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A Highly Efficient Gold-Catalyzed Photoredox α-C(sp^3)–H Alkynylation of Tertiary Aliphatic Amines with Sunlight

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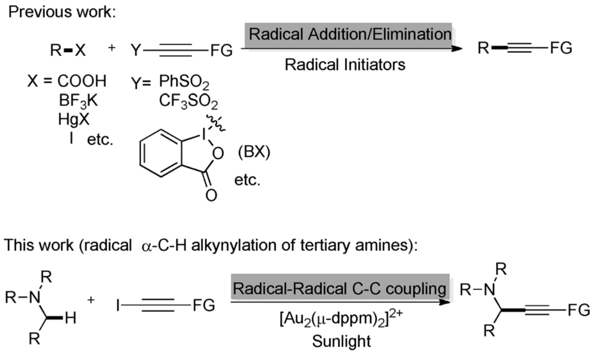
Abstract: *A new α-C(sp^3)–H alkynylation of unactivated tertiary aliphatic amines with 1-iodoalkynes as radical alkynylating reagents in the presence of $[Au_2(\mu\text{-dppm})_2]^{2+}$ in sunlight provides propargylic amines. Based on mechanistic studies, a C–C coupling of an α-aminoalkyl radical and an alkynyl radical is proposed for the C(sp^3)–C(sp) bond formation. The mild, convenient, efficient, and highly selective C(sp^3)–H alkynylation reaction shows excellent regioselectivity and good functional-group compatibility. A scale-up to gram quantities is possible with sunlight used as a clean and sustainable energy source.*

C-Alkynylation reactions are important for organic synthesis, as alkyne moieties are not only versatile building blocks, but also important structural motives in organic materials and biologically active molecules.[1] Sonogashira coupling is a very powerful method for the formation of C(sp^2)–C(sp) bonds,[2] but the chemospecific construction of C(sp^3)–C(sp) bonds still remains a challenge, which was addressed during the past decade by the development of nucleophilic[3] and electrophilic[4] C(sp^3)–C(sp) bond formation, but much less by radical alkynylation of C(sp^3) centers. The pioneering contributions in this field used alkylmercury halides,[5] alkyl halides,[6] and even C–H bonds[7] as C(sp^3) radical precursors and combined them with alkynyl sulfones and radical initiators under UV conditions. In 2006, a radical deboronative alkynylation of *B*-alkylcatecholboranes with alkynyl sulfones using di-*tert*-butylhyponitrite as a radical initiator was reported.[8] Recently, the silver-catalyzed oxidative decarboxylative alkynylation of aliphatic carboxylic acids[9] and visible-light-induced deboronative alkynylation of alkyl trifluoroborates were achieved by using ethynylbenziodoxolones (EBX) as a radical alkynylating reagent.[10] The broad substrate scope is a further advantage of the radical C(sp^3)–C(sp) coupling methods—but most of these methods rely on the use of hazardous radical initiators or external oxidants (organostannanes, iodine(III) reagents, AIBN, $K_2S_2O_8$ etc.) and require prefunctionalization of the substrates or special photoreactors. In a continuation of our work on gold-catalyzed C–H activation,[12,13] we now present the first example of a gold-catalyzed redox-neutral radical α-C(sp^3)–H alkynylation of unactivated tertiary aliphatic amines that is based on photoredox catalysis with sunlight[11] and thus obviates prefunctionalization of the substrates (Scheme 1). The products are formed by the coupling of an α-aminoalkyl radical[14] and an alkynyl radical[15] instead of the previously reported radical addition/elimination pathways.



Scheme 1. Different strategies for radical C(sp^3)–C(sp) coupling reactions.

