DOI: 10.1002/adsc.201600221

Advanced Synthesis & Catalysis

# Lewis Acid-Catalyzed [3+2] Cycloaddition of Donor-Acceptor Cyclopropanes and Enamines: Enantioselective Synthesis of Nitrogen-Functionalized Cyclopentane Derivatives

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Received: February 24, 2016; Revised: April 11, 2016; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201600221.

**Abstract:** A straightforward and efficient method for the synthesis of nitrogen-functionalized cyclopentane derivatives *via* [3+2] cycloaddition of enamines with donor-acceptor cyclopropanes in the presence of catalytic amounts of various Lewis acids at room temperature has been developed; furthermore, the corresponding β-amino acid was synthesized by monodecarboxylation and hydrogenolysis. An enantioenriched synthesis of nitrogen-functionalized cyclopentane derivatives through dynamic kinetic asymmetric transformation of racemic donor-acceptor cyclopropanes has also been achieved employing a copper complex [$Cu(OTf)_2$-**L1**] as the catalyst affording an enantiomeric ratio up to 8:1.

**Keywords:** β-amino acids; donor-acceptor cyclopropanes; enamines; nitrogen-functionalized cyclopentanes

Nitrogen-functionalized carbocycles are ubiquitously found in numerous bioactive compounds relevant to pharmaceutical interest.[1] In this context, the nitrogen-functionalized cyclopentane (NFC) ring is of particular importance (Figure 1). Cispentacin, an antifungal antibiotic,[2] pactamycin, reported to act as an antitumor, antiviral and antiprotozoal agent,[3] and peramivir having potential for the treatment of H1N1 influenza,[4] are some illustrative examples of synthetic drugs containing an NFC ring. Owing to their biological activities, the development of a new synthetic protocol for NFCs is of greater interest.

It has widely been demonstrated that donor-acceptor cyclopropanes (DACs) serve as all-carbon centered 1,3-zwitterionic synthons which, in the presence of different Lewis acids, undergo [3+n] cycloadditions to form cyclic skeletons.[5] Mainly two types of [3+2] annulations are known for the construction of cyclopentane derivatives using DACs. These are (i) annulation between various transition metal π-allyl activated vinyl DACs and electron-deficient alkenes[6] and (ii) Lewis acid-activated DACs and different alkenes.[7] However, only a few reports are available in the literature wherein DACs have been used for the synthesis of NFCs. The two major approaches used for the construction of NFCs differ significantly by using different substrates: (i) nitrogen functionality attached to the cyclopropane moiety, and (ii) nitrogen functionality attached to the alkyne moiety (Scheme 1). The

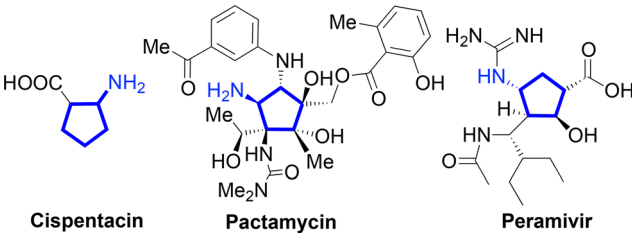
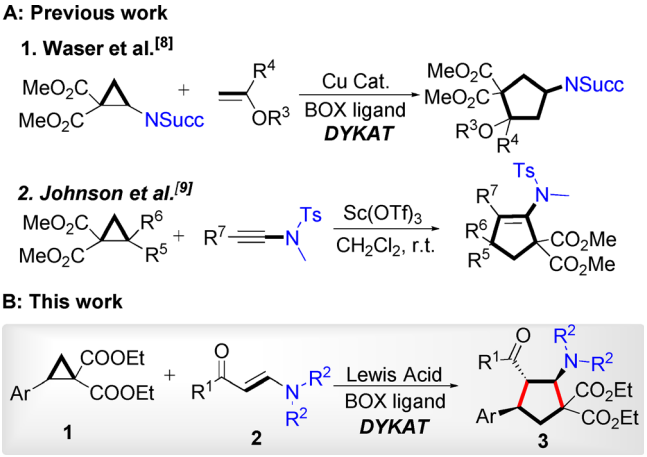



