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Ligand-free Ag(I)-catalyzed carboxylative coupling of terminal alkynes, chloride compounds, and CO_2

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ABSTRACT

Simple silver(I) slats were found to be highly efficient and selective catalyst for carboxylative coupling of aryl- or alkyl-substituted terminal alkynes, CO_2, and various allylic, propargylic or benzylic chlorides to exclusively yield functionalized 2-alkynoates. The activity is about 300 times that of the previously reported *N*-heterocyclic carbene copper(I) catalytic system. The ligand-free silver(I) catalytic system showed the wide generality of substrates involving both functionalized terminal alkynes and chloride compounds.

1. Introduction

The utilization of CO_2 in the production of high value-added chemicals has received much attention over the past decade. This is a consequence of CO_2 being an abundant, inexpensive and non-toxic renewable carbon resource.[1] In the present strategies for homogeneous transformation of CO_2, especially in the carboxylation of various nucleophiles[2–7] or relatively C–H bonds[8] with CO_2 to yield synthetically important carboxylic acids and derivatives,[9] relatively high loading of transition-metal catalysts bearing appropriate ligands were frequently used to overcome the limitation from the thermodynamically and kinetically stable CO_2 and maximize synthetic efficiency. In view of the cost and availability for the potential applications, the development of simple catalytic systems for CO_2 transformation, which particularly show increased activity and selectivity at lower catalyst loadings, is thus of paramount importance.

Catalytic carboxylation of terminal alkynes with CO_2 attracted considerable interest and is emerging as a powerful tool in the straightforward synthesis of functionalized propiolic acids and 2-alkynoates,[10–16] which are versatile synthetic intermediates of natural products and other bioactive compounds.[17] Inoue and co-workers reported copper(I)- or silver(I)-catalyzed carboxylative coupling reaction of terminal alkynes, alkyl bromides and CO_2 at 100 °C.[10] However, this methodology sometimes suffered from the major formation of direct coupling or dialkyl carbonate by-products. In 2008, Anastas and co-workers disclosed silver(I)-catalyzed reaction of phenylacetylene, CO_2, and 3-bromo-1-phenyl-1-propyne, affording arylnaphthalene lactones in poor to moderate yield.[11] (4,7-Diphenyl-1,10-phenanthroline) bis[tris(4-fluorophenyl)phosphine]–copper(I) nitrate catalyst developed by Goossen and co-workers[12] and *N*-heterocyclic carbene copper(I) catalysts employed by Zhang and co-workers[13] were proven to exhibit promising activity in catalyzing the direct carboxylation of a wide range of terminal alkynes with CO_2 to provide the corresponding propiolic acids in good yield. More recently, Kondo and co-workers reported a CuI/PEt_3 catalyzed carboxylative coupling reaction of terminal alkynes, CO_2, and alkyl bromides or iodides, providing a variety of functionalized alkyl 2-alkynoates under ambient conditions.[14]

In 2010, we developed a novel Cu(I)-catalyzed carboxylative coupling reaction of terminal alkynes, allylic chlorides, and CO_2,[15] wherein 10 mol % loading of *N*-heterocyclic carbene copper(I) catalyst (IPr)CuCl (IPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was turned out to effectively suppress the non-carboxylative direct coupling reaction (Scheme 1, B).[18] A variety of carboxylative coupling (Scheme 1, A) products, functionalized allylic 2-alkynoates were straightforwardly obtained in good yield with high selectivity. Recently, we disclosed that only 1 mol % loading of AgI could efficiently catalyze the direct carboxylation of terminal alkynes under ligand-free conditions, affording functionalized

