Boron-Catalyzed Michael Reaction of Donor-Acceptor Carboxylic Acid Pairs Enabling Direct Synthesis of 1,5-Dicarboxylic Acids

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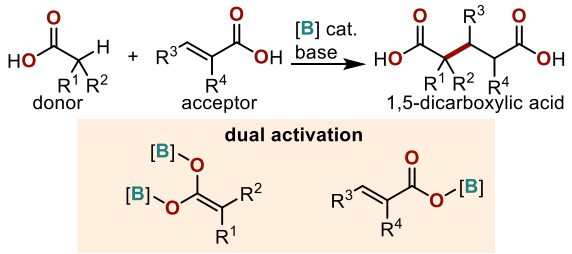
Supporting Information Placeholder



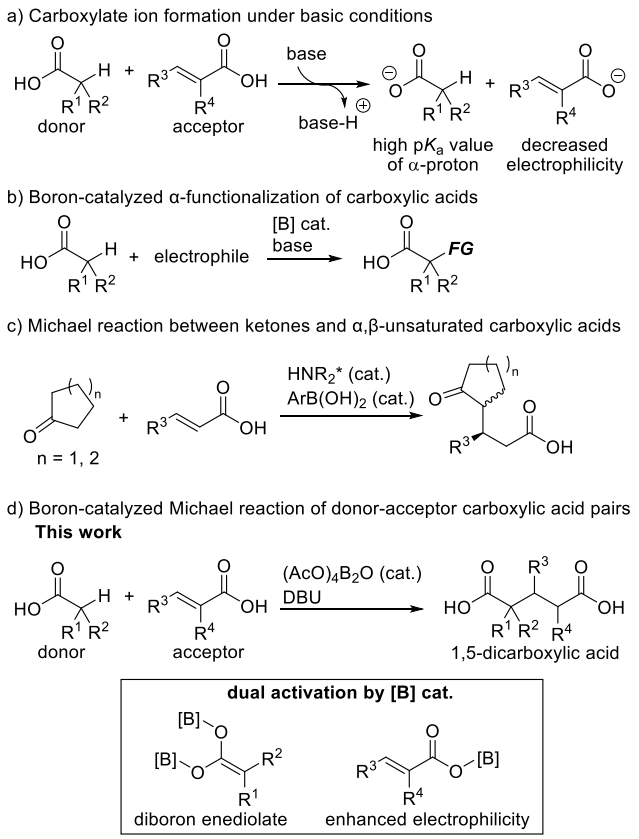
ABSTRACT: A boron-catalyzed Michael reaction using pairs of carboxylic acids was developed. The reaction occurs through dual activation of the two substrates by a boron catalyst, which facilitates boron enolate formation from the donor carboxylic acid with simultaneous activation of the α,β-unsaturated carboxylic acid as the acceptor. α-Aryl and α-alkenyl carboxylic acids were applicable as donors. The versatility and utility of this reaction were demonstrated by the direct use of pharmaceuticals as donor carboxylic acids.

The Michael reaction is a powerful carbon–carbon bond formation reaction that provides synthetically valuable 1,5-dicarbonyl compounds from easily available Michael donors and acceptors.[1] Despite continuous development of the reaction, readily available carboxylic acids have rarely been applied to the Michael reaction as either donors or acceptors. The high pK_a value of the α-protons of carboxylic acids hampers the catalytic generation of enolates, making carboxylic acids unsuitable as Michael donors (Scheme 1a). Therefore, the use of excess amounts of strong bases such as *n*BuLi and LDA[2,3] or pre-formation of a mixed acid anhydride using acylchloride[4] has been indispensable for promoting the Michael reaction.[5] Additionally, under the basic conditions required for enolate formation, α,β-unsaturated carboxylic acids are transformed to carboxylate ions, resulting in a loss of reactivity as electrophiles.

