

Supporting Information Part 1

Stereoselective Synthesis of 2,4,5-Trisubstituted Tetrahydropyrans using an Intramolecular Allylation Strategy

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General Experimental

Infra-red spectra were recorded either neat as thin films between sodium chloride discs, or as a Nujol mull between sodium chloride discs. The intensity of each band is described as s (strong), m (medium) or w (weak) and with the prefix v (very) and suffix br (broad) where appropriate. ^1H -NMR and ^{13}C -NMR spectra were recorded in CDCl_3 unless stated otherwise, at 500 and 125 MHz, 400 and 100 MHz, or 300 and 75 MHz, respectively. Chemical shifts are reported as δ values (ppm) referenced to the following solvent signals: CHCl_3 , δ_{H} 7.26; CDCl_3 , δ_{C} 77.0. The term, 'stack' is used to describe a region where resonances arising from non-equivalent nuclei are coincident, and multiplet, m, to describe a region where resonances arising from a single nucleus (or equivalent nuclei) are coincident but coupling constants cannot be readily assigned. In analyzing AB systems, where the resonance pattern forms two well-separated groups, each of two lines, these are separately reported as "A of AB" and "B of AB", along with $J_{\text{A-B}}$. In analyzing ABX (and similar systems), where the resonance pattern forms two, clearly separated groups of lines (two sets of four lines for an ABX system), these are reported as "A of ABX" and "B of ABX", along with $J_{\text{A-B}}$, which can be directly measured from the spectra. Whilst $J_{\text{A-X}}$ cannot strictly be measured directly from the spectrum, the value obtained from the spectrum is sufficiently close to the actual value for it still to be useful; however it is acknowledged that the value quoted for $J_{\text{A-X}}$ is not the true value. Connectivities were deduced from COSY90, HSQC and HMBC experiments. GOESY experiments were used to elucidate relative stereochemistry. Mass spectra were recorded on a LCT spectrometer utilizing electrospray ionization (and a methanol mobile phase), or electron impact ionization, and are reported as (m/z (%)). HRMS were recorded on

a LCT spectrometer using a lock mass incorporated into the mobile phase. Melting points were determined using open capillaries and are uncorrected.

Reactions were monitored by thin layer chromatography using pre-coated glass-backed silica plates (60A F₂₅₄) and visualized by UV detection (at 254 nm) and with ammonium molybdate(IV) - cerium(IV) sulfate staining dip or potassium manganate(VII) staining dip or 2,4-dinitrophenylhydrazine staining dip (for aldehydes). Column chromatography was performed on silica gel (particle size 40-63 μm mesh).

All reactions were conducted in oven-dried (140 °C) or flame-dried glassware under a nitrogen atmosphere, and at ambient temperature (20 to 25 °C) unless otherwise stated, with magnetic stirring. Volumes of 1 mL or less were measured and dispensed with gastight syringes. Evaporation and concentration under reduced pressure was performed at 50 - 500 mbar. Residual solvent was removed under high vacuum (1 mbar).

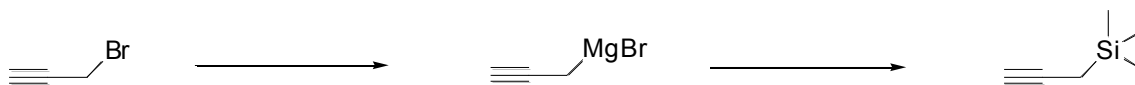
All reagents were obtained from commercial sources and used without further purification unless stated otherwise. Trimethylsilyl trifluoromethanesulfonate (triflate) was stored in a Schlenk tube under nitrogen at 4 °C and used whilst ever the compound was colorless. Over time, a pink coloration was observed whereupon fresh TMSOTf was used. Dichloromethane and cyclohexane were freshly distilled under nitrogen from CaH₂. Diethyl ether was freshly distilled under nitrogen from sodium benzophenone ketyl. Toluene was freshly distilled from sodium. All solutions are aqueous and saturated unless stated otherwise. TMSCl was distilled under nitrogen from CaH₂. 2,4,6-Tri-*tert*-butylpyrimidine (TTBP) was synthesized

following a known procedure.¹ Dess Martin Periodinane was synthesized according to a known procedure.²

References

1. Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis*, **2001**, 323-326.
2. (a) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899; (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.

Propargyltrimethylsilane



A 1 L round-bottom, triple-necked flask fitted with a condenser and a dropping funnel was charged with magnesium turnings (10.6 g, 440 mmol). Et₂O (80 mL) was then added and the mixture stirred vigorously. HgCl₂ (1.493 g, 5 mmol) was added in one portion whereupon the reaction mixture turned cloudy. After the solution had assumed a dark grey appearance (usually 10-15 min), the metal was considered activated and a solution of propargyl bromide [1 mL of a solution prepared from propargyl bromide 40 mL, 220 mmol, 80% solution in toluene) and Et₂O (220 mL)] was added quickly to initiate the reaction (1 min). The remaining propargyl bromide solution was then added dropwise at such a rate (2-4 drops per second) so as to maintain a gentle reflux of the ether solvent. Efficient stirring was maintained for a further 30 min before leaving the reaction to settle (1 h). Transfer and filtration of the ethereal solution *via* a cannula fitted with an oven-dried Whatman 1 filter paper afforded a solution of propargylmagnesium bromide in Et₂O which was titrated using the method described below (typically 85-100%). The resulting solution was cooled to 0 °C and stirred vigorously. TMSCl (23.8 mL, 1.86 mmol) was then added dropwise over 15 min and the resulting mixture was stirred for a further 45 min at 0 °C and then 1 h at rt. The ethereal solution was transferred to a dry, round-bottom flask and filtered *via* cannula fitted with an oven-dried Whatman 1 filter paper and then left at 4 °C overnight. The less dense, colourless solution was then removed *via* cannula from the more dense, orange-coloured liquid (comprising principally propargyl bromide) and the Et₂O then removed by distillation (atmospheric pressure,

20 cm Vigreux column). The resulting liquid was further purified by reduced pressure distillation (140 mmHg) to afford propargyltrimethylsilane as a colourless liquid (18.0 g of a 59.0 : 30.8 : 6.2 : 4.1 mixture of $\text{HC}\equiv\text{CCH}_2\text{SiMe}_3$: PhMe : $\text{CH}_2=\text{C}=\text{CHSiMe}_3$: Et_2O ; 95 mmol, 43% from propargyl bromide). b.p. 34-36 °C (140 mmHg).

Titration of Propargyl Grignard

Anhydrous 1,10-phenanthroline (a spatula tip) was added to the propargyl Grignard solution prepared above (2.5 mL). The resulting dark pink solution was then diluted with Et_2O (2.5 mL). $i\text{PrOH}$ (distilled from Mg/I_2) was then added dropwise and the quantity of alcohol required to turn the solution yellow was equivalent to the quantity of organomagnesium compound.

Trimethylsilylbut-2-yn-1-ol (9)

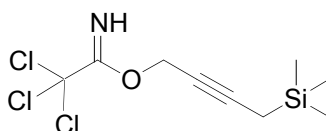


$n\text{-BuLi}$ (27.04 mL of a 2.5 M solution in hexane, 67.6 mmol) was added over 20 min to a solution of propargyltrimethylsilane (7.57 g, 67.6 mmol) in Et_2O (300 mL) at -78 °C. The temperature was raised to 0 °C and the reaction mixture stirred for 1 h. Paraformaldehyde (5.68 g, 135.2 mmol) was added in one portion and the reaction mixture warmed to room temperature. After 48 h, the reaction was quenched by the addition of NH_4Cl solution (200 mL). The phases were separated and the aqueous phase was washed with Et_2O (2 x 200 mL). The combined organic extracts were

washed with brine (200 mL), dried (MgSO_4) and concentrated under reduced pressure. Flash column chromatography of the residue (15% EtOAc in hexane) afforded propargyl alcohol **9** as a colourless oil (8.56 g, 89%); $R_f = 0.22$ (15 % EtOAc in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3362s br (OH), 2957s, 2898s, 2333w, 2297w, 2217m ($\text{C}\equiv\text{C}$), 1947w, 1949w, 1709w, 1658w, 1640w, 1639w, 1548w, 1512w, 1414m, 1397m, 1360m, 1298m, 1250s, 1169m, 1126s, 1011s, 846s, 786m, 760m, 699s, 666m; δ_{H} (300 MHz) 0.09 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.49 (2H, t, J 2.6, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 4.24 (2H, t, J 2.6, $\text{HOCH}_2\text{C}\equiv\text{C}$); δ_{C} (75 MHz) -2.3 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 6.8 (CH_2 , $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 50.9 (CH_2 , $\text{HOCH}_2\text{C}\equiv\text{C}$), 77.1 (quat. C, $\text{C}\equiv\text{C}$), 83.6 (quat. C, $\text{C}\equiv\text{C}$); m/z (EI) 142 ($[\text{M}]^+$, 10%), 90 (100, $[\text{Si}(\text{CH}_3)_3\text{OH}]^+$), 73 (6, $[\text{Si}(\text{CH}_3)_3]^+$).

Data were in agreement with those reported in the literature.¹

4-trimethylsilanyl-but-2-ynyl-2',2',2'-trichloroacetimidate (**10**)



Sodium (15 mg, 0.702 mmol) was added to a cooled (0 °C) solution of propargyl alcohol **9** (0.50 g, 3.51 mmol) in trichloroacetonitrile (1.013 g, 7.02 mmol). The reaction mixture was warmed to room temperature and then stirred for 3 h. The liquid was decanted from the residual solid sodium and the residue was washed with Et_2O (20 mL). The combined organic phases were washed with water (2 x 20 mL) and brine (20 mL), dried (MgSO_4) and concentrated under reduced pressure to afford acetimidate **10** as a colourless liquid, which was used in the next step without

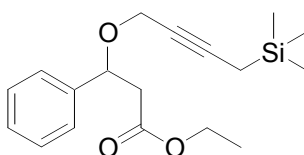
¹ McGarvey, G. J.; Bajwa, J. S. *J. Org. Chem.* **1984**, *49*, 4092.

further purification (1.01 g, quantitative yield); selected data: δ_{H} (300 MHz) 0.09 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.52 (2H, t, J 2.5, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 4.90 (2H, t, J 2.5, $\text{HOCH}_2\text{C}\equiv\text{C}$), 8.39 (1H, s, NH).

General procedure for etherification: formation of **12**

TMSOTf (1 equiv.) was added to a solution of trichloroacetimidate **10** (1 equiv), β -hydroxy ester **11** (1.5 equiv) and TTBP (1.1 equiv) in cyclohexane (0.1 M reaction concentration) at 0 °C. The reaction mixture was warmed to room temperature and then stirred for 5-6 h (consumption of the starting material was monitored by TLC). The reaction was quenched by the addition of NaHCO_3 solution (1 x volume of organic phase). The two phases were separated and the aqueous phase was extracted with Et_2O (2 x volumes of aqueous phase). The combined organic extracts were washed with water (1/6 x volume of organic phase) and brine (1/6 x volume of organic phase), dried (MgSO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography.

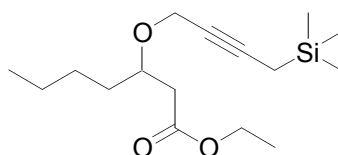
Ethyl 3-phenyl-3-(4'-trimethylsilanyl-but-2'-ynyloxy)propionate (**12a**)



Ether **12a** was prepared from trichloroacetimidate **10** (0.636 g, 2.22 mmol) and β -hydroxy ester **11a** (0.646 g, 3.33 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et_2O in hexane) afforded ether **12a** as a colourless oil (0.502 g, 71%); R_f = 0.23 (10% Et_2O in

hexane); (Found: C, 67.60; H, 8.00. $C_{18}H_{26}O_3Si$ requires C, 67.88; H, 8.23%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3454w, 3064w, 3032w, 2957s, 2902m, 2857m, 2335w, 2250w, 2215m ($C\equiv C$), 1960w, 1738vs ($C=O$), 1679w, 1641w, 1603w, 1565w, 1546w, 1529w, 1513w, 1494m, 1478m, 1393m, 1372m, 1348m, 1309m, 1250s, 1197m, 1170s, 1127m, 1078s, 1060s, 1030s, 912s, 852vs, 789w, 761m, 734s, 701s, 666m, 648m; δ_H (300 MHz) 0.10 (9H, s, $Si(CH_3)_3$), 1.20 (3H, t, J 7.2, $CO_2CH_2CH_3$), 1.49 (2H, t, J 2.4, $CH_2Si(CH_3)_3$), 2.62 (1H, A of ABX, J_{A-B} 15.1, J_{A-X} 5.9, $CH_aH_bC=O$), 2.86 (1H, B of ABX, J_{B-A} 15.1, J_{B-X} 8.1, $CH_aH_bC=O$), 3.86 (1H, A of ABX_2 , J_{A-B} 15.1, J_{A-X} 2.4, $OCH_aH_bC\equiv C$), 4.03-4.15 (3H, stack including [4.08 (1H, B of ABX_2 , J_{B-A} 15.1, J_{B-X} 2.4, $OCH_aH_bC\equiv C$)], [4.10 (2H, q, J 7.2, $CO_2CH_2CH_3$)], $OCH_aH_bC\equiv C$, $CO_2CH_2CH_3$), 4.98 (1H, dd, J 8.1, 5.9, 3- H), 7.26-7.37 (5H, stack, Ph H); δ_C (75 MHz) -2.2 (CH_3 , $Si(CH_3)_3$), 7.0 (CH_2 , $C\equiv CCH_2Si$), 13.9 (CH_3 , OCH_2CH_3) 43.1 (CH_2 , $CH_2C=O$), 56.3 (CH_2 , $OCH_2C\equiv C$), 60.2 (CH_2 , OCH_2CH_3), 74.2 (quat. C, $C\equiv C$), 76.2 (CH, C-3), 84.5 (quat. C, $C\equiv C$), 126.7 (CH, Ph), 127.9 (CH, Ph), 128.3 (CH, Ph), 140.0 (quat. C, *ipso*Ph), 170.3 (quat. C, $C=O$); m/z (TOF ES+) 341.1 ($[M+Na]^+$, 100%); HRMS m/z (TOF ES+) 341.1562. $C_{18}H_{26}NaO_3Si$ requires 341.1549.

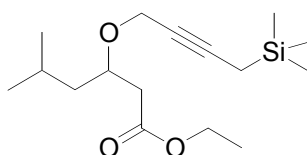
Ether **12b** (3-(4'-trimethylsilanyl-but-2'-ynyl-oxy)heptanoate (**12b**))



Ether **12b** was prepared from trichloroacetimidate **10** (0.730 g, 2.55 mmol) and β -hydroxy ester **11b** (0.667 g, 3.83 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et_2O in hexane) afforded ether **12b** as a colourless oil (0.563 g, 74%); R_f = 0.22 (10% Et_2O in

hexane); (Found: C, 64.54; H, 10.10. C₁₆H₃₀O₃Si requires C, 64.38; H, 10.13%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3445w, 2956s, 2860m, 2212m (C≡C), 1957w, 1735s (C=O), 1652w, 1558w, 1540w, 1506w, 1457m, 1374m, 1350m, 1301m, 1250s, 1213m, 1175m, 1125m, 1064m, 1036m, 851s, 790w, 760w, 699w, 666w; δ_{H} (300 MHz); 0.09 (9H, s, Si(CH₃)₃), 0.89 (3H, t, *J* 6.6, CH₃(CH₂)₃), 1.22-1.35 (7H, stack including [1.25 (3H, t, *J* 7.0, CO₂CH₂CH₃], 2 x CH₂, CO₂CH₂CH₃), 1.47-1.58 (4H, stack including [1.49 (2H, t, *J* 2.2, CH₂Si(CH₃)₃], 1 x CH₂, CH₂Si(CH₃)₃), 2.41 (1H, A of ABX, *J*_{A-B} 15.2, *J*_{A-X} 6.2, CH_aH_bC=O), 2.57 (1H, B of ABX, *J*_{B-A} 15.2, *J*_{B-X} 6.2, CH_aH_bC=O), 3.91 (1H, app. quintet, *J* 6.2, 3-*H*), 4.01-4.26 (4H, stack including [4.13 (2H, q, *J* 6.6, CO₂CH₂CH₃], OCH₂C≡C, CO₂CH₂CH₃)); δ_{C} (75 MHz) -2.2 (CH₃, Si(CH₃)₃), 7.1 (CH₂, C≡CCH₂Si), 13.9 (CH₃), 14.1 (CH₃), 22.6 (CH₂), 27.2 (CH₂), 33.9 (CH₂), 39.5 (CH₂, CH₂C=O), 57.2 (OCH₂C≡C), 60.2 (CH₂, OCH₂CH₃), 74.80 (CH, C-3), 74.83 (quat. C, C≡C), 84.1 (quat. C, C=C), 171.4 (quat. C, C=O); *m/z* (TOF ES+) 321.1 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 321.1859. C₁₆H₃₀NaO₃Si requires 321.1862.

