Magnesium-mediated intramolecular reductive coupling: a stereoselective synthesis of C_2-symmetric 3,4-bis-silyl-substituted adipic acid derivatives†

Pintu K. Kundu and Sunil K. Ghosh*

Received 2nd June 2009, Accepted 7th August 2009
First published as an Advance Article on the web 14th September 2009
DOI: 10.1039/b910784c

Chiral C_2-symmetric 3,4-bis-silyl-substituted adipic acid derivatives have been synthesised by a Mg/trimethylsilyl chloride-mediated intramolecular reductive coupling of symmetrical disiloxanes of β-silylacrylic acid *N*-oxazolidinone derivatives. Efficient and short syntheses of enantiomerically pure enantiomers of 2,6-dioxabicyclo[3.3.0]octane-3,7-dione have been achieved from the bis-silylated adipic acid derivatives using Fleming–Tamao oxidation as the key step.

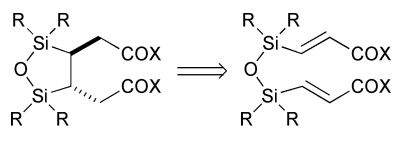
Introduction

Molecules containing two (or more) stereochemically defined silicon-bearing centres and terminal functionalities are useful intermediates in organic synthesis. A silicon group can effect stereochemical control[1] in a 1,2-related and a 1,3-related fashion. Therefore, molecules with two adjacent silicon-bearing centres can effectively control stereocentres which are 1,4-related and beyond.[2] Highly stereoselective syntheses of the *meso* diastereoisomer of 3,4-bis-silylated adipates by a SmI_2[3] induced hydrodimerisation of β-dimethyl(aryl)silylacrylates have been reported[4] and used in the stereocontrol of 1,4-related centres to achieve the synthesis of both enantiomers of nonactic acid as well as nonactin.[5] Thus, the C_2-symmetric *racemic* diastereoisomer of 3,4-bis-silylated adipate is also expected to be a starting point for syntheses of complex molecules. Besides, C_2-symmetric molecules have *privileged* structures with high potential for the generation of molecular species suitable for asymmetric catalysis. Herein, we report our successful approach to the stereoselective syntheses of chiral C_2-symmetric 3,4-bis-silyl-substituted adipic acid derivatives and the utility of some of these intermediates for short and efficient syntheses of enantiomerically pure enantiomers of 2,6-dioxabicyclo[3.3.0]octane-3,7-dione.

Results and discussion

Besides electrochemical methods,[6] intermolecular reductive hydrocoupling of α,β-unsaturated carbonyl compounds is known to be mediated by metals like Na,[7] Yb[8] and Sm[9] or reducing agents like SmI_2[10] and $TiCl_4$–Zn.[11] Amongst these, SmI_2, which is frequently used for this purpose, can induce hydrodimerisation of β-aryl/alkyl acrylic acid derivatives to give 3,4-diaryl/alkyl-substituted adipates/adipamides[12] in favour (66–100%) of the C_2-symmetric diastereoisomer. However, the same hydrodimerisation of β-silylacrylic acid esters[3] favoured the *meso* diastereoisomer (76–100%). An intramolecular version of this reaction with bis-α,β-unsaturated esters linked by a tether underwent reductive coupling–Dieckmann condensation leading to bicyclic oxacyclopentanecarboxylate with varying degrees of preference for the *cis* or *trans* ring junction products, depending upon the olefin geometry, tether length and reaction conditions.[13] Using reagents other than SmI_2, some recent reports[14-21] have shown that the intramolecular reductive coupling of α,β-unsaturated carbonyl compounds joined by a suitable tether led to cyclic systems with preferential formation of the *trans*-diastereoisomers. Magnesium in methanol can induce intramolecular reductive cyclisation of ketones[17] tethered to activated olefins. The same combination has been used[18,19] for activated olefins connected by a tether to give cyclic products with 3- and 5-membered rings, associated with varying quantities of double bond reduction products. The diastereoisomer ratio in the products depended on the substituents at the activated olefins and the tether. In most cases, it varied between 1.1 and 2.8, favouring the *trans*-isomers. Electroreductive cyclisation[15] of a bis-enoate tethered by a propyl chain has been reported to give a 1,2-disubstituted cyclopentane system with moderate to high *trans*-selectivity depending upon the proton source.[15d] The chrysene radical anion-induced intramolecular reductive cyclisation[16] of bis(enone) led to a *cis* ring junction preferentially. Photocatalysts in combination with sacrificial electron donors have also been developed[20] for photoinduced electron transfer to the β-position of α,β-unsaturated esters and ketones. The resulting carbon-centred radicals led to intramolecular C–C bond formation providing 5- or 6-membered rings with a strong preference for *trans*-1,2-stereochemistry. The tin hydride[21] induced intramolecular reductive cyclisations of α,β-unsaturated ketones with electronically deficient olefins also favoured high *trans*-selectivity.

We, therefore, decided to resolve our problem of making C_2-symmetric *racemic* diastereoisomer **1** by using a five-membered ring formation (Scheme 1). This can be expected to be achieved



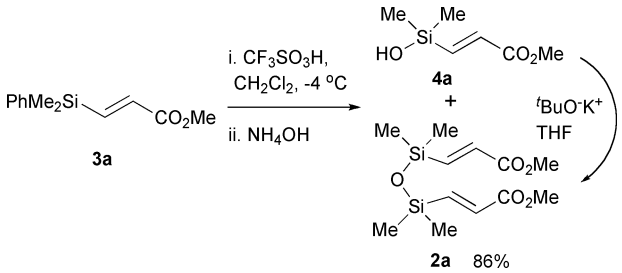
Scheme 1 Retrosynthesis of cyclic disiloxane **1**.

Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai, India. E-mail: ghsunil@barc.gov.in; Fax: +91-22-25505151; Tel: +91-22-25595012

† Electronic supplementary information (ESI) available: Copies of ^1H and ^{13}C spectra of new compounds. See DOI: 10.1039/b910784c

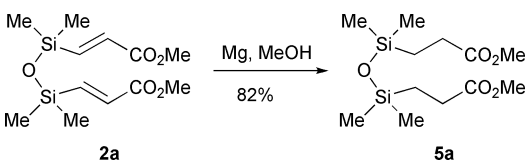
by intramolecular reductive cyclisation of symmetrical disiloxane tethered bis-acrylates **2** (X = OR′).

Our first task was, therefore, to make the symmetric disiloxane **2a** (R = Me, X = OMe), as syntheses of these types of molecule are not known. Recently, we have reported[22] the synthesis of vinylsilanols and vinyldisiloxanes from dimethyl(phenyl)vinylsilanes by a selective proteodephenylation using trifluoromethanesulfonic (TfOH) or trifluoroacetic acid (TFA). We were pleased to see that under these conditions, the silylacrylate **3a** gave the desired disiloxane **2a** in excellent yield (Scheme 2). It is worth mentioning that sometimes the product is contaminated with a small amount of silanol **4a**, which either on standing or treatment with a sub-stoichiometric amount of potassium *tert*-butoxide gets converted to the desired disiloxane **2a**.



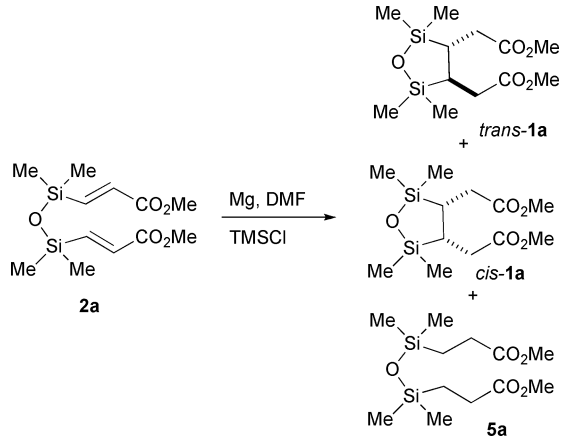
Scheme 2 Synthesis of disiloxane **2a**.

The intramolecular reductive cyclisation of the disiloxane **2a** was then attempted with SmI_2 in THF–DMPU following the literature[3] procedure without much success. Moreover, SmI_2 is reactive to certain carboxylic acid derivatives such as *N*-acyl oxazolidinones,[23] highly air-sensitive and requires THF as a co-solvent. While searching for a cheaper and more environmentally friendly reagent, we found that Mg metal and SmI_2 have similar reduction potentials.[24] Magnesium has already been used in reductive reactions involving unsaturated esters as well as in intramolecular reductive cyclisations.[18,19] When we carried out the reductive cyclisation of disiloxane **2a** with Mg metal in dry MeOH following the protocol of Chavan and Ethiraj,[19] only the double bond reduced product **5a** (Scheme 3) was isolated. The reaction did not proceed at all in solvents like THF, acetonitrile or DMF even after prolonged stirring at room temperature.



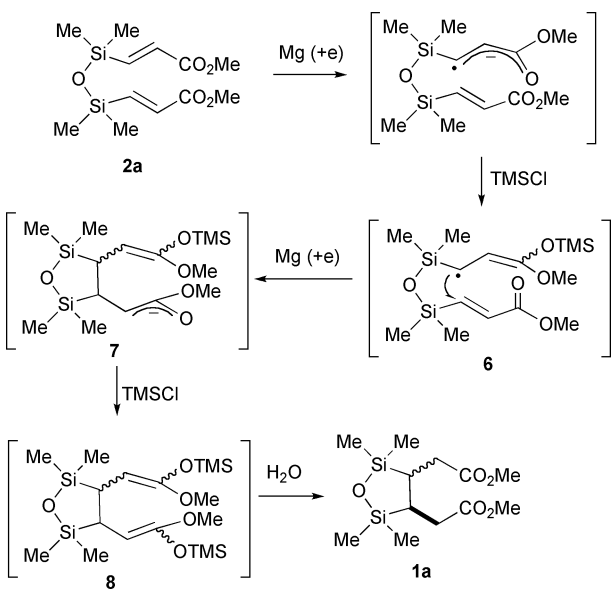
Scheme 3 Reaction of **2a** with Mg in MeOH.

Recently, Nishiguchi *et al.*[25] have shown that in the presence of trimethylsilyl chloride (TMSCl) as an additive, the Mg metal-promoted reductive dimerisation of α,β-unsaturated aldehydes and ketones in DMF generates bis-(silyl enol) ethers with very high regioselectivity. We were gratified to note that the reaction with disiloxane **2a** under the reported conditions,[25] took place with complete consumption of starting material (Scheme 4; Table 1, entry 1). Analysis of the crude product by ^{1}H NMR spectroscopy revealed the formation of a mixture of diastereoisomeric cyclic products, *cis*-**1a** and *trans*-**1a**, along with the double bond reduced



Scheme 4 Mg/TMSCl mediated reductive coupling of **2a**.

product **5a** and some unidentified oligomeric materials. We then modified the procedure by adding the disiloxane **2a** to the mixture of Mg and TMSCl in DMF under various conditions as presented in Table 1. Under all these conditions, the formation of the double bond reduction product **5a** (10–24%) could not be avoided. The role of TMSCl in this reaction was manifold. Without it, the reaction did not take place in DMF.‡ Therefore, the presence of TMSCl accelerated the redox process between Mg and the disiloxane substrate. Its presence also increases the chemoselectivity of the reaction in favour of the reductive cyclisation products over the double bond reduction product. This can be explained by the mechanism proposed in Scheme 5. The reductive cyclisation process was probably accelerated by quenching the radical anion, formed by electron transfer from Mg to the substrate **2a**, with TMSCl to give the radical **6**. This radical underwent intramolecular conjugate addition to the unsaturated



Scheme 5 Proposed mechanism for reductive cyclisation of disiloxane **2a** promoted by Mg/TMSCl.

