Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Stereocontrolled asymmetric synthesis of syn-*E*-1,4-diol-2-enes using allyl boronates and its application in the total synthesis of solandelactone F

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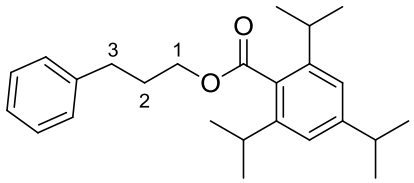
1. General Information

All air and water sensitive reactions were carried out in oven dried glassware under argon using standard manifold techniques.[1] All chemicals were purchased from Acros, Aldrich, Alfa Aesar, Fluka, Fluorochem, Lancaster or Merck and used without further purification unless otherwise stated. Compounds that are not described in the experimental part were synthesised according to literature procedures. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (TMEDA) was distilled over CaH_2 under reduced pressure prior to use. The following solvents were obtained from a purification column composed of activated alumina:[2] diethyl ether, tetrahydrofuran, dichloromethane and toluene. (*E*)-Me_3Si-C=C-*B*-9BBN (**2**) was prepared according to the procedure by Singleton.[3] Molecular sieves were activated before use by microwave irradiation in a reaction microwave for 5 min at 150 °C. Flash chromatography was performed on silica gel (Merck Kieselgel 60 F254 230–400 mesh). Thin layer chromatography was performed on aluminium backed plates pre-coated with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualised by exposure to UV light or by dipping the plates in a solution of 5 % $(NH_4)_2Mo_7O_{24}•4H_2O$ in 95% EtOH (w/v) followed by heating. Petroleum ether was distilled before use and refers to the 40-60 °C boiling point fractions. Chiral HPLC separations were performed on Agilent 1100 series normal phase high performance liquid chromatography units using HP Chemstation for LC or LC/MS. Daicel Chiralcel/Chiralpak columns (0.46 × 25 cm or 0.46 × 5 cm) were used for normal phase separations. Details of chromatographic conditions are indicated under each compound. Chiral GC separations were performed on an Agilent 6890N. NMR spectra were recorded on Varian 500 MHz, Varian 400 MHz, JEOL 400 MHz, JEOL 300 MHz or JEOL 270 MHz spectrometers using deuturated chloroform as the solvent. The residual signal of the undeuturated solvent was used as the internal standard. Mass spectra were recorded by the University of Bristol Spectrometry Services Laboratory using electron impact (EI), electrospray (ESI) or chemical (CI) ionization techniques. Low resolution mass spectra (m/z) were recorded with only major peaks being reported with intensities quoted as percentages of the base peak. IR data was obtained on a PerkinElmer Spectrum 100 FT-IR-spectrometer with only major peaks being reported. Optical rotations were obtained on a PerkinElmer 241MC polarimeter. Melting points were determined using a Kopfler hot stage apparatus and are uncorrected.

2. Stannanes

3-phenylpropyl 2,4,6-triisopropylbenzoate



3-Phenylpropan-1-ol (1.4 ml, 10 mmol) was added over 10 min to a stirring suspension of NaH (400 mg, 60% in mineral oil, 10 mmol) in THF (5 ml). After evolution of gas had ceased 2,4,6-trichlorobenzoyl chloride (1.3 g, 5.0 mmol) was added and the reaction heated at 80 °C in a sealed tube for 16 hours. The reaction was cooled to room temperature and quenched with H_2O (50 ml). The layers were separated, aqueous layer extracted with Et_2O (3 × 50 ml), organic fractions combined, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/petroleum ether 2:98) to yield the *benzoate* (1.73 g, 94%) as a colourless oil.

$\boldsymbol{R_f}$ = 0.38 (EtOAc/Petroleum Ether 3:98);

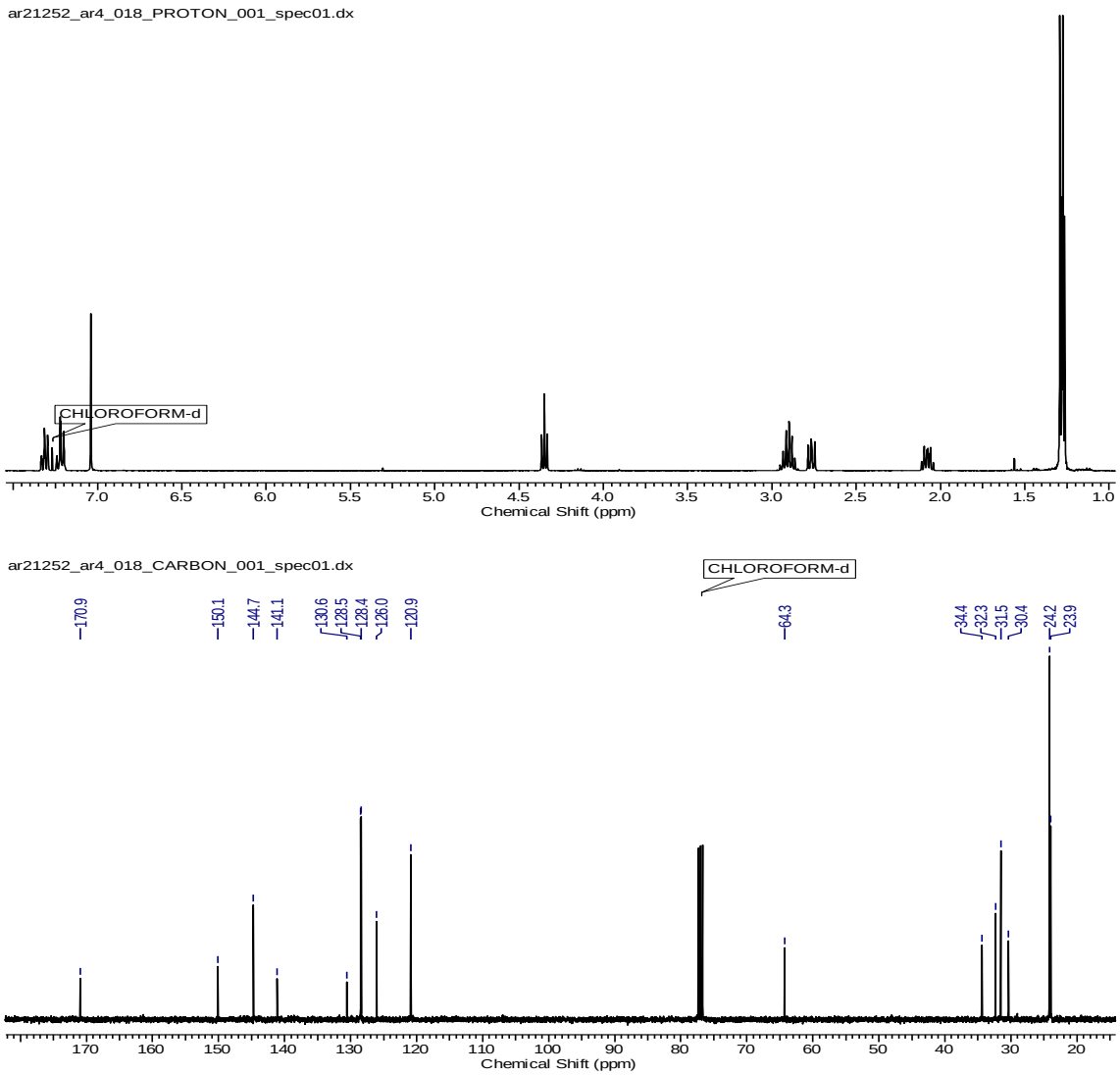
^{13}C NMR (100 MHz, $CHCl_3$) δ ppm 170.9 (C=O), 150.1 (C), 144.7 (C), 141.1 (C), 130.6 (C), 128.5 (CH), 128.4 (CH), 126.0 (CH), 120.9 (CH), 64.3 (CH_2), 34.4 (CH), 32.3 (CH_2), 31.5 (CH), 30.4 (CH_2), 24.2 (CH_3), 23.9 (CH_3);

^{1}H NMR: (400 MHz, $CDCl_3$) δ ppm 7.35 - 7.28 (2H, m, ArH), 7.25 - 7.18 (3H, m, ArH), 7.04 (2H, s, ArH), 4.35 (2H, t, *J* = 6.5 Hz, H1), 2.92 (3H, spt, *J* = 6.8 Hz, C*H*$(CH_3)_2$), 2.80 - 2.73 (2H, m, H3), 2.12 - 2.03 (2H, m, H2), 1.29 (12H, d, *J* = 6.8 Hz, CH(C*H*$_3)_2$), 1.27 (6H, d, *J* = 6.8, Hz, CH(C*H*$_3)_2$);

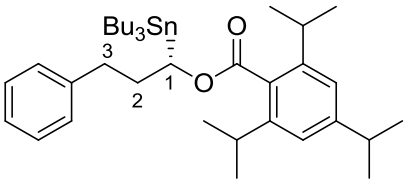
IR ($\tilde{\nu}$ /cm^{-1}, neat): 2956, 2925, 2854, 1730, 1462, 1378, 1251, 1076;

HRMS (EI): calc. for $C_{25}H_{34}O_2$: 366.2559, found: 366.2552;

MS (EI): 366.3 (15), 248 (35), 233.2 (50), 118 (100), 91 (50);



(*S*)-3-Phenyl-1-(tributylstannyl)propyl 2,4,6-triisopropylbenzoate 19



(−)-Sparteine (0.80 ml, 3.5 mmol) and 3-phenyl-1-propyl-2,4,6-triisopropylbenzoate (1.0 g, 2.7 mmol) were dissolved in Et_2O (13.5 ml) and cooled to −78 °C. *s*BuLi (1.3 M in hexanes, 2.7 ml, 3.5 mmol) was added dropwise over 15 min and the reaction stirred at this temperature for 5 h. Bu_3SnCl (1.3 ml, 4.6 mmol) was added dropwise and the reaction allowed to warm to room temperature overnight, upon which it was quenched with aqueous KF (1 M solution, 20 ml), layers separated and the aqueous extracted with Et_2O (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and solvent removed under reduced pressure. The crude material was purified by column chromatography (EtOAc/petroleum ether 1:99) to yield the *stannane* (1.59 g, 90%) as a colourless oil. The racemic was made using TMEDA in place of (–)-Sparteine.

R_f = 0.58 (EtOAc/Petroleum Ether 3:97)

^{13}C NMR (100 MHz, $CHCl_3$) δ ppm 171.2 (C=O), 149.9 (C), 144.8 (C), 141.8 (C), 130.9 (C), 128.4 (CH), 128.3 (CH), 125.9 (CH),120.8 (CH), 71.6 (CH), 36.7 (CH_2), 34.8 (CH_2), 34.4 (CH), 31.6 (CH), 29.1 (CH_2), 27.5 (CH_2), 24.6 (CH_3), 24.2 (CH_3), 24.0 (CH_3), 13.7 (CH_3), 9.9 (CH_2);

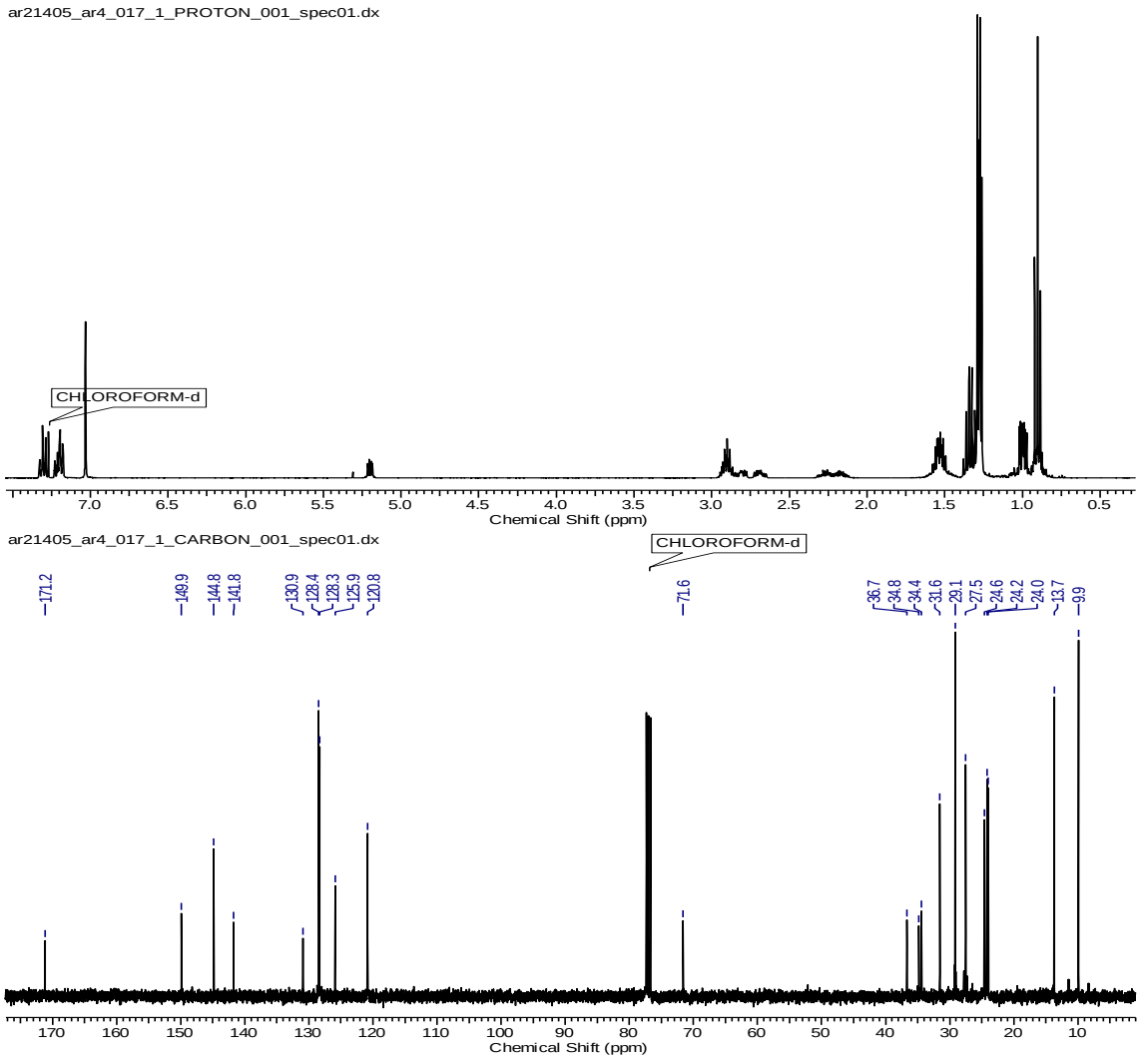
^{1}H NMR (400 MHz, $CHCl_3$) δ ppm 7.35 - 7.28 (2H, m, ArH), 7.25 - 7.17 (3H, m, ArH), 7.04 (2H, s, ArH), 5.21 (1H, dd, *J* = 9.0, 4.0 Hz, H1), 2.97 - 2.87 (3H, m, C*H*$(CH_3)_2$), 2.83 (1H, ddd, *J* = 13.5, 10.9, 5.2 Hz, one of H3), 2.70 (1H, ddd, *J* = 13.5, 10.7, 5.9 Hz, one of H3), 2.28 (1H, dddd, *J* = 14.3, 10.7, 9.0, 5.2 Hz, one of H2), 2.17 (1H, dddd, *J* = 14.3, 10.9, 5.9, 4.0 Hz, one of H2), 1.60 - 1.49 (6H, m, $SnBu_3$), 1.40 - 1.31 (6H, m, $SnBu_3$), 1.29 (12H, d, *J* = 6.8 Hz, 2 × CH(CH_3)$_2$), 1.28 (6H, d, *J* = 6.9 Hz, CH(CH_3)$_2$), 1.05 – 0.96 (6H, m, $SnBu_3$), 0.89 - 0.94 (9H, m, $SnBu_3$);

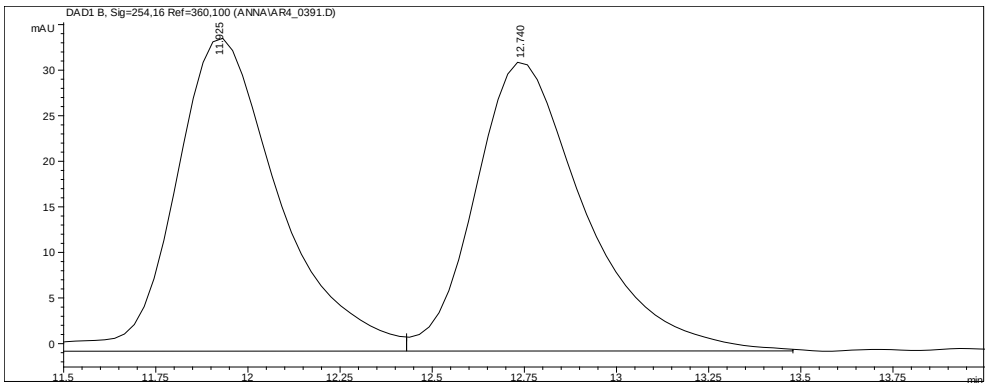
IR ($\tilde{\nu}$ /cm^{-1}, neat): 2960, 1706, 1607, 1463, 1384, 1285, 1250, 1074;

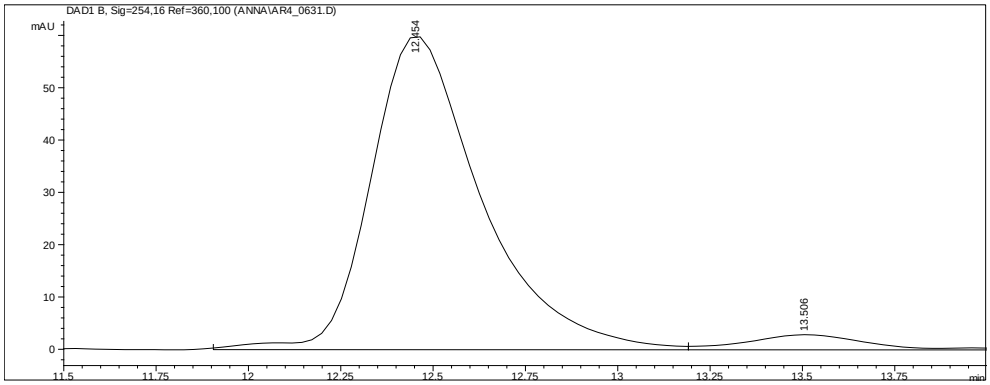
HRMS (CI): calc. for $C_{37}H_{61}O_2Sn$: m/z = 657.3694, found: m/z = 657.3710;

$[\alpha]_D^{23}$ = + 31 (*c* 1.00, $CHCl_3$);

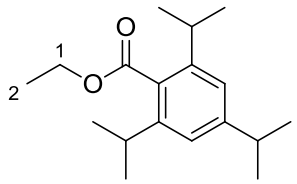
Chiral HPLC (Daicel Chiralcel-IB column (25 cm), hexane,0.5 mL/min, 0 °C, 254 nm); t_R = 12.5 (major), 13.5 (minor), e. r. = 95:5;







Ethyl 2,4,6-triisopropylbenzoate



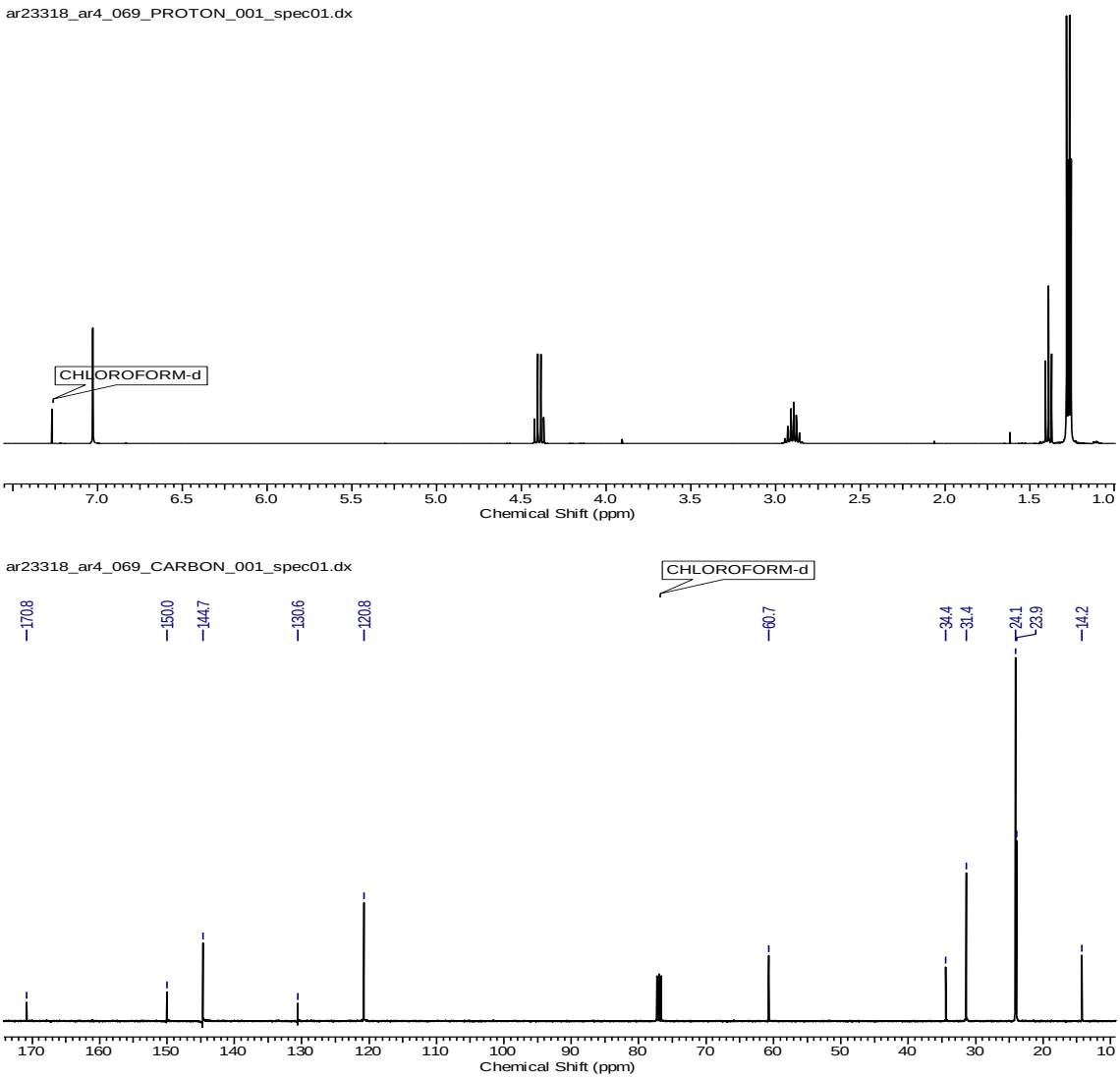
Ethanol (1.75 ml, 30 mmol) was added over 10 min to a stirring suspension of NaH (1.20 g, 60% in mineral oil, 30 mmol) in THF (15 ml). After evolution of gas had ceased 2,4,6-trichlorobenzoyl chloride (4.0 g, 15 mmol) was added and the reaction heated at 80 °C in a sealed tube for 16 hours. The reaction was cooled to room temperature and quenched with H_2O (100 ml). The layers were separated, aqueous layer extracted with Et_2O (3 × 100 ml), organic fractions combined, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/petroleum ether 1:99) to yield the benzoate[4] (3.63 g, 88%) as a colourless oil.

