$B(C_6F_5)_3$: Stoichiometric and Catalytic C–C and C–H Bond Formation *via* Cationic Intermediates

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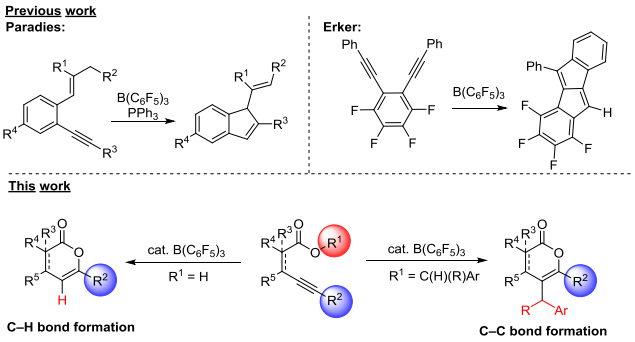
Dedicated to the memory of Bernd Wrackmeyer.

Abstract: This work showcases a new method of catalytic cyclization reaction using a highly Lewis acidic borane with concomitant C–H or C–C bond formation. Activation of alkyne containing substrates using $B(C_6F_5)_3$ allows catalytic intramolecular cyclizations of carboxylic acid substrates to be achieved for the first time using this Lewis acid. In addition, intramolecular cyclizations of esters enables C–C bond formation in which catalytic $B(C_6F_5)_3$ is used to effect formal 1,5-alkyl migrations from ester functionalities to unsaturated carbon-carbon frameworks. Using this new methodology, the catalytic formation of complex dihydropyrones and isocoumarins in extremely good yields under relatively mild conditions with excellent atom efficiency can be achieved in a metal-free manner.

A major development in the field of main group chemistry over the last decade is that of frustrated Lewis pairs (FLPs).[1] These act as cooperative reagents in small molecule activation and metal-free hydrogenation catalysis. Subsequently, FLP chemistry has led to new ways of thinking about Lewis acidity and basicity and now encompass broader applications across synthetic organic chemistry.[2] Yet, this thriving field is still in its naissance, with avenues still remaining uncovered and many practical applications still await development. One Lewis acid which has come to light through these advancements is $B(C_6F_5)_3$.[3] This electron deficient borane has been shown to act as a hard Lewis acid with particular oxophilic character, but has also displayed the proclivity to act as a π-Lewis acid through the activation of softer Lewis basic centers such as alkynes and alkenes[4] which is reminiscent of soft transition metal catalysts such as gold,[5] palladium[6] and platinum.[7] Indeed, there has been a great deal of work by Erker, Oestreich, Paradies, Piers and ourselves *inter alia* to establish the wide range of transformations this reagent can effect such as 1,n-carboborations,[8] benzannulations,[9] cyclizations,[3a, 10] and hydrosilylations[11] (Scheme 1, top).

In this paper, we demonstrate that this Lewis acid can catalyze the rearrangement of alkynyl carboxylic acids and esters to give 3,4-dihydropyrones and isocoumarins in high yields under relatively mild conditions (Scheme 1, bottom). Naturally occurring or synthetic dihydropyrones are omnipresent motifs in numerous biologically active compounds[12] with derivatives having extensive uses in anti-inflammatory, antidiabetic, and antimicrobial agents, amongst others.[13] In addition to their biological activity, dihydropyrones also serve as synthetically useful intermediates for the synthesis of oxygen-containing heterocycles such as pyridones and γ-lactones.[14] The combination of biological activity and synthetic utility of dihydropyrones has led to considerable interest in their preparation. Although many synthetic routes to pyrones exist,[15] many involve heavy or noble metals in the latter stages of preparation thus making these syntheses less attractive within the pharmaceutical and industrial setting.[16]



Scheme 1. Examples of $B(C_6F_5)_3$ catalysis.

Initially, a variety of alkynyl carboxylic acids (**1a–k**) and esters (**2a–u**) were synthesized according to literature procedures (Figure 1).[16a] The reaction of the electron rich alkynyl functionalized carboxylic acids **1a–c** with $B(C_6F_5)_3$ in a 1:1 molar ratio in $CDCl_3$ produced the cyclized lactone products **3a–c** quantitatively within 30 minutes when monitored by *in situ* NMR spectroscopy with excellent isolated yields above 90%. However, when functionalizing the backbone with unsaturated moieties (**1i-j**), lower isolated yields of 45% for **3d** and 52% for **3e** were recorded (Scheme 2). A crop of colorless crystals of **3a** and **3d–e** were grown from a saturated CH_2Cl_2/hexane solution stored at -40 °C, which were suitable for single-crystal X-ray diffraction (Figure 2 and SI).

