Asymmetric Catalysis

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Enantioselective Addition of Boronates to Chromene Acetals Catalyzed by a Chiral Brønsted Acid/Lewis Acid System**

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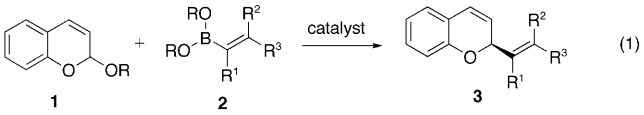
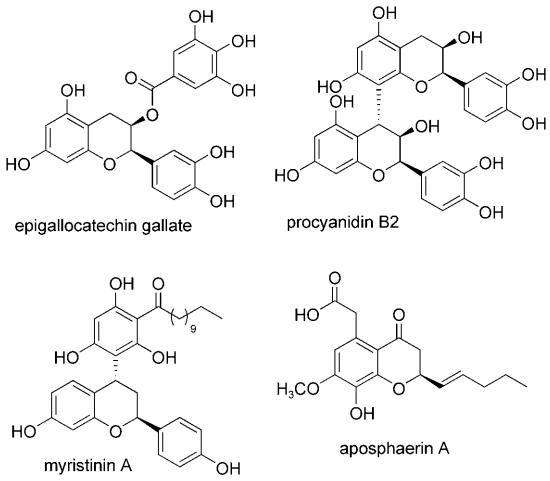
Boronates exhibit wide-ranging utility in synthesis.[1] As carbon donors in cross-coupling reactions[2] and metal-based nucleophiles in π addition reactions,[3] their utility is characterized by their ease of preparation, stability towards isolation and storage, and predictable reactivity patterns to afford valuable products.[4] In a seminal discovery Petasis and coworkers demonstrated how boronates could be activated towards addition to iminiums.[5] However, an elusive area of reactivity is the addition of vinyl and aryl boronates to carbonyl and oxonium compounds.[6] While less reactive than imines and iminium compounds, carbonyl-based electrophiles would significantly expand the utility of boronates in synthesis. Coincident with our interest in new reaction methodology[7] we sought to expand the repertoire of nucleophilic boronate reactions to enantioselective addition to acetals.[8] We identified 2-alkoxy-2*H*-chromenes as our first substrate class for investigation [Eq. (1)].[9]



1 2 3 (1)

The addition of vinyl- and aryl-based nucleophiles to this class of electrophiles give rise to chiral chromene products[10] that could readily be utilized in the synthesis of benzopyran-containing natural products (Scheme 1) such as epigallocatechin-3-gallate, a nutraceutical with potent antioxidant properties,[11] procyanidin B2, a proapoptotic polyphenol,[12] myristinin A, an inhibitor of DNA polymerase B,[13] and the antibacterial fungal metabolite aposphaerin A.[14] A general synthetic method to access this structural class in enantioenriched form would be attractive.[15] Herein, we describe the development of an enantioselective boronate addition to chromene acetals catalyzed by a chiral Brønsted acid/metal salt Lewis acid system.



Scheme 1. Natural product benzopyrans.

We initiated our study by investigating the addition of boronate **5** to 2-ethoxy-2*H*-chromene (**4**) (Table 1). A brief survey of Lewis acids failed, providing none of the desired addition product when used in catalytic amount and led to substantial decomposition of the chromene **4**. We postulated that organic acids would serve as mild catalysts for the formation of the pyrylium, thereby promoting the reaction. Indeed, the use of acetic acid and trifluoroacetic acid (TFA) provided the desired addition product **6** in modest yields (Table 1, entries 1 and 2).