**Figure 1.** Bioactive compounds containing NFC rings.




**Scheme 1.** Synthesis of NFC derivatives.

Waser group reported dynamic kinetic asymmetric [3+2] annulations of *N-succinimido*-substituted cyclopropanes with both enol ethers and aldehydes using a copper catalyst and commercially available BOX ligands. Excellent enantiomeric ratios (*er*) with good yields of the NFCs containing a cyclopentyl or nucleobase have been achieved.[8] Johnson and his co-workers reported an $Sc(OTf)_3$-catalyzed [3+2] cycloaddition of DACs with ynamides to provide cyclopentene sulfonamide derivatives.[9] Although excellent regioselectivity with respect to ynamides was accomplished in this report, the catalytic enantioselective version of the titled transformation could not be achieved due to the significant steric hindrance of the $MgI_2$(PyBOX) catalyst system. Herein, we report [3+2] cycloadditions of DACs with enamines to construct NFC derivatives in the presence of various Lewis acids. An approach towards the asymmetric variant through dynamic kinetic asymmetric transformation (DyKAT)[10] of racemic DAC **1b** is presented by using the $Cu(OTf)_2$-**L1** complex as catalyst, whereby an *er* up to 8:1 was achieved with good yield.

We started this investigation to explore the reaction conditions that could effect the desired transformation (Table 1). Previously, we demonstrated that ring opening reactions of DACs with other strained rings (epoxides, aziridines) could best be achieved in the presence of $MgI_2$.[11] Based on our previous experiences, initially we performed the reaction between **1b** and **2a** in the presence of 5 mol% $MgI_2$, which produced two separable diastereomers **3ba** and **4ba** in a 3:1 ratio with a combined 40% yield (Table 1, entry 2). Both **3ba** and **4ba** were characterized by NMR spectroscopy. In addition, a single crystal X-ray structure was sought for **3ba**[12] (Figure 2, also see the Supporting Information). Encouraged by this preliminary result, we next varied the loading of the catalyst to improve the yield. The best yield of the products was obtained when 20 mol% of $MgI_2$ were used (Table 1, entry 4). However, higher loadings (50 or 100 mol%) caused inferior results. To our delight, $Cu(OTf)_2$ shows a similar efficiency as that of $MgI_2$ producing the cycloadducts in excellent yield (Table 1, entry 7). While other Lewis acids, such as $Sc(OTf)_3$, $Sn(OTf)_2$, $Yb(OTf)_3$ and $InCl_3$, failed to produce the desired product (Table 1, entryies 8–11), $MgCl_2$ and $MgBr_2$ gave moderate yields (Table 1, entries 12 and 13). Various solvents were also explored in the course of this optimization. A chlorinated solvent, such as $ClCH_2CH_2Cl$ or $CH_2Cl_2$ is found to be better than non-chlorinated solvents (Table 1, entries 4 and 14). While THF and acetonitrile provided moderate yields (Table 1, entries 15 and 16).Toluene and hexane gave low yield or no reaction, respectively (Table 1, entries 17 and 18). Therefore, the optimal reaction conditions for the cycloaddition were identified as 20 mol% of $MgI_2$ or $Cu(OTf)_2$ in $CH_2Cl_2$ at room temperature.

With the optimized reaction conditions in hand, the substrate scope was examined with a variety of DACs

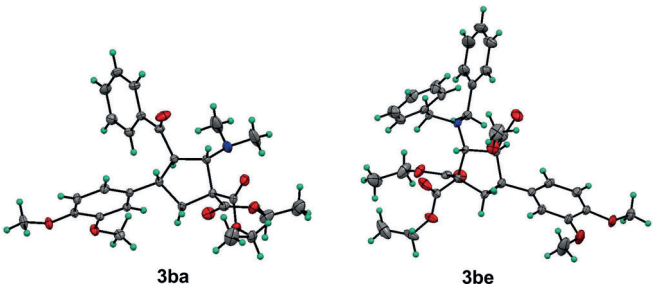
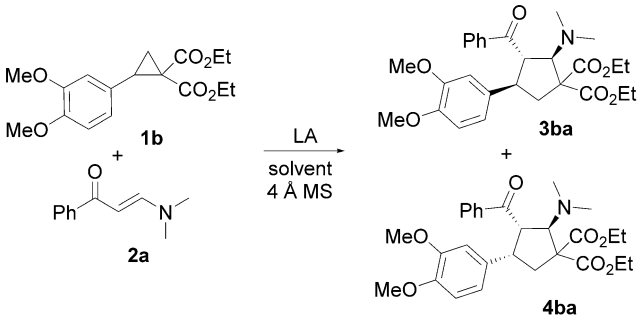



