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

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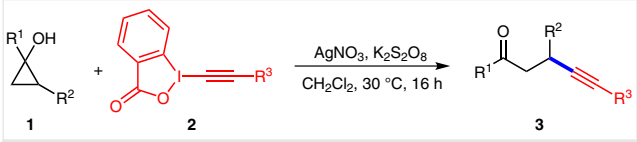
Abstract A new silver-promoted oxidative ring opening/alkynylation of cyclopropanols with ethynylbenziodoxolones (EBX) is described. This method enables the formation of alkylated alkynes via a sequence of ring opening and alkynylation. Control experiments support a radical mechanism in this silver-promoted 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 alkynylating reagents, particularly with special reaction characteristics for the formation of the C(sp)–C(sp^3) bond, have gained wide interest in the past decade.[4,5] Typically, attractive electrophilic alkynylating reagents include ethynylbenziodoxolones (EBX),[4] which are appealing alkynylating reagents for the construction of diverse ynone 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 cyclopropanols[7] by various terminal alkynes, including aryl- and alkyl-substituted alkynes, and represents a mild and practical route for the assembly of alkylated alkynes.[8]



Scheme 1 The ring opening and alkynylation reaction

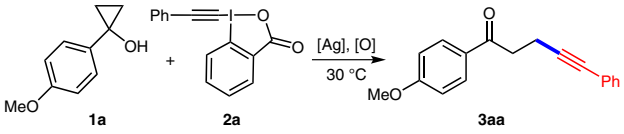
We began our study by investigating the reaction between 1-(4-methoxyphenyl)cyclopropan-1-ol (**1a**) and 1-(phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (**2a**, Ph-EBX) to optimize the reaction conditions (Table 1). The results demonstrated that the ring opening/alkynylation reaction occurred in the 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, acetonitrile, 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(1*H*)-one **2** (Tables 2 and 3). As shown in Table 2, a variety of 1-(arylethynyl)-1,2-benziodoxol-3(1*H*)-ones **2b**–**h** and 1-(3,3-dimethylbut-1-ynyl)-1,2-benziodoxol-3(1*H*)-one (**2i**) were viable for the construction of the corresponding alkynes **3ab**–**ai** in moderate to good yields, however, 1-[(trimethylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (**2j**; TMS-EBX) did not give **3aj**. Using 1-(phenylethynyl)-1,2-benziodoxol-3(1*H*)-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(1*H*)-one (**2b**) gave **3ab** in 70% yield. 1-(4-Cyanophenylethynyl)-1,2-benziodoxol-3(1*H*)-one (**2f**) and 1-(3-acetylphenylethynyl)-1,2-benziodoxol-3(1*H*)-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(1*H*)-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(1*H*)-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(1*H*)-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(1*H*)-one (**2a**), silver(I) nitrate, and potassium persulfate. We found that

Table 1 Optimization of the Reaction Conditions[a]



