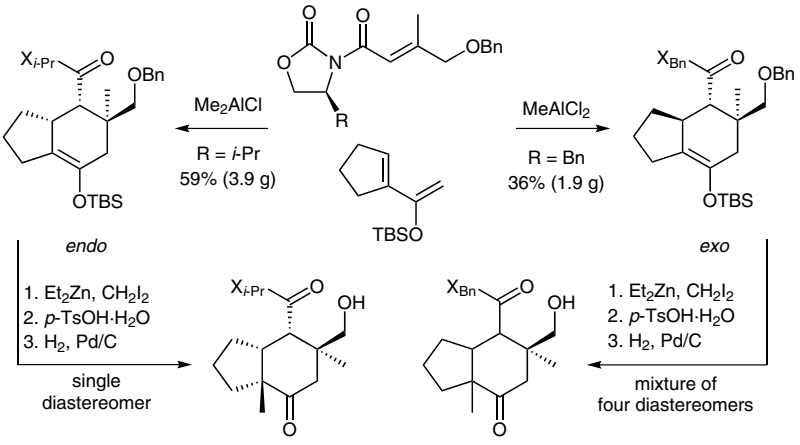
Synthesis S. Steffen et al. Paper

Substituted *cis*-Hydrindan-4-ones by Sequential Cycloadditions

Sara Steffen
Andreas Schäfer
Martin Hiersemann*

Fakultät für Chemie und Chemische Biologie, Technische Universität Dortmund, 44227 Dortmund, Germany
martin.hiersemann@tu-dortmund.de



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Abstract The synthesis of substituted *cis*-hydrindan-4-ones is reported. Particular emphasis was placed on the diastereoselective construction of quaternary stereogenic ring carbon atoms. An intermolecular asymmetric Al(III)-promoted (4+2)-cycloaddition served as the principal C/C-connecting tool. Opportunities for the further structural elaboration of the (4+2)-cycloadducts were explored.

Key words cycloaddition, Diels–Alder reaction, Lewis acids, ring opening, Grignard reaction

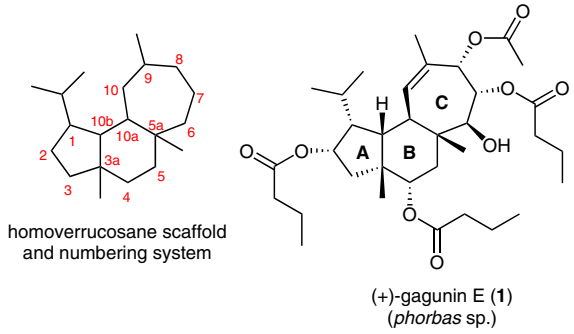
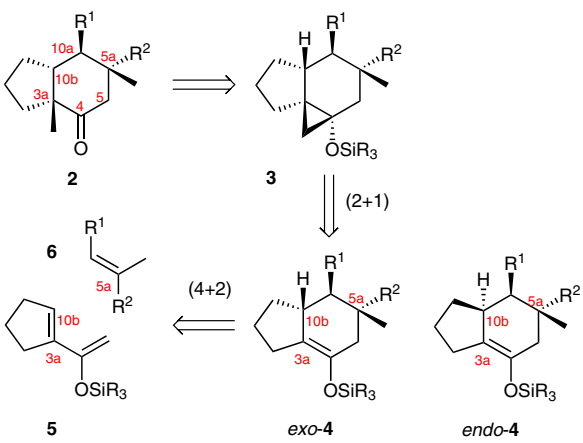


Figure 1 Proposed structure of (+)-gagunin E (**1**). The absolute configuration of **1** is unknown. The illustrated homoverrucosane numbering system is used throughout this article.

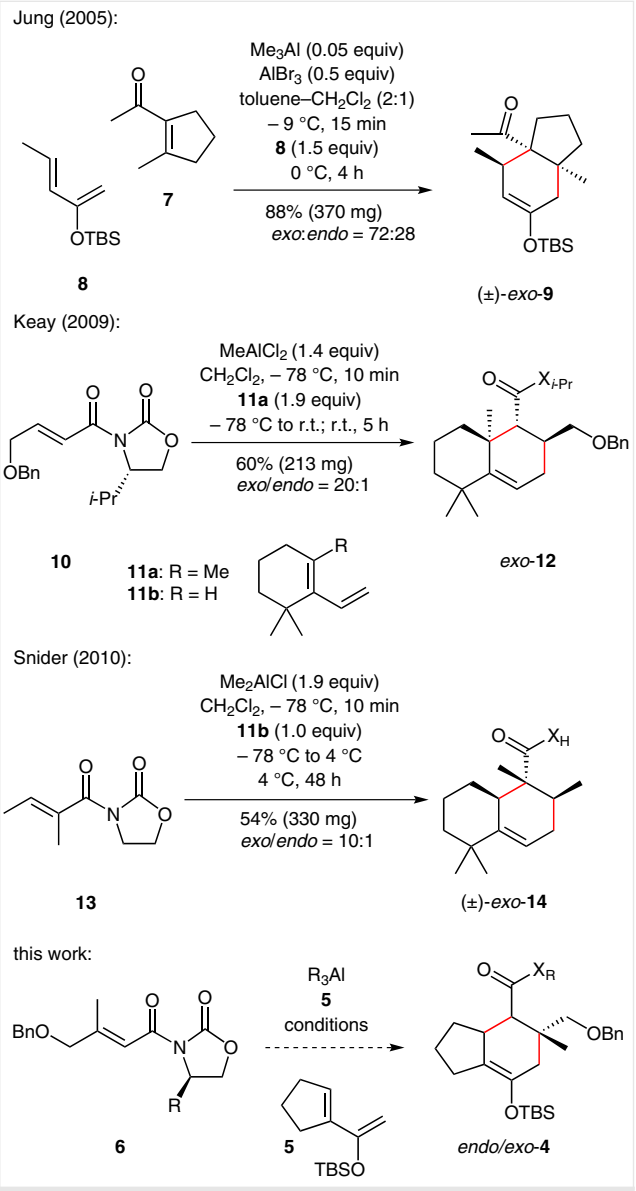
In the context of a research program aimed at the development of C/C-bond forming transformations that are useful for the total synthesis of architecturally challenging and biologically active terpenoids of marine and terrestrial origin,[1] our attention was recently drawn to a report by Shin and co-workers on the isolation of gagunin E (**1**) from a sponge of the genus *Phorbas*.[2] The homoverrucusane diterpenoid **1** is characterized by a densely substituted 5(A)-6(B)-7(C)-tricyclic cyclohepta[*e*]hydrindane scaffold featuring an A,B-*cis*-B,C-*trans* annulation pattern, which is rare within the family of homoverrucosanoids (Figure 1).

From our retrosynthetic point of view, the *cis*-hydrindane nucleus represents the key element to the architecture of gagunin E. As outlined in Scheme 1, we envisioned a sequence of two intermolecular cycloadditions as a suitable answer to the synthetic challenge and decided to explore the feasibility of such a synthetic approach.[3] In light of the exploratory nature of our endeavor, we selected the easily accessible silyl enol ether **5**[4] as an A-ring building block. The (4+2)-cycloaddition between **5** and a suitable dienophile **6** would afford the desired hydrindane architectural



Scheme 1 Proposed sequence of diastereoselective cycloadditions to the 3a,5a-dimethyl substituted *cis*-hydrindan-4-one scaffold **2**

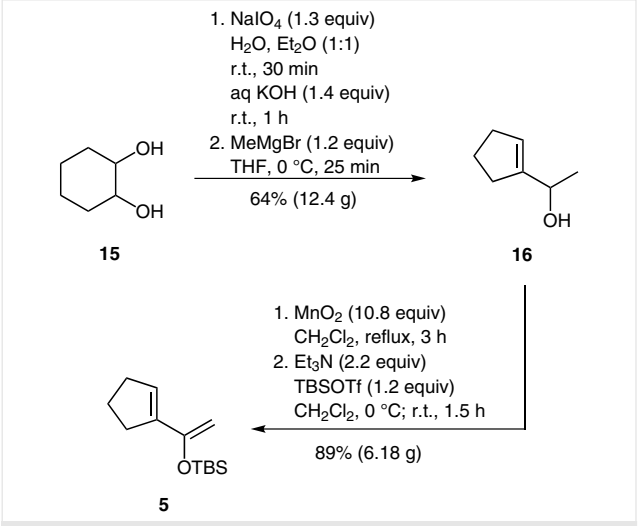
motif **4**, fittingly substituted with the angular methyl group at carbon atom C5a. By controlling the *exo*/*endo* diastereoselectivity of the (4+2)-cycloaddition, the relative configuration of the carbon atoms C10b and C5a would be predetermined; internal or external asymmetric induction would be required to render the (4+2)-cycloaddition enantioselective. With respect to the stereochemical course of the subsequent (2+1)-cycloaddition, we ventured to assume that the configuration of the carbon atom C10b of the (4+2)-cycloadduct would trigger an electrophilic cyclopropanation from the *convex* face of the bicyclic silyl enol ether **4**. Subsequent regioselective ring-opening of the siloxycyclopropane moiety would finalize our approach to the substituted B-ring of gagunin E (**1**).



Scheme 2 Guiding literature examples and the object of this work

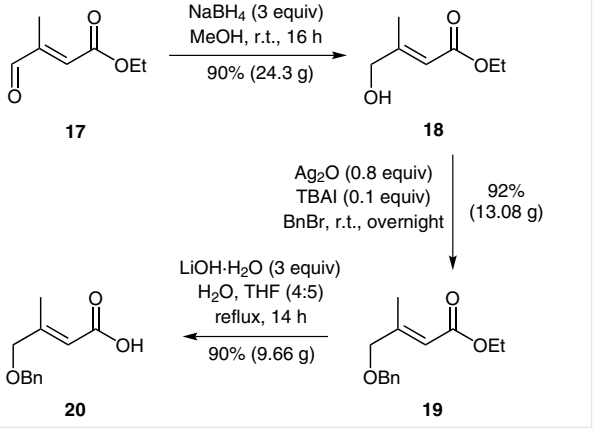
Our planning with respect to the structure of the dienophile and the reaction conditions was guided by examples for *exo* diastereoselective intermolecular (4+2)-cycloadditions from the literature (Scheme 2);[5–10] thus, α,β-unsaturated carbonyl compounds were used as dienophiles in conjunction with aluminum(III) Lewis acid activation. The desired *exo* diastereoselectivity was experimentally observed regardless of the nature of the Al(III) Lewis acid promoter. Evans type *N*-acryloyl oxazolidinones as deployed by Keay (**10**) appeared particularly promising to us because of the solid experimental and mechanistic basis provided by Evans as well as by the opportunity for auxiliary-induced diastereoselectivity.[11] Thus, we decided to study the Al(III) promoted (4+2)-cycloaddition between cross-conjugated silyl dienol ether **5** and an appropriately substituted 3-acryloyloxazolidin-2-one **6**.

The synthesis of silyl enol ether **5** commenced with the one-pot oxidative cleavage of cyclohexane-1,2-diol (**15**) and subsequent 5-*enolexo* aldol condensation to provide the crude 1-cyclopentene-1-carbaldehyde as a solution in ether (Scheme 3).[12] Reacting the crude aldehyde with methylmagnesium bromide delivered allylic alcohol **16** on a gram scale after chromatographic purification (64%, 12.4 g of analytically pure compound isolated).[13] Oxidation of the allylic alcohol **16** with manganese(IV) oxide afforded the crude volatile enone as a solution in CH_2Cl_2. Formation of the desired acid labile silyl enol ether **5** was then accomplished by treatment of the crude enone with an excess of triethylamine and *tert*-butyldimethylsilyl trifluoromethansulfonate (89%, 6.18 g).[14] The crude silyl enol ether **5** was purified by Kugelrohr distillation and could be stored for several weeks at low temperature and under the rigorous exclusion of acid.[15]



Scheme 3 Preparation of silyl enol ether **5** on a gram scale requires only a single column chromatographic purification; the acid-labile silyl enol ether can be purified by Kugelrohr distillation.

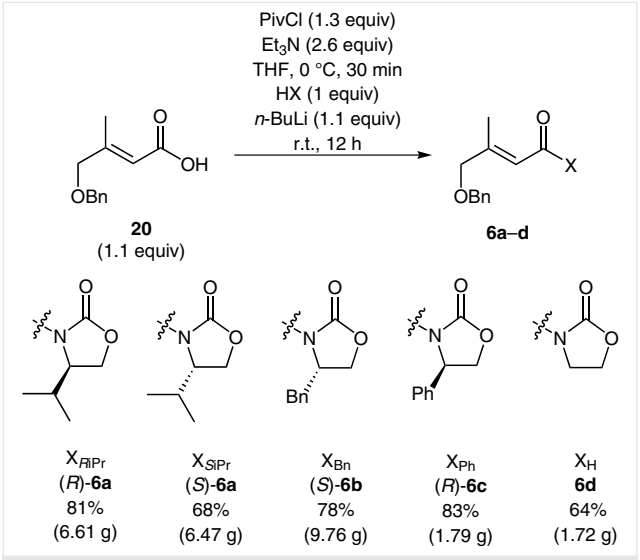
The synthesis of *N*-acryloyl oxazolidinones required access to (*E*)-4-(benzyloxy)-3-methylbut-2-enoic acid (**20**) for covalent attachment to the corresponding chiral auxiliaries (Scheme 4). The synthesis of the acid **20** started with the commercially available ethyl (*E*)-3-methyl-4-oxobut-2-enoate (**17**), which was chemoselectively reduced with sodium borohydride to afford allylic alcohol **18** (90%, 24.3 g). The allylic alcohol was subjected to a silver(I) oxide mediated and tetra-*n*-butylammonium iodide catalyzed benzylation to provide benzylic ether **19** (92%, 13.08 g).[16] Saponification by exposure to aqueous lithium hydroxide at elevated temperature finally delivered the desired acid **20** (90%, 9.66 g).



