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Ferrocene as a scaffold for effective bifunctional amine–thiourea organocatalysts†

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A simple and readily accessible prototype of the ferrocene-based bifunctional amine–thioureas shows high enantioselectivity in the Michael addition of acetylacetone to nitroolefins, giving the enantioselectivity of up to 96% ee. This work demonstrates that, in accord with metal catalysis, ferrocene could be an excellent scaffold for chiral organocatalysts.

Since the pioneering work of Jacobsen,[1] Schreiner[2] and Takemoto,[3] bifunctional amine–thiourea, which incorporates both Lewis/Brønsted acid and base functionalities into a chiral scaffold within the same molecule, has become one of the most versatile catalysts in asymmetric organocatalysis and has been used in very successful catalysts for numerous enantioselective reactions.[4,5] Despite their tremendous utility, these organocatalysts are derived from a very limited range of chiral structural scaffolds. The typical catalysts of this family include the 1,2-diamine derivatives A (Takemoto catalyst) (Fig. 1),[3] the *cinchona*-alkaloid-derived catalysts such as B, developed independently by four research groups,[6] and binaphthyl based catalysts C.[7] The key to the success of these catalysts is their ability to activate both nucleophilic and electrophilic substrates independently and simultaneously by the discrete functionalities, amine and thiourea, within the same catalyst, and to control their encounter in a well-defined chiral environment.

Ferrocene is 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.[8] Surprisingly, ferrocene has not been exploited as a backbone of organocatalysts[9] except for the use of the planar chiral DMAP[10] and PIP[11] as acyl transfer catalysts for the kinetic resolution of racemic alcohols and amines, as well as simple chiral ferrocene-based phosphines as nucleophilic organocatalysts for the enantioselective boration of olefins,[12] dimerizations of ketenes,[13] [3 + 2] cyclizations[14] and (aza-)Morita–Baylis–Hillman reaction.[15] As a part of our continuous research on the development of ferrocene-based chiral ligands and catalysts,[16] we are interested in exploring the potential of the ferrocene

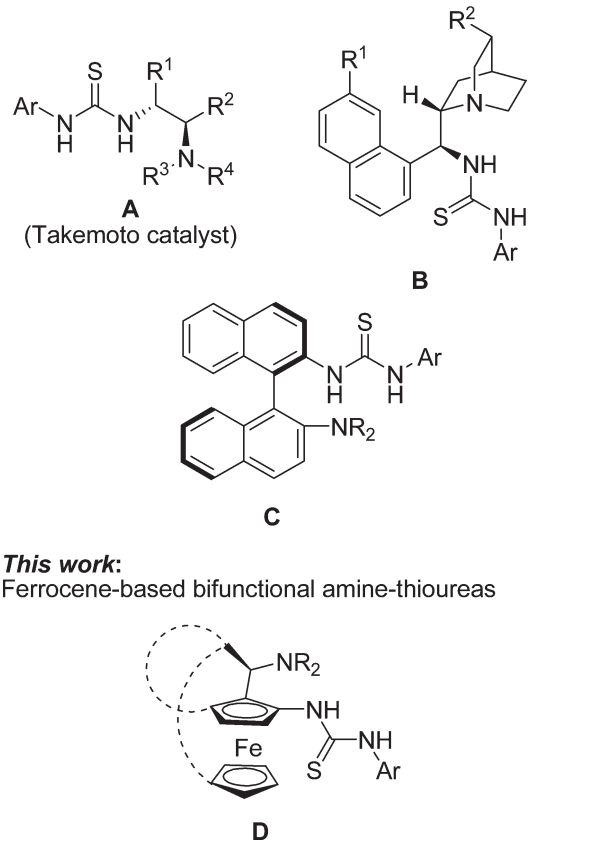

Fig. 1 Structure of bifunctional amine–thioureas.

