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Organocatalytic Asymmetric Conjugate Addition and Cascade Acyl Transfer Reaction of α-Nitroketones

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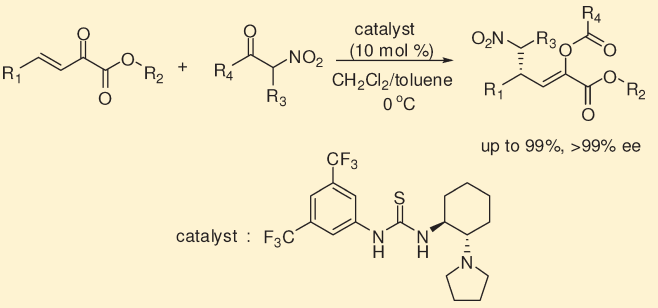
Supporting Information

ABSTRACT: Organocatalytic asymmetric conjugate addition of α-nitroketones to β,γ-unsaturated α-keto esters has been developed. A pyrrolidine-based thiourea−tertiary amine was identified as the best catalyst. The reaction was found to proceed via cascade conjugate addition and acyl transfer reaction. A number of α-nitroketones and β,γ-unsaturated α-keto esters were examined in this transformation. 5-Nitro-2-acyloxypent-2-enoates were obtained in good yields (up to 99%) and enantioselectivities (up to 99% ee). The products could be hydrolyzed to provide 5-nitro-2-oxopentanoates, which are not available from the direct addition of nitromethane to β,γ-unsaturated α-keto esters.



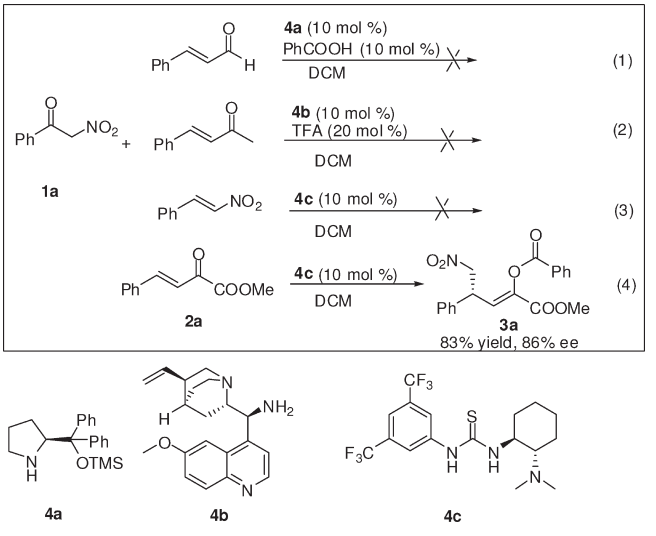
INTRODUCTION

The conjugate addition of stabilized carbon anions to Michael acceptors is one of the most useful carbon−carbon bond formation reactions in organic synthesis.[1] In recent years, organocatalytic asymmetric conjugate additions have proved to be powerful tools for the synthesis of chiral compounds.[2,3] 1,3-Dicarbonyl compounds, nitroalkanes, and other carbon anion precursors have been applied as the nucleophilic reagents with great successes. α-Nitroketones are active nucleophilic reagents with very acidic α-hydrogen atoms ($pK_a \approx 4.0$). α-Nitroketones are readily deprotonated by many weak bases to generate enolate anions. In addition, α-nitroketones can be converted into a number of useful functionalized compounds via different derivation pathways.[4,5] Recently we have developed a series of organocatalytic conjugate additions with various nucleophiles.[6] We speculate that α-nitroketones are valuable nucleophiles for organocatalytic asymmetric conjugate additions. To the best of our knowledge, the application of α-nitroketones in organocatalytic reactions has not yet been explored.[7] In this paper, we report the organocatalytic asymmetric conjugate addition of α-nitroketones to β,γ-unsaturated α-keto esters. The reaction provided 5-nitro-2-acyloxypent-2-enoates in good yields and with excellent enantioselectivities via cascade conjugate addition and acyl transfer reaction.

RESULTS AND DISCUSSION

Initially we examined the reaction of 2-nitro-1-phenylethanone **1a** with several typical Michael acceptors, including cinnamaldehyde, benzylidene acetone, and β-nitrostyrene. On the basis of previous studies, appropriate organocatalysts were selected for each reaction and the results are summarized in Scheme 1. Unfortunately, none of the three reactions was successful (Scheme 1, eqs 1−3). The expected conjugate addition products could not be obtained in substantial yields. To our delight, the reaction of **1a** with β,γ-unsaturated α-keto ester **2a** provided a product in good yield and enantioselectivity when Takemoto's thiourea−tertiary

Scheme 1. Organocatalytic Conjugate Addition of α-Nitroketones to Michael Acceptors



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Scheme 2. Organocatalysts 4d−4j

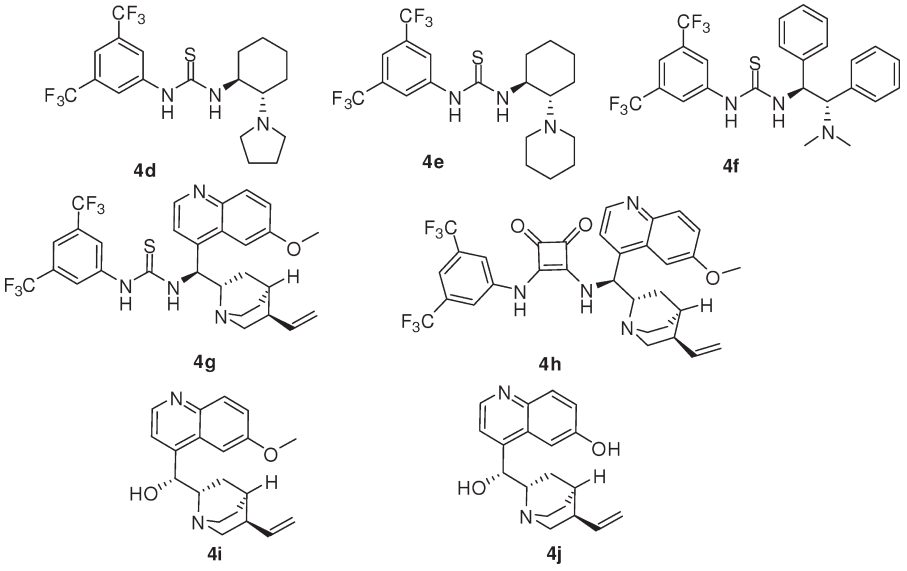
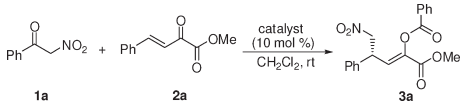


Table 1. Screening of Catalysts[a]



entry	catalyst	time (h)	yield[b] (%)	ee[c] (%)
1	**4c**	8	83	86
2	**4d**	4	87	90
3	**4e**	72	trace	nd[d]
4	**4f**	24	37	79
5	**4g**	24	58	76
6	**4h**	72	trace	nd[d]
7	**4i**	24	70	25
8	**4j**	24	65	30

[a] The reactions were carried out with **1a** (0.100 mmol), **2a** (0.110 mmol), and catalyst (0.010 mmol) in dichloromethane (0.5 mL) at room temperature. [b] Isolated yields. [c] Determined by chiral HPLC. [d] Not determined.

amine (**4c**) was used as the catalyst (Scheme 1, eq 4).[8] The product was identified as (*Z*)-1-methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl benzoate **3a** by ^{1}H and ^{13}C NMR analysis. The normal conjugate addition product was not observed in the reaction.

