Silver-Promoted Oxidative Ring Opening/Alkynylation of Cyclopropanols: Facile Synthesis of 4-Yn-1-ones

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Abstract
A new silver-promoted oxidative ring opening/alkynylation of cyclopropanols with ethynylbenziodoxolones (EBX) is described. This method enables the formation of alkylated alkynes via a sequence of ring opening and alkynylation. Control experiments support a radical mechanism in this silver-promoted method.

Key words silver, ring opening, alkynylation, cyclopropanol, alkyne

Alkynes are common and versatile building blocks with wide application in synthesis.1 Therefore, the development of new efficient methods for their synthesis continues to receive the attention of synthetic chemists.1-3 Although the Sonogashira cross-coupling reaction, 2,3 which starts from aryl or alkenyl halides and terminal alkynes, is well-established for the incorporation of alkyne moieties into organic molecules, the synthesis of aliphatic alkynes from alkyl electrophiles remains a formidable challenge.3 For example, the Fu group has extended the Sonogashira cross-coupling reaction to the use of primary alkyl halides as the electrophile.3a The Hu group has also reported an efficient nickel-catalyzed Sonogashira cross-coupling of alkyl halides for the construction of alkylated alkynes.3b,c However, the majority of these transformations require a copper cocatalyst, base, and a ligand to improve the yield. To overcome these disadvantages, the development of new electrophilic alkynylation reagents, particularly with special reaction characteristics for the formation of the C(sp)–C(sp3) bond, have gained wide interest in the past decade.4,5 Typically, attractive electrophilic alkynylation reagents include ethynylbenziodoxolones (EBX),4 which are appealing alkynylation reagents for the construction of diverse ynones molecules by C-alkynylation with aldehydes.

Herein, we report a new oxidative ring opening/alkynylation of cyclopropanols with ethynylbenziodoxolones for the synthesis of alkylated alkynes using a combination of silver(I) nitrate and potassium persulfate as the catalytic system (Scheme 1);6 this method allows selective radical cleavage of the C–C bond in a wide range of cyclopropanols7 by various terminal alkynes, including aryl- and alkyl-substituted alkynes, and represents a mild and practical route for the assembly of alkylated alkynes.8

We began our study by investigating the reaction between 1-(4-methoxyphenyl)cyclopropan-1-ol (1a) and 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-one (2a, Ph-EBX) to optimize the reaction conditions (Table 1). The results demonstrated that the ring opening/alkynylation reaction occurred in the presence of silver(I) nitrate alone and it enabled the formation of the desired product 3aa in 33% yield (entry 1). Gratifyingly, the addition of oxidants, such as potassium persulfate, sodium persulfate, ammonium persulfate, and dibenzoyl peroxide (BPO), improved the yield of 3aa (entries 2–5), and potassium persulfate showed the most reactivity. Identical results to those obtained using two equivalents of potassium persulfate were obtained when using three equivalents of potassium persulfate (cf. entries 2 and 6). A number of other silver catalysts (entries 7–10), including silver(I) acetate, tetrafluoroborate, triflate, and carbonate, also had high catalytic activity in this reaction, but they were less effective than silver(I) nitrate. We found that the amount of silver(I) nitrate used also affected
the reaction result: using 30 mol% of silver(I) nitrate did not improve the yield compared to the use of 20 mol% of silver(I) nitrate (entry 11), but using 10 mol% of silver(I) nitrate reduced the yield to 60% (entry 12). Surprisingly, the reaction took place in the absence of a silver salt, albeit with lower yield (45%) (entry 13). A similar yield (49%) of 3aa was isolated when three equivalents of potassium persulfate were used in the absence of silver(I) nitrate (entry 14). The results suggest that silver(I) nitrate may play two roles, both as a accelerator and an oxidant. The use of other solvents, dichloromethane–water, 1,2-dichloroethane, acetone, tetrahydrofuran, and N,N-dimethylformamide, was also examined, but the yields of 3aa were lower than with dichloromethane (entries 15–19). Screening the effects of the reaction temperature revealed that a reaction temperature of 30 °C gave optimal results (entries 2, 20, and 21).

