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Stereoselective Synthesis of Hexahydroisobenzofuran-4(1*H*)-ones from Chiral Substituted Cyclohex-2-enyl Carbamates via Asymmetric Homoaldol Reaction and THF Cyclocondensation

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Dedicated to Professor Peter Welzel on the occasion of his 70th birthday

Keywords: Asymmetric synthesis / Heterocycles / Metallated allyl carbamates / Homoaldol reactions / Tetrahydrofuran synthesis

The diastereofacial selectivity of the homoaldol reaction of metalated substituted cyclohex-2-enyl carbamates with aldehydes is controlled by the nature of the metal complex. Allyllithiums yield *syn*-configured products whereas transmetallation to $Ti(NEt_2)_3$ gives access to *anti*-configured 3-(1-hydroxyalkyl)cyclohexenes. The *syn*-configured homoaldol products were transformed into annulated *all-cis*-tetrahydrofurans by Lewis acid-mediated cyclocondensation with aldehydes. Analogous *cis,trans,cis*-substituted hexahydroisobenzofuran-4(1*H*)-ones, the core structure of many biologically active natural products, were synthesized starting from *anti*-configured homoaldol products. The configurations of the products were determined by ^1H NMR coupling constants, nOe-studies, and X-ray crystal structure analysis.

Introduction

The eunicellin and briarelin diterpenes,[1] such as sclerophytin A (**1a**)[2] or briarelin E (**1b**)[3] have a tetra-C-substituted hydroisobenzofuran core within the cyclic framework. Several strategies for the synthesis of these important structures have recently been published.[4] In the preceeding paper[5] we reported a highly stereocontrolled synthesis of simpler *all-cis*-hexahydroisobenzo-furan-4(1*H*)-ones which is based on the asymmetric deprotonation[6] of cyclohex-2-enyl *N*,*N*-diisopropylcarbamate, its homoaldol reaction with aldehydes,[7] and subsequent cyclocondensation with aldehydes[8] (Figure 1).

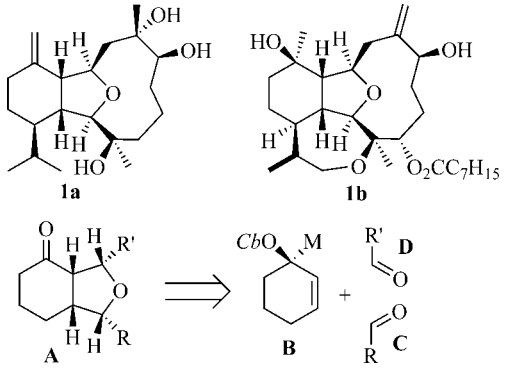

Figure 1. Sclerophytin A (**1a**), briarelin E (**1b**) and synthesis of *all-cis*-hexahydroisobenzofuran-4(1*H*)-ones **A** from metalated cyclohex-2-enyl carbamates **B**.

One crucial feature is the question whether it is possible to construct a 1,3-*cis*-3,3a-*trans*-3a,7a-*cis*-tetrasubstituted hexahydroisobenzofuran-4(1*H*)-one instead of the *all-cis*-substituted tetrahydrofuran moiety.

We now investigated the homoaldol reaction and tetrahydrofuran cyclocondensation of substituted cyclohex-2-enyl carbamates **2** and **3** (Figure 2), which were previously found to be easily lithiated with retention of the configuration as shown in a study of lithiation-stannylation reactions.[6]

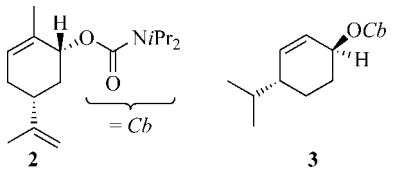

Figure 2. Investigated substituted cyclohex-2-enyl *N*,*N*-diisopropylcarbamates.

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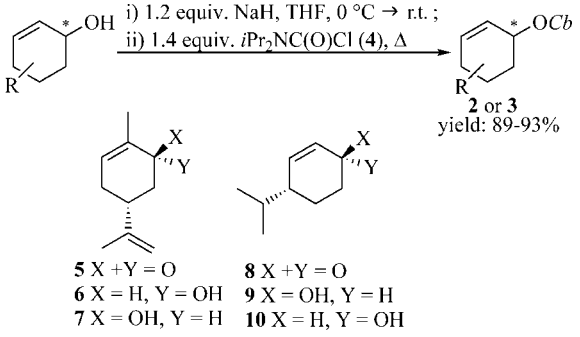
Results and Discussion

Synthesis of the Carbamates 2 and 3

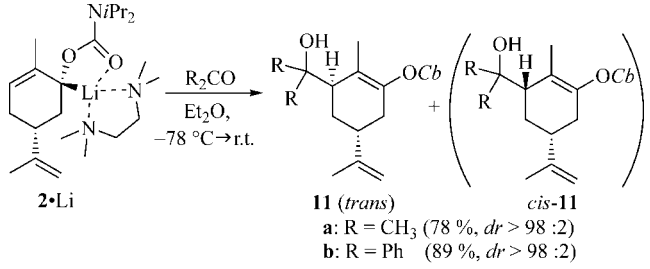
Carbamates **2** and **3** were obtained from the corresponding alcohols by the usual method via acylation of the sodium alcoholates with *N*,*N*-diisopropylcarbamoyl chloride (**4**) (Scheme 1).[9] (5*R*)-*cis*-Carveol (**6**) is readily available by reduction of commerically available (*R*)-(–)-carvone (**5**).[10] The *cis*-isomer **2** (99% *ee*) was isolated after carbamoylation and chromatography. Reduction of (*R*)-(–)-crypton (**8**) by $LiAlH_4$ afforded a mixture (80:20) of *trans*-(1*S*,4*R*)- and *cis*-(1*R*,4*R*)-4-isopropyl-cyclohex-2-enol (**9** and **10**).[11] Their carbamates **3** (*trans*) and *cis*-**3** were obtained in stereoisomerically pure form after chromatography.



Scheme 1. Carbamoylation of cyclohex-2-en-1-ols.

Lithiation and Homoaldol Reactions

We previously reported that the cyclohex-2-enyl carbamates **2** and **3** are deprotonated by means of alkyllithium/diamine with retention of the configuration to form configurationally stable allyllithiums, which reacted stereospecifically in an *anti*-S_E'-process with tin-electrophiles.[6] Our actual investigations show, that the reaction of the lithium intermediate **2**·Li with acetone or benzophenone affords the pure *trans*-homoaldol products **11a** or **11b**, respectively (Scheme 2). The stereochemistry of the subsequent carbonyl addition is determined by the configuration of the metal-bearing carbon atom, proceeding in a strict suprafacial manner, which also is supported by the steric shielding of the "rear face" by the bulky isopropenyl group and the axial protons in 4 and 6 position.



Scheme 2. Homoaldol reaction of **2**·Li with ketones.

The configuration of **11b** was determined by an X-ray crystal structure analysis (Figure 3).[12,13] **11a** is also *trans*-configured as determined by comparison of the coupling pattern of 3-H, 4-H_{ax}, and 4-H_{eq} with that of **11b**. The small axial-equatorial coupling constants observed at the 4-H proton $^3J_{3,4ax}$ = 5.0 Hz (**11a**) and 4.8 Hz (**11b**) support the *trans* substitution.

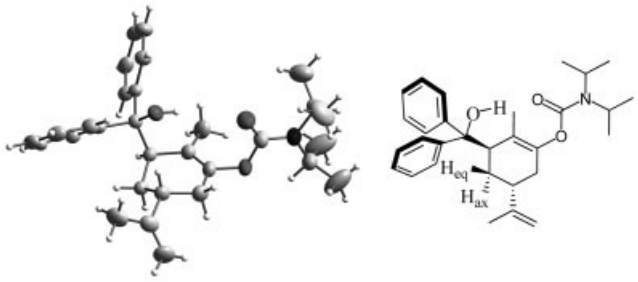
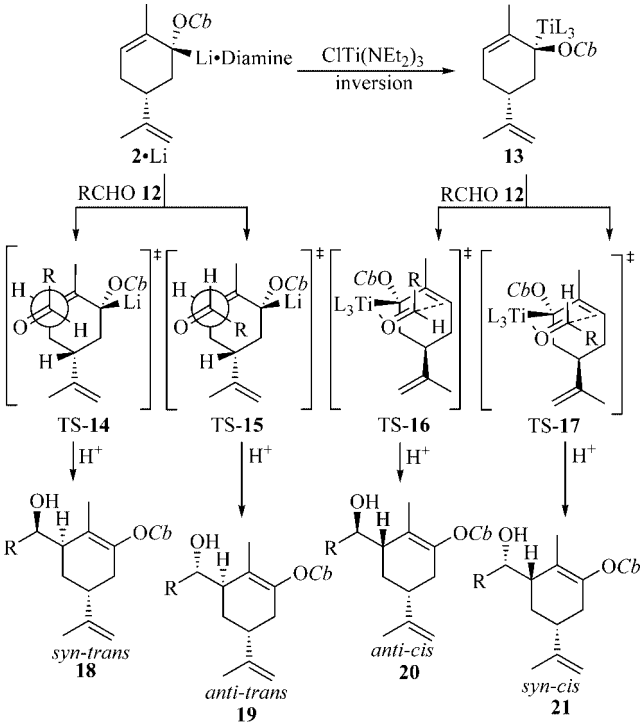


Figure 3. Solid state structure of the benzophenone adduct **11b**.[12,13]

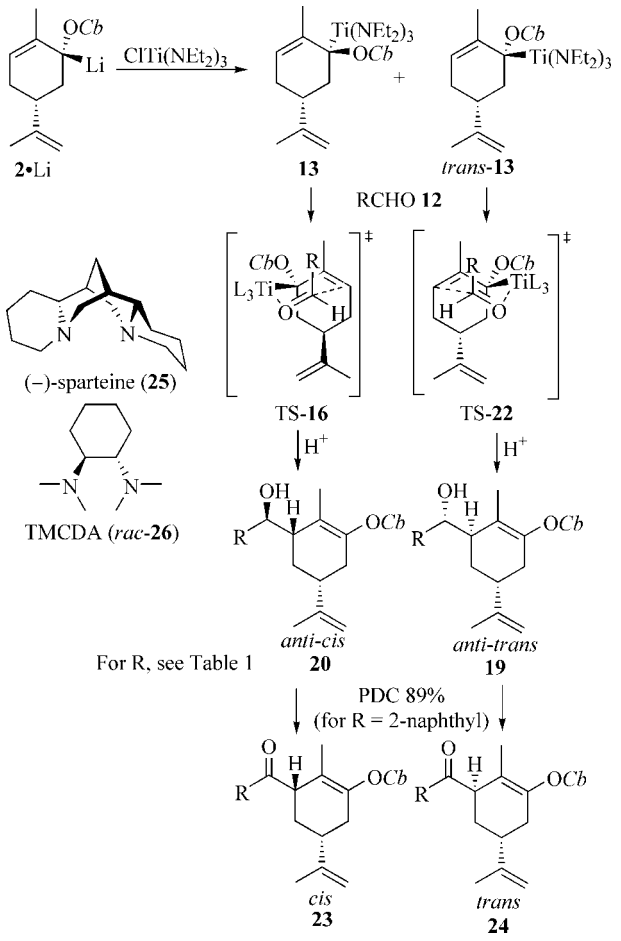
With naphthalene-2-carbaldehyde (**12a**) and cyclohexanecarbaldehyde (**12b**) the *trans*-diastereoselectivity is maintained, but *syn*/*anti* mixtures of **18a**/**19a** (79%, 90:10) and **18b**/**19b** (71%, 75:25) were obtained, which could be separated by flash chromatography. The *syn*-*trans* configuration of **18a** was determined by nOe-experiments after conversion to the annulated tetrahydrofuran **35a** and by comparisation of the analytical data with those of the diastereomers which were obtained in the titanium-mediated reaction (vide infra).

Usually, lithium–titanium exchange inverts the configuration.[7,14] From the aldehyde addition of metalated **2** in principle four diastereomers can be formed (Scheme 3).



Scheme 3. Possible diastereomers **18**–**21** arising from the homoaldol reaction of **2**·Li with aldehydes.

Metal-exchange of lithium with $ClTi(NEt_2)_3$[15] in intermediate **2**·Li is expected to proceed as an antarafacial process to form **13** which subsequently reacts with aldehydes **12a**–**g** through a Zimmerman–Traxler transition state[16] leading to the *anti-cis* or *syn-cis* diastereomers **20** or **21**, respectively. The stereochemical pathway of the reaction of cyclic allyltitaniums with aldehydes or imines is not exclusively controlled by the 1,3-diaxial interactions of the substituents R of the aldehyde and the β-substituent of the allylmetal. Here steric interactions with the cycloalkene moiety are of great influence. Thus, many diversities are found in the literature for the diastereofacial selectivity, and a sure prediction is not available: 7-, 8- and nine-membered cyclic diisopropoxytitaniumallyl compounds have shown to yield *syn* products after addition of aldehydes, whereas a cyclohexenyltitanium afforded only a low (2:1) stereoselectivity in favor of the *syn* product.[17] In contrast, the reaction of a cyclooctenyltitanium species with imines yielded addition products with *anti*-configuration, which was explained by a six-membered chair-like transition state in which the imine substituent occupies an axial position.[18] An *anti* selectivity was also observed in the reaction of a cyclic six-membered β-silyloxy-substituted allyltitanium compound with aldehydes.[19] The reaction of **13** with several aldehydes **12a**–**g** yielded *anti-cis*-configured diastereomers **20a**–**g** in good yields, but these were accompanied by up to 20% of *anti-trans* diastereomers **19a**–**g** if the TMEDA complex of **2**·Li was the intermediate (Scheme 4, Table 1, for an example see Entry 3). These results can be explained by a highly ordered chair-like transition state TS-**16**, in which the substituent R has to occupy an axial position. Here, the – usually large – 1,3-diaxial interactions of the methyl group and substituent R have to be smaller than the severe interactions of R with the cyclohexene moiety. A twist-boat-like transition state can not be excluded and would also explain the simple diastereoselectivity.[20,21] The formation of the minor diastereomers **19** via TS-**22** is the result of a not completely stereospecific metal exchange, presuambly due to steric interactions with the isopropenyl group. We increased the steric demand of the diamine ligand by applying (–)-sparteine (**25**) or *rac-trans*-1,2-bis(dimethylamino)cyclohexane (TMCDA, *rac*-**26**) in order to hinder the attack of the titanium reagent from the "upper face". TMCDA (*rac*-**26**) gave the best stereospecifities with a diastereoselectivity of up to 95:5 (Table 1; Entries 5–11).



Scheme 4. Mechanism of the titanium-mediated homoaldol reactions of **2**.

The observed *anti*-selectivity even in the *trans*-series is a hint for a complete metal exchange. The optimization reactions were performed using benzaldehyde, which afforded inseparable mixtures of **20c/19c** (R = Ph), all other diastereomeric pairs **20/19** could be separated by flash chromatography. A mixture of separable diastereomers **20a** and **19a** (R = 2-naphthyl) was oxidized with PDC in 89%

Table 1. Results of the homolaldol reactions of **2**.

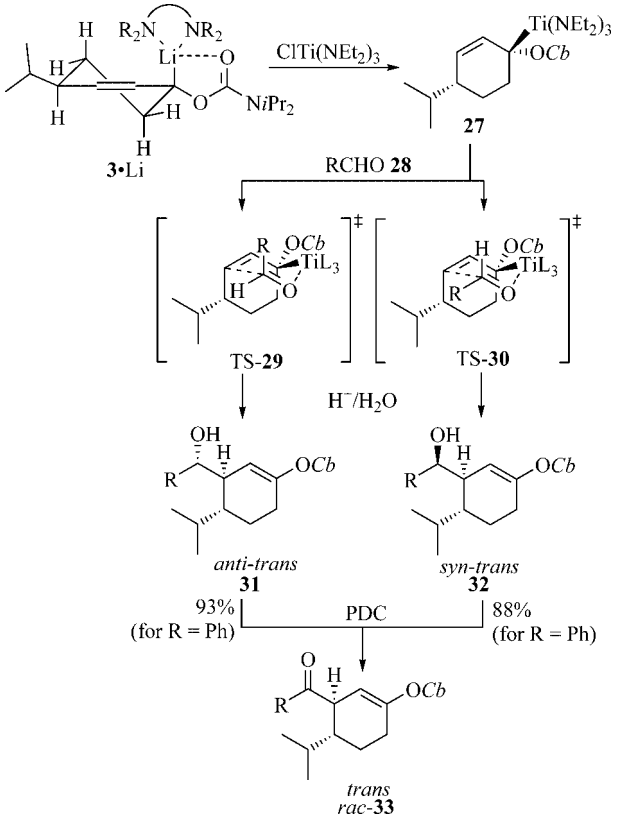
Entry	Diamine	$ClTi(NEt_2)_3$	Aldehyde, R	% Yield[a]	Product *dr*[b]
1	TMEDA	–	**12a**, 2-naphthyl	78	**18a/19a** = 90:10
2	TMEDA	–	**12b**, cyclohexyl	71	**18b/19b** = 75:25
3[c]	TMEDA	1.6 equiv.	**12c**, Ph	69	**20c/19c** = 80:20
4[c]	**25**	1.6 equiv.	**12c**, Ph	71	**20c/19c** = 87:13
5	*rac*-**26**	1.6 equiv.	**12c**, Ph	65	**20c/19c** = 95:5
6	*rac*-**26**	1.6 equiv.	**12a**, 2-naphthyl	81	**20a/19a** = 94:6
7	*rac*-**26**	2.0 equiv.	**12d**, 4-BrPh	58	**20d/19d** = 93:7
8	*rac*-**26**	1.6 equiv.	**12e**, vinyl	71	**20e/19e** = 95:5
9	*rac*-**26**	1.6 equiv.	**12f**, $C(=CH_2)(CH_3)$	80	**20f/19f** = 95:5
10	*rac*-**26**	1.6 equiv.	**12g**, $CH(CH_3)_2$	55	**20g/19g** = 93:7
11	*rac*-**26**	1.6 equiv.	**12b**, cyclohexyl	35	**20b/19b** = 91:9

[a] Isolated yields. [b] The diastereomeric ratio was determined from the crude product by GC (HP-5). [c] Other aldehydes yielded the same diastereoselectivity when applying these conditions.[22]

yield. The diastereomeric ratio remained; **20a** yielded the *cis*-configured ketone **23** and **19a** the *trans*-diastereomer **24**, which were easily separable by chromatography. The *cis* configurations of the *anti-cis* products **20** and of ketone **23** were secured by the large constants of the ^{1}H NMR coupling of 3-H and 4-H_{ax}, which were in the range of 10.2 Hz (**20d**) to 11.6 Hz (**23**). Starting from **20a** the hexahydroisobenzofuran-4(1*H*)-one **38a** was obtained, clearly establishing the *anti* configuration for the series of compounds **20** (see Scheme 9). The reversal of *syn* (M = Li) to *anti* (M = TiR_3) diastereoselectivity can be rationalized in terms of an open transition state in the lithium-method (TS-**14**, Scheme 3). Interestingly, the reaction of the six-membered cyclic trichlorotitaniumallyl carbamate with aldehydes afforded exclusively *syn*-homoaldol products.[5,23]

Homoaldol Reactions with 3

The lithiated *trans*-configured cryptyl carbamate **3**·Li was not subjected to a direct carbonyl addition. We expected that the isopropyl group in 4-position would hinder a *syn* addition of the carbonyl electrophile. But the preferred conformation of **3**·Li bears good conditions for an metal-exchange with inversion by $ClTi(NEt_2)_3$ (Scheme 5). The reaction of the allyltitanium intermediate *rac*-**27** with benzaldehyde afforded a solid product *rac*-**31a** from which crystals suitable for X-ray crystallographic analysis were obtained (Figure 4).[12,24] It conclusively established the anticipated *anti-trans*-configuration for this series of compounds.



Scheme 5. Transmetallation and homoaldol reactions of **3**.

