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Construction of All-Carbon Quaternary Centers through Cu-Catalyzed Sequential Carbene Migratory Insertion and Nucleophilic Substitution/Michael Addition

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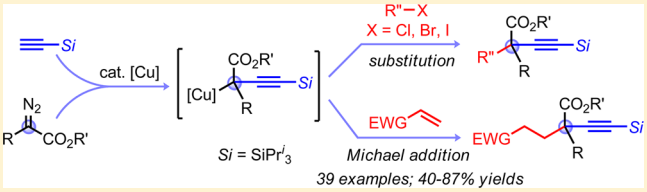
Supporting Information

ABSTRACT: A Cu-catalyzed three-component cross-coupling reaction of terminal alkyne, α-diazo ester, and alkyl halide has been developed. This transformation involves sequent migratory insertion of copper-carbene and nucleophilic substitution, in which a C(sp)−C(sp^3) bond and a C(sp^3)−C(sp^3) bond are formed successively on a carbenic center. Michael addition acceptors can also be employed instead of alkyl halides that enable Michael addition to be an alternative way to build C(sp^3)−C(sp^3) bond. This transformation represents a highly efficient method for the construction of all-carbon quaternary centers.

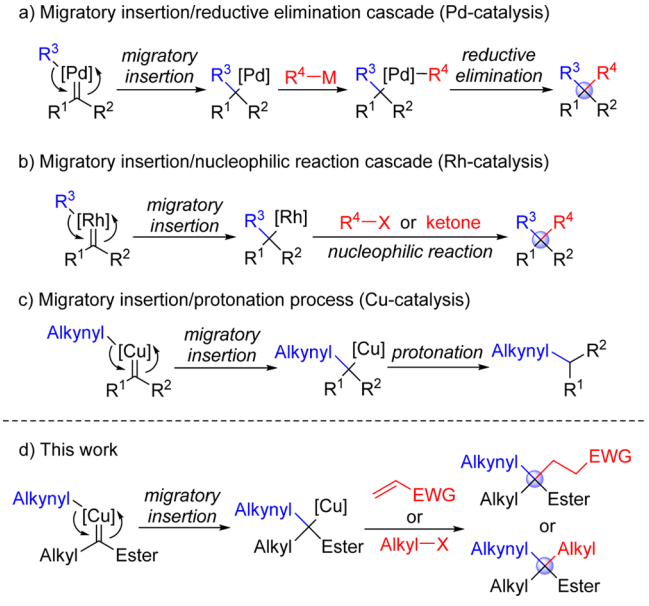


INTRODUCTION

Diazo compounds, which are commonly utilized as carbene precursors, have been recently extensively employed as versatile cross-coupling partners in various transition-metal-catalyzed reactions.[1] A series of novel C−C bond forming reactions have been established through the carbene-based coupling reactions. In this context, the formation of two separate carbon−carbon σ-bonds on the carbenic center through cascade reactions provides an accessible way toward the highly efficient construction of all-carbon quaternary centers. Such an approach was initially reported by Van Vranken and co-workers.[2] Wang[3a] and Liang[3b] have then developed palladium-catalyzed three-component reactions combining migratory insertion and reductive elimination, which renders two different groups to connect successively to the carbenic center (Scheme 1a). Yu,[4a] Wang,[4b,d] and Murakami[4c] have also developed relevant rhodium-carbene migratory insertion and nucleophilic reaction cascade that realizes sequent C−C bond formations (Scheme 1b). Notably, in addition to carbene migratory insertion, the strategy of electrophilic trapping of the metal-carbene induced zwitterionic intermediate established by Hu and others provides an alternative approach to quaternary center construction.[5,6]

On the other hand, the efficient construction of quaternary carbon centers has remained a crucial issue in organic synthesis.[7] Since quaternary carbon centers are widely found in various natural products, pharmaceuticals, and bioactive molecules, significant efforts have been devoted to the effective construction of quaternary centers in their total syntheses.[8,9] Transition-metal-catalyzed cross-coupling reactions have recently emerged as a powerful tool that significantly complements the synthetic methodology of quaternary carbon centers, among which palladium[10] and rhodium[11] catalysis played an important role in their development. Copper catalysts are also efficient in quaternary center construction,[12] especially in the enantioselective conjugate addition reactions,[13] but the stoichiometric use of highly reactive organometallic reagents is usually inevitable. Compared to carbene-involved cascade

Scheme 1. Construction of All-Carbon Quaternary Centers through Carbene-Based Coupling Reactions



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reactions, these methods typically form only one C−C bond, which are obviously less efficient than the successive C−C bond formation strategy in one-pot manner.

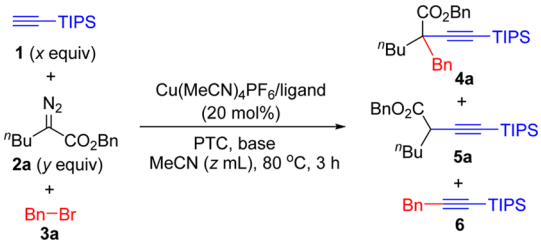
In contrast, transition-metal-catalyzed carbene-involved cross-coupling reactions of alkynes have been successfully developed that form either C(sp)−C(sp^2) bonds[14] or C(sp)−C(sp^3) bonds,[3,4d,15] introducing the alkyne moiety into the product. Among these reports, copper-catalyzed C(sp)−C(sp^3) bond forming reactions show significant advantages as they employ cheap and bench-stable copper catalysts and avoid the use of complex ligands (Scheme 1c).[15] Despite the preceding developments, however, copper-catalyzed sequential formation of two C−C bonds on a carbenic center based on metal-carbene migratory insertion has not yet been reported. Herein, we report a Cu-catalyzed three-component reaction of terminal alkyne, α-alkyl-α-diazo esters, and alkyl halides or Michael addition acceptors, which involve sequential carbene migratory insertion and nucleophilic substitution or Michael addition in one-pot manner. This reaction realizes successive C(sp)−C(sp^3) and C(sp^3)−C(sp^3) bond formation and provides a powerful and tunable method for the construction of all-carbon quaternary centers (Scheme 1d).

RESULTS AND DISCUSSION

At the beginning of our investigation, terminal alkyne **1**, α-diazo ester **2a**, and benzyl bromide **3a** were selected as the model substrates to test the three-component coupling reaction (Table 1). Employing $Cu(MeCN)_4PF_6$ as the catalyst and 1,10-phenanthroline as the ligand, the desired product **4a** was isolated in 27% yield (entry 1). The main byproducts include **5a** and **6**, which were the coupling products of **1** with **2a** and **1** with **3a**, respectively. To our delight, the replacement of the 1,10-phenanthroline with 4,5-diazafluoren-9-one (DAFO) resulted in suppressing the formation of **6** (entry 2). The yield was improved to 57% when 2 equiv of α-diazo ester **2a** was added (entry 3). Although an increased amount of base would inhibit the protonation process which generated **5a**, excessive NaH was proved to be detrimental to this reaction, which accelerated the nucleophilic substitution of alkyne and benzyl bromide that led to the formation of **6** (entry 4). Alternatively, mixed bases were necessary to repress both byproducts (entries 5−6). Furthermore, raising the amount of **1** enhanced the yield to 76% (entry 7). To our delight, the amount of **2a** could be reduced to 1.6 equiv, and an adjustment in concentration improved the yield to 78% (entries 8−9). Moreover, we were glad to find that the scale-up experiment could be conducted successfully, and the desired product was isolated in gram scale with only slight decrease in yield (entry 9, 65%, 1.23 g), which illustrated the practicality of this methodology.

In addition, further experiments revealed that NaH was not indispensable, as a diminished amount of NaH was also effective to this reaction (entries 10−11). The phase-transfer catalyst was found to be necessary, as the yield declined due to the replacement of TBAI to TBAB, and only a trace amount of product was detected in the absence of phase-transfer catalysts (entries 12−13). The effect of TBAI might be two-fold: it enhanced the solubility of the substrates, and a halogen exchange reaction might occur between iodide anion and benzyl bromide, thus increasing its electrophilicity. Finally, the control experiment indicates the Cu(I) catalyst is necessary (entry 14).

