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Organocatalytic desymmetrization of cyclic *meso*-anhydrides through enantioselective alcoholysis with functionalized primary nitroallylic alcohols

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ABSTRACT

The direct organocatalytic desymmetrization of cyclic *meso*-anhydrides was achieved by alcoholysis with nitroallylic alcohols. The reaction between primary nitroallylic alcohols and cyclic *meso*-anhydrides catalyzed by cinchonidine derived thiourea organocatalyst **II** (10 mol %) proceeded smoothly. The corresponding hemiesters were obtained in high chemical yields with high to excellent levels of stereoselectivity (up to 90% yield and 99% ee). On the other hand, the reversal of enantioselectivity was observed when an amino cinchonidine derivative (**III**) was used as the organocatalyst under the similar reaction conditions. This demonstrated an example of activation of the nucelophilic component in the desymmetrization of cyclic *meso*-anhydrides.

1. Introduction

Over the past several decades, many efficient asymmetric protocols have been developed for synthesizing chiral nonracemic substances through either metal-mediated[1] or metal-free catalysis.[2] Catalytic asymmetric desymmetrization is a conventional method that allows access to versatile enantioenriched chiral building blocks without creating new stereogenic centers.[3] Numerous naturally occurring biologically active complex molecular structures can be easily synthesized using these chiral products.[4] Many functional prochiral and *meso* starting substrates have been used in the simple symmetry-breaking operation, including olefinic 1,3-diol,[5] 3-substituted oxetane,[6] epoxide,[7] cyclohexadienone,[8] cyclic ketone,[9] cyclohexadiene,[10] aziridine,[11] 1,3-dione,[12] cyclohexanone,[13] and bis(phenol).[14] The use of a chiral Lewis acid catalysis in enantioselective desymmetrization has been documented.[15] By contrast, organocatalysis is an alternative and environmentally benign approach for performing desymmetrization reaction, which possesses several synthetic advantages such as easy accessibility of the starting substrates, creation of multiple stereogenic centers, and the possibility of the final products undergoing additional chemical transformations.[16] The desymmetrization of anhydrides catalyzed by a small organic molecule *cinchona* alkaloid was first reported by Oda.[17] An enantioselective ring-opening of cyclic *meso*-anhydrides yielded chemically differentiated carboxyl groups, which are useful building blocks for numerous synthetic transformations.[18] The use of the privileged *cinchona* alkaloids and their derivatives has pervaded a substantial part of organocatalysis.[19] Many efficient synthetic methodologies have been developed using these bifunctional catalysts to activate both the nucleophilic and electrophilic components synergistically.[20] Therefore, we report an enantioselective alcoholysis of cyclic *meso*-anhydrides with primary nitroallylic alcohols to prepare both enantiomers of hemiesters by using cinchonidine derived amino and thiourea catalysts (Fig. 1).

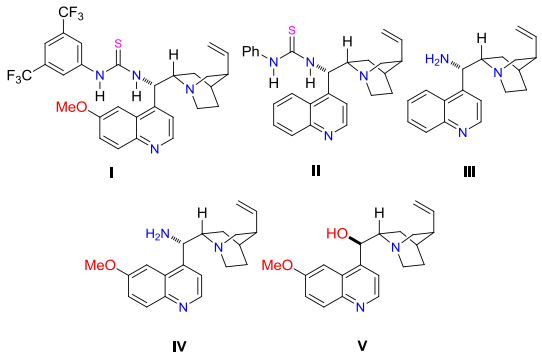

Fig. 1. Structures of various bifunctional organocatalysts **I**–**V**.

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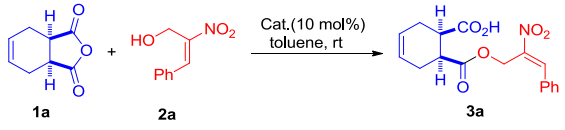
2. Results and discussion

Most enantioselective desymmetrization of cyclic *meso*-anhydrides involves using a simple alcohol in the presence of a catalyst. The alcoholysis process requires the activation of the electrophilic cyclic anhydrides followed by deprotonation of the alcoholic proton. The activation of the nucleophilic components has not been extensively studied. The presence of a thiourea moiety in the catalyst has been known to activate the nitro group in various enantioselective reactions. Incorporating an auxiliary nitro group in the nucleophilic alcohols might facilitate the desymmetrization of the cyclic *meso*-anhydrides. To test this hypothesis, various *cinchona* alkaloid based catalysts (**I**–**V**) were used in this study to catalyze the asymmetric ring opening of *meso*-anhydrides. The primary nitroallylic alcohol (**2a**) and *cis*-1,2-cyclohexene dicarboxylic anhydride (**1a**) were used as model substrates for the reaction at ambient temperature. Both the chemical yield and enantioselectivity were moderate when the thiourea catalyst **I** was used (Table 1, entry 1). The use of catalyst **II** was able to improve the reactivity and stereoselectivity (86% ee) in toluene (Table 1, entry 2). The corresponding hemiester **3a** was obtained with stereochemistry opposite to that observed when primary amino organocatalysts **III**–**IV** were used (Table 1, entries 3 and 4). Finally, using a quinine catalyst to give the desired product with inferior results (Table 1, entry 5).