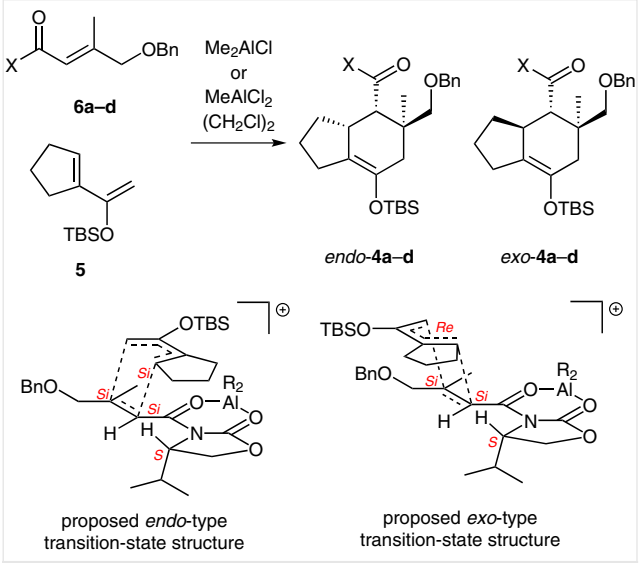
Scheme 4 Preparation of carboxylic acid **20** from commercially available aldehyde **17**

Model studies by Evans have revealed that the phenylalaninol-derived auxiliary exerted an enhanced auxiliary-induced diastereoselectivity in the Et_2AlCl promoted (4+2)-cycloaddition of *N*-acryloyl oxazolidinones with acyclic dienes.[11] To test the significance of this auxiliary effect, we set out to synthesize a small collection of 3-acryloyloxazolidin-2-ones using differently substituted 1,3-oxazolidin-2-ones (Scheme 5). In our hands, reacting the mixed anhydride of acid **20** with pivalic acid and the lithiated 1,3-oxazolidin-2-one in the absence of additional lithium chloride delivered the desired 3-acryloyloxazolidin-2-ones **6a–d** most effectively.[17,18]

With diene **5** and a collection of dienophiles **6a–d** in hand, we proceeded to investigate the envisioned (4+2)-cycloaddition (Scheme 6, Table 1 and Table 2). By following the reported procedures (Scheme 2), *N*-acryloyl oxazolidinones **6a–d** were treated at low temperature with an excess of dimethylaluminum chloride (1.4 equiv) to allow for chelate formation (1,2-dichloroethane, –25 °C, 10 min). Subsequent addition of diene **5** (2 equiv) at –25 °C followed by stirring at ambient temperature delivered the cycloadducts **4a–d** (Table 1). The (4+2)-cycloaddition promoted by Me_2AlCl proceeded in a highly *endo* diastereoselective fashion and with complete auxiliary-induced diastereoselectivity.[19] The valinol-based auxiliary X_{iPr} was particularly effective in this regard, and a single *endo* diastereomer (*endo*-**4a**) was obtained after chromatographic purification (Table 1, entries 1 and 2). Diminished *endo*/*exo* diastereoselectivities were detected for the dienophiles **6b** or **6c**, equipped with phenylalanine- and phenylglycine-based auxiliaries X_{Bn} or X_{Ph} (Table 1, entries 3 and 4). To determine the intrinsic *endo*/*exo* diastereoselectivity without interference by a chiral auxiliary, the achiral dienophile **6d**, containing the simple 1,3-oxazolidin-2-one X_H, was subjected to our standard conditions for the dimethylaluminum chloride-promoted



Scheme 5 Preparation of (*E*)-3-[4-(benzyloxy)-3-methylbut-2-enoyl]oxazolidin-2-ones **6a–d**



Scheme 6 Diastereoselective (4+2)-cycloadditions promoted by Me_2AlCl or $MeAlCl_2$. Absolute configuration proposed for (*S*)-configured auxiliaries (X). For conditions see Table 1 (Me_2AlCl) and Table 2 ($MeAlCl_2$).

Table 1 *Endo*-Diastereoselective (4+2)-Cycloadditions Promoted by Me_2AlCl (Scheme 4)[a]

Entry	Dienophile	X	*endo*/*exo*[b]	opt. rot.[c]	*endo*-**4a**–**d**[b]
1	(*S*)-**6a**	X_{SiPr}	>95:5	(+)	59% (3.94 g)
2	(*R*)-**6a**	X_{RiPr}	>95:5	(–)	50% (2.13 g)
3	(*S*)-**6b**	X_{Bn}	83:17	(+)	38% (70 mg)
4	(*R*)-**6c**	X_{Ph}	87:13	(–)	50% (651 mg)
5	**6d**	X_H	>95:5	(±)	54% (107 mg)

[a] Reaction conditions: **6a**–**d** (1 equiv), $(CH_2Cl)_2$, Me_2AlCl (1.4 equiv), –25 °C, 10 min; **5** (2 equiv), –25 °C to r.t., then r.t., 2 h.
[b] Determined by ^1H NMR spectroscopic analysis.
[c] Sign of optical rotation of the pure *endo* diastereomer determined as specified in the Experimental Section.
[d] Isolated yield (isolated mass) of pure *endo* diastereomer after purification by chromatography.

Table 2 *Exo*-Diastereoselective (4+2)-Cycloadditions Promoted by $MeAlCl_2$ (Scheme 4)[a]

Entry	Dienophile	X	*endo*/*exo*[b]	opt. rot.[c]	*exo*-**4a**–**c**[d]
1	(*S*)-**6a**	X_{SiPr}	17:83	(–)	29% (98 mg)
2	(*S*)-**6b**	X_{Bn}	6:94	(–)	36% (1.9 g)
3	(*R*)-**6c**	X_{Ph}	13:87	(+)	43% (70 mg)

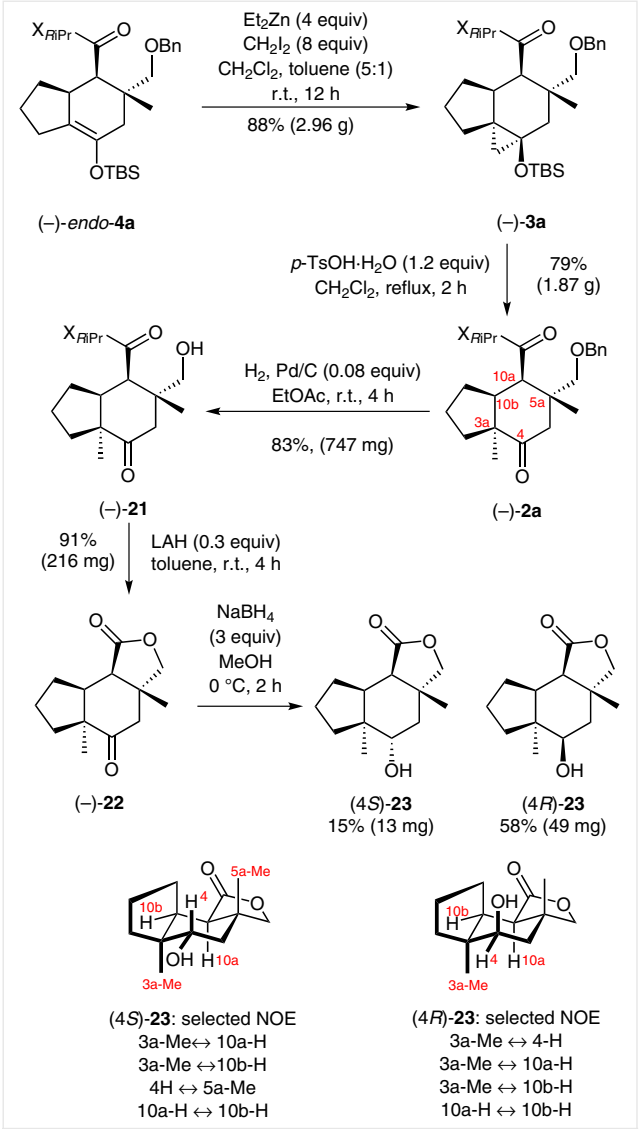
[a] Reaction conditions: **6a**–**c** (1 equiv), $(CH_2Cl)_2$, $MeAlCl_2$ (1.4 equiv), –25 °C, 10 min; **5** (2 equiv), –25 °C to r.t., then r.t., 12 h.
[b] Determined by ^1H NMR spectroscopic analysis.
[c] Sign of optical rotation of the pure *exo* diastereomer determined as specified in the Experimental Section.
[d] Isolated yield (isolated mass) of pure *exo* diastereomer after purification by chromatography.

(4+2)-cycloaddition (Table 1, entry 5). In the event, the *endo* configured cycloadduct **4d** was obtained exclusively. In light of the examples from the literature (Scheme 2), the high *endo*-diastereoselectivity of the dimethylaluminum chloride-promoted (4+2)-cycloaddition between **5** and **6** caught us by surprise. We speculate that diene **5** is sterically less demanding compared with dienophiles such as **11a**,**b** and, hence, the intrinsic preference for an *endo*-type transition-state prevails.

Somewhat surprisingly, switching the Lewis acid to methylaluminum dichloride had a profound influence on the *exo*/*endo* diastereoselectivity of the (4+2)-cycloaddition (Table 2). Regardless of the nature of the chiral auxiliary, the formation of the *exo*-configured cycloadducts **4a**–**c** was favored, albeit in inferior isolated yields (29–43%) compared with the dimethylaluminum chloride promoted *endo* diastereoselective (4+2)-cycloaddition (38–59%). Nevertheless, by employing the phenylalanine-derived chiral auxiliary X_{Bn}, the diastereomerically pure (4+2)-cycloadduct *exo*-**4b** was accessible on a gram scale (Table 2, entry 2).

We next set out to evaluate opportunities for structural elaboration of the diastereomerically pure (4+2)-cycloadducts **4**. According to our plan (Scheme 1), we initially focused on the introduction of the 3a-methyl group by electrophilic cyclopropanation of the silyl enol ether moiety. Departing from our initial expectations, given that the *exo*- and *endo*-configured cycloadducts **4** were available, we opted to address the (2+1)-cycloaddition for both diastereomers.

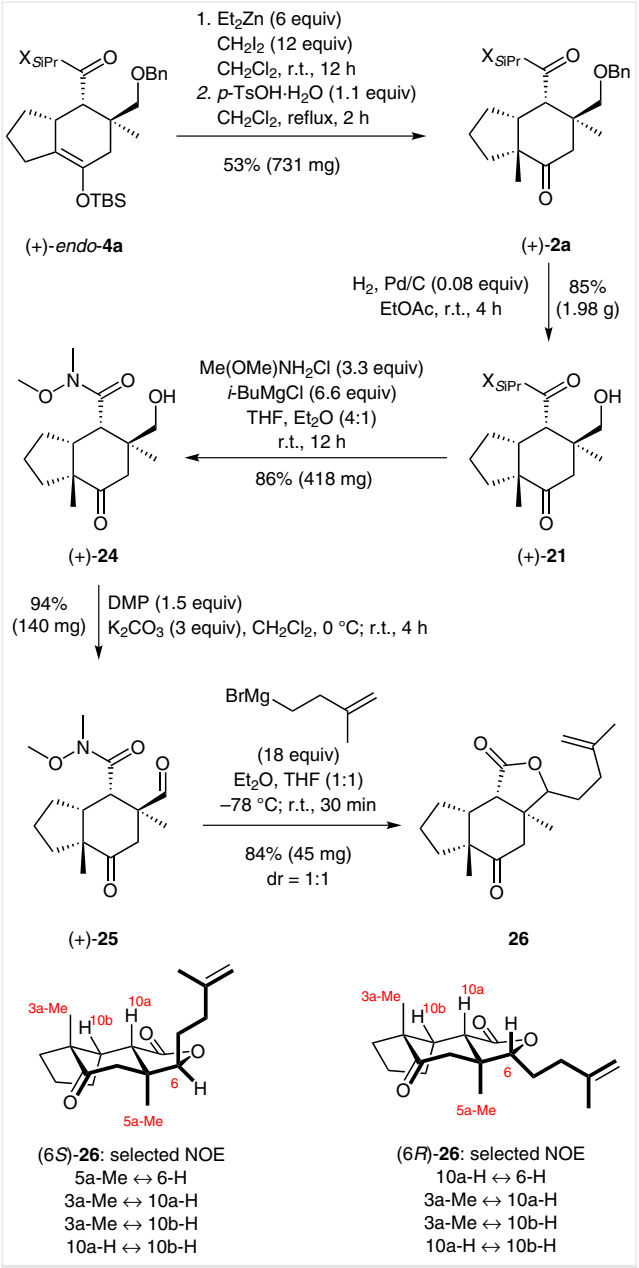
Installation of the siloxycyclopropane moiety by Furukawa type cyclopropanation of (–)-*endo*-**4a** proceeded uneventfully and provided imide (–)-**3a** (88%, 2.96 g) as a single diastereomer (Scheme 7).[17] Subsequent Brønsted acid mediated ring-opening of the siloxycyclopropane (–)-**3a** delivered the *cis*-hydrindan-4-one **2** (79%, 1.87 g).[20] In accordance with our original plan (Scheme 1), the cyclopropanation proceeded from the *convex* face of the bicyclic silyl enol ether *endo*-**4a** leading to the *trans*-arrangement of the 3a- and 5a-methyl groups on the six-membered B-ring of **2**.



Scheme 7 Introduction of the 3a-methyl group and subsequent structural elaboration

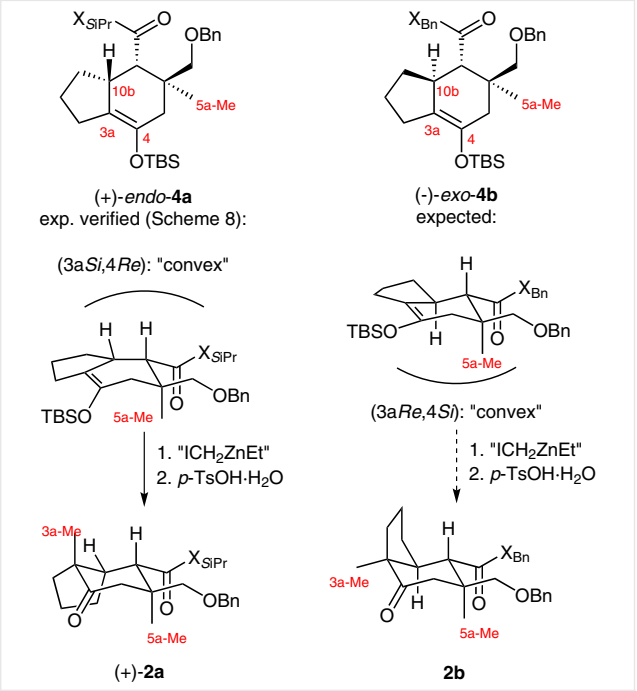
We next focused on the extrusion of the chiral auxiliary by lactonization.[21] Accordingly, the benzyl protecting group was removed by hydrogenolysis to afford the γ-hydroxy imide (–)-**21** (83%, 747 mg). In our hands, lactonization was then triggered by treatment of the γ-hydroxy imide (–)-**21** with substoichiometric amounts (0.3 equiv) of lithium aluminum hydride in toluene at ambient temperature (91%, 216 mg) and without reduction of the C4 carbonyl group.[22] We hypothesized that aluminum alkoxide formation and a directing effect could be responsible for the success of the lactonization. Having established conditions for extrusion of the chiral auxiliary, we finally investigated the chemo- and diastereoselective reduction of ketone **22**. Preliminary experiments revealed that the application of L- or K-Selectride,[23] DIBAL-H,[24] or Red-Al at low temperature in tetrahydrofuran (THF) led to no conversion, possibly as a consequence of the steric congestion in **22**. Exposure of ketone **22** to an excess of sodium borohydride in methanol finally delivered the desired alcohol **23** as a mixture of diastereomers (4*R*/4*S* ratio 4:1) that were separable by chromatography. This result indicates a moderate preference for an equatorial attack of the hydride from the *convex* face of the molecule. A similar result was obtained for the reduction of ketone **22** by using $NaBH_4$ (1.5 equiv) in the presence of $CeCl_3$ (1.5 equiv) in MeOH at –30 °C (86%, dr = 69:31).[25]

Aiming to add structural elements of the homoverrucosane scaffold to the *cis*-hydrindan-4-one building block **2**, we next set out to explore additional opportunities for the structural elaboration of the (4+2)-cycloadducts. Thus, exposure of (+)-*endo*-**4a** to the chemistry described above delivered alcohol (+)-**21** (Scheme 8). Treatment of the γ-hydroxy imide (+)-**21** with an excess of magnesium chloride methoxy(methyl)amide led to the exposure of the auxiliary and formation of the corresponding Weinreb amide **24** (86%, 418 mg).[26] Notably, attempts to convert the benzyl ether (–)-**2a** into the corresponding Weinreb amide had proven unsuccessful. Dess–Martin oxidation of alcohol **24** proceeded uneventfully and delivered the aldehyde **25** (94%, 140 mg).[27] The aldehyde was then subjected to reaction with (3-methylbut-3-en-1-yl)magnesium bromide[28] to afford the *trans*-γ-lactones (6*S*)- and (6*R*)-**26** as an equimolar but separable mixture of diastereomers (84%, 45 mg). The thus installed C7 to C9 tether could later serve as a handle for the annulation of the seven-membered C-ring of the homoverrucosane scaffold.

