Accepted Manuscript

Ferrocenophane-based bifunctional organocatalyst for highly enantioselective Michael reactions

Wei Yao, Junchao Zhu, Xiaowei Zhou, Ru Jiang, Pingan Wang, Weiping Chen

PII: S0040-4020(18)30736-1

DOI: 10.1016/j.tet.2018.06.036

Reference: TET 29632

To appear in: *Tetrahedron*

Received Date: 11 April 2018

Revised Date: 11 June 2018

Accepted Date: 15 June 2018

Please cite this article as: Yao W, Zhu J, Zhou X, Jiang R, Wang P, Chen W, Ferrocenophane-based bifunctional organocatalyst for highly enantioselective Michael reactions, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.06.036.

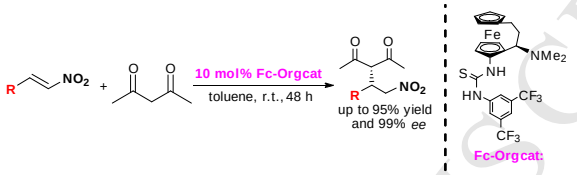
Graphical Abstract

Ferrocenophane-based bifunctional organocatalyst for highly enantioselective Michael reactions

Leave this area blank for abstract info.

Wei Yao, Junchao Zhu, Xiaowei Zhou, Ru Jiang, PinganWang‡andWeiping Chen‡

Department of Medicinal Chemistry, School of Pharmacy, The Fourth Military Medical University, Changle West Road 169, Xi'an, 710032, P. R. China.



Tetrahedron
journal homepage: www.elsevier.com

Ferrocenophane-based bifunctionalorganocatalyst for highly enantioselective Michael reactions

Wei Yao, Junchao Zhu, Xiaowei Zhou, Ru Jiang, PinganWang‡andWeiping Chen‡

Department of Medicinal Chemistry, School of Pharmacy, The Fourth Military Medical University, Changle West Road 169, Xi'an, 710032, P. R. China.
‡Corresponding authors: ping_an1718@outlook.com, wpchen@fmmu.edu.cn.

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Ferrocenophane-based organocatalysts
Michael addition
acetylacetone
trans-β-nitroolefins

ABSTRACT

Highly enantioselective Michael reactions between acetylacetoneand*trans*-β-nitroolefinsare achieved by a novel ferrocenophane-based tertiary amine-thioureaorganocatalyst to provide the corresponding products in good to excellent yields (up to 95%) and enantioselectivities (up to 99% *ee*).

1. Introduction

Michael addition has been played an import role in the field of organic synthesis. Chemists have synthesized numerous organocatalysts used in the Michael additions of different substrates in the past decade[1].Among them, bifunctional amine-thiourea[2] has become one of the most versatilecatalysts. Despite their tremendous utility, these organocatalysts are derived from a very limited range of chiral structural scaffolds.Thetypical bifunctional amine-thioureas include the 1,2-diamine derivatives(Takemoto catalysts)[3], the cinchona-alkaloid-derived catalysts[4]and binaphthyl-based catalysts[5]. Ferrocene is regarded as a "privileged framework" for the construction of effective chiral ligands in metal catalysis due to its specific and unique geometries (adequate rigidity, steric bulkiness and planar chirality), electronic (redox) properties, easy accessibility and derivatization, as well as stability[6]. Ferrocene-based organocatalysts have been developed rapidly in recent decade, and some of them have been synthesized and used in several enantioselective transformations[7].As a part of our continuous research on the development of ferrocene-based chiral ligands and catalysts[8], in 2014, we prepared the first ferrocene-based tertiary amine-thioureaorganocatalysts**1** and investigated its catalytic performance in asymmetric Michael addition[9]. After that, anotherferrocene-based organocatalyst**2** was synthesized by our group[10] and presented excellent catalytic performance in the asymmetric Michael addition of acetylacetone to nitroolefins with high enatioselectivities(up to 96% *ee*).

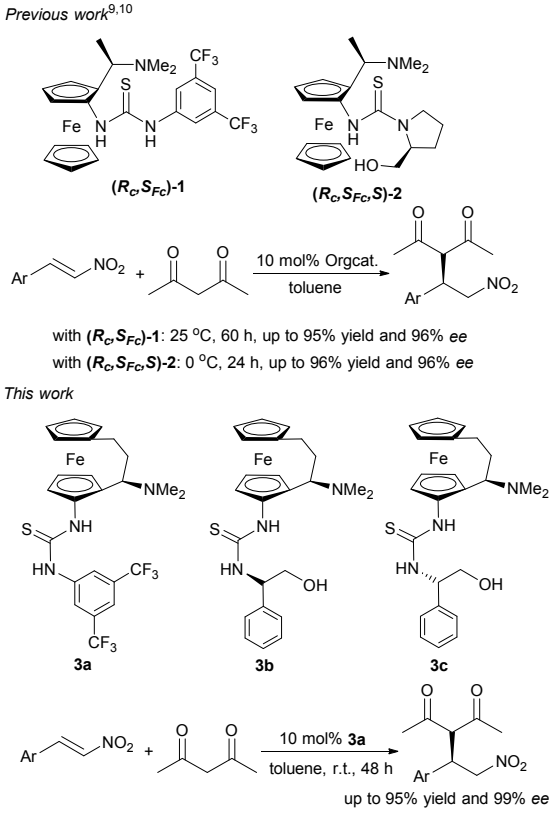


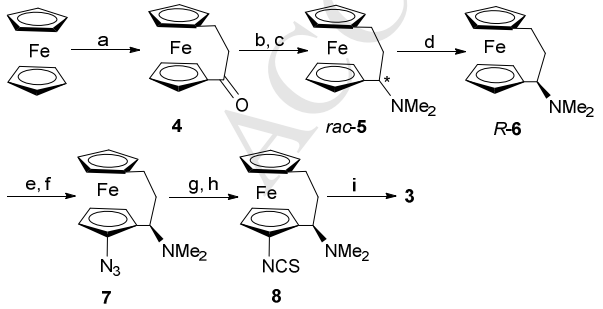
Figure 1. Ferrocene-based chiral organocatalysts for asymmetric Michael additions.

