Hosomi-Sakurai Reactions of Silacyclohexenes.


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1,1,1,3,3,3-hexamethyl-2-[hydroxy(4'-methoxyphenyl)methyl]-2-phenyltrisilane, 8c

\[
\text{Si(SiMe}_3\text{)Ph}^\text{OH}
\]

\(v_{\text{max}}\) (thin film) 3729, 2954, 2894, 2834, 1606, 1506, 1296, 1244, 1035, 830 cm\(^{-1}\); \(\delta_H\) (500 MHz, CDCl\(_3\)); 7.60 (2H, m, Ar-H), 7.36 (3H, m, Ar-H), 7.12 (2H, d, J = 8.7 Hz, Ar-H), 6.82 (2H, d, J = 8.7 Hz, Ar-H), 5.13 (1H, s, CH\(_2\)OH), 3.79 (3H, s, Ar-OMe), 0.191 (9H, s, Si(CH\(_3\))\(_3\)), 0.158 (9H, s, Si(CH\(_3\))\(_3\)); \(\delta_C\) (126 MHz, CDCl\(_3\)); 158.3 (C-4'), 138.0 (Ar-C), 136.5 (Ar-C), 135.6 (Ar-C), 128.7 (Ar-C), 128.2 (Ar-C), 126.9 (Ar-C), 113.9 (Ar-C), 69.6 (OCH\(_3\)); \(\delta_{Si}\) (99 MHz) -16.0 (Si(CH\(_3\))\(_3\)), -16.2 (Si(CH\(_3\))\(_3\)), -35.2 (-Si-Ph); m/z (ES\(^+\)); 411 (M'Na), HRMS (ES\(^+\)) MNa\(^+\) Found 411.1602, C\(_{20}\)H\(_{32}\)O\(_2\)Si\(_3\)Na requires \(M^+\) 411.1602.

1,1,1,3,3,3-Hexamethyl-2-[hydroxy(3',4'-methylenedioxyphenyl)methyl]-2-phenyltrisilane, 8d

\[
\text{Si(SiMe}_3\text{)Ph}^\text{OH}
\]

\(R_f\) (pet. ether/ether[9:1]) 0.4; mp; 80-83°C; \(v_{\text{max}}\) (thin film); 3567, 2951, 2895, 1503, 1482, 1429, 1254, 1035, 1014 cm\(^{-1}\); \(\delta_H\) (400 MHz, CDCl\(_3\)); 7.55 (2H, m Ar-H), 7.33 (3H, m, Ar-
(1RS,2RS,3RS)-3-methyl-2-(4'-methoxyphenyl)-1-phenyl-1-trimethylsilyl-silacyclohex-4-ene, 10c.

Isolated as a mixture of three diastereoisomers in a ratio of 83:14:3 % by GC; $\nu_{\text{max}}$ (thin film); 1681, 1603, 1508, 1427, 1297, 1246, 1175, 1034, 835 cm$^{-1}$; NMR data for major isomer; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$); 7.20-7.30 (5H, m, Ar-H), 7.01 (2H, d, J = 8.6Hz, Ar-H), 6.83 (2H, d, J 8.6Hz, Ar-H), 5.97 (1H, m, 5-H), 5.64 (1H, m, 4-H), 3.82 (3H, s, Ar-OC$_2$H$_5$), 2.78 (1H, m, 3-H), 2.28 (1H, d, J 10.0Hz, 2-H), 1.85 (2H, m, 6-H$_2$), 0.97 (3H, d, J 7.1Hz, 3-CH$_3$), -0.01 (9H, s, Si(CH$_3$)$_3$) $\delta_{\text{C}}$ (126 MHz, CDCl$_3$); 157.2 (Ar-OMe), 136.6 (4-C), 134.5 (Ar-C), 128.9 (Ar-C), 128.5 (Ar-C), 127.5 (2 x Ar-C), 124.5 (5-C), 113.7 (2 x Ar-C), 55.2 (Ar-OMe), 39.7 (2-C), 36.7 (3-C), 22.0 (3-CH$_3$), 9.7 (6-C), -1.19 (Si(CH$_3$)$_3$); $\delta_{\text{Si}}$ (99 MHz); -19.03 (Si(CH$_3$)$_3$), -22.89 (Si-Ph); m/z GC/MS (El); 366 (M$, 16\%$), 351 (M$+$-Me, 5%), 298 (100\%), 283 (72\%) 135 (58\%), 73 (54\%); HRMS (El); M$^+$Found 366.1826, C$_{22}$H$_{30}$O$_2$Si$_3$Na requires M$^+$ 336.1830.

(1RS,2RS,3RS)-3-methyl-2-(3',4'-methylenedioxyphenyl)-1-phenyl-1-trimethylsilyl-silacyclohex-4-ene, 10d.
Isolated as a mixture of three diastereoisomers in a ratio of 80:15:5% by GC/MS; $\nu_{\text{max}}$ (CHCl$_3$) 3072, 3012, 2960, 2894, 1506, 1485, 1440, 1440, 1246, 1044, 837 cm$^{-1}$; NMR data for the major isomer; $\delta$ (H) (400 MHz, CDCl$_3$); 7.48-7.22 (5H, m, Si-Ph), 6.71 (1H, d, J 7.8Hz, 5'-H), 6.61 (1H, d, J 1.8Hz, 2'-H), 6.50 (1H, dd, J 1.8Hz, 7.8Hz, 6'-H), 5.92 (2H, s, OCH$_2$O), 5.90 (1H, m, 5-H), 5.61 (1H, dt, J 10.3, 9.1, 1.5Hz, 4-H), 2.72 (1H, m, 3-H), 2.24 (1H, d, J 10.0Hz, 2-H), 1.6 (2H, m, 6-HH), 0.96 (3H, d, J 7.0Hz, 3-C$_3$H$_3$), -0.01 (Si(C$_3$H$_3$)$_3$); $\delta$ (C) (126 MHz, CDCl$_3$) 147.6 (Ar'-C), 144.6 (Ar'-C), 136.5 (4'-C), 134.4 (Ar-C), xx (Ar-C), 128.6 (Ar-C), 127.9 (Ar-C), 127.6 (Ar-C), 124.6 (5-C), 120.8 (Ar'-C) 108.5 (2'-C), 108.2 (5'-C), 100.6 (OCH$_2$O), 40.5 (2-C), 36.8 (3-C), 21.9 (3-CH$_3$), 9.7 (6-C), -1.20 (Si(C$_3$H$_3$)$_3$); $\delta$ (Si (99 MHz) -19.0 (Si(CH$_3$)$_3$), -22.4 (Si-Ph); m/z GC/MS (EI); 380 (M+, 24%), 365 (M'-Me, 5%), 311 (100%), 297 (78%), 134 (74%), 73 (78%); HRMS (EI); M$^+$ Found 380.1626, C$_{22}$H$_{28}$O$_2$Si$_2$ requires M$^+$ 380.1622.

