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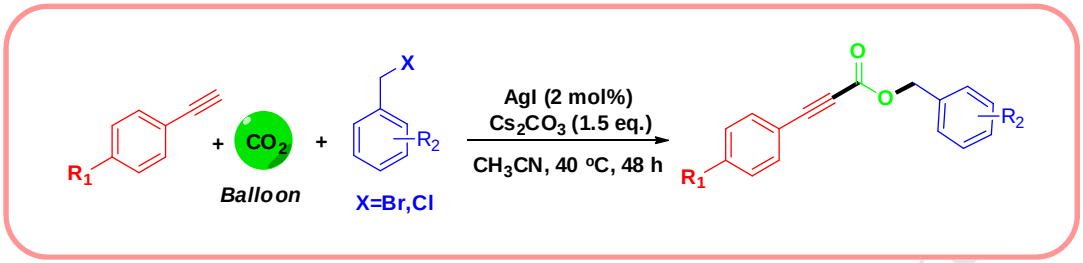
Graphical abstract:



Synthesis of benzyl 2-alkynoates via one-pot carboxylative coupling of terminal alkynes, benzyl halides and CO_2 using silver iodide as the catalyst and Cs_2CO_3 as the base.

Silver-catalyzed one-pot synthesis of benzyl 2-alkynoates under ambient pressure of CO_2 and ligand-free conditions

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Abstract: The carboxylative coupling of aryl / alkyl terminal alkynes, CO_2 and benzyl halides was investigated using silver iodide as the catalyst and Cs_2CO_3 as the base in CH_3CN under ligand-free conditions. This reaction protocol shows a wide substrate scope and high functional group tolerance ability for benzyl halides, in which various functionalized benzyl 2-alkynoates were achieved in good yields. This one-pot, ligand-free and CH_3CN mediated reaction proved to be easy to handle and could be facilitated under atmospheric CO_2 pressure.

Keywords: silver catalysis; benzyl 2-alkynoates; carboxylative coupling; carbon dioxide

1 Introduction

CO_2 is one of ideal C1 building blocks for producing fuels, polymers and fine chemicals [1]. However, CO_2 is a thermodynamic stable molecule with very low reactivity which makes its transformation particularly difficult [2]. Accordingly, transition metal catalyst usually has to be involved in most reactions [3]. Among various catalytic transformations, the carboxylation of terminal alkynes with CO_2 to produce propiolic acids or the corresponding 2-alkynote derivatives is regarded as one of very promising route, whereas copper (I) or silver (I) is commonly used as an effective catalyst in the presence of a strong base [4]. On the other hand, propiolic

acids and 2-alkynotes are also value-added fine chemicals, which can be used to produce medicine, synthetic intermediates and other bio-active compounds [5]. Inoue [6], Lu [3a-3c,4d], Kondo [4e], He [7] and other research groups have make significant efforts on the three-component carboxylative coupling of terminal alkyne, halide and CO_2 to produce various functionalized alkyl, allylic and benzyl 2-alkynoates. However, when reviewing these reported processes carefully, we found that most reaction conditions still suffer from some drawbacks. For example, Inoue and co-workers have firstly described the synthesis of hexyl alkynoates from alkynes, CO_2 and 1-bromohexane using 4 mol% of copper (I) or silver (I) iodide as the catalyst in the presence of 6 equiv. of K_2CO_3. However, the reaction has to be performed at 100 ^oC and this method could not be applied to the synthesis of allylic or benzyl 2-alkynoates [6]. Lu et al. reported a N-heterocyclic carbene copper (I) complex ((IPr)CuCl) catalyzed carboxylation of terminal alkenes, allylic chlorides and CO_2 in the presence of K_2CO_3 and DMF, which provides an effective method for the synthesis of allylic 2-alkynoates. Nevertheless, the reaction has to be carried out at 1.5 MPa with a high catalyst loading (10 mol%) [4d]. Kondo [4e] and He [7] have respectively described the CuI promoted carboxylation of aryl / alkyl terminal alkynes, CO_2 with alkyl halides using Cs_2CO_3 as the base. 8 mol% of PEt_3 was involved in Kondo's process, while the reaction was completed under ligand-free conditions in He's process. Notably, in both cases the reactions could be facilitated under ambient pressure of CO_2. Comparing to Cu (I), the application of Ag (I) seems to be more advantageous since Ag (I) is more stable and the carboxylation can be smoothly completed with rather low catalyst loading. Lu et al. have successfully developed a AgI / Cs_2CO_3 catalyzed carboxylative coupling of aryl / alkyl terminal alkynes, CO_2 with various chlorides using only 0.1 mol% of AgI under ligand-free conditions. Nevertheless, when reducing the reaction pressure from 1.5 to 0.5 MPa, the product yield was also significantly decreased [3a]. In addition, Zhang et al. disclosed a poly-NHC-Ag(I) promoted carboxylation of terminal alkyne and CO_2, and excellent product yields could be achieved with merely 0.3 mol% of catalyst [8]. Recently, our group also reported a 1 mol% NHC-Ag(I) complex catalyzed carboxylation of aryl /

