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Noyori's Ts-DPEN ligand: an efficient bifunctional primary amine-based organocatalyst in enantio- and diastereoselective Michael addition of 1,3-dicarbonyl indane compounds to nitroolefins

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ABSTRACT

Noyori's Ts-DPEN ligand bearing an amino sulfonamide moiety and with a primary amino group on a chiral scaffold was found to be a simple and efficient bifunctional organocatalyst for the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroolefins, which gave highly functional Michael adduct with quaternary stereocenters in good enantioselectivities (up to 84%ee) and dr (up to 5.7:1 dr).

Chiral bifunctional catalysts have attracted growing attention in the past decades.[1] It is considered that by imitating nature, the principle of bifunctional catalysis could offer many advantages.[2] Catalysts that contain two reaction partners in close proximity and with the correct relative geometry could activate and facilitate both reagent and substrate in a controlled environment or, alternatively, one reactive center could be used to bind to the substrate, whilst the second active site performs the chemical transformation.[3] Such synergistic cooperation or dual activation between two functionalities would be similar to enzymatic catalysis. Aspiring to imitate enzymatic synergistic cooperation of multicenters, chemists have succeeded in designing and developing many kinds of bifunctional and multifunctional catalysts for asymmetric synthesis, such as CBS reduction, aminoalcohol-mediated addition of dialkylzinc, Shibasaki's hetero- and homobimetallic catalysts, Jacobsen's metal–salen complexes, and Trost's chiral semiazacrown Zn complex.[4] Since the pioneering works in 2000,[5] impressive progress has been made recently in the development of bifunctional organocatalysis for organic synthesis.[6] And pyrrolidine- and imidazoline-type catalysts with secondary amines are widely used organocatalysts in the past years, in which the asymmetric enamine catalysis of ketone or aldehyde has been commonly accepted.[7] By comparison, chiral primary amine-based bifunctional organocatalysts also received increasing attention.[8] Primary amine catalysis is effectively exploited by enzymes such as type I aldolases, decarboxylases, and dehydratases, each of which contain catalytically active lysine or threonine residues.[9] Considering the particularities and potentials of primary amine-based organocatalysis, we herein report that Noyori's Ts-DPEN ligand with an amino sulfonamide moiety and a primary amino group on a chiral scaffold is revealed to be highly efficient for the asymmetric Michael addition of 1,3-dicarbonyl indane compounds to nitroolefins, which gave highly functional Michael adduct with quaternary stereocenters in good enantioselectivities.

Michael reaction of nitroolefins represents a direct and most appealing approach to chiral nitroalkanes that are versatile intermediates in organic synthesis, which is tied to their propensity to undergo facile α-alkylation reaction and interconversions to other important organic functional groups.[10] Although the catalytic asymmetric versions of this reactions were achieved, most required metal catalyst or strict reactions conditions,[11] and the chiral construction of a quaternary carbon atom via Michael addition is rare.[12] Recently, the utility of urea (thiourea)-based organocatalysts has been proved to be effective in the Michael addition of ketones to nitroolefins, which is due to their strong activation of carbonyl and nitro groups through efficient double-hydrogen-bonding interactions.[13] Notably, *N*-sulfonylcarboxamides, which contain an acidic hydrogen with a pK_a value similar to that of the carboxyl acid group, also represent a novel fine-tuning class of