$\left(3R^*,4S^*,5R^*,6R^*\right)$-2,4-Dimethyl-5-ethenyl-6-methoxy-6-(4'-trifluoromethylphenyl)hexan-3-ol

Reaction of silacycle 10a and trifluoromethylbenzaldehyde dimethylacetal afforded, following column chromatography, the title alcohol 36 as a colourless oil as a 2:1 mixture of diastereoisomers (23%); R$_f$ 0.3 (pet. ether/ether 9:1); $\nu_{\text{max}}$ (thin film) 3386 (broad-OH), 2960, 2931, 2872, 1736, 1600, 1517, 1416, 1364, 1325, 1256, 1228, 1128 cm$^{-1}$; $\delta$ (H) (500 MHz, CDCl$_3$) 7.58 (2H, d, J 8, Ar- H), 7.38 (2H, d, J 8, Ar-H), 6.01 (1H, ddd, J 17, 11, 10, 5-C=H), 5.09 (1H, dd, J 10, 2, =CHH), 4.77 (1H, dd, J 17, 2, =CHH), 4.59 (1H, d, J 4, 6-H), 3.30 (1H, m, 3-H), 3.23 (3H, s, 6-(OC$_2$H$_3$)), 3.08 (1H, d, J 4, -OCH), 2.24 (1H, m, 5-H), 1.79-1.73 (2H, m, 4-H & 2-H), 1.00 (3H, d, J 7, 2-CH$_3$), 0.85 (3H, d, J 7, 4-CH$_3$), 0.80 (3H, d, J 7, 1-H$\beta$); $\delta$ (C) (126 MHz, CDCl$_3$) 145.6 (C-1'), 134.7 (CH=), 128.3 (Ar-C), 127.9 (C-4'), 125.4 (ArCF$_3$), 125.2 (Ar-C), 119.1 (=CH$_2$), 86.2 (C-6), 78.8 (C-3), 57.5 (C-5), 57.4 (OCH$_3$), 40.5 (C-4), 29.8 (C-2), 20.8 (2-CH$_3$), 17.2 (4-CH$_3$), 14.0 (C-1); $\delta$ (F) (300 MHz, CDCl$_3$) -62.73 (3F, m, CF$_3$); m/z (ES$^+$) 353 (MNa$^+$); HRMS (ES$^+$) Found MNa$^+$ 353.1700 C$_{18}$H$_{26}$O$_2$F$_3$Na requires M$^+$ 353.1699.
**Supplementary Material for Organic & Biomolecular Chemistry**

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(3R*,4S*,5R*,6R*)-2,4-Dimethyl-5-ethenyl-6-methoxy-6-(4′-bromophenyl)hexan-3-ol

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Reaction of silacycle 10a and 4-bromobenzaldehyde dimethylacetal afforded, following column chromatography, the title alcohol as a colourless oil as a 2:1 mixture of diastereoisomers (23%); Rf 0.3 (pet. ether/ether 9:1) \( \nu \text{max} \) (thin film) 3391 (broad –OH), 2961, 2961, 2932, 2875, 2241, 1737, 1486, 1436, 1405, 1364, 1259, 1072, 1011, 840, 821 cm\(^{-1}\); NMR data for major isomer \( \delta \) (500 MHz, CDCl\(_3\)) 7.47 (2H, d, \( J \) 9, Ar-H), 7.16 (2H, d, J 9, Ar-H), 6.01 (1H, ddd, J 17, 11, 10, 5-CH=), 5.12 (1H, dd, J 10, 2, =CHH), 5.81 (1H, dd, J 17, 2, =CHH), 4.50 (1H, d, J 4, 6-H), 3.76 (1H, d, J 6, -OH), 3.30 (1H, m, 3-H), 3.23 (3H, s, OC\(_3\)H), 2.22 (1H, m, 5-H), 1.80-1.74 (2H, m, 4-H, 2-H), 1.02 (3H, d, J 7, 1-H), 0.87 (3H, d, J 7, 4-CH\(_3\)), 0.82 (3H, d, J 7, 2-CH\(_3\)), \( \delta \) (126MHz, CDCl\(_3\)) 135.4 (ipso-Ar-C), 134.5 (ipso-Ar-C), 131.1 (Ar-C), 129.1 (Ar-C), 118.8 (=CH\(_2\)), 86.0 (C-6), 76.6 (C-3), 57.5 (C-5), 57.0 (OCH\(_3\)), 40.3 (C-4), 29.6 (C-2), 20.6 (C-1), 17.1 (4-CH\(_3\)), 13.7 (2-CH\(_3\)), \( m/z \) (ES\(^+\)) 363 ([\(^{79}\)Br]MNa\(^+\)); HRMS (ES\(^+\)) Found [\(^{79}\)Br]MNa\(^+\) 363.0931, C\(_{17}\)H\(_{25}\)O\(_2\)\(^{79}\)BrNa requires \( M^+ \) 363.0930.

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(3R*,4S*,5R*,6R*) 2,4-Dimethyl-5-ethenyl-6-methoxyheptan-3-ol

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Reaction of silacycle 10a and acetaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol 38 as a 2:1 mixture of diastereoisomers. Rf 0.2 (pet. ether/ether 9:1); \( \nu \text{max} \) (thin film) 3374 (broad OH), 2960, 2928, 2878, 1737, 1678, 1600, 1520, 1468, 1428, 1364, 1256, 1232, 1120, 1072, 1042 cm\(^{-1}\); \( \delta \) (500 MHz, CDCl\(_3\)) 5.93 (1H, ddd, J 17, 10, 5-CH=), 5.19 (1H, dd, J 10, 2, =CHH), 5.03 (1H, m, =CHH), 4.42 (1H, s, -OH), 3.52 (1H, m, 6-H), 3.34 (3H, s, OCH\(_3\)), 3.21 (1H, m, 3-H), 2.02 (1H, d, J 10, 5-H), 1.80-1.68 (2H, m, 4-H, 2-H), 1.12 (3H, m, 7-H), 0.92 (3H, m, 2-CH\(_3\)), 0.87 (3H, d, J 7, 4-CH\(_3\)), 0.83 (3H, d, J 7, 1-CH\(_3\)), \( \delta \) (126MHz, CDCl\(_3\)) 137.2 (5-CH=CH\(_2\)), 119.1 (5-CH=CH\(_2\)), 80.2 (C-6), 76.0 (C-3), 57.3 (C-5), 56.6 (6-(OCH\(_3\))), 42.0 (C-4), 30.0 (C-2).
(1S*,2S*,3R*,4S*) 1,4-Diphenyl-3-ethenyl-4-methoxy-2-methylbutan-1-ol 39

