

Cobalt-Catalyzed Intramolecular Cycloadditions of Alkenylenecyclopropanes with Alkenes and Dienes

Eduardo da Concepción,^a Israel Fernández,^b José L. Mascareñas,^{a,*} and Fernando López^{a, c,*}

^a Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela
Santiago de Compostela 15782 (Spain)

E-mail: joseluis.mascarenas@usc.es

^b Departamento de Química Orgánica I and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid (Spain)

^c Misión Biológica de Galicia (MBG), Consejo Superior de Investigaciones Científicas (CSIC)
36680, Pontevedra (Spain)

E-mail: fernando.lopez@csic.es

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Dedicated with admiration to Prof. Miquel Pericás, in recognition of his impactful career



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Abstract: Low-valent cobalt complexes equipped with phosphorous type of ligands can promote the intramolecular (3+2) cycloaddition of alkylenecyclopropanes (ACPs) with alkenes and with allenes. Dienes can also be used as partners, but they afford seven-membered cycloadducts. The reactions are fully diastereoselective and, in some cases, we also observed moderate enantioselectivities, especially when using chiral phosphite ligands.

Keywords: Cobalt; alkylenecyclopropane; cycloaddition; allene; diene

Transition metal-catalyzed (TMC) formal cycloadditions are among the most practical and versatile methods to construct polycyclic products from simple acyclic materials.^[1] Among the different cycloaddition strategies so far developed, those involving the activation of C–C bonds in strained carbocyclic reactants are especially attractive.^[2]

In this regard, we and others have shown that readily accessible alkylenecyclopropanes (ACPs) can

behave as versatile three-carbon components in a wide variety of synthetically powerful (3+2), (3+4) and (3+2+n) formal cycloadditions.^[3,4] These and other TMC annulations based on the C–C activation of strained carbocycles,^[2] typically require catalysts featuring noble transition metals like Rh, Pd or Ir. The use of earth-abundant first-row transition metals, which would offer a more sustainable and attractive option, has been mostly limited to nickel derivatives,^[5] and to a few examples based on iron and cobalt catalysts.^[6,7] This scarcity of examples is very likely due to the difficulties associated with controlling the redox steps of the catalytic cycles, owing to the wide range of accessible oxidation states exhibited by these metals. However, we have recently demonstrated that low-valent cobalt catalysts can also be used for the intramolecular (3+2) cycloadditions of ACPs and alkynes,^[7c] a reaction that had been originally developed with Pd, Ru and Rh-based reagents.^[4a,b,i] Moreover, we discovered that the cobalt-catalyzed annulation exhibits a different mechanism than those promoted by noble metals, which usually entail an initial oxidative addition cleavage of the cyclopropane ring. In the case of cobalt chemistry, the reaction prefers to start with the coordination of the enyne to a

cationic Co(I) species to deliver a highly stable intermediate **I**, that undergoes an oxidative cyclization to the key spirocobaltacyclopentene intermediate **II** (Scheme 1a).^[7c-d]

Considering this mechanistic pathway, we questioned whether alkenes could also be partners in the cycloaddition, as this would allow to enrich the stereochemical build-up of the reaction. However, alkenes might exhibit poorer coordination properties than alkynes, which would make the annulation more challenging.

Herein, we disclose our preliminary efforts in this direction, which allowed us to find cobalt complexes that can catalyze formal (3+2) intramolecular cycloadditions between ACPs and alkenes, and hence produce synthetically appealing 5,5-fused bicyclic scaffolds. Moreover, a slight modification of the catalytic system allows to expand this methodology to allenyl partners. We have also found that with 1,3-dienes, the reaction leads to appealing bicycles featuring seven-membered carbocycles.

Whereas the current scope of the processes is moderate, in some cases the cobalt-catalyzed reactions provide better results and complementary outcomes than those promoted by noble transition metals.^[4] Moreover, Density Functional Theory (DFT) calculations confirmed that the reactions do not start with the distal activation of the cyclopropane, but involve an oxidative cyclometallation step.