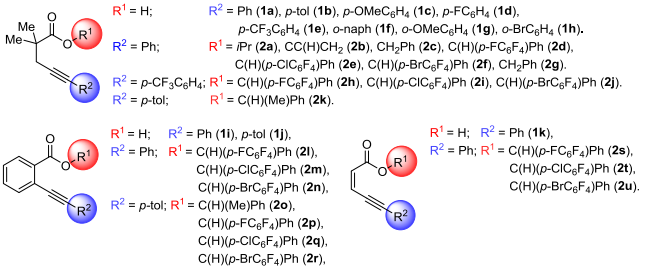


Figure 1. Substrates **1** and **2** used in this study.

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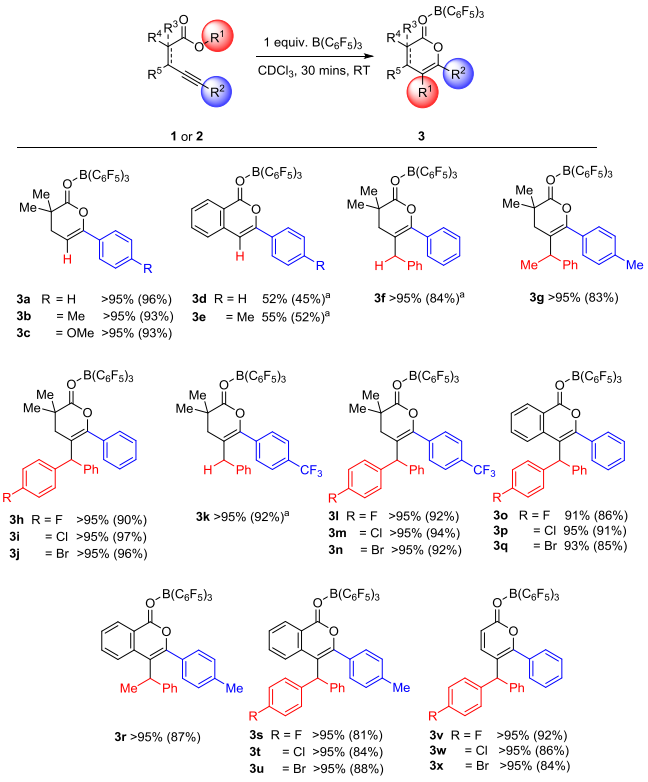
These results were surprising since carboxylic acids are not usually tolerated in $B(C_6F_5)_3$ related chemistry, other than the few reports of coordinative structural investigations as well as $B(C_6F_5)_3$ catalyzed deoxygenations, amongst a small number of others.[17] Electron poor, or more sterically demanding *ortho*-substituted alkynes **1d**–**1h**, exhibited reduced reactivity. In these cases, multinuclear NMR spectroscopy showed a mixture of products, with the expected target molecule presenting only as a minor component.

The limited scope and the propensity of carboxylic acids to interfere with $B(C_6F_5)_3$ chemistry encouraged us to undertake the related ester chemistry which also led to an increase in complexity of the subsequent lactone product (Scheme 2). Reactions of isopropyl or allyl esters (**2a**–**b**) resulted in no discernible formation of the target dihydropyrone, however, exposing benzyl or benzhydrol derivatives (**2c**–**u**) to the same reaction conditions triggered the analogous rearrangement as the carboxylic acids to give γ-functionalized 3,4-dihydropyrones and isocoumarins **3** as the borane adduct through a C–C bond forming reaction.

Notably, compounds **3g–j** and **3l–x** could be formed in excellent yields (>90% conversion; 81%–97% isolated) in as little as 30 minutes at room temperature, whereas formation of **3f** and **3k** exhibited slightly longer reaction times (24 h) to give the corresponding rearrangement product in very high yields (91% and 92% respectively). The crystal structures of **3h–i**, **3m** and **3v** were determined by X-ray diffraction and confirmed atomic connectivity (Figure 2 and SI).



In situ NMR conversion (isolated yield). [a] 24 h reaction time.

Scheme 2. Substrate scope for the cyclization reaction of **1** with $B(C_6F_5)_3$.

