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Metal-free synthesis of ynones via direct C–H alkynylation of aldehydes with ethynylbenziodoxolones

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ABSTRACT

A metal-free synthesis of ynones via direct alkynlyation of C–H bonds in aldehydes with ethynylbenziodoxolones is described. A variety of unactivated aldehydes undergo this transformation, affording ynones in good yields. These ynones could be further transformed into important heterocycles without purification.

1. Introduction

Alkynones are abundant structural motifs found in numerous biologically active molecules.[1] More importantly, they are often employed as important key intermediates in the organic synthesis. They are precursors to valuable organic functional groups, such as pyrimidines,[2] quinolones,[3] furans,[4] pyrazoles,[5] pyrroles,[6] isoxazoles,[7] benzodiazepines,[8] flavones,[9] oximes,[10] chiral propargylic alcohols.[11] Therefore, developing new strategies for the synthesis of ynones is of significance.

Several approaches have been reported for the preparation of ynones. Classical methods involve the addition of acetylide anion to aldehydes followed by further oxidization (Scheme 1, Eq. 1),[12] transition metal-catalyzed Sonogashira coupling of terminal alkynes with activated carboxylic acid derivatives, or carbonylative Sonogashira coupling of alkynes with aryl halides (Scheme 1, Eq. 2).[1b,2b–d,13] Other methods, including Au-catalyzed decarbonylative alkynylation of aldehydes with ethynylbenziodoxolones,[14] Lewis acid-promoted alkynylation of acyl chlorides with alkynyltrifluoroborate salts,[15] homogeneous gold-catalyzed Meyer–Schuster rearrangement of propargylicpivalates followed by oxidation,[16] have also been reported. Very recently, Zhou et al. developed the first Rh(III)- or Ir(III)- catalyzed direct alkynylation from aldehydes via chelation-assisted C–H bond activation with suitable directing group for the synthesis of ynones (Scheme 1, Eq. 3).[17] However, the largest part of these methods required the use of transition metals. To avoid the drawbacks of metal usage such as toxicity and heavy transition metal impurities in final products, the development of transition-metal-free cross-coupling reactions is of special importance. In view of previous successful radical-induced alkynylation reactions of ethynylbenziodoxolones,[18] we envisioned that acyl radicals generated from aldehydes could be trapped by suitable alkynylating reagents, providing an efficient synthesis of ynones from easily available aldehydes. Herein, we describe a metal-free direct alkynylation of common aldehydes with ethynylbenziodoxolones to afford ynones (Scheme 1, Eq. 4).[19]

2. Results and discussion

Initially, benzaldehyde and 1-[(tri*iso*propylsilyl)-ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) (**2a**) were utilized to optimize the reaction conditions. With *tert*-butylhydroperoxide (TBHP) as the initiator, the desired product **3a** was isolated in 56% yield (Table 1, entry 1). Then, several solvents were tested, but the yield got no further increase (Table 1, entries 2–4). When the reaction temperature was raised to 100 °C with the reaction time shortened to 12 h, the yield increased to 61% (Table 1, entries 1, 5–7). Several different initiators were also screened in an effort to promote the reaction. Unfortunately, these initiators were not effective (Table 1, entries 8–10). After optimization of the ratio of **1a** and **2a**, we are pleased to obtain the desired product in 80% yield (Table 1, entry 16).

The substrate scope was subsequently investigated under the optimized conditions. First, various substituted aldehydes were applied to the direct coupling with TIPS-EBX. As shown in Fig. 1, various benzaldehydes bearing electron-donating (**3b**–**3d**, **3i**–**3j**, **3l**, **3n**, **3o**) and electron-withdrawing (**3e**–**3h**, **3k**) substituents at different positions furnished the corresponding ynones in moderate to good yields, and the electron-donating substituents resulted