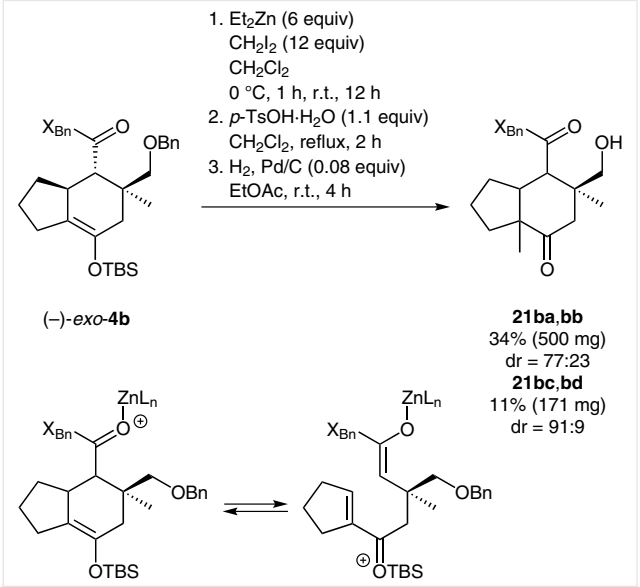


Scheme 8 Structural elaboration of cycloadduct (+)-*endo*-**4a** by chain elongation at carbon atom C6

The productive combination of substrate- and auxiliary-induced diastereoselectivity enabled access to the diastereomerically pure *cis*-hydrindan-4-ones (+)-**2a** and (–)-**2a** (Scheme 7 and Scheme 8). To explain the complete diastereoselectivity of the Furukawa cyclopropanation of *endo*-**4a**, we propose the qualitative stereochemical model depicted in Scheme 9.[29] Assuming that the absolute configuration of the carbon atom C10b induces a curvature in the bicyclic silyl enol ether scaffold of *endo*-**4a**, the *convex* face should be more easily accessible by the cyclopropanation reagent. The preference for an attack from the *convex* face may be reinforced, or at least not attenuated, because of the concavely directed 5a-methyl group. We then utilized the stereochemical model to predict the outcome of the (2+1)-cycloaddition of the *exo*-configured (4+2)-cycloadduct *exo*-**4b** (Scheme 9). Accordingly, we expected a preference for the attack of the cyclopropanation reagent from the *convex* face of *exo*-**4b** to deliver the desired *cis*-hydrindan-4-one building block **2b**. In this case, however, the pseudo-axial 5a-



Scheme 9 Stereochemical model used to explain and predict the diastereoface-differentiation of the electrophilic cyclopropanation using conditions reported by Furukawa



Scheme 10 Cyclopropanation of *exo*-**4b** delivered a mixture of four diastereomers **21ba–bd**

methyl group is directed toward the *convex* face of the bicyclic silyl enol ether. Thus, we could not a priori preclude an attenuated diastereoselectivity for the Furukawa cyclopropanation of *exo*-**4b**.

Being confident of the validity of our stereochemical model (Scheme 9), we proceeded to investigate the (2+1)-cycloaddition of *exo*-**4b** (Scheme 10). Much to our dismay, however, exposure of the *exo*-**4b** cycloaddition product to the Furukawa cyclopropanation led to the formation of an inseparable mixture of *four* diastereomers. Exposure of the diastereomeric mixture to Brønsted acidic conditions triggered siloxycyclopropane ring-opening. Subsequent benzyl ether cleavage by hydrogenolysis delivered two separable pairs of two diastereomers each (**21ba**,**bb** and **21bc**,**bd**). Chromatographic purification allowed isolation of one pure diastereomer **21bc**, however, NOE studies of the mixtures as well as the pure diastereomer **21bc** were inconclusive or ambiguous; thus, we refrain from assigning relative configurations for **21ba**–**bd**.

The formation of four diastereomers and the failure of our stereochemical model to predict the outcome of the cyclopropanation of *exo*-**4b** may be explained by assuming that the orientation of the 5a-methyl group toward the *convex* face of the bicyclic silyl enol ether decelerates the cyclopropanation of *exo*-**4b** to a degree that a Lewis acid (ZnL_n)-mediated retro-Michael/Michael reaction equilibrium emerges as a competitive reaction pathway. Retrospectively, this result and its interpretation support the assumption that the high diastereoselectivities of the initial (4+2)-cycloadditions between **5** and **6** originate from a certainly asynchronous but still concerted bond reorganization process (Diels–Alder reaction).

In conclusion, we have studied a sequence composed of consecutive (4+2)- and (2+1)-cycloadditions that provides access to substituted *cis*-hydrindan-4-one building blocks from simple starting materials. Deploying a chiral dienophile, the aluminum(III)-promoted (4+2)-cycloaddition proceeded with complete auxiliary-induced diastereoselectivity. The *exo*/*endo*-diastereoselectivity of the (4+2)-cycloaddition could be controlled by the appropriate choice of the Lewis acid promoter. The diastereoselectivity of the subsequent Furukawa cyclopropanation turned out to depend on the relative configuration of the (4+2)-cycloadduct. The (2+1)-cycloaddition of the *endo*-configured (4+2)-cycloadduct was highly diastereoselective, whereas the cyclopropanation of the *exo*-configured (4+2)-cycloadduct afforded a complex mixture of diastereomers. A stereochemical model was proposed to account for this experimental finding. Removal of the auxiliary by functional group interconversion, redox chemistry, and C/C-bond formation by Grignard reaction served to illustrate opportunities for structural elaboration of the available *cis*-hydrindan-4-one building block.

Unless otherwise stated, commercially available reagents, catalysts and solvents were used as purchased. Tetrahydrofuran, dichloromethane, acetonitrile, and diethyl ether were dried by deploying a commercially available solvent purification system. Triethylamine (Et_3N) was dried over KOH followed by distillation from CaH_2 and

stored under an atmosphere of Argon. $CDCl_3$ was stored over activated 4 Å molecular sieves. All moisture-sensitive reactions were performed in flame-dried septum-sealed glassware under an atmosphere of argon. Reagents were transferred by using a syringe. Solids were introduced under a counter-flow of argon. The concentration of commercially available *n*-BuLi solutions were confirmed by titration against diphenylacetic acid.[30]

Analytical TLC was performed using precoated silica gel foils (4 cm). Visualization was achieved by using 254 nm ultraviolet irradiation followed by staining with the Kägi–Miescher reagent (*p*-anisaldehyde 2.53% v/v, acetic acid 0.96% v/v, EtOH 93.06% v/v, concd H_2SO_4 3.45% v/v) or the $KMnO_4$ reagent [$KMnO_4$ (3 g), K_2CO_3 (20 g), NaOH (0.25 g in 5 mL H_2O), H_2O (300 mL)].[31] Unless otherwise specified, chromatographic purification[32] was performed on silica gel (particle size 0.040–0.063 mm). Mixtures of cyclohexane and EtOAc or *n*-pentane and diethyl ether were used as eluents.

^1H NMR spectra were recorded at 400 or 500 MHz. Chemical shifts (δ) are reported in ppm relative to chloroform (δ = 7.26 ppm).[33] Signal splitting patterns are labeled as: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sext = sextet, sept = septet, oct = octet, m = multiplet or overlap of nonequivalent resonances, br = broad, Ar = aryl, cPr = cyclopropyl, iPr = isopropyl. Coupling constants (Hz) are given as reported by the NMR processing and analysis software. ^{13}C NMR spectra were recorded at 101 or 126 MHz. Unless otherwise reported, all ^{13}C NMR spectra were obtained with broadband proton decoupling. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 77.16 ppm); the total number of reported ^{13}C atom signals may fall short of the expected number because of coincidental chemical shifts, even for constitutopic or diastereotopic carbon atoms. The NMR peak assignment as well as the assignment of the relative configuration rests on the interpretation of $^1H^1H$ COSY, $^1H^{13}C$ HSQC and $^1H^1H$ NOESY experiments. Atom numbering is based on the homoverrucosane numbering system (Figure 1).

Unless stated otherwise, IR spectra were recorded as a thin film on a KBr disk. Infrared absorptions are reported in reciprocal wavelength ν (cm^{-1}) and are adjusted down- or upward to 0 or 5 cm^{-1}. Relative intensities are indicated as they appeared as: s = strong, m = medium, w = weak.

Molecular formula assignment was confirmed by combustion elemental analysis using the elemental analyzers Leco CHNS-932 or Elementar Vario Micro Cube.

High-resolution mass spectra were recorded with a LTQ Orbitrap mass spectrometer using electrospray ionization (ESI).

Melting points (m.p.) are uncorrected and were recorded with a Büchi B-540 melting point apparatus.

Synthesis of Allylic Alcohol 16 from Cyclohexan-1,2-diol

To a solution of $NaIO_4$ (47.90 g, 223.95 mmol, 1.3 equiv) in H_2O (300 mL), was added at r.t. a solution of cyclohexan-1,2-diol (20.0 g, 172.18 mmol, 1 equiv) in Et_2O (300 mL). The pH of the reaction mixture was measured and, if necessary, adjusted to pH 4 by the addition of aq HNO_3 (25% v/v). After being stirred for 30 min at ambient temperature, a solution (20% w/v, 67 mL) of KOH (13.4 g, 238.8 mmol, 1.4 equiv) in H_2O was added and the resulting mixture was stirred at r.t. for 1 h. The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated at 900 mbar and 40 °C bath temperature to a volume of 100 mL. The ethereal solution was diluted with THF (150 mL) and activated 4 Å MS (20 g, beads) were added. To the ethereal solution was added MeMgBr (1 M in THF, 202.22 mL, 202.22 mmol 1.17 equiv) at 0 °C over a period of 25 min. After addition of the Grignard reagent was complete, the reaction mixture was diluted by the addition of sat. aq NH_4Cl (200 mL). The phases were separated and the aqueous layer was extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by chromatography (cyclohexane–EtOAc, 50:1→20:1→10:1) afforded allylic alcohol (±)-**16**.

Yield: 12.42 g (110.72 mmol, 64%); colorless liquid; R_f = 0.48 (cyclohexane–EtOAc, 2:1).

IR (film): 3345 (s), 2970 (s), 2950 (s), 2930 (s), 2895 (s), 2845 (s), 1365 (s), 1070 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, *J* = 6.5 Hz, 3 H), 1.88 (m, 3 H), 2.31 (t, *J* = 7.6 Hz, 4 H), 4.40 (q, *J* = 6.5 Hz, 1 H), 5.56 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.1, 23.4, 31.4, 32.2, 67.3, 124.2, 148.3.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.9; H, 10.8.

Silyl Enol Ether 5

MnO_2 Oxidation: To a solution of allylic alcohol **16** (12.42 g, 110.72 mmol, 1 equiv) in CH_2Cl_2 (600 mL) at ambient temperature was added pretreated (2 d at 150 °C) MnO_2 (90% w/w, 115.54 g, 103.99 g MnO_2, 1196.07 mmol, 10.8 equiv). The reaction mixture was heated to reflux for 3 h and subsequently filtered through a pad of Celite. The filter cake was rinsed with CH_2Cl_2 and the filtrate was concentrated at 800 mbar and 40 °C to a volume of 100 mL. According to NMR analysis, the solution contained the corresponding enone (11.20 g, 101.68 mmol, 92%) that was sufficiently pure for further transformation. For analytical purposes, a sample of the enone was purified by chromatography (pentane–Et_2O, 50:1→20:1, solvent evaporation at 700 mbar and 40 °C) to deliver the enone as a clear colorless liquid; R_f = 0.65 (cyclohexane–EtOAc, 2:1).

IR (film): 2955 (s), 2855 (m), 1705 (m), 1665 (s), 1615 (s), 1375 (s), 1295 (s), 1265 (s), 1045 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.93 (tt, *J* = 7.6, 7.6 Hz, 2 H), 2.32 (s, 3 H), 2.52–2.58 (m, 4 H), 6.73 (tt, *J* = 2.0, 2.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 23.0, 26.8, 30.6, 34.0, 144.4, 146.3, 196.9.

Silyl Enol Ether Formation: To a solution of the enone (3.12 g, 28.33 mmol, 1 equiv) in CH_2Cl_2 (200 mL) at 0 °C was successively added Et_3N (0.73 g/mL, 8.70 mL, 6.35 g, 62.76 mmol, 2.2 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.151 g/mL, 7.81 mL, 8.99 g, 34.0 mmol, 1.2 equiv). The reaction mixture was stirred at r.t. for 1.5 h. Evaporation of the volatiles afforded a biphasic residue; the lower layer was discarded whereas the upper layer was subjected to Kugelrohr distillation to deliver the acid-labile silyl enol ether **5** at 0.66 mbar and 95–100 °C. The silyl enol ether could be stored up to four weeks under an atmosphere of argon at –30 °C.[15]

Yield: 6.18 g (27.54 mmol, 97%); pale-yellow oil; R_f = 0.72 (cyclohexane–EtOAc, 2:1)

^1H NMR (500 MHz, $CDCl_3$): δ = 0.18 (s, 6 H), 0.97 (s, 9 H), 1.93 (tt, *J* = 7.5, 7.5 Hz, 2 H), 2.43 (t, *J* = 7.5 Hz, 4 H), 4.27 (d, *J* = 2.5 Hz, 2 H), 6.00 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 4.6, 18.3, 23.7, 25.9, 32.2, 33.0, 92.6, 128.8, 141.3, 154.1.

Allylic Alcohol 18 by $NaBH_4$ Reduction

To a solution of ethyl (*E*)-3-methyl-4-oxobut-2-enoate (**17**) (1.063 g/mL, 25.0 mL, 26.575 g, 186.95 mmol, 1 equiv) in MeOH (500 mL) at 0 °C was added $NaBH_4$ (20.84 g, 550.89 mmol, 3 equiv). After stirring at ambient temperature for 16 h, the reaction mixture was diluted with sat. aq $NaHCO_3$ (400 mL). The phases were separated and the aqueous layer was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 10:1→5:1) to give allylic alcohol **18**.

Yield: 24.30 g (168.55 mmol, 90%); colorless liquid; R_f = 0.33 (cyclohexane–EtOAc, 2:1).

IR (film): 3440 (br. s), 2985 (s), 2905 (s), 1715 (s), 1660 (s), 1445 (s), 1385 (s), 1370 (s), 1320 (s), 1280 (s), 1225 (s), 1150 (s), 1080 (s), 1045 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz, 3 H), 1.95 (t, *J* = 6.0 Hz, 1 H), 2.08 (d, *J* = 1.1 Hz, 3 H), 4.13 (dd, *J* = 7.1 Hz, 2 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 5.98 (tq, *J* = 1.1, 1.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.4, 15.7, 59.8, 67.1, 113.7, 157.3, 166.9.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.3; H, 8.6.

Benzyl Ether 19

To a solution of allylic alcohol **18** (8.75 g, 60.69 mmol, 1 equiv) in benzyl bromide (36 mL) was added at r.t. tetra-*n*-butyl-ammonium iodide (2.24 g, 6.06 mmol, 0.1 equiv). After stirring for 20 min at r.t., the reaction mixture was chilled to 0 °C and Ag_2O (11.24 g, 48.50 mmol, 0.8 equiv) was added in portions. The cooling bath was removed and the reaction mixture was stirred at r.t. overnight. The mixture was filtered through a plug of Celite and the filter cake was rinsed with Et_2O. The filtrate was dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 100:1→50:1) to give benzyl ether **19**.

Yield: 13.08 g (55.83 mmol, 92%); clear colorless oil; R_f = 0.68 (cyclohexane–EtOAc, 2:1).

IR (film): 2980 (s), 2855 (s), 1715 (s), 1660 (s), 1455 (s), 1370 (s), 1320 (s), 1270 (s), 1225 (s), 1150 (s), 1105 (s), 1030 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3 H), 2.11 (d, *J* = 1.1 Hz, 3 H), 4.00 (d, *J* = 1.4 Hz, 2 H), 4.18 (q, *J* = 7.1 Hz, 2 H), 4.54 (s, 2 H), 6.01 (tq, *J* = 1.1, 1.4 Hz, 1 H), 7.28–7.38 (m, 5 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 15.9, 59.8, 72.6, 74.2, 115.4, 127.7, 127.8, 128.5, 137.9, 154.5, 166.8.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.7; H, 7.8.