Indeed, the transmetallation proceeded stereospecifically with inversion of the configuration, but besides the major *anti-trans* diastereomers **31**, small amounts of the *syn-trans* homoaldol products **32** were obtained (Table 2). The configuration of the minor diastereomers **32** was prooven by the PDC oxidation of *rac*-**31a** and *rac*-**32a** (R = Ph), which yielded the same *trans*-configured ketone *rac*-**33**. The energy difference of transition states **TS-29** and **TS-30** depends on the substituent R of the aldehyde and is not as large as observed for the transition states in the investigations of the carveyl carbamate **2**.[20]

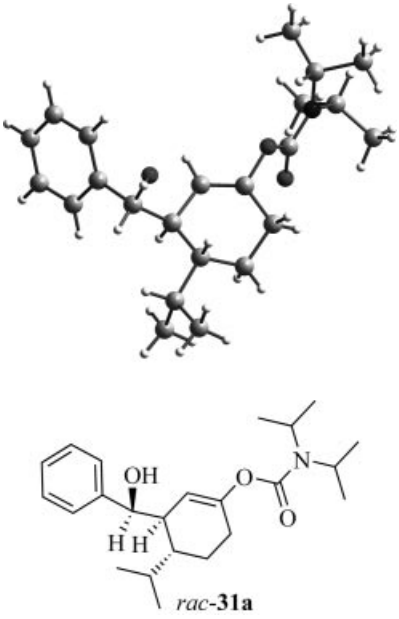
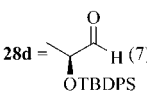


Figure 4. Solid state structure of *rac*-**31a**.[12,24]

Table 2. Results of the homoaldol reactions of carbamate **3**.

Entry	**3**	Aldehyde, R (equiv.)	% Yield[a]	*dr*
1	**3**	**28a** Ph (12)	63[b] (58)[c]	**31a**:**32a** = 93:7[d] (94:6)[c, d]
3	*rac*-**3**	**28b** C(=CH_2)(CH_3) (10)	83	*rac*-**31b**:*rac*-**32b** = 95:5[d]
2	*rac*-**3**	**28c** $CH(CH_3)_2$ (10)	62	*rac*-**31c**:*rac*-**32c** = 85:15[e]
4	**3**	**28d** =  H (7)[f]	45	**31d**:**32d** > 95:5[d]

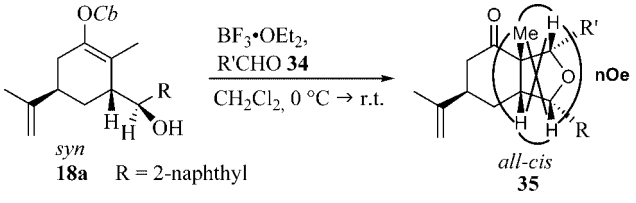
[a] Isolated yields. [b] 99% *ee* (HPLC). [c] Yield and *dr* of the racemate starting from *rac*-**3**. [d] The *dr* was determined from the crude product by GC (HP-5). [e] The *dr* was determined by ^{1}H NMR spectroscopy. [f] 59% of the chiral aldehyde **28d** were reisolated.

Good *dr*s are observed for arylic and vinylic aldehydes as well as for enantiopure TBDPS protected (*R*)-lactaldehyde **28a**[25] (Table 2, Entry 4). The major products **31** have a higher polarity than **32** and all diastereomeric pairs **31a–c**/**32a–c** are easily separable by flash chromatography. Unfortunately, the allyltitanium compound **27** seems to suffer partially from decomposition because the reaction with the

usual excess (3.0 equiv.) of the aldehyde afforded only low yields. Increasing the amount of the aldehyde to 7–12 equiv. resulted in acceptable yields (45–83%). As expected, the enantio-enrichments of **3** (99% *ee*) and **31a** (99% *ee*) are equal, indicating that the stereogenic centres of the alkyl-substituted cyclohex-2-enyl carbamates do not epimerize at all in the homoaldol reactions.

Cyclizations to Form Hexahydroisobenzofuran-4(1*H*)-ones

The *syn* homoaldol product **18a** (R = 2-naphthyl) was subjected to the Mukaiyama-type reaction conditions[8] by addition of 1.3 equiv. aldehyde **34** and BF_3·OEt_2 to yield the diastereomerically pure bicycles **35** in good yields (Scheme 6). As observed with unsubstituted cyclohex-2-enyl carbamate the *syn* configuration of the homoaldol product leads to *all-cis*-configured hexahydroisobenzofuran-4(1*H*)-ones,[5] which is not influenced by substituents on the cyclohexene ring. The configuration of the tetrahydrofuran moiety of **35b** (R = 2-naphthyl, R′ = Ph) was determined by nOe-experiments.

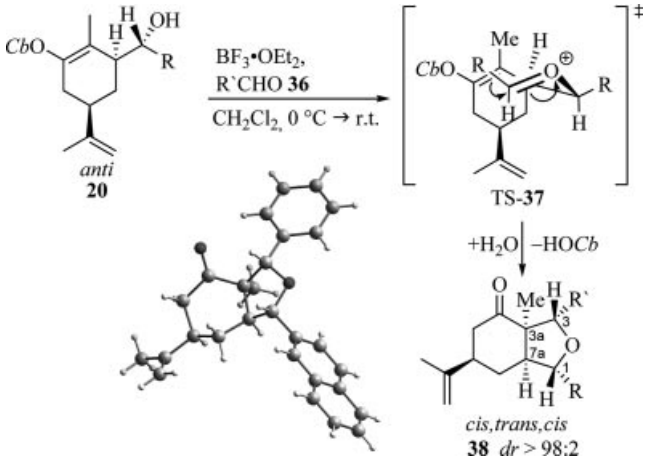


Scheme 6. Synthesis of *all-cis*-6-isopropenylhexahydroisobenzofuran-4(1*H*)-ones **35**.

When *anti-cis*-configured homoaldol products **20** were treated with BF_3·OEt_2 and aldehydes **36**, again diastereomerically pure bicycles were obtained (Scheme 7, Table 3). The X-ray crystal structure analysis[12,26] of solid compound **38a** established that the homoaldol products **20** formed hexahydroisobenzofuran-4(1*H*)-ones **38** with the desired 1,3-*cis*-3,3a-*trans*-3a,7a-*cis*-substitution pattern at the tetrahydrofuran moiety. The "carbamoyl-protected enolate" **37** is even nucleophilic enough to form the quaternary stereocentre at the carbon atom 3a.

The annulation proceeded in a *cis*-fashion, but the *anti*-configuration of the starting material afforded the (*E*)-oxonium ion TS-**37**, whose conformational bias lead to an *Si*,*Si*-attack. Aryl, α,β-unsaturated, and aliphatic aldehydes provided the diastereomerically pure products **38** in good yields (73–83%).

The condensation of *anti*-configured homoaldol product **31a** (R = Ph) with 4-bromobenzaldehyde (**39a**) resulted in the formation of diastereomerically pure tetrahydrofuran **41a** (Scheme 8, Table 4, Entry 1). As shown by HPLC measurements, the enantio-enrichment of the starting carbamate **3** (99% *ee*) remains unchanged after homoaldol reaction and THF cyclocondensation. The absolute configuration of the solid product **41a** was secured by X-ray structure analysis with anomalous dispersion.[12,27,28]

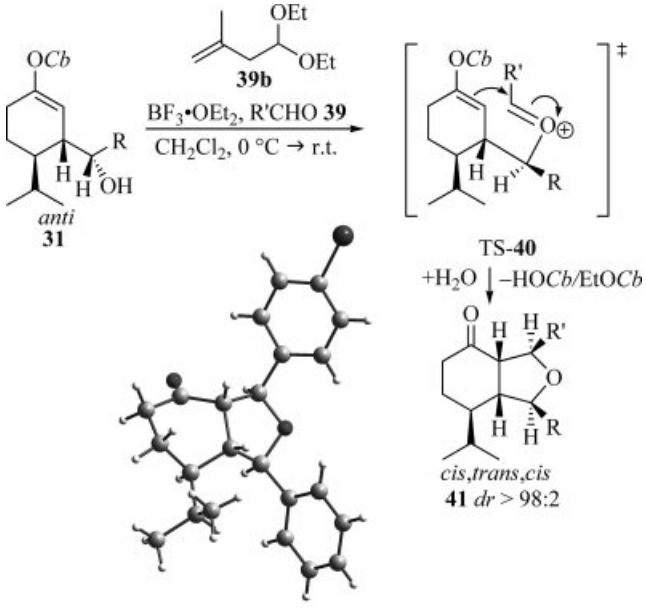


Scheme 7. Synthesis of 1,3-*cis*-3,3a-*trans*-3a,7a-*cis*-6-isopropenylhexahydroisobenzofuran-4(1*H*)-ones **38** and solid-state structure of **38a** (R = 2-naphthyl, R′ = Ph).[12,26]

Table 3. Synthesis of annulated *cis*,*trans*,*cis*-tetrahydrofurans **38**.

Entry	**20**	R	Aldehyde, R′	**38**	% Yield[a]
1	**20a**	2-naphthyl	**36a**, Ph	**38a**	73
2	**20d**	*p*-BrPh	**36b**, Me	**38b**	83
3	**20f**	$C(CH_2)Me$	**36c**, $CHMe_2$	**38c**	73
4	**20g**	$CHMe_2$	**36a**, Ph	**38d**	80
5	**20b**	cyclohexyl	**36a**, Ph	**38e**	83

[a] Isolated yields. *dr* >98:2 for all reactions as determined by GC (HP-5) from the crude product.



Scheme 8. Synthesis of 1,3-*cis*-3,3a-*trans*-3a,7a-*cis*-7-isopropylhexahydroisobenzofuran-4(1*H*)-ones **41** and solid-state structure of **41a** (R = Ph, R′ = 4-BrPh).[12,27,28]

The configuration of all four stereogenic centres at the tetrahydrofuran moiety arises from the stereoselective reduction of (*R*)-(–)-crypton, the *anti*-selective homoaldol reaction and the *cis*-selective annulation via the (*E*)-oxonium intermediate **40**. In order to obtain potential precursors for

Table 4. Results of the cyclocondensation reactions.

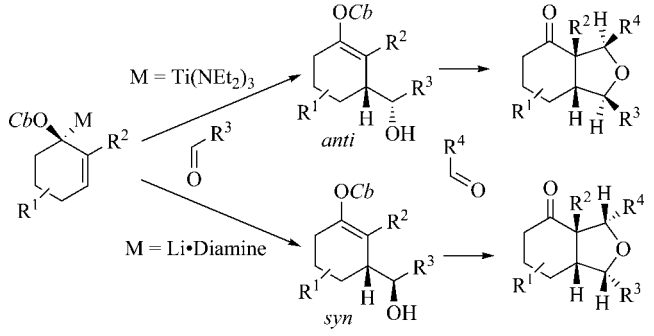
Entry	31	R	Aldehyde, R′	41	% Yield[a]
1	**31a**	Ph	**39a**, 4-Br-Ph	**41a**	91 (84)[b]
2	*rac*-**31a**	Ph	**39b**, $CH_2C(CH_2)Me$	*rac*-**41b**	70
3	*rac*-**31b**	$C(CH_2)Me$	**39b**, $CH_2C(CH_2)Me$	*rac*-**41c**	68

[a] Isolated Yields. *dr* >98:2 for all reactions as determined by GC (HP-5) from the crude product. [b] Yield of the racemate starting from *rac*-**31a**.

the soft coral diterpenes (Figure 1) we performed condensation reactions with 3-methyl-3-butenal diethyl acetal **48b**[29] (Table 4, Entries 2 and 3). The annulation proceeded again smoothly and stereoselectively to yield compounds *rac*-**41b** and *rac*-**41c** with an *exo*-double bound. The great variety of olefin and ketone reactions makes this compounds versatile chiral building blocks for further transformations.

Conclusions

We have shown, that the simple diastereoselectivity of the homoaldol reaction of metalated substituted cyclohex-2-enyl *N*,*N*-diisopropylcarbamates with aldehydes can be controlled by the nature of the applied metal (Scheme 9). The tris(diethylamino)titanium complexes led preferentially to *anti*-configured homoaldol products, whereas the lithium complexes afforded *syn* homoaldol products, which were also observed with trichlorotitaniumallyl carbamates.[5] Condensation of the *anti* products with aldehydes in a Mukaiyama-type reaction yielded *cis*,*trans*,*cis*-substituted hexahydroisobenzofuran-4(1*H*)-ones; *syn* homoaldol products afforded an *all*-*cis*-substitution pattern. This methodology provides a stereoselective approach to valuable building blocks in a two step sequence starting from metalated cyclohexenyl carbamates.



Scheme 9. Diversity in the stereoselective synthesis of 3-(1-hydroxyalkyl)cyclohexenes and hexahydroisobenzofuran-4(1*H*)-ones.

Experimental Section

General Remarks: Details concerning purification of solvents, reagents and a list of the applied analysis systems can be found in the preceeding puplication.[5]

Carbamoylation of Cyclohex-2-enols: A detailed procedure can be found in the preceeding paper.[5]

(1*R*,5*R*)-5-Isopropenyl-2-methylcyclohex-2-enyl *N*,*N*-Diisopropylcarbamate (2): NaH (3.84 g, 96 mmol, 1.2 equiv.), (5*R*)-carveol[10] (12.25 g, 80.5 mmol, **6**/**7** = 97:3) and **4** (18.3 g, 112 mmol, 1.4 equiv.) were refluxed in THF (170 mL) for 18 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:16 to 1:8) yielded 20.61 g (74 mmol, 92%)[30] **2**:*trans*-**2** = 97:3[31] as colorless liquids. **2**: t_R = 13.98 min (HP-5). R_F = 0.59 (Et_2O/PE = 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18, 1.20 (2 s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.49 (ddd, $^3J_{5,6A}$ = 12.0 Hz, $^2J_{6A,6B}$ = 11.7 Hz, 1 H, 6-H_A), 1.64 (s, 3 H, 5-C$(CH_2)(CH_3)$), 1.70 (s, 3 H, 2-CH_3), 1.95 (ddm, $^3J_{4A,5}$ = 12.0 Hz, $^2J_{4A,4B}$ = 17.1 Hz, 1 H, 4-H_A), 2.06 (dm, $^2J_{4A,4B}$ = 17.1 Hz, 1 H, 4-H_B), 2.19 (ddt, $^3J_{5,6B}$ = 5.9 Hz, $^2J_{6A,6B}$ = 11.7 Hz, 1 H, 6-H_B), 2.29 (tt, $^3J_{4A,5}$ = $^3J_{5,6A}$ = 12.0 Hz, $^3J_{4B,5}$ = $^3J_{5,6B}$ = 5.9 Hz, 1 H, 5-H), 3.88 (br. s, 2 H, *N*-*i*Pr CH), 4.69 (s, 2 H, 5-C$(CH_2)(CH_3)$), 5.40 (m, 1 H, 1-H), 5.52 (m, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0 (CH_3, 2-CH_3), 20.5 (CH_3, 5-C$(CH_2)(CH_3)$), 20.9 (CH_3, *N*-*i*Pr $(CH_3)_2$), 30.7 (CH_2, C-4), 34.5 (CH_2, C-6), 40.4 (CH, C-5), 45.6 (CH, *N*-*i*Pr CH), 73.6 (CH, C-1), 109.0 (CH_2, 5-C$(CH_2)(CH_3)$), 124.9 (CH, C-3), 134.1 (C_q, C-2), 148.5 (C_q, 5-C$(CH_2)(CH_3)$), 155.4 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 2999 (m), 2968 (s), 2930 (m) [$\nu(C_{aliph}$-H)], 1681 (s) [ν(C=O)], 1644 (s) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 302.21 [M + Na]$^+$. $C_{17}H_{29}NO_2$ (279.42): calcd. C 73.07, H 10.46, N 5.01; found C 72.86, H 10.40, N 4.90. $[\alpha]_D^{20}$ = +5.1 (*c* = 0.97, $CHCl_3$) at 99% *ee*; HPLC Chiralcel OD-H (4.6×250 mm), λ = 200 nm, *i*PrOH:*n*-hexane = 1:2000, 1.0 mL/min, 8.98 min (*ent*-**2**), 13.03 min (**2**). *rac*-**2** was prepared by mixing equal amounts of **2** and *ent*-**2**, which was prepared from (*S*)-(+)-carvon.

(1*S*,4*R*)-4-Isopropylcyclohex-2-enyl *N*,*N*-Diisopropylcarbamate (3): NaH (370 mg, 9.24 mmol, 1.2 equiv.), (4*R*)-cryptol[11] (1.080 g, 7.70 mmol, **9**/**10** = 80:20) and **4** (1.38 g, 10.8 mmol, 1.4 equiv.) were refluxed in THF (25 mL) for 3.5 h. Purification and separation of the diastereomers by FCC (Et_2O/PE = 1:12) yielded 1.450 g (5.42 mmol, 70%) **3** and 377 mg (1.41 mmol, 18%) *cis*-**3** (total yield 89%, **3**:*cis*-**3** = 80:20[31]) as colorless liquids. *rac*-**3** and *rac*-*cis*-**3** were obtained from NaH (3.1 g, 77 mmol, 1.2 equiv.), *rac*-cryptol (9.0 g, 64 mmol, *rac*-**9**:*rac*-**10** = 80:20) and **4** (14.8 g, 90 mmol, 1.4 equiv.). Yield 15.91 g (60 mmol, 93%)[30] *rac*-**3**: *rac*-*cis*-**3** = 80:20.[31] *rac*-**3** becomes a colourless solid when stored in a freezer at 4 °C. **3**: t_R = 13.08 min (HP-5). R_F = 0.40 (Et_2O/PE = 1:9). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.80, 0.83 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 7.1 Hz, 6 H, 4-*i*Pr $(CH_3)_2$), 1.13 (s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.32 (m, 1 H, 5-H_A), 1.50 (m, 2 H, 6-H_A, 4-*i*Pr CH), 1.70 (m, 1 H, 5-H_B), 1.94 (m, 1 H, 4-H), 2.07 (m, 1 H, 6-H_B), 3.62, 4.06 (2 br. s, 2 H, *N*-*i*Pr CH), 5.17 (m, 1 H, 1-H), 5.65 (m, 2 H, 2-H, 3-H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ = 19.3, 19.6 (CH_3, 4-*i*Pr $(CH_3)_2$), 20.8, 21.4 (CH_3, *N*-*i*Pr $(CH_3)_2$), 23.4 (CH_2, C-5), 28.8 (CH_2, C-6), 31.9 (CH, 4-*i*Pr CH), 41.6 (CH_2, C-4), 45.0, 46.2 (CH, *N*-*i*Pr CH), 70.1 (CH, C-1), 128.4 (CH, C-2), 133.6 (CH, C-3), 155.6 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 2996 (m), 2961 (s), 2935 (s), 2871 (s) [$\nu(C_{aliph}$–H)], 1688 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 290.2088 [M + Na]$^+$. $C_{16}H_{29}NO_2$ (267.41): calcd. C 71.86, H 10.93, N 5.24; found C 71.99, H 11.05, N 5.11. $[\alpha]_D^{20}$ = –117.4 (*c* = 0.70, $CHCl_3$) at 99% *ee*; HPLC Chiralcel OD-H (4.6×250 mm), λ = 210 nm, *i*PrOH:*n*-hexane = 1:600, 0.3 mL/min, 35.62 min (*ent*-**3**), 38.83 min (**3**). *cis*-**3**: t_R = 12.84 min (HP-5). R_F = 0.28 (Et_2O/PE = 1:9). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90, 0.92 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 7.0 Hz, 6 H, 4-*i*Pr $(CH_3)_2$), 1.20, 1.21 (2 br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.50 (m, 1 H, 5-H_A), 1.61 (m, 1 H, 5-H_B), 1.69 (m, 2 H, 6-H_A, 4-*i*Pr CH), 1.95 (m, 2 H, 6-H_B, 4-H), 3.89 (br. s, 2 H, *N*-*i*Pr CH), 5.14 (m, 1 H, 1-H), 5.86 (s, 2 H, 2-H, 3-H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ = 19.1, 19.5 (CH_3, 4-*i*Pr $(CH_3)_2$), 20.6 (CH_2, C-5), 20.9 (CH_3, *N*-*i*Pr $(CH_3)_2$), 28.2 (CH_2, C-6), 31.7 (CH, 4-*i*Pr

CH), 41.8 (CH, C-4), 45.8 (CH, *N*-*i*Pr CH), 66.7 (CH, C-1), 125.9 (CH, C-2), 136.2 (CH, C-3), 155.6 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 2995 (m), 2961 (m), 2940 (m), 2873 (m) [$\nu(C_{aliph}–H)$], 1688 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 290.2072 $[M + Na]^+$. $C_{16}H_{29}NO_2$ (267.41): calcd. C 71.86, H 10.93, N 5.24; found C 71.71, H 11.10, N 5.10. $[\alpha]_D^{20}$ = +129.1 (*c* = 0.70, $CHCl_3$).

Deprotonation of Cyclohex-2-enyl Carbamates and Trapping with Carbonyl Electrophiles. General Procedure A (GP A): A Solution of the cyclohex-2-enyl carbamate (1.0 mmol) and TMEDA (151 mg, 1.3 equiv.) or TMCDA *rac*-**26** (221 mg, 1.3 equiv.) in Et_2O (5 mL) was cooled to –78 °C. 1.36 M *sec*-BuLi solution (0.95 mL, 1.3 equiv.) was added dropwise and the solution was stirred for 2 h. The carbonyl compound (3.0 equiv.) was then added dropwise by syringe and stirring at –78 °C was continued for 2–14 h until complete consumption of the starting material (TLC). The reaction was quenched with satd. aq. NH_4Cl solution (2 mL) and the mixture was warmed to room temperature. The layers were separated and the aqueous layer was extracted with TBME (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed in vacuo. FCC on silica gel and removal of the solvent in vacuo yielded the addition products.

