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Asymmetric Synthesis of α-Substituted Nitriles and Cyanohydrins by Oxidative Cleavage of Chiral Aldehyde Hydrazones with Magnesium Monoperoxyphthalate

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Abstract: Optically active α- and α,β-substituted aldehyde hydrazones **2**, **4**, and **7**, which are readily available by asymmetric alkylation, Michael addition or [2,3]-Wittig rearrangement of chiral hydrazones can be transformed into nitriles **3** and **5** or cyanohydrins **8** by MMPP mediated oxidation, respectively. This synthetic sequence offers a C-C connective entry into optically active functionalised nitriles with good overall yields (30 - 75 %) together with high diastereo- and enantioselectivities (*de* = 76 - ≥ 96 %, *ee* ≥ 72 - ≥ 97 %).

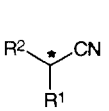
Due to the rich chemistry of the cyano group[1], nitriles, cyanohydrins and aminonitriles are of particular interest in preparative organic chemistry. Apart from the reduction of nitriles into amines, their conversion into carboxylic acids, amides and ketones is of conciderable interest, particularly in the light of recent developments in enzymatic processes[2,3].

Racemic nitriles can be synthesised by nucleophilic substitution with cyanide anion[1], by dehydration of amides[4], oxidation of primary amines[5], or from ketones using tosylmethyl isocyanide[6]. Starting from aldehydes they can also be prepared *via* dehydration of intermediate aldoximes[7] or by elimination-reactions of the corresponding N,N-dimethylhydrazones. The latter can be accomplished by using strong bases[8], by base promoted elimination of trimethylamine from hydrazonium salts intermediates[9] or by the use of several oxidising reagents[10].

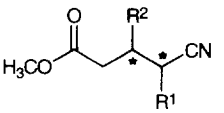
Although many processes for the synthesis of racemic nitriles already exist, there is a great need for flexible and practical methods leading to optically active nitriles. It has only been recently that syntheses have been reported starting from enantiopure precursors[11], chromatographic[12] or enzymatic[3] resolutions or asymmetric syntheses[13]. Due to the unsatisfactory enantioselectivity or the limited availability of the enantiopure starting materials, the number of nitriles available in high enantiomeric purity is still rather limited.

In 1990 we introduced the oxidative cleavage of N,N-dialkylhydrazones to ketones by magnesium monoperoxyphthalate hexahydrate (MMPP· 6 H_2O)[14]. This procedure is applicable to N,N-dimethylhydrazones and to hydrazones derived from (*S*)-1-amino-2-methoxymethyl-pyrrolidine (SAMP) in good yields without racemisation. MMPP is a save, mild reagent which is superior to other peroxy systems in many oxidation reactions and has enjoyed increasing popularity[15]. We have recently described the enantioselective syntheses of nitriles by asymmetric α-alkylation of aldehyde SAMP hydrazones with subsequent MMPP mediated hydrazone cleavage[16], which was discovered during our work on the oxidative cleavage of ketone hydrazones[14]. This methodology has been extended to the diastereo- and enantioselective synthesis of cyanohydrins *via* [2,3]-Wittig rearrangement of chiral allyloxyacetaldehyde hydrazones, followed by MMPP-cleavage[17].

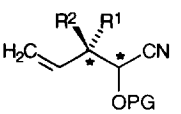
Independently, Lassaletta et al. also reported on the conversion of N,N-dialkylhydrazones to nitriles[10c,18].We now wish to describe the results of our investigations for the flexible C-C connective, diastereo- and enantioselective synthesis of nitriles **A** and **B** as well as protected cyanohydrins **C** (PG = protecting group).



A



B



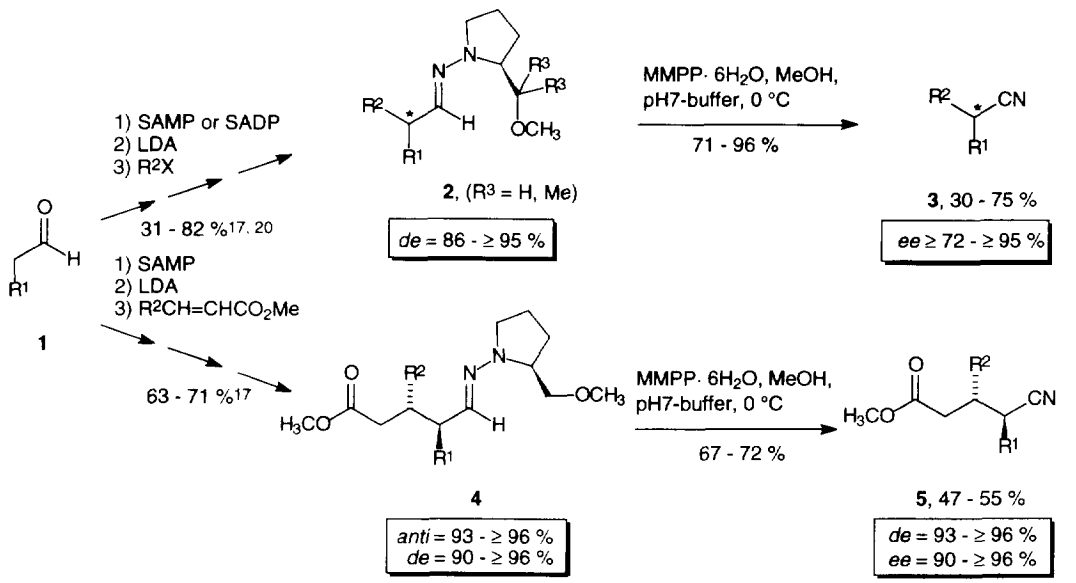
C

Cyanohydrins possess an even greater synthetic potential than nitriles through manipulation of both, the cyano and the hydroxy group. They can be easily converted into α-hydroxycarboxylic acids, -esters, -ketones, -aldehydes and β-hydroxyamines as well as α-amino acids, without racemisation[19a,b]. Optically active cyanohydrins are usually synthesised by enantioselective stoichiometric or catalytic addition of cyanide sources to aldehydes, employing enzymes, polymeric reagents, organometallic species and peptides as catalysts[19]. In particular the stereoselective synthesis of aliphatic cyanohydrins warrants further investigation.

The alkylation of aldehyde SAMP hydrazones is a well established method for asymmetric C-C bond construction and usually gives the alkylated hydrazones in excellent yields and asymmetric inductions[20]. As depicted in Scheme 1, aldehydes **1** were converted into their chiral hydrazones, followed by metalation with lithium diisopropylamide (LDA) and alkylation according to literature procedure to give the α-substituted hydrazones **2a-d** in excellent yields and diastereomeric excesses (*de* ≥ 95 %)[16,20]. Starting from protected α-hydroxyacetaldehydes the protected α-hydroxyhydrazones **2e,f** were prepared with good diastereomeric excesses (*de* = 86 - 95 %) after condensation with SAMP or (*S*)-1-amino-2-(1-methoxy-1-methylethyl)-pyrrolidine (SADP) and subsequent alkylation[21].

Oxidative cleavage of hydrazones **2** was accomplished by stirring with MMPP in a mixed MeOH/ phosphate buffer solvent system at 0 °C until starting material could no longer be detected (5 min to 5 h). Simple work up procedures and purification by Kugelrohr distillation or column chromatography afforded the nitriles **3a-d** and cyanohydrins **3e,f** in good overall yields (30 - 67 %) starting from aldehyde **1**. The *ee*-values of nitriles **3a-d** were determined by ^{1}H and ^{13}C NMR spectroscopy after reduction with lithium aluminium hydride and preparation of the corresponding Mosher amides[22] and those of the cyanohydrins **3e,f** after reduction to the corresponding aldehydes (Table 2). With the exception of α-benzyloxyhydrazone **2f** (*de* = 86 %, *ee* ≥ 72 % for **3f**) no racemisation was observed and enantiomeric excesses of the products were high (*ee* ≥ 93 %). The absolute configuration of nitriles **3a-e** follows from the established mechanism for alkylation of SAMP hydrazones[20,21]. The enantiomeric nitriles are of course available by employing RAMP instead of SAMP as chiral auxiliary but, as can be seen from the results in Table 1, the absolute configuration can also be predicted by proper choice of the starting material and the alkylating reagent (synthon control, **3a,b**) or by use of the sterically more demanding SADP instead of SAMP (**3e,f**).