We started our study with the precursor **1a**, which bears an unsubstituted alkene tethered to the alkydidecyclopropane, and tested the cobalt catalysts previously found successful for the (3+2) cycloaddition of alkynylidene cyclopropanes.^[7c] In consonance with a more challenging process, treatment of **1a** with the low-valent cobalt catalyst *in situ* generated from

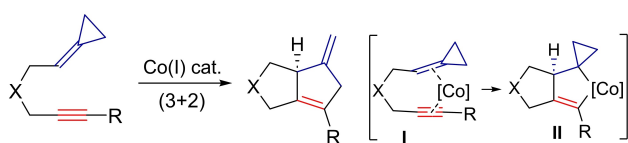
CoBr₂, dppp, Zn and ZnI₂ led to complete recovery of the starting material, even upon heating at 110 °C for several hours (Table 1, entry 1). The use of a stoichiometric amount of Zn, allowed to observe a modest conversion (27%) towards the desired product (**2a**), which was obtained in a low 20% yield (entry 2). Gratifyingly, we found that changing the reducing agent and additive to In (50 mol%) and InBr₃ (20 mol%), respectively, has a significant impact on the catalysis, so that the (3+2) adduct **2a** could now be isolated in 51% yield (entry 3). Importantly, the reaction was fully diastereoselective towards the *cis*-fused adduct.

Alternative bisphosphines such as dppf, instead of dppp, were also effective; however, besides the adduct **2a** (47% yield), the reaction also delivered the isomerized product **2a'**, in 27% yield (entry 4). Further optimizations led us to find out that the reaction was more efficient when using dppp as ligand and NaBARf instead of InBr₃ as additive (entry 5), as well as by increasing the reaction temperature up to 140 °C. Under these conditions, **2a** was isolated in 71% yield and also with complete stereoselectivity (entry 7).

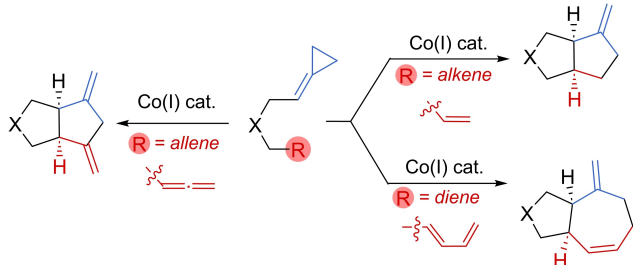
The use of Binap, which had provided good yields and enantioselectivities in the cycloadditions of ACPs with alkynes, led to **2a** with decent yield, but null enantioselectivity (entry 8). This complete lack of enantioselectivity was also observed with cobalt complexes equipped with other chiral bisphosphine ligands such as Segphos, Garphos or Ph-BPE (entries 9–11). Josiphos ligands like **L1** or **L2** led to poorer yields, but produced some asymmetric induction (entries 12 and 13). The reaction could also be achieved using monodentate phosphorous ligands, such as the bulky phosphite **L3** (entry 14), a result that encouraged us to test chiral monodentate phosphites. Indeed, the chiral cobalt catalyst generated *in situ* from CoBr₂ and the phosphite **L4**^[8] provides the cycloadduct **2a** in a good 80% yield and with a notable 85:15 er (entry 15). Unfortunately, all attempts to increase this value by altering the reaction conditions or by using structurally related chiral phosphites were unfruitful (Table S2).^[9] These results confirmed that tuning the reaction conditions allows to perform the desired (3+2) annulations, and with excellent diastereoselectivity; however, reaching high enantioselectivities is more challenging.^[10] One of the reasons for this poor asymmetric induction could be partially associated with a competitive background reaction promoted by achiral cobalt species that lack the phosphorous-based ancillary ligands (entry 16, 43% conversion, 31% yield).

The best conditions to promote the reaction, based on the catalyst derived from CoBr₂, dppp, In and NaBARf (Table 1, entry 6), could also be applied to promote the cycloaddition of ACP **1b**, bearing a fully carbonade tether, which gave the desired bicarbocyclic

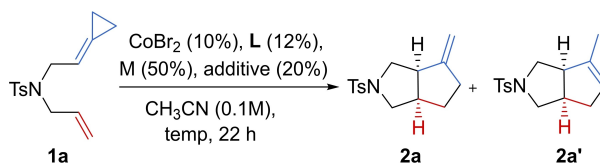
a) Cobalt-catalyzed (3+2) cycloadditions between ACP and alkynes



