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Sugar-Based Pyrrolidine as a Highly Enantioselective Organocatalyst for Asymmetric Michael Addition of Ketones to Nitrostyrenes

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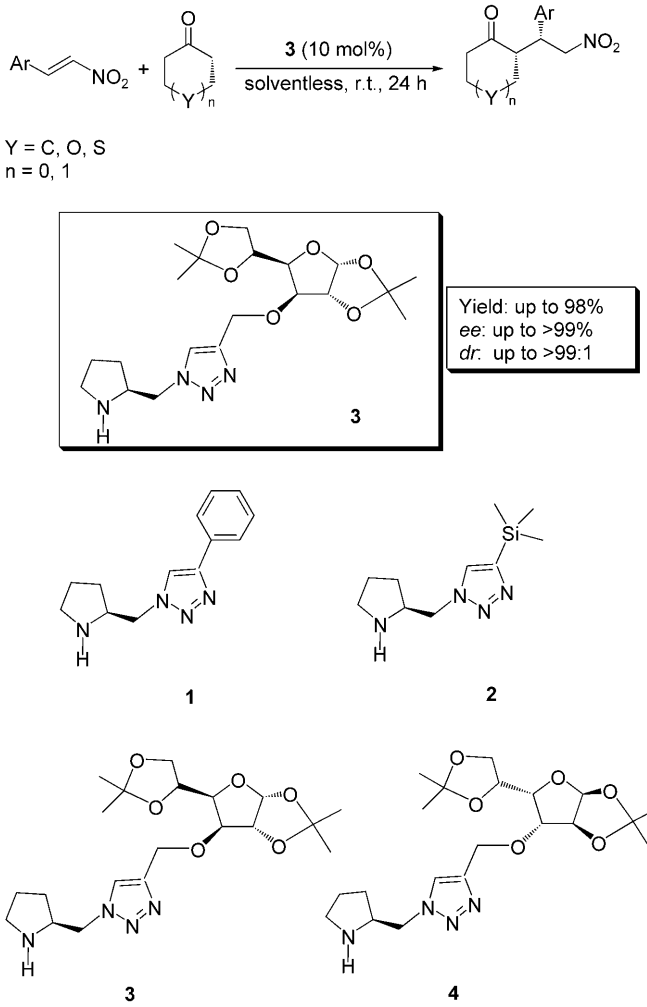
Abstract: A modular sugar-based pyrrolidine (**3**) was prepared and was found to be a highly enantioselective organocatalyst for the asymmetric Michael addition of ketones to nitrostyrenes. In the presence of 10 mol% of **3**, a pyrrolidine unit anchored to a natural D-glucose backbone through click chemistry, the Michael additions of ketones to nitrostyrenes proceeded smoothly to generate the corresponding adducts in good yields (up to 98%), high enantioselectivities (up to >99% *ee*) and excellent diastereoselectivities (up to >99:1 *dr*) under solvent-free reaction conditions.

Keywords: asymmetric Michael addition; D-glucose; nitrostyrenes; organocatalysts; pyrrolidine unit; solvent-free reaction conditions

Introduction

The asymmetric Michael addition of a carbon nucleophile to a nitroalkene plays a particularly important role among the numerous carbon-carbon bond forming reactions since it represents a very useful synthetic method for the preparation of chiral nitroalkanes with at least two vicinal stereogenic centers in a single step.[1–6] Chiral nitroalkanes are valuable building blocks in organic synthesis because they can be transformed into a wide variety of different functional groups such as amines, carboxylic acids, nitrile oxides, etc.[7,8] Their versatile utility in organic synthesis has stimulated tremendous research interest in the development of asymmetric Michael catalysts, especially metal-free organo-catalysts. In 2001, Barbas[9] and List[10] independently reported that L-proline could catalyze the asymmetric Michael addition of ketone to *trans*-β-nitrostyrene, but the natural catalysts, such as L-proline failed to demonstrate good enantioselectivity (0–23% *ee*). Since then, a variety of asymmetric organocatalysts have been explored for the Michael addition of ketones or aldehydes to nitroolefins, such as pyrrolidine-based diamines,[11–17] chiral diamines,[18,19] chiral guanidines,[20] *Cinchona* alkaloid-based bifunctional organocatalysts,[21,22] and thiourea-amine bifunctional catalysts.[23–29] Currently, asymmetric organocatalysis has attracted considerable attention as a new, powerful, and environmentally friendly methodology for the catalytic production of enantiomerically pure organic compounds and also as one of the most rapidly growing and competitive research areas in synthetic organic chemistry. Therefore, the design of new effective organocatalysts for asymmetric synthesis is of great importance.

With their configurations being assigned as the D-family, natural carbohydrates which are the most abundant class of organic compounds found in living organisms among the natural products perform numerous roles. Besides, natural amino acids with the L-configuration found within proteins convey a vast array of chemical versatility and play central roles both as building blocks of proteins and as intermediates in metabolism. Recently carbohydrate-based bidentate ligands have been successfully used in some enantioselective reactions.[30–34] In this context, a modular and more efficient approach constructs the sugar-based pyrrolidine through a click reaction, which introduces a chiral pyrrolidine moiety into a common and inexpensive carbohydrate. Sugar-based pyrrolidine organocatalyst (**3**) was prepared uneventfully from natural D-glucose and L-proline as shown in