With the optimal conditions in hand, we set out to investigate the scope and limitations of this oxidative ring opening/alkynylation protocol with regard to cyclopropanols 1 and 1-(substituted ethynyl)-1,2-benziodoxol-3(1H)-one 2 (Tables 2 and 3). As shown in Table 2, a variety of 1-(arylthynyl)-1,2-benziodoxol-3(1H)-ones 2b–h and 1-(3,3-dimethylbut-1-ynyl)-1,2-benziodoxol-3(1H)-one (2i) were viable for the construction of the corresponding alkyne 3ab–ai in moderate to good yields, however, 1-[(trimethylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one (2j; TMS-EBX) did not give 3aj. Using 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-ones 2b–h, several substituents, such as Me, Br, CN, Ac, and Ph groups, on the phenyl ring attached to the acetylene were well tolerated giving products 3ab–ah. For example, 1-(p-tolylethynyl)-1,2-benziodoxol-3(1H)-one (2b) gave 3ab in 70% yield. 1-(4-Cyanophenylethynyl)-1,2-benziodoxol-3(1H)-one (2f) and 1-(3-acetylphenylethynyl)-1,2-benziodoxol-3(1H)-one (2g) with a para-cyano or para-acetyl group were also converted into products 3af and 3ag in moderate yields. Importantly, bromo-substituted 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-ones 2c–e utilized under the optimal conditions gave bromo-substituted products 3ac–ae that could undergo subsequent modifications at the halogenated positions. In the case of 1-(biphenyl-2-ylethynyl)-1,2-benziodoxol-3(1H)-one (2h) containing an ortho phenyl group the desired product 3ah was obtained in 51% yield. We found that the optimal conditions were compatible with 1-(3,3-dimethylbut-1-ynyl)-1,2-benziodoxol-3(1H)-ones (2i) giving product 3ai in moderate yield.

The optimal conditions were applicable to a wide range of cyclopropanols, namely 1-arylcyclopropanols 1b–i and 1-alkylcyclopropanols 1j–m (Table 3). Initially, a variety of 1-arylcyclopropanols 1b–f were investigated in the presence of 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-one (2a), silver(I) nitrate, and potassium persulfate. We found that several substituents, such as OMe, Cl, F, and CF3, were tolerated on the phenyl ring. 1-Phenylcyclopropanol (1b) displayed high reactivity and furnished the desired product 3ba in 78% yield. A substrate containing a bulky ortho group, 2-methoxybenzyl-substituted cyclopropanol 1c, gave 3ca in moderate (60%) yield. Using 4-chlorophenyl-, 4-fluorophenyl-, and 4-(trifluoromethyl)benzyl-substituted cyclopropanols 1d–f gave 3da–fa in 72%, 75%, and 53% yields, respectively. The reaction was applicable to heterocycle-containing substrates 1g and 1h, and successfully delivered products 3ga and 3ha in good yields. We were pleased to find that 1-(4-methoxyphenyl)-2-pentylcyclopropan-1-ol (1i) was a suitable substrate and it successfully gave product 3ia. The optimal conditions were compatible with 1-alkylcyclopropanols 1j–l, even bulky 1-[(1-adaman-