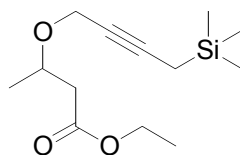
Ethyl 5-methyl-3-(4'-trimethylsilanyl-but-2'-ynyloxy)hexanoate (**12c**)



Ether **12c** was prepared from trichloroacetimidate **10** (0.650 g, 2.27 mmol) and β -hydroxy ester **11c** (0.590 g, 3.40 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et₂O in hexane) afforded ether **12c** as a colourless oil (0.393 g, 58%); *R_f* = 0.28 (10% Et₂O in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3454w, 2958s, 2939s, 2873m, 2220w (C≡C), 1735s (C=O), 1467w, 1375m, 1251s, 1179s, 1127m, 1067m, 1034m, 853m, 665m; δ_{H} (300 MHz)

0.09 (9H, s, Si(CH₃)₃), 0.88-0.93 (6H, stack, (CH₃)₂CH), 1.19-1.37 (4H, stack including [1.25 (3H, t, *J* 7.2, CO₂CH₂CH₃)], ⁱPrCH_aH_b, CO₂CH₂CH₃), 1.41-1.55 (3H, stack including [1.49 (2H, t, *J* 2.4, CH₂Si(CH₃)₃)], ⁱPrCH_aH_b, CH₂Si(CH₃)₃), 1.68-1.83 (1H, m, (CH₃)₂CH), 2.39 (1H, A of ABX, *J*_{A-B} 15.0, *J*_{A-X} 6.4, CH_aH_bC=O), 2.59 (1H, B of ABX, *J*_{B-A} 15.0, *J*_{B-X} 5.9, CH_aH_bC=O), 3.89-4.03 (1H, m, 3-*H*), 4.08-5.01 (4H, stack, CO₂CH₂CH₃, OCH₂C≡C); δ_C (75 MHz) -2.1 (CH₃, Si(CH₃)₃), 7.1 (CH₂, C≡CCH₂Si), 14.1 (CH₃, OCH₂CH₃), [22.3, 23.1, 24.4 (2 x CH₃, 1 x CH, (CH₃)₂CH)], 39.8 (CH₂, CH₂C=O), 44.0 (CH₂, ⁱPrCH₂), 57.2 (CH₂, OCH₂C≡C), 60.2 (CH₂, OCH₂CH₃), 73.3 (CH, C-3), 74.8 (quat. C, C≡C), 84.2 (quat. C, C≡C), 171.4 (quat. C, C=O); *m/z* (TOF ES+) 321.2 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 321.1874. C₁₆H₃₀NaO₃Si requires 321.1862.

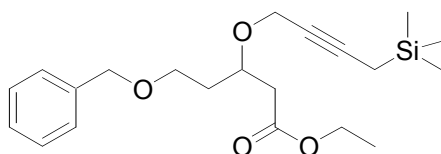
Ethyl 3-(4'-trimethylsilanyl-but-2'-ynyloxy)butyrate (**12d**)



Ether **12d** was prepared from trichloroacetimidate **10** (0.774 g, 2.70 mmol) and β-hydroxy ester **11d** (0.535 g, 4.05 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et₂O in hexane) afforded ether **12d** as a colourless oil (0.512 g, 74%); *R_f* = 0.19 (10% Et₂O in hexane); ν_{max}(film)/cm⁻¹ 3583w, 2959m, 2901m, 2360w, 2214m (C≡C), 1738s (C=O), 1448m, 1376m, 1303m, 1250s, 1186s, 1134m, 1082s, 1041s, 852s, 790w, 761w, 699m, 666m; δ_H (300 MHz) 0.09 (9H, s, Si(CH₃)₃), 1.19-1.29 (6H, stack including [1.22 (3H, d, *J* 5.9, CH₃)], [1.25 (3H, t, *J* 7.2, CO₂CH₂CH₃)], CH₃, CO₂CH₂CH₃), 1.49 (2H, t, *J* 2.6, CH₂Si(CH₃)₃), 2.36 (1H, dd, *J* 15.0, 6.6,

$\text{CH}_a\text{H}_b\text{C}=\text{O}$), 2.62 (1H, dd, J 15.0, 6.6, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 4.01-4.18 (5H, stack, $\text{CO}_2\text{CH}_2\text{CH}_3$, $\text{OCH}_2\text{C}\equiv\text{C}$, 3- H); δ_{C} (75 MHz) -2.2 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 7.0 (CH_2 , $\text{C}\equiv\text{CCH}_2\text{Si}$), 14.0 (CH_3 , OCH_2CH_3), 19.6 (CH_3 , C-4), 41.6 (CH_2 , $\text{CH}_2\text{C}=\text{O}$), 56.5 (CH_2 , $\text{OCH}_2\text{C}\equiv\text{C}$), 60.1 (CH_2 , OCH_2CH_3), 70.5 (CH , C-3), 74.6 (quat. C, $\text{C}\equiv\text{C}$), 84.2 (quat. C, $\text{C}\equiv\text{C}$), 171.0 (quat. C, $\text{C}=\text{O}$); m/z (TOF ES+) 279.9 ($[\text{M}+\text{Na}]^+$, 100%); HRMS m/z (TOF ES+) 279.1399. $\text{C}_{13}\text{H}_{24}\text{NaO}_3\text{Si}$ requires 279.1392.

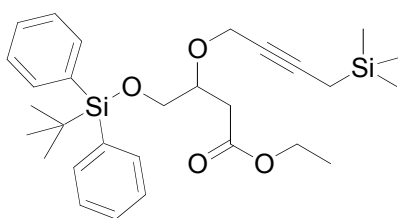
Ethyl 5-benzyloxy-3-(4'-trimethylsilanyl-but-2'-ynyloxy)pentanoate (**12e**)



Ether **12e** was prepared from trichloroacetimidate **10** (0.601g, 2.10 mmol) and β -hydroxy ester **11e** (0.795 g, 3.15 mmol) according to the general procedure. After 6 h, work-up and purification by flash column chromatography (10% Et_2O in hexane) afforded ether **12e** as a colourless oil (0.530 g, 67%); R_f = 0.21 (10% Et_2O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3582w, 3064w, 3030m, 2213m ($\text{C}\equiv\text{C}$), 1958w, 1735s ($\text{C}=\text{O}$), 1496w, 1454m, 1367m, 1306m, 1249s, 1214m, 1174s, 1096s, 852s, 791w, 737m, 699m, 666m; δ_{H} (300 MHz) 0.08 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.24 (3H, t, J 7.0, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.47 (2H, t, J 2.6, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.88 (2H, app. q, J 6.2, $\text{BnOCH}_2\text{CH}_2$), 2.48 (1H, A of ABX, $J_{\text{A-B}}$ 15.2, $J_{\text{A-X}}$ 6.1, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 2.61 (1H, B of ABX, $J_{\text{B-A}}$ 15.2, $J_{\text{B-X}}$ 6.6, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 3.56-3.61 (2H, m, BnOCH_2), 3.98-4.21 (5H, stack including [4.12 (2H, q, J 7.0, $\text{CO}_2\text{CH}_2\text{CH}_3$], $\text{OCH}_2\text{C}\equiv\text{C}$, 3- H , $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.49 (2H, s, PhCH_2), 7.26-7.37 (5H, stack, PhH); δ_{C} (75 MHz) -2.3 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 6.9 (CH_2 , $\text{C}\equiv\text{CCH}_2\text{Si}$), 14.0 (CH_3 , OCH_2CH_3), 34.3 (CH_2 , $\text{BnOCH}_2\text{CH}_2$), 39.6 (CH_2 , $\text{CH}_2\text{C}=\text{O}$), 57.5 (CH_2 , $\text{OCH}_2\text{C}\equiv\text{C}$), 60.1 (CH_2 , OCH_2CH_3), 66.4 (CH_2 , BnOCH_2), 72.3 (CH , C-3), 72.6 (CH_2 , PhCH_2O),

74.6 (quat. C, C \equiv C), 84.2 (quat. C, C \equiv C), [127.3, 128.1, (3 x CH, Ph, overlapping resonance)], 138.2 (quat. C, *ipso*Ph), 171.0 (quat. C, C=O); *m/z* (TOF ES+) 399.3 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 399.1971. C₂₁H₃₂NaO₄Si requires 399.1968.

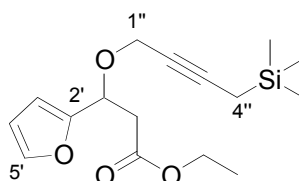
Ethyl 4-(*tert*-butyl-diphenyl-silanyloxy)-3-(4'-trimethylsilanyl-but-2'-ynyloxy)butyrate (12f)



Ether **12f** was prepared from trichloroacetimidate **10** (0.350 g, 1.22 mmol) and β -hydroxy ester **11f** (0.748 g, 1.83 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et₂O in hexane) afforded ether **12f** as a colourless oil (0.380 g, 61%); *R_f* = 0.22 (10% Et₂O in hexane); ν_{max} (film)/cm⁻¹ 3583w, 3354w, 2979m, 2360w, 2226 (C \equiv C), 1735s (C=O), 1448w, 1378m, 1305m, 1251s, 1190s, 1134m, 1075m, 954w, 852s, 700w, 666m; δ_{H} (300 MHz) 0.04 (9H, s, Si(CH₃)₃), 1.02 (9H, s, C(CH₃)₃), 1.22 (3H, t, *J* 7.2, CO₂CH₂CH₃), 1.42 (2H, t, *J* 2.4, CH₂Si(CH₃)₃), 2.52 (1H, A of ABX, *J*_{A-B} 15.7, *J*_{A-X} 7.53, CH_aH_bC=O), 2.66 (1H, B of ABX, *J*_{B-A} 15.7, *J*_{B-X} 5.1, CH_aH_bC=O), 3.60 (1H, A of ABX, *J*_{A-B} 10.7, *J*_{A-X} 5.5, SiOCH_aH_b), 3.75 (1H, B of ABX, *J*_{B-A} 10.7, *J*_{B-X} 5.1, SiOCH_aH_b), 3.99-4.21 (5H, stack including [4.10 (2H, q, 7.2, CO₂CH₂CH₃)], OCH₂C \equiv C, 3-*H*, CO₂CH₂CH₃), 7.31-7.45 (6H, stack, Ph*H*), 7.61-7.67 (4H, stack, Ph*H*); δ_{C} (75 MHz) -2.1 (CH₃, Si(CH₃)₃), 7.1 (CH₂, C \equiv CCH₂Si), 14.2 (CH₃, OCH₂CH₃), 19.2 (quat. C, C(CH₃)₃), 26.8 (CH₃, C(CH₃)₃), 37.4 (CH₂, CH₂C=O), 58.4

(CH₂, OCH₂C≡C), 60.3 (CH₂, OCH₂CH₃), 65.0 (CH₂, SiOCH₂), 74.8 (quat. C, C≡C), 75.4 (CH, C-3), 84.5 (quat. C, C≡C), 127.6 (CH, *m*-Ph), 129.6 (CH, *p*-Ph), [133.25, 133.32, (quat. C, *ipso*Ph)], [135.5, 135.6 (CH, *o*-Ph)], 171.4 (quat. C, C=O); *m/z* (TOF ES+) 533.1 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 533.2501. C₂₉H₄₂NaO₄Si₂ requires 533.2519.

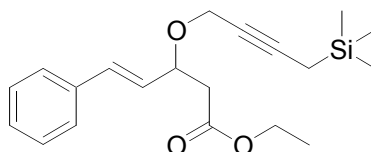
Ethyl 3-(furan-2'-yl)-3-(4''-trimethylsilanyl-but-2''-ynyloxy)propionate (**12g**)



Ether **12g** was prepared from trichloroacetimidate **10** (0.700 g, 2.09 mmol) and β-hydroxy ester **11g** (0.574 g, 3.14 mmol) according to the general procedure. After 5 h, work-up and purification by flash column chromatography (10% Et₂O in hexane) afforded ether **12g** as a colourless oil (0.348 g, 54%); *R_f* = 0.18 (10% Et₂O in hexane); *v*_{max}(film)/cm⁻¹ 3583w, 3374w, 2957m, 2901m, 2214w (C≡C), 1739s (C=O), 1585w, 1503w, 1446w, 1372m, 1335w, 1290m, 1250s, 1210w, 1166m, 1127w, 1057m, 1014m, 926w, 852s, 789w, 742w, 699w, 655w; δ_H (300 MHz) 0.11 (9H, s, Si(CH₃)₃), 1.22 (3H, t, *J* 7.2, CO₂CH₂CH₃), 1.51 (2H, t, *J* 2.2, CH₂Si(CH₃)₃), 2.81 (1H, A of ABX, *J*_{A-B} 15.4, *J*_{A-X} 6.6, CH_aH_bC=O), 2.97 (1H, B of ABX, *J*_{B-A} 15.4, *J*_{B-X} 7.7, CH_aH_bC=O), 3.94 (1H, A of ABX₂, *J*_{A-B} 15.1, *J*_{A-X} 2.4, OCH_aH_bC≡C), 4.07-4.19 (3H, stack, CO₂CH₂CH₃, OCH_aH_bC≡C), 5.04 (1H, app. t, *J* 7.0, 3-*H*), 6.30-6.37 (2H, stack, furyl CCHCH), 7.39 (1H, s with unresolved fine coupling, furyl OCH); δ_C (75 MHz) -2.1 (CH₃, Si(CH₃)₃), 7.1 (CH₂, C≡CCH₂Si), 14.0 (CH₃, OCH₂CH₃), 39.4 (CH₂, CH₂C=O), 56.4 (CH₂, OCH₂C≡C), 60.4 (CH₂, OCH₂CH₃), 69.0 (CH, C-3), 74.0

(quat. C, C \equiv C), 85.0 (quat. C, C \equiv C), 108.8 (CH, furyl CH), 109.9 (CH, furyl CH), 142.8 (CH, furyl OCH), 152.2 (quat. C, furyl C), 170.1 (quat. C, C=O); *m/z* (TOF ES+) 331.1 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 331.1339. C₁₆H₂₄NaO₄Si requires 331.1342.