Ferrocenophaneisa kind of orbicular compound which combinesferrocene with cyclic structure, and in the ferrocenophanes, many of the important properties of the ferrocene are retained, such as high electron density, aromaticity, derivatization. Moreover,ferrocenophanes is more rigid and stable than ferrocene. Therefore, those compounds have been developed rapidly from the new century[11]. A class of ferrocenophane-based chiral monophosphines as organocatalysts have been developed by Marinetti[12] and Štěpnička[13] independently for highly enantioselectivecyclization and MBH reaction. Herein, in order to improve the catalytic activity and enantioselectivity, we designed and synthesized novel α-dimethylamino[3]-ferrocenophanethiourea catalysts **3**. We envisioned that, these newly-designed catalysts would be more rigid and stable than previously reported ferrocene-based organocatalysts, andbetter catalytic results should be obtained in the asymmetric Michael addition.

2. Results and discussion

The novel α-dimethylamino[3]-ferrocenophanethiourea catalysts **3** were synthesized using ferrocene as starting material (**Scheme 1**). Thus,Friedel-Crafts reaction of ferrocene with acryloyl chloride gave **4** in 17% yield[14]. Reductionof **4** with $NaBH_4$, followed by esterification (Ac_2O, pyridine) and amination($HNMe_2$, Et_3N) affordedthe well-known *rac*-**5**[14b] in 59% overall yield.(*R*)-**6** was obtained by resolution of *rac*-**5**using L-tartaric acid. Lithiation of (*R*)-**6** with *t*-BuLi (0°C~rt, 1~2 h) followed by reaction with*p*-toluenesulfonylazide gave the azide**7** in 83% yield. **7** was hydrogenated in the presence of 5% Pd–C at 1 barH_2 pressure to afford the diamine,and then followed by reaction with CS_2 and EDC gave isothiocyanate**8** in 68% yield. Finally, **8** was treated with 3,5-Bis(trifluoromethyl)aniline or L/D-plenylglycinol to give the corresponding thiourea catalysts **3** in 84-90% yields.

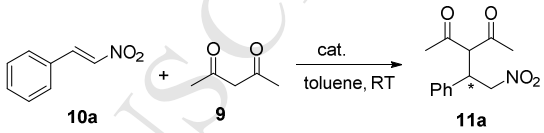
Scheme1. Synthesis of α-dimethylamino[3]-ferrocenophanethiourea catalysts **3**.



Reagents and conditions: a) acryloyl chloride, $AlCl_3$, DCM, -78°C, overnight; b) $NaBH_4$, Ac_2O, pyridine, r.t., overnight; c) $HNMe_2$, Et_3N, methanol, 75°C reflux, 4~6 h; d) L-tartaric acid, methanol, NaOHaq.; e) *t*-BuLi, TBME, 0 °C–r.t., 1-2 h; f) *p*-toluenesulfonylazide, TBME, −78 °C–r.t., 5 h; g) H_2, 5% Pd–C,MeOH, r.t., 4 h; h) CS_2, EDC, THF, -10 °C–r.t., overnight; i) 3,5-$(CF_3)_2C_6H_3NH_2$ (for **3a**) or L/D-plenylglycinol (for **3b** and **3c**), THF, r.t., 6~8 h.

The performances of **3** were initially evaluted in the model Michael addition of acetylacetone **9** to trans-β-nitrostyrene**10a** in the presence of 10 mol% of catalyst at room temperature, and the results are summarized in Table 1. Compared to catalysts **1** and **2**, the more rigid and stable dimethylamino[3]-ferrocenophanethiourea catalyst **3a** exhibited better catalytic results (Table 1, entry 3); compared with **1**,**3b** and **3c** also significantly enhanced the catalytic activity, but theenantioseletivity dropped sharply, especially **3c** (Table 1,entries 4-5), it proves that the configuration of the β-amino alcohol moiety in the catalysts is an important factor for enantioselectivities. Therefore, we chose the [3]-ferrocenophanethiourea catalyst **3a** as the organocatalyst for the rest of the study.

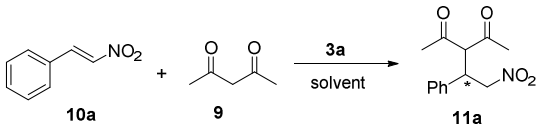
Table 1.Ferrocene-based catalysts screening[a].



Entry	catalyst（10 mol%）	Yield (%)[b]	*ee* (%)[c,]
1	**1**	55	80
2	**2**	91	80
3	**3a**	**85**	**86**
4	**3b**	78	51
5	**3c**	73	6

[a]Unless otherwise specified, the reactions were performed with 0.2mmol of **10a** and 0.4mmol of **9** in 1.0 mL of toluene for 48h.[b]Isolated yield. [c]Determined by chiral HPLC analysis [d]Absolute configuration was confirmed by comparing the HPLC data with that reported in the literature[16].

Table 2 Reaction conditions screening[a].



Entry	Solvent	Temp.	Yield(%)[b]	*ee*(%)[c,d]
1	$CHCl_3$	r.t.	65	55
2	CH_2Cl_2	r.t.	72	68
3	CH_3CN	r.t.	82	21
4	1,4-dioxane	r.t.	85	38
5	MeOH	r.t.	65	3
6	Et_2O	r.t.	45	64
7	xylene	r.t.	78	72
8	THF	r.t.	87	61
9	toluene	r.t.	85	86
10	toluene	0°C	65	78
11	toluene	-20°C	62	76
12	toluene	50°C	90	69
13[e]	toluene	rt	87	81
14[f]	toluene	rt	82	78

[a]Unless otherwise specified, the reactions were performed with 0.2 mmol of **10a** and 0.4mmol of **9** in 1.0 mL of toluene for 48h.[b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Absolute configuration was confirmed by comparing the

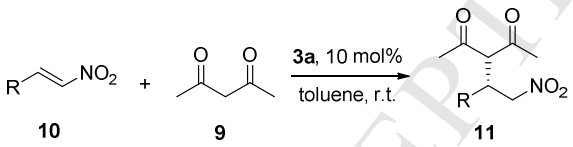
HPLC data with that reported in the literature[16]. [e]Reaction with catalyst loading of 20 mol%.[f]Reaction with catalyst loading of 5 mol%, 60h.

