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Chiral bifunctional organocatalysts for enantioselective synthesis of 3-substituted isoindolinones†

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A series of chiral bifunctional organocatalysts were prepared and used for enantioselective synthesis of 3-substituted isoindolinones from 2-formylarylnitriles and malonates through aldol-cyclization rearrangement tandem reaction in excellent yields and enantioselectivities (up to 87% yield and 95% ee) without recrystallization. In this investigation, we found that chiral tertiary-amine catalysts with a urea group can afford 3-substituted isoindolinones both in higher yields (87% vs. 77%) and enantioselectivities (95% ee vs. 46% ee) than chiral bifunctional phase-transfer catalysts.

1 Introduction

3-Substituted isoindolinones are important heterocycles present in many bioactive molecules, for examples, an anxiolytic agent (*S*)-pagoclone,¹ a potent dopamine D₄ ligand (*S*)-PD172938,² anti-tumor agents NMS-P515 (ref. 3) and (*R*)-NU8165 (ref. 4) and so on (Fig. 1). Due to their versatile physiological activities, many synthetic routes to 3-substituted isoindolinones have been developed by organic chemists. Recently, the catalytic asymmetric synthesis of isoindolinones has been summarized well by Peng and colleagues.⁵ On one hand, metal-catalyzed asymmetric preparation of 3-substituted isoindolinones was developed rapidly, Mg(II),⁶ Cu(I),⁷ Cu(II),⁸ Rh(III),⁹ Pd(II)¹⁰ and other metals with various chiral ligands as catalysts were used to produce isoindolinones in good to excellent yields and enantioselectivities, the reaction types of aza-Wacker type cyclization, tandem Michael–Mannich reaction, intramolecular dearomatization and hydrogenation are involved. In these metal-catalyzed reactions, α,β -unsaturated ketones with *N*-tosyl imines,⁷ 2-formylarylcarboxylic esters, arylamines with terminal alkynes,⁸ aryl hydroxamates with diazo esters,^{9a} *N*-methoxy arylamides with α,α -difluoromethylene alkynes,^{9b} were used as starting materials. On the other hand, many chiral organocatalysts including chiral phosphoric acids, ammonium salts, (thio)ureas and proline-

derived silyl ethers have shown good chiral induction in asymmetric synthesis of 3-substituted isoindolinones with moderate to good enantio-selectivities (Fig. 2).¹¹ In some organocatalyzed synthetic routes to chiral 3-substituted isoindolinones, excellent *ee* values of products were obtained through recrystallization,^{11a} which resulted in a loss of yield. Therefore, it is necessary to find an effective method to prepare 3-substituted isoindolinones with high yields and enantioselectivities in one pot without tedious recrystallization. We have reported asymmetric amination of nitrooleins by chiral phase-transfer catalysts (CPTCs) under neutral and water-rich conditions with high yields and enantioselectivities.¹² The precursors of these CPTCs are chiral bifunctional organocatalysts. For our continuous interest on the application of these CPTCs and bifunctional organocatalysts,¹³ herein, we have demonstrated the comparison of chiral induction of them for preparation of 3-substituted isoindolinones from 2-

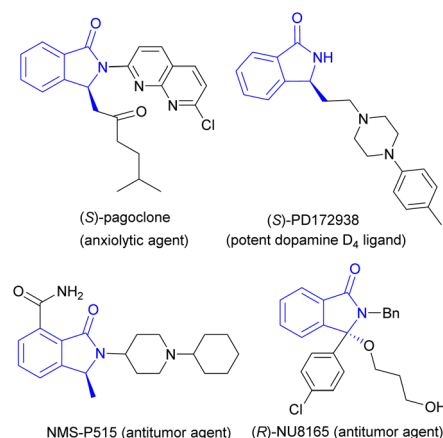


Fig. 1 Representative bioactive compounds containing 3-substituted isoindolinone core.

