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# Catalytic *anti*-selective asymmetric Henry (nitroaldol) reaction catalyzed by Cu(I)–amine–imine complexes

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ABSTRACT

Chiral complex derived from *N*-methyl-$C_1$-tetrahydro-1,1′-bisisoquinolines (*R*)-**1b** and Cu(I)Cl promoted the diastereoselective Henry reaction of nitroethane with a series of aromatic and aliphatic aldehydes. The nitroalcohol adducts were obtained in excellent yields (up to 95%), moderate *anti*-selectivity (up to 2.6:1), and good enantioselectivity (up to 92% ee) without any special precautions to exclude moisture or air.



## 1. Introduction

The asymmetric nitroaldol (Henry) reaction[1–6] provides an atom-economical route to synthetically important enantioenriched α-hydroxy nitroalkanes. Manipulation of the nitro group can generate chiral compounds such as α-hydroxy ketones, β-amino alcohols, azides, aldehydes, carboxylic acids, and sulfides.[7–19] While highly enantioselective Henry reactions using nitromethane has been achieved successfully using various chiral metal catalysts,[20–28] organocatalysts[29–34] and enzymes,[35,36] highly diastereo- and enantioselective Henry reactions using other nitroalkanes still remain a challenge and are quite limited.[2] The first example of a direct *syn*-selective Henry reaction was reported by Shibasaki et al. in 1995 using modified BINOL heterobimetallic complexes.[37,38] Subsequently other *syn*-diastereoselective ligands such as guanidinium–thiourea,[39,40] bisimadozoline,[41] bisoxazolidine,[42,43] brucine,[44] and diamines[45–48] were reported with variable successes. On the other hand, the more notorious *anti*-diastereoselective version has been reported using enzymes,[36] tetraaminophosphonium salts,[49] quaternary ammonium biflourides,[50] amino alcohols,[51] amides[52], and amine-type ligands.[53–56] Two distinctive mechanistic models have been proposed to account for the *syn* and *anti*-selectivities: the chelation model gives *syn*-selectivity while a non-chelation model gives *anti*-selectivity.[57] Some of the limitations encountered in diastereoselective Henry reactions include the use of a narrow range of aldehydes and nitroalkanes as well as the requirement for activated substrates, low reaction temperatures, and long reaction times.[2] Therefore, more robust and efficient catalysts for diastereoselective (especially *anti*-selective) Henry reactions are highly desirable.

A closer look at the above reported ligands for diastereoselective Henry reactions reveals their wide diversity and the lack of common characteristic features between them. We previously reported a highly enantioselective Henry reaction between various aldehydes and nitromethane using a chiral $C_1$-1,1′-bisisoquinoline/Cu(I)Cl catalyst and briefly mentioned its potential for diastereoselective applications.[58–61] To expand the application of this amine–imine type catalyst, it was logical to further examine its application in the diastereoselective Henry reaction considering that these ligands have been utilized in many other asymmetric transformations.[62–70] We report herein the application of amine–imine chiral ligands based on 1,1′-bisisoquinoline framework (Fig. 1) in the diastereoselective Henry reaction between nitroethane and various aromatic and aliphatic aldehydes.

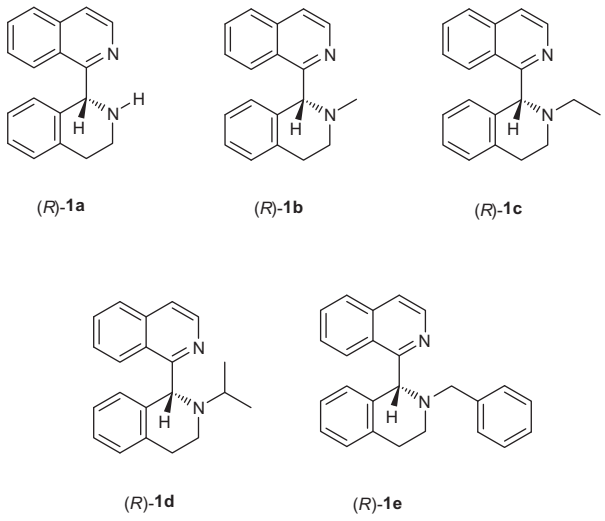


**Figure 1.** $C_1$-Tetrahydro-1,1′-bisisoquinoline and its chiral *N*-alkyl derivatives.

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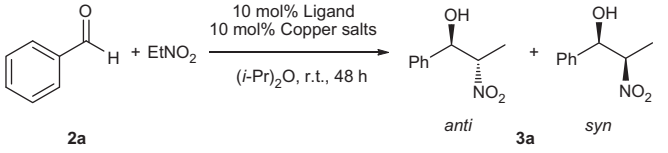
## 2. Results and discussion