After screening of catalysts, we investigated the influence of different experimental conditions, and the results are summarized in Table 2. The choice of solvent plays a critical role in the reaction. Reactions in chlorinated solvents (CH_2Cl_2, $CHCl_3$) afforded the desired Michael adduct**(*S*)-11a** with moderate to good yields (65-72%) and enantioselectivities (55-68% *ee*) (Table 2, entries 1-2). More polar solvents such as dioxane and CH_3CN decreased remarkably the enantioselectivity (Table 2, entries 3-4). Moreover, the use of a protic solvent, such as MeOH, afforded an almost racemic mixture (Table 2, entry 5). While the nonpolar solvents improved the enantioseletivity significantly (Table 2, entries 6-9). Like most Michael addition of β-nitrostyrene with acetylacetone catalyzed by bifunctionalamine–thioureas[15], toluene is the best solvent in the reaction (Table 2, entry 9), possibly due to the increased hydrogen bondingactivation of β-nitrostyrene by **3a** in the nonpolarsolvents.

We also explored the effect of reaction temperature. As shown in Table 2, increasing the reaction temperature from r.t. to 50°C, the selectivity decreased remarkably (Table 2, entry 12). Surprisingly, lowering the reaction temperature from r.t. to 0°C or -20°C had no beneficial effect on the enantioselectivity (Table 2, entries 10-11). In addition, increasing the catalyst loading to 20 mol% had only a marginal effect on both yield and enantioselectivity (Table 2, entry 13).

Next we explored the scope of this organocatalyzed conjugate addition reaction by variousnitroalkenes under the optimal conditions: **9** (0.4 mmol, 2.0 equiv) and **10a** (0.2 mmol, 1.0 equiv)

Table 3 Asymmetric Michael addition of acetylacetone to *trans*-β-nitrostyrene catalyzed **3a**[a].



Entry	R	Product	Yield(%)[b]	*ee*(%)[c,d]
1	C_6H_5(**10a**)	**11a**	85	86
2	2-F-C_6H_4(**10b**)	**11b**	90	91
3	2-Cl-C_6H_4(**10c**)	**11c**	89	97
4	**2-Br-C_6H_4 (10d)**	**11d**	**88**	**99**
5	2-NO_2-C_6H_4 (**10e**)	**11e**	67	91
6	2,3-Cl_2-C_6H_3 (**10f**)	**11f**	95	87
7	3-Br-C_6H_4 (**10g**)	**11g**	86	89
8	3-OMe-C_6H_4 (**10h**)	**11h**	86	95
9	3,5-Cl_2-C_6H_3 (**10i**)	**11i**	87	80
10	4-F-C_6H_4(**10j**)	**11j**	78	90
11	4-Cl-C_6H_4 (**10k**)	**11k**	85	87
12	4-Br-C_6H_4 (**10l**)	**11l**	82	93
13	4-CH_3-C_6H_4 (**10m**)	**11m**	78	94
14	1-naphthyl (**10n**)	**11n**	80	91
15	2-naphthyl (**10o**)	**11o**	82	90
16	2-furyl (**10p**)	**11p**	90	92

[a]Unless otherwise specified, the reactions were performed with0.2mmol of **10a** and 0.4mmol of **9** in 1.0 mL of toluene for 48h.[b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Absolute configuration was confirmed by comparing the HPLC data with that reported in the literature[16].

in 1.0 mL of toluene with 10 mol% of **3a** at room temperature for 48 h, the obtained results are summarized in Table 3. All the nitrostyrenes bearing either electron-donating or electron-withdrawing substituents on the aromatic ring, as shown in Table 3, afforded the desired Michael adduct in excellent yields and enantioselectivities. The*ortho* substituents on the phenyl ring gave relatively higher enantioselectivity, and the 2-bromo derivative gave the highest enantioselectivity (99% *ee*, entry 4). The results indicate that the more rigid and stable [3]-ferrocenophanethiourea catalyst **3a**indeed hashigher catalytic activity and enantioselectivity than the first ferrocene-based thiourea catalysts**1**doesin the asymmetric Michael addition of acetylacetone to nitroolefins. It also proved that, in accord with metal catalysis, the rigid, bulky, planar and carbon-centered chiral [3]-ferrocenophane moiety is an excellent scaffold for chiral organocatalysts.

3. Conclusion

In summary, the novel [3]-ferrocenophanethiourea catalysts have been designed and synthesized. Good levels of reactivity, and excellent enantioselectivities were achieved in the asymmetric Michael addition of acetylacetone tonitroolefinsusing the novel [3]-ferrocenophanethiourea catalyst **3a**,givingthe products with up to 95% yield and 99% *ee*. The results indicate that, compared with the first ferrocene-based thiourea catalyst **1**, the more rigid and stable [3]-ferrocenophanethiourea catalysts have better catalytic activity and enantioselectivity in the asymmetric Michael addition. It again proved that ferrocene can not only be used as the skeleton of ligands in metal catalysis, but alsoan ideal skeleton for building organocatalysts. In this work, we successfully expand the structural types of ferrocene-based organocatalysts. Further work in our lab is still ongoing to expand theirapplications to other valuable transformations and develop other types of organocatalysts based on the ferrocene backbone.

4. Experimental Section

General methods

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer using TMS as an internal reference. Coupling constant (*J*) values were given in Hz. HRMS were recorded on ZAB-HS spectrometer with ES ionization (ESI). All commercially available reagents were used as received. Solvents and reagents were purified and dried by standard methods prior to use. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. All reactions involving air or moisture sensitive species were performed under inert atmosphere in oven-dried glassware. Enantiomeric excesses (*ee*) were determined by HPLC analysis using an Agilent 1100 Series instrumentwith Daicel Chiralpak AD-H column, as indicated.