‡ The reaction did not proceed at all in solvents like THF and acetonitrile even in the presence of TMSCl.

Table 1 Reductive cyclisation of disiloxane **2a** promoted by Mg/TMSCl

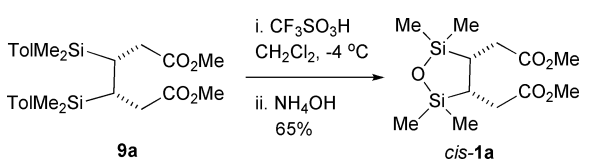
Entry	Mg/TMSCl (equiv.)	Conc. of **2a** in DMF	Temp (°C)/addition time	Ratio of products[a] *cis*-**1a**: *trans*-**1a**: **5a**	Yield (%)[b]
1	12/12	100 mM	28/1 min	42:40:18	25
2	12/6	100 mM	0/10 min	43:40:17	70
3	12/12	12 mM	28/3 h	39:40:21	75
4	12/24	15 mM	10/3 h	42:38:20	75
5	24/24	8 mM	28/5 h	46:30:24	80
6	12/12	10 mM	10/1 h	52:30:18	80[c]
7	12/12	30 mM	0/1.3 h	42:42:16	87
8	12/6	15 mM	28/3 h	63:27:10	85[d]

[a] Obtained from ^{1}H-NMR spectrum of the crude product. [b] Isolated combined yield of *cis*-**1a**, *trans*-**1a** and **5a**. [c] Reaction performed under sonication. [d] SmI_3 (0.2 equiv.) was added as an additive.

ester functionality and finally one more electron addition gave the intermediate anion **7** which was then quenched by TMSCl to give bis silyl ketene acetal **8**. The silyl acetal **8** underwent hydrolysis during aqueous work-up conditions and provided the diester **1a**. By this process, TMSCl also protected the reductive cyclisation product from further reactions like Dieckmann condensation or oligomerisations.

The stereoselectivity of the cyclisation was marginal in all these conditions as shown in Table 1. A catalytic amount of SmI_2 or SmI_3 and a stoichiometric amount of a reducing agent like Mg can induce various types of reactions on carbonyl compounds including pinacol type self couplings[26] or couplings with activated olefins.[27] Being a lanthanide, samarium in the trivalent state is known to be a good complexing agent[28] and thus can activate the substrate as well as make the transition state compact for a better stereocontrol. Therefore, we were interested to see the effect of SmI_3 in this coupling reaction and a marginal preference for *cis*-**1a** was observed when SmI_3 (0.2 equiv.) was added to the above reagents (Table 1, entry 8). The optimised conditions for the cyclisation were therefore to use 12 equiv. each of Mg and TMSCl in DMF with a 30 millimolar concentration of the unsaturated ester **2a** at 0 °C which gave a mixture of *cis*-**1a**, *trans*-**1a** and reduced diester **5a** in 87% isolated combined yield (Table 1, entry 7). Although little selectivity in the cyclisation was observed, the formation of the reduction product was substantially reduced (**1a**:**5a** = 84/16) under the optimised conditions. *Racemic trans*-**1a** is a crystalline solid and easily crystallises out from a hexane solution of the crude reaction product leaving behind the *cis*-**1a** and the reduced product **5a** in the solution, which were then separated by chromatography.

The stereochemistry of the cyclic products was confirmed by converting the known[3] *meso* diester **9a** to the *cis*-**1a** (Scheme 6). For this, the *meso* diester **9a** was briefly treated with TfOH in dichloromethane at –4 °C and quenched with ammonium hydroxide to provide *cis*-**1a**. By comparing the ^{1}H NMR spectra, the stereochemistry of the crystalline product from the Mg-mediated reaction was confirmed to be the *racemic trans*-**1a**.



9a *cis*-**1a**

Scheme 6 Confirmation of stereochemistry.

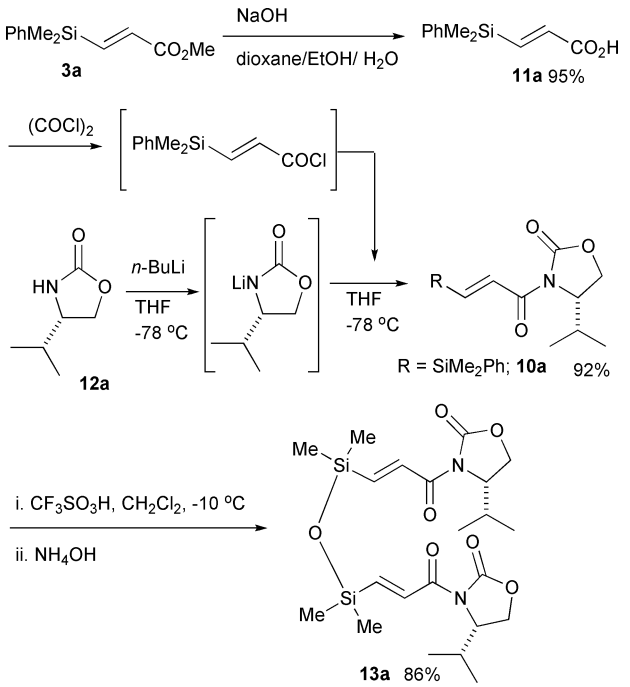
Our next attempt was to improve the relative stereochemistry (*trans*/*cis*) as well as control the absolute configuration during the cyclisation to obtain the *trans*-isomer(s) in pure and enantiomeric form. It was envisaged that instead of an ester, the Mg/TMSCl-mediated coupling of the corresponding amide, possessing a suitable chiral amine, might be useful for this purpose. Amongst the amides, chiral oxazolidinones,[29] initially introduced by Evans *et al*.[30] are widely used as chiral auxiliaries. These oxazolidinones, when attached to carboxylic acids, control the diastereoselectivity[31] of reactions at the position α to the carboxylic acid group. Oxazolidinones are also known for their strong directing effect[32] on the conjugate addition of nucleophiles to the β position of unsaturated acid derivatives and in electroreductive hydrodimerisation.[33] Sibi *et al.*[34] have shown that various oxazolidinone derivatives of α,β-unsaturated carboxylic acids can control the stereoselectivity of C–C bond formation at the β-position in radical reactions. Unlike alkyl amides, the oxazolidinone amide bond is easily hydrolysed to give acids. In view of all of this, we prepared the (*S*)-valine derived oxazolidinone derivative of β-silylacrylic acid **10a** as shown in Scheme 7. The *trans*-β-silylacrylic ester **3a** was hydrolysed to the acid **11a**, which was converted to the intermediate acid chloride by reacting with oxalyl chloride, which was then reacted with the lithium salt of Evans' oxazolidinone **12a** to give the oxazolidinone derivative **10a** in high yield. Reaction of this amide **10a** with TfOH (3.6 equiv.) in dichloromethane at –10 °C, followed by quenching with ammonium hydroxide, produced the disiloxane **13a** in very good yield.

Next, we subjected the disiloxane **13a** to the optimised reductive cyclisation conditions (Table 1, entry 7) described for disiloxane **2a**, using Mg/TMSCl in DMF at 0 °C, which led to complete consumption of the starting material. Interestingly, the crude reaction product showed the formation of a mixture of diastereoisomeric cyclic products, *cis*-**14a** and two *trans*-products (*trans*-**14a**:*trans*-**15a** = 60/40) with a strong preference for the desired *trans* isomers (*trans*:*cis* = 85/15) (Scheme 8 and Table 2, entry 1). Also, the formation of the double bond reduced product was significantly reduced (not seen in the ^{1}H-NMR spectrum of the crude product). The isolated yield of the cyclic products was also very high (85%), and the *trans*-isomers could be easily separated from the *cis*-**14a** by crystallisation. Notably, even the two diastereoisomeric *trans*-**14a** and *trans*-**15a** could be individually isolated by fractional crystallisation with nearly quantitative recovery. To see the effect of SmI_3 in the reductive cyclisation, the reaction was also carried out using disiloxane **13a**, TMSCl and SmI_3 (0.2 equiv.) as an additive

Table 2 Mg/TMSCl promoted reductive cyclisation of oxazolidinone-attached disiloxanes **13a–13c**

		Cyclised products		
Entry	Disiloxane	*trans*:*cis*[a]	*trans*-**14**: *trans*-**15**	%Yield[b]
1	**13a**	85:15	60:40	85
2	**13a**	67:33	53:47	75[c]
3	**13b**	88:12	45:55	83
4	**13c**	87:13	45:55	83

[a] Obtained from ^{1}H-NMR spectrum of the crude product. [b] Combined isolated yield of all isomers. [c] SmI_3 (0.2 equiv.) was used as an additive.

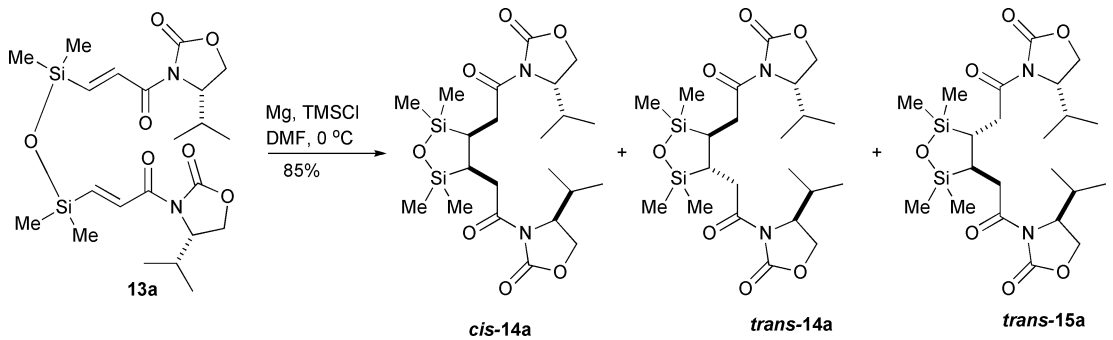


Scheme 7 Synthesis of disiloxane **13a**.