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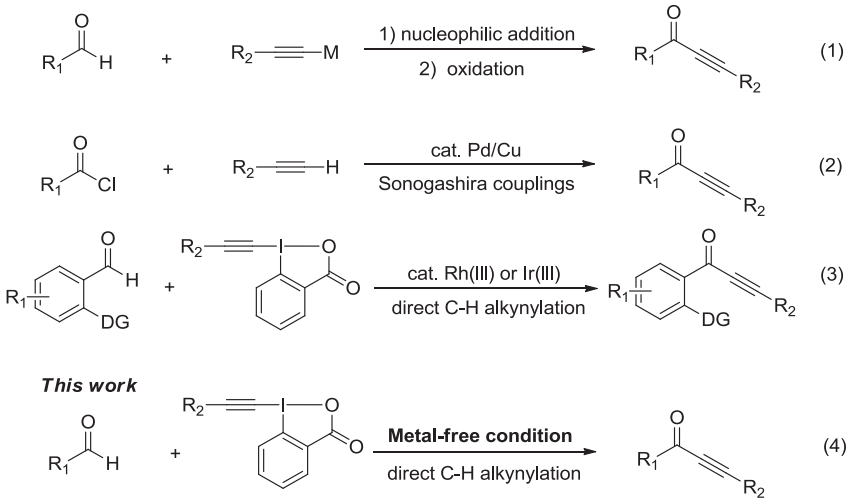
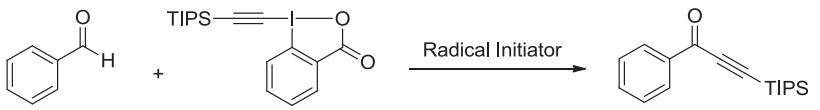


Scheme 1. Methods for the synthesis of ynones.

Table 1
Optimization of reaction conditions[a]



1a **2a** **3a**

Entry	**1a**:**2a** (equiv)	Initiators (equiv)	Solvent	t (h)/T (°C)	Yield (%)[b]
1	4:1	TBHP (4)	DCE	24/80	56
2	4:1	TBHP (4)	MeCN	24/80	53
3	4:1	TBHP (4)	Toluene	24/80	18
4	4:1	TBHP (4)	1,4-Dioxane	24/80	18
5	4:1	TBHP (4)	DCE	12/80	41
6	4:1	TBHP (4)	DCE	24/100	46
7	4:1	TBHP (4)	DCE	12/100	61
8	4:1	DTBP (4)	DCE	12/100	40
9	4:1	*m*-CPBA (4)	DCE	12/100	Trace
10	4:1	H_2O_2 (4)	DCE	12/100	13
11	4:1	TBHP (3)	DCE	12/100	58
12	4:1	TBHP (5)	DCE	12/100	59
13	2:1	TBHP (2)	DCE	12/100	51
14	1:2	TBHP (2)	DCE	12/100	53
15	1:3	TBHP (2)	DCE	12/100	75
16	1:3	TBHP (3)	DCE	12/100	80

[a] All reactions were carried out on a 0.2 mmol scale in 1 mL of solvent under an argon atmosphere. TBHP (anhydrous, 5.5 M in decane) was used.
[b] Yield of isolated product.

in comparatively better yields. The reaction was not sensitive to steric effects. High yields were observed for both *para*- and *ortho*-substituted benzaldehydes derivatives (**3b** vs **3j**). To our delight, the phenolic hydroxyl group was survived in this transformation under oxidation conditions (**3l**). Subsequently, we found that other aromatic aldehydes (**3m**, **3p**, **3q**, **3r**), such as 2-naphthaldehyde, thiophene-2-carbaldehyde, thiophene-3-carbaldehyde, picolinaldehyde, etc. were also suitable for this transformation. Interestingly, unprotected 1*H*-indole-3-carbaldehyde was also good substrate for this coupling reaction (**3s**), providing a convenient synthetic method for important indole derivatives.