Preparation of 4

To a solution of $AlCl_3$(13.3 g, 0.1 mol) in dry DCM was added a solution of ferrocene(18.6 g, 0.1 mol) which was dissolved in DCM under argon. Then the mixture was cooled to -78°C, a solution of acryloyl chloride(4.06 mL, 0.05mol) was added dropwise 10 minutes later. After stirring overnight at –78°C, the mixture was poured into ice water, added some 1M HCl and extracted with CH_2Cl_2 (2×50 mL). The combined organic solutions were washed with sodium hydrogen carbonate and water,dried over MgSO4 and the solvent was removed in *vacuo*.The crude product was purified by column chromatography to afford a red brown solid**4** (4.1 g, 17.1%).

Preparation of *rac*-5

4(1.37 g, 5.0 mmol) was weighed into a 100 mL round bottom flask, dissolved with DCM and slowly added a solution of $NaBH_4$(0.57 g, 15 mmol) in MeOH. The reaction was completed after 4~6h, and the solvent was removed. The residue was dissolved with pyridine and acetic anhydride was added to the mixture. The reaction was completed after stirring overnight, the residual acetic anhydride and solvent were removed in vacuo, washed with water and saturated salt solution, dried over $MgSO_4$. The ester compound was obtained, red brown solid.

The ester compound(1.59 g, 5.0 mmol) was dissolved with 10 mL of MeOH, dimethylamine methanol solution(50 mL, 2.0 mol/L in methanol) and trimethylamine(1.4 mL, 10 mmol) were added. The mixture was heated to 75°C and refluxed for 4~6h, cooled to room temperature and removed the solvent. The crude product was obtained and purified by column chromatography to afford a red brown solid *rac*-**5**(1.21 g, 72.9%).

Preparation of *R*-6

L-tartaric acid (3.0 g, 20 mmol) was added to a solution of *rac*-**5** (5.38 g, 20 mmol) in CH_3OH(20 mL) and then heated to 70°C. More methanol were slowly added until the solid was completely dissolved. Then the mixture was cooled to 0°C.After several hours,the solid precipitates were filtered. The solids were added to NaOH solution (10%, 200 mL). The mixture was extracted with diethyl ether (2×50 mL), washed with water. The combined organic solutions were dried over Na_2SO_4, and the solvent was removed *in vacuo* and resulting red brown solid *R*-**6** (>99% *ee*, 2.1 g, 78%).

Preparation of 7

To a degassed solution of *R*-**6**(>99%*ee*, 2.0 g, 7.43 mmol) in TBME (8 mL) was added dropwise at 0°C a solution of *t*-BuLi in pentane (1.6M, 5.62 mL, 9.0 mmol). After stirring for 1 h at ambient temperature, the mixture was cooled to -78°C. A solution of *p*-tosylazide (1.77 g, 9.0 mmol, 1.2equiv) in TBME (8 mL) was added dropwise. The mixture was stirred at –78°C for 5 h, warmed to 0°C, stirred for 10 min, and then $Na_4P_2O_7.10H_2O$(3.73 g, 8.36 mmol, 1.1equiv) in H_2O (100 mL) was added. After stirring overnight at room temperature, the mixture was extracted with CH_2Cl_2 (3×25 mL). The combined organic solutions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography to afford a red brown oil **7** (1.58 g, 83.7%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.43 (q, *J* = 2.0 Hz, 1H), 4.35 (t, *J* = 2.0 Hz, 1H), 4.12 – 4.10 (m, 1H), 3.98 (q, *J* = 2.5 Hz, 2H), 3.93 (dt, *J* = 2.6, 1.5 Hz, 2H), 2.61 (dt, *J* = 15.6, 11.3 Hz, 3H), 2.33 (m, 1H), 2.28 (s, 6H), 2.04 – 1.94 (m, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 98.15, 89.70, 74.83, 72.37, 71.62, 70.77, 70.33, 66.77, 66.52, 64.47, 61.06, 44.69, 37.86, 25.80.

Preparation of 8

7(1.5 g, 5.9 mmol) was dissolved in MeOH (40 mL). The solution was degassed by passing nitrogen for 5 min. Then 5% Pd/C (0.25 g) was added and the mixture was stirred for 4 h at a H_2 pressure of 1bar. The mixture was filtered through Celite and washed with a small amount of CH_2Cl_2. The solvent was removed and resulting crude primary amine product. Then 10 mL THF was added under the nitrogen, cooled to -10 °C. A solution of CS_2 (2 mL, 36 mmol) and EDC (1.5 g, 6 mmol) in THF (10 mL) was added dropwise, The mixture was stirred at –10°C for 2 h, warmed to room temperature, stirred overnight. The solvent was removed, washed with water and extracted with CH_2Cl_2 (3×10 mL). The combined organic solutions were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by column chromatography to afford **8** (1.3 g, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.49 – 4.42 (m, 2H), 4.11 (dd, *J* = 2.5, 1.3 Hz, 1H), 4.00 (dd, *J* = 8.0, 1.8 Hz, 3H), 3.93 (td, *J* = 2.4, 1.2 Hz, 1H), 2.97 (dd, *J* = 11.4, 2.3 Hz, 1H), 2.66 (ddd, *J* = 14.4, 4.1, 2.9 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.38 – 2.32 (m, 1H), 2.29 (s, 6H), 2.07 (td, *J* = 13.5, 3.0 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 90.05, 84.66, 74.27, 71.83, 71.48, 70.72, 68.51, 67.60, 66.19, 65.56, 43.51, 38.48, 25.95, 15.29.

General procedure for the synthesis of catalyst 3

To a solution of **8**(300 mg, 0.92 mmol) in THF was added a solution of primary amino compounds(0.95 mmol) in THF at 0°C under the argon, warmed to room temperature, stirred for 12 h. The solvent was removed and then purified by column chromatography to give the products of **3a**,**3b** and **3c**.