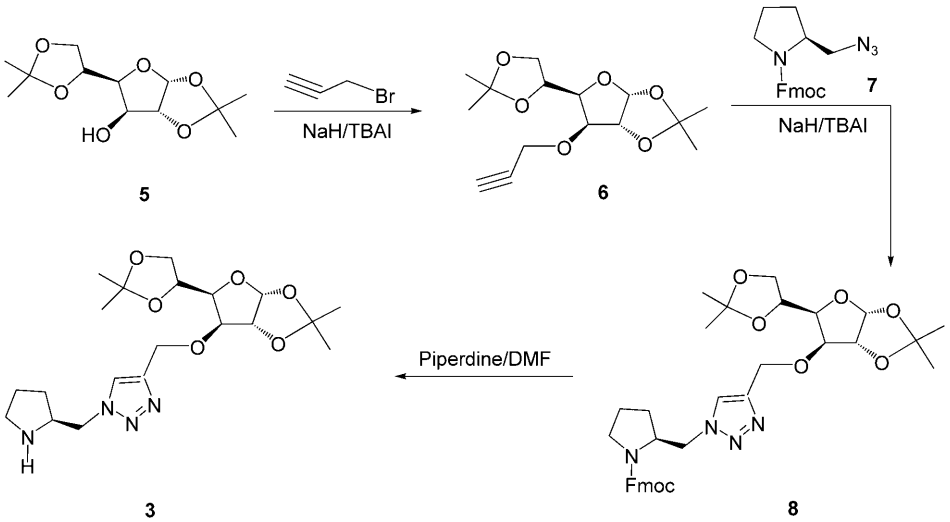
Scheme 1. Sugar-based pyrrolidine **3** as catalyst and screened organocatalysts **1**–**4** for the asymmetric Michael addition.

Scheme 1. We were pleased to find that the newly designed organocatalyst **3** catalyzed the reaction of cyclohexanone to arylnitroolefins smoothly to generate the corresponding adducts in good yields (up to 98%), high enantioselectivities (up to >99% *ee*) and excellent diastereoselectivities (up to >99:1 *dr*) under solvent-free reaction conditions.

In comparison with the above-mentioned similar pyrrolidine-based organocatalysts used in the asymmetric Michael addition to nitrostyrenes,[16] this sugar-based pyrrolidine organocatalyst **3** showed particular advantages: (i) high yields attained; (ii) excellent enantioselectivities (up to >99% *ee*) and diastereoselectivities (up to >99:1 *dr*) obtained; (iii) solvent-free reaction conditions without any organic solvent in the reaction; (iv) free of TFA as additive in the reaction; and (v) simple and easy experimental operation. In this paper, we will describe our experimental results.

Results and Discussion

Organocatalysts **1** and **2** were prepared according to the literature,[16c] and the synthesis of sugar-based pyrrolidine catalyst **3** (or **4**) is illustrated in Scheme 2. It was readily prepared through a three-step procedure for the synthsis of **3** (or **4**). Diacetone-D-glucose **5** in dry THF reacted with propargyl bromide in the presence of NaH (60% dispersion in mineral oil) and tetraethylammonium iodide (TEAI, 20 mol%) at room temperature and 70 °C for 20 h to afford **6** as pale yellow oil in 76% yield.[35] The obtained **6** reacted with **7**, obtained according to the synthetic route[36] in the presence of DIPEA and CuI (20 mol%) in the mixed solvent ($CHCl_3$/EtOH/H_2O = 9/1/1) at room temperature for 16 h to form the corresponding **8** as a pale yellow oil, followed by deprotection of the Fmoc

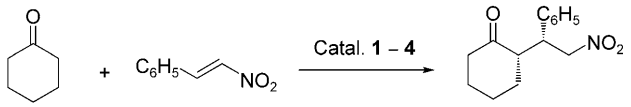


Scheme 2. Typical synthesis route to sugar-based pyrrolidine **3**.

group in DMF/piperidine (v/v 8/2) at room temperature with shaking for 0.5 h. The desired **3** was obtained as a colorless oil in 78% yield.[37] When diacetone-L-glucose was used as starting material through the same synthetic procedure, the corresponding **4** was obtained as a colorless oil.

For optimization of the reaction conditions and the identification of the best organocatalyst, solvent and reaction temperature, a model reaction of cyclohexanone with *trans*-β-nitrostyrene was chosen. The results are summarized in Table 1. Initially, organocatalysts with different skeletons were explored. As shown in Table 1, when the model reactions were carried out in the presence of organocatalysts **1–4** (10 mol%) respectively in EtOH at room temperature for 24 h, **3** was found to be the most effective one in reaction activity and stereoselectivity (Table 1, entries 1–4). It is important to note that **4** derived from L-glucose showed lower enantioselectivity than **3** derived from D-glucose (Table 1, entry 3 *vs.* 4). The reason for the difference of this type of catalyst is unclear at present, but the size of substituted group on the 1,2,3-triazole and stereochemistry mating of the substituted group on the 1,2,3-triazole with the pyrrolidine unit derived from L-proline have a certain effect on its activity and stereoselectivity. In the following reaction, **3** was chosen as catalyst considering its high activity, high stereoselectivity and the low cost of natural D-glucose. Next, various solvents were examined on the model reaction at room temperature using 10 mol% of **3** as a catalyst. As shown in Table 1, in polar or non-polar solvents, such as EtOH, CH_3CN, DMF, H_2O, $CHCl_3$, THF, hexane or toluene, the model Michael addition reaction proceeded smoothly to give the product in moderate to good yields with high diastereoselectivities and enantioselectivities (Table 1, entries 3, and 5–11). To our delight, almost quantitative isolated yield and excellent diastereoselectivity and enantioselectivity were obtained when the model reaction was carried out under solvent-free reaction conditions (Table 1, entry 12). With respect to the catalyst loading, when less than 10 mol% of **3** was used, the reaction did not go to completion, but that a higher loading (up to 10 mol%) of the catalyst **3** gave a very good result (Table 1, entries 13 and 12). However, with an increased loading of the catalyst **3** up to 15 mol%, there was no increase in the isolated yield of the product (Table 1, entry 14). In addition, a slightly higher enantioselectivity and almost same diastereoselectivity were achieved when the reaction temperature was down to 10 °C without a significant decrease of the reaction rate (Table 1, entry 15). Interestingly, the addition of a catalytic amount of organic acid, such as TFA, could reduce the reaction rate along with loss of enantiomeric excess (Table 1, entry 16). In addition, it was also found that the reaction was accomplished as the reaction was carried out for more than 24 h (Table 1, entries 17 and 18).