Reaction of silacycle 10b and benzaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol 39 as a 2:1 mixture of diastereoisomers Rf 0.3 (pet. ether/ether 9:1). \( \nu_{\text{max}} \) (thin film) 3355 (broad –OH), 2362, 2333, 1491, 1452, 1084, 1068, 914, 841, 754, 698 cm\(^{-1}\); NMR data for major isomer \( \delta_H \) (500 MHz, CDCl\(_3\)) 7.30-7.16 (10H, m, Ar-H), 6.05 (1H, ddd, J 17, 10, 10, 3-C\(=\)H), 5.14 (1H, dd J 10, 3, =CH\(=\)H), 4.80 (1H, dd, J 17, 3, =CH\(=\)H), 3.26 (3H, s, OCH\(_3\)), 4.55 (1H, m, 4-H), 4.31 (1H, d, J 10, 1-H), 3.81 (1H, s, -OH), 2.29 (1H, m, 3-H), 1.98 (1H, m, 2-H), 0.55 (3H, d, J 7, 2-CH\(_3\)); \( \delta_C \) (126MHz, CDCl\(_3\)) 144.1 (Ar-C), 140.8 (Ar-C), 134.6 (3-CH=), 128.2 (Ar-C), 128.1 (Ar-C), 127.6 (Ar-C), 127.4 (Ar-C), 127.2 (Ar-C), 126.6 (Ar-C), 119.2 (=CH\(_2\)), 86.6 (C-4), 77.0 (C-1), 57.2 (4-(OCH\(_3\))), 57.0 (C-3), 43.8 (C-2), 17.2 (2-CH\(_3\)); m/z (ES\(^+\)) 319 (MNa\(^+\)); HRMS (ES\(^+\)) Found MNa\(^+\) 319.1667, C\(_{20}\)H\(_{24}\)O\(_2\)Na requires M\(^+\) 319.1669.

(1S*,2S*,3R*,4R*)-3-Ethenyl-2-methyl-4-methoxy-1-phenyl-4-(4’-trifluoromethylphenyl)butan-1-ol 41

Reaction of silacycle 10b and trifluoromethylbenzaldehyde dimethylacetal afforded, following column chromatography, the title alcohol 41 as a colourless oil as a 8:3:2 mixture of diastereoisomers (50%); Rf 0.3 (pet. ether/ether 9:1). Major isomer, \( \nu_{\text{max}} \) (thin film) 3370 (broad –OH), 2960, 2931, 2876, 1736, 1618, 1599, 1417, 1325, 1167, 1129 cm\(^{-1}\); NMR data given for the major isomer \( \delta_H \) (500 MHz, CDCl\(_3\)) 7.45 (2H, d, J 9, Ar-H), 7.45 (2H, d, J 9, Ar-H), 6.09 (1H, ddd, J 17, 11, 10, 3-CH=), 6.09 (1H, ddd, J 17, 11, 10, 3-CH=), 5.21 (1H, dd, J 10, 2, =CH\(=\)H), 4.86 (1H, dd, J 17, 2, =CH\(=\)H), 4.70 (1H, d, J 6, 4-H), 4.43 (1H, d, J 9, 1-H), 3.43 (1H, s, -OH), 3.27 (3H, s, 4-(OCH\(_3\))), 2.30 (1H, m, 3-H), 2.04 (1H,
(1S*,2S*,3R*,4R*) 4-(4’-Bromophenyl)-3-ethenyl-4-methoxy-2-methyl-1-phenylbutan-1-ol

Reaction of silacycle 10b and 4-bromobenzaldehyde dimethylacetal afforded, following column chromatography, the title alcohol 42 as a colourless oil as a 3:1 mixture of diastereoisomers (46%); Rf 0.3 (pet. ether/ether 9:1); \( \nu \) max (thin film) 3605, 3362 (broad-OH), 2960, 2929, 2243, 1719, 1591, 1487, 1453, 1405, 1269, 1081, 1072, 1011, 839, 818 cm\(^{-1}\); NMR data for major isomer \( \delta \) (500 MHz, CDCl\(_3\)) 7.49 (2H, d, \( J \) 9, Ar-H), 7.40-7.25 (5H, m, Ar-H), 7.21 (2H, d, J 9, Ar-H), 6.07 (1H, ddd, J 17, 10, 10, 3-CH=), 5.21 (1H, dd, J 10, 2, =CHH), 4.88 (1H, dd, J 17, 2, =CHH), 4.60 (1H, d, J 4, 4-H), 4.40 (1H, d, J 9, 1-H), 3.45 (1H, s, -OH), 3.25 (3H, s, OCH\(_3\)), 2.26 (1H, m, 3-H), 1.99 (1H, m, 2-H), 0.61 (3H, d, J 7, 2-CH\(_3\)); \( \delta \) C (126MHz, CDCl\(_3\)) 144.2 (ipso-Ar-C), 140.4 (ipso-Ar-C), 135.0 (3-CH=), 132.1 (Ar-C), 131.5 (Ar-C), 129.6 (Ar-C), 128.5 (Ar-C), 127.4 (Ar-C), 121.5 (ipso-Ar-C), 119.6 (=CH\(_2\)), 86.0 (C-4), 57.3 (OCH\(_3\)), 57.2 (C-3), 43.4 (C-2), 17.2 (2-CH\(_3\)); m/z (ES\(^+\)) 397 ([\(^{79}\)Br]MNa\(^+\)); HRMS (ES\(^+\)) Found [\(^{79}\)Br]MNa\(^+\) 397.0775, C\(_{20}\)H\(_{23}\)O\(_2\)\(^{79}\)BrNa requires M\(^+\) 397.0775.

(1S*,2S*,3R*,4R*) 3-Ethenyl-4-methoxy-2-methyl-4-(4’-nitrophenyl)-1-phenyl butan-1-ol

Reaction of silacycle 10b and 4-nitrobenzaldehyde dimethylacetal afforded, following column chromatography, the title alcohol as a colourless oil as a pale yellow oil as a
mixture of 3.5:2:1 diastereoisomers (63%); Rf 0.3 (pet. ether/ether 9:1); $\nu_{\text{max}}$ (thin film) 3474-3228 (broad-OH), 3079, 2932, 2884, 2361, 2244, 1600, 1522, 1346, 1107, 1084 cm$^{-1}$; Major isomer $\delta_{\text{H}}$ (500 MHz, CDCl$_3$) 8.23 (2H, d, $J$ 8.0, Ar-H), 7.52 (2H, d, $J$ 8.0, Ar-H), 7.36-7.24 (5H, m, Ar-H), 6.06 (1H, ddd, $J$ 17, 10, 10, 3-C=H), 5.21 (1H, dd, $J$ 10, 2, =CH(H)), 4.86 (1H, dd, $J$ 17, 2, =CHH), 4.77 (1H, d, $J$ 6, 4-H), 4.47 (1H, d, $J$ 8, 1-H), 3.28 (3H, s, OCH$_3$), 2.29 (1H, m, 3-H), 1.96 (1H, m, 2-H), 0.66 (3H, d, $J$ 8, 2-C$_3$H$_3$); $\delta_{\text{C}}$ (126MHz, CDCl$_3$) 149.4 (ipso-Ar-C), 147.6 (ipso-Ar-C), 143.8 (ipso-Ar-C), 134.9 (3-C=H), 128.5 (Ar-C), 128.0 (Ar-C), 127.3 (Ar-C), 125.8 (Ar-C), 123.6 (Ar-C), 119.8 (=CH$_3$), 85.3 (C-4), 77.1 (C-1), 57.6 (OCH$_3$), 56.7 (C-3), 42.9 (C-2), 16.5 (2-C$_3$H$_3$); m/z (ES$^+$) 364 (MNa$^+$); HRMS (ES$^+$) Found MNa$^+$ 364.1519, C$_{20}$H$_{23}$NO$_4$Na requires M$^+$ 364.1519.

