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Organocatalytic Mannich-Type Reactions of Trifluoroethyl Thioesters

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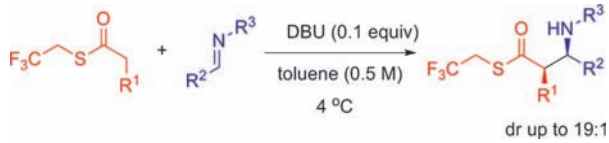
ABSTRACT



Direct organocatalytic Mannich-type reactions of thioesters provide for the expedient and diastereoselective synthesis of protected β-amino acids. A variety of thioesters were found to be reactive with different imines under mild conditions to provide β-amino acids in good yields. This chemistry was extended to a diastereo- and enantioselective variant.

Direct organocatalytic Mannich and Mannich-type reactions provide expedient access to α- and β-amino acids, amino alcohols and sugars, and amino carbonyl derivatives that are synthons of import in the pharmaceutical and other industries and have, therefore, received much attention.[1–3] We have devoted considerable effort toward addressing this reaction using enamine-based mechanisms and toward solving the stereochemical challenges of direct organocatalytic enantioselective *syn*- or *anti*-selective syntheses of these types of products based on the use of ketone or aldehyde donors.[3] A significant unmet challenge in this area is the development of direct organocatalytic Mannich and Mannich-type reactions that utilize donors in the ester oxidation state and are either diastereoselective or both diastereo- and enantioselective. Such reactions are not amenable to enamine-based organocatalytic approaches. Recently, we have described a new approach[4] to direct organocatalytic ester-based reactions that utilizes electronic tuning of thioesters to provide ester donor reactivity without need to resort to decarboxylative approaches[5] for enolate generation. Herein we report the application of this strategy to direct asymmetric Mannich-type reactions that utilize thioester donors.

(1) For recent reviews that consider the contributions of the many laboratories that have studied the organocatalytic Mannich reaction, see: (a) Ting, A.; Schaus, S. E. *Eur. J. Org. Chem.* **2007**, 5797. (b) Dondoni, A.; Massi, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4638.

(2) For recent leading references from other laboratories concerning organocatalytic Mannich and Mannich-type reactions, see: (a) Wang, W.; Wang, J.; Li, H. *Tetrahedron Lett.* **2004**, *45*, 7243. (b) Westermann, B.; Neuhaus, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4077. (c) Fustero, S.; Jimenez, D.; Sanz-Cervera, J. F.; Sanchez-Rosello, M.; Esteban, E.; Simon-Fuentes, A. *Org. Lett.* **2005**, *7*, 3433. (d) Cobb, A. J. A.; Shaw, D. M.; Longbottom, D. A.; Gold, J. B.; Ley, S. V. *Org. Biomol. Chem.* **2005**, *3*, 84. (e) Kano, T.; Yamaguchi, Y.; Tokuda, O.; Maruoka, K. *J. Am. Chem. Soc.* **2005**, *127*, 16408. (f) Franzen, J.; Marigo, M.; Fielenbach, D.; Wabnitz, T. C.; Kjaersgaard, A.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 18296. (g) Poulsen, T. B.; Alemparte, C.; Saaby, S.; Bella, M.; Jørgensen, K. A. *Angew. Chem.* **2005**, *117*, 2956; *Angew. Chem., Int. Ed.* **2005**, *44*, 2896. (h) Enders, D.; Grondal, C.; Vrettou, M. *Synthesis* **2006**, 3597. (i) Kano, T.; Hato, Y.; Maruoka, K. *Tetrahedron Lett.* **2006**, *47*, 8467. (j) Janey, J. M.; Hsiao, Y.; Armstrong, J. D., III. *J. Org. Chem.* **2006**, *71*, 390. (k) Chi, Y.; Gellman, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 6804. (l) Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048. (m) Ting, A.; Lou, S.; Schaus, S. E. *Org. Lett.* **2006**, *8*, 2003. (n) Song, J.; Shih, H. W.; Deng, L. *Org. Lett.* **2007**, *9*, 603. (o) Lou, S.; Dai, P.; Schaus, S. E. *J. Org. Chem.* **2007**, *72*, 9998. (p) Chi, Y.; English, E. P.; Pomerantz, W. C.; Horne, W. S.; Joyce, L. A.; Alexander, L. R.; Fleming, W. S.; Hopkins, E. A.; Gellman, S. H. *J. Am. Chem. Soc.* **2007**, *129*, 6050. (q) Cheng, L. L.; Han, X.; Huang, H. M.; Wong, M. W.; Lu, Y. X. *Chem. Commun.* **2007**, *40*, 4143. (r) Hashimoto, T.; Maruoka, K. *J. Am. Chem. Soc.* **2007**, *129*, 10054. (s) Yang, J. W.; Stadler, M.; List, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 609. (t) Marianacci, O.; Micheletti, G.; Bernardi, L.; Fini, F.; Fochi, M.; Pettersen, D.; Sgarzani, V.; Ricci, A. *Chem. Eur. J.* **2007**, *13*, 8338. (u) Guo, Q.-X.; Liu, H.; Guo, C.; Luo, S.-W.; Gu, Y.; Gong, L.-Z. *J. Am. Chem. Soc.* **2007**, *129*, 3790. (v) Cheng, L.; Wu, X.; Lu, Y. *Org. Biomol. Chem.* **2007**, *5*, 1018. (w) Kano, T.; Hato, Y.; Yamamoto, A.; Maruoka, K. *Tetrahedron* **2008**, *64*, 1197. (x) Yang, J. W.; Chandler, C.; Stadler, M.; Kampen, D.; List, B. *Nature* **2008**, *452*, 453. (y) Hayashi, Y.; Urushima, T.; Aratake, S.; Okano, T; Obi, K. *Org. Lett.* **2008**, *10*, 21. (z) Zhang, Y.; Liu, Y.-K.; Kang, T.-R.; Hu, Z.-K.; Chen, Y. -C. *J. Am. Chem. Soc.* **2008**, *130*, 2456.