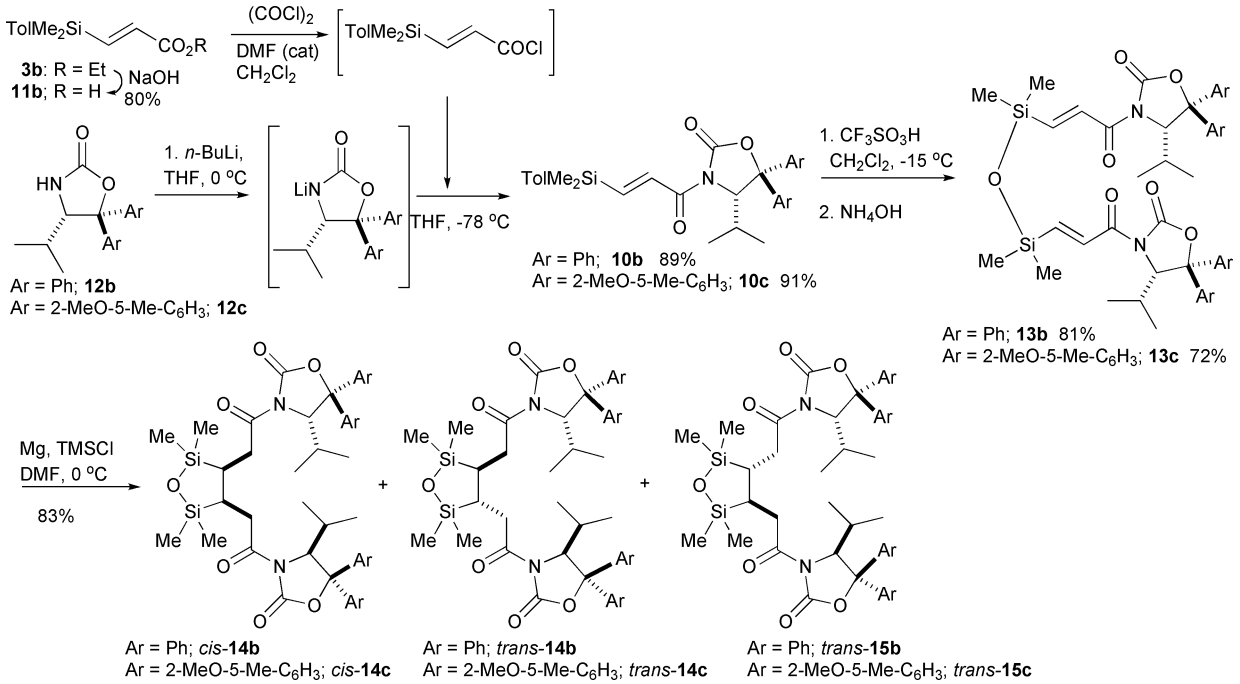
under the above conditions. This reduced the *trans*/*cis* ratio to 67/33, with a marginal change in the selectivity between the *trans*-isomers (Table 2, entry 2).

For further improvement in stereoselectivity, we decided to modify the oxazolidin-2-one with various substituents. A number of research groups[35-37] had independently introduced 5,5-disubstituted oxazolidin-2-ones, called 'SuperQuats', as chiral auxiliaries mainly to obviate the problems *viz*. purification of products by crystallisation, and limit endocyclic cleavage during removal, which is known to be problematic with Evans' oxazolidin-2-one **12a**.[30] We were specifically interested to see the effect of 5,5-disubstituted oxazolidin-2-ones on the reductive cyclisation because we had already seen a dramatic improvement in diastereoselective anhydride opening[38] when using them. We prepared 4-isopropyl-5,5-diphenyloxazolidin-2-one **12b** and 4-isopropyl-5,5-diaryloxazolidin-2-one **12c** from (*S*)-valine following the reported procedures.[38,39] The lithium salts of the oxazolidin-2-ones **12b**, **12c** were made in THF using *n*-BuLi at 0 °C and reacted with the intermediate acid chloride generated from acid **11b** (obtained from the hydrolysis of **3b**) at –78 °C in THF to give the amides **10b** and **10c**, respectively. The $TolMe_2Si$ group was chosen in these cases because this group is expected to proteodearylate under milder conditions compared to the $PhMe_2Si$ group. This was essential to prevent degradation of the oxazolidinone moieties in **10b** and **10c**. Unlike amide **10a**, the conversion of the amides **10b** and **10c** to the corresponding disiloxanes **13b** and **13c** was performed with less TfOH (2.5–3 equiv.) and at a lower temperature (–15 °C) (Scheme 9). Reductive cyclisation of disiloxane **13b**, under the conditions described for amide **13a**, resulted in the formation of a mixture of diastereoisomeric cyclic products, *cis*-**14b** and two diastereoisomeric *trans*-products (*trans*-**14b**: *trans*-**15b** = 45/55) with a marginally higher preference for the desired *trans*-isomers (*trans*: *cis* = 88/12) (Table 2, entry 3). Similarly, the disiloxane **13c** also gave a mixture of *cis*-**14c** and two diastereoisomeric *trans*-products (*trans*-**14c**: *trans*-**15c** = 45/55) on reductive cyclisation with Mg and TMSCl. Fractional crystallisation then provided pure *trans*-**15b** or *trans*-**15c** but other isomers *viz*. *cis*-**14b** or *cis*-**14c** and *trans*-**14b** or *trans*-**14c** could not be separated by crystallisation or chromatography.

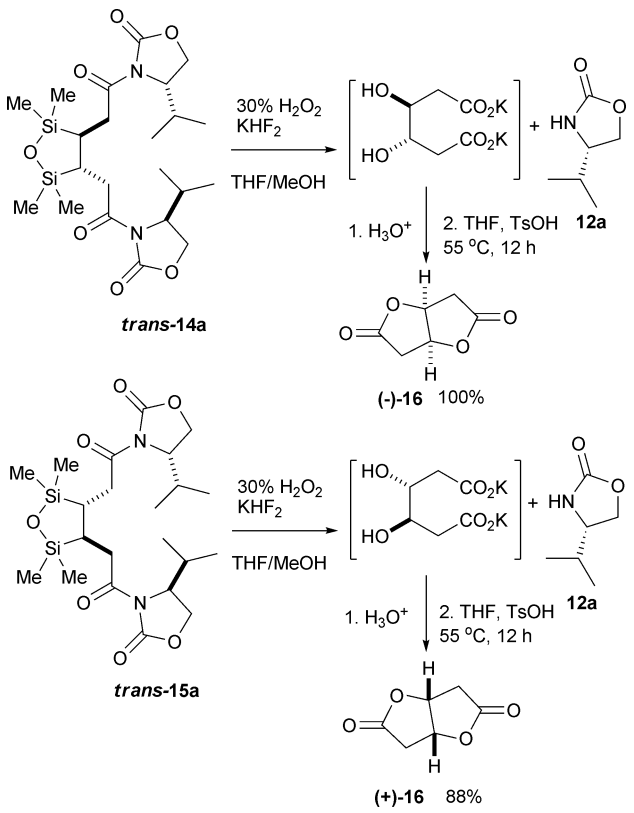
To establish the absolute stereochemistry of the individual *trans*-diastereoisomers *viz*. *trans*-**14a** and *trans*-**15a**, each of these was converted to known bislactone **16**. For this, *trans*-**14a** was subjected to Fleming–Tamao[40,41] oxidation using KHF_2–H_2O_2 in 1/1 THF–MeOH at 60 °C (Scheme 10). Besides conversion of the silyloxy groups to hydroxyl groups, the oxazolidinone group was also removed under these conditions to give the intermediate dipotassium salt. At this stage, a simple extraction of the reaction mixture with ethyl acetate gave back the oxazolidinone **12a** (90%) and acidification of the residue gave the dilactone (–)-**16**. The



Scheme 8 Reductive cyclisation of disiloxane **13a**.



Scheme 9 Synthesis of disiloxanes **13b**,**c** and their reductive cyclisation.



Scheme 10 Synthesis of dioxabicyclo[3.3.0]octane-3,7-diones.

(3*S*,4*S*)-configuration of the silicon-bearing asymmetric centres in *trans*-**14a** was confirmed from the specific rotation data of (−)-**16** ($[\alpha]_D^{23} = -145.3$, *c* 0.64, H_2O) (lit.:[42] $[\alpha]_D^{19} = +143 \pm 2.5$, *c* 0.785, H_2O for the antipode). Similarly, the minor *trans*-**15a** gave (+)-2,6-dioxabicyclo[3.3.0]octane-3,7-dione (+)-**16**[42] as confirmed from the specific rotation data of (+)-**16** ($[\alpha]_D^{25} = +142.1$, *c* 0.38, H_2O) (lit.:[42] $[\alpha]_D^{19} = +143 \pm 2.5$, *c* 0.785, H_2O), thus confirming its (3*R*,4*R*)-configuration.

Interestingly, the major *trans*-diastereoisomers containing 'SuperQuat' oxazolidinones, *trans*-**15b** and *trans*-**15c**, after Fleming–Tamao oxidation gave (+)-2,6-dioxabicyclo[3.3.0]-octane-3,7-dione (+)-**16**. The marginal difference in stereocontrol behaviour between oxazolidinones **12a** and **12b** or **12c** is probably due to the steric crowding caused by the 5,5-diaryl groups in **12b** or **12c**. It is important to note that the bis-lactone **16** has been shown to be a useful intermediate in the synthesis of some important biologically active compounds such as eldanolide,[43] the Geissman-Waiss lactone,[44] prostaglandin analogues,[45] *trans*-lauredials,[46] 8,9-epoxyeicosatrienoic acid[47] and enantiomerically pure butenolides.[48] However, in spite of the significant utility of the bis-lactone **16**, to our knowledge, only two reports[20f,48] are available for the asymmetric synthesis of the (+)-**16** and none for (−)-**16**.

Conclusions

In conclusion, we have successfully developed a Mg/TMSCl-mediated intramolecular reductive cyclisation of symmetric disiloxanes made from chiral oxazolidinone derivatives of β-silylacrylic acid to give C_2-symmetric *trans*-diastereoisomers with high stereoselectivity; however, the stereocontrol is marginal amongst the *trans*-diastereoisomers. The *trans*-diastereoisomers attached to Evans' oxazolidinones were easily separated from the *cis*-diastereoisomer and individual *trans*-diastereoisomers were also separated by fractional crystallisation with ease and high

recoveries. The individual isomers of cyclic products containing "SuperQuat" oxazolidinones were difficult to separate.

Experimental

General methods

Compounds **3a**,[49] **3b**,[3] **9a**[3] and **12a–12c**[30,38,39] were prepared following the published procedures. DMF was dried over CaH_2 followed by storage over 4 Å molecular sieves. Mg turnings were purified by washing with dilute hydrochloric acid then water followed by washing with acetone and dried under vacuum. TMSCl was distilled over CaH_2 before use. *n*-BuLi (~1.6 M in hexanes) was purchased from Aldrich and its strength was determined by titration prior to use. Trifluoromethanesulfonic acid, KHF_2, H_2O_2 (30%), $KOBu^t$ and oxalyl chloride were used as received from commercial sources.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200/500 MHz spectrometers. Spectra were referenced to residual chloroform (δ 7.25 ppm, ^1H; 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (pentet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. C, H and N analyses were performed at the Indian Institute of Technology, Mumbai and at the Hydrometallurgy Division, BARC, Mumbai. High resolution mass spectra were recorded at 60–70 eV on a Waters Micromass Q-TOF spectrometer (ESI, Ar). Optical rotations were measured in a JASCO DIP 360 polarimeter. Infrared spectra (IR) were recorded on a JASCO FT IR spectrophotometer in NaCl cells or in KBr discs. Peaks are reported in cm^{-1}. Melting points (mp) were determined on a Fischer John's melting point apparatus and are uncorrected. Analytical thin-layer chromatography was performed using home made silica gel plates (about 0.5 mm).