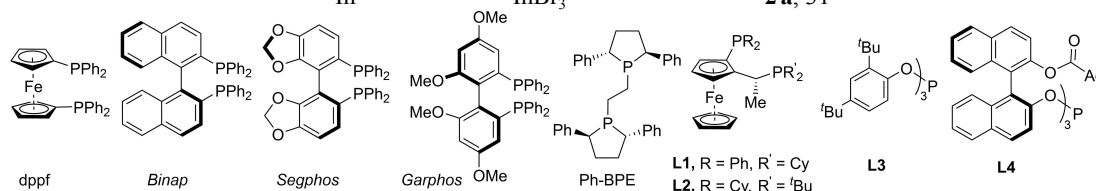
b) This work



Scheme 1. Previous cobalt-catalyzed (3+2) cycloadditions of ACPs and alkynes and this work.

Table 1. Optimization of the Co-catalyzed (3 + 2) cycloaddition of **1a**.^[a]

entry	L	M	Additive	2/3, yield %	er
1	dppp	Zn	ZnI_2	–	–
2 ^[b]	dppp	Zn	ZnI_2	2a , 20	–
3	dppp	In	InBr_3	2a , 51	–
4	dppf	In	InBr_3	2a , 47/ 2a' , 27	–
5	dppp	In	InI_3	2a , 52	–
6	dppp	In	NaBARF	2a , 61	–
7	dppp	In	NaBARF ^[c]	2a , 71	–
8	Binap	In	InBr_3	2a , 50	50:50
9	Segphos	In	InBr_3	2a , 50	50:50
10	Garphos	In	InBr_3	2a , 72	50:50
11	Ph-BPE	In	InBr_3	2a , 43	50:50
12	L1	In	InBr_3	2a , 20	65:35
13	L2	In	InBr_3	2a , 15	72:28
14	L3 ^[d]	In	InBr_3	2a , 61	–
15	L4 ^[d]	In	InBr_3	2a , 80	85:15
16	–	In	InBr_3	2a , 31 ^[e]	–



^[a] Conditions: Carried out with CoBr_2 (10 mol%) **L** (12 mol%), **M** (50 mol%), additive (20 mol%) in MeCN at 110 °C, unless otherwise noted.

^[b] Carried out with 1 equiv. of Zn. Conversion = 27%.

^[c] Carried out at 140 °C.

^[d] Carried out with 20 mol% of ligand (**L**).

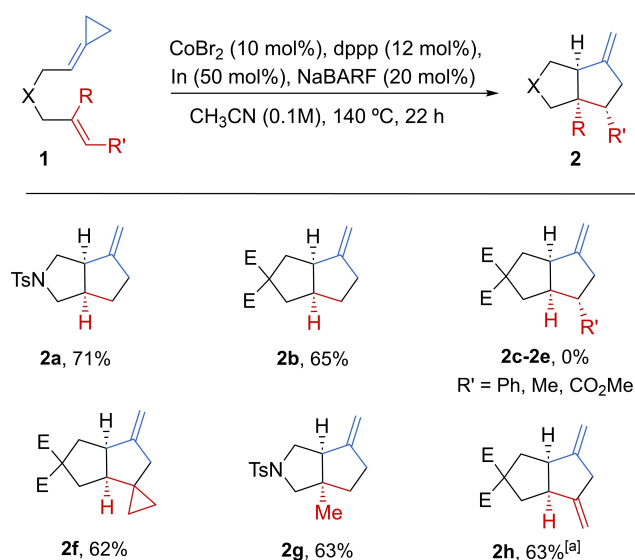
^[e] Conversion = 43%.

adduct **2b** in 65% yield (Scheme 2). In consonance with the assumption that alkenes are more challenging partners than alkynes, substrates with substituted alkenes like **1c–1e** ($\text{R}' = \text{Ph}, \text{Me}$ or CO_2Me) failed to give the expected cycloadducts. However, the cycloaddition of the bisalkylidenecyclopropane **1f** proceeded smoothly to afford the corresponding 5,5-bicyclic system **2f** in a good 62% yield. Interestingly, contrary to the Pd catalyzed processes,^[4c] the cobalt-catalyzed cycloaddition does allow the participation of alkenes that bear substituents at their internal position. Therefore, substrate **1g** ($\text{R} = \text{Me}$) delivered the (3 + 2) adduct **2g**, as the only isomer, in a good 63% yield.

