Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Electronic Supplementary Information

Synthetic studies towards garsubellin A: Synthesis of model systems and potential mimics by regioselective lithiation of bicyclo[3.3.1]nonane-2,4,9-trione derivatives from catechinic acid

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Compounds prepared using procedure A (Table 1)

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-5-trimethylsilanyl-bicyclo[3.3.1]non-2-en-4-one 19. Colorless oil (46%); $[\alpha]_D^{20}$ +173 (*c* 0.25 in $CHCl_3$); υ_{max} ($CHCl_3$) 2900, 1644, 1612, 1461, 1380, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H, Si(C*H*$_3$)$_3$), 0.65 (m, 21H, OSi(C*H*(C*H*$_3$)$_2$)$_3$), 1.89 (m, 2H, C*H*$_2$), 2.73 (dd, *J* 4.1, 1.6, 1H, 5-C*H*), 2.98 (s, 3H, OC*H*$_3$), 3.05 (dd, *J* 10.4, 4.1, 1H, ArC*H*), 3.32 (s, 3H, OC*H*$_3$), 3.60 (s, 3H, OC*H*$_3$), 3.64 (s, 3H, ArOC*H*$_3$), 3.67 (s, 3H, ArOC*H*$_3$), 4.01 (ddd, *J* 10.4, 10.4, 6.3, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 5.31 (s, 1H, C=C*H*), 6.43 (m, 2H, 2 x Ar*H*), 6.58 (d, *J* 8.7, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 2.8 (CH_3), 12.6 (CH), 17.9 (CH_3), 43.4 (CH_2), 47.9 (CH), 49.6 (CH_3), 50.9 (CH_3), 51.5 (CH), 55.6 (CH_3), 55.8 (CH_3), 56.0 (CH_3), 68.5 (CH), 83.4 (C), 101.5 (C), 101.7 (CH), 110.8 (CH), 112.1 (CH), 120.7 (CH), 129.3 (C), 132.9 (C), 147.9 (C), 148.5 (C), 175.4 (C), 198.6 (C); HRMS (ESI) *m/z* 607.3488 $[M+H]^+$, $[C_{32}H_{55}O_7Si_2]^+$ requires 607.3486.

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-5-Allyl-8-(3,4-dimethoxyphenyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 20. Clear oil (46%); $[\alpha]_D^{30}$ +160 (*c* 0.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2939, 2865, 1730, 1650, 1616, 1462, 1380, 1114, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.74-90 (m, 21H, OSi(C*H*(C*H*$_3$)$_2$)$_3$), 1.79-1.90 (m, 2H, 8-C*H*$_2$), 2.54 (dd, *J* 15.0, 7.2, 1H, C*H*HCH=CH$_2$), 2.67 (dd, *J* 15.0, 7.2, 1H, CH*H*CH=CH$_2$), 2.92 (d, *J* 4.0, 1H, 5-C*H*), 3.11 (dd, *J* 10.6, 4.0, 1H, ArC*H*), 3.22 (s, 3H, OC*H*$_3$), 3.49 (s, 3H, OC*H*$_3$), 3.56 (s, 3H, OC*H*$_3$), 3.83 (s, 3H, ArOC*H*$_3$), 3.85 (s, 3H, ArOC*H*$_3$), 4.22 (ddd, *J* 10.6, 10.6, 5.7, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 4.94 (d, *J* 10.0, 1H, CH*H*=CH), 5.01 (d, *J* 17.1, 1H, C*H*H=CH), 5.55 (s, 1H, C=C*H*), 6.10 (ddt, *J* 17.1, 10.0, 7.2, 1H, CH$_2$=C*H*CH$_2$), 6.61 (br s, 1H, Ar*H*), 6.65 (d, *J* 8.2, 1H, Ar*H*), 6.78 (d, *J* 8.2, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH), 17.6 (CH_3), 18.1 (CH_3), 37.1 (CH_2), 41.9 (CH_2), 48.2 (CH), 50.1 (CH_3), 50.7 (CH), 50.7 (CH_3), 55.5 (CH_3), 55.8 (CH_3), 56.0 (CH_3), 56.9 (C), 68.7 (CH), 103.5 (CH), 103.9 (C), 110.8 (CH), 111.9 (CH), 115.2

(CH_2), 120.9 (CH), 133.2 (C), 136.9 (CH), 147.9 (C), 148 (C), 174.9 (C), 200.7 (C); HRMS (ES) *m/z* 575.3404 $[M+H]^+$, $[C_{32}H_{51}O_7Si]^+$ requires 575.3405.

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-5-Benzyl-8-(3,4-dimethoxyphenyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 21. Clear oil (56%); $[\alpha]_D^{22}$ +115 (*c* 1.0 in $CHCl_3$);); υ_{max} ($CHCl_3$) 2940, 2865, 1730, 1650, 1616, 1462, 1379, 1100, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.58-0.88 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.48 (dd, *J* 12.0, 5.4, 1H, 8-CH*H*), 1.65-1.74 (m, 1H, 8-C*H*H), 3.00 (d, *J* 10.4, 3.7, 1H, ArC*H*), 3.04 (d, *J* 3.7, 1H, 5-C*H*), 3.19 (d, *J* 13.7, 1H, PhCH*H*), 3.28 (d, *J* 13.7, 1H, PhC*H*H), 3.32 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.83 (s, 3H, ArOCH_3), 3.85 (s, 3H, ArOCH_3), 4.20 (ddd, *J* 10.4, 10.4, 5.4, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.57 (s, 1H, C=C*H*), 6.58-6.60 (m, 1H, Ar*H*), 6.64 (d, *J* 8.3, 1H, Ar*H*), 6.75 (dd, *J* 8.3, 0.84, 1H, Ar*H*), 7.14 (t, *J* 7.0, 1H, Ar*H*), 7.22 (dd, *J* 8.0, 7.0, 2H, Ar*H*, Ar*H*), 7.45 (d, *J* 8.0, 2H, Ar*H*, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2 (CH), 18.0 (CH_3), 35.4 (CH_2), 40.9 (CH_2), 48.0 (CH), 49.2 (CH_3), 49.5 (CH), 52.4 (CH_3), 55.6 (CH_3), 55.7 (CH_3), 55.9 (CH_3), 57.4 (c), 68.8 (CH), 103.5 (C), 103.7 (CH), 110.8 (CH), 111.8 (CH), 121.0 (CH), 125.6 (CH), 127.4 (CH), 131.8 (CH), 133.1 (C), 139.2 (C), 147.9 (C), 148.4 (C), 174.7 (C), 201.3 (C); HRMS (ES) *m/z* 625.3539 $[M+H]^+$, $[C_{36}H_{53}O_7Si]^+$ requires 625.3561.