1,1,3,3-Tetramethyl-1,3-di-[(2-methoxycarbonyl)ethenyl]-disiloxane 2a

Trifluoromethanesulfonic acid (4.8 mL, 54.6 mmol, 5.5 equiv.) was added to a stirred solution of (*E*)-methyl 3-dimethyl-(phenyl)silylpropenoate **3a** (2.2 g, 10 mmol) in dry dichloromethane (70 mL) at –4 °C. The reaction mixture was stirred for 20 min at that temperature, poured slowly into a stirred ice-cold aqueous ammonia solution (25%, 230 mL) and extracted with chloroform. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The residue was dissolved in THF (7 mL) and potassium *tert*-butoxide (8 mg, 0.07 mmol) was added. The reaction mixture was stirred at room temperature overnight, diluted with water and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica using hexane-EtOAc (95:5) as eluent to give the disiloxane **2a** (1.3 g, 86%) as a colourless liquid. R_f 0.64 (hexane-EtOAc, 90:10); ν_{max} (film)/cm^{-1} 3033, 2956, 2904, 2844, 1731, 1601, 1436, 1308, 1273, 1257, 1227, 1192, 1170, 1054, 998, 844, 802, 702; δ_H(200 MHz; $CDCl_3$) 0.20 (12 H, s, 4 × Si*Me*), 3.75 (6 H, s, 2 × CO_2CH_3), 6.25 (2 H, d, *J* 19.0, 2 × CH=C*H*CO_2CH_3), 7.12 (2 H, d, *J* 19.0, 2 × C*H*=CHCO_2CH_3); δ_C(50 MHz; $CDCl_3$) –0.3 (4 C), 50.9 (2 C), 133.9 (2 C), 146.5 (2 C), 165.3 (2 C); *m*/*z* (EI) 287 (M – 15, 30%), 233 (18), 179 (100), 163 (60), 149 (68), 133 (53), 119 (24), 73 (18).

1,1,3,3-Tetramethyl-1,3-di-[(2-methoxycarbonyl)ethyl]-disiloxane 5a

Magnesium turnings (101 mg, 4.1 mmol) were added to a stirred solution of the diester **2a** (125 mg, 0.41 mmol) in dry methanol (6 mL) at room temperature under an argon atmosphere. After 4 h, the reaction mixture was poured into cold aqueous HCl (0.3 N, 30 mL) and extracted with ethyl acetate. The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was quickly filtered through a plug of silica gel to give the diester **5a** (103 mg, 82%) as a colourless oil; R_f 0.67 (hexane-EtOAc, 90:10); ν_{max} (film)/cm^{-1} 2954, 2900, 1742, 1437, 1353, 1255, 1212, 1162, 1125, 1051, 843, 793; δ_H(200 MHz; $CDCl_3$) 0.05 (12 H, s, 4 × Si*Me*), 0.83 (4 H, t, *J* 8.4, 2 × Me_2SiCH_2), 2.27 (4 H, t, *J* 8.4, 2 × CH_2CO_2Me), 3.64 (6 H, s, 2 × CO_2CH_3); δ_C(50 MHz; $CDCl_3$) 0.0 (4 C), 13.1 (2 C), 27.9 (2 C), 51.5 (2 C), 175.3 (2 C); m/z (EI) 291 (M – 15, 3%), 219 (75), 163 (100), 145 (74), 133 (45), 119 (13). 89 (15), 73 (15).

Reductive cyclisation of 2a to give *trans*-1a, *cis*-1a and 5a

Freshly distilled TMSCl (5.2 mL, 41 mmol) was added to a stirred suspension of magnesium turnings (1 g, 41 mmol) in dry DMF (95 mL) at room temperature under an argon atmosphere. After 30 min, the reaction mixture was cooled on an ice-water bath and a solution of disiloxane **2a** (1 g, 3.3 mmol) in dry DMF (15 mL) was added slowly over 1.3 h to the stirred reaction mixture. After the addition was over, the reaction mixture was stirred for 5.5 h and the cold bath was removed. The reaction mixture was allowed to warm to room temperature (about 30 min) and poured into cold saturated sodium bicarbonate solution and then extracted three times with 10% ethyl acetate-hexane. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica using benzene-EtOAc (99:1) as eluent to give the reduction product **5a** (125 mg, 12%) as a colourless liquid, the *trans*-**1a** (380 mg, 38%) as a colourless solid, and the *cis*-**1a** (375 mg, 37%) as a colourless liquid.

Data for *trans*-**1a**: mp 99–100 °C (from hexane); R_f 0.60 (hexane-EtOAc, 90:10); (Found: C, 47.18; H, 8.08. $C_{12}H_{24}O_5Si_2$ requires C, 47.33; H, 7.94%); ν_{max} (KBr)/cm^{-1} 3005, 2985, 2956, 2899, 2856, 1731, 1436, 1421, 1357, 1306, 1250, 1205, 1176, 1145, 1052, 930, 873, 841, 789; δ_H(200 MHz; $CDCl_3$) 0.09 (6 H, s, 2 × Si*Me*), 0.24 (6 H, s, 2 × Si*Me*), 0.86-1.10 (2 H, m, 2 × $Me_2SiCHCH_2$), 2.22 (2 H, dd, *J* 15.8 and 10.6, 2 × $Me_2SiCHCH_AH_B$), 2.65 (2 H, dd, *J* 15.8 and 3.6, 2 × $Me_2SiCHCH_AH_B$), 3.64 (6 H, s, 2 × CO_2CH_3); δ_C(50 MHz; $CDCl_3$) –2.5 (2 C), 0.6 (2 C), 27.0 (2 C), 35.4 (2 C), 51.5 (2 C), 174.2 (2 C); m/z (EI) 289 (M – 15, 7%), 245 (10), 231 (56), 179 (10), 163 (100), 149 (23), 133 (92), 119 (23), 73(46).

Data for *cis*-**1a**: (Found: C, 47.49; H, 7.95. $C_{12}H_{24}O_5Si_2$ requires C, 47.33; H, 7.94%); R_f 0.51 (hexane-EtOAc, 90:10); ν_{max} (film)/cm^{-1} 3021, 2954, 2917, 2848, 1738, 1437, 1356, 1254, 1204, 1164, 1114, 924, 847, 794, 758; δ_H(200 MHz; $CDCl_3$) 0.14 (6 H, s, 2 × Si*Me*), 0.18 (6 H, s, 2 × Si*Me*), 1.60-1.73 (2 H, m, 2 × $Me_2SiCHCH_2$), 2.30 (2 H, dd, *J* 15.8 and 9.4, 2 × $Me_2SiCHCH_AH_B$), 2.46 (2 H, dd, *J* 15.8 and 6.2,

2 × $Me_2SiCHCH_AH_B$), 3.65 (6 H, s, 2 × CO_2CH_3); δ_C(50 MHz; $CDCl_3$) −1.4 (2 C), 0.2 (2 C), 23.8 (2 C), 31.8 (2 C), 51.7 (2 C), 174.2 (2 C); m/z (EI) 289 (M − 15, 9%), 231 (54), 179 (15), 163 (100), 149 (22), 133 (63), 119 (16), 73 (28). This compound was also prepared in 65% yield from diester **9a** following the procedure for the preparation of disiloxane **2a**.

(*E*)-3-[Dimethyl(phenyl)silyl]propenoic acid 11a

A solution of sodium hydroxide (15 *M*, 30 mL, 450 mmol) in water was added portionwise to a stirred solution of (*E*)-methyl 3-[dimethyl(phenyl)silyl]propenoate **3a** (32.5 g, 147.5 mmol) in 1,4 dioxane (580 mL). Ethanol (20 mL) was added to the reaction mixture to make it homogeneous and it was then stirred overnight. The solvent was removed under reduced pressure, diluted with water (300 mL) and extracted with ether. The aqueous phase was acidified with citric acid (pH ~ 4) and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated to give acid **11a** (29 g, 95%) as a thick gum. ν_{max} (film)/cm^{-1} 3500-2500 (br), 3070, 3022, 2959, 1696, 1594, 1427, 1411, 1300, 1253, 1117, 997, 938, 843, 822, 732, 700; δ_H(200 MHz; $CDCl_3$) 0.44 (6 H, s, 2 × Si*Me*), 6.28 (1 H, d, *J* 18.8, CH=C*H*CO_2H), 7.34-7.54 (6 H, m, C*H*=CHCO$_2$H, Ar). δ_C(50 MHz; $CDCl_3$) −3.4 (2 C), 128.0 (2 C), 129.5, 133.7 (2 C), 134.5, 135.8, 150.7, 171.0; *m/z* (EI) 206 (M^+, 9%), 205 (32), 191 (32), 163 (25), 145 (21), 135 (26), 121 (28), 105 (19), 75 (100), 69 (25).

(*E*)-3-[Dimethyl(tolyl)silyl]propenoic acid 11b

Following the procedure for the preparation of **11a**, (*E*)-ethyl 3-[dimethyl(tolyl)silyl]propenoate **3b** (12.5 g, 50.3 mmol) gave acid **11b** (8.9 g, 80%) as a crystalline solid. mp 78–80 °C (from hexane); ν_{max} (KBr)/cm^{-1} 3500-2500 (br), 3066, 3011, 2968, 2921, 1697, 1611, 1402, 1298, 1247, 1110, 1001, 935, 838, 795, 777; δ_H(200 MHz; $CDCl_3$) 0.40 (6 H, s, 2 × Si*Me*), 2.35 (3 H, s, Ar-*Me*), 6.25 (1 H, d, *J* 18.8, CH=C*H*CO_2H), 7.19 (2 H, d, *J* 7.6, Ar), 7.39 (2 H, d, *J* 7.6, Ar), 7.46 (1 H, d, *J* 18.8, C*H*=CHCO$_2$H); δ_C(50 MHz; $CDCl_3$) −3.3 (2 C), 21.4, 128.9 (2 C), 132.2, 133.8 (2 C), 134.4, 139.5, 151.1, 171.2; *m/z* (EI) 220 (M^+, 11%), 219 (14), 205 (51), 177 (28), 159 (25), 149 (22), 135 (25), 91 (22), 75 (100), 69 (24).

(4*S*)-3-*trans*-(2-Dimethylphenylsilyl)acryloyl-4-isopropyl-2-oxazolidinone 10a

Dry DMF (0.03 mL, 0.38 mmol) was added to a stirred solution of acid **11a** (15 g, 72.7 mmol) in dry dichloromethane (100 mL) and the reaction mixture was cooled in an ice-water bath. Oxalyl chloride (25.4 mL, 291 mmol) was added and the reaction mixture was allowed to attain to room temperature. After 3.5 h, the solvent and volatiles were removed under reduced pressure to give the crude acid chloride which was dissolved in dry THF (68 mL). The acid chloride solution was added into a stirred solution of lithium salt of oxazolidinone at −78 °C which was prepared from oxazolidinone **12a** (9.4 g, 72.7 mmol) and *n*-BuLi (48.5 mL, 1.5 M solution in hexane, 72.7 mmol) in dry THF (136 mL) at −78 °C. The reaction mixture was stirred under the same conditions for 30 min followed by 15 min in an ice-water bath. A saturated aqueous ammonium chloride solution (600 mL) was added into the reaction mixture and extracted with ether. The extract was washed successively with saturated aqueous sodium bicarbonate and brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica using hexane-EtOAc (93:7) as eluent to give the pure amide **10a** (21.2 g, 92%) as a colourless solid. (Found: C, 64.16; H, 7.58; N, 4.38. $C_{17}H_{23}NO_3Si$ requires C, 64.32; H, 7.30; N, 4.41%); mp 59–60 °C (from hexane); $[\alpha]_D^{25}$ +78.52 (c 1.08 in EtOH); R_f 0.53 (hexane-EtOAc, 85:15); ν_{max} ($CHCl_3$)/cm^{-1} 3070, 3049, 2963, 2876, 1781, 1683, 1592, 1487, 1428, 1364, 1337, 1254, 1207, 1116, 1060, 974, 860, 819, 774; δ_H(200 MHz; $CDCl_3$) 0.45 (6 H, s, 2 × Si*Me*), 0.88 (3 H, d, *J* 7.2, $CH*Me_A*Me_B$), 0.92 (3 H, d, *J* 7.2, $CHMe_A*Me_B*$), 2.33-2.49 (1 H, m, NCHC*H*Me_2), 4.18-4.32 (2 H, m, NCO_2CH_2CH), 4.44-4.51 (1 H, m, NC*H*$CHMe_2$), 7.33-7.40 (3 H, m, Ar), 7.50 (1 H, d, *J* 18.7, CH=C*H*CON), 7.47-7.60 (2 H, m, Ar), 7.70 (1 H, d, *J* 18.7, C*H*=CHCO); δ_C(50 MHz; $CDCl_3$) −3.3 (2 C), 14.6, 17.9, 28.3, 58.5, 63.3, 127.9 (2 C), 129.3, 133.7 (2 C), 133.9, 136.4, 148.8, 153.8, 164.2; m/z (EI) 302 (M − 15, 43%), 240 (17), 230 (31), 216 (60), 202 (90), 189 (46), 161 (54), 145 (55), 135 (100), 105 (40), 75 (26), 69 (42).

