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Enantioselective Intermolecular Rauhut–Currier Reaction of Electron-Deficient Allenes with Maleimides

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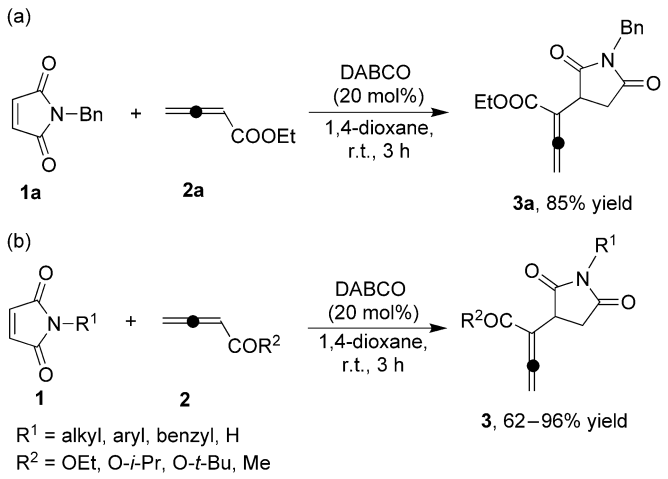
Abstract: The 1,4-diazabicyclic[2.2.2]octane (DABCO)-catalyzed intermolecular Rauhut–Currier reaction of maleimides with electron-deficient allenes has been investigated, affording the corresponding products in good to high yields under mild conditions. The first example of a β-isocupreidine (β-ICD)-catalyzed highly enantioselective intermolecular Rauhut–Currier reaction of maleimides with allenoates and penta-3,4-dien-2-one has been also developed, allowing the synthesis of optically active functionalized allene derivatives in good to high yields along with good to excellent enantioselectivities.

Keywords: allenes; chiral γ-butenolides; 1,4-diazabicyclic[2.2.2]octane (DABCO); enantioselectivitve Rauhut–Currier reaction; β-isocupreidine (β-ICD); maleimides

The Rauhut–Currier (RC) reaction, also known as vinylogous Morita–Baylis–Hillman (MBH) reaction, involves the coupling of one active alkene/latent enolate to a second Michael acceptor, producing a new C–C bond between the α-position of one activated alkene and the β-position of a second alkene under the catalysis of a nucleophilic species.[1] This reaction was first reported by Rauhut and Currier in 1963 in the dimerization of electron-deficient alkenes catalyzed by tertiary phosphine.[1b] A few years later, a series of phosphine-catalyzed intermolecular RC reactions was subsequently explored, demonstrating the wide synthetic utility of this reaction.[2] Moreover, in 1986, Amri and Villieras[3] first disclosed that tertiary amines such as 1,4-diazabicyclic[2.2.2]octane (DABCO) could also efficiently catalyze the intermolecular RC reactions under mild conditions and since then, this type of tertiary amine-catalyzed intermolecular RC reactions has been further developed by Basavaiah and co-workers as well as other researchers during the last decades.[4] The first asymmetric version of an intermolecular Rauhut–Currier reaction was presented by Wang and co-workers using a *Cinchona* alkaloid thiourea as a catalyst in a novel asymmetric Michael–Michael cascade reaction of *trans*-3-(2-mercaptophenyl)-2-propenoic acid ethyl ester with *trans*-β-nitrostyrene in 2008.[5] Almost at the same time, scandium triflate [$Sc(OTf)_3$] combined with (*R*,*R*)-Phpybox was used as a catalyst by Scheidt and co-workers in an intermolecular RC reaction of silyloxyallenes with α,β-unsaturated ketones, affording the corresponding product in 72% yield, 20:1 (*Z*:*E*) and 70% *ee*.[6] However, to the best of our knowledge, there has been no report on the asymmetric intermolecular RC reaction involving electron-deficient alkenes with allenes promoted by the amine-based organocatalyst, although enantioselective intramolecular RC-type reactions have achieved a great progress in recent years.[7,8] In this paper, we would like to disclose the application of quinidine-derived β-isocupreidine (β-ICD) as organocatalyst for the asymmetric intermolecular RC reaction of maleimides with electron-deficient allenes, giving the corresponding products in high yields and good to high *ee* values under mild conditions.