Encouraged by these preliminary results, we explored the use of available chiral acids. (+)-Mandelic acid (**9**) and dihydroxy acid **10** were nominally successful at promoting the enantioselective addition reaction (Table 1, entries 3 and 4). However, the use of catalytic *N*-Boc amino acids derived from L-serine and L-threonine resulted in a more selective reaction. Notably, L-threonine **12** afforded the product in lower selectivity than L-serine **11** (entries 5 and 6), enantioselectivity that returned upon use of the epimeric *allo*-L-threonine **13** (entry 7). These results led us to consider chiral acids that possess hydroxy groups at the β-position of the carboxylic acid; namely tartaric acid and derivatives. (+)-Tartaric acid (**14**) provided similar levels of enantioselectivity to serine-derived catalyst **11** (entry 8); however, conversion of one of the hydroxy groups to an ester (**15**) ablated selectivity (entry 9). Alternatively, amides of tartaric acid (**16**–**19**) provided the highest enantioselectivities in the reaction (entries 10–13) and were thusly selected as the catalyst design for further investigation.

The initial results were promising but far from ideal. Tartaric acid derived amides[16] were an excellent starting point as asymmetric catalysts but despite relatively high

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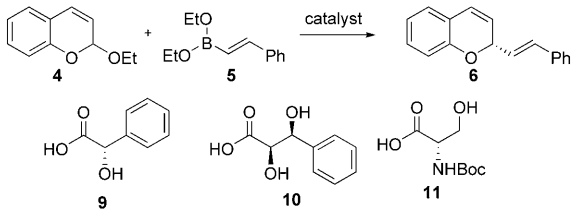
Table 1: Acid-catalyzed addition of boronate **5** to 2-ethoxy-2*H*-chromene (**4**).[a]



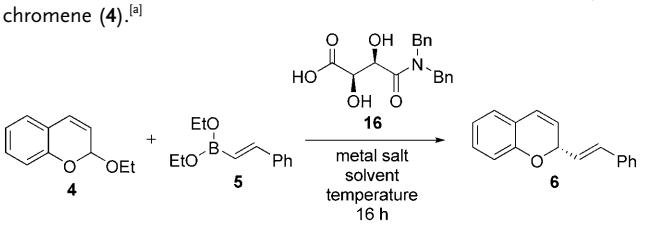
14: R^1 = H, R^2 = H, R^3 = OH
15: R^1 = H, R^2 = Bz, R^3 = OH
16: R^1 = H, R^2 = H, R^3 = NBn_2
17: R^1 = Bn, R^2 = H, R^3 = NBn_2
18: R^1 = H, R^2 = H, R^3 = 1-NH-2,6-(*i*Pr)$_2$-C_6H_3
19: R^1 = H, R^2 = H, R^3 = piperidine

Entry	Catalyst	Yield[b]	e.r.[c]
1	AcOH (**7**)	33%	–
2	TFA (**8**)	43%	–
3	**9**	50%	59:41
4	**10**	26%	50:50
5	**11**	55%	63:37
6	**12**	38%	54:46
7	**13**	46%	66:34
8	**14**	81%	63:37
9	**15**	59%	55:45
10	**16**	44%	83:17
11	**17**	0%	–
12	**18**	54%	82:18
13	**19**	40%	81:19

[a] Reactions were run with 0.50 mmol chromene **4**, 0.75 mmol boronate **5**, and 0.15 mmol catalyst in EtOAc (1 mL) for 16 h at room temperature under Ar, followed by flash chromatography on silica gel. [b] Yield of isolated product. [c] Enantiomeric ratios determined by HPLC analysis using a chiral stationary phase.

catalyst concentrations, the enantioselectivities were moderate and catalytic efficiency low. Solvent selection could provide some increase in catalysis but failed to give rise to correspondingly higher levels of enantioselectivity (Table 2, entries 1–4). We postulated that the addition of a metal-derived Lewis acid would increase the catalytic efficiency of the Brønsted acid catalyst. A concept pioneered by Yamamoto et al., Lewis acid assisted Brønsted acids[17] were originally developed for enantioselective protonation reactions.[18] Furthermore, Lewis acids are capable of facilitating allylboration reactions according to observations made in the groups of Hall,[19] Ishiyama, and Miyaura.[20] The addition of $Zn(OTf)_2$ to the reaction of **4** and **5** in the presence of acid **16** resulted in a slight increase in selectivity but almost no change in the yield of the isolated product (Table 2, entry 5). A noticeable change to the reaction was significant levels of decomposition; the additional Lewis acid either degraded the starting material or product. Reducing the amount of the Brønsted acid/Lewis acid combination resulted in a substantial increase in the enantioselectivity of the reaction and a slight increase in yield, again due to decomposition (entry 6). The triflate counterion appeared to be the best and $Zn(OTf)_2$