Chiral ligands (*R*)-**1a**–**1e** (Fig. 1) have been easily synthesized.[58–60] Having alkyl substituents with differing bulkiness at the $sp^3$ nitrogen allows us to examine the crowding effect on the reactivity, diastereo- and enantioselectivities in the Henry reaction. We have started our screening of ligands (*R*)-**1a**–**1e** (Fig. 1) using the optimal conditions developed for the reaction of benzaldehyde with nitromethane (10 mol % ligand, 10% CuCl in $(i\text{-Pr})_2O$, rt, 48 h).[60] The results are summarized in Table 1. The reaction of benzaldehyde **2a** with nitroethane proceeded smoothly to give adducts *anti*- and *syn*-**3a**. Among ligands (*R*)-**1a**–**1e**, the parent ligand (*R*)-**1a** bearing no substituent afforded **3a** with the lowest diastereoselectivity (*anti*/*syn* = 1.7:1) while ligand (*R*)-**1b** bearing the smallest *N*-alkyl (i.e. *N*–$CH_3$) substituent proved to be the most efficient giving a 64% yield of **3a** with an *anti*/*syn* diastereoselectivity of 2.0:1 and with ee values of 72:78, respectively (Table 1, entry 2). Ligands (*R*)-**1c**–**1e** having relatively larger *N*-alkyl substituents afforded **3a** in comparable diastereoselectivities to (*R*)-**1b** but in lower yields and ee's (Table 1, entries 3–5). The reaction conditions were then optimized.

**Table 1**
Screening of ligands (*R*)-**1a**–**1e** and copper sources for the diastereoselective Henry reaction




**2a** **3a**

| Entry | Ligand | Copper source | Yield[a] (%) | *anti*/*syn*[b] | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | (*R*)-**1a** | CuCl | 49 | 1.7:1 | 64:70 |
| 2 | (*R*)-**1b** | CuCl | 64 | 2.0:1 | 72:78 |
| 3 | (*R*)-**1c** | CuCl | 50 | 2.1:1 | 68:64 |
| 4 | (*R*)-**1d** | CuCl | 43 | 1.9:1 | 66:67 |
| 5 | (*R*)-**1e** | CuCl | 36 | 2.0:1 | 65:68 |
| 6 | (*R*)-**1b** | CuBr | 55 | 2.0:1 | 63:73 |
| 7 | (*R*)-**1b** | CuI | 34 | 1.9:1 | 56:61 |
| 8 | (*R*)-**1b** | $CuCl_2$ | 17 | 1.7:1 | 54:40 |
| 9 | (*R*)-**1b** | $Cu(OAc)_2$ | 79 | 2.0:1 | 30:24 |
| 10 | (*R*)-**1b** | Cu(OAc) | 70 | 1.7:1 | 44:47 |

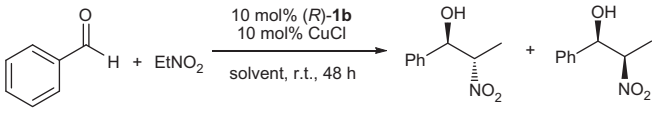
[a] Yields of isolated products.
[b] Determined by $^1H$ NMR analysis and HPLC using a Chiralpak AD-H column.
[c] Enantiomeric excesses values were determined by HPLC using Chiralpak AD-H column.[55]

The effects of different copper sources (Table 1) were examined using the most efficient ligand (*R*)-**1b**. The results obtained revealed that Cu(I) sources are superior to Cu(II) sources in terms of enantioselectivities (Table 1, entries 2, 6, and 7 vs entries 8–10). The use of different Cu(I) sources did not alter the diastereoselectivity of **3a** indicating that the counterions have little effect. However, CuCl gave better yields and enantioselectivities compared to CuBr and CuI (Table 1, entry 2 vs entry 6 vs entry 7) and thus was used for further reactions.

Subsequently, the effects of various solvents were examined (Table 2). THF gave the best *anti*/*syn* selectivity of 2.6:1, and the ee values were 83% (*anti*) and 90% (*syn*) (Table 2, entry 3). Further reactions were conducted using THF as the solvent.

Next, the effects of ratio of (*R*)-**1b** to CuCl and catalyst loading were examined. While keeping the amount of ligand (*R*)-**1b** constant at 10 mol %, a gradual increase in the amount of CuCl from 5, 10, 15 to 20 mol % gave comparable diastereoselectivities but resulted in a remarkable decrease in the yield of **3a** (Table 3, entries 1–4). The optimal ratio of ligand (*R*)-**1b** to CuCl is 1:1 (Table 3, entry 2) and the use of 20 mol % CuCl caused inhibition of the

**Table 2**
Screening of solvents for the diastereoselective Henry reaction using ligand (*R*)-**1b**



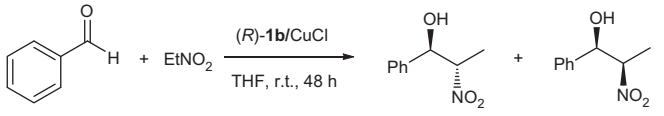

**2a** **3a**

| Entry | Solvent | Yield[a] (%) | *anti*/*syn*[b] | ee[c] (%) |
|---|---|---|---|---|
| 1 | $(i\text{-Pr})_2O$ | 64 | 2.0:1 | 72:78 |
| 2 | Dioxane | 55 | 2.1:1 | 74:80 |
| 3 | THF | 65 | 2.6:1 | 83:90 |
| 4 | $CH_2Cl_2$ | 38 | 2.3:1 | 72:80 |
| 5 | EtOH | 89 | 1.3:1 | 73:64 |
| 6 | $CH_3CN$ | 22 | 2.3:1 | 82:80 |
| 7 | Toluene | 19 | 1.3:1 | 47:53 |

