Supplementary Material for Organic & Biomolecular Chemistry

Hosomi-Sakurai Reactions of Silacyclohexenes.

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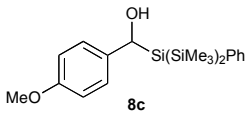
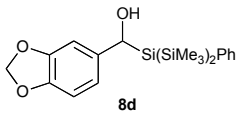
1,1,1,3,3,3-hexamethyl-2-[hydroxy(4'-methoxyphenyl)methyl]-2-phenyltrisilane, 8c



8c

ν_{max} (thin film) 3729, 2954, 2894, 2834, 1606, 1506, 1606, 1506, 1296, 1244, 1035, 830 cm^{-1}; δ_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, C*H*OH), 3.79 (3H, s, Ar-O*Me*), 0.191 (9H, s, $Si(CH_3)_3$), 0.158 (9H, s, $Si(CH_3)_3$); δ_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); δ_{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, $C_{20}H_{32}O_2Si_3Na$ requires M^+ 411.1602.

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

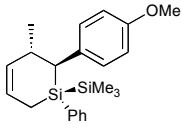


8d

R_f (pet. ether/ether[9:1]) 0.4; mp; 80-83°C; ν_{max} (thin film); 3567, 2951, 2895, 1503, 1482, 1429, 1254, 1035, 1014 cm^{-1}; δ_H (400 MHz, $CDCl_3$); 7.55 (2H, m *Ar*-H), 7.33 (3H, m, *Ar*-

H), 6.68 (1H, d, J 8.0Hz, *Ar*-H), 6.66 (1H, s, *Ar*-H), 6.61 (1H, d, J 8.0Hz, *Ar*-H), 5.90 (2H, s, OCH_2O), 5.07 (1H, s, C*H*OH), 0.15 (9H, s, Si(CH_3)$_3$), 0.12 (9H, s, Si(CH_3)$_3$); δ_C (101 MHz) 147.6 (*Ar*-C), 145.8 (*Ar*-C), 139.7 (*Ar*-C), 136.2 (*Ar*-C), 135.2 (*Ar*-C), 128.5 (*Ar*-C), 127.9 (*Ar*-C), 118.2 (*Ar*-C), 108.0 (*Ar*-C), 106.4 (*Ar*-C) 100.7 (O*C*H_2O), 69.7 (*C*HOH), 0.2 (-Si(*C*H_3)$_3$) 0.1 (-Si(*C*H_3)$_3$); δ_{Si} (99 MHz) -16.0 (-*Si*(CH_3)$_3$), -16.3 (-*Si*(CH_3)$_3$), -34.6 (-*Si*-Ph); *m/z* (ES^+); found 425 (MNa^+); HRMS (ES^+) MNa^+ Found 425.1396, $C_{20}H_{30}O_3Si_3Na$ requires M^+ 425.1395.

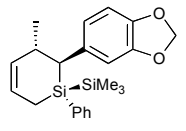
(1*RS*,2*RS*,3*RS*)-3-methyl-2-(4'-methoxyphenyl)-1-phenyl-1-trimethylsilyl-silacyclohex-4-ene, 10c.



10c

Isolated as a mixture of three diastereoisomers in a ratio of 83:14:3 % by GC; ν_{max} (thin film); 1681, 1603, 1508, 1427, 1297, 1246, 1175, 1034, 835 cm^{-1}; NMR data for major isomer; δ_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-OCH_3), 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)$_3$) δ_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-O*Me*), 39.7 (*2*-C), 36.7 (*3*-C), 22.0 (*3*-*C*H_3), 9.7 (*6*-C), -1.19 (Si(*C*H_3)$_3$); δ_{Si} (99 MHz); -19.03 (Si(CH_3)$_3$), -22.89 (Si-Ph); m/z GC/MS (EI); 366 (M^+, 16%), 351 (M+-Me, 5%), 298 (100%), 283 (72%) 135 (58%), 73 (54%); HRMS (EI); M^+Found 366.1826, $C_{22}H_{30}OSi_2$ requires M^+ 336.1830).

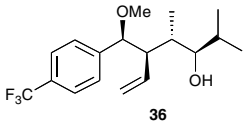
(1*RS*,2*RS*,3*RS*)-3-methyl-2-(3',4'-methylenedioxyphenyl)-1-phenyl-1-trimethylsilyl-silacyclohex-4-ene, 10d.



10d

Isolated as a mixture of three diastereoisomers in a ratio of 80:15:5 % by GC/MS; ν_{max} ($CHCl_3$) 3072, 3012, 2960, 2894, 1506, 1485, 1440, 1440, 1246, 1044, 837 cm^{-1}; NMR data for the major isomer; δ_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_2O), 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-CH_3), -0.01 ($Si(CH_3)_3$); δ_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_2O), 40.5 (*2*-C), 36.8 (*3*-C), 21.9 (*3*-CH_3), 9.7 (*6*-C), -1.20 ($Si(CH_3)_3$); δ_{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, $C_{22}H_{28}O_2Si_2$ requires M^+380.1622.