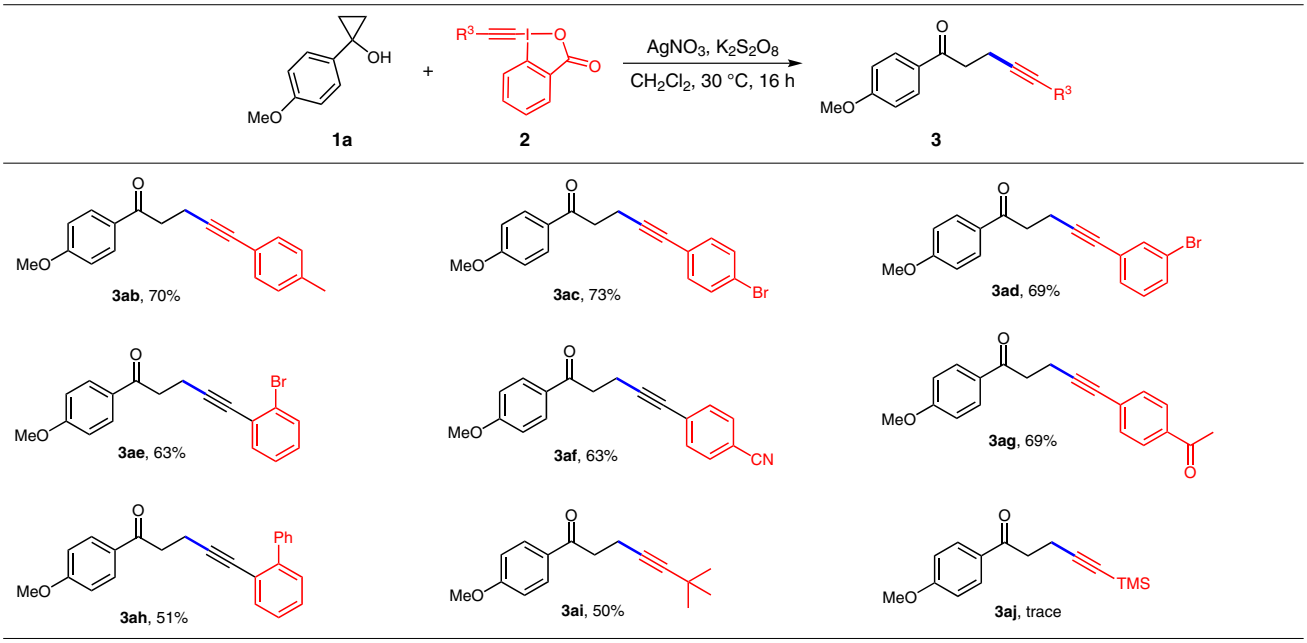
1a 2a 3aa

Entry	[Ag] (mol%)	[O] (equiv)	Solvent	Yield[b] (%)
1	$AgNO_3$ (20)	–	CH_2Cl_2	33
2	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	81
3	$AgNO_3$ (20)	$Na_2S_2O_8$ (2)	CH_2Cl_2	73
4	$AgNO_3$ (20)	$(NH_2)_2S_2O_8$ (2)	CH_2Cl_2	43
5	$AgNO_3$ (20)	BPO (2)	CH_2Cl_2	65
6	$AgNO_3$ (20)	$K_2S_2O_8$ (3)	CH_2Cl_2	80
7	AgOAc (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	53
8	$AgBF_4$ (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	20
9	AgOTf (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	52
10	Ag_2CO_3 (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	47
11	$AgNO_3$ (30)	$K_2S_2O_8$ (2)	CH_2Cl_2	78
12	$AgNO_3$ (10)	$K_2S_2O_8$ (2)	CH_2Cl_2	60
13	–	$K_2S_2O_8$ (2)	CH_2Cl_2	45
14	–	$K_2S_2O_8$ (3)	CH_2Cl_2	49
15[c]	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	CH_2Cl_2/H_2O	50
16	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	DCE	70
17	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	MeCN	19
18	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	THF	35
19	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	DMF	61
20[d]	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	67
21[e]	$AgNO_3$ (20)	$K_2S_2O_8$ (2)	CH_2Cl_2	62

[a] 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] CH_2Cl_2–H_2O (1:1).
[d] At r.t.
[e] At 40 °C.

several substituents, such as OMe, Cl, F, and CF_3, 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-

Table 2 Variation of the Ethynylbenziodoxolone **2**[a]