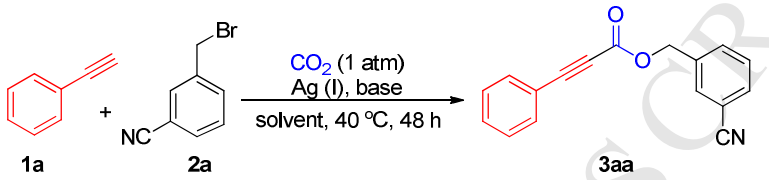
alkyl terminal alkyne with CO_2, and a wide range of aryl or alkyl substituted propiolic acids could be obtained in good yields under ambient temperature and pressure [9]. In continue our study on the carboxylation of CO_2, we were interested in further investigating the Ag(I)-catalyzed three-component carboxylative coupling of terminal alkynes, CO_2 and benzyl halide to produce benzyl 2-alkynoates. It has been reported that the carboxylative coupling using benzyl halide as the substrate often lead to a low selectivity since the side reaction - formation of dibenzyl carbonate - could not be avoided, therefore this reaction is so far still rarely reported [6]. In this context, a convenient approach to preparing benzyl 2-alkynoates via the one-pot carboxylative coupling of terminal alkynes, benzyl halides and CO_2 using AgI as the effective catalyst and Cs_2CO_3 as the base under mild condition is developed.

2 Results and discussion

To explore the reactivity, phenylacetylene **1a** and 3-cyanobenzyl bromide **2a** were initially chosen as the model substrates to react with CO_2 (Table 1). Control experiment showed that the reaction could not be proceeded without the involvement of the catalyst or the base (Table 1, entries 1 and 2). Different Ag salts including $AgNO_3$, AgOAc and AgI were then applied as the catalyst in the presence of 1.5 equiv. Cs_2CO_3 in CH_3CN at 40 ^oC. The results showed that AgI was the most active catalyst, in which 85% of the desired product **3aa** could be obtained (Table 1, entries 3-5). Thus, AgI was used as the catalyst for further studies. Reducing the amount of AgI from 2 to 0.5 mol%, the yield of **3aa** was also reduced (Table 1, entries 5-7). Nevertheless, the yield was similar to that of 2 mol% while using 5 mol% of AgI (Table 1, entry 8). As most reported carboxylation reactions [3b, 6, 10], the base played very important roles on the formation of 2-alkynoates. Despite K_2CO_3 proved to be effective, it resulted in much lower yields of products as compared to Cs_2CO_3 (Table 1, entry 9). Moreover, the reaction could not be promoted when applying other bases such as Na_2CO_3, KOH, NaOH, KO^{t}Bu and NaO^{t}Bu (Table 1, entries 10-14). Reducing the amount of Cs_2CO_3 from 1.5 to 1.0 equiv. or increasing to 2.0 equiv., the product yields were also reduced (Table 1, entries 15-17). The reaction was further screened by the variation of solvents, and CH_3CN proved to be the most efficient

solvent (Table 1, entries 18-21). Further optimization indicated that lowering or elevating the reaction temperature only led to the decreased yield of compound **3aa** (Table 1, entries 22-24). Lastly, the reaction was carried out under the conditions in references 7a and 9, affording **3aa** in 40% and 61% yield respectively (Table 1, entries 25-26). Accordingly, a standard reaction condition **A** (2 mol % of AgI, 1.5 equiv. of Cs_2CO_3, 1 atm of CO_2 at 40 °C in CH_3CN for 48 h) was obtained.

Table 1 Optimization of reaction conditions[a]



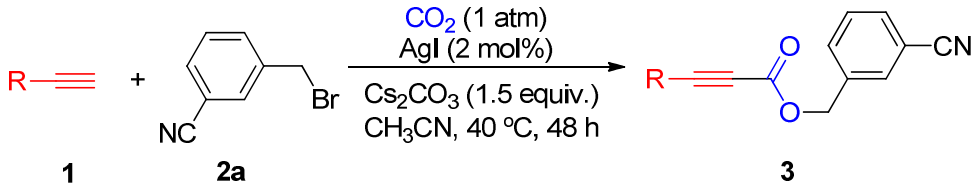
Entry	Catalyst (mol%)	Base (equiv.)	Solvent	Yield[b] (%)
1	-	Cs_2CO_3 (1.5)	CH_3CN	0
2	AgI (2)	-	CH_3CN	nr
3	$AgNO_3$ (2)	Cs_2CO_3 (1.5)	CH_3CN	31
4	AgOAc (2)	Cs_2CO_3 (1.5)	CH_3CN	51
5	AgI (2)	Cs_2CO_3 (1.5)	CH_3CN	85
6	AgI (1)	Cs_2CO_3 (1.5)	CH_3CN	74
7	AgI (0.5)	Cs_2CO_3 (1.5)	CH_3CN	66
8	AgI (5)	Cs_2CO_3 (1.5)	CH_3CN	88
9	AgI (2)	K_2CO_3 (1.5)	CH_3CN	40
10	AgI (2)	Na_2CO_3 (1.5)	CH_3CN	nr
11	AgI (2)	KOH (1.5)	CH_3CN	nr
12	AgI (2)	NaOH (1.5)	CH_3CN	nr
13	AgI (2)	KO^{t}Bu (1.5)	CH_3CN	nr
14	AgI (2)	NaO^{t}Bu (1.5)	CH_3CN	nr
15	AgI (2)	Cs_2CO_3 (1.0)	CH_3CN	75
16	AgI (2)	Cs_2CO_3 (1.2)	CH_3CN	75
17	AgI (2)	Cs_2CO_3 (2.0)	CH_3CN	77
18	AgI (2)	Cs_2CO_3 (1.5)	DMF	73

