Supporting Information for

Intramolecular Cyclopropanation of Unsaturated Terminal Epoxides and Chlorohydrins

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Full list of authors for references from main paper with 16 or more authors

[3a] Bueno, A. B.; Collado, I.; de Dios, A.; Dominguez, C.; Martin, J. A.; Martin, L. M.; Martinez-Grau, M. A.; Montero, C.; Pedregal, C.; Catlow, J.; Coffey, D. S.; Clay, M. P.; Dantzig, A. H.; Lindstrom, T.; Monn, J. A.; Jiang, H.; Schoepp, D. D.; Stratford, R. E.; Tabas, L. B.; Tizzano, J. P.; Wright, R. A.; Herin, M. F. *J. Med. Chem.* **2005**, *48*, 5305–5320.

[3b] McBriar, M. D.; Guzik, H.; Shapiro, S.; Paruchova, J.; Xu, R.; Palani, A.; Clader, J. W.; Cox, K.; Greenlee, W. J.; Hawes, B. E.; Kowalski, T. J.; O'Neill, K.; Spar, B. D.; Weig, B.; Weston, D. J.; Farley, C.; Cook, J.; *J. Med. Chem.* **2006**, *49*, 2294–2310.

General details

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon or nitrogen. THF and Et_2O were distilled from benzophenone ketyl; *t*-BuOMe, 2,2,6,6-tetramethylpiperidine (TMP) and 1,2-epoxy-5-hexene from CaH_2; all other reagents were used as received, unless stated otherwise. Column chromatography was carried out on silica gel (Kieselgel 60, 40-63 μm) as stationary phase. TLC was performed on aluminium sheets pre-coated with silica (Merck Silica Gel 60 F_{254}), which were visualised by staining either with 5% w/v phosphomolybdic acid in EtOH, or $KMnO_4$ solutions. Petrol refers to the petroleum fraction boiling between 30 ˚C and 40 ˚C. IR spectra were recorded at rt on a Perkin-Elmer 1750 FTIR

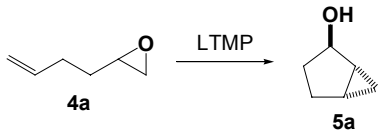
spectrophotometer using KBr discs or thin films on film plates as stated. Peak intensities are specified as broad (b), strong (s), medium (m) or weak (w), and all absorptions are reported in wavenumbers (cm^{-1}). Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded in $CDCl_3$ at room temperature, with Bruker DPX250, DPX400, DQX400 or AMX500 spectrometers unless stated otherwise; Chemical shifts (δ_H and δ_C) are reported in parts per million (ppm), and are referenced relative to the $CHCl_3$ (^{1}H NMR 7.27) and $CDCl_3$ (^{13}C NMR 77.0, central signal of triplet) signals, unless stated otherwise. Assignments were aided by COSY, DEPT, HMQC and NOE experiments. Coupling constants (*J*) are given in Hertz to the nearest ±0.1 Hz. Multiplicities are given as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), multiplet (m) and broad (b) where applicable. Diastereotopic protons in the molecule are assigned as H-X and H-X′ in the NMR spectra, where X is the proton number indicated in the structure. Mass spectra (*m/z*, low and high resolution) were recorded on a Micromass GCT spectrometer using the techniques of chemical ionisation (CI+) or field ionisation (FI+), or by the EPSRC National Mass Spectrometry Service Centre at the University of Swansea on a 900 XLT high resolution double focusing mass spectrometer using the technique of electrospray ionisation (ES+). Chiral stationary phase HPLC was performed using a Daicel Chiralcel OD column (4.6 mm × 250 mm) or Daicel Chiralpak AD column (4.6 mm × 250 mm) on a Gilson System with 712 Controller Software and a 118 UV/vis detector at the appropriate wavelength for the sample under analysis. Chiral GC analysis was performed using a ThermoQuest CE Instruments TRACE GC, running Chrom-Card for TRACE software, fitted with a CYDEX-β column at the stated temperature. All enantioenriched samples were verified by the preparation of racemic samples. Enantiomeric excesses (ees) were determined by chiral HPLC or GC to the nearest 1%. Retention times (t_R) are given in minutes to the nearest 0.01 min. Optical rotations $[\alpha]^{T}_{D}$ were measured using a Perkin Elmer 241 Polarimeter with a cell of path length 1.0 dm, at T ºC and are given in 10^{-1} deg cm^2 g^{-1}. Concentrations (*c*) are given in g/100 mL.

Optimization of the intramolecular cyclopropanation reaction using 1,2-epoxy-5-hexene 4a

For our initial study, direct application of Yamamoto's conditions to epoxide **4a** [addition of epoxide (1 mmol) to a solution of LTMP (2 equiv., 0.2 M in THF, 25 ˚C, 1 h)] gave alcohol **5a** in 47% yield (Table 1, entry 1). Volatile 5-hexanal (derived from hydrolysis of the corresponding enamine) was also observed on TLC, indicating that enamine formation was in competition with the cyclopropanation process. Since enamination proceeds efficiently in THF but is sluggish in Et_2O,[1] and is conducted at rt, therefore we envisaged that the use of Et_2O as solvent and a lower addition temperature (0 ˚C) in subsequent runs might favor the intramolecular cyclopropanation pathway. The rate of LTMP addition to the epoxide was investigated with these changes implemented. Solutions of LTMP at 0 ˚C were added via cannula to stirred solutions of **4a** at 0 ˚C over 15, 40 and 60 min, resulting in the isolation of **5a** in 67, 66 and 79% yields, respectively (entries 2 - 4). There was no significant difference in the yield within experimental error as the rate varied between 15 to 60 min; thus an addition time of 40 to 60 min was considered to be the most practical for controlled addition of a relatively small amount of LTMP solution via cannula. Subsequently, epoxide **4a** was treated with LTMP and the resulting mixture was only allowed to react at room temperature for 2 h (entry 5). This led to a 1:1 mixture of **4a** and **5a** in the crude product after ^{1}H NMR analysis, and we concluded that the cyclopropanation reaction is significantly slower than enamine formation, which requires only 1 h. We then investigated the molar equivalents of the base required for the cyclopropanation reaction by changing the amount of LTMP to 1.5 and 2.5 equiv. Incomplete consumption of **4a** was observed with 1.5 equiv. of LTMP (entry 6), and **5a** was isolated in only 62% yield when 2.5 equiv. of LTMP was used (entry 7). This indicates the use of 2 equiv. of LTMP is optimal. The reaction was reexamined in hexane and THF under the conditions applied in entry 4 (entries 8 and 9). Bicyclic alcohol **5a** was cleanly isolated in 62% yield from the hexane reaction. In contrast, ^{1}H NMR analysis of **5a** isolated after column chromatography from the THF reaction revealed a significant amount of side-products (~10%) present, which gave rise to distinctive vinylic signals (δ 4.7 - 5.7 ppm). The latter side-products were postulated to be a mixture of *cis*- and *trans*-cyclopropanes **9** (R = H, ratio not determined), formed via allylic deprotonation followed by

intramolecular epoxide ring-opening. Apparu and Barelle[2,3] have previously reported the formation of *trans*-**9** in the reaction between **4a** and *N*-lithioethylenediamine in HMPA as solvent at room temperature. However, their NMR data were obtained in CCl_4, making direct comparison difficult.

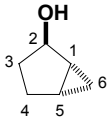
Table 1. Optimization of the intramolecular cyclopropanation reaction



Entry[a]	LTMP[b] (equiv.)	Solvent	Time (h)	Yield (%)[c]
1	2	THF	1	47
2[d]	2	Et_2O	40	67
3[e]	2	Et_2O	40	66
4[f]	2	Et_2O	12	79
5	2	Et_2O	2	**4a**:**5a** = 1:1[g]
6	1.5	Et_2O	20	**4a** = 29, **5a** = 46
7	2.5	Et_2O	18	62
8	2	Hexane	16	62
9	2	THF	16	48[h]

[a] Performed with 1 mmol of **4a** at 0.2 M. [b] 0.2 M. [c] Isolated yields. [d] LTMP added over 15 min. [e] LTMP added over 40 min. [f] LTMP added over 60 min. [g] Crude residue analyzed by ^{1}H NMR. [h] The presence of **9** (R = H, ~10%) observed in ^{1}H NMR.

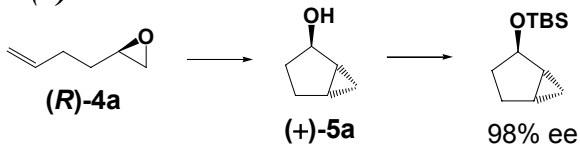
Typical cyclopropanation procedure: formation of bicyclic alcohol 5a from terminal epoxide 4a and LTMP



n-BuLi (1.6 M in hexane, 1.3 mL, 2.0 mmol) was added to a stirred solution of 2,2,6,6-tetramethylpiperidine (0.34 mL, 2.00 mmol) in *t*-BuOMe (10 mL) at –78 ˚C. The pale yellow LTMP solution formed was stirred at rt for 15 min and cooled to 0 ˚C in an ice bath. To a stirred solution of unsaturated terminal epoxide (1.00 mmol) in *t*-BuOMe (5 mL) at 0 ˚C was added the LTMP solution dropwise *via* cannula over 45 - 60 min. The resulting mixture was stirred at rt for the duration specified, quenched with MeOH (0.5 mL) and concentrated. The residue was dry-loaded onto a small amount of silica and purified by column chromatography (30% Et_2O in petrol) to give bicyclo[3.1.0]hexan-2-ol **5a**[3] (77 mg, 0.79 mmol, 79%) as a pale yellow oil.

Procedures for the formation of bicyclic alcohols 5a-q from epoxides 4a-q and LTMP (Table 1 in main paper)

(+)-Bicyclo[3.1.0]hexan-2-ol (+)-5a

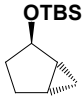


(R)-1,2-Epoxy-5-hexene **(*R*)-4a**

According to Jacobsen's procedure,[4] (*R,R*)-*N,N´*-Bis(3,5-di-*tert*-butylsalicylidinene)-1,2-cyclohexanediaminocobalt (II) (495 mg, 0.82 mmol, 2 mol%) was treated with 1,2-epoxy-5-hexene **4a** (4.00 g, 40.8 mmol), AcOH (47 μl, 0.82 mmol, 0.02 equiv.) and THF (0.5 mL). The mixture was cooled to 0 ˚C, followed by addition of water (403 μl, 22.4 mmol, 0.55 equiv.) in one portion and stirred at rt for 20 h. Subjection of the crude mixture to bulb-to-bulb Kugelrohr distillation (at rt and 0.07 mbar) gave (*R*)-1,2-epoxy-5-hexene **(*R*)-4a** (1.54 g, 15.7 mmol, 39%) as a colorless liquid; $[\alpha]_D^{22}$ = +5.3 (*c*, 1.0 in $CHCl_3$) {lit.[4] = $[\alpha]_D^{25}$ = +9.36 (neat)}; ^1H and ^{13}C NMR spectra were identical to the starting epoxide. The enantiomeric excess of **(*R*)-4a** (ee > 98%) was confirmed by chiral HPLC (OD column, 0.1/0.4 $mLmin^{-1}$/98.5% heptane and 1.5% EtOH) analysis of the 2-naphthalene thiol derivative.[5]

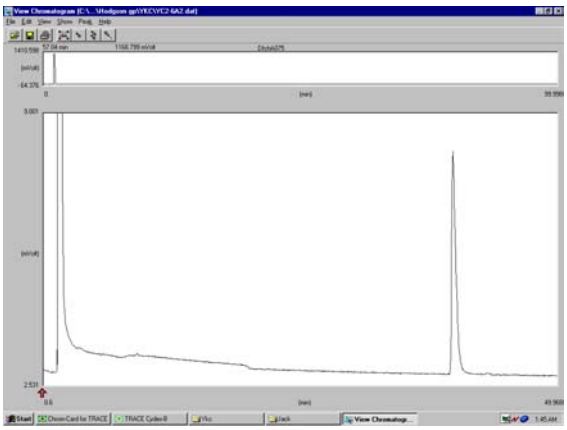
(+)-Bicyclo[3.1.0]hexan-2-ol ***(+)-5a***

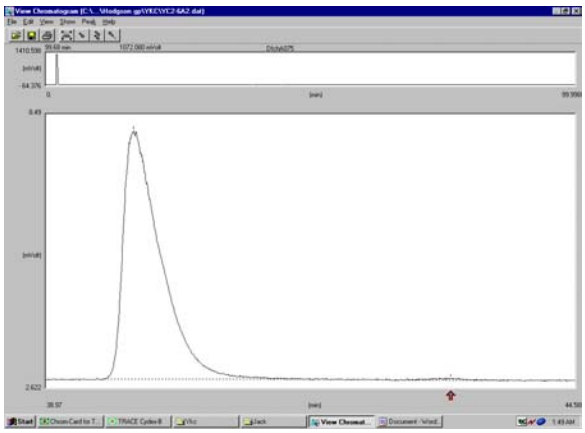
Following the typical cyclopropanation procedure, (*R*)-1,2-epoxy-5-hexene **(*R*)-4a** (196 mg, 2.0 mmol) was treated with LTMP in Et_2O for 16 h to give (+)-bicyclo[3.1.0]hexan-2-ol **(+)-5a** (137 mg, 1.40 mmol, 70%) as a pale yellow oil, $[\alpha]_D^{22}$ = +31.0 (*c*, 1.0 in $CHCl_3$). NMR data see **5a** above. The enantiomeric excess of **(+)-5a** (ee = 98%) was confirmed by chiral GC (Cydex-β column, 80 ˚C/0.6 $mLmin^{-1}$) analysis of the *tert*-butyldimethylsilyl derivative below:



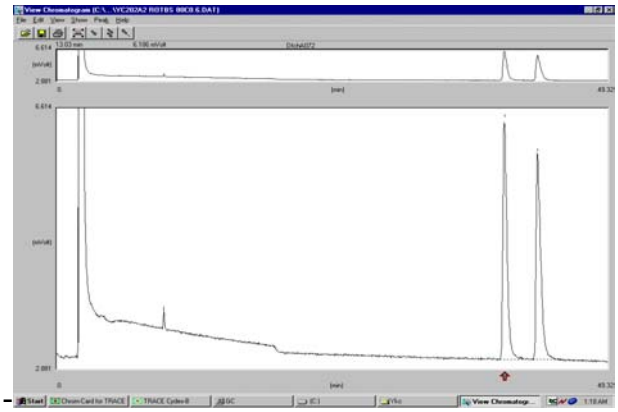
tert-Butyldimethylsilyl chloride (230 mg, 1.53 mmol, 1.5 equiv.) was added to a stirred solution of (+)-bicyclo[3.1.0]hexan-2-ol **(+)-5a** (100 mg, 1.02 mmol) and imidazole (139 mg, 2.04 mmol, 2.0 equiv.) in CH_2Cl_2 (4 mL) at rt. The reaction mixture was stirred for 4 h, then diluted with

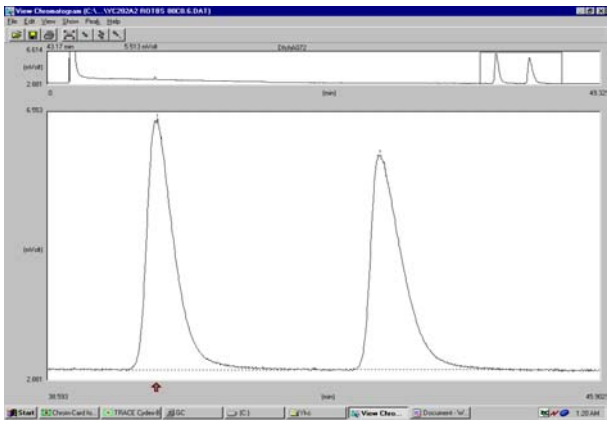
CH_2Cl_2 (50 mL), washed with sat. aq. $NaHCO_3$ (50 mL) and the layers were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave the desired chiral silylether (178 mg, 0.84 mmol, 82%) as a colorless oil; R_f = 0.7 (10% Et_2O in petrol); $[\alpha]_D^{22}$ = +8.7 (*c*, 1.0 in $CHCl_3$); *ee* = 98%; IR (film) 2950s (C-H), 1466m, 1365m, 1253s (C-Si), 1106s (C-O), 1060s, 1023s; ^{1}H NMR (400 MHz) –0.07 - –0.04 (m, 1H, H-6), 0.08 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.33 - 0.38 (m, 1H, H-6′), 0.91 (s, 9H, $SiC(CH_3)_3$), 1.24 - 1.34 (m, 2H, H-1, H-4′), 1.38 - 1.43 (m, 1H, H-5), 1.46 (dd, 1H, H-4, *J* = 8.8, 14.0), 1.60 (dd, 1H, H-3, *J* = 8.8, 12.4), 1.90 - 2.01 (m, 1H, H-3′), 4.22 (d, 1H, H-2, *J* = 4.8); ^{13}C NMR ($CDCl_3$, 100 MHz) –4.5 ($Si(CH_3)_2$), 6.5 (C-6), 16.7 (C-5), 18.3 ($SiC(CH_3)_3$), 24.5 (C-1), 24.9 (C-3), 26.0 ($SiC(CH_3)_3$), 31.0 (C-4), 75.0 (C-2); MS (CI+) *m/z*: 213.2 (MH^+, 100%), 172.1 (15%), 155.1 (21%), 133.1 (4%); HRMS *m/z*: MH^+ found 213.1670, $C_{12}H_{25}OSi$ requires 213.1675.



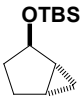


Peak Number	Area %	Ret.Time	Area	BC
1	99.2157	39.90	1449302	mi
2	0.7843	43.26	11457	mi
Totals	100.0000		1460759	



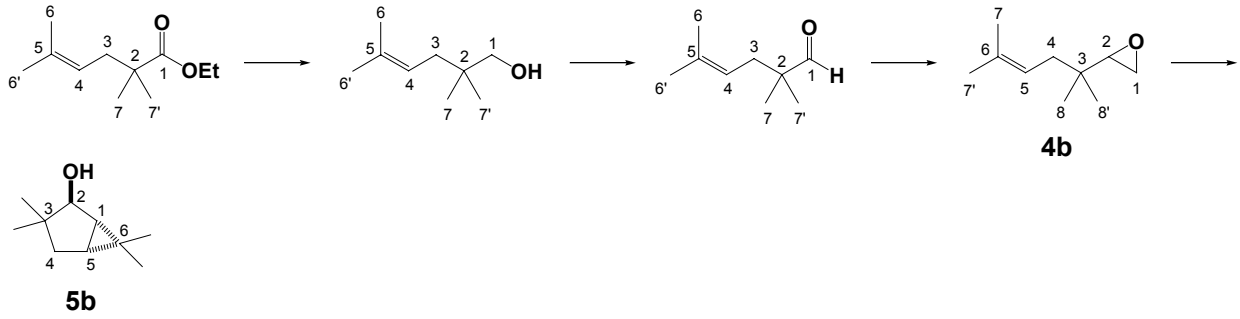


Peak Number	Area %	Ret.Time	Area	BC
1	49.9017	40.04	840979	mi
2	50.0983	42.99	844291	mi
Totals	100.0000		1685270	



The racemic substrate was prepared according to the procedure above.

3,3,6,6-Tetramethylbicyclo[3.1.0]hexan-2-ol 5b



1,2-Epoxy-3,3,6-trimethyl-5-heptene ***4b***

n-BuLi (1.6 M in hexane, 11.8 mL, 18.9 mmol, 1.1 equiv.) was added to a stirred solution of diisopropylamine (1.91 g, 18.9 mmol, 1.1 equiv.) in THF (90 mL) at –78 ˚C. The LDA solution formed was warmed to rt and then cooled to –78 ˚C. Ethyl isobutyrate (2.0 g, 2.3 mL, 17.2 mmol) was added slowly to the LDA solution and the resulting mixture was stirred at the same temperature for 1 h, and then treated with prenyl bromide (2.1 mL, 18.1 mmol, 1.05 equiv.). After 30 min, the mixture was warmed to rt and stirred for 12 h. The reaction mixture was diluted with Et_2O (200 mL) and washed with water (200 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated

to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave 2,2,5,5-tetramethylpent-4-enoate (2.75 g, 14.9 mmol, 87%) as a colorless oil, R_f = 0.4 (5% Et_2O in petrol); IR (film) 2980s, 2933s (C-H), 1733s (C=O), 1471m, 1448m, 1387m, 1364w, 1308m, 1251m, 1181s, 1130s, 1032m; ^{1}H NMR (400 MHz) 1.16 (s, 6H, 3 × H-7, 3 × H-7′), 1.25 (t, 3H, OCH_2CH_3, J = 7.2), 1.61, 1.70 (s, 6H, 3 × H-6, 3 × H-6′), 2.22 (d, 2H, 2 × H-3, J = 7.6), 4.11 (q, 2H, OCH_2, J = 7.2), 5.06 - 5.10 (m, 1H, H-4); ^{13}C NMR (100 MHz) 14.2 (OCH_2CH_3), 17.9 (C-6), 24.8 (C-7, 7′), 26.0 (C-6′), 38.7 (C-3), 42.7 (C-2), 60.2 (OCH_2), 119.9 (C-4), 134.0 (C-5), 177.9 (C-1).

$LiAlH_4$ (2.3 M in THF, 10.6 mL, 24.4 mmol, 2.0 equiv.) was added slowly to a stirred solution of ethyl 2,2,5,5-tetramethylpent-4-enoate (2.25 g, 12.2 mmol) in THF (112 mL) at 0 ˚C. The resulting mixture was stirred at the same temperature for 4 h, and then quenched by sequential addition of water (0.93 mL), aq. NaOH (15%, 0.93 mL) and water (2.8 mL). The solids formed were filtered and washed through with Et_2O (100 mL). The filtrate was dried ($MgSO_4$), filtered and concentrated to give crude 2,2,5,5-tetramethylpent-4-en-1-ol (1.64 g, 11.5 mmol, 94%) as a colorless oil, which was sufficiently pure to be sued in the next step; IR (film) 3351bs (O-H), 2965s, 2928s, 2871s (C-H), 1472m, 1451m, 1378m, 1363w, 1263w, 1186w, 1104w, 1042s; ^{1}H NMR (400 MHz) 0.88 (s, 6H, 3 × H-7, 3 × H-7′), 1.63, 1.73 (2 × s, 6H, 3 × H-6, 3 × H-6′), 1.95 (d, 2H, 2 × H-3, J = 7.2), 3.33 (s, 2H, 2 × H-1), 5.19 - 5.23 (m, 1H, H-4); ^{13}C NMR (100 MHz) 17.8 (C-6), 23.9 (C-7, 7′), 26.0 (C-6′), 36.3 (C-2), 37.0 (C-3), 72.0 (C-1), 120.6 (C-4), 133.4 (C-5).

DMSO (1.99 mL, 28.0 mmol, 2.5 equiv.) was added dropwise to a stirred solution of oxalyl chloride (1.04 mL, 12.3 mmol, 1.1 equiv.) in CH_2Cl_2 (80 mL) at –78 ˚C. After 5 min, the mixture was treated slowly with 2,2,5,5-tetramethylpent-4-en-1-ol (1.60 g, 11.2 mmol), stirred for 15 min and then treated slowly with Et_3N (7.9 mL, 56.0 mmol, 5.0 equiv.). After 5 min, the resulting mixture was warmed to rt and stirred for 3 h. The reaction mixture was poured into water (100 mL), the layers were separated and then the aqueous layer extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried ($MgSO_4$), filterd and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave 2,2,5,5-tetramethylpent-4-enal (1.24 g, 8.83

mmol, 79%) as a yellow oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 2969s, 2930s (C-H), 1725s (C=O), 1470m, 1379m, 1104w, 1080w; ^{1}H NMR (400 MHz) 1.05 (s, 6H, 3 × H-7, 3 × H-7′), 1.61, 1.71 (2 × s, 6H, 3 × H-6, 3 × H-6′), 2.16 (d, 2H, 2 × H-3, J = 8.0), 5.04 - 5.09 (m, 1H, H-4), 9.48 (s, 1H, H-1); ^{13}C NMR (100 MHz) 17.8 (C-6), 21.1 (C-7, 7′), 25.9 (C-6′), 35.5 (C-2), 118.7 (C-4), 134.7 (C-5), 206.5 (C-1).

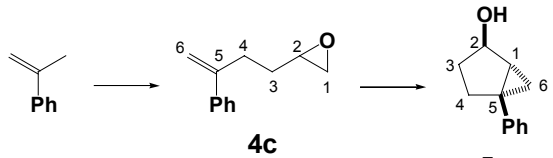
n-BuLi (1.6 M in hexane, 3.3 mL, 5.2 mmol, 1.05 equiv.) was added dropwise (~1 drop/s) to a stirred solution of 2,2,5,5-tetramethylpent-4-enal **(**694 mg, 4.95 mmol) and dibromomethane (0.42 mL, 5.94 mmol, 1.2 equiv.) in THF (20 mL) at –78 ˚C.[6] The resulting mixture was warmed to rt and stirred for 14 h. The reaction mixture was poured into sat. aq. NH_4Cl (50 mL), the layers were separated and the aqueous layer extracted with Et_2O (50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4b** (425 mg, 2.76 mmol, 56%) as a colorless oil, R_f = 0.45 (10% Et_2O in petrol); IR (film) 3050w (epoxide), 2966s, 2929s (C-H), 1466m, 1452m, 1397w, 1379m, 1360m, 1260w, 1104w; ^{1}H NMR (400 MHz) 0.81 (s, 3H, $COC(CH_3)$), 0.87 (s, 3H, $COC(CH_3)$), 1.61 (s, 3H, $C=C(CH_3)_2$), 1.72 (s, 3H, $C=C(CH_3)_2$), 1.95 - 2.06 (m, 2H, 2 × H-4), 2.59 - 2.64 (m, 2H, H-1, H-1′), 2.76 (dd, 1H, H-2, J = 2.8, 4.0), 5.19 - 5.24 (m, 1H, H-5); ^{13}C NMR (100 MHz) 17.8 ($C=C(CH_3)_2$), 21.9 ($COC(CH_3)_2$), 23.1 ($COC(CH_3)_2$), 26.0 ($C=C(CH_3)_2$), 34.3 (C-3), 38.3 (C-4), 44.0 (C-1), 59.4 (C-2), 119.9 (C-5), 133.7 (C-6); MS (CI+) *m/z*: 172.2 (MNH_4^+ 5%), 155.1 (MH^+ 6%), 137.1 (100%), 135.1 (23%), 133.1 (5%), 121.1 (10%), 109.1 (3%); HRMS *m/z*: MNH_4^+ found 172.1709, $C_{10}H_{22}NO$ requires 172.1701.

3,3,6,6-Tetramethylbicyclo[3.1.0]hexan-2-ol ***5b***

Following the typical cyclopropanation procedure, 1,2-epoxy-3,3,6-trimethyl-5-heptene **4b** (154 mg, 1.00 mmol) was treated with LTMP in Et_2O for 8 h to give bicyclic alcohol **5b** (116 mg, 0.75 mmol, 75%) as a white solid, R_f = 0.2 (20 % Et_2O in petrol); mp = 73 - 75 ˚C; IR (KBr) 3306bs (O-H), 3016w (cyclopropane), 2938s (C-H), 2740s, 1456s, 1372w, 1345w, 1288w, 1266w, 1238w, 1207w, 1131w, 1095w, 1053m, 1010w; ^{1}H NMR (400 MHz) 0.95 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.01 (s,

6H, 2 × CH_3), 1.05 - 1.06 (m, 1H, H-4), 1.08 - 1.09 (m, 1H, H-2), 1.15 - 1.20 (m, 1H, H-3), 1.46 (s, 1H, OH), 1.52 (dd, 1H, H-4, *J* = 7.6, 13.6), 3.42 (d, 1H, H-1, *J* = 2.0); ^{13}C NMR (100 MHz) 14.4 (CH_3), 22.0 (CH_3), 23.8 (C-6), 24.4 (CH_3), 27.2 (CH_3), 28.2 (C-3), 37.2 (C-2), 37.5 (C-4), 52.7 (C-2), 79.3 (C-1); Elemental analysis: found C, 77.81; H, 11.79; O, 10.40; $C_{10}H_{18}O$ requires C, 77.87; H, 11.76; O, 10.37.

