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Indolinol-catalyzed asymmetric Michael reaction of aldehydes to nitroalkenes in brine

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ABSTRACT

(2*S*,3a*S*,7a*S*)-Perhydroindolinol **A** facilitated the reaction of a wide range of aldehyde and nitroalkene substrates to provide Michael adducts with excellent enantioselectivities (up to 98% *ee*), excellent yields and high diastereoselectivities (*syn*/*anti* up to 99:1). Our results indicated that perhydroindolinols were also highly efficient organocatalysts for asymmetric Michael reactions in brine, while also being environmentally friendly.

1. Introduction

Organomolecule-catalyzed asymmetric Michael additions play a significant role in various organocatalytic C–C bond-forming reactions.[1] In particular, the conjugate addition reactions of carbonyl compounds to nitroalkenes result in the formation of γ-nitro carbonyl compounds, which are versatile synthetic intermediates.[2] Since Barbas et al. demonstrated the first organocatalytic asymmetric Michael reaction of unmodified aldehydes to nitroalkenes using chiral secondary amine catalyst,[3a] more and more selective and efficient organocatalysts have been developed for organocatalyzed Michael reactions of carbonyl compounds to nitroalkenes, such as proline-derived diamines,[3] pyrrolidinyltetrazoles,[4] ethers **1**,[5] amides **2**,[6] thioureas[7] and chiral quaternary ammonium salt oganocatalysts.[8] Other organocatalysts such as cinchona alkaloid derivatives **3**,[9] cyclohexylene diamine derivatives **4**[10] and some special organocatalysts[11] have also been developed for the asymmetric Michael reactions of nitroalkenes (Scheme 1).

Although great progress has been achieved in asymmetric Michael additions of nitroalkenes, most of the organocatalysts were designed to be poorly water soluble, or even water insoluble because of a large hydrophobic group. Recently, environmentally friendly and metal-free reactions have been gained intensive focus.[12] Therefore, the design of organocatalysts within the principle of 'green chemistry' is a challenging task. Aqueous reactions catalyzed by organocatalysts are recognized as 'green chemistry' for the advantages of being environmentally safe.[13]

Additional efforts have been made to develop efficient organocatalysts for asymmetric reactions in water.[14] However, there are very limited examples of reported organocatalytic Michael reactions under aqueous conditions. For example, Wang et al. reported on multifluoro-substituted phenyl silicone ether organocatalysts for asymmetric Michael addition reactions.[5b] Headley and Ni developed two examples of water-soluble imidazole and aniline-substituted silicone ether organocatalysts for asymmetric Michael addition reactions of aldehydes to nitroalkenes.[5g]

We found that chiral proline derivatives were of significant importance in many enantioselective organocatalytic transformations,[15] and that slight changes on catalyst structure can sometimes improve the catalytic activity dramatically. We previously reported on effective diphenylperhydroindolinol silyl ether organocatalysts for asymmetric Michael addition reactions of aldehydes to nitroalkenes, providing Michael adducts in nearly enantiomerically pure form (99%), good yields and high diastereoselectivities (*syn*/*trans* 99:1).[16] In our previous report, however, organic solvents were used, which is not consistent with 'green chemistry'. Herein we report the synthesis of new perhydroindole derivatives and then applied them to the asymmetric Michael reactions of aldehydes to nitroalkenes in aqueous solution (Scheme 2).

2. Results and discussions

2.1. Effects of catalysts

At first, we synthesized the perhydroindole derivatives organocatalysts according to the literature.[17] With these catalysts

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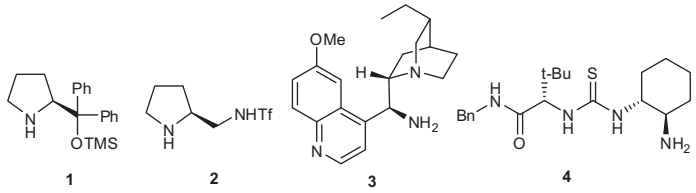
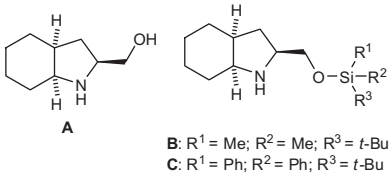


Scheme 1. Some representative organocatalysts for asymmetric Michael reactions.