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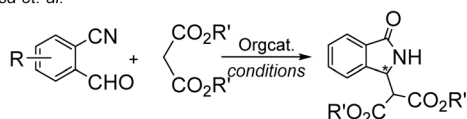
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**Conditions A:**

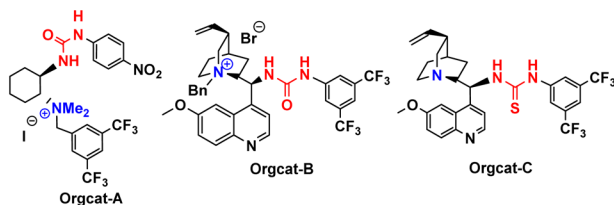
R = H, R' = Me, 5 mol% **Orgcat-A**, CH₂Cl₂, 1 eq. K₂CO₃, -10 °C, 10 h
98% yield and 78% *ee* (77% yield and 95% *ee* after a recrystallization)

Conditions B:

R = H, R' = Me, 5 mol% **Orgcat-B**, CH₂Cl₂, 1 eq. K₂CO₃, r.t., 4 h
99% yield and 43% *ee*

Conditions C:

R = H, R' = Bn, 5 mol% **Orgcat-C**, CH₂Cl₂, r.t., 70 h
95% yield and 55% *ee* (45% yield and 99% *ee* after a recrystallization)



This work

Conditions D:

R = H, R' = *i*-Pr, 5 mol% **Orgcat-D**, CH₂Cl₂, 2.0 eq. K₂CO₃, 0 °C, 16 h
77% yield and 46% *ee*

Conditions E:

R = 5-F, R' = Bn, 10 mol% **Orgcat-E**, CH₂Cl₂, r.t., 48 h
88% yield and 95% *ee* without a recrystallization

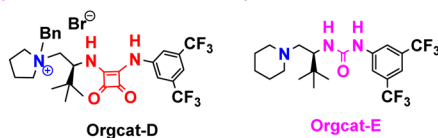


Fig. 2 The synthesis of chiral 3-substituted isoindolinones by organocatalyzed aldol-cyclization rearrangement reaction.

formylarylnitriles and malonates through aldol-cyclization rearrangement in good yields and excellent enantioselectivities (up to 87% yield and 95% *ee*) without recrystallization.

2 Results and discussion

2.1. Chiral bifunctional phase-transfer catalysts for synthesis of 3-substituted isoindolinones

Massa and colleagues have developed catalytic enantioselective synthesis of 3-substituted isoindolinones by chiral phase-

Table 1 The screening of CPTCs

Entry ^a	CPTC	Yield ^b (%)	<i>ee</i> ^c (%)	Config. ^d
1	None	67	0	—
2	CPTC-1	79	32	<i>S</i>
3	CPTC-2	72	26	<i>S</i>
4	CPTC-3	53	15	<i>S</i>
5	CPTC-4	48	11	<i>S</i>
6	CPTC-5	56	25	<i>S</i>
7	CPTC-6	78	24	<i>S</i>
8	CPTC-7	70	34	<i>S</i>
9	CPTC-8	75	13	<i>S</i>
10	CPTC-9	51	15	<i>S</i>
11	CPTC-10	74	22	<i>S</i>
12	CPTC-11	73	11	<i>S</i>
13	CPTC-12	77	46	<i>S</i>
14	CPTC-13	76	44	<i>S</i>
15	CPTC-14	76	13	<i>S</i>
16	CPTC-15	79	17	<i>S</i>
17	CPTC-16	71	10	<i>S</i>
18 ^e	CPTC-12	71	19	<i>S</i>
19 ^f	CPTC-12	78	0	—
20 ^g	CPTC-12	52	0	—
21 ^h	CPTC-12	49	27	<i>S</i>
22 ⁱ	CPTC-12	N. R.	—	—
23 ^j	CPTC-12	78	7	<i>S</i>
24 ^k	CPTC-12	N. R.	—	—

^a 1.0 mmol of **1a** and 1.1 mmol of **2c** in 5 mL dry CH₂Cl₂ were stirred under inert atmosphere. ^b Isolated yield based on **1a**. ^c Determined by chiral HPLC. ^d Compare to literature report. ^e r. t. reaction. ^f THF as solvent. ^g Toluene as solvent. ^h CHCl₃ as solvent. ⁱ EtOH as solvent, N. R. is no reaction. ^j 2.0 eq. Cs₂CO₃ as additive. ^k 2.0 eq. Na₂CO₃ as additive.

transfer catalysts (CPTCs).¹¹ These CPTCs are derived from 1,2-diaminocyclohexane and cinchona alkaloids, respectively. The enantiomeric 3-substituted isoindolinones were obtained in excellent yields (98%) and good *ee* values (up to 78% *ee* at -10 °C). The *ee* values of products can be promoted to be 99% *ee* after a recrystallization with a sacrifice for half original chemical yields. Chiral bifunctional phase-transfer catalysts with