(3R,4S*,5R*,6R*)-2,4-Dimethyl-5-ethenyl-6-methoxy-6-(4'-trifluoromethylphenyl)hexan-3-ol* **36**

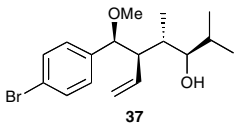


36

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); υ_{max} (thin film) 3386 (broad-OH), 2960, 2931, 2872, 1736, 1600, 1517, 1416, 1364, 1325, 1256, 1228, 1128 cm^{-1}; δ_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, =C*H*H), 4.77 (1H, dd, *J* 17, 2, =CH*H*), 4.59 (1H, d, *J* 4, 6-*H*), 3.30 (1H, m, 3-*H*), 3.23 (3H, s, 6-(OCH_3)), 3.08 (1H, d, *J* 4, -O*H*), 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_3); δ_C (126MHz, $CDCl_3$) 145.6 (*C-1'*), 134.7 (*C*H=), 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); δ_F (300 MHz, $CDCl_3$) -62.73 (3F, m, CF_3); *m/z* (ES^+) 353 (MNa^+); HRMS (ES^+) Found MNa^+ 353.1700 $C_{18}H_{25}O_2F_3Na$ requires M^+ 353.1699.

Comment [JS1]: Patrick, this was a 2:1 ratio by NMR, I don't have good data for the crude oxidation product to check before I columned it.

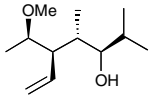
(3R,4S*,5R*,6R*)-2,4-Dimethyl-5-ethenyl-6-methoxy-6-(4'-bromophenyl)hexan-3-ol* **37**



37

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%); R_f 0.3 (pet. ether/ether 9:1) υ_{max} (thin film) 3391 (broad –OH), 2961, 2932, 2875, 2241, 1737, 1486, 1463, 1405, 1364, 1259, 1072, 1011, 840, 821 cm^{-1}; NMR data for major isomer δ_H (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-C*H*=), 5.12 (1H, dd, *J* 10, 2, =C*H*H), 4.81 (1H, dd, *J* 17, 2, =CH*H*), 4.50 (1H, d, *J* 4, 6-*H*), 3.76 (1H, d, *J* 6, -O*H*), 3.30 (1H, m, 3-*H*), 3.23 (3H, s, OCH_3), 2.22 (1H, m, 5-*H*), 1.80-1.74 (2H, m, 4-*H*, 2-*H*), 1.02 (3H, d, *J* 7, 1-H_3), 0.87 (3H, d, *J* 7, 4-CH_3), 0.82 (3H, d, *J* 7, 2-CH_3); δ_C (126MHz, $CDCl_3$) 139.5 (*ipso*-Ar-*C*), 135.4 (*ipso*-Ar-*C*), 134.5 (*CH*=), 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.

(3R,4S*,5R*,6R*) 2,4-Dimethyl-5-ethenyl-6-methoxyheptan-3-ol* **38**

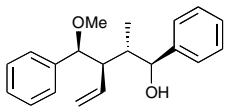


38

Reaction of silacycle **10a** and acetaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol **38** as a 2:1 mixture of diastereoisomers. R_f 0.2 (pet. ether/ether 9:1); υ_{max} (thin film) 3374 (broad-OH), 2960, 2928, 2878, 1737, 1678, 1600, 1520, 1468, 1428, 1364, 1256, 1232, 1120, 1072, 1042; cm^{-1}; δ_H (500 MHz, $CDCl_3$) 5.93 (1H, ddd, *J* 17, 10, 10, 5-C*H*=), 5.19 (1H, dd, *J* 10, 2, =C*H*H), 5.03 (1H, m, =CH*H*), 4.42 (1H, s, -O*H*), 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_3), 0.92 (3H, m, 2-CH_3), 0.87 (3H, d, *J* 7, 4-CH_3), 0.83 (3H, d, *J* 7, 1-H_3); δ_C (126MHz, $CDCl_3$) 137.2 (5-*C*H=CH_2), 119.1 (5-CH=*C*H_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),

20.4 (2-*C*H_3), 18.0 (4-*C*H_3), 17.4 (7-*C*), 14.0 (*C*-1); *m/z* (ES^+) 223 (MNa^+); HRMS (ES^+) Found MNa^+ 223.1669, $C_{12}H_{24}O_2Na$ requires M^+ 223.1668.