[a] Yields of isolated products.
[b] Determined by $^1H$ NMR analysis and HPLC using a Chiralpak AD-H column.
[c] Enantiomeric excesses values were determined by HPLC using Chiralpak AD-H column.[55]

reaction (Table 3, entry 4). Attempts to increase the catalyst loading from 10 to 20 mol % provided **3a** in a higher yield (79%) but with lower diastereo- and enantioselectivities (Table 3, entries 2 vs 5). At a lower catalyst loading of 5 mol %, the nitroaldol adduct **3a** was obtained in comparable diastereoselectivity (*anti*/*syn* = 2.4:1; ee values 84% and 87%, respectively) but at a disappointingly lower yield (17%) (Table 2, entry 2 vs 6). Overall, the most effective condition used 10 mol % loading of (*R*)-**1b** and CuCl in a ratio of 1:1 (Table 3, entry 2).

**Table 3**
Screening of catalyst loading and ratios of (*R*)-**1b** to CuCl for the diastereoselective Henry reaction



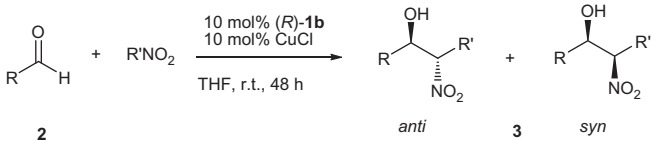

**2a** **3a**

| Entry | Ratio (*R*)-**1b**/CuCl | Yield[a] (%) | *anti*/*syn*[b] | ee[c] (%) |
|---|---|---|---|---|
| 1 | 1:0.5 | 70 | 2.3:1 | 81:80 |
| 2 | 1:1.0 | 65 | 2.6:1 | 83:90 |
| 3 | 1:1.5 | 36 | 2.3:1 | 76:83 |
| 4 | 1:2.0 | — | — | — |
| 5 | 2:2.0 | 79 | 2.0:1 | 61:75 |
| 6[d] | 0.5:0.5 | 17 | 2.4:1 | 84:87 |

[a] Yields of isolated products.
[b] Determined by $^1H$ NMR analysis and HPLC using Chiralpak AD-H column.
[c] Enantiomeric excesses values were determined by HPLC using Chiralpak AD-H column.[55]
[d] Reaction time is 120 h.

The scope for the reaction was studied under the optimized conditions as described in Table 3, entry 2. For a variety of aldehydes, the reaction proceeded cleanly to afford the desired nitroaldol adducts as single product with predominately *anti* diastereoselectivity in good ee values and yields. In case of aromatic aldehydes, the electronic nature of the substituent on the aromatic ring has little effect on the diastereoselectivity, irrespective of its electron withdrawing or donating effect (Table 4, entries 2–9). However, electron donating substituents exhibited higher ee (Table 4, entries 2–5 vs entries 6–9). 2-Naphthylaldehyde (Table 4, entry 10) gave a lower *anti* adduct and ee in comparison to the *syn* isomer possibly due to fast retro-Henry reaction and

**Table 4**
Diastereoselective Henry reaction of aldehydes with nitroethane catalyzed by (*R*)-**1b**/CuCl




**2** **3**

| Entry | R | R′ | Product | Yield[a] (%) | *anti*/*syn*[b] | ee[c] (%) |
|---|---|---|---|---|---|---|
| 1 | Ph | $CH_3CH_2$ | **3a** | 65 | 2.6:1 | 83:90 |
| 2 | 2-$FC_6H_4$ | $CH_3CH_2$ | **3b** | 80 | 2.1:1 | 72:86 |
| 3 | 4-$ClC_6H_4$ | $CH_3CH_2$ | **3c** | 83 | 1.5:1 | 63:86 |
| 4 | 4-$BrC_6H_4$ | $CH_3CH_2$ | **3d** | 85 | 1.6:1 | 61:87 |
| 5 | 4-$NO_2C_6H_4$ | $CH_3CH_2$ | **3e** | 95 | 1.5:1 | 50:66 |
| 6[d] | 2-$MeC_6H_4$ | $CH_3CH_2$ | **3f** | 70 | 1.6:1 | 75:92 |
| 7[d] | 3-$MeC_6H_4$ | $CH_3CH_2$ | **3g** | 65 | 1.6:1 | 77:87 |
| 8[d] | 4-$MeC_6H_4$ | $CH_3CH_2$ | **3h** | 75 | 1.7:1 | 85:91 |
| 9[d] | 2-MeOC6H4 | $CH_3CH_2$ | **3i** | 70 | 2.1:1 | 84:90 |
| 10 | 2-Naphthyl | $CH_3CH_2$ | **3j** | 70 | 0.8:1 | 40:75 |
| 11 | *i*-Bu | $CH_3CH_2$ | **3k** | 80 | 1.3:1 | 90:91 |
| 12 | *n*-Pr | $CH_3CH_2$ | **3l** | 81 | 1.3:1 | 90:89 |
| 13 | *i*-Bu | $CH_3CH_2CH_2$ | **3m** | 73 | 1.3:1 | 86:90 |
| 14 | *n*-Pr | $CH_3CH_2CH_2$ | **3n** | 79 | 1.1:1 | 85:87 |
| 15 | Et | $CH_3CH_2CH_2$ | **3o** | 77 | 1.1:1 | 86:89 |