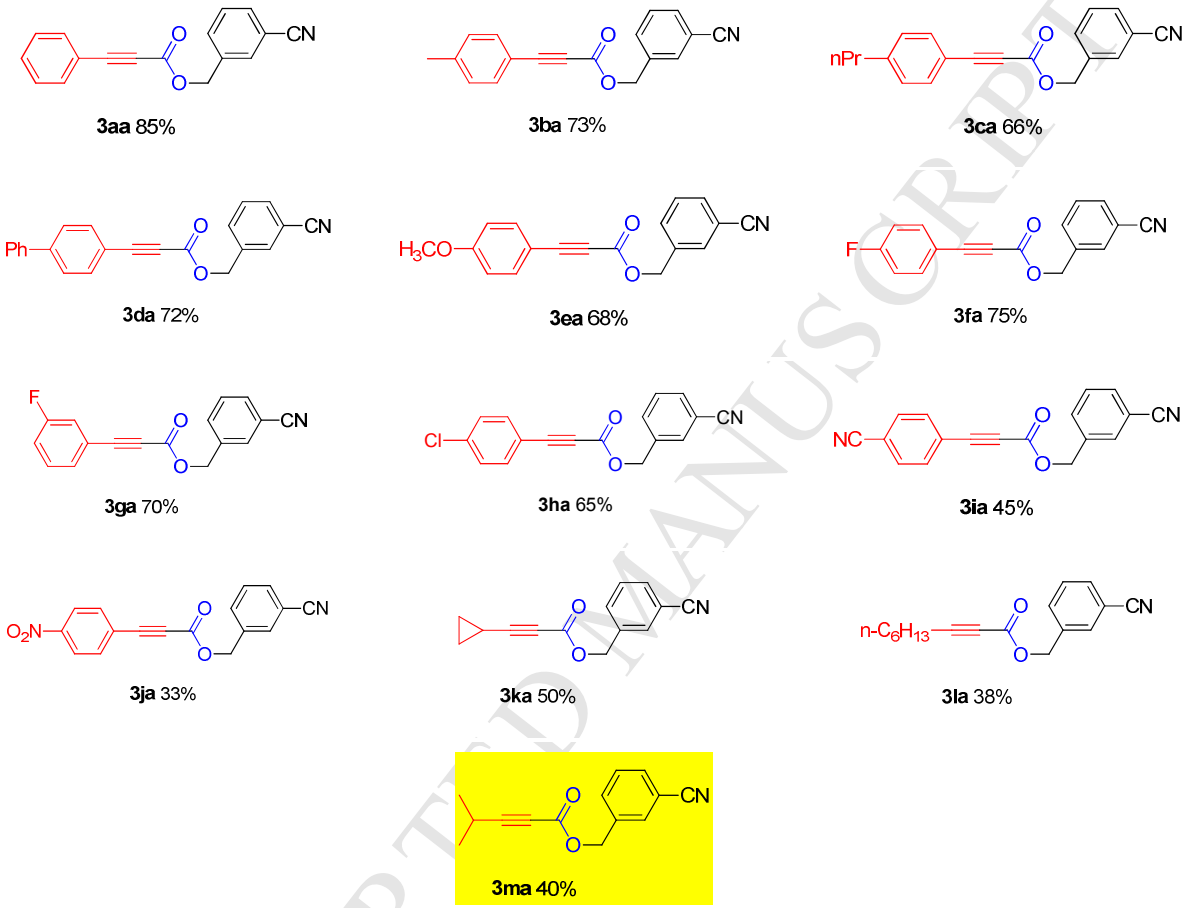
19	AgI (2)	Cs_2CO_3 (1.5)	DMSO	21
20	AgI (2)	Cs_2CO_3 (1.5)	CH_2Cl_2	0
21	AgI (2)	Cs_2CO_3 (