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Transition-Metal-Free Synthesis of Ynones via Decarboxylative Alkynylation of α-Keto Acids under Mild Conditions

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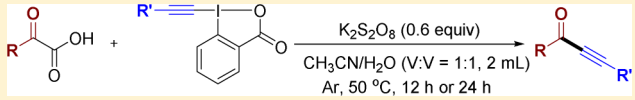
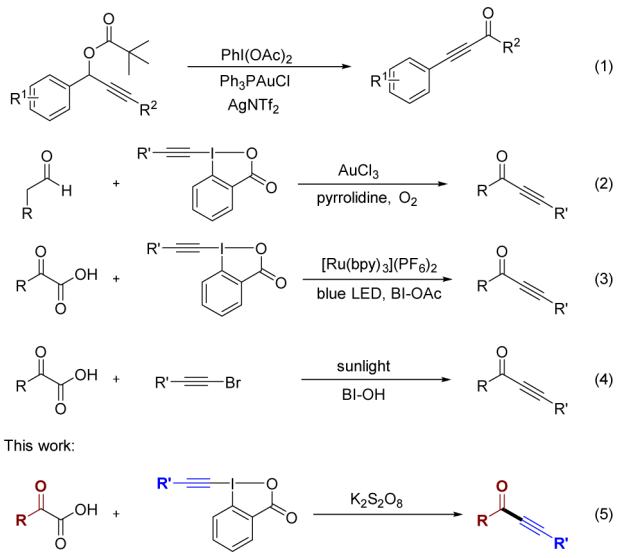
Supporting Information

ABSTRACT: A transition-metal-free synthetic method of various ynones via decarboxylative alkynylation of α-keto acids is described. The reaction is carried out under mild conditions and exhibits remarkable tolerance of functional groups. The mechanism of a radical process is proposed in the reaction.



Ynones are highly valuable and amusing compounds that are widely employed as fascinating precursors of heterocyclic compounds in organic synthesis.[1] Typical approaches for the synthesis of ynones involve Sonogashira couplings reactions of terminal alkynes with acyl chlorides utilizing Pd/Cu as catalysts[2] or carbonylative couplings reactions between terminal alkynes and aryl or alkyl halides,[3] aryl triflates,[4] aryl amines[5] with CO insertion. Recently, other methods have also emerged as new strategies for the synthesis of ynones. For example, Hashmi et al. reported a gold-catalyzed dehydrogenative Meyer−Schuster-like rearrangement to produce ynones (Scheme 1, eq 1).[6] Huang et al. reported a general synthesis of ynones from aldehydes via oxidative C−C bond cleavage under aerobic conditions (Scheme 1, eq 2).[7] More recently, direct alkynylation of aldehydes to synthesize ynones via nucleophilic addition/Oppenauer oxidation and C−H activation has also been reported.[8] When our study work is accomplished, Chen et al. reported that dual hypervalent iodine(III) reagents and photoredox catalysis enabled decarboxylative ynonylation (Scheme 1, eq 3).[9] Almost meanwhile, Wang et al. reported a sunlight-driven decarboxylative alkynylation of α-keto acids with bromoacetylenes by hypervalent iodine reagent catalysis (Scheme 1, eq 4).[10] Although considerable efforts and significant progress have been made to prepare ynones, most synthetic methods have some shortcomings, such as the usage of toxic CO, harsh reaction conditions, limited substrate scope, and expensive catalysts. Therefore, further development of preparing ynones is of great demand to enable mild reaction conditions as well as available raw materials. In order to achieve this goal, it is greatly important to explore new approaches for the efficient synthesis of ynones.

Scheme 1. Synthetic methods of Ynones



Transition-metal-catalyzed decarboxylative cross-coupling reactions of carboxylic acids represent one of most important methods for the construction of C−C and C-heteroatom bonds.[11−16] These reactions do not require expensive organometallic reagents and produce nontoxic CO_2. In 2002, Myers first reported a palladium-catalyzed Heck-type olefination of arene carboxylates,[11] and subsequently considerable studies on the decarboxylative coupling reactions were conducted by Forgione,[12] Goossen,[13] Liu[14] and others.[15,16] These reactions reveal that decarboxylative couplings provide an alternative method for catalytic synthesis purpose. Although many significant contributions are achieved in this field, decarboxylation of α-keto acids receives relatively less attention. Decarboxylation of α-keto acids can afford acyl donors which are crucial for the preparation of carbonyl compounds. We are interested in developing new strategies to prepare ynones from α-keto acids under mild conditions. In particular, the reactions

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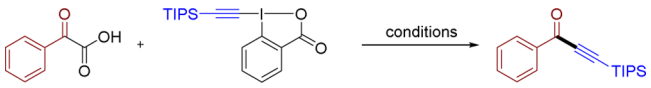
that are conducted under transition-metal-free condition are highly desirable to enable potential application because of the significance of ynones. Herein, we report a general and efficient synthesis of ynones via $K_2S_2O_8$-promoted decarboxylative alkynylation of α-keto acids under mild conditions (Scheme 1 eq 5).[17]