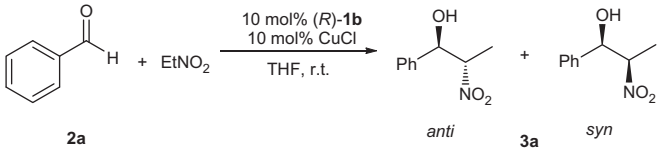
[a] Yields of isolated products.
[b] Determined by $^1$H NMR analysis and HPLC using Chiralcel OD-H, OJ-H and OB-H, Chiralpak AD-H, AS-H columns.
[c] Enantiomeric excesses values were determined by HPLC using Chiralcel OD-H, OJ-H and OB-H, Chiralpak AD-H, AS-H columns.[39,43,51,53–55]
[d] Reaction time is 96 h.

epimerization (see below for an explanation). Addition of nitroethane to aliphatic aldehydes gave lower diastereoselectivities, however, the products were obtained in very good yields and excellent ee's (up to 80% yield and 91% ee) (Table 4, entries 11–15).

Under the reaction conditions utilized (Table 4), we observed that reaction time greatly affects the *anti*/*syn* ratio of the nitroaldol adducts. This is not surprising considering that yjr Henry reaction is known to be reversible (retro-nitroaldol or retro-Henry) and the nitroaldol adducts are easily epimerized at the carbon α to the $NO_2$ group. Therefore, we decided to further elucidate the stereochemistry of the reaction by conducting both cross-over and time-course studies.[71]

In the cross-over reaction, treatment of a THF solution of nitroaldol adducts *anti*-**3a** and *syn*-**3a** with (*R*)-**1b**/CuCl (10 mol %, 1:1) and $MeNO_2$ (20 mol %) resulted in the formation of benzaldehyde **2a** and 1-phenyl-2-nitroethanol along with *anti*-**3a** and *syn*-**3a**. This result clearly indicates that a retro-Henry reaction is taking place. Further evidence for a retro-Henry reaction comes from the time-course studies (Table 5). As clearly seen from Table 5, entries 1–4, the amount of the more dominant *anti*-**3a** gradually decreases as the reaction proceeds and then equilibrates with *syn*-**3a** (Table 5, entries 4–9).[38,72] We believe that there is a competing kinetic versus thermodynamic control. Initially, we have a reaction that allows for the formation of the more dominant and thermodynamically stable *anti*-**3a** along with the kinetically formed *syn*-**3a**, indicating thermodynamic control. As the reaction proceeds over time and as a result of retro-Henry reaction, the kinetically *syn*-**3a** equilibrates with the thermodynamically *anti*-**3a** and an equilibrium is established after ca. 30 h (Fig. 2).[38,52,73] In addition, after 63 h, more of the *anti*-**3a** slowly converts to the *syn*-**3a**. Moreover, as shown in Table 4, the ee values of the *anti*- and *syn*-nitroaldol adducts are similar but with a slight bias toward the *syn*-product, indicating the probability of in situ epimerization of the *anti*-**3a** adduct to the *syn*-**3a** adduct.[38,52,73]

**Table 5**
Time-course studies of diastereoselective Henry reaction of benzaldehyde with $EtNO_2$ catalyzed by (*R*)-**1b**/CuCl[a]




**2a** **3a**

| Entry | Time (h) | *anti*-**3a**/*syn*-**3a**[b] |
|---|---|---|
| 1 | 8 | 3.7:1 |
| 2 | 14.5 | 3.0:1 |
| 3 | 23.5 | 2.7:1 |
| 4 | 31.5 | 2.6:1 |
| 5 | 48.5 | 2.6:1 |
| 6 | 55.5 | 2.6:1 |
| 7 | 62.5 | 2.6:1 |
| 8 | 80.5 | 2.5:1 |
| 9 | 96 | 2.4:1 |

[a] All reactions were performed on a 0.2 mmol scale of benzaldehyde in the presence of ligand (*R*)-**1b** (10 mol %) and CuCl (10 mol %) using $EtNO_2$ (20 equiv) in THF (1.5 ml).
[b] Determined by $^1$H NMR analysis.