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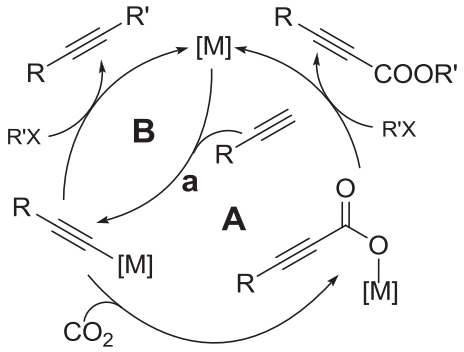
propiolic acids in high yield.[16] With this success in hand, we envisioned whether the simple silver(I) catalytic system could also serve as highly active and selective catalyst for the above-mentioned carboxylative coupling reaction. Herein, we report highly selective and efficient carboxylative coupling of terminal alkynes, various chloride compounds, and CO_2 catalyzed by low loading of simple silver(I) salt under ligand-free conditions to exclusively afford functionalized 2-alkynoates.[19]

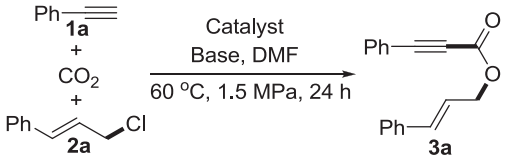


Scheme 1. Carboxylative coupling (A) and direct coupling (B) of terminal alkynes and halides.

2. Results and discussion

The activity of the Ag(I)-based catalyst was initially tested by the carboxylative coupling reaction of phenylacetylene (**1a**), cinnamyl chloride (**2a**), and CO_2 (Table 1). It was delightedly found that the catalytic system used in the previous direct carboxylation reaction (1 mol % of AgI as catalyst and Cs_2CO_3 as base) gave 84% yield of carboxylative coupling product cinnamyl phenylpropiolate (**3a**) (Table 1, entry 2). Notably, the decreased loading (0.1 mol %) of AgI catalyst led to the increased yield, which could be comparable to the result from 10 mol % of (IPr)CuCl catalytic system (Table 1, entries 1 and 3). Furthermore, simple kinetic studies of the two catalyst systems by monitoring the reaction with LC revealed that the activity of AgI/Cs_2CO_3 catalyst system was about 300 times that of our previously reported $(IPr)CuCl/K_2CO_3$ system (Fig. 1). Importantly, no direct coupling by-product was detected even in complete conversion and only carboxylative coupling product was formed exclusively. Those results imply that the insertion of CO_2 into silver(I) acetylide species proceeds significantly faster than that of CO_2 to the sp-hybridized carbon–copper(IPr) bond (Scheme 1).

Table 1
Ag(I)-catalyzed carboxylative coupling of phenylacetylene, cinnamyl chloride, and CO_2[a]



Entry	Cat. (mol %)	Base	Yield[b] (%)
1[c]	(IPr)CuCl (10)	K_2CO_3	91
2	AgI (1)	Cs_2CO_3	84
3	AgI (0.1)	Cs_2CO_3	91
4	AgI (0.05)	Cs_2CO_3	70
5	—	Cs_2CO_3	11
6	AgI (0.1)	—	4
7	AgI (0.1)	K_2CO_3	74
8	AgI (0.1)	KO^{t}Bu	16
9	AgF (0.1)	Cs_2CO_3	81
10	AgCl (0.1)	Cs_2CO_3	80
11	AgBr (0.1)	Cs_2CO_3	83
12	AgOAc (0.1)	Cs_2CO_3	86
13	$AgNO_3$ (0.1)	Cs_2CO_3	77
14	Ag_2CO_3 (0.1)	Cs_2CO_3	88
15	$AgBF_4$ (0.1)	Cs_2CO_3	94
16	$AgPF_6$ (0.1)	Cs_2CO_3	77
17[d]	AgI (0.1)	Cs_2CO_3	84
18[e]	AgI (0.1)	Cs_2CO_3	78
19[f]	AgI (0.1)	Cs_2CO_3	80
20[g]	AgI (0.1)	Cs_2CO_3	—

[a] Reaction condition: **1a** (2 mmol), **2a** (3 mmol), base (3 mmol), 20 mL of DMF, 1.5 MPa, 24 h, 60 °C.
[b] Isolated yield.
[c] See Ref. 15.
[d] 50 °C.
[e] 16 h.
[f] 0.5 MPa.
[g] In the absence of CO_2.