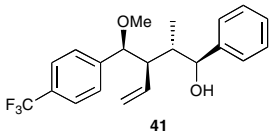
(1S,2S*,3R*,4S*) 1,4-Diphenyl-3-ethenyl-4-methoxy-2-methylbutan-1-ol* **39**



39

Reaction of silacycle **10b** and benzaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol **39** as a 2:1 mixture of diastereoisomers R_f 0.3 (pet. ether/ether 9:1). υ_{max} (thin film) 3355 (broad –OH), 2362, 2333, 1491, 1452, 1084, 1068, 914, 841, 754, 698 cm^{-1}; NMR data for major isomer δ_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, =C*H*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, -O*H*), 2.29 (1H, m, 3-*H*), 1.98 (1H, m, 2-*H*), 0.55 (3H, d, *J* 7, 2-CH_3); δ_C (126MHz, $CDCl_3$) 144.1 (Ar-*C*), 140.8 (Ar-*C*), 134.6 (3-*C*H=), 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 (=*C*H_2), 86.6 (*C*-4), 77.0 (*C*-1), 57.2 (4-(O*C*H_3)), 57.0 (*C*-3), 43.8 (*C*-2), 17.2 (2-*C*H_3); *m/z* (ES^+) 319 (MNa^+); HRMS (ES^+) Found MNa^+ 319.1667, $C_{20}H_{24}O_2Na$ requires M^+ 319.1669.

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

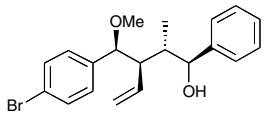


41

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%); R_f 0.3 (pet. ether/ether 9:1). Major isomer; υ_{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 δ_H (500 MHz, $CDCl_3$) 7.62 (2H, d, *J* 9, Ar-*H*), 7.45 (2H, d, *J* 9, Ar-*H*), 7.33-7.26 (5H, m, Ar-*H*), 6.09 (1H, ddd, *J* 17, 11, 10, 3-C*H*=), 5.21 (1H, dd, *J* 10, 2, =C*H*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*), 3.34 (1H, s, -O*H*), 3.27 (3H, s, 4-(OCH_3)), 2.30 (1H, m, 3-*H*), 2.04 (1H,

m, 2-*H*), 0.65 (3H, d, *J* 7, 2-CH_3); δ_C (126MHz, $CDCl_3$) 145.3 (*C*-4'), 143.8 (*ipso*-Ar-*C*), 140.6 (*ipso*-Ar-*C*), 134.6 (*C*H=), 128.3 (Ar-*C*), 127.8 (Ar-*C*), 127.6 (Ar-*C*), 127.1 (Ar-*C*), 125.0 (Ar-*C*), 119.5 (=*C*H_2), 85.6 (*C*-4), 57.2 (O*C*H_3), 56.7 (*C*-3), 43.1 (*C*-1), 16.7 (2-*C*H_3); δ_F (300 MHz, $CDCl_3$) -62.72 (3F, m, Ar-C*F*$_3$); *m/z* (CI, NH_3) 382 (MNH_4^+); HRMS (CI) Found 382.1985 ($C_{21}H_{27}O_2NF_3$ requires 382.1988).

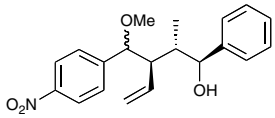
(1S,2S*,3R*,4R*) 4-(4'-Bromophenyl)-3-ethenyl-4-methoxy-2-methyl-1-phenylbutan-1-ol* **42**



42

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%); R_f 0.3 (pet. ether/ether 9:1); υ_{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 δ_H (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-C*H*=), 5.21 (1H, dd, *J* 10, 2, =C*H*H), 4.88 (1H, dd, *J* 17, 2, =CH*H*), 4.60 (1H, d, *J* 4, 4-*H*), 4.40 (1H, d, *J* 9, 1-*H*), 3.45 (1H, s, -O*H*), 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); δ_C (126MHz, $CDCl_3$) 144.2 (*ipso*-Ar-*C*), 140.4 (*ipso*-Ar-*C*), 135.0 (3-*C*H=), 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 (=*C*H_2), 86.0 (*C*-4), 57.3 (O*C*H_3), 57.2 (*C*-3), 43.4 (*C*-2), 17.2 (2-*C*H_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* **43**

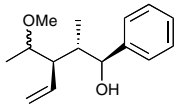


43

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%); R_f 0.3 (pet. ether/ether 9:1); υ_{max} (thin film) 3474-3228 (broad-OH), 3079, 2932, 2884, 2361, 2244, 1600, 1522, 1346, 1107, 1084 cm^{-1}; Major isomer δ_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, =C*H*H), 4.86 (1H, dd, *J* 17, 2, =CH*H*), 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-CH_3); δ_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 (=*C*H_2), 85.3 (*C*-4), 77.1 (*C*-1), 57.6 (O*C*H_3), 56.7 (*C*-3), 42.9 (*C*-2), 16.5 (2-*C*H_3); *m/z* (ES^+) 364 (MNa^+); HRMS (ES^+) Found MNa^+ 364.1519, $C_{20}H_{23}NO_4Na$ requires M^+ 364.1519.