Several ethynylbenziodoxolones were then prepared[20] to widen the reaction scope. As shown in Fig. 2, most of the corresponding products were obtained in moderate to good yields. In addition to silyl substituted EBX reagents, aryl and alkyl substituted EBX reagents were also good substrates for this transformation.

Addtionally, the reaction could be carried out smoothly on water affording product **3a** in moderate yield (Scheme 2). It is worth mentioning that a series of benzyl alcohols could afford ynones through oxidation/alkynylation cascade reaction (Scheme 3). Moreover, we performed one-pot syntheses of pyrazoles starting from inexpensive readily available aldehydes. Here, tosylhydrazide or phenylhydrazine was added after the coupling reaction without isolation of ynones, and pyrazole products were successfully obtained in good yield (Scheme 4).[5]

To investigate the mechanism, a series of controlled experiments were conducted (Scheme 5). The addition of radical scavenger 2, 2, 6, 6-tetramethylpiperidine *N*-oxide (TEMPO) or 1, 1-diphenylethylene decreased the yield of the model reaction obviously. This results indicate that this reaction most likely proceeds via a radical pathway, and the reaction may proceed through a similar mechanism as proposed in our previous work.[18a] Firstly, the benzoyl radicals are generated from aldehydes in the presence of TBHP. Then, the addition of the radical species to the triple bond forms new radical intermediates (Scheme 6, **B**). Subsequently, β-elimination of the adduct radicals occurs to afford the final product with the formation of a benziodoxolonyl radical, which is further transformed to 2-iodobenzoic acid via a reduction-protonation sequence (see Scheme 6).

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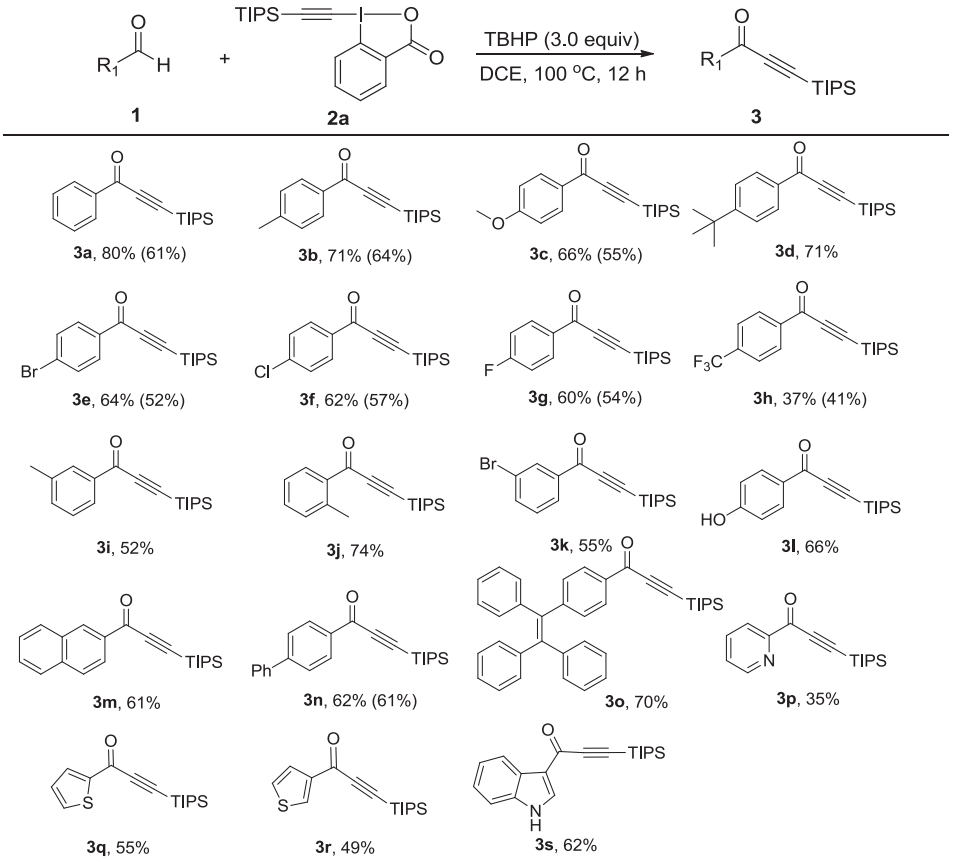
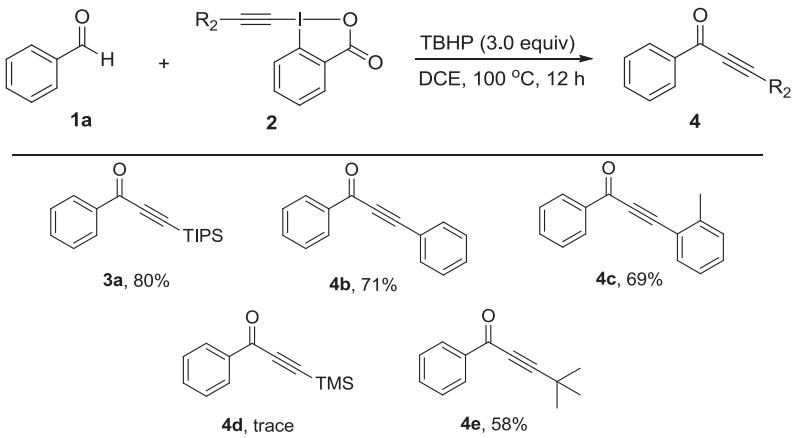


