Tetrahedron: *Asymmetry* 25 (2014) 212–218

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Enantioselective Michael addition of cyclic ketones to nitroolefins catalyzed by a novel fluorine-insertion organocatalyst

Yanan Wang, Min Jiang, Jin-Tao Liu *

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

ARTICLE INFO

Article history:
Received 16 October 2013
Accepted 12 December 2013

ABSTRACT

A novel fluorine-insertion organocatalyst, which was designed based on the fluorine–ammonium ion *gauche* effect, was synthesized and used successfully to catalyze the asymmetric Michael addition of cyclic ketones to nitroolefins. High yields and excellent diastereo- and enantioselectivities were achieved under mild conditions. A possible stereochemical model is also proposed.

1. Introduction

Fluorine is an important atom in organic chemistry. The C–F bond is dramatically different from a C–H bond due to the high electronegativity of fluorine.[1,2] The properties of organic compounds, such as the conformations of molecules, can often be altered by the introduction of a fluorine atom. For instance, the proline molecule has two conformations for the pyrrolidine ring, C^{γ}-*exo* and C^{γ}-*endo* (Fig. 1).[3] When R^1 = H and R^2 = OH, N_3, or F, C^{γ}-*endo* is the favored conformation. When R^2 = H and R^1 = OH, F, C^{γ}-*exo* is the favored one. Therefore, the different substituent has a dramatic impact on the conformation of the pyrrolidine ring. Furthermore, the electronegativity of the substituent can alter the relative energies of the conformers and make a single conformer more popular.[4–7]

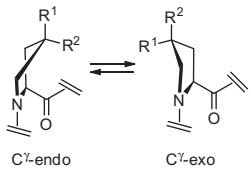

Figure 1. The conformation of 4-substituted proline derivatives.

When a fluorine atom is incorporated into a pyrrolidine ring, the main factors for controlling the molecular topology are charge–dipole interactions. Due to the high electronegativity of fluorine, the C–F bond is highly polarized and has a vacant low-energy σ*C–F orbital that can interact with adjacent σ bonds, such as a C–H bond. Furthermore, the polarized nature of $C^{\delta+}$–$F^{\delta-}$ bond evokes the *gauche* effect (Fig. 2).[8,9] Therefore, a single C–F bond can establish a conformational rigidity and tip the balance between multiple conformers to favor a single species.

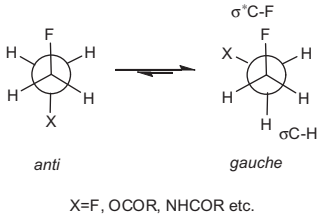

Figure 2. The fluorine *gauche* effect.

Recently, some fluorine-insertion catalysts were reported which utilize the unique properties of fluorine. Marson et al. synthesized a C_2-symmetric, enantiopure vicinal difluoropyrrolidine catalyst.[10] A few years later, List et al. reported on the *trans*-4-fluoroproline catalyzed transannular aldolization of cyclic diketones, which were used as a key step in a short synthesis of (+)-hirsutene.[11] Recently, Gilmour et al. showcased a series of novel fluorinated organocatalysts and investigated their potential uses in organic synthesis.[12] Alexakis et al. also designed a novel fluorine stabilized catalyst.[13]

Although *N*-(2-pyrrolidinylmethyl)pyrrolidine **1** is an ideal organocatalyst,[14] poor results were obtained in some asymmetric reactions, such as the Michael addition of cyclohexanone and nitrostyrene. We envisioned that introducing a fluorine atom at the 4-position of the pyrrolidine may result in an efficient fluorinated organocatalyst **1-F**, which is conformationally stable (Fig. 3). Alexakis has already confirmed that this conformational

* Corresponding author. Tel.: +86 21 54925188.
E-mail address: jtliu@sioc.ac.cn (J.-T. Liu).

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http://dx.doi.org/10.1016/j.tetasy.2013.12.015

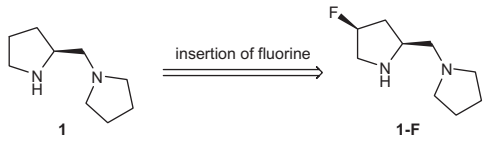


Figure 3. New fluorinated aminocatalyst.

change does not lead to any extra steric hindrance, because the atomic radius of fluorine is close to that of a hydrogen atom.[13] Herein we report the synthesis and application of this new fluorinated pyrrolidine-based catalyst.

2. Results and discussion

Our first goal was the synthesis of fluorinated pyrrolidine **1-F**. According to the literature,[15] the esterification of (2*S*,4*R*)-4-hydroxypyrrolidine-2-carboxylic acid **1-A** and subsequent N-protection afforded compound **1-B** in high yield. The fluorination of the hydroxyl group with diethylaminosulfurtrifluoride (DAST) took place smoothly and **1-B** was converted into (2*S*,4*S*)-4-fluoro-substituted pyrrolidine **1-C** stereoselectively. The reduction of the ester group in **1-C** with DIBAL-H afforded aldehyde **1-D**, which produced **1-E** via condensation with pyrrolidine and the following reduction of the imine. The target compound **1-F** was obtained via the N-deprotection of **1-E** (Scheme 1).