1,1,3,3-Tetramethyl-1,3-di-{2-[3-(4*S*)-3-carbonyl-4-isopropyl-2-oxazolidinone]ethenyl}disiloxane 13a

Trifluoromethanesulfonic acid (13.8 mL, 157 mmol, 2.5 equiv.) was added to a stirred solution of **10a** (20 g, 63 mmol) in dry dichloromethane (400 mL) at −10 °C. After 1 h, another portion of TfOH (6 mL, 68.3 mmol, 1.1 equiv) was added to the reaction mixture and it was stirred under the same conditions for 1 h. The reaction mixture was poured slowly into a stirred ice-cold aqueous ammonia solution (25%, 1.4 L) and stirred for 2.5 h. The reaction mixture was extracted with chloroform and the extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica using hexane-EtOAc (85:15) as eluent to give the disiloxane **13a** (13.5 g, 86%) as a colourless solid. (Found: C, 53.34; H, 7.62; N, 5.77. $C_{22}H_{36}N_2O_7Si_2$ requires C, 53.20; H, 7.31; N, 5.64%); mp 87–88 °C (from hexane-EtOAc); $[\alpha]_D^{23}$ +93.1 (*c* 1.01 in EtOH); R_f 0.72 (hexane-EtOAc, 70:30); ν_{max} ($CHCl_3$)/cm^{-1} 3020, 2964, 2877, 1781, 1683, 1487, 1388, 1365, 1337, 1256, 1208, 1120, 1098, 1060, 840, 756; δ_H(200 MHz; $CDCl_3$) 0.25 (12 H, s, 4 × Si*Me*), 0.89 (6 H, d, *J* 7.8, 2 × $CH*Me_A*Me_B$), 0.93 (6 H, d, *J* 7.8, 2 × $CHMe_A*Me_B*$), 2.33–2.49 (2 H, m, 2 × NCHC*H*Me_2), 4.18-4.34 (4 H, m, 2 × NCO_2CH_2CH), 4.44-4.51 (2 H, m, 2 × NC*H*$CHMe_2$), 7.28 (2 H, d, *J* 18.6, 2 × CH=C*H*CON), 7.67 (2 H, d, *J* 18.6, 2 × C*H*=CHCON); δ_C(50 MHz; $CDCl_3$) 0.3 (2 C), 0.4 (2 C), 14.7 (2 C), 18.0 (2 C), 28.4 (2 C), 58.6 (2 C), 63.4 (2 C), 133.4 (2 C), 148.7 (2 C), 153.9 (2 C), 164.5 (2 C); m/z (EI) 481 (M – 15, 19%), 324 (16), 261 (22), 260 (100), 186 (19), 157 (41), 133 (22), 69 (15).

Reductive cyclisation of 13a to give *trans*-14a, *trans*-15a and *cis*-14a

Following the procedure for the intramolecular reductive cyclisation of disiloxane **2a**, disiloxane **13a** (7 g, 14.1 mmol), magnesium turnings (4.1 g, 168.8 mmol) and TMSCl (21.4 mL, 168.8 mmol) gave a mixture of *trans*-**14a**, *trans*-**15a** and *cis*-**14a** (6 g, 85%).

The mixture was dissolved in ethyl acetate and the *trans* isomers were precipitated out by adding hexane into the solution. The mixture was filtered to give a solid mixture of *trans*-**14a** and *trans*-**15a** (3.9 g, 55%) and the filtrate was evaporated to give a gummy mixture containing all three isomers (2.1 g, 30%). The solid mixture was crystallised from benzene-hexane to give pure major *trans*-**14a** product (2.1 g, 30%) followed by crystallisation of the residual mass from hexane-ethyl acetate to give minor *trans*-**15a** (1.4 g, 20%). Separation of isomers by chromatography was not easy because of very similar R_f values. A pure sample of *cis*-**14a** for characterisation purposes was obtained by careful column chromatography of the gummy residue containing mixture of all isomers.

Data for *trans*-**14a**: (Found: C, 52.95; H, 7.85; N, 5.88. $C_{22}H_{38}N_2O_7Si_2$ requires C, 52.98; H, 7.68; N, 5.62%); Crystalline solid; mp 162–163 °C (from hexane-EtOAc); $[\alpha]_D^{28}$ −5.3 (c 0.87 in EtOH); R_f 0.71 (hexane-EtOAc, 70:30); ν_{max} ($CHCl_3$)/cm^{-1} 3019, 2966, 1780, 1697, 1388, 1376, 1302, 1252, 1215, 1098, 919, 846, 759; δ_H(200 MHz; $CDCl_3$) 0.04 (6 H, s, 2 × Si*Me*), 0.32 (6 H, s, 2 × Si*Me*), 0.87 (6 H, d, *J* 7.8, 2 × CH*Me*$_A$Me$_B$), 0.92 (6 H, d, *J* 7.8, 2 × CHMe$_A$*Me*$_B$), 1.10-1.51 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 2.27–2.43 (2 H, m, 2 × NCHC*H*Me$_2$), 2.81 (2 H, dd, *J* 18.6 and 10.8, 2 × -C*H*$_A$H$_B$CON), 3.43 (2 H, dd, *J* 18.6 and 4.4, 2 × -CH$_A$*H*$_B$CON), 4.17-4.33 (4 H, m, 2 × NCO$_2$C*H*$_2$CH), 4.37-4.44 (2 H, m, 2 × NC*H*CHMe$_2$); δ_C(50 MHz; $CDCl_3$) −2.4 (2 C), 1.1 (2 C), 14.6 (2 C), 17.9 (2 C), 25.8 (2 C), 28.4 (2 C), 38.2 (2 C), 58.4 (2 C), 63.5 (2 C), 154.1 (2 C), 173.7 (2 C); m/z (EI) 483 (M − 15, 5%), 327 (27), 328 (100), 260 (81), 228 (15), 213 (19), 199 (71), 174 (34), 149 (32), 133 (66), 117 (19), 73 (22), 69 (21).

Data for *trans*-**15a**: (Found: C, 52.99; H, 7.74; N, 6.21. $C_{22}H_{38}N_2O_7Si_2$ requires C, 52.98; H, 7.68; N, 5.62%); Crystalline solid; mp 141–142 °C (from hexane-EtOAc); $[\alpha]_D^{27}$ +152.9 (c 0.90 in EtOH); R_f 0.71 (hexane-EtOAc, 70:30); ν_{max} ($CHCl_3$)/cm^{-1} 3019, 2965, 2877, 1779, 1696, 1487, 1388, 1302, 1251, 1210, 1096, 920, 846, 751; δ_H(200 MHz; $CDCl_3$) 0.05 (6 H, s, 2 × Si*Me*), 0.30 (6 H, s, 2 × Si*Me*), 0.88 (6 H, d, *J* 7.8, 2 × CH*Me*$_A$Me$_B$), 0.92 (6 H, d, *J* 7.8, 2 × CHMe$_A$*Me*$_B$), 1.15-1.19 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 2.28–2.44 (2 H, m, 2 × NCHC*H*Me$_2$), 2.82 (2 H, dd, *J* 17.8 and 10.4, 2 × -C*H*$_A$H$_B$CON), 3.41 (2 H, dd, *J* 17.8 and 4.6, 2 × -CH$_A$*H*$_B$CON), 4.17-4.33 (4 H, m, 2 × NCO$_2$C*H*$_2$CH), 4.38-4.45 (2 H, m, 2 × NC*H*CHMe$_2$); δ_C(50 MHz; $CDCl_3$) −2.3 (2 C), 1.0 (2 C), 14.5 (2 C), 18.0 (2 C), 25.9 (2 C), 28.1 (2 C), 38.1 (2 C), 58.4 (2 C), 63.2 (2 C), 154.0 (2 C), 173.7 (2 C); m/z (EI) 483 (M − 15, 5%), 327 (26), 328 (100), 260 (80), 228 (15), 213 (19), 199 (69), 174 (35), 149 (32), 133 (64), 117 (18), 73 (22), 69 (21).

Data for *cis*-**14a**: Colourless thick gum; $[\alpha]_D^{31}$ +58.2 (c 0.67 in EtOH); R_f 0.71 (hexane-EtOAc, 70:30); ν_{max} ($CHCl_3$)/cm^{-1} 2963, 2977, 1780, 1698, 1387, 1302, 1252, 1208, 1097, 10120, 919; δ_H(500 MHz; $CDCl_3$) 0.16 (3 H, s, Si*Me*), 0.17 (3 H, s, Si*Me*), 0.23 (3 H, s, Si*Me*), 0.25 (3 H, s, Si*Me*), 0.88 (6 H, d, *J* 7.0, 2 × CH*Me*$_A$Me$_B$), 0.92 (6 H, d, *J* 7.8, 2 × CHMe$_A$*Me*$_B$), 1.69-1.73 (1 H, m, Me$_2$SiC*H*CH$_2$), 1.82-1.86 (1 H, m, Me$_2$SiC*H*CH$_2$), 2.30–2.43 (2 H, m, 2 × NCHC*H*Me$_2$), 2.95 (2 H, dd, *J* 17.5 and 9.0, 2 × -C*H*$_A$H$_B$CON), 3.15 (1 H, dd, *J* 17.5 and 6.0, -CH$_A$*H*$_B$CON), 3.22 (1 H, dd, *J* 18.0 and 7.5, -CH$_A$*H*$_B$CON), 4.18-4.23 (2 H, m, NCO$_2$C*H*$_2$CH), 4.26-4.34 (2 H, m, NCO$_2$C*H*$_2$CH), 4.39-4.42 (1 H, m, NC*H*CHMe$_2$), 4.44-4.47 (1 H, m, NC*H*CHMe$_2$); δ_C(125 MHz; $CDCl_3$) −1.3, −1.1, 0.1, 0.5, 14.5, 14.5, 18.0 (2 C), 22.4, 22.9, 28.2, 28.3, 32.9, 33.5, 58.5 (2 C), 63.2, 63.3, 154.1, 154.2, 173.4, 173.6; Found: MH$^+$ 499.2275, $C_{22}H_{39}N_2O_7Si_2$ requires MH$^+$ 499.2290; *m/z* (ES)521 (M + Na, 69%), 499 (M + H, 100), 481 (26), 370 (19), 279 (41), 132 (16).

