# Diastereo- and Enantioselective Synthesis of Vicinal Amino Alcohols by Oxa Michael Addition of *N*-Formylnorephedrine to Nitro Alkenes

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Received April 27, 1998

**Keywords:** Amino alcohols / Asymmetric synthesis / Oxa Michael addition / Nitro alkenes / C–O bond cleavage

The first intermolecular asymmetric oxa Michael additions with removable chirality information within the hydroxide source are reported. As enantiopure oxygen nucleophile functioning as chiral hydroxide equivalent *N*-formylnorephedrine (**7**) was used and conjugate additions to aliphatic (*E*)-nitro alkenes **2a–j** were carried out in good yields (35–87%) and excellent diastereomeric excesses (*de* = 94–≥98%). After reduction of the nitro group and protection of the amino function (**11a–h**, 73–87%, both steps), the cleavage of the auxiliary occurred without epimerisation (69–99%) using $Na/NH_3$. The Boc-protected 2-amino alcohols **12a–h** could be obtained in good overall yields (30–58 %, four steps) and excellent diastereomeric and enantiomeric excesses (*de*, *ee* = 94–≥98%). Transition states explaining the overall stereochemical outcome are presented based on the absolute configuration determined by X-ray structure analysis on **8b**.

## Introduction

The oxa-analogous Michael addition was reported for the first time in 1878 by Loydl in his work on the synthesis of artificial malic acid, starting from fumaric acid and sodium hydroxide. Interestingly, the reaction mixture was heated up to 100°C for 100 h in a soldered tin can[1]. In 1881 Purdie reported the addition of sodium alkoxides to fumaric acid at 270°C[2]. After acidic ether cleavage he obtained malic acid, too. The discovery of the actual Michael addition by Komnenos[3a], Claisen and Crismer[3b][3c] five years later in 1883 and by Michael[4a][4b][4c][4d][4e] in 1887 led to one of the most important methods for C–C bond formation.

After early work on the oxa Michael addition[5a][5b][5c], diastereo- and enantioselective, inter- and intramolecular additions of alkoxides to enantiopure Michael acceptors have been developed[6]. The intramolecular reaction has often been used as key step in natural product synthesis, for example as by Nicolaou et al. in the synthesis of *Brevetoxin B* in 1989[7]. The addition of oxygen nucleophiles to nitro alkenes was described for example by Barrett et al.[8], Kamimura et al.[9a][9b], and Brade et al.[10].

To the best of our knowledge, the removable chirality information in diastereo- and enantioselective oxa Michael additions was placed so far in the Michael acceptors[11a][11b] or was present in form of a chiral catalyst, e.g. enzymes like fumarases[12a][12b][12c]. We have already reported our new method for the stereoselective addition of an enantiopure hydroxide equivalent, using the sodium alkoxide of *N*-formylnorephedrine (**7**) as nucleophile in a short communication[13]. The addition to (*E*)-nitro alkenes **2a–m** has opened a new enantioselective pathway to vicinal amino alcohols **11a–h**, which cannot be obtained by reduction of amino acids[14a][14b]. 2-Amino alcohols are characteristic structural features of many natural products and drugs, and play an important role as building blocks, auxiliaries, and ligands in catalysis[15a][15b][15c][15d][15e][15f][15g].

We now want to report the experimental details and further investigations on the addition of chiral sodium alkoxides to nitro alkenes as well as the influence on the diastereomeric excesses. The addition of different *N*-acylephedrine derivatives **5a–c**, **7** to nitro alkene **2d** allowed us to present a possible transition state of the oxa Michael addition in order to explain the high diastereomeric excesses obtained with *N*-formylnorepehdrine (**7**) as oxygen nucleophile.

## Results and Discussion

Our first interest in the additon reaction of chiral alkoxides **1a–g** to nitro alkenes was the investigation into the steric demands of the nucleophile with regard to diastereomeric excesses and yields. The addition of enantiomerically not pure sodium alkoxides to 3,3-dimethyl-1-nitrobutene (**2e**) as a sterically hindred acceptor was used in small-scale test reactions. It was possible in these cases to determine diastereomeric excesses using $^1$H-NMR spectroscopy.

Scheme 1. Oxa Michael addition of chiral sodium alkoxides to nitro alkene **2e**

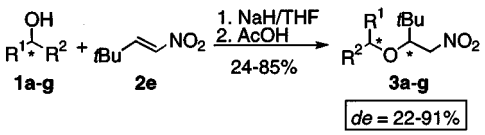


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Table 1. Reaction conditions, yields and diastereomeric excesses of the oxa Michael addition of chiral sodium alkoxides to nitro alkene **2e**

| Alcohol | $R^1$ | $R^2$ | $T$ [°C] | Yield [%] | *de* of **3a**−**g** [%] |
|---|---|---|---|---|---|
| **1a** | Me | Et | −78 | 85 | 35 |
| **1b** | Me | *i*Pr | −78 | 70 | 61 |
| **1c** | Me | *t*Bu | −25 | 30 | 22 |
| **1d** | Me | $Ph[CH_2]_2$ | −78 | 80 | 31 |
| **1e** | Me | Ph | −78 | 54 | 91 |
| **1e** | Me | Ph | −90 | − | − |
| **1f** | Me | naphthyl | −78 | 24 | 87 |
| **1g** | Et | Ph | −78 | 85 | 54 |

Table 1 points out the effects of steric hindrance with respect to the resulting diastereomeric excesses and chemical yields. The best *de* values were obtained at −78°C, with lower temperatures decreasing the reaction rate resulting in lower yields, and higher temperatures resulting in lower diastereomeric excesses. Increasing diastereomeric excesses were observed following the concept of one small, one medium, and one large residue at the C atom attached to the oxygen atom. The best result in this case was a *de* = 91% achieved using 1-phenyleth-1-oxide (**1e**) as a nucleophile. The greater the size of the large residue, the lower the reaction rate, so much so, that no reaction took place at −78°C in the case of 3,3-dimethylbut-2-oxide (**1c**) as a nucleophile, requiring a temparature of −25°C for satisfactory reaction rate.

1-Phenylethan-1-ol (**1e**), as the best nucleophile, was now tested using different nitro alkenes (**2b**,**d**,**e**,**k**). The results of the oxa Michael addition of the sodium alkoxide are shown in Table 2.

Scheme 2. Oxa Michael addition of sodium 1-phenylethoxide to different nitro alkenes

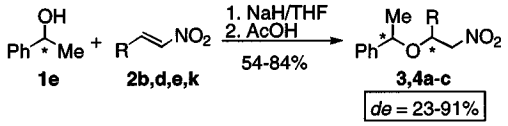



Table 2. Yields and diastereomeric excesses of the oxa Michael addition of sodium 1-phenylethoxide to different nitro alkenes

| Nitro alkene | R | $T$ [°C] | Yield [%] | *de* of **3e**, **4a**−**c** [%] |
|---|---|---|---|---|
| **2b** | Et | −78 | 58 | 35 |
| **2d** | *i*Pr | −78 | 84 | 50 |
| **2e** | *t*Bu | −78 | 54 | 91 |
| **2k** | Ph | −78 | 61 | 23 |

The results in Table 2 demonstrate that the diastereomeric execess depends on the steric bulk of the Michael acceptor. This concept of simple steric effects is not sufficient for a general diastereoselective oxa Michael addition to different nitro alkenes.

### Oxa Michael Addition of Ephedrine Derivatives 5a−c and 7

The concept of steric effects based on a pre-orientation of nucleophile and acceptor and attractive interaction seemed to be a more promising approach. Amino alcohols with an amide protecting group were used to avoid aza Michael addition as side reaction. *N*-Acyl derivatives show a partial double bond character in $^1$H-NMR spectra, which is well known from formamides (e.g. DMF). This partial double bond leads to hindred rotation about the C−N bond and a further polarisation of this bond[16]. The result of this formal separation of charges is a dipolar character which may allow a pre-orientation with the nitro group of the Michael acceptor. The steric demand of ephedrine derivatives **5a**−**c**, **7** is similar to 1-phenylethan-1-ol (**1e**). The results of the oxa Michael addition are shown in Table 3.

Scheme 3. Oxa Michael addition of ephedrine derivatives to nitro alkene **2d**

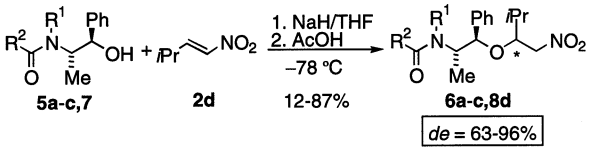



Table 3. Yields and diastereomeric excesses of the oxa Michael addition of ephedrine derivatives to nitro alkene **2d** at −78°C

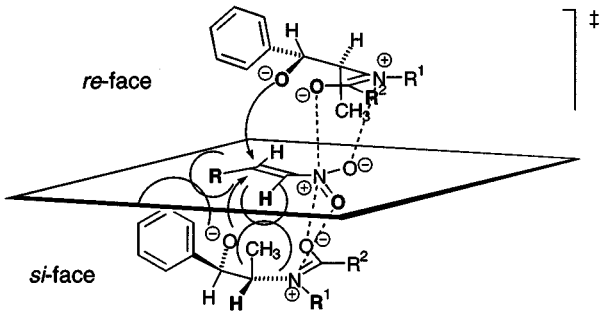
| Ephedrine derivative | $R^1$ | $R^2$ | Yield[a] [%] | *de* of **8d**, **6a**−**c** [%][a][b] |
|---|---|---|---|---|
| **7** | H | H | 87 (84) | 96 (≥ 98) |
| **5a** | H | Me | 14 (11) | 76 (≥ 96) |
| **5b** | H | $CF_3$ | 12 (12) | 75 (75) |
| **5c** | Me | H | 44 (29) | 63 (≥ 96) |

[a] Values in parentheses obtained after separation of the diastereomers by column chromatography. − [b] The *de* values are obtained by $^1$H-NMR spectroscopy (**8d**: 500 MHz; **6a**−**c**: 300 MHz).

The highest diastereomeric excess and yield could be obtained by using *N*-formylnorephedrine (**7**) as nucleophile. For the other ephedrine derivatives **5a**−**b**, the diasteromeric excesses were between 69% and 76% but with lower yields. The choice of the amide protecting group seemed to be as important as the substitution at the nitrogen atom (hydrogen atom in **7**, **5a**−**b** or methyl group in **5c**). This led to the idea, that these interactions involving these groups may be important in the transition state. In a further oxa Michael addition *N*-formylpseudonorephedrine was used to investigate the influence of relative stereochemistry of the alkoxides (*de* = 77%, 80% yield). These results led us to suggest a possible transition state in the oxa Michael addition of ephedrine derivatives **5a**−**c**, **7** to the nitro alkene **2d** (cf. Figure 1).

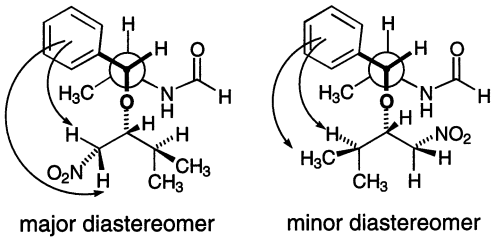
By assuming that the pre-orientation between nitro functionality and amide group exists, Figure 1 shows that the attack at the *si* face of the nitro alkene is much more disfavored due to repulsive interactions between the methyl group and the hydrogen atom and especially between the phenyl group and the substituent R of the nitro alkene. The relative conformation of the ephedrine derivatives given in Figure 1 is a favoured conformation which was determined by the NMR spectra of the addition products **8a**−**j**. This also allowed the determination of the relative and therefore

Figure 1. Presumed transition state for the oxa Michael addition of ephedrine derivatives **5a**−**c**, **7** to nitro alkenes **2**




the absolute configuration of the products, using NOE measurements, ring-current effects and the chemical shifts, as described in the literature for the determination of configuration of alcohols and amines[17a][17b][17c][17d][17e][17f]. In our case, the ring-current effect of the phenyl group of the *N*-formylnorephedrine causes a high-field shift of the signals of the protons in α position to the nitro group for the major diastereomer in comparison to the minor diastereomer and a shift to low field for the isopropyl group. Based on the favoured conformation of the norephedrine derivative obtained from NOE experiments we were able to assign the relative and therefore absolute configuration as indicated in Figure 2.

Figure 2. Ring-current effects for the major and the minor diastereomer of **8d**



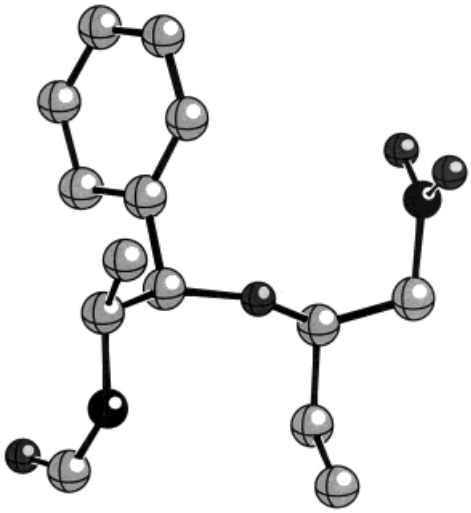

The relative and absolute configuration of the new stereogenic center was determined as *R* for (**8a**−**f**, **i**, **k**−**m**) and *S* for (**8g**−**h**, **j**) in the addition of (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**]. These results were confirmed by the X-ray structure determination of (*S*,*R*,*R*)-**8b**[13] (cf. Figure 3).

The suggested transition state may explain that small variations in the protecting groups on the nitrogen atom and the relative configuration of the nucleophile have a large influence on the diastereomeric excesses and yields (cf. Figure 1).

The use of *N*-formylnorephedrine (**7**) as an widely applicable oxygen nucleophile was demonstrated by the oxa Michael addition to various nitro alkenes (Table 4).

Aromatic residues (**8k**−**m**) resulted in only low yields and lower diastereomeric excesses, compared to aliphatic substituents (**8a**−**j**). Elimination to the starting material and changing electronic effects of the nitro alkene may be responsible for these observations. Compound **8d** shows, that

Figure 3. X-ray structure of **8b**



Scheme 4. Oxa Michael addition of (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] to nitro alkenes **2a**−**m**

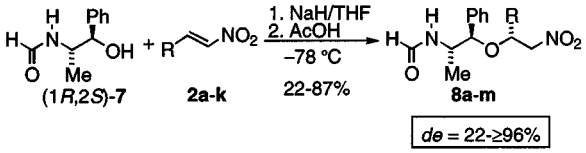



Table 4. Yields, diastereomeric excesses, and rotational values of the oxa Michael addition products of (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] to nitro alkenes **2a**−**m**

| | R | Yield of **8a**−**m** [a] [%] | *de* of **8a**−**m** [a][b] [%] | $[\alpha]_D^{24}$ (*c*, $CHCl_3$) |
|---|---|---|---|---|
| **2a** | Me | 60 (56) | 94 (≥96) | −128.8 (1.09) |
| **2b** | Et | 75 (72) | 93 (97) | −136.3 (1.06) |
| **2c** | *n*Pr | 52 (50) | 94 (≥96) | −127.0 (0.82) |
| **2d** | *i*Pr | 87 (84) | 96 (≥98) | −130.5 (1.00) |
| **2d** | *i*Pr | 87 (84) | 96 (≥98) | +129.8 (1.08)[c] |
| **2e** | *t*Bu | 67 (67) | 98 (≥98) | −106.6 (1.46) |
| **2f** | cyclohexyl | 85 (85) | 94 (94) | −155.1 (1.08) |
| **2g** | $(EtO)_2CH$ | 35 (34) | 96 (≥96) | −78.2 (0.95) |
| **2h** | 1-naphthyl-$OCH_2$ | 48 (47) | 96 (≥96) | −145.7 (0.65) |
| **2i** | $PhCH{=}CH(CH_2)_2$ | 48 (43) | 89 (≥96) | −124.4 (0.62) |
| **2j** | $PhCH{=}CHCH_2OCH_2$ | 65 (63) | 96 (≥96) | −77.6 (0.70) |
| **2k** | Ph | 23 | 71 (71) | −104.6 (0.63) |
| **2l** | furyl | 22 | 22 (22) | −37.5 (1.00) |
| **2m** | ferrocenyl | 26 | 94 (94) | −74.9 (0.30) |

[a] Values in parentheses obtained after separation of the diastereomers by column chromatography. − [b] The *de* values are obtained by $^1$H-NMR spectroscopy (**8a**,**c**,**f**−**m**: 300 MHz; **8b**,**d**,**e**: 500 MHz). − [c] Oxa Michael addition product of (1*S*,2*R*)-(+)-*N*-formylnorephedrine [(1*S*,2*R*)-**7**] to nitro alkenes **2d**.

the other enantiomer could be obtained by using the optical antipode of *N*-formylnorephedrine (**7**).

With the oxa Michael addition to α-substituted nitro alkenes **9a**−**c** it was necessary to control the relative stereochemistry by diastereoselective protonation avoiding partial

Scheme 5. Oxa Michael addition of (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] to α-substituted nitro alkenes **9a**−**c**

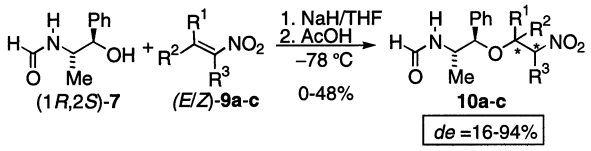



Table 5. Yields and ratios of diastereomers of the oxa Michael addition products of *N*-formylnorephedrine (**7**) to nitro alkenes **9a**−**c**

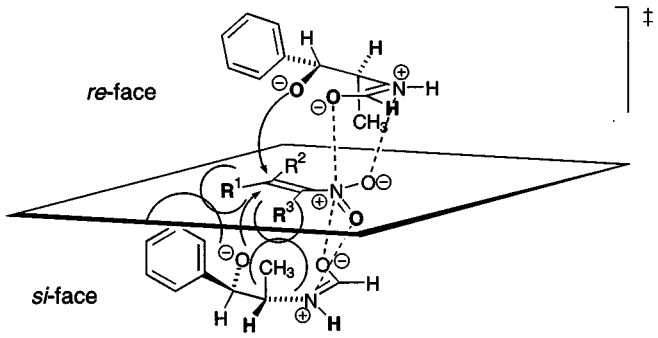
| | $R^1$ | $R^2$ | $R^3$ | Yield [%][a] | Ratio of diastereomers of **10a**−**c** (*de*) [%][b] |
|---|---|---|---|---|---|
| (*E*)-**9a** | H | *i*Pr | Me | 48 | 76:23:0.5:0.5 (52) |
| (*Z*)-**9a** | *i*Pr | H | Me | traces | – |
| (*E*)-**9b** | H | *i*Pr | $TBSOCH_2$ | 38 | 58:40:1:1 (16) |
| (*Z*)-**9b** | *i*Pr | H | $TBSOCH_2$ | traces | – |
| **9c** | H | | $[CH_2]_4$ | 46 | 97:2:0.5:0.5 (94)[c] |

[a] Yield of all diastereomers after column chromatography. – [b] The ratio of diastereomers and *de* values are obtained by $^1$H-NMR spectroscopy (300 MHz) referred to values after reaction. – [c] The major diastereomer could be isolated with *de* ≥ 96 after chromatography.

epimerisation via the nitro and aci forms to an equilibrium mixture of *syn* and *anti* product at room temperature.

For the additon of *N*-formylnorephedrine (**7**) to 1-nitrocyclohexene (**9c**), both stereogenic centers could be controlled. In the case of acyclic nitro alkenes the control of the stereochemistry of the second stereogenic center could not be achieved. The possible transition state (cf. Figure 1) may explain why the (*E*)-nitro alkenes (*E*)-**9a**−**c** were found to react under these conditions, whereas the (*Z*)-nitro alkenes (*Z*)-**9a,b** were unreactive.

Figure 4. Presumed transition state for the oxa Michael addition of (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] to α-substituted (*E*/*Z*)-nitro alkenes **9a**−**c**




If $R^1$ and $R^3$ are aliphatic substituents ($R^2$ = H) in the case of (*E*)-nitro alkenes (*E*)-**9a**−**c**, the reaction takes place favourably from the *re* face with the same stereoselectivity as mentioned above. Using (*Z*)-nitro alkenes (*Z*)-**9a,b** ($R^3$, $R^2$ = substituents, $R^1$ = H) there should be a steric interaction so that *si* face attack as well as *re* face attack is hindered preventing the oxa Michael addition under the reaction conditions (cf. Figure 4).

### Synthesis of Vicinal Amino Alcohols 12a−h by Removal of the Auxiliary

The reduction of the oxa Michael adducts to the corresponding amines, followed by protection (**11a**−**h**) and the cleavage of the benzylic ether bond with sodium in liquid ammonia was carried out in good yields and without loss of stereochemical information.

We were able to synthesize *N*-Boc-protected amino alcohols **12a**−**h** with high enantio- and diastereomeric excesses as it is shown in Table 6. On the other hand we iso-

Scheme 6. Enantioselective synthesis of vicinal amino alcohols **12a**−**h** and *N*-formylamphetamine (**13**)

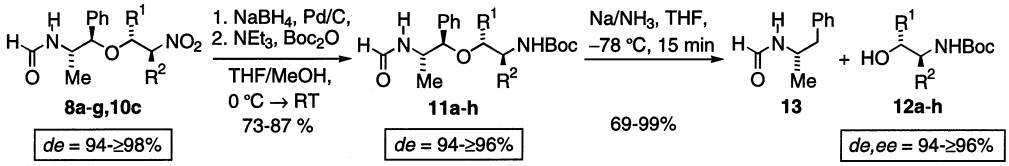
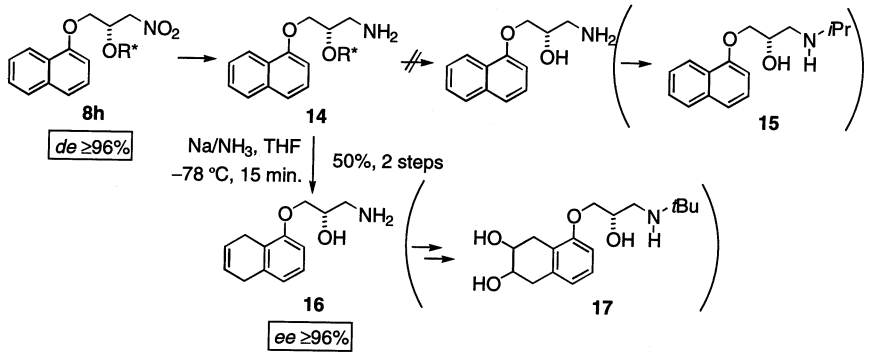



Table 6. Yields, diastereomeric and enantiomeric excesses, and rotational values of the *N*-Boc-protected aminoethers **11a**−**h** and amino alcohols **12a**−**h**

| | $R^1$ | $R^2$ | Yield of **11a**−**h** [%] | *de* of **11a**−**h** [%][a] | $[\alpha]_D^{24}$ (*c*, $CHCl_3$) | Yield of **12a**−**h** [%] | *ee*/*de* of **12a**−**h** [%] | $[\alpha]_D^{24}$ (*c*, $CHCl_3$) |
|---|---|---|---|---|---|---|---|---|
| (*S*,*R*,*R*)-**8a** | Me | H | 80 | ≥ 96 | −78.5 (1.06) | 75 | ≥ 96[c] | −23.2 (0.65) |
| (*S*,*R*,*R*)-**8b** | Et | H | 83 | ≥ 96 | −70.0 (0.97) | 69 | ≥ 96[c] | −16.2 (1.06) |
| (*S*,*R*,*R*)-**8c** | *n*Pr | H | 79 | ≥ 96 | −78.3 (1.11) | 73 | ≥ 96[c] | −13.2 (0.98) |
| (*S*,*R*,*R*)-**8d** | *i*Pr | H | 84 | ≥ 96 | −75.4 (0.50) | 74 | ≥ 96[c] | −19.4 (0.94) |
| (*R*,*S*,*S*)-**8d** | *i*Pr | H | 86 | ≥ 96 | +75.1 (0.94)[b] | 78 | ≥ 96[c] | +19.5 (0.98)[b] |
| (*S*,*R*,*R*)-**8e** | *t*Bu | H | 84 | ≥ 96 | −96.1 (1.34) | 76 | ≥ 96[c] | −28.8 (1.19) |
| (*S*,*R*,*R*)-**8f** | cyclohexyl | H | 83 | 94 | −73.3 (1.40) | 75 | ≥ 94[d] | −19.4 (1.25) |
| (*S*,*R*,*S*)-**8g** | $(EtO)_2CH$ | H | 73 | ≥ 96 | −49.1 (0.54) | 96 | ≥ 96[c] | −13.1 (0.83) |
| (*S*,*R*,*R*,*S*)-**10c** | $[CH_2]_4$ | | 87 | ≥ 96 | −84.7 (1.07) | 99 | ≥ 96[c] | −32.8 (0.99) |

[a] The *de* values are obtained by $^1$H-NMR spectroscopy (300 MHz). – [b] Obtained by the use of (1*S*,2*R*)-(+)-*N*-formylnorephedrine [(1*S*,2*R*)-**7**]. – [c] Determined by $^1$H-NMR spectroscopy (300 MHz) with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol as cosolvent. – [d] Determined after conversion to the corresponding ester with MTPA chloride (Mosher's reagent) by $^1$H-NMR spectroscopy[19a][19b].

Scheme 7. Enantioselective synthesis of a precursor of nadolol (**17**)




lated the *N*-formylamphetamine **13** as by-product. In the case of the oxa Michael adduct **8h**, we wanted to obtain a precursor compound for the β-adrenergic blocker (*S*)-propranolol (**15**). However, the Birch reduction of the aromatic ring was faster than the cleavage of the C−O bond so that we obtained an amino alcohol **16** which could be used as starting material for the synthesis of nadolol (**17**).[18a][18b][18c][18d][18e]

## Conclusion

In summary, our new method using *N*-formylnorephedrine (**7**) as oxygen nucleophile in oxa Michael additions to (*E*)-nitro alkenes **2** has opened a new way for the synthesis of vicinal Boc-protected amino alcohols in good overall yields (30−58%, four steps) and excellent diastereomeric and enantiomeric excesses (*de*, *ee* = 94−≥98%) for both enantiomers. The nitro compounds **8a**−**m**, especially **8i** and **8j** should also be starting materials for further reactions, using simple transformations. For example, the conversion of the aliphatic nitro moiety could pave the way for subsequent inter- or intramolecular 1,3-dipolar cycloaddition reactions opening novel routes to a variety of 2-amino-1,4-diols.

This work was supported by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* (*Leibniz* award, *Sonderforschungbereich 380*). We are grateful to the *BASF AG*, the *Bayer AG*, the *Degussa AG*, the *Hoechst AG* and the *Wacker-Chemie* for the generous donation of chemicals.

## Experimental Section

*General:* All solvents were dried and distilled before use. − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh) (flash). − Optical rotation values: Perkin-Elmer P 241, solvent UVASOL quality. − Melting points (uncorrected): Büchi 510. − IR: Perkin-Elmer FT 1750. − NMR: Varian VXR 300 and Gemini 300 (300 and 75 MHz for $^1H$ and $^{13}C$, respectively), Varian Unity 500 (500 and 125 MHz for $^1H$ and $^{13}C$, respectively), $CDCl_3$ as solvent, TMS as internal standard. − MS: Finnigan MAT (70 eV) and Finnigan SSQ 7000 (70 eV). − Elemental analyses (C,H,N): Elementar vario EL. − High Resolution MS: Finnigan MAT, MAT 95. − The diastereomeric and enantiomeric excesses were determined by $^1H$-NMR spectroscopy. The different two sets of signals in the NMR spectra − assigned as (*Z*) and (*E*) − resulted by the observable rotamers of the formyl group of the auxiliary.

*General Procedure 1 (GP 1): Oxa Michael Additions:* A solution of *N*-formylnorephedrine (**7**) (1.2 equiv.) in THF (12.5 ml/mmol alcohol) was added to a suspension of sodium hydride (1.1 equiv.) in THF (10 ml/mmol NaH) at room temp. This reaction mixture was then cooled to −78°C and a solution of the (*E*)-nitro alkene **2** (1.0 equiv.) in THF (1 ml/mmol nitro alkene) was added dropwise (the reaction was monitored by TLC). The reaction was quenched by the addition of glacial acetic acid. After aqueous work-up and extraction with diethyl ether, the organic layer was dried with $Na_2SO_4$. The crude product **8** was obtained by removing the solvent under vacuum and purified by flash chromatography.

*General Procedure 2 (GP 2): Reduction of the Nitro Function and Protection of Amines:* To a suspension of the nitro ether **8** (1.0 equiv.) and Pd/C (50 mg/mmol) in methanol/THF (1:1) was added $NaBH_4$ (4.0 equiv.) at 0°C. The reaction mixture was kept at this temp. for 2 h, then allowed to warm up to room temp. and stirred for 3 d. The catalyst was removed by filtration through Celite and washed with methanol. $Boc_2O$ (1.0 equiv.) and triethylamine (5 ml/mmol) were added to the solution of the crude amine. The reaction, monitored by TLC, was stopped by removing the solvent, and dissolving the residue in dichlormethane. After drying with $Na_2SO_4$, the crude product **11** was obtained by removing the solvent under vacuum and purified by flash chromatography.

*General Procedure 3 (GP 3): Cleavage of the Auxiliary:* Sodium (2.5 equiv.) was added to liquid ammonia (25 ml/mmol) at −78°C. The *N*-Boc-protected amino ether **11** (1.0 equiv.), dissolved in THF (10 ml/mmol), was slowly added. After 15 min, the reaction was stopped by the addition of solid $NH_4Cl$ at −78°C. After removal of the ammonia, the residue was dissolved in dichlormethane and dried with $Na_2SO_4$. The crude product **12** was obtained by removing the solvent under vacuum and purified by flash chromatography.

*Synthesis of Ephedrine Derivatives* **5a**−**c, 7**[20a][20b][20c][20d]: Compounds **5a**−**c**, **7** were prepared according to literature procedures starting from commercially available ephedrine or norephedrine in good to excellent yields (80−98%).

*Synthesis of (E)-Nitro Alkenes* **2a**−**m, 9a**−**b**: The aliphatic nitro alkenes **2a**−**j** were prepared according to literature procedures by dehydrating the nitro alcohols which were obtained by basically catalyzed nitro aldol reaction of the nitro alkane and the corresponding aldehyde (Henry reaction)[21]. The elimination of water was carried out with *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of CuCl which afforded an *E*/*Z* ratio larger than 98:2 in good overall yields (**2a**−**g**). The nitro alkenes **2h**−**j** were prepared after esterification of the nitro alcohols with $Ac_2O$ and elemination of acetic acid. The *E*/*Z* ratios were 95:5 to 98:2. In the case of the higher substituted aliphatic nitro alkenes **9a**−**b**, the *E*/*Z* ratio was

1.5:1 to 1:1, but the separation of isomers was possible by flash chromatography. 1-Nitrocyclohexene (**9c**) is comercially available[22a][22b][22c][22d]. Aromatic nitro alkenes **2k**−**m** were obtained as described by nitro aldol condensation of the aromatic aldehydes with nitromethane only in (*E*) configuration[23a][23b][23c].

*1-(3-Nitroallyloxy)naphthalene* (**2h**) was obtained as an orange solid by esterification of 3-naphthoxy-1-nitropropan-2-ol (600 mg, 2.43 mmol) in 35 ml of diethyl ether, using $Ac_2O$ (1.94 ml) and pyridine (2.4 ml). Elemination took place during chromatography ($SiO_2$; diethyl ether/pentane, 1:5) and the product was purified by recrystallisation from diethyl ether/pentane. Yield 139 mg (25%), m.p. 70−75°C (decomp.) − IR (KBr): $\tilde{\nu}$ = 3061 $cm^{-1}$ (m), 1630 (m), 1596 (m), 1529 (s), 1335 (s), 929 (s), 788 (s), 772 (s). − $^1$H NMR (300 MHz): δ = 5.02 (d/d, *J* = 2.88/1.51 Hz, 2 H, $CH_2$), 6.82 (d, *J* = 7.42 Hz, 1 H, $CH_{ar.}$), 7.38 (d/d, *J* = 7.97/7.42 Hz, 1 H, $CH_{ar.}$), 7.47 (d/d, *J* = 13.74/1.55 Hz, 1 H, $CH_2CHCH$), 7.48−7.56 (m, 3 H, $CH_{ar.}$), 7.55 (d, *J* = 13.46/2.90 Hz, 1 H, $CH_2CHCH$), 7.83 (m, Σ*J* = 16 Hz, 1 H, $CH_{ar.}$), 8.25 (m, Σ*J* = 17 Hz, 1 H, $CH_{ar.}$). − $^{13}$C NMR (75 MHz): δ = 63.81 ($CH_2$), 105.09, 121.55, 121.72, 125.56 ($CH_{ar.}$), 125.71 (*i*-$C_{ar.}$), 125.80, 126.84, 127.71 ($CH_{ar.}$), 134.63 (*i*-$C_{ar.}$), 136.69 ($CH_2CH$), 140.21 ($CHNO_2$), 153.04 (*i*-$C_{ar.}$). − MS (70 eV); *m*/*z* (%): 229 (25.2) [$M^+$], 144 (13.3), 143 (68.5), 115 (100.0). − $C_{13}H_{11}NO_3$ (229.07): calcd. C 68.11, H 4.84, N 6.11; found C 68.02, H 4.97, N 5.96.

*(E,E)-6-Phenyl-1-nitrohexa-1,5-diene* (*E*,*E*/*Z*,*E* = 98:2) (**2i**) was obtained as a yellow liquid by esterification of 1-nitro-6-phenylhex-5-en-2-ol (570 mg, 2.60 mmol) in 39 ml of diethyl ether, using $Ac_2O$ (2.1 ml) and pyridine (2.6 ml). Elemination took place during chromatography ($SiO_2$; diethyl ether/pentane, 1:10). Yield 441 mg (83%) − IR (film): $\tilde{\nu}$ = 3058 $cm^{-1}$ (m), 2973 (m), 2929 (m), 1648 (m), 1598 (m), 1524 (s), 1353 (s), 966 (s), 746 (m). − $^1$H NMR (300 MHz): δ = 2.43 (m, 4 H, $CH_2CH_2$), 6.15 (d/t, *J* = 15.66/6.73 Hz, 1 H, $C_{ar.}CHCHCH_2$), 6.45 (d, *J* = 15.66 Hz, 1 H, $CHCHCH_2$), 7.01 (d/t, *J* = 14.56/1.01 Hz, 1 H, $CHCHNO_2$), 7.19−7.37 (m, 6 H, $CHCHNO_2$, $CH_{ar.}$). − $^{13}$C NMR (75 MHz): δ = 28.28 ($CHCH_2$), 31.05 ($CH_2CH$), 126.12 (*o*-$CH_{ar.}$), 127.46 (*p*-$CH_{ar.}$), 127.49 (*m*-$CH_{ar.}$), 128.63 ($CHCH_2$), 131.88 ($C_{ar.}CH$), 137.00 (*i*-$C_{ar.}$), 140.00 ($CHCHNO_2$), 141.64 ($CHNO_2$). − MS (70 eV); *m*/*z* (%): 203 (6.0) [$M^+$ + 1], 157 (10.3), 129 (27.8), 91 (100.0). − $C_{12}H_{13}NO_2$ (202.23), calcd. C 71.27, H 6.48, N 6.93; found C 70.85, H 6.54, N 6.65.

