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Gold-Catalyzed *syn*-1,2-Difunctionalization of Ynamides via Nitrile Activation

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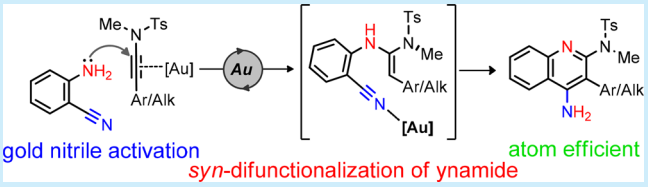
Supporting Information

ABSTRACT: Developed is an unprecedented Au(I)-catalyzed *syn*-1,2-difunctionalization of ynamides with 2-aminobenzonitriles via nitrile activation. The coupling between ynamides and 2-aminobenzonitriles is explicitly regioselective, providing a straightforward access to 2,4-diamino-substituted quinolines. Density functional theory (DFT) study provides insightful information and rationalizes the reaction pathway. It shows how the synergy between ynamide π-activation and nitrile σ-coordination by the Au(I) catalyst makes the cyclization viable.



Nitrogen heteroarenes are widely present in natural products, molecules of pharmaceutical importance, and materials of various significance.[1] The ynamide motif has been broadly used for the construction of such complex *N*-heterocycles.[2] In this context, gold-catalyzed transformations of ynamides have proven efficient, highly selective, and are synthetically relevant. Notably, the cyclization/cycloisomerization of yne-surrogates under homogeneous Au catalysis has led to novel synthetic transformations that allow the construction of diverse molecular scaffolds.[3] Generally, the cyclization of diynes proceeds via a vinyl carbocation[4] or a gold-vinylidene[5] intermediate through π-coordination and dual σ- and/or π-coordination of the alkyne moieties, followed by the attack of a nucleophile, respectively (Scheme 1A). For example, cyclization of terminal alkyne tethered ynamides/diynes involves gold-vinylidene intermediate (developed by Hashmi's and Gagosz's groups; Scheme 1A, path a).[5] In the yne-tethered ynamide series, nucleophile-promoted attack of the ynamide to the activated alkyne via vinyl carbocation is demonstrated (path b).[6] A recent report by Gagosz et al. based on intermolecular dimerization of ynamides followed by intramolecular C−H attack to a vinyl-carbocation intermediate (Scheme 1B, right), and the demonstration of Hashmi's on intermolecular trapping of a gold carbene with an ynamide (Scheme 1B, left), provides a direct access to novel heterocycles.[7] The Au-catalyzed hydroamination of anilines with ynamides (developed by Skrydstrup's and Liu's groups),[8] and the intramolecular trapping of vinyl-[Au] species, generated from aniline attack to ynamides, by alkynes, have also been reported.[9] Within this context, trying to devise an intermolecular method based on the concomitant attack of a nucleophile at the α-position of a keteniminium species, obtained in situ from an ynamide under the influence of a gold catalyst, followed by the β-attack of the resulting vinyl-[Au] species to an unsaturated-heteroatom motif, is a challenging endeavor (Scheme 1C).

Intrigued by the significant challenges involved in the multiple activation of π-bonds, we planned a reaction of ynamides with 2-aminobenzonitriles (having a nucleophilic amine moiety and a weakly coordinating CN group) in the presence of a Au(I) catalyst. We envisaged that the attack of the NH_2 group at the α-position of the Au-activated ynamide would be favored over that of the nitrile. The hydroamination and protodeauration would provide a helically chiral nitrile-gold complex **D**.[10] Finally, intramolecular enamine addition to the nitrile-gold ligated species, followed by the imine/enamine tautomerism would produce unusual 2,4-diamino-substituted quinolines (a core structure present in various natural products), as shown in eq 1.[11] The current demonstration is synthetically different from previously described Au-catalyzed transformations of ynamides involving nitriles in the sense that the −CN species here acts as an electrophile and not as a nucleophile.[12]

To accomplish the envisaged process, ynamide **1a** was reacted with 2-aminobenzonitrile **2a** in the presence of various Au-catalysts (Table 1). To our delight, product **3a** was formed in 53% yield when the reaction was conducted with $Ph_3PAuNTf_2$ (1.0 mol %) in 1,2-dichloroethane (DCE) at