In order to improve the enantioselectivity of the reaction, a series of organocatalysts **4d**−**4i** were screened (Scheme 2). The results are summarized in Table 1. Pyrrolidine-based thiourea−tertiary amine **4d** provided better yield (87%) and enantioselectivity (90% ee) (Table 1, entry 2).[6d] Interestingly, the more sterically demanding catalyst **4e** was found to be completely inactive for the reaction (Table 1, entry 3). In our previous study, **4e** was the most efficient catalyst for asymmetric conjugate addition of malononitrile to conformationally restricted dienones.[6b] The result is contrary to the recent report by Wang and coworkers,[7] where a piperidine-based indanyl thiourea−tertiary amine was found to be the most efficient catalyst. The small structural difference between **4d** and **4e** seems to result in a significant change of their catalytic activities. 1,2-Diphenylethane-1,2-diamine-derived catalyst **4f** gave poor yield and moderate enantioselectivity (Table 1, entry 4). 9-Amino-9-deoxyepiquinine-derived thiourea **4g** also provided inferior yield and enantioselectivity (Table 1, entry 5). Chiral squaramide **4h** was completely inefficient (Table 1, entry 6). We also extended our screening to quinine **4i** and 6-demethyl quinine **4j**, but only low enantioselectivities were obtained (Table 1, entries 7 and 8).

Furthermore the effects of reaction solvent and temperature were examined and the results are summarized in Table 2. Toluene provided a similar result as dichloromethane (Table 2, entries 1 and 2). Chloroform, 1,2-dichloroethane, ether, tetrahydrofuran (THF), dioxane, and ethyl acetate afforded **3a** with good enantioselectivities but in lower yields (Table 2, entries 3−8). More polar solvents, such as acetonitrile, methanol, *N*, *N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were detrimental for the enantioselectivity (Table 2, entries 9−12). When the reaction was carried out at 0 °C in dichloromethane or toluene, the enantioselectivity was improved slightly but at the expense of the yield (Table 2, entries 13 and 14). Optimal result was achieved in a mixed solvent of dichloromethane/toluene (v/v = 1/1) (Table 2, entry 15). Further decrease in temperature did not improve the enantioselectivity but rather decreased the yield substantially (Table 2, entry 16).

With the optimal reaction conditions in hand, the scope of α-nitroketones was investigated and the results are summarized in Table 3. 1-(4-Methoxyphenyl)-2-nitroethanone **1c** provided better yield and enantioselectivity than **1a** (Table 3, entry 3). When 4-halogen substitutions were introduced, the enantioselectivities decreased in a sequence of F > Cl > Br (Table 3, entries 4−6). 4-Nitro substitution resulted in a significant loss of the enantioselectivity (Table 3, entry 7). 3-Chloro substitution was found to have slight effect on the enantioselectivity (Table 3, entry 8). 3,5-Dimethoxy substitution afforded better yield and similar enantioselectivity (Table 3, entry 9). Best yield and enantioselectivity were achieved with 2-methoxy-substituted α-nitroketone **1j** (Table 3, entry 10). Heteroaryl α-nitroketone **1k** provided the product with excellent enantioselectivity but in

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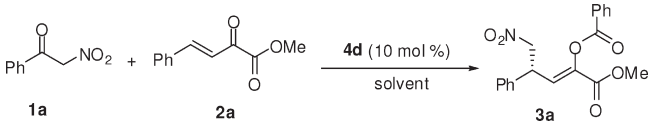
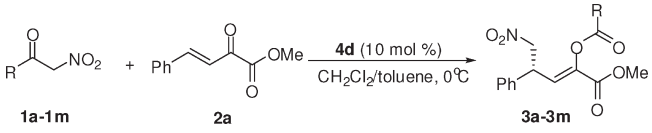
Table 2. Optimization of Reaction Conditions[a]



entry	solvent	T (°C)	time (h)	yield[b] (%)	ee[c] (%)
1	dichloromethane	rt	4	87	90
2	toluene	rt	12	86	89
3	chloroform	rt	24	54	83
4	1,2-dichloroethane	rt	24	56	87
5	ether	rt	24	59	88
6	THF	rt	24	59	86
7	dioxane	rt	24	45	85
8	ethyl acetate	rt	24	65	86
9	acetonitrile	rt	24	60	42
10	methanol	rt	24	99	21
11	DMF	rt	24	73	8
12	DMSO	rt	24	54	0
13	dichloromethane	0	12	82	92
14	toluene	0	48	79	94
15	dichloromethane/toluene (1/1)	0	24	82	93
16	dichloromethane/toluene (1/1)	−20	>96	66	93

[a] The reactions were carried out with **1a** (0.100 mmol), **2a** (0.110 mmol), and **4d** (0.010 mmol) in solvent (0.5 mL). [b] Isolated yields. [c] Determined by chiral HPLC.

Table 3. Conjugate Addition of α-Nitroketones 1a−1m to 2a[a]

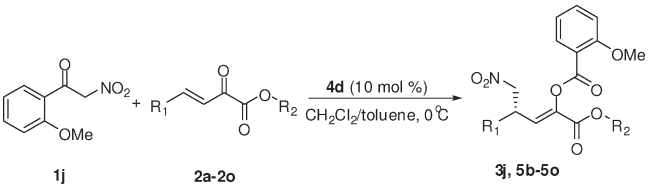


entry	reactant 1	R	time (h)	product	yield[b] (%)	ee[c] (%)
1	**1a**	C_6H_5	24	**3a**	81	93
2	**1b**	4-Me-C_6H_4	36	**3b**	87	88
3	**1c**	4-MeO-C_6H_4	36	**3c**	86	95
4	**1d**	4-F-C_6H_4	24	**3d**	82	93
5	**1e**	4-Cl-C_6H_4	24	**3e**	83	86
6	**1f**	4-Br-C_6H_4	24	**3f**	96	80
7	**1g**	4-NO_2-C_6H_4	24	**3g**	82	62
8	**1h**	3-Cl-C_6H_4	24	**3h**	81	91
9	**1i**	3,5-diMeO-C_6H_4	48	**3i**	92	90
10	**1j**	2-MeO-C_6H_4	36	**3j**	94	95
11	**1k**	2-thiophenyl	48	**3k**	55	94
12	**1l**	*i*-Pr	24	**3l**	76	79
13	**1m**	*c*-hex	24	**3m**	66	79

[a] The reactions were carried out with **1a−1m** (0.100 mmol), **2a** (0.110 mmol) and **4d** (0.010 mmol) in toluene/CH_2Cl_2 (v/v = 1/1, 0.5 mL) at 0 °C. [b] Isolated yields. [c] Determined by chiral HPLC.

moderate yield (Table 3, entry 11). Moderate yields and enantioselectivities were obtained for 1-alkyl α-nitroketones **1l** and **1m** (Table 3, entries 12 and 13).

Table 4. Conjugate Addition of 1j to β,γ-Unsaturated α-Keto Esters 2a−2o[a]



entry	reactant 2	R_1	R_2	time (h)	product	yield[b] (%)	ee[c] (%)
1	**2a**	C_6H_5	CH_3	36	**3j**	94	95
2	**2b**	4-Me-C_6H_4	CH_3	36	**5b**	92	97
3	**2c**	4-MeO-C_6H_4	CH_3	48	**5c**	90	95
4	**2d**	4-F-C_6H_4	CH_3	24	**5d**	86	94
5	**2e**	4-Cl-C_6H_4	CH_3	24	**5e**	92	95
6	**2f**	4-Br-C_6H_4	CH_3	24	**5f**	96	95
7	**2g**	4-NO_2-C_6H_4	CH_3	36	**5g**	80	95
8	**2h**	2-F-C_6H_4	CH_3	36	**5h**	87	93
9	**2i**	3-Cl-C_6H_4	CH_3	24	**5i**	99	93
10	**2j**	2-thiophenyl	CH_3	36	**5j**	99	92
11	**2k**	C_6H_5	C_2H_5	36	**5k**	83	96
12	**2l**	C_6H_5	allyl	36	**5l**	85	96
13	**2m**	C_6H_5	*i*-Pr	36	**5m**	85	97
14	**2n**	*i*-Pr	C_2H_5	144	**5n**	85	91
15	**2o**	*c*-Hex	C_2H_5	192	**5o**	82	91

[a] The reactions were carried out with **1j** (0.100 mmol), **2a−2o** (0.110 mmol), and **4d** (0.010 mmol) in toluene/CH_2Cl_2 (v/v = 1/1, 0.5 mL) at 0 °C. [b] Isolated yields. [c] Determined by chiral HPLC.