3a, 90% yield; yellow crystals; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.21 (s, 1H), 8.80(s, 1H), 8.13 (s, 2H), 7.72 (s, 1H), 4.39 (s, 1H), 4.30 (s, 1H), 4.22 (s, 1H), 4.05 (t, *J* = 2.2 Hz, 4H), 3.98 (s, 1H), 2.64 (d, *J* = 13.0 Hz, 2H), 2.37 (s, 6H), 2.21 (d, *J* = 12.6 Hz, 1H), 1.97 (t, *J* = 14.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.00, 140.94, 132.06 (d, *J* = 33.7 Hz), 124.45, 123.69, 121.73, 118.87 (d, *J* = 31.0 Hz), 91.98, 89.45, 81.96, 72.84, 70.80, 70.27, 68.97, 67.93, 65.88, 65.29, 60.73, 45.06, 37.95, 24.71. HRMS(ESI) Calcd for $C_{24}H_{23}F_6FeN_3S$+H $(M+H)^+$: 556.0945, Found: 556.0942.

3b, 84% yield; yellow crystals; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.37 (d, *J* = 5.3 Hz, 1H), 6.02 (s, 1H), 4.52 (s, 1H), 4.23 – 4.15 (m, 3H), 4.03 (s, 4H), 3.94 (d, *J* = 2.4 Hz, 1H), 2.56 (dt, *J* = 25.6, 9.7 Hz, 4H), 2.30 (s, 6H), 2.16 (q, *J* = 12.5 Hz, 1H), 1.90 (t, *J* = 13.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.43, 138.47, 129.05, 127.89, 126.86, 92.44, 89.24, 80.88, 72.52, 70.85, 70.18 67.68 (d, *J* = 12.6 Hz), 66.55, 65.06 (d, *J* = 8.9 Hz), 60.31, 57.98, 45.20, 38.32, 24.53. HRMS(ESI) Calcd for $C_{24}H_{29}F_6FeN_3OS$+H $(M+H)^+$: 464.1459, Found: 464.1452.

3c, 86% yield; yellow crystals; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.72 – 7.67 (m, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz,

1H), 5.85 (s, 1H), 4.23 (ddd, *J* = 15.1, 9.1, 4.7 Hz, 3H), 4.11 (s, 1H), 3.98 (s, 1H), 3.91 (t, *J* = 2.6 Hz, 1H), 3.85 (d, *J* = 3.0 Hz, 1H), 3.63 (s, 1H), 3.49 (s, 1H), 2.65 – 2.42 (m, 4H), 2.30 (s, 6H), 2.16 – 2.00 (m, 1H), 1.83 (t, *J* = 13.5 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.31, 138.79, 129.11, 128.30, 127.57, 92.68, 88.91, 80.50, 72.24, 70.29 (d, *J* = 23.5 Hz), 67.69, 67.43, 65.66, 65.04, 60.32, 57.71, 45.13. HRMS(ESI) Calcd for $C_{24}H_{29}F_6FeN_3OS$+H $(M+H)^+$: 464.1459, Found: 464.1446.

General procedure for asymmetric Michael addition

The catalyst **3a**(5.55 mg, 0.01 mmol) was added to a vial containing 2,4-pentanedione (0.4 mmol) and nitroolefin (0.2 mmol) in 1 mL of dried toluene. After 48 hours of stirring at room temperature, TLC analysis indicated completion of the reaction. The reaction mixture wasconcentrated and purified by column chromatography to afford the Michael addition products **11a-11p**. Spectral data match those previously reported[16].

(*S*)-3-(2-Nitro-1-phenyl-ethyl)-pentane-2,4-dione(11a), white solid, 85%yield, 86% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*)δ7.35 – 7.29 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 2H), 4.68 – 4.59 (m, 2H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.29 – 4.21 (m, 1H), 2.29 (s, 3H), 1.94(s, 3H). ChiralpakAD-H column, Hex:*i*-Pro =90:10, 1mL/min, wavelength=210 nm. t_r =10.6 min [major(*S*)-enantiomer], t_r = 14.0 min [minor (*R*)-enantiomer].

(*S*)-3-[1-(2-Fluoro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11b),white solid, 90% yield, 91%*ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 1H), 7.19 (td, *J* = 7.7, 1.9 Hz, 1H), 7.15 – 7.06 (m, 2H), 4.79 – 4.72 (m, 1H), 4.68 – 4.62 (m, 1H), 4.50 (q, *J* = 3.3, 2.8 Hz, 2H), 2.32 (s, 3H), 2.04 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =95:5, 1mL/min, wavelength=210 nm. t_r =15.0min [major(*S*)-enantiomer], t_r = 17.5min [minor(*R*)-enantiomer].

(*S*)-3-[1-(2-Chloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11c), White solid, 89% yield, 97% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 1H), 7.31 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 4.86 (dd, *J* = 12.2, 6.6 Hz, 1H), 4.77 (ddd, *J* = 10.4, 6.6, 3.9 Hz, 1H), 4.68 (dd, *J* = 12.2, 4.0 Hz, 1H), 4.62 (d, *J* = 10.0 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H).ChiralpakAD-H column, Hex:*i*-Pro =98:2, 1mL/min, wavelength=210nm.t_r=16.1 min [major(*S*)-enantiomer], t_r = 17.6min [minor(*R*)-enantiomer].

(*S*)-3-[1-(2-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11d),white solid, 88% yield, 99% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ7.65 (d, *J* = 7.9 Hz, 1H), 7.32 (td, *J* = 7.5, 1.1 Hz, 1H), 7.23 – 7.14 (m, 2H), 4.86 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.79 – 4.73 (m, 1H), 4.69 (dd, *J* = 12.2, 3.8 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H). Chiralpak AD-H column, Hex:*i*-Pro =98:2, 1mL/min, wavelength=210 nm. t_r =20.7 min [major(*S*)-enantiomer], t_r = 22.1 min [minor(*R*)-enantiomer].