Table 1. Optimization of the Reaction Conditions[a]



entry	base (equiv)	x	y	z	PTC	**4a**, yield (%)
1[b]	NaH (2.0)	1.0	1.0	0.5	TBAI	27
2	NaH (2.0)	1.0	1.0	0.75	TBAI	32
3	NaH (2.0)	1.0	2.0	0.75	TBAI	57
4	NaH (3.0)	1.0	2.0	0.75	TBAI	19
5	NaH (1.0) + Cs_2CO_3 (1.0)	1.0	2.0	0.75	TBAI	61
6	NaH (1.0) + Cs_2CO_3 (2.0)	1.0	2.0	0.75	TBAI	65
7	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	2.0	0.75	TBAI	76
8	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	1.6	0.75	TBAI	74
9	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	1.6	1.0	TBAI	78(65)[c]
10	NaH (0.5) + Cs_2CO_3 (2.0)	1.5	1.6	1.0	TBAI	71
11	Cs_2CO_3 (3.5)	1.5	1.6	1.0	TBAI	71
12	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	1.6	1.0	TBAB	42
13	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	1.6	1.0	none	trace
14	NaH (1.0) + Cs_2CO_3 (2.0)	1.5	1.6	1.0	TBAI	trace[d]

[a]Unless otherwise noted, all the reactions were carried out with **1**, **2a**, **3a** (0.10 mmol), $Cu(MeCN)_4PF_6$ (20 mol %), DAFO (20 mol %), base, and PTC (20 mol %) in MeCN under nitrogen atmosphere at 80 °C for 3 h. [b]1,10-phenanthroline (20 mol %) was used as the ligand instead of DAFO. [c]The yield in the parentheses was obtained in 4.0 mmol scale. PTC = phase-transfer catalyst. [d]The reaction was carried out in the absence of Cu(I) catalyst. TIPS = triisopropylsilyl. DAFO = 4,5-diazafluoren-9-one. TBAI = tetrabutylammonium iodide. TBAB = tetrabutylammonium bromide.

With the optimized reaction conditions, we then explored the substrate scope of α-diazo esters containing a series of alkyl groups (Scheme 2). α-Diazo esters with primary and secondary alkyl groups including butyl, ethyl, methyl, and isopropyl were all suitable substrates for this reaction (**4a**−**d**). In addition, benzyl and cinnamyl groups could also be introduced into the products (**4e**,**f**). Alkenes, cyclopropyl group and esters were also well tolerated in the reaction system, giving the corresponding products in moderate to good yields (**4f**−**j**). Furthermore, α-diazo ester containing γ-butyrolactone moiety could also undergo this reaction smoothly, generating a quaternary carbon center in the ring (**4k**).

Next, we investigated the scope of benzyl bromides with various functional groups (Scheme 3). Benzyl bromides bearing electron-donating and -withdrawing groups were all subject to the identical reaction conditions. Functional groups including ester, nitro, cyano, methyl, and methoxy groups were well tolerated in this reaction (**7a**−**d**,**h**,**i**). Also, benzyl bromides with substituents on *para*, *meta*, and *ortho* positions, as well as 2-naphthyl group, were proved to be suitable substrates for this transformation (**7a**−**j**). Notably, the halogen substituents on

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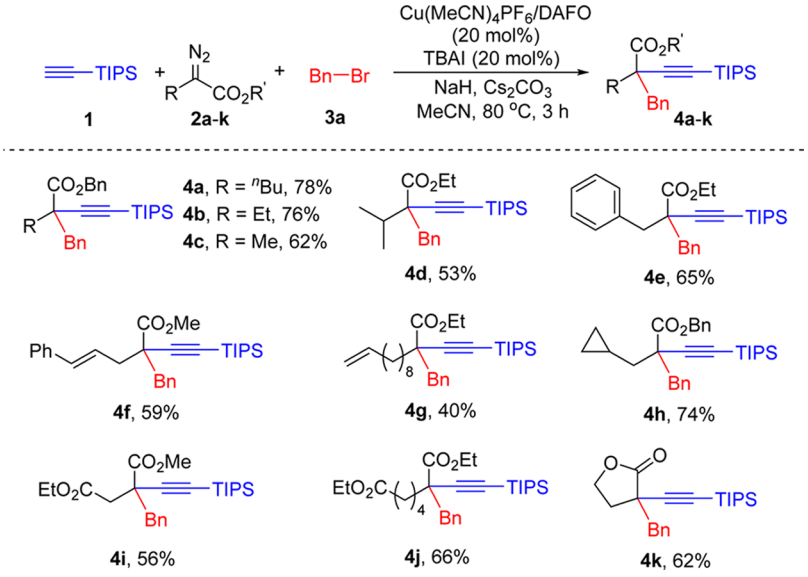
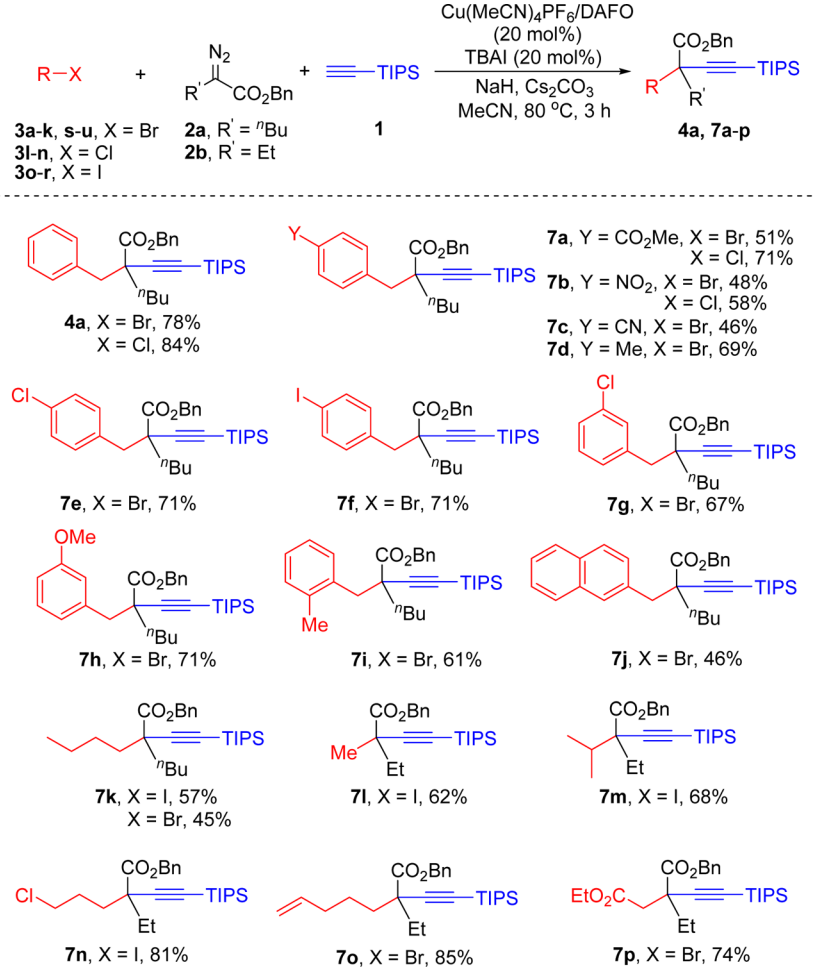
Scheme 2. Substrate Scope of α-Diazo Esters[a]



[a]All the reactions were carried out with **1** (0.15 mmol), α-diazo esters **2a−k** (0.16 mmol), **3a** (0.10 mmol), $Cu(MeCN)_4PF_6$ (20 mol %), DAFO (20 mol %), NaH (1 equiv), Cs_2CO_3 (2 equiv), and TBAI (20 mol %) in MeCN (1 mL) under nitrogen atmosphere at 80 °C for 3 h.

Scheme 3. Substrate Scope of Alkyl Halides[a]



[a]All the reactions were carried out with **1** (0.15 mmol), α-diazo ester **2a** or **2b** (0.16 mmol), alkyl halides **3a−u** (0.10 mmol), $Cu(MeCN)_4PF_6$ (20 mol %), DAFO (20 mol %), NaH (1 equiv), Cs_2CO_3 (2 equiv), and TBAI (20 mol %) in MeCN (1 mL) under nitrogen atmosphere at 80 °C for 3 h.

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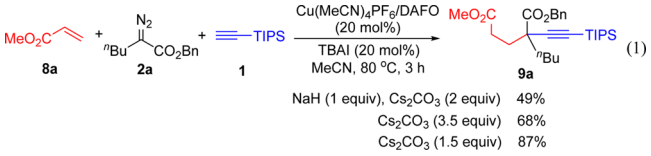
the aromatic ring, especially iodide, remained inert in the reaction, allowing further transformations through cross-coupling reactions (**7e**–**g**). It is interesting to note that benzyl chlorides were successfully converted into the products in even better yields than the corresponding benzyl bromides despite their lower reactivity (**4a**, **7a**,**b**). This could be attributed to the compatibility of benzyl chlorides with the reaction system, thus decelerating certain side reactions.