We next check whether the reaction could be performed using allenes as 2 C-unsaturated partners. Allenes had been tested before in intramolecular (3 + 2) cycloadditions with ACPs with Pd catalysts,^[4d] but not with group 9 metals, including rhodium.^[11] Gratifyingly, substrate **1h** underwent the desired

annulation using a cobalt catalyst generated *in situ* from CoBr_2 and dppp, with In and InBr_3 as reducing mixture, to give the expected (3 + 2) adduct **2h** as the only product, in 63% yield. The cycloaddition of analogue precursors bearing terminally substituted allenes led to the recovery of the starting material.^[9]

While the introduction of alkyl substituents at the terminal position of the double bond hampered the reactivity, we envisioned that conjugated dienes might participate in the annulation, as they might coordinate better to the cobalt reagent and facilitate the reductive elimination step of the catalytic cycle.^[12] However, the diene could behave as a 2 C or as a 4 C cycloaddition partner. Dienes had been assayed in the palladium chemistry, and tend to provide mixtures of both, the (3 + 2) and the (4 + 3) cycloadduct.^[4e] To our delight, the cobalt-catalyzed cycloaddition of **1i**, which bears a terminally unsubstituted 1,3-diene provides the 5,7-fused bicyclic system **3i** in a good 54% yield, without



Scheme 2. Scope of the (3+2) cycloaddition with alkenes. $\text{E}=\text{CO}_2\text{Et}$.^[a] Carried out with InBr_3 at 110 °C.

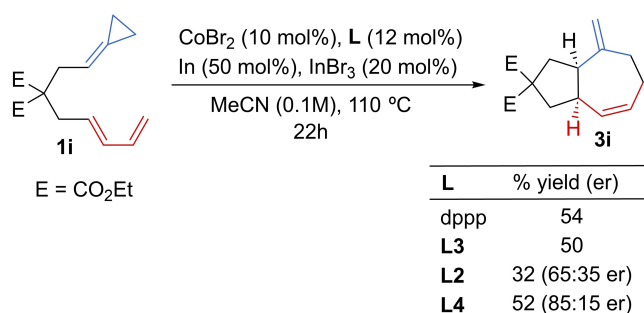
traces of the cyclopentane adduct (Scheme 3). The reaction can be performed not only using dppp as ligand but also with the ligand **L3**, with similar efficiency. We also tested chiral ligands, and the best results were obtained with the chiral phosphite ligand **L4**, which allowed to obtain a 52% yield of the product and a 85:15 enantiomeric ratio.

This proof of concept demonstrates the viability of the process, but expanding the reaction to other dienylnyl precursors will require further tuning of the conditions.

At this point, we considered important to obtain mechanistic information that could shed light on the above processes. Therefore, we carried out DFT calculations at the dispersion-corrected PCM(MeCN)-B3LYP-D3/def2-SVP level.^[9,13] We used the precursor **1a'** and the cationic Co(I) complex $[(\text{dppp})\text{Co}]^+$ as model reactant and catalyst, respectively (Figure 1). Compared to the previously described cobalt-catalyzed intramolecular (3+2) cycloaddition of ACPs and alkynes,^[7c] it is worth highlighting that, despite the

lower coordinating abilities of an alkene, the formation of a Co(I)-complex in which both the alkene of the ACP and the tethered alkene are both coordinated to the Co(I) center is still highly favoured over other possibilities.