*(E,E)-1-Nitro-3-(3-phenylallyloxy)prop-1-ene* (*E*,*E*/*Z*,*E* = 95:5) (**2j**) was obtained as a yellow liquid by esterification of 1-nitro-6-phenylhex-5-en-2-ol (1860 mg, 7.85 mmol) in 115 ml of diethyl ether, using $Ac_2O$ (6.3 ml) and pyridine (7.9 ml). Elemination took place during chromatography ($SiO_2$; diethyl ether/pentane, 1:5). Yield 820 mg (48%) − IR ($Et_2O$): $\tilde{\nu}$ = 3027 $cm^{-1}$ (w), 2854 (m), 1657 (m), 1526 (s), 1357 (s), 1228 (m), 1030 (m), 969 (m), 745 (m). − $^1$H NMR (300 MHz): δ = 4.22 (d/d, *J* = 6.04/1.37 Hz, 2 H, $C_{ar.}CHCHCH_2O$), 4.27 (d/d, *J* = 2.61/1.23 Hz, 2 H, $OCH_2CHCHNO_2$), 6.26 (d/t, *J* = 15.93/6.04 Hz, 1 H, $C_{ar.}CHCHCH_2$), 6.63 (d/t, *J* = 15.94/1.37 Hz, 1 H, $CHCHCH_2$), 7.19−7.42 (m, 7 H, $CHCHNO_2$, $CH_{ar.}$). − $^{13}$C NMR (75 MHz): δ = 65.49 ($OCH_2$), 71.85 ($OCH_2$), 124.66 ($C_{ar.}CHCHCH_2$), 126.57 (*o*-$CH_{ar.}$), 128.07 (*p*-$CH_{ar.}$), 128.67 (*m*-$CH_{ar.}$), 133.53 ($C_{ar.}CH$), 136.22 (*i*-$C_{ar.}$), 138.48 ($CHCHNO_2$), 139.73 ($CHCHNO_2$). − MS (70 eV); *m*/*z* (%): 219 (4.6) [$M^+$], 133 (17.4), 117 (48.6), 115 (34.1), 105 (100.0). − $C_{12}H_{13}NO_3$ (219.24): calcd. C 65.74, H 5.98, N 6.39; found C 65.41, H 6.24, N 6.59.

*(E/Z) 1-tert-Butyldimethylsilyloxy-5-methyl-2-nitropent-2-ene* (**9b**) was obtained as a yellow liquid by dehydratisation of (±)-1-*tert*-butyldimethylsilyloxy-4-methyl-2-nitropentan-3-ol (2.0 g, 7.2 mmol) using DCC (1.8 g, 8.6 mmol) and CuCl (288 mg) in 72 ml of diethyl ether. The separation of the *E*/*Z* isomeres was possbile by chromatography ($SiO_2$, pentane). Yield 1.06g (57%). − IR (film): $\tilde{\nu}$ = 2931 $cm^{-1}$ (s), 2859 (s), 1530 (s), 1471 (s), 1385 (m), 1361 (m), 1258 (s), 1076 (s), 839 (s), 780 (s). − $^1$H NMR (300 MHz): (*E*): δ = 0.11 [s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $SiC(CH_3)_3$], 1.13 (d, *J* = 6.60 Hz, 6 H, $CH(CH_3)_2$], 2.78 (d/sept, *J* = 10.71/6.59 Hz, 1 H, $CH(CH_3)_2$], 4.62 (s, 2 H, $OCH_2$), 6.98 (d, *J* = 10.71 Hz, 1H CHC*H*), (*Z*): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $SiC(CH_3)_3$], 1.09 [d, *J* = 6.59 Hz, 6 H, $CH(CH_3)_2$], 3.13 [d/sept, *J* = 10.17/6.60 Hz, 1 H, $CH(CH_3)_2$], 4.48 (d, *J* = 1.37 Hz, 2 H, $OCH_2$), 5.85 (d/d, *J* = 10.16/1.37 Hz, 1H CC*H*). − $^{13}$C NMR (75 MHz): (*E*): δ = −5.45 [$Si(CH_3)_2$], 18.24 [$C(CH_3)_3$], 22.18 [$CH(CH_3)_2$], 25.75 [$C(CH_3)_3$], 27.80 [$CH(CH_3)_2$], 56.14 ($CH_2$), 145.38 ($CH_2CCH$), 148.98 ($CH_2CCH$); (*Z*): δ = −5.42 [$Si(CH_3)_2$], 18.26 [$C(CH_3)_3$], 22.15 [$CH(CH_3)_2$], 25.75 [$C(CH_3)_3$], 27.42 [$CH(CH_3)_2$], 61.59 ($CH_2$), 140.08 ($CH_2CCH$), 147.58 ($CH_2CCH$). − MS (70 eV); *m*/*z* (%): 202 (15.7, $M^+-C_4H_9$), 75 (100.0). − $C_{12}H_{25}NO_3Si$ (259.42): calcd. C 55.56, H 9.71, N 5.40; found C 55.50, H 10.01, N 5.36.

*Addition of Chiral Alkoxides to (E)-Nitro Alkenes*

*3,3-Dimethyl-2-(1-methylpropoxy)-1-nitrobutane* (**3a**) was obtained according to *GP 1* by adding (±)-butan-2-ol (**1a**) (74 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The yield and the *de* were determined by $^1$H NMR. Yield 85%. − *de* = 35%. − $^1$H NMR (300 MHz): major diastereomer: δ = 0.84 (t, *J* = 6.38 Hz, 3 H, $CH_2CH_3$), 0.95 [s, 9 H, $C(CH_3)_3$], 1.10 (d, *J* = 6.04 Hz, 3 H, $CHCH_3$), 1.28−1.68 (m, 2 H, $CH_2CH_3$), 3.38 (sext, *J* = 6.04 Hz, 1 H, $CHCH_3$), 3.83 (d/d, *J* = 7.05/3.36 Hz, 1 H, $CHCH_2NO_2$), 4.37 (d/d, *J* = 12.43/7.05 Hz, 1 H, $CH_2NO_2$), 4.53 (d/d, *J* = 12.42/3.36 Hz, 1 H, $CH_2NO_2$); minor diastereomer: δ = 0.89 (t, *J* = 6.38 Hz, 3 H, $CH_2CH_3$), 0.96 [s, 9 H, $C(CH_3)_3$], 1.00 (d, *J* = 6.38 Hz, 3 H, $CHCH_3$), 1.28−1.68 (m, 2 H, $CH_2CH_3$), 3.42 (sext, *J* = 6.38 Hz, 1 H, $CHCH_3$), 3.80 (d/d, *J* = 8.05/3.35 Hz, $CHCH_2NO_2$), 4.36 (d/d, *J* = 11.75/8.06 Hz, 1 H, $CH_2NO_2$), 4.52 (d/d, *J* = 11.76/3.35 Hz, 1 H, $CH_2NO_2$). − $^{13}$C NMR (75 MHz): major diastereomer: δ = 9.67 ($CH_2CH_3$), 18.90 ($CHCH_3$), 26.04 [$C(CH_3)_3$], 29.58 ($CH_2CH_3$), 35.33 [$C(CH_3)_3$], 76.21 ($CHCH_3$), 78.39 ($CH_2NO_2$), 81.66 ($CHCH_2NO_2$); minor diastereomer: δ = 9.89 ($CH_2CH_3$), 19.13 ($CHCH_3$), 26.04 [$C(CH_3)_3$], 29.44 ($CH_2CH_3$), 35.83 [$C(CH_3)_3$], 77.56 ($CHCH_3$), 78.73 ($CH_2NO_2$), 82.40 ($CHCH_2NO_2$).

*2-(1,2-Dimethylpropoxy)-3,3-dimethyl-1-nitrobutane* (**3b**) was obtained according to *GP 1* by adding (±)-3-methylbutan-2-ol (**1b**) (88 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The yield and the *de* were determined by $^1$H NMR.Yield 70%. − *de* = 61%. − $^1$H NMR (300 MHz): major diastereomer: δ = 0.90 (d, *J* = 6.71 Hz, 3 H, $CH(CH_3)_2$], 0.92 (d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 0.95 [s, 9 H, $C(CH_3)_3$], 1.14 (d, *J* = 6.05 Hz, 3 H, $CH_2CH_3$), 1.65 [sept/d, *J* = 6.71/6.05 Hz, 1 H, $CH(CH_3)_2$], 3.27 (pent, *J* = 6.05 Hz, 1 H, $CHCH_3$), 3.85 (d/d, *J* = 6.05/3.70 Hz, 1 H, $CHCH_2NO_2$), 4.37 (d/d, *J* = 12.76/6.38 Hz, 1 H, $CH_2NO_2$), 4.54 (d/d, *J* = 12.76/3.70 Hz, 1 H, $CH_2NO_2$); minor diastereomer: δ = 0.85 [d, *J* = 6.71 Hz, 3 H, $CH(CH_3)_2$], 0.89 [d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 0.91 [s, 9 H, $C(CH_3)_3$], 1.05 (d, *J* = 6.05 Hz, 3 H, $CH_2CH_3$), 1.84 [sept/d, *J* = 6.71/6.05 Hz, 1 H, $CH(CH_3)_2$], 3.36 (quint, *J* = 6.05 Hz, 1 H, $CHCH_3$), 3.78 (d/d, *J* = 6.05/3.70 Hz, 1 H, $CHCH_2NO_2$), 4.35 (d/d, *J* = 12.76/6.38 Hz, 1 H, $CH_2NO_2$), 4.51 (d/d, *J* = 12.76/3.70 Hz, 1 H, $CH_2NO_2$). − $^{13}$C NMR (75 MHz): major diastereomer: δ = 15.08 [$CH(CH_3)_2$], 17.66 [$CH(CH_3)_2$], 19.81 ($CHCH_3$), 26.02 [$C(CH_3)_3$], 33.44 [$C(CH_3)_3$],

34.95 [*C*H(CH$_3$)$_2$], 78.12 (*C*H$_2$NO$_2$), 78.72 (*C*HCH$_3$), 80.82 (*C*HCH$_2$NO$_2$); minor diastereomer: δ = 14.95 [CH(*C*H$_3$)$_2$], 17.06 [CH(*C*H$_3$)$_2$], 20.78 (CH*C*H$_3$), 26.19 [C(*C*H$_3$)$_3$], 33.92 [*C*(CH$_3$)$_3$], 35.34 [*C*H(CH$_3$)$_2$], 78.73 (*C*H$_2$NO$_2$), 80.35 (*C*HCH$_3$), 82.19 (*C*HCH$_2$NO$_2$).

*3,3-Dimethyl-1-nitro-2-(1,2,2-trimethylpropoxy)butane* (**3c**) was obtained according to *GP 1* by adding (±)-3,3-dimethylbutan-2-ol (**1c**) (102 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −25°C. The yield and the *de* were determined by $^1$H NMR. Yield 30%. − *de* = 22%. − $^1$H NMR (300 MHz): major diastereomer δ = 0.86 [s, 9 H, C(C*H*$_3$)$_3$], 0.93 [s, 9 H, C(C*H*$_3$)$_3$], 1.04 (d, *J* = 6.04 Hz, 3 H, C*H*$_3$), 3.13 (q, *J* = 6.05 Hz, 1 H, C*H*CH$_3$), 3.87 (d/d, *J* = 5.37/4.03 Hz, 1 H, C*H*CH$_2$), 4.37 (d/d, *J* = 13.43/5.37 Hz, 1 H, C*H*$_2$NO$_2$), 4.50 (d/d, *J* = 13.43/4.03 Hz, 1 H, C*H*$_2$NO$_2$); minor diastereomer δ = 0.89 [s, 9 H, C(C*H*$_3$)$_3$], 0.97 [s, 9 H, C(C*H*$_3$)$_3$], 1.12 (d, *J* = 6.38 Hz, 3 H, C*H*$_3$), 3.30 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 3.84 (d/d, *J* = 7.73/3.36 Hz, 1 H, C*H*CH$_2$), 4.32 (d/d, *J* = 12.76/3.36 Hz, 1 H, C*H*$_2$NO$_2$), 4.50 (d/d, *J* = 12.76/7.72 Hz, 1 H, C*H*$_2$NO$_2$). $^{13}$C NMR (75 MHz): major diastereomer δ = 12.81 (CH*C*H$_3$), 25.90, 25.91 [C(*C*H$_3$)$_3$], 34.83, 35.25 [*C*(CH$_3$)$_3$], 77.59 (*C*H$_2$NO$_2$), 79.28 (*C*HCH$_3$), 79.93 (*C*HCH$_2$); minor diastereomer δ = 12.28 (CH*C*H$_3$), 26.20, 26.92 [C(*C*H$_3$)$_3$], 35.35, 36.52 [*C*(CH$_3$)$_3$], 78.83 (*C*H$_2$NO$_2$), 80.59 (*C*HCH$_3$), 82.44 (*C*HCH$_2$).

*3,3-Dimethyl-2-(1-methyl-3-phenylpropoxy)-1-nitrobutane* (**3d**) was obtained according to *GP 1* by adding (±)-4-phenylbutan-2-ol (**1d**) (150 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The yield and the *de* were determined by $^1$H NMR. Yield 80%. − *de* = 31%. − $^1$H NMR (300 MHz): major diastereomer δ = 0.94 [s, 9 H, C(C*H*$_3$)$_3$], 1.16 (d, *J* = 6.05 Hz, 3 H, CHC*H*$_3$), 1.62−1.95 (m, 2 H, C*H*$_2$CH$_2$C$_{ar.}$), 2.52−2.73 (m, 2 H, CH$_2$C*H*$_2$C$_{ar.}$), 3.52 (sext, *J* = 6.04 Hz, 1 H, C*H*CH$_3$), 3.84 (d/d, *J* = 6.71/3.35 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.34 (d/d, *J* = 12.42/3.35 Hz, 1 H, C*H*$_2$NO$_2$), 4.52 (d/d, *J* = 12.42/6.71 Hz, 1 H, C*H*$_2$NO$_2$), 7.14−7.20 (m, 2 H, C*H*$_{ar.}$), 7.23−7.31 (m, 3 H, C*H*$_{ar.}$); minor diastereomer δ = 0.95 [s, 9 H, C(C*H*$_3$)$_3$], 1.08 (d, *J* = 6.05 Hz, 3 H, CHC*H*$_3$), 1.62−1.95 (m, 2 H, C*H*$_2$CH$_2$C$_{ar.}$), 2.52−2.73 (m, 2 H, CH$_2$C*H*$_2$C$_{ar.}$), 3.54 (sext, *J* = 6.05 Hz, 1 H, C*H*CH$_3$), 3.81 (d/d, *J* = 7.72/3.02 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.36 (d/d, *J* = 12.09/7.72 Hz, 1 H, C*H*$_2$NO$_2$), 4.52 (d/d, *J* = 12.09/3.02 Hz, 1 H, C*H*$_2$NO$_2$), 7.14−7.20 (m, 2 H, C*H*$_{ar.}$), 7.23−7.31 (m, 3 H, C*H*$_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer δ = 19.29 (CH*C*H$_3$), 26.02 [C(*C*H$_3$)$_3$], 31.69 (*C*H$_2$CH$_2$C$_{ar.}$), 35.22 [*C*(CH$_3$)$_3$], 38.61 (CH$_2$*C*H$_2$C$_{ar.}$), 74.35 (*C*HCH$_3$), 78.18 (*C*H$_2$NO$_2$), 81.29 (*C*HCH$_2$NO$_2$), 125.75 (*p*-*C*H$_{ar.}$), 128.31 (*o*-*C*H$_{ar.}$), 128.35 (*m*-*C*H$_{ar.}$), 142.14 (*i*-*C*$_{ar.}$); minor diastereomer δ = 19.51 (CH*C*H$_3$), 26.14 [C(*C*H$_3$)$_3$], 31.80 (*C*H$_2$CH$_2$C$_{ar.}$), 35.84 [*C*(CH$_3$)$_3$], 38.52 (CH$_2$*C*H$_2$C$_{ar.}$), 75.90 (*C*HCH$_3$), 78.69 (*C*H$_2$NO$_2$), 82.47 (*C*HCH$_2$NO$_2$), 125.81 (*p*-*C*H$_{ar.}$), 128.26 (*o*-*C*H$_{ar.}$), 128.38 (*m*-*C*H$_{ar.}$), 142.13 (*i*-*C*$_{ar.}$).

*3,3-Dimethyl-2-(1-naphthylethoxy)-1-nitrobutane* (**3f**) was obtained according to *GP 1* by adding (±)-1-β-naphthylethan-1-ol (**1f**) (172 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The yield and the *de* were determined by $^1$H NMR. Yield 24%. − *de* = 87%. − $^1$H NMR (300 MHz): major diastereomer δ = 1.00 [s, 9 H, C(C*H*$_3$)$_3$], 1.50 (d, *J* = 6.38 Hz, 3 H, CHC*H*$_3$), 3.96 (d/d, *J* = 6.71/4.03 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.23 (d/d, *J* = 13.09/6.72 Hz, 1 H, C*H*$_2$NO$_2$), 4.33 (d/d, *J* = 13.10/4.03 Hz, 1 H, C*H*$_2$NO$_2$), 4.65 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 7.37−7.48 (m, 3 H, C*H*$_{ar.}$), 7.67 (m, 1 H, C*H*$_{ar.}$), 7.74−7.83 (m, 3 H, C*H*$_{ar.}$); minor diastereomer δ = 0.78 [s, 9 H, C(C*H*$_3$)$_3$], 1.44 (d, *J* = 6.38 Hz, 3 H, CHC*H*$_3$), 3.78 (d/d, *J* = 6.71/3.69 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.49 (d/d, *J* = 12.42/6.72 Hz, 1 H, C*H*$_2$NO$_2$), 4.59 (d/d, *J* = 12.42/3.69 Hz, 1 H, C*H*$_2$NO$_2$), 4.61 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 7.37−7.48 (m, 3 H, C*H*$_{ar.}$), 7.67 (m, 1 H, C*H*$_{ar.}$), 7.74−7.83 (m, 3 H, C*H*$_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer δ = 25.07 (CH*C*H$_3$), 26.02 [C(*C*H$_3$)$_3$], 35.71 [*C*(CH$_3$)$_3$], 77.69 (*C*H$_2$NO$_2$), 79.17 (*C*HCH$_3$), 83.00 (*C*HCH$_2$); minor diastereomer δ = 20.68 (CH*C*H$_3$), 23.10 [C(*C*H$_3$)$_3$], 35.23 [*C*(CH$_3$)$_3$], 78.28 (*C*H$_2$NO$_2$), 78.35 (*C*HCH$_3$), 82.71 (*C*HCH$_2$), aromatic Carbons for both diastereomers: δ = 123.80, 123.87, 124.05, 125.07, 125.73, 125.83, 127.65, 127.72, 128.21, 128.31, 132.89, 133.08, 133.19, 133,34 (*o*,*m*,*p*-*C*H$_{ar.}$), 140.89, 143.17 (*i*-*C*$_{ar.}$).

*3,3-Dimethyl-1-nitro-2-(1-phenylpropoxy)butane* (**3g**) was obtained according to *GP 1* by adding (±)-1-phenylpropan-1-ol (**1g**) (136 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The yield and the *de* were determined by $^1$H NMR. Yield 85%. − *de* = 54%. − $^1$H NMR (300 MHz): major diastereomer δ = 0.79 (t, *J* = 7.55 Hz, 3 H, CH$_2$C*H*$_3$), 0.99 [s, 9 H, C(C*H*$_3$)$_3$], 1.54−2.01 (m, 2 H, C*H*$_2$CH$_3$), 3.88 (d/d, *J* = 6.04/4.03 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.16 (d/d, *J* = 13.10/6.05 Hz, 1 H, C*H*$_2$NO$_2$), 4.24 (t, *J* = 6.72 Hz, 1 H, CH$_2$C*H*C$_{ar.}$), 4.27 (d/d, *J* = 13.10/4.03 Hz, 1 H, C*H*$_2$NO$_2$), 7.19−7.34 (m, 5 H, C*H*$_{ar.}$); minor diastereomer δ = 0.80 (t, *J* = 7.39 Hz, 3 H, CH$_2$C*H*$_3$), 0.99 [s, 9 H, C(C*H*$_3$)$_3$], 1.54−2.01 (m, 2 H, C*H*$_2$CH$_3$), 3.68 (d/d, *J* = 6.04/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.19 (t, *J* = 6.71 Hz, 1 H, CH$_2$C*H*C$_{ar.}$), 4.47 (d/d, *J* = 12.76/6.05 Hz, 1 H, C*H*$_2$NO$_2$), 4.27 (d/d, *J* = 12.76/3.36 Hz, 1 H, C*H*$_2$NO$_2$), 7.19−7.34 (m, 5 H, C*H*$_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer δ = 10.09 (CH$_2$*C*H$_3$), 26.07 [C(*C*H$_3$)$_3$], 30.14 (*C*H$_2$CH$_3$), 36.01 [*C*(CH$_3$)$_3$], 77.57 (*C*H$_2$NO$_2$), 83.14 (*C*HCH$_2$NO$_2$), 85.12 (CH$_2$*C*HC$_{ar.}$), 127.03 (*o*-*C*H$_{ar.}$), 127.90 (*p*-*C*H$_{ar.}$), 128.34 (*m*-*C*H$_{ar.}$), 141.84 (*i*-*C*$_{ar.}$); minor diastereomer δ = 10.22 (CH$_2$*C*H$_3$), 25.94 [C(*C*H$_3$)$_3$], 30.27 (*C*H$_2$CH$_3$), 35.16 [*C*(CH$_3$)$_3$], 78.17 (*C*H$_2$NO$_2$), 81.47 (*C*HCH$_2$NO$_2$), 82.82 (CH$_2$*C*HC$_{ar.}$), 127.81 (*o*-*C*H$_{ar.}$), 127.86 (*p*-*C*H$_{ar.}$), 128.14 (*m*-*C*H$_{ar.}$), 140.90 (*i*-*C*$_{ar.}$).

*1-Nitro-2-(1-phenylethoxy)butane* (**4a**) was obtained as colourless oil according to *GP 1* by adding (±)-1-phenylethanol (**1e**) (122 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-1-nitrobut-1-ene (**2b**) (101 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography (SiO$_2$; diethyl ether/pentane, 1:10). Yield 58%. − *de* = 35%. − IR (film): ṽ = 2975 cm$^{-1}$ (s), 2932 (m), 1556 (s), 1494 (m) 1385 (m), 1355(m), 1328 (m), 1086 (s). − $^1$H NMR (300 MHz): major diastereomer: δ = 0.96 (t, *J* = 7.69 Hz, 3 H, CH$_2$C*H*$_3$), 1.42 (d, *J* = 6.38 Hz, 3 H, CHC*H*$_3$), 1.58−1.70 (m, 2 H, C*H*$_2$CH$_3$), 3.94 (m, 1 H, C*H*CH$_2$NO$_2$), 4.18 (d/d, *J* = 12.09/4.36 Hz, 1 H, C*H*$_2$NO$_2$), 4.35 (d/d, *J* = 12.09/8.06 Hz, 1 H, C*H*$_2$NO$_2$), 4.52 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 7.22−7.37 (m, 5 H, C*H*$_{ar.}$); minor diastereomer: δ = 0.78 (t, *J* = 7.69 Hz, 3 H, CH$_2$C*H*$_3$), 1.40 (d, *J* = 6.38 Hz, 3 H, CHC*H*$_3$), 1.58−1.70 (m, 2 H, C*H*$_2$CH$_3$), 3.94 (m, 1 H, C*H*CH$_2$NO$_2$), 4.42 (d/d, *J* = 12.09/4.67 Hz, 1 H, C*H*$_2$NO$_2$), 4.48 (d/d, *J* = 12.09/6.87 Hz, 1 H, C*H*$_2$NO$_2$), 4.51 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 7.22−7.37 (m, 5 H, C*H*$_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer: δ = 9.27 (CH$_2$*C*H$_3$), 23.99 (CH*C*H$_3$), 25.81 (*C*H$_2$CH$_3$), 75.57 (*C*HCH$_2$NO$_2$), 76.28 (*C*HCH$_3$), 78.73 (*C*H$_2$NO$_2$), 126.46 (*o*-*C*H$_{ar.}$), 127.94 (*p*-*C*H$_{ar.}$), 128.52 (*m*-*C*H$_{ar.}$), 143.22 (*i*-*C*$_{ar.}$); minor diastereomer: δ = 8.73 (CH$_2$*C*H$_3$), 23.66 (CH*C*H$_3$), 23.99 (*C*H$_2$CH$_3$), 74.35 (*C*HCH$_2$NO$_2$), 77.59 (*C*HCH$_3$), 78.46 (*C*H$_2$NO$_2$), 126.34 (*o*-*C*H$_{ar.}$), 127.82 (*p*-*C*H$_{ar.}$), 128.44 (*m*-*C*H$_{ar.}$), 142.62 (*i*-*C*$_{ar.}$). − MS (70 eV); *m*/*z* (%): 223 (0.2) [M$^+$] 121 (55.0) 105 (100.0). − C$_{12}$H$_{17}$NO$_3$ (223.27): calcd. C 64.55; H 7.67, N 6.27; found C 64.52, H 7.92, N 5.93.

*3-Methyl-1-nitro-2-(1-phenylethoxy)butane* (**4b**) was obtained as colourless oil according to *GP 1* by adding (±)-1-phenylethanol (**1e**) (122 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (115 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether/pentane, 1:10). Yield 84%. − *de* = 50%. − IR (film): $\tilde{\nu}$ = 2973 $cm^{-1}$ (s), 2932 (s), 2878 (m), 1557 (s), 1467 (m), 1453(s), 1371 (s), 1283 (m), 1031 (m). − $^1H$ NMR (300 MHz): major diastereomer: δ = 0.93 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 0.98 [d, *J* = 6.86 Hz, 3 H, CH(C$H_3$)$_2$], 1.43 (d, *J* = 6.59 Hz, 3 H, CHC$H_3$), 2.07 [sept/d, *J* = 6.87/4.40 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.86 (d/d/d, *J* = 8.24/4.40/4.12 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.20 (d/d, *J* = 12.08/4.12 Hz, 1 H, C$H_2$NO$_2$), 4.31 (d/d, *J* = 12.09/8.24 Hz, 1 H, C$H_2$NO$_2$), 4.51 (q, *J* = 6.59 Hz, 1 H, C*H*CH$_3$), 7.20−7.36 (m, 5 H, C$H_{ar.}$); minor diastereomer: δ = 0.79 [d, *J* = 7.01 Hz, 3 H, CH(C$H_3$)$_2$], 0.82 [d, *J* = 7.01 Hz, 3 H, CH(C$H_3$)$_2$], 1.39 (d, *J* = 6.60 Hz, 3 H, CHC$H_3$), 1.74 [sept/d, *J* = 6.90/5.00 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.87 (d/d/d, *J* = 7.42/5.22/3.85 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.42 (d/d, *J* = 12.08/3.85 Hz, 1 H, C$H_2$NO$_2$), 4.47 (q, *J* = 6.59 Hz, 1 H, C*H*CH$_3$), 4.49 (d/d, *J* = 12.09/7.42 Hz, 1 H, C$H_2$NO$_2$), 7.20−7.36 (m, 5 H, C$H_{ar.}$). − $^{13}C$ NMR (75 MHz): major diastereomer: δ = 17.00 [CH(*C*H$_3$)$_2$], 17.83 [CH(*C*H$_3$)$_2$], 23.89 (CH*C*H$_3$), 29.10 [*C*H(CH$_3$)$_2$], 76.69 (*C*HCH$_2$NO$_2$), 76.76 (*C*H$_2$NO$_2$), 78.25 (*C*HCH$_3$), 124.34 (*o*-*C*H$_{ar.}$), 127.90 (*p*-*C*H$_{ar.}$), 128.47 (*m*-*C*H$_{ar.}$), 142.71 (*i*-*C*$_{ar.}$); minor diastereomer: δ = 17.39 [CH(*C*H$_3$)$_2$], 18.08 [CH(*C*H$_3$)$_2$], 23.56 (CH*C*H$_3$), 30.62 [*C*H(CH$_3$)$_2$], 76.96 (*C*HCH$_2$NO$_2$), 77.88 (*C*H$_2$NO$_2$), 79.41 (*C*HCH$_3$), 126.53 (*o*-*C*H$_{ar.}$), 127.75 (*p*-*C*H$_{ar.}$), 128.35 (*m*-*C*H$_{ar.}$), 143.24 (*i*-*C*$_{ar.}$). MS (70 eV); *m*/*z* (%): 237 (0.5) [$M^+$] 121 (49.0), 105 (100.0). − $C_{13}H_{19}NO_3$ (237.20): calcd. C 65.84, H 8.07, N 5.90; found, C 66.34, H 8.32, N 6.18.

*3,3-Dimethyl-1-nitro-2-(1-phenylethoxy)butane* (**3e**) was obtained as colourless oil according to *GP 1* by adding (±)-1-phenylethanol (**1e**) (122 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (129 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$, diethyl ether/pentane 1:10). Yield 54%. − *de* = 91%. − IR (film): $\tilde{\nu}$ = 2974 $cm^{-1}$ (s), 1556 (s), 1494 (m), 1423 (s), 1399 (s), 1380 (s), 1284 (m), 1082 (s). − $^1H$ NMR (300 MHz): major diastereomer: δ = 0.99 [s, 9 H, C(C$H_3$)$_3$], 1.44 (d, *J* = 6.38 Hz, 3 H, CHC$H_3$), 3.92 (d/d, *J* = 6.71/4.03 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.22 (d/d, *J* = 12.76/6.72 Hz, 1 H, C$H_2$NO$_2$), 4.34 (d/d, *J* = 12.75/4.03 Hz, 1 H, C$H_2$NO$_2$), 4.48 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 7.22−7.35 (m, 5 H, C$H_{ar.}$); minor diastereomer: δ = 0.80 [s, 9 H, C(C$H_3$)$_3$], 1.38 (d, *J* = 6.38 Hz, 3 H, CHC$H_3$), 3.74 (d/d, *J* = 7.05/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.45 (q, *J* = 6.38 Hz,1 H, C*H*CH$_3$), 4.47 (d/d, *J* = 12.42/7.05 Hz, 1 H, C$H_2$NO$_2$), 4.55 (d/d, *J* = 12.42/3.36 Hz, 1 H, C$H_2$NO$_2$), 7.22−7.35 (m, 5 H, C$H_{ar.}$). − $^{13}C$ NMR (75 MHz): major diastereomer: δ = 23.10 (CH*C*H$_3$), 26.02 [C(*C*H$_3$)$_3$], 35.69 [*C*(CH$_3$)$_3$], 77.73 (*C*H$_2$NO$_2$), 79.11 (*C*HCH$_2$NO$_2$), 82.93 (*C*HCH$_3$), 126.19 (*o*-*C*H$_{ar.}$), 127.76 (*p*-*C*H$_{ar.}$), 128.38 (*m*-*C*H$_{ar.}$), 143.49 (*i*-*C*$_{ar.}$); minor diastereomer: δ = 23.60 (CH*C*H$_3$), 26.02 [C(*C*H$_3$)$_3$], 35.20 [*C*(CH$_3$)$_3$], 78.20 (*C*H$_2$NO$_2$), 78.37 (*C*HCH$_2$NO$_2$), 82.55 (*C*HCH$_3$), 126.91 (*o*-*C*H$_{ar.}$), 127.72 (*p*-*C*H$_{ar.}$), 128.24 (*m*-*C*H$_{ar.}$), 142.62 (*i*-*C*$_{ar.}$). − MS (70 eV); *m*/*z* (%): 165 (4.5), 130 (4.1), 121 (41.3), 105 (100.0). − $C_{14}H_{21}NO_3$ (251.32): calcd. C 66.91, H 8.42, N 5.57; found C 66.65, H 8.56, N 5.77.

*1-Nitro-2-phenyl-2-(1-phenylethoxy)ethane* (**4c**) was obtained as colourless oil according to *GP 1* by adding (±)-1-phenylethanol (**1e**) (122 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-ω-nitrostyrene (**2k**) (149 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether/pentane, 1:10). Yield 61%. − *de* = 23%. − IR (film): $\tilde{\nu}$ = 2976 $cm^{-1}$ (m), 1557 (s), 1493 (m), 1380 (s), 1353 (m), 1094 (s), 1029 (m) 763 (s), 700 (s). − $^1H$ NMR (300 MHz): major diastereomer: δ = 1.43 (d, *J* = 6.38 Hz, 3 H, CHC$H_3$), 4.41 (d/d, *J* = 12.42/3.36 Hz, 1 H, C$H_2$NO$_2$), 4.47 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 4.66 (d/d, *J* = 12.76/9.73 Hz, 1 H, C$H_2$NO$_2$), 5.26 (d/d, *J* = 10.07/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 7.12−7.44 (m, 10 H, C$H_{ar.}$); minor diastereomer: δ = 1.38 (d, *J* = 6.38 Hz, 3 H, CHC$H_3$), 4.26 (d/d, *J* = 12.09/3.36 Hz, 1 H, C$H_2$NO$_2$), 4.27 (q, *J* = 6.38 Hz, 1 H, C*H*CH$_3$), 4.63 (d/d, *J* = 12.42/10.07 Hz, 1 H, C$H_2$NO$_2$), 4.83 (d/d, *J* = 10.07/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 7.12−7.44 (m, 10 H, C$H_{ar.}$). − $^{13}C$ NMR (75 MHz): major diastereomer: δ = 21.72 (CH*C*H$_3$), 75.10 (*C*HCH$_3$), 76.20 (*C*HCH$_2$NO$_2$), 80.60 (*C*H$_2$NO$_2$), 126.14, 126.82 (*o*-*C*H$_{ar.}$), 127.44, 128.18 (*p*-*C*H$_{ar.}$), 128.79, 129.09 (*m*-*C*H$_{ar.}$), 136.83, 143.02 (*i*-*C*$_{ar.}$); minor diastereomer: δ = 24.15 (CH*C*H$_3$), 75.18 (*C*HCH$_3$), 76.35 (*C*HCH$_2$NO$_2$), 80.56 (*C*H$_2$NO$_2$), 126.57, 127.05 (*o*-*C*H$_{ar.}$), 128.03, 128.18 (*p*-*C*H$_{ar.}$), 128.57, 128.76 (*m*-*C*H$_{ar.}$), 136.53, 141.84 (*i*-*C*$_{ar.}$). − MS (70 eV); *m*/*z* (%): 271 (0.7) [$M^+$], 105 (81.5), 104 (100.0), 77 (23.7). − $C_{16}H_{17}NO_3$ (271.32): calcd. C 70.83, H 6.32, N 5.16; found C 70.36, H 6.53, N 5.31.

