Nonracemic, Chiral Homoenolate Reagents Derived from (Cycloalk-1-enyl)methyl Carbamates and Evaluation of Their Configurational Stabilities

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Dedicated to Professor Joachim Thiem on the occasion of his 60th birthday

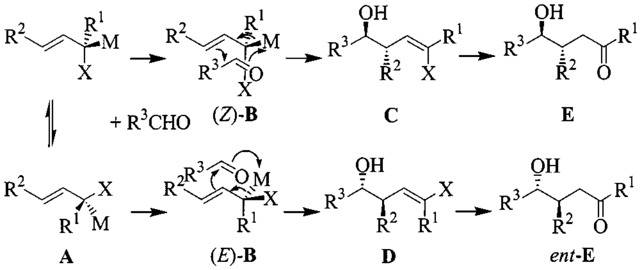
Keywords: Asymmetric synthesis / Carbanions / Chirality / Lithiation

Several (cycloalk-1-enyl)methyl *N*,*N*-diisopropylcarbamates **11** were synthesised by three different methods and their asymmetric deprotonation by butyllithium/(–)-sparteine was investigated. The ratios of epimeric ion pairs **18·4**/*epi*-**18·4** were determined by (stereospecific) trimethylsilylation, forming the products **19**/*ent*-**19**. Lithiated 2-unsubstituted (cyclopent-1-enyl)methyl carbamates, such as **11a** or **11h**, epimerise rapidly at –78 °C and the thermodynamically controlled ratio is opposite to the kinetically achieved ratio. High configurational stability was found for the 2-methylcycloalk-1-enyl derivatives **11d**, **11e** and **11j**. These turned out to be valuable reagents for enantioselective homoaldol reaction; *er* values of up to 96:4 could be achieved. X-ray crystal structure analyses with anomalous diffraction, obtained from the heavy atom containing products **22**, **23b**, **27d**, and **27e** derived from (2-methylcyclopentenyl)methyl and (2-methylcyclohexenyl)methyl reagents, established the (1*S*) configuration of the major lithium compound. Thus, the kinetically controlled deprotonation of the corresponding allyl carbamates removes the (*pro-S*) proton. Overall, a simple method for the enantioselective synthesis of cyclic homoaldol adducts from achiral precursors is reported.

Introduction

Among the nonracemic, chiral homoenolate reagents,[1] 1-hetero-substituted 2-alkenylmetal derivatives of type **A** are the most powerful intermediates for performing stereocontrolled homoaldol reactions.[2] Compounds of type **A** reliably add aldehydes, through cyclic Zimmerman−Traxler transition states[3] **B**, to form the homoaldol adducts **C** or **D** with essentially complete γ-regio- and *anti*-diastereoselectivity. Covalently bound "cations" M give rise to complete transfer of chirality from position 1 in **A** to position 3 in the addition products **C** and **D**. Depending on whether the heterosubstituent X takes a pseudoaxial or a pseudoequatorial position [(*Z*)-**B** or (*E*)-**B**],[4] an opposite sense of chirality is induced in the products **C** and **D**, with enantiomeric γ-hydroxy carbonyl compounds **E** and *ent*-**E**, respectively, being formed after hydrolysis (Scheme 1).

(1-Alkoxyallyl)boronates,[5] [(1-methoxymethoxy)but-2-enyl]tributylstannane[6] and metallated cinnamylamides[7,8] have been applied in this respect. We have introduced α-metallated 2-alkenyl *N*,*N*-diisopropylcarbamates as versatile homoenolate reagents.[9,2] Because of the strongly activating properties of *N*,*N*-diisopropylcarbamoyloxy groups, these are easily prepared by facile deprotonation, and the cation is fixed in the α-position by chelation.[10] Exchange of lithium by tetra(isopropoxy)titanium enhances the regioselectivity and diastereoselectivity of the aldehyde addition dramatically.[11,12]



M = $B(OR')_2$, $Ti(OR')_3$, SnR'_3, Li
X = OR', Cl, OC(O)N*i*Pr_2, NR'R"

Scheme 1

Enantioenriched (α-lithio-2-alkenyl)carbamates, derived from secondary esters such as **1**, are configurationally stable at −78 °C and can be obtained by deprotonation of the optically active precursors[13] or through kinetic resolution of the racemic carbamates during deprotonation by *sec*-bu-

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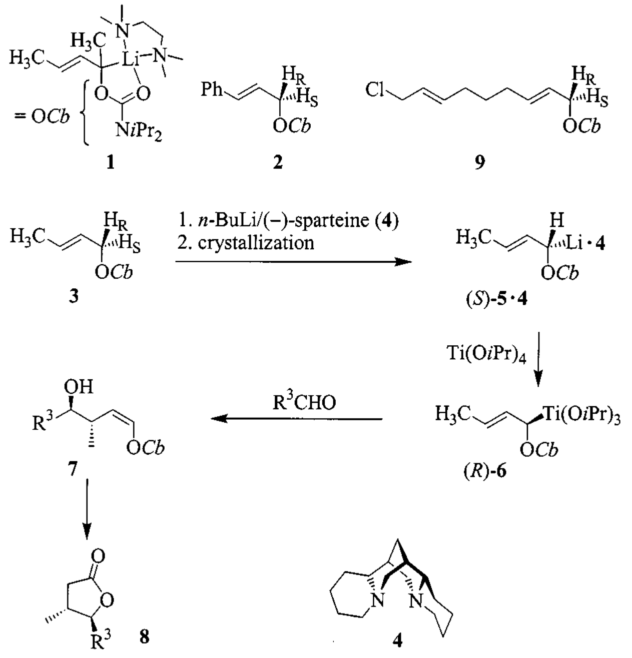
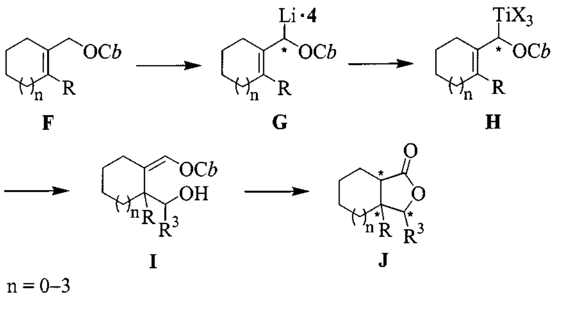
tyllithium/(−)-sparteine (**4**).[14] The lithium ion pairs produced from primary 2-alkenyl carbamates such as **3**[15] or **2**[16] with butyllithium/(−)-sparteine (**4**) turned out to be configurationally unstable in solution even at −78 °C. However, the sparteine complex (*S*)-**5·4** crystallised from the pentane/cyclohexane solution[15] with concomitant dynamic kinetic resolution,[17] resulting in up to 92% *de* in the solid. The metal exchange proceeded with inversion of the configuration and gave rise to the allyltitanium intermediate (*R*)-**6**, which was stable in solution (Scheme 2). The homoaldol adducts of aldehydes and ketones were obtained with > 90% *ee* values. These are easily transformed into optically active γ-lactones **8**,[18] and have frequently been utilised in natural product synthesis.[19]



Scheme 2

From investigations of the carbamates **2**[16] and **9**[20] it is known that removal of the (*pro-S*) protons by butyllithium/**4** is kinetically favoured, as found for the *O*-alkyl derivatives;[7a,21] however, a rapid epimerisation took place even at low temperatures.

Because of the importance of bicyclic γ-lactones **J** in natural product chemistry, we undertook a study of whether the corresponding homoenolate reagents of type **G** might be accessible in enantioenriched forms through (−)-sparteine-induced deprotonation of the achiral allyl carbamates **F** (Scheme 3).

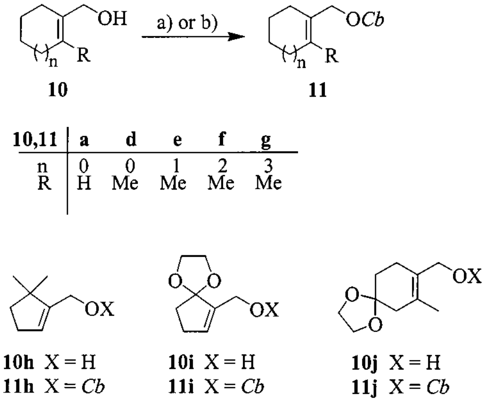


Scheme 3

Results and Discussion

Synthesis of the Allyl Carbamates

Carbamates **11a**, **d−g**, **i** and **j** were prepared from the corresponding allylic alcohols **10** by carbamoylation with *N*,*N*-diisopropylcarbamoyl chloride by use of the pyridine[22] or the sodium hydride methods[23] (Method A or B). The known allylic alcohols **10a**,[24] **10d**,[25] **10e**,[26] **10i**[27] and **10j**[28] were prepared by literature methods (see Scheme 4 and Table 1).



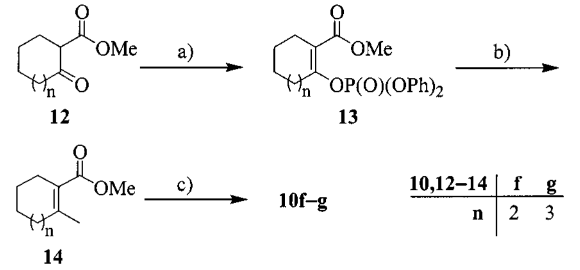
Scheme 4. a) Method A: 1.25 equiv. *N*,*N*-diisopropylcarbamoyl chloride, 10 mol % DMAP, pyridine, 12 h reflux; b) Method B: 1.2 equiv. NaH, 1.4 equiv. *N*,*N*-diisopropylcarbamoyl chloride, THF, 16 h reflux

Table 1. Prepared 1-cycloalk-1-enyl *N*,*N*-diisopropylcarbamates **11**

Entry	Substrate	Method	Product	*n*	R	Yield (%)
1	**10a**	B	**11a**	0	H	75
2	**10d**	B	**11d**	0	Me	58
3	**10e**	B	**11e**	1	Me	90[a]
4	**10f**	A	**11f**	2	Me	58
5	**10g**	A	**11g**	3	Me	66
6	**10i**	B	**11i**	–	–	68
7	**10j**	B	**11j**	–	–	84

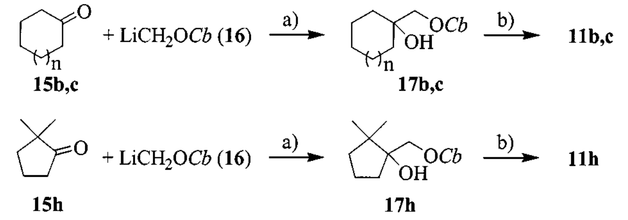
[a] Based on the ester **14e**.

The 2-methyl-substituted alcohols **10f−g** were obtained in a three-step synthetic sequence starting from the corresponding 2-oxocycloalkanecarboxylic esters, via the enol phosphates, nucleophilic methylation by lithium dimethylcuprate and DIBALH reduction (Scheme 5).[29] Carbamates **11b**, **11c** and **11h** were synthesised directly from the cycloalkanones **15b**, **15c** or **15h** by nucleophilic addition of lithiomethyl *N*,*N*-diisopropylcarbamate **16**[30] and elimination of water from the intermediate tertiary alcohols **17b**, **17c** or **17h**, respectively (Scheme 6).



10,12–14	f	g
n	2	3

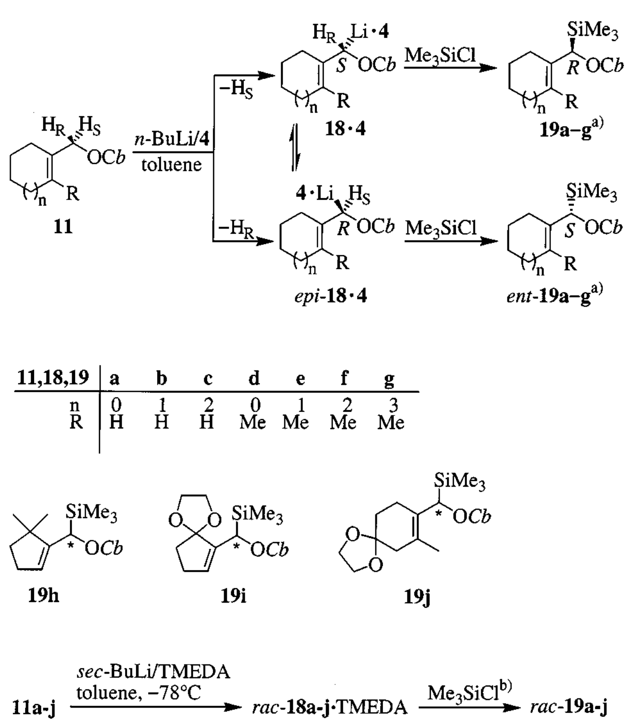
Scheme 5. a) NaH, THF, ClP(O)(OPh)$_2$, yields: **13f**: 86%;[29] **13g**: 90%; b) LiCuMe$_2$, Et$_2$O, yields: **14f**: 85%;[29] **14g**: 86%; c) DIBALH, THF, yields: **10f**: 94%; **10g**: 90%



Scheme 6. a) −78 °C, THF, 4 h, yields (n = 1): **17b** used without purification; (n = 2): **17c**: 56%, **17h**: 64%; b) POCl$_3$ or SOCl$_2$, pyridine, 3−20 h, yields (n = 1): **11b**: 54% over two steps; (n = 2): **11c**: 63%, **11h**: 55%

Deprotonations and Silylation Reactions

In a series of deprotonation experiments with *n*-butyllithium/(−)-sparteine (**4**), the efficiency of the enantiotopic differentiation in carbamates **11** and the configurational stability of the lithioallyl carbamate/**4** complexes were investigated (Scheme 7). Silylations of α-substituted lithioallyl carbamates are known to proceed rapidly, with high α-selectivity[31] and with reliable inversion of the configuration. Consequently, we selected chlorotrimethylsilane as the trapping reagent for establishing the ratios of the epimeric ion pairs. The ratio of the enantiomers **19**/*ent*-**19** roughly reflects the diastereomer ratio in the lithiated intermediates **18·4**/*epi*-**18·4** (Table 2), although kinetic resolution originating from different reactivities of the diastereomers may cause some error. (Time-dependent changes in the ratios are a strong hint of configurational lability.) When a very high lability was suspected, **18·4**/*epi*-**18·4** were produced "in situ" by deprotonation of **11** in the presence of chlorotrimethylsilane. The enantiomeric ratios were determined by ^{1}H NMR spectroscopy in the presence of chiral shift reagents or by GC on a chiral column, by comparison with the corresponding racemates *rac*-**19**, prepared by deprotonation under "achiral conditions", with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as the chelating diamine.