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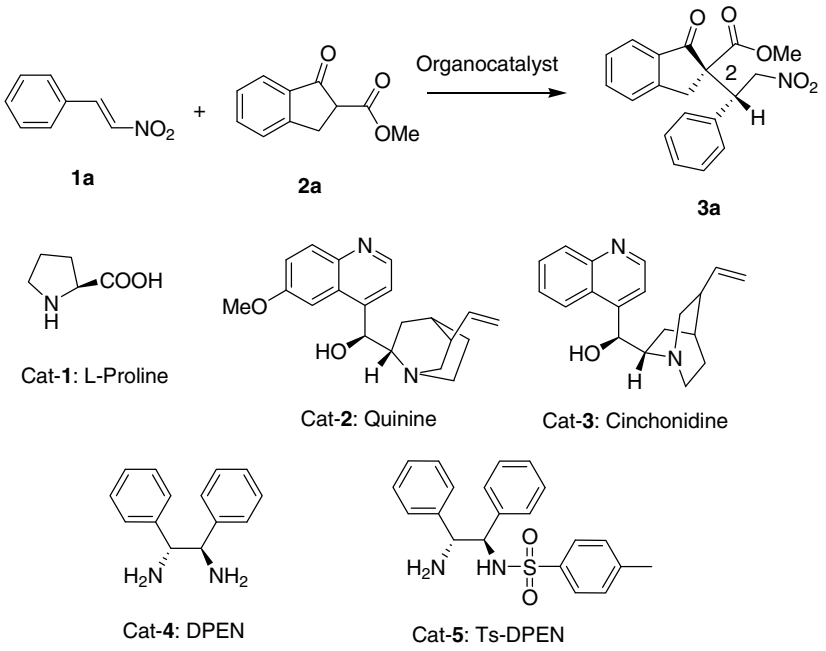


Scheme 1.

highly enantioselective organocatalysts for aldol and Michael addition;[14] however, simple amino *N*-sulfonamides with weak single-hydrogen-bonding interaction received little attractions. Up to date, there are only a few literatures that reported the simple organocatalyst bearing amino *N*-sulfonamides-catalyzed organic transformations.[15] Inspired by the proven ability of thiourea and *N*-sulfonylamides with hydrogen-bonding functionality in the asymmetric addition reactions, we envisioned that an appropriate combination of *N*-sulfonamide and primary amine in a chiral scaffold could result in a potential bifunctional organocatalyst. Herein, we described the asymmetric organocatalytic Michael addition containing tertiary stereocenters, which is promoted by a simple bifunctional organocatalyst bearing an amino sulfonamide moiety and with a primary amino group on a chiral scaffold.

There are few reports of Michael reaction of ketoesters to nitroolefins constructing a stereogenic quaternary carbon center with high diastereo- and enantioselectivity.[12] Therefore the Michael reaction of nitrostyrene (**1a**) and α-substituted cyclic β-ketoester (methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate, **2a**) was selected as model reactions (Scheme 1). Initially, different commercially available organocatalysts were examined, and the results are summarized in Table 1. L-Proline and other chiral Lewis base, including primary diamine, (*R,R*)-1,2-diphenylethylenediamine (DPEN), showed low enantioselectivities and dr (Table 1, entries 1–4). We then synthesized a simple organocatalyst, Ts-DPEN, bearing an amino sulfonamide moiety from (*R,R*)-1,2-diphenylethylenediamine (DPEN), which could activate the nitrostyrene with hydrogen-bonding interactions. It is known that the Ts-DPEN and Noyori's Ts-DPEN ligand, in combination with Ru(II)Cl(^{6}η-arene), exhibited high enantiofacial discrimination ability in hydrogenation.[16] However, to the best of our knowledge, no report is known of Ts-DPEN-catalyzed organic reaction. Herein, to our surprise, as shown in Table 1 (entry 5), the Noyori's Ts-DPEN ligand showed the best enantioselectivities (73% ee and 4:1 dr) compared to previous organocatalyst (cat-1 to cat-4). These results indicated that *N*-sulfonamide is crucial for a high yield and selectivity. We then carried out Michael reaction of nitrostyrene (**1a**) and cyclic β-ketoester (**2a**) in different solvent. Evaluation of usual reaction media led to the further identification of toluene as the best solvent (Table 1, entries 5–9). Further optimization of standard parameters revealed that the reaction carried out at −20 °C in the presence of 5% to 10 mol % of the catalytic Ts-DPEN represents the best reactivity and enantioselectivity (Table 1, entries 10–13).