5-Phenylbicyclo[3.1.0]hexan-2-ol 5c



4c **5c**

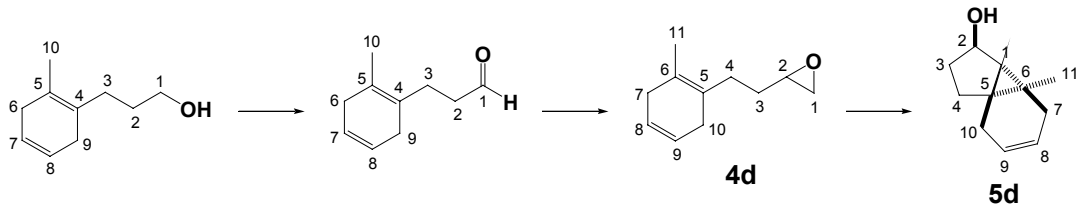
1,2-Epoxy-5-phenyl-5-hexene ***4c***

n-BuLi (1.6 M in hexanes, 6.25 mL, 10.0 mmol) was added dropwise to a stirred solution of *t*-BuOK (1.12 g, 10.0 mmol) in THF (40 mL) at –78 ˚C. After 5 min, α-methylstyrene (1.30 mL, 10.0 mmol) was added dropwise and following further stirring for 30 min, epichlorohydrin (0.39 mL, 5.00 mmol) was added in one portion. Following stirring for 90 min, sat. aq. NH_4Cl (5 mL) and Et_2O (5 mL) were added and the layers separated. The aqueous layer was washed with Et_2O (3 × 10 mL), the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue by column chromatography gave a crude oil. Bulb-to-bulb distillation (75 ˚C, 0.07 mbar) of the crude oil gave 1,2-epoxy-5-phenyl-5-hexene **4c** as a colorless oil (454 mg, 2.61 mmol, 52%), R_f = 0.20 (3% Et_2O in petrol); IR (film) 3082w, 3053m, 2987m, 2923s, 1627s (C=C), 1600m, 1495s, 1444m, 1410m, 1079w; ^{1}H NMR (400 MHz) 1.78 - 1.65 (m, 2H, 2 × H-3), 2.48 (dd, 1H, H-1, *J* = 5.0, 3.0), 2.76 - 2.62 (m, 3H, H-1´, 2 × H-4), 2.99 - 2.95 (1H, m, H-2), 5.13 (d, 1H, H-6, *J* = 1), 5.33 (d, 1H, H-6´, *J* = 1.0), 7.44 - 7.28 (m, 5H, 5 × Ar-H); ^{13}C NMR (100 MHz) 31.2 (C-4), 31.7 (C-3), 47.2 (CH_2O), 51.9 (C-2), 112.8 (C-6), 126.1 (Ar-C), 127.5 (2 × Ar-C), 128.4 (2 × Ar-C), 140.1 (Ar-C_{quat}), 147.5 (=C); MS (CI+) *m/z*: 192 (MNH_4^+, 35), 175 (MH^+, 95), 157 (100); HRMS *m/z*: MH^+ found 175.1129, $C_{12}H_{15}O$ requires 175.1123.

5-Phenylbicyclo[3.1.0]hexan-2-ol ***5c***

Following the typical cyclopropanation procedure, 1,2-epoxy-5-phenyl-5-hexene **4c** (174 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give 5-phenylbicyclo[3.1.0]hexan-2-ol **5c** (139 mg, 0.80 mmol, 80%) as a colorless oil, R_f = 0.2 (30% Et_2O in petrol); IR (film) 3346 (OH), 3060 (cyclopropane), 3028, 2933, 1603, 1498, 1447, 1326, 1166, 1107, 1031, 755, 698; ^{1}H NMR (400 MHz) 0.76 (t, 1H, H-6, *J* = 4.8), 0.94 (dd, 1H, H-6′, *J* = 5.2, 8.4), 1.51-1.61 (m, 1H, H-4), 1.69 (s, 1H, OH), 1.73-1.78 (m, 2H, H-1, H-4′), 2.08 (dd, 1H, H-3, *J* = 8, 12.4), 2.29 (td, 1H, H-3′, *J* = 8.4, 12.1), 4.34 (d, 1H, H-2, *J* = 3.6), 7.17-7.32 (5H, H aromatic); ^{13}C NMR (100 MHz) 17.1 (C-6), 29.7 (C-3), 31.6 (C-4), 32.1 (C-5), 33.6 (C-1), 74.7 (C-2), 125.6 (Ar-C), 126.5 (Ar-C), 128.2 (Ar-C), 144.3 (Ar-C); MS (CI+) *m/z*: 157 ([M–OH]$^+$, 100), 173 (M-H$^+$, 10); HMRS *m/z*: [M–OH]$^+$ found 157.1017, $C_{12}H_{13}$ requires 157.1017.

3b-Methyl-2,3,3a,3b,4,7-hexahydro-1H-cyclopenta[1,3]cyclopropa[1,2]benzen-3-ol 5d



4-(6-Methylcyclohexa-5,8-dienyl)-1,2-epoxybutane ***4d***

$LiAlH_4$ (2.3 M in THF, 26.2 mL, 60.3 mmol, 3.0 equiv.) was added slowly to a stirred solution of 3-*o*-tolylpropionic acid (3.30 g, 20.1 mmol) in THF (180 mL) at −78 ˚C. The resulting mixture was warmed to rt slowly over 2 h and then stirred at the same temperature for 4 h. The reaction mixture was then quenched slowly by sequential addition of water (2.3 mL), aq. NaOH (15%, 2.3 mL) and water (6.9 mL). The solids formed were filtered and washed through with Et_2O (250 mL). The filtrate was dried ($MgSO_4$), filtered and concentrated to give crude 3-*o*-tolylpropan-1-ol (3.00 g, 20.0 mmol, 100%) as a colorless oil, which was sufficiently pure to be used without further purification.

A solution of 3-*o*-tolylpropan-1-ol (2.00 g, 13.3 mmol) in THF (20 mL) was added slowly to a stirred dark blue solution of Li (554 mg, 79.8 mmol, 6.0 equiv.), *t*-BuOH (4.6 mL), THF (30 mL) in NH_3 (80 mL) at −78 ˚C. After 7 h, the mixture was quenched slowly with $NH_4Cl_{(s)}$ until no blue

color was observed, then warmed to rt slowly and stirred until the excess NH_3 was evaporated. The mixture was washed with water (100 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 60 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (60% Et_2O in petrol) gave 3-(5-methylcyclohexa-4,7-dienyl)propan-1-ol (1.11 g, 7.29 mmol, 55%) as a colorless oil, R_f = 0.4 (60% Et_2O in petrol); IR (film) 3333bs (O-H), 3026m, 2927s, 2871s (C-H), 2815s, 1428m, 1059s; ^{1}H NMR (400 MHz) 1.51 (bs, 1H, OH), 1.63 - 1.70 (m, 5H, 3 × H-10, 2 × H-2), 2.12 (t, 2H, 2 × H-3, J = 8.0), 2.59 - 2.66 (m, 4H, 2 × H-6, 2 × H-9), 3.66 (td, 2H, 2 × H-1, J = 1.6, 6.4), 5.66 - 5.73 (m, 2H, H-7, H-8); ^{13}C NMR (100 MHz) 18.4 (C-10), 29.0 (C-3), 30.5 (C-2), 30.9, 33.0 (C-6, C-9), 63.0 (C-1), 124.3 (C-4), 124.4 (C-7), 124.6 (C-8), 126.8 (C-5); MS (CI+) *m/z*: 170.2 (MNH_4^+, 47%), 153.1 (MH^+, 100%), 135.1 (61%), 119.1 (16%), 108.1 (41%), 105.1 (36%), 91.1 (48%); HRMS *m/z*: MNH_4^+ found 170.1543, $C_{10}H_{20}NO$ requires 170.1545.

TPAP (56 mg, 0.16 mmol, 5 mol%) was added to a stirred solution of 3-(5-methylcyclohexa-4,7-dienyl)propan-1-ol (500 mg, 3.28 mmol), powdered 3 Å sieves (900 mg) and 4-methylmorpholine *N*-oxide (769 mg, 6.56 mmol, 2.0 equiv.) in CH_2Cl_2 (25 mL) at rt. The resulting mixture was stirred for 4 h, and then filtered through a thin pad of silica. The filtrate was concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave 3-(5-methylcyclohexa-4,7-dienyl)propionaldehyde (320 mg, 2.13 mmol, 65%) as a colorless oil, R_f = 0.3 (10% Et_2O); IR (film) 3028m, 2816m (C-H), 1725s (C=O), 1428m; ^{1}H NMR (400 MHz) 1.65 (s, 3H, 3 × H-10), 2.36 (t, 2H, 2 × H-3, J = 7.2), 2.51 (td, 2H, 2 × H-2, J = 0.8, 7.6), 2.60 (s, 4H, 2 × H-6, 2 × H-9), 5.65 - 5.71 (m, 2H, H-7, H-8), 9.80 (s, 1H, CHO); ^{13}C NMR (100 MHz) 18.4 (C-10), 25.2 (C-3), 30.3, 32.9 (C-6, C-9), 42.2 (C-2), 124.3 (C-7), 124.4 (C-8), 125.3 (C-4), 125.4 (C-5), 202.4 (C-1); MS (CI+) *m/z*: 168.1 ((MNH_4^+, 53%), 151.2 (MH^+, 11%), 133.0 (34%), 117.1 (73%), 106.1 (100%); HRMS *m/z*: MNH_4^+ found 168.1393, $C_{10}H_{18}NO$ requires 168.1388.

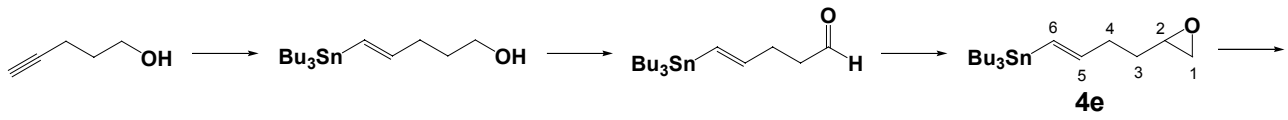
n-BuLi (1.6 M in hexane, 4.3 mL, 6.9 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of 3-(5-methylcyclohexa-4,7-dienyl)propionaldehyde (939 mg, 6.25 mmol) and

dibromomethane (0.53 mL, 7.50 mmol, 1.2 equiv.) in THF (25 mL) at –78 °C.[6] The resulting mixture was warmed to rt and stirred for 20 h. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4d** (684 mg, 4.16 mmol, 67%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3027m, 2921s, 2872s (C-H), 2815s, 1430m, 1252w, 1161w, 1011w; ^{1}H NMR (400 MHz) 1.54 - 1.64 (m, 2H, 2 × H-3), 1.66 (s, 3H, 3 × H-11), 2.20 (t, 2H, 2 × H-4, J = 8.0), 2.48 (dd, 1H, H-1, J = 2.8, 5.2), 2.58 - 2.66 (m, 4H, 2 × H-7, 2 × H-10), 2.75 (dd, 1H, H-1′, J = 4.0, 4.8), 2.90 - 2.94 (m, 1H, H-2), 5.66 - 5.73 (m, 2H, H-8, H-9); ^{13}C NMR (100 MHz) 18.8 (C-11), 29.5 (C-4), 30.9 (C-7), 31.3 (C-3), 33.4 (C-10), 47.6 (C-1), 52.6 (C-2), 124.9, 125.0 (C-8, C-9, C-5), 126.7 (C-6); MS (CI+) *m/z*: 182.2 (MNH_4^+, 14%), 165.7 (MH^+, 53%), 147.1 (100%), 131.1 (66%), 118.1 (26%), 105.1 (63%); HRMS *m/z*: MH^+ found 165.1287, $C_{11}H_{17}O$ requires 165.1279.

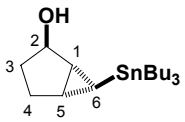
3b-Methyl-2,3,3a,3b,4,7-hexahydro-1H-cyclopenta[1,3]cyclopropa[1,2]benzen-3-ol ***5d***

Following the typical cyclopropanation procedure, 4-(6-methylcyclohexa-5,8-dienyl)-1,2-epoxybutane **4d** (164 mg, 1.0 mmol) was treated with LTMP in *t*-BuOMe for 24 h to give bicyclic alcohol **5d** (101 mg, 0.61 mmol, 61%) as a colorless oil, R_f = 0.3 (60% Et_2O in petrol); IR (film) 3318bs (O-H), 3026s, 2868s (C-H), 2825s, 1661w, 1434m, 1324m, 1214m, 1136s, 1056s, 1018s; ^{1}H NMR (400 MHz) 1.02 (s, 3H, 3 × H-11), 1.23 (s, 1H, H-1), 1.59 (bs, 1H, OH), 1.72 - 1.96 (m, 4H, 2 × H-3, 2 × H-4), 2.02 - 2.09 (m, 1H, H-7), 2.32 - 2.41 (m, 3H, H-7′, 2 × H-10), 4.21 (d, 1H, H-2, J = 5.2), 5.44 - 5.61 (m, 2H, H-8, H-9); ^{13}C NMR (100 MHz) 16.4 (C-11), 21.7 (C-6), 29.7 (C-7), 30.0 (C-4), 34.2 (C-10), 37.2 (C-1), 38.1 (C-3), 75.2 (C-2), 124.7, 125.6 (C-8, C-9); MS (FI+) *m/z*: 164.1 (M^+, 100%); HRMS *m/z*: M^+ found 164.1205, $C_{11}H_{16}O$ requires 164.1201.

***exo*-6-Tributylstannylbicyclo[3.1.0]hexan-2-ol 5e**



4e



5e

(5E)-1,2-Epoxy-6-tributylstannyl-5-hexene ***4e***

A mixture of 4-pentyn-1-ol (2.00 g, 23.8 mmol) and AIBN (39 mg, 0.24 mmol, 1 mol%) in Bu_3SnH (7.0 mL, 26.2 mmol, 1.1 equiv.) was heated from rt to 80 ˚C. After heating for 2 h at 80 ˚C, the mixture was cooled to rt and chromatographed (10 - 30% Et_2O in petrol) three times to give (5*E*)-5-tributylstannylpent-4-en-1-ol (4.62 g, 12.3 mmol, 52%) as a colorless oil, R_f = 0.3 (40% Et_2O in petrol); ^{1}H NMR (400 MHz) 0.73 - 0.91 (m, 15H, 3 × $Sn(CH_2)_3CH_3$, 3 × $Sn(CH_2)_2CH_2$), 1.23 - 1.35 (m, 6H, 3 × $SnCH_2CH_2$), 1.41 - 1.55 (m, 6H, 3 × $SnCH_2$), 1.63 - 1.69 (m, 2H, 2 × H-2), 2.13 - 2.21 (m, 2H, 2 × H-3), 3.58 - 3.63 (m, 2H, 2 × H-1), 5.83 - 5.95 (m, 2H, H-4, H-5); ^{13}C NMR (100 MHz) 9.3 (3 × $SnCH_2$, $J_{Sn\text{-}C}$ = 174), 13.7 (3 × $Sn(CH_2)_3CH_3$), 27.2 (3 × $Sn(CH_2)_2CH_2$), 29.1 (3 × $SnCH_2CH_2$), 31.7 (C-2), 34.1 (C-3), 62.4 (C-1), 128.1 (C-5), 148.6 (C-4).

DMSO (1.9 mL, 26.8 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (1.2 mL, 12.8 mmol, 1.2 equiv.) in CH_2Cl_2 (50 mL) at –78 ˚C. After 5 min, the mixture was treated slowly with a solution of (5*E*)-5-tributylstannylpent-4-en-1-ol (4.0 g, 10.7 mmol) in CH_2Cl_2 (10 mL), stirred for 15 min and then treated slowly with Et_3N (7.5 mL, 53.5 mmol, 5.0 equiv.). After 5 min, the resulting mixture was warmed to rt and stirred for a further 12 h. The reaction mixture was poured into water (100 mL), the layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 × 60 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave (5*E*)-5-tributylstannylpent-4-enal (1.65 g, 4.43 mmol, 42%) as a light yellow oil, R_f = 0.6 (10% Et_2O in petrol); IR (film) 2957s, 2925s (C-H), 2872m, 2852m, 1730s (C=O), 1599w, 1464w, 1417w, 1377w; ^{1}H NMR (400 MHz) 0.78 - 0.95 (m, 15H, 3 × $Sn(CH_2)_3CH_3$, 3 × $Sn(CH_2)_2CH_2$), 1.24 - 1.35 (m, 6H, 3 × $SnCH_2CH_2$), 1.41 - 1.54 (m, 6H, 3 × $SnCH_2$), 2.45 - 2.57 (m, 4H, 2 × H-2, 2 × H-3), 5.88 - 6.06

(m, 2H, H-4, H-5), 9.78 (t, (1H, H-1, J = 1.6); ^{13}C NMR (100 MHz) 9.4 (3 × Sn*C*H$_2$, $J_{Sn\text{-}C}$ = 171), 13.7 (3 × Sn(CH$_2$)$_3$*C*H$_3$), 27.2 (3 × Sn(CH$_2$)$_2$*C*H$_2$), 29.0 (3 × SnCH$_2$*C*H$_2$), 29.9 (C-2), 42.7 (C-3), 129.2 (C-5), 146.3 (C-4), 202.4 (C-1).

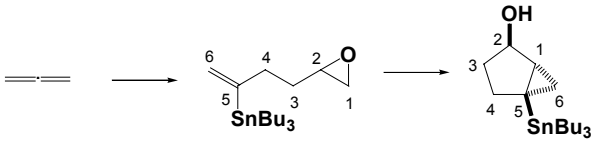
n-BuLi (1.6 M in hexane, 3.1 mL, 4.9 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of (5*E*)-5-tributylstannylpent-4-enal (1.65 g, 4.42 mmol) and dibromomethane (0.37 mL, 5.32 mmol, 1.2 equiv.) in THF (15 mL) at –78 °C.[6] The resulting mixture warmed to rt and stirred for 16 h. The reaction mixture was poured into sat. aq. NH_4Cl (40 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4e** (475 mg, 1.23 mmol, 28%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3043w (epoxide), 2957s, 2925s (C-H), 2872m, 2853m, 1600w, 1464w, 1376w, 1340w, 1292w; ^{1}H NMR (400 MHz) 0.79 - 0.95 (m, 15H, 3 × Sn(CH$_2$)$_3$C*H*$_3$, 3 × Sn(CH$_2$)$_2$C*H*$_2$), 1.26 - 1.35 (m, 6H, 3 × SnCH$_2$C*H*$_2$), 1.41 - 1.55 (m, 6H, 3 × SnC*H*$_2$), 1.61 - 1.70 (m, 2H, 2 × H-3), 2.23 - 2.38 (m, 2H, 2 × H-4), 2.49 (dd, 1H, H-1, J = 2.8, 5.2), 2.76 (t, 1H, H-1′, J = 4.8), 2.92 - 2.97 (m, 1H, H-2), 5.87 - 6.06 (m, 2H, H-5, H-6); ^{13}C NMR (100 MHz) 9.4 (3 × Sn*C*H$_2$, $J_{Sn\text{-}C}$ = 164), 13.7 (3 × Sn(CH$_2$)$_3$*C*H$_3$), 27.3 (3 × Sn(CH$_2$)$_2$*C*H$_2$), 29.1 (3 × SnCH$_2$*C*H$_2$), 31.8 (C-3), 34.0 (C-4), 47.3 (C-1), 51.9 (C-2), 128.4 (C-6), 147.8 (C-5); ^{119}Sn NMR ($CDCl_3$, 93 MHz) –50.0; MS (CI+) *m/z*: 389.2 (MH$^+$, 1%), 348.1 (9%), 308.1 (100%), 291.1 (40%), 252.2 (5%); HRMS *m/z*: MH$^+$ found 389.1852, $C_{18}H_{37}OSn$ requires 389.1866.

exo-6-Tributylstannylbicyclo[3.1.0]hexan-2-ol ***5e***

Following the typical cyclopropanation procedure, (5*E*)-1,2-epoxy-6-tributylstannyl-5-hexene **4e** (300 mg, 0.77 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give bicyclic alcohol **5e** (200 mg, 0.52 mmol, 68%) as a colorless oil, R_f = 0.3 (30% Et_2O in petrol); IR (film) 3319bs (O-H), 3008w, 2957s, 2925s (C-H), 2871m, 1463m, 1418m, 1377m, 1318m, 1157m; ^{1}H NMR (400 MHz) –0.52 - –0.45 (m, 1H, H-6), 0.78 - 0.82 (m, 6H, 3 × Sn(CH$_2$)$_2$C*H*$_2$), 0.89 (t, 9H, 3 × Sn(CH$_2$)$_3$C*H*$_3$), 1.23 - 1.56 (m, 17H, 3 × SnCH$_2$C*H*$_2$, 3 × SnC*H*$_2$, OH, H-1, H-5, one of cyclopentyl CH$_2$), 1.66 -

1.72 (m, 1H, one of cyclopentyl CH_2), 1.94 - 2.03 (m, 1H, one of cyclopentyl CH_2), 4.23 - 4.24 (m, 1H, H-2); ^{13}C NMR (100 MHz) 2.5 (C-6), 8.6 (3 × Sn*C*H_2, $J_{Sn\text{-}C}$ = 161), 13.7 (3 × Sn$(CH_2)_3$*C*H_3), 20.7, 25.7 (one of cyclopentyl CH_2), 27.3 (3 × Sn$(CH_2)_2$*C*H_2), 28.7, 29.1 (3 × SnCH_2*C*H_2), 30.6, 75.5 (C-2); ^{119}Sn NMR (93 MHz) –7.6; MS (ES+) *m/z*: 411.2 (MNa^+, 54%), 388.3 (39%), 323.2 (47%), 267.1 (41%), 235.0 (19%); HRMS *m/z*: MNa^+ found 411.1685, $C_{18}H_{36}NaOSn$ requires 411.1680.

5-Tributylstannylbicyclo[3.1.0]hexan-2-ol 5f



4f **5f**

*1,2-Epoxy-5-tributylstannyl-5-hexene **4f***

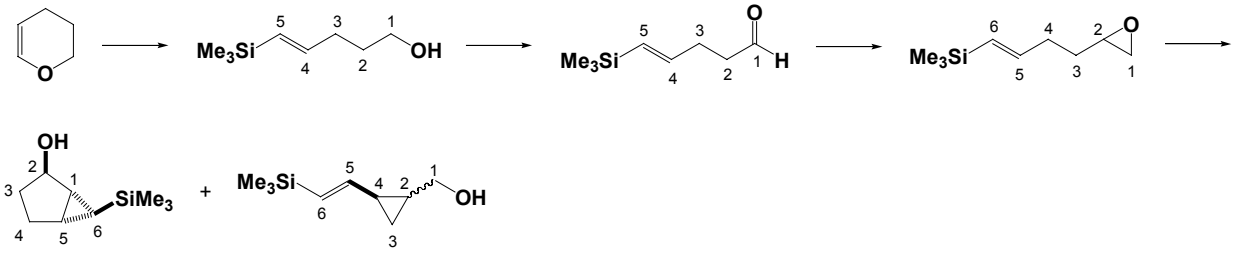
A solution of Bu_3SnLi (6.00 mmol, 2.0 equiv.) [prepared by addition of Bu_3SnH (1.61 mL, 6.00 mmol) to a stirred solution of LDA (6.00 mmol) in THF (12 mL) at 0 ˚C, and then stirred for 5 min] was added by syringe to a stirred suspension of CuCN (269 mg, 3.00 mmol) in THF (10 mL) at –78 ˚C.[7] The resulting brown solution was stirred at the same temperature for 30 min, and then treated with allene (~200 cm^3 in a balloon, ~3.30 mmol, ~1.1 equiv.). Completion of addition was indicated by deflation of the balloon. The resulting orange/brown stannyl-cuprate solution was stirred at –78 ˚C for 30 min then treated with epichlorohydrin (0.94 mL, 12.0 mmol, 4.0 equiv.). After 1 h, the mixture was warmed to 0 ˚C and stirred for a further 5 h. The reaction mixture was poured into sat. aq. NH_4Cl (50 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave epoxide **4f** (673 mg, 1.74 mmol, 29%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3040w (epoxide), 2957s, 2927s, 2872s (C-H), 1464m, 1377w, 1340w, 1261w, 1072m; ^{1}H NMR (400 MHz) 0.82 - 0.98 (m, 15H, 3 × Sn$(CH_2)_3$C*H*$_3$, 3 × Sn$(CH_2)_2$C*H*$_2$), 1.28 - 1.37 (m, 6H, 3 × SnCH_2C*H*$_2$), 1.44 - 1.53 (m, 6H, 3 × SnC*H*$_2$), 1.59 - 1.66 (m, 2H, 2 × H-3), 2.34 - 2.47 (m, 2H, 2 × H-4), 2.49 (dd, 1H, H-1, *J* = 2.4, 4.8), 2.77 (t, 1H, H-1′, *J* = 4.0), 2.91 - 2.96 (m, 1H, H-2), 5.15 (d, 1H, H-6, *J* = 2.4), 5.73 (s, 1H,

H-6′); ^{13}C NMR (100 MHz) 9.5 (3 × Sn*C*H$_2$, J_{Sn-C} = 166), 13.7 (3 × Sn(CH$_2$)$_3$*C*H$_3$), 27.4 (3 × Sn(CH$_2$)$_2$*C*H$_2$), 29.1 (3 × SnCH$_2$*C*H$_2$), 32.4 (C-3), 37.1 (C-4), 47.3 (C-1), 51.9 (C-2), 125.3 (C-6), 154.00 (C-5); ^{119}Sn NMR (93 MHz) –44.9; MS (CI–) *m/z*: 387.3 ([M–H]$^-$, 46%), 361.1 (70%), 313.1 (100%), 291.2 (70%), 269.1 (30%), 218.2 (22%); HRMS *m/z*: [M–H]$^-$ found 387.1713, $C_{18}H_{35}O^{120}Sn$ requires 387.1715.

5-Tributylstannylbicyclo[3.1.0]hexan-2-ol ***5f***

Following the typical cyclopropanation procedure, 1,2-epoxy-5-tributylstannyl-5-hexene **4f** (387 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 24 h to give bicyclic alcohol **5f** (256 mg, 0.66 mmol, 66%) as a colorless oil; R_f = 0.3 (20% Et$_2$O in petrol); IR (film) 3345bs (O-H), 2956s, 2925s, 2872s (C-H), 1464s, 1418m, 1376s, 1340m, 1292m, 1250m, 1212m, 1185m, 1058m; ^{1}H NMR (500 MHz) 0.18 (dd, 1H, H-6, *J* = 3.5, 4.5), 0.36 (dd, 1H, H-6′, *J* = 5.5, 7.5), 0.84 (t, 6H, 3 × Sn(CH$_2$)$_2$C*H*$_2$, *J* = 8.5), 0.90 (t, 9H, 3 × Sn(CH$_2$)$_3$C*H*$_3$, *J* = 7.5), 1.24 (d, 1H, OH, *J* = 6.0), 1.28 - 1.54 (m, 15H, 3 × SnC*H*$_2$, 3 × SnCH$_2$C*H*$_2$, H-1, 2 × H-3), 1.76 (dd, 1H, H-4, *J* = 8.5, 12.5), 1.86 - 1.92 (m, 1H, H-4′), 4.35 (t, 1H, H-2, *J* = 5.5); ^{13}C NMR (100 MHz) 8.5 (3 × Sn*C*H$_2$, J_{Sn-C} = 158), 11.1 (C-6), 12.1 (C-5), 13.7 (3 × Sn(CH$_2$)$_3$*C*H$_3$), 27.4 (3 × Sn(CH$_2$)$_2$*C*H$_2$), 29.1 (3 × SnCH$_2$*C*H$_2$), 29.2 (C-1), 30.2 (C-3), 30.3 (C-4), 75.1 (C-2); ^{119}Sn NMR (125 MHz) –10.0; MS (CI–, ^{120}Sn) *m/z*: 387.3 ([M–H]$^-$, 100%), 361.1 (65%), 313.1 (100%), 291.2 (15%), 269.1 (30%); HRMS *m/z*: [M–H]$^-$ found 387.1718, $C_{18}H_{35}O^{120}Sn$ requires 387.1715.