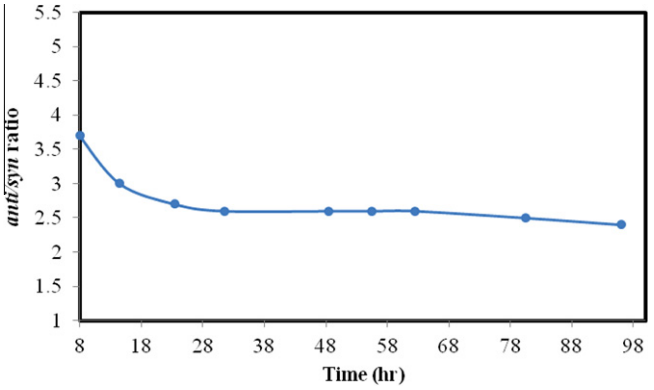



**Figure 2.** Time-course studies of diastereoselective Henry reaction of benzaldehyde with $EtNO_2$ catalyzed by (*R*)-**1b**/CuCl.

## 3. Conclusion

We have shown that chiral $C_1$-1,1′-bisisoquinoline (*R*)-**1b** is an effective ligand in the Cu(I)-catalyzed diastereoselective Henry reaction. The desired products were obtained in very good yields (up to 95%), moderate diastereoselectivities and good enantioselectivities (up to 92%) using a range of aliphatic and aromatic aldehydes. The major diastereomer obtained is the *anti* isomer which has proven difficult to obtain using various ligands. Cross-over and time-course studies suggest a competition between the kinetically and thermodynamically controlled products. The enantioinduction is governed by the substituents at the nitrogen of (*R*)-**1a**. The operational procedure using the present catalyst system is simple and no exclusion of air or moisture is required. Further investigation of the detailed reaction mechanism is still in progress.

## 4. Experimental

### 4.1. General

All commercial chemicals were reagent grade unless otherwise specified. Analytical thin layer chromatography (TLC) was performed using $F_{254}$ pre-coated silica gel plates (0.2 mm thickness). Separation of products was achieved using column chromatography

on Silica Gel 60 (230–400 mesh). FTIR were recorded as thin films (KBr). NMR spectra were recorded at 300 MHz for $^1$H and at 75.6 MHz for $^{13}$C. Chemical shifts are given in ppm relative to TMS ($\delta$ = 0 ppm) or solvent residual peaks ($CDCl_3$: $^1$H, $\delta$ = 7.26 ppm; $^{13}$C, $\delta$ = 75 ppm) as internal standards. $^1$H NMR multiplicities were designated as singlet (s), doublet (d), doublet of doublet (dd), doublet of doublet of doublet (ddd), triplet (t), triplet of doublet (td), quartet (q), pentet (p), multiplet (m) and broad (br). HPLC separations were performed on using Diacel Chiralcel OD-H, OJ-H, AS-H and AD-H chiral columns.

### 4.2. General procedure for the asymmetric Henry reaction

T first, (*R*)-**1b** (0.02 mmol, 10 mol %) and CuCl (0.02 mmol, 10 mol %) were mixed in THF (1.5 mL) and allowed to stir at rt for 1 h. Aldehydes (0.2 mmol) and nitroethane/nitropropane (4 mmol, 20 equiv) were then added sequentially. The reaction mixture was then stirred at the given temperature for a specific time (TLC). The β-nitroalcohol product was purified on silica gel by flash column chromatography.

#### 4.2.1. 1-Phenyl-2-nitropropan-1-ol 3a

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (65% yield); diastereomeric ratios (*anti*/*syn*, 2.6:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (90:10 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 8.38 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 9.16 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 10.69 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 11.83 min. *anti*/*syn* = 83%/90% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.48 (3H, d, *J* = 6.9 Hz), 3.05 (1H, s), 4.65–4.82 (1H, m), 5.33–5.39 (1H, m), 7.31–7.42 (5H, m); *syn* isomer—1.30 (3H, d, *J* = 6.9 Hz), 3.05 (1H, s), 4.65–4.82 (1H, m), 5.01 (1H, d, *J* = 9.0 Hz), 7.31–7.42 (5H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.1, 73.9, 87.4, 125.9, 128.6, 128.8, 138.4; *syn* isomer—16.5, 76.3, 88.4, 126.9, 129.0, 129.2, 138.3.

#### 4.2.2. 1-(2-Fluorophenyl)-2-nitropropan-1-ol 3b

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (80% yield); diastereomeric ratios (*anti*/*syn*, 2.1:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (95:5 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 11.54 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 14.12 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 18.89 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 22.64 min. *anti*/*syn* = 72%/86% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.49 (3H, d, *J* = 6.9 Hz), 2.91 (1H, d, *J* = 6.9 Hz), 4.79–4.88 (1H, m), 5.70–5.76 (1H, m), 7.03–7.13 (1H, m), 7.19–7.59 (3H, m); *syn* isomer—1.41 (3H, d, *J* = 6.9 Hz), 2.77 (1H, s), 4.79–4.88 (1H, m), 5.38–5.39 (1H, m), 7.03–7.13 (1H, m), 7.19–7.59 (3H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—11.9, 68.3, 85.2, 115.4, 124.6, 125.4, 127.8, 130.1, 157.5; *syn* isomer—16.2, 70.0, 87.9, 115.8, 125.0, 125.6, 128.3, 130.6, 160.8.