In addition to benzyl bromides and chlorides, gratifyingly, unactivated alkyl halides were also found to be efficient through this transformation, which significantly broadened the substrate scope that enabled a wider range of potential products to be synthesized (Scheme 3). First, both 1-iodobutane and 1-bromobutane could give the dibutyl-substituted product with a lower yield for the bromide (**7k**). Other primary alkyl iodides were employed as the substrates, including iodomethane (**7l**) and 1-chloro-3-iodopropane (**7n**). Moreover, secondary alkyl iodide was also a suitable electrophile (**7m**). Besides alkyl iodides, alkyl bromides were subject to the reaction, giving the corresponding alkene- and ester-containing products in excellent yields (**7o**,**p**).

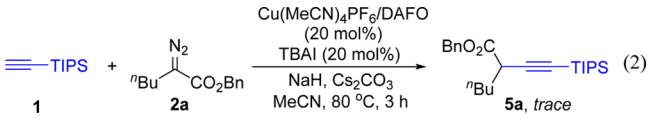
Encouraged by the results above, we proceeded to explore an alternative way to realize the $C(sp^3)$–$C(sp^3)$ bond formation in addition to nucleophilic substitution. As expected, methyl acrylate **8a** was a suitable electrophile, providing the Michael addition product in 49% yield under the identical reaction conditions eq 1. Considering that a protonation step was



required after the Michael addition, NaH was removed, and 3.5 equiv of Cs_2CO_3 was added instead, which enhanced the yield to 68%. Further reducing the amount of base proved to be beneficial to this reaction, and 1.5 equiv of Cs_2CO_3 was found to be optimal, producing the Michael addition product in 87% yield. However, in the absence of any base, only a trace amount of product could be detected.

With the optimized reaction conditions in hand, the scope of various Michael addition acceptors was examined (Scheme 4). To our delight, α,β-unsaturated esters (**9a**–**c**), amide (**9d**), ketones (**9e**,**f**), nitrile (**9g**), sulfone (**9h**), and phosphonate (**9i**) all gave satisfactory results, indicating a new method toward the sequential construction of C–C bonds. Michael addition acceptors bearing substituent on the β-position of the electron-withdrawing group underwent the reaction smoothly, while no diastereoselectivity was observed in this case (**9f**).

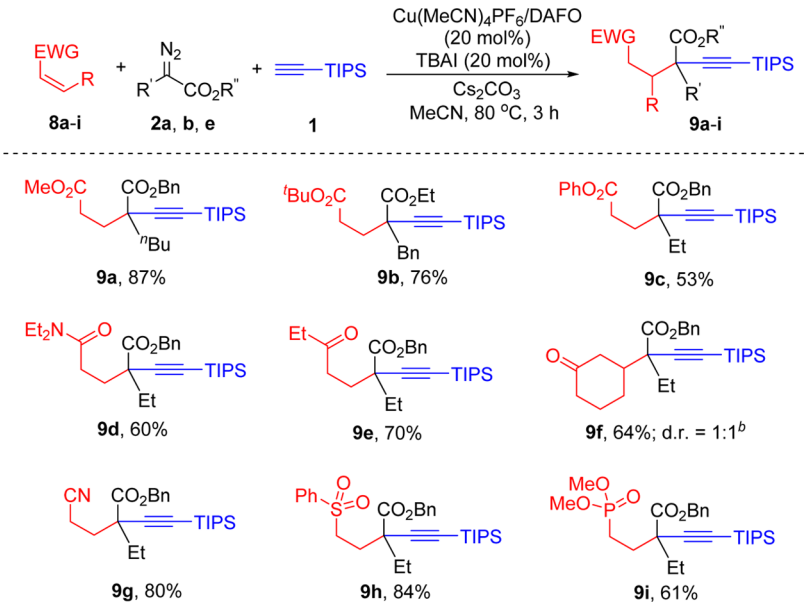
To gain insight into the mechanism, we tried the reaction of terminal alkyne **1** and α-diazo ester **2a** under the identical reaction conditions in the absence of the electrophile. According to our previous studies,[15b] we initially expected that the corresponding protonation product **5a** would be obtained eq 2. However, only a trace amount of **5a** was



detected, and the starting materials either remained or decomposed, indicating that the basic conditions in this reaction significantly suppressed the protonation of the organocopper species.

Furthermore, we employed the protonation products **5a** and **5b** to react with methyl acrylate **8a** and benzyl bromide **3a** in the absence of copper catalyst, respectively, eqs 3 and 4. Not surprisingly, the corresponding Michael addition and substitution reaction occurred smoothly, giving the products **9a** and **4b** in excellent yields. These results suggest that the copper

Scheme 4. Substrate Scope of Michael Addition Acceptors[a]



[a]All the reactions were carried out with **1** (0.15 mmol), α-diazo ester **2a**, **2b**, or **2e** (0.16 mmol), Michael addition acceptors **8a**–**i** (0.10 mmol), $Cu(MeCN)_4PF_6$ (20 mol %), DAFO (20 mol %), Cs_2CO_3 (1.5 equiv), and TBAI (20 mol %) in MeCN (1 mL) under nitrogen atmosphere at 80 °C for 3 h. [b]The diastereomeric ratio (dr) was determined by ^1H NMR analysis. EWG = electron-withdrawing group.

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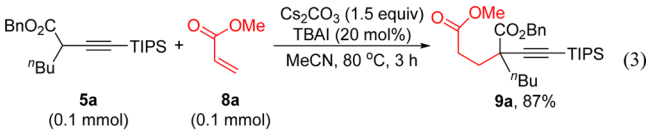
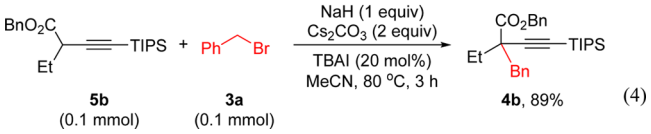
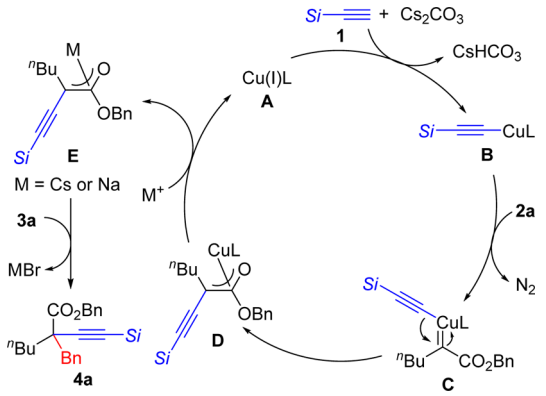




catalyst probably does not participate in the nucleophilic reaction step.

Based on our understanding of Cu-catalyzed reactions involving diazo compounds,[1,15b,16] a plausible mechanism is depicted in Scheme 5. First, the ligand coordinates to Cu(I) to

Scheme 5. Proposed Reaction Mechanism



generate the catalyst **A**, which activates the terminal alkyne **1** with the assistance of base to afford alkynyl copper species **B**. Cu(I)-carbene intermediate **C** is then formed, followed by migratory insertion of the alkynyl group to generate the copper enolate species **D**. Subsequently, according to the experiments shown above, an alkali metal-copper exchange occurs that regenerates the active copper catalyst **A** and forms a sodium or cesium enolate species **E**, which affords the final product via nucleophilic reaction. However, the possibility that the formation of the product may arise from the direct nucleophilic reaction of organocopper species **D**, and the electrophile cannot strictly be ruled out.

CONCLUSION

In summary, we have developed a highly efficient Cu-catalyzed three-component cross-coupling reaction, in which a C(sp)−C(sp^3) bond and a C(sp^3)−C(sp^3) bond form successively on a carbenic center in one-pot manner. This reaction has a wide range of substrate scope and can be realized in gram-scale synthesis, thus representing a promising methodology for the construction of all-carbon quaternary centers with readily available starting materials. Further investigation will be focused on the enantioselective version of this approach and the results will be reported in due course.

EXPERIMENTAL SECTION

Unless otherwise noted, all the copper-catalyzed reactions were performed under nitrogen atmosphere in a 10 mL Schlenk tube. The gram-scale synthesis was performed under nitrogen atmosphere in a 250 mL Schlenk flask. All the solvents were distilled under nitrogen atmosphere prior to use. MeCN was dried over calcium hydride. THF was dried over Na. For chromatography, 200−300 mesh silica gel was employed. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C{^{1}H}-NMR (100 MHz) spectra are reported relative to the chemical shift of tetramethylsilane (TMS): chemical shifts (δ) were reported in ppm, and coupling constants (J) are in Hertz (Hz). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. PE: petroleum either; EA: ethyl acetate. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. α-Diazo esters **2a−j** were prepared by a modified two-step procedure reported in the literature.[17] α-Diazobutyrolactone **2k** was prepared following a reported procedure.[18]

General Procedure for the Preparation of α-Diazo Esters 2a−j.[17] Under nitrogen atmosphere, NaH (60% in oil, 1.20 g, 30 mmol) was added into dried THF (30 mL), and the mixture was cooled to 0 °C. With magnetic stirring, acetoacetate (30 mmol) was added dropwise. When the vigorous generation of hydrogen gas ceased, the mixture was warmed to room temperature. Alkyl halide (20 mmol) was then added dropwise, and the mixture was allowed to reflux for 12 h. After the mixture was cooled to room temperature, NH_4Cl saturated solution (10 mL) was added to quench the reaction. The mixture was further diluted with water and extracted with CH_2Cl_2 twice. The combined organic layer was dried over Na_2SO_4, filtered, and evaporated *in vacuo* to remove the volatile compounds. The residue was purified by column chromatography (silica gel, eluting with PE:EA = 10:1) to give 2-alkyl acetoacetate as a colorless or light yellow oil, which was used for the next step.

