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Catalytic Asymmetric Henry Reaction of Nitroalkanes and Aldehydes Catalyzed by a Chiral *N,N′*-Dioxide/Cu(I) Complex

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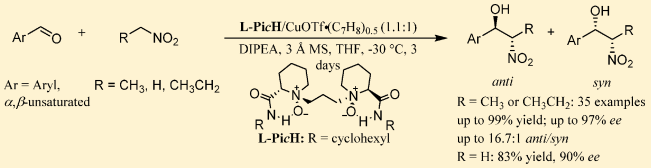
Supporting Information

ABSTRACT: An easily available *N,N′*-dioxide/Cu(I) complex has been developed for the catalytic asymmetric nitroaldol (Henry) reaction of aldehydes with nitroethane. Under mild reaction conditions, a series of substituted aromatic, heteroaromatic and *α,β*-unsaturated aldehydes are transformed to the corresponding *anti*-*β*-nitroalcohols in good to excellent yields (up to 99%) with moderate to good *dr* (up to 16.7:1 *anti*/*syn*) and high *ee* values (up to 97%). Besides nitroethane, nitromethane and 1-nitropropane were also employed as nucleophiles, and good enantioselectivities were obtained.



INTRODUCTION

Henry reaction is a powerful and efficient method for the construction of carbon−carbon bond.[1] The resulting products, *β*-nitroalcohols, can be easily transformed into 2-hydroxycarboxylic acids,[2] 2-nitro ketones,[3] nitro alkenes[4] and *β*-amino alcohols.[5] As we know, *β*-amino alcohol is a very important structure in various biologically active natural products,[6] pharmaceuticals[7] and chiral ligands.[8] Thus, the catalytic asymmetric protocols for Henry reaction have gained particular attention.[9,10] Comparing with the well developed Henry reaction of aldehydes with nitromethane,[9c,h,i] the Henry reaction of aldehydes with other nitroalkanes is more challenging for often suffering from low reactivity and poor stereoselectivity. An alternative approach is the application of trimethylsilyl nitronates.[10a,b] Taking into account the atom economy, the direct reactions of aldehydes with nitroalkanes are more attractive. After several years, impressive progress in asymmetric Henry reaction of aldehydes with nitroethane has been achieved.[10e−j] Ooi's tetraaminophosphonium salt-mediated catalyst[10c] and Shibasaki's heterobimetallic complexes[1i,j,10p−r] are quite efficient for the Henry reaction of nitroethane with different types of aldehydes. Although great progress has been achieved, developing new catalysts for the diastereoselective and enantioselective Henry reaction of aldehydes with nitroethane is still necessary.

In our group, *N,N′*-dioxide/metal complexes have been used to catalyze a number of enantioselective reactions.[11] And, they were also proven to be efficient for the enantioselective Henry reaction of nitromethane with aromatic aldehydes and alkyl substituted *α*-ketoesters, giving the corresponding products in moderate to excellent yields with good to excellent *ee* values.[12] As a matter of course, we want to know whether *N,N′*-dioxide/metal complexes can also be efficient for the Henry reaction about nitroethane. Herein, we present our intensive study of applying the *N,N′*-dioxide/metal catalysts to the diastereo- and enantioselective Henry reaction of nitroalkanes with aldehydes.

RESULTS AND DISCUSSION

In the initial study, benzaldehyde (**1a**) and nitroethane were chosen as the model substrate and nucleophilic reagent. First, the reaction was performed in THF at 0 °C using 5 mol % of *N,N′*-dioxide **L-PicP** in combination with various metal salts. When the complexes of $NiBr_2$, $Cu(OTf)_2$ and $Zn(OTf)_2$ were applied as the catalysts, no or trace amount of products were detected (Table 1, entries 1 to 3). Delightedly, when using the complex of $CuOTf{\cdot}(C_7H_8)_{0.5}$ as catalyst, the corresponding **2a** was obtained in 65% yield with 66/34 *anti*/*syn* and 51/63% *ee* (Table 1, entry 4). The quite different behavior between $Cu(OTf)_2$ and $CuOTf{\cdot}(C_7H_8)_{0.5}$ might be caused by their different coordination nature. $Cu(OTf)_2$ can coordinate with the four oxygen atoms of *N,N′*-dioxides;[13] thus, next only either aldehyde or nitroethane can be activated, which cannot promote the reaction. Meanwhile, $CuOTf{\cdot}(C_7H_8)_{0.5}$ can coordinate with two or three oxygen atoms of the ligand,[10n] and next active both the aldehyde and nitroethane, and nitroethane is deprotonated by the counterion of Cu(I) to generate the active nucleophile through a possible complex of nitronate, which attacks aldehyde to yield corresponding adduct. Then, the counterion of Cu(I) was screened. When CuBr and $[Cu(CH_3CN)_4]PF_6$ were used, the reactivity and enantioselectivity of the reaction decreased dramatically (Table 1, entries 5 and 6). Next, the efficiency of $CuOTf{\cdot}(C_7H_8)_{0.5}$ with other *N,N′*-dioxide ligands was explored (Figure 1), which showed that the reactivity and enantioselectivity were closely dependent on both the substituent R_1 of the amide moiety and

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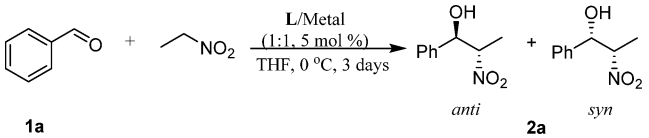
Table 1. Screen of Lewis Acids and *N,N′*-Dioxide Ligands



entry[a]	metal	ligand	yield (%)[b]	*anti/syn* (%)[c]	*ee* (%)[c]
1	$NiBr_2$	**L-PicP**	n.r.[d]	–	–
2	$Cu(OTf)_2$	**L-PicP**	trace	n.d.[e]	n.d.[e]
3	$Zn(OTf)_2$	**L-PicP**	n.r.[d]	–	–
4	$CuOTf{\cdot}(C_7H_8)_{0.5}$	**L-PicP**	65	66/34	51/63
5	CuBr	**L-PicP**	36	62/38	6/−2
6	$[Cu(CH_3CN)_4]PF_6$	**L-PicP**	10	58/42	11/−12
7	$CuOTf{\cdot}(C_7H_8)_{0.5}$	**L-PiPr$_2$**	trace	n.d.[e]	n.d.[e]
8	$CuOTf{\cdot}(C_7H_8)_{0.5}$	**L-PicH**	17	69/31	65/60
9	$CuOTf{\cdot}(C_7H_8)_{0.5}$	**L-PrcH**	78	67/33	6/−11
10	$CuOTf{\cdot}(C_7H_8)_{0.5}$	**L-RacH**	66	64/36	5/10

[a]Unless otherwise noted, all reactions were performed with **L**/Metal (1:1, 5 mol %), **1a** (0.2 mmol, 20 μL), nitroethane (10 equiv, 142 μL) in THF (0.5 mL) under N_2 at 0 °C for 3 days. [b]Isolated yield. [c]Determined by chiral HPLC analysis (Chiralcel AD-H). [d]n.r. = no reaction. [e]n.d. = not determined.

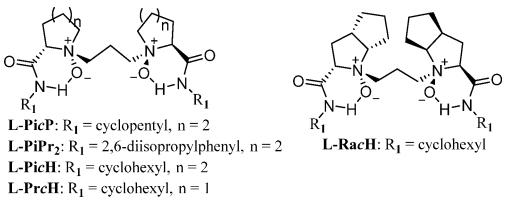


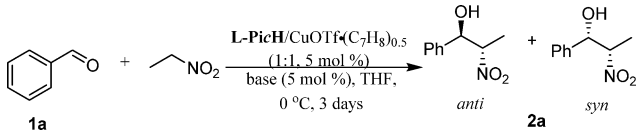
Figure 1. Ligands screened in this work.

the chiral backbone. As shown in Table 1, when the substituent R_1 was 2,6-diisopropylphenyl group, trace amount of product **2a** was detected (Table 1, entry 7), while alkyl cyclohexyl subunit could promote the reaction in 65/60% *ee* and 69/31 *anti/syn* albeit with 17% yield (Table 1, entry 8). When different backbones were investigated, it was found that L-pipecolic acid derived **L-PicH** was much superior to L-proline-derived **L-PrcH** and L-ramipril-derived **L-RacH** in enantioselectivity but inferior in reactivity (Table 1, entry 8 vs entries 9 and 10).