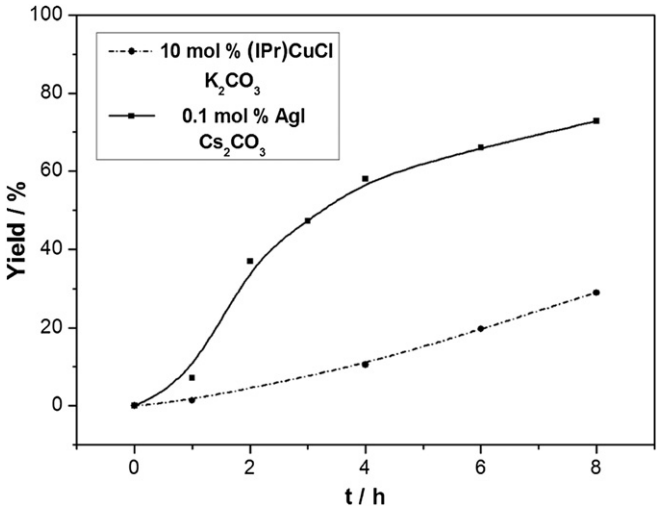


Fig. 1. Plot of yield versus time for the carboxylative coupling reaction catalyzed by (IPr)CuCl and AgI. Yields were determined by LC.

The control experiment showed that extremely low yield of **3a** was obtained in the absence of AgI or Cs_2CO_3, testifying the vital roles of catalyst and base in this catalytic system (Table 1, entries 5 and 6). Using K_2CO_3 as base gave moderate yield (Table 1, entry 7), while KO^{t}Bu was proven to be unsuitable base to the reaction (Table 1, entry 8). Other simple silver(I) salts were also tested as catalyst and the silver counter-ions had an evident effect on their catalytic activities (Table 1, entries 9–16). The superior catalytic activity of AgI could be presumably ascribed to its good solubility in DMF. $AgBF_4$ was more efficient in catalyzing this reaction (Table 1, entry 15). Because of the highly hygroscopic nature of $AgBF_4$, AgI was still used in our subsequent investigations.

When the reaction was conducted under 0.5 MPa of CO_2, decreased yield of carboxylative coupling product was obtained, although the direct coupling by-product was also not observed (Table 1, entry 19). No carboxylative coupling product was formed in the absence of CO_2, which clearly demonstrated that the CO_2 unit in **3a** came from gaseous CO_2 rather than the base (Table 1, entry 20), similar to the previously reported (IPr)CuCl system.

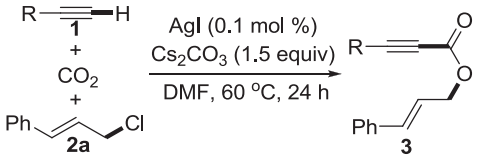
Even the carboxylative coupling reaction could be smoothly carried out using very low loading of catalyst, the AgI still could be recycled in this catalytic system. No obvious decrease in catalytic efficiency was observed for AgI catalyst after four times recycle (see Supplementary data).

Under the optimized reaction condition, the kinetics of the carboxylative coupling reaction of phenylacetylene, cinnamyl chloride, and CO_2 was also studied. The dependence of the initial rate on phenylacetylene, cinnamyl chloride concentration, and CO_2 pressure was evaluated, respectively, by monitoring the formation of product

using LC (see Supplementary data). The rate exhibited a saturation rate dependence on the cinnamyl chloride concentration and CO_2 pressure, and first-order dependence on phenylacetylene concentration, which might suggest that deprotonation of terminal alkyne to form silver(I) acetylide is the rate limiting step (Scheme 1, a).