Carboxylic Acid 20 by Saponification

To a solution of $LiOH{\cdot}H_2O$ (6.48 g, 154.43 mmol, 3 equiv) in H_2O (117 mL) was added at r.t. a solution of the ester **19** (12.14 g, 51.81 mmol, 1 equiv) in THF (149 mL). After heating to reflux for 14 h, the reaction mixture was cooled to r.t. and the phases were separated. The organic layer was extracted twice with H_2O. The combined clear yellow aqueous solutions were acidified (pH 1) with aq HCl (1 M) and the resulting white suspension was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 20:1) to give carboxylic acid **20**.

Yield: 9.66 g (46.84 mmol, 90%); colorless oil that solidified at r.t. to afford colorless crystals; mp 27–28 °C; R_f = 0.23 (cyclohexane–EtOAc, 2:1).

IR (film): 3300–2500 (br. s), 3065 (s), 3030 (s), 2920 (s), 2860 (s), 1695 (s), 1650 (s), 1455 (s), 1425 (s), 1365 (s), 1295 (s), 1255 (s), 1170 (s), 1105 (s), 735 (s), 700 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 1.1 Hz, 3 H), 4.03 (d, *J* = 1.4 Hz, 2 H), 4.56 (s, 2 H), 6.08 (tq, *J* = 1.1, 1.4 Hz, 1 H), 7.29–7.40 (m, 5 H), 11.80 (br. s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 16.2, 72.7, 74.0, 114.5, 127.7, 127.9, 128.6, 137.7, 157.8, 172.3.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.0; H, 7.2.

Preparation of 3-Acryloyloxazolidin-2-ones 6a–d from Carboxylic Acid 20; General Procedure

To a solution of acid **20** (1.1 equiv) and Et_3N (0.73 g/mL, 2.6 equiv) in THF at 0 °C was added freshly distilled pivaloyl chloride (PivCl; 0.98 g/mL, 1.3 equiv). The resulting suspension was stirred for 30 min at 0 °C. Meanwhile, to a solution of the representative oxazolidin-2-one (1 equiv) in THF was added *n*-BuLi (1.1 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and subsequently transferred to the suspension by syringe. After stirring for 12 h at r.t., the mixture was diluted with H_2O (10 mL/mmol oxazolidin-2-one). The phases were separated and the aqueous layer was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by chromatography (cyclohexane–EtOAc, 50:1→20:1→10:1→5:1) to give the corresponding imide.

(*R*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-isopropyloxazolidin-2-one [(*R*)-6a]

According to the general procedure, (*R*)-**6a** was prepared from acid **20** (6.03 g, 29.24 mmol, 1.1 equiv), Et_3N (0.73 g/mL, 9.63 mL, 7.03 g, 69.47 mmol, 2.7 equiv) and PivCl (0.98 g/mL, 4.25 mL, 4.165 g, 34.54 mmol, 1.3 equiv) in THF (230 mL) as well as (*R*)-4-isopropyloxazolidin-2-one (HX_{RiPr}; 3.32 g, 25.70 mmol, 1 equiv) and added *n*-BuLi (2.48 M in hexanes, 11.77 mL, 29.19 mmol, 1.1 equiv) in THF (93 mL) to give imide (*R*)-**6a**.

Yield: 6.61 g (20.83 mmol, 81%); colorless solid; mp 88 °C; R_f = 0.51 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –64.7 (*c* 0.97, $CHCl_3$).

IR (film): 1775 (s), 1680 (s), 1640 (s), 1385 (s), 1365 (s), 1255 (s), 1210 (s), 1185 (s), 1105 (s), 1065 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 7.0 Hz, 3 H), 0.92 (d, *J* = 7.0 Hz, 3 H), 2.11 (d, *J* = 1.1 Hz, 3 H), 2.38–2.46 (m, 1 H), 4.07 (d, *J* = 1.3 Hz, 2 H), 4.21 (dd, *J* = 9.0, 3.4 Hz, 1 H), 4.28 (dd, *J* = 9.0, 8.4 Hz, 1 H), 4.48–4.52 (m, 1 H), 4.58 (s, 2 H), 7.27 (tq, *J* = 1.1, 1.3 Hz, 1 H), 7.26–7.40 (m, 5 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.8, 16.8, 18.1, 28.6, 58.4, 63.2, 72.6, 74.5, 115.3, 127.8, 127.8, 128.5, 137.9, 154.0, 156.5, 165.2.

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 68.3; H, 7.3; N, 4.2.

(*S*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-isopropyloxazolidin-2-one [(*S*)-6a]

According to the general procedure, (*S*)-**6a** was prepared from acid **20** (7.0 g, 33.94 mmol, 1.1 equiv), Et_3N (0.73 g/mL, 11.18 mL, 8.16 g, 80.64 mmol, 2.7 equiv) and PivCl (0.98 g/mL, 4.94 mL, 4.84 g, 40.14 mmol, 1.3 equiv) in THF (230 mL) as well as (*S*)-4-isopropyloxazolidin-2-one (HX_{SiPr}; 3.86 g, 29.89 mmol, 1 equiv) and added *n*-BuLi (2.48 M in hexanes, 13.69 mL, 33.95 mmol, 1.1 equiv) in THF (93 mL) to give imide (*S*)-**6a**.

Yield: 6.47 g (20.39 mmol, 68%); colorless solid; mp 85 °C; R_f = 0.50 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +63.4 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those reported for (*R*)-**6a**.

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 68.5; H, 7.5; N, 4.3.

(*S*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-benzyloxazolidin-2-one [(*S*)-6b]

According to the general procedure, (*S*)-**6b** was prepared from acid **20** (7.70 g, 37.34 mmol, 1.1 equiv), Et_3N (0.73 g/mL, 12.33 mL, 9.0 g, 88.95 mmol, 2.6 equiv) and PivCl (0.98 g/mL, 5.41 mL, 5.30 g, 43.95 mmol, 1.3 equiv) in THF (360 mL) as well as (*S*)-4-benzyloxazolidin-2-one (HX_{Bn}; 6.03 g, 34.03 mmol, 1 equiv) and added *n*-BuLi (2.46 M in hexanes, 15.22 mL, 37.44 mmol, 1.1 equiv) in THF (200 mL) to give imide (*S*)-**6b**.

Yield: 9.76 g (26.71 mmol, 78%); colorless solid; mp 53 °C; R_f = 0.47 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +38.9 (*c* 1.315, $CHCl_3$).

IR (film): 3030 (w), 2915 (w), 2855 (w), 1775 (s), 1685 (s), 1385 (s), 1325 (s), 1250 (s), 1200 (s), 1180 (s), 1110 (s), 1065 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.03 (d, *J* = 1.1 Hz, 3 H), 2.78 (dd, *J* = 13.4, 9.8 Hz, 1 H), 3.37 (dd, *J* = 13.4, 3.3 Hz, 1 H), 4.09 (d, *J* = 1.3 Hz, 2 H), 4.16 (dd, *J* = 9.0, 3.1 Hz, 1 H), 4.18–4.22 (m, 1 H), 4.59 (s, 2 H), 4.71–4.76 (m, 1 H), 7.28 (tq, *J* = 1.1, 1.3 Hz, 1 H), 7.28–7.40 (m, 10 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 16.9, 38.1, 55.3, 66.1, 72.6, 74.4, 115.2, 127.3, 127.8, 128.5, 129.0, 129.5, 135.6, 137.9, 153.4, 157.0, 165.1.

Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.2; H, 6.3; N, 3.7.

(*R*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-phenyloxazolidin-2-one [(*R*)-6c]

According to the general procedure, (*R*)-**6c** was prepared from acid **20** (1.39 g, 6.74 mmol, 1.1 equiv), Et_3N (0.73 g/mL, 2.22 mL, 1.62 g, 16.0 mmol, 2.6 equiv) and PivCl (0.98 g/mL, 0.98 mL, 0.96 g, 7.96 mmol, 1.3 equiv) in THF (70 mL) as well as (*R*)-4-phenyloxazolidin-2-one (HX_{Ph}; 1.0 g, 6.13 mmol, 1 equiv) and added *n*-BuLi (2.48 M in hexanes, 2.72 mL, 6.75 mmol, 1.1 equiv) in THF (mL) to give imide (*R*)-**6c**.

Yield: 1.79 g (5.09 mmol, 83%); colorless solid; mp 91 °C; R_f = 0.45 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –44.2 (*c* 0.965, $CHCl_3$).

IR (film): 3065 (m), 3030 (m), 2915 (m), 2855 (m), 1780 (s), 1680 (s), 1640 (s), 1495 (s), 1455 (s), 1385 (s), 1325 (s), 1250 (s), 1180 (s), 1110 (s), 1065 (s), 1030 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.03 (d, *J* = 1.2 Hz, 3 H), 4.05 (s, 2 H), 4.25 (dd, *J* = 8.8, 4.1 Hz, 1 H), 4.58 (d, *J* = 1.8 Hz, 2 H), 4.69 (dd, *J* = 8.8, 8.8 Hz, 1 H), 5.48–5.51 (m, 1 H), 7.29 (tq, *J* = 1.2, 1.8 Hz, 1 H), 7.28–7.40 (m, 10 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.8, 57.7, 69.9, 72.7, 74.4, 115.0, 126.0, 127.8, 128.5, 128.7, 129.2, 137.9, 139.3, 153.7, 157.3, 164.6.

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.4; H, 6.3; N, 3.9.

(*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]oxazolidin-2-one (6d)

To a solution of oxazolidin-2-one (HX_H; 2.08 g, 23.9 mmol, 2.46 equiv) in THF (50 mL) was added *n*-BuLi (2.3 M in *n*-hexane, 10.5 mL, 24.15 mmol, 2.5 equiv) at 0 °C. The colorless suspension was stirred at 0 °C for 15 min and at r.t. for 15 min. Meanwhile, to a solution of acid **20** (2.00 g, 9.70 mmol, 1 equiv) in THF (70 mL) at 0 °C was added Et_3N (0.73 g/mL, 3.25 mL, 2.36 g, 23.3 mmol, 2.4 equiv) and, slowly, PivCl (0.98 g/mL, 1.43 mL, 1.41 g, 11.6 mmol, 1.2 equiv). The mixture was stirred for 30 min at 0 °C, then the suspension was added to the above solution at 0 °C over 10 min. The reaction mixture was warmed to r.t. and, after stirring for 17 h at r.t., the reaction mixture was diluted with sat. aq NH_4Cl (150 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were extracted with sat. aq $NaHCO_3$ (250 mL), and the organic layer was separated, dried ($MgSO_4$), and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 10:1→5:1) to give imide **6d**.

Yield: 1.72 g (6.24 mmol, 64%); clear colorless oil; R_f = 0.43 (cyclohexane–EtOAc, 1:1).

IR (film): 3030 (w), 2920 (m), 2855 (m), 1775 (s), 1680 (s), 1640 (s), 1385 (s), 1360 (s), 1270 (s), 1220 (s), 1185 (s), 1110 (s), 1045 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 1.3 Hz, 3 H), 4.06 (dd, *J* = 8.8, 7.4 Hz, 2 H), 4.07 (d, *J* = 1.6 Hz, 2 H), 4.40 (dd, *J* = 8.8, 7.4 Hz, 2 H), 4.57 (s, 2 H), 7.26 (tq, *J* = 1.3, 1.6 Hz, 1 H), 7.26–7.39 (m, 5 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.8, 42.7, 61.9, 72.6, 74.5, 114.8, 127.8, 128.5, 137.9, 153.4, 156.8, 165.3.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.2; H, 6.5; N, 5.1.

Me_2AlCl-Promoted *Endo*-Diastereoselective (4+2)-Cycloadditions: General Procedure

To a solution of dienophile **6** (1 equiv) in 1,2-dichloroethane (4 mL/mmol dienophile) was slowly added Me_2AlCl (0.9 M in heptane, 1.4 equiv) at –25 °C. The reaction mixture was stirred at –25 °C for 10 min. A solution of silyl enol ether **5** (2 equiv) in 1,2-dichloroethane (4 mL/mmol dienophile) was added. The reaction mixture was warmed to r.t. and stirred for 2 h, then the reaction mixture was diluted with sat. aq $NaHCO_3$. The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford the cycloaddition product *endo*-**4**.

$MeAlCl_2$-Promoted *Exo*-Diastereoselective (4+2)-Cycloadditions: General Procedure

To a solution of dienophile **6** (1 equiv) in 1,2-dichloroethane (4 mL/mmol dienophile) was added $MeAlCl_2$ (1 M in hexane, 1.4 equiv) between –25 and –30 °C. After stirring the reaction mixture for 10 min at –25 to –30 °C, a solution of silyl enol ether **5** (2 equiv) in 1,2-dichloroethane (4 mL/mmol dienophile) was added. After stirring for 12 h at r.t., the reaction mixture was diluted with sat. aq $NaHCO_3$. The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→50:1→20:1) to deliver cycloaddition product *exo*-**4**.

Me_2AlCl-Promoted (4+2)-Cycloaddition of (*S*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-isopropyloxazolidin-2-one [(+)-6a]: Silyl Enol Ether (+)-*endo*-4a (Table 1, entry 1)

To a solution of dienophile (+)-**6a** (3.91 g, 12.32 mmol, 1 equiv) in 1,2-dichloroethane (50 mL) was added Me_2AlCl (0.9 M in heptane, 19.20 mL, 17.28 mmol, 1.4 equiv) at –25 °C. The reaction mixture was stirred for 10 min at –25 °C and a solution of silyl enol ether **5** (5.54 g, 24.67 mmol, 2 equiv) in 1,2-dichloroethane (50 mL) was added. After stirring for 2 h at r.t., the reaction mixture was diluted with sat. aq

$NaHCO_3$ (80 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→50:1→20:1) to deliver (+)-*endo*-**4a**.

Yield: 3.94 g (7.27 mmol, 59%); viscous oil that solidified upon storage in the refrigerator; mp 113 °C; R_f = 0.65 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +77.4 (*c* 1.0, $CHCl_3$).

IR (film): 2960 (s), 2930 (s), 1780 (s), 1700 (s), 1385 (s), 1360 (s), 1095 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.12 (s, 3 H, TBS-CH_3), 0.13 (s, 3 H, TBS-CH_3), 0.87 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.90 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.93 (s, 9 H, TBS-CH_3), 0.93–0.99 (m, 1 H, 1-CH_2), 1.03 (s, 3 H, 5a-CH_3), 1.37–1.48 (m, 1 H, 2-CH_2), 1.71 (dddd, *J* = 12.3, 7.1, 5.6, 2.3 Hz, 1 H, 2-CH_2), 1.80 (dddd, *J* = 16.9, 2.6, 2.6, 1.3 Hz, 1 H, 5-CH_2), 1.90 (ddd, *J* = 10.9, 6.1, 5.6 Hz, 1 H, 1-CH_2), 2.13–2.18 (m, 1 H, 3-CH_2), 2.21–2.27 (m, 1 H, 3-CH_2), 2.31 (dddd, *J* = 16.9, 2.6, 2.6, 3.1 Hz, 1 H, 5-CH_2), 2.33–2.39 (m, 1 H, X_{iPr}-CH), 2.48–2.55 (m, 1 H, 10b-CH), 3.18 (d, *J* = 8.7 Hz, 1 H, 6-CH_2), 3.36 (d, *J* = 8.7 Hz, 1 H, 6-CH_2), 4.17 (dd, *J* = 9.2, 3.3 Hz, 1 H, X_{iPr}-CH_2^{Re}), 4.20 (dd, *J* = 9.2, 7.3 Hz, 1 H, X_{iPr}-CH_2^{Si}), 4.45 (ddd, *J* = 7.3, 3.6, 3.3 Hz, 1 H, X_{iPr}-CH), 4.46 (d, *J* = 10.5 Hz, 1 H, 6-OCH_2Ph), 4.52 (d, *J* = 4.9 Hz, 1 H, 10a-CH), 4.54 (d, *J* = 10.5 Hz, 1 H, 6-OCH_2Ph), 7.24–7.37 (m, 5 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –4.0 (TBS-CH_3), –3.6 (TBS-CH_3), 14.5 (X_{iPr}-CH_3), 18.2 (TBS-C), 18.3 (X_{iPr}-CH_3), 23.5 (5a-CH_3), 24.2 (2-CH_2), 25.9 (TBS-CH_3), 26.0 (3-CH_2), 28.4 (X_{iPr}-CH), 30.3 (1-CH_2), 37.7 (5-CH_2), 39.5 (5a-C), 40.8 (10b-CH), 42.6 (10a-CH), 58.9 (X_{iPr}-CH), 62.6 (X_{iPr}-CH_2), 73.2 (6-OCH_2Ph), 76.7 (6-CH_2), 116.1 (3a-C), 127.4 (Ar-CH), 127.5 (Ar-CH), 128.3 (Ar-CH), 138.8 (Ar-C), 140.8 (4-C), 154.1 (X_{iPr}-C), 172.7 (10-C).

