Enantio- and Diastereoselective Synthesis of Highly Substituted Acylcyclopropanes from Homoaldol Products by Stereospecific Homoallylic Cyclization

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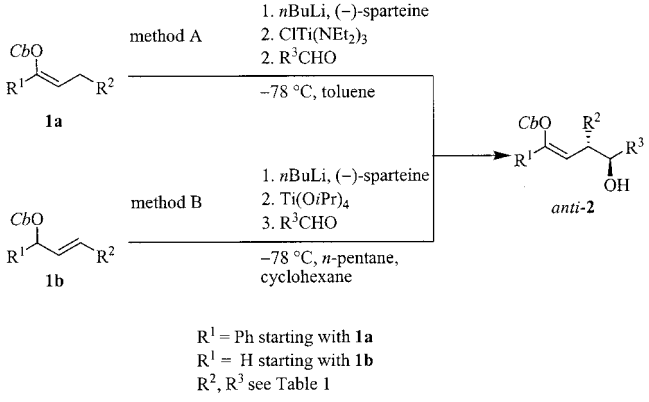
Highly enantioenriched 4-hydroxy-1-alkenyl *N*,*N*-diisopropylcarbamates, easily available by asymmetric homoaldol reaction, cyclize by treatment with sodium hydride to form (1*r*,2*t*,3*t*)-configured 1-acylcyclopropanes with high diastereoselectivity. The decisive steps are the migration of the *N*,*N*-diisopropylcarbamoyl group onto the alkoxide oxygen atom, followed by an intramolecular homoallylic substitution reaction of the intermediate γ-carbamoyloxy enolate with inversion of the configuration at the γ-C atom.

Introduction

Enantioenriched acylcyclopropanes are versatile electrophilic substrates for the construction of optically active, cyclopropane-containing molecules.[1] Various groups have described in the last years the asymmetric synthesis of enantiomerically enriched highly substituted cyclopropanes. However, only few ring-forming syntheses are known which lead to enantioenriched acylcyclopropanes.[2–6] Suzuki and co-workers reported a method for synthesizing enantiopure *trans*-disubstituted vinylcyclopropanes by homoallylic participation which can be afterwards ozonolysed to the corresponding acylcyclopropanes.[3e] The direct formation of functionalized acylcyclopropanes was shown by Hanessian and co-workers. They used a stereocontrolled conjugate 1,4-addition of a lithiated phosphonamide reagent to α,β-unsaturated carbonyl compounds with a subsequent intramolecular attack of the enolate upon the intermediate allylic chloride leading to cyclopropanes.[3f]

We and Taylor recently reported a facile single-step synthesis of acylcyclopropanes,[7,8] based on *O*-(4-hydroxy-1-alkenyl) carbamates, which are readily accessible by asymmetric homoaldol reaction (Scheme 1).[9,10]

The homoaldol products *anti*-**2** can be obtained by enantiotopos-differentiating γ-deprotonation of 1-aryl-1-alkenyl *N*,*N*-diisopropylcarbamates **1a** by *n*-butyllithium/(–)-sparteine (method A, Scheme 1) or by α-deprotonation of alkenyl *N*,*N*-diisopropylcarbamates **1b** (method B, Scheme 1). The *N*,*N*-diisopropylcarbamoyloxy group (*Cb*O) enhances the kinetic acidity of the proton in the deprotonation step and fixes the lithium cation in the α-position by chelation.[11]



Scheme 1.

After the enantiotopos-differentiating deprotonation of **1a** or **1b**, the lithiated carbamates react under inversion of configuration with the titanium reagents, $ClTi(NEt_2)_3$ (method A, Scheme 1) or $Ti(OiPr)_4$ (method B, Scheme 1).[12] The α-titanated carbamate added aldehydes or ketones via a Zimmerman–Traxler transition state with complete 1,3-transfer of chirality to the optically active *anti*-homoaldol products *anti*-**2** in high yields, diastereo- and enantioselectivities.[13] Only for the homoaldol product **2a** did we obtain moderate enantioselectivities but high diastereoselectivities. This can be attributed to the configurational lability of the lithium intermediate.

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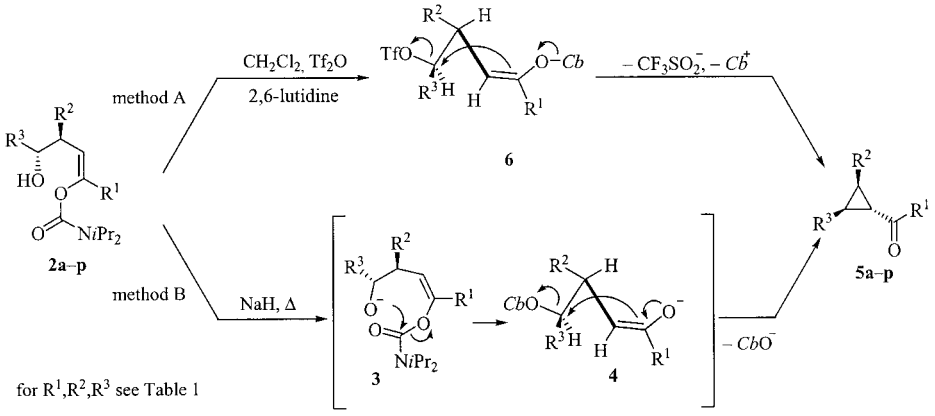


Scheme 2.

According to Taylor et al., these homoallylic alcohols undergo cyclopropane formation after activation of the hydroxy group by means of triflic anhydride (method A, Scheme 2).[8]

Results and Discussion

As we found, after converting the adduct **2** into its sodium alkoxide **3**, an $O \rightarrow O'$ migration of the *N*,*N*-diisopropylcarbamoyl group takes place,[14] thus activating the electrofugic leaving group and the nucleophilic enol moiety simultaneously for cycloalkylation. The enantioenriched and essentially diastereomerically pure (1*r*,2*t*,3*t*)-configured cyclopropane **5** is formed with high yield and complete conservation of the chirality at C-3 (method B, Scheme 2). We have now explored the scope of our extremely simple method.

The intramolecular substitution step in the enolate **4** to form the cyclopropane **5** proceeds with complete stereoinversion from the *exo* conformation (shown in formula **4**). Since the *N*,*N*-diisopropylcarbamate group in **4** is a poorer leaving group than the triflate group in intermediate **6**, for the application of method B, a dipolar aprotic solvent, such as DMF, and higher reaction temperatures (60 °C vs. 20 °C) are required in a few cases for achieving high yields (Table 1).

Table 1. Syntheses of (1*r*,2*t*,3*t*)-configured cyclopropanes **5**.

Entry	Method	Solvent	Compound **2** (% *ee*)	Product **5** (% *ee*)	R^1	R^2	R^3	Yield [%]	*dr*	$[\alpha]_D^{20}$[a]
1	A	CH_2Cl_2	**2a** (30)[b]	**5a** (30)[c]	H	$(CH_2)_2CH_3$	$(CH_2)_2C_6H_4$	70 (76)[d]	>98:2	+2
2	A	CH_2Cl_2	**2b** (71)[b]	**5b** (71)[c]	H	CH_3	Ph	>99 (65)[d]	>95:5	+110
3	B	DMF	**2b** (71)[b]	**5b** (71)[b]	H	CH_3	Ph	71	>95:5	+110
4	A	CH_2Cl_2	**2c** (87)[b]	**5c** (87)[c]	H	CH_3	$(CH_2)_2C_6H_4$	48 (70)[d]	>95:5	+3
5	B	DMF	**2c** (87)[b]	**5c** (87)[b]	H	CH_3	$(CH_2)_2C_6H_4$	58	>98:2	+3
6	A	CH_2Cl_2	**2d** (82)[c]	**5d** (82)[c]	H	CH_3	$CH(CH_3)_2$	>99 (75)[d]	>98:2	–4
7	A	CH_2Cl_2	**2e** (83)[c]	**5e** (83)[c]	H	CH_3	cyclopropyl	39 (15)[d]	88:12	–[e]
8	A	CH_2Cl_2	**2f** (86)[c]	**5f** (>80)[c]	H	CH_3	$(CH_2)_4CH_3$	61 (63)[d]	>98:2	+1
9	A	CH_2Cl_2	**2g** (96)[b]	**5g** (96)[b]	Ph	CH_3	Ph	80	>98:2	+153
10	B	THF	**2g** (92)[b]	**5g** (91)[b]	Ph	CH_3	Ph	98 (87)[d]	>98:2	+142
11	A	CH_2Cl_2	**2h** (93)[b]	**5h** (93)[b]	Ph	CH_3	$C(CH_3)_3$	83	>98:2	–17
12	B	DMF	**2h** (95)[b]	**5h** (94)[b]	Ph	CH_3	$C(CH_3)_3$	66 (59)[d]	>98:2	–17
13	A	CH_2Cl_2	**2i** (91)[b]	**5i** (91)[b]	Ph	CH_3	*p*-BrC_6H_4	41	92:8	+148
14	B	THF	**2i** (93)[b]	**5i** (93)[b]	Ph	CH_3	*p*-BrC_6H_4	91 (77)[d]	>98:2	+151
15	B	DMF	**2f** (86)[b]	**5f** (>80)[b]	H	CH_3	$(CH_2)_4CH_3$	62	>98:2	+1
16	B	THF	**2j** (94)[b]	**5j** (92)[b]	Ph	CH_3	2-naphthyl	84 (80)[d]	>98:2	+206
17	B	THF	**2k** (92)[f]	**5k** (92)[f]	Ph	CH_3	2-furyl	98 (80)[d]	>98:2	+177
18	B	THF	**2l** (91)[b]	**5l**[g]	Ph	CH_3	CH_3	84	>98:2	–
19	B	THF	**2m** (96)[b]	**5m**[h]	Ph	CH_3	CH_2CH_3	96 (88)[d]	>98:2	–85
20	B	DMF	**2n** (96)[b]	**5n** (96)[b]	Ph	CH_3	$CH(CH_3)_2$	62 (58)[d]	>98:2	–19
21	B	THF	**2o** (95)[b]	**5o** (95)[b]	Ph	CH_3	cyclopropyl	74 (70)[d]	>98:2	–50
22	B	THF	**2p** (95)[b]	**5p** (95)[c]	Ph	CH_3	cyclohexyl	78 (70)[d]	>98:2	–9

[a] c = 0.15–0.92, $CHCl_3$. [b] Enantiomeric excesses were determined by HPLC (column: Chira Grom-2, solvent: *n*-hexane/2-propanol). [c] Enantiomeric excesses were determined by chiral GC (column: β-Dex™ 120). [d] Yield of *rac*-**5**, starting from *rac*-**2**. [e] Due to the volatility of the compound it was not possible to determine the specific optical rotation. [f] Enantiomeric excesses were determined by HPLC (column: Chira Grom-1, solvent: *n*-hexane/2-propanol). [g] Achiral. [h] Not determined.