Table 2: Use of Lewis acids in the addition of boronates to 2-ethoxy-2*H*-chromene (**4**).[a]



Entry	Mol% **16**	Metal salt	mol%	Solvent	*T* [°C]	Yield[b]	e.r.[c]
1	30	–	–	EtOAc	20	44%	83:17
2	30	–	–	$PhCH_3$	20	72%	80:20
3	30	–	–	THF	20	<5%	ND
4	30	–	–	CH_2Cl_2	20	51%	82:18
5	30	$Zn(OTf)_2$	30	EtOAc	20	45%	84:16
6	5	$Zn(OTf)_2$	4.5	EtOAc	20	54%	94:6
7	5	$Zn(OTs)_2$	4.5	EtOAc	20	18%	84:16
8	5	$Zn(TFA)_2$	4.5	EtOAc	20	8%	65:35
9	5	$Sc(OTf)_3$	4.5	EtOAc	20	18%	66:34
10	5	$Ce(OTf)_4$	4.5	EtOAc	20	65%	97.5:2.5
11	–	$Ce(OTf)_4$	4.5	EtOAc	20	<2%	ND
12	5	$Ce(OTf)_4$	4.5	EtOAc	−20	75%	97.5:2.5
13	5	$Ce(OTf)_4$	4.5	EtOAc	−40	83%	99:1
14	5	$Yb(OTf)_3$	4.5	EtOAc	−40	87%	98.5:1.5
15	5	$Ce(OTf)_3$	4.5	EtOAc	−40	78%	96:4

[a] Reactions were run with 0.50 mmol chromene **4**, 0.75 mmol boronate **5**, **16**, and metal salt in solvent (1 mL) for 16 h at the indicated temperature under Ar, followed by flash chromatography on silica gel. [b] Yield of isolated product. [c] Enantiomeric ratios determined by HPLC analysis using a chiral stationary phase. ND = not determined.

was substantially better than the more commonly employed triflate salt $Sc(OTf)_3$ (entry 9). However, the use of $Ce(OTf)_4$[21] resulted in a substantially improved reaction obtaining good yields and the highest enatioselectivities (39:1 e.r., entry 10).

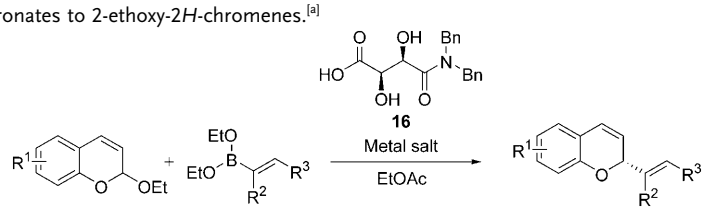
The omission of acid catalyst **16** resulted in almost no conversion indicating that the primary mode of enantioselective catalysis had not changed (entry 11). Lower temperatures improved the chemo- and enantioselectivity of the reaction (entries 12 and 13) while Ce^{III}, Ce^{IV}, and Yb^{III} triflate salts all gave comparably high yields and enantioselectivities. At the conclusion of the initial optimization studies, we had identified a set of conditions that utilized a chiral Brønsted acid/metal triflate Lewis acid catalytic system to achieve a highly enantioselective reaction.