6-(Trimethylsilyl)-bicyclo[3.1.0]hexan-1-ol 5e (SnBu$_3$ = SiMe$_3$) and 2-(2-trimethylsilylvinyl)-cyclopropyl-methanol 9 (R = SiMe$_3$)



(5E)-Trimethylsilylpent-4-en-1-ol[8]

SOLUTION A: *t*-BuLi (1.7 M in pentane, 7.1 mL, 12 mmol) was added slowly to a stirred solution of freshly distilled 3,4-dihydro-2*H*-pyran (0.841 g, 10.0 mmol) in THF (8 mL) at −60 ˚C. After 10 min, the mixture was placed in an ice-bath for 50 min.

SOLUTION B: MeLi (1.6 M in Et_2O, 13.3 mL, 21 mmol) was added to a stirred solution of hexamethyldisilane (3.28 g, 22.4 mmol) and HMPA (4.12 g, 23.0 mmol) in THF (20 mL) at 0 ˚C. After 15 min, this mixture was added *via* cannula to a stirred suspension of CuCN (896 mg, 10.0 mmol) in THF (24 mL) at –40 ˚C. The resulting mixture was stirred at –25 ˚C for 30 min.

Solution A [diluted with THF (8 mL)] was added *via* cannula to solution B [diluted with THF (28 mL)] at –30 ˚C. The reaction mixture was subsequently stirred for 1.5 h at –5 ˚C, cooled to –40 ˚C and then treated with NH_4Cl (4.79 g, 89.6 mmol) in one portion. The mixture was allowed to reach rt overnight, poured into a solution of sat. aq. NH_4Cl:NH_3 (4:1) at 0 ˚C, stirred for 30 min, and then extracted with Et_2O (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to give the crude product. Purification by column chromatography (50% Et_2O in petrol) gave (5*E*)-trimethylsilylpent-4-en-1-ol as a colorless oil (1.423 g, 8.99 mmol, 90 %), R_f = 0.22 (50% Et_2O in petrol); IR (film) 3400s, 2954s, 1640m, 1247s; ^{1}H NMR (400 MHz) 0.05 (s, 9H, $Si(CH_3)_3$), 1.36 (s, 1H, OH), 1.65 - 1.72 (m, 2H, 2 × H-2), 2.18 - 2.29 (m, 2H, 2 × H-3), 3.66 (t, 2H, 2 × H-1, J = 6.8), 5.68 (d, 1H, H-5, J = 18.4), 6.01 - 6.08 (m, 1H, H-4); ^{13}C NMR (100 MHz) –1.2 ($Si(CH_3)_3$), 31.5 (C-3), 32.9 (C-2), 62.5 (C-1), 130.5 (C-5), 146.2 (C-4); MS (CI+) *m/z*: 176.1 (MNH_4^+, 35%), 159.1 (MH^+, 100%), 103.1 (20%).

(5E)-Trimethylsilyl-pent-4-enal

DMSO (1.56 g, 19.91 mmol) was added slowly to a stirred solution of oxalyl chloride (1.21 g, 9.51 mmol) in CH_2Cl_2 (40 mL) at −78 ˚C. After 5 min, a solution of 5(*E*)-trimethylsilylpent-4-en-1-ol (1.26 g, 7.95 mmol) in CH_2Cl_2 (10 mL) was added dropwise. After 15 min Et_3N (4.03 g, 39.81 mmol) was added slowly, and then after 5 min the reaction mixture was warmed to rt and stirred overnight. The reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the crude product by column chromatography (20% Et_2O in petrol) gave (5*E*)-trimethylsilyl-pent-4-enal (1.240 g, 7.93 mmol, 99 %) as a colorless oil, R_f = 0.5 (20% Et_2O in petrol); IR (film) 2959s, 2821w, 2720w, 1728s, 1618m, 1411w, 1248s; ^{1}H NMR (400 MHz) 0.03 (s, 9H, $Si(CH_3)_3$), 2.45 - 2.58 (m, 4H, 2 × H-2, 2 × H-3), 5.66 - 5.71 (m, 1H, H-5), 5.99 - 6.06 (m, 1H, H-4), 9.78 (s, 1H, H-1); ^{13}C NMR (100 MHz) −1.3 ($Si(CH_3)_3$), 28.7 (C-3), 42.5 (C-2), 131.3 (C-5), 144.0 (C-4), 202.1 (C-1); MS (CI+) *m/z*: 174.2 (MNH_4^+, 100%), 157.1 (MH^+, 90%), 113.1 (20%).

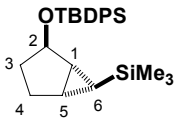
(5E)-1,2-Epoxy-6-trimethylsilyl-5-hexene ***4e*** *($SnBu_3$ = $SiMe_3$)*

n-BuLi (1.6 M solution in hexane, 1.5 mL, 2.34 mmol) was added over 1.5 h *via* a syringe pump to a solution of (5*E*)-trimethylsilyl-pent-4-enal (350 mg, 2.24 mmol) and dibromomethane (443 mg, 2.55 mmol) in THF (10 mL) −78 ˚C. The resulting solution was warmed to rt and stirred overnight. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the organic phase was dried ($MgSO_4$) and then concentrated *in vacuo*. Purification of the crude product by column chromatography (20% Et_2O in petrol) gave (5*E*)-1,2-epoxy-6-trimethylsilyl-5-hexene **4e** ($SnBu_3$ = $SiMe_3$) (267 mg, 1.57 mmol, 70 %), R_f = 0.65 (20% Et_2O in petrol); IR (film) 3000w, 2955m, 1738w, 1618m, 1410w, 1248s; ^{1}H NMR (400 MHz) 0.05 (s, 9H, $Si(CH_3)_3$), 1.61 - 1.68 (m, 2H, 2 × H-4), 2.24 - 2.32 (m, 2H, 2 × H-3), 2.48 (dd, 1H, H-1, *J* = 3.2, 5.0), 2.75 - 2.77 (m, 1H, H-1´), 2.91 - 2.96 (m, 1H, H-2), 5.70 (d, 1H, H-6, *J* = 18.4), 6.01 - 6.08 (m, 1H, H-5); ^{13}C NMR (100 MHz) −1.2 ($Si(CH_3)_3$), 31.6 (C-4), 32.8 (C-3), 47.2 (C-1), 51.9 (C-2), 130.8 (C-6), 145.5 (C-5); MS (CI+) *m/z*: 188.2 (MNH_4^+, 95%), 171.2 (MH^+, 100%), 164.2 (15%), 155.2 (50%), 129.1 (50%), 103.1 (55%).

6-(Trimethylsilyl)-bicyclo[3.1.0]hexan-1-ol ***5e*** *($SnBu_3$ = $SiMe_3$) and 2-(2-trimethylsilylvinyl)-cyclopropyl-methanol* ***9*** *(R = $SiMe_3$)*

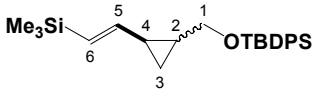
Following the typical cyclopropanation procedure, (5*E*)-1,2-epoxy-6-trimethylsilyl-5-hexene (390 mg, 2.29 mmol) was treated with LTMP for 16 h to give an inseparable mixture of 6-(trimethylsilyl)-bicyclo[3.1.0]hexan-1-ol **5e** ($SnBu_3$ = $SiMe_3$) and 2-(2-trimethylsilylvinyl)-cyclopropyl-methanol **9** (R = $SiMe_3$) as colorless oils (273 mg, 1.60 mmol, 70%), in a ratio of 5:2 (determined by integration of olefin signals and C*H*$SiMe_3$). Separation of their *tert*-butyldiphenyl silyl ether derivatives was achieved, see below.

2-(tert-Butyldiphenylsilyloxy)-6-trimethylsilyl-bicyclo[3.1.0]hexane



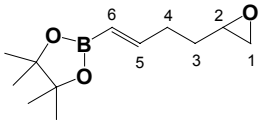
TBDPSCl (0.52 g, 1.91 mmol) was added portionwise to a stirred solution of a mixture of **5e** ($SnBu_3$ = $SiMe_3$) and **9** (R = $SiMe_3$) (in ratio 5:2) (270 mg, 1.59 mmol) and imidazole (0.27 g, 3.98 mmol) in DMF (2 mL) at 0 ˚C. Following stirring for 1 h the solution was warmed to rt and then stirred overnight. The reaction mixture was dry-loaded onto silica and then chromatographed (petrol) to give 2-(tert-butyldiphenylsilyloxy)-6-trimethylsilyl-bicyclo[3.1.0]hexane (464 mg, 1.14 mmol, 100 %) as a colorless oil as the first eluted compound, R_f = 0.2 (petrol); IR (film) 3071m, 3016m, 2956s, 2895m, 2859s, 1437m, 1428s, 1361w, 1248s, 1164s, 1111s, 1071s, 1026s; ^{1}H NMR (400 MHz) –0.77 - –0.76 (m, 1H, H-6), –0.07 (s, 9H, $Si(CH_3)_3$), 1.19 - 1.23 (m, 10H, H-1, $SiC(CH_3)_3$), 1.40 - 1.45 (m, 2H, 2 × H-3), 1.64 - 1.72 (m, 2H, 2 × H-4), 2.13 - 2.21 (m, 1H, 2 × H-5), 4.39 - 4.40 (m, 1H, H-2), 7.42 - 7.51 (m, 6H, 6 × Ar-H), 7.76 - 7.82 (m, 4H, 4 × Ar-H); ^{13}C NMR (100 MHz) –2.1 ($Si(CH_3)_3$, 6.3 (C-5), 19.3 ($SiC(CH_3)_3$), 21.4 (C-6), 26.0 (C-4), 27.1 ($SiC(CH_3)_3$), 28.6 (C-1), 31.1 (C-3), 76.9 (C-2), 127.5 (2 × Ar-C), 129.5 (2 × Ar-C), 134.9 (2 × Ar-C), 135.1 (2 × Ar-C), 135.8 (2 × Ar-C), 135.9 (2 × Ar-C); MS (CI+) *m/z*: 409.4 (MH+, 60%), 368.3 (100%), 351.3 (80%), 331.3 (25%), 288.2 (65%), 268.3 (80%), 216.2 (90%), 170.29 (90%), 153.1 (90%), 135.1 (30%).

tert-Butyl-(2-trimethylsilylvinyl-cyclopropylmethoxy)-diphenylsilane



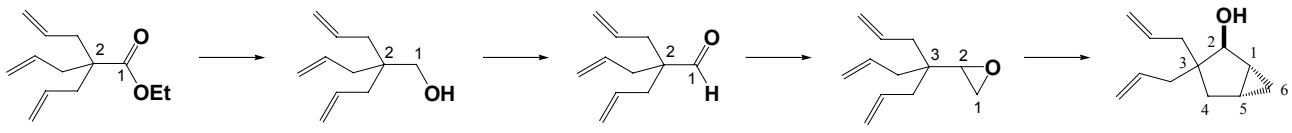
The second eluted product in the reaction above was *tert*-butyl-(2-trimethylsilylvinyl-cyclopropylmethoxy)-diphenylsilane (0.185 g, 0.45 mmol, 100 %) (*cis:trans* = 1:7.8) as a colorless oil, R_f = 0.05 (petrol); IR (film) 3071m, 3000s, 2955s, 2895s, 2859s, 1613s, 1473m, 1428m, 1247s, 1112s; ^{1}H NMR (400 MHz) 0.05 (s, 9H, Si(CH$_3$)$_3$), 0.60 - 0.71 (m, 2H, 2 × H-3), 0.84 - 0.91 (m, 1H, H-2), 1.05 (s, 9H, SiC(CH$_3$)$_3$), 1.30 - 1.38 (m, 1H, H-4), 3.48 - 3.52 (m, 2H, 2 × H-1), 5.49 - 5.56 (m, 1H, H-5), 5.62 - 5.80 (m, 1H, H-6), 7.37 - 7.45 (m, 6H, 6 × Ar-H), 7.61 - 7.71 (m, 4H, 4 × Ar-H); ^{13}C NMR (100 MHz) −1.1 (Si(CH$_3$)$_3$), 12.0 (C-3), 19.3 (Si*C*(CH$_3$)$_3$), 22.8 (C-2), 23.1 (C-4), 26.9 (SiC(*C*H$_3$)$_3$), 66.1 (C-1), 126.8 (4 × Ar-C), 127.6 (Ar-C), 129.5 (C-6), 134.0 (Ar-C), 135.6 (4 × Ar-C), 149.3 (C-5); MS (CI+) *m/z*: 409.2 (MH$^+$, 30%), 297.2 (15%), 245.1 (15%), 173.1 (35%).

***4,4,5,5-Tetramethyl-2-(4-oxiranylbut-1-enyl)[1,3,2]dioxaborolane 4e (SnBu$_3$* = B(OCMe$_2$)$_2$)**



A solution of Grubbs 2nd generation catalyst (42 mg, 5 mol%), 1,2-epoxy-5-hexene **4a** (196 mg, 2.0 mmol, 2.0 equiv.) and 4,4,5,5-tetramethyl-2-vinyl-[1,3,2]dioxaborolane (154 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) was heated under reflux at 45 ˚C for 12 h. The solvent was evaporated and the residue was purified by column chromatography (20% Et_2O in petrol) to give the title epoxide (168 mg, 0.75 mmol, 75%) as a brown oil, R_f = 0.2 (20% Et_2O in petrol); IR (film) 2979s, 2931s (C-H), 1640s, 1446m, 1363s, 1265m, 1146s; ^{1}H NMR (400 MHz) 1.26 (s, 12H, 4 × CH$_3$), 1.64 - 1.70 (m, 2H, 2 × H-4), 2.26 - 2.37 (m, 2H, 2 × H-3), 2.48 (dd, 1H, H-1, *J* = 2.8, 4.8), 2.75 (dd, 1H, H-1′, *J* = 4.4, 4.8), 2.92 - 2.96 (m, 1H, H-2), 5.48 (dt, 1H, H-6, *J* = 1.6, 18.0), 6.64 (dt, 1H, H-5, *J* = 6.0, 18.0); ^{13}C NMR (100 MHz) 24.7 (CH$_3$), 30.1 (C-3), 31.9 (C-4), 47.1 (C-1), 51.8 (C-2), 83.1 (*C*(CH$_3$)$_2$), 152.7 (C-5, C-6); MS (CI+) *m/z*: 242.2 (MNH$_4^+$, 100%), 225.2 (6%); HRMS *m/z*: MNH$_4^+$ found 242.1935, $C_{12}H_{25}BNO_3$ requires 242.1927.

3,3-Diallylbicyclo[3.1.0]hexan-2-ol 5g



3,3-Diallyl-1,2-epoxy-5-hexene ***4g***

n-BuLi (1.6 M in hexane, 0.81 mL, 1.3 mmol, 1.1 equiv.) was added to a stirred solution of diisopropylamine (0.18 mL, 1.31 mmol, 1.1 equiv.) in THF (6 mL) at –78 ˚C. The LDA solution formed was warmed to rt over 15 min, cooled to –78 ˚C and then treated slowly with ethyl 2-allylpent-4-enoate[9] (200 mg, 1.19 mmol). After 1 h, the mixture was treated with allyl bromide (0.11 mL, 1.31 mmol, 1.1 equiv.), then stirred for 30 min and then left at at rt for 20 h. The reaction mixture was poured into sat. aq. NH_4Cl (30 mL) and the aqueous layer extracted with Et_2O (2 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave ethyl 2,2-diallylpent-4-enoate (234 mg, 1.12 mmol, 94%) as a colorless oil, R_f = 0.4 (5% Et_2O in petrol); IR (film) 3076m (C=C), 2980m, 2932m (C-H), 1725s (C=O), 1638m (C=C), 1441m, 1369w, 1340w, 1297w, 1278w, 1205s, 1148m, 1037m; ^{1}H NMR (400 MHz) 1.26 (t, 3H, OCH_2CH_3, J = 7.2), 2.34 (d, 6H, 3 × $CH_2CH{=}CH_2$, J = 7.6), 4.15 (q, 2H, OCH_2CH_3, J = 7.2), 5.07 - 5.10 (m, 6H, 3 × $CH_2CH{=}CH_2$), 5.67 - 5.78 (m, 3H, 3 × $CH_2CH{=}CH_2$); ^{13}C NMR (100 MHz) 14.3 (OCH_2CH_3), 38.9 ($CH_2CH{=}CH_2$), 49.1 (C-2), 60.4 (OCH_2CH_3), 118.3 ($CH_2CH{=}CH_2$), 133.5 ($CH_2CH{=}CH_2$), 175.4 (C=O).

DIBALH (1.0 M in hexane, 27.1 mL, 27.1 mmol, 2.2 equiv.) was added slowly to a stirred solution of ethyl 2,2-diallylpent-4-enoate (2.56 g, 12.3 mmol) in CH_2Cl_2 (55 mL) at –78 ˚C. After 3 h, the mixture was treated slowly with MeOH (0.5 mL) and then warmed to rt. The reaction mixture was washed successively with water (150 mL) and aq. HCl (2 M, 50 mL), and the aqueous layers were extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give 2,2-diallylpent-4-en-1-ol (1.934 g, 11.63 mmol, 95%) as a pale yellow oil, which was sufficiently pure to be used without further purification, R_f = 0.2 (30% Et_2O in petrol); IR (film) 3399bs (O-H), 3075m (C=C), 3005w, 2978m, 2924m (C-H), 1639m (C=C), 1444m, 1415w,

1262m, 1213w, 1045s, 1017s; ^{1}H NMR (400 MHz) 2.07 (d, 6H, 3 × CH_2CH=CH$_2$, J = 7.2), 3.42 (s, 2H, CH_2OH), 5.09 - 5.12 (m, 6H, 3 × CH$_2$CH=CH_2), 5.82 - 5.93 (m, 3H, 3 × CH$_2$CH=CH$_2$); ^{13}C NMR (100 MHz) 38.8 (CH$_2$=CHCH$_2$), 41.2 (C-2), 67.5 (C-1), 117.8 (CH$_2$CH=CH$_2$), 134.5 (CH$_2$$C$H=CH$_2$); MS (CI+) *m/z*: 184.2 (MNH$_4^+$, 100%), 167.1 (MH$^+$, 70%), 151.1 (10%), 137.1 (50%), 124.1 (20%), 107.1 (18%); HRMS *m/z*: MNH$_4^+$ found 184.1693, $C_{11}H_{22}NO$ requires 184.1701.

DMSO (2.1 mL, 29.0 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (1.1 mL, 12.8 mmol, 1.1 equiv.) in CH_2Cl_2 (70 mL) at –78 ˚C. The resulting mixture was stirred for 5 min, treated slowly with a solution of 2,2-diallylpent-4-en-1-ol (1.93 g, 11.6 mmol) in CH_2Cl_2 (10 mL) and then stirred for a further 15 min. The mixture was treated slowly with Et_3N (8.1 mL, 58.0 mmol, 5.0 equiv.), stirred for 5 min and then warmed to rt. After 3 h, water (100 mL) was added to the reaction mixture, the layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave 2,2-diallylpent-4-enal (1.86 g, 11.3 mmol, 97%) as a colorless oil, R_f = 0.6 (10% Et_2O in petrol); IR (film) 3076m (C=C), 2980m, 2922m (C-H), 2836w, 2720w, 1725s (C=O), 1638m (C=C), 1441m, 1417w; ^{1}H NMR (400 MHz) 2.28 (dt, 6H, 3 × CH_2CH=CH$_2$, J = 1.2, 7.6), 5.07 - 5.12 (m, 6H, 3 × CH$_2$CH=CH_2), 5.65 - 5.75 (m, 3H, 3 × CH$_2$CH=CH$_2$), 9.52 (s, 1H, CHO); ^{13}C NMR (100 MHz) 36.7 (CH$_2$CH=CH$_2$), 51.8 (C-2), 118.9 (CH$_2$CH=CH$_2$), 132.5 (CH$_2$$C$H=CH$_2$), 205.6 (C=O); MS (CI+) *m/z*: 182.2 (MNH$_4^+$, 100%), 165.1 (MH$^+$, 15%), 135.1 (17%), 123.1 (20%), 109.1 (7%); HRMS *m/z*: MNH$_4^+$ found 182.1545, $C_{11}H_{20}NO$ requires 182.1545.

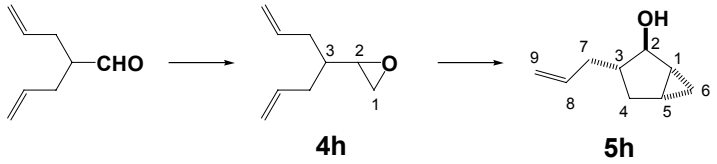
n-BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of 2,2-diallylpent-4-enal (600 mg, 3.65 mmol) and dibromomethane (0.38 mL, 5.48 mmol, 1.5 equiv.) in THF (15 mL) at –78 ˚C.[6] The resulting mixture was warmed to rt and stirred for a further 16 h. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separarted and the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers

were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4g** (437 mg, 2.45 mmol, 67%) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 3076m (epoxide), 3006w, 2979m, 2924s (C-H), 1640m (C=C), 1485w, 1445m, 1274w; ^{1}H NMR (400 MHz) 2.01 - 2.14 (m, 6H, 3 × C*H*$_2$CH=CH$_2$), 2.64 - 2.69 (m, 2H, 2 × H-1), 2.88 (dd, 1H, H-2, *J* = 3.2, 4.0), 5.06 - 5.10 (m, 6H, 3 × CH$_2$CH=C*H*$_2$), 5.80 - 5.91 (m, 3H, 3 × CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz) 38.6 (C-3), 38.8 (*C*H$_2$CH=CH$_2$), 43.6 (C-1), 57.9 (C-2), 118.0 (CH$_2$CH=*C*H$_2$), 134.0 (CH$_2$*C*H=CH$_2$); MS (CI+) *m/z*: 196.2 (MNH_4^+, 75%), 179.1 (MH^+, 100%), 161.1 (100%), 137.1 (30%), 119.1 (30%), 107.1 (10%); HRMS *m/z*: MNH_4^+ found 196.1700, $C_{12}H_{22}NO$ requires 196.1701, MH^+ found 179.1432, $C_{12}H_{19}O$ requires 179.1436.

3,3-Diallylbicyclo[3.1.0]hexan-2-ol ***5g***

Following the typical cyclopropanation procedure, 3,3-diallyl-1,2-epoxy-5-hexene **4g** (178 mg, 1.00 mmol) was treated with LTMP in Et_2O for 8 h. TLC analysis of the reaction mixture revealed the presence of the starting epoxide, R_f = 0.8 (50 % Et_2O in petrol) and product, R_f = 0.3 (50 % Et_2O in petrol). The reaction mixture was cooled to 0 ˚C and treated with another batch of LTMP (1.5 equiv.) under the standard conditions. After a further 8 h, TLC analysis showed complete consumption of starting material. Bicyclic alcohol **5g** (149 mg, 0.84 mmol, 84%) was subsequently isolated as a colorless oil following the standard purification procedures, R_f = 0.3 (50% Et_2O in petrol); IR (film) 3390bs (O-H), 3074s (cyclopropane), 3030w, 2978s, 2919s, 2861s (C-H), 1638s (C=C), 1440m, 1328w, 1303w, 1244w, 1077m, 1057m, 1028s; ^{1}H NMR (400 MHz) 0.24 - 0.27 (m, 1H, H-6$_{endo}$), 0.78 - 0.83 (m, 1H, H-6$_{exo}$), 1.22 (dd, 1H, H-4, *J* = 2.0, 14.0), 1.29 - 1.38 (m, 2H, H-1, H-5), 1.76 (s, OH), 1.91 (dd, 1H, H-4, *J* = 6.0, 14.0), 1.97 - 2.09 (m, 2H, C*H*$_2$CH=CH$_2$), 2.27 (d, 2H, C*H*$_2$CH=CH$_2$, *J* = 7.2), 3.75 (d, 1H, H-2, *J* = 4.8), 5.01 - 5.15 (m, 4H, 2 × CH$_2$CH=C*H*$_2$), 5.78 - 6.01 (m, 2H, 2 × CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz) 17.2 (C-5, C-6), 26.0 (C-1), 38.1 (*C*H$_2$CH=CH$_2$), 38.2 (C-4), 42.7 (*C*H$_2$CH=CH$_2$), 55.0 (C-3), 82.2 (C-2), 117.1 (CH$_2$CH=*C*H$_2$), 117.3 (CH$_2$CH=*C*H$_2$), 135.4 (CH$_2$*C*H=CH$_2$),136.2 (CH$_2$*C*H=CH$_2$); MS (CI+) *m/z*: 196.2 (MNH_4^+, 20%), 179.1 (MH^+, 35%), 161.1 (100%), 137.1 (10%), 119.1 (20%), 108.1 (4%); HRMS *m/z*: MNH_4^+ found 196.1703, $C_{12}H_{22}NO$ requires 196.1701.

3-Allylbicyclo[3.1.0]hexan-2-ol 5h



4h **5h**

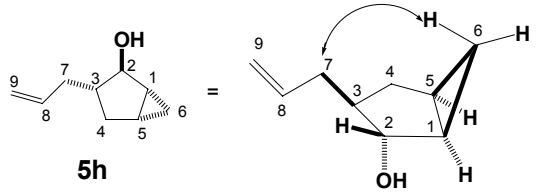
2-(1-Allylbut-3-enyl)oxirane ***4h***

n-BuLi (1.6 M in hexane, 2.2 mL, 3.5 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/3 s) to a stirred solution of 2-allylpent-4-enal[10] (400 mg, 3.22 mmol) and dibromomethane (0.27 mL, 3.86 mmol, 1.2 equiv.) in THF (10 mL) at –78 °C.[6] The resulting mixture was warmed to rt and stirred for 16 h. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separated and the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4h** (289 mg, 2.09 mmol, 65%) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 3078m (C=C), 2997m, 2979s, 2920s (C-H), 1641s (C=C), 1442m, 1417w, 1261w; ^{1}H NMR (400 MHz) 1.30 - 1.38 (m, 1H, H-3), 2.06 - 2.34 (m, 4H, 2 × C*H*$_2$CH=CH$_2$), 2.52 - 2.54 (m, 1H, H-1), 2.76 - 2.80 (m, 2H, H-1′, H-2), 5.02 - 5.12 (m, 4H, 2 × CH$_2$CH=C*H*$_2$), 5.73 - 5.90 (m, 2H, 2 × CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz) 35.1, 36.3 (2 × *C*H$_2$CH=CH$_2$), 41.3 (C-3), 46.9 (C-1), 55.2 (C-2), 116.6, 116.7 (CH$_2$CH=*C*H$_2$), 135.9, 136.0 (CH$_2$*C*H=CH$_2$); MS (CI+) *m/z*: 156.1 (MNH_4^+, 100%), 139.1 (MH^+, 53%), 121.1 (74%), 107.1 (17%); HRMS *m/z*: MNH_4^+ found 156.1391, $C_9H_{18}NO$ requires 156.1388.

3-Allylbicyclo[3.1.0]hexan-2-ol ***5h***

Following the typical cyclopropanation procedure, 2-(1-allylbut-3-enyl)oxirane **4h** (138 mg, 1.00 mmol) was treated with LTMP for 10 h to give 3-allylbicyclo[3.1.0]hexan-2-ol **5h (**96 mg, 0.69 mmol, 69%) as a colorless oil, R_f = 0.3 (50% Et_2O in petrol); IR (film) 3330bs (O-H), 3070m (cyclopropane), 2926s, 2868s (C-H), 1636m (C=C), 1438m, 1414m, 1356m, 1342m, 1265w, 1212w, 1029s; ^{1}H NMR (400 MHz) 0.07 - 0.10 (m, 1H, H-6$_{endo}$), 0.56 - 0.62 (m, 1H, H-6$_{exo}$), 1.34 - 1.41 (m, 2H, H-1, H-4), 1.43 - 1.50 (m, 1H, H-5), 1.70 (s, 1H, OH), 1.88 - 1.96 (m, 1H, H-7), 2.04 - 2.18 (m, 2H, H-3, H-7′), 2.25 - 2.32 (m, 1H, H-4′), 3.95 (d, 1H, H-2, *J* = 2.8), 4.97 - 5.02 (m, 2H, 2 × H-9),

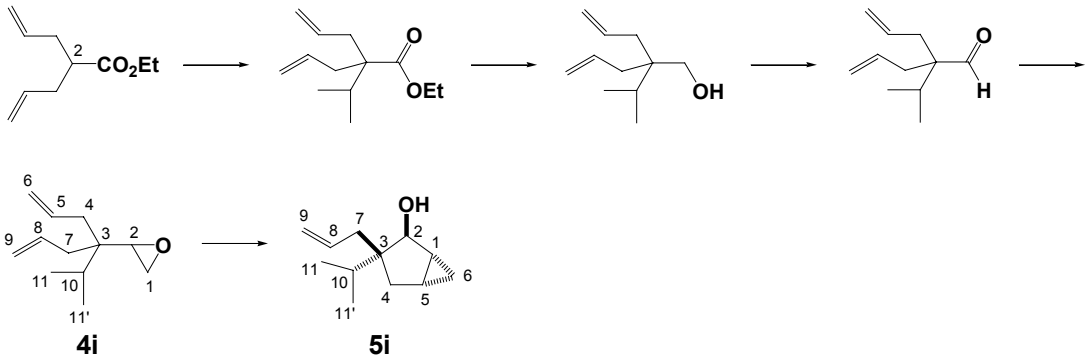
5.69 - 5.79 (m, 1H, H-8); ^{13}C NMR (100 MHz) 10.6 (C-6), 18.5 (C-5), 26.4 (C-1), 32.0 (C-4), 40.6 (C-7), 50.0 (C-3), 80.2 (C-2), 115.5 (C-9), 137.5 (C-8); MS (CI+) *m/z*: 156.1 (MNH_4^+, 10%), 139.1 (MH^+, 20%), 121.1 (67%), 105.1 (4%); HRMS *m/z*: MNH_4^+ found 156.1384, $C_9H_{18}NO$ requires 156.1388.

