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Enantioselective Organocatalytic Three-Component Petasis Reaction among Salicylaldehydes, Amines, and Organoboronic Acids

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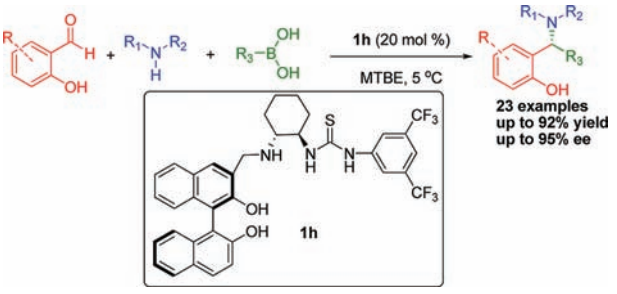
ABSTRACT



The catalytic enantioselective three-component Petasis reaction among salicylaldehydes, amines, and organoboronic acids with a newly designed thiourea-binol catalyst is presented. A broad range of alkylaminophenols can be obtained in good yield (up to 92%) and good to high enantioselectivity (up to 95% ee). A possible reaction pathway for this catalytic enantioselective Petasis reaction is tentatively proposed.

As a multicomponent reaction,[1] the Petasis reaction enjoys a history of nearly two decades and makes a significant contribution to the preparation of an assortment of compounds depending on the nature of the aldehyde component involved.[2] Among them, α-amino acids starting from glyoxylic acid and derivatives, α-hydroxyl amines starting from glycolaldehyde and derivatives, and alkylaminophenols starting from salicylaldehyde and derivatives are the most easily accessible.[3] In particular, studies on asymmetric induction by using various chiral reactants have achieved remarkable success in this area.[2b,2d,4] However, to date, there are only three examples concerning the catalytic enantioselective Petasis reaction reported by Takemoto[5] and Schaus,[6] respectively (Scheme 1, eqs 1−3). Notably, the three existing catalytic

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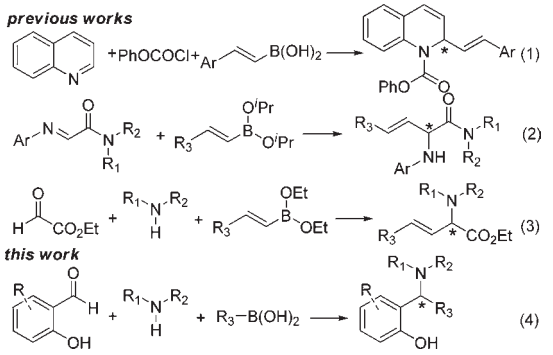
enantioselective versions are limited to substrates including quinolines,[5a] *N*-aryl-α-imino amides,[5b] and ethyl glyoxylates.[6] *Obviously, there is a lack of catalytic enantioselective Petasis reactions that tolerate variations of both aromatic aldehydes and readily available arylboronic acids.* Indeed, the Petasis reaction with salicylaldehydes as substrates (Scheme 1, eq 4) should be an attractive approach for the construction of alkylaminophenols,[2e] which have gathered considerable interest due to their accessibility to various reagents in organic synthesis and potential applications in drug discovery and material science. Therefore, the development of a catalytic enantioselective Petasis reaction for the three-component reaction among salicylaldehydes, amines, and organoboronic acids remains a highly desirable yet elusive goal.

Scheme 1. Existing Catalytic Enantioselective Versions of Petasis Reaction



Significant progress has been made on the reactions involving organoboronic reagents with chiral biphenol-derived diols as catalysts[4a,6,7] and on the development of chiral boronate esters based on the chiral BINOL backbone for asymmetric synthesis[8] and determination of the enantiomeric excess of chiral compounds.[9] Concurrently, asymmetric catalysis by chiral H-bond donors represents an attractive option in organic synthesis.[10] As part of our ongoing program on asymmetric organocatalysis,[11] we have recently found that various alkylaminophenols can be obtained in high yield and good to high enantioselectivity with a newly designed thiourea-binol catalyst **1h** which bears multiple H-bond donors. To the best of our knowledge, this represents the first catalytic enantioselective Petasis reaction among salicylaldehydes, amines, and organoboronic acids. Herein we wish to report our preliminary results on this subject.