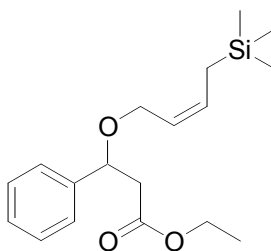
(E) Ethyl 5-phenyl-3-(4'-trimethylsilanyl-but-2'-ynyloxy)pent-4-enoate (12h)



Ether **12h** was prepared from trichloroacetimidate **10** (0.616 g, 2.15 mmol) and β -hydroxy ester **11h** (0.710 g, 3.23 mmol) according to the general procedure. After 6 h, work-up and purification by flash column chromatography (10% Et₂O in hexane) afforded ether **12h** as a yellow oil (0.474 g, 64%); *R_f* = 0.26 (10% Et₂O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3583w, 3366w, 3027w, 2957m, 2900m, 2360w, 2340w, 2213w (C \equiv C), 1737s (C=O), 1627m (C=C), 1495w, 1449m, 1369m, 1344m, 1302m, 1249s, 1167m, 1133m, 1055s, 969m, 851s, 790w, 751m, 694m, 666m; δ_{H} (300 MHz) 0.11 (9H, s, Si(CH₃)₃), 1.23 (3H, t, *J* 7.3, CO₂CH₂CH₃), 1.51 (2H, t, *J* 2.4, CH₂Si(CH₃)₃), 2.56 (1H, A of ABX, *J*_{A-B} 15.0, *J*_{A-X} 6.4, CH_aCH_bC=O), 2.75 (1H, B of ABX, *J*_{B-A} 15.0, *J*_{B-X} 7.4, CH_aCH_bC=O), 3.96-4.25 (4H, stack including [4.13 (2H, q, *J* 7.3, CO₂CH₂CH₃)], OCH₂C \equiv C, CO₂CH₂CH₃), 4.55 (1H, app. q, *J* 7.4, 3-*H*), 6.05 (1H, dd, *J* 16.1, 8.3, PhCH=CH), 6.64 (1H, d, *J* 16.1, PhCH=CH), 7.21-7.50 (5H, stack, PhH); δ_{C} (75 MHz) -2.2 (CH₃, Si(CH₃)₃), 7.0 (CH₂, C \equiv CCH₂Si), 14.0 (CH₃, OCH₂CH₃), 41.0 (CH₂, CH₂C=O), 56.1 (CH₂, OCH₂C \equiv C), 60.2 (CH₂, OCH₂CH₃), 74.4 (quat. C, C \equiv C), 75.1 (CH, C-3), 84.5 (quat. C, C \equiv C), 126.4 (CH), 127.6 (CH), 127.7 (CH), 128.3 (CH), 133.4 (CH), 136.0 (quat. C, *ipso*Ph), 170.2 (quat. C, C=O); *m/z* (TOF ES+) 367.2

([M+Na]⁺, 100%); HRMS *m/z* (TOF ES⁺) 367.1700. C₂₀H₂₈NaO₃Si requires 367.1705.

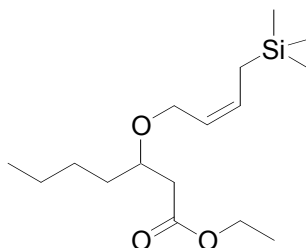
(Z) Ethyl 3-phenyl-3-(4'-trimethylsilanyl-but-2'-enyloxy)propionate (13a)



Raney nickel (a spatula tip) was added to a solution of alkyne **12a** (0.400 g, 1.34 mmol) in EtOH (39 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution stirred for 8 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13a** as a colourless oil (0.395 g, 92%); *R_f* = 0.24 (10% Et₂O in hexane); *v*_{max}(film)/cm⁻¹ 3583w, 3074w, 3027m, 2956s, 2896m, 1950w, 1739s (C=O), 1643w (C=C), 1603w, 1548w, 1530w, 1512w, 1494w, 1454m, 1415m, 1372m, 1336m, 1309m, 1249s, 1164m, 1094m, 1030m, 912w, 854s, 762m, 733m, 701s, 665m; *δ*_H (300 MHz) -0.07 (9H, s, Si(CH₃)₃), 1.21 (3H, t, *J* 7.1, CO₂CH₂CH₃), 1.37 (2H, d, *J* 8.8, CH₂Si(CH₃)₃), 2.57 (1H, A of ABX, *J*_{A-B} 15.3, *J*_{A-X} 5.0, CH_aCH_bC=O), 2.81 (1H, B of ABX, *J*_{B-A} 15.3, *J*_{B-X} 9.0, CH_aCH_bC=O), 3.84 (2H, d, *J* 6.2, OCH₂CH=CH), 4.12 (2H, q, *J* 7.1, CO₂CH₂CH₃), 4.78 (1H, dd, *J* 9.0, 5.0, 3-*H*), 5.39-5.69 (1H, m, OCH₂CH=CH), 5.51-5.68 (1H, m, OCH₂CH=CH), 7.25-7.41 (5H, stack, PhH); *δ*_C (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 14.1 (CH₃, OCH₂CH₃), 19.0 (CH₂, CH=CHCH₂Si), 43.6 (CH₂, CH₂C=O), 60.4 (CH₂, OCH₂CH₃), 64.3 (CH₂, OCH₂CH=CH), 77.5 (CH, C-3),

123.4 (CH, CH=CH), 126.6 (CH, Ph), 127.8 (CH, Ph), 128.4 (CH, Ph), 129.8 (CH, CH=CH), 141.1 (quat. C, *ipso*Ph), 170.8 (quat. C, C=O); *m/z* (TOF ES+) 343.3 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 343.1701. C₁₈H₂₈NaO₃Si requires 343.1705.

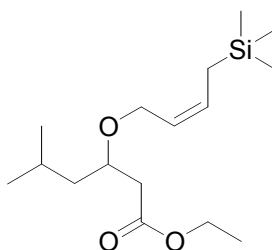
(Z) Ethyl 3-(4'-trimethylsilanyl-but-2'-enyloxy)heptanoate (13b)



Raney nickel (a spatula tip) was added to a solution of alkyne **12b** (0.325 g, 1.09 mmol) in EtOH (31 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution stirred for 15 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13b** as a colourless oil (311 mg, 95%); *R_f* = 0.23 (10% Et₂O in hexane); *v*_{max}(film)/cm⁻¹ 3446w, 2955s, 2872m, 1738s (C=O), 1646m (C=C), 1558w, 1540w, 1506w, 1465m, 1418m, 1374m, 1338m, 1301m, 1248s, 1176m, 1094m, 1036m, 944w, 854s, 773w, 727m, 702m, 665m; *δ*_H (300 MHz) -0.01 (9H, s, Si(CH₃)₃), 0.89 (3H, t, *J* 7.0, CH₃(CH₂)₃), 1.21-1.39 (7H, stack including [1.25 (3H, t, *J* 7.2, CO₂CH₂CH₃), 2 x CH₂, CO₂CH₂CH₃], 1.34-1.56 (4H, stack including [1.50 (2H, d, *J* 8.8, CH₂Si(CH₃)₃), 1 x CH₂, CH₂Si(CH₃)₃], 2.40 (1H, A of ABX, *J*_{A-B} 15.1, *J*_{A-X} 5.5, CH_aH_bC=O), 2.55 (1H, B of ABX, *J*_{B-A} 15.1, *J*_{B-X} 7.0, CH_aH_bC=O), 3.75 (1H, app. quintet, *J* 6.1, 3-*H*), 4.00 (2H, d, *J* 6.6, OCH₂CH=CH), 4.13 (2H, q, *J* 7.2,

CO₂CH₂CH₃), 5.41 (1H, dt, *J* 11.0, 6.6, OCH₂CH=CH), 5.51-5.69 (1H, m, OCH₂CH=CH); δ_C (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 13.9 (CH₃), 14.1 (CH₃), 19.1 (CH₂, CH=CHCH₂Si), 22.7 (CH₂), 27.3 (CH₂), 34.2 (CH₂), 40.0 (CH₂, CH₂C=O), 60.2 (CH₂, OCH₂CH₃), 64.9 (OCH₂CH=CH), 75.6 (CH, C-3), 123.9 (CH, CH=CH), 129.2 (CH, CH=CH), 171.8 (quat. C, C=O); *m/z* (TOF ES+) 323.2 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 323.2007. C₁₆H₃₂NaO₃Si requires 323.2018.

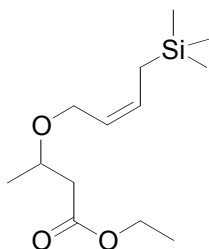
(Z) Ethyl 5-methyl-3-(4'-trimethylsilanyl-but-2'-enyloxy)hexanoate (13c)



Raney nickel (a spatula tip) was added to a solution of alkyne **12c** (0.300 g, 1.01 mmol) in EtOH (30 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution stirred for 12 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13c** as a colourless oil (0.276 g, 91%); *R_f* = 0.26 (10% Et₂O in hexane); ν_{max}(film)/cm⁻¹ 3583w, 3384w, 2956s, 2871m, 2360w, 2842w, 1737s (C=O), 1648w (C=C), 1467w, 1419w, 1369m, 1340w, 1306m, 1249s, 1179m, 1144m, 1096m, 1037m, 856s, 772w, 702w, 667m; δ_H (300 MHz) 0.00 (9H, s, Si(CH₃)₃), 0.87-0.93 (6H, stack, (CH₃)₂CH), 1.13-1.29 (4H, stack including [1.53 (3H, t, *J* 7.1, CO₂CH₂CH₃)], ⁱPrCH_aH_b, CO₂CH₂CH₃), 1.42-1.59 (3H, stack including [1.51 (2H, d, *J* 8.8, CH₂Si(CH₃)₃)], ⁱPrCH_aH_b, CH₂Si(CH₃)₃), 1.66-1.83 (1H, m, (CH₃)₂CH), 2.39 (1H, A of ABX, *J*_{A-B} 15.0,

J_{A-X} 6.1, $CH_aH_bC=O$), 2.57 (1H, B of ABX, J_{B-A} 15.0, J_{B-X} 6.6, $CH_aH_bC=O$), 3.76-3.87 (1H, m, 3-*H*), 3.97 (1H, A of ABX, J_{A-B} 11.8, J_{A-X} 6.8, $OCH_aH_bCH=CH$), 4.06 (1H, B of ABX, J_{B-A} 11.8, J_{B-X} 6.5, $OCH_aH_bCH=CH$), 4.14 (2H, q, J 7.1, $CO_2CH_2CH_3$), 5.37-5.45 (1H, m, $OCH_2CH=CH$), 5.51-5.66 (1H, m, $OCH_2CH=CH$); δ_C (75 MHz) -2.0 (CH_3 , $Si(CH_3)_3$), 14.1 (CH_3 , OCH_2CH_3), 19.1 (CH_2 , $CH=CHCH_2Si$), [22.3, 23.1, 24.5 (2 x CH_3 , 1 x CH , $(CH_3)_2CH$)], 40.3 (CH_2 , $CH_2C=O$), 44.2 (CH_2 , $iPrCH_2$), 60.2 (CH_2 , OCH_2CH_3), 64.8 (CH_2 , $OCH_2CH=CH$), 74.1 (CH , C-3), 123.8 (CH , $CH=CH$), 129.2 (CH , $CH=CH$), 171.7 (quat. C, $C=O$); m/z (TOF ES+) 323.2 ($[M+Na]^+$, 100%); HRMS m/z (TOF ES+) 323.2010. $C_{16}H_{32}NaO_3Si$ requires 323.2018.

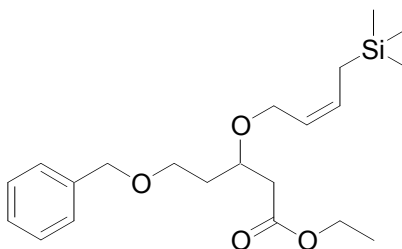
(Z) Ethyl 3-(4'-trimethylsilanyl-but-2'-enyloxy)butyrate (13d)



Raney nickel (a spatula tip) was added to solution of alkyne **12d** (0.350 g, 1.36 mmol) in EtOH (40 mL) at rt. The solution was charged with H_2 gas (3 x vacuum- H_2 flushes) and the resulting solution stirred for 10 min under an atmosphere of H_2 . Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et_2O in hexane) to afford alkene **13d** as a colourless oil (0.341 g, 97%); R_f = 0.19 (10% Et_2O in hexane); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3583w, 2956s, 1738s ($C=O$), 1650w ($C=C$), 1448w, 1376m, 1334m, 1302m, 1249s, 1187s, 1144m, 1096s, 1033m, 948w, 918w, 858s, 729w, 702w, 666m; δ_H (300 MHz) -0.01 (9H, s, $Si(CH_3)_3$), 1.21 (3H, d, J 6.3, CH_3), 1.25 (3H, t, J

7.1, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.51 (2H, d, J 8.8, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 2.35 (1H, A of ABX, $J_{\text{A-B}}$ 15.1, $J_{\text{A-X}}$ 5.9, $\text{CH}_a\text{CH}_b\text{C}=\text{O}$), 2.59 (1H, B of ABX, $J_{\text{B-A}}$ 15.1, $J_{\text{B-X}}$ 7.0, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 3.82-4.03 (3H, stack, $\text{OCH}_2\text{CH}=\text{CH}$, 3- H), 4.13 (2H, q, J 7.1, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.41 (1H, dt, J 11.0, 6.3, $\text{OCH}_2\text{CH}=\text{CH}$), 5.52-5.67 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}$); δ_{C} (75 MHz) -1.9 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 14.2 (CH_3 , OCHCH_3), 19.1 (CH_2 , $\text{CH}=\text{CHCH}_2\text{Si}$), 19.9 (CH_3 , C-4), 42.0 (CH_2 , $\text{CH}_2\text{C}=\text{O}$), 60.2 (CH_2 , OCH_2CH_3), 64.2 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}$), 71.5 (CH , C-3), 123.8 (CH , $\text{CH}=\text{CH}$), 129.4 (CH , $\text{CH}=\text{CH}$), 171.5 (quat. C, $\text{C}=\text{O}$); m/z (TOF ES+) 281.1 ($[\text{M}+\text{Na}]^+$, 100%); HRMS m/z (TOF ES+) 281.1553. $\text{C}_{13}\text{H}_{26}\text{NaO}_3\text{Si}$ requires 281.1549.

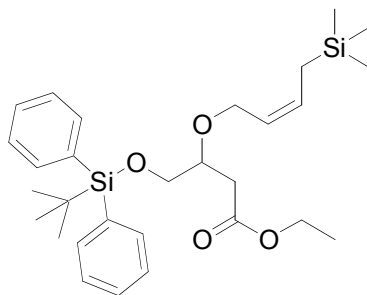
(Z) Ethyl 5-benzyloxy-3-(4'-trimethylsilanyl-but-2'-enyloxy)pentanoate (13e)



Raney nickel (a spatula tip) was added to a solution of alkyne **12e** (0.250 g, 0.66 mmol) in EtOH (19 mL) at rt. The solution was charged with H_2 gas (3 x vacuum- H_2 flushes) and the resulting solution stirred for 10 min under an atmosphere of H_2 . Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et_2O in hexane) to afford alkene **13e** as a colourless oil (0.225 g, 90%); R_f = 0.22 (10% Et_2O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3019m, 2954s, 2858m, 2354w, 1946w, 1890w, 1735s ($\text{C}=\text{O}$), 1649w ($\text{C}=\text{C}$), 1496w, 1454m, 1420m, 1373m, 1337m, 1306m, 1248s, 1214m, 1174s, 1096s, 1030m, 948w, 857s, 799w, 774w, 732m, 697m; δ_{H} (300 MHz) -0.02 (9H, s,

Si(CH₃)₃), 1.25 (3H, t, *J* 7.2, CO₂CH₂CH₃), 1.49 (2H, d, *J* 8.8, CH₂Si(CH₃)₃), 1.85 (2H, app. q, *J* 6.3, BnOCH₂CH₂), 2.47 (1H, A of ABX, *J*_{A-B} 15.1, *J*_{A-X} 5.5, CH_aH_bC=O), 2.57 (1H, B of ABX, *J*_{B-A} 15.1, *J*_{B-X} 7.0, CH_aH_bC=O), 3.48-3.65 (2H, m, BnOCH₂), 3.92-4.19 (5H, stack including [4.13 (2H, q, *J* 7.2, CO₂CH₂CH₃], OCH₂CH=CH, 3-*H*, CO₂CH₂CH₃), 4.49 (2H, s, PhCH₂), 5.38 (1H, dt, *J* 11.0, 6.6, OCH₂CH=CH), 5.53-5.67 (1H, m, OCH₂CH=CH), 7.23-7.43 (5H, stack, PhH); δ_C (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 14.1 (CH₃, OCH₂CH₃), 19.1 (CH₂, CH=CHCH₂Si), 34.7 (CH₂, BnOCH₂CH₂), 40.2 (CH₂, CH₂C=O), 60.3 (CH₂, OCH₂CH₃), 65.1 (CH₂, (OCH₂CH=CH), 66.5 (BnOCH₂), 72.8 (CH₂, PhCH₂O), 73.0 (CH, C-3), 123.6 (CH, CH=CH), 127.4 (CH, Ph), 127.5 (CH, Ph), 128.2 (CH, Ph), 129.3 (CH, CH=CH), 138.3 (CH, *ipso*Ph), 171.5 (quat. C, C=O); *m/z* (TOF ES+) 401.3 ([M+Na]⁺, 100%), 485.2 (23, [M+Ag]⁺); HRMS *m/z* (TOF ES+) 401.2122. C₂₁H₃₄NaO₄Si requires 401.2124.