$\boldsymbol{R_f}$ = 0.55 (EtOAc/Petroleum Ether 10:90);

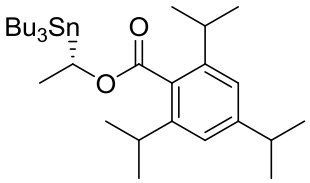
^{13}C NMR (100 MHz, $CHCl_3$) δ ppm 170.8 (C=O), 150.0 (C), 144.7 (C), 130.6 (C), 120.8 (CH), 60.7 (CH_2), 34.4 (CH), 31.4 (CH), 24.1 (CH_3), 23.9 (CH_3), 14.2 (CH_3)

^{1}H NMR: (400 MHz, $CDCl_3$) δ ppm 7.03 (2H, s, ArH), 4.39 (2H, q, *J* = 7.1 Hz, H1), 2.95 - 2.83 (3H, m, C*H*(CH_3)$_2$), 1.39 (3H, t, *J* = 7.1 Hz, H2), 1.27 (12H, d, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.26 (6 H, d, *J* = 6.8 Hz, , CH(C*H*$_3$)$_2$);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 2958, 2926, 2871, 1709, 1461, 1251, 1066;



(*S*)- Tributylstannyl)ethyl 2,4,6-triisopropylbenzoate 23



(–)-Sparteine (1.2 ml, 5.2 mmol) and ethyl-2,4,6-triisopropylbenzoate (1.1 g, 4.0 mmol) were dissolved in Et_2O (20 ml) and cooled to −78 °C. sBuLi (1.3 M in hexanes, 4.0 ml, 5.2 mmol) was added dropwise over 15 min and the reaction stirred at this temperature for 5 h. Bu_3SnCl (1.8 ml, 6.8 mmol) was added dropwise and the reaction allowed to warm to room temperature overnight, upon which it was quenched with aqueous KF (1 M solution, 30 ml), layers separated and the aqueous extracted with Et_2O (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and solvent removed under reduced pressure. The crude material was purified by column

chromatography (EtOAc/petroleum ether 1:99) to yield the stannane4 (1.89 g, 83%) as a colourless oil. The racemic was made using TMEDA in place of (−)-Sparteine.

R_f = 0.39 (EtOAc/Petroleum Ether 2:98);

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2 (C=O), 149.8 (C), 144.7 (C), 131.0 (C), 120.7 (CH), 66.8 (CH), 34.4 (CH), 31.3 (CH), 29.1 (CH_2), 27.5 (CH_2), 24.5 (CH_3), 24.0 (CH_3), 23.9 (CH_3), 20.0 (CH_3), 13.7 (CH_3), 9.2 (CH_2);

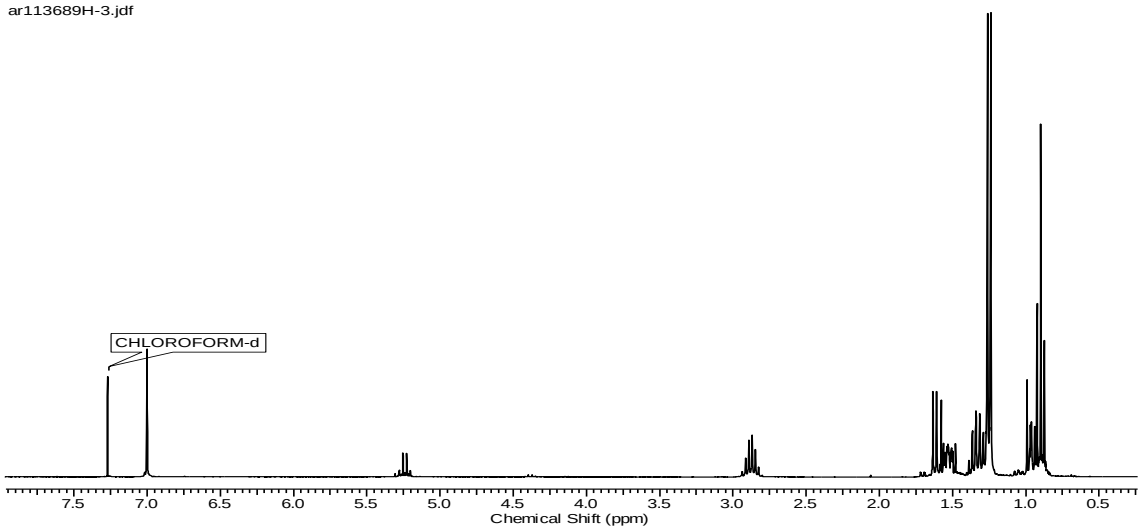
^{1}H NMR: ^{1}H NMR (301 MHz, $CDCl_3$) δ ppm 7.00 (2H, s, ArH), 5.24 (1H, m, $CHSnBu_3$), 2.87 (3H, spt, *J* = 6.9 Hz, $CH(CH_3)_2$), 1.62 (3H, d, *J* = 7.6 Hz, CH_3), 1.46 - 1.57 (6H, m, $SnBu_3$), 1.40 - 1.28 (6H, m, $SnBu_3$), 1.25 (6H, d, *J* = 6.9 Hz, $CH(CH_3)_2$), 1.25 (12H, d, *J* = 6.9 Hz, $CH(CH_3)_2$), 0.93 - 1.01 (6H, m, $SnBu_3$), 0.90 (9H, t, *J* = 7.3 Hz, $SnBu_3$);

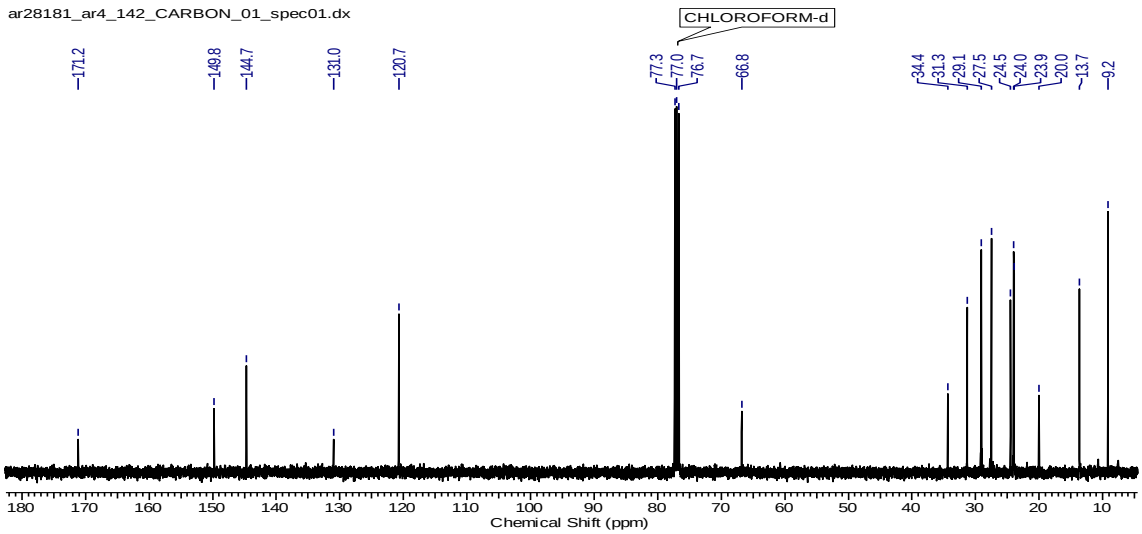
IR ($\tilde{\nu}$ /cm^{-1}, neat): 2958, 2926, 1710, 1607, 1461, 1251, 1066;

HRMS (ESI): calc. for $C_{30}H_{54}O_2SnNa$: m/z = 589.3038, found: m/z = 589.3046;

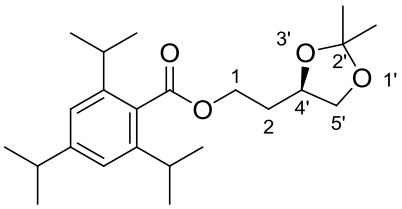
$[\alpha]_D^{23}$ = + 17 (*c* = 1.00, $CHCl_3$);

Chiral HPLC: This product could not be separated by HPLC or chiral GC





(*R*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl 2,4,6-triisopropylbenzoate 29



2-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]ethanol (1.4 ml, 10 mmol) was added over 10 min to a stirring suspension of NaH (400 mg, 60% in mineral oil, 10 mmol) in THF (10 ml). After evolution of gas had ceased 2,4,6-trichlorobenzoyl chloride (2.7 g, 10 mmol) was added and the reaction heated at 80 °C in a sealed tube for 16 hours. The reaction was cooled to room temperature and quenched with H_2O (50 ml). The layers were separated, aqueous layer extracted with Et_2O (3 × 50 ml), organic fractions combined, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/petroleum ether 5:95) to yield the *benzoate* (2.63 g, 70%) as a colourless oil.

$\boldsymbol{R_f}$ = 0.39 (EtOAc/Petroleum Ether 10:90)

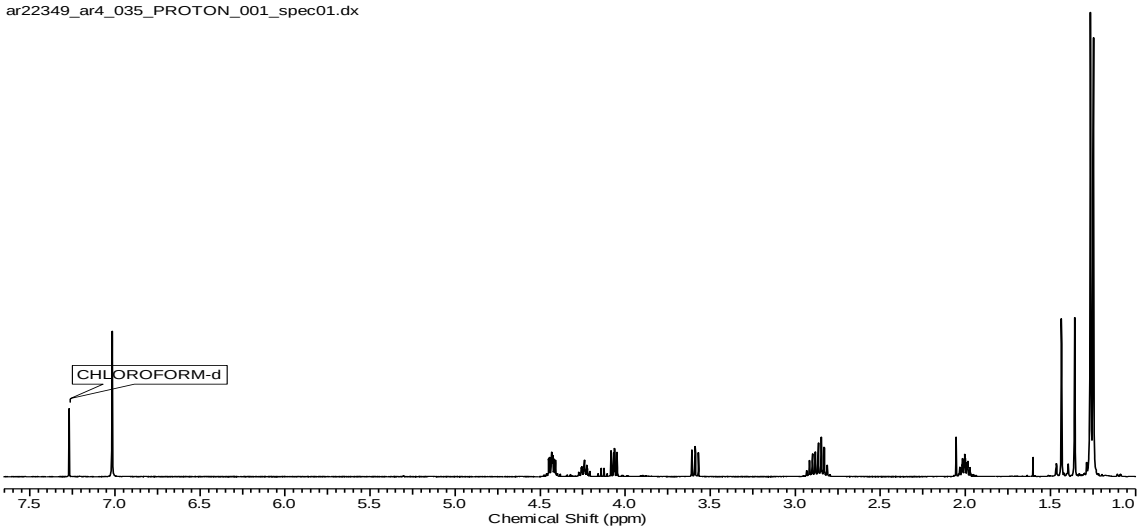
^{13}C NMR (100 MHz, $CHCl_3$) δ ppm 170.7 (C=O), 150.2 (C), 144.7 (C), 130.3 (C), 120.8 (CH), 109.0 (C), 72.9 (CH), 69.3 (CH_2), 61.8 (CH_2), 34.4 (CH), 32.6 (CH_2), 31.5 (CH), 26.9 (CH_3), 25.6 (CH_3), 24.1 (CH_3), 24.1 (CH_3), 23.9 (CH_3);

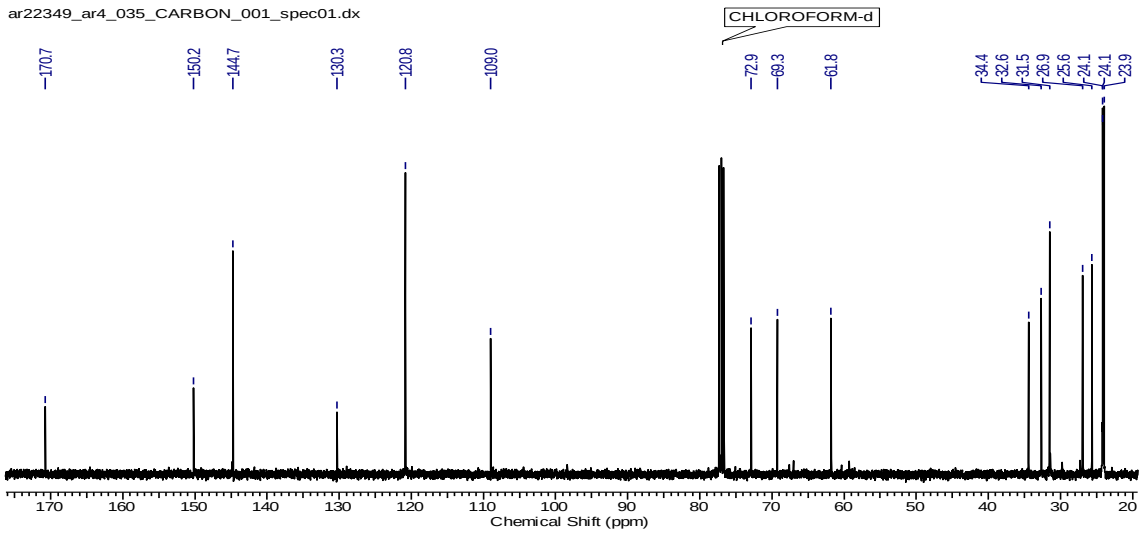
^{1}H NMR: ^{1}H NMR (301 MHz, $CDCl_3$) δ ppm 7.02 (2H, s, ArH), 4.43 (2H, ddd, *J* = 7.1, 6.1, 2.6 Hz, H1), 4.24 (1H, dddd, *J* = 7.4, 7.2, 6.0, 5.8 Hz, H4'), 4.07 (1H, dd, *J* = 7.9, 6.0 Hz, one of H5'), 3.59 (1H, dd, *J* = 7.9, 7.4 Hz, one of H5'), 2.95 - 2.80 (3H, m, C*H*$(CH_3)_2$), 2.04 – 1.96 (2H, m, H2), 1.43 (3H, s, C$(CH_3)_2$), 1.36 (3H, s, C$(CH_3)_2$), 1.26 (18H, d, *J* = 7.1 Hz, CH(C$H_3)_2$);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 2961, 2871, 1730, 1607, 1465, 1370, 1251, 1075;

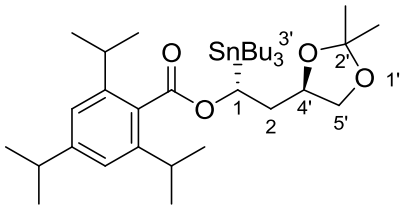
HRMS (ESI): calc. for $C_{23}H_{36}O_4Na$: m/z = 399.2506, found: m/z = 399.2512;

$[\alpha]_D^{23}$ = + 9 (*c* = 1.00, $CHCl_3$);





(*R*)-2-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-1-(tributylstannyl)ethyl 2,4,6-triisopropylbenzoate 30



(*R*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethyl 2,4,6-triisopropylbenzoate (1.51 g, 4.00 mmol) was dissolved in Et_2O (20 ml) and cooled to −78 °C. sBuLi (1.3 M in hexanes, 4.40 mmol, 3.38 ml) was added dropwise over 30 min and the reaction stirred at this temperature for 5 h. Bu_3SnCl (1.84 ml, 6.80 mmol) was added dropwise and the reaction allowed to warm to room temperature overnight, upon which it was quenched with aqueous KF (1 M solution, 50 ml), layers separated and the aqueous extracted with Et_2O (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and solvent removed under reduced pressure. The crude material was purified by column chromatography (EtOAc/petroleum ether 1:99) to yield the *stannane* (1.89 g, 71%) as a colourless oil (as a 10:1 mixture of diastereomers, major product characterised).

R_f = 0.43 (EtOAc/Petroleum Ether 10:90)

^{13}C NMR (101 MHz, $CHCl_3$) δ ppm 171.1 (C), 149.9 (C), 144.7 (C), 130.7 (C), 120.8 (CH), 109.0 (C), 73.8 (CH), 69.6 (CH_2), 68.1 (CH), 38.0 (CH_2), 34.4 (CH), 31.5 (CH), 29.1 (CH_2), 27.5 (CH_2), 26.9 (CH_3), 25.6 (CH_3), 24.5 (CH_3), 24.1 (CH_3), 23.9 (CH_3), 13.7 (CH_3), 10.2 (CH_2);

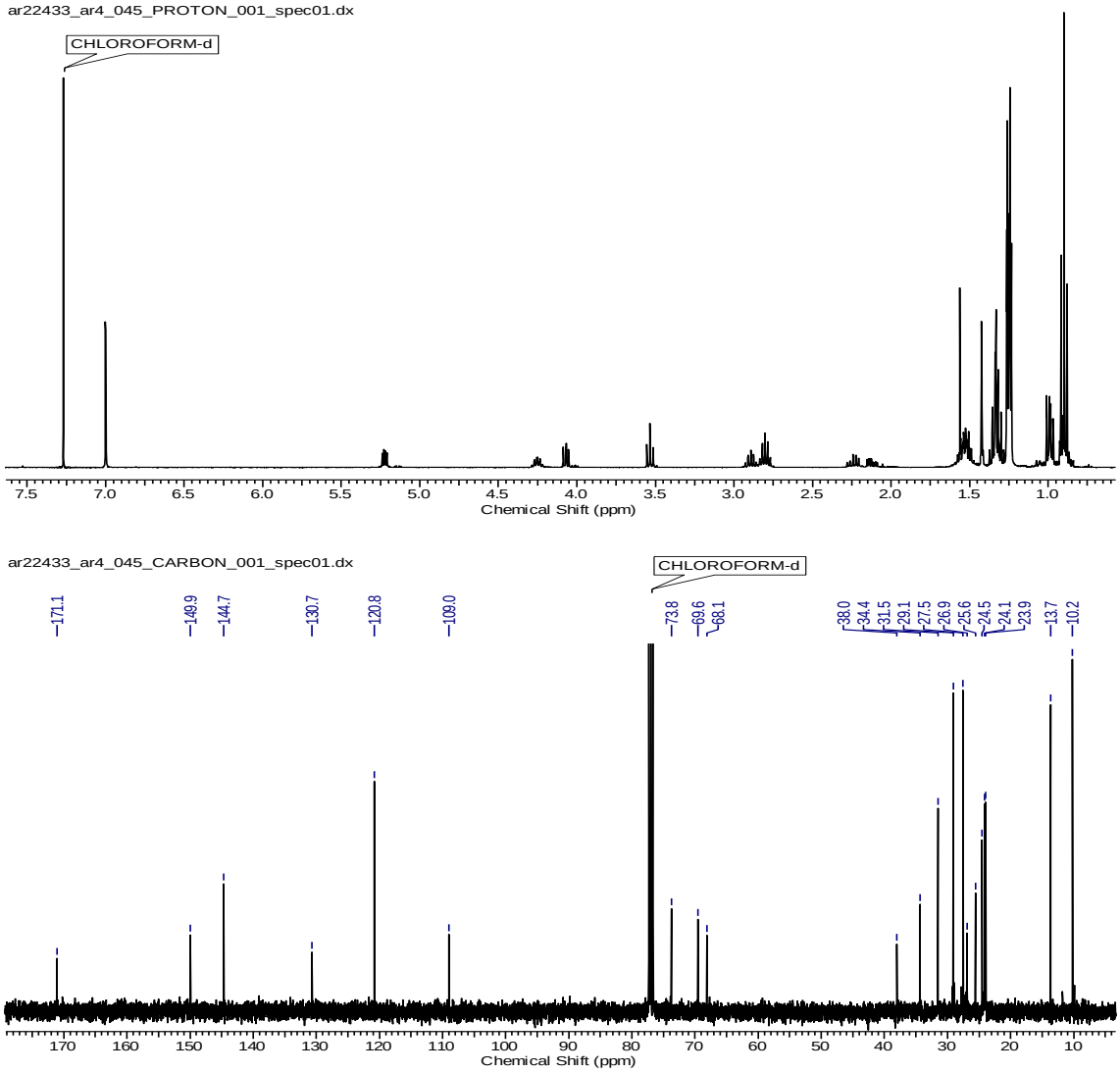
^{1}H NMR: ^{1}H NMR (400MHz, $CDCl_3$) δ ppm 7.00 (2H, s, ArH), 5.22 (1H, dd, *J* = 7.6, 4.4 Hz, H1), 4.25 (1H, dddd, *J* = 7.9, 6.9, 6.2, 5.9 Hz, H4'), 4.07 (1H, dd, *J* = 7.9, 5.9 Hz, one of H5'), 3.54 (1H, t, *J* = 7.9 Hz, one of H5'), 2.89 (1H, spt, *J* = 6.8 Hz, C*H*(CH_3)$_2$), 2.80 (2H, spt, *J* = 6.9 Hz, C*H*(CH_3)$_2$), 2.29 - 2.18 (1H, ddd, *J* = 14.5, 7.6, 6.9 Hz, one of H2), 2.12 (1H, ddd, *J* = 14.6, 6.2, 4.4

Hz, one of H2), 1.59 - 1.47 (6H, m, $SnBu_3$), 1.42 (3H, s, one of $C(CH_3)_2$), 1.38 - 1.27 (9H, m, $SnBu_3$, one of $C(CH_3)_2$), 1.27 - 1.22 (18H, m, $CH(CH_3)_2$), 1.02 – 0.95 (6H, m, $SnBu_3$), 0.92 - 0.87 (9H, m, $SnBu_3$);

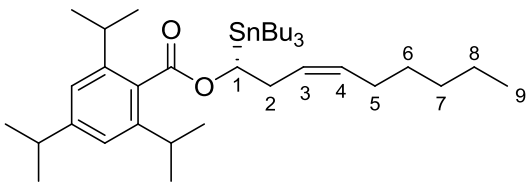
IR ($\tilde{\nu}$ /cm^{-1}, neat): 2960, 1927, 1715, 1608, 1465, 1379, 1363 1252, 1064;

HRMS (ESI): calc. for $C_{35}H_{62}O_4SnNa$: m/z = 689.3562, found: m/z = 689.3567;

$[\alpha]_D^{22}$ = – 13 (*c* = 1.00, $CHCl_3$);



(*R*,*Z*)-1-(Tributylstannyl)non-3-enyl 2,4,6-triisopropylbenzoate 27



(*R*)-2-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-1-(tributylstannyl) ethyl 2,4,6-triisopropylbenzoate (350 mg, 0.52 mmol) was dissolved in MeOH (15 ml) and aqueous HCl (1 M, 0.5 ml) added. The reaction was monitored by TLC and after complete deprotection $NaHCO_3$ was added until the solution reached pH 8, then $NaIO_4$ (0.89 g, 4.2 mmol) was added. After 1 h H_2O (20 ml) and CH_2Cl_2 (20 ml) were added, the layers separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 ml). The combined organic extracts were dried ($MgSO_4$) and solvent removed under reduced pressure. The crude aldehyde was immediately subjected to Wittig reaction. NaHMDS (1 M solution in THF, 0.57 ml, 0.57 mmol) was added to a solution of n-hexylphosphonium bromide (244 mg, 0.57 mmol) in THF (5 ml) at 0 °C. After 30 min at 0 °C and 30 min at room temperature the reaction mixture was cooled to -78 °C and the crude aldehyde in THF (3 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight, quenched with H_2O (20 ml), layers separated, and the aqueous phase extracted with Et_2O (3 × 20 ml). The organic extracts were combined, dried ($MgSO_4$) and solvent removed under reduced pressure. The product was purified by column chromatography (EtOAc/petroleum ether 1:99) to give the *stannane* (195 mg, 57%) as a colourless oil.