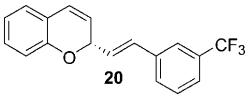
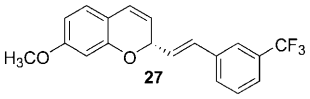
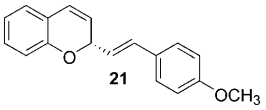
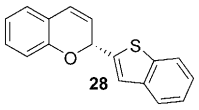
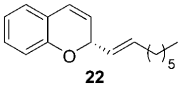
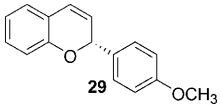
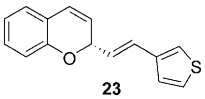
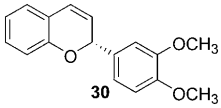
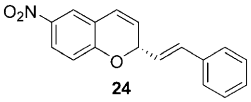
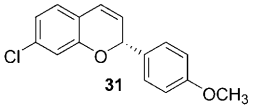
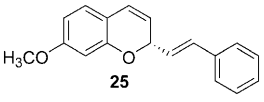
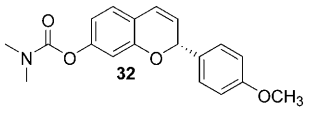
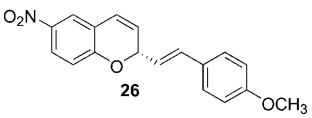
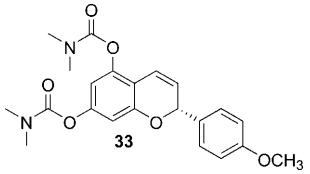
The Brønsted acid/Lewis acid catalytic reaction conditions proved general for a range of boronate additions to chromene acetals. However, optimal yields and selectivities required further experimentation and were found to be dependent on the electronic nature of the chromene acetal and boronate employed in the reaction. The parameters used to moderate the reaction were temperature, catalyst identity and concentration, and *t*BuOH (an additive that decreases the rate of starting material decomposition, but unfortunately, also the rate of the addition reaction). For example, reactions using less reactive boronates could be executed at 4 °C, whereas more reactive boronates required lower temperatures (−40 °C) and the addition of *t*BuOH to attenuate the reactivity (Table 3, entries 1 and 2). Similar observations were made of electron-deficient and electron-rich chromene ace-

tals (entries 5–8). However, good yields and high enantioselectivities were achieved with alkenyl boronate nucleophiles (entries 1–8). Aryl boronates proved to be less reactive and required activating groups on the aromatic ring such as methoxy substitution. Higher catalyst loadings were used to achieve the desired reaction rates, but increased catalyst concentrations also led to product decomposition. The addition of *t*BuOH tempered the amount of decomposition observed (entries 9–14). Oxygenation of the chromene acetal led to low reaction yields and selectivities with the addition of aryl boronates. However, the donating capability of the oxygen substitution could be attenuated using a dimethyl carbamate rather than a methoxy group achieving good yields and high selectivities in the addition reaction (entries 13 and 14). While no single set of reaction conditions were applicable to all of the substrates evaluated, an optimal set could be identified for each substrate based on an understanding of the reactivity.

Studies were performed to ascertain the roles of the catalysts and the species formed during the course of the reaction. First, the addition of boronate **5** to diol **16** results in an exchange process to form the dioxaborolane **34** (Figure 1). ^{1}H NMR analysis of the catalyst–boronate complex **34** illustrated the methine protons, doublets at $\delta = 4.87$ and 4.46 ppm, shifted downfield to $\delta = 5.62$ and 5.29 ppm within 2 min of boronate addition. Direct injection electron spray ionization mass spectrometry (ESI-MS) analysis of the complex detected the sodium salt dioxaborolane **35** (calculated [M−H+Na]: 463.2; measured: 463.7). The spectroscopic and spectrometric evidence supported the formation of dioxoborolane **35**; however, the role of the carboxylic acid and amide moieties was not clear. While the carboxylic acid is necessary for catalysis (Table 1, entry 11), a structural or catalytic role could not be discerned. Although there was evidence for dioxaborolane **34**, the possibility remained that the dioxaborolane might be forming by exchange with one of

Table 3: Enantioselective addition of boronates to 2-ethoxy-2*H*-chromenes.[a]