11,18,19	a	b	c	d	e	f	g
n	0	1	2	0	1	2	3
R	H	H	H	Me	Me	Me	Me

Scheme 7. a) For individual conditions, yields and *ee* values see Table 2; b) yields: *rac*-**11a**: 59%; *rac*-**11b**: 87%; *rac*-**11c**: 88%; *rac*-**11d**: 73%; *rac*-**11e**: 85%; *rac*-**11f**: 68%; *rac*-**11g**: 66%; *rac*-**11**h: 69%; *rac*-**11i**: 71%; *rac*-**11j**: 56%

With the (cyclopentenyl)methyl carbamate **11a**, after a short deprotonation time at −78 °C, the enantiomer (+)-**19a** was obtained with a low *ee* (Table 2, Entries 1). Prolonged reaction times gave rise to excess (−)-**19a** (Entries 2 and 3). When the deprotonation was performed at −110 °C for 120 min, (+)-**19a** was isolated with 58% *ee* and in 21% yield. A 71% *ee* of (+)-**19a** and a 34% yield were obtained when the deprotonation was carried out in the presence of chlorotrimethylsilane (Entry 5). The value of 71% *ee* roughly reflects a kinetically determined **18a·4**/*ent*-**18a·4** ratio of 85.5:14.5. A rapid epimerisation proceeded and after 120 min (Entry 3) the thermodynamically determined opposite **18a·4**/*ent*-**18a·4** ratio (38.5:61.5) had essentially been established. The use of pentane as a solvent or of *sec*-butyllithium instead of *n*-butyllithium changed the situation only slightly. In summary, the epimeric (−)-sparteine/lithium complexes, derived from **11a** have a high degree of configurational lability; the half-times of epimerisation are of the magnitude of few minutes. The equilibrium between the epimers (approx. 3:7) in solution is less distinct and dynamic kinetic resolution by preferential crystallisation has not been achieved so far.

The situation was similar for the (5,5-dimethylcyclopentenyl)methyl derivative **11h** (Entries 8 and 9). However, it was interesting to find that bulky substituents in the α-position, where the lithium cation is attached, do not increase the configurational stability significantly. The 5,5-ethylenedioxy-substituted complexes **18·4**/*ent*-**18·4** derived from **11i**

Table 2. (−)-Sparteine-mediated lithiation, silylation and stannylation of allyl carbamates **11**

Entry	Substrate (solvent)[a]	*n*	R	Time [min], base[b]	Product[c]	Yield (%) [recovered. **11** (%)]	*er* **19**/*ent*-**19** (*ee*)	$[\alpha]_D^{20}$[d]
1	**11a** (pentane)[e]	0	H	10	**19a**/*ent*-**19a**	54 [[f]]	67:33 (34)	+6.8
2	**11a** (pentane)	0	H	40	**19a**/*ent*-**19a**	71 [[f]]	42:58 (16)	−3.4
3	**11a** (pentane)	0	H	120	**19a**/*ent*-**19a**	57 [[f]]	38.5:61.5 (23)	−4.9
4	**11a** (pentane)	0	H	120[g][h]	**19a**/*ent*-**19a**	21 [[f]]	79:21 (58)	+12.9
5	**11a** (toluene)	0	H	0[i]	**19a**/*ent*-**19a**	34 [43]	85:5:14:5 (71)	+15.2
6	**11a** (toluene)	0	H	[j]	**19a**/*ent*-**19a**	67 [[f]]	38.5:61.5 (23)	−4.4
7	**11a** (toluene)	0	H	180[h]	**19a**/*ent*-**19a**	71 [[f]]	39: 61 (22)	−4.8
8	**11h** (pentane)	[k]	[k]	40	**19h**/*ent*-**19h**	25 [50]	43: 57 (14)	+4.1
9	**11h** (pentane)	[k]	[k]	240	**19h**/*ent*-**19h**	18 [70]	62.5:37.5 (25)	−7.4
10	**11i** (pentane)	[k]	[k]	10	**19i**/*ent*-**19i**	64 [19]	30:70 (40)	+6.8
11	**11i** (pentane)	[k]	[k]	120	**19i**/*ent*-**19i**	49 [2]	34:66 (32)	+5.5
12	**11d** (toluene)	0	Me	10	**19d**/*ent*-**19d**	44 [[f]]	94.5:6.5 (89)	+7.9
13	**11d** (toluene)	0	Me	180	**19d**/*ent*-**19d**	70 [[f]]	85:15 (70)	+6.0
14	**11d** (toluene)	0	Me	0[i]	**19d**/*ent*-**19d**	34 [[f]]	96.5:3.5 (93)	+8.0
15	**11b** (toluene)	1	H	30	**19b**/*ent*-**19b**	78 [0]	77:23 (54)	[f]
16	**11b** (toluene)	1	H	180	**19b**/*ent*-**19b**	[f]	75.5:24.5 (51)	[f]
17	**11b** (toluene)	1	H	0[i]	**19b**/*ent*-**19b**	88 [0]	76:24 (52)	+4.1
18	**11b** (toluene)	1	H	15[h]	**19b**/*ent*-**19b**	45 [[f]]	*rac*	−
19	**11e** (toluene)	1	Me	10	**19e**/*ent*-**19e**	20 [62]	92.5:7.5 (85)	−12.0
20	**11e** (toluene)	1	Me	120	**19e**/*ent*-**19e**	88 [0]	92.5:7.5 (85)	−12.0
21	**11j** (toluene)	[k]	[k]	10	**19j**/*ent*-**19j**	45 [45]	88:12 (76)	−9.3
22	**11j** (toluene)	[k]	[k]	120	**19j**/*ent*-**19j**	69 [0]	87.5:12.5 (75)	−10.1
23	**11c** (toluene)	2	H	10[h]	**19c**/*ent*-**19c**	15 [43]	46.5:53.5 (7)	−1.1
24	**11f** (toluene)	2	Me	10	**19f**/*ent*-**19f**	30 [54]	3:97 (94)	−25.2
25	**11f** (toluene)	2	Me	120	**19f**/*ent*-**19f**	48 [25]	12.5:87.5 (75)	−18.4
26	**11f** (toluene)	2	Me	5[h]	**19f**/*ent*-**19f**	78 [0]	9.5:90.5 (81)	−20.8
27	**11f** (toluene)	2	Me	10[h]	**19f**/*ent*-**19f**	74 [0]	87:13 (74)	[f]
28	**11g** (toluene)	3	Me	10	**19g**/*ent*-**19g**	7 [89]	3.5:96.5 (93)	−13.8
29	**11g** (toluene)	3	Me	120	**19g**/*ent*-**19g**	35 [39]	13.5:86.5 (73)	−10.4
30	**11g** (toluene)	3	Me	10[h]	**19g**/*ent*-**19g**	68 [14]	12.5:87.5 (75)	−11.7

[a] In toluene, other solvent stated. [b] Deprotonation with *n*-butyllithium at −78 °C; other bases stated. [c] All products are oils. [d] c = 0.2−2.0 in $CHCl_3$. [e] Approx. 0.15 M solution. [f] Not determined. [g] At −110 °C. [h] Deprotonation with *sec*-butyllithium. [i] In situ experiment, see text. [j] The reaction mixture was kept at −40 °C for 30 min prior to silylation. [k] See Scheme 4.

(Entries 10 and 11) seem to have a higher configurational stability,[31] which might be caused by the presence of an additional complexing intramolecular oxy group in the molecule. If this is the case, the rate of enantiotopic differentiation in the (−)-sparteine-induced deprotonation step is low (approx. 70:30).

The introduction of a γ-methyl group onto the allylic moiety causes a dramatic increase in the configurational stability. With the (2-methylcyclopentyl)methyl carbamate **11d**, the original, kinetically achieved, **18d**/*ent*-**18d** ratio of 96.5:3.5 (Entry 14) decreased only to 85:15 after 3 h at −78 °C (Entry 13). It is obvious from this series of experiments that a compromise between achievable yield and *ee* has to be chosen, since a little epimerisation does already take place during complete deprotonation. After 10 min, the *ee* is 89% but the yield is low (44%) (Entry 12). A better yield (70%) is offset by a lower *ee* (70%, Entry 13).

Deprotonation of the (cyclohexenyl)methyl carbamate **11b** by *n*-butyllithium/(−)-sparteine in toluene afforded the silane **19b** with very similar enantiomeric excesses (51−54%), irrespective of the standing time of the intermediate lithium carbanion (Entries 15 and 16). Even the in situ experiment (Entry 17) gave a 52% *ee*. From these results, the following is concluded: The intermediate lithium carbanion pair **18b·4** is configurationally stable in toluene, but the ability of the *n*-butyllithium/(−)-sparteine reagent to discriminate between the enantiotopic protons is only moderate. If *n*-butyllithium was replaced by *sec*-butyllithium (Entry 18), a racemic mixture of silane *rac*-**19b** was isolated. A control experiment revealed that *sec*-butyllithium deprotonates **11b** (toluene, −78 °C) even in the absence of a complexing diamine.

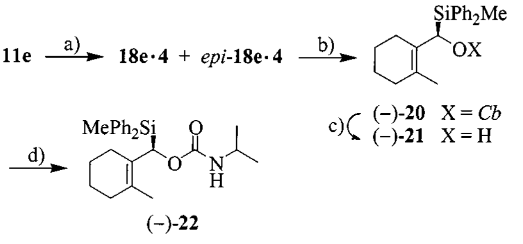
On introduction of a 2-methyl group into the six-membered ring, almost complete configurational stability of the lithium intermediates **18e·4**/*ent*-**18e·4** was achieved at −78 °C. The enantiomeric ratio (92.5:7.5; 85% *ee*) did not change after 120 min, but the yield of **19e**/*ent*-**19e** increased from 20% after 10 min to 88% after 2 h (Entries 19 and 20). Even more highly functionalised substrates of this type, such as the ketal **11j**, also exhibit these characteristics (Entries 21 and 22).

The lithium intermediates derived from the (2-methylcycloheptenyl)methyl (**11f**) and the (2-methylcyclooctenyl)methyl (**11g**) carbamates (Entries 24−27 and 28−30, respectively) also have very high configurational stabilities. It turned out that the use of *sec*-butyllithium/**4** is advantageous over that of *n*-butyllithium/**4** here, since the deprotonation of **11f** or **11g** proceeds within 10 min at −78 °C. The racemates *rac*-**19a−g** were obtained in good yields by use of *sec*-butyllithium/TMEDA.

Further Reactions for Assignment of Absolute Configurations

Unfortunately, none of the trimethylsilanes **19** could be crystallised to furnish crystals suitable for X-ray analysis with use of anomalous diffraction methods for assignment of the absolute configuration. Therefore, a number of reactions offering the potential for formation of crystalline, heavy atom containing compounds were performed.

Quenching of the lithium intermediates produced from **11e** with *n*-butyllithium/**4** with chloromethyldiphenylsilane yielded the substitution product (−)-**20** as a noncrystalline solid (Scheme 8). Deprotection with diisobutylaluminium hydride provided the liquid α-silyl alcohol (−)-**21**, which was converted into the crystalline urethane (−)-**22** by addition of isopropyl isocyanate. X-ray analysis of (−)-**22** (Figure 1)[32] established the (*R*) configuration at the stereogenic centre.