We have developed various boron-catalyzed reactions based on chemoselective enolate formation from carboxylic acids.[6] The reversible B–O covalent bond formation between the carboxylic acids and the Lewis acidic boron catalysts increases the acidity of the α-proton, thus enabling generation of nucleophilic diboron enediolates under mild basic conditions. Hence, the boron catalysis was applicable to various α-functionalizations of carboxylic acids including the Mannich reaction, aldol reaction, allylation, amination, and trifluoromethylthiolation (Scheme 1b). On the other hand, Ishihara recently developed an asymmetric Michael reaction between ketone donors and α,β-unsaturated carboxylic acid acceptors using a chiral amine/boronic acid two-component catalyst, which increased the electrophilicity of the α,β-unsaturated carboxylic acids by B–O bond formation (Scheme 1c).[7-9] Regardless of these advances in boron catalysis for activation of carboxylic acids,[10] there have been no reports on Michael reactions that employ carboxylic acids as both Michael donors and acceptors to provide 1,5-dicarboxylic acids directly. Herein, we report a new

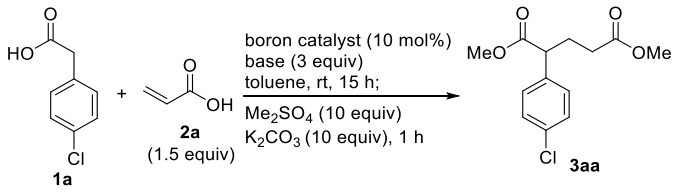
boron catalysis that allows Michael reaction of donor-acceptor carboxylic acid pairs for the first time (Scheme 1d). Dual activation of donor and acceptor carboxylic acids by the boron catalysts was crucial to achieve C–C bond formation.

Scheme 1. Boron-Catalyzed Michael Reaction of Carboxylic Acids.



We commenced the search for boron catalysts effective for the Michael reaction of carboxylic acid pairs using 2-(4-chlorophenyl)acetic acid (**1a**) as the Michael donor and acrylic acid (**2a**) as the acceptor (1.5 equiv) with DBU (3 equiv) as a base in toluene at room temperature (Table 1). For the sake of expeditious analysis of the reaction outcome, crude reaction products were subjected to methyl esterification using dimethyl sulfate to obtain diester **3aa**. While no reaction occurred in the absence of a boron catalyst (entry 1), addition of 10 mol% of $(AcO)_4B_2O$, which is a competent catalyst to form the diboron enediolate,[6] caused the reaction to afford 1,5-diester **3aa** in 76% yield with concomitant formation of significant amounts of tricarbonyl compounds, which seem to be produced through double Michael addition with a single molecule of **1a** and two molecules of acrylic acid (**2a**) (entry 2). $BH_3{\cdot}SMe_2$, which has also been used for catalytic reactions involving diboron enediolate intermediate formation, promoted the Michael reaction with only 33% yield of **3aa** (entry 3). 3,4,5-Trifluorophenylboronic acid, which was a competent catalyst for the dehydrative amidation of carboxylic acids,[9a] was not effective at all (entry 4). Screening of bases showed that DBU was the only effective base, while other organic bases such as NEt_3, DBN, and 2,6-lutidine or inorganic bases such as Cs_2CO_3, LiH, and KO*t*Bu caused no or traces of reaction (entries 5–10). To inhibit the double Michael addition by facilitating the protonation of the initially formed enolate intermediate, we reduced the amount of DBU to 2 equiv (entry 11). As a result, the reaction became much cleaner, giving **3aa** in 93% yield.

Table 1. Optimization of Boron-catalyzed Michael Reaction of Donor-Acceptor Carboxylic Acid Pair.[a]

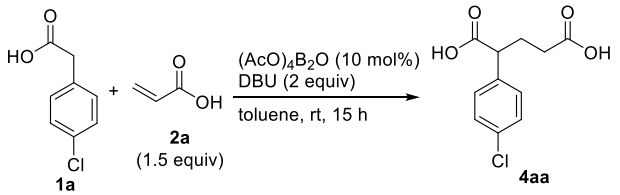


entry	Boron catalyst	base	**3aa**[b] (%)
1	None	DBU	0
2	$(AcO)_4B_2O$	DBU	76
3	$BH_3{\cdot}SMe_2$	DBU	33
4	3,4,5-F_3-$C_6H_2B(OH)_2$	DBU	0
5	$(AcO)_4B_2O$	NEt_3	<5[f]
6	$(AcO)_4B_2O$	DBN	9
7	$(AcO)_4B_2O$	2,6-lutidine	0
8	$(AcO)_4B_2O$	Cs_2CO_3	<5[f]
9	$(AcO)_4B_2O$	LiH	0
10	$(AcO)_4B_2O$	KO*t*Bu	0
11[c]	$(AcO)_4B_2O$	DBU	93