Scheme 2. Perhydroindole derivatives for asymmetric Michael reaction.

in hand, we next investigated the asymmetric Michael addition of aldehydes to nitroalkenes. The Michael reaction of propanal and (*E*)-(2-nitrovinyl)-benzene was chosen as the model reaction. The reaction was performed with 20 mol % catalyst as the catalytic system in NaCl aq at room temperature. Initial screening of the catalysts demonstrated that the cyclohexyl ring plays an important role both in terms of the stereoselectivity and enantioselectivity when compared with (*S*)-prolinol (Table 1). Good enantioselectivity (93% *ee*) and yield (98%) were achieved when (2*S*,3a*S*,7a*S*)-(octahydro-indol-2-yl)-methanol **A** was employed (Table 1, entry 1). Chiral perhydroindolinol silyl ethers **B** and **C**, the hydroxyl groups of which were protected by a siloxy group, exhibited lower reactivities and enantioselectivities (Table 1, entries 2–3). In the presence of **B** and **C**, the reaction was complete in 4 h at room temperature to afford the corresponding Michael adduct with the same enantioselectivity (90%) (Table 1, entries 2, 3). Only 23% *ee* was observed when using (*S*)-prolinol as the catalyst (Table 1, entry 4). In comparison to prolinol, (2*S*,3a*S*,7a*S*)-diphenylperhydroindolinol **A**, prolinol silyl ethers **B** and **C**, which incorporates a rigid cyclohexyl ring in the backbone, which in turn contributes toward differentiating between the diastereofacial approaches, showed better efficiencies in Michael reactions between aldehydes and nitroalkenes.[16] Catalyst loading can also be reduced to 10 mol % without compromising the enantioselectivity (Table 1, entry 6), although a further increase to 30 mol % increased the reactivity and decreased the reaction time to 0.5 h (Table 1, entry 5). From the catalyst loading optimization, we found that lower stereoselectivity was obtained with 30 mol % catalyst loading or lower enantioselectivity was obtained with 10 mol % catalyst loading. Hence we used 20 mol % catalyst loading in order to further study this catalytic system.

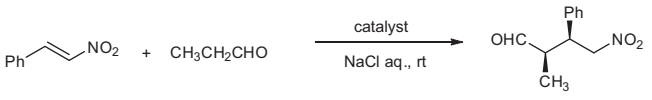
2.2. Influence of the solvent

In order to obtain better reaction conditions (both reactivity and selectivity) of **A**, we next screened the effects of several common organic solvents (Table 2, entries 1–10). Throughout this study, we used 20 mol % catalyst and 10 equiv of aldehyde. As can be seen in Table 2, a strong solvent effect was observed. CH_2Cl_2, hexane, toluene, THF and MeOH were the solvents of choice in this reaction, providing good *ee*s and excellent diastereoselectivities (*syn*/*trans* 99:1) (Table 2, entries 1–6). No Michael adduct was observed when DMF was used as the solvent (Table 2, entry 7). When H_2O was used as the solvent, the enantioselectivity was increased to 90% (Table 2, entry 8), while in saturated NaCl, 93% *ee* was obtained and the reaction was complete in 1 h (Table 2, entry 9). The reaction can even be performed at 0 °C to give the desired product with 98% *ee* (Table 2, entry 10). From the solvent screening, it can be seen that H_2O and saturated NaCl gave good results, with saturated NaCl providing the best results. We believe catalyst **A** with a hydroxy group interacts with brine by hydrogen bonding and thus strengthens the catalytic effects.

2.3. Michael addition of various aldehydes and nitroalkenes

Under the optimized reaction conditions, the asymmetric Michael addition of aldehydes and nitroalkenes were screened (Table 3). As can be seen in Table 3, a variety of aldehydes and

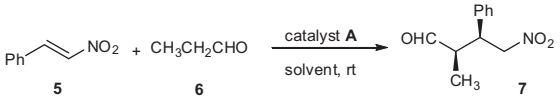
Table 1
The effects of catalysts in the Michael reaction of propanal and (*E*)-(2-nitrovinyl)-benzene



Entry	Catalyst	Time [h]	Yield [%][a]	*syn*/*anti*[b]	*ee* [%][c]
1	**A**	1	98	99:1	93
2	**B**	4	85	99:1	90
3	**C**	4	98	99:1	90
4	Prolinol	1	98	85:15	23
5[d]	**A**	0.5	98	97:3	93
6[e]	**A**	5	90	99:1	91

[a] Yield of isolated product.
[b] Determined by HPLC analysis.
[c] The *ee* value was determined by HPLC analysis on a chiral phase (Chiralcel OD-H).
[d] 30 mol % catalyst loading.
[e] 10 mol % catalyst loading.