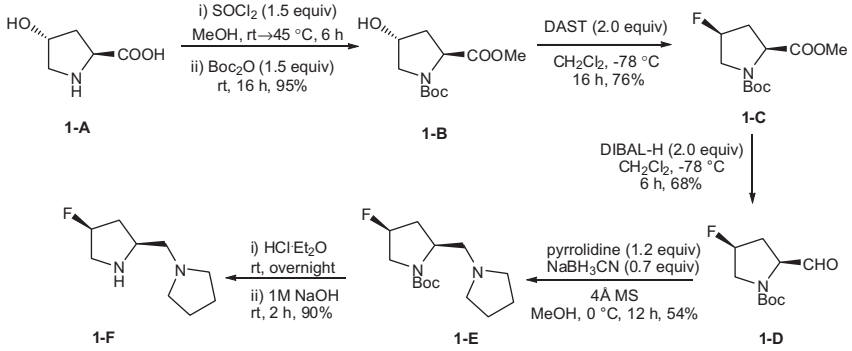
In order to test the catalytic potential of this new fluorine-insertion organocatalyst, the Michael addition of ketones to nitroolefins was selected as a model reaction.[16] In a preliminary experiment, *trans*-nitrostyrene **2a** was treated with cyclohexanone **3a** (5.0 equiv) and catalyst **1-F** (10 mol %) at room temperature under solvent free conditions. The corresponding adduct **4a** was obtained in 97% yield with 51:1 dr and 96% ee after 23 h. The relative and absolute configuration of **4a** was determined by comparison of its ^{1}H NMR spectra and specific rotation with those in the literature as shown in Table 1.[16]

Encouraged by the results, we further screened a range of reaction parameters for the selective formation of *syn*-**4a** and the key results are shown in Table 1. Decreasing the amount of cyclohexanone (3.0 equiv) or catalyst (5 mol %) lowered the yield and diastereoselectivity (entries 2 and 3). Examination of the solvents revealed that acetonitrile, methanol, and dimethyl sulfoxide (DMSO) gave much lower yields (entries 4–6). Excellent diastereoselectivity or enantioselectivity was achieved with a decrease of the yield in hexane, tetrahydrofuran (THF), or dichloromethane (entries 7–9). Although toluene was a suitable solvent, affording adduct **4a** in 93% yield with 57:1 dr and 96% ee, we chose the solvent-free conditions for this transformation because of it being environmentally friendly. The effect of an additive was also examined. In the presence of 10 mol % trifluoroacetic acid, the reaction proceeded well to afford **4a** in 93% yield with 16:1 dr and 98% ee in 20 h. Other additives such as 2,4-dinitro-benzenesulfonic acid and benzoic acid, gave **4a** with high ee (up to 99%), but the yield decreased slightly. As a control experiment, the reaction catalyzed by **1** was also examined and a notable loss in enantioselectivity (86% ee) was observed (entry 15).[17]

Next, we studied the Michael addition reaction between cyclohexanone **3a** and a variety of nitroolefins and the results are summarized in Table 2. It was found that better stereoselectivities were obtained in the absence of an additive for electron-rich β-nitrostyrenes **2b** and **2c** (entries 2 and 3). However, the reactions of electron-deficient β-nitrostyrenes **2d**–**2g** with substituents at the *para*- or *ortho*-position occurred smoothly in the presence of TFA to give the corresponding products **4d**–**4g** with high enantioselectivities, ranging from 91% to 99%, and relatively lower yields and enantioselectivities were afforded without TFA (entries 5–9). Therefore, TFA might contribute in activating the substrate and make the preferred conformation of the transition state more favored by the coordination effect of the proton in these reactions. The reactions of a naphthyl nitroolefin (entry 10) and a heteroaryl nitroolefin (entry 11) also proceeded well and afforded adducts **4h** and **4i** with 98% and 98% ee, respectively, when an additive was added. However, the results were unsatisfactory for β-cyclohexyl nitroolefin **2j**, and adduct **4j** was obtained in low yield with moderate stereoselectivities after 6.5 days along with the recovery of some starting material (entry 12); similar results were obtained with *n*-butyl substituted nitroolefin **2k**, probably due to the less reactive nature of the alkyl nitroolefin (entry 13).

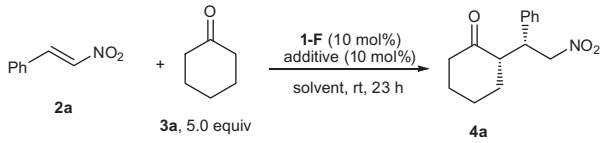
The Michael addition of different ketones with *trans*-nitrostyrene was also investigated (Table 3). When heterocyclic ketone **3b** was used as the Michael donor, better results were obtained in the presence of CF_3COOH and the desired product **4l** was isolated in 92% yield with 39:1 dr and 95% ee (Table 3, entry 2). The reaction of cyclopentanone afforded product **4m** with lower diastereoselectivity and moderate enatioselectivity, with or without TFA as the additive (entry 3). Both cycloheptanone **3d** and acetone **3e** showed low activity, which might be attributed to a less favored coordination. By prolonging the reaction time to 14 days, their reactions with **2a** in the absence of an additive afforded the corresponding adducts **4n** and **4o** with 80% and 49% ee, respectively (entries 4 and 5). Unfortunately, the reaction of aromatic ketone **3f** was unsuccessful and no adduct was formed under any conditions (entry 6).