A single crystal of product **3e** was obtained. Its absolute configuration (*4R*) and (*Z*)-geometry of β,γ-double bond were determined by X-ray diffraction analysis.[9,10] Other products were assigned as the same absolute configuration and (*Z*)-geometry analogously. The reaction of a series of β,γ-unsaturated α-keto esters with 1-(2-methoxyphenyl)-2-nitroethanone **1j** were examined and the results are summarized in Table 4. In general, good yields and excellent enantioselectivities were obtained for γ-aryl-β,γ-unsaturated α-keto esters (Table 4, entries 1−13). The substitutions at 4-phenyl with electron-donating or -withdrawing groups did not exert significant effect on the enantioselectivity. 4-Nitro-substituted substrate **2g** gave lower yield than 4-methoxy-substituted substrate **2c** (Table 4, entry 3 versus entry 7). γ-Heteroaryl-β,γ-unsaturated α-keto ester **2j** provided excellent yield and good enantioselectivity (Table 4, entry 10). The ester groups of β,γ-unsaturated α-keto esters showed negligible effect on the enantioselectivity, but ester groups bigger than methyl resulted in lower yields (Table 4, entries 11−13). γ-Alkyl-β,γ-unsaturated α-keto esters **2n** and **2o** were also applicable for the reaction. Although extended reaction time was required, good yields and enantioselectivities were still achieved (Table 4, entries 14 and 15).

The reaction of α-methyl- and α-ethyl-substituted α-nitroketones **1n** and **1o** with β,γ-unsaturated α-keto ester **2b** were also examined (Scheme 3). The products **3n** and **3o** were obtained with excellent enantioselectivities but in moderate yields and low diastereoselectivities. The bigger steric hindrance of **1n** and **1o** obviously decreases their reactivities.

The reaction is proposed to proceed through a stepwise mechanism (Scheme 4).[7] α-Nitroketone **1a** is deprotonated by

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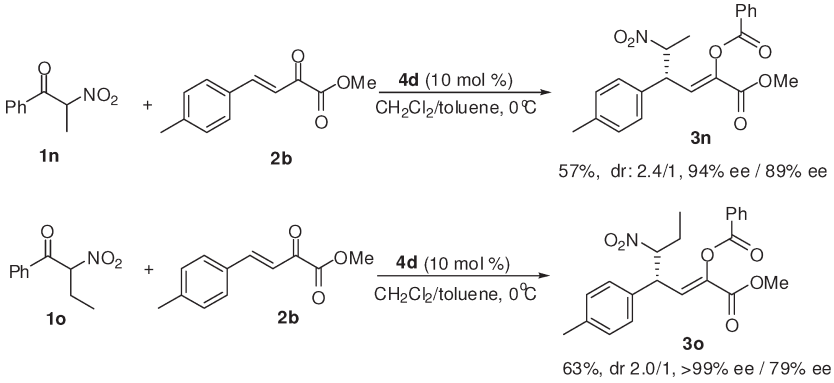
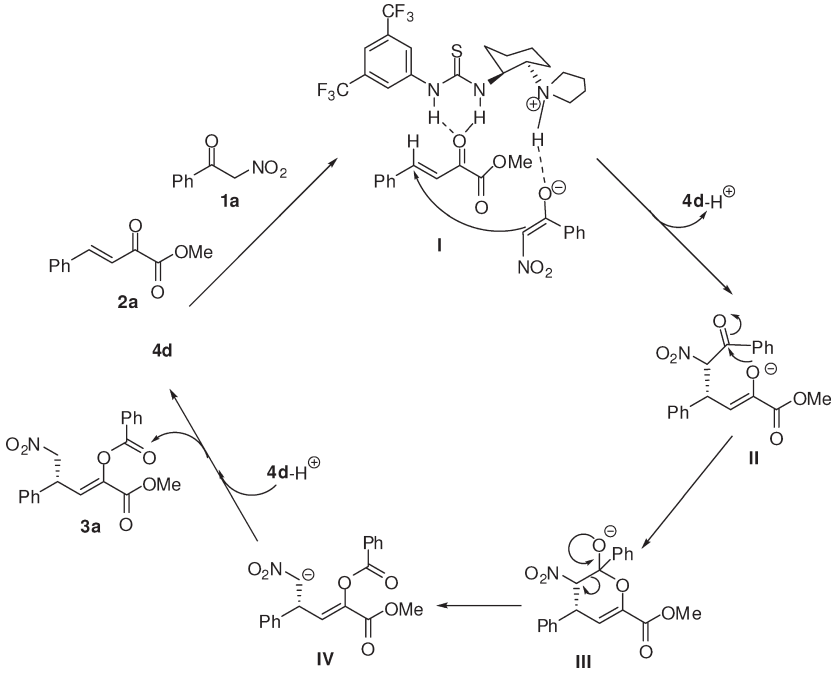
Scheme 3. Conjugate Addition of α-Alkyl-α-Nitroketones 1n and 1o to 2b



Scheme 4. Proposed Reaction Mechanism



the tertiary amine group of catalyst **4d.** The resulted ammonium cation generates a hydrogen bond with the nitro enolate. β,γ-Unsaturated α-keto ester **2a** is activated though the formation of hydrogen bonds with the thiourea group of **4d**. The attack of nitro enolate from the *re*-face of the double bond gives the intermediate **II**. The resulting enolate anion attacks the carbonyl group to give the cyclic intermediate **III.** The consequent C−C bond cleavage provides the nitro anion **IV**, which removes a proton from **4d**-H^+ to regenerate catalyst **4d** and provide product **3a**.[6c] The transformation of **II** to **III** is proposed to proceed very quickly, since no normal conjugate addition product is observed in the reaction. In addition, the formation of cyclic hemiketal intermediate **III** is supported by the fact that only (*Z*)-products were obtained in the reaction.

For a comparison, we examined **4d**-catalyzed addition of nitromethane to **2a** (Scheme 5, eq 1). Only a trace amount of double addition product **6** was obtained if 1 equiv of nitromethane was used. When 10 equiv of nitromethane was used, the reaction gave **6** (50% yield) and **7** (5% yield). The result is different from the previous report by Deng and co-workers.[11] 1, 2-Addition is preferential when γ-alkyl-β,γ-unsaturated α-keto ester and 6-demethylquinine-derived catalyst are used (Scheme 5, eq 2).

Product **3a** was hydrolyzed by concentrate H_2SO_4 in methanol. The resulting ketal intermediate was treated with trifluoroacetic acid (TFA) to give compound **8** in moderate yield (Scheme 6).[12] The enantiopurity of **3a** was kept during the elaboration. Since compound **8** could not be prepared directly from the conjugate addition of nitromethane to β,γ-unsaturated α-keto ester **2a**, α-nitroketone **1a** may be used as a surrogate of nitromethane for overcoming unfavorable chemoselectivity. Compound **8** was also treated under the standard reaction condition (catalyst **4d**, α-nitroketone **1a**, toluene/CH_2Cl_2, 0 °C) for 48 h. The formation of product **3a** was not observed by thin-layer chromatography or ^{1}H NMR analysis. The fact