We initiated our investigations by seeking the best conditions for the intermolecular RC reaction between maleimide **1a** and ethyl allenoate **2a**. After screening of the catalysts and investigating the effects of solvent, reaction time and temperature on the reaction outcomes, we determined that the optimized reaction conditions are to carry out the reaction in 1,4-dioxane at room temperature for 3 h using DABCO (20 mol%) as the catalyst [Scheme 1, Eq. (a)] (see



Scheme 1. DABCO-catalyzed RC reactions of maleimides **1** with allenes **2**.

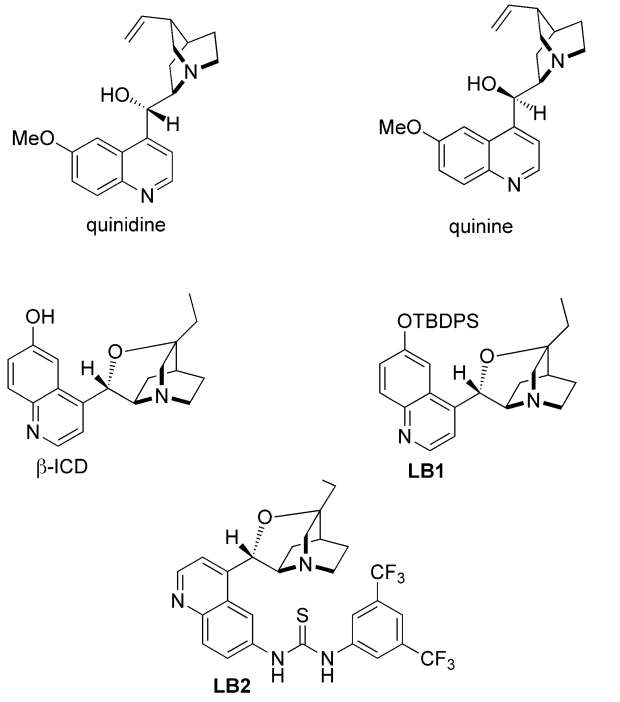


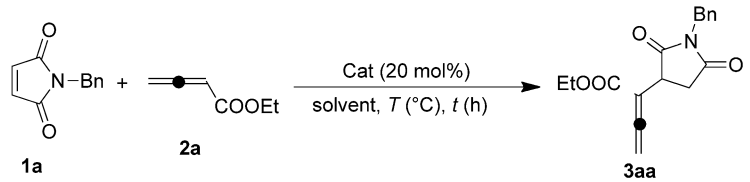
Figure 1. Nitrogen-containing chiral organocatalysts screened.

Table SI-1 in the Supporting Information for details). Under the optimal reaction conditions, we next set out to examine the scope and limitations of this reaction using various maleimides **1** and electron-deficient allenes **2** and it was found that all of these *N*-alkyl-, *N*-aryl-, and *N*-benzyl-substituted maleimides **1** could react with **2** smoothly to give the corresponding RC products **3** in moderate to good yields (62–96%) under the standard conditions [Scheme 1, Eq. (b)] (see Table SI-2 in the Supporting Information for details).

In view of our results on the intermolecular RC reactions of maleimides **1** with allenoates and penta-3,4-dien-2-one effectively catalyzed by DABCO, the next logical step was to investigate the asymmetric version of this reaction by using nitrogen-containing chiral organocatalysts (Figure 1). First, quinidine and quinine were used as the catalysts in this RC reaction of **1a** with **2a**. We found that using quinidine (20 mol%) as the catalyst afforded **3aa** in 65% yield along with 66% *ee* in 1,4-dioxane at 25 °C for 7 days (Table 1, entry 1); using quinine as the catalyst, a similar result was obtained, giving **3aa** in 63% yield and 61% *ee* with the reversed absolute configuration (determined by chiral HPLC) under the same reaction conditions (Table 1, entry 2). Gratifyingly, it was found that β-ICD was the more effective catalyst in this reaction, giving **3aa** in 93% yield and 81% *ee* within 16 h (Table 1, entry 3). Catalyst **LB1** synthesized from β-ICD by protecting the OH group with *tert*-butyl-(diphenyl)chlorosilane (TBDPSCl) could not catalyze this reaction under the standard conditions, suggesting that the C-6′-OH group of β-ICD is very important for the reaction (Table 1, entry 4). Another *Cinchona* alkaloid-derived catalyst **LB2** was also examined in this reaction, giving **3aa** in 92% yield and 71% *ee* within one day (Table 1, entry 5).