*Addition of N-Acyl Derivatives* **5a**−**c** *of Ephedrine and Norephedrine to (E)-3-Methyl-1-nitrobut-1-ene* (**2d**)

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]acetamide* (**6a**) was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-acetylnorephedrine (**5a**) (193 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (115 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 43 mg (14%). − *de* = 76% (≥ 96%, after chromatography). − Major diastereomer: $[\alpha]_D^{24}$ = −98.6 (*c* = 0.70, $CHCl_3$); minor diastereomer: $[\alpha]_D^{24}$ = −7.5 (*c* = 0.23, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3029 $cm^{-1}$ (m), 2966 (s), 2935 (m), 1653 (s), 1557 (s), 1494 (m), 1454 (s), 1423 (m), 1372 (s) 1220 (m), 1141 (m), 1080 (s), 1029 (m), 757 (s), 726 (m), 705 (s). − $^1H$ NMR (300 MHz): major diastereomer: δ = 0.92 [d, *J* = 6.86 Hz, 3 H, CH(C$H_3$)$_2$], 0.98 [d, *J* = 7.14 Hz, 3 H, CH(C$H_3$)$_2$], 1.03 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.97 [s, 3 H, C$H_3$CO), 2.16 [sept/d, *J* = 6.87/3.85 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.97 (d/d/d, *J* = 9.07/3.85/3.57 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.12 (d/q/d, *J* = 8.51/7.15/3.57 Hz, 1 H, NC*H*CH$_3$), 4.30 (d/d, *J* = 11.81/3.57 Hz, 1 H, C$H_2$NO$_2$), 4.43 (d/d, *J* = 11.81/9.06 Hz, 1 H, C$H_2$NO$_2$), 4.69 (d, *J* = 3.57 Hz, 1 H, C*H*C$_{ar.}$), 5.65 (br. d, *J* = 8.24 Hz, 1 H, N*H*), 7.19−7.23 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.39 (m, 3 H, *p,m*-C$H_{ar.}$); minor diastereomer: δ = 0.84 (d, *J* = 6.86 Hz, 3 H, CH(C$H_3$)$_2$], 0.88 [d, *J* = 7.14 Hz, 3 H, CH(C$H_3$)$_2$], 0.96 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.85 [sept/d, *J* = 6.87/4.39 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.03 (s, 3 H, C$H_3$CO), 3.96 (d/d/d, *J* = 8.79/4.40/3.03 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.06 (d/q/d, *J* = 8.79/6.87/2.75 Hz, 1 H, NC*H*CH$_3$), 4.46 (d/d, *J* = 12.08/3.02 Hz, 1 H, C$H_2$NO$_2$), 4.58 (d/d, *J* = 12.09/8.79 Hz, 1 H, C$H_2$NO$_2$), 4.62 (d, *J* = 2.75 Hz, 1 H, C*H*C$_{ar.}$), 5.85 (br. d, *J* = 8.73 Hz, 1 H, N*H*), 7.27−7.38 (m, 5 H, C$H_{ar.}$). − $^{13}C$ NMR (75 MHz): major diastereomer: δ = 13.76 (NCH*C*H$_3$), 16.05 [CH(*C*H$_3$)$_2$], 18.04 [CH(*C*H$_3$)$_2$], 23.45 [*C*H(CH$_3$)$_2$], 27.67 (*C*H$_3$CO), 50.33 (N*C*HCH$_3$), 76.24 (*C*H$_2$NO$_2$), 78.12 (*C*HCH$_2$NO$_2$), 80.32 (*C*HC$_{ar.}$), 127.09 (*o*-*C*H$_{ar.}$), 128.19 (*p*-*C*H$_{ar.}$), 128.46 (*m*-*C*H$_{ar.}$), 137.72 (*i*-*C*$_{ar.}$), 169.20 (*C*O); minor diastereomer: δ = 12.75 (NCH*C*H$_3$), 16.34 [CH(*C*H$_3$)$_2$], 18.81 [CH(*C*H$_3$)$_2$], 23.38 (*C*H$_3$CO), 29.83 [*C*H(CH$_3$)$_2$], 50.90 (N*C*HCH$_3$), 75.95 (*C*H$_2$NO$_2$), 82.90 (*C*HCH$_2$NO$_2$), 83.62 (*C*HC$_{ar.}$), 127.73 (*o*-*C*H$_{ar.}$), 126.74 (*p*-*C*H$_{ar.}$), 128.20 (*m*-*C*H$_{ar.}$), 139.59 (*i*-*C*$_{ar.}$), 169.81 (*C*O). − MS (70 eV); *m*/*z* (%): 309 (1.6) [$M^+$ + 1], 222 (9.7), 134 (25.5), 107 (78.2), 86 (100). − $C_{16}H_{24}N_2O_4$ = 308.38): calcd. C 62.32, H 7.84, N 9.08; found C 62.41, H 8.03, N 9.52.

*(1S,2R,1′R)-(−)-2,2,2-Trifluoro-N-[1-methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]acetamide* (**6b**) was obtained as

colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-trifluoracetylnorephedrine (**5b**) (247 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (115 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether/pentane 1:3). Yield 44 mg (12%). − *de* = 75% . − $[\alpha]_D^{24}$ = −90.7 (*c* = 1.70, $CHCl_3$). − IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3035 $cm^{-1}$ (m), 2968 (s), 2938 (m), 1713 (s), 1558 (s), 1494 (m), 1455 (s), 1424 (s), 1386 (s), 1371 (s), 1276 (m), 1210 (s), 1181 (s), 1078 (s), 1029 (m), 759 (m), 739 (m), 728 (s), 705 (s). − $^1$H NMR (300 MHz): major diastereomer: δ = 0.92 [d, *J* = 7.14 Hz, 3 H, $CH(CH_3)_2$], 0.96 [d, *J* = 6.86 Hz, 3 H, $CH(CH_3)_2$], 1.14 (d, *J* = 6.87 Hz, 3 H, $NCHCH_3$), 2.14 [sept/d, *J* = 6.86/3.84 Hz, 1 H, $CH(CH_3)_2$], 3.99 (d/d/d, *J* = 9.07/3.57/3.30 Hz, 1 H, $CHCH_2NO_2$), 4.19 (d/q/d, *J* = 7.97/6.87/3.57 Hz, 1 H, $NCHCH_3$), 4.31 (d/d, *J* = 12.09/3.29 Hz, 1 H, $CH_2NO_2$), 4.44 (d/d, *J* = 12.08/9.07 Hz, 1 H, $CH_2NO_2$), 4.68 (d, *J* = 3.58 Hz, 1 H, $CHC_{ar.}$), 6.48 (br. d, *J* = 7.97 Hz, 1 H, N*H*), 7.17−7.22 (m, 2 H, *o*-$CH_{ar.}$), 7.30−7.42 (m, 3 H, *p*,*m*-$CH_{ar.}$); minor diastereomer: δ = 0.85 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 0.91 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 1.10 (d, *J* = 6.86 Hz, 3 H, $NCHCH_3$), 1.85 [sept/d, *J* = 6.84/4.67 Hz, 1 H, $CH(CH_3)_2$], 3.93 (d/d/d, *J* = 7.97/4.94/3.29 Hz, 1 H, $CHCH_2NO_2$), 4.17 (d/q/d, *J* = 8.40/6.86/3.03 Hz, 1 H, $NCHCH_3$), 4.49 (d/d, *J* = 12.91/3.30 Hz, 1 H, $CH_2NO_2$), 4.57 (d/d, *J* = 12.91/7.96 Hz, 1 H, $CH_2NO_2$), 4.63 (d, *J* = 3.02 Hz, 1 H, $CHC_{ar.}$), 6.81 (br. d, *J* = 8.40 Hz, 1 H, N*H*), 7.17−7.22 (m, 1 H, *o*-$CH_{ar.}$), 7.30−7.42 (m, 3 H, *p*,*m*-$CH_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer: δ = 13.67 ($NCHCH_3$), 15.82 [$CH(CH_3)_2$], 18.09 [$CH(CH_3)_2$], 27.68 [$CH(CH_3)_2$], 51.00 ($NCHCH_3$), 76.20 ($CH_2NO_2$), 78.29 ($CHCH_2NO_2$), 79.84 ($CHC_{ar.}$), 115.85 (q, $J_{C-F}$ = 288.0 Hz, $CF_3$), 127.13 (*o*-$CH_{ar.}$), 128.76 (*p*-$CH_{ar.}$), 128.79 (*m*-$CH_{ar.}$), 136.46 (*i*-$C_{ar.}$), 156.41 (q, $J_{C-F}$ = 36.6 Hz, $COCF_3$); minor diastereomer: δ = 13.05 ($NCHCH_3$), 16.68 [$CH(CH_3)_2$], 18.72 [$CH(CH_3)_2$], 29.99 [$CH(CH_3)_2$], 51.64 ($NCHCH_3$), 75.49 ($CH_2NO_2$), 81.51 ($CHCH_2NO_2$), 82.54 ($CHC_{ar.}$), 109.57 (q, $J_{C-F}$ = 282.2 Hz, $CF_3$), 127.13 (*o*-$CH_{ar.}$), 128.44 (*p*-$CH_{ar.}$), 128.54 (*m*-$CH_{ar.}$), 138.07 (*i*-$C_{ar.}$), 150.44 (q, $J_{C-F}$ = 34.2 Hz, $COCF_3$). − MS (70 eV); *m*/*z* (%): 230 (12.3), 223 (12.6), 222 (86.4), 139 (12.8), 107 (68.9), 105 (15.7) 69 (100). − $C_{16}H_{21}N_2O_4F_3$ (362.35): calcd. C 53.04, H 5.84, N 7.73; found C 53.22, H 6.06, N 8.15.

*(1S,2R,1′R)-(−)-N-Methyl-N-[1-methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]formamide* (**6c**) was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylephedrine (**5c**) (193 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (115 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether/pentane, 30:1). Yield 135 g (44%). − *de* = 63% (≥ 96% after chromatography). − Major diastereomer: $[\alpha]_D^{24}$ = −70.4 (*c* = 1.20, $CHCl_3$). − M.p. 97°C. − IR (KBr): $\tilde{\nu}$ = 2963 $cm^{-1}$ (s), 2935 (m), 2898 (m), 1681 (s), 1660 (s), 1550 (s), 1496 (m), 1466 (m), 1426 (s), 1405 (s), 1383 (s), 1370 (m), 1289 (m), 1240 (m), 1115 (s), 1074 (s), 1057 (s), 766 (m), 723 (m), 710 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.88 [d, *J* = 6.71 Hz, 3 H, $CH(CH_3)_2$], 0.95 [d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 1.34 (d, *J* = 7.05 Hz, 3 H, $NCHCH_3$), 2.16 [sept/d, *J* = 7.05/3.70 Hz, 1 H, $CH(CH_3)_2$], 2.76 (s, 3 H, $NCH_3$), 3.88 (d/t, *J* = 9.06/3.60 Hz, 1 H, $CHCH_2NO_2$), 4.20 (quint, *J* = 7.05 Hz, 1 H, $NCHCH_3$), 4.22 (d/d, *J* = 11.75/3.35 Hz, 1 H, $CH_2NO_2$), 4.33 (d/d, *J* = 12.09/9.07 Hz, 1 H, $CH_2NO_2$), 4.76 (d, *J* = 7.05 Hz, 1 H, $CHC_{ar.}$), 7.11−7.39 (m, 5 H, $CH_{ar.}$), 7.83 (s, 1 H, C*H*O); (*E*): δ = 0.91 [d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 0.98 [d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 1.45 (d, *J* = 6.72 Hz, 3 H, $NCHCH_3$), 2.16 [sept/d, *J* = 7.05/3.70 Hz, 1 H, $CH(CH_3)_2$], 2.68 (s, 3 H, $NCH_3$), 3.72 (d/q, *J* = 7.72/6.89 Hz, 1 H, $NCHCH_3$), 3.88 (d/t, *J* = 9.06/3.60 Hz, 1 H, $CHCH_2NO_2$), 4.21 (d/d, *J* = 12.09/3.35 Hz, 1 H, $CH_2NO_2$), 4.36 (d, *J* = 8.39 Hz, 1 H, $CHC_{ar.}$), 4.35 (d/d, *J* = 12.09/9.07 Hz, $CH_2NO_2$), 7.11−7.39 (m, 5 H, $CH_{ar.}$), 7.66 (s, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.76 [d, *J* = 6.71 Hz, 3 H, $CH(CH_3)_2$], 0.79 [d, *J* = 6.72 Hz, 3 H, $CH(CH_3)_2$], 1.44 (d, *J* = 7.09 Hz, 3 H, $NCHCH_3$), 1.68 [sept/d, *J* = 7.05/4.68 Hz, 1 H, $CH(CH_3)_2$], 2.70 (s, 3 H, $NCH_3$), 3.50 (m, 1 H, $NCHCH_3$), 3.70 (m, 1 H, $CHCH_2NO_2$), 4.20−4.55 (m, 3 H, $CHC_{ar.}$, $CH_2NO_2$), 7.20−7.37 (m, 5 H, $CH_{ar.}$), 7.74 (s, 1 H, C*H*O); (*E*): δ = 0.79 [d, *J* = 6.72 Hz, 3 H, $CH(CH_3)_2$], 0.81 [d, *J* = 7.05 Hz, 3 H, $CH(CH_3)_2$], 1.36 (d, *J* = 6.71 Hz, 3 H, $NCHCH_3$), 1.68 [sept/d, *J* = 7.05/4.68 Hz, 1 H, $CH(CH_3)_2$], 2.63 (s, 3 H, $NCH_3$), 3.74 (d/q, *J* = 8.05/7.05 Hz, 1 H, $NCHCH_3$), 3.89 (d/d/d, *J* = 8.05/4.70/3.35 Hz, 1 H, $CHCH_2NO_2$), 4.28 (d, *J* = 8.40 Hz, 1 H, $CHC_{ar.}$), 4.43 (d/d, *J* = 12.75/3.36 Hz, 1 H, $CH_2NO_2$), 4.52 (d/d, *J* = 12.42/7.72 Hz, 1 H, $CH_2NO_2$), 7.20−7.37 (m, 5 H, $CH_{ar.}$), 7.64 (s, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 12.79 ($NCHCH_3$), 15.96 [$CH(CH_3)_2$], 18.08 [$CH(CH_3)_2$] 27.57 [$CH(CH_3)_2$], 33.08 ($NCH_3$), 54.52 ($NCHCH_3$), 76.28 ($CH_2NO_2$), 77.40 ($CHCH_2NO_2$), 80.53 ($CHC_{ar.}$), 127.56 (*o*-$CH_{ar.}$), 128.54 (*p*-$CH_{ar.}$), 129.15 (*m*-$CH_{ar.}$), 137.54 (*i*-$C_{ar.}$), 162.71 (*C*HO); (*E*): δ = 15.79 [$CH(CH_3)_2$], 16.17 ($NCHCH_3$), 18.08 [$CH(CH_3)_2$], 26.77 [$CH(CH_3)_2$], 27.77 ($NCH_3$), 59.13 ($NCHCH_3$), 76.19 ($CH_2NO_2$), 77.91 ($CHCH_2NO_2$), 81.34 ($CHC_{ar.}$), 127.22 (*o*-$CH_{ar.}$), 128.39 (*m*-$CH_{ar.}$), 128.92 (*p*-$CH_{ar.}$), 137.10 (*i*-$C_{ar.}$), 162.84 (*C*HO); minor diastereomer: (*Z*): δ = 13.32 ($NCHCH_3$), 17.21 [$CH(CH_3)_2$], 18.08 [$CH(CH_3)_2$], 24.70 [$CH(CH_3)_2$], 26.50 ($NCH_3$), 55.74 ($NCHCH_3$), 76.10 ($CH_2NO_2$), 79.14 ($CHCH_2NO_2$), 83.17 ($CHC_{ar.}$), 127.59 (*o*-$CH_{ar.}$), 128.29 (*p*-$CH_{ar.}$), 129.04 (*m*-$CH_{ar.}$), 137.94 (*i*-$C_{ar.}$), 165.55 (*C*HO); (*E*): δ = 16.99 [$CH(CH_3)_2$], 18.08 ($NCHCH_3$), 18.16 [$CH(CH_3)_2$], 27.75 [$CH(CH_3)_2$], 30.71 ($NCH_3$), 58.89 ($NCHCH_3$), 76.37 ($CH_2NO_2$), 77.32 ($CHCH_2NO_2$), 83.53 ($CHC_{ar.}$), 127.50 (*o*-$CH_{ar.}$), 127.97 (*m*-$CH_{ar.}$), 128.78 (*p*-$CH_{ar.}$), 138.01 (*i*-$C_{ar.}$), 162.96 (*C*HO). − MS (70 eV); *m*/*z* (%): 309 (5.4) [$M^+$ + 1], 249 (3.4), 222 (36.7), 116 (25.7), 107 (44.4), 91 (15.0), 86 (100), 69 (65.0). − $C_{16}H_{24}N_2O_4$ (308.38): calcd. C 62.32, H 7.84, N 9.08; found C 62.32, H 7.72, N 8.83.

*(1S,2S,1′S)-(+)-N-[1-Methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]formamide* was obtained as colourless solid according to *GP 1* by adding (1*R*,2*R*)-(+)-*N*-formylpseudonorephedrine (**5b**) (179 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (115 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether/pentane, 20:1). Yield 235 mg (80%). − *de* = 77% (83% after chromatography). − $[\alpha]_D^{24}$ = +68.5 (*c* = 1.01, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3032 $cm^{-1}$ (m), 2969 (s), 2936 (m), 1689 (s), 1556 (s), 1495 (m), 1423 (m), 1384 (s), 1303 (m), 1229 (m), 1146 (m), 1082 (s), 1029 (m), 757 (s), 724 (m), 705 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.92 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 1.00 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 1.17 (d, *J* = 6.59 Hz, 3 H, $NCHCH_3$), 2.17 [sept/d, *J* = 6.87/3.85 Hz, 1 H, $CH(CH_3)_2$], 3.94 (d/d/d, *J* = 9.07/3.85/3.57 Hz, 1 H, $CHCH_2NO_2$), 4.28 (d/d, *J* = 12.09/3.30 Hz, 1 H, $CH_2NO_2$), 4.29 (d/q/d, *J* = 8.79/6.60/4.12 Hz, 1 H, $NCHCH_3$), 4.41 (d/d, *J* = 12.09/9.06 Hz, 1 H, $CH_2NO_2$), 4.54 (d, *J* = 4.12 Hz, 1 H, $CHC_{ar.}$), 5.77 (br. d, *J* = 8.52 Hz, 1 H, N*H*), 7.16 (m, 2 H, *o*-$CH_{ar.}$), 7.27−7.41 (m, 3 H, *p*,*m*-$CH_{ar.}$), 8.06 (d, *J* = 1.10 Hz, 1 H, C*H*O); (*E*): δ = 0.90 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 0.96 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 1.06 (d, *J* = 6.87 Hz, 3 H, $NCHCH_3$), 2.14 [sept/d, *J* = 6.86/3.84 Hz, 1 H, $CH(CH_3)_2$], 3.61 (d/q/d, *J* = 9.62/6.87/6.87 Hz, 1 H, $NCHCH_3$), 3.89 (d/d/d, *J* = 9.07/3.84/3.57 Hz, 1 H, $CHCH_2NO_2$), 4.19 (d, *J* = 6.59 Hz, 1 H, $CHC_{ar.}$), 4.22 (d/d, *J* = 12.09/3.30 Hz, 1 H, $CH_2NO_2$), 4.35 (d/d, *J* = 12.09/9.07 Hz, 1 H, $CH_2NO_2$), 5.99 (br. t, *J* = 10.17 Hz, 1 H, N*H*), 7.15 (m, 2 H, *o*-$CH_{ar.}$), 7.27−7.41

(m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.97 (d, *J* = 11.81 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.78 [d, *J* = 6.87 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.82 [d, *J* = 6.87 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.00 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 4.49 (d, *J* = 3.57 Hz, 1 H, C*H*C$_{ar.}$), 8.11 (d, *J* = 1.65 Hz, 1 H, C*H*O); (*E*): δ = 0.81 [d, *J* = 6.87 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.84 [d, *J* = 6.87 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.08 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 7.88 (d, *J* = 11.82 Hz, 1 H, C*H*O), other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 16.22 (NCH*C*H$_3$), 17.09 [CH(*C*H$_3$)$_2$], 18.09 [CH(*C*H$_3$)$_2$], 28.02 [*C*H(CH$_3$)$_2$], 48.72 (N*C*HCH$_3$), 76.37 (*C*H$_2$NO$_2$), 78.35 (*C*HCH$_2$NO$_2$), 80.43 (*C*HC$_{ar.}$), 127.42 (*o*-*C*H$_{ar.}$), 128.47 (*m*-*C*H$_{ar.}$), 128.56 (*p*-*C*H$_{ar.}$), 137.21 (*i*-*C*$_{ar.}$), 160.66 (*C*HO); (*E*): δ = 16.17 [CH(*C*H$_3$)$_2$], 18.09 (NCH*C*H$_3$), 18.17 [CH(*C*H$_3$)$_2$], 27.91 [*C*H(CH$_3$)$_2$], 53.20 (N*C*HCH$_3$), 76.27 (*C*H$_2$NO$_2$), 78.03 (*C*HCH$_2$NO$_2$), 83.13 (*C*HC$_{ar.}$), 127.50 (*o*-*C*H$_{ar.}$), 128.86 (*m*-*C*H$_{ar.}$), 129.01 (*p*-*C*H$_{ar.}$), 137.29 (*i*-*C*$_{ar.}$), 164.81 (*C*HO). − MS (70 eV); *m*/*z* (%): 295 (0.2) [M$^+$ + 1], 222 (41.9), 178 (15.0), 116 (45.5), 107 (77.0), 69 (100). − $C_{15}H_{22}N_2O_4$ (294.35): calcd. C 61.21, H 7.53, N 9.52; found C 61.14, H 7.76, N 9.71.

*Addition of N-Formylnorephedrine* (**7**) *to (E)-Nitro Alkenes* **2a−m**

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(1′-methyl-2′-nitroethoxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8a**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-1-nitroprop-1-ene (**2a**) (435 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 799 mg (60%) − *de* = 94% (≥ 96% after chromatography). − Major diastereomer: $[\alpha]_D^{24}$ = −128.8 (*c* = 1.09, $CHCl_3$); minor diastereomer: $[\alpha]_D^{24}$ = −41.8 (*c* = 1.01, $CHCl_3$). − M.p. 71°C. − IR (KBr): $\tilde{\nu}$ = 3035 cm$^{-1}$ (m), 2977 (m), 2969 (m), 2931 (m), 1694 (s), 1661 (s), 1554 (s), 1492 (m), 1452 (m), 1389 (s), 1364 (m), 1350 (m), 1233 (s), 1204 (m), 1154 (s), 1054 (s), 1029 (m). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 1.03 (d, *J* = 6.88 Hz, 3 H, NCHC*H*$_3$), 1.23 (d, *J* = 6.30 Hz, 3 H, CHC*H*$_3$), 4.16 (d/d/d, *J* = 8.31/6.22/3.78 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.21 (d/q/d/d, *J* = 9.40/6.88/3.76/0.75 Hz, 1 H, NC*H*CH$_3$), 4.35 (d/d, *J* = 11.92/3.77 Hz, 1 H, C*H*$_2$NO$_2$), 4.47 (d/d, *J* = 11.92/8.39 Hz, 1 H, C*H*$_2$NO$_2$), 4.66 (d, *J* = 3.78 Hz, 1 H, C*H*C$_{ar.}$), 6.34 (br. d, *J* = 8.73 Hz, 1 H, N*H*), 7.24 (m, 2 H, *o*-C*H*$_{ar.}$), 7.28−7.40 (m, 3 H, *m*,*p*-C*H*$_{ar.}$), 8.11 (d, *J* = 0.69 Hz, 1 H, C*H*O); (*E*): δ = 1.03 (d, *J* = 6.80 Hz, 3 H, NCHC*H*$_3$), 1.24 (d, *J* = 6.29 Hz, 3 H, CHC*H*$_3$), 3.69 (d/q/d, *J* = 9.65/6.92/5.03 Hz, 1 H, NC*H*CH$_3$), 4.14 (d/d/d, *J* = 8.23/6.04/4.03 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.30 (d/d, *J* = 12.00/3.78 Hz, 1 H, C*H*$_2$NO$_2$), 4.38 (d, *J* = 5.12 Hz, 1 H, C*H*C$_{ar.}$), 4.45 (d/d, *J* = 12.00/8.65 Hz, 1 H, C*H*$_2$NO$_2$), 6.06 (br. d/d, *J* = 11.20/10.08 Hz, 1 H, N*H*), 7.19 (m, 2 H, *o*-C*H*$_{ar.}$), 7.28−7.40 (m, 3 H, *m*,*p*-C*H*$_{ar.}$), 7.81 (d, *J* = 11.75 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.95 (d, *J* = 6.88 Hz, 3 H, NCHC*H*$_3$), 1.15 (d, *J* = 6.46 Hz, 3 H, CHC*H*$_3$), 4.23 (d/q/d/d, *J* = 9.48/6.46/3.94/0.84 Hz, 1 H, NC*H*CH$_3$), 4.24 (d/d/d, *J* = 6.37/6.04/5.29 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.50 (d, *J* = 5.22 Hz, 1 H, C*H*$_2$NO$_2$), 4.50 (d, *J* = 5.87 Hz, 1 H, C*H*$_2$NO$_2$), 4.63 (d, *J* = 3.89 Hz, 1 H, C*H*C$_{ar.}$), 6.05 (br. d, *J* = 8.85 Hz, 1 H, N*H*), 7.27−7.40 (m, 5 H, C*H*$_{ar.}$), 8.18 (d, *J* = 0.85 Hz, 1 H, C*H*O); (*E*): δ = 1.08 (d, *J* = 6.97 Hz, 3 H, NCHC*H*$_3$), 1.09 (d, *J* = 6.47 Hz, 3 H, CHC*H*$_3$), 3.73 (d/q/d, *J* = 9.73/6.50/4.45 Hz, 1 H, NC*H*CH$_3$), 4.22 (d/d/d, *J* = 7.56/6.92/3.44 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.30 (d, *J* = 4.45 Hz, 1 H, C*H*C$_{ar.}$), 4.41 (d/d, *J* = 12.33/3.95 Hz, 1 H, C*H*$_2$NO$_2$), 4.43 (d/d, *J* = 12.51/7.55 Hz, 1 H, C*H*$_2$NO$_2$), 5.52 (br. d/d, *J* = 11.50/10.00 Hz, 1 H, N*H*), 7.27−7.40 (m, 5 H, C*H*$_{ar.}$), 7.91 (d, *J* = 11.75 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.80 (NCH*C*H$_3$), 15.95 (CH*C*H$_3$), 48.75 (N*C*HCH$_3$), 69.28 (*C*HCH$_2$NO$_2$), 79.85 (*C*HC$_{ar.}$), 80.45 (*C*H$_2$NO$_2$), 127.00 (*o*-*C*H$_{ar.}$), 128.21 (*p*-*C*H$_{ar.}$), 128.48 (*m*-*C*H$_{ar.}$), 137.55 (*i*-*C*$_{ar.}$), 160.56 (*C*HO); (*E*): δ = 15.90 (CH*C*H$_3$), 17.02 (NCH*C*H$_3$), 52.87 (N*C*HCH$_3$), 69.17 (*C*HCH$_2$NO$_2$), 80.35 (*C*H$_2$NO$_2$), 81.55 (*C*HC$_{ar.}$), 127.63 (*o*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 128.75 (*p*-*C*H$_{ar.}$), 136.30 (*i*-*C*$_{ar.}$), 164.03 (*C*HO); minor diastereomer: (*Z*): δ = 12.95 (NCH*C*H$_3$), 18.23 (CH*C*H$_3$), 49.18 (N*C*HCH$_3$), 73.33 (*C*HCH$_2$NO$_2$), 79.73 (*C*HC$_{ar.}$), 82.95 (*C*H$_2$NO$_2$), 126.50 (*o*-*C*H$_{ar.}$), 127.92 (*p*-*C*H$_{ar.}$), 128.38 (*m*-*C*H$_{ar.}$), 139.21 (*i*-*C*$_{ar.}$), 160.75 (*C*HO); (*E*): δ = 17.07 (NCH*C*H$_3$), 18.23 (CH*C*H$_3$), 52.66 (N*C*HCH$_3$), 72.44 (*C*HCH$_2$NO$_2$), 79.81 (*C*H$_2$NO$_2$), 84.80 (*C*HC$_{ar.}$), 127.61 (*o*-*C*H$_{ar.}$), 128.63 (*m*-*C*H$_{ar.}$), 128.71 (*p*-*C*H$_{ar.}$), 137.33 (*i*-*C*$_{ar.}$), 164.08 (*C*HO). − MS (70 eV); *m*/*z* (%): 267 (0.2) [M$^+$ + 1], 221 (1.7), 194 (30.3), 107 (39.0), 105 (13.3), 88 (100), 72 (40.1). − $C_{13}H_{18}N_2O_4$ (266.30): calcd. C 58.64, H 6.81, N 10.52; found C 58.81, H 6.86, N 10.56.

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(1′-nitromethylpropoxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8b**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-1-nitrobut-1-ene (**2b**) (506 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 1.05 g (75%), m.p. 92°C. − *de* = 93% (97% after chromatography). − $[\alpha]_D^{24}$ = −136.3 (*c* = 1.06, $CHCl_3$) − IR (KBr): $\tilde{\nu}$ = 3032 cm$^{-1}$ (m), 2972 (s), 2942 (m), 2877 (m), 1681 (s), 1653 (s), 1627 (m), 1553 (s), 1525 (s), 1491 (m), 1469 (m), 1458 (m), 1392 (s), 1374 (s), 1234 (m), 1233 (s), 1152 (m), 1120 (m), 1097 (s), 1029 (s), 999 (m). − $^1$H NMR (500 MHz): major diastereomer: (*Z*): δ = 0.93 (t, *J* = 7.48 Hz, 3 H, CH$_2$C*H*$_3$), 1.06 (d, *J* = 6.86 Hz, 3 H, NCHC*H*$_3$), 1.63 (d/q/d, *J* = 14.57/7.40/7.17 Hz, 1 H, C*H*$_2$CH$_3$), 1.71 (d/q/d, *J* = 14.57/7.62/4.12 Hz, 1 H, C*H*$_2$CH$_3$), 4.02 (d/d/d/d, *J* = 8.72/7.02/4.27/3.89 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.23 (d/q/d/d, *J* = 8.85/6.87/3.66/0.84 Hz, 1 H, NC*H*CH$_3$), 4.36 (d/d, *J* = 11.90/3.74 Hz, 1 H, C*H*$_2$NO$_2$), 4.48 (d/d, *J* = 11.90/8.31 Hz, 1 H, C*H*$_2$NO$_2$), 4.68 (d, *J* = 3.66 Hz, 1 H, C*H*C$_{ar.}$), 5.91 (br. d, *J* = 8.16 Hz, 1 H, N*H*), 7.24 (m, 2 H, *o*-C*H*$_{ar.}$), 7.32 (m, 1 H, *p*-C*H*$_{ar.}$), 7.34−7.40 (m, 2 H, *m*-C*H*$_{ar.}$), 8.14 (d/d, *J* = 1.68/0.73 Hz, 1 H, C*H*O); (*E*): δ = 0.94 (t, *J* = 7.48 Hz, 3 H, CH$_2$C*H*$_3$), 1.17 (d, *J* = 6.86 Hz, 3 H, NCHC*H*$_3$), 1.61−1.75 (m, 2 H, C*H*$_2$CH$_3$), 3.72 (d/q/d, *J* = 9.77/6.79/4.96 Hz, 1 H, NC*H*CH$_3$), 4.01 (d/d/d/d, *J* = 8.54/7.18/3.81/3.74 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.30 (d/d, *J* = 12.05/3.81 Hz, 1 H, C*H*$_2$NO$_2$), 4.34 (d, *J* = 5.03 Hz, 1 H, C*H*C$_{ar.}$), 4.44 (d/d, *J* = 12.05/8.47 Hz, 1 H, C*H*$_2$NO$_2$), 5.68 (br. d/d, *J* = 10.90/10.45 Hz, 1 H, N*H*), 7.19 (m, 2 H, *o*-C*H*$_{ar.}$), 7.31 (m, 1 H, *p*-C*H*$_{ar.}$), 7.34−7.40 (m, 2 H, *m*-C*H*$_{ar.}$), 7.87 (d, *J* = 11.67 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.86 (t, *J* = 7.48 Hz, 3 H, CH$_2$C*H*$_3$), 0.98 (d, *J* = 6.95 Hz, 3 H, NCHC*H*$_3$), 1.49 (d/d/q, *J* = 14.35/7.84/7.47 Hz, 1 H, C*H*$_2$CH$_3$), 1.61 (d/q/d, *J* = 14.34/7.63/4.96 Hz, 1 H, C*H*$_2$CH$_3$), 4.00 (d/d/d/d, *J* = 7.86/7.17/4.96/3.59 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.22 (d/q/d/d, *J* = 8.93/6.94/3.05/0.92 Hz, 1 H, NC*H*CH$_3$), 4.53 (d/d, *J* = 12.13/7.17 Hz, 1 H, C*H*$_2$NO$_2$), 4.57 (d/d, *J* = 12.13/3.58 Hz, 1 H, C*H*$_2$NO$_2$), 4.65 (d, *J* = 3.05 Hz, 1 H, C*H*C$_{ar.}$), 6.06 (br. d, *J* = 7.93 Hz, 1 H, N*H*), 7.26−7.40 (m, 5 H, C*H*$_{ar.}$), 8.17 (d/d, *J* = 1.61/0.84 Hz, 1 H, C*H*O); (*E*): δ = 0.83 (t, *J* = 7.47 Hz, 3 H, CH$_2$C*H*$_3$), 1.08 (d, *J* = 6.94 Hz, 3 H, NCHC*H*$_3$), 1.44−1.64 (m, 2 H, C*H*$_2$CH$_3$), 3.76 (d/q/d, *J* = 9.84/7.09/4.50 Hz, 1 H, NC*H*CH$_3$), 4.00 (m, 1 H, C*H*CH$_2$NO$_2$), 4.32 (d, *J* = 4.50 Hz, 1 H, C*H*C$_{ar.}$), 4.50 (d, *J* = 5.80 Hz, 1 H, C*H*$_2$NO$_2$), 4.50 (d, *J* = 5.04 Hz, 1 H, C*H*$_2$NO$_2$), 5.47 (br. d/d, *J* = 10.84/10.60 Hz, 1 H, N*H*), 7.26−7.40 (m, 5 H, C*H*$_{ar.}$), 7.93 (d, *J* = 11.83 Hz, 1 H, C*H*O). − $^{13}$C NMR (125 MHz): major diastereomer: (*Z*): δ = 8.55 (CH$_2$*C*H$_3$), 13.90 (NCH*C*H$_3$), 22.87 (*C*H$_2$CH$_3$), 48.94 (N*C*HCH$_3$), 74.38 (*C*HCH$_2$NO$_2$), 78.48 (*C*H$_2$NO$_2$), 80.27 (*C*HC$_{ar.}$), 127.14 (*o*-*C*H$_{ar.}$), 128.38 (*p*-*C*H$_{ar.}$), 128.59 (*m*-*C*H$_{ar.}$), 137.55 (*i*-*C*$_{ar.}$), 160.45

(*C*HO); (*E*): δ = 8.48 ($CH_2CH_3$), 17.16 ($NCHCH_3$), 22.94 ($CH_2CH_3$), 52.85 ($NCHCH_3$), 74.38 ($CHCH_2NO_2$), 78.43 ($CH_2NO_2$), 82.29 ($CHC_{ar.}$), 127.72 (*o*-$CH_{ar.}$), 128.81 (*m*-$CH_{ar.}$), 128.94 (*p*-$CH_{ar.}$), 136.37 (*i*-$C_{ar.}$), 163.88 (*C*HO); minor diastereomer: (*Z*): δ = 9.32 ($CH_2CH_3$), 13.03 ($NCHCH_3$), 25.30 ($CH_2CH_3$), 49.28 ($NCHCH_3$), 77.73 ($CH_2NO_2$), 78.23 ($CHCH_2NO_2$), 82.82 ($CHC_{ar.}$), 126.71 (*o*-$CH_{ar.}$), 128.02 (*p*-$CH_{ar.}$), 128.42 (*m*-$CH_{ar.}$), 139.13 (*i*-$C_{ar.}$), 160.82 (*C*HO); (*E*): δ = 9.21 ($CH_2CH_3$), 17.22 ($NCHCH_3$), 25.80 ($CH_2CH_3$), 52.61 ($NCHCH_3$), 77.94 ($CH_2NO_2$), 78.23 ($CHCH_2NO_2$), 84.32 ($CHC_{ar.}$), 127.85 (*o*-$CH_{ar.}$), 128.68 (*m*-$CH_{ar.}$), 128.82 (*p*-$CH_{ar.}$), 136.90 (*i*-$C_{ar.}$), 164.18 (*C*HO). − MS (70 eV); *m*/*z* (%): 281 (0.2) [$M^+$ + 1], 208 (38.9), 178 (15.4), 107 (80.6), 102 (100), 79 (25.6). − $C_{14}H_{20}N_2O_4$ (280.32): calcd. C 59.99, H 7.19, N 9.99; found C 60.32, H 7.19, N 10.21.