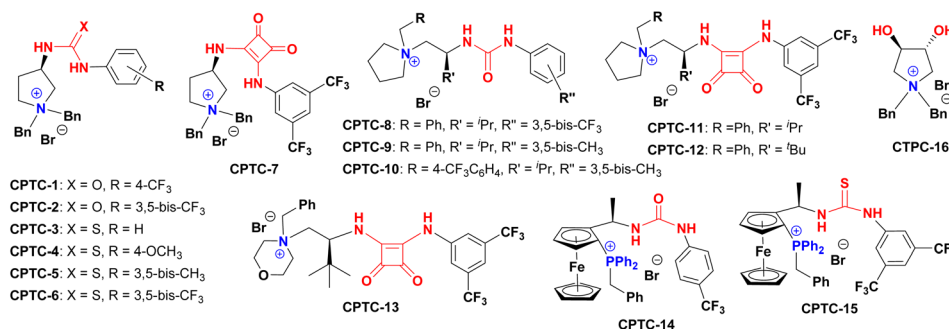


Fig. 3 The chemical structures of CPTCs.

various privileged scaffolds have been developed in recent years for many enantioselective transformations.¹⁴ we have reported catalytic asymmetric amination of β -nitrostyrenes by CPTCs in high yields and enantioselectivities. Inspired by these above-mentioned researches, herein, we have demonstrated a group of CPTCs for enantioselective synthesis of 3-substituted isoindolinones from 2-formylbenzonitriles and malonates. The chemical structures of CPTCs are illustrated in Fig. 3. At first, we choose the substrates 2-formylbenzonitrile **1a** and diisopropyl malonate **2c** as model substrates to investigate the enantioinduction of all listed CPTCs. The catalytic results are shown in Table 1. It was found that all CPTCs can catalyze this reaction under standard conditions (entries 2–17), **3ac** was obtained in moderate to good yields and low to moderate *ee* values. Among them, **CPTC-12** is the best catalyst to provide **3ac** in good yield (77%) but with a moderate enantioselectivity (46% *ee*, entry 13). When the reaction was performed at room temperature (r. t.), the enantioselectivity is decreased to 19% *ee* (entry 18). The solvent was switched to THF and toluene, **3ac** was obtained as racemate respectively (entries 19 and 20). CHCl_3 was used as a solvent to give **3ac** in both low yield and enantioselectivity (entry 21). No reaction was found when EtOH was used as a solvent (entry 22). More basic additive Cs_2CO_3 can spoil the reaction to produce **3ac** in high yield (78%) but very low *ee* (7% *ee*, entry 23), and less basic additive Na_2CO_3 resulted in no reaction (entry 24). Due to unfavourable results were obtained under phase-transfer catalysis conditions, no further substrate-extending was carried out.

2.2. Chiral bifunctional organocatalysts for synthesis of 3-substituted isoindolinones

Cinchona-derived ureas and thioureas have been used as chiral organocatalysts for preparation of chiral 3-substituted isoindolinones in excellent yield and moderate enantioselectivities by Massa and colleagues.^{11a} Inspired by their research work, we thought that chiral bifunctional organocatalysts (Bif-OCs) containing one tertiary amine and one hydrogen-bonding donor group (such as hydroxyl, amide, urea, thiourea and squaramide group) can sever as catalysts in this aldol-cyclization rearrangement reaction to prepare enantio-rich 3-substituted isoindolinones. Then, the catalytic activities of sixteen chiral bifunctional organocatalysts based privileged scaffolds (Fig. 4) were investigated in aldol-cyclization rearrangement reaction for preparation of chiral 3-substituted isoindolinones, and the results are listed in Table 2. L-Proline-derived **Bif-OC-1** with a secondary amine group can not catalyze this reaction at standard conditions (10 mol% of catalyst, r. t., 48 h, in CH_2Cl_2). Neither **Bif-OC-2** nor **Bif-OC-3** can provide the corresponding product **3ac** even possessing a tertiary amine group (entries 2 and 3). Thiourea **Bif-OC-4** and squaramide **Bif-OC-5** with 3-amino pyrrolidine backbone can afford **3ac** in good yield but with low *ees* (entries 4 and 5). 1,2-Diaminocyclohexane based ureas **Bif-OC-6** and **Bif-OC-7** demonstrate good chiral induction in this model reaction to furnish **3ac** in 76% and 75% yields with 69% and 68% *ee* values (entries 6 and 7). However, 1,2-diaminocyclohexane derived squaramides **Bif-OC-8** and **Bif-OC-9** with a bulky tertiary amine group can lead to a significant