(4*S*)-3-*trans*-(2-Dimethyltolylsilyl)acryloyl-5,5-diphenyl-4-isopropyl-2-oxazolidinone 10b

Following the procedure for the preparation of **10a**, (*E*)-3-[dimethyl(tolyl)silyl]propenoic acid **11b** (1.06 g, 4.8 mmol), oxazolidinone **12b** (1.36 g, 4.8 mmol) and *n*-BuLi (3.2 mL, 1.5 *M* solution in hexane, 4.8 mmol) gave *N*-substituted oxazolidinone **10b** (2.06 g, 89%) as a crystalline solid. (Found: C, 75.02; H, 6.78; N, 2.91. $C_{30}H_{33}NO_3Si$ requires C, 74.50; H, 6.88; N, 2.90%); mp 105–107 °C (from hexane-EtOAc); $[\alpha]_D^{25}$ −163.95 (c 1.03 in $CHCl_3$); R_f 0.62 (hexane-EtOAc, 90:10); ν_{max} ($CHCl_3$)/cm^{-1} 3065, 3031, 2965, 2878, 1784, 1683, 1602, 1495, 1450, 1394, 1363, 1334, 1250, 1108, 1001, 762; δ_H(200 MHz; $CDCl_3$) 0.39 (3 H, s, Si*Me*), 0.40 (3 H, s, Si*Me*), 0.76 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.89 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$), 1.91-2.06 (1 H, m, NCHC*H*Me$_2$), 2.33 (3 H, s, Ar-*Me*), 5.46 (1 H, d, *J* 3.2, NC*H*CHMe$_2$), 7.16-7.66 (16 H, m, 2 × Ph, Ar, CH=CHCON); δ_C(50 MHz; $CDCl_3$) −3.2 (2 C), 16.3, 21.4, 21.7, 30.1, 64.4, 89.2, 125.6 (2 C), 125.9 (2 C), 127.9, 128.3 (2 C), 128.5, 128.8 (2 C), 128.8 (2 C), 132.7, 133.2, 133.8 (2 C), 138.2, 139.3, 142.2, 149.8, 152.8, 164.2; m/z (EI) 468 (M − 15, 5%), 424 (16), 337 (21), 262 (14), 222 (34), 207 (100), 167 (40), 149 (55), 129 (22), 105 (24), 91 (16).

1,1,3,3-Tetramethyl-1,3-di-{2-[3-(4*S*)-3-carbonyl-5,5-diphenyl-4-isopropyl-2-oxazolidinone]ethenyl}disiloxane 13b

Following the procedure for the preparation of disiloxane **13a**, oxazolidinone **10b** (1.8 g, 3.7 mmol) and trifluoromethanesulfonic acid (0.98 mL, 11.15 mmol, 3 equiv) at −15 °C gave the disiloxane **13b** (1.2 g, 81%) as a colourless solid. (Found: C, 68.83; H, 6.59; N, 3.59. $C_{46}H_{52}N_2O_7Si_2$ requires C, 68.97; H, 6.54; N, 3.50%); mp 148–150 °C (from hexane-EtOAc); $[\alpha]_D^{24}$ −193.2 (c 1.03 in $CHCl_3$); R_f 0.52 (hexane-EtOAc, 85:15); ν_{max} ($CHCl_3$)/cm^{-1} 3024, 2965, 2877, 1782, 1683, 1450, 1364, 1335, 1256, 1213, 1176, 1053, 752; δ_H(200 MHz; $CDCl_3$) 0.18 (6 H, s, 2 × Si*Me*), 0.19 (6 H, s, 2 × Si*Me*), 0.77 (6 H, d, *J* 6.8, 2 × CH*Me*$_A$Me$_B$), 0.89 (6 H, d, *J* 7.0, 2 × CHMe$_A$*Me*$_B$), 1.91-2.06 (2 H, m, 2 × NCHC*H*Me$_2$), 5.45 (2 H, d, *J* 3.2, 2 × NC*H*CHMe$_2$), 7.20-7.62 (24 H, m, 4 × Ph, 2 × CH=CHCON); δ_C(50 MHz; $CDCl_3$) 0.2 (4 C), 16.2 (2 C), 21.6 (2 C), 29.9 (2 C), 64.4 (2 C), 89.1 (2 C), 125.4 (4 C), 125.7 (4 C), 127.7 (2 C), 128.1 (4 C), 128.3 (2 C), 128.7 (4 C), 132.7 (2 C), 138.1 (2 C), 142.1 (2 C), 149.2 (2 C), 152.5 (2 C), 164.1 (2 C); *m/z* (ES) 823 (M + Na, 8%), 801 (M + H, 100).

Reductive cyclisation of 13b to give *trans*-14b, *trans*-15b and *cis*-14b

Following the procedure of intramolecular reductive cyclisation of disiloxane **2a**, disiloxane **13b** (0.945 g, 1.18 mmol), magnesium turnings (0.344 g, 14.2 mmol) and TMSCl (1.8 mL, 14.2 mmol) gave a mixture of *trans*-**14b**, *trans*-**15b** and *cis*-**14b** (0.79 g, 83%). The residue was crystallised from hexane-ethyl acetate to give the major *trans*-**15b** (0.28 g, 29%). The remaining portion (0.5 g, 54%) consisted of a mixture of all three isomers from which the individual isomers could not be separated by crystallisation or chromatography.

Data for *trans*-**15b**: Solid; mp 93–95 °C (from hexane-EtOAc); $[\alpha]_D^{26}$ –98.3 (c 0.6 in $CHCl_3$); R_f 0.51 (hexane-EtOAc, 85:15); ν_{max} ($CHCl_3$)/cm^{-1} 3062, 3029, 2966, 2878, 1783, 1701, 1450, 1369, 1251, 1176, 929, 758; δ_H(200 MHz; $CDCl_3$) –0.43 (6 H, s, 2 × Si*Me*), 0.20 (6 H, s, 2 × Si*Me*), 0.77 (6 H, d, *J* 6.0, 2 × CH*Me*$_A$Me$_B$), 0.86 (6 H, d, *J* 8.0, 2 × CHMe$_A$*Me*$_B$), 1.00-1.05 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 1.91-2.06 (2 H, m, 2 × NCHC*H*Me$_2$), 2.65 (2 H, dd, *J* 18.6 and 11.0, 2 × -C*H*$_A$H$_B$CON), 3.32 (2 H, dd, *J* 18.6 and 3.4, 2 × -CH$_A$*H*$_B$CON), 5.34 (2 H, d, *J* 4.0, 2 × NC*H*CHMe$_2$), 7.26-7.50 (20 H, m, 4 × Ph); δ_C(50 MHz; $CDCl_3$) –3.0 (2 C), 1.1 (2 C), 16.5 (2 C), 21.5 (2 C), 25.4 (2 C), 29.8 (2 C), 37.6 (2 C), 64.7 (2 C), 89.5 (2 C), 125.5 (4 C), 125.8 (4 C), 127.9 (2 C), 128.3 (4 C), 128.6 (2 C), 128.9 (4 C), 137.9 (2 C), 142.3 (2 C), 153.1 (2 C), 173.3 (2 C); Found: MH$^+$ 803.3507, $C_{46}H_{55}N_2O_7Si_2$ requires MH$^+$ 803.3542; *m*/*z* (ES) 825 (M + Na, 6%), 803 (M + H, 63), 279 (100), 132 (33).

Data for *trans*-**14b** from the mixture containing about 55% of *trans*-**15b**: δ_H(200 MHz; $CDCl_3$) 0.03 (6 H, s, 2 × Si*Me*), 0.20 (6 H, s, 2 × Si*Me*), 0.72 (6 H, d, *J* 6.0, 2 × CH*Me*$_A$Me$_B$), 0.86 (6 H, d, *J* 8.0, 2 × CHMe$_A$*Me*$_B$), 0.93-1.05 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 1.91-2.06 (2 H, m, 2 × NCHC*H*Me$_2$), 2.74 (2 H, dd, *J* 19.6 and 11.0, 2 × -C*H*$_A$H$_B$CON), 3.17 (2 H, dd, *J* 19.6 and 3.2, 2 × -CH$_A$*H*$_B$CON), 5.32 (2 H, d, *J* 4.0, 2 × NC*H*CHMe$_2$), 7.23-7.50 (20 H, m, 4 × Ph).

(4*S*)-3-*trans*-(2-dimethyltolylsilyl)acryloyl-4-isopropyl-5,5-di(2-methoxy-5-methyl)-2-oxazolidinone 10c

Following the procedure for the preparation of **10a**, (*E*)-3-[dimethyl(tolyl)silyl]propenoic acid **11b** (1.02 g, 4.6 mmol), oxazolidinone **12c** (1.7 g, 4.6 mmol) and *n*-BuLi (3.1 mL, 1.5 *M* solution in hexane, 4.6 mmol) gave *N*-substituted oxazolidinone **10c** (2.4 g, 91%) as a crystalline solid. (Found: C, 71.61; H, 7.38; N, 2.89. $C_{34}H_{41}NO_5Si$ requires C, 71.42; H, 7.23; N, 2.45%); mp 160–161 °C (from hexane-EtOAc); $[\alpha]_D^{28}$ –215.8 (c 1.05 in EtOAc); R_f 0.69 (hexane-EtOAc, 85:15); ν_{max} ($CHCl_3$)/cm^{-1} 3072, 3035, 3012, 2999, 2964, 2835, 1772, 1683, 1604, 1504, 1465, 1342, 1250, 1201, 1107, 1034, 910, 821, 730; δ_H(200 MHz; $CDCl_3$) 0.39 (3 H, s, Si*Me*), 0.40 (3 H, s, Si*Me*), 0.73 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$), 0.97 (3 H, d, *J* 7.0, CHMe$_A$*Me*$_B$), 1.67-1.82 (1 H, m, NCHC*H*Me$_2$), 2.23 (3 H, s, Ar-*Me*), 2.34 (3 H, s, Ar-*Me*), 2.36 (3 H, s, Ar-*Me*), 3.48 (3 H, s, O*Me*-Ar), 3.49 (3 H, s, O*Me*-Ar), 5.85 (1 H, d, *J* 1.8, NC*H*CHMe$_2$), 6.66 (2 H, dd, *J* 8.2 and 10.0, Ar), 6.98-7.10 (2 H, m, Ar), 7.16-7.70 (8 H, m, Ar, CH=CHCON); δ_C(50 MHz; $CDCl_3$) –3.1 (2 C), 16.0, 20.7 (2 C), 21.4, 22.6, 30.1, 55.4, 56.0, 62.3, 89.0, 111.0, 113.8, 126.7, 127.6, 128.1, 128.7 (3 C), 128.9, 129.0, 129.1, 130.0, 133.0, 133.9 (3 C), 139.2, 148.4, 152.7, 153.3, 156.2, 164.4; m/z (EI) 571(M$^+$, 3%), 556 (M – 15, 2), 512 (15), 310 (26), 293 (18), 271 (20), 255 (28), 203 (55), 149 (100), 135 (45), 105 (20), 91 (14).