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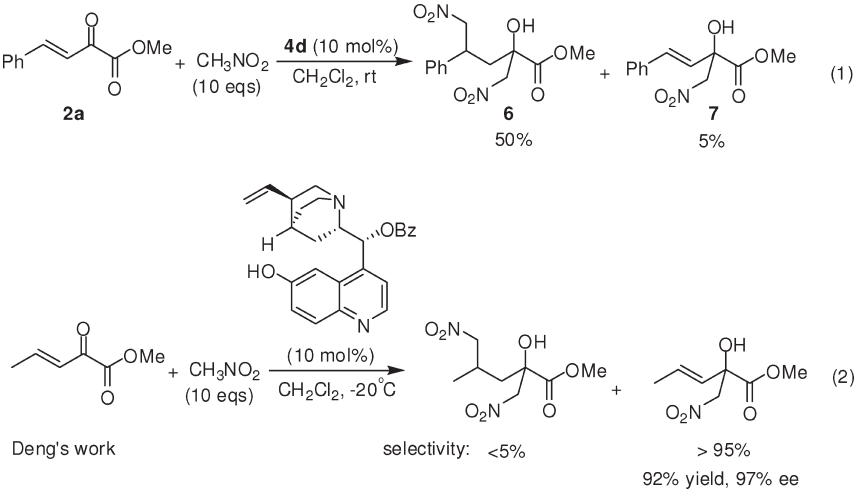
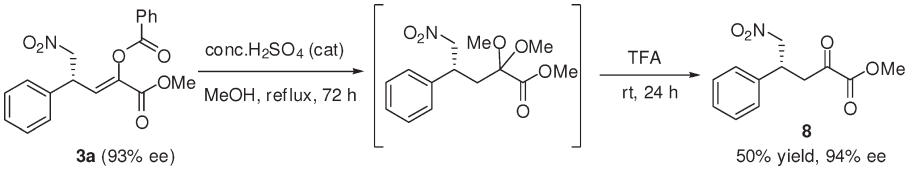
Scheme 5. Conjugate Addition of Nitromethane to β,γ-Unsaturated α-Keto Esters



Scheme 6. Hydrolysis of Product 3a



confirms that the cascade conjugate addition and acyl transfer steps are necessary for the generation of product **3a**.

CONCLUSIONS

In summary, we have developed an organocatalytic asymmetric conjugate addition of α-nitroketones to β,γ-unsaturated α-keto esters. The reaction proceeds via conjugate addition and consequent acyl transfer steps. A pyrrolidine-based thiourea–tertiary amine was identified as the best catalyst. A number of 5-nitro-2-acyloxypent-2-enoates were prepared in good yields and enantioselectivities. By comparison with the recent report of Wang and co-workers,[7] the present work offers several distinct improvements: (1) catalyst **4d** is more readily prepared from commercially available *trans*-cyclohexane-1,2-diamine, (2) wider scope of the substrates concerning both α-nitroketones and β,γ-unsaturated α-keto esters were examined (in particular, α-alkyl-α-nitroketones were found to provide excellent enantioselectivities); (3) two-step acidic hydrolysis of the products was developed to give 5-nitro-2-oxopentanoates in acceptable yield; and (4) the (*Z*)-configuration of β,γ-double bond in the products was reassigned.

EXPERIMENTAL SECTION

General Information. All solvents were used as commercial anhydrous grade without further purification. Flash column chromatography was carried out over silica gel (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0 ppm). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High-resolution mass spectra were obtained with a LCMS-IT-TOF mass spectrometer. Infrared (IR) peaks are represented as frequency of absorption (cm^{-1}). Enantiomeric excesses of the products were determined by HPLC on a Daicel Chiralpak IC column. α-Nitroketones **1a**–**1o** and β,γ-unsaturated α-keto esters **2a**–**2o** were prepared according to reported procedures.[13,14]

General Procedure for Conjugate Addition of α-Nitroketones to β,γ-Unsaturated α-Keto Esters. A mixture of **1a** (16.5 mg, 0.10 mmol), **2a** (22.8 mg, 0.12 mmol), and **4d** (4.4 mg, 0.01 mmol) in CH_2Cl_2/toluene (v/v = 1/1, 0.5 mL) was stirred for 24 h at 0 °C. After evaporation of the solvent under vacuum, the residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate = 10/1) to give **3a** as a white solid.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl Benzoate (**3a**).* White solid (28.7 mg, yield 81%), mp 67–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.09 (m, 2H), 7.72–7.62 (m, 1H), 7.57–7.46 (m, 2H), 7.42–7.14 (m, 5H), 6.78 (d, J = 9.6 Hz, 1H), 4.73 (d, J = 7.8 Hz, 2H), 4.64–4.55 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.7, 140.1, 136.5, 134.1, 130.4, 129.4, 128.7, 128.3, 128.1, 127.7, 127.4, 78.4, 52.7, 41.1; IR (thin film) ν/cm^{-1} 1739, 1722, 1554, 1294, 1258, 1055, 712; HRMS (ESI) calcd for $C_{19}H_{17}NO_6$ $(M - H)^-$ 354.0978, found 354.0975; $[\alpha]^{20}_D$ = −93.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 7.8 min, t_r(major) = 10.0 min, 93% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Methylbenzoate (**3b**).* White solid (32.1 mg, yield 87%), mp