[a] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv), TBHP (anhydrous, 5.5 M in decane, 3.0 equiv) , DCE (1 mL) under an argon atmosphere at 100 °C for 12 h. [b] Yield of isolated product. [C] Number in parentheses is the yield of isolated product under the reaction conditions of **2a** (0.2 mmol), **1** (4.0 equiv), TBHP (anhydrous, 5.5 M in decane, 4.0 equiv), DCE (1 mL) under an argon atmosphere at 100 °C for 12 h.

Fig. 1. Scope of aldehydes **1**.[a]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (3.0 equiv), TBHP (anhydrous, 5.5 M in decane, 3.0 equiv) , DCE (1 mL) under an argon atmosphere at 100 °C for 12 h.
[b] Yield of isolated product.

Fig. 2. Scope of ethynylbenziodoxolones **2**.[a]

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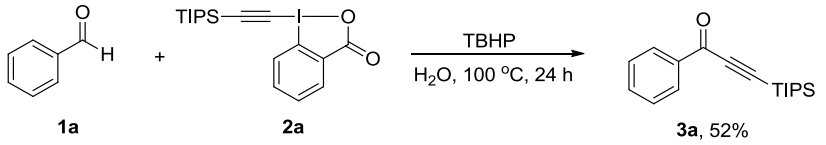
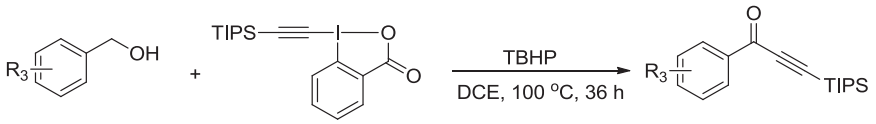
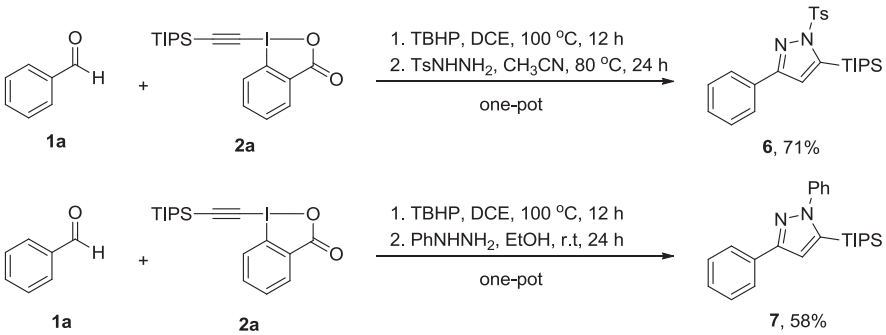