The SAMP/ RAMP hydrazone method not only allows the enantioselective α-alkylation of aldehydes and ketones but can also be applied to other electrophilic substitutions alpha to the carbonyl group, for example, the asymmetric Michael addition[20,23]. Reaction of the deprotonated SAMP hydrazones with enoates cleanly gave the Michael adducts **4** in good yields (67 - 71 %) and very good selectivities (*anti* = 93 - ≥ 96 %, *de* = 90 - ≥ 96 %). The relative and absolute configurations of ketoester SAMP hydrazones **4a-c** has already



Scheme 1. Asymmetric synthesis of nitriles and cyanohydrins by electrophilic substitution of chiral hydrazones and subsequent oxidative cleavage with MMPP

Table 1. Optically Active Nitriles and Cyanohydrins.

compounds 3, 5	R^1	R^2	yield[a] [%]	$[\alpha]_D^{RT}$ (c, $CHCl_3$)	de[b] [%]	ee [%]	config.
3a	Me	Bn	78 (56)	+ 31.1 (1.2)	—	≥ 95[c]	(*S*)
3b	Bn	Me	72 (55)	− 29.4 (1.5)	—	≥ 95[c]	(*R*)
3c	Ph	Me	73 (67)	+ 18.5 (1.2)	—	≥ 95[c]	(*R*)
3d	*n*-Non	Me	71 (57)	− 20.8 (1.1)	—	≥ 95[c]	(*R*)
3e	OTBDPS	Allyl	96 (30)	− 27.9 (0.6)	—	93[d]	(*S*)
3f	OBn	Allyl	91 (75)	+ 115.5 (1.0)	—	72[d]	(*R*)[e]
5a	Me	Me	72 (48)	+ 34.6 (1.1)	94	90[f]	(*S*,*S*)
5b	Bn	Ph	67 (42)	− 40.8 (1.1)	93	≥ 96[f]	(*S*,*S*)
5c	*n*-Non	Me	70 (50)	+ 1.2 (1.4)	≥ 96	≥ 96[f]	(*S*,*S*)

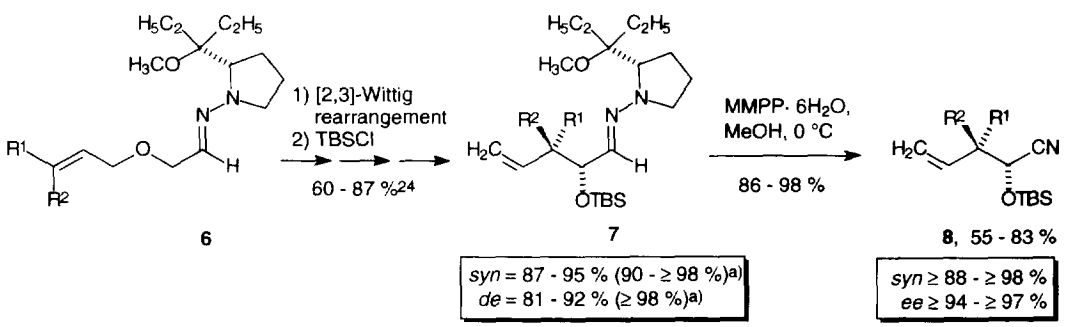
a) In parantheses: Overall yield of the three step procedure starting from aldehyde **1**; b) Determined by ^1H and ^{13}C NMR spectroscopy and by gas chromatography; c) Determined by ^1H and ^{13}C NMR spectroscopy on the Mosher amides derived from the corresponding amines after $LiAlH_4$ reduction; d) Determined after DIBAH reduction furnishing the corresponding aldehyde **9h,i**; e) Using SADP as chiral auxiliary; f) Determined by gas chromatography employing a chiral stationary phase [50 m, H_2, 200 °C, heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin].

unambiguously been established[23].

Oxidative removal of the auxiliary with MMPP afforded the α,β-substituted nitriles **5** and gas chromatographic analysis of the crude products showed only very small amounts of the corresponding aldehydes (≤ 5 %)[16]. Again the hydrazone nitrile conversion proceeded without epimerisation at the new α-stereogenic center (^{1}H and ^{13}C NMR) furnishing cyano esters **5** in high diastereo- and enantiomeric excesses (*de* = 93 - ≥ 96 %, *ee* = 90 - ≥ 96 %). We have also been able to demonstrate that the cyano esters **5** are valuable building blocks in organic synthesis as they could be converted to *cis*-4,5-disubstituted piperidin-2-ones by reductive lactamisation with Raney nickel[16].

By employing the [2,3]-Wittig rearrangement as key reaction, protected β,γ-unsaturated cyanohydrins with variable substitution in α-position were available from α-allyloxyacetaldehyde (*S*)-1-amino-2-(1-ethyl-1-methoxypropyl)-pyrrolidine (SAEP) hydrazones **6**, which can be readily prepared from the corresponding Weinreb amides in two steps[17]. Metallation of the hydrazones **6** with LDA in THF/ HMPA and subsequent silylation with *tert*-butyldimethylsilyl chloride (TBSCl) afforded the α-silyloxyhydrazones **7** in good to very good yields (60 - 87 %) and *syn*/ *anti*-selectivities (*syn* = 90 - ≥ 98 %) together with high diastereomeric excesses (*de* ≥ 98 %), after purification by HPLC[17] (Scheme 2).

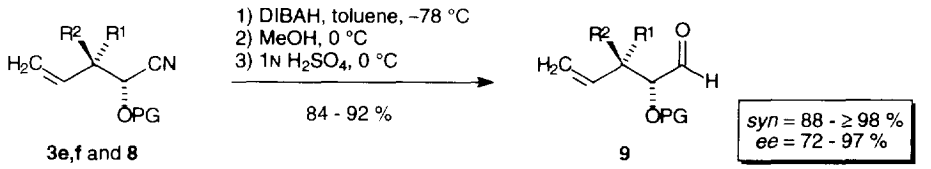
Oxidative cleavage of the chiral auxiliary from the hydrazones **7** was carried out by stirring with MMPP in MeOH at 0 °C, the reaction beeing followed by TLC control. The reaction was much faster in the absence of buffer due to the homogeneous nature of the solution and was complete within 30 to 90 minutes. Again the cleavage proceeded in very good yields (86 - 98 %) and purification by column chromatography gave the α-substituted, β,γ-unsaturated cyanohydrins **8** in good overall yields (55 - 83 %) with high *syn*-selectivity (*syn* ≥ 88 - ≥ 98 %) and enantiomeric excesses (*ee* ≥ 94 - ≥ 97 %).



Scheme 2. Asymmetric synthesis of cyanohydrins by [2,3]-Wittig rearrangement of SAEP hydrazones and subsequent oxidative cleavage with MMPP

In order to demonstrate the synthetic potential of the functionalised cyanohydrins **3e,f** and **8** they were converted into protected α-hydroxyaldehydes **9** by employing a method recently described by Oguni et al.[25] (Scheme 3). Standard work up and purification by column chromatography furnished the aldehydes **9** in very good yields (85 - 92 %). The enantiomeric excesses were determined by ^{1}H NMR spectroscopy using (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (**9a-g**) or acetalisation with (*R,R*)-2,3-bis-(trimethylsilyloxy)-butane and analysis of the product by GC or ^{1}H and ^{13}C NMR spectroscopy (**9h,i**)[21]. The observed slight

racemisation (1 - 4 %) over two steps can be attributed to nitrile reduction and the ease of racemisation of protected α-hydroxyaldehydes.



Scheme 3. Conversion of cyanohydrins to protected α-hydroxyaldehydes

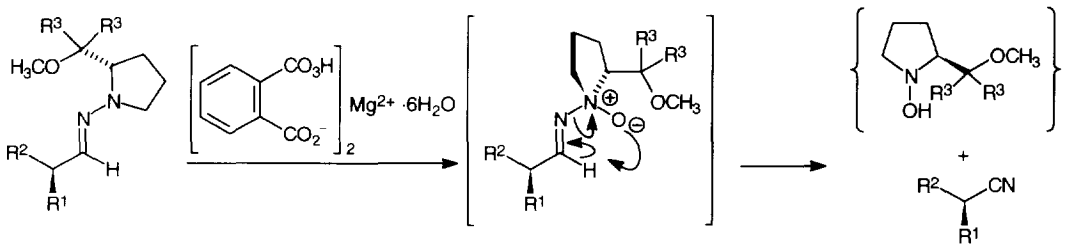
The relative and absolute configuration of products **8** follows from derivatisation of aldehydes **9**[17] and has further been confirmed by the total synthesis of naturally occurring (–)-oudemansin A[24].

Table 2. Optically Active Cyanohydrins **8** and α-Hydroxyaldehydes **9**.

8, 9	R^1	R^2	PG	yield **8**[a] [%]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)	overall[b] yield **9** [%]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)	*syn*[c] [%]	*ee*[d] [%]	config.
a	Me	H	TBS	96 (77)	+ 44.1 (1.0)	65	+ 15.1 (1.1)	> 98	96	(*R,S*)
b	Me	Me	TBS	86 (58)	+ 49.1 (1.0)	49	+ 7.5 (1.0)	—	95	(*R*)
c	Et	H	TBS	93 (68)	+ 68.9 (1.1)	58	+ 26.3 (1.0)	93	97	(*R,S*)
d	*n*-Pr	H	TBS	88 (74)	+ 63.8 (1.1)	68	+ 28.9 (1.0)	94	94	(*R,S*)
e	*i*-Pr	H	TBS	88 (83)	+ 66.5 (1.0)	71	+ 26.1 (1.1)	88	95	(*R,S*)
f	*n*-Bu	H	TBS	98 (79)	+ 58.6 (1.1)	71	+ 26.1 (1.0)	96	95	(*R,S*)
g	*i*-Bu	H	TBS	92 (55)	+ 70.6 (1.0)	49	+ 41.4 (1.0)	98	96	(*R,S*)
h	H	H	TBDPS	—	—	27[e]	- 4.2 (0.7)	—	93[f]	(*S*)
i	H	H	Bn	—	—	63[e]	+ 52.3 (0.9)	—	72[f]	(*R*)

a) In parantheses: Overall yield of the three step procedure starting from hydrazone **6**; b) Overall yield of the four step procedure starting from hydrazone **6**; c) Determined by ^1H and ^{13}C NMR spectroscopy; d) Determined by ^1H NMR spectroscopy using (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent; e) Overall yield of the four step procedure starting from aldehyde **1**; f) Determined by acetalisation with (*R,R*)-2,3-bis-(trimethylsilyloxy)-butane and analysis of the product by GC or ^1H and ^{13}C NMR spectroscopy[21].

Concerning the mechanism of nitrile formation we and others[10c] assume an aza Cope-type elemination after intermediate formation of an N-oxide (Scheme 4). This process was first proposed by Albright and Smith[10a] for the oxidative cleavage of N,N-dimethylhydrazones with hydrogen peroxide. This mechanistic pathway remains to be unambiguously confirmed by isolation of the putative hydroxylamine cleavage product (or a derivative thereof), thus allowing recycling of the chiral auxiliary.