Scheme 8. a) nBuLi/**4**, toluene, 2 h, −78 °C; b) $Ph_2MeSiCl$, 76%; c) DIBALH (10 equiv.), THF, 15 h, room temp., 87%; d) iPrN=C=O (3 equiv.), DMAP (0.1 equiv.), CH_2Cl_2, 24 h, 40 °C, 90%

Treatment of the analogously generated solution of **18e·4**/*ent*-**18e·4** with chlorotrimethylstannane gave a mixture of the α-adduct (−)-**23a** (13%, 67% *ee*) and the γ-adduct (+)-**24a** (47%, 85% *ee*) (Scheme 9), while *rac*-**18e**-TMEDA afforded the α-adduct *rac*-**23a** (50%) in excess over *rac*-**24a** (18%). When chlorotriphenylstannane was used as the scavenger, we exclusively isolated the α-adduct *rac*-**23b** in 80% yield. However, the sparteine complexes **18e·4**/*ent*-**18e−4** gave rise to (+)-**23b** (34%) besides an inseparable mixture of **24b** and **11e**; we were unable to determine the enantiomeric excesses in these triphenylstannanes. Compound (+)-**23b** was subjected to a crystal structure analysis, which clearly indicated its (*R*) configuration (Figure 2).[32]

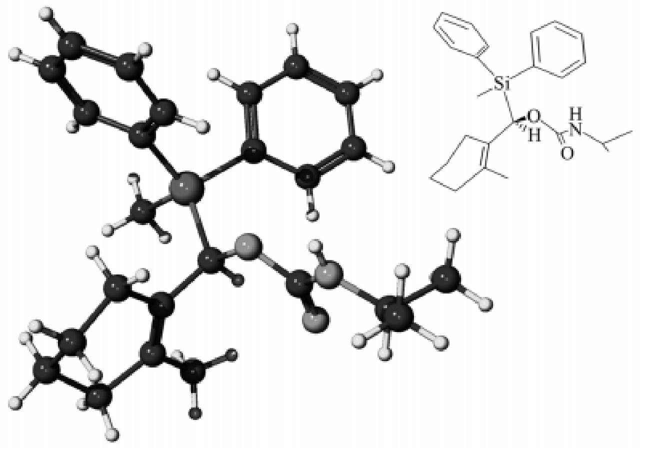
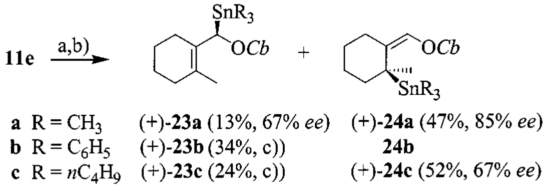


Figure 1. Structure of (*R*)-(2-methyl-1-cyclohexenyl)(methyldiphenylsilyl)methyl *N*,*N*-diisopropylcarbamate [(−)-**22**][32]



Scheme 9. a) nBuLi/**4**, toluene, 2 h, −78 °C; b) R_3SnCl (1.5 equiv.); 1 h, −78 °C, −78 °C to room temp.; c) attempts to determine the *ee* failed

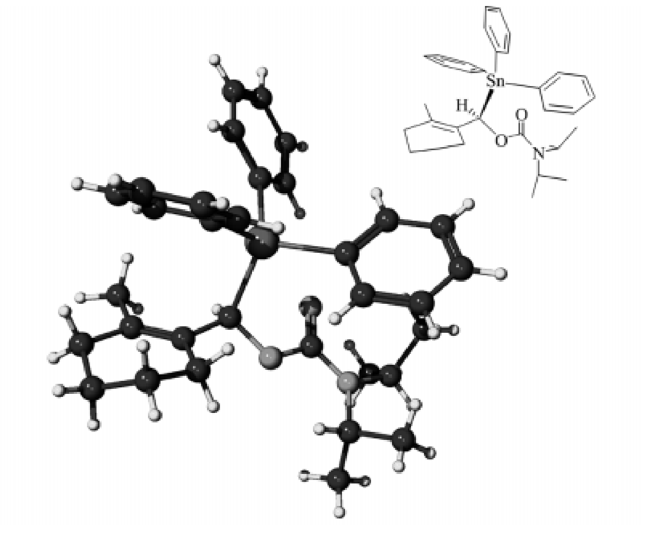
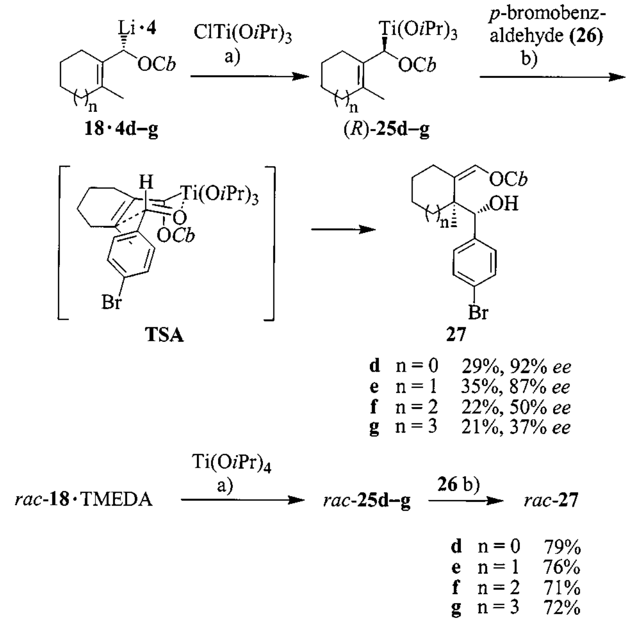


Figure 2. Structure of (*R*)-(2-methyl-1-cyclohexenyl)(triphenylstannyl)methyl *N*,*N*-diisopropylcarbamate [(+)-**23b**][32]

Addition of tetra(isopropoxy)titanium (3 equiv.) to a toluene solution of *rac*-**18d−g** at −78 °C resulted in smooth metal exchange, which in each case was apparent in the formation of a single *rac*-**27d−g** diastereomer after homoaldol addition with *p*-bromobenzaldehyde, in yields between 71 and 79% (Scheme 10). When the same conditions were applied to the corresponding sparteine complexes **18d−g·4**/*epi*-**18d−g·4**, inseparable diastereomeric mixtures resulted. Obviously, no lithium/titanium exchange had taken place. However, after use of the more reactive chlorotri(isopropoxy)titanium, the optically active homoaldol adducts **27d−g** were formed, although in low yields (21−35%). Compounds (+)-**27d** and (−)-**27e** could be subjected to X-ray analysis with anomalous diffraction (Figure 3 and Figure 4),[32] establishing (*S*) configurations at the stereogenic ring carbon atoms and (*R*) configurations at the benzylic position of each of them.



Scheme 10. a) −78 °C, toluene, 1 h; b) −78 °C, 1 h, warm to room temp.

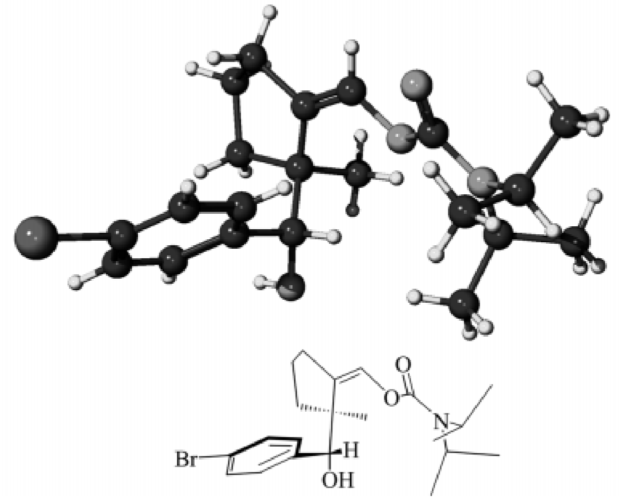


Figure 3. Structure of {1*Z*,1[2*S*,2(1*R*)]}-{2-[(4-bromophenyl)(hydroxy)methyl]-2-methylcyclohexylidene}methyl *N*,*N*-diisopropylcarbamate [(+)-**27e**][32]

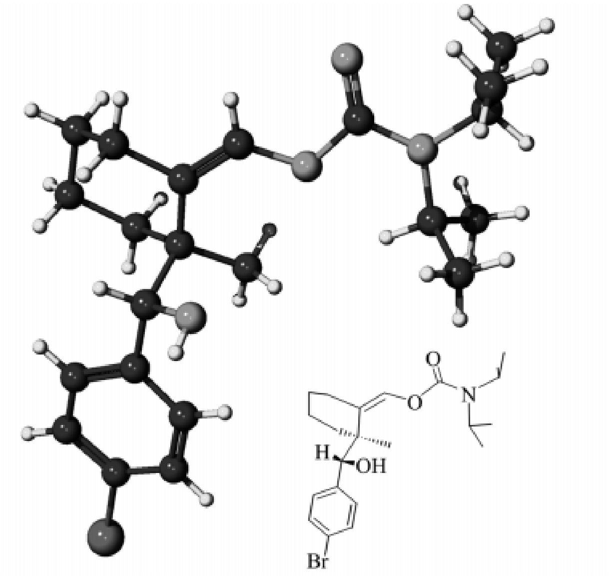


Figure 4. Structure of {1*Z*,1[2*S*,2(1*R*)]}-{2-[(4-bromophenyl)(hydroxy)methyl]-2-methylcyclopentylidene}methyl *N*,*N*-diisopropylcarbamate [(+)-**27d**][32]

Because of the highly ordered nature of the Zimmerman−Traxler transition state TS **A**, the titanium intermediates (*R*)-**25d** and (*R*)-**25e** are assumed to be the direct precursors. Since the lithium/titanium exchange in lithiated allyl carbamates has been recognised to proceed with stereoinversion,[15c] the major lithium complexes **18d·4** and **18e·4** must have the (*S*) configuration. The same conclusion results for **18e·4** from the analysis of the mode of formation of the silane (−)-(*R*)-**20** and the stannane (+)-(*R*)-**23b**, since similar silylations and stannylations have regularly been observed to proceed with stereoinversion.[16,33] Thus, in the kinetically controlled deprotonation processes of **11d** and **11e**, the (*pro*-*S*) proton is removed preferentially. The (*pro*-*S*) preference of alkyllithium/(−)-sparteine has also been found for the primary allyl carbamates **2**[16] and **9**.[20] Therefore, it is quite likely that the remaining major intermediates **18·4**, formed under kinetic control, and the resulting products **19** and **27** have the proposed analogous absolute configurations. The assumption is less certain for the derivatives of the 2,2-disubstituted (cyclopentenyl)methyl carbamates **11h** and **11i**, since there are substantial structural differences compared to the "usual" allyl carbamates seen.

Conclusion

2-Alkyl-substituted (cycloalk-1-enyl)methyl carbamates such as **10d**, **10e** and **10f** are deprotonated by butyllithium/(−)-sparteine with efficient enantiotopic differentiation in favour of the α-(*pro*-*S*) proton. The resulting lithium/(−)-sparteine complexes exhibit satisfactory configurational stability at −78 °C, and can be converted into highly enantioenriched products in stereospecific reactions with electrophiles. The analogous 2-unsubstituted compounds **10a** and **10c**, but not the (cyclohex-1-enyl)methyl derivative **10b**, epimerise within a few minutes under these conditions. The mechanism of the epimerisation, which requires the formal migration of the lithium cation from one face to the other, is still unknown, although attempts to achieve better insight have been performed.[34] The semiquantitative relationships observed in this paper may be explained by an *anti*-S_E' substitution reaction at the γ-position of the ion pairs **17·4** by "vagabonding" lithium cation in the solution; its rate should be decreased with increasing steric shielding of this position. Further efforts are necessary to uncover the mechanism. From the synthetic point of view, a simple and efficient route to structurally complex homoaldol adducts has been established, and has been utilised in the stereoselective synthesis of highly substituted, bicyclic γ-lactones.[35]

Experimental Section

General Remarks: All solvents were dried and distilled prior to use. Unless otherwise specified, materials were obtained from commercial sources and used without purification. TMEDA and TMSCl were distilled from calcium hydride and stored under argon. All air- and moisture-sensitive reactions were performed in oven-dried glassware under argon. Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates (Macherey−Nagel & Co.), or on Merck silica gel (60 F_{254}) plates. For flash column chromatography, silica gel 60, 0.040−0.063 mm (230−400 mesh) was used. Melting points are uncorrected. IR: Nicolet 5 DXC Fourier transform IR spectrometer. Optical rotations: Perkin−Elmer 241 polarimeter. Elemental analyses: Heraeus CHN-O-rapid elemental analyser. HRMS: Finnigan MAT 8200 or Micromass Quattro LC-Z mass spectrometer. NMR: Bruker spectrometer 200 P-FT NMR, ARX 300, AM360, AMX400 or Varian Associated Unity Plus 600 spectrometer. X-ray: Enraf−Nonius CAD4-diffractometer. The following abbreviations are used in the text: C_q = quaternary C; PE = petroleum ether.