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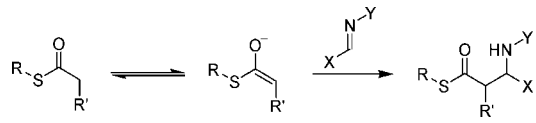
In order to expand the scope of direct organocatalytic reactions of trifluoroethyl thioesters,[4,6] we have evaluated thioesters as nucleophiles in Mannich-type reactions. Our goal was to study their general reactivity in direct Mannich-type reactions with preformed imines with the hope of developing a diastereoselective transformation en route to an enantioselective one (Scheme 1). We initially studied the

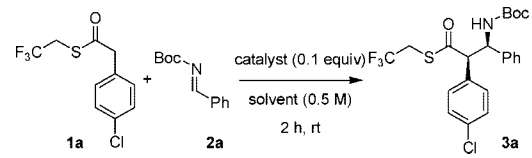
Scheme 1. Thioester Enolization and Addition to an Imine



reaction of thioester **1a** with the *N*-Boc-imine of benzaldehyde, **2a**, using a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Table 1).

In our preliminary study of the related aldol reaction,[4] we found that DBU was an effective catalyst. As noted in entries 1−9, we observed significant solvent effects on both the overall yield of the reaction and the diastereoselectivity of the reaction. Polar aprotic solvents such as DMF, CH_2Cl_2, and THF provided the product in good yield after 2 h; however, the reaction demonstrated only modest diastereoselectivity, slightly favoring the *syn*-product **3a** (entries 1−4). The protic solvent methanol provided the product with slight

Table 1. Catalyst and Solvent Screening for the Mannich Reaction of Thioester with *N*-Boc-imine[a]



entry	catalyst	solvent	yield[b] (%)		*syn*/*anti*[c]
1	DBU	DMF	96		57/43
2[d]	DBU	DMF	78		57/43
3	DBU	CH_2Cl_2	89		50/50
4	DBU	THF	86		57/43
5[e]	DBU	MeOH	17	(19)	41/59
6	DBU	CH_3CN	85		80/20
7[f]	DBU	hexane	quant		88/12
8[f]	DBU	Et_2O	quant		89/11
9[f]	DBU	toluene	94		83/17
10[f]	KO^{t}Bu	toluene	quant		41/59
11	Et_3N	toluene	22	(73)	50/50
12	^{i}Pr$_2$EtN	toluene	18	(80)	47/53
13	K_2CO_3	toluene	13	(87)	44/56

[a] Catalyst (0.01 mmol) was added to a mixture of thioester **1a** (0.1 mmol) with imine **2a** (0.12 mmol) in solvent (0.2 mL), and the reaction was stirred at room temperature for 2 h. [b] Yields were calculated from crude ^{1}H NMR spectra using anisole as a internal standard. Recovered yield of thioester is shown in parentheses. [c] Determined by crude ^{1}H NMR spectra. [d] MS4A was used as an additive. [e] MeOH adduct of imine (69% based on imine) and methyl 4-chlorophenylacetate (39% yield) were formed. [f] Products were precipitated during the reaction.