1,1,3,3-Tetramethyl-1,3-di-{2-[3-(4*S*)-3-carbonyl-5,5-di(2-methoxy-5-methyl)-4-isopropyl-2-oxazolidinone]-ethenyl}disiloxane 13c

Following the procedure for the preparation of disiloxane **13a**, oxazolidinone **10c** (1.32 g, 2.3 mmol) and TfOH (0.51 mL, 5.8 mmol, 2.5 equiv) at –15 °C gave the disiloxane **13c** (0.81 g, 72%) as a colourless solid. (Found: C, 66.70; H, 7.17; N, 2.92. $C_{54}H_{68}N_2O_{11}Si_2$ requires C, 66.36; H, 7.01; N, 2.87%); mp 179–180 °C (from hexane-EtOAc); $[\alpha]_D^{24}$ –235.8 (c 1.02 in EtOAc); R_f 0.65 (hexane-EtOAc, 75:25); ν_{max} ($CHCl_3$)/cm^{-1} 3019, 2964, 2879, 2836, 1778, 1683, 16011, 1503, 1465, 1343, 1253, 1201, 1033, 760; δ_H(200 MHz; $CDCl_3$) 0.20 (12 H, s, 4 × Si*Me*), 0.74 (6 H, d, *J* 6.8, 2 × CH*Me*$_A$Me$_B$), 0.98 (6 H, d, *J* 7.2, 2 × CHMe$_A$*Me*$_B$), 1.69-1.77 (2 H, m, 2 × NCHC*H*Me$_2$), 2.23 (6 H, s, 2 × Ar-*Me*), 2.35 (6 H, s, 2 × Ar- *Me*), 3.49 (12 H, s, 4 × O*Me*-Ar), 5.85 (2 H, d, *J* 1.8, 2 × NC*H*CHMe$_2$), 6.65 (4 H, t, *J* 9.2, Ar), 6.95-7.10 (4 H, m, Ar), 7.16 (1 H, s, Ar), 7.26 (2 H, d, *J* 18.6, 2 × CH=C*H*CON), 7.36 (1 H, s, Ar), 7.61 (2 H, d, *J* 18.6, 2 × C*H*=CHCON), 7.69 (1 H, s, Ar), 7.70 (1 H, s, Ar); δ_C(50 MHz; $CDCl_3$) 0.1 (4 C), 15.8 (2 C), 20.4 (4 C), 22.4 (2 C), 29.8 (2 C), 55.0 (2 C), 55.5 (2 C), 62.1 (2 C), 88.8 (2 C), 110.8 (2 C), 113.4 (2 C), 126.3 (2 C), 127.4 (2 C), 127.7 (2 C), 128.4 (2 C), 128.6 (2 C), 128.6 (2 C), 128.9 (2 C), 129.8 (2 C), 133.2 (2 C), 148.0 (2 C), 152.4 (2 C), 153.0 (2 C), 155.9 (2 C), 164.2 (2 C); *m*/*z* (ES) 999 (M + Na, 19%), 977 (M + H, 15), 500 (100).

Reductive cyclisation of 13c to give *trans*-14c, *trans*-15c and *cis*-14c

Following the procedure of intramolecular reductive cyclisation of disiloxane **2a**, disiloxane **13c** (0.695 g, 0.71 mmol), magnesium turnings (0.21 g, 8.64 mmol) and TMSCl (1.1 mL, 8.68 mmol) gave a mixture of *trans*-**14c**, *trans*-**15c** and *cis*-**14c** (0.58 g, 83%). The residue was crystallised from hexane-ethyl acetate to give the major *trans*-**15c** (0.21 g, 30%). The remaining portion (0.37 g, 53%) consisted of a mixture of all three isomers from which the individual isomers could not be separated.

Data for *trans*-**15c**: Colourless solid; mp 250–252 °C (from hexane-EtOAc); $[\alpha]_D^{24}$ –135.1 (c 0.6 in $CHCl_3$); R_f 0.63 (hexane-EtOAc, 75:25); ν_{max} ($CHCl_3$)/cm^{-1} 2957, 2926, 2856, 1779, 1695, 1502, 1464, 1372, 1252, 1200, 1032, 924; δ_H(200 MHz; $CDCl_3$) -0.20 (6 H, s, 2 × Si*Me*), 0.34 (6 H, s, 2 × Si*Me*), 0.74 (6 H, d, *J* 6.6, 2 × CH*Me*$_A$Me$_B$), 0.95 (6 H, d, *J* 7.2, 2 × CHMe$_A$*Me*$_B$), 1.09-1.14 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 1.61-1.75 (2 H, m, 2 × NCHC*H*Me$_2$), 2.23 (6 H, s, 2 × Ar-*Me*), 2.35 (6 H, s, 2 × Ar-*Me*), 2.74 (2 H, dd, *J* 19.0, 11.4, 2 × -C*H*$_A$H$_B$CON), 3.44 (2 H, dd, *J* 19.0 and 3.0, -CH$_A$*H*$_B$CON), 3.48 (12 H, s, 4 × O*Me*-Ar), 5.75 (2 H, d, *J* 2.0, 2 × NC*H*CHMe$_2$), 6.65 (4 H, dd, *J* 12.8 and 8.2, Ar), 6.96-7.10 (4 H, m, Ar), 7.21 (1 H, s, Ar), 7.22 (1 H, s, Ar), 7.70 (1 H, s, Ar), 7.71 (1 H, s, Ar); δ_C(50 MHz; $CDCl_3$) –2.6 (2 C), 1.5 (2 C), 16.0 (2 C), 20.6 (2 C), 20.8 (2 C), 22.4 (2 C), 25.1 (2 C), 29.9 (2 C), 38.1 (2 C), 55.3 (2 C), 56.0 (2 C), 61.7 (2 C), 89.0 (2 C), 111.0 (2 C), 114.1 (2 C), 126.3 (2 C), 126.9 (2 C), 127.9 (2 C), 128.9 (6 C), 129.1 (2 C), 130.1 (2 C), 152.7 (2 C), 153.5 (2 C), 156.4 (2 C), 173.5 (2 C); Found: MH$^+$ 979.4545, $C_{54}H_{71}N_2O_{11}Si_2$ requires MH$^+$ 979.4591; *m*/*z* (ES) 1001 (M + Na, 11%), 979 (M + H, 100), 318 (14), 279 (45), 132 (7).

Data for *trans*-**14c** from the mixture containing about 5% of *trans*-**15c:** δ_H(200 MHz; $CDCl_3$) 0.07 (6 H, s, 2 × Si*Me*), 0.37 (6 H, s, 2 × Si*Me*), 0.69 (6 H, d, *J* 6.6, 2 × CH*Me*$_A$Me$_B$), 0.95 (6 H, d, *J* 7.0, 2 × CHMe$_A$*Me*$_B$), 1.09-1.14 (2 H, m, 2 × Me$_2$SiC*H*CH$_2$), 1.61-1.75 (2 H, m, 2 × NCHC*H*Me$_2$), 2.24 (6 H, s, 2 × Ar-*Me*), 2.34 (6 H, s, 2 × Ar-*Me*), 2.93 (2 H, dd, *J* 19.0, 11.2, 2 × -C*H*$_A$H$_B$CON), 3.12 (2 H, dd, *J* 19.0 and 4.0, -CH$_A$*H*$_B$CON), 3.46 (6 H, s, 2 × O*Me*-Ar), 3.48 (6 H, s, 2 × O*Me*-Ar), 5.76 (2 H, d, *J* 1.5, 2 × NC*H*CHMe$_2$), 6.64 (4 H, dd, *J* 12.0 and 8.4, Ar), 6.96-7.10 (4 H, m, Ar), 7.14 (1 H, s, Ar), 7.15 (1 H, s, Ar), 7.66 (1 H, s, Ar), 7.67 (1 H, s, Ar).

(3*S*,4*S*)-Dihydroxyadipic-γ,γ′-dilactone (–)-16

Hydrogen peroxide (0.6 mL, 30%) was added to a stirred mixture of *trans*-**14a** (0.15 g, 0.3 mmol) and KHF_2 (0.14 g, 1.8 mmol) in THF/MeOH (6 mL, 1:1). After 24 h at 60 °C, H_2O_2 (0.3 mL) was added to the reaction mixture followed by addition of THF/MeOH (2 mL, 1:1). After 15 h, the solvent was evaporated under reduced pressure. The white residue was triturated with hot EtOAc and filtered. The filtrate on evaporation gave the oxazolidinone (35 mg, 90%). The solid residue was taken up in 0.2 molar methanolic HCl (10 mL) and evaporated. The residue was triturated with ethyl acetate and filtered. The filtrate was evaporated under reduced pressure and the residue was dissolved in THF (2 mL), TsOH (2 mg, 0.01 mmol) was added into it and the mixture was heated at 55 °C for 12 h. Sodium bicarbonate (3 mg) was added and the reaction mixture was diluted with hot EtOAc and filtered, then the filtrate was evaporated to give the lactone (–)-**16** (44 mg, 100%) as a solid. mp 122–124 °C (hexane-EtOAc) (lit.[42] mp 122–123 °C); $[\alpha]_D^{23}$ –145.3 (c 0.64 in H_2O) (lit.[42]; $[\alpha]_D^{19} = +143 \pm 2.5$, *c* 0.785, H_2O for the antipode); R_f 0.57 (hexane-EtOAc, 2:8); ν_{max} ($CHCl_3$)/cm^{-1} 3023, 2993, 2958, 1783, 1401, 1343, 1309, 1191, 1165, 1051; δ_H(200 MHz; $CDCl_3$) 2.83-3.04 (4 H, m, 2 × CH_2), 5.18-5.24 (2 H, m, 2 × C*H*); δ_C(50 MHz; $CDCl_3$) 35.1 (2 C), 78.3 (2 C), 172. 9 (2 C).

(3*R*,4*R*)-Dihydroxyadipic-γ,γ′-dilactone (+)-16

Following the procedure for conversion of *trans*-**14a** to (–)-**16**, disiloxane *trans*-**15a** (0.1 g, 0.2 mmol) and H_2O_2 (0.7 mL, 30%) gave lactone (+)-**16** (25 mg, 88%) as a solid. mp 121–123 °C (hexane-EtOAc) (lit.[42] mp 122–123 °C); $[\alpha]_D^{25}$ +142.11 (c 0.38 in H_2O) (lit.[42]; $[\alpha]_D^{19} = +143 \pm 2.5$, *c* 0.785, H_2O); R_f 0.57 (hexane-EtOAc, 20:80); ν_{max} ($CHCl_3$)/cm^{-1} 3023, 2993, 2958, 1783, 1401, 1343, 1309, 1191, 1165, 1051, 927, 836; δ_H(200 MHz; $CDCl_3$) 2.83-3.04 (4 H, m, 2 × CH_2), 5.18-5.24 (2 H, m, 2 × C*H*); δ_C(50 MHz; $CDCl_3$) 35.1 (2 C), 78.3 (2 C), 172. 9 (2 C). Recovery of oxazolidinone **12a** (27 mg, 80%). This compound was also obtained by Fleming–Tamao oxidation of *trans*-**15b** in 85% yield. Recovery of oxazolidinone **12b** was 75%. This compound was also obtained by Fleming–Tamao oxidation of *trans*-**15c** in 84% yield. Recovery of oxazolidinone **12c** was 70%.