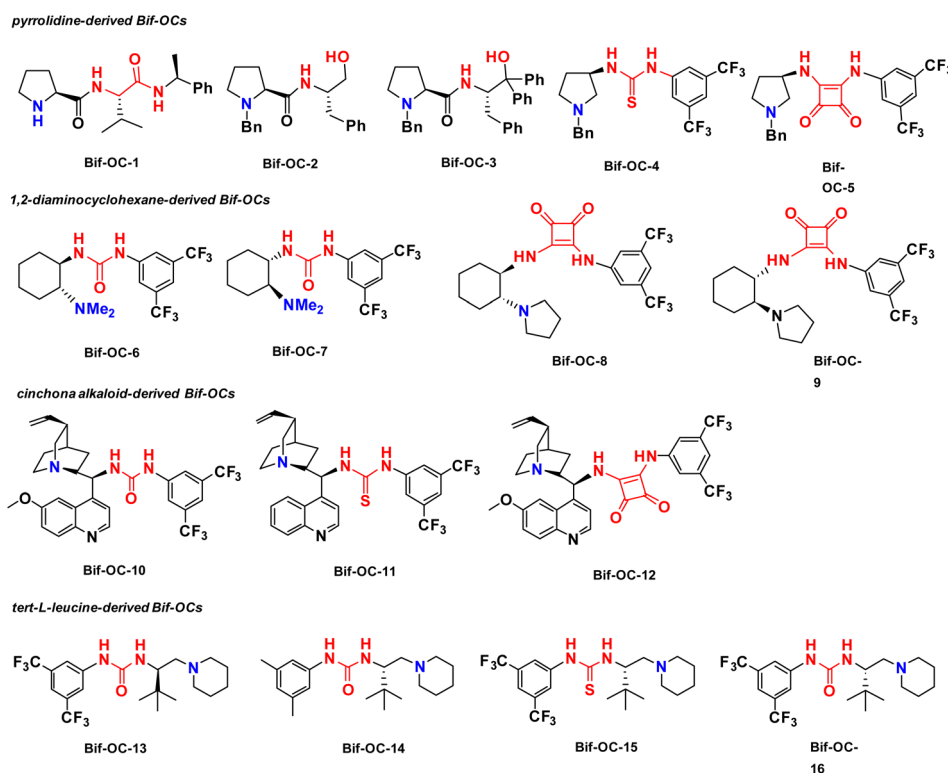
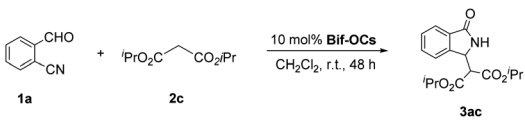


Fig. 4 The chemical structures of Bif-OCs.