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(1′-nitromethylbutoxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8c**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-1-nitropent-1-ene (**2c**) (576 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 765 mg (52%), m.p. 87°C. − *de* = 94% (≥ 96% after chromatography). − $[\alpha]_D^{24}$ = −127.0 (*c* = 0.82, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3034 $cm^{-1}$ (m), 2974 (m), 2928 (m), 2879 (m), 2860 (s), 1681 (s), 1655 (s), 1553 (s), 1527 (s), 1454 (m), 1413 (m), 1388 (s), 1373 (s), 1238 (s), 1152 (m), 1095 (s), 1038 (s), 753 (s), 706 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.93 (t, *J* = 7.28 Hz, 3 H, $CH_2CH_3$), 1.06 (d, *J* = 6.94 Hz, 3 H, $NCHCH_3$), 1.20−1.45 (m, 2 H, $CH_2CH_3$), 1.50−1.72 (m, 2 H, $CHCH_2CH_2$), 4.04 (d/d/d/d, *J* = 7.67/7.67/3.95/3.95 Hz, 1 H, $CHCH_2NO_2$), 4.22 (d/q/d/d, *J* = 9.75/6.87/3.71/0.90 Hz, 1 H, $NCHCH_3$), 4.36 (d/d, *J* = 11.92/3.88 Hz, 1 H, $CH_2NO_2$), 4.46 (d/d, *J* = 11.92/8.14 Hz, 1 H, $CH_2NO_2$), 4.66 (d, *J* = 3.71 Hz, 1 H, $CHC_{ar.}$), 6.02 (br. d, *J* = 7.96 Hz, 1 H, N*H*), 7.22−7.26 (m, 2 H, *o*-$CH_{ar.}$), 7.30−7.40 (m, 3 H, *p*,*m*-$CH_{ar.}$), 8.12 (d, *J* = 0.89 Hz, 1 H, C*H*O); (*E*): δ = 0.94 (t, *J* = 7.32 Hz, 3 H, $CH_2CH_3$), 1.17 (d, *J* = 6.79 Hz, 3 H, $NCHCH_3$), 1.20−1.45 (m, 2 H, $CH_2CH_3$), 1.50−1.72 (m, 2 H, $CHCH_2CH_2$), 3.71 (d/q/d, *J* = 8.11/6.90/5.02 Hz, 1 H, $NCHCH_3$), 4.04 (m, Σ*J* = 23.8 Hz, 1 H, $CHCH_2NO_2$), 4.30 (d/d, *J* = 12.01/3.77 Hz, 1 H, $CH_2NO_2$), 4.34 (d, *J* = 5.01 Hz, 1 H, $CHC_{ar.}$), 4.42 (d/d, *J* = 12.02/7.77 Hz, 1 H, $CH_2NO_2$), 5.82 (br. d/d, *J* = 11.54/9.00 Hz, 1 H, N*H*), 7.16−7.20 (m, 2 H, *o*-$CH_{ar.}$), 7.27−7.41 (m, 3 H, *p*,*m*-$CH_{ar.}$), 7.84 (d, *J* = 11.88 Hz, 1 H, C*H*O); minor diastereomer: (*Z*) δ = 0.80 (t, *J* = 7.22 Hz, 3 H, $CH_2CH_3$), 1.09 (d, *J* = 6.97 Hz, 3 H, $NCHCH_3$), 4.50 (d/d, *J* = 12.10/6.71 Hz, 1 H, $CH_2NO_2$), 4.58 (d/d, *J* = 12.10/3.36 Hz, 1 H, $CH_2NO_2$), 4.63 (d, *J* = 3.35 Hz, 1 H, $CHC_{ar.}$), 8.14 (d, *J* = 0.84 Hz, 1 H, C*H*O); (*E*): δ = 7.86 (d, *J* = 11.95 Hz, 1 H, C*H*O), other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.95 ($NCHCH_3$), 14.08 ($CH_2CH_3$), 17.82 ($CH_2CH_3$), 32.34 ($CHCH_2CH_2$), 48.90 ($NCHCH_3$), 73.58 ($CHCH_2NO_2$), 78.84 ($CH_2NO_2$), 80.38 ($CHC_{ar.}$), 127.08 (*o*-$CH_{ar.}$), 128.30 (*p*-$CH_{ar.}$), 128.51 (*m*-$CH_{ar.}$), 137.56 (*i*-$C_{ar.}$), 160.45 (*C*HO); (*E*): δ = 14.08 ($CH_2CH_3$), 17.20 ($NCHCH_3$), 17.82 ($CH_2CH_3$), 32.34 ($CHCH_2CH_2$), 52.88 ($NCHCH_3$), 73.58 ($CHCH_2NO_2$), 78.84 ($CH_2NO_2$), 82.35 ($CHC_{ar.}$), 127.67 (*o*-$CH_{ar.}$), 128.73 (*m*-$CH_{ar.}$), 128.86 (*p*-$CH_{ar.}$), 136.39 (*i*-$C_{ar.}$), 163.95 (*C*HO). − MS (70 eV); *m*/*z* (%): 295 (0.5) [$M^+$ + 1], 249 (2.5), 223 (8.4), 222 (59.0), 178 (18.2), 116 (54.6), 107 (100), 69 (69.6). − $C_{15}H_{22}N_2O_4$ (294.35): calcd. C 61.21, H 7.53, N 9.52; found C 61.54, H 7.52, N 10.01.

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8d**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (576 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 1.28 g (87%). − *de* = 96% (≥ 98% after chromatography). − $[\alpha]_D^{24}$ = −130.5 (*c* = 1.00, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2967 $cm^{-1}$ (m), 2937 (m), 1670 (s), 1557 (s), 1454 (m), 1386 (s), 1304 (w), 1230 (m), 1078 (m), 1029 (m). − $^1$H NMR (500 MHz): major diastereomer: (*Z*): δ = 0.91 [d, *J* = 6.95 Hz, 3 H, $CH(CH_3)_2$], 0.98 [d, *J* = 6.95 Hz, 3 H, $CH(CH_3)_2$], 1.09 (d, *J* = 6.87 Hz, 3 H, $NCHCH_3$), 2.16 [sept/d, *J* = 6.95/3.51 Hz, 1 H, $CH(CH_3)_2$], 3.98 (d/d/d, *J* = 9.08/3.66/3.51 Hz, 1 H, $CHCH_2NO_2$), 4.23 (d/q/d/d, *J* = 8.77/6.79/3.97/0.77 Hz, 1 H, $NCHCH_3$), 4.30 (d/d, *J* = 12.05/3.32 Hz, 1 H, $CH_2NO_2$), 4.42 (d/d, *J* = 12.06/9.01 Hz, 1 H, $CH_2NO_2$), 4.68 (d, *J* = 3.97 Hz, 1 H, $CHC_{ar.}$), 5.95 (br. d, *J* = 8.39 Hz, 1 H, N*H*), 7.21 (m, 2 H, *o*-$CH_{ar.}$), 7.30 (m, 1 H, *p*-$CH_{ar.}$), 7.35 (m, 2 H, *m*-$CH_{ar.}$), 8.13 (d, *J* = 1.01 Hz, 1 H, C*H*O); (*E*): δ = 0.91 [d, *J* = 6.95 Hz, 3 H, $CH(CH_3)_2$], 0.99 [d, *J* = 6.94 Hz, 3 H, $CH(CH_3)_2$], 1.19 (d, *J* = 6.79 Hz, 3 H, $NCHCH_3$), 2.14 [sept/d, *J* = 6.95/3.51 Hz, 1 H, $CH(CH_3)_2$], 3.73 (d/q/d, *J* = 9.61/6.86/5.34 Hz, 1 H, $NCHCH_3$), 3.96 (d/d/d, *J* = 8.85/3.74/3.43 Hz, 1 H, $CHCH_2NO_2$), 4.32 (d/d, *J* = 12.21/*J* = 3.36 Hz, 1 H, $CH_2NO_2$), 4.32 (d, *J* = 5.95 Hz, 1 H, $CHC_{ar.}$), 4.38 (d/d, *J* = 12.21/8.85 Hz, 1 H, $CH_2NO_2$), 5.76 (br. d/d, *J* = 11.13/10.08 Hz, 1 H, N*H*), 7.15 (m, 2 H, *o*-$CH_{ar.}$), 7.34 (m, 1 H, *p*-$CH_{ar.}$), 7.35 (m, 2 H, *m*-$CH_{ar.}$), 7.87 (d, *J* = 11.75 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.84 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 0.89 [d, *J* = 6.94 Hz, 3 H, $CH(CH_3)_2$], 1.02 (d, *J* = 6.87 Hz, 3 H, $NCHCH_3$), 1.85 [sept/d, *J* = 6.95/4.58 Hz, 1 H, $CH(CH_3)_2$], 3.98 (d/d/d, *J* = 8.39/4.58/2.97 Hz, 1 H, $CHCH_2NO_2$), 4.18 (d/q/d/d, *J* = 9.47/6.95/3.21/0.92 Hz, 1 H, $NCHCH_3$), 4.48 (d/d, *J* = 12.28/2.97 Hz, 1 H, $CH_2NO_2$), 4.57 (d/d, *J* = 12.29/8.40 Hz, 1 H, $CH_2NO_2$), 4.63 (d, *J* = 3.20 Hz, 1 H, $CHC_{ar.}$), 5.93 (br. d, *J* = 7.86 Hz, 1 H, N*H*), 7.28 (m, 1 H, *p*-$CH_{ar.}$), 7.34 (m, 2 H, *m*-$CH_{ar.}$), 7.35 (m, 2 H, *o*-$CH_{ar.}$), 8.15 (d, *J* = 1.01 Hz, 1 H, C*H*O); (*E*): δ = 0.84 [d, *J* = 6.87 Hz, 3 H, $CH(CH_3)_2$], 0.86 [d, *J* = 6.94 Hz, 3 H, $CH(CH_3)_2$], 1.08 (d, *J* = 6.87 Hz, 3 H, $NCHCH_3$), 1.79 [sept/d, *J* = 6.87/4.81 Hz, 1 H, $CH(CH_3)_2$], 3.78 (d/q/d, *J* = 9.84/7.01/4.50 Hz, 1 H, $NCHCH_3$), 3.94 (d/d/d, *J* = 8.39/4.58/2.97 Hz, 1 H, $CHCH_2NO_2$), 4.29 (d, *J* = 4.43 Hz, 1 H, $CHC_{ar.}$), 4.46 (d/d, *J* = 12.52/7.63 Hz, 1 H, $CH_2NO_2$), 4.54 (d/d, *J* = 12.51/3.28 Hz, 1 H, $CH_2NO_2$), 5.39 (br. d/d, *J* = 11.52/11.06 Hz, 1 H, N*H*), 7.25 (m, 2 H, *o*-$CH_{ar.}$), 7.26 (m, 1 H, *p*-$CH_{ar.}$), 7.36 (m, 2 H, *m*-$CH_{ar.}$), 7.94 (d, *J* = 11.82 Hz, 1 H, C*H*O). − $^{13}$C NMR (125 MHz): major diastereomer: (*Z*): δ = 14.25 ($NCHCH_3$), 16.12 [$CH(CH_3)_2$], 18.08 [$CH(CH_3)_2$], 27.72 [$CH(CH_3)_2$], 49.08 ($NCHCH_3$), 76.29 ($CH_2NO_2$), 78.14 ($CHCH_2NO_2$), 80.46 ($CHC_{ar.}$), 127.26 (*o*-$CH_{ar.}$), 128.41 (*p*-$CH_{ar.}$), 128.55 (*m*-$CH_{ar.}$), 137.50 (*i*-$C_{ar.}$), 160.47 (*C*HO); (*E*): δ = 16.35 [$CH(CH_3)_2$], 17.46 ($NCHCH_3$), 17.97 [$CH(CH_3)_2$], 28.03 [$CH(CH_3)_2$], 52.90 ($NCHCH_3$), 76.37 ($CH_2NO_2$), 78.32 ($CHCH_2NO_2$), 82.72 ($CHC_{ar.}$), 127.81 (*o*-$CH_{ar.}$), 128.78 (*m*-$CH_{ar.}$), 128.97 (*p*-$CH_{ar.}$), 136.15 (*i*-$C_{ar.}$), 163.83 (*C*HO); minor diastereomer: (*Z*): δ = 13.16 ($NCHCH_3$), 16.52 [$CH(CH_3)_2$], 18.67 [$CH(CH_3)_2$], 30.02 [$CH(CH_3)_2$], 49.50 ($NCHCH_3$), 75.99 ($CH_2NO_2$), 82.35 ($CHCH_2NO_2$), 83.34 ($CHC_{ar.}$), 126.92 (*o*-$CH_{ar.}$), 128.02 (*p*-$CH_{ar.}$), 128.34 (*m*-$CH_{ar.}$), 139.15 (*i*-$C_{ar.}$), 160.83 (*C*HO); (*E*): δ = 17.09 [$CH(CH_3)_2$], 17.42 ($NCHCH_3$), 18.32 [$CH(CH_3)_2$], 30.79 [$CH(CH_3)_2$], 52.54 ($NCHCH_3$), 76.39 ($CH_2NO_2$), 80.52 ($CHCH_2NO_2$), 84.46 ($CHC_{ar.}$), 128.05 (*o*-$CH_{ar.}$), 128.63 (*m*-$CH_{ar.}$), 128.84 (*p*-$CH_{ar.}$), 136.69 (*i*-$C_{ar.}$), 164.22 (*C*HO). − MS (70 eV); *m*/*z* (%): 295 (0.2) [$M^+$ + 1], 222 (41.9), 178 (15.0), 116 (45.5), 107 (77.0), 69 (100). − $C_{15}H_{22}N_2O_4$ (294.35): calcd. C 61.21, H 7.53, N 9.52; found C 61.14, H 7.76, N 9.71.

*(1R,2S,1′S)-(+)-N-[1-Methyl-2-(2′-methyl-1′-nitromethylpropoxy)-2-phenylethyl]formamide* (1*R*,2*S*,1′*S*)-**8d** was obtained as

colourless oil according to *GP 1* by adding (1*S*,2*R*)-(+)-*N*-formylnorephedrine [(1*S*,2*R*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-3-methyl-1-nitrobut-1-ene (**2d**) (576 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 1.27 g (86%). − $[\alpha]_D^{24}$ = +129.8 (*c* = 1.08, $CHCl_3$).

*(1S,2R,1′R)-(−)-N-[2-(2′,2′-Dimethyl-1′-nitromethylpropoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8e**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (896 mg, 5.0 mmol) and NaH (182 mg, 5.5 mmol 80%) to (*E*)-3,3-dimethyl-1-nitrobut-1-ene (**2e**) (646 mg, 5.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 1.03 g (67%). − *de* ≥ 96% (≥ 98% after chromatography). − $[\alpha]_D^{24}$ = −106.6 (*c* = 1.46, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2968 $cm^{-1}$ (s), 2913 (m), 2875 (s), 1683 (s), 1556 (s), 1509 (s), 1482 (s), 1455 (s), 1384 (s), 1344 (m), 1220 (s), 1083 (s), 1044 (m), 1030 (m). − $^1$H NMR (500 MHz): (*Z*): δ = 1.04 (s, 9 H, C(C$H_3$)$_3$], 1.11 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 3.98 (d/d, *J* = 5.72/3.89 Hz, 1 H, C*H*C$H_2$NO$_2$), 4.21 (d/d, *J* = 13.88/5.73 Hz, 1 H, C$H_2$NO$_2$), 4.33 (d/d, *J* = 13.89/4.04 Hz, 1 H, C$H_2$NO$_2$), 4.38 (d/q/d/d, *J* = 9.01/6.87/4.20/0.84 Hz, 1 H, NC*H*CH$_3$), 4.58 (d, *J* = 4.19 Hz, 1 H, C*H*C$_{ar.}$), 5.76 (br. d, *J* = 8.74 Hz, 1 H, N*H*), 7.27 (m, 2 H, *o*-C$H_{ar.}$), 7.29−7.37 (m, 3 H, *m*,*p*-C$H_{ar.}$), 8.08 (d/d, *J* = 1.14/0.85 Hz, 1 H, C*H*O); (*E*): δ = 1.02 [s, 9 H, C(C$H_3$)$_3$], 1.12 (d, *J* = 6.86 Hz, 3 H, NCHC$H_3$), 3.88 (d/q/d, *J* = 9.61/6.87/4.58 Hz, 1 H, NC*H*CH$_3$), 3.99 (d/d, *J* = 5.95/3.51 Hz, 1 H, C*H*C$H_2$NO$_2$), 4.22 (d/d, *J* = 13.96/6.18 Hz, 1 H, C$H_2$NO$_2$), 4.30 (d/d, *J* = 13.96/3.51 Hz, 1 H, C$H_2$NO$_2$), 4.33 (d, *J* = 4.50 Hz, 1 H, C*H*C$_{ar.}$), 5.57 (br. d/d, *J* = 10.83/10.38 Hz, 1 H, N*H*), 7.19 (m, 2 H, *o*-C$H_{ar.}$), 7.29−7.37 (m, 3 H, *m*,*p*-C$H_{ar.}$), 7.96 (d, *J* = 11.82 Hz, 1 H, C*H*O). − $^{13}$C NMR (125 MHz): (*Z*): δ = 15.65 [C(*C*H$_3$)$_3$], 26.15 (NCH*C*H$_3$), 36.12 [*C*(CH$_3$)$_3$], 48.61 (N*C*HCH$_3$), 77.03 (*C*H$_2$NO$_2$), 84.27 (*C*HC$_{ar.}$), 84.68 (*C*HCH$_2$NO$_2$), 127.18 (*o*-*C*H$_{ar.}$), 128.40 (*p*-*C*H$_{ar.}$), 128.56 (*m*-*C*H$_{ar.}$), 138.66 (*i*-*C*$_{ar.}$), 160.45 (*C*HO); (*E*): δ = 17.80 [C(*C*H$_3$)$_3$], 26.17 (NCH*C*H$_3$), 36.03 [*C*(CH$_3$)$_3$], 52.38 (N*C*HCH$_3$), 77.30 (*C*H$_2$NO$_2$), 84.76 (*C*HCH$_2$NO$_2$), 85.94 (*C*HC$_{ar.}$), 127.80 (*o*-*C*H$_{ar.}$), 128.69 (*m*-*C*H$_{ar.}$), 128.88 (*p*-*C*H$_{ar.}$), 137.07 (*i*-*C*$_{ar.}$), 163.95 (C*H*O). − MS (70 eV); *m*/*z* (%): 263 (1.1), 236 (48.0), 178 (12.1), 130 (31.4), 107 (69.1), 83 (100). − $C_{16}H_{24}N_2O_4$ (308.38): calcd. C 62.32, H 7.84, N 9.08; found C 62.37, H 8.04, N 9.02.

*(1S,2R,1′R)-(−)-N-[2-(1′-Cyclohexyl-2′-nitroethoxy)-1-methyl2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8f**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (359 mg, 2.0 mmol) and NaH (73 mg, 2.2 mmol 80%) to (*E*)-(2-nitrovinyl)cyclohexane (**2f**) (310 mg, 2.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 569 mg (85%), m.p. 76°C − *de* = 94%. − $[\alpha]_D^{24}$ = −155.1 (*c* = 1.08, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2978 $cm^{-1}$ (m), 2929 (s), 2855 (s), 1668 (s), 1556 (s), 1495 (m), 1452 (s), 1376 (m), 1221 (m), 1091 (m), 1068 (s), 1029 (m). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.85−1.07 (m, 2 H, C$H_2$), 1.00 (d, *J* = 7.05 Hz, 1 H, NCHC$H_3$), 1.12−1.35 (m, 3 H, C$H_2$), 1.60 (m, 1 H, C$H_2$), 1.67−1.92 (m, 5 H, C*H*CH$_2$), 3.94 (d/d/d, *J* = 8.73/7.05/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.22 (d/q/d/d, *J* = 8.73/6.97/3.77/0.68 Hz, 1 H, NC*H*CH$_3$), 4.31 (d/d, *J* = 12.09/3.56 Hz, 1 H, C$H_2$NO$_2$), 4.44 (d/d, *J* = 12.09/8.72 Hz, 1 H, C$H_2$NO$_2$), 4.67 (d, *J* = 3.86 Hz, 1 H, C*H*C$_{ar.}$), 5.90 (br. d, *J* = 8.73 Hz, 1 H, N*H*), 7.22 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.40 (m, 3 H, *m*,*p*-C$H_{ar.}$), 8.12 (d, *J* = 0.70 Hz, 1 H, C*H*O); (*E*): δ = 0.85−1.07 (m, 2 H, C$H_2$), 1.18 (d, *J* = 7.05 Hz, 1 H, NCHC$H_3$), 1.12−1.35 (m, 3 H, C$H_2$), 1.60 (m, 1 H, C$H_2$), 1.67−1.92 (m, 5 H, C*H*CH$_2$), 3.74 (d/q/d, *J* = 9.74/6.71/4.36 Hz, 1 H, NC*H*CH$_3$), 3.93 (d/d/d, *J* = 8.64/7.03/3.69 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.27 (d/d, *J* = 12.76/3.69 Hz, 1 H, C$H_2$NO$_2$), 4.31 (d, *J* = 5.38 Hz, 1 H, C*H*C$_{ar.}$), 4.39 (d/d, *J* = 12.76/8.64 Hz, 1 H, C$H_2$NO$_2$), 5.69 (br. t, *J* = 10.75 Hz, 1 H, N*H*), 7.16 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.40 (m, 3 H, *m*,*p*-C$H_{ar.}$), 7.85 (d, *J* = 11.75 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 4.50 (d/d, *J* = 12.34/3.19 Hz, 1 H, C$H_2$NO$_2$), 4.59 (d/d, *J* = 12.34/7.64 Hz, 1 H, C$H_2$NO$_2$), 4.60 (d, *J* = 3.35 Hz, 1 H, C*H*C$_{ar.}$), other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 14.19 (NCH*C*H$_3$), 26.13 (*C*H$_2$CH$_2$CH), 26.24 (CHCH$_2$*C*H$_2$), 26.39 (CH$_2$*C*H$_2$CH$_2$), 27.33 (CH*C*H$_2$), 28.81 (*C*H$_2$CH), 38.42 (CH$_2$*C*HCH$_2$), 49.07 (N*C*HCH$_3$), 76.88 (*C*H$_2$NO$_2$), 78.12 (*C*HCH$_2$NO$_2$), 80.58 (*C*HC$_{ar.}$), 127.15 (*o*-*C*H$_{ar.}$), 128.33 (*p*-*C*H$_{ar.}$), 128.50 (*m*-*C*H$_{ar.}$), 137.53 (*i*-*C*$_{ar.}$), 160.29 (*C*HO); (*E*): δ = 17.40 (NCH*C*H$_3$), 26.13 (*C*H$_2$CH$_2$CH), 26.24 (CHCH$_2$*C*H$_2$), 26.39 (CH$_2$*C*H$_2$CH$_2$), 27.54 (CH*C*H$_2$), 28.67 (*C*H$_2$CH), 38.79 (CH$_2$*C*HCH$_2$), 52.77 (N*C*HCH$_3$), 76.88 (*C*H$_2$NO$_2$), 78.34 (*C*HCH$_2$NO$_2$), 82.99 (*C*HC$_{ar.}$), 127.73 (*o*-*C*H$_{ar.}$), 128.72 (*m*-*C*H$_{ar.}$), 128.90 (*p*-*C*H$_{ar.}$), 136.37 (*i*-*C*$_{ar.}$), 163.76 (*C*HO). − MS (70 eV); *m*/*z* (%): 335 (19.7) [$M^+$ + 1], 262 (14.6), 162 (100), 134 (46.5), 117 (21.7), 109 (62.9). − $C_{18}H_{26}N_2O_4$ (334.41): calcd. C 64.65, H 7.84, N 8.38; found C 64.85, H 7.60, N 8.64.

*(1S,2R,1′S)-(−)-N-[2-(1′-Diethoxymethyl-2′-nitroethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*S*)-**8g**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (125 mg, 0.70 mmol) and NaH (23 mg, 0.77 mmol 80%) to (*E*)-3,3-diethoxy-1-nitroprop-1-ene (**2g**) (123 mg, 0.70 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 87 mg (35%), m.p. 70°C − *de* = 96% (≥ 96% after chromatography). − $[\alpha]_D^{24}$ = −78.2 (*c* = 0.95, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2978 $cm^{-1}$ (s), 2931 (m), 2879 (m), 1685 (s), 1556 (s), 1495 (m), 1453 (s), 1425 (s), 1383 (s), 1314 (m), 1267 (m), 1223 (m), 1102 (s), 1064 (s), 1029 (m), 746 (m), 704 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 1.01 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.23 (t, *J* = 7.14 Hz, 3 H, CH$_2$C$H_3$), 1.24 (t, *J* = 7.14 Hz, 3 H, CH$_2$C$H_3$), 3.58 (d/q, *J* = 9.34/7.14, 1 H, C$H_2$CH$_3$), 3.61 (d/q, *J* = 9.34/7.14 Hz, 1 H, C$H_2$CH$_3$), 3.76 (d/q, *J* = 10.71/7.14 Hz, 1 H, C$H_2$CH$_3$), 3.79 (d/q, *J* = 10.72/7.14, 1 H, C$H_2$CH$_3$), 4.12 (d/d/d, *J* = 6.95/4.53/4.43 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.25 (d/q/d/d, *J* = 9.07/6.87/3.30/0.83 Hz, 1 H, NC*H*CH$_3$), 4.53 (d/d, *J* = 12.91/4.39 Hz, 1 H, C$H_2$NO$_2$), 4.58 (d/d, *J* = 12.91/6.60 Hz, 1 H, C$H_2$NO$_2$), 4.73 (d, *J* = 4.67 Hz, 1 H, OC*H*O), 4.78 (d, *J* = 3.29 Hz, 1 H, C*H*C$_{ar.}$), 6.17 (br. d, *J* = 8.52 Hz, 1 H, N*H*), 7.16−7.26 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.41 (m, 3 H, *p*,*m*-C$H_{ar.}$), 8.15 (d, *J* = 0.83 Hz, 1 H, C*H*O); (*E*): δ = 1.13 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.22 (t, *J* = 7.14 Hz, 3 H, CH$_2$C$H_3$), 1.25 (t, *J* = 7.14 Hz, 3 H, CH$_2$C$H_3$), 3.53−3.67 (m, 2 H, C$H_2$CH$_3$), 3.70−3.81 (m, 2 H, *C*H$_2$CH$_3$), 3.87 (d/q/d, *J* = 9.61/6.90/4.40 Hz, 1 H, NC*H*CH$_3$), 4.06 (d/d/d, *J* = 7.69/4.95/3.84 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.48 (d/d, *J* = 12.84/6.94 Hz, 1 H, C$H_2$NO$_2$), 4.55 (d/d, *J* = 12.84/6.94 Hz, 1 H, C$H_2$NO$_2$), 4.63 (d, *J* = 4.67 Hz, 1 H, C*H*C$_{ar.}$), 4.68 (d, *J* = 4.94 Hz, 1 H, OC*H*O), 5.94 (br. t, *J* = 11.81 Hz, 1 H, N*H*), 7.16−7.26 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.41 (m, 3 H, *p*,*m*-C$H_{ar.}$), 7.94 (d, *J* = 11.81 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 13.63 (NCH*C*H$_3$), 15.30, 15.37 (CH$_2$*C*H$_3$), 48.97 (N*C*HCH$_3$), 64.53, 64.70 (*C*H$_2$CH$_3$), 75.91 (*C*H$_2$NO$_2$), 76.11 (*C*HCH$_2$NO$_2$), 83.30 (*C*HC$_{ar.}$), 101.30 (O*C*HO), 126.71 (*o*-*C*H$_{ar.}$), 128.32 (*p*-*C*H$_{ar.}$), 128.53 (*m*-*C*H$_{ar.}$), 137.61 (*i*-*C*$_{ar.}$), 160.25 (*C*HO); (*E*): δ = 15.30, 15.37 (CH$_2$*C*H$_3$), 16.83 (NCH*C*H$_3$), 52.85 (N*C*HCH$_3$), 64.53, 64.70 (*C*H$_2$CH$_3$), 75.41 (*C*H$_2$NO$_2$), 76.11 (*C*HCH$_2$NO$_2$), 84.45 (*C*HC$_{ar.}$), 101.49 (O*C*HO), 127.42 (*o*-*C*H$_{ar.}$), 128.72 (*m*-*C*H$_{ar.}$), 128.82 (*p*-*C*H$_{ar.}$), 136.61 (*i*-*C*$_{ar.}$), 163.75 (*C*HO). − MS (70 eV); *m*/*z* (%): 283 (2.7), 282 (17.2), 178 (2.5), 162 (6.1), 135 (100), 103 (43.9). −

$C_{17}H_{26}N_2O_6$ (354.40): calcd. C 57.61, H 7.39, N 7.90; found C 57.54, H 6.98, N 8.25.

*(1S,2R,1′S)-(−)-N-{1-Methyl-2-[1-(α-naphth-1′-yloxymethyl)-2-nitroethoxy]-2-phenylethyl}formamide* [(1*S*,2*R*,1′*S*)-**8h**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (109 mg, 0.61 mmol) and NaH (22 mg, 0.67 mmol 80%) to (*E*)-1-(3-nitroallyloxy)naphthalene (**2h**) (139 mg, 0.61 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 119 mg (48%), m.p. 47°C. − *de* = 96% (≥ 96% after chromatography). − $[\alpha]_D^{24}$ = −145.7 (*c* = 0.65, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2979 $cm^{-1}$ (m), 2932 (m), 2874 (m), 1685 (s), 1580 (s), 1556 (s), 1509 (s), 1456 (s), 1388 (s), 1269 (s), 1241 (s), 1179 (m), 1157 (m), 1102 (s), 1072 (m), 1022 (m), 794 (s), 774 (s), 746 (m), 704 (m). − $^1$H NMR (300 MHz): (*Z*): δ = 1.00 (d, *J* = 6.78 Hz, 3 H, NCHC$H_3$), 4.18 (d/q/d/d, *J* = 9.09/7.15/3.57/0.82 Hz, 1 H, NC*H*$CH_3$), 4.20 (d/d, *J* = 10.72/3.02 Hz, 1 H, O*H*CH), 4.41 (d/d, *J* = 10.71/3.55 Hz, 1 H, OHC*H*), 4.49 (d/d/d/d, *J* = 7.96/3.85/3.57/3.02 Hz, 1 H, C*H*$CH_2NO_2$), 4.64 (d/d, *J* = 12.63/3.84 Hz, 1 H, C$H_2NO_2$), 4.78 (d, *J* = 3.29 Hz, 1 H, C*H*$C_{ar.}$), 4.92 (d/d, *J* = 12.63/7.96 Hz, 1 H, C$H_2NO_2$), 5.90 (br. d, *J* = 8.79 Hz, 1 H, N*H*), 6.79 (d, *J* = 6.87 Hz, 1 H, C$H_{naphth.}$), 7.24−7.29 (m, 2 H, *o*-C$H_{ar.}$), 7.31−7.41 (m, 4 H, C$H_{naphth.}$, *p*,*m*-C$H_{ar.}$), 7.45 (d, $^4$*J* = 0.82 Hz, 1 H, C*H*O), 7.47−7.55 (m, 3 H, C$H_{naphth.}$), 7.82 (m, Σ*J* = 16.8 Hz, 1 H, C$H_{naphth.}$), 8.19 (m, Σ*J* = 16.1 Hz, 1 H, C$H_{naphth.}$); (*E*): δ = 1.11 (d, *J* = 6.59 Hz, 3 H, NCHC$H_3$), 3.69 (d/q/d, *J* = 9.61/6.59/5.22 Hz, 1 H, NC*H*$CH_3$), 4.24 (d/d, *J* = 10.72/4.12 Hz, 1 H, O*H*CH), 4.30 (d/d, *J* = 10.71/4.67 Hz, 1 H, OHC*H*), 4.49 (m, 1 H, C*H*$C_{ar.}$), 4.50 (m, 1 H, C*H*$CH_2NO_2$), 4.58 (d/d, *J* = 12.63/3.85 Hz, 1 H, C$H_2NO_2$), 4.75 (d/d, *J* = 12.63/7.96 Hz, 1 H, C$H_2NO_2$), 5.57 (br. d/d, *J* = 11.27/10.43 Hz, 1 H, N*H*), 6.77 (d, *J* = 6.87 Hz, 1 H, C$H_{naphth.}$), 7.19−7.24 (m, 2 H, *o*-C$H_{ar.}$), 7.27−7.40 (m, 4 H, C$H_{naphth.}$, *p*,*m*-C$H_{ar.}$), 7.47−7.56 (m, 3 H, C$H_{naphth.}$), 7.78 (d, *J* = 11.82 Hz, 1 H, C*H*O), 7.83 (m, Σ*J* = 17.5 Hz, 1 H, C$H_{naphth.}$), 8.14 (m, Σ*J* = 18.2 Hz, 1 H, C$H_{naphth.}$). − $^{13}$C NMR (75 MHz): (*Z*): δ = 13.39 (NCH*C*$H_3$), 48.78 (N*C*HCH$_3$), 65.51 (O*C*$H_2$), 72.76 (*C*H$CH_2NO_2$), 77.09 (*C*$H_2NO_2$), 81.43 (*C*H$C_{ar.}$), 105.19, 120.95, 121.65 (*C*H$_{naphth.}$), 125.12 (*i*-$C_{naphth.}$), 125.83, 125.98 (*C*H$_{naphth.}$), 126.81 (*o*-*C*H$_{ar.}$), 126.88 (*C*H$_{naphth.}$), 127.98 (*p*-*C*H$_{ar.}$), 128.50 (*C*H$_{naphth.}$), 128.67 (*m*-*C*H$_{ar.}$), 134.57 (*i*-$C_{naphth.}$), 137.08 (*i*-$C_{ar.}$), 153.41 (*i*-$C_{naphth.}$), 160.30 (*C*HO); (*E*): δ = 17.31 (NCH*C*$H_3$), 52.66 (N*C*HCH$_3$), 66.14 (O*C*$H_2$), 72.24 (*C*H$CH_2NO_2$), 77.09 (*C*$H_2NO_2$), 83.51 (*C*H$C_{ar.}$), 104.90, 121.42, 121.51 (*C*H$_{naphth.}$), 125.20 (*i*-$C_{naphth.}$), 125.67, 125.76, 126.81 (*C*H$_{naphth.}$) 127.76 (*o*-*C*H$_{ar.}$), 128.67 (*C*H$_{naphth.}$), 128.92 (*m*-*C*H$_{ar.}$), 129.17 (*p*-*C*H$_{ar.}$), 135.40 (*i*-$C_{naphth.}$), 135.78 (*i*-$C_{ar.}$), 153.59 (*i*-$C_{naphth.}$), 163.88 (*C*HO). − MS (70 eV); *m*/*z* (%): 408 (5.2) [$M^+$], 336 (7.4), 229 (18.2), 143 (60.5), 115 (100). − $C_{23}H_{24}N_2O_5$ (408.45): calcd. C 67.63, H 5.92, N 6.85; found C 67.15, H 6.09, N 6.51.