The relative configuration of ketone **5h** was determined by an X-ray structure analysis (Figure 1).[15] The absolute configuration of the precursor **2** is retained at C-3, and the enantiomeric excesses of the products **5** correspond to those of the starting materials **2** (Table 1).

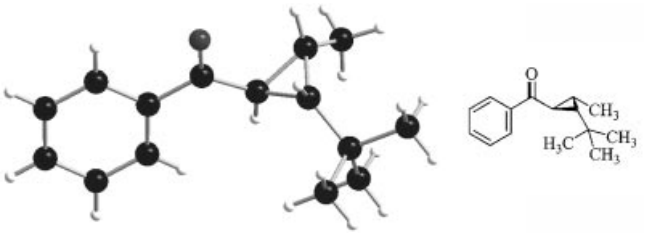
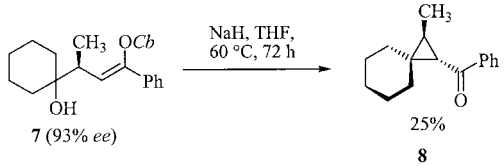


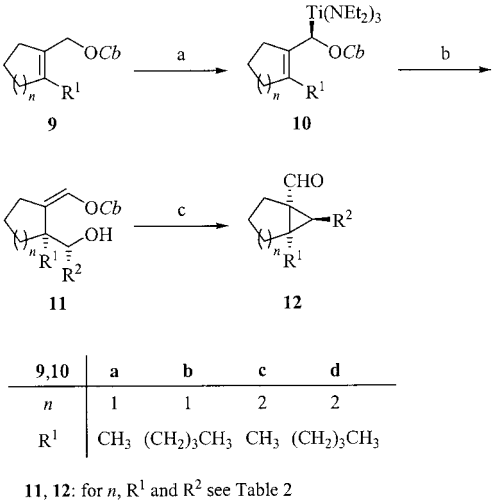
Figure 1. Solid-state structure of (1*S*,2*R*,3*R*)-1-(2-*tert*-butyl-3-methylcyclopropyl)-1-phenylmethanone (**5h**).

Homoaldol products such as **7**, arising from ketones, and, thus, bearing a tertiary hydroxy group, gave low yields of cyclopropyl ketones **8** (Scheme 3). Here, the carbamoyl migration is hampered and, in addition, a retro-homoaldol reaction competes.[16]



Scheme 3.

(2-Alkyl-1-cycloalkenyl)methyl carbamates **9**, upon (–)-sparteine-mediated deprotonation, lead to lithium intermediates of high configurational stability and, thus, have been used for the synthesis of highly enantioenriched homoaldol products **11** (Scheme 4).[17–19]



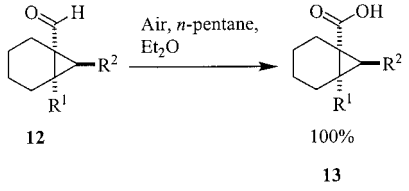
9,10	a	b	c	d
n	1	1	2	2
R^1	CH_3	$(CH_2)_3CH_3$	CH_3	$(CH_2)_3CH_3$

11, **12**: for *n*, R^1 and R^2 see Table 2

Scheme 4. a) 1. *n*- or *s*BuLi, (–)-sparteine, toluene, –78 °C; 2. $(Et_2N)_3TiCl$; b) R^2CHO, –78 °C, 82–87%, 72–86% *ee*; c) NaH, THF, 65 °C.

Treatment of **11** with sodium hydride in THF causes a rapid cyclization to form the bicyclic, bis(tertiary) cyclopropane-1-carboxaldehydes **12** (Table 2); these pentasubstituted cyclopropanes are isolated in the form of pure diastereomers.

Compounds *rac*-**12a**, *rac*-**12b**, *rac*-**12e** and *rac*-**12d** (prepared from the racemic homoaldol products *rac*-**11a**, *rac*-**11b**, *rac*-**11e** and *rac*-**11d**) were oxidized to the corresponding carboxylic acids by exposing them in a 4:1 mixture of *n*-pentane and diethyl ether to air for 7 d (Scheme 5). The carboxylic acids *rac*-**13** were obtained in almost quantitative yields.



Scheme 5.

Table 2. Syntheses of bicyclic cyclopropane-1-carboxaldehydes **11** (method C).

Entry	Compound **11** (% *ee*)	Product **12** (% *ee*)	*n*	R^1	R^2	Yield [%]	*dr*	$[\alpha]_D^{20}$[a]
1	**11a** (86)[b]	**12a** (86)[c]	1	CH_3	*p*-BrC_6H_4	81 (84)[e]	>98:2	+37
2	**11b** (74)[b]	**12b** (74)[d]	1	CH_3	*p*-ClC_6H_4	85 (86)[e]	>98:2	+23
3	**11c** (83)[b]	**12c** (83)[d]	1	CH_3	2-naphthyl	83 (86)[e]	>98:2	–11
4	**11d** (86)[b]	**12d** (86)[c]	2	CH_3	*p*-BrC_6H_4	84 (85)[e]	>98:2	–85
5	**11e** (82)[b]	**12e** (82)[d]	2	$(CH_2)_3CH_3$	Ph	85 (87)[e]	>98:2	–114
6	**11f** (72)[b]	**12f** (72)[d]	2	$(CH_2)_3CH_3$	*p*-BrC_6H_4	80 (80)[e]	>98:2	+22

[a] c = 0.50–1.00, $CHCl_3$. [b] Enantiomeric excesses were determined by ^1H NMR shift experiments. [c] Enantiomeric excesses were determined by HPLC (column: Chira Grom-2, solvent: *n*-hexane/2-propanol). [d] Enantiomeric excesses were determined by HPLC (column: Chira Grom-1, solvent: *n*-hexane/2-propanol). [e] Yield of *rac*-**12**, starting from *rac*-**11**.

rac-**13d** crystallized well and furnished an X-ray crystal structure analysis (Figure 2), which clearly supports the assumed relative configuration.[15]

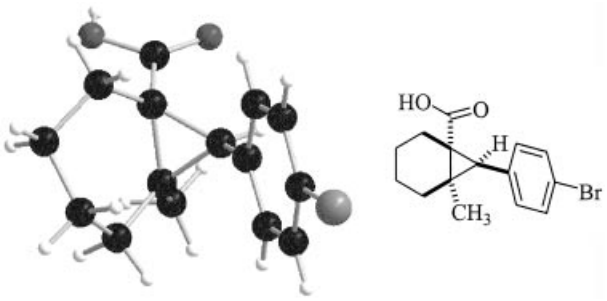


Figure 2. Solid-state structure of (1*R**,6*S**,7*R**)-6-(4-bromophenyl)-5-methylbicyclo[4.1.0]heptane-1-carboxylic acid (*rac*-**13d**).

Conclusions

The *N*,*N*-diisopropylcarbamoyl group is removed in the cycloalkylation step, in which it activated the enolate moiety and the homoallylic hydroxy group simultaneously by a base-induced migration. In the previous steps it served for the enhancement of the kinetic acidity in the allylic carbamate and contributed to the configurational stability of the chiral lithium intermediate. In summary, a simple, highly stereoselective approach to the title compounds, starting from allyl carbamates and aldehydes, has been developed.

Experimental Section

General Remarks: All solvents were dried and purified prior to use. Unless otherwise specified, materials were obtained from commercial sources and used without purification. THF was distilled from potassium benzophenone ketyl and CH_2Cl_2 was distilled from CaH_2. All reactions were performed under argon in flame-dried glassware. Flash column chromatography (FCC) was performed on Merck 60 silica gel, 0.040–0.063 mm, and monitored by thin layer chromatography (TLC) on Merck 60 F_{254} silica gel. Melting points: Gallenkamp MFB 595 (uncorrected values). IR: Nicolet 5 DXC. MS: Finnigan MAT 8230 (EI); Micromass Quattro LCZ (ESI), Micromass MAT 8200 (GC-TOF/HRMS). Optical rotations: Perkin–Elmer 341 polarimeter. NMR: Bruker ARX 300, AM 360, AMX 400 or Varian Associated Unity Plus 600; spectra from solutions in $CDCl_3$ (δ_C = 77.0 ppm) are calibrated relative to residual content of $CHCl_3$ (δ_H = 7.24 ppm) or $SiMe_4$ (δ_H = 0.0 ppm). Elemental analyses: Heraeus CHN-O-Rapid or Elementar Analysensysteme Vario EL III. GC: Agilent 6890, 30 m × 0.32 mm HP 5, 1.5 mL × min^{-1} H_2 start at 50 °C/10 °C × min^{-1} 20 min at 270 °C; Hewlett–Packard 6890, cyclodextrins from Supelco (30 m × 0.32 mm) or Macherey–Nagel (25 m × 0.2 mm), 100 kPa pre-column pressure N_2, isothermal runs. HPLC: Waters 600E Multisolvent Delivery System and 996 PDA detector.

