2876, 1724, 1452, 1144, 1104, 1068, 1008, 972, 736, 700 cm^{-1} ; ^1H -NMR δ 7.45-7.25 (m, 5 H, Ar), 6.50 (d, $J = 1.7$ Hz, 1 H, H7), 5.00 (d, $J = 5.0$ Hz, 1 H, H5), 4.80 (q, $J = 6.4$ Hz, 1 H, H8), 4.68 (dd, $J = 5.1$, 1.7 Hz, 1 H, H1), 3.92 (d, $J = 5.1$ Hz, 1 H, H2), 2.66 (dd, $J = 15.3$, 5.0 Hz, 1 H, H4_{ax}), 2.26 (d, $J = 15.3$ Hz, 1 H, H4_{eq}), 1.48 (d, $J = 6.4$ Hz, 3 H, H9), 0.94 (t, $J = 8.1$ Hz, 9 H, TES-CH₃), 0.63 (q, $J = 8.1$ Hz, 6 H, TES-CH₂); ^{13}C -NMR δ 205.32 (4 $^\circ$, C3), 146.48 (4 $^\circ$, C6), 143.44 (4 $^\circ$, Ar), 141.45 (3 $^\circ$, C7), 128.59 (3 $^\circ$, Ar), 127.85 (4 $^\circ$, Ar), 126.39 (3 $^\circ$, Ar), 83.09, 82.20, 81.05, 79.05 (C1, C2, C5, C8), 46.40 (2 $^\circ$, C4), 24.21 (1 $^\circ$, C9), 7.18 (1 $^\circ$, TES-CH₃), 3.14 (2 $^\circ$, TES-CH₂); MS m/z 310 (1), 254 (11), 225 (13), 195 (2), 181 (3), 115 (12), 105 (100), 87 (12), 77 (7); HRMS calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Si}$ 254.1338, found 254.1338. Data for **9 C**, colourless oil, $[\alpha]_{\text{D}}^{25} = +45.9^\circ$ ($c = 1$, CHCl_3). IR (film) ν 3084, 3060, 3028, 2952, 2908, 2872, 2808, 1724, 1452, 1144, 1112, 1068, 1008, 972, 732, 700 cm^{-1} ; ^1H NMR δ 7.45-7.25 (m, 5 H, Ar), 6.45 (d, $J = 1.7$ Hz, 1 H, H7), 4.92 (m, 1 H, H1), 4.85 (m, 2 H, H5, H8), 3.91 (d, $J = 2.76$ Hz, 1 H, H2), 2.63

(dd, $J = 15.3, 5.0$ Hz, 1 H, H_{4ax}), 2.27 (d, $J = 15.3$ Hz, 1 H, H_{4eq}), 1.47 (d, $J = 6.4$ Hz, 3 H, H₉), 0.95 (t, $J = 8.0$ Hz, 9 H, TES-CH₃), 0.73 (q, $J = 8.0$ Hz, 6 H, TES-CH₂); NOE, H₂ irradiated: H₁ (18.6%), H_{4ax} (1.8%); H_{4ax} irradiated: H₅ (7.4%), H₂ (3.7%), H_{4eq} (37.5%); H₆ irradiated: H₅ (6.2%), H_{4eq} (1.2%); H_{4eq} irradiated: H₅ (4.0%), H₆ (3.0%), H_{4ax} (38.7%); ¹³C NMR δ 205.86 (4°, C₃), 144.64 (4°, C₆), 144.32 (3°, C₇), 143.34 (4°, Ar), 128.67 (3°, Ar), 127.89 (4°, Ar), 126.46 (3°, Ar), 84.53, 82.69, 79.16, 78.74 (3°, C₁, C₂, C₅, C₈), 46.09 (2°, C₄), 24.09 (1°, C₉), 7.33 (1°, TES-CH₃), 3.47 (2°, TES-CH₂); MS m/z 286 (1), 254 (3), 225 (15), 182 (4), 172 (5), 153 (10), 115 (13), 105 (100), 87 (12), 77 (3); HRMS calcd. for C₁₃H₂₂O₃Si 254.1338, found 254.1336.