Entry	Product	Conditions	T [°C]	Yield	e.r.	Entry	Product	Conditions	T [°C]	Yield	e.r.
1	 **20**	A	4	71%	96.5:3.5	8	 **27**	A	4	77%	87.0:13.0
								B	4	72%	94.0:6.0
2	 **21**	A	−40	92%	88.0:12.0	9	 **28**	A	4	75%	86.0:14.0
		B	−40	71%	98.5:1.5			D	4	72%	95.5:4.5
3	 **22**	A	−20	75%	99.0:1.0	10	 **29**	A	4	60%	98.5:1.5
								D	−10	71%	98.5:1.5
4	 **23**	B	−40	77%	99.5:0.5	11	 **30**	A	4	50%	97.5:2.5
								D	4	68%	97.5:2.5
5	 **24**	A	10	59%	93.0:7.0	12	 **31**	A	4	75%	97.0:3.0
		C	20	79%	96.0:4.0			D	4	85%	97.0:3.0
6	 **25**	A	−20	74%	96.0:4.0	13	 **32**	A	4	40%	96.0:4.0
								D	4	71%	97.0:3.0
7	 **26**	C	4	70%	91.0:9.0	14	 **33**	D	−10	75%	95.0:5.0

[a] Reactions listed under Condition A were run with 1.5 equiv boronate, 5 mol% **16**, and 4.5 mol% $Ce(OTf)_4$; those under Condition B were run with 1.5 equiv boronate, 5 mol% **16**, 4.5 mol% $Ce(OTf)_4$, and 1 equiv *t*BuOH; those under Condition C were run with 1.5 equiv boronate, 5 mol% **16**, 4.5 mol% $Yb(OTf)_3$, and 1 equiv *t*BuOH; those under Condition D were run with 3.0 equiv boronate, 10 mol% **16**, and 9.0 mol% $Yb(OTf)_3$ except entry 14 which was run with 4.0 equiv boronate, 15 mol% **16**, and 13.5 mol% $Yb(OTf)_3$.

