Organic LETTERS

Letter

pubs.acs.org/OrgLett

One-Pot Catalytic Asymmetric Synthesis of Tetrahydrocarbazoles

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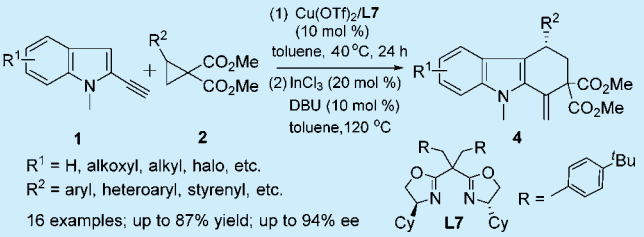
Supporting Information

ABSTRACT: A one-pot asymmetric synthesis of 1,2,3,4-tetrahydrocarbazoles has been developed via an enantioselective [3 + 3] annulation of 2-alkynylindoles and donor−acceptor cyclopropanes. In the presence of chiral Lewis acids as catalysts, a series of optically active tetrahydrocarbazoles were furnished in high yields (63−87%) with good to excellent levels of enantioselectivity (up to 94% ee).



Polycyclic indoles, such as carbazoles and their derivatives, are important heterocyclic compounds owing to their frequent occurrence as key motifs in various bioactive nature products and drug molecules (Figure 1).[1,2] It was found that

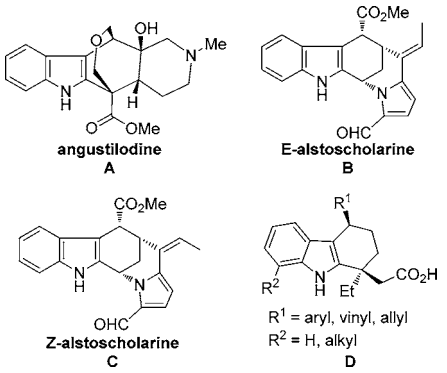


Figure 1. Natural products containing tetrahydrocarbazole.

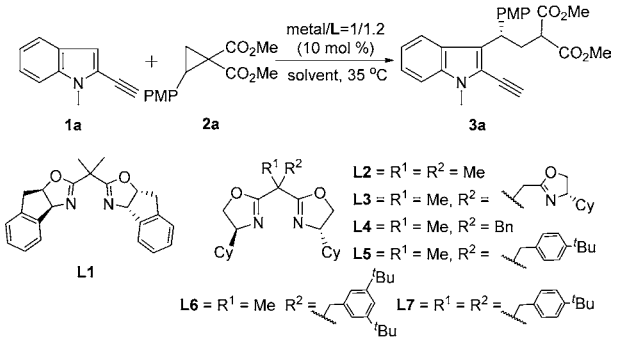
the tetrahydrocarbazoles **D**, especially in their optically active forms, usually show high bioactivities, such as analgesic potency and anti-inflammatory potency.[2a] Great efforts have been made to explore the effective methods for the enantioselective construction of this subunit, including Friedel−Crafts alkylation, the Diels−Alder reaction, and others.[3−5] In 2009, Kerr and co-workers reported an extraordinarily efficient approach that led to tetrahydrocarbazoles,[6] which involved ring-opening of the donor−acceptor (D−A) cyclopropanes with indole[7,8] and Conia−ene cyclization.[9,10] Recently, we have developed a series of catalytic processes for enantioselective ring opening and annulation reactions of D−A cyclopropanes with versatile reagents such as nitrones, amines, enol silyl ethers, and indoles,[11] by Lewis acid based on side arm modified chiral bisoxazoline ligands.[12,13] Here, we report our recent results on the development of catalytic system for enantioselective [3 + 3] annulation of 2-alkynylindoles with donor−acceptor cyclopropanes, which provides a one-pot access to a variety of optically active tetrahydrocarbazoles.