**Figure 2.** ORTEP structures of **3ba** and **3be**.

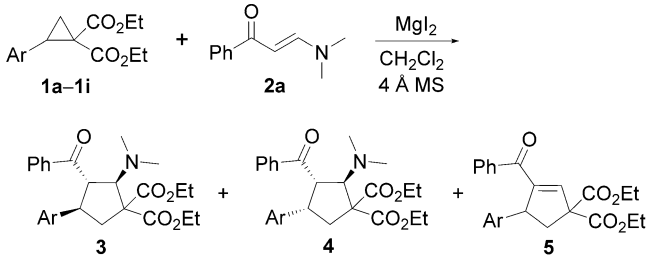
**Table 1.** Optimization of the reaction conditions.[a]




| Entry | LA | LA (mol%) | Solvent | *t* [h] | Yield [%][b] of **3ba/4ba** |
|---|---|---|---|---|---|
| 1 | none | 0 | $CH_2Cl_2$ | 24 | n.r[c] |
| 2 | $MgI_2$ | 5 | $CH_2Cl_2$ | 4 | 40/3:1 |
| 3 | $MgI_2$ | 10 | $CH_2Cl_2$ | 4 | 69/1.7:1 |
| 4 | $MgI_2$ | 20 | $CH_2Cl_2$ | 2 | 85/1.8:1 |
| 5 | $MgI_2$ | 50 | $CH_2Cl_2$ | 2 | 81/1.7:1 |
| 6 | $MgI_2$ | 100 | $CH_2Cl_2$ | 2 | 72/1.9:1 |
| 7 | $Cu(OTf)_2$ | 20 | $CH_2Cl_2$ | 4.5 | 83/3:1 |
| 8 | $Sc(OTf)_3$ | 20 | $CH_2Cl_2$ | 40 | n.r[c] |
| 9 | $Sn(OTf)_2$ | 20 | $CH_2Cl_2$ | 40 | n.r[c] |
| 10 | $Yb(OTf)_3$ | 20 | $CH_2Cl_2$ | 40 | n.r[c] |
| 11 | $InCl_3$ | 20 | $CH_2Cl_2$ | 40 | n.r[c] |
| 12 | $MgBr_2$ | 20 | $CH_2Cl_2$ | 24 | 53/3:1 |
| 13 | $MgCl_2$ | 20 | $CH_2Cl_2$ | 24 | 45/2.3:1 |
| 14[f] | $MgI_2$ | 20 | DCE[d] | 2 | 84/1.9:1 |
| 15 | $MgI_2$ | 20 | THF[e] | 8 | 72/3:1 |
| 16 | $MgI_2$ | 20 | $CH_3CN$ | 25 | 67/2.3:1 |
| 17 | $MgI_2$ | 20 | toluene | 28 | 22/1.8:1 |
| 18 | $MgI_2$ | 20 | hexane | 24 | n.r[c] |

[a] All reactions were carried out under a nitrogen atmosphere: **1b** (0.15 mmol, 1 equiv.), **2a** (0.15 mmol, 1 equiv.), Lewis acid (0.03 mmol, 0.2 equiv.), 4 Å MS (200 mg), solvent (1 mL) at 25 °C.
[b] Isolated yield after flash column chromatography.
[c] n.r = no reaction.
[d] DCE = 1,2-dichloroethane.
[e] THF = Tetrahydrofuran,
[f] Temperature = 80 °C.

**Table 2.** Scope with respect to DACs.[a]




| Entry | DAC | Ar | *t* [h] | Products and Yields [%][b] | | |
|---|---|---|---|---|---|---|
| | | | | **3** | **4** | **5** |
| 1 | **1a** | 4-MeOC$_6$H$_4$ | 3 | 61 | 19 | – |
| 2 | **1b** | 3,4-(MeO)$_2$C$_6$H$_3$ | 2 | 55 | 30 | – |
| 3 | **1c** | 3,4-(CH$_2$O$_2$)C$_6$H$_3$ | 2.5 | 58 | 15 | 9 |
| 4 | **1d** | 2,4,6-(MeO)$_3$C$_6$H$_2$ | 0.32 | 71 | – | – |
| 5 | **1e** | 2-furyl | 3.5 | 56 | 22 | – |
| 6 | **1f** | *N*-benzylindol-3-yl | 0.32 | 68 | – | – |
| 7 | **1g** | 4-MeC$_6$H$_4$ | 7 | 54 | 14 | – |
| 8 | **1h** | *p*-isopropylC$_6$H$_4$ | 6.5 | 38 | – | – |
| 9 | **1i** | (*E*)-CH=CHC$_6$H$_5$ | 8 | 22 | 35 | 23 |