Table 1. Optimization of the reaction conditions.[a]

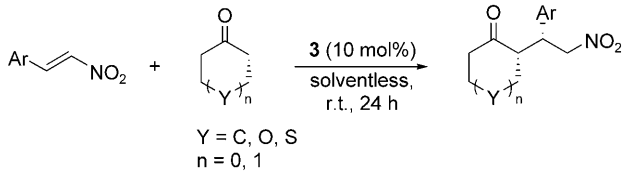


Entry	Catalyst	Solvent	Yield[b] [%]	*ee*[c] [%]	*dr*[d]
1	**1**	EtOH	82	91	49:1
2	**2**	EtOH	75	90	24:1
3	**3**	EtOH	88	99	99:1
4	**4**	EtOH	87	85	49:1
5	**3**	CH_3CN	86	98	98:2
6	**3**	DMF	85	99	98:2
7	**3**	H_2O	73	99	99:1
8	**3**	$CHCl_3$	78	99	99:1
9	**3**	THF	80	98	99:1
10	**3**	hexane	87	98	98:2
11	**3**	toluene	83	99	98:2
12	**3**	neat	98	99	99:1
13[e]	**3**	neat	64	99	99:1
14[f]	**3**	neat	98	99	99:1
15[g]	**3**	neat	90	>99	99:1
16[h]	**3**	neat	78	97	99:1
17[i]	**3**	neat	86	99	99:1
18[j]	**3**	neat	98	99	99:1

[a] Nitrostyrene (1.0 mmol), cyclohexanone (2.0 mmol), organocatalyst **1**, **2**, **3**, or **4** (0.10 mmol), in solvent (2.0 mL) or under solventless reaction condition at room temperature for 24 h.
[b] Isolated yields.
[c] Enantiomeric excess, *ee*, determined by HPLC using chiralpak AD-H column.
[d] Diasteromeric ratio, *dr* (*syn*/*anti*), determined by ^{1}H NMR spectroscopy.
[e] 5 mol% of **3** was used in the reaction.
[f] 15 mol% of **3** was used in the reaction.
[g] The reaction temperature was 10 °C for 36 h.
[h] 5 mol% of TFA was added in the reaction.
[i] The reaction time was 12 h.
[j] The reaction time was 36 h.

Under the optimized Michael additions of nitroolefins with ketones the reaction involved the use of 10 mol% of **3** as catalyst in the absence of solvent at room temperature for 24 h. The reactions of a variety of nitroolefins with different substituents and ketones were investigated, and the results are summarized in Table 2. Various styrene-type nitroolefins reacted smoothly with cyclohexanone in high yields with excellent diastereoselectivities and enantioselectivities (Table 2, entries 1–14). Generally, substituents on the aryl groups in nitroolefins slightly influenced the diastereoselectivities and enantioselectivities, as well as the yields. For example, phenyl rings in nitroolefins bearing both electron-withdrawing and electron-donating groups gave the desired Michael addition products with high stereoselectivities (up to >99:1 *dr* and

Table 2. Michael additions of ketones to *trans*-β-nitrostyrenes catalyzed by **3**.[a]



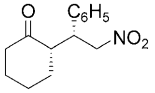
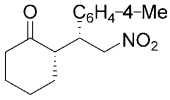
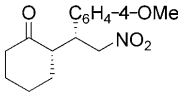
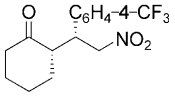
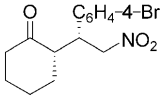
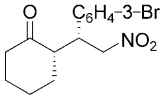
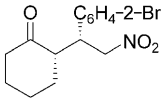
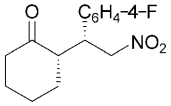
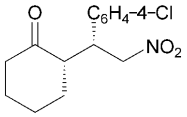
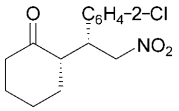
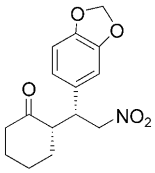
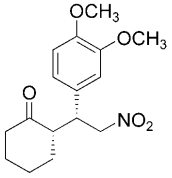
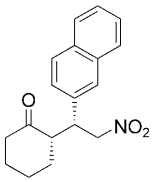
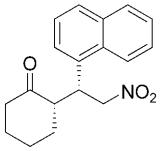
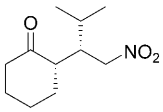
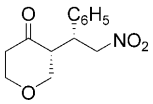
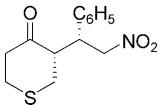
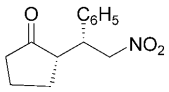
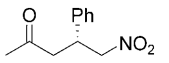
Entry	Product	Yield[b] [%]	*ee*[c] [%]	*dr*[d]
1		98	99	99:1
2		96	>99	>99:1
3		97	99	99:1
4		98	>99	>99:1
5		95	99	99:1
6		90	93	98:2
7		93	98	99:1
8		97	96	99:1
9		94	99	98:2
10		90	91	99:1
11		84	99	99:1
12		90	>99	>99:1