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110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.95 (m, 2H), 7.37−7.27 (m, 5H), 7.25−7.20 (m, 2H), 6.76 (d, J = 9.6 Hz, 1H), 4.72 (d, J = 7.8 Hz, 2H), 4.65−4.52 (m, 1H), 3.77 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.8, 145.1, 140.1, 136.5, 130.5, 129.4, 129.4, 128.3, 127.5, 127.4, 125.3, 78.4, 52.7, 41.1, 21.8; IR (thin film) ν/cm^{-1} 1736, 1609, 1296, 1258, 762; HRMS (ESI) calcd for $C_{20}H_{19}NO_6$ $(M - H)^-$ 368.1134, found 368.1127; $[\alpha]^{20}_D$ = −109.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 9.5 min, t_r(major) = 13.5 min, 88% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Methoxybenzoate (**3c**).* White solid (33.1 mg, yield 86%), mp 96−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−7.86 (m, 2H), 7.37−7.27 (m, 3H), 7.25−7.20 (m, 2H), 7.12−6.94 (m, 2H), 6.75 (d, J = 9.6 Hz, 1H), 4.73 (d, J = 7.8 Hz, 2H), 4.64−4.54 (m, 1H), 3.90 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.8, 161.9, 140.2, 136.6, 132.6, 129.3, 128.3, 127.4, 120.3, 114.0, 78.4, 55.6, 52.7, 41.1; IR (thin film) ν/cm^{-1} 1729, 1723, 1605, 1553, 1255, 1165, 1082, 767; HRMS (ESI) calcd for $C_{20}H_{19}NO_7$ $(M - H)^-$ 384.1083, found 384.1076; $[\alpha]^{20}_D$ = −109.1 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 261 nm), t_r(minor) = 11.8 min, t_r(major) = 18.8 min, 95% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Fluorobenzoate (**3d**).* White solid (30.6 mg, yield 82%), mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20−8.04 (m, 2H), 7.37−7.27 (m, 3H), 7.25−7.15 (m, 4H), 6.79 (d, J = 9.6 Hz, 1H), 4.72 (d, J = 7.8 Hz, 2H), 4.64−4.53 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (d, $J_{(CF)}$ = 256.0 Hz), 162.4 (d, $J_{(CF)}$ = 153.7 Hz), 140.00, 136.41, 133.1 (d, $J_{(CF)}$ = 9.6 Hz), 129.39, 128.35, 127.82, 127.42, 124.3 (d, $J_{(CF)}$ = 3.0 Hz), 116.0 (d, $J_{(CF)}$ = 22.2 Hz), 78.47, 52.77, 41.16; IR (thin film) ν/cm^{-1} 1739, 1722, 1678, 1555, 1295, 1256, 1080, 1058, 766, 751; HRMS (ESI) calcd for $C_{19}H_{16}FNO_6$ $(M - H)^-$ 372.0883, found 372.0880; $[\alpha]^{20}_D$ = −107.5 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 7.5 min, t_r(major) = 11.0 min, 93% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Chlorobenzoate (**3e**).* White solid (32.3 mg, yield 83%), mp 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.00 (m, 2H), 7.51−7.46 (m, 2H), 7.36−7.28 (m, 3H), 7.23−7.19 (m, 3H), 6.79 (d, J = 9.6 Hz, 1H), 4.72 (d, J = 7.8 Hz, 2H), 4.61−4.53 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.5, 140.8, 140.0, 136.4, 131.8, 129.4, 129.1, 128.4, 127.9, 127.4, 126.5, 78.5, 52.8, 41.2; IR (thin film) ν/cm^{-1} 1737, 1555, 1299, 1255, 1132, 754; HRMS(ESI) calcd for $C_{19}H_{16}ClNO_6$ $(M - H)^-$ 388.0588, found 388.0581; $[\alpha]^{20}_D$ = −104.1 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 7.8 min, t_r(major) = 11.2 min, 86% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Bromobenzoate (**3f**).* White solid (41.6 mg, yield 96%), mp 101−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.88 (m, 2H), 7.73−7.59 (m, 2H), 7.36−7.26 (m, 3H), 7.24−7.19 (m, 2H), 6.79 (d, J = 9.6 Hz, 1H), 4.71 (d, J = 7.8 Hz, 2H), 4.61−4.51 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.5, 140.0, 136.4, 132.1, 131.8, 129.5, 129.4, 128.4, 127.9, 127.4, 127.0, 78.5, 52.8, 41.2; IR (thin film) ν/cm^{-1} 1737, 1721, 1554, 1297, 1255, 1083, 1069, 750; HRMS (ESI) calcd for $C_{19}H_{16}BrNO_6$ $(M - H)^-$ 432.0083, found 432.0081; $[\alpha]^{20}_D$ = −101.1 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 7.9 min, t_r(major) = 11.1 min, 90% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 4-Nitrobenzoate (**3g**).* Yellow solid (32.8 mg, yield 82%), mp 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45−8.31 (m, 2H), 8.31−8.22 (m, 2H), 7.38−7.28 (m, 3H), 7.21 (m, 2H), 6.84 (d, J = 9.4 Hz, 1H), 4.76−4.69 (m, 2H), 4.64−4.51 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 161.2, 151.2, 139.8, 136.2, 133.4, 131.5, 129.5, 128.5, 128.3, 127.4, 123.8, 78.5, 52.9, 41.2; IR (thin film) ν/cm^{-1} 1756, 1555, 1528, 1259, 1169, 1087, 717, 698; HRMS (ESI) calcd for $C_{19}H_{16}N_2O_8$ $(M - H)^-$ 399.0828, found 399.0822; $[\alpha]^{20}_D$ = −88.4 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm), t_r(minor) = 30.0 min, t_r(major) = 32.2 min, 62% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 3-Chlorobenzoate (**3h**).* Colorless oil (31.5 mg, yield 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.04 (m, 1H), 8.04−7.96 (m, 1H), 7.68−7.60 (m, 1H), 7.51−7.44 (m, 1H), 7.39−7.28 (m, 3H), 7.26−7.20 (m, 2H), 6.82 (d, J = 9.6 Hz, 1H), 4.74 (d, J = 7.8 Hz, 2H), 4.64−4.52 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 161.5, 140.0, 136.31, 134.9, 134.1, 130.4, 130.0, 129.8, 129.4, 128.5, 128.4, 128.0, 127.4, 78.5, 52.8, 41.2; IR (thin film) ν/cm^{-1} 1753, 1733, 1555, 1283, 1250, 1126, 1083, 749, 729, 699; HRMS (ESI) calcd for $C_{19}H_{16}ClNO_6$ $(M - H)^-$ 388.0588, found 388.0579; $[\alpha]^{20}_D$ = −103.7 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 206 nm), t_r(minor) = 7.4 min, t_r(major) = 9.0 min, 91% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 3,5-Dimethoxybenzoate (**3i**).* White solid (38.2 mg, yield 92%), mp 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.26 (m, 4H), 7.26−7.20 (m, 3H), 6.78 (d, J = 9.6 Hz, 1H), 6.74 (t, J = 2.4 Hz, 1H), 4.73 (d, J = 7.8 Hz, 2H), 7.64 −7.54 (m, 1H), 3.86 (s, 6H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 160.8, 140.1, 136.4, 129.7, 129.4, 128.4, 127.7, 127.4, 107.9, 107.1, 78.5, 55.7, 52.8, 41.2; IR (thin film) ν/cm^{-1} 2360, 1745, 1731, 1550; HRMS (ESI) calcd for $C_{21}H_{21}NO_8$ $(M - H)^-$ 414.1189, found 414.1185; $[\alpha]^{20}_D$ = −82.5 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 203 nm), t_r(minor) = 11.7 min, t_r(major) = 15.2 min, 90% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 2-Methoxybenzoate (**3j**).* Colorless oil (36.2 mg, yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.92 (m, 1H), 7.61−7.54 (m, 1H), 7.37−7.27 (m, 4H), 7.26−7.24 (m, 1H), 7.08−7.02 (m, 2H), 6.71 (d, J = 9.4 Hz, 1H), 4.77 (dd, J = 7.6, 3.6 Hz, 2H), 4.73−4.65 (m, 1H), 3.96 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.8, 160.00, 140.0, 136.7, 134.9, 132.6, 129.3, 128.2, 127.4, 127.4, 120.4, 117.6, 112.1, 78.2, 56.0, 52.7, 41.0; IR (thin film) ν/cm^{-1} 1734, 1669, 1602, 1555, 1292, 1228, 753, 700; HRMS (ESI) calcd for $C_{20}H_{19}NO_7$ $(M - H)^-$ 384.1083, found 384.1079; $[\alpha]^{20}_D$ = −63.8 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 254 nm), t_r(minor) = 14.0 min, t_r(major) = 23.2 min, 95% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl Thiophene-2-carboxylate (**3k**).* Colorless oil (19.9 mg, yield 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.92 (m, 1H), 7.74−7.68 (m, 1H), 7.37−7.27 (m, 3H), 7.25−7.17 (m, 3H), 6.77

(d, J = 9.6 Hz, 1H), 4.77−4.70 (m, 2H), 4.66−4.54 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.4, 139.7, 136.4, 135.6, 134.4, 131.0, 129.4, 128.3, 128.2, 128.0, 127.4, 78.3, 52.8, 41.2; IR (thin film) ν/cm^{-1} 1735, 1556, 1295, 756; HRMS (ESI) calcd for $C_{17}H_{15}NO_6S$ $(M - H)^-$ 360.0542, found 360.0533; $[\alpha]^{20}_D$ = −70.9 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 246 nm), t_r(minor) = 10.0 min, t_r(major) = 16.7 min, 94% ee.

*(R,Z)-Methyl 2-(Isobutyryloxy)-5-nitro-4-phenylpent-2-enoate (**3l**).* Colorless oil (24.4 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.27 (m, 3H), 7.25−7.18 (m, 2H), 6.65 (d, J = 9.6 Hz, 1H), 4.78−4.58 (m, 2H), 4.51 (dd, J = 9.6, 7.8 Hz, 1H), 3.77 (s, 3H), 2.85−2.68 (m, 1H), 1.33−1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 161.7, 140.0, 136.6, 129.4, 128.3, 127.4, 127.1, 78.5, 52.6, 41.0, 33.8, 18.8, 18.7; IR (thin film) ν/cm^{-1} 2978, 1963, 1736, 1556, 1123, 760, 700; HRMS (ESI) calcd for $C_{16}H_{19}NO_6$ $(M - H)^-$ 320.1134, found 320.1133; $[\alpha]^{20}_D$ = −47.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 6.2 min, t_r(major) = 7.4 min, 79% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl Cyclohexanecarboxylate (**3m**).* White solid (23.8 mg, yield 66%), mp 101−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.27 (m, 3H), 7.25−7.19 (m, 2H), 6.64 (d, J = 9.6 Hz, 1H), 4.75−4.59 (m, 2H), 4.56−4.44 (m, 1H), 3.76 (s, 3H), 2.60−2.47 (m, 1H), 2.10−1.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 161.7, 140.0, 136.6, 129.4, 128.3, 127.4, 127.1, 78.4, 52.6, 42.7, 41.0, 28.8, 28.7, 25.6, 25.2, 25.2; IR (thin film) ν/cm^{-1} 2938, 2853, 1756, 1722, 1553, 1282, 1116, 698; HRMS (ESI) calcd for $C_{19}H_{23}NO_6$ $(M - H)^-$ 360.1447, found 360.1442; $[\alpha]^{20}_D$ = −70.6 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 6.7 min, t_r(major) = 9.5 min, 79% ee.