#### 4.2.3. 1-(4-Chlorophenyl)-2-nitropropan-1-ol 3c

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (83% yield); diastereomeric ratios (*anti*/*syn*, 1.5:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (95:5 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 16.13 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 17.29 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 22.84 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 25.37 min. *anti*/*syn* = 63%/86% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.49 (3H, d, *J* = 6.0 Hz), 2.82 (1H, s), 4.62–4.75 (1H, m), 5.66 (1H, br s), 7.30–7.40 (4H, m); *syn* isomer—1.33 (3H, d, *J* = 6.0 Hz), 2.71 (1H, s), 4.62–4.75 (1H, m), 5.39 (1H, d, *J* = 8.1 Hz), 7.30–7.40 (4H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.0, 73.2, 87.2, 127.4, 129.0, 134.4, 136.9; *syn* isomer—16.4, 75.5, 88.2, 128.3, 129.2, 135.1, 136.8.

#### 4.2.4. 1-(4-Bromophenyl)-2-nitropropan-1-ol 3d

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (85% yield); diastereomeric ratios (*anti*/*syn*, 1.6:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (90:10 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 9.84 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 10.45 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 13.26 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 15.27 min. *anti*/*syn* = 61%/87% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.40 (3H, d, *J* = 6.9 Hz), 2.89 (1H, d, *J* = 3.9 Hz), 4.53–4.69 (1H, m), 5.25–5.31 (1H, m), 7.16–7.20 (2H, m), 7.42–7.47 (2H, m); *syn* isomer—1.24 (3H, d, *J* = 6.9 Hz), 2.83 (1H, d,, *J* = 3.9 Hz), 4.53–4.69 (1H, m), 4.90–4.94 (1H, m), 7.16–7.20 (2H, m), 7.42–7.47 (2H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.0, 73.3, 87.2, 122.5, 127.7, 131.9, 137.6; *syn* isomer—16.3, 75.5, 88.2, 123.2, 128.6, 132.1, 137.4.

#### 4.2.5. 1-(4-Nitrophenyl)-2-nitropropan-1-ol 3e

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 4:1) to give a yellow oil (95% yield); diastereomeric ratios (*anti*/*syn*, 1.5:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralcel OD-H + Chiralpak AD-H (80:20 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{major}$ (1*R*,2*S*) $t_r$ = 16.95 min, $anti_{minor}$ (1*S*,2*R*) $t_r$ = 18.65 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 21.60 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 24.81 min. *anti*/*syn* = 50%/66% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.49 (3H, d, *J* = 6.9 Hz), 3.10 (1H, s), 4.68–4.82 (1H, m), 5.54–5.61 (1H, m), 7.58–7.62 (2H, m), 8.24–8.28 (2H, m); *syn* isomer—1.39 (3H, d, *J* = 6.9 Hz), 3.10 (1H, s), 4.68–4.82 (1H, m), 5.20 (1H, d, *J* = 9.0 Hz), 7.58–7.62 (2H, m), 8.24–8.28 (2H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—11.9, 72.9, 86.8, 124.0, 127.0, 145.6, 148.5; *syn* isomer—16.1, 75.0, 87.8, 124.1, 127.9, 145.6, 148.0.

#### 4.2.6. 2-Nitro-1-*o*-tolylpropan-1-ol 3f

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (70% yield); diastereomeric ratios (*anti*/*syn*, 1.6:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (95:5 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 11.44 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 12.80 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 15.60 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 19.43 min. *anti*/*syn* = 75%/92% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.43 (3H, d, *J* = 6.9 Hz), 2.29 (3H, s), 2.58 (1H, s), 4.54–4.57 (1H, m), 5.54 (1H, s), 7.08–7.19 (3H, m), 7.46 (1H, d, *J* = 7.2 Hz); *syn* isomer—1.22 (3H, d, *J* = 6.9 Hz), 2.36 (3H, s), 2.48 (1H, s), 4.77–4.80 (1H, m), 5.27–5.30 (1H, m), 7.08–7.19 (3H, m), 7.29–7.32 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—11.5, 18.9, 70.9, 85.4, 126.0, 126.4, 128.4, 130.8, 134.3, 136.7; *syn* isomer—16.1, 19.6, 72.2, 88.8, 126.5, 126.8, 128.8, 131.0, 135.9, 136.6.

#### 4.2.7. 2-Nitro-1-*m*-tolylpropan-1-ol 3g

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (65% yield); diastereomeric ratios (*anti*/*syn*, 1.6:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AS-H column (90:10 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 8.74 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 9.73 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 10.44 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 12.91 min. *anti*/*syn* = 77%/87% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.44 (3H, d, *J* = 6.9 Hz), 2.29 (3H, s), 2.63 (1H, d, *J* = 3.6 Hz),

4.57–4.74 (1H, m), 5.28 (1H, dd, $J$ = 3.6, 3.4 Hz), 7.05–7.11 (3H, m), 7.17–7.24 (1H, m); *syn* isomer—1.23 (3H, d, $J$ = 6.9 Hz), 2.30 (3H, s), 2.51 (1H, d, $J$ = 3.6 Hz), 4.57–4.74 (1H, m), 4.90 (1H, dd, $J$ = 3.6, 3.6 Hz), 7.05–7.11 (3H, m), 7.17–7.24 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.1, 21.4, 74.0, 87.5, 123.0, 126.6, 128.6, 129.3, 138.5, 138.6; *syn* isomer—16.5, 21.5, 76.3, 88.5, 124.1, 127.5, 128.9, 130.0, 138.3, 138.9.