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**Table 1** Optimization of the Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Ag] (mol%)</th>
<th>[O] (equiv)</th>
<th>Solvent</th>
<th>Yield (b) (%)</th>
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<tr>
<td>1</td>
<td>AgNO3 (20)</td>
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<td>CH2Cl2</td>
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<td>2</td>
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<td>CH2Cl2</td>
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<td>4</td>
<td>AgNO3 (20)</td>
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<td>5</td>
<td>AgNO3 (20)</td>
<td>BPO (2)</td>
<td>CH2Cl2</td>
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<td>6</td>
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<tr>
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<td>53</td>
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<td>8</td>
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<td>20</td>
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<td>CH2Cl2</td>
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<td>13</td>
<td>–</td>
<td>K2S2O8 (2)</td>
<td>CH2Cl2</td>
<td>45</td>
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<td>14</td>
<td>–</td>
<td>K2S2O8 (3)</td>
<td>CH2Cl2</td>
<td>49</td>
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<td>15*</td>
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<td>CH2Cl2/H2O</td>
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<td>DCE</td>
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<td>67</td>
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<td>21*</td>
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<td>K2S2O8 (2)</td>
<td>CH2Cl2</td>
<td>62</td>
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*Reaction conditions: 1a (0.3 mmol), 2a (1.5 equiv), [Ag], oxidant, solvent (1 mL), 30 °C, under argon, 16 h.

b Isolated yield.

c CH2Cl2–H2O (1:1).

d At r.t.

e At 40 °C.
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Table 2 Variation of the Ethynylbenziodoxolone 2

<table>
<thead>
<tr>
<th>R3</th>
<th>Additive</th>
<th>Yield</th>
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<tr>
<td>MeO</td>
<td>TEMPO</td>
<td>trace</td>
</tr>
<tr>
<td>MeO</td>
<td>2,6-di-tert-butyl-4-methylphenol (BHT)</td>
<td>trace</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3aa 70%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3ab 73%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3ac 69%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3af 63%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3ag 69%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3ah 51%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3ai 50%</td>
</tr>
<tr>
<td>MeO</td>
<td>AgNO3, K2S2O8</td>
<td>3aj trace</td>
</tr>
</tbody>
</table>

As shown in Scheme 2, the reaction of cyclopropanol 1a with 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-one (2a) was completely suppressed when using a stoichiometric amount of radical inhibitor (3 equiv), including 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT). The results suggest that this reaction involves a free radical process.

Therefore, the proposed mechanism outlined in Scheme 2 for this ring opening of cyclopropanols 1 by silver(I) nitrate and potassium persulfate begins by the formation of the alkyl radical intermediate A. The addition of intermedi-
ate A to the C≡C bond in 2 produces the vinyl radical intermediate B, followed by C–I bond cleavage by single-electron transfer and this is followed by β-elimination to give the desired products 3 and radical C. Within this process, silver salts might play at least two roles: as the catalyst to initiate the formation of the radical intermediate A and as Lewis acid to stabilize the radical intermediates.

In summary, we have developed a new silver-promoted oxidative ring opening/alkynylation of cyclopropanols with ethynylbenziodoxolones for the synthesis of alkylated alkenes in the presence of potassium persulfate. In this method, both silver(I) nitrate and potassium persulfate have two roles as catalysts and oxidants, thus achieving ring opening and alkynylation with broad substrate scope and excellent selectivity.

NMR spectroscopy was performed on a Bruker advanced spectrometer operating at 400 MHz (1H NMR) and 100 MHz (13C NMR) or 500 MHz (1H NMR) and 125 MHz (13C NMR). MS analysis was performed on GC-MS analysis (Shimazu GCMS-QP2010) and ESI-Q-TOF (Bruker MicroQTOF-II). All melting points are uncorrected.

Silver-Promoted Oxidative Ring Opening/Alkynylation of Cyclopropanols; Typical Procedure

To a Schlenk tube were added 1 (0.3 mmol), 2a (1.5 equiv), AgNO₃ (20 mol%), K₂S₂O₈ (2 equiv), CH₂Cl₂ (1 mL), 30 °C, under argon, 16 h. The reaction was charged with argon (1 atm) and stirred at 30 °C for 16 h until complete consumption of the starting material (TLC monitoring). When the reaction had finished, the mixture was washed with aq sat. NaHCO₃. The aqueous phase was re-extracted with CH₂Cl₂. The combined organic extracts were dried (Na₂SO₄), concentrated under vacuum, and the resulting residue was purified by column chromatography (silica gel, hexane–EtOAc) to afford the desired product.