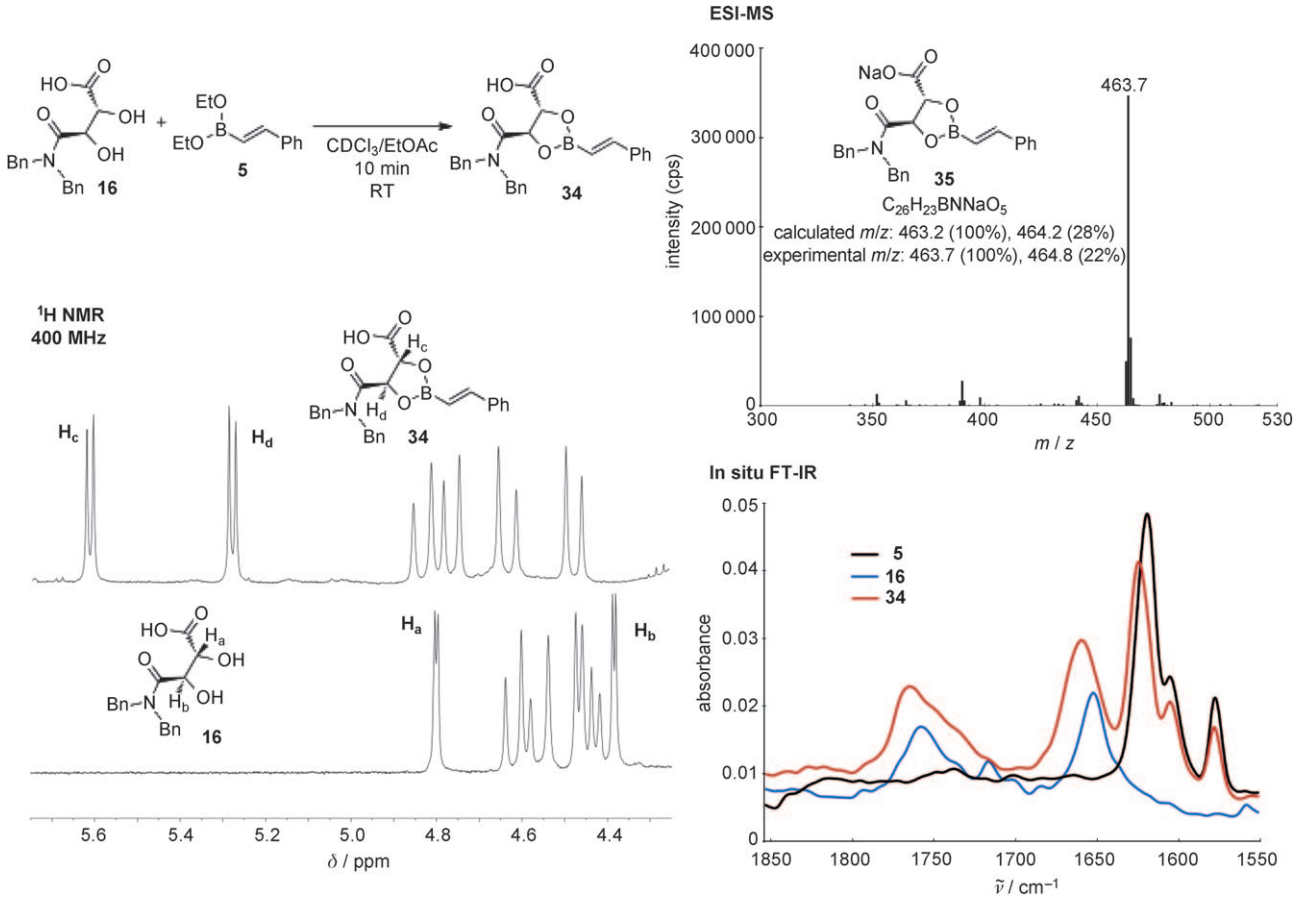
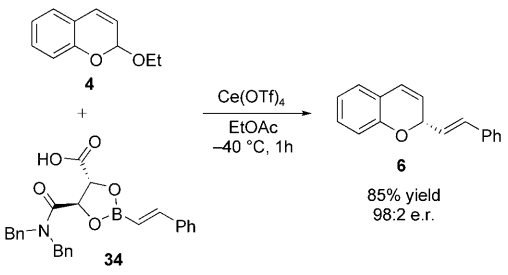
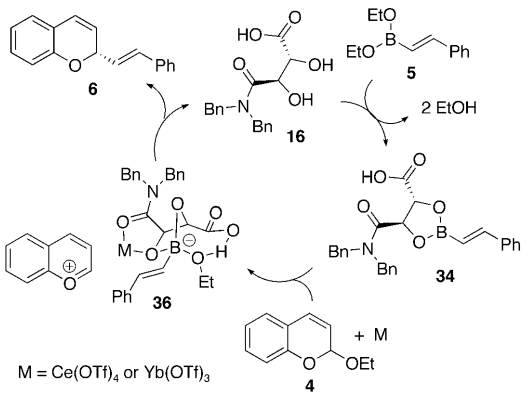


Figure 1. Characterization of boronate **34**. Formation of boronate **34** was accomplished by addition of boronate **5** in a solution of ethyl acetate to a solution of acid **16** in $CDCl_3$ at room temperature. The ^{1}H NMR chemical shift change of H_a and H_b to H_c and H_d indicates the formation of boronate **34**. Analysis of the reaction mixture using electron spray ionization mass spectrometry resulted in the characterization of sodium salt **35**. In situ IR spectroscopic analysis of the reaction indicated only minor shifts in the carbonyl absorbance (**16**: acid 1757 cm^{-1}, amide 1653 cm^{-1}; **34**: acid 1765 cm^{-1}, amide 1659 cm^{-1}). Bn = benzyl, Ph = phenyl.