Table 1
Catalysts screening for the desymmetrization reaction of *cis*-1,2-cyclohexene dicarboxylic anhydride (**1a**) with nitroallylic alcohol (**2a**)[a]

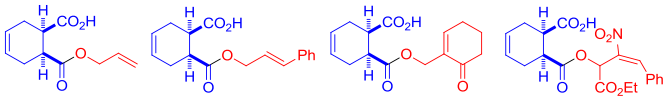


1a **2a** **3a**

Entry	Catalyst	*t*/h	Yield (%)[b]	ee (%)[c]
1	**I**	20	37	68
2	**II**	15	79	86
3	**III**	20	58	−61
4	**IV**	20	47	−55
5	**V**	21	41	−31

[a] All reactions were carried out with *cis*-1,2-cyclohexene dicarboxylic acid anhydride **1a** (1.0 equiv), nitroallylic alcohol **2a** (1.0 equiv), and 10 mol % of organocatalysts (**I**–**V**) in toluene (0.8 mL) at ambient temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

The phenomenon of reversal of stereochemistry when thiourea catalysts (**I** and **II**) and amino catalysts (**III** and **IV**) were used is compelling. Presumably, the nitro group of the nucleophilic alcohol was activated by the catalyst through hydrogen bond formation. To confirm the hypothesis, we conducted ^{1}H NMR studies on the interaction between the nitroallylic alcohol **2a** and the catalyst **II** in deuterium toluene-d_8. Examining the spectrum indicated the signals of methylene protons in nitroallylic alcohol **2a** shifted slightly downfield from δ (ppm) 4.16 (d) to 4.19 (s) while the olefinic proton shifted upfield to 7.77 (s) from 7.79 (s).[21] No changes in chemical shifts were observed when cyclic *meso*-anhydride **1a** and catalyst **II** were mixed, potentially indicating the proximity between the nitro group and the thiourea functionalities in the solution. Next, the use of other allylic alcohols was investigated to verify the importance of the nitro group in the desymmetrization reaction. Thus, we applied the present protocol to other allylic alcohols as nucleophiles in the presence of cinchonidine derived thiourea catalyst **II**. Using allylic alcohol afforded the desired hemiester **4a** with reasonable enantioselectivity (Fig. 2). The reaction of cinnamyl alcohol resulted in the expected product **4b** in favorable chemical yield and moderate enantioselectivity (58% ee). The use of 2-(hydroxymethyl)cyclohex-2-enone produced the corresponding product in 64% chemical



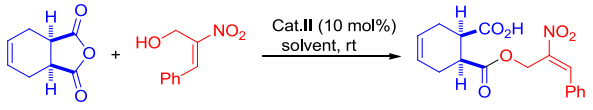
4a (91%, 68% ee) **4b** (77%, 58% ee) **4c** (64%, 42% ee) **4d** (48%, 93% ee)

Fig. 2. The structures of other hemisters **4a**–**d** when different allylic alcohols were used catalyzed by **II**.

yield with moderate enantioselectivity (42% ee). The reaction of racemic nitroallylic alcohol provided the desired hemiester **4d** with excellent enantioselectivity (93% ee).[22] These data indicate that the presence of a nitro group in allylic alcohols is essential in the cyclic anhydride ring opening.

To determine whether any other solvents could be suitable for this protocol, a survey of reaction media was conducted. We performed the reaction in different solvents, including toluene, *n*-pentane, benzene, and halogenated solvents in the presence of catalyst **II**. Screening the solvents revealed that toluene was the optimal solvent for the reaction (Table 2, entry 1). Both the reactivity and selectivity were slightly decreased when benzene was used (Table 2, entry 3). No reaction occurred when nonpolar *n*-pentane was used (Table 2, entry 4). The desired product **3a** was obtained with high enantioselectivity (85% ee) in halogenated solvents (Table 2, entries 5–7). The reactivity decreased considerably when polar solvent, such as CH_3CN were used (Table 2, entry 8). Surprisingly, an excellent chemical yield was obtained (96%) when the amount of cyclic anhydride **1a** was increased from 1.0 to 2.0 equiv with comparable enantioselectivity (Table 2, entry 9). The enantioselectivity was further improved to 94% ee when the reaction was performed at −20 °C (Table 2, entry 10).