In order to improve the reactivity of **L-PicH**/$CuOTf{\cdot}(C_7H_8)_{0.5}$ complex catalysis, Brønsted bases were designed to add in the catalytic system to achieve the goal by helping to generate the nitronate and hence enhancing the nucleophilic capability. As expected, when the bases were added, the yield of the nitroaldol product was improved dramatically and in most cases nearly quantitative yields were obtained (Table 2, entries 1−6). However, the enantioselectivity and diastereoselectivity of the reaction were decreased in varying degrees. The *N,N*-diisopropylethylamine (DIPEA) decreased the *dr* to 58/42 and the *ee* to 57/68% (Table 2, entry 1). Other bases, such as DBU, DABCO, DMAP, pyridine and Cs_2CO_3, decreased the enantioselectivity of the reaction more seriously (Table 2, entries 2−6). The base might not only affect the generation of the nitronate, but also inhibit the formation of beneficial catalytic species in varying degrees depending on their structures in this catalytic system.

The effect of solvents was also examined (Table 3, entries 1−5). Aprotic solvents toluene, acetonitrile, and THF (Table 3,

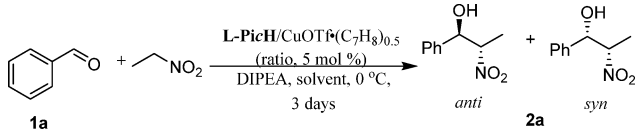
Table 2. Screen of Additive



entry[a]	base	yield (%)[b]	*anti/syn* (%)[c]	*ee* (%)[c]
1	DIPEA[d]	99	58/42	57/68
2	DBU[e]	99	60/40	14/4
3	DABCO[f]	99	41/59	2/−32
4	DMAP[g]	93	57/43	17/−16
5	Pyridine	96	59/41	43/25
6	Cs_2CO_3	99	63/37	36/40

[a]Unless otherwise noted, all reactions were performed with **L-PicH**/$CuOTf{\cdot}(C_7H_8)_{0.5}$ (1:1, 5 mol %), **1a** (0.2 mmol, 20 μL), nitroethane (10 equiv, 142 μL) and base (5 mol %) in THF (0.5 mL) under N_2 at 0 °C for 3 days. [b]Isolated yield. [c]Determined by chiral HPLC analysis (Chiralcel AD-H). [d]DIPEA = *N,N*-Diisopropenyl ethylamine. [e]DBU = 1,8-Diazabicyclo-[5.4.0]undec-7-ene. [f]DABCO = 1,4-Diazabicyclo-[2.2.2]octane. [g]DMAP = 4-Dimethylaminopyridine.

Table 3. Screen of Solvents and the Ratio of Ligand to Metal



entry[a]	solvent	ratio (**L**/**M**)	yield (%)[b]	*anti/syn* (%)[c]	*ee* (%)[c]
1	THF	1:1	99	58/42	57/68
2	toluene	1:1	86	60/40	26/15
3	CH_3CN	1:1	93	57/43	33/50
4	CH_2Cl_2	1:1	85	53/47	16/13
5	^iPrOH	1:1	99	61/39	4/−18
6	THF	0.5:1	92	60/40	37/13
7	THF	1.1:1	89	57/43	60/74
8	THF	1.5:1	93	55/45	55/73
9	THF	2:1	92	56/44	52/64

[a]Unless otherwise noted, all reactions were performed with **L-PicH**/$CuOTf{\cdot}(C_7H_8)_{0.5}$ (ratio, 5 mol %), **1a** (0.2 mmol, 20 μL), nitroethane (10 equiv, 142 μL) and DIPEA (5 mol %) in solvent (0.5 mL) under N_2 at 0 °C for 3 days. [b]Isolated yield. [c]Determined by chiral HPLC analysis (Chiralcel AD-H).

entries 1−3) gave better enantioselectivity than halogenated solvent dichloromethane (Table 3, entry 4) and protic solvent isopropanol (Table 3, entry 5). And THF was shown to be suitable solvent for this reaction in terms of the yield and enantioselectivity (Table 3, entry 1). When the ratio of ligand **L-PicH** to $CuOTf{\cdot}(C_7H_8)_{0.5}$ was investigated from 0.5:1 to 2:1 (Table 3, entries 7−10). The results suggested that the better ratio of ligand **L-PicH**/$CuOTf{\cdot}(C_7H_8)_{0.5}$ was 1.1:1, and the *ee* of the product **2a** was improved to 60/74% without decreasing the *anti/syn* ratio, albeit with a slightly decreased reactivity (Table 3, entry 8).

When the reaction temperature was lowered to −20 °C, the enantioselectivity was increased to 84/85% (Table 4, entry 2). Encouraged by the hopeful results obtained, the loading of DIPEA was surveyed under −20 °C. When the loading of DIPEA was increased from 5 to 30 mol %, the yield was increased sharply from 72% to 99% with *dr* and *ee* maintained (Table 4, entries 2−5). The *dr* and *ee* was further improved to 78/22 and 93/89% when the reaction temperature was further

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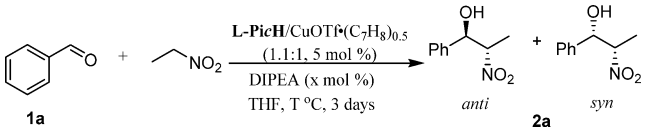
Table 4. Screen of Reaction Temperature and the Loading of DIPEA



entry[a]	T (°C)	x (mol %)	yield (%)[b]	*anti*/*syn* (%)[c]	*ee* (%)[c]
1	0	5	89	57/43	60/74
2	−20	5	72	67/33	84/85
3	−20	10	99	69/31	86/85
4	−20	20	99	65/35	83/84
5	−20	30	99	69/31	86/84
6	−30	30	89	78/22	93/89
7[d]	−30	30	93	71/29	96/94

[a]Unless otherwise noted, all reactions were performed with **L-PicH**/CuOTf·$(C_7H_8)_{0.5}$ (1.1:1, 5 mol %), **1a** (0.2 mmol, 20 μL), nitroethane (10 equiv, 142 μL) and DIPEA (5 mol %) in solvent (0.5 mL) under N_2 at 0 °C for 3 days. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]30 mg of 3 Å molecular sieves were added.

lowered to −30 °C (Table 4, entry 6). When 30 mg of 3 Å MS were employed, the enantioselectivity improved substantially to 96/94% *ee*. According our previous work,[14] the molecular sieves might help to form the benificial catalytic species in the catalytic system.

Thus, the optimal reaction conditions were determined to be 5 mol % of **L-PicH**/Cu(I) (1.1:1), 30 mol % of DIPEA, 10 equiv of nitroethane, 30 mg of 3 Å MS at −30 °C in THF.

With the optimized conditions in hand, the substrate scope of the reaction was evaluated, and the results were summarized in Table 5. Various substituted benzaldehydes proceeded smoothly to provide the corresponding products in moderate to excellent yields (up to 99%) with moderate to good *dr* (up to 16.7:1 *anti*/*syn*) and high *ee* values (up to 97%). Generally, the reaction of *ortho*-substituted benzaldehydes provided much higher diastereoselectivity than those with *meta*- or *para*-substituted benzaldehydes. For example, the reaction of *ortho*-bromobenzaldehyde **1l** afforded the corresponding product **2l** with 14.3:1 *anti*/*syn*, while the *meta*- or *para*-bromobenzaldehyde **1m** and **1n** gave a ratio of 3.2:1 and 3.9:1, respectively (Table 5, entry 12 vs entries 13 and 14). Besides, electron-donating substituents on the *para*-position of the phenyl ring had a negative influence on the reactivity. **1w** and **1y** with a *para*-electron-donating substitutent gave the corresponding adduct **2w** only in 66% yield and **2y** in 46% yield (Table 5, entries 23 and 25). 1-Naphthaldehyde **1ab** and 2-naphthaldehyde **1ac** proceeded also well to afford the nitroaldol products in 85 and 95% yields with moderate *anti*/*syn* ratios (3.7:1 and 2.7:1) and high *ee* values (93/84% and 94/95%), respectively (Table 5, entries 28 and 29). α,β-Unsaturated aldehyde **1ad** afforded the corresponding product in 95% yield with 1.3:1 *anti*/*syn* ratio and 81/79% *ee* values (Table 5, entry 30). Finally, heteroaromatic aldehydes **1ae**−**1ah** were also tested, giving the optically active nitroaldol adducts in 81−95% yields with 1.0:1−1.9:1 *anti*/*syn* selectivities and 90−96% *ee* values (Table 5, entries 31−34). Besides, nitromethane and 1-nitropropane were also employed as nucleophiles to react with benzaldehyde. The corresponding products **2ai** was obtained in 83% yield and 90% *ee* (Table 5, entry 35), while **2aj** was obtained in 35% yield with 84/56% *ee* and 1.8:1 *anti*/*syn* (Table 5, entry 36). The poor reactivity of 1-nitropropane was caused by its steric hindrance. The absolute configuration of major *anti*-isomer of **2a** was determined to be (1*R*,2*S*)[10b,15a−g] and that of **2ai** was determined to be *R*[12] by comparison of the HPLC with literature data.

In summary, a highly efficient catalytic asymmetric Henry reaction of aldehydes with nitroalkanes has been realized by using a *N*,*N*′-dioxide/Cu(I) complex. Various β-nitro alcohols were obtained in moderate to high yields with high to excellent enantioselectivities and moderate to good diastereoselectivities.