Table 2. (Continued)

Entry	Product	Yield[b] [%]	*ee*[c] [%]	*dr*[d]
13		91	>99	>99:1
14		86	99	99:1
15		75	93	94:6
16		89	95	99:1
17		87	98	99:1
18		95	85; 83	34:66
19		93	63	–

[a] Nitroolefin (1.0 mmol), ketone (2.0 mmol), **3** (0.10 mmol), under solvent-free reaction conditions at room temperature for 24 h.
[b] Isolated yields.
[c] Enantiomeric excess, *ee*, determined by HPLC using chiralpak AS-H and AD-H columns.
[d] Diasteromeric ratio, *dr* (*syn*/*anti*), determined by ^{1}H NMR spectroscopy.

up to >99% *ee*) in excellent yields. However, an average yield but good enantioselectivity of product was obtained when aliphatic substituted nitroolefin was used as one of the reaction substrate (Table 2, entry 15). Moreover, the Michael reactions were evaluated with other ketones and we found that tetrahydrothiopyran-4-one and tetrahydro-4*H*-pyran-4-one were also suitable substrates as Michael donors (Table 2, entries 16 and 17). However, cyclopentanone and acetone served as efficient Michael donors and generated the desired adducts with excellent yield, but moderate to good diastereoselectivity and enantioselectivity were observed (Table 2, entries 18 and 19).

Conclusions

In summary, we have developed a new type of sugar-based pyrrolidine organocatalyst, which is capable of catalyzing Michael addition reaction of ketones to nitrostyrenes, a remarkably better catalytic performance was provided by the reactions in terms of productivity (up to 98%), diastereoselectivity (*syn/anti* 99:1), enantioselectivity (up to 99%) under solvent-free reaction conditions at room temperature. Further investigations on the application of this kind of organocatalyst in asymmetric catalysis are still underway in our laboratory.

Experimental Section

General Remarks

All reactions were carried out under an air atmosphere. All reagents were purchased from commercial suppliers and used after further purification. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2. All ^1H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard.

Typical Procedure for Sugar-Based Pyrrolidine 3 as Organocatalyst for Asymmetric Michael Addition of Ketones to Nitrostyrenes

A 5.0-mL of reaction tube was charged with organocatalyst **3** (44 mg, 0.10 mmol), *trans*-β-nitrostyrene (150 mg, 1.0 mmol), cyclohexanone (2.0 mmol). The mixture was stirred at room temperature (25 °C) for 24 h, and then washed with ethyl acetate (3.0 mL × 3), the combined ethyl acetate fraction was concentrated. Flash chromatography (hexane:ethyl acetate = 3:1, v/v) furnished the corresponding (*S*)-2-[(*R*)-2-nitro-1-phenylethyl]cyclohexanone as colorless crystals; yield: 242 mg (98%).

Procedure for the Preparation of Pyrrolidine-Type Organocatalyst 1 (or 2)

Organocatalyst **1** was prepared according to synthetic procedure shown in the literature[16c] as a pale yellow solid; overall yield: 90%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (s, 1H), 7.63 (t, $J = 6.8$ Hz, 2H), 7.35–7.26 (m, 3H), 4.94–4.89 (dd, $J = 8.8$, 6.0, 8.4 Hz, 1H), 4.68–4.63 (dd, $J = 4.8$, 10.0, 4.8 Hz, 1H), 4.23–4.16 (m, 1H), 3.40–3.24 (m, 2H), 2.23–2.15 (m, 1H), 2.12–1.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.7$, 129.7, 128.8, 128.4, 125.5, 121.4, 59.2, 50.3, 45.5, 28.1, 23.3.

Organocatalyst **2** was prepared also according to synthetic procedure shown in the literature[16c] as a pale yellow oil; overall yield: 91%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.74$ (s, 1H), 4.94–4.88 (dd, $J = 8.0$, 6.4, 8.0 Hz, 1H), 4.67–4.62 (dd, $J = 4.8$, 9.6, 4.8 Hz, 1H), 4.20–4.18 (m, 1H), 3.36–3.29 (m, 2H), 2.17–2.11 (m, 1H), 2.05–1.78 (m, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 130.7, 59.1, 49.7, 45.5, 28.2, 23.3, −1.47; anal. calcd. for $C_{10}H_{20}N_4Si$: C 53.53, H 8.98, N 24.97; found: C 53.81, H 8.76, N 24.85.

Procedure for the Preparation of Sugar-Based Pyrrolidine 3 (or 4)

Sodium hydride (800 mg, 60% dispersion in mineral oil, 20 mmol) was added to a solution of diacetone-D-glucose **5** (5.0 g, 19 mmol) in dry THF (20.0 mL) at room temperature and the mixture was stirred and heated up to 70 °C for 2 h. Tetraethylammonium iodide (1.0 g, 3.8 mmol) and propargyl bromide (4.0 g, 27 mmol) in toluene (6.0 mL) were then added to the mixture and stirred at room temperature for 16 h. After the reaction was complete, the reaction mixture was diluted with Et_2O (100.0 mL) and washed with water. The organic layer was separated and dried with $MgSO_4$. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate 70/30 v/v) to afford **6** as a pale yellow oil; yield: 4.3 g (76%).[35] ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.85 (d, $J = 4.0$ Hz, 1H, CH), 4.62 (d, $J = 3.6$ Hz, 1H, CH), 4.60–4.23 (m, 3H, CH_2 and CH), 4.13–4.05 (m, 3H, CH_2 and CH), 3.98–3.94 (m, 1H, CH), 2.56 (s, 1H, CH), 1.48 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 111.5$, 108.6, 104.9, 82.6, 81.3, 80.7, 79.1, 74.9, 72.2, 66.9, 57.8, 26.5, 26.0, 25.1.