Table 2
Optimization of the desymmetrization reaction of *cis*-1,2-cyclohexene dicarboxylic acid anhydride (**1a**) with nitroallylic alcohol (**2a**)[a]



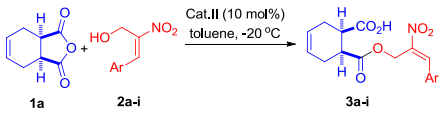
1a **2a** **3a**

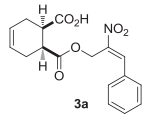
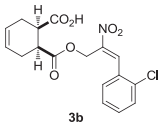
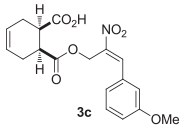
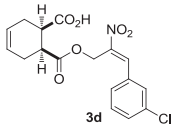
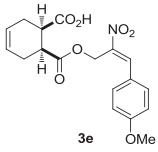
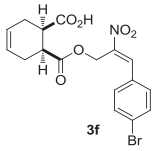
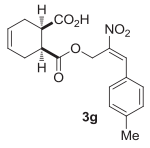
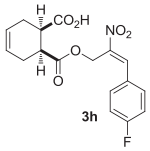
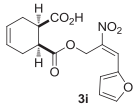
Entry	Solvent	*t*/h	Yield (%)[b]	ee (%)[c]
1	Toluene	15	79	86
2	Mesitylene	18	73	77
3	Benzene	15	63	82
4	*n*-Pentane	48	—	—
5	CCl_4	20	77	76
6	$CHCl_3$	18	61	85
7	CH_2Cl_2	20	60	81
8	CH_3CN	30	<10	—
9[d]	Toluene	18	96	84
10[e]	Toluene	48	88	94

[a] All reactions were carried out with *cis*-1,2-cyclohexene dicarboxylic acid anhydride **1a** (1.0 equiv), nitroallylic alcohol **2a** (1.0 equiv), and 10 mol % of organocatalyst **II** in the solvent indicated (0.8 mL) at ambient temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] *cis*-1,2-Cyclohexene dicarboxylic acid anhydride:nitroallylic alcohol=2:1 at ambient temperature.
[e] *cis*-1,2-Cyclohexene dicarboxylic acid anhydride:nitroallylic alcohol=2:1 at −20 °C.

After optimizing the reaction conditions, we evaluated the scope of this methodology by using *cis*-1,2-cyclohexene dicarboxylic acid anhydride **1a** with various nitroallylic alcohols. The results were summarized in Table 3. Various nitroallylic alcohols **2a**–**i** were investigated to establish the general utility of this asymmetric transformation. Regardless of the substituent functionality and orientation in the aromatic nucleus, the desymmetrization of ring openings proceeded smoothly to give the desired products with comparable results. Employing a 2-chloro substituted aryl group in

Table 3
The reaction of various nitroallylic alcohols **2a**–**i** with *cis*-1,2-cyclohexene dicarboxylic acid anhydride **1a** mediated by catalyst **II**[a]



Entry	Product	*t*/h	Yield (%)[b]	ee (%)[c]
1		48	88	94
2		72	81	99
3		72	77	91
4		66	80	84
5		50	85	92
6		72	84	92
7		72	72	92
8		48	85	91
9		48	84	81

[a] All reactions were carried out with *cis*-1,2-cyclohexene dicarboxylic acid anhydride **1a** (2.0 equiv), nitroallylic alcohols **2a**–**i** (1.0 equiv), and 10 mol % of organocatalyst **II** in toluene (0.8 mL) at −20 °C.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

the nucleophile yielded excellent enantioselectivity; however, the stereoselectivity dropped when 3-chloro substituted substrate was used (Table 3, entries 2 and 4). Comparable stereoselectivities were observed when 4-substituent substrates was used (Table 3, entries 5–8). Using of 2-furyl substituted nitroallylic alcohol 2i provided **3i** with reasonable selectivity (81% ee) (Table 3, entry 9). The desymmetrization products were characterized by IR, HRMS, ^{1}H, ^{13}C NMR spectroscopic data, and the absolute stereochemistry was tentatively assigned by single crystal X-ray analysis of a representative product (1*R*,6*S*)-**3b** (Fig. 3).[23]

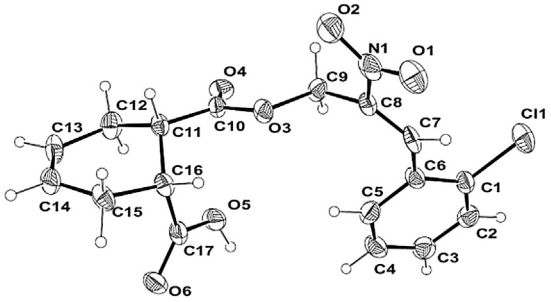


Fig. 3. Thermal ellipsoid representation of **3b** at 30% probability level.

To explore the scope of the asymmetric protocol further, we examined the reaction between nitroallylic alcohol **2a** and various cyclic *meso*-anhydrides. As depicted in Fig. 4, the desymmetrization reaction tolerated six-, five-, and three-membered cyclic anhydrides in the presence of catalyst **II**. Various anhydrides reacted readily with nitroallylic alcohol **2a** to provide the corresponding hemiesters in high chemical yields with high levels of enantioselectivity (**3j**–**l**, 93–95% ee).