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-5-methyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 22. Yellow oil (48%); $[\alpha]_D^{23}$ +123 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 2941, 2866, 1650, 1462, 1374, 1103, 1061, 882 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78-0.90 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.44 (s, 3H, CH_3), 1.79-1.90 (m, 2H, CH_2), 2.92 (d, *J* 4.1, 1H, 5-C*H*), 3.17 (dd, *J* 10.5, 4.1, 1H, ArC*H*), 3.19 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.84 (s, 3H, ArOCH_3), 3.86 (s, 3H, ArOCH_3), 4.22 (dd, *J* 10.5, 10.5, 5.8, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.52 (s, 1H, C=C*H*), 6.62 (d, *J* 1.8, 1H, Ar*H*), 6.65 (dd, *J* 8.2, 1.8, 1H, Ar*H*), 6.78 (d, *J* 8.2, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1 (CH), 16.7 (CH_3), 16.8 (CH_3), 42.1 (CH_2), 46.9 (CH), 48.7 (CH_3), 48.8

(CH_3), 49.3 (CH), 52.6 (C), 53.9 (CH_3), 54.2 (CH_3), 54.5 (CH_3), 67.0 (CH), 101.1 (C), 101.5 (CH), 109.4 (CH), 110.6 (CH), 119.4 (CH), 131.9 (C), 146.4 (C), 147.0 (C), 173.5 (C), 199.8 (C); HRMS (ES) *m/z* 549.3259 $[M+H]^+$, $[C_{30}H_{49}O_7Si]^+$ requires 549.3248.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-dimethoxyphenyl)-5-(hydroxyphenylmethyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 23. Less polar diastereoisomer; clear oil (26%): $[\alpha]_D^{22}$ +131 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 3494, 2942, 1614, 1462, 1382, 1109, 1053, 882 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.64-0.79 (m, 21H, OSi((C*H*(CH_3)$_2$)$_3$), 1.82-1.84 (m, 2H, CH_2), 2.98 (dd, *J* 10.3, 3.9, 1H, ArC*H*), 3.11 (d, *J* 3.9, 1H, 5-C*H*), 3.32 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.82 (s, 3H, ArOCH_3), 3.85 (s, 3H, ArOCH_3), 4.14-4.19 (m, 1H, C*H*OSi((CH(CH_3)$_2$)$_3$), 4.67 (br s, 1H, O*H*), 5.39 (s, 1H, C*H*OH), 5.62 (s, 1H, C=C*H*), 6.56 (d, *J* 1.9, 1H, Ar*H*), 6.61 (dd, *J* 8.2, 1.9, 1H, Ar*H*), 6.77 (d, *J* 8.2, 1H, Ar*H*), 7.21 (t, *J* 7.4, 1H, Ar*H*), 7.29 (dd, *J* 7.7, 7.4, 2H, 2 x Ar*H*), 7.51 (d, *J* 7.7, 2H, 2 x Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5 (CH), 17.8 (CH_3), 18.0 (CH_3), 37.9 (CH_2), 48.2 (CH), 48.3 (CH), 49.3 (CH_3), 52.9 (CH_3), 55.8 (CH_3), 55.8 (CH_3), 60.3 (C), 68.8 (CH), 73.9 (CH), 104.1 (C), 104.7 (CH), 110.8 (CH), 111.7 (CH), 120.9 (CH), 126.8 (CH), 127.2 (CH), 128.7 (CH), 132.7 (C), 141.9 (C), 148.0 (C), 148.5 (C), 175.3 (C), 202.2 (C); HRMS (ES) *m/z* 663.3335 $[M + Na]^+$, $[C_{36}H_{52}NaO_8Si]^+$ requires 663.3324; more polar distereosiomer; clear oil (26%); $[\alpha]_D^{20}$ +155 (*c* 1.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2866, 1652, 1619, 1115, 1048, 1028, 882 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.79-0.87 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.87-1.94 (m, 1H, CH*H*), 2.21 (dd, *J* 12.0, 5.4, 1H, C*H*H), 2.95 (dd, *J* 10.3, 3.9, 1H, ArC*H*), 3.17 (d, *J* 3.9 1H, 5-C*H*), 3.27 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.82 (s, 3H, ArOCH_3), 3.85 (s, 3H, ArOCH_3), 4.23 (ddd, *J* 10.3, 10.3, 5.4, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.26 (s, 1H, C*H*OH), 5.73 (s, 1H, C=C*H*), 6.57 (s, 1H, Ar*H*), 6.61 (d, *J* 8.2, 1H, Ar*H*), 6.78 (d, *J* 8.2, 1H, Ar*H*), 7.17-7.20 (m, 1H, Ar*H*), 7.24-7.27 (m, 2H, 2 x Ar*H*), 7.33-7.35 (m, 2H,

2 x Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 18.0 (CH_3), 40.3 (CH_3), 46.9 (CH), 48.5 (CH), 49.1 (CH_3), 53.4 (CH_3), 55.8 (CH_3), 55.8 (CH_3), 56.0 (CH_3), 59.8 (C), 68.7 (CH), 77.7 (CH), 104.8 (CH), 106.1(C), 110.0 (CH), 111.9 (CH), 120.9 (CH), 126.5 (CH), 126.7 (CH), 128.4 (CH), 132.6 (C), 143.3 (C), 148.2 (C), 148.6 (C), 174.1 (C), 200.0 (C); HRMS (ES) *m/z* 663.3324 $[M + H]^+$, $[C_{36}H_{52}O_8Si]^+$ requires 663.3329.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-5-(1*R*/*S*)-(1-hydroxy-2-methylpropyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 24. A Yellow oil (31%); $[\alpha]_D^{22}$ +151 (*c* 0.8 in $CHCl_3$); υ_{max} ($CHCl_3$) 3414 (br), 2940, 1730, 1614, 1592, 1462, 1382, 1305, 1106, 1028, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.90 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.01 (d, *J* 7.0, 3H, CH(C*H*$_3$)$_2$), 1.02 (d, *J* 7.0, CH(C*H*$_3$)$_2$), 1.92-1.96 (m, 1H, CH*H*), 2.56 (m, 1H, C*H*(CH_3)$_2$), 2.83 (dd, *J* 12.4, 5.2, 1H, C*H*H), 3.00 (d, *J* 4.4, 1H, 5-C*H*), 3.18 (s, 3H, OC*H*$_3$), 3.22 (dd, *J* 10.8, 4.4, 1H, ArC*H*), 3.45 (s, 3H, OC*H*$_3$), 3.55 (s, 3H, OC*H*$_3$), 3.78 (dd, *J* 10.4, 2.0, 1H, C*H*(OH)), 3.83 (s, 3H, ArOC*H*$_3$), 3.85 (s, 3H, ArOC*H*$_3$), 4.14 (ddd, *J* 10.8, 10.8, 5.2, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.09 (d, *J* 10.4, 1H, CHO*H*), 5.53 (s, 1H, C=C*H*), 6.61 (d, *J* 1.8, Ar*H*), 6.64 (dd, *J* 8.2, 1.8, 1H, Ar*H*), 6.78 (d, *J* 8.2, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0 (CH), 18.0 (CH_3), 22.4 (CH_3), 29.5 (CH), 40.5 (CH_2), 48.6 (CH), 50.1 (CH_3), 50.7 (CH), 51.8 (CH_3), 55.6 (CH_3), 55.8 (CH_3), 56.0 (CH_3), 58.3 (C), 68.3 (CH), 81.3 (CH), 104.1 (CH), 110.9 (CH), 112.1 (CH), 120.8 (CH), 133.1 (C), 148.0 (C), 148.5 (C), 175.5 (C), 205.3 (C); HRMS (ES) *m/z* 607.3698 $[M + H]^+$, $[C_{33}H_{55}O_8Si]^+$ requires 607.3666.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-5-phenylsulfanyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 25. Pale oil (67%); $[\alpha]_D^{22}$ +126 (*c* 0.6 in $CHCl_3$); υ_{max} ($CHCl_3$) 2941, 1731, 1617, 1462, 1374, 1128, 1046 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.50-0.75 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.75 (dd, *J* 12.0, 6.0, 1H, CH*H*), 1.78-1.82 (m, 1H, C*H*H), 2.96 (dd, *J* 4.4, 1H, 5-C*H*), 3.24 (s, 3H, OC*H*$_3$), 3.26 (dd, *J* 10.4, 4.4, 1H, ArC*H*), 3.54 (s, 3H, OC*H*$_3$), 3.81 (s, 3H,

