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Article

Chemistry

Copper(I)/SaBOX catalyzed highly diastereo- and enantio-selective cyclopropanation of *cis*-1,2-disubstituted olefins with α-nitrodiazoacetates

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Abstract A copper-catalyzed highly stereoselective cyclopropanation of 1,2-disubstituted olefins with α-nitrodiazo acetates has been developed, giving the desired products in up to 97 % yields, up to >99/1 dr and up to 98 % ee, which provides an efficient access to the synthesis of optical active cyclopropane α-amino acids and unnatural α-amino acid derivatives.

Keywords Asymmetric catalysis · Cyclopropanation · Sidearm · Bisoxazoline · α-Amino acids

1 Introduction

Nitrocyclopropane carboxylates are an important class of compounds that are suitable precursors of biologically important cyclopropane α-amino acids [1, 2] as well as various unnatural α-amino acid derivatives that could be easily accessed by ring-opening transformations [3, 4]. One of the most effective methods for the stereoselective synthesis of nitrocyclopropane carboxylates is the transition-metal-catalyzed asymmetric cyclopropanation of olefins with nitrodiazoacetates [5–7]. However, like other diacceptor diazo compounds, the nitrodiazoacetate was inherently less reactive to form metal carbene [8–23]. Charette and co-workers developed an efficient access to disubstituted α-nitrocyclopropyl ketones by using chiral rhodium(II) carboxylate as catalyst, in which 54 %–91 % yields, 94/6–99/1 dr and 87 %–95 % ee were achieved [6]. Zhang and co-workers [7] succeeded in the chiral radical cobalt/porphyrin complex-catalyzed asymmetric *Z*-cyclopropanation of both electron-rich and electron-deficient terminal alkenes with α-nitrodiazoacetates under carbene radical process (42 %–97 % yields, 53/47–>99/1 and 75 %–95 % ee). When copper was used as catalyst, harsh conditions such as elevated temperature [24, 25] and extra activator [5] are required, but both the reactivity and stereoselectivity are unsatisfactory. For example, Charette and Wurz [5] found that compared with Rh(II) catalysts, the Cu(I)-bisoxazoline (BOX) catalysts were less reactive in the cyclopropanation of styrene with nitrodiazoacetate, and up to 55 % yield and up to 72 % ee were obtained. Later on, they [26] successfully realized asymmetric cyclopropanation of terminal alkenes in 45 %–84 % yields with 82/18–95/5 dr and 68 %–93 % ee by employing iodonium ylides [26–29] as carbene sources. To date, less active 1,2-disubstituted olefins [30, 31] have barely been employed in this reaction, except one example of indene substrate was reported in 72 % yield, 95/5 dr and 98 % ee after recrystallization [28]. Herein, we wish to report our recent efforts on the asymmetric cyclopropanation of *cis*-1,2-disubstituted olefins with α-nitrodiazoacetates by using copper(I)/SaBOX as catalyst.

Liang-Wen Feng and Peng Wang have contributed equally to this work.

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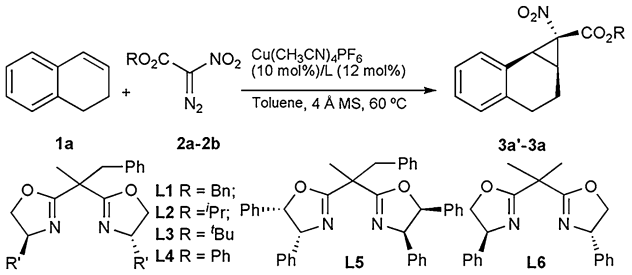
2 Materials and methods