[a] All reactions were carried out under a nitrogen atmosphere: **1** (0.15 mmol, 1 equiv.), **2a** (0.15 mmol, 1 equiv.), MgI$_2$ (0.03 mmol, 0.2 equiv.), 4 Å MS (200 mg), CH$_2$Cl$_2$ (1 mL) at 25 °C.

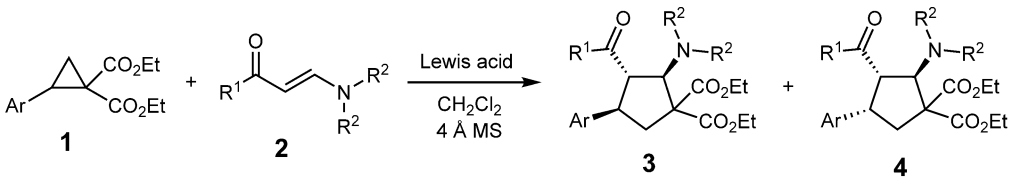
[b] Isolated yield after flash column chromatography.

(**1a**–**1l**) as well as enamines (**2a**–**2e**) and the results are presented in Table 2 and Table 3.

The reactivity of aryl-substituted DACs depends upon the various groups present on the aryl ring. Initially, we tested the methodology with more activated DACs containing an electron-donating group, such as methoxy (**1a** and **1b**) and methylenedioxy (**1c**) present in different positions of the aryl ring. Gratifyingly, these variants of DACs gave the best yield of the products **3aa** & **4aa**, **3ba** & **4ba** and **3ca** & **4ca** (Table 2, entries 1–3). Notably, a conjugated cyclopentenone **5** was observed in some cases (from cyclopropanes **1c** and **1i**), resulting from elimination of the amine functionality. However, the reason behind this specific elimination is not clear at this time. The 2,4,6-trimethoxyphenyl substituted DAC **1d** gave only isomer **3da** in 20 min (Table 2, entry 4). When a heterocyclic ring was incorporated and the respective DACs **1e** and **1f** were subjected to the above transformation, they also yielded the products **3ea** & **4ea** and **3fa** (Table 2, entries 5 and 6). Noticeably, the more reactive and highly substituted cyclopropanes **1d** and **1f** each produce the single isomer. The yields of the reactions were suppressed when *p*-tolyl- and *p*-isopropylphenyl-substituted DACs were used. Thus, a less electron-donating alkyl group could cause a lower yield of the reaction (Table 2, entries 7 and 8). Simple phenyl-substituted **1k** and *o*-methylphenyl-substituted **1j** DACs failed to undergo the cycloaddition reactions even at higher temperature (DCE, 80 °C). This may be due to electronic and steric effect of the *ortho* substitution at the phenyl ring. To install an easily cleavable group at NFCs, the reaction was tested with 2-styryl DAC **1i** and the corresponding products **3ia**, **4ia** & **5ia** were obtained in high yield (Table 2, entry 9).

The scope of the reaction was further extended by employing various β-aminoacrylates or enone **2b**–**2e**