(1*S*,2*R*,5*S*)-2-[(1*R*)-Naphth-2-yl-ethoxy]-6-triethylsilyl-8-oxabicyclo[3.2.1]oct-6-en-3-one **10 A** and (1*R*,2*R*, 5*S*)-2-[(1*R*)-Naphth-2-yl-ethoxy]-7-triethylsilyl-8-oxabicyclo[3.2.1]oct-6-en-3-one **10 C**. 3-Triethylsilylfuran (49 mg, 0.269 mmol) and silyl enol ether **1b** were allowed to react according to the general procedure (method B) to afford **10 A** (41 mg, 37%) and **10 C** (30 mg, 27%). Data for **10 A**, colourless oil, IR (CHCl₃) ν 3056, 2952, 2908, 1724, 1456, 1399, 1176, 1140, 1104 s 1072, 1016, 972, 860, 820, 736, 664 cm⁻¹; ¹H NMR δ 7.90-7.44 (m, 7 H, Ar), 6.52 (d, $J = 1.66$ Hz, 1 H, H₇), 4.98 (m, 2 H, H₅, H₈), 4.68 (dd, $J = 5.14, 1.66$ Hz, 1 H, H₁), 3.95 (d, $J = 5.14$ Hz, 1 H, H₂), 2.64 (dd, $J = 15.26, 4.96$ Hz, 1 H, H_{4ax}), 2.26 (d, $J = 15.26$ Hz, 1 H, H_{4eq}), 1.56 (d, $J = 6.43$ Hz, 3 H, H₉), 0.94 (t, $J = 8.1$ Hz, 9 H, TES-CH₃), 0.63 (q, $J = 8.1$ Hz, 6 H, TES-CH₂); ¹³C NMR δ 205.34 (4°, C₃), 146.53 (4°, C₆), 141.48 (4°, Ar), 140.69 (3°, C₇), 133.22, 128.67, 127.84, 127.74, 126.28, 125.99, 125.69, 124.04 (3°, Ar), 83.08, 82.20, 81.05, 79.19 (3°, C₁, C₂, C₅, C₈), 46.41 (2°, C₄), 24.04 (1°, C₉), 7.19 (1°, TES-CH₃), 3.16 (2°, TES-CH₂); MS m/z 408 (M⁺, 15), 379 (10), 361 (11), 299 (10), 254 (59), 225 (100), 211 (10); HRMS calcd for C₁₃H₂₂O₃Si 254.1338, found 254.1339. Data for **10 C**, IR (CHCl₃) ν 3052, 2952, 2908, 2872, 1724, 1456, 1300, 1176, 1144, 1112, 1072, 972, 820, 720 cm⁻¹; ¹H NMR δ 7.90-7.43 (m, 7 H, Ar), 6.45 (d, $J = 1.68$ Hz, 1 H, H₆), 5.02 (q, $J = 6.43$ Hz, 1 H, H₈), 4.90 (d, $J = 4.96$ Hz, 1 H, H₅), 4.85 (d, 5.14 Hz, 1 H, H₂), 3.93 (d, $J = 5.14$ Hz, 1 H, H₁), 2.62 (dd, $J = 15.26, 4.96$ Hz, 1 H, H_{4ax}), 2.28 (d, $J = 15.26$ Hz, 1 H, H_{4eq}), 1.55 (d, $J = 6.43$ Hz, 3 H, H₉), 0.95 (t, $J = 8.1$ Hz, 9 H, TES-CH₃), 0.72 (q, $J = 8.1$ Hz, 6 H, TES-CH₂); ¹³C NMR δ 206 (4°, C₃), 146.95 (4°, C₆), 144.64 (4°, Ar), 144.27 (3°, C₇), 140.52, 133.21, 128.70, 127.83, 127.75, 126.28, 125.98, 125.91, 123.98 (3°, Ar), 84.46, 82.62, 79.09, 78.85 (3°, C₁, C₂, C₅, C₈), 46.03 (2°, C₄), 23.83 (1°, C₉), 7.32 (1°, TES-CH₃), 3.48 (2°, TES-CH₂); MS (60 °C) m/z 408 (M⁺, 1), 253 (1), 225 (3), 198 (1), 183 (1), 155 (100), 127 (3), 115 (9), 87 (7), 75 (2); HRMS calcd. for C₁₃H₂₂O₃Si 254.1338, found 254.1326.