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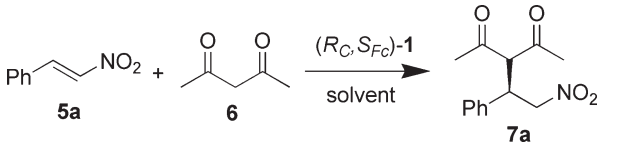
moiety as a scaffold for effective organocatalysts.[17] We envisioned that, in the ferrocene-based bifunctional amine–thioureas with a general structure D (Fig. 1), the rigid, bulky, planar and carbon-centered chiral ferrocene moiety provided effective spatial arrangement and should be an ideal scaffold for organocatalysts, allowing the catalytic transformation with excellent enantioselectivity. Herein, we describe the preliminary results of a simple and readily accessible prototype of the ferrocene-based bifunctional amine–thioureas as an organocatalyst for the enantioselective Michael addition of acetylacetone to nitroolefins. To the best of our knowledge, this is the first example of ferrocene-based bifunctional amine–thioureas.

A simple prototype of the ferrocene-based bifunctional amine–thioureas, (R_C,S_{Fc})-**1** is readily synthesized from (*R*)-Ugi's amine (*R*)-**2** in three steps (Scheme 1). Thus, lithiation of (*R*)-**2** with *t*-BuLi (0 °C ~ rt, 1 h) followed by reaction with *p*-toluenesulfonyl azide gave the azide (R_C,S_{Fc})-**3** in 82% yield. (R_C,S_{Fc})-**3** was hydrogenated in the presence of 5% Pd–C at a H_2 pressure of 1 bar to afford the diamine (R_C,S_{Fc})-**4** in 93% yield. Finally, the bifunctional amine–thiourea (R_C,S_{Fc})-**1** was obtained in 86% yield from the reaction of (R_C,S_{Fc})-**4** with 3,5-bis(trifluoromethyl)phenyl isothiocyanate.

In order to demonstrate the potential of ferrocene as a scaffold for organocatalysts, the performance of (R_C,S_{Fc})-**1** was initially evaluated in the model Michael addition of acetylacetone **6** to *trans*-β-nitrostyrene **5a** in the presence of 10 mol% of catalyst at room temperature, and the results are summarized in Table 1. The choice of solvent plays a critical role in the reaction. Reactions in chlorinated solvents (dichloromethane, $CHCl_3$ and 1,2-dichloroethane) afforded the desired Michael adduct (*R*)-**7a** with moderate to good yields (55–78%) and enantioselectivities (41–70% ee) (Table 1, entries 1–3). More polar solvents, such as CH_3CN, dioxane and *N*,*N*-dimethylformide, decreased remarkably the enantioselectivity (entries 4–6) while an almost racemic mixture was obtained with a protic solvent, such as MeOH and EtOH, or the very polar solvent dimethylsulfoxide (entries 7–9). Nonpolar solvents improved the enantioselectivity (entries 10–13). Like most Michael additions of β-nitrostyrene with acetylacetone catalyzed by bifunctional amine–thioureas,[18] toluene is the best solvent in the reaction (entry 12), possibly due to the increased hydrogen bonding activation of β-nitrostyrene by (R_C,S_{Fc})-**1** in the nonpolar solvent. Lowering the catalyst loading to 5 mol% led to a significant decrease in the enantioselectivity (entry 15). Interestingly, increasing the reaction temperature from 25 °C to 40 °C had only a marginal effect on enantioselectivity (entry 12 *vs.* 16) while the selectivity decreased remarkably when the temperature was changed from 40 °C to 50 °C (entry 16 *vs.* 17). Surprisingly, lowering the reaction temperature from 25 °C to 0 °C had no beneficial effects on the enantioselectivity (entry 18).