Using β-ICD (20 mol%) as the catalyst, we next examined the solvent effects and reaction temperature on the reaction outcome to further optimize the reaction conditions. In solvents such as CH_2Cl_2 (DCM), THF, toluene, CH_3CN and Et_2O, the corresponding product **3aa** was obtained in moderate to high yields (from 68% to 96%) but with lower *ee* values (from 29% to 75%) (Table 1, entries 6–10). Protic solvents such as methanol were not suitable media for this reaction, affording complex product mixtures (Table 1, entry 11). In the mixed solvent system CH_2Cl_2/dioxane = 1:2 (v/v), **3aa** was forme3d in 93% yield and 88% *ee* after 24 h (Table 1, entries 3 *vs.* 12) and no improvement was observed when the reaction was carried out at −20 °C (Table 1, entry 13). On further decreasing the reaction temperature to −40 °C and using the mixed solvent system CH_2Cl_2/dioxane = 3:2 (v/v), **3aa** was obtained in 85% yield and up to 90% *ee* (Table 1, entry 14). Since 1,4-dioxane will freeze at lower temperature in the reaction system, DCM was used as the solvent instead of 1,4-dioxane to accurately examine the temperature effect. Upon decreasing the reaction temperature from to 0 °C to −20 °C or −40 °C, we found that **3aa** could be obtained in up to 92% yield and 96% *ee* when the reaction was carried out at −20 °C within 24 h (Table 2, entries 15–17). Reducing the employed amount of β-ICD from 20 mol% to 10 mol% or 5 mol% resulted in the same reaction outcomes (Table 1, entries 18 and 19). Therefore, the best reaction conditions have been identified as those

Table 1. Optimization of the reaction conditions in the asymmetric RC reaction of **1a** with **2a**.[a]



Entry	Catalyst	Solvent	Temp. [°C]	Time [h]	Yield [%][b] 3aa	*ee* [%][c] 3aa
1	quinidine	dioxane	25	168	65	66
2	quinine	dioxane	25	168	63	-61
3	β-ICD	dioxane	25	16	93	81
4	**LB1**	dioxane	25	24	trace	-
5	**LB2**	dioxane	25	24	92	71
6	β-ICD	DCM	25	16	93	75
7	β-ICD	THF	25	16	86	67
8	β-ICD	toluene	25	16	68	69
9	β-ICD	CH_3CN	25	16	90	29
10	β-ICD	Et_2O	25	16	96	50
11	β-ICD	MeOH	25	16	complex	-
12	β-ICD	DCM/dioxane = 1:2 (v/v)	0	24	93	88
13	β-ICD	DCM/dioxane = 1:2 (v/v)	–20	24	89	88
14	β-ICD	DCM/dioxane = 3:2 (v/v)	–40	24	85	90
15	β-ICD	DCM	0	24	93	92
16	β-ICD	DCM	–20	24	92	96
17	β-ICD	DCM	–40	24	91	96
18[d]	β-ICD	DCM	–20	24	92	96
19[e]	β-ICD	DCM	–20	24	92	96

[a] The reaction was carried out on a 0.15 mmol scale, and the ratio of **1**/**2** was 1.0/2.0.
[b] Isolated yields.
[c] Determined by chiral HPLC.
[d] 10 mol% β-ICD was used.
[e] 5 mol% β-ICD was used.

using 5 mol% of β-ICD as the catalyst and carrying out the reaction in CH_2Cl_2 at −20 °C for 24 h.