Organic halides and tertiary amines were usually used in photoredox reactions as the oxidative and reductive quencher, respectively, undergoing reductive dehalogenation reactions.[16] As the radical C(sp^3)–H alkynylation of tertiary amines was unprecedented,[17] we studied the feasibility of radical C(sp^3)–C(sp) coupling reactions of α-aminoalkyl radicals and alkynyl radicals generated from tertiary amines and electrophilic alkynes under photoredox conditions. The bench-stable and easily available $[Au_2(\mu\text{-dppm})_2]^{2+}$ (dppm = bis(diphenylphosphanyl)methane) is a promising photosensitizer,[18] which was recently applied by Barriault and coworkers in elegant photoredox reactions with unactivated halogen-substituted starting materials.[16c] As a consequence, we started to investigate the reaction of *N,N*-diisopropylmethylamine (**2a**) with various electrophilic alkynes **3a–c** in sunlight and using $[Au_2(\mu\text{-dppm})_2]Cl_2$ **1a** as a photocatalyst (Table 1, entries 1–3). Trace amounts of the desired redox-neutral coupling product **4aa** were obtained with **3a** or **3b** as the alkynylating reagents (entries 1 and 2). A 53% yield of **4aa** (the by-products **5a** and diyne **6a** were observed by GC-MS analysis) was obtained with **3c**[19] (entry 3). The use of K_2HPO_4 as an additional base delivered slightly higher yields (51% versus 40% without K_2HPO_4; entry 4). Of the gold

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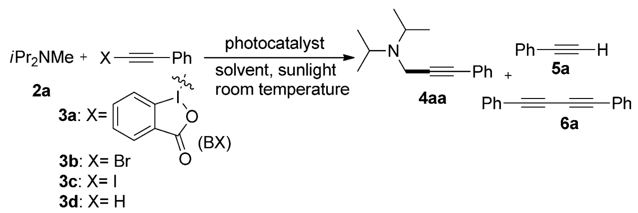
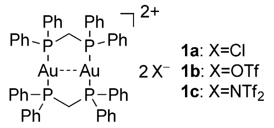
Table 1: Optimization of the reaction conditions.[a]



Entry	Photocatalyst (mol %)	X	Base (2.0 equiv)	Equiv **2a**	Time [h]	Yield of **4aa** [%][b]
1	**1a** (3)	BX	K_2HPO_4	3	6	trace
2	**1a** (3)	Br	K_2HPO_4	3	6	trace
3	**1a** (3)	I	K_2HPO_4	3	6	53
4	**1a** (3)	I	–	3	6	40
5	**1b** (3)	I	K_2HPO_4	3	6	62
6	**1c** (3)	I	K_2HPO_4	3	6	60
7	***1b** (3)*	*I*	–	*5*	*1.5*	*81*
8	***1b** (1)*	*I*	–	*5*	*1.5*	*81*
9	$[Ru(bpy)_3]Cl_2$ (1)	I	–	5	6	62
10	$[Ir(ppy)_3]$ (1)	I	–	5	1.5	76
11[c]	**1b** (1)	I	–	5	1.5	trace
12[d]	**1b** (1)	I	–	5	2	78
13[e]	**1b** (1)	I	–	5	1.5	trace
14[f]	**1b** (1)	I	–	5	1.5	trace
15	–	I	–	5	1.5	28
16[g]	–	H	–	5	6	0

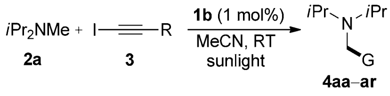
[a] Reaction conditions: **3a–d** (0.1 mmol), **2a** (3–5 equiv), MeCN (0.25 mL), sunlight. [b] Yield of isolated product. [c] UV light ($\lambda = 254$ nm). [d] UVA light ($\lambda = 315$–400 nm). [e] 35 W fluorescent bulb. [f] In the dark. [g] 10 mol% I_2 and 3.0 equiv TBHP at room temperature. bpy = 2,2′-bipyridine, ppy = 2-phenylpyridine, TBHP = *tert*-butyl hydroperoxide.