Notes and references

1 (*a*) For a review on silicon controlled stereoselective reactions, see: I. Fleming, A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063; (*b*) For usefulness of β-silyl carbonyl compounds, see: I. Fleming, in *Science of Synthesis*, ed. I. Fleming, Thieme, Stuttgart, 2002, vol. 4, pp. 927.
2 (*a*) A. Barbero, D. C. Blakemore, I. Fleming and R. N. Wesley, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1329; (*b*) M. Ahmar, C. Duyck and I. Fleming, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2721.
3 (*a*) P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693; (*b*) K. Gopalaiah and H. B. Kagan, *New J. Chem.*, 2008, **32**, 607; (*c*) H. B. Kagan, *Tetrahedron*, 2003, **59**, 10351; (*d*) G. A. Molander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
4 (*a*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1992, 1775; (*b*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1992, 1777; (*c*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2711.
5 (*a*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1994, 2285; (*b*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1994, 2287; (*c*) I. Fleming and S. K. Ghosh, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2733.
6 (*a*) M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, 1964, **111**, 223; (*b*) A. J. Fry, in *Synthetic Organic Electrochemistry*, John Wiley and Sons, New York, NY, 2nd edn., 1989, pp. 208.
7 (*a*) E. L. Totton, N. C. Camp, III, G. M. Cooper, B. D. Haywood and D. P. Lewis, *J. Org. Chem.*, 1967, **32**, 2033; (*b*) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger and D. K. Roe, *J. Am. Chem. Soc.*, 1970, **92**, 2783; (*c*) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan and J. P. Simeone, *J. Am. Chem. Soc.*, 1970, **92**, 2800.
8 K. Takaki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku and Y. Fujiwara, *J. Chem. Soc., Chem. Commun.*, 1990, 516.
9 (*a*) Y. Liu, N. Dai, Y. Qi and S. Zhang, *Synth. Commun.*, 2009, **39**, 799; (*b*) For a review, see: B. K. Banik, *Eur. J. Org. Chem.*, 2002, 2431.
10 D. Y. Jung and Y. H. Kim, *Synlett*, 2005, 3019.
11 L. Zhou, D. Shi, Y. Gao, W. Shen, G. Dai and W. Chen, *Tetrahedron Lett.*, 1997, **38**, 2729.
12 (*a*) J. Inanaga, Y. Handa, T. Tabuchi, K. Otsubo, M. Yamaguchi and T. Hanamoto, *Tetrahedron Lett.*, 1991, **32**, 6557; (*b*) S. Kanemasa, H. Yamamoto and S. Kobayashi, *Tetrahedron Lett.*, 1996, **37**, 8505; (*c*) T. Kikukawa, T. Hanamoto and J. Inanaga, *Tetrahedron Lett.*, 1999, **40**, 7497.
13 (*a*) I. Shinohara, M. Okue, Y. Yamada and H. Nagaoka, *Tetrahedron Lett.*, 2003, **44**, 4649; (*b*) A. Cabrera, R. L. Lagadec, P. Sharma, J. L. Arias, R. A. Toscano, L. Velasco, R. Gavino, C. Alvarez and M. Salmon, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3609.
14 M. E. Osborn, J. F. Pegues and L. A. Paquette, *J. Org. Chem.*, 1980, **45**, 167.
15 (*a*) H. E. Bode, C. G. Sowell and R. D. Little, *Tetrahedron Lett.*, 1990, **31**, 2525; (*b*) R. D. Little, D. P. Fox, L. V. Hijfte, R. Dannecker, G. Sowell, R. L. Wolin, L. Mones and M. M. Baizer, *J. Org. Chem.*, 1988, **53**, 2287; (*c*) D. P. Fox, R. D. Little and M. M. Baizer, *J. Org. Chem.*, 1985, **50**, 2202; (*d*) L. Moens, M. M. Baizer and R. D. Little, *J. Org. Chem.*, 1986, **51**, 4497.
16 J. Yang, G. A. N. Felton, N. L. Bauld and M. J. Krische, *J. Am. Chem. Soc.*, 2004, **126**, 1634.
17 S. R. Angle and J. D. Rainier, *J. Org. Chem.*, 1992, **57**, 6883.
18 (*a*) G. H. Lee, E. B. Choi, E. Lee and C. S. Pak, *J. Org. Chem.*, 1994, **59**, 1428; (*b*) For a review, see: G. H. Lee, I. K. Youn, E. B. Choi, H. K. Lee, G. H. Yon, H. C. Yang and C. S. Pak, *Curr. Org. Chem.*, 2004, **8**, 1263.
19 S. P. Chavan and K. S. Ethiraj, *Tetrahedron Lett.*, 1995, **36**, 2281.
20 (*a*) G. Pandey and S. Hajra, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1169; (*b*) G. Pandey, S. Hajra and M. K. Ghorai, *Tetrahedron Lett.*, 1994, **35**, 7837; (*c*) G. Pandey, S. Hajra, M. K. Ghorai and K. R. Kumar, *J. Am. Chem. Soc.*, 1997, **119**, 8777; (*d*) G. Pandey, S. Hajra and M. K. Ghorai, *J. Org. Chem.*, 1997, **62**, 5966; (*e*) G. Pandey, M. K. Ghorai and S. Hajra, *Tetrahedron Lett.*, 1998, **39**, 1831; (*f*) G. Pandey, A. L. Gaikwad and S. R. Gadre, *Tetrahedron Lett.*, 2006, **47**, 701.
21 (*a*) E. J. Enholm and K. S. Kinter, *J. Org. Chem.*, 1995, **60**, 4850; (*b*) E. J. Enholm and K. S. Kinter, *J. Am. Chem. Soc.*, 1991, **113**, 7784; (*c*) D. S. Hays and G. C. Fu, *J. Org. Chem.*, 1996, **61**, 4.
22 (*a*) S. K. Ghosh, R. Singh and G. C. Singh, *Eur. J. Org. Chem.*, 2004, 4141; (*b*) R. Singh, G. C. Singh and S. K. Ghosh, *Tetrahedron Lett.*, 2005, **46**, 4719; (*c*) R. Singh, G. C. Singh and S. K. Ghosh,, *Eur. J. Org. Chem.*, 2007, 5376.
23 (*a*) C. M. Jensen, K. B. Lindsay, R. H. Taaning, J. Karaffa, A.-M. Hansen and T. Skrydstrup, *J. Am. Chem. Soc.*, 2005, **127**, 6544; (*b*) R. H. Taaning, L. Thim, J. Karaffa, A. C. Campana, A.-M. Hansen and T. Skrydstrup,, *Tetrahedron*, 2008, **64**, 11884.
24 (*a*) M. Shabangi and R. A. Flowers, II, *Tetrahedron Lett.*, 1997, **38**, 1137; (*b*) P. W. Atkins, *Physical Chemistry*, ELBS, Oxford, Fifth Ed, pp. C20.
25 H. Maekawa, M. Sakai, T. Uchida, Y. Kita and I. Nishiguchi, *Tetrahedron Lett.*, 2004, **45**, 607.
26 (*a*) R. Nomura, T. Matsuno and T. Endo, *J. Am. Chem. Soc.*, 1996, **118**, 11666; (*b*) H. C. Aspinall, N. Greeves and C. Valla, *Org. Lett.*, 2005, **7**, 1919; (*c*) F. Helion and J.-L. Namy, *J. Org. Chem.*, 1999, **64**, 2944.
27 E. J. Corey and G. Z. Zheng, *Tetrahedron Lett.*, 1997, **38**, 2045.
28 K. Mikami, M. Terada and H. Matsuzawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 3554.
29 (*a*) D. A. Evans, *Aldrichimica Acta*, 1982, **15**, 23; (*b*) D. A. Evans and A. S. Kim, in *Encyclopedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, Wiley, NY, 1995, vol.11, pp. 345; (*c*) D. Ager, I. Prakash and D. R. Schaad, *Chem. Rev.*, 1996, **96**, 835.

30 (*a*) D. A. Evans and A. E. Weber, *J. Am. Chem. Soc.*, 1986, **108**, 6757; (*b*) D. A. Evans, K. T. Chapman and J. Bisaha, *J. Am. Chem. Soc.*, 1988, **110**, 1238.
31 D. A. Evans, M. D. Ennis and D. J. Mathre, *J. Am. Chem. Soc.*, 1982, **104**, 1737.
32 M. P. Sibi and S. Manyem, *Tetrahedron*, 2000, **56**, 8033.
33 N. Kise, S.-I. Mashiba and N. Ueda, *J. Org. Chem.*, 1998, **63**, 7931.
34 M. P. Sibi, S. Manyem and J. Zimmerman, *Chem. Rev.*, 2003, **103**, 3263.
35 (*a*) S. G. Davies and H. J. Sanganee, *Tetrahedron: Asymmetry*, 1995, **6**, 671; (*b*) S. D. Bull, S. G. Davies, A. C. Garner, D. Kruchinin, M.-S. Key, P. M. Roberts, E. D. Savory, A. D. Smith and J. E. Thomson, *Org. Biomol. Chem.*, 2006, **4**, 2945.
36 T. Hintermann and D. Seebach, *Helv. Chim. Acta*, 1998, **81**, 2093.
37 (*a*) C. L. Gibson, K. Gillon and S. Cook, *Tetrahedron Lett.*, 1998, **39**, 6733; (*b*) S. D. Bull, S. G. Davis, S. Jones, M. E. C. Polywka, R. S. Prasad and H. J. Sanganee, *Synlett*, 1998, 519.
38 N. Chaubey, S. M. Date and S. K. Ghosh, *Tetrahedron: Asymmetry*, 2008, **19**, 2721.
39 M. Brenner, L. L. Vecchia, T. Leutert and D. Seebach, *Org. Synth.*, 2002, **80**, 57.
40 I. Fleming, *Chemtracts-Org. Chem.*, 1996, **9**, 1.
41 K. Tamao, N. Ishida, Y. Ito and M. Kumada, *Org. Synth.*, 1990, **69**, 96.
42 T. Posternak and J.-P. Susz, *Helv. Chim. Acta*, 1956, **39**, 2032.
43 M. Hizuka, N. Hayashi, T. Kamashita, H. Suemune and K. Sakai, *Chem. Pharm. Bull.*, 1988, **36**, 1550.
44 M. Tanaka, T. Murakami, H. Suemune and K. Sakai, *Heterocycles*, 1992, **33**, 697.
45 M. Hizuka, C. Fang, H. Suemune and K. Sakai, *Chem. Pharm. Bull.*, 1989, **37**, 1185.
46 B. Anorbe, V. S. Martin, J. M. Palazone and J. M. Trujillo, *Tetrahedron Lett.*, 1986, **27**, 4991.
47 (*a*) C. A. Moustakis, J. Viala, J. Capdevila and J. R. Falck, *J. Am. Chem. Soc.*, 1985, **107**, 5283; (*b*) F. Mosset, P. Yadagiri, S. Lumin, J. Capdevila and J. R. Falck, *Tetrahedron Lett.*, 1986, **27**, 6035; (*c*) M. D. Ennis and M. E. Base, *Tetrahedron Lett.*, 1986, **27**, 6031.
48 J. Kiegiel, J. Nowacki, A. Tarnowska, M. Stachurska and J. Jurczak, *Tetrahedron Lett.*, 2000, **41**, 4003.
49 K. Takeshita, Y. Seki, K. Kawamoto, S. Murai and N. Sonoda, *J. Org. Chem.*, 1987, **52**, 4864.