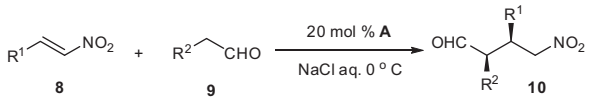
Table 2
Influences of solvents on Michael addition of propanal and (*E*)-(2-nitrovinyl)-benzene

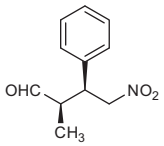
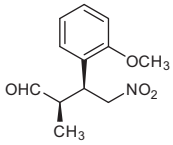
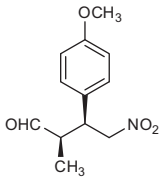
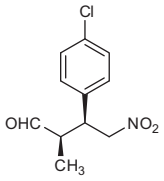
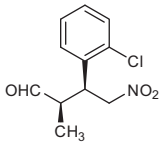
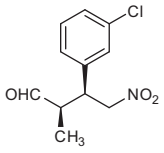
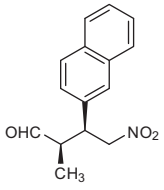
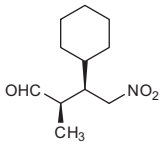
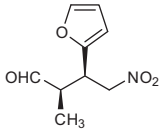
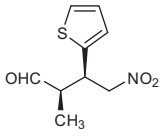


Entry	Solvent	Time [h]	Yield [%][a]	*syn*/*anti*[b]	*ee* [%][c]
1	CH_2Cl_2	5	95	99:1	83
3	Hexane	5	91	99:1	89
4	Toluene	5	93	99:1	88
5	THF	3	90	99:1	77
6	MeOH	5	85	99:1	86
7	DMF	12	<5	ND	ND
8	H_2O	5	93	99:1	90
9	NaCl aq	1	98	99:1	93
10[d]	NaCl aq	5	95	99:1	98

[a] Yield of isolated product.
[b] Determined by ^1H NMR Spectroscopy (400 MHz).
[c] The *ee* value was determined by HPLC analysis on a chiral phase (Chiralcel OD-H).
[d] The reaction was performed at 0 °C.

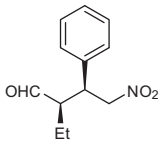
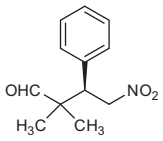
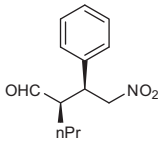
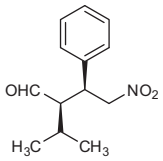
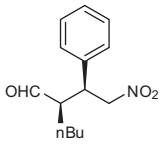
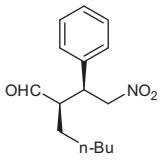
Table 3
Asymmetric Michael reaction of aldehydes and nitroalkenes



Entry	Product	Time [h]	Yield [%][a]	*syn*/*anti* [b]	*ee* [%][c]
1		5	98	99:1	98
2		7	95	97:3	96
3		7	96	98:2	92
4		5	98	98:2	94
5		9	91	99:1	95
6		8	93	88:12	95
7		7	91	99:1	93
8		16	92	45:55	91(80)
9		18	93	97:3	90
10		18	93	82:18	84(84)

(*continued on next page*)

Table 3 (*continued*)

Entry	Product	Time [h]	Yield [%][a]	*syn*/*anti* [b]	*ee* [%][c]
11		7	93	99:1	96
12		12	93	—	88
13		7	93	95:5	92
14		18	91	99:1	88
15		7	93	98:2	97
16		8	91	93:7	95

[a] Yield of isolated product.
[b] Determined by HPLC.
[c] The *ee* value was determined by HPLC analysis on a chiral phase (Chiralcel OD-H, AD-H or AS-H).

nitroalkenes could be used in the conjugate addition reaction, to afford the desired γ-nitroaldehyde products in excellent yields and enantioselectivities (Table 3, entries 1–16). Aryl-substituted (Table 3, entries 1–7), alkyl-substituted (Table 3, entry 8) and heteroaryl-substituted nitroalkenes (Table 3, entries 9 and 10) were excellent Michael acceptors. However in comparison to aryl substituted nitroalkenes, longer reaction times were needed for alkyl-substituted (Table 3, entry 8) and heteroaryl-substituted nitroalkenes (Table 3, entries 9 and 10). For example, 16–18 h were needed to ensure complete conversion, while worse diastereoselectivities (*syn*/*trans* 45:55) were obtained when alkyl-substituted or heteroaryl-substituted nitroalkenes were used (Table 3, entries 8–10). Straight and branched aldehydes were good Michael donors (Table 3, entries 11–16), although longer reaction times were also required for branched aldehydes (Table 3, entries 12 and 14).