Methyl 2-[(Diphenoxyphosphoryl)oxy]-1-cycloheptene-1-carboxylate (13f): Compound **12f** (8.51 g, 50.0 mmol) was added to a suspension of sodium hydride (60% in mineral oil, 2.20 g, 55.0 mmol, 1.1 equiv.) in THF (50 mL), cooled to −30 °C, and the mixture was stirred for 1 h at −30 °C. Diphenyl chlorophosphate (14.8 g, 55.0 mmol) was then added and the mixture was stirred for 1 h at −30 °C. After this had warmed to room temperature, satd. aq. NH_4Cl (40 mL) and water (100 mL) were added. The aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column (PE/Et_2O, 1:1) to afford the pure product **13f**. Yield: 17.3 g (86%) colourless oil. R_F = 0.33 (PE/Et_2O, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56−1.80 (2 m, 6 H), 2.41−2.66 (2 m, 4 H), 3.54 (s, 3 H), 7.14−7.37 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0 (CH_2), 25.9 (CH_2), 27.7 (CH_2), 31.0 (CH_2), 34.3 (CH_2), 51.6 (CH_3), 120.0 [120.1] (C_q), 122.0 [122.1] (CH), 125.4 (CH), 129.7 (CH), 150.5 [150.6] (C_q, Ph), 155.9 [156.0] (C_q), 167.6 (C_q). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1719 ν(C=O); 1596 ν(C=C). $C_{21}H_{23}O_6P$ (402.380): calcd. C 62.68, H 5.76; found C 62.49, H 5.77.

Methyl 2-[(Diphenoxyphosphoryl)oxy]-1-cyclooctene-1-carboxylate (13g): In the same manner as described for **13f**, **12g** (9.21 g, 50.0 mmol) was converted into 18.8 g (90%) of **13g**. Colourless oil. R_F = 0.33 (PE/Et_2O, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48−1.79 (2 m, 8 H), 2.37−2.60 (2 m, 4 H), 3.56 (s, 3 H), 7.13−7.38 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.8 (CH_2), 26.3 (CH_2), 27.9 (CH_2), 27.9 (CH_2), 29.8 (CH_2), 31.5 (CH_2), 51.5 (CH_3), 119.1 [119.2] (C_q), 120.0 [120.1] (CH), 125.3 (CH), 129.7 (CH), 150.5 [150.6] (C_q, Ph), 153.4 [153.5] (C_q), 166.9 (C_q). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1719 ν(C=O), 1592 ν(C=C). $C_{22}H_{25}O_6P$ (416.40): calcd. C 63.46, H 6.05; found C 63.62, H 6.30.

Methyl 2-Methyl-1-cycloheptene-1-carboxylate (14f): Methyllithium (1.6 M, 31.6 mL, 50.6 mmol) was added to a suspension of copper(I) iodide (4.81 g, 25.3 mmol) in Et_2O (175 mL), cooled to 0 °C. After the mixture had been cooled to −40 °C, **13f** (8.50 g, 21.1 mmol), dissolved in Et_2O (10 mL), was added over 30 min. The mixture was stirred for 3 h at this temperature and quenched at room temperature with 2 N aq. HCl. The aqueous phase was extracted with Et_2O (4 × 30 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (PE/Et_2O, 4:1). Yield: 3.02 (85%) colourless oil. R_F = 0.65 (PE/Et_2O, 4:1). For experimental details see ref.[29]

Methyl 2-Methyl-1-cyclooctene-1-carboxylate (14g): In the same manner as described for **14f**, **13g** (8.79 g, 21.1 mmol) was converted into 3.29 (86%) of **14g**. Colourless oil. R_F = 0.63 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27−1.46 (2 m, 8 H), 1.98 (s, 3 H), 2.20−2.42 (2 m, 4 H), 3.68 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 26.5 (CH_2), 26.5 (CH_2), 28.3 (CH_2), 28.3 (CH_2), 30.1 (CH_2), 34.9 (CH_2), 51.1 (CH_3), 127.1 (C_q), 148.6 (C_q), 169.9 (C=O).

(2-Methyl-1-cycloheptenyl)methanol (10f): DIBALH (1 M, 42.7 mL, 42.7 mmol, 2.5 equiv.) was added to a solution of ester **14f** (2.87 g, 17.1 mmol, 2.5 equiv.) in THF (100 mL) at 0 °C and the mixture was stirred for 2 h at 0 °C. It was allowed to warm up to room temperature before addition of methanol (10 mL), followed by satd. aq. NH_4Cl (10 mL) and 2 N aq. HCl (50 mL). The aqueous layer was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The remaining residue was purified by flash column chromatography on silica gel (PE/Et_2O, 1:1) to give 2.25 g (94%) of alcohol **10f**. Colourless oil. R_F = 0.48 (PE/Et_2O, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34−1.49 (m, 4 H), 1.44 (s, 1 H), 1.61−1.79 (m, 5 H), 2.16 (m_c, 2 H), 2.22 (m_c, 2 H), 4.05 (s, 2 H).

(2-Methyl-1-cyclooctenyl)methanol (10g): In the same manner as described for **10f**, **14g** (3.17 g, 17.4 mmol) was converted into 2.43 (90%) of **10g**. R_F = 0.46 (PE/Et_2O, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34−1.59 (m, 8 H), 1.72 (s, 3 H), 2.12−2.30 (2 m, 4 H), 4.20 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1 (CH_3), 26.4 (CH_2), 26.8 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 30.0 (CH_2), 33.1 (CH_2), 62.7 (CH_2), 132.5 (C_q), 134.0 (Cq,). IR (film): $\tilde{\nu}$ [cm^{-1}] = 3334 ν(OH), 1666 ν(C=C). $C_{10}H_{18}O$ (154.25): calcd. C 77.87, H 11.76; found C 77.32, H 11.71.

(2-Methyl-1-cycloheptenyl)methyl *N*,*N*-Diisopropylcarbamate (11f) (Method A): *N*,*N*-Diisopropylcarbamoyl chloride (3.11 g, 19.0 mmol, 1.25 equiv.) in THF (10 mL) was added to a solution of allylic alcohol **10f** (2.15 g, 15.2 mmol), DMAP (186 mg 1.52 mmol) and pyridine (20 mL). The reaction mixture was heated under reflux for 12 h. After cooling to room temperature, the solution was poured into 2 N aq. HCl (30 mL). The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (PE/Et_2O, 4:1). Yield: 2.36 g (58%) **11f** as a colourless oil; 366 mg (17%) of **10f** was also recovered. R_F = 0.47 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.9 Hz, 12 H), 1.36−1.74 (2 m, 6 H), 1.75 (s, 3 H), 2.16 (m_c, 4 H), 3.87 (br. s, 2

H), 4.53 (d, J = 0.5 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (CH_3), 25.8 (CH_2), 26.8 (CH_2), 31.9 (CH_2), 32.4 (CH_2), 36.1 (CH_2), 45.7 (CH), 66.3 (CH_2), 131.6 (C_q), 139.2 (C_q), 156.2 (C=O). IR (film): ṽ [cm^{-1}] = 1693 ν(C=O). $C_{16}H_{29}NO_2$ (267.41): calcd. C 71.86, H 10.93, N 5.24; found C 71.61, H 11.04, N 5.39.

(2-Methyl-1-cyclooctenyl)methyl *N,N*-Diisopropylcarbamate (11g) (Method A): In the same manner as described for **11f**, **10g** (2.31 g, 15.0 mmol), DMAP (183 mg 1.50 mmol), and *N,N*-diisopropylcarbamoyl chloride (3.07 g, 18.8 mmol) in pyridine (20 mL) were heated under reflux for 12 h. After cooling to room temperature, the mixture was worked up. Flash chromatography (PE/Et_2O, 4:1) gave **11g**. Yield: 2.80 g (66%) colourless oil; 570 mg (25%) of **10g** were also recovered. R_F = 0.54 (PE/Et_2O, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.7 Hz, 12 H), 1.36−1.58 (m, 8 H), 1.74 (s, 3 H), 2.14−2.27 (m, 4 H), 3.88 (br. s, 2 H), 4.58 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 (CH_3), 21.0 (CH_3), 26.4 (CH_2), 26.8 (CH_2), 28.3 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 33.3 (CH_2), 45.7 (CH), 65.0 (CH_2), 128.7 (C_q), 135.9 (C_q), 156.0 (C=O). IR (film): ṽ [cm^{-1}] = 1691 ν(C=O). $C_{16}H_{29}NO_2$ (267.41): calcd. C 72.55, H 11.10, N 4.98; found C 72.45, H 11.09, N 5.20.

1-Cyclopentenylmethyl *N,N*-Diisopropylcarbamate (11a): A solution of allylic alcohol **10a** (5.60 g, 57.1 mmol) in THF (10 mL) was added dropwise to a suspension of sodium hydride (60% in mineral oil, 2.74 g, 68.6 mmol, 1.2 equiv.) in hexane (75 mL) at 0 °C. The reaction mixture was stirred for 1 h at room temperature, after which *N,N*-diisopropylcarbamoyl chloride (11.2 g, 73.2 mmol, 1.28 equiv.) was added in small portions over 5 min, and the mixture was then heated under reflux for 16 h. After cooling to room temperature, the solution was poured into 2 N aq. HCl (20 mL). The aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. Distillation of the crude product yielded 1.72 g (75%) **11a** as a colourless oil. b.p. 75−80 °C (0.01 Torr). ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.0 Hz, 12 H), 1.60−2.40 (m, 6 H), 3.81 (sept, J = 7.0 Hz, 2 H), 4.55 (m, 2 H), 5.55 (m, 1 H). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 21.0 (CH_3), 23.4 (CH_2), 32.4 (CH_2), 33.1 (CH_2), 45.8 (CH), 63.4 (CH_2), 126.9 (CH), 140.1 (C_q), 155.3 (C=O). $C_{13}H_{23}NO_2$ (255.32): calcd. C 69.30, H 10.29; found C 69.25, H 10.25.

(2-Methyl-1-cyclopentenyl)methyl *N,N*-Diisopropylcarbamate (11d): In the same manner as described for **11a**, **10d** (1.40 g, 12.5 mmol) in hexane (20 mL) was deprotonated with sodium hydride (60% in mineral oil, 0.60 g, 15.0 mmol, 1.2 equiv.) and *N,N*-diisopropylcarbamoyl chloride (2.46 g, 16.0 mmol, 1.28 equiv.) was added. The crude product was purified by silica gel column chromatography (PE/Et_2O, 4:1). Yield: 2.36 g (58%) **11d** as a colourless oil. R_F = 0.54 (PE/Et_2O, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.9 Hz, 12 H), 1.67 (s, 3 H), 1.71−1.82 (m, 2 H), 2.37−2.24 (m, 4 H), 3.87 (br. s, 2 H), 4.60 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 21.0 (CH_3), 21.6 (CH_2), 34.8 (CH_2), 38.7 (CH_2), 45.7 (CH), 61.2 (CH_2), 130.7 (C_q), 137.1 (C_q), 156.0 (C=O). IR (film): ṽ [cm^{-1}] = 1696 ν(C=O). $C_{14}H_{25}NO_2$ (239.35): calcd. C 70.25, H 10.53, N 5.85; found C 69.85, H 10.43, N 6.20.

(2-Methyl-1-cyclohexenyl)methyl *N,N*-Diisopropylcarbamate (11e): In the same manner as described for **11a**, **10e** (1.93 g, 15 mmol) in THF (10 mL) was deprotonated with sodium hydride (60% in mineral oil, 0.96 g, 24.0 mmol) and *N,N*-diisopropylcarbamoyl chloride (3.93 g, 24.0 mmol) was added. Purification of the crude product by silica gel column chromatography (PE/Et_2O, 4:1) gave **11e** in 86% yield (3.51 g) over two steps as a colourless oil. R_F = 0.44 (PE/Et_2O, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, J = 6.7 Hz, 12 H), 1.60 (m, 4 H), 1.70 (s, 3 H), 1.94−2.09 (m, 4 H), 3.80−4.2 (m, 2 H), 4.58 (d, J = 0.5 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 20.9, 20.9, 27.9, 31.9, 45.6, 64.9, 125.9, 132.1, 156.0. $C_{15}H_{27}NO_2$ (253.38): calcd. C 71.10, H 10.74, N 5.53, found C 70.94, H 10.81, N 5.85.

