# Supplementary Material (ESI) for Chemical Communications


# *SUPPORTING INFORMATION*

## *Synthesis of a simplified analogue of eleutherobin* via *a Claisen rearrangement and ring-closing metathesis strategy*

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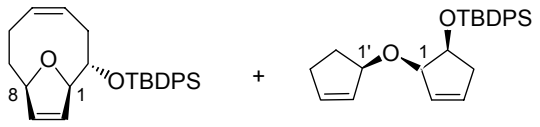
***(1S,2S,4Z,8R,9Z)*-2-(*tert*-Butyldiphenylsilanyloxy)-11-oxabicyclo[6.2.1]-undeca-4,9-diene, 6.**

**(1S,2S,4Z,1'R,2'Z)-*[2-(*tert-*Butyldiphenylsilanyloxy)-(bis-cyclopent-4-enyloxy-cyclopent-2'-enyloxy)], 9.**



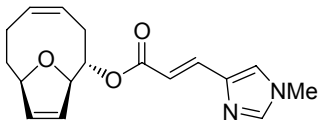

**6** **9**

*Method A towards* **4**

To a stirred solution of Grubbs ruthenium catalyst **10** (1 mg, 0.002 mmol, 5 mol%) in $CH_2Cl_2$ (1 $cm^3$) was added a solution of the *bis*-alkene **5** (14 mg, 0.032 mmol) in $CH_2Cl_2$ (1 $cm^3$, 0.5 $cm^3$ rinse) *via* cannula. The mixture was stirred for 18 h at room temperature. The solvent was removed *in vacuo* and purification by flash chromatography (petroleum ether 40-60:ether, 10:1) gave the *bicyclic [6.2.1] ring system* **6** (9 mg, 69%) and the *bis-cyclopentene* **8** (3 mg, 22%); Data for **6**: $R_f$ 0.21 (petroleum ether 40-60:ether, 10:1); $[\alpha]_D^{22}$ +18.0 (*c* 0.51 in $CHCl_3$); $\nu_{max}$ (neat)/$cm^{-1}$ 3014w, 2930w, 2856w, 1761w, 1589w, 1472w, 1453w, 1427m, 1390m, 1361w, 1216w, 1178w, 1103s, 1084s, 1008m, 936m, 866m, 822m, 738s and 700s; $\delta_H$ (400 MHz; $CDCl_3$, -30 °C) 7.61-7.74 (4H, m, Ar), 7.30-7.46 (6H, m, Ar), 5.71-5.78 (2H, m, alkene), 5.60-5.67 (1H, m, alkene), 5.52-5.53 (1H, d, *J* 5.9), 5.23 and 5.18 (2H, brs, H-1 and H-8), 3.54-3.56 (1H, d, *J* 6.4, H-2), 2.29-2.37 (2H, m, ring C$H_2$), 1.94-1.98 (1H, m, ring CH*H*), 1.80-1.91 (1H, m, ring CH*H*), 1.60-1.66 (1H, m, ring CH*H*), 1.50-1.55 (1H, dd, *J* 14.4 and 6.7, ring CH*H*) and 1.05 [9H, s, (C$H_3$)$_3$C]; $\delta_C$ (125 MHz; $CDCl_3$, 25 °C) 136.1, 135.9, 134.2, 134.0, 131.4, 129.8, 129.7, 129.5, 128.9, 127.7, 127.6, 127.5 and 125.9 (Ar and CH=CH), 92.5, 87.5 and 70.6 (C-1, C-2 and C-8), 28.6, 27.9 and 21.8 (C-3, C-6 and C-7) and 27.1 and 19.4 [C(C$H_3$)$_3$]; *m/z* (CI; $NH_3$) 422 [$(M+NH_4)^+$, 85%], 405 [$(M+H)^+$, 10%], 347 (10), 329 (30), 327 (100) 148 (30) and 52 (30); [*m/z* (ES) Found: $(M+H)^+$, 405.2258. $C_{26}H_{33}O_2Si$ requires *M*, 405.2250]. Data for **9**: $R_f$ 0.27 (petroleum ether 40-60:ether, 10:1); $\nu_{max}$ (neat)/$cm^{-1}$ 2927m, 2855m, 1730w, 1460m, 1427m, 1360w, 1261w, 1189w, 1110s, 1051m, 973w, 924w, 874w, 821m, 737s and 700s; $[\alpha]_D^{22}$ –6.0 (*c* 0.52 in $CHCl_3$, 25 °C); $\delta_H$ (250 MHz;

