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COMMUNICATION

Phosphine-Catalyzed Activation of Cyclopropenones: A Versatile C_3 Synthon for (3+2) Annulations with Unsaturated Electrophiles

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We herein report a phosphine-catalyzed (3+2) annulation of cyclopropenones with a wide variety of electrophilic π systems, including aldehydes, ketoesters, imines, isocyanates, and carbodiimides, offering products of butenolides, butyrolactams, maleimides, and iminomaleimides, respectively, in high yields with broad substrate scope. An α-ketenyl phosphorous ylide is validated as the key intermediate, which undergoes preferential catalytic cyclization with aldehydes rather than stoichiometric Wittig olefinations. This phosphine-catalyzed activation of cyclopropenones thus supplies a versatile C_3 synthon for formal cycloadditon reactions.

The development of effective strategies to construct cyclic molecular architectures has attracted long-standing interest from the chemistry community.[1] In this regard, phosphine catalysis[2] has emerged as a powerful and versatile approach for the construction of various carbo- and heterocyles. Lu's (3+2),[3] Kwon's (4+2),[4] and Tong's (4+1)[5] annulations represent seminal advances in this field, from which a plethora of reactions[6] and asymmetric variants[2b] have been inspired. Since phosphine-catalyzed reactions are usually initiated by the conjugate addition of a phosphine to a polar double or triple bond to generate reactive zwitterionic intermediates, the prevalent substrates of phosphine catalysis rely almost entirely on electron-deficient alkenes, alkynes, allenes, and their derivatives[2a] (Figure 1a). These substrate entities serve as effective C_1 to C_4 synthons for generating various ring systems. Alternatively, we envisaged that the integration of the C–C bond activation of strained carbocycles within phosphine catalysis would significantly expand the scope. In 2018, we disclosed that electron-deficient vinylcyclopropanes (VCPs) undergo phosphine-catalyzed activation to generate zwitterions **A** that triggers the rearrangement of vinylcyclopropylketones to cycloheptenones (Figure 1b, up).[7] Very recently, an elegant phosphine-catalyzed enantioselective (3+2) annulation of electron-deficient vinylcyclopropanes with *N*-tosylaldimines with a zwitterion **B** as the key intermediate has been developed by Lu and co-workers[8] (Figure 1b, down). In the meantime, we have established that electron-deficient alkylidenecyclopropanes (ACPs) also readily undergo phosphine-catalyzed substrate-controlled rearrangements to afford polysubstituted furans and dienones.[9]

