Atom-economic and stereoselective catalytic synthesis of fully substituted enol esters/carbonates of amides in acyclic systems enabled by boron Lewis acid catalysis†

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Carboacyloxylation of internal alkynes is emerging as a powerful and straightforward strategy for enol ester synthesis. However, the reported examples come with limitations, including the utilization of noble metal catalysts, the control of regio- and Z/E selectivity, and an application in the synthesis of enol carbonates. Herein, a boron Lewis acid-catalyzed intermolecular carboacyloxylation of ynamides with esters to access fully substituted acyclic enol esters in high yield with generally high Z/E selectivity (up to >96 : 4) is reported. Most importantly, readily available allylic carbonates are also compatible with this difunctionalization reaction, representing an atom-economic, catalytic and stereoselective protocol for the construction of acyclic β,β-disubstituted enol carbonates of amides for the first time. The application of the carboacyloxylation products to decarboxylative allylations provided a ready access to enantioenriched α-quaternary amides. Moreover, experimental studies and theoretical calculations were performed to illustrate the reaction mechanism and rationalize the stereochemistry.

Introduction

The chemistry of enolates can be considered one of the cornerstone areas in organic chemistry, driven by this compound class’s role as carbon nucleophiles.1 As a crucial subclass of enolates endowed with a delicate balance of reactivity and stability, enol ester/carbonate derivatives have proven to be fascinating building blocks due to their versatility for further synthetic transformations such as aldol2 and Mannich-type reactions,3 cross-coupling reactions,4 asymmetric hydrogenations,5 cyclizations,6 and decarboxylative allylations.7 The enol ester skeleton is also found in an array of natural products and pharmaceuticals.8 Due to the importance of enol esters/carbonates, many efforts have been focused on their synthesis. Most of the conventional methods for their preparation rely on α-deprotonation of the corresponding carbonyl compounds and subsequent O-acylation of enolates, a route that is typically plagued with regio- or stereoselectivity issues and incompatible with base-sensitive functional groups (Scheme 1A).9 Recently, several attractive catalytic approaches for the preparation of enol esters have been reported including the hydroacyloxylation of alkynes,10 rearrangements of propargylic esters,11 Chan-Lam couplings,12 organocatalyzed Michael addition-rearrangement of ynals with carboxylic acids,13 and others.14 Despite significant progress, construction of fully substituted acyclic enol esters remains limited because of inevitable issues including significant steric hindrance and the difficulty to distribute the various substituents in a stereo- and regioselective way.

Attractive solutions to this problem have been described, and one of the most straightforward catalytic routes to rapidly build these valuable enol esters is the 1,2-difunctionalization of internal alkynes.15 For example, the Cramer group performed pioneering work on the heteroaryl acyloxylation of alkynes by cooperative rhodium/copper catalysis. However, the substrates were mainly symmetrical dialkyl alkynes, and the reaction transcribed...
afforded the desired products with poor regioselectivities when unsymmetrically substituted alkynes were used (Scheme 1B, top). On the other hand, pioneered by Lu, trans-acetoxy palladation of alkynes followed by olefin insertion and depalladation of the C–Pd bond was demonstrated by the groups of Lu,17e–d Chen,17e and Jiang17f as an efficient method for accessing fully substituted acyclic enol esters (Scheme 1B, middle). It has been reported that unsymmetrical internal alkynes activated by an electron-withdrawing group showed improved regioselectivity for the reaction,17e,f probably due to the polarization of the triple bonds. However, as for normal unactivated unsymmetrical alkynes, their regioselective carboacyloxylation is still a formidable challenge. Ynamides are versatile nitrogen-containing alkyne synthons in organic synthesis. Owing to their unique reactivity and regioselectivity, ynamides have been regarded as versatile building blocks to react with diverse starting materials providing a concise and flexible approach to construct various useful nitrogen-containing molecules.18,19 Thus, ynamides are accordingly selected as the reaction substrates in the investigation of the 1,2-difunctionalization process.20 Along these lines, the Hashmi group reported an impressive example of a regio- and stereoselective intermolecular acyloxyalknylation of ynamides based on an Au(i)/Au(III) catalytic cycle using ethynylbenziodoxolones as bifunctional reagents (Scheme 1B, bottom).21