We initiated optimization of the reaction conditions by selecting benzoylformic acid (**1a**) with 1-[(triisopropylsilyl)-ethynyl]-1,2-benziodoxol-3(1H)-one (**2a**) as model substrates (Table 1). With $AgNO_3$ (20 mol %) as a catalyst and $K_2S_2O_8$ (3 equiv) as an oxidant, it was found that CH_3CN was used as a solvent to give the desired product **3a** in 12% yield at 50 °C under an argon atmosphere (entry 1). Next, other solvents such as H_2O, acetone/H_2O (V:V = 1:1), CH_2Cl_2/H_2O (V:V = 1:1), and CH_3CN/H_2O (V:V = 1:1) were examined (entries 2−5). It was found that CH_3CN/H_2O was the optimal medium for the transformation, which brought about an obviously increasing yield of 88%. Then the use of other silver salts such as $AgBF_4$, Ag_2CO_3, and Ag_2SO_4 also showed similar yields (entries 6−8). Furthermore, the use of $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$ as oxidants led to the reduction of yield (entries 9−10). Reducing or increasing the reaction temperature did not improve the yield of **3a** (entries 11−13). The control experiment proved that $K_2S_2O_8$ was essential, and the reaction still could be conducted to give the desired product **3a** in high yield in the absence of $AgNO_3$ (entries 14−15). Finally, by changing the amount of $K_2S_2O_8$, the yield of **3a** was further improved to 92% (entries 16−19).

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	catalyst	oxidant (equiv)	solvent	temp (°C)	yield (%)[b]
1	$AgNO_3$	$K_2S_2O_8$ (3)	CH_3CN	50	12
2	$AgNO_3$	$K_2S_2O_8$ (3)	H_2O	50	trace
3	$AgNO_3$	$K_2S_2O_8$ (3)	acetone/H_2O	50	64
4	$AgNO_3$	$K_2S_2O_8$ (3)	CH_2Cl_2/H_2O	50	trace
5	$AgNO_3$	$K_2S_2O_8$ (3)	CH_3CN/H_2O	50	88
6	$AgBF_4$	$K_2S_2O_8$ (3)	CH_3CN/H_2O	50	87
7	Ag_2CO_3	$K_2S_2O_8$ (3)	CH_3CN/H_2O	50	85
8	Ag_2SO_4	$K_2S_2O_8$ (3)	CH_3CN/H_2O	50	84
9	$AgNO_3$	$Na_2S_2O_8$ (3)	CH_3CN/H_2O	50	79
10	$AgNO_3$	$(NH_4)_2S_2O_8$ (3)	CH_3CN/H_2O	50	77
11	$AgNO_3$	$K_2S_2O_8$ (3)	CH_3CN/H_2O	rt(24)	28
12	$AgNO_3$	$K_2S_2O_8$ (3)	CH_3CN/H_2O	40	70
13	$AgNO_3$	$K_2S_2O_8$ (3)	CH_3CN/H_2O	60	82
14	$AgNO_3$	–	CH_3CN/H_2O	50	–
15	–	$K_2S_2O_8$ (3)	CH_3CN/H_2O	50	89
16	–	$K_2S_2O_8$ (0.2)	CH_3CN/H_2O	50	58
17	–	$K_2S_2O_8$ (0.4)	CH_3CN/H_2O	50	87
18	–	**$K_2S_2O_8$ (0.6)**	**CH_3CN/H_2O**	**50**	**92**
19	–	$K_2S_2O_8$ (0.8)	CH_3CN/H_2O	50	91

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), $K_2S_2O_8$ (1 equiv = 0.2 mmol), silver salt catalyst (20 mol %), solvent (2 mL), 12 h under an argon atmosphere. [b]Isolated yields based on **1a**. TIPS = triisopropylsilyl

With the optimal conditions in hand, we explored the scope of α-keto acids to examine the compatibility of the present reaction (Scheme 2). It was found that various α-keto acids could smoothly perform decarboxylative alkynylation to generate the desired ynones products in modest to high yields. Both electron-donating substituents such as methy (**3b**, **3k**, **3p**, **3u**), ethyl (**3e**), and methoxyl (**3c**, **3l**, **3q**, **3v**) and electron-withdrawing groups such as trifluoromethyl (**3j**) could be well tolerated in current reaction system. It is interesting to note that the reaction could tolerate an unprotected OH group (**3o**), and the corresponding product could further perform cyclization to led to the formation of chromone.[8b] Additionally, the halide groups, such as F (**3f**, **3m**, **3r**), Cl (**3g**, **3n**, **3s**), Br (**3h**, **3t**), and I (**3i**) were also well compatible with the reaction, enabling possibly further functionalization at these positions. The α-keto acids bearing ortho- and meta-substituents could work well to give the corresponding ynones of 29−87% yields (**3k-t**). The reactions of disubstituted α-keto acids gave the desired products in 68−82% yields under the above conditions (**3u−y**). Furthermore, the reaction could also tolerate heterocyclic α-keto acids such as thiophene, benzo[*b*]thiophene and indole, giving the desired products in low yields of 31−36% (**3z**, **3aa−ab**). However, no product was detected when 2-(furan-2-yl)-2-oxoacetic acid was employed as a heterocyclic substrate (**3ac**). On the other hand, when aliphatic α-keto acids were employed for the transformation, the corresponding products were obtained in 48−72% yields (**3ad−ag**).