[a]**1a** (0.1 mmol), **2a** (0.15 mmol), boron catalyst (0.01mmol), DBU (0.3 mmol), toluene (0.2 M), 15 h; then Me_2SO_4 (1 mmol), K_2CO_3 (1 mmol), 1 h. When methyl esterification of the product was incomplete, additional methyl esterification was performed using Me_2SO_4 (1 mmol), K_2CO_3 (1 mmol) in THF, 1 h. [b]Yields of the isolated products. [c]2 equiv of DBU were used.

The boron-catalyzed Michael reaction proceeded cleanly on both 1 mmol and 10 mmol scale with 2 equiv of DBU. The product could be isolated as dicarboxylic acid **4aa** in 93% and 63% yields, respectively, after reverse phase chromatography on an ODS-packed column with MeCN/0.1% TFA aq. eluent (Scheme 2).

Scheme 2. Over 1 mmol-scale Reactions.

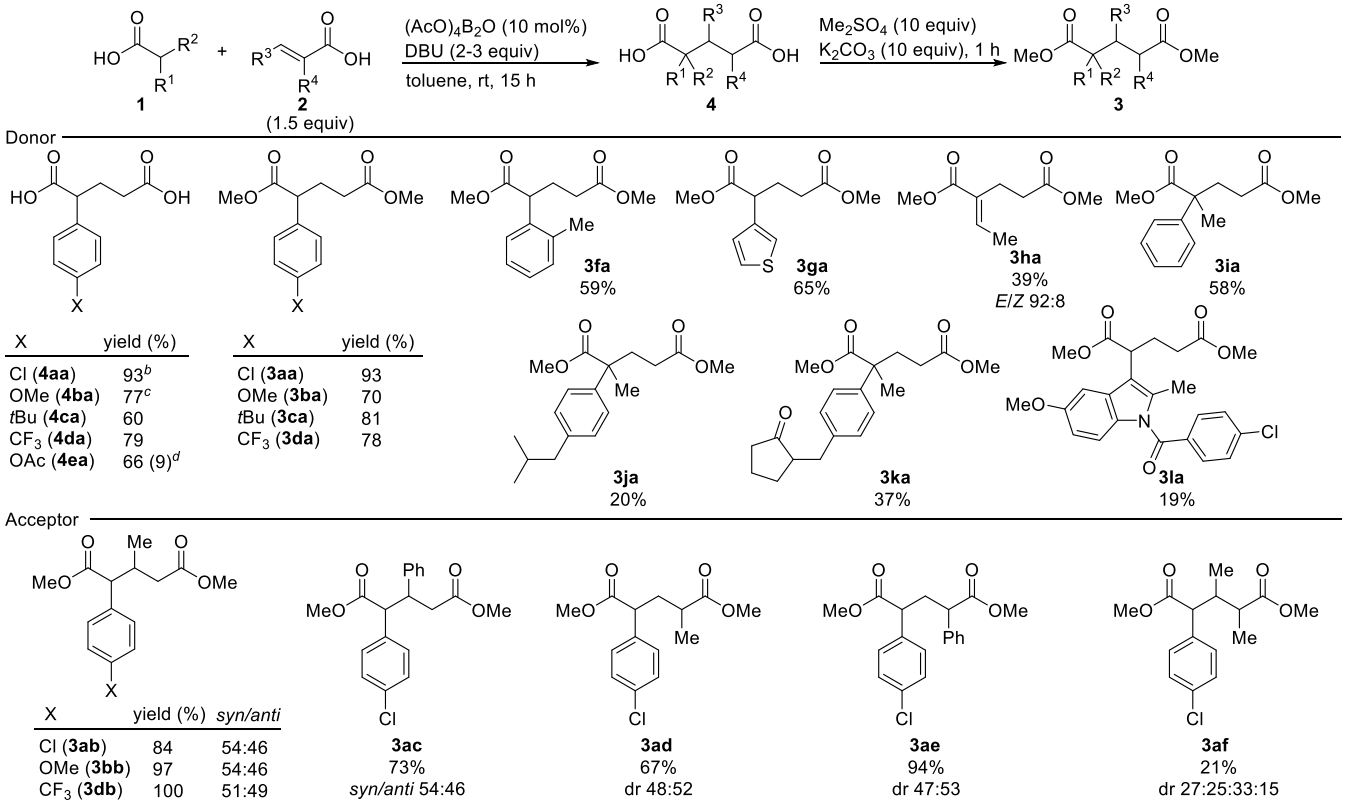


Next, scope of donor carboxylic acids (**1b–l**) was explored with an acrylic acid (**2a**) acceptor (Scheme 3). Electron-donating methoxy (**1b**) and *tert*-butyl (**1c**) groups, and an electron-withdrawing trifluoromethyl (**1d**) group at the *para* position of the α-substituted aromatic ring were amenable, giving the corresponding products in good yields in both dicarboxylic acid form (**4ba**: 77%; **4ca**: 60%; **4da**: 79%) and diester form (**3ba**: 70%; **3ca**: 81%; **3da**: 78%). In the reaction of acetoxy-substituted substrate **1e** with an

enolizable carbonyl group, C–C bond formation occurred exclusively at the α-position of the carboxy group to give **4ea** in 66% yield along with a small amount of deacetylated product **4ea'** (X = OH, 9%). A carboxylic acid with a sterically congested *ortho*-methyl substituted α-aryl group (**1f**) and that with an α-3-thiophenyl group (**1g**) were also applicable to this reaction, giving **3fa** and **3ga** in 59% and 65% yields, respectively. The reaction with 3-butenoic acid (**1h**), an α-alkenyl carboxylic acid, produced **3ha** in 39% yield (*E*/*Z* 92:8), with the C–C