Despite the progress made, the carboacyloxylation of alkynes continues to face several challenges such as (a) the carboacyloxylation strategy could not be extended to benzyl acyloxyations and secondary alkyl acyloxyations of alkynes; (b) in contrast to transition-metal catalysis, the complementary main group-catalyzed carboacyloxylation of alkynes in a sustainable manner is still scarce. A landmark in this field was described by Melen and co-workers, yet this reaction proceeds in an intramolecular fashion.22 (c) So far, most of the transformations were focused on the carboacyloxylation of alkynes for synthesis of enol esters while less work was reported on the selective delivery of a carbon atom and a carbonate across an alkyne for synthesis of enol carbonates, probably due to the carbonate's ability to undergo decarboxylation.23 Marek's group developed a state-of-the-art strategy for preparation of stereodefined acyclic z,1-dialkylsubstituted amide enol carbonates through a regio- and stereoselective carbocupration reaction of ynamides followed by a stereoretentive oxidation with an oxenoid and subsequent enolate trapping with allyl chloroformate (AllocCl; Scheme 1C, bottom).24 Of note, other elegant methods for the generation of stereo-defined amide enolates mentioned above typically require highly specialized substrates, often incorporating chiral auxiliaries to impart selectivity in the enolate formation step (Scheme 1A).25 Thus, the development of a catalytic protocol for accessing this important structural motif would be highly desirable. As a rare example, Dérien and co-workers reported a ruthenium-catalyzed synthesis of dienyl carbonates from propargylic carbonates and silyl diazo compounds by 1,2-carbonate migration of the propargylic carbonates, affording the desired products with poor to moderate Z/E ratios (Scheme 1C, top).26

An ester is one of the most common functional groups in organic chemistry. Carboxylates, especially carbonate, were always utilized as ideal leaving groups for the electrophile.27 In contrast to the studies on the difunctionalization reactions by using carboxylic acids, the successful use of esters as the bifunctional reagents28 in difunctionalization of unsaturated hydrocarbons to build molecular complexity still lags behind and had been limited to the intramolecular reaction.29 In line with our interest in developing atom-economic reactions and
main group catalysis, we report here a complementary and main-group-catalyzed intermolecular 1° and 2° alkyl acylation of nymades with benzyl carboxylates or carbonates, in which the RCO₂-C(sp³) bond is formally cleaved and added across nymades to generate the acyclic β,β-disubstituted enol esters/carbonates of amid es. The synthetic utility is illustrated by the late-stage modification of natural products and drug derivatives and the construction of acyclic quaternary carbon centers by palladium-catalyzed decarboxylylation allylic alkylation of fully substituted amide enolates.

Results and discussion

Catalytic synthesis of fully substituted enol esters

Given that geminal diaryl skeletons are prevalent in many natural products and pharmaceuticals, benzhydryl carboxylate 2a was selected as the model substrate, which can be easily prepared and also serves as a suitable cation precursor. Initially, diarly ester 2a and ynamide 1a were treated with commonly used metal-based Lewis acid catalysts such as Cu(OTf)₂, Zn(OTf)₂, and ZnCl₂ in toluene at 80 °C for 12 h. These catalysts led to no conversion (Table 1, entries 1–3). Using Sc(OTf)₃ or BF₃·Et₂O as the catalyst, a mixture of 3aa with a poor Z/E ratio and yield and some hydro-oxycarbonylation side product 4aa was obtained (entries 4 and 5). Bronsted acid TFOH failed to afford the desired product (entry 6). In light of Komeyama’s and Takaki’s as well as Melen’s elegant work on intramolecular carbo-oxycarbonylation of alkenyl enolates, we tried to perform the current intermolecular 1,2-difunctionalization reaction by means of bismuth and boron Lewis acid catalysis, respectively. Gratifyingly, with the use of Bi(C₆F₅)₃, the reaction provided the desired stereodefined fully substituted enol ester (Z)-3aa in 94% NMR yield (entry 8). The structure and configuration of (Z)-3aa were confirmed by X-ray diffraction. In contrast, Bi(OTf)₃ failed to give the desired product (entry 7 versus 8). A decrease in the yield and stereoselectivity was observed when the reaction was conducted at 60 °C (entry 9) or in the presence of a hindered Lewis basic phospine (entries 10 and 11).