To a reaction vessel, **6** (142.2 mg, 0.5 mmol), **7** (174.2 mg, 0.5 mmol) obtained according to the reported synthetic route,[36] DIPEA (64.5 mg, 0.5 mmol), CuI (10 mg, 0.1 mmol) and the mixed solvent (5.0 mL, $CHCl_3$/EtOH/$H_2O = 9/1/1$) were added and stirred vigorously at room temperature for 16 h. After completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by column chromatography (with hexane/ethyl acetate 70/30 v/v) and **8** was obtained as a pale yellow oil. The obtained yellow oil **8** was dissolved in DMF/piperidine (5.0 mL, 8/2 v/v) at room temperature and shaken for 0.5 h. After the reaction was completed (TLC monitoring), H_2O (15.0 mL) was added. The mixture was extracted with ethyl acetate (10.0 mL × 3), and the combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography to afford the desired **3** as a colorless oil; yield: 172 mg (78%).[37] ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (s, 1H, C=CH), 5.88 (s, 1H, CH), 4.81–4.79 (m, 2H, CH), 4.60 (s, 1H, CH), 4.40–4.38 (m, 2H, CH), 4.31–3.99 (m, 5H, CH), 3.63–3.60 (m, 1H, CH), 2.97–2.93 (m, 2H, CH), 2.10 (s, 1H, CH), 1.97–1.94 (m, 1H, CH), 1.79–1.73 (m, 2H, CH), 1.49 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.4$, 123.3, 111.8, 108.9, 105.2, 82.6, 81.6, 81.0, 72.4, 67.3, 64.0, 57.8, 55.4, 46.5, 29.0, 26.7, 26.2, 25.4; anal. calcd. for $C_{20}H_{32}N_4O_6$: C 56.59, H 7.60, N 13.20; found: C 56.78, H 7.46, N 13.41.

Organocatalyst **4** was obtained through the same synthetic procedure from diacetone-L-glucose as starting material as a colorless oil; overall yield: 61%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (s, 1H, C=CH), 5.87 (s, 1H, CH), 4.83–4.80 (m, 2H, CH), 4.61 (s, 1H, CH), 4.43–4.39 (m, 2H, CH), 4.30–3.95 (m, 5H, CH), 3.64–3.60 (m, 1H, CH), 2.99–2.95 (m, 2H, CH), 2.12 (s, 1H, CH), 1.98–1.94 (m, 1H, CH), 1.80–1.74 (m, 2H, CH), 1.49 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 144.5, 123.4, 111.9, 108.9, 105.2, 82.8, 81.7, 81.1, 72.4, 67.4, 64.1, 57.9, 55.5, 46.7, 29.1, 26.8, 26.2, 25.5; anal. calcd. for $C_{20}H_{32}N_4O_6$: C 56.59, H 7.60, N 13.20; found: C 56.81, H 7.38, N 13.52.