NOE study 

5h

NOE study: irradiation of H-6_{endo} and H-7s showed reciprocal signal enhancement, but no signal enhancement was observed between H-6_{endo} and H-3.

3-Allyl-3-isopropylbicyclo[3.1.0]hexan-2-ol 5i



4i **5i**

2-(1-Allyl-1-isopropylbut-3-enyl)oxirane ***4i***

n-BuLi (1.6 M in hexane, 0.8 mL, 1.3 mmol, 1.1 equiv.) was added to a stirred solution of diisopropylamine (0.18 mL, 1.31 mmol, 1.1 equiv.) in THF (6 mL) at –78 ˚C. The LDA solution formed was warmed to rt over 15 min, then cooled to –78 ˚C. Ethyl 2-allylpent-4-enoate[9] (200 mg, 1.19 mmol) was added slowly to the mixture. The resulting mixture was stirred for a 1 h at the same temperature and treated with isopropyliodide (3.57 mmol, 608 mg, 0.35 mL, 3.0 equiv.). After 30 min, the mixture was warmed to rt and then stirred for 20 h. The reaction mixture was poured into sat. aq. NH_4Cl (40 mL), the layers were separated and the aqueous layer extracted with Et_2O (50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave ethyl 2-allyl-2-isopropylpent-4-enoate (197 mg, 0.94 mmol, 79%) as a colorless oil, R_f = 0.4 (5% Et_2O in petrol); IR (film) 3076m (C=C), 2970s (CH), 1725s (C=O), 1638m (C=C), 1446m, 1388w, 1369w, 1210s,

1143s, 1032m; ^{1}H NMR (400 MHz) 0.93 (d, 6H, CH(C*H*$_3$)$_2$, *J* = 6.8), 1.27 (t, 3H, OCH$_2$C*H*$_3$, *J* = 7.2), 1.93 (sept, 1H, C*H*(CH$_3$)$_2$, *J* = 7.2), 2.32 (dd, 2H, C*H*$_2$CH=CH$_2$, *J* = 8.0, 14.4), 2.50 (dd, 2H, C*H*$_2$CH=CH$_2$, *J* = 6.8, 14.4), 4.15 (q, 2H, OC*H*$_2$CH$_3$, *J* = 7.6), 5.02 - 5.10 (m, 4H, 2 × CH$_2$CH=C*H*$_2$), 5.74 - 5.85 (m, 2H, 2 × CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz) 14.3 (OCH$_2$*C*H$_3$), 17.9 (CH(*C*H$_3$)$_2$), 33.1 (*C*H(CH$_3$)$_2$), 37.1 (*C*H$_2$CH=CH$_2$), 52.0 (C-2), 60.1 (O*C*H$_2$CH$_3$), 117.6 (CH$_2$CH=*C*H$_2$), 134.9 (CH$_2$*C*H=CH$_2$), 175.2 (C-1); MS (CI+) *m/z*: 228.2 (MNH$_4^+$, 5%), 211.2 (MH$^+$, 100%), 167.1 (5%), 148.1 (5%), 137.1 (2%); HRMS *m/z*: MNH$_4^+$ found 228.1967, C$_{13}$H$_{26}$NO$_2$ requires 228.1964.

DIBALH (1.0 M in hexane, 32.3 mL, 32.3 mmol, 2.1 equiv.) was added slowly to a stirred solution of ethyl 2-allyl-2-isopropylpent-4-enoate (3.23 g, 15.4 mmol) in CH$_2$Cl$_2$ (60 mL) at –78 ˚C. After 3 h, the mixture was treated slowly with MeOH (0.5 mL) and then warmed to rt. The reaction mixture was washed with water (150 mL), followed by aq. HCl (2 M, 50 mL). The aqueous layers were extracted with CH$_2$Cl$_2$ (100 mL), and then the combined organic layers were dried (MgSO$_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et$_2$O in petrol) gave 2-allyl-2-isopropylpent-4-en-1-ol (2.54 g, 15.1 mmol, 98%) as a colorless oil, R_f = 0.3 (10% Et$_2$O in petrol); IR (film) 3433bs (O-H), 3078m (C=C), 2969s, 2889s (C-H), 1630m (C=C), 1467m, 1442m, 1383w, 1363w, 1038m; ^{1}H NMR (400 MHz) 0.93 (d, 6H, CH(C*H*$_3$)$_2$, *J* = 6.8), 1.46 (bs, 1H, OH), 1.82 (sept, 1H, C*H*(CH$_3$)$_2$, *J* = 6.8), 2.13 (d, 4H, 2 × C*H*$_2$CH=CH$_2$, *J* = 7.6), 3.55 (d, 2H, 2 × H-1, *J* = 3.6), 5.04 - 5.14 (m, 4H, 2 × CH$_2$CH=C*H*$_2$), 5.89 - 6.00 (m, 2H, 2 × CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz) 17.3 (CH(*C*H$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 37.8 (*C*H$_2$CH=CH$_2$), 43.0 (C-2), 67.8 (C-1), 117.2 (CH$_2$CH=*C*H$_2$), 135.9 (CH$_2$*C*H=CH$_2$); MS (CI+) *m/z*: 186.2 (MNH$_4^+$, 100 %), 169.2 (MH$^+$, 93%), 151.1 (15%), 137.1 (20%), 125.1 (15%), 109.1 (30%); HRMS *m/z*: MNH$_4^+$ found 186.1862, C$_{11}$H$_{24}$NO requires 186.1858, MH$^+$ found 169.1586, C$_{11}$H$_{21}$O requires 169.1592.

DMSO (2.7 mL, 37.8 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (1.4 mL, 16.6 mmol, 1.1 equiv.) in CH$_2$Cl$_2$ (85 mL) at –78 ˚C. After 5 min, the mixture was treated slowly with a solution of 2-allyl-2-isopropylpent-4-en-1-ol (2.54 g, 15.1 mmol) in CH$_2$Cl$_2$ (15 mL),

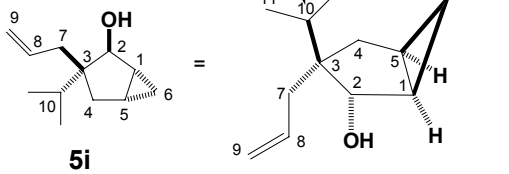
stirred for 15 min and then treated slowly with Et_3N (10.5 mL, 75.5 mmol, 5.0 equiv.). The resulting mixture was stirred at the same temperature for 5 min, warmed to rt and stirred for a further 3 h. The reaction mixture was poured into water (100 mL), the layers were separated, and the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave 2-allyl-2-isopropylpent-4-enal (2.29 g, 13.8 mmol, 91%) as a colorless oil, R_f = 0.6 (10% Et_2O in petrol); IR (film) 3076m (C=C), 2970s (C-H), 2720w, 1725s (C=O), 1638m (C=C), 1465w, 1441w, 1174w; ^{1}H NMR (400 MHz) 0.97 (d, 6H, CH(CH_3)$_2$, J = 7.2) 1.98 (sept, 1H, CH(CH$_3$)$_2$, J = 7.2), 2.26 - 2.44 (m, 4H, 2 × CH_2CH=CH$_2$), 5.07 - 5.13 (m, 4H, 2 × CH$_2$CH=CH_2), 5.70 - 5.80 (m, 2H, 2 × CH$_2$CH=CH$_2$); ^{13}C NMR (100 MHz) 17.5 (CH(*C*H$_3$)$_2$), 31.2 (*C*H(CH$_3$)$_2$), 34.8 (2 × *C*H$_2$CH=CH$_2$), 53.9 (C-2), 118.3 (2 × CH$_2$CH=*C*H$_2$), 133.6 (CH$_2$*C*H=CH$_2$), 206.8 (C-1); MS (CI+) *m/z*: 184.2 (MNH$_4^+$ 100%), 167.1 (MH$^+$, 30%), 151.1 (12%), 137.1 (17%), 124.1 (25%), 109.1 (10%); HRMS *m/z*: MNH$_4^+$ found 184.1706, $C_{11}H_{22}NO$ requires 184.1701.

n-BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/3 s) to a stirred solution of 2-allyl-2-isopropylpent-4-enal (600 mg, 3.61 mmol) and dibromomethane (0.38 mL, 5.42 mmol, 1.5 equiv.) in THF (15 mL) at –78 °C.[6] The resulting mixture was warmed to rt and stirred for a further 16 h. The mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separated and the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4i** (453 mg, 2.51 mmol, 70%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3076m (CH=C), 2977s, 2930s (C-H), 1631m (C=C), 1469w, 1440w, 1386w, 1273w, 1175w; ^{1}H NMR (400 MHz) 0.98, 0.99 (2d, 6H, CH(CH_3)$_2$, J = 6.8), 1.79 (sept, 1H, CH(CH$_3$)$_2$, J = 6.8), 1.96 - 2.18 (m, 4H, 2 × CH_2CH=CH$_2$), 2.63 (dd, 1H, H-1, J = 4.4), 2.67 (dd, 1H, H-1′, J = 2.8, 4.4), 2.90 (dd, 1-H, H-2, J = 2.8, 4.0), 5.02 - 5.12 (m, 4H, 2 × CH$_2$CH=CH_2), 5.76 - 5.94 (m, 2H, 2 × CH$_2$CH=CH$_2$); ^{13}C NMR (100 MHz) 17.3 (CH(*C*H$_3$)$_2$), 17.6 (CH(*C*H$_3$)$_2$), 33.1 (*C*H(CH$_3$)$_2$), 35.9 (*C*H$_2$CH=CH$_2$), 36.1 (*C*H$_2$CH=CH$_2$), 40.4 (C-3), 43.2 (C-1), 56.5 (C-2), 117.3 (CH$_2$CH=*C*H$_2$), 117.4 (CH$_2$CH=*C*H$_2$), 134.7 (CH$_2$*C*H=CH$_2$), 134.8 (CH$_2$*C*H=CH$_2$); MS (CI+) *m/z*:

198.2 (MNH_4^+ 30%), 181.2 (MH^+, 60%), 163.1 (100%), 151.1 (10%), 139.1 (15%), 123.1 (20%), 107.1 (15%); HRMS *m/z*: MNH_4^+ found 198.1849, $C_{12}H_{24}NO$ requires 198.1858.

3-Allyl-3-isopropylbicyclo[3.1.0]hexan-2-ol ***5i***

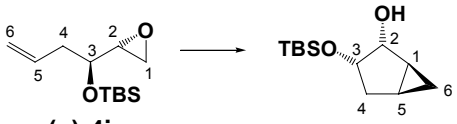
Following the typical cyclopropanation procedure, 2-(1-allyl-1-isopropylbut-3-enyl)oxirane **4i** (180 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 8 h to give bicyclic alcohol **5i** (148 mg, 0.82 mmol, 82%) as a colorless oil, R_f = 0.4 (20% Et_2O in petrol); IR (film) 3435bs (O-H), 3059m (cyclopropane), 3029w, 2960s, 2872s (C-H), 1631m (C=C), 1465m, 1411w, 1386m, 1371m, 1342w, 1322w, 1180w, 1077s, 1057s, 1028m; ^{1}H NMR (400 MHz) 0.05 - 0.08 (m, 1H, H-6$_{endo}$), 0.85 (d, 3H, CH_3, *J* = 6.8), 0.89 - 0.96 (m, 4H, CH_3, H-6$_{exo}$), 1.19 - 1.34 (m, 3H, H-1, H-5, H-4), 1.51 (sept, 1H, H-10, *J* = 6.8), 1.90 (d, 1H, OH, *J* = 6.0), 2.01 (dd, 1H, H-4′, *J* = 6.8, 14.0), 2.15 (dd, 1H, H-7, *J* = 6.8, 14.0), 2.41 (dd, 1H, H-7′, *J* = 7.6, 13.6), 3.72 (d, 1H, H-2, *J* = 5.6), 5.09 (d, 1H, H-9, *J* = 10.0), 5.18 (d, 1H, H-9′, *J* = 16.8), 6.15 - 6.26 (m, 1H, H-8); ^{13}C NMR (100 MHz) 17.3 (C-5), 18.0 (CH_3), 18.4 (CH_3), 19.0 (C-6), 27.5 (C-1), 34.9 (C-7), 36.4 (C-10), 38.8 (C-4), 60.3 (C-3), 82.8 (C-2), 115.6 (C-9), 137.8 (C-8); MS (CI+) *m/z*: 198.2 (MNH_4^+ 10%), 180.2 (MH^+, 45%), 163.1 (100%), 137.1 (5%), 121.1 (15%), 107.1 (7%); HRMS *m/z*: MNH_4^+ found 198.1852, $C_{12}H_{24}NO$ requires 198.1858.

NOE study 

5i

NOE study: irradiation of H-6$_{endo}$, H-10, H-11 and H-11′ showed reciprocal signal enhancement, but no signal enhancement was observed between H-6$_{endo}$ and H-7s.

(2R,3S)-3-tert-Butyldimethylsilanyloxybicyclo[3.1.0]hexan-2-ol (+)-5j



(+)-4j **(+)-5j**

(2R,3S)-3-tert-butyldimethylsilyloxy-1,2-Epoxy-5-hexene ***(+)-4j***

Ti(*i*-PrO)$_4$ (0.41 mL, 1.4 mmol, 0.1 equiv.) was added to a stirred solution of 1,5-hexadien-3-ol (1.37 g, 14.0 mmol), (+)-dicyclohexyl tartrate (717 mg, 2.1 mmol, 0.15 equiv.) and powdered 4 Å molecular sieves (627 mg) in CH_2Cl_2 (16 mL) at –20 ˚C. After 30 min, the mixture was treated dropwise with *t*-BuOOH (6.0 M in decane, 1.4 mL, 8.4 mmol, 0.6 equiv.), and then stirred at the same termperature for a further 19 h. The reaction mixture was poured into a solution of iron (III) sulfate heptahydrate (5.17 g) and citric acid (1.72 g) in water (16 mL) at 0 ˚C, then stirred for 30 min. The reaction was filtered through a pad of celite. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (30% Et_2O in petrol) gave (2*R*,3*S*)-1,2-epoxy-3-hydroxy-5-hexene[11] (1.02 g, assumed to be 7.0 mmol, 50% yield) as a cloudy oil. ^{1}H NMR analysis of the product showed the presence of a significant amount of (+)-dicyclohexyl tartrate, and was used without further purification.

tert-Butyldimethylsilyl chloride (2.11 g, 14.0 mmol, 2.0 equiv.) was added to a stirred solution of (2*R*,3*S*)-1,2-epoxy-3-hydroxy-5-hexene (7.0 mmol) and imidazole (1.19 g, 17.5 mmol, 2.5 equiv.) in CH_2Cl_2 (60 mL) at rt for 5 h. The reaction mixture was washed with sat. aq. $NaHCO_3$ (50 mL), the layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave (2*R*,3*S*)-3-*tert*-butyldimethylsilyloxy-1,2-epoxy-5-hexene **(+)-4j** (1.166 g, 5.11 mmol, 37% from 1,5-hexadien-3-ol) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol), $[\alpha]_D^{25}$ = +32.4˚ (*c* = 1.0, in $CHCl_3$), *ee* = 97%; IR (film) 3079w (epoxide), 2930s, 2858s (C-H), 1643w, 1473m, 1362w, 1253s, 1112s; ^{1}H NMR (400 MHz) 0.05 (s, 6H, 2 × $SiCH_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 2.29 - 2.43 (m, 2H, 2 × H-4), 2.67 (dd, 1H, H-1, *J* = 2.8, 5.6), 2.71

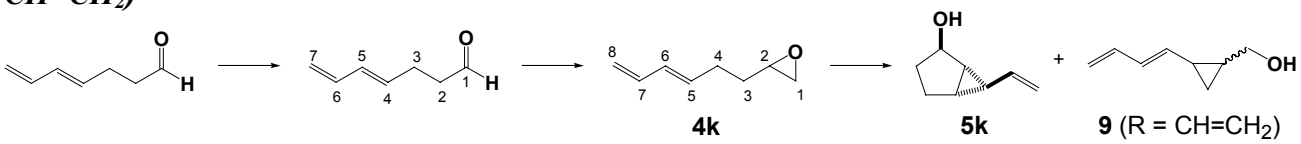
(dd, 1H, H-1′, J = 3.6, 5.2), 2.90 - 2.93 (m, 1H, H-2), 3.61 - 3.65 (m, 1H, H-3), 5.07 - 5.14 (m, 2H, 2 × H-6), 5.82 - 5.93 (m, 1H, H-5); ^{13}C NMR (100 MHz) –4.8 ($SiCH_3$), –4.5 ($SiCH_3$), 18.1 ($SiC(CH_3)_3$), 25.8 ($SiC(CH_3)_3$), 40.0 (C-4), 44.8 (C-1), 54.3 (C-2), 71.0 (C-3), 117.4 (C-6), 134.2 (C-5); MS (CI+) *m/z*: 229.2 (MH^+, 38%), 213.1 (20%), 199.2 (9%), 187.1 (48%), 171.1 (100%), 141.1 (55%), 129.0 (87%), 117.0 (18%); HRMS *m/z*: found 229.1622 $C_{12}H_{25}O_2Si$ required 229.1624.

(2R,3S)-3-tert-Butyldimethylsilanyloxybicyclo[3.1.0]hexan-2-ol ***(+)-5j***

Following the typical cyclopropanation procedure, (2*R*,3*S*)-3-*tert*-butyldimethylsilyloxy-1,2-epoxy-5-hexene **(+)-4j** (228 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give (2*R*,3*S*)-3-*tert*-butyldimethylsilanyloxybicyclo[3.1.0]hexan-2-ol **(+)-5j** (139 mg, 0.61 mmol, 61%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); $[\alpha]_D^{25}$ = +1.0° (*c* = 1.0, in $CHCl_3$), *ee* = 96%; IR (film) 3544bs (O-H), 2931s, 2859s (C-H), 1472m, 1362m, 1253s, 1174m, 1118s, 1086s (Si-O), 1049m, 1019m; ^{1}H NMR (400 MHz) 0.06 (s, 6H, 2 × $SiCH_3$), 0.08 - 0.11 (m, 1H, H-6_{endo}), 0.43 - 0.49 (m, 1H, H-6_{exo}), 0.89 (s, 9H, $SiC(CH_3)_3$), 1.35 - 1.41 (m, 1H, H-5), 1.50 - 1.54 (m, 1H, H-1), 1.74 - 1.80 (m, 1H, H-4), 1.96 (dd, 1H, H-4′, J = 7.2, 12.4), 2.93 (s, 1H, OH), 3.78 - 3.83 (m, 1H, H-3), 3.91 (d, 1H, H-2, J = 4.8); ^{13}C NMR (100 MHz) –5.1 ($SiCH_3$), –4.7 ($SiCH_3$), 7.4 (C-6), 15.6 (C-5), 18.0 ($SiC(CH_3)_3$), 21.0 (C-1), 25.7 ($SiC(CH_3)_3$), 33.4 (C-4), 72.3 (C-3), 72.4 (C-2); MS (CI+) *m/z*: 229.2 (MH^+, 6%), 211.1 (100%), 187.1 (10%), 171.1 (93%), 153.1 (6%), 132.1 (7%), 115.1 (10%), 105.0 (13%); HRMS *m/z*: MH^+ found 229.1618 $C_{12}H_{25}O_2Si$ required 229.1624.

Procedures for the formation of bicyclic alcohols 5k-o and 18a-b from epoxides 4k-o and LTMP (Table 2 in main paper)

exo-6-Vinylbicyclo[3.1.0]hexan-2-ol 5k and (2-buta-1,3-dienyl-cyclopropyl)-methanol 9 (R = CH=CH₂)



4k **5k** **9** (R = CH=CH$_2$)

1,2-Epoxy-5,7-octadiene ***4k***

DIBALH (1.0 M in hexane, 2.9 mL, 2.9 mmol, 1.0 equiv.) was added slowly to a stirred solution of methyl (4*E*)-hepta-4,6-dienoate (400 mg, 2.85 mmol) in CH_2Cl_2 (12 mL) at –78 ˚C. After 1 h, the

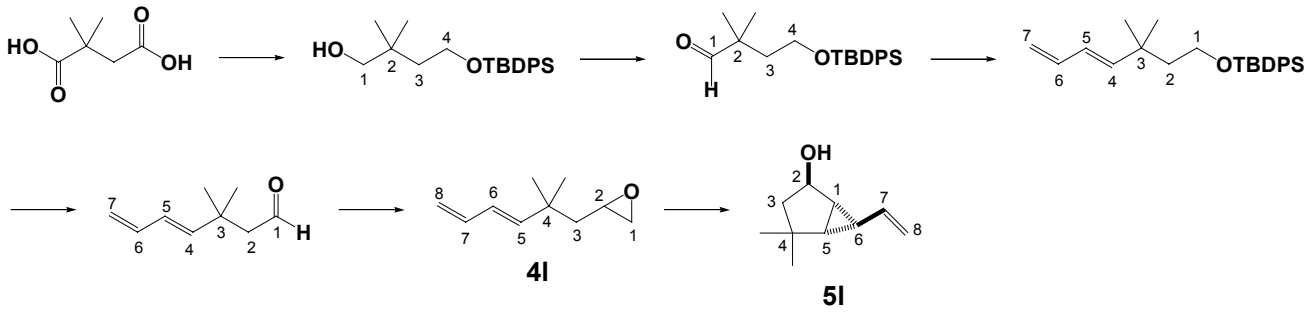
mixture was treated slowly with MeOH (2 drops) and then warmed to rt. The mixture was washed with water (30 mL) and the layers were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave (4*E*)-hepta-4,6-dienal (228 mg, 2.07 mmol, 73%) as a colorless oil, R_f = 0.2 (10 % Et_2O in petrol); IR (film) 3086w, 3009w, 2913w, 2826w (C-H), 2720w, 1725s (C=O), 1653w (C=C), 1600w, 1446w, 1412w, 1388w, 1008m; ^{1}H NMR (400 MHz) 2.40 - 2.45 (m, 2H, 2 × H-3), 2.53 - 2.58 (m, 2H, 2 × H-2), 5.00 (d, 1H, H-7, *J* = 10.0), 5.12 (d, 1H, H-7′, *J* = 17.2), 5.65 - 5.73 (m, 1H, H-4), 6.06 - 6.12 (m, 1H, H-5), 6.24 - 6.34 (m, 1H, H-6), 9.78 (t, 1H, H-1, *J* = 1.2); ^{1}H NMR (100 MHz) 25.0 (C-3), 43.1 (C-2), 115.9 (C-7), 132.1 (C-5), 132.3 (C-4), 136.7 (C-6), 201.7 (C=O); MS (CI+) *m/z*: 128.2 (MNH_4^+, 100%), 112.6 (35%); HRMS *m/z*: MNH_4^+ found 128.1925, $C_7H_{14}NO$ requires 128.1922.

n-BuLi (1.6 M in hexane, 4.6 mL, 7.32 mmol, 1.05 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of (4*E*)-hepta-4,6-dienal (768 mg, 6.97 mmol) and dibromomethane (0.74 mL, 10.50 mmol, 1.5 equiv.) in THF (28 mL) at –78 ˚C. The resulting mixture was warmed to rt and stirred for 15 h. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4k** (579 mg, 4.66 mmol, 67%) as a colorless oil, R_f = 0.6 (10% Et_2O in petrol); IR (film) 3038w (epoxide), 2990s, 2922s, 2855w (C-H), 1715w, 1648w, 1600w, 1480w, 1441m, 1412m, 1258w (epoxide), 1133w, 1003s; ^{1}H NMR (400 MHz) 1.61 - 1.68 (m, 2H, 2 × H-3), 2.21 - 2.32 (m, 2H, 2 × H-4), 2.48 - 2.50 (m, 1H, H-1), 2.75 - 2.77 (m, 1H, H-1′, 2.91 - 2.96 (m, 1H, H-2), 4.99 (d, 1H, H-8, *J* = 10.0), 5.10 (d, 1H, H-8′, *J* = 16.8), 5.69 - 5.76 (m, 1H, H-5), 6.10 (dd, 1H, H-6, *J* = 10.4, 15.2), 6.31 (dt, 1H, H-7, *J* = 10.4, 16.8); ^{13}C NMR (100 MHz) 29.0 (C-4), 32.0 (C-3), 47.1 (C-1), 51.8 (C-2), 115.4 (C-8), 131.7 (C-6), 133.6 (C-5), 136.9 (C-7); MS (CI+) *m/z*: 142.1230 (MNH_4^+ 100%), 125.0946 (MH^+, 50%), 107.0878 (20%); HRMS *m/z*: MNH_4^+ found 142.1230, $C_8H_{16}NO$ requires 142.1232.

exo-6-Vinylbicyclo[3.1.0]hexan-2-ol ***5k*** *and (2-buta-1,3-dienyl-cyclopropyl)-methanol* ***9*** *(R = CH=CH$_2$)*

Following the typical cyclopropanation procedure, 1,2-epoxy-5,7-octadiene **4k** (124 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give an inseparable 1:1.5 mixture of bicyclic alcohol **5k** and cyclopropane **9** (R = CH=CH$_2$) (80 mg, 0.65 mmol, 65%) as a light yellow oil, R_f = 0.5 (50% Et$_2$O in petrol). Ratio determined in ^{1}H NMR using the CHOH signal of **5r** and CH$_2$OH signal of **9** (R = CH=CH$_2$).

exo-4,4-Dimethyl-6-vinylbicyclo[3.1.0]hexan-2-ol 5l



(5E)-1,2-Epoxy-4,4-dimethylocta-3,5-diene ***4l***

LiAlH$_4$ (2.3 M in THF, 52.2 mL, 120 mmol, 6.0 equiv.) was added slowly to a stirred solution of 2,2-dimethylsuccinic acid (2.92 g, 20.0 mmol) in THF (250 mL) at –78 ˚C and stirred at rt for 5 h. The reaction mixture was cooled to –78 ˚C and quenched by sequential addition of water (4.6 mL), aq. NaOH (15 w%, 4.6 mL) and water (13.8 mL). The solid precipitates formed were filtered and washed through with Et$_2$O (2 × 150 mL). The filtrate was dried (MgSO$_4$), filtered and concentrated to give the 2,2-dimethyl-butane-1,4-diol (2.33 g, 19.7 mmol, 99%) as a coulourless oil, which was sufficiently pure to be used without further purification. *tert*-Butyldiphenylsilyl chloride (0.52 mL, 2.0 mmol, 1.0 equiv.) was added to a stirred solution of 2,2-dimethyl-butane-1,4-diol (236 mg, 2.0 mmol) and imidazole (204 mg, 3.0 mmol, 1.5 equiv.) in anhydrous DMF (5 mL) at rt. After 20 h, the mixture was diluted with Et$_2$O (20 mL) washed with sat. aq. NaHCO$_3$ (25 mL), the layers were separated and then the aqueous layer extracted with Et$_2$O (20 mL). The combined organic layers were dried (MgSO$_4$), filtered and concentrated to give the crude product. Purification by column chromatography (30% Et$_2$O in petrol) gave 4-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylbutan-1-ol (522 mg, 1.46 mmol, 73%) as a colorless oil, R_f = 0.3 (30% Et$_2$O in petrol); IR (film) 3431bs (O-H),

3072m, 2957s (C-H), 1472s, 1428s, 1391m, 1363m, 1111s (Si-O), 1056s; ^{1}H NMR (400 MHz) 0.92 (s, 6H, 2 × CH_3), 1.08 (s, 9H, SiC(CH_3)$_3$), 1.57 (t, 2H, 2 × H-3, J = 4.0), 3.40 (d, 2H, 2 × H-1, J = 4.0), 3.74 (t, 2H, 2 × H-4, J = 4.0), 7.40 - 7.48 (m, 6H, 6 × Ar-H), 7.69 - 7.71 (m, 4H, 4 × Ar-H); ^{13}C NMR (100 MHz) 19.0 (SiC(CH$_3$)$_3$), 25.0 (CH_3), 26.8 (SiC(CH$_3$)$_3$), 26.0 (C-2), 42.0 (C-3), 61.1 (C-4), 71.6 (C-1), 127.8 (Ar-C), 129.8 (Ar-C), 133.0 (Ar-C), 135.5 (Ar-C); MS (CI+) *m/z*: 357.2 (MH^+, 3%), 279.2 (16%), 229.1 (11%), 216.1 (4%), 199.1 (100%), 181.0 (11%); HRMS *m/z*: MH^+ found 357.2233, $C_{22}H_{33}O_2Si$ requires 357.2250.