(3*R*,5*R*)-3-(1-Hydroxy-1-methylethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (11a): (1*R*,5*R*)-Carveyl carbamate **2** (279 mg, 1.00 mmol) was lithiated according to GP A with TMEDA (151 mg, 1.30 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (0.95 mL, 1.30 mmol, 1.3 equiv.) in Et_2O (5 mL) at –78 °C for 2 h. Acetone (174 mg, 3.0 mmol, 3.0 equiv.) was then added and the solution was warmed to room temperature within 8 h. FCC on silica gel (TBME/PE = 1:20 to 1:12) yielded 263 mg (0.78 mmol, 78%) **11a** (*dr* > 98:2) as a colourless liquid. t_R = 16.56 min (HP-5). R_F = 0.33 (TBME/PE = 1:12). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24, 1.26 (2 br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.29, 1.31 (2 s, 6 H, 2′-H), 1.54 (dt, $^3J_{3,4A}$ = 5.0 Hz, $^2J_{4A,4B}$ = $^3J_{4A,5}$ = 13.3 Hz, 1 H, 4-H_A), 1.72 (br. s, 6 H, 2-CH_3, 5-C$(CH_2)(CH_3)$), 1.94 (m, 1 H, 4-H_B), 2.02 (dm, $^2J_{6A,6B}$ = 17.5 Hz, 1 H, 6-H_A), 2.22 (dm, $^2J_{6A,6B}$ = 17.5 Hz, 1 H, 6-H_B), 2.26 (m, 1 H, 3-H), 2.36 (s, 1 H, OH), 3.00 (m, 1 H, 5-H), 3.82, 4.09 (2 br. s, 2 H, *N*-*i*Pr CH), 4.70, 4.75 (2 s, 2 H, 5-C$(CH_2)(CH_3)$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 (CH_3, 2-CH_3), 20.3 (CH_3, 5-C$(CH_2)(CH_3)$), 21.1 (CH_3, *N*-*i*Pr $(CH_3)_2$), 27.8 (CH_2, C-4), 30.3 (CH, C-5), 32.4 (CH_3, C-2′), 36.6 (CH_2, C-6), 46.1 (CH, *N*-*i*Pr CH), 49.5 (CH, C-3), 72.9 (C_q, C-OH), 108.7 (CH_2, 5-C$(CH_2)(CH_3)$), 120.7 (C_q, C-2), 145.3 (C_q, C-1), 149.3 (C_q, 5-C$(CH_2)(CH_3)$), 153.6 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3457 (br.) [ν(OH)], 2970 (s), 2934 (s), 2877 (s) [$\nu(C_{aliph}–H)$], 1699 (s) [ν(C=O)], 1645 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 360.25 $[M + Na]^+$. $C_{20}H_{35}NO_3$ (337.50): calcd. C 71.18, H 10.45, N 4.15; found C 70.81, H 10.52, N 4.05. $[\alpha]_D^{20}$ = +22.4 (*c* = 0.98, $CHCl_3$).

(3*R*,5*R*)-3-(1-Hydroxy-1,1-diphenylmethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (11b): (1*R*,5*R*)-Carveyl carbamate **2** (279 mg, 1.00 mmol) was lithiated according to GP A with TMEDA (151 mg, 1.30 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (0.95 mL, 1.30 mmol, 1.3 equiv.) in Et_2O (5 mL) at –78 °C for 2 h. Benzophenone (550 mg, 3.0 mmol, 3.0 equiv.) in Et_2O (2 mL) was added and the solution was warmed to room temperature during 8 h. FCC on silica gel (TBME/PE = 1:20 to 1:10) yielded 409 mg (0.89 mmol, 89%) **11b** (*dr* > 98:2) as a colourless solid. M.p. 174 °C (TBME/PE). t_R = 16.56 min (HP-5). R_F = 0.34 (TBME/PE = 1:10). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (m, 3 H, 2-CH_3), 1.22 (d, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.44 (s and dt, $^3J_{3,4A}$ = 4.8 Hz, $^2J_{4A,4B}$ = $^3J_{4A,5}$ = 13.2 Hz, 4 H, 5-C$(CH_2)(CH_3)$, 4-H_A), 1.67 (dt, $^2J_{4A,4B}$ = 13.2 Hz, $^3J_{3,4B}$ = $^3J_{4B,5}$ = 2.5 Hz, 1 H, 4-H_B), 2.05 (dd, $^3J_{5,6A}$ = 10.4 Hz, $^2J_{6A,6B}$ = 17.6 Hz, 1 H, 6-H_A), 2.23 (dd, $^3J_{5,6B}$ = 7.0 Hz, $^2J_{6A,6B}$ = 17.6 Hz, 1 H, 6-H_B), 3.06 (dddd, $^3J_{4A,5}$ = 13.2 Hz, $^3J_{4B,5}$ = 2.5 Hz, $^3J_{5,6A}$ = 10.4 Hz, $^3J_{5,6B}$ = 7.0 Hz, 1 H, 5-H), 3.58 (br. s, 1 H, 3-H), 3.77, 4.09 (2 br. s, 2 H, *N*-*i*Pr CH), 4.52, 4.55 (2 s, 2 H, 5-C$(CH_2)(CH_3)$), 7.12 (m, 2 H, *p*-PhCH), 7.25 (m, 4 H, *o*-PhCH), 7.68, 7.79 (2 m, 4 H, *m*-PhCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3, 2-CH_3), 20.3 (CH_3, 5-C$(CH_2)(CH_3)$), 21.5 (CH_3, *N*-*i*Pr $(CH_3)_2$), 30.7 (CH_2, C-4), 32.4 (CH_2, C-6), 35.8 (CH, C-5), 45.5, 46.9 (CH, *N*-*i*Pr CH), 48.0 (CH, C-3), 78.8 (CH, C-OH), 108.3 (CH_2, 5-C$(CH_2)(CH_3)$), 120.3 (C_q, C-2), 125.6, (CH, *m*-Ph), 126.2 (CH, *p*-Ph), 127.8 (CH, *o*-Ph), 145.7 (C-1), 149.2 (C_q, 5-C$(CH_2)(CH_3)$), 149.6 (C_q, *i*-C-Ph), 153.9 (C_q, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3492 (br.) [ν(OH)], 3076 (m) [$\nu(C_{arom}–H)$], 2972 (s), 2937 (m), 2919 (m) [$\nu(C_{aliph}–H)$], 1700 (s) [ν(C=O)], 1642 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 484.28 $[M + Na]^+$. $C_{30}H_{39}NO_3$ (461.64): calcd. C 78.05, H 8.52, N 3.01; found C 77.87, H 8.51, N 2.92. $[\alpha]_D^{20}$ = –34.7 (*c* = 1.01, $CHCl_3$).

[3*R*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-[1-Hydroxy-1-(naphthalen-2-yl)-methyl]-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (18a and 19a): (1*R*,5*R*)-Carveyl carbamate **2** (849 mg, 3.0 mmol) was lithiated according to GP A with TMEDA (453 mg, 3.9 mmol, 1.3 equiv.) and 0.59 M *s*BuLi solution (6.6 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h. 2-Naphthaldehyde (**12a**, 1.4 g, 9.0 mmol, 3.0 equiv.) in Et_2O (10 mL) was added and the solution was stirred for 2 h at –78 °C. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 to 1:3) yielded yielded 914 mg (2.10 mmol, 70%) **18a** and 103 mg (0.24 mmol, 8%) **19a** (total yield 78%, **18a**/**19a** = 90:10[31]) as colourless oils. **18a**: t_R = 24.30 min (HP-5). R_F = 0.42 (Et_2O/PE = 1:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.56 (m, 1 H, 4-H_A), 1.60 (s, 3 H, 2-CH_3), 1.71 (s and m, 4 H, 5-C$(CH_2)(CH_3)$, 4-H_B), 2.15 (m, 2 H, 6-H), 2.58 (br. s, 1 H, 3-H), 3.06 (br. m, 1 H, 5-H), 3.87, 4.09 (2 br. s, 2 H, *N*-*i*Pr CH), 4.62 (s, 2 H, 5-C$(CH_2)(CH_3)$), 5.25 (d, *J* = 3.7 Hz, 1 H, CH-O), 7.44 (m, 3 H, ArCH), 7.82 (m, 3 H, ArCH), 7.94 (s, 7 H, ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH_3, 2-CH_3), 20.6 (CH_3, 5-C$(CH_2)(CH_3)$), 21.5 (CH_3, *N*-*i*Pr $(CH_3)_2$), 27.6 (CH_2, C-4), 32.4 (CH_2, C-6), 37.9 (CH, C-5), 45.9 (CH, *N*-*i*Pr CH), 46.9 (CH, C-3), 73.3 (CH, C-OH), 108.8 (CH_2, 5-C$(CH_2)(CH_3)$), 119.9 (C_q, C-2), 124.2, 124.5, 125.4, 125.9, 127.6, 127.7, 128.0 (CH, C-Ar), 132.6, 133.4, 140.1 (C_q, C-Ar), 145.4 (C-1), 148.8 (C_q, 5-C$(CH_2)(CH_3)$), 153.7 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3422 (br.) [ν(OH)], 3052 (w) [$\nu(C_{arom}–H)$], 2965 (s), 2930 (s), 2870 (s) [$\nu(C_{aliph}–H)$], 1678 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 458.2653 $[M + Na]^+$. $C_{28}H_{37}NO_3$ (435.60): calcd. C 77.20, H 8.56, N 3.22; found C 77.10, H 8.54, N 2.88. $[\alpha]_D^{20}$ = +31.5 (*c* = 0.86, $CHCl_3$). **19a**: t_R = 24.30 min (HP-5). R_F = 0.35 (Et_2O/PE = 1:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27, 1.29 (2 br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.58 (br. s, 4 H, 4-H_A, 2-CH_3), 1.79 (s, 3 H, 5-C$(CH_2)(CH_3)$), 2.03, 2.18 (2 m, 4 H, 3-H, 6-H, 4-H_B), 2.82 (m, 1 H, 5-H), 3.92, 4.04 (2 br. s, 2 H, *N*-*i*Pr CH), 4.59 (s, 2 H, 5-C$(CH_2)(CH_3)$), 5.30 (d, *J* = 2.1 Hz, 1 H, CH-O), 7.45 (m, 3 H, ArCH), 7.82 (m, 3 H, ArCH), 7.89 (s, 1 H, ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4 (CH_3, 2-CH_3), 20.9 (CH_3, 5-C$(CH_2)(CH_3)$), 21.4 (CH_3, *N*-*i*Pr $(CH_3)_2$), 27.0 (CH_2, C-4), 33.6 (CH_2, C-6), 41.0 (CH, C-5), 45.5 (CH, *N*-*i*Pr CH), 47.3 (CH, C-3), 71.7 (CH, C-OH), 109.4 (CH_2, 5-C$(CH_2)(CH_3)$), 119.8 (C_q, C-2), 124.0, 124.3, 125.4, 125.8 127.6, 127.9, 128.0 (CH, C-Ar), 132.6, 133.4, 140.0 (C_q, C-Ar), 146.3 (C-1), 148.6 (C_q, 5-C$(CH_2)(CH_3)$), 153.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3424 (br.) [ν(OH)], 3047 (w) [$\nu(C_{arom}–H)$], 2970 (s), 2929 (s), 2872 (s) [$\nu(C_{aliph}–H)$], 1683 (m) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 458.2648 $[M + Na]^+$. $C_{28}H_{37}NO_3$ (435.59): calcd. C 77.20, H 8.56, N 3.22; found C 76.82, H 8.52, N 3.10. $[\alpha]_D^{20}$ = +117.3 (*c* = 0.48, $CHCl_3$).

[3*R*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-(1-Cyclohexyl-1-hydroxymethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (18b and 19b): (1*R*,5*R*)-Carveyl carbamate **2** (840 mg, 3.0 mmol) was lithiated according to GP A with TMEDA (453 mg, 3.9 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (2.9 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h. Cyclohexanecarbaldehyde (**12b**, 1.0 g, 9.0 mmol, 3.0 equiv.) was added and the solution was warmed to room temperature during 16 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4) yielded 932 mg (2.14 mmol, 71%)[30] **18b/19b** = 75:25[31] as colourless oils. **18b**: t_R = 20.47 min (HP-5). R_F = 0.48 (TBME/PE = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–1.03 (m, 2 H, $CyCH_2$), 1.26 (m, 14 H, *N*-*i*Pr $(CH_3)_2$, $CyCH_2$), 1.43–1.54 (m, 2 H, 4-H_A, CyCH), 1.57 (s, 3 H, 2-CH_3), 1.64–1.70 (m, 3 H, $CyCH_2$), 1.73 (s, 3 H, 5-C$(CH_2)(CH_3)$), 1.75 (m, 2 H, $CyCH_2$), 1.85 (dtr, $^3J_{3,4B}$ = $^3J_{4A,5}$ = 2.7 Hz, $^2J_{4A,4B}$ = 13.3 Hz, 1 H, 4-H_B), 2.05–2.15 (m, 2 H, 6-H), 2.22 (m, 1 H, $CyCH_2$), 2.33 (s, 1 H, 3-H), 2.41 (br. s, 1 H, OH), 2.95 (m, 1 H, 5-H), 3.43 (dd, *J* = 9.5 Hz, 2.8 Hz, 1 H, CH-OH), 3.83, 4.09 (2 br. s, 2 H, *N*-*i*Pr CH), 4.72, 4.75 (2 s, 2 H, 5-C$(CH_2)(CH_3)$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3, 2-CH_3), 20.5, 21.6 (CH_3, *N*-*i*Pr $(CH_3)_2$), 20.7 (CH_3, 5-C$(CH_2)(CH_3)$), 25.7, 26.1, 26.6, 26.9, 28.8, (CH_2, C-Cy), 31.0 (CH_2, C-4), 32.5 (CH_2, C-6), 38.0 (CH, C-5), 39.8 (CH, C-Cy), 41.4 (CH, C-3), 45.7, 46.7 (CH, *N*-*i*Pr CH), 75.1 (CH, C-OH), 108.8 (CH_2, 5-C$(CH_2)(CH_3)$), 120.3 (C_q, C-2), 144.7 (C_q, C-1), 149.3 (C_q, 5-C$(CH_2)(CH_3)$), 153.6 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3473 (br.) [ν(OH)], 2998 (s), 2970 (s), 2932, 2874 (s) [$\nu(C_{aliph}–H)$], 1698 (s) [ν(C=O)], 1645 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 414.2985 $[M + Na]^+$. $C_{24}H_{41}NO_3$ (391.58): calcd. C 73.61, H 10.55, N 3.58; found C 73.41, H 10.55, N 3.43. $[\alpha]_D^{20}$ = +31.8 (*c* = 1.01, $CHCl_3$). **19b**: t_R = 20.50 min (HP-5). R_F = 0.34 (TBME/PE = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–1.13 (m, 3 H, $CyCH_2$), 1.25 (br. s, 14 H, *N*-*i*Pr $(CH_3)_2$, $CyCH_2$), 1.40 (m, 1 H, CyCH), 1.58 (dt, $^3J_{3,4A}$ = 2.5 Hz, $^2J_{4A,4B}$ = 12.8 Hz, $^3J_{4A,5}$ = 2.5 Hz, 1 H, 4-H_A), 1.65 (s, 3 H, 2-CH_3), 1.66–1.73 (m, 2 H, $CyCH_2$), 1.73 (s, 3 H, 5-C$(CH_2)(CH_3)$), 1.75–1.78 (m, 3 H, $CyCH_2$), 1.95–2.08 (m, 2 H, 4-H_B, 6-H_A), 2.17 (dd, $^3J_{5,6B}$ = 6.8 Hz, $^2J_{6A,6B}$ = 16.8 Hz, 1 H, 6-H_B), 2.31 (br. s, 1 H, OH), 2.49 (br. s, 1 H, 3-H), 2.72 (m, 1 H, 5-H), 3.30 (dd, *J* = 6.5 Hz, 4.4 Hz, 1 H, CH-O), 3.81, 4.10 (2 br. s, 2 H, *N*-*i*Pr CH), 4.71, 4.73 (2 s, 2 H, 5-C$(CH_2)(CH_3)$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2 (CH_3, 2-CH_3), 20.4 (CH_3, 5-C$(CH_2)(CH_3)$), 20.5, 21.5 (CH_3, *N*-*i*Pr $(CH_3)_2$), 26.2, 26.4, 26.6, 28.2, 30.0 (CH_2, C-Cy), 32.7 (CH_2, C-4), 33.2 (CH_2, C-6), 37.2 (CH, C-5), 41.6 (CH, C-Cy), 43.4 (CH, C-3), 45.6, 46.7 (CH, *N*-*i*Pr CH), 80.1 (CH_2, C-OH), 109.0 (CH_2, 5-C$(CH_2)(CH_3)$), 120.9 (C_q, C-2), 144.2 (C_q, C-1), 148.9 (C_q, 5-C$(CH_2)(CH_3)$), 153.5 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3455 (br.) [ν(OH)], 2969 (s), 2925 (s), 2851 (s) [$\nu(C_{aliph}–H)$], 1695 (s) [ν(C=O)], 1646 (m) [ν(C=C)] cm^{-1}. HR-MS (ESI, $C_{24}H_{41}NO_3$, 391.58): calcd. 414.2985 $[M + Na]^+$, found *m*/*z* = 414.2979 $[M + Na]^+$. $[\alpha]_D^{20}$ = +69.8 (*c* = 1.00, $CHCl_3$).

Transmetallation and Homoaldol Reactions of 2. General Procedure B (GP B): To a stirred solution of carbamate **2** (838 mg, 3.0 mmol) and TMCDA (*rac*-**26**, 663 mg, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C 1.36 M *s*BuLi solution (2.9 mL, 3.9 mmol, 1.3 equiv.) was added dropwise. After 2 h $ClTi(NEt_2)_3$[15b] (1.44 g, 4.8 mmol, 1.6 equiv.) in Et_2O (3 mL) was added over a period of 10 min and stirring at –78 °C was continued for 3 h. The aldehyde (9.0 mmol, 3.0 equiv.) was then added dropwise. After complete consumption of the starting material (TLC) the reaction was quenched with satd. aq. NH_4Cl solution (5 mL). The slurry was stirred for 10 min at room temperature, satd. aq. K Na tartrate solution (5 mL) was added and stirring was continued for 15 min. The precipitate was decanted and the solution filtered through a Büchner funnel. The solid residue was washed with TBME (3 × 10 mL), filtered and the filter cake was washed with TBME (20 mL). The aqueous layer was separated and extracted with TBME (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was removed in vacuo. FCC on silica gel (Et_2O/PE or TBME/PE mixtures) and removal of the solvent in vacuo yielded the homoaldol products.

