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Diastereoselective and enantioselective capture of chiral zinc enolate using nitroolefins: a rapid access to chiral γ-nitro carbonyl compounds†

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Highly diastereoselective and enantioselective catalytic capture of chiral zinc enolates using nitroolefins as electrophiles is described. The tandem products γ-nitro ketones were obtained in good yields with high diastereoselectivities and enantioselectivities. The γ-nitro ketones were readily hydrogenated to the optically enriched and diastereomerically pure chiral pyrrolidines with four contiguous stereocentres under mild conditions.

The pyrrolidine motifs are important structural scaffolds found in many bioactive molecules.[1] Chiral pyrrolidines form the core of numerous natural products and synthetic analogues displaying a broad and interesting range of biological activities (Fig. 1).[2] They are also useful as synthetic intermediates as well as organocatalysts in asymmetric catalysis.[3]

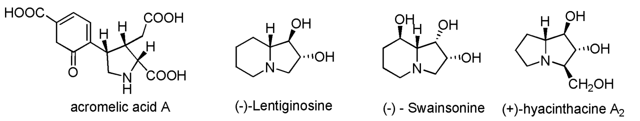
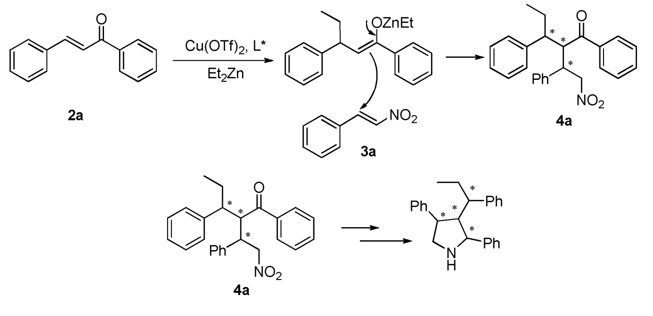


Fig. 1 Representative natural products containing the chiral pyrrolidine motif.

The chiral pyrrolidine derivatives can be readily synthesized from naturally occurring α-amino acids.[4] Other approaches such as the ring closure metathesis (namely RCM) or ring exposure,[5] azomethine ylide cycloaddition,[6] and asymmetric 1,3-dipolar addition[7] and other methods are also employed. Despite the great successes achieved in the past years, highly efficient access to these structurally complex molecules is still urgently required. In this regard, asymmetric tandem C–C bond formations are attractive methodologies which provide access to complex molecules with excellent regio-, chemo-, diastereo-, and enantioselectivities by using a single catalyst in *one pot*, without the isolation of the intermediates formed.[8] The tandem reactions have been successfully applied in the synthesis of structurally and functionally diverse organic compounds.[9] Michael addition of nucleophiles to α,β-unsaturated carbonyl compounds represents one of the most important transformations in organic chemistry.[10] Diethylzinc has been employed in the enantioselective conjugate addition to α,β-unsaturated ketones.[10–11] The chiral zinc enolates formed *in situ* in the process can be captured by a series of electrophiles such as aldehydes, ketones, nitriles, oxocarbenium ions, carboxylates, alkyl halides, imines, nitrosos and tosylates forming molecules with complex stereochemistry and functionalities.[12] Up to now, there is no report of using α,β-unsaturated systems as electrophiles to trap the formed chiral zinc enolate. In this regard, nitroolefins are attractive Michael acceptors because the corresponding Michael product can be conveniently converted to important nitrogen-containing compounds *via* Nef reaction, Meyer reaction and other transformations.[13] Employment of nitroolefins as electrophiles to trap the chiral zinc enolates formed in the copper catalyzed Michael addition of diethylzinc to α,β-unsaturated ketones would yield valuable γ-nitro substituted carbonyl compounds.[14] The γ-nitro substituted carbonyl compounds would be readily transformed to the corresponding chiral pyrrolidine bearing multiple contiguous chiral centres using the known procedures (Scheme 1). Based on this concept, we initiated the copper catalyzed enantioselective addition of diethylzinc to α,β-unsaturated systems and capture of the chiral zinc enolate using nitroolefins as electrophiles. Herein we report our results toward the efforts.