anti-selectivity albeit in very low yield (entry 5). A significant improvement in both yield and diastereoselectivity was observed for reactions in nonpolar solvents such as hexane, diethyl ether, and toluene (entries 7−9). Under these conditions, quantitative or near-quantitative yields of **3a** were obtained and the *syn*/*anti* ratio reached ∼8:1. We also observed that the reaction product **3a** precipitated during the course of the reaction when these solvents were used but remained soluble in the polar solvents studied (entries 1−5).

We then studied the role of the catalyst under the toluene solvent conditions. As noted in entry 10, the base KO^{t}Bu proved an effective substitute for DBU in terms of overall yield of the desired product; however, the reaction was poorly diastereoselective (entry 10). Reactions using the other three bases tested (Et_3N, ^{i}Pr$_2$EtN, K_2CO_3) gave reduced product yield and diastereoselectivity after 2 h relative to reactions in DBU. Most of thioester **1a** was recovered intact following reactions using Et_3N, ^{i}Pr$_2$EtN, and K_2CO_3, indicating that substrate decomposition was not responsible for the low yields under these conditions.

Next we optimized reaction time and temperature across the three most promising solvents (toluene, diethylether, and hexane) (Table 2). Our preliminary study of the reaction in toluene indicated that the reaction was complete in less than 2 h. Given that the product was insoluble using this and the other high-yielding solvent systems and that the diastereoselectivity of the reaction was low under solvent conditions wherein the product was soluble (polar solvents), we speculated that diastereoselectivity was under thermodynamic control driven by precipitation of the *syn*-product. To test this hypothesis, we studied both longer and shorter reaction times and reductions in reaction temperature. No significant change in

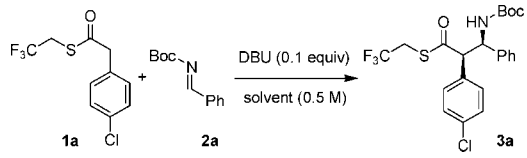
(3) For studies from this laboratory concerning organocatalytic Mannich and Mannich-type reactions, see: (a) Notz, W.; Sakthivel, K.; Bui, T.; Barbas, C. F., III. *Tetrahedron Lett.* **2001**, *42*, 199. (b) Sakthivel, K.; Notz, W.; Bui, T.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2001**, *123*, 5260. (c) Cordova, A.; Notz, W.; Zhong, G.; Betancort, J.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2002**, *124*, 1842. (d) Cordova, A.; Watanabe, S.; Tanaka, F.; Notz, W.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2002**, *124*, 1866. (e) Cordova, A.; Barbas, C. F., III. *Tetrahedron. Lett.* **2002**, *43*, 7749. (f) Watanabe, S.; Cordova, A.; Tanaka, F.; Barbas, C. F., III. *Org. Lett.* **2002**, *4*, 4519. (g) Notz, W.; Tanaka, F.; Watanabe, S.; Chowdari, N. S.; Turner, J. M.; Thayumanuvan, R.; Barbas, C. F., III. *J. Org. Chem.* **2003**, *68*, 9624. (h) Chowdari, N. S.; Ramachary, D. B.; Barbas, C. F., III. *Synlett* **2003**, 1906. (i) Cordova, A.; Barbas, C. F., III. *Tetrahedron Lett.* **2003**, *44*, 1923. (j) Notz, W.; Watanabe, S.; Chowdari, N. S.; G.; Zhong, Betancort, J. M.; Tanaka, F.; Barbas, C. F., III. *Adv. Synth. Catal* **2004**, *346*, 1131. (k) Chowdari, N. S.; Suri, J.; Barbas, C. F., III. *Org. Lett.* **2004**, *6*, 2507. (l) Notz, W.; Tanaka, F.; Barbas, C. F., III. *Acc. Chem. Res.* **2004**, *37*, 580. (m) Chowdari, N. S.; Ahmad, M.; Albertshofer, K.; Tanaka, F.; Barbas, C. F., III. *Org. Lett.* **2006**, *8*, 2839. (n) Cheong, P. H.-Y.; Zhang, H.; Thayamanavan, R.; Tanaka, F.; Houk, K. N.; Barbas, C. F., III. *Org. Lett.* **2006**, *8*, 811. (o) Mitsumori, S.; Zhang, H.; Cheong, P. H. Y.; Houk, K. N.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2006**, *128*, 1040. (p) Zhang, H. L.; Mifsud, M.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2006**, *128*, 9630. (q) Ramasastry, S. S. V.; Zhang, H.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2007**, *129*, 288. (r) Zhang, H.; Ramasastry, S. S. V.; Tanaka, F.; Barbas, C. F., III. *Adv. Synth. Catal.* **2008**, *350*, 791. (s) Zhang, H. L.; Mitsumori, S.; Utsumi, N.; Imai, M.; Garcia-Delgado, N.; Mifsud, M.; Albertshofer, K.; Cheong, P. H.-Y.; Houk, K. N.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2008**, *130*, 875.