2-Alkyl acetoacetate (10 mmol) prepared from the previous step was added to MeCN (30 mL), and 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 3.60 g, 15 mmol) was added. With magnetic stirring, DBU (2.25 mL, 15 mmol) was added dropwise, and the mixture was stirred at room temperature for 5 h. The mixture was then concentrated *in vacuo* to give a dark-red solution, which was eluted through a short path of silica gel (eluting with PE:EA = 5:1) to give a bright yellow filtrate. The solution was evaporated *in vacuo* to remove the volatile compounds, and the residue was purified by column chromatography (silica gel, eluting with PE:EA = 30:1) to give the corresponding α-diazo ester **2a−j** as a bright yellow oil (except **2f**, which is an orange oil).

Procedure for the Preparation of α-Diazobutyrolactone 2k.[18] NaN_3 (260 mg, 4.0 mmol), NaOH (8 mL of 2 M in water, 16 mmol), and TBAB (3.2 mg, 0.01 mmol) were combined in petroleum ether (5 mL), and the mixture was cooled to 0 °C. With vigorous magnetic stirring, Tf_2O (564 mg, 2.0 mmol) was added dropwise. After 10 min, a solution of 2-acetylbutyrolactone (128 mg, 1.0 mmol) in MeCN (4 mL) was added, and the mixture was stirred at 0 °C for another 30 min. The mixture was then diluted with water (5 mL) and ethyl acetate (10 mL), and the aqueous layer was further extracted with ethyl acetate twice. The combined organic layer was dried over Na_2SO_4, filtered, and evaporated *in vacuo* to remove the volatile compounds. The residue was eluted through a short path of silica gel (eluting with PE:EA = 1:1), and the solvent was removed *in vacuo* to give the pure product **2k** as a light yellow solid.

General Procedure for the Cu(I)-Catalyzed Reaction of Triisopropylsilylethyne, α-Diazo Ester, and Alkyl Halide. $Cu(MeCN)_4PF_6$ (7.5 mg, 0.02 mmol), 4,5-diazafluoren-9-one (3.6 mg, 0.02 mmol), TBAI (7.4 mg, 0.02 mmol), NaH (60% in oil, 4.0 mg, 0.10 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), and alkyl halide (0.10 mmol) were suspended in MeCN (1.0 mL) in a 10 mL Schlenk tube under nitrogen atmosphere. Triisopropylsilylethyne (27.4 mg, 0.15 mmol) and α-diazo ester (0.16 mmol) were then added, and the resulting solution was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile compounds. The residue was purified by preparative thin-layer chromatography (TLC) (silica gel) to give the corresponding product.

*Benzyl 2-Benzyl-2-((triisopropylsilyl)ethynyl)hexanoate (**4a**).* Colorless oil; yield 78% (37 mg) for benzyl bromide, 84% (40 mg) for benzyl chloride. The TLC plate was stained with $KMnO_4$, and a bright

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yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 5H), 7.19−7.17 (m, 5H), 5.03 (AB q, J = 12.5 Hz, 2H), 3.13 (d, J = 13.1 Hz, 1H), 2.95 (d, J = 13.1 Hz, 1H), 1.98−1.91 (m, 1H), 1.71−1.64 (m, 1H), 1.62−1.54 (m, 1H), 1.33−1.26 (m, 3H), 1.04−0.93 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 136.6, 135.5, 130.2, 128.3, 128.0, 127.9, 127.8, 126.7, 107.0, 86.4, 66.8, 50.9, 45.3, 39.6, 27.6, 22.7, 18.5, 13.9, 11.2; IR (film) 2957, 2942, 2864, 2169, 1732, 1456, 1199, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{45}O_2Si$ [(M + H)$^+$] 477.3183, found: 477.3189.

*Benzyl 2-Benzyl-2-ethyl-4-(triisopropylsilyl)but-3-ynoate (**4b**).* Colorless oil; yield 76% (34 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 5H), 7.19−7.18 (m, 5H), 5.04 (AB q, J = 12.4 Hz, 2H), 3.13 (d, J = 13.1 Hz, 1H), 2.96 (d, J = 13.1 Hz, 1H), 2.03−1.94 (m, 1H), 1.76−1.68 (m, 1H), 1.05−1.04 (m, 3H), 1.02−0.95 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 136.6, 135.6, 130.3, 128.3, 128.0, 127.9, 127.8, 126.7, 106.8, 86.5, 66.8, 51.5, 45.0, 32.8, 18.5, 11.2, 9.8; IR (film) 2942, 2865, 2169, 1732, 1456, 1214, 997, 883 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{41}O_2Si$ [(M + H)$^+$] 449.2870, found: 449.2872.

*Benzyl 2-Benzyl-2-methyl-4-(triisopropylsilyl)but-3-ynoate (**4c**).* Colorless oil; yield 62% (27 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.20 (m, 10H), 5.10 (AB q, J = 12.5 Hz, 2H), 3.15 (d, J = 13.1 Hz, 1H), 2.98 (d, J = 13.1 Hz, 1H), 1.48 (s, 3H), 1.00−0.95 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 136.5, 135.6, 130.4, 128.4, 128.0, 127.9, 127.8, 126.8, 108.3, 84.9, 67.0, 45.6, 45.0, 25.5, 18.5, 11.2; IR (film) 2942, 2865, 2171, 1738, 1455, 1221, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{39}O_2Si$ [(M + H)$^+$] 435.2714, found: 435.2716.

*Ethyl 2-Benzyl-2-isopropyl-4-(triisopropylsilyl)but-3-ynoate (**4d**).* Colorless oil; yield 53% (21 mg). $KMnO_4$ staining showed no spot on TLC plate; the spot was detected by weak UV absorption (254 nm); R_f = 0.55 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.29 (m, 2H), 7.22−7.18 (m, 3H), 3.98−3.89 (m, 2H), 3.00 (AB q, J = 12.8 Hz, 2H), 2.23 (heptet, J = 6.7 Hz, 1H), 1.15−0.98 (m, 30H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 137.2, 130.2, 127.6, 126.6, 105.3, 87.3, 60.8, 56.5, 43.8, 36.4, 19.3, 18.6, 17.5, 13.9, 11.4; IR (film) 2963, 2943, 2865, 2166, 1728, 1464, 1256, 1215, 1043, 883 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{41}O_2Si$ [(M + H)$^+$] 401.2870, found: 401.2872.

*Ethyl 2,2-Dibenzyl-4-(triisopropylsilyl)but-3-ynoate (**4e**).* Colorless oil; yield 65% (29 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.30 (m, 4H), 7.24−7.20 (m, 6H), 3.92 (q, J = 7.2 Hz, 2H), 3.26 (d, J = 13.0 Hz, 2H), 2.96 (d, J = 13.0 Hz, 2H), 1.00−0.93 (m, 24H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2, 136.5, 130.4, 127.7, 126.7, 106.4, 88.4, 61.2, 52.2, 45.5, 18.5, 13.7, 11.3; IR (film) 2942, 2865, 2167, 1727, 1456, 1226, 883 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{41}O_2Si$ [(M + H)$^+$] 449.2870, found: 449.2874.

*(E)-Methyl 2-Benzyl-5-phenyl-2-((triisopropylsilyl)ethynyl)pent-4-enoate (**4f**).* Colorless oil; yield 59% (27 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected immediately, which later turned to bright yellow after 10 min at room temperature; R_f = 0.6 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.20 (m, 10H), 6.47 (d, J = 15.8 Hz, 1H), 6.38−6.30 (m, 1H), 3.60 (s, 3H), 3.17 (d, J = 13.2 Hz, 1H), 3.01 (d, J = 13.2 Hz, 1H), 2.82−2.77 (m, 1H), 2.63−2.57 (m, 1H), 1.05−0.99 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 137.3, 136.4, 133.4, 130.3, 128.4, 127.8, 127.2, 126.8, 126.2, 125.1, 106.5, 87.3, 62.3, 50.7, 44.5, 42.8, 18.6, 11.3; IR (film) 3031, 2945, 2865, 2173, 1734, 1463, 1229, 966, 883 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{41}O_2Si$ [(M + H)$^+$] 461.2870, found: 461.2872.