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Scheme 1. (A and B) Cyclization Methods of Ynamides; (C) Intermolecular *syn*-1,2-Difunctionalization of Ynamides

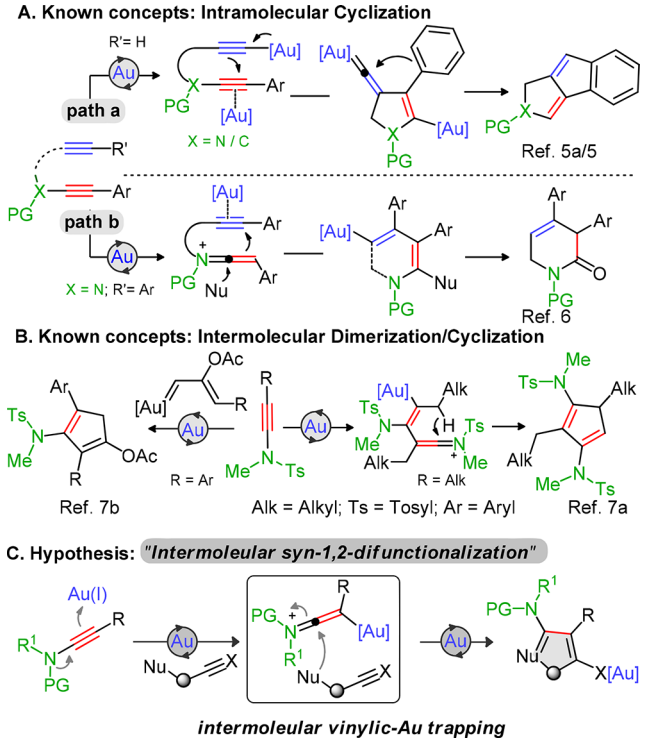
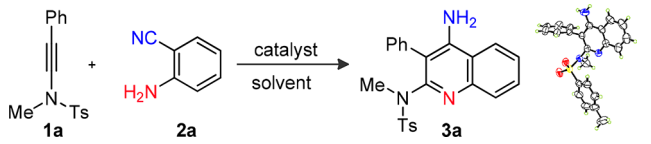


Table 1. Optimization of Reaction Conditions[a]



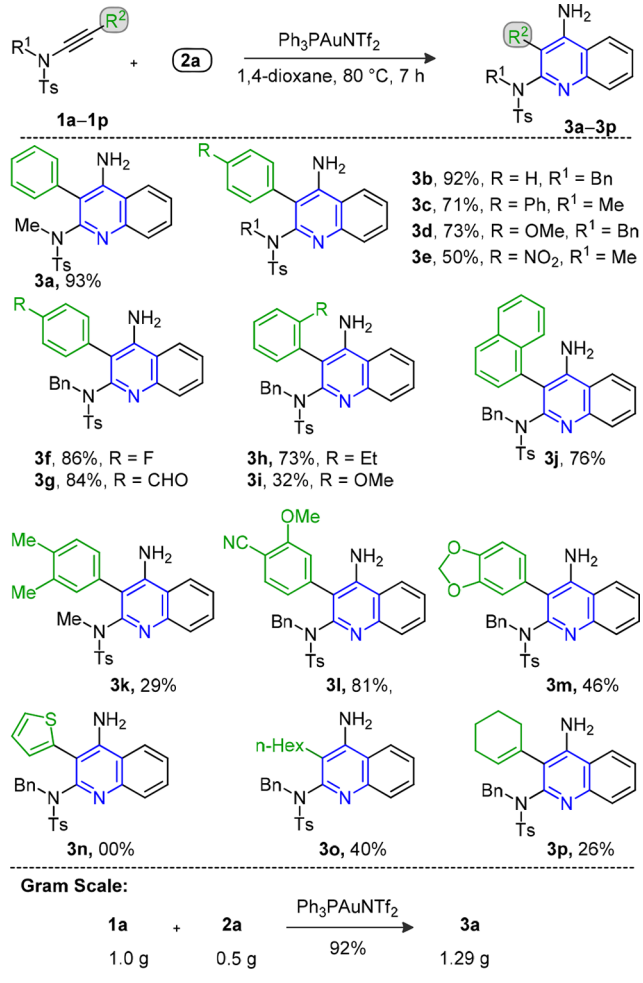
entry	catalyst	solvent	yield of **3a**[b] (%)
1	$Ph_3PAuNTf_2$	$ClCH_2CH_2Cl$	53[c]
2	$Ph_3PAuNTf_2$	$ClCH_2CH_2Cl$	86
3	$Ph_3PAuNTf_2$	acetone	79
4	$Ph_3PAuNTf_2$	toluene	82
5	**$Ph_3PAuNTf_2$**	**dioxane**	**93**
6	$Ph_3PAuNTf_2$	dioxane	85[d]
7	JohnPhosAu(MeCN)SbF_6	dioxane	44
8	CyJohnPhosAuNTf_2	dioxane	38
9	IprAuNTf_2	dioxane	24
10	IMesAuNTf_2	dioxane	58
11	$Cu(OAc)_2$	dioxane	0
12	$Pd(OAc)_2$	dioxane	0
13	$AgNTf_2$	dioxane	11