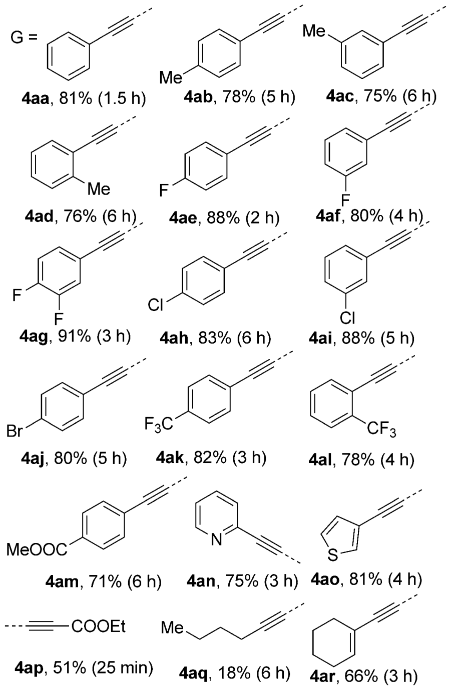


photocatalysts screened, **1b** showed the highest catalytic activity (entries 3, 5, and 6). By adding 2.0 equiv *N,N*-diisopropylmethylamine, K_2HPO_4 could not only be substituted as an external base, but the yield of the reaction improved to 81% of **4aa** in 1.5 h (entry 7). Even the loading of photocatalyst **1b** could be reduced to 1 mol% (entry 8). MeCN was the best solvent.[20] The use of $[Ru(bpy)_3]Cl_2$ or *fac*-$[Ir(ppy)_3]$ instead of the gold complex **1b** resulted in a lower yield (entries 9 and 10). Besides sunlight, UVA light ($\lambda = 315$–400 nm) could also efficiently promote the reaction (entry 12). However, irradiation of the reaction mixture with either UV light ($\lambda = 254$ nm) or a fluorescent bulb delivered only traces of the desired product (entries 11 and 13). The control experiments demonstrated that both light and photocatalyst were necessary for the formation of **4aa** (entries 14 and 15). **3d** and the tertiary amine **2a** did not provide **4aa** with the very efficient I_2-TBHP oxidative catalytic system (entry 16).[21]

A variety of substituted 1-iodoalkynes were examined under the optimized reaction conditions (Table 2). Both donor and acceptor substituents in the *o*-, *m*-, or *p*-position of the phenylacetylene derivatives gave the corresponding coupling products **4aa–am** selectively in 71–91% yield. The heteroaromatic **4an** and **4ao** were isolated in yields of 75% and 81%. 3-Iodopropiolate furnished **4ap** in 51% yield. When an aliphatic group was present, **4aq** was obtained in only 18% yield; hex-1-yne was the main product—which suggests that a hydrogen abstraction seems to be favored over a radical–radical cross-coupling for alkylalkynyl radicals. 1-(Iodoethynyl)cyclohex-1-ene furnished the desired **4ar** in 66% yield.

Table 2: Reaction scope with regard to the 1-iodoalkynes.[a]

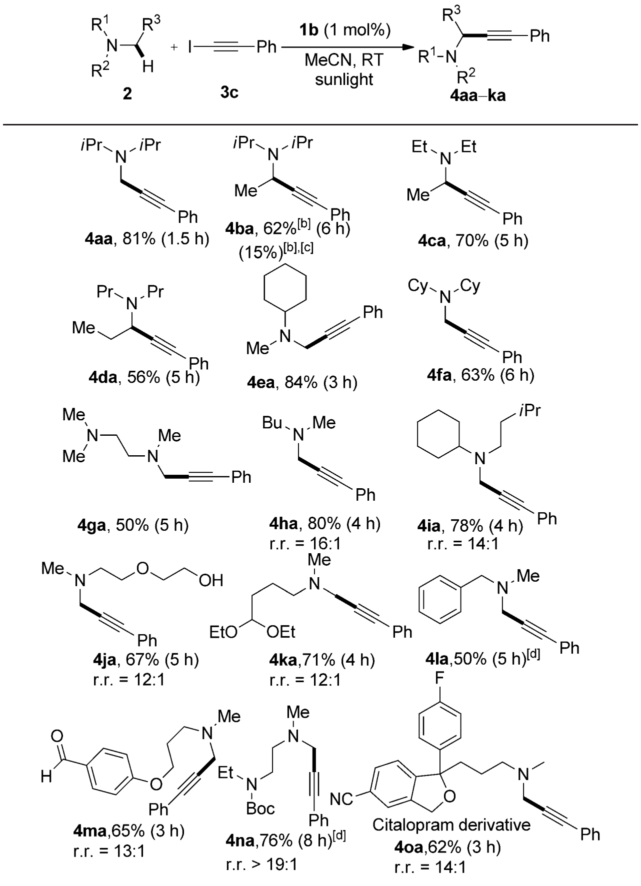




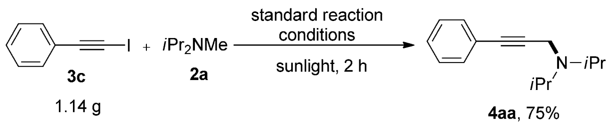
[a] Reaction conditions: $[Au_2(\mu\text{-dppm})_2](OTf)_2$ (1 mol%), 1-iodoalkyne (0.2 mmol), **2a** (5.0 equiv), MeCN (0.5 mL), room temperature, sunlight.