EXPERIMENTAL SECTION

General Remarks. Reactions were carried out using commercial available reagents in overdried apparatus. THF was dried over Na and distilled prior to use. Nitroalkanes were dried over anhydrous $CaCl_2$ and distilled prior to use. Aldehydes were obtained from commercial sources and were distilled or recrystallized before use. Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV detector at 210 nm. The ratio of *anti*/*syn* was determined by ^{1}H NMR spectroscopy analysis. ^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.16 ppm).

General Procedure for the Catalytic Asymmetric Henry Reaction. A dry reaction tube was charged with CuOTf·$(C_7H_8)_{0.5}$ (2.6 mg, 0.01 mmol), **L-PicH** (5.4 mg, 0.011 mmol) and 30 mg 3 Å MS under an N_2 atmosphere. Then, THF (0.5 mL) was added and the mixture was stirred at 35 °C for 0.5 h. Next, substrate **1** (0.2 mmol) was added and the mixture was stirred at 35 °C for 0.5 h. Finally, 30 mol % DIPEA (10.5 μL, 0.06 mmol) and 10 equiv of nitroalkanes (2.0 mmol) were added with being stirred at the indicated temperature. The mixture was stirred at the indicated temperature for 3 days. The residue was purified by flash chromatography (petroleum ether/AcOEt, 9:1 to 3:1) on silica gel to afford the products. The enantiomeric excesses (*ee*) were determined by high-performance liquid chromatography (HPLC). The ratio of *anti*/*syn* was determined by ^{1}H NMR spectroscopy analysis.

2-Nitro-1-phenylpropan-1-ol (**2a**).[10g,l,m,15a−g] $C_9H_{11}NO_3$. Yellow oil in 93% yield, 33.7 mg. Enantiomeric excesses (96% for *anti*, 94% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): (1*S*,2*R*) t_R (*anti* minor) = 15.74 min, (1*R*,2*S*) t_R (*anti* major) = 17.31 min, (1*S*,2*S*) t_R (*syn* minor) = 20.15 min, (1*R*,2*R*) t_R (*syn* major) = 22.17 min. Absolute configuration of major *anti*-isomer was determined to be (1*R*,2*S*) by comparison of the retention time with literature data. Diastereomeric ratio (*anti*/*syn* = 2.6:1, Table 5, entry 1) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.32−7.30 (m, 5H, *anti*+*syn*), 5.32 (s, 0.72H, *anti*), 4.94 (q, 0.28H, *syn*), 4.73−4.66 (m, 0.28H, *syn*), 4.65−4.59 (m, 0.72H, *anti*), 2.66 (s, 0.72H, *anti*), 2.55 (s, 0.28H, *syn*), 1.43 (d, 2.16H, J = 6.8 Hz, *anti*), 1.24 (d, 0.84H, J = 7.6 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 138.6, 128.9, 128.7, 126.1, 87.6, 74.0, 12.2.

1-(2-Fluorophenyl)-2-nitropropan-1-ol (**2b**).[10m,15g] $C_9H_{10}FNO_3$. Yellow oil in 93% yield, 37.0 mg. Enantiomeric excesses (94% for *anti*, 90% for *syn*) HPLC (DAICEL CHIRALPAK IA, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 6.30 min, t_R (*anti* major) = 7.03 min, t_R (*syn* minor) = 8.34 min, t_R (*syn* major) = 9.36 min. Diastereomeric ratio (*anti*/*syn* = 3.0:1, Table 5, entry 2) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58−7.54 (m, 0.75H, *anti*), 7.48−7.45 (m,0.25H, *syn*), 7.39−7.31 (m, 1H, *anti*+*syn*), 7.23−7.19 (m, 1H, *anti*+*syn*), 7.12−7.04 (m, 1H, *anti*+*syn*), 5.73 (s, 0.75H, *anti*), 5.40 (q, 0.25H, *syn*), 4.88−4.78 (m, 1H, *anti*+*syn*), 2.95 (d, 0.75H, J = 3.6 Hz, *anti*), 2.82 (d,

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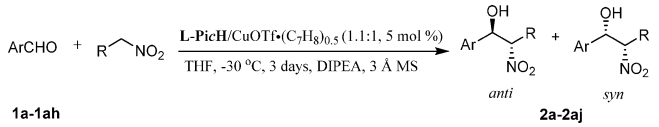
Table 5. Substrate Scope of Aldehydes and Nitroalkanes in the Asymmetric Henry Reaction



1a-1ah 2a-2aj

entry[a]	aldehyde (Ar)	nitroalkanes (R)	product	yield (%)[b]	*anti*/*syn* (%)[c]	*ee* (%)[d]
1	Ph (**1a**)	CH_3	**2a**	93	2.6:1	96(1*R*,2*S*)/94(1*S*,2*S*)
2	2-FC_6H_4 (**1b**)	CH_3	**2b**	93	3.0:1	94/90
3	3-FC_6H_4 (**1c**)	CH_3	**2c**	91	3.0:1	92/82
4	4-FC_6H_4 (**1d**)	CH_3	**2d**	80	3.2:1	94/84
5	2,6-diFC_6H_3 (**1e**)	CH_3	**2e**	99	2.8:1	93/97
6	2-ClC_6H_4 (**1f**)	CH_3	**2f**	99	16.7:1	90/n.d.[e]
7	3-ClC_6H_4 (**1g**)	CH_3	**2g**	86	10.0:1	94/58
8	4-ClC_6H_4 (**1h**)	CH_3	**2h**	88	2.9:1	90/84
9	2,4-diClC_6H_3 (**1i**)	CH_3	**2i**	96	11.1:1	90/n.d.[e]
10	2,6-diClC_6H_3 (**1j**)	CH_3	**2j**	99	7.1:1	95/98
11	3,4-diClC_6H_3 (**1k**)	CH_3	**2k**	99	3.7:1	89/77
12	2-BrC_6H_4 (**1l**)	CH_3	**2l**	99	14.3:1	95/n.d.[e]
13	3-BrC_6H_4 (**1m**)	CH_3	**2m**	96	3.2:1	93/85
14	4-BrC_6H_4 (**1n**)	CH_3	**2n**	98	3.9:1	92/82
15	2-$F_3CC_6H_4$ (**1o**)	CH_3	**2o**	88	2.7:1	91/76
16	4-$F_3CC_6H_4$ (**1p**)	CH_3	**2p**	91	3.6:1	92/83
17	4-$O_2NC_6H_4$ (**1q**)	CH_3	**2q**	90	2.5:1	85/76
18	2-MeC_6H_4 (**1r**)	CH_3	**2r**	93	10.0:1	92/n.d.[e]
19	3-MeC_6H_4 (**1s**)	CH_3	**2s**	82	3.3:1	90/92
20	4-MeC_6H_4 (**1t**)	CH_3	**2t**	80	3.0:1	90/86
21	2-$MeOC_6H_4$ (**1u**)	CH_3	**2u**	93	11.1:1	94/n.d.[e]
22	3-$MeOC_6H_4$ (**1v**)	CH_3	**2v**	86	2.9:1	97/95
23	4-$MeOC_6H_4$ (**1w**)	CH_3	**2w**	66	2.9:1	93/92
24	3-$PhOC_6H_4$ (**1x**)	CH_3	**2x**	93	3.0:1	96/92
25	4-BnC_6H_4 (**1y**)	CH_3	**2y**	46	2.1:1	94/95
26	4-F-3-$PhOC_6H_3$ (**1z**)	CH_3	**2z**	77	4.8:1	93/79
27	4-PhC_6H_4 (**1aa**)	CH_3	**2aa**	93	2.4:1	93/89
28	1-naphthyl (**1ab**)	CH_3	**2ab**	85	3.7:1	93/84
29	2-naphthyl (**1ac**)	CH_3	**2ac**	95	2.7:1	94/95
30	PhC≡C (**1ad**)	CH_3	**2ad**	95	1.3:1	81/79
31	2-furyl (**1ae**)	CH_3	**2ae**	95	1.0:1	96/96
32	3-furyl (**1af**)	CH_3	**2af**	90	1.7:1	96/90
33	2-thienyl (**1ag**)	CH_3	**2ag**	81	1.1:1	90/90
34	3-thienyl (**1ah**)	CH_3	**2ah**	94	1.9:1	96/93
35	Ph (**1a**)	H	**2ai**	83	–	90(*R*)
36	Ph (**1a**)	CH_3CH_2	**2aj**	35	1.8:1	84/56

[a]Reactions were carried out on a 0.2 mmol scale of aldehyde with 10 equiv of nitroalkane in 0.5 mL THF in the presence of **L-PicH**/CuOTf·$(C_7H_8)_{0.5}$ (1.1:1, 5 mol %), 30 mol % DIPEA, and 30 mg of 3 Å MS at −30 °C for 3 days. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy analysis. [d]Determined by chiral HPLC analysis. [e]n.d. = not determined.