OCH_3), 3.83 (s, 3H, ArOCH_3), 3.84 (s, 3H, ArOCH_3), 4.13 (ddd, *J* 10.4, 10.4, 6.0, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.61 (s, 1H, C=C*H*), 6.59 (d, *J* 2.0, 1H, Ar*H*), 6.60 (dd, *J* 8.4, 2.0, 1H, Ar*H*), 6.75 (d, *J* 8.4, 1H, Ar*H*), 7.21-7.23 (m, 3H, 3 x SPh*H*), 7.76-7.78 (m, 2H, 2 x SPh*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4 (CH), 17.7 (CH_3), 41.0 (CH_2), 48.3 (CH), 50.3 (CH_3), 52.0 (CH), 52.2 (CH_3), 55.7 (CH_3), 55.8 (CH_3), 55.9 (CH_3), 66.1 (C), 69.2 (CH), 102.9 (C), 103.2 (CH), 110.9 (CH), 112.0 (CH), 120.7 (CH), 128.1 (CH), 128.4 (CH), 131.5 (C), 132.8 (C), 137.7 (CH), 148.0 (C), 148.5 (C), 174.5 (C), 198.0 (C); HRMS (ES) *m/z* 643.3098 $[M + H]^+$, $[C_{35}H_{51}O_7Ssi]^+$ requires 643.3125.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-5-tributylstannyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 26. Clear oil (63%); $[\alpha]_D^{18}$ +96 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 2866, 1613, 1517, 1104, 1069, 1028, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70-0.99 (m, 27H, OSi(C*H*(CH_3)$_2$)$_3$), Sn(CH_2CH$_2$CH$_2$CH$_3$)$_3$), 1.24-1.69 (m, 21H, Sn(CH$_2$CH_2CH_2CH_3)$_3$), 2.21 (m, 2H, *CH*$_2$), 3.01 (dd, *J* 10.3, 3.9, 1H, ArC*H*), 3.18 (d, *J* 3.9, 1H, 5-C*H*), 3.29 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.83 (s, 3H, ArOCH_3), 3.86 (s, 3H, ArOCH_3), 4.19 (ddd, *J* 10.3, 10.3, 5.8, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 5.52 (s, 1H, C=C*H*), 6.61 (d, *J* 1.6, 1H, Ar*H*), 6.66 (dd, *J* 1.6, 8.0, 1H, Ar*H*), 6.79 (d, *J* 8.0, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0 (CH_2), 12.4 (CH), 13.8 (CH_3), 17.9 (CH_3), 18.0 (CH_3), 26.8 (CH_2), 29.1 (CH_2), 39.4 (CH_2), 47.0 (CH), 49.1 (CH), 53.1 (CH_3), 55.5 (CH_3), 55.8 (CH_3), 56.0 (CH_3), 58.6 (C), 69.2 (CH), 104.1 (C), 104.1 (CH), 111.0 (CH), 111.9 (CH), 121.0 (CH), 133.8 (C), 148.0 (C), 148.5 (C), 174.7 (C), 203.1 (C); HRMS (ESI) *m/z* 847.3972 $[M+Na]^+$, $[C_{41}H_{72}NaO_7SiSn]^+$ requires 847.3962.

Compounds prepared using procedure B (Table 2)

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-3-methyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 32. Clear viscous oil (36%); $[\alpha]_D^{20}$ +76 (*c* 0.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2961, 1713, 1356, 1090, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75-0.90 (m,

21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.78 (s, 3H, CH_3), 1.83-1.91 (m, 1H, CH*H*), 2.15 (ddd, *J* 12.6, 9.2, 5.5, 1H, C*H*H), 2.91 (s, 3H, OCH_3), 2.91-2.94 (m, 1H, 1-C*H*), 3.10 (s, 3H, OCH_3), 3.17 (dd, *J* 10.5, 4.0, 1H, ArC*H*), 3.26-3.29 (m, 1H, 5-C*H*), 3.32 (s, 3H, OCH_3), 3.84 (s, 3H, ArOCH_3), 3.86 (s, 3H, ArOCH_3), 4.19 (ddd, *J* 10.5, 10.5, 5.5, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 6.72 (d, *J* 1.8, 1H, Ar*H*), 6.76 (dd, *J* 8.2, 1.8, 1H, Ar*H*), 6.81 (d, *J* 8.2, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.3 (CH_3), 12.6 (CH), 17.9 (CH_3), 18.0 (CH_3), 43.6 (CH_3), 47.2 (CH_3), 48.5 (CH_3), 48.6 (CH), 49.2 (CH), 54.7 (CH_3), 55.6 (CH_3), 56.0 (CH_3), 68.1 (CH), 101.1 (C), 111.1 (CH), 112.0 (CH), 116.1 (C), 121.0 (CH), 132.8 (C), 148.2 (C), 148.7 (C), 169.9 (C), 198.1 (C); HRMS (ES) *m/z* 549.3242 $[M+H]^+$, $[C_{30}H_{48}O_7Si]^+$ requires 549.3247.

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-3-Benzoyl-8-(3,4-dimethoxyphenyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 33. Pale yellow solid (60mg, 50%); $[\alpha]_D^{20}$ +191 (*c* 0.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2943, 1647, 1646, 1602, 1370, 1112, 1100, 1059, 1026, 882, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79-0.94 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.89-1.98 (m, 1H, CH*H*), 2.22 (ddd, *J* 12.7, 9.2, 5.6, 1H, C*H*H), 2.99-3.03 (m, 1H, 1-C*H*), 3.11 (s, 3H, OCH_3), 3.19-3.26 (m, 2H, 5-C*H*, ArC*H*), 3.29 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.86 (s, 3H, ArOCH_3), 3.92 (s, 3H, ArOCH_3), 4.54 (ddd, *J* 10.6, 10.6, 5.6, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 6.80-6.91 (m, 3H, 3 x Ar*H*), 7.46 (t, *J* 7.7, 2H, 2 x Ar*H*), 7.54 (t, 7.0, 1H, Ar*H*), 7.91 (d, *J* 7.3, 2H, 2 x Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 18.0 (CH_3), 34.3 (CH_2), 47.5 (CH_3), 47.8 (CH), 48.6 (CH_3), 49.0 (CH), 49.5 (CH), 55.9 (CH_3), 56.0 (CH_3), 57.3 (CH_3), 67.9 (CH), 101.3 (C), 111.1 (CH), 111.1 (CH), 120.6 (CH), 121.4 (C), 128.6 (CH), 129.3 (CH), 132.7 (C), 133.3 (CH), 137.6 (C), 148.2 (C), 148.9 (C), 173.0 (C), 195.0 (C), 196.9 (C); HRMS (ES) *m/z* 639.3348 $[M+H]^+$, $[C_{36}H_{51}O_8Si]^+$ requires 639.3353.