Synthesis of Homoaldol Products. Method A, Representative Procedure:[9a] To a solution of (–)-sparteine (353 mg, 1.50 mmol, 1.5 equiv.) in dry toluene (2 mL) was added dropwise at –78 °C *n*-butyllithium (1.6 M in *n*-hexane, 0.89 mL, 1.40 mmol, 1.4 equiv.). After 10 min, a solution of the carbamate **1a** (275 mg, 1.0 mmol, 1.0 equiv.) in toluene (1 mL) was added slowly. Stirring was continued for 1.5 h before a solution of $ClTi(NEt_2)_3$ (897 mg, 3.0 mmol, 3.0 equiv.) in toluene (2 mL) was injected. After a transmetallation time of 2 h, the aldehyde (3.0 mmol, 3.0 equiv.) was added at –78 °C, and stirring was continued for additional 2 h. For workup 2 N HCl (10 mL) was injected and the solution was warmed to room temperature.The aqueous phase was separated and extracted with diethyl ether (3 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was subjected to FCC on silica gel (diethyl ether/*n*-pentane, 1:1) yielding the pure homoaldol adduct **2**.

Synthesis of Homoaldol Products. Method B, Representative Procedure:[9b,20] In a three-necked flask with cooled dropping funnel and mechanical stirrer were dissolved (–)-sparteine (3.64 g, 15.5 mmol, 1.03 equiv.) and carbamate **1b** (R^2 = CH_3, 2.99 g, 15.0 mmol, 1.0 equiv.) in a mixture of *n*-pentane (20 mL) and cyclohexane (3 mL) and cooled to –78 °C. *n*-Butyllithium (1.6 M in *n*-hexane, 10.0 mL, 16.0 mmol, 1.07 equiv.) was added dropwise. After 2 h of stirring, a solution of $Ti(OiPr)_4$ (12.8 g, 45.0 mmol, 3.0 equiv.) in *n*-pentane (35 mL), precooled to –78 °C, was added. After a transmetallation time of 30 min, a solution of the aldehyde (16.5 mmol, 1.1 equiv.) in *n*-pentane (5 mL) was added at –78 °C, and stirring was continued for additional 2 h. The solution was warmed to room temperature, diethyl ether (20 mL) was added and the reaction mixture was poured onto 2 N HCl (150 mL). The aqueous phase was separated and extracted with diethyl ether (3 × 30 mL) and washed with saturated $NaHCO_3$ solution (30 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was subjected to FCC on silica gel (diethyl ether/*n*-pentane, 1:1) yielding the pure homoaldol adduct **2**.

Synthesis of Homoaldol Products. Method C, Representative Procedure:[19] To a solution of carbamate **9a** (239 mg, 1.0 mmol, 1.0 equiv.) and (–)-sparteine (257 mg, 1.1 mmol, 1.1 equiv.) in toluene (5 mL) was added at –78 °C *n*-butyllithium (1.6 M in *n*-hexane, 0.68 mL, 1.1 mmol, 1.1 equiv.). After 10 min, a solution of $ClTi(NEt_2)_3$ (897 mg, 3.0 mmol, 3.0 equiv.) in toluene (1 mL) was injected. The reaction mixture was stirred at –78 °C for 2 h and then the aldehyde (3.0 mmol, 3.0 equiv.) was added. The solution was warmed to room temperature and poured onto diethyl ether (10 mL) and 2 N HCl (10 mL). The aqueous phase was separated and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was subjected to FCC on silica gel (ethyl acetate/*n*-pentane, 1:10) to give the pure homoaldol adduct **11**.

3-(1-Hydroxycyclohexyl)-1-phenylbut-1-enyl (*R*,*Z*)-*N*,*N*-Diisopropylcarbamate (7): Method A: (–)-Sparteine (353 mg, 1.50 mmol, 1.5 equiv.), *n*-butyllithium (1.6 M in *n*-hexane, 0.89 mL, 1.40 mmol, 1.4 equiv.) and 1-phenylbut-1-enyl *N*,*N*-diisopropylcarbamate [(*Z*)/(*E*) = 92:8, 275 mg, 1.00 mmol, 1.0 equiv.], dissolved in toluene (3 mL), were treated according to method A. After 1.5 h, cyclohexanone (216 mg, 3.00 mmol, 3.0 equiv.) was added. Workup was done after additional 2 h according to method A. Purification by FCC yielded (+)-**7** (216 mg, 0.58 mmol, 58%) as colourless oil. R_F = 0.37 (PE/Et_2O, 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.08 (d, $^3J_{3\text{-H},4\text{-H}}$ = 6.8 Hz, 3 H, 4-H), 1.24–1.64 (m, 22 H, CH_3-*Cb*, H-*c*-Hex), 1.89 (br. s, 1 H, OH), 2.58 (m, $^3J_{2\text{-H},3\text{-H}}$ = 10.4, $^3J_{3\text{-H},4\text{-H}}$ = 6.8 Hz, 1 H, 3-H), 3.97, 4.08 (m, 2 H, CH-*Cb*), 5.80 (d, $^3J_{2\text{-H},3\text{-H}}$ = 10.4 Hz, 1 H, 2-H), 7.21–7.43 (m, 5 H, *o*, *m*-,*p*-Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.8 (CH_3, C4), 20.4 (CH_3, *Cb*), 21.5, 21.7, 21.8, 25.8, 34.3 (CH_2, C-*c*-Hex), 35.7 (CH_2, C3), 41.3 (CH, C-*c*-Hex), 46.3, 46.4 (CH, *Cb*), 72.8

(OH), 119.7 (CH, C2), 124.6, 127.7, 128.2 (CH, *o*-, *m*-, *p*-Ph), 136.2 (C_q, *i*-Ph), 146.6 (C_q, C1), 153.8 (C=O). IR (film) $\tilde{\nu}$ [cm^{-1}] = 3491 ν(O–H), 2969, 2921, 2856 ν(C_{aliph}–H), 1700 ν(C=O). $C_{23}H_{35}NO_3$ (373.26): calcd. C 73.96, H 9.44, N 3.75 found C 73.76, H 9.59, N 3.67. $[\alpha]_D^{20}$ = +49.0 (*c* = 1.00, $CHCl_3$) at 93% *ee* (*er* = 96.5:3.5).

Synthesis of Cyclopropanecarboxaldehydes and Cyclopropyl Ketones. Method A, Representative Procedure: A flask was charged with carbamate **2a** (199 mg, 0.66 mmol, 71% *ee*, 1.0 equiv.) in CH_2Cl_2 (10 mL). 2,6-Lutidine (280 mg, 2.64 mmol, 4.0 equiv.) was added by syringe, the solution was cooled to –78 °C, and then freshly distilled triflic anhydride (553 mg, 1.98 mmol, 3.0 equiv.) was injected. The reaction mixture was stirred for 1 h, quenched with water (5 mL), and allowed to warm to room temperature. The mixture was diluted with CH_2Cl_2 (25 mL), the aqueous phase was separated, and the organic layer was washed with saturated $NaHCO_3$ solution (10 mL). The organic phase was dried with $MgSO_4$ and the solvent evaporated in vacuo. The crude product was subjected to FCC on silica gel (diethyl ether/*n*-pentane, 1:10) yielding pure cyclopropanecarboxaldehyde **5a** (104 mg, 0.66 mmol, quant., 71% *ee*) as colourless liquid.

Synthesis of Cyclopropanecarboxaldehydes and Cyclopropyl Ketones. Method B, Representative Procedure: To the *anti*-homoaldol adduct **2i** (169 mg, 0.37 mmol, 93% *ee*, 1.0 equiv.) was added sodium hydride (60% in mineral oil, 18 mg, 0.45 mmol, 1.2 equiv.). The flask was placed under argon, THF (10 mL) was injected, and the resulting solution was heated at 60 °C for 3–14 h (TLC control). When DMF was used as solvent the solution was stirred at room temperature for 1 h and then heated at 60 °C for 2–12 h (TLC control). For workup saturated sodium chloride solution (10 mL) was added. The aqueous phase was separated and extracted with diethyl ether (3 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was subjected to FCC on silica gel (diethyl ether/*n*-pentane, 1:10) yielding pure cyclopropyl ketone **5i** (106 mg, 0.34 mmol, 92%, 93% *ee*) as colourless solid.

Synthesis of Cyclopropanecarboxaldehydes and Cyclopropyl Ketones. Method C, Representative Procedure: To the homoaldol adduct **11a** (109 mg, 0.25 mmol, 86% *ee*, 1.0 equiv.) was added sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) The flask was placed under argon, THF (5 mL) was injected, and the resulting solution was heated at 65 °C for 10 h (TLC control). For workup saturated $NaHCO_3$ solution (10 mL) was added. The aqueous phase was separated and extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was subjected to FCC on silica gel (diethyl ether/*n*-pentane, 1:4) yielding pure cyclopropanecarboxaldehyde **12a** (60 mg, 0.20 mmol, 81%, 86% *ee*) as colourless solid.

(1*S*,2*S*,3*R*)-2-(2-Phenylethyl)-3-propylcyclopropane-1-carboxaldehyde (5a): Method A: **2a** (101 mg, 0.28 mmol, 30% *ee*, 1.0 equiv.), 2,6-lutidine (120 mg, 1.12 mmol, 4.0 equiv.) and triflic anhydride (237 mg, 0.84 mmol, 3.0 equiv.), dissolved in CH_2Cl_2 (5 mL), were treated according to method A. Purification by FCC yielded (+)-**5a** (42 mg, 0.19 mmol, 70%, 30% *ee*) as colourless liquid. R_F = 0.36 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.90 (t, $J_{2'',3''}$ = 7.2 Hz, 3 H, 3″-H), 1.15–1.90 (m, 6 H, 1′-H/1″-H/2″-H), 1.33 (q, $^3J_{1,2}$ = 4.5, $^3J_{1,CHO}$ = 4.5 Hz, $^3J_{1,3}$ = 4.5 Hz, 1 H, 1-H), 1.56–1.66 (m, 2 H, 2-H/3-H), 2.70 (t, $^3J_{1',2'}$ = 7.5 Hz, 2 H, 2′-H), 7.11–7.30 (m, 5 H, Ph-H), 9.03 (d, $^3J_{1,CHO}$ = 4.5 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.1 (CH_3, C3″), 22.8 (CH_2, C2″), 27.9 (CH, C2), 28.1 (CH, C3), 29.3 (CH_2, C1′), 29.4 (CH_2, C1″), 35.9 (CH_2, C2″), 37.9 (CH, C1), 126.2 (CH, *p*-Ph), 128.5 (CH, *o*-Ph), 128.6 (CH, *m*-Ph), 141.5 (C_q, *i*-Ph), 201.3 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 3084, 3063, 3023, 2957, 2926, 2860 ν(C_{aliph}–H), 1702 ν(C=O). Exact mass (EI): $C_{15}H_{20}O$ calcd. 216.1514; found 216.1541. $[\alpha]_D^{20}$ = +2.4 (*c* = 0.38, $CHCl_3$) at 30% *ee* (*er* = 65:35). *rac*-**5a** (46 mg, 0.21 mmol, 76%) was obtained from *rac*-**2a** (101 mg, 0.28 mmol, 1.0 equiv.) as colourless liquid by method A.