1-(4-Methoxyphenyl)-5-phenylpent-4-yn-1-one (3aa)
White solid; yield: 64.2 mg (81%); mp 52.9–54.0 °C.
IR (KBr): 1677 cm⁻¹.
1H NMR (400 MHz, CDCl₃): δ = 7.96 (d, J = 8.8 Hz, 2 H), 7.39–7.37 (m, 2 H), 7.26–7.25 (m, 3 H), 6.93 (d, J = 8.8 Hz, 2 H), 3.84 (s, 3 H), 3.27–3.23 (m, 2 H), 2.84–2.81 (m, 2 H).
13C NMR (100 MHz, CDCl₃): δ = 196.4, 163.5, 131.5, 130.2, 129.6, 128.1, 127.6, 123.6, 113.7, 89.0, 80.9, 55.4, 37.4, 14.3.
LR-MS (EI, 70 eV): m/z (%) = 264 (M +, 37), 233 (18), 221 (18), 135 (100).

1-(4-Methoxyphenyl)-5-(p-tolyl)pent-4-yn-1-one (3ab)
White solid; yield: 58.4 mg (70%); mp 72.5–74.2 °C.
IR (KBr): 1675 cm⁻¹.
1H NMR (400 MHz, CDCl₃): δ = 7.97 (d, J = 8.8 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.07 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.28–3.24 (m, 2 H), 2.82 (t, J = 8.0 Hz, 2 H), 2.32 (s, 3 H).

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Variation of the Cyclopropanol 1a</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1O  Ph</td>
<td>3ba, 78%</td>
</tr>
<tr>
<td>R1O  F</td>
<td>3ea, 75%</td>
</tr>
<tr>
<td>R1OH</td>
<td>3ha, 57%</td>
</tr>
<tr>
<td>R1</td>
<td>3ka, 72%</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1 (0.3 mmol), 2a (1.5 equiv), AgNO₃ (20 mol%), K₂S₂O₈ (2 equiv), CH₂Cl₂ (1 mL), 30 °C, under argon, 16 h.
5-(4-Bromophenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ac)
White solid; yield: 74.9 mg (73%); mp 112.6–113.7 °C.

IR (KBr): 3424, 2927, 1669 cm⁻¹.

1H NMR (400 MHz, CDCl 3): δ = 7.97 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.27–3.24 (m, 2 H), 2.87 (t, J = 7.2 Hz, 2 H), 2.84–2.80 (m, 2 H).

13C NMR (100 MHz, CDCl 3): δ = 196.4, 163.5, 137.6, 131.4, 130.2, 129.7, 128.9, 120.5, 113.7, 88.2, 81.0, 55.4, 37.5, 21.4, 14.4.

HRMS (ESI): m/z (%) = 328 (M⁺, 52), 235 (23), 135 (100).

5-(4-Acetylphenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ag)
Yellow liquid; yield: 52.0 mg (51%).

IR (KBr): 1711 cm⁻¹.

1H NMR (400 MHz, CDCl 3): δ = 7.98 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 1 H), 7.41 (d, J = 7.6 Hz, 1 H), 7.21 (t, J = 7.2 Hz, 1 H), 7.11 (t, J = 7.6 Hz, 1 H), 6.94 (d, J = 8.4 Hz, 2 H), 3.87 (s, 3 H), 3.31 (t, J = 7.6 Hz, 2 H), 2.92–2.88 (m, 2 H).

13C NMR (100 MHz, CDCl 3): δ = 196.5, 163.6, 134.4, 130.8, 130.3, 130.1, 129.6 (2 C), 125.7, 122.0, 113.8, 90.6, 79.6, 55.5, 37.2, 14.4.

LR-MS (EI, 70 eV): m/z (%) = 289 (M⁺, 30), 288 (23), 258 (29), 135 (100).


1-(4-Methoxyphenyl)-1,6,6-dimethylhept-4-yn-1-one (3ai)
Colorless liquid; yield: 36.7 mg (50%).

IR (KBr): 1711 cm⁻¹.