With these optimal reaction conditions in hand, we subsequently turned our attention to examine the substrate scope of this interesting asymmetric RC reaction with respect to a variety of maleimides and electron-deficient allenes. The results of these experiments are summarized in Table 2. As can be seen from Table 2, *N*-benzylmaleimide **1a** and a variety of *N*-benzylmaleimide derivatives **1b**–**1i** having electron-rich or electron-poor aromatic groups on their R^1 groups or *N*-2-thienylmethylmaleimide **1j** bearing a heteroaromatic group as its R^1 group could react with electron-deficient allenes **2a**, **2b** and **2d** smoothly to give the corresponding RC products **3bb**–**3pp** in good to high yields along with 91–98% enantiomeric excesses (Table 2, entries 1–16). In the cases of maleimides **1k**–**1r** in which R^1 are aromatic groups, the reaction should be carried out at −60 °C in DCM for 72 h, affording the corresponding products **3qq**–**3yy** in

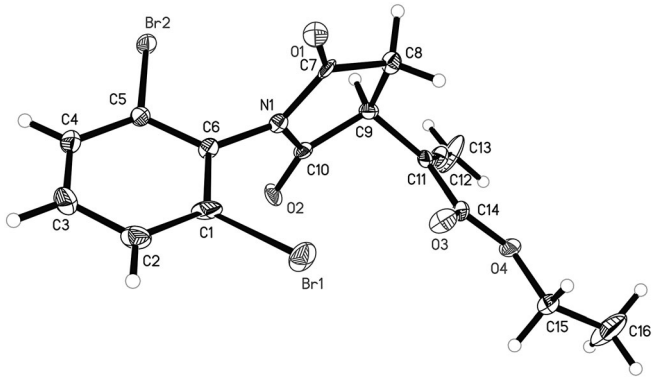
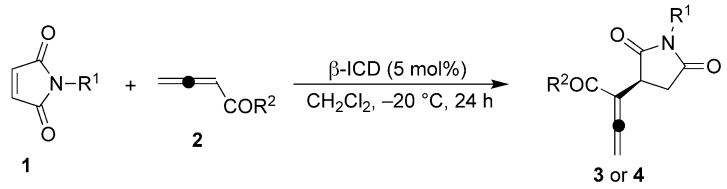
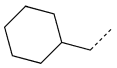
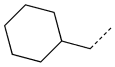


Figure 2. ORTEP drawing of **3ww**.

Table 2. Substrate scope of the asymmetric RC reaction of maleimides **1** with electron-deficient allenes **2** catalyzed by β-ICD[a].