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (1.2 equiv), catalyst (1.0 mol %), solvent (1 M) at 80 °C for 7 h. [b]Isolated yield. [c]At room temperaure (rt). [d]50 °C.

room temperature (rt) for 7 h (Table 1, entry 1). At 80 °C, the yield was improved to 86% (Table 1, entry 2). The reaction in acetone or toluene was equally efficient (Table 1, entries 3 and 4). The best solvent proved to be 1,4-dioxane, providing **3a** in 93% yield at 80 °C (Table 1, entry 5), or in 85% yield at 50 °C (Table 1, entry 6). Of note, the nature of the ligated gold species substantially influenced the outcome. The product yield was diminished when JohnPhos and CyJohnPhos ligated Au-catalysts were employed (44%, Table 1, entry 7; 38%, Table 1, entry 8). Similarly, the use of IPr- or IMes-derived catalysts gave **3a** in 24% and 58% yield, respectively (Table 1, entries 9 and 10). Not surprisingly, the use of copper and palladium catalysts did not yield the desired product (Table 1, entries 11 and 12), whereas **3a** was isolated in 11% yield when the reaction was performed with $AgNTf_2$ (Table 1, entry 13).

The scope of this Au(I)-catalyzed reaction between ynamides and 2-aminobenzonitrile **2a** was then surveyed (Schemes 2 and 3). Under the optimized condition (Table 1, entry 5), the ynamides having aryl motifs [electron-neutral, electron-rich (*p*-Ph, *p*-OMe), electron-poor (*p*-F, *p*-NO_2, *p*-CHO)] at the ynamide terminus furnished the desired 2,4-diamino-substituted quinolines **3a**–**3g** in good yields in most cases. The *N*-Me/Bn protected ynamides effectively partici-

Scheme 2. Scope I: Reaction of Ynamides (1) with 2-Aminobenzonitrile (2a)[a]



[a]Reaction conditions: **1a** (1.0 equiv), **2a** (1.2 equiv), Au-cat (1.0 mol %), 1,4-dioxane (1 M) at 80 °C for 7 h. Isolated yield.

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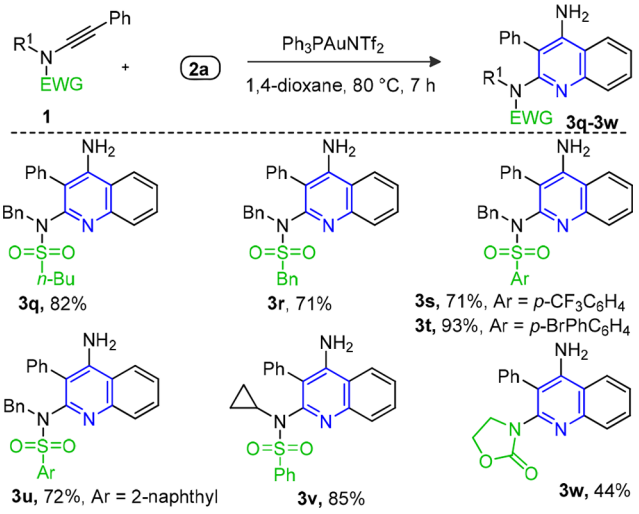
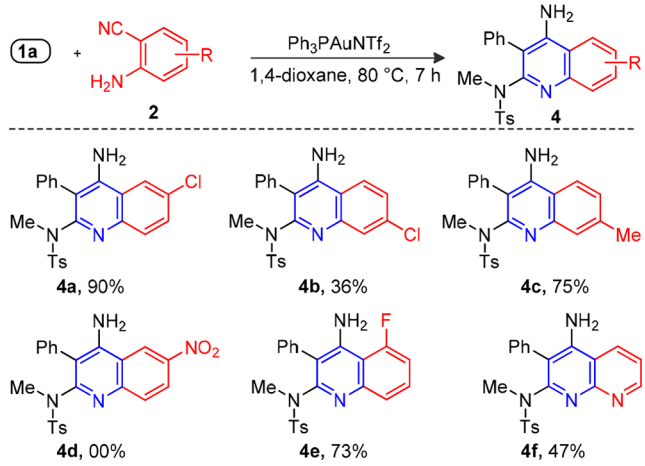
Scheme 3. Scope II: Reactivity of Various *N*-Protected Ynamides with 2a[a]