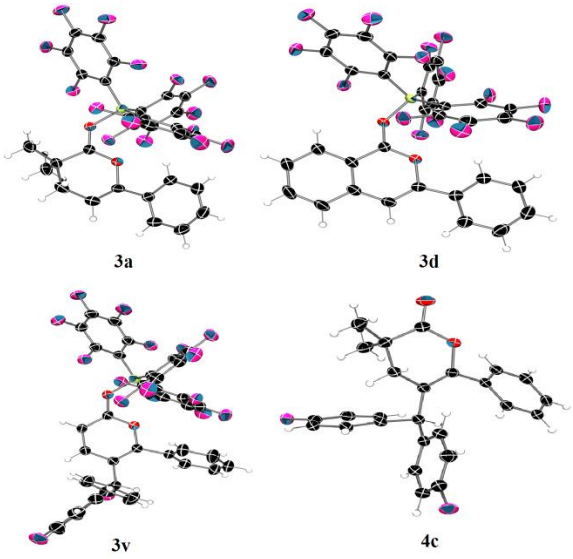


Figure 2. Solid-state structure of compound **3a**, **3d**, **3v** and **4c**. Disordered F atom modelled over two sites (**3v** and **4c**). Thermal ellipsoids shown at 50% probability.

Since the resulting lactone products **3** sequester the borane as the O–B adduct, it was posited that if the boron-oxygen bond could be thermally cleaved, catalytic turnover should be permitted to give compounds **4** (Scheme 3). Indeed, using **2d** as the model system, the catalytic reaction in $CDCl_3$ at ambient temperature using 10 mol% $B(C_6F_5)_3$ resulted in >95% conversion to the product after 6 h at 70 °C. The catalytic system was subsequently established through optimization of the reaction conditions *viz.* borane catalyst, solvent, and catalytic loading (Table 1).

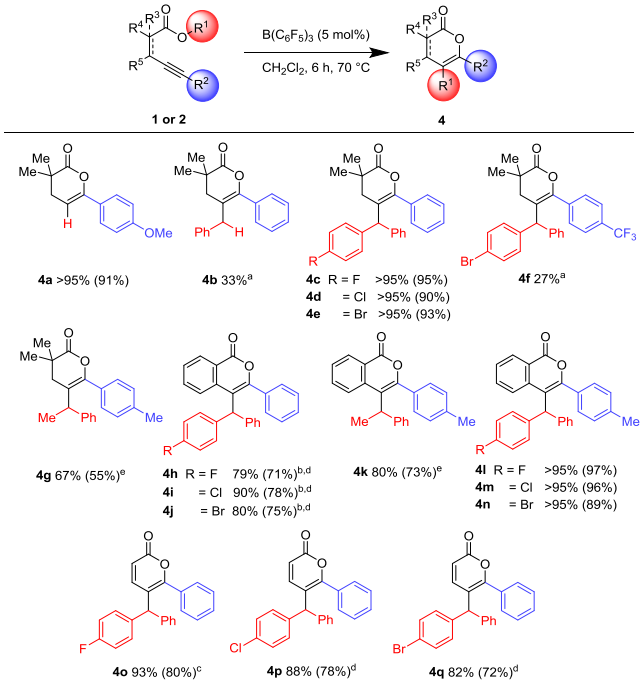
Less Lewis acidic boranes such as BPh_3, and other fluorinated aryl boranes BR_3 [R = (2,6-$F_2C_6H_3$) or (2,4,6-$F_3C_6H_2$)][18] resulted in no detectable product after 24 h at 70 °C (entries 1–3, Table 1). In addition, less sterically hindered boranes such as $BF_3{\cdot}OEt_2$ also showed no appreciable conversion even though the Lewis acidity is only deemed slightly less than that of $B(C_6F_5)_3$ (entry 4, Table 1).[19] Further reduction of the catalyst loading did not negatively affect the catalytic efficiency, giving excellent conversion using as little as 1 mol% (entry 7, Table 1). However, for the interests of tandem catalytic processes, a catalyst loading of 5 mol% was used in subsequent reactions (entries 5–7, Table 1).

Table 1. Optimization for the catalytic cyclization.