DMSO (3.0 mL, 42.9 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (1.6 mL, 18.9 mmol, 1.1 equiv.) in CH_2Cl_2 (80 mL) at –78 ˚C and stirred for 5 min. The mixture was treated slowly with a solution of 4-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylbutan-1-ol (6.12 g, 17.2 mmol) in CH_2Cl_2 (20 mL), stirred for 15 min and then treated slowly with Et_3N (12.0 mL, 86.0 mmol, 5.0 equiv.). After 5 min, the resulting mixture was warmed to rt and stirred for a further 12 h. The reaction mixture was washed with water (100 mL), the layers were separated and then the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave 4-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylbutyraldehyde (5.55 g, 15.7 mmol, 91%) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 3072m, 2932s (C-H), 2707m, 1732s (C=O), 1472s, 1428s, 1391m, 1363m, 1188w, 1111s (Si-O), 1053m; ^{1}H NMR (400 MHz) 1.07 (s, 9H, SiC(CH_3)$_3$), 1.10 (s, 6H, 2 × CH_3), 1.83 (t, 2H, 2 × H-3, J = 4.0), 3.68 (t, 2H, 2 × H-4, J = 4.0), 7.40 - 7.48 (m, 6H, Ar-H), 7.68 - 7.70 (m, 4H, Ar-H), 9.59 (s, 1H, CHO); ^{1}H NMR (100 MHz) 19.0 (SiC(CH$_3$)$_3$), 21.5 (CH_3), 26.7 (SiC(CH$_3$)$_3$), 40.6 (C-3), 44.5 (C-2), 60.1 (C-4), 127.6 (Ar-C), 129.6 (Ar-C), 133.3 (Ar-C), 135.5 (Ar-C), 205.3 (C=O); MS (CI+) *m/z*: 372.2 (MNH_4^+, 2%), 355.2 (MH^+, 86%), 325.2 (5%), 297.1 (83%), 277.2 (23%), 267.1 (12%), 216.1 (11%), 199.1 (28%), 148.1 (24%); HRMS *m/z*: MNH_4^+ found 372.2364, $C_{22}H_{34}NO_2Si$ requires 372.2359.

n-BuLi (1.6 M in hexane, 8.7 mL, 13.9 mmol, 1.2 equiv.) was added to a stirred solution of allyl diethyl phosphonate (2.47 g, 13.9 mmol, 1.2 equiv.) in THF (85 mL) at –78 °C[12] and stirred for 15 min. The mixture was treated slowly with a solution of 4-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylbutyraldehyde (4.10 g, 11.6 mmol) and HMPA (4.0 mL, 23.2 mmol, 2.0 equiv.) in THF (10 mL), and then stirred for 2 h. The resulting mixture was warmed to rt, and then stirred for a further 12 h. The reaction mixture was washed with aq. HCl (1 N, 200 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10 % Et_2O in petrol) gave (4*E*)-*tert*-butyl-(3,3-dimethylhepta-4,6-dienyloxy)diphenylsilane (3.73 g, 9.85 mmol, 85%) as a colorless oil, R_f = 0.7 (10% Et_2O in petrol); IR (film) 3071m, 2960s (C-H), 2858s, 1649w, 1602w, 1472m, 1390m, 1362m, 1188w, 1111s (Si-O), 1044m, 1005s; ^{1}H NMR (400 MHz) 1.00 (s, 6H, 2 × CH_3), 1.07 (s, 9H, (SiC(CH_3)$_3$), 1.66 (t, 2H, 2 × H-2, *J* = 8.0), 3.69 (t, 2H, 2 × H-1, *J* = 8.0), 4.97 (d, 1H, H-7, *J* = 12.0), 5.10 (d, 1H, H-7′, *J* = 20.0), 5.62 (d, 1H, H-4, *J* = 16.0), 5.93 (dd, 1H, H-5, *J* = 12.0, 16.0), 6.23 - 6.30 (m, 1H, H-6); ^{13}C NMR (100 MHz) 19.1 (Si*C*(CH$_3$)$_3$), 26.8 (SiC(*C*H$_3$)$_3$), 27.5 (CH_3), 35.1 (C-3), 45.1 (C-2), 61.2 (C-1), 114.8 (C-7), 126.8 (C-5), 127.6 (Ar-C), 129.5 (Ar-C), 134.0 (C-6), 135.6 (Ar-C), 137.6 (Ar-C), 144.7 (C-5); MS (CI+) *m/z*: 379.2 (MH^+, 100%), 321.2 (59%), 199.1 (21%), 148.1 (100%), 123.1 (61%); HRMS *m/z*: MH^+ found 379.2452, $C_{22}H_{35}OSi$, requires 379.2457.

TBAF (1.0 M in THF, 19.7 mL, 19.7 mmol, 2.0 equiv.) was added to a stirred solution of (4*E*)-*tert*-butyl-(3,3-dimethylhepta-4,6-dienyloxy)diphenylsilane (3.73 g, 9.85 mmol) in THF (20 mL) at rt. After 12 h, the mixture was poured into water (80 mL) and the aqueous layer extracted with Et_2O (80 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give (4*E*)-3,3-dimethylhepta-4,6-dien-1-ol (1.43 g, 10.2 mmol) as a colorless oil, which was sufficiently pure to be used without further purification. DMSO (1.8 mL, 25.5 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (1.1 mL, 11.2 mmol, 1.1 equiv.) in CH_2Cl_2 (40 mL) at –78 °C and stirred for 5 min. The mixture was treated slowly with a solution of the above alcohol (1.43 g, 10.2 mmol) in CH_2Cl_2 (10 mL), stirred for a 15 min and then treated slowly with Et_3N (7.1 mL, 51.0

mmol, 5.0 equiv.). After 5 min, the mixture was warmed to rt and stirred for a further 5 h. The reaction mixture was washed with water (100 mL), the layers were separated and then the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave (4*E*)-3,3-dimethylhepta-4,6-dienal (1.20 g, 8.68 mmol, 88% from (4*E*)-*tert*-butyl-(3,3-dimethylhepta-4,6-dienyloxy)diphenylsilane) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 2964s (C-H), 2735w, 1722s (C=O), 1649w, 1603w, 1470w, 1386w, 1045w, 1007s; ^{1}H NMR (400 MHz) 1.18 (s, 6H, 2 × CH_3), 2.36 (d, 2H, 2 × H-2, *J* = 2.8), 5.04 (d, 1H, H-7, *J* = 10.0), 5.17 (d, 1H, H-7′, *J* = 16.9), 5.78 (d, 1H, H-4, *J* = 15.2), 6.05 (dd, 1H, H-5, *J* = 10.0, 15.2), 6.27 - 6.37 (m, 1H, H-6); ^{13}C NMR (100 MHz) 27.6 (CH_3), 35.4 (C-3), 55.0 (C-2), 116.4 (C-7), 128.1 (C-5), 136.9 (C-6), 142.2 (C-4), 203.0 (C-1); MS (CI+) *m/z*: 156.1 (MNH_4^+, 91%), 148.1 (76%), 139.1 (100%), 131.1 (4%), 123.1 (6%), 109.1 (10%); HRMS *m/z*: MNH_4^+ found 156.1391, $C_9H_{18}NO$, requires 156.1388.

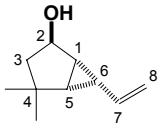
n-BuLi (1.6 M in hexane, 6.0 mL, 9.6 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of (4*E*)-3,3-dimethylhepta-4,6-dienal (1.20 g, 8.68 mmol) and dibromomethane (0.73 mL, 10.4 mmol, 1.2 equiv.) in THF (35 mL) at –78 °C.[6] The resulting mixture was warmed to rt and stirred for 16 h. The reaction mixture was washed with sat. aq. NH_4Cl (40 mL), the layers were separated and then the aqueous aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave (5*E*)-1,2-epoxy-4,4-dimethylocta-3,5-diene **4l** (695 mg, 4.57 mmol, 53%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3086w (epoxide), 3039m, 2963s (C-H), 1649m, 1603w, 1469m, 1385m, 1365m, 1260w, 1190w, 1006s; ^{1}H NMR (400 MHz) 1.12 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.49 - 1.59 (m, 2H, 2 × H-3), 2.40 - 2.42 (m, 1H, H-1), 2.73 (dd, 1H, H-1′, *J* = 4.0, 8.0), 2.88 - 2.93 (m, 1H, H-2), 5.00 (d, 1H, H-8, *J* = 12.0), 5.15 (d, 1H, H-8′, *J* = 16.0), 5.74 (d, 1H, H-5, *J* = 16.0), 6.04 (dd, 1H, H-6, *J* = 12.0, 16.0), 6.29 - 6.38 (m, 1H, H-7); ^{13}C NMR (100 MHz) 27.1 (CH_3), 27.7 (CH_3), 35.9 (C-4), 45.5 (C-3), 46.8 (C-1), 49.5 (C-2), 115.5 (C-8), 127.4 (C-6), 137.3 (C-7), 143.9 (C-5); MS (CI+) *m/z*: 170.2 (MNH_4^+, 34%), 153.1

(100%), 148.1 (19%), 135.1 (71%), 119.1 (11%), 109.0 (16%); HRMS *m/z*: MNH_4^+ found 170.1537 $C_{10}H_{20}NO$, requires 170.1545.

exo-4,4-Dimethyl-6-vinylbicyclo[3.1.0]hexan-2-ol ***5l***

Following the typical cyclopropanation procedure, (5*E*)-1,2-epoxy-4,4-dimethylocta-3,5-diene **4l** (152 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give bicyclic alcohol **5l** (114 mg, 0.75 mmol, 75%) as a colorless oil, R_f = 0.5 (50% Et_2O in petrol); IR (film) 3357bs (O-H), 3082w, 2954s (C-H), 2868m, 1638s, 1466m, 1364m, 1337m, 1151s, 1036m; ^{1}H NMR (400 MHz) 1.05 (s, 3H, CH_3), 1.08 - 1.11 (m, 1H, H-6), 1.26 (s, 3H, CH_3), 1.27 - 1.44 (m, 3H, H-3, H-3′, H-5), 1.51 - 1.52 (m, 1H, H-1), 1.62 (bs, 1H, OH), 4.32 (d, 1H, H-2, *J* = 4.0), 4.83 (dd, 1H, H-8, *J* = 4.0, 12.0), 4.99 (d, 1H, H-8′, *J* = 20.0), 5.31 - 5.41 (m, 1H, H-7); ^{13}C NMR (100 MHz) 23.2 (C-6), 26.6 (CH_3), 30.4 (CH_3), 33.9 (C-1), 38.5 (C-5), 39.1 (C-3), 46.3 (C-4), 75.1 (C-2), 111.4 (C-8), 139.5 (C-7); MS (CI+) *m/z*: 170.2 (MNH_4^+, 3%), 152.1 (MH^+, 50%), 135.1 (100%), 119.1 (8%), 108.1 (6%); HRMS *m/z*: MNH_4^+ found 170.1544 $C_{10}H_{20}NO$, requires 170.1545.

endo-4,4-Dimethyl-6-vinylbicyclo[3.1.0]hexan-2-ol 5m



5m

(5Z)-1,2-Epoxy-4,4-dimethylocta-5,7-diene ***4m***

t-BuLi (1.5 M in hexane, 2.2 mL, 3.3 mmol, 1.0 equiv.) was added to a stirred solution of allyl trimethylsilane (377 mg, 3.30 mmol) and TMEDA (0.5 mL, 3.3 mmol, 1.0 equiv.) in THF (11 mL) at –78 ˚C. The mixture was warmed to –30 ˚C, stirred for 2 h and then cooled to –78 ˚C. The mixture was treated with Ti(*i*-PrO)$_4$ (1.0 mL, 3.3 mmol), stirred for 1 h and then treated slowly with a solution of 4-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylbutyraldehyde (see synthesis of **4l**, 1.06 g, 3.0 mmol,) in THF (2 mL). After 3.5 h at –78 ˚C, the mixture was quenched by slow addition of aq.

HCl (2 M, 10 mL) and then warmed to rt. The layers were separated and the aqueous layer extracted with Et_2O (40 mL). The combine organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave 1-(*tert*-butyldiphenylsilyloxy)-3,3-dimethyl-5-trimethylsilylhept-6-en-4-ol (1.00 g, 2.13 mmol, 71%) as a colorless oil; R_f = 0.6 (10% Et_2O in petrol); IR (film) 3412bs (O-H), 3072s, 2958s (C-H), 2892s, 1620m, 1472s, 1428s, 1390s, 1364m, 1245s, 1158s, 1112s (Si-O), 1029s; ^{1}H NMR (400 MHz) 0.07 (s, 9H, $Si(CH_3)_3$), 0.90 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 1.08 (s, 9H, $SiC(CH_3)_3$), 1.40 - 1.46 (m, 1H, H-2), 1.74 - 1.81 (m, 1H, H-2′), 1.94 (d, 1H, H-5, J = 10.4), 3.68 - 3.74 (m, 3H, 2 × H-1, H-4), 3.89 (s, 1H, OH), 4.81 (d, 1H, H-7, J = 17.2), 4.89 (d, 1H, H-7′, J = 10.0), 6.10 - 6.20 (m, 1H, H-6); ^{13}C NMR (100 MHz) – 2.4 ($Si(CH_3)_3$), 19.0 ($SiC(CH_3)_3$), 23.6 (CH_3), 25.9 (CH_3), 26.8 ($CSi(CH_3)_3$), 38.5 (C-5), 40.1 (C-3), 44.1 (C-2), 61.2 (C-1), 76.5 (C-4), 111.3 (C-7), 127.8 (Ar-C), 129.8 (Ar-C), 132.8 (Ar-C), 132.9 (Ar-C), 135.6 (Ar-C), 137.7 (C-6); MS (CI+) *m/z*: 451.3 ($[M–H_2O]H^+$, 1%), 379.2 (100%), 321.2 (66%), 297.1 (18%), 243.1 (14%), 216.1 (21%), 199.1 (43%), 123.1 (82%); HRMS *m/z*: $[M–H_2O]H^+$ found 451.2835 $C_{28}H_{43}OSi_2$, requires 451.2852.

KH (30% in mineral oil, 340 mg, 2.55 mmol, 3.0 equiv.) was washed with dry petrol four times and then dried under a flow of argon. A stirred suspension of KH in THF (12 mL) at rt was treated slowly with a solution of 1-(*tert*-butyldiphenylsilyloxy)-3,3-dimethyl-5-trimethylsilylhept-6-en-4-ol (398 mg, 0.85 mmol). Hydrogen evolution ceased after 5 min and the mixture was stirred for 1 h. The mixture was poured slowly into sat. aq. NH_4Cl (25 mL), the layers were separated and then the aqueous layer extracted with Et_2O (20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave (4*Z*)-*tert*-butyl-(3,3-dimethyl-hepta-4,6-dienyloxy)diphenylsilane (286 mg, 0.76 mmol, 89%) as a colorless oil; R_f = 0.8 (5% Et_2O in petrol); IR (film) 3071w, 2959s (C-H), 2858s, 1589m, 1472s, 1428s, 1389m, 1363m, 1111s (Si-O), 1047m; ^{1}H NMR (400 MHz) 1.08 (s, 9H, $SiC(CH_3)_3$), 1.15 (s, 6H, 2 × CH_3), 1.77 - 1.81 (m, 2H, 2 × H-2), 3.73 - 3.77 (m, 2H, 2 × H-1), 5.08 - 5.15 (m, 2H, 2 × H-7), 5.27 (d, 1H, H-4, J = 12.0), 5.81 - 5.88 (m, 1H, H-5), 6.75 - 6.85 (m, 1H, H-6), 7.38 - 7.47 (m, 6H, Ar-H), 7.69 - 7.72 (m, 4H, Ar-H); ^{13}C NMR (100 MHz) 19.1 ($SiC(CH_3)_3$),

26.9 (SiC(CH$_3$)$_3$), 29.8 (CH$_3$), 36.0 (C-3), 46.4 (C-2), 61.3 (C-1), 117.8 (C-7), 127.6 (Ar-C), 128.4 (C-5), 129.5 (Ar-C), 133.2 (C-6), 134.0 (Ar-C), 135.6 (Ar-C), 140.6 (C-4); MS (CI+) *m/z*: 379.2 (MH$^+$, 100%), 321.2 (75%), 243.1 (14%), 199.1 (27%), 123.1 (72%); HRMS *m/z*: MH$^+$ found 379.2459 $C_{25}H_{35}OSi$, requires 379.2457.

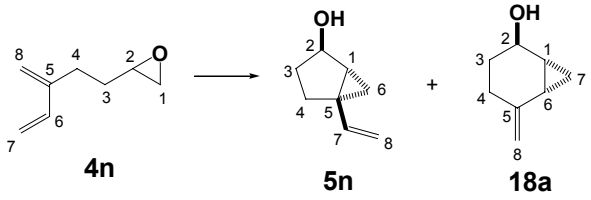
TBAF (1.0 M in THF, 49.2 mL, 49.2 mmol, 2.0 equiv.) was added to a stirred solution of (4*Z*)-*tert*-butyl-(3,3-dimethyl-hepta-4,6-dienyloxy)diphenylsilane (9.30 g, 24.6 mmol) in THF (80 mL) at rt and then stirred for 12 h. The mixture was washed with water (200 mL), the layers were separated and then the aqueous layer extracted with Et_2O (200 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give (4*Z*)-3,3-dimethylhepta-4,6-dien-1-ol (3.45 g, 24.6 mmol) as a colorless oil, which was sufficiently pure to be used without further purification. DMSO (4.4 mL, 61.5 mmol, 2.5 equiv.) was added slowly to a stirred solution of oxalyl chloride (2.6 mL, 27.1 mmol, 1.1 equiv.) in CH_2Cl_2 (110 mL) at –78 ˚C and stirred for 5 min. The mixture was treated slowly with a solution of the above alcohol (3.45 g, 24.6 mmol) in CH_2Cl_2 (20 mL), stirred for 15 min and then treated slowly with Et_3N (17.1 mL, 123 mmol, 5.0 equiv.). After 5 min, the mixture was warmed to rt and stirred for a further 12 h. The reaction mixture was washed with water (100 mL), the layers were separated and then the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O in petrol) gave (4*Z*)-3,3-dimethylhepta-4,6-dienal (2.78 g, 20.1 mmol, 82% from (4*Z*)-*tert*-butyl-(3,3-dimethyl-hepta-4,6-dienyloxy)diphenylsilane) as a colorless oil, R_f = 0.5 (10% Et_2O in petrol); IR (film) 3089w, 2963s (C-H), 2734m, 1722s (C=O), 1586w, 1470m, 1389w, 1367m, 1254w, 1154w, 1047m; ^{1}H NMR (400 MHz) 1.30 (s, 6H, 2 × CH$_3$), 2.49 (d, 2H, 2 × H-2, J = 2.0), 5.17 - 5.21 (m, 2H, 2 × H-7), 5.44 (d, 1H, H-4, J = 12.0), 5.96 (t, 1H, H-5, J = 12.0), 6.74 - 6.83 (m, 1H, H-6), 9.74 (t, 1H, H-1, J = 4.2); ^{3}C NMR (100 MHz) 29.8 (CH$_3$), 35.8 (C-3), 56.5 (C-2), 119.4 (C-7), 129.5 (C-5), 132.4 (C-6), 138.2 (C-4), 202.8 (C-1); MS (CI+) *m/z*: 156.1 (MNH$_4^+$, 63%), 148.1 (21%), 139.1 (28%), 121.1 (14%), 109.1 (16%), 95.1 (100%); HRMS *m/z*: MNH$_4^+$ found 156.1386 $C_9H_{18}NO$, requires 156.1388.

n-BuLi (1.6 M in hexane, 6.0 mL, 9.6 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of (4*Z*)-3,3-dimethylhepta-4,6-dienal (1.20 g, 8.68 mmol) and dibromomethane (0.73 mL, 10.4 mmol, 1.2 equiv.) in THF (35 mL) at –78 ˚C.[6] The resulting mixture was warmed to rt and stirred for 16 h. The reaction mixture was washed with sat. aq. NH_4Cl (40 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave epoxide **4m** (707 mg, 4.64 mmol, 53%) as a colorless oil, R_f = 0.4 (10% Et_2O in petrol); IR (film) 3088w (epoxide), 3045w, 2962s, 2926s (C-H), 2873m, 1722m, 1470m, 1434w, 1410w, 1366m, 1168m; ^{1}H NMR (400 MHz) 1.24 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.60 - 1.70 (m, 2H, 2 × H-3), 2.44 (dd, 1H, H-1, *J* = 2.8, 5.2), 2.74 (dd, 1H, H-1′, *J* = 4.4), 2.94 - 2.98 (m, 1H, H-2), 5.12 - 5.18 (m, 2H, 2 × H-8), 5.40 (d, 1H, H-5, *J* = 12.4), 5.94 (t, 1H, H-6, *J* = 11.6), 6.78 - 6.88 (m, 1H, H-7); ^{13}C NMR (100 MHz) 29.5 (CH_3), 29.8 (CH_3), 36.8 (C-4), 46.6 (C-3), 46.9 (C-1), 49.8 (C-2), 118.4 (C-8), 128.9 (C-6), 132.9 (C-7), 139.8 (C-5); MS (CI+) *m/z*: 170.2 (MNH_4^+, 39%), 153.1 (MH^+, 45%), 135.1 (89%), 119.1 (16%), 109.1 (20%); HRMS *m/z*: MNH_4^+ found 170.1539 $C_{10}H_{20}NO$, requires 170.1545.

endo-4,4-Dimethyl-6-vinylbicyclo[3.1.0]hexan-2-ol ***5m***

Following the typical cyclopropanation procedure, (5*Z*)-1,2-epoxy-4,4-dimethylocta-3,5-diene **4m** (152 mg, 1.0 mmol) was treated with LTMP in *t*-BuOMe for 16 h to give bicyclic alcohol **5m** (119 mg, 0.78 mmol, 78%) as a colorless oil, R_f = 0.3 (40% Et_2O in petrol); IR (film) 3355bs (O-H), 3081w, 2953s (C-H), 2869m, 1626m, 1455m, 1335m, 1221w, 1145m, 1005s (C=C); ^{1}H NMR (400 MHz) 1.05 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.42 - 1.46 (m, 1H, H-6), 1.56 - 1.77 (m, 5H, H-1, 2 × H-3, H-5, OH), 4.27 (d, 1H, H-2, *J* = 5.2), 5.05 (dd, 1H, H-8, *J* = 1.2, 10.0), 5.22 (dd, 1H, H-8′, *J* = 1.2, 16.8), 5.69 - 5.78 (m, 1H, H-7); ^{13}C NMR (100 MHz) 24.4 (CH_3), 25.8 (CH_3), 31.8 (C-6), 32.9 (C-1), 37.0 (C-5), 39.8 (C-3), 49.5 (C-4), 74.8 (C-2), 117.0 (C-8), 135.4 (C-7); MS (CI+) *m/z*: 170.2 (MNH_4^+, 2%), 152.1 (8%), 135.1 (100%), 119.1 (25%), 107.1 (6%); HRMS *m/z*: MNH_4^+ found 170.1546 $C_{10}H_{20}NO$, requires 170.1545.

5-Vinylbicyclo[3.1.0]hexan-2-ol 5n and 5-methylenebicyclo[4.1.0]heptan-2-ol 18a



1,2-Epoxy-5-methylene-6-heptene ***4n***

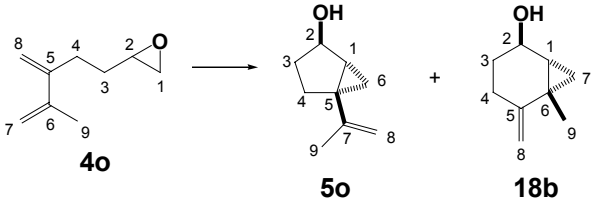
n-BuLi (1.6 M in hexane, 7.5 mL, 12.0 mmol) was added slowly to a stirred solution of *t*-BuOK (1.35 g, 12.0 mmol) and 2,2,6,6-tetramethylpiperidine (1.69 mL, 10.0 mmol) in THF (15 mL) at –78 ˚C. After 45 min, the mixture was treated with isoprene (2.0 mL, 20 mmol), and then stirred for a further 45 min to give a red solution. Epichlorohydrin (0.47 mL, 6.0 mmol) was added to the reaction mixture in one portion. After 2 h at –78 ˚C, the mixture was poured into sat. aq. NH_4Cl (40 mL). The layers were separated and the aqueous layer extracted with Et_2O (40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave 1,2-epoxy-5-methylene-6-heptene **4n** (263 mg, 2.12 mmol, 35%) as a colorless oil; R_f = 0.4 (5% Et_2O in petrol); IR (film) 3090w, 3048w (epoxide), 2981s, 2924s (C-H), 1596s, 1410w, 1261w; ^{1}H NMR (400 MHz) 1.66 - 1.83 (m, 2H, 2 × H-3), 2.32 - 2.47 (m, 2H, 2 × H-4), 2.50 (dd, 1H, H-1, *J* = 2.8, 4.8), 2.77 (t, 1H, H-1′, *J* = 4.4), 2.95 - 2.99 (m, 1H, H-2), 5.04 (d, 2H, 2 × H-8, *J* = 8.0), 5.09 (d, 1H, H-7, *J* = 10.8), 5.25 (d, 1H, H-7′, *J* = 17.6), 6.38 (dd, 1H, H-67, *J* = 10.8, 17.6); ^{13}C NMR (100 MHz) 27.5 (C-4), 31.0 (C-3), 47.2 (C-1), 52.0 (C-2), 113.5 (C-7), 116.1 (C-8), 138.5 (C-6), 145.2 (C-5); MS (CI+) *m/z*: 142.1 (MNH_4^+, 100%), 125.1 (MH^+, 41%), 107.1 (43%); HRMS *m/z*: MNH_4^+ found 142.1233, $C_8H_{16}NO$ requires 142.1232.