[3*S*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-(1-Hydroxyphenylmethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20c and 19c): (1*R*,5*R*)-Carveyl carbamate **2** (838 mg, 3.0 mmol) was lithiated according to GP C with TMCDA (*rac*-**26**, 663 mg, 3.9 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (2.9 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (1.8 g, 6.0 mmol, 2.0 equiv.) for 3 h. Benzaldehyde (**12c**, 954 mg, 9.0 mmol, 3.0 equiv.) was added and the solution was warmed to room temperature during 14 h. Purification by FCC (TBME/PE = 1:4) yielded 749 mg (1.94 mmol, 65%) **20c/19c** = 95:5[31] as colourless oil. The diastereomers were not separable by chromatography. The optimisation reactions were performed with the same conditions but with variation of the diamine ligand (see Table 1). **20c**: t_R = 20.68 min (HP-5). R_F = 0.41 (TBME/PE = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23, 1.25 (2 br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.38 (dt, $^3J_{3,4A}$ = 10.6 Hz, $^2J_{4A,4B}$ = 12.6 Hz, $^3J_{4A,5}$ = 12.6 Hz, 1 H, 4-H_A), 1.47 (s, 3 H, 2-CH_3), 1.68 (s, 3 H, 5-C$(CH_2)(CH_3)$), 1.82 (m, 1 H, 4-H_B), 2.06, 2.09 (2 m, 2 H, 6-H), 2.31 (m, 1 H, 5-H), 2.40 (br. s, 1 H, OH), 2.94 (br. dd, $^3J_{3,4A}$ = 10.6 Hz, $^3J_{3,4B}$ = 5.3 Hz, 1 H, 3-H), 3.86, 4.00 (2 br. s, 2 H, *N*-*i*Pr CH), 4.87, 4.68 (2 s, 2 H, 5-C$(CH_2)(CH_3)$), 4.89 (d, *J* = 3.8 Hz, 1 H, CH-O), 7.20–7.40 (m, 5 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (CH_3, 2-CH_3), 20.6 (CH_3, 5-C$(CH_2)(CH_3)$), 21.3 (CH_3, *N*-*i*Pr $(CH_3)_2$), 32.2 (CH_2, C-4), 33.4 (CH_2, C-6), 41.3 (CH, C-5), 46.1 (CH, *N*-*i*Pr CH), 47.2 (CH, C-3), 75.9 (CH, C-OH), 109.2 (CH_2, 5-C$(CH_2)(CH_3)$), 118.9 (C_q, C-2), 125.9 (CH, *m*-Ph), 126.8 (CH, *p*-Ph), 128.0 (CH, *o*-Ph), 143.8 (C_q, C-1), 145.3 (C_q, 5-C$(CH_2)(CH_3)$), 148.6 (C_q, *i*-C-Ph), 153.2 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3441 (s, br.) [ν(OH)], 3084 (m), 3064 (m) [$\nu(C_{arom}–H)$], 2969 (s), 2932 (s), 2873 (s) [$\nu(C_{aliph}–H)$], 1681 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 408.25 $[M + Na]^+$. $C_{24}H_{35}NO_3$ (385.54, mixture of diastereomers): calcd. C 74.77, H 9.15, N 3.63; found C 74.53, H 9.36, N 3.50. $[\alpha]_D^{20}$ = +1.6 (*c* = 1.02, $CHCl_3$, **20c/19c** = 95:5). **19c**: t_R = 20.54 min (HP-5). R_F = 0.41 (TBME/PE = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 6 H, 5-C$(CH_2)(CH_3)$, 2-CH_3), 2.66 (br. m, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7 (CH_3, 2-CH_3), 49.4 (CH, C-3), 109.0 (CH_2, 5-C$(CH_2)(CH_3)$) ppm.

[3*S*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-(1-Hydroxy-1-naphthalen-2-ylmethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20a and 19a): (1*R*,5*R*)-Carveyl carbamate **2** (1.397 g, 5.0 mmol) was lithiated according to GP C with TMCDA (*rac*-**26**, 1.105 g, 6.5 mmol, 1.3 equiv.) and 1.32 M *s*BuLi solution (5.0 mL, 6.5 mmol, 1.3 equiv.) in Et_2O (25 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (2.4 g, 8.0 mmol, 1.6 equiv.) for 3 h. A solution of 2-naphthaldehyde (**12a**, 2.3 g, 15.0 mmol, 3.0 equiv.) in Et_2O (25 mL) was added and the solution was warmed to room temperature within 14 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 to 1:3) yielded 1.754 g (4.03 mmol, 81%)[30] **20a/19a** = 94:6[31] as colourless oils. **20a**: t_R = 24.28 min (HP-5). R_F = 0.31 (Et_2O/PE = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22, 1.24 (2 br. s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.47 (m and s, 4 H, 4-H_A, 2-CH_3), 1.67 (s, 3 H, 5-C$(CH_2)(CH_3)$), 1.89 (m, 1 H, 4-H_B), 2.04 (br. d, 1 H, 6-H_A), 2.13 (m, 1 H, 6-H_B), 2.33 (br. t, 1 H, 5-H), 2.76 (br. s, 1 H, OH), 3.05 (br. s, 1 H, 3-H), 3.82, 4.04 (2 br. s, 2 H, *N*-*i*Pr CH), 4.67 (s, 2 H, 5-C$(CH_2)(CH_3)$), 5.04 (d,

$^3J_{3,CH-O}$ = 3.2 Hz, 1 H, CH-O), 7.44 (m, 2 H, ArCH), 7.51 (m, 1 H, ArCH), 7.79 (m, 3 H, ArCH), 7.89 (s, 1 H, ArCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (CH_3, 2-CH_3), 20.6 (CH_3, 5-C(CH_2)(CH_3)), 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 32.4 (CH_2, C-4), 33.5 (CH_2, C-6), 41.3 (CH, C-5), 46.2 (CH, *N*-*i*Pr CH), 47.1 (CH, C-3), 76.0 (CH, C-OH), 109.3 (CH_2, 5-C(CH_2)(CH_3)), 119.9 (C_q, C-2), 124.2, 124.6, 125.5, 125.9, 127.5, 127.7, 128.1 (CH, C-Ar), 132.6, 133.3, 141.4 (C_q, C-Ar), 145.4 (C_q, C-1), 148.5 (C_q, 5-C(CH_2)(CH_3)), 153.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3435 (s, br.) [ν(OH)], 3081 (w) [$\nu(C_{arom}–H)$], 2970 (s), 2932 (s), 2872 (m) [$\nu(C_{aliph}–H)$], 1677 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 458.2642 [M + Na]$^+$. $C_{28}H_{37}NO_3$ (435.60): calcd. C 77.20, H 8.56, N 3.22; found C 77.10, H 8.57, N 3.06. $[\alpha]_D^{20}$ = –3.6 (*c* = 1.13, $CHCl_3$). **19a**: See above.

[3*S*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-[1-Hydroxy-1-(4-bromophenyl)-methyl]-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20d and 19d): (1*R*,5*R*)-Carveyl carbamate **2** (1.395 g, 5.0 mmol) was lithiated according to GP B with TMCDA (*rac*-**26**, 1.11 g, 6.5 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (4.77 mL, 6.5 mmol, 1.3 equiv.) in Et_2O (25 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (3.00 g, 10.0 mmol, 2.0 equiv.) for 3 h. A solution of 4-bromobenzaldehyde (**12d**, 2.31 g, 12.5 mmol, 2.5 equiv.) in Et_2O (25 mL) was added and the solution was warmed to room temperature during 7 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 to 1:2) yielded 1.336 g (2.88 mmol, 58%)[30] **20d/19d** = 93:7[31] as colourless oils. **20d**: t_R = 22.71 min (HP-5). R_F = 0.35 (TBME/PE = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.37 (dt, $^3J_{3,4A}$ = 10.2 Hz, $^2J_{4A,4B}$ = 12.8 Hz, $^3J_{4A,5}$ = 12.8 Hz, 1 H, 4-H_A), 1.43 (s, 3 H, 2-CH_3), 1.69 (s, 3 H, 5-C(CH_2)(CH_3)), 1.87 (m, 1 H, 4-H_B), 2.04 (m, 1 H, 6-H_A), 2.10 (m, 1 H, 6-H_B), 2.30 (m, 1 H, 5-H), 2.67 (br. s, 1 H, 3-H), 2.92 (br. s, 1 H, OH), 3.83, 4.05 (2 br. s, 2 H, *N*-*i*Pr CH), 4.68, 4.70 (2 s, 2 H, 5-C(CH_2)(CH_3)), 4.87 (s, 1 H, CH-O), 7.28 (d, *J* = 8.6 Hz, 2 H, *o*-ArCH), 7.44 (d, *J* = 8.6 Hz, 2 H, *m*-ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3, 2-CH_3), 20.5, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.7 (CH_3, 5-C(CH_2)(CH_3)), 32.0 (CH_2, C-4), 33.5 (CH_2, C-6), 41.1 (CH, C-5), 45.7, 46.6 (CH, *N*-*i*Pr CH), 47.3 (CH, C-3), 75.0 (CH, C-OH), 109.4 (CH_2, 5-C(CH_2)(CH_3)), 119.4 (C_q, C-2), 120.5 (C_q, *p*-Ar), 127.6 (CH, *o*-Ar), 131.1 (CH, *m*-Ar), 142.8 (C_q, C-1), 145.6 (C_q, 5-C(CH_2)(CH_3)), 148.4 (C_q, *i*-C-Ar), 153.2 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3429 (s, br.) [ν(OH)], 3081 (w) [$\nu(C_{arom}–H)$], 2970 (s), 2932 (s), 2872 (m) [$\nu(C_{aliph}–H)$], 1678 [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 486.16 [M + Na]$^+$. $C_{24}H_{34}BrNO_3$ (464.44): calcd. C 62.07, H 7.38, N 3.02; found C 62.12, H 7.59, N 2.73. $[\alpha]_D^{20}$ = –9.7 (*c* = 1.04, $CHCl_3$). **19d**: t_R = 22.53 min (HP-5). R_F = 0.41 (TBME/PE = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25, 1.26 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.30 (m, 1 H, 4-H_A), 1.56 (s, 3 H, 2-CH_3), 1.59 (m, 1 H, 4-H_B), 1.63 (s, 3 H, 5-C(CH_2)(CH_3)), 2.04, 2.08 (2 m, 2 H, 6-H), 2.34 (m, 1 H, 5-H), 2.63 (br. t, $^3J_{3,CH-O}$ = 4.5 Hz, 1 H, 3-H), 3.06 (br. s, 1 H, OH), 3.82, 4.08 (2 br. s, 2 H, *N*-*i*Pr CH), 4.62, 4.66 (2 s, 2 H, 5-C(CH_2)(CH_3)), 4.83 (d, $^3J_{3,CH-O}$ = 4.5 Hz, 1 H, CH-O), 7.25 (d, *J* = 8.6 Hz, 2 H, *o*-ArCH), 7.45 (d, *J* = 8.6 Hz, 2 H, *m*-ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6 (CH_3, 2-CH_3), 20.3 (CH_3, 5-C(CH_2)(CH_3)), 20.6, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 31.1 (CH_2, C-4), 32.5 (CH_2, C-6), 37.1 (CH, C-5), 45.8, 46.6 (CH, *N*-*i*Pr CH), 47.5 (C_q, C-3), 76.1 (CH, C-OH), 109.2 (CH_2, 5-C(CH_2)(CH_3)), 119.8 (C_q, C-2), 120.5 (C_q, *p*-Ar), 127.6 (CH, *o*-Ar), 131.2 (CH, *m*-Ar), 143.6 (C_q, C-1), 145.0 (C_q, 5-C(CH_2)(CH_3)), 148.6 (C_q, *i*-C-Ar), 153.5 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3423 (br.) [ν(OH)], 3081 (w) [$\nu(C_{arom}–H)$], 2969 (s), 2931 (s), 2874 (m) [$\nu(C_{aliph}–H)$], 1701 (s), 1677 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 486.16 [M + Na]$^+$. $C_{24}H_{34}BrNO_3$ (464.44): calcd. C 62.07, H 7.38, N 3.02; found C 62.05, H 7.52, N 2.82. $[\alpha]_D^{20}$ = +46.6 (*c* = 1.01, $CHCl_3$, **19d**/**20d** = 86:14).

[3*S*,3(1*R*),5*R*]- and [3*R*,3(1*S*),5*R*]-3-(1-Hydroxyprop-2-enyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20e and 19e): (1*R*,5*R*)-Carveyl carbamate **2** (1.397 g, 5.0 mmol) was lithiated according to GP C with TMCDA (*rac*-**26**, 1.105 g, 6.5 mmol, 1.3 equiv.) and 1.23 M *s*BuLi solution (5.28 mL, 6.5 mmol, 1.3 equiv.) in Et_2O (25 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (3.0 g, 10.0 mmol, 2.0 equiv.) for 3 h. Freshly distilled acroleine (**12e**, 1.4 g, 15 mmol, 3.0 equiv.) was added and the solution was stirred for 3 h at –78 °C. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 to 1:3) yielded 886 mg (2.64 mmol, 53%)[30] **20e**/**19e** = 94:6 and 298 mg (0.89 mmol, 18%) **20e** (total yield 71%, **20e**/**19e** = 95:5[31]) as colourless oils. **20e**: t_R = 17.24 min (HP-5). R_F = 0.19 (TBME/PE = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.30 (m, 1 H, 4-H_A), 1.59 (s, 3 H, 2-CH_3), 1.73 (s, 3 H, 5-C(CH_2)(CH_3)), 1.90 (dm, $^3J_{4B,5}$ = 12.7 Hz, 1 H, 4-H_B), 2.02 (br. d, $^3J_{6A,6B}$ = 15.9 Hz, 1 H, 6-H_A), 2.08 (s, 1 H, OH), 2.17 (dd, $^3J_{5,6B}$ = 12.7 Hz, $^3J_{6A,6B}$ = 15.9 Hz, 1 H, 6-H_B), 2.33 (br. t, $^3J_{4B,5}$ = $^3J_{5,6B}$ = 12.7 Hz, 1 H, 5-H), 2.69 (br. m, 1 H, 3-H), 3.82, 4.06 (2 br. s, 2 H, *N*-*i*Pr CH), 4.56 (m, 1 H, CH-O), 4.72 (s, 2 H, 5-C(CH_2)(CH_3)), 5.21 (dd, $^2J_{3'A,3'B}$ = 1.6 Hz, $^3J(Z)_{2',3'A}$ = 10.6 Hz, 1 H, 3′-H_A), 5.33 (dd, $^2J_{3'A,3'B}$ = 1.6 Hz, $^3J(E)_{2',3'B}$ = 17.3 Hz, 1 H, 3′-H_B), 5.94 (ddd, $^3J_{CH-O,2'}$ = 4.3 Hz, $^3J(Z)_{2',3'A}$ = 10.6 Hz, $^3J(E)_{2',3'B}$ = 17.3 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (CH_3, 2-CH_3), 20.5, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.6 (CH_3, 5-C(CH_2)(CH_3)), 28.5 (CH_2, C-4), 33.3 (CH_2, C-6), 40.7 (CH, C-5), 45.2 (CH, C-3), 72.9 (CH, C-OH), 109.1 (CH_2, 5-C(CH_2)(CH_3)), 115.2 (CH_2, C-3′), 119.1 (C_q, C-2), 138.0 (CH, C-2′), 144.4 (C_q, C-1), 148.7 (C_q, 5-C(CH_2)(CH_3)), 153.2 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3446 (s, br.) [ν(OH)], 2970 (s), 2932 (s), 2877 (s) [$\nu(C_{aliph}–H)$], 1682 (s) [ν(C=O)], 1645 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 358.2300 [M + Na]$^+$. $C_{20}H_{35}NO_3$ (335.48): calcd. C 71.60, H 9.91, N 4.18; found C 71.33, H 10.03, N 3.90. $[\alpha]_D^{20}$ = +93.8 (*c* = 1.03, $CHCl_3$). **19e**: t_R = 17.04 min (HP-5). R_F = 0.24 (TBME/PE = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24, 1.26 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.58 (dt, $^3J_{3,4A}$ = 5.5 Hz, $^2J_{4A,4B}$ = 13.0 Hz, $^3J_{4A,5}$ = 13.0 Hz, 1 H, 4-H_A), 1.65 (s, 3 H, 2-CH_3), 1.71 (s, 3 H, 5-C(CH_2)(CH_3)), 1.84 (br. d, $^2J_{4A,4B}$ = 13.0 Hz, 1 H, 4-H_B), 1.95 (br. s, 1 H, OH), 2.05–2.16 (m, 2 H, 6-H), 2.44 (br. t, $^3J_{3,4A}$ = 5.5 Hz, *J* = 5.5 Hz, 1 H, 3-H), 2.72 (m, 1 H, 5-H), 3.84, 4.07 (2 br. s, 2 H, *N*-*i*Pr CH), 4.34 (t, $^3J_{CH-O,2'}$ = $^3J_{3,CH-O}$ = 4.8 Hz, 1 H, CH-O), 4.71 (s, 2 H, 5-C(CH_2)(CH_3)), 5.12 (dt, $^3J(Z)_{2',3'A}$ = 10.5 Hz, $^2J_{3'A,3'B}$ = 1.7 Hz, *J* = 1.7 Hz, 1 H, 3′-H_A), 5.27 (dt, $^3J(E)_{2',3'B}$ = 17.3 Hz, $^2J_{3'A,3'B}$ = 1.7 Hz, *J* = 1.7 Hz, 1 H, 3′-H_B), 5.94 (ddd, $^3J_{CH-O,2'}$ = 4.8 Hz, $^3J(Z)_{2',3'A}$ = 10.5 Hz, $^3J(E)_{2',3'B}$ = 17.3 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2 (CH_3, 2-CH_3), 20.5, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.6 (CH_3, 5-C(CH_2)(CH_3)), 26.9 (CH_2, C-4), 32.5 (CH_2, C-6), 37.5 (CH, C-5), 45.1 (CH, C-3), 75.3 (CH, C-OH), 108.9 (CH_2, 5-C(CH_2)(CH_3)), 113.9 (CH_2, C-3′), 119.1 (C_q, C-2), 138.0 (CH, C-2′), 144.4 (C_q, C-1), 148.7 (C_q, 5-C(CH_2)(CH_3)), 153.5 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3440 (s, br.) [ν(OH)], 2970 (s), 2933 (s), 2874 (s) [$\nu(C_{aliph}–H)$], 1681 (s) [ν(C=O)], 1645 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 358.2300 [M + Na]$^+$. $C_{20}H_{35}NO_3$ (335.48): calcd. C 71.60, H 9.91, N 4.18; found C 71.36, H 9.97, N 4.11. $[\alpha]_D^{20}$ = +45.9 (*c* = 1.01, $CHCl_3$).

[3*S*,3(1*S*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-(1-Hydroxy-2-methylprop-2-enyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20f and 19f): (1*R*,5*R*)-Carveyl carbamate **2** (842 mg, 3.0 mmol) was lithiated according to GP C with TMCDA (*rac*-**26**,

665 mg, 3.9 mmol, 1.3 equiv.) and 1.37 M *s*BuLi solution (2.85 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (1.44 g, 4.8 mmol, 1.6 equiv.) for 4 h. Freshly distilled methacroleine (**12f**, 0.63 g, 9.0 mmol, 3.0 equiv.) was added and the solution was stirred for 2 h at –78 °C. Purification and separation of the mayor diastereomer by FCC (TBME/PE = 1:4 to 1:3) yielded 642 mg (1.84 mmol, 61%)[30] **20f/19f** = 94:6 and 201 mg (0.58 mmol, 19%) **20f** (total yield 80%, **20f/19f** = 95:5[31]) as colourless oils. **20f**: t_R = 17.78 min (HP-5). R_F = 0.21 (TBME/PE = 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24, 1.25 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.43 (dt, $^3J_{3,4A}$ = 10.7 Hz, $^2J_{4A,4B}$ = $^3J_{4A,5}$ = 12.7 Hz, 1 H, 4-H_A), 1.65 (s, 3 H, 2-CH_3), 1.73 (s, 3 H, 2′-CH_3), 1.78 (s, 3 H, 5-C(CH_2)(CH_3)), 1.83 (m, 1 H, 4-H_B), 1.95 (br. s, 1 H, OH), 2.05 (br. d, 1 H, 6-H_A), 2.20 (br. m, 1 H, 6-H_B), 2.48 (m, 1 H, 5-H), 2.71 (br. dd, $^3J_{3,4A}$ = 10.7 Hz, $^3J_{3,CH\text{-}O}$ = 3.4 Hz, 1 H, 3-H), 3.87, 4.02 (2 br. s, 2 H, *N*-*i*Pr CH), 4.20 (d, $^3J_{3,CH\text{-}O}$ = 3.4 Hz, 1 H, CH-O), 4.73 (s, 2 H, 5-C(CH_2)(CH_3)), 4.90 (br. s, 1 H, 3′-H_A), 5.05 (br. s, 1 H, 3′-H_B) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_3, 2-CH_3), 19.5 (CH_3, 5-C(CH_2)(*C*H_3)), 20.4, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.6 (CH_3, 2′-CH_3), 31.6 (CH_2, C-4), 33.5 (CH_2, C-6), 41.3 (CH, C-5), 43.6 (CH, C-3), 46.0, 46.6 (CH, *N*-*i*Pr CH), 77.4 (CH, C-OH), 109.2 (CH_2, 5-C(*C*H_2)(CH_3)), 111.1 (CH_2, C-3′), 120.3 (C_q, C-2), 144.6 (C_q, C-2′), 146.8 (C_q, C-1), 148.8 (C_q, 5-*C*(CH_2)(CH_3)), 153.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3443 (s, br.) [ν(OH)], 2965 (s), 2926 (s), 2874 (s) [ν(C_{aliph}–H)], 1687 (m) [ν(C=O)], 1644 (s) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 372.2572 [M + Na]$^+$. $C_{21}H_{35}NO_3$ (349.51): calcd. C 72.17, H 10.09, N 4.01; found C 71.88, H 10.12, N 3.86. $[\alpha]_D^{20}$ = +39.1 (*c* = 0.88, $CHCl_3$). **19f**: t_R = 17.59 min (HP-5). R_F = 0.22 (TBME/PE = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.56 (m, 1 H, 4-H_A), 1.69 (s, 3 H, 2-CH_3), 1.71 (s, 3 H, 2′-CH_3), 1.79 (s, 3 H, 5-C(CH_2)(CH_3)), 1.81–1.85 (m, 1 H, 4-H_B), 1.98–2.11 (m, 2 H, OH, 6-H_A), 2.16–2.25 (br. m, 1 H, 6-H_B), 2.46 (m, 1 H, 5-H), 2.71 (m, 1 H, 3-H), 3.83, 4.07 (2 br. s, 2 H, *N*-*i*Pr CH), 4.20 (br. s, 1 H, CH-O), 4.70 (s, 2 H, 5-C(CH_2)(CH_3)), 4.86 (m, 1 H, 3′-H_A), 5.02 (m, 1 H, 3′-H_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (CH_3, 2-CH_3), 18.1 (CH_3, 5-C(CH_2)(*C*H_3)), 20.4, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.5 (CH_3, 2′-CH_3), 31.4 (CH_2, C-4), 32.6 (CH_2, C-6), 37.2 (CH, C-5), 42.7 (CH, C-3), 46.0, 46.6 (CH, *N*-*i*Pr CH), 79.4 (CH, C-OH), 108.9 (CH_2, 5-C(*C*H_2)(CH_3)), 111.5 (CH_2, C-3′), 121.0 (C_q, C-2), 144.1 (C_q, C-15), 147.2 (C_q, C-1), 148.9 (C_q, 5-*C*(CH_2)(CH_3)), 153.5 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3443 (s, br.) [ν(OH)], 2969 (s), 2935 (s), 2874 (s) [ν(C_{aliph}–H)], 1700 (m) [ν(C=O)], 1647 (s) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 372.2566 [M + Na]$^+$. $C_{21}H_{35}NO_3$ (349.51, mixture of diastereomers): calcd. C 72.17, H 10.09, N 4.01; found C 72.08, H 10.31, N 3.83. $[\alpha]_D^{20}$ = +45.2 (*c* = 1.02, **19f/20f** = 23:77, $CHCl_3$).