Preparing both enantiomeric products without resorting to the antipodal catalyst is synthetically attractive. The use of the same chirality of amino cinchonidine catalyst **III** (as to **II**) to obtain a functionalized hemiester with opposite stereochemistry is of worth noting (Table 1). Desymmetrization of various cyclic *meso*-anhydrides with nitroallylic alcohol **2a** in the presence of catalyst **III** yields the enantiomeric hemiesters (Fig. 4, ent-**3a**, ent-**3e**, ent-**3f**, and ent-**3j**–**l**) with decreased stereoselectivity. The relative weak interaction between the amino group and nitro functionality might account for the low reactivity, which the reaction required to proceed at ambient temperature. Two working mechanisms that involve general base catalysis[17] and nucleophilic catalysis[24] have been proposed for the cyclic *meso*-anhydride ring opening.[25]

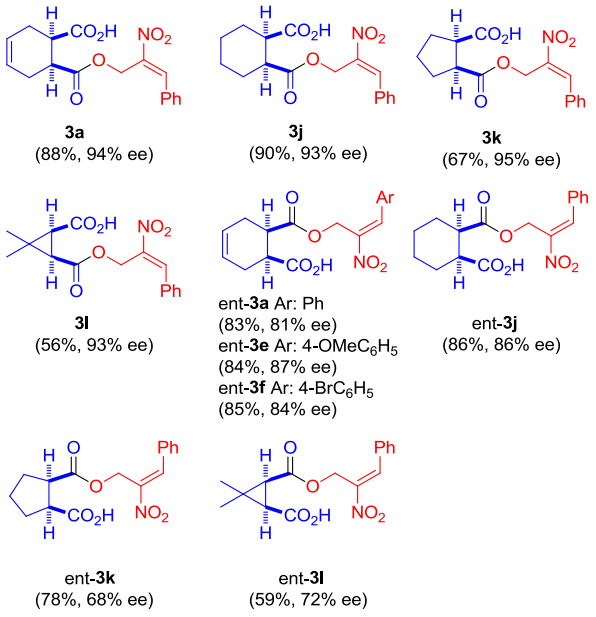


Fig. 4. Examples of various nitroallylic alcohol **2a**, **2e**, and **2f** react with different cyclic anhydrides **1j**–**l** mediated by catalysts **II** and **III**, respectively.

Although the mechanism of the current work remains to be clarified, a plausible reaction mode for the formation of hemiesters was proposed. As illustrated in Fig. 5, hydrogen bonds were formed between the thiourea moiety in organocatalyst **II** and the nitro group in the nucleophile. The orientation of the six-membered carbocycle in **1a** toward the bicyclic skeleton in catalyst **II** might cause steric repulsion. The formation of a desymmetrized product (1*R*,6S) from the transition structure TS-II is energetically more favorable than the structure of TS-I. The oxyanion that was generated was stabilized by the protonated tertiary amino group in catalyst **II**.

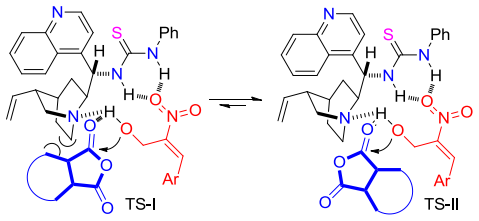


Fig. 5. Plausible reaction mechanism.

3. Conclusions

In conclusion, we demonstrated a practical desymmetrization reaction catalyzed by using *cinchona* alkaloid derived thiourea organocatalyst **II**. A wide range of nitroallylic alcohols **2a**–**i** were used for the asymmetric ring opening of cyclic *meso*-anhydrides. The products were obtained in high chemical yields (72–88%) with high to excellent enantioselectivity (81–99% ee) under optimized reaction conditions. The activation of the nitro group in the nucleophilic alcohols by the thiourea moiety is essential. In particular, activation of the nitroallylic alcohols with the amino catalyst (**III**) yields enantiomeric hemiesters with reasonable to high stereoselectivity (68–87% ee). The use of *cinchona* alkaloids and their derivatives as catalysts in organocatalytic reactions is currently under investigation.

4. Experimental

4.1. General remarks

Chemicals and solvents were purchased from commercial suppliers and used as received. The cyclic *meso*-anhydrides were purchased from Sigma–Aldrich and used as received. IR spectra were recorded with a Perkin–Elmer 500 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz), Bruker Avance 500 (500 MHz), and Bruker Avance III HD 600 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (TMS, δ 0.00), carbon ($CDCl_3$, δ 77.0); proton (MeOH-d_4, δ 4.87), carbon (MeOH-d_4, δ 49.1); proton (DMSO-d_6, δ 2.50), carbon (DMSO-d_6, δ 39.5). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiple), dd (doublet of doublet), br. s (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained with a JEOL, JMS-700, Japan or Waters, LCT, UK spectrometer. The X-ray diffraction measurements were carried out at 200 K with a KAPPA APEX II CCD area detector system equipped with a graphite monochromator and a Mo-$K\alpha$ fine-focus sealed tube (k=0.71073 Å). Merck precoated TLC plates (Merck 60 F254) were used for thin layer chromatography, and compounds were visualized under UV light at 254 nm. Solutions were evaporated to dryness under reduced pressure with a rotary evaporator, and the residues were purified by flash column chromatography on silica gel (230–400 mesh) with the indicated eluents. The enantiomeric excess value for a product was determined by chiral-phase HPLC analysis.