$\boldsymbol{R_f}$ = 0.66 (EtOAc/Petroleum Ether 5:95)

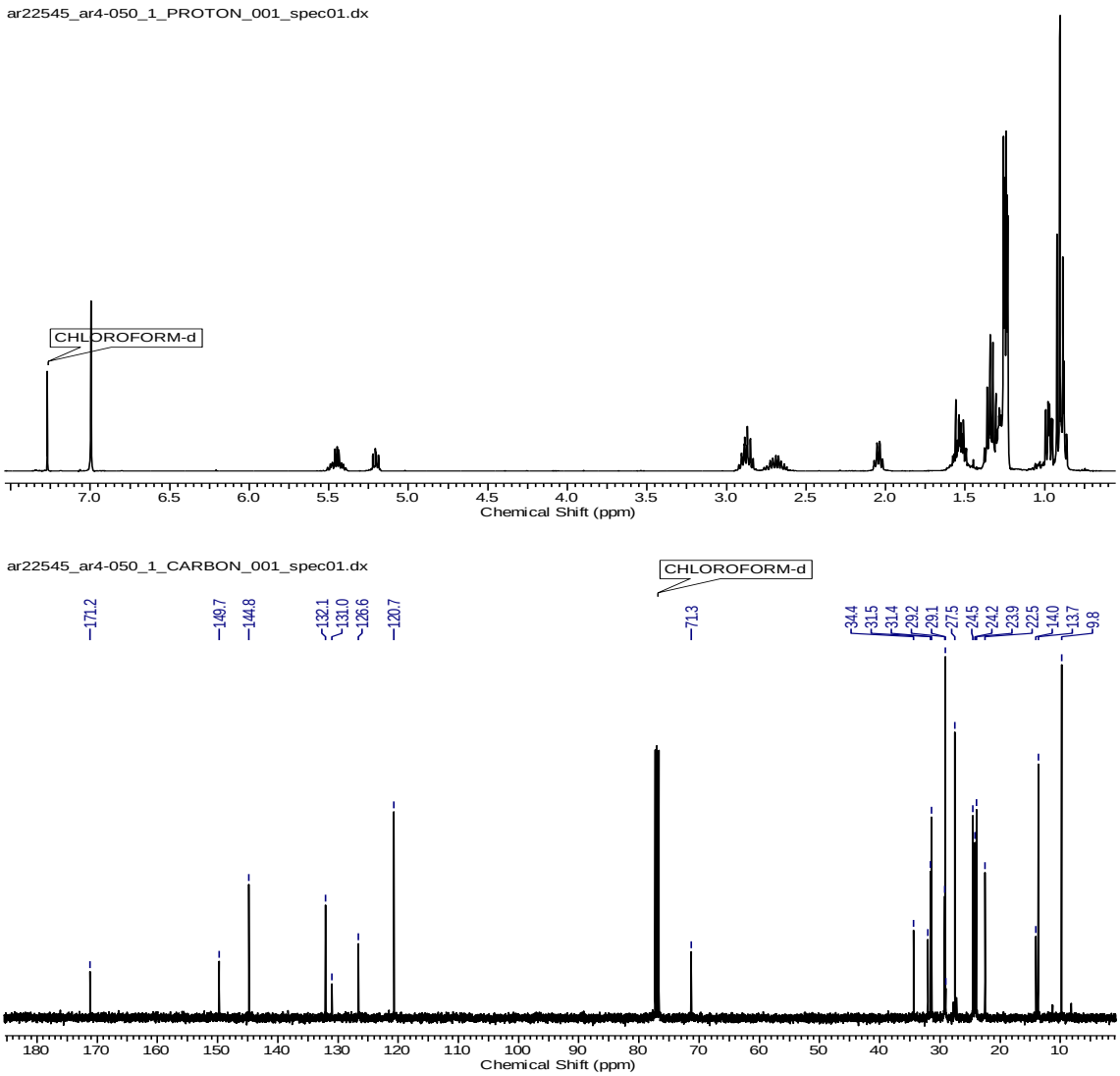
^{13}C NMR (101 MHz, $CHCl_3$) δ ppm 171.2 (C), 149.7 (C), 144.8 (C), 132.1 (CH), 131.0 (C), 126.6 (CH), 120.7 (CH), 71.3 (CH), 34.4 (CH), 31.5 (CH_2), 31.4 (CH), 29.2 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 27.5 (CH_2), 24.5 (CH), 24.2 (CH_3), 23.9 (CH_3), 22.5 (CH_2), 14.0 (CH_3), 13.7 (CH_3), 9.8 (CH_2);

^{1}H NMR: (400MHz, $CDCl_3$) δ ppm 7.00 (2H, s, ArH), 5.52 - 5.37 (2H, m, H3 and H4), 5.20 (1H, dd, *J* = 7.8, 6.3 Hz, H1), 2.93 - 2.82 (3H, m, C*H*(CH_3)$_2$), 2.78 - 2.59 (2H, m, H5), 2.05 (2H, m, H2), 1.63 - 1.45 (6H, m, $SnBu_3$), 1.40 - 1.21 (30H, m, CH(C*H*$_3$)$_2$, H6-H8 and $SnBu_3$), 1.01 – 0.93 (6H, m, $SnBu_3$), 0.90 (9H, t, *J* = 7.3 Hz, $SnBu_3$), 0.88 (3H, t, *J* = 6.7 Hz, H9);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 2960, 2958, 2925, 2856, 1710, 1607, 1462, 1250, 1067;

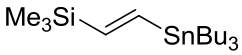
HRMS (ESI): calc. for $C_{37}H_{66}O_2SnNa$: m/z = 685.3977, found: m/z = 685.4006;

$[\alpha]_D^{25}$ = + 16 (*c* = 0.50, $CHCl_3$);



3. Boronic ester

(*E*)-trimethyl(2-(tributylstannyl)vinyl)silane

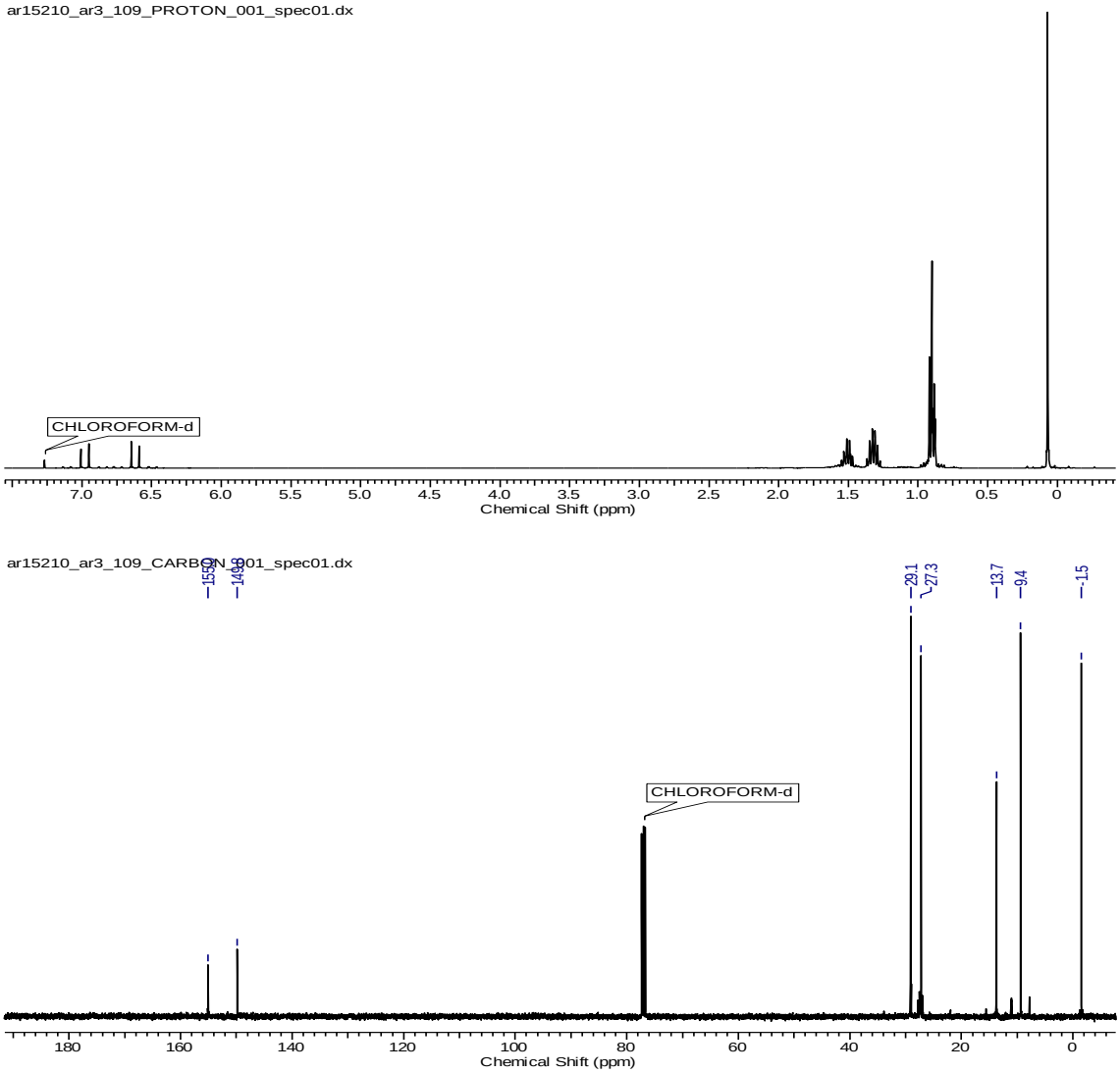


Tributyltin hydride (5.4 ml, 20 mmol) was added to a suspension of 1,1'-azobis(cyclohexanecarbonitrile) (0.49 g, 2.0 mmol) in trimethylsilylacetelene (2.8 ml, 20 mmol) and the reaction heated to 80 °C for 16 h. After cooling to rt the reaction was filtered through silica (the filter cake being washed with pentane (100 ml)) and solvent removed *in vacuo* to yield the stannane[5] (7.1 g, 91%) as a colourless oil.

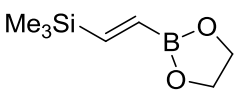
^{13}C NMR (101 MHz, $CHCl_3$) δ ppm 155.0 (CH), 149.8 (CH), 29.1 (CH_2, d satellite $J_{C\text{-}Sn}$ = 20.2 Hz), 27.3 (CH_2, d satellite $J_{C\text{-}Sn}$ = 52.2 Hz), 13.7 (CH_3), 9.4 (CH_2, 2 × d satellites $J_{C\text{-}Sn}$ = 318, 332 Hz), -1.5 (CH_3);

^{1}H NMR: (400MHz, $CDCl_3$) δ ppm 6.98 (1H, d, *J* = 22.4 Hz, CH=C*H*), 6.62 (1H, d, *J* = 22.4 Hz, C*H*=CH), 1.56 - 1.44 (6H, m, $SnBu_3$), 1.32 (6H, dq, *J* = 14.9, 7.3 Hz, $SnBu_3$), 0.99 - 0.79 (15H, m, 3 × $SnCH_2$, 3× $Sn(CH_2)_3CH_3$), 0.07 (9 H, s, $SiMe_3$);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 2956, 2926, 1464, 1246, 859, 835;



[(*E*)-2-(1,3,2-Dioxaborolan-2-yl)vinyl](trimethyl)silane 6



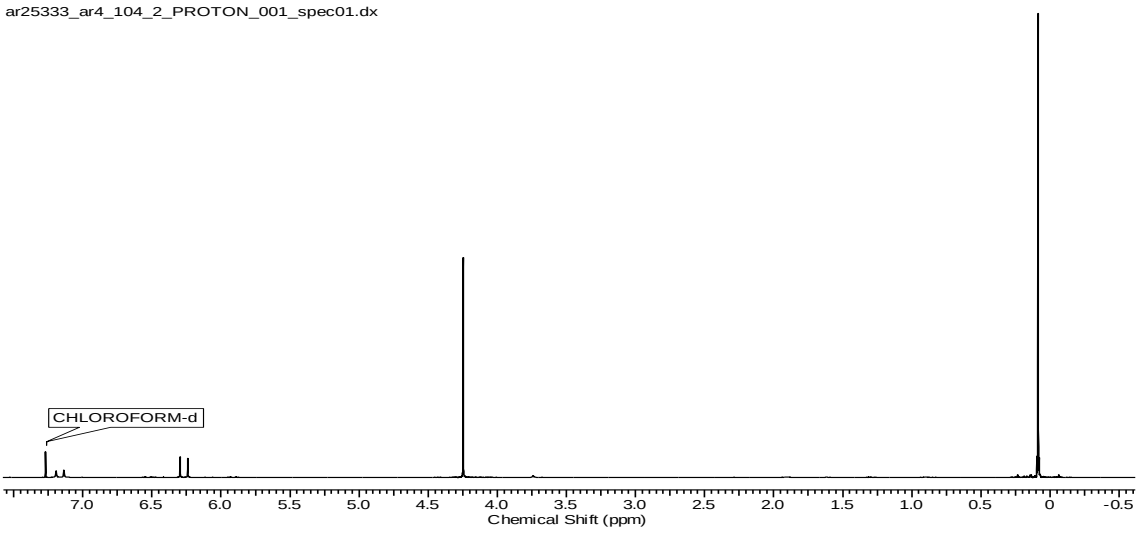
The stannane **231**[5] (6.29 g, 16.1 mmol) was dissolved in THF (44 ml) and cooled to −78 °C. A solution of *n*BuLi (1.6 M in hexane, 11.1 ml, 17.7 mmol) was added dropwise and the mixture was stirred for 2 hours at −78 °C followed by 1 hour at −45 °C. The reaction flask was then cooled back to −78 °C and $B(OMe)_3$ (1.97 ml, 17.7 mmol) was added dropwise. The mixture was stirred for 1

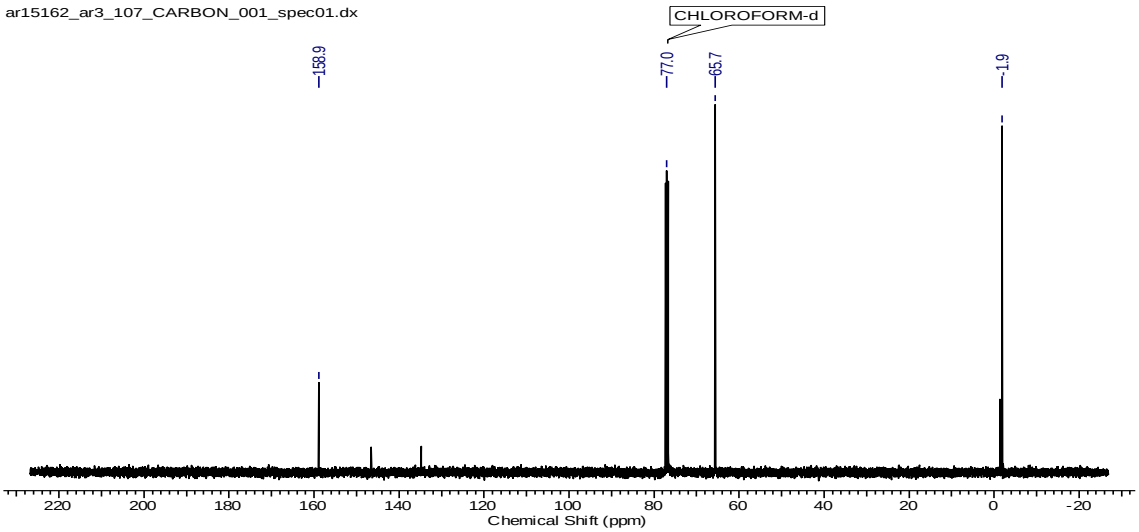
hour at this temperature followed by 2 hours at 0 °C and was then quenched with aqueous HCl (1 M, 100 ml) and extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude boronic ester was dissolved in dichloromethane (32 ml) and magnesium sulphate (10 g) and ethylene glycol (1.80 ml, 32.2 mmol) were added. This mixture was stirred for 3 days at room temperature, filtered (the magnesium sulfate was washed with pentane) and concentrated *in vacuo*. Careful distillation (b. p. 35−40 °C at 2 mbar) gave the boronic ester5 (1.31 g, 48 %).

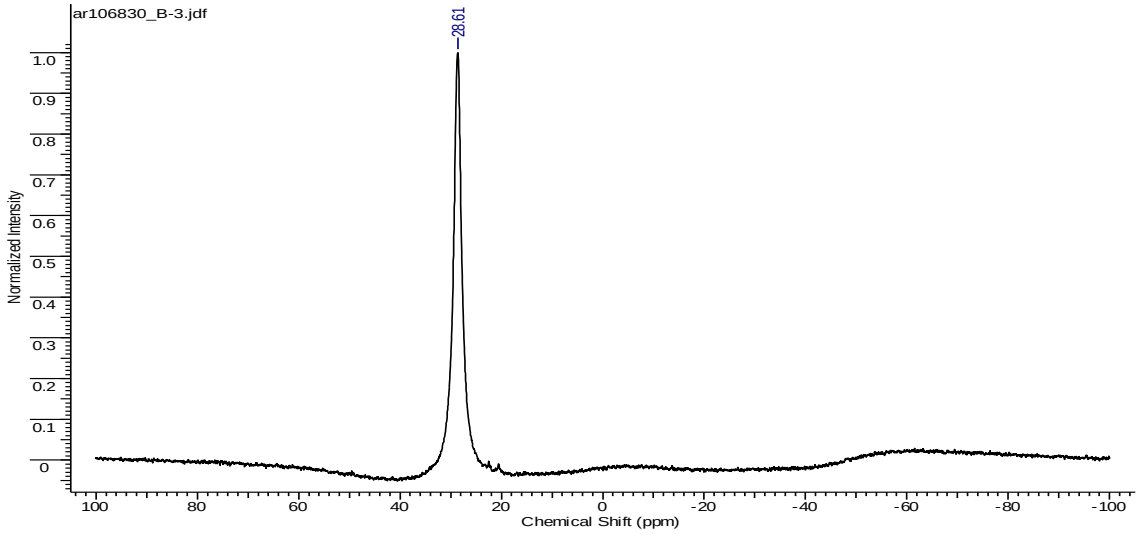
^{13}C NMR (101 MHz, $CHCl_3$) δ ppm 158.9 (CH), 65.7 (2 × CH_2), -1.9 (3 × CH_3);

^{1}H NMR: (400MHz, $CDCl_3$) δ ppm 7.17 (1H, d, *J* = 21.7 Hz, CH=C*H*), 6.27 (1H, d, *J* = 21.6 Hz, C*H*=CH), 4.26 (4H, s, OCH_2CH_2O), 0.09 (9 H, s, $SiMe_3$);

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm = 28.6;





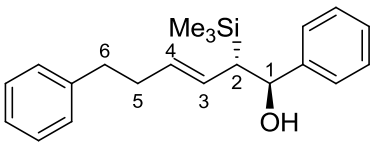


4. E-allyl silanes

General Procedure

The respective stannane (0.5 mmol) was dissolved in Et_2O (2.5 ml) and cooled to –78 °C. *n*BuLi (1.6 M in hexanes, 0.34 ml, 0.55 mmol) was added dropwise and the mixture was stirred at –78 °C for 1 hour. A solution of **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) was added dropwise and the mixture was stirred at −78 °C for 1 hour followed by warming to 23 °C over 30 minutes. Diethyl ether was then removed under vacuum and replaced with CH_2Cl_2 (2.5 ml), the mixture was refluxed for 1 h, before being cooled to −30 °C. In a seperate pot magnesium bromide was prepared by stirring Mg (18 mg, 1.5 eq) and 1,2- dibromoethane (0.043 ml, 1.0 eq) in 1 ml diethyl ether for 2 hours and this solution was then added to the reaction mixture at −30 °C. Aldehyde (1 mmol) was added dropwise and the reaction stirred until complete by TLC (15-24 hours). The reaction was quenched with a pre-mixed solution of aqueous NaOH (1 M)/H_2O_2 (2 ml of a 2:1 ratio solution). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 25 ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography.