Initially, the reaction was carried out with 1.0 equiv of 2-ethynylindole **1a** and 2.0 equiv of cyclopropane **2a** in 1,2-dichloroethane (Table 1). After evaluation of several Lewis acids,[14] copper complexes were proven to be competent catalysts for the asymmetric ring-opening reaction. By using in situ generated $Cu(SbF_6)_2$/**L1** as catalyst, the reaction proceeded very fast at 35 °C, affording the desired product **3a** in 98% yield with 55% ee after 50 min (entry 1). When $Cu(OTf)_2$ was employed, it gave rise to a 91% yield with a moderate level of enantioselectivity (59% ee, entry 2). Although the reaction provided a similar yield and enantioselectivity in dichloromethane (entry 3), a dramatic increase of enantioselectivity (77% ee) was observed by employing toluene as solvent (entry 4). Aiming at improving both the reactivity and the enantioselectivity of the ring-opening reaction, a variety of chiral ligands were investigated. Importantly, it was found that bisoxazoline ligands bearing cyclohexyl backbones provided better enantioinduction. With ligand **L2**, the ring-opening product **3a** was afforded in 72% yield with 83% ee (entry 5). Although trisoxazoline **L3** led to a lower reactivity and enantioselectivity, SaBOX ligand **L4** bearing a benzyl side arm could promote the reaction and gave a higher ee value (entries 6 and 7). Notably, SaBOX ligand **L5** containing a sterically demanding side arm could promote the reaction efficiently, affording the ring-opening product **3a** in 95% yield with 87% ee (entry 8). Since a further increase in steric hindrance of the side arm group resulted in no improvement of enantioselectivity of the reaction (entry 9), the SaBOX ligand **L7** with two side arm groups was employed. To our delight, with **L7**, the product **3a** was obtained in 97% yield with 90% ee (entry 10). In addition, when the ratio of **1a**/

Received: July 3, 2015
Published: August 7, 2015

DOI: 10.1021/acs.orglett.5b01909
Org. Lett. 2015, 17, 4014−4017

Table 1. Reaction Optimization[a]



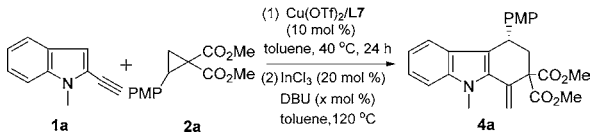
entry	metal precursor	L	solvent	yield[b] (%)	ee[c] (%)
1	$Cu(SbF_6)_2$	L1	DCE	98	55
2	$Cu(OTf)_2$	L1	DCE	91	59
3	$Cu(OTf)_2$	L1	DME	93	59
4	$Cu(OTf)_2$	L1	toluene	72	77
5	$Cu(OTf)_2$	L2	toluene	72	83
6	$Cu(OTf)_2$	L3	toluene	44	77
7	$Cu(OTf)_2$	L4	toluene	75	88
8	$Cu(OTf)_2$	L5	toluene	95	87
9	$Cu(OTf)_2$	L6	toluene	96	85
10	$Cu(OTf)_2$	L7	toluene	97	90
11[d]	$Cu(OTf)_2$	L7	toluene	90	90

[a]Performed with 0.2 mmol of **1a**, 0.4 mmol of **2a**, and 3 mL of solvent. [b]Isolated yields. [c]Determined by chiral HPLC. [d]**1a**/**2a** = 1.5/1, at 40 °C.

2a was 1.5/1, both high yield and an excellent level of enantioselectivity could be afforded as well (entry 11).

Next, we turned our attention to investigate the *one-pot* [3 + 3] annulation reaction of 2-alkynylindole **1a** with cyclopropane **2a** (Table 2). With $InCl_3$ as catalyst, the cyclization reaction

Table 2. One-Pot [3 + 3] Annulation Reaction[a]



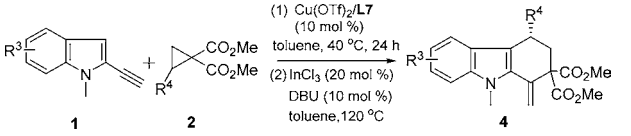
entry	DBU (mol %)	time (h)	yield[b] (%)	ee[c] (%)
1	0	5	73	85
2	5	6	80	87
3	10	6	82	89
4	15	72	78	90