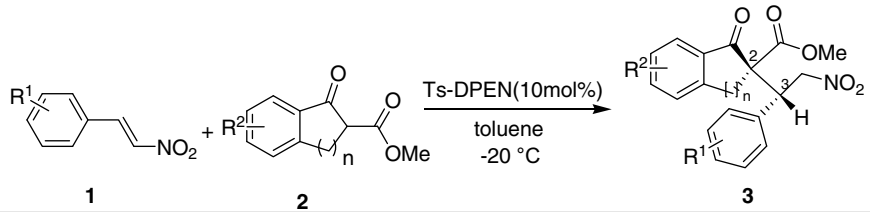
Table 1
Michael reaction of nitrostyrene with various catalysts under different conditions

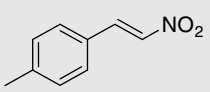
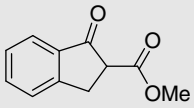
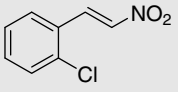
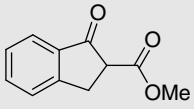
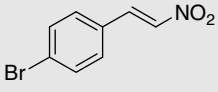
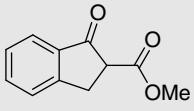
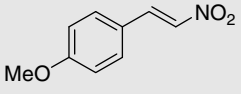
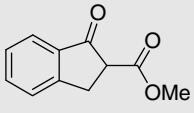
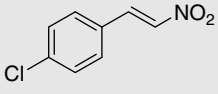
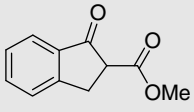
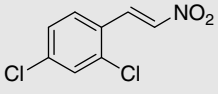
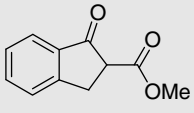
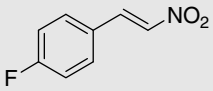
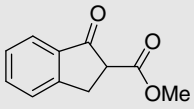
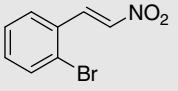
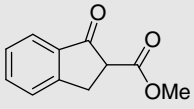
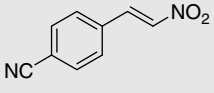
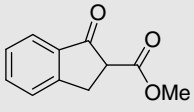
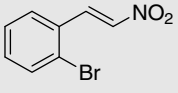
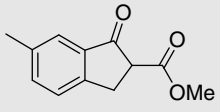
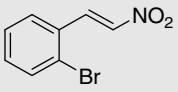
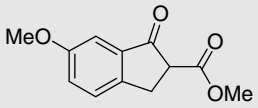
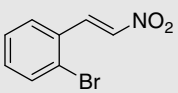
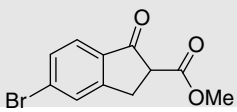
Entry[a]	Cat.	Solvent	*T* (°C)	Yield[b] (%)	dr (2*R*/2*S*)[c]	ee % (major)[d]
1	Cat-1	Toluene	−20	40	1.2:1	2
2	Cat-2	Toluene	−20	67	1.0:1	20
3	Cat-3	Toluene	−20	81	1.4:1	3
4	Cat-4	Toluene	−20	80	1.9:1	11
5	Cat-5	Toluene	−20	87	4.0:1	73
6	Cat-5	MeOH	−20	93	1.2:1	4
7	Cat-5	THF	−20	66	2.3:1	26
8	Cat-5	CH_3CN	−20	60	1.5:1	11
9	Cat-5	DCM	−20	51	2.8:1	42
10	Cat-5	Toluene	20	81	4.0:1	65
11	Cat-5	Toluene	0	90	4.0:1	66
12	Cat-5	Toluene	−78	50	2.3:1	59
13[e]	Cat-5	Toluene	−20	86	4.6:1	70

[a] *Note*: The reaction was performed with 1.0 mmol of nitrostyrene, 1.1 mmol of cyclic β-ketoester (2a), 10 mol % of catalyst, for 24 h.
[b] GC yield.
[c] Determined by ^{1}H NMR.
[d] The ee values of major products were determined by HPLC (see Supplementary data).
[e] 5 mol % of Ts-DPEN.