Scheme 4. Proposed mechanism for the aldehyde hydrazone nitrile conversion with MMPP

In summary, the combination of asymmetric electrophilic α-substitutions of chiral aldehyde hydrazones or the [2,3]-Wittig rearrangement of allyloxyacetaldehyde hydrazones with the MMPP mediated hydrazone cleavage allows a flexible C-C connective entry into optically active nitriles and cyanohydrins in good overall yields and very good enantiomeric and diastereomeric excesses. By employing the whole repertoire of the SAMP/ RAMP hydrazone method, the synthetic access to optically active molecules bearing the cyano group can be further extended. For example, recent work in colaboration with Lassaletta et al. has shown that α-substituted β-nitronitriles can be synthesised in high enantiomeric excess[26].

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EXPERIMENTAL

Chemicals. Toluene was freshly distilled from sodium under argon. Light petroleum refers to the fraction with b.p. 40 - 80 °C. Reagents of commercial quality were used from freshly opened containers unless otherwise stated. MMPP· $6H_2O$ (85 % content) was purchased from Fluka; DIBAH (1.0 M in *n*-hexane) was purchased from Aldrich. The hydrazones **2**[16,20], **4**[16,22], **6**[23,24] and **7**[24] and nitrile **5a**[16] were prepared according to literature procedures.

Apparatus. TLC: Merck glass-backed silica gel 60 F_{254} plates. - Preparative column chromatography: Merck silica gel 60, practical size 0.040 - 0.063 mm (230 - 400 mesh) (flash) and Florisil®, 0.160 - 0.240 mm, purchased from Aldrich. - Analytical GC: Siemens Sichromat 2 or 3 equipped with a SE-54-CB column (25 m x 0.25 mm) and SE-30 column (50 m x 0.25 mm), carrier gas nitrogen, FID. - Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality. - IR spectra: Perkin-Elmer 1420 and Perkin-Elmer FT/IR 1750. - ^1H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz): Varian VXR 300 and Gemini 300 (solvent: $CDCl_3$, TMS as internal standard). - Mass spectra: Varian MAT 212 (EI 70 eV) (relative intensities in paranthesis). - GC-MS: GC: Varian 3700, FS 15 column (25 m x 0.25 mm); MS: Varian MAT 212 (EI 70 eV) (relative intensities in paranthesis) - HRMS: Finnigan MAT, MAT 95.

General procedure for the MMPP-mediated hydrazone nitrile conversion of hydrazones ***2*** *and* ***4****:*
MMPP· $6H_2O$ (3.0 mmol, 7.5 mmol for **2e,f**) is suspended in a rapidly stirred mixture of MeOH and pH7 phosphate buffer (20 ml, 1:1, 4:1 for **2e**) at 0 °C. The corresponding hydrazone (2.5 mmol) dissolved in

MeOH (2 ml) is added dropwise and the mixture is stirred at 0 °C until the reaction is complete (TLC control, 5 min to 5 h). The suspension is charged to a separating funnel along with 100 ml of diethyl ether and saturated aqueous $NaHCO_3$ solution (10 ml). The organic layer is separated and the aqueous phase is extracted with diethyl ether (50 ml). The combined organic phases are washed with water (10 ml) and brine (10 ml) and dried over $MgSO_4$. Evaporation of the solvent and purfication by Kugelrohr distillation or column chromatography gives the pure nitrile or cyanohydrin **3,4** as a colourless liquid or solid.

General procedure for the MMPP-mediated cleavage of hydrazone 7:
The corresponding aldehyde hydrazone **7** (2.0 mmol) is dissolved in MeOH and stirred at 0 °C. MMPP· $6H_2O$ is added (5.0 mmol) and stirring is continued until the reaction is complete (TLC control, 30 - 90 min.). The mixture is charged to a seperating funnel together with diethyl ether (200 ml) and saturated aqueous $NaHCO_3$ solution and the organic layer is separated. The aqueous phase is extracted twice with diethyl ether (20 ml) and the combined organic phases are washed several times with brine and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography affords the pure cyanohydrins **8** as colourless liquids.

General procedure for the reduction of cyanohydrins to α-hydroxyaldehydes 9 with DIBAH[25]
A flame dried Schlenk flask is charged with the corresponding cyanohydrin (1 mmol) dissolved in toluene (20 ml) and the solution is cooled to –78 °C. DIBAH (2 ml, 2 mmol) is added dropwise and stirring is continued for 1 h at –78 °C. MeOH (4 ml) is added and stirring is continued for 1 h at 0 °C followed by addition of 1 N H_2SO_4 (4 ml) and additional vigorous stirring for 1 h. The mixture is transferred to a separating funnel and diluted with diethyl ether (100 ml) and water (20 ml). The organic layer is separated , the aqueous phase is extracted twice with diethyl ether (20 ml) and the combined organic phases are washed (neutral) with brine. Drying over $MgSO_4$, evaporation of the solvent and purification by column chromatography affords aldehyde **9** as a colourless liquid.

(S)-2-Methyl-3-phenyl-propionitrile [(*S*)-**3a**]: 78% Yield from hydrazone **2b** after Kugelrohr distillation (170 °C, 12 Torr). - $[\alpha]_D^{RT}$: +31.1 (*c* = 1.2, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction with lithium aluminium hydride and preparation of the corresponding Mosher amide. - IR (film): ν = 2240 (w, CN), 1490 (s), 1450 (s), 1080 (s), 1030 (s), 740 (s), 700 (s) cm^{-1}. - ^1H NMR: δ = 1.23 (d, *J* = 6.4 Hz, 3H, CH_3), 2.71-2.86 (m, 3H, $CHCH_2$), 7.20 (m, 5H, $CH_{arom.}$) ppm. - ^{13}C NMR: δ = 17.21 (CH_3), 27.11 (2-CH), 39.55 (3-CH_2), 122.15 (1-C), 126.84 (CH_{para}), 128.31 (CH_{meta}), 128.72 (CH_{ortho}), 136.63 (C_{ipso}) ppm. - MS: *m/z* = 145 (16, M^+), 91 (100). - $C_{10}H_{11}N$ (145.2): calcd. C 82.72, H 7.64, N 9.65; found C 82.53, H 7.78, N 10.06.

(R)-2-Methyl-3-phenyl-propionitrile [(*R*)-**3b**]: 72% Yield from hydrazone **2b** after Kugelrohr distillation (100 °C, 0.2 Torr). - $[\alpha]_D^{RT}$: –29.4 (*c* = 1.5, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction with lithium aluminium hydride and preparation of the corresponding Mosher amide. - IR (film): ν = 2240 (w, CN), 1490 (s), 1450 (s), 1080 ,(s), 1030 (s), 740 (s), 700 (s) cm^{-1}. - ^1H NMR: δ = 1.20 (d, *J* = 6.7 Hz, 3H, CH_3), 2.70-2.89 (m, 3H, $CHCH_2$), 7.15-7.31 (m, 5H, CH_{arom}) ppm. - ^{13}C NMR: δ = 17.10 (CH_3), 26.96 (2-CH), 39.40 (3-CH_2), 122.05 (1-C), 126.71 (CH_{para}), 128.18 (CH_{meta}), 128.63 (CH_{ortho}), 136.58 (C_{ipso}) ppm. - MS: *m/z* = 145 (13, M^+), 91 (100). - $C_{10}H_{11}N$ (145.2): calcd. C 82.72, H 7.64, N 9.65; found C 82.56, H 7.81, N 10.01.

(R)-2-Phenyl-propionitrile [(*R*)-**3c**]: 73% Yield from hydrazone **2c** after Kugelrohr distillation (70 °C, 0.2 Torr). - $[\alpha]_D^{RT}$: +18.5 (*c* = 1.1, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction with lithium aluminium hydride and preparation of the corresponding Mosher amide. - IR (film): ν = 2240 (w, CN), 1495 (s), 1450 (s), 760 (s), 700 (s) cm^{-1}. - ^1H NMR: δ = 1.57 (d, *J* = 7.4 Hz, 3H, CH_3), 3.84 (q, *J* = 7.4 Hz, 3H, $CHCH_3$), 7.25-7.38 (m, 5H, $CH_{arom.}$) ppm. - ^{13}C NMR: δ = 21.13 (3-CH_3), 30.89 (2-CH), 121.32 (1-C), 126.43 (CH_{meta}), 127.73 (CH_{para}), 128.85 (CH_{ortho}), 136.93 (C_{ipso}) ppm. - MS: *m/z* = 131 (35, M^+), 116 (100), 89 (24), 78 (19), 77 (16), 63 (29), 51 (24), 50 (14), 39 (21). - C_9H_9N (131.18): calcd. C 82.41, H 6.91, N 10.68; found C 82.26, H 7.17, N 10.79.

(R)-2-Methyl-undecanenitrile [(*R*)-**3d**]: 71% Yield from hydrazone **2d** after Kugelrohr distillation (95 °C, 0.1 Torr). - $[\alpha]_D^{RT}$: –20.8 (*c* = 1.1, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction with lithium aluminium hydride and preparation of the corresponding Mosher amide. - IR (film): ν = 2240 (w, CN), 1460 (s) cm^{-1}. - ^1H NMR: δ = 0.88 (t, *J* = 6.7 Hz, 3H, 1.31-1.34 (m, 17H, 4-CH_2, 5-CH_2, 6-CH_2, 7-CH_2, 8-CH_2, 9-CH_2, 10-CH_2, 11-CH_3), 1.40-1.64 (m, 2H, $CHCH_2$), 2.60 (m, 1H, $CHCH_2$) ppm. - ^{13}C NMR: δ = 13.87 (11-CH_3), 17.85 (2-$CHCH_3$), 24.49 (3-CH_2), 25.33 (2-CH), 26.88, 28.93, 29.10, 29.22, 29.31, 31.70, 33.96 (4-CH_2, 5-CH_2, 6-CH_2, 7-CH_2, 8-CH_2, 9-CH_2, 10-CH_2), 122.77 (1-C) ppm. - MS: *m/z* = 181 (3, M^+), 124 (23), 111 (30), 110 (31), 97 (37), 96 (37), 83 (42), 63 (37), 57 (34), 55 (58), 43 (62), 41 (100). - $C_{12}H_{23}N$ (181.32): calcd. C 79.49, H 12.78, N 7.73; found C 79.38, H 12.81, N 7.42.