*Ethyl 2-Benzyl-2-((triisopropylsilyl)ethynyl)dodec-11-enoate (**4g**).* Colorless oil; yield 40% (20 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected immediately, which later turned to bright yellow after 10 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.27 (m, 2H), 7.23−7.20 (m, 3H), 5.86−5.76 (m, 1H), 5.01−4.92 (m, 2H), 4.11−3.99 (m, 2H), 3.10 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 13.1 Hz, 1H), 2.06−2.01 (m, 2H), 1.93−1.87 (m, 1H), 1.66−1.55 (m, 2H), 1.38−1.27 (m, 11H), 1.14−0.99 (m, 24H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 139.2, 136.7, 130.3, 127.7, 126.6, 114.1, 107.4, 86.2, 61.1, 50.7, 45.2, 39.6, 33.8, 29.5, 29.4, 29.3, 29.1, 28.9, 25.3, 18.6, 14.0, 11.3; IR (film) 2927, 2864, 2170, 1730, 1463, 1220, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{53}O_2Si$ [(M + H)$^+$] 497.3809, found: 497.3815.

*Benzyl 2-Benzyl-2-(cyclopropylmethyl)-4-(triisopropylsilyl)but-3-ynoate (**4h**).* Colorless oil; yield 74% (35 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.24 (m, 5H), 7.21−7.18 (m, 5H), 5.05 (AB q, J = 12.5 Hz, 2H), 3.16 (d, J = 13.1 Hz, 1H), 2.96 (d, J = 13.1 Hz, 1H), 1.86 (dd, J = 5.8 Hz, J = 13.4 Hz, 1H), 1.71 (dd, J = 7.8 Hz, J = 13.4 Hz, 1H), 1.04−0.95 (m, 22H), 0.49−0.42 (m, 1H), 0.37−0.30 (m, 1H), 0.18−0.12 (m, 1H), 0.09−0.03 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 136.6, 135.5, 130.3, 128.3, 128.1, 127.9, 127.7, 126.7, 107.1, 86.8, 66.9, 51.1, 45.1, 44.9, 18.5, 11.3, 7.3, 4.4, 4.2; IR (film) 2943, 2865, 2172, 1731, 1456, 1203, 833 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{43}O_2Si$ [(M + H)$^+$] 475.3027, found: 475.3029.

*4-Ethyl 1-Methyl 2-benzyl-2-((triisopropylsilyl)ethynyl)succinate (**4i**).* Colorless oil; yield 56% (24 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 5H), 4.11 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 3.18 (d, J = 13.1 Hz, 1H), 3.06 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 16.1 Hz, 1H), 2.72 (d, J = 16.1 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.05−0.98 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.3, 169.9, 135.6, 130.4, 127.9, 127.1, 105.7, 86.7, 60.7, 52.6, 47.0, 43.8, 42.6, 18.5, 14.0, 11.2; IR (film) 2944, 2866, 2171, 1738, 1464, 1244, 1177, 1031, 883 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{39}O_4Si$ [(M + H)$^+$] 431.2612, found: 431.2612.

*Diethyl 2-Benzyl-2-((triisopropylsilyl)ethynyl)heptanedioate (**4j**).* Colorless oil; yield 66% (32 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.4 (PE:EA = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2H), 7.23−7.20 (m, 3H), 4.14−4.04 (m, 4H), 3.10 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 13.1 Hz, 1H), 2.28 (t, J = 7.3 Hz, 2H), 1.96−1.89 (m, 1H), 1.69−1.60 (m, 4H), 1.43−1.34 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H), 1.05−0.99 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 172.5, 136.5, 130.3, 127.7, 126.7, 107.1, 86.4, 61.2, 60.2, 50.5, 45.2, 38.9, 34.2, 25.1, 24.9, 18.6, 14.2, 13.9, 11.2; IR (film) 2942, 2865, 2171, 1736, 1464, 1221, 883 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{47}O_4Si$ [(M + H)$^+$] 487.3238, found: 487.3240.

*3-Benzyl-3-((Triisopropylsilyl)ethynyl)dihydrofuran-2(3H)-one (**4k**).* Colorless oil; yield 62% (22 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.65 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 5H), 4.37−4.31 (m, 1H), 4.19−4.15 (m, 1H), 3.25 (d, J = 13.7 Hz, 1H), 3.02 (d, J = 13.7 Hz, 1H), 2.34−2.21 (m, 2H), 1.05−0.99 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.2, 135.8, 130.1, 128.3, 127.2, 104.6, 86.7, 65.9, 44.6, 41.9, 35.8, 18.5, 11.1; IR (film) 2943, 2866, 2170, 1779, 1463, 1370, 1160, 1025, 883 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{33}O_2Si$ [(M + H)$^+$] 357.2244, found: 357.2244.

*Methyl 4-(2-((Benzyloxy)carbonyl)-2-((triisopropylsilyl)ethynyl)-hexyl)benzoate (**7a**).* Colorless oil; yield 51% (27 mg) for methyl 4-(bromomethyl)benzoate, 71% (38 mg) for methyl 4-(chloromethyl)benzoate. The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.27−7.26 (m, 3H), 7.18−7.16 (m, 2H), 5.03 (br, 2H), 3.90 (s, 3H), 3.18 (d, J = 13.1 Hz, 1H), 2.98 (d, J = 13.1 Hz, 1H), 1.98−1.91 (m, 1H), 1.73−1.65 (m, 1H), 1.62−1.54 (m, 1H), 1.32−1.26 (m, 3H), 1.03−0.97 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.3, 167.1, 142.0, 135.4, 130.2, 129.1, 128.6, 128.3, 128.1, 128.0, 106.6,

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87.0, 66.9, 51.4, 50.6, 45.1, 39.9, 27.5, 22.6, 18.5, 13.9, 11.2; IR (film) 2955, 2865, 2170, 1726, 1463, 1278, 1196, 1111, 883 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{47}O_4Si$ $[(M + H)^+]$ 535.3238, found: 535.3238.

*Benzyl 2-(4-Nitrobenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7b**).* Colorless oil; yield 48% (25 mg) for 4-nitrobenzyl bromide, 58% (30 mg) for 4-nitrobenzyl chloride. The TLC plate was stained with $KMnO_4$, and an orange spot was detected after 15 min at room temperature; R_f = 0.6 (PE:EA = 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.29−7.24 (m, 3H), 7.19−7.16 (m, 2H), 5.05 (AB q, J = 12.2 Hz, 2H), 3.22 (d, J = 13.0 Hz, 1H), 2.98 (d, J = 13.0 Hz, 1H), 2.01−1.93 (m, 1H), 1.76−1.69 (m, 1H), 1.62−1.55 (m, 1H), 1.35−1.28 (m, 3H), 1.05−0.97 (m, 21H), 0.88 (t, J = 7.1 Hz, 3H), ; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.0, 146.9, 144.3, 135.2, 131.0, 128.33, 128.27, 128.25, 122.8, 106.1, 87.7, 67.1, 50.6, 44.7, 40.3, 27.5, 22.6, 18.5, 13.9, 11.2; IR (film) 2943, 2865, 2168, 1731, 1523, 1462, 1347, 1199, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{44}NO_4Si$ $[(M + H)^+]$ 522.3034, found: 522.3036.

*Benzyl 2-(4-Cyanobenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7c**).* Colorless oil; yield 46% (23 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.3 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.3 Hz, 2H), 7.32−7.29 (m, 5H), 7.19−7.16 (m, 2H), 5.04 (AB q, J = 12.3 Hz, 2H), 3.18 (d, J = 13.0 Hz, 1H), 2.93 (d, J = 13.0 Hz, 1H), 1.99−1.92 (m, 1H), 1.74−1.67 (m, 1H), 1.62−1.54 (m, 1H), 1.34−1.26 (m, 3H), 1.03−0.95 (m, 21H), 0.87 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.1, 142.2, 135.2, 131.5, 130.9, 128.4, 128.3, 128.2, 119.0, 110.6, 106.2, 87.5, 67.1, 50.6, 45.0, 40.2, 27.5, 22.6, 18.5, 13.9, 11.2; IR (film) 2956, 2943, 2865, 2229, 2173, 1731, 1462, 1214, 997, 883 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{44}NO_2Si$ $[(M + H)^+]$ 502.3136, found: 502.3133.