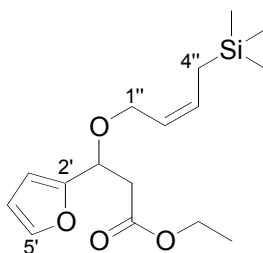
(Z) Ethyl 4-(*tert*-butyl-diphenyl-silanyloxy)-3-(4'-trimethylsilanyl-but-2'-enyloxy)butyrate (13f)



Raney nickel (a spatula tip) was added to a solution of alkyne **12f** (0.300 g, 0.59 mmol) in EtOH (18 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution stirred for 12 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which

was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13f** as a colourless oil (0.269 g, 89%); R_f = 0.23 (10% Et₂O in hexane); $\nu_{\max}(\text{film})$ /cm⁻¹ 3583w, 3379w, 3064w, 3029m, 2955s, 2364w, 1749s (C=O), 1648w (C=C), 1604w, 1496m, 1454m, 1370m, 1249s, 1205m, 1178s, 1110m, 1073m, 1029m, 855s, 731s, 696s, 666m; δ_H (300 MHz) -0.04 (9H, s, Si(CH₃)₃), 1.04 (9H, s, C(CH₃)₃), 1.25 (3H, t, J 7.2, CO₂CH₂CH₃), 1.45 (2H, d, J 8.5, CH₂Si(CH₃)₃), 2.50 (1H, A of ABX, J_{A-B} 15.6, J_{A-X} 8.3, CH_aCH_bC=O), 2.66 (1H, B of ABX, J_{B-A} 15.6, J_{B-X} 4.6, CH_aCH_bC=O), 3.58 (1H, A of ABX, J_{A-B} 10.4, J_{A-X} 5.7, SiOCH_aH_b), 3.72 (1H, B of ABX, J_{B-A} 10.4, J_{B-X} 5.5, OSiCH_aH_b), 3.85-4.18 (5H, stack including [4.04 (1H, app. t, J 6.6, OCH_aH_bCH=CH), [4.13 (2H, q, J 7.2, CO₂CH₂CH₃), 3-*H*, OCH_aH_bCH=CH, CO₂CH₂CH₃), 5.31-5.43 (1H, m, OCH₂CH=CH), 5.48-5.62 (1H, m, OCH₂CH=CH), 7.33-7.46 (6H, stack, Ph*H*), 7.64-7.71 (4H, stack, Ph*H*); δ_C (75 MHz) -1.9 (CH₃, Si(CH₃)₃), 14.2 (CH₃, OCH₂CH₃), 19.1 (quat. C, C(CH₃)₃), 19.2 (CH₂, CH=CHCH₂Si), 26.8 (CH₃, C(CH₃)₃), 37.8 (CH₂, CH₂C=O), 60.4 (CH₂, OCH₂CH₃), 65.3 (CH₂), 66.0 (CH₂), 76.2 (CH, C-3), 123.8 (CH, CH=CH), 127.6 (CH, *m*-Ph), 129.3 (CH, CH=CH), 129.6 (CH, *p*-Ph), [133.27, 133.34, (quat. C, *ipso*Ph)], [135.54, 135.56 (CH, *o*-Ph)], 171.7 (quat. C, C=O); m/z (TOF ES+) 535.3 ([M+Na]⁺, 100%); HRMS m/z (TOF ES+) 535.2669. C₂₉H₄₄NaO₄Si₂ requires 535.2676.

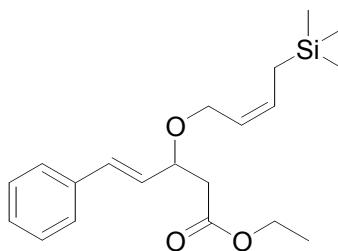
(Z) Ethyl 3-(furan-2'-yl)-3-(4''-trimethylsilanyl-but-2''-enyloxy)propionate (13g)



Raney nickel (a spatula tip) was added to a solution of alkyne **12g** (0.250 g, 0.81 mmol) in EtOH (24 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution stirred for 12 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13g** as a colourless oil (0.234 g, 93%); *R_f* = 0.19 (10% Et₂O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2955m, 2897m, 1740s (C=O), 1684w, 1653w (C=C), 1559w, 1540w, 1522w, 1506w, 1458w, 1419w, 1374m, 1352w, 1332w, 1287m, 1249s, 1210w, 1165m, 1078m, 1043m, 1012m, 926w, 855s, 738m, 703m, 665m; δ_{H} (300 MHz) -0.03 (9H, s, Si(CH₃)₃), 1.24 (3H, t, *J* 7.0, CO₂CH₂CH₃), 1.37 (2H, d, *J* 9.2, CH₂Si(CH₃)₃), 2.76 (1H, A of ABX, *J*_{A-B} 15.4, *J*_{A-X} 5.6, CH_aCH_bC=O), 2.96 (1H, B of ABX, *J*_{B-A} 15.4, *J*_{B-X} 8.5, CH_aCH_bC=O), 3.95 (2H, d with unresolved fine coupling, *J* 5.5, OCH₂CH=CH), 4.14 (2H, q, *J* 7.1, CO₂CH₂CH₃), 4.83 (1H, dd, *J* 8.5, 5.6, 3-*H*), 5.35-5.48 (1H, m, OCH₂CH=CH), 5.55-5.69 (1H, m, OCH₂CH=CH), 6.28-6.41 (2H, stack, furyl CCHCH), 7.38-7.43 (1H, m, furyl OCH); δ_{C} (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 14.1 (CH₃, OCH₂CH₃), 19.1 (CH₂, CH=CHCH₂Si), 40.0 (CH₂, CH₂C=O), 60.4 (CH₂, OCH₂CH₃), 64.3 (CH₂, OCH₂CH=CH), 70.2 (CH, C-3), 107.9 (CH, furyl CH), 109.9 (CH, furyl CH), 123.1 (CH, CH=CH), 130.1 (CH, CH=CH), 142.4 (CH, furyl OCH), 153.3 (quat. C, furyl C) 170.4 (quat. C, C=O); *m/z* (TOF ES⁺) 333.1

$[M+Na]^+$, 100%); HRMS m/z (TOF ES+) 333.1487. $C_{16}H_{26}NaO_4Si$ requires 333.1487.

(4*E*, 2'*Z*) Ethyl 5-phenyl-3-(4'-trimethylsilanyl-but-2'-enyloxy)pent-4-enoate
(13h)



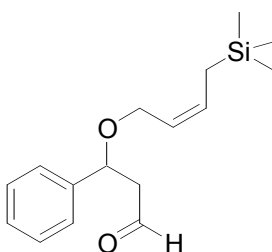
Raney nickel (a spatula tip) was added to a solution of alkyne **12h** (0.280 g, 0.81 mmol) in EtOH (23 mL) at rt. The solution was charged with H₂ gas (3 x vacuum-H₂ flushes) and the resulting solution was stirred for 10 min under an atmosphere of H₂. Filtration and removal of the solvent under reduced pressure left a residue which was purified by flash column chromatography (10% Et₂O in hexane) to afford alkene **13h** as a yellow oil (0.255 g, 91%); R_f = 0.23 (10% Et₂O in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3582w, 2954m, 2357w, 1737s (C=O), 1656w, 1649w, 1626m (C=C), 1547w, 1511w, 1495m, 1463w, 1449m, 1369m, 1248s, 1159s, 1094m, 1041m, 968m, 854s, 805w, 795w, 751, 692m, 665s; δ_H (300 MHz) -0.03 (9H, s, Si(CH₃)₃), 1.24 (3H, t, J 7.2, CO₂CH₂CH₃), 1.48 (2H, d, J 8.5, CH₂Si(CH₃)₃), 2.52 (1H, A of ABX, J_{A-B} 15.1, J_{A-X} 5.5, CH_aH_bC=O), 2.71 (1H, B of ABX, J_{B-A} 15.1, J_{B-X} 8.1, CH_aH_bC=O), 3.94 (1H, A of ABX, J_{A-B} 11.8, J_{A-X} 7.0, OCH_aH_bCH=CH), 4.01 (1H, B of ABX, J_{B-A} 11.8, J_{B-X} 6.3, OCH_aH_bCH=CH), 4.14 (2H, q, J 7.2, CO₂CH₂CH₃), 4.37 (1H, app. q, J 7.1, 3-*H*), 5.44 (1H, dt, J 11.0, 7.0, OCH₂CH=CH), 5.54-5.69 (1H, m, OCH₂CH=CH), 6.10 (1H, dd, J 16.0, 7.7, PhCH=CH), 6.61 (1H, d, J 16.0, PhCH=CH), 7.22-7.48 (5H, stack, PhH);

δ_{C} (100 MHz) -1.9 (CH₃, Si(CH₃)₃), 14.2 (CH₃, OCH₂CH₃), 19.2 (CH₂, CH=CHCH₂Si), 41.4 (CH₂, CH₂C=O), 60.4 (CH₂, OCH₂CH₃), 64.1 (CH₂, OCH₂CH=CH), 75.3 (CH, C-3), 123.5 (CH), 126.5 (CH), 127.8 (CH), 128.5 (CH), 128.8 (CH), 129.8 (CH), 132.6 (CH), 136.3 (quat. C, *ipso*Ph), 170.7 (quat. C, C=O); m/z (TOF ES⁺) 369.3 ([M+Na]⁺, 100%); HRMS m/z (TOF ES⁺) 369.1854. C₂₀H₃₀NaO₃Si requires 369.1862.

General procedure for DIBALH reduction: formation of **7**

DIBALH (1.1 equiv of a 1.5 M solution in toluene) was added dropwise over 30 min to a solution of ester **13** (1 equiv) in CH₂Cl₂ (0.06 M reaction concentration) at -78 °C. After 1 h (consumption of the starting material was monitored by TLC), the reaction was quenched with MeOH (1 equiv) and H₂O (6 equiv) at -78 °C, and the resulting slurry was allowed to warm to rt. It was then filtered through MgSO₄ and Celite and the solvent was evaporated under reduced pressure to leave a yellow liquid which was purified by flash column chromatography.

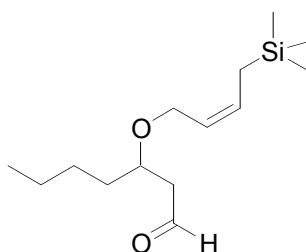
(*Z*) 3-Phenyl-3-(4'-trimethylsilanyl-but-2'-enyloxy)propionaldehyde (**7a**)



Aldehyde **7a** was prepared from ester **13a** (0.300 g, 0.94 mmol) and DIBALH (0.69 mL of a 1.5 M solution in toluene, 1.03 mmol) according to the general procedure.

After 1 h, work-up and purification by flash column chromatography (6% EtOAc in hexane) afforded aldehyde **7a** as a colourless oil (0.236 g, 91%); R_f = 0.22 (6% EtOAc in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3583w, 3436w, 3064w, 3027m, 2955s, 2895m, 2726m, 1952w, 1727s (C=O), 1681m (C=C), 1647m (C=C), 1627w, 1604w, 1494m, 1454m, 1401m, 1335m, 1307m, 1289m, 1248s, 1217w, 1192w, 1146m, 1090s, 1041m, 921w, 855m, 762m, 702s, 666m; δ_H (300 MHz) -0.07 (9H, s, Si(CH₃)₃), 1.37 (2H, d, J 8.8, CH₂Si(CH₃)₃), 2.59 (1H, A of ABXY, J_{A-B} 16.5, J_{A-X} 4.3, J_{A-Y} 1.6, CH_aH_bC=O), 2.92 (1H, B of ABXY, J_{B-A} 16.5, J_{B-X} 9.0, J_{B-Y} 2.4, CH_aH_bC=O), 3.79-3.97 (2H, m, OCH₂CH=CH), 4.84 (1H, dd, J 9.0, 4.3, 3-*H*), 5.42 (1H, dt, J 10.3, 5.1, OCH₂CH=CH), 5.55-5.68 (1H, m, OCH₂CH=CH), 7.23-7.47 (5H, stack, Ph*H*), 9.80 (1H, app. t, J 2.0, CHO); δ_C (75 MHz) -2.5 (CH₃, Si(CH₃)₃), 18.7 (CH₂, CH=CHCH₂Si), 51.5 (CH₂, CH₂C=O), 64.1 (CH₂, OCH₂CH=CH), 76.1 (CH, C-3), 123.3 (CH, CH=CH), 126.8 (CH, Ph), 128.3 (CH, Ph), 128.9 (CH, Ph), 130.6 (CH, CH=CH), 141.2 (quat. C, *ipso*Ph), 201.4 (CH, C=O); m/z (TOF ES+) 299.1 ([M+Na]⁺, 100%), 331.1 (93, [M+Na+MeOH]⁺); HRMS m/z (TOF ES+) 299.1454. C₁₆H₂₄NaO₂Si requires 299.1443.

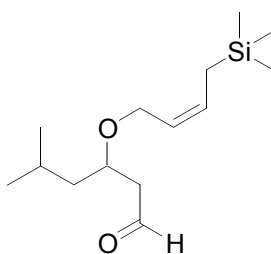
(Z) 3-(4'-trimethylsilanyl-but-2'-enyloxy)heptanal (7b)



Aldehyde **7b** was prepared from ester **13b** (0.250 g, 0.83 mmol) and DIBALH (0.61 mL of a 1.5 M solution in toluene, 0.91 mmol) according to the general procedure.