(1*R*,2*S*,*E*)-1,6-diphenyl-2-(trimethylsilyl)hex-3-en-1-ol 10a



Prepared according to the general method from **(***S***)**-3-phenyl-1-(tributylstannyl)propyl 2,4,6-triisopropylbenzoate (328 mg, 0.50 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and benzaldehyde (0.01 ml, 1 mmol). The crude product was

purified by flash column chromatography (alumina, EtOAc/petroleum ether 5:95) to give the *alcohol* (98 mg, 61 %) as a colourless oil.

R_f = 0.39 (EtOAc/petroleum ether 1:9);

^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 143.5 (C), 141.7 (C), 132.0 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.0 (CH), 125.8 (CH), 74.7 (CH), 44.1 (CH), 36.0 (CH_2), 34.6 (CH_2), -2.4 (CH_3);

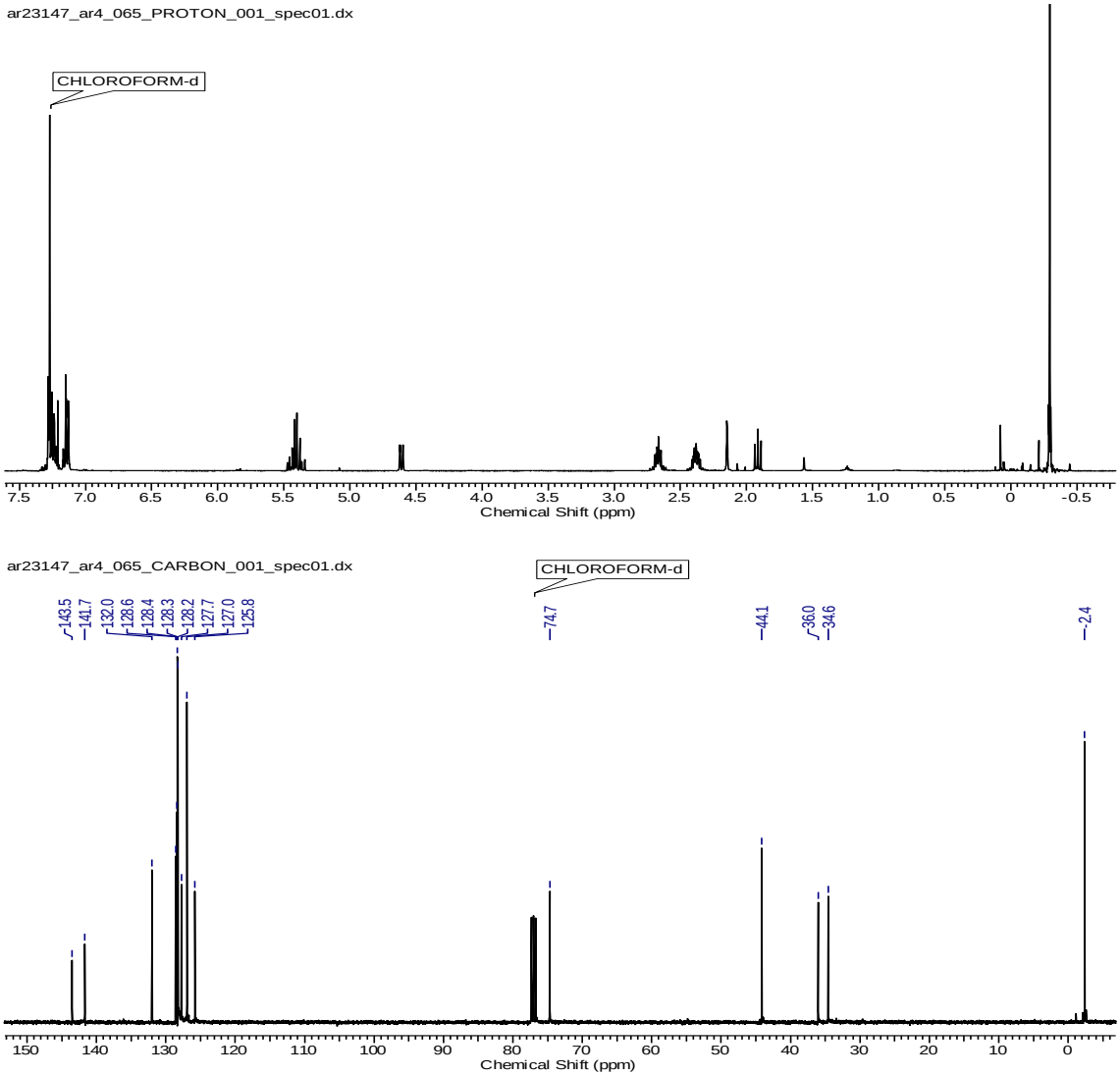
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.30 - 7.20 (6H, m, ArH), 7.18 - 7.11 (4H, m, ArH), 5.48 - 5.33 (2H, m, H3 & H4), 4.61 (1H, dd, *J* = 8.9, 1.8 Hz, H1), 2.67 (2H, ddd, *J* = 7.5, 7.5, 4.4 Hz, H6), 2.42 - 2.33 (2H, m, H5), 2.15 (1H, d, *J* = 1.8 Hz, OH), 1.91 (1H, t, *J* = 9.2 Hz, H2), -0.29 (9H, s, $SiMe_3$);

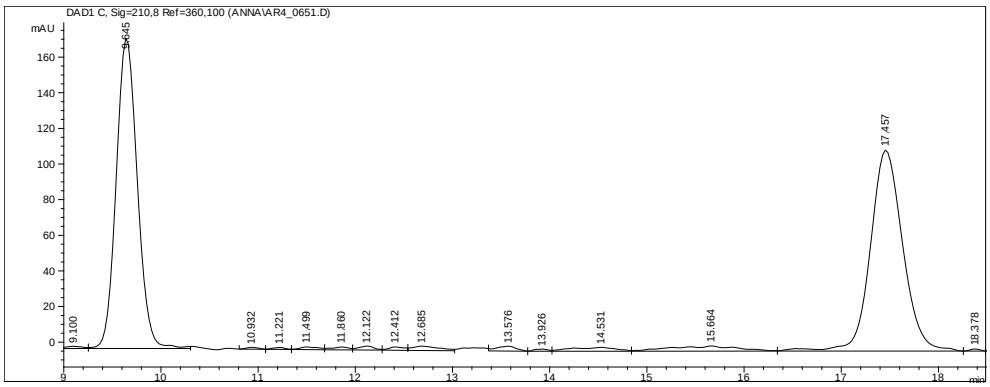
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3447, 3028, 2953, 1496, 1454, 1247, 1083, 1030;

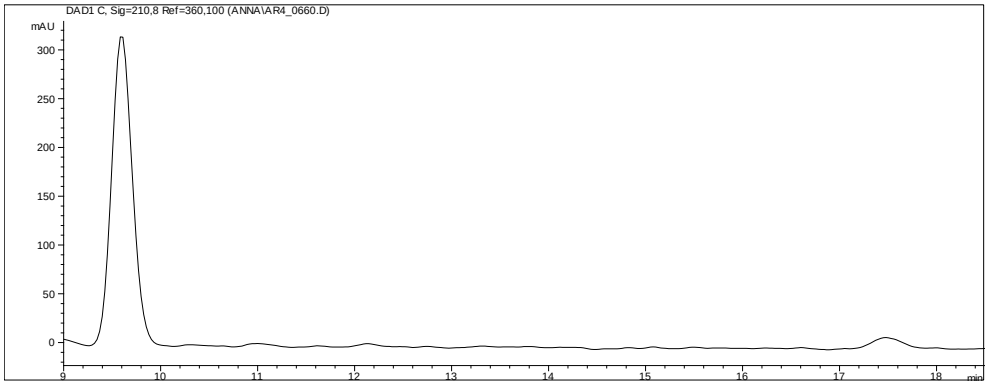
HRMS (ESI): calc. for $C_{21}H_{28}OSiNa$: m/z = 347.1802, found: m/z = 347.1811;

$[\alpha]_D^{23}$ = − 39 (*c* = 1.00, $CHCl_3$);

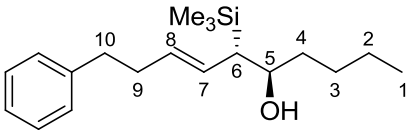
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), 5% IPA in hexane, 0.8 mL/min, rt, 210.8 nm); t_R = 9.6 (major), 17.5 (minor), e.r. = 95:5;







(5*R*,6*S*,*E*)-10-Phenyl-6-(trimethylsilyl)dec-7-en-5-ol 10b



Prepared according to the general method from (*S*)-3-phenyl-1-(tributylstannyl)propyl 2,4,6-triisopropylbenzoate (328 mg, 0.5 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), boronic ester **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and pentanal (110 µl, 1 mmol). The crude product was purified by flash column chromatography (alumina, EtOAc/petroleum ether 5:95) to give the *alcohol* (107 mg, 70 %) as a colourless oil.

$\boldsymbol{R_f}$ = 0.37 (EtOAc/petroleum ether 1:9);

^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 141.9 (C), 130.7 (CH), 128.4 (CH), 128.3 (CH), 127.8 (CH), 125.7 (CH), 71.7 (CH), 40.8 (CH), 36.8 (CH_2), 36.3 (CH_2), 34.6 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3), -1.9 (CH_3);

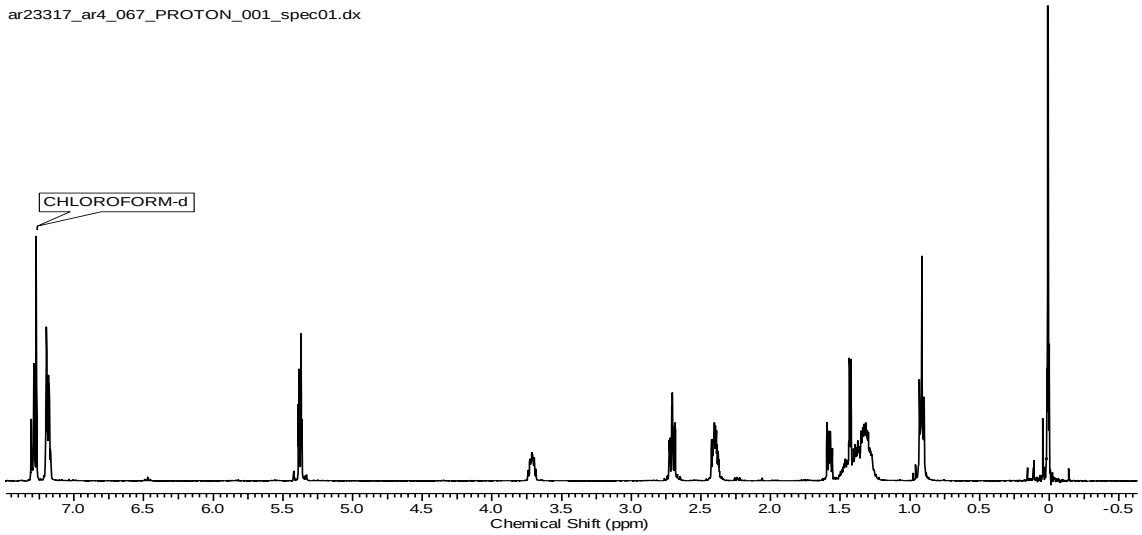
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.31 - 7.26 (2H, m, ArH), 7.22 - 7.15 (3H, m, ArH), 5.40 - 5.36 (2H, m, H7 & H8), 3.71 (1H, dddd, *J* = 7.4, 5.6, 4.5, 4.3 Hz, H5), 2.71 (2H, ddd, *J* = 7.5, 7.5, 1.5 Hz, H10), 2.45 - 2.34 (2H, m, H9), 1.60 - 1.54 (1H, m, H6), 1.43 (1H, d, *J* = 4.3 Hz, OH), 1.53 - 1.23 (6H, m, H2-H4), 0.91 (3H, t, *J* = 7.0 Hz, H1), 0.01 (9H, s, $SiMe_3$);

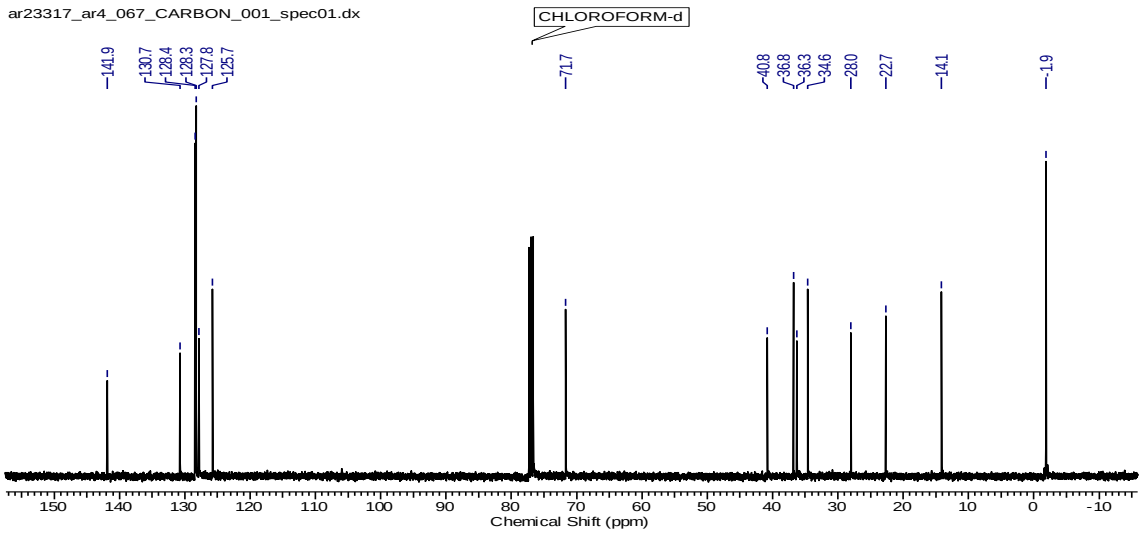
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3467, 2955, 2928, 1454, 1245, 1030, 835;

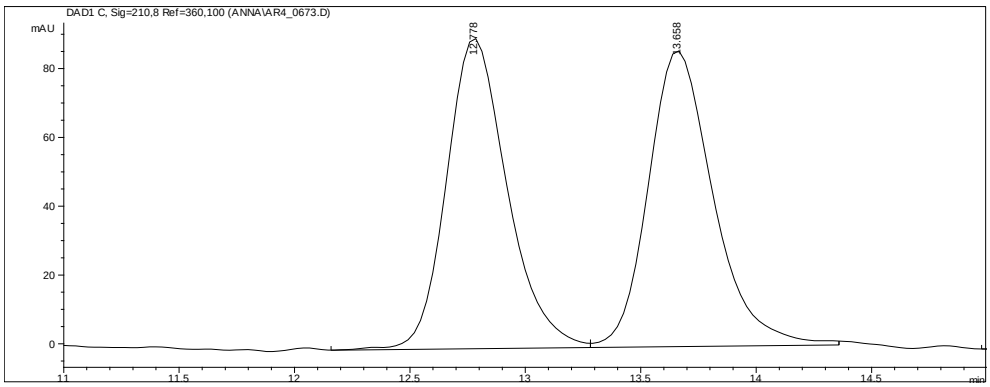
HRMS (ESI): calc. for $C_{19}H_{32}OSiNa$: m/z = 327.2115, found: m/z = 327.2123;

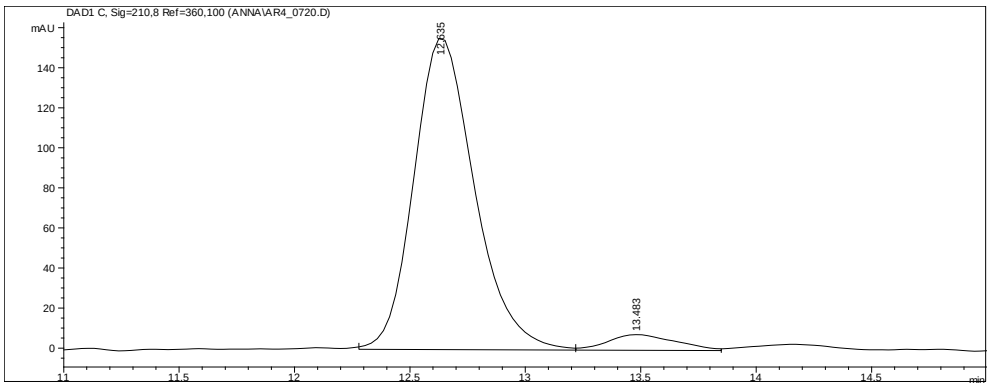
$[\alpha]_D^{23}$ = + 6 (*c* = 1.00, $CHCl_3$);

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), 1% IPA in hexane, 0.5 mL/min, rt, 210.8 nm); t_R = 12.6 (major), 13.7 (minor), e.r. = 95:5;

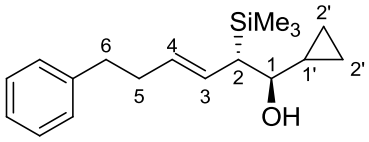








(1*R*,2*S*,*E*)-1-Cyclopropyl-6-phenyl-2-(trimethylsilyl)hex-3-en-1-ol 10c



Prepared according to the general method from (*S*)-3-phenyl-1-(tributylstannyl)propyl 2,4,6-triisopropylbenzoate (328 mg, 0.50 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), boronic ester **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and cyclopropanecarbaldehyde (0.075 ml, 1 mmol). The crude product was purified by flash column chromatography (alumina, EtOAc/petroleum ether 5:95) to give the *alcohol* (108 mg, 75 %) as a colourless oil.

R_f = 0.27 (EtOAc/petroleum ether 1:9);

^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 141.9 (C), 130.4 (CH), 128.5 (CH), 128.2 (CH), 128.2 (CH), 125.7 (CH), 77.1 (CH), 41.5 (CH), 36.3 (CH_2), 34.6 (CH_2), 17.6 (CH), 3.8 (CH_2), 3.3 (CH_2), -1.9 (CH_3)

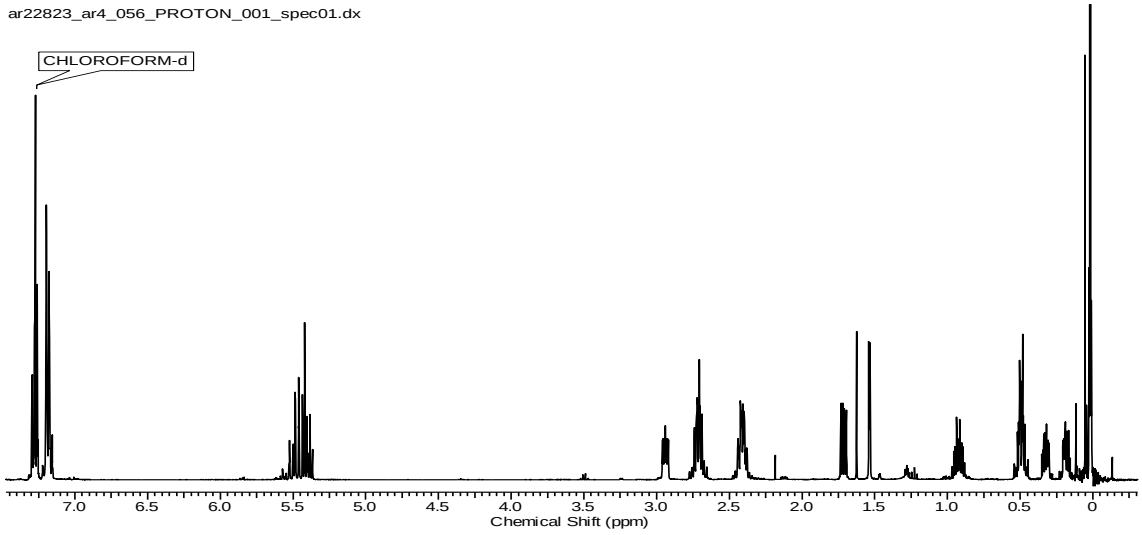
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.31 - 7.24 (2H, m, ArH), 7.21 - 7.14 (3H, m, ArH), 5.49 (1H, dddd, *J* = 15.2, 10.2, 1.0, 1.0 Hz, H3), 5.40 (1H, ddd, *J* = 15.2, 6.3, 6.3 Hz, H4), 2.94 (1H, ddd, *J* = 8.7, 5.0, 2.7 Hz, H1), 2.78 - 2.64 (2H, m, H6), 2.36 - 2.45 (2H, m, H5), 1.71 (1H, dd, *J* = 10.2, 5.0 Hz, H2), 1.54 (1H, d, *J* = 2.7 Hz, OH), 0.93 (1H, qt, *J* = 8.3, 4.9 Hz, H1'), 0.55 - 0.43 (2H, m, two of H2'), 0.36 - 0.29 (1H, m, one of H2'), 0.21 - 0.16 (1H, m, one of H2'), 0.02 (9H, s, $SiMe_3$);

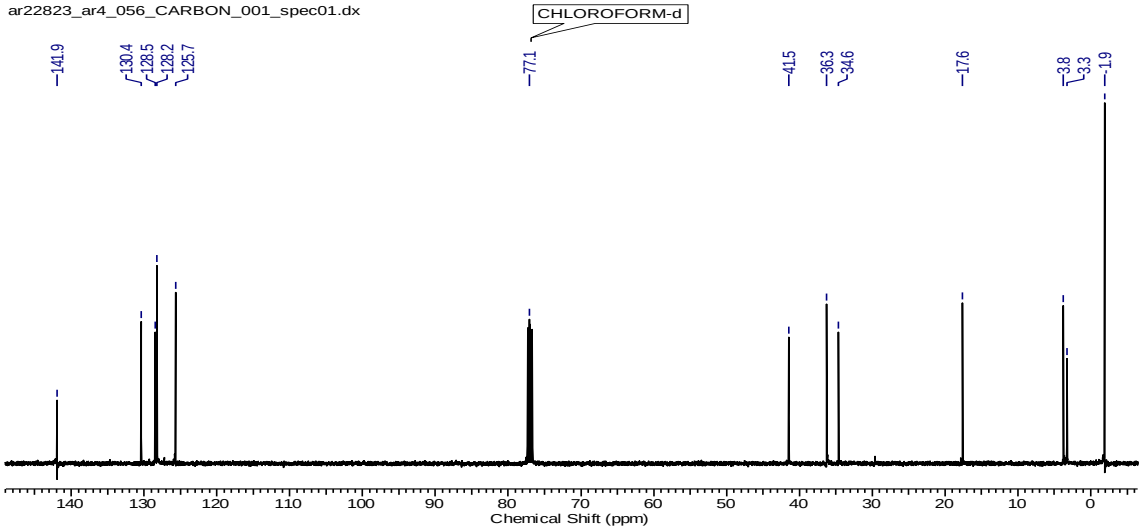
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3467, 2925, 2855, 1454, 1246, 1083;