*Benzyl 2-(4-Methylbenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7d**).* Colorless oil; yield 69% (34 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.26 (m, 3H), 7.18−7.16 (m, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 7.9 Hz, 2H), 5.03 (br, 2H), 3.08 (d, J = 13.1 Hz, 1H), 2.92 (d, J = 13.1 Hz, 1H), 2.28 (s, 3H), 1.96−1.89 (m, 1H), 1.70−1.63 (m, 1H), 1.60−1.55 (m, 1H), 1.32−1.26 (m, 3H), 1.01−0.94 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 136.2, 135.6, 133.5, 130.1, 128.4, 128.2, 128.0, 127.9, 107.3, 86.2, 66.7, 50.9, 45.0, 39.4, 27.6, 22.7, 21.0, 18.5, 13.9, 11.3; IR (film) 2942, 2864, 2170, 1731, 1463, 1198, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{47}O_2Si$ $[(M + H)^+]$ 491.3340, found: 491.3342.

*Benzyl 2-(4-Chlorobenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7e**).* Colorless oil; yield 71% (36 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 40:1).^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.28 (m, 3H), 7.18−7.16 (m, 4H), 7.13−7.11 (m, 2H), 5.03 (AB q, J = 12.3 Hz, 2H), 3.09 (d, J = 13.1 Hz, 1H), 2.88 (d, J = 13.1 Hz, 1H), 1.96−1.89 (m, 1H), 1.71−1.64 (m, 1H), 1.61−1.54 (m, 1H), 1.32−1.26 (m, 3H), 1.04−0.97 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.4, 135.4, 135.1, 132.7, 131.5, 128.3, 128.1, 128.0, 127.9, 106.8, 86.9, 66.9, 50.8, 44.5, 39.8, 27.5, 22.6, 18.5, 13.9, 11.2; IR (film) 2945, 2865, 2170, 1731, 1493, 1462, 1214, 1017, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{44}ClO_2Si$ $[(M + H)^+]$ 511.2794, found: 511.2792.

*Benzyl 2-(4-Iodobenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7f**).* Colorless oil; yield 71% (43 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.65 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.30−7.29 (m, 3H), 7.17−7.15 (m, 2H), 6.98 (d, J = 8.2 Hz, 2H), 5.03 (AB q, J = 12.3 Hz, 2H), 3.06 (d, J = 13.1 Hz, 1H), 2.85 (d, J = 13.1 Hz, 1H), 1.96−1.89 (m, 1H), 1.70−1.63 (m, 1H), 1.61−1.53 (m, 1H), 1.34−1.24 (m, 3H), 1.03−0.95 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.4, 136.8, 136.3, 135.4, 132.2, 128.4, 128.1, 128.0, 106.7, 92.4, 86.9, 66.9, 50.7, 44.7, 39.8, 27.5, 22.6, 18.5, 13.9, 11.2; IR (film) 2941, 2864, 2168, 1731, 1462, 1214, 1008, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{44}IO_2Si$ $[(M + H)^+]$ 603.2150, found: 603.2145.

*Benzyl 2-(3-Chlorobenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7g**).* Colorless oil; yield 67% (34 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 4H), 7.21−7.15 (m, 3H), 7.09−7.08 (m, 2H), 5.04 (br, 2H), 3.11 (d, J = 13.1 Hz, 1H), 2.89 (d, J = 13.1 Hz, 1H), 1.98−1.90 (m, 1H), 1.72−1.65 (m, 1H), 1.60−1.54 (m, 1H), 1.33−1.27 (m, 3H), 1.01−0.95 (m, 21H), 0.87 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.4, 138.7, 135.4, 133.6, 130.3, 129.0, 128.4, 128.3, 128.1, 127.0, 106.5, 87.0, 67.0, 50.7, 44.8, 39.9, 27.5, 22.6, 18.5, 13.9, 11.2 (one peak was missed because of overlap); IR (film) 2956, 2943, 2865, 2171, 1731, 1463, 1212, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{44}ClO_2Si$ $[(M + H)^+]$ 511.2794, found: 511.2798.

*Benzyl 2-(3-Methoxybenzyl)-2-((triisopropylsilyl)ethynyl)-hexanoate (**7h**).* Colorless oil; yield 71% (36 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.4 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 3H), 7.21−7.18 (m, 2H), 7.10 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.80 (br, 1H), 6.73 (dd, J = 2.4 Hz, J = 7.9 Hz, 1H), 5.08−5.02 (m, 2H), 3.71 (m, 3H), 3.12 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 13.1 Hz, 1H), 1.98−1.91 (m, 1H), 1.72−1.65 (m, 1H), 1.62−1.55 (m, 1H), 1.32−1.25 (m, 3H), 1.03−0.95 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 159.2, 138.2, 135.6, 128.7, 128.3, 127.9, 122.7, 116.1, 112.0, 107.1, 86.3, 66.8, 55.0, 50.7, 45.3, 39.6, 27.6, 22.7, 18.5, 13.9, 11.2 (one peak was missed because of overlap); IR (film) 2954, 2864, 2171, 1732, 1601, 1456, 1264, 1052, 882 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{47}O_3Si$ $[(M + H)^+]$ 507.3289, found: 507.3287.

*Benzyl 2-(2-Methylbenzyl)-2-((triisopropylsilyl)ethynyl)hexanoate (**7i**).* Colorless oil; yield 61% (30 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.5 Hz, 1H), 7.28−7.27 (m, 3H), 7.21−7.19 (m, 2H), 7.07 (d, J = 4.1 Hz, 2H), 7.02−6.98 (m, 1H), 5.06 (AB q, J = 12.5 Hz, 2H), 3.18 (d, J = 13.9 Hz, 1H), 3.04 (d, J = 13.9 Hz, 1H), 2.33 (s, 3H), 2.04−1.96 (m, 1H), 1.75−1.68 (m, 1H), 1.64−1.55 (m, 1H), 1.33−1.26 (m, 3H), 0.97−0.91 (m, 21H), 0.86 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 137.0, 135.6, 135.4, 130.2, 130.1, 128.3, 128.1, 127.9, 126.5, 125.4, 107.2, 86.5, 67.0, 50.4, 41.1, 40.2, 27.6, 22.7, 20.3, 18.5, 13.9, 11.2; IR (film) 2942, 2865, 2169, 1731, 1463, 1215, 1017, 883 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{47}O_2Si$ $[(M + H)^+]$ 491.3340, found: 491.3343.

*Benzyl 2-(Naphthalen-2-ylmethyl)-2-((triisopropylsilyl)ethynyl)-hexanoate (**7j**).* Colorless oil; yield 46% (24 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78−7.76 (m, 1H), 7.72−7.69 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.43−7.40 (m, 3H), 7.20−7.13 (m, 3H), 7.07−7.05 (m, 2H), 5.01 (AB q, J = 12.4 Hz, 2H), 3.30 (d, J = 13.1 Hz, 1H), 3.12 (d, J = 13.1 Hz, 1H), 2.04−1.97 (m, 1H), 1.77−1.70 (m, 1H), 1.65−1.58 (m, 1H), 1.34−1.27 (m, 3H), 1.01−0.95 (m, 21H), 0.87 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 135.4, 134.3, 133.2, 132.5, 128.8, 128.7, 128.2, 127.9, 127.8, 127.7, 127.5, 127.2, 125.6, 125.3, 107.2, 86.6, 66.9, 51.0, 45.5, 39.8, 27.6, 22.7, 18.5, 13.9, 11.2; IR (film) 3062, 2942, 2865, 2169, 1731, 1462, 1213, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{47}O_2Si$ $[(M + H)^+]$ 527.3340, found: 527.3337.

*Benzyl 2-Butyl-2-((triisopropylsilyl)ethynyl)hexanoate (**7k**).* Colorless oil; yield 57% (25 mg) for 1-iodobutane, 45% (20 mg) for 1-bromobutane. The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.7 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 5H), 5.15 (s, 2H), 1.86−1.78 (m, 2H), 1.67−1.60 (m, 2H), 1.55−1.48 (m, 2H), 1.30−1.21 (m, 6H), 1.05−1.01 (m, 21H), 0.85 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 135.9, 128.4, 128.0, 127.9, 108.1, 84.3, 66.7, 49.3, 39.4, 27.5, 22.7, 18.6, 13.9, 11.3; IR (film) 2957, 2942, 2865, 2170, 1735, 1463, 1202, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{47}O_2Si$ $[(M + H)^+]$ 443.3340, found: 443.3341.

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*Benzyl 2-Ethyl-2-methyl-4-(triisopropylsilyl)but-3-ynoate (**7l**).* Colorless oil; yield 62% (23 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.30 (m, 5H), 5.16 (br, 2H), 1.95−1.86 (m, 1H), 1.74−1.65 (m, 1H), 1.47 (s, 3H), 1.04−0.97 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.4, 135.9, 128.4, 128.0, 127.8, 108.8, 83.2, 66.8, 44.3, 33.4, 25.3, 18.6, 11.2, 9.6; IR (film) 2942, 2865, 2172, 1740, 1462, 1231, 1147, 883 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{37}O_2Si$ [(M + H)$^+$] 373.2557, found: 373.2558.