(1*S*,2*R*,5*S*)-Benzenecarbothioic acid, S-[2-[(1*R*)-naphth-2-yl-ethoxy]-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-6-yl] ester **12 A** and (1*R*,2*S*,5*R*)-Benzenecarbothioic acid, S-[2-[(1*R*)-naphth-2-yl-ethoxy]-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-6-yl] ester **12 B**. Benzenecarbothioic acid S-(3-

furanyl) ester (120 mg, 0.59 mmol) and silyl enol ether **1b** were allowed to react according to the general procedure (method B) to afford **12 A** (96 mg, 38%) and **12 B** (63 mg, 25%). Data for **12 A**, colourless solid, mp 132-135 °C, $[\alpha]_D^{25} = +73.8^\circ$ ($c = 1$, CHCl₃). IR (CHCl₃) ν 3060, 3000, 2980, 2932, 2868, 1724, 1680, 1448, 1300, 1176, 1104, 1072, 976, 896, 860, 820 cm⁻¹; ¹H NMR δ 8.00-7.40 (m, 10 H, Ar), 6.70 (d, $J = 1.9$ Hz, 1 H, H₇), 5.33 (d, $J = 4.9$ Hz, 1 H, H₅), 5.03 (q, $J = 6.4$ Hz, 1 H, H₈), 4.81 (dd, $J = 5.2, 1.9$ Hz, 1 H, H₁), 3.99 (d, $J = 5.2$ Hz, 1 H, H₂), 2.66 (dd, $J = 16, 4.9$ Hz, 1 H, H_{4ax}), 2.55 (d, $J = 16$ Hz, 1 H, H_{4eq}), 1.59 (d, $J = 6.4$ Hz, 3 H, H₉); ¹³C NMR δ 206.49 (4°, C₃), 189.47 (4°, C₁₀), 140.24 (4°, C₆), 136.22 (3°, C₇), 136.07, 135.62 (4°, Ar), 134.14 (3°, Ar), 133.27, 133.18 (4°, Ar), 128.88, 128.83, 127.84, 127.76, 127.56, 126.39, 126.12, 125.83, 123.88 (3°, Ar), 81.31, 80.80, 79.64, 79.61 (3°, C₁, C₂, C₅, C₈), 45.18 (2°, C₄), 24.06 (1°, C₉); MS (170 °C) m/z 276 (2), 195 (1), 155 (100), 127 (3), 105 (45), 77 (9); HRMS calcd. for C₁₄H₁₂O₄S 276.0456, found 276.0457. Data for **12 B**, colourless solid, mp 105-110 °C, $[\alpha]_D^{25} = +37.0^\circ$ ($c = 0.5$, CHCl₃). IR (CHCl₃) ν 3060, 3000, 2980, 2928, 2928, 1728, 1680, 1448, 1304, 1176, 1096, 980, 900, 860, 820 cm⁻¹; ¹H NMR δ 8.00-7.40 (m, 10 H, Ar), 6.74 (d, $J = 1.9$ Hz, 1 H, H₇), 5.39 (dd, $J = 4.6, 1.25$ Hz, 1 H, H₅), 5.23 (dd, $J = 4.9$ Hz, 1 H, H₁), 4.94 (q, $J = 6.4$ Hz, 1 H, H₈), 4.14 (d, $J = 4.9$ Hz, 1 H, H₂), 2.61 (dd, $J = 16, 4.6$ Hz, 1 H, H_{4ax}), 2.53 (dd, $J = 16, 1.25$ Hz, 1 H, H_{4eq}), 1.61 (d, $J = 6.4$ Hz, 3 H, H₉); ¹³C NMR δ 202.33 (4°, C₃), 188.33 (4°, C₁₀), 139.65 (4°, C₆), 136.05 (3°, C₇), 136.00, 135.89 (4°, Ar), 134.18 (3°, Ar), 133.22, 133.17 (4°, Ar), 128.90, 128.56, 128.00, 127.93, 127.71, 127.58, 126.18, 126.01, 125.48, 124.34 (3°, Ar), 81.30, 79.75, 79.57, 79.59 (3°, C₁, C₂, C₅, C₈), 44.74 (2°, C₄), 23.58 (1°, C₉); MS (170 °C) m/z 276 (2), 155 (100), 129 (4), 105 (28), 77 (6); HRMS calcd. for C₁₄H₁₂O₄S 276.0456, found 276.0457.