We further examined the Michael addition of (*E*,*E*)-(4-nitro-1,3-butadienyl) benzene **2k** with cyclohexanone **3a**. The corresponding



Scheme 1. Synthesis of fluorinated pyrrolidine **1-F**.

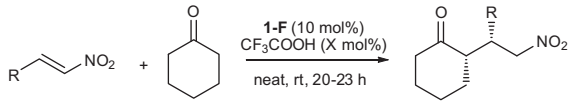
Table 1
Optimization of the **1-F** catalyzed asymmetric Michael addition reaction of cyclohexanone and *trans*-nitrostyrene



Entry[a]	Solvent	Additive	Yield[b] (**4a**, %)	dr[c]	ee[d] (%)
1	Neat	—	97	51:1	96
2[e]	Neat	—	84	27:1	94
3[f]	Neat	—	80	33:1	98
4	Acetonitrile	—	67	21:1	>99
5	Methanol	—	50	21:1	99
6	DMSO	—	24	16:1	88
7	Hexane	—	81	99:1	76
8	THF	—	88	99:1	98
9	CH_2Cl_2	——	84	65:1	98
10	Toluene	—	93	57:1	96
11[g]	Neat	Trifluoroacetic acid	93	16:1	98
12	Neat	2,4-Dinitro-benzenesulfonic acid	86	58:1	99
13	Neat	3,5-Dinitrobenzoic acid	90	85:1	95
14	Neat	Benzoic acid	90	16:1	99
15[h]	Neat	Trifluoroacetic acid	73	35:1	86

[a] Reactions were performed with *trans*-nitrostyrene (0.47 mmol), cyclohexanone (2.35 mmol, 5.0 equiv), additive (0 or 10 mol %), and **1-F** (10 mol %) for 23 h at room temperature.
[b] Yield of isolated product.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Determined by chiral HPLC analysis (Chiralpak PC, hexane-*i*-PrOH, 95:5).
[e] 5 mol % catalyst was used and the reaction time was 35 h.
[f] 3.0 equiv of cyclohexanone was used and the reaction time was 25 h.
[g] The reaction time was 20 h.
[h] **1** was used as the catalyst.

Table 2
Michael addition of cyclohexanone with various nitroolefins



Entry[a]	X (mol %)	**2**, R	**4**	Yield[b] (%)	dr[c]	ee[d] (%)
1	0	**2a**, C_6H_5	**4a**	97	51:1	96
	10			93	16:1	98
2	0	**2b**, 4-$MeOC_6H_4$	**4b**	91	99:1	93
	10			85	28:1	87
3	0	**2c**, 4-^{t}BuC_6H_4	**4c**	80	30:1	88
	10			43	18:1	86
4	0	**2d**, 4-ClC_6H_4	**4d**	78	60:1	92
	10			92	33:1	91
5	0	**2e**, 4-BrC_6H_4	**4e**	80	50:1	90
	10			86	49:1	98
6	0	**2f**, 2-BrC_6H_4	**4f**	83	99:1	87
	10			92	99:1	76
7	0	**2g**, 2,4-$Cl_2C_6H_3$	**4g**	77	26:1	97
	10			94	99:1	99
8	0	**2h**, 1-Naphthyl	**4h**	76	66:1	95
	10			77	99:1	98
9	0	**2i**, 2-Furyl	**4i**	89	21:1	94
	10			90	21:1	98
10[e]	0	**2j**, Cyclohexyl	**4j**	30	11:1	78
	10			16	15:1	84
11[f]	0	**2k**, ^{n}Bu	**4k**	58	8:1	91
	10			43	20:1	96

[a] Conditions: **2** (0.47 mmol), **3a** (2.35 mmol, 5.0 equiv), catalyst **1-F** (10 mol %), CF_3COOH (X mol %), neat, rt, 20–23 h.
[b] Yield of isolated product.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Determined by chiral HPLC analysis.
[e] The reaction time was 6.5 d.
[f] The reaction time was 5.5 d.

product **4q** was isolated in 84% yield with 14:1 dr and 99% ee in the absence of an additive. Good yield and excellent enantioselectivity were also obtained while using 10 mol% TFA as the additive (Scheme 2).

Based on the above experimental results, a stereochemical model was proposed to account for the high enantio- and diastereoselectivity of the Michael addition reaction of six-membered ketones and nitroolefins. The pyrrolidine derivative reacted with carbonyl compounds to form the favored (*E*)-*trans*-enamine. As shown in Figure 4, (*E*)-*trans*-C$^\gamma$-*endo* is the favored conformation. When a fluorine atom was introduced at the 4-position of the pyrrolidine ring, the stabilization of the C$^\gamma$-*exo* conformer decreased due to the *gauche* effect.[13] The lower enatioselectivity (86% vs 98% ee), which was obtained by unfluorinated catalyst **1** (Table 1, entry 15), confirmed the conformational stabilization for catalyst **1-F** and intermediate **A**.