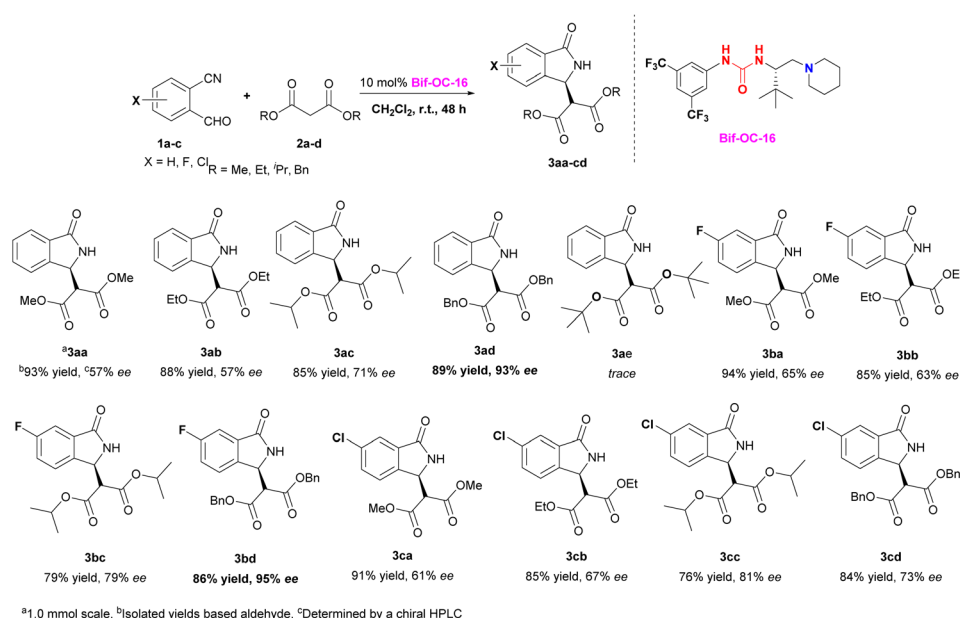
Table 2 The screening of Bif-OCs

				
Entry ^a	CPTC	Yield ^b (%)	ee ^c (%)	Config. ^d
1	Bif-OC-1	N. R.	—	—
2	Bif-OC-2	N. R.	—	—
3	Bif-OC-3	N. R.	—	—
4	Bif-OC-4	73	37	<i>S</i>
5	Bif-OC-5	77	10	<i>S</i>
6	Bif-OC-6	76	69	<i>S</i>
7	Bif-OC-7	75	68	<i>R</i>
8	Bif-OC-8	41	19	<i>S</i>
9	Bif-OC-9	48	21	<i>R</i>
10	Bif-OC-10	68	69	<i>S</i>
11	Bif-OC-11	72	68	<i>S</i>
12	Bif-OC-12	73	66	<i>S</i>
13	Bif-OC-13	83	70	<i>R</i>
14	Bif-OC-14	52	32	<i>S</i>
15	Bif-OC-15	77	36	<i>S</i>
16	Bif-OC-16	85	71	<i>S</i>
17 ^e	Bif-OC-16	N. R.	—	—
18 ^f	Bif-OC-16	49	33	<i>S</i>
19 ^g	Bif-OC-16	34	73	<i>S</i>
20 ^h	Bif-OC-16	78	70	<i>S</i>
21 ⁱ	Bif-OC-16	52	42	<i>S</i>
22 ^j	Bif-OC-16	44	30	<i>S</i>
23 ^k	Bif-OC-16	86	<i>rac</i> -	—
24 ^l	Bif-OC-16	82	<i>rac</i> -	—

^a 1.0 mmol of **1a** and 1.1 mmol of **2c** in 5 mL dry CH₂Cl₂ were stirred under inert atmosphere. N. R. is no reaction. ^b Isolated yield based on **1a**. ^c Determined by chiral HPLC. ^d Compare to literature report. ^e THF as solvent. ^f CH₃CN as solvent. ^g Toluene as solvent. ^h At 0 °C. ⁱ 5 mol% **Bif-OC-16** was used. ^j 1 mol% **Bif-OC-16** was used. ^k 2.0 eq. Cs₂CO₃ as additive. ^l 2.0 eq. K₂CO₃ as additive.