Anal. Calcd for $C_{31}H_{47}NO_5Si$: C, 68.72; H, 8.74; N, 2.59. Found: C, 68.8; H, 8.9; N, 2.6.

Me_2AlCl-Promoted (4+2)-Cycloaddition of (*R*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-isopropyloxazolidin-2-one [(–)-6a]: Silyl Enol Ether (–)-*endo*-4a (Table 1, entry 2)

To a solution of the dienophile (–)-**6a** (2.49 g, 7.85 mmol, 1 equiv) in 1,2-dichloroethane (30 mL) was added Me_2AlCl (0.9 M in heptane, 12.21 mL, 10.99 mmol, 1.4 equiv) at –25 °C. The reaction mixture was stirred for 10 min at –25 °C and a solution of silyl enol ether **5** (3.0 g, 13.37 mmol, 1.7 equiv) in 1,2-dichloroethane (30 mL) was added. After stirring for 2 h at r.t., the reaction mixture was diluted with sat. aq $NaHCO_3$ (50 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→50:1→20:1) to deliver (–)-*endo*-**4a**.

Yield: 2.13 g (3.93 mmol, 50%); viscous oil that solidified upon storage in the refrigerator; mp 113 °C; R_f = 0.64 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –78.4 (*c* 1.085, $CHCl_3$). The spectrocopic data were identical to those reported for (+)-*endo*-**4a**.

Anal. Calcd for $C_{31}H_{47}NO_5Si$: C, 68.72; H, 8.74; N, 2.59. Found: C, 69.1; H, 9.0; N, 2.2.

$MeAlCl_2$-Promoted (4+2)-Cycloaddition of (*S*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-isopropyloxazolidin-2-one [(+)-6a]: Silyl Enol Ether (–)-*exo*-4a (Table 2, entry 1)

To a solution of dienophile (+)-**6a** (200 mg, 0.63 mmol, 1 equiv) in 1,2-dichloroethane (2 mL) was slowly added $MeAlCl_2$ (1 M in hexane, 0.88 mL, 0.88 mmol, 1.4 equiv) at –30 °C, and the reaction mixture was stirred at –30 °C for 10 min. A solution of silyl enol ether **5** (282 mg, 1.26 mmol, 2 equiv) in 1,2-dichloroethane (2 mL) was added and the reaction mixture was warmed to r.t. After stirring for 12 h at r.t., the reaction mixture was diluted with sat. aq $NaHCO_3$ (2 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford a mixture of diastereomers (35%, dr = 83:17). Further purification delivered the pure cycloadduct (–)-*exo*-**4a**.

Yield: 98 mg (0.181 mmol, 29%); viscous oil that solidified upon storage in the refrigerator; mp 113 °C; R_f = 0.69 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –60.5 (*c* 0.7, $CHCl_3$).

IR (film): 2955 (s), 2930 (s), 2855 (s), 1775 (s), 1700 (s), 1385 (s), 1375 (s), 1360 (s), 1250 (s), 1205 (s), 1120 (s), 1095 (s), 1025 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.12 (s, 3 H, TBS-CH_3), 0.13 (s, 3 H, TBS-CH_3), 0.77 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.78 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.94 (s, 9 H, TBS-CH_3), 1.13 (ddd, *J* = 11.5, 7.8, 3.9 Hz, 1 H, 1-CH_2), 1.28 (s, 3 H, 5a-CH_3), 1.50–1.58 (m, 1 H, 2-CH_2), 1.67 (dddd, *J* = 16.7, 2.6, 2.6, 1.9 Hz, 1 H, 5-CH_2), 1.71–1.78 (m, 2 H, 1-CH_2, 2-CH_2), 2.09 (dddd, *J* = 16.7, 2.6, 2.6, 3.5 Hz, 1 H, 5-CH_2), 2.18–2.25 (m, 2 H, X_{iPr}-CH, 3-CH_2), 2.31–2.38 (m, 1 H, 3-CH_2), 2.70–2.76 (m, 1 H, 10b-CH), 3.11 (dd, *J* = 8.8, 8.8 Hz, 1 H, X_{iPr}-CH_2^{Si}), 3.24 (d, *J* = 8.7 Hz, 1 H, 6-CH_2), 3.57 (d, *J* = 8.6 Hz, 1 H, 6-CH_2), 3.76 (dd, *J* = 8.8, 3.3 Hz, 1 H, X_{iPr}-CH_2^{Re}), 3.80 (d, *J* = 10.5 Hz, 1 H, 10a-CH), 4.06 (ddd, *J* = 8.8, 3.6, 3.3 Hz, 1 H, X_{iPr}-CH), 4.38 (d, *J* = 12.0 Hz, 1 H, 6-OCH_2Ph), 4.47 (d, *J* = 12.0 Hz, 1 H, 6-OCH_2Ph), 7.24–7.34 (m, 5 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –3.8 (TBS-CH_3), –3.7 (TBS-CH_3), 14.6 (X_{iPr}-CH_3), 17.9 (X_{iPr}-CH_3), 18.2 (TBS-C), 19.6 (5a-CH_3), 23.9 (2-CH_2), 25.8 (TBS-CH_3), 26.4 (3-CH_2), 28.4 (X_{iPr}-CH), 32.0 (1-CH_2), 41.3 (5a-C), 41.8 (5-CH_2), 43.1 (10b-CH), 48.3 (10a-CH), 58.5 (X_{iPr}-CH), 62.2 (X_{iPr}-CH_2), 72.9 (6-OCH_2Ph), 79.9 (6-CH_2), 120.0 (3a-C), 126.8 (Ar-CH), 127.5 (Ar-CH), 128.3 (Ar-CH), 138.8 (Ar-C), 138.8 (4-C), 154.7 (X_{iPr}-C), 175.4 (10-C).

Anal. Calcd for $C_{31}H_{47}NO_5Si$: C, 68.72; H, 8.74; N, 2.59. Found: C, 68.4; H, 8.7; N, 2.5.

$MeAlCl_2$-Promoted (4+2)-Cycloaddition of (*S*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-benzyloxazolidin-2-one [(+)-6b]: Silyl Enol Ether (–)-*exo*-4b (Table 2, entry 2)

To a solution of the dienophile (+)-**6b** (3.29 g, 9.0 mmol, 1 equiv) in 1,2-dichloroethane (35 mL) was slowly added $MeAlCl_2$ (1 M in hexane, 12.6 mL, 12.6 mmol, 1.4 equiv) at –25 °C. The mixture was stirred at –25 °C for 10 min, then a solution of silyl enol ether **5** (4.04 g, 18.0 mmol, 2 equiv) in 1,2-dichloroethane (2 mL) was added. The reaction mixture was warmed to r.t. and stirred for 12 h and then diluted with sat. aq $NaHCO_3$ (30 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by

chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford a mixture of diastereomers (dr = 94:6). Further purification delivered the pure cycloadduct (–)-*exo*-**4b**.

Yield: 1.90 g (3.22 mmol, 36%); viscous oil; R_f = 0.76 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –8.3 (*c* 1.1, $CHCl_3$).

IR (film): 2955 (s), 2930 (s), 1780 (s), 1695 (s), 1375 (s), 1350 (s), 1250 (s), 1205 (s), 1100 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 3 H, TBS-CH_3), 0.14 (s, 3 H, TBS-CH_3), 0.94 (s, 9 H, TBS-CH_3), 1.09–1.21 (m, 1 H, 1-CH_2), 1.31 (s, 3 H, 5a-CH_3), 1.50–1.61 (m, 1 H, 2-CH_2), 1.69 (dddd, *J* = 16.8, 2.6, 2.6, 1.9 Hz, 1 H, 5-CH_2), 1.74–1.84 (m, 2 H, 2-CH_2, 1-CH_2), 2.12 (dddd, *J* = 16.8, 2.6, 2.6, 3.3 Hz, 1 H, 5-CH_2), 2.20–2.28 (m, 1 H, 3-CH_2), 2.31–2.40 (m, 1 H, 3-CH_2), 2.51 (dd, *J* = 13.2, 10.1 Hz, 1 H, X_{Bn}-CH_2Ph), 2.72–2.82 (m, 1 H, 10b-CH), 3.12 (dd, *J* = 8.8, 8.8 Hz, 1 H, X_{Bn}-CH_2^{Si}), 3.25 (dd, *J* = 13.2, 3.0 Hz, 1 H, X_{Bn}-CH_2Ph), 3.26 (d, *J* = 8.6 Hz, 1 H, 6-CH_2), 3.57 (d, *J* = 8.6 Hz, 1 H, 6-CH_2), 3.71 (dd, *J* = 8.8, 3.2 Hz, 1 H, X_{Bn}-CH_2^{Re}), 3.79 (d, *J* = 10.6 Hz, 1 H, 10a-CH), 4.26–4.32 (m, 1 H, X_{Bn}-CH), 4.36 (d, *J* = 12.0 Hz, 1 H, 6-OCH_2Ph), 4.46 (d, *J* = 12.0 Hz, 1 H, 6-OCH_2Ph), 7.11–7.31 (m, 10 H, Ar-CH).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –3.8 (TBS-CH_3), –3.7 (TBS-CH_3), 18.2 (TBS-C), 19.5 (5a-CH_3), 23.9 (2-CH_2), 25.8 (TBS-CH_3), 26.4 (3-CH_2), 32.0 (1-CH_2), 38.4 (X_{Bn}-CH_2Ph), 41.4 (5a-C), 41.7 (5-CH_2), 43.0 (10b-CH), 48.5 (10a-CH), 55.3 (X_{Bn}-CH), 65.3 (X_{Bn}-CH_2), 73.0 (6-OCH_2Ph), 79.8 (6-CH_2), 120.0 (3a-C), 126.8 (Ar-CH), 127.1 (Ar-CH), 127.5 (Ar-CH), 128.3 (Ar-CH), 128.8 (Ar-CH), 129.3 (Ar-CH), 135.8 (Ar-C), 138.6 (Ar-C), 138.8 (4-C), 154.1 (X_{Bn}-C), 175.5 (10-C).

Anal. Calcd for $C_{35}H_{47}NO_5Si$: C, 71.27; H, 8.03; N, 2.37. Found: C, 71.1; H, 8.2; N, 2.3.

Me_2AlCl-Promoted (4+2)-Cycloaddition of (*S*,*E*)-3-(4-(benzyloxy)-3-methylbut-2-enoyl)-4-benzyloxazolidin-2-one (+)-6b: Silyl Enol Ether (+)-*endo*-4b (Table 1, entry 3)

To a solution of dienophile (+)-**6b** (115 mg, 0.315 mmol, 1 equiv) in 1,2-dichloroethane (1.5 mL) was slowly added Me_2AlCl (0.9 M in heptane, 0.48 mL, 0.43 mmol, 1.4 equiv) at –25 °C. The reaction mixture was stirred at –25 °C for 10 min, then a solution of silyl enol ether **5** (141 mg, 0.63 mmol, 2 equiv) in 1,2-dichloroethane (1.5 mL) was added. The reaction mixture was warmed to r.t. and stirred for 12 h, then diluted with sat. aq $NaHCO_3$ (1.5 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford a mixture of diastereomers (dr = 83:17). Further purification delivered the pure cycloadduct (+)-*endo*-**4b**.

Yield: 70 mg (0.12 mmol, 38%); viscous oil; R_f = 0.74 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +159.7 (*c* 0.85, $CHCl_3$).

IR (film): 3065 (w), 3030 (w), 2955 (s), 2930 (s), 2855 (s), 1780 (s), 1700 (s), 1455 (s), 1385 (s), 1350 (s), 1260 (s), 1210 (s), 1175 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.16 (s, 3 H, TBS-CH_3), 0.16 (s, 3 H, TBS-CH_3), 0.95 (s, 9 H, TBS-CH_3), 0.97–1.05 (m, 1 H, 1-CH_2), 1.08 (s, 3 H, 5a-CH_3), 1.40–1.50 (m, 1 H, 2-CH_2), 1.73 (dddd, *J* = 12.3, 7.3, 6.2, 2.2 Hz, 1 H, 2-CH_2), 1.82 (dddd, *J* = 16.9, 2.7, 2.7, 1.3 Hz, 1 H, 5-CH_2), 1.94 (ddd, *J* = 11.0, 6.0, 5.5 Hz, 1 H, 1-CH_2), 2.16–2.24 (m, 1 H, 3-CH_2), 2.23–2.31 (m, 1 H, 3-CH_2), 2.40 (dddd, *J* = 16.9, 2.7, 2.7, 3.0 Hz, 1 H, 5-CH_2), 2.52–2.58 (m, 1 H, 10b-CH), 2.57 (dd, *J* = 13.1, 10.9 Hz, 1 H, X_{Bn}-CH_2Ph), 3.19 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 3.39 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 3.42 (dd, *J* = 13.1, 3.0 Hz, 1 H, X_{Bn}-CH_2Ph), 4.09 (dd, *J* = 9.4, 3.5 Hz, 1 H, X_{Bn}-CH_2^{Re}), 4.11 (dd, *J* = 9.4, 7.0 Hz, 1 H, X_{Bn}-CH_2^{Si}), 4.48 (d, *J* = 12.1 Hz, 1 H, 6-CH_2OBn), 4.51 (d, *J* = 7.0 Hz, 1 H, 10a-CH), 4.55 (d, *J* = 12.1 Hz, 1 H, 6-OCH_2Ph), 4.65–4.69 (m, 1 H, X_{Bn}-CH), 7.24–7.37 (m, 10 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –4.1 (TBS-CH_3), –3.5 (TBS-CH_3), 18.2 (TBS-C), 23.6 (5a-CH_3), 24.2 (2-CH_2), 25.9 (TBS-CH_3), 26.1 (3-CH_2), 30.3 (1-CH_2), 37.8 (5-CH_2), 38.2 (X_{Bn}-CH_2Ph), 39.5 (5a-C), 40.8 (10b-CH), 42.8 (10a-CH), 56.0 (X_{Bn}-CH), 65.6 (X_{Bn}-CH_2), 73.2 (6-OCH_2Ph), 76.7 (6-CH_2), 116.2 (3a-C), 127.3 (Ar-CH), 127.4 (Ar-CH), 127.6 (Ar-CH), 128.3 (Ar-CH), 129.0 (Ar-CH), 129.5 (Ar-CH), 135.9 (Ar-C), 138.7 (Ar-C), 140.9 (4-C), 153.4 (X_{Bn}-C), 172.6 (10-C).

Anal. Calcd for $C_{35}H_{47}NO_5Si$: C, 71.27; H, 8.03; N, 2.37. Found: C, 71.4; H, 8.2; N, 2.3.