After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **7b** as a colourless oil (0.204 g, 96%); *R*_f = 0.20 (6% Et₂O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3234w, 3019m, 2956s, 2862m, 2724w, 2368w, 2340w, 1726s (C=O), 1691w, 1679w, 1650m (C=C), 1548w, 1529w, 1513w, 1468m, 1415m, 1379m, 1336m, 1249s, 1147m, 1077m, 915w, 855s, 773w, 733m, 702m, 666m; δ_{H} (300 MHz) 0.00 (9H, s, Si(CH₃)₃), 0.90 (3H, t, *J* 7.0, CH₃), 1.24-1.41 (4H, stack 2 x CH₂), 1.42-1.55 (4H, stack including [1.50 (2H, d, *J* 8.8, CH₂Si(CH₃)₃)], 1 x CH₂, CH₂Si(CH₃)₃), 2.51 (1H, A of ABXY, *J*_{A-B} 16.3, *J*_{A-X} 5.0, *J*_{A-Y} 2.0, CH_aH_bC=O), 2.62 (1H, B of ABXY, *J*_{B-A} 16.3, *J*_{B-X} 7.0, *J*_{B-Y} 2.4, CH_aH_bC=O), 3.83 (1H, app. quintet, *J* 6.0, 3-*H*), 4.00 (2H, d, *J* 6.6, OCH₂CH=CH), 5.40 (1H, dt with unresolved fine coupling, *J* 11.0, 6.6, OCH₂CH=CH), 5.51-5.69 (1H, m, OCH₂CH=CH), 9.81 (1H, app. t, *J* 2.4, CHO); δ_{C} (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 13.9 (CH₃, CH₃(CH₂)₃), 19.1 (CH₂, CH=CHCH₂Si), 22.6 (CH₂), 27.2 (CH₂), 34.0 (CH₂), 48.3 (CH₂, CH₂C=O), 64.5 (OCH₂CH=CH), 74.1 (CH, C-3), 123.5 (CH, CH=CH), 129.6 (CH, CH=CH), 201.7 (CH, C=O); *m/z* (TOF ES⁺) 279 ([M+Na]⁺, 100%), 311 (96, [M+Na+MeOH]⁺); HRMS *m/z* (TOF ES⁺) 279.1759. C₁₄H₂₈NaO₂Si requires 279.1756.

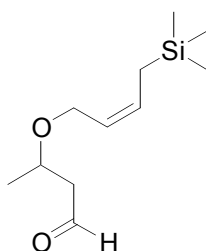
(Z) 5-Methyl-3-(4'-trimethylsilanyl-but-2'-enyloxy)hexanal (7c)



Aldehyde **7c** was prepared from ester **13c** (0.250 g, 0.83 mmol) and DIBALH (0.61 mL of a 1.5 M solution in toluene, 0.91 mmol) according to the general procedure.

After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **7c** as a colourless oil (0.201 g, 94%); *R_f* = 0.26 (6% Et₂O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3583w, 3444w, 3030w, 2954s, 2360w, 1731s (C=O), 1646w (C=C), 1494w, 1454m, 1418m, 1249s, 1098s, 854s, 670s, 666s; (300 MHz) - 0.00 (9H, s, Si(CH₃)₃), 0.89-0.94 (6H, stack, (CH₃)₂CH), 1.16-1.32 (1H, m, ⁱPrCH_aH_b), 1.41-1.63 (3H, stack including [1.51 (2H, d, *J* 9.2, CH₂Si(CH₃)₃)], ⁱPrCH_aH_b, CH₂Si(CH₃)₃), 1.65-1.83 (1H, m, (CH₃)₂CH), 2.55-2.60 (2H, stack, CH₂C=O), 3.84-3.93 (1H, m, 3-*H*), 3.97-4.04 (2H, stack, OCH₂CH=CH), 5.35-5.44 (1H, m, OCH₂CH=CH), 5.54-5.68 (1H, m, OCH₂CH=CH), 9.82-9.83 (1H, m, CHO); δ_{C} (75 MHz) -1.9 (CH₃, Si(CH₃)₃), 19.2 (CH₂, CH=CHCH₂Si), [22.5, 22.9, 24.6 (2 x CH₃, 1 x CH, (CH₃)₂CH)], 44.1 (CH₂, ⁱPrCH₂), 48.6 (CH₂, CH₂C=O), 64.6 (CH₂, OCH₂CH=CH), 72.6 (CH, C-3), 123.5 (CH, CH=CH), 129.8 (CH, CH=CH), 201.8 (CH, C=O); *m/z* (TOF ES+) 311 ([M+Na+MeOH]⁺, 95%), 279 (100, [M+Na]⁺); HRMS *m/z* (TOF ES+) 279.1758. C₁₄H₂₈NaO₂Si requires 279.1756.

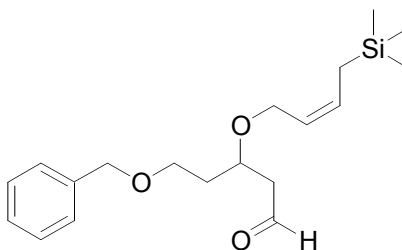
(Z) 3-(4'-Trimethylsilanyl-but-2'-enyloxy)butanal (7d)



Aldehyde **7d** was prepared from ester **13d** (0.210 g, 0.98 mmol) and DIBALH (0.72 mL of a 1.5 M solution in toluene, 1.08 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **7d** as a colourless oil (1.912 g, 91%); *R_f* = 0.18 (6%

Et₂O in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3583w, 3435w, 3018w, 2956s, 2856s, 2724w, 1727s (C=O), 1647w (C=C), 1455w, 1418w, 1376m, 1330m, 1249s, 1146m, 1113m, 1070m, 1044m, 855s, 772w, 729w, 701m, 666m; δ_{H} (300 MHz) 0.00 (9H, s, Si(CH₃)₃), 1.24 (3H, d, *J* 6.3, CH₃), 1.51 (2H, d, *J* 8.8, CH₂Si(CH₃)₃), 2.47 (1H, A of ABXY, *J*_{A-B} 16.4, *J*_{A-X} 5.1, *J*_{A-Y} 2.0, CH_aCH_bC=O), 2.65 (1H, B of ABXY, *J*_{B-A} 16.4, *J*_{B-X} 7.2, *J*_{B-Y} 2.3, CH_aCH_bC=O), 3.87-4.13 (3H, stack, OCH₂CH=CH, 3-*H*), 5.40 (1H, dt, *J* 10.7, 6.6, OCH₂CH=CH), 5.56-5.65 (1H, m, OCH₂CH=CH), 9.79 (1H, app. t, *J* 2.2, CHO); δ_{C} (75 MHz) -2.4 (CH₃, Si(CH₃)₃), 18.8 (CH₂, CH=CHCH₂Si), 19.5 (CH₃, C-4), 50.3 (CH₂, CH₂C=O), 63.9 (CH₂, OCH₂CH=CH), 69.9 (CH, C-3), 123.7 (CH, CH=CH), 130.1 (CH, CH=CH), 202.2 (CH, C=O); *m/z* (TOF ES+) 237.1 ([M+Na]⁺, 100%), 269.2 (97, [M+Na+MeOH]⁺); HRMS *m/z* (TOF ES+) 237.1283. C₁₁H₂₂NaO₂Si requires 237.1287.

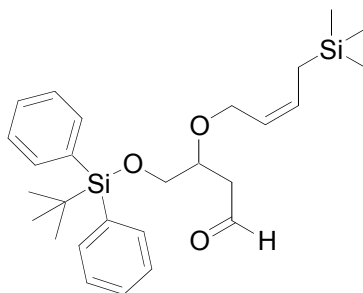
(Z) 5-Benzyloxy-3-(4'-trimethylsilanyl-but-2'-enyloxy)pentanal (7e)



Aldehyde **7e** was prepared from ester **13e** (0.200 g, 0.53 mmol) and DIBALH (0.39 mL of a 1.5 M solution in toluene, 0.59 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **7e** as a colourless oil (0.157 g, 89%); *R_f* = 0.26 (6% EtOAc in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3583w, 3430w, 3027w, 2954s, 2859s, 2726w, 1725s (C=O), 1646w (C=C), 1496w, 1454m, 1418w, 1362m, 1337w, 1248s, 1205w,

1099s, 855s, 773w, 736m, 698m, 666m; δ_{H} (300 MHz) -0.01 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.50 (2H, d, J 8.8, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.76-1.99 (2H, m, $\text{BnOCH}_2\text{CH}_2$), 2.57-2.65 (2H, m, $\text{CH}_2\text{C}=\text{O}$), 3.49-3.66 (2H, m, BnOCH_2), 3.91-4.16 (3H, stack, $\text{OCH}_2\text{CH}=\text{CH}$, 3- H), 4.49 (2H, s, PhCH_2O), 5.39 (1H, dt, J 10.7, 6.6, $\text{OCH}_2\text{CH}=\text{CH}$), 5.54-5.68 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}$), 7.20-7.42 (5H, stack, PhH), 9.79 (1H, app. t, J 2.0, CHO); δ_{C} (75 MHz) -1.9 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 19.1 (CH_2 , $\text{CH}=\text{CHCH}_2\text{Si}$), 34.6 (CH_2 , $\text{BnOCH}_2\text{CH}_2$), 48.5 (CH_2 , $\text{CH}_2\text{C}=\text{O}$), 64.9 (CH_2), 66.3 (CH_2), 71.5 (CH , C-3), 72.9 (CH_2 , PhCH_2O), 123.3 (CH , $\text{CH}=\text{CH}$), 127.52 (CH , Ph), 127.54 (CH , Ph), 128.3 (CH , Ph), 129.8 (CH , $\text{CH}=\text{CH}$), 138.2 (quat. C, *ipso*Ph), 201.4 (CH , $\text{C}=\text{O}$); m/z (TOF ES+) 357.2 ($[\text{M}+\text{Na}]^+$, 92%), 389.2 [92, $[\text{M}+\text{Na}+\text{MeOH}]^+$]; HRMS m/z (TOF ES+) 357.1871. $\text{C}_{19}\text{H}_{30}\text{NaO}_3\text{Si}$ requires 357.1862.

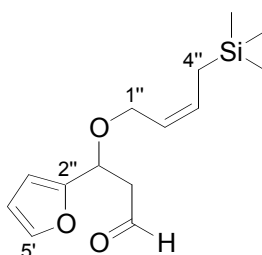
(Z) 4-(tert-Butyl-diphenyl-silanyloxy)-3-(4'-trimethylsilanyl-but-2'-enyloxy)butanal (7f)



Aldehyde **7f** was prepared from ester **13f** (0.200 g, 0.39 mmol) and DIBALH (0.29 mL of a 1.5 M solution in toluene, 0.44 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et_2O in hexane) afforded aldehyde **7f** as a colourless oil (0.159 g, 87%); R_f = 0.22 (6% Et_2O in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3583w, 3072m, 3017m, 2955s, 2939s, 2894s, 2858s, 2723s, 2360w, 2342w, 1728s ($\text{C}=\text{O}$), 1648w ($\text{C}=\text{C}$), 1590w, 1472m, 1428s, 1390m,

1362m, 1333w, 1248s, 1188w, 1113s, 1000m, 998m, 940w, 854s, 825s, 741s, 702s, 666m, 614s; δ_{H} (300 MHz) -0.04 (9H, s, Si(CH₃)₃), 1.04 (9H, s, C(CH₃)₃), 1.45 (2H, d, *J* 8.8, CH₂Si(CH₃)₃), 2.63-2.69 (2H, stack, CH₂C=O), 3.61 (1H, A of ABX, *J*_{A-B} 10.3, *J*_{A-X} 5.9, SiOCH_aH_b), 3.74 (1H, B of ABX, *J*_{B-A} 10.3, *J*_{B-X} 5.0, SiOCH_aH_b), 3.88-4.08 (3H, stack, OCH₂CH=CH, 3-*H*), 5.35 (1H, dt, *J* 10.7, 6.6, OCH₂CH=CH), 5.55-5.68 (1H, m, OCH₂CH=CH), 7.31-7.49 (6H, stack, Ph*H*), 7.57-7.69 (4H, stack, Ph*H*), 9.82 (1H, app. t, *J* 2.0, CHO); δ_{C} (75 MHz) -1.9 (CH₃, Si(CH₃)₃), 19.16 (quat. C, C(CH₃)₃), 19.22 (CH₂, CH=CHCH₂Si), 26.8 (CH₃, C(CH₃)₃), 46.4 (CH₂, CH₂C=O), 65.2 (CH₂), 65.6 (CH₂), 74.6 (CH, C-3), 123.4 (CH, CH=CH), 127.7 (CH, *m*-Ph), 129.8 (CH, CH=CH), 129.9 (CH, *p*-Ph), [133.1, 133.2 (quat. C, *ipso*Ph)], [135.5, 135.6 (CH, *o*-Ph)], 201.4 (CH, C=O); *m/z* (TOF ES⁺) 523.2 ([M+Na+MeOH]⁺, 100%), 491.3 (25, [M+Na]⁺); HRMS *m/z* (TOF ES⁺) 491.2435. C₂₇H₄₀NaO₃Si₂ requires 491.2412.

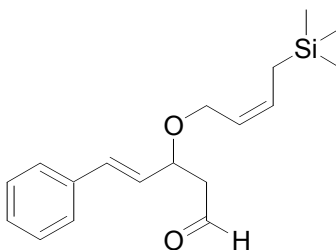
(Z) 3-Furan-2'-yl-3-(4''-trimethylsilanyl-but-2''-enyloxy)propionaldehyde (7g)



Aldehyde **7g** was prepared from ester **13g** (0.180 g, 0.58 mmol) and DIBALH (0.43 mL of a 1.5 M solution in toluene, 0.64 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **7g** as a colourless oil (0.138 g, 89%); *R_f* = 0.20 (6% Et₂O in hexane); ν_{max} (film)/cm⁻¹ 3583w, 3120w, 2955m, 2894m, 2726w, 1728s

(C=O), 1647w (C=C), 1504w, 1401w, 1326w, 1249s, 1150m, 1079s, 1041m, 1011m, 928w, 855s, 740m, 702w, 666m; (300 MHz) -0.03 (9H, s, Si(CH₃)₃), 1.46 (2H, d, *J* 9.6, CH₂Si(CH₃)₃), 2.81 (1H, A of ABXY, *J*_{A-B} 16.6, *J*_{A-X} 4.9, *J*_{A-Y} 1.5, CH_aH_bC=O), 3.06 (1H, B of ABXY, *J*_{B-A} 16.6, *J*_{B-X} 8.4, *J*_{B-Y} 2.6, CH_aH_bC=O), 3.91-3.99 (2H, stack, OCH₂CH=CH), 4.88 (1H, dd, *J* 8.4, 4.9, 3-*H*), 5.40 (1H, dt, *J* 10.7, 6.6, OCH₂CH=CH), 5.57-5.71 (1H, m, OCH₂CH=CH), 6.32-6.33 (1H, m, furyl CH), 6.35-6.37 (1H, m, furyl CH), 7.41 (1H, d, *J* 1.1, 5'-*H*), 9.80-9.81 (1H, m, CHO); δ_C (75 MHz) -1.9 (CH₃, Si(CH₃)₃), 19.2 (CH₂, CH=CHCH₂Si), 47.8 (CH₂, CH₂C=O), 64.1 (CH₂, OCH₂CH=CH), 68.7 (CH, C-3), 108.3 (CH, furyl CH), 110.1 (CH, furyl CH), 122.8 (CH, CH=CH), 130.6 (CH, CH=CH), 142.6 (CH, furyl OCH), 152.9 (quat. C, furyl C), 202.2 (CH, C=O); *m/z* (TOF ES⁺) 321.4 ([M+Na+MeOH]⁺, 98%), 289.4 (100, [M+Na]⁺); HRMS *m/z* (TOF ES⁺) 289.1230. C₁₄H₂₂NaO₃Si requires 289.1236.