(1*S*,2*R*,5*S*)-Benzenecarbothioic acid, S-[4-methyl-2-[(1*R*)-naphth-2-yl-ethoxy]-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-6-yl] ester **14 A**. Benzenecarbothioic acid S-(3-furanyl) ester (40 mg, 0.19 mmol) and silyl enol ether **1b** were allowed to react according to the general procedure (method B) to afford **14 A** (57 mg, 65%), colourless crystals, mp 128 °C, $[\alpha]_D^{25} = +95.1^\circ$ ($c = 1$, CHCl₃). IR (CHCl₃) ν 3060, 3012, 2980, 2932, 2876, 1724, 1676, 1448, 1176, 1124, 1084, 900 cm⁻¹; ¹H NMR δ 8.00-7.40 (m, 16 H, Ar), 6.79 (d, $J = 2.0$ Hz, 1 H, H₇), 5.22 (d, $J = 4.5$ Hz, 1 H, H₅), 5.0 (q, $J = 6.4$ Hz, 1 H, H₉), 4.83 (dd, $J = 5.3, 2.0$ Hz, 1 H, H₁), 4.05 (d, $J = 5.3$ Hz, 1 H, H₂), 2.84 (dq, $J = 7.2, 4.5$ Hz, 1 H, H₄), 1.60 (d, $J = 6.4$ Hz, 3 H, H₁₀), 1.11 (d, $J = 7.2$ Hz, 3 H, H₈); ¹³C NMR δ 206.76 (4°, C₃), 188.17 (4°, C₁₁), 140.35 (4°, C₆), 137.69 (3°, C₇), 136.23, 134.54 (4°, Ar), 134.06 (3°, Ar), 133.27, 133.21 (4°, Ar), 128.88, 128.80, 127.83, 127.76, 127.49, 126.36, 126.09, 125.74, 123.91 (3°, Ar), 83.65, 81.59, 81.42, 79.34 (3°, C₁, C₂, C₅, C₉), 50.56 (3°, C₄), 23.95 (1°, C₁₀), 9.14 (1°, C₈); MS (120 °C) m/z 317 (1), 290 (3), 232 (2), 209 (3), 167 (6), 155 (100), 141 (24), 127 (7), 105 (37), 91 (8), 75 (31); HRMS calcd. for C₁₅H₁₅O₄S 289.0535, found 289.0533.

(1R,2R,5S)-6,7-Dibromo-2-[(1R)-phenylethoxy]-8-oxabicyclo[3.2.1]oct-6-en-3-one **15 A**. 3,4-Dibromofuran (140 mg, 0.621 mmol) and silyl enol ether **1a** were allowed to react according to the general procedure (method B) to afford **15 A** (125 mg, 50%), colourless oil. IR (CHCl₃) ν 3084, 3064, 2980, 2932, 2868, 1732, 1608, 1452, 1300, 1264, 1120, 1080, 900 cm⁻¹; ¹H NMR δ 7.40–7.27 (m, 5 H, Ar), 4.83 (q, J = 6.43 Hz, 1 H, H8), 4.78 (dd, J = 4.22, 1.66 Hz, 1 H, H5), 4.59 (d, J = 4.97 Hz, 1 H, H1), 3.94 (d, J = 4.97 Hz, 1 H, H2), 2.67 (d, J = 4.22 Hz, 1 H, H4a), 2.65 (d, J = 1.65 Hz, 1 H, H4b), 1.51 (d, J = 6.43 Hz, 3 H, H9); ¹³C NMR 203.68 (4°, C3), 142.85 (4°, Ph), 128.69 (3°, Ph), 128.13 (3°, Ph), 126.54 (3°, Ph), 124.17 (4°, C7), 122.17 (4°, C6), 83.70, 82.60, 81.06, 79.91 (3°, C1, C2, C5, C8), 44.10 (2°, C4), 23.95 (1°, C9); MS m/z 403 (M⁺+1, 2), 373 (1), 321 (1), 298 (100), 255 (25), 239 (12), 226 (47), 189 (24), 161 (15), 131 (8), 121 (21); HRMS calcd. for C₇H₆Br₂O₃ 297.8663, found 297.8662.