(1*S*, 5*S*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-2,9,9-trimethoxy-3-tri-*tert*-butylstannanyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 34. Clear oil (61%); $[\alpha]_D^{24}$ +121 (*c* 1.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2932, 2867, 1710, 1627, 1568, 1463, 1361, 1108, 882 cm^{-1}; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 0.75-1.01 (m, 33H, OSi(C*H*(CH_3)$_2$)$_3$), Sn(CH_2CH_2CH_2CH_3)$_3$), 1.25-1.36 (m, 9H, Sn($CH_2CH_2CH_2CH_3$)$_3$), 1.45-1.54 (m, 6H, Sn($CH_2CH_2CH_2CH_3$)$_3$), 1.81-1.86 (m, 1H, CH*H*), 2.12 (ddd, *J* 12.0, 9.0, 5.4, 1H, C*H*H), 2.83 (s, 3H, OCH_3), 2.84-2.89 (m, 1H, 1-C*H*), 3.04 (s, 3H, OCH_3), 3.14 (dd, *J* 10.2, 3.8, 1H, ArC*H*), 3.23 (dd, *J* 3.8, 2.4, 1H, 5-C*H*), 3.32 (s, 3H, OCH_3), 3.85 (s, 3H, ArOCH_3), 3.86 (s, 3H, ArOCH_3), 4.24 (ddd, *J* 10.2, 10.2, 5.4, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 6.76-6.83 (m, 3H, 3 x Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9 (CH), 12.3 (CH), 13.8 (CH_3), 17.9 (CH_3), 18.1 (CH_3), 27.4 (CH_2), 29.1 (CH_2), 34.1 (CH_2), 44.5 (CH), 47.3 (CH_3), 48.4 (CH), 48.5 (CH_3), 49.6 (CH), 54.3, CH_3), 55.8 (CH_3), 56.0 (CH_3), 68.5 (CH), 102.0 (C), 111.2 (CH), 111.3 (CH), 119.0 (C), 133.1 (C), 148.2 (C), 148.8 (C), 180.0 (C), 202.0 (C); HRMS (ES) *m/z* 847.3961 $[M+Na]^+$ $[C_{41}H_{72}NaO_7SiSn]^+$ requires 847.3967.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-5,3-Dibenzoyl-8-(3,4-dimethoxyphenyl)-2,9,9-trimethoxy-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-2-en-4-one 35. A solution of LTMP was prepared by adding ^{n}BuLi (1.18 mL, 1.86 mmol, 1.6M solution in hexanes) to tetramethylpiperidine (0.38 mL, 1.86 mmol, 10 eq.) in THF (2 mL) at −78 °C. The solution was allowed to warm to RT and after 10 min re-cooled to −78 °C. This LTMP/THF solution was added dropwise *via* syringe to a solution of bridged ketone **16** (100 mg, 0.19 mmol) in THF (1 mL) at −78 °C resulting in a deep yellow-coloured solution. The solution was stirred at −78 °C for 3 h, followed by addition of benzoyl chloride (0.22 mL, 1.88 mmol, 10 eq.) and stirring for a further 3 h at −78 °C. The reaction mixture was quenched after this period with H_2O (5 mL) followed by extraction with EtOAc (3 x 5 mL). The organic layers were combined and washed with saturated aqueous NaCl (5 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification by column chromatography (petroleum ether-EtOAc 4:1) gave the title compound **35** as a pale yellow solid (77 mg, 55%); $[\alpha]_D^{20}$ +161 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 2944, 2866, 1672, 1643, 1605, 1462, 1368, 1133, 1087, 1052, 882 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82-0.98 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 2.39 (dd, *J* 13.0, 5.6, 1H, CH*H*), 2.55-2.61 (m, 1H, C*H*H), 3.19 (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3), 3.23

(s, 3H, OCH_3), 3.36 (d, *J* 4.5, 1H, 5-C*H*), 3.45 (dd, *J* 10.5, 4.5, 1H, ArC*H*), 3.86 (br s, 6H, ArOCH_3), 4.55 (td, *J* 10.5, 10.5, 5.6, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 6.81 (d, *J* 8.2, 1H, Ar*H*), 6.91-6.92 (m, 2H, Ar*H*, Ar*H*), 7.20-7.25 (m, 2H, Ar*H*, Ar*H*), 7.36-7.74 (m, 1H, Ar*H*), 7.50-7.55 (m, 2H, Ar*H*, Ar*H*), 7.59-7.64 (m, 1H, Ar*H*), 7.84-7.88 (m, 2H, Ar*H*, Ar*H*), 8.02-8.06 (m, 2H, Ar*H*, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 39.8 (CH_2), 49.0 (CH_3), 49.1 (CH), 49.7 (CH), 50.1 (CH_3), 55.9 (CH_3), 56.0 (CH_3), 57.4 (CH_3), 67.6 (CH), 68.6 (C), 103.1 (C), 111.2 (CH),120.1 (CH), 121.5 (C), 127.1 (CH), 128.6 (CH), 129.3 (CH), 130.7 (CH), 130.9 (CH), 131.8 (CH), 132.4 (C), 133.6 (CH), 137.7 (C), 137.7 (C), 148.2 (C), 149.0 (C), 172.8 (C), 194.5 (C), 196.1 (C), 199.3 (C); HRMS (ES) *m/z* 743.3610 $[M+H]^+$, $[C_{43}H_{55}O_9Si]^+$ requires 743.3615.

(1*R*, 5*R*, 7*S*, 8*R*)-(-)-8-(3,4-Dimethoxyphenyl)-4,9,9-trimethoxy-7-triisopropylsilanyloxy-3-trimethylsilanyl-bicyclo[3.3.1]non-3-en-2-one 36. According to procedure A. Clear oil (31%); $[\alpha]_D^{30}$ –40 (*c* 0.4 in $CHCl_3$);); υ_{max} ($CHCl_3$) 2869, 1661, 1540, 1469, 1376, 1149, 1110, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.22 (s, 9H, Si(CH_3)$_3$), 0.72-0.94 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 2.00-2.02 (m, 2H, CH_2), 2.86 (dd, *J* 3.9, 1H, 5-C*H*), 3.00 (dd, *J* 10.8, 3.9, 1H, ArC*H*), 3.12 (s, 3H, OCH_3), 3.17-3.20 (m, 1H, 1-C*H*), 3.32 (s, 3H, OCH_3), 3.83 (s, 9H, OCH_3), 4.32-4.38 (m, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 6.55-6.57 (m, 2H, 2 x Ar*H*), 6.73 (d, *J* 8.1, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.78 (CH_3), 12.6 (CH), 17.9 (CH_3), 19.1 (CH_3), 32.3 (CH_2), 37.7 (CH), 47.1 (CH_3), 48.6 (CH_3), 50.2 (CH), 54.9 (CH_3), 55.9 (CH_3), 57.5 (CH), 68.7 (CH), 100.7 (C), 110.8 (CH), 112.8 (CH), 117.4 (C), 121.5 (CH), 132.6 (C), 147.8 (C), 148.4 (C), 179.9 (C), 200.3 (C); HRMS (ES) *m/z* 607.3479 $[M+H]^+$, $[C_{32}H_{55}O_7Si_2]^+$ requires 607.3486.

(1*R*, 5*R*, 7*S*, 8*R*)-(-)-8-(3,4-Dimethoxyphenyl)-4,9,9-trimethoxy-3-methyl-7-triisopropylsilanyloxy-bicyclo[3.3.1]none-3-en-2-one 37. According to procedure A. Clear viscous oil (60%); $[\alpha]_D^{22}$ –40 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 2940, 1651, 1623, 1462, 1380, 1357, 1101, 1028, 882 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70-0.90 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.79 (s, 3H, CH_3), 1.97-2.09

(m, 2H, CH_2), 2.96 (dd, *J* 4.2, 2.2, 1H, 5-C*H*), 3.02 (dd, *J* 10.5, 4.2, 1H, ArC*H*), 3.10 (s, 3H, CH_3), 3.18-3.22 (m, 1H, 1-C*H*), 3.32 (s, 3H, OCH_3), 3.81 (br s, 6H, ArOCH_3), 3.87 (s, 3H, OCH_3), 4.26 (ddd, *J* 10.5, 10.5, 5.2, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 6.51 (br s, 1H, Ar*H*), 6.53 (d, *J* 1.9, 1H, Ar*H*), 6.74 (d, *J* 7.9, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.46 (CH_3), 12.6 (CH), 17.9 (CH_3), 18.0 (CH_3), 31.9 (CH_2), 37.4 (CH), 47.1 (CH_3), 48.6 (CH_3), 50.0 (CH), 55.4 (CH_3), 55.6 (CH_3), 55.8 (CH_3), 56.4 (CH), 68.7 (CH), 100.5 (C), 110.9 (CH), 112.7 (CH), 116.2 (CH), 121.2 (C), 132.4 (C), 147.8 (C), 148.2 (C), 168.8 (C), 197.0 (C); HRMS (ES) *m/z* 549.3248 $[M+H]^+$, $[C_{30}H_{49}O_7Si]^+$ requires 549.3248.