[a]Performed with 0.3 mmol of **1a** and 0.2 mmol of **2a** in 3 mL of toluene for the first step; an additional 1 mL of toluene was added for the second step. [b]Isolated yields. [c]Determined by chiral HPLC.

proceeded smoothly at 120 ° C after 5 h, furnishing the desired product **4a** in 73% yield but with a slight drop of the ee value (85% ee, entry 1). When 5 mol % of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added as additive, both the yield and enantioselectivity were improved (entry 2). Increasing the amount of the base to 10 mol %, the annulation product **4a** was obtained in 82% yield with 89% ee (entry 3). However, a further increase of DBU to 15 mol % led to a dramatically sluggish reaction, delivering the [3 + 3] annulation product in 78% yield with 90% ee even after 3 days (entry 4).

Under the optimized reaction conditions, the substrate scope of the enantioselective *one-pot* [3 + 3] annulation reaction of 2-alkynylindoles with cyclopropanes was examined. As shown in Table 3, electron-rich indole derivatives, such as those bearing a

Table 3. Substrate Scope of Annulation Reaction[a]



entry	R^3	R^4	4	yield[b] (%)	ee[c] (%)
1	H (**1a**)	PMP (**2a**)	**4a**	82	89
2	4-Me (**1b**)	PMP (**2a**)	**4b**	86	93
3	5-Me (**1c**)	PMP (**2a**)	**4c**	87	90
4	6-Me (**1d**)	PMP (**2a**)	**4d**	76	89
5	7-Me (**1e**)	PMP (**2a**)	**4e**	71	88
6	4-OMe (**1f**)	PMP (**2a**)	**4f**	85	94
7	5-OMe (**1g**)	PMP (**2a**)	**4g**	77	91
8	5-Cl (**1h**)	PMP (**2a**)	**4h**	77	77
9	6-Cl (**1i**)	PMP (**2a**)	**4i**	69	77
10	5-F (**1j**)	PMP (**2a**)	**4j**	79	84
11	H (**1a**)	2-furyl (**2b**)	**4k**	68	57
12	H (**1a**)	2-thienyl (**2c**)	**4l**	71	77
13	H (**1a**)	4-TBSOC_6H_4 (**2d**)	**4m**	86	82
14	H (**1a**)	3,4-$(MeO)_2C_6H_3$ (**2e**)	**4n**	77	87
15	H (**1a**)	3,4,5-$(MeO)_3C_6H_2$ (**2f**)	**4o**	78	90
16	H (**1a**)	CH=CHPh (**2g**)	**4p**	63	86

[a]Performed with 0.6 mmol of **1a** and 0.4 mmol of **2a** in 6 mL of toluene for the first step; an additional 2 mL of toluene was added for the second step. [b]Isolated yields. [c]Determined by chiral HPLC.

methyl group at the 4-, 5-, 6-, and 7-positions (**1b**−**e**), could react smoothly with cyclopropane **2a**, giving the corresponding [3 + 3] products **4b**−**e** in 71−87% yields with 88−93% ee (entries 2−5). Similar product yields (77−85% yields) and slightly higher levels of enantioselectivity (91−94% ee) were obtained for the reactions of **2a** with indoles **1f** and **1g**, which contain methoxy groups at the 4- and 5-positions, respectively (entries 6 and 7). Halo-substituted indole substrates **1h**−**j** were also tolerated in the current catalyst system, furnishing the desired products **4h**−**j** in good yields with up to 84% ee (entries 8−10). In addition to **2a**, a variety of D−A cyclopropanes were compatible with this asymmetric [3 + 3] annulation reaction. For example, the reactions of cyclopropanes bearing heterocyclic substituents such as 2-furyl (**2b**) and 2-thienyl (**2c**) with **1a** resulted in the desired products in good yields with moderate to good enantioselectivities (entries 11 and 12).

D−A cyclopropanes with other aromatic substituents, such as **2d**−**f** containing electron-donating groups on the phenyl ring, could also perform well in the asymmetric [3 + 3] annulation reaction, affording the corresponding products **4m**−**o** in high yields with high levels of enantioselectivity (entries 13−15). In addition, styrenyl-substituted D−A cyclopropane **2g** was also a suitable substrate, delivering the corresponding product **4p** in 63% yield with 86% ee (entry 16). The absolute configuration of **4h** was established as *S* by X-ray crystallography (Figure 2).