(1*S*,2*S*,3*R*)-3-Methyl-2-phenylcyclopropane-1-carboxaldehyde (5b): Method B: Sodium hydride (60% in mineral oil, 29 mg, 0.73 mmol 1.1 equiv.) and carbamate **2b** (200 mg, 0.66 mmol, 68% *ee*, 1.0 equiv.), suspended in DMF (10 mL), were treated according to method B. Purification by FCC yielded (+)-**5b** (82 mg, 0.51 mmol, 78%) as colourless liquid. R_F = 0.38 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.91 (d, $^3J_{3,3\text{-}CH3}$ = 6.3 Hz, 3 H, 3-CH_3), 1.83 (m, 1 H, 3-H), 2.05 (q, $^3J_{1,2}$ = 4.6, $^3J_{1,CHO}$ = 4.8, $^3J_{1,3}$ = 4.8 Hz, 1 H, 1-H), 2.82 (dd, $^3J_{1,2}$ = 4.6, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 7.09–7.27 (m, 5 H, Ph-H), 9.30 (d, $^3J_{1,CHO}$ = 4.8 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.8 (3-CH_3), 24.4 (CH, C1), 26.6 (CH, C3), 32.8 (CH, C2), 126.9 (CH, *p*-Ph), 128.5, 128.6 (CH, *o*-Ph/*m*-Ph), 136.1 (C_q, *i*-Ph), 201.3 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 3062, 3030; 2960, 2928, 2826 ν(C_{aliph}–H), 1700 ν(C=O). Exact mass (EI): $C_{11}H_{12}O$ calcd. 160.0888; found 160.0884. $[\alpha]_D^{20}$ = +109.5 (*c* = 0.43, $CHCl_3$) at 68% *ee* (*er* = 84:16). Method A: From **2b** (199 mg, 0.66 mmol, 68% *ee*, 1.0 equiv.) (+)-**5b** (104 mg, 0.66 mmol, > 99%, 68% *ee*) was obtained as colourless liquid. *rac*-**5b** (34 mg, 0.21 mmol, 65%) was obtained as colourless liquid from *rac*-**2b** (100 mg, 0.33 mmol, 1.0 equiv.) by method A.

(1*S*,2*S*,3*R*)-3-Methyl-2-(2-phenylethyl)cyclopropane-1-carboxaldehyde (5c): Method B: Sodium hydride (60% in mineral oil, 26 mg, 0.65 mmol 1.1 equiv.) and carbamate **2c** (200 mg, 0.60 mmol, 87% *ee*, 1.0 equiv.), suspended in DMF (10 mL), were treated according to method B. Purification by FCC yielded (+)-**5c** (71 mg, 0.38 mmol, 62%) as colourless liquid. R_F = 0.34 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.00 (d, $^3J_{3,3\text{-}CH3}$ = 6.3 Hz, 3 H, 3-CH_3), 1.21 (q, $^3J_{1,2}$ = 4.5, $^3J_{1,3}$ = 4.5 Hz, 1 H, 1-H), 1.45 (m, 2 H, 2/3-H), 1.64 (m, 2 H, 1′-H), 2.61 (t, $^3J_{1',2'}$ = 7.6 Hz, 2 H, 2′-H), 7.03–7.19 (m, 5 H, Ph-H), 8.94 (d, $^3J_{1,CHO}$ = 5.2 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.1 (CH, C2), 22.3 (CH_3, 3-CH_3), 27.7 (CH, C3), 28.8 (CH_2, C2′), 35.8 (CH_2, C1′), 38.9 (CH, C1), 126.2 (CH, *p*-Ph), 128.6 (CH, *o*-Ph/*m*-Ph), 141.9 (C_q, *i*-Ph), 201.3 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 3026–2751 ν(C_{aliph}–H), 1636 ν(C=O). Exact mass (EI): $C_{13}H_{16}O$ calcd. 188.1201; found 188.1187. $[\alpha]_D^{20}$ = +3.1 (*c* = 0.45, $CHCl_3$) at 87% *ee* (*er* = 93.5:6.5). Method A: From **2c** (100 mg, 0.30 mmol, 87% *ee*, 1.0 equiv.) (+)-**5b** (27 mg, 0.14 mmol, 48%, 87% *ee*) was obtained as colourless liquid. *rac*-**5c** (39 mg, 0.21 mmol, 70%) was obtained as colourless liquid from *rac*-**2c** (100 mg, 0.30 mmol, 1.0 equiv.) by method A.

(1*S*,2*S*,3*R*)-2-Isopropyl-3-methylcyclopropane-1-carboxaldehyde (5d): Method A: From **2d** (200 mg, 0.74 mmol, 82% *ee* 1.0 equiv.), 2,6-lutidine (317 mg, 2.96 mmol, 4.0 equiv.) and triflic anhydride (626 mg, 2.22 mmol, 3.0 equiv.), dissolved in CH_2Cl_2 (10 mL) (–)-**5d** (93 mg, 0.74 mmol, >99%, 82% *ee*) was obtained after purification by FCC as colourless liquid. R_F = 0.39 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.97 (d, $^3J_{1',2'}$ = 6.1 Hz, 3 H, 2′-H), 0.98 (d, $^3J_{1',2'}$ = 6.1 Hz, 3 H, 2′-H), 1.15 (d, $^3J_{3,3\text{-}CH3}$ = 6.5 Hz, 3 H, 3-CH_3), 1.18–1.35 (m, 3 H, 1/2/1′-H), 1.60–1.67 (m, 1 H, 3-H), 9.02 (d, $^3J_{1,CHO}$ = 5.1 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 11.8 (CH_3, 3-CH_3), 22.1 (CH_3, C2′), 22.3 (CH, C3), 22.6 (CH_3, C2′), 27.1 (CH, C1′), 36.4 (CH, C2), 38.3 (CH, C1), 201.3 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2961, 2930, 2870 ν(C_{aliph}–H), 1687 ν(C=O). Exact mass (EI): $C_8H_{14}O$ calcd. 126.1045; found 126.1080. $[\alpha]_D^{20}$ = –4.0 (*c* = 0.92, $CHCl_3$) at 82%

ee (*er* = 91:9). *rac*-**5d** (35 mg, 0.28 mmol, 75%) was obtained from *rac*-**2d** (100 mg, 0.37 mmol, 1.0 equiv.) by method A as colourless liquid.

(1*S*,2*R*,3*R*)-2-Cyclopropyl-3-methylcyclopropane-1-carboxaldehyde (5e): Method A: From **2e** (150 mg, 0.56 mmol, 83% *ee*, 1.0 equiv.), 2,6-lutidine (240 mg, 2.24 mmol, 4.0 equiv.) and triflic anhydride (474 mg, 1.68 mmol, 3.0 equiv.), dissolved in CH_2Cl_2 (7 mL) **5e** (27 mg, 0.31 mmol, 39%, 83% *ee*) was obtained after purification by FCC as colourless liquid. R_F = 0.48 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.17–0.26 (m, 2 H, 2′a-H), 0.47–0.66 (m, 3 H, 1′/2′b-H), 1.21 (d, $^3J_{3,3\text{-}CH3}$ = 6.7 Hz, 3 H, 3-CH_3), 1.28 (ddd, $^3J_{H1,H2}$ = 4.6, $^3J_{H2,H3}$ = 10.7, $^3J_{H2,H1'}$ = 6.7 Hz, 1 H, 2-H), 1.43 (q, 1 H, 1-H), 1.61–1.69 (m, 1 H, 3-H), 9.05 (d, $^3J_{1,CHO}$ = 5.1 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 4.6 (CH_2, C2′), 4.7 (CH_2, C2′), 7.8 (CH, C1′), 12.5 (CH_3, 3-CH_3), 23.4 (CH, C3), 32.5 (CH, C2), 37.6 (CH, C1), 201.5 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 3004, 2960, 2927, 2874 ν(C_{aliph}–H), 1690 ν(C=O). 83% *ee* (*er* = 91.5:8.5). Due to the volatility of the compound it was not possible to determine the specific optical rotation. *rac*-**5e** (7 mg, 0.06 mmol, 15%) was obtained from *rac*-**2e** (100 mg, 0.37 mmol, 1.0 equiv.) by method A as colourless liquid.

(1*S*,2*R*,3*S*)-2-Methyl-3-pentylcyclopropane-1-carboxaldehyde (5f): Method B: Sodium hydride (60% in mineral oil, 29 mg, 0.73 mmol, 1.1 equiv.) and carbamate **2f** (200 mg, 0.67 mmol, 86% *ee*, 1.0 equiv.), suspended in DMF (10 mL), were treated according to method B. Purification by FCC yielded (+)-**5f** (64 mg, 0.42 mmol, 62%, >80% *ee*) as colourless liquid. R_F = 0.48 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): 0.84 (t, $^3J_{4',5'}$ = 7.2 Hz, 3 H, 5′-H), 0.98 (d, $^3J_{2,2\text{-}CH3}$ = 6.0 Hz, 3 H, 2-CH_3), 1.04–1.56 (m, 10 H, 1/3/1′/2′/3′/4′-H), 1.56–1.65 (m, 1 H, 2-H); 9.03 (d, $^3J_{1,CHO}$ = 5.1 Hz, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 11.8 (CH_3, 2-CH_3), 14.0 (CH_3, C5′), 22.1 (CH, C2), 22.3, 28.4, 29.1, 31.5, 34.1, 38.7 (CH and CH_2, C1/C3/C1′/C2′/C3′/C4′), 201.1 (CHO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2961, 2829, 2859, 2723 ν(C_{aliph}–H), 1708 ν(C=O). Exact mass (EI): $C_{10}H_{18}O$ calcd. 154.1358; found 154.1362. $[\alpha]_D^{20}$ = +1.2 (*c* = 0.52, $CHCl_3$) at >80% *ee*. Method A: From **2f** (300 mg, 1.00 mmol, 86% *ee*, 1.0 equiv.) (+)-**5f** (94 mg, 0.61 mmol, 61%, >80% *ee*) was obtained as colourless liquid. *rac*-**5f** (33 mg, 0.21 mmol, 63%) was obtained from *rac*-**2f** (100 mg, 0.33 mmol, 1.0 equiv.) by method A as colourless liquid.