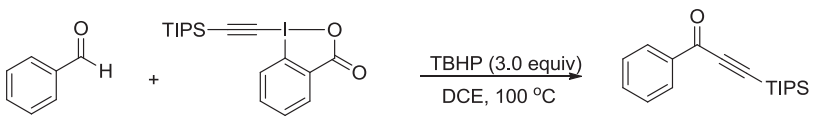
Scheme 2. The synthesis of ynone on water.



Scheme 3. Oxidation/alkynylation cascade reaction for the synthesis of ynones.

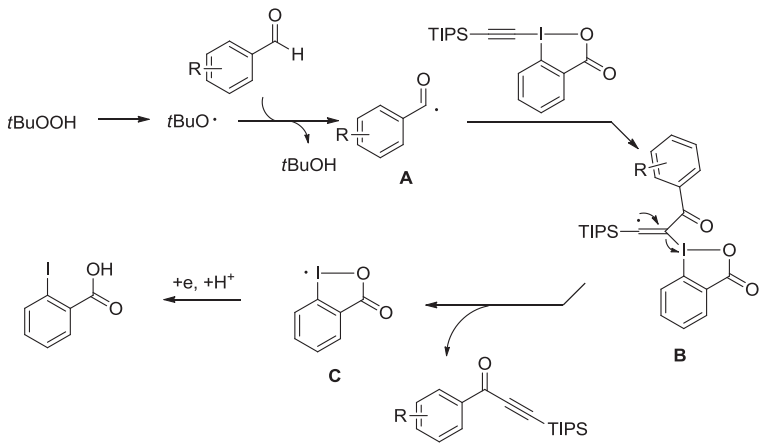


Scheme 4. One-pot synthesis of pyrazoles from aldehydes with ethynylbenziodoxolones.



TEMPO	(1.0 equiv)	32 %
TEMPO	(3.0 equiv)	n.d
1,1-Diphenylethylene	(1.0 equiv)	43 %
1,1-Diphenylethylene	(3.0 equiv)	trace

Scheme 5. The radical inhibition experiments.



Scheme 6. Proposed reaction mechanism.

3. Conclusion

In conclusion, we have developed a simple and convenient metal-free synthesis of ynones from readily available starting materials under mild conditions. The reaction proceeds via direct C–H alkynylation with ethynylbenziodoxolones. A series of (hetero) aromatic aldehydes were alkynylated smoothly to provide targets ynones in moderate to good yields. Based on the control experiments, a radical mechanism was proposed. Here, our work represents a worthy supplement and development over existing methods for the synthesis of the valuable ynones.

4. Experimental section

4.1. General information

^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) with $CDCl_3$ as solvent and recorded in parts per million (ppm) relative to internal tetramethylsilane (TMS) standard. ESI-MS spectral data were recorded on a Finnigan LCQDECA mass spectrometer. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Ethynylbenziodoxolones were prepared according to the literature procedure.

4.2. General procedure for ynones

In a sealed 25 mL Schlenk tube equipped with a magnetic stir bar were added aldehydes (0.2 mmol), ethynylbenziodoxolones (0.6 mmol, 3.0 equiv), TBHP (anhydrous, 5.5 M in decane, 3.0 equiv), DCE (1 mL), and the reaction mixture was heated under argon atmosphere at 100 °C for 12 h. Then, the reaction mixture was allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL). The organic layer was separated and dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, GC–MS and HRMS.

*4.2.1. 1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-one (**3a**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.17 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.47 (m, 2H), 1.17–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.70, 136.88, 134.21, 129.70, 128.73, 103.17, 98.20, 18.72, 11.25. HRMS (ESI) calcd for $C_{18}H_{27}OSi^+$ $[M+H]^+$: 287.1826, found: 287.1835.