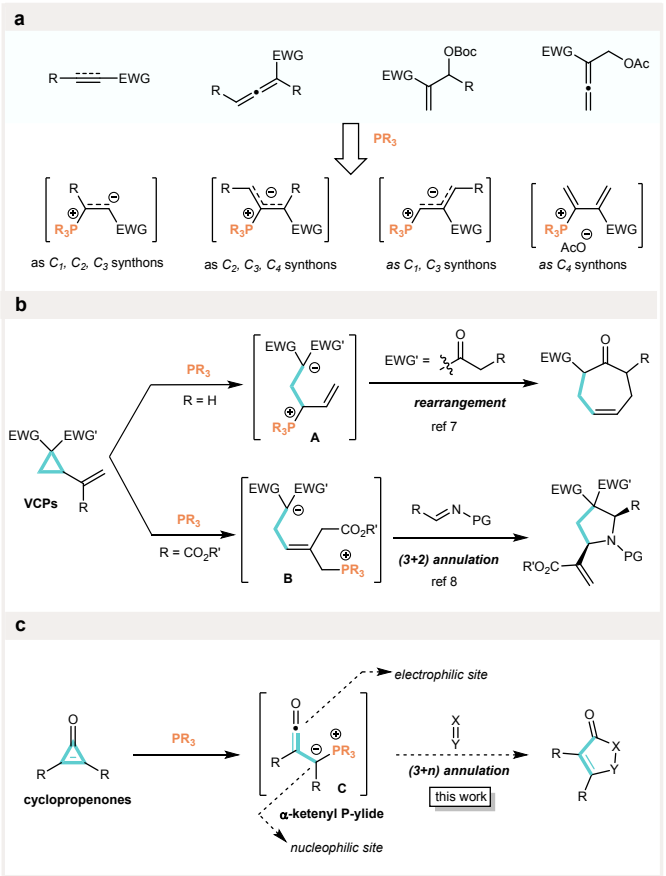

Figure 1 Substrates of phosphine-catalyzed annulation reactions. (a) Commonly used substrates of phosphine catalysis. (b) The use of electron-deficient vinylcyclopropanes (VCPs) as substrates in a phosphine-catalyzed rearrangement reaction (up), and (3+2) annulation with *N*-tosylaldimines (down). (c) This work describes the use of cyclopropenones as a versatile C_3 synthon for annulation reactions under phosphine catalysis.

As part of ongoing studies, we hypothesized that cyclopropenones, as triggered by phosphines, would serve as C_3 synthons for possible (3+n) annulations (Figure 1c). Mechanistically, the nucleophilic

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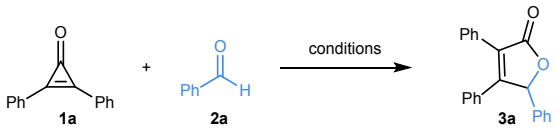
addition of a phosphine to cyclopropenones followed by ring cleavage would generate an α-ketenyl phosphorus ylide **C**.[10] Prescher and co-workers[11] have previously employed such ylides to react with *nucleophiles*, *e.g.* primary amines, for applications in bioorthogonal ligations. By virtue of its amphiphilic structure bearing both a nucleophilic ylide and an electrophilic ketene moiety, we proposed that it might be used as a 1,3-dipole surrogate for annulation reactions with unsaturated *electrophiles* (Figure 1c).

As a subclass of "non-benzenoid aromatic compounds", cyclopropenones[12] are strained, highly unsaturated, and readily available building blocks which have drawn tremendous interest in contemporary organic synthesis due to their unique and versatile reactivities.[13] The activation of these strained compounds is typically achieved through transition metal catalysis, *via* oxidative addition to the C–C single bond[14] to bring about various transformations,[13b] especially annulation reactions.[15] Wender and co-workers[15b] pioneered the Rh-catalyzed (3+2) cycloaddition of cyclopropenones with alkynes to build cyclopentadienones, whereas Li and co-workers[15f] developed a Ni-catalyzed (3+2) annulation of cyclopropenones with α,β-unsaturated ketones/imines to access butenolides and lactams. Gleiter and co-workers[15k, 15l] also demonstrated an interesting Co-mediated dimerization of cyclopropenones to form Co-capped benzoquinones. Other metal complexes involving Pd,[15c, 15i] Ru,[15a, 16] Ag,[17] and so forth,[18] are also known to facilitate a range of annulations with cyclopropenones. Compared to transition metal-catalyzed methods, however, the organocatalytic activation of cyclopropenones toward practical transformations remains far less explored.[19] Stemming from our interest in Lewis base catalysis,[7, 9, 20] we now report the phosphine-catalyzed activation of cyclopropenones as a new subset of C_3 synthons that are capable of undergoing (3+2) annulations with various unsaturated electrophiles (*vide infra*).

Table 1. Survey on conditions.[a]



entry	catalyst	additive	solvent	time	yield (%)[b]
1[c]	PPh_3	/	CH_2Cl_2	3 h	trace
2[c]	PBu_3	/	CH_2Cl_2	3 h	22
3[c]	PMe_3	/	CH_2Cl_2	3 h	30
4[c]	PMe_3	4Å MS	CH_2Cl_2	30 min	73
5	PMe_3	4Å MS	CH_2Cl_2	30 min	99
6[d]	PMe_3	4Å MS	CH_2Cl_2	2 h	92
7[e]	PMe_3	4Å MS	CH_2Cl_2	24 h	78
8[f]	PMe_3	4Å MS	CH_2Cl_2	5 d	20
9	PMe_3	4Å MS	THF	1 h	88
10	PMe_3	4Å MS	CH_3CN	1 h	35
11	PMe_3	4Å MS	toluene	1 h	95
12	PMe_3	4Å MS	cyclohexane	1 h	69
13	PMe_3	4Å MS	DMF	1 h	44

[a] Reaction conditions: **1a** (0.30 mmol), **2a** (0.20 mmol), and catalyst (0.02 mmol, 10 mol %) were stirred in the solvent (2.0 mL) at r.t. under N_2 atmosphere. [b] Yield of isolated product. [c] 0.20 mmol **1a** was used. [d] 5 mol % of PMe_3 was adopted. [e] 2 mol % of PMe_3 was used. [f] 0.1 mol % of PMe_3 was adopted.