1H NMR (400 MHz, CDCl 3): δ = 7.96 (d, J = 8.8 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.14–3.10 (m, 2 H), 2.58–2.55 (m, 2 H), 1.17 (s, 9 H).

13C NMR (100 MHz, CDCl 3): δ = 197.2, 163.5, 130.4, 130.2, 113.7, 89.5, 77.2, 55.5, 38.0, 31.3, 27.3, 14.0.

LR-MS (EI, 70 eV): m/z (%) = 244 (M⁺, 29), 255 (21), 135 (100).


1,5-Diphenylpent-4-yn-1-one (3ba)
White solid; yield: 54.8 mg (78%); mp 57.7–58.7 °C.

IR (KBr): 1685 cm⁻¹.

1H NMR (400 MHz, CDCl 3): δ = 7.99 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 7.39–7.37 (m, 2 H), 7.27–7.25 (m, 3 H), 3.31 (t, J = 7.2 Hz, 2 H), 2.85 (t, J = 7.2 Hz, 2 H).

13C NMR (100 MHz, CDCl 3): δ = 197.9, 136.5, 133.2, 131.5, 128.6, 128.1, 128.0, 127.7, 123.6, 88.8, 81.0, 37.8, 14.3.

LR-MS (EI, 70 eV): m/z (%) = 234 (M⁺, 49), 233 (64), 128 (32), 105 (100), 77 (73).
1-(2-Methoxyphenyl)-6-phenylhex-5-yn-2-one (3ca)
White solid; yield: 57.9 mg (72%); mp 49.8–52.4 °C.
IR (KBr): 1688 cm⁻¹.
¹H NMR (400 MHz, CDCl₃): δ = 7.93 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.38–7.36 (m, 2 H), 7.28–7.26 (m, 3 H), 3.29 (t, J = 8.6 Hz, 2 H), 2.85 (t, J = 7.2 Hz, 2 H).
¹³C NMR (100 MHz, CDCl₃): δ = 196.8, 139.7, 134.9, 131.5, 129.5, 129.0, 128.2, 127.8, 123.5, 88.5, 81.2, 37.8, 14.3.
LR-MS (EI, 70 eV): m/z (%) = 278 (M⁺, 23), 157 (82), 115 (100), 91 (91).

1-(4-Chlorophenyl)-5-phenylpent-4-yn-1-one (3da)
White solid; yield: 48.0 mg (61%); mp 63.4–64.8 °C.
IR (KBr): 1674 cm⁻¹.
¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.58 (m, 1 H), 7.46 (d, J = 1.2 Hz, 1 H), 7.39–7.37 (m, 2 H), 7.27–7.26 (m, 3 H), 6.85 (d, J = 8.0 Hz, 1 H), 6.03 (s, 2 H), 2.82 (t, J = 7.2 Hz, 2 H), 2.82 (t, J = 7.2 Hz, 2 H).
¹³C NMR (100 MHz, CDCl₃): δ = 196.0, 151.8, 148.2, 131.5, 131.4, 128.1, 127.7, 124.3, 123.6, 107.9, 107.8, 101.8, 88.9, 81.0, 37.5, 14.4.
LR-MS (EI, 70 eV): m/z (%) = 278 (M⁺, 53), 277 (41), 235 (20), 149 (100).

1-(Furan-2-yl)-5-phenylpent-4-yn-1-one (3fa)
White yellow liquid; yield: 38.3 mg (57%).
IR (KBr): 1663 cm⁻¹.
¹H NMR (400 MHz, CDCl₃): δ = 7.60 (s, 1 H), 7.38–7.36 (m, 2 H), 7.27–7.24 (m, 4 H), 6.56–6.54 (m, 1 H), 3.17 (t, J = 7.2 Hz, 2 H), 2.83 (t, J = 7.2 Hz, 2 H).
¹³C NMR (100 MHz, CDCl₃): δ = 187.2, 152.5, 146.5, 131.6, 128.2, 127.7, 123.6, 117.3, 112.3, 88.4, 81.2, 37.5, 14.2.
LR-MS (EI, 70 eV): m/z (%) = 224 (M⁺, 54), 223 (100), 181 (75), 167 (64), 128 (54), 95 (63).