(1R,2R,5S)-6,7-Dibromo-2-[(1R)-naphth-2-yl-ethoxy]-8-oxabicyclo[3.2.1]oct-6-en-3-one **16 A**. 3,4-Dibromofuran (61 mg, 0.27 mmol) and silyl enol ether **1b** were allowed to react according to the general procedure (method B) to afford **16 A** (60 mg, 49%), colourless oil. IR (CHCl₃) ν 3060, 2980, 2932, 2876, 1732, 1608, 1296, 1120, 1080, 900, 860 cm⁻¹; ¹H NMR δ 7.92–7.40 (m, 7 H, Ar), 5.00 (q, J = 6.43 Hz, 1 H, H8), 4.76 (dd, J = 3.68, 2.21 Hz, 1 H, H5), 4.57 (d, J = 4.97 Hz, 1 H, H1), 3.98 (d, J = 5.00 Hz, 1 H, H2), 2.65 (d, J = 2.57 Hz, 1 H, H4a), 2.65 (d, J = 1.29 Hz, 1 H, H4b), 1.59 (d, J = 6.43 Hz, 3 H, H9); ¹³C NMR δ 203.71 (4°, C3), 140.06 (4°, Ar), 133.31, 133.15 (4°, C6, C7), 128.83, 127.86, 127.78, 126.41, 126.17, 126.01 (3°, Ar), 124.22 (4°, Ar), 124.03 (3°, Ar), 122.18 (4°, Ar), 83.69, 82.59, 81.09, 80.09 (3°, C1, C2, C5, C8), 44.10 (3°, C4), 23.77 (1°, C9); MS m/z 452 (0.3), 318 (0.2), 298 (0.7), 258 (0.4), 229 (0.4), 215 (1), 198 (2), 155 (100), 127 (5), 115 (3), 84 (8), 73 (12); HRMS calcd. for C₇H₆Br₂O₃ 297.8663, found 297.8662.

2 α -(1-Phenylethoxy)-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one **17**. 2,5-Dimethylfuran (0.11 ml, 1 mmol) and silyl enol ether **1a** were allowed to react according to the general procedure (method A) to afford **17 A** (74.5 mg, 27%) and **17 B** (60.4 mg, 22%). Data for **17 A**, colourless oil. IR (film) ν 3364, 3084, 3064, 3032, 2972, 2932, 2896, 2872, 1724, 1492, 1452, 1408, 1376, 1336, 1316, 1268, 1240, 1208, 1172, 1104, 1044, 1016, 948, 912, 892, 848, 752, 700, 668 cm⁻¹; ¹H NMR δ 7.30 (m, 5 H, Ar), 6.08 (d, J = 5.9 Hz, 1 H, H7), 5.98 (d, J = 5.9 Hz, 1 H, H6), 4.79 (q, J = 6.4 Hz, 1 H, H8), 3.88 (s, 1 H, H2), 2.52 (d, J = 15.0 Hz, 1 H, H4_{ax}), 2.37 (d, J = 15.0 Hz, 1 H, H4_{eq}), 1.61 (s, 3 H, CH₃), 1.48 (d, J = 6.4 Hz, 3 H, H9), 1.45 (s, 3 H, CH₃); ¹³C NMR δ 204.76 (4°, C3), 142.83 (4°, Ar), 137.09, 134.85 (3°, C6, C7), 128.18, 127.55, 126.58 (3°, Ar), 87.12 (4°, C1), 86.16 (3°, C8), 84.88 (4°, C5), 78.84 (3°, C2), 51.53 (2°, C4), 23.00, 22.22, 20.68 (1°, C9, CH₃, CH₃); FAB-MS m/z 272 (M⁺, 3), 201 (11), 175 (7), 167 (69), 152 (18), 100 (100); HRMS calcd. for C₁₇H₂₀O₂ 272.1412, found 272.1404. Data for **17 B**, colourless oil. IR (CHCl₃) ν 3084, 3064, 3008, 2976, 2932, 2872, 2812, 1720, 1492,

1452, 1408, 1380, 1336, 1316, 1280, 1268, 1240, 1171, 1148, 1112, 1076, 1044, 1028, 1008, 948, 912, 888, 848, 813, 612, 548, 520 cm⁻¹; ¹H NMR δ 7.30 (m, 5 H, Ar), 6.07 (d, J = 5.9 Hz, 1 H, H7), 5.98 (d, J = 5.9 Hz, 1 H, H6), 4.84 (q, J = 6.4 Hz, 1 H, H8), 3.63 (s, 1 H, H2), 2.55 (d, J = 15.0 Hz, 1 H, H4_{ax}), 2.39 (d, J = 15.0 Hz, 1 H, H4_{eq}), 1.52 (d, J = 6.4 Hz, 3 H, H9), 1.42 (s, 3 H, CH₃), 1.30 (s, 3 H, CH₃); ¹³C NMR δ 206.97 (4°, C3), 142.42 (4°, Ar), 136.94, 135.02 (3°, C6, C7), 128.34, 127.96, 127.28 (3°, Ar), 86.73 (4°, C1), 85.44 (3°, C8), 84.77 (4°, C5), 78.78 (3°, C2), 51.87 (2°, C4), 23.51, 22.09, 20.47 (1°, C9, CH₃, CH₃); FAB-MS m/z 273 (M⁺+1, 7), 201 (9), 176 (10), 167 (30), 154 (25), 137 (23), 121 (8), 105 (100).