0.25H, *J* = 4.8 Hz, *syn*), 1.48 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.41 (d, 0.75H, *J* = 7.6 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 160.5, 158.0, 130.3, 130.2, 128.0, 127.9, 125.7, 125.5, 124.8, 124.7, 115.6, 115.4, 85.3, 85.3, 68.4, 68.4, 12.0.

*1-(3-Fluorophenyl)-2-nitropropan-1-ol (**2c**).*[10m] $C_9H_{10}FNO_3$. Yellow oil in 91% yield, 36.2 mg. Enantiomeric excesses (92% for *anti*, 82% for *syn*) HPLC (DAICEL CHIRALPAK ID, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.54 min, t_R (*anti* minor) = 6.95 min, t_R (*syn* minor) = 8.58 min, t_R (*syn* major) = 10.54 min. Diastereomeric ratio (*anti*/*syn* = 3.0:1, Table 5, entry 3) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.33−7.19 (m, 1H, *anti*+*syn*), 7.07−6.93 (m, 3H, *anti*+*syn*), 5.34 (s, 0.75H, *anti*), 4.96 (d, 0.25H, *J* = 8.8 Hz, *syn*), 4.69−4.57 (m, 1H, *anti*+*syn*), 2.81 (br, 0.75H, *anti*), 2.74 (br, 0.25H, *syn*), 1.41 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.271 (d, 0.75H, *J* = 7.6 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 164.4, 161.9, 141.2, 141.1, 130.5, 130.5, 121.7, 121.6, 115.7, 115.5, 113.4, 113.2, 87.3, 73.2, 73.3, 12.0.

*1-(4-Fluorophenyl)-2-nitropropan-1-ol (**2d**).*[10m] $C_9H_{10}FNO_3$. Yellow oil in 80% yield, 31.8 mg. Enantiomeric excesses (94% for *anti*, 84% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.88 min, t_R (*anti* minor) = 7.74 min, t_R (*syn* minor) = 10.21 min, t_R (*syn* major) = 11.18 min. Diastereomeric ratio (*anti*/*syn* = 3.2:1, Table 5, entry 4) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.28−7.19 (m, 2H, *anti*+*syn*), 7.04−6.98 (m, 2H, *anti*+*syn*), 5.29 (s, 0.76H, *anti*), 4.95 (d, 0.24H, *J* = 9.2 Hz, *syn*), 4.69−4.58 (m, 1H, *anti*+*syn*), 2.77−2.68 (m, 1H, *anti*+*syn*), 1.43 (d, 2.28H, *J* = 6.4 Hz, *syn*), 1.24 (d, 0.72H, *J* = 6.4 Hz, *anti*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 163.0, 160.6, 133.3, 126.9, 126.9, 115.0, 114.7, 86.6, 72.5, 11.3.

*1-(2,6-Difluorophenyl)-2-nitropropan-1-ol (**2e**).*[15] $C_9H_{10}F_2NO_3$. Yellow oil in 99% yield, 43.0 mg. Enantiomeric excesses (93% for

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anti, 97% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*syn* major) = 5.20 min, t_R (*syn* minor) = 5.56 min, t_R (*anti* minor) = 10.63 min, t_R (*anti* major) = 11.72 min. Diastereomeric ratio (*anti*/*syn* = 2.8:1, Table 5, entry 5) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.32−7.20 (m, 1H, *anti*+*syn*), 6.92−6.83 (m, 2H, *anti*+*syn*), 5.47−5.40 (m, 1H, *anti*+*syn*), 5.10−5.02 (m, 0.74H, *anti*), 4.96−4.89 (m, 0.26H, *syn*), 2.81 (s, 1H, *anti*+*syn*), 1.66 (d, 1.22H, J = 6.8 Hz, *syn*), 1.31 (d, 1.78H, J = 7.8 Hz, *anti*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 161.2, 161.1, 158.7, 158.6, 130.2, 130.1, 130.0, 111.3, 111.1, 85.4, 66.7, 15.3. HRMS (ESI-TOF) calcd for $C_9H_9{}^{18.9984}F_2NNaO_3^+$ ([M + Na^+]) = 240.0450, found 240.0448.

1-(2-Chlorophenyl)-2-nitropropan-1-ol (**2f**).[10m] $C_9H_{10}ClNO_3$ Yellow oil in 99% yield, 42.7 mg. Enantiomeric excesses (90% for *anti*, n.d. for *syn*) HPLC (DAICEL CHIRALPAK ID, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, detection at 210 nm) t_R (*anti* minor) = 8.70 min, t_R (*anti* major) = 9.04 min, t_R (*syn* minor) = 12.07 min, t_R (*syn* major) = 14.69 min. Diastereomeric ratio (*anti*/*syn* = 16.7:1, Table 5, entry 6) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.57 (d, 0.93H, J = 7.6 Hz, *anti*), 7.43 (d, 0.07H, J = 7.2 Hz, *syn*), 7.31−7.19 (m, 3H, *anti*+*syn*), 5.77 (s, 0.94H, *anti*), 5.53 (q, 0.06H, J = 4.8 Hz, *syn*), 4.84−4.78 (m, 1H, *anti*+*syn*), 2.89−2.80 (m, 1H, *ant*+*syn*), 1.38−1.36 (m, 3H, *anti*+*syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 135.9, 131.6, 129.8, 129.8, 128.3, 127.4, 84.2, 70.6, 11.3.

1-(3-Chlorophenyl)-2-nitropropan-1-ol (**2g**).[10l] $C_9H_{10}ClNO_3$. Yellow oil in 86% yield, 37.1 mg. Enantiomeric excesses (94% for *anti*, 58% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 0.5 mL/min, detection at 210 nm): (1*S*,2*R*) t_R (*anti* minor) = 13.22 min, (1*R*,2*S*) t_R (*anti* major) = 15.57 min, (1*S*,2*S*) t_R (*syn* minor) = 19.81 min, (1*R*,2*R*) t_R (*syn* major) = 25,53 min. Diastereomeric ratio (*anti*/*syn* = 10:1, Table 5, entry 7) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58−7.56 (m, 0.91H, *anti*), 7.44−7.42 (m,0.09H, *syn*), 7.34−7.19 (m, 3H, *anti*+*syn*), 5.77 (s,0.91H, *anti*), 5.52 (q, 0.09H, J = 3.2 Hz, *syn*), 4.84−4.75 (m, 1H, *anti*+*syn*), 2.88 (br, 0.91H, *anti*), 2.82 (br, 0.09H, *syn*), 1.37−1.36 (m, 3H, *anti*+*syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 135.9, 131.6, 129.8, 129.7, 128.2, 127.4, 84.2, 70.6, 11.3.

1-(4-Chlorophenyl)-2-nitropropan-1-ol (**2h**).[10l,15d,h] $C_9H_{10}ClNO_3$. Yellow oil in 88% yield, 37.9 mg. Enantiomeric excesses (90% for *anti*, 84% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 5.71 min, t_R (*anti* major) = 6.77 min, t_R (*syn* minor) = 9.79 min, t_R (*syn* major) = 11.65 min Diastereomeric ratio (*anti*/*syn* = 2.9:1, Table 5, entry 8) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.40−7.31 (m, 4H, *anti*+*syn*), 5.38 (t, 0.74H, J = 3.6 Hz, *anti*), 5.02 (q, 0.26H, J = 4.0 Hz, *syn*), 4.76−4.71 (m, 0.26H, *syn*), 4.69−4.63 (m, 0.74H, *anti*), 2.79−2.78 (m, 0.74H, *anti*), 2.67−2.66 (m, 0.26H, *syn*), 1.49 (d, 2.25H, J = 6.8 Hz, *anti*), 1.33 (d, 0.75H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 137.0, 134.5, 129.1, 127.5, 87.3, 73.3, 12.2.

1-(2,4-Dichlorophenyl)-2-nitropropan-1-ol (**2i**).[15] $C_9H_{10}Cl_2NO_3$. Yellow oil in 96% yield, 48.0 mg. Enantiomeric excesses (91% for *anti*, n.d. for *syn*) HPLC (DAICEL CHIRALPAK ID, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 5.72 min, t_R (*anti* minor) = 6.87 min, t_R (*syn* minor) = 8.53 min, t_R (*syn* major) = 8.72 min. Diastereomeric ratio (*anti*/*syn* = 11.1:1, Table 5, entry 9) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60−7.58 (m, 1H, *anti*+*syn*), 7.40−7.33 (m, 2H, *anti*+ *syn*), 5.79 (s, 0.92H, *anti*), 5.56−5.54 (m, 0.08H, *syn*), 4.84−4.83 (m, 1H, *anti*+*syn*), 3.05 (s, 1H, *anti*+*syn*), 1.44−1.42 (m, 3H, *ant* +*syni*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 135.1, 134.6, 132.2, 129.6, 129.3, 127.8, 83.9, 70.2, 11.2.