*(R,Z)-1-Methoxy-5-nitro-1-oxo-4-p-tolylpent-2-en-2-yl 2-Methoxybenzoate (**5b**).* Colorless oil (36.7 mg, yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.91 (m, 1H), 7.62−7.52 (m, 1H), 7.17−7.12 (m, 4H), 7.08−7.02 (m, 2H), 6.69 (d, J = 9.6 Hz, 1H), 4.71−4.78 (m, 2H), 4.71−4.55 (m, 1H), 3.96 (s, 3H), 3.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.9, 160.0, 139.8, 138.0, 134.9, 133.6, 132.6, 130.0, 127.6, 127.3, 120.3, 117.7, 112.1, 78.3, 56.0, 52.7, 40.7, 21.1; IR (thin film) ν/cm^{-1} 2954, 1734, 1556, 1295, 1228, 1022, 756; HRMS (ESI) calcd for $C_{21}H_{21}NO_7$ $(M - H)^-$ 398.1240, found 398.1236; $[\alpha]^{20}_D$ = −117.6 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 203 nm), t_r(minor) = 13.4 min, t_r(major) = 22.7 min, 97% ee.

*(R,Z)-1-Methoxy-4-(4-methoxyphenyl)-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5c**).* Colorless oil (37.4 mg, yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.91 (m, 1H), 7.62−7.52 (m, 1H), 7.21−7.14 (m, 2H), 7.12−7.00 (m, 2H), 6.96−6.74 (m, 2H), 6.69 (d, J = 9.6 Hz, 1H), 4.77−4.69 (m, 2H), 4.69−4.56 (m, 1H), 3.95 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.9, 160.0, 159.4, 139.7, 134.9, 132.6, 128.5, 127.6, 120.3, 117.7, 114.7, 112.1, 78.4, 56.0, 55.3, 52.7, 40.4; IR (thin film) ν/cm^{-1} 2955, 2841, 1733, 1556, 1297,1255, 1123, 1028, 832, 756; HRMS (ESI) calcd for $C_{21}H_{21}NO_8$ $(M - H)^-$ 414.1189, found 414.1187; $[\alpha]^{20}_D$ = −103.8 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 16.5 min, t_r(major) = 27.6 min, 95% ee.

*(R,Z)-4-(4-Fluorophenyl)-1-methoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5d**).* Colorless oil (34.7 mg, yield 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 −7.90 (m, 1H), 7.63−7.53 (m, 1H), 7.28−7.21 (m, 2H), 7.10−7.03 (m, 3H), 7.01−6.96 (m, 1H), 6.68 (d, J = 9.2 Hz, 1H), 4.78−4.71 (m, 2H), 4.71−4.57 (m, 1H), 3.95(s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.8, 160.0, 140.1, 135.0, 132.6, 132.5, 132.5, 129.16 (d, $J_{(CF)}$ = 8.3 Hz), 127.0, 120.4, 117.5, 116.28 (d, $J_{(CF)}$ = 21.7 Hz), 112.1, 78.2, 56.0, 52.8, 40.4; IR (thin film) ν/cm^{-1} 1733, 1602, 1296, 1227, 756; HRMS (ESI) calcd for $C_{20}H_{18}FNO_7$ $(M - H)^-$ 402.0989, found 402.0983; $[\alpha]^{20}_D$ = −77.4 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 11.0 min, t_r(major) = 17.7 min, 94% ee.

*(R,Z)-4-(4-Chlorophenyl)-1-methoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5e**).* Colorless oil (38.6 mg, yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.89 (m, 1H), 7.63−7.53 (m, 1H), 7.33−7.28 (m, 2H), 7.23−7.16 (m, 2H), 7.10−6.99 (m, 2H), 6.67 (d, J = 9.4 Hz, 1H), 4.78−4.71 (m, 2H), 4.70−4.59 (m, 1H), 3.95 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.8, 160.0, 140.3, 135.2, 135.0, 134.2, 132.6, 129.5, 128.8, 126.7, 120.4, 117.4, 112.1, 78.0, 56.0, 52.8, 40.4; IR (thin film) ν/cm^{-1} 1733, 1636, 1557, 1123, 757; HRMS (ESI) calcd for $C_{20}H_{18}ClNO_7$ $(M - H)^-$ 418.0694, found 418.0693; $[\alpha]^{20}_D$ = −96.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 11.0 min, t_r(major) = 17.8 min, 95% ee.

*(R,Z)-4-(4-Bromophenyl)-1-methoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5f**).* Colorless oil (44.4 mg, yield 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.89 (m, 1H), 7.65−7.52 (m, 1H), 7.51−7.42 (m, 2H), 7.20−7.00 (m, 5H), 6.66 (d, J = 9.6 Hz, 1H), 4.74 (d, J = 7.8 Hz, 2H), 4.69−4.59 (m, 1H), 3.95 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.7, 160.0, 140.3, 135.8, 135.0, 132.6, 132.4, 129.2, 126.6, 122.3, 120.4, 117.4 112.1, 77.8, 56.0, 52.8, 40.5; IR (thin film) ν/cm^{-1} 1733, 1602, 1556, 1491, 1437, 1296, 1122, 755; HRMS (ESI) calcd for $C_{20}H_{18}BrNO_7$ $(M - H)^-$ 462.0188, found 462.0180; $[\alpha]^{20}_D$ = −104.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 11.4 min, t_r(major) = 18.5 min, 95% ee.

*(R,Z)-1-Methoxy-5-nitro-4-(4-nitrophenyl)-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5g**).* Colorless oil (34.4 mg, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.09 (m, 2H), 7.95−7.88 (m, 1H), 7.64−7.54 (m, 1H), 7.49−7.42 (m, 2H), 7.09−7.01 (m, 2H), 6.69 (d, J = 9.0 Hz, 1H), 4.89−4.66 (m, 3H), 3.95 (s, 3H,), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.5, 160.0, 144.0, 141.1, 135.2, 132.6, 128.6, 125.4, 124.4, 120.4, 117.1, 112.2, 77.4, 56.0, 52.9, 40.7, 25.4; IR (thin film) ν/cm^{-1} 1733, 1603, 1557, 1349, 1297, 1227, 1123, 1020, 758, 696; HRMS (ESI) calcd for $C_{20}H_{18}N_2O_9$ $(M - H)^-$ 429.0934, found 429.0933; $[\alpha]^{20}_D$ = −129.6 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 20.3 min, t_r(major) = 25.2 min, 92% ee.

*(R,Z)-4-(2-Fluorophenyl)-1-methoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5h**).* Colorless oil (35.1 mg, yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.90 (m, 1H),

7.62−7.52 (m, 1H), 7.32−7.27 (m, 1H), 7.25−7.21 (m, 1H), 7.12−7.02 (m, 4H), 6.80 (dd, J = 9.2, 1.4 Hz, 1H), 4.93−4.71 (m, 3H), 3.95 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.8, 160.0, 140.6, 134.9, 132.6, 130.1 (d, $J_{(CF)}$ = 8.4 Hz), 129.9 (d, $J_{(CF)}$ = 4.2 Hz), 125.7 (d, $J_{(CF)}$ = 1.9 Hz), 124.9 (d, $J_{(CF)}$ = 3.4 Hz), 123.6 (d, $J_{(CF)}$ = 13.6 Hz), 120.3, 117.6, 116.4, 116.2, 112.1, 76.9 (d, $J_{(CF)}$ = 3.3 Hz), 56.0, 52.7, 36.8; IR (thin film) ν/cm^{-1} 2955, 1735, 1556, 1492, 1297, 1230, 756; HRMS (ESI) calcd for $C_{20}H_{18}FNO_7$ (M − H)$^-$ 402.0989, found 402.0982; $[\alpha]^{20}_D$ = −72.7 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 11.2 min, t_r(major) = 20.2 min, 93% ee.