Once it was established that low loading of AgI and Cs_2CO_3 as base was highly selective and efficient catalytic system for the carboxylative coupling of phenylacetylene, cinnamyl chloride, and CO_2, the functional group compatibility was then investigated under the optimized condition. As shown in Table 2, a wide range of aryl- and alkyl-substituted terminal alkynes successfully underwent the carboxylative coupling reaction with cinnamyl chloride and CO_2 to afford the corresponding cinnamyl 2-alkynoates exclusively in the presence of 0.1 mol% loading of AgI. Various functional groups including aryl-OMe, -F, -Cl, -Br, $-CF_3$, cyclopropane, and cyclopentane were tolerated (Table 2, entries 4–9, 14, and 15). The chloride group in 5-chloro-1-pentyne proved to be inert toward this catalytic system at 60 °C (Table 2, entry 12).

Table 2
Ag(I)-catalyzed carboxylative coupling of terminal alkynes, cinnamyl chloride, and CO_2[a]



Entry	R	Yield[b] (%)
1	Ph	91 (**3a**)
2	4-MeC_6H_4	91 (**3b**)
3	4-$^tBuC_6H_4$	92 (**3c**)
4	4-$MeOC_6H_4$	85 (**3d**)
5	4-(n-C_5H_{11})C_6H_4	83 (**3e**)
6	4-FC_6H_4	82 (**3f**)
7	2-ClC_6H_4	74 (**3g**)
8	4-BrC_6H_4	80 (**3h**)
9	4-$CF_3C_6H_4$	89 (**3i**)
10	*n*-Hexyl	74 (**3j**)
11	*n*-Octyl	86 (**3k**)
12	3-Chloropropyl	77 (**3l**)
13	2-Phenylethyl	81 (**3m**)
14	Cyclopropyl	71 (**3n**)
15	Cyclopentyl	75 (**3o**)
16	Cyclohexylmethyl	60 (**3p**)

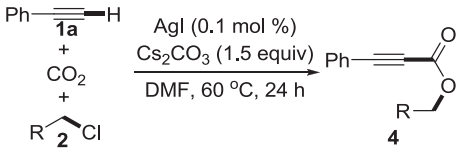
[a] Reaction condition: **1** (2 mmol), **2a** (3 mmol), Cs_2CO_3 (3 mmol), 20 mL of DMF, 1.5 MPa, 24 h, 60 °C.
[b] Isolated yield.

Furthermore, the low loading of silver(I) catalytic system also showed broad substrate scope for chloride compounds (Table 3). Besides cinnamyl chloride, alkyl-substituted allylic chlorides, propargylic chlorides proved applicable for the carboxylative coupling reaction (Table 3, entries 1–6). A series of benzylic chlorides bearing methyl, methoxyl, fluorine, bromine, nitryl, and vinyl substituents could also serve as reactive carboxylative coupling partners (Table 3, entries 7–15). α-Chloro carbonyl compounds were also found to be suitable substrates (Table 3, entries 16 and 17). When *n*-hexyl chloride was used as a carboxylative partner, only 25% yield of carboxylative coupling product *n*-hexyl phenylpropiolate (**4s**) was obtained (Table 3, entry 18). When the same reaction was conducted at elevated temperature (100 °C), the yield of **4s** increased to 77% (Table 3, entry 19).

3. Conclusion

In summary, we have successfully developed a simple ligand-free silver(I) catalytic system for the carboxylative coupling of aryl- or alkyl-substituted terminal alkynes, CO_2, and various allylic, propargylic or benzylic chlorides to exclusively afford functionalized 2-alkynoates in good yield. Compared with the previously reported *N*-heterocyclic carbene copper(I) catalytic system, the ligand-free silver(I) catalytic system shows greatly enhanced activity and selectivity at much lower catalyst loading.