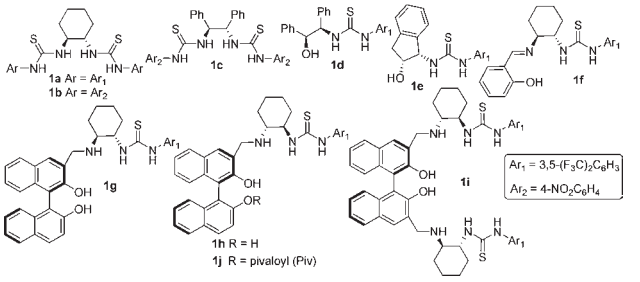


Figure 1. Chiral catalysts evaluated in this study.

Our initial studies started with the reaction of salicylaldehyde (**2a**), morpholine (**3a**), and (*E*)-styrylboronic acid (**4a**) in ethyl ether at 5 °C for the screening of a series of chiral organocatalysts **1a**−**i** (Figure 1).[12] As shown in Table 1, in the presence of 20 mol % chiral 1,2-diamine-derived thiourea catalysts **1a**−**c**, the reaction delivered the desired product **5aaa** in only moderate yield and poor enantioselectivity (entries 1−3). Further investigations into catalysts **1d**−**e** which bear thiourea moieties and hydroxyl groups revealed that **5aaa** also could be obtained with moderate yield and low ee (entries 4−5). Catalyst **1f** rendered the product in 64% yield and 42% ee (entry 6). Meanwhile, with a multiple H-bond donor thiourea-binol catalyst **1g**, a 68% yield and 8% ee were observed (entry 7). Because an appropriate match between chiral diamine moiety and the axial chiral BINOL moiety in **1g** was likely crucial for the enantiocontrol, catalyst **1h** was prepared and examined. To our delight, product **5aaa** could be obtained in 73% yield with a significantly improved enantioselectivity of 69% ee (entry 8). Another catalyst **1i** which bears more H-bond donors was not superior to **1h** in terms of enantioselectivity (entry 9). We then focused on the optimization of a **1h**-

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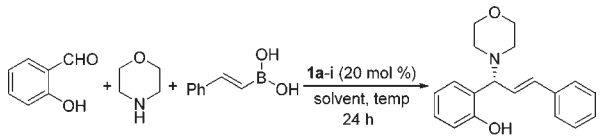
(12) For details about the preparation of some selected catalysts, see Supporting Information.

Table 1. Optimization Studies[a]



2a 3a 4a 5aaa

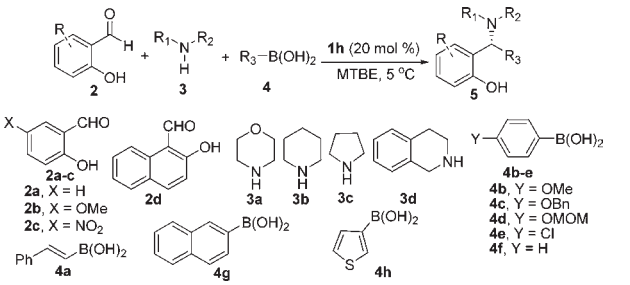
entry	1	solvent	temp (°C)	yield (%)[b]	ee (%)[c]
1	**1a**	Et_2O	5	53	39
2	**1b**	Et_2O	5	42	9
3	**1c**	Et_2O	5	43	12
4	**1d**	Et_2O	5	59	0
5	**1e**	Et_2O	5	55	9
6	**1f**	Et_2O	5	64	-42
7	**1g**	Et_2O	5	68	-8
8	**1h**	Et_2O	5	73	69
9	**1i**	Et_2O	5	82	45
10	**1h**	CH_2Cl_2	5	76	45
11	**1h**	toluene	5	83	56
12	**1h**	MTBE	5	83	73
13	**1h**	THF	5	25	55
14	**1h**	MTBE	15	86	70
15	**1h**	MTBE	-10	72	73[d]
16	**1h**	MTBE	-30	63	73[e]