*(R,Z)-4-(3-Chlorophenyl)-1-methoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5i**).* Colorless oil (41.5 mg, yield 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.90 (m, 1H), 7.61−7.55 (m, 1H), 7.29−7.26 (m, 3H), 7.19−7.11 (m, 1H), 7.09−7.02 (m, 2H), 6.67 (d, J = 9.4 Hz, 1H), 4.80−4.72 (m, 2H), 4.72−4.60 (m, 1H), 3.96 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.7, 160.0, 140.4 138.7, 135.1, 135.0, 132.6, 130.6, 128.5, 127.8, 126.4, 125.6, 120.4, 117.4, 112.1, 77.8, 56.0, 52.8, 40.7; IR (thin film) ν/cm^{-1} 1734, 1556, 1294, 756, 696; HRMS (ESI) calcd for $C_{20}H_{18}ClNO_7$ (M − H)$^-$ 418.0694, found 418.0694; $[\alpha]^{20}_D$ = −87.8 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 13.8 min, t_r(major) = 25.1 min, 93% ee.

*(S,Z)-1-Methoxy-5-nitro-1-oxo-4-(thiophen-2-yl)pent-2-en-2-yl 2-Methoxybenzoate (**5j**).* Colorless oil (38.7 mg, yield 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.93 (m, 1H), 7.62−7.53 (m, 1H), 7.26−7.23 (m, 1H), 7.11−7.01 (m 2H), 6.98−6.93 (m, 2H), 6.69 (d, J = 9.8 Hz, 1H), 5.06−4.95 (m, 1H), 4.83−4.63 (m, 2H), 3.95 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.8, 160.0, 140.2, 138.9, 135.0, 132.7, 127.4, 126.5, 125.7, 125.4, 120.4, 117.5, 112.1, 78.6, 56.0, 52.8, 36.3; IR (thin film) ν/cm^{-1} 1734, 1556, 1296, 1229, 1122, 756, 705; HRMS (ESI) calcd for $C_{18}H_{17}NO_7S$ (M − H)$^-$ 390.0647, found 390.0640; $[\alpha]^{20}_D$ = −66.5 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r-(minor) = 14.0 min, t_r(major) = 21.6 min, 95% ee.

*(R,Z)-1-Ethoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 2-Methoxybenzoate (**5k**).* Colorless oil (33.1 mg, yield 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.92 (m, 1H), 7.59−7.50 (m, 1H), 7.38−7.26 (m, 5H), 7.10−6.97 (m, 2H), 6.69 (d, J = 9.4 Hz, 1H), 4.83−4.75 (m, 2H), 4.74−4.66 (m, 1H), 4.32−4.18 (m, 2H), 3.96 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.4, 159.9, 140.3, 136.8, 134.8, 132.5, 129.3, 128.2, 127.5, 127.0, 120.3, 117.9, 112.1, 78.2, 61.9, 56.0, 41.0, 14.1; IR (thin film) ν/cm^{-1} 2982, 1728, 1556, 1294, 1228, 1124, 1083, 756, 700; HRMS (ESI) calcd for $C_{21}H_{21}NO_7$ (M − H)$^-$ 398.1240, found 398.1237; $[\alpha]^{20}_D$ = −91.8 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r-(minor) = 10.9 min, t_r(major) = 14.3 min, 96% ee.

*(R,Z)-1-(Allyloxy)-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 2-Methoxybenzoate (**5l**).* Colorless oil (34.9 mg, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.90 (m, 1H), 7.62−7.52 (m, 1H), 7.37−7.26 (m, 5H), 7.10−6.98 (m, 2H), 6.72 (d, J = 9.2 Hz, 1H), 5.98−5.81 (m, 1H), 5.37−5.18 (m, 2H), 4.83−4.75 (m, 2H), 4.74−4.70 (m, 1H), 4.70−4.66 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.1, 159.9, 140.0, 136.7, 134.8, 132.5, 131.4, 129.3, 128.2, 127.5, 120.4, 118.9, 117.8, 112.1, 78.2, 66.4, 56.0, 41.1; IR (thin film) ν/cm^{-1} 2360, 1732, 1640, 1555, 1120; HRMS (ESI) calcd for $C_{22}H_{21}NO_7$ (M − H)$^-$ 410.1240, found 410.1232; $[\alpha]^{20}_D$ = −91.0 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 9.7 min, t_r(major) = 12.0 min, 96% ee.

*(R,Z)-1-Isopropoxy-5-nitro-1-oxo-4-phenylpent-2-en-2-yl 2-Methoxybenzoate (**5m**).* Colorless oil (35.1 mg, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.87 (m, 1H), 7.61−7.51 (m, 1H), 7.38−7.26 (m, 5H), 7.11−6.99 (m, 2H), 6.65 (d, J = 9.2 Hz, 1H), 5.15−5.02 (m, 1H), 4.84−4.74 (m, 2H), 4.74−4.66 (m, 1H), 3.95 (s, 3H), 1.26 (dd, J = 6.2, 2.0Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 160.9, 159.7, 140.6, 136.9, 134.6, 132.3, 129.3, 128.2, 127.5, 126.5, 120.3, 118.1, 112.1, 78.2, 69.9, 56.0, 41.0, 21.7; IR (thin film) ν/cm^{-1} 2983, 1725, 1556, 1293, 756, 700; HRMS (ESI) calcd for $C_{22}H_{23}NO_7$ (M − H)$^-$ 412.1396, found 412.1393; $[\alpha]^{20}_D$ = −83.1 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 8.3 min, t_r(major) = 9.3 min, 97% ee.

*(S,Z)-1-Ethoxy-5-methyl-4-(nitromethyl)-1-oxohex-2-en-2-yl 2-Methoxybenzoate (**5n**).* Colorless oil (31.0 mg, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.92 (m, 1H), 7.59−7.51 (m, 1H), 7.07−6.99 (m, 2H), 6.45 (d, J = 10.6 Hz, 1H), 4.54 (dd, J = 12.4, 6.6 Hz, 1H), 4.43 (dd, J = 12.4, 7.6 Hz, 1H), 4.30−4.23 (m, 2H), 3.93 (s, 3H), 3.32 (ddt, J = 10.6, 7.6, 6.6 Hz, 1H), 1.94−1.81 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H), 0.99 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.4, 160.0, 141.6, 134.7, 132.5, 126.4, 120.3, 118.0, 112.1, 61.8, 56.0, 41.4, 29.7, 20.4, 18.6, 14.1; IR (thin film) ν/cm^{-1} 2964, 2921, 2383, 1729, 1601, 1297, 1255, 1095, 758; HRMS (ESI) calcd for $C_{18}H_{23}NO_7$ (M − H)$^-$ 364.1396, found 364.1391; $[\alpha]^{20}_D$ = −2.4 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 10.8 min, t_r(major) = 14.3 min, 91% ee.

*(S,Z)-4-Cyclohexyl-1-ethoxy-5-nitro-1-oxopent-2-en-2-yl 2-Methoxybenzoate (**5o**).* Colorless oil (33.2 mg, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.91 (m, 1H), 7.59−7.49 (m, 1H), 7.08−6.98 (m, 2H), 6.46 (d, J = 10.8 Hz, 1H), 4.56 (dd, J = 12.4, 6.4 Hz, 1H), 4.43 (dd, J = 12.4, 7.8 Hz, 1H), 4.30−4.21 (m, 2H), 3.93 (s, 3H), 3.39−3.21 (m, 1H), 1.73−1.45 (m, 5H), 1.29 (t, J = 7.2 Hz, 3H), 1.23−0.82 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.4, 160.0, 141.4, 134.7, 132.5, 127.1, 120.3, 118.0, 112.1, 76.8, 61.8, 56.0, 40.9, 39.4, 30.8, 29.2, 26.1, 26.0, 26.0, 14.1; IR (thin film) ν/cm^{-1} 2929, 2854, 1729, 1555, 1295, 756; HRMS (ESI) calcd for $C_{21}H_{27}NO_7$ (M − H)$^-$ 404.1709, found 404.1700; $[\alpha]^{20}_D$ = −18.2 (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/i-PrOH = 60:40, 1.0 mL/min, 230 nm), t_r(minor) = 12.6 min, t_r(major) = 15.5 min, 91% ee.