Initially, we examined the phosphine-catalyzed reaction of diphenylcyclopropenone **1a** with several activated alkenes such as acrylates and maleates. These attempts were unsuccessful; however, the employment of benzaldehyde **2a** as the reaction partner led to the anticipated (3+2) annulation to afford a butenolide product **3a** (Table 1). To our knowledge, the (3+2) annulation of cyclopropenones with simple aldehydes is unprecedented, even under transition metal catalysis.[21] Another point of note is that the aforementioned α-ketenyl phosphorus ylide **C** does not undergo the usual Wittig reaction with aldehydes but enters into a catalytic cycloaddition pathway (see mechanism discussions below).

It was found that PPh_3 did not promote the reaction, whereas PBu_3 and PMe_3 catalyzed the reaction with yields of 22% and 30% of **3a**, respectively (entries 1–3). Nitrogen-containing Lewis bases such as DABCO, DMAP, and DBU were inefficient catalysts for the reaction (not shown). Interestingly, the addition of 4Å molecular sieves (4Å MS) improved the yield to 73% in a shorter time (entry 4), suggesting the progress of the reaction to be water sensitive. Increasing the amount of **1a** to 1.5 equivalents led to quantitative conversion, and halving the catalyst loading to 5 mol % still furnished an excellent yield of 92% in 2 h (entries 5 and 6). Further reducing the catalyst loading to 2 mol % gave 78% yield over 24 h, while 0.1 mol % of catalyst resulted in a substantially lower yield (entries 7 and 8). Examination of common solvents indicated dichloromethane to be optimal, although toluene gave comparable results (entries 9–13).

With optimized conditions in hand, the scope of the (3+2) heteroannulation of cyclopropenones with aldehydes was investigated first (Figure 2). A series of benzaldehydes with electron-donating groups (-Me, -^{t}Bu, -OMe, -OCF_3), halogens (-F, -Cl, -Br), or electron-withdrawing groups (-CO_2Me, -CF_3, -NO_2), substituted at either *para*, *ortho*, or *meta* position, all proceeded smoothly producing the corresponding adducts **3b**–**3r** in 55–96% yields. While naphthalene formaldehyde produced butenolide **3s** in 88% yield, heteroaryl aldehydes such as 2-furaldehyde, 2-thienaldehyde, and 3-indole aldehyde, yielded their respective annulated products **3t–3v** in 94–99% yields. The structure of **3v** was confirmed by single-crystal X-ray analysis. Notably, aliphatic aldehydes, such as butyraldehyde and pentanal, were also highly efficient substrates, providing adducts **3w** and **3x** in 89% and 87% yields, respectively. Even paraformaldehyde was found to undergo the (3+2) annulation with **1a** to give butenolide **3y** in 82% yield. To explore the scope of cyclopropenones, fluoro- and methyl-substituted diphenylcyclopropenones (**1b** and **1c**) were reacted with 4-methylbenzaldehyde, which produced the adducts **3z** and **3aa** in 91% and 93% yields, respectively. When cyclopropenones with unsymmetric substituents (R^1 = aryl, R^2 = methyl) were adopted, the annulated products **3ab–3ad** were obtained in 89–92% yields with excellent regioselectivity, possibly due to the preferential attack of the phosphine catalyst to the less sterically hindered side of the cyclopropenone. However, when a bigger ethyl is incorporated in the cyclopropenone (R^1 = phenyl, R^2 = ethyl), the annulated product **3ae** was obtained in 51% yield with a poor regioselectivity (1.5:1). It was then found that 1,2-dibutylcyclopropenone failed in the annulation (not shown), probably due to its less electrophilicity retarding the nucleophilic attack of the phosphine catalyst. Among aldehyde substrates, it is noteworthy that salicylic aldehyde reacted differently to form the enolate ester **4**, presumably *via* phenolate addition to a protonated ketenyl phosphonium intermediate.[22] Besides