With optimized reaction conditions established, we examined the reactions of benzhydryl esters 2 containing various carbonates with 1a. Esters 2a–q derived from aryl carboxylic acids were subjected to Conditions A described in Scheme 2. This protocol is amenable to a variety of esters bearing different R¹ functional groups, including halogen (2a–d), trifluoromethyl (2e), carboxyl (2f), methoxy (2i), and vinyl (2j) groups in the para position of the aromatic ring, and led to the corresponding enol esters in good to excellent yields and diastereoselection with Z/E up to >96 : 4. In general, substrates with an electron-withdrawing group showed higher yield and Z/E ratio than the other substrates bearing an electron-donating group (2e versus 2h and 2f versus 2i). As expected, functional groups at the meta- and ortho-positions gave satisfactory results for 10 mol% catalyst loading (2k and 2l). In addition, disubstituted (2m and 2n) and polysubstituted (2o and 2p) substrates were found to function exceptionally well in this reaction. Of note, benzhydryl propiolate 2r reacted chemoselectively (ynamides over electron-deficient alkynes) in good yield. The present protocol can also be efficiently applied to benzhydryl acetate derivative 2s and pivalic acid ester 2t to afford the corresponding products 3as and 3at in high yields and with excellent Z/E ratios. Importantly, our protocol allowed the incorporation of the enol ester fragment into bioactive molecules such as ketoprofen, isoxepac, menthol, estrone, and borneol (2u–ab). Notably, when benzhydryl esters 2z–ab bearing an additional ester functional group were subjected to the standard reaction conditions, only the benzhydryl ester motif was successfully incorporated into the products, affording corresponding products in good yields and Z/E ratios. We next investigated the scope of the aryl ester. Symmetrical diaryl esters bearing electron-withdrawing (4-F as in 2ac and 4-Cl as in 2ad) and electron-donating (4-Me as in 2ae) groups all worked well for the reactions when coupled with 1a generating 3aae–3aae in good yields; The unsymmetrical diaryl esters containing halogen (2af–ah and 2aj), electron-neutral (H as in 2ai), alkyl in the ortho- (2aj) or meta-position (2ak), and even alkynyl (2al) groups on the aryl ring were all tolerated and gave the corresponding products (3aaf–aal) in good yields and Z/E ratios ranging from 89 : 11 to >96 : 4. Rather than diaryl esters, alkynyl(aryl) esters were also competent to afford products 3aam–aaq, albeit with a lower yield and stereoselectivity. It is particularly noteworthy that the reaction of 4-methoxybenzyl 4-fluorobenzoate 2ap was successful under Conditions A, yielding 3aap in reasonable yield and with an excellent Z/E ratio. Besides benzyl ester derivatives, the reaction of alkynyl(alkenyl)...

<table>
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<th>Entry</th>
<th>Catalyst</th>
<th>Conv. [b] [%]</th>
<th>(Z)-3aa [b,c] [%]</th>
<th>(Z)-3aa : (E)-3aa [d]</th>
<th>4aa [b,c] [%]</th>
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<tr>
<td>1</td>
<td>Cu(OTf)₂</td>
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<td>—</td>
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<tr>
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<td>Zn(OTf)₂</td>
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<tr>
<td>3</td>
<td>ZnCl₂</td>
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<td>—</td>
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<tr>
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<td>75 : 25</td>
<td>10</td>
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<tr>
<td>5</td>
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<td>20</td>
<td>12</td>
<td>79 : 21</td>
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<td>—</td>
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<tr>
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<td>8</td>
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<td>96</td>
<td>65</td>
<td>78 : 22</td>
<td>4</td>
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[a] Unless otherwise noted, the reactions were performed with 1a (0.24 mmol), 2a (Ar = 4-FC₆H₄; 0.2 mmol) and catalyst (5.0 mol%) in toluene (2 mL) at 80 °C for 12 h. [b] Determined by 1H NMR spectroscopy of the crude reaction mixture with CH₃Br₂ as an internal standard. [c] NMR yield. [d] The reaction was run at 60 °C. 5 mol% B(C₆F₅)₃ and 5 mol% Mes₃P used. [e] B(C₆F₅)₃ (0.2 mmol) and Mes₃P (0.2 mmol) used.
ester 2aq with 1a at 80 °C for 12 h resulted in a mixture of regioisomers in 54% total yield (see the ESI† for details).