[a] Unless otherwise noted, the reactions were run with **2a** (0.1 mmol), **3a** (0.1 mmol), and **4a** (0.1 mmol) in specified solvent (2.0 mL) with 20 mol % **1** at 5 °C for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC. [d] Run for 64 h. [e] Run for 96 h. MTBE = methyl *tert*-butyl ether.

catalyzed reaction to improve the Petasis reaction efficiency. A screen of solvents revealed that MTBE was the best solvent (entry 12 vs entries 8, 10, 11, and 13). Afterward, a survey of reaction temperatures indicated that performing the reaction at 5 °C afforded the best results (entry 12 vs entries 14−16).

With the optimal reaction conditions in hand (Table 1, entry 12), the substrate scope of the three-component Petasis reaction was surveyed. As shown in Table 2, the reaction can be extended to a wide variety of salicylaldehydes **2a**−**d**, amines **3a**−**d**, and organoboronic acids **4a**−**h** for the generation of a broad range of alkylaminophenols in up to 92% yield and up to 95% ee. For the aldehyde component, not only the salicyaldehyde but also electron-donating (**2b**) or -withdrawing (**2c**) substituent incorporation to the aromatic ring of salicyaldehyde showed good activities and enantioselectivities for giving the corresponding products (entries 1−22). The ee value of **5aaa** could be readily improved from 73% to 99% after recrystallization from a mixture of petroleum ether and ethyl acetate (entry 1). A sterically demanding aldehyde **2d** was also accommodated but with certain impact on the yield and enantiocontrol (entry 23). We also found that cyclic secondary amine, including morpholine (**3a**), piperidine (**3b**), pyrrolidine (**3c**), and even 1,2,3,4-tetrahydroisoquinoline (**3d**), was the most competent partner for this process. As to the organoboronic acid component, besides vinyl boronic acid (**4a**), a variety of arylboronic acids bearing either an electron-donating (**4b**−**d**) or −withdrawing group (**4e**) are also good substrates for the reaction. 2-Naphthyl-based boronic acid **4g** also underwent the Petasis reaction with different amines affording the expected products with good results (entries 12−13). Importantly, further extension of this protocol to heteroaryl boronic acid **4h** revealed that thiophen-3-ylboronic acid was also tolerated (entry 14). However, it should be noted that the current reaction system is ineffective for benzaldehyde derivatives lacking an *o*-hydroxy substituent, primary amines, acyclic secondary amines, and alkyl boronic acids reagents.[13]

Table 2. Substrate Scope[a]



entry	2	3	4	5	time (h)	yield (%)[b]	ee (%)[c]
1	**2a**	**3a**	**4a**	**5aaa**	24	83	73(99)[d]
2	**2a**	**3b**	**4a**	**5aba**	24	83	79
3	**2a**	**3c**	**4a**	**5aca**	24	73	73
4	**2a**	**3b**	**4b**	**5abb**	96	78	85
5	**2a**	**3c**	**4b**	**5acb**	96	92	90
6	**2a**	**3a**	**4d**	**5aad**	120	68	83
7	**2a**	**3b**	**4d**	**5abd**	120	65	82
8	**2a**	**3c**	**4d**	**5acd**	96	74	95
9	**2a**	**3b**	**4c**	**5abc**	96	68	87
10	**2a**	**3c**	**4c**	**5acc**	96	70	95
11	**2a**	**3c**	**4e**	**5ace**	36	61	74[e]
12	**2a**	**3a**	**4g**	**5aag**	36	90	82[e]
13	**2a**	**3c**	**4g**	**5acg**	36	92	86[e]
14	**2a**	**3a**	**4h**	**5aah**	96	88	86[f]
15	**2a**	**3d**	**4b**	**5adb**	96	67	74
16	**2b**	**3b**	**4b**	**5bbb**	96	89	80
17	**2b**	**3c**	**4b**	**5bcb**	96	91	95
18	**2c**	**3a**	**4b**	**5cab**	48	83	83
19	**2c**	**3b**	**4b**	**5cbb**	48	85	90
20	**2c**	**3c**	**4b**	**5ccb**	48	85	88
21	**2c**	**3b**	**4c**	**5cbc**	48	82	94
22	**2c**	**3c**	**4c**	**5ccc**	48	83	90
23	**2d**	**3c**	**4f**	**5dcf**	36	48	62[e,g]