(*S*)-3-[2-Nitro-1-(2-nitro-phenyl)-ethyl]-pentane-2,4-dione(11e),white solid, 67% yield, 91% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.64 – 7.48 (m, 2H), 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.00 (dd, *J* = 13.4, 7.1 Hz, 1H), 4.86 (dd, *J* = 13.4, 3.7 Hz, 1H), 4.79 – 4.66 (m, 2H), 2.33 (s, 3H), 2.15 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =98:2, 1mL/min, wavelength=210 nm. t_r = 42.0min [major(*S*)-enantiomer], t_r = 45.6min [minor(*R*)-enantiomer].

(*S*)-3-[1-(2,3-Dichloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11f),colorless oil, 95% yield, 87% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.69 (dd, *J* = 12.0, 3.4 Hz, 1H), 4.60 (d, *J* = 9.4 Hz, 1H), 2.32 (s, 3H), 2.09 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =99.5:0.5, 0.6mL/min, wavelength=210 nm. t_r = 52.2min [major(*S*)-enantiomer], t_r = 59.0min [minor(*R*)-enantiomer].

(*S*)-3-[1-(3-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11g),white solid, 86% yield, 89% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (ddq, *J* = 8.0, 2.3, 1.2 Hz, 1H), 7.38 (t, *J* = 1.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (dt, *J* = 7.9, 1.3 Hz, 1H), 4.70 – 4.58 (m, 2H), 4.36 (d, *J* = 10.6 Hz, 1H), 4.23 (ddd, *J* = 10.7, 7.6, 4.9 Hz, 1H), 2.32 (s, 1H), 2.02 (s, 2H).Chiralpak AD-H column, Hex:*i*-Pro=98:2, 1mL/min, wavelength=210 nm. t_r =22.9min [major(*S*)-enantiomer], t_r = 25.8min [minor(*R*)-enantiomer].

(*S*)-3-[1-(3-Methoxy-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11h),yellow oil, 86% yield, 95%*ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 1H), 6.86 – 6.76 (m, 1H), 6.73 (d, *J* = 2.2 Hz, 1H), 4.71 – 4.57 (m, 2H), 4.39 (dd, *J* = 10.7, 1.7 Hz, 1H), 4.28 – 4.16 (m, 1H), 3.80 (d, *J* = 1.7 Hz, 3H), 2.32 (d, *J* = 1.7 Hz, 3H), 1.99 (d, *J* = 1.7 Hz, 3H).ChiralpakAD-H column, Hex:*i*-Pro =90:10, 1mL/min, wavelength=210 nm. t_r =12.5 min [major(*S*)-enantiomer], t_r = 16.2min [minor(*R*)-enantiomer].

(*S*)-3-[1-(3,5-Dichloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11i),colorless oil, 87%yield, 80% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 2H), 4.70 – 4.58 (m, 2H), 4.34 (d, *J* = 10.4 Hz, 1H), 4.22 (ddd, *J* = 10.4, 7.6, 4.8 Hz, 1H), 2.33 (s, 3H), 2.09 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro=95:5, 1mL/min, wavelength=210nm. t_r=12.6min [major(*S*)-enantiomer], t_r = 14.9min [minor(*R*)-enantiomer].

(*S*)-3-[1-(4-Fluoro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11j), white solid, 78% yield, 90% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 2H), 7.09 – 7.01 (m, 2H), 4.66 – 4.60 (m, 2H), 4.36 (d, *J* = 10.8 Hz, 1H), 4.30 – 4.22 (m, 1H), 2.32 (s, 3H), 1.99 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =85:15, 1mL/min, wavelength=210 nm. t_r =9.8min [major(*S*)-enantiomer], t_r = 18.0min [minor(*R*)-enantiomer].

(*S*)-3-[1-(4-Chloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11k),white solid, 85% yield, 87% *ee*.^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.30 (m, 2H), 7.19 – 7.13 (m, 2H), 4.68 – 4.59 (m, 2H), 4.35 (d, *J* = 10.7 Hz, 1H), 4.29 – 4.20 (m, 1H), 2.32 (s, 3H), 2.00 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =80:20, 1mL/min, wavelength=210 nm. t_r =8.5min [major(*S*)-enantiomer], t_r = 20.8min [minor(*R*)-enantiomer].

(*S*)-3-[1-(4-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione(11l),white solid, 82% yield, 93%*ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 2H), 7.12 – 7.06 (m, 2H), 4.68 – 4.57 (m, 2H), 4.35 (d, *J* = 10.7 Hz, 1H), 4.23 (ddd, *J* = 10.7, 7.4, 5.2 Hz, 1H), 2.32 (s, 3H), 2.00 (s, 3H). Chiralpak AD-H column, Hex:*i*-Pro =80:20, 1mL/min,

wavelength=210 nm. t_r =9.1min [major(*S*)-enantiomer], t_r = 26.7min [minor(*R*)-enantiomer].

(*S*)-3-(2-Nitro-1-p-tolyl-ethyl)-pentane-2,4-dione(11m),white solid, 78% yield, 94% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.67 – 4.57 (m, 2H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.22 (ddd, *J* = 10.9, 7.6, 5.1 Hz, 1H), 2.32 (d, *J* = 4.4 Hz, 6H), 1.96 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =90:10, 1mL/min, wavelength=210 nm. t_r =10.1min [major(*S*)-enantiomer], t_r = 16.2min [minor(*R*)-enantiomer].

(*S*)-3-(1-Naphthalen-1-yl-2-nitro-ethyl)-pentane-2,4-dione(11n),yellow solid, 80% yield, 91%*ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.6 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.44 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 1H), 5.22 (dd, *J* = 10.5, 5.4 Hz, 1H), 4.84 (dd, *J* = 12.2, 6.5 Hz, 1H), 4.79 – 4.68 (m, 2H), 2.35 (s, 3H), 1.90 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =99:1, 1mL/min, wavelength=210nm. t_r=33.9min [major(*S*)-enantiomer], t_r = 35.6min [minor(*R*)-enantiomer].