While *N,N*-dialkylanilines[3d] and *N*-aryltetrahydroisoquinolines[3p] are more reactive, mild alkynylations of α-C(sp^3)–H bonds of tertiary aliphatic amines are relatively rare.[22] Our new procedure gave moderate to good yields of **4aa–4oa** (Table 3). In the absence of **1b**, only a small amount of **4ba** is obtained, thus emphasizing the necessity of a photocatalyst. For the unsymmetrical tertiary amines bearing various functional groups (-OH, ether, acetal, -CHO, *N*-Boc, etc.) from Table 3, exclusively **4aa**, **4ba** and **4ea–4ga**, or mainly **4ha–4oa** were obtained, which indicated a reaction at the methyl group adjacent to the nitrogen atom instead of the methylene or methine group. The redox-neutral radical alkynylation procedure was applied in the selective C(sp^3)–H alkynylation of the antidepressant drug citalopram (**4oa**). *N*-Arylamines failed to undergo the radical alkynylation reaction.[20] A gram-scale conversion gave a 75% yield of **4aa** (Scheme 2).

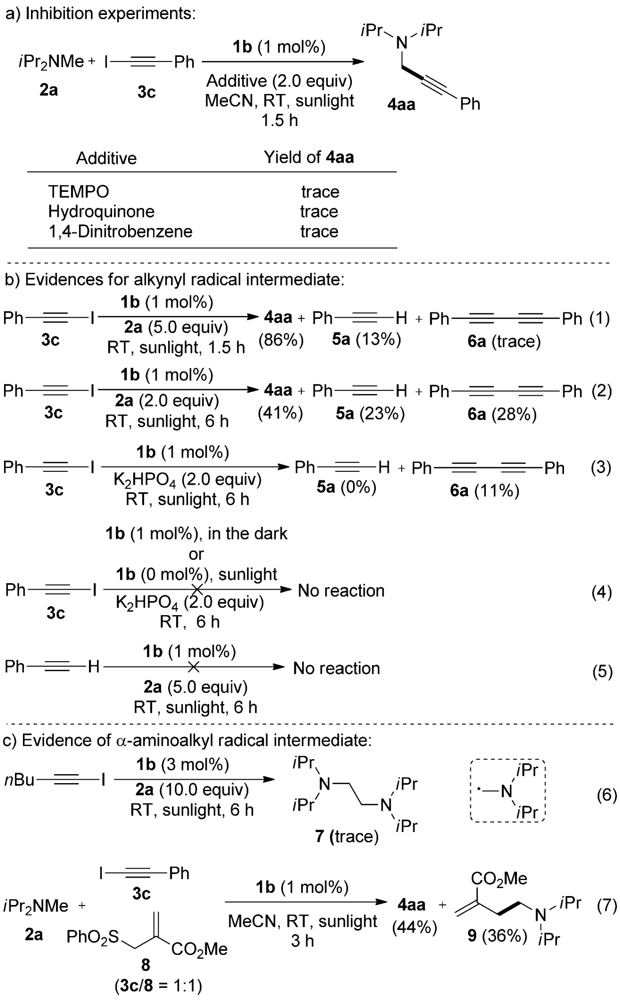
Table 3: Reaction scope with regard to the tertiary aliphatic amines.[a]



[a] Reaction conditions: $[Au_2(\mu\text{-dppm})_2](OTf)_2$ (1 mol%), **3c** (0.2 mmol), tertiary amines (5.0 equiv), MeCN (0.5 mL), room temperature, sunlight. The regioisomeric ratio (r.r.) was determined by ^1H NMR. Yields of the isolated product. [b] 1.2 equiv 4-dimethylaminopyridine (DMAP) was added. [c] Without photocatalyst **1b**. [d] UVA light was used instead of sunlight.



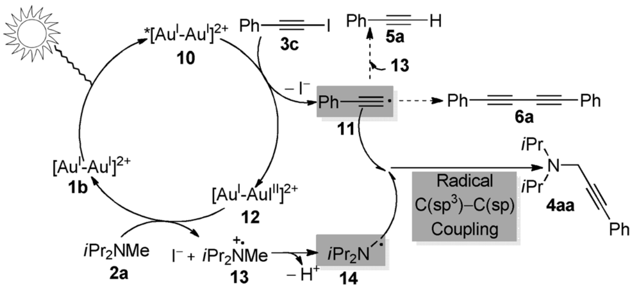
Scheme 2. Gram-scale experiment.