the alcohols and the carboxylate.[22] In situ Fourier transform infrared spectroscopy (FT-IR) was used to characterize the structure of the dioxaborolane. The catalyst was dissolved in EtOAc and the C=O of the carboxylic acid absorbance was assigned to 1757 cm^{-1} and the amide was assigned to 1653 cm^{-1} (in situ FT-IR, Figure 1). Boronate **5** and carboxylic acid **16** were mixed and the carbonyl shifts monitored. The absorbances did not shift indicating the exchange occurred exclusively to form dioxoborolane **34**. Next, the interaction of $Ce(OTf)_4$ with **34** was investigated using ESI-MS and FT-IR. The addition of $Ce(OTf)_4$ to **34** under the reaction conditions was then analyzed by ESI-MS. A 1:1 complex of **34** and $Ce(OTf)_4$ was detected (**34** + $Ce(OTf)_3$, mass: 1027). However, the presence of the complex does not demonstrate how the $Ce(OTf)_4$ interacts with the dioxaborolane. To ascertain the type of complexation, in situ FT-IR was used. To a solution of boronate **34** was added $Ce(OTf)_4$. The carboxylic acid absorbance did not shift, whereas the amide began to shift from 1653 to 1609 cm^{-1}. Continued addition of $Ce(OTf)_4$ (> 1 mol equiv) began to affect the carbonyl of the carboxylic acid. Complexation of the metal appears to be selective for the amide carbonyl under the reaction conditions, and in line with previous work involving boronates and Lewis acids, the $Ce(OTf)_4$ is likely to bind with the oxygen of the boronate as well.[23] Detection of the oxocarbenium species was also performed. Benzopyrylium species exhibit UV/Vis absorbances at 400–600 nm.[24] The spectroscopic analysis showed a distinct peak at 449 nm over the course of time indicating the formation of a pyrylium intermediate. Kinetic evaluation of the reaction demonstrated a first-order dependence of tartaramide acid catalyst **16** and $Ce(OTf)_4$, consistent with the spectroscopic data. Finally, the addition of chiral dioxoborolane **34** to chromene acetal **4** promoted by $Ce(OTf)_4$ afforded the addition product **6** in 85% isolated yield and 98:2 e.r. [Eq. (2)], supporting the intermediacy of **34** in the catalytic process.



(2)



Scheme 2. Proposed catalytic cycle.

Our preliminary studies indicate a possible catalytic cycle (Scheme 2). The catalytic cycle begins with the formation of dioxaborolane **34** from the boronate and tartaramide acid **16**. The addition of Lewis acid to complex **34** enhances the acidity of the boronate. Thusly with the addition of chromene acetal, the boronate serves to facilitate pyrylium formation concomitant with generation of boronate **36**. Activation through formation of the "ate" complex **36** leads to the nucleophilic addition of the styryl group to the electrophile. Nucleophilic delivery serves to provide the necessary reservoir of tartaramide acid **16** for re-entry into the catalytic cycle. The proposed activation of the boronate accounts for the enhancing role of the Lewis acid, although not crucial for reactivity and is consistent with the spectroscopic, spectrometric, and kinetic studies. Continued investigations focus on the physical characteristics of boronate **34**, the mode of enantioselectivity, and the catalytic turnover processes.

In summary, we have developed a dual catalyst system for the enantioselective addition of boronates to oxoniums. The catalyst system is a tartaric acid derived Brønsted acid used in conjunction with a lanthanide triflate Lewis acid used in catalytic amounts to promote the enantioselective addition of alkenyl and aryl boronates to chromene acetals. The reaction was optimized for a range of chromene acetals possessing both electron-deficient and electron-rich substitution patterns. Mechanistic studies demonstrate an exchange process leading to a reactive dioxoborolane intermediate. Ongoing studies include further mechanistic investigations, expansion of the scope, and utility for the synthesis of natural products.

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Keywords: asymmetric catalysis · boronates · Brønsted acids · enantioselective synthesis · natural products

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