3. Conclusions

In conclusion, new perhydroindole derivatives have been synthesized in excellent yields and evaluated as chiral organocatalysts in asymmetric Michael reactions of aldehydes to nitroalkenes. (2*S*,3*aS*,7*aS*)-Perhydroindolinol **A** facilitated the reaction of a wide range of aldehydes and nitroalkenes substrates, providing Michael adducts with excellent enantioselectivities (up to 98% *ee*), excellent yields and high diastereoselectivities (*syn*/*trans* up to 99:1). These results indicated that perhydroindolinols are also highly efficient organocatalysts for asymmetric Michael reactions in water. Further applications of this catalytic system to other asymmetric reactions are currently in progress.

4. Experimental

4.1. General

All reactions were carried out under air in glassware with magnetic stirring. The solvents were directly used with commercial purchase. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of the reaction products was carried out by flash chromatography using Qing Dao Sea chemical reagent silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on a Bruker XL 400 (400 MHz) spectrometer and the spectra are referenced internally to the residual proton resonance in $CDCl_3$ (δ = 7.26 ppm), or with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. Chemical shifts re reported as parts per million (ppm) in the δ scale downfield from TMS. ^{13}C NMR spectra were recorded on Bruker (400 MHz) spectrometer with complete proton decoupling, and chemical shifts are reported in ppm from TMS with the solvent as the internal reference ($CDCl_3$, δ = 77.0 ppm). HPLC analyses were conducted on a Shimadzu 10A

instrument using CHIRALCEL OD-H, AD-H or AS-H columns (0.46 cm diameter × 25 cm length). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

4.2. Procedures for the preparation of organocatalysts

4.2.1. Synthesis of catalyst A[17]

Amino alcohol **A** was prepared from (2*S*,3a*S*,7a*S*)-methyl octahydro-1*H*-indole-2-carboxylate (3.66 g, 20 mmol) as the material by using lithium aluminum hydride (1.9 g, 50 mmol) as the reductant in THF in excellent yield as a yellow oil. **A** (2.8 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25–1.30 (3H, m), 1.44–1.88 (8H, m), 1.97–2.02 (1H, m), 3.04–3.08 (1H, m), 3.26–3.29 (2H, m), 3.39–3.44 (1H, m), 3.58–3.62 (1H, m). ^{13}C (100 MHz, $CDCl_3$): δ 22.4, 23.6, 28.2, 29.6, 33.1, 38.4, 57.6, 59.2, 65.9.

4.2.2. Synthesis of catalyst B[16]

A solution of $(CH_3)_2t$-BuSiCl (3.45 mL, 20 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of (2*S*,3a*S*,7a*S*)-octahydro-1*H*-indol-2-yl)methanol **A** (1.55 g, 10 mmol) and Et_3N (4.16 mL, 30 mmol) in 20 mL of CH_2Cl_2 at 0 °C. The reaction was stirred for 24 h at ambient temperature until full conversion of the starting material. The reaction was quenched with water, extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by flash chromatography and **B** (2.53 g, 94% yield) was isolated as yellow oil. $[\alpha]_D^{20} = -9.5$ (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (6H, s), 0.86 (9H, s),1.21–1.32 (2H, m), 1.41–1.48 (5H, m),1.64–1.68 (2H, m), 1.79–1.82 (1H, m), 2.05–2.10 (1H, m), 3.12–3.17 (1H, m), 3.33–3.37 (1H, m), 3.58–3.62 (1H, m), 3.72–3.76 (1H, m), 4.34 (1H, s). ^{13}C (100 MHz, $CDCl_3$): δ −5.33, −5.27, 18.43, 22.22, 23.30, 26, 32.83, 37.95, 57.98, 59.42, 64.70.; HRMS (ESI) *m*/*z*: calculated for $C_{15}H_{31}NOSi$ 269.2175; found: 269.2179.