aldehydes, it was found that the ketoester **5** also underwent (3+2) annulation readily with representative cyclopropenones to afford fully-substituted butenolides **6a**–**6c** in 91–98% yields (Figure 2, bottom left). Normal ketones like acetone and benzophenone, however, were ineffective under the current reaction conditions. More intriguingly, *N*-tosylimine **7** was also found to be an efficient partner for (3+2) annulation with **1**, which produced the butyrolactams **8a**–**8c** in 71–88% yields (Figure 2, bottom right).

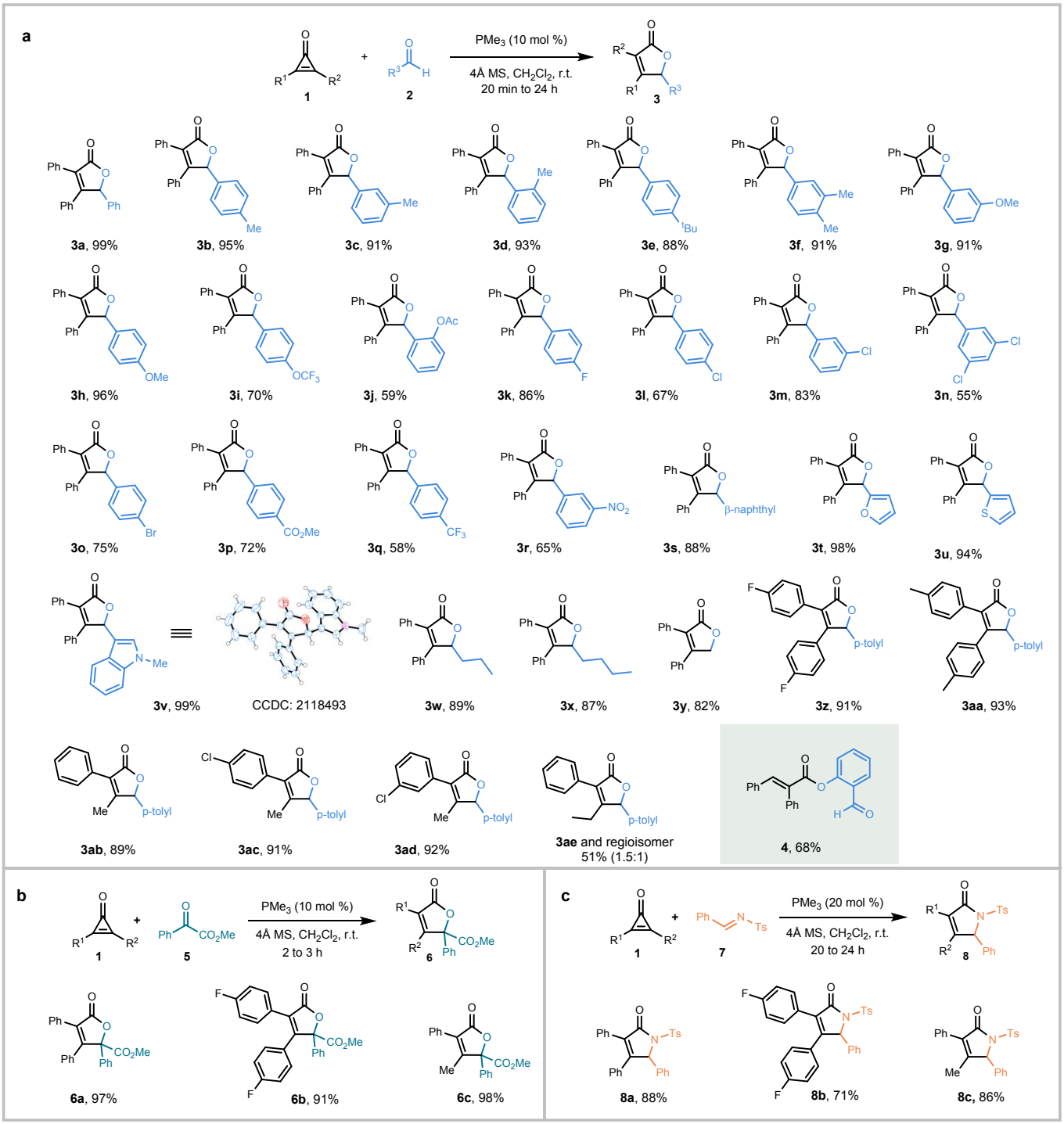


Figure 2 Scope of PMe_3-catalyzed (3+2) annulation with electrophilic C=X partners. (a) Reaction with aldehydes. (b) Reaction with ketoester. (c) Reaction with imines.

As C=O and C=N bonds can be both successfully integrated into annulations, we next examined the reaction of isocyanates possessing cumulated C=O and C=N bonds. Under optimized conditions (see Supplementary information for details), the phosphine-catalyzed (3+2) annulation of cyclopropenones with isocyanates **9** occurred exclusively at the C=N bond to provide the maleimide derivatives **10** in high yield (Figure 3). The scope of the reaction was therefore found to be broad. Aryl isocyanates with varied electron properties substituted at either *para*, *ortho*, or *meta* position typically reacted well to produce **10a**–**10k** in good yields. A trend can be discerned, such that groups with increased electron-withdrawing ability on the

benzene ring decreased the productivity. It was found that both alkyl and allyl isocyanates also readily coupled with cyclopropenones to provide *N*-substituted maleimides **10l**–**10q** in 60–83% yields. The structure of **10e** was confirmed by single-crystal X-ray analysis. Substitution of the phenyl groups of cyclopropenones was tolerated, as shown by the formation of **10r**–**10u** in 72–81% yields. *Bis*-isocyanates were also found efficient, which annulated with two molecules of **1a** to form adducts **10v** and **10w** in excellent yields. It is noteworthy that the convenient synthesis of polysubstituted maleimides by our current strategy stands in sharp contrast with transition-metal catalyzed ones, for example, as reported by Kondo and co-workers[16] through ruthenium-catalyzed (2+2+1) cocyclization of isocyanates, alkynes, and CO. To further demonstrate the generality of our phosphine-catalyzed annulation method, two commercially available carbodiimides **11** were employed as annulation partners with representative cyclopropenones (Figure 3, bottom). These reactions smoothly generated the iminomaleimides **12a**–**12f** in excellent yields (81–91%; single-crystal X-ray structure confirming **12a** unequivocally).