(S)-2-tert-Butyldiphenylsilyloxy-pent-4-enenitrile [(*S*)-**3e**]: 96% Yield from hydrazone **2e** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:8). - R_f = 0.36 (diethyl ether/ light petroleum, 1:8). - $[\alpha]_D^{27}$: –27.9 (*c* = 0.6, $CHCl_3$). - *ee* ≥ 93 %, Determined after reduction to aldehyde **9h**. - IR (film): ν = 3073, 3051, 3014 (m, $CH_{arom.}$), 2959 (s), 2932 (s), 2885 (m), 2852 (s), 1641 (w, C=C), 1488 (w), 1473 (m), 1427 (s), 1395 (m), 1365 (m), 1335 (m), 1190 (m), 1100 (s, br, SiOC), 1025 (s), 995 (s), 925 (s, $HC{=}CH_2$), 823 (s, CSi-O), 741 (s, OSi-C), 700 (s), 610 (s) cm^{-1}. - ^1H NMR: δ = 1.10 [s, 9H, $C(CH_3)_3$], 2.48 (m, 2H, $CHCH_2CH$), 4.36 (dd, *J* = 7.1 Hz/ 5.4 Hz, 1H, CHO), 5.16 (m, 2H, $HC{=}CH_2$), 5.77 (ddt, *J* = 16.8 Hz/ 10.4 Hz/ 7.1 Hz, 1H, $HC{=}CH_2$), 7.36-7.50 (m, 6H, CH_{meta}; CH_{para}), 7.64-7.74 (m, 4H, CH_{ortho}) ppm - ^{13}C NMR: δ = 19.25 [$SiC(CH_3)_3$], 26.67 [$SiC(CH_3)_3$], 40.47 (3-CH), 62.76 (2-CH), 119.05 (1-C), 120.26 (5-CH_2), 127.70 (CH_{meta}), 130.39, 130.41, 130.61 (CH_{para}, 4-CH), 131.50, 131.98 (C_{ipso}), 135.73, 135.82 (CH_{ortho}) ppm. - MS: *m/z* = 335 (0.7, M^+), 280 (7), 279 (25), 278 (100, M^+–C_4H_9), 252 (19), 251 (81), 223 (11), 208 (37), 181 (21), 173 (17), 147 (24), 135 (11), 123 (30), 105 (15), 77 (11) - $C_{21}H_{25}NOSi$ (335.5): calcd. C 75.18, H 7.51, N 4.18; found C 75.06, H 7.60, N 4.47.

(R)-2-Benzyloxy-pent-4-enenitrile [(*R*)-**3f**]: 91% Yield from hydrazone **2f** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:5). - R_f = 0.50 (diethyl ether/ light petroleum, 1:5). - $[\alpha]_D^{27}$: +115.5 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 72 %, Determined after reduction to aldehyde **9i**. - IR (film): ν = 3084, 3068, 3034 (m, $CH_{arom.}$), 2984 (s), 2926 (s), 2872 (s), 1645 (m, C=C), 1497 (m), 1456 (s), 1433 (s), 1397 (m), 1372 (m), 1334 (s), 1275 (m), 1209 (m), 1094 (s), 1029 (s), 992 (s), 927 (s, $HC{=}CH_2$), 744 (s), 699 (s), 613 (m) cm^{-1}. - ^1H NMR: δ = 2.49 (m, 2H, $CHCH_2CH$), 4.17 (t, *J* = 6.5 Hz, 1H, CHO), 4.53 (d, *J* = 11.4 Hz, $PhCHH$), 4.84 (d, *J* = 11.8 Hz, $PhCHH$), 5.22 (m, 1H, $HC{=}CH_{trans}H$), 5.29 (m, 1H, $HC{=}CH_{cis}H$), 5.81 (ddt, *J* = 16.1 Hz/ 10.1 Hz/ 7.1 Hz, 1H, $HC{=}CH_2$), 7.31-7.39 (m, 5H, $CH_{arom.}$) ppm - ^{13}C NMR: δ = 37.61 (3-CH), 67.34

(2-CH), 72.67 (Ph*C*H_2), 117.75 (1-C), 120.02 (5-CH_2), 128.21, 128.67, 128.46 ($CH_{arom.}$), 130.71 (4-CH), 135.83 (C_{ipso}) ppm - MS: *m/z* = 187 (1.2, M^+), 105 (10), 91 (100, $C_7H_7^+$), 65 (18), 57 (10), 55 (10), 51 (10), 41 (18) - $C_{12}H_{13}NO$ (187.2): calcd. C 76.98, H 7.00, N 7.48; found C 76.58, H 7.16, N 4.42.

Methyl (S,S)-4-Benzyl-4-cyano-3-phenyl-butanoate [(*S,S*)-**5b**]: 67% Yield from hydrazone **4b** after recristallization from light petroleum/ diethyl ether. - colourless solid: mp 107-108 °C. - $[\alpha]_D^{RT}$: –40.8 (*c* = 1.1, $CHCl_3$). - *ee* ≥ 96 %, Determined by gas chromatography employing a chiral stationary phase: [50m, H_2, 200 °C, heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin]. - IR (film): ν = 2240 (w, CN), 1725 (s, C=O), 1495 (s), 1455 (s), 1340 (s), 760 (s), 725 (s), 700 (s) cm^{-1}. - ^1H NMR: δ = 2.60 (dd, J = 14 Hz/ 8.7 Hz, 1H, C*H*HPh), 2.72 (dd, J = 14 Hz/ 8.7 Hz, 1H, CH*H*Ph), 2.84 (dd, J = 16 Hz/ 6.4 Hz, 1H, C*H*HCO), 2.97 (dd, J = 16 Hz/ 7.7 Hz, 1H, CH*H*CO), 3.32-3.41 (m, 2H, CHCN, CHPh), 3.59 (s, 3H, OCH_3), 7.12-7.38 (m, 10H, $CH_{arom.}$) ppm. - ^{13}C NMR: δ = 36.86 (CH_2Ph), 38.83 (2-CH_2), 38.77 (3-CH), 42.31 (4-CH), 51.81 (OCH_3), 120.00 (CN), 127.21 (4-$CHCH_2CH_{para}$), 128.03 (3-$CHCH_{para}$), 128.40, 128.72, 128.82, 128.83 (CH_{ortho}, CH_{meta}), 136.79 (4-$CHCH_2C_{ipso}$), 138.29 (3-CHC_{ipso}), 171.63 (1-C) ppm. - MS: *m/z* = 294 (7, M^++1), 293 (32, M^+), 164 (41), 133 (65), 121 (100), 104 (60), 91 (99), 43 (23). - $C_{19}H_{19}NO_2$ (181.32): calcd. C 77.79, H 6.53, N 4.78; found C 77.78, H 6.56, N 4.64.

Methyl (S,S)-4-Cyano-3-methyl-tridecanoate [(*S,S*)-**5c**]: 70% Yield from hydrazone **4c** after Kugelrohr distillation (160 °C, 0.1 Torr). - $[\alpha]_D^{RT}$: +1.2 (*c* = 1.4, $CHCl_3$). - *ee* ≥ 96 %, Determined by gas chromatography employing a chiral stationary phase: [50m, H_2, 200 °C, heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin]. - IR (film): ν = 2240 (w, CN), 1740 (s, C=O), 1460 (s), 1440 (s), 1370 (s), 1195 (s), 1175 (s) cm^{-1}. - ^1H NMR: δ = 0.88 (t, 3H, J = 6.7 Hz, 3H, CH_2CH_3), 1.09 (d, J = 6.7 Hz, 3H, $CHCH_3$), 1.25-1.75 (m, 16H, 5-CH_2, 6-CH_2, 7-CH_2, 8-CH_2, 9-CH_2, 10-CH_2, 11-CH_2, 12-CH_2), 2.21 (m, 1H, C*H*CH_3), 2.36 (dd, J = 16 Hz/ 7.0 Hz, 1H, C*H*HCO), 2.48 (dd, J = 16 Hz/ 7.4 Hz, 1H, CH*H*O), 2.73 (m, 1H, CHCN), 3.69 (s, 3H, OCH_3) ppm. - ^{13}C NMR: δ = 13.85 (13-CH_3), 15.61 (3-$CHCH_3$), 22.46, 27.34, 28.87, 29.06, 29.15, 29.27, 30.22 (6-CH_2, 7-CH_2, 8-CH_2, 9-CH_2, 10-CH_2, 11-CH_2, 12-CH_2), 31.49 (3-CH), 31.66 (5-CH_2), 36.66 (4-CH), 39.23 (2-CH_2), 51.41 (OCH_3), 120.15 (CN), 171.97 (1-C) ppm. - MS: *m/z* = 267 (1, M++1), 236 (13), 194 (24), 134 (49), 105 (100), 97 (56), 43 (22). - $C_{16}H_{29}NO_2$ (267.40): calcd. C 71.89, H 10.93, N 5.24; found C 71.59, H 10.91, N 5.42.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-methyl-pent-4-enenitrile [(*R,S*)-**8a**]: 96% Yield from hydrazone **7a** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:40). - R_f = 0.21 (diethyl ether/ light petroleum, 1:40). - $[\alpha]_D^{RT}$: +44.4 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 96 %, Determined after reduction to aldehyde **9a**. - IR (film): ν = 2960 (s), 2930 (s), 2890 (s), 2860 (s), 1645 (w, C=C), 1475 (s), 1465 (s), 1420 (m), 1365 (m), 1260 (s), 1070 (s, br, SiOC), 1040 (m), 1005 (m), 925 (m, HC=CH_2), 840 (s, CSi-O), 780 (s, OSi-C), 675 (m) cm^{-1}. - ^1H NMR: δ = 0.13, 0.19 [s, 6H, $Si(CH_3)_2$], 0.92 [s, 9H, $C(CH_3)_3$], 1.15 (d, *J* = 6.7 Hz, 3H, $CHCH_3$), 2.54 (m, 1H, C*H*CH_3), 4.27 (d, *J* = 5.7 Hz, 1H, CHO), 5.20 (m, 2H, HC=CH_2), 5.81 (m, 1H, *H*C=CH_2) ppm. - ^{13}C NMR: δ = –5.42, –5.19 [$Si(CH_3)_2$], 14.73 ($CHCH_3$), 18.11 [$SiC(CH_3)_3$], 25.51 [$SiC(CH_3)_3$], 43.18 (3-CH), 66.43 (2-CH), 117.47 (5-CH_2), 119.12 (1-C), 137.17 (4-CH) ppm. - GC-MS: *m/z* = 225 (0.3, M^+), 171 (11), 169 (14), 168 (100, M^+–C_4H_9), 142 (89, 168–CHN), 140 (13), 138 (21), 127 (31), 115 [12, $C_4H_9Si(CH_3)_2^+$], 113 (21), 99 (11), 85 (15), 84 (15), 75 [46, $(CH_3)_2SiOH^+$], 73 (50), 59 (20), 57