[3*S*,3(1*R*),5*R*]- and [3*R*,3(1*S*),5*R*]-3-(1-Hydroxy-2-methylpropyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20g and 19g): (1*R*,5*R*)-Carveyl carbamate **2** (850 mg, 3.0 mmol) was lithiated according to GP C with 680 mg TMCDA *rac*-**26** (3.9 mmol, 1.3 equiv.) and 1.37 M *s*BuLi solution (2.85 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (1.44 g, 4.8 mmol, 1.6 equiv.) for 3 h. Isobutyraldehyde (**12g**, 0.66 g, 9.0 mmol, 3.0 equiv.) was then added and the solution was warmed to room temperature during 14 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 → 1:3) yielded 47 mg (0.13 mmol, 5%) **19g** and 530 mg (1.51 mmol, 50%) **20g** (total yield 55%, **20g/19g** = 93:7[31]) as colourless oils. **20g**: t_R = 17.70 min (HP-5). R_F = 0.14 (TBME/PE = 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94, 0.99 (2 d, $^3J_{2',3'}$ = 8.2 Hz, 6 H, 3′-H), 1.24, 1.26 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.46 (dt, $^3J_{3,4A}$ = 10.8 Hz, $^3J_{4A,4B}$ = $^3J_{4A,5}$ = 12.6 Hz, 1 H, 4-H_A), 1.64 (s, 3 H, 2-CH_3), 1.71 (br. s, 1 H, 1-H), 1.74 (s, 3 H, 5-C(CH_2)(CH_3)), 1.88 (m, 1 H, 4-H_B), 1.94 (m, 1 H, 2′-H), 2.07 (br. d, $^2J_{6A,6B}$ = 14.8 Hz, 1 H, 6-H_A), 2.19 (m, 1 H, 6-H_B), 2.29 (m, 1 H, 5-H), 2.63 (m, 1 H, 3-H), 3.38 (dd, $^3J_{3,CH\text{-}O}$ = 3.4 Hz, $^3J_{CH\text{-}O,2'}$ = 8.2 Hz, 1 H, CH-O), 3.86, 4.01 (2 br. s, 2 H, *N*-*i*Pr CH), 4.74 (m, 2 H, 5-C(CH_2)(CH_3)) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3, 2-CH_3), 19.5 (CH_3, 5-C(CH_2)(*C*H_3)), 19.6 (CH_3, C-3′), 20.7 (CH_3, *N*-*i*Pr (CH_3)$_2$), 27.0 (CH_2, C-2′), 31.8 (CH_2, C-4), 32.0 (CH_2, C-6), 33.6 (CH, C-5), 41.5 (CH, C-3), 46.4 (CH, *N*-*i*Pr CH), 79.9 (CH, C-OH), 109.2 (CH_2, 5-C(*C*H_2)(CH_3)), 120.6 (C_q, C-2), 144.3 (C_q, C-1), 148.8 (C_q, 5-*C*(CH_2)(CH_3)), 153.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3465 (s, br.) [ν(OH)], 2965 (s), 2926 (s), 2870 (s) [ν(C_{aliph}–H)], 1687 (m) [ν(C=O)], 1639 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 374.2661 [M + Na]$^+$. $C_{21}H_{37}NO_3$ (351.52): calcd. C 71.75, H 10.61, N 3.98; found C 71.62, H 10.80, N 3.84. $[\alpha]_D^{20}$ = +28.4 (*c* = 1.00, $CHCl_3$). **19g**: t_R = 17.36 min (HP-5). R_F = 0.25 (TBME/PE = 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96, 0.98 (2 d, $^3J_{2',3'}$ = 6.4 Hz, 6 H, 3′-H), 1.24, 1.26 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.65 (s and m, 4 H, 2-CH_3, 4-H_A), 1.72 (s and m, 4 H, 5-C(CH_2)(CH_3), 2′-H), 2.05 (br. d, $^2J_{4A,4B}$ = 11.4 Hz, 1 H, 4-H_B), 2.17 (m, 2 H, 6-H), 2.45 (br. s, 1 H, 3-H), 2.71 (tt, $^3J_{4A,5}$ = $^3J_{5,6A}$ = 10.7 Hz, $^3J_{4B,5}$ = $^3J_{5,6B}$ = 5.8 Hz, 1 H, 5-H), 3.28 (br. s, 1 H, CH-O), 3.82, 4.07 (2 br. s, 2 H, *N*-*i*Pr CH), 4.72, 4.73 (2 s, 2 H, 5-C(CH_2)(CH_3)) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH_3, 2-CH_3), 18.2 (CH_3, 5-C(CH_2)(*C*H_3)), 20.1 (CH_3, C-3′), 20.8 (CH_3, *N*-*i*Pr (CH_3)$_2$), 27.0 (CH, C-2′), 33.1 (CH_2, C-4), 33.6 (CH_2, C-6), 33.7 (CH, C-5), 37.7 (CH, C-3), 42.5 (CH, *N*-*i*Pr CH), 81.4 (CH, C-OH), 109.4 (CH_2, 5-C(*C*H_2)(CH_3)), 121.3 (C_q, C-2), 144.7 (C_q, C-1), 149.4 (C_q, 5-*C*(CH_2)(CH_3)), 154.1 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3465 (s, br.) [ν(OH)], 2965 (s), 2926 (s), 2870 (s) [ν(C_{aliph}–H)], 1687 (m) [ν(C=O)], 1639 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 374.2684 [M + Na]$^+$. $C_{21}H_{37}NO_3$ (351.52): calcd. C 71.75, H 10.61, N 3.98; found C 71.49, H 10.74, N 3.80. $[\alpha]_D^{20}$ = +77.4 (*c* = 1.00, $CHCl_3$).

[3*S*,3(1*R*),5*R*]- and [3*R*,3(1*R*),5*R*]-3-(1-Cyclohexyl-1-hydroxymethyl)-5-isopropenyl-2-methylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (20b and 19b): (1*R*,5*R*)-Carveyl carbamate **2** (845 mg, 3.0 mmol) was lithiated according to GP C with TMCDA *rac*-**26** 675 mg (3.9 mmol, 1.3 equiv.) and 1.37 M *s*BuLi solution (2.85 mL, 3.9 mmol, 1.3 equiv.) in Et_2O (15 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (1.44 g, 4.8 mmol, 1.6 equiv.) for 3 h. Cyclohexancarbaldehyde (**12a**, 1.1 g, 9.0 mmol, 3.0 equiv.) was then added and the solution was warmed to room temperature during 15 h. Purification and separation of the diastereomers by FCC (TBME/PE = 1:4 → 1:3) yielded 69 mg (0.18 mmol, 6%)[30] **19b/20b** = 75:25 and 348 mg (0.89 mmol, 30%) **20b** (total yield 36%, **20b/19b** = 91:9[31]) as colourless oils. **20b**: t_R = 20.64 min (HP-5). R_F = 0.23 (TBME/PE = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.93 (m, 2 H, $CyCH_2$), 1.12 (m, 1 H, $CyCH_2$), 1.22 (br. s, 14 H, *N*-*i*Pr (CH_3)$_2$, $CyCH_2$), 1.43 (dt, $^3J_{3,4A}$ = 10.6 Hz, $^2J_{4A,4B}$ = 12.7 Hz, $^3J_{4A,5}$ = 12.7 Hz, 1 H, 4-H_A), 1.50 (m, 1 H, CyCH), 1.61 (s, 3 H, 2-CH_3), 1.72 (s, 3 H, 5-C(CH_2)(CH_3)), 1.75 (m, 2 H, $CyCH_2$), 1.78 (br. s, 1 H, $CyCH_2$), 1.85 (m, 1 H, 4-H_B), 2.02–2.05 (m, 2 H, 6-H_A, $CyCH_2$), 2.17 (dm, 1 H, 6-H_B), 2.29 (m, 1 H, 5-H), 2.63 (br. s, 1 H, 3-H), 3.36 (d, *J* = 7.7 Hz, 1 H, CH-O), 3.79, 4.04 (2 br. s, 2 H, *N*-*i*Pr CH), 4.71, 4.72 (2 s, 2 H, 5-C(CH_2)(CH_3)) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.8 (CH_3, 2-CH_3), 20.5, 21.6 (CH_3, *N*-*i*Pr (CH_3)$_2$), 20.7 (CH_3, 5-C(CH_2)(*C*H_3)), 26.1, 26.3, 26.5, 29.5, 30.0 (CH_2, C-Cy), 32.1 (CH_2, C-4), 33.5 (CH_2, C-6), 41.5 (CH, C-5), 41.9 (CH, C-Cy), 43.4 (CH, C-3), 45.6, 46.5 (CH, *N*-*i*Pr CH), 78.9 (CH, C-OH), 109.1 (CH_2, 5-C(*C*H_2)(CH_3)), 120.5 (C_q, C-2), 144.2 (C_q, C-1), 148.8 (C_q, 5-*C*(CH_2)(CH_3)), 153.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3471 (s, br.) [ν(OH)], 2968 (s), 2925 (s), 2852 (s) [ν(C_{aliph}–H)], 1682 (s) [ν(C=O)], 1645 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* =

414.2980 [M + Na]$^+$. $C_{24}H_{41}NO_3$ (391.58): calcd. C 73.61, H 10.55, N 3.58; found C 73.32, H 10.45, N 3.46. $[\alpha]_D^{20}$ = +17.7 (*c* = 0.99, $CHCl_3$). **19b**: see above.

(3*S*,5*R*)- and (3*R*,5*R*)-5-Isopropenyl-2-methyl-3-(naphthalen-2-ylcarbonyl)cyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (23 and 24): The homoaldol products **20a/19a** = 73:27 (383 mg, 0.88 mmol), dissolved in CH_2Cl_2 (16 mL), were treated with PDC (1.65 g, 4.4 mmol, 5.0 equiv.) and powdered molecular sieves (4 Å) (30 mg) and stirred for 3 h at room temperature. The suspension was diluted with Et_2O (20 mL) and filtered through silica gel. Purification by FCC (TBME/PE = 1:8 to 1:4) yielded 219 mg (0.56 mmol, 64%) **23** as colourless oil and 85 mg (0.22 mmol, 25%) **24** as colourless solid (total yield 89%, **23/24** = 76:24[31]). **23**: t_R = 24.25 min (HP-5). R_F = 0.49 (TBME/PE = 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27, 1.29 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.57 (s, 3 H, 2-CH_3), 1.73 (s, 3 H, 5-C(CH_2)(CH_3)), 1.80 (dtr, $^3J_{3,4A}$ = 11.6 Hz, $^2J_{4A,4B}$ = $^3J_{4A,5}$ = 12.6 Hz, 1 H, 4-H_A), 2.12 (dd, $^3J_{3,4B}$ = 5.9 Hz, $^2J_{4A,4B}$ = 12.6 Hz, 1 H, 4-H_B), 2.34 (m, 2 H, 6-H), 2.61 (m, 1 H, 5-H), 3.91, 4.04 (2 br. s, 2 H, *N*-*i*Pr CH), 4.36 (br. dd, $^3J_{3,4A}$ = 11.6 Hz, $^3J_{3,4B}$ = 5.9 Hz, 1 H, 3-H), 4.73, 4.75 (2 s, 2 H, 5-C(CH_2)(CH_3)), 7.57 (m, 2 H, ArCH), 7.86 (d, *J* = 7.7 Hz, 1 H, ArCH), 7.86 (d, *J* = 8.9 Hz, 1 H, ArCH), 8.08 (m, 2 H, ArCH), 8.72 (s, 1 H, ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3, 2-CH_3), 20.5 (CH_3, 5-C(CH_2)(CH_3)), 20.7, 21.5 (CH_3, *N*-*i*Pr (CH_3)$_2$), 33.1, 33.4 (CH_2, C-4/C-6), 41.3 (CH, C-5), 46.4 (CH, *N*-*i*Pr CH), 51.1 (CH, C-3), 109.9 (CH_2, 5-C(CH_2)(CH_3)), 118.8 (C_q, C-2), 124.4, 126.6, 127.6, 128.5, 130.0, 130.5 (CH, C-Ar), 132.7, 133.7, 135.6 (C_q, C-Ar), 144.6 (C_q, C-1), 147.8 (C_q, 5-*C*(CH_2)(CH_3)), 153.3, 202.2 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3059 (w) [ν(C_{arom}–H)], 2969 (s), 2934 (s), 2871 (m) [ν(C_{aliph}–H)], 1705 (s), 1676 (s) [ν(C=O)], 1627 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 456.2477 [M + Na]$^+$. $C_{28}H_{35}NO_3$ (433.58): calcd. C 77.56, H 8.14, N 3.23; found C 77.33, H 8.18, N 3.19. $[\alpha]_D^{20}$ = –7.2 (*c* = 0.39, $CHCl_3$). **24**: M.p. 136.5 °C (*n*-hexane). t_R = 24.37 min (HP-5). R_F = 0.21 (TBME/PE = 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27, 1.29 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.58 (s, 3 H, 2-CH_3), 1.66 (s, 3 H, 5-C(CH_2)(CH_3)), 2.02 (dm, $^2J_{4A,4B}$ = 11.3 Hz, 1 H, 4-H_A), 2.10 (dt, $^3J_{3,4B}$ = 7.0 Hz, $^2J_{4A,4B}$ = 11.3 Hz, $^3J_{4B,5}$ = 11.4 Hz, 1 H, 4-H_B), 2.24 (dd, $^3J_{5,6A}$ = 5.6 Hz, $^2J_{6A,6B}$ = 15.5 Hz, 1 H, 6-H_A), 2.35 (m, 1 H, 6-H_B), 2.49 (m, 1 H, 5-H), 3.98 (br. s, 2 H, *N*-*i*Pr CH), 4.36 (d, $^3J_{3,4B}$ = 7.0 Hz, 1 H, 3-H), 4.69, 4.72 (m, s, 2 H, 5-C(CH_2)(CH_3)), 7.58 (m, 2 H, ArCH), 7.90 (m, 2 H, ArCH), 8.02 (m, 2 H, ArCH), 8.53 (s, 1 H, ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5 (CH_3, 2-CH_3), 20.7 (CH_3, 5-C(CH_2)(CH_3)), 21.4 (CH_3, *N*-*i*Pr (CH_3)$_2$), 31.2 (CH_2, C-4), 33.0 (CH_2, C-6), 37.7 (CH, C-5), 46.4 (CH, *N*-*i*Pr CH), 47.8 (CH, C-3), 109.7 (CH_2, 5-C(CH_2)(CH_3)), 117.4 (C_q, C-2), 124.4, 126.8, 127.7, 128.5, 129.7, 130.0 (CH, C-Ar), 132.6, 133.7, 135.6 (C_q, C-Ar), 145.1 (C_q, C-1), 147.8 (C_q, 5-*C*(CH_2)(CH_3)), 153.3 (C_q, C=O), 201.1 (C_q, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (w) [ν(C_{arom}–H)], 2969 (s), 2933 (s), 2874 (m) [ν(C_{aliph}–H)], 1701 (s) [ν(C=O)], 1647 (m) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 456.2513 [M + Na]$^+$. $C_{28}H_{35}NO_3$ (433.58): calcd. C 77.56, H 8.14, N 3.23; found C 77.28, H 8.28, N 3.11. $[\alpha]_D^{20}$ = +31.0 (*c* = 0.21, $CHCl_3$).

Transmetallation and Homoaldol Reactions of 3. General Procedure C (GP C): To a stirred solution of carbamate **2** (267 mg, 1.0 mmol) and TMCDA (*rac*-**26**, 179 mg, 1.05 mmol, 1.05 equiv.) in Et_2O (8 mL) at –78 °C 1.22 M *s*BuLi solution (0.86 mL, 1.05 mmol, 1.05 equiv.) was added dropwise.[32] After 2 h $ClTi(NEt_2)_3$[15b] (479 mg, 1.6 mmol, 1.6 equiv.) in Et_2O (2 mL) was added over a period of 10 min and stirring at –78 °C was continued for 3 h. The aldehyde (10.0 mmol, 10.0 equiv.) was then added dropwise over a period of 15 min. After complete consumption of the starting material (TLC) the reaction was quenched with satd. aq. NH_4Cl solution (2 mL) and worked up as described in GP B.