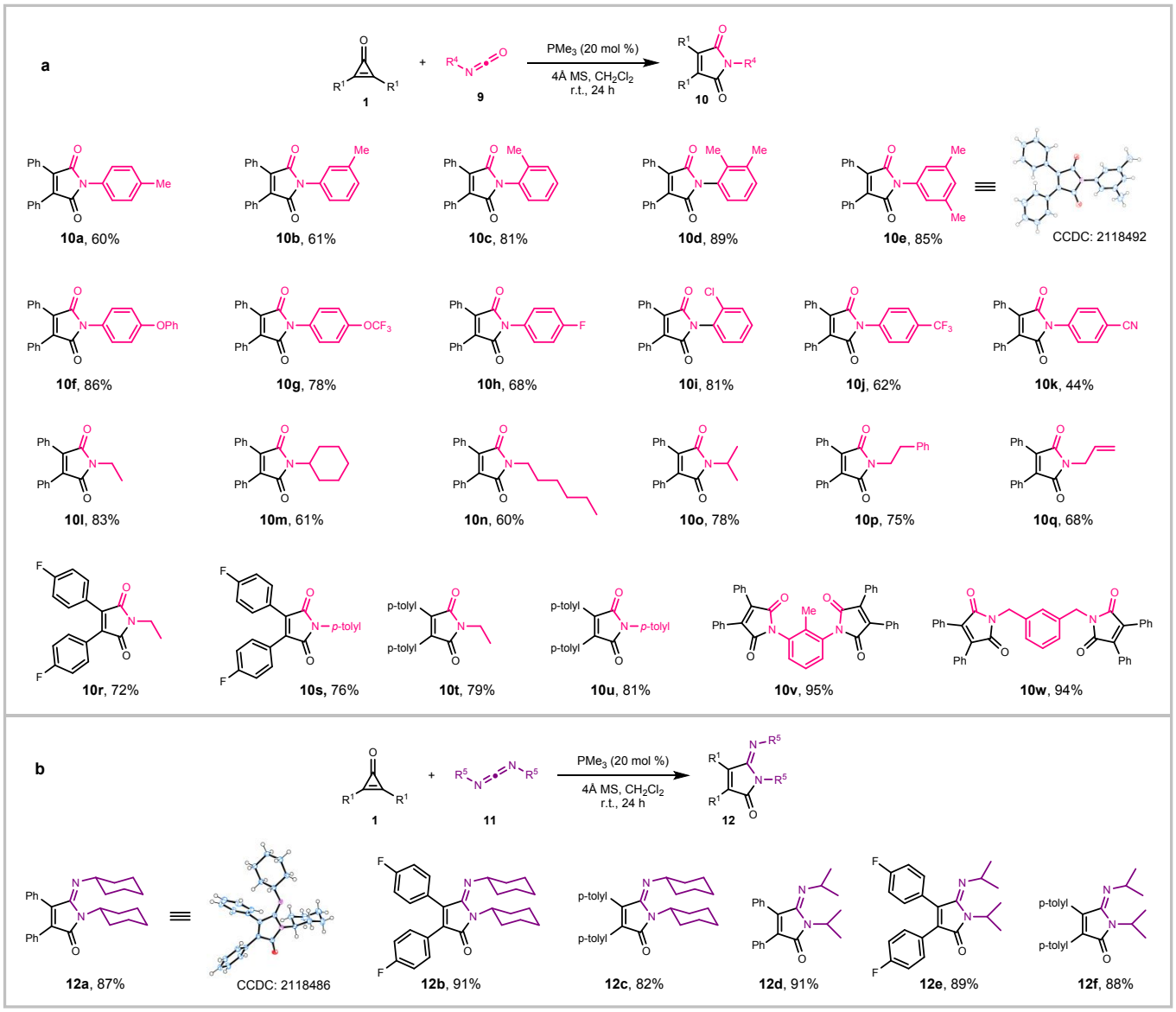


Figure 3 Scope of PMe_3-catalyzed (3+2) annulation with cummulated X=C=N partners. (a) Reaction with isocyanates. (b) Reaction with carbodiimides.

Collectively, our findings clearly indicate that the phosphine-catalyzed (3+2) heteroannulation of cyclopropenones is general for a broad range of C=X substrates including aldehydes, ketoesters, imines, isocyanates and carbodiimides. Notably, the products butenolide, butyrolactam, maleimide, and iminomaleimide are of high biologically relevance[23] and synthetic utility[24], which can now be readily generated in high efficiencies under mild conditions. This annulation strategy also constitutes a highly attractive alternative to transition metal-based variants.[15f, 15i]

A ^{31}P NMR tracking experiment was conducted in order to detect any essential intermediates in the PMe_3-catalyzed (3+2) annulation (See ESI for details). When mixing cyclopropenone **1a**, isocyanate **9a** with PMe_3 in $CDCl_3$ for 3 h, it was found that,

with the disappearance of PMe_3, several new species with signals at 5.8, 15.6, 22.9, and 38.6 ppm appeared in the ^{31}P NMR spectrum. This result supports the involvement of the phosphine in the catalysis, and implies that free phosphine is not the resting state of the catalytic cycle. In addition, when the reaction mixture was subjected to HRMS, a peak at 283.1248 ($C_{18}H_{19}OP$ [M + H]$^+$) corresponding to the adduct of **1a** and PMe_3 was detected, which may also support the formation of the proposed α-ketenyl ylide intermediate (See ESI for details).