(1*R*, 5*R*, 7*S*, 8*R*)-(+)-8-(3,4-Dimethoxyphenyl)-4,9,9-trimethoxy-3-(preny)-7-triisopropylsilanyloxy-bicyclo[3.3.1]non-3-en-2-one 38. According to procedure A. Yellow oil (25%); $[\alpha]_D^{30}$ +11 (*c* 0.9 in $CHCl_3$); υ_{max} ($CHCl_3$) 2940, 1670, 1630, 1469, 1349, 1111, 1035, 890 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.69 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.98-2.04 (m, 1H, 6-CH*H*), 2.05-2.10 (m, 1H, 6-C*H*H), 2.92-2.97 (m, 2H, CH_2CH=C(CH_3)$_2$), 3.00 (dd, *J* 10.6, 4.1, 1H, ArC*H*), 3.11 (s, 3H, OCH_3), 3.15-3.22 (m, 2H, 1-C*H*, 5-C*H*), 3.3 (s, 3H, OCH_3), 3.80 (s, 3H, ArOCH_3), 3.82 (s, 3H, ArOCH_3), 3.88 (s, 3H, OCH_3), 4.33 (ddd, *J* 10.6, 10.6, 5.5, 1H, C*H*OSi(CH(CH_3)$_2$)$_3$), 5.17 (t, *J* 7.0, 1H, C*H*=C(CH_3)$_2$), 6.53-6.57 (m, 2H, 2 x Ar*H*), 6.70 (d, *J* 8.7, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 17.8 (CH_3), 18.0 (CH_3), 21.4 (CH_2), 25.7 (CH_3), 32.5 (CH_2), 37.1 (CH), 47.1 (CH_3), 48.5 (CH_3), 50.3, (CH), 55.2 (CH_3), 55.7 (CH_3), 55.9 (CH_3), 56.5 (CH), 68.5 (CH), 100.6 (C), 110.9 (CH), 113.0 (CH), 120.6 (C), 121.6 (CH), 122.2 (CH), 131.7 (C), 132.6 (C), 147.8 (C), 148.3 (C), 168.4 (C), 196.0 (C); HRMS (ES) *m/z* 603.3711 $[M+H]^+$, $[C_{34}H_{55}O_7Si]^+$ requires 603.3717.

(1*R*, 3*S*, 8*R*, 9*R*, 10*S*)-(+)-9-(3,4-Dimethoxy-phenyl)-3-(1-hydroxy-1-methyl-ethyl)-12,12-dimethoxy-10-triisopropylsilanyloxy-4-oxa-tricyclo[6.3.1.0$^{1.5}$]dodec-5-en-7-ones 39 and (1*R*, 3*R*, 8*R*, 9*R*, 10*S*)-(-)-9-(3,4-Dimethoxy-phenyl)-3-(1-hydroxy-1-methyl-ethyl)-12,12-dimethoxy-10-

triisopropylsilanyloxy-4-oxa-tricyclo[6.3.1.0^{1,5}]dodec-5-en-7-ones 40. Dimethyldioxirane (15 mL, 0.05 M in acetone) was added to substrate **18** (180 mg, 0.29 mmol) in CH_2Cl_2 (4 mL) at 0 °C and the reaction mixture was stirred at 0 °C for 3.5 h. $MgSO_4$ was then added to the solution which was filtered, then concentrated *in vacuo*. The crude orange oil was re-dissolved in CH_2Cl_2 (4 mL), cooled to 0 °C, then trimethylsilyl chloride (0.045 ml, 1.2 eq.) added and the reaction mixture was further stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl (6 mL), the organic layer was separated and washed with saturated NaCl (8 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a 2:1 mixture of diastereoisomers. Purification by column chromatography (EtOAc-petroleum ether 1:9) gave firstly **40** as a white solid (115 mg, 66%); mp 82-85 °C; $[\alpha]_D^{18}$ –0.6 (*c* 1.0 in $CHCl_3$); υ_{max} ($CHCl_3$) 2865, 1632, 1578, 1184, 1088, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.25 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.80 (m, 2H, 11-CH*H, 2-CH*H), 2.49 (dd, *J* 13.1, 5.5, 1H, 11-CH*H*), 2.83 (dd, *J* 12.3, 10.5, 1H, 2-C*H*H), 2.97 (dd, *J* 4.3, 0.8, 1H, 8-C*H*), 3.17 (s, 3H, OCH_3), 3.28 (dd, *J* 10.8, 4.3, 1H, ArC*H*), 3.35 (s, 3H, OCH_3), 3.82 (s, 3H, ArOCH_3), 3.84 (s, 3H, ArOCH_3), 4.32 (m, 2H, C*H*OSi(CH(CH$_3$)$_2$)$_3$, C*H*C(CH$_3$)$_2$OH), 5.72 (s, 1H, C=CH), 6.63 (m, 2H, Ar*H*, Ar*H*), 6.76 (d, *J* 8.0, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 18.1 (CH_3), 25.7 (CH_3), 27.2 (CH_3), 30.0 (CH_2), 40.2 (CH_2), 49.2 (CH_3), 49.4 (CH), 53.0 (C), 55.7 (CH_3), 56.0 (CH_3), 57.7 (CH), 69.7 (CH), 70.8 (C), 91.0 (CH), 101.6 (CH), 103.4 (CH), 110.9 (CH), 113.2 (CH), 121.3 (C), 132.2 (C), 147.9 (C), 148.4 (C), 181.5 (C), 197.1 (C); HRMS (ES) *m/z* 605.3504 $[M+H]^+$, $[C_{33}H_{53}O_8Si]^+$ requires 605.3509; and secondly **39** as a clear oil (47 mg, 27%); $[\alpha]_D^{22}$ +27 (*c* 1.65 in CH_2Cl_2); υ_{max} ($CHCl_3$) 831, 968, 1028, 1053, 1088, 1518, 1632, 1711, 2865, 2921 3583 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.94 (m, 21H, OSi(C*H*(CH_3)$_2$)$_3$), 1.25 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.75 (dd, *J* 12.0, 5.6, 1H, 2-CH*H*), 1.95 (dd, *J* 12.8, 10.7, 1H, 11-CH*H*), 2.10 (dd, *J* 12.8, 5.6, 1H, 11-C*H*H), 2.74-2.82 (m, 1H, 2-C*H*H), 2.97 (d, *J* 4.4, 1H, 8-C*H*), 3.16 (s, 3H, OCH_3), 3.29 (dd, *J* 10.7, 4.4, 1H, ArC*H*), 3.35 (s, 3H, OCH_3), 3.82 (s, 3H, ArOCH_3), 3.85 (s, 3H, ArOCH_3), 4.39 (ddd, *J* 10.7, 10.7, 5.6, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 4.49 (dd, *J* 10.7, 5.6, 1H, C*H*(CH$_3$)$_2$OH), 5.68 (s, 1H, C=C*H*),

6.62 (d, *J* 1.9, 1H, Ar*H*), 6.65 (dd, *J* 8.2, 1.9, 1H, Ar*H*), 6.78 (d, *J* 8.2, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6 (CH), 17.9 (CH_3), 18.1 (CH_3), 24.1 (CH_3), 26.7 (CH_3), 31.4 (CH_2), 38.0 (CH_2), 49.1 (CH_3), 49.8 (CH), 53.9 (C), 55.7 (CH_3), 55.9 (CH_3), 57.5 (CH), 69.1 (CH), 71.2 (C), 90.2 (CH), 100.7 (C), 101.8 (CH), 110.8 (CH), 113.0 (CH), 121.1 (CH), 132.1 (C), 147.9 (C), 148.3 (C), 181.2 (C), 197.1 (C); HRMS (ES) *m/z* 604.3433 $[M]^+$, $[C_{33}H_{52}O_8Si]^+$ requires 604.3431.