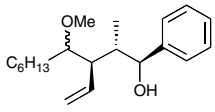
(1S,2S*,3R*,4R*) 3-Ethenyl-4-methoxy-2-methyl-1-phenylpentan-1-ol* **44**



44

Reaction of silacycle **10b** and acetaldehyde dimethyl acetal afforded, following column chromatography, the title alcohol **44** as a 2:1 mixture of diastereoisomers R_f 0.2 (pet. ether/ether 9:1); υ_{max} (thin film) 3332 (broad-OH), 3071, 3027, 2974, 2930, 2831, 2359, 2338, 1716, 1683, 1652, 1558, 1540, 1455, 1260, 1197, 1119, 1074, 843 cm^{-1}; δ_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, =C*H*H), 4.91 (1H, dd, *J* 17, 2, =CH*H*), 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-CH_3); δ_C (126MHz, $CDCl_3$) 144.5 (*ipso*-Ar-*C*), 138.3 (*C*H=), 128.1 (Ar-*C*), 126.9 (Ar-*C*), 126.7 (Ar-*C*), 118.7 (=*C*H_2), 56.1 (4-(O*C*H_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^+ 257.1510, $C_{15}H_{22}O_2Na$ requires M^+ 257.1512.

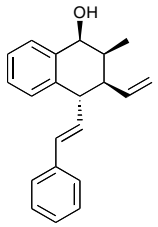
(1S,2S*,3R*,4R*) 3-Ethenyl-4-methoxy-2-methyl-1-phenylnonan-1-ol* **46**



46

Reaction of silacycle **10b** and hexanal dimethyl acetal afforded, following column chromatography, the title alcohol as a 1:1 mixture of diastereoisomers R_f 0.3 (pet. ether/ether 9:1); υ_{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}; δ_H (500 MHz, $CDCl_3$) 7.32-7.14 (5H, m, Ar-*H*), 5.90 (1H, ddd, *J* 17, 11, 10, 3-C*H*=), 5.08 (1H, dd, *J* 10, 2, =CH*H*), 4.96 (1H, dd, *J* 17, 2, =C*H*H), 4.63 (1H, s, -O*H*), 4.44 (1H, d, *J* 8, 1-*H*), 3.43 (3H, s, OCH_3), 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); δ_C (126MHz, $CDCl_3$) 144.6 (*ipso*-Ar-*C*), 138.0 (3-*C*H=), 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, $C_{19}H_{30}O_2Na$ 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**

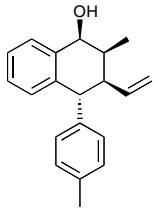


48

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; R_f 0.3 (pet. ether/ether 9:1); υ_{max} (thin film) 3428 (broad-OH), 2958, 2365, 2357, 1599, 1493, 1448, 1384, 1259, 1091, 1029, 964, 915, 795, 759, 692 cm^{-1}; δ_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-C*H*=), 5.14 (1H, d, *J* 17, =CH*H*), 5.07 (1H, d, *J* 8, =C*H*H), 4.98 (1H, t, *J* 5, 1-*H*), 4.36 (1H, d, *J* 5, -O*H*), 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); δ_C (126MHz, $CDCl_3$) 140.2 (4a-*C*), 139.2 (8a-*C*), 137.9 (Ar-*C*), 136.6 (Ar-*C*), 131.9 (4-CH=*C*HAr), 129.0 (4-*C*H=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

(=*C*H_2), 71.2 (*C*-1), 47.5 (*C*-3), 45.2 (*C*-4), 38.9 (*C*-2), 7.6 (2-*C*H_3); *m/z* (EI) 290 (M^+); HRMS (EI) Found M^+ 290.1663, $C_{21}H_{22}O$ requires M^+ 290.1665.

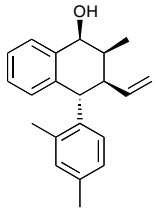
(1R,2S*,3S*,4S*)-2-Ethenyl-4-hydroxy-3-methyl-1-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene* **49**



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%); R_f 0.2 (pet. ether:ether [1:1]); ν_{max}(thin film); 3464, 2926, 2931, 2252, 1720, 1601, 1463, 1381 cm^{-1}; NMR data for major isomer; δ_H (500 MHz, $CDCl_3$); 7.62 (1H, d, *J* 7.8, Ar-*H*) 7.28 (1H, t, *J* 7.8, Ar-*H*), 7.15 (1H, t *J* 7.8, Ar-*H*), 7.07 (2H, d, *J* 7.9, Ar-*H*), 6.99 (1H, d, *J* 7.8, Ar-*H*), 6.91 (2H, d *J* 7.9, Ar-*H*), 5.95 (1H, m, 2-CH=) 5.02 (1H, dd, *J* 9.6, 1.0, =C*H*H) 4.99 (1H, d, *J* 6.5, *4*-H) 4.97 (1H, dd, *J* 17.3, 1.0, =C*H*H), 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'-CH_3), 1.00 (3H, d, *J* 7.0, *3*-CH_3); δ_C (126 MHz, $CDCl_3$); 142.7 (*Ar*-C), 139.8 (2-*C*H=), 138.6 (*Ar*-C), 138.4 (*Ar*-C), 135.9 (*Ar*-C), 129.5 (Ar-*C*), 129.4 (Ar-*C)* 129.2 (Ar-*C)* 127.7 (Ar-*C*), 127.3 (Ar-*C)*, 126.9 (Ar-*C)* 116.3 (=*C*H_2*)*, 72.4 (*C-4)*, 50.0 (*C-2)*, 47.6 (*C-1)*, 37.2 (*C-3)*, 21.3 (4'-*C*H_3), 9.6 (3-*C*H_3); m/z (ES^+); 333 (M^+ + [Na+MeOH]); HRMS (ES^+); found $[MNa+MeOH]^+$ 333.1827, $C_{21}H_{26}O_2Na$ requires M^+ 333.1825.