Previous studies on the crystal structures of SaBOX/Cu(II) complexes indicated that the aryl groups of the side arms always bend toward the metal center. Accordingly, an asymmetric induction model was proposed to explain the observed enantioselectivity (Scheme 1). In this model, it is evident that the upper and lower sides of the Cu(II)/oxazoline ring square

DOI: 10.1021/acs.orglett.5b01909
Org. Lett. 2015, 17, 4014−4017

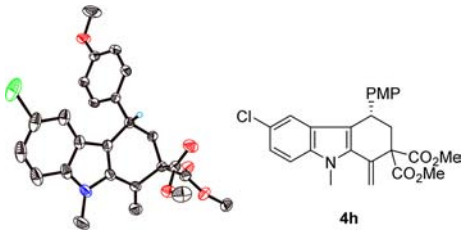
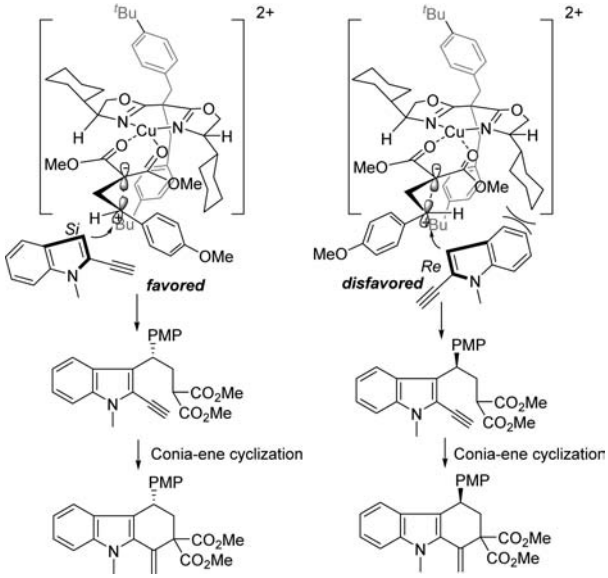


Figure 2. X-ray crystal structure of annulation product **4h**.

Scheme 1. Proposed Stereochemical Model



are blocked by the side arms while the top-left and low-right corners are sterically hindered by the cyclohexyl group. Upon interacting with the Lewis acidic Cu center through its two ester groups, the D−A cyclopropane is further activated to give rise to positive charge at the carbon center bearing electron-rich substituent. In combination with the stabilization effect from the donor−acceptor synergistic system, the reaction undergo an asymmetric transformation of D−A cyclopropanes through a chiral Lewis acid-catalyzed ring opening with indoles. Due to the steric demand of the nucleophilic attack of C3-position of indole, the Si face of the indole is preferred to approach the transient (*R*)-cyclopropane (left), suffering less steric interaction with the ligand cyclohexyl substituent.

In summary, we have developed a one-pot catalytic system for asymmetric synthesis of 1,2,3,4-tetrahydrocarbazoles via an enantioselective [3 + 3] annulation of 2-alkynyl indoles with donor−acceptor cyclopropanes. In the presence of Lewis acids as catalysts, a series of chiral tetrahydrocarbazoles were furnished in high yields (63−87%) with good to excellent levels of enantioselectivity (up to 94% ee). In addition, a rational model for stereoinduction was provided. Together with the ready accessibility of both the catalysts and starting materials, the simple operation and the broad substrate scope should make this current protocol synthetically useful.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01909.

Experimental procedures, characterization data for all new compounds, and crystallographic data (PDF)
X-ray data for enantiopure product **4h** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (Nos. 21121062, 21432011, and 21272250), the National Basic Research Program of China (973 Program) (2015CB856600), the Chinese Academy of Sciences, the National Science Foundation (CHE-1152767 and CHE-1465106; X.P.Z.), and the National Institutes of Health (R01-GM098777; X.P.Z.).

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DOI: 10.1021/acs.orglett.5b01909
Org. Lett. 2015, 17, 4014−4017