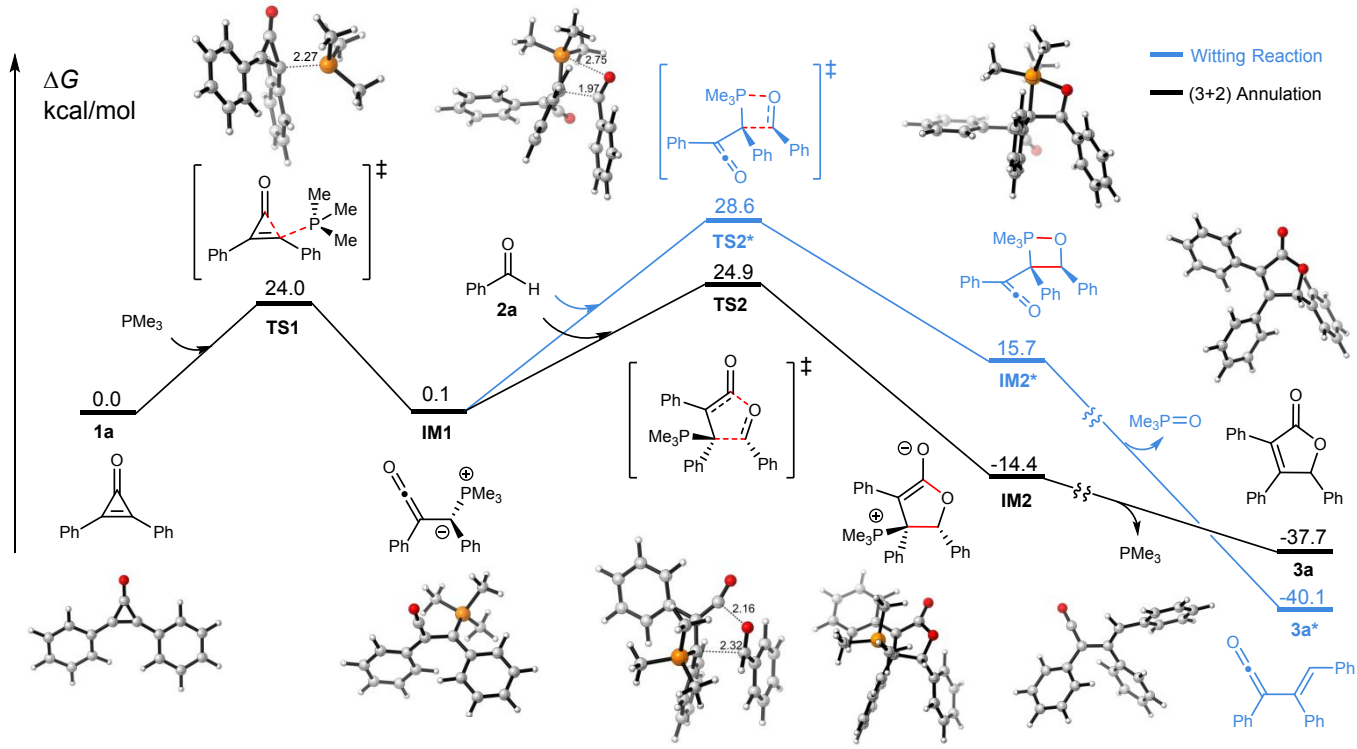


Figure 4 Calculated reaction profiles. The (3+2) annulation reaction is in black; Wittig olefination reaction is in blue. Energies are in kcal/mol and distances are given in Å.

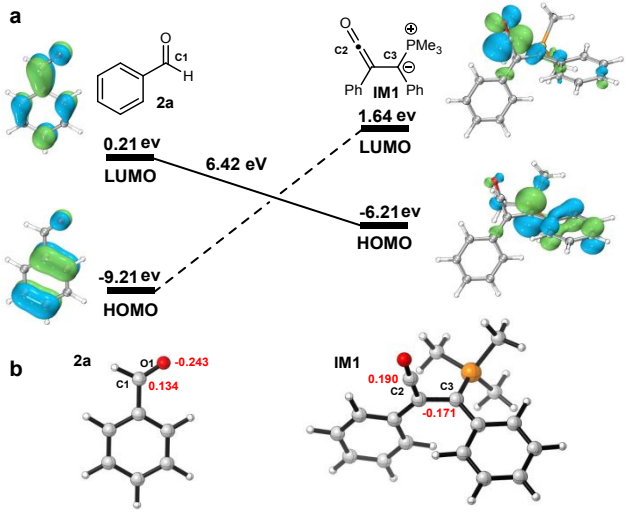


Figure 5 The frontier molecular orbitals (FMOs) and Hirshfeld charges. (a) FMOs interactions stabilizing **TS2** (see Figure 4). (b) Hirshfeld charges of **2a** and **IM1**.