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(2′-nitromethyl-5′-phenylpent-4′-enyloxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8i**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (179 mg, 1.0 mmol) and NaH (33 mg, 1.1 mmol 80%) to (*E*,*E*)-6-phenyl-1-nitrohexa-1,5-diene (**2i**) (203 mg, 1.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 119 mg (48%), m.p. 144°C. − *de* = 89% (≥ 96% after chromatography). − $[\alpha]_D^{24}$ = −124.4 (*c* = 0.62, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2967 $cm^{-1}$ (m), 2927 (m), 2862 (m), 1659 (s), 1550 (s), 1520 (s), 1451 (s), 1382 (s), 1344 (m), 1262 (m), 1077 (s), 1047 (s), 971 (m), 784 (m), 741 (m), 700 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 1.06 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.81 (m, 2 H, Σ*J* = 69.6 Hz, OCHC$H_2$), 2.27 (m, 2 H, Σ*J* = 56.7 Hz, CHC$H_2$C$H_2$), 4.10 (d/d/d/d, *J* = 7.73/6.87/6.59/4.05 Hz, 1 H, C*H*$CH_2NO_2$), 4.25 (d/q/d/d, *J* = 9.13/6.87/3.60/0.82 Hz, 1 H, NC*H*$CH_3$), 3.78 (d/d, *J* = 10.64/4.12 Hz, 1 H, OCHC$H_2$O), 4.37 (d/d, *J* = 11.95/4.05 Hz, 1 H, C$H_2NO_2$), 4.49 (d/d, *J* = 11.95/7.73 Hz, 1 H, C$H_2NO_2$), 4.68 (d, *J* = 3.57 Hz, 1 H, C*H*$C_{ar.}$), 5.81 (br. d, *J* = 8.86 Hz, 1 H, N*H*), 6.12 (d/t, *J* = 15.73/6.94 Hz, 1 H, C*H*CHC$_{ar.}$), 6.40 (d/t, *J* = 15.73/1.26 Hz, 1 H, CHC*H*C$_{ar.}$), 7.16−7.38 (m, 10 H, C$H_{ar.}$), 8.10 (d, *J* = 0.80 Hz, 1 H, C*H*O); (*E*): δ = 1.15 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.81 (m, 2 H, Σ*J* = 69.6 Hz, OCHC$H_2$), 2.27 (m, 2 H, Σ*J* = 56.7 Hz, CHC$H_2$C$H_2$), 3.72 (d/q/d, *J* = 9.80/6.87/4.12 Hz, 1 H, NC*H*$CH_3$), 4.10 (m, Σ*J* = 24.5 Hz, 1 H, C*H*$CH_2NO_2$), 4.31 (d/d, *J* = 11.76/4.05 Hz, 1 H, C$H_2NO_2$), 4.35 (d, *J* = 3.02 Hz, 1 H, C*H*$C_{ar.}$), 4.42 (d/d, *J* = 11.76/7.90 Hz, 1 H, C$H_2NO_2$), 5.61 (br. d/d, *J* = 10.58/9.61 Hz, 1 H, N*H*), 6.11 (d/t, *J* = 15.72/6.59 Hz, 1 H, C*H*CHC$_{ar.}$), 6.40 (d/t, *J* = 15.73/1.26 Hz, 1 H, CHC*H*C$_{ar.}$), 7.16−7.38 (m, 10 H, C$H_{ar.}$), 7.88 (d, *J* = 11.88 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 1.04 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 4.43 (d/d, *J* = 13.30/5.10 Hz, 1 H, *H*CHNO$_2$), 4.56 (d/d, *J* = 13.15/7.39 Hz, 1 H, C$H_2NO_2$), 4.65 (d, *J* = 3.69 Hz, 1 H, C*H*C$_{ar.}$), 8.02 (d, *J* = 1.50 Hz, 1 H, C*H*O); (*E*): δ = 1.18 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 7.86 (d, *J* = 11.75 Hz, 1 H, C*H*O), other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 14.04 (NCH*C*$H_3$), 27.98 (*C*H$_2$), 30.04 (*C*H$_2$), 48.91 (N*C*HCH$_3$), 73.49 (*C*H$CH_2NO_2$), 78.06 (*C*H$_2NO_2$), 80.85 (*C*HC$_{ar.}$), 126.06 (*o*-*C*H$_{ar.}$), 127.11 (*o*-*C*H$_{ar.}$), 127.41 (CH$_2$*C*H), 128.35 (*p*-*C*H$_{ar.}$), 128.44 (*p*-*C*H$_{ar.}$), 128.61 (*m*-*C*H$_{ar.}$), 128.63 (*m*-*C*H$_{ar.}$), 131.36 (*C*HC$_{ar.}$), 137.00 (*i*-$C_{ar.}$), 137.44 (*i*-$C_{ar.}$), 160.43 (*C*HO); (*E*): δ = 17.21 (NCH*C*$H_3$), 27.91 (*C*H$_2$), 30.04 (*C*H$_2$), 52.76 (N*C*HCH$_3$), 73.40 (*C*H$CH_2NO_2$), 78.66 (*C*H$_2NO_2$), 82.72 (*C*HC$_{ar.}$), 126.06 (*o*-*C*H$_{ar.}$), 127.11 (*o*-*C*H$_{ar.}$), 127.41 (OCH$_2$*C*H), 128.24 (*p*-*C*H$_{ar.}$), 128.61 (*m*-*C*H$_{ar.}$), 128.84 (*m*-*C*H$_{ar.}$), 129.01 (*p*-*C*H$_{ar.}$), 131.36 (*C*HC$_{ar.}$), 136.14 (*i*-$C_{ar.}$), 137.00 (*i*-$C_{ar.}$), 163.89 (*C*HO). − MS (70 eV); *m*/*z* (%): 382 (0.6) [$M^+$], 310 (8.0), 249 (2.7), 167 (23.3), 162 (66.9), 134 (46.8), 117 (100), 91 (42.5). − $C_{22}H_{26}N_2O_4$ (382.46): calcd. C 69.09, H 6.85, N 7.33; found C 68.69, H 6.79, N 7.21.

*(1S,2R,1′S)-(E)-(−)-N-[1-Methyl-2-(2′-nitro-1′-(3′-phenyl allyloxymethyl)ethoxy]-2-phenylethyl]formamide* [(1*S*,2*R*,1′*S*)-**8j**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (358 mg, 2.0 mmol) and NaH (73 mg, 2.2 mmol 80%) to (*E*,*E*)-1-nitro-3-(3-phenyl-allyloxy)prop-1-ene (**2j**) (438 mg, 2.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 517 mg (65%), m.p. 87°C. − *de* = 96% (≥ 96% after chromatography). − $[\alpha]_D^{24}$ = −77.6 (*c* = 0.70, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2927 $cm^{-1}$ (m), 2861 (m), 1682 (s), 1556 (s), 1383 (s), 1309 (m), 1112 (s), 1027 (m), 970 (m), 756 (s), 703 (m). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.99 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 3.57 (d/d, *J* = 10.64/4.12 Hz, 1 H, OCHC$H_2$O), 3.78 (d/d, *J* = 10.64/4.12 Hz, 1 H, OCHC$H_2$O), 4.19 (d/d, *J* = 6.18/1.30 Hz, 2 H, OC$H_2$CH), 4.23 (d/q/d/d, *J* = 9.13/6.87/3.23/0.82 Hz, 1 H, NC*H*$CH_3$), 4.25 (d/d/d/d, *J* = 7.83/4.19/4.12/4.02 Hz, 1 H, C*H*$CH_2NO_2$), 4.48 (d/d, *J* = 12.57/4.19 Hz, 1 H, C$H_2NO_2$), 4.67 (d/d, *J* = 12.57/7.83 Hz, 1 H, C$H_2NO_2$), 4.72 (d, *J* = 3.23 Hz, 1 H, C*H*C$_{ar.}$), 6.25 (d/t, *J* = 15.93/6.18 Hz, 1 H, C*H*CHC$_{ar.}$), 6.51 (br. d/d, *J* = 9.13/1.70 Hz, 1 H, N*H*), 6.62 (d/t, *J* = 15.93/1.23 Hz, 1 H, CHC*H*C$_{ar.}$), 7.16−7.44 (m, 10 H, C$H_{ar.}$), 8.09 (d/d, *J* = 1.70/0.82 Hz, 1 H, C*H*O); (*E*): δ = 1.10 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 3.57 (d/d, *J* = 10.64/4.12 Hz, 1 H, OCHC$H_2$O), 3.70 (d/d, *J* = 10.44/4.39 Hz, 1 H, OCHC$H_2$O), 3.70 (m Σ*J* = 20.1 Hz, 1 H, NC*H*$CH_3$), 4.16−4.30 (m, 3 H, OC$H_2$CH, C*H*$CH_2NO_2$), 4.45 (d/d, *J* = 12.64/3.85 Hz, 1 H, C$H_2NO_2$), 4.51 (d, *J* = 5.22 Hz, 1 H, C*H*C$_{ar.}$), 4.60 (d/d, *J* = 12.63/7.96 Hz, 1 H, C$H_2NO_2$), 5.90 (br. t, *J* = 10.0 Hz, 1 H, N*H*), 6.29 (d/t, *J* = 15.93/6.32 Hz, 1 H,

C*H*CHC$_{ar.}$), 6.61 (br. d, $J$ = 15.93 Hz, 1 H, CHC*H*C$_{ar.}$), 7.16−7.44 (m, 10 H, C*H*$_{ar.}$), 7.97 (d, $J$ = 11.81 Hz, 1 H, C*H*O); minor diastereomer: δ = 0.96 [d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$ (*Z*)], 1.11 [d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$ (*E*)], 6.41 [br. d, $J$ = 7.97 Hz, 1 H, N*H* (*Z*)], 7.94 [d, $J$ = 11.81 Hz, 1 H, C*H*O (*E*)], 8.17 [br. s, 1 H, C*H*O (*Z*)], other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.36 (NCH*C*H$_3$), 49.02 (N*C*HCH$_3$), 66.67 (OCH*C*H$_2$), 72.21 (O*C*H$_2$CH), 73.69 (*C*HCH$_2$NO$_2$), 77.12 (*C*H$_2$NO$_2$), 81.67 (*C*HC$_{ar.}$), 124.44 (OCH$_2$*C*H), 125.56 (*o*-*C*H$_{ar.}$), 126.61 (*o*-*C*H$_{ar.}$), 128.22 (*p*-*C*H$_{ar.}$), 128.27 (*p*-*C*H$_{ar.}$), 128.56 (*m*-*C*H$_{ar.}$), 128.75 (*m*-*C*H$_{ar.}$), 133.81 (*C*HC$_{ar.}$), 136.02 (*i*-*C*$_{ar.}$), 137.48 (*i*-*C*$_{ar.}$), 160.33 (*C*HO); (*E*): δ = 16.56 (NCH*C*H$_3$), 52.88 (N*C*HCH$_3$), 67.75 (OCH*C*H$_2$), 72.21 (O*C*H$_2$CH), 73.34 (*C*HCH$_2$NO$_2$), 77.12 (*C*H$_2$NO$_2$), 82.27 (*C*HC$_{ar.}$), 124.85 (OCH$_2$*C*H), 126.61 (*o*-*C*H$_{ar.}$), 127.24 (*o*-*C*H$_{ar.}$), 128.05 (*p*-*C*H$_{ar.}$), 128.56 (*m*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 128.75 (*p*-*C*H$_{ar.}$), 133.72 (*C*HC$_{ar.}$), 136.26 (*i*-*C*$_{ar.}$), 136.46 (*i*-*C*$_{ar.}$), 163.68 (*C*HO). − MS (70 eV); *m*/*z* (%): 399 (0.4) [M$^+$ + 1], 381 (0.6), 327 (1.0), 266 (2.3), 162 (63.7), 134 (37.0), 117 (100), 116 (13.9), 115 (47.5), 91 (23.0). − $C_{22}H_{26}N_2O_5$ (398.46): calcd. C 66.32, H 6.58, N 7.03; found C 66.30, H 6.47, N 6.88.

*(1S,2R,1′R)-(−)-N-[1-Methyl-2-(2′-nitro-1′-phenylethoxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8k**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (358 mg, 2.0 mmol) and NaH (73 mg, 2.2 mmol 80%) to (*E*)-ω-nitrostyrene (**2k**) (298 mg, 2.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 151 mg (23%), m.p. 74°C. − *de* = 71%. − $[\alpha]_D^{24}$ = −104.6 (*c* = 0.63, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2980 cm$^{-1}$ (m), 2857 (m), 1678 (s), 1555 (s), 1497 (s), 1455 (m), 1380 (s), 1203 (m), 1061 (m), 1029 (m), 755 (m), 702 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 1.15 (d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$), 4.16 (d, $J$ = 5.22 Hz, 1 H, C*H*C$_{ar.}$), 4.42 (d/q/d, $J$ = 9.75/6.80/5.22 Hz, 1 H, NC*H*CH$_3$), 4.51 (d/d, $J$ = 10.71/3.02 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.75 (d/d, $J$ = 13.74/3.30 Hz, 1 H, C*H*$_2$NO$_2$), 4.95 (d/d, $J$ = 13.74/10.98 Hz, 1 H, C*H*$_2$NO$_2$), 5.50 (br. d, $J$ = 10.07 Hz, 1 H, N*H*), 7.10−7.41 (m, 10 H, C*H*$_{ar.}$), 8.00 (br. s, 1 H, C*H*O); (*E*): δ = 1.18 (d, $J$ = 6.80 Hz, 3 H, NCHC*H*$_3$), 3.81 (d/q/d, $J$ = 9.50/6.82/6.04 Hz, 1 H, NC*H*CH$_3$), 3.92 (d, $J$ = 6.04 Hz, 1 H, C*H*C$_{ar.}$), 4.52 (d/d, $J$ = 11.26/8.24 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.92 (d/d, $J$ = 13.73/11.26 Hz, 1 H, C*H*$_2$NO$_2$), 5.06 (d/d, $J$ = 13.75/8.24 Hz, 1 H, C*H*$_2$NO$_2$), 5.35 (br. d, $J$ = 9.80 Hz, 1 H, N*H*), 7.10−7.41 (m, 10 H, C*H*$_{ar.}$), 7.88 (d, $J$ = 11.81 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 1.00 (d, $J$ = 6.94 Hz, 3 H, NCHC*H*$_3$), 4.27 (d, $J$ = 3.48 Hz, 1 H, C*H*C$_{ar.}$), 4.40 (d/q/d, $J$ = 9.07/6.90/3.52 Hz, 1 H, NC*H*CH$_3$), 4.59 (d/d, $J$ = 13.74/3.29 Hz, 1 H, C*H*$_2$NO$_2$), 4.78 (d/d, $J$ = 13.74/10.09 Hz, 1 H, C*H*$_2$NO$_2$), 5.20 (d/d, $J$ = 9.89/3.32 Hz, 1 H, C*H*CH$_2$NO$_2$), 5.96 (br. d, $J$ = 9.80 Hz, 1 H, N*H*), 7.10−7.45 (m, 10 H, C*H*$_{ar.}$), 7.95 (br. s, 1 H, C*H*O); (*E*): δ = 1.10 (d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$), 3.65 (m, Σ$J$ = 19.5 Hz, 1 H, NC*H*CH$_3$), 4.07 (d, $J$ = 5.49 Hz, 1 H, C*H*C$_{ar.}$), 4.66 (d/d, $J$ = 10.72/4.39 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.81 (d/d, $J$ = 13.46/4.39 Hz, 1 H, C*H*$_2$NO$_2$), 5.13 (d/d, $J$ = 13.48/10.98 Hz, 1 H, C*H*$_2$NO$_2$), 5.72 (br. d, $J$ = 10.07 Hz, 1 H, N*H*), 7.10−7.41 (m, 10 H, C*H*$_{ar.}$), 7.72 (d, $J$ = 12.08 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.68 (NCH*C*H$_3$), 49.71 (N*C*HCH$_3$), 74.93 (*C*HCH$_2$NO$_2$), 76.81 (*C*H$_2$NO$_2$), 81.31 (*C*HC$_{ar.}$), 127.52 (*o*-*C*H$_{ar.}$), 127.94 (*o*-*C*H$_{ar.}$), 128.00 (*p*-*C*H$_{ar.}$), 128.11 (*p*-*C*H$_{ar.}$), 129.10 (*m*-*C*H$_{ar.}$), 129.29 (*m*-*C*H$_{ar.}$), 134.18 (*i*-*C*$_{ar.}$), 136.12 (*i*-*C*$_{ar.}$), 160.23 (*C*HO); (*E*): δ = 16.17 (NCH*C*H$_3$), 53.54 (N*C*HCH$_3$), 73.80 (*C*HCH$_2$NO$_2$), 77.85 (*C*H$_2$NO$_2$), 80.73 (*C*HC$_{ar.}$), 126.75 (*o*-*C*H$_{ar.}$), 126.91 (*o*-*C*H$_{ar.}$), 127.21 (*p*-*C*H$_{ar.}$), 127.95 (*m*-*C*H$_{ar.}$), 128.74 (*m*-*C*H$_{ar.}$), 129.41 (*p*-*C*H$_{ar.}$), 133.40 (*i*-*C*$_{ar.}$), 136.10 (*i*-*C*$_{ar.}$), 163.81 (*C*HO); minor diastereomer: (*Z*): δ = 14.33 (NCH*C*H$_3$), 47.65 (N*C*HCH$_3$), 70.85 (*C*HCH$_2$NO$_2$), 79.14 (*C*H$_2$NO$_2$), 80.02 (*C*HC$_{ar.}$), 127.86 (*o*-*C*H$_{ar.}$), 127.98 (*o*-*C*H$_{ar.}$), 128.00 (*p*-*C*H$_{ar.}$), 128.74 (*p*-*C*H$_{ar.}$), 129.04 (*m*-*C*H$_{ar.}$), 129.20 (*m*-*C*H$_{ar.}$), 134.80 (*i*-*C*$_{ar.}$), 136.08 (*i*-*C*$_{ar.}$), 160.77 (*C*HO); (*E*): δ = 16.51 (NCH*C*H$_3$), 50.35 (N*C*HCH$_3$), 71.53 (*C*HCH$_2$NO$_2$), 78.69 (*C*H$_2$NO$_2$), 79.57 (*C*HC$_{ar.}$), 127.20 (*o*-*C*H$_{ar.}$), 127.43 (*o*-*C*H$_{ar.}$), 128.50 (*p*-*C*H$_{ar.}$), 128.83 (*m*-*C*H$_{ar.}$), 129.75 (*m*-*C*H$_{ar.}$), 129.80 (*p*-*C*H$_{ar.}$), 136.20 (*i*-*C*$_{ar.}$), 136.45 (*i*-*C*$_{ar.}$), 163.90 (*C*HO). − MS (70 eV); *m*/*z* (%): 252 (5.8), 251 (4.0), 221 (15.7), 203 (36.1), 192 (26.8), 191 (100), 178 (30.8), 115 (70.8), 104 (89.9), 91 (37.3). − $C_{18}H_{20}N_2O_4$ (328.37): calcd. C 65.84, H 6.14, N 8.53; found C 65.48, H 6.45, N 8.48.

*(1S,2R,1′R)-(−)-N-[2-(1′′-Furan-2′-yl-2′-nitroethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8l**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (358 mg, 2.0 mmol) and NaH (73 mg, 2.2 mmol 80%) to (*E*)-2-(2-nitrovinyl)furane (**2l**) (278 mg, 2.0 mmol) at −78°C. The product was purified by column chromatography ($SiO_2$; diethyl ether). Yield 140 mg (22%), m.p. 103°C. − *de* = 22%. − $[\alpha]_D^{24}$ = −37.5 (*c* = 1.00, $CHCl_3$). − IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2982 cm$^{-1}$ (m), 2931 (m), 2875 (m), 1677 (s), 1558 (s), 1500 (s), 1452 (s), 1426 (s), 1383 (s), 1265 (m), 1234 (m), 1203 (m), 1151 (m), 1072 (s), 1059 (s), 1014 (m), 926 (m), 880 (m), 748 (s), 704 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.99 (d, $J$ = 6.71 Hz, 3 H, NCHC*H*$_3$), 4.16 (d/q/d/d, $J$ = 9.40/6.72/3.69/0.90 Hz, 1 H, NC*H*CH$_3$), 4.38 (d, $J$ = 3.35 Hz, 1 H, C*H*C$_{ar.}$), 4.53 (d/d, $J$ = 11.54/2.47 Hz, 1 H, C*H*$_2$NO$_2$), 5.01 (d/d, $J$ = 11.54/10.01 Hz, 1 H, C*H*$_2$NO$_2$), 5.07 (d/d, $J$ = 9.88/2.48 Hz, 1 H, C*H*CH$_2$NO$_2$), 5.94 (br. d, $J$ = 8.72 Hz, 1 H, N*H*), 6.33−6.41 (m, 2 H, C*H*C*H*$_{fur.}$), 7.18−7.22 (m, 2 H, *o*-C*H*$_{ar.}$), 7.30−7.42 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.43 (m, Σ$J$ = 4.5 Hz, 1 H, OC*H*CH$_{fur.}$), 7.98 (d, $J$ = 1.01 Hz, 1 H, C*H*O); (*E*): δ = 1.11 (d, $J$ = 6.71 Hz, 3 H, NCHC*H*$_3$), 3.60 (d/q/d, $J$ = 9.40/6.72/5.04 Hz, 1 H, NC*H*CH$_3$), 3.99 (d, $J$ = 5.37 Hz, 1 H, C*H*C$_{ar.}$), 4.49 (d/d, $J$ = 10.58/2.02 Hz, 1 H, C*H*$_2$NO$_2$), 4.97 (d/d, $J$ = 10.40/9.74 Hz, 1 H, C*H*$_2$NO$_2$), 5.03 (d/d, $J$ = 9.70/2.20 Hz, 1 H, C*H*CH$_2$NO$_2$), 5.63 (br. d/d, $J$ = 11.08/10.00 Hz, 1 H, N*H*), 6.33−6.41 (m, 2 H, C*H*C*H*$_{fur.}$), 7.12−7.18 (m, 2 H, *o*-C*H*$_{ar.}$), 7.29−7.42 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.43 (m, Σ$J$ = 4.5 Hz, 1 H, OC*H*CH$_{fur.}$), 7.75 (d, $J$ = 11.75 Hz, 1 H, C*H*O); minor diastereomer: (*Z*): δ = 0.95 (d, $J$ = 7.05 Hz, 3 H, NCHC*H*$_3$), 4.24 (d/q/d/d, $J$ = 8.73/7.05/2.96/0.80 Hz, 1 H, NC*H*CH$_3$), 4.59 (d/d, $J$ = 13.09/3.02 Hz, 1 H, C*H*$_2$NO$_2$), 4.71 (d, $J$ = 3.02 Hz, 1 H, C*H*C$_{ar.}$), 5.06 (d/d, $J$ = 13.10/10.07 Hz, 1 H, C*H*$_2$NO$_2$), 5.22 (d/d, $J$ = 10.08/3.02 Hz, 1 H, C*H*CH$_2$NO$_2$), 5.88 (br. d, $J$ = 9.02 Hz, 1 H, N*H*), 6.06−6.14 (m, 2 H, C*H*C*H*$_{fur.}$), 7.10−7.23 (m, 2 H, *o*-C*H*$_{ar.}$), 7.10−7.23 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.37 (m, Σ$J$ = 4.5 Hz, 1 H, OC*H*CH$_{fur.}$), 8.20 (d, $J$ = 0.90 Hz, 1 H, C*H*O); (*E*): δ = 1.08 (d, $J$ = 7.05 Hz, 3 H, NCHC*H*$_3$), 3.78 (m, Σ$J$ = 26.0 Hz, 1 H, NC*H*CH$_3$), 4.35 (d, $J$ = 4.37 Hz, 1 H, C*H*C$_{ar.}$), 4.56 (d/d, $J$ = 13.10/3.36 Hz, 1 H, C*H*$_2$NO$_2$), 4.96 (d/d, $J$ = 13.09/9.74 Hz, 1 H, C*H*$_2$NO$_2$), 5.23 (d/d, $J$ = 10.08/3.36 Hz, 1 H, C*H*CH$_2$NO$_2$), 5.72 (br. t, $J$ = 10.00 Hz, 1 H, N*H*), 6.06−6.14 (m, 2 H, C*H*C*H*$_{fur.}$), 7.01−7.09 (m, 2 H, *o*-C*H*$_{ar.}$), 7.10−7.24 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.37 (m, Σ$J$ = 4.5 Hz, 1 H, OC*H*CH$_{fur.}$), 7.89 (d, $J$ = 11.76 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.39 (NCH*C*H$_3$), 48.60 (N*C*HCH$_3$), 68.76 (*C*HCH$_2$NO$_2$), 77.43 (*C*H$_2$NO$_2$), 80.00 (*C*HC$_{ar.}$), 110.83 (*C*H$_{fur.}$), 112.11 (*C*H$_{fur.}$), 126.90 (*o*-*C*H$_{ar.}$), 128.38 (*p*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 136.69 (*i*-*C*$_{ar.}$), 144.06 (*C*H$_{fur.}$), 147.62 (*i*-*C*$_{fur.}$), 160.45 (*C*HO); (*E*): δ = 16.69 (NCH*C*H$_3$), 53.13 (N*C*HCH$_3$), 68.37 (*C*HCH$_2$NO$_2$), 77.37 (*C*H$_2$NO$_2$), 81.48 (*C*HC$_{ar.}$), 110.53 (*C*H$_{fur.}$), 111.70 (*C*H$_{fur.}$), 127.62 (*o*-*C*H$_{ar.}$), 128.86 (*m*-*C*H$_{ar.}$), 128.95 (*p*-*C*H$_{ar.}$), 135.68 (*i*-*C*$_{ar.}$), 144.30 (*C*H$_{fur.}$), 147.53 (*i*-*C*$_{fur.}$), 163.65 (*C*HO); minor diastereomer: (*Z*): δ = 14.73

(NCH*C*H$_3$), 47.99 (N*C*HCH$_3$), 70.65 (*C*HCH$_2$NO$_2$), 73.88 (*C*H$_2$NO$_2$), 81.53 (*C*HC$_{ar.}$), 110.51 (*C*H$_{fur.}$), 113.27 (*C*H$_{fur.}$), 127.35 (*o*-*C*H$_{ar.}$), 127.72 (*p*-*C*H$_{ar.}$), 128.23 (*m*-*C*H$_{ar.}$), 136.20 (*i*-*C*$_{ar.}$), 144.54 (*C*H$_{fur.}$), 146.56 (*i*-*C*$_{fur.}$), 160.20 (*C*HO); (*E*): δ = 15.27 (NCH*C*H$_3$), 48.55 (N*C*HCH$_3$), 71.02 (*C*HCH$_2$NO$_2$), 73.63 (*C*H$_2$NO$_2$), 80.19 (*C*HC$_{ar.}$), 111.17 (*C*H$_{fur.}$), 114.48 (*C*H$_{fur.}$), 126.99 (*o*-*C*H$_{ar.}$), 128.51 (*m*-*C*H$_{ar.}$), 129.23 (*p*-*C*H$_{ar.}$), 136.45 (*i*-*C*$_{ar.}$), 144.73 (*C*H$_{fur.}$), 146.36 (*i*-*C*$_{fur.}$), 164.98 (*C*HO). − MS (70 eV); *m*/*z* (%): 319 (0.3) [M$^+$ + 1], 226 (1.9), 178 (11.8), 140 (17.8), 94 (96.3), 72 (100). − C$_{16}$H$_{18}$N$_2$O$_5$ (318.33): calcd. C 60.37, H 5.70, N 8.80; found C 59.99, H 5.70, N 8.66.

*(1S,2R,1′R)-(−)-N-[2-(1′′-Ferrocenyl-2′-nitroethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**8m**] was obtained as a yellow-orange solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (90 mg, 0.5 mmol) and NaH (18 mg, 0.55 mmol 80%) to (*E*)-2-(2-nitrovinyl)ferrocene (**2m**) (129 mg, 0.5 mmol) at −78°C. The product was purified by column chromatography (SiO$_2$; diethyl ether). Yield 57 mg (26%), m.p. 68°C.− *de* = 94%. − [α]$_D^{24}$ = −74.9 (*c* = 0.30, CHCl$_3$). − IR (CHCl$_3$): ṽ = 2927 cm$^{-1}$ (m), 2872 (m), 1680 (s), 1556 (s), 1494 (s), 1452 (s), 1426 (s), 1383 (s), 1314 (m), 1242 (m), 1106 (m), 1087 (m), 1059 (s), 1041 (s), 754 (s), 705 (s). − $^1$H NMR (300 MHz): major diastereomer: (*Z*): δ = 0.90 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 4.04 (d/d/d, *J* = 2.48/1.24/1.24 Hz, 1H C$_5$*H*$_4$R), 4.11 (m, Σ*J* = 12.5 Hz, 1 H, C$_5$*H*$_4$R), 4.12 (s, 5 H, C$_5$*H*$_5$), 4.28 (m, Σ*J* = 19.5 Hz, 2 H, NC*H*CH$_3$, C$_5$*H*$_4$R), 4.46 (d, *J* = 3.30 Hz, 1 H, C*H*C$_{ar.}$), 4.86 (d/d, *J* = 10.44/1.65 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.92 (d/d, *J* = 10.72/10.43 Hz, 1 H, C*H*$_2$NO$_2$), 5.08 (d/d, *J* = 10.71/1.65 Hz, 1 H, C*H*$_2$NO$_2$), 5.51 (br. d, *J* = 8.79 Hz, 1 H, N*H*), 7.15−7.20 (m, 2 H, *o*-C*H*$_{ar.}$), 7.30−7.42 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.85 (d, *J* = 0.82 Hz, 1 H, C*H*O); (*E*): δ = 0.99 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 3.96 (d/d/d, *J* = 2.48/1.24/1.24 Hz, 1H C$_5$*H*$_4$R), 4.07 (m, Σ*J* = 9.5 Hz, 1 H, NC*H*CH$_3$), 4.11 (s, 5 H, C$_5$*H*$_5$), 4.12 (m, 2 H, C$_5$*H*$_4$R), 4.28 (m, 2 H, C$_5$*H*$_4$R, C*H*C$_{ar.}$), 4.81 (d/d, *J* = 10.43/2.47 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.89 (d/d, *J* = 12.64/10.17 Hz, 1 H, C*H*$_2$NO$_2$), 5.04 (d/d, *J* = 12.36/2.47 Hz, 1 H, C*H*$_2$NO$_2$), 5.36 (br. t, *J* = 10.50 Hz, 1 H, N*H*), 7.10−7.15 (m, 2 H, *o*-C*H*$_{ar.}$), 7.22−7.44 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.76 (d, *J* = 11.81 Hz, 1 H, C*H*O); minor diastereomer: δ = 0.89 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 4.08 (s, 5 H, C$_5$*H*$_5$), other signals are overlapped. − $^{13}$C NMR (75 MHz): major diastereomer: (*Z*): δ = 13.50 (NCH*C*H$_3$), 48.40 (N*C*HCH$_3$), 65.09 (*C*HCH$_2$NO$_2$), 65.63 (*C*$_5$H$_4$R), 69.00 (C$_5$H$_5$), 69.10 (*i*-*C*$_5$H$_4$R), 69.79 (*C*$_5$H$_4$R), 70.58 (*C*$_5$H$_4$R), 71.99 (*C*$_5$H$_4$R), 78.77 (*C*HC$_{ar.}$), 79.89 (*C*H$_2$NO$_2$), 127.06 (*o*-*C*H$_{ar.}$), 127.78 (*p*-*C*H$_{ar.}$), 128.56 (*m*-*C*H$_{ar.}$), 137.19 (*i*-*C*$_{ar.}$), 160.07 (*C*HO); (*E*): δ = 16.89 (NCH*C*H$_3$), 52.56 (N*C*HCH$_3$), 65.60 (*C*HCH$_2$NO$_2$), 68.38 (*C*$_5$H$_4$R), 69.00 (C$_5$H$_5$), 69.15 (*i*-*C*$_5$H$_4$R), 69.89 (*C*$_5$H$_4$R), 70.28 (*C*$_5$H$_4$R), 71.42 (*C*$_5$H$_4$R), 80.20 (*C*HC$_{ar.}$), 81.36 (*C*H$_2$NO$_2$), 127.78 (*o*-*C*H$_{ar.}$), 127.79 (*m*-*C*H$_{ar.}$), 129.06 (*p*-*C*H$_{ar.}$), 133.10 (*i*-*C*$_{ar.}$), 163.61 (*C*HO). − MS (70 eV); *m*/*z* (%): 436 (2.4) [M$^+$], 259 (16.1), 258 (100), 210 (35.8), 121 (53.9), 56 (36.0). − HR-MS; C$_{22}$H$_{24}$FeN$_2$O$_4$ (436.29): calcd. 436.108543; found 436.108686.