[3*R*,3(1*R*),4*R*]- and [3*R*,3(1*S*),4*R*]-3-(1-Hydroxyphenylmethyl)-4-isopropylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (31a and 32a): (1*S*,4*R*)-Cryptyl carbamate **3** (67 mg, 0.25 mmol, 99% *ee*) was lithiated according to GP C with TMCDA (*rac*-**26**, 58 mg, 0.33 mmol, 1.3 equiv.) and 1.38 M *s*BuLi solution (0.24 mL, 0.33 mmol, 1.3 equiv.) in Et_2O (2 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (244 mg, 0.75 mmol, 3.0 equiv.) for 3 h. Benzaldehyde (**28a**, 313 mg, 2.95 mmol, 11.9 equiv.) was added and the solution was warmed to room temperature during 17 h. Purification and separation of the diastereomers by FCC (Et_2O/PE = 1:2) yielded 7 mg (0.02 mmol, 7%) **32a** and 52 mg (0.14 mmol, 56%) **31a** as colourless solids (total yield 63%, **31a/32a** = 93:7[31]). *rac*-**31a**/*rac*-**32a** were prepared from *rac*-**3** (535 mg, 2.0 mmol) by lithiation with TMCDA (443 mg, 2.6 mmol, 1.3 equiv.) and 1.38 M *s*BuLi solution (2.13 mL, 2.6 mmol, 1.3 equiv.), transmetallation with $ClTi(NEt_2)_3$ (1.8 g, 6.0 mmol, 3.0 equiv.) and addition of **28a** (2.54 g, 24 mmol, 12 equiv.). Yield 32 mg (0.09 mmol, 4%) **32a** and 398 mg (1.07 mmol, 54%) **31a** as colourless solids (total yield 58%, *rac*-**31a**:*rac*-**32a** = 94:6[31]). **31a**: M.p. 132 °C (for **31a** at 99% *ee*, Et_2O/PE), m.p. 137 °C (for *rac*-**31a**, Et_2O/PE). t_R = 19.91 min (HP-5). R_F = 0.29 (Et_2O/PE = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89, 0.98 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 7.4 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 1.21, 1.23 (2 d, $^3J_{N\text{-}i\text{PrCH},N\text{-}i\text{Pr(Me)}}$ = 3.4 Hz, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.49 (m, 1 H, 5-H_A), 1.56 (m, 1 H, 4-H), 1.82 (m, 1 H, 5-H_B), 1.98 (m, 1 H, 4-*i*Pr CH), 2.14 (m, 2 H, 6-H), 2.60 (m, 1 H, 3-H), 3.81, 4.01 (2 br. s, 2 H, *N*-*i*Pr CH), 4.85 (d, $^3J_{3,CH\text{-}O}$ = 3.4 Hz, 1 H, CH-O), 5.03 (d, $^3J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 7.24 (m, 1 H, *p*-PhCH), 7.34 (m, 4 H, *o*/*m*-PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6, 21.7 (CH_3, 4-*i*Pr (CH_3)$_2$), 20.9 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.8 (CH_2, C-5), 26.6 (CH_2, C-6), 28.1 (CH, 4-*i*Pr CH), 40.3 (CH, C-4), 45.6 (CH, C-3), 45.8 (CH, *N*-*i*Pr CH), 74.5 (CH, C-OH), 111.4 (CH, C-2), 125.7 (CH, *o*-Ph), 126.7 (CH, *p*-Ph), 128.1 (CH, *m*-Ph), 144.2 (C_q, *i*-C-Ph), 153.1 (C_q, C-1), 154.1 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3416 (s) [ν(C–OH)], 3083 (w), 3060 (w), 3024 (w) [ν(C_{arom}–H)], 2965 (s), 2933 (s), 2884 (m), [ν(C_{aliph}–H)], 1684 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 396.2511 [M + Na]$^+$. $C_{23}H_{35}NO_3$ (373.53): calcd. C 73.96, H 9.44, N 3.75; found C 73.74, H 9.54, N 3.52. $[\alpha]_D^{20}$ = +94.5 (*c* = 1.02, $CHCl_3$) at 99% *ee*; HPLC Chira Grom 1 (2 × 250 mm), λ = 210 nm, *i*PrOH:*n*-hexane = 1:200, 0.3 mL/min, 21.04 min (*ent*-**31a**), 27.75 min (**31a**). **32a**: M.p. 102.2 °C (for **32a** at 99% *ee*, Et_2O/PE), m.p. 111.6 °C (for *rac*-**32a**, Et_2O/PE). t_R = 19.64 min (HP-5). R_F = 0.40 (Et_2O/PE = 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.82, 0.84 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.7 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 1.21 (m, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.44 (m, 1 H, 4-H), 1.56 (m, 1 H, 4-*i*Pr CH), 1.69 (m, 1 H, 5-H_A), 1.82 (m, 1 H, 5-H_B), 1.96 (m, 1 H, 6-H_A), 2.16 (m, 1 H, 6-H_B), 2.63 (br. d, $^3J_{2,3}$ = 4.8 Hz, 1 H, 3-H), 3.75, 4.03 (2 br. s, 2 H, *N*-*i*Pr CH), 4.72 (d, $^3J_{3,CH\text{-}O}$ = 6.2 Hz, 1 H, CH-O), 5.03 (d, $^3J_{2,3}$ = 4.8 Hz, 1 H, 2-H), 7.25 (tt, $^4J_{o\text{-}PhCH,p\text{-}PhCH}$ = 1.4 Hz, $^3J_{m\text{-}PhCH,p\text{-}PhCH}$ = 7.2 Hz, 1 H, *p*-PhCH), 7.33 (t, $^3J_{m\text{-}PhCH,p\text{-}PhCH}$ = 7.2 Hz, 2 H, *m*-PhCH), 7.37 (dd, $^3J_{o\text{-}PhCH,m\text{-}PhCH}$ = 7.2 Hz, $^4J_{o\text{-}PhCH,p\text{-}PhCH}$ = 1.4 Hz, 2 H, *o*-PhCH) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ = 19.5, 21.6 (CH_3, 4-*i*Pr (CH_3)$_2$), 20.5, 21.3 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.2 (CH_2, C-5), 24.6 (CH_2, C-6), 27.6 (CH, C-7), 38.0 (CH, C-4), 44.6 (CH, C-3), 45.6 (CH, *N*-*i*Pr CH), 76.1 (CH, C-OH), 113.4 (CH, C-2), 126.5 (CH, *o*-Ph), 127.2 (CH, *p*-Ph), 128.1 (CH, *m*-Ph), 142.7 (C_q, *i*-C-Ph), 150.8 (C_q, C-1), 154.0 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3442 (s, br.) [ν(C–OH)], 3086 (w), 3061 (w), 3028 (m) [ν(C_{arom}–H)], 2965 (s), 2933 (s), 2873 (s) [ν(C_{aliph}–H)], 1695 (s), 1681 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 396.2507 [M + Na]$^+$. $C_{23}H_{35}NO_3$ (373.53): calcd. C 73.96, H 9.44,

N 3.75; found C 73.85, H 9.36, N 3.54. $[\alpha]_D^{20}$ = +18.9 (*c* = 0.76, $CHCl_3$) at 99% *ee*.

[3*RS*,3(1*RS*),4*RS*]- and [3*RS*,3(1*SR*),4*RS*]-3-(1-Hydroxy-2-methylprop-2-enyl)-4-isopropylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (*rac*-31b and *rac*-32b): Cryptyl carbamate *rac*-**3** (267 mg, 1.0 mmol) was lithiated according to GP C with TMCDA *rac*-**26** (179 mg, 1.05 mmol, 1.3 equiv.) and 1.22 M *s*BuLi solution (0.86 mL, 1.05 mmol, 1.05 equiv.) in Et_2O (8 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (480 mg, 1.6 mmol, 1.6 equiv.) for 3 h. Methacroleine (**28b**, 0.70 g, 10 mmol, 10.0 equiv.) was added and the solution was warmed to room temperature during 14 h. Purification and separation of the diastereomers by FCC (Et_2O/PE = 1:2 → 1:1) yielded 16 mg (0.05 mmol, 5%) *rac*-**32b** as colourless oil and 264 mg (0.78 mmol, 78%) *rac*-**31b** as colourless solid (total yield 83%, *rac*-**31b**:*rac*-**32b** = 95:5[31]). *rac*-**31b**: M.p. 77 °C (Et_2O/PE). t_R = 19.09 min (HP-5). R_F = 0.17 (Et_2O/PE = 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86, 0.99 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.8 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 1.22, 1.24 (2 s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.53 (m, 2 H, 4-H, 4-*i*Pr CH), 1.72 (br. s, 3 H, 2′-CH_3), 1.79 (m, 1 H, 5-H_A), 1.91 (m, 1 H, 5-H_B), 2.24 (m, 2 H, 6-H), 2.35 (br. s, 1 H, OH), 2.63 (m, 1 H, 3-H), 3.83, 4.11 (2 br. s, 2 H, *N*-*i*Pr CH), 4.72 (br. s, 1 H, CH-O), 4.93 (m, 1 H, 3′-H_A), 5.02 (br. s, 1 H, 2-H), 5.15 (m, 1 H, 3′-H_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 21.9 (CH_3, 4-*i*Pr (CH_3)$_2$), 19.2 (CH_3, 2′-CH_3), 20.6, 21.2 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.7 (CH_2, C-5), 26.7 (CH_2, C-6), 27.7 (CH, C-7), 40.1 (CH, C-4), 40.2 (CH, C-3), 46.2 (CH, *N*-*i*Pr CH), 75.6 (CH, C-OH), 110.9 (CH, C-2), 111.4 (CH_2, C-3′), 146.3 (C_q, C-2′), 151.9 (C_q, C-1), 154.0 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3425 (br.) [ν(OH)], 2963 (s), 2934 (m), 2877 (w) [ν(C_{aliph}–H)], 1691 (m) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 360.2507 $[M + Na]^+$. $C_{20}H_{35}NO_3$ (337.50): calcd. C 71.18, H 10.45, N 4.15; found C 71.00, H 10.57, N 3.91. *rac*-**32b**: t_R = 18.95 min (HP-5). R_F = 0.26 (Et_2O/PE = 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83, 0.86 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.7 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 1.15, 1.17 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.43 (m, 1 H, 4-H), 1.64 (m, 1 H, 4-*i*Pr CH), 1.69 (br. s, 3 H, 2′-CH_3), 1.68 (m, 1 H, 5-H_A), 1.75 (dt, $^2J_{5A,5B}$ = 17.2 Hz, $^3J_{4,5B}$ = $^3J_{5B,6}$ = 4.9 Hz, 1 H, 5-H_B), 2.10 (m, 2 H, 6-H), 2.40 (br. s, 1 H, 3-H), 3.72, 3.94 (2 br. s, 2 H, *N*-*i*Pr CH), 3.96 (d, $^3J_{3,CH\text{-}O}$ = 6.4 Hz, 1 H, CH-O), 4.84 (br. s, 1 H, 3′-H_A), 4.98 (br. s, 1 H, 2-H), 5.15 (d, *J* = 4.4 Hz, 1 H, 3′-H_B) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 21.9 (CH_3, 4-*i*Pr (CH_3)$_2$), 19.7 (CH_3, 2′-CH_3), 20.7, 21.2 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.8 (CH_2, C-5), 24.6 (CH_2, C-6), 27.6 (CH, 4-*i*Pr CH), 37.9 (CH, C-4), 40.8 (CH, C-3), 45.7, 46.4 (CH, *N*-*i*Pr CH), 77.3 (CH, C-OH), 112.2, 113.5 (CH/CH_2, C-2/C-3′), 145.4 (C_q, C-2′), 150.5 (C_q, C-1), 154.1 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3432 (br.) [ν(OH)], 2964 (s), 2930 (m), 2876 (w) [ν(C_{aliph}–H)], 1692 (m) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 360.2508 $[M + Na]^+$. $C_{20}H_{35}NO_3$ (337.50): calcd. C 71.18, H 10.45, N 4.15; found C 70.94, H 10.68, N 3.82.

[3*RS*,3(1*SR*),4*RS*]- and [3*RS*,3(1*RS*),4*RS*]-3(1-Hydroxy-2-methylpropyl)-4-isopropylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (*rac*-31c and *rac*-32c): Cryptyl carbamate *rac*-**3** (267 mg, 1.0 mmol) was lithiated according to GP C with *rac*-**26** (179 mg, 1.05 mmol, 1.05 equiv.) and 1.22 M *s*BuLi solution (0.86 mL, 1.05 mmol, 1.05 equiv.) in Et_2O (8 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (479 mg, 1.6 mmol, 1.6 equiv.) for 3 h. Isobutyraldehyde (**28c**, 0.72 g, 10 mmol, 10.0 equiv.) was then added and the solution was warmed to room temperature within 14 h. Purification and separation of the diastereomers by FCC (Et_2O/PE = 1:2) yielded 34 mg (0.10 mmol, 10%) *rac*-**32c** and 175 mg (0.52 mmol, 52%) *rac*-**31c** as colourless oils (total yield 62%, *rac*-**31c**:*rac*-**32c** = 85:15). *rac*-**31c**: t_R = 18.79 min (HP-5). R_F = 0.26 (Et_2O/PE = 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82, 0.88 (2 d, $^3J_{i\text{PrCH},i\text{Pr(Me)}}$ = 6.8 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 0.97, 1.03 (2 d, $^3J_{2',3'}$ = 6.7 Hz, 6 H, 3′-H), 1.23, 1.24 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.51 (m, 1 H, 4-H), 1.68 (dsept, $^3J_{2',CH\text{-}O}$ = 1.9 Hz, $^3J_{2',3'}$ = 6.7 Hz, 1 H, 2′-H), 1.75–1.89 (m, 3 H, 4-*i*Pr CH, 5-H), 2.13 (m, 2 H, 6-H), 2.48 (br. s, 1 H, 3-H), 3.20 (dd, $^3J_{2',CH\text{-}O}$ = 1.9 Hz, $^3J_{3,CH\text{-}O}$ = 8.8 Hz, 1 H, CH-O), 3.79, 4.05 (2 br. s, 2 H, *N*-*i*Pr CH), 5.21 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 19.3 (CH_3, 4-*i*Pr (CH_3)$_2$), 20.9 (CH_2, C-3′), 20.9, 21.7 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.8 (CH_2, C-5), 26.9 (CH_2, C-6), 27.8 (CH, 4-*i*Pr CH), 32.1 (CH, C-2′), 39.8 (CH, C-3), 40.8 (CH, C-4), 45.9, 46.6 (CH, *N*-*i*Pr CH), 78.2 (CH, C-OH), 111.4 (CH, C-2), 152.2 (C_q, C-1), 154.0 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3400 (br.) [ν(OH)], 2958 (s), 2936 (m), 2872 (w) [ν(C_{aliph}–H)], 1699 (m) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 362.2668 $[M + Na]^+$. $C_{20}H_{37}NO_3$ (339.51): calcd. C 70.75, H 10.98, N 4.13; found C 70.57, H, 11.03, N 3.88. *rac*-**32c**: t_R = 18.79 min (HP-5). R_F = 0.44 (Et_2O/PE = 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93, 0.94 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.6 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 0.95, 0.96 (2 d, $^3J_{2',3'}$ = 6.6 Hz, 6 H, 3′-H), 1.22, 1.24 (2 br. s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.53 (m, 1 H, 4-H), 1.61 (br. s, 1 H, OH), 1.68–1.80 (m, 2 H, 2′-H/4-*i*Pr CH), 1.86–1.97 (m, 2 H, 5-H), 1.92, 2.20 (2 m, 2 H, 6-H), 2.36 (t, $^3J_{2,3}$ = $^3J_{3,CH\text{-}O}$ = 5.4 Hz, 1 H, 3-H), 3.20 (t, $^3J_{2',CH\text{-}O}$ = $^3J_{3,CH\text{-}O}$ = 5.4 Hz, 1 H, CH-O), 3.77, 4.05 (2 br. s, 2 H, *N*-*i*Pr CH), 5.21 (d, $^3J_{2,3}$ = 5.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1, 20.3 (CH_3, 4-*i*Pr (CH_3)$_2$), 20.5 (CH_3, C-3′), 20.8, 21.9 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.0 (CH_2, C-5), 24.0 (CH_2, C-6), 27.5 (CH, 4-*i*Pr CH), 29.7 (CH, C-2′), 38.4 (CH, C-3), 40.6 (CH, C-4), 46.0 (CH, *N*-*i*Pr CH), 78.4 (CH, C-OH), 113.3 (CH, C-2), 150.3 (C_q, C-1), 154.1 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3410 (br.) [ν(OH)], 2961 (s), 2933 (m), 2873 (w) [ν(C_{aliph}–H)], 1682 (m) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 362.2670 $[M + Na]^+$. $C_{20}H_{37}NO_3$ (339.51): calcd. C 70.75, H 10.98, N 4.13; found C 70.48, H 10.96, N 3.91.

[3*R*,3(1*R*,2*S*),4*R*]-3-(2-(*tert*-Butyldiphenylsilyloxy)-1-hydroxypropyl)-4-isopropylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (31d): (1*S*,4*R*)-Cryptyl carbamate **3** (134 mg, 0.50 mmol, 99% *ee*) was lithiated according to GP C with TMCDA (*rac*-**26**, 116 mg, 0.65 mmol, 1.3 equiv.) and 1.36 M *s*BuLi solution (0.48 mL, 0.65 mmol, 1.3 equiv.) in Et_2O (4 mL) at –78 °C for 2 h and transmetallated with $ClTi(NEt_2)_3$ (450 mg, 1.5 mmol, 3.0 equiv.) for 3 h. (2*R*)-2-(*tert*-Butyldiphenylsilyloxy)propanal[25] (**28d**, 1.13 g, 3.6 mmol, 7.3 equiv.) ($[\alpha]_D^{20}$ = +19.4 (*c* = 0.94, $CHCl_3$); ref.[25] $[\alpha]_D^{20}$ = –15.0 (*c* = 1.07, $CHCl_3$) for (2*S*)-**28d**), were then added and the solution was warmed to room temperature during 17 h. Purification by FCC (Et_2O/PE = 1:4) yielded 129 mg (0.22 mmol, 45%) **31d** as a colourless oil. 668 mg (2.14 mmol) of the enantiopure aldehyde **28d** were reisolated. t_R = decomposition (HP-5). R_F = 0.18 (Et_2O/PE = 1:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.78, 0.95 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.9 Hz, 6 H, 4-*i*Pr (CH_3)$_2$), 0.97 (d, $^3J_{2',3'}$ = 6.4 Hz, 6 H, 3′-H), 1.06 (s, 9 H, C(CH_3)$_3$), 1.22, 1.23 (2 s, 12 H, *N*-*i*Pr (CH_3)$_2$), 1.50 (m, 2 H, 4-H, 5-H_A), 1.79 (m, 1 H, 5-H_B), 1.92 (dsept, $^3J_{4,4\text{-}i\text{PrCH}}$ = 3.6 Hz, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.9 Hz, 1 H, 4-*i*Pr CH), 2.09 (m, 1 H, 6-H_A), 2.19 (m, 1 H, 6-H_B), 2.36 (m, 1 H, 3-H), 2.70 (br. s, 1 H, OH), 3.56 (dd, $^3J_{1',2'}$ = 6.4 Hz, $^3J_{1',3}$ = 2.1 Hz, 1 H, 1′-H), 3.84, 3.98 (2 br. s, 2 H, *N*-*i*Pr CH), 3.91 (quint, $^3J_{1',2'}$ = $^3J_{2',3'}$ = 6.4 Hz, 1 H, 2′-H), 5.12 (br. s, 1 H, 2-H), 7.36–7.43, 7.70–7.72 (2 m, 10 H, PhCH) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ = 16.9, 19.9 (CH_3, 4-*i*Pr (CH_3)$_2$), 19.3 (C_q; *C*(CH_3)$_3$), 20.5, 21.3 (CH_3, *N*-*i*Pr (CH_3)$_2$), 21.4 (CH_2, C-5), 21.8 (CH_3, C-3′), 26.4 (CH_2, C-6), 27.0 (CH_3, C(*C*H_3)$_3$), 27.1 (CH, 4-*i*Pr CH), 38.9 (CH_2, C-3), 40.9 (CH, C-4), 45.7, 46.3 (CH, *N*-*i*Pr CH), 71.9 (CH, C-2′), 78.4 (CH, C-1′), 112.6 (CH, C-2), 127.5, 127.7 (CH, *m*-Ph), 129.6, 129.7 (CH, *p*-Ph), 133.4, 134.2 (CH, *i*-C-Ph), 135.8, 135.9 (CH, *o*-Ph), 150.7 (C_q, C-1), 153.9 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3459 (br.)

[ν(OH)], 2961 (s), 2932 (m), 2892 (w), 2859 (w) [ν(C_{aliph}–H)], 1702 (m) [ν(C=O)] cm^{-1}. MS (ESI): m/z = 602.3636 $[M + Na]^+$. $C_{35}H_{53}NO_4Si$ (579.89): calcd. C 72.49, H 9.21, N 2.42; found C 72.48, H 9.38, N 2.11. $[\alpha]_D^{20}$ = +40.8 (c = 1.04, $CHCl_3$).

(3*RS*,4*RS*)-3-Benzoyl-4-isopropylcyclohex-1-enyl *N*,*N*-Diisopropylcarbamate (*rac*-33): The homoaldol product *rac*-**31a** (126 mg, 0.34 mmol), dissolved in 5 mL CH_2Cl_2, was treated with PDC (0.64 g, 1.7 mmol, 5.0 equiv.) and powdered molecular sieves (4 Å) (20 mg) and stirred for 16 h at room temperature. The suspension was diluted with Et_2O (20 mL), filtered through silica gel and the solvent was removed in vacuo. Purification by FCC (Et_2O/PE = 1:4) yielded 118 mg (0.32 mmol, 93%) *rac*-**33** as a colourless solid. Oxidation of *rac*-**32a** (17 mg, 0.046 mmol) for 28 h using the conditions above yielded 15 mg (0.040 mmol, 88%) *rac*-**33**. M.p. 78 °C (Et_2O/PE). t_R = 19.81 min (HP-5). R_F = 0.40 (Et_2O/PE = 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85, 0.95 (2 d, $^3J_{4\text{-}i\text{PrCH},4\text{-}i\text{Pr(Me)}}$ = 6.8 Hz, 6 H, 4-*i*Pr $(CH_3)_2$), 1.20, 1.21 (2 s, 12 H, *N*-*i*Pr $(CH_3)_2$), 1.68 (m, 2 H, 5-H), 1.88 (m, 1 H, 4-*i*Pr CH), 2.11 (m, 1 H, 6-H_A), 2.24 (m, 1 H, 6-H_B), 2.30 (m, 1 H, 4-H), 3.79, 3.99 (2 br. s, 2 H, *N*-*i*Pr CH), 4.23 (m, 1 H, 3-H), 5.27 (m, 1 H, 2-H), 7.48 (m, 2 H, *m*-PhCH), 7.57 (tt, $^3J_{m\text{-PhCH},p\text{-PhCH}}$ = 7.5 Hz, $^4J_{o\text{-PhCH},p\text{-PhCH}}$ = 1.4 Hz, 1 H, *p*-PhCH), 8.02 (dd, $^3J_{o\text{-PhCH},m\text{-PhCH}}$ = 8.5 Hz, $^4J_{o\text{-PhCH},p\text{-PhCH}}$ = 1.4 Hz, 2 H, *o*-PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 21.4 (CH_3, 4-*i*Pr $(CH_3)_2$), 20.4, 21.3 (CH_3, *N*-*i*Pr $(CH_3)_2$), 22.0 (CH_2, C-5), 26.7 (CH_2, C-6), 29.2 (CH, 4-*i*Pr CH), 40.4 (CH, C-4), 45.8, 46.3 (CH, *N*-*i*Pr CH), 46.5 (CH, C-3), 111.1 (CH, C-2), 128.6, 128.7 (CH, *o*/*m*-Ph), 133.0 (C_q, *i*-C-Ph), 136.6 (CH, *p*-Ph), 151.0 (C_q, C-1), 153.5 (C_q, *i*-C-Ph), 201.2 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3060 (w), 3001 (m), [ν(C_{arom}–H)], 2961 (s), 2874 (m) [ν(C_{aliph}–H)], 1688 (s), [ν(C=O)] cm^{-1}. MS (ESI): m/z = 394.2351 $[M + Na]^+$. $C_{23}H_{33}NO_3$ (371.51): calcd. C 74.36, H 8.95, N 3.77; found C 74.39, H 9.00, N 3.62.