Typical procedure for the asymmetric cyclopropanation (**3a** as an example): A mixture of $Cu(MeCN)_4PF_6$ (0.04 mmol) and the ligand (**L5**, 0.048 mmol) in toluene (3 mL) with activated 4 Å molecular sieve (MS) was stirred at 50 °C for 2 h under an atmosphere of nitrogen. Then, **1a** (2.0 mmol) and diazo **2b** (0.4 mmol) were added to the mixture of catalyst via microsyringes, followed by washing with 1 mL toluene. The resulting suspension was allowed to stir at 50 °C. After the reaction was complete (monitoring by thin-layer chromatography), the reaction was filtered through a glass funnel with a thin layer (20 mm) of silica gel (100–200 mesh) with CH_2Cl_2 (~30 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/petroleum, 1/80) to afford **3a** as white solid in 85 % with >99/1 dr and 98 % ee (determined by high-performance liquid chromatography (HPLC) analysis: chiralcel OD-3 column (25 cm), heptane/*i*-PrOH = 99/1, 1.0 mL/min, 254 nm; tr (major) = 10.4 min, tr (minor) = 12.4 min); $[\alpha]_D^{20} = +65.6°$ (c = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 1H), 7.22–7.17 (m, 2H), 7.05–7.02 (m, 1H), 4.16–3.99 (m, 2H), 3.32 (d, J = 10.4 Hz, 1H), 2.94–2.89 (m, 1H), 2.76–2.69 (m, 1H), 2.44–2.32 (m, 2H), 2.17–2.07 (m, 1H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 134.5, 130.7, 128.7, 128.5, 127.8, 126.6, 73.2, 62.4, 32.5, 29.8, 25.0, 16.9, 13.3; IR (neat, cm^{-1}): 2,986, 2,938, 1,739, 1,537, 1,335, 1,184, 1,107, 1,089, 1,019, 796, 755, 730, 687; HRMS-ESI: $[M+H]^+$ Calcd. for $C_{14}H_{16}NO_4$, 262.1079; Found, 262.1076.

3 Results and discussion

Recently, we have developed a series of sidearm-modified bisoxazoline ligands (SaBOX), which could improve the reactivity and stereoselectivity in the asymmetric cyclopropanation of multisubstituted olefins with diazoacetates [32, 33]. Thus, we tried to extend this strategy to the asymmetric cyclopropanation of 1,2-disubstituted olefins with α-nitrodiazoacetates. Initially, the study was carried out in toluene at 60 °C under nitrogen atmosphere using dialin **1a** and methyl nitrodiazoacetate **2a** as starting material. With phenyl-sidearmed SaBOX **L1**, when $Cu(MeCN)_4PF_6$/**L1** was employed as catalyst, the reaction proceeded slowly, furnishing the nitrocyclopropane **3a** in only 9 % yield with >99/1 dr and 94 % ee after 24 h (Table 1, entry 1). In order to further increase the yield, several SaBOX ligands bearing different substituents on the oxazoline backbone were then examined. With *iso*propyl group, **L2** gave 14 % yield (entry 2), while with

Table 1 Reaction optimization[a]

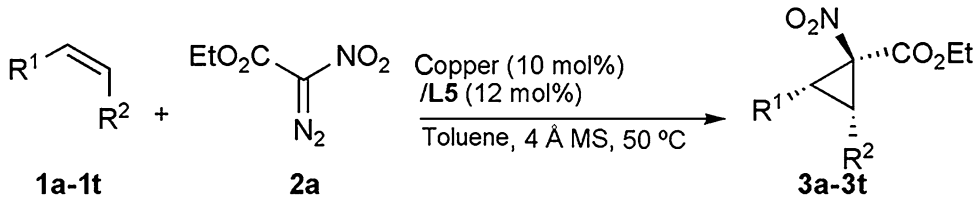


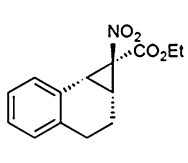
Entry	Ligand	R	Time (h)	Yield (%)[b]	dr[c]	ee (%)[d]
1	**L1**	Me	24	9	>99/1	94
2	**L2**	Me	24	14	>99/1	95
3	**L3**	Me	24	Trace	–	–
4	**L4**	Me	11	66	>99/1	97
5	**L5**	Me	3	80	>99/1	97[e]
6[f]	**L5**	Me	6	81	>99/1	98[e]
7[f,g]	**L5**	Me	2.5	81	>99/1	98[e]
8[f]	**L5**	Et	3	85	>99/1	98[e]
9[f,g]	**L6**	Et	3	15	>99/1	86