**Table 3.** Scope with respect to enamines.[a]



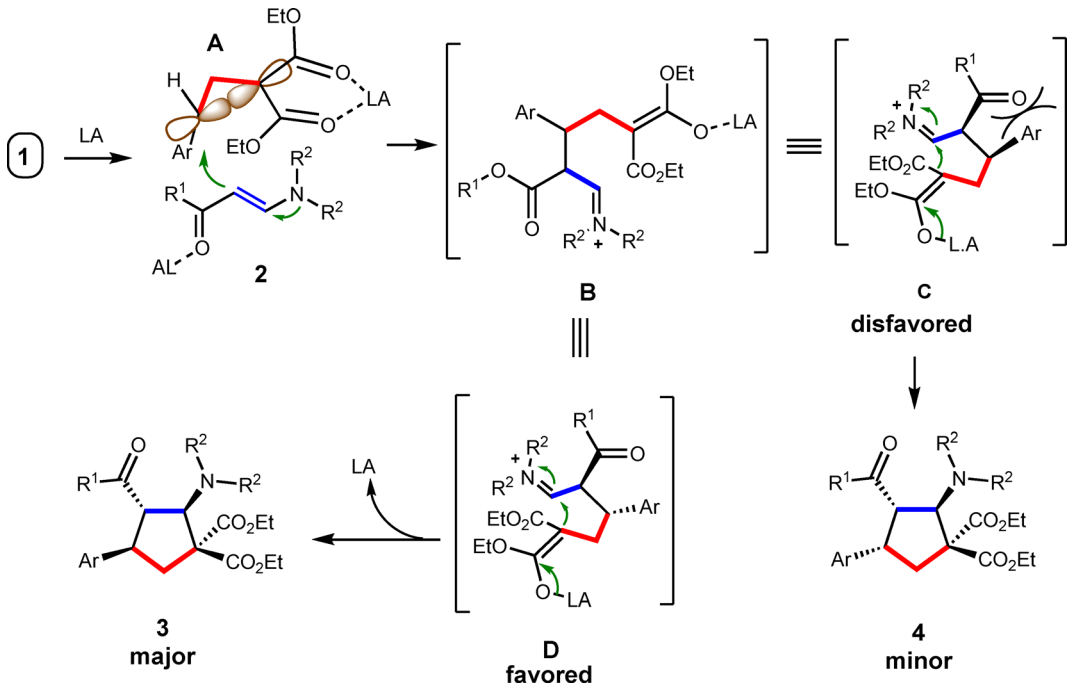

| Entry | **1** | **2** | Ar | R$^1$ | R$^2$ | *t* [h] | Product and Yields [%][d] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | **3** | **4** |
| 1[b] | **1b** | **2b** | 3,4-(MeO)$_2$C$_6$H$_3$ | 2-naphthyl | Me | 4 | 50 | – |
| 2[b] | **1b** | **2c** | 3,4-(MeO)$_2$C$_6$H$_3$ | OMe | -(CH$_2$)$_2$- | 2.4 | 84 | – |
| 3[b] | **1b** | **2d** | 3,4-(MeO)$_2$C$_6$H$_3$ | OMe | -(CH$_2$)$_2$O- | 3 | 82 | – |
| 4[c] | **1b** | **2e** | 3,4-(MeO)$_2$C$_6$H$_3$ | OMe | CH$_2$Ph | 2 | 88 | – |
| 5[c] | **1l** | **2e** | NPhTh | OMe | CH$_2$Ph | 2 | 82 | – |
| 6[c] | **1k** | **2e** | C$_6$H$_5$ | OMe | CH$_2$Ph | 5 | 61 | 14 |
| 7[c] | **1g** | **2e** | 4-MeC$_6$H$_4$ | OMe | CH$_2$Ph | 4.5 | 63 | 16 |

[a] All reactions were carried out under a nitrogen atmosphere: **1** (0.15 mmol, 1 equiv.), **2** (0.15 mmol, 1 equiv.), Lewis acid (0.03 mmol, 0.2 equiv.), 4 Å MS (200 mg), CH$_2$Cl$_2$ (1 mL) at 25 °C,

[b] Lewis acid = MgI$_2$,

[c] Lewis acid = Cu(OTf)$_2$,

[d] Isolated yield after column chromatography.




**Scheme 2.** Plausible mechanism.

with DAC **1b** (Table 3). Reaction of **1b** and dibenzylamine-substituted enamine **2e** in the presence of $Cu(OTf)_2$ gave only the single isomer **3be** in 88% isolated yield (Table 3, entry 4). The configuration of the compound **3be** was confirmed by NOE and single crystal X-ray studies (Figure 2, see the Supporting Information).[12] To have more nitrogen functionality in the cycloadduct, **2e** was also treated with *N*-containing cyclopropane **1l** which gave **3le** in 82% yield (Table 3, entry 5). We further examined the reaction of enamine **2e** with less activated DACs. To our delight, phenyl- (**1k**) and *p*-methyl-substituted (**1g**) DACs gave the corresponding diastereomeric mixtures of the products **3ke** & **4ke** and **3ge** & **4ge** with combined yields of 75% and 79%, respectively (Table 3, entries 6 and 7). The enamines (**1c** or **1d**) that contain a pyrrolidine or morpholine amino functionality afforded **3bc** and **3bd**, respectively, in good yields (Table 3, entries 2 and 3). When the phenyl group was replaced by a naphthyl in enamine **2b**, the yield of the reaction was decreased to 50% (Table 3, entry 1).