$MeAlCl_2$-Promoted (4+2)-Cycloaddition of (*R*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-phenyloxazolidin-2-one [(–)-6c]: Silyl Enol Ether (+)-*exo*-4c (Table 2, entry 3)

To a solution of dienophile (–)-**6c** (100 mg, 0.28 mmol, 1 equiv) in 1,2-dichloroethane (1 mL) was slowly added $MeAlCl_2$ (1 M in hexane, 0.39 mL, 0.39 mmol, 1.4 equiv) at –25 °C. The reaction mixture was stirred at –25 °C for 10 min and then a solution of silyl enol ether **5** (128 mg, 0.57 mmol, 2 equiv) in 1,2-dichloroethane (1 mL) was added. The reaction mixture was warmed to r.t. and stirred for 12 h, then diluted with sat. aq $NaHCO_3$ (2 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford a mixture of diastereomers (dr = 87:13). Further purification delivered the pure cycloadduct (+)-*exo*-**4c**.

Yield: 70 mg (0.12 mmol, 43%); viscous oil; R_f = 0.72 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +15.4 (*c* 0.98, $CHCl_3$).

IR (film): 2955 (s), 2929 (s), 1780 (s), 1705 (s), 1383 (s), 1175 (s), 1099 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 3 H, TBS-CH_3), 0.11 (s, 3 H, TBS-CH_3), 0.93 (s, 9 H, TBS-CH_3), 0.93–1.02 (m, 1 H, 1-CH_2), 1.24 (s, 3 H, 5a-CH_3), 1.24–1.40 (m, 2 H, 1-CH_2, 2-CH_2), 1.60–1.67 (m, 1 H, 2-CH_2), 1.67 (dddd, *J* = 16.8, 2.7, 2.7, 1.7 Hz, 1 H, 5-CH_2), 2.10 (dddd, *J* = 16.8, 2.7, 2.7, 3.2 Hz, 1 H, 5-CH_2), 2.13–2.19 (m, 1 H, 3-CH_2), 2.23–2.34 (m, 1 H, 3-CH_2), 2.49–2.57 (m, 1 H, 10b-CH), 3.29 (d, *J* = 8.6 Hz, 1 H, 6-CH_2), 3.57 (dd, *J* = 8.9, 8.9 Hz, 1 H, X_{Ph}-CH_2^{Re}), 3.66 (d, *J* = 8.9 Hz, 1 H, 6-CH_2), 3.74 (d, *J* = 10.5 Hz, 1 H, 10a-CH), 3.79 (dd, *J* = 8.9, 4.8 Hz, 1 H, X_{Ph}-CH_2^{Si}), 4.40 (d, *J* = 11.8 Hz, 1 H, 6-OCH_2Ph), 4.52 (d, *J* = 11.8 Hz, 1 H, 6-OCH_2Ph), 4.79 (dd, *J* = 8.9, 4.8 Hz, 1 H, X_{Ph}-CH), 7.13–7.42 (m, 10 H, Ar-CH).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –3.9 (TBS-CH_3), –3.8 (TBS-CH_3), 18.2 (TBS-C), 19.7 (5a-CH_3), 23.8 (2-CH_2), 25.8 (TBS-CH_3), 26.3 (3-CH_2), 31.7 (1-CH_2), 41.4 (5a-C), 41.7 (5-CH_2), 43.0 (10b-CH), 48.6 (10a-CH), 58.0 (X_{Ph}-CH), 68.9 (X_{Ph}-CH_2), 73.0 (6-OCH_2Ph), 80.0 (6-CH_2), 120.1 (3a-C), 125.9 (Ar-CH), 127.1 (Ar-CH), 127.6 (Ar-CH), 128.3 (Ar-CH), 128.4 (Ar-CH), 129.0 (Ar-CH), 138.6 (Ar-C), 138.8 (Ar-C), 139.9 (4-C), 154.4 (X_{Ph}-C), 174.8 (10-C).

Anal. Calcd for $C_{34}H_{45}NO_5Si$: C, 70.92; H, 7.88; N, 2.43. Found: C, 71.0; H, 7.7; N, 2.4.

Me_2AlCl-Promoted (4+2)-Cycloaddition of (*R*,*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]-4-phenyloxazolidin-2-one [(–)-6c]: Silyl Enol Ether (–)-*endo*-4c (Table 1, entry 4)

To a solution of dienophile (–)-**6c** (800 mg, 2.28 mmol, 1 equiv) in 1,2-dichloroethane (12 mL) was slowly added Me_2AlCl (0.9 M in heptane, 3.54 mL, 3.19 mmol, 1.4 equiv) at –25 °C. The reaction mixture was stirred at –25 °C for 10 min and then a solution of silyl enol ether **5** (1.02 g, 4.55 mmol, 2 equiv) in 1,2-dichloroethane (12 mL) was added. The reaction mixture was warmed to r.t. and stirred for 2 h, then the reaction mixture was diluted with sat. aq $NaHCO_3$ (10 mL). The phases were separated and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was first purified by chromatography on basic Al_2O_3 (particle size 0.05–0.20 mm, cyclohexane–EtOAc, 100:0→100:1→50:1) and then by chromatography on silica gel (cyclohexane–EtOAc, 100:1→75:1→50:1) to afford a mixture of diastereomers (dr = 83:17). Further purification delivered the pure cycloadduct (–)-*endo*-**4c**.

Yield: 651 mg (1.13 mmol, 50%); viscous oil; R_f = 0.70 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –125.9 (*c* 0.75, $CHCl_3$).

IR (film): 2955 (s), 2929 (s), 2855 (s), 1780 (s), 1705 (s), 1385 (s), 1320 (s), 1260 (s), 1175 (s), 1100 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, TBS-CH_3), 0.07 (s, 3 H, TBS-CH_3), 0.39–0.48 (m, 1 H, 1-CH_2), 0.89 (s, 9 H, TBS-CH_3), 1.08 (s, 3 H, 5a-CH_3), 1.20–1.31 (m, 1 H, 2-CH_2), 1.36–1.43 (m, 1 H, 2-CH_2), 1.65 (ddd, *J* = 11.1, 6.1, 5.5 Hz, 1 H, 1-CH_2), 1.75 (dddd, *J* = 16.9, 2.7, 2.7, 1.3 Hz, 1 H, 5-CH_2), 1.93–2.04 (m, 2 H, 3-CH_2), 2.27 (dddd, *J* = 16.9, 2.7, 2.7, 3.1 Hz, 1 H, 5-CH_2), 2.41–2.47 (m, 1 H, 10b-CH), 3.16 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 3.35 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 4.28 (dd, *J* = 8.8, 2.8 Hz, 1 H, X_{Ph}-CH_2^{Si}), 4.45 (d, *J* = 12.4 Hz, 1 H, 6-OCH_2Ph), 4.53 (d, *J* = 6.8 Hz, 1 H, 10a-CH), 4.54 (d, *J* = 12.4 Hz, 1 H, 6-OCH_2Ph), 4.62 (dd, *J* = 8.8, 8.8 Hz, 1 H, X_{Ph}-CH_2^{Re}), 5.43 (dd, *J* = 2.8, 8.8 Hz, 1 H, X_{Ph}-CH), 7.24–7.37 (m, 10 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –4.2 (TBS-CH_3), –3.7 (TBS-CH_3), 18.1 (TBS-C), 23.5 (5a-CH_3), 24.0 (2-CH_2), 25.8 (3-CH_2), 25.9 (TBS-CH_3), 29.7 (1-CH_2), 37.7 (5-CH_2), 39.5 (5a-C), 41.0 (10b-CH), 42.7 (10a-CH), 57.9 (X_{Ph}-CH), 69.3 (X_{Ph}-CH_2), 73.2 (6-OCH_2Ph), 76.7 (6-CH_2), 116.2 (3a-C), 126.7 (Ar-CH), 127.4 (Ar-CH), 127.5 (Ar-CH), 128.3 (Ar-CH), 128.7 (Ar-CH), 128.9 (Ar-CH), 138.8 (Ar-C), 139.4 (Ar-C), 140.5 (4-C), 153.7 (X_{Ph}-C), 172.1 (10-C).

Anal. Calcd for $C_{34}H_{45}NO_5Si$: C, 70.92; H, 7.88; N, 2.43. Found: C, 70.8; H, 7.8; N, 2.5.

Me_2AlCl-Promoted (4+2)-Cycloaddition of (*E*)-3-[4-(Benzyloxy)-3-methylbut-2-enoyl]oxazolidin-2-one (6d): Silyl Enol Ether (±)-*endo*-4d (Table 1, entry 5)

To a solution of dienophile **6d** (110 mg, 0.40 mmol, 1 equiv) in 1,2-dichloroethane (1 mL) was slowly added a solution of Me_2AlCl (0.9 M in *n*-heptane, 0.62 mL, 0.56 mmol, 1.4 equiv). The colorless turbid reaction mixture was stirred at –25 °C for 10 min. A stock solution of the silyl enol ether **5** in 1,2-dichloroethane (0.1 M, 1.2 mL, 1.2 mmol, 3 equiv) was added. The reaction mixture was warmed to r.t., stirred for 21.5 h, then diluted with sat. aq potassium sodium tartrate (2 mL). The mixture was diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL), and subsequently stirred at r.t. for 3 h. The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were extracted with sat. aq NaCl (10 mL) and then dried ($MgSO_4$). Evaporation of all volatiles delivered a residue that was purified by chromatography on silica gel (cyclohexane–EtOAc, 100:1) to afford the silyl enol ether (±)-*endo*-**4d**.

Yield: 107 mg (0.214 mmol, 54%); colorless viscous oil; R_f = 0.24 (cyclohexane–EtOAc, 5:1).

IR (film): 3065 (m), 3030 (m), 2930 (s), 2855 (s), 1770 (s), 1700 (s), 1470 (s), 1385 (s), 1360 (s), 1335 (s), 1255 (s), 1220 (s), 1175 (s), 1100 (s), 1040 (s), 1010 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.13 (s, 3 H, TBS-CH_3), 0.13 (s, 3 H, TBS-CH_3), 0.84 (m, 1 H, 1-CH_2^{Re}), 0.93 (s, 9 H, TBS-CH_3), 1.06 (s, 3 H, 5a-CH_3), 1.42 (m, 1 H, 2-CH_2^{Re}), 1.70 (dddd, *J* = 12.7, 7.8, 5.6, 2.4 Hz, 1 H, 2-CH_2^{Si}), 1.79 (dddd, *J* = 17.0, 2.6, 2.6, 1.5 Hz, 1 H, 5-CH_2^{Re}), 1.84 (ddd, *J* = 11.4, 6.8, 5.6 Hz, 1 H, 1-CH_2^{Si}), 2.14–2.27 (m, 2 H, 3-CH_2), 2.35 (dddd, *J* = 17.0, 2.6, 2.6, 3.2 Hz, 1 H, 5-CH_2^{Si}), 2.49 (m, 1 H, 10b-CH), 3.18 (d, *J* = 8.8 Hz, 1 H, 6-CH_2^{Re}), 3.38 (d, *J* = 8.8 Hz, 1 H, 6-CH_2^{Si}), 3.98 (m, 2 H, X_H-CH_2), 4.34 (m, 2 H, X_H-CH_2), 4.47 (d, *J* = 12.3 Hz, 1 H, 6-OCH_2Ph^{Re}), 4.55 (d, *J* = 12.3 Hz, 1 H, 6-OCH_2Ph^{Si}), 4.56 (d, *J* = 7.0 Hz, 1 H, 10a-CH), 7.24–7.37 (m, 5 H, Ph-CH).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –4.0 (TBS-CH_3), –3.5 (TBS-CH_3), 18.2 (TBS-C), 23.6 (5a-CH_3), 24.1 (2-CH_2), 25.9 (TBS-CH_3), 26.1 (3-CH_2), 30.4 (1-CH_2), 37.7 (5-CH_2), 39.4 (5a-C), 40.6 (10b-CH), 42.6 (X_H-CH_2), 42.9 (10a-CH), 61.4 (X_H-CH_2), 73.2 (6-OCH_2Ph), 76.6 (6-CH_2), 115.9 (3a-C), 127.4 (Ar-CH), 127.5 (Ar-CH), 128.3 (Ar-CH), 138.7 (Ar-C), 140.9 (4-C), 153.5 (X_H-C), 173.1 (10-C).

Anal. Calcd for $C_{28}H_{41}NO_5Si$: C, 67.30; H, 8.27; N, 2.80. Found: C, 67.6; H, 8.5; N, 2.7.

Siloxycyclopropane (–)-3a by Cyclopropanation

To a solution of (–)-*endo*-**4a** (3.29 g, 6.07 mmol, 1 equiv) in CH_2Cl_2 (135 mL) was successively added Et_2Zn (1.1 M in toluene, 22.07 mL, 24.28 mmol, 4 equiv) and CH_2I_2 (3.325 g/mL, 3.91 mL, 13.0 g 48.54 mmol, 8 equiv) at 0 °C. The cooling bath was removed and the reaction mixture was stirred at r.t. for 12 h, then sat. aq $NaHCO_3$ (100 mL) was added and the phases were separated. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were extracted once with aq NaS_2O_3 and then dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 100:1→50:1) to provide siloxycyclopropane (–)-**3a**.

Yield: 2.96 g (5.33 mmol, 88%); colorless viscous oil that solidified upon storage in the refrigerator; mp 74 °C; R_f = 0.52 (cyclohexane–EtOAc, 5:1); $[\alpha]_D^{20}$ –52.8 (*c* 1.0, $CHCl_3$).

IR (film): 2955 (s), 2935 (s), 2855 (m), 1780 (s), 1700 (s), 1245 (s), 1225 (s), 1205 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, TBS-CH_3), 0.13 (s, 3 H, TBS-CH_3), 0.60 (d, *J* = 5.2 Hz, 1 H, cPr-CH_2), 0.76 (d, *J* = 5.2 Hz, 1 H, cPr-CH_2), 0.83 (d, *J* = 6.9 Hz, 3 H, X_{iPr}-CH_3), 0.86 (d, *J* = 6.9 Hz, 3 H, X_{iPr}-CH_3), 0.86 (s, 9 H, TBS-CH_3), 1.23 (s, 3 H, 5a-CH_3), 1.43–1.53 (m, 2 H, 3-CH_2, 1-CH_2), 1.60–1.67 (m, 1 H, 2-CH_2), 1.72 (d, *J* = 14.3 Hz, 1 H, 5-CH_2), 1.76–1.83 (m, 2 H, 1-CH_2, 2-CH_2), 1.96 (d, *J* = 14.3 Hz, 1 H, 5-CH_2), 2.10–2.16 (m, 1 H, 3-CH_2), 2.22–2.29 (m, 1 H, X_{iPr}-CH), 2.55 (ddd, *J* = 10.1, 7.4, 2.7 Hz, 1 H, 10b-CH), 3.05 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 3.38 (d, *J* = 8.8 Hz, 1 H, 6-CH_2), 3.73 (d, *J* = 7.4 Hz, 1 H, 10a-CH), 3.81 (dd, *J* = 8.8, 8.8 Hz, 1 H, X_{iPr}-CH_2^{Re}), 4.02 (dd, *J* = 8.8, 2.6 Hz, 1 H, X_{iPr}-CH_2^{Si}), 4.23 (ddd, *J* = 8.8, 3.1, 2.6 Hz, 1 H, X_{iPr}-CH), 4.30 (d, *J* = 12.2 Hz, 1 H, 6-OCH_2Ph), 4.47 (d, *J* = 12.2 Hz, 1 H, 6-OCH_2Ph), 7.22–7.33 (m, 5 H, Ph-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –3.5 (TBS-CH_3), –3.3 (TBS-CH_3), 14.5 (X_{iPr}-CH_3), 17.9 (TBS-C), 18.1 (X_{iPr}-CH_3), 19.3 (5a-CH_3), 25.5 (2-CH_2), 25.8 (TBS-CH_3), 26.5 (cPr-CH_2), 28.3 (X_{iPr}-CH), 29.4 (3a-C), 31.7 (1-CH_2), 31.9 (3-CH_2), 38.6 (5a-C), 40.1 (10b-CH), 42.1 (10a-CH), 47.5 (5-CH_2), 57.1 (4-C), 58.2 (X_{iPr}-CH), 62.6 (X_{iPr}-CH_2), 73.0 (6-OCH_2Ph), 77.7 (6-CH_2), 126.9 (Ar-CH), 127.3 (Ar-CH), 128.3 (Ar-CH), 138.9 (Ar-C), 153.5 (X_{iPr}-C), 174.5 (10-C).