(*S*)-3-(1-Naphthalen-2-yl-2-nitro-ethyl)-pentane-2,4-dione(11o),light yellow solid, 82% yield, 90%*ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.77 (m, 3H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.32 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.81 – 4.68 (m, 2H), 4.52 (d, *J* = 10.7 Hz, 1H), 4.44 (ddd, *J* = 10.7, 7.9, 4.4 Hz, 1H), 2.35 (s, 3H), 1.97 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =90:10, 1mL/min, wavelength=210nm.t_r =16.0min [major(*S*)-enantiomer], t_r = 20.3min [minor(*R*)-enantiomer].

(*R*)-3-(1-Furan-2-yl-2-nitro-ethyl)-pentane-2,4-dione(11p),colorless oil, 90% yield, 92% *ee*.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.32 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.20 (d, *J* = 3.3 Hz, 1H), 4.68 (d, *J* = 5.5 Hz, 2H), 4.44 – 4.33 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H).Chiralpak AD-H column, Hex:*i*-Pro =90:10, 1mL/min, wavelength=210 nm. t_r =11.1min [major(*R*)-enantiomer], t_r= 13.1min [minor(*S*)-enantiomer].

Acknowledgments

We thank the National Natural Science Foundation of China(21272271, 21372259) for financial support.

References

1 For reviews on organocatalytic Michael reaction, see:
(a) Dalko PIandMoisan L.*Angew. Chem. Int. Ed.***2004**; 43; 5138;
(b) List B.*Chem. Rev.***2007**; 107; 5413
(c) MacMillan DWC. *Nature.***2008**; 455; 304;
(d) Butler RN and Coyne AG.*Chem. Rev*. **2010**; 110; 6302;
(e) List B and Yamamoto H.*Synlett.***2011**; 461;
(f) Hernández JGandJuaristi E.*Chem. Commun.***2012**; 48; 5396;
(g) Scheffler UandMahrwald R.*Chem. Eur. J.***2013**; 19; 14346;
(h)*ComprehensiveEnantioselective Organocatalysis;*Dalko, PI, Ed., Wiley: Weinheim: Germany, **2013**.
(i) Hou XH, Ma ZW, Wang JL and Liu HM.*Chin. J. Org. Chem.***2014**; 34; 1509 (in Chinese);
(j) Mondal A, Bhowmick S, Ghosh A, Chanda TandBhowmick KC.*Tetrahedron: Asymmetry*.**2017**; 28; 849;
(k) Alonso DA, Baeza A, Chinchilla R, Gomez C, Guillena G, Pastor IM and Ramon DJ.*Molecules*.**2017**; 22; 895;
(l) Pellissier H.*Curr.Org. Chem.***2018**; 22; 323.
2 Select reviews on bifunctional amine-thiourea, see:
(a) Zhang Z and Schreiner PR.*Chem. Soc. Rev.***2009**; 38; 1187;
(b) Connon SJ.*Synlett.***2009**; 354;
(c) Siau WY and Wang J.*Catal. Sci. Technol.***2011**; 1; 1298;
(d) Narayanaperumal S, Rivera DG, Silva RCandPaixaoWM.*ChemCatChem*.**2013**; 5; 2756;

(e) Serdyuk OV, Heckel CM, Tsogoeva SB.*Org. Biomol. Chem.***2013**; 11; 7051;
(f) Jakab G, Schreiner PR. In*Comprehensive Enantioselective Organocatalysis;*Dalko, P. I., Ed.; Wiley: Weinheim: Germany, **2013**; pp. 315–342.
(g) Held FE, Tsogoeva SB.*Catal. Sci. Technol.***2016**; 6; 645;
(h) Chen XW, Xin YJ, Liu Q, Lan ZL.*Chin. J. Org. Chem.***2016**; 36; 306 (in Chinese);
(i) Sun YL, Wei Y, Shi M., *ChemCatChem*.**2017**; 9; 718.

3 (a) OkinoT, HoashiY and TakemotoY.*J Am ChemSoc*.**2003**;125;12672;
(b) OkinoT, HoashiY, TakemotoY., et al.*J Am ChemSoc*.**2005**;127;119.
(c)Miyabe H, Takemoto Y.*Bull. Chem. Soc. Jpn*.**2008**;81;785;
(d) Takemoto Y.*Chem. Pharm. Bull.***2010**; 58; 593.

4 (a) VakulyaB, VargaS, CsámpaiA and SoósT.*Org Lett*.**2005**;7;1967;
(b) McCooeySH and ConnonSJ.*AngewChemInt Ed*.**2005**;44;6367;
(c) YeJ, DixonDJ and HynesPS.*ChemCommun*.**2005**;4481;
(d) LiB-J, JiangL, LiuM, WuY., et al.*Synlett*.**2005**;603.
(e) Rao KS, Trivedi R, Kantam ML, *Synlett.* **2015**; 26; 221.

5 (a) WangJ, LiH, DuanW, ZuL and WangW.*Org Lett*.**2005**;7;4713;
(b) RabalakosC and WulffWD.*J Am ChemSoc*.**2008**;130;13524.

6 Selected reviews on ferrocene-based chiral ligands, see:
(a) Hayashi T.In*Ferrocenes*, TogniA, Hayashi T, Ed., Wiley-VCH, Weinheim, **1995**; pp. 105–142;
(b) ArrayásRG,AdrioJandCarretero JC.*Angew. Chem. Int. Ed.***2006**; 45;7674;
(c) Blaser HC, Chen W, Camponovo F andTogni A.In*Ferrocenes: Ligands, Materials and Biomolecules*,Stepnicka P, Ed.,Wiley-VCH, Weinheim, **2008**, pp. 205–236;
(d) Chen W andBlaser HU.In*Phosphorus Ligands in Asymmetric Catalysis*,Börner A, Ed., **2008**, pp. 359–392;
(e) *Chiral Ferrocenes in AsymmetricCatalysis*, DaiL,Hou X, Ed.Wiley-VCH, **2010**.