1-(2,6-Dichlorophenyl)-2-nitropropan-1-ol (**2j**).[15] $C_9H_{10}Cl_2NO_3$. Yellow oil in 99% yield, 49.5 mg. Enantiomeric excesses (95% for *anti*, 98% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*syn* minor) = 6.49 min, t_R (*syn* major) = 7.87 min, t_R (*anti* minor) = 11.53 min, t_R (*anti* major) = 12.88 min. Diastereomeric ratio (*anti*/*syn* = 7.1:1, Table 5, entry 10) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.39−7.33 (m, 2H, *anti*+*syn*), 7.28−7.20 (m, 1H, *anti*+*syn*), 6.01−5.97 (m, 0.88H, *anti*), 5.81−5.77 (m, 0.12H, *syn*), 5.52−5.35 (m, 1H, *anti*+*syn*), 3.61−3.24 (m, 1H, *anti*+*syn*), 1.80 (d, 0.87H, J = 6.8 Hz, *syn*), 1.37 (d, 2.13H, J = 6.8 Hz, *anti*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 135.1, 132.7, 130.7, 130.5, 129.9, 86.0, 70.9, 16.1. HRMS (ESI-TOF) calcd for $C_9H_9{}^{34.9689}Cl_2KNO_3^+$ ([M + K^+]) = 287.9589, found 287.9597; $C_9H_9{}^{36.9659}Cl_2KNO_3^+$ ([M + K^+]) = 291.9538, found 291.9585.

1-(3,4-Dichlorophenyl)-2-nitropropan-1-ol (**2k**).[15h] $C_9H_{10}Cl_2NO_3$. Yellow oil in 99% yield, 49.5 mg. Enantiomeric excesses (89% for *anti*, 76% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 5.64 min, t_R (*anti* minor) = 6.43 min, t_R (*syn* minor) = 8.49 min, t_R (*syn* major) = 10.61 min. Diastereomeric ratio (*anti*/*syn* = 3.7:1, Table 5, entry 11) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.52−7.46 (m, 2H, *anti*+*syn*), 7.23−7.20 (m, 1H, *anti*+*syn*), 5.39 (t, 1H, J = 3.2 Hz, *anti*), 5.02 (q, 0.27H, J = 3.6 Hz, *anti*), 2.92−2.91 (m, 0.73H, *anti*), 2.84 (m, 0.27H, *syn*), 1.48 (d, 2.19H, J = 7.2 Hz, *anti*), 1.36 (d, 0.81H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 138.7, 133.2, 132.8, 130.9, 128.2, 125.4, 87.1, 72.7, 12.0.

1-(2-Bromophenyl)-2-nitropropan-1-ol (**2l**).[15g] $C_9H_{10}BrNO_3$. Yellow oil in 99% yield, 51.5 mg. Enantiomeric excesses (95% for *anti*, n.d. for *syn*) HPLC (DAICEL CHIRALPAK IA, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 6.42 min, t_R (*anti* major) = 7.31 min, t_R (*syn* minor) = 9.07 min, t_R (*syn* major) = 11.09 min. Diastereomeric ratio (*anti*/*syn* = 14.3:1, Table 5, entry 12) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS):δ = 7.64−7.62 (m, 1H, *anti*+*syn*), 7.60−7.55 (m, 1H, *anti*+*syn*), 7.40 (t, 1H, J = 7.6 Hz, *anti*+*syn*), 7.26−7.20 (m, 1H, *anti* +*syn*), 5.80 (s, 0.93H, *anti*), 5.58 (d, 0.07H, J = 8.4 Hz, *syn*), 4.93−4.85 (m, 1H, *ant*+*syn*), 3.52−3.51 (m, 0.07H, *syn*), 3.01 (m, 0.93H, *anti*), 1.47−1.43 (m, 3H, *anti*+*syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 137.4, 133.1, 130.1, 128.6, 128.0, 121.6, 84.1, 72.6, 11.1.

1-(3-Bromophenyl)-2-nitropropan-1-ol (**2m**).[15i] $C_9H_{10}BrNO_3$. Yellow oil in 96% yield, 49.9 mg. Enantiomeric excesses (93% for *anti*, 85% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 0.5 mL/min, detection at 210 nm): (1*S*,2*R*) t_R (*anti* minor) = 15.00 min, (1*R*,2*S*) t_R (*anti* major) = 16.92 min, (1*S*,2*S*) t_R (*syn* minor) = 18.97 min, (1*R*,2*R*) t_R (*syn* major) = 27.41 min. Diastereomeric ratio (*anti*/*syn* = 3.2:1, Table 5, entry 13) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.49−7.38 (m, 2H, *anti*+*syn*), 7.24−7.17 (m, 2H, *anti*+ *syn*), 5.32 (d, 0.75H, J = 2.8 Hz, *anti*), 4.93 (d, 0.25H, J = 9.2 Hz, *anti*), 4.69−4.63 (m, 0.25H, *syn*), 4.62−4.56 (m, 0.75H, *anti*), 2.82−2.75 (m, 1H, *anti*+*syn*), 1.41 (d, 2.25H, J = 7.8 Hz, *anti*), 1.27 (d, 0.75H, J = 7.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 140.8, 131.7, 130.4, 129.2, 124.7, 123.0, 87.2, 73.1, 12.0.

1-(4-Bromophenyl)-2-nitropropan-1-ol (**2n**).[10g,l] $C_9H_{10}BrNO_3$. Yellow oil in 98% yield, 51.4 mg. Enantiomeric excesses (92% for *anti*, 82% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 5.98 min, t_R (*anti* minor) = 7.15 min, t_R (*syn* minor) = 10.48 min, t_R (*syn* major) = 12.61 min. Diastereomeric ratio (*anti*/*syn* = 3.9:1, Table 5, entry 14) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.48−7.44 (m, 2H, *anti*+*syn*), 7.20−7.17 (m, 2H, *anti*+*syn*), 5.29 (t, 0.79H, J = 3.6 Hz, *anti*), 4.93 (q, 0.21H, J = 3.6 Hz, *syn*), 4.68−4.62 (m, 0.21H, *syn*), 4.51−4.55 (m, 0.79H, *anti*), 2.77 (d, 0.79H, J = 3.6 Hz, *anti*), 2.68 (d, 0.21H, J = 4.0 Hz, *syn*), 1.41 (d, 2.37H, J = 7.6 Hz, *anti*), 1.25 (d, 0.63H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 137.5, 132.0, 127.8, 122.5, 87.2, 73.3, 12.1.

2-Nitro-1-(2-(trifluoromethyl)phenyl)propan-1-ol (**2o**).[15] $C_{10}H_{10}F_3NO_3$. Yellow oil in 88% yield, 43.8 mg. Enantiomeric excesses (91% for *anti*, 74% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 4.59 min, t_R (*anti* minor) = 5.20 min, t_R (*syn* major) = 6.80 min, t_R (*syn* minor) = 7.92 min. Diastereomeric

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ratio (*anti*/*syn* = 2.7:1, Table 5, entry 15) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.87−7.62 (m, 3H, *anti*+*syn*), 7.52−7.46 (m, 1H, *anti*+*syn*), 5.90 (s, 0.73H, *anti*), 5.54 (d, 0.27H, *J* = 8.8 Hz, *syn*), 4.95−4.87 (m, 0.27H, *syn*), 4.75−4.70 (m, 0.73H, *anti*), 2.99 (d, 0.73H, *J* = 3.2 Hz, *anti*), 2.87 (d, 0.27H, *J* = 3.2 Hz, *syn*), 1.54 (d, 2.19H, *J* = 6.8 Hz, *anti*), 1.31 (d, 0.81H, *J* = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 136.9, 132.4, 128.9, 128.6, 126.4, 126.3, 85.7, 69.3, 69.3, 11.5. HRMS (ESI-TOF) calcd for $C_{10}H_{10}{}^{18.9984}F_3KNO_3^+$ ([M + K$^+$]) = 288.0259, found 288.0250.

2-Nitro-1-(4-(trifluoromethyl)phenyl)propan-1-ol (**2p**).[15j] $C_{10}H_{10}F_3NO_3$. Yellow oil in 88% yield, 43.8 mg. Enantiomeric excesses (92% for *anti*, 83% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 4.59 min, t_R (*anti* minor) = 5.20 min, t_R (*syn* minor) = 6.80 min, t_R (*syn* major) = 7.92 min. Diastereomeric ratio (*anti*/*syn* = 3.6:1, Table 5, entry 16) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.59−7.57 (m, 2H, *anti*+*syn*), 7.46−7.44 (m, 2H, *anti*+*syn*), 5.42 (d, 0.78H, *J* = 1.6 Hz, *anti*), 5.03 (d, 0.22H, *J* = 8.4 Hz, *syn*), 4.72−4.59 (m, 1H, *anti* +*syn*), 2.94 (br, 1H, *anti*+*syn*), 1.40 (d, 2.34H, *J* = 6.8 Hz, *anti*), 1.27 (d, 0.66H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 142.5, 127.5, 126.5, 125.9, 125.8, 87.2, 73.3, 11.9.