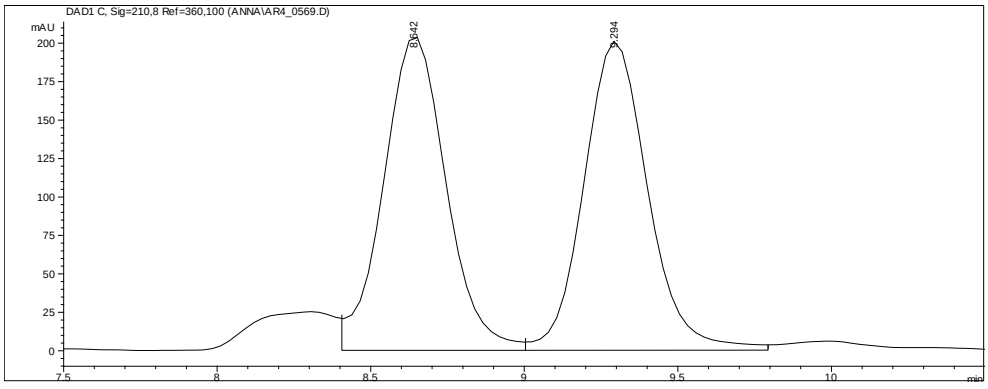
HRMS (ESI): calc. for $C_{18}H_{28}OSiNa$: m/z = 311.1802, found: m/z = 311.1801;

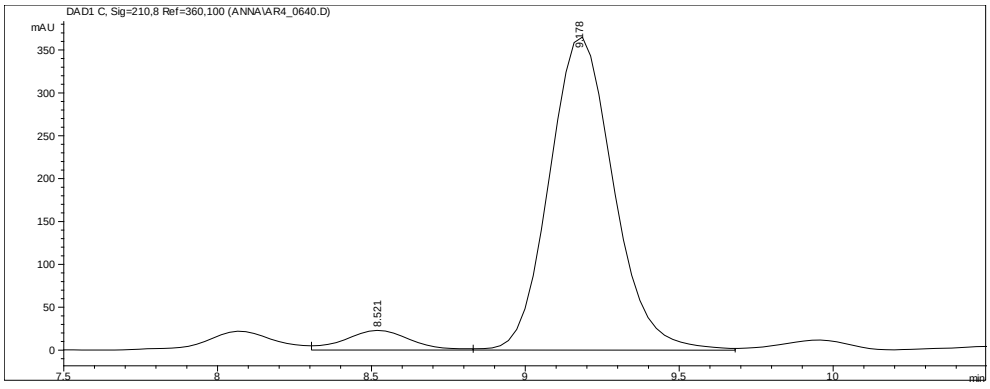
$[\alpha]_D^{23}$ = − 8 (*c* = 0.50, $CHCl_3$);

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), 1% IPA in hexane,0.8 mL/min, rt, 210.8 nm); t_R = 8.5 (minor), 9.2 (major), e.r. = 95:5;

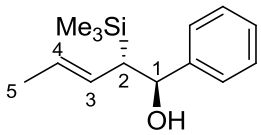








(1*R*,2*S*,*E*)-1-Phenyl-2-(trimethylsilyl)pent-3-en-1-ol 10d



Prepared according to the general method from (*S*)-tributylstannyl)ethyl 2,4,6-triisopropylbenzoate (283 mg, 0.50 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), (*E*)-Me_3Si-=-*B*-ethyleneglycol (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and benzaldehyde (100 µl, 1.0 mmol). The crude product was purified by flash column chromatography (neutralised silica, EtOAc/petroleum ether 5:95) to give the allylsilane[6] (103 mg, 88%) as a colourless oil.

R_f = 0.36 (EtOAc/petroleum ether 1:9);

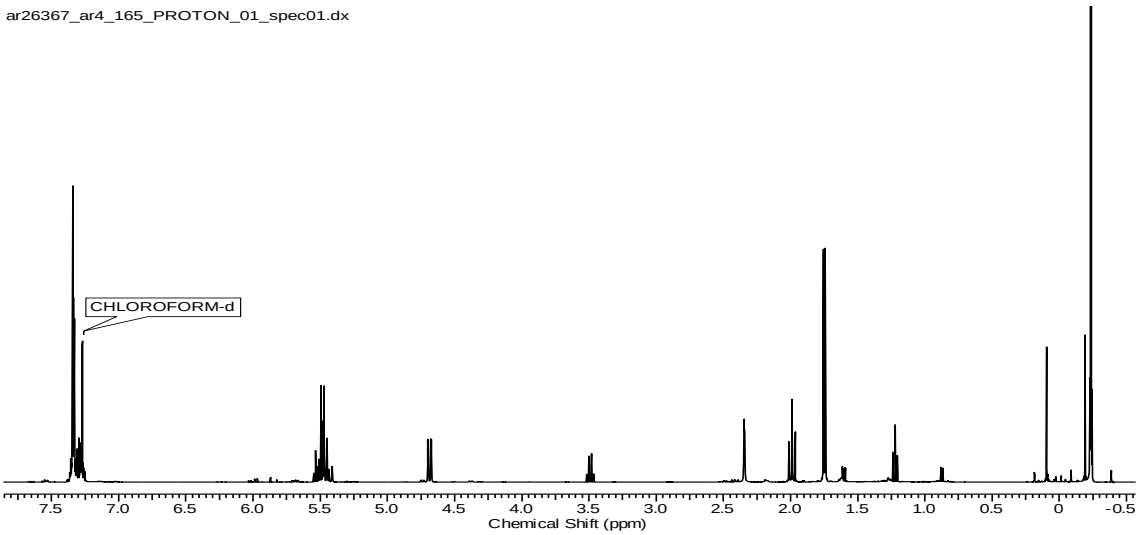
^{13}C NMR: δ ppm 143.6 (C), 128.8 (CH), 128.3 (CH), 127.8 (CH), 127.6 (CH), 127.0 (CH), 74.8 (CH), 44.2 (CH), 18.2 (CH_3), -2.4 (CH_3);

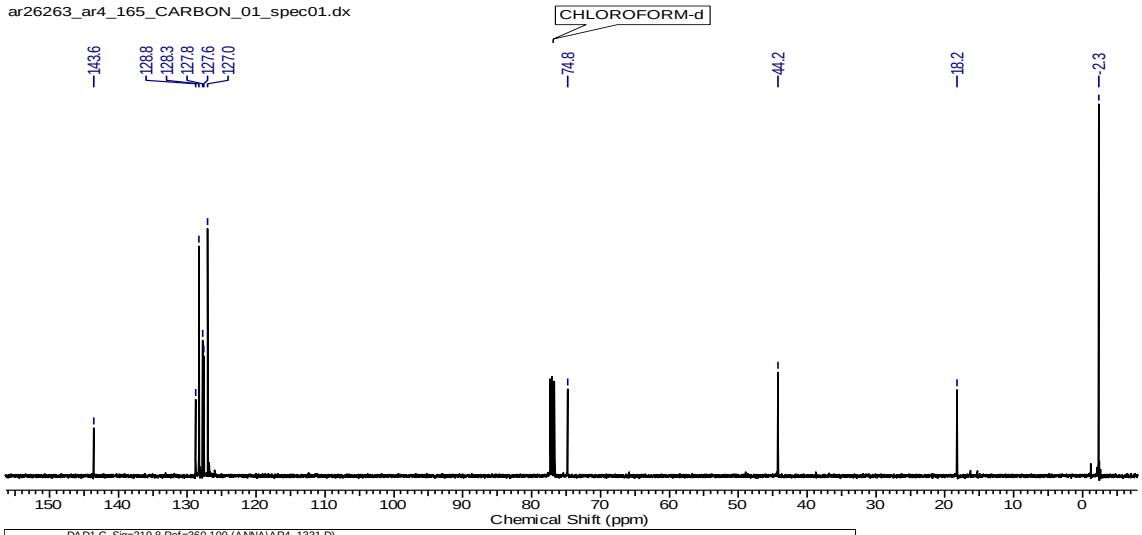
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.32 - 7.15 (5H, m, ArH), 5.48 - 5.33 (2H, m, H3, H4), 4.62 (1H, dd, *J* = 9.0, 1.8 Hz, H1), 2.26 (1H, d, *J* = 1.8 Hz, OH), 1.92 (1H, dd, *J* = 9.2, 9.0 Hz, H2), 1.68 (3H, d, *J* = 4.8 Hz, H5), -0.30 (9H, s, $SiMe_3$);

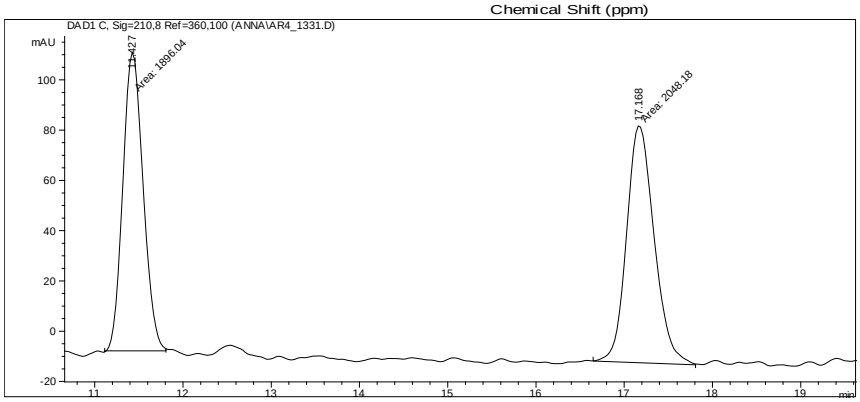
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3432, 2956, 1453, 1246, 834;

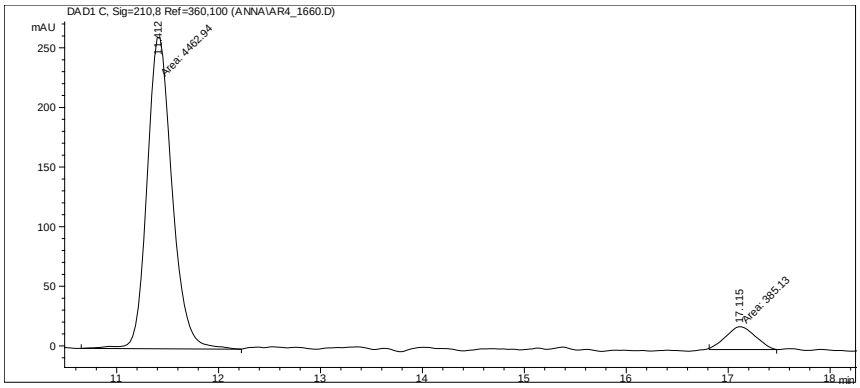
$[\alpha]_D^{23}$ = − 2 (*c* = 0.5, $CHCl_3$);

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), 5% IPA in hexane, 0.5 mL/min, rt, 210.8 nm); t_R = 11.4 (major), 17.2 (minor), e.r. = 91:9; (e.r. 94:6 when reaction carried out from (*S*)-3-phenyl-1-(triphenylstannyl)propyl 2,4,6-triisopropylbenzoate (e.r. of stannane 94:6))

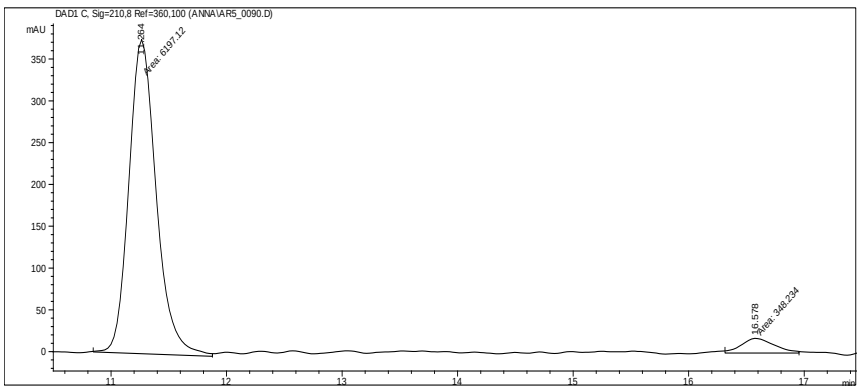






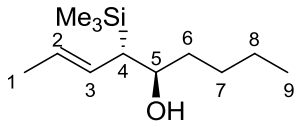


(from (*S*)-3-phenyl-1-(tributylstannyl)propyl 2,4,6-triisopropylbenzoate)



(from (*S*)-3-phenyl-1-(triphenylstannyl)propyl 2,4,6-triisopropylbenzoate)

(4*S*,5*R*,*E*)-4-(Trimethylsilyl)non-2-en-5-ol 10e



Prepared according to the general method from (*S*)-tributylstannyl)ethyl 2,4,6-triisopropylbenzoate (283 mg, 0.50 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), boronic ester **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and pentanal (110 µl, 1.0 mmol). The crude product was purified by flash column chromatography (neutralised silica, EtOAc/petroleum ether 5:95) to give the *alcohol* (69 mg, 64 %) as a colourless oil.

R_f = 0.38 (EtOAc/Petroleum Ether 1:9);

^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 128.0 (CH), 126.3 (CH), 71.7 (CH), 40.9 (CH), 36.8 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 18.2 (CH_3), 14.1 (CH_3), -1.8 (CH_3);

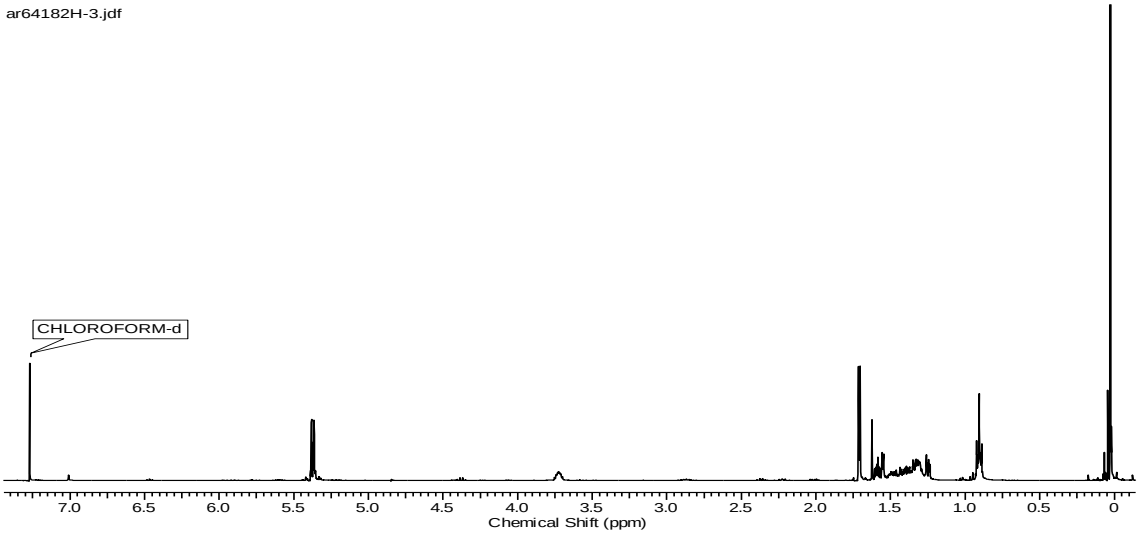
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 5.43 - 5.31 (2H, m, H2, H3), 3.77 - 3.69 (1H, m, H5), 1.71 (3H, d, *J* = 4.6 Hz, H1), 1.62 - 1.56 (1H, m, H4), 1.55 (1H, d, *J* = 4.0 Hz, OH), 1.52 - 1.27 (6H, m, H6, H7, H8), 0.91 (3H, t, *J* = 7.0 Hz, H9), 0.03 (9 H, s, $SiMe_3$);

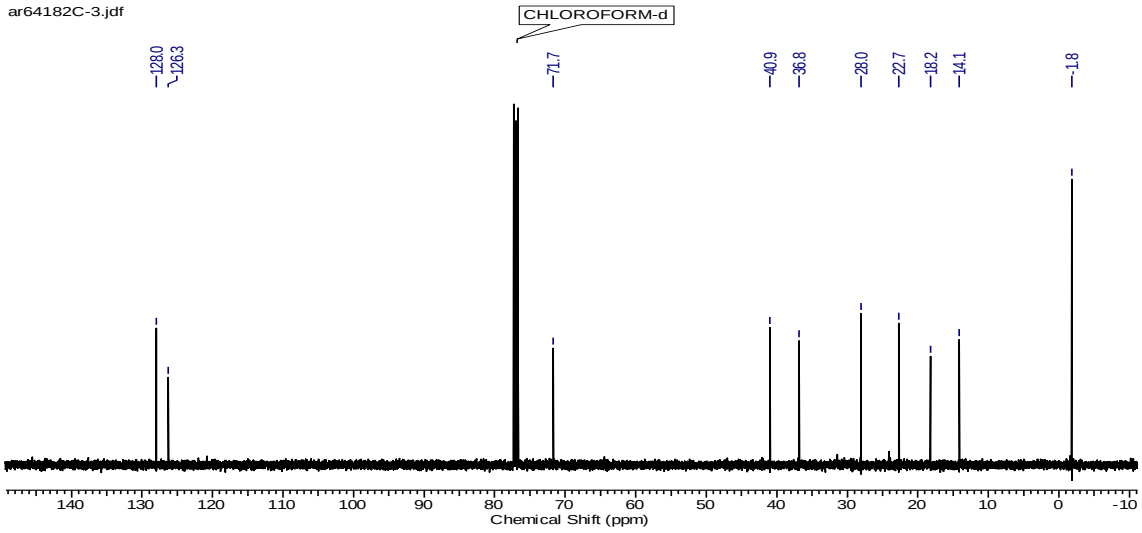
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3449, 2957, 2930, 2859, 1455, 1379, 1245, 974, 834;

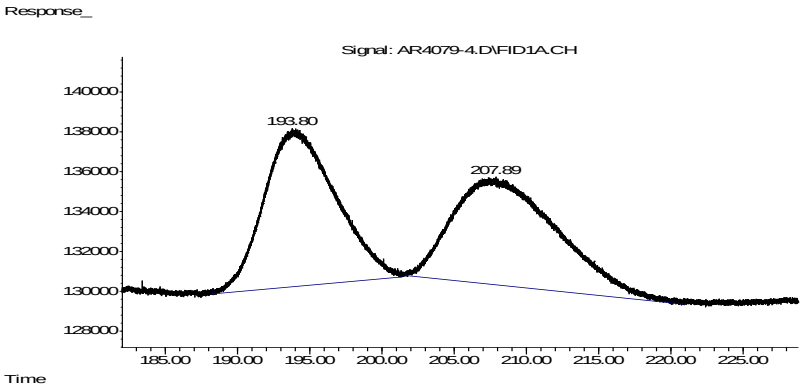
HRMS (ESI): calc. for $C_{12}H_{26}OSiNa$: m/z = 237.1645, found: m/z = 237.1650;

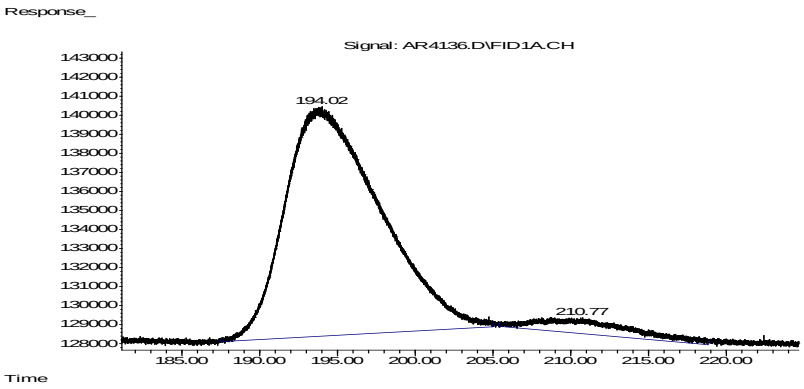
$[\alpha]_D^{23}$ = + 4 (*c* = 1.00, $CHCl_3$);

Chiral GC: (Astec CHIRALDEX™ G-TA column, 30 m × 0.25 mm × 0.12 µm), 70 °C for 240 min then 5 °C/min to 180 °C, hold 10 min, 25 psi, split 50:1. t_R = 194 minutes (major), 208 minutes (minor), e.r. = 91:9;

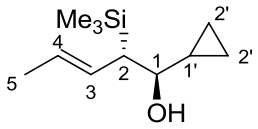








(1*R*,2*S*,*E*)-1-Cyclopropyl-2-(trimethylsilyl)pent-3-en-1-ol 10f



Prepared according to the general method from (*S*)-tributylstannyl)ethyl 2,4,6-triisopropylbenzoate (283 mg, 0.5 mmol), *n*BuLi (1.6 M in hexanes, 0.34 mL, 0.55 mmol), boronic ester **6** (1 M in diethyl ether, 0.65 mL, 0.65 mmol) and cyclopropanecarboxaldehyde (75 µl, 1.0 mmol). The crude product was purified by flash column chromatography (neutralised silica, EtOAc/petroleum ether 5:95) to give the *alcohol* (63 mg, 64 %) as a colourless oil.