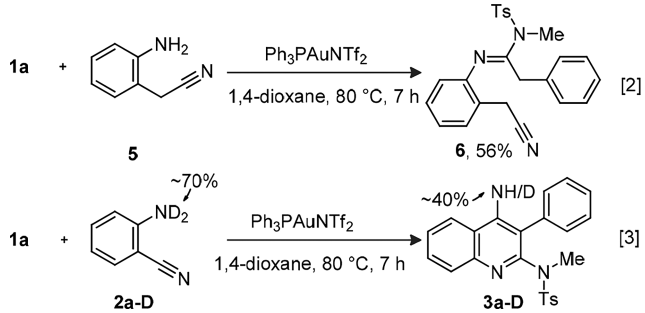
[a]Reaction conditions: **1** (1.0 equiv), **2** (1.2 equiv), Au-cat (1.0 mol %), 1,4-dioxane (1 M) at 80 °C for 7 h. Isolated yield.

Scheme 4. Scope III: Screening of 2-Aminobenzonitriles (2)[a]



[a]Reaction conditions: **1** (1.0 equiv), **2** (1.2 equiv), Au-cat (1.0 mol %), 1,4-dioxane (1 M) at 80 °C for 7 h. Isolated yield.

Scheme 5. Mechanistic Experiments



pated. Similarly, the reaction of ynamides displaying *ortho*-substituted aryls with **2a** provided **3h** (73%) and **3i** (32%). The π-extended 1-naphthyl-substituted quinoline **3j** was also successfully constructed. Quinolines **3k**–**3m** were accessed from multisubstituted aryl-bearing ynamides. Disappointingly, the 2-thienyl-substituted quinoline **3n** was formed only in trace, which is a possible consequence from the quench of the Au-catalyst. Alkyl- and alkenyl-bearing ynamides showed moderate reactivity with **2a**, delivering **3o** and **3p** in 40% and 26% yield, respectively. Gratifyingly, this transformation was scalable with no change in yield: 1.29 g of **3a** was obtained from 1.0 g of **1a** and 0.5 g of **2a**.

Sulfonamide-substituted heterocycles are widely present in the molecules of biological importance.[13] In this context, transformation of various *N*-sulfonyl protected ynamides using **2a** was probed (Scheme 3). Accordingly, several 4-amino-2-*N*-sulfonyl protected 3-phenyl quinolines **3q**–**3u** [having *N*-Bn-$SO_2{}^nBu$/SO_2Bn/$SO_2C_6H_4$-*p*-CF_3/$SO_2C_6H_4$-*p*-Br/SO_2-β-naphthyl] and **3v** [*N*-cyclopropyl-SO_2Ph] were synthesized. In addition, the carbamate derivative **3w** was prepared, albeit in moderate yield compared to sulfonyls.

We next explored the generality of the transformation by reacting **1a** with various 2-aminobenzonitriles having substituents at different positions of the arene periphery (Scheme 4). Thus, the reaction of 5-Cl/4-Cl/4-Me-substituted 2-aminobenzonitriles with **1a** delivered the corresponding highly substituted quinolines **4a**–**4c**. Unfortunately, the reaction with a nitro-substituted 2-aminobenzonitrile was unsuccessful, a likely consequence of the strong electron-withdrawing nature of the nitro group that reduces the nucleophilicity of the amine moiety. The desired quinoline **4e** (73%) was accessed from 2-amino-6-fluorobenzonitrile. The strong coordination ability of the pyridine scaffold did not hamper the reaction, delivering **4f** in 47% yield.