3. Conclusion

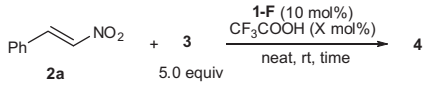
In conclusion, we have designed and synthesized a novel fluorine-insertion organocatalyst, which was successfully applied in the Michael addition reaction of six-membered ketones to nitroolefins. The *gauche* effect plays an important role in the transformation and results in a high diastereoselectivity and enatioselectivity.

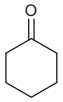
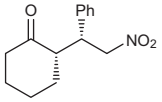
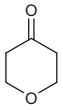
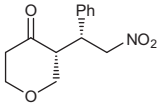
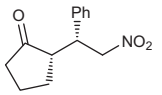
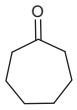
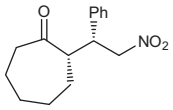
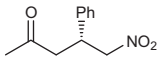
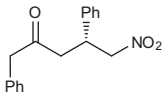
4. Experimental

4.1. General

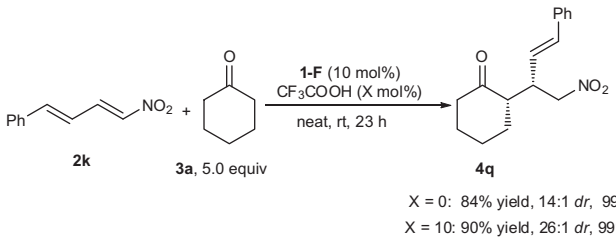
^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer (400 MHz) with TMS as an internal standard. ^{19}F NMR spectra were taken on a Bruker AM-400 (376 MHz) spectrometer using $CFCl_3$ as an external standard. ^{13}C NMR spectra were

Table 3
Michael addition of various Michael donors **3** with *trans*-nitrostyrene



Entry[a]	X (mol %)	3	Time	4	Yield[b] (%)	dr[c]	ee[d] (%)
1	0 10		23 h 20 h		97 93	51:1 16:1	96 98
		3a		**4a**			
2	0 10		25 h 23 h		98 92	13:1 39:1	78 95
		3b		**4l**			
3	0 10		25 h 24 h		71 84	4:1 2:1	84 88
		3c		**4m**			
4	0 10		14 d 14 d		69 46	17:1 18:1	80 69
		3d		**4n**			
5	0 10		14 d 14 d		56 58	— —	49 37
		3e		**4o**			
6[e]	0 10		23 h 23 h		NR NR	— —	— —
		3f		**4p**			

[a] Conditions: **2a** (0.47 mmol), **3** (2.35 mmol, 5.0 equiv), catalyst **1-F** (10 mol %), CF_3COOH (X mol %), neat, rt.
[b] Yield of isolated product.
[c] Determined by ^1H NMR spectroscopy.
[d] Determined by chiral HPLC analysis.
[e] NR = no reaction.



Scheme 2. Michael addition of diene **2k** and ketone **3a**.

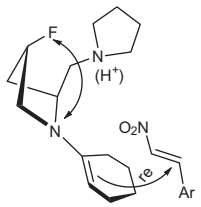


Figure 4. Proposed stereochemical model.

recorded in $CDCl_3$ on a Bruker AM-400 spectrometer (100 MHz) with TMS as internal standard. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz). IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Melting points were measured on a melt-Temp apparatus and are uncorrected. Mass spectra were obtained on a Finnigan GC–MS 4021. HRMS data were obtained on a high-resolution mass spectrometer. Enantiomeric excesses were determined by chiral HPLC using a Waters instrument. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gels. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. CH_2Cl_2 was freshly distilled by standard procedure prior to use.

4.2. Synthesis of 1-F

4.2.1. N-Boc-*trans*-4-hydroxy-L-proline methyl ester 1-B[15a]

This is a known compound; a white solid, 95% yield; $[\alpha]_D^{20} = -65.8$ (*c* 0.5, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 4.32–4.41 (m, 2H), 3.68 (s, 3H), 3.50–3.55 (m, 2H), 2.19–2.28 (m, 1H), 1.99–2.02 (m, 1H), 1.40 (s, 3H), 1.35 (s, 6H) ppm.

4.2.2. *N*-Boc-*cis*-4-fluoro-L-proline methyl ester 1-C[15b]

This is a known compound; pale yellow solid, 76% yield; $[\alpha]_D^{20} = -59.6$ (*c* 0.7, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 5.21 (d, *J* = 53.6 Hz, 1H), 4.46 (dd, *J* = 31.8, 10 Hz, 1H), 3.46–3.80 (m, 2H), 3.65 (s, 3H), 2.14–2.44 (m, 2H), 1.39 (s, 4H), 1.34 (s, 5H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −173.5 (m, 1F) ppm.