double bond conjugated to the carbonyl group, likely due to the isomerization of the doble bond after the conjugate addition. On the other hand, no Michael reaction product was obtained with propionic acid lacking the aryl or alkenyl group at the α-position, showing that the α-aryl or alkenyl substitution is indispensable. This boron catalysis was applicable to the construction of quaternary carbons using α-phenylpropionic acid (**1i**), giving **3ia** in 58% yield. Furthermore, direct transformation of pharmaceutical carboxylic acids such as ibuprofen (**1j**), loxoprofen (**1k**), and indomethacin (**1l**) were feasible with acceptable yields (**3ja**: 20%; **3ka**: 37%; **3la**: 19%).

Next, acceptor carboxylic acids were investigated. Reactions of crotonic acid (**2b**) with **1a**, **1b**, and **1d** proceeded smoothly to provide the corresponding products in high yields (**3ab**: 84%; **3bb**: 97%; **3db**: 100%), albeit with nearly 1:1 diastereomeric ratios.[11] Cinnamic acid (**2d**), bearing a phenyl group at the β-position, was also reactive, giving **3ac** in 73% yield with *syn*/*anti* 54:46. Methacrylic acid (**2d**) and atropic acid (**2e**), bearing a methyl or a phenyl substituent at the α-position, were also compatible to afford **3ad** (67%, dr 48:52) and **3ae** (94%, dr 47:53), respectively. Tiglic acid (**2f**), α,β-unsaturated carboxylic acid doubly methylated at the α- and β-positions, reacted with **1a** to afford Michael adduct **3af** in 21% yield with 27:25:33:15 dr.

Scheme 3. Substrate Scope[a]

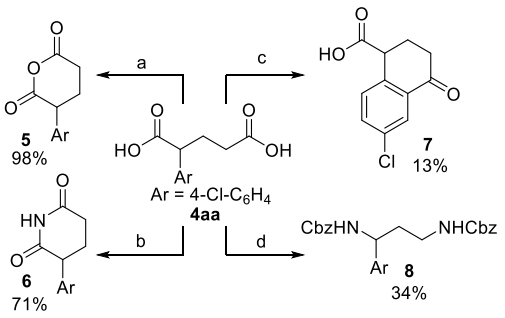


[a]**1a** (0.1 mmol), **2a** (0.15 mmol), $(AcO)_4B_2O$ (0.01 mmol), DBU (0.2-0.3 mmol), toluene (0.2 M), 15 h. To isolate the products as diesters, the esterification was conducted with Me_2SO_4 and K_2CO_3. [b]1 mmol scale. [c]0.5 mmol scale. [d]Yield of the deacetylated product (**4ea'**, X = OH) is in the parentheses.