$CDCl_3$) 7.72-7.77 (4H, m, Ar), 7.36-7.44 (6H, m, Ar), 5.94-5.96 (1H, m, C*H*=CH), 5.88-5.90 (1H, m, CH=C*H*), 5.78-5.81 (2H, m, C*H*=CH and CH=C*H*), 4.76-4.77 (1H, m, H-1'), 4.27-4.31 (1H, q, *J* 6.6, H-1), 4.10-4.11 (1H, d, *J* 5.7, H-2), 2.40-2.50 (2H, m, ring C$H_2$), 2.09-2.22 (3H, m, ring C$H_2$), 1.80-1.85 (1H, m, ring CH*H*) and 1.09 [9H, s, (C$H_3$)$_3$C]; $\delta_C$ (62.5 MHz; $CDCl_3$) 136.0, 136.0, 135.9, 135.8, 134.8, 134.5, 134.2, 133.4, 131.8, 130.8, 129.6, 127.6, 127.5 and 127.4 (Ar and alkene), 84.2, 80.2 and 73.9 (C-1, C-1' and C-2), 38.7, 31.0, and 30.9 (C-4', C-5' and C-5) and 27.0 and 19.3 [C(C$H_3$)$_3$]; *m/z* (ES) 422 [$(M+NH_4)^+$, 100%]; [Found: $(M+NH_4)^+$, 422.2516. $C_{26}H_{36}NO_2Si$ requires *M*, 422.2515].

***(1R,2S,4Z,8R,9Z)*-2-(N(τ)-methyl urocanic acid)-11-oxabicyclo[6.2.1]undeca-4,9-dien-2-yl ester, 7.**




**7**

Data for **7**: $R_f$ 0.18 ($CH_2Cl_2$:EtOAc:EtOH, 5:5:1); $[\alpha]_D^{25}$ +36.5 (*c* 0.2 in $CHCl_3$); $\nu_{max}$ ($CHCl_3$)/cm$^{-1}$ 3013w, 2921ms, 2850m, 1703s, 1638s, 1542w, 1496w, 1453w, 1383w, 1337w, 1295m, 1271ms, 1163s, 1085m, 1049w, 1002m, 980m, 779m and 749m; $\delta_H$ (500 MHz; $CDCl_3$) 7.60-7.63 (1H, d, *J* 15.7, H-12), 7.44 (1H, s, H-16), 7.08 (1H, s, H-15), 6.60-6.63 (1H, d, *J* 15.7, H-13), 5.84-5.87 (2H, m, H-4 and H-5), 5.52-5.62 (2H, m, H-9 and H-10), 5.20-5.24 (2H, m, H-1 and H-8), 4.98-5.00 (1H, d, *J* 7.3, H-2), 3.69 (3H, s, NMe), 2.69 (1H, brs, ring CH*H*), 1.84-196 (2H, m, ring C$H_2$) and 2.35-2.54 (3H, m, ring C$H_2$); $\delta_C$ (62.5 MHz; $CDCl_3$) 167.2 (C=O), 139.1, 138.7, 136.7, 132.7, 132.3, 128.2, 124.7, 122.2, 116.0 (alkene), 88.6, 70.5, 65.8 (C-1, C-2 and C-8), 33.5 (NMe), 29.7, 21.8 and 15.3 (C-3, C-6 and C-7); *m/z* (CI; $NH_3$) 301 [$(M+H)^+$, 100%] and 249 (20); [*m/z* (ES) Found: $(M+H)^+$, 301.1553. $C_{17}H_{21}N_2O_3$ requires *M*, 301.1552].