Scheme 2 depicts a proposed mechanism of the reaction between **1** and **2** using different Lewis acids. The Lewis acid activates the DAC ring and transforms it to the intermediate **A**. Enamine **2** attacks on the intermediate **A** to generate the intermediate **B**. This intermediate can adopt two possible conformations **C** and **D**. In conformer **C**, the two bulky groups repel each other and result in minor product **4**. On the other hand, the conformer **D** featuring less steric hindrance leads to the major product **3**. The configuration of **3** and **4** was confirmed by NOE spectroscopy techniques (see the Supporting Information and Figure 3).

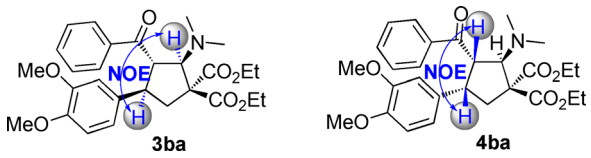
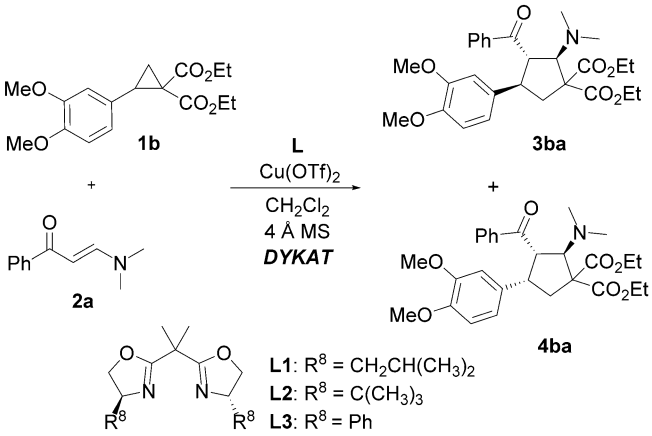



**Figure 3.** NOE observations of products **3ba** and **4ba**.

Next, we became interested in examining the feasibility of performing an asymmetric variant of our methodology. Following the previous reports on DyKAT,[13,8] we conducted the asymmetric reaction through DyKAT using racemic cyclopropane **1b** with enamine **2a** in the presence of broad range of bisoxazoline ligands (BOX) (**L1**–**L3**) in combination with $Cu(OTf)_2$ (Table 4). Initially, we attempted the asymmetric reaction with racemic DAC **1b** with **2a** in the presence of $Cu(OTf)_2$-**L1** complex, which gives an *er* of 8:1 and a 5.2:1 ratio of diastereomers **3ba** and **4ba** with 78% yield (Table 4, entry 1). DAC **1b** was fully consumed in the reaction and yielded 78% of NFC products (**3ba** and **4ba**). Compared to **L1**, the ligands **L2** & **L3** were found to give moderate *er* of both diastereomers (Table 4, entries 2 and 3). Other variants of ligand were also studied for the above transformation for optimization (see the Supporting Information).

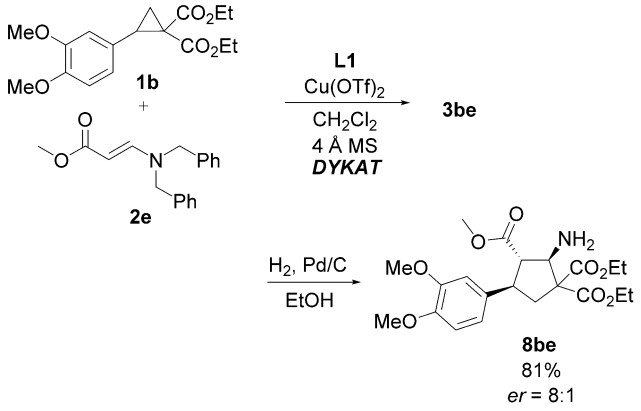
To synthesize enantioenriched free amine-functionalized cyclopentane derivative, the reaction of **1b** and