(1S,2R,5S)-1,5-Dimethyl-2-[(1R)-naphth-2-yl-ethoxy]-8-oxabicyclo[3.2.1]oct-6-en-3-one **18 A** and (1R,2S, 5R)-1,5-Dimethyl-2-[(1R)-naphth-2-yl-ethoxy]-8-oxabicyclo[3.2.1]oct-6-en-3-one **18 B**. 2,5-Dimethylfuran (30 mg, 0.31 mmol) and silyl enol ether **1b** were allowed to react according to the general procedure (method B) to afford **18 A** (28 mg, 28%) and **18 B** (19 mg, 19%). Data for **18 A**, colourless solid, mp 88–91 °C. IR (CHCl₃) ν 3060, 2980, 2932, 2868, 1720, 1452, 1380, 1336, 1240, 1176, 1116, 1100, 1072, 944, 860 cm⁻¹; ¹H NMR δ 7.88–7.42 (m, 7 H, Ar), 6.03 (d, J = 5.7 Hz, 1 H, H7), 5.98 (d, J = 5.7 Hz, 1 H, H6), 5.03 (q, J = 6.43 Hz, 1 H, H10), 3.65 (s, 1 H, H2), 2.55 (d, J = 15.08 Hz, 1 H, H4a), 2.40 (d, J = 15.08 Hz, 1 H, H4b), 1.60 (d, J = 6.43 Hz, 3 H, H11), 1.40 (s, 3 H, H8), 1.30 (s, 3 H, H9); ¹³C NMR δ 206.98 (4°, C3), 139.71 (4°, Ar), 137.00 (3°, C7), 135.07 (3°, C6), {133.25, 133.06} (4°, Ar), 128.42, 127.83, 127.70, 126.73, 126.21, 126.01, 124.64 (3°, Ar), 86.74 (3°, C1), 85.45, 78.92 (3°, C2, C10), 84.77 (3°, C5), 51.92 (3°, C4), 23.45 (1°, C8), 23.00 (1°, C9), 20.59 (1°, C11); MS m/z 322 (M⁺, 2), 293 (1), 191 (2), 167 (79), 155 (100), 139 (5), 127 (8), 109 (7), 96 (23), 79 (6); HRMS calcd. for C₂₁H₂₂O₃ 322.1569, found 322.1569. Data for **18 B**, colourless oil. IR (CHCl₃) ν 3056, 2972, 2928, 2896, 2868, 1724, 1448, 1372, 1336, 1312, 1240, 1172, 1112, 948, 752 cm⁻¹; ¹H NMR δ 7.88–7.40 (m, 7 H, Ar), 6.10 (d, J = 5.7 Hz, 1 H, H7), 5.98 (d, J = 5.7 Hz, 1 H, H6), 4.97 (q, J = 6.44 Hz, 1 H, H10), 3.90 (s, 1 H, H2), 2.48 (d, J = 15.08 Hz, 1 H, H4a), 2.40 (d, J = 15.08 Hz, 1 H, H4b), 1.65 (s, 3 H, H8), 1.57 (d, J = 6.44 Hz, 3 H, H11), 1.43 (s, 3 H, H9); ¹³C NMR δ 204.58 (4°, C3), 140.25 (4°, Ar), 137.17 (3°, C7), 134.85 (3°, C6), 133.12, 133.10 (4°, Ar), 128.04, 127.99, 127.64, 125.91, 125.76, 125.41, 124.95 (3°, Ar), 87.19 (3°, C1), 86.34, 79.20 (3°, C2, C10), 84.91 (3°, C5), 51.54 (3°, C4), 23.06 (1°, C8), 22.33 (1°, C9), 20.77 (1°, C11); MS m/z 322 (M⁺, 2), 288 (3), 241 (2), 231 (7), 182 (31), 167 (32), 155 (27), 139 (16), 125 (15), 109 (52), 91 (100), 84 (56), 72 (29); HRMS calcd. for C₂₁H₂₂O₃ 322.1569, found 322.1568.