To get some insight into the reaction pathway, a few control experiments were designed. The coupling of 2-aminobenzyl-cyanide **5** with **1a** provided the uncyclized product **6** (eq 2 in Scheme 5); this ascertains the plausible involvement of hydroamination/enamine intermediates. The reaction of *N*-deuterated-**2a** (70% D) under the standard conditions provided **3a** with 40% deuterium incorporation; the proton source from **2a** is thus confirmed (eq 3 in Scheme 5).

To further explore the mechanistic details of the reaction of ynamide **1a** with 2-aminobenzonitrile (**2a**), DFT computations were executed at the M06/def2-QZVP(Au)-6-311+G(2d,p)//B3LYP/LANL2DZ(Au)-6-31G(d,p) level of theory (see the Supporting Information for details). Complex **A**, which results from the coordination of AuL^+ to ynamide **1a** and **2a**, were selected as reference for the free energies of system [**AB**] (Figure 1). The geometry of this complex is actually closer to a σ-ketiminium species than a π-complex (see the SI). The *trans*-hydroamination of **1a** with **2a** was first modeled. This step requires a low free energy of activation of 17.0 kcal/mol and is endergonic by 15.2 kcal/mol. In fact, iminium **C** shows two elements of chirality, because of its helicity and the C–N axis connecting the alkene and the amide fragment. Thus, diastereomer **C′** displaying the same helix but an inverted C–N axis can be defined.[9] It is more stable than **C**, by 6.2 kcal/mol, but slightly slower to form. The transformation of **C'** into the final product has been computed and the corresponding energy profile is presented in the Supporting Information. The protodeauration from intermediate **C** is exergonic, providing the nitrile-gold complex **D** lying at −19.6 kcal/mol on the potential energy surface (PES). Next, intramolecular enamine addition to the helically and axially chiral nitrile-gold ligated species gives **E**. This step is endergonic by 10.2 kcal/mol and requires 20.7 kcal/mol of