R_f = 0.33 (EtOAc/petroleum ether 1:9)

^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 128.3 (CH), 125.9 (CH), 77.1 (CH), 41.6 (CH), 18.2 (CH_3), 17.6 (CH), 3.9 (CH_2), 3.2 (CH_2), -1.9 (CH_3);

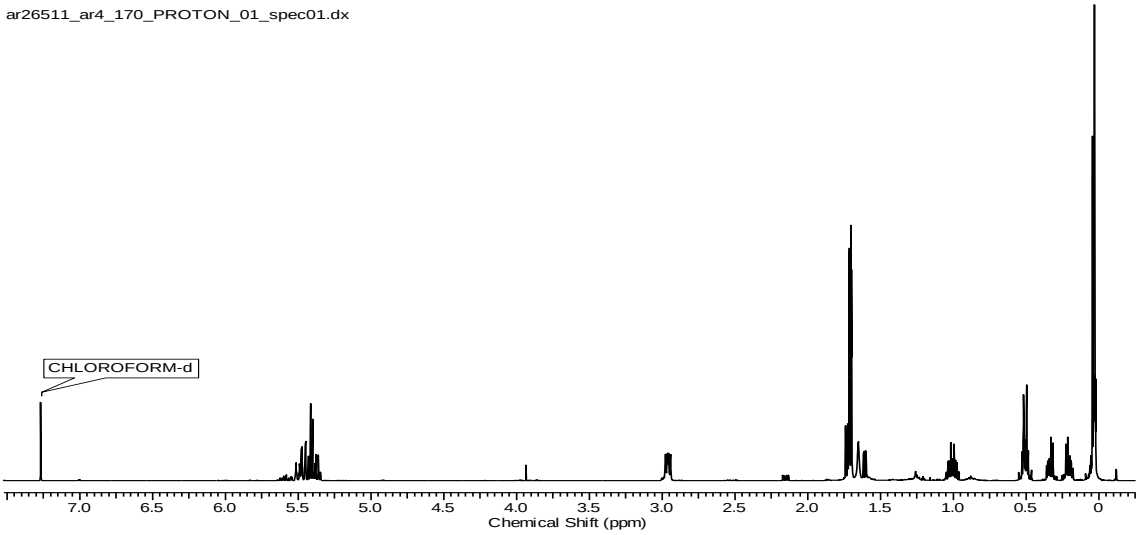
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 5.53 - 5.33 (2H, m, H3, H4), 2.96 (1H, dd, *J* = 8.4, 5.6 Hz, H1), 1.74-1.71 (1H, m, H2), 1.71 (3H, dd, *J* = 5.9, 1.0 Hz, H5), 1.01 (1H, dtt, *J* = 8.4, 8.2, 5.0 Hz, H1'), 0.54 - 0.48 (2H, m, two of H2'), 0.37 - 0.31 (1H, m, one of H2'), 0.24 - 0.17 (1H, m, one of H2'), 0.03 (9H, s, $SiMe_3$);

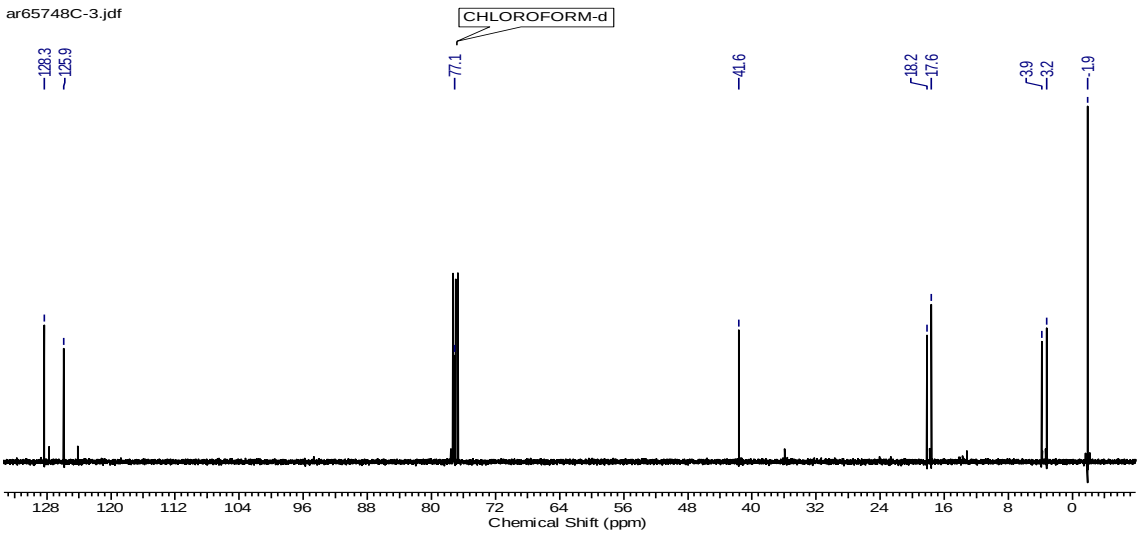
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3454, 2956, 2857, 1404, 1245, 1026, 971, 833;

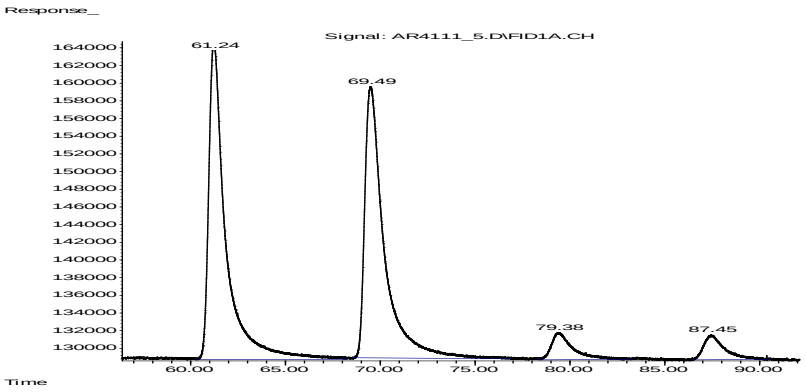
HRMS (ESI): calc. for $C_{11}H_{22}OSiNa$: m/z = 221.1332, found: m/z = 221.1336;

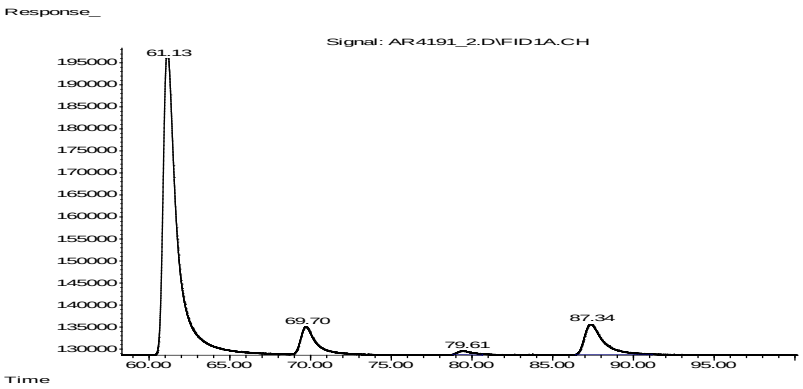
$[\alpha]_D^{23}$ = + 16 (*c* = 0.19, $CHCl_3$);

Chiral GC: (Supelco Beta Dex™ column, ≈29 m × 0.25 mm × 0.12 μm), 80 °C for 100 min then 10 °C/min to 180 °C hold for 5.0 min. t_R = 61.1 minutes (major), 69.7 minutes (minor), e. r. = 91:9;







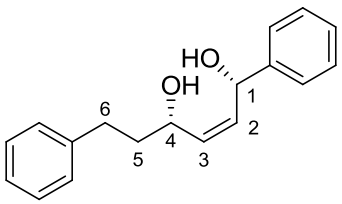


5. 1,4-diols

General procedure (syn-*Z*)

Ligand A (2.9 mg, 4.0 µmol) was dissolved in toluene (0.05 ml) and $VO(OiPr)_3$ (0.47 µl, 2.0 µmol) added. The mixture was stirred at room temperature for 8 hours before cumene hydroperoxide (44 µl, 0.30 mmol) and the respective homoallylic alcohol (0.2 mmol) were added. The reaction was stirred until complete by TLC, quenched with aqueous sodium thiosulphate (saturated., 1 ml) and the layers separated. The aqueous layer was extracted with Et_2O (3 × 20 ml), organic extracts combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The crude epoxide was dissolved in methanol (2 ml), cooled to 0 °C and glacial AcOH added (0.1 ml). The reaction was stirred at this temperature for 16 h, quenched with aqueous $NaHCO_3$ (saturated, 2 ml). The layers were separated, the aqueous layer extracted with EtOAc (3 × 20 ml). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography.

(1*S*,4*S*,*Z*)-1,6-Diphenylhex-2-ene-1,4-diol 26b



Prepared according to the general method from (5*R*,6*S*,*E*)-10-phenyl-6-(trimethylsilyl)dec-7-en-5-ol (65mg, 0.2 mmol). The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether 4:6) to give the *1,4-diol* (36mg, 67 %) as a colourless oil.

R_f = 0.11 (EtOAc/petroleum ether 4:6);

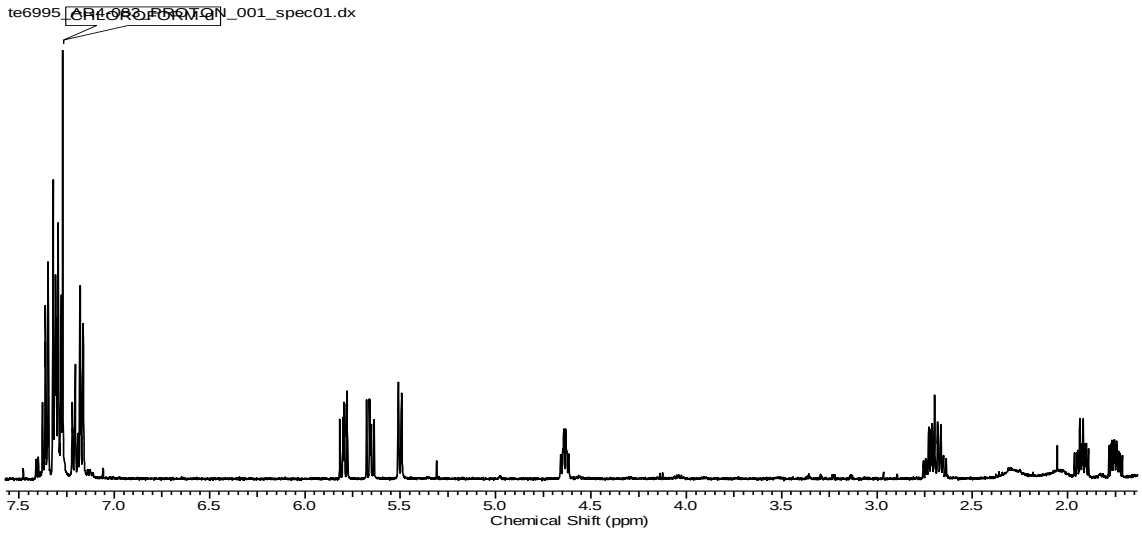
^{13}C NMR: (126 MHz, $CDCl_3$) δ ppm 143.0 (C), 141.5 (C), 134.4 (CH), 134.0 (CH), 128.7 (CH), 128.4 (2 x CH), 127.8 (CH), 126.1 (CH), 125.9 (CH), 70.3 (CH), 67.1 (CH), 38.7 (CH_2), 31.5 (CH_2);

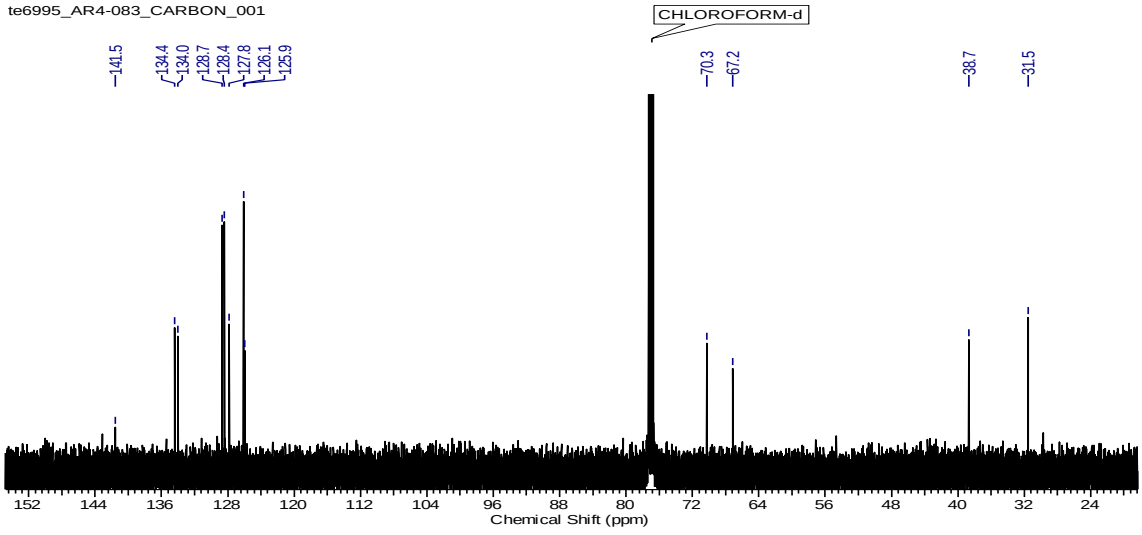
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.42 - 7.28 (5H, m, ArH), 7.25 - 7.08 (5H, m, ArH), 5.78 (1H, ddd, *J* = 11.1, 8.3, 1.1 Hz, H3), 5.64 (1H, ddd, *J* = 11.1, 8.4, 1.1 Hz, H2), 5.49 (1H, d, *J* = 8.4 Hz, H1), 4.68 - 4.60 (1H, m, H4), 2.77 - 2.60 (2H, m, H6), 1.94 (1H, dddd, *J*=13.7, 9.0, 7.7, 6.1 Hz, H5), 1.75 (1H, dddd, *J*=13.7, 9.4, 6.9, 5.4 Hz, H5);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 3350, 3063, 3028, 2927, 1648, 1603, 1495, 1454, 1031;

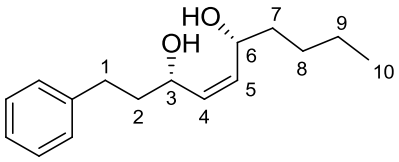
HRMS (ESI): calc. for $C_{18}H_{20}O_2SiNa$: m/z = 291.1356, found: m/z = 291.1363;

$[\alpha]_D^{24}$ = + 140 (*c* = 0.50, $CHCl_3$);





(3*S*,6*R*,*Z*)-1-Phenyldec-4-ene-3,6-diol 26c



Prepared according to the general method from (5*R*,6*S*,*E*)-10-phenyl-6-(trimethylsilyl)dec-7-en-5-ol (61 mg, 0.2 mmol), The crude product was purified by flash column chromatography (silica, EtOAc/Petroleum ether 4:6) to give the *1,4-diol* (34 mg, 69 %) as a colourless oil.

R_f = 0.16 (EtOAc/petroleum ether 4:6);

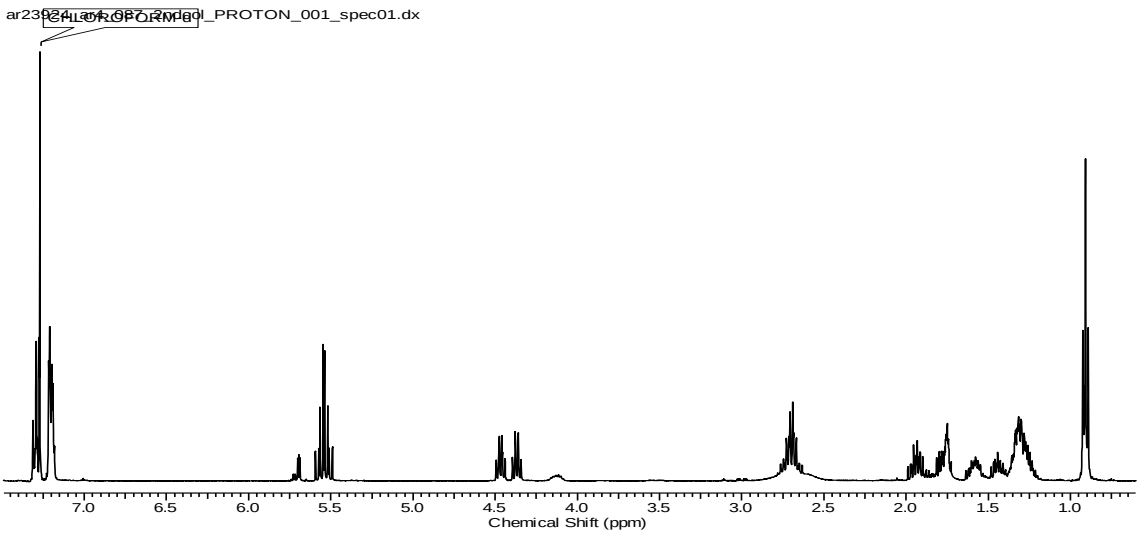
^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 141.6 (C), 134.9 (CH), 134.5 (CH), 128.3 (2 x CH), 125.9 (CH), 67.5 (CH), 66.8 (CH), 38.7 (CH_2), 37.0 (CH_2), 31.6 (CH_2), 27.5 (CH_2), 22.6 (CH_2), 14.0 (CH_3);

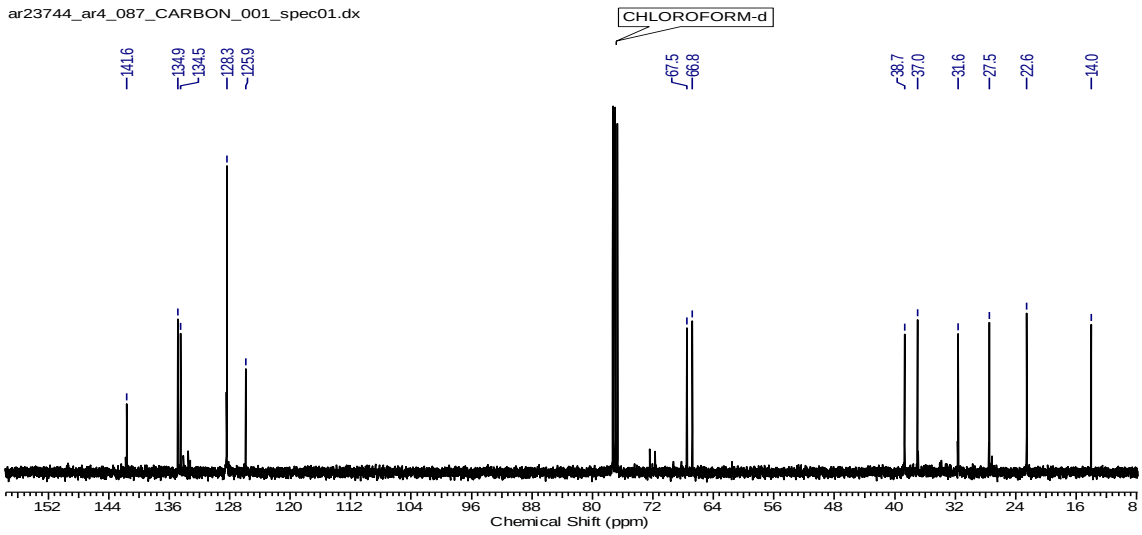
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.33 - 7.27 (2H, m, ArH), 7.23 - 7.16 (3H, m, ArH), 5.60 - 5.48 (2H, m, H4, H5), 4.47 (1H, ddd, *J* = 7.5, 7.4, 5.7 Hz, H3), 4.37 (1H, q, *J* = 6.9 Hz, H6), 2.78 - 2.62 (2H, m, H1), 1.94 (1H, dddd, *J* = 13.6, 9.2, 7.4, 6.2 Hz, one of H2), 1.77 (1H, dddd, *J* = 13.6, 9.5, 6.7, 5.6 Hz, one of H2), 1.61 - 1.54 (1H, m, one of H7), 1.49 - 1.39 (1H, m, one of H7), 1.39 - 1.20 (4H, m, H8, H9), 0.91 (3H, t, *J* = 7.0 Hz, H10);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 3332, 2929, 2859, 1496, 1455, 1054, 1030, 1005;

HRMS (ESI): calc. for C16H24O_2SiNa: m/z = 271.1669, found: m/z = 271.1673;

$[\alpha]_D^{24}$ = – 60 (*c* = 0.50, $CHCl_3$);

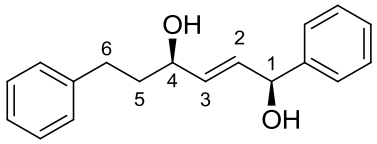




General procedure (Syn-*E*)

The respective allyl silane (0.2 mmol) was dissolved in dichloromethane (3 mL) and cooled to –20 °C. Sodium hydrogen carbonate (67 mg, 0.8 mmol) and *m*CPBA (≤77 % (Aldrich), 90 mg, 0.4 mmol) were added and the mixture was stirred at –20 °C for 2.5 hours. Then the excess *m*CPBA was destroyed by adding sodium thiosulfate (1 M in water, 0.4 ml, 0.4 mmol). The mixture was allowed to warm to 0 °C over 0.5 hours, stirred for another 1.5 h at 0 °C and was finally extracted with diethyl ether (3 × 20 ml). The solvent was removed *in vacuo* and the crude epoxide was dissolved in methanol (2 mL), cooled to 0 °C and treated with glacial acetic acid (0.1 ml). This mixture was stirred overnight and then quenched with aqueous $NaHCO_3$ (saturated, 10 ml). The diol was extracted with ethyl acetate (3 × 20 ml), dried (Na_2SO_4), filtered and the solvent was removed *in vacuo*. The crude material was purified by flash column chromatography (EtOAc/petroleum ether) to give the *diol* as a colourless oil (as a mixture of diastereomers, major product characterised).

(1*S*,4*R*,*E*)-1,6-Diphenylhex-2-ene-1,4-diol 11c



Prepared according to the general method from (1*R*,2*S*,*E*)-1,6-diphenyl-2-(trimethylsilyl)hex-3-en-1-ol (47 mg, 0.15 mmol), The crude product was purified by flash column chromatography (EtOAc/petroleum ether 1:1) to give the *1,4-diol* (29 mg, 73 %) as a colourless oil (as a mixture of diastereomers; syn-*E*:syn-*Z* ≈ 3:1; major product characterised).