**Table 4.** Asymmetric [3+2] cycloaddition reaction between **2a** and **1b**: Screening with various BOX ligands.[a]




| Entry | L | *t* [h] | Yield [%][c] | 3ba:4ba | 3ba (*er*[b]) | 4ba (*er*[b]) |
|---|---|---|---|---|---|---|
| 1 | **L1** | 8 | 78 | 2.5:1 | 8:1 | 5.2:1 |
| 2 | **L2** | 9 | 77 | 3:1 | 3.7:1 | 2.7:1 |
| 3 | **L3** | 9 | 80 | 2.3:1 | 2.1:1 | 1.8:1 |

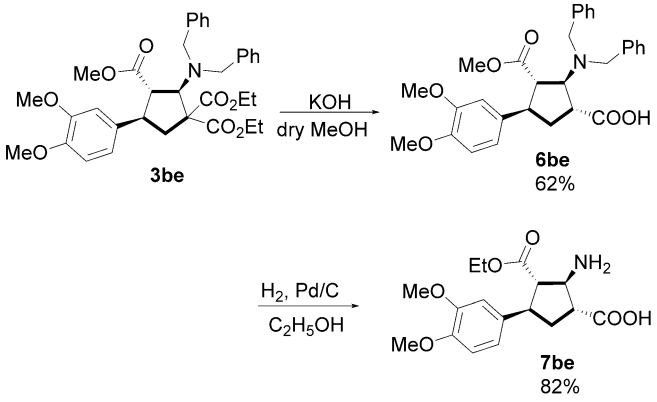
[a] All reactions were carried out under a nitrogen atmosphere: **2a** (0.15 mmol, 1 equiv.), **1b** (0.15 mmol, 1 equiv.), ligand (0.22 equiv.), Lewis acid (0.03 mmol, 0.2 equiv.), 4 Å MS (200 mg), $CH_2Cl_2$ (1 mL), room temperature.
[b] *er* = enantiomeric ratio,
[c] Isolated yield after flash column chromatography.




**Scheme 3.** Asymmetric synthesis of a cyclopentane derivative containing a free amine **8be**.

**2e** in the presence of Cu(OTf)$_2$-**L1** complex as catalyst yielded **3be**, which on hydrogenolysis gave an 81% yield of **8be** with 8:1 *er* (Scheme 3).

A synthetic application of the NFCs was demonstrated further for the preparation of β-amino acids, which have a great pharmacological potential.[14] An NFC derivative **3be** was partially decarboxylated in the presence of KOH at 70 °C to give a single diastereoisomer **6be**[15] and further hydrogenolysis using $H_2$, 10% Pd/C afforded **7be** with good yield of 82% (Scheme 4).




**Scheme 4.** Decarboxylation and hydrogenolysis steps.

In conclusion, we have developed a [3+2] cycloaddition reaction of enamines and DACs in the presence of various Lewis acids, providing a workable access to functionalized NFCs that are otherwise difficult to prepare. We have also shown an effective synthesis of enantiomerically pure NFC using the Cu(OTf)$_2$-**L1** catalytic system. Furthermore, decarboxylation and hydrogenolysis of an NFC derivative to a cyclic β-amino acid derivative may open up further synthetic potential of this protocol. Studies on the further applications of this protocol to the synthesis of natural products are in progress.

## Experimental Section

### General Procedure for the Cycloaddition Reaction

A two-necked round-bottom flask was charged with donor-acceptor cyclopropane **1** (1.0 equiv.), enamines **2** (1.0 equiv.), 4 Å MS (200 mol%) and Lewis acid (0.2 equiv.) under a nitrogen atmosphere. DCM was added to the reaction mixture and solution was stirred at room temperature until consumption of the cyclopropane (as monitored by TLC). The reaction mixture was filtered through thin pad of celite and solvent was concentrated in a rotary evaporator. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane as eluent.

## Acknowledgements

*KV thanks to the UGC, New Delhi, India for a research fellowship. PB acknowledges the DST-India for financial support. The authors are also thankful to Dr. C. M. Nagaraja, Department of Chemistry, IIT Ropar for solving the single crystal X-ray structure mentioned in this paper.*

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