Next, we further explored the scope of various hypervalent iodine alkynyl reagents (Scheme 3). Alkyne bearing alkyl-substituent such as linear hexyl group could well react with benzoylformic acid **1a** to give the desired products in 52% yield (**4a**). Substrates with bulky silyl groups including $SiEt_3$, $SiMe_2{}^tBu$, and Si^tBuPh_2 groups could be also well applicable for the reaction (**4b−d**). Furthermore, various aryl-substituent alkynes, bearing electron-rich methyl, methoxyl, phenyl, and diphenyl and electron-deficient chloride, nitrile, ketone, and aldehyde could successfully convert to the corresponding ynones in 25−81% yields (**4e−l**).

To elucidate the plausible mechanism of reaction, the following experiment was conducted (Scheme 4). Under the optimal conditions, when a radical-trapping reagent TEMPO (2,2,6,6-tetramethyl-1-oxylpiperidine) was added to the reaction, no product was detected. The result suggested that the reaction may proceed by a radical pathway.

According to the above experimental result and the previous studies,[18] we proposed a possible reaction mechanism shown in Scheme 5. First, peroxydisulfate ion, $S_2O_8{}^{2-}$, performs homolysis to give sulfate ion radical, which reacts with α-keto acids **1** to produce carboxyl radicals. Carboxyl radical undergoes fast decarboxylation to generate acyl radical and then attacks the triple bonds of hypervalent iodine alkynyl reagents **2** to achieve the radical intermediate **I**. Subsequently, **I** through β-elimination gives the desired products and benziodoxolonyl radical **II**. Finally, 2-iodobenzoic acid is afforded via reduction−protonation of benziodoxolonyl radical **II**.

In conclusion, we developed a new efficient reaction system for decarboxylative alkynylation of α-keto acids using $K_2S_2O_8$ as an oxidant. The present reaction can tolerate many important functional groups and be conducted under very mild conditions. Furthermore, the reaction provided a general and efficient method for the synthesis of ynones without transition-metal catalysts.

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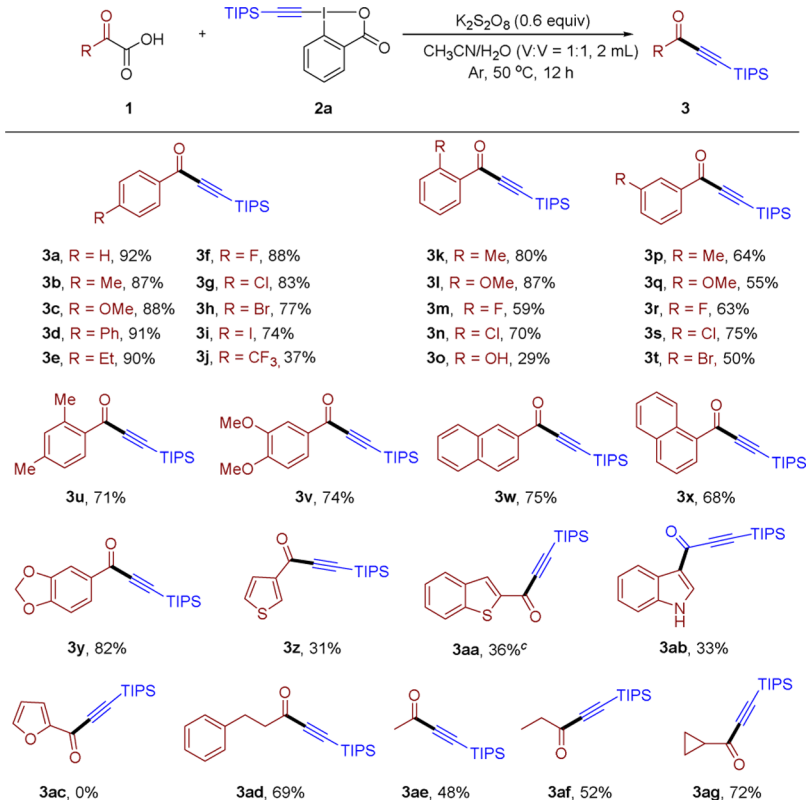
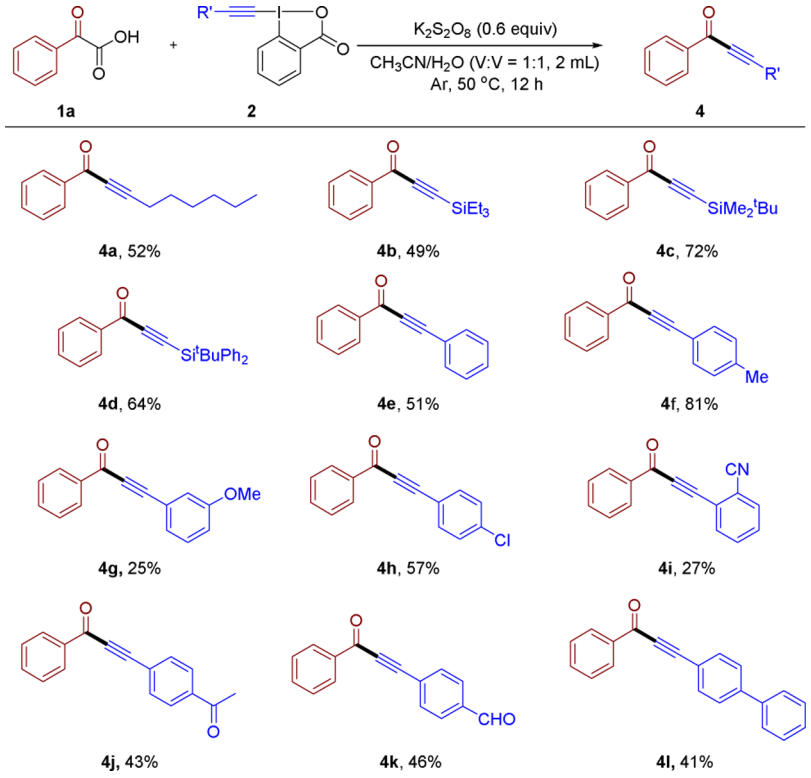
Scheme 2. Scope of α-Keto Acids[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), $K_2S_2O_8$ (0.12 mmol, 0.6 equiv), CH_3CN/H_2O (V:V = 1:1, 2 mL), 50 °C for 12 h under an argon atmosphere. [b]Isolated yields based on **1**. [c]The reaction was carried out for 24 h.