[a] **1/2** = 5/1 and [**2**] = 0.1 mol/L in toluene (4 mL) with 4 Å MS under N_2 at 60 °C. [b] Isolated yields; [c] determined by ^1H NMR analysis; [d] determined by chiral HPLC; [e] the enantioselectivity is reversed; [f] at 50 °C; [g] with CuI (10 mol%) and $AgSbF_6$ (12 mol%)

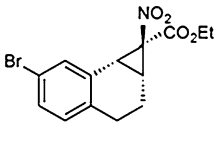
tert-butyl group, **L3** led to only trace cyclopropanation product (entry 3). Then, we attempted to use *L*-phenylglycine-derived **L4** as ligand. To our delight, the reactivity was promoted obviously giving the desired product **3a′** in 66 % yield after 11 h; meanwhile, the enantioselectivity was also raised slightly with 97 % ee (entry 4). After an extensive screening of SaBOX ligands (see Supporting information, online), **L5** derived from 2-amino-1,2-diphenylethanol was emerged as the best ligands, which speeded up the reaction sharply and accomplished 80 % yield within 3 h without any erosion of the stereocontrol but the reversed enantioselectivity (entry 5). Lowering the reaction temperature from 60 to 50 °C increased the ee to 98 %, but it needs 6 h to finish the reaction (entry 6). In addition, $CuSbF_6$ proved also to be a more efficient metal salt and 81 % yield, >99/1 dr and 98 % ee was obtained in only 2.5 h, with **L5** as ligand (entry 6 vs. entry 7). Changing the ester group of nitrodiazoacetate from methyl **2a** to ethyl **2b**, leading to a little bit of improvement in the yield of **3a** with maintenance of the stereoselectivity after 3 h (85 % yield, >99/1 dr and 98 % ee, entry 8). However, as to BOX ligand [34–39] **L6**, which proved very efficient in the asymmetric cyclopropanation of terminal olefin with iodonium ylides [26], only gave 30 % yield of **3a** after 3 h even in the presence of more active $CuSbF_6$ (entry 6 vs. entry 7), indicating that the SaBOX ligand is more efficient (entry 8 vs. entry 9).

Table 2 Reaction scope[a]