4.2.3. N-Boc-*cis*-4-fluoro-L-prolinal 1-D[15c]

At first, DIBAL-H (1.5 M in toluene, 2.9 mL, 4.36 mmol) was added via syringe pump over 26 min to a stirred and cooled (−78 °C) solution of **1-C** (539 mg, 2.18 mmol) in CH_2Cl_2 (7 mL) under an Ar atmosphere. After stirring for 6 h, 0.5 mL of MeOH was added at the same temperature. The mixture was warmed to room temperature and a solution of potassium sodium tartrate (2 M, 11 mL) was added and the resulting mixture was stirred vigorously for 0.5 h. The organic layer was separated and the aqueous layer was extracted further with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, concentrated, and purified by flash column chromatography to yield **1-D** as a light yellow solid. 421.1 mg, 54% yield; mp 57–59 °C; $[\alpha]_D^{20} = -80.7$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 9.50 (t, *J* = 2.2 Hz, 1H), 5.17 (d, *J* = 52.3 Hz, 1H), 4.19 (dd, *J* = 44.3, 9.4 Hz, 1H), 3.71–3.88 (m, 1H), 3.44–3.59 (m, 1H), 2.12–2.43 (m, 2H), 1.45 (s, 4H), 1.39 (s, 5H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −172.8 (m, 1F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0 (minor), 201.8 (major), 154.6 (minor), 153.7 (major), 92.2 (J_{C-F} = 176.8 Hz, minor), 91.2 (J_{C-F} = 176.8 Hz, major), 81.0 (major), 80.8 (minor), 63.4 (major), 63.2 (minor), 53.3 (J_{C-F} = 23.2 Hz, minor), 53.0 (J_{C-F} = 23.2 Hz, major), 36.1 (J_{C-F} = 21.2 Hz, major), 34.9 (J_{C-F} = 21.2 Hz, minor), 28.2 (minor), 28.1 (major). HRMS (ESI) calcd for $C_{10}H_{16}FNNaO_3$ ($M+Na^+$) 240.1012, found 240.1006. IR (KBr, cm^{-1}): 2984, 2888, 2836, 2824, 1728, 1698, 1402, 1368, 1168.

4.2.4. (*S,S*)-2-((Pyrrolidin-1-yl)methyl)-4-fluoro-pyrrolidine-1-carboxylic acid *tert*-butyl ester 1-E

Powdered 4 Å molecular sieves (ca. 1.5 g) were added to a solution of **1-D** (1.5 g, 6.90 mmol) in MeOH (13 mL) under an Ar atmosphere, and the resulting suspension was cooled to −2 °C. Pyrrolidine was added dropwise (0.68 mL, 8.30 mmol), and the mixture was stirred for 20 min. A solution of sodium cyanoborohydride (291 mg, 4.60 mmol) in MeOH (9 mL) was added via syringe pump over 3.6 h. The reaction mixture was stirred for another 12 h at −2 °C before it was filtered through a pad of Celite. The filter cake was washed with MeOH, and the filtrate was concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water. The aqueous layer was washed with ethyl acetate. The combined organic extract was dried over K_2CO_3, concentrated, and purified by flash column chromatography to yield **1-E** as a pale yellow oil. 1.0 g, 53% yield. $[\alpha]_D^{20} = -50.1$ (*c* 1.1, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 5.17 (d, *J* = 53.1 Hz, 1H), 3.91–4.02 (m, 1H), 3.48–3.65 (m, 2H), 2.38–2.74 (m, 7H), 1.94–2.10 (m, 1H), 1.71 (s, 4H), 1.44 (s, 5H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −169.9 (m, 1F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 93.3 (J_{C-F} = 177.8 Hz, minor), 92.5 (J_{C-F} = 175.7 Hz, major), 79.2, 60.0, 59.2 (major), 58.5 (minor), 55.4 (minor), 54.0 (major), 53.1 (major), 52.8 (minor), 35.5 (J_{C-F} = 20.2 Hz, major), 34.7 (J_{C-F} = 20.2 Hz, minor), 28.1, 23.2. HRMS (EI) calcd for $C_{14}H_{25}FN_2O_2$ (M^+) 272.1900, found 272.1905. IR (KBr, cm^{-1}): 2972, 2934, 2824, 2798, 2769, 1693, 1455, 1408, 1365, 1243, 1182, 1116, 1084, 883.