(4) Alonso, D. A.; Kitagaki, S.; Utsumi, N.; Barbas, C. F., III. *Angew. Chem., Int. Ed.* **2008**, *47*, 4588.

(5) (a) Magdziak, D.; Lalic, G.; Lee, H. M.; Fortner, K. C.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 7284. (b) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852. (c) Orlandi, S.; Benaglia, M.; Cozzi, F. *Tetrahedron Lett.* **2004**, *45*, 1747. (d) Yost, J. M.; Zhou, G.; Coltart, D. M. *Org. Lett.* **2006**, *8*, 1503. (e) Ricci, A.; Pettersen, D.; Bernardi, L.; Fini, F.; Fochi, M.; Perez Herrera, R.; Sgarzani, V. *Adv. Synth. Catal.* **2007**, *349*, 1037. (f) Lubkoll, J.; Wennemers, H. *Angew. Chem.* **2007**, *119*, 6965; *Angew. Chem., Int. Ed.* **2007**, *46*, 6841.

(6) Um, P. -J.; Drueckhammer, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 5605.

Table 2. Effect of Temperature and Reaction Time on the Reaction of Thioester with *N*-Boc-imine[a]



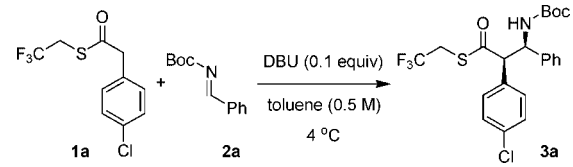
entry	solvent	T (°C)	time (h)	yield[b] (%)	*syn*/*anti*[c]
1	toluene	25	2	89	83/17
2	toluene	25	6	89	83/17
3	toluene	4	5 min	98	75/25
4	toluene	4	2	96	92/8
5	toluene	−15	4	quant	91/9
6	toluene	−40	2	93	29/71
7	toluene	−78	2	8 (83)	50/50
8	Et_2O	25	2	quant	89/11
9	Et_2O	4	2	91	89/11
10	Et_2O	−15	4	quant	89/11
11	hexane	25	2	quant	88/12
12	hexane	4	2	quant	88/12
13	hexane	−15	4	quant	75/25

[a] Catalyst (0.01 mmol) was added to a mixture of thioester **1a** (0.1 mmol) with imine **2a** (0.12 mmol) in a solvent (0.2 mL). The reaction was stirred at specified temperature for the specified time. [b] Yield was calculated by NMR of the crude product using anisole as an internal standard. Recovered yield of thioester is shown in parentheses. [c] Determined by ^{1}H NMR of crude product.

either yield or diastereoselectivity was noted when we increased the reaction time from 2 to 6 h (entries 1 and 2). However, when we slowed the reaction by lowering the temperature to 4 °C and worked up the reaction after just 5 min, the yield remained high but the diastereoselectivity was reduced (entry 3). Significantly, the *syn*:*anti* ratio of the 4 °C reaction was improved to 92:8 (from 75:35 after 5 min) simply by extending the reaction time to 2 h (entry 4). Interestingly, reduction of the reaction temperature to −40 °C (entry 6) resulted in a slightly *anti*-selective reaction, whereas reduction of the temperature to −78 °C significantly slowed the reaction (8% yield after 2 h) and no selectivity was obtained (entry 7). Reactions in diethyl ether were high yielding over the +4 to −15 °C range, providing the *syn*-product with ∼8:1 (*syn*:*anti*) diastereoselection (entries 8−10). Reactions in hexane did not provide diastereoselectivities exceeding ∼7:1 (entries 11−13).