(*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.23 (m, 3H, ArH), 7.16 (d, J = 7.3 Hz, 2H, ArH), 4.92 (dd, J = 4.5, 12.3 Hz, 1H, CH), 4.66 (dd, J = 9.9, 12.0 Hz, 1H, CH), 3.75 (dt, J = 4.5, 9.9 Hz, 1H, CH), 2.70–2.67 (m, 1H, CH), 2.49–2.45 (m, 1H, CH), 2.43–2.36 (m, 1H, CH), 2.14–2.05 (m, 1H, CH), 1.78–1.60 (m, 4H, 2 × CH_2), 1.28–1.21 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.6, 137.5, 128.9, 128.3, 127.6, 78.8, 52.4, 43.9, 42.9, 33.1, 28.4, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 10.34 min, t_{major} = 13.23 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 99%; $[\alpha]_D^{25}$: −23.2 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Methylphenyl)-2-nitroethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, J = 8.2 Hz, 2H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 4.90 (dd, J = 4.7, 12.0 Hz, 1H, CH), 4.62 (dd, J = 9.3, 11.9 Hz, 1H, CH), 3.73 (dt, J = 4.6, 10.0 Hz, 1H, CH), 2.64–2.58 (m, 1H, CH), 2.46–2.43 (m, 1H, CH), 2.39–2.35 (m, 1H, CH) 2.32 (s, 3H, CH_3), 1.78–1.76 (m, 1H, CH), 1.76–1.55 (m, 4H, 2 × CH_2), 1.24–1.21(m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.1, 137.5, 134.6, 129.6, 128.0, 79.2, 52.6, 43.7, 42.5, 33.4, 28.5, 25.1, 21.0; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 8.99 min, t_{major} = 12.34 min; *dr* (*syn*/*anti*) > 99:1; *ee* > 99%; $[\alpha]_D^{25}$: −25.8 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Methoxyphenyl)-2-nitroethyl]cyclohexanone:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, J = 8.3 Hz, 2H, ArH), 6.82 (d, J = 8.9 Hz, 2H, ArH), 4.94 (dd, J = 4.5, 12.2 Hz, 1H, CH), 4.56 (dd, J = 10.2, 12.3 Hz, 1H, CH), 3.77 (s, 3H, OCH_3), 3.72 (dt, J = 4.8, 10.4 Hz, 1H, CH), 2.65–2.63 (m, 1H, CH), 2.54–2.43 (m, 1H, CH), 2.44–2.36 (m, 1H, CH), 2.13–2.06 (m, 1H, CH), 1.82–1.57 (m, 4H, 2 × CH_2), 1.25–1.20 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.2, 137.4, 134.6, 129.6, 128.2, 79.0, 52.6, 43.5, 42.6, 33.4, 28.5, 25.1, 21.0; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 11.99 min, t_{major} = 15.75 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 99%; $[\alpha]_D^{25}$: −21.8 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Trifluoromethylphenyl)-2-nitroethyl]cyclohexanone:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.0 Hz, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH), 4.97 (dd, J = 12.8, 4.5 Hz, 1H, CH), 4.65 (dd, J = 12.8, 10.0 Hz, 1H, CH), 3.87 (dt, 1H, J = 10.0, 4.5 Hz, ArCH), 2.73–2.65 (m, 1H, CH), 2.50–2.49 (m, 1H, CH), 2.41–2.33 (m, 1H, CH), 2.15–2.05 (m, 1H, CH), 1.82–1.75 (m, 1H, CH), 1.75–1.66 (m, 2H, CH_2), 1.64–1.56 (m, 1H, CH), 1.29–1.20 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.3, 149.2, 148.7, 130.2, 120.5, 111.8, 79.4, 56.2, 52.6, 43.8, 42.6, 33.4, 28.5, 27.6, 25.1; HPLC (Chiralpak AD-H, 2-propanol/hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 16.78 min, t_{major} = 36.24 min; *dr* (*syn*/*anti*) > 99:1; *ee* > 99%; $[\alpha]_D^{25}$: −20.6 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Bromophenyl)-2-nitroethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.7 Hz, 2H, ArH), 7.05 (d, J = 8.4 Hz, 2H, ArH), 4.93 (dd, J = 4.5, 12.6 Hz, 1H, CH), 4.62 (dd, J = 9.9, 12.6 Hz, 1H, CH), 3.76 (dt, J = 4.5, 9.9 Hz, 1H, CH), 2.68–2.57 (m, 1H, CH), 2.53–2.30 (m, 2H, CH_2), 2.14–2.05 (m, 1H, CH), 1.82–1.53 (m, 4H, 2 × CH_2), 1.30–1.17 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.8, 148.4, 140.2, 134.6, 129.9, 122.8, 78.2, 52.0, 43.4, 42.5, 33.3, 28.2, 25.0; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 11.92 min, t_{major} = 18.67 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 99%; $[\alpha]_D^{25}$: −28.2 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(3-Bromophenyl)-2-nitroethyl]cyclohexanone:[39] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.7 Hz, 1H, ArH), 7.38 (s, 1H, ArH), 7.20 (t, J = 7.9 Hz, 1H, ArH), 7.12 (d, J = 7.2 Hz, 1H, ArH), 4.93 (dd, J = 4.5, 12.7 Hz, 1H, CH), 4.62 (dd, J = 10.0, 12.7 Hz, 1H, CH), 3.77–3.71 (m, 1H, CH), 2.64–2.58 (m, 1H, CH), 2.48–2.37 (m, 2H, CH_2), 2.07–2.04 (m, 1H, CH), 1.78–1.55 (m, 4H, 2 × CH_2), 1.31–1.21 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.1, 140.2, 131.2, 130.8, 130.5, 126.8, 122.7, 78.2, 52.2, 43.7, 42.7, 33.1, 28.4, 25.1; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 9.41 min, t_{major} = 10.35 min; *dr* (*syn*/*anti*) = 98:2; *ee* = 93%; $[\alpha]_D^{25}$: −31.5 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(2-Bromophenyl)-2-nitroethyl]cyclohexanone:[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.2 Hz, 1H, ArH), 7.31–7.20 (m, 2H, ArH), 7.14–7.12 (m, 1H, ArH), 4.88 (d, J = 8.0 Hz, 2H, CH_2), 4.31 (dd, J = 6.3, 6.8 Hz, 1H, CH), 2.91–2.85 (m, 1H, CH), 2.48–2.34 (m, 2H, CH_2), 2.12–2.06 (m, 1H, CH), 1.82–1.57 (m, 4H, 2 × CH_2), 1.40–1.22 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.4, 137.3, 133.4, 129.2, 127.8, 77.2, 52.4, 43.1, 42.5, 41.8, 32.7, 28.4, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 10.34 min, t_{major} = 18.06 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 98%; $[\alpha]_D^{25}$: −51.8 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Fluorophenyl)-2-nitroethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 8.2 Hz, 2H, ArH), 7.02 (d, J = 8.5 Hz, 2H, ArH), 4.93 (dd, J = 4.5, 12.6 Hz, 1H, CH), 4.57 (dd, J = 10.0, 12.4 Hz, 1H, CH), 3.81–3.73 (m, 1H, CH), 2.64–2.60 (m, 1H, CH), 2.48–2.38 (m, 2H, CH_2), 2.09–2.07 (m, 1H, CH), 1.79–1.58 (m, 4H, 2 × CH_2), 1.24–1.21 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.5, 133.4, 129.6, 129.4, 124.7, 124.6, 116.5, 115.3, 78.9, 52.3, 43.1, 42.7, 33.0, 28.4, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 16.45 min, t_{major} = 25.57 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 96%; $[\alpha]_D^{25}$: −32.6 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(4-Chlorophenyl)-2-nitroethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.3 Hz, 2H, ArH), 7.16 (d, J = 8.4 Hz, 2H, ArH), 4.92 (dd, J = 4.6, 12.5 Hz, 1H, CH), 4.64 (dd, J = 10.0, 12.6 Hz, 1H, CH), 3.78–3.72 (m, 1H, CH), 2.73–2.64 (m, 1H, CH), 2.46–2.36 (m, 2H, CH_2), 2.12–2.04 (m, 1H, CH), 1.77–1.56 (m, 4H, 2 × CH_2), 1.26–1.23 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.4, 136.3, 133.4, 129.7, 129.1, 122.8, 78.4, 52.4, 43.2, 42.6, 33.4, 29.5, 28.4, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 27.41 min, t_{major} = 41.83 min; *dr* (*syn*/*anti*) = 98:2; *ee* = 99%; $[\alpha]_D^{25}$: −38.1 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(2-Chlorophenyl)-2-nitroethyl]cyclohexanone:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.27–7.21 (m, 3H, ArH), 4.94–4.88 (m, 2H, CH_2), 4.31–4.25 (m, 1H, CH), 2.96–2.90 (m, 1H, CH), 2.46–2.38 (m, 2H, CH_2), 2.12–2.07 (m, 1H, CH), 1.82–1.57 (m, 4H, 2 × CH_2), 1.27–1.23 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.4, 135.5, 134.4, 130.3, 129.3, 128.7, 127.2,