Table 3
Ag(I)-catalyzed carboxylative coupling of phenylacetylene, chloride compounds, and CO_2[a]



Entry	R	Yield[b] (%)
1	Vinyl	47 (**4b**)
2	Isocrotyl	90 (**4c**)
3	Isopropenyl	83 (**4d**)
4	2-Chlorovinyl	87 (**4e**)
5	Heptynyl	80 (**4f**)
6	Phenylethynyl	60 (**4g**)
7	Ph	85 (**4h**)
8	2-MeC_6H_4	79 (**4i**)
9	4-$MeOC_6H_4$	70 (**4j**)
10	4-FC_6H_4	80 (**4k**)
11	2-FC_6H_4	77 (**4l**)
12	4-BrC_6H_4	77 (**4m**)
13	4-$NO_2C_6H_4$	75 (**4n**)
14	2-$NO_2C_6H_4$	78 (**4o**)
15	4-(CH_2=CH)C_6H_4	84 (**4p**)
16	Ethoxycarbonyl	79 (**4q**)
17	(Diethylamino)carbonyl	76 (**4r**)
18	*n*-Pentyl	25 (**4s**)
19[c]	*n*-Pentyl	77 (**4s**)

[a] Reaction condition: **1a** (2 mmol), **2** (3 mmol), Cs_2CO_3 (3 mmol), 20 mL of DMF, 1.5 MPa, 24 h, 60 °C.
[b] Isolated yield.
[c] 100 °C.

4. Experimental section

4.1. General information

Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or CO_2 atmosphere. DMF was distilled from CaH_2 at 60 °C under reduced pressure and stored over 4 Å molecular sieves. NMR spectra were recorded on a Bruker AvanceII 400M type (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. Multiplicity abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. High-resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer. Carbon dioxide (99.999%), commercially available terminal alkynes, chloride compounds, silver(I) salt, and other all reagents were used without further purification.

4.2. Representative experimental procedure for carboxylative coupling reaction

Taking the carboxylative coupling of 4-methylphenylacetylene, cinnamyl chloride (**2a**), and CO_2 as example: A 70 mL oven dried autoclave containing a stir bar was charged with AgI (0.5 mg, 0.002 mmol) and Cs_2CO_3 (978 mg, 3.0 mmol). 4-Methylpheny lacetylene (232 mg, 2.0 mmol), cinnamyl chloride (458 mg, 3.0 mmol), and 20 mL dry DMF were added with syringe, respectively,

after purging the autoclave with CO_2 three times. The sealed autoclave was pressurized to appropriate pressure with CO_2. The reaction mixture was stirred at 60 °C for 24 h, then the autoclave was cooled to room temperature and the remaining CO_2 was vented slowly. The reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed under vacuum. The product (*E*)-cinnamyl 4-methylphenyl propiolate (**3b**) (502 mg, 1.82 mmol, 91% yield) was isolated by column chromatography on silica gel (ethyl acetate/petroleum ether: 1:25).

4.3. Characterization of new compounds

*4.3.1. Cinnamyl 4-pentylphenylpropiolate (**3e**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52 (2H, d, *J*=8.0 Hz), 7.42 (2H, d, *J*=8.0 Hz), 7.32 (2H, t, *J*=8.0 Hz), 7.28 (1H, t, *J*=8.0 Hz), 7.18 (2H, d, *J*=8.0 Hz), 6.73 (1H, d, *J*=16.0 Hz), 6.35 (1H, dt, *J*=16.0, 8.0 Hz), 4.89 (2H, d, *J*=8.0 Hz), 2.62 (2H, t, *J*=7.6 Hz), 1.61 (2H, m), 1.32 (4H, m), 0.89 (3H, t, *J*=6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.1, 146.5, 136.1, 135.3, 133.2, 128.8, 128.7, 128.4, 126.8, 122.3, 116.7, 87.4, 80.3, 66.6, 36.1, 31.5, 30.9, 22.6, 14.1. IR (cm^{-1}) (neat) 2217, 1708. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}O_2Na$ $[M+Na]^+$: 355.1674, found: 355.1684.