To further probe the reaction mechanism and the origins of chemoselectivity toward the formation of **3a** over Wittig-based pathways to **3a***, density functional theory (DFT) calculations were performed as shown in Figure 4 (see Supplementary information for details). The reaction of cyclopropenone with PMe_3 has a 24.0 kcal/mol energy barrier to form the α-ketenyl phosphorus ylide **IM1**. The reaction involves concerted P–C bond formation and C–C cleavage, and no stable intermediate resulting from the phosphine addition on the cyclopropenone was found. The ketene and the phosphorus ylide are not conjugated, as the ylide C and P lie in a plane perpendicular to the plane of the ketene and its substituents. **IM1** was shown to computationally undergo a concerted cycloaddition with benzaldehyde **2a** to form **IM2**, *via* a five-membered ring transition state **TS2** with a 24.9 kcal/mol barrier. This may be a pseudo-pericyclic reaction[25] and does not involve a cyclic delocalized 6-electron transition state. Instead, the nucleophilic carbon of the ylide attacks the electrophilic aldehyde π system, while the oxygen of the aldehyde attacks the highly electrophilic π system of the ketene, in the plane of the forming lactone ring. The cyclization is more favorable than the Wittig-type attack of the aldehyde oxygen at the ylide phosphorus *via* a four-membered ring transition state **TS2***, which is higher in energy than **TS2** by 3.7 kcal/mol, even though the product **3a*** is more stable by 2.4 kcal/mol. The adduct of the cycloaddition (**IM2**) is unstable, which readily undergoes 1,4-elimination to form product **3a**. These pathway calculations are in accord with the fact that only product **3a** is observed experimentally. The frontier molecular orbitals (FMOs) of the reactants are shown in Figure 5a. The nucleophilic carbon terminus of the phosphorus ylide, HOMO of **IM1**, interacts with the large LUMO coefficient at C1 of **2a.** These orbitals differ in energy by 6.42 eV. Hirshfeld charges of corresponding atoms are shown in red in Figure 5b. From the perspective of molecular charge reorganizations, these charges are very complementary to the

transition state of the observed reaction. The two steps of the observed reaction have similar barriers, so that substituents that influence the rate of either step can have an effect on the overall reaction rate. Interestingly, the normally good dienophiles and dipolarophiles, acrylates and maleates, are not reactive in these cases. The low reactivity of acrylates as compared to aldehydes is likely due to the necessity for strong electrostatic interactions between the heteroatom of the electrophile and the central carbon of the ketene. In addition, it is known[2a, 26] that these Michael acceptors would react with PMe_3 catalysts to form off cycle intermediates thereby deactivating the desired reaction mode.

In summary, we report the development of a phosphine-catalyzed (3+2) heteroannulation of cyclopropenones with an extensive range of electrophilic C=X π systems including aldehydes, ketoesters, imines, isocyanates, and carbodiimides. This valuable alternative to transition metal-based methods not only provides efficient access to highly substituted sets of butenolides, butyrolactams, maleimides, and iminomaleimides, but also highlights the versatility and generality of the organocatalytic (3+2) annulative approach. Computational mechanistic investigations confirmed that an α-ketenyl phosphorus ylide is formed as a key intermediate. This species then undergoes a cycloaddition with aldehydes in a catalytic manner, rather than a stoichiometric Wittig olefination pathway, thus showcasing a unique and interesting reactivity. The organocatalytic activation of cyclopropenones also expands the scope of phosphine catalysis by supplying a new subset of 1,3-dipole surrogates that complements existing well-studied synthons, for example, allene substrates. Reaction development based on new modes of phosphine-catalyzed C–C bond activations is being explored in our laboratory.

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