Scheme 3. Scope of Alkynyl Reagents[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), $K_2S_2O_8$ (0.12 mmol, 0.6 equiv), CH_3CN/H_2O (V:V = 1:1, 2 mL), 50 °C for 12 h under an argon atmosphere. [b]Isolated yields based on **1a**.

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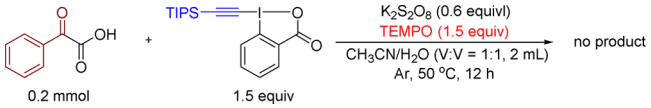
Scheme 4. Investigation of the Mechanism



EXPERIMENTAL SECTION

General Information and Materials. All the reactions were conducted in oven-dried Schlenk tubes under an argon atmosphere. All solvents were obtained from commercial suppliers and used without further purification. α-Keto acids were obtained from commercial suppliers or prepared according to the literature reported procedures.[19] Hypervalent iodine alkynyl reagents were prepared according to the literature reported procedure.[20] ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a 600 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift (δppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δppm), multiplicity, and coupling constant (Hz). Data for ^{19}F NMR are reported in chemical shift and multiplicity. High-resolution mass spectra were obtained by ESI on a TOF mass analyzer.

Typical Procedure for the Synthesis of Ynones via Decarboxylative Alkynylation of α-Keto Acids. A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with benzoylformic acid **1a** (0.2 mmol), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one **2a** (1.5 equiv), and $K_2S_2O_8$ (0.6 equiv). The tube was evacuated and backfilled with argon (this operation was repeated three times). CH_3CN (1 mL) and H_2O (1 mL) were added by syringe under a flow of argon. The tube was sealed, and the mixture was allowed to stir at 50 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature. Then the mixture was diluted with EtOAc and washed with water. The organic phase was separated, and the aqueous phase was extracted with EtOAc in three times. The combined organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed under vacuo. The residue was purified by column chromatography on silica gel to give the desired product **3a**.

Characterization Data for the Products. *1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-one* (**3a**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (52.8 mg, 92% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19−8.15 (m, 2H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 1.25−1.14 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 136.8, 134.0, 129.5, 128.6, 103.1, 98.0, 18.6, 11.1.

1-(p-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3b**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (52.3 mg, 87% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 1.23−1.05 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 145.1, 134.5, 129.7, 129.3, 103.2, 97.3, 21.8, 18.6, 11.1.

1-(4-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3c**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a light yellow oil (55.8 mg, 88% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 1.22−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 164.4, 131.9, 130.2, 113.8, 103.2, 96.8, 55.6, 18.6, 11.1.

1-([1,1′-Biphenyl]-4-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3d**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (66.1 mg, 91% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26−8.21 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 1.26−1.11 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1, 146.7, 139.7, 135.7, 130.1, 129.0, 128.4, 127.3, 127.2, 103.2, 98.0, 18.6, 11.2. HRMS calcd for $C_{24}H_{31}OSi$ $[M + H]^+$ 363.2144; found: 363.2140.

1-(4-Ethylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3e**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (56.7 mg, 90% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.23−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 151.3, 134.7, 129.8, 128.1, 103.2, 97.3, 29.1, 18.6, 15.1, 11.1. HRMS calcd for $C_{20}H_{31}OSi$ $[M + H]^+$ 315.2144; found: 315. 2142.

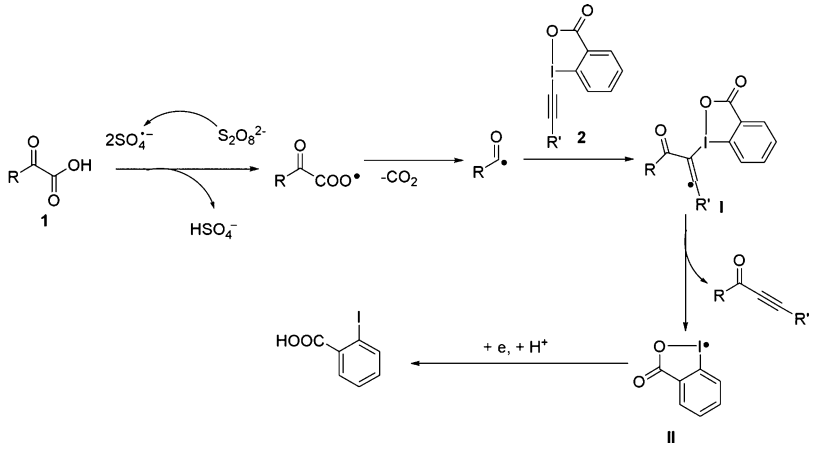
1-(4-Fluorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3f**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (53.6 mg, 88% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 5.7 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 1.25−1.01 (m, 21H).^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 166.4 (d, *J* = 256.5 Hz), 133.3 (d, *J* = 2.8 Hz), 132.2 (dd, *J* = 9.6, 3.3 Hz), 115.8 (d, *J* = 22.2 Hz), 102.7, 98.4, 18.6, 11.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ −103.27 − −103.39 (m).