Anal. Calcd for $C_{32}H_{49}NO_5Si$: C, 69.15; H, 8.89; N, 2.52. Found: C, 69.3; H, 9.1; N, 2.4.

Ketone (–)-2a by Brønsted Acid Mediated Cyclopropane Ring-Opening

To a solution of siloxycyclopropane (–)-**3** (2.96 g, 5.33 mmol, 1 equiv) in CH_2Cl_2 (70 mL) was added *p*-toluenesulfonic acid monohydrate (1.22 g, 6.41 mmol, 1.2 equiv). The reaction mixture was heated to reflux for 2 h and subsequently diluted with H_2O (10 mL) at r.t. The pH of the resulting mixture was adjusted to 8–9 by the addition of aq NaOH (1 M). The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated. Purification of the residue by chromatography (cyclohexane–EtOAc, 50:1→20:1→10:1) delivered ketone (–)-**2a**.

Yield: 1.87 g (4.23 mmol, 79%); colorless viscous oil; R_f = 0.57 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ –103.5 (*c* 1.05, $CHCl_3$).

IR (film): 2965 (s), 2875 (s), 1780 (s), 1735 (m), 1705 (s), 1455 (s), 1385 (s), 1375 (s), 1300 (s), 1225 (s), 1205 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.86 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 1.20 (s, 3 H, 5a-CH_3), 1.26–1.32 (m, 1 H, 3-CH_2), 1.33 (s, 3 H, 3a-CH_3), 1.48–1.60 (m, 1 H, 1-CH_2; 2 H, 2-CH_2), 1.73–1.80 (m, 1 H, 1-CH_2), 1.99 (d, *J* = 14.1 Hz, 1 H, 5-CH_2), 2.20–2.27 (m, 1 H, X_{iPr}-CH), 2.47–2.52 (m, 1 H, 3-CH_2), 2.54 (ddd, *J* = 12.7, 5.8, 3.0 Hz, 1 H, 10b-CH), 2.84 (d, *J* = 14.0 Hz, 1 H, 5-CH_2), 3.10 (d, *J* = 8.9 Hz, 1 H, 6-CH_2), 3.36 (d, *J* = 8.9 Hz, 1 H, 6-CH_2), 3.91 (dd, *J* = 9.0, 9.0 Hz, 1 H, X_{iPr}-CH_2^{Re}), 4.07 (dd, *J* = 9.0, 3.0 Hz, 1 H, X_{iPr}-CH_2^{Si}), 4.26 (ddd, *J* = 9.0, 3.5, 3.0 Hz, 1 H, X_{iPr}-CH), 4.41 (d, *J* = 12.3 Hz, 1 H, 6-OCH_2Ph), 4.49 (d, *J* = 12.3 Hz, 1 H, 6-OCH_2Ph), 4.78 (d, *J* = 5.8 Hz, 1 H, 10a-CH), 7.26–7.35 (m, 5 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.7 (X_{iPr}-CH_3), 18.0 (X_{iPr}-CH_3), 20.6 (5a-CH_3), 23.3 (2-CH_2), 25.9 (3a-CH_3), 28.4 (X_{iPr}-CH), 28.7 (1-CH_2), 36.0 (3-CH_2), 41.8 (10a-CH), 42.9 (5a-C), 48.5 (5-CH_2), 49.0 (10b-CH), 55.6 (3a-C), 58.2 (X_{iPr}-CH), 62.8 (X_{iPr}-CH_2), 73.2 (6-OCH_2Ph), 78.1 (6-CH_2), 127.4 (Ar-CH), 127.6 (Ar-CH), 128.4 (Ar-CH), 138.4 (Ar-C), 153.7 (X_{iPr}-C), 173.8 (10-C), 214.9 (4-C)

Anal. Calcd for $C_{26}H_{35}NO_5$: C, 70.72; H, 7.99; N, 3.17. Found: C, 70.6; H, 8.2; N, 3.0.

Alcohol (–)-21 by Benzyl Ether Cleavage

To a solution of the ketone (–)-**2a** (1.13 g, 2.56 mmol, 1 equiv) in EtOAc (20 mL) was added Pd/C (10% w/w, 218 mg, 22 mg Pd, 106.42 g/mol, 0.20 mmol, 0.08 equiv). The flask was evacuated and vented with argon three times. Hydrogen was then passed through the reaction mixture at r.t. for 4 h, then the reaction mixture was filtered through a plug of Celite. The Celite cake was rinsed with EtOAc and the solvent was evaporated. The residue was purified by chromatography (cyclohexane–EtOAc, 10:1→5:1) to give alcohol (–)-**21**.

Yield: 747 mg (2.12 mmol, 83%); colorless solid; mp 134 °C; R_f = 0.63 (cyclohexane–EtOAc, 0:1); $[\alpha]_D^{20}$ –147.8 (*c* 1.0, $CHCl_3$).

IR (film): 3435 (m), 2965 (s), 2930 (m), 2875 (m), 1770 (s), 1705 (s), 1385 (s), 1375 (s), 1205 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 0.91 (d, *J* = 7.0 Hz, 3 H, X_{iPr}-CH_3), 1.15 (s, 3 H, 5a-CH_3), 1.28–1.32 (m, 1 H, 3-CH_2), 1.33 (s, 3 H, 3a-CH_3), 1.48–1.64 (m, 2 H, 2-CH_2; 1 H, 1-CH_2), 1.72–1.80 (m, 1 H, 1-CH_2), 1.95 (d, *J* = 14.0 Hz, 1 H, 5-CH_2), 1.99 (br, 1 H, OH), 2.26–2.32 (m, 1 H, X_{iPr}-CH), 2.50 (ddd, *J* = 12.6, 6.4, 6.0 Hz, 1 H, 3-CH_2), 2.58 (ddd, *J* = 12.6, 6.0, 3.2 Hz, 1 H, 10b-CH), 2.78 (d, *J* = 14.0 Hz, 1 H, 5-CH_2), 3.25 (d, *J* = 11.0 Hz, 1 H, 6-CH_2), 3.50 (d, *J* = 11.0 Hz, 1 H, 6-CH_2), 4.20 (dd, *J* = 9.0, 3.2 Hz, 1 H, X_{iPr}-CH_2^{Si}), 4.29 (dd, *J* = 9.0, 9.0 Hz, 1 H, X_{iPr}-CH_2^{Re}), 4.52 (ddd, *J* = 9.0, 3.5, 3.2 Hz, 1 H, X_{iPr}-CH), 4.71 (d, *J* = 6.0 Hz, 1 H, 10a-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.6 (X_{iPr}-CH_3), 18.1 (X_{iPr}-CH_3), 19.9 (5a-CH_3), 23.3 (2-CH_2), 25.9 (3a-CH_3), 28.3 (X_{iPr}-CH), 28.8 (1-CH_2), 36.0 (3-CH_2), 41.5 (10a-CH), 43.6 (5a-C), 47.7 (5-CH_2), 49.1 (10b-CH), 55.5 (3a-C), 58.4 (X_{iPr}-CH), 63.0 (X_{iPr}-CH_2), 70.7 (6-CH_2), 154.1 (X_{iPr}-C), 174.1 (10-C), 215.0 (4-C).

Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.93; H, 8.32; N, 3.99. Found: C, 64.7; H, 8.2; N, 3.9.

γ-Lactone (–)-22 by LAH-Mediated Lactonization

To a solution of alcohol (–)-**21** (375 mg, 1.07 mmol, 1 equiv) in toluene (17 mL) was added $LiAlH_4$ (12 mg, 0.32 mmol, 0.3 equiv) at –78 °C. After 10 min, the reaction mixture was warmed to r.t., stirred for 4 h and then diluted with sat. aq NH_4Cl (10 mL). The layers were separated and the aqueous phase was extracted three times with EtOAc. The combined organic phases were dried and concentrated. Purification of the residue by chromatography (cyclohexane–EtOAc, 10:1→5:1→3.5:1) delivered lactone (–)-**22**.

Yield: 216 mg (0.97 mmol, 91%); colorless solid; mp 80 °C; R_f = 0.5 (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ –58.3 (*c* 1.0, $CHCl_3$).

IR (film): 2965 (s), 1780 (s), 1705 (s), 1115 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 3 H, 5a-CH_3), 1.26 (s, 3 H, 3a-CH_3), 1.39–1.47 (m, 1 H, 3-CH_2), 1.48–1.61 (m, 1 H, -CH_2; 2 H, 2-CH_2), 2.06–2.12 (m, 1 H, 1-CH_2), 2.36–2.41 (m, 1 H, 3-CH_2), 2.40 (d, *J* = 13.8 Hz, 1 H, 5-CH_2), 2.46–2.51 (m, 1 H, 10b-CH), 2.68 (d, *J* = 13.8 Hz, 1 H, 5-CH_2), 3.03 (d, *J* = 6.0 Hz, 1 H, 10a-CH), 4.01 (d, *J* = 8.5 Hz, 1 H, 6-CH_2), 4.05 (d, *J* = 8.5 Hz, 1 H, 6-CH_2).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.7 (5a-CH_3), 24.5 (2-CH_2), 26.7 (3a-CH_3), 28.3 (1-CH_2), 36.9 (3-CH_2), 44.0 (10b-CH), 44.0 (5a-C), 47.2 (10a-CH), 48.8 (5-CH_2), 55.3 (3a-C), 78.5 (6-CH_2), 174.7 (10-C), 212.5 (4-C).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.9; H, 7.8.

Hydroxylactones (4*R*)-23 and (4*S*)-23 by $NaBH_4$ Reduction

To a solution of lactone (–)-**22** (85 mg, 0.38 mmol, 1 equiv) in MeOH (8 mL) was added $NaBH_4$ (43 mg, 1.14 mmol, 3 equiv) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was diluted with sat. aq NH_4Cl (6 mL), the layers were separated and the aqueous phase was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 2:1→1:1→0:1) to deliver a mixture of the diastereomeric alcohols (73%, dr = 4:1). The diastereomers were separated by chromatography to provide the major diastereomer (4*R*)-**23** and the minor diastereomer (4*S*)-**23** as colorless solids.

Major Diastereomer (4*R*)-23

Yield: 49 mg (0.22 mmol, 58%); colorless solid; mp 196 °C; R_f = 0.4 (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ –45.7 (c 1.0, $CHCl_3$).

IR (film): 3515 (s), 2960 (m), 2930 (m), 1760 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H, 3a-CH_3), 1.44 (s, 3 H, 5a-CH_3), 1.51 (ddd, *J* = 13.3, 10.4, 6.4 Hz, 1 H, 3-CH_2), 1.64 (br. s, 1 H, OH), 1.65–1.73 (m, 1 H, 2-CH_2), 1.78–1.84 (m, 1 H, 2-CH_2), 1.86 (d, *J* = 4.0 Hz, 2 H, 5-CH_2), 1.84–1.90 (m, 1 H, 1-CH_2), 1.98–2.02 (m, 1 H, 1-CH_2), 2.00–2.04 (m, 1 H, 3-CH_2), 2.13–2.18 (m, 1 H, 10b-CH), 2.52 (d, *J* = 4.9 Hz, 1 H, 10a-CH), 3.78 (t, *J* = 4.0 Hz, 1 H, 4-CH), 3.82 (d, *J* = 7.8 Hz, 1 H, 6-CH_2), 3.98 (d, *J* = 7.8 Hz, 1 H, 6-CH_2).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.7 (5a-CH_3), 24.2 (2-CH_2), 27.2 (1-CH_2), 27.6 (3a-CH_3), 36.4 (3-CH_2), 38.2 (5-CH_2), 40.3 (5a-C), 42.9 (10b-CH), 47.1 (3a-C), 47.4 (10a-CH), 74.9 (4-CH), 82.1 (6-CH_2), 176.3 (10-C)

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.2; H, 8.9.

Minor Diastereomer (4*S*)-23

Yield: 13 mg (0.06 mmol, 15%); colorless solid; mp 176 °C; R_f = 0.22 (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ –121.5 (*c* 0.75, $CHCl_3$).

IR (film): 3515 (s), 2960 (m), 2930 (m), 1760 (s) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, 3a-CH_3), 1.23 (s, 3 H, 5a-CH_3), 1.41 (ddd, *J* = 13.1, 9.3, 5.4 Hz, 1 H, 3-CH_2), 1.53 (dd, *J* =12.0, 12.0 Hz, 1 H, 5-CH_2), 1.55–1.61 (m, 1 H, 1-CH_2), 1.69–1.76 (m, 2 H, 2-CH_2), 1.83 (dd, *J* = 12.0, 4.4 Hz, 1 H, 5-CH_2), 1.92–2.04 (m, 2 H, 3-CH_2, 1-CH_2), 2.21 (ddd, *J* = 10.1, 5.0, 5.1 Hz, 1 H, 10b-CH), 2.51 (d, *J* = 5.0 Hz, 1 H, 10a-CH), 3.82 (dd, *J* = 12.0, 4.4 Hz, 1 H, 4-CH), 3.89 (d, *J* = 8.2 Hz, 1 H, 6-CH_2), 3.98 (d, *J* = 8.2 Hz, 1 H, 6-CH_2); no OH-signal detected.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.0 (3a-CH_3), 20.7 (5a-CH_3), 23.1 (2-CH_2), 26.0 (1-CH_2), 38.0 (3-CH_2), 39.4 (5-CH_2), 42.9 (5a-C), 43.8 (10b-CH), 47.4 (3a-C), 47.6 (10a-CH), 69.9 (4-CH), 80.6 (6-CH_2), 175.8 (10-C).

Ketone (+)-2a

Cyclopropanation: To a solution of (+)-*endo*-**4a** (1.70 g, 3.14 mmol, 1 equiv) in CH_2Cl_2 (70 mL) were successively added Et_2Zn (1.1 M in toluene, 17.13 mL, 18.84 mmol, 6 equiv) and CH_2I_2 (3.325 g/mL, 3.04 mL, 10.11 g, 37.75 mmol, 12 equiv) at 0 °C. The cooling bath was removed and the reaction mixture was stirred at r.t. for 12 h. Sat. aq $NaHCO_3$ (60 mL) was added, the phases were separated, and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were extracted with aq $Na_2S_2O_3$ and then dried ($MgSO_4$). The solvents were removed and the residue was purified by chromatography (cyclohexane–EtOAc, 100:1→50:1) to afford the corresponding siloxycyclopropane (1.16 g, 2.09 mmol, 67%).

Siloxycyclopropane Ring-Opening: To a solution of the siloxycyclopropane (1.16 g, 2.09 mmol, 1 equiv) in CH_2Cl_2 (27 mL) was added *p*-toluenesulfonic acid monohydrate (477 mg, 2.51 mmol, 1.2 equiv). After stirring and heating to reflux for 2 h, the reaction mixture was diluted with H_2O (5 mL). The pH of the biphasic mixture was adjusted to 8–9 by the addition of aq NaOH (1 M). The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and the solvents were evaporated. The residue was purified by chromatography (cyclohexane–EtOAc, 50:1→20:1→10:1) to give ketone (+)-**2a**.

Yield: 731 mg (1.66 mmol, 79%); colorless viscous oil; R_f = 0.57 (cyclohexane–EtOAc, 2:1); $[\alpha]_D^{20}$ +105.5 (*c*, 1.0 $CHCl_3$).