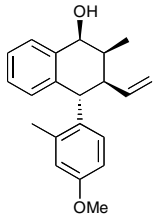
(1R,2S*,3S*,4S*)-2-Ethenyl-4-hydroxy-3-methyl-1-(4',6'-dimethylphenyl)-1,2,3,4-tetrahydronaphthalene* **50**



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%); R_f 0.15 (pet. ether:ether [1:1]); ν_{max}(thin film); 3464, 2924, 2252, 1602, 1465, 1380 cm^{-1}; NMR data for major isomer; δ_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-C*H*=) 5.02 (1H bd, *J* 11.7, =CH*H*) 4.94 (1H d, *J* 6.0, *4*-H) 4.96 (1H, bd, J, 16.7, =C*H*H), 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-CH_3), 1.08 (3H, d, *J* 7.0, *3*-CH_3) δ_C (126 MHz, $CDCl_3$) 140.7 (Ar-*C*), 139.4 (2-*C*H=*)*, 138.6 (Ar-*C*), 138.1 (Ar-*C*), 136.0 (*Ar*-C), 135.4 (Ar-C), 131.1 (Ar-C), 130.0 (Ar-*C*), 129.4 (*Ar*-C), 127.8 (2x *Ar*-C), 126.5 (2x *Ar*-C), 116.0 (=*C*H_2*)*, 72.1 (*C-4)*, 48.7 (*C-2)*, 44.2 (*C-1)*, 36.0 (*C-3)*, 21.2 (Ar-*C*H_3), 20.1 (Ar-*C*H_3), 9.5 (*3*-*C*H_3); m/z (ES^+) 347 (M^+ +[Na+MeOH]); HRMS (ES^+) found $[MNa+MeOH]^+$ 347.1985, $C_{22}H_{28}O_2Na$ 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**

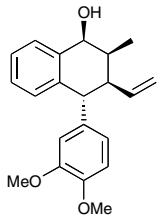


51

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 ˚C; R_f 0.2 (pet. ether:ether [1:1]); ν_{max}(thin film) 3543, 3164, 2944, 2627, 2410, 2293, 2250, 1630, 1443cm^{-1}; NMR data for major isomer; δ_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, OCH_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, O*H*), 1.05 (3H, d, *J* 7.0, 3-CH_3); δ_C (125 MHz, $CDCl_3$) 157.5 (Ar-*C*), 139.4 (2-*C*H=), 138.6 (Ar-*C*), 138.3 (Ar-*C*), 137.4 (Ar-*C*), 136.0 (Ar-*C*), 130.0 (Ar-*C*), 127.8 (2x Ar-*C*), 126.5 (2x Ar-*C*), 115.7 (Ar-*C*, =*C*H_2*)*, 111.0

(Ar-*C*), 71.9 (*C-4)*, 55.0 (O*C*H_3), 48.6 (*C-2)*, 43.5 (*C-1)*, 35.6 (*C-3)* 20.1 (Ar-*C*H_3), 10.8 (3-*C*H_3); m/z (ES^+) 331 (MNa^+); HRMS (ES^+); found MNa^+ 331.1665; $C_{21}H_{24}O_2Na$ requires M^+ 331.1668.

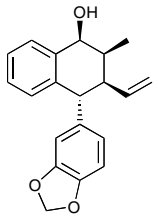
(1R,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-1-(3',4'-dimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene* **52**



52

Silacycle **10b** (98.7mg, 0.29mmol) 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 (15.9mg, 17%); Rf 0.2 (pet. ether:ether [1:1]); ν_{max}(thin film) 3540, 3165, 3002, 2943, 2627, 2408, 2292, 2251, 1828, 1740, 1440cm^{-1}; NMR data for major isomer; δ_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-CH=)*, 5.00 (1H, bd, *J* 10.8, =CH*H*) 4.98 (1H, d, *J* 14, *4*-H), 4.95 (1H, bd, *J* 17.4, =C*H*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-*H*), 2.38 (1H, m, 3-*H*), 1.83 (1H, s, O*H*), 1.01 (3H, d, *J* 7.0, *3*-CH_3); δ_C (126 MHz, $CDCl_3$) 149.0 (Ar-*C*), 1.47.6 (Ar-*C*), 139.7 (2-*C*H=*)*, 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 (=*C*H_2*)*, 112.6 (Ar-*C)*, 110.9 (Ar-*C)*, 72.3 (*C-4)*, 56.1 (O*C*H_3), 56.0 (O*C*H_3), 49.9 (*C-2)*, 47.6 (*C-1)*, 37.4 (*C-3)*, 9.4 (3-*C*H_3); m/z (ES^+) 347 (MNa^+); HRMS (ES^+) found MNa^+ 347.1617; $C_{21}H_{24}O_3Na$ requires M^+ 347.1618.