1-(4-Chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3g**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (53.3 mg, 83% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 1.25−1.01 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 140.7, 135.2, 130.8, 129.0, 102.7, 98.8, 18.6, 11.1.

1-(4-Bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3h**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (56.3 mg, 77% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 1.25−1.01 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 135.6, 131.9, 130.9, 129.5, 102.6, 98.9, 18.6, 11.1.

1-(4-Iodophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3i**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (60.9 mg, 74% yield);

Scheme 5. Proposed Reaction Mechanism



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^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 4H), 1.21−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 138.0, 136.1, 130.7, 102.6, 102.5, 98.9, 18.6, 11.1.

1-(4-(Trifluoromethyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3j**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (26.2 mg, 37% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 1.25−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 139.2, 135.2 (d, J = 32.8 Hz), 129.8 (d, J = 2.4 Hz), 125.7 (q, J = 3.6 Hz), 123.5 (d, J = 272.8 Hz), 102.5, 99.9, 18.6, 11.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ −63.22 (s).

1-(o-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3k**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (48.1 mg, 80% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.23 (s, 1H), 2.63 (s, 3H), 1.22−1.05 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.2, 140.6, 135.4, 133.4, 132.9, 132.1, 125.8, 104.5, 96.3, 22.0, 18.6, 11.1.

1-(2-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3l**).[21] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a colorless oil (55.1 mg, 87% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.02−6.95 (m, 2H), 3.89 (s, 3H), 1.20−1.04 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 159.7, 134.8, 132.9, 126.7, 120.1, 112.0, 105.1, 96.0, 55.7, 18.5, 11.1.

1-(2-fluorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3m**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (35.9 mg, 59% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 10.8, 4.3 Hz, 1H), 7.55 (dd, J = 13.1, 7.2 Hz, 1H), 7.23 (d, J = 7.4 Hz, 1H), 7.14 (dd, J = 10.4, 8.8 Hz, 1H), 1.23−1.07 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 162.1 (d, J = 262.5 Hz), 135.5 (d, J = 9.2 Hz), 132.0, 125.5 (d, J = 7.8 Hz), 124.1 (d, J = 4.0 Hz), 117.1 (d, J = 21.8 Hz), 104.2, 98.2 (d, J = 3.0 Hz), 18.5, 11.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ −110.86 to −111.15 (m).

1-(2-Chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3n**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (44.9 mg, 70% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (t, J = 6.7 Hz, 1H), 7.45 (d, J = 4.0 Hz, 2H), 7.36 (dt, J = 8.3, 4.3 Hz, 1H), 1.21−1.07 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 135.5, 133.6, 133.3, 132.8, 131.5, 126.7, 104.0, 99.1, 18.5, 11.1.

1-(2-hydroxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3o**).[8b] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (17.6 mg, 29% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 6.96 (dd, J = 13.8, 7.8 Hz, 2H), 1.26−1.07 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.7, 162.9, 137.1, 133.0, 120.7, 119.4, 118.1, 101.6, 101.5, 18.6, 11.1.

1-(m-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3p**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (38.5 mg, 64% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00−7.96 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 2.41 (s, 3H), 1.24−1.09 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 138.4, 136.8, 134.8, 130.0, 128.5, 126.9, 103.2, 97.7, 21.2, 18.6, 11.1. HRMS calcd for $C_{19}H_{29}OSi$ $[M + H]^+$ 301.1988; found:301.1985.

1-(3-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3q**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (34.8 mg, 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 1H), 7.66 (s, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.15 (dd, J = 8.2, 2.5 Hz, 1H), 3.85 (s, 3H), 1.23−1.09 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 159.7, 138.1, 129.6, 122.6, 121.3, 112.7, 103.1, 97.8, 55.4, 18.6, 11.1.

1-(3-Fluorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3r**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (38.4 mg, 63% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.46 (td, J = 7.9, 5.6 Hz, 1H), 7.30 (td, J = 8.2, 2.4 Hz, 1H), 1.23−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1 (d, J = 2.6 Hz), 162.7 (d, J = 248.4 Hz), 138.8 (d, J = 6.6 Hz), 130.3 (d, J = 7.6 Hz), 125.4 (d, J = 2.9 Hz), 121.1 (d, J = 21.6 Hz), 115.9 (d, J = 22.8 Hz), 102.6, 99.0, 18.5, 11.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ −111.75 to −111.85 (m). HRMS calcd for $C_{18}H_{26}FOSi$ 305.1737; found: 305.1739.