#### 4.2.8. 2-Nitro-1-*p*-tolylpropan-1-ol 3h

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a yellow oil (75% yield); diastereomeric ratios (*anti*/*syn*, 1.7:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (95:5 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 14.56 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 16.40 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 22.50 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 26.66 min. *anti*/*syn* = 85%/91% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.51 (3H, d, $J$ = 6.9 Hz), 2.36 (3H, s), 2.62 (1H, br s), 4.67–4.79 (1H, m), 5.32–5.39 (1H, m), 7.21–7.28 (4H, m); *syn* isomer—1.31 (3H, d, $J$ = 6.9 Hz), 2.36 (3H, s), 2.49 (1H, br s), 4.67–4.79 (1H, m), 5.06 (1H, d, $J$ = 8.1 Hz), 7.21–7.28 (4H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.3, 21.1, 73.9, 87.5, 125.9, 129.4, 135.4, 138.4; *syn* isomer—16.5, 29.7, 76.2, 88.5, 126.8, 129.7, 133.4, 139.2.

#### 4.2.9. 1-(2-Methoxyphenyl)-2-nitropropan-1-ol 3i

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 8:1) to give a yellow oil (70% yield); diastereomeric ratios (*anti*/*syn*, 2.1:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak OJ-H column (95:5 *n*-hex–IPA, 0.6 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 47.22 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 53.95 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 60.84 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 64.25 min. *anti*/*syn* = 84%/90% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.47 (3H, d, $J$ = 6.9 Hz), 3.11 (1H, br s), 3.88 (3H, s), 4.86–4.97 (1H, m), 5.53 (1H, s), 6.88–7.02 (2H, m), 7.26–7.37 (2H, m); *syn* isomer—1.33 (3H, d, $J$ = 6.9 Hz), 3.32 (1H, d, $J$ = 3 Hz), 3.88 (3H, s), 5.00–5.03 (1H, m), 5.11–5.17 (1H, m), 6.88–7.02 (2H, m), 7.41–7.44 (2H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.6, 55.4, 70.8, 85.1, 110.4, 121.0, 126.3, 127.6, 129.5, 155.8; *syn* isomer—16.6, 55.5, 74.1, 87.7, 111.0, 121.2, 125.9, 129.0, 130.1, 156.8.

#### 4.2.10. 1-(Naphthyalen-2-yl)-2-nitropropan-1-ol 3j

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (70% yield); diastereomeric ratios (*anti*/*syn*, 0.8:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (90:10 *n*-hex–IPA, 1.0 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 11.55 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 13.91 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 17.96 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 20.55 min. *anti*/*syn* = 40%/75% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—1.52 (3H, d, $J$ = 6.9 Hz), 2.84 (1H, br s), 4.79–4.93 (1H, m), 5.58 (1H, s), 7.43–7.55 (3H, m), 7.84–7.94 (4H, m); *syn* isomer—1.33 (3H, d, $J$ = 6.9 Hz), 2.69 (1H, br s), 4.79–4.93 (1H, m), 5.20 (1H, d, $J$ = 9.3 Hz), 7.43–7.55 (3H, m), 7.84–7.94 (4H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—12.0, 74.0, 87.3, 123.3, 125.3, 126.5, 126.6, 127.7, 128.09, 128.7, 133.11, 133.2, 135.7; *syn* isomer—16.6, 76.5, 88.4, 123.8, 126.7, 126.74, 126.8, 127.8, 128.07, 129.1, 133.09, 133.6, 135.6.

#### 4.2.11. 5-Methyl-2-nitrohexan-3-ol 3k

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (80% yield); diastereomeric ratios (*anti*/*syn*, 1.3:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (98:2 *n*-hex–IPA, 0.8 ml/min, 220 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 20.18 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 21.70 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 26.09 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 28.00 min. *anti*/*syn* = 90%/91% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—0.86–0.91 (6H, m), 1.15–1.23 (1H, m), 1.48 (3H, d, $J$ = 6.6 Hz), 1.76–1.80 (2H, m), 2.28 (1H, br s), 4.20 (1H, d, $J$ = 6.6 Hz), 4.40–4.46 (1H, m); *syn* isomer—0.86–0.91 (6H, m), 1.06–1.14 (1H, m), 1.30–1.39 (2H, m), 1.49 (3H, d, $J$ = 6.9 Hz), 2.28 (1H, br s), 3.86–3.90 (1H, m), 4.40–4.46 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—16.3, 21.7, 23.6, 24.3, 42.0, 71.2, 86.7; *syn* isomer—12.4, 21.4, 23.3, 24.5, 41.8, 70.2, 88.2.