Following the establishment of a set of acceptable reaction conditions: **6** (0.40 mmol, 2.0 equiv) and **5a** (0.20 mmol, 1.0 equiv) in 1.0 mL of toluene with 10 mol% of (R_C,S_{Fc})-**1** at 25 °C for 60 h, the substrate scope was explored. As shown in Table 2, all the nitrostyrenes bearing either electron-donating or electron-withdrawing substituents on the aromatic ring gave the desired Michael adducts in good to excellent yields and enantioselectivities. Normally, higher enantioselectivities were obtained with the nitrostyrenes having a substituent at

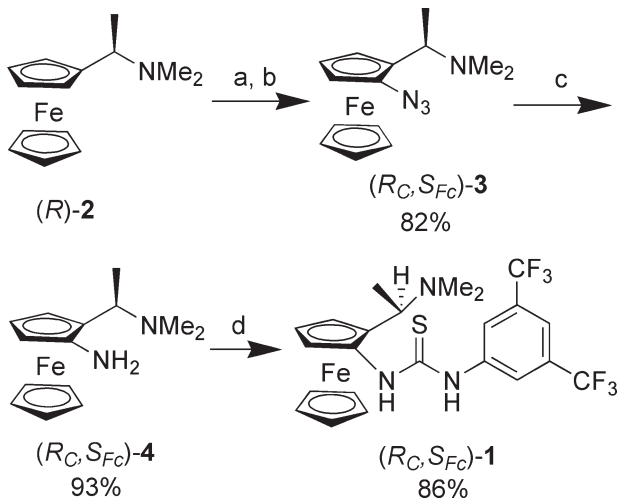
Table 1 Asymmetric Michael addition of acetylacetone to trans-β-nitrostyrene catalyzed by amine–thiourea (R_C,S_{Fc})-**1**[a]



5a **6** **7a**

Entry	Solvent	(R_C,S_{Fc})-**1** (*x* mol%)	Temp (°C)	Yield (%)[b]	ee (%)[c,d]
1	CH_2Cl_2	10	25	55	41
2	$CHCl_3$	10	25	65	40
3	$(ClCH_2)_2$	10	25	78	70
4	MeCN	10	25	69	12
5	Dioxane	10	25	45	19
6	DMF	10	25	80	13
7	MeOH	10	25	35	~0
8	EtOH	10	25	40	~0
9	DMSO	10	25	55	~0
10	THF	10	25	65	64
11	CCl_4	10	25	82	71
12	Toluene	10	25	75	81
13	*o*-Xylene	10	25	85	79
14	Toluene	15	25	78	80
15	Toluene	5	25	50	68
16	Toluene	10	40	90	78
17	Toluene	10	50	90	56
18[e]	Toluene	10	0	65	73

[a] Unless otherwise specified, the reactions were performed using 0.2 mmol of **5a** and 0.4 mmol of **6** in 1.0 mL of solvent for 60 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Absolute configuration was assigned by comparing the optical rotation values with those reported in the literature. [e] Reacted for 72 h.



Scheme 1 Synthesis of ferrocene-based bifunctional amine–thiourea (R_C,S_{Fc})-**1**. Reagents and conditions: a) *t*-BuLi, TBME, 0 °C–rt, 1 h; b) *p*-toluenesulfonyl azide, TBME, −78 °C–rt, 5 h; c) H_2, 5% Pd–C, MeOH, rt, 4 h; d) 3,5-$(CF_3)_2C_6H_3NCS$; CH_2Cl_2, rt, 4 h.

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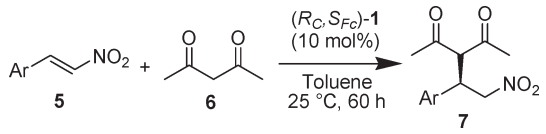
Table 2 Asymmetric Michael addition of acetylacetone to trans-β-nitrostyrene catalyzed by amine–thiourea (R_C,S_{Fc})-**1**[a]