5-Vinylbicyclo[3.1.0]hexan-2-ol ***5n*** *and 5-methylenebicyclo[4.1.0]heptan-2-ol* ***18a***

Following the typical cyclopropanation procedure, 1,2-epoxy-5-methylene-6-heptene **4n** (124 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 24 h to give an inseparable mixture of 5-vinylbicyclo[3.1.0]hexan-2-ol **5n** and 5-methylenebicyclo[4.1.0]heptan-2-ol **18a** (**5n**:**18a** = 2.4:1, 60 mg, 0.48 mmol, 48%) as a colorless oil, R_f = 0.3 (60% Et_2O in petrol); IR (film) 3348bs (O-H), 3064w, 2945s, 2873s (C-H), 1642s, 1450m, 1278m; ^{1}H NMR (400 MHz) 0.35 - 0.39 (m, 1H, H-7B), 0.57 (t, 1H, H-6_{5u}, *J* = 4.8), 0.74 (dd, 1H, H-6′A, *J* = 5.6, 8.4), 0.85 - 0.89 (m, 1H, H-7′B), 1.30 -

2.37 (m, 13H, H-1$_{5u}$, 2 × H-3$_{5u}$, 2 × H-4A, H-1$_{18a}$, 2 × H-3$_{18a}$, 2 × H-4$_{18a}$, H-6$_{18a}$, 2 × OH), 4.19 (s, 1H, H-2B), 4.22 (d, 1H, H-2$_{5u}$, J = 2.0), 4.78 (d, 1H, H-8$_{18a}$, J = 1.6), 4.89 (s, 1H, H-8′$_{18a}$), 4.95 (dd, 1H, H-8$_{5u}$, J = 1.6, 10.0), 5.06 (dd, 1H, H-8′$_{5u}$, J = 1.2, 17.2), 5.74 (dd, 1H, H-7$_{5u}$, J = 10.8, 17.6); ^{13}C NMR (100 MHz) 10.9 (C-7$_{18a}$), 15.2 (C-6$_{5u}$), 17.8, 20.3, 24.3, 25.9, 28.6, 31.1, 33.7, 66.3 (C-2$_{18a}$), 74.3 (C-2$_{5u}$), 142.2 (C-7$_{5u}$), 145.0 (C-5$_{18a}$); MS (CI+) *m/z*: 142.1 (MNH_4^+, 27%), 124.1 (27%), 107.1 (100%); HRMS *m/z*: MNH_4^+ found 142.1236, $C_8H_{16}NO$ requires 142.1232.

5-Isopropenylbicyclo[3.1.0]hexan-2-ol 5o and 6-methyl-5-methylenebicyclo[4.1.0]heptan-2-ol 18b



*1,2-Epoxy-6-methyl-5-methylene-6-heptene **4o***

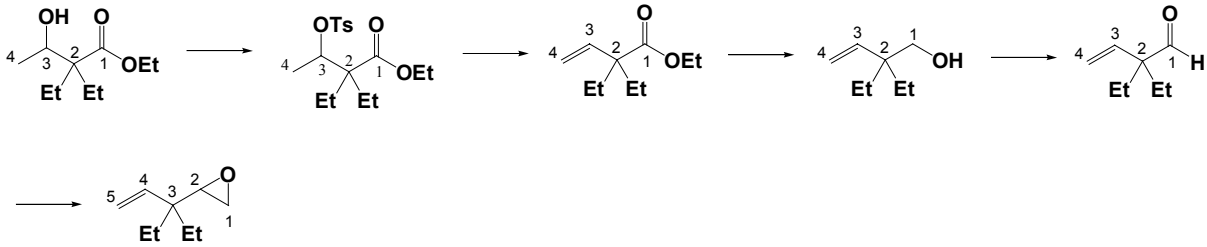
n-BuLi (1.6 M in hexane, 7.5 mL, 12 mmol) was added slowly to a stirred solution of *t*-BuOK (1.35 g, 12 mmol) and 2,2,6,6-tetramethylpiperidine (1.69 mL, 10 mmol) in THF at –78 ˚C. After 45 min, the mixture was treated with 2,3-dimethyl-1,3-butadiene (2.3 mL, 20 mmol), and then stirred for a further 45 min to give a red solution. Epichlorohydrin (0.47 mL, 6.0 mmol) was added rapidly to the red mixture in one portion. After 2 h at –78 ˚C, the reaction mixture was poured into sat. aq. NH_4Cl (40 mL), the layers were separated and then the aqueous layer extracted with Et_2O (40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave 1,2-epoxy-6-methyl-5-methylene-6-hepctene **4o** (314 mg, 2.27 mmol, 38%) as a colorless oil; R_f = 0.4 (5% Et_2O in petrol); IR (film) 3094w (epoxide), 2948s (C-H), 1598s, 1444m, 1410m, 1262w; ^{1}H NMR (400 MHz) 1.67 - 1.80 (m, 2H, 2 × H-3), 1.92 (s, 3H, 3 × H-9), 2.37 - 2.53 (m, 3H, 2 × H-4, H-1), 2.77 (t, 1H, H-1′, J = 4.8), 2.93 - 2.98 (m, 1H, H-2), 5.00 (s, 2H, H_2C=C), 5.09 (s, 1H, one of H_2C=C), 5.13 (s, 1H, one of H_2C=C); ^{13}C NMR (100 MHz) 21.1 (C-9), 29.9 (C-4), 31.7 (C-3), 47.2 (C-1), 52.1 (C-2), 112.6 (H_2C=C), 112.8 (H_2C=C), 142.3 (C-6), 146.8 (C-5); MS (CI+) *m/z*: 156.1 (MNH_4^+, 100%), 139.1 (MH^+, 25%), 121.1 (18%); HRMS *m/z*: MNH_4^+ found 156.1385, $C_9H_{18}NO$ requires 156.1388.

5-Isopropenylbicyclo[3.1.0]hexan-2-ol ***5o*** *and 6-methyl-5-methylenebicyclo[4.1.0]heptan-2-ol* ***18b***

Following the typical cyclopropanation procedure, 1,2-epoxy-6-methyl-5-methylene-6-heptene **4o** (138 mg, 1.0 mmol) was treated with LTMP in *t*-BuOMe for 24 h to give an inseparable mixture of 5-isopropenylbicyclo[3.1.0]hexan-2-ol **5o** and 6-methyl-5-methylenebicyclo[4.1.0]heptan-2-ol **18b** (**5o**:**18b** = 1.1:1, 96 mg, 0.69 mmol, 69%) as a colorless oil, R_f = 0.3 (50% Et_2O in petrol); IR (film) 3346bs (O-H), 3083w, 2947s (C-H), 1634s, 1449s, 1288m, 1171m; ^{1}H NMR (400 MHz) 0.43 (dd, 1H, H-6_{5v}, J = 4.4, 5.6), 0.54 (t, 1H, H-7_{18b}, J = 5.2), 0.72 (dd, 1H, H-$7'_{18b}$, J = 6.8, 9.2), 0.80 - 0.83 (m, 1H, H-$6'_{5v}$), 1.11 - 1.15 (m, 1H, H-1_{18b}), 1.25 (s, 3H, 3 × H-9_{18b}), 1.42 - 1.54 (m, 3H), 1.62 - 1.66 (m, 3H), 1.68 (s, 3H, 3 × H-9_{5v}), 1.77 (dd, 1H, J = 8.0, 12.4), 1.87 (bs, 1H, OH), 1.94 - 2.02 (m, 1H), 2.07 - 2.15 (m, 1H), 2.28 - 2.36 (m, 1H), 4.14 (s, 1H, H-2_{18b}), 4.23 (s, 1H, H-2_{5v}), 4.787 - 4.88 (m, 4H, 2 × H_2C=C); ^{13}C NMR (100 MHz) 13.7 (C-6_{5v}), 18.4 (C-7_{18b}), 20.3 (C-9_{5v}), 21.2, 24.3 (C-9_{18b}), 26.2, 27.7, 30.0, 30.1, 31.4, 31.5, 33.9, 67.7 (C-2_{18b}), 74.6 (C-2_{5v}), 107.7 (H_2C=C), 109.3 (H_2C=C), 146.8 (H_2C=C), 149.4 (H_2C=C); MS (CI+) *m/z*: 139.1 (MH^+, 72%), 121.1 (100%); HRMS *m/z*: MH^+ found 139.1122, $C_9H_{15}O$ requires 139.1123.

Synthesis of epoxides 20 and 22

1,2-Epoxy-3,3-diethyl-4-pentene 20



20

n-BuLi (1.6 M in hexane, 4.8 mL, 7.6 mmol, 1.1 equiv.) was added to a stirred solution of diisopropylamine (7.3 mL, 7.62 mmol, 1.1 equiv.) in THF (20 mL) at –78 ˚C. The LDA solution was stirred at rt for 15 min, cooled to –78 ˚C and then treated slowly with a solution of ethyl 2-ethylbut-1-anoate (1.0 g, 6.93 mmol) in THF (5 mL). The resulting mixture was stirred for 1 h and treated with acetaldehyde (0.5 mL, 9.01 mmol, 1.3 equiv.). After 30 min, the reaction mixture was quenched by slow addition of sat. aq. NH_4Cl (5 mL) and then warmed to rt. The solution was washed with sat. aq. NH_4Cl (30 mL), the layers were separated and then the aqueous layer extracted

with Et_2O (30 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (30% Et_2O in petrol) gave ethyl 2,2-diethyl-3-hydroxybutyrate (1.03 g, 5.47 mmol, 79%) as a colorless oil, R_f = 0.3 (30% Et_2O in petrol); IR (film) 3498bs (O-H), 2976s, 2944s, 2884s (C-H), 1723s (C=O), 1462s, 1383s, 1341w, 1294m, 1232s, 1141s, 1098s, 1025s; ^{1}H NMR (500 MHz) 0.81 (t, 3H, α-CH_2CH_3, J = 7.5), 0.87 (t, 3H, α-CH_2CH_3, J = 7.5), 1.13 (d, 3H, 3 × H-4, J = 6.5), 1.27 (t, 3H, OCH_2CH_3, J = 7.5), 1.46 - 1.82 (m, 4H, 2 × α-CH_2CH_3), 3.03 (d, 1H, OH, J = 7.0), 3.89 - 3.94 (m, 1H, H-3), 4.17 (q, 2H, OCH_2CH_3, J = 7.0); ^{13}C NMR (125 MHz) 8.6 (α-CH_2CH_3), 8.7 (α-CH_2CH_3), 14.2 (OCH_2CH_3), 17.9 (C-4), 23.8 (α-CH_2CH_3), 25.5 (α-CH_2CH_3), 53.7 (C-2), 60.4 (OCH_2CH_3), 69.8 (C-3), 176.9 (C-1); MS (CI+) *m/z*: 206.2 (MNH_4^+, 2%), 189.1 (MH^+, 100%), 171.1 (80%), 160.1 (18%), 144.1 (91%), 129.1 (25%), 115.1 (13%); HRMS *m/z*: MNH_4^+ found 206.1758, $C_{10}H_{24}NO_3$ requires 206.1756.

p-Toluenesulfonyl chloride (11.4 g, 59.8 mmol, 2.0 equiv.) was added to a stirred solution of ethyl 2,2-diethyl-3-hydroxybutyrate (5.63 g, 29.9 mmol) in dry pyridine (20 mL) at 0 ˚C. The resulting mixture was stirred at rt for 48 h. The mixture was diluted with EtOAc (150 mL), washed with aq. HCl (1 M) until pH of the aqueous layer <3 and the layers were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% EtOAc in petrol) gave ethyl 2,2-diethyl-3-(toluene-4-sulfonyloxy)butyrate (8.01 g, 23.4 mmol, 78%) as a colorless oil; R_f = 0.3 (10% EtOAc in petrol); IR (film) 1278s, 2885s (C-H), 1732s (C=O), 1599m, 1496w, 1454m, 1363s, 1306w, 1235s, 1189s, 1177s, 1144m, 1098m, 1076w, 1020m; ^{1}H NMR (400 MHz) 0.81 (t, 3H, α-CH_2CH_3, J = 7.0), 0.83 (t, 3H, α-CH_2CH_3, J = 7.0), 1.22 (t, 3H, OCH_2CH_3, J = 7.5), 1.31 (d, 3H, 3 × H-4, J = 6.5), 1.54 - 1.77 (m, 4H, 2 × α-CH_2CH_3), 2.44 (s, 3H, $ArCH_3$), 4.06 - 4.13 (m, 2H, OCH_2CH_3), 4.99 - 5.03 (m, 1H, H-3), 7.32 (d, 2H, 2 × Ar-H, J = 8.5), 7.78 (d, 2H, 2 × Ar-H, J = 8.0); ^{1}H NMR (100 MHz) 8.5 (α-CH_2CH_3), 8.7 (α-CH_2CH_3), 14.1 (OCH_2CH_3), 16.8 (C-4), 21.6 ($ArCH_3$), 23.9 (α-CH_2CH_3), 24.4 (α-CH_2CH_3), 53.6 (C-2), 60.6 (OCH_2CH_3), 82.3 (C-3), 127.5 (Ar-C), 129.6 (Ar-C), 135.0 (Ar-C), 144.3 (Ar-C), 173.5 (C-1); MS (CI+) *m/z*: 360.2 (MNH_4^+, 5%), 343.2 (MH^+, 2%), 298.1 (2%), 188.16 (5%), 171.1

(100%), 148.1 (17%), 141.1 (29%), 124.1 (9%), 113.1 (5%); HRMS *m/z*: MNH_4^+ found 360.1838, $C_{17}H_{30}NO_5$ requires 360.1845.

A mixture of ethyl 2,2-diethyl-3-(toluene-4-sulfonyloxy)butyrate (8.01 g, 23.4 mmol) in DBU (9.5 mL) was heated under reflux at 140 ˚C for 3 h. The resulting mixture was cooled to rt, diluted with Et_2O (150 mL), washed with aq. HCl (1 M, 150 mL) until the aqueous layer reached pH <3 and the layers were separated. The organic layer was dried ($MgSO_4$), filtered and concentrated to give ethyl 2,2-diethylbut-3-enoate (3.67 mg, 21.6 mmol, 92%) as a light yellow oil, which was sufficiently pure to be used without further purification; IR (film) 2973s, 2941s, 2882s (C-H), 1731s (C=O), 1639w, 1462s, 1413w, 1382m, 1369m, 1345w, 1296w, 1228s, 1133s, 1028m, 1002w; ^{1}H NMR (500 MHz) 0.82 (t, 6H, 2 × α-CH_2CH_3, J = 7.5), 1.26 (t, 3H, OCH_2CH_3, J = 7.0), 1.73 (q, 4H, 2 × α-CH_2CH_3, J = 7.0), 4.16 (q, 2H, OCH_2CH_3, J = 7.0), 5.08 (d, 1H, H-4, J = 17.5), 5.19 (d, 1H, H-4′, J = 12.0), 5.97 (dd, 1H, H-3, J = 11.0, 18.0); ^{13}C NMR (125 MHz) 8.7 (α-CH_2CH_3), 14.2 (OCH_2CH_3), 28.3 (α-CH_2CH_3), 53.0 (C-2), 60.4 (OCH_2CH_3), 114.4 (C-4), 139.8 (C-3), 175.4 (C-1); MS (CI+) *m/z*: 188.2 (MNH_4^+, 9%), 171.1 (MH^+, 100%), 155.1 (3%), 148.1 (11%), 141.1 (42%), 124.1 (15%), 113.1 (4%); HRMS *m/z*: MNH_4^+ found 188.1650, $C_{10}H_{22}NO_2$ requires 188.1651.

$LiAlH_4$ (2.3 M in THF, 71.7 mL, 165 mmol, 2.2 equiv.) was added slowly to a stirred solution of ethyl 2,2-diethylbut-3-enoate (12.8 g, 75.2 mmol) in THF (350 mL) at 0 ˚C. After 4 h, the mixture was cooled to –78 ˚C and quenched by sequential addition of water (6.3 mL), aq. NaOH (15 w%, 6.3 mL) and water (18.9 mL). The precipitates formed were filtered and washed through with Et_2O (200 mL). The filtrate was dried ($MgSO_4$), filtered and concentrated to give 2,2-diethylbut-3-en-1-ol (8.17 g, 63.7 mmol, 85%) as a colorless oil, which was sufficiently pure to be used without further purification; R_f = 0.3 (30% Et_2O in petrol); IR (film) 3370bs (O-H), 3082m (C=C), 2967s, 2880s (C-H), 1638m, 1462s, 1416m, 1380m, 1244w, 1165w, 1078m, 1030s, 1003m; ^{1}H NMR (400 MHz) 0.81 (t, 6H, 2 × α-CH_2CH_3, J = 7.6), 1.29 - 1.48 (m, 4H, 2 × α-CH_2CH_3), 3.42 (s, 1H, OH), 5.02 (dd, 1H, H-4, J = 1.2, 17.6), 5.21 (dd, 1H, H-4′, J = 1.2, 6.7), 5.63 (dd, 1H, H-3, J = 10.8, 17.6); ^{13}C NMR (100 MHz) 7.5 (α-CH_2CH_3), 24.7 (α-CH_2CH_3), 44.8 (C-2), 66.1 (C-1), 115.0 (C-4), 143.8 (C-

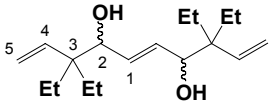
3); MS (CI+) *m/z*: 148.1 (34%), 146.2 (MNH_4^+, 41%), 131.1 (6%), 110.1 (38%); HRMS *m/z*: MNH_4^+ found 146.1545, $C_8H_{20}NO$ requires 146.1544.

TPAP (137 mg, 0.39 mmol, 5 mol%) was added to a stirred solution of 2,2-diethylbut-3-en-1-ol (1.00 g, 7.80 mmol), 4-methylmorpholine *N*-oxide (15.62 mmol, 1.83 g, 2.0 equiv.) and powdered 3 Å molecular sieves (2.0 g) in CH_2Cl_2 (50 mL) at rt. After 4 h, the solution was filtered through a pad of silica (11 cm × 3 cm) topped with a small amount of celite, and then eluted through with CH_2Cl_2 (100 mL). The filtrate was concentrated to give 2,2-diethylbut-3-enal (756 mg, 6.00 mmol, 77%) as a colorless oil, which was sufficiently pure to be used without further purification; R_f = 0.6 (10% Et_2O in petrol); IR (film) 3085w (C=C), 2970s, 2940s, 2882s (C-H), 1727s (C=O), 1632m, 1459m, 1414w, 1383m, 1001m; ^{1}H NMR (400 MHz) 0.82 (t, 6H, 2 × α-CH_2CH_3, *J* = 7.6), 1.60 - 1.75 (m, 4H, 2 × α-CH_2CH_3), 5.13 (d, 1H, H-4, *J* = 18.0), 5.34 (d, 1H, H-4′, *J* = 10.8), 5.71 (dd, 1H, H-3, *J* = 10.8, 17.6), 9.38 (s, 1H, CHO); ^{13}C NMR (100 MHz) 8.0 (α-CH_2CH_3), 24.6 (α-CH_2CH_3), 56.5 (C-2), 117.5 (C-4), 137.6 (C-3), 203.7 (C-1); MS (CI+) *m/z*: 144.1 (MNH_4^+, 100%), 141.1 (3%), 131.1 (9%), 126.1 (M^+, 27%); HRMS *m/z*: MNH_4^+ found 144.1382, $C_8H_{18}NO$ requires 144.1388.

n-BuLi (1.6 M in hexane, 3.8 mL, 6.1 mmol, 1.1 equiv.) was added dropwise (~ 1 drop/2 s) to a stirred solution of 2,2-diethylbut-3-enal (700 mg, 5.55 mmol) and dibromomethane (0.47 mL, 6.66 mmol, 1.2 equiv.) in THF (20 mL) at –78 ˚C. The resulting mixture was warmed to rt and stirred for 20 h. The reaction mixture was washed with sat. aq. NH_4Cl (50 mL), the layers were separated and then the aqueous layer extracted with Et_2O (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (10% Et_2O) gave 1,2-epoxy-3,3-diethyl-4-pentene **20** (598 mg, 4.26 mmol, 77%) as a colorless oil, R_f = 0.6 (10% Et_2O in petrol); IR (film) 3084w (C=C), 3051w (epoxide), 2969s, 2927s, 2882s (C-H), 1636m, 1462s, 1414m, 1383m, 1261w, 1082w, 1014m; ^{1}H NMR (400 MHz) 0.85 (t, 3H, α-CH_2CH_3, *J* = 7.2), 0.87 (t, 3H, α-CH_2CH_3, *J* = 7.2), 1.40 - 1.58 (m, 4H, 2 × α-CH_2CH_3), 2.57 (dd, 1H, H-1, *J* = 3.2, 4.8), 2.64 (dd, 1H, H-1′, *J* = 4.4, 4.8), 2.85 (dd, 1H, H-2, *J* =

3.2, 3.6), 5.03 (dd, 1H, H-5, J = 1.2, 18.0), 5.14 (d, 1H, H-5′, J = 11.2), 5.56 (dd, 1H, H-4, J = 11.2, 18.0); ^{13}C NMR (100 MHz) 7.9, 8.0 (α-CH_2CH_3), 25.5 (α-CH_2CH_3), 27.4 (α-CH_2CH_3), 42.2 (C-3), 43.5 (C-1), 57.5 (C-2), 114.9 (C-5), 140.0 (C-4); MS (CI+) *m/z*: 158.2 (MNH_4^+, 6%), 141.1 (MH^+, 8%), 123.1 (56%), 111.1 (100%); HRMS *m/z*: MNH_4^+ found 158.1537, $C_9H_{20}NO$ requires 158.1545.

Dimerization of epoxide 20



Following the typical procedure, 1,2-epoxy-3,3-diethyl-4-pentene **20** (140 mg, 1.00 mmol) was treated with LTMP in *t*-BuOMe for 20 h to give the corresponding dimer A (16 mg, 11%) as a pale brown solid, R_f = 0.6 (Et_2O) and dimer B (78 mg, 56%) as a white solid, R_f = 0.5 (Et_2O).

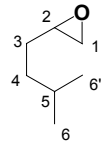
Characterisation data for dimer A:

IR (film) 3368bs (O-H), 3079s (C=C), 2965s, 2930s, 2881s (C-H), 1636w, 1477s, 1428m, 1383m; ^{1}H NMR (400 MHz) 0.77 - 0.90 (m, 12H, 4 × CH_2CH_3), 1.31 - 1.69 (m, 8H, 4 × CH_2CH_3), 4.36 - 4.40 (m, 2H, H-2, H-2′), 5.06 (dd, 2H, 2 × H-5, J = 1.6, 17.6), 5.26 (dd, 2H, 2 × H-5′, J = 1.6, 11.2), 5.73 - 5.82 (m, 4H, H-1, H-1′, H-4, H-4′); ^{13}C NMR (100 MHz) 7.6, 7.7 ($CHCH_3$), 23.6, 23.9 (CH_2CH_3), 46.1 (C-3, 3′), 70.2 (C-2, 2′), 116.0 (C-5, 5′), 133.2 (C-1, 1′), 141.5 (C-4, 4′).

Characterisation data for dimer B:

IR (film) 3365bs (O-H), 3079s (C=C), 2965s, 2932s, 2887s (C-H), 1633w, 1479s, 1431m, 1397m; ^{1}H NMR (400 MHz) 0.75 - 0.84 (m, 12H, 4 × CH_2CH_3), 1.31 - 1.67 (m, 8H, 4 × CH_2CH_3), 3.97 - 3.98 (m, 2H, H-2, H-2′), 5.04 (d, 2H, 2 × H-5, J = 18.0), 5.25 (d, 2H, 2 × H-5′, J = 10.8), 5.69 - 5.76 (m, 4H, H-1, H-1′, H-4, H-4′); ^{13}C NMR (100 MHz) 7.6, 7.7 (CH_2CH_3), 23.5, 24.5 (CH_2CH_3), 46.8 (C-3, 3′), 75.9 (C-2, C-2′), 115.9 (C-5, C-5′), 132.1 (C-1, C-1′), 141.8 (C-4, C-4′).

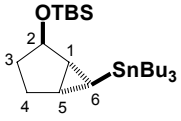
***1,2-Epoxy-5-methylhexane* 22**[13]



m-Chloroperbenzoic acid (77%, 2.73 g, 12.2 mmol, 1.2 equiv.) was added to a stirred solution of 5-methylhex-1-ene (1.00 g, 10.2 mmol) in CH_2Cl_2 (50 mL) at rt After 12 h, the solution was successively washed with sat. aq $NaHCO_3$ (30 mL) and sat. aq. Na_2SO_3 (30 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (5% Et_2O in petrol) gave 1,2-epoxy-5-methylhexane **22** (862 mg, 7.55 mmol, 74%) as a colorless oil; R_f = 0.4 (5% Et_2O in petrol); IR (film) 2956s (C-H), 2870m, 1771m, 1725s, 1575w, 1469m, 1427m, 1385m, 1283m, 1255s, 1217s; ^{1}H NMR (400 MHz) 0.88 (s, 3H, CH_3), 090 (s, 3H, CH_3), 1.25 - 1.43 (m, 2H, 2 × H-4), 1.50 - 1.63 (m, 3H, 2 × H-3, H-5), 2.46 (dd, 1H, H-1, J = 2.4, 4.8), 2.74 (t, 1H, H-1′, J = 4.8), 2.87- 2.91 (m, 1H, H-2); ^{13}C NMR (100 MHz) 22.4 (C-6), 27.8 (C-5), 30.3 (C-3), 34.8 (C-4), 47.1 (C-1), 52.5 (C-2).

Synthesis of cyclopropanes 23, 24a-g, 25, 26 and 27

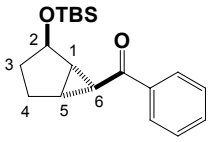
tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane 23



tert-Butyldimethylsilyl chloride (271 mg, 1.80 mmol, 1.5 equiv.) was added to a stirred solution of *exo*-6-tributylstannylbicyclo[3.1.0]hexan-2-ol **5e** (464 mg, 1.20 mmol) and imidazole (163 mg, 2.40 mmol, 2.0 equiv.) in CH_2Cl_2 (10 mL) at rt. The resulting mixture was stirred for 3 h, and then dry-loaded onto a small amount of silica. Purification by column chromatography (2% Et_2O in petrol) gave silylated bicyclic alcohol **23** (512 mg, 1.02 mmol, 85%) as a colorless oil, R_f = 0.5 (2% Et_2O in petrol); IR (film) 2957s, 2928s, 2857s (C-H), 1463m, 1376w, 1254s, 1183m, 1094m, 1072s (Si-O), 1026s; ^{1}H NMR (400 MHz) –0.61 - –0.54 (m, 1H, H-6), 0.08 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.77 - 0.82 (m, 6H, 3 × $Sn(CH_2)_2CH_2$), 0.88 - 0.92 (m, 18H, $SiC(CH_3)_3$, 3 × $Sn(CH_2)_3CH_3$), 1.25 - 1.53 (m, 16H, 3 × $SnCH_2CH_2$, 3 × $SnCH_2$, H-1, H-5, two of cyclopentyl CH_2), 1.60 - 1.64 (m, 1H, one of cyclopentyl CH_2), 1.96 - 2.05 (m, 1H, one of cyclopentyl CH_2), 4.22 - 4.24 (m, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz) –4.5 ($SiCH_3$), 2.1 (C-6),

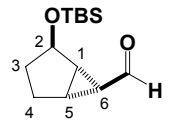
8.7 (3 × Sn*C*H$_2$, J_{Sn-C} = 161), 13.7 (3 × Sn(CH$_2$)$_3$*C*H$_3$), 18.5 (Si*C*(CH$_3$)$_3$), 21.4, 26.1 (Si*C*(*C*H$_3$)$_3$), 27.3 (3 × Sn(CH$_2$)$_2$*C*H$_2$), 28.9, 29.0, 29.1 (3 × SnCH$_2$*C*H$_2$), 31.3, 76.1 (C-2); ^{119}Sn NMR (93 MHz) –7.9; MS (EI+) *m/z*: 445.3 (62%), 389.2 (26%), 253.0 (8%), 209.0 (17%), 195.0 (29%), 117.0 (23%), 166.2 (15%), 137.0 (9%), 121.0 (8%); HRMS *m/z*: M^+ found 502.2647, $C_{24}H_{50}OSiSn$ requires 502.2638.