4.2. Typical reaction procedure

To a solution of (*E*)-2-nitro-3-phenylprop-2-en-1-ol **2a** (30 mg, 0.16 mmol) and 1-phenyl-3-((*S*)-quinolin-4-yl((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)thiourea **II** (7.1 mg, 0.01 mmol) in anhydrous toluene (0.80 mL) was added cyclic *meso* anhydride **1a** (50.8 mg, 0.33 mmol) in one portion at −20 °C. The reaction mixture was stirred at −20 °C for the needed time period. The reaction was monitored by TLC analysis and quenched with H_2O (5 mL). The mixture was extracted with CH_2Cl_2 (10 mL) and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (ethyl acetate/hexanes=1:3) afforded the desired adducts **3a**–**i**.

*4.2.1. (1R,6S)-6-((((E)-2-Nitro-3-phenylallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3a**).* Colorless oil. Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.35–2.42 (m, 2H), 2.56–2.62 (m, 2H), 3.10–3.16 (m, 2H), 5.17–5.25 (m, 2H), 5.70 (s, 2H), 7.42–7.48 (m, 5H), 8.34 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.6, 25.6, 39.5, 39.6, 58.3, 125.0, 125.1, 129.3, 130.1, 130.91, 131.3, 140.2, 145.0, 172.4, 178.9 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3030, 2977, 2954, 2926, 1736, 1702, 1527, 1447, 1329 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{17}NO_6$ $[M+Na]^+$ 354.0954, found 354.0945; The ee value of **3a** was 94%, t_R (minor)=25.8 min, t_R (major)=27.0 min; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.2. (1R,6S)-6-((((E)-3-(2-Chlorophenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3b**).* Greenish solid. Yield: 81%; mp 68.5–69.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.37–2.41 (m, 2H), 2.55–2.60 (m, 2H), 3.05–3.22 (m, 2H), 5.09–5.11 (m, 2H), 5.69 (s, 2H), 7.26–7.35 (m, 2H), 7.40–7.49 (m, 2H), 8.47 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.5, 39.3, 39.6, 58.0, 124.9, 125.0, 127.5, 129.8, 130.0, 130.3, 132.1, 135.1, 137.0, 146.2, 172.2, 179.7 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3022, 2923, 2839, 1740, 1706, 1527, 1436, 1340 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{16}ClNO_6$ $[M+Na]^+$ 388.0564, found 388.0564; $[M+2+Na]^+$ 390.0534, found 390.0578; The ee value of **3b** was 99%, t_R (major)=49.1 min, t_R (minor)=58.0 min; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 7% ^{i}PrOH/hexanes, flow rate=0.5 mL/min).

4.2.3. Crystal structure data of 3b at 200 K. $C_{17}H_{16}ClNO_6$, M=365.76 g mol^{-1}; tetragonal, point group I 41/a, bond precision: C–C=0.0099 Å, a=26.779(13), b=26.779(13), c=9.116(4), α=90, β=90, γ=90, V=6537(5) Å^3, F(000)=3040, λ (Mo-$K\alpha$)=0.71073 Å, D=1.487 cm^{-3}, Nref=2872, R (reflections)=0.0836(1076), wR_2 (reflections)=0.2096(2872) for all data.

*4.2.4. (1R,6S)-6-((((E)-3-(3-Methoxyphenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3c**).* Colorless oil. Yield: 77%; ^{1}H NMR (400 MHz, MeOD): δ=2.27–2.32 (m, 2H), 2.44–2.51 (m, 2H), 2.97–3.24 (m, 2H), 3.76 (s, 3H), 5.10–5.16 (m, 2H), 5.59 (s, 2H), 6.99–7.06 (m, 3H), 7.33 (t, J=8.0 Hz, 1H), 8.29 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=27.0, 27.1, 40.9, 56.2, 59.4, 116.2, 118.5, 123.8, 126.1, 126.6, 131.5, 134.0, 141.0, 147.0, 161.7, 174.6, 176.9 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=2916, 2854, 1733, 1706, 1691, 1600, 1523, 1451, 1451 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{19}NO_7$ $[M]^+$ 361.1162, found 361.1164; The ee value of **3c** was 91%, t_R (minor)=40.6 min, t_R (major)=43.2; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.5. (1R,6S)-6-((((E)-3-(3-Chlorophenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3d**).* Colorless oil. Yield: 80%; ^{1}H NMR (400 MHz, MeOD): δ=2.33–2.39 (m, 2H), 2.40–2.58 (m, 2H), 3.07–3.31 (m, 2H), 5.16–5.22 (m, 2H), 5.67 (s, 2H), 7.48–7.51