Additive	Yield of **4aa**
TEMPO	trace
Hydroquinone	trace
1,4-Dinitrobenzene	trace

Scheme 3. Mechanistic experiments.

The mechanistic experiments are shown in Scheme 3. The addition of the radical inhibitors TEMPO or hydroquinone or the electron-transfer scavenger 1,4-dinitrobenzene significantly inhibits the transformation. This finding implies a radical pathway that proceeds through a single-electron-transfer (SET) process should be involved. Under the optimized reaction conditions, besides the desired **4aa**, **5a** (13%) and diyne **6a** (trace) were also detected as by-products by GC-MS analysis [Eq. (1)]. Lowering the concentration of the tertiary amine slowed down the α-deprotonation of the amino-centered radical, thus favoring the competing homodimerization and hydrogen abstraction. Indeed, **5a** and **6a** were formed in 23% and 28% yield, respectively, with only two equivalents of amine **2a** [Eq. (2)]. Thus, an excess of tertiary amines/base is essential for the reaction, as the generation of the α-aminoalkyl radical is favored under basic conditions.[14g] With K_2HPO_4 instead of the tertiary amine, **6a** was produced in 11% yield (substoichiometric with respect to the catalyst), despite a low conversion of **3c** [Eq. (3)]. The conversion of **3c** failed in the absence of a photocatalyst or in the dark [Eq. (4)]. No reaction occurred if phenylacetylene was employed instead of the iodoalkyne [Eq. (5)]. Electron-rich furan was used to trap the alkynyl radical,[15a,b] and the expected $C(sp^2)$–$C(sp)$ coupling product was observed (see the Supporting Information for details). These control experiments indicate the generation of an alkynyl radical from 1-iodoalkyne in the presence of photocatalyst **1b** in sunlight. The dimerization of **2a** to **7**[14c] was observed by GC-MS analysis during optimization of the reaction with aliphatic 1-iodohex-1-yne [Eq. (6)].[20] The nucleophilicity of an α-aminoalkyl radical[14a–d] results in the addition of Michael acceptor **8** delivering the expected addition product **9** [Eq. (7)]. These results strongly indicate that an α-aminoalkyl radical is another important intermediate. The model reaction (1) needed continuous irradiation with sunlight; no conversion of (iodoethynyl)benzene **3c** was detected in the dark.[20]



Scheme 4. Possible reaction mechanism.

A possible mechanism is shown in Scheme 4 based on the visible-light-mediated α-C(sp^3)–H arylation of tertiary amines with 1,4-dicyanobenzene[14g] and on our results. First the excited-state form of dinuclear gold complex **10** is generated by irradiation with sunlight. Owing to its powerful reducing ability [$E^o(\mathrm{Au_2}^{3+}/{*}\mathrm{Au_2}^{2+}) = -1.5$ to -1.7 V versus SSCE],[23] it should be possible to donate an electron to **3c**,[24] which then fragments, thereby forming the alkynyl radical species **11**.[15a,b,20] Then, the resulting dimeric gold complex **12** would be reduced through a SET process from tertiary amines **2a** to give amine radical cation **13**, which can afford α-aminoalkyl radical **14** by a deprotonation process. Finally, the radical–radical coupling of the α-aminoalkyl radical **14** and alkynyl radical **11** affords the desired product **4aa**.[25] Alternatively, the abstraction of a hydrogen atom by the alkynyl radical **11** from the α-position of the amino-centered radical **13** or the homocoupling of two alkynyl radicals **11** can generate by-products **5a** and **6a**. The selectivity for the preferred cross-recombination of two different radicals can easily be explained by the "persistent" radical effect.[26,27]

In summary, a highly efficient gold-catalyzed radical C(sp^3)–H alkynylation of tertiary aliphatic amines using readily available 1-iodoalkynes as a radical alkynylating reagent in the presence of $[\mathrm{Au_2}(\mu\text{-dppm})_2]^{2+}$ under mild reaction conditions was developed. Mechanistic studies indicate a coupling of an α-aminoalkyl radical and an alkynyl radical.