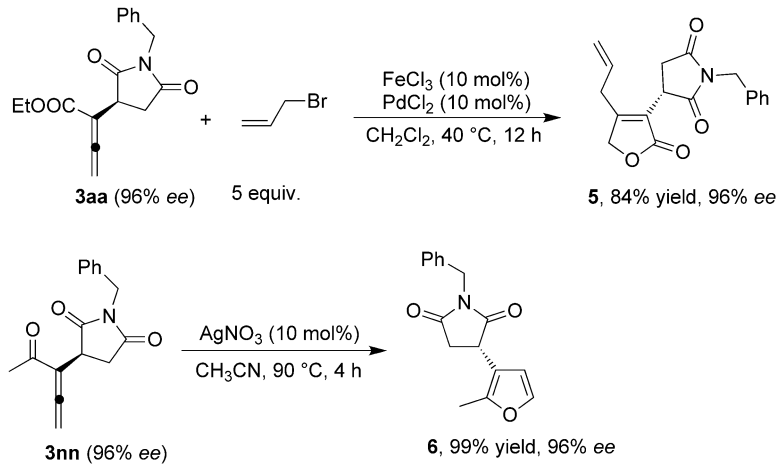
1 2 3 or 4

Entry	R^1	R^2	Yield [%][b]	ee [%][c,d]
1	**1a**, Bn	**2a**, OEt	**3aa**, 92	96 (*S*)
2	**1b**, $(C_6H_5)_2CH$	**2a**, OEt	**3bb**, 99	96 (*S*)
3	**1c**, 1-naphthalenemethyl	**2a**, OEt	**3cc**, 97	98 (*S*)
4	**1d**, 4-$MeOC_6H_4CH_2$	**2a**, OEt	**3dd**,92	94 (*S*)
5	**1e**, 3-$MeOC_6H_4CH_2$	**2a**, OEt	**3ee**, 96	96 (*S*)
6	**1f**, 3, 4-$(MeO)_2C_6H_3CH_2$	**2a**, OEt	**3ff**, 93	96 (*S*)
7	**1g**, 4-$BrC_6H_4CH_2$	**2a**, OEt	**3gg**, 98	92 (*S*)
8	**1h**, 4-$FC_6H_4CH_2$	**2a**, OEt	**3hh**, 94	94 (*S*)
9	**1i**, $(4\text{-}BrC_6H_4)_2CH$	**2a**, OEt	**3ii**, 89	95 (*S*)
10	**1j**, 2-thienylmethyl	**2a**, OEt	**3jj**, 93	95 (*S*)
11	**1b**, $(C_6H_5)_2CH$	**2b**, O-*i*-Pr	**3kk**, 89	91 (*S*)
12	**1c**, 1-naphthalenemethyl	**2b**, O-*i*-Pr	**3ll**, 91	95 (*S*)
13	**1a**, Bn	**2b**, O-*i*-Pr	**3mm**, 77	91 (*S*)
14	**1a**, Bn	**2d**, Me	**3nn**, 89	96 (*S*)
15	**1d**, 4-$MeOC_6H_4CH_2$	**2d**, Me	**3oo**, 92	96 (*S*)
16	**1g**, 4-$BrC_6H_4CH_2$	**2d**, Me	**3pp**, 86	95 (*S*)
17	**1k**, Ph	**2a**, OEt	**3qq**, 70[e], 84[f]	82[e], 73[f] (*S*)
18	**1l**, 4-$MeOC_6H_4$	**2a**, OEt	**3rr**, 90[e], 85[f]	81[e], 71[f] (*S*)
19	**1m**, 3,5-$(MeO)_2C_6H_3$	**2a**, OEt	**3ss**, 88[e], 92[f]	83[e], 75[f] (*S*)
20	**1n**, 3-MeC_6H_4	**2a**, OEt	**3tt**, 90[e], 86[f]	75[e], 75[f] (*S*)
21	**1o**, 4-$NO_2C_6H_4$	**2a**, OEt	**3uu**, 88[e], 89[f]	72[e], 57[f] (*S*)
22	**1p**, 4-ClC_6H_4	**2a**, OEt	**3vv**, 91[e], 91[f]	80[e], 67[f] (*S*)
23	**1q**, 2,6-$Br_2C_6H_3$	**2a**, OEt	**3ww**, 91[e]	85[e] (99)[g] (*S*)
24	**1r**, 2,4,6-$Br_3C_6H_2$	**2a**, OEt	**3xx**, 83[e]	75[e] (*S*)
25	**1k**, Ph	**2b**, O-*i*-Pr	**3yy**, 68[e]	73[e] (*S*)
26	**1s**, H	**2a**, OEt	**3zz**, 81[e], 92[f]	81[e], 72[f] (*S*)
27	**1t**, Me	**2a**, OEt	**4aa**, 84[e], 80[f]	78[e], 67[f] (*S*)
28	**1u**, 	**2a**, OEt	**4bb**, 86[e], 87[f]	75[e], 55[f] (*S*)
29	**1u**, 	**2c**, O-*t*-Bu	**4cc**, 68[e]	73[e] (*S*)

[a] The reaction was carried out on a 0.15-mmol scale with 5 mol% β-ICD under Ar in CH_2Cl_2 (1.0 mL) at −20 °C for 24 h and the ratio of **1**/**2** was 1.0/2.0.
[b] Isolated yields.
[c] Determined by chiral HPLC analysis.
[d] Absolute configuration was determined by X-ray diffraction of **3ww** (see the Supporting Information).
[e] The reaction was carried out at −60 °C for 72 h.
[f] The yields and *ee* values were obtained by carrying out the reactions at −20 °C for 24 h.
[g] The *ee* value in the parenthesis was that of **3ww** after a single recrystallization.