Synthesis of Hexahydroisobenzofuran-4(1*H*)-ones: General Procedure D (GP D): To a stirred solution of the homoaldol product (0.5 mmol) and the aldehyde (0.65 mmol, 1.3 equiv.) in CH_2Cl_2 (2 mL) at 0 °C, $BF_3{\cdot}OEt_2$ (92 mg 0.65 mmol, 1.3 equiv.) was added through a syringe within 1 min. The solution was warmed to room temperature and stirring was continued until complete consumption of the starting material (TLC). The reaction was quenched with satd. aq. NaCl solution (3 mL), diluted with CH_2Cl_2 (5 mL) and the aqueous layer was extracted with TBME (3 × 10 mL). The combined organic layers were washed with satd. aq. $NaHCO_3$ solution (5 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by FCC on silica gel (Et_2O/PE or TBME/PE mixtures).

(1*S*,3*S*,3a*S*,6*R*,7a*R*)-6-Isopropenyl-3a-methyl-1,3-di(naphthalen-2-yl)-hexahydroisobenzofuran-4(1*H*)-one (35a): According to GP D **18a** (218 mg, 0.50 mmol), 2-naphthaldehyde (**34a**, 101 mg, 0.65 mmol, 1.3 equiv.) and $BF_3{\cdot}OEt_2$ (92 mg, 0.65 mmol, 1.3 equiv.), were stirred for 30 min. FCC (Et_2O/PE = 1:10) yielded 183 mg (0.41 mmol, 82%) **35a** as a colourless oil. t_R = 29.61 min (HP-5). R_F = 0.10 (Et_2O/PE = 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32–1.38 (m, 2 H, 5-H_A, 7-H_A), 1.47 (s, 3 H, 6-C(CH_2)(CH_3)), 1.69 (s and m, 4 H, 3a-CH_3, 7-H_B), 2.17 (ddd, $^2J_{5A,5B}$ = 16.8 Hz, $^3J_{5B,6}$ = 3.8 Hz, $^4J_{5B,7A}$ = 2.0 Hz, 1 H, 5-H_B), 2.43–2.50 (m, 2 H, 7a-H, 6-H), 4.44, 4.72 (2 s, 2 H, 6-C(CH_2)(CH_3)), 4.15 (s, 1 H, 3-H), 5.56 (d, $^3J_{1,7a}$ = 4.8 Hz, 1 H, 1-H), 7.44–7.57 (m, J = 7.5 Hz, 6 H, ArCH), 7.81 (d, J = 8.7 Hz, 1 H, ArCH), 7.88–7.93 (m, 3 H, ArCH), 7.96 (d, J = 8.7 Hz, 1 H, ArCH), 8.05 (s, 1 H, ArCH), 8.13 (s, 1 H, ArCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (CH_3, 3a-CH_3), 26.0 (CH_3, 6-C(CH_2)(CH_3)), 27.1 (CH_2, C-7), 38.9 (CH, C-6), 45.2 (CH_2, C-5), 50.5 (CH, C-7a), 60.3 (C_q, C-3a), 82.5 (CH, C-3), 90.0 (CH, C-1), 111.5 (CH_2, 6-C(CH_2)(CH_3)), 123.8, 124.4, 124.7, 125.9, 126.0, 126.2, 126.3, 127.7, 127.8, 128.0, 128.2, 132.7 (CH, C-Ar), 132.9, 133.4, 136.0, 136.7 (C_q, C-Ar), 146.8 (C_q, 6-$C(CH_2)(CH_3)$), 212.1 (C_q, C-4) ppm. IR (film): $\tilde{\nu}$ = 3407 (br.) [ν(OH)], 3052 (m) [ν(C_{arom}–H)], 2962 (s), 2925 (m), 2860 (w), 2859 (w) [ν(C_{aliph}–H)], 1695 (s) [ν(C=O)] cm^{-1}. MS (ESI): m/z = 469.2157 $[M + Na]^+$. $C_{32}H_{30}O_2$ (446.58): calcd. C 86.06, H 6.77; found C 85.72, H 6.61. $[\alpha]_D^{20}$ = +36.2 (c = 1.00, $CHCl_3$).

(1*S*,3*S*,3a*S*,6*R*,7a*R*)-6-Isopropenyl-3a-methyl-1-(naphthalen-2-yl)-3-phenyl-hexahydroisobenzofuran-4(1*H*)-one (35b): According to GP D **18a** (219 mg, 0.50 mmol), benzaldehyde (**34b**, 70 mg, 0.65 mmol, 1.3 equiv.), and $BF_3{\cdot}OEt_2$ (92 mg, 0.65 mmol, 1.3 equiv.) were stirred for 30 min. FCC (TBME/PE = 1:10) yielded 164 mg (0.41 mmol, 83%) **35b** as a colourless solid. M.p. 79 °C (PE). t_R = 24.55 min (HP-5). R_F = 0.19 (TBME/PE = 1:10). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.31 (ddt, $^2J_{7A,7B}$ = 14.1 Hz, $^3J_{6,7A}$ = $^3J_{7a,7A}$ = 5.4 Hz, $^4J_{5B,7A}$ = 2.1 Hz, 1 H, 7-H_A), 1.40 (dd, $^2J_{5A,5B}$ = 16.9 Hz, $^3J_{5A,6}$ = 5.9 Hz, 1 H, 5-H_A), 1.48 (s, 3 H, 6-C(CH_2)(CH_3)), 1.63 (s and m, 4 H, 3a-CH_3, 7-H_B), 2.17 (ddd, $^2J_{5A,5B}$ = 16.9 Hz, $^3J_{5B,6}$ = 3.9 Hz, $^4J_{5B,7A}$ = 2.1 Hz, 1 H, 5-H_B), 2.43 (dt, $^3J_{1,7a}$ = 5.1 Hz, $^3J_{7a,7A}$ = $^3J_{7a,7B}$ = 5.4 Hz, 1 H, 7a-H), 2.50 (br. s, 1 H, 6-H), 4.44, 4.72 (2 s, 2 H, 6-C(CH_2)(CH_3)), 4.99 (s, 1 H, 3-H), 5.56 (d, $^3J_{1,7a}$ = 5.1 Hz, 1 H, 1-H), 7.27 (t, J = 7.5 Hz, 1 H, *p*-PhCH), 7.36 (t, J = 7.5 Hz, 2 H, *m*-PhCH), 7.46–7.50 (m, 4 H, ArCH, *o*-PhCH), 7.53 (m, 1 H, ArCH), 7.86 (d, J = 8.0 Hz, 1 H, ArCH), 7.89 (d, J = 8.5 Hz, 1 H, ArCH), 7.92 (d, J = 8.0 Hz, 1 H, ArCH), 8.06 (s, 1 H, ArCH) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ = 21.7 (CH_3, 3a-CH_3), 25.9 (CH_3, 6-C(CH_2)(CH_3)), 27.0 (CH_2, C-7), 38.9 (CH, C-6), 45.0 (CH_2, C-5), 50.4 (CH, C-7a), 60.2 (C_q, C-3a), 82.4 (CH, C-3), 89.9 (CH, C-1), 111.5 (CH_2, 6-C(CH_2)(CH_3)), 123.8 (CH, *o*-Ph), 124.4, 125.8, 126.1 (CH, C-Ar), 126.3 (CH, *m*-Ph), 127.7 (CH, C-Ar), 128.0 (CH, *p*-Ph), 128.1 (CH, C-Ar), 132.7 (C_q, *i*-C-Ph), 133.4, 136.0, 139.0 (C_q, C-Ar), 146.9 (C_q, 6-$C(CH_2)(CH_3)$), 212.3 (C_q, C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 3024 (w) [ν(C_{arom}–H)], 2968 (s), 2932 (w), 2866 (w) [ν(C_{aliph}–H)], 1691 (s) [ν(C=O)] cm^{-1}. MS (ESI): m/z = 419.1978 $[M + Na]^+$. $C_{28}H_{28}O_2$ (396.52): calcd. C 84.81, H 7.12; found C 84.46, H 7.14. $[\alpha]_D^{20}$ = +9.80 (c = 1.01, $CHCl_3$).

(1*S*,3*S*,3a*R*,6*R*,7a*S*)-6-Isopropenyl-3a-methyl-1-(naphthalen-2-yl)-3-phenylhexahydroisobenzofuran-4(1*H*)-one (38a): According to GP D **20a** (219 mg, 0.50 mmol), benzaldehyde (**36a**, 70 mg, 0.65 mmol, 1.3 equiv.) and $BF_3{\cdot}OEt_2$ (92 mg, 0.65 mmol, 1.3 equiv.), were stirred for 1 h. FCC (Et_2O/PE = 1:10) yielded 145 mg (0.37 mmol, 73%) **38a** as a colourless solid. M.p. 79 °C (PE). t_R = 25.54 min (HP-5). R_F = 0.21 (Et_2O/PE = 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (br. s, 3 H, 6-C(CH_2)(CH_3)), 1.56 (dt, $^2J_{7A,7B}$ = 13.1 Hz, $^3J_{6,7A}$ = $^3J_{7A,7a}$ = 12.4 Hz, 1 H, 7-H_A), 1.76 (s, 3 H, 3a-CH_3), 2.14 (ddt, $^2J_{7A,7B}$ = 13.1 Hz, $^3J_{6,7B}$ = 6.5 Hz, $^4J_{5B,7B}$ = 2.3 Hz, 1 H, 7-H_B), 2.38 (dd, $^3J_{1,7a}$ = 7.5 Hz, $^3J_{7A,7a}$ = 12.4 Hz, 1 H, 7a-H), 2.40 (dd, $^2J_{5A,5B}$ = 17.0 Hz, $^3J_{5A,6}$ = 11.0 Hz, 1 H, 5-H_A), 2.65 (m, 1 H, 6-H), 2.75 (ddd, $^2J_{5A,5B}$ = 17.0 Hz, $^3J_{5B,6}$ = 6.5 Hz, $^4J_{5B,7B}$ = 2.3 Hz, 1 H, 5-H_B), 4.74 (d, $^3J_{1,7a}$ = 7.5 Hz, 1 H, 1-H), 4.79, 4.80 (2 s, 2 H, 6-C(CH_2)(CH_3)), 5.54 (s, 1 H, 3-H), 7.28 (tt, $^3J_{m\text{-PhCH},p\text{-PhCH}}$ = 7.3 Hz, $^3J_{o\text{-PhCH},p\text{-PhCH}}$ = 1.7 Hz, 1 H, *p*-PhCH), 7.37 (br. t, $^3J_{m\text{-PhCH},p\text{-PhCH}}$ = $^3J_{m\text{-PhCH},o\text{-PhCH}}$ = 7.5 Hz, 2 H, *m*-PhCH), 7.47–7.53 (m, 2 H, ArCH), 7.59 (d, $^3J_{m\text{-PhCH},o\text{-PhCH}}$ = 7.4 Hz, 2 H, *o*-PhCH), 7.62 (dd, J = 8.4 Hz, J = 1.6 Hz, 2 H, ArCH), 7.84–7.89 (m, 2 H, ArCH), 7.91 (br. s, 1 H, ArCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (CH_3, 3a-CH_3), 23.1 (CH_3, 6-C(CH_2)(CH_3)), 33.1 (CH_2, C-7), 41.0 (CH_2, C-6), 43.3 (CH, C-5), 57.5 (C_q, CH, C-3a, C-7a), 83.1 (CH, C-3), 86.3 (CH, C-1), 110.3 (CH_2, 6-C(CH_2)(CH_3)), 123.7 (CH, *o*-Ph), 124.6, 125.9, 126.2, 127.0, 127.3 (CH, C-Ar), 127.7 (CH, *m*-Ph), 127.8, 127.9 (CH, C-

Ar), 128.4 (CH, *p*-Ph), 133.1 (CH, C-Ar), 133.2 (C_q, *i*-C-Ph), 138.0, 138.4 (C_q, C-Ar), 147.0 (C_q, 6-*C*(CH_2)(CH_3)), 213.7 (C_q, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3079 (w), 3057 (w), 3029 (w) [$\nu(C_{arom}–H)$], 2933 (m), 2932 (w), 2865 (w) [$\nu(C_{aliph}–H)$], 1698 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 419.1957 $[M + Na]^+$. $C_{28}H_{28}O_2$ (396.52): calcd. C 84.81, H 7.12; found C 84.49, H 7.07. $[\alpha]_D^{20}$ = +72.8 (*c* = 0.99, $CHCl_3$).

(1*S*,3*S*,3a*R*,6*R*,7a*S*)-1-(4-Bromophenyl)-6-isopropenyl-3,3a-dimethyl-hexahydroisobenzofuran-4(1*H*)-one (38b): According to GP D **20d** (232 mg, 0.50 mmol), acetaldehyde (**36b**, 29 mg, 0.65 mmol, 1.3 equiv.), and BF_3·OEt_2 (92 mg, 0.65 mmol, 1.3 equiv.) were stirred for 3 h. FCC (Et_2O/PE = 1:9) yielded 151 mg (0.42 mmol, 83%) **38b** as a colourless oil. t_R = 19.15 min (HP-5). R_F = 0.23 (Et_2O/PE = 1:9). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (br. s, 3 H, 6-C(CH_2)(CH_3)), 1.35 (d, $^3J_{3,3\text{-}CH3}$ = 6.3 Hz, 3 H, 3-CH_3), 1.48 (m, 1 H, 7-H_A), 1.74 (s, 3 H, 3a-CH_3), 2.08 (m, 1 H, 7-H_B), 2.14 (m, 1 H, 7a-H), 2.23 (dd, $^2J_{5A,5B}$ = 17.0 Hz, $^3J_{5A,6}$ = 11.4 Hz, 1 H, 5-H_A), 2.49–2.58 (m, 1 H, 6-H), 2.64 (ddd, $^2J_{5A,5B}$ = 17.0 Hz, $^3J_{5B,6}$ = 5.4 Hz, *J* = 2.3 Hz, 1 H, 5-H_B), 4.74 (q, $^3J_{3,3\text{-}CH3}$ = 6.3 Hz, 1 H, 3-H), 5.54 (d, $^3J_{1,7a}$ = 6.1 Hz, 1 H, 1-H), 4.76, 4.79 (s, m, 2 H, 6-C(CH_2)(CH_3)), 7.24 (dm, $^3J_{m\text{-}PhCH,o\text{-}PhCH}$ = 8.2 Hz, 1 H, *o*-PhCH), 7.47 (dm, $^3J_{m\text{-}PhCH,o\text{-}PhCH}$ = 8.2 Hz, 1 H, *m*-PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (CH_3, 3-CH_3), 20.2 (CH_3, 3a-CH_3), 20.8 (CH_3, 6-C(CH_2)(*C*H_3)), 34.2 (CH_2, C-7), 41.4 (CH_2, C-6), 43.7 (CH, C-5), 55.7 (C_q, CH, C-7a), 57.3 (C_q, C-3a), 78.1 (CH, C-3), 85.8 (CH, C-1), 110.3 (CH_2, 6-C(*C*H_2)(CH_3)), 121.3 (CH, *p*-Ph), 127.2 (CH, *o*-Ph), 131.6 (CH, *m*-Ph), 140.9 (C_q, *i*-C-Ph), 146.9 (C_q, 6-*C*(CH_2)(CH_3)), 213.6 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3084 (w), 3047 (w) [$\nu(C_{arom}–H)$], 2966 (s), 2934 (s), 2909 (s), 2868 (m) [$\nu(C_{aliph}–H)$], 1691 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 385.3 $[M + Na]^+$. $C_{19}H_{23}BrO_2$ (363.29): calcd. C 62.82, H 6.38; found C 62.78, H 6.44. $[\alpha]_D^{20}$ = +57.0 (*c* = 0.53, $CHCl_3$).

(1*S*,3*S*,3a*R*,6*R*,7a*S*)-1,6-Diisopropenyl-3-isopropyl-3a-methyl-hexahydroisobenzofuran-4(1*H*)-one (38c): According to GP D **20f** (174 mg, 0.50 mmol), isobutyraldehyde (**36c**, 47 mg, 0.65 mmol, 1.3 equiv.), and BF_3·OEt_2 (92 mg, 0.65 mmol, 1.3 equiv.) were stirred for 1 h. FCC (TBME/PE = 1:20) yielded 101 mg (0.37 mmol, 73%) **38c** as a colourless oil. t_R = 14.13 min (HP-5). R_F = 0.24 (Et_2O/PE = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73, 1.07 (2 d, $^3J_{3\text{-}i\text{Pr(Me)},3\text{-}i\text{PrCH}}$ = 6.7 Hz, 6 H, 3-*i*Pr (CH_3)$_2$), 1.13 (s, 3 H, 3a-CH_3), 1.72 (s and m, 4 H, 6-C(CH_2)(CH_3), 7-H_A), 1.76 (s, 3 H, 1-C(CH_2)(CH_3)), 1.88 (m, 1 H, 3-*i*Pr CH), 1.98 (dm, $^2J_{5A,5B}$ = 13.8 Hz, 1 H, 5-H_A), 2.16 (ddd, $^3J_{1,7a}$ = 2.8 Hz, $^3J_{7A,7a}$ = 6.5 Hz, $^3J_{7B,7a}$ = 12.4 Hz, 1 H, 7a-H), 2.48 (m, 3 H, 5-H_B, 6-H, 7-H_B), 3.85 (d, $^3J_{3,3\text{-}i\text{PrCH}}$ = 8.9 Hz, 1 H, 3-*i*Pr CH), 4.02 (br. s, 1 H, 1-H), 4.76, 4.79 (2 s, 2 H, 6-C(CH_2)(CH_3)), 4.83, 5.12 (2 s, 2 H, 1-C(CH_2)(CH_3)) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1, 18.9 (CH_3, 3-*i*Pr (CH_3)$_2$), 18.2 (CH_3, 3a-CH_3), 20.3 (CH_3, 1-C(CH_2)(*C*H_3)), 21.1 (CH_3, 6-C(CH_2)(*C*H_3)), 29.4 (CH_2, C-7), 36.3 (CH_3, 3-*i*Pr CH), 44.3 (CH, C-6), 44.7 (CH_2, C-5), 55.0 (CH, C-7a), 57.0 (C_q, C-3a), 87.2 (CH, C-3), 88.0 (CH, C-1), 109.5 (CH_2, 1-C(*C*H_2)(CH_3)), 110.1 (CH_2, 6-C(*C*H_2)(CH_3)), 144.8 (C_q, 1-*C*(CH_2)(CH_3)), 147.1 (C_q, 6-*C*(CH_2)(CH_3)), 213.3 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 2978 (m), 2958 (m), 2933 (m), 2917 (m) [$\nu(C_{aliph}–H)$], 1699 (s) [ν(C=O)], 1650 (s) [ν(C=C)] cm^{-1}. MS (ESI): *m*/*z* = 299.1983 $[M + Na]^+$. $C_{18}H_{28}O_2$ (276.41): calcd. C 78.21, H 10.21; found C 77.93, H 10.12. $[\alpha]_D^{20}$ = +93.3 (*c* = 1.00, $CHCl_3$).