(4 *E*, 2' *Z*) 5-Phenyl-3-(4'-trimethylsilylbut-2'-enyloxy)pent-4-enal (7h)



Aldehyde **7h** was prepared from ester **13h** (0.220 g, 0.73 mmol) and DIBALH (0.53 mL of a 1.5 M solution in toluene, 0.80 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6 % Et₂O in hexane) afforded aldehyde **7h** as a yellow oil (0.203 g, 92%); *R_f* = 0.20 (6% Et₂O in hexane); ν_{max}(film)/cm⁻¹ 3433w, 3023m, 2954s, 2727m, 1950w, 1726s (C=O), 1679m (OCH₂CH=CH), 1621m (PhCH=CH), 1994 w, 1450w, 1405m, 1332m, 1250s,

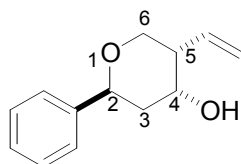
1148m, 1078s, 972m, 852s, 749m, 695m, 663m; δ_{H} (300 MHz) -0.03 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.49 (2H, d, J 8.8, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 2.60 (1H, A of ABXY, $J_{\text{A-B}}$ 16.3, $J_{\text{A-X}}$ 4.9, $J_{\text{A-Y}}$ 1.8, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 2.80 (1H, B of ABXY, $J_{\text{B-A}}$ 16.3, $J_{\text{B-X}}$ 8.0, $J_{\text{B-Y}}$ 2.5, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 3.95 (1H, ABX, $J_{\text{A-B}}$ 11.7, $J_{\text{A-X}}$ 7.0, $\text{OCH}_a\text{H}_b\text{CH}=\text{CH}$), 4.08 (1H, B of ABX, $J_{\text{B-A}}$ 11.7, $J_{\text{B-X}}$ 6.1, $\text{OCH}_a\text{H}_b\text{CH}=\text{CH}$), 4.45 (1H, td, J 8.0, 4.9, 3- H), 5.43 (1H, dt, J 11.0, 6.6, $\text{OCH}_2\text{CH}=\text{CH}$), 5.44-5.67 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}$), 6.11 (1H, dd, J 15.9, 8.0, $\text{PhCH}=\text{CH}$), 6.63 (1H, d, J 15.9, $\text{PhCH}=\text{CH}$), 7.22-7.45 (5H, stack, PhH), 9.81 (1H, app. t, J 2.1, CHO); δ_{C} (75 MHz) -1.9 (CH_3 , $\text{Si}(\text{CH}_3)_3$), 19.3 (CH_2 , $\text{CH}=\text{CHCH}_2\text{Si}$), 49.5 (CH_2 , $\text{CH}_2\text{C}=\text{O}$), 64.0 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}$), 74.9 (CH , C-3), 123.1 (CH), 126.5 (CH), 128.0 (CH), 128.5 (CH), 128.6 (CH), 130.3 (CH), 132.8 (CH), 136.0 (quat. C, *ipso*Ph), 201.0 (CH , $\text{C}=\text{O}$); m/z (TOF ES+) 325.2 ($[\text{M}+\text{Na}]^+$, 100%), 357.2 (87, $[\text{M}+\text{Na}+\text{MeOH}]^+$); HRMS m/z (TOF ES+) 325.1607. $\text{C}_{18}\text{H}_{26}\text{NaO}_2\text{Si}$ requires 325.1600.

General procedure for allylation reactions: formation of **14**

MeSO_3H (1.1 equiv) was added to a solution of aldehyde **7** (1.0 equiv) in toluene (0.1 M reaction concentration) at -78°C and the reaction was stirred for 30-50 min (consumption of the starting material was monitored by TLC). The reaction was then quenched by the addition of NaHCO_3 solution (1 x volume of organic phase) at -78°C and then the reaction mixture was allowed to warm to rt over 30 min. The two phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x volumes of aqueous phase). The combined organic extracts were washed with water (1 x volume of organic phase) and brine (1 x volume of organic phase) and dried over MgSO_4 . Filtration and evaporation under reduced pressure produced the homoallylic alcohol as a mixture of two diastereoisomers (**14,15**), which were

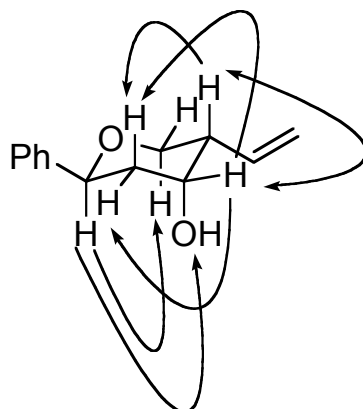
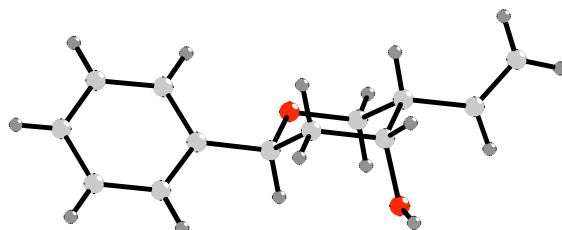
separated by flash column chromatography. Reactions were carried out a minimum of two times.

(2*S, 4*R**, 5*S**) 4-Hydroxy-2-phenyl-5-vinyl-tetrahydropyran (**14a**)**



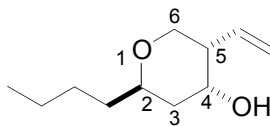
Aldehyde **7a** (0.220 g, 0.80 mmol) was reacted with MeSO₃H (57 μ L, 0.88 mmol) according to the general procedure. After 45 min, work-up provided a mixture of alcohol diastereoisomers **14a** and **14b** (>50:1 **14a**:**14b**, quantitative yield). Purification of this mixture by flash column chromatography afforded the major alcohol **14a** as a white crystalline solid (0.144 g, 88%): mp 58-60 °C; R_f = 0.21 (20% EtOAc in hexane); (Found: C, 76.54; H, 7.70. C₁₃H₁₆O₂ requires C, 76.44; H, 7.90%); ν_{\max} (film)/cm⁻¹ 3582w, 3407s br (OH), 3065w, 3030w, 2921s, 2852s, 2348w, 1962w, 1727w, 1640m (C=C), 1605w, 1496m, 1453s, 1421m, 1370m, 1290m, 1249m, 1184m, 1142s, 1082s, 1029s, 994m, 919m, 896m, 854m, 803w, 759s, 699s, 665s; δ_H (300 MHz) 1.75 (1H, s, OH), 1.86 (1H, ddd, J 14.1, 11.6, 2.8, 3- H_{ax}), 2.05 (1H, app. dt, J 14.1, 2.7, 3- H_{eq}), 2.55-2.69 (1H, m, 5- H), 3.86-4.03 (2H, stack, 6- H_{ax} , 6- H_{eq}), 4.14-4.22 (1H, m, 4- H), 4.78 (1H, dd, J 11.6, 2.4, 2- H), 5.16 (1H, d with unresolved fine coupling, J 17.6, CH=CH_{cis}H_{trans}), 5.26 (1H, d with unresolved fine coupling, J 10.7, CH=CH_{cis}H_{trans}), 5.83 (1H, ddd, J 17.6, 10.7, 6.4, CH=CH₂), 7.20-7.42 (5H, stack, PhH); δ_C (125 MHz) 40.3 (CH₂, C-3), 44.0 (CH, C-5), 65.7 (CH₂, C-6), 66.7 (CH, C-4), 73.3 (CH, C-2), 117.6 (CH₂, CH=CH₂), 125.8 (CH, Ph), 127.4 (CH, Ph), 128.3 (CH, Ph), 135.8 (CH, CH=CH₂), 142.4 (quat. C, *ipso*Ph); m/z (EI) 204 ([M]⁺, 7%), 184 (19), 159 (17), 148 (13), 120 (32), 105 (100), 91 (13,

[PhCH₂]⁺, 77 (31, [Ph]⁺), 70 (88), 54 (66), 43 (7); HRMS *m/z* (EI) 204.1155. C₁₃H₁₆O₂ requires 204.1150. The structure of this product was also confirmed by X-ray crystallography.

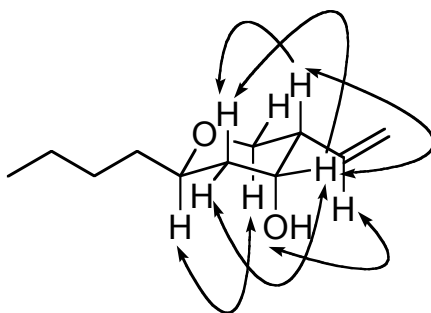


Selected nOes (GOESY) for **14a**

(2*R, 4*R**, 5*S**) 2-Butyl-4-hydroxy-5-vinyl-tetrahydropyran (**14b**)**

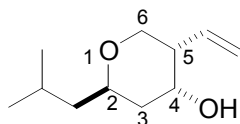


Aldehyde **7b** (0.210 g, 0.82 mmol) was reacted with MeSO₃H (58 μ L, 0.90 mmol) according to the general procedure. After 50 min, work-up provided a mixture of alcohol diastereoisomers **14b** and **15b** (50:1 **14b**:**15b**, 96%). Flash column chromatography of this mixture afforded the major alcohol **14b** as a colourless oil (0.138 g, 91%); R_f = 0.22 (20% EtOAc in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3442s br (OH), 3076m, 2930s, 2866s, 1840w, 1684w, 1640m (C=C), 1461m, 1421m, 1380m, 1282m, 1225m, 1082s, 1060s, 1000s, 919m, 866m, 776w, 710m, 663m; δ_H (300 MHz) 0.88 (3H, t, J 7.0, CH₃), 1.21-1.43 (6H, stack, CH₃(CH₂)₃), 1.50 (1H, app. t with unresolved fine coupling, J 12.7, 3- H_{ax}), 1.73 (1H, s, OH), 1.79 (1H, d with unresolved fine coupling, J 13.2, 3- H_{eq}), 2.41-2.51 (1H, m, 4-H), 3.61-3.79 (3H, stack, 2-H, 6- H_{ax} , 6- H_{eq}), 4.11-4.19 (1H, m, 4-H), 5.08 (1H, d, J 17.8, CH=CH_{cis}H_{trans}), 5.19 (1H, d, J 10.9, CH=CH_{cis}H_{trans}), 5.76 (1H, ddd, J 17.8, 10.9, 6.5, CH=CH₂); δ_C (125 MHz); 14.0 (CH₃, CH₃(CH₂)₃), 22.7 (CH₂, CH₃CH₂), 27.7 (CH₂, CH₃CH₂CH₂), 35.7 (CH₂, CH₃(CH₂)₂CH₂), 38.4 (CH₂, C-3), 44.4 (CH, C-5), 65.3 (CH₂, C-6), 66.6 (CH, C-4), 71.1 (CH, C-2), 117.4 (CH₂, CH=CH₂), 136.1 (CH, CH=CH₂); m/z (EI) 184 ([M]⁺, 1%), 129 (10), 117 (22), 111 (14), 101 (4), 95 (7), 87 (56), 70 (68), 54 (100), 49 (10), 43 (12, [CH₃(CH₂)₂]⁺); HRMS m/z (EI) 184.1461. C₁₁H₂₀O₂ requires 184.1463.



Selected nOes (GOESY) for **14b**.

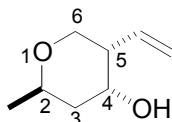
(2*R, 4*R**, 5*S**) 2-iso-butyl-4-hydroxy-5-vinyl-tetrahydropyran (**14c**)**



Aldehyde **7c** (0.180 g, 0.70 mmol) was reacted with MeSO₃H (50 μ L, 0.77 mmol) according to the general procedure. After 45 min, work-up provided a mixture of alcohol diastereoisomers **14c** and **15c** (32:1 **14c**:**15c**, 95%). Flash column chromatography of this mixture afforded the major alcohol **14c** as a colourless oil (0.118 g, 87%); R_f = 0.26 (20% EtOAc in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3427s br (OH), 3075w, 2955s, 2919s, 2870s, 2349w, 1640w (C=C), 1468m, 1421w, 1382m, 1368m, 1229m, 1171w, 1147m, 1113m, 1087s, 1053s, 999s, 958m, 917m, 877m, 840m, 786w, 713w, 665m; δ_H (300 MHz) 0.90 (6H, d, J 6.6, (CH₃)₂CH), 1.14 (1H, A of ABXY, J_{A-B} 14.0, J_{A-X} 8.5, J_{A-Y} 4.4, ^{*i*}PrCH_aH_b), 1.24 (1H, s, OH), 1.37-1.56 (3H, stack including [1.50, ddd, J 14.3, 11.4, 2.6, 3- H_{ax}], ^{*i*}PrCH_aH_b, 3- H_{eq} , 3- H_{ax}), 1.72-1.83 (1H, m, (CH₃)₂CH), 2.41-2.52 (1H, m, 5- H), 3.69-3.81 (3H, stack, 2- H , 6- H_{ax} , 6- H_{eq}), 4.02-4.10 (1H, m, 4- H), 5.09 (1H, d with unresolved fine coupling, J 17.6, CH=CH_{cis}H_{trans}), 5.21 (1H, d with unresolved fine coupling, J 10.7, CH=CH_{cis}H_{trans}), 5.77 (1H, ddd, J 17.6, 10.7, 6.6, CH=CH₂); δ_C (100 MHz) [22.3, 23.3, 24.4 (2 x CH₃, 1 x CH, (CH₃)₂CH)], 38.9 (CH₂, ^{*i*}PrCH₂), 44.3 (CH, C-5), 45.2 (CH₂, C-3), 65.2 (CH₂, C-6),

66.7 (CH, C-4), 69.2 (C-2), 117.5 (CH₂, CH=CH₂), 136.1 (CH, CH=CH₂); *m/z* (EI) 184 ([M]⁺, 1%), 127 (17), 117 (39), 111 (23), 95 (11), 87 (95), 70 (90), 54 (100), 43 (22); HRMS *m/z* (EI) 184.1455. C₁₁H₂₀O₂ requires 184.1463.

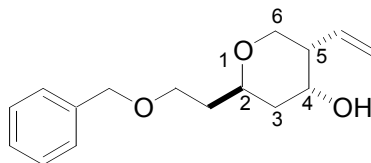
(2*R, 4*R**, 5*S**) 4-Hydroxy-2-methyl-5-vinyl-tetrahydropyran (**14d**)**



Aldehyde **7d** (0.240 g, 1.12 mmol) was reacted with MeSO₃H (80 μL, 1.23 mmol) according to the general procedure. After 45 min, work-up provided a mixture of alcohol diastereoisomers **14d** and **15d** (7:1 **14d**:**15d**, 93%). Flash column chromatography of this mixture afforded the major alcohol **14d** as a colourless oil (0.131 g, 82%); *R_f* = 0.18 (20% EtOAc in hexane); *v*_{max}(film)/cm⁻¹ 3854w, 3745w, 3583w, 3583w, 3406s br (OH), 3066w, 3031w, 2922s, 2852s, 2360w, 2341w, 1963w, 1734w, 1734w, 1684w, 1640m (C=C), 1605w, 1559w, 1540w, 1496m, 1454m, 1420m, 1371m, 1249m, 1183m, 1142m, 1081m, 1081s, 1029s, 995m, 919m, 896m, 854m, 804w, 759m, 699s, 666s; δ_H (300 MHz) 1.15 (3H, d, *J* 6.3, CH₃), 1.50 (1H, ddd, *J* 13.9, 11.4, 2.7, 3-*H*_{ax}), 1.70 (1H, s, OH), 1.80 (1H, d with unresolved fine coupling, *J* 13.9, 3-*H*_{eq}), 2.37-2.53 (1H, m, 5-*H*), 3.62-3.92 (3H, stack, 2-*H*, 6-*H*_{ax}, 6-*H*_{eq}), 4.02-4.11 (1H, m, 4-*H*), 5.10 (1H, d with unresolved fine coupling, *J* 17.6, CH=CH_{cis}*H*_{trans}), 5.20 (1H, d with unresolved fine coupling, *J* 11.0, CH=CH_{cis}*H*_{trans}), 5.76 (1H, ddd, *J* 17.6, 11.0, 6.2, CH=CH₂); δ_C (75 MHz) 21.5 (CH₃), 40.0 (CH₂, C-3), 44.0 (CH, C-5), 65.2 (CH₂, C-6), 66.6 (CH, C-2 or C-4), 67.2 (CH, C-2 or C-4), 117.5 (CH₂, CH=CH₂), 136.0 (CH, CH=CH₂); *m/z* (EI) 142 ([M]⁺, 12%),

96 (8), 87 (35), 84 (27), 75 (37), 70 (68), 54 (100), 49 (5), 45 (46); HRMS m/z (EI) 142.0991. $C_8H_{14}O_2$ requires 142.0994.