1-(3-Chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3s**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (48.1 mg, 75% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.57 (dd, J = 7.9, 0.7 Hz, 1H), 7.42 (t, J = 7.9 Hz, 1H), 1.25−1.09 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 138.2, 134.9, 133.9, 129.9, 129.6, 127.5, 102.5, 99.3, 18.5, 11.1.

1-(3-bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3t**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a yellow oil (36.5 mg, 50% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 1.23−1.09 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 138.4, 136.8, 132.6, 130.2, 127.9, 122.8, 102.5, 99.5, 18.6, 11.1.

1-(2,4-Dimethylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3u**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (44.7 mg, 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 7.05 (s, 1H), 2.60 (s, 3H), 2.36 (s, 3H), 1.22−1.05 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 143.8, 140.8, 133.9, 132.94, 132.93, 126.5, 104.6, 95.5, 22.0, 21.5, 18.6, 11.1.

1-(3,4-Dimethoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3v**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:30) as a colorless oil (51.3 mg, 74% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.3, 1.7 Hz, 1H), 7.64 (d, J = 1.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 1.21−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 154.2, 148.9, 130.3, 125.2, 110.6, 110.2, 103.1, 96.8, 56.1, 56.0, 18.6, 11.1. HRMS calcd for $C_{20}H_{31}O_3Si$ $[M + H]^+$ 347.2042; found:347.2041.

1-(Naphthalen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3w**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate: petroleum ether =1:50) as a yellow oil (50.5 mg, 75% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.15 (dd, J = 8.6, 1.3 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 (t, J = 7.8 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 1.28−1.14 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 136.1, 134.4, 133.0, 132.4, 129.8, 129.0, 128.4, 127.9, 126.9, 123.8, 103.2, 97.9, 18.6, 11.2.

1-(Naphthalen-1-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3x**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a yellow oil (45.8 mg, 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (d, J = 8.7 Hz, 1H), 8.62 (d, J = 7.3 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.67−7.63 (m, 1H), 7.56 (td, J = 7.4, 4.1 Hz, 2H), 1.24−1.11 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.2, 135.0, 134.6, 133.8, 132.8, 130.7, 128.9, 128.5, 126.7, 126.0, 124.4, 104.6, 96.2, 18.6, 11.2.

1-(Benzo[d][1,3]dioxol-5-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3y**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a colorless oil (54.2 mg, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.1, 1.4 Hz, 1H), 7.56 (d, J = 1.3 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.06 (s, 2H), 1.25−1.03 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 152.8, 148.2, 132.0, 127.1, 108.3, 108.0, 103.0, 102.1, 97.1, 18.6, 11.1. HRMS calcd for $C_{19}H_{27}O_3Si$ $[M + H]^+$ 331.1729; found: 331.1728.

1-(Thiophen-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3z**).[8d] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a colorless oil (18.2 mg, 31% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28−8.25 (m, 1H), 7.61 (t, J = 4.5 Hz, 1H), 7.32 (dd, J = 4.9, 3.1 Hz, 1H), 1.21−1.08 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 143.0, 135.4, 126.77, 126.75, 103.6, 95.9, 18.6, 11.1.

1-(Benzo[b]thiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3aa**).[8d] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a yellow oil (24.7

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mg, 36% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 1.24−1.11 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 144.3, 143.1, 138.7, 132.6, 128.0, 126.4, 125.2, 123.1, 102.4, 97.6, 18.6, 11.1.

1-(1H-Indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3ab**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:5) as a light yellow solid (21.5 mg, 33% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.41−8.38 (m, 1H), 8.11 (d, J = 2.9 Hz, 1H), 7.48−7.45 (m, 1H), 7.29 (m, 2H), 1.18−1.07 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 136.8, 135.8, 125.0, 124.2, 123.1, 122.2, 119.8, 111.9, 104.2, 92.1, 18.6, 11.1. HRMS calcd for $C_{20}H_{28}NOSi$ $[M + H]^+$ 326.1940; found: 326.1943.

5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-one (**3ad**).[8d] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a colorless oil (43.4 mg, 69% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.3 Hz, 3H), 3.01 (t, J = 7.7 Hz, 2H), 2.90 (t, J = 7.7 Hz, 2H), 1.15−1.02 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.5, 140.2, 128.5, 128.3, 126.3, 104.0, 96.1, 47.2, 30.1, 18.5, 11.0.

4-(Triisopropylsilyl)but-3-yn-2-one (**3ae**).[17] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a colorless oil (21.5 mg, 48% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (d, J = 4.6 Hz, 3H), 1.14−1.03 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 184.2, 104.7, 95.2, 32.8, 18.4, 11.0.

1-(Triisopropylsilyl)pent-1-yn-3-one (**3af**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a colorless oil (24.8 mg, 52% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.58 (q, J = 7.4 Hz, 2H), 1.15 (dd, J = 9.8, 5.0 Hz, 3H), 1.14−1.03 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.3, 104.0, 95.5, 38.9, 18.5, 11.0, 8.2. HRMS calcd for $C_{14}H_{27}OSi$ $[M + H]^+$ 239.1831; found: 239.1829.