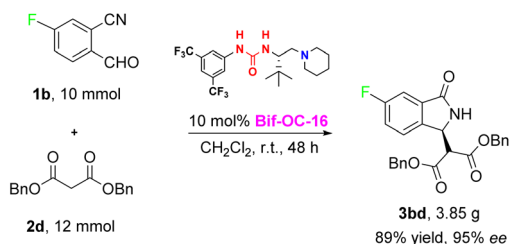
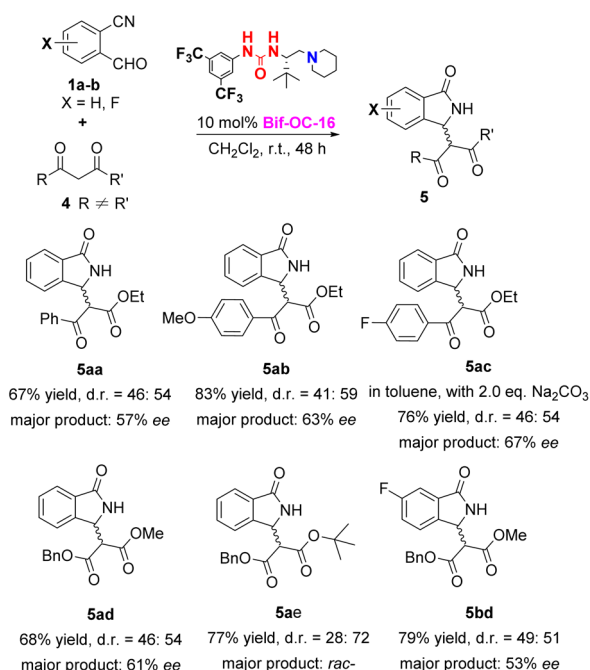
decrease both in yield and enantioselectivity of **3ac** (entries 8 and 9). Cinchona alkaloid-derived **Bif-OC-10**, **Bif-OC-11** and **Bif-OC-12** are very attractive organocatalysts for this aldol-cyclization rearrangement reaction to give **3ac** both in high yield (68–72%) and enantioselectivity (66–69% *ee*, entries 10 to 12). Chiral bifunctional urea organocatalysts from *tert*-leucine containing an electron-withdrawing aryl group (3,5-bis-CF₃C₆H₃) **Bif-OC-13** and **Bif-OC-16** have shown the same and satisfactory catalytic activity in this model reaction, and **3ac** was obtained in high yield (85%) and good enantioselectivity (71% *ee*, entries 13 and 16). Urea **Bif-OC-14** with an electron-donating aryl group (3,5-bis-MeC₆H₃) can make a sharp decline in yield and *ee* of **3ac** which compared to **Bif-OC-16** (entry 14). Thiourea **Bif-OC-15** has provided a inferior result to **Bif-OC-16** in this aldol-cyclization rearrangement reaction (entry 15). Therefore, **Bif-OC-16** was chosen as the best catalyst for this reaction. When THF was used as a solvent, no reaction was found at the same time (entry 17), while **3ac** was afforded in 49% yield and 34% *ee* in CH₃CN (entry 18). The solvent was switched to toluene, **3ac** was obtained in higher enantioselectivity (73% *ee*) than in CH₂Cl₂ but with a low yield (34%, entry 19). The reaction was performed at 0 °C, no significant change in yield and *ee* of **3ac** was found (entry 20). The yield and enantioselectivity of **3ac** were decreased along with a decrease of amount of **Bif-OC-16** (entries 21 and 22, 5 mol% and 1 mol% **Bif-OC-16** was used, respectively). Additives Cs₂CO₃ and K₂CO₃ can overwhelm catalyst and lead to *rac*-**3ac** in high yield (entries 23 and 24). The optimal reaction conditions are listed here: 10 mol% of **Bif-OC-16**, CH₂Cl₂ as a solvent, and the reaction mixture was stirred at r. t. in 48 h.

With the optimal conditions in hand, the substrate scope of this reaction was investigated and the results are shown in Scheme 1. 3-Substituted isoindolinones **3aa–3cd** were obtained in good to excellent yields and enantioselectivities under

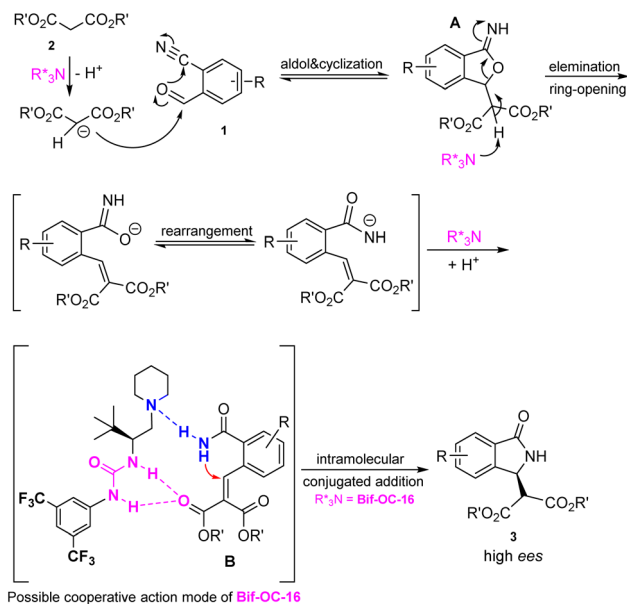


Scheme 1 Bif-OC-16 catalyzed aldol-cyclization rearrangement reactions.