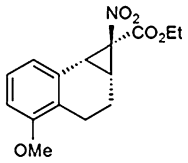




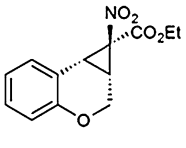
3a[b]
3 h, 85% yield
>99/1 dr
98% ee



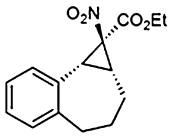
3b
5 h, 73% yield
>99/1 dr
97% ee



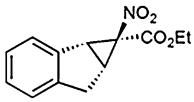
3c
4 h, 97% yield
>99/1 dr
94% ee



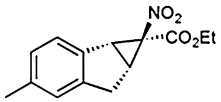
3d[c]
5 h, 67% yield
>99/1 dr
93% ee



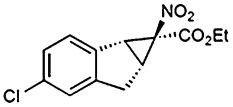
3e[c]
26 h, 77% yield
96/4 dr
98% ee



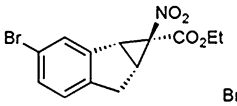
3f[b]
1 h, 88% yield
>99/1 dr
98% ee



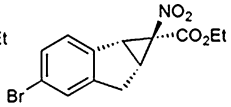
3g[b]
1 h, 83% yield
>99/1 dr
93% ee



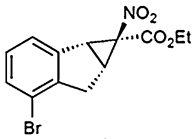
3h[b]
2 h, 90% yield
>99/1 dr
98% ee



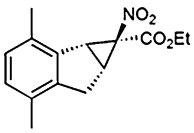
3i[b]
1.5 h, 87% yield
>99/1 dr
96% ee



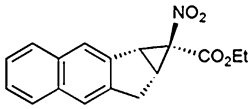
3j[b, e]
1 h, 83% yield
>99/1 dr
98% ee



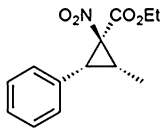
3k[b]
8 h, 69% yield
94/6 dr
96% ee



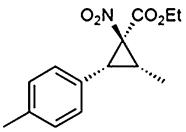
3l[b]
2 h, 79% yield
>99/1 dr
96% ee



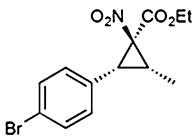
3m[b]
1 h, 90% yield
>99/1 dr
97% ee



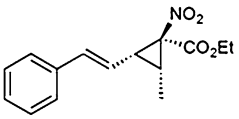
3n[c]
40 h, 56% yield
>99/1 dr
95% ee



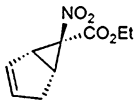
3o[c]
60h, 83% yield
>99/1 dr
93% ee



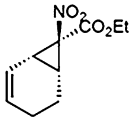
3p[d]
73h, 59% yield
>99/1 dr
97% ee



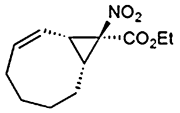
3q[c, d, e]
8.5 h, 65% yield
93/7 dr
85% ee



3r[c]
3 h, 60% yield
>99/1 dr
92% ee



3s[c]
2 h, 90% yield
>99/1 dr
93% ee



3t[c]
15 h, 56% yield
96/4 dr
78% ee

[a] CuI (0.04 mmol) and $AgSbF_6$ (0.04 mmol), **L5** (0.048 mmol), **1/2b** = 5/1 and [**2b**] = 0.1 mol/L in toluene (4 mL) with 4 Å MS under N_2 at 50 °C. The yield is of the isolated product. The dr was determined by ^1H NMR analysis, and the ee values were determined by chiral HPLC analysis. [b] $Cu(CH_3CN)_4PF_6$ (10 mol%) was used. [c] Benzene was used as solvent. [d] [**2b**] = 0.2 mol/L. [e] The absolute configuration of **3j** and **3q** were determined as (*1S,1aR,6aR*)- and (*1S,2R,3S*)-configuration by X-ray crystallographic analysis. CCDC 994351 (**3f**) and 995729 (**3q**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif

We next evaluated the reaction scope of this catalyst system. As shown in Table 2, the reaction proceeded smoothly with various dialin derivatives **1b-1c** by using $CuSbF_6$/**L5** as catalyst, including both electron-withdrawing and electron-donating group substituted substrates (73 %–97 % yields, >99/1 dr and 94 %–97 % ee). The current catalytic system is also compatible with a variety of heterocyclic alkenes and seven-membered cyclic alkenes (**1d** and **1e**), furnishing the nitrocyclopropane carboxylates (**3d** and **3e**) in high level of ee values (93 % and 98 % ee). For indene substrates **1f-1m**, the reaction finished even faster by employing $Cu(MeCN)_4PF_6$/**L5** as catalyst. Various functional groups such as –Me, –Cl, and –Br substituted at different position were all well tolerated. Both high yields and excellent stereoselectivities can be achieved within 1–8 h (69 %–90 % yields, >99/1 dr and 93 %–98 % ee). It is noteworthy that the catalyst loading was able to decrease to 2 mol%, giving the corresponding nitrocyclopropane **3f** after 7 h without erosion of both yield and enantioselectivity. Disubstituted indene **1l** and fused cyclic substrate **1m** were both reacted very fast to give the desired products **3l** and **3m** within 1 or 2 h, in 79 % yield with >99/1 dr and 96 % ee, as well as 90 % yield with >99/1 dr and 97 % ee, respectively. Meanwhile, a series of acyclic alkenes **1n-1p** readily participated in this cyclopropanation, and products with 93 %–97 % ee were obtained. For acyclic diene substrate **1q**, the cyclopropanation of the *cis* double bond gave 65 % yield with 86 % ee value by using $CuSbF_6$/**L5**. Aliphatic olefins **1r** and **1s** could also process well to afford the cyclopropane **3r** and **3s** in 60 %–90 % yield with >99/1 dr and 92 %–93 % ee. In addition, eight-membered cyclic diene **1t** was also tolerated in this reaction system, leading to moderate yield and good enantioselectivity.