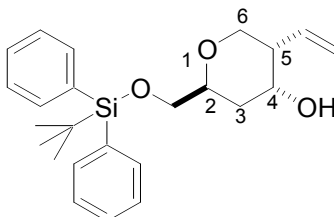
(2*R, 4*R**, 5*S**) 2-(2-Benzyloxyethyl)-4-hydroxy-5-vinyl-tetrahydropyran**
(14e)



Aldehyde **7e** (0.200 g, 0.67 mmol) was reacted with $MeSO_3H$ (48 μL , 0.74 mmol) according to the general procedure. After 40 min, work-up provided a mixture of diastereoisomers **14e** and **15e** (12:1 **14e**:**15e**, 94%). Flash column chromatography of this mixture afforded the major alcohol **14e** as a colourless oil (0.142 g, 81%); R_f = 0.24 (20% EtOAc in hexane); (Found: C, 73.20; H, 8.32. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.45%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3583w, 3442s br (OH), 3067w, 3030w, 2917s, 2862s, 2362w, 1640m (C=C), 1496m, 1454m, 1422m, 1364m, 1220m, 1098s, 1051s, 1028m, 1000m, 918m, 871m, 802w, 738s, 698s, 666m; δ_H (300 MHz) 1.55 (1H, ddd, J 14.0, 11.4, 2.6, 3- H_{ax}), 1.63 (1H, s, OH), 1.70-1.87 (3H, stack, 3- H_{eq} , $BnOCH_2CH_2$), 2.39-2.55 (1H, m, 5- H), 3.58 (2H, t, J 6.6, $BnOCH_2$), 3.66-3.80 (2H, stack, 6- H_{ax} , 6- H_{eq}), 3.81-3.94 (1H, m, 2- H), 4.05-4.12 (1H, m, 4- H), 4.50 (2H, s, $PhCH_2O$), 5.09 (1H, dt, J 17.6, 1.5, $CH=C_{cis}H_{trans}$), 5.21 (1H, d with unresolved fine coupling, J 10.7, $CH=CH_{cis}H_{trans}$), 5.77 (1H, ddd, J 17.6, 10.7, 6.4, $CH=CH_2$), 7.24-7.49 (5H, stack, PhH); δ_C (75 MHz) 36.1 (CH_2), 38.6 (CH_2), 44.3 (CH, C-5), 65.3 (CH_2), 66.5 (CH), 66.9 (CH_2), 68.4 (CH), 72.9 (CH_2 , $PhCH_2$), 117.4 (CH_2 , $CH=CH_2$), 127.4 (CH, Ph), 127.6 (CH, Ph), 128.3 (CH, Ph), 136.0 (CH, $CH=CH_2$), 138.5 (quat.

C, *ipso*Ph); m/z (TOF ES+) 285.2 ($[M+Na]^+$, 100%); HRMS m/z (TOF ES+) 285.1458. $C_{16}H_{22}NaO_3$ requires 285.1467.

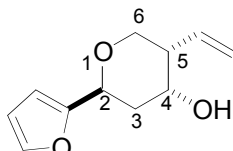
(2*S, 4*R**, 5*S**) 2-(tert-Butyl-diphenyl-silanyloxymethyl)-4-hydroxy-5-vinyl-tetrahydropyran (**14f**)**



Aldehyde **7f** (0.150 g, 0.32 mmol) was reacted with $MeSO_3H$ (23 μ L, 0.35 mmol) according to the general procedure. After 40 min, work-up provided a mixture of alcohol diastereoisomers **14f** and **15f** (18:1 **14f**:**15f**, 89%). Flash column chromatography of this mixture afforded the major alcohol **14f** as a colourless oil (0.104 g, 82%); R_f = 0.31 (20% EtOAc in hexane); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3444s br (OH), 3068w, 3031w, 2918s, 2863s, 1640w (C=C), 1496w, 1454m, 1422w, 1364m, 1204m, 1090s, 1050s, 1028m, 1000m, 918m, 871m, 803w, 737m, 698m, 666m; δ_H (300 MHz) 1.07 (9H, s, $C(CH_3)_3$), 1.28 (1H, d, J 1.8, OH), 1.59-1.72 (1H, m, 3- H_{ax}), 1.88 (1H, d with unresolved fine coupling, J 14.0, 3- H_{eq}), 2.41-2.56 (1H, m, 5- H), 3.61 (1H, A of ABX, J_{A-B} 10.3, J_{A-X} 5.1, $SiOCH_aH_b$), 3.68-3.80 (3H, stack including [3.73, B of ABX, J_{B-A} 10.3, J_{B-X} 5.2, $SiOCH_aH_b$), 6- H , $SiOCH_aH_b$), 3.81-3.93 (1H, m, 2- H), 4.11-4.18 (1H, m, 4- H), 5.12 (1H, d with unresolved fine coupling, J 17.6, $CH=CH_{cis}H_{trans}$), 5.23 (1H, d with unresolved fine coupling, J 10.7, $CH=CH_{cis}H_{trans}$), 5.80 (1H, ddd, J 17.6, 10.7, 6.6, $CH=CH_2$), 7.33-7.45 (6H, stack, PhH), 7.65-7.72 (4H, stack, PhH); δ_C (75 MHz) 19.3 (quat. C, $C(CH_3)_3$), 26.9 (CH_3 , $C(CH_3)_3$), 34.9 (CH, C-5), 44.2 (CH_2 , C-3), 65.1 (CH_2), 66.4 (CH, C-4), 67.0 (CH_2), 71.7 (CH, C-2),

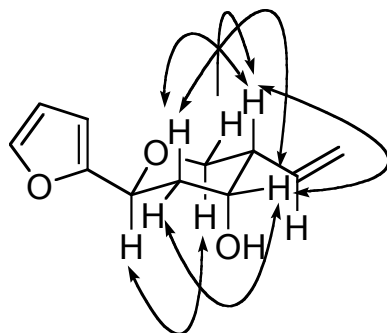
117.5 (CH₂, CH=CH₂), 127.6 (CH, Ph), 129.6 (CH, Ph), 133.7 (quat. C, *ipso*Ph), 135.6 (CH, Ph), 136.0 (CH, CH=CH₂); *m/z* (TOF ES+) 419.2 ([M+Na]⁺, 100%); HRMS *m/z* (TOF ES+) 419.2009. C₂₄H₃₂NaO₃Si requires 419.2018.

(2*S, 4*R**, 5*S**) 2-(Furan-2'-yl)-4-hydroxy-5-vinyl-tetrahydropyran (**14g**)**



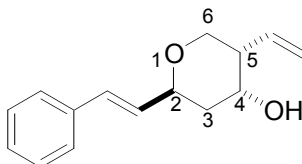
Aldehyde **7g** (0.125 g, 0.47 mmol) was reacted with MeSO₃H (32 μL, 0.52 mmol) according to the general procedure. After 45 min, work-up provided a mixture of alcohol diastereoisomers **14g** and **15g** (25:1 **14g**:**15g**, 94%). Flash column chromatography of this mixture afforded the major alcohol **14g** as a colourless oil (78 mg, 86%); *R_f* = 0.21 (20% EtOAc in hexane); *v*_{max}(film)/cm⁻¹ 3417s br, 2951m, 2920m, 2865m, 1640m (C=C), 1500w, 1456w, 1408m, 1349m, 1314w, 1238m, 1216m, 1178w, 1152m, 1107m, 1076m, 1046s, 1006s, 954m, 934m, 875m, 836m, 812w, 753m, 666m; *δ*_H (500 MHz) 1.71 (1H, s, OH), 2.02 (1H, app. dt, *J* 13.8, 2.9, 3-*H*_{eq}), 2.11 (1H, ddd, *J* 13.8, 11.7, 2.8, 3-*H*_{ax}), 2.51-2.60 (1H, m, 5-*H*), 3.80 (1H, dd, *J* 11.3, 2.8, 6-*H*_{eq}), 3.92 (1H, app. t, *J* 11.3, 6-*H*_{ax}), 4.13-4.20 (1H, m, 4-*H*), 4.82 (1H, dd, *J* 11.6, 2.4, 2-*H*), 5.12 (1H, d with unresolved fine coupling, *J* 17.8, CH=CH_{cis}*H*_{trans}), 5.22 (1H, d with unresolved fine coupling, *J* 10.7, CH=CH_{cis}*H*_{trans}), 5.79 (1H, ddd, *J* 17.8, 10.7, 6.6, CH=CH₂), 6.25 (1H, d, *J* 3.1, furyl CCH), 6.29-6.31 (1H, m, furyl CH), 6.36 (1H, d, *J* 1.4, OCH₂); *δ*_C (125 MHz) 36.1 (CH₂, C-3), 43.9 (CH, C-5), 65.6 (CH₂, C-6), 66.2 (CH, C-4), 66.8 (CH, C-2), 106.8 (CH, furyl CCH), 110.1 (CH, furyl OCHCH), 117.9 (CH₂, CH=CH₂), 135.6 (CH, CH=CH₂), 142.3 (CH, furyl OCH), 154.5 (quat. C, furyl C); *m/z* (EI) 194 ([M]⁺, 11%), 147 (7), 138 (7), 122

(9), 110 (28), 95 (100), 86 (10), 81 (27), 77 (9), 70 (11), 66 (33), 55 (40), 49 (37), 43 (18); HRMS m/z (EI) 194.0952. $C_{11}H_{14}O_3$ requires 194.0943.



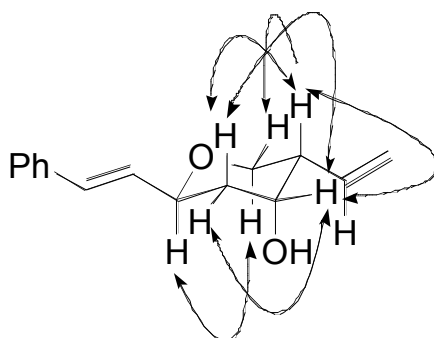
Selected nOes (GOESY) for **14g**.

(*E*, 2*S*^{*}, 4*R*^{*}, 5*R*^{*}) 4-Hydroxy-2-styryl-5-vinyl-tetrahydropyran (14h**)**



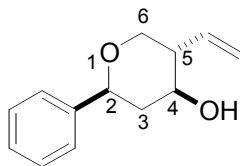
Aldehyde **7h** (0.215 g, 0.71 mmol) was reacted with $MeSO_3H$ (51 μL , 0.78 mmol) according to the general procedure. After 40 min, work-up provided a mixture of alcohol diastereoisomers **14h** and **15h** (19:1 **14h**:**15h**, quantitative yield). Flash column chromatography of this mixture afforded the major alcohol **14h** as a yellow oil (0.137 g, 84%); R_f = 0.23 (20% EtOAc in hexane); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3583w, 3403s br (OH), 3081m, 3027s, 2919s, 2862s, 2360w, 2341w, 1951w, 1880w, 1718w, 1639m (C=C), 1598w, 1578w, 1495m, 1448m, 1421m, 1355m, 1266m, 1241m, 1201m, 1072s, 997s, 968s, 919m, 875m, 833w, 793w, 740s, 692s, 666s; δ_H (500 MHz) 1.66 (1H, s, OH), 1.74 (1H, app. t with unresolved fine coupling, J 12.6, 3- H_{ax}),

1.97 (1H, app. dt, J 12.6, 2.6, 3- H_{eq}), 2.51-2.60 (1H, m, 5- H), 3.79-3.94 (2H, stack, 6- H_{ax} , 6- H_{eq}), 4.13-4.19 (1H, m, 4- H), 4.43 (1H, app. dd, J 12.6, 6.0, 2- H), 5.15 (1H, d, J 17.6, $CH=C_{cis}H_{trans}$), 5.25 (1H, d, J 10.9, $CH=CH_{cis}H_{trans}$), 5.81 (1H, ddd, J 17.6, 10.9, 6.4, $CH=CH_2$), 6.19 (1H, dd, J 16.1, 6.0, $PhCH=CH$), 6.63 (1H, d, J 16.1, $PhCH=CH$), 7.22 (1H, t, J 7.3, p - PhH), 7.30 (2H, app. t, J 7.6, m - PhH), 7.38 (2H, d, J 7.4, o - PhH); δ_C (125 MHz) 38.6 (CH_2 , C-3), 44.0 (CH , C-5), 65.2 (CH_2 , C-6), 66.4 (CH , C-4), 71.6 (CH , C-2), 117.8 (CH_2 , $CH=CH_2$), 126.4 (CH , Ph), 127.5 (CH , Ph), 128.5 (CH , Ph), 130.0 (CH , $PhCH=CH$), 130.4 (CH , $PhCH=CH$), 135.8 (CH , $CH=CH_2$), 136.9 (quat. C, *ipso*Ph); m/z (TOF ES+) 285.1 ($[M+Na+MeOH]^+$, 20%), 253.1 (100, $[M+Na]^+$); HRMS m/z (TOF ES+) 253.1200. $C_{15}H_{18}NaO_2$ requires 253.1204.



Selected nOes (GOESY) for **14h**.

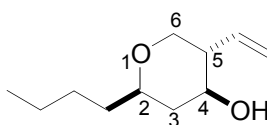
(2S*, 4S*, 5S*) 4-Hydroxy-2-phenyl-5-vinyl-tetrahydropyran (15a)



Dess-Martin periodinane (0.438 g, 1.03 mmol) was added to a solution of alcohols **14a** and **15a** (crude allylation product) (0.140 g, 0.69 mmol) in CH₂Cl₂ (7 mL) at rt and the reaction mixture was stirred for 1 h. The reaction was then quenched with NaHCO₃ solution (3.5 mL) and sodium thiosulfate solution (3.5 mL) and stirred for a further 30 min. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (2 x 7 mL). The combined organic extracts were washed with water (7 mL) and brine (7 mL) and dried over MgSO₄. Filtration and evaporation under reduced pressure produced a residue which was dissolved in Et₂O (6 mL). NaBH₄ (52 mg, 1.38 mmol) was added and the reaction mixture was stirred at rt for 5 h. The reaction was then quenched with NH₄Cl solution (7 mL) and stirred for 30 min. The phases were separated and the aqueous phase was extracted with Et₂O (2 x 7 mL). The combined organic extracts were washed with water (6 mL) and brine (6 mL) and dried over MgSO₄. Evaporation under reduced pressure produced alcohol **15a** as a colourless oil (0.122 g, 87%); *R_f* = 0.17 (20% EtOAc in hexane); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3583w, 3408s br (OH), 3066w, 3031w, 2911m, 2840m, 2359w, 1640m (C=C), 1605w, 1496m, 1453m, 1371m, 1215w, 1283w, 1141m, 1070s, 1028s, 992m, 917m, 896m, 855w, 803w, 759s, 733m, 699m, 655m; δ_{H} (300 MHz) 1.64 (1H, app. q, *J* 11.8, 3-*H_{ax}*), 1.89 (1H, s, OH), 2.21-2.40 (2H, stack including [2.25 (1H, ddd, *J* 11.8, 4.5, 2.0, 3-*H_{eq}*), 3-*H_{eq}*, 5-H), 3.40 (1H, app. t, *J* 11.4, 6-*H_{ax}*), 3.70 (1H, app. td, *J* 10.3, 4.5, 4-H), 4.05 (1H, dd, *J* 11.4, 4.8, 6-*H_{eq}*), 4.40 (1H, dd, *J* 11.8, 2.0, 2-H), 5.24-5.39 (2H, stack, CH=CH₂), 5.54-5.75 (1H, m, CH=CH₂), 7.21-7.43 (5H, stack,

PhH); δ_{C} (75 MHz) 41.1 (CH₂, C-3), 50.2 (CH, C-5), 70.0 (CH₂, C-6), 71.1 (CH, C-4), 78.8 (CH, C-2), 119.8 (CH₂, CH=CH₂), 125.9 (CH, Ph), 127.7 (CH, Ph), 128.4 (CH, Ph), 135.0 (CH, CH=CH₂), 141.6 (quat. C, *ipso*Ph); *m/z* (EI) 204 ([M]⁺, 7%), 159 (11), 148 (10), 120 (40), 105 (100), 91 (11, [PhCH₂]⁺), 77 (28, [Ph]⁺), 70 (91), 54 (76), 43 (8); HRMS *m/z* (EI) 204.1144. C₁₃H₁₆O₂ requires 204.1150.