[a] The reactions were run with **2** (0.2 mmol), **3** (0.2 mmol), and **4** (0.2 mmol) in MTBE (4.0 mL) with 20 mol % **1h** at 5 °C. [b] Isolated yield. [c] Determined by chiral HPLC. [d] The result in parentheses was obtained with recrystallization. [e] Run at 60 °C. [f] Run at rt. [g] The absolute configuration of **5dcf** was determined to be *R* configuration by comparing the optical rotation with the literature known compound.[14] The absolute configurations of remaining products were tentatively assigned by analogy.

We also performed a preparative scale reaction to demonstrate the practical features of this process. The reaction of **2a**, **3c**, and **4c** was carried out on a gram scale with 20 mol % catalyst **1h** in MTBE. As shown in Scheme 2, the reaction proceeded well to afford the corresponding product **5acc** in an improved isolated yield up to 87% without any loss of enantioselectivity (95% ee).

Although a detailed mechanism has yet to be elucidated, we attempted to conduct preliminary studies on the origin

(13) No desired product was observed when benzaldehyde, phenylmethanamine, aniline, dicyclohexylamine, dipentylamine, and cyclopropylboronic acid were used as one component, respectively. However, when dibenzylamine was used, the expected product could be obtained in only 32% yield, but it was racemate. For details, see Supporting Information.

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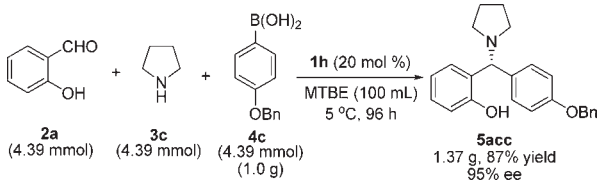
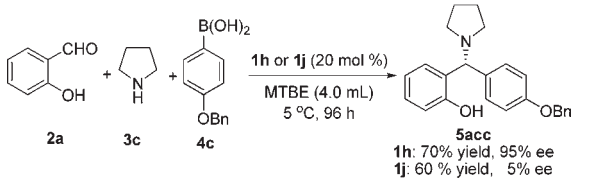
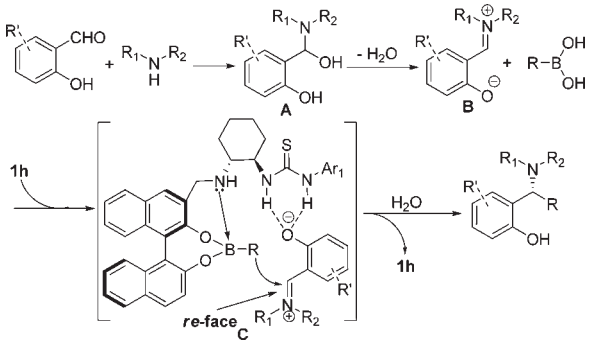
Scheme 2. Reaction on a Gram Scale



Scheme 3. Comparative Experiments with **1h** and **1j** as Catalyst



Scheme 4. Possible Reaction Pathway



of the enantioselective induction of this process. As shown in Scheme 3, the use of **1j** as the catalyst for the reaction afforded **5acc** in 60% yield but with only 5% ee. In sharp contrast, with **1h** as the catalyst under the same reaction conditions, a 70% yield and up to 95% ee were observed. Accordingly, we speculate that the diol functional group of BINOL in **1h** plays a crucial role in asymmetric induction. Additionally, to obtain further insight into the possible reaction pathway, we analyzed the 1:5 mixture of **1h** and **4b** in MTBE by ESI-MS, observing the mass of the 1:1 complex of **1h** and **4b**.[15] This result indicates that a cyclic binaphthyl-derived boronate ester fragment was likely formed by the exchange of the diol group of BINOL in **1h** with the hydroxyl groups of boronic acid.[15] Nevertheless, we also carried out a control experiment with a two-component catalyst composed of (*R*)-BINOL and (*R,R*)-bithiourea, furnishing the desired product in 62% yield but the ee lowered from 95% (Table 2, entry 10) to 31%.[16]