1-(4-Fluorophenyl)-5-phenylpent-4-yn-1-one (3ea)
White colorless liquid; yield: 50.1 mg (50%).
IR (KBr): 1680 cm⁻¹.
¹H NMR (400 MHz, CDCl₃): δ = 7.99 (d, J = 8.8 Hz, 2 H), 7.34–7.31 (m, 2 H), 7.26–7.24 (m, 3 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.87 (s, J = 3.3 Hz), 3.32–3.26 (m, 2 H), 3.11–3.04 (m, 1 H), 1.64–1.61 (m, 1 H), 1.56–1.52 (m, 1 H), 1.39–1.23 (m, 6 H), 0.92–0.86 (m, 3 H).
¹³C NMR (100 MHz, CDCl₃): δ = 196.7, 163.5, 131.6, 130.5, 130.2, 128.1, 127.3, 123.8, 113.7, 81.8, 55.5, 43.6, 34.9, 31.6, 28.2, 27.1, 22.6, 14.0.
LR-MS (EI, 70 eV): m/z (%) = 334 (M⁺, 4), 263 (83), 215 (23), 135 (100).

2,7-Diphenylhept-6-yn-3-one (3ja)
White solid; yield: 48.0 mg (61%); mp 63.4–64.8 °C.
IR (KBr): 1690 cm⁻¹.
¹H NMR (400 MHz, CDCl₃): δ = 7.80 (d, J = 8.0 Hz, 2 H), 7.73–7.72 (m, 3 H), 7.28–7.25 (m, 3 H), 3.82 (s, 2 H), 2.82–2.78 (m, 2 H), 2.69–2.65 (m, 2 H).
¹³C NMR (100 MHz, CDCl₃): δ = 205.1, 137.7, 131.5, 129.8, 129.5 (q, J_C-C = 32.3 Hz), 128.2, 127.8, 125.6 (q, J_C-C = 3.8 Hz), 123.8 (q, J_C-C = 251.0 Hz), 123.4, 88.1, 81.2, 49.6, 41.2, 14.0.
¹⁹F NMR (375 MHz, CDCl₃): δ = –62.5.
LR-MS (EI, 70 eV): m/z (%) = 296 (M⁺, 72), 157 (73), 128 (25), 115 (100).

1-Phenylnonadec-1-yn-5-one (3ka)
Light yellow liquid; yield: 52.3 mg (72%).
IR (KBr): 1710 cm⁻¹.

1H NMR (500 MHz, CDCl₃): δ = 7.38–7.36 (m, 2 H), 7.27–7.26 (m, 3 H), 2.74–2.65 (m, 4 H), 2.45 (t, J = 7.5 Hz, 2 H), 1.61–1.57 (m, 2 H), 1.30–1.26 (m, 6 H), 0.89–0.86 (m, 3 H).

13C NMR (100 MHz, CDCl₃): δ = 209.0, 131.5, 128.1, 127.6, 123.6, 88.6, 80.8, 42.8, 41.4, 31.5, 28.8, 23.7, 22.4, 13.9.

LR-MS (EI, 70 eV): m/z (%) = 242 (M⁺, 14), 171 (16), 157 (100), 129 (27), 115 (35).


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Supporting Information
Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560374.

Reference
(c) Diederich, F.; Stang, P. J.; Tykwinski, R. R. Acetylene Chemistry; Chemistry, Biology and Material Science; Wiley-VCH: Weinheim, 2005.
During our preparation for this paper, a very similar report has come out. In this paper, excess amount of AcOH was required to promote the reaction with cyclopropanols. Furthermore, the scope is limited to silyl- and phenyl-substituted alkynes, see: (i) Wang, S.; Guo, L. N.; Wang, H.; Duan, X. H. Org. Lett. 2015, 17, 4798.