4.2.5. (*S,S*)-2-((Pyrrolidin-1-yl)methyl)-4-fluoro-pyrrolidine 1-F

Compound **1-E** (435.5 mg, 1.60 mmol) was treated with $HCl{\cdot}Et_2O$ solution (3 mL), and the mixture was stirred overnight at room temperature. The solvent was then evaporated in vacuo, and the residue was dissolved in a 1 M NaOH solution. The reaction mixture was stirred for 2 h at room temperature, and then extracted with ethyl acetate. The combined organic extract was dried over Na_2SO_4, and the solvent was evaporated in vacuo to give **1-F** as a pale yellow oil, 275.4 mg, 90% yield. $[\alpha]_D^{20} = +13.5$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, MeOH-d_4): δ 5.23 (dt, *J* = 55.1, 4.2, 1H), 3.16–3.25 (m, 2H), 2.85 (ddd, *J* = 35.4, 13.0, 3.8 Hz, 1H), 2.52–2.68 (m, 6H), 2.19–2.34 (m, 1H), 1.65–1.80 (m, 5H) ppm. ^{19}F NMR (376 MHz, MeOH-d_4): δ −170.94 (m, 1F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 94.8 (J_{C-F} = 173.0 Hz), 61.6, 57.0, 54.5, 53.7 (J_{C-F} = 23.0 Hz), 38.0 (J_{C-F} = 20.0 Hz), 23.5. HRMS (ESI) calcd for $C_9H_{18}FN_2$ ($M+H^+$) 173.1454, found 173.1449. IR (KBr, cm^{-1}): 3338 (br), 2928, 2855, 2798, 1456, 1406, 1378, 1304, 1156, 861.

4.3. General Michael addition procedure

To a solution of **1-F** (0.1 equiv) in ketone (5.0 equiv) was added TFA (0.1 equiv) at room temperature. Next, nitroolefin **2** (1.0 equiv) was added to the solution. The mixture was stirred at room temperature until TLC showed complete conversion. The solvents were removed in vacuo, and the products were purified by flash column chromatography on silica gel.

4.3.1. (*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]cyclohexanone 4a

A white solid, 97% yield; 50:1 dr (*syn*/*anti*), 96% ee; $[\alpha]_D^{20} = -29.6$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.31 (m, 3H), 7.14–7.16 (m, 2H), 4.92 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.60 (dd, *J* = 11.7, 10.9 Hz, 1H), 3.74 (td, *J* = 10.0, 4.4 Hz, 1H), 2.66–2.72 (m, 1H), 2.35–2.46 (m, 2H), 2.06–2.08 (m, 1H), 1.52–1.76 (m, 4H), 1.19–1.22 (m, 1H) ppm. HPLC (Chiralpak PC column, hexanes/*i*-PrOH = 95:5, flow rate = 0.6 mL/min, λ = 214 nm): t_R (*syn* isomer) = 50.73 (minor), 59.13 (major) min.

4.3.2. (*S*)-2-[(*R*)-2-Nitro-1-*p*-methoxyphenylethyl]cyclohexanone 4b

A white solid, 91% yield; 99:1 dr (*syn*/*anti*), 93% ee; $[\alpha]_D^{20} = -23.5$ (*c* 1.1, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.90 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.57 (dd, *J* = 12.3, 10.1 Hz, 1H), 3.77 (s, 3H), 3.70 (td, *J* = 10.1, 4.5 Hz, 1H), 2.59–2.64 (m, 1H), 2.36–2.45 (m, 2H), 2.03–2.06 (m, 1H), 1.52–1.76 (m, 4H), 1.20–1.25 (m, 1H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 214 nm): t_R (*syn* isomer) = 17.18 (minor), 20.78 (major) min.

4.3.3. (*S*)-2-[(*R*)-2-Nitro-1-*p*-tert-butylphenylethyl]cyclohexanone 4c

A colorless oil, 80% yield; 30:1 dr (*syn*/*anti*), 88% ee; $[\alpha]_D^{20} = -15.6$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.91 (dd, *J* = 12.5, 4.6 Hz, 1H), 4.63 (dd, *J* = 12.5, 9.9 Hz, 1H), 3.74 (td, *J* = 9.9, 4.5 Hz, 1H), 2.59–2.80 (m, 1H), 2.26–2.53 (m, 2H), 2.05–2.09 (m, 1H), 1.58–1.75 (m, 5H), 1.29 (s, 9H) ppm. HPLC (Chiralpak PA-2 column, hexanes/*i*-PrOH = 70:30, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 10.58 (major), 16.58 (minor) min.

4.3.4. (*S*)-2-[(*R*)-2-Nitro-1-*p*-chlorophenylethyl]cyclohexanone 4d

A white solid, 92% yield; 33:1 dr (*syn*/*anti*), 91% ee; $[\alpha]_D^{20} = -27.0$ (*c* 1.5, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.91 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.58 (dd, *J* = 12.6, 10.3 Hz, 1H), 3.74 (td, *J* = 10.3, 4.4 Hz, 1H), 2.60–2.65 (m, 1H), 2.34–2.46 (m, 2H), 2.05–2.08 (m, 1H), 1.24–1.79 (m, 4H), 1.19–1.22 (m, 1H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 90:10, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 17.68 (minor), 26.73 (major) min.

4.3.5. (*S*)-2-[(*R*)-2-Nitro-1-*p*-bromophenylethyl]cyclohexanone 4e

A white solid, 86% yield; 49:1 dr (*syn*/*anti*), 98% ee; $[\alpha]_D^{20} = -25.7$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.92 (dd, *J* = 12.6, 4.5 Hz, 1H), 4.59 (dd, *J* = 12.6, 10.1 Hz, 1H), 3.74 (td, *J* = 10.1, 4.5 Hz, 1H), 2.61–2.68 (m, 1H), 2.33–2.49 (m, 2H), 2.07–2.11 (m, 1H), 1.54–1.82 (m, 4H), 1.20–1.27 (m, 1H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, λ = 214 nm): t_R (*syn* isomer) = 17.23 (minor), 29.78 (major) min.