Keywords: C–H activation · gold catalysis · photoredox catalysis · radical C–C coupling · sunlight

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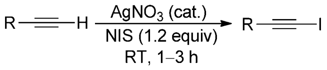
[17] The oxidative α-C(sp^3)–H nucleophilic alkynylation of tertiary amines were developed in the last decade, but sacrificial external oxidants were usually required.

[18] The dinuclear gold complex absorbs light at about 300 nm to form a high-energy and long-lived photoexcited state with a quantum yield of 0.23, see D. Li, C.-M. Che, H.-L. Kwong, V. W.-W. Yam, *J. Chem. Soc. Dalton Trans.* **1992**, 3325 – 3329.

[19] The 1-iodoalkynes can be easily prepared in high yields from various commercially available alkynes, see



$$\mathrm{R{-}{\equiv}{-}H} \xrightarrow[\text{NIS (1.2 equiv)}\atop \text{RT, 1–3 h}]{\text{AgNO}_3\text{ (cat.)}} \mathrm{R{-}{\equiv}{-}I}$$

[20] See the Supporting Information.

[21] a) Z.-J. Cai, S.-Y. Wang, S.-J. Ji, *Org. Lett.* **2013**, *15*, 5226 – 5229; b) T. Nobuta, N. Tada, A. Fujiya, A. Kariya, T. Miura, A. Itoh, *Org. Lett.* **2013**, *15*, 574 – 577; c) F. Xiao, H. Chen, H. Xie, S. Chen, L. Yang, G.-J. Deng, *Org. Lett.* **2014**, *16*, 50 – 53.

[22] A dehydorogenative nucleophilic alkynylation of branched tertiary aliphatic amines catalyzed by a Shvo complex has been achieved in moderate yields, but the harsh reaction reactions (150 °C, 24 h) and poor functional-group compatibility seriously limited the utility of this method, see Ref. [3i].

[23] C.-M. Che, H.-L. Kwong, K.-C. Poon, V. W.-W. Yam, *J. Chem. Soc. Dalton Trans.* **1990**, 3215 – 3219.

[24] The cyclic voltammogram of (iodoethynyl)benzene (**3c**) exhibited an irreversible reduction with $E_{1/2} = -1.29$ V versus Fc in MeCN.[20]

[25] The SOMO energy of α-aminoalkyl radical **14** and alkynyl radical **11** were calculated as −7.12 eV and −10.07 eV, respectively.

[26] Although initially discovered with "persistent" radicals, this kinetic phenomenon also applies to short-lived radicals. It is only necessary that the lifetimes of the two radicals involved show a significant difference (which is the case, Ref. [27]): a) A. Studer, *Chem. Eur. J.* **2001**, *7*, 1159 – 1164; b) H. Fischer, *Chem. Rev.* **2001**, *101*, 3581 – 3610.

[27] The lifetime of an α-aminoalkyl radical (Et$_2$NCHMe) and phenylethynyl radical are about 700 ns and 2 ns, respectively; see a) J. C. Scaiano, *J. Phys. Chem.* **1981**, *85*, 2851 – 2855; b) X. Gu, Y. Guo, F. Zhang, A. M. Mebel, R. I. Kaiser, *Chem. Phys. Lett.* **2007**, *436*, 7 – 14. Thus, α-aminoalkyl radical **14** is more long-lived and the initially preferred dimerization of the alkynyl radical is in full accord with the mechanistic model.

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Communications

Gold Photocatalysis

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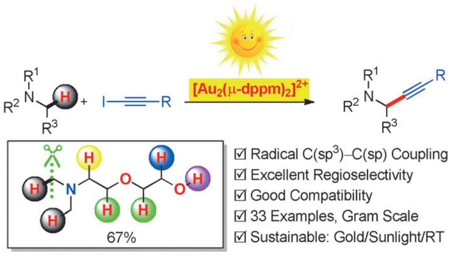
A Highly Efficient Gold-Catalyzed Photoredox α-C(sp^3)—H Alkynylation of Tertiary Aliphatic Amines with Sunlight



Golden sunshine: With 1-iodoalkynes as radical alkynylation reagents, unactivated tertiary aliphatic amines react in the presence of $[Au_2(\mu\text{-dppm})_2]^{2+}$ (dppm = bis(diphenylphosphanyl)methane) in sunlight to afford propargylamines. A C—C coupling of an α-aminoalkyl radical and an alkynyl radical was proposed as the mechanism.