The NMR and IR data matched those reported for (–)-**2a**.

Alcohol (+)-21 by Benzyl Ether Cleavage

To a solution of the ketone (+)-**2** (2.92 g, 6.61 mmol, 1 equiv) in EtOAc (52 mL) was added Pd/C (10% w/w, 562.7 mg, 56.3 mg Pd, 106.42 g/mol, 0.53 mmol, 0.08 equiv) at r.t.. The reaction mixture was degassed three times by evacuation and venting with argon. Hydrogen was then bubbled through the reaction mixture over 4 h, then the reaction mixture was filtered through a plug of Celite. The filter cake was rinsed with EtOAc. The solvent was removed and the residue was purified by chromatography (cyclohexane–EtOAc, 10:1 to 5:1) to deliver the alcohol (+)-**21**.

Yield: 1.98 g (5.63 mmol, 85%); colorless solid; mp 137 °C; R_f = 0.63 (cyclohexane–EtOAc, 0:1); $[\alpha]_D^{20}$ +131.2 (*c* 1.55, $CHCl_3$).

Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.93; H, 8.32; N, 3.99. Found: C, 65.3; H, 8.5; N, 4.0.

The NMR and IR data matched those reported for (–)-**21**.

Weinreb Amide (+)-24

To a solution of alcohol (+)-**21** (600 mg, 1.71 mmol, 1 equiv) in THF (22 mL) was successively added *N*,*O*-dimethylhydroxylamine hydrochloride (549 mg, 5.63 mmol, 3.3 equiv) and *i*-BuMgCl (2 M in Et_2O, 5.64 mL, 11.3 mmol, 6.6 equiv) at 0 °C. The cooling bath was removed and the reaction mixture was stirred at r.t. for 12 h. Sat. aq NH_4Cl (16 mL) was added, the phases were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by chromatography (cyclohexane–EtOAc, 5:1→2:1→1:1) provided amide (+)-**24**.

Yield: 418 mg (1.48 mmol, 86%); colorless solid; mp 98 °C; R_f = 0.38 (cyclohexane–EtOAc, 0:1); $[\alpha]_D^{20}$ +80.2 (*c* 1.05, $CHCl_3$).

IR (film): 3445 (s), 2960 (s), 2875 (s), 1700 (s), 1650 (s), 1455 (s), 1425 (s), 1375 (s) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (s, 3 H, 5a-CH_3), 1.26 (s, 3 H, 3a-CH_3), 1.34 (ddd, *J* = 12.7, 7.7, 6.4 Hz, 1 H, 3-CH_2), 1.46–1.62 (m, 2 H, 2-CH_2), 1.78 (dt, *J* = 8.5, 7.6 Hz, 2 H, 1-CH_2), 2.09 (dd, *J* = 5.8, 4.5 Hz, 1 H, OH), 2.17 (d, *J* = 14.8 Hz, 1 H, 5-CH_2), 2.36–2.44 (m, 2 H, 10b-CH, 3-CH_2), 2.65 (d, *J* = 14.8 Hz, 1 H, 5-CH_2), 3.19 (s, 3 H, *N*-CH_3), 3.26 (dd, *J* = 10.9, 5.8 Hz, 1 H, 6-CH_2), 3.47 (dd, *J* = 10.9, 4.5 Hz, 1 H, 6-CH_2), 3.67 (d, *J* = 5.7 Hz, 1 H, 10a-CH), 3.77 (s, 3 H, N-OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.6 (5a-CH_3), 23.3 (2-CH_2), 26.5 (3a-CH_3), 29.5 (1-CH_2), 32.2 (N-CH_3), 36.3 (3-CH_2), 39.1 (10a-CH), 43.1 (5a-C), 46.9 (5-CH_2), 48.9 (10b-CH), 54.6 (3a-C), 61.8 (N-OCH_3), 70.5 (6-CH_2), 175.0 (10-C), 215.6 (4-C).

Anal. Calcd for $C_{15}H_{25}NO_4$: C, 63.58; H, 8.89; N, 4.94. Found: C, 63.7; H, 9.0; N, 4.9.

Aldehyde (+)-25 By Dess–Martin Oxidation

To a solution of amide (+)-**24** (150 mg, 0.53 mmol, 1 equiv) in CH_2Cl_2 (12 mL) at 0 °C was added K_2CO_3 (219 mg, 1.59 mmol, 3 equiv) and Dess–Martin periodinane (337 mg, 0.80 mmol, 1.5 equiv). After stirring at r.t. for 4 h, sat. aq $Na_2S_2O_3$ (10 mL) was added. The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 5:1→2:1→1:1) to deliver aldehyde (+)-**25**.

Yield: 140 mg (0.50 mmol, 94%); colorless solid; mp 80 °C; R_f = 0.52 (cyclohexane–EtOAc, 0:1); $[\alpha]_D^{20}$ +45.4 (*c* 1.1, $CHCl_3$).

IR (film): 2960 (s), 1725 (s), 1700 (s), 1650 (s), 1460 (s) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H, 3a-CH_3), 1.19 (s, 3 H, 5a-CH_3), 1.37–1.51 (m, 2 H, 1-CH_2, 2-CH_2), 1.52–1.62 (m, 2 H, 3-CH_2, 2-CH_2), 1.89–1.95 (m, 1 H, 1-CH_2), 2.07–2.13 (m, 1 H, 3-CH_2), 2.16 (ddd, *J* = 9.8, 8.3, 6.2 Hz, 1 H, 10b-CH), 2.33 (d, *J* = 17.3 Hz, 1 H, 5-CH_2), 2.95 (d, *J* = 17.3 Hz, 1 H, 5-CH_2), 3.20 (s, 3 H, N-CH_3), 3.68 (d, *J* = 6.2 Hz, 1 H, 10a-CH), 3.76 (s, 3 H, N-OCH_3), 9.48 (s, 1 H, 6-H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.0 (5a-CH_3), 23.4 (2-CH_2), 27.5 (3a-CH_3), 31.2 (1-CH_2), 32.7 (N-CH_3), 37.0 (3-CH_2), 40.6 (10a-CH), 41.2 (5-CH_2), 47.0 (10b-CH), 50.9 (5a-C), 52.5 (3a-C), 61.6 (N-OCH_3), 161.7 (10-C), 202.7 (6-C), 212.9 (4-C).

Anal. Calcd for $C_{15}H_{23}NO_4$: C, 64.03; H, 8.24; N, 4.98. Found: C, 64.2; H, 8.2; N, 4.8.

Lactone 26 by Grignard Reaction

To a solution of aldehyde (+)-**25** (52 mg, 0.185 mmol, 1 equiv) in THF (2 mL) at –78 °C was slowly added a solution of Grignard reagent prepared from Mg (81 mg, 3.33 mmol, 18 equiv) and 4-bromo-2-methylbut-1-ene (500 mg, 3.35 mmol, 18 equiv) in Et_2O (2 mL). When the addition was complete, the cooling bath was removed and the reaction mixture was stirred at r.t. for 30 min. The reaction mixture was diluted with sat. aq NH_4Cl (1 mL), the phases were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 10:1→5:1→2:1→1:1) to provide lactone **26**.

Yield: 45 mg (0.155 mmol, 84%); colorless solid; mixture of C-6 diastereomers (1:1); mp 71 °C; R_f = 0.57 (cyclohexane–EtOAc, 1:1).

IR (film): 2965 (s), 1780 (s), 1705 (s), 1450 (s), 1370 (s) cm^{-1}.

NMR data are listed for the mixture of diastereomers using the label '*' to assign distinguishable signals.

^1H NMR (500 MHz, $CHCl_3$): δ = 0.92 (s, 3 H, 5a*-CH_3), 1.11 (s, 3 H, 5a-CH_3), 1.25 (s, 3 H, 3a-CH_3; 3 H, 3a*-CH_3), 1.38–1.45 (m, 1 H, 3-CH_2; 1 H, 3*-CH_2), 1.47–1.56 (m, 1 H, 1-CH_2; 1 H, 1*-CH_2), 1.54–1.67 (m, 2 H, 2-CH_2; 2 H, 2*-CH_2; 1 H, 7-CH_2; 1 H, 7*-CH_2), 1.72 (s, 3 H, 9*-CH_3), 1.73 (s, 3 H, 9-CH_3), 1.75–1.86 (m, 1 H, 7-CH_2; 1 H, 7*-CH_2), 2.07–2.14 (m, 1 H, 1-CH_2; 1 H, 1*-CH_2; 1 H, 8-CH_2; 1 H, 8*-CH_2), 2.21–2.29 (m, 1 H, 8-CH_2; 1 H, 8*-CH_2), 2.26 (d, *J* = 13.5 Hz, 1 H, 5-CH_2), 2.34 (d, *J* = 13.7 Hz, 1 H, 5*-CH_2), 2.36–2.41 (m, 1 H, 3-CH_2; 1 H, 3*-CH_2), 2.45–2.51 (m, 1 H, 10b*-CH; 1 H, 10b-CH), 2.61 (d, *J* = 13.7 Hz, 1 H, 5*-CH_2), 2.69 (d, *J* = 13.5 Hz, 1 H, 5-CH_2), 3.06 (d, *J* = 5.9 Hz, 1 H, 10a*-CH), 3.18 (d, *J* = 6.0 Hz, 1 H, 10a-CH), 4.06 (dd, *J* = 3.6, 10.8 Hz, 1 H, 6-CH), 4.11 (dd, *J* = 3.7, 9.3 Hz, 1 H, 6*-CH), 4.71 (s, 2 H, 9*-CH_2), 4.78 (s, 2 H, 9-CH_2).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.8 (5a*-CH_3), 22.4 (9*-CH_3), 22.6 (9-CH_3), 23.6 (5a-CH_3), 24.4 (2-CH_2), 24.5 (2*-CH_2), 26.7 (7*-CH_2), 26.7 (3a*-CH_3), 26.9 (3a-CH_3), 27.3 (7-CH_2), 28.6 (1*-CH_2), 28.7 (1-CH_2), 33.7 (8-CH_2), 33.9 (8*-CH_2), 36.9 (3-CH_2), 36.9 (3*-CH_2), 43.9 (10a-CH), 44.0 (10b-CH), 44.0 (10b*-CH), 45.0 (5a-C), 46.5 (5a*-C), 47.1 (5-CH_2), 48.6 (5*-CH_2), 49.3 (10a*-CH), 55.1 (3a*-C), 55.3 (3a-C), 87.3 (6*-CH), 87.7 (6-CH), 111.1 (9-CH_2), 111.2 (9*-CH_2), 144.0 (9*-C), 144.1 (9-C), 174.5 (10-C), 174.6 (10*-C), 212.6 (4*-C), 213.1 (4-C).

Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.4; H, 9.2.

Hydroxyketone 21bc

Cyclopropanation: To a solution of cycloadduct (–)-*exo*-**4b** (2.20 g, 3.73 mmol, 1 equiv) in CH_2Cl_2 (88 mL) at 0 °C were successively added CH_2I_2 (3.325 g/mL, 3.61 mL, 12.0 g, 44.80 mmol, 12 equiv) and Et_2Zn (1.1 M in toluene, 20.34 mL, 22.37 mmol, 6 equiv). After stirring at 0 °C for 1 h and at r.t. for 12 h, the reaction mixture was diluted with sat. aq $NaHCO_3$ (60 mL). The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 100:1→50:1) to deliver the corresponding siloxycyclopropane as an inseparable mixture of four diastereomers (1.60 g, 2.65 mmol, 71%).

Siloxycyclopropane Ring-Opening: To a solution of the siloxycyclopropane (1.60 g, 2.65 mmol, 1 equiv) in CH_2Cl_2 (35 mL) was added *p*-toluenesulfonic acid monohydrate (557 mg, 2.93 mmol, 1.1 equiv). After stirring and heating to reflux for 2 h, the reaction mixture was cooled to r.t. and subsequently diluted with H_2O (5 mL). The pH of the biphasic mixture was adjusted to 8–9 by the addition of aq NaOH (1 M). The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (cyclohexane–EtOAc, 50:1→20:1) to afford the corresponding ketone as an inseparable mixture of four diastereomers (934 mg, 1.91 mmol, 72%).

*Alcohol **21bc** by Benzyl Ether Cleavage*: To a solution of the ketone (934 mg, 1.91 mmol, 1 equiv) in EtOAc (30 mL) at ambient temperature was added Pd/C (10% w/w, 162 mg, 16.2 mg Pd, 106.42 g/mol, 0.152 mmol, 0.08 equiv). The flask was evacuated and vented with argon three times. Hydrogen from a balloon was bubbled through the reaction mixture over 4 h, then the reaction mixture was filtered through Celite and the filter cake was rinsed with EtOAc. The solvent was removed and the residue was purified by chromatography (cyclohexane–EtOAc, 10:1→5:1→3.5:1) to deliver alcohol **21ba–bd** ($C_{23}H_{29}NO_5$, 399.49 g/mol) as two mixtures (**21ba**,**bb**: colorless viscous oil, 500 mg, 1.25 mmol, 66%, dr = 77:23; **21bc**,**bd**: colorless viscous oil, 171 mg, 0.43 mmol, 22%, dr = 91:9) of two diastereomers each. A diastereomerically pure sample of **21bc** [R_f = 0.48 (cyclohexane–EtOAc, 1:1)] was obtained and its analytical data are listed below.

IR (film): 3500 (m, OH), 2965 (s), 1775 (s), 1700 (s), 1385 (s), 1350 (s), 1210 (s), 1100 (s), 1050 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 (s, 3 H, 5a-CH_3), 1.15 (s, 3 H, 3a-CH_3), 1.32–1.43 (m, 1 H, 1-CH_2), 1.52 (ddd, *J* = 12.9, 8.9, 3.5 Hz, 1 H, 3-CH_2), 1.79–1.87 (m, 1 H, 1-CH_2), 1.89–1.97 (m, 1 H, 2-CH_2), 1.97 (d, *J* = 14.7 Hz, 1 H, 5-CH_2), 2.00–2.08 (m, 1 H, 2-CH_2; 1 H, 3-CH_2), 2.60 (dd, *J* = 11.9, 6.7 Hz, 1 H, 10b-CH), 2.67 (dd, *J* = 10.6, 13.3 Hz, 1 H, X_{Bn}-CH_2Ph), 2.72 (br. s, 1 H, 6-OH), 2.96 (d, *J* = 14.7 Hz, 1 H, 5-CH_2), 3.35 (d, *J* = 12.0 Hz, 1 H, 6-CH_2), 3.40 (d, *J* = 12.0 Hz, 1 H, 6-CH_2), 3.43 (dd, *J* = 3.4, 13.3 Hz, 1 H, X_{Bn}-CH_2Ph), 4.21 (dd, *J* = 9.4, 6.8 Hz, 1 H, X_{Bn}-CH_2^{Si}), 4.22 (dd, *J* = 9.4, 3.2 Hz, 1 H, X_{Bn}-CH_2^{Re}), 4.27 (d, *J* = 11.9 Hz, 1 H, 10a-CH), 4.73–4.78 (m, 1 H, X_{Bn}-CH), 7.23–7.37 (m, 5 H, Ar-CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.6 (5a-CH_3), 21.8 (2-CH_2), 21.9 (3a-CH_3), 30.2 (1-CH_2), 36.6 (3-CH_2), 38.0 (X_{Bn}-CH_2Ph), 44.5 (5a-C), 46.1 (10a-CH), 46.4 (5-CH_2), 50.4 (10b-CH), 54.9 (3a-C), 56.4 (X_{Bn}-CH), 66.4 (X_{Bn}-CH_2), 70.6 (6-CH_2), 127.5 (Ar-CH), 129.1 (Ar-CH), 129.4 (Ar-CH), 135.4 (Ar-C), 154.7 (X_{Bn}-C), 174.1 (10-C), 213.9 (4-C).

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Supporting Information

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