(m, 3H), 7.51–7.60 (m, 1H), 8.35 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=26.9, 27.13, 40.9, 41.0, 59.1, 126.1, 126.6, 129.5, 131.2, 131.9, 132.1, 134.8, 136.3, 139.3, 148.0, 174.4, 176.9 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3330, 2938, 2908, 1706, 1649, 1558, 1527, 1337 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{16}ClNO_6$ $[M+Na]^+$ 388.0564, found 388.0569; $[M+2+Na]^+$ 390.0534, found 390.0576; The ee value of **3d** was 84%, t_R (minor)=31.1 min, t_R (major)=37.1 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.6. (1R,6S)-6-((((E)-3-(4-Methoxyphenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3e**).* Colorless oil. Yield: 85%; ^{1}H NMR (400 MHz, DMSO): δ=2.25–2.34 (m, 2H), 2.36–2.50 (m, 2H), 2.99–3.05 (m, 2H), 3.82 (s, 3H), 5.07–5.19 (m, 2H), 5.61 (s, 2H), 7.07 (d, *J*=8.4 Hz, 2H), 7.59 (d, *J*=8.4 Hz, 2H), 8.38 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO): δ=25.8, 26.4, 56.2, 58.9, 115.5, 123.7, 125.5, 126.0, 133.7, 140.7, 143.4, 162.8, 173.4, 175.0 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3434, 2257, 2129, 1737, 1654, 1603, 1523, 1508 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{19}NO_7$ $[M-H]^-$ 360.1084, found 360.1092; The ee value of **3e** was 91%, t_R (minor)=40.5 min, t_R (major)=46.0; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.7. (1R,6S)-6-((((E)-3-(4-Bromophenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3f**).* Colorless oil. Yield: 84%; ^{1}H NMR (400 MHz, MeOD): δ=2.34–2.39 (m, 2H), 2.40–2.58 (m, 2H), 3.08–3.31 (m, 2H), 5.14–5.23 (m, 2H), 5.67 (s, 2H), 7.48 (d, *J*=8.4 Hz, 2H), 7.68 (d, *J*=6.4 Hz, 2H), 8.36 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=26.7, 27.3, 40.9, 41.0, 59.3, 126.1, 126.5, 126.9, 131.9, 133.2, 133.7, 139.9, 147.3, 174.6, 177.0 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3434, 3030, 2977, 2923, 2826, 1738, 1706, 1655, 1587, 1529, 1409 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{16}BrNO_6$ $[M+Na]^+$ 432.0059, found 432.0052; $[M+2+Na]^+$ 434.0038, found 434.0023; The ee value of **3f** was 92%, t_R (minor)=31.7 min, t_R (major)=36.9 min; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.8. (1R,6S)-6-((((E)-2-Nitro-3-(p-tolyl)allyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3g**).* Colorless oil. Yield: 72%; ^{1}H NMR (400 MHz, MeOD): δ=2.33–2.36 (m, 2H), 2.40 (s, 3H), 2.51–2.60 (m, 2H), 3.08–3.31 (m, 2H), 5.17–5.26 (m, 2H), 5.67 (s, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 7.46 (d, *J*=8.0 Hz, 2H), 8.38 (s, 1H) ppm; ^{13}C NMR (125 MHz, MeOD): δ=21.7, 26.8, 27.2, 40.8, 40.9, 59.6, 126.1, 126.5, 129.8, 131.1, 131.8, 141.3, 143.6, 145.9, 174.6, 176.8 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3424, 2961, 2862, 2076, 1729, 1653, 1638, 1527, 1512 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{19}NO_6$ $[M+Na]^+$ 368.1110, found 368.1108; The ee value of **3g** was 92%, t_R (minor)=17.5 min, t_R (major)=18.9 min; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.9. (1R,6S)-6-((((E)-3-(4-Fluorophenyl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3h**).* Colorless oil. Yield: 85%; ^{1}H NMR (400 MHz, MeOD): δ=2.34–2.40 (m, 2H), 2.41–2.59 (m, 2H), 3.10–3.31 (m, 2H), 5.16–5.24 (m, 2H), 5.67 (s, 2H), 7.25 (t, *J*=8.8 Hz, 2H), 7.61–7.65 (m, 2H), 8.40 (s, 1H) ppm; ^{13}C NMR (150 MHz, MeOD): δ=25.2, 25.7, 39.3, 39.4, 57.8, 116.0, 124.6, 125.0, 127.6, 132.7, 138.5, 145.1, 164.4, 173.1, 175.4 ppm; ^{19}F NMR (564 MHz, MeOD): δ=−111.14 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3434, 3030, 2961, 2908, 2854, 2083, 1737, 1702, 1654, 1603, 1528, 1508 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{16}FNO_6$ $[M+Na]^+$ 372.0859, found 372.0861; The ee value of **3h** was 91%, t_R (minor)=32.4 min, t_R (major)=34.3; HPLC analysis (Chiralcel OJ-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.10. (1R,6S)-6-((((E)-3-(Furan-2-yl)-2-nitroallyl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**3i**).