(10), 55 (13), 47 (10), 45 (11), 43 (11), 41 (14). - $C_{12}H_{23}NOSi$ (225.4): calcd. C 63.94, H 10.28, N 6.21; found C 64.21, H 10.32, N 6.49.

(R)-2-tert-Butyldimethylsilyloxy-3,3-dimethyl-pent-4-enenitrile [(*R*)-**8b**]: 86% Yield from hydrazone **7b** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:40). - R_f = 0.58 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +49.1 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction to aldehyde **9b**. - IR (film): ν = 2960 (s), 2940 (s), 2890 (m), 2860 (s), 1640 (w, C=C), 1470 (s), 1420 (m), 1385 (m), 1365 (m), 1260 (s), 1105 (s, br, SiOC), 1005 (m), 920 (m, $HC=CH_2$), 840 (s, CSi-O), 780 (s, OSi-C), 680 (m) cm^{-1}. - ^1H NMR: δ = 0.12, 0.20 [s, 6H, $Si(CH_3)_2$], 0.92 [s, 9H, $C(CH_3)_3$], 1.13, 1.14 [s, 6H, $C(CH_3)_2$], 4.07 (s, 1H, CHO), 5.15 (dd, *J*= 17.7 Hz/ 1.0 Hz, 1H, $HC=CH_{cis}H$), 5.15 (dd, *J*= 10.4 Hz/ 1.0 Hz, $HC=CH_{trans}H$), 5.86 (d/d, *J*= 17.5 Hz/ 10.4 Hz, 1H, $HC=CH_2$) ppm. - ^{13}C NMR: δ = –5.50, –5.24 [$Si(CH_3)_2$], 18.10 [$SiC(CH_3)_3$], 22.19, 22.25 [$C(CH_3)_2$], 25.52 [$SiC(CH_3)_3$], 41.73 (3-C), 70.31 (2-CH), 114.90 (5-CH_2), 118.91 (1-C), 141.92 (4-CH) ppm. - GC-MS: *m/z* = 183 (17), 182 (100, $M^+-C_4H_9$), 171 (21), 156 (48), 155 (89, 182-CHN), 141 (70), 140 (27), 127 (25), 113 (10), 99 (21), 85 (15), 84 (14), 75 [75, $(CH_3)_2SiOH^+$], 73 (47), 69 [69, $H_2C=CHC(CH_3)_2^+$], 59 (17), 57 (10), 47 (10), 43 (10), 41 (44), 39 (10). - $C_{13}H_{25}NOSi$ (239.4): calcd. C 65.21, H 10.52, N 5.85; found C 65.52, H 10.57, N 6.30.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-ethyl-pent-4-enenitrile [(*R,S*)-**8c**]: 91 % Yield from hydrazone **7c** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:40). - R_f = 0.60 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +68.9 (*c* = 1.1, $CHCl_3$). - *ee* ≥ 97 %, Determined after reduction to aldehyde **9c**. - IR (Film): ν = 2960 (s), 2930 (s), 2890 (m), 2860 (s), 1645 (w, C=C), 1470 (m), 1465 (m), 1390 (m), 1365 (m), 1260 (s), 1120 (s, br, SiOC), 1055 (m), 995 (m), 920 (m, $HC=CH_2$), 840 (s, CSi-O), 770 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.13, 0.19 [s, 6H, $Si(CH_3)_2$], 0.91 [s, 9H, $C(CH_3)_3$], 0.91 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.40 (m, 1H, $HCHCH_3$), 1.69 (m, 1H, $HCHCH_3$), 2.26 (m, 1H, $CHHC=CH_2$), 4.33 (d, *J* = 6.1 Hz, 1H, CHO), 5.23 (m, 2H, $HC=CH_2$), 5.63 (ddd, *J* = 17.1 Hz/ 10.4 Hz/ 9.1 Hz, 1H, $HC=CH_2$) ppm. - ^{13}C NMR: δ = –5.41, –5.16 [$Si(CH_3)_2$], 11.39 (CH_2CH_3), 18.11 [$SiC(CH_3)_3$], 22.45 (CH_2CH_3), 25.53 [$SiC(CH_3)_3$], 51.15 (3-CH), 65.66 (2-CH), 119.19 (1-C), 119.30 (5-CH_2), 135.81 (4-CH) ppm. - GC-MS: *m/z* = 183 (17), 182 (100, $M^+-C_4H_9$), 171 (16), 156 (17), 155 (43, 182–CHN), 141 (30), 127 (11), 115 [11, $C_4H_9Si(CH_3)_2^+$], 114 (10), 113 (13), 101 (12), 99 (28), 84 (14), 75 [96, $(CH_3)_2SiOH^+$], 73 (33), 69 [15, $H_2C=CHCH(Et)^+$], 59 (17), 47 (10). - $C_{13}H_{25}NOSi$ (239.4): calcd. C 65.21, H 10.52, N 5.85; found C 65.12, H 10.54, N = 6.35.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-propyl-pent-4-enenitrile [(*R,S*)-**8d**]: 88% Yield from hydrazone **7d** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:100). - R_f = 0.83 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +63.8 (*c* = 1.1, $CHCl_3$). - *ee* ≥ 94 %, Determined after reduction to aldehyde **9d**. - IR (film): ν = 2960 (s), 2940 (s), 2860 (s), 1645 (w, C=C), 1470 (m), 1420 (m), 1390 (m), 1365 (m), 1260 (s), 1110 (s, br, SiOC), 1045 (m), 920 (m, $HC=CH_2$), 840 (s, CSi-O), 780 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.13, 0.19 [s, 6H, $Si(CH_3)_2$], 0.91 [(s, 9H, $C(CH_3)_3$], 0.91 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.20-1.70 (m, 4H, $CH_2CH_2CH_3$), 2.35 (m, 1H, $CHHC=CH_2$), 4.33 (d, *J* = 5.7 Hz, 1H, CHO), 5.21 (m, 2H, $HC=CH_2$), 5.64 (ddd, *J* = 17.1 Hz/ 10.4 Hz/ 9.1 Hz, 1H, $HC=CH_2$) ppm. - ^{13}C NMR: δ = –5.40, –5.16 [$Si(CH_3)_2$], 13.90 (CH_2CH_3), 18.11 [$SiC(CH_3)_3$], 19.98 (CH_2CH_3), 25.53 [$SiC(CH_3)_3$], 31.48 ($CH_2CH_2CH_3$), 49.19 (3-CH),