*Addition of N-Formylnorephedrine to α-Substituted Nitro Alkenes*

*(1S,2R,1′R/S,1′′R/S)-N-{1-Methyl-2-[2′-methyl-1′-(1′′-nitroethyl)propoxy]-2-phenylethyl}formamide* [(1*S*,2*R*,1′*R*/*S*,1′′*R*/*S*)-**10a**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (717 mg, 4.0 mmol) and NaH (145 mg, 4.4 mmol 80%) to (*E*)- or (*Z*)-5-methyl-2-nitropent-2-ene (**9a**) (517 mg, 4.0 mmol) at −78°C. The product was purified by column chromatography (SiO$_2$; diethyl ether) isolated as mixtures of diastereomers. Yield 592 mg (48%) (*E*), traces (≤ 1%) (*Z*). − Ratio of diastereomers 76:23:0.5:0.5, *ds* = 76%, *de* = 52%. − IR (film): ṽ = 2968 cm$^{-1}$ (s), 2937 (m), 2877 (m), 1673 (s), 1550 (s), 1495 (s), 1453 (s), 1391 (s), 1357 (m), 1219 (m), 1091 (s), 1061 (s), 1029 (m), 757 (s), 704 (s). − $^1$H NMR (300 MHz): diastereomer 1: (*Z*): δ = 1.00 [d, *J* = 6.94 Hz, 3 H, CHC*H*$_3$)$_2$], 1.01 [d, *J* = 7.01 Hz, 3 H, CHC*H*$_3$)$_2$], 1.13 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.54 (d, *J* = 6.86 Hz, 1 H, C*H*$_3$CHNO$_2$), 2.07 [sept/d, *J* = 7.01/4.81 Hz, 1 H, C*H*CH$_3$)$_2$], 3.86 (d/d, *J* = 4.81/3.37 Hz, 1 H, C*H*CHNO$_2$), 4.36 (d/q/d/d, *J* = 8.93/6.87/4.12/0.82 Hz, 1 H, NC*H*CH$_3$), 4.53 (d/q, *J* = 6.79/3.37 Hz, 1 H, CH$_3$C*H*NO$_2$), 4.60 (d, *J* = 4.12 Hz, 1 H, C*H*C$_{ar.}$), 5.58 (br. d/d, *J* = 9.0/1.7 Hz, 1 H, N*H*), 7.20−7.25 (m, 2 H, *o*-C*H*$_{ar.}$), 7.29−7.41 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 8.12 (d/d, *J* = 1.65/0.82 Hz, 1 H, C*H*O); (*E*): δ = 1.02 [d, *J* = 6.86 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.02 [d, *J* = 6.87 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.14 (d, *J* = 6.93 Hz, 3 H, NCHC*H*$_3$), 1.51 (d, *J* = 6.79 Hz, 1 H, C*H*$_3$CHNO$_2$), 2.05 [sept/d, *J* = 6.87/5.16 Hz, 1 H, CH(CH$_3$)$_2$], 3.84 (d/q/d, *J* = 9.07/6.94/4.39 Hz, 1 H, NC*H*CH$_3$), 3.86 (d/d, *J* = 5.16/3.43 Hz, 1 H, C*H*CHNO$_2$), 4.31 (d, *J* = 4.39 Hz, 1 H, C*H*C$_{ar.}$), 4.48 (d/q, *J* = 6.80/3.50 Hz, 1 H, CH$_3$C*H*NO$_2$), 5.40 (br. d/d, *J* = 11.88/9.07 Hz, 1 H, N*H*), 7.13−7.18 (m, 2 H, *o*-C*H*$_{ar.}$), 7.29−7.41 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.96 (d, *J* = 11.88 Hz, 1 H, C*H*O); diastereomer 2: (*Z*): δ = 0.99 [d, *J* = 7.08 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.04 [d, *J* = 7.14 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.09 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.43 (d, *J* = 6.87 Hz, 1 H, C*H*$_3$CHNO$_2$), 2.02 [sept/d, *J* = 7.07/2.99 Hz, 1 H, CH(CH$_3$)$_2$], 3.71 (d/d, *J* = 7.83/2.99 Hz, 1 H, C*H*CHNO$_2$), 4.27 (d/q/d/d, *J* = 8.92/6.80/3.85/0.83 Hz, 1 H, NC*H*CH$_3$), 4.61 (d/q, *J* = 7.83/6.86 Hz, 1 H, CH$_3$C*H*NO$_2$), 4.68 (d, *J* = 3.84 Hz, 1 H, C*H*C$_{ar.}$), 5.72 (br. d/d, *J* = 9.0/1.7 Hz, 1 H, N*H*), 7.20−7.25 (m, 2 H, *o*-C*H*$_{ar.}$), 7.29−7.41 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 8.12 (d/d, *J* = 1.70/0.83 Hz, 1 H, C*H*O); (*E*): δ = 1.00 [d, *J* = 7.07 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.06 [d, *J* = 7.08 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.15 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.39 (d, *J* = 6.87 Hz, 1 H, C*H*$_3$CHNO$_2$), 2.00 [sept/d, *J* = 7.01/3.09 Hz, 1 H, CH(CH$_3$)$_2$], 3.73 (d/d, *J* = 7.76/3.16 Hz, 1 H, C*H*CHNO$_2$), 3.85 (d/q/d, *J* = 7.90/6.87/4.87 Hz, 1 H, NC*H*CH$_3$), 4.35 (d, *J* = 4.87 Hz, 1 H, C*H*C$_{ar.}$), 4.56 (d/q, *J* = 7.76/6.87 Hz, 1 H, CH$_3$C*H*NO$_2$), 5.42 (br. d/d, *J* = 11.88/7.90 Hz, 1 H, N*H*), 7.13−7.18 (m, 2 H, *o*-C*H*$_{ar.}$), 7.29−7.41 (m, 3 H, *p*,*m*-C*H*$_{ar.}$), 7.92 (d, *J* = 11.88 Hz, 1 H, C*H*O); diastereomer 3: (*Z*): δ = 8.14 (br. s, 1 H, C*H*O); (*E*): 7.98 (d, *J* = 11.90 Hz, 1 H, C*H*O); diastereomer 4: (*Z*): δ = 8.17 (br. s, 1 H, C*H*O); (*E*): 8.02 (d, *J* = 11.50 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): diastereomer 1: (*Z*): δ = 14.12 (NCH*C*H$_3$), 15.48 [CH(*C*H$_3$)$_2$], 17.83 [CH(*C*H$_3$)$_2$], 18.42 (*C*H$_3$CHNO$_2$), 29.36 [*C*H(CH$_3$)$_2$], 48.53 (N*C*HCH$_3$), 81.00 (*C*HCHNO$_2$), 81.43 (*C*HC$_{ar.}$), 83.23 (*C*HNO$_2$), 127.53 (*o*-*C*H$_{ar.}$), 127.62 (*p*-*C*H$_{ar.}$), 128.50 (*m*-*C*H$_{ar.}$), 137.15 (*i*-*C*$_{ar.}$), 160.45 (*C*HO); (*E*): δ = 13.96 [CH(*C*H$_3$)$_2$], 17.83 (NCH*C*H$_3$), 18.11 [CH(*C*H$_3$)$_2$], 18.56 (*C*H$_3$CHNO$_2$), 29.71 [*C*H(CH$_3$)$_2$], 52.50 (N*C*HCH$_3$), 81.52 (*C*HCHNO$_2$), 83.13 (*C*HC$_{ar.}$), 83.23 (*C*HNO$_2$), 128.06 (*o*-*C*H$_{ar.}$), 128.66 (*m*-*C*H$_{ar.}$), 128.94 (*p*-*C*H$_{ar.}$), 135.90 (*i*-*C*$_{ar.}$), 164.02 (*C*HO); diastereomer 2: (*Z*): δ = 14.85 (NCH*C*H$_3$), 16.28 [CH(*C*H$_3$)$_2$], 17.49 [CH(*C*H$_3$)$_2$], 17.79 (*C*H$_3$CHNO$_2$), 28.41 [*C*H(CH$_3$)$_2$], 48.94 (N*C*HCH$_3$), 81.69 (*C*HCHNO$_2$), 83.17 (*C*HC$_{ar.}$), 84.94 (*C*HNO$_2$), 128.35 (*o*-*C*H$_{ar.}$), 128.41 (*p*-*C*H$_{ar.}$), 128.63 (*m*-*C*H$_{ar.}$), 137.29 (*i*-*C*$_{ar.}$), 160.53 (*C*HO); (*E*): δ = 16.11 [CH(*C*H$_3$)$_2$], 17.34 (NCH*C*H$_3$), 17.79 [CH(*C*H$_3$)$_2$], 18.97 (*C*H$_3$CHNO$_2$), 28.65 [*C*H(CH$_3$)$_2$], 52.80 (N*C*HCH$_3$), 82.06 (*C*HCHNO$_2$), 83.84 (*C*HC$_{ar.}$), 85.02 (*C*HNO$_2$), 128.15 (*o*-*C*H$_{ar.}$), 128.41 (*m*-*C*H$_{ar.}$), 128.57 (*p*-*C*H$_{ar.}$), 137.21 (*i*-*C*$_{ar.}$), 164.01 (*C*HO). − MS (70 eV); *m*/*z* (%): 263 (2.0), 238 (1.3), 237 (11.6), 236 (78.9), 162 (12.0), 134 (35.7), 130 (46.8), 107 (45.9), 83 (100). − C$_{16}$H$_{24}$N$_2$O$_4$ (308.38): calcd. C 62.32, H 7.84, N 9.08; found C 62.18, H 7.80, N 8.84.

*(1S,2R,1′R/S,2′R/S)-N-[2-(3′-tert-Butyldimethylsilyloxy-1′-isopropyl-2′-nitropropoxy)-1-methyl-2-phenylethyl]formamide*

[(1*S*,2*R*,1′*R*/*S*,2′*R*/*S*)-**10b**] was obtained as colourless oil according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (537 mg, 3.0 mmol) and NaH (109 mg, 3.3 mmol 80%) to (*E*)- or (*Z*)-1-*tert*-butyldimethylsilyloxy-5-methyl-2-nitropent-2-ene (**9b**) (778 mg, 3.0 mmol) at −78 °C. The product was purified by column chromatography ($SiO_2$; diethyl ether) and isolated as mixtures of diastereomers. Yield 500 mg (38%) (*E*), traces (≤ 1%) (*Z*). − Ratio of diastereomers 58:40:1:1, *ds* = 58%, *de* = 16%. − IR (film): $\tilde{\nu}$ = 2958 $cm^{-1}$ (s), 2932 (s), 2884 (s), 2858 (s), 1668 (s), 1557 (s), 1463 (s), 1388 (s), 1362 (m), 1309 (m), 1259 (s), 1204 (m), 1114 (s), 1071 (s), 1030 (m), 840 (s), 781 (s), 741 (m), 704 (s). − $^1$H NMR (300 MHz): diastereomer 1: (*Z*): δ = −0.02 (s, 3 H, SiC$H_3$), 0.01 (s, 3 H, SiC$H_3$), 0.82 [s, 9 H, C(C$H_3$)$_3$], 0.95 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.06 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.08 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 2.00 [sept/d, *J* = 6.87/3.02 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.61 (d/d, *J* = 7.14/3.02 Hz, 1 H, C*H*CHNO$_2$), 3.65 (d/d, *J* = 10.99/3.85 Hz, 1 H, *H*CHOSi), 4.03 (d/d, *J* = 10.99/9.62 Hz, 1 H, HC*H*OSi), 4.25 (d/q/d/d, *J* = 9.61/6.87/3.85/0.83 Hz, 1 H, NC*H*CH$_3$), 4.69 (d, *J* = 3.85 Hz, 1 H, C*H*C$_{ar.}$), 4.70 (d/d/d, *J* = 9.62/7.15/3.84 Hz, 1 H, C*H*NO$_2$), 5.72 (br. d, *J* = 9.51 Hz, 1 H, N*H*), 7.22−7.27 (m, 2 H, *o*-CH$_{ar.}$), 7.29−7.42 (m, 3 H, *p*,*m*-CH$_{ar.}$), 8.09 (d, *J* = 0.82 Hz, 1 H, C*H*O); (*E*): δ = −0.02 (s, 3 H, SiC$H_3$), 0.01 (s, 3 H, SiC$H_3$), 0.80 [s, 9 H, C(C$H_3$)$_3$], 0.97 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.07 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.16 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 1.99 [sept/d, *J* = 6.87/3.02 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.64 (d/d, *J* = 4.75/3.02 Hz, 1 H, C*H*CHNO$_2$), 3.69 (d/d, *J* = 10.99/3.85 Hz, 1 H, *H*CHOSi), 3.78 (d/q/d, *J* = 9.61/6.87/4.67 Hz, 1 H, NC*H*CH$_3$), 3.96 (d/d, *J* = 10.99/9.34 Hz, 1 H, HC*H*OSi), 4.32 (d, *J* = 4.94 Hz, 1 H, C*H*C$_{ar.}$), 4.61 (d/d/d, *J* = 9.34/4.95/3.85 Hz, 1 H, C*H*NO$_2$), 5.39 (br. t, *J* = 10.44 Hz, 1 H, N*H*), 7.15−7.19 (m, 2 H, *o*-CH$_{ar.}$), 7.29−7.42 (m, 3 H, *p*,*m*-CH$_{ar.}$), 7.90 (d, *J* = 11.81 Hz, 1 H, C*H*O); diastereomer 2: (*Z*): δ = −0.04 (s, 3 H, SiC$H_3$), −0.01 (s, 3 H, SiC$H_3$), 0.82 [s, 9 H, C(C$H_3$)$_3$], 0.96 [d, *J* = 6.86 Hz, 3 H, CH(C$H_3$)$_2$], 1.06 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.16 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 2.02 [sept/d, *J* = 6.87/3.30 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.70 (d/d, *J* = 5.49/3.30 Hz, 1 H, C*H*CHNO$_2$), 3.89 (d/d, *J* = 11.54/3.85 Hz, 1 H, *H*CHOSi), 4.00 (d/d, *J* = 11.54/9.34 Hz, 1 H, HC*H*OSi), 4.36 (d/q/d/d, *J* = 7.42/6.87/5.22/0.82 Hz, 1 H, NC*H*CH$_3$), 4.55 (d, *J* = 4.67 Hz, 1 H, C*H*C$_{ar.}$), 4.62 (d/d/d, *J* = 9.61/5.77/3.84 Hz, 1 H, C*H*NO$_2$), 5.47 (br. d, *J* = 9.34 Hz, 1 H, N*H*), 7.19−7.43 (m, 5 H, CH$_{ar.}$), 8.13 (d, *J* = 0.82 Hz, 1 H, C*H*O); (*E*): δ = −0.04 (s, 3 H, SiC$H_3$), −0.01 (s, 3 H, SiC$H_3$), 0.83 [s, 9 H, C(C$H_3$)$_3$], 0.97 [d, *J* = 7.15 Hz, 3 H, CH(C$H_3$)$_2$], 1.07 [d, *J* = 6.87 Hz, 3 H, CH(C$H_3$)$_2$], 1.15 (d, *J* = 6.87 Hz, 3 H, NCHC$H_3$), 2.02 (d/sept, *J* = 7.14/6.87 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.69 (d/d, *J* = 7.14/4.12 Hz, 1 H, C*H*CHNO$_2$), 3.85 (d/q/d, *J* = 9.61/6.87/4.94 Hz, 1 H, NC*H*CH$_3$), 3.87 (d/d, *J* = 11.54/4.13 Hz, 1 H, *H*CHOSi), 3.94 (d/d, *J* = 11.54/9.34 Hz, 1 H, HC*H*OSi), 4.30 (d, *J* = 4.67 Hz, 1 H, C*H*C$_{ar.}$), 4.65 (d/t, *J* = 9.34/4.13 Hz, 1 H, C*H*NO$_2$), 5.40 (br. t, *J* = 10.50 Hz, 1 H, N*H*), 7.19−7.43 (m, 5 H, CH$_{ar.}$), 7.95 (d, *J* = 11.88 Hz, 1 H, C*H*O); diastereomer 3: (*Z*): δ = 8.17 (br. s, 1 H, C*H*O); (*E*): 8.01 (d, *J* = 11.88 Hz, 1 H, C*H*O); diastereomer 4: (*Z*): δ = 8.18 (br. s, 1 H, C*H*O); (*E*): δ = 7.97 (d, *J* = 11.78 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): diastereomer 1: (*Z*): δ = −5.73, −5.61 [Si(*C*H$_3$)$_2$], 14.73 (NCH*C*H$_3$), 17.29 [CH(*C*H$_3$)$_2$], 17.83 [CH(*C*H$_3$)$_2$], 18.09 [Si*C*(CH$_3$)$_3$], 25.62 [SiC(*C*H$_3$)$_3$], 28.65 [*C*H(CH$_3$)$_2$], 48.91 (N*C*HCH$_3$), 62.00 (*C*H$_2$OSi), 77.51 (*C*HCHNO$_2$), 81.19 (*C*HC$_{ar.}$), 90.73 (*C*HNO$_2$), 127.66 (*o*-*C*H$_{ar.}$), 128.16 (*p*-*C*H$_{ar.}$), 128.50 (*m*-*C*H$_{ar.}$), 136.83 (*i*-*C*$_{ar.}$), 160.29 (*C*HO); (*E*): δ = −5.73, −5.61 [Si(*C*H$_3$)$_2$], 17.15 [CH(*C*H$_3$)$_2$], 17.65 (NCH*C*H$_3$), 17.92 [Si*C*(CH$_3$)$_3$], 18.60 [CH(*C*H$_3$)$_2$], 25.68 [SiC(*C*H$_3$)$_3$], 29.01 [*C*H(CH$_3$)$_2$], 52.65 (N*C*HCH$_3$), 61.81 (*C*H$_2$OSi), 78.67 (*C*HCHNO$_2$), 83.78 (*C*HC$_{ar.}$), 90.94 (*C*HNO$_2$), 128.43 (*o*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 128.97 (*p*-*C*H$_{ar.}$), 135.77 (*i*-*C*$_{ar.}$), 163.72 (*C*HO); diastereomer 2: (*Z*): δ = −5.72, −5.63 [Si(*C*H$_3$)$_2$], 15.96 (NCH*C*H$_3$), 17.35 [CH(*C*H$_3$)$_2$], 17.75 [CH(*C*H$_3$)$_2$], 18.14 [Si*C*(CH$_3$)$_3$], 25.62 [SiC(*C*H$_3$)$_3$], 29.68 [*C*H(CH$_3$)$_2$], 48.29 (N*C*HCH$_3$), 62.15 (*C*H$_2$OSi), 79.92 (*C*HCHNO$_2$), 82.23 (*C*HC$_{ar.}$), 90.08 (*C*HNO$_2$), 127.66 (*o*-*C*H$_{ar.}$), 128.43 (*p*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 136.88 (*i*-*C*$_{ar.}$), 160.23 (*C*HO); (*E*): δ = −5.72, −5.63 [Si(*C*H$_3$)$_2$], 17.39 [CH(*C*H$_3$)$_2$], 17.95 (NCH*C*H$_3$), 18.01 [CH(*C*H$_3$)$_2$], 18.09 [Si*C*(CH$_3$)$_3$], 25.61 [SiC(*C*H$_3$)$_3$], 29.81 [*C*H(CH$_3$)$_2$], 52.23 (N*C*HCH$_3$), 62.18 (*C*H$_2$OSi), 80.33 (*C*HCHNO$_2$), 83.74 (*C*HC$_{ar.}$), 89.96 (*C*HNO$_2$), 128.49 (*o*-*C*H$_{ar.}$), 128.84 (*m*-*C*H$_{ar.}$), 129.14 (*p*-*C*H$_{ar.}$), 135.59 (*i*-*C*$_{ar.}$), 163.68 (*C*HO). − MS (70 eV); *m*/*z* (%): 382 (4.8) [M$^+$ − C$_4$H$_8$], 381 (19.6) [M$^+$ − C$_4$H$_9$], 367 (7.2), 366 (28.2), 213 (22.9), 162 (100), 134 (79.5), 117 (27.8), 81 (29.6). − $C_{22}H_{38}N_2O_5$ (438.64): calcd. C 60.24, H 8.73, N 6.39; found C 60.55, H 8.76, N 6.40.

*(1S,2R,1′R,2′S)-(−)-N-[1-Methyl-2-(2′-nitrocyclohexyloxy)-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*,2′*S*)-**10c**] was obtained as colourless solid according to *GP 1* by adding (1*R*,2*S*)-(−)-*N*-formylnorephedrine [(1*R*,2*S*)-**7**] (717 mg, 4.0 mmol) and NaH (145 mg, 4.4 mmol 80%) to 1-nitrocyclohex-1-ene (**9c**) (509 mg, 4.0 mmol) at −78 °C. The product was purified by column chromatography ($SiO_2$; diethyl ether) and isolated as single diastereomer. Yield 558 mg (46%), m.p. 104 °C. − Ratio of diastereomers 97:2:0.5:0.5 (*cis*/*trans* 31:1), *ds* = 97%, *de* = 94%. − *de* ≥ 98% [major diastereomer (1*S*,2*R*,1′*R*,2′*S*), after chromatography]. − $[\alpha]_D^{24}$ = −153.7 (*c* = 1.06, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2982 $cm^{-1}$ (m), 2941 (m), 2892 (m), 1678 (s), 1658 (s), 1540 (s), 1522 (s), 1385 (s), 1355 (m), 1097 (m), 1080 (m), 1069 (m), 1029 (s), 960 (m), 893 (m), 753 (s), 703 (m). − $^1$H NMR (500 MHz): major diastereomer (1*S*,2*R*,1′*R*,2′*S*): (*Z*): δ = 1.06 (d, *J* = 6.87 Hz, NCHC$H_3$), 1.30 (m, Σ*J* = 32.5 Hz, 1 H, NO$_2$CHCH$_2$C*H*$_2$), 1.34 (m, Σ*J* = 25.0 Hz, 1 H, C*H*$_2$CHCHNO$_2$), 1.48 (m, 1 H, Σ*J* = 38.0 Hz, C*H*$_2$CH$_2$CHCHNO$_2$), 1.56 (m, Σ*J* = 58.5 Hz, 1 H, C*H*$_2$CH$_2$CHCHNO$_2$), 1.92 (m, Σ*J* = 22.5 Hz, C*H*$_2$CHCHNO$_2$), 2.02 (m, 1 H, Σ*J* = 30.0 Hz, C*H*$_2$CHNO$_2$), 2.16 (m, Σ*J* = 23.0 Hz, 1 H, C*H*$_2$CHCHNO$_2$), 2.35 (m, Σ*J* = 57.0 Hz, 1 H, C*H*$_2$CHNO$_2$), 4.15 (m, Σ*J* = 10.5 Hz, 1 H, C*H*CHNO$_2$), 4.18 (d/q/d/d, *J* = 8.78/6.86/3.58/0.77 Hz, 1 H, NC*H*CH$_3$), 4.36 (d/d/d, *J* = 11.45/4.12/3.28 Hz, 1 H, C*H*NO$_2$), 4.64 (d, *J* = 3.89 Hz, 1 H, C*H*C$_{ar.}$), 6.07 (br. d, *J* = 8.39 Hz, 1 H, N*H*), 7.19 (m, Σ*J* = 9.5 Hz, 2 H, *o*-CH$_{ar.}$), 7.31 (m, Σ*J* = 9.5 Hz, 1 H, *p*-CH$_{ar.}$), 7.35 (m, Σ*J* = 17.5 Hz, 2 H, *m*-CH$_{ar.}$), 8.13 (d, *J* = 0.99 Hz, 1 H, C*H*O); (*E*): δ = 1.21 (d, *J* = 6.79 Hz, NCHC$H_3$), 1.28 (m, Σ*J* = 32.5 Hz, 1 H, NO$_2$CHCH$_2$C*H*$_2$), 1.35 (m, Σ*J* = 25.0 Hz, 1 H, C*H*$_2$CHCHNO$_2$), 1.48 (m, 1 H, Σ*J* = 38.0 Hz, C*H*$_2$CH$_2$CHCHNO$_2$), 1.59 (m, Σ*J* = 58.5 Hz, 1 H, C*H*$_2$CH$_2$CHCHNO$_2$), 1.93 (m, Σ*J* = 22.5 Hz, C*H*$_2$CHCHNO$_2$), 2.03 (m, 1 H, Σ*J* = 30.0 Hz, C*H*$_2$CHNO$_2$), 2.15 (m, Σ*J* = 23.0 Hz, 1 H, C*H*$_2$CHCHNO$_2$), 2.30 (m, Σ*J* = 57.0 Hz, 1 H, C*H*$_2$CHNO$_2$), 3.68 (d/q/d, *J* = 9.69/6.72/5.65 Hz, 1 H, NC*H*CH$_3$), 4.15 (m, Σ*J* = 10.5 Hz, 1 H, C*H*CHNO$_2$), 4.28 (d, *J* = 5.42 Hz, 1 H, C*H*C$_{ar.}$), 4.29 (d/d/d, *J* = 11.83/4.19/3.20 Hz, 1 H, C*H*NO$_2$), 5.92 (br. t, *J* = 10.72 Hz, 1 H, N*H*), 7.12 (m, Σ*J* = 9.5 Hz, 2 H, *o*-CH$_{ar.}$), 7.29 (m, Σ*J* = 9.5 Hz, 1 H, *p*-CH$_{ar.}$), 7.35 (m, Σ*J* = 17.5 Hz, 2 H, *m*-CH$_{ar.}$), 7.70 (d, *J* = 11.83 Hz, 1 H, C*H*O); minor diastereomer (1*S*,2*R*,1′*R*,2′*R*): (*Z*): δ = 0.95 (d, *J* = 6.71 Hz, NCHC$H_3$), 1.18−1.38 (m, 3 H, NO$_2$CHCH$_2$C*H*$_2$, C*H*$_2$CHCHNO$_2$, C*H*$_2$CH$_2$CHCHNO$_2$), 1.50 (m, Σ*J* = 55.0 Hz, 1 H, C*H*$_2$CH$_2$CHCHNO$_2$), 1.80 (m, 1 H, Σ*J* = 32.0 Hz, C*H*$_2$CHNO$_2$), 1.93 (m, Σ*J* = 40.0 Hz, C*H*$_2$CHCHNO$_2$), 2.10 (m, Σ*J* = 26.5 Hz, 1 H, C*H*$_2$CHCHNO$_2$), 2.35 (m, Σ*J* = 45.0 Hz, 1 H, C*H*$_2$CHNO$_2$), 4.14 (d/q/d/d, *J* = 9.07/6.72/4.89/0.80 Hz, 1 H, NC*H*CH$_3$), 4.33 (m, Σ*J* = 13.0 Hz, 1 H, C*H*CHNO$_2$), 4.40 (d/d/d,

$J$ = 11.29/3.66/3.28 Hz, 1 H, C*H*$NO_2$), 4.56 (d, $J$ = 3.05 Hz, 1 H, C*H*$C_{ar.}$), 5.79 (br. d, $J$ = 7.63 Hz, 1 H, N*H*), 7.25−7.38 (m, 5 H, C*H*$_{ar.}$), 8.15 (s, 1 H, C*H*O); (*E*): δ = 1.02 (d, $J$ = 7.02 Hz, NCHC*H*$_3$), 1.18−1.38 (m, 3 H, $NO_2CHCH_2CH_2$, $CH_2CHCHNO_2$, $CH_2CH_2CHCHNO_2$), 1.50 (m, Σ$J$ = 55.0 Hz, 1 H, $CH_2CH_2CHCHNO_2$), 1.80 (m, 1 H, Σ$J$ = 32.0 Hz, $CH_2CHNO_2$), 1.93 (m, Σ$J$ = 40.0 Hz, $CH_2CHCHNO_2$), 2.10 (m, Σ$J$ = 26.5 Hz, 1 H, $CH_2CHCHNO_2$), 2.35 (m, Σ$J$ = 45.0 Hz, 1 H, $CH_2CHNO_2$), 3.74 (d/q/d, $J$ = 10.99/7.02/3.36 Hz, 1 H, NC*H*$CH_3$), 4.15 (d, $J$ = 4.27 Hz, 1 H, C*H*$C_{ar.}$), 4.32 (d/d/d, $J$ = 10.50/4.27/3.36 Hz, 1 H, C*H*$NO_2$), 4.36 (m, Σ$J$ = 12.0 Hz, 1 H, C*H*$CHNO_2$), 5.22 (br. t, $J$ = 10.72 Hz, 1 H, N*H*), 7.25−7.38 (m, 5 H, C*H*$_{ar.}$), 7.94 (d, $J$ = 11.90 Hz, 1 H, C*H*O); signals of (1*S*,2*R*,1′*S*,2′*S*) and (1*S*,2*R*,1′*S*,2′*R*) are overlapped. − $^{13}$C NMR (125 MHz): major diastereomer (1*S*,2*R*,1′*R*,2′*S*): (*Z*): δ = 14.04 (NCH*C*H$_3$), 19.33 (OCHCH$_2$*C*H$_2$), 23.06 ($NO_2CHCH_2CH_2$), 24.34 ($NO_2CHCH_2$), 26.27 (OCH*C*H$_2$), 49.15 (N*C*HCH$_3$), 71.25 (*C*HCHNO$_2$), 78.91 (*C*HC$_{ar.}$), 85.79 (*C*HNO$_2$), 127.28 (*o*-*C*H$_{ar.}$), 128.27 (*p*-*C*H$_{ar.}$), 128.49 (*m*-*C*H$_{ar.}$), 137.20 (*i*-*C*$_{ar.}$), 160.51 (*C*HO); (*E*): δ = 17.39 (NCH*C*H$_3$), 19.12 (OCHCH$_2$*C*H$_2$), 23.22 ($NO_2CHCH_2CH_2$), 24.09 ($NO_2CHCH_2$), 26.31 (OCH*C*H$_2$), 53.15 (N*C*HCH$_3$), 71.23 (*C*HCHNO$_2$), 80.95 (*C*HC$_{ar.}$), 85.61 (*C*HNO$_2$), 127.83 (*o*-*C*H$_{ar.}$), 128.72 (*m*-*C*H$_{ar.}$), 128.83 (*p*-*C*H$_{ar.}$), 136.13 (*i*-*C*$_{ar.}$), 163.91 (*C*HO); minor diastereomer (1*S*,2*R*,1′*R*,2′*R*): (*Z*): δ = 12.77 (NCH*C*H$_3$), 19.43 (OCHCH$_2$*C*H$_2$), 22.99 ($NO_2CHCH_2CH_2$), 24.39 ($NO_2CHCH_2$), 29.30 (OCH*C*H$_2$), 49.62 (N*C*HCH$_3$), 77.56 (*C*HCHNO$_2$), 83.85 (*C*HC$_{ar.}$), 85.86 (*C*HNO$_2$), 126.64 (*o*-*C*H$_{ar.}$), 127.88 (*p*-*C*H$_{ar.}$), 128.27 (*m*-*C*H$_{ar.}$), 139.81 (*i*-*C*$_{ar.}$), 160.86 (*C*HO), other signals of the (*E*) minor diastereomers (1*S*,2*R*,1′*R*,2′*R*), (1*S*,2*R*,1′*S*,2′*S*), and (1*S*,2*R*,1′*S*,2′*R*) are not detected. − MS (70 eV); *m*/*z* (%): 307 (13.2) [$M^+$ + 1], 261 (15.0), 235 (73.6), 234 (100), 178 (61.8), 162 (88.1), 134 (81.3), 107 (91.5), 81 (91.9), 67 (74.8). − $C_{16}H_{22}N_2O_4$ (306.36): calcd. C 62.73, H 7.24, N 9.14; found C 62.45, H 7.21, N 8.95.

*Reduction to Amines and Reaction to N-Boc-Protected Amino Ethers*

*(1S,2R,1′R)-(−)-N-[2-(2′-tert-Butoxycarbonylamino-1′-methylethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11a**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8a** (533 mg, 2 mmol) reacted with $NaBH_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with $Boc_2O$ (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white solid after flash chromatography. Yield 538 mg (80%). − *de* ≥ 96%. − $[\alpha]_D^{24}$ = −78.5 (*c* = 1.06, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2976 $cm^{-1}$ (s), 2932 (m), 1690 (s), 1514 (s), 1453 (s), 1384 (s), 1367 (s), 1275 (s), 1250 (s), 1172 (s), 1125 (s), 1104 (s), 1085 (m), 1027 (m), 753 (s), 703 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 1.04 (d, $J$ = 6.72 Hz, 3 H, CHC*H*$_3$), 1.11 (d, $J$ = 6.04 Hz, 3 H, NCHC*H*$_3$), 1.43 [s, 9 H, C(C*H*$_3$)$_3$], 3.11 (br. m, 1 H, C*H*$_2$N), 3.19 (br. m, 1 H, C*H*$_2$N), 3.49 (br. m, 1 H, C*H*CH$_2$NH), 4.35 (br. m, 1 H, NC*H*CH$_3$), 4.55 (br. d, $J$ = 4.03 Hz, 1 H, C*H*C$_{ar.}$), 4.97 (br. m, 1 H, N*H*Boc), 6.38 (br. m, 1 H, N*H*CHO), 7.24−7.38 (m, 5 H, C*H*$_{ar.}$), 8.11 (d, $J$ = 1.01 Hz, 1 H, C*H*O); (*E*): δ = 1.00 (d, $J$ = 7.05 Hz, 3 H, CHC*H*$_3$), 1.15 (d, $J$ = 6.72 Hz, 3 H, NCHC*H*$_3$), 1.40 [s, 9 H, C(C*H*$_3$)$_3$], 3.00 (br. m, 1 H, C*H*$_2$N), 3.05 (br. m, 1 H, C*H*CH$_2$NH), 3.24 (br. m, 1 H, C*H*$_2$N), 3.68 (br. m, 1 H, NC*H*CH$_3$), 4.31 (br. d, $J$ = 5.03 Hz, 1 H, C*H*C$_{ar.}$), 5.02 (br. m, 1 H, N*H*Boc), 6.64 (br. m, 1 H, N*H*CHO), 7.24−7.38 (m, 5 H, C*H*$_{ar.}$), 7.89 (d, $J$ = 11.75 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 14.20 (CH*C*H$_3$), 16.36 (NCH*C*H$_3$), 28.41 [C(*C*H$_3$)$_3$], 46.14 (*C*H$_2$NHBoc), 48.67 (N*C*HCH$_3$), 71.96 (CH*C*H$_3$), 79.15 [*C*(CH$_3$)$_3$], 79.55 (*C*HC$_{ar.}$), 127.05 (*o*-*C*H$_{ar.}$), 127.84 (*p*-*C*H$_{ar.}$), 128.41 (*m*-*C*H$_{ar.}$), 138.86 (*i*-*C*$_{ar.}$), 156.09 (*C*O), 160.53 (*C*HO); (*E*): δ = 13.93 (CH*C*H$_3$), 18.05 (NCH*C*H$_3$), 28.41 [C(*C*H$_3$)$_3$], 48.49 (*C*H$_2$NHBoc), 53.07 (N*C*HCH$_3$), 71.96 (*C*HCH$_3$), 73.99 [*C*(CH$_3$)$_3$], 82.36 (*C*HC$_{ar.}$), 127.62 (*o*-*C*H$_{ar.}$), 128.33 (*p*-*C*H$_{ar.}$), 128.58 (*m*-*C*H$_{ar.}$), 137.72 (*i*-*C*$_{ar.}$), 151.62 (*C*O), 164.26 (*C*HO). − MS (70 eV); *m*/*z* (%): 337 (0.2) [$M^+$ + 1], 264 (12.8), 162 (33.3), 134 (37.1), 102 (100), 57 (64.1). − $C_{18}H_{28}N_2O_4$ (336.43): calcd. C 64.26, H 8.39, N 8.33; found C 64.75, H 8.02, N 8.22.