(1*S*,2*S*,3*R*)-1-(3-Methyl-2-phenylcyclopropyl)-1-phenylmethanone (5g): Method B: From sodium hydride (60% in mineral oil, 13 mg, 0.43 mmol, 1.65 equiv.) and carbamate **2g** (100 mg, 0.26 mmol, 91% *ee*, 1.0 equiv.), suspended in THF (2 mL), (+)-**5g** (63 mg, 0.26 mmol, 98%, 91% *ee*) was obtained after purification by FCC as colourless solid. M.p. 95–96 °C (PE/E). R_F = 0.47 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.98 (d, $^3J_{3',3'\text{-}CH3}$ = 6.9 Hz, 3 H, 3′-CH_3), 1.99 (ddq, $^3J_{3',3'\text{-}CH3}$ = 6.9, $^3J_{1',3'}$ = 4.6, $^3J_{2',3'}$ = 9.5 Hz, 1 H, 3′-H), 2.80 (t, $^3J_{1',3'}$ = 4.6, $^3J_{1',2'}$ = 4.6 Hz, 1 H, 1′-H), 2.96 (dd, $^3J_{1',2'}$ = 4.6, $^3J_{2',3'}$ = 9.5 Hz, 1 H, 2′-H), 7.11–7.54 (m, 5 H, 3′′′/4′′/2′′′/3′′′/4′′′-H), 7.98 (td, $^3J_{2'',3''}$ = 7.0, $^4J_{2'',4''}$ = 1.6 Hz, 2 H, 2′′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.9 (CH_3, 3′-CH_3), 26.9 (CH, C3′), 31.9 (CH, C-2′), 35.4 (CH, C-1′), 126.6, 128.1, 128.3, 128.6, 129.1 (CH, C2′′/C3′′/C2′′′/C3′′′/C4′′′), 132.8 (CH, C4′′), 136.9 (C_q, C1′′), 138.1 (C_q, C1′′′), 199.3 (CO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2971, 2946, 2923, 2890 ν(C_{aliph}–H), 1659 ν(C=O). Exact mass (ESI): $C_{17}H_{16}O + Na^+$ calcd. 259.1093; found 259.1086. $[\alpha]_D^{20}$ = +142.0 (*c* = 0.53, $CHCl_3$) at 91% *ee* (*er* = 95.5:4.5). Method A: From **2g** (75 mg, 0.20 mmol, 91% *ee*, 1.0 equiv.) (+)-**5g** (37 mg, 0.74 mmol, 80%, 91% *ee*) was obtained as colourless crystals. *rac*-**5g** (64 mg, 0.27 mmol, 87%) was obtained from carbamate *rac*-**2g** (119 mg, 0.31 mmol, 1.0 equiv.) by method B as colourless solid.

(1*S*,2*S*,3*R*)-1-(2-*tert*-Butyl-3-methylcyclopropyl)-1-phenylmethanone (5h): Method B: Sodium hydride (60% in mineral oil, 17 mg, 0.43 mmol, 1.2 equiv.) and carbamate **2h** (128 mg, 0.35 mmol, 94% *ee*, 1.0 equiv.), suspended in DMF (5 mL), were treated according to method B. Purification by FCC yielded (–)-**5h** (49 mg, 0.23 mmol, 66%, 94% *ee*) as colourless solid. M.p. 38–39 °C (PE/E). R_F = 0.63 (PE/Et_2O, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.98 [s, 9 H, 2′-C(CH_3)$_3$], 1.28 (d, $^3J_{3',3'\text{-}CH3}$ = 5.7 Hz, 3 H, 3′-CH_3), 1.55 (dd, $^3J_{1',2'}$ = 5.1, $^3J_{2',3'}$ = 9.7 Hz, 1 H, 2′-H), 1.75 (m, 1 H, 3′-H), 2.39 (t, $^3J_{1',2'}$ = 5.1, $^3J_{1',3'}$ = 5.1 Hz, 1 H, 1′-H), 7.37–7.44 (m, 2 H, *m*-Ph), 7.48 (tt, $^3J_{p\text{-}Ph,m\text{-}Ph}$ = 7.6, $^4J_{p\text{-}Ph,o\text{-}Ph}$ = 2.2 Hz, 1 H, *p*-Ph), 7.92 (td, $^4J_{p\text{-}Ph,o\text{-}Ph}$ = 2.2, $^3J_{o\text{-}Ph,m\text{-}Ph}$ = 8.1 Hz, 2 H, *o*-Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.4 (CH, C-3′), 26.5 (CH_3, 3′-CH_3), 29.8 (CH, C-1′), 30.3 [CH_3, 2′-C(*C*H_3)$_3$], 31.4 [C_q, 2′-*C*(CH_3)$_3$], 43.5 (CH, C-2′), 127.8, 128.4 (CH, *o*-Ph/*m*-Ph), 132.4 (CH, *p*-Ph), 138.3 (C_q, *i*-Ph), 200.6 (CO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2953, 2900, 2869 ν(C_{aliph}–H), 1663 ν(C=O). Exact mass (EI): $C_{15}H_{20}O$ calcd. 216.1514; found 216.1513. $[\alpha]_D^{20}$ = –16.9 (*c* = 0.15, $CHCl_3$) at 94% *ee* (*er* = 97:3). Method A: From **2h** (101 mg, 0.28 mmol, 93% *ee*, 1.0 equiv.) (–)-**5h** (50 mg, 0.23 mmol, 83%, 93% *ee*) was obtained as colourless crystals. *rac*-**5h** (19 mg, 0.09 mmol, 59%) was obtained from *rac*-**2h** (54 mg, 0.15 mmol, 1.0 equiv.) by method B as colourless solid.

X-ray Crystal Structure Analysis of 5h:[15] Colourless crystal 0.50×0.15×0.10 mm, *a* = 5.975(1), *b* = 10.359(1), *c* = 11.161(1) Å, β = 103.30(1)°, *V* = 672.3(1) Å^3, $\rho_{calcd.}$ = 1.069 g cm^{-3}, μ = 4.96 cm^{-1}, empirical absorption correction (0.790 ≤ *T* ≤ 0.952), *Z* = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, *T* = 223 K, ω- and φ-scans, 3002 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.59 $Å^{-1}$, 1640 independent (R_{int} = 0.036) and 1590 observed reflections [$I \geq 2\,\sigma(I)$], 149 refined parameters, *R* = 0.039, wR^2 = 0.111, Flack parameter 0.1(4), max. residual electron density 0.09 (–0.12) e·$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

(1*S*,2*R*,3*R*)-1-[2-(4-Bromophenyl)-3-methylcyclopropyl]-1-phenylmethanone (5i): Method B: From sodium hydride (60% in mineral oil, 18 mg, 0.45 mmol, 1.2 equiv.) and carbamate **2i** (169 mg, 0.37 mmol, 93% *ee*, 1.0 equiv.), suspended in THF (10 mL), (+)-**5i** (106 mg, 0.34 mmol, 92%, 93% *ee*) was obtained after purification by FCC as colourless solid. M.p. 154–157 °C (PE/E). R_F = 0.62 (PE/Et_2O, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.25 (d, $^3J_{3',3'\text{-}CH3}$ = 6.3 Hz, 3 H, 3′-CH_3), 1.96 (ddq, $^3J_{3',3'\text{-}CH3}$ = 6.3, $^3J_{1',3'}$ = 4.8, $^3J_{2'\text{-}H,3'\text{-}H}$ = 9.7 Hz, 1 H, 3′-H), 2.74 (t, $^3J_{1',3'}$ = 4.8 Hz, 1 H, 1′-H), 2.92 (dd, $^3J_{1',2'}$ = 4.8, $^3J_{2'\text{-}H,3'\text{-}H}$ = 9.7 Hz, 1 H, 2′-H), 7.01 (m, 2 H, 2′′′-H), 7.36–7.51 (m, 5 H, 2′′/3′′/3′′′-H), 7.98 (m, 2 H, 4′′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 11.6 (CH_3, 3′-CH_3), 28.6 (CH, C3′), 32.1 (CH, C2′), 34.7 (CH, C1′), 119.9 (C_q, C4′′′), 128.0 (CH, C3′′), 128.6 (CH, C2′′), 130.7 (CH, C2′′′), 131.4 (CH, C3′′′), 132.8 (CH, C4′′), 138.6 (C_q, C1′′), 140.1 (C_q, C1′′′), 197.0 (CO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2996, 2965, 2906 ν(C_{aliph}–H), 1649 ν(C=O). $C_{17}H_{15}BrO$ (315.20): calcd. C 64.78, H 4.80, found C 64.54, H 4.68. $[\alpha]_D^{20}$ = +151.8 (*c* = 0.85, $CHCl_3$) at 93% *ee* (*er* = 96.5:3.5). Method A: From **2i** (193 mg, 0.42 mmol, 93% *ee*, 1.0 equiv.) (+)-**5i** (55 mg, 0.17 mmol, 42%, 93% *ee*) was obtained as colourless solid. *rac*-**5i** (173 mg, 0.55 mmol, 77%) was obtained from *rac*-**2i** (334 mg, 0.72 mmol, 1.0 equiv.) by method B as colourless solid.