(1*R*, 3*S*, 8*R*, 9*R*, 10*S*)-(-)-9-(3,4-Dimethoxyphenyl)-12,12-dimethoxy-3-(1-methyl-1-trimethylsilanyloxyethyl)-10-triisopropylsilanyloxy-4-oxa-tricyclo [6.3.1.0$^{1.5}$]dodec-5-en-7-one 41 and (1*R*, 3*R*, 8*R*, 9*R*, 10*S*)-(+)-9-(3,4-Dimethoxyphenyl)-12,12-dimethoxy-3-(1-methyl-1-trimethylsilanyloxyethyl)-10-triisopropylsilanyloxy-4-oxa-tricyclo [6.3.1.0$^{1.5}$]dodec-5-en-7-one 42. Imidazole (110 mg, 10 eq.), DMAP (6 mg, 10 mol %), and trimethylsilyl chloride (0.10 mL, 0.81 mmol, 5 eq.) were added to a solution of tricyclic compounds **39** and **40** (98 mg, 0.16 mmol, 1:2 diastereoisomeric mixture) in DMF (0.5 mL) at 0 °C was added respectively. The reaction mixture was stirred for 2 h at 0 °C after which time the reaction was complete by TLC. Purification by column chromatography (10% EtOAc in petroleum ether) afforded firstly title compound **42** as a clear oil (70 mg, 65%); $[\alpha]^{22}_D$ +57 (*c* 1.25 in $CHCl_3$); υ_{max} ($CHCl_3$) 2927, 1736, 1628, 1604, 1369, 1112, 1057, 998, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H, Si(C*H*$_3$)$_3$), 0.81 (m, 21H, OSi(C*H*(C*H*$_3$)$_2$)$_3$), 1.32 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.74 (dd, *J* 12.8, 6.3, 1H, 2-CH*H*), 1.87 (dd, *J* 12.9, 10.2, 1H, 11-CH*H*), 2.16 (dd, J 12.9, 5.6, 1H, 11-C*H*H), 2.77 (dd, *J* 12.8, 10.1, 1H, 2-C*H*H), 2.96 (dd, *J* 4.3, 0.8, 1H, 8-C*H*), 3.16 (s, 3H, OC*H*$_3$), 3.29 (dd, *J* 10.8, 4.3, 1H, ArC*H*), 3.37 (s, 3H, OC*H*$_3$), 3.83 (s, 3H, ArOC*H*$_3$), 3.84 (s, 3H, ArOC*H*$_3$), 4.18 (dd, *J* 10.1, 6.3, 1H, C*H*C(CH$_3$)$_2$OSi), 4.35 (ddd, *J* 10.2, 10.2, 5.6, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 5.70 (d, *J* 0.9, 1H, C=C*H*), 6.68 (m, 2H, 2 x ArH), 6.76 (d, *J* 8.0, 1H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 2.5 (CH_3), 12.7 (CH), 18.0 (CH_3), 18.1 (CH_3), 25.4 (CH_3), 27.4 (CH_3), 30.1 (CH_2), 41.3 (CH_2), 49.2 (CH_3), 49.3 (CH_3), 49.5 (CH), 52.8 (C), 55.7 (CH_3), 55.9 (CH_3), 57.6 (CH), 69.7 (CH), 73.5 (C), 91.5 (CH), 101.7 (C), 101.7 (CH), 103.7 (CH), 110.9 (CH), 113.2 (CH), 132.2 (C),

147.9 (C), 148.4 (C), 181.6 (C), 197.0 (C); HRMS (ES) *m/z* 677.3905 $[M+H]^+$, $[C_{36}H_{60}O_8Si_2]^+$ requires 677.3905; and then title compound **41** as a clear oil (33 mg, 30%); $[\alpha]_D^{22}$ –10 (*c* 1.75 in $CHCl_3$); υ_{max} ($CHCl_3$) 2865, 1730, 1631, 1462, 1137, 1047, 883 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9H, Si(C*H*$_3$)$_3$), 0.69-0.92 (m, 21H, OSi(C*H*(C*H*$_3$)$_2$)$_3$), 1.32 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.74 (dd, *J* 12.7, 6.3, 1H, 2-CH*H*), 1.86 (dd, *J* 12.8, 10.8, 1H, 11-CH*H*), 2.15 (dd, *J* 12.8, 5.6, 1H, 11-C*H*H), 2.77 (dd, *J* 12.7, 10.2, 1H, 2-C*H*H), 2.96 (d, *J* 4.3, 1H, 8-C*H*), 3.17 (s, 3H, OC*H*$_3$), 3.29 (dd, *J* 10.8, 4.3, 1H, ArC*H*), 3.37 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, ArOC*H*$_3$), 3.83 (s, 3H, ArOC*H*$_3$), 4.18 (dd, 10.2, 6.3, 1H, 3-C*H*), 4.35 (ddd, *J* 10.8, 10.8, 5.6, 1H, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 5.70 (s, 1H, C=CH), 6.62-6.66 (m, 2H, 2 x Ar*H*), 6.76 (d, *J* 8.0, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.5 (CH_3), 12.6 (CH), 18.0 (CH_3), 18.1 (CH_3), 25.3 (CH_3), 27.3 (CH_3), 30.1 (CH_2), 41.3 (CH_2), 49.2 (CH_3), 49.3 (CH_3), 49.5 (CH), 52.8 (C), 55.6 (CH_3), 55.9 (CH_3), 57.6 (CH), 69.7 (CH), 73.4 (C), 91.3 (CH), 101.6 (C), 103.6 (CH), 110.8 (CH), 113.1 (CH), 121.3 (CH), 132.2 (C), 147.8 (C), 148.3 (C), 181.6 (C), 197.0 (C); HRMS (ES) *m/z* 677.3905 $[M+H]^+$, $[C_{36}H_{60}O_8Si_2]^+$ requires 677.3905.

(1*R*, 3*R*, 8*R*, 9*R*, 10*S*)-(-)-6-Bromo-9-(3,4-dimethoxyphenyl)-12,12-dimethoxy-3-(1-methyl-1-trimethylsilanyloxy-ethyl)-10-triisopropylsilanyloxy-4-oxa-tricyclo[6.3.1.0^{1,5}]dodec-5-en-7-one 44.