*4.2.2. 1-(p-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.06 (m, 2H), 7.30–7.28 (m, 2H), 2.43 (s, 3H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.42, 145.29, 134.68, 129.84, 129.46, 103.35, 97.53, 21.95, 18.72, 11.28. HRMS (ESI) calcd for $C_{19}H_{29}OSi^+$ $[M+H]^+$: 301.1982, found: 301.1978.

*4.2.3. 1-(4-Methoxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3c**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.13 (m, 2H), 6.97–6.95 (m, 2H), 3.89 (s, 3H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.37, 164.56, 132.09, 130.36, 113.98, 103.33, 97.05, 55.74, 18.73, 11.26. HRMS (ESI) calcd for $C_{19}H_{29}O_2Si^+$ $[M+H]^+$: 317.1931, found: 317.1940.

*4.2.4. 1-(4-(tert-Butyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3d**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.10 (m, 2H), 7.52–7.50 (m, 2H), 1.35 (s, 9H), 1.17–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.38, 158.20, 134.50, 129.70, 125.74, 103.35, 97.46, 35.44, 31.21, 18.73, 11.27. HRMS (ESI) calcd for $C_{22}H_{35}OSi^+$ $[M+H]^+$: 343.2452, found: 343.2455.

*4.2.5. 1-(4-Bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3e**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H), 7.65–7.63 (m, 2H), 1.16–1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.55, 135.68, 132.11, 131.04, 129.69, 102.74, 99.07, 26.74, 18.70, 11.21. HRMS (ESI) calcd for $C_{18}H_{25}BrNaOSi^+$ $[M+Na]^+$: 387.0750, found: 387.0748.

*4.2.6. 1-(4-Chlorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3f**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.09 (m, 2H), 7.48–7.46 (m, 2H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.35, 140.84, 135.33, 130.97, 129.13, 102.82, 99.98, 26.75, 18.71, 11.25. HRMS (ESI) calcd for $C_{18}H_{26}ClOSi^+$ $[M+H]^+$: 321.1436, found: 321.1442.

*4.2.7. 1-(4-Fluorophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3g**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.18 (m, 2H), 7.18–7.14 (m, 2H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.07, 166.57 (d, J=254.8 Hz), 133.42, 132.33 (d, J=9.6 Hz), 115.98 (d, J=22.2 Hz), 102.86, 98.59, 26.74, 18.71, 11.23. HRMS (ESI) calcd for $C_{18}H_{25}FNaOSi^+$ $[M+Na]^+$: 327.1551, found: 327.1556.

*4.2.8. 1-(4-(Trifluoromethyl)phenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3h**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.27 (m, 2H), 7.78–7.76 (m, 2H), 1.17–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.39, 139.34, 135.47 (t, J=32.2 Hz), 129.92, 125.86 (q, J=3.6 Hz), 123.67 (d, J=271.0 Hz), 102.67, 100.11, 18.71, 11.23. HRMS (ESI) calcd for $C_{19}H_{26}F_3OSi^+$ $[M+H]^+$: 355.1700, found: 355.1695.

*4.2.9. 1-(m-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3i**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.97 (m, 2H), 7.43–7.36 (m, 2H), 2.42 (s, 3H), 1.17–1.16 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.91, 138.55, 136.93, 135.01, 130.21, 128.62, 127.05, 103.29, 97.96, 21.42, 18.72, 11.26. HRMS (ESI) calcd for $C_{19}H_{28}NaOSi^+$ $[M+Na]^+$: 323.1802, found: 323.1804.

*4.2.10. 1-(o-Tolyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3j**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.28 (m, 1H), 7.47–7.43 (m, 1H), 7.35–7.31 (m, 1H), 7.26–7.24 (m, 1H), 2.64 (s, 3H), 1.15–1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.41, 140.81, 135.51, 133.58, 133.03, 132.27, 125.97, 104.62, 94.46, 22.16, 18.72, 11.26. HRMS (ESI) calcd for $C_{19}H_{28}NaOSi^+$ $[M+Na]^+$: 323.1802, found: 323.1801.