After the investigation of the ester scope, we studied the scope with respect to the ynamides (Scheme 3). Several 2-aryl ynamides 1b–k were tested with the ester 2a. Different substitution patterns of the aromatic substituent were tolerated independent of their electronic nature, providing products 3ba–ka in yields between 63% and 87% and with Z/E ratios ranging from 89 : 11 to >96 : 4. The naphthyl-containing ynamides 1l and 1m also afforded the corresponding products in good yields. Moreover, ynamides bearing different primary or secondary alkyl groups afforded the desired products with exclusive trans selectivity with a higher catalyst loading (1n–p). The amide moiety was not limited to oxazolidin-2-one; ynamides featuring a urea functionality and a thiazolidine-2-one were also competent in this reaction, resulting in the desired products 3qa–ra in excellent yields, albeit with a low stereoselectivity for product 3qa. Meanwhile, it should be noted that an ynamide containing a sulfonamide group, which readily undergoes hydrocarboxylation as reported by Mayr and co-workers, gave a complex reaction mixture, and attempts to isolate any pure compound failed. It is probably due to the ynamide containing a sulfonamide group, which readily undergoes hydrocarboxylation as reported by Mayr and co-workers.

**Catalytic synthesis of fully substituted enol carbonates**

Enol carbonate derivatives have served as versatile synthons in organic transformations. After the implementation of the carboacyloxylation of ynamides for the synthesis of enol esters, we wondered whether we could expand this catalytic methodology to build enol carbonates. To examine this hypothesis, readily available allyl benzhydryl carbonate 5a and ynamide 1o were selected as the model substrates (Scheme 4). In contrast to esters 2, the employment of carbonates 5 as bifunctional reagents in the current reaction poses formidable challenges. On the one hand, the main challenge is the issue of site selectivity because of the presence of two C–O reactive sites (e.g. bond a versus b). On the other hand, a competitive side reaction encountered in this case is the formation of ethers via decarboxylative etherification.

Treatment of 1o and 5a with B(C₆F₅)₃ under Conditions A did afford the desired product 6oa. However, a lower yield (50%)
and E/Z ratio (69:31) of 6oa together with side product ether 7 were obtained. After further investigations leading to the reoptimized reaction conditions B, the carboacyloxylation reaction provided the desired (E)-6oa in 81% NMR yield with E/Z > 96:4 at room temperature. Of note, the solvent (PhCl/HFIP) and the reaction temperature played an important role in controlling the stereoselectivity and the inhibition of side reactions (see Table S2 in the ESI†).

Under the optimal reaction conditions B, a series of carbonate derivatives 5 were prepared and examined. As shown in Scheme 5, allyl benzhydryl carbonate derivatives 5a-f bearing either electron-withdrawing or electron-donating groups on the aromatic ring were effectively converted into the stereodefined enol carbonates 6oa-of in moderate to good yields. The reaction was not limited to allyl benzhydryl carbonates; carbonates 5g derived from a primary benzylic alcohol and 5h derived from the alkynyl(aryl) alcohol were also tolerated. Furthermore, the substituent R² can be 2-methylallyl (5i), alkyl (5j), propargyl (5k) or phenyl (5l). The reactions proceeded smoothly to give the desired stereodefined enol carbonates in reasonable yields.

Having demonstrated the scope of the carbonates, our attention moved towards exploring the versatility of the ynamides. Various alkyl-substituted ynamides were screened and the desired enol carbonates (6sa-ta and 6na) were obtained in excellent yields. Aryl-substituted ynamide 1a was also compatible, albeit in lower yield. Also, thiazolidine-2-one-

![](image_url)
derived ynamide 1u and chiral ynamide 1v reacted smoothly to afford the corresponding stereodefined enol carbonates in good yields.

Synthetic transformations
The practicality of this method was demonstrated by performing a gram-scale synthesis of \((Z)-3aa\) (1.23 g) and a scale-up synthesis of \((E)-6oa\) (1.0 mmol) with maintaining selectivity and yield (Scheme 6, top). \(3as\) was found to be unstable and was expected to hydrolyze on silica gel during purification by flash column chromatography. Thus, amide 8 was isolated in 92% yield after subjecting crude \(3as\) to the silica gel and Et\(_3\)N (Scheme 6a). By contrast, both the enol ester group and oxazolidinone were hydrolyzed to give N-acyl ethanolamine 9 in 71% yield in the presence of LiOH, which can be readily converted into oxazole 10 (Schemes 6b and c). The functionalized enol ester 11 can be prepared from \(3aa\) by chemoselective Sonogashira coupling (Scheme 6d).

The C-C triple bond in \((Z)-3aan\) was hydrogenated over Pd/C to produce 12 in 90% yield (Scheme 6e). Selective semi-reduction of the alkyne for obtaining \(Z\)-alkene in 13 was achieved by using Prabhu’s protocol (Scheme 6f). These two transformations as alternative strategies have, to a certain extent, served the purposes of the synthesis of corresponding enol esters from alkyl aryl esters or alkenyl aryl esters with ynamides.