Scheme 2 Gram-scale preparation of **3bd**.Scheme 3 Unsymmetric methylene compounds **4** in preparation of 3-substituted isoindolinones.

standard conditions (up to 94% yield and 95% ee) except **3ae** (trace yield) due to its bulky *tert*-Bu group. Dibenzyl malonate is a good substrate for this reaction to provide the corresponding products **3ad** and **3bd** in satisfactory yields (89% and 86% yields) and excellent ees (93% and 95% ees) without recrystallization, however, when 5-chloro-2-formylbenzonitrile was used as substrate, **3cd** was obtained in somewhat low enantioselectivity (73% ee of **3cd** vs. 95% ee of **3bd**). In order to show the practical use of this method, **3bd** was prepared in 10 mmol scale in 89% yield and 95% ee. This product **3bd** can be transformed to the corresponding chiral acid through hydrolysis and decarboxylation, and this chiral acid can be used as a building block for preparation of F-containing Pazinaclone and (*S*)-PD-172938 (Scheme 2).^{11a} No corresponding products were obtained when malononitrile and acetylacetone were used as substrates under the same conditions. There is a limitation of functional group transformation (FGT) when activated symmetric methylene compounds (such as dialkyl malonate or malononitrile) were used, decarboxylation following hydrolysis is common conversion of products **3aa–3cd**. It should be more

Fig. 5 The proposed mechanism for **Bif-OC-16** catalyzed aldol-cyclization.

interesting and useful to take activated unsymmetric methylene compounds (such as ethyl acetoacetate, ethyl 2-nitroacetate, ethyl 2-cyanoacetate, or nitromethane) as substrates. And then, we have investigated the performance of these activated unsymmetric methylene compounds **4** in this aldol-cyclization rearrangement reaction, and the results are listed in Scheme 3. All activated unsymmetric methylene compounds **4** used can take place the aldol-cyclization rearrangement reaction to provide corresponding products **5** in good yields (67–83%) but with poor diastereoselectivities (d. r. is about 1:1), and the enantioselectivities of major product are moderate (53–67% ee) except **5ae**.

A plausible mechanism for the formation of enantiomeric 3-substituted isoindolinones **3** in the presence of **Bif-OC-16** is shown in Fig. 5. Initially, the aldol-cyclization of 2-formylbenzonitriles **1** and malonates **2** took place in the presence of **Bif-OC-16** to form intermediate **A**, which underwent elimination and rearrangement to provide intermediate **B**. **Bif-OC-16** may play cooperative action mode with intermediate **B** through H-bonding between amide moiety and carboxylic group to activate both Michael donor and acceptor. The facial contact with the nucleophiles could be assisted by this cooperative action. The effect of this urea-based catalyst (**Bif-OC-16**) was significant, providing the desired products **3** in up to 95% ee. This catalytic mode is different from the chiral phase-transfer catalyst (CPTCs), and the chiral induction of CPTCs mainly depends on the electrostatic attraction of chiral ion pair between substrate and CPTCs.

3 Experimental

3.1 Typical procedure for synthesis of compound **3aa**

To a dried reaction tube, 2-formylbenzonitrile **1a** (1 mmol), dimethyl malonate **2a** (1.1 mmol), **Bif-OC-16** (45 mg, 0.1 mmol)



and 5.0 mL of dry CH_2Cl_2 were added successively. The mixture is stirred at room temperature for 48 h, and the reaction was monitored by TLC. When TLC indicates that **1a** was consumed, solvent CH_2Cl_2 was removed under reduced pressure to yield a yellow foam, which was purified by a flash column chromatography to give pure **3aa** as white solid.

4 Conclusions

In conclusion, we have developed a facile access to enantiomeric 3-substituted isoindolinones through aldol-cyclization rearrangement reaction catalyzed by chiral bifunctional organocatalysts in high yields and excellent enantioselectivities without recrystallization. It was found that chiral tertiary-amine urea catalyst can afford 3-substituted isoindolinones both in higher yields (87% vs. 77%) and enantioselectivities (95% *ee* vs. 46% *ee*) than chiral bifunctional phase-transfer catalysts.

Author contributions

P. A. W., Y. Y. Jia and G. Q. B. guided the research. X. M. H., H. D. and R. Z. conducted the experiments, analysed the results, and wrote the ESI and manuscript. Y. Y. J. and G. Q. B. helped revise the ESI and manuscript.

Conflicts of interest

There are no conflicts to declare.

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