We next examined the scope of this class of Michael reactions with a series of nitroolefins and cyclic β-ketoesters under the optimized reaction conditions. Table 2 summarizes the results using different substrates. The Michael reaction of different substituted nitroolefins with methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2a**) proceeded smoothly with good enantioselectivities (Table 2, entries 1–9, 67–84% ee). In this way, it was revealed that all the Michael adducts with various nitroolefins were obtained in good yields and enantioselectivities. Furthermore, the Michael reaction of various cyclic β-ketoesters and nitroolefins gave corresponding adducts with good enantioselectivities and yields (entries 10–15, up to 71% ee, up to 5.3 dr). The scope of the reaction

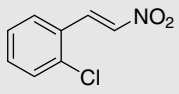
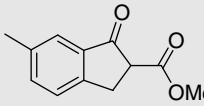
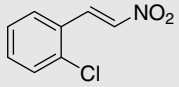
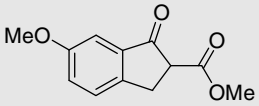
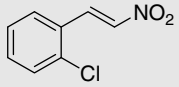
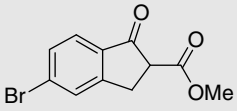
Table 2
Enantio- and diastereoselective Michael reactions of nitroolefins in the presence of catalytic Ts-DPEN



Entry[a]	Nitroolefins	Cyclic β-ketoesters	Time (h)	Yield[b] (%)	dr (2*R*/2*S*)[c]	ee[d] (%)
1			24	85	3.2:1	68
2			24	81	5.7:1	80
3			24	72	4.6:1	73
4			24	78	3.0:1	71
5			24	81	4.9:1	71
6			24	79	4.6:1	69
7			24	85	4.9:1	77
8			24	77	3.3:1	84
9			24	76	5.7:1	67
10			48	72	2.7:1	71
11			48	87	4.8:1	73
12			48	78	3.0:1	68

(*continued on next page*)

Table 2 (*continued*)

Entry[a]	Nitroolefins	Cyclic β-ketoesters	Time (h)	Yield[b] (%)	dr (2*R*/2*S*)[c]	ee[d] (%)
13			48	83	3.2:1	60
14			48	85	5.3:1	70
15			48	87	2.8:1	64

[a] The reaction was performed with 1.0 mmol of nitrostyrene, 1.1 mmol of cyclic β-ketoester **2a**), 10 mol % of Ts-DPEN, in toluene (2 mL), at −20 °C.
[b] Isolated yield.
[c] Determined by ^{1}H NMR.
[d] The ee values of major prodcuts were determined by HPLC (see Supplementary data), and the relative configuration was determined by comparing the retention time of HPLC of products with that of the literature data.[12e]

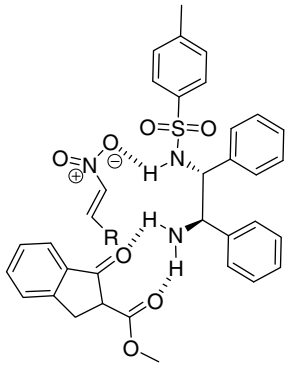


Figure 1. Proposed catalytic reaction mode via dual activation model.

proved to be quite broad to give Michael adducts with quaternary stereocenters in good enantioselectivities.

On the basis of the experimental results described above, the reaction may proceed by the dual activation model,[4,12e,17] the two substrates involved in the reaction are activated simultaneously by Ts-DPEN as shown in Figure 1. The carbonyl group of ketoesters is assumed to interact with primary amine moiety of Ts-DPEN via multiple H-bonds, thus increasing the nucleophilic ability of the reacting carbon center. The *H*-sulfonamide activated nitroolefins via a single hydrogen bond enhanced the electrophilicities of olefin.

In conclusion, Noyori's Ts-DPEN ligand bearing an amino sulfonamide moiety and with a primary amino group on a chiral scaffold was first found to be a simple and efficient bifunctional organocatalyst for the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroolefins, which gave highly functional Michael adduct with quaternary stereocenters in good enantioselectivities (up to 84% ee) and good dr (up to 5.7:1). This provides a new strategy to give practical, synthetically useful, and highly functionalized chiral substituted nitro compounds with quaternary carbon center.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.025.

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