Our calculations indicate that this intermediate (**INT0**) can undergo an oxidative cyclometallation to a cobaltacycle intermediate, **INT1**, through **TS1**, with an accessible energy barrier of 14.3 kcal/mol, almost identical to that previously observed for the Co-catalyzed cycloaddition with alkynes.^[7c] **INT1** holds the hydrogen atoms at the ring fusion in a *cis* disposition. The formation of the corresponding *trans*-fused stereoisomer **INT1'** could also be computationally located from **INT0'**, through the analogous transition state **TS1'**. From the data in Figure 1, it becomes evident that the formation of the *cis*-adduct **INT1** is favoured from both thermodynamic ($\Delta\Delta G_{\text{R}} = 3.2$ kcal/mol) and kinetic ($\Delta\Delta G^\ddagger = 4.6$ kcal/mol) points of view, which is consistent with the exclusive formation of the *cis*-fused bicyclic system observed experimentally (see above). The *cis*-fused spiro-metalacyclic intermediate (**INT1**) can be transformed into the highly stable π -allyl derivative **INT2**, via a cyclopropyl to π -allyl rearrangement (via **TS2**), a canonical β -carboelimination consisting of a distal opening of the cyclopropyl ring (C...C bond distance of 2.105 Å in **TS2**). Curiously, the barrier for this step is almost 7 kcal/mol lower than that of the analogous process involving an alkyne instead of alkene as cycloaddition partner (18.6 vs 25.3 kcal/mol).^[7c] This might be due to the higher conformational flexibility of the current cobaltacyclic system **INT2**, featuring a $\text{C}(sp^3)\text{-Co}$ bond. From this intermediate, a C–C reductive elimination provides the experimentally observed carbocycle. This last step conveys an energy barrier of almost 30 kcal/mol, significantly higher than that of the corresponding step for the cycloaddition with alkynes, reflecting the higher energetic cost associated with reductive eliminations involving $\text{C}(sp^3)$ carbons. Moreover, our calculations indicate that the addition of a substituent at the terminal position of the alkene (e. g. a methyl group), further increases the reductive elimination barrier by ≈ 6 kcal/mol ($\Delta G^\ddagger = 33.6$ kcal/mol, Figure S1). Therefore, our calculations suggest that the reluctance of ACP precursors like **1c** or **1d**, bearing a substituent at the alkene terminal position, to provide the (3+2) adducts of type **2**, might be related to a difficult C–C reductive elimination, so that alternative side processes, such as β -H eliminations, might compete. At variance, when the substituent at the alkene is a C–C double bond (i. e. cycloaddition with a conjugated diene), a π -allyl intermediate **INT4''** would be obtained, from which a facile reductive elimination (ΔG^\ddagger of only 10.5 kcal/mol) takes place to give the corresponding seven-membered cycle (Figure 2). This cyclization reaction is greatly favored over



Scheme 3. Co-catalyzed (4+3) cycloaddition of dienylnyl ACPs.