(1,4-Dioxaspiro[4.4]non-6-en-6-yl)methyl *N,N*-Diisopropylcarbamate (11i) (Method B): In the same manner as described for **11a**, **10i** (2.05 g, 13.1 mmol) in hexane (20 mL) was deprotonated with sodium hydride (60% in mineral oil, 0.63 g, 15.7 mmol, 1.2 equiv.) and *N,N*-diisopropylcarbamoyl chloride (2.78 g, 17.0 mmol, 1.30) was added. After workup, the residue was purified by silica gel column chromatography (PE/Et_2O, 1:2). Yield 2.51 g (68%) **11i** as a colourless oil. R_F = 0.67 (PE/Et_2O, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 [1.17] (d, J = 6.8 Hz, 12 H), 2.00−2.08 (m, 2 H), 2.29−2.32 (m, 2 H), 3.78−3.99 (m, 6 H), 4.64 (dd, J = 3.8, 2.2 Hz, 2 H), 5.99 (ddd, J = 3.9, 2.5, 1.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (CH_3), 28.0 (CH_2), 36.0 (CH_2), 45.9 (CH), 59.7 (CH_2), 65.2 (CH_2), 109.5 (C_q), 133.7 (CH), 139.2 (C_q), 155.4 (C=O). IR (film): ṽ [cm^{-1}] = 1700 ν(C=O). $C_{15}H_{24}NO_4$ (283.36): calcd. C 63.58, H 8.89, N 4.94, found C 63.47, H 8.98, N 5.17.

(7-Methyl-1,4-dioxaspiro[4.5]dec-7-en-8-yl)methyl *N,N*-Ddiisopropylcarbamate (11j): In the same manner as described for **11a**, **10j** (3.90 g, 21.2 mmol) in THF (20 mL) was deprotonated with sodium hydride (60% in mineral oil, 600 mg, 25.2 mmol, 1.2 equiv.) and *N,N*-diisopropylcarbamoyl chloride (4.47 g, 27.5 mmol, 1.3 equiv.) was added. The crude product was purified by silica gel column chromatography (PE/Et_2O, 1:1). Yield: 5.56 g (84%) **11d** as a colourless oil. R_F = 0.46 (PE/Et_2O, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (d, J = 6.9 Hz, 12 H), 1.64−1.72 (m, 2 H), 1.67 (s, 3 H), 2.17−2.30 (m, 4 H), 3.69−4.00 (m, 6 H), 4.56 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (CH_3), 21.0 (CH_3), 26.9 (CH_2), 31.2 (CH_2), 41.8 (CH_2), 45.7 (CH), 63.9 (CH_2), 64.3 (CH_2), 64.3 (CH_2), 107.9 (C_q), 125.6 (C_q), 129.6 (C_q), 155.8 (C=O). IR (film): ṽ [cm^{-1}] = 1690 ν(C=O). $C_{17}H_{29}NO_4$ (311.42): calcd. C 65.57, H 9.39, N 4.50, found C 65.51, H 9.40, N 4.79.

(1-Hydroxycycloheptyl)methyl *N,N*-Diisopropylcarbamate (17c): *sec*-Butyllithium (1.3 M, 8.5 mL, 11.0 mmol, 1.1 equiv.) was added dropwise to a solution of methyl *N,N*-diisopropylcarbamate (1.95 g, 10.0 mmol) and TMEDA (1.79 g, 15.0 mmol, 1.5 equiv.) in THF (30 mL), cooled to −78 °C. Stirring was continued at −78 °C for 2 h, after which cycloheptanone (2.24 g, 20.0 mmol, 2.0 equiv.) was added in small portions over 1 h. Finally the reaction mixture was stirred at −78 °C for 4 h and 2 N aq. HCl (40 mL) was added at room temperature. The aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/Et_2O, 1:1) to afford the pure product (*R*)-**20**. Yield: 1.53 mg (56%) colourless oil. R_F = 0.43 (PE/Et_2O, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, J = 6.7 Hz, 12 H), 1.30−1.72 (m, 12 H), 2.25 (br. s, 1 H), 3.90 (br. s, 2 H), 3.98.(s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (CH_3), 22.2 (CH_2), 29.8 (CH_2), 37.9 (CH_2), 45.9 (CH), 72.4 (CH_2), 156.0 (C=O). IR (film): ṽ [cm^{-1}] = 3449 ν(OH), 1683 ν(C=O). $C_{15}H_{29}NO_3$ (271.40): calcd. C 66.38, H 10.77, N 5.16, found C 66.26, H 10.59, N 5.49.

(1-Hydroxycyclohexyl)methyl *N,N*-Diisopropylcarbamate (17b): In the same manner as described for **17c**, methyl *N,N*-diisopropylcarbamate (2.41 g, 15.1 mmol) and TMEDA (3.43 g, 22.7 mmol, 1.16 equiv.) were dissolved in THF (40 mL) and cooled to −78 °C, after which *sec*-butyllithium (1.25 M, 14.8 mL, 18.5 mmol, 1.23 equiv.) was added. Stirring was continued at −78 °C for 2 h, after which cyclohexanone (2.05 g, 19.6 mmol) was added over a period of 1.5 h. After workup, the crude product was used without further purification.

1-(Hydroxy-2,2-dimethylcyclopentyl)methyl *N,N*-Diisopropylcarbamate (17h): In the same manner as described for **17c**, methyl *N,N*-diisopropylcarbamate (2.72 g, 17.1 mmol, 2.1 equiv.) and TMEDA (2.94 g, 25.7 mmol, 3.0 equiv.) in THF (30 mL), cooled to −78 °C, was deprotonated with *sec*-butyllithium (1.23 M, 15.3 mL, 18.8 mmol). Stirring was continued at −78 °C for 2.5 h, after which 2,2-dimethylcyclopentanone (1.00 g, 8.56 mmol) was added over 1.5 h. The crude product was purified by silica gel column chromatography (PE/Et_2O, 5:1). Yield: 1.48 g (64%) of **17h** as a colourless oil. $R_F = 0.36$ (PE/Et_2O, 5:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (s, 3 H), 1.01 (s, 3 H), 1.18 (d, $J = 6.9$ Hz, 12 H), 1.33−1.97 (m, 6 H), 2.59 (s, 1 H), 3.87 (sept, $J = 6.9$ Hz, 2 H), 4.09 (d, $J = 11.4$ Hz, 2 H), 4.19 (d, $J = 11.4$ Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.2$ (CH_2), 20.9 (CH_3), 22.3 (CH_3), 24.5 (CH_3), 35.9 (CH_2), 39.7 (CH_2) 44.5 (C_q), 46.1 (CH), 69.1 (CH), 82.8 (C_q), 156.1 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 3467 ν(OH), 1683 ν(C=O). $C_{15}H_{29}NO_3$ (271.40): calcd. C 66.38, H 10.77, N 5.16, found C 66.14, H 10.93, N 5.40.

1-Cycloheptenylmethyl *N,N*-Diisopropylcarbamate (11c): Compound **17c** (1.31 g, 4.83 mmol) was dissolved in pyridine (12 mL), cooled to 0 °C and $POCl_3$ (2.5 mL) was added dropwise. The mixture was stirred for 20 h at 0 °C, after which it was poured into crushed ice (50 g). The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EtOAc, 10:1) to afford the pure product **11c**. Yield: 768 mg (63%), colourless oil. $R_F = 0.54$ (PE/EtOAc, 10:1) ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$−1.26 (m, 12 H), 1.43−2.23 (3 m 10 H), 3.89 (br. s, 2 H), 4.42 (s, 2 H), 5.83 (t, $J = 6.1$ Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.0$ (CH_3), 26.7 (CH_2), 26.9 (CH_2), 28.3 (CH_2), 30.4 (CH_2), 32.3 (CH_2), 45.8 (CH), 70.4 (CH_2), 130.2 (CH), 140.0 (C_q), 155.8 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1701 ν(C=O). $C_{15}H_{27}NO_2$ (253.38): calcd. C 71.10, H 10.74, N 5.53, found C 70.73, H 10.71, N 5.86.

1-Cyclohexenylmethyl *N,N*-Diisopropylcarbamate (11b): In the same manner as described for **17c**, the crude product **17b** was dissolved in pyridine (30 mL) and cooled to 0 °C, after which $SOCl_2$ (1.65 mL, 22.7 mmol) was added dropwise. The mixture was stirred at 0 °C for 3 h. After workup, the residue was purified by silica gel column chromatography (PE/Et_2O, 9:1) to yield **11b** (1.95 g, 54% over two steps) as a colourless oil. $R_F = 0.58$ (PE/Et_2O, 9:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.22$ (d, $J = 6.7$ Hz), 1.55−1.75 (m, 4 H), 1.96−2.10 (m, 4 H), 3.70−4.20 (m, 2 H), 4.46 (br. s, 2 H), 5.71 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.1$, 22.4, 22.6, 25.1, 26.2, 45.9, 69.0, 124.8, 133.8, 155.6.

(5,5-Dimethyl-1-cyclopentenyl)methyl *N,N*-Diisopropylcarbamate (11h): In the same manner as described for **17c**, **17h** (271 mg, 1.0 mmol) was dissolved in pyridine (2.5 mL), cooled to 0 °C and $SOCl_2$ (238 mg, 2.0 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred for 3 h at room temperature. After workup, the residue was purified by silica gel column chromatography (PE/Et_2O, 4:1) to yield **11h** (138 mg, 55%) as a colourless oil together with 20 mg of an isomer that was not characterised. $R_F = 0.42$ (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.04$ (s, 6 H), 1.19 (d, $J = 6.9$ Hz, 12 H), 1.71 (t, $J = 7.0$ Hz, 2 H), 2.19−2.27 (m, 2 H), 3.89 (sept, $J = 6.9$ Hz, 2 H), 4.58 (m_c, 2 H), 5.52 (m_c, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.0$ (CH_3), 26.9 (CH_3), 29.3 (CH_2), 41.1 (CH_2), 45.2 (C_q), 45.8 (CH), 61.3 (CH_2), 125.7 (CH), 147.1 (C_q), 155.3 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1699 ν(C=O). $C_{15}H_{27}NO_2$ (253.38): calcd. C 71.10, H 10.74, N 5.53, found C 70.91, H 10.96, N 5.75.

General Procedure for Deprotonation of Allyl Carbamates (GP1): Butyllithium (1.2 equiv.) was added dropwise with vigorous stirring to a 0.15 M solution of allyl carbamates **11** and diamine (1.2 equiv.) in toluene or pentane at −78 °C. After this had been stirred for 0−180 min (see Table 2) at the same temperature, the electrophile (1.5 equiv.) was added. The mixture was stirred for 1 h at −78 °C, after which it was allowed to warm to room temperature and poured into an ice-cooled mixture of Et_2O (10 mL) and 2 N aq. HCl (10 mL). The aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography.

In situ Silylation of Carbamates: *n*-Butyllithium (1.2 equiv.) was added over 10 min to a solution of **11** and TMSCl (1.5 equiv.) in toluene (5 mL) at −78 °C. Stirring was continued for 30 min and the mixture was quenched with methanol (1 mL) at −78 °C. After usual workup, the crude product was purified by silica gel flash column chromatography.

(1-Cyclopentenyl)(trimethylsilyl)methyl *N,N*-Diisopropylcarbamate (19a): As described under GP1, **11a** (158 mg, 0.70 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (10 min) and quenched with TMSCl. Yield: 112 mg (54%) colourless oil. $R_F = 0.67$ (PE/Et_2O, 4:1). $[\alpha]_D^{20} = +6.8$ ($c = 1.08$, $CHCl_3$). Shift experiment: *er* 67:33 (34% *ee*), 9.4 mg + 11 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at $\delta = 0.05$] = 0.03, signal of major enantiomer appears at lower field. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.05$ (s, 9 H), 1.20 (d, $J = 6.9$ Hz, 12 H), 1.72−1.92 (m, 2 H), 2.14−2.40 (m, 4 H), 3.90 (br. s, 2 H), 5.12−5.20 (m, 1 H), 5.31−5.37 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 0.7$ (CH_3), 21.1 (CH_3), 23.1 (CH_2), 32.3 (CH_2), 34.0 (CH_2), 45.8 (CH), 69.6 (CH), 122.1 (CH), 143.3 (C_q), 155.8 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1693 ν(C=O), 1645 ν(C=C). $C_{16}H_{31}NO_2Si$ (297.51): calcd. C 64.59, H 10.50, N 4.71, found C 64.60, H 10.49, N 4.91.

(1-Cyclohexenyl)(trimethylsilyl)methyl *N,N*-Diisopropylcarbamate (19b): As described under GP1, **11b** (145 mg, 0.61 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (30 min) and quenched with TMSCl. Yield: 167 mg (88%) colourless oil. $R_F = 0.63$ (PE/Et_2O, 9:1). $[\alpha]_D^{20} = +4.1$ ($c = 0.75$, $CHCl_3$). Shift experiment: *er* 77:23 (54% *ee*), 50 mol % Eu(hfc)$_3$ in $CDCl_3$. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.09$ (s, 9 H), 1.15 (d, $J = 6.7$ Hz, 12 H), 1.45−1.70 (m, 4 H), 1.90−2.10 (m, 4 H), 3.95 (br. s, 2 H), 4.93 (s, 1 H), 5.49 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -2.8$, 21.0, 22.4, 22.6, 24.9, 26.9, 45.9, 73.4, 119.9.136.5, 155.6. $C_{17}H_{33}NO_2Si$ (311.53): calcd. C 65.54, H 10.68, N 4.50, found C 65.58, H 10.59, N 4.76.