*Benzyl 2-Ethyl-2-isopropyl-4-(triisopropylsilyl)but-3-ynoate (**7m**).* Colorless oil; yield 68% (27 mg). $KMnO_4$ staining showed no spot on TLC plate; the spot was detected by weak UV absorption (254 nm); R_f = 0.6 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 5H), 5.15 (AB q, J = 12.5 Hz, 2H), 2.08 (heptet, J = 6.7 Hz, 1H), 1.82−1.72 (m, 2H), 1.06−1.00 (m, 24H), 0.97−0.93 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 135.9, 128.4, 128.0, 105.6, 85.5, 66.6, 55.7, 35.7, 31.0, 19.3, 18.6, 17.5, 11.3, 10.1; IR (film) 2963, 2941, 2865, 2165, 1733, 1461, 1224, 998, 883 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{41}O_2Si$ [(M + H)$^+$] 401.2870, found: 401.2872.

*Benzyl 5-Chloro-2-ethyl-2-((triisopropylsilyl)ethynyl)pentanoate (**7n**).* Colorless oil; yield 81% (35 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected after 20 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.16 (br, 2H), 3.54−3.48 (m, 2H), 2.02−1.87 (m, 3H), 1.80−1.67 (m, 3H), 1.05−0.96 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.7, 135.7, 128.4, 128.1, 128.0, 106.8, 85.3, 66.9, 49.4, 44.8, 36.3, 32.9, 28.8, 18.6, 11.2, 9.6; IR (film) 2942, 2865, 2169, 1736, 1461, 1217, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{40}ClO_2Si$ [(M + H)$^+$] 435.2481, found: 435.2483.

*Benzyl 2-Ethyl-2-((triisopropylsilyl)ethynyl)hept-6-enoate (**7o**).* Colorless oil; yield 85% (36 mg). The TLC plate was stained with $KMnO_4$, and a dark yellow spot was detected immediately, which later turned to bright yellow after 10 min at room temperature; R_f = 0.65 (PE:EA = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.25 (m, 5H), 5.79−5.69 (m, 1H), 5.18−5.12 (m, 2H), 5.00−4.92 (m, 2H), 2.05−2.00 (m, 2H), 1.92−1.80 (m, 2H), 1.73−1.61 (m, 3H), 1.43−1.35 (m, 1H), 1.08−0.95 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 138.3, 135.9, 128.4, 128.0, 127.9, 114.6, 107.5, 84.6, 66.7, 49.9, 38.6, 33.6, 32.8, 24.6, 18.6, 11.2, 9.7; IR (film) 2941, 2865, 2168, 1736, 1459, 1205, 995, 883 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{43}O_2Si$ [(M + H)$^+$] 427.3027, found: 427.3029.

*1-Benzyl 4-Ethyl 2-ethyl-2-((triisopropylsilyl)ethynyl)succinate (**7p**).* Colorless oil; yield 74% (33 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (m, 5H), 5.19 (AB q, J = 12.6 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 2.98 (d, J = 15.7 Hz, 1H), 2.72 (d, J = 15.7 Hz, 1H), 1.96−1.87 (m, 1H), 1.81−1.72 (m, 1H), 1.19 (t, J = 7.1 Hz, 3H), 1.03−0.97 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.1, 169.8, 135.7, 128.3, 128.0, 105.9, 85.0, 67.2, 60.6, 46.7, 43.3, 32.5, 18.5, 14.0, 11.1, 9.4 (one peak was missed because of overlap); IR (film) 2941, 2865, 2172, 1739, 1462, 1189, 1018, 883 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{41}O_4Si$ [(M + H)$^+$] 445.2769, found: 445.2773.

General Procedure for the Cu(I)-Catalyzed Reaction of Triisopropylsilylethyne, α-Diazo Ester, and Michael Reaction Acceptor. $Cu(MeCN)_4PF_6$ (7.5 mg, 0.02 mmol), 4,5-diazafluoren-9-one (3.6 mg, 0.02 mmol), TBAI (7.4 mg, 0.02 mmol), and Cs_2CO_3 (48.9 mg, 0.15 mmol) were suspended in MeCN (1.0 mL) in a 10 mL Schlenk tube under nitrogen atmosphere. Michael reaction acceptor (0.10 mmol), triisopropylsilylethyne (27.4 mg, 0.15 mmol), and α-diazo ester (0.16 mmol) were then added, and the resulting solution was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile compounds. The residue was purified by preparative TLC (silica gel) to give the corresponding product.

*1-Benzyl 5-Methyl 2-butyl-2-((triisopropylsilyl)ethynyl)-pentanedioate (**9a**).* Colorless oil; yield 87% (41 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.65 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.15 (br, 2H), 3.65 (s, 3H), 2.64−2.56 (m, 1H), 2.39−2.31 (m, 1H), 2.22−2.15 (m, 1H), 2.02−1.94 (m, 1H), 1.88−1.81 (m, 1H), 1.70−1.63 (m, 1H), 1.51−1.45 (m, 1H), 1.30−1.23 (m, 3H), 1.04−0.99 (m, 21H), 0.85 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.4, 172.4, 135.6, 128.4, 128.1, 128.0, 106.6, 85.6, 67.0, 51.6, 48.4, 39.4, 33.9, 30.4, 27.4, 22.6, 18.5, 13.8, 11.2; IR (film) 2956, 2944, 2865, 2169, 1741, 1462, 1214, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{45}O_4Si$ [(M + H)$^+$] 473.3082, found: 473.3086.

*5-tert-Butyl 1-Ethyl 2-benzyl-2-((triisopropylsilyl)ethynyl)-pentanedioate (**9b**).* Colorless oil; yield 76% (37 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.7 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.21 (m, 5H), 4.12−4.00 (m, 2H), 3.13 (d, J = 13.1 Hz, 1H), 2.96 (d, J = 13.1 Hz, 1H), 2.61−2.53 (m, 1H), 2.35−2.17 (m, 2H), 2.00−1.92 (m, 1H), 1.43 (s, 9H), 1.14−1.00 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.3, 172.0, 136.2, 130.3, 127.8, 126.8, 106.3, 87.1, 80.3, 61.4, 49.9, 45.2, 34.2, 31.8, 28.0, 18.6, 13.9, 11.2; IR (film) 2943, 2866, 2171, 1732, 1456, 1367, 1154, 883 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{46}NaO_4Si$ [(M + Na)$^+$] 509.3058, found: 509.3057.

*1-Benzyl 5-Phenyl 2-ethyl-2-((triisopropylsilyl)ethynyl)-pentanedioate (**9c**).* Colorless oil; yield 53% (27 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.7 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 7H), 7.23−7.20 (m, 1H), 7.07−7.05 (m, 2H), 5.18 (br, 2H), 2.90−2.82 (m, 1H), 2.66−2.58 (m, 1H), 2.34−2.27 (m, 1H), 2.13−2.08 (m, 1H), 2.00−1.91 (m, 1H), 1.81−1.72 (m, 1H), 1.06−1.00 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.3, 171.5, 150.7, 135.6, 129.4, 128.5, 128.2, 128.0, 125.7, 121.5, 106.2, 86.0, 67.1, 49.1, 33.5, 32.8, 30.8, 18.6, 11.2, 9.7; IR (film) 2945, 2866, 2172, 1763, 1737, 1456, 1197, 1163, 1138, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{42}KO_4Si$ [(M + K)$^+$] 545.2484, found: 545.2482.

*Benzyl 5-(Diethylamino)-2-ethyl-5-oxo-2-((triisopropylsilyl)-ethynyl)pentanoate (**9d**).* Light red oil; yield 60% (29 mg). The TLC plate was stained with $KMnO_4$, and a light yellow spot was detected after 20 min at room temperature; R_f = 0.35 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.16 (AB q, J = 12.4 Hz, 2H), 3.42−3.27 (m, 2H), 3.25−3.13 (m, 2H), 2.61−2.52 (m, 1H), 2.30−2.15 (m, 2H), 2.06−2.01 (m, 1H), 1.99−1.89 (m, 1H), 1.78−1.69 (m, 1H), 1.10−0.98 (m, 30H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 171.2, 135.8, 128.4, 128.1, 128.0, 107.0, 85.3, 66.8, 49.3, 41.7, 40.0, 34.3, 32.9, 29.5, 18.6, 14.2, 13.0, 11.2, 9.7; IR (film) 2941, 2865, 2169, 1735, 1648, 1460, 1224, 883 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{48}NO_3Si$ [(M + H)$^+$] 486.3398, found: 486.3396.