(1*S*,2*R*,3*S*)-1-[3-Methyl-2-(naphth-2-yl)cyclopropyl]-1-phenylmethanone (5j): Method B: Sodium hydride (60% in mineral oil, 36 mg, 0.91 mmol, 1.2 equiv.) and carbamate **2j** (328 mg, 0.76 mmol, 92% *ee*, 1.0 equiv.), suspended in THF (10 mL), were treated according to method B. Purification by FCC yielded (+)-**5j** (106 mg,

0.34 mmol, 92%, 92% *ee*) as colourless oil. R_F = 0.63 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.38 (d, $^3J_{3',3'\text{-}CH3}$ = 6.6 Hz, 3 H, 3′-CH_3), 2.14 (ddq, $^3J_{3',3'\text{-}CH3}$ = 6.6 Hz, $^3J_{1',3'}$ = 4.5, $^3J_{2',3'}$ = 9.3 Hz, 1 H, H-3′), 3.00 (t, $^3J_{1',2'}$ = 4.5, $^3J_{1',3'}$ = 4.5 Hz, 1 H, H-1′), 3.20 (dd, $^3J_{1',2'}$ = 4.5, $^3J_{2',3'}$ = 9.3 Hz, 1 H, H-2′), 7.39–8.17 (m, 12 H, *o*-,*m*-,*p*-Ph, Naphthyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 13.4 (CH_3, 3′-CH_3), 27.5 (CH, C3′), 32.4 (CH, C2′); 35.7 (CH, C-1′), 125.9, 126.5, 127.5, 127.9, 128.1, 128.2, 128.5, 129.0, 132.7, 133.2, 133.8, 135.0, 138.5 (CH and C_q, C-Ph, C-Naphthyl), 199.6 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2919, 2882, 2874 ν(C_{aliph}–H), 1647 ν(C=O). $C_{21}H_{18}O$ (286.37): calcd. C 88.08, H 6.34, found C 87.76, H 6.13. $[\alpha]_D^{20}$ = +206.0 (*c* = 0.77, $CHCl_3$) at 92% *ee* (*er* = 96:4). *rac*-**5j** (46 mg, 0.16 mmol, 80%) was obtained from carbamate *rac*-**2j** (82 mg, 0.20 mmol, 1.0 equiv.) by method B as colourless oil.

(1*S*,2S,3*R*)-1-[2-(Furan-2-yl)-3-methylcyclopropyl]-1-phenylmethanone (5k): Method B: From sodium hydride (60% in mineral oil, 13 mg, 0.32 mmol, 92% *ee*, 1.2 equiv.) and carbamate **2k** (101 mg, 0.27 mmol, 1.0 equiv.), suspended in THF (10 mL), (+)-**5k** (61 mg, 0.27 mmol, 98%, 92% *ee*) was obtained as colourless oil after purification by FCC. R_F = 0.78 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.11 (d, $^3J_{3',3'\text{-}CH3}$ = 6.0 Hz, 3 H, 3′-CH_3), 1.86–1.98 (m, 1 H, 3′-H), 2.7–2.83 (m, 1 H, 1′/2′-H), 6.08 (d, $^3J_{1'',2''}$ = 3.3 Hz, 1 H, Fu-H), 6.24 (dd, $^3J_{1'',2''}$ = 3.3, $^3J_{2'',3''}$ = 1.8 Hz, 2 H, Fu-H), 7.25 (dd, $^4J_{1'',3''}$ = 0.6, $^3J_{2'',3''}$ = 1.8 Hz, 1 H,Fu-H), 7.36–7.50 (m, 3 H, *m*-,*p*-Ph), 7.92–7.95 (m, 2H *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 13.3 (CH_3, 3′-CH_3), 26.6 (CH, C3′), 27.9 (CH, C2′), 32.6 (CH, C1′), 107.6, 110.8 (CH, C-Fu), 128.5, 128.9 (CH, *o*-,*m*-Ph), 133.3 (CH, *p*-Ph), 138.2 (C_q, *i*-Ph), 141.8, 152.4 (CH and C_q, C-Fu), 199.8 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2960, 2926, 2873 ν(C_{aliph}–H), 1669 ν(C=O). $C_{15}H_{14}O_2$ (226.09): calcd. C 79.62, H 6.24, found C 79.69, H 6.42. $[\alpha]_D^{20}$ = +177.0 (*c* = 0.53, $CHCl_3$) at 92% *ee* (*er* = 96:4). *rac*-**5k** (134 mg, 0.59 mmol, 80%) was obtained from carbamate *rac*-**2k** (277 mg, 0.75 mmol, 1.0 equiv.) by method B as colourless oil.

(1*r*,2*t*,3*t*)-1-(2,3-Dimethylcyclopropyl)-1-phenylmethanone (5l): Method B: Sodium hydride (60% in mineral oil, 27 mg, 0.68 mmol 1.2 equiv.) and carbamate **2l** (183 mg, 0.57 mmol, 91% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method B. Purification by FCC yielded **5l** (83 mg, 0.48 mmol, 84%) as colourless oil. R_F = 0.44 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.42 (m, 6 H, 2′-CH_3, 3′-CH_3), 1.98 (m, 2 H, 2′/3′-H), 2.26 (t, $^3J_{1',2'}$ = 4.5, $^3J_{1',3'}$ = 4.5 Hz,1 H, 1′-H), 7.62–7.77 (m, 3 H, Ph-H), 8.14–8.18 (m, 2 H, Ph-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.5 (CH, C2′, C3′), 26.5 (CH_3, 2′/3′-CH_3), 30.1 (CH, C1′), 128.3, 128.8 (CH, *o*-, *m*-Ph), 132.8 (CH, *p*-Ph), 138.8 (C_q, *i*-Ph), 200.4 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2953, 2928, 2871 ν(C_{aliph}–H), 1665 ν(C=O). $C_{12}H_{14}O$ (174.10): calcd. C 82.72, H 8.10, found C 82.52, H 8.02.

(1*S*,2*S*,3*R*)-1-(2-Ethyl-3-methylcyclopropyl)-1-phenylmethanone (5m): Method B: Sodium hydride (60% in mineral oil, 26 mg, 0.66 mmol 1.2 equiv.) and carbamate **2m** (185 mg, 0.55 mmol, 96% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method B. Purification by FCC yielded (–)-**5m** (101 mg, 0.53 mmol, 96%) as colourless oil. R_F = 0.50 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.04 (t, $^3J_{CH2CH3,CH2CH3}$ = 5.7 Hz, 3 H, CH_2CH_3), 1.22 (d, $^3J_{3',3'\text{-}CH3}$ = 4.8 Hz, 3 H, 3′-CH_3), 1.53 (m, 2 H, CH_2CH_3), 1.68–1.75 (m, 1 H, 3′-H), 1.78–1.87 (m, 1 H, 2′-H), 2.11 (t, $^3J_{1',2'}$ = 3.9, $^3J_{1',3'}$ = 3.9 Hz, 1 H, 1′-H), 7.44–7.57 (m, 2 H, Ph-H), 7.96–7.98 (m, 2 H, *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.2 (CH_3, CH_2CH_3), 13.8 (CH_3, 3′-CH_3), 20.8 (CH_2, CH_2CH_3), 26.0 (CH, C3′), 33.4 (CH, C2′), 34.0 (CH, C1′), 127.8, 128.3 (CH, *o*-/*m*-Ph), 132.3 (CH, *p*-Ph), 138.2 (C_q, *i*-Ph), 200.0 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2960, 2930, 2869 ν(C_{aliph}–H), 1665 ν(C=O). $C_{13}H_{16}O$ (188.12): calcd. C 82.94, H 8.57, found C 82.78, H 8.72. $[\alpha]_D^{20}$ = –85.0 (*c* = 0.59, $CHCl_3$). *rac*-**5m** (41 mg, 0.22 mmol, 88%) was obtained from *rac*-**2m** (84 mg, 0.25 mmol, 1.0 equiv.) by method B as colourless liquid.

(1*S*,2*S*,3*R*)-1-(2-Isopropyl-3-methylcyclopropyl)-1-phenylmethanone (5n): Method B: Sodium hydride (60% in mineral oil, 15 mg, 0.38 mmol 1.2 equiv.) and carbamate **2n** (113 mg, 0.32 mmol, 96% *ee*, 1.0 equiv.), suspended in DMF (5 mL), were treated according to method B. Purification by FCC yielded (–)-**5n** (40 mg, 0.20 mmol, 62%, 96% *ee*) as colourless liquid. R_F = 0.85 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.97 [d, $^3J_{CH(CH3)2,CH(CH3)2}$ = 6.0 Hz, 6 H, 2′-CH(CH_3)$_2$], 1.17 (d, $^3J_{3',3'\text{-}CH3}$ = 6.3 Hz, 3 H, 3′-CH_3), 1.33–1.50 [m, 2 H, 2′-CH(CH_3)$_2$/2′-H], 1.71–1.82 (m, 1 H, 3′-H), 2.07 (t, $^3J_{1',2'}$ = 4.2, $^3J_{1',3'}$ = 4.2 Hz, 1 H, 1′-H), 7.35–7.48 (m, 3 H, *p*-/*m*-Ph), 7.86–7.91 (m, 2 H, *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.8 (CH_3, 3′-CH_3), 22.6, 23.3 [CH_3, CH(CH_3)$_2$], 26.8 [CH, $CH(CH_3)_2$], 28.2 (CH, C1′), 33.5 (CH, C2′), 41.1 (CH, C1′), 128.3, 128.8 (CH, *o*-/*m*-Ph), 132.8 (CH, *p*-Ph), 138.7 (C_q, *i*-C-Ph), 200.4 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2948, 2920, 2865 ν(C_{aliph}–H), 1660 ν(C=O). $C_{14}H_{18}O$ (202.13): calcd. C 83.12, H 8.97, found C 82.95, H 9.17. $[\alpha]_D^{20}$ = –19.0 (*c* = 0.70, $CHCl_3$) at 96% *ee* (*er* = 98:2). *rac*-**5n** (75 mg, 0.37 mmol, 58%) was obtained from carbamate *rac*-**2n** (224 mg, 0.64 mmol, 1.0 equiv.) by method B as colourless liquid.