N-Bromosuccinimide (66 mg, 0.370 mmol, 10 eq.) was added to tricyclic compound **42** (25 mg, 0.037 mmol) in CCl_4 (2 mL) at 0 °C. The reaction mixture was stirred for 3 h at 0 °C, then at RT for 16 h. The solution was diluted with CH_2Cl_2 (5 mL), washed with saturated Na_2CO_3 (aq.), dried ($MgSO_4$), then concentrated *in vacuo*. Purification by column chromatography (petroleum ether-EtOAc 5:1) gave the title compound **44** as as a yellow oil (20 mg, 65%); $[\alpha]_D^{24}$ –11 (*c* 0.5 in $CHCl_3$); υ_{max} ($CHCl_3$) 2866, 1668, 1619, 1463, 1379, 1064, 980, 882 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H, Si(C*H*$_3$)$_3$), 0.80-0.96 (m, 21H, OSi(C*H*(C*H*$_3$)$_2$)$_3$), 1.38 (s, 3H, C*H*$_3$), 1.41 (s, 3H, C*H*$_3$), 1.87 (dd, *J* 12.7, 6.3, 1H, 2-CH*H*), 1.97 (dd, *J* 12.9, 10.1, 1H, 11-CH*H*), 2.24 (dd, *J* 12.9, 5.6, 1H, 11-C*H*H), 2.92 (dd, *J* 12.7, 10.1, 1H, 2-C*H*H), 3.19-3.20 (m, 1H, C*H*), 3.21 (s, 3H, OC*H*$_3$), 3.41 (s, 3H, OC*H*$_3$), 3.83 (s, 3H, ArOC*H*$_3$),

3.84 (s, 3H, ArOC*H*$_3$), 3.97 (dd, *J* 10.1, 4.4, 1H, ArC*H*), 4.27-4.37 (m, 2H, C*H*C(CH$_3$)$_2$OSi(CH$_3$)$_3$, C*H*OSi(CH(CH$_3$)$_2$)$_3$), 6.35 (s, 1H, Ar*H*), 7.00 (s, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.8 (CH_3), 13.0 (CH), 18.1 (CH_3), 18.3 (CH_3), 25.8 (CH_3), 27.4 (CH_3), 31.2 (CH_2), 41.4 (CH), 47.7 (CH), 49.7 (CH), 50.1 (CH_3), 55.5 (C), 56.0 (CH_3), 56.4 (CH_3), 56.6 (CH_3), 69.5 (CH), 73.7 (C), 92.9 (CH), 96.6 (C), 101.1 (C), 112.8 (CH), 115.8 (CH), 117.0 (C), 130.3 (C), 147.7 (C), 148.5 (C), 178.0 (C), 189.4 (C); HRMS (ESI) *m/z* 833.2121 $[M+H]^+$, $[C_{36}H_{59}Br_2O_8Si_2]^+$ requires 833.2037.

7-(tert-Butyl-dimethyl-silanyloxy)-8-(3,4-dihydroxy-phenyl)-2-methoxy-bicyclo[3.3.1]non-2-ene-4,9-dione 46 and 7-(tert-butyl-dimethyl-silanyloxy)-8-(3,4-dihydroxy-phenyl)-4-methoxy-bicyclo[3.3.1]non-3-ene-2,9-dione 47. To a solution of crude catechinic acid (**8**) (4.30 g, 13.7 mmol) in DMF (100 mL) was added DMAP (15.0 g, 123 mmol, 9 eq.) followed by TBSCl (12.5 g, 82.0 mmol, 6 eq.). The resulting mixture was stirred at RT for 48 h. The reaction mixture was then filtered through a short pad of celite, rinsing with DMF (4 mL). To the resulting brown solution was added K_2CO_3 (18.0 g, 130 mmol, 9.5 eq.), then Me_2SO_4 (6.60 mL, 65.0 mmol, 5 eq.) and the reaction mixture was stirred 1 h at RT, then 2 h at 80 °C. The solid was filtered off and DMF was removed under high vacuum. The residue was diluted with AcOEt, and washed with a saturated aqueous NH_4Cl solution. The aqueous phase was then extracted twice with AcOEt. The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product as a brown oil. Purification by flash column chromatography (petroleum ether-EtOAc 9:1 to 7:3) afforded a white foam (4.40 g). To this solid (550 mg, 852 µmol) in MeCN (20 mL) was added $(HF)_3.Et_3N$ (300 µL, 1.88 mmol) and the resulting mixture was stirred at RT overnight. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and extracted with AcOEt. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as a beige solid. Purification by flash column chromatography (petroleum ether-CH_2Cl_2-EtOAc 4:4:2 to 4:2:4) afford compound **46** (amorphous white solid, 170 mg, 24%); $[\alpha]_D^{20}$ +191.3 (*c* = 1.1, $CHCl_3$); ν_{max} ($CHCl_3$) 3599, 2930, 1735, 1650, 1597, 1374,

1108 /cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.35 (s, 3H, MeSi), -0.05 (s, 3H, MeSi), 0.62 (s, 9H, ^{t}Bu), 1.95 (ddd, *J* 13.2, 10.5, 4.4, 1H, CH*Hax*-CHOTBS), 2.49 (ddd, *J* 13.2, 5.5, 3.2, 1H, C*Heq*H-CHOTBS), 3.04 (dd, *J* 10.5, 4.5, 1H, C*H*-Ar), 3.30 (m, 2H, 2 C=O-C*H*), 3.66 (s, 3H, OMe), 4.30 (td, *J* 10.5, 5.5, 1H, C*H*-OTBS), 5.18 (br s, 1H, ArO*H*), 5.33 (br s, 1H, ArO*H*), 5.78 (s, 1H, C*H*=C(OMe)), 6.52 (dd, *J* 8.0, 2.0, 1H, Ar*H*), 6.61 (d, *J* 2.0, 1H, Ar*H*), 6.79 (d, *J* 8.0, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -5.3, -4.4, 17.7, 25.4, 38.9, 54.0, 56.6, 59.0, 59.5, 67.5, 105.0, 115.0, 115.3, 120.5, 131.5, 143.0, 143.9, 157.7, 195.9, 204.4; HRMS (EI) *m/z* 419.1894 $[M+H]^+$ $[C_{22}H_{31}O_6Si]^+$ requires 419.1890; and then compound **47** (amorphous white solid, 121 mg, 17%); $[\alpha]_D^{20}$ +66.3 (*c* = 0.7, $CHCl_3$); ν_{max} ($CHCl_3$) 3552, 2929, 1736, 1650, 1601, 1460, 1375, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.41 (s, 3H, MeSi), -0.08 (s, 3H, MeSi), 0.62 (s, 9H, ^{t}Bu), 1.97 (ddd, *J* 13.5, 10.5, 4.0, 1H, CH*Hax*-CHOTBS), 2.44 (ddd, *J* 13.5, 5.5, 3.0, 1H, C*Heq*H-CHOTBS), 3.04 (dd, *J* 10.5, 4.5, 1H, C*H*-Ar), 3.30 (br s, 1H, C=O-C*H*), 3.42 (br d, *J* 4.5, 1H, C=O-C*H*-C=O), 3.89 (s, 3H, OMe), 4.31 (td, *J* 10.5, 5.5, 1H, C*H*-OTBS), 5.84 (s, 1H, C*H*=C(OMe)), 6.15 (br s, 1H, ArO*H*), 6.38 (dd, *J* 8.0, 2.0, 1H, Ar*H*), 6.53 (d, *J* 2.0, 1H, Ar*H*), 6.59 (d, *J* 8.0, 1H, Ar*H*), 6.93 (br s, 1H, Ar-O*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -5.2, -4.6, 17.7, 24.4, 37.0, 51.7, 55.6, 57.4, 67.6, 67.7, 104.8, 115.7, 115.8, 120.5, 129.6, 143.4, 144.0, 177.2, 194.7, 203.7.