These data are consistent with our hypothesis that *syn*-selectivity was driven by product solubility and that the *syn* and *anti* isomers could interconvert under the reaction conditions wherein the *syn* product was less soluble than the *anti* product. To further test this hypothesis, we reexamined the reaction in toluene at 4 °C (Table 2, entries 3 and 4). We isolated the reaction product by extractive workup and compared the isolated product with product isolated by filtration (insoluble precipitate was formed during the reaction) (Table 3, entries 1 and 2). We found that the product isolated via filtration was *syn*-enriched compared to that obtained from extractive workup. However, when the reaction time was extended to 2 h, which allowed the reaction to equilibrate, there was little difference in the selectivities of products isolated using the two methods (Table 3, entries 3 and 4).

Table 3. Selectivities when Products Were Isolated Using Extraction vs Filtration[a]

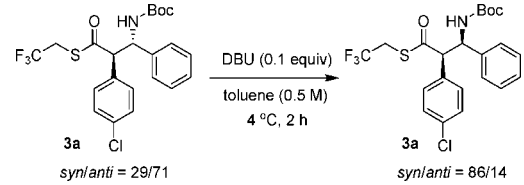


entry	workup method	time (min)	yield[b] (%)	*syn*/*anti*[c]
1	extraction[d]	5	98	75/25
2	filtration[e]	5	70	83/17
3	extraction[d]	120	96	92/8
4	filtration[e]	120	65	96/4

[a] DBU (0.1 equiv) was added to a mixture of thioester **1a** (1 equiv) with imine **2a** (1.2 equiv) in toluene (0.5 M), and the reaction was stirrred at 4 °C for specified time. [b] Isolated yield. [c] Determined by ^{1}H NMR spectra. [d] Extraction by EtOAc/brine followed by purification by flash column chromatography. [e] The precipitated solid was collected by filteration and washed using small amount of cold toluene.

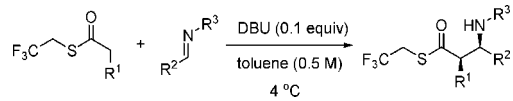
As final evidence for a dynamic thermodynamic mechanism, purified product **3a** (Table 2, entry 6), which had a *syn*:*anti* ratio of 29:71, was incubated with fresh DBU catalyst in toluene for 2 h at 4 °C and **3a** was reisolated (Scheme 2, 3). We found that this product had a *syn*:*anti* ratio of 86:14 indicating that epimerization of the α-position was facile under these conditions and that selective precipitation of the *syn*-product increased the diastereoselectivity of the reaction in nonpolar solvents.

Scheme 2. *Syn*/*Anti* Isomerization of Mannich Adduct **3a** Catalyzed by DBU



The optimized reaction conditions were suitable for a range of thioester donors and imine acceptors (Table 4). Boc-imines derived from benzaldehyde were substantially more reactive than the corresponding tosyl (Ts) imines; compare entries 1 and 2 to entries 6 and 7. Modest to insignificant differences in diastereoselectivites were observed between Boc- and Ts-imine reactions. The *N*-*p*-methoxyphenyl (PMP)-protected imine of ethyl glyoxylate provided product with low yield and diastereoselectivity. Of the eight thioesters studied, those with insoluble products were obtained in good diastereoselectivity. Product **3h**, for example, was obtained in 94% yield with 19:1 *syn*:*anti* diastereoselection (entry 8). In addition to thioesters functionalized with an aromatic group at the α-position, chloro-substitution at this position led to generation of a reactive enolate under these mild organocatalytic conditions (entry 12). The relative *syn*-stereochemistry of product **3f** was determined

Table 4. Scope of Diastereoselective Mannich-Type Reaction of Thioesters[a]