(1*R*,3*S*,3a*R*,6*R*,7a*S*)-6-Isopropenyl-1-isopropyl-3a-methyl-3-phenyl-hexahydroisobenzofuran-4(1*H*)-one (38d): According to GP D **20g** (179 mg, 0.50 mmol), benzaldehyde (**36a**, 70 mg, 0.65 mmol, 1.3 equiv.), and BF_3·OEt_2 (92 mg, 0.65 mmol, 1.3 equiv.) were stirred for 30 min. FCC (TBME/PE = 1:10) yielded 124 mg (0.40 mmol, 80%) **38d** as a colourless oil. t_R = 17.94 min (HP-5). R_F = 0.22 (TBME/PE = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 3 H, 3a-CH_3), 1.02, 1.10 (2 d, $^3J_{1\text{-}i\text{Pr(Me)},1\text{-}i\text{PrCH}}$ = 6.9 Hz, 6 H, 1-*i*Pr (CH_3)$_2$), 1.50 (dt, $^3J_{6,7A}$ = $^3J_{7a,7A}$ = 12.2 Hz, $^2J_{7A,7B}$ = 13.3 Hz, 1 H, 7-H_A), 1.76 (s, 3 H, 6-C(CH_2)(CH_3)), 1.92 (oct, $^3J_{1,1\text{-}i\text{PrCH}}$ = $^3J_{1\text{-}i\text{Pr(Me)},1\text{-}i\text{PrCH}}$ = 6.9 Hz, 1 H, 1-*i*Pr CH), 2.01 (dm, $^2J_{7A,7B}$ = 13.3 Hz, 1 H, 7-H_B), 2.15 (dt, $^3J_{1,7a}$ = $^3J_{7a,7B}$ = 6.3 Hz, $^3J_{7a,7A}$ = 12.2 Hz, 1 H, 7a-H), 2.35 (dd, $^2J_{5A,5B}$ = 16.0 Hz, $^3J_{5A,6}$ = 11.4 Hz, 1 H, 5-H_A), 2.59 (m, 1 H, 6-H), 2.68 (ddd, $^2J_{5A,5B}$ = 16.0 Hz, $^3J_{5B,6}$ = 5.3 Hz, *J* = 2.3 Hz, 1 H, 5-H_B), 3.39 (dd, $^3J_{1,7a}$ = 6.3 Hz, $^3J_{1,1\text{-}i\text{PrCH}}$ = 6.9 Hz, 1 H, 1-H), 4.78, 4.80 (2 s, 2 H, 6-C(CH_2)(CH_3)), 5.11 (s, 1 H, 3-H), 7.29 (m, 5 H, PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (CH_3, 3a-CH_3), 19.3 (CH_3, 1-*i*Pr (CH_3)$_2$), 21.8 (CH_3, 6-C(CH_2)(*C*H_3)), 32.6 (CH, 1-*i*Pr CH), 35.6 (CH_2, C-7), 42.1 (CH, C-6), 44.2 (CH_2, C-5), 52.4 (CH, C-7a), 57.5 (C_q, C-3a), 82.3 (CH, C-1), 90.4 (CH, C-3), 110.1 (CH_2, 6-C(*C*H_2)(CH_3)), 127.0, 127.3, 127.6 (CH, *o*/*m*/*p*-Ph), 137.8 (C_q, *i*-C-Ph), 147.2 (C_q, 6-*C*(CH_2)(CH_3)), 213.2 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 2978 (m), 2958 (m), 2933 (m), 2917 (m) [$\nu(C_{aliph}–H)$], 1699 (s) [ν(C=O)], 1650 (s) [ν(C=C)] cm^{-1}. HR-MS (ESI, $C_{21}H_{28}O_2$, 312.45): calcd. *m*/*z* = 335.1982 $[M + Na]^+$, found *m*/*z* = 335.1950 $[M + Na]^+$. $[\alpha]_D^{20}$ = –0.45 (*c* = 1.01, $CHCl_3$).

(1*R*,3*S*,3a*R*,6*R*,7a*S*)-1-Cyclohexyl-6-isopropenyl-3a-methyl-3-phenyl-hexahydroisobenzo-furan-4(1*H*)-one (38e): According to GP D **20b** (196 mg, 0.50 mmol), benzaldehyde (**36a**, 70 mg, 0.65 mmol, 1.3 equiv.), and BF_3·OEt_2 (92 mg, 0.65 mmol, 1.3 equiv.) were stirred for 1 h. FCC (TBME/PE = 1:20) yielded 146 mg (0.41 mmol, 83%) **38d** as a colourless oil. t_R = 21.22 min (HP-5). R_F = 0.37 (TBME/PE = 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 3 H, 3a-CH_3), 1.18–1.23 (m, 6 H, $CyCH_2$), 1.50 (dt, $^3J_{6,7a}$ = $^3J_{7a,7A}$ = 12.1 Hz, $^2J_{7A,7B}$ = 13.4 Hz, 1 H, 7-H_A), 1.61 (m, 1 H, CyCH), 1.76 (s and m, 7 H, 6-C(CH_2)(CH_3)), $CyCH_2$), 1.99 (ddt, *J* = 13.4 Hz, *J* = 6.3 Hz, *J* = 2.5 Hz, 1 H, $CyCH_2$), 2.08 (br. d, $^2J_{7A,7B}$ = 13.4 Hz, 1 H, 7-H_B), 2.18 (dt, $^3J_{1,7a}$ = $^3J_{7a,7B}$ = 6.2 Hz, $^3J_{7a,7A}$ = 12.1 Hz, 1 H, 7a-H), 2.35 (dd, $^2J_{5A,5B}$ = 16.0 Hz, $^3J_{5A,6}$ = 11.3 Hz, 1 H, 5-H_A), 2.59 (m, 1 H, 6-H), 2.68 (ddd, $^2J_{5A,5B}$ = 16.0 Hz, $^3J_{5B,6}$ = 5.3 Hz, *J* = 2.3 Hz, 1 H, 5-H_B), 3.42 (dd, $^3J_{1,7a}$ = 6.2 Hz, $^3J_{1,CyCH}$ = 7.0 Hz, 1 H, 1-H), 4.78, 4.80 (2 s, 2 H, 6-C(CH_2)(CH_3)), 5.09 (s, 1 H, 3-H), 7.28 (m, 5 H, PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (3a-CH_3), 21.8 (CH_3, 6-C(CH_2)(*C*H_3)), 26.0, 26.1, 26.5, 29.3, 29.9 (CH_2, C-Cy), 35.6 (CH_2, C-7), 42.1 (CH, C-6), 42.5 (CH, C-Cy), 44.2 (CH_2, C-5), 52.2 (CH, C-7a), 57.4 (C_q, C-3a), 82.2 (CH, C-1), 89.5 (CH, C-3), 110.1 (CH_2, 6-C(*C*H_2)(CH_3)), 127.0, 127.3, 127.6 (CH, *o*/*m*/*p*-Ph), 137.8 (C_q, *i*-C-Ph), 147.3 (C_q, 6-*C*(CH_2)(CH_3)), 213.4 (C_q, C=O) ppm. IR (film): $\tilde{\nu}$ = 3082 (w), 3060 (w), 3030 (w) [$\nu(C_{arom}–H)$], 2960 (m), 2926 (s), 2848 (s) [$\nu(C_{aliph}–H)$], 1700 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 375.2308 $[M + Na]^+$. $C_{24}H_{32}O_2$ (352.51): calcd. C 81.77, H 9.15; found C 81.75, H 9.43. $[\alpha]_D^{20}$ = +70.7 (*c* = 0.54, $CHCl_3$).

(1*R*,3*S*,3a*S*,7*R*,7a*R*)-3-(4-Bromophenyl)-7-isopropyl-1-phenyl-hexahydroisobenzofuran-4(1*H*)-one (41a): According to GP D **31a** (45 mg, 0.12 mmol), 4-bromobenzaldehyde (**39a**, 29 mg, 0.16 mmol, 1.3 equiv.) and 23 mg (0.16 mmol, 1.3 equiv.) BF_3·OEt_2 were stirred for 1 h. FCC (Et_2O/PE = 1:6) yielded 45 mg (0.11 mmol, 91%) **41a** as a colourless solid. *rac*-**41a** was prepared from *rac*-**31a** (187 mg, 0.50 mmol), **39a** (120 mg, 0.65 mmol, 1.3 equiv.) and BF_3·OEt_2 (92 mg, 0.65 mmol, 1.3 equiv.). Yield 174 mg (0.42 mmol, 84%), colourless solid. M.p. 108 °C (for **41a** at 99% *ee*, Et_2O/PE), m.p. 117 °C (for *rac*-**41a**, PE). t_R = 22.54 min (HP-5). R_F = 0.38 (Et_2O/PE = 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67, 0.85 (2 d, $^3J_{7\text{-}i\text{Pr(Me)},7\text{-}i\text{PrCH}}$ = 6.8 Hz, 6 H, 7-*i*Pr (CH_3)$_2$), 1.50 (m, 2 H, 6-H_A, 7-H), 1.71 (m, 1 H, 7-*i*Pr CH), 1.91 (m, 1 H, 6-H_B), 2.39 (m, 1 H, 5-H_A), 2.53 (dt, $^2J_{5A,5B}$ = 17.1 Hz, $^3J_{5B,6A}$ =

$^3J_{5B,6B}$ = 5.4 Hz, 1 H, 5-H_B), 2.71 (dt, $^3J_{1,7a}$ = $^3J_{7,7a}$ = 8.2 Hz, $^3J_{3a,7a}$ = 10.1 Hz, 1 H, 7a-H), 2.93 (dd, $^3J_{3,3a}$ = 6.2 Hz, $^3J_{3a,7a}$ = 10.1 Hz, 1 H, 3a-H), 4.59 (d, $^3J_{1,7a}$ = 8.2 Hz, 1 H, 1-H), 5.45 (d, $^3J_{3,3a}$ = 6.2 Hz, 1 H, 3-H), 7.33–7.42 (m, 7 H, PhCH/ArCH), 7.49 (dt, *J* = 8.5 Hz, *J* = 2.0 Hz, 2 H, ArCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6, 21.4 (CH_3, 7-*i*Pr (CH_3)$_2$), 22.2 (CH_2, C-6), 28.0 (CH, 7-*i*Pr CH), 38.4 (CH_2, C-5), 41.7 (CH, C-7), 51.2 (CH, C-7a), 59.0 (CH, C-3a), 78.9 (CH, C-3), 86.4 (CH, C-1), 121.3 (C_q, *p*-Ar), 126.9 (CH, *p*-Ph), 127.7 (CH, *o*-Ph), 128.4 (CH, *m*-Ph), 128.6 (CH, *o*-Ar), 131.5 (CH, *o*-Ar), 140.1 (C_q, *i*-C-Ar), 141.0 (C_q, *i*-C-Ph), 210.6 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3092 (w), 3063 (m), 3040 (w) 3013 (w) [ν(C_{arom}–H)], 2957 (s), 2848 (m) [ν(C_{aliph}–H)], 1707 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 435.0934 [M + Na]$^+$. $C_{23}H_{25}BrO_2$ (413.35): calcd. C 66.83, H 6.10; found C 66.88, H 5.92. $[\alpha]_D^{20}$ = –41.2 (*c* = 1.03, $CHCl_3$) at 99% *ee*; HPLC Chiralcel OD-H (4.6 × 250 mm), λ = 200 nm, *i*PrOH: *n*-hexane = 1:50, 1.0 mL/min, 11.28 min (*ent*-**41a**), 12.85 min (**41a**).

(1*RS*,3*RS*,3a*SR*,7*RS*,7a*RS*)-7-Isopropyl-3-(2-methylprop-2-enyl)-1-phenyl-hexahydroisobenzofuran-4(1*H*)-one (*rac*-41b): According to GP D *rac*-**31a** (93 mg, 0.25 mmol), 3-methyl-3-butenal diethyl acetal[29] (**39b**, 52 mg, 0.33 mmol, 1.3 equiv.) and BF_3·OEt_2 (46 mg, 0.33 mmol, 1.3 equiv.) were stirred for 1 h. FCC (Et_2O/PE = 1:4) yielded 55 mg (0.18 mmol, 70%) *rac*-**41b** as a colourless liquid. t_R = 17.18 min (HP-5). R_F = 0.32 (Et_2O/PE = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73, 0.91 (2 d, $^3J_{7\text{-}i\text{Pr(Me)},7\text{-}i\text{PrCH}}$ = 6.8 Hz, 6 H, 7-*i*Pr (CH_3)$_2$), 1.54 (m, 1 H, 7-H), 1.66 (m, 1 H, 6-H_A), 1.74 (m, 1 H, 7-*i*Pr CH), 1.82 (s, 3 H, 2′-CH_3), 1.93 (m, 1 H, 6-H_B), 2.34–2.41 (m, 2 H, 1′-H), 2.43–2.49 (m, 2 H, 5-H), 2.51 (dt, $^3J_{1,7a}$ = $^3J_{7,7a}$ = 6.4 Hz, $^3J_{3a,7a}$ = 8.7 Hz, 1 H, 7a-H), 2.71 (dd, $^3J_{3,3a}$ = 7.4 Hz, $^3J_{3a,7a}$ = 8.7 Hz, 1 H, 3a-H), 4.57 (dt, $^3J_{1'A,3}$ = $^3J_{3,3a}$ = 7.4 Hz, $^3J_{1'B,3}$ = 5.2 Hz, 1 H, 3-H), 4.65 (d, $^3J_{1,7a}$ = 6.4 Hz, 1 H, 1-H), 4.84 (s, 3 H, 3′-H), 7.24–7.34 (m, 5 H, *o*/*m*/*p*-PhCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6, 21.5 (CH_3, 7-*i*Pr (CH_3)$_2$), 22.9 (CH_3, 2′-CH_3), 23.0 (CH_2, C-6), 28.2 (CH, 7-*i*Pr CH), 38.4 (CH_2, C-5), 41.5 (CH, C-7), 43.5 (CH_2, C-1′), 51.8 (CH, C-7a), 55.8 (CH, C-3a), 77.7 (CH, C-3), 85.6 (CH, C-1), 112.7 (CH_2, C-3′), 126.2, 127.7, 128.4 (CH, *o*/*m*/*p*-Ph), 141.7 (C_q, *i*-C-Ph), 142.7 (C_q, C-2′), 210.6 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3071 (w), 3032 (w) [ν(C_{arom}–H)], 2960 (s), 2877 (m) [ν(C_{aliph}–H)], 1708 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 335.1985 [M + Na]$^+$. $C_{21}H_{28}O_2$ (312.45): calcd. C 80.73, H 9.03; found C 80.51, H 9.18.

(1*RS*,3*RS*,3a*SR*,7*RS*,7a*RS*)-1-Isopropenyl-7-isopropyl-3-(2-methylprop-2-enyl)-hexahydroisobenzofuran-4(1*H*)-one (*rac*-41c): According to GP D *rac*-**31b** (193 mg, 0.52 mmol), **39b**[29] (106 mg, 0.67 mmol, 1.3 equiv.) and BF_3·OEt_2 (81 mg, 0.57 mmol, 1.1 equiv.) were stirred for 35 min at 0 °C. FCC (Et_2O/PE = 1:9) yielded 97 mg (0.35 mmol, 68%) *rac*-**41c** as a colourless, volatile liquid. t_R = 12.42 min (HP-5). R_F = 0.22 (Et_2O/PE = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84, 1.00 (2 d, $^3J_{7\text{-}i\text{Pr(Me)},7\text{-}i\text{PrCH}}$ = 6.8 Hz, 6 H, 7-*i*Pr (CH_3)$_2$), 1.49 (m, 1 H, 7-H), 1.61 (m, 1 H, 6-H_A), 1.71 (s, 1 H, 1-C(CH_2)(CH_3)), 1.82 (s, 3 H, 2′-CH_3), 1.85–1.94 (m, 2 H, 6-H_B, 7-*i*Pr CH), 2.25–2.48 (m, 5 H, 1′-H, 5-H, 7a-H), 2.60 (dd, $^3J_{3,3a}$ = 7.4 Hz, $^3J_{3a,7a}$ = 8.5 Hz, 1 H, 3a-H), 4.12 (d, $^3J_{1,7a}$ = 5.9 Hz, 1 H, 1-H), 4.43 (dt, $^3J_{1'A,3}$ = $^3J_{3,3a}$ = 7.4 Hz, $^3J_{1'B,3}$ = 5.3 Hz, 1 H, 3-H), 4.78, 4.80 (2 m, 1 H, 3′-H), 4.88, 5.00 (2 m, 1 H, 1-C(CH_2)(CH_3)) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6, 21.7 (CH_3, 7-*i*Pr (CH_3)$_2$), 17.4 (CH_3, 1-C(CH_2)(*C*H_3)), 22.9 (CH_3, 2′-CH_3), 23.0 (CH_2, C-6), 28.0 (CH, 7-*i*Pr CH), 38.5 (CH_2, C-5), 41.9 (CH, C-7), 43.3 (CH_2, C-1′), 46.9 (CH, C-7a), 56.1 (CH, C-3a), 77.5 (CH, C-3), 87.5 (CH, C-1), 112.5 (CH_2, 1-C(*C*H_2)(CH_3)), 113.0 (CH_2, C-3′), 142.6 (C_q, 1-*C*(CH_2)(CH_3)), 144.3 (C_q, C-2′), 210.7 (C_q, C=O) ppm. IR (ATR): $\tilde{\nu}$ = 2958 (s), 2920 (s), 2874 (m), 2852 (m) [ν(C_{aliph}–H)], 1708 (s) [ν(C=O)] cm^{-1}. MS (ESI): *m*/*z* = 299.1980 [M + Na]$^+$. $C_{18}H_{28}O_2$ (276.41): calcd. C 78.21, H 10.21; found C 77.82, H 10.31.

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[24] X-ray crystal structure analysis for *rac*-**31a**: formula $C_{23}H_{35}NO_3$, M = 373.52, colorless crystal 0.50 × 0.25 × 0.05 mm, a = 11.395(1), b = 18.803(6), c = 10.359(1) Å, V = 2219.5(3) Å^3, ρ_{calc} = 1.118 g cm^{-3}, μ = 0.572 mm^{-1}, empirical absorption correction (0.763 ≤ T ≤ 0.972), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, T = 223 K, ω and φ scans, 9789 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3647 independent (R_{int} = 0.041) and 3346 observed reflections [$I \geq 2\sigma(I)$], 251 refined parameters, R = 0.049, wR_2 = 0.133, Flack parameter 0.5(3), max. residual electron density 0.12 (–0.15) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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[26] X-ray crystal structure analysis for **38a**: formula $C_{28}H_{28}O_2$, M = 396.50, colorless crystal 0.55 × 0.15 × 0.06 mm, a = 8.811(1), b = 12.110(1), c = 11.188(1) Å, β = 110.23(1)°, V = 1120.1(2) Å^3, ρ_{calc} = 1.176 g cm^{-3}, μ = 0.561 mm^{-1}, empirical absorption correction (0.748 ≤ T ≤ 0.967), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, ω and φ scans, 11166 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.58 Å^{-1}, 2749 independent (R_{int} = 0.051) and 2409 observed reflections [$I \geq 2\sigma(I)$], 273 refined parameters, R = 0.041, wR_2 = 0.110, Flack parameter –0.2(4), max. residual electron density 0.10 (–0.11) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

[27] X-ray crystal structure analysis for **41a**: formula $C_{23}H_{25}BrO_2$, M = 413.34, colorless crystal 0.45 × 0.10 × 0.10 mm, a = 11.838(1), b = 5.945(1), c = 14.515(1) Å, β = 98.72(1)°, V = 1009.7(2) Å^3, ρ_{calc} = 1.360 g cm^{-3}, μ = 2.871 mm^{-1}, empirical absorption correction (0.358 ≤ T ≤ 0.761), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, ω and φ scans, 6521 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 2642 independent (R_{int} = 0.036) and 2560 observed reflections [$I \geq 2\sigma(I)$], 237 refined parameters, R = 0.038, wR_2 = 0.101, Flack parameter 0.07(2), max. residual electron density 0.32 (–0.45) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

[28] The relative configuration of *rac*-**41a**, which crystallizes in a different space group than **41a**, was also determined by X-ray crystal structure analysis: formula $C_{23}H_{25}BrO_2$, M = 413.34, colorless crystal 0.35 × 0.25 × 0.10 mm, a = 38.648(1), b = 11.462(6), c = 17.901(1) Å, V = 7929.8(8) Å^3, ρ_{calc} = 1.385 g cm^{-3}, μ = 2.924 mm^{-1}, empirical absorption correction (0.428 ≤ T ≤ 0.759), Z = 16, orthorhombic, space group $Fdd2$ (No. 43), λ = 1.54178 Å, T = 223 K, ω and φ scans, 8967 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3251 independent (R_{int} = 0.033) and 3226 observed reflections [$I \geq 2\sigma(I)$], 238 refined parameters, R = 0.028, wR_2 = 0.075, Flack parameter 0.00(7), max. residual electron density 0.44 (–0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

[29] J. W. Conforth, M. E. Firth, *J. Chem. Soc.* **1958**, 1091–1099.

[30] Besides the pure diastereomers, fractions of diastereomeric mixtures where obtained, which were separated by repeated chromatography.

[31] The diastereomeric ratio was determined from the crude products by GC (HP-5).

[32] The concentration of the carbamate solution is critical for good yields. 1.3 equiv. *s*BuLi can be used in small scale reactions (0.25 mmol), at scales of ≥ 1.0 mmol 1.0 to 1.05 equiv. of carefully titrated *s*BuLi and *rac*-**26** are recommended for optimum yields.

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