(+)-3-[(1*S*, 2*R*, 3*S*, 5*R*)-3-(tert-Butyl-dimethyl-silanyloxy)-8-methoxy-6-oxo-bicyclo[3.3.1]non-7-en-2-yl]-hexa-2,4-dienedioic acid dimethyl ester 48. To a solution of catechol **44** (100 mg, 239 μmol) in MeOH / toluene (800 μL, 1:1) was addded a solution of freshly recrystallised $Pb(OAc)_4$ (233 mg, 526 μmol, 2.2 eq.) in MeOH-toluene (1.4 mL, 1:1). The solution was stirred at RT for 36 h, then the solvents were evaporated. The residue was dissolved in AcOEt-H_2O, the phases separated, and the aqueous layer extracted with AcOEt. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give crude product as a yellow oil. Purification by flash column chromatography (petroleum ether-EtOAc 3:2 to 1:1) afforded diester **48** as a colorless oil (105 mg, 92%); $[\alpha]_D^{30}$ +164.7 (*c* = 0.95, $CHCl_3$); ν_{max} ($CHCl_3$)

2953, 2931, 2858, 1730, 1680, 1595, 1362, 1105 /cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.00 (s, 3H, MeSi), 0.02 (s, 3H, MeSi), 0.81 (s, 9H, tBu), 1.87 (ddd, *J* 12.8, 10.5, 4.4, 1H, CH*H*-CHOTBS), 2.41 (ddd, *J* 12.8, 5.5, 3.6, 1H, C*H*H-CHOTBS), 2.96 (dd, *J* 10.5, 3.6, 1H, C*H*-CHOTBS), 3.22 (br s, 1H, CH_2-C*H*-C=O), 3.65 (s, 3H, OMe), 3.70 (s, 3H, OMe), 3.73 (overlap, 1H, C*H*-C=O), 3.76 (s, 3H, OMe), 4.08 (td, *J* 10.5, 5.5, 1H, C*H*OTBS), 5.66 (d, *J* 2.0, 1H, C=C*H*-CO_2Me), 5.75 (s, 1H, C*H*=C(OMe)), 5.91 (d, *J* 12.4, 1H, CH=C*H*-CO_2Me), 7.02 (dd, 1H, *J* 12.4, 2.0, 1H, C*H*=CH-CO_2Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -5.1, -3.9, 17.8, 25.7, 38.4, 51.5, 51.6, 53.9, 55.6, 56.7, 59.3, 68.5, 105.7, 118.6, 120.4, 144.5, 153.1, 165.5, 165.7, 174.3, 194.5, 202.8; HRMS (ES) *m/z* found 497.2098 $[M+H]^+$ $[C_{24}H_{35}O_8Si]^+$ requires 479.2101.

(1*S*, 5*R*, 7*S*, 8*R*)-(+)-7-(tert-Butyl-dimethyl-silanyloxy)-8-(3,4-dioxo-cyclohexa-1,5-dienyl)-4-methoxy-bicyclo[3.3.1]non-3-ene-2,9-dione 49. To a solution of catechol **47** (300 mg, 0.72 mmol) in THF (50 mL) was added Fetizon's reagent (Ag_2CO_3 on celite, ~50% w/w, 1.6 g, 2.87 mmol, 4 eq.), and the resulting suspension was vigorously stirred at 60 °C for 3 h. The solid was filtered off, and the filtrate was evaporated *under vacuo*. The title compound **49** was obtained as an amorphous green solid (290 mg, 96%); $[\alpha]_D^{20}$ +132.0 (*c* = 0.3, $CHCl_3$); ν_{max} ($CHCl_3$) 2955, 1711, 1666, 1599, 1361, 1111 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.04 (s, 3H, MeSi), 0.03 (s, 3H, MeSi), 0.74 (s, 9H, ^{t}Bu), 1.96 (ddd, *J* 13.5, 10.5, 4.0, 1H, CH*Hax*-CHOTBS), 2.45 (ddd, *J* 13.5, 5.5, 3.5, 1H, C*Heq*H-CHOTBS), 2.88 (dd, *J* 10.5, 3.5, 1H, C*H*-Ar), 3.31 (m, 1H, C=O-C*H*), 3.34 (m, 1H, C=O-C*H*), 3.87 (s, 3H, OMe), 4.27 (td, *J* 10.5, 5.5, 1H, C*H*-OTBS), 5.77 (s, 1H, C*H*=C(OMe)), 6.17 (br d, *J* 2.0, 1H, C=C*H*-C=O), 6.37 (d, *J* 10.0, 1H, CH-C*H*-C=O), 6.82 (dd, *J* 10.0, 2.0, 1H, C*H*-CH-C=O); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -5.0, -4.0, 17.8, 25.5, 36.2, 51.4, 54.5, 57.5, 63.5, 66.1, 105.2, 129.2, 129.6, 140.7, 150.0, 175.9, 178.9, 179.7, 190.3, 201.7.

(+)-4-[(1*S*, 2*R*, 3*S*, 5*R*)-3-(tert-Butyl-dimethyl-silanyloxy)-6-methoxy-8,9-dioxo-bicyclo[3.3.1]non-6-en-2-yl]-furan-2-carboxylic acid methyl ester 50. To a solution of quinone **49** (100 mg, 240 μmol) in *i*PrOH (3.5 mL) and H_2O (1.5 mL) was added $NaIO_4$ (900 mg, 4. mmol, 18 eq) and OsO_4 (240 μL, 10% in *t*BuOH, 24 μmol, 0.1 eq.). The resulting mixture was stirred at rt overnight, then the white precipitate was removed by filtration, and the filtrate diluted with AcOEt and NH_4Cl aq. The phases were separated, and the aqueous layer extracted with AcOEt (4 × 10 mL). The organic phases were dried ($MgSO_4$) and concentrated *in vacuo* to give crude acid as a yellow solid (106 mg). This crude acid was dissolved in acetone, and treated with K_2CO_3 (100 mg, 720 μmol, 3 eq) and Me_2SO_4 (46 μL, 480 μmol, 2 eq). The mixture was stirred at rt for 3 h, then the solid was removed by filtration and the solvent evaporated. The residue was purified by column chromatography (petroleum ether-EtOAc 7:3) to provide furan **50** (50 mg, 47%); mp 197-199 °C (petroleum ether-AcOEt); $[\alpha]_D^{20}$ + 30.3 (c = 0.9, $CHCl_3$); ν_{max} ($CHCl_3$) 2955, 2858, 1731, 1658, 1603, 1364, 1323, 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) δ -0.31 (s, 3H, MeSi), -0.08 (s, 3H, MeSi), 0.70 (s, 9H, ^{t}Bu), 1.94 (ddd, J 13.5, 11.0, 4.0, 1H, CH*Hax*-CHOTBS), 2.40 (ddd, J 13.5, 5.0, 3.0, 1H, C*Heq*H-CHOTBS), 3.05 (dd, J 10.5, 4.0, 1H, C*H*-furan), 3.26 (br s, 1H, C=O-C*H*), 3.36 (m, 1H, C=O-C*H*), 3.85 (s, 3H, OMe), 3.86 (s, 3H, OMe), 4.06 (td, J 10.5, 5.5, 1H, C*H*-OTBS),), 5.78 (s, 1H, C*H*=C(OMe)), 7.01 (s, 1H, C*H*=C), 7.47 (s, 1H, C*H*=C); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ -5.0, -4.5, 17.7, 25.4, 37.1, 46.4, 51.6, 51.9, 57.2, 65.2, 68.5, 105.2, 118.6, 124.8, 144.1, 144.5, 159.0, 175.7, 192.3, 203.1; HRMS (EI) *m/z* found 435.1828 $[M+H]^+$ $[C_{22}H_{31}O_7Si]^+$ requires 435.1839.