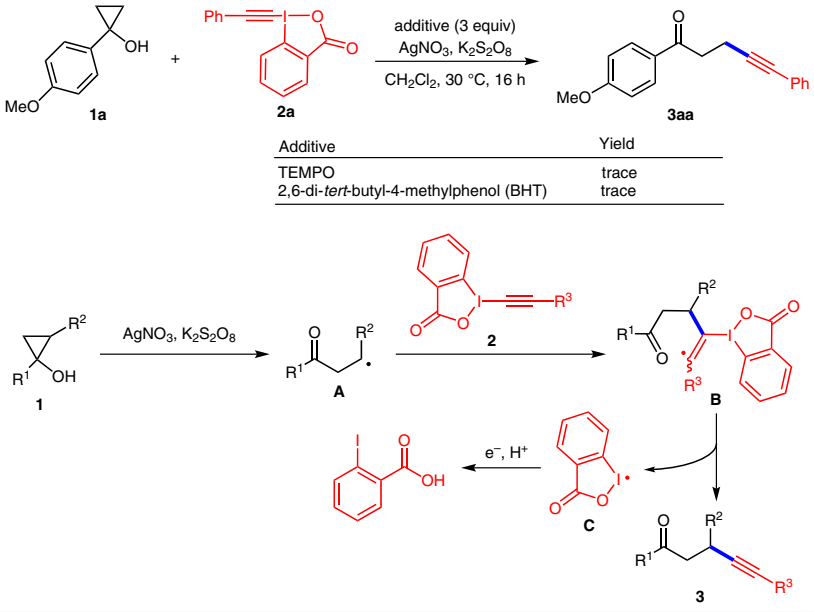


[a] Reaction conditions: **1a** (0.3 mmol), **2** (1.5 equiv), $AgNO_3$ (20 mol%), $K_2S_2O_8$ (2 equiv), CH_2Cl_2 (1 mL), 30 °C under argon, 16 h.

tyl)cyclopropan-1-ol (**1l**), affording products **3ja**–**la** in high yields. Gratifyingly, 1-styrylcyclopropan-1-ol (**1m**) was also a viable substrate for the construction of **3ma** in 55% yield.

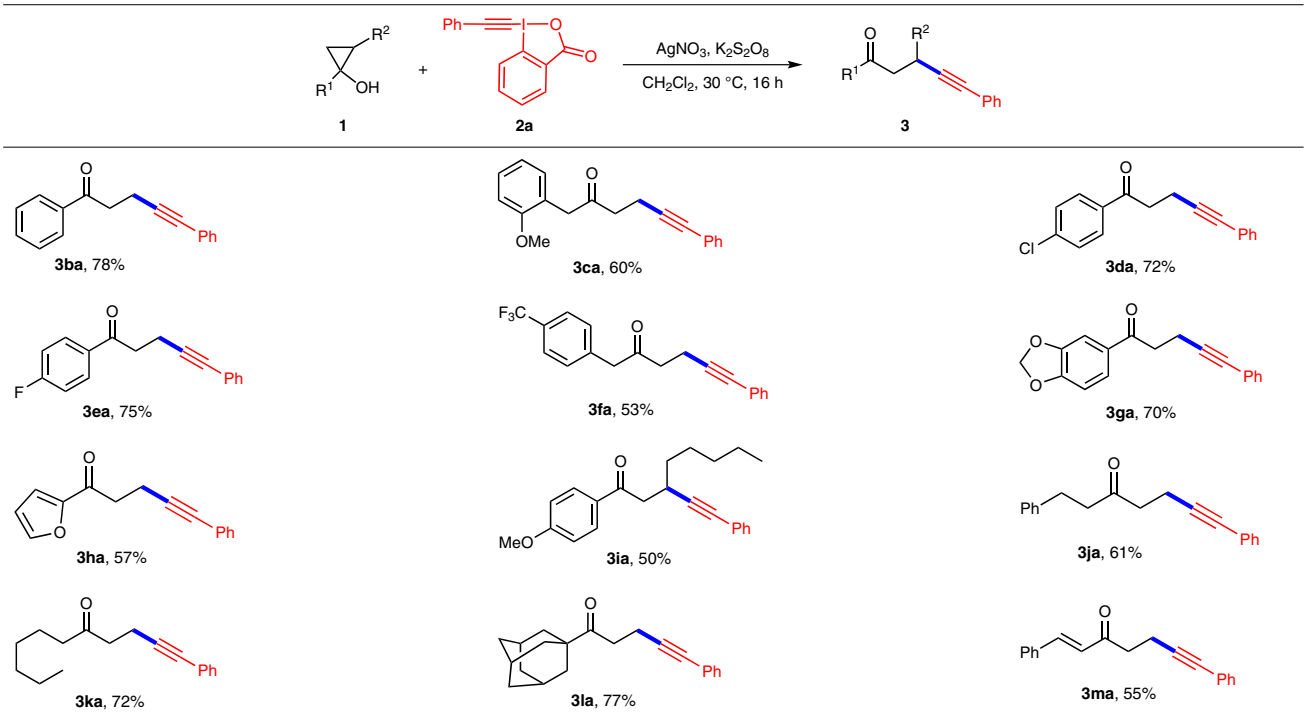
As shown in Scheme 2, the reaction of cyclopropanol **1a** with 1-(phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (**2a**) was completely suppressed when using a stoichiometric amount of radical inhibitor (3 equiv), including 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (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-