Entry	Catalyst	Solvent	Loading (mol%)	Conv. (%)[a]	Product
1	BPh_3	$CDCl_3$	10	<5	**4c**
2	(2,6-$F_2C_6H_3$)$_3$B	$CDCl_3$	10	<5	**4c**
3	(2,4,6-$F_3C_6H_2$)$_3$B	$CDCl_3$	10	<5	**4c**
4	$BF_3{\cdot}OEt_2$	$CDCl_3$	10	7	**4c**
5	$B(C_6F_5)_3$	$CDCl_3$	10	>95	**4c**
6	$B(C_6F_5)_3$	$CDCl_3$	5	>95	**4c**
7	$B(C_6F_5)_3$	$CDCl_3$	1	>95	**4c**
8	$B(C_6F_5)_3$	THF	10	52	**4c**
9	$B(C_6F_5)_3$	1,4-Dioxane	10	54	**4c**
10	$B(C_6F_5)_3$	Toluene	10	>95	**4c**
11	$B(C_6F_5)_3$	Et_2O	10	>95	**4c**
12	$B(C_6F_5)_3$	CH_2Cl_2	10	>95	**4c**
13	$B(C_6F_5)_3$	$CDCl_3$	5	>95	**4a**
14	CF_3CO_2H	$CDCl_3$	5	0	**4a**
15	CF_3SO_3H	$CDCl_3$	5	Traces[b]	**4a**

[a] *In situ* NMR conversion after 6 hours at 70 °C. [b] Multiple products observed.

Once the optimal borane and catalyst loading had been elucidated, various solvents were screened with the observation that the catalytic reactions proceeded rapidly in high yields (over 95%) in a variety of solvents ($CDCl_3$, CH_2Cl_2, Et_2O and toluene) but less well in more coordinating solvents such as THF and 1,4-dioxane (entries 5, 8–12, Table 1) which likely leads to catalyst deactivation processes through formation of solvent-borane adducts. When applying these conditions to the electron rich carboxylic acid **1c**, clean quantitative formation of **4a** was also observed (entry 13, Table 1). Additionally, trifluoroacetic acid was trialled in the synthesis of **4a** using 5 mol% loading at 70 °C for 6 h to interrogate whether the cyclisation is proton mediated as a result of borane coordination to the carbonyl of the carboxylic acid fragment, or whether it is indeed the borane that activates the alkynyl fragment. Using these conditions, *in situ* monitoring of the reaction showed no conversion (entry 14, Table 1). Using a stronger acid, trifluoromethylsulfonic acid (entry 15, Table 1), in 5 mol% loading garnered a mixture of products with little indication of the target molecule (see SI).

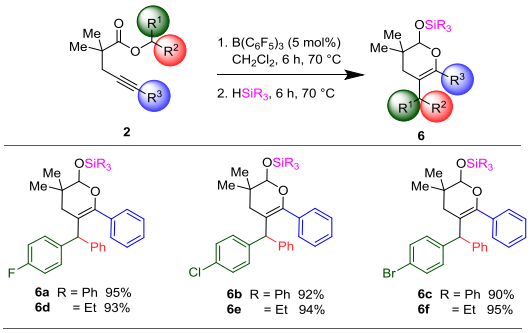


In situ NMR conversion (isolated yield). [a] Isolated yield after 120 h. [b] 10 mol% catalyst. [c] 16 h reaction time. [d] 24 h reaction time. [e] 48 h reaction time.

Scheme 3. Catalytic formation of **4** using $B(C_6F_5)_3$.

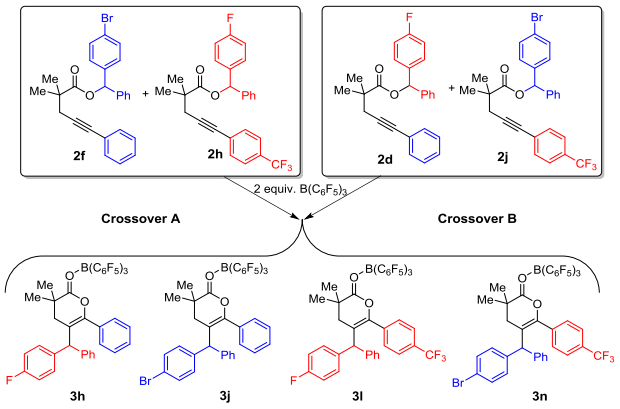
The alkynyl carboxylic acids and esters were then tested in the borane catalyzed rearrangement reactions using these optimized conditions. Whilst the most electron rich alkynyl carboxylic acid generated the corresponding dihydropyrone **4a** in excellent yields, less activated substrates (**1a–b**, **1d–e**) showed little reactivity under the established conditions. Conversely, favorable returns were observed for the vast majority of the lactone products with many being isolated in yields over 90% (**4c–e**, **4l–m**, Scheme 3). Lower conversions were noted for products **4b** and **4f** with isolated yields of 33% and 27% respectively. Additionally, to generate **4h–j** in good yields (71–78%), 10 mol% catalyst was used with a reaction time of 24 h (Scheme 3). In the case of **4a**, **4c** and **4f**, storing the saturated hexane/CH_2Cl_2 solutions at -40 °C yielded colorless crystals that were characterized by single-crystal X-ray diffraction (Figure 2 and SI). Further functionalization of these products was evidenced through a subsequent Suzuki-Miyaura coupling reaction of the *para*-bromo substituted derivative **4e** showcasing its candidacy as an excellent building block for further derivatizations and uses in organic synthesis (see SI, compound **5**).