Palladium-catalyzed decarboxylative asymmetric allylic alkylation (DAAA) of fully substituted enol carbonates represents a practical strategy to set a quaternary carbon stereocenter in an acyclic system. In 2017, utilizing chemistry developed by the Marek group for the synthesis of acyclic enolates, the Stoltz group disclosed the elegant DAAA reactions of acyclic amide enolates utilizing Trost’s ligand (Scheme 1C). The use of acyclic carbamate substrates proved to be crucial to afford products in high enantioselectivities. In contrast, the DAAA of oxazolidinone-based allyl enol carbonates only gave the desired product with up to e.r. = 88:12. With a library of stereodefined oxazolidinone-based allyl enol carbonates in hand, we decided to evaluate the palladium-catalyzed DAAA of \((E)-6oa\) to afford \(Z\)-quaternary amide 14 that is not reported for Stoltz’s system. Gratifyingly, with the use of Pd\(_2\)(dba)\(_3\)/((S)-DTBM-SEGPHOS as the catalyst, the reaction provided the desired product 14 in 88% yield with e.r. = 94.5:5.5 e.r. (Scheme 6g; see also Table S3 in the ESI†).

Mechanistic studies
To gain insight into the reaction mechanism, several control experiments were conducted. When an enantiomerically pure...
sample of ester (R)-2ar was subjected to Conditions A, the resulting enol ester was obtained in racemic form, thus revealing that carboacyloxylation proceeds through a carboxylation intermediate (Scheme 7A). Subsequently, electrophilic addition of the in situ-generated carboxylation to ynamide 1 could give a keteniminium ion as an intermediate. To verify this proposal, ester 2as bearing electron-rich aromatic moieties was prepared, and then treated with 1a under Conditions A. Interestingly, the reaction afforded 1-amidoindene 15 in 78% NMR yield along with 13% NMR yield of 4aa (Scheme 7B).\textsuperscript{19} Given that 4aa was observed in current carboacyloxylation, we subjected 4aa and ester 2a to Conditions A to test whether the carboacyloxylation product arose from downstream benzylaion of the hydroacyloxylation product, but 3aa was not formed (Scheme 7C).

Furthermore, we performed crossover experiments with a mixture of equimolar amounts of ynamide 1a, and esters 2f and 2ai under conditions A (Scheme 7D). Analysis of the products by liquid chromatography-mass spectrometry revealed the presence of all four possible product masses, indicating that the addition of the carboxylate and the benzyl group to the ynamide is proceeding in a stepwise manner, and the resonance-stabilized anion may facilitate crossover by dissociation from the carboxylation center.

To further elucidate the mechanistic details of this reaction and to explain the observed stereoselectivity, DFT calculations on a model reaction of ynamide 1a with diaryl ester 2a using the B(C₆F₅)₃ catalyst were conducted at the M06-2X/cc-pVTZ//M06-2X/6-31G(d,p) level\textsuperscript{38} using the Gaussian 16 program.\textsuperscript{39} The solvent effect for toluene was taken into consideration using the polarizable continuum model.\textsuperscript{40} 3D structures were generated with CYLview.\textsuperscript{41} According to our calculations and the aforementioned control experiments (see Table 1, entries 10 and 11), the reaction proceeds through an ionic mechanism rather than a radical pathway due to the high energies required for the related single electron transfer (SET) process\textsuperscript{27ab} (see Fig. S1 in the ESI\textsuperscript{†}). Therefore, the following discussion will be focused on the possible two-electron processes involved in this reaction.
As shown in Fig. 1A, the carboacyloxylation reaction starts with the complexation of 2a with B(C₆F₅)₃ to give the Lewis adduct IM1. The formation of IM1 is exergonic by 4.2 kcal mol⁻¹. Although it is thermodynamically less favorable compared to 1a·B(C₆F₅)₃ carbonyl adduct IM¹ (ΔG = −6.4 kcal mol⁻¹), our computational results show that the ynamide activation pathway through the complexation of B(C₆F₅)₃ with the oxygen atom of 1a (IM¹) can be excluded (see Fig. S2, Table S1+ and related discussions for details). IM1 undergoes C–O cleavage to form ion pair IM2 with a barrier of 23.1 kcal mol⁻¹ (via TS1). IM2 consists of an electrophilic carbocation ionium and a borate anion [Ar¹CO₂B(C₆F₅)₃] as the carbanion, which readily undergo an electrophilic addition reaction with ynamide 1a to afford the new ion pair IM3 (via TS2). This step has a barrier of 22.9 kcal mol⁻¹, and the formation of IM3 is endergonic by 2.8 kcal mol⁻¹ relative to 2a and B(C₆F₅)₃. The borate anion [Ar¹CO₂B(C₆F₅)₃] of IM3 can attack at the carbocationic center of IM3 from the same and opposite side of the 1,1-diaryl methyl group to give the syn- (via E-TS3) and anti-addition (via Z-TS3) products, respectively (Fig. 1B). The formation of E-3aa requires a higher barrier than that of Z-3aa (3.5 versus 5.1 kcal mol⁻¹), and Z-3aa is thermodynamically more favorable than the syn-addition product by 0.8 kcal mol⁻¹. In E-TS3, the ketene iminium fragment is in a more distorted conformation than it is in the favored transition state Z-TS3 (C1–C2–N3 bond angle: 156° versus 164°). This might be attributed to the steric hindrance imparted by the 1,1-diaryl methyl moiety. The calculated free energy difference ΔGTS1 = 1.6 kcal mol⁻¹ is in good agreement with the experimentally observed stereoselectivity [(Z)-3aa/(E)-3aa > 96 : 4].