77.2, 51.6, 42.8, 41.2, 33.4, 28.6, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 23.34 min, t_{major} = 39.63 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 91%; $[\alpha]_D^{25}$: −21.8 (*c* 1.1, $CHCl_3$).

(*S*)-2-[(*R*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-2-nitroethyl]cyclohexanone:[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 7.9 Hz, 1H, ArH), 6.63–6.62 (m, 2H, ArH), 5.95 (s, 2H, CH_2), 4.92 (dd, *J* = 4.5, 12.4 Hz, 1H, CH), 4.56 (dd, *J* = 4.5, 10.0 Hz, 1H, CH), 3.67 (dt, *J* = 4.5, 9.9 Hz, 1H, CH), 2.64–2.57 (m, 1H, CH), 2.52–2.36 (m, 2H, CH_2), 2.14–2.06 (m, 1H, CH), 1.78–1.56 (m, 4H, 2×CH_2), 1.35–1.24 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 148.2, 147.2, 131.5, 121.7, 108.4, 108.0, 101.3, 78.8, 52.3, 43.4, 42.5, 33.2, 28.3, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 16.56 min, t_{major} = 18.72 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 99%; $[\alpha]_D^{25}$: −45.3 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(3,4-Dimethoxyphenyl)-2-nitroethyl]cyclohexanone:[40] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.2 Hz, 1H, ArH), 6.67–6.63 (m, 2H, ArH), 4.92 (dd, *J* = 4.6, 7.8 Hz, 1H, CH), 4.63 (dd, *J* = 2.4, 9.9 Hz, 1H, CH), 3.88 (s, 6H, 2×CH_3), 3.72–3.64 (m, 1H, CH), 2.65–2.63 (m, 1H, CH), 2.48–2.43 (m, 1H, CH), 2.42–2.36 (m, 1H, CH), 2.06–2.03 (m, 1H, CH), 1.80–1.62 (m, 4H, 2×CH_2), 1.27–1.24 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.1, 149.3, 148.4, 130.0, 120.4, 111.6, 79.1, 56.1, 52.6, 43.8, 42.6, 33.4, 28.5, 27.4, 25.2; HPLC (Chiralpak As-H, 2-propanol/hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 12.35 min, t_{major} = 23.37 min; *dr* (*syn*/*anti*) > 99:1; *ee* > 99%; $[\alpha]_D^{25}$: −29.3 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-2-(Naphthalen-1-yl)-2-nitroethyl)cyclohexanone:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.78 (m, 2H, ArH), 7.63 (s, 1H, ArH), 7.50–7.45 (m, 2H, ArH), 7.28 (dd, *J* = 8.5, 2.0 Hz, 2H, ArH), 5.01 (dd, *J* = 12.0, 4.7 Hz, 1H, CH), 4.74 (dd, *J* = 12.0, 10.0 Hz, 1H, CH), 3.95 (dt, *J* = 10.0, 4.7 Hz, 1H, ArCH), 2.81–2.75 (m, 1H, CH), 2.52–2.48 (m, 1H, CH), 2.44–2.37 (m, 1H, CH), 2.10–2.04 (m, 1H, CH), 1.78–1.61 (m, 4H, 2×CH_2), 1.31–1.23 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.1, 134.5, 128.9, 128.1, 126.3, 125.7, 125.1, 123.5, 122.4, 78.6, 53.5, 42.7, 36.5, 33.1, 28.5, 25.1; HPLC (Chiralpak AS-H, 2-propanol/hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 10.17 min, t_{major} = 16.22 min; *dr* (*syn*/*anti*) > 99:1; ee > 99%; $[\alpha]_D^{25}$: −65.7 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-1-(Naphthalen-1-yl)-2-nitroethyl]cyclohexanone:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H, ArH), 7.84 (d, *J* = 7.7 Hz, 1H, ArH), 7.75 (d, *J* = 8.2 Hz, 1H, ArH), 7.56–7.43 (m, 3H, ArH), 7.36 (d, *J* = 7.2 Hz, 1H, ArH), 5.07 (dd, *J* = 12.5, 4.5 Hz, 1H, CH_2), 4.72 (br, t, 1H, *J* = 12.5 Hz, CH), 4.74–4.73 (br, m, 1H, CH), 2.87 (s, 1H, CH), 2.53–2.46 (m, 1H, CH), 2.44–2.34 (m, 1H, CH), 2.08–2.04 (m, 1H, CH), 1.76–1.58 (m, 4H, 2×CH_2), 1.30–1.22 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.7, 135.2, 133.4, 132.7, 128.9, 127.9, 127.7, 126.4, 126.2, 125.2, 78.8, 76.6, 52.6, 44.1, 42.4, 33.3, 28.5, 25.0; HPLC (Chiralpak AD-H, 2-propanol/hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 8.83 min, t_{major} = 14.45 min; *dr* (*syn*/*anti*) = 99:1; *ee* = 99%; $[\alpha]_D^{25}$: −97.6 (*c* 1.2, $CHCl_3$).