68–91% yields and 72–85% *ee* values (Table 2, entries 17–25). A single recrystallization of **3ww** with 85% *ee* from DCM/petroleum ether (1:4) afforded the corresponding product in nearly enantiomeric pure product (99% *ee*), indicating that a simple recrystallization can improve the enanatiomeric excess of the obtained product (Table 2, entry 23). As for N-H maleimide **1s**, as well as the *N*-alkylmaleimide derivatives **1t** and **1u**, the reactions also proceeded smoothly to give the corresponding RC products **3zz** and **4aa**–**4cc** in 68–86% yields along with 73–81% enantiomeric excesses at −60 °C (Table 2, entries 26–29). The relatively lower yields and enantiomeric excesses for entries 17–29 in Table 2 were presumably due to the electronic and steric effects of *N*-aryl- or *N*-alkylmaleimides **1k**–**1u**.

The absolute configuration of products **3** or **4** was unambiguously assigned as the *S*-configuration on the basis of the X-ray crystallographic analysis of product **3ww** which has two bromine atoms on the aromatic ring (Figure 2).



Scheme 2. Further transformation of the obtained chiral Rauhut–Currier reaction products **3aa** and **3nn**.

To illustrate the synthetic utility of the thus obtained optically active RC reaction products **3** or **4**, the further transformation of **3aa** or **3nn** was performed in the presence of transition metal catalysts (Scheme 2). As shown in Scheme 2, the $FeCl_3/PdCl_2$-cocatalyzed coupling cyclization[9] of optically active RC product **3aa** (96% *ee*) with allylic bromide afforded the corresponding β-allylic substituted γ-butenolide derivative **5** in 84% isolated yield with *ee* value retained. Optically active product **3nn** could be also readily transformed into the corresponding functionalized furan derivative **6** in 99% yield with *ee* value retained in acetonitrile by the silver-catalyzed rearrangement of the allenic moiety.[10] Furthermore, isomerization of product **3** catalyzed by PPh_3 has been also performed in toluene and the result has been summarized in Scheme SI-1 in the Supporting Information.