4.3.6. (*S*)-2-[(*R*)-2-Nitro-1-*ortho*-bromophenylethyl]cyclohexanone 4f

A white solid, 92% yield; 99:1 dr (*syn*/*anti*), 96% ee; $[\alpha]_D^{20} = -54.0$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.27–7.31 (m, 1H), 7.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.11–7.15 (m, 1H), 4.88 (d, *J* = 6.0 Hz, 2H), 4.30–4.34 (m, 1H), 2.85–2.87 (m, 1H), 2.35–2.50 (m, 2H), 2.08–2.13 (m, 1H), 1.61–1.84 (m, 4H), 1.33–1.42 (m, 1H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, λ = 214 nm): t_R (*syn* isomer) = 14.83 (minor), 19.83 (major) min.

4.3.7. (*S*)-2-[(*R*)-2-Nitro-1-(2,4-dichlorophenyl)-ethyl]cyclohexanone 4g

A white solid, 94% yield; 99:1 dr (*syn*/*anti*), 99% ee; $[\alpha]_D^{20} = -59.6$ (*c* 0.9, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.15–7.25 (m, 2H), 4.85–4.87 (m, 2H), 4.24 (td, *J* = 9.5, 7.1 Hz, 1H), 2.81–2.87 (m, 1H), 2.31–2.47 (m, 2H), 2.08–2.10 (m, 1H), 1.62–1.82 (m, 4H), 1.30–1.36 (m, 1H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 95:5, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 22.63 (minor), 44.63 (major) min.

4.3.8. (*S*)-2-[(*R*)-1-(Naphthalene-1-yl)-2-nitroethyl]cyclohexanone 4h

A white solid, 77% yield; 99:1 dr (*syn*/*anti*), 98% ee; $[\alpha]_D^{20} = -84.5$ (*c* 0.5, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.43–7.56 (m, 3H), 7.36 (d, *J* = 7.0 Hz, 1H), 5.08 (dd, *J* = 12.4, 3.8 Hz, 1H), 4.87–4.93 (m, 1H), 4.77 (br, 1H), 2.85 (s, 1H), 2.47–2.50 (m, 1H), 2.37–2.43 (m, 1H), 2.05–2.06 (m, 1H), 1.44–1.67 (m, 4H), 1.19–1.27 (m, 1H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 50:50, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 11.28 (minor), 15.23 (major) min.

4.3.9. (*S*)-2-[(*S*)-1-(Furan-2-yl)-2-nitroethyl]cyclohexanone 4i

A white solid, 90% yield; 21:1 dr (*syn*/*anti*), 98% ee; $[\alpha]_D^{20} = -13.2$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 1.7, 0.5 Hz, 1H), 6.26 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.14–6.16 (m, 1H), 4.78 (dd, *J* = 12.5, 4.7 Hz, 1H), 4.64 (dd, *J* = 12.5, 9.5 Hz, 1H), 3.95 (td, *J* = 9.3, 4.7 Hz, 1H), 2.69–2.76 (m, 1H), 2.34–2.45 (m, 2H), 2.04–2.08 (m, 1H), 1.80–1.83 (m, 1H), 1.70–1.75 (m, 1H), 1.59–1.65 (m, 2H), 1.21–1.31 (m, 1H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 90:10, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 15.13 (major), 18.48 (minor) min.

4.3.10. (*S*)-2-[(*S*)-2-Nitro-1-cyclohexylethyl]cyclohexanone 4j

Pale yellow oil, 16% yield; 15:1 dr (*syn*/*anti*), 84% ee; $[\alpha]_D^{20} = -25.0$ (*c* 0.3, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 4.69 (dd, *J* = 13.8, 5.8 Hz, 1H), 4.36 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.65–2.70 (m, 1H), 2.28–2.37 (m, 3H), 2.07–2.10 (m, 2H), 1.93–1.97 (m, 1H), 1.57–1.75 (m, 9H), 1.12–1.25 (m, 3H), 0.87–1.03 (m, 2H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 214 nm): t_R (*syn* isomer) = 13.98 (major), 15.33 (minor) min.

4.3.11. (*S*)-2-((*S*)-1-Nitrohexan-2-yl)cyclohexanone 4k

Pale yellow oil, 43% yield; 20:1 dr (*syn*/*anti*), 96% ee; $[\alpha]_D^{20} = -20.1$ (*c* 0.9, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 4.55 (dd, *J* = 12.3, 6.0 Hz, 1H), 4.39 (dd, *J* = 12.3, 6.5 Hz, 1H), 2.54–2.60 (m, 1H), 2.45–2.51 (m, 1H), 2.37–2.41 (m, 1H), 2.26–2.34 (m, 1H), 2.07–2.13 (m, 2H), 1.92–1.95 (m, 1H), 1.61–1.70 (m, 2H), 1.42–1.49 (m, 1H), 1.25–1.32 (m, 6H), 0.87–0.92 (m, 3H) ppm. HPLC (Chiralpak AD-H column, hexanes/*i*-PrOH = 70:30, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 10.70 (major), 12.57 (minor) min.