#### 4.2.12. 2-Nitrohexan-3-ol 3l

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (81% yield); diastereomeric ratios (*anti*/*syn*, 1.3:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (98:2 *n*-hex–IPA, 0.8 ml/min, 220 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 25.40 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 27.92 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 31.55 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 35.12 min. *anti*/*syn* = 90%/89% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—0.87–0.92 (5H, m), 1.34–1.40 (2H, m), 1.46 (3H, d, $J$ = 6.9 Hz), 2.13 (1H, br s), 4.12–4.15 (1H, m), 4.45–4.50 (1H, m); *syn* isomer—0.87–0.92 (5H, m), 1.34–1.40 (2H, m), 1.49 (3H, d, $J$ = 6.9 Hz), 2.22 (1H, br s), 3.75–3.85 (1H, m), 4.45–4.50 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—13.8, 16.3, 18.4, 35.1, 72.7, 86.4; *syn* isomer—12.4, 13.9, 19.0, 29.7, 71.8, 87.7.

#### 4.2.13. 2-Methyl-5-nitroheptan-4-ol 3m

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (73% yield); diastereomeric ratios (*anti*/*syn*, 1.3:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (99:1 *n*-hex–IPA, 0.6 ml/min, 210 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 22.13 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 25.02 min, $syn_{minor}$ (1*S*,2*S*) $t_r$ = 30.79 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 32.07 min. *anti*/*syn* = 86%/90% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—0.84–0.96 (9H, m), 1.11–1.23 (2H, m), 1.34–1.41 (1H, m), 1.76–1.84 (2H, m), 2.02–2.19 (1H, m), 4.08–4.13 (1H, m), 4.25–4.30 (1H, m); *syn* isomer—0.84–0.96 (9H, m), 1.11–1.23 (2H, m), 1.34–1.41 (1H, m), 1.76–1.84 (2H, m), 2.02–2.19 (1H, m), 3.89–3.92 (1H, m), 4.25–4.30 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—10.5, 21.3, 21.5, 23.5, 24.5, 42.0, 70.4, 94.2; *syn* isomer—10.2, 21.5, 23.4, 23.9, 24.3, 42.5, 70.0, 94.8.

#### 4.2.14. 3-Nitroheptan-4-ol 3n

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (79% yield); diastereomeric ratios (*anti*/*syn*, 1.1:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak AD-H column (99.5:0.5 *n*-hex–IPA, 1.0 ml/min, 215 nm); $anti_{minor}$ (1*S*,2*R*) $t_r$ = 27.38 min, $anti_{major}$ (1*R*,2*S*) $t_r$ = 29.19 min, $syn_{minor}$ (1*S*, 2*S*) $t_r$ = 38.67 min, $syn_{major}$ (1*R*,2*R*) $t_r$ = 40.70 min. *anti*/*syn* = 85%/87% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—0.85–0.95 (6H, m), 1.32–1.49 (4H, m), 1.80–1.85 (1H, m), 2.00–2.06 (2H, m), 3.90–4.00 (1H, m), 4.30–4.39 (1H, m); *syn* isomer—0.85–0.95 (6H, m), 1.32–1.49 (4H, m), 1.80–1.85 (1H, m), 2.00–2.06 (2H, m), 3.81–3.88 (1H, m), 4.30–4.39 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—10.5, 13.7, 18.8, 21.5, 35.2, 72.0, 93.9; *syn* isomer—10.2, 13.8, 18.5, 23.9, 35.5, 71.6, 94.4.

#### 4.2.15. 3-Nitrohexan-4-ol 3o

This compound was prepared according to the General Procedure and purified by column chromatography (Hexane–EtOAc 5:1) to give a clear oil (77% yield); diastereomeric ratios (*anti*/

*syn*, 1.1:1) were determined by $^1$H NMR and HPLC. HPLC analysis: Chiralpak OB-H column (98:2 *n*-hex–IPA, 0.6 ml/min, 210 nm); *anti*$_{minor}$ (1*S*,2*R*) $t_r$ = 18.71 min, *anti*$_{major}$ (1*R*,2*S*) $t_r$ = 22.05 min, *syn*$_{major}$ (1*R*,2*R*) $t_r$ = 28.02 min, *syn*$_{minor}$ (1*S*,2*S*) $t_r$ = 32.17 min. *anti*/*syn* = 86%/89% ee. $^1$H NMR (300 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—0.96–0.99 (6H, m), 1.26–1.41 (2H, m), 1.65–1.91 (2H, m), 2.33–2.60 (1H, m), 3.77–3.83 (1H, m), 4.16–4.21 (1H, m); *syn* isomer—0.96–0.99 (6H, m), 1.26–1.41 (2H, m), 1.65–1.91 (2H, m), 2.33–2.60 (1H, m), 3.60–3.75 (1H, m), 4.16–4.21 (1H, m); $^{13}$C NMR (75.6 MHz, $CDCl_3$, $\delta$ ppm): *anti* isomer—10.0, 10.5, 21.5, 26.3, 73.6, 93.7; *syn* isomer—9.6, 10.2, 24.0, 26.5, 73.1, 94.1.

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