2-Nitro-1-(4-nitrophenyl)propan-1-ol (**2q**).[10l,15d,f,g] $C_9H_{10}N_2O_5$. White solid in 90% yield, 40.7 mg. Enantiomeric excesses (91% for *anti*, 74% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 10.08 min, t_R (*anti* minor) = 11.92 min, t_R (*syn* minor) = 16.38 min, t_R (*syn* major) = 17.96 min. Diastereomeric ratio (*anti*/*syn* = 2.5:1, Table 5, entry 17) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.27−8.24 (m, 2H, *anti*+*syn*), 7.62−7.58 (m, 2H, *anti*+*syn*), 5.57 (d, 0.71H, *J* = 2.8 Hz, *anti*), 5.20 (d, 0.29H, *J* = 8.4 Hz, *syn*), 4.81−4.70 (m, 1H, *anti*+*syn*), 3.16 (br, 1H, *anti*+*syn*), 1.49 (d, 2.13H, *J* = 6.8 Hz, *anti*), 1.39 (d, 0.87H, *J* = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 148.0, 145.7, 127.1, 124.1, 86.9, 73.0, 12.0.

2-Nitro-1-o-tolylpropan-1-ol (**2r**).[10l,15d,g] $C_{10}H_{13}NO_3$. Yellow oil in 99% yield, 38.6 mg. Enantiomeric excesses (92% for *anti*, n.d. for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.11 min, t_R (*anti* minor) = 7.12 min, t_R (*syn* minor) = 11.86 min, t_R (*syn* major) = 13.02 min. Diastereomeric ratio (*anti*/*syn* = 10.0:1, Table 5, entry 18) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS):δ = 7.55−7.53 (m, 0.91H, *anti*), 7.40−7.38 (m, 0.09H, *syn*), 7.29−7.16 (m, 3H, *anti*+*syn*), 5.62 (t, 0.91H, J = 2.4 Hz, *anti*), 5.36 (q, 0.09H, *J* = 3.6 Hz, *syn*), 4.89−4.82 (m, 0.09H, *syn*), 4.67−4.61 (m, 0.91H, *anti*), 2.44 (s, 0.27H, *syn*), 2.37 (s, 2.73H, *anti*), 1.51 (d, 2.73H, *J* = 6.8 Hz, *anti*), 1.32 (d, 0.27H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 136.7, 134.4, 130.9, 128.5, 126.6, 126.1, 85.4, 71.0, 19.0, 11.7.

2-Nitro-1-m-tolylpropan-1-ol (**2s**).[15k] $C_{10}H_{13}NO_3$. Yellow oil in 99% yield, 38.6 mg. Enantiomeric excesses (90% for *anti*, 92% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.36 min, t_R (*anti* minor) = 7.37 min, t_R (*syn* minor) = 11.29 min, t_R (*syn* major) = 12.75 min. Diastereomeric ratio (*anti*/*syn* = 3.3:1, Table 5, entry 19) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.22−7.05 (m, 5H, *anti*+*syn*), 5.27 (t, 0.77H, *J* = 3.6 Hz, *anti*), 4.89 (q, 0.23H, *J* = 3.6 Hz, *syn*), 4.72−4.65 (m, 0.25H, *syn*), 2.67−2.66 (m, 0.75H, *anti*), 2.57−2.56 (m, 0.25H, *syn*), 2.30 (s, 0.71H, *syn*), 2.29 (s, 2.29H, *anti*), 1.42 (d, 2.30H, *J* = 6.8 Hz, *anti*), 1.23 (d, 0.70H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 138.6, 138.6, 129.4, 128.8, 126.7, 123.1, 87.6, 74.1, 21.6, 12.2.

2-Nitro-1-p-tolylpropan-1-ol (**2t**).[10l] $C_{10}H_{13}NO_3$. Yellow oil in 62% yield, 24.2 mg. Enantiomeric excesses (90% for *anti*, 86% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.80 min, t_R (*anti* minor) = 7.94 min, t_R (*syn* minor) = 13.05 min, t_R (*syn* major) = 15.45 min. Diastereomeric ratio (*anti*/*syn* = 3.0:1, Table 5, entry 20) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.26−7.23 (m, 2H, *anti*+*syn*), 7.21−7.17 (m, 2H, *anti*+*syn*), 5.32 (d, 0.75H, *J* = 3.6 Hz, *anti*), 5.97 (d, 0.25H, *J* = 9.2 Hz, *syn*), 4.78−4.71 (m, 0.25H, *syn*), 4.70−4.64 (m, 0.75H, *anti*), 2.71 (br, 0.75H, *anti*), 2.59 (br, 0.25H, *syn*), 2.36 (s, 1H, *syn*), 2.35 (s, 3H, *anti*), 1.49 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.29 (d, 0.75H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 138.5, 135.6, 129.5, 126.0, 87.6, 74.0, 21.3, 12.3.

1-(2-Methoxyphenyl)-2-nitropropan-1-ol (**2u**).[10m,l,15d,g] $C_{10}H_{13}NO_4$. Yellow oil in 93% yield, 39.2 mg. Enantiomeric excesses (94% for *anti*, n.d. for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 9.21 min, t_R (*anti* major) = 9.95 min, t_R (*syn* minor) = 18.43 min, t_R (*syn* major) = 19.28 min. Diastereomeric ratio (*anti*/*syn* = 11.1:1, Table 5, entry 21) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.43−7.41 (m, 1H, *anti* +*syn*), 7.33−7.29 (m, 1H, *anti*+*syn*), 7.00 (t, 1H, *J* = 3.6 Hz, *anti*+*syn*), 6.91 (q, 1H, *J* = 8.4 Hz, *anti*+*syn*), 5.53 (t, 0.92H, *J* = 4.4 Hz, *anti*), 5.13 (t, 0.08H, *J* = 8.8 Hz, *syn*), 5.04−4.97 (m, 0.08H, *syn*), 4.93−4.88 (m, 0.92H, *anti*), 3.89 (s, 0.23H, *syn*), 3.87 (s, 2.77H, *anti*), 3.31−3.29 (m, 0.08H, *syn*), 3.08−3.06 (m, 0.92H, *anti*), 1.48 (d, 2.78H, *J* = 6.8 Hz, *anti*), 1.33 (d, 0.22H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 155.9, 129.6, 127.8, 126.3, 121.1, 110.5, 85.1, 70.9, 55.5, 12.7.

1-(3-Methoxyphenyl)-2-nitropropan-1-ol (**2v**).[10m] $C_{10}H_{13}NO_4$. Yellow oil in 86% yield, 36.3 mg. Enantiomeric excesses (97% for *anti*, 95% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 8.99 min, t_R (*anti* minor) = 10.54 min, t_R (*syn* minor) = 15.24 min, t_R (*syn* major) = 16.97 min. Diastereomeric ratio (*anti*/*syn* = 2.9:1, Table 5, entry 22) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.33−7.26 (m, 1H, *anti*+*syn*), 6.94−6.85 (m, 3H, *anti*+*syn*), 5.38 (br, 0.75H, *anti*), 4.98 (d, 0.25H, *J* = 8.4 Hz, *syn*), 4.79−4.74 (m, 0.25H, *syn*), 4.73−4.66 (m, 0.75H, *anti*), 3.82 (s, 0.77H, syn), 3.81 (s, 2.23H, *anti*), 2.77 (d, 0.75H, *J* = 2.8 Hz, *anti*), 2.67 (d, 0.25H, *J* = 2.4 Hz, *syn*), 1.49 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.32 (d, 0.75H, *J* = 6.8, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 160.0, 140.2, 130.0, 118.2, 114.0, 111.7, 87.5, 73.8, 55.4, 12.1.

1-(4-Methoxyphenyl)-2-nitropropan-1-ol (**2w**).[10g,l,15d,f] $C_{10}H_{13}NO_4$. Yellow oil in 66% yield, 27.8 mg. Enantiomeric excesses (90% for *anti*, 86% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): (1*S*,2*R*)t_R (*anti* minor) = 10.99 min, (1*R*,2*S*) t_R (*anti* major) = 12.32 min, (1*S*,2*S*) t_R (*syn* minor) = 15.28 min, (1*R*,2*R*) t_R (*syn* major) = 17.36 min. Diastereomeric ratio (*anti*/*syn* = 2.9:1, Table 5, entry 23) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.24−7.19 (m, 2H, *anti*+*syn*), 6.87−6.83 (m, 2H, *anti*+*syn*), 5.24 (br, 0.75H, *anti*), 4.91 (q, 0.25H, *J* = 0.4 Hz, *syn*), 4.772−4.57 (m, 1H, *anti*+*syn*), 3.75 (s, 0.77H, *syn*), 3.74 (s, 2.23H, *anti*), 2.54 (d, 0.75H, *J* = 2.4 Hz, *anti*), 2.40 (d, 0.25H, *J* = 2.4 Hz, *syn*), 1.45 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.23 (d, 0.75H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 159.8, 130.5, 127.4, 114.3, 87.7, 73.9, 55.5, 12.6.