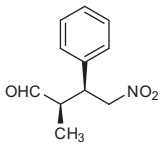
4.2.3. Synthesis of catalyst C[16]

A solution of Ph_2t-BuSiCl (4.50 mL, 20 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of (2*S*,3a*S*,7a*S*)-octahydro-1*H*-indol-2-yl) methanol **A** (1.55 g, 10 mmol) and Et_3N (4.16 mL, 30 mmol) in 20 mL of CH_2Cl_2 at 0 °C. The reaction was stirred for 24 h at ambient temperature until full conversion of the starting material. The reaction was quenched with water, extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by flash chromatography and **C** (3.45 g, 88% yield) was isolated as a yellow oil. $[\alpha]_D^{20} = -8.7$ (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (9H, s), 1.22–1.71 (9H, m), 1.82–1.89 (1H, m), 2.01–2.03 (1H, m), 2.22 (1H, s), 3.03–3.07 (1H, m), 3.25–3.31 (1H, m), 3.65–3.68 (1H, m), 7.39–7.44 (6H, m), 7.69–7.72 (4H, m). ^{13}C (100 MHz, $CDCl_3$): δ 19.29, 21.91, 23.96, 26.89, 28.37, 29.03, 33.86, 39.14, 57.76, 59.24, 67.02, 127.52, 127.63, 127.67, 129.60, 133.60, 133.66, 134.93, 135.69.; HRMS (ESI) *m*/*z*: calculated for $C_{25}H_{35}NOSi$ 393.2488; found: 393.2493.

4.3. Typical experimental procedure[16]

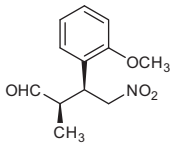
Propanal (0.48 mL, 6.7 mmol) was added to a solution of nitroalkenes (100 mg, 0.67 mmol) and **A** (20.8 mg, 0.134 mmol) in NaCl aq (2.0 mL) at 0 °C. After the reaction mixture had been stirred for 5 h at that temperature, the reaction mixture was purified by flash chromatography to afford the Michael adduct (136 mg, 98%) as a clear oil. *syn*/*trans* 99:1 (by ^{1}H NMR spectroscopy of the crude mixture), 98% *ee* (by HPLC using Daicel Chiralcel OD-H column, λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 15.05 min (minor), t_R = 17.26 min (major).[16]

4.3.1. (2*R*,3*S*)-2-Methyl-4-nitro-3-phenylbutanal[16]



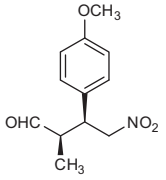
Prepared from (*E*)-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 98%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 15.05 min (minor), t_R = 17.26 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, d, *J* = 7.3 Hz), 2.66–2.72 (1H, m), 3.70–3.76 (1H, m), 4.57–4.62 (1H, m), 4.69–4.74 (1H, m), 7.07–7.27 (5H, m), 9.61 (1H, d, *J* = 1.5 Hz).

4.3.2. (2*R*,3*S*)-2-Methyl-4-nitro-3-(2-methoxyphenyl)-butanal[16]



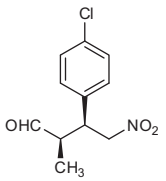
Prepared from (*E*)-1-methoxy-2-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 96%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 15.89 min (minor), t_R = 16.85 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (3H, d, *J* = 7.3 Hz), 2.90–2.94 (1H, m), 3.74 (3H, s), 3.92–3.98 (1H, m), 4.63–4.68 (1H, m), 4.75–4.80 (1H, m), 6.79–6.84 (2H, m), 6.98–7.00 (1H, m), 7.16–7.20 (1H, m), 9.62 (1H, d, *J* = 1.8 Hz).

4.3.3. (2*R*,3*S*)-2-Methyl-4-nitro-3-(4-methoxyphenyl)-butanal[16]



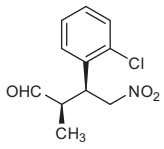
Prepared from (*E*)-1-methoxy-4-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 92%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel AS-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 28.68 min (minor), t_R = 32.91 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, d, *J* = 7.3 Hz), 2.60–2.66 (1H, m), 3.66 (3H, s), 3.68–3.71 (1H, m), 4.51–4.57 (1H, m), 4.64–4.70 (1H, m), 6.75–6.78 (2H, m), 6.98–7.05 (2H, m), 9.58 (1H, d, *J* = 1.6 Hz).