(1-Cycloheptenyl)(trimethylsilyl)methyl *N,N*-Diisopropylcarbamate (19c): As described under GP1, **11c** (127 mg, 0.50 mmol) was deprotonated with *sec*-butyllithium/(−)-sparteine (10 min) and quenched with TMSCl. Yield: 15 mg (15%) colourless oil and 33 mg (43%) **11c** recovered. $R_F = 0.63$ (PE/Et_2O, 4:1). $[\alpha]_D^{20} = -1.1$ ($c = 0.75$, $CHCl_3$). Shift experiment: *er* 53.5:46.5 (7% *ee*), 18.0 mg + 75 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at $\delta = 0.04$] = 0.03, signal of major enantiomer appears at higher field. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9 H), 1.20 (d, $J = 6.8$ Hz, 12 H), 1.30−2.22 (2 m, 10 H), 3.91 (m, 2 H), 4.91 (s, 1 H), 5.55 (t, $J = 6.4$ Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -2.3$ (CH_3), 21.5 (CH_3), 27.2 (CH_2), 27.6 (CH_2), 28.8 (CH_2), 31.4 (CH_2), 33.1 (CH_2), 46.3 (CH), 75.3 (CH), 125.5 (CH), 143.3 (C_q), 156.0 (C=O). IR (film): ṽ [cm^{-1}] = 1701 ν(C=O).

(2-Methyl-1-cyclopentenyl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19d): As described under GP1, **11d** (120 mg, 0.50 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (180 min) and quenched with TMSCl. Yield: 109 mg (70%) colourless oil. R_F = 0.66 (PE/Et_2O, 4:1). $[\alpha]_D^{20}$ = +4.0 (*c* = 1.02, $CHCl_3$). Shift experiment: *er* 85:15 (70% *ee*), 4.0 mg + 10 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ(3 H at δ = 1.68) = 0.28, signal of major enantiomer appears at lower field. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.06 (s, 9 H), 1.21 (d, *J* = 6.7 Hz, 12 H), 1.68 (s, 3 H), 1.75 (m_c, 2 H), 2.26−2.40 (m, 4 H,), 3.91 (br. s, 2 H), 5.41 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.5 (CH_3), 14.6 (CH_3), 21.1 (CH_3), 22.0 (CH_2), 34.7 (CH_2), 38.6 (CH_2), 45.8 (CH), 68.1 (CH), 131.5 (C_q), 133.5 (C_q), 156.1 (C=O). IR (film): ṽ [cm^{-1}] = 1694 ν(C=O). $C_{17}H_{33}NO_2Si$ (311.53): calcd. C 65.54, H 10.68, N 4.50, found C 65.41, H 10.76, N 4.70.

(2-Methyl-1-cyclohexenyl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19e): As described under GP1, **11e** (177 mg, 0.70 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (120 min) and quenched with TMSCl. Yield: 141 mg (88%) colourless oil. R_F = 0.74 (PE/Et_2O, 9:1). $[\alpha]_D^{20}$ = −12.0 (*c* = 0.54, $CHCl_3$). Shift experiment: *er* 92.5:7.5 (85% *ee*), 35 mol % Eu(hfc)$_3$ in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 1.15 (d, *J* = 6.9 Hz, 2 H), 1.42−155 (m, 4 H), 1.60 (s, 2 H), 1.75−2.00 (m, 4 H), 3.85 (br. s,2 H), 5.46 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.2, 19.7, 21.0, 22.96, 23.02, 26.7, 32.1, 45.7, 70.5, 126.1, 128.7, 155.9. $C_{18}H_{35}NO_2Si$ (325.56): calcd. C 66.41, H 10.84, N 4.30, found C 66.49, H 10.83, N 4.71.

(2-Methyl-1-cycloheptenyl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19f): As described under GP1, **11f** (134 mg, 0.50 mmol) was deprotonated with *sec*-butyllithium/(−)-sparteine (5 min) and quenched with TMSCl. Yield: 132 mg (78%) colourless oil. R_F = 0.39 (PE/EtOAc, 20:1). $[\alpha]_D^{20}$ = −20.8 (*c* = 0.65, $CHCl_3$). Shift experiment: *er* 90.5:9.5 (81% *ee*), 11.4 mg + 80 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at δ = 0.02] = 0.07, signal of major enantiomer appears at higher field. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 1.19 (br. s, 12 H), 1.28−1.82 (m, 6 H), 1.75 (s, 3 H), 2.00−2.21 (m, 4 H), 3.75 [4.08] (br. s, 2 H), 5.46 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.4 (CH_3), 20.7 [21.3] (CH_3), 21.4 (CH_3), 25.9 (CH_2), 27.2 (CH_2), 29.9 (CH_2), 32.8 (CH_2), 36.5 (CH_2), 45.2 [46.4] (CH), 71.1 (CH), 133.5, (C_q), 134.2 (C_q), 156.2 (C=O). IR (film): ṽ [cm^{-1}] = 1691 ν(C=O). $C_{19}H_{37}NO_2Si$ (339.59): HR-MS: calcd. 339.25937, found 339.26040.

(2-Methyl-1-cyclooctenyl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19g): As described under GP1, **11g** (141 mg, 0.50 mmol) was deprotonated with *sec*-butyllithium/(−)-sparteine (10 min) and quenched with TMSCl. Yield: 121 mg (68%) colourless oil and 20 mg (14%) of starting compound was recovered. R_F = 0.20 (PE/Et_2O, 40:1). $[\alpha]_D^{20}$ = −11.2 (*c* = 0.56, $CHCl_3$). Shift experiment: *er* 87.5:12.5 (75% *ee*), 16.7 mg + 100 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at δ = 0.03] = 0.12, signal of major enantiomer appears at higher field. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9 H), 1.18 [1.20] (d, *J* = 6.8 Hz, 12 H), 1.23−1.62 (m, 8 H), 1.70 (s, 3 H), 1.84−2.40 (m, 4 H), 3.90 (br. s, 2 H), 5.47 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.3 (CH_3), 21.0 (CH_3), 23.0 (CH_3), 28.0 (CH_2), 28.9 (CH_2), 29.4 (CH_2), 30.9 (CH_2), 33.1 (CH_2), 34.8 (CH_2), 47.8 (CH), 73.1 (CH), 121.2 (C_q), 133.4 (C_q), 157.8 (C=O). IR (film): ṽ [cm^{-1}] = 1696 ν(C=O), 1654 ν(C=C). $C_{20}H_{39}NO_2Si$ (353.61): calcd. C 67.93, H 11.12, N 3.96, found C 68.09, H 11.33, N 4.48.

(5,5-Dimethyl-1-cyclopentenyl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19h): As described under GP1, **11h** (152 mg, 0.60 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (40 min) and quenched with TMSCl. Yield: 48 mg (25%) colourless oil and 76 mg (50%) of **11h**. R_F = 0.65 (PE/Et_2O, 4:1). $[\alpha]_D^{20}$= +4.1 (*c* = 0.54, $CHCl_3$. Shift experiment: *er* 57:43 (14% *ee*), 22.1 mg + 10 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at δ = 0.05] = 0.03, signal of major enantiomer appears at higher field. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 0.99 (s, 3 H), 1.01 (s, 3 H), 1.18[1.16] (d, *J* = 6.8 Hz, 12 H), 1.54−1.72 (m, 2 H), 2.22 (m_c, 2 H), 3.87 (sept, *J* = 6.8 Hz, 2 H), 5.21 (m, 1 H), 5.55 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.4 (CH_3), 21.1 (CH_3), 26.5 (CH_3), 27.5 (CH_3), 29.5 (CH_2), 40.5 (CH_2), 45.8 (CH), 46.3 (C_q), 64.7 (CH), 127.3 (CH), 150.2 (C_q), 155.4 (C=O). IR (film): ṽ [cm^{-1}] = 1690 ν(C=O), 1634 ν(C=C). $C_{18}H_{35}NO_2Si$ (325.56): calcd. C 66.41, H 10.84, N 4.30, found C 66.02, H 10.96, N 4.42.

(+)-(1,4-Dioxaspiro[4.4]non-6-en-6-yl)(trimethylsilyl)methyl *N*,*N*-Diisopropylcarbamate (19i): As described under GP1, **11i** (170 mg, 0.60 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (10 min) and quenched with TMSCl. Yield: 138 mg (64%) colourless oil and 33 mg (19%) of **11i**. R_F = 0.61 (PE/EtOAc, 2:1). $[\alpha]_D^{20}$ = +6.8 (*c* = 1.02, $CHCl_3$). Shift experiment: *er* 70:30 (40% *ee*), 16.1 mg + 35 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ[Si(CH_3)$_3$ at δ = 0.05] = 0.16, signal of major enantiomer appears at higher field. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 1.18 (d, *J* = 6.8 Hz, 12 H), 1.94 (ddd, *J* = 13.5, *J* = 6.5, *J* = 5.5 Hz, 1 H), 2.02 (ddd, *J* = 13.5, *J* = 7.1, *J* = 6.3 Hz, 1 H), 2.30−2.33 (m, 2 H), 3.78−4.04 (m, 6 H), 5.21 (dd, *J* = 1.5, *J* = 2.9, 1 H), 5.83 (td, *J* = 2.5, *J* = 1.5, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = −2.7 (CH_3), 21.1 (CH_3), 28.1 (CH_2), 35.7 (CH_2), 45.8 (CH), 64.6 (CH_2), 64.9 (CH_2), 65.3 (CH), 119.5 (C_q), 131.5 (CH), 142.5 (C_q), 155.2 (C=O). IR (film): ṽ [cm^{-1}] = 1690 ν(C=O). $C_{18}H_{33}NO_4Si$ (355.54): calcd. C 60.81, H 9.35, N 3.94, found C 60.65, H 9.53, N 4.08.

(−)-(7-Methyl-1,4-dioxaspiro[4.5]dec-7-en-8-yl)(trimethylsilyl)methyl-*N*,*N*-Diisopropylcarbamate (19j): As described under GP1, **11i** (249 mg, 0.80 mmol) was deprotonated with *n*-butyllithium/(−)-sparteine (10 min) and quenched with TMSCl. Yield: 211 mg (69%) colourless oil. R_F = 0.77 (PE/EtOAc, 1:1). $[\alpha]_D^{20}$ = −9.3 (*c* = 0.53, $CHCl_3$). Shift experiment: *er* 88:12 (76% *ee*), 15.9 mg + 5 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ(3 H at δ = 1.66) = 0.07, signal of major enantiomer appears at lower field. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 1.19 (d, *J* = 6.9 Hz, 12 H), 1.57−1.78 (m, 5 H), 2.02−2.31 (m, 4 H), 3.84−3.99 (m, 6 H), 5.55 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.2 (CH_3), 19.5 (CH_3), 21.1 (CH_3), 25.8 (CH_2), 31.4 (CH_2), 42.1 (CH_2), 45.8 (CH), 64.2 (CH_2), 70.0 (CH), 108.1 (C_q), 123.8 (C_q), 128.5 (C_q), 155.8 (C=O). IR (film): ṽ [cm^{-1}] = 1688 ν(C=O). $C_{20}H_{37}NO_4Si$ (383.60): calcd. C 62.62, H 9.72, N 3.65, found C 62.53, H 9.58, N 3.83.

(*R*)-(2-Methyl-1-cyclohexenyl)(methyldiphenylsilyl)methyl *N*,*N*-Diisopropylcarbamate [(*R*)-20]: As described under GP1, *n*-butyllithium (1.6 M, 1.88 mL, 3.0 mmol, 1.2 equiv.) was added to a solution of **11e** (633 mg, 2.50 mmol) and (−)-sparteine (703 mg, 3.0 mmol, 1.2 equiv.) in toluene (18 mL) at −78 °C and the mixture was stirred for 2 h at −78 °C, after which chloromethyldiphenylsilane (873 mg, 3.75 mmol) was added. After workup, the residue was purified by silica gel column chromatography (PE/Et_2O, 10:1) to afford the pure product (*R*)-**20**. Yield: 855 mg (76%) colourless oil. R_F = 0.41 (PE/Et_2O, 10:1). $[\alpha]_D^{20}$ = −19.1 (*c* = 0.67, $CHCl_3$), determination of the *ee* value failed. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 3 H), 1.16 (br. s, 12 H), 1.33 (s, 3 H), 1.36−1.63 (m, 4 H), 1.72−1.95 (m, 4 H), 3.82 (br. s, 2 H), 6.12 (s, 1 H), 7.25−7.64 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.4 (CH_3), 19.7 (CH_3), 20.9 (CH_3), 22.95 (CH_2), 22.97 (CH_2), 26.8 (CH_2), 32.1 (CH_2), 45.8 (CH), 68.5 (CH), 127.50 (C_q), 127.53 (CH), 127.7 (CH), 127.8 (C_q), 129.3 (CH), 129.4 (CH), 135.2 (CH), 135.3 (CH), 135.3 (C_q), 155.5 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1691 ν(C=O).