65.83 (2-CH), 119.01 (5-CH_2), 119.18 (1-C), 136.13 (4-CH) ppm. - GC-MS: *m/z* = 253 (0.3, M^+), 197 (12), 196 (75, M^+–C_4H_9), 171 (21), 169 (29, 196–CHN), 166 (22), 156 (12), 155 (14), 141 (17), 127 (12), 114 (10), 113 (11), 99 (10), 83 [16, H_2C=CHCH(*n*-Pr)$^+$], 75 (100, $[CH_3)_2SiOH^+$], 73 (49), 59 (18), 57 (6), 55 (16), 41 (13). - $C_{14}H_{27}NOSi$ (253.5): calcd. C 66.34, H 10.74, N 5.53; found C 66.15, H 10.94, N 5.98.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-isopropyl-pent-4-enenitrile [(*R,S*)-**8e**]: 88% Yield from hydrazone **7e** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:100). - R_f = 0.62 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +66.5 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction to aldehyde **9e**. - IR (film): ν = 2960 (s), 2930 (s), 2890 (m), 2860 (s), 1640 (w, C=C), 1470 (s), 1425 (m), 1390 (m), 1365 (m), 1255 (s), 1135 (s), 1110 (s, br, SiOC), 1000 (m), 920 (m, HC=CH_2), 840 (s, CSi-O), 780 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.15, 0.21 [(s, 6H, $Si(CH_3)_2$], 0.87, 0.95 [d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$], 0.91 [s, 9H, $C(CH_3)_3$], 2.00 [m, 1H, $CH(CH_3)_2$], 2.20 (m, 1H, CHHC=CH_2), 4.23 (d, *J* = 7.4 Hz, 1H, CHO), 5.19 (ddd, *J* = 16.8 Hz/ 1.9 Hz/ 0.7 Hz, 1H, HC=CH_{cis}), 5.29 (dd, *J* = 10.2 Hz/ 1.9 Hz, 1H, HC=CH_{trans}), 5.62 (ddd, *J* = 16.8 Hz/ 10.4 Hz/ 9.6 Hz, 1H, HC=CH_2) ppm. - ^{13}C NMR: δ = –5.42, –5.09 [$Si(CH_3)_2$], 17.93, 21.11 [$CH(CH_3)_2$], 18.07 [$SiC(CH_3)_3$], 25.52 [$SiC(CH_3)_3$], 26.82 [$CH(CH_3)_2$], 55.81 (3-CH), 63.87 (2-CH), 119.42 (1-C), 120.67 (5-CH_2), 133.08 (4-CH) ppm. - GC-MS: *m/z* = 253 (1.0, M^+), 197 (16), 196 (100, M^+–C_4H_9), 171 (14), 169 (21, 196–CHN), 168 (14), 156 (12), 155 (15), 154 (36), 141 (11), 140 (18), 128 (10), 127 (39), 115 [15, $C_4H_9Si(CH_3)_2^+$], 114 (16), 113 (22), 101 (10), 99 (24), 95 (12), 83 [57, H_2C=CHCH(*i*-Pr)$^+$], 75 [91, $(CH_3)_2SiOH^+$], 73 (48), 59 (19), 55 (33), 43 (15), 41 (21). - $C_{14}H_{27}NOSi$ (253.5): calcd. C 66.34, H 10.74, N = 5.53; found C 66.32, H 10.76, N = 6.00.

(2R,3S)-3-Butyl-2-tert-butyldimethylsilyloxy-pent-4-enenitrile [(*R,S*)-**8f**]: 98% Yield from hydrazone **7f** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:60). - R_f = 0.61 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +66.5 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 95 %, Determined after reduction to aldehyde **9f**. - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 1645 (w, C=C), 1470 (m), 1420 (m), 1390 (m), 1360 (m), 1260 (s), 1130 (s), 1110 (s, br, SiOC), 995 (m), 920 (m, HC=CH_2), 840 (s, CSi-O), 780 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.13, 0.19 [s, 6H, $Si(CH_3)_2$], 0.90 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 0.91 [s, 9H, $C(CH_3)_3$], 1.10-1.70 (m, 6H, CH_2), 2.33 (m, 1H, CHHC=CH_2), 4.32 (d, *J* = 5.8 Hz, 1H, CHO), 5.21 (m, 2H, HC=CH_2), 5.64 (ddd, *J* = 17.0 Hz/ 10.4 Hz/ 8.8 Hz, 1H, HC=CH_2) ppm. - ^{13}C NMR: δ = –5.39, –5.10 [$Si(CH_3)_2$], 13.92 (CH_2CH_3), 18.12 [$SiC(CH_3)_3$], 22.53 29.00, 29.06 (*n*-Bu-CH_2), 25.53 [$SiC(CH_3)_3$], 49.43 (3-CH), 65.84 (2-CH), 119.05 (5-CH_2), 119.18 (1-C), 136.18 (4-CH) ppm. - GC-MS: *m/z* = 211 (18), 210 (100, M^+–C_4H_9), 183 (31, 210–CHN), 182 (10), 180 (17), 171 (24), 156 (11), 154 (10), 141 (13), 140 (27), 127 (14), 114 (12), 99 (12), 97 [23, H_2C=CHCH(*n*-Bu)$^+$], 84 (11), 75 [93, $(CH_3)_2SiOH^+$], 73 (42), 67 (11), 59 (18), 55 (30), 41 (17). - $C_{15}H_{29}NOSi$ (267.5): calcd. C 67.35, H 10.93, N 5.24; found C 67.22, H 10.88, N 5.54.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-isobutyl-pent-4-enenitrile [(*R,S*)-**8g**]: 92% Yield from hydrazone **7g** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:60). - R_f = 0.58 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +70.6 (*c* = 1.0, $CHCl_3$). - *ee* ≥ 96 %, Determined after reduction to aldehyde **9g**. - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 1645 (w, C=C), 1470 (m), 1420 (m), 1390 (m), 1365 (m), 1260 (s), 1110 (s, br, SiOC), 995 (m), 920 (m, HC=CH_2), 840 (s, CSi-O), 780 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.13, 0.19 (s, 6H, $Si(CH_3)_2$), 0.86, 0.93 [(d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$], 0.92 [s, 9H, $C(CH_3)_3$],

1.36 (m, 2H, CH_2), 1.61 [m, 1H, $CH(CH_3)_2$], 2.43 (m, 1H, $CHHC{=}CH_2$), 4.30 (d, J = 5.4 Hz, 1H, CHO), 5.20 (m, 2H, $HC{=}CH_2$), 5.63 (ddd, J = 17.1 Hz/ 10.7 Hz/ 9.1 Hz, 1H, $HC{=}CH_2$) ppm. - ^{13}C NMR: δ = –5.38, –5.16 [$Si(CH_3)_2$], 18.11 [$SiC(CH_3)_3$], 21.32, 23.65 [$CH(CH_3)_2$], 25.09 [$CH(CH_3)_2$], 25.53 [$SiC(CH_3)_3$], 38.51 (*i*-Bu-CH_2), 47.60 (3-CH), 66.10 (2-CH), 118.94 (5-CH_2), 119.11 (1-C), 136.27 (4-CH) ppm. - GC-MS: *m/z* = 211 (11), 210 (61, $M^+–C_4H_9$), 183 (34, 210–CHN), 182 (14), 171 (23), 156 (12), 155 (17), 154 (19), 141 (12), 127 (21), 115 [11, $C_4H_9Si(CH_3)_2^+$], 114 (12), 109 (42), 102 (14), 99 (13), 97 [39, $H_2C{=}CHCH(i\text{-}Bu)^+$], 85 (8), 84 (10), 75 [100, $(CH_3)_2SiOH^+$], 73 (49), 69 (11), 67 (14), 59 (17), 55 (31), 43 (13), 41 (20). - $C_{15}H_{29}NOSi$ (267.5): calcd. C 67.35, H 10.93, N 5.24; found C 67.29, H 10.50, N 5.59.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-methyl-pent-4-enal [(*R,S*)-**9a**]: 85% Yield from cyanohydrin **8a** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:40). - R_f = 0.26 (diethyl ether/ light petroleum, 1:40). - $[\alpha]_D^{RT}$: +15.1 (*c* = 1.1, $CHCl_3$). - *ee* = 96 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (9 eq.). - IR (film): ν = 2950 (s), 2920 (s), 2880 (s), 2855 (s), 2800 (m), 1735 (s, C=O), 1640 (w, C=C), 1465 (m), 1420 (m), 1365 (m), 1255 (s), 1130 (m), 1100 (s, br, SiOC), 1030 (m), 910 (m, $HC{=}CH_2$), 835 (s, CSi-O), 775 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.06 (s, 6H, $Si(CH_3)_2$), 0.93 [s, 9H, $C(CH_3)_3$], 1.04 (d, J = 6.7 Hz, 3H, $CHCH_3$), 2.60 (m, 1H, $CHCH_3$), 3.85 (dd, J = 4.7 Hz/ 2.0 Hz, 1H, CHOSi), 5.07 (m, 2H, $HC{=}CH_2$), 5.82 (ddd, J = 17.5 Hz/ 9.8 Hz/ 7.5 Hz, 1H, $HC{=}CH_2$), 9.58 (d, J = 2.0 Hz, 1H, HC=O) ppm. - ^{13}C NMR : δ = –4.99, –4.57 [$Si(CH_3)_2$], 14.11 ($CHCH_3$), 18.25 [$SiC(CH_3)_3$], 25.76 [$SiC(CH_3)_3$], 41.04 (3-CH), 80.85 (2-CH), 115.55 (5-CH_2), 139.35 (4-CH), 203.84 (1-CH) ppm. - GC-MS: *m/z* = 199 (25, M^+–CHO), 171 (65, $M^+–C_4H_9$), 141 (38), 127 (33), 117 (11), 115 [19, $C_4H_9Si(CH_3)_2^+$], 101 (13), 75 [65, $(CH_3)_2SiOH^+$], 73 (100), 59 (14), 55 (39, $H_2C{=}CHCH(CH_3)^+$). - $C_{12}H_{24}O_2Si$ (228.4): calcd. C 63.10, H 10.59; found C 63.08, H 10.70.