To demonstrate the synthetic utility of the dicarboxylic acids obtained by the Michael reaction of the donor-acceptor carboxylic acid pairs, transformations of **4aa** were conducted (Scheme 4). Under the dehydrative conditions, cyclic acid anhydride **5** was obtained in 98% yield. Reaction of **4aa** with urea at 200 °C afforded cyclic imide **6** in 71% yield. Intramolecular Friedel-Crafts acylation to produce 1-tetralone-4-carboxylic acid **7** (13%) could be achieved by converting **4aa** into acid anhydride **5** followed by the addition of $AlCl_3$ as a Lewis acid. Double Curtius rearrangement using DPPA followed by the addition of benzyl alcohol gave Cbz-protected 1,3-diamine **8** in 34% yield.

Following reactions were conducted to gain mechanistic insights of the reaction (Scheme 5). In accord with our previous reports,[6] no **3aa** was obtained when the methyl ester **9** was used as the Michael donor (Scheme 5a), indicating that boron enolate formation was specific to carboxylic acids. In addition, **3aa** was obtained only in a trace amount when methyl acrylate (**10**) was used instead of acrylic acid (**2a**), showing that the *in situ* generated boron carboxylate

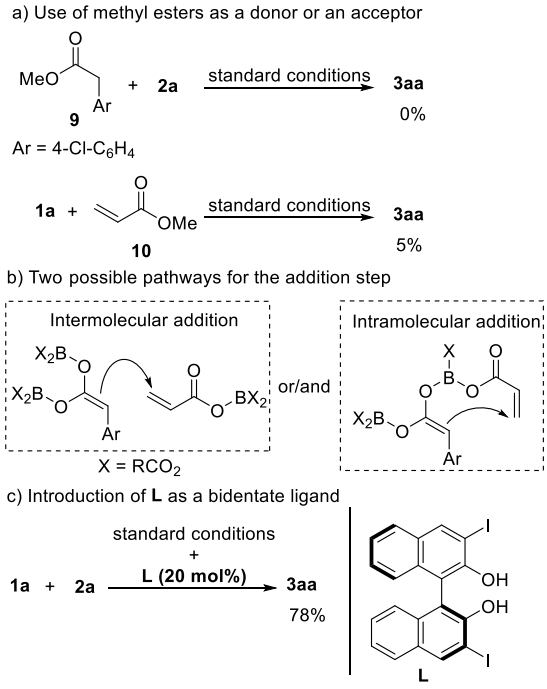
Scheme 4. Transformations of Dicarboxylic Acid 4aa.



[a]TFAA (2.2 equiv), CH_2Cl_2, 0 °C to rt. [b]urea (1.5 equiv), 1,2-diglyme, 140 to 200 °C. [c]TFAA (2.2 equiv), CH_2Cl_2, 0 °C to rt.; $AlCl_3$ (2.3 equiv), 1,2-dichloroethane, rt. [d]DPPA (2 equiv), NEt_3 (2 equiv), toluene, 80 °C; BnOH (3 equiv), reflux.

of **2a** is more reactive than **10**. Regarding the 1,4-addition step, two possible pathways are expected (Scheme 5b): an intermolecular addition and an intramolecular addition where the donor and the acceptor are connected by the single boron atom. To confirm the contribution of intermolecular addition pathway, a binaphthol-type ligand **L** was introduced to the standard conditions (Scheme 5c). Given the nature of **L** as a bidentate ligand, which occupies two of the three covalent bonds on a boron atom, the intramolecular addition pathway is not feasible under these conditions. Although the reactivity was lower than the reaction without **L**, production of **3aa** in 78% yield strongly indicates the existence of the intermolecular addition pathway. Nevertheless, the intramolecular addition pathway cannot be ruled out at this stage.