Scheme 2 Control experiments and possible mechanism

Table 3 Variation of the Cyclopropanol **1**[a]



[a] Reaction conditions: **1** (0.3 mmol), **2a** (1.5 equiv), $AgNO_3$ (20 mol%), $K_2S_2O_8$ (2 equiv), CH_2Cl_2 (1 mL), 30 °C, under argon, 16 h.

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 alkynes 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 (^{1}H NMR) and 100 MHz (^{13}C NMR) or 500 MHz (^{1}H NMR) and 125 MHz (^{13}C 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), **2** (0.45 mmol), $AgNO_3$ (0.06 mmol), $K_2S_2O_8$ (0.6 mmol), and CH_2Cl_2 (1 mL). The tube 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. $NaHCO_3$. The aqueous phase was re-extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4), 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)[9]

White solid; yield: 64.2 mg (81%); mp 52.9–54.0 °C.

IR (KBr): 1677 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}O_2$: 265.1223; found: 265.1230.

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}.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 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.

LR-MS (EI, 70 eV): *m*/*z* (%) = 278 (M^+, 52), 235 (23), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O_2$: 279.1380; found: 279.1385.

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): 1683 cm^{-1}.

^{1}H 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), 2.84–2.80 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 163.6, 133.0, 131.4, 130.3, 129.6, 122.6, 121.7, 113.7, 90.4, 79.9, 55.4, 37.2, 14.4.

LR-MS (EI, 70 eV): *m*/*z* (%) = 344 (M^+ + 2, 20), 342 (M^+, 18), 313 (10), 311 (9), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}BrO_2$: 343.0328; found: 343.0335.

5-(3-Bromophenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ad)

White solid; yield: 70.8 mg (69%); mp 78.2–79.5 °C.

IR (KBr): 1678 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.8 Hz, 2 H), 7.51 (s, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 7.13 (t, *J* = 8.0 Hz, 1 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.26 (t, *J* = 7.6 Hz, 2 H), 2.83 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 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* (%) = 344 (M^+ + 2, 15), 342 (M^+, 15), 313 (11), 311 (10), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}BrO_2$: 343.0328; found: 343.0336.

5-(2-Bromophenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ae)

White solid; yield: 64.6 mg (63%); mp 83.6–85.2 °C.

IR (KBr): 1671 cm^{-1}.

^{1}H 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 163.6, 133.3, 132.2, 130.3, 129.6, 128.8, 126.9, 125.7, 125.4, 113.7, 94.2, 79.7, 55.4, 37.2, 14.6.

LR-MS (EI, 70 eV): *m*/*z* (%) = 344 (M^+ + 2, 4), 342 (M^+, 4), 264 (20), 263 (100), 135 (95).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}BrO_2$: 343.0328; found: 343.0333.

4-[5-(4-Methoxyphenyl)-5-oxopent-1-ynyl]benzonitrile (3af)

White solid; yield: 54.6 mg (63%); mp 108.3–109.5 °C.

IR (KBr): 1669 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H), 3.28 (t, *J* = 7.2 Hz, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 163.7, 132.1, 131.9, 130.3, 129.5, 128.7, 118.6, 113.8, 111.0, 94.2, 79.7, 55.5, 37.0, 14.0.

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

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}NO_2$: 290.1176; found: 290.1186.

5-(4-Acetylphenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ag)

Light yellow solid; yield: 63.4 mg (69%); mp 56.6–57.8 °C.

IR (KBr): 1685, 1600 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H), 3.31–3.27 (m, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 2.59 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 196.3, 163.7, 135.8, 131.7, 130.3, 129.6, 128.7, 128.1, 113.8, 92.9, 80.5, 55.5, 37.2, 26.6, 14.5.

LR-MS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 27), 291 (28), 263 (12), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{19}O_3$: 307.1329; found: 307.1335.