Entry	Ar	Product	Yield (%)[b]	ee (%)[c,d]
1	C_6H_5 (**5a**)	**7a**	75	81
2	2-Cl-C_6H_4 (**5b**)	**7b**	85	96
3	2-Br-C_6H_4 (**5c**)	**7c**	88	92
4	2-F-C_6H_4 (**5d**)	**7d**	92	89
5	2-NO_2-C_6H_4 (**5e**)	**7e**	78	90
6	2-CH_3O-C_6H_4 (**5f**)	**7f**	81	83
7	2,3-Cl_2-C_6H_3 (**5g**)	**7g**	95	95
8	2,4-Cl_2-C_6H_3 (**5h**)	**7h**	90	83
9	3-CH_3O-C_6H_4 (**5i**)	**7i**	78	85
10	3-Br-C_6H_4 (**5j**)	**7j**	75	80
11	4-CH_3O-C_6H_4 (**5k**)	**7k**	72	74
12	4-Cl-C_6H_4 (**5l**)	**7l**	70	84
13	4-Br-C_6H_4 (**5m**)	**7m**	64	80
14	4-F-C_6H_4 (**5n**)	**7n**	65	90
15	4-CF_3-C_6H_4 (**5o**)	**7o**	75	78
16	4-CH_3-C_6H_4 (**5p**)	**7p**	68	89
17	4-EtO-C_6H_4 (**5q**)	**7q**	72	78
18	1-naphthyl (**5r**)	**7r**	72	88
19	2-naphthyl (**5s**)	**7s**	65	77
20	2-furyl (**5t**)	**7t**	80	81

[a] Reaction conditions: **6** (0.40 mmol, 2.0 equiv) and **5** (0.20 mmol, 1.0 equiv) in 1.0 mL of toluene with 10 mol% of (R_C,S_{Fc})-**1** at 25 °C for 60 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Absolute configuration was assigned by comparing the optical rotation values with those reported in the literature.

the 2-position of the phenyl ring (Table 1, entries 2–5), and the 2-chloro derivative gave the highest enantioselectivity (96% ee, entry 2). The preliminary results indicate that the rigid, bulky, planar and carbon-centered chiral ferrocene moiety is indeed an excellent scaffold for bifunctional amine–thiourea, which catalyzes the Michael addition of a variety of *trans*-β-nitrostyrenes with acetylacetone in high enantioselectivity.

The absolute configuration of the Michael adducts was assigned as (*R*) by comparing the optical rotation values with those reported in the literature.[18] A plausible transition state for (R_C,S_{Fc})-**1** catalyzed Michael reaction was proposed (Fig. 2). The dimethylamino group of (R_C,S_{Fc})-**1** deprotonates an acidic proton of acetylacetone, generating the enolate.

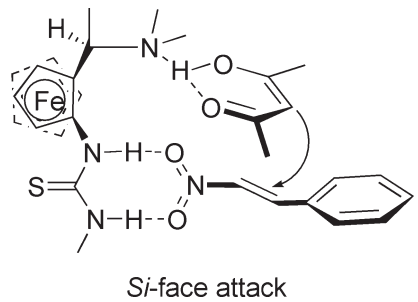


Fig. 2 Plausible transition-state model of Michael reaction.

Meanwhile, the nitrostyrene is activated by the hydrogen bonding interaction of the nitro group with thiourea, in which the bottom Cp ring of ferrocene forces the phenyl ring to orient above the upper Cp ring of ferrocene. Then, the activated acetylacetone enolate attacks the thiourea-activated nitroolefin from the *Si*-face, leading to the formation of (*R*)-adducts.

Conclusions

In summary, a simple and readily accessible ferrocene-based bifunctional amine–thiourea (R_C,S_{Fc})-**1** is highly effective in the Michael addition of acetylacetone to nitroolefins, giving the enantioselectivity of up to 96% ee. This work demonstrates that, in accord with metal catalysis, ferrocene could be an excellent scaffold for chiral organocatalysts for the first time. Work is actively under way in our lab to modify the structure of ferrocene-based bifunctional amine–thioureas, unravel its structure–reactivity–enantioselectivity relationships, expand its application to other valuable transformations and develop other types of organocatalysts based on the ferrocene backbone.

Acknowledgements

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