(R)-2-tert-Butyldimethylsilyloxy-3,3-dimethyl-pent-4-enal [(*R*)-**9b**]: 85% Yield from cyanohydrin **8b** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:40). - R_f = 0.26 (diethyl ether/ light petroleum, 1:40). - $[\alpha]_D^{RT}$: +7.5 (*c* = 1.0, $CHCl_3$). - *ee* = 95 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (6 eq.). - IR (film): ν = 2960 (s), 2930 (s), 2885 (m), 2860 (s), 1735 (s, C=O), 1640 (w, C=C), 1470 (m), 1415 (m), 1380 (m), 1360 (m), 1255 (s), 1140 (m), 1100 (s, br, SiOC), 1005 (m), 920 (m, $HC{=}CH_2$), 855 (m), 840 (s, CSi-O), 780 (s, OSi-C), 670 (m) cm^{-1}. - ^1H NMR: δ = 0.02, 0.05 [s, 6H, $Si(CH_3)_2$], 0.93 [s, 9H, $C(CH_3)_3$], 1.06, 1.07 [s, 6H, $C(CH_3)_2$], 3.58 (d, J = 3.1 Hz, 1H, CHOSi), 5.01 (dd, J = 17.6 Hz/ 1.4 Hz, 1H, $HC{=}CH_{cis}H_{cis}$), 5.06 (dd, J = 10.9 Hz/ 1.0 Hz, $HC{=}CH_{trans}H_{trans}$), 5.95 (dd, J = 17.7 Hz/ 10.9 Hz, 1H, $HC{=}CH_2$), 9.51 (d, J = 3.1 Hz, HC=O) ppm. - ^{13}C NMR: δ = –5.09, –4.49 [$Si(CH_3)_2$], 18.22 [$SiC(CH_3)_3$], 22.96, 23.03 [$C(CH_3)_2$], 25.76 [$SiC(CH_3)_3$], 41.33 (3-CH), 83.42 (2-CH), 113.17 (5-CH_2), 143.19 (4-CH), 203.68 (1-CH) ppm. - GC-MS: *m/z* = 213 (19, M^+–CHO), 185 (37, $M^+–C_4H_9$), 155 (12), 127 (16), 117 (24), 75 [32, $(CH_3)_2SiOH^+$], 73 (67), 69 [100, $H_2C{=}CHC(CH_3)_2^+$], 41 (30). - $C_{13}H_{26}O_2Si$ (242.4): calcd. C 64.41, H 10.81; found C 64.20, H 11.09.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-ethyl-pent-4-enal [(*R,S*)-**9c**]: 85% Yield from cyanohydrin **8c** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:50). - R_f = 0.57 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +26.3 (*c* = 1.0, $CHCl_3$). - *ee* = 97 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (8 eq.). - IR (film): ν = 2960 (s), 2940 (s), 2880 (m),

2860 (s), 1740 (s, C=O), 1640 (w, C=C), 1470 (m), 1460 (m), 1380 (m), 1360 (m), 1255 (s), 1130 (s), 1100 (s, br, SiOC), 1005 (m), 920 (m, HC=CH_2), 880 (m), 840 (s, CSi-O), 780 (s, OSi-C), 670 (w) cm^{-1}. - ^1H NMR: δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.85 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 0.93 [s, 9H, $C(CH_3)_3$], 1.36 (m, 1H, *H*CHCH$_3$), 1.55 (m, 1H, HC*H*CH$_3$), 2.32 (m, 1H, C*H*HC=CH_2), 3.88 (dd, *J* = 5.1 Hz/ 2.0 Hz, 1H, CHOSi), 5.09 (m, 2H, HC=CH_2), 5.63 (ddd, *J* = 17.0 Hz/ 10.2 Hz/ 8.8 Hz, 1H, *H*C=CH_2), 9.58 (d, *J* = 2.0 Hz, 1H, HC=O) ppm. - ^{13}C NMR: δ = –5.01, –5.53 [$Si(CH_3)_2$], 11.77 (CH_2CH_3), 18.24 [Si*C*$(CH_3)_3$], 21.99 (CH_2CH_3), 25.76 [SiC(CH_3)$_3$], 49.27 (3-CH), 80.55 (2-CH), 117.35 (5-CH_2), 137.73 (4-CH), 203.86 (1-CH) ppm. - GC-MS: *m/z* = 213 (34, M^+–CHO), 185 (56, M^+–C_4H_9), 155 (25), 129 (12), 127 (33), 117 (17), 115 [12, $C_4H_9Si(CH_3)_2^+$], 93 (18), 75 [58, $(CH_3)_2SiOH^+$], 73 (100), 69 [100, H_2C=CHC(Et)$^+$], 59 (12), 41 (35). - $C_{13}H_{26}O_2Si$ (242.4): calcd. C 64.41, H 10.81; found C 64.12, H 11.15.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-propyl-pent-4-enal [(*R,S*)-**9d**]: 92% Yield from cyanohydrin **8d** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:50). - R_f = 0.58 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +28.9 (*c* = 1.0, $CHCl_3$). - *ee* = 94 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (8 eq.). - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 2800 (m), 1740 (s, C=O), 1640 (w, C=C), 1470 (m), 1465 (m), 1370 (m), 1360 (m), 1255 (s), 1130 (s), 1100 (s, br, SiOC), 1000 (m), 920 (m, HC=CH_2), 840 (s, CSi-O), 780 (s, OSi-C) cm^{-1}. - ^1H NMR: δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.87 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 0.93 [s, 9H, $C(CH_3)_3$], 1.05-1.55 (m, 4H, $CH_2CH_2CH_3$), 2.43 (m, 1H, C*H*HC=CH_2), 3.87 (dd, *J* = 5.1 Hz/ 2.0 Hz, 1H, CHOSi), 5.08 (m, 2H, HC=CH_2), 5.65 (ddd, *J* = 16.9 Hz/ 10.5 Hz/ 9.2 Hz, 1H, *H*C=CH_2) ppm. - ^{13}C NMR: δ = –5.01, –4.54 [$Si(CH_3)_2$], 13.67 (CH_2CH_3), 18.24 [Si*C*$(CH_3)_3$], 20.29 (CH_2CH_3), 25.76 [SiC(CH_3)$_3$], 31.12 (CH_2CH_2CH), 47.28 (3-CH), 80.72 (2-CH), 117.03 (5-CH_2), 138.08 (4-CH), 203.87 (1-CH) ppm. - GC-MS: *m/z* = 227 (7, M^+–CHO), 199 (13, M^+–C_4H_9), 127 (18), 117 (12), 107 (13), 101 (7), 83 [11, H_2C=CHCH(*n*-Pr)$^+$], 75 [52, $(CH_3)_2SiOH^+$], 73 (100), 59 (14), 55 (51), 41 (26). - $C_{14}H_{28}O_2Si$ (256.5): C 65.57, H 11.00; found C 65.88, H 11.00.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-isopropyl-pent-4-enal [(*R,S*)-**9e**]: 86% Yield from cyanohydrin **8e** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:50). - R_f = 0.53 (diethyl ether/ light petroleum, 1:10). - $[\alpha]_D^{RT}$: +26.1 (*c* = 1.1, $CHCl_3$). - *ee* = 95 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (8 eq.). - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 2800 (m), 1740 (s, C=O), 1640 (w, C=C), 1475 (m), 1465 (m), 1390 (m), 1370 (m), 1255 (s), 1145 (s), 1100 (s, br, SiOC), 1005 (m), 920 (m, HC=CH_2), 885 (m), 840 (s, CSi-O), 780 (s, OSi-C) cm^{-1}. - ^1H NMR: δ = 0.06, 0.07 [s, 6H, $Si(CH_3)_2$], 0.85, 0.89 [d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$], 0.93 [s, 9H, $C(CH_3)_3$], 2.01 [m, 1H, C*H*$(CH_3)_2$], 2.33 (m, 1H, C*H*HC=CH_2), 3.94 (dd, *J* = 7.1 Hz/ 2.7 Hz, 1H, CHOSi), 5.05 (ddd, *J* = 17.0 Hz/ 2.0 Hz/ 0.7 Hz, 1H, HC=CHH_{cis}), 5.14 (dd, *J* = 10.2 Hz/ 2.0 Hz, 1H, HC=CHH_{trans}), 5.62 (dt, *J* = 17.0 Hz/ 10.2 Hz, 1H, *H*C=CH_2), 9.54 (d, *J* = 2.7 Hz, 1H, HC=O) ppm. - ^{13}C NMR: δ = –5.04, –4.42 [$Si(CH_3)_2$], 18.03, 21.71 [$CH(CH_3)_2$], 18.17 [Si*C*$(CH_3)_3$], 25.74 [SiC(CH_3)$_3$], 26.44 [*C*H$(CH_3)_2$], 53.72 (3-CH), 79.08 (2-CH), 118.67 (5-CH_2), 135.00 (4-CH), 203.42 (1-CH) ppm. - GC-MS: *m/z* = 227 (28, M^+–CHO), 200 (8), 199 (51, M^+–C_4H_9), 169 (10), 157 (21), 143 (14), 127 (23), 117 (36), 115 [19, $C_4H_9Si(CH_3)_2^+$], 107 (26), 89 (41), 83 [22, H_2C=CHCH(*i*-Pr)$^+$], 75 [70, $(CH_3)_2SiOH^+$], 74 (9), 73 (100), 69 (12), 59 (13), 55 (48), 43 (10), 41 (19). - $C_{14}H_{28}O_2Si$ (256.5): calcd. C 65.57, H 11.00; C 65.45, H =1.40.