Scheme 5. Control Experiments.



In summary, we have developed the first Michael reaction between carboxylic acids and α,β-unsaturated carboxylic acids by the boron catalyst. Simultaneous activation of donor and acceptor carboxylic acids through formation of B–O covalent bonds was essential to achieve C–C bond formation. The utility of the substituted 1,5-dicarboxylic acid products was demonstrated by transformations via cyclization reactions and double Curtius rearrangement. Extension of the catalytic reaction to asymmetric variants by introducing chiral ligands on the boron catalyst is on-going in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data, and NMR spectra (PDF).

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Knochel, P.; Molander, G. A. Carbon-Carbon Bond Formation. In *Comprehensive Organic Synthesis*, 2nd ed. Eds.; Elsevier: Amsterdam, 2014; Vol. 3.

(2) (a) Kuo, Y.-N.; Yahner, J. A.; Ainsworth, C. Reactions of Dianions of Carboxylic Acids with Esters and α,β-Unsaturated Esters, Nitriles, and Aldehydes. *J. Am. Chem. Soc.* **1971**, *93*, 6321-6323. (b) Mulzer, J.; Hartz, G.; Kühl, U.; Brüntrup, G. The Reaction of Dilithium Carboxylates with Acyclic α.β-Enones - a Continuous Transition from 1.2- to 1.4-Addition. *Tetrahedron Lett.* **1978**, *19*, 2949-2952.

(3) For asymmetric Michael reaction of carboxylic acid donors using chiral lithium amides, see: (a) Yu, K.; Lu, P.; Jackson, J. J.; Nguyen, T. D.; Alvarado, J.; Stivala, C. E.; Ma, Y.; Mack, K. A.; Hayton, T. W.; Collum, D. B.; Zakarian, A. Lithium Enolates in the Enantioselective Construction of Tetrasubstituted Carbon Centers with Chiral Lithium Amides as Noncovalent Stereodirecting Auxiliaries. *J. Am. Chem. Soc.* **2017**, *139*, 527-533. (b) Lu, P.; Jackson, J. J.; Eocljpff, J. A.; Zakarian. A. Direct Enantioselective Conjugate Addition of Carboxylic Acids with Chiral Lithium Amides as Traceless Auxiliaries. *J. Am. Chem. Soc.* **2015**, *137*, 656-659.

(4) For selected examples, see: (a) Belmessieri, D.; Morrill, L. C.; Simal, C.; Slawin, A. M. Z.; Smith, A. D. Organocatalytic Functionalization of Carboxylic Acids: Isothiourea-Catalyzed Asymmetric Intra- and Intermolecular Michael Addition–Lactonizations. *J. Am. Chem. Soc.* **2011**, *133*, 2714–2720. (b) Simal, C.; Lébl, T.; Slawin, A. M. Z.; Smith, A. D. Dihydropyridones: Catalytic Asymmetric Synthesis, N- to C-Sulfonyl Transfer, and Derivatizations. *Angew. Chem., Int. Ed.* **2012**, *51*, 3653–3657. (c) Morrill, L. C.; Douglas, J.; Lébl, T.; Slawin, A. M. Z.; Fox, D. J.; Smith, A. D. Isothiourea-mediated Asymmetric Michael-lactonisation of Trifluoromethylenones: a Synthetic and Mechanistic Study. *Chem. Sci.* **2013**, *4*, 4146–4155. (d) Stark, D. G.; Morrill, L. C.; Yeh, P.-P.; Slawin, A. M. Z.; O'Riordan, T. J. C.; Smith, A. D. Isothiourea-Mediated One-Pot Synthesis of Functionalized Pyridines. *Angew. Chem., Int. Ed.* **2013**, *52*, 11642–11646.

(5) As related reactions, carboxy-directed conjugate addition of C–H bonds to Michael acceptors were reported. (a) Han, W.-J.; Pu, F.; Li, C-J.; Liu, Z.-W.; Fan, J.; Shi, X.-Y. Carboxyl-Directed Conjugate Addition of C–H Bonds to α,β-Unsaturated Ketones in Air and Water. *Adv. Synth. Catal.* **2018**, *360*, 1358–1363. (b) Zhang, G.; Jia, F.; Gooßen, L. J. Regioselective C–H Alkylation via Carboxylate-Directed Hydroarylation in Water. *Chem. Eur. J.* **2018**, *24*, 4537–4541.