(*R*)-(2-Methyl-1-cyclohexenyl)(methyldiphenylsilyl)methanol [(*R*)-21]: DIBALH in hexane (1 M, 18.7 mL, 18.7 mmol, 10 equiv.) was added to a solution of (*R*)-**21** (842 mg, 1.87 mmol, $[\alpha]_D^{20} = -19.1$) in THF (10 mL), cooled to 0 °C, and the mixture was stirred for 15 h at room temperature. After this had again been cooled to 0 °C, methanol (2 mL) was added followed by satd. aq. NH_4Cl (10 mL) and 2 N aq. HCl (50 mL). The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. Flash chromatography (PE/Et_2O, 4:1) of the crude product gave 525 mg (87%) of **11f** as a colourless oil. $R_F = 0.25$ (PE/Et_2O, 4:1). $[\alpha]_D^{20} = -11.1$ ($c = 0.95$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.60 (s, 3 H), 1.01−2.23 (m, 11 H), 5.01 (s, 1 H), 7.27−7.64 (m, 10 H). IR (film): $\tilde{\nu}$ [cm^{-1}] = 3445 ν(OH).

(*R*)-(2-Methyl-1-cyclohexenyl)(methyldiphenylsilyl)methyl *N*-Isopropylcarbamate [(*R*)-22]: A solution of (*R*)-**21** (113 mg, 0.35 mmol, $[\alpha]_D^{20} = -11.1$), isopropyl isocyanate (98 μL, 1.0 mmol, 2.86 equiv.) and DMAP (5 mg, 0.04 mmol, 10 mol %) was heated for 24 h at 50 °C. The solution was allowed to cool to room temperature and was poured into a mixture of Et_2O (10 mL) and 2 N aq. HCl (10 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. Flash chromatography (PE/Et_2O, 4:1) of the crude product gave 129 mg (90%) of (*R*)-**22** as a colourless solid. $R_F = 0.20$ (PE/Et_2O, 4:1). M.p. 102−103 °C (PE). $[\alpha]_D^{20} = -19.8$ ($c = 0.42$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.60 (s, 3 H), 1.07 (d, J = 6.4 Hz, 6 H), 1.23−1.99 (m, 11 H), 3.74 (br. s, 1 H), 4.33 (br. s, 1 H), 6.02 (s, 1 H), 7.20−7.69 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.75 (CH_3), 19.6 (CH), 22.9 (CH_2), 22.9 (CH_2), 23.1 (CH_3), 26.6 (CH_2), 32.1 (CH_2), 43.2 (CH), 68.7 (CH), 127.6 (CH), 127.7 (CH), 128.2 (C_q), 129.4 (CH), 129.4 (CH), 135.0 (CH), 135.1 (CH), 135.3 (C_q), 156.1 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3308 ν[N(H)], 1702/1680 ν[(C=O)/amide I], 1534 (amide II). $C_{25}H_{33}NO_2Si$ (407.62): calcd. C 73.66, H 8.16, N 3.44, found C 73.56, H 8.44, N 3.29.

X-ray Crystal Structure Analysis of (*R*)-22: Colourless crystal 0.40 × 0.05 × 0.05 mm, a = 12.216(2), b = 12.497(2), c = 14.168(1) Å, α = 83.99(1), β = 87.88(1), γ = 60.95(2)°, V = 1880.2(5) Å^3, $\rho_{calcd.} = 1.080$ g cm^{-3}, μ = 9.61 cm^{-1}, empirical absorption correction by ψ scan data (0.700 ≤ T ≤ 0.954), Z = 3, triclinic, space group $P1$ (no. 1), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 7988 reflections collected (±h, ±k, +l), [(sinθ)/λ] = 0.62 Å^{-1}, 7988 independent and 5734 observed reflections [$I \geq 2\,\sigma(I)$], 806 refined parameters, R = 0.045, wR^2 = 0.112, max. residual electron density 0.25 (−0.24) e Å^{-3}, Flack parameter −0.07(3), contains three almost identical molecules in the unit cell, connected by hydrogen bonds, hydrogen atoms calculated and refined as riding atoms.[32]

(*R*)-(2-Methyl-1-cyclohexenyl)(trimethylstannyl)methyl *N*,*N*-Diisopropylcarbamate [(*R*)-23a)] and [(1*Z*,2*S*)-2-Methyl-2-(trimethylstannyl)cyclohexylidene]methyl *N*,*N*-Diisopropylcarbamate [(*S*)-24a]: As described under GP1, *n*-butyllithium (1.6 M, 1.38 mL, 2.2 mmol) was added to a solution of **11e** (506 mg, 2.0 mmol) and (−)-sparteine (516 mg, 2.2 mmol) in 5 mL toluene at −78 °C. After this had been stirred for 2 h at −78 °C, chlorotrimethylstannane (1 M, 3.0 mL, 3.0 mmol) was added. Flash chromatography (PE/Et_2O, 100:1 to 10:1) of the crude product gave 107 mg (13%) of (*R*)-**23a**, 391 mg (47%) of (*S*)-**24a** and 37 mg of an unknown impurity.

(*R*)-23a: Colourless oil. $R_F = 0.60$ (PE/Et_2O, 10:1). $[\alpha]_D^{20} = +6.9$ ($c = 0.82$, $CHCl_3$). Shift experiment: *er* 83.7:16.3 (67% *ee*), 15.9 mg + 10.1 mol % Eu(hfc)$_3$ in C_6D_6, Δδ[Sn(CH_3)$_3$ at δ = 0.06] = 0.04, signal of major enantiomer appears at higher field. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 1.19[1.18] (d, J = 6.9 Hz, 12 H), 1.45−1.72 (m, 7 H), 1.74−2.25 (m, 4 H), 3.88 (br. s, 2 H), 5.41 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = (8.4 (CH_3), 19.2 (CH_3), 21.0 (CH_3), 23.0 (CH_2), 23.2 (CH_2), 27.3 (CH_2), 32.0 (CH_2), 45.9 (CH), 74.5 (CH), 122.9 (C_q), 130.0 (C_q), 156.1 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1674 ν(C=O). $C_{18}H_{35}NO_2Sn$ (416.19): calcd. C 51.95, H 8.48, N 3.37, found C 52.08, H 8.69, N 3.48.

(*R*)-24a: Amorphous solid. $R_F = 0.45$ (PE/Et_2O, 10:1). $[\alpha]_D^{20} = +15.3$ ($c = 0.15$, $CHCl_3$). Shift experiment: *er* 92.6:7.4 (85% *ee*), 20.5 mg + 20.4 mol % Eu(hfc)$_3$ in C_6D_6, Δδ[Sn(CH_3)$_3$ at δ = 0.06] = 0.05, signal of major enantiomer appears at lower field. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 0.99−1.83 (m, 6 H), 1.22[1.23] (d, J = 6.9 Hz, 12 H), 1.22 (s, 3 H), 1.83 (dm, J = 14.1 Hz, 1 H), 2.86 (dm, J = 14.1 Hz, 1 H), 3.92 (br. s, 2 H), 6.69 (m$_c$, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −9.0 (CH_3), 21.0 (CH_3), 24.7 (CH_3), 25.6 (CH_2), 25.6 (CH_2), 26.5 (CH_2), 35.5 (C_q), 40.2 (CH_2), 46.1 (CH), 126.9 (CH), 129.6 (C_q), 153.6 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1711 ν(C=O). $C_{18}H_{35}NO_2Sn$ (416.19): calcd. C 51.95, H 8.48, N 3.37, found C 52.07, H 8.31, N 3.17.

(*R*)-(2-Methyl-1-cyclohexenyl)(tributylstannyl)methyl *N*,*N*-Diisopropylcarbamate [(*R*)-23b] and [(1*Z*,2*S*)-2-Methyl-2-(tributylstannyl)cyclohexylidene]methyl *N*,*N*-Diisopropylcarbamate [(*S*)-24b]: As described under GP1, *n*-butyllithium (1.6 M, 2.75 mL, 4.4 mmol) was added to a solution of **11e** (957 mg, 3.78 mmol) and (−)-sparteine (1.03 g, 4.4 mmol, 1.16 equiv.) in 5 mL toluene at −78 °C. After this had been stirred for 2 h at −78 °C, chlorotributylstannane (1.95 g, 6.0 mmol, 1.6 equiv.) in toluene (2 mL) was added. Flash chromatography (PE/Et_2O, 100:1 to 10:1) of the crude product gave 497 mg (24%) of (*R*)-**23b** and 1.06 g (52%) of (*S*)-**24b**.

(*R*)-23b: Colourless oil. $R_F = 0.48$ (PE/Et_2O, 10:1). $[\alpha]_D^{20} = +14.4$ ($c = 0.48$, $CHCl_3$), determination of the *ee* value failed. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.80−0.88 (m, 15 H), 1.17[1.18] (d, J = 6.9 Hz, 12 H), 1.28 (m, 6 H), 1.35−1.70 (m, 10 H), 1.58 (s, 3 H), 1.76−2.21 (m, 4 H), 3.78[3.97] (br. s, 2 H), 5.55 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =10.5 (CH_3), 13.6 (CH_3), 19.3 (CH_3), 21.1 (CH_3), 23.0 (CH_2), 23.2 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 27.6 (CH_2), 29.1 (CH_2), 45.6 (CH), 73.9 (CH), 122.7 (C_q), 130.5 (C_q), 155.9 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1675 ν(C=O). $C_{27}H_{53}NO_2Sn$ (542.43): calcd. C 59.78, H 9.85, N 2.58, found C 59.50, H 10.04, N 2.42.

(*R*)-24b: Colourless oil. $R_F = 0.51$ (PE/Et_2O, 10:1). $[\alpha]_D^{20} = +12.0$ ($c = 0.74$, $CHCl_3$). Shift experiment: *er* 83.4:16.6 (67% *ee*), 19.5 mg + 30 mol % Eu(hfc)$_3$ in C_6D_6, Δδ(1 H at δ = 2.83) = 0.13, signal of major enantiomer appears at higher field. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.76−0.93 (m, 15 H), 1.13−1.85 (2 m, 33 H), 1.89 (d, J = 14.0 Hz, 1 H), 2.83 (d, J = 14.0 Hz, 1 H), 3.82 [4.02] (br. s, 2 H), 6.69 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.2 (CH_2), 13.6 (CH_3), 20.9 (CH_3), 25.2 (CH_3), 25.7 (CH_2), 25.8 (CH_2), 26.5 (CH_2), 27.6 (CH_2), 29.3 (CH_2), 37.5 (C_q), 40.9 (CH_2), 46.1 (CH), 126.7 (CH), 130.0 (C_q), 153.6 (C=O). IR (film): $\tilde{\nu}$ [cm^{-1}] = 1707 ν(C=O), 1653 ν(C=C). $C_{27}H_{53}NO_2Sn$ (542.43): calcd. C 59.78, H 9.85, N 2.58, found C 59.75, H 10.09, N 2.48.

(*R*)-(2-Methyl-1-cyclohexenyl)(triphenylstannyl)methyl *N*,*N*-Diisopropylcarbamate [(*R*)-23c] and [(1*Z*,2*S*)-2-Methyl-2-(triphenylstannyl)cyclohexylidene]methyl *N*,*N*-Diisopropylcarbamate [(*S*)-24c]: As described under GP1, *n*-butyllithium (1.6 M, 2.75 mL, 4.4 mmol) was added to a solution of **11e** (957 mg, 3.78 mmol) and (−)-sparteine (1.03 g, 4.4 mmol, 1.16 equiv.) in 5 mL toluene at −78 °C. After this had been stirred for 2 h at −78 °C, chlorotriphenylstannane (2.75, 6.0 mmol, 1.6 equiv.) in toluene (2 mL) was added. Flash chromatography (PE/Et_2O, 100:1 to 10:1) of the crude product gave 774 mg (34%) of (*R*)-**23b** and 928 mg (52%) of an inseparable mixture of (*S*)-**24b** and **11e**.

(*R*)-23c: Colourless solid. A first attempt to grow crystals at room temperature by diffusion of pentane into a solution of (*R*)-**23c** gave racemic material only. After removal of the racemic crystals, the same sample was stored at −30 °C for 2 d and then gave crystals suitable for single-crystal X-ray analysis. R_F = 0.46 (PE/Et_2O, 10:1). $[\alpha]_D^{20}$ = +48.9 (*c* = 0.93, $CHCl_3$), determination of the *ee* value failed. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.78−1.34 (2 m, 16 H), 1.57 (s, 3 H), 1.68−2.37 (2 m, 4 H), 3.75 (br. s, 2 H), 5.87 (s, 1 H), 7.25−7.35 (m, 9 H), 7.54−7.61 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (CH_3), 20.4 [21.1] (CH_3), 22.3 (CH_2), 22.7 (CH_2), 27.8 (CH_2), 32.1 (CH_2), 45.2 [46.1] (CH), 75.8 (CH), 125.8 (C_q), 128.0 (CH), 128.4 (CH), 129.0 (C_q), 137.3 (CH), 140.6 (C_q), 156.0 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1678 ν(C=O). $C_{33}H_{41}NO_2Sn$ (602.39): calcd. C 65.80, H 6.86, N 2.33, found C 65.66, H 6.65, N 2.16.