*4.3.2. Cinnamyl 2-chlorophenylpropiolate (**3g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61 (1H, d, *J*=8.0 Hz), 7.45–7.27 (8H, m), 6.74 (1H, d, *J*=16.0 Hz), 6.35 (1H, dt, *J*=16.0, 8.0 Hz), 4.92 (2H, d, *J*=4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.7, 137.5, 136.1, 135.6, 134.9, 131.8, 129.8, 128.8, 128.4, 126.9, 126.8, 122.2, 120.0, 84.9, 82.9, 66.9. IR (cm^{-1}) (neat) 2224, 1707. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{13}O_2NaCl$ $[M+Na]^+$: 319.0502, found: 319.0510.

*4.3.3. Cinnamyl 4-bromophenylpropiolate (**3h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51–7.26 (9H, m), 6.71 (1H, d, *J*=15.6 Hz), 6.32 (1H, dt, *J*=16.0, 6.4 Hz), 4.88 (2H, d, *J*=6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.7, 136.0, 135.6, 134.4, 132.1, 128.8, 126.9, 122.1, 118.6, 85.5, 81.6, 66.8. IR (cm^{-1}) (neat) 2213, 1693. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{13}O_2NaBr$ $[M+Na]^+$: 362.9997, found: 362.9998.

*4.3.4. Cinnamyl hept-2-ynoate (**3k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.23 (5H, m), 6.65 (1H, d, *J*=16.0 Hz), 6.26 (1H, dt, *J*=16.0, 8.0 Hz), 4.78 (2H, d, *J*=4.0 Hz), 2.30 (2H, t, *J*=8.0 Hz), 1.59–1.51 (2H, m), 1.38–1.25 (10H, m), 0.85 (3H, t, *J*=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.8, 136.0, 135.1, 128.8, 128.4, 126.7, 122.2, 90.1, 73.0, 66.2, 31.8, 29.1, 29.0, 28.9, 27.5, 22.6, 18.7, 14.1. IR (cm^{-1}) (neat) 2234, 1712. HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{26}O_2Na$ $[M+Na]^+$: 321.1831, found: 321.1839.

*4.3.5. Cinnamyl 5-phenyl-2-pentynoate (**3m**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.37–7.17 (10H, m), 6.65 (1H, d, *J*=16.0 Hz), 6.26 (1H, dt, *J*=16.0, 8.0 Hz), 4.78 (2H, d, *J*=4.0 Hz), 2.86 (2H, t, *J*=8.0 Hz), 2.59 (2H, t, *J*=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.5, 139.6, 136.1, 135.1, 128.7, 128.6, 128.4, 128.3, 126.8, 126.7, 122.2, 89.0, 73.6, 66.3 33.9, 20.9. IR (cm^{-1}) (neat) 2233, 1708. HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1204, found: 313.1205.

*4.3.6. Cinnamyl 3-cyclopentyl-2-propynoate (**3o**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.38–7.25 (5H, m), 6.66 (1H, d, *J*=16.0 Hz), 6.28 (1H, dt, *J*=16.0, 8.0 Hz), 4.79 (2H, d, *J*=8.0 Hz), 2.81–2.74 (1H, m), 2.00–1.59 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.0, 136.2, 135.3, 128.7, 128.3, 126.8, 122.4, 94.2, 72.7, 66.4, 33.2, 29.9, 25.4. IR (cm^{-1}) (neat) 2228, 1708. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{18}O_2Na$ $[M+Na]^+$: 277.1204, found: 277.1202.

*4.3.7. Benzyl phenylpropiolate (**4h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54 (2H, d, *J*=7.2 Hz), 7.41–7.31 (8H, m), 5.24 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.0, 134.9, 133.0, 130.8, 128.8, 128.7, 128.6, 119.5, 86.8, 80.6, 67.8. IR (cm^{-1}) (neat) 2220, 1708. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{12}O_2Na$ $[M+Na]^+$: 259.0735, found: 259.0727.