(6) (a) Morita, Y.; Yamamoto, T.; Nagai, H.; Shimizu, Y.; Kanai, M. Chemoselective Boron-Catalyzed Nucleophilic Activation of Carboxylic Acids for Mannich-Type Reactions. *J. Am. Chem. Soc.* **2015**, *137*, 7075–7078. (b) Nagai, H.; Morita, Y.; Shimizu, Y.; Kanai, M. Ligand-Promoted, Boron-Mediated Chemoselective Carboxylic Acid Aldol Reaction. *Org. Lett.* **2016**, *18*, 2276–2279. (c) Ishizawa, K.; Nagai, H.; Shimizu, Y.; Kanai, M. Boron-Catalyzed Carboxylic Acid-Selective Aldol Reaction with Trifluoromethyl Ketones. *Chem. Pharm. Bull.* **2018**, *66*, 231–234. (d) Morisawa, T.; Sawamura, M.; Shimizu, Y. Boron-Catalyzed α-Amination of Carboxylic Acids. *Org. Lett.* **2019**, *21*, 7466–7469. (e) Fujita, T.; Yamamoto, T.; Morita, Y.; Chen, H.; Shimizu, Y.; Kanai, M. Chemo- and Enantioselective Pd/B Hybrid Catalysis for the Construction of Acyclic Quaternary Carbons: Migratory Allylation of *O*-Allyl Esters to α-*C*-Allyl Carboxylic Acids. *J. Am. Chem. Soc.* **2018**, *140*, 5899–5903. (f) Chen, H.; Yamaguchi, S.; Morita, Y.; Nakao, H.; Zhai, X.; Shimizu, Y.; Mitsunuma, H.; Kanai, M. Data-driven Catalyst Optimization for Stereodivergent Asymmetric Synthesis by Iridium/Boron Hybrid Catalysis. *Cell Rep. Phys. Sci.* **2021**, *2*, 100679. (g) Sun, K.; Ueno, M.; Imaeda, K.; Ueno, K.; Sawamura, M.; Shimizu, Y. Visible-Light-Driven α-Allylation of Carboxylic Acids. *ACS Catal.* **2021**, *11*, 9722–9728. (h) Fujita, T.; Yamane, M.; Sameera, W. M. C.; Mitsunuma, H.; Kanai, M. Siloxy Esters as Traceless Activators of Carboxylic Acids: Boron-Catalyzed Chemoselective Asymmetric Aldol Reaction. *Angew. Chem. Int. Ed.* **2021**, *60*, 24598–24604. (i) Sun, K.; Huang, C.-Y.; Sawamura, M.; Shimizu, Y. Direct α-Trifluoromethylthiolation of Carboxylic Acids Enabled by Boron Catalysis. *Synlett* **2023**, 2210–2214. (j) Shimizu,Y.; Kanai, M. Boron-Catalyzed α-Functionalizations of Carboxylic Acids. *Chem. Rec.* **2023**, e202200273.

(7) Horibe, T.; Hazeyama, T.; Nakata, Y.; Takeda, K.; Ishihara, K. Enantioselective 1,4-Addition Reaction of α,β-Unsaturated Carboxylic Acids with Cycloalkanones Using Cooperative Chiral Amine–Boronic Acid Catalysts. *Angew. Chem. Int. Ed.* **2020**, *59*, 17256–17260.