Alternatively, IM1 could also react with ynamide via a concerted S₄₂ transition state to afford the ion pair IM3 (via TS1). Our computations exclude this pathway due to the involvement of a high-energy transition state. This result is supported by the control experiment shown in Scheme 7A. Besides, a pathway proceeding through borane activation of the alkyne for the intramolecular carboacyloxylation of alkenyl carboxylic esters was proposed by Melen and co-workers. Although the addition of B(C₆F₅)₃ to ynamide is kinetically feasible (ΔGTS1 = 15.7 kcal mol⁻¹), the subsequent nucleophilic attack of diaryl ester 2a to the 1a·B(C₆F₅)₃ adduct IM4 is kinetically less favored than the above pathway by 4.3 kcal mol⁻¹. Therefore, a pathway involving the activation of the carboxylate of the diaryl ester by B(C₆F₅)₃ by an S₄₂₁-type mechanism is likely responsible for this carboacyloxylation process.

Conclusion

In summary, by taking advantage of esters as bifunctional reagents in the metal-free carboacyloxylation reaction of ynamides, an atom-economic and highly selective method for the synthesis of fully substituted acyclic enol esters was developed. To the best of our knowledge, this is the first B(C₆F₅)₃-catalyzed intermolecular 1,2-difunctionalization reaction of internal alkynes for the synthesis of acyclic tetrasubstituted alkenes. The salient features of this transformation include readily available starting materials, broad substrate scope, and scalability. The applicability was further illustrated in the late-stage modification of natural products and drug-like molecules. Notably, the protocol is also amenable to the synthesis of stereodefined acyclic β,β-disubstituted enol carbonates of amides, especially amide enol allyl carbonates, in one step. They are difficult to synthesize using transition-metal-catalyzed methods and can only be prepared by non-catalytic processes. Furthermore, we applied a palladium-catalyzed decarboxylative asymmetric allylic alkylation to the amide enol allyl carbonate to generate an α-quaternary amide in high yield and enantioselectivity (up to 88% yield and e.r. = 94.5 : 5.5). Control experiments combined with DFT studies support an SN1 pathway and rule out a concerted S₄₂ mechanism as well as a pathway involving the activation of the alkyne by B(C₆F₅)₃.

Data availability

The datasets supporting this article have been uploaded as part of the ESL†

Author contributions

Y. X., L. T., T.-T. X., and J.-Y.-H. S. performed the experiments and conducted the analytical characterization. Z. Z. and L. Y. conducted the crossover experiments described in Scheme 7D. G. W. executed the theoretical calculations. G. W., M. O. and J.-J. F. wrote the manuscript. J.-J. F. conceived the catalytic system.

Conflicts of interest

There are no conflicts to declare.

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References


The stereochemistry of the enol esters/carbonates was unambiguously assigned by X-ray crystal structure analysis of (Z)-3aa (CCDC 2236736) and (Z)-6oa (CCDC 2236734).


M. J. Frisch, et al, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford, CT, 2019, see the ESI† for the full citation.