Scheme 1 Copper catalyzed Michael addition/Michael trapping and a possible route to the pyrrolidine derivative.

Initially, using the reported procedure, chalcone was exposed to diethylzinc in the presence of 2 mol% of $Cu(OTf)_2$ and monodentate phosphoramidite **1a** (4 mol%) which was found to

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be effective in the asymmetric Michael addition of diethylzinc to α,β-unsaturated ketones.[15] The intermediate zinc enolate formed was captured by *trans*-β-nitrostyrene at –20 °C affording the three component product. Only one diastereoisomer was observed in 79% yield with 85% *ee*. The major side product was the Michael addition of diethylzinc to nitroolefins (<10% yield), no other side reactions such as the polymerization of nitroolefins were observed. This result encouraged us to further evaluate other phosphoramidites (Fig. 2).

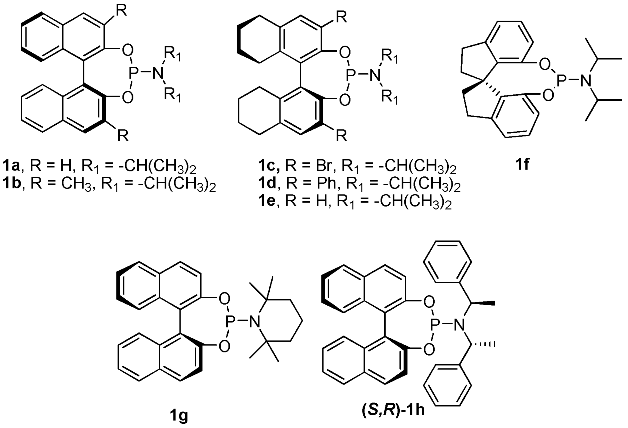
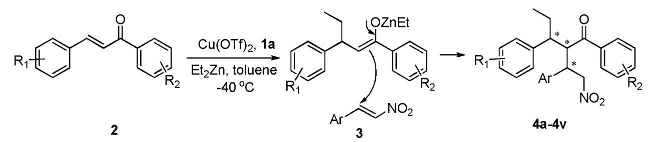


Fig. 2 The phosphoramidites investigated in the work.

Among the phosporamidites investigated, **1a** was best for the reaction in terms of yield and enantioselectivity. Further optimization was thus carried out (see Supporting Information†). When the reaction was carried out at –40 °C in the presence of 3 mol% of copper triflate in combination with 6 mol% of phosphoramidite using toluene as the reaction medium, the corresponding three component product **4a** was isolated in 71% yield with 89% *ee* (see Supporting Information†).

Table 1 The scope of the substrates



Entry[a]	R_1, R_2	Ar	Product	Yield%[b]	Ee[c]
1	H, H	H	**4a**	71	89
2	H, H	4-ClC_6H_5	**4b**	76	91
3	H, H	4-FC_6H_5	**4c**	56	86
4	H, H	4-BrC_6H_5	**4d**	60	90
5[d]	H, H	2-ClC_6H_5	**4e**	27	89
6	H, H	4-$CH_3C_6H_5$	**4f**	81	88
7	H, H	3-$OMeC_6H_5$	**4g**	74	96
8	H, H	4-$OMeC_6H_5$	**4h**	89	90
9	H, H	2-furyl	**4i**	64	92
10	H, H	1-naphthyl	**4j**	42	90
11	H, H	2-thienyl	**4k**	68	93
12	H, H	cyclohexyl	**4l**	25	79
13	4-Cl, H	H	**4m**	61	94
14[e]	4-NO_2, H	H	**4n**	72	90
15	4-Br, H	H	**4o**	66	95
16	4-OMe, H	H	**4p**	76	80
17	4-F, H	H	**4q**	68	90
18	2-CH_3, H	H	**4r**	78	78
19	3-OMe, H	H	**4s**	46	89
20	1-Nap, H	H	**4t**	53	76
21	H, 4-Cl	H	**4u**	63	80
22	H, 4-OMe	H	**4v**	56	87

[a] Unless otherwise stated, 0.2 mmol of chalcone was exposed to 0.24 mmol of diethylzinc in the presence of 3 mol% of $Cu(OTf)_2$ and 6 mol% of chiral phosphoramidite **1a**, unless otherwise stated, the diastereomerically pure (dr > 20 : 1, determined by the ^{1}HNMR of the crude products) products were obtained. [b] Isolated yields. [c] Enantioselectivities were determined by chiral HPLC. [d] Diastereomerically mixed product was obtained (dr: 5 : 1, the ee value of the major isomer was 89% ee, the configuration of major isomer was deduced from ^{1}HNMR); [e] Diastereomerically mixed product was obtained (dr: 10 : 1).