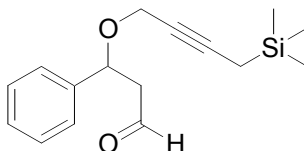
(2*R, 4*S**, 5*S**) 2-Butyl-4-hydroxy-5-vinyl-tetrahydropyran (**15b**)**



Dess-Martin periodinane (0.382 g, 0.90 mmol) was added to a solution of tetrahydropyrans **14a** and **15b** (crude allylation product) (0.110 g, 0.60 mmol) in CH₂Cl₂ (6 mL) at rt and the reaction mixture was stirred for 1 h. The reaction was then quenched with NaHCO₃ solution (3 mL) and sodium thiosulfate solution (3 mL) and stirred for a further 30 min. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (2 x 6 mL). The combined organic extracts were washed with water (6 mL) and brine (6 mL) and dried over MgSO₄. Filtration and evaporation under reduced pressure produced a residue which was dissolved in Et₂O (6 mL). NaBH₄ (45 mg, 1.20 mmol) was added and the reaction mixture was stirred at RT for 5 h. The reaction was then quenched with NH₄Cl solution (6 mL) and stirred for 30 min. The phases were separated and the aqueous phase was extracted with Et₂O (2 x 6 mL). The combined organic extracts were washed with water (6 mL) and brine (6 mL) and dried over MgSO₄. Evaporation under reduced pressure produced alcohols **15b** and **14b** (15:1 **15b**:**14b**). Flash column chromatography afforded the major alcohol **15b** as a colourless oil (91 mg, 83%); *R_f* = 0.18 (20% EtOAc in

hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3583m, 3405s br (OH), 3080w, 3056s, 2933s, 2860s, 1642m (C=C), 1460m, 1378m, 1248w, 1143m, 1084s, 1036m, 992m, 917m, 862w, 803w, 778w, 666m; δ_{H} (300 MHz) 0.88 (3H, t, J 7.0, CH_3), 1.18-1.68 (7H, stack, $\text{CH}_3(\text{CH}_2)_3$, 3- H_{ax}), 1.87 (1H, s, OH), 1.99 (1H, ddd, J 12.6, 4.6, 1.9, 3- H_{eq}), 2.16 (1H, app. qd, J 11.0, 4.6, 5-H), 3.18 (1H, app. t, J 11.0, 6- H_{ax}), 3.23-3.48 (1H, m, 2-H), 3.50 (1H, app. td, J 11.0, 4.6, 4-H), 3.86 (1H, dd, J 11.0, 4.6, 6- H_{eq}), 5.18-5.32 (2H, stack, $\text{CH}=\text{CH}_2$), 4.47-6.64 (1H, m, $\text{CH}=\text{CH}_2$); δ_{C} (75 MHz) 14.0 (CH_3 , $\text{CH}_3(\text{CH}_2)_3$), 22.6 (CH_2 , CH_3CH_2), 27.6 (CH_2 , $\text{CH}_3\text{CH}_2\text{CH}_2$), 35.7 (CH_2 , $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 39.4 (CH_2 , C-3), 50.4 (CH, C-5), 69.6 (CH_2 , C-6), 70.9 (CH, C-4), 76.6 (CH, C-2), 119.4 (CH_2 , $\text{CH}=\text{CH}_2$), 135.3 (CH, $\text{CH}=\text{CH}_2$); m/z (EI) 184 ($[\text{M}]^+$, 3%), 127 (12), 117 (24), 111 (14), 99 (3), 95 (7), 87 (74), 79 (22), 70 (87), 58 (3), 54 (100), 49 (20), 43 (17); HRMS m/z (EI) 184.1470. $\text{C}_{11}\text{H}_{20}\text{O}_2$ requires 184.1463.

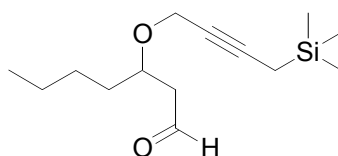
3-Phenyl-3-(4-trimethylsilanyl-but-2-ynyl)oxypropionaldehyde (**16a**)



Aldehyde **16a** was prepared from ester **12a** (0.263 g, 0.88 mmol) and DIBALH (0.65 mL of a 1.5 M solution in toluene, 0.97 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et_2O in hexane) afforded aldehyde **16a** as a colourless oil (0.229 g, 95%); R_f = 0.23 (6% EtOAc in hexane); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3583w, 3436w, 3063w, 3031w, 2956s, 2898m, 2856m, 2725w, 2335w, 2213m ($\text{C}\equiv\text{C}$), 1727s ($\text{C}=\text{O}$), 1681m, 1627w, 1494m, 1454m, 1396m, 1356m, 1307w, 1250s, 1169w, 1126m, 1066s, 1044s, 852s, 791w, 762m, 701s, 666m; δ_{H} (300 MHz) 0.11 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.47-1.54 (2H, m,

$\text{CH}_2\text{Si}(\text{CH}_3)_3$, 2.65 (1H, A of ABXY, $J_{\text{A-B}}$ 16.4, $J_{\text{A-X}}$ 4.5, $J_{\text{A-Y}}$ 1.7, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 2.91 (1H, B of ABXY, $J_{\text{B-A}}$ 16.4, $J_{\text{B-X}}$ 9.0, $J_{\text{B-Y}}$ 2.6, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 3.87 (1H, A of ABX₂, $J_{\text{A-B}}$ 15.3, $J_{\text{A-X}}$ 2.4, $\text{CH}_a\text{H}_b\text{C}\equiv\text{C}$), 4.12 (1H, B of ABX₂, $J_{\text{B-A}}$ 15.3, $J_{\text{B-X}}$ 2.4, $\text{CH}_a\text{H}_b\text{C}\equiv\text{C}$), 5.09 (1H, dd, J 8.8, 4.4, 3-*H*), 7.21-7.45 (5H, stack, Ph*H*), 9.76-9.83 (1H, m, CHO); δ_{C} (75 MHz) -2.0 (CH₃, Si(CH₃)₃), 7.2 (CH₂, C \equiv CCH₂Si), 51.2 (CH₂, CH₂C=O), 56.4 (CH₂, OCH₂C \equiv C), 74.2 (quat. C, C \equiv C), 74.8 (CH, C-3), 85.2 (quat. C, C \equiv C), 126.7 (CH, Ph), 128.2 (CH, Ph), 128.7 (CH, Ph), 139.8 (quat. C, *ipso*Ph), 200.6 (CH, C=O); m/z (TOF ES+) 329.2 ([M+Na+MeOH]⁺, 100%), 297.2 (53, [M+Na]⁺); HRMS m/z (TOF ES+) 297.1275. C₁₆H₂₂O₂NaSi requires 297.1287.

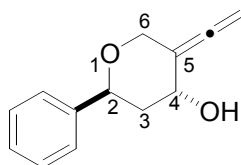
3-(4-Trimethylsilanyl-but-2-ynyloxy)heptanal (**16b**)



Aldehyde **16b** was prepared from ester **12b** (0.293 g, 0.98 mmol) and DIBALH (0.72 mL of a 1.5 M solution in toluene, 1.08 mmol) according to the general procedure. After 1 h, work-up and purification by flash column chromatography (6% Et₂O in hexane) afforded aldehyde **16b** as a colourless oil (0.239 g, 96%); R_f = 0.21 (6%EtOAc in hexane); ν_{max} (film)/cm⁻¹ 3583w, 3429w, 2957s, 2861m, 2360w, 2340w, 2212w (C \equiv C), 1726s (C=O), 1458w, 1350w, 1250s, 1169w, 1126m, 1060m, 852s, 791w, 698w, 666m; δ_{H} (300 MHz) 0.10 (9H, s, Si(CH₃)₃), 0.82-0.99 (3H, m, CH₃), 1.12-1.44 (4H, stack, CH₃(CH₂)₂CH₂), 1.47-1.79 (4H, stack including [1.50 (2H, t, J 2.4, CH₂Si(CH₃)₃), CH₃(CH₂)₂CH₂, CH₂Si(CH₃)₃), 2.57 (1H, A of ABXY, $J_{\text{A-B}}$ 16.3, $J_{\text{A-X}}$ 5.1, $J_{\text{A-Y}}$ 2.2, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 2.62 (1H, B of ABXY, $J_{\text{B-A}}$ 16.3, $J_{\text{B-X}}$ 6.8, $J_{\text{B-Y}}$ 2.6, $\text{CH}_a\text{H}_b\text{C}=\text{O}$), 4.04 (1H, app. quintet, J 6.0, 3-*H*), 4.18 (2H, t, J 2.4, OCH₂CH=CH),

9.82 (1H, t, J 2.4, CHO); δ_C (75 MHz) -2.6 (CH₃, Si(CH₃)₃), 6.6 (CH₂, C \equiv CCH₂Si), 13.5 (CH₃), 22.2 (CH₂), 26.8 (CH₂), 33.4 (CH₂), 47.7 (CH₂, CH₂C=O), 56.8 (OCH₂C \equiv C), 73.0 (CH, C-3), 74.6 (quat. C, C \equiv C), 84.7 (quat. C, C \equiv C), 202.4 (CH, C=O). Satisfactory mass spectra could not be obtained on this compound.

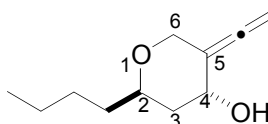
(2S*, 4R*) 4-Hydroxy-2-phenyl-5-vinylidene-tetrahydropyran (17a)



MeSO₃H (61 μ L, 0.94 mmol) was added to a solution of aldehyde **16a** (0.235 g, 0.86 mmol) in CH₂Cl₂ (8.6 mL) at -78 °C. After 2 min, work-up as described for the formation of **14**, and purification by flash column chromatography (20% EtOAc in hexane) afforded allene **17a** as a colourless oil (0.153 g, 88%); R_f = 0.22 (20% EtOAc in hexane); ν_{\max} (film)/cm⁻¹ 3583w, 3412s br (OH), 3063w, 3032w, 2921m, 2850m, 2359w, 1962s (C=C=C), 1724w, 1605w, 1495w, 1495w, 1454s, 1371m, 1328w, 1252m, 1204m, 1174w, 1062s, 1003m, 906w, 886m, 853s, 774w, 757m, 700s, 666s; δ_H (500 MHz) 1.90 (1H, s, OH), 1.94-2.02 (1H, m, 3- H_{ax}), 2.06 (1H, app. dt, J 13.1, 3.1, 3- H_{eq}), 4.34 (1H, d, J 12.2, 6- H_{eq}), 4.61 (1H, dt, J 12.2, 3.0, 6- H_{ax}), 4.65 (1H, app. t, J 2.7, 4- H), 4.80 (1H, A of ABX, J_{A-B} 13.1, J_{A-X} 3.1, C=C=CH_aH_b), 4.86-4.98 (2H, stack, 2- H , C=C=CH_aH_b), 7.24-7.28 (2H, m, m -PhH), 7.29-7.39 (3H, stack, o -PhH, p -PhH); δ_C (125 MHz) 40.7 (CH₂, C-3), 65.5 (CH₂, C-6), 67.4 (CH, C-4), 73.9 (CH, C-2), 76.3 (CH₂, C=C=CH₂), 98.9 (quat. C, C=C=CH₂), 125.9 (CH, Ph), 127.6 (CH, Ph), 128.4 (CH, Ph), 142.0 (quat. C, $ipso$ Ph), 203.2 (quat. C, C=C=CH₂); m/z (EI) 202 ([M⁺], 1%), 184 (100, [M - H₂O]⁺), 155 (3), 141 (3), 133 (6), 128 (10),

105 (92), 91 (6, [PhCH₂]⁺), 77 (19, [Ph]⁺), 68 (38), 51 (27), 43 (10); HRMS *m/z* (EI) 202.0985. C₁₃H₁₄O₂ requires 202.0994.

(2*R, 4*R**) 2-Butyl-4-hydroxy-5-vinylidene-tetrahydropyran (17b)**



MeSO₃H (56 μL, 0.86 mmol) was added to a solution of aldehyde **16b** (0.200 g, 0.79 mmol) in CH₂Cl₂ (7.9 mL) at -78 °C. After 2 min, work-up as described for the formation of **14**, provided a mixture of allenes **17b** and **18b** (10:1 **17b**:**18b**, 94%). Purification by flash column chromatography (20% EtOAc in hexane) afforded the major allene **17b** as a colourless oil (0.124 g, 86%); *R_f* = 0.23 (20% EtOAc in hexane); *v*_{max}(film)/cm⁻¹ 3416s br (OH), 2956s, 2931s, 2860m, 2361w, 1963s (C=C=C), 1711w, 1658w, 1642w, 1549w, 1453m, 1377m, 1327m, 1268m, 1210m, 1176m, 1088s, 1061s, 1037s, 845m, 792w, 772w, 732w; *δ*_H (300 MHz) 0.89 (3H, t, *J* 7.0, CH₃), 1.22-1.56 (6H, stack, CH₃(CH₂)₃), 1.63 (1H, ddd, *J* 13.2, 11.2, 3.3, 3-*H*_{ax}), 1.71 (1H, s, OH), 1.83 (1H, dt, *J* 13.2, 2.8, 3-*H*_{eq}), 3.72-3.86 (1H, m, 2-*H*), 4.18 (1H, d, *J* 12.2, 6-*H*_{eq}), 4.41 (1H, dt *J* 12.2, 3.4, 6-*H*_{ax}), 4.57 (1H, app. t, *J* 2.8, 4-*H*), 4.74 (1H, A of ABX, *J*_{A-B} 10.8, *J*_{A-X} 3.5, C=C=CH_aH_b), 4.82 (1H, B of ABX, *J*_{B-A} 10.8, *J*_{B-X} 3.1, C=C=CH_aH_b); *δ*_C (75 MHz) 13.6 (CH₃, CH₃(CH₂)₃), 22.4 (CH₂, CH₃CH₂), 27.3 (CH₂, CH₃CH₂CH₂), 35.2 (CH₂, CH₃(CH₂)₂CH₂), 38.7 (CH₂, C-3), 65.0 (CH₂, C-6), 67.2 (CH, C-4), 71.7 (CH, C-2), 76.0 (CH₂, C=C=CH₂), 99.5 (quat. C, C=C=CH₂), 203.9 (C=C=CH₂); *m/z* (EI) 182 ([M]⁺, 6%), 164 (33, [M - H₂O]⁺), 135 (7), 131 (10), 125 (74), 122 (24), 117 (11), 113 (8), 107 (30), 99 (14), 96 (100), 91 (40); HRMS *m/z* (EI) 182.1301. C₁₁H₁₈O₂ requires 182.1307.