1-Cyclopropyl-3-(triisopropylsilyl)prop-2-yn-1-one (**3ag**).[8d] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a colorless oil (36.1 mg, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.02 (ddd, J = 12.6, 8.1, 4.6 Hz, 1H), 1.26 (td, J = 7.3, 3.5 Hz, 2H), 1.14−1.00 (m, 23H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.1, 101.9, 94.9, 24.6, 18.5, 11.0, 10.8.

1-Phenylnon-2-yn-1-one (**4a**).[22] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a light yellow oil (22.3 mg, 52% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.70−1.64 (m, 2H), 1.47 (dt, J = 14.7, 7.3 Hz, 2H), 1.35−1.30 (m, 4H), 0.93−0.86 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 136.9, 133.8, 129.5, 128.5, 96.9, 79.7, 31.2, 28.6, 27.8, 22.5, 19.2, 14.0.

1-Phenyl-3-(triethylsilyl)prop-2-yn-1-one (**4b**).[23] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (24.1 mg, 49% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 1.07 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 136.6, 134.1, 129.6, 128.6, 102.1, 98.8, 7.4, 4.0.

3-(tert-Butyldimethylsilyl)-1-phenylprop-2-yn-1-one (**4c**).[24] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a colorless oil (35.2 mg, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 1.02 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 136.6, 134.1, 129.6, 128.6, 101.6, 99.4, 26.1, 16.7, −5.1.

3-(tert-Butyldiphenylsilyl)-1-phenylprop-2-yn-1-one (**4d**). The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (47.2 mg, 64% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, J = 7.4 Hz, 2H), 7.83 (d, J = 6.8 Hz, 4H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.43 (dt, J = 22.6, 7.3 Hz, 6H), 1.19 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 136.7, 135.6, 134.3, 131.5, 130.1, 129.6, 128.7, 128.0, 104.4, 96.0, 27.1, 18.9. HRMS calcd for $C_{25}H_{25}OSi$ $[M + H]^+$ 369.1675; found:369.1673.

1,3-Diphenylprop-2-yn-1-one (**4e**).[24] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:100) as a light yellow oil (21.1 mg, 51% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (dt, J = 20.2, 7.6 Hz, 3H), 7.42 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 136.9, 134.1, 133.1, 130.8, 129.6, 128.7, 128.6, 120.1, 93.1, 86.9.

1-Phenyl-3-(p-tolyl)prop-2-yn-1-one (**4f**).[10] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a white solid (35.7 mg, 81% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 141.5, 137.0, 134.0, 133.1, 129.53, 129.47, 128.6, 117.0, 93.8, 86.8, 21.8.

3-(3-Methoxyphenyl)-1-phenylprop-2-yn-1-one (**4g**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a yellow oil (11.8 mg, 25% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.35−7.26 (m, 2H), 7.19 (s, 1H), 7.05−7.00 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 159.4, 136.8, 134.1, 129.8, 129.6, 128.6, 125.6, 121.0, 117.56, 117.55, 93.0, 86.5, 55.4.

3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-one (**4h**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a light yellow solid (27.4 mg, 57% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 2H), 7.62 (dd, J = 17.5, 7.9 Hz, 3H), 7.51 (t, J = 7.7 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 137.2, 136.7, 134.24, 134.22, 129.6, 129.2, 128.7, 118.6, 91.6, 87.6.

2-(3-Oxo-3-phenylprop-1-yn-1-yl)benzonitrile (**4i**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:20) as a white solid (12.5 mg, 27% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.69−7.62 (m, 2H), 7.59 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 136.3, 134.6, 134.4, 133.0, 132.7, 130.8, 129.9, 128.8, 124.1, 117.1, 116.3, 91.2, 86.9.

3-(4-Acetylphenyl)-1-phenylprop-2-yn-1-one (**4j**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:20) as a light yellow solid (21.4 mg, 43% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 7.3 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 177.7, 138.0, 136.6, 134.4, 133.1, 129.6, 128.7, 128.4, 124.7, 91.1, 88.7, 26.7.

4-(3-Oxo-3-phenylprop-1-yn-1-yl)benzaldehyde (**4k**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:20) as a light yellow solid (21.6 mg, 46% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.20 (d, J = 7.5 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.1, 177.6, 137.1, 136.5, 134.5, 133.4, 129.6, 128.7, 126.1, 90.7, 89.1.

3-([1,1′-Biphenyl]-4-yl)-1-phenylprop-2-yn-1-one (**4l**).[9] The product was isolated by column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) as a light yellow solid (23.2 mg, 41% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.67−7.60 (m, 5H), 7.53 (t, J = 7.7 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 143.6, 139.8, 136.9, 134.1, 133.6, 129.6, 129.0, 128.6, 128.2, 127.3, 127.1, 118.8, 93.2, 87.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01387.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Van den Hoven, B. G.; Ali, B. E.; Alper, H. *J. Org. Chem.* **2000**, *65*, 4131. (b) Jeevanandam, A.; Narkunan, K.; Ling, Y.-C. *J. Org. Chem.* **2001**, *66*, 6014. (c) Xiong, X.; Bagley, M. C.; Chapaneri, K. *Tetrahedron Lett.* **2004**, *45*, 6121. (d) Liang, J. T.; Mani, N. S.; Jones, T. K. *J. Org. Chem.* **2007**, *72*, 8243. (e) Kirkham, J. D.; Edeson, S. J.; Stokes, S.; Harrity, J. P. A. *Org. Lett.* **2012**, *14*, 5354.