[2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hex-6-yl]phenyl methanone 24a



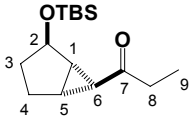
tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol) was reacted with a suspension of *N,N*-dimethylbenzamide (298 mg, 2.00 mmol, 2.0 equiv.) in THF (2 mL) as described in the typical procedure. Purification of the crude product by column chromatography (5% Et_2O in petrol) gave a mixture of cyclopropane **24a** and a side-product (derived from the reaction of excess *n*-BuLi with the electrophile). Subsequent vacuum Kugelrohr distillation (70 ˚C and 0.07 mbar) gave pure cyclopropane **24a** (273 mg, 0.86 mmol, 86%) as a white solid, R_f = 0.3 (5% Et_2O in petrol); mp = 57 - 58 ˚C; IR (film) 2930s, 2857s (C-H), 1668s (C=O), 1599m, 1582m, 1449s, 1401s, 1360s, 1267s, 1220s, 1168s, 1097s, 1034s; ^{1}H NMR (400 MHz) 0.09 (s, 3H, SiCH$_3$), 0.10 (s, 3H, SiCH$_3$), 0.91 (s, 9H, SiC(CH$_3$)$_3$), 1.43 - 1.52 (m, 1H, H-3), 1.64 (dd, 1H, H-3′, *J* = 8.4, 14.4), 1.83 (dd, 1H, H-4, *J* = 8.4, 12.8), 2.11 - 2.24 (m, 3H, H-4′, H-5, H-6), 2.29 (t, 1H, H-6, *J* = 2.8), 4.37 (d, 1H, H-2, *J* = 5.2), 7.47 (t, 2H, 2 × Ar-H, *J* = 8.0), 7.56 (t, 1H, Ar-H, *J* = 6.8), 7.94 (d, 2H, 2 × Ar-H, *J* = 8.4); ^{13}C NMR (100 MHz) –4.7 (SiCH$_3$), –4.6 (SiCH$_3$), 18.2 (Si*C*(CH$_3$)$_3$), 25.5 (C-4), 25.9 (SiC(*C*H$_3$)$_3$), 26.7 (C-6), 31.8 (C-3), 32.2 (C-5), 38.1 (C-1), 74.3 (C-2), 127.9 (Ar-C), 128.4 (Ar-C), 133.0 (Ar-C), 138.0 (Ar-C), 198.8 (C=O); MS (CI+) *m/z*: 334.2 (MNH_4^+, 4%), 317.2 (MH^+, 100%), 259.1 (23%), 185.1 (20%), 131.1 (17%); HRMS *m/z*: MNH_4^+ found 334.2203, $C_{19}H_{32}NO_2Si$ requires 334.2202; Elemental analysis: found C, 72.08; H, 8.93; $C_{19}H_{28}O_2Si$ requires C, 72.10; H, 8.92.

2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hexane-6-carbaldehyde 24b



tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (5012 mg, 1.00 mmol) was reacted with *N,N*-dimethylformamide (0.15 mL, 2.00 mmol, 2.0 equiv.) as described in the typical procedire. Purification of the crude product by column chromatography (10% Et_2O in petrol) gave cyclopropane **24b** (137 mg, 0.57 mmol, 57%) as a colorless oil, R_f = 0.3 (10% Et_2O in petrol); IR (film) 2952s (C-H), 1684s (C=O), 1463s, 1361m, 1317m, 1257s, 1217m, 1169m, 1007s; ^{1}H NMR (400 MHz) 0.07 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.90 (s, 9H, $SiC(CH_3)_3$), 1.28 - 1.37 (m, 1H, H-3), 1.48 - 1.50 (m, 1H, H-6), 1.56 (dd, 1H, H-3´, *J* = 8.8, 14.8), 1.78 (dd, 1H, H-4, *J* = 8.4, 12.4), 2.03 (dd, 1H, H-1, *J* = 3.6, 5.6), 2.08 - 2.16 (m, 2H, H-4´, H-5), 4.32 (d, 1H, H-2, *J* = 4.8), 9.04 (d, 1H, CHO, *J* = 5.6); ^{13}C NMR (100 MHz) –4.7 ($SiCH_3$), –4.7 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 24.9 (C-4), 25.8 ($SiC(CH_3)_3$), 27.6 (C-5), 31.3 (C-3), 32.1 (C-6), 34.1 (C-1), 74.0 (C-2), 200.0 (C=O); MS (CI+) *m/z*: 258.2 (MNH_4^+, 26%), 241.2 (MH^+, 100%), 200.1 (11%), 183.1 (15%), 126.1 (5%), 109.1 (15%); HRMS *m/z*: MNH_4^+ found 258.1877, $C_{13}H_{28}NO_2Si$ requires 258.1889.

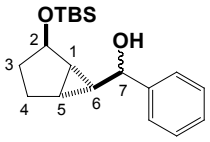
1-[2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hex-6-yl]propan-1-one 24c



tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol) was reacted with *N,N*-dimethylpropioamide (0.22 mL, 2.00 mmol, 2.0 equiv.) as described in the typical procedure. Purification of the crude product by column chromatography (10% Et_2O in petrol) gave a mixture of cyclopropane **24c** and a side-product (derived from the reaction of excess *n*-BuLi with the electrophile). Subsequent vacuum Kugelrohr distillation (60 ˚C and 10 mbar) gave pure cyclopropane **24c** (161 mg, 0.62 mmol, 62%) as a colorless oil, R_f = 0.3 (10% Et_2O in petrol); IR (film) 2932s, 2858s (C-H), 1702s (C=O), 1462m, 1406m, 1360m, 1256s, 1171s, 1124s, 1097m, 1034s; ^{1}H NMR (400 MHz) 0.06 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.88 (s, 9H, $SiC(CH_3)_3$), 1.05 (t, 3H, 3 × H-9, *J* = 7.2), 1.27 - 1.37 (m, 1H, H-3), 1.51 - 1.56 (m, 2H, H-3´, H-6), 1.71 (dd, 1H, H-4, *J* = 8.0, 12.8), 1.92 - 2.10 (m, 3H, H-1, H-4´, H-5), 2.50 (q, 2H, 2 × H-8, *J*

= 7.2), 4.27 (d, 1H, H-2, J = 4.4); ^{13}C NMR (100 MHz) –4.7 ($SiCH_3$), –4.6 ($SiCH_3$), 7.9 (C-9), 18.2 ($SiC(CH_3)_3$), 25.3 (C-4), 25.9 ($SiC(CH_3)_3$), 29.8 (C-5), 30.5 (C-6), 31.6 (C-3), 36.5 (C-8), 36.8 (C-1), 74.3 (C-2), 209.5 (C=O); MS (CI+) *m/z*: 286.2 (MNH_4^+, 15%), 269.2 (MH^+, 100%), 228.1 (24%), 211.1 (34%), 154.1 (29%), 137.1 (74%); HRMS *m/z*: MNH_4^+ found 286.2205, $C_{15}H_{32}NO_2Si$ requires 286.2202.

[2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hex-6-yl]phenyl methanol 24d



tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol) was reacted with benzamide (0.20 mL, 2.00 mmol, 2.0 equiv.) as described in the typical procedure. Purification of the crude product by column chromatography (20% Et_2O in petrol) gave two diastereoisomers, both contaminated with the side-product (derived from the reaction of excess *n*-BuLi with the electrophile). Subsequent vacuum Kugelrohr distillation (95 ˚C and 0.07 mbar) gave pure diastereomer A (108 mg, 0.34 mmol, 34%) as a pale yellow oil, R_f = 0.2 (20% Et_2O in petrol), and diastereomer B (80 mg, 0.25 mmol, 25%) as a pale yellow oil, R_f = 0.1 (20% Et_2O in petrol).

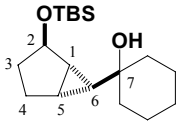
Characterisation data for diastereomer A:

IR (film) 3384bs (O-H), 3030w (Ar), 2928s, 2856s (C-H), 1494w, 1462s, 1361s, 1255s, 1169s, 1071s; ^{1}H NMR (400 MHz) 0.09 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.84 - 0.88 (m, 1H, H-6), 0.92 (s, 9H, $SiC(CH_3)_3$), 1.27 - 1.34 (m, 1H, H-3), 1.48 - 1.64 (m, 4H, H-1, H-3´, H-4, H-5), 1.92 (d, 1H, OH, J = 3.2), 1.94 - 2.00 (m, 1H, H-4´), 4.05 (dd, 1H, H-7, J = 2.8, 8.4), 4.32 (d, 1H, H-2, J = 4.4), 7.29 - 7.41 (m, 5H, 5 × Ar-H); ^{13}C NMR (100 MHz) –4.5 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 22.7 (C-5), 24.7 (C-4), 26.0 ($SiC(CH_3)_3$), 27.9 (C-6), 31.2 (C-1), 32.2 (C-3), 74.5 (C-2), 76.8 (C-7), 125.8 (Ar-C), 127.5 (Ar-C), 128.4 (Ar-C), 143.8 (Ar-C); MS (CI+) *m/z*: 336.3 (MNH_4^+, 1%), 319.2 (MH^+, 2%), 301.2 (16%), 260.2 (4%), 243.1 (8%), 204.1 (5%), 187.1 (40%), 169.1 (100%), 143.1 (6%), 115.1 (3%); HRMS *m/z*: MNH_4^+ found 336.2355, $C_{19}H_{34}NO_2Si$ requires 336.2359.

Characterisation data for diastereomer B:

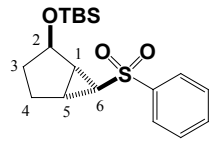
IR (film) 3357bs (O-H), 3030w (Ar), 2929s (C-H), 1361s, 1255s, 1169s, 1039s; ^{1}H NMR (400 MHz) 0.05 (s, 3H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.83 - 0.86 (m, 1H, H-6), 0.89 (s, 9H, $SiC(CH_3)_3$), 1.28 - 1.34 (m, 1H, H-3), 1.37 (dd, 1H, H-1, J = 3.2, 6.0), 1.51 (dd, 1H, H-3′, J = 8.4, 14.4), 1.64 - 1.68 (m, 1H, H-5), 1.74 (dd, 1H, H-4, J = 8.8, 13.2), 2.00 (d, 1H, OH, J = 2.8), 1.98 - 2.04 (m, 1H, H-4′), 4.08 (dd, 1H, H-7, J = 2.4, 8.4), 4.17 (d, 1H, H-2, J = 4.8), 7.28 - 7.42 (m, 5H, 5 × Ar-H); ^{13}C NMR (100 MHz) –4.6 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 23.5 (C-5), 25.1 (C-4), 25.9 ($SiC(CH_3)_3$), 27.9 (C-6), 30.4 (C-1), 32.3 (C-3), 74.4 (C-2), 76.5 (C-7), 125.8 (Ar-C), 127.5 (Ar-C), 128.3 (Ar-C), 143.9 (Ar-C); MS (CI+) *m/z*: 336.2 (MNH_4^+, 1%), 319.2 (MH^+, 5%), 301.2 (100%), 261.1 (11%), 243.1 (9%), 204.1 (9%), 187.1 (75%), 169.1 (81%), 143.1 (9%); HRMS *m/z*: MNH_4^+ found 336.2355, $C_{19}H_{34}NO_2Si$ requires 336.2359.

1-[2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hex-6-yl]cyclohexanol 24e



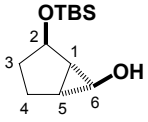
tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol) was reacted with cyclohexanone (0.21 mL, 2.00 mmol, 2.0 equiv.) as described in the typical procedure. Purification of the crude product by column chromatography (20% Et_2O in petrol) gave a mixture of cyclopropane **24e** and a side-product (derived from the reaction of excess *n*-BuLi with the electrophile). Subsequent vacuum Kugelrohr distillation (65 ˚C and 0.07 mbar) gave pure cyclopropane **24e** (186 mg, 0.60 mmol, 60%) as a colorless oil; R_f = 0.2 (20% Et_2O in petrol); IR (film) 3423bs (O-H), 2934s, 2858s (C-H), 1462m, 1360m, 1312w, 1254s, 1178s, 1079s, 1041s, 1004s; ^{1}H NMR (400 MHz) 0.07 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$), 0.48 (t, 1H, H-6, J = 4.0), 0.90 (s, 9H, $SiC(CH_3)_3$), 0.94 (s, 1H, OH), 1.18 - 1.62 (m, 15H), 1.95 - 2.02 (m, 1H), 4.22 (d, 1H, H-2, J = 4.8); ^{13}C NMR (100 MHz) –4.5 ($SiCH_3$), 18.3 ($SiC(CH_3)_3$), 20.0 (C-5), 21.9 (CH_2), 25.3 (CH_2), 25.8 (CH_2), 26.0 ($SiC(CH_3)_3$), 27.8 (C-1), 30.7 (C-6), 32.6 (CH_2), 37.2 (CH_2), 37.3 (CH_2), 69.7 (C-7), 75.3 (C-2); MS (CI+) *m/z*: 293.2 ($[M–H_2O]H^+$, 3%), 235.2 (3%), 161.1 (100%), 134.1 (11%); HRMS *m/z*: $[M–H_2O]H^+$ found 293.2295, $C_{19}H_{33}OSi$ requires 293.2301.

(6-Benzenesulfonylbicyclo[3.1.0]hex-2-yloxy)-tert-butyldimethylsilane 24f



tert-Butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol) was reacted with benzenesulfonyl floride (0.24 mL, 2.00 mmol, 2.0 equiv.) as described in the typical procedure. Purification of the crude product by column chromatography (20% Et_2O in petrol) gave pure cyclopropane **24f** (176 mg, 0.50 mmol, 50%) as a white solid, R_f = 0.2 (20% Et_2O in petrol); mp = 72 - 73 ˚C; IR (KBr) 3063w (Ar), 2954s, 2895s, 2857s (C-H), 1472m, 1447m, 1360m, 1308s, 1256m, 1169m, 1149s, 1087s, 1031s; ^{1}H NMR (400 MHz) 0.04 (s, 3H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.87 (s, 9H, $SiC(CH_3)_3$), 1.15 - 1.24 (m, 1H, H-3), 1.53 (dd, 1H, H-3´, *J* = 8.4, 14.4), 1.69 (dd, 1H, H-4, *J* = 7.6, 13.2), 2.00 (t, 1H, H-6, *J* = 3.6), 2.03 - 2.12 (m, 1H, H-4´), 2.21 (dd, 1H, H-1, *J* = 3.2, 7.2), 2.29 - 2.32 (m, 1H, H-5), 4.25 (d, 1H, H-2, *J* = 4.8), 7.55 (t, 2H, 2 × *m*Ar-H, *J* = 7.2), 7.64 (t, 1H, *p*Ar-H, *J* = 7.2), 7.88 (d, 2H, 2 × *o*Ar-H, *J* = 6.8); ^{1}H NMR (100 MHz) –4.8 ($SiCH_3$), –4.8 ($SiCH_3$), 18.0 ($SiC(CH_3)_3$), 24.7 (C-4), 25.5 (C-5), 25.7 ($SiC(CH_3)_3$), 31.4 (C-3), 32.0 (C-1), 40.0 (C-6), 73.6 (C-2), 127.3 (Ar-C), 129.2 (Ar-C), 133.3 (Ar-C), 140.9 (Ar-C); Elemental analysis: found C, 61.48; H, 8.05; $C_{18}H_{28}O_3SSi$ requires C, 61.32; H, 8.00.

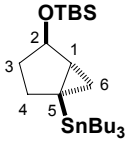
2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hexan-6-ol 24g



n-BuLi (1.6 M in hexane, 0.6 mL, 1.0 mmol, 1.1 equiv.) was added to a stirred solution of *tert*-butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (450 mg, 0.90 mmol) in THF (5 mL) at 0 ˚C. After 1 h, the mixture was cooled to −78 ˚C, treated with a suspension of MoOPH[14] (586 mg, 1.35 mmol, 1.5 equiv.) in THF (1.5 mL) and then stirred at the same temperature for a further 3 h. The resulting mixture was warmed to rt, dry-loaded onto a small amount of silica and purified by column chromatography (40% Et_2O in petrol) to give cyclopropylalcohol **24g** (125 mg, 0.55 mmol, 61%) as a colorless oil, R_f = 0.3 (40% Et_2O in petrol); IR (film) 3319bs (O-H), 2930s, 2858s (C-H), 1463s, 1362s, 1319m, 1256s, 1168s, 1133s, 1076s, 1034s, 1012s; ^{1}H NMR (400 MHz) 0.07 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$), 0.89 (s, 9H,

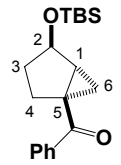
$SiC(CH_3)_3$), 1.00 - 1.09 (m, 1H, H-3), 1.43 - 1.50 (m, 2H, H-1, H-3′), 1.57 (t, 1H, H-5, J = 6.4), 1.68 (dd, 1H, H-4, J = 8.4, 12.4), 1.89 - 1.98 (m, 2H, H-4′, OH), 3.02 (s, 1H, H-6), 4.25 (d, 1H, H-2, J = 4.8); ^{13}C NMR (100 MHz) –4.6 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 24.6 (C-4), 25.9 ($SiC(CH_3)_3$), 26.3 (C-5), 33.4 (C-3), 34.3 (C-1), 53.4 (C-6), 73.8 (C-2); MS (CI+) *m/z*: 229.2 (MH^+, 100%), 171.1 (34%); HRMS *m/z*: MH^+ found 229.1616, $C_{12}H_{25}O_2Si$ requires 229.1624.

***tert*-Butyldimethyl-(5-tributylstannylbicyclo[3.1.0]hex-2-yloxy)silane 25**



tert-Butyldimethylsilyl chloride (226 mg, 1.50 mmol, 1.5 equiv.) was added to a stirred solution of 5-tributylstannylbicyclo[3.1.0]hexan-2-ol **5f** (387 mg, 1.00 mmol) and imidazole (136 mg, 2.00 mmol, 2.0 equiv.) in CH_2Cl_2 (10 mL) at rt, and then stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) then washed with sat. aq. $NaHCO_3$ (20 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to give the crude product. Purification by column chromatography (3% Et_2O in petrol) gave protected alcohol **25** (456 mg, 0.91 mmol, 91%) as a colorless oil; R_f = 0.6 (10% Et_2O in petrol); IR (film) 2957s, 2927s, 2856s (C-H), 1463m, 1362m, 1254s, 1089s, 1070s, 1038s; ^{1}H NMR (500 MHz) 0.06 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.10 (t, 1H, H-6, J = 4.0), 0.26 (dd, 1H, H-6′, J = 5.5, 8.0), 0.82 (t, 6H, 3 × $Sn(CH_2)_2CH_2$, J = 8.0), 0.89 - 0.92 (m, 18H, 3 × $Sn(CH_2)_3CH_3$, $SiC(CH_3)_3$), 1.24 - 1.56 (m, 15H, 3 × $SnCH_2$, 3 × $SnCH_2CH_2$, H-1, 2 × H-3), 1.68 (dd, 1H, H-4, J = 7.5, 11.5), 1.87 - 1.93 (m, 1H, H-4′), 4.33 (d, 1H, H-2, J = 4.5); ^{13}C NMR (125 MHz) –4.6 ($SiCH_3$), 8.4 (3 × $SnCH_2$, J_{Sn-C} = 164), 10.4 (C-6), 12.6 (C-5), 13.7 (3 × $Sn(CH_2)_3CH_3$), 18.1 ($SiC(CH_3)_3$), 25.9 ($SiC(CH_3)$, 27.5 (3 × $Sn(CH_2)_2CH_2$), 29.0 (C-1), 29.1 (3 × $SnCH_2CH_2$), 30.7 (C-3), 30.8 (C-4), 75.2 (C-2); ^{119}Sn NMR (125 MHz) –9.8; MS (CI–, ^{120}Sn) *m/z*: 501.3 ($[M–H]^-$, 56%), 467.1 (9%), 419.3 (28%), 387.3 (85%), 361.1 (56%), 313.1 (100%), 291.2 (29%), 269.1 (29%), 250.1 (9%), 222.1 (24%); HRMS *m/z*: ($[M–H]^-$) found 497.2574, $C_{24}H_{49}O^{116}Sn$ requires 497.2576.

[2-(tert-Butyldimethylsilanyloxy)bicyclo[3.1.0]hex-5-yl]phenylmethanone 26



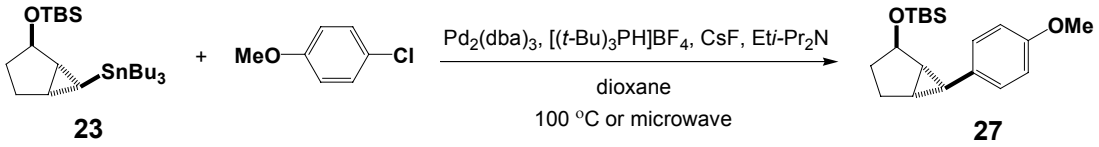
tert-Butyldimethyl-(6-tributylstannylbicyclo[3.1.0]hex-2-yloxy)silane **25** (501 mg, 1.00 mmol) was reacted with a suspension of *N,N*-dimethylbenzamide (298 mg, 2.00 mmol, 2.0 equiv.) in THF (2 mL) as described in the typical procedure. Purification of the crude product by column chromatography (10% Et_2O in petrol) gave a mixture of cyclopropane **26** and a side-product (derived from the reaction of excess *n*-BuLi with the electrophile). Subsequent vacuum Kugelrohr distillation (70 ˚C and 0.07 mmbar) gave pure cyclopropane **26** (260 mg, 0.82 mmol, 82%) as a colorless oil, R_f = 0.3 (10% Et_2O in petrol); IR (film) 3062m, 2955s (C-H), 1669s (C=O), 1599s, 1580m, 1471s, 1448s, 1380s, 1342s, 1313s, 1295s, 1257s, 1199s, 1181s; ^{1}H NMR (400 MHz) 0.14 (s, 6H, 2 × $SiCH_3$), 0.61 (t, 1H, H-6, *J* = 4.8), 0.97 (s, 9H, $SiC(CH_3)_3$), 1.58 (dd, 1H, H-6′, *J* = 3.2, 5.2), 1.60 - 1.61 (m, 1H, H-3), 1.75 (dd, 1H, H-3′, *J* = 8.4, 14.0), 1.92 (dd, 1H, H-4, *J* = 8.0, 12.4), 1.98 (dd, 1H, H-1, *J* = 4.8, 8.8), 2.48 - 2.56 (m, 1H, H-4′), 4.39 (d, 1H, H-2, *J* = 4.8), 7.41 (m, 2H, 2 × *m*Ar-H), 7.48 - 7.52 (m, 1H, *p*Ar-H), 8.06 (dd, 2H, 2 × *o*Ar-H, *J* = 1.2, 8.4); ^{13}C NMR (100 MHz) –4.7 ($SiCH_3$), 13.2 (C-6), 18.1 ($SiC(CH_3)_3$), 25.8 ($SiC(CH_3)_3$), 28.9 (C-4), 32.8 (C-3), 38.0 (C-1), 38.1 (C-5), 47.7 (C-2), 128.1 (Ar-C), 128.8 (Ar-C), 131.8 (Ar-C), 137.9 (Ar-C), 203.0 (C=O); MS (CI+) *m/z*: 334.2 (MNH_4^+, 6%), 317.2 (MH^+, 40%), 259.1 (63%), 202.1 (4%), 185.1 (100%), 105.0 (19%); HRMS *m/z*: MNH_4^+ found 334.2206, $C_{19}H_{32}NO_2Si$ requires 334.2202.

Stille cross-coupling of cyclopropylstannane 23 with 4-chloroanisole

A mixture of **23** (1.0 mmol), 4-chloroanisole (1.2 equiv.), $Pd_2(dba)_3$ (1.5 mol%), $[(t\text{-}Bu)_3PH]BF_4$ (6 mol%), CsF (2.2 equiv.) and ethyl diisopropylamine (6 mol%) in dioxane (2 mL) was heated in a sealed tube at 100 ˚C for 48 h. Under these conditions, incomplete consumption of the starting cyclopropylstanne was observed (entry 1). The yield based on recovered starting material (brsm) improved with a reaction duration of 72 h (entry 2), while use of a higher catalytic loading resulted in similar yield of product, but with much less recovered starting material (entry 3). Surprisingly, no reaction was observed between **23** and the more reactive 4-bromobenzonitrile (entry 4). The Pd/P*t*-

Bu_3 catalytic system was previously shown to be stable in a microwave assisted cross-coupling reaction between aryl halides and aryl zinc halides.[15] Therefore we considered worthwhile to conduct the coupling reaction under microwave irradiation. Coupled adduct **27** was isolated in 35% yield (95% yield brsm) after irradiation at 75W/110 ˚C for 15 min (entry 5). No improvement was observed with a higher catalyst loading (4 mol%) and a longer irradiation period (entry 6). Although incomplete reaction was observed in each case, nonetheless the direct functionalization of precursor **23** via Stille cross-coupling was shown to be viable.

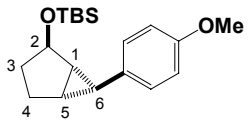
Table 2. Stille cross-coupling reactions



Entry[a]	$Pd_2(dba)_3$ (mol%)	$[(t\text{-}Bu)_3PH]BF_4$ (mol%)	Microwave[c] Conditions	Time (h)	**23**[d] (%)	**27**[d] (%)
1	1.5	6.0	–	48	40	33
2	1.5	6.0	–	72	44	48
3	5.0	20.0	–	72	4	37
4[b]	1.5	6.0	–	72	100	–
5	2.0	8.0	75W/110 ˚C	0.25	63	35
6	4.0	16.0	75W/120 ˚C	1	37	43

[a] All reactions were performed with **23** (1.0 mmol), *p*-4-chloroanisole (1.2 equiv.), Et^iPr_2N {same as $[(t\text{-}Bu)_3PH]BF_4$} and CsF (2.2 equiv.) in dioxane (2 mL) at 100 ˚C. After the reaction, the mixture was dry-loaded onto a small amount of silica and purified by column chromatography (2% Et_2O in petrol). Unreacted **23** was separated from the chromatographed material *via* vacuum Kugelrohr distillation (65 ˚C, 0.06 mbar) to give pure product **27**. [b] Reaction performed with *p*-4-bromobenzonitrile (1.2 equiv.). [c] Reactor type: CEM Discover. [d] Isolated yields.

tert-Butyl-[6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-yloxy]dimethylsilane 27



Procedure for Entry 2, Table 2: A suspension of *tert*-butyldimethyl-{6-(tributylstannyl)bicyclo[3.1.0]hex-2-yloxy}silane **23** (501 mg, 1.00 mmol), $Pd_2(dba)_3$ (1.5 mol%), $[(t\text{-}Bu)_3PH]BF_4$ (6 mol%), CsF (334 mg, 2.2 equiv.) and $i\text{-}Pr_2EtN$ (6 mol%) in dioxane (2 mL) was heated in a small sealed tube at 100 ˚C for 72 h. The mixture was cooled to rt, dry-loaded onto a small amount of silica, and then purified by column chromatography (3% Et_2O in petrol) to give arylcyclopropane **27** (153 mg, 0.48 mmol, 48%) as a colorless oil, R_f = 0.4 (3% Et_2O in petrol), and recovered starting material **23** (221 mg, 0.44 mmol, 44%); IR (film) 3034w, 2954s (C-H), 2857s (C-

O), 1614m (Ar), 1516s, 1464s, 1442m, 1361m, 1301m, 1255s, 1169s, 1078s, 1035s; ^{1}H NMR (400 MHz) 0.11 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.94 (s, 9H, $Si(CH_3)_3$), 1.48 (t, 1H, H-6, J = 4.0), 1.50 - 1.53 (m, 1H, H-3), 1.57 - 1.63 (m, 2H, H-1, H-3′), 1.69 - 1.72 (m, 1H, H-5), 1.82 (dd, 1H, H-4, J = 7.6, 12.4), 2.06 - 2.15 (m, 1H, H-4′), 3.79 (s, 3H, OCH_3), 4.39 (d, 1H, H-2, J = 4.8), 6.82 (d, 2H, 2 × Ar-H, J = 9.2), 6.97 (d, 2H, 2 × Ar-H, J = 8.8); ^{13}C NMR (100 MHz) –4.5 ($SiCH_3$), 18.3 ($SiC(CH_3)_3$), 23.5 (C-6), 25.6 ($SiC(CH_3)_3$), 26.0 (C-4), 28.7 (C-5), 32.1 (C-3), 36.3 (C-1), 55.3 (OCH_3), 75.0 (C-2), 113.7 (Ar-C), 126.4 (Ar-C), 134.7 (Ar-C), 157.5 (Ar-C); MS (EI+) *m/z*: 318.3 (M^+, 1%), 261.2 (9%), 187.2 (11%), 160.1 (70%), 145.1 (9%), 129.1 (15%), 121.1 (46%); HRMS *m/z*: M^+ found 318.2011, $C_{19}H_{30}O_2Si$ requires 318.2010.