The generality of this reaction was further investigated (Table 1). Under the optimal conditions, various nitroolefins substituted with electron withdrawing or donating groups at the benzene ring uniformly provided the diastereomerically pure products with excellent enantioselectivities. For example, the introduction of methyl, fluoro, chloro, bromo, or methoxy group at the *para* position of the benzene ring appended to the nitroolefins did not significantly affect the reactivity and enantioselectivity of the reaction (entries 2–4, 6 and 8, Table 1). The steric hindrance in the nitroolefins had much effect on the reaction, for example, 2-chlorobenzaldehyde derived nitroolefin yielded the product **4e** in only 27% yield albeit with excellent *ee* (entry 5, Table 1). Similarly, 42% yield was obtained with 90% *ee* when the 1-naphthaldehyde derived nitroolefin was employed (entry 10, Table 1). Among the substrates investigated, only the nitroolefin derived from 2-chlorobenzaldehyde provided a diastereomerically mixed product (dr: 5 : 1). Generally speaking, larger steric hindrance in the nitroolefins led to better enantioselectivities but lower yields. It should be noted that heteroaromatic aldehydes such as furyl and thienyl aldehyde derived nitroolefins were tolerable under the reaction conditions affording excellent enantioselectivities and good yields (entries 9 and 11, Table 1). The aliphatic aldehyde derived nitroolefins were also tested and only the nitroolefin derived from cyclohexanecarbaldehyde afforded the corresponding diastereomerically pure product in low yield with good enantioselectivity (entry 12, Table 1). The low yield may result from the steric hindrance caused by the cyclohexyl group. Other aliphatic substituted olefins were not tolerable under the conditions investigated.

A brief survey of the scope of the reaction with respect to the structure of α,β-unsaturated ketones was also carried out. Varieties of α,β-unsaturated ketones reacted smoothly with diethylzinc and were captured by *trans*-β-nitrostyrene affording **4** in good yields with good to excellent enantioselectivities. The steric hindrance and electronic property of the ketones had little effect on the reaction. All the 4, 3, and 2-substitution patterns of the aromatic ring of the ketones afforded the corresponding product in 46–78% yield and with good to excellent enantioselectivities (entries 13–22, Table 1). For a specific substituent pattern, the substituents that are helpful to the polarization of the double bond led to better yields. For all 4-substituted enones, (entries 13–15, 17 *vs.* 16), electron-withdrawing groups on the phenyl ring attached to the C=C bond afforded the products in a less satisfactory yield. This is also the case for the substitution of phenyl ring attached to carbonyl. (Entries 21–22). The *ortho* and *meta* substituted substrates also provided similar results (entries 18–19).

The absolute configuration of **4d** was determined to be (2*R*,3*R*,1′*S*) by X-ray analysis (Fig. 3). The structure of other

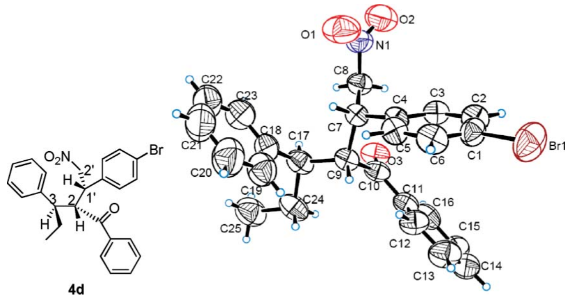


Fig. 3 The molecular structure of **4d**.