*(1S,2R,1′R)-(−)-N-[2-(1′-tert-Butoxycarbonylaminomethylpropoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11b**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8b** (561 mg, 2 mmol) reacted with $NaBH_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with $Boc_2O$ (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 582 mg (83%). − *de* ≥ 96%. − $[\alpha]_D^{24}$ = −70.0 (*c* = 0.97, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2976 $cm^{-1}$ (s), 2933 (m), 1695 (s), 1510 (s), 1454 (s), 1391 (m), 1367 (s), 1272 (m), 1217 (m), 1171 (s), 1099 (m), 1069 (m), 757 (s), 704 (m). − $^1$H NMR (300 MHz): (*Z*): δ = 0.89 (t, $J$ = 7.42 Hz, 3 H, CH$_2$C*H*$_3$), 1.07 (d, $J$ = 6.59 Hz, 3 H, NCHC*H*$_3$), 1.42 [s, 9 H, C(C*H*$_3$)$_3$], 1.40−1.70 (m, 2 H, C*H*$_2$CH$_3$), 2.95−3.25 (m, 2 H, C*H*$_2$N), 3.30 (br. m, 1 H, C*H*CH$_2$NH), 4.25 (br. m, 1 H, NC*H*CH$_3$), 4.56 (br. d, $J$ = 3.84 Hz, 1 H, C*H*C$_{ar.}$), 4.80 (br. m, 1 H, N*H*Boc), 6.20 (br. m, 1 H, N*H*CHO), 7.24−7.38 (m, 5 H, C*H*$_{ar.}$), 8.12 (br. s, 1 H, C*H*O); (*E*): δ = 1.03 (t, $J$ = 6.87 Hz, 3 H, CH$_2$C*H*$_3$), 1.16 (d, $J$ = 6.86 Hz, 3 H, NCHC*H*$_3$), 1.40 [s, 9 H, C(C*H*$_3$)$_3$], 1.40−1.70 (m, 2 H, C*H*$_2$CH$_3$), 2.95−3.25 (m, 2 H, C*H*$_2$N), 3.20 (br. m, 1 H, C*H*CH$_2$NH), 3.72 (br. m, 1 H, NC*H*CH$_3$), 4.30 (br. d, $J$ = 4.95 Hz, 1 H, C*H*C$_{ar.}$), 4.92 (br. m, 1 H, N*H*Boc), 6.42 (br. m, 1 H, N*H*CHO), 7.24−7.38 (m, 5 H, C*H*$_{ar.}$), 7.91 (d, $J$ = 11.81 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 9.28 (CH$_2$*C*H$_3$), 14.40 (NCH*C*H$_3$), 23.41 (*C*H$_2$CH$_3$), 28.42 [C(*C*H$_3$)$_3$], 43.34 (*C*H$_2$NHBoc), 48.82 (N*C*HCH$_3$), 77.56 (*C*HCH$_2$), 79.13 [*C*(CH$_3$)$_3$], 80.56 (*C*HC$_{ar.}$), 127.15 (*o*-*C*H$_{ar.}$), 127.71 (*p*-*C*H$_{ar.}$), 128.47 (*m*-*C*H$_{ar.}$), 139.06 (*i*-*C*$_{ar.}$), 156.04 (*C*O), 160.45 (*C*HO); (*E*): δ = 9.19 (CH$_2$*C*H$_3$), 17.32 (NCH*C*H$_3$), 29.70 (*C*H$_2$CH$_3$), 28.42 [C(*C*H$_3$)$_3$], 48.82 (*C*H$_2$NHBoc), 53.00 (N*C*HCH$_3$), 77.56 (*C*HCH$_2$), 81.15 [*C*(CH$_3$)$_3$], 82.19 (*C*HC$_{ar.}$), 127.94 (*o*-*C*H$_{ar.}$), 128.47 (*p*-*C*H$_{ar.}$), 128.66 (*m*-*C*H$_{ar.}$), 137.90 (*i*-*C*$_{ar.}$), 156.45 (*C*O), 164.14 (*C*HO). − MS (70 eV); *m*/*z* (%): 351 (0.1) [$M^+$ + 1], 278 (7.7), 222 (6.2), 178 (10.2), 162 (31.2), 116 (100), 57 (50.6). − $C_{19}H_{30}N_2O_4$ (350.46): calcd. C 65.12, H 8.63, N 7.99; found C 64.97, H 8.94, N 7.98.

*(1S,2R,1′R)-(−)-N-[2-(1′-tert-Butoxycarbonylaminomethylbutoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11c**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8c** (589 mg, 2 mmol) reacted with $NaBH_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with $Boc_2O$ (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 576 mg (79%). − *de* ≥ 96%. − $[\alpha]_D^{24}$ = −78.3 (*c* = 1.11, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2960 $cm^{-1}$ (s), 2939 (s), 2870 (s), 1683 (s), 1658 (s), 1518 (s), 1456 (s), 1429 (s), 1386 (s), 1368 (s), 1292 (s), 1217 (s), 1175 (s), 1078 (s), 1058 (s), 998 (m), 786 (m), 746 (m), 701 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 0.90 (t, $J$ = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.07 (d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.23−1.60 (m, 4 H, C*H*$_2$C*H*$_2$), 1.42 [s, 9 H, C(C*H*$_3$)$_3$], 3.10 (m, 1 H, C*H*$_2$N), 3.27 (m, 1 H, C*H*$_2$N), 3.34 (br. m, 1 H, C*H*CH$_2$NH), 4.27 (br. m, 1 H, NC*H*CH$_3$), 4.56 (br. d, $J$ = 3.57 Hz, 1 H, C*H*C$_{ar.}$), 4.76 (br. m, 1 H, N*H*Boc), 6.04 (br. d, $J$ = 7.97 Hz, 1 H, N*H*CHO), 7.24−7.40 (m, 5 H, C*H*$_{ar.}$), 8.13 (br. s, 1 H, C*H*O); (*E*): δ = 0.91 (t, $J$ = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.16 (d, $J$ = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.23−1.60 (m, 4 H, C*H*$_2$C*H*$_2$), 1.40 [s, 9 H, C(C*H*$_3$)$_3$], 3.04 (m, 1 H, C*H*$_2$N), 3.20 (br. m, 1 H,

C*H*CH$_2$NH), 3.24 (m, 1 H, C*H*$_2$N), 3.72 (br. m, 1 H, NC*H*CH$_3$), 4.30 (br. d, $J$ = 4.94 Hz, 1 H, C*H*C$_{ar.}$), 4.60 (br. m, 1 H, N*H*Boc), 5.98 (br. d, $J$ = 10.72 Hz, 1 H, N*H*CHO), 7.24−7.40 (m, 5 H, C*H*$_{ar.}$), 7.91 (d, $J$ = 11.91 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 14.30 (CH$_2$*C*H$_3$), 14.40 (NCH*C*H$_3$), 18.39 (*C*H$_2$CH$_3$), 28.42 [C(*C*H$_3$)$_3$], 33.06 (CH*C*H$_2$CH$_2$), 43.84 (*C*H$_2$NHBoc), 48.80 (N*C*HCH$_3$), 76.60 (*C*HCH$_2$), 80.68 [*C*(CH$_3$)$_3$], 82.30 (*C*HC$_{ar.}$), 127.13 (*o*-*C*H$_{ar.}$), 127.70 (*p*-*C*H$_{ar.}$), 128.47 (*m*-*C*H$_{ar.}$), 139.10 (*i*-*C*$_{ar.}$), 156.01 (*C*O), 160.40 (*C*HO); (*E*): δ = 14.41 (CH$_2$*C*H$_3$), 17.37 (NCH*C*H$_3$), 18.34 (*C*H$_2$CH$_3$), 28.42 [C(*C*H$_3$)$_3$], 32.40 (CH*C*H$_2$CH$_2$), 48.80 (*C*H$_2$NHBoc), 52.95 (N*C*HCH$_3$), 79.12 (*C*HCH$_2$), 79.14 [*C*(CH$_3$)$_3$], 79.75 (*C*HC$_{ar.}$), 127.95 (*o*-*C*H$_{ar.}$), 128.47 (*p*-*C*H$_{ar.}$), 128.67 (*m*-*C*H$_{ar.}$), 137.92 (*i*-*C*$_{ar.}$), 156.01 (*C*O), 164.10 (*C*HO). − MS (70 eV); *m*/*z* (%): 365 (1.6) [M$^+$ + 1], 292 (25.8), 162 (77.0), 134 (54.6), 130 (98.0), 86 (31.1), 57 (100). − C$_{20}$H$_{32}$N$_2$O$_4$ (364.48): calcd. C 65.91, H 8.85, N 7.69; found C 65.87, H 8.65, N 7.33.

*(1S,2R,1′R)-(−)-N-[2-(1′-tert-Butoxycarbonylaminomethyl-2′-methylpropoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11d**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8d** (589 mg, 2 mmol) reacted with NaBH$_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 612 mg (84%). − *de* ≥ 96%. − [α]$_D^{24}$ = −75.4 (*c* = 0.50, CHCl$_3$). − IR (CHCl$_3$): ṽ = 2973 cm$^{-1}$ (s), 2934 (s), 1694 (s), 1604 (m), 1505 (s), 1454 (s), 1390 (s), 1367 (s), 1337 (s), 1250 (s), 1173 (s), 1080 (s), 1029 (s), 755 (s), 703 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 0.93 [d, $J$ = 7.57 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.97 [d, $J$ = 7.57 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.12 [d, $J$ = 6.72 Hz, 3 H, NCHC*H*$_3$), 1.40 [s, 9 H, C(C*H*$_3$)$_3$], 2.00 (m, 1 H, C*H*(CH$_3$)$_2$], 3.03 (br. m, 1 H, C*H*$_2$N), 3.20 (br. m, 2 H, C*H*$_2$N, C*H*CH$_2$NH), 4.27 (br. m, 1 H, NC*H*CH$_3$), 4.56 (br. m, 2 H, C*H*C$_{ar.}$, N*H*Boc), 5.98 (br. d, $J$ = 7.72 Hz, 1 H, N*H*CHO), 7.24−7.40 (m, 5 H, C*H*$_{ar.}$), 8.10 (br. s, 1 H, C*H*O); (*E*): δ = 0.93 [d, $J$ = 7.57 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.97 [d, $J$ = 7.57 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.17 (d, $J$ = 6.71 Hz, 3 H, NCHC*H*$_3$), 1.37 [s, 9 H, C(C*H*$_3$)$_3$], 2.02 (m, 1 H, C*H*(CH$_3$)$_2$], 2.97 (br. m, 1 H, C*H*$_2$N), 3.15 (br. m, 2 H, C*H*$_2$N, C*H*CH$_2$NH), 3.80 (br. m, 1 H, NC*H*CH$_3$), 4.27 (br. d, $J$ = 4.59 Hz, 1 H, C*H*C$_{ar.}$), 4.58 (br. m, 1 H, N*H*Boc), 5.80 (br. m, 1 H, N*H*CHO), 7.24−7.40 (m, 5 H, C*H*$_{ar.}$), 7.91 (d, $J$ = 11.75 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 14.81 (NCH*C*H$_3$), 16.93 [CH(*C*H$_3$)$_2$], 18.57 [CH(*C*H$_3$)$_2$], 28.40 [C(*C*H$_3$)$_3$], 28.53 [*C*H(CH$_3$)$_2$], 40.49 (*C*H$_2$NHBoc), 48.97 (N*C*HCH$_3$), 79.02 [*C*(CH$_3$)$_3$], 81.24 (*C*HCH$_2$), 81.50 (*C*HC$_{ar.}$), 127.27 (*o*-*C*H$_{ar.}$), 128.00 (*p*-*C*H$_{ar.}$), 128.46 (*m*-*C*H$_{ar.}$), 139.20 (*i*-*C*$_{ar.}$), 155.87 (*C*O), 160.35 (*C*HO); (*E*): δ = 17.06 [CH(*C*H$_3$)$_2$], 17.67 (NCH*C*H$_3$), 18.46 [CH(*C*H$_3$)$_2$], 28.40 [C(*C*H$_3$)$_3$], 28.76 [*C*H(CH$_3$)$_2$] 40.64 (*C*H$_2$NHBoc), 52.86 (N*C*HCH$_3$), 81.79 (*C*HCH$_3$), 82.99 [*C*(CH$_3$)$_3$], 83.00 (*C*HC$_{ar.}$), 127.84 (*o*-*C*H$_{ar.}$), 128.51 (*m*-*C*H$_{ar.}$), 128.68 (*p*-*C*H$_{ar.}$), 137.88 (*i*-*C*$_{ar.}$), 156.92 (*C*O), 164.03 (*C*HO). − MS (70 eV); *m*/*z* (%): 365 (0.3) [M$^+$ + 1], 292 (24.0), 236 (24.6), 192 (24.6), 162 (95.1), 134 (67.0), 130 (100), 121 (38.3), 57 (81.1). − C$_{20}$H$_{32}$N$_2$O$_4$ (364.48): calcd. C 65.91, H 8.85, N 7.69; found C 65.70, H 8.80, N 7.50.

*(1S,2R,1′S)-(+)-N-[2-(1′-tert-Butoxycarbonylaminomethyl-2′-methylpropoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*S*)-**11d**]: According to *GP 2* (1*S*,2*R*,1′*S*)-**8d** (589 mg, 2 mmol) reacted with NaBH$_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 313 mg (86%). − *de* ≥ 96%. − [α]$_D^{24}$ = +75.1 (*c* = 0.94, CHCl$_3$).

*(1S,2R,1′R)-(−)-N-[2-(1′-tert-Butoxycarbonylaminomethyl-2′,2′-dimethylpropoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11e**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8e** (617 mg, 2 mmol) reacted with NaBH$_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 636 mg (84%). − *de* ≥ 96%. − [α]$_D^{24}$ = −96.1 (*c* = 1.34, CHCl$_3$). − IR (CHCl$_3$): ṽ = 2976 cm$^{-1}$ (s), 2936 (s), 2872 (s), 1695 (s), 1509 (s), 1482 (s), 1454 (s), 1391 (s), 1367 (s), 1247 (s), 1081 (s), 1030 (m), 757 (s), 704 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 1.03 [s, 9 H, C(C*H*$_3$)$_3$], 1.13 (d, $J$ = 6.38 Hz, 3 H, NCHC*H*$_3$), 1.36 [s, 9 H, C(C*H*$_3$)$_3$], 2.87 (d/d/d, $J$ = 14.44/6.38/6.38 Hz, 1 H, C*H*$_2$N), 3.14 (br. m, 1 H, C*H*CH$_2$NH), 3.25 (d/d/d, $J$ = 14.44/6.04/2.68 Hz, 1 H, C*H*$_2$N), 4.13 (br. m, 1 H, NC*H*CH$_3$), 4.35 (br. m, 1 H, N*H*Boc), 4.56 (br. d, $J$ = 4.08 Hz, 1 H, C*H*C$_{ar.}$), 5.92 (br. d, $J$ = 8.06 Hz, 1 H, N*H*CHO), 7.26−7.42 (m, 5 H, C*H*$_{ar.}$), 8.06 (br. s, 1 H, C*H*O); (*E*): δ = 1.01 [s, 9 H, C(C*H*$_3$)$_3$], 1.11 (d, $J$ = 6.38 Hz, 3 H, NCHC*H*$_3$), 1.33 [s, 9 H, C(C*H*$_3$)$_3$], 2.82 (br. m, 1 H, C*H*$_2$N), 3.14 (br. m, 1 H, C*H*CH$_2$NH), 3.25 (br. m, 1 H, C*H*$_2$N), 4.13 (br. m, 1 H, NC*H*CH$_3$), 4.28 (br. d, $J$ = 4.37 Hz, 1 H, C*H*C$_{ar.}$), 4.35 (br. m, 1 H, N*H*Boc), 5.72 (br. m, 1 H, N*H*CHO), 7.26−7.42 (m, 5 H, C*H*$_{ar.}$), 8.01 (br. d, $J$ = 11.75 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 15.47 (NCH*C*H$_3$), 26.87 [C(*C*H$_3$)$_3$], 28.36 [C(*C*H$_3$)$_3$], 35.67 (*C*H$_2$NHBoc), 41.62 [*C*(CH$_3$)$_3$], 49.00 (N*C*HCH$_3$), 78.84 [*C*(CH$_3$)$_3$], 84.35 (*C*HCH$_2$), 87.36 (*C*HC$_{ar.}$), 127.14 (*o*-*C*H$_{ar.}$), 127.74 (*p*-*C*H$_{ar.}$), 128.60 (*m*-*C*H$_{ar.}$), 140.10 (*i*-*C*$_{ar.}$), 155.53 (*C*O), 160.38 (*C*HO); (*E*): δ = 17.93 (NCH*C*H$_3$), 26.79 [C(*C*H$_3$)$_3$], 28.32 [C(*C*H$_3$)$_3$], 35.62 (*C*H$_2$NHBoc), 41.62 [*C*(CH$_3$)$_3$], 52.41 (N*C*HCH$_3$), 79.50 [*C*(CH$_3$)$_3$], 86.09 (*C*HCH$_2$), 88.06 (*C*HC$_{ar.}$), 127.90 (*o*-*C*H$_{ar.}$), 128.60 (*p*-*C*H$_{ar.}$), 128.80 (*m*-*C*H$_{ar.}$), 138.38 (*i*-*C*$_{ar.}$), 160.65 (*C*O), 164.08 (*C*HO). − MS (70 eV); *m*/*z* (%): 379 (0.4) [M$^+$ + 1], 306 (31.0), 250 (35.3), 162 (100), 144 (83.3), 134 (68.7), 118 (29.3), 57 (85.0). − C$_{21}$H$_{34}$N$_2$O$_4$ (378.51): calcd. C 66.64, H 9.05, N 7.40; found C 66.18, H 9.20, N 7.22.

*(1S,2R,1′R)-(−)-N-[2-(2′-tert-Butoxycarbonylamino-1′-cyclohexylethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*)-**11f**]: According to *GP 2* (1*S*,2*R*,1′*R*)-**8f** (669 mg, 2 mmol) reacted with NaBH$_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 672 mg (83%). − *de* = 94%. − [α]$_D^{24}$ = −73.3 (*c* = 1.40, CHCl$_3$). − IR (CHCl$_3$): ṽ = 2978 cm$^{-1}$ (s), 2929 (s), 2854 (s), 1700 (s), 1510 (s), 1453 (s), 1386 (s), 1367 (s), 1333 (m), 1252 (s), 1173 (s), 1086 (s), 1068 (s), 1028 (m), 746 (m), 703 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 0.95−1.29 (m, 9 H, C*H*$_2$, NCHC*H*$_3$), 1.39 [s, 9 H, C(C*H*$_3$)$_3$], 1.60−1.90 (m, 5 H, C*H*$_2$, C*H*), 3.04−3.29 (m, 3 H, C*H*C*H*$_2$NH), 4.24 (br. m, 1 H, NC*H*CH$_3$), 4.55 (br. m, 2 H, C*H*C$_{ar.}$, N*H*Boc), 5.92 (br. d, $J$ = 7.97 Hz, 1 H, N*H*CHO), 7.18−7.40 (m, 5 H, C*H*$_{ar.}$), 8.11 (br. s, 1 H, C*H*O); (*E*): δ = 0.95−1.29 (m, 9 H, C*H*$_2$, NCHC*H*$_3$), 1.36 [s, 9 H, C(C*H*$_3$)$_3$], 1.60−1.90 (m, 5 H, C*H*$_2$, C*H*), 2.94−3.23 (br. m, 3 H, C*H*C*H*$_2$NH), 3.76 (br. m, 1 H, NC*H*CH$_3$), 4.24 (br. d, $J$ = 4.67 Hz, 1 H, C*H*C$_{ar.}$), 4.64 (br. m, 1 H, N*H*Boc), 5.68 (br. m, N*H*CHO), 7.18−7.40 (m, 5 H, C*H*$_{ar.}$), 7.92 (br. d, $J$ = 11.81 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 14.75 (NCH*C*H$_3$), 26.44, 26.48, 26.59 (*C*H$_2$), 28.38 [C(*C*H$_3$)$_3$], 39.28 (*C*H), 41.13 (*C*H$_2$NHBoc), 49.03 (N*C*HCH$_3$), 79.03 (*C*HCH$_2$), 81.44 [*C*(CH$_3$)$_3$], 81.70 (*C*HC$_{ar.}$), 127.23 (*o*-*C*H$_{ar.}$), 127.83 (*p*-*C*H$_{ar.}$), 128.50 (*m*-

$CH_{ar.}$), 139.39 (*i*-$C_{ar.}$), 155.86 (*C*O), 160.33 (*C*HO); (*E*): δ = 17.64 (NCH*C*H$_3$), 27.94, 28.21 (*C*H$_2$), 28.38 [C(*C*H$_3$)$_3$], 29.23 (*C*H$_2$), 39.28 (*C*H), 41.13 (*C*H$_2$NHBoc), 52.82 (N*C*HCH$_3$), 79.64 [*C*(CH$_3$)$_3$], 82.02 (*C*HCH$_2$), 83.35 (*C*HC$_{ar.}$), 128.00 (*o*-*C*H$_{ar.}$), 128.50 (*m*-*C*H$_{ar.}$), 128.70 (*p*-*C*H$_{ar.}$), 138.03 (*i*-$C_{ar.}$), 157.20 (*C*O), 164.02 (*C*HO). − MS (70 eV); *m*/*z* (%): 405 (0.1) [M$^+$ + 1], 332 (8.1), 276 (6.8), 232 (6.0), 170 (100), 162 (83.0), 134 (50.0), 57 (56.0). − $C_{23}H_{36}N_2O_4$ (404.55): calcd. C 68.29, H 8.97, N 6.92; found C 68.09, H 8.99, N 6.63.

*(1S,2R,1′S)-(−)-N-[2-(1′-tert-Butoxycarbonylaminomethyl-2′,2′-diethoxyethoxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*S*)-**11g**]: According to *GP 2* (1*S*,2*R*,1′*S*)-**8g** (87 mg, 0.245 mmol) reacted with NaBH$_4$ (38 mg, 1 mmol) in the presence of 13 mg of 10% Pd/C in 5 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (101 mg, 0.5 mmol) and triethylamine (1.2 ml). The product was obtained as a white, waxy solid after flash chromatography. Yield 76 mg (73%). − *de* ≥ 96%. − [α]$_D^{24}$ = −49.1 (*c* = 0.54, CHCl$_3$). − IR (CHCl$_3$): ṽ = 2979 cm$^{-1}$ (s), 2932 (s), 2899 (s), 2880 (s), 1681 (s), 1510 (s), 1453 (s), 1390 (s), 1367 (s), 1250 (s), 1219 (s), 1060 (s), 1029 (s), 885 (m), 757 (s), 704 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 0.99 (d, *J* = 6.87 Hz, 3 H, NCHC*H*$_3$), 1.24 (t, *J* = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.29 (t, *J* = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.37 [s, 9 H, C(C*H*$_3$)$_3$], 3.19 (m, 1 H, C*H*$_2$N), 3.23 (m, 1 H, C*H*$_2$N), 3.56 (br. m, 1 H, C*H*CH$_2$NH), 3.53−3.82 (m, 4 H, C*H*$_2$CH$_3$), 4.26 (d/q/d, *J* = 9.62/7.14/3.30 Hz, 1 H, NC*H*CH$_3$), 4.53 (d, *J* = 5.22 Hz, 1 H, OC*H*O), 4.60 (br. m, 1 H, N*H*Boc), 4.71 (br. d, *J* = 3.29 Hz, 1 H, C*H*C$_{ar.}$), 6.34 (br. d, *J* = 9.70 Hz, 1 H, N*H*CHO), 7.26−7.40 (m, 5 H, C*H*$_{ar.}$), 8.16 (br. s, 1 H, C*H*O); (*E*): δ = 1.10 (d, *J* = 6.86 Hz, 3 H, NCHC*H*$_3$), 1.22 (t, *J* = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.30 (t, *J* = 7.14 Hz, 3 H, CH$_2$C*H*$_3$), 1.37 [s, 9 H, C(C*H*$_3$)$_3$], 3.15 (m, 1 H, C*H*$_2$N), 3.33 (m, 1 H, C*H*$_2$N), 3.53−3.82 (m, 4 H, C*H*$_2$CH$_3$), 3.56 (br. m, 1 H, C*H*CH$_2$NH), 3.85 (br. d/q/d, *J* = 9.34/7.14/3.29 Hz, 1 H, NC*H*CH$_3$), 4.48 (d, *J* = 5.50 Hz, 1 H, OC*H*O), 4.60 (br. m, 1 H, N*H*Boc), 4.67 (br. d, *J* = 3.85 Hz, 1 H, C*H*C$_{ar.}$), 6.09 (br. t, *J* = 10.16 Hz, 1 H, N*H*CHO), 7.26−7.40 (m, 5 H, C*H*$_{ar.}$), 8.04 (d, *J* = 12.09 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 13.63 (NCH*C*H$_3$), 15.38 (CH$_2$*C*H$_3$), 15.44 (CH$_2$*C*H$_3$), 28.35 [C(*C*H$_3$)$_3$], 41.83 (*C*H$_2$NHBoc), 49.23 (N*C*HCH$_3$), 63.65 (*C*H$_2$CH$_3$), 64.08 (*C*H$_2$CH$_3$), 79.18 [*C*(CH$_3$)$_3$], 79.82 (O*C*HCH$_2$), 84.76 (*C*HC$_{ar.}$), 103.14 (O*C*HO), 126.50 (*o*-*C*H$_{ar.}$), 127.87 (*p*-*C*H$_{ar.}$), 128.52 (*m*-*C*H$_{ar.}$), 139.36 (*i*-$C_{ar.}$), 155.73 (*C*O), 160.21 (*C*HO); (*E*): δ = 15.25 (CH$_2$*C*H$_3$), 16.87 (CH$_2$*C*H$_3$), 18.05 (NCH*C*H$_3$), 28.35 [C(*C*H$_3$)$_3$], 41.80 (*C*H$_2$NHBoc), 52.79 (N*C*HCH$_3$), 63.57 (*C*H$_2$CH$_3$), 64.08 (*C*H$_2$CH$_3$), 77.95 [*C*(CH$_3$)$_3$], 80.24 (O*C*HCH$_2$), 86.82 (*C*HC$_{ar.}$), 101.70 (O*C*HO), 126.69 (*o*-*C*H$_{ar.}$), 127.42 (*m*-*C*H$_{ar.}$), 128.34 (*p*-*C*H$_{ar.}$), 138.14 (*i*-$C_{ar.}$), 158.33 (*C*O), 163.85 (*C*HO). − MS (70 eV); *m*/*z* (%): 425 (0.3) [M$^+$ + 1], 352 (12.5), 252 (24.5), 206 (37.6), 135 (52.5), 103 (100), 75 (35.1), 57 (34.8). − $C_{22}H_{36}N_2O_6$ (424.54): calcd. C 62.24, H 8.55, N 6.60; found C 61.94, H 8.10, N 6.36.

*(1S,2R,1′R,2′S)-(−)-N-[2-(2′-tert-Butoxycarbonylamino-cyclohexyloxy)-1-methyl-2-phenylethyl]formamide* [(1*S*,2*R*,1′*R*,2′*S*)-**11h**]: According to *GP 2* (1*S*,2*R*,1′*R*,2′*S*)-**8h** (613 mg, 2 mmol) reacted with NaBH$_4$ (303 mg, 8.0 mmol) in the presence of 100 mg of 10% Pd/C in 40 ml of THF/methanol (1:1) to the corresponding amine, which was protected with Boc$_2$O (405 mg, 2 mmol) and triethylamine (10 ml). The product was obtained as a white solid after flash chromatography. Yield 655 mg (87%). − *de* ≥ 96%. − [α]$_D^{24}$ = −84.7 (*c* = 1.07, CHCl$_3$). − M.p. 59°C. − IR (KBr): ṽ = 2977 cm$^{-1}$ (m), 2935 (s), 2863 (m), 1698 (s), 1604 (m), 1499 (s), 1454 (s), 1385 (s), 1366 (s), 1309 (s), 1250 (s), 1173 (s), 1080 (m), 1048 (s), 1027 (s), 975 (m), 875 (m), 782 (m), 748 (m), 704 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 1.15 (t, *J* = 7.14 Hz, 3 H, NCHC*H*$_3$), 1.25−1.52 (m, 4 H, C*H*$_2$), 1.43 [s, 9 H, C(C*H*$_3$)$_3$], 1.62 (m, 2 H, C*H*$_2$), 1.70 (m, 1 H, C*H*$_2$), 1.93 (m, 1 H, C*H*$_2$), 3.53 (br. m, 2 H, OC*HCH*NHBoc), 4.30 (br. m, 1 H, NC*H*CH$_3$), 4.52 (d, *J* = 3.85 Hz, 1 H, C*H*C$_{ar.}$), 4.85 (br. d, *J* = 9.07 Hz, 1 H, N*H*Boc), 5.72 (br. d, *J* = 8.50 Hz, 1 H, N*H*CHO), 7.23−7.39 (m, 5 H, C*H*$_{ar.}$), 8.11 (br. s, 1 H, C*H*O); (*E*): δ = 1.18 (t, *J* = 7.14 Hz, 3 H, NCHC*H*$_3$), 1.25−1.52 (m, 4 H, C*H*$_2$), 1.40 [s, 9 H, C(C*H*$_3$)$_3$], 1.50 (m, 1 H, C*H*$_2$), 1.60 (m, 1 H, C*H*$_2$), 1.70 (m, 1 H, C*H*$_2$), 1.93 (m, 1 H, C*H*$_2$), 3.53 (br. m, 2 H, OC*HCH*NHBoc), 3.78 (br. m, 1 H, NC*H*CH$_3$), 4.26 (d, *J* = 4.95 Hz, 1 H, C*H*C$_{ar.}$), 4.81 (br. d, *J* = 9.50 Hz, 1 H, N*H*Boc), 5.54 (br. t, *J* = 10.99 Hz, 1 H, N*H*CHO), 7.23−7.39 (m, 5 H, C*H*$_{ar.}$), 7.95 (d, *J* = 12.09 Hz, 1 H, C*H*O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 15.13 (NCH*C*H$_3$), 19.95, 24.38, 26.95, 28.05 (*C*H$_2$), 28.45 [C(*C*H$_3$)$_3$], 48.97 (N*C*HCH$_3$), 51.56 (*C*HNHBoc), 73.27 (O*C*HCH$_2$), 79.00 [*C*(CH$_3$)$_3$], 79.95 (*C*HC$_{ar.}$), 127.39 (*o*-*C*H$_{ar.}$), 128.02 (*p*-*C*H$_{ar.}$), 128.49 (*m*-*C*H$_{ar.}$), 138.36 (*i*-$C_{ar.}$), 155.21 (*C*O), 160.20 (*C*HO); (*E*): δ = 17.66 (NCH*C*H$_3$), 19.71, 24.54, 27.04, 27.87 (*C*H$_2$), 28.45 [C(*C*H$_3$)$_3$], 51.56 (*C*HNHBoc), 52.96 (N*C*HCH$_3$), 73.44 (O*C*HCH$_2$), 79.00 [*C*(CH$_3$)$_3$], 81.04 (*C*HC$_{ar.}$), 127.89 (*o*-*C*H$_{ar.}$), 128.49 (*p*-*C*H$_{ar.}$), 128.68 (*m*-*C*H$_{ar.}$), 137.09 (*i*-$C_{ar.}$), 155.21 (*C*O), 163.98 (*C*HO). − MS (70 eV); *m*/*z* (%): 305 (7.8), 304 (32.6), 248 (66.8), 204 (23.1), 162 (18.4), 142 (100), 98 (73.3), 81 (40.9), 57 (94.5). − $C_{21}H_{32}N_2O_4$ (376.49): calcd. C 66.99, H 8.57, N 7.44; found C 66.79, H 8.48, N 7.18.

*Synthesis of N-Boc-Protected Amino Alcohols*

*(2R)-(−)-1-tert-Butoxycarbonylaminopropan-2-ol* [(2*R*)-**12a**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11a** (336 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 131 mg (75%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz) and by GC (7-CD-Perme 25, *p*(H$_2$) = 1 bar, $R_t$ = 26.5 min. Enantiomer 1 (*S*): $R_t$ = 27.1 min; enantiomer 2 (*R*). − [α]$_D^{24}$ = −23.2 (*c* = 0.65, CHCl$_3$). − IR (CHCl$_3$): ṽ = 3356 cm$^{-1}$ (s), 2976 (s), 2932 (s), 1962 (s), 1525 (s), 1456 (m), 1393 (s), 1367 (s), 1330 (m), 1277 (s), 1253 (s), 1174 (s), 993 (m). − $^1$H NMR (300 MHz): δ = 1.18 (d, *J* = 6.31 Hz, 3 H, C*H*$_3$), 1.45 [s, 9 H, C(C*H*$_3$)$_3$], 2.56 (br. s, 1 H, O*H*), 3.00 (d/d/d, *J* = 14.01/7.56/5.56 Hz, 1 H, C*H*$_2$N), 3.27 (d/d/d, *J* = 14.01/6.50/3.30, 1 H, C*H*$_2$N), 3.90 (d/q/d, *J* = 7.60/6.30/3.00 Hz, 1 H, C*H*CH$_2$N), 5.00 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 20.63 (*C*H$_3$), 28.34 [C(*C*H$_3$)$_3$], 47.95 (CH*C*H$_2$N), 67.55 (*C*HCH$_2$N), 79.60 [*C*(CH$_3$)$_3$], 156.85 (*C*O). − MS (70 eV); *m*/*z* (%): 175 (1.2) [M$^+$], 131 (16.7), 119 (13.8), 75 (48.6), 57 (100), 41 (24.2). − $C_8H_{17}NO_3$ (175.23): calcd. C 54.84, H 9.78, N 7.99; found C 54.99, H 9.89, N 7.93.

*(2R)-(−)-1-tert-Butoxycarbonylaminobutan-2-ol* [(2*R*)-**12b**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11b** (350 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 131 mg (69%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz). − [α]$_D^{24}$ = −16.2 (*c* = 1.06, CHCl$_3$). − IR (CHCl$_3$): ṽ = 3360 cm$^{-1}$ (s), 2976 (s), 2932 (s), 2879 (s), 1694 (s), 1520 (s), 1457 (s), 1393 (s), 1367 (s), 1275 (s), 1253 (s), 1174 (s), 1086 (m), 1041 (m), 1030 (m). − $^1$H NMR (300 MHz): δ = 0.80 (t, *J* = 7.38 Hz, 3 H, CH$_2$C*H*$_3$), 1.40−1.54 (m, 2 H, C*H*$_2$CH$_3$), 1.45 [s, 9 H, C(C*H*$_3$)$_3$], 3.00 (d/d/d, *J* = 13.90/7.39/5.23 Hz, 1 H, C*H*$_2$N), 3.12 (br. s, 1 H, O*H*), 3.30 (d/d/d, *J* = 13.90/6.63/3.30 Hz, 1 H, C*H*$_2$N), 3.90 (d/t/d, *J* = 7.40/

7.39/3.00 Hz, 1 H, C*H*$CH_2$N), 5.20 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 9.90 ($CH_2CH_3$), 27.64 ($CH_2CH_3$), 28.40 [$C(CH_3)_3$], 46.25 ($CHCH_2$N), 72.81 ($CHCH_2$N), 79.51 [$C(CH_3)_3$], 156.88 (*C*O). − MS (70 eV); *m/z* (%): 189 (0.6) [$M^+$], 133 (8.3), 131 (10.1), 76 (36.9), 75 (61.4), 59 (34.2), 57 (100), 41 (34.4). − $C_9H_{19}NO_3$ (189.25): calcd. C 57.12, H 10.12, N 7.40; found C 57.53, H 10.29, N 7.21.