* Colorless oil. Yield: 84%; ^{1}H NMR (400 MHz, MeOD): δ=2.29–2.36 (m, 2H), 2.47–2.54 (m, 2H), 3.00–3.09 (m, 1H), 3.30–3.31 (m, 1H), 5.40–5.53 (m, 2H), 5.62 (s, 2H), 6.70 (t, *J*=2.0 Hz, 1H), 7.17 (d, *J*=3.2 Hz, 1H), 7.86 (d, *J*=1.2 Hz, 1H), 8.12 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=27.0, 27.0, 40.9, 59.5, 114.6, 124.0, 126.0, 126.3, 126.5, 142.7, 148.4, 150.0, 174.8, 176.9 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3439, 2923, 2865, 1733, 1699, 1647, 1512, 1436 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{15}H_{15}NO_6$ $[M+Na]^+$ 344.0746, found 344.0749; The ee value of **3i** was 81%, t_R (major)=33.5 min, t_R (minor)=38.6 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.11. (1R,2S)-2-((((E)-2-Nitro-3-phenylallyl)oxy)carbonyl)cyclohexanecarboxylic acid (**3j**).* Colorless oil. Yield: 90%; ^{1}H NMR (400 MHz, MeOD): δ=1.41–1.54 (m, 4H), 1.74–1.85 (m, 2H), 1.93–2.08 (m, 2H), 2.86–2.92 (m, 2H), 5.14 (d, *J*=13.2 Hz, 1H), 5.25 (d, *J*=12.8 Hz, 1H), 7.49–7.58 (m, 5H), 8.40 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=23.4, 23.5, 25.7, 26.2, 42.2, 42.3, 57.7, 128.9, 130.0, 130.8, 131.2, 139.5, 145.4, 173.5, 175.7 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=2938, 2862, 1736, 1702, 1655, 1599, 1526, 1451 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{19}NO_6$ $[M+Na]^+$ 356.1110, found 356.1100; The ee value of **3j** was 93%, t_R (major)=23.1 min, t_R (minor)=27.1 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.12. (1R,2S)-2-((((E)-2-Nitro-3-phenylallyl)oxy)carbonyl)cyclopentanecarboxylic acid (**3k**).* Colorless oil. Yield: 67%; ^{1}H NMR (400 MHz, MeOD): δ=1.63–1.74 (m, 1H), 1.79–1.99 (m, 1H), 2.00–2.05 (m, 4H), 3.11–3.15 (m, 2H), 5.12 (d, *J*=12.8 Hz, 1H), 5.27 (d, *J*=13.2 Hz, 1H), 7.50–7.51 (m, 2H), 7.52–7.59 (m, 3H), 8.40 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=23.2, 28.1, 28.7, 46.3, 57.7, 78.1, 128.9, 130.1, 130.8, 131.2, 139.5, 145.4, 173.8, 176.2 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3431, 2969, 2877, 2648, 2549, 1739, 1702, 1649, 1527 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{17}NO_6$ $[M+Na]^+$ 342.0954, found 342.0947; The ee value of **3k** was 95%, t_R (major)=28.0 min, t_R (minor)=29.2 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.13. (1S,3R)-2,2-Dimethyl-3-((((E)-2-nitro-3-phenylallyl)oxy)carbonyl)cyclopropanecarboxylic acid (**3l**).* Colorless oil. Yield: 56%; ^{1}H NMR (400 MHz, MeOD): δ=1.23 (s, 3H), 1.41 (s, 3H), 1.98–2.05 (m, 2H), 5.11 (d, *J*=13.2 Hz, 1H), 5.31 (d, *J*=13.2 Hz, 1H), 7.50–7.51 (m, 3H), 7.58–7.60 (m, 2H), 8.40 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=14.6, 25.7, 26.5, 31.2, 31.8, 57.9, 128.9, 130.1, 130.8, 131.2, 139.5, 168.8, 171.2 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3062, 3027, 2964, 2928, 2744, 2679, 1783, 1743, 1704, 1654, 1600, 1576, 1526 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{17}NO_6$ $[M+Na]^+$ 342.0954, found 342.0955; The ee value of **3l** was 93%, t_R (minor)=21.6 min, t_R (major)=23.0 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.14. (1R,6S)-6-((Allyloxy)carbonyl)cyclohex-3-enecarboxylic acid (**4a**).* Colorless oil. Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.34–2.40 (m, 2H), 2.55–2.64 (m, 2H), 3.08–3.10 (m, 2H), 4.56–4.65 (s, 2H), 5.20–5.33 (m, 2H), 5.66–5.69 (m, 2H), 5.72–5.94 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.6, 25.8, 39.5, 39.6, 65.4, 118.1, 125.1, 125.1, 132.0, 172.9, 178.3 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3445, 3031, 2641, 1731, 1713, 1421 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{11}H_{14}O_4$ $[M+Na]^+$ 233.0790 found 233.0786; The ee value of **4a** was 68%, t_R (minor)=16.4 min, t_R (major)=20.2; HPLC analysis (Chiralcel AS-H, λ=220 nm, 10% ^{i}PrOH/hexanes, flow rate=0.5 mL/min).