X-ray Crystal Structure Analysis of (*R*)-23c: Colourless crystal 0.20 × 0.20 × 0.10 mm, *a* = 8.085(1), *b* = 12.026(1), *c* = 31.722(2) Å, *V* = 3084.3(5) $Å^3$, $\rho_{calcd.}$ = 1.297 g cm^{-3}, μ = 67.92 cm^{-1}, empirical absorption correction by ψ scan data (0.344 ≤ *T* ≤ 0.550), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 3559 reflections collected (−*h*, −*k*, +*l*), [(sinθ)/λ] = 0.62 $Å^{-1}$, 3559 independent and 3284 observed reflections [*I* ≥ 2 σ(*I*)], 339 refined parameters, *R* = 0.043, wR^2 = 0.116, max. residual electron density 1.52 (−1.06) e $Å^{-3}$ close to Sn, Flack parameter 0.007(12), hydrogen atoms calculated and refined as riding atoms.[32]

{(1*Z*,2*S*)-2-[(*R*)-(4-Bromophenyl)(hydroxy)methyl]-2-methylcyclopentylidene}methyl *N*,*N*-Diisopropylcarbamate (27d): *n*-Butyllithium (1.6 M, 0.48 mL, 0.77 mmol, 1.1 equiv.) was added to a solution of **11d** (120 mg, 0.50 mmol) and (−)-sparteine (129 mg, 0.55 mmol, 1.1 equiv.) in toluene (5 mL) at −78 °C. The reaction mixture was stirred for 10 min, after which a precooled (−78 °C) solution of chlorotri(isopropoxy)titanium (Cl-TiPT) (390 mg, 1.5 mmol, 3.0 equiv.) was added. The dark reaction mixture was stirred for 1 h at −78 °C, and *p*-bromobenzaldehyde (278 mg, 1.5 mmol, 3.0 equiv.) in toluene (1 mL) was then added. Finally, the mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature. The yellow solution was poured into an ice-cooled mixture of Et_2O (10 mL) and 2 N aq. HCl (10 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (PE/EtOAc, 20:1) to give 61 mg (29%) **27d** as a colourless solid. Crystals suitable for single-crystal X-ray analysis were grown by diffusion of pentane into a solution of **27d** in Et_2O. R_F = 0.14 (PE/EtOAc, 10:1). $[\alpha]_D^{20}$ = +112.5 (*c* = 0.20, $CHCl_3$). Shift experiment: *er* 95.8:4.2 (92% *ee*), 4.1 mg + 10.5 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ(1 H at δ = 4.96) = 0.06, signal of major enantiomer appears at lower field. M.p. 116 °C (PE/EtOAc). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14−1.54 (m, 14 H), 1.38 (s, 3 H), 1.76−1.94 (m, 2 H), 2.16−2.38 (m, 2 H), 3.69 [4.24] (br. s, 2 H), 4.96 (s, 1 H), 6.95 (t, *J* = 1.9 Hz, 1 H), 7.26 (m, 2 H), 7.44 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (CH_3), 22.4 (CH_3), 23.5 (CH_2), 31.5 (CH_2), 36.0 (CH_2), 46.4 (CH), 50.4 (C_q), 76.4 (CH), 120.0 (C_q), 129.0 (CH), 129.5 (CH), 130.0 (C_q), 130.5 (CH), 140.5(C_q), 151.6 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3496 ν(OH), 1691 ν(C=O). $C_{21}H_{30}BrNO_3$ (424.37): calcd. C 59.43, H 7.13, N 3.30, found C 59.62, H 6.88, N 3.53.

X-ray Crystal Structure Analysis of 27d: Colourless crystal 0.40 × 0.25 × 0.15 mm, *a* = 13.758(2), *b* = 20.135(3), *c* = 7.671(1) Å, *V* = 2125.0(5) $Å^3$, $\rho_{calcd.}$ = 1.326 g cm^{-3}, μ = 27.84 cm^{-1}, empirical absorption correction by ψ scan data (0.402 ≤ *T* ≤ 0.680), *Z* = 4, orthorhombic, space group $Pna2_1$ (no. 33), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2338 reflections collected (−*h*, −*k*, +*l*), [(sinθ)/λ] = 0.62 $Å^{-1}$, 2338 independent and 2197 observed reflections [*I* ≥ 2 σ(*I*)], 241 refined parameters, *R* = 0.035, wR^2 = 0.103, max. residual electron density 0.39 (−0.57) e $Å^{-3}$, Flack parameter 0.02(2), hydrogen atoms calculated and refined as riding atoms.[32]

{(1*Z*,2*S*)-2-[(*R*)-(4-Bromophenyl)(hydroxy)methyl]-2-methylcyclohexylidene}methyl *N*,*N*-Diisopropylcarbamate (27e): In the same manner as described for **27d**, *n*-butyllithium (1.6 M, 0.48 mL, 0.77 mmol, 1.1 equiv.) was added dropwise to a solution of **11e** (177 mg, 0.70 mmol) and (−)-sparteine (180 mg, 0.77 mmol, 1.1 equiv.) in toluene (5 mL) at −78 °C. The reaction mixture was stirred for 10 min, after which precooled (−78 °C) Cl-TiPT in toluene (1 M, 2.1 mL, 2.1 mmol, 3.0 equiv.) was added. The dark mixture was stirred for 2 h at −78 °C, and *p*-bromobenzaldehyde (389 mg, 2.1 mmol, 3 equiv.) in toluene (1 mL) was then added. After workup, the residue was purified by flash chromatography (PE/EtOAc, 10:1) to give 107 mg (35%) **27d** as a colourless solid. Crystals suitable for single-crystal X-ray analysis were grown by diffusion of pentane into a solution of **27e** in Et_2O. R_F = 0.26 (PE/EtOAc, 10:1). $[\alpha]_D^{20}$= −46.3 (*c* = 0.44, $CHCl_3$). Shift experiment: *er* 93.6:6.4 (87% *ee*), 4.7 mg + 14.9 mol % Eu(hfc)$_3$ in $CDCl_3$, Δδ(1 H at δ = 5.02) = 0.39, signal of major enantiomer appears at lower field. M.p. 119−120 °C (PE/EtOAc). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82−1.92 (m, 18 H), 1.08 (s, 3 H), 2.07−2.33 (m, 2 H), 3.66 [4.17] (br. s, 2 H), 5.02 (s, 1 H), 6.95 (s, 1 H), 7.25 (m, 2 H), 7.44 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CH_3), 21.6 (CH_3), 21.9 (CH_2), 26.9 (CH_2), 29.3 (CH_2), 36.9 (CH_2), 44.6 (C_q), 45.9 [47.0] (CH), 74.2 (CH), 121.1 (C_q), 124.6 (C_q), 129.6 (CH), 130.5 (CH), 133.2 (CH), 139.1 (C_q), 152.4 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3453 ν(OH), 1680 ν(C=O). $C_{22}H_{32}BrNO_3$ (438.40): calcd. C 60.27, H 7.36, N 3.19, found C 60.25, H 7.55, N 3.11.

X-ray Crystal Structure Analysis of 27e: Colourless crystal 0.50 × 0.30 × 0.10 mm, *a* = 7.933(1), *b* = 11.157(1), *c* = 25.162(1) Å, *V* = 2227.1(4) $Å^3$, $\rho_{calcd.}$ = 1.308 g cm^{-3}, μ = 18.66 cm^{-1}, empirical absorption correction by SORTAV (0.456 ≤ *T* ≤ 0.835), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 0.71073 Å, *T* = 293 K, ω and scans, 8818 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 $Å^{-1}$, 4356 independent (R_{int} = 0.036) and 2989 observed reflections [*I* ≥ 2 σ(*I*)], 250 refined parameters, *R* = 0.041, wR^2 = 0.084, max. residual electron density 0.19 (−0.39) e $Å^{-3}$, Flack parameter 0.015(10), hydrogen atoms calculated and refined as riding atoms.[32]

(+)-{(1*Z*,2*SR*)-2-[(*RS*)-(4-Bromophenyl)(hydroxy)methyl]-2-methylcycloheptylidene}methyl *N*,*N*-Diisopropylcarbamate (27f): In the same manner as described for **27d**, *sec*-butyllithium (1.32 M, 0.64 mL, 0.84 mmol, 1.2 equiv.) was added dropwise to a solution of **11f** (188 mg, 0.70 mmol) and (−)-sparteine (196 mg, 0.84 mmol, 1.2 equiv.) in toluene (5 mL) at −78 °C. The mixture was stirred for 15 min, after which a precooled (−78 °C) solution of Cl-TiPT (657 mg, 2.52 mmol, 3.6 equiv.) in toluene was added. The dark reaction mixture was stirred for 2 h at −78 °C, and *p*-bromobenzaldehyde (194 mg, 1.05 mmol, 1.5 equiv.) in toluene (1 mL) was then added. After workup, the residue was purified by flash chromatography (PE/EtOAc, 20:1) to give 68 mg (22%) **27d** as a colourless solid. R_F = 0.08 (PE/EtOAc, 20:1). $[\alpha]_D^{20}$ = +34.4 (*c* = 0.22, $CHCl_3$). Shift experiment: *er* 74.9:25.1 (50% *ee*), 6.2 mg + 7.3 mol % $Eu(hfc)_3$ in $CDCl_3$, $\Delta\delta$(1 H at δ = 4.64) = 0.09, signal of major enantiomer appears at lower field. M.p. 166 °C (PE/EtOAc). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98−1.75 (m, 20 H), 1.37 (s, 3 H), 1.75−1.88 (m, 1 H), 1.94−2.07 (m, 1 H), 2.25 (s, 1 H), 3.68 [4.11] (br. s, 2 H), 4.64 (s, 1 H), 6.94 (s, 1 H), 7.20 (m_c, 2 H), 7.38 (m_c, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CH_3), 22.3 (CH_3), 23.6 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 32.0 (CH_2), 35.8 (CH_2), 46.5 (CH), 46.5 (C_q), 78.9 (CH), 121.1 (C_q), 128.4 (C_q), 129.8 (CH), 130.4 (CH), 135.2 (CH), 140.0 (C_q), 152.0 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3445 ν(OH), 1691 ν(C=O), 1653 ν(C=C). $C_{23}H_{34}BrNO_3$ (452.43): calcd. C 61.06, H 7.57, N 3.10, found C 61.88, H 7.73, N 2.84.

(+)-{(1*Z*,2*SR*)-2-[(*RS*)-(4-Bromophenyl)(hydroxy)methyl]-2-methylcyclooctylidene}methyl *N*,*N*-Diisopropylcarbamate (27g): In the same manner as described for **27d**, *sec*-butyllithium (1.32 M, 0.64 mL, 0.84 mmol, 1.2 equiv.) was added dropwise to a solution of **11g** (197 mg, 0.70 mmol) and (−)-sparteine (196 mg, 0.84 mmol, 1.2 equiv.) in toluene (5 mL) at −78 °C. The reaction mixture was stirred for 15 min, after which a precooled (−78 °C) solution of Cl-TiPT (657 mg, 2.52 mmol, 3.6 equiv.) in toluene was added. The dark mixture was stirred for 2 h at −78 °C, and *p*-bromobenzaldehyde (194 mg, 1.05 mmol, 1.5 equiv.) in toluene (1 mL) was then added. After workup, the residue was purified by flash chromatography (PE/EtOAc, 20:1) to give 66 mg (21%) **27d** as a colourless solid. R_F = 0.12 (PE/EtOAc, 20:1). $[\alpha]_D^{20}$ = +6.8 (*c* = 0.19, $CHCl_3$). Shift experiment: *er* 68.3:31.7 (37% *ee*), 6.0 mg + 7.8 mol % $Eu(hfc)_3$ in $CDCl_3$, $\Delta\delta$(1 H at δ = 4.40) = 0.15, signal of major enantiomer appears at lower field. M.p. 66 °C (PE/EtOAc). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03−1.95 (m, 23 H), 1.27 (s, 3 H), 2.08−2.20 (m, 1), 2.22 (br. s, 1 H), 3.65 [4.08] (br. s, 2 H), 4.40 (s, 1 H), 6.93 (s, 1 H), 7.19 (m_c, 2 H), 7.38 (m_c, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (CH_3), 20.8 (CH_3), 24.7 (CH_2), 25.0 (CH_2), 26.3 (CH_2), 29.4 (CH_2), 31.3 (CH_2), 33.9 (CH_2), 46.1 (C_q), 46.5 (CH), 79.2 (CH), 121.2 (C_q), 126.9 (C_q), 130.0 (CH), 130.4 (CH), 136.6 (CH), 139.6 (C_q), 152.3 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3462 ν(OH), 1693, ν(C=O), 1654 ν(C=C). $C_{24}H_{36}BrNO_3$ (466.45): calcd. C 61.80, H 7.78, N 3.00, found C 61.54, H 7.81, N 2.83.

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