4.3.4. (2*R*,3*S*)-3-(4-Chlorophenyl)-2-methyl-4-nitrobutanal[16]



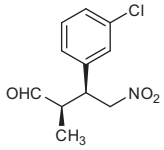
Prepared from (*E*)-1-chloro-4-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 93.5%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel AD-H column (λ = 208 nm, hexane/*i*-PrOH = 99:1, 1.0 mL/min), t_R = 15.41 min (minor), t_R = 16.98 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (3H, d, *J* = 7.3 Hz), 2.66–2.71 (1H, m), 3.69–3.75 (1H, m), 4.54–4.60 (1H, m), 4.67–4.74 (1H, m), 7.03–7.10 (2H, m), 7.20–7.25 (2H, m), 9.61 (1H, s).

4.3.5. (2*R*,3*S*)-3-(2-Chlorophenyl)-2-methyl-4-nitrobutanal[18]



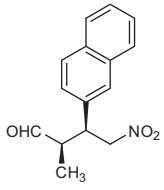
Prepared from (*E*)-1-chloro-2-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 95%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 210 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 11.68 min (minor), t_R = 16.98 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (3H, d, *J* = 7.3 Hz), 2.66–2.71 (1H, m), 3.69–3.75 (1H, m), 4.54–4.60 (1H, m), 4.67–4.74 (1H, m), 7.03–7.10 (2H, m), 7.20–7.25 (2H, m), 9.61 (1H, s).

4.3.6. (2*R*,3*S*)-3-(3-Chlorophenyl)-2-methyl-4-nitrobutanal[19]



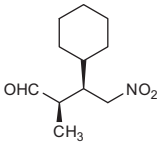
Prepared from (*E*)-1-chloro-3-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 95%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 210 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 13.52 min (minor), t_R = 17.02 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82–2.70 (m, 1H), 1.01 (d, *J* = 7.3 Hz, 3H), 3.82–3.74 (m, 1H), 4.69–4.61 (m, 1H), 4.84–4.75 (m, 1H), 7.32–6.97 (m, 4H), 9.69 (d, *J* = 1.5 Hz, 1H).

4.3.7. (2*R*,3*S*)-2-Methyl-3-(2-naphthyl)-4-nitrobutanal[16]



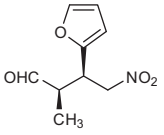
Prepared from (*E*)-2-(2-nitrovinyl)-naphthalene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 93%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 26.93 min (minor), t_R = 28.67 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, d, *J* = 7.3 Hz), 2.86–2.91 (1H, m), 4.67–4.85 (3H, m), 7.25–7.50 (4H, m), 7.71 (1H, d, *J* = 8.2 Hz), 7.78 (1H, d, *J* = 8.0 Hz), 8.01–8.03 (1H, m), 9.65 (1H, d, *J* = 1.6 Hz).

4.3.8. (2*R*,3*R*)-3-Cyclohexyl-2-methyl-4-nitro-butanal[16]



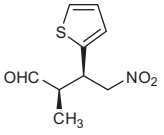
Prepared from (*E*)-(2-nitrovinyl)-cyclohexane and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 91%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel AD-H column (λ = 210 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 6.78 min (major), t_R = 7.51 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81–0.93 (3H, m), 0.96–1.00 (2H, m), 1.13 (3H, d, *J* = 6.8 Hz), 1.34–1.70 (6H, m), 2.48–2.67 (2H, m), 4.29–4.36 (1H, m), 4.50–4.55 (1H, m), 9.61 (1H, s).

4.3.9. (2*R*,3*R*)-3-Furyl-2-methyl-4-nitrobutanal[16]



Prepared from (*E*)-2-(2-nitrovinyl)-furan and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 90%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel AD-H column (λ = 210 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 19.47 min (major), t_R = 24.68 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (3H, d, *J* = 7.3 Hz), 2.69–2.79 (1H, m), 3.91–4.05 (1H, m), 4.60–4.71 (2H, m), 6.06–6.23 (2H, m), 7.29 (1H, s), 9.63 (1H, s).

4.3.10. (2*R*,3*R*)-2-Methyl-4-nitro-3-(2-thiophyl)butanal[16]



Prepared from (*E*)-2-(2-nitrovinyl)-thiophene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 84%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel AD-H column (λ = 238 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 16.69 min (major), t_R = 27.95 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, d, *J* = 7.3 Hz), 2.74–2.85 (1H, m), 4.16–4.27 (1H, m), 4.65–4.80 (2H, m), 6.89–6.96 (2H, m), 7.21–7.27 (1H, m), 9.67 (1H, d, *J* = 0.9 Hz).