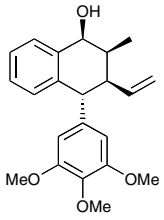
(1R,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-1-(3',4'-methylenedioxyphenyl)-1,2,3,4-tetrahydronaphthalene* **53**



53

Silacycle **10b** (81.4mg, 0.24mmol) was combined with piperonal benzaldehyde dimethylacetal to afford the title alcohol **53** as a white solid as a 9:1 mixture of diastereoisomers (8mg, 11%); mp; 73-76°C; R_f 0.2 (pet. ether:ether [1:1]); ν_{max}(thin film); 3358, 1709, 1500, 1163, 969, 920 cm^{-1}; NMR data for major isomer; δ_H (500 MHz, $CDCl_3$); 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-C*H*=), 5.93 (2H, s, OCH_2O), 5.01 (1H, dd, *J* 5.6, 10.6, =C*H*H), 4.98 (1H, d, *J* 5.1, *4*-H), 4.95 (1H, dd, *J* 5.6, 16.2, =CH*H*), 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-CH_3); δ_C (126 MHz, $CDCl_3$) 147.9 (Ar-*C*), 146.1 (Ar-*C*), 139.6 (2-*C*H=*)*, 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 (=*C*H_2*)*, 109.6 (Ar-*C*), 108.0 (Ar-*C*), 101.1 (O*C*H_2O*)*, 72.3 (*C-4*), 50.1 (*C-2*), 47.7 (*C-1*), 37.5 (*C-3*), 9.3 (3-*C*H_3); m/z (ES^+) 331 (MNa^+); HRMS (ES^+) found MNa^+ 331.1310 ; $C_{20}H_{20}O_3Na$ 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**

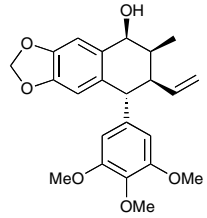


54

Silacycle **10b** was combined with trimethoxybenzaldehyde dimethylacetal to afford the title alcohol **54** which crystallised as a white solid (32 %); R_f: (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, $CDCl_3$) 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-C*H*=), 5.01 (1H, dd, *J* 3, 10.6, =CH*H*), 4.95 (1H, dd, *J* 3, 16.0, =C*H*H), 4.97 (1H, d, *J* 5.4, 4-*H*), 3.99 (1H, d, *J* 8.4, 1-*H*), 3.85 (3H, s, 4'-OCH_3), 3.78 (6H, s, 3'-OCH_3 , 5'-OCH_3), 2.69 (1H. m, 2-*H*), 2.39 (1H, m, 3-*H*), 1.76 (1H, br, 4-O*H*), 1.00 (3H, d, *J* 7.0, 3-CH_3); δ_C (126 MHz, $CDCl_3$) 152.9 (Ar-*C*), 141.0 (1'-*C*), 139.3 (2-*C*H=), 138.3 (Ar-*C*), 137.6 (Ar-*C*), 136.4 (4'-*C*), 130.0 (Ar-*C*), 127.5 (Ar-*C*), 127.1 (Ar-*C*), 126.8 (Ar-*C*), 116.0 (=*C*H_2), 106.4 (2'-*C*, 6'-*C*), 72.0 (4-*C*), 60.8 (4'-O*C*H_3), 56.1 (3'-O*C*H_3, 5'-O*C*H_3), 49.4 (2-*C*), 48.2 (1-*C*), 37.1 (3-*C*), 9.2 (3-*C*H_3); *m/z* (ES^+) 377 (MNa^+); HRMS (ES^+) found MNa^+: 377.1722, $C_{22}H_{26}O_4Na$ requires M^+ 377.1723.

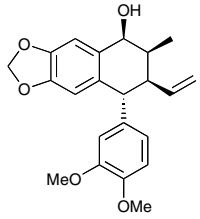
(1R, 2S*, 3S*, 4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(3'4'5'-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene* **55**