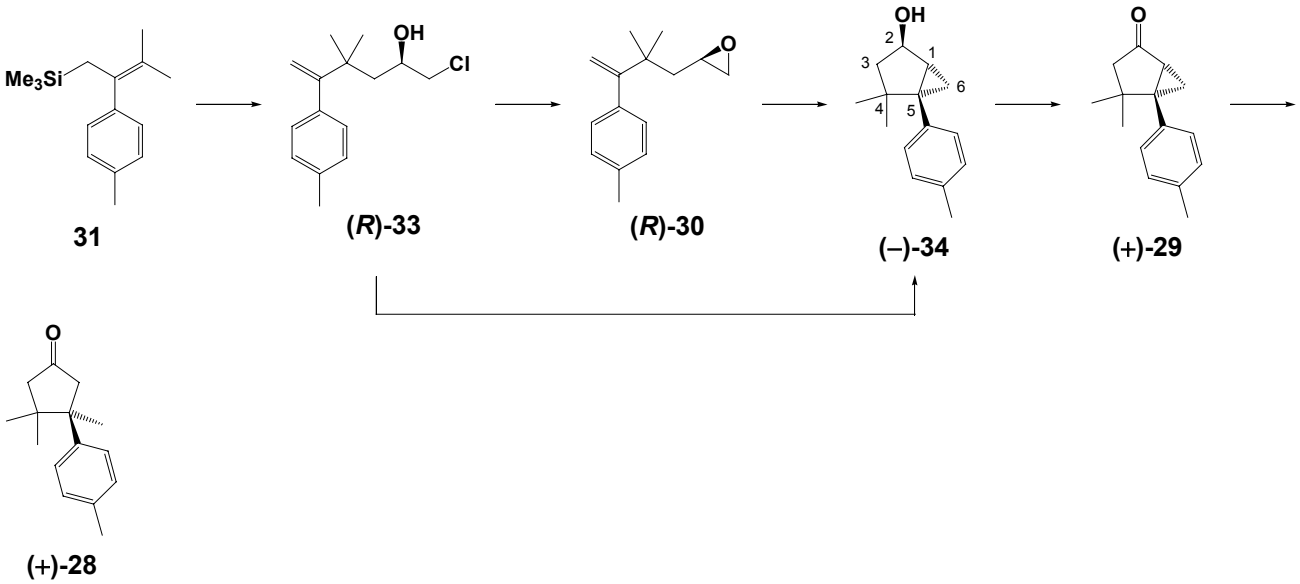
Model study of (+)-β-cuparenone

Formation of 5-phenylbicyclo[3.1.0]hexan-2-ol 5c using substoichiometric TMP

n-BuLi (1.6 M in hexanes, 1.07 mL, 1.72 mmol, 2.0 equiv.) was added slowly over 40 min to a stirred solution of epoxide **4c** (150 mg, 0.86 mmol) and tetramethylpiperidine (0.073 ml, 0.43 mmol, 0.5 equiv.) in *t*-BuOMe (4 ml) at 0 - –5 ˚C. The resulting pale-yellow mixture was stirred at the same temperature for 4.5 h. The reaction was then quenched with aq. HCl (3 M, 2.0 equiv.), diluted with Et_2O (10 mL) and washed twice with aq. HCl (3 M, 0.5 equiv.). The aqueous layer was back extracted with Et_2O (2 × 5 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by column chromatography (30% Et_2O in petrol) gave **5c** (120 mg, 0.69 mmol, 80%) as a colorless oil. Data as above. [When the same reaction was performed under identical conditions using 1.1 equiv. of *n*-BuLi added slowly over 20 min, it gave **5c** (79 mg, 53%, 58% brsm)].

Asymmetric synthesis of (+)-β-cuparenone (+)-28

(+)-β-Cuparenone (+)-28



*2-p-Tolyl-3-methyl-but-2-en-1-yl-trimethylsilane **31***

A 50 mL round-bottom flask containing $Pd(dba)_2$ (518 mg, 0.9 mmol) was purged with Argon (× 3). To the flask were then added toluene (54 mL), 4-iodotoluene (3.92 g, 18 mmol), 3-methyl-1,2-butadiene (3.57 mL, 36.0 mmol), and tributyl(trimethylsilyl)stannane (6.28 mL, 18 mmol). The reaction mixture was heated with stirring at 80 ˚C for 7 h. The solution changed rapidly from purple red to pale yellow in the first few minutes and maintained the same color during the reaction. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. The solution was filtered through celite, the filtrate was concentrated, and the residue was purified by distillation (90 ˚C, 0.045 mmHg) to give allylsilane **31** (2.08 g, 8.95 mmol, 50%) as a colorless oil, R_f = 0.88 (20% Et_2O in petrol); IR (film) 2922s, 1510m, 1248s, 1166w, 833s; ^{1}H NMR (200 MHz) –0.15 (s, 9H, $Si(CH_3)_3$), 1.62 (s, 3H, CH_3), 1,76 (s, 3H, CH_3), 1.89 (s, 2H, CH_2Si), 2.34 (s, 3H, CH_3Ph), 7.03 (d, 2H, 2 × Ar-H, J = 8.2), 7.09 (d, 2H, 2 × Ar-H, J = 8.2); ^{13}C NMR (100 MHz) –0.9 ($Si(CH_3)_3$), 21.1 ($(CH_3)_2C$=C), 22.1 (CH_3Ph), 25.7 (CH_2), 123.5 ($(CH_3)_2C$=C), 128.3 (2 × Ar-C), 129.0 (2 × Ar-C), 132.2 (Ar-C), 135.1 ($(CH_3)_2C$=C), 142.1 (Ar-C); MS (CI+) *m/z*: 233 (MH^+, 100%,), 232 (27%), 90 (84%), 73 (27%); HRMS *m/z*: MH^+ found 233.1716, $C_{15}H_{25}Si$ requires 233.1726.

(R)-1-Chloro-4,4-dimethyl-5-p-tolyl-hex-5-en-2-ol ***(R)-33***

To a stirred solution of allylsilane **31** (284 mg, 1.22 mmol) and (*R*)-epichlorohydrin **(*R*)-32** (0.12 mL, 140 mg, 1.46 mmol) in CH_2Cl_2 (2.6 mL) at −78 ˚C was added a solution of $TiCl_4$ (1 M in CH_2Cl_2, 1.46 mL, 1.46 mmol) through the cold inner surface of the flask over a period of 2 - 3 min. The violet-red mixture was stirred at −78 ˚C for 30 min and then removed from the cold bath. 30% aq. NaOH (0.8 mL) and Et_2O (3.73 mL) were immediately added, and the resulting mixture was stirred vigorously while being allowed to warm to rt. The organic phase was separated, washed with half-saturated aq. NaCl (2 × 10 mL), dried ($MgSO_4$), filtered and evaporated *in vacuo*. Purification of the residue by column chromatography (20% Et_2O in petrol) gave chlorohydrin **(*R*)-33** (184 mg, 0.73 mmol, 60%) as a colorless oil, R_f = 0.58 (20% Et_2O in petrol); $[\alpha]_D^{21}$ = +0.48 (*c*, 1.0 in $CHCl_3$); IR (film) 3442m, 2966s, 1623w, 1511m, 1430m, 1382m, 1090m, 909s, 825s; ^{1}H NMR (400 MHz) 1.20 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.55 (dd, 1H, CH_AH_BCHOH, *J* = 2.5, 14.6), 1.71 (dd, 1H, CH_AH_BCHOH, *J* = 8.1, 14.6), 2.34 (br s, OH), 2.36 (s, 3H, CH_3Ph), 3.44 (dd, 1H, CH_AH_BCl, *J* = 7.3, 11.0), 3.53 (dd, 1H, CH_AH_BCl, *J* = 3.5, 11.0), 3.99 - 4.03 (m, 1H, C*H*OH), 4.96 (d, 1H, $H_AH_BC{=}C$, *J* = 1.5), 5.27 (d, 1H, $H_AH_BC{=}C$, *J* = 1.5), 7.09 (d, 2H, *J* = 8.3, 2 × Ar-H), 7.12 (d, 2H, *J* = 8.3, 2 × Ar-H); ^{13}C NMR (100 MHz) 21.0 (CH_3Ph), 28.3 ($(CH_3)_2C$), 38.7 ($(CH_3)_2C$), 44.8 (CH_2CHOH), 51.4 (CH_2Cl), 69.5 (CHOH), 114.3 ($H_2C{=}C$), 128.2 (2 × Ar-C), 128.8 (2 × Ar-C), 136.2 (Ar-C), 139.8 (Ar-C), 158.1 ($H_2C{=}C$); MS (CI+) *m/z*: 270 (MNH_4^+, 100%,), 253 (MH^+, 27%,), 235 (12%), 199 (64%), 160 (7%), 135 (26%), 119 (15%); HRMS *m/z*: MNH_4^+ found 270.1628, $C_{15}H_{25}NOCl$ requires 270.1625.

(R)-1,2-Epoxy-4,4-dimethyl-5-p-tolyl-5-hexene ***(R)-30***

Powdered NaOH (29 mg, 0.72 mmol) was added to a stirred solution of chlorohydrin **(*R*)-33** (150 mg, 0.59 mmol) in MeOH (0.56 mL) at 0 ˚C. The resulting mixture was stirred at rt for 1 h, diluted with Et_2O (30 mL), and washed with water (30 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% Et_2O in petrol) to give epoxide **(*R*)-30** (128 mg, 0.59 mmol, 99%) as colorless oil, R_f = 0.71 (20% Et_2O in petrol); $[\alpha]_D^{21}$ = +3.4 (*c*, 1.0 in $CHCl_3$); IR (film) 2968m, 1592m, 824s; ^{1}H NMR (400 MHz) 1.21 (s,

3H, CH_3), 1.23 (s, 3H, CH_3), 1.61 - 1.63 (m, 2H, CH_2CHO), 2.36 (s, 3H, CH_3Ph), 2.43 (dd, 1H, CH_AH_BO, J = 2.8, 5.0), 2.77 (dd, 1H, CH_AH$_B$O, J = 4.0, 5.0), 3.00 - 3.04 (m, 1H, CHO), 4.92 (d, 1H, H_AH$_B$C=C, J = 1.5), 5.24 (d, 1H, H$_A$$H_B$C=C, J = 1.5), 7.06 (d, 2H, 2 × Ar-H, J = 8.0), 7.12 (d, 2H, 2 × Ar-H, J = 8.0); ^{13}C NMR (100 MHz) 21.0 (CH_3Ph), 27.7 (CH_3CCH_3), 27.9 (CH_3CCH_3), 38.9 ($C(CH_3)_2$), 43.5 (CH_2CHO), 46.9 (CH_2O), 49.7 (CHO), 113.7 (CH_2=C), 128.2 (Ar-C), 128.9 (Ar-C), 136.1, 139.9 (2 × Ar-C), 157.4 (H_2C=C); MS (CI+) *m/z*: 234 (MNH_4^+, 13%,), 217 (MH^+, 100%,), 199 (17%), 160 (14%); HRMS *m/z*: MH^+ found 217.1599, $C_{15}H_{21}O$ requires 217.1592.

Formation of (1R, 2R, 5R)-4,4-dimethyl-5-p-tolyl-bicyclo[3.1.0]hexan-2-ol ***(–)-34*** *from epoxide* ***(R)-30*** *under standard conditions*

Following the typical cyclopropanation procedure, epoxide **(*R*)-30** (100 mg, 0.46 mmol) was treated with LTMP in *t*-BuOMe for 20 h to give bicyclic alcohol **(–)-34 (**71 mg, 0.33 mmol, 72%) as a colorless oil, R_f = 0.3 (30% Et_2O in petrol); $[\alpha]_D^{21}$ = –3 (*c*, 1.0 in $CHCl_3$); IR (film) 3356m, 2956s, 1516m, 1465m, 1034m, 998m, 820m; ^{1}H NMR (400 MHz) 0.60 - 0.62 (m, 1H, H-6), 0.66 (dd, 1H, H-6′, J = 4.9, 8.5), 1.00 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.56 - 1.57 (m, 2H, H-3, H-3′), 1.68 (s, 1H, OH), 1.73 (dd, 1H, CH-1, J = 3.8, 8.6), 2.35 (s, 3H, CH_3Ph), 4.32-4.33 (m, 1H, H-2), 7.11 (d, 2H, 2 × Ar-H, J = 7.8), 7.26 (d, 2H, 2 × Ar-H, J = 7.8); ^{13}C NMR (100 MHz) 13.9 (C-6), 21.1 (CH_3Ph), 25.6 (CH_3), 29.1 (CH_3), 32.0 (C-1), 41.2 (C-4), 42.3 (C-5), CPh), 47.3 (C-3), 74.5 (C-2), 128.4 (Ar-C), 130.8 (Ar-C), 135.9, 138.2 (2 × Ar-C); MS (CI+) *m/z*: 199 ($[M–H_2O]H^+$, 100%,), 198 (52%), 183 (15%); HRMS *m/z*: M^+ found 216.1513, $C_{15}H_{20}O$ requires 216.1514.

Formation of (1R, 2R, 5R)-4,4-dimethyl-5-p-tolyl-bicyclo[3.1.0]hexan-2-ol ***(–)-34*** *from chlorohydrin* ***(R)-33***

Following the typical cyclopropanation procedure, chlorohydrin **(*R*)-33** (253 mg, 1.00 mmol) was treated with LTMP (3.5 equiv.) in *t*-BuOMe for 20 h to give bicyclic alcohol **(–)-34 (**128 mg, 0.59 mmol, 59%) as a colorless oil. Data as above.

Formation of (1R, 2R, 5R)-4,4-dimethyl-5-p-tolyl-bicyclo[3.1.0]hexan-2-ol ***(–)-34*** *from epoxide* ***(R)-30*** *using substoichiometric TMP*

n-BuLi (1.6 M in hexanes, 0.58 mL, 0.93 mmol) was added very slowly over 25 min to a stirred solution of epoxide **(*R*)-30** (100 mg, 0.46 mmol) and tetramethylpiperidine (33 mg, 0.23 mmol, 0.039 mL) in *t*-BuOMe (2.3 mL) at –2 ˚C. The resulting pale-yellow mixture was stirred at the same temperature for 4.5 h (complete consumption of the epoxide). The reaction was then quenched with aq. HCl (3 M, 2 equiv.), diluted with Et_2O (10 mL) and washed twice with aq. HCl (3 M, 0.5 equiv.); the aqueous phase was extracted twice with Et_2O (2 × 5 mL) and the combined organic phases dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by column chromatography (30% Et_2O in petrol) gave **(–)-34** (84 mg, 0.39 mmol, 85%) as a colorless oil. Data as above. [When the same reaction was performed under identical conditions using 1.1 equiv. of *n*-BuLi added slowly over 13 min, it gave **(–)-34** in 72% yield].

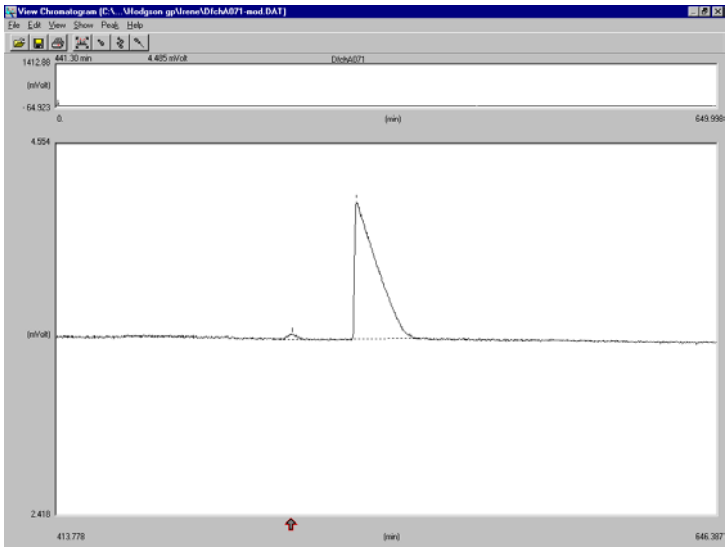
(1R,5R)-4,4-dimethyl-5-p-tolyl-bicyclo[3.1.0]hexan-2-one (+)-29[16]

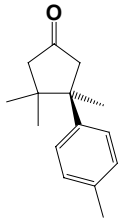
TPAP (5.3 mg, 0.015 mmol) was added to a stirred solution of bicyclic alcohol **(–)-34** (65 mg, 0.30 mmol), 4-methylmorpholine *N*-oxide (71 mg, 0.60 mmol), and powdered 3Å molecular sieves (83 mg) in CH_2Cl_2 (2.2 mL) at 20 ˚C. After 2 h the mixture was filtered through a short pad of silica (2.5 × 8 cm) and eluted with Et_2O (100 ml). The solvent was evaporated *in vacuo* to give ketone **(+)-29** (64 mg, 0.30 mmol, 99%) as a white solid, R_f = 0.59 (30% Et_2O in petrol); $[\alpha]_D^{20}$ = +19.5 (*c*, 1.0 in $CHCl_3$), {lit.[16] $[\alpha]_D$ = –16.1, (*c*, 2.6 in $CHCl_3$ for (–)-enantiomer)}; IR (KBr) 1717s; ^{1}H NMR (400 MHz) 0.92 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.36 - 1.40 (m, 1H, CH_AH_BCHCO), 1.58 (dd, 1H, CH_AH_BCHCO, *J* = 3.0, 4.5), 1.90 (d, 1H, CH_AH_BCO, *J* = 17.3), 2.12 (dd, 1H, CHCO, *J* = 8.6, 2.8), 2.21 (d, 1H, CH_AH_BCO, *J* = 17.3), 2.35 (s, 3H, CH_3Ph), 7.12 (d, 2H, *J* = 8.2), 7.20 (d, 2H, *J* = 8.2); ^{13}C NMR (100 MHz) 20.7 (CH_2CHCO), 21.1 (CH_3Ph), 24.1 (CH_3), 28.4 (CH_3), 35.2 (*C*HCO), 38.9, 47.1 ($C(CH_3)_2$, CPh), 48.1 (CH_2CO), 128.7 (2 × Ar-C), 130.4 (2 × Ar-C), 135.1, 137.2 (2 × Ar-C_{quat}), 213.2 (CO); MS (CI+) *m/z*: 232 (MNH_4^+, 87%), 215 (MH^+, 100%), 158 (17%); HRMS *m/z*: MNH_4^+ found 232.1693, $C_{15}H_{22}NO$ requires 232.1701.

(R)-(+)-β-cuparenone ***(+)-28***

Small pieces of lithium wire (20 mg, 2.88 mmol, prewashed with anhydrous pentane) were placed in a three-necked flask under argon. Ammonia (~8 mL) was condensed into the flask at −78 ˚C and a solution of ketone **(+)-29** (65 mg, 0.30 mmol) and *t*-BuOH (0.18 mL) in anhydrous Et_2O (3.6 mL) were added. After 15 min, NH_4Cl (600 mg) was added to the blue solution. Ammonia was allowed to evaporate by warming to rt and the remaining solution was diluted with Et_2O (30 mL). The solution was extracted with water (30 mL), the layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by column chromatography (30% Et_2O in petrol) gave **(+)-28 (**56 mg 0.259 mmol, 85%) as a colorless oil, R_f = 0.67 (30% Et_2O in petrol); $[\alpha]_D^{21}$ = +42 (*c*, 1 in $CHCl_3$); lit.[17] $[\alpha]_D^{29}$ = +45 (*c*, 1.4 in $CHCl_3$), lit.[18] $[\alpha]_D^{23}$ = +44.4 (*c*, 2.47 in $CHCl_3$); IR (film) 2961s, 1742s (C=O), 1517m, 1457m, 1406m, 1203m, 1020m, 818m; ^{1}H NMR (200 MHz) 0.74 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.43 (s, 3H, CH_3CPh), 2.28 - 2.39 (m, 3H), 2.34 (s, 3H, CH_3Ph), 3.14 (d, 1H, *J* = 18.2), 7.14 (d, 2H, 2 × Ar-H, *J* = 8.2), 7.21 (d, 2H, 2 × Ar-H, *J* = 8.2); ^{13}C NMR (100 MHz) 20.8 (CH_3Ph), 24.1 (CH_3), 24.4 (CH_3CPh), 26.2 (CH_3), 41.8, 47.8 ($C(CH_3)_2$, CPh), 50.7 (CH_2), 52.4 (CH_2), 126.5 (2 × Ar-C), 128.7 (2 × Ar-C), 135.8, 141.2 (2 × Ar-C), 218.3 (CO); MS (CI+) *m/z*: 234 (MNH_4^+, 100%,), 217 (MH^+, 13%), 132 (97%); HRMS *m/z*: MNH_4^+ found 234.1849, $C_{15}H_{24}NO$ requires 234.1858.

Chiral GC (Cydex-β column, 100 ˚C, 1.0 mLmin^{-1}) analysis of **(+)-28** showed a resultant ee = 97%





(+)-28

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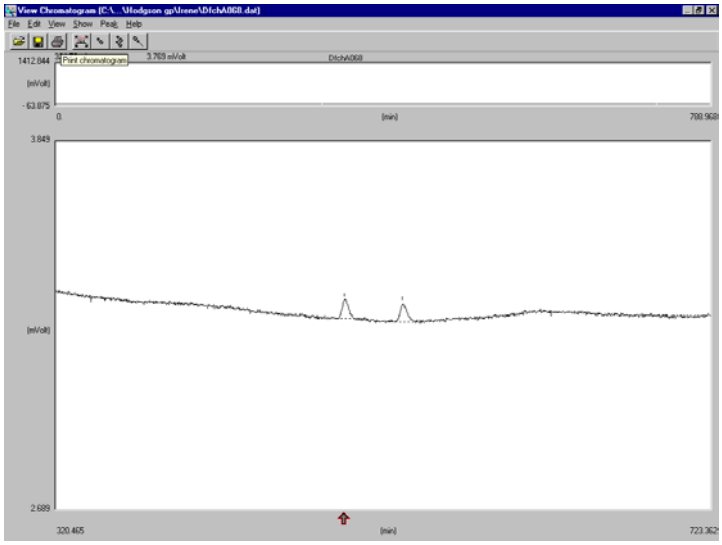

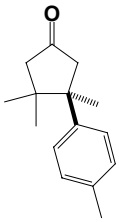

28

Peak Number #	Area %	Ret.Time	Area BC
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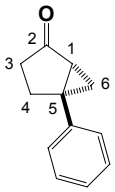
2	50.0670	533.54	168136 mi
Totals	100.0000		335822

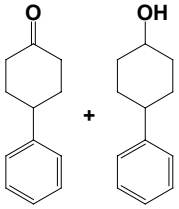
5-Phenylbicyclo[3.1.0]hexan-2-one



TPAP (24.3 mg, 0.069 mmol) was added to a stirred solution of alcohol **5f** (241 mg, 1.38 mmol), 4-methylmorpholine *N*-oxide (325 mg, 2.77 mmol), and powdered 3Å molecular sieves (380 mg) in CH_2Cl_2 (10.2 mL) at 20 ˚C. After 2 h the mixture was filtered through a short pad of silica (10·3 cm) and eluted with Et_2O (200 mL); the organic solvent was evaporated *in vacuo* to give 5-phenylbicyclo[3.1.0]hexan-2-one (238 mg, 100%) as a pale yellow oil, R_f = 0.29 (30% Et_2O in petrol); IR (film) 2940w, 1728s (C=O), 1180m, 759m, 699m; ^{1}H NMR (400 MHz) 1.50 (dd, 1H, H-6 J = 3.5, 4.8), 1.61 (ddt, 1H, H-6′, J = 1.4, 4.8, 9.3), 2.15 (dd, 1H, H-1, J = 3.5, 9.3), 2.21 - 2.31 (m,

2H, 2·H-3), 2.3 - 2.49 (m, 2H, 2 × H-4), 7.24 - 7.29 (m, 3H, 3 × Ar-H), 7.32 - 7.37 (m, 2H, 2 × Ar-H); ^{13}C NMR (100 MHz) 21.1 (C-6), 29.0 (C-4), 33.4 (C-3), 35.7 (C-1), 37.1 (C-5), 126.9 (2 × Ar-C), 128.6 (2 × Ar-C), 141.7 (Ar-C), 213.4 (CO); MS (CI+) *m/z*: 190 (20%, MNH_4^+), 173 (MH^+, 100%), 130 (100%), 115 (98%), 91 (15%); HRMS *m/z*: MNH_4^+ found 190.1230, $C_{12}H_{16}NO$ requires 190.1232.

4-Phenyl cyclohexanone and 4-phenyl cyclohexanol



Small pieces of lithium wire (82 mg, 11.8 mmol, prewashed with anhydrous pentane) were placed in a three-necked flask. Ammonia (~30 mL) was condensed into the flask at –78 ˚C and a solution of 5-phenylbicyclo[3.1.0]hexan-2-one (200 mg, 1.16 mmol) and *t*-BuOH (0.70 mL) in Et_2O (15 mL) was added. The mixture was allowed to reflux for 15 min by removing the dry ice-acetone bath and then NH_4Cl (1.47 g) was added. The remaining ammonia was allowed to evaporate, the resulting solution was diluted with Et_2O (50 mL) and then extracted with water (50 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), the combined organic layers were dried ($MgSO_4$), filtered and evaporated *in vacu*o to give the crude product. Purification by column chromatography (30% Et_2O in petrol) gave 4-phenyl cyclohexanone[19] (70 mg, 0.40 mmol, 35%) as a white solid, and 4-phenyl cyclohexanol[20] (90 mg, 0.51 mmol, 44%, as an inseparable mixture of two diastereoisomers, dr 6.7/3.3 determined by ^{1}H NMR analysis of the crude product) as a white solid.

Characterization data for 4-phenyl cyclohexanone:

R_f = 0.47 (30% Et_2O in petrol); IR (KBr) 2960m, 1716s, 1450m, 1163m, 738s; ^{1}H NMR (400 MHz) 1.91 - 2.02 (m, 2H, CH_2), 2.21 - 2.26 (m, 2H, CH_2), 2.51 - 2.58 (m, 4H, 2 × CH_2CO), 3.00 - 3.08 (m, 1H, CH), 7.22 - 7.36 (m, 5H, Ar-H); ^{13}C NMR (100 MHz) 34.0 (2 × CH_2), 41.4 (2 × *C*H_2CO), 42.8

(CH), 126.6 (Ar-C), 126.7 (2 × Ar-C), 128.6 (2 × Ar-C), 144.8 (Ar-C), 211.2 (C=O); MS (CI+) *m/z*: 194 (MNH_4^+, 100%), 174 (7%); HRMS *m/z*: MH^+ found 175.1123, $C_{12}H_{15}O$ requires 175.1123.

Characterization data for 4-phenyl cyclohexanol:

R_f = 0.19 (30% Et_2O in petrol); IR (KBr) 3375m, 2924s, 1494m, 1062m, 966w, 739m; ^1H NMR (400 MHz), inseparable mixture of two diastereoisomers: 1.27 - 1.33 (m), 1.39 - 1.64 (m), 1.73 - 1.82 (m), 1.92 - 2.13 (m), 2.47 - 2.55 (m), 2.60 - 2.72 (m), 3.55 - 3.60 (m, C*H*OH), 3.67 - 3.74 (m, C*H*OH), 5.42 - 5.44 (m, OH), 5.69 - 5.77 (m, OH), 7.18 - 7.22 (m, Ar-H), 7.27-7.32 (m, Ar-H); discernable data for major diastereoisomer: 3.67 - 3.74 (m, C*H*OH), 5.69 - 5.77 (m, OH); discernable data for minor diastereisomer: 3.55 - 3.60 (m, C*H*OH), 5.42 - 5.44 (m, OH); ^{13}C NMR (100 MHz), inseparable mixture of two diastereisomer: 26.7 (CH_2), 27.4 (CH_2), 29.5 (CH_2), 32.4 (CH_2), 35.7 (CH_2), 35.8 (CH_2), 43.4 (CH), 44.2 (CH), 70.6 (CHOH), 70.9 (CHOH), 117.0, 124.3, 124.4, 126.0, 126.7, 128.3 (Ar-C), 138.8 (Ar-C), 146.5 (Ar-C); discernable data for major diastereoisomer: 43.4 (CH), 70.6 (CHOH), 146.5 (Ar-C); discernable data for minor diastereisomer: 44.2 (CH), 70.9 (CHOH), 138.8 (Ar-C); MS (CI+) *m/z*: 159 ($[M–H_2O]H^+$, 5%), 158 ($M–H_2O$, 100%), 143 (8%); HRMS *m/z*: MNH_4^+ found 194.1552, $C_{12}H_{20}NO$ requires 194.1545.

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