*4.2.11. 1-(3-Bromophenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3k**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.32 (m, 1H), 8.10–8.08 (m, 1H), 7.75–7.72 (m, 1H), 7.39–7.36 (m, 1H), 1.17–1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.13, 138.57, 136.96, 132.77, 130.33, 128.07, 122.98, 102.59, 99.65, 18.71, 11.23. HRMS (ESI) calcd for $C_{18}H_{26}BrOSi^+$ $[M+H]^+$: 365.0931, found: 365.0939.

*4.2.12. 1-(4-Hydroxyphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3l**).* White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.10 (m, 2H), 6.57 (s, 2H), 1.14–1.13 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.49, 162.85, 132.83, 129.50, 115.96, 103.04, 99.11, 18.66, 11.21. HRMS (ESI) calcd for $C_{18}H_{26}NaO_2Si^+$ $[M+Na]^+$: 325.1594, found: 325.1604.

*4.2.13. 1-(Naphthalen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3m**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80–8.79 (m, 1H), 8.17–8.15 (m, 1H), 7.97–7.95 (m, 1H), 7.92–7.89 (m, 2H), 7.65–7.56 (m, 2H), 1.21–1.20 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.65, 136.27, 134.50, 133.22, 132.52, 130.00, 129.18, 128.62, 128.05, 127.09, 123.93, 103.30, 98.15, 18.77, 11.30. HRMS (ESI) calcd for $C_{22}H_{29}OSi^+$ $[M+H]^+$: 337.1982, found: 337.1991.

*4.2.14. 1-([1,1′-Biphenyl]-4-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3n**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.24 (m, 2H),

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7.73–7.71 (m, 2H), 7.66–7.64 (m, 2H), 7.50–7.46 (m, 2H), 7.43–7.40 (m, 1H), 1.18–1.17 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.27, 146.89, 139.86, 135.75, 130.29, 129.13, 128.56, 127.47, 127.39, 103.27, 98.16, 18.74, 11.26. HRMS (ESI) calcd for $C_{24}H_{31}OSi^+$ $[M+H]^+$: 363.2139, found: 363.2144.

*4.2.15. 3-(Triisopropylsilyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)prop-2-yn-1-one (**3o**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.89 (m, 2H), 7.12–7.11 (m, 11H), 7.04–7.00 (m, 6H), 1.14–1.13 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.16, 150.32, 143.28, 143.16, 143.12, 139.94, 134.85, 131.65, 131.45, 131.39, 129.18, 128.07, 128.05, 127.86, 127.18, 126.98, 126.95, 103.37, 97.70, 29.85, 18.72, 11.27. HRMS (ESI) calcd for $C_{38}H_{41}OSi^+$ $[M+H]^+$: 541.2921, found: 541.2922.

*4.2.16. 1-(Pyridin-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3p**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78–8.77 (m, 1H), 8.17–8.15 (m, 1H), 7.87–7.84 (m, 1H), 7.50–7.47 (m, 1H), 1.17–1.16 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.46, 153.20, 150.21, 136.97, 127.44, 124.06, 103.85, 100.95, 18.70, 11.29. HRMS (ESI) calcd for $C_{17}H_{26}NOSi^+$ $[M+H]^+$: 288.1778, found: 288.1787.

*4.2.17. 1-(Thiophen-2-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3q**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.93 (m, 1H), 7.71–7.69 (m, 1H), 7.17–7.15 (m, 1H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.40, 145.15, 135.33, 135.10, 128.49, 102.79, 96.71, 18.71, 11.24. HRMS (ESI) calcd for $C_{16}H_{25}OSSi^+$ $[M+H]^+$: 293.1390, found: 293.1392.