55

Silacycle **10d** was combined with trimethoxybenzaldehyde dimethylacetal to afford the title alcohol **55** as a white solid (28 %); R_f: (petroleum ether/diethyl ether [1:1]) 0.18; m.p. 168-170°C (from petroleum ether/diethyl ether); ν_{max} (ATR) 3397 br, 3100 m, 2904 m, 2800 m, 1588 s, 1504 m, 1461 m, 1418 m, 1328 m, 1235 m, 1125 s, 1032 m, 1004 m, 911 m, 822 m, 751 m, 709 m cm^{-1}; δ_H (500 MHz, $CDCl_3$) 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-C*H*=), 5.90 (2H, d, *J* 6.3, OCH_2O), 5.00 (1H, dd, *J* 3, 10.3, =CH*H*), 4.95 (1H, dd, *J* 3, 17.3, 2-CH=C*H*H), 4.84 (1H, m, 4-*H*), 3.88 (1H, d, *J* 8.0, 1-*H*), 3.83 (3H, s, 4'-OCH_3), 3.78 (6H, s, 3'-OCH_3, 5'-OCH_3), 2.61 (1H, m, 2-*H*), 2.32 (1H, m, 3-*H*), 1.74 (1H, d, *J* 8.0, 4-O*H*), 0.99 (3H, d, *J* 7.0, 3-CH_3); δ_C (126 MHz, $CDCl_3$) 153.0 (3'-*C*, 5'-*C*), 147.0 (Ar-*C*), 146.6 (Ar-*C*), 140.9 (1'-*C*), 139.3 (2-*C*H=), 136.4 (4'-*C*), 131.9 (Ar-*C*), 131.0 (Ar-*C*), 116.0 (=*C*H_2), 109.4 (8-*C*), 107.0 (5-*C*), 106.3 (2'-*C*, 6'-*C*), 100.9 (O*C*H_2O), 71.9 (4-*C*), 60.8 (4'-O*C*H_3), 56.1 (3'-O*C*H_3, 5'-O*C*H_3), 49.4 (2-*C*), 48.4 (1-*C*), 36.7 (3-*C*), 9.5 (3-*C*H_3); *m/z* (ES^+) 398 (M^+), 421 (MNa^+); HRMS (ES^+) found MNa^+ 421.1622, $C_{23}H_{26}O_6Na$ requires M^+ 421.1621.

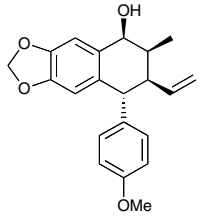
(1R,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(3'4'-dimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene* **56.**



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]); ν_{max}(thin film); 3461, 3156, 2945, 2838, 1794, 1644, 1468, 1383, 1096, 1016, 917cm^{-1}; δ_H (500 MHz, $CDCl_3$) 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, OCH_2O), 4.96 (2H, dd, *J* 10.5, 17.1, =CH_2), 4.83 (1H, d, *J* 4.4, *4*-H), 3.9 (1H, d, *J* 7.8, *1*-H), 3.85 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 2.60 (1H, m, *2*-H), 2.30 (1H, m, *3*-H), 0.99 (3H, d, *J* 7.0, 3-CH_3); δ_C (126 MHz, $CDCl_3$) 148.8 (Ar-*C*), 147.4 (Ar-*C*), 146.9 (Ar-*C*), 146.5 (Ar-*C*), 139.4 (2-*C*H=), 137.8 (Ar-*C*), 131.9 (Ar-*C*), 131.3 (Ar-*C*), 121.4 (Ar-*C)* 116.0 (=*C*H_2), 112.1 (Ar-*C)*, 110.7 (Ar-*C)*, 109.4 (Ar-*C*), 106.9 (Ar-*C)*, 100.8 (O*C*H_2O*)*, 71.9 (*C-4)*, 55.9 (O*C*H_3), 55.8 (O*C*H_3), 49.6 (*C-2)*, 47.6 (*C-1)*, 36.6 (*C-3)*, 9.5 (3-*C*H_3); *m/z* (ES$^+$) 351 (M^+-OH, 100%), 759 (M_2Na^+, 60%); HRMS (ES$^+$) found [M^+-OH] 351.1590, $C_{22}H_{23}O_4$ 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**

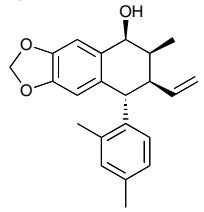


57

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 ^{o}C; ν_{max}(thin film); 3400, 3155, 2986, 2902, 1793, 1644, 1470, 1383, 1096, 905 cm^{-1}; NMR data for

major isomer; δ_H (500 MHz, $CDCl_3$) 7.05 (1H, s, Ar-*H*), 6.95 (2H, d *J* 8.6, Ar-*H*), 6.79 (2H, d, *J* 8.6, Ar-*H*), 6.29 (1H, s, Ar-*H*), 5.92 (1H, m, *2-CH=)*, 5.88 (2H, s, OCH_2O), 4.96 (2H, dd, *J* 10.4, 17.3, $=CH_2$), 4.83 (1H, m, *4*-H), 3.92 (1H, d, *J* 7.6, *1*-H), 3.78 (3H, s, OCH_3), 2.57 (1H, m, *3*-H), 2.28 (1H, m, *2*-H), 1.72 (1H, d, *J* 8.2, 4-O*H*), 0.98 (3H, d, *J* 8.2, 3-CH_3), δ_C (126 MHz, $CDCl_3$) 157.9 (C-4'), 147.0 (Ar-*C*), 146.5 (Ar-*C*), 139.5 (2-*C*H=), 137.4 (Ar-*C*), 131.9 (Ar-*C*), 131.5 (Ar-*C*), 130.0 (Ar-*C)*, 116.0 ($=CH_2$), 113.6 (Ar-*C)*, 109.5 (Ar-*C*), 107.0 (Ar-*C)*, 101.1 (OCH_2O*)*, 71.9 (*C-4)*, 55.2 (OCH_3), 49.8 (*C-2)*, 47.2 (*C-1)*, 36.5 (*C-3)*, 9.6 (3-CH_3); m/z (ES^+) 321 (M^+-OH), HRMS (ES^+) found [M^+-OH] 321.1485, $C_{21}H_{21}O_3$ requires M^+ 321.1485.