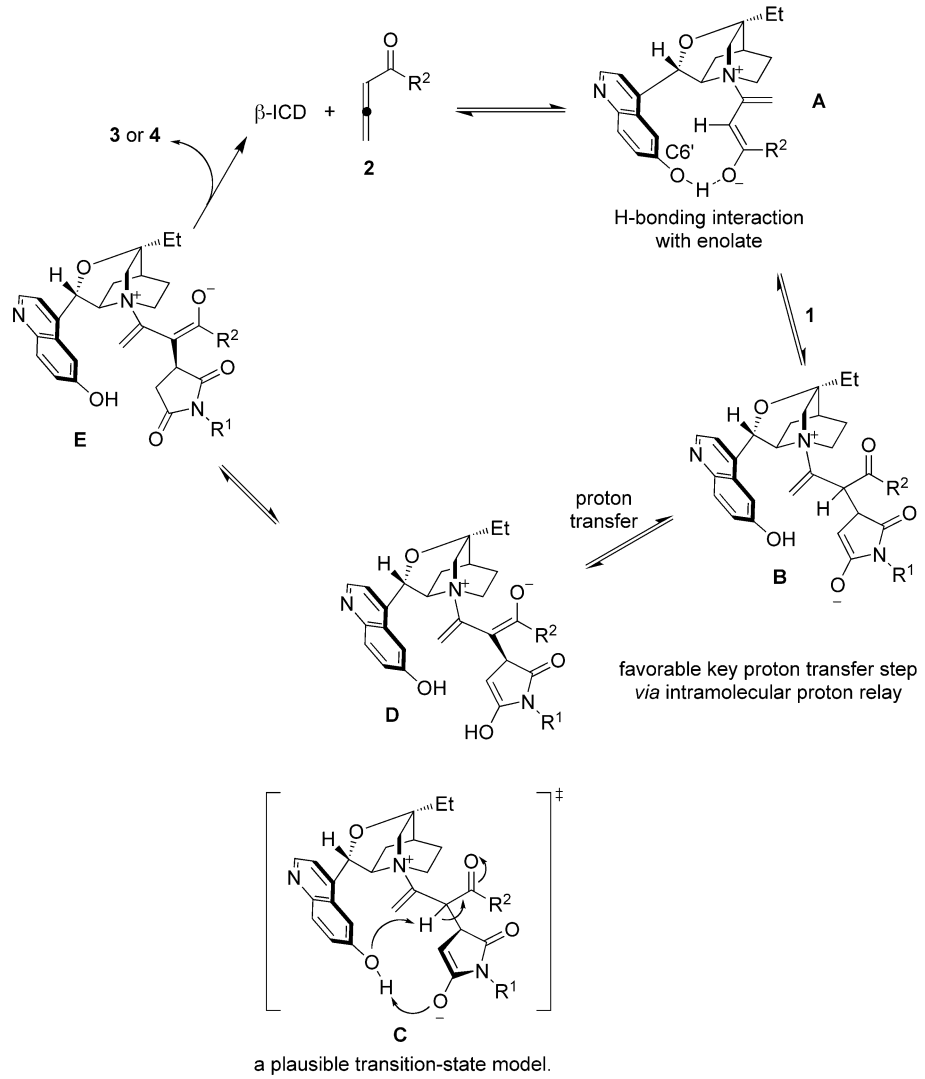
Based on the above experimental findings and previous mechanistic studies,[11] we propose a plausible mechanism of β-ICD-catalyzed asymmetric RC reaction in Scheme 3. The enolate **A** is generated upon nucleophilic addition of β-ICD to the allenic substrate, which is stabilized by the C-6′-OH group of β-ICD *via* an intramolecular hydrogen bonding interaction. The subsequent 1,4-addition of **A** with maleimide **1** leads to the formation of zwitterionic intermediate **B**. The following proton transfer is the key step (rate-determining step) on the basis of previous literature.[12] We believe that the acidic proton of the C-6′-OH group serves as a "proton shuttle" to facilitate the intramolecular proton transfer from the α-carbon to the oxygen anion. A plausible transition-state model **C** indicating the favorable key proton transfer step *via* intramolecular proton relay is also shown in Scheme 3. This proton transfer step also likely differentiates the four diastereomers of **B** and the major stereoisomer has been indicated in Scheme 3, leading to the production of the desired isomer **D**, which is then isomerized to intermediate **E**. Finally, intermediate **E** undergoes β-elimination to afford the RC adduct **3** or **4** and regenerate β-ICD at the same time to complete the catalytic cycle.

In summary, we have developed an efficient DABCO-catalyzed intermolecular Rauhut–Currier reaction of maleimides with electron-deficient allenes to afford the corresponding products in good to high yields under mild conditions. Furthermore, the first example of the highly enantioselective intermolecular Rauhut–Currier reaction of maleimides with allenoates and penta-3,4-dien-2-one has also been disclosed to produce the corresponding functionalized allenic derivatives in good to high yields along with good to excellent enantioselectivities in the presence of β-ICD (5 mol%) in CH_2Cl_2 at −20 °C or −60 °C. These chiral functionalized allenic derivatives can be further transformed to the corresponding chiral γ-butenolide derivatives and furan derivatives in good yields in the presence of transition metal catalysts.

Experimental Section

General Procedure for the DABCO- or β-ICD-Catalyzed Intermolecular Rauhut–Currier Reaction of Maleimide 1 with Electron-deficient Allene 2

Maleimide **1** (0.15 mmol), allene **2** (0.30 mmol), DABCO (0.030 mmol) or β-ICD (0.0075 mmol), and 1,4-dioxane or dichloromethane (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for 3 h or at −20 °C for 24 h, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (PE/EA = 4/1–2/1).



Scheme 3. A plausible mechanism.

Supporting Information

Experimental procedures, chiral HPLC traces, and spectroscopic data for all new compounds, X-ray crystal structure and CIF data for **3ww** are available in the Supporting Information.

Acknowledgements

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