5-(Biphenyl-2-yl)-1-(4-methoxyphenyl)pent-4-yn-1-one (3ah)

Yellow liquid; yield: 52.0 mg (51%).

IR (KBr): 1684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 9.2 Hz, 2 H), 7.56 (d, *J* = 7.2 Hz, 2 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.38–7.29 (m, 5 H), 7.28–7.24 (m, 1 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H), 3.10–3.06 (m, 2 H), 2.73–2.69 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 163.6, 143.7, 140.8, 132.9, 130.3, 129.7, 129.3 (2C), 127.9, 127.8, 127.2, 126.9, 122.0, 113.7, 92.1, 80.6, 55.5, 37.1, 14.5.

LR-MS (EI, 70 eV): *m*/*z* (%) = 340 (M^+, 12), 339 (14), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{21}O_2$: 341.1536; found: 341.1538.

1-(4-Methoxyphenyl)-6,6-dimethylhept-4-yn-1-one (3ai)

Colorless liquid; yield: 36.7 mg (50%).

IR (KBr): 1711 cm^{-1}.

^{1}H 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).

^{13}C 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^+, 7), 229 (21), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{21}O_2$: 245.1536; found: 245.1541.

1,5-Diphenylpent-4-yn-1-one (3ba)[8c]

White solid; yield: 54.8 mg (78%); mp 57.7–58.7 °C.

IR (KBr): 1685 cm^{-1}.

^{1}H 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).

^{13}C 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{15}O$: 235.1117; found: 235.1124.

1-(2-Methoxyphenyl)-6-phenylhex-5-yn-2-one (3ca)

Light yellow liquid; yield: 50.1 mg (60%).

IR (KBr): 1683 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.35 (m, 2 H), 7.27–7.25 (m, 4 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 6.94–6.87 (m, 2 H), 3.80 (s, 3 H), 3.71 (s, 2 H), 2.78–2.74 (m, 2 H), 2.67–2.63 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 157.3, 131.5, 131.2, 128.6, 128.2, 127.7, 123.6, 123.2, 120.7, 110.5, 88.8, 80.8, 55.3, 44.7, 40.7, 14.0.

LR-MS (EI, 70 eV): *m*/*z* (%) = 278 (M$^+$, 23), 157 (82), 115 (100), 91 (91).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O_2$: 279.1380; found: 279.1384.

1-(4-Chlorophenyl)-5-phenylpent-4-yn-1-one (3da)[9]

White solid; yield: 57.9 mg (72%); mp 49.8–52.4 °C.

IR (KBr): 1688 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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* = 7.6 Hz, 2 H), 2.85 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): 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* (%) = 270 (M$^+$ + 2, 15), 268 (M$^+$, 45), 233 (49), 111 (52).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{14}ClO$: 269.0728; found: 269.0736.

1-(4-Fluorophenyl)-5-phenylpent-4-yn-1-one (3ea)[9]

Colorless liquid; yield: 56.7 mg (75%).

IR (KBr): 1690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.00 (m, 2 H), 7.37 (d, *J* = 3.6 Hz, 2 H), 7.27 (d, *J* = 3.2 Hz, 3 H), 7.14 (t, *J* = 8.4 Hz, 2 H), 3.29 (t, *J* = 8.0 Hz, 2 H), 2.85 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 166.3 (d, J_{C-F} = 253.0 Hz), 133.0 (d, J_{C-F} = 2.0 Hz), 131.5, 130.7 (d, J_{C-F} = 9.0 Hz), 128.2, 127.7, 123.5, 115.7 (d, J_{C-F} = 21.0 Hz), 88.6, 81.1, 37.7, 14.3.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –104.9.

LR-MS (EI, 70 eV): *m*/*z* (%) = 252 (M$^+$, 58), 251 (78), 209 (20), 128 (27), 123 (100), 95 (57).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{14}FO$: 253.1023; found: 253.1029.

6-Phenyl-1-[4-(trifluoromethyl)phenyl]hex-5-yn-2-one (3fa)

Light yellow solid; yield: 50.3 mg (53%); mp 50.6–52.4 °C.