*4.3.8. 4-Methoxybenzyl phenylpropiolate (**4j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54 (2H, d, *J*=7.6 Hz), 7.43–7.32 (5H, m), 6.80 (2H, d, *J*=8.0 Hz), 5.19 (2H, s), 3.79 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.0, 154.0, 133.0, 130.7, 130.6, 128.6, 127.1, 119.6, 114.1, 86.5, 80.7, 67.6, 55.3. IR (cm^{-1}) (neat) 2218, 1709. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{14}O_3Na$ $[M+Na]^+$: 289.0841, found: 289.0836.

*4.3.9. 4-Fluorobenzyl phenylpropiolate (**4k**).* ^{1}H NMR (400 MHz, CD_3OD): δ=7.57–7.04 (9H, m), 5.22 (2H, s). ^{13}C NMR (100 MHz, CD_3OD): δ=164.2, 161.7, 153.9, 133.1, 130.9, 130.8, 128.7, 119.5, 115.8, 115.6, 87.0, 80.5. IR (cm^{-1}) (neat) 2221, 1710. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{11}FO_2Na$ $[M+Na]^+$: 277.0641, found: 277.0649.

*4.3.10. 2-Fluorobenzyl phenylpropiolate (**4l**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56 (2H, d, *J*=7.7 Hz), 7.46–7.06 (7H, m), 5.32 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=162.4, 159.9, 153.8, 133.1, 130.9, 128.7, 124.4, 119.5, 115.8, 115.6, 87.0, 80.4, 61.6. IR (cm^{-1}) (neat) 2220, 1710. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{11}FO_2Na$ $[M+Na]^+$: 277.0641, found: 277.0643.

*4.3.11. 4-Nitrobenzyl phenylpropiolate (**4n**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22 (2H, d, *J*=8.8 Hz), 7.58–7.34 (7H, m), 5.32 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.5, 147.9, 142.1, 133.1, 131.0, 128.7, 128.6, 124, 119.2, 87.8, 80.0, 66.0. IR (cm^{-1}) (neat) 2219, 1709. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{11}NO_4Na$ $[M+Na]^+$: 304.0586, found: 304.0588.

*4.3.12. 2-Nitrobenzyl phenylpropiolate (**4o**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.16 (1H, d, *J*=8.0 Hz), 7.71–7.39 (8H, m), 5.69 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.4, 147.3, 134.1, 133.2, 131.4, 131.0, 129.1, 128.7, 125.3, 119.3, 87.6, 80.1, 64.2. IR (cm^{-1}) (neat) 2223,1715. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{11}NO_4Na$ $[M+Na]^+$: 304.0586, found: 304.0596.

*4.3.13. 4-Vinylbenzyl phenylpropiolate (**4p**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.57–7.32 (9H, m), 6.67 (1H, dd, *J*=17.6, 10.8 Hz), 5.76 (1H, d, *J*=17.6 Hz), 5.26 (1H, d, *J*=10.8 Hz), 5.23 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.9, 138.0, 136.3, 134.4, 133.1, 130.8, 129.0, 128.6, 126.5, 119.5, 114.6, 86.8, 80.6, 67.5. IR (cm^{-1}) (neat) 2219, 1708. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{14}O_2Na$ $[M+Na]^+$: 285.0891, found: 285.0881.

*4.3.14. n-Hexyl phenylpropiolate (**4s**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59–7.36 (5H, m), 4.23 (2H, t, *J*=6.8 Hz), 1.73–1.69 (2H, m), 1.34–1.31 (6H, m), 0.90 (3H, t, *J*=7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.2, 132.9, 130.6, 128.5, 119.7, 86.0, 80.8, 66.2, 31.4, 28.4, 25.5, 22.5, 14.0. IR (cm^{-1}) (neat) 2221, 1710. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{18}O_2Na$ $[M+Na]^+$: 253.1204, found: 253.1203.

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Supplementary data

Reuse of AgI catalyst, kinetic studies, and copies of NMR spectra. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.08.053.

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