7 For the review of ferrocene-based organocatalysts, see:
Zhu J-C, Cui D-X, Li Y-D, Wang P-A, et al.*ChemCatChem*.**2018**;10;907.

8 (a) Chen W, Mbafor W, Roberts SM and Whittall J.*J. Am.Chem. Soc.***2006**; 128; 3922;
(b)Chen W, Roberts M and Whittall J.*ChemCommu.* **2016**;916;
(c) Chen W, Mbafor W, Roberts SM and Whittall J.*Tetrahedron: Asymmetry*.**2006**; 17; 1161;
(d) Chen W, McCormack PJ, Whittall J, et al.*AngewChemInt Ed.* **2007**;46;4141;
(e) Chen W, Spindler F, Pugin B, Nettekoven U.*AngewChemInt Ed.* **2013**;52;8652;
(f) NieHF, ZhouG, WangQ, ChenW and ZhangS.*Tetrahedron: Asymmetry*. **2013**;24;1567;
(g) WangQ, LiuXY, LiuX, ChenW, et al. *ChemCommun*. **2014**;50;978;
(h) NieH, YaoL, LiB, ZhangS and ChenW.*Organometallics*.**2014**;33;2109;
(i)Zhang X, Ma P, Zhang D, Lei Y, Zhang S, et al.*Org. Biomol. Chem.***2014**; 12; 2423;
(j) Ma J, Li C, Zhang D, Lei Y, Li M, et al.*RSC Adv.***2015**; 5; 35888;
(k) Liu R, Zhou G, Hall TH, Clarkson GJ, Wills M, et al.*Adv. Synth. Catal.***2015**; 357; 3453;
(l) Li C, Ma P, Lei Y, Chen H, Guan S, et al.*Catal.Lett.***2016**; 146; 1429;
(m) YaoL, WenJ, WoodN, ChenW, ZhangX, et al.*ChemCommun.* **2016**;52;2273;
(n) Yao L, Nie H, Zhang D, Wang L, Zhang Y, et al.*ChemCatChem*.**2018**;10; 804.

9 YaoW, ChenM, LiuX, JiangR, ZhangS and ChenW.*CatalSciTechnol*.**2014**;4;1726.

10 RenXC, ChaiYH, YaoW, ChenW, ZhangS.*Org BiomolChem*.**2015**;13;5054.

11 Selected recent examples, see:
(a) JongSJ and FangJM.*Org Lett*. **2000**;2;1947;
(b) SteudelR, HassenbergK, ZanelloP, et al.*Organometallics*. **2002**;21;2604;
(c) TarragaA, OtonF, EspinosaA, EvansDJ, et al. *ChemCommun*.**2004**;458;
(d) OtonF, TarragaA,EspinosaA, MolinaP, et al.*J Org Chem*.**2005**;70;6603;
(e) MiyaharaY, NishimuraE and SugimuraT.*J Org Chem*.**200**8;73;1783;
(f) TebbenL, BussamannK, ErkerG, et al.*Organometallics*.**2008**;27;4269;
(g) UsenerG, KehrG, FrohlichR, ErkerG, et al.*Organometallics*.**2010**;29;3852;
(h) BaghB, BreitN, GilroyJ, SchatteG, MullerJ.*ChemCommun*.**2012**;48;7823;
(i) VamadoCD, RosenEL, BielawskiCW, et al.*Dalton Trans*.**2013**;42;13251;
(j) ErhardM, LamK, HaddowM, MannersI, et al.*PolymChem*.**2014**;5;1264;
(k) LikA, KarginD, IsenbergS, HeltenH, et al.*ChemCommun*.**2018**;54;2471.

12 (a) VoituriezA, PanossianA, MarinettiA, et al.*J Am ChemSoc*.**2008**;130;14030;
(b) VoituriezA, PanossianA, MarinettA, et al.*Adv Synth Catal*.**2009**;351;1968;
(c) PintoN, NeelM, PanossianA, MarinettiA, et al.*ChemEur J*.**2010**;16;1033;
(d) PintoN, RetailleauP, VoituriezA and MarinettiA.*ChemCommun*.**2011**;47;1015.

13 ŠtěpničkaP, ŠkochK and CísařovăI.*Organometallics*.**2013**;32;623.

14 (a) RosenblumM, BanerjeeAK, SchlatterV, et al.*J Am ChemSoc*.**1963**;85;316;
(b)ChenC, FrohlichR, KehrG and ErkerG.*Organometallics*.**2008**;27;3248.

15 (a) AndresJM, ManzanoR and PedrosaR.*ChemEur J*.**2008**;14;5116;
(b) GaoP, TangC, WangC, WuY and ZhouZ.*Eur J Org Chem*.**2008**;4563;

(c) JiangX, LaiL, LiuX, WangR, WangR, et al.*J Org Chem*.**2009**;74;5562;

(d) PengF-Z, PuX-W, ShaoZ-H and ZhangH-B.*Tetrahedron*.**2010**;66;3655;

(e) GavinDP and StephensJC.*ARKIVOC*.**2011**;407;

(f) Gao X, HuoL-J, LiuY-X, MaZ-W, TaoJ-C, et al.*Tetrahedron: Asymmetry*.**2012**;23;443;

(g) BlochV, GandelmanM, NisnevichG and SuezG.*Eur J Org Chem*.**2012**;118.

16 (a) WangJ, LiH,DuanW, ZuL and WangW.*Org Lett*.**2005**;7;4713;

(b) MalerichJP, HagiharaK and RawalVH.*J Am ChemSoc*.**2008**;130;14416;

(c) YaoW, ChenM, LiuX, ChenW, et al.*CatalSciTechnol*.**2014**;4;1726.

(d) Tukhvatshin, Rinat S, Kucherenko, Alexander S, Nelyubina, Yulia V, Zlotin, Sergei G. *ACS Catalysis*. **2017**;7;2981.