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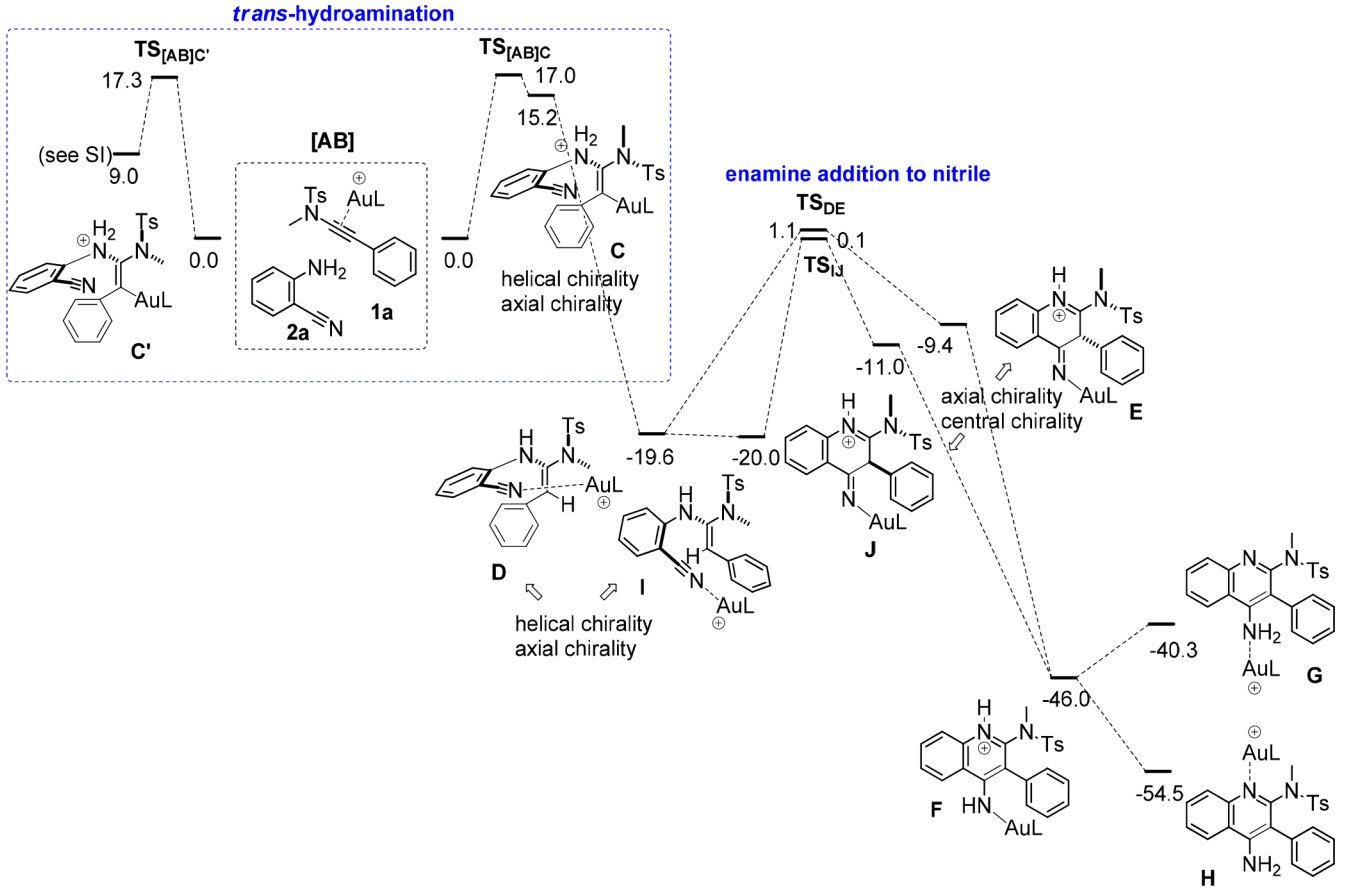

Figure 1. Free-energy profile (ΔG_{353}, kcal/mol, L = dimethylJohnPhos).

free energy of activation. The diastereomer **I**, obtained through enamine/iminium tautomerism of **D** (this step requires an unknown proton shuttle to avoid the symmetry-forbidden intramolecular 1,3-H shift, it thus cannot be computed), is more stable than **D** by 0.4 kcal/mol. The cyclization of **I** demands 20.1 kcal/mol free energy of activation and provides **J**, which is a diastereomer of **E**. This cyclization **I** → **J** imposes a different sense of rotation around the chiral C−N axis, compared to **D** → **E**; thus, **E** and **J** are diastereomers. The imine/enamine tautomerism of **E**/**J** gives pyridinium species **F**, lying at −46.0 kcal/mol on the PES. Finally, protodeauration of **F** leads to the amine-gold complex **G** (−40.3 kcal/mol), or the pyridine-gold complex **H** (−54.5 kcal/mol). The formation of **H** is thus more favorable. Overall, the transformation of the [**AB**] system to **H** is strongly exergonic by 54.5 kcal/mol.

On the basis of this DFT study, the transformation begins with the attack of amine to the gold ketiniminium species (**I**), obtained in situ via selective π-coordination with the Au(I) catalyst and generates enamine intermediate **II** (which exists as *cis* and *trans* diastereomers).[14] The intramolecular enamine attack to the activated CN moiety then provides **III**. Finally, aromatization of **III** and the proto-deauration of **IV** leads to the desired quinoline product **3** and regenerating the Au(I) catalyst.[14]

We have herein demonstrated an Au(I)-catalyzed direct coupling of ynamides with 2-aminobenzonitriles for the synthesis of 2,4-diamino-substituted quinolines. This transformation highlights the *syn*-1,2-difunctionalization of ynamide through the intramolecular 6-*exo*-dig cyclization of ketene aminal to the σ-coordinated nitrile moiety by Au(I). The catalytic system is robust, showcasing broad scope, and tolerates various functional groups. The mechanistic details are rationalized by DFT calculations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03830.

Experimental procedures and methods, substrate synthesis and isolated product characterization, analytical data, computational details, coordinates and energy of the computed species (PDF)

Accession Codes

CCDC 1870573 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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