*4.2.15. (1R,6S)-6-((Cinnamyloxy)carbonyl)cyclohex-3-enecarboxylic acid (**4b**).* Colorless oil. Yield: 77%; ^{1}H NMR (400 MHz, MeOD): δ=2.23–2.40 (m, 2H), 2.54–2.60 (m, 2H), 3.08–3.11 (m, 2H), 4.73–4.75 (dd, *J*=6.0, 1.2 Hz, 2H), 5.67 (s, 2H), 6.26 (d, *J*=12.0 Hz, 1H), 6.27–6.34 (m, 1H), 7.21–7.23 (m, 2H), 7.25–7.28 (m, 1H), 7.30–7.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=27.0, 27.2,

40.9, 41.1, 66.3, 124.6, 126.3, 126.5, 127.8, 129.1, 129.8, 134.8, 138.1, 175.2, 177.2 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3029, 2921, 2854, 2349, 1861, 1842, 1777, 1729, 1708 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{18}O_4$ $[M-H]^-$ 285.1127, found 285.1124; The ee value of **4b** was 58%, t_R (minor)=15.2 min, t_R (major)=16.6 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.16. (1R,6S)-6-(((6-Oxocyclohex-1-en-1-yl)methoxy)carbonyl)cyclohex-3-enecarboxylic acid (**4c**).* Colorless oil. Yield: 64%; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.99–2.04 (m, 2H), 2.32–2.48 (m, 6H), 2.53–2.61 (m, 2H), 3.06–3.08 (m, 2H), 4.77–4.78 (m, 2H), 5.68 (s, 2H), 7.00 (t, *J*=4.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.6, 25.6, 25.7, 38.0, 39.3, 39.5, 39.6, 61.6, 125.0, 125.1, 134.3, 148.6, 172.8, 178.6, 198.1 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3420, 3037, 2918, 2852, 1772, 1736, 1717, 1697, 1646, 1636, 1559, 1539 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{15}H_{18}O_5$ $[M+Na]^+$ 301.1052, found 301.1044; The ee value of **4c** was 42%, t_R (minor)=19.1 min, t_R (major)=21.8 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

*4.2.17. (1R,6S)-6-((((S,E)-1-Ethoxy-3-nitro-1-oxo-4-phenylbut-3-en-2-yl)oxy)carbonyl)cyclohex-3-enecarboxylic acid (**4d**).* Colorless oil. Yield: 48%; ^{1}H NMR (400 MHz, MeOD): δ=1.20 (t, *J*=7.2 Hz, 3H), 2.37–2.38 (m, 2H), 2.42–2.66 (m, 2H), 3.08–3.11 (m, 1H), 3.18–3.31 (m, 1H), 4.15–4.21 (m, 2H), 5.61–5.70 (m, 2H), 6.52 (s, 1H), 7.47–7.53 (m, 5H), 8.50 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD): δ=14.4, 26.9, 27.2, 40.8, 40.9, 63.7, 67.4, 126.1, 126.7, 130.5, 131.2, 131.2, 132.6, 142.3, 146.4, 167.6, 173.5, 176.7 ppm; IR (CH_2Cl_2): $\tilde{\nu}$=3431, 3055, 3033, 2590, 2059, 1767, 1738, 1705, 1653 cm^{-1}; HRMS (ESI-TOF): *m*/*z* calcd for $C_{20}H_{21}NO_8$ $[M+Na]^+$, 426.1165, found 426.1171; The ee value of **4d** was 93%, t_R (major)=18.9 min, t_R (minor)=34.8 min; HPLC analysis (Chiralcel AD-H, λ=254 nm, 10% ^{i}PrOH/hexanes, flow rate=1.0 mL/min).

4.3. General procedure for the synthesis of enantiomeric products ent-3

To a solution of *meso*-anhydride **1a** (50.8 mg, 0.33 mmol) in anhydrous toluene (0.80 mL) was sequentially added (*E*)-2-nitro-3-phenylprop-2-en-1-ol **2a** (30 mg, 0.16 mmol) and (*S*)-quinolin-4-yl((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanamine **III** (4.9 mg, 0.01 mmol). The reaction vial was then capped, and the reaction mixture was stirred at ambient temperature for 24 h. The reaction was quenched with H_2O (5 mL) and extracted with EtOAc (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (ethyl acetate/hexanes=1:3) afforded the desired ent-products: ent-**3a**, ent-**3e**, ent-**3f**, and ent-**3j**–**l**.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.10.008.

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