(1S*,2S*,3R*,4R*) 3-Ethenyl-4-methoxy-2-methyl-1-phenylpentan-1-ol 44

Reaction of silacycle 10b and acetaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol 44 as a 2:1 mixture of diastereoisomers Rf 0.2 (pet. ether/ether 9:1); $\nu_{\text{max}}$ (thin film) 3332 (broad-OH), 3071, 2974, 2930, 2831, 2359, 2338, 1716, 1683, 1652, 1558, 1540, 1455, 1260, 1197, 1119, 1074, 843 cm$^{-1}$; $\delta_{\text{H}}$ (500 MHz, CDCl$_3$) 7.33-7.32 (5H, m, Ar-H), 5.80 (1H, ddd, $J$ 17, 11, 10, 3-C=H), 5.04 (1H, dd, $J$ 10, 2, =CHH), 4.91 (1H, dd, $J$ 17, 2, =CHH), 4.50 (1H, m, 1-H), 3.46 (1H, m, 4-H), 3.42 (3H, s, OCH$_3$), 2.24 (1H, m, 3-H), 2.18 (1H, m, 2-H), 1.13 (3H, d, $J$ 6, 5-H$_3$), 0.83 (3H, d, $J$ 7, 2-C$_3$H$_3$); $\delta_{\text{C}}$ (126MHz, CDCl$_3$) 144.5 (ipso-Ar-C), 138.3 (CH=), 128.1 (Ar-C), 126.9 (Ar-C), 126.7 (Ar-C), 118.7 (=CH$_3$), 56.1 (4-(OCH$_3$)), 52.0 (C-3), 42.8 (C-2), 17.2 (C-5), 14.8 (C-2); m/z (ES$^+$) 257 (MNa$^+$); HRMS (ES$^+$) Found MNa$^+$ 257.1519, C$_{15}$H$_{22}$O$_3$Na requires M$^+$ 257.1512.

(1S*,2S*,3R*,4R*) 3-Ethenyl-4-methoxy-2-methyl-1-phenylnonan-1-ol 46
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Reaction of silacycle 10b and hexanal dimethyl acetal afforded, following column chromatography, the title alcohol as a 1:1 mixture of diastereoisomers Rf 0.3 (pet. ether/ether 9:1); \( \nu_{\text{max}} \) (thin film) 3689, 3602, 3343 (broad –OH), 2958, 2831, 2872, 2860, 2243, 1681, 1600, 1493, 1455, 1378, 1260, 1197, 1111, 1081, 1011 cm\(^{-1}\); \( \delta_{\text{H}} \) (500 MHz, CDCl\(_3\)) 7.32-7.14 (5H, m, Ar-\( \text{H} \)), 5.90 (1H, ddd, \( J \) 17, 11, 10, 3-\( CH= \)), 5.08 (1H, dd, \( J \) 10, 2, =CHH), 4.96 (1H, dd, \( J \) 17, 2, =CHH), 4.63 (1H, s, -OH), 4.44 (1H, d, \( J \) 8, 1-H), 3.43 (3H, s, OC\(_3\)H), 3.37 (1H, m, 4-\( H \)), 2.37 (1H, m, 3-\( H \)), 2.14 (1H, m, 2-\( H \)), 1.66-1.25 (8H, m, 5-\( H_2 \), 6-\( H_2 \), 7-\( H_2 \), 8-\( H_2 \)), 0.87 (3H, m, 9-\( H_3 \)), 0.76 (3H, d, \( J \) 7, 2-\( CH_3 \)); \( \delta_{\text{C}} \) (126MHz, CDCl\(_3\)) 144.6 (ipso-Ar-C), 138.0 (3-\( CH= \)), 128.0 (Ar-C), 127.0 (Ar-C), 126.9 (Ar-C), 116.8 (=CH\(_2\)), 81.7 (C-4), 76.6 (C-1), 57.1 (4- (OCH\(_3\))), 49.7 (C-3), 42.0 (C-2), 32.1, 30.4, 23.7, 22.6 (5-C, 6-C, 7-C, 8-C), 15.6 (2-CH\(_3\)), 14.0 (C-9); \( m/z \) (ES\(^+\)) 313 (MNa\(^+\)), 603 (2MNa\(^+\)); HRMS (ES\(^+\)) Found MNa\(^+\) 313.2138, C\(_{19}\)H\(_{30}\)O\(_2\)Na requires \( M^+ \) 313.2138.

\((1R^*,2R^*,3R^*,4R^*)\) 2-Methyl-4-(2'-phenylethen-1'-yl)-3-ethenyl-1,2,3,4-tetrahydronaphthalen-1-ol 48

Reaction of silacycle 10b and cinnamaldehyde dimethylacetal afforded, following column chromatography, the title tetralol 48 as a white solid (44%) as a 7:2 mixture of diastereoisomers; m.p. 119-121; Rf 0.3 (pet. ether/ether 9:1); \( \nu_{\text{max}} \) (thin film) 3428 (broad-OH), 2958, 2365, 2357, 1599, 1493, 1448, 1384, 1259, 1091, 1029, 964, 915, 795, 759, 692 cm\(^{-1}\); \( \delta_{\text{H}} \) (500 MHz, CDCl\(_3\)) 7.67 (1H, d, \( J \) 7, Ar-\( H \)), 7.44 (1H, d, \( J \) 7, Ar-H), 7.32 (1H, t, \( J \) 7, Ar-H), 7.25-7.19 (6H, m, Ar-\( H \)), 6.56 (1H, d \( J \) 16, 2'-\( H \)), 6.14 (1H, dd, \( J \) 16, 10, 1'-\( H \)), 6.00 (1H, ddd, \( J \) 17, 10, 8, 3-\( CH= \)), 5.14 (1H, d, \( J \) 17, =CHH), 5.07 (1H, d, \( J \) 8, =CHH), 4.98 (1H, t, \( J \) 5, 1-H), 4.36 (1H, d, \( J \) 5, -OH), 3.60 (1H, t, \( J \) 9, 4-H), 2.64 (1H, m, 3-\( H \)), 2.36 (1H, m, 2-\( H \)), 0.92 (3H, d, \( J \) 7, 2-CH\(_3\)); \( \delta_{\text{C}} \) (126MHz, CDCl\(_3\)) 140.2 (4a-C), 139.2 (8a-C), 137.9 (Ar-C), 136.6 (Ar-C), 131.9 (4-CH=CHAr), 129.0 (4-CH=CHAr), 128.7 (Ar-C), 127.3 (Ar-C), 126.7 (Ar-C), 126.5 (Ar-C), 126.4 (Ar-C), 126.1 (Ar-C), 115.1
Supplementary Material for Organic & Biomolecular Chemistry

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\((=\text{CH}_2)\), 71.2 (C-1), 47.5 (C-3), 45.2 (C-4), 38.9 (C-2), 7.6 (2-\text{CH}_3); m/z (EI) 290 (M⁺);

HRMS (EI) Found M⁺ 290.1663, C₂₁H₂₂O requires M⁺ 290.1665.