(1*S*,2*S*,3*R*)-1-(2-Cyclopropyl-3-methylcyclopropyl)-1-phenylmethanone (5o): Method B: From sodium hydride (60% in mineral oil, 33 mg, 0.83 mmol 1.3 equiv.) and carbamate **2o** (218 mg, 0.64 mmol, 95% *ee*, 1.0 equiv.), suspended in THF (5 mL), (–)-**5o** (95 mg, 0.47 mmol, 74%, 95% *ee*) was obtained after purification by FCC as colourless oil. R_F = 0.58 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.11–0.17 (m, 2 H, H-*c*-Pr), 0.34–0.48 (m, 2 H, H-*c*-Pr), 0.52–0.62 (m, 1 H, H-*c*-Pr), 1.15 (d, $^3J_{3',3'\text{-}CH3}$ = 7.5 Hz, 3 H, 3′-CH_3), 1.24–1.30 (ddd, $^3J_{1',2'}$ = 4.5, $^3J_{2',3'}$ = 9.3 Hz, 1 H, 2′-H), 1.63–1.73 (m, 1 H, 3′-H), 2.07 (t, $^3J_{1',2'}$ = 4.5, $^3J_{1',3'}$ = 4.5 Hz, 1 H, 1′-H), 7.27–7.40 (m, 3 H, *p*-/*m*-Ph), 7.78–7.81 (m, 2 H, *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 5.3, 5.4, 8.8 (CH and CH_2, *c*–Pr–C), 13.36 (CH_3, 3′-CH_3), 26.7 (CH, C-3′), 33.2 (CH, C-2′), 36.5 (CH, C-1′), 128.3, 128.8 (CH, *o*-/*m*-Ph), 132.8 (CH, *p*-C-Ph), 138.7 (C_q, *i*-C-Ph), 200.4 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2956, 2926, 2865 ν(C_{aliph}–H), 1656 ν(C=O). $C_{14}H_{16}O$ (200.12): calcd. C 83.96, H 8.05, found C 83.83, H 8.27. $[\alpha]_D^{20}$ = –50.0 (*c* = 0.57, $CHCl_3$) at 95% *ee* (*er* = 97.5:2.5). *rac*-**5o** (28 mg, 0.14 mmol, 70%) was obtained from carbamate *rac*-**2o** (68 mg, 0.20 mmol, 1.0 equiv.) by method B as colourless oil.

(1*S*,2*S*,3*R*)-1-(2-Cyclohexyl-3-methylcyclopropyl)-1-phenylmethanone (5p): Method B: Sodium hydride (60% in mineral oil, 17 mg, 0.43 mmol, 1.3 equiv.) and carbamate **2p** (145 mg, 0.37 mmol, 95% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method B. Purification by FCC yielded (–)-**5p** (70 mg, 0.29 mmol, 78%, 95% *ee*) as colourless solid. M.p. 111–112 °C (PE/Et_2O). R_F = 0.83 (PE/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.12–1.31, 1.51–1.89 (m, $^3J_{3',3'\text{-}CH3}$ = 6.6 Hz, 16 H, 2′/3′-H/3′-CH_3/H-*c*-Hex), 2.14 (t, $^3J_{1',2'}$-H = 4.2, $^3J_{1',3'}$ = 4.2 Hz, 1 H, 1′-H), 7.42–7.56 (m, 2 H, H-Ph), 7.96–8.00 (m, 2 H, *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 12.9, 26.3, 26.4, 26.6, 26.7, 32.9, 33.4 (CH and CH_2, C2′, C3′, C-*c*-Hex), 37.4, 39.7 (CH and CH_2, C1′, C-*c*-Hex), 128.6, 128.8 (CH, *o*-/*m*-Ph), 132.8 (CH, *p*-Ph), 138.7 (C_q, *i*-Ph), 200.5 (CO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2978, 2886, 2843 ν(C_{aliph}–H), 1656 ν(C=O). $C_{17}H_{22}O$ (242.16): calcd. C 84.25, H 9.15, found C 83.91, H 8.84. $[\alpha]_D^{20}$ = –9.0 (*c* = 0.57, $CHCl_3$) at 95%

ee (*er* = 97.5:2.5). *rac*-**5p** (59 mg, 0.24 mmol, 70%) was obtained from *rac*-**2p** (137 mg, 0.35 mmol, 1.0 equiv.) by method B as colourless solid.

(1*S*,2*S*)-(2-Methylspiro[2.5]oct-1-yl)-1-phenylmethanone (8): Method B: Sodium hydride (60% in mineral oil, 33 mg, 0.83 mmol, 1.4 equiv.) and allyl carbamate **7** (258 mg, 0.69 mmol, 93% *ee*, 1.0 equiv.), suspended in THF (10 mL), were heated at 60 °C for 3 d. Workup was done according to method B. Purification by FCC yielded (–)-**8** (40 mg, 0.17 mmol, 25%) as colourless oil. R_F = 0.66 (PE/Et_2O, 3:1). ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.14 (d, $^3J_{3',3'\text{-CH3}}$ = 6.0 Hz, 3 H, 3′-CH_3), 1.31–1.58 (m, 10 H, H-*c*-Hex); 1.78 (q, 1 H, 3-H′); 2.09 (d, $^3J_{1',3'}$ = 5.2 Hz, 1 H, 1′-H); 7.36–7.47, 7.84–7.92 (m, 5 H, *o*, *m*-,*p*-Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 12.6, 26.0, 26.2, 26.4, 28.1, 30.0, 32.0 (CH and CH_2, C2′, C3′, C-*c*-Hex), 39.6, 40.5 (CH and CH_2, C1′, C-*c*-Hex), 127.9, 128.4 (CH, *o*-/*m*-Ph), 132.2 (CH, *p*-Ph), 139.2 (C_q, *i*-Ph), 198.6 (CO). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2922, 2847 $\nu(C_{aliph}–H)$, 1664 ν(C=O). $C_{16}H_{20}O$, Exact mass (ESI): $C_{16}H_{20}O + Na^+$ calcd. 251.1406; found 251.1403. $[\alpha]_D^{20}$ = +7.0 (*c* = 0.26, $CHCl_3$).

(1*R*,5*R*,6*R*)-6-(4-Bromophenyl)-5-methylbicyclo[3.1.0]pentane-1-carboxaldehyde (12a): Method C: Sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and allyl carbamate **11a** (106 mg, 0.25 mmol, 86% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method C. Purification by FCC yielded (+)-**12a** (60 mg, 0.20 mmol, 81%, 86% *ee*) as colourless solid. M.p. 126 °C (PE/E). R_F = 0.22 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.18 (s, 3 H, CH_3), 1.74–2.39 (m, 6 H, 2/3/4-H), 2.80 (s, 1 H, 7-H), 6.96 (d, $J_{8,9}$ = 8.3 Hz, 2 H, 8-H), 7.34 (d, $J_{8,9}$ = 8.3 Hz, 2 H, 9-H), 9.36 (s, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 19.4 (CH_3), 22.2 (CH_2, C3), 28.7 (CH_2, C2), 29.7 (C_q, C5), 30.4 (CH_2, C4), 32.3 (CH, C6), 43.7 (C_q, C1), 120.8 (C_q, C10), 130.9 (CH, C8), 131.7 (CH, C9), 135.8 (C_q, C7), 202.6 (C=O). IR (KBr) $\tilde{\nu}$[cm^{-1}] = 2960, 2921, 2852 $\nu(C_{aliph}–H)$, 1682 ν(C=O). According to oxidized product **13a** $C_{14}H_{15}O_2Br$ (295.17): calcd. C 56.87, H 5.12, found C 56.98, H 5.19. $[\alpha]_D^{20}$ = +36.9 (*c* = 0.90, $CHCl_3$), at 86% *ee* (*er* = 93:7). *rac*-**12a** (62 mg, 0.22 mmol, 84%) was obtained from carbamate *rac*-**11a** (106 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless solid.

(1*R*,5*R*,6*R*)-6-(4-Chlorophenyl)-5-methylbicyclo[3.1.0]pentane-1-carboxaldehyde (12b): Method C: From sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and carbamate **11b** (94 mg, 0.25 mmol, 74% *ee*, 1.0 equiv.), suspended in THF (5 mL), (+)-**12b** (53 mg, 0.21 mmol, 85%, 74% *ee*) was obtained after purification by FCC as colourless solid. M.p. 125 °C (PE/E). R_F = 0.24 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.07 (s, 3 H, CH_3), 1.74–2.40 (m, 6 H, 2/3/4-H), 2.81 (s, 1 H, 7-H), 7.02 (d, $J_{8,9}$ = 8.3 Hz, 2 H, 8-H), 7.18 (d, $J_{8,9}$ = 8.3 Hz, 2 H, 9-H), 9.68 (s, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 18.3 (CH_3), 26.9 (CH_2, C3), 28.4 (CH_2, C2), 28.9 (C_q, C5), 30.7 (CH_2, C4), 32.9 (CH, C6), 42.4 (C_q, C1), 121.8 (C_q, C10), 131.5 (CH, C8), 132.4 (CH, C9), 135.3 (C_q, C7), 203.1 (CHO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2952, 2924, 2853 $\nu(C_{aliph}–H)$, 1684 ν(C=O). According to oxidized product **13b**, $C_{14}H_{15}ClO_2$ (250.72): calcd. C 67.07, H 6.03, found C 67.17, H 6.18. $[\alpha]_D^{20}$ = +22.9 (*c* = 0.85, $CHCl_3$) at 74% *ee* (*er* = 87:13). *rac*-**12b** (54 mg, 0.22 mmol, 86%) was obtained from carbamate *rac*-**11b** (94 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless oil.