IR (KBr): 1669 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2 H), 7.35–7.32 (m, 4 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.1, 137.7, 131.5, 129.8, 129.5 (q, J_{C-F} = 32.3 Hz), 128.2, 127.8, 125.6 (q, J_{C-F} = 3.8 Hz), 123.8 (q, J_{C-F} = 251.0 Hz), 123.4, 88.1, 81.2, 49.6, 41.2, 14.0.

^{19}F NMR (375 MHz, $CDCl_3$): δ = –62.5.

LR-MS (EI, 70 eV): *m*/*z* (%) = 316 (M$^+$, 7), 157 (73), 128 (25), 115 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}F_3O$: 317.1148; found: 317.1143.

1-(1,3-Benzodioxol-5-yl)-5-phenylpent-4-yn-1-one (3ga)

White solid; yield: 58.4 mg (70%); mp 79.6–82.3 °C.

IR (KBr): 1674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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), 3.23 (t, *J* = 7.2 Hz, 2 H), 2.82 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}O_3$: 279.1016; found: 279.1022.

1-(Furan-2-yl)-5-phenylpent-4-yn-1-one (3ha)

Light yellow liquid; yield: 38.3 mg (57%).

IR (KBr): 1663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_2$: 225.0910; found: 225.0917.

1-(4-Methoxyphenyl)-3-(phenylethynyl)octan-1-one (3ia)

Colorless liquid; yield: 50.1 mg (50%).

IR (KBr): 1680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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, 3 H), 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 163.5, 131.6, 130.5, 130.2, 128.1, 127.5, 123.8, 113.7, 92.7, 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{27}O_2$: 335.2006; found: 335.2011.

1,7-Diphenylhept-6-yn-3-one (3ja)

White solid; yield: 48.0 mg (61%); mp 63.4–64.8 °C.

IR (KBr): 1690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 2 H), 7.28–7.25 (m, 5 H), 7.20–7.16 (m, 3 H), 2.92 (t, *J* = 7.6 Hz, 2 H), 2.78 (t, *J* = 7.6 Hz, 2 H), 2.72–2.63 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.8, 140.8, 131.5, 128.5, 128.3, 128.2, 127.7, 126.1, 123.5, 88.5, 81.0, 44.3, 41.7, 29.6, 13.9.

LR-MS (EI, 70 eV): *m*/*z* (%) = 262 (M$^+$, 14), 171 (60), 157 (100), 105 (92), 91 (82).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}O$: 263.1430; found: 263.1438

1-Phenylundec-1-yn-5-one (3ka)

Light yellow liquid; yield: 52.3 mg (72%).

IR (KBr): 1710 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{23}O$: 243.1743; found: 243.1747.

1-(Adamantan-1-yl)-5-phenylpent-4-yn-1-one (3la)

Colorless liquid; yield: 67.5 mg (77%).

IR (KBr): 1700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.36 (m, 2 H), 7.27–7.25 (m, 3 H), 2.80–2.77 (m, 2 H), 2.65–2.61 (m, 2 H), 2.07–2.02 (m, 3 H), 1.85–1.82 (m, 5 H), 1.81–1.68 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 131.5, 128.1, 127.6, 123.7, 89.3, 80.7, 46.2, 38.1, 36.5, 35.5, 27.9, 14.0.

LR-MS (EI, 70 eV): *m*/*z* (%) = 292 (M^+, 5), 157 (7), 135 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{25}O$: 293.1900; found: 293.1908.

(*E*)-1,7-Diphenylhept-1-en-6-yn-3-one (3ma)

Yellow solid; yield: 42.9 mg (55%); mp 46.7–47.9 °C.

IR (KBr): 1696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 16.4 Hz, 1 H), 7.57–7.55 (m, 2 H), 7.41–7.37 (m, 5 H), 7.27–7.26 (m, 3 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 3.04–3.01 (m, 2 H), 2.81–2.77 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 143.1, 134.4, 131.6, 130.6, 129.0, 128.3, 128.2, 127.7, 125.9, 123.6, 88.8, 81.1, 39.7, 14.3.

LR-MS (EI, 70 eV): *m*/*z* (%) = 260 (M^+, 4), 217 (81), 203 (42), 131 (56), 103 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}O$: 261.1274; found: 261.1280.

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Supporting Information

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