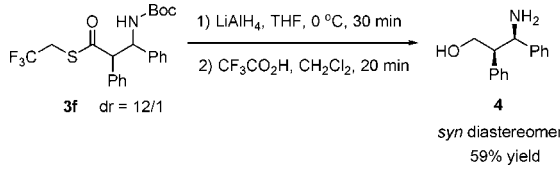


entry	R^1	R^2	R^3	product	time (h)	yield[b] (%)	*syn/anti*[c]
1[d]	4-ClC_6H_4	Ph	Boc	**3a**	2	93	92/8
2[d,e,f]	4-ClC_6H_4	Ph	Ts	**3b**	30	88	92/8
3[g]	4-ClC_6H_4	CO_2Et	4-$MeOC_6H_4$	**3c**	4	65	75/25[h]
4[d]	4-$CF_3C_6H_4$	Ph	Boc	**3d**	2	88	92/8
5[d]	4-$NO_2C_6H_4$	Ph	Boc	**3e**	72	90	94/6
6[d]	Ph	Ph	Boc	**3f**	2	87	89/11
7[d,i]	Ph	Ph	Ts	**3g**	4	78	92/8
8[d]	4-$MeOC_6H_4$	Ph	Boc	**3h**	2	94	19/1
9[g]	2-ClC_6H_4	Ph	Boc	**3i**	2	quant	33/67
10[g]	1-Naphtyl	Ph	Boc	**3j**	2	98	40/60
11[d]	2-Thienyl	Ph	Boc	**3k**	17	94	22/78
12[g]	Cl	Ph	Boc	**3l**	2	39	55/45[h]

[a] Unless specified, DBU (0.01 mmol) was added to a mixture of thioester (0.1 mmol) with a imine (0.12 mmol) in toluene (0.2 mL), and the reaction was stirred at 4 °C for specified time. [b] Isolated yield. [c] Determined by ^{1}H NMR of crude product. [d] Products were precipitated during the reaction. [e] Reaction was performed in 0.25 M concentration. [f] Thioester (1.2 equiv) and imine (1 equiv) were used. [g] Product did not precipitate during the reaction. [h] Major/minor (*syn/anti* was not asssigned). [i] Reaction was performed at 0.16 M concentration.

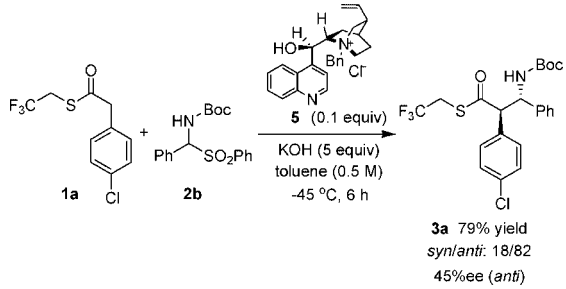
following conversion to the known amino alcohol **4**.[7] *Syn*-stereochemistry of other products was assigned if they demonstrated strong ^{1}H NMR spectral correlations with **3f**.

Scheme 3. Determination of Relative Stereochemistry



We were also interested in exploring the potential of an enantioselective version of this reaction. As noted in Scheme 4, we adopted phase-transfer conditions with in situ *N*-Boc-imine generation from the α-amido sulfone **2b**.[8] Using a *Cinchona* alkaloid-based catalyst **5**, good yields of **3a** were obtained with modest diastereo- and enantioselectivity. Interestingly, this reaction (performed at −45 °C) was modestly *anti*-selective, like the DBU reaction performed at −40 °C (Table 2, entry 6). Although the enantioselectivity of this reaction was modest, 45% ee, the reactivity of our system compares very favorably with direct Mannich-type reactions based on malonic acid half-thioesters that typically require reaction times of 3 days.

Scheme 4. Enantioselective Mannich Reaction of a Thioester



In conclusion, we report the first direct diastereoselective Mannich-type reactions of thioesters using the simple tertiary amine DBU as a catalyst. This methodology provides expedient access to β-amino acids. These s*yn*-selective direct Mannich-type reactions are the first of their kind involving thioesters. The reactions described here compare favorably with and serve to complement the *anti*-selective direct Mannich-type reaction of sulfonylimidates recently described by Kobayashi et al.[9] These studies provide a foundation for future development of highly diastereo- and enantioselective direct ester-based Mannich reactions.

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

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(7) The major product was found to have the *syn* relative stereochemistry as determined by ^{1}H NMR coupling constant analysis; see:(a) Fodor, G.; Reavill, R. E.; Stefanovsky, J.; Kurtev, B. *Tetrahedron* **1966**, *22*, 235. (b) Kunz, H.; Burgard, A.; Schanzenbach, D. *Angew. Chem.* **1997**, *109*, 394; *Angew Chem., Int. Ed.* **1997**, *36*, 386.

(8) (a) Fini, F.; Sgarzani, V.; Pettersen, D.; Herrera, R. P.; Bernardi, L.; Ricci, A. *Angew. Chem.* **2005**, *117*, 8189; *Angew Chem., Int. Ed.* **2005**, *44*, 7975.

(9) Matsubara, R.; Berthiol, F.; Kobayashi, S. *J. Am. Chem. Soc.* **2008**, *130*, 1804.