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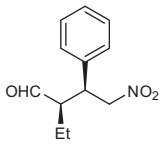
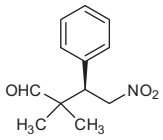
4.3.11. (2*R*,3*S*)-2-Ethyl-4-nitro-3-phenylbutanal[16]



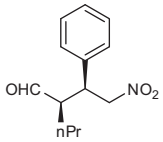
Prepared from (*E*)-(2-nitrovinyl)-benzene and butyraldehyde according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 96%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 11.26 min (major), t_R = 14.01 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71 (3H, t, *J* = 7.5 Hz), 1.35–1.44 (2H, m), 2.56–2.62 (1H, m), 3.68–3.74 (1H, m), 4.51–4.69 (2H, m), 7.09–7.25 (5H, m), 9.67 (1H, d, *J* = 2.5 Hz).

4.3.12. (*R*)-2,2-Dimethyl-4-nitro-3-phenylbutanal[16]



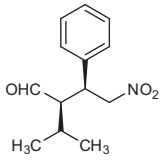
Prepared from (*E*)-(2-nitrovinyl)-benzene and isobutyraldehyde according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 88%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 14.26 min (minor), t_R = 20.65 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, s), 0.99 (3H, s), 3.67–3.71 (2H, m), 4.59 (1H, dd, *J* = 4.2, 13.1 Hz), 4.73–4.79 (1H, m), 7.09–7.21 (5H, m), 9.39 (1H, s).

4.3.13. (2*R*,3*S*)-2-Propyl-4-nitro-3-phenylbutanal[16]



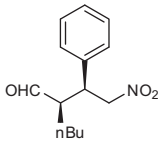
Prepared from (*E*)-(2-nitrovinyl)-benzene and pentanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 92%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 14.47 min (minor), t_R = 16.19 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69 (3H, t, *J* = 7.1 Hz), 1.06–1.42 (4H, m), 2.59–2.66 (1H, m), 3.67–3.73 (1H, m), 4.53–4.65 (2H, m), 7.08–7.27 (5H, m), 9.60 (1H, d, *J* = 2.5 Hz).

4.3.14. (2*R*,3*S*)-2-Isopropyl-4-nitro-3-phenylbutanal[16]



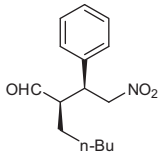
Prepared from (*E*)-(2-nitrovinyl)-benzene and 3-methylbutanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 88%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 14.65 min (minor), t_R = 16.51 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, d, *J* = 7.0 Hz), 1.09 (3H, d, *J* = 7.2 Hz), 1.66–1.75 (1H, m), 2.76–2.80 (1H, m), 4.54–4.69 (2H, m), 7.18–7.36 (5H, m), 9.91 (1H, d, *J* = 2.4 Hz).

4.3.15. (2*R*,3*S*)-2-Butyl-4-nitro-3-phenylbutanal[16]



Prepared from (*E*)-(2-nitrovinyl)-benzene and hexanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 97%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 15.70 min (minor), t_R = 18.68 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 6.7 Hz), 1.02–1.18 (4H, m), 1.30–1.41 (2H, m), 2.59–2.65 (1H, m), 3.67–3.73 (1H, m), 4.53–4.66 (2H, m), 7.09–7.27 (5H, m), 9.61 (1H, d, *J* = 2.7 Hz).

4.3.16. (2*R*,3*S*)-2-Pentyl-4-nitro-3-phenylbutanal[16]



Prepared from (*E*)-(2-nitrovinyl)-benzene and heptanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; *ee* = 95%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (λ = 208 nm, hexane/*i*-PrOH = 85:15, 1.0 mL/min), t_R = 15.12 min (minor), t_R = 17.31 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72 (3H, t, *J* = 6.8 Hz), 1.01–1.42 (8H, m), 2.59–2.65 (1H, m), 3.67–3.73 (1H, m), 4.53–4.65 (2H, m), 7.09 (2H, d, *J* = 7.2 Hz), 7.18–7.27 (3H, m), 9.61 (1H, d, *J* = 2.6 Hz).

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2016.03.006.

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