Supplementary investigations sought to conduct tandem catalytic rearrangements/reduction reactions using a one-pot synthesis from **2** to give γ-functionalized cyclic silylacetals (Scheme 4). Initially we hoped to effect a one-pot catalytic cyclization followed by an FLP hydrogenation of the lactone functionality using $B(C_6F_5)_3$ as the catalyst. Unfortunately, these reactions proved unsuccessful at 5 atm of H_2 using **2d** as a substrate and 10 mol% borane. However, we subsequently turned our attention to the hydrosilylation reaction for the second step which is well-documented using $B(C_6F_5)_3$ to much greater success.[11] Indeed, the simple addition of either $HSiPh_3$ or $HSiEt_3$ after the initial cyclization reaction resulted in the quantitative formation of the hydrosilylated products **6a–f** after a further 6 h at 70 °C with excellent isolated yields from the tandem reaction (90–95%). Single crystals of **6a** could be grown from a saturated CH_2Cl_2/hexane solution stored at -40 °C and whose structure was confirmed by X-ray diffraction (see SI).



Scheme 4. Tandem catalytic one-pot cyclization/hydrosilylation to yield **6**.

The method by which the benzylic fragment undergoes the 1,5-migration in these rearrangements was hence probed *via* a set of crossover reactions. Using a 1:1 mixture of **2f** and **2h**, the presence (or absence) of any mixing of the $[Ar^1C(H)Ar^2]^+$ moiety upon reaction with 2 equivalents of $B(C_6F_5)_3$ was studied (Crossover A, Scheme 5). Similarly, the analogous reaction was also carried out using **2d** and **2j** in a bid to clarify further whether the reaction proceeds *via* an *inter-* or *intra*-molecular pathway (Crossover B, Scheme 5). It was observed that in both cases scrambling of the migratory group does indeed occur giving mixtures of **3h**, **3j**, **3l** and **3n**, lending credence to a proposed *inter*molecular pathway with generation of a carbenium ion in solution. When probing this further, it was seen that in crossover experiment A, very little variance was seen in the generation of all four products, however, when looking at crossover B, the formation of **3h** was preferential over **3j**, **3l** and **3n**.



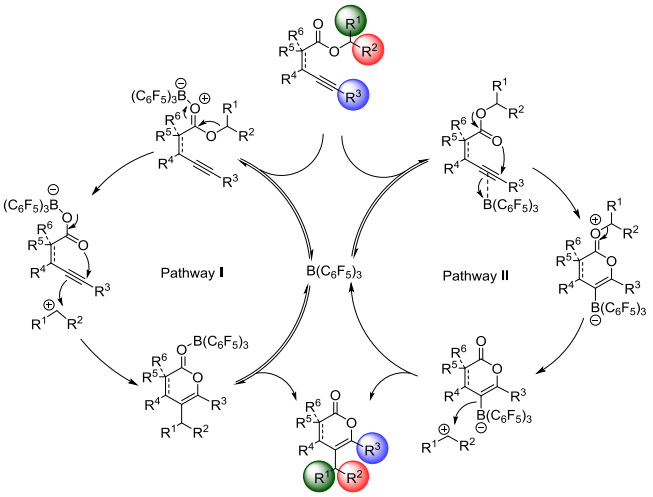
Scheme 5. Crossover reactions.

This is presumably due to the substrate containing a more activated alkyne (more electron rich) than the CF_3 substituted phenyl acetylene. This also explains the reduced reactivity of the CF_3 substituted precursors **2h–j** in the catalytic experiments described earlier. In addition, the *p*-F substituted benzhydrol starting material results in the formation of a more stable carbenium ion than the *p*-Br substituted benzhydrol starting material (the σ_p Hammett constant for *p*-F>*p*-Br).