2-Nitro-1-(3-phenoxyphenyl)propan-1-ol (**2x**).[15] $C_{15}H_{15}NO_4$. Yellow oil in 93% yield, 50.8 mg. Enantiomeric excesses (95% for *anti*, 92% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 8.69 min, t_R (*anti* major) = 9.50 min, t_R (*syn* minor) = 12.12 min, t_R (*syn* major) = 16.40 min. Diastereomeric ratio (*anti*/*syn* = 3.0:1, Table 5, entry 24) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38−7.32 (m, 3H, *anti*+*syn*), 7.17−6.94 (m, 6H, *anti*+*syn*), 5.37 (br, 0.75H, *anti*), 4.99 (q, 0.25H, *J* = 2.0 Hz, *syn*), 4.76−4.64 (m, 1H, *anti*+*syn*), 2.74 (d, 75H, *J* = 3.2 Hz, *anti*), 2.64 (d, 0.25H, *J* = 3.2 Hz, *syn*), 1.50 (d, 2.25H, *J* = 6.8 Hz, *anti*), 1.34 (d, 0.75H, *J* = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 157.9, 156.8, 140.6, 130.3, 130.0, 123.8, 119.2, 116.1, 87.4, 73.6, 12.2. HRMS (ESI-TOF) calcd for $C_{15}H_{15}NNaO_4^+$ ([M + Na$^+$]) = 296.0895, found 296.0899.

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1-(4-Benzylphenyl)-2-nitropropan-1-ol (**2y**).[15] $C_{16}H_{17}NO_3$. White solid in 46% yield, 25.0 mg. Enantiomeric excesses (96% for *anti*, 91% for *syn*) HPLC (DAICEL CHIRALPAK IB, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 24.29 min, t_R (*anti* minor) = 25.89 min, t_R (*syn* major) = 29.21 min, t_R (*syn* minor) = 31.13 min. Diastereomeric ratio (*anti*/*syn* = 2.1:1, Table 5, entry 25) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44−7.28 (m, 7H, *anti*+*syn*), 7.01−6.97 (m, 2H, *anti*+*syn*), 5.31 (d, 0.68H, J = 4.0 Hz, *anti*), 5.07−5.06 (m, 2H, *anti* +*syn*), 4.98 (d, 0.32H, J = 5.2 Hz, *syn*), 4.78−4.71 (m, 0.32H, *syn*), 4.70−4.64 (m, 0.68H, *anti*), 2.59 (s, 0.68H, *anti*), 2.44 (s, 0.32H, *syn*), 1.52 (d, 2.04H, J = 6.8 Hz, *anti*), 1.31 (d, 0.96H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 159.1, 130.8, 128.8, 128.3, 128.2, 127.6, 127.4, 115.2, 87.7, 73.9, 70.2, 12.6. HRMS (ESI-TOF) calcd for $C_{16}H_{17}KNO_3^+$ ([M + K$^+$]) = 310.0846, found 310.0846.

1-(4-Fluoro-3-phenoxyphenyl)-2-nitropropan-1-ol (**2z**).[15] $C_{15}H_{14}FNO_4$. Yellow oil in 93% yield, 54.1 mg. Enantiomeric excesses (93% for *anti*, 89% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 6.70 min, t_R (*anti* minor) = 7.26 min, t_R (*syn* minor) = 10.62 min, t_R (*syn* major) = 12.77 min. Diastereomeric ratio (*anti*/*syn* = 4.8:1, Table 5, entry 26) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7. 30−7.24 (m, 2H, *anti* +*syn*), 7.16−7.09 (m, 1H, *anti*+*syn*), 7.08−6.95 (m, 3H, *anti*+*syn*), 6.90−6.88 (m, 2H, *anti*+*syn*), 5.23 (t, 0.82H, J = 3.2 Hz, *anti*), 4.88 (q, 0.18H, J = 4.0 Hz, *anti*), 4.62−4.51 (m, 1H, *anti*+*syn*), 2.70 (s, 0.82H, *anti*), 2.62 (s,0.18H, *syn*), 1.40 (d, 2.46H, J = 6.8 Hz, *anti*), 1.25 (d, 0.54H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 157.0, 155.4, 152.9, 144.3, 144.2, 135.3, 130.0, 123.6, 117.7, 117.6, 117.5, 117.4, 87.3, 73.1, 12.3. HRMS (ESI-TOF) calcd for $C_{15}H_{14}{}^{18.9984}FNNaO_4^+$ ([M + Na$^+$]) = 314.0804, found 314.0805.

1-(Biphenyl-4-yl)-2-nitropropan-1-ol (**2aa**).[10m] $C_{15}H_{15}NO_3$. White solid in 93% yield, 47.8 mg. Enantiomeric excesses (93% for *anti*, 89% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 8.09 min, t_R (*anti* minor) = 9.96 min, t_R (*syn* minor) = 15.42 min, t_R (*syn* major) = 17.83 min. Diastereomeric ratio (*anti*/*syn* = 2.4:1, Table 5, entry 27) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62−7.56 (m, 4H, *anti*+*syn*), 7.46−7.41 (m, 4H, *anti*+*syn*), 7.39−7.34 (m, 1H, *anti*+*syn*), 5.43−5.42 (m, 0.70H, *anti*), 5.06−5.04 (m, 0.3H, *syn*), 4.83−4.76 (m, 0.30H, *syn*), 4.75−4.69 (m, 0.70H, *anti*), 2.80 (s, 1H, *anti*+*syn*), 2.59 (s, 0.25H, *syn*), 1.52 (d, 2.10H, J = 6.8 Hz, *anti*), 1.35 (d, 0.90H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 140.5, 140.4, 137.5, 129.0, 127.8, 127.5, 127.2, 126.5, 87.5, 73.8, 12.2.

1-(Naphthalen-1-yl)-2-nitropropan-1-ol (**2ab**).[10g] $C_{13}H_{13}NO_3$. Yellow oil in 85% yield, 32.3 mg. Enantiomeric excesses (93% for *anti*, 84% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): (1*S*,2*R*) t_R (*anti* minor) = 8.28 min, (1*R*,2*S*) t_R (*anti* major) = 9.82 min, (1*S*,2*S*) t_R (*syn* minor) = 13.20 min, (1*R*,2*R*) t_R (*syn* major) = 14.88 min. Diastereomeric ratio (*anti*/*syn* = 3.7:1, Table 5, entry 28) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.28 (d, 0.78H, J = 8.4 Hz, *syn*), 8.00 (d, 0.22H, J = 8.4 Hz, *anti*), 7.92−7.77 (m, 3H, *anti*+*syn*), 6.27 (s, 0.78H, *anti*), 5.79 (d, 0.22H, J = 5.6 Hz, *syn*), 5.16−5.09 (m, 0.22H, *syn*), 4.94−4.88 (m, 0.78H, *anti*), 2.77 (br, 1H, *anti*+*syn*), 1.43 (d, 2.34H, J = 6.8 Hz, *anti*), 1.26 (d, 0.66H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 157.9, 156.8, 140.6, 130.3, 130.0, 123.8, 119.2, 116.1, 87.4, 73.6, 12.2.

1-(Naphthalen-2-yl)-2-nitropropan-1-ol (**2ac**).[10g] $C_{13}H_{13}NO_3$. Yellow oil in 95% yield, 43.9 mg. Enantiomeric excesses (95% for *anti*, 92% for *syn*) HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): (1*S*,2*R*) t_R (*anti* minor) = 10.57 min, (1*R*,2*S*) t_R (*anti* major) = 12.24 min, (1*S*,2*S*) t_R (*syn* minor) = 16.32 min, (1*R*,2*R*) t_R (*syn* major) = 18.72 min. Diastereomeric ratio (*anti*/*syn* = 2.7:1, Table 5, entry 29) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.79−7.71 (m, 4H, *anti*+*syn*), 7.46−7.39 (m, 2H, *anti*+*syn*), 7.37−7.32 (m, 1H, *anti*+*syn*), 5.45 (s, 0.73H, *anti*), 5.07 (q, 0.27H, J = 2.8 Hz, *syn*), 4.81−4.73 (m, 0.27H, *syn*), 4.73−4.66 (m, 73H, *anti*), 2.85 (br, 0.73H, *anti*), 2.75 (br, 0.27H, *syn*), 1.41 (d, 2.19H, J = 6.8 Hz, *anti*), 1.22 (d, 0.81H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 135.9, 133.2, 128.8, 128.2, 127.8, 126.7, 126.6, 125.4, 123.4, 87.4, 74.1, 12.1.