*Benzyl 2-Ethyl-5-oxo-2-((triisopropylsilyl)ethynyl)heptanoate (**9e**).* Colorless oil; yield 70% (31 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.18−5.12 (m, 2H), 2.71−2.63 (m, 1H), 2.45−2.38 (m, 1H), 2.34 (q, J = 7.4 Hz, 2H), 2.13−2.06 (m, 1H), 1.96−1.87 (m, 2H), 1.75−1.66 (m, 1H), 1.05−0.96 (m, 27H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.4, 172.5, 135.7, 128.4, 128.1, 128.0, 106.7, 85.4, 66.9, 49.1, 38.4, 35.9, 32.8, 32.5, 18.6, 11.2, 9.7, 7.8; IR (film) 2942, 2865, 2168, 1735, 1721, 1460, 1227, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{43}O_3Si$ [(M + H)$^+$] 443.2976, found: 443.2981.

*Benzyl 2-Ethyl-2-(3-oxocyclohexyl)-4-(triisopropylsilyl)but-3-ynoate (**9f**).* Colorless oil; yield 64% (29 mg), d.r. = 1:1. The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.6 (PE:EA = 10:1). Diastereoisomers are hard to separate, so mixture NMR is given. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (m, 5H), 5.23−5.11 (m, 2H), 2.55−2.35 (m, 2.5H), 2.27−2.15 (m, 2.5H), 2.03−1.98 (m, 1H), 1.86−1.82 (m, 1H), 1.80−1.70 (m, 1.5H), 1.68−1.52 (m, 2.5H), 1.06−0.91 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 211.1, 210.6, 172.2, 171.9, 135.5, 135.4, 128.4, 128.22, 128.18, 128.1, 104.9, 104.6, 87.3, 87.1, 67.1, 67.0, 55.1, 54.9, 45.5, 45.3, 44.4, 42.9, 41.3,

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41.1, 30.84, 30.80, 27.8, 25.8, 24.50, 24.46, 18.6, 11.2, 10.0, 9.8; IR (film) 2943, 2864, 2171, 1731, 1719, 1460, 1221, 997, 883 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{43}O_3Si$ $[(M + H)^+]$ 455.2976, found: 455.2978.

*Benzyl 2-(2-Cyanoethyl)-2-ethyl-4-(triisopropylsilyl)but-3-ynoate (**9g**).* Colorless oil; yield 80% (33 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.4 (PE:EA = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 5H), 5.17 (AB q, J = 12.3 Hz, 2H), 2.64−2.55 (m, 1H), 2.43−2.34 (m, 1H), 2.30−2.23 (m, 1H), 1.98−1.86 (m, 2H), 1.78−1.69 (m, 1H), 1.05−0.97 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 135.2, 128.5, 128.4, 128.1, 119.2, 104.8, 87.1, 67.4, 48.9, 33.9, 32.8, 18.5, 13.7, 11.1, 9.4; IR (film) 2942, 2865, 2251, 2170, 1736, 1461, 1215, 1125, 883 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{38}NO_2Si$ $[(M + H)^+]$ 412.2666, found: 412.2665.

*Benzyl 2-Ethyl-2-(2-(phenylsulfonyl)ethyl)-4-(triisopropylsilyl)but-3-ynoate (**9h**).* Light red oil; yield 84% (44 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.55 (PE:EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 2H), 7.67−7.63 (m, 1H), 7.56−7.53 (m, 2H), 7.35−7.29 (m, 5H), 5.11 (AB q, J = 12.3 Hz, 2H), 3.40−3.32 (m, 1H), 3.15−3.07 (m, 1H), 2.24−2.17 (m, 1H), 2.05−1.98 (m, 1H), 1.90−1.81 (m, 1H), 1.74−1.66 (m, 1H), 1.00−0.92 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4, 138.9, 135.3, 133.7, 129.2, 128.5, 128.3, 128.1, 127.9, 105.1, 86.8, 67.3, 53.1, 48.4, 32.7, 31.0, 18.5, 11.0, 9.4; IR (film) 2943, 2865, 2171, 1736, 1460, 1448, 1308, 1225, 1153, 1087, 883 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{43}O_4SSi$ $[(M + H)^+]$ 527.2646, found: 527.2660.

*Benzyl 2-(2-(Dimethoxyphosphoryl)ethyl)-2-ethyl-4-(triisopropylsilyl)but-3-ynoate (**9i**).* Colorless oil; yield 61% (30 mg). The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 20 min at room temperature; R_f = 0.45 (PE:EA = 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 5H), 5.16 (br, 2H), 3.70 (d, J = 10.8 Hz, 6H), 2.13−2.03 (m, 2H), 1.93−1.84 (m, 2H), 1.78−1.68 (m, 2H), 1.06−0.96 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.0, 135.5, 128.5, 128.2, 128.0, 106.0, 86.0, 67.1, 52.3 (d, J = 6.5 Hz), 52.2 (d, J = 6.4 Hz), 50.0 (d, J = 19.3 Hz), 32.6, 31.5 (d, J = 3.0 Hz), 20.9 (d, J = 141.6 Hz), 18.5, 11.1, 9.6; IR (film) 2944, 2865, 2169, 1737, 1462, 1258, 1230, 1061, 1032, 883 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{43}KO_5PSi$ $[(M + K)^+]$ 533.2249, found: 533.2252.

Procedure for the Gram-Scale Synthesis. $Cu(MeCN)_4PF_6$ (298 mg, 0.8 mmol), 4,5-diazafluoren-9-one (146 mg, 0.8 mmol), TBAI (295 mg, 0.8 mmol), NaH (60% in oil, 160 mg, 4.0 mmol), and Cs_2CO_3 (2.61 g, 8.0 mmol) were suspended in MeCN (40 mL) in a 250 mL Schlenk flask under nitrogen atmosphere. Triisopropylsilylethyne **1** (1.09 g, 6.0 mmol), benzyl 2-diazohexanoate **2a** (1.48 g, 6.4 mmol), and benzyl bromide **3a** (684 mg, 4.0 mmol) were then added, and the resulting solution was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile compounds. The residue was purified by column chromatography (silica gel, eluting with PE:EA = 60:1) to give the product **4a** as a colorless oil (1.23 g, 65%).

General Procedure for the Preparation of 5a and 5b through Cu(I)-Catalyzed Reaction of Triisopropylsilylethyne and α-Diazo Ester. The reaction conditions for this transformation were established during the condition screening of the three-component reaction, and the products were used for mechanistic study (note: the reaction was not optimized). $Cu(MeCN)_4PF_6$ (22.3 mg, 0.06 mmol), 1,10-phenanthroline (10.8 mg, 0.06 mmol), TBAI (22.1 mg, 0.06 mmol), and NaOMe (32.4 mg, 0.60 mmol) were suspended in MeCN (1.5 mL) in a 10 mL Schlenk tube under nitrogen atmosphere. Triisopropylsilylethyne (54.7 mg, 0.30 mmol) and α-diazo ester (0.30 mmol) were then added, and the resulting solution was stirred at 50 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile compounds. The residue was purified by preparative TLC (silica gel) to give the corresponding product.

*Benzyl 2-((Triisopropylsilyl)ethynyl)hexanoate (**5a**).* Colorless oil. The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 10 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 5H), 5.16 (AB q, J = 12.7 Hz, 2H), 3.41 (dd, J = 6.2 Hz, J = 8.1 Hz, 1H), 1.90−1.74 (m, 2H), 1.49−1.26 (m, 4H), 1.05−0.99 (m, 21H), 0.89 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 135.7, 128.5, 128.1, 128.0, 104.0, 84.3, 66.8, 39.1, 32.1, 29.1, 22.1, 18.5, 13.9, 11.2; IR (film) 2943, 2865, 2175, 1746, 1463, 1162, 996, 883 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{39}O_2Si$ $[(M + H)^+]$ 387.2714, found: 387.2721.

*Benzyl 2-Ethyl-4-(triisopropylsilyl)but-3-ynoate (**5b**).* Colorless oil. The TLC plate was stained with $KMnO_4$, and a bright yellow spot was detected after 10 min at room temperature; R_f = 0.5 (PE:EA = 40:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.31 (m, 5H), 5.17 (AB q, J = 12.5 Hz, 2H), 3.37 (dd, J = 5.9 Hz, J = 7.9 Hz, 1H), 1.93−1.79 (m, 2H), 1.06−1.02 (m, 24H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.6, 135.7, 128.5, 128.2, 128.0, 103.8, 84.4, 66.8, 60.6, 26.0, 18.6, 11.4, 11.2; IR (film) 2943, 2866, 2176, 1745, 1463, 1165, 998, 883 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{35}O_2Si$ $[(M + H)^+]$ 359.2401, found: 359.2400.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01592.

^1H and ^{13}C spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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