*(4R,5R/5S,Z)-1-Methoxy-5-nitro-1-oxo-4-p-tolylhex-2-en-2-yl Benzoate (**3n**).* Colorless oil (21.8 mg, yield 57%), a mixture of two diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.07 (m, 2H + 0.8H*), 7.74−7.61 (m, 1H + 0.4H*), 7.58−7.44 (m, 2H + 0.8H*), 7.16−7.06 (m, 4H + 1.6H*), 6.85 (d, J = 10.0 Hz, 0.4H*), 6.69 (d, J = 10.6 Hz, 1H), 5.06−4.83 (m, 1H + 0.4H*), 4.24 (t, J = 10.2 Hz, 1H), 4.15 (t, J = 9.8 Hz, 0.4H*), 3.77 (s, 3H), 3.76 (s, 1.2H*), 2.31 (s, 1.2H*), 2.30 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H), 1.39 (d, J = 6.8 Hz, 1.2H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.8, 140.2, 138.1, 134.1, 133.6, 130.4, 129.9, 128.8, 128.1, 127.9, 127.5, 86.3, 52.7, 47.0, 21.0, 18.1; IR (thin film)

ν/cm^{-1} 2957, 2923, 1752, 1555, 1289, 1264, 1228, 1020, 708, 579; HRMS (ESI) calcd for $C_{21}H_{21}NO_6$ $(M - H)^-$ 382.1291, found 382.1290; $[\alpha]^{20}_D = -139.5$ (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm), t_r(minor) = 8.1 min, t_r(major) = 8.7 min, 89% ee; t_r(minor) = 14.7 min, t_r(major) = 20.4 min, 94% ee.

*(4R,5R/5S,Z)-1-Methoxy-5-nitro-1-oxo-4-p-tolylhept-2-en-2-yl Benzoate (**3o**).* Colorless oil (25.0 mg, yield 63%), a mixture of two diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.06 (m, 2H + 1.6H*), 7.72−7.61 (m, 1H + 0.8H*), 7.57−7.47 (m, 2H + 1.6H*), 7.15−7.00 (m, 4H + 3.2H*), 6.86 (d, J = 10.1 Hz, 1H), 6.67 (d, J = 10.7 Hz, 0.8H*), 4.80 (td, J = 10.4, 3.6 Hz, 0.8H*), 4.71 (td, J = 10.4, 3.2 Hz, 1H), 4.21 (t, J = 10.6 Hz, 0.8H*), 4.15 (t, J = 10.0 Hz, 1H), 3.76 (s, 2.4H*), 3.75 (s, 3H), 2.31 (s, 3H), 2.29 (s, 2.4H*), 2.08−1.49 (m, 2H + 1.6H*), 0.98 (t, J = 7.4 Hz, 2.4H*), 0.86 (t, J = 7.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.7, 140.0, 138.1, 133.9, 133.4, 130.4, 130.1, 128.6, 128.3, 127.8, 127.7, 127.5, 93.6, 52.6, 46.2, 25.2, 21.0, 10.2; IR (thin film) ν/cm^{-1} 2976, 2922, 2851, 1753, 1728, 1554, 1021, 708, 581; HRMS (ESI) calcd for $C_{22}H_{23}NO_6$ $(M - H)^-$ 396.1447, found 396.1444; $[\alpha]^{20}_D = -118.7$ (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm), t_r(minor) = 6.1 min, t_r(major) = 6.5 min, 79% ee; t_r(minor) = 21.8 min, t_r(major) = 33.0 min, >99% ee.

*Methyl 2-Hydroxy-5-nitro-2-(nitromethyl)-4-phenylpentanoate (**6**).* Colorless oil (15.6 mg, yield 50%), a mixture of two diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.14 (m, 5H + 1.7H*), 4.74 (d, J = 13.6 Hz, 1H), 4.68−4.57 (m, 1H + 0.3H*), 4.50 (dd, J = 12.8, 8.4 Hz, 2H + 0.6H*), 4.36 (d, J = 13.8 Hz, 0.3H*), 3.99 (s, 1H), 3.85 (s, 1H*), 3.74 (ddd, J = 16.2, 8.4, 4.0 Hz, 1H + 0.3H*), 3.60 (s, 0.3H*), 3.29 (s, 3H), 2.37−2.16 (m, 1H + 0.3H*), 2.06 (ddd, J = 18.0, 14.4, 4.2 Hz, 1H + 0.3H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 171.8, 138.7, 137.6, 129.4, 128.9, 128.3, 128.2, 128.1, 127.6, 81.4, 80.8, 80.2, 80.0, 74.9, 74.1, 53.9, 53.3, 39.5, 39.2, 39.0, 38.6; IR (thin film) ν/cm^{-1} 3032, 2959, 2924, 2075, 1751, 1734, 1567,1545, 1495, 1140, 1085, 702, 522; HRMS (ESI) calcd for $C_{13}H_{16}N_2O_7$ $(M + Na)^+$ 335.0855, found 335.0851.

Procedure for Hydrolysis of 3a. Compound **3a** (213.0 mg, 0.60 mmol), concentrated H_2SO_4 (30 μL), and MeOH (12 mL) were refluxed for 72 h. After evaporation of the solvent under vacuum, trifluoroacetic acid (90% aqueous solution, 6 mL) was added. The reaction mixture was stirred for 24 h at room temperature and then diluted with EtOAc (20 mL). The organic layer was separated and washed with H_2O (10 mL × 3) and brine (10 mL). Then it was dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate = 5:1) to give **8** as a colorless oil.

*(R)-Methyl 5-Nitro-2-oxo-4-phenylpentanoate (**8**).* Colorless oil (12.6 mg, yield 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 3H), 7.25−7.21 (m, 2H), 4.66 (qd, J = 12.6, 7.4 Hz, 2H), 4.14−4.00 (m, 1H), 3.84 (s, 3H), 3.43 (dd, J = 18.8, 7.4 Hz, 1H), 3.31 (dd, J = 18.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 160.6, 137.9, 129.2, 128.2, 127.4, 79.2, 53.2, 42.2, 38.6; IR (thin film) ν/cm^{-1} 3363, 2960, 2920, 2851, 1758, 1562, 1379, 1296, 1261, 1093, 1070, 796, 702; HRMS (ESI) calcd for $C_{12}H_{13}NO_5$ $(M - H)^-$ 250.0715, found 250.0714; $[\alpha]^{20}_D = +12.5$ (c = 1.0, CH_2Cl_2); enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexane/*i*-PrOH = 60:40, 1.0 mL/min, 220 nm), t_r(minor) = 9.9 min, t_r(major) = 12.7 min, 94% ee.

■ ASSOCIATED CONTENT

Supporting Information. X-ray structural data (CIF) and NMR spectra and HPLC chromatograms of products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) CCDC 822112 contains the supporting crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. An ORTEP drawing of **3e** is also provided in the Supporting Information.

(10) (*E*)-Products were claimed on the basis of X-ray structural analysis in the report of Wang and co-workers.[7] We checked the ORTEP drawing supplied in the paper and found that the product actually has a (*Z*)-configuration. We also compared the NMR spectra of several products prepared both in our and Wang's studies and confirmed that the spectra are identical within the scope of instrumental errors. In addition, the assignment of (*Z*)-geometry is further supported by the NOESY analysis of product **3a**. The NOE signal was observed between the methyl ester group and the proton of the double bond. The result indicates that they are positioned at the same side of the double bond. We think the configurations of the products in Wang's study were not assigned correctly.

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(12) Compound **8** and its analogues were prepared previously from the reaction of α-keto esters with nitroalkenes catalyzed by chiral Ni(II) or Cu(II) complexes. See (a) Nakamura, A.; Lectard, S.; Hashizume, D.; Hamashima, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2010**, *132*, 4036. (b) Nakamura, A.; Lectard, S.; Shimizu, R.; Hamashima, Y.; Sodeok, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1682.

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