(1*R*,6*R*,7*R*)-6-Methyl-7-(naphth-2-yl)bicyclo[3.1.0]heptane-1-carboxaldehyde (12c): Method C: Sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and carbamate **11c** (98 mg, 0.25 mmol, 83% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method C. Purification by FCC yielded (–)-**12c** (52 mg, 0.21 mmol, 83%, 83% *ee*) as colourless solid. M.p. 138 °C (PE/E). R_F = 0.22 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.03 (s, 3 H, CH_3), 1.83–2.49 (m, 6 H, 2/3/4-H), 2.81 (s, 1 H, 5-H), 7.16–7.74 (m, 7 H, Naphthyl-H), 9.64 (s, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 19.6 (CH_3), 26.1 (CH_2, C3), 28.6 (CH_2, C2), 28.8 (C_q, C5), 31.2 (CH_2, C4), 33.8 (C_q, C6), 40.2 (C_q, C1), 125.8, 126.3, 127.2, 127.9, 128.3, 130.2, 132.4, 133.9, 134.6, 136.2 (CH and C_q), 203.6 (CHO). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2960, 2926, 2856 $\nu(C_{aliph}–H)$, 1683 ν(C=O). According to oxidized product **13c**, $C_{18}H_{18}O_2$ (266.33): calcd. C 81.17, H 6.81, found C 81.22, H 6.72. $[\alpha]_D^{20}$ = –11.2 (*c* = 0.85, $CHCl_3$) at 83% *ee* (*er* = 91.5:8.5). *rac*-**12c** (54 mg, 0.22 mmol, 86%) was obtained from *rac*-**11c** (98 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless solid.

(1*R*,6*S*,7*R*)-7-(4-Bromophenyl)-6-methylbicyclo[4.1.0]heptane-1-carboxaldehyde (12d): Method C: From sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and allyl carbamate **11d** (109 mg, 0.25 mmol, 86% *ee*, 1.0 equiv.), suspended in THF (5 mL) (–)-**12d** (65 mg, 0.22 mmol, 85%, 86% *ee*) was obtained after purification by FCC as colourless oil. R_F = 0.22 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.93 (s, 3 H, CH_3), 1.19–1.55 (m, 4 H, 3/4-H), 1.60 (m, 2 H, 2-H), 1.75 (m, 2 H, 5-H), 3.05 (s, 1 H, 7-H), 7.24 (d, $J_{9,10}$ = 8.3 Hz, 2 H, 9-H), 7.72 (d, $J_{9,10}$ = 8.3 Hz, 2 H, 10-H), 9.68 (s, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 18.9 (CH_3), 15.3 (CH_2, C3), 26.9 (C_q, C6), 29.4 (CH_2, C2), 30.2 (CH_2, C4), 36.6 (CH_2, C5), 37.5 (CH, C7), 45.1 (C_q, C1), 121.1 (C_q, C11), 131.1 (CH, C9), 132.6 (CH, C10), 135.0 (C_q, C8), 203.1 (C=O). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2954, 2913, 2849 $\nu(C_{aliph}–H)$, 1706 ν(C=O). According to oxidized product **13d**, $C_{16}H_{21}BrO_2$ (309.20): calcd. C 58.27, H 5.54, found C 58.62, H 5.80. $[\alpha]_D^{20}$ = –85.0 (*c* = 0.53, $CHCl_3$), at 86% *ee* (*er* = 93:7). *rac*-**12d** (65 mg, 0.21 mmol, 84%) was obtained from carbamate *rac*-**11d** (109 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless oil.

(1*R*,6*R*,7*R*)-6-Butyl-7-phenylbicyclo[4.1.0]heptane-1-carboxaldehyde (12e): Method C: Sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and allyl carbamate **11e** (100 mg, 0.25 mmol, 82% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method C. Purification by FCC yielded (–)-**12e** (65 mg, 0.21 mmol, 85%, 82% *ee*) as colourless oil. R_F = 0.23 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, $J_{3',4'}$ = 6.9 Hz, 3 H, 4′-H), 1.21–1.56 (m, 4 H, 3/4-H), 1.62 (m, 2 H, 2-H), 1.73 (m, 2 H, 2′-H), 1.81–1.92 (m, 4 H, 1′/3′-H), 2.41 (m, 2 H, 5-H), 2.85 (s, 1 H, 7-H), 7.07–7.21 (m, 5 H, 9/10/11-H), 9.38 (s, 1 H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.2 (CH_3, C4′), 15.1 (CH_2, C2′), 15.8 (CH_2, C3), 26.1 (C_q, C1), 29.4 (CH_2, C2), 30.4 (CH_2, C4), 34.8–35.7 (CH_2, C1′/3′), 36.7 (CH_2, C5), 37.5 (CH_2, C7), 39.9 (C_q, C6), 125.7, 128.9, 131.2, 140.6 (C_q and CH), 202.2 (C=O). IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2960, 2926, 2860 $\nu(C_{aliph}–H)$, 1691 ν(C=O). According to oxidized product **13e**, $C_{18}H_{23}O_2$ (272.38): calcd. C 79.37, H 8.88, found C 79.53, H 8.97. $[\alpha]_D^{20}$ = –114.0 (*c* = 0.64, $CHCl_3$), at 82% *ee* (*er* = 91.5:9.5). *rac*-**12e** (83 mg, 0.22 mmol, 87%) was obtained from carbamate *rac*-**11e** (100 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless oil.

(1*R*,6*R*,7*R*)-7-(4-Bromophenyl)-6-butylbicyclo[4.1.0]heptane-1-carboxaldehyde (12f): Method C: Sodium hydride (60% in mineral oil, 14 mg, 0.35 mmol, 1.4 equiv.) and allyl carbamate **11f** (100 mg, 0.25 mmol, 72% *ee*, 1.0 equiv.), suspended in THF (5 mL), were treated according to method C. Purification by FCC yielded (+)-**12f** (68 mg, 0.20 mmol, 80%, 72% *ee*) as colourless oil. R_F = 0.24 (PE/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.93 (t, $J_{3',4'}$ = 7.1 Hz, 3 H, 4′-H), 1.15–1.52 (m, 4 H, 3/4-H), 1.65 (m, 2 H, 2-H), 1.75 (m, 2 H, 2′-H), 1.85–1.92 (m, 1 H, 1′/3′-H), 2.40 (m, 2 H, 5-H), 2.82 (s, 1 H, 7-H), 7.17–7.25 (m, 4 H, 9/10-H), 9.35 (s,

1 H, CHO).^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.4 (CH_3, C4′), 22.3 (CH_2, C3), 23.1 (CH_2, C3′), 24.3 (CH_2, C4), 23.4 (CH_2, C2′), 25.8 (CH_2, C2), 26.7 (C_q, C6), 27.7 (CH_2, C1′), 33.9 (CH_2, C5), 34.4 (C_q, C7), 45.7 (C_q, C1), 125.9 (C_q, C11), 127.8 (CH, C10), 128.7 (CH, C9), 139.6 (C_q, C8), 203.2 (C=O). IR (film) $\tilde{\nu}$ [cm^{-1}] = 2951, 2916, 2846 $\nu(C_{aliph}–H)$, 1700 ν(C=O). According to oxidized product **13f**, $C_{18}H_{23}OBr$ (335.29): calcd. C 64.48, H 6.91, found C 64.53, H 6.96. $[\alpha]_D^{20}$ = +22.0 (*c* = 0.53, $CHCl_3$), at 72% *ee* (*er* = 86:14). *rac*-**12f** (67 mg, 0.20 mmol, 80%) was obtained from *rac*-**11f** (120 mg, 0.25 mmol, 1.0 equiv.) by method C as colourless oil.

***rac*-6-(4-Bromophenyl)-5-methylbicyclo[3.1.0]pentane-1-carboxylic Acid (*rac*-13a):** *rac*-**12a** (62 mg, 0.22 mmol) was dissolved in *n*-pentane (2 mL) and diethyl ether (0.5 mL). The solution was allowed to stand at room temperature without any stirring for 7 d. The solvents were evaporated in vacuo yielding pure carboxylic acid *rac*-**13a** (66 mg, 0.22 mmol, >99%) as colourless solid. M.p. 126 °C (PE/E). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.18 (s, 3 H, CH_3), 1.14–1.59 (m, 4 H, 2/3-H), 1.69 (m, 2 H, 4-H), 2.80 (s, 1 H, 7-H), 6.96 (m, 2 H, 8-H), 7.34 (d, 2 H, 9-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 19.4 (CH_3), 22.2 (CH_2, C3), 29.7 (C_q, C5), 30.4 (CH_2, C2), 31.4 (CH_2, C4), 34.3 (CH, C6), 42.3 (C_q, C1), 120.8 (C_q, C10), 130.9 (CH, C8), 131.7 (CH, C9), 135.8 (C_q, C7), 182.6 (COOH). IR (KBr) $\tilde{\nu}$[cm^{-1}] = 2960, 2921, 2852 $\nu(C_{aliph}–H)$. $C_{14}H_{15}O_2Br$ (295.17): calcd. C 56.87, H 5.12, found C 56.98, H 5.19.

***rac*-7-(4-Bromophenyl)-6-methylbicyclo[4.1.0]heptane-1-carboxylic Acid (*rac*-13d):** *rac*-**12d** (65 mg, 0.22 mmol) was dissolved in *n*-pentane (2 mL) and diethyl ether (0.5 mL). The solution was allowed to stand at room temperature without any stirring for 7 d. The solvents were evaporated in vacuo yielding pure carboxylic acid *rac*-**13d** (68 mg, 0.22 mmol, >99%) as colourless solid. M.p. 160 C° (PE/E). $C_{16}H_{21}BrO_2$ (309.20): calcd. C 58.27, H 5.54, found C 58.62, H 5.80.

X-ray Crystal Structure Analysis of *rac*-13d:[15] M = 309.20, colourless crystal 0.35 × 0.15 × 0.15 mm, a = 7.141(1), b = 10.698(1), c = 17.997(1) Å, β = 90.66(1)°, V = 1374.8(2) Å^3, $\rho_{calcd.}$ = 1.494 g cm^{-3}, μ = 29.82 cm^{-1}, empirical absorption correction ($0.422 \leq T \leq 0.663$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω- and φ-scans, 10278 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 3274 independent (R_{int} = 0.045) and 2346 observed reflections [$I \geq 2\,\sigma(I)$], 165 refined parameters, R = 0.037, wR^2 = 0.090, max. residual electron density 0.31 (–0.70) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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