The stereoinductive model shown in Fig. 1 was proposed to explain the accomplished high stereoselectivity. According to previous studies on the structure of SaBOX–metal complexes [40–43], the pendant aryl groups of BOX–metal complexes always bend toward the metal center [32, 44, 45]. In this model, the top of the Cu(I)/oxazoline ring square is occupied by the phenyl group of the sidearm, and the upper right corner as well as the lower left corner are blocked by the phenyl groups of the chiral backbone. We proposed that in the presence of the Cu(I) complex, the diazo compound [46–49] decomposed to form copper carbene with the bigger ester group pointed to the less hindered lower side of the Cu(I)/oxazoline ring square. The olefin might tend to place in the right side of the copper carbene, by way of avoiding the steric repulsion between the substituents of the olefin and the sidearm as well as the chiral backbone (Fig. 1). This model is consistent with stereochemical results and the configuration of the cyclopropane determined by X-ray crystallographic analysis.

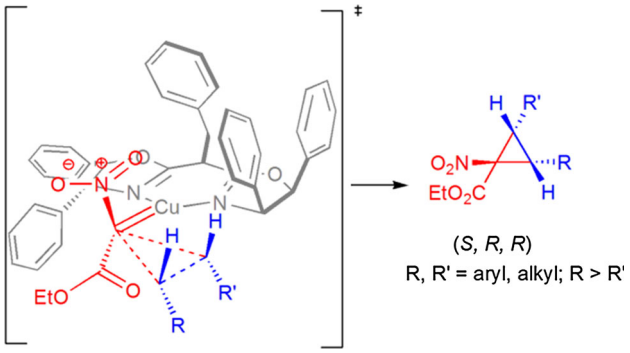
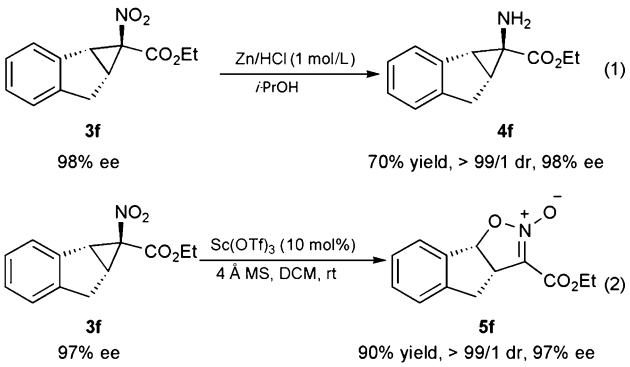


Fig. 1 (Color online) Possible stereochemical model

The products are potentially synthetically useful. For example, the product **3f** was readily reduced to optically active cyclopropane α-amino acid derivative in 70 % yield with total reservation of the ee value (Eq. (1) in Scheme 1). Meanwhile, **3f** was also easily transformed to give the corresponding ring-opening product **5f** in 90 % yield with >99/1 dr and maintained ee value (Eq. (2) in Scheme 1).

4 Conclusions

In summary, we have developed a copper(I)/SaBOX catalyzed highly diastereo- and enantio-selective cyclopropanation of 1,2-disubstituted olefins with α-nitrodiazoacetates. With this cheap and readily available sidearm-modified bisoxazoline-copper(I) complex, the cyclopropanation was performed well over a wide scope of *cis*-disubstituted olefins, giving the desired products in good to high yields (up to 97 %), excellent diastereoselectivities (up to >99/1 dr) and enantioselectivities (up to 98 % ee). This method provides an efficient access to the synthesis of optical active cyclopropane α-amino acids as well as various chiral unnatural α-amino acid derivatives, which made this reaction potentially useful in organic synthesis.



Scheme 1 Transformations of product **3f**

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Conflict of interest The authors declare that they have no conflict of interest.

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