products was assigned by analogy. In the ^{1}HNMR spectrum of **4d** (Fig. 3), 2′-H proton signals were observed as two ABC resonances at δ_H 4.98 and 4.91 ppm (J = 13.6 Hz, 11.2 Hz, 4.0 Hz). 1′-H was observed as dt signal at δ_H 3.57 ppm (J = 11.2 Hz and 4.4 Hz). 2-H appeared as dd at δ_H 4.10 ppm (J = 10.0 Hz and 4.8 Hz). This indicates that 1′-H has a *cis* relationship in respect to 2-H with a coupling constant J = 4.4 Hz. The 3-H signal appeared at δ_H 2.92 ppm as td with J = 10.6 Hz and 4.0 Hz. The coupling constant between 3-H and 2-H should be 10.6 Hz and revealed that the two protons are *trans* relationship. The ^{1}HNMR signals unequivocally proved the molecular structure of **4d**.

The approach of the chiral zinc enolate from chalcone **3a** to *trans*-β-nitrostyrene **2a** is possible two ways (Fig. 4). *Si*-face approach provided the product **4a** observed in the experiment. The attack of enolates to *Si*-face of nitroolefins would be favorable for the removal of the steric repulsion. *Re*-face approach would yield the minor diastereoisomer **4a′** which was not observed in most cases.

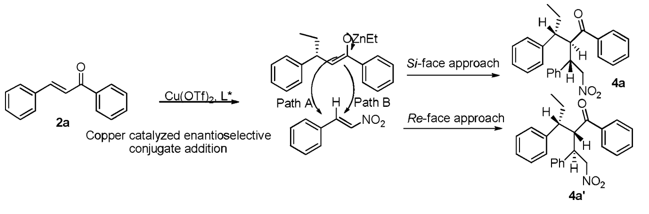
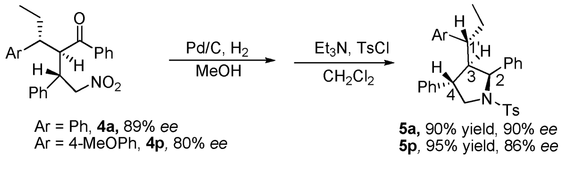


Fig. 4 Diastereoselective capture of chiral zinc enolate with nitroolefin **2a**.

To demonstrate the utility of the tandem chemistry, the products for the tandem reaction **4a** and **4p** can be conveniently hydrogenated to the chiral pyrrolidine derivatives with four contiguous stereocentres (Scheme 2). The three component product **4** was transformed to the cyclic amine **5** under 1 atm of hydrogen using Pd/C as catalyst at 40 °C with subsequent protection of amine with toluenesulfonyl chloride in CH_2Cl_2 in excellent yields in the presence of triethylamine. The enantiomeric excess of **5a** and **5p** were determined to be 90% and 86% *ee* respectively by HPLC. During the hydrogenation, no erosions of enantioselectivity and diastereoselectivity were observed. Recrystallization from the mixed solvent of hexane and ethyl acetate afforded the enantiomerically pure **5d** in 81% yield. It should be noted that bromine containing **4d** underwent dehalogenation under the present hydrogenation conditions forming the corresponding product **5a**. The absolute configuration of **5a** was determined to be 2*S*,3*R*,4*S*,1′*R* by X-ray diffraction (Fig. 5).



Scheme 2 Synthesis of chiral pyrrolidine derivatives and the determination of absolute configuration.

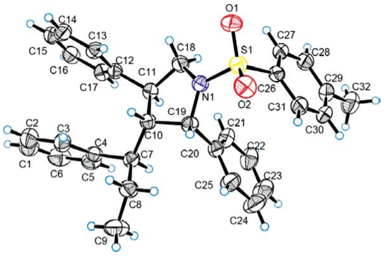


Fig. 5 The crystal structure of **5a**.

In summary, highly diastereoselective and enantioselective catalytic capture of chiral enolates using nitroolefins as electrophile was developed. The tandem products γ-nitro ketones were obtained in good yields with high diastereoselectivities and enantioselectivities. The γ-nitro ketones were readily hydrogenated to optically enriched and diastereomerically pure chiral pyrrolidines with four stereocentres under mild conditions. The absolute configuration of both γ-nitro ketones and pyrrolidines were established by X-ray diffraction. Using other α,β-unsaturated systems as electrophiles for trapping the chiral zinc enolates is being investigated, and these results will be reported in due course.

Acknowledgements

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