(8) Electrophilic activation of α,β-unsaturated carboxylic acids by boron catalysts: (a) Furuta, K.; Miwa, Y.; Iwanaga, K.; Yamamoto, H. Acyloxyborane: an Activating Device for Carboxylic Acids. *J. Am. Chem. Soc.* **1988**, *110*, 6254–6255. (b) Al-Zoubi, R. M.; Marion, O.; Hall, D. G. Direct and Waste-Free Amidations and Cycloadditions by Organocatalytic Activation of Carboxylic Acids at Room Temperature. *Angew. Chem., Int. Ed.* **2008**, *47*, 2876–2879. (c) Zheng, H.; McDonald, R.; Hall, D. G. Boronic Acid Catalysis for Mild and Selective [3+2] Dipolar Cycloadditions to Unsaturated Carboxylic Acids. *Chem. Eur. J.* **2010**, *16*, 5454–5460. (d) Azuma, T.; Murata, A.; Kobayashi, Y.; Inokuma, T.; Takemoto, Y. A Dual Arylboronic Acid–Aminothiourea Catalytic System for the Asymmetric Intramolecular Hetero-Michael Reaction of α,β-Unsaturated Carboxylic Acids. *Org. Lett.* **2014**, *16*, 4256–4259. (e) Hayama, N.; Azuma, T.; Kobayashi, Y.; Takemoto, Y. Chiral Integrated Catalysts Composed of Bifunctional Thiourea and Arylboronic Acid: Asymmetric Aza-Michael Addition of α,β-Unsaturated Carboxylic Acids. *Chem. Pharm. Bull.* **2016**, *64*, 704–717. (f) Hayama, N.; Kuramoto, R.; Földes, T.; Nishibayashi, K.; Kobayashi, Y.; Pápai, I.; Takemoto, Y. Mechanistic Insight into Asymmetric Hetero-Michael Addition of α,β-Unsaturated Carboxylic Acids Catalyzed by Multifunctional Thioureas. *J. Am. Chem. Soc.* **2018**, *140*, 12216–12225. (g) Michigami, K.; Murakami, H.; Nakamura, T.; Hayama, N.; Takemoto, Y. Catalytic Asymmetric Aza-Michael Addition of Fumaric Monoacids with Multifunctional Thiourea/Boronic Acids. *Org. Biomol. Chem.* **2019**, *17*, 2331–2335. (h) Hayama, N.; Kobayashi, Y.; Sekimoto, E.; Miyazaki, A.; Inamoto, K.; Kimachi, T.; Takemoto, Y. A Solvent-dependent Chirality-switchable Thia-Michael Addition to α,β-Unsaturated Carboxylic Acids using a Chiral Multifunctional Thiourea Catalyst. *Chem. Sci.* **2020**, *11*, 5572–5576. (i) Tanaka, R.; Hirata, Y.; Kojima, M.; Yoshino, T.; Matsunaga, S. Cp*Rh(III)/Boron Hybrid Catalysis for Directed C–H Addition to β-Substituted α,β-Unsaturated Carboxylic Acids. *Chem. Commun.* **2022**, *58*, 76–79.

(9) Boron compounds are also competent catalysts for dehydrative amidation and esterification of carboxylic acids. A pioneering work of Ishihara and Yamamoto, see: (a) Ishihara, K.; Ohara, S.; Yamamoto, H. 3,4,5-Trifluorobenzeneboronic Acid as an Extremely Active Amidation Catalyst. *J. Org. Chem.* **1996**, *61*, 4196–4197. For selected reviews, see: (b) Chrville, H.; Jackson, D.; Hodges, G.; Whiting, A. The Thermal and Boron-catalysed Direct Amide Formation Reactions: Mechanistically Understudied Yet Important Processes. *Chem. Commun.* **2010**, *46*, 1813–1823. (c) Lundberg, H.; Tinnis, F.; Selander, N.; Adolfsson, H. Catalytic Amide Formation from Non-activated Carboxylic Acids and Amines. *Chem. Soc. Rev.* **2014**, *43*, 2714–2742. (d) de Figueiredo, R. M.; Suppo, J.-S.; Campagne, J.-M. Nonclassical Routes for Amide Bond Formation. *Chem. Rev.* **2016**, *116*, 12029–12122. (e) Hall, D. G. Boronic Acid Catalysis. *Chem. Soc. Rev.* **2019**, *48*, 3475–3496.

(10) Sawamura, M.; Shimizu, Y. Boron Catalysis in the Transformation of Carboxylic Acids and Carboxylic Acid Derivatives. *Eur. J. Org. Chem.* **2023**, *26*, e202201249.

(11) The stereochemistries of **3ab**, **3bb**, and **3db** were determined by analogy to the known compounds reported in reference 3b.