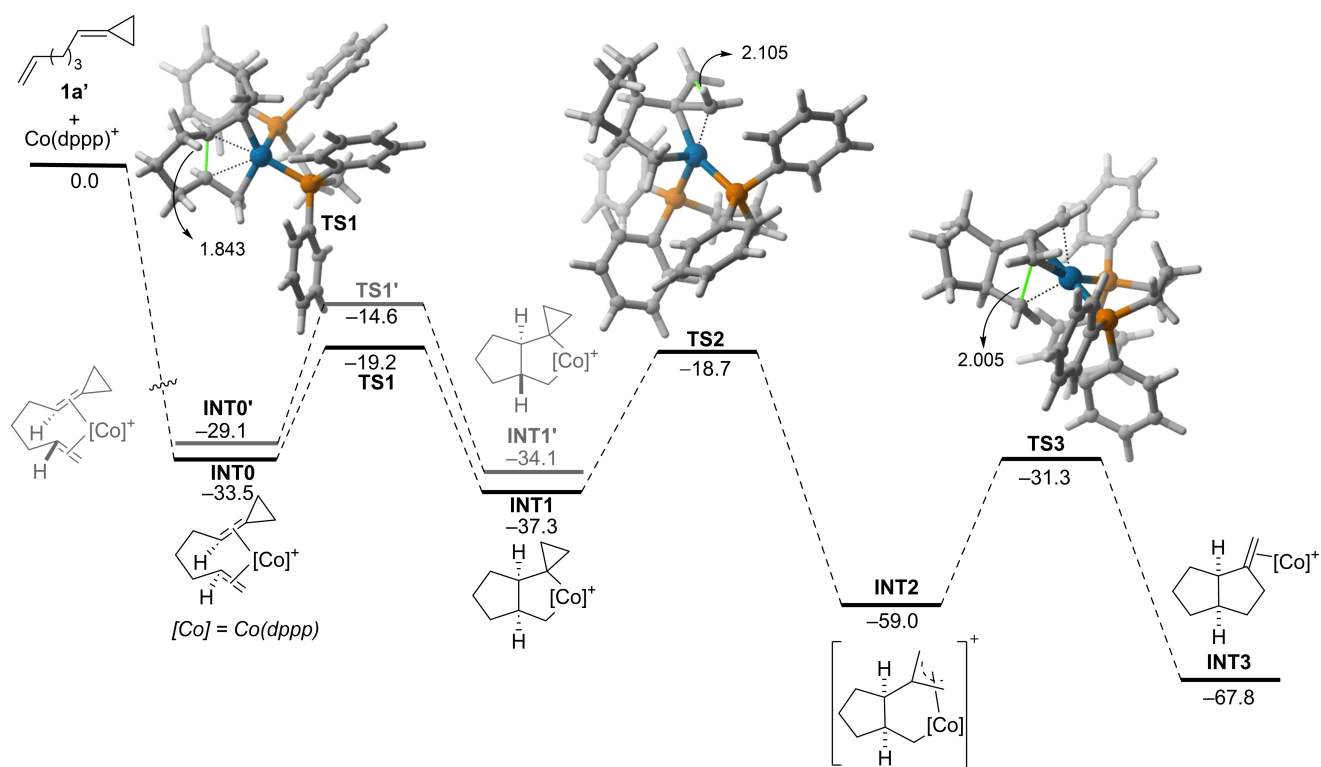


Figure 1. Computed reaction profile for the reaction model ACP **1a'** and $[\text{Co}(\text{dppp})]^+$. Relative free energies (ΔG , at 298 K) are given in kcal/mol. All data have been computed at the PCM(MeCN)-B3LYP-D3/def2-SVP level.

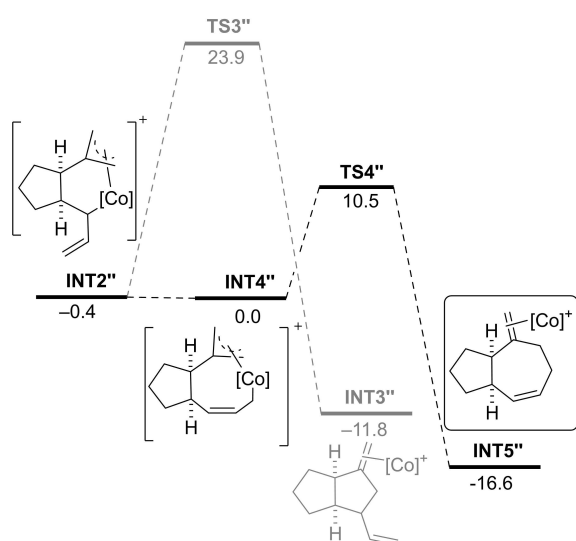


Figure 2. Computed reaction profile for the competitive cyclization reactions involving a model ACP of **1i**. Relative free energies (ΔG , at 298 K) are given in kcal/mol. All data have been computed at the PCM(MeCN)-B3LYP-D3/def2-SVP level.

the possible (3+2) process (via **TS3''** from **INT3''**) from both thermodynamic ($\Delta\Delta G = 4.8$ kcal/mol) and kinetic ($\Delta\Delta G^\ddagger = 13.4$ kcal/mol) points of view, which is fully consistent with the exclusive formation of the

bicyclic species **3h** observed experimentally (Scheme 3).

In conclusion, this study demonstrates that earth-abundant low-valent cobalt catalysts are capable of promoting the intramolecular (3+2) cycloaddition between ACPs and alkenes or allenes. Preliminary assays demonstrate that dienes are also suitable partners to provide (4+3) cycloadducts in a chemoselective manner. We have also found that asymmetric versions are feasible, however optimizing the processes will need further ligand screening. Using DFT calculations, we have obtained important mechanistic information that suggests that the difficulties associated with these annulation processes are mainly due to the reductive elimination step.

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- [13] a) This level was selected to enable a direct comparison with the data reported by us on the related Co(I)-catalyzed intramolecular (3+2) cycloadditions of ACPs and alkynes (see reference [7c]); b) For additional DFT results using the precursor **1a**, see Figure S2 (Supporting Information).

COMMUNICATIONS

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 E. da Concepción, I. Fernández, J. L. Mascareñas*, F. López*