(2) (a) Karpov, A. S.; Müller, T. J. J. *Org. Lett.* **2003**, *5*, 3451. (b) Chen, L.; Li, C.-J. *Org. Lett.* **2004**, *6*, 3151.

(3) (a) Mohamed Ahmed, M. S.; Mori, A. *Org. Lett.* **2003**, *5*, 3057. (b) Karpov, A. S.; Merkul, E.; Rominger, F.; Müller, T. J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6951. (c) Fusano, A.; Fukuyama, T.; Nishitani, S.; Inouye, T.; Ryu, I. *Org. Lett.* **2010**, *12*, 2410.

(4) Wu, X.-F.; Sundararaju, B.; Neumann, H.; Dixneuf, P. H.; Beller, M. *Chem. - Eur. J.* **2011**, *17*, 106.

(5) Wu, X.-F.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11142.

(6) Yu, Y.; Yang, W.; Pflästerer, D.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 1144.

(7) Wang, Z.; Li, L.; Huang, Y. *J. Am. Chem. Soc.* **2014**, *136*, 12233.

(8) (a) Yuan, J.; Wang, J.; Zhang, G.; Liu, C.; Qi, X.; Lan, Y.; Miller, J. T.; Kropf, A. J.; Bunel, E. E.; Lei, A. *Chem. Commun.* **2015**, *51*, 576. (b) Wang, H.; Xie, F.; Qi, Z.; Li, X. *Org. Lett.* **2015**, *17*, 920. (c) Ai, W.; Wu, Y.; Tang, H.; Yang, X.; Yang, Y.; Li, Y.; Zhou, B. *Chem. Commun.* **2015**, *51*, 7871. (d) Liu, X.; Yu, L.; Luo, M.; Zhu, J.; Wei, W. *Chem. - Eur. J.* **2015**, *21*, 8745.

(9) Huang, H.; Zhang, G.; Chen, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 7872.

(10) Tan, H.; Li, H.; Ji, W.; Wang, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 8374.

(11) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250.

(12) Forgione, P.; Brochu, M.-C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350.

(13) (a) Goossen, L. J.; Rodriguez, N.; Melzer, B.; Linder, C.; Deng, G. J.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (b) Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248. (c) Goossen, L. J.; Rodriguez, N.; Lange, P. P.; Linder, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 1111.

(14) (a) Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H.-Z.; Liu, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 9350. (b) Shang, R.; Yang, Z.-W.; Wang, Y.; Zhang, S.-L.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 14391. (c) Shang, R.; Ji, D.-S.; Chu, L.; Fu, Y.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4470. (d) Shang, R.; Xu, Q.; Jiang, Y.-Y.; Wang, Y.; Liu, L. *Org. Lett.* **2010**, *12*, 1000. (e) Shang, R.; Huang, Z.; Chu, L.; Fu, Y.; Liu, L. *Org. Lett.* **2011**, *13*, 4240.

(15) Some examples: (a) Burger, E. C.; Tunge, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 10002. (b) Becht, J.-M.; Catala, C.; Drian, C. L.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781. (c) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. *Chem. Commun.* **2008**, 6312. (d) Hu, P.; Zhang, M.; Xie, X.; Su, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 227. (e) Liu, J.; Liu, Q.; Yi, H.; Qin, C.; Bai, R.; Qi, X.; Lan, Y.; Lei, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 502.

(16) Our previous work: (a) Feng, Y.-S.; Wu, W.; Xu, Z.-Q.; Li, Y.; Li, M.; Xu, H.-J. *Tetrahedron* **2012**, *68*, 2113. (b) Li, Y.; Chen, H.-H.; Wang, C.-F.; Xu, X.-L.; Feng, Y.-S. *Tetrahedron Lett.* **2012**, *53*, 5796. (c) Feng, Y.-S.; Xu, Z.-Q.; Mao, L.; Zhang, F.-F.; Xu, H.-J. *Org. Lett.* **2013**, *15*, 1472. (d) Wang, P.-F.; Wang, X.-Q.; Dai, J.-J.; Feng, Y.-S.; Xu, H.-J. *Org. Lett.* **2014**, *16*, 4586.

(17) Wang, H.; Guo, L.-N.; Wang, S.; Duan, X.-H. *Org. Lett.* **2015**, *17*, 3054.

(18) (a) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 1651. (b) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330.

(19) Wadhwa, K.; Yang, C.; West, P. R.; Deming, K. C.; Chemburkar, S. R.; Reddy, R. E. *Synth. Commun.* **2008**, *38*, 4434.

(20) (a) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem. - Eur. J.* **2012**, *18*, 5655. (b) Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136*, 2280.

(21) Feng, L.; Kumar, D.; Kerwin, S. M. *J. Org. Chem.* **2003**, *68*, 2234.

(22) Reddy, K. R.; Suresh, M.; Kantam, M. L.; Bhargava, S. K.; Srinivasu, P. *Ind. Eng. Chem. Res.* **2014**, *53*, 18630.

(23) Shintani, R.; Okamoto, K.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, *127*, 2872.

(24) Cox, R. J.; Ritson, D. J.; Dane, T. A.; Berge, J.; Charmant, J. P. H; Kantacha, A. *Chem. Commun.* **2005**, 1037.

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