*(2R)-(−)-1-tert-Butoxycarbonylaminopentan-2-ol* [(2*R*)-**12c**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11c** (364 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 148 mg (73%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz). $-[\alpha]_D^{24}$ = −13.2 (*c* = 0.98, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3365 $cm^{-1}$ (s), 2961 (s), 2933 (s), 2873 (s), 1692 (s), 1520 (s), 1457 (s), 1392 (s), 1367 (s), 1276 (s), 1252 (s), 1174 (s), 1089 (m), 1060 (m), 1027 (m), − $^1$H NMR (300 MHz): δ = 0.93 (t, *J* = 7.14 Hz, 3 H, $CH_2CH_3$), 1.33−1.52 (m, 4 H, $CH_2CH_2$), 1.45 [s, 9 H, $C(CH_3)_3$], 2.62 (br. s, 1 H, O*H*), 3.00 (d/d/d, *J* = 14.01/7.97/6.05 Hz, 1 H, C$H_2$N), 3.32 (d/d/d, *J* = 14.01/6.32/3.02 Hz, 1 H, C$H_2$N), 3.90 (br. m, 1 H, C*H*$CH_2$N), 5.03 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 14.06 ($CH_2CH_3$), 18.72 ($CH_2CH_3$), 28.41 [$C(CH_3)_3$], 36.95 ($CH_2CH_2CH$), 46.72 ($CHCH_2$N), 71.32 ($CHCH_2$N), 79.58 [$C(CH_3)_3$], 156.88 (*C*O). − MS (70 eV); *m/z* (%): 203 (0.1) [$M^+$], 147 (5.1), 76 (29.9), 75 (55.6), 59 (21.4), 57 (100). − $C_{10}H_{21}NO_3$ (203.28): calcd. C 59.09, H 10.41, N 6.89; found C 58.80, H 10.15, N 6.83.

*(2R)-(−)-1-tert-Butoxycarbonylamino-3-methylbutan-2-ol* [(2*R*)-**12d**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11d** (364 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 150 mg (74%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz) and ≥ 98% after gaschromatography. $-[\alpha]_D^{24}$ = −19.4 (*c* = 0.94, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3385 $cm^{-1}$ (s), 2966 (s), 2933 (s), 1694 (s), 1515 (s), 1454 (s), 1392 (s), 1368 (s), 1274 (s), 1252 (s), 1172 (s), 1075 (m). − $^1$H NMR (300 MHz): δ = 0.93 [d, *J* = 6.86 Hz, 3 H, $CH(CH_3)_2$], 0.95 [d, *J* = 6.86 Hz, 3 H, $CH(CH_3)_2$], 1.45 [s, 9 H, $C(CH_3)_3$], 1.69 (oct, *J* = 6.87 Hz, 1 H, C*H*$(CH_3)_2$], 2.85 (br. s, 1 H, O*H*), 3.02 (d/d/d, *J* = 14.09/8.40/5.42 Hz, 1 H, C$H_2$N), 3.34 (d/d/d, *J* = 14.08/6.73/2.95 Hz, 1 H, C$H_2$N), 3.41 (d/t/d, *J* = 8.52/6.87/3.00 Hz, 1 H, C*H*$CH_2$N), 5.11 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 17.83 [$CH(CH_3)_2$], 18.67 [$CH(CH_3)_2$], 28.41 [$C(CH_3)_3$], 32.01 [$CH(CH_3)_2$], 44.56 ($CHCH_2$N), 76.45 ($CHCH_2$N), 79.55 [$C(CH_3)_3$], 156.91 (*C*O). − MS (70 eV); *m/z* (%): 203 (1.9) [$M^+$], 131 (12.7), 104 (16.1), 76 (39.2), 75 (74.0), 59 (19.8), 57 (100), 41 (36.5). − $C_{10}H_{21}NO_3$ (203.28): calcd. C 59.09, H 10.41, N 6.89; found C 59.31, H 10.38, N 6.63.

*(2S)-(+)-1-tert-Butoxycarbonylamino-3-methylbutan-2-ol* [(2*S*)-**12d**]: According to *GP 3* (1*S*,2*R*,1′*S*)-**11d** (291 mg, 0.8 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (46 mg, 2.0 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 127 mg (78%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz) and ≥ 98% after gaschromatography. − $[\alpha]_D^{24}$ = +19.5 (*c* = 0.98, $CHCl_3$).

*(2R)-(−)-1-tert-Butoxycarbonylamino-3,3-dimethylbutan-2-ol* [(2*R*)-**12e**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11e** (379 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a white solid after flash chromatography. Yield 165 mg (76%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz) and ≥ 98% after gaschromatography. − $[\alpha]_D^{24}$ = −28.8 (*c* = 1.19, $CHCl_3$). − M.p. 80°C. − IR (KBr): $\tilde{\nu}$ = 3418 $cm^{-1}$ (s), 2970 (s), 2954 (s), 1690 (s), 1524 (s), 1512 (s), 1481 (s), 1467 (s), 1455 (s), 1431 (s), 1393 (s), 1367 (s), 1323 (s), 1279 (s), 1254 (s), 1176 (s), 1144 (s), 1092 (s), 1067 (s). − $^1$H NMR (300 MHz): δ = 0.93 [s, 9 H, $C(CH_3)_3$], 1.45 [s, 9 H, $C(CH_3)_3$], 2.70 (br. s, 1 H, O*H*), 2.96 (d/d/d, *J* = 13.70/9.49/4.20 Hz, 1 H, C$H_2$N), 3.32 (d/d, *J* = 9.57/2.40 Hz, 1 H, C*H*$CH_2$N), 3.41 (d/d, *J* = 13.70/7.38/2.35 Hz, 1 H, C$H_2$N), 5.08 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 25.68 [$C(CH_3)_3$], 28.42 [$C(CH_3)_3$], 34.18 [$C(CH_3)_3$], 42.67 ($CHCH_2$N), 79.34 ($CHCH_2$N), 79.53 [$C(CH_3)_3$], 157.04 (*C*O). − MS (70 eV); *m/z* (%): 217 (1.3) [$M^+$], 161 (9.6), 104 (37.1), 87 (17.8), 76 (44.5), 75 (75.2), 57 (100), 41 (31.4). − $C_{11}H_{23}NO_3$ (217.31): calcd. C 60.80, H 10.69, N 6.45; found C 61.27, H 10.45, N 6.16.

*(2R)-(−)-1-tert-Butoxycarbonylamino-3-cyclohexylethan-2-ol* [(2*R*)-**12f**]: According to *GP 3* (1*S*,2*R*,1′*R*)-**11f** (405 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a white solid after flash chromatography. Yield 183 mg (75%). − *ee* = 94%, determined by diastereomeric excess as MTPA (Mosher) ester[19a][19b]. − $[\alpha]_D^{24}$ = −19.4 (*c* = 1.25, $CHCl_3$). − M.p. 78°C. − IR (KBr): $\tilde{\nu}$ = 3429 $cm^{-1}$ (s), 2980 (s), 2962 (s), 2927 (s), 1690 (s), 1647 (m), 1542 (s), 1432 (m), 1408 (m), 1391 (m), 1366 (s), 1297 (s), 1252 (s), 1179 (s), 1116 (s), 1067 (m), 1047 (m). − $^1$H NMR (300 MHz): δ = 0.95−1.14 (m, 2 H, $CH_2$), 1.14−1.28 (m, 3 H, $CH_2$), 1.36 (m, 1 H, $CH_2$), 1.45 [s, 9 H, $C(CH_3)_3$], 1.62−1.81 (m, 4 H, $CH_2$), 1.86 (m, 1 H, C*H*CHOH), 2.87 (br. s, 1 H, O*H*), 3.04 (d/d/d, *J* = 13.43/7.89/4.55 Hz, 1 H, C$H_2$N), 3.36 (d/d/d, *J* = 13.44/6.78/2.77 Hz, 1 H, C$H_2$N), 3.39 (br. m, 1 H, C*H*$CH_2$N), 5.13 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 26.02 ($CH_2$), 26.14 ($CH_2$), 26.40 ($CH_2$), 28.32 ($CH_2$), 28.41 [$C(CH_3)_3$], 28.93 ($CH_2$), 41.83 (*C*HCHOH), 44.45 ($CHCH_2$N), 75.74 ($CHCH_2$N), 79.47 [$C(CH_3)_3$], 156.87 (*C*O). − MS (70 eV); *m/z* (%): 243 (3.0) [$M^+$], 187 (19.8), 131 (13.4), 104 (21.9), 95 (31.7), 76 (68.9), 75 (100), 57 (90.1), 41 (20.2). − $C_{13}H_{25}NO_3$ (243.35): calcd. C 64.17, H 10.36, N 5.76; found C 64.19, H 10.39, N 5.73.

*2-[(tert-Butoxycarbonyl)amino]-1-cyclohexylethyl 3,3,3-Trifluoro-2-methoxyphenylpropanoate:* To a solution of (2*R*)-(−)-1-*tert*-butoxycarbonylamino-3-cyclohexylethan-2-ol [(2*R*)-**12f**] (24 mg, 0.10 mmol) in 10 ml of dichlormethane a solution of DMAP (37 mg, 0.30 mmol) and (*S*)-(+)-MTPA chloride (28 mg, 0.11 mmol) in 10 ml of dichlormethane was slowly added dropwise at −78°C. The reaction mixture was allowed to warm up to room temp. (monitoring by TLC) and poured into 5 ml of pH 7 buffer, the organic phase was dried with $Na_2SO_4$. The product was obtained as a colourless oil after flash chromatography. Yield 42 mg (91%). − *de* = 94% (determined by signals at δ = 3.54 and 3.57). − $[\alpha]_D^{24}$ = +9.9 (*c* = 0.80, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2978 $cm^{-1}$ (m), 2931 (s), 2855 (s), 1747 (s), 1711 (s), 1510 (s), 1452 (s), 1393 (m), 1368 (s), 1254 (s), 1170 (s), 1124 (s), 1110 (s), 1083 (m), 1067 (m), 1019 (s), 962 (m), 760 (s), 719 (m), 698 (m). − $^1$H NMR (300 MHz): major diastereomer: δ = 0.82−1.30 (m, 6 H, $CH_2$), 1.43 [s, 9 H, $C(CH_3)_3$], 1.52−1.76 (m, 5 H, $CHCH_2$), 3.27 (d/d/d, *J* = 14.29/7.70/6.59 Hz, 1 H, C$H_2$N), 3.46 (d/d/d, *J* = 14.29/6.33/2.75

Hz, 1 H, C$H_2$N), 3.54 (q, $J_{H-F}$ = 1.23 Hz, 3 H, OC$H_3$), 4.55 (br. t, $J$ = 6.6 Hz, 1 H, N*H*), 5.03 (d/d/d, $J$ = 7.96/5.30/2.74 Hz, 1 H, C*H*CH$_2$N), 7.39−7.45 (m, 3 H, *o,p*-C$H_{ar.}$), 7.52−7.58 (m, 2 H, *m*-C$H_{ar.}$); minor diastereomer: δ = 0.82−1.30 (m, 6 H, C$H_2$), 1.43 [s, 9 H, C(C$H_3$)$_3$], 1.52−1.76 (m, 5 H, *C*HC$H_2$), 3.14 (d/d/d, $J$ = 14.28/7.97/5.77 Hz, 1 H, C$H_2$N), 3.46 (d/d/d, $J$ = 14.29/6.33/2.75 Hz, 1 H, C$H_2$N), 3.57 (q, $J_{H-F}$ = 1.23 Hz, 3 H, OC$H_3$), 4.36 (br. t, $J$ = 6.6 Hz, 1 H, N*H*), 5.04 (d/d/d, $J$ = 8.52/5.77/2.75 Hz, 1 H, C*H*CH$_2$N), 7.39−7.45 (m, 3 H, *o,p*-C$H_{ar.}$), 7.52−7.58 (m, 2 H, *m*-C$H_{ar.}$). − $^{13}$C NMR (75 MHz): major diastereomer: δ = 25.80 (*C*H$_2$), 25.90 (*C*H$_2$), 26.09 (*C*H$_2$), 27.71 (*C*H$_2$), 28.34 [C(*C*H$_3$)$_3$], 28.61 (*C*H$_2$), 39.47 (*C*H), 41.76 (CH*C*H$_2$N), 55.44 (O*C*H$_3$), 79.66 [*C*(CH$_3$)$_3$], 80.30 (*C*HCH$_2$N), 83.92 (q, $J_{C-F}$ = 21 Hz, *C*CF$_3$), 123.15 (q, $J_{C-F}$ = 287 Hz, C*C*F$_3$), 127.43 (*o*-*C*H$_{ar.}$), 128.47 (*m*-*C*H$_{ar.}$), 129.67 (*p*-*C*H$_{ar.}$), 132.20 (*i*-*C*$_{ar.}$), 154.79 (N*C*O), 166.12 (*C*O$_2$); minor diastereomer: δ = 25.83 (*C*H$_2$), 26.07 (*C*H$_2$), 26.15 (*C*H$_2$), 28.11 (*C*H$_2$), 28.34 [C(*C*H$_3$)$_3$], 28.73 (*C*H$_2$), 39.53 (*C*H), 41.51 (CH*C*H$_2$N), 55.62 (O*C*H$_3$), 80.05 [*C*(CH$_3$)$_3$], 80.38 (*C*HCH$_2$N), 83.92 (q, $J_{C-F}$ = 21 Hz, *C*CF$_3$), 123.28 (q, $J_{C-F}$ = 282 Hz, C*C*F$_3$), 127.31 (*o*-*C*H$_{ar.}$), 128.52 (*m*-*C*H$_{ar.}$), 129.69 (*p*-*C*H$_{ar.}$), 132.44 (*i*-*C*$_{ar.}$), 153.81 (N*C*O), 166.44 (*C*O$_2$). − MS (70 eV); *m/z* (%): 235 (5.7), 226 (4.5), 225 (28.5), 189 (84.2), 179 (65.7), 169 (73.3), 109 (29.1), 57 (100). − $C_{23}H_{32}NO_5F_3$ (459.50): calcd. C 60.12, H 7.02, N 3.05; found C 60.13, H 7.35, N 3.43.

*(2S)-(−)-3-tert-Butoxycarbonylamino-1,1-diethoxypropan-2-ol* [(2*S*)-**12g**]: According to *GP 3* (1*S*,2*R*,1′*S*)-**11g** (75 mg, 0.18 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 10 ml of liquid ammonia, containing dissolved sodium (11 mg, 0.45 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 46 mg (96%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz). − $[\alpha]_D^{24}$ = −13.1 (*c* = 0.83, CHCl$_3$). − IR (film): $\tilde{\nu}$ = 3375 cm$^{-1}$ (s), 2977 (s), 2930 (s), 1699 (s), 1515 (s), 1455 (s), 1392 (s), 1367 (s), 1346 (m), 1252 (s), 1173 (s), 1143 (s), 1103 (s), 1062 (s). − $^1$H NMR (300 MHz): δ = 1.23 (t, $J$ = 7.14 Hz, 3 H, CH$_2$C$H_3$), 1.24 (t, $J$ = 7.14 Hz, 3 H, CH$_2$C$H_3$), 1.45 [s, 9 H, C(C$H_3$)$_3$], 2.65 (br. s, 1 H, O*H*), 3.21 (d/d/d, $J$ = 14.01/6.87/5.77 Hz, 1 H, C$H_2$N), 3.44 (d/d/d, $J$ = 14.01/6.36/3.85 Hz, 1 H, C$H_2$N), 3.58 (d/q, $J$ = 9.62/7.14 Hz, 1 H, C$H_2$CH$_3$), 3.59 (d/q, $J$ = 9.62/7.14 Hz, 1 H, C$H_2$CH$_3$), 3.66 (br. d/d/d, $J$ = 6.32/5.77/3.75 1 H, C*H*CH$_2$N), 3.75 (d/q, $J$ = 9.34/7.14 Hz, 1 H, C$H_2$CH$_3$), 3.77 (d/q, $J$ = 9.34/7.14 Hz, 1 H, C$H_2$CH$_3$), 4.36 (d, $J$ = 5.77 Hz, 1 H, OC*H*O), 5.01 (br. m, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 15.38 (CH$_2$*C*H$_3$), 15.38 (CH$_2$*C*H$_3$), 28.41 [C(*C*H$_3$)$_3$], 46.08 (CH*C*H$_2$N), 63.53 (*C*H$_2$CH$_3$), 64.02 (*C*H$_2$CH$_3$), 71.23 (*C*HCH$_2$N), 79.43 [*C*(CH$_3$)$_3$], 103.32 (O*C*HO), 156.64 (*C*O). − MS (70 eV); *m/z* (%): 190 (0.5), 162 (4.6), 144 (3.6), 116 (8.4), 103 (100), 75 (51.9), 57 (33.1), 47 (41.7). − $C_{12}H_{25}NO_5$ (263.33): calcd. C 54.73, H 9.57, N 5.32; found C 54.80, H 9.66, N 5.13.

*(1R,2S)-(−)-1-tert-Butoxycarbonylaminocyclohexan-2-ol* [(2*R*,2*S*)-**12h**]: According to *GP 3* (1*S*,2*R*,1′*R*,2′*S*)-**11h** (376 mg, 1 mmol) was dissolved in 10 ml of THF and slowly added dropwise to 25 ml of liquid ammonia, containing dissolved sodium (58 mg, 2.5 mmol), at −78°C. The product was obtained as a colourless liquid after flash chromatography. Yield 214 mg (99%). − *ee*, *de* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz) and comparing with spectroscopical data of *trans*-(±)-1-*tert*-butoxycarbonylaminocyclohexan-2-ol. − $[\alpha]_D^{24}$ = −32.8 (*c* = 0.99, CHCl$_3$). − M.p. 93°C. − IR (KBr): $\tilde{\nu}$ = 3328 cm$^{-1}$ (s) 2979 (s), 2935 (s), 2860 (s), 1680 (s), 1537 (s), 1445 (m), 1390 (m), 1301 (m), 1179 (s), 1080 (m), 1069 (m). − $^1$H NMR (300 MHz): δ = 1.28−1.46 (m, 2 H, C$H_2$), 1.45 [s, 9 H, C(C$H_3$)$_3$], 1.49−1.66 (m, 5 H, C$H_2$), 1.73 (m, Σ$J$ = 32 Hz, 1 H, C$H_2$), 2.26 (br. d, $J$ = 3.02 Hz, 1 H, C*H*NH), 3.60 (br. s, 1 H, O*H*), 3.93 (br. d, $J$ = 1.65 Hz, 1 H, C*H*OH), 4.94 (br. d, $J$ = 6.90 Hz, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 19.95 (*C*H$_2$), 23.66 (*C*H$_2$), 27.46 (*C*H$_2$), 28.42 [C(*C*H$_3$)$_3$], 31.53 (*C*H$_2$), 52.08 (*C*HN), 69.30 (*C*HOH), 79.45 [*C*(CH$_3$)$_3$], 155.96 (*C*O). − MS (70 eV); *m/z* (%): 160 (1.8), 159 (8.6), 158 (9.5), 142 (8.6), 114 (15.8), 98 (56.6), 59 (23.6), 57 (100), 56 (48.2). − $C_{11}H_{21}NO_3$ (215.29): calcd. C 61.37, H 9.83, N 6.51; found C 61.52, H 9.99, N 6.35.

*trans-(±)-1-tert-Butoxycarbonylaminocyclohexan-2-ol: trans*-(±)-2-Aminocyclohexan-1-ol hydrochloride was treated with an excess of triethylamine and $Boc_2O$ in diethyl ether/methanol (1:1). − $^1$H NMR (300 MHz): δ = 1.10−1.39 (m, 4 H, C$H_2$), 1.45 [s, 9 H, C(C$H_3$)$_3$], 1.70 (m, Σ$J$ = 27.5 Hz, 2 H, C$H_2$), 2.00 (m, Σ$J$ = 40.0 Hz, 2 H, C$H_2$), 3.24−3.35 (m, 2 H, C*H*OH,C*H*NH), 3.45 (br. s, 1 H, O*H*), 4.76 (br. s, 1 H, N*H*). − $^{13}$C NMR (75 MHz): δ = 24.08 (*C*H$_2$), 24.71 (*C*H$_2$), 28.39 [C(*C*H$_3$)$_3$], 31.78 (*C*H$_2$), 34.15 (*C*H$_2$), 56.62 (*C*HN), 75.14 (*C*HOH), 79.88 [*C*(CH$_3$)$_3$], 157.12 (*C*O).

*(2S)-(+)-1-Amino-3-(5′,8′-dihydronaphth-1′-yloxy)propan-2-ol* [(2*S*)-**16**]: According to *GP 2* (1*S*,2*R*,1′*S*)-**8h** (90 mg, 0.22 mmol) was reduced by adding $NaBH_4$ (33 mg, 0.88 mmol) to a suspension of 11 mg of Pd/C in 5 ml of THF/methanol. According to *GP 3* the free amine (2*S*)-**14** was dissolved in 10 ml of THF and slowly added dropwise to 10 ml of liquid ammonia, containing dissolved sodium (15 mg, 0.65 mmol), at −78°C. The product was obtained as a white solid recrystallizing from diethyl ether/pentane. Yield 25 mg (50%). − *ee* ≥ 96%, determined by a shift experiment with (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent in the $^1$H-NMR spectrum (300 MHz). − $[\alpha]_D^{24}$ = +38.0 (*c* = 0.21, CHCl$_3$). − M.p. 114°C. − IR (CHCl$_3$): $\tilde{\nu}$ = 3350 cm$^{-1}$ (m), 2916 (s), 2860 (s), 1668 (m), 1584 (s), 1455 (s), 1385 (s), 1345 (m), 1310 (m), 1258 (s), 1208 (m), 1167 (m), 1096 (s), 1003 (s), 969 (s), 954 (s), 910 (m), 877 (m), 858 (m), 765 (s), 709 (m). − $^1$H NMR (300 MHz): δ = 2.08 (br. s, 3 H, N$H_2$, O*H*), 2.89 (br. m, 1 H, *H*CHNH$_2$), 3.01 (br. m, 1 H, HC*H*NH$_2$), 3.28 (br. d, $J$ = 6.38 Hz, 2 H, CHC$H_2$C$_{ar.}$), 3.38 (br. d, $J$ = 5.64 Hz, 2 H, CHC$H_2$C$_{ar.}$), 3.98 (br. m, 3 H, OC$H_2$C*H*), 5.88 (br. m, 2 H, C*H*C*H*), 6.67 (d, $J$ = 8.31 Hz, 1 H, C$H_{ar.}$), 6.74 (d, $J$ = 7.38 Hz, 1 H, C$H_{ar.}$), 7.10 (t, $J$ = 7.97 Hz, 1 H, C$H_{ar.}$). − $^{13}$C NMR (75 MHz): δ = 24.26, 29.47 (CH*C*H$_2$C$_{ar.}$), 44.10 (CH*C*H$_2$NH$_2$), 69.90 (OCH$_2$CH), 70.39 (*C*HOH), 108.10 (*o*-*C*H$_{ar.}$), 121.16 (*p*-*C*H$_{ar.}$), 123.31 (*o*-*i*-*C*$_{ar.}$), 124.01 (*C*HCH), 124.19 (CH*C*H), 126.40 (*m*-*C*H$_{ar.}$), 135.53 (*m*-*i*-*C*$_{ar.}$), 155.81 (O-*i*-*C*$_{ar.}$). − MS (70 eV); *m/z* (%): 221 (12.6, M$^+$+2), 220 (21.5) [M$^+$ + 1], 219 (100) [M$^+$], 148 (25.4), 146 (66.8), 145 (91.6), 128 (24.0), 115 (41.5), 74 (21.0), 56 (16.3). − CI, (*methane*) 2000 mTorr: *m/z* (%): 222 (36.6, M$^+$+3), 221 (38.3, M$^+$+2), 220 (100) [M$^+$ + 1], 219 (26.0) [M$^+$], 218 (19.1, M$^+$−1). − HR-MS, $C_{13}H_{17}NO_2$ (219.28): calcd. 219.125930; found 219.125811.

*(S)-(−)-N-Formylamphetamine* [(*S*)-**13**]: The compound was obtained as a by-product of the diethyl ether cleavage in the synthesis of the protected amino alcohols **12a**−**h** as a white solid. Yield 75−80%. − $[\alpha]_D^{24}$ = −23.2 (*c* = 0.50, CHCl$_3$). − M.p. 48°C. − IR (KBr): $\tilde{\nu}$ = 2968 cm$^{-1}$ (s), 2949 (m), 2923 (s), 2879 (s), 2786 (m), 2728 (m), 1655 (s), 1538 (s), 1493 (s), 1386 (s), 1337 (s), 1257 (s), 1130 (s), 1029 (m), 906 (m), 857 (m), 770 (s), 740 (s), 701 (s). − $^1$H NMR (300 MHz): (*Z*): δ = 1.16 (d, $J$ = 6.73 Hz, 3 H, NCHC$H_3$), 2.75 (d/d, $J$ = 13.46/7.08 Hz, 1 H, C$H_2$), 2.85 (d/d, $J$ = 13.46/6.15 Hz, 1 H, C$H_2$), 4.36 (d/q/d, $J$ = 7.07/6.66/6.11 Hz, 1 H, NC*H*CH$_3$), 5.43 (br. m, 1 H, N*H*), 7.12−7.35 (m, 5 H, C$H_{ar.}$), 8.09 (br. s, 1 H, C*H*O); (*E*): δ = 1.27 (d, $J$ = 6.66 Hz, 3 H, NCHC$H_3$), 2.70 (d/d, $J$ = 13.53/7.69 Hz, 1 H, C$H_2$), 2.82 (d/d, $J$ = 13.46/5.42

Hz, 1 H, C$H_2$), 3.74 (p/d, $J$ = 7.39/5.49 Hz, 1 H, NC$H$CH$_3$), 5.61 (br. d, $J$ = 12.50 Hz, 1 H, N$H$), 7.12−7.35 (m, 5 H, C$H_{ar.}$), 7.83 (d, $J$ = 11.53 Hz, 1 H, C$H$O). − $^{13}$C NMR (75 MHz): (*Z*): δ = 20.04 (NCH$C$H$_3$), 42.33 ($C$H$_2$), 45.00 (N$C$HCH$_3$), 128.50 (*o*-$C$H$_{ar.}$), 128.74 (*p*-$C$H$_{ar.}$), 129.46 (*m*-$C$H$_{ar.}$), 137.57 (*i*-$C_{ar.}$), 160.46 ($C$HO); (*E*): δ = 21.95 (NCH$C$H$_3$), 44.59 ($C$H$_2$), 49.68 (N$C$HCH$_3$), 126.64 (*o*-$C$H$_{ar.}$), 126.93 (*p*-$C$H$_{ar.}$), 129.46 (*m*-$C$H$_{ar.}$), 140.12 (*i*-$C_{ar.}$), 163.57 ($C$HO). − MS (70 eV); *m*/*z* (%): 164 (1.3) [M$^+$ + 1], 163 (1.9) [M$^+$], 119 (10.7), 118 (100), 91 (33.2), 72 (81.9). − $C_{10}H_{13}NO$ (163.22): calcd. C 73.59, H 8.03, N 8.58; found C 73.47, H 7.92, N 8.53.

*(R)-(+)-N-Formylamphetamine* [(*R*)-**13**]: $[\alpha]_D^{24}$ = +22.8 (*c* = 0.99, $CHCl_3$).


[1] F. Loydl, *Justus Liebigs Ann. Chem.* **1878**, *192*, 80.
[2] T. Purdie, *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 2238.
[3] [3a] T. Komnenos, *Justus Liebigs Ann. Chem.* **1883**, *218*, 145. − [3b] L. Claisen, *Justus Liebigs Ann. Chem.* **1883**, *218*, 170. − [3c] L. Claisen, *Justus Liebigs Ann. Chem.* **1887**, *35*, 413.
[4] [4a] A. Michael, *J. Prakt. Chem.* **1887**, *35*, 349. − [4b] A. Michael, O. Schulthess, *J. Prakt. Chem.* **1892**, *45*, 55. − [4c] A. Michael, *Am. Chem. J.* **1887**, *9*, 112. − [4d] A. Michael, *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 2126. − [4e] A. Michael, *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3731.
[5] [5a] L. Claisen, L. Crismer, *Justus Liebigs Ann. Chem.* **1883**, *218*, 129. − [5b] C. Liebermann, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 1876. − [5c] C. F. Koelsch, *J. Am. Chem. Soc.* **1943**, *65*, 437.
[6] A. Berkessel, in *Methods of Organic Chemistry* (Houben-Weyl), 4th ed., **1995**, vol. E 21e, p. 4818, and references cited therein.
[7] K. C. Nicolaou, C.-K. Hwang, M. E. Duggan, *J. Am. Chem. Soc.* **1989**, *111*, 6682.
[8] A. G. M. Barrett, P. D. Weipert, D. Dhanak, R. K. Husa, S. A. Lebold, *J. Am. Chem. Soc.* **1991**, *113*, 9820.
[9] [9a] A. Kamimura, N. Ono, *Tetrahedron Lett.* **1989**, *30*, 731. − [9b] K. Hori, S. Higuchi, A. Kamimura, *J. Org. Chem.* **1990**, *55*, 5900.
[10] W. Brade, A. Vasella, *Helv. Chim. Acta* **1990**, *73*, 1923.
[11] For example: [11a] A. Bernardi, S. Cardani, C. Scolastico, R. Villa, *Tetrahedron* **1990**, *46*, 1987. − [11b] S. Cardani, C. Scolastico, R. Villa, *Tetrahedron* **1990**, *46*, 7283.
[12] [12a] I. Chibata, *Immobilized Enzymes − Research and Development*, Halsted Press, New York, **1978**, p. 190. − [12b] T. Kitazume, T. Ikeya, K. Murata, *J. Chem. Soc., Chem. Commun.* **1986**, 1331. − [12c] M. A. Findeis, G. M. Whitesides, *J. Org. Chem.* **1987**, *52*, 2838.
[13] D. Enders, A. Haertwig, G. Raabe, J. Runsink, *Angew. Chem.* **1996**, *108*, 2540, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2388, and references cited therein.
[14] Reviews: [14a] A. G. M. Barrett, *Chem. Soc. Rev.* **1991**, *20*, 95. − [14b] V. V. Perealkin, E. S. Lipina, V. M. Berestovitskaya, D. A. Efremov, *Nitroalkenes*, John Wiley & Sons Ltd., Chichester, **1994**, p. 67, and references cited therein.
[15] Reviews: [15a] R. Henning, *Nachr. Chem. Tech. Lab.* **1990**, *38*, 460. − [15b] K. Tomioka, *Synthesis* **1990**, 541. − [15c] R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49. − [15d] Y. Ohfune, *Acc. Chem. Res.* **1992**, *25*, 360. − [15e] A. Golebiowski, J. Jurczak, *Synlett* **1993**, 241. − [15f] T. Kunieda, T. Ishizuka in *Studies in Natural Products Chemistry*, vol.12 (Ed.: Atta-ur-Rahman), Elsevier, New York, **1993**, p. 411 and references cited therein. − [15g] A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497.
[16] D. Lauvergnat, P. C. Hiberty, *J. Am. Chem. Soc.* **1997**, *119*, 9478, and references cited therein.
[17] [17a] B. M. Trost, J. L. Belletire, S. Godleski, P. G. McDougal, J. M. Balkovec, *J. Org. Chem.* **1986**, *51*, 2370. − [17b] B. M. Trost, R. C. Bunt, S. R. Pulley, *J. Org. Chem.* **1994**, *59*, 4202. − [17c] F. Hammerschmidt, Y. F. Li, *Tetrahedron* **1994**, *50*, 10253. − [17d] M. Kobayashi, S. Aoki, I. Kitagawa, *Tetrahedron Lett.* **1994**, *35*, 1243. − [17e] J. M. Seco, Sh. K. Latypov, E. Quiñoá, R. Riguera, *Tetrahedron: Asymmetry* **1995**, *6*, 107. − [17f] J. M. Seco, Sh. K. Latypov, E. Quiñoá, R. Riguera, *J. Org. Chem.* **1997**, *62*, 7556.
[18] [18a] D. Parker, R. J. Taylor *Tetrahedron* **1987**, *43*, 5451. − [18b] E. Mutschler, *Arzneimittelwirkungen*, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, **1991**, p. 247, and references cited therein. − [18b] J. Knabe, H.-D. Höltje, *Lehrbuch der pharmazeutischen Chemie*, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, **1991**, p. 502, and references cited therein. − [18b] H. Sasai, N. Itoh, T. Suzuki, M. Shibasaki, *Tetrahedron Lett.* **1993**, *34*, 855. − [18b] R. R. Ruffolo, W. Bondinell, J. P. Hieble, *J. Med. Chem.* **1995**, *38*, 3681.
[19] [19a] J. A. Dale, D. L. Dull, H. S. Mosher, *J. Org. Chem.* **1969**, *34*, 2543. − [19b] J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc.* **1973**, *95*, 512.
[20] [20a] R. Vilvala, T. Haapanen, *Acta Pharm. Fenn.* **1980**, *89*, 253. − [20b] B. D. Berrang, A. H. Lewin, F. I. Carroll, *J. Org. Chem.* **1982**, *47*, 2643. − [20c] I. A. Al-Meshal, M. Nasir, F. S. El-Feraly, *Phytochemistry* **1986**, *25*, 2241. − [20d] D. Enders, J. Zhu, L. Kramps *Liebigs Ann.* **1997**, 1101−1113 and references cited therein.
[21] L. Henry, *C. R. Hebd. Seances Acad. Sci.* **1895**, *120*, 1265.
[22] [22a] N. L. Drake, A. B. Ross, *J. Org. Chem.* **1958**, *23*, 717. − [22b] D. Seebach, P. Knochel, *Synth. Commun.* **1982**, 1017. − [22c] G. Rosini, R. Ballini, *Synthesis* **1988**, 833. − [22d] R. Syrig, Dissertation, RWTH Aachen, **1996** and references cited therein.
[23] [23a] D. E. Worrall, *J. Am. Chem. Soc.* **1934**, *56*, 1556. − [23b] A. McCarthy, W. Kahl, *J. Org. Chem.* **1956**, *21*, 1118. − [23c] M. Shiga, H. Kono, I. Motoyama, K. Hata *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1897.


[98193]