R_f = 0.14 (EtOAc/petroleum ether 6:4);

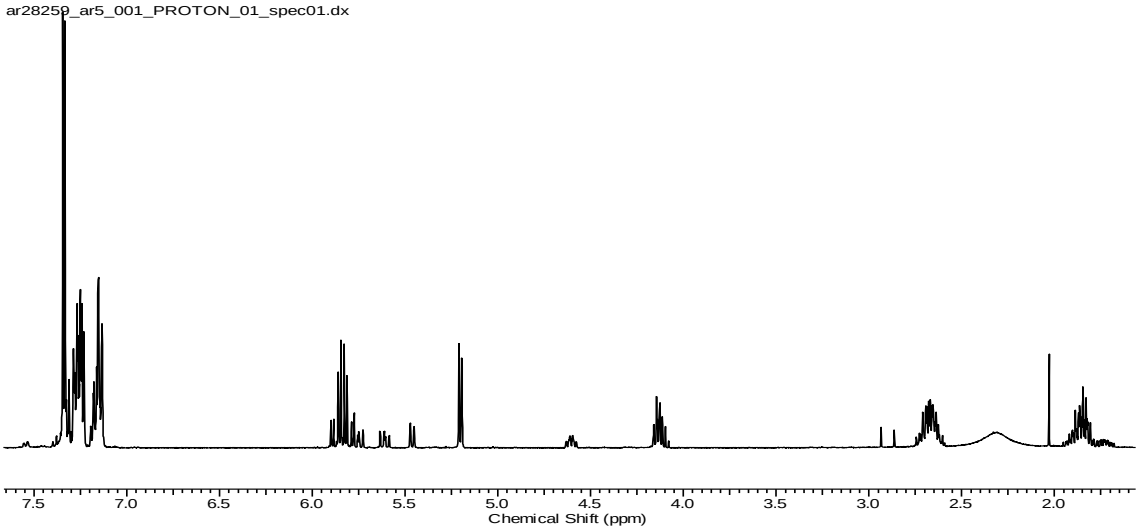
^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 142.7 (C), 141.7 (C), 133.8 (CH), 133.1 (CH), 128.6 (CH), 128.4 (CH), 128.4 (CH), 127.8 (CH), 126.2 (CH), 125.9 (CH), 74.5 (CH), 71.5 (CH), 38.6 (CH_2), 31.6 (CH_2);

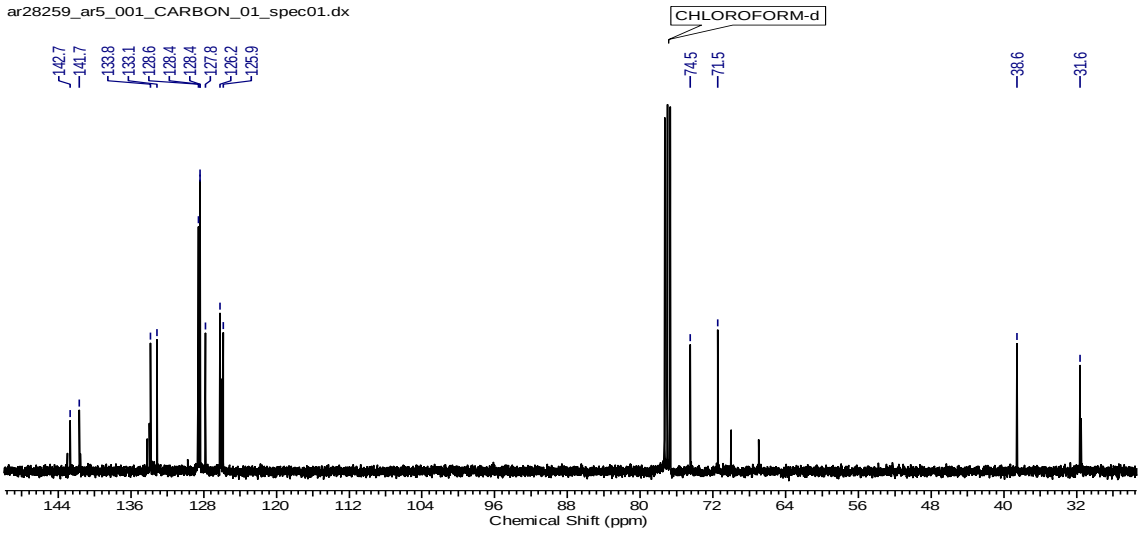
^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.16 - 7.42 (10H, m, ArH), 5.90 (1H, dd, *J* = 15.5, 5.7 Hz, H2), 5.84 (1H, dd, *J* = 15.5, 5.7 Hz, H3), 5.24 (1H, d, *J* = 5.7 Hz, H1), 4.17 (1H, dt, *J* = 7.3, 5.7 Hz, H4), 2.79 - 2.64 (2H, m, H6), 1.96 - 1.83 (2H, m, H5);

IR ($\tilde{\nu}$ /cm^{-1}, neat): 3321, 2925, 2860, 1603, 1495, 1453, 1286, 1029, 970;

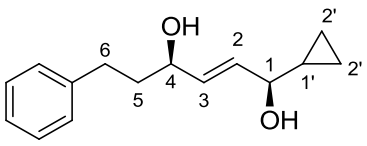
HRMS (ESI): calc. for $C_{18}H_{20}O_2Na$: m/z = 291.1356, found: m/z = 291.1366;

[α]$_D^{24}$ = + 17 (*c* = 1.00, $CHCl_3$);





(1*R*,4*R*,*E*)-1-Cyclopropyl-6-phenylhex-2-ene-1,4-diol 11d



Prepared according to the general method from (1*R*,2*S*,*E*)-1-cyclopropyl-6-phenyl-2-(trimethylsilyl)hex-3-en-1-ol (58 mg, 0.2 mmol), The crude product was purified by flash column chromatography (EtOAc/petroleum ether 4:6) to give the *1,4-diol* (30 mg, 93 %) as a colourless oil (as a mixture of diastereomers; *syn-E*:*syn-Z* ≈ 4:1; somewhat separable, major product characterised).

R_f = 0.10 (EtOAc/Petroleum Ether 1:1);

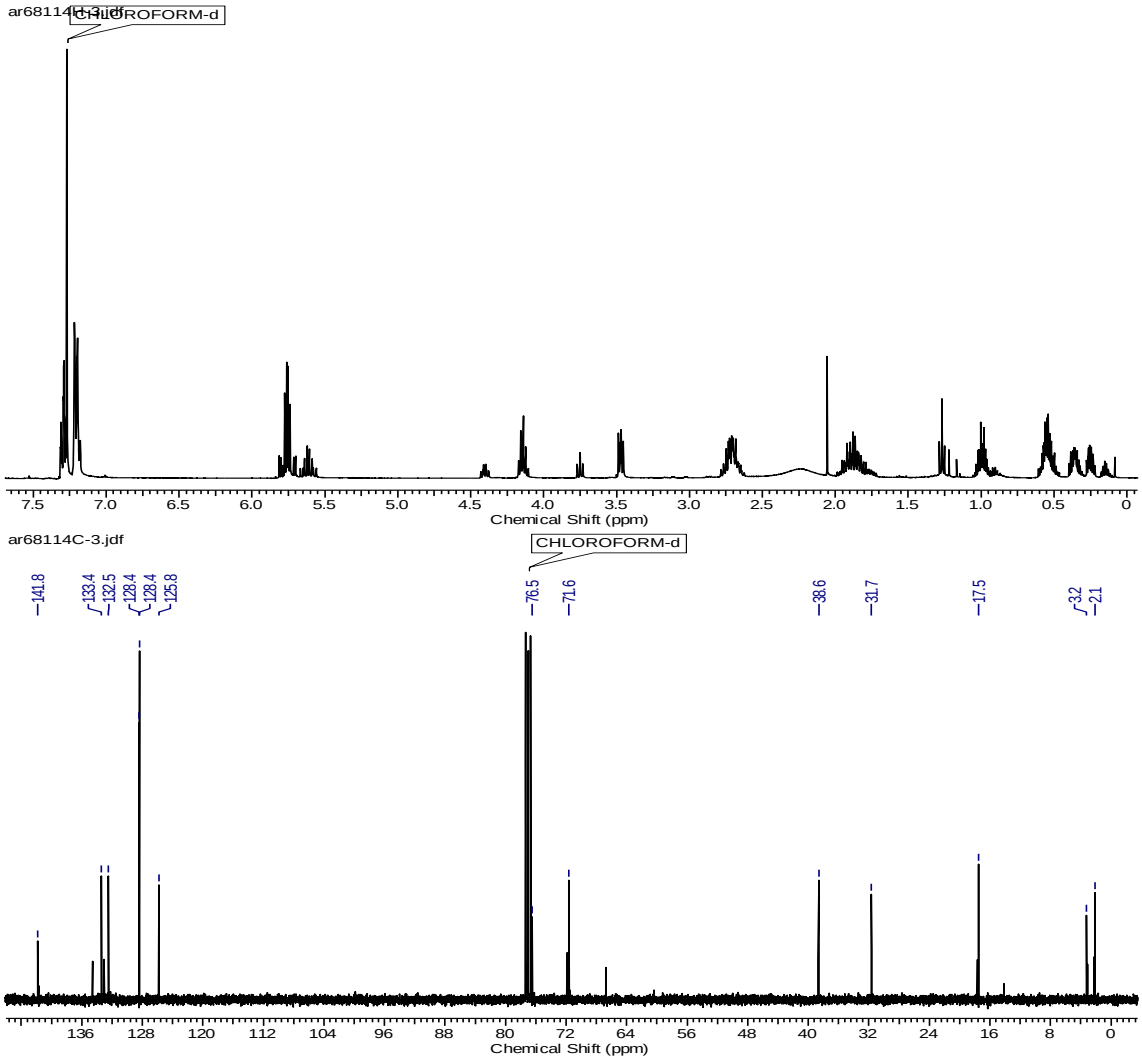
^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 141.8 (C), 133.4 (CH), 132.5 (CH), 128.4 (CH), 128.4 (CH), 125.8 (CH), 76.5 (CH), 71.6 (CH), 38.6 (CH_2), 31.7 (CH_2), 17.5 (CH), 3.2 (CH_2), 2.1 (CH_2);

^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.33 - 7.25 (2H, m, ArH), 7.24 - 7.16 (3H, m, ArH), 5.79 (1H, dd, *J* = 15.7, 5.2 Hz, H2), 5.73 (1H, dd, *J* = 15.7, 5.8 Hz, H3), 4.18 - 4.09 (1H, m, H4), 3.47 (1H, dd, *J* = 8.2, 5.2 Hz, H1), 2.80 - 2.62 (2H, m, H6), 1.78 - 2.00 (2H, m, H5), 1.06 - 0.93 (1H, m, H1'), 0.62 - 0.46 (2H, m, H2'), 0.41 - 0.30 (1H, m, H2'), 0.28 - 0.21 (1H, m, H2');

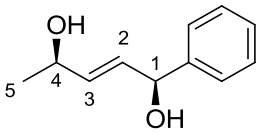
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3334, 2925, 2861, 1719, 1496, 1454, 1261, 1022, 1002, 970;

HRMS (ESI): calc. for $C_{15}H_{20}O_2Na$: m/z = 255.1356, found: m/z = 255.1365;

$[\alpha]_D^{24}$ = + 2 (*c* = 0.50, $CHCl_3$);



(1*S*,4*R*,*E*)-1-Phenylpent-2-ene-1,4-diol 11a



Prepared according to the general method (1*R*,2*S*,*E*)-1-phenyl-2-(trimethylsilyl)pent-3-en-1-ol (47 mg, 0.20 mmol), The crude product was purified by flash column chromatography (EtOAc/petroleum ether 1:1) to give the 1,4-diol[6]**Error! Bookmark not defined.** (27 mg, 75 %) as colourless oil (as a mixture of diastereomers syn-*E*:syn-*Z* ≈ 3:1; major product characterised).

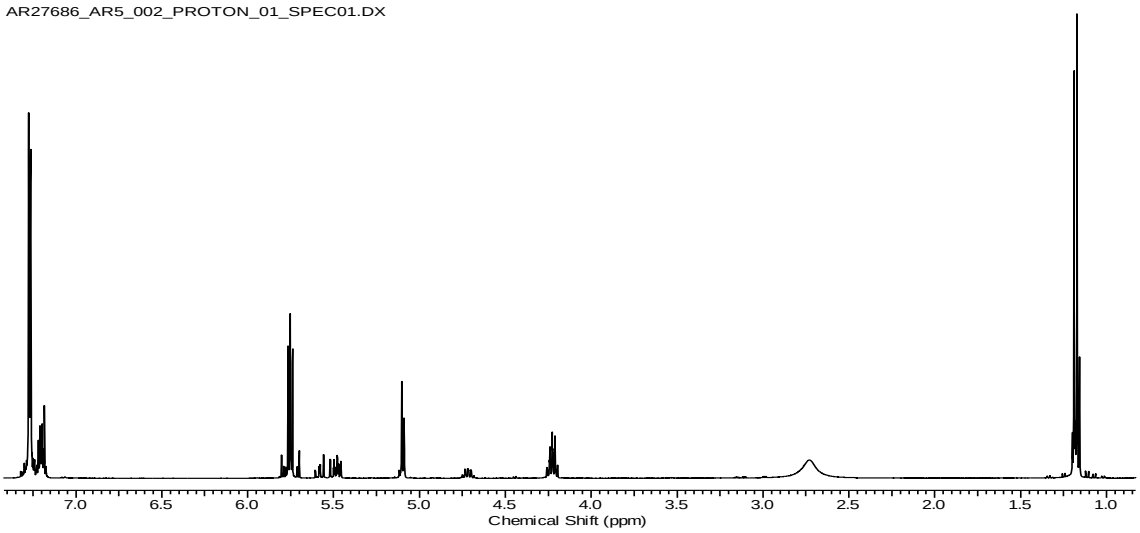
R_f = 0.10 (EtOAc/petroleum ether 6:4);

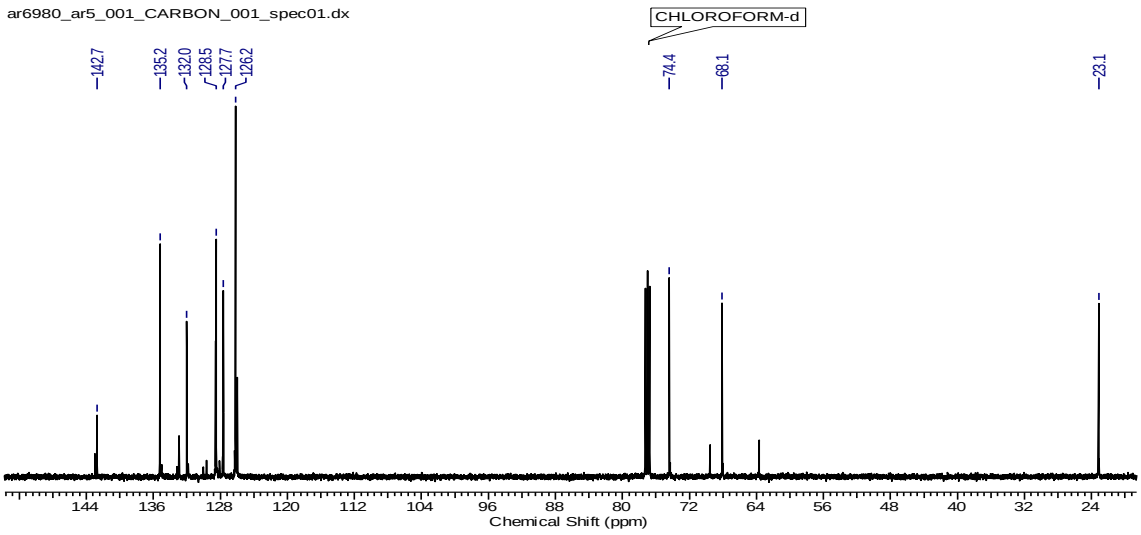
^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 142.7 (C) 135.2 (CH) 132.0 (CH) 128.5 (CH) 127.7 (CH) 126.2 (CH) 74.4 (CH) 68.1 (CH) 23.1 (CH_3);

^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 7.30 - 7.23 (5H, m, ArH) 5.81 - 5.69 (2H, m, H2, H3) 5.10 (1H, d, *J* = 5.5 Hz, H1) 4.26 - 4.19 (1H, m, H4) 1.18 (3H, d, *J* = 6.4 Hz, H5);

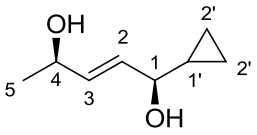
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3300, 2970, 2878, 1492, 1451, 1372, 1064;

$[\alpha]_D^{22}$ = + 20 (*c* = 1.00, $CHCl_3$);





(1*R*,4*R*,*E*)-1-Cyclopropylpent-2-ene-1,4-diol 11b



Prepared according to the general method from (1*R*,2*S*,*E*)-1-cyclopropyl-2-(trimethylsilyl)pent-3-en-1-ol (40 mg, 0.20 mmol), The crude product was purified by flash column chromatography (EtOAc/petroleum ether 1:1) to give the *1,4-diol* (20 mg, 73 %) as a colourless oil (as a mixture of diastereomers; syn-*E*:syn-*Z* ≈ 2.9:1; major product characterised).

R_f = 0.5 (EtOAc/petroleum ether 1:1);

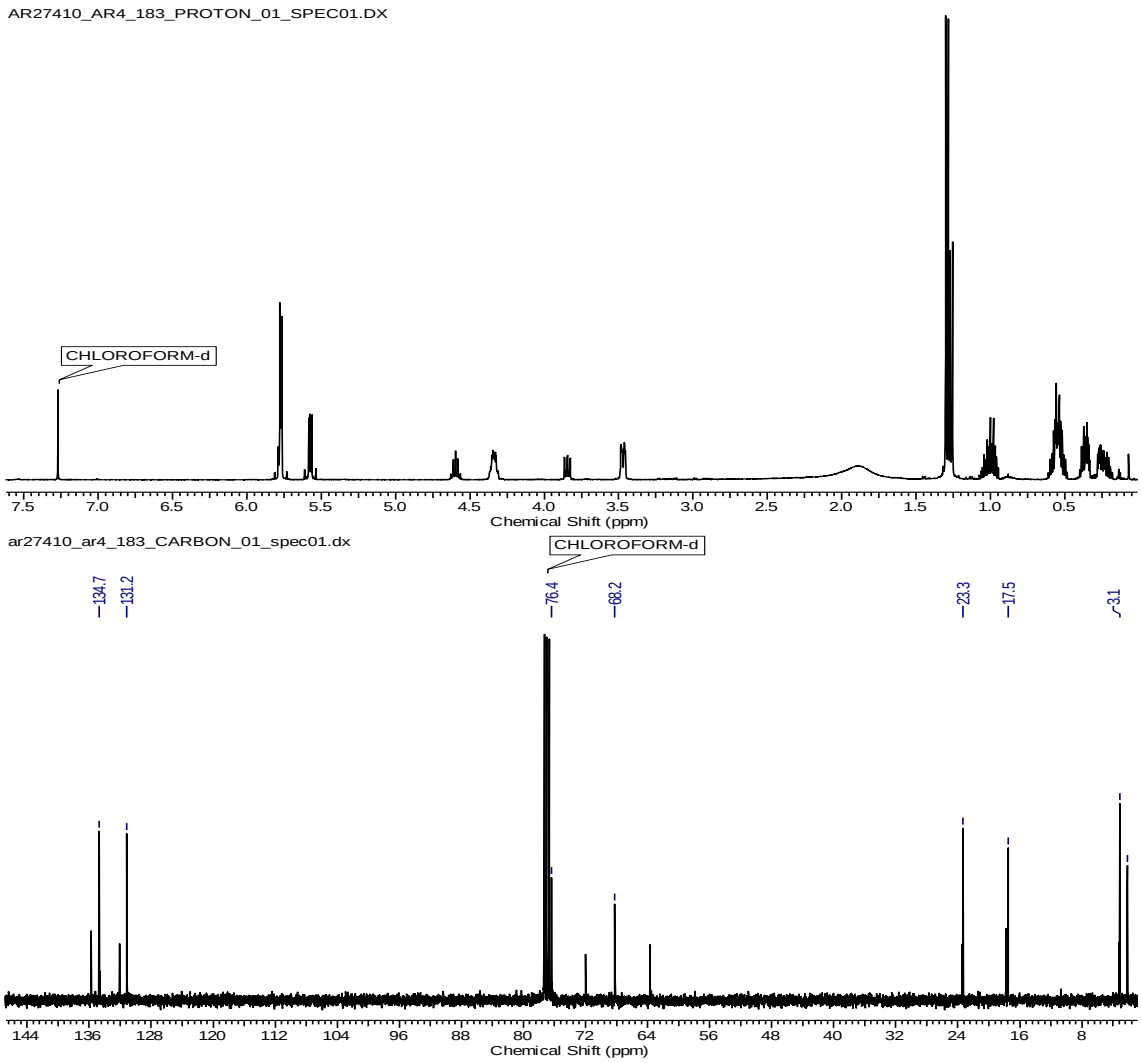
^{13}C NMR: (101 MHz, $CDCl_3$) δ ppm 134.7 (CH), 131.2 (CH), 76.4 (CH), 68.2 (CH), 23.3 (CH), 17.5 (CH_3), 3.1 (CH_2), 2.1 (CH_2);

^{1}H NMR: (400 MHz, $CHCl_3$) δ ppm 5.82 - 5.72 (2H, m, H2, H3), 4.39 - 4.28 (1H, m, H4), 3.51 - 3.43 (1H, m, H1), 1.90 (2H, br. s., OH), 1.29 (3H, d, *J* = 6.4 Hz, H5), 1.00 (1H, dtt, *J* = 16.4, 8.2, 4.9, Hz, H1'), 0.62 - 0.47 (2 H, m, two of H2'), 0.41 - 0.32 (1 H, m, one of H2'), 0.29 - 0.21 (1 H, m, one of H2');

IR ($\tilde{\nu}$ /cm^{-1}, neat): 3321, 2972, 2873, 1662, 1413, 1288, 1115, 1061, 1021;

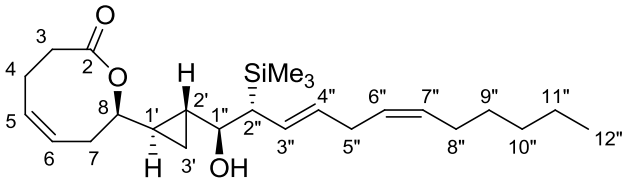
HRMS (ESI): calc. for $C_8H_{14}O_2Na$: m/z = 165.0886, found: m/z = 165.0890;

$[\alpha]_D^{24}$ = + 22 (*c* = 1.00, $CHCl_3$);



6. *Solandelactone F*

(*R*,*Z*)-8-((1*R*,2*R*)-2-((1*S*,2*R*,3*E*,6*Z*)-1-Hydroxy-2-(trimethylsilyl)dodeca-3,6-dienyl)cyclopropyl)-3,4,7,8-tetrahydro-2H-oxocin-2-one 8



(*R*,*Z*)-1-(Tributylstannyl)non-3-enyl 2,4,6-triisopropylbenzoate (131 mg, 0.2 mmol) was dissolved in diethyl ether (1 mL) and cooled to –78 °C. *n*BuLi (1.6 M in hexanes, 0.14 mL, 0.22 mmol) was added dropwise and the mixture was stirred at –78 °C for 1 hour. A solution of boronic ester **6** (1 M in diethyl ether, 0.26 mL, 0.26 mmol) was added dropwise and the mixture was stirred at −78 °C for 1 hour followed by warming to 23 °C over 30 minutes. Diethyl ether was then removed under vacuum and replaced with CH_2Cl_2 (1 ml), the mixture was then refluxed at 40 °C for 1 hour, before

being cooled to −20 °C. In a separate pot magnesium bromide was prepared by stirring Mg (7.3 mg, 0.3 mmol) and 1,2- dibromoethane (0.017 mL, 0.2 mmol) in 0.5 mL diethyl ether for 2 hours and this solution was then added to the reaction mixture at −20 °C. Aldehyde **3** (50 mg, 0.26 mmol) was added dropwise and the reaction stirred for 24 h. The reaction was quenched with a aqueous $NaHCO_3$ (saturated solution, 2 ml). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (petroleum ether/EtOAc 95:5) to yield the *allylsilane* as a colourless oil (42 mg, 50%).