Mechanistically, two possible cyclization pathways are possible; borane activation of the carbonyl resulting in elimination of a carbenium ion, followed by a 6-*endo*-*dig* cyclization reaction (pathway **I**, Scheme 6). Alternatively, borane activation of the alkyne followed by a 1,2-*trans* oxyboration reaction with subsequent proto- or carbodeboration could occur (pathway **II**, Scheme 6). Both pathways have been observed previously in other reactions with $B(C_6F_5)_3$. For example, we have previously noted the deprotection of Boc groups using catalytic amounts of $B(C_6F_5)_3$ reminiscent of pathway **I**,[20] while the oxyboration pathway **II** has also been observed in work by ourselves[20,21] and others[10b,22] in the synthesis of oxazoles, dioxaborinines, pyrylium and lactone systems.

It could be argued that the hard Lewis acidic $B(C_6F_5)_3$ coordinates preferentially to the harder carbonyl oxygen over the softer π-bond of the alkyne, lending credence to pathway **I** which may also detected in the ^{11}B NMR spectrum (*ca.* 40 ppm). However, a transient sharp singlet at *ca.* -15 ppm is observed in the ^{11}B NMR spectrum, indicative of a vinyl borate suggesting that pathway **II** is indeed witnessed. This may be further reinforced by the lack of selectivity and reactivity when using *ortho*-substituted alkynyl carboxylic acids (**1f** and **1g**). Although these groups, or derivatives thereof, have been shown to activate the alkyne fragment, the increased steric bulk may obstruct the approach of the bulky Lewis acid. Both proposed mechanisms proceed through carbenium intermediates which explains the lack of reactivity with substrates **3a** and **3b** and the lower reactivity/activity with **3c,** which are less able to stabilize a carbocation intermediate than the diaryl or ethylphenyl substituted benzhydrol units. In addition to these observations, when conducting the control reaction of substrate **1c** with catalytic amounts of trifluoroacetic acid at elevated temperatures, no reaction occurred after 6 h (see SI). When **1c** was subjected to 5 mol% of the stronger triflic acid, some reactivity was seen however, conversion to the target molecule was not observed.

This was also repeated with substrate **1a** using 5 mol% and stoichiometric amounts of triflic acid, however no change was noted *via* the *in situ* ^1H NMR spectrum. This leads us to believe that pathway **II** is perhaps more plausible, due to the rapid reaction with $B(C_6F_5)_3$ and distinct lack thereof when utilising a direct proton source however, further mechanistic investigations are ongoing in the group.



Scheme 6. Proposed mechanistic pathways.

In conclusion, this work has shown how the strong Lewis acid $B(C_6F_5)_3$ can be utilized to great effect in the catalytic cyclization reactions, showcasing a powerful new metal-free pathway to C–H and C–C bonds in the formation of structurally complex pyrones and isocoumarins. Indeed, the reactions are quantitative in most stoichiometric examples after just 30 minutes at ambient temperature with the catalytic systems requiring mild heating to give generally good to excellent yields. Further functionalization of these systems has also been displayed through tandem cyclization/hydrosilylation reactions afford complex cyclic silylacetals in excellent yields, with exceptional atom efficiency. Further studies into catalytic C–C bond forming processes as well as tandem $B(C_6F_5)_3$ catalysis is ongoing in our group.

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Keywords: $B(C_6F_5)_3$ • Boron • Catalysis • Cyclization • Lewis acid

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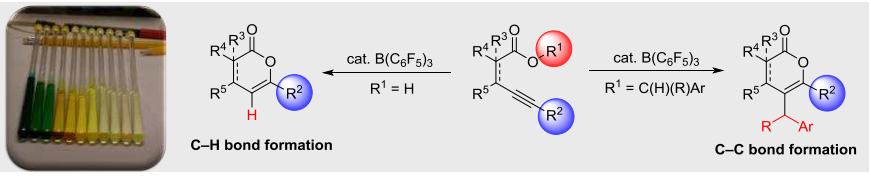

The highly Lewis acidic borane, $B(C_6F_5)_3$, is used in C–H and C–C bond forming reactions. Activation of alkynyl substrates using the Lewis acid allows catalytic intramolecular cyclizations of carboxylic acid substrates to be achieved for the first time. Additionally, intramolecular cyclizations of esters enables C–C bond formation in which catalytic $B(C_6F_5)_3$ is used to effect 1,5-alkyl migrations from ester functionalities to unsaturated carbon-carbon frameworks in good to excellent yields and outstanding atom efficiency in a metal-free manner.

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$B(C_6F_5)_3$: Stoichiometric and Catalytic C–C and C–H Bond Formation *via* Cationic Intermediates