(*R*)-Tetrahydro-3-[(*R*)-2-nitro-1-phenylethyl]pyran-4-one:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 3H, ArH), 7.21 (d, *J* = 7.4 Hz, 2H, ArH), 4.96 (dd, *J* = 12.5, 4.7 Hz, 1H, CH), 4.68 (dd, *J* = 12.5, 10.0 Hz, 1H, CH), 4.20–4.15 (m, 1H, PhCH), 3.89–3.79 (m, 2H, CH_2), 3.73 (dd, *J* = 11.0, 5.3 Hz, 1H, CH), 3.31 (dd, *J* = 11.0, 8.8 Hz, 1H, CH), 2.94–2.89 (m, 1H, CH), 2.72–2.67 (m, 1H, CH), 2.62–2.58 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 136.4, 129.2, 128.4, 128.1, 78.7, 54.6, 44.7, 43.4, 35.1, 31.6; HPLC (Chiralpak AS-H, 2-propanol/hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 11.63 min, t_{major} = 16.93 min; *dr* (*syn*/*anti*) > 99/1; *ee* = 95%; $[\alpha]_D^{25}$: −34.7 (*c* 1.2, $CHCl_3$).

(*R*)-Tetrahydro-3-[(*R*)-2-nitro-1-phenylethyl]thiopyran-4-one:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.33 (m, 2H, ArH), 7.33–7.29 (m, 1H, ArH), 7.19 (d, *J* = 6.5 Hz, 2H, ArH), 4.73 (dd, *J* = 12.7, 4.5 Hz, 1H, CH), 4.63 (dd, *J* = 12.7, 10.0 Hz, 1H, CH), 3.98 (dt, *J* = 10.0, 4.5 Hz, 1H, PhCH), 3.07–3.00 (m, 1H, CH), 3.00–2.94 (m, 2H, CH_2), 2.88–2.84 (m, 1H, CH), 2.84–2.77 (m, 1H, CH), 2.61 (ddd, *J* = 2.0, 4.0, 13.8 Hz, 1H, CH), 2.45 (dd, *J* = 13.8, 9.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.4, 136.6, 129.3, 128.5, 127.7, 78.9, 71.8, 69.2, 53.4, 43.2, 41.4; HPLC (Chiralpak AS-H, 2-propanol/hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 11.85 min, t_{major} = 17.63 min; *dr* (*syn*/*anti*) = 99/1; *ee* = 98%; $[\alpha]_D^{25}$: −40.4 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]cyclopentanone:[41] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.20 (m, 3H, ArH), 7.15–7.05 (m, 2H, ArH), 5.31–5.24 (m, 1H, CH), 4.97 (dd, *J* = 9.9, 12.8 Hz, 1H, CH), 3.69–3.62 (m, 1H, CH), 2.36–2.28 (m, 2H, CH_2), 2.13–2.09 (m, 1H, CH), 1.87–1.75 (m, 2H, CH_2), 1.70–1.68 (m, 1H, CH), 1.56–1.39 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 218.6, 137.5, 137.3, 128.9, 128.5, 127.8, 78.3, 50.5, 44.2, 38.7, 28.1, 25.2; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): *syn*: t_{major} = 9.96 min, t_{minor} = 11.42 min, *anti*: t_{minor} = 12.90 min, t_{major} = 17.32 min; *dr* (*syn*/*anti*) = 34:66; *ee* = 83%, 85%; $[\alpha]_D^{25}$: −40.6 (*c* 1.2, $CHCl_3$).

(*S*)-2-[(*S*)-3-Methyl-1-nitrobutan-2-yl]cyclohexanone:[39] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.61 (dd, *J* = 5.8, 12.9 Hz, 1H), 4.39 (dd, *J* = 5.3, 13.3 Hz, 1H), 2.69–2.61 (m, 1H), 2.45–2.29 (m, 3H), 2.16–2.07 (m, 2H), 1.99–1.88 (m, 2H), 1.74–1.54 (m, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.8, 76.8, 50.8, 43.3, 41.9, 32.1, 28.4, 26.2, 25.3, 19.8; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 6.63 min, t_{minor} = 7.95 min; *dr* (*syn*/*anti*) = 94/6; *ee* = 93%; $[\alpha]_D^{25}$: −30.2 (*c* 1.2, $CHCl_3$).

(*R*)-5-Nitro-4-phenylpentan-2-one:[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 5H), 4.71–4.58 (m, 2H), 4.02–3.97 (m, 1H), 2.91 (d, *J* = 6.8 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.3, 138.9, 129.2, 127.9, 127.2, 109.1, 79.5, 46.2, 39.0, 30.5; HPLC (Chiralpak AD-H, 2-propanol/hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 9.12 min, t_{major} = 11.05 min; *ee* = 63%; $[\alpha]_D^{25}$: −8.9 (*c* 1.2, $CHCl_3$).

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