$\boldsymbol{R_f}$ = 0.21 (EtOAc/Petroleum Ether 1:9);

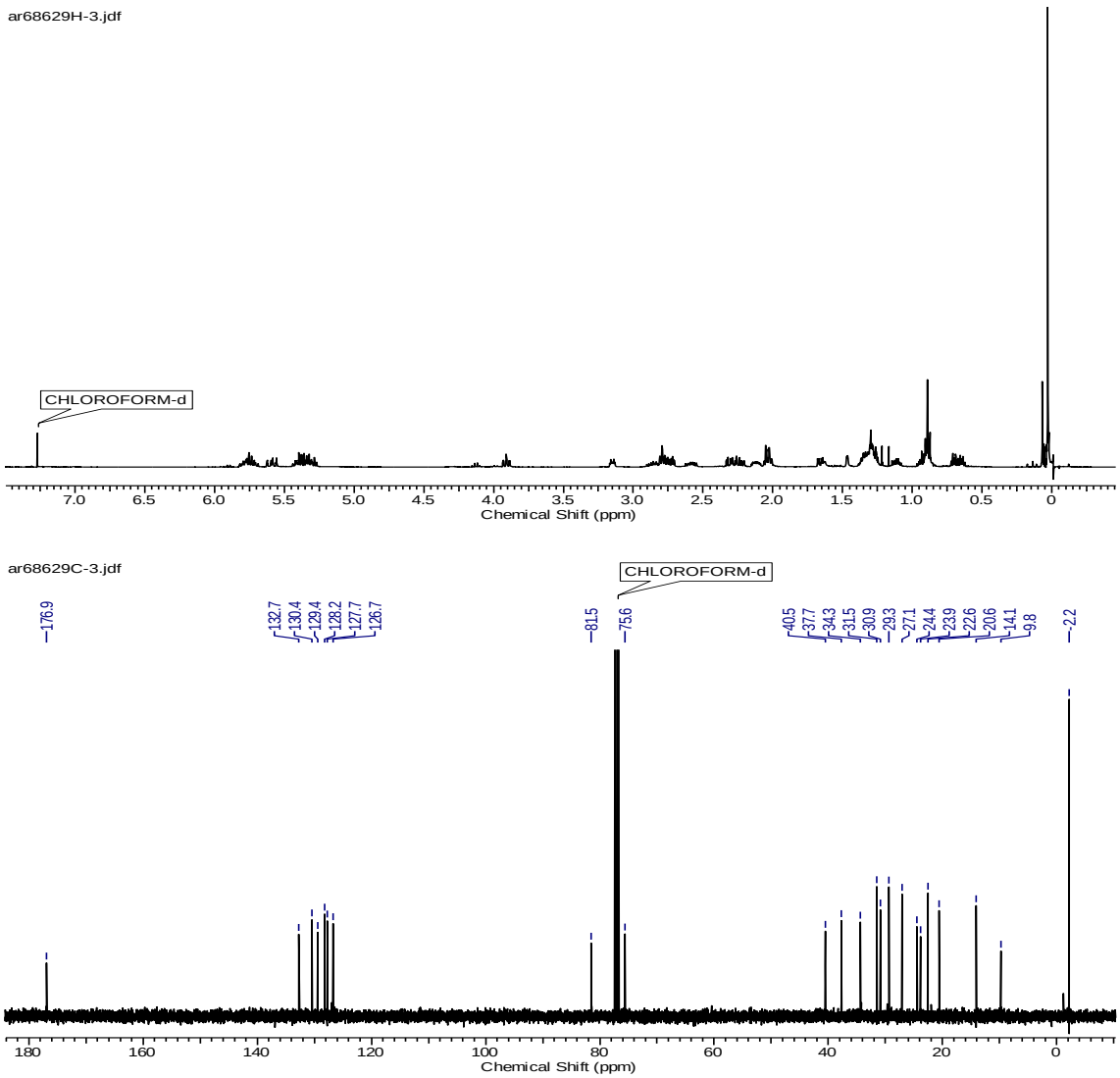
^{13}C NMR: ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.9 (C=O), 132.7 (CH), 130.4 (CH), 129.4 (CH), 128.2 (CH), 127.7 (CH), 126.7 (CH), 81.5 (CH), 75.6 (CH), 40.5 (CH), 37.7 (CH_2), 34.3 (CH_2), 31.5 (CH_2), 30.9 (CH_2), 29.3 (CH_2), 27.1 (CH_2), 24.4 (CH_2), 23.9 (CH), 22.6 (CH_2), 20.6 (CH), 14.1 (CH_3), 9.8 (CH_2), -2.2 (CH_3);

^{1}H NMR: ^{1}H NMR (400 MHz, $CHCl_3$) δ ppm 5.84 - 5.68 (2H, m, H5 & H6), 5.59 (1H, ddt, *J* = 15.3, 10.5, 1.4 Hz, H3”), 5.46 - 5.25 (3H, m, H4”, H6” & H7”), 3.91 (1H, ddd, *J* = 10.3, 8.8, 1.6 Hz, H8), 3.15 (1H, dt, *J* = 8.3, 3.2 Hz, H1”), 2.91 - 2.82 (1H, m, one of H4), 2.79 (2H, t, *J* = 6.7 Hz, H5”), 2.74 (1H, ddd, *J* = 13.2, 5.8, 2.9 Hz, one of H3), 2.63 - 2.54 (1H, m, one of H7), 2.30 (1H, ddd, *J* = 13.2, 11.7, 4.7 Hz, one of H3), 2.23 (1H, ddd, *J* = 14.0, 8.0, 2.0 Hz, one of H7), 2.17 - 2.08 (1H, m, one of H4), 2.04 (2H, q, *J* = 7.0 Hz, H8”), 1.66 (1H, dd, *J* = 10.5, 3.2 Hz, H2”), 1.40 - 1.22 (6H, m, H9”-H11”), 1.12 (1H, tt, *J* = 8.3, 4.7 Hz, H2’), 0.97 - 0.92 (1H, m, H1’), 0.89 (3H, t, *J* = 6.9 Hz, H12”), 0.70 (1H, ddd, *J* = 8.3, 5.2, 4.7 Hz, one of H3’), 0.65 (1H, dt, *J* = 8.3, 5.2 Hz, one of H3’), 0.03 (9H, s, $SiMe_3$);

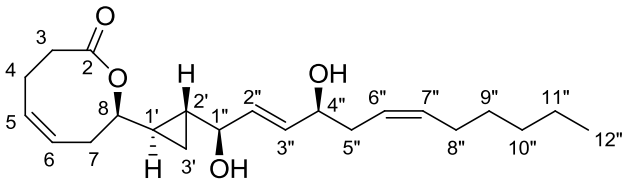
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3502, 2955, 2929, 2857, 1734, 1332, 1244, 1213, 1052;

HRMS (ESI): calc. for $C_{25}H_{42}O_3SiNa$: m/z = 441.4795, found: m/z = 441.2786;

$[\alpha]_D^{24}$ = + 21 (*c* = 1.00, $CHCl_3$);



Solandelactone F



Allyl silane **8** (24 mg, 0.06 mmol) was dissolved in dichloromethane (1 mL) and cooled to –20 °C. Sodium hydrogen carbonate (20 mg, 0.24 mmol) and *m*CPBA (≤77 % (Aldrich), 13 mg, 0.06 mmol) were added and the mixture was stirred at –20 °C for 5 hours. Then the excess *m*CPBA was destroyed by adding sodium thiosulfate (1 M in water, 0.1 mL, 0.1 mmol). The mixture was allowed to warm to 0 °C over 0.5 hours, stirred for another 1.5 h at 0 °C and was finally extracted with diethyl ether (3 × 20 ml). The solvent was removed *in vacuo* and the crude epoxide was dissolved in methanol (1 mL), cooled to 0 °C and treated with glacial acetic acid (0.05 mL). This mixture was stirred overnight and then quenched with a sodium bicarbonate solution (saturated in water, 10 mL).

The diol was extracted with ethyl acetate (3 × 20 ml), dried (sodium sulfate), filtered and the solvent was removed *in vacuo*. The crude material was purified by flash column chromatography (silica gel, 50 % ethyl acetate in Petroleum Ether) to give the solandelactone F[7] as a colourless oil (5.9 mg, 30% (51% brsm)).

R_f = 0.18 (EtOAc/Petroleum Ether 6:4);

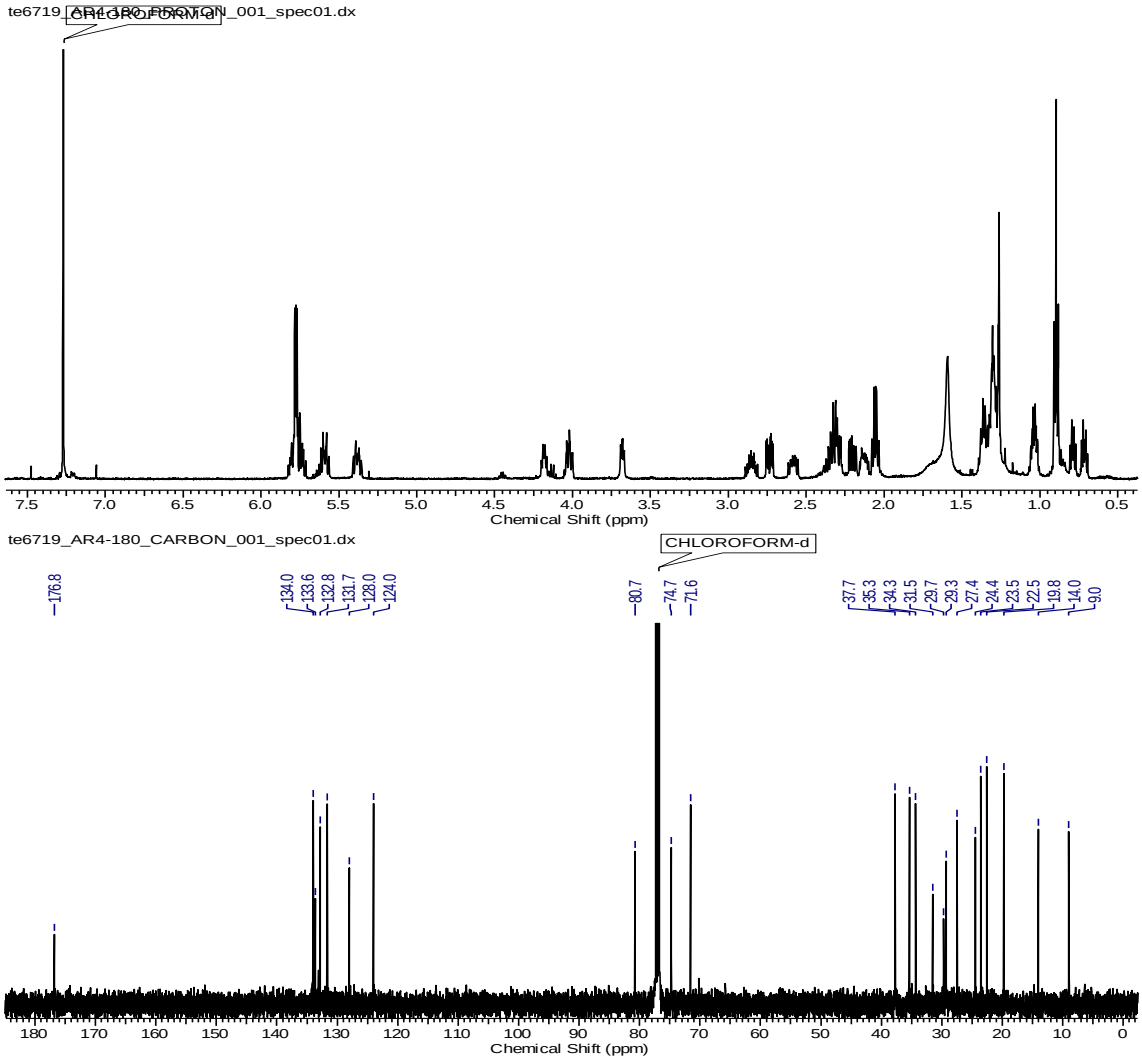
^{13}C NMR: ^{13}C NMR (126 MHz, $CDCl_3$) ppm 176.8 (C=O), 134.0 (CH), 133.6 (CH), 132.8 (CH), 131.7 (CH), 128.0 (CH), 124.0 (CH), 80.7 (CH), 74.7 (CH), 71.6 (CH), 37.7 (CH_2), 35.3 (CH_2), 34.3 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 27.4 (CH_2), 24.4 (CH_2), 23.5 (CH), 22.5 (CH_2), 19.8 (CH), 14.0 (CH_3), 9.0 (CH_2);

^{1}H NMR: ^{1}H NMR (500 MHz, $CHCl_3$) δ ppm 5.84 - 5.70 (4H, m, H5, H6, H2”, H3”), 5.64 - 5.55 (1H, m, H7”), 5.42 - 5.34 (1H, m, H6”), 4.21 - 4.16 (1H, m, H4”), 4.02 (1H, ddd, *J* = 10.0, 8.1, 1.7 Hz, H8), 3.68 (1H, dd, *J* = 6.9, 5.1 Hz, H1”), 2.85 (1H, tdd, *J* = 12.2, 9.3, 5.7 Hz, H4), 2.73 (1H, ddd, *J* = 13.4, 5.8, 3.1 Hz, one of H3), 2.63 - 2.54 (1H, m, one of H7), 2.38 - 2.27 (3H, m one of H3, H5”), 2.20 (1H, ddd, *J* = 14.0, 8.0, 1.9 Hz, one of H7), 2.16 - 2.10 (1H, m, one of H4), 2.09 - 2.03 (2H, m, H8”), 1.24 - 1.40 (6 H, m, H9”-H11”), 1.07 - 1.00 (2H, m, H1’, H2’), 0.89 (3H, t, *J* = 7.0 Hz, H12”), 0.79 (1H, dt, *J* = 8.1, 5.2 Hz, H3’), 0.71 (1H, dt, *J* = 8.3, 5.2 Hz, H3’);

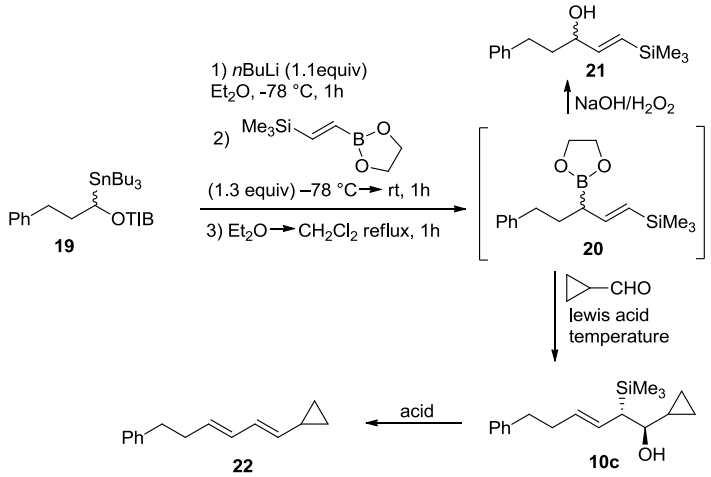
IR ($\tilde{\nu}$ /cm^{-1}, neat): 3367, 2926, 2856, 1746, 1332, 1214, 1054;

HRMS (ESI): calc. for $C_{22}H_{34}O_4Na$: m/z = 385.2349, found: m/z = 385.2357;

$[\alpha]_D^{22}$ = + 2 (*c* = 0.50, $CHCl_3$);



7. *Optimization of the allylboration reaction: full results*



Entry	Lewis acid (equiv)	T/ °C	Time/ h	Yield **21** (%)	Yield **22** (%)	Yield **10c** (%)
1	$MgBr_2$•Et_2O (1 equiv)	-20	18	-	75	-

2	$MgBr_2$•Et_2O (1 equiv)	-40	18	26	-	43
3	$MgBr_2$•Et_2O (1 equiv)	-40	36	28	-	58
4	$Sc(OTf)_3$ (0.5 equiv)	-40	18	7	44	41
5	$Sc(OTf)_3$ (0.2 equiv)	-40	42	16	-	45
6	BF_3•Et_2O (0.2 equiv)	-40	36	26	12	56
7	$Sc(OTf)_3$ (0.5 equiv)	-60	26	13	-	41
8	BF_3•Et_2O (1 equiv)	-60	18	14	34	38
9	BF_3•Et_2O (0.5 equiv)	-60	19	13	33	43
10	$MgBr_2$•Et_2O (2 equiv)	-60	19	46	9	30
11	$MgBr_2$•Et_2O (2 equiv)	-80	very little allylation after 4 days			
12	BF_3•Et_2O (1 equiv)	-80	mainly elimination product **22**			
13	$Sc(OTf)_3$ (0.2 equiv)	-80	mainly elimination product **22**			
14	**$MgBr_2$•Et_2O (1 equiv)**	**-30**	**24**	**-**	**12**	**75**
15	BF_3•Et_2O (0.2 equiv)	-30	17	20	12	63

Table 2. Optimization of the allylboration reaction

8. Model for selectivity in epoxidation using Yamamoto's catalyst

Placing our substrate into his transition state model (Figure 1, **TS6**), it is clear that there is a large steric clash between the ligand backbone and the R^2 substituent of the substrate and so will be disfavored. Rotation around the C-O bond would alleviate this steric interaction and epoxidation could ensue *via* the more 'boat-like' **TS7.**

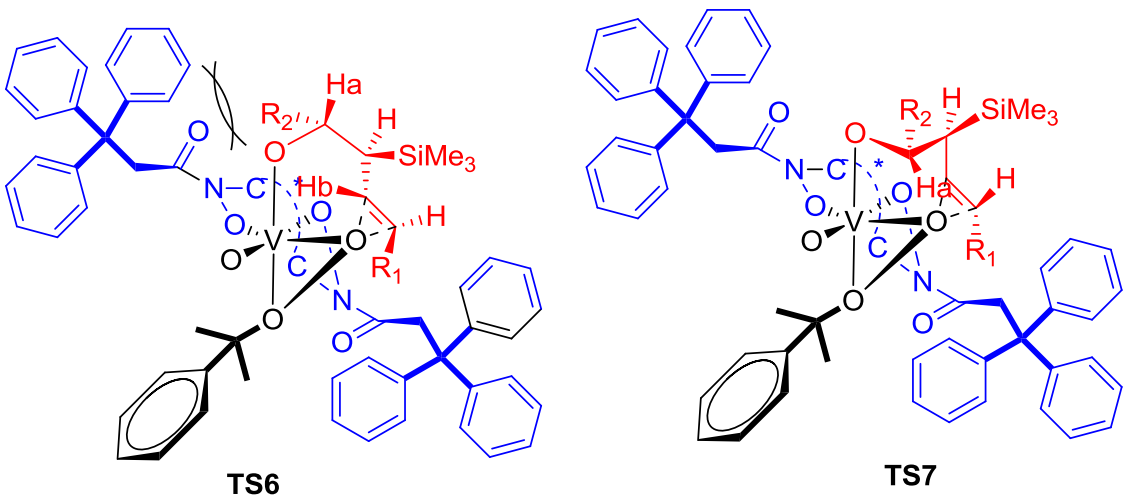


Figure 1 Model to account for selectivity in epoxidation using Yamamoto's catalyst

[1] Leonard, J.; Lygo, B.; Procter, G. *Advanced Practical Organic Chemistry*, Taylor & Francis, **1998**.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[3] Singleton, D. A.; Martinez, J. P. *Tetrahedron Lett.* **1991**, *32*, 7365–7368.

[4] Beak, P.; Baillargeon, M.; Carter, L. G. *J. Org. Chem.* **1978**, *43*, 4255-4256

[5] Prinz, P.; Lansky, A.; Haumann, T.; Boese, R.; Noltemeyer, M.; Knieriem, B.; de Meijere, A. *Angew. Chem.* **1997**, 1343−1346; *Angew. Chem. Int. Ed.* **1997**, *36*, 1289−1292

[6] Binanzer, M.; Fang, G.Y.; Aggarwal, V.K. *Angew. Chem. Int. Ed.* **2010**, *49*, 4264-4268

[7] a) White, J. D.; Martin, W. H. C.; Lincoln, C.; Yang, J. *Org. Lett.* **2007**, *9*, 3481-3483; b) White, J. D.; Lincoln, C.; Yang, J.; Martin, W. H. C.; Chan, D. B. *J. Org. Chem* **2008**, *73*, 4139-4150; c) Pietruszka, J.; Rieche, A. C. *Adv. Synth. Catal.* **2008**, *350*, 1407-1412.