*4.2.18. 1-(Thiophen-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3r**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.27 (m, 1H), 7.63–7.62 (m, 1H), 7.34–7.32 (m, 1H), 1.17–1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ171.06, 143.16, 135.52, 126.92, 103.74, 96.08, 18.72, 11.24. HRMS (ESI) calcd for $C_{16}H_{25}OSSi^+$ $[M+H]^+$: 293.1390, found: 293.1397.

*4.2.19. 1-(1H-Indol-3-yl)-3-(triisopropylsilyl)prop-2-yn-1-one (**3s**).* White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.42–8.40 (m, 1H), 8.09–8.08 (m, 1H), 7.46–7.44 (m, 1H), 7.31–7.29 (m, 2H), 1.14–1.13 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.87, 136.81, 135.46, 125.12, 124.34, 123.24, 122.50, 120.14, 111.82, 104.47, 91.93, 18.75, 11.29. HRMS (ESI) calcd for $C_{20}H_{28}NOSi^+$ $[M+H]^+$: 326.1935, found: 326.1937.

*4.2.20. 1,3-Diphenylprop-2-yn-1-one (**4b**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.22 (m, 2H), 7.70–7.62 (m, 3H), 7.54–7.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.18, 137.06, 134.27, 133.23, 130.95, 129.74, 128.84, 128.78, 120.30, 93.26, 87.04. HRMS (ESI) calcd for $C_{15}H_{11}O^+$ $[M+H]^+$: 207.0804, found: 207.0806.

*4.2.21. 1-Phenyl-3-(o-tolyl)prop-2-yn-1-one (**4c**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.23 (m, 2H), 7.67–7.62 (m, 2H), 7.55–7.51 (m, 2H), 7.38–7.36 (m, 1H), 7.31–7.29 (m, 1H), 7.26–7.24 (m, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.21, 142.33, 137.20, 134.18, 133.82, 130.95, 130.03, 129.70, 128.78, 126.09, 120.17, 92.32, 90.91, 21.04. HRMS (ESI) calcd for $C_{16}H_{13}O^+$ $[M+H]^+$: 221.0961, found: 221.0964.

*4.2.22. 4,4-Dimethyl-1-phenylpent-2-yn-1-one (**4e**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.11 (m, 2H), 7.62–7.58 (m, 1H), 7.50–7.46 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.55, 133.95, 130.16, 129.67, 128.62, 104.15, 78.27, 30.33, 26.44. HRMS (ESI) calcd for $C_{13}H_{15}O^+$ $[M+H]^+$: 187.1117, found: 187.1116.

*4.2.23. 3-Phenyl-1-tosyl-5-(triisopropylsilyl)-1H-pyrazole (**6**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.87–7.82 (m, 4H), 7.37–7.36 (m, 3H), 7.32–7.29 (m, 2H), 2.40 (s, 3H), 1.39 (s, 9H), 1.16–1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.43, 136.06, 135.76, 133.75, 130.27, 129.88, 128.58, 127.98, 126.67, 110.12, 94.14, 21.73, 18.78, 11.17. HRMS (ESI) calcd for $C_{25}H_{35}N_2O_2SSi^+$ $[M+H]^+$: 455.2183, found: 455.2184.

*4.2.24. 1,3-Diphenyl-5-(triisopropylsilyl)-1H-pyrazole (**7**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.96–7.94 (m, 2H), 7.42–7.38 (m, 2H), 7.34–7.30 (m, 3H), 7.19–7.17 (m, 2H), 6.96–6.92 (m, 1H), 1.24–1.21 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.69, 135.68, 129.55, 128.51, 128.22, 126.12, 125.49, 121.17, 113.48, 107.70, 96.16, 18.90, 11.32. HRMS (ESI) calcd for $C_{24}H_{32}N_2NaSi^+$ $[M+Na]^+$: 399.2227, found: 399.2231.

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Supplementary data

Supplementary data (The detailed experimental procedures and compounds characterization can be found in the online version) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.06.091.

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