(2R,3S)-3-Butyl-2-tert-butyldimethylsilyloxy-pent-4-enal [(*R,S*)-**9f**]: 86% Yield from cyanohydrin **8f** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:60). - R_f = 0.33 (diethyl ether/ light petroleum, 1:60). - $[\alpha]_D^{RT}$: +26.1 (*c* = 1.0, $CHCl_3$). - *ee* = 95 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (7 eq.). - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 2800 (m), 1740 (s, C=O), 1640 (w, C=C), 1470 (m), 1465 (m), 1380 (m), 1360 (m), 1255 (s), 1130 (s), 1100 (s, br, SiOC), 1000 (m), 920 (m, $HC=CH_2$), 840 (s, CSi-O), 780 (s, OSi-C) cm^{-1}. - ^1H NMR: δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.87 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 0.93 [s, 9H, $C(CH_3)_3$], 1.00-1.60 (m, 6H, $CH_2CH_2CH_2$), 2.41 (m, 1H, $CHHC=CH_2$), 3.86 (dd, *J* = 5.5 Hz/ 2.2 Hz, 1H, CHOSi), 5.08 (m, 2H, $HC=CH_2$), 5.65 (ddd, *J* = 17.0 Hz/ 10.4 Hz/ 9.1 Hz, 1H, $HC=CH_2$), 9.58 (d, *J* = 1.9 Hz, 1H, HC=O) ppm. - ^{13}C NMR: δ = –5.01, –4.54 [$Si(CH_3)_2$], 13.96 (CH_2CH_3), 18.23 [$SiC(CH_3)_3$], 22.59, 28.65, 29.34 (*n*-Bu-CH_2), 25.76 [$SiC(CH_3)_3$], 47.51 (3-CH), 80.73 (2-CH), 117.11 (5-CH_2), 138.14 (4-CH), 203.06 (1-CH) ppm. GC-MS: *m/z* = 241 (28, M^+–CHO), 213 (34, M^+–C_4H_9), 183 (14), 157 (10), 141 (11), 129 (24), 127 (25), 111 (29), 109 (23), 99 (20), 97 [42, $H_2C=CHCH(n\text{-Bu})^+$], 85 (31), 83 (40), 75 [54, $(CH_3)_2SiOH^+$], 73 (90), 71 (51), 57 (77), 55 (100), 43 (60). - $C_{15}H_{30}O_2Si$ (270.5): calcd. C 66.61, H 11.18; C 66.61, H 11.18.

(2R,3S)-2-tert-Butyldimethylsilyloxy-3-isobutyl-pent-4-enal [(*R,S*)-**9g**]: 87% Yield from cyanohydrin **8g** after column chromatography (Florisil®, diethyl ether/ light petroleum, 1:60). - R_f = 0.27 (diethyl ether/ light petroleum, 1:60). - $[\alpha]_D^{RT}$: +41.4 (*c* = 1.0, $CHCl_3$). - *ee* = 95 %, Determined by ^1H NMR spectroscopy with (–)-(*R*)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (7 eq.). - IR (film): ν = 2960 (s), 2930 (s), 2860 (s), 2800 (m), 1740 (s, C=O), 1640 (w, C=C), 1470 (m), 1465 (m), 1380 (m), 1360 (m), 1255 (s), 1130 (s), 1100 (s, br, SiOC), 1000 (m), 920 (m, $HC=CH_2$), 840 (s, CSi-O), 780 (s, OSi-C) cm^{-1}. - ^1H NMR: δ = 0.06 [s, 6H, $Si(CH_3)_2$], 0.82, 0.88 [d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$], 0.93 [s, 9H, $C(CH_3)_3$], 1.22 [m, 1H, $HCHCH(CH_3)_2$], 1.35 [m, 1H, $HCHCH(CH_3)_2$], 1.53 [m, 1H, $CH(CH_3)_2$], 2.53 (m, 1H, $CHHC=CH_2$), 3.85 (dd, *J* = 5.2 Hz/ 2.2 Hz, 1H, CHOSi), 5.08 (m, 2H, $HC=CH_2$), 5.66 (ddd, *J* = 16.5 Hz/ 11.0 Hz/ 9.1 Hz, 1H, $HC=CH_2$), 9.58 (d, *J* = 2.2 Hz, 1H, HC=O) ppm. - ^{13}C NMR: δ = –5.00, –4.55 [$Si(CH_3)_2$], 18.24 [$SiC(CH_3)_3$], 21.28, 23.41 [$CH(CH_3)_2$], 25.10 [$CH(CH_3)_2$], 25.76 [$SiC(CH_3)_3$], 38.11 ($CHCH_2CH$), 45.54 (3-CH), 81.00 (2-CH), 116.96 (5-CH_2), 138.24 (4-CH), 203.90 (1-CH) ppm. - GC/MS: *m/z* = 241 (30, M^+-CHO), 213 (39, M^+-C_4H_9), 157 (19), 127 (25), 121 (20), 117 (20), 115 [10, $C_4H_9Si(CH_3)_2^+$], 109 (17), 105 (11), 101 (16), 95 (10), 93 (17), 89 (10), 75 [58, $(CH_3)_2SiOH^+$], 73 (100), 69 (11), 67 (11), 59 (14), 55 (61), 43 (20), 41 (24). - $C_{15}H_{30}O_2Si$ (270.5): calcd. C 66.61, H 11.18; found C 66.77, H 11.15.

(S)-2-tert-Butyldiphenylsilyloxy-pent-4-enal [(*S*)-**9h**]: 89% Yield form cyanohydrin **3e** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:4). - R_f = 0.33 (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{25}$: –4.2 (*c* = 0.7, $CHCl_3$). - *ee* = 93 %, Determined after acetalisation with (*R,R*)-2,3-bis-(trimethylsilyloxy)-butane[21] - IR (film): ν = 3073, 3051, 3014 (m, $CH_{arom.}$), 2959 (s), 2932 (s), 2895 (s), 2859 (s), 1738 (s, C=O), 1642 (w, C=C), 1473 (s), 1464 (m), 1429 (s), 1392 (m), 1374 (m), 1363 (m), 1190 (m), 1113 (s, br, SiOC), 1030 (m), 1007 (m), 999 (s), 919 (s, $HC=CH_2$), 823 (s, CSi-O), 741 (s, OSi-C), 703 (s), 622 (m), 612 (s), 507 (s), 488 (s) cm^{-1}. - ^1H NMR: δ = 1.12 [s, 9H, $C(CH_3)_3$], 2.38 (ddd, *J* = 7.1 Hz/ 6.1 Hz/ 1.4 Hz, 1H, $CHCHHCH$), 2.40 (ddd, *J* = 7.1 Hz/ 6.1 Hz/ 1.3 Hz, 1H, $CHCHHCH$), 4.08 (dt, *J* = 1.7 Hz/ 5.9 Hz, 1H, CHOSi), 5.05 (m, 1H, $HC=CH_{trans}$), 5.04 (m, 1H, $HC=CH_{cis}$), 5.77 (m, 1H, $HC=CH_2$), 7.32-7.48 (m, 6H, CH_{meta}, CH_{para}), 7.65 (m, 4H, CH_{ortho}), 9.57 (d, *J* = 1.7 Hz, 1H, CH=O) ppm. - ^{13}C NMR: δ =

19.36 [SiC(CH$_3$)$_3$], 26.92 [SiC(CH$_3$)$_3$], 37.55 (3-CH), 77.58 (2-CH), 118.58 (5-CH$_2$), 127.78, 127.83 (CH$_{meta}$), 130.05, 130.07 (CH$_{para}$), 132.33 (4-CH), 132.94, 133.05 (C$_{ipso}$), 135.81, 135.83 (CH$_{ortho}$), 203.36 (1-C) ppm. - MS: *m/z* = 309 (5, M$^+$–CHO), 282 (23), 281 (100, M$^+$–C$_4$H$_9$), 251 (15), 239 (11, C$_4$H$_9$Ph$_2$Si$^+$), 203 (43), 199 (18, Ph$_2$SiO$^+$), 197 (12), 185 (16), 173 (15), 163 (12), 161 (41), 141 (15), 139 (14), 135 (39), 105 (17). - HRMS [C$_{17}$H$_{17}$O$_2$Si (M–C$_4$H$_9$)]: calcd. 283.0998; found 283.0995.

(R)-2-Benzyloxy-pent-4-enal [(*R*)-**9i**]: 84% Yield from cyanohydrin **3f** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:4). - R_f = 0.33 (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{23}$: +52.3 (*c* = 0.9, CHCl$_3$). - *ee* = 72 %, Determined after acetalisation with (*R,R*)-2,3-bis-(trimethylsilyloxy)-butane[21] - IR (film): ν = 3067, 3032 (m, CH$_{arom.}$), 2981 (m), 2915 (m), 2867 (ms), 1736 (s, C=O), 1643 (m), 1497 (m), 1455 (s), 1433 (m), 1416 (m), 1372 (m), 1340 (m), 1308 (m), 1262 (m), 1209, (m), 1101 (s, br, O–C), 1029 (s), 996 (s), 920 (s), 740 (s), 699 (s) cm^{-1}. - ^{1}H NMR: δ = 2.49 (m, 2H, CHC*H*$_2$CH), 3.82 (ddd, *J* = 7.7 Hz/ 5.7 Hz/ 2.0 Hz, 1H, C*H*OCH$_2$), 4.60 (d, *J* = 11.8 Hz, PhC*H*H), 4.68 (d, *J* = 11.8 Hz, PhCH*H*), 5.00-5.20 (m, 2H, HC=C*H*$_2$), 5.82 (ddt, *J* = 17.1 Hz/ 10.1 Hz /7.1 Hz, 1H, *H*C=CH$_2$), 7.28-7.38 (m, 5H, CH$_{arom.}$), 9.66 (d, *J* = 2.0 Hz, CH$_2$CHC*H*O) ppm. - ^{13}C NMR: δ = 34.69 (3-CH), 72.55 (Ph*C*H$_2$), 82.83 (2-CH), 72.67 (Ph*C*H$_2$), 118.51 (5-CH$_2$), 128.01, 128.57, 128.14, 132.40 (CH$_{arom.}$, 4-CH), 130.71 (4-CH), 135.83 (C$_{ipso}$), 203 (1-C) ppm. - MS: *m/z* = 161 (13, M$^+$–CHO), 91 (100, C$_7$H$_7^+$), 65 (12). - HRMS [C$_{11}$H$_{13}$O$_2$ (M$^+$–CHO)]: calcd. 161.0966; found 161.0966.

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