4.3.12. (*R*)-Tetrahydro-3-[(*R*)-2-nitro-1-phenylethyl]pyran-4-one 4l

A white solid, 92% yield; 39:1 dr (*syn*/*anti*), 95% ee; $[\alpha]_D^{20} = -36.2$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.34 (m, 3H), 7.17–7.19 (m, 2H), 4.92 (dd, *J* = 12.8, 4.5 Hz, 1H), 4.62 (dd, *J* = 12.7, 10.2 Hz, 1H), 4.10–4.15 (m, 1H), 3.65–3.85 (m, 3H), 3.25 (dd, *J* = 11.5, 9.0 Hz, 1H), 2.84–2.90 (m, 1H), 2.61–2.65 (m, 1H), 2.50–2.65 (m, 1H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 214 nm): t_R (*syn* isomer) = 28.83 (minor), 60.48 (major) min.

4.3.13. 2-Nitro-1-phenylethyl cyclopentanone (*syn* and *anti*) 4m

A white solid, mixture, 84% yield; 2:1 dr (*syn*/*anti*), 88% ee (*syn*), 86% ee (*anti*); $[\alpha]_D^{20} = -44.2$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.33 (m, 4.5H), 7.15–7.19 (m, 3H), 5.32 (dd, *J* = 12.9, 5.5 Hz, 1.5H), 4.70 (dd, *J* = 12.9, 10.0 Hz, 1.5H), 3.80–3.85 (m, 0.5H, *anti*-isomer), 3.69 (td, *J* = 9.6, 5.5 Hz, 1H, *syn*-isomer), 2.30–2.42 (m, 3H), 2.06–2.18 (m, 1.5H), 1.85–1.92 (m, 3H), 1.66–1.71 (m, 3H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 214 nm): t_R (*syn* isomer) = 22.58 (minor), 36.38 (major) min; t_R (*anti* isomer) = 23.93 (major), 29.38 (minor) min.

4.3.14. (*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]cycloheptanone 4n

A colorless oil, 69% yield; 17:1 dr (*syn*/*anti*), 80% ee; $[\alpha]_D^{20} = -14.6$ (*c* 1.0, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.33 (m, 3H), 7.15–7.17 (m, 2H), 4.64 (dd, *J* = 6.8, 2.6 Hz, 2H), 3.65–3.71 (m, 1H), 2.98 (td, *J* = 10.4, 3.4 Hz, 1H), 2.49–2.53 (m, 2H), 1.83–1.90 (m, 2H), 1.54–1.75 (m, 3H), 1.13–1.24 (m, 3H) ppm. HPLC (Chiralpak AD column, hexanes/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 214 nm): t_R (*syn* isomer) = 12.23 (minor), 15.23 (major) min.

4.3.15. (*S*)-2-[(*R*)-1-(2,3-Dimethoxyphenyl)-2-nitroethyl]cyclohexanone 4o

A white solid, 56% yield; 49% ee; $[\alpha]_D^{20} = -1.5$ (*c* 0.6, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$, 589 nm): δ 7.19–7.33 (m, 5H), 4.67 (dd, *J* = 12.3, 6.8 Hz, 1H), 4.58 (dd, *J* = 12.3, 7.8 Hz, 1H), 3.96–4.03 (m, 1H), 2.89 (d, *J* = 7.0 Hz, 2H), 2.10 (s, 3H) ppm. HPLC (Chiralpak AS column, hexanes/*i*-PrOH = 80:20, flow rate = 0.5 mL/min, λ = 214 nm): t_R = 30.53 (minor), 40.88 (major) min.

4.3.16. (*E*)-(*S*)-2-((*S*)-1-Nitro-4-phenylbut-3-en-2-yl)cyclohexanone 4q

A white solid, 84% yield, 14:1 dr (*syn*/*anti*), 99% ee; $[\alpha]_D^{20} = -60.1$ (*c* 1.1, $CHCl_3$, 589 nm). ^1H NMR (400 MHz, $CDCl_3$): δ 7.20–7.33 (m, 5H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 9.6 Hz, 1H), 4.65 (dd, *J* = 11.9, 4.7 Hz, 1H), 4.54 (dd, *J* = 11.9, 8.5 Hz, 1H), 3.33 (qd, *J* = 8.5, 4.8 Hz, 1H), 2.33–2.64 (m, 1H), 2.40–2.44 (m, 1H), 2.29–2.37 (m, 1H), 2.12–2.17 (m, 1H), 2.05–2.09 (m, 1H), 1.86–1.90 (m, 1H), 1.62–1.68 (m, 2H), 1.38–1.48 (m, 1H) ppm. HPLC (Chiralpak PA column, hexanes/*i*-PrOH = 80:20, flow rate = 0.7 mL/min, λ = 214 nm): t_R (*syn* isomer) = 16.28 (major), 19.41 (minor) min.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 21172243) is gratefully acknowledged.

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