Finally, we tentatively propose a possible reaction pathway for the **1h**-catalyzed enantioselective Petasis reaction. As shown in Scheme 4, the nucleophilic addition of the secondary amines to salicylaldehydes produces the carbinolamine intermediate **A**. Then, the dehydration of the carbinolamine readily generates a key iminium intermediate **B** with the assistance of the *o*-phenolic hydroxyl group.[3,17] Afterward, a possible reaction intermediate **C** is proposed, in which the thiourea is associated to the phenol anion of **B**.[17,18] Simultaneously, a cyclic binaphthyl-derived boronate ester fragment is formed by the exchange of the diol group of the BINOL moiety in **1h** with the hydroxyl groups of boronic acid.[9,15] Subsequently, the R moiety of boronic acids favorably attacks the iminium ion from the *re*-face affording the desired product with *R*-configuration, while **1h** is released by hydrolysis. Further studies are currently underway to precisely understand the mechanism of this reaction.

In summary, we have developed an enantioselective three-component Petasis reaction among salicylaldehydes, secondary amines, and organoboronic acids catalyzed by a newly designed thiourea-binol catalyst. A broad range of alkylaminophenols bearing various functional groups can be obtained in good yield (up to 92%) and good to high enantioselectivity (up to 95% ee). The potential utility of the protocol has also been demonstrated by gram-scale reaction. Preliminary studies on the reaction mechanism were conducted, and a possible reaction pathway for this catalytic enantioselective Petasis reaction was tentatively proposed. Further mechanistic investigations and expanding the substrate scope are currently underway in our laboratory.

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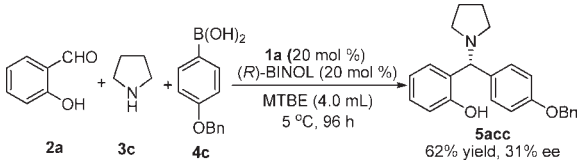
Supporting Information Available. Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(15) The ESI-MS spectrum is shown in the Supporting Information.

(16) A control experiment with a two-component catalyst composed of bithiourea **1a** and (*R*)-BINOL.



(17) For selected examples related to intermediates **A** and **B**, see: (a) Candeias, N. R.; Cal, P. M. S. D.; André, V.; Duarte, M. T.; Veiros, L. F.; Gois, P. M. P. *Tetrahedron* **2010**, *66*, 2736. (b) Tao, J. C.; Li, S. H. *Chin. J. Chem.* **2010**, *28*, 41. (c) Candeias, N. R.; Veiros, L. F.; Afonso, C. A. M.; Gois, P. M. P. *Eur. J. Org. Chem.* **2009**, 1859.

(18) For selected examples related to H-bond catalysis by anion binding, see: (a) Singh, R. P.; Foxman, B. M.; Deng, L. *J. Am. Chem. Soc.* **2010**, *132*, 9558. (b) Burns, N. Z.; Witten, M. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2011**, *133*, 14578. (c) Birrell, J. A.; Desrosiers, J.-N.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2011**, *133*, 13872. (d) De, C. K.; Mittal, N.; Seidel, D. *J. Am. Chem. Soc.* **2011**, *133*, 16802. (e) De, C. K.; Seidel, D. *J. Am. Chem. Soc.* **2011**, *133*, 14538. (f) Brown, A. R.; Kuo, W.-H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2010**, *132*, 9286. (g) Klauber, E. G.; De, C. K.; Shah, T. K.; Seidel, D. *J. Am. Chem. Soc.* **2010**, *132*, 13624. (h) De, C. K.; Klauber, E. G.; Seidel, D. *J. Am. Chem. Soc.* **2009**, *131*, 17060. (i) Reisman, S. E.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008**, *130*, 7198.