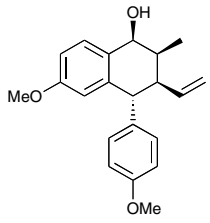
(1R,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-6,7-methylenedioxy-1-(2',4'-dimethylphenyl)-1,2,3,4-tetrahydronaphthalene* **58**



58

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]); ν_{max} (thin film); 3604, 3155, 2982, 2925, 1793, 1482, 1383, 1239, 1096, 1042, 991 cm^{-1}; NMR data for major isomer; δ_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_2O), 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, O*H*), 1.03, (3H, d, *J* 7.0, 3-CH_3); δ_C (126 MHz, $CDCl_3$) 147.5 (Ar-C), 147.3 (Ar-*C*), 146.5 (Ar-*C*), 139.5 (2-*C*H=), 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_2O), 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^+); 319 (M^+-OH); HRMS (ES^+) found [M^+-OH] 319.1692, $C_{22}H_{23}O_2$ requires M^+ 319.1693.

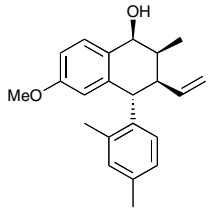
(1R,2S*,3S*,4S*) 2-Ethenyl-4-hydroxy-3-methyl-7-methoxy-1-(4'-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene* **59**



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. ν_{max} (thin film) 3400, 3155, 2986, 2902, 1794, 1644, 1470, 1383, 1095, 910 cm^{-1} δ_H (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, =CH_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, O*H*), 0.99 (3H, d, *J* 7.1, 3-CH_3); δ_C (126 MHz, $CDCl_3$) 158.8 (Ar-*C)*, 157.9 (Ar-*C)*, 139.6 (2-*C*H=*)*, 139.5 (Ar-*C*), 137.4 (Ar-*C*), 131.0 (Ar-*C)*, 130.0 (Ar-*C)*, 128.7 (Ar-*C*), 115.9 (=*C*H_2*)*, 114.7 (Ar-*C*), 113.6 (Ar-*C')*, 112.8 (Ar-*C*), 71.6 (*C-4*), 55.2 (7-O*C*H_3, 4'-O*C*H_3), 49.8 (*C-2)*, 47.4 (*C-1)*, 36.4 (*C-3)*, 9.9 (3-*C*H_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.**



60

Silacycle **10c** (50.0mg, 0.14mmol) was combined with 2,4-dimethyl benzaldehyde dimethyl acetal to afford the title alcohol **60** as a 3:1 mixture of diastereoisomers; (6.9mg, 15%); ν_{max}(thin film) 3693, 3155, 2986, 2902, 1794, 1644, 1469, 1383, 1096, 909 cm-1; NMR data for major isomer; δ_H (500 MHz, $CDCl_3$) 7.47 (1H, d, *J* 8.6, Ar-*H*), 6.99 (1H, s, Ar-*H*), 6.83 (2H, m, *J* 2.9, Ar-*H*), 6.46 (1H, bs, Ar-*H*), 6.34 (1H, d, *J* 2.7, Ar-*H*), 6.02 (1H, m, *2-CH=)*, 5.01 (1H, bd, *J* 4.5, =C*H*H), 4.98 (1H, bd, *J* 12.0, =CH*H*), 4.80 (1H, broad, *4*-H), 4.36 (1H, broad, *1*-H), 3.67 (3H, s, 6-OCH_3), 2.52 (1H, broad, *2*-H), 2.36-2.26 (7H, Ar-CH_3-, *3*-H), 1.67 (1H, d, *J* = 8.0, 4-O*H*), 1.05 (3H, d, *J* = 7.0, 3-CH_3); δ_C

(126 MHz, $CDCl_3$) 159.1 (C-*7*), 139.7 (-*C*H=*)*, 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 (=*C*H_2*)*, 114.5 (Ar-*C*), 112.9 (Ar-*C*), 110.0 (Ar-*C*), 71.4 (*C*-4*)*, 55.1 (O*C*H_3) 48.2 (*C*-2), 44.7 (*C-1*), 36.7 (*C-3*), 20.9 (Ar-*C*H_3), 19.7 (Ar-*C*H_3); m/z (ES^+) 305 (M^+-OH); HRMS (ES^+) found $[M\text{-}OH]^+$ 305.1900, $C_{22}H_{25}O$ requires M^+ 305.1900.