4-Nitro-1-phenylpent-1-yn-3-ol (**2ad**).[10c] $C_{11}H_{11}NO_3$. Yellow oil in 95% yield, 39.0 mg. Enantiomeric excesses (81% for *anti*, 79% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 19.31 min, t_R (*anti* minor) = 20.13 min, t_R (*syn* minor) = 23.90 min, t_R (*syn* major) = 26.44 min. Diastereomeric ratio (*anti*/syn = 1.3:1, Table 5, entry 30) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.45−7.43 (m, 2H, *anti*+*syn*), 7.39−7.30 (m, 3H, *anti*+*syn*), 5.16−5.14 (m, 0.56H, *anti*), 5.03−4.99 (m, 0.44H, *syn*), 4.80−4.71 (m, 1H, *anti*+*syn*), 4.75−4.70 (m, 1H, *anti*+*syn*), 2.90 (s, 0.56H, *anti*) 2.78 (s, 0.44H, *syn*), 1.73 (d, 1.69H, J = 6.8 Hz, *anti*), 1.71 (d, 1.31H, J = 6.8 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 132.0, 129.3, 128.5, 121.4, 87.8, 85.5, 84.0, 64.3, 13.5.

1-(Furan-2-yl)-2-nitropropan-1-ol (**2ae**).[15e,f] $C_7H_9NO_4$. Yellow oil in 95% yield, 32.5 mg. Enantiomeric excesses (96% for *anti*, 97% for *syn*) HPLC (DAICEL CHIRALPAK ID, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, detection at 210 nm): t_R (*syn* minor) = 12.03 min, t_R (*syn* major) = 13.19 min, t_R (*anti* minor) = 19.04 min, t_R (*anti* major) = 20.09 min. Diastereomeric ratio (*anti*/*syn* = 1.0:1, Table 5, entry 31) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.36−7.33 (m, 1H, *anti*+*syn*), 6.35−6.31 (m, 2H, *anti*+*syn*), 5.28 (s, 0.50H, *anti*), 5.00−4.99 (m, 0.50H, *syn*), 4.94−4.86 (m, 0.50H, *syn*), 4.83−4.77 (m, 0.50H, *anti*), 2.72 (d, 0.50H, J = 4.0 Hz, *anti*), 2.63 (d, 50H, J = 4.0 Hz, *syn*), 1.54 (d, 1.50H, J = 6.8 Hz, *anti*), 1.33 (d, 1.50H, J = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 150.3, 149.9, 142.5, 142.0, 109.8, 109.7, 108.5, 107.4, 85.4, 84.0, 68.7, 68.1, 15.4, 12.3.

1-(Furan-3-yl)-2-nitropropan-1-ol (**2af**).[15e,f] $C_7H_9NO_4$. Yellow oil in 90% yield, 30.8 mg. Enantiomeric excesses (96% for *anti*, 90% for *syn*) HPLC (DAICEL CHIRALPAK ID, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* minor) = 6.81 min, t_R (*anti* major) = 7.51 min, t_R (*syn* minor) = 7.93 min, t_R (*syn* major) = 8.54 min. Diastereomeric ratio (*anti*/*syn* = 1.7:1, Table 5, entry 32) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.50−7.43 (m, 2H, *anti*+*syn*), 6.42 (s, 0.40H, *syn*), 6.37 (s, 0.60H, *anti*), 5.31 (m, 0.60H, *anti*), 5.06−5.04 (m, 0.40H, *syn*), 4.80−4.72 (m, 0.40H, *syn*), 4.71−4.65 (m, 0.40H, *anti*), 2.71 (s, 0.60H, *anti*), 2.59 (s, 0.40H, *syn*), 1.58 (d, 1.80H, J = 6.8 Hz, *anti*), 1.43 (d, 1.20H, J = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 144.0, 140.4, 123.8, 108.1, 86.6, 68.3, 12.9.

2-Nitro-1-(thiophen-2-yl)propan-1-ol (**2ag**).[15f] $C_7H_9NO_3S$. Yellow oil in 94% yield, 35.2 mg. Enantiomeric excesses (92% for *anti*, 92% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 95/5, flow rate 0.8 mL/min, detection at 210 nm): t_R (*syn* major) = 18.37 min, t_R (*syn* minor) = 19.67 min, t_R (*anti* minor) = 29.60 min, t_R (*anti* major) = 34.25 min. Diastereomeric ratio (*anti*/*syn* = 1.1:1, Table 5, entry 33) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.30−7.29 (d, 0.50H, J = 5.2 Hz, *syn*), 7.25−7.23 (q, 0.50H, J = 1.6 Hz, *anti*), 7.02−6.93 (m, 2H, *anti*+*syn*), 5.53 (d, 0.50H, J = 4.0 Hz, *anti*), 5.25 (m, 0.50H, J = 8.8 Hz, *syn*), 4.78−4.65 (m, 1H, *anti*+*syn*), 2.89−2.80 (m, 1H, *anti*+*syn*), 1.54 (d, 1.50H, J = 6.8 Hz, *anti*), 1.33 (d, 1.50H, J = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 141.4, 127.3, 127.2, 126.8, 125.8, 87.5, 71.0, 13.0.

2-Nitro-1-(thiophen-3-yl)propan-1-ol (**2ah**).[15f] $C_7H_9NO_3S$. Yellow oil in 94% yield, 35.1 mg. Enantiomeric excesses (92% for *anti*, 92% for *syn*) HPLC (DAICEL CHIRALPAK IE, hexane/2-propanol = 95/5, flow rate 0.8 mL/min, detection at 210 nm): t_R (*anti* major) = 18.37 min, t_R (*anti* minor) = 19.67 min, t_R (*syn* minor) = 29.60 min, t_R (*syn* major) = 34.25 min. Diastereomeric ratio (*anti*/*syn* = 1.9:1, Table 5, entry 34) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.32−7.24 (m, 2H, *anti*+*syn*), 7.02 (q, 0.34H, J = 1.2 Hz, *syn*), 6.97 (q, 0.66H, J = 1.2 Hz, *anti*), 5.38 (d, 0.67H, J = 3.6 Hz, *anti*), 5.08 (m, 0.33H, *syn*), 4.76−4.70 (m, 0.33H, *syn*), 4.68−4.620 (m, 0.67H, *anti*), 2.74−2.63 (m, 1H, *anti*+*syn*), 1.46 (d, 2.01H, J = 6.8 Hz, *anti*), 1.309 (d, 0.99H, J = 6.4 Hz, *syn*). ^{13}C NMR (100 MHz,

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$CDCl_3$, 25 °C): (*anti*) δ = 139.9, 127.0, 125.1, 122.6, 86.9, 71.2, 12.6. HRMS (ESI-TOF) calcd for $C_7H_9KNO_3{}^{31.9721}S^+$ ([M + K^+]) = 225.9901, found 225.9940.

*2-Nitro-1-phenylethan-1-ol (**2ai**).*[12] $C_8H_9NO_3$. Colorless oil in 83% yield, 27.7 mg (Table 5, entry 35). HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): major (*R*) t_R = 14.33 min, minor (*S*) t_R = 18.05 min. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.42−7.34 (m, 5H), 5.48−5.42 (m, 1H), 4.59 (q, 1H, *J* = 9.6 Hz), 4.50 (q, 1H, *J* = 2.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.2, 129.2, 129.1, 126.1, 81.3, 71.1.

*2-Nitro-1-phenylbutan-1-ol (**2aj**).*[15d] $C_{10}H_{13}NO_3$. Colorless oil in 35% yield, 13.7 mg. Enantiomeric excesses (84% for *anti*, 56% for *syn*) HPLC (DAICEL CHIRALPAK IC, hexane/2-propanol = 90/10, flow rate 1.0 mL/min, detection at 210 nm): t_R (*anti* major) = 5.51 min, t_R (*anti* minor) = 6.73 min, t_R (*syn* minor) = 11.78 min, t_R (*syn* major) = 12.82 min. Diastereomeric ratio (*anti*/*syn* = 1.8:1, Table 5, entry 36) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.43−7.31 (m, 5H, *anti*+*syn*), 5.18 (q, 0.64H, *J* = 3.2 Hz, *anti*), 5.03 (q, 0.36H, *J* = 4.0 Hz, *syn*), 4.65−4.56 (m, 1H, *anti*+*syn*), 2.69 (d, 0.64H, *J* = 3.2 Hz, *anti*), 2.48 (d, 0.36H, *J* = 4.0 Hz, *syn*), 2.23−2.11 (m, 0.64H, *anti*), 1.96−1.80 (m, 1H, *anti*+*syn*), 1.47−1.37 (m, 0.36H, *syn*), 0.94 (t, 1.92H, *J* = 7.6 Hz, *anti*), 0.87 (t, 1.08H, *J* = 7.6 Hz, *syn*). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): (*anti*) δ = 138.6, 129.2, 128.9, 126.3, 94.8, 74.4, 21.4, 10.5.

■ ASSOCIATED CONTENT

Supporting Information

HPLC data, ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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