\((1R^*,2S^*,3S^*,4S^*)\)-2-Ethenyl-4-hydroxy-3-methyl-1-(4-methylphenyl)-1,2,3,4-
tetrahydronaphthalene 49

Silacycle 10b (180mg, 0.53mmol) was combined with 4-methyl benzaldehyde dimethyl acetal to afford the title alcohol as a colourless oil as a 2:1 mixture of diastereoisomers (34.4mg, 23%); R₂ 0.2 (pet. ether:ether [1:1]); \(\nu\) max (thin film); 3464, 2926, 2931, 2252, 1720, 1601, 1463, 1381 cm⁻¹; NMR data for major isomer;

\(\delta^H (500 \text{ MHz, CDCl}_3); 7.62 (1H, d, J 7.8, \text{Ar-H}), 7.28 (1H, t, J 7.8, \text{Ar-H}), 7.15 (1H, t J 7.8, \text{Ar-H}), 7.07 (2H, d, J 7.9, \text{Ar-H}), 6.99 (1H, d, J 7.8, \text{Ar-H}), 6.91 (2H, d J 7.9, \text{Ar-H}), 5.95 (1H, m, 2-\text{CH}=) 5.02 (1H, dd, J 9.6, 1.0, =\text{CHH}) 4.99 (1H, d, J 6.5, 4-H) 4.97 (1H, dd, J 17.3, 1.0, =\text{CHH}), 4.05 (1H, d, J 8.1, 1-H), 2.69 (1H, m, 2-H), 2.36 (1H, m, 3-H), 2.32 (3H, s, 4'-\text{CH}_3), 1.00 (3H, d, J 7.0, 3-\text{CH}_3); \delta^C (126 \text{ MHz, CDCl}_3); 142.7 (\text{Ar-C}), 139.8 (2-\text{CH}=), 138.6 (\text{Ar-C}), 138.4 (\text{Ar-C}), 135.9 (\text{Ar-C}), 129.5 (\text{Ar-C}), 129.4 (\text{Ar-C}) 129.2 (\text{Ar-C}) 127.7 (\text{Ar-C}), 127.3 (\text{Ar-C}), 126.9 (\text{Ar-C}) 116.3 (=\text{CH}_2), 72.4 (\text{C-4}), 50.0 (\text{C-2}), 47.6 (\text{C-1}), 37.2 (\text{C-3}), 21.3 (4'-\text{CH}_3), 9.6 (3-\text{CH}_3); m/z (ES⁺); 333 (M⁺ + [Na+MeOH]); HRMS (ES⁺); found [MNa+MeOH]⁺ 333.1825.

\((1R^*,2S^*,3S^*,4S^*)\)-2-Ethenyl-4-hydroxy-3-methyl-1-(4',6'-dimethylphenyl)-1,2,3,4-
tetrahydronaphthalene 50
Silacycle 10b (99.2mg, 0.29mmol) was combined with 2,4-dimethyl benzaldehyde dimethyl acetal to afford the title alcohol 50 as a colourless oil as a (9:1) mixture of diastereoisomers (28.6mg, 34%); Rf 0.15 (pet. ether:ether [1:1]); ν\text{max}(\text{thin film}); 3464, 2924, 2252, 1602, 1465, 1380 cm\(^{-1}\); NMR data for major isomer; δ\text{H} (500 MHz, CDCl\(_3\)) 7.60 (1H, d, J 7.8, Ar-H), 7.29 (1H, d, J 7.0, Ar-H), 7.27 (1H, d, J 7.0, Ar-H), 7.16 (1H, t, J 7.4, Ar-H), 7.02 (1H, bs, Ar-H), 6.87 (1H, d, J 7.8, Ar-H), 6.84 (1H, d, J 7.8, Ar-H), 6.02 (1H, m, 2-CH=) 5.02 (1H bd, J 11.7, =CHH) 4.94 (1H d, J 6.0, 4-H) 4.96 (1H, bd, J, 16.7, =CHH), 4.36 (1H, d, J 6.6 1-H) 2.65 (1H, m, 2-H), 2.38 (1H, m, 3-H), 2.30 (6H, s, Ar-C\(_3\)), 1.08 (3H, d, J 7.0, 3-C\(_3\)H\(_3\)) δ\text{C} (126 MHz, CDCl\(_3\)) 140.7 (Ar-C\(_{\text{Ar}}\)), 139.4 (2-C=C), 138.6 (Ar-C\(_{\text{Ar}}\)), 138.1 (Ar-C\(_{\text{Ar}}\)), 136.0 (Ar-C\(_{\text{Ar}}\)), 135.4 (Ar-C\(_{\text{Ar}}\)), 131.1 (Ar-C\(_{\text{Ar}}\)), 130.0 (Ar-C\(_{\text{Ar}}\)), 129.4 (Ar-C\(_{\text{Ar}}\)), 127.8 (2x Ar-C\(_{\text{Ar}}\)), 126.5 (2x Ar-C\(_{\text{Ar}}\)), 116.0 (=CH\(_2\)), 72.1 (C-4), 48.7 (C-2), 44.2 (C-1), 36.0 (C-3), 21.2 (Ar-CH\(_3\)), 20.1 (Ar-CH\(_3\)), 9.5 (3-CH\(_3\)); m/z (ES\(^{+}\)) 347 (M\(^{+}\) +[Na+MeOH]); HRMS (ES\(^{+}\)) found [MNa+MeOH]\(^{+}\) 347.1985, C\(_{22}\)H\(_{28}\)O\(_2\)Na requires M\(^{+}\) 347.1982.

(1R\(^*\),2S\(^*\),3S\(^*\),4S\(^*\)) 2-Ethenyl-4-hydroxy-3-methyl-1-(4'-methoxy-2'-methylphenyl)-1,2,3,4-tetrahydronaphthalene 51

Silacycle 10b (97.2mg, 0.29mmol) was combined with 2-methyl-4-methoxy benzaldehyde dimethyl acetal to afford the title alcohol as a white solid as a 9:1 mixture of diastereoisomers (14.3mg, 16%); mp 96-98 \(^\circ\)C; Rf 0.2 (pet. ether:ether [1:1]); ν\text{max}(\text{thin film}) 3543, 3164, 2944, 2627, 2410, 2293, 2250, 1630, 1443cm\(^{-1}\); NMR data for major isomer; δ\text{H} (500 MHz, CDCl\(_3\)) 7.57 (1H, d, J 7.7, Ar-H), 7.25 (1H, t, J 7.5, Ar-H), 7.24 (1H, d, J 5.5, Ar-H), 7.14 (1H, t, J = 7.5, Ar-H), 6.80 (1H, d, J 7.7, Ar-H) 6.72 (1H, s, Ar-H), 6.58 (1H, d, J 7.3, Ar-H) 5.98 (1H, m, 2-CH=), 4.98 (2H, dd, J 17.4, 10.5, =CH\(_2\)), 4.92 (1H, d, J 10.1, 4-H), 4.29 (1H, d, J = 4.2, 1-H), 3.76 (3H, s, OC\(_3\)H\(_3\)), 2.59 (1H, m, 2-H), 2.38-2.28 (4H, m, 2'-CH\(_3\), 3-H), 1.80 (1H, d, J 7.8, OH), 1.05 (3H, d, J 7.0, 3-CH\(_3\)); δ\text{C} (125 MHz, CDCl\(_3\)) 157.5 (Ar-C\(_{\text{Ar}}\)), 139.4 (2-CH=), 138.6 (Ar-C\(_{\text{Ar}}\)), 138.3 (Ar-C\(_{\text{Ar}}\)), 137.4 (Ar-C\(_{\text{Ar}}\)), 136.0 (Ar-C\(_{\text{Ar}}\)), 130.0 (Ar-C\(_{\text{Ar}}\)), 127.8 (2x Ar-C\(_{\text{Ar}}\)), 126.5 (2x Ar-C\(_{\text{Ar}}\)), 115.7 (Ar-C\(_{\text{Ar}}\), =CH\(_2\)), 111.0
Silacycle 10b (98.7 mg, 0.29 mmol) was combined with 3,4-dimethoxy benzaldehyde dimethyl acetal to afford the title alcohol 52 as a colourless oil as a 9:1 mixture of diastereoisomers (15.9 mg, 17%); Rf 0.2 (pet. ether:ether [1:1]); ν\text{max}(\text{thin film}) 3540, 3165, 3002, 2943, 2408, 2292, 2251, 1828, 1740, 1440 cm\(^{-1}\); NMR data for major isomer; δ\text{H} (500 MHz, CDCl\(_3\)) 7.62 (1H, d, J 7.7, Ar-H), 7.27 (1H, t, J 7.7, Ar-H), 7.15 (1H, t, J 7.7, Ar-H), 6.89 (1H, d, J 7.7, Ar-H), 6.76 (1H, d, J 7.9, Ar-H), 6.55 (1H, s, Ar-H), 6.54 (1H, d, J = 7.9, Ar-H), 5.95 (1H, m, 2-\text{CH=}), 5.00 (1H, bd, J 10.8, =CH\text{H}), 4.98 (1H, d, J 14, 4-H), 4.95 (1H, bd, J 17.4, =CH\text{H}), 4.02 (1H, d, J 8.2, 1-H), 3.86 (3H, s, OCH\(_3\)), 3.81 (3H, s, OCH\(_3\)), 2.70 (1H, m, 2-\text{CH=}), 2.38 (1H, m, 3-H), 1.83 (1H, s, OH), 1.01 (3H, d, J 7.0, 3-\text{CH}_3); δ\text{C} (126 MHz, CDCl\(_3\)) 149.0 (Ar-C), 147.6 (Ar-C), 139.7 (2-\text{CH=}), 138.6 (Ar-C), 138.3 (Ar-C), 138.2 (Ar-C), 130.3 (Ar-C) 127.7 (Ar-C), 127.3 (Ar-C), 126.9 (Ar-C), 121.8 (Ar-C), 116.3 (=CH\text{H}), 112.6 (Ar-C), 110.9 (Ar-C), 72.3 (C-4), 56.1 (OCH\(_3\)), 56.0 (OCH\(_3\)), 49.9 (C-2), 47.6 (C-1), 37.4 (C-3), 9.4 (3-\text{CH}_3); m/z (ES\(^+\)) 347 (MNa\(^+\)); HRMS (ES\(^+\)) found MNa\(^+\) 347.1617; C\(_21\)H\(_{20}\)O\(_3\)Na requires M\(^+\) 347.1618.

(1R\(^*,\)2S\(^*,\)3S\(^*,\)4S\(^*)\) 2-Ethenyl-4-hydroxy-3-methyl-1-(3',4'-methylenedioxyphenyl)-1,2,3,4-tetrahydronaphthalene 53
Silacycle 10b (81.4 mg, 0.24 mmol) was combined with piperonal benzaldehyde dimethylacetal to afford the title alcohol 53 as a white solid as a 9:1 mixture of diastereoisomers (8 mg, 11%); mp; 73-76°C; Rf 0.2 (pet. ether:ether [1:1]); ν max (thin film); 3358, 1709, 1563, 920 cm⁻¹; NMR data for major isomer; δ H (500 MHz, CDCl₃); 7.61 (1H, d, J 8.0, Ar-H), 7.27 (1H, t, J 7.8, Ar-H), 7.15 (1H, t, J 7.8, Ar-H) 6.88 (1H, d, J 7.8, Ar-H), 6.71 (1H, d, J 7.8, Ar-H), 6.52 (1H, dd, J 7.8, 1.6, Ar-H), 6.47 (1H, d, J 1.6, Ar-H), 5.95 (1H, m, 2-CH=), 5.93 (2H, s, OCH₂O), 5.01 (1H, dd, J 5.6, 10.6, =CH₂), 4.98 (1H, d, J 5.1, 4-H), 4.95 (1H, dd, J 5.6, 16.2, =CHH), 3.98 (1H, d, J 8.7, 1-H), 2.64 (1H, m, 2-H) 2.35 (1H, m, 3-H), 0.98 (3H, d, J 7.6, 3-CH₃); δ C (126 MHz, CDCl₃) 147.9 (Ar-C), 146.1 (Ar-C), 139.6 (2-CH=), 138.6 (Ar-C), 138.2 (Ar-C), 130.3 (Ar-C), 127.7 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 122.8 (Ar-C), 116.4 (=CH₂), 109.6 (Ar-C), 108.0 (Ar-C), 101.1 (OCH₂O), 72.3 (C-4), 50.1 (C-2), 47.7 (C-1), 37.5 (C-3), 9.3 (3-CH₂); m/z (ES⁺) 331 (MNa⁺); HRMS (ES⁺) found MNa⁺ 331.1310; C₂₀H₂₀O₃Na requires M⁺ 331.1310.

(1R*, 2S*, 3S*, 4S*) 2-ethenyl-4-hydroxy-3-methyl-1-(3’4’5’-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene 54

Silacycle 10b was combined with trimethoxybenzaldehyde dimethylacetal to afford the title alcohol 54 which crystallised as a white solid (32%); Rf (petroleum ether/diethyl ether [1:1]) 0.30; m.p. 62-64°C (from petroleum ether/diethyl ether); ν max (ATR) 3317 br, 3000 w, 2926 m, 2900 m, 1588 s, 1501 m, 1450 m, 1418 s, 132 m, 1234 s, 1124 s, 1032 m, 1006 m, 914 m, 751 m, 709 m cm⁻¹; δ H (500 MHz, CDCl₃) 7.60 (1H, d, J 7.6, Ar-H),

Silacycle 10b was combined with trimethoxybenzaldehyde dimethylacetal to afford the title alcohol 54 which crystallised as a white solid (32%); Rf (petroleum ether/diethyl ether [1:1]) 0.30; m.p. 62-64°C (from petroleum ether/diethyl ether); ν max (ATR) 3317 br, 3000 w, 2926 m, 2900 m, 1588 s, 1501 m, 1450 m, 1418 s, 132 m, 1234 s, 1124 s, 1032 m, 1006 m, 914 m, 751 m, 709 m cm⁻¹; δ H (500 MHz, CDCl₃) 7.60 (1H, d, J 7.6, Ar-H),
7.26 (1H, t, J 7.6, Ar-H), 7.15 (1H, t, J 7.6, Ar-H), 6.90 (1H, d, J 7.6, Ar-H), 6.20 (2H, s, 2'-H, 6'H), 5.93 (1H, m, 2'-CH=), 5.01 (1H, dd, J 3, 10.6, =CHH), 4.95 (1H, dd, J 3, 16.0, =CHH), 4.97 (1H, d, J 5.4, 4'-H), 3.99 (1H, d, J 8.4, 1'-H), 3.85 (3H, s, 4'-OCCH3), 3.78 (6H, s, 3'-OCCH3, 5'-OCCH3), 2.69 (1H, m, 2'-H), 2.39 (1H, m, 3'-H), 1.76 (1H, br, 4-OH), 1.00 (3H, d, J 7.0, 3-C3H3).

δC (126 MHz, CDCl3) 152.9 (Ar-C), 141.0 (1'-C), 139.3 (2-C=), 138.3 (Ar-C), 137.6 (Ar-C), 136.4 (4'-C), 130.0 (Ar-C), 127.5 (Ar-C), 127.1 (Ar-C), 116.0 (=CH2), 106.4 (2'-C, 6'-C), 72.0 (4'-C), 60.8 (4'-OCCH3), 56.1 (3'-OCCH3, 5'-OCCH3), 49.4 (2'-C), 48.2 (1'-C), 37.1 (3-C), 9.2 (3-C3H3).

m/z (ES+) 377 (MNa+); HRMS (ES+) found MNa+ 377.1722, C22H26O4Na requires M+ 377.1723.

(1R*, 2S*, 3S*, 4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(3'4'5'-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene 55

Silacycle 10d was combined with trimethoxybenzaldehyde dimethylacetal to afford the title alcohol 55 as a white solid (28 %); Rf (petroleum ether/diethyl ether [1:1]) 0.18; m.p. 168-170°C (from petroleum ether/diethyl ether); νmax (ATR) 3397 br, 3100 m, 2904 m, 2800 m, 1588 s, 1504 m, 1461 m, 1418 s, 1328 m, 1235 m, 1125 s, 1032 m, 1004 m, 911 m, 822 m, 751 m, 709 m cm⁻¹; δH (500 MHz, CDCl3) 7.07 (1H, s, 5-H), 6.34 (1H, s, 8-H), 6.20 (2H, s, 2'-H, 6'-H), 5.92 (1H, m, 2'-CH=), 5.90 (2H, d, J 6.3, OCH2O), 5.00 (1H, dd, J 3, 10.3, =CHH), 4.95 (1H, dd, J 3, 17.3, 2'-CH=CHH), 4.84 (1H, m, 4'-H), 3.88 (1H, d, J 8.0, 1-H), 3.83 (3H, s, 4'-OCH3), 3.78 (6H, s, 3'-OCH3, 5'-OCH3), 2.61 (1H, m, 2-H), 2.32 (1H, m, 3-H), 1.74 (1H, d, J 8.0, 4-OH), 0.99 (3H, d, J 7.0, 3-C3H3); δC (126 MHz, CDCl3) 153.0 (3'-C, 5'-C), 147.0 (Ar-C), 146.6 (Ar-C), 140.9 (1'-C), 139.3 (2'-CH=), 136.4 (4'-C), 131.9 (Ar-C), 131.0 (Ar-C), 116.0 (=CH2), 109.4 (8-C), 107.0 (5-C), 106.3 (2'-C, 6'-C), 100.9 (OCH2O), 71.9 (4'-C), 60.8 (4'-OCH3), 56.1 (3'-OCH3, 5'-OCH3), 49.4 (2'-C), 48.4 (1'-C), 36.7 (3-C), 9.5 (3-C3H3); m/z (ES+) 398 (M+), 421 (MNa+); HRMS (ES+) found MNa+ 421.1622, C22H26O4Na requires M' 421.1621.
(1R*,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(3′4′-dimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene 56.

Silacycle 10d (149.4mg, 0.39mmol) was combined with 3,4-dimethoxy benzaldehyde dimethyl acetal to afford the title alcohol 56 as a white solid as a single diastereoisomer (21.8mg, 15%); mp: 74-76 °C; Rf 0.2 (pet. ether:ether [1:1]); νmax(thin film): 3461, 3156, 2945, 2838, 1794, 1644, 1468, 1383, 1096, 917 cm⁻¹; δH (500 MHz, CDCl₃) 7.06 (1H, s, Ar-H), 6.75 (1H, d, J 8.2, Ar-H), 6.52 (2H, m, Ar-H), 6.31 (1H, s, Ar-H), 5.92 (1H, m, 2-CH=), 5.89 (2H, s, OC₆H₂O), 4.96 (2H, dd, J 10.5, 17.1, =CH₂), 4.83 (1H, d, J 4.4, 4-H), 3.9 (1H, d, J 7.8, 1-H), 3.85 (3H, s, OCH₃), 3.81 (3H, s, OCH₃), 2.60 (1H, m, 2-H), 2.30 (1H, m, 3-H), 0.99 (3H, d, J 7.0, 3-CH₃); δC (126 MHz, CDCl₃) 148.8 (Ar-C), 147.4 (Ar-C), 146.9 (Ar-C), 146.5 (Ar-C), 139.4 (2-CH=), 137.8 (Ar-C), 131.9 (Ar-C), 131.3 (Ar-C), 121.4 (Ar-C) 116.0 (=CH₂), 112.1 (Ar-C), 110.7 (Ar-C), 109.4 (Ar-C), 106.9 (Ar-C), 100.8 (OCH₂O), 71.9 (C-4), 55.9 (OCH₃), 55.8 (OCH₃), 49.6 (C-2), 47.6 (C-1), 36.6 (C-3), 9.5 (3-CH₃); m/z (ES⁺) 351 (M⁺-OH, 100%), 759 (M₂Na⁺, 60%); HRMS (ES⁺) found [M⁺-OH] 351.1590, C₂₂H₂₃O₄ requires M⁺ 351.1591.

(1R*,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(4′methoxyphenyl)-1,2,3,4-tetrahydronaphthalene 57

Silacycle 10d (123.4mg, 0.32mmol) was combined with 4-methoxy benzaldehyde dimethyl acetal to afford the title alcohol 57 as a colourless oil as a 13:1 mixture of diastereoisomers (16.4mg, 15%); Rf 0.2 (pet. ether:ether [1:1]); mp 94-96 °C; νmax(thin film): 3400, 3155, 2986, 2902, 1793, 1644, 1470, 1383, 1096, 905 cm⁻¹; NMR data for
Silacycle 10d (97.8mg, 0.26mmol) was combined with 2,4-dimethyl benzaldehyde dimethyl acetal to afford the title alcohol 58 as a colourless oil as a 3:1 mixture of diastereoisomers (16.4mg, 18%). Rf 0.2 (pet. ether:ether [1:1]); \( \nu_{\text{max}} \) (thin film); 3604, 3155, 2982, 2925, 1793, 1482, 1383, 1239, 1096, 1042, 991 cm\(^{-1}\); NMR data for major isomer; \( \delta_{\text{H}} \) (500 MHz, CDCl\(_3\)) 7.01 (1H, s, Ar-H), 6.98 (1H, s, Ar-H), 6.84 (1H, d, J 8.2, Ar-H), 6.52 (1H, broad, Ar-H), 6.25 (1H, s, Ar-H), 6.0 (1H, m, 2-CH=), 5.9 (2H, s, OCH\(_2\)O), 5.0 (2H, dd, J 10.8, 17.2, =CH\(_2\)), 4.75 (1H, broad, 4-H), 4.2 (1H, broad, 1-H), 2.51 (1H, broad, 2-H), 2.38-2.24 (7H, m, Ar-CH\(_3\), 3-H), 1.71 (1H, d, J 7.9, OH), 1.03, (3H, d, J 7.0, 3-CH\(_3\)); \( \delta_{\text{C}} \) (126 MHz, CDCl\(_3\)) 147.5 (Ar-C), 147.3 (Ar-C), 146.5 (Ar-C), 139.5 (2-CH=), 135.8 (Ar-C), 135.5 (Ar-C), 132.2 (Ar-C), 131.4 (Ar-C), 131.2 (2xAr-C), 126.5 (Ar-C), 115.7 (=CH\(_2\)), 109.6 (Ar-C), 107.9 (Ar-C), 100.9 (OCH\(_2\)O), 71.8 (C-4), 48.2 (C-2), 44.4 (C-1), 36.5 (C-3), 20.9 (Ar-CH\(_3\)), 19.7 (Ar-CH\(_3\)), 14.2 (3-CH\(_3\)); m/z (ES\(^{+}\)) 321 (M\(^{+}\)-OH); HRMS (ES\(^{+}\)) found [M+OH] 321.1485, C\(_{22}\)H\(_{23}\)O\(_2\) requires M\(^{+}\) 321.1485.

(1R\(^{*}\),2S\(^{*}\),3S\(^{*}\),4S\(^{*}\)) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-((2',4'-dimethylphenyl)-1,2,3,4-tetrahydronaphthalene 59
Silacycle 10c (61.6mg, 0.17mmol) was combined with 4-methoxy benzaldehyde dimethyl acetal to afford the title alcohol 59 as a single diastereoisomer (10mg, 18%); m; 126-128 °C. ν̇max (thin film) 3400, 3155, 2986, 2902, 1794, 1644, 1470, 1383, 1095, 910 cm$^{-1}$ δH (500 MHz, CDCl$_3$) 7.50 (1H, d, J 8.6, Ar-H), 6.91 (2H, d, J 8.6, Ar-H), 6.80 (1H, dd, J 8.6, 2.7, Ar-H), 6.78 (2H, d, J 8.6, Ar-H), 6.39 (1H, d, J 2.44, Ar-H), 5.94 (1H, m, 2-Ch=), 4.97 (2H, dd, J 10.6, 17.1, =C=H$_2$), 4.88 (1H, m, 4-H) 4.00 (1H, d, J 7.6, 1-H), 3.78 (3H, s, OCH$_3$), 3.67 (3H, s, OCH$_3$), 2.61 (1H, m, 2-H), 2.29 (1H, m, 3-H), 1.69 (1H, d J 8.2, OH), 0.99 (3H, d, J 7.1, 3-CH$_3$); δC (126 MHz, CDCl$_3$) 158.8 (Ar-C), 157.9 (Ar-C), 139.6 (2-Ch=), 139.5 (Ar-C), 137.4 (Ar-C), 131.0 (Ar-C), 130.0 (Ar-C), 128.7 (Ar-C), 115.9 (=CH$_2$), 114.7 (Ar-C), 113.6 (Ar-C'), 112.8 (Ar-C), 111.6 (C-4), 112.8 (Ar-C), 71.6 (C-1), 55.2 (7-OCH$_3$, 4'-OCH$_3$), 49.8 (C-2), 47.4 (C-1), 36.4 (C-3), 9.9 (3-CH$_3$); m/z (ES+) 307 (M'-OH); HRMS (ES') Found [M'-OH] 307.1693, C$_{21}$H$_{23}$O$_2$ requires M' 307.1693.

(1R*,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-7-methoxy-1-(2',4'-dimethylphenyl)-1,2,3,4-tetrahydronaphthalene, 60.
(126 MHz, CDCl$_3$) 159.1 (C-7), 139.7 (-CH=), 139.3 (Ar-C), 135.8 (Ar-C), 135.4 (Ar-C),
131.1 (2xAr-C), 129.6 (Ar-C), 126.5 (Ar-C), 121.5 (Ar-C), 115.6 (=CH$_2$), 114.5 (Ar-C),
112.9 (Ar-C), 110.0 (Ar-C), 71.4 (C-4), 55.1 (OCH$_3$) 48.2 (C-2), 44.7 (C-1), 36.7 (C-3),
20.9 (Ar-CH$_3$), 19.7 (Ar-CH$_3$); m/z (ES$^+$) 305 (M$^+$-OH); HRMS (ES$^+$) found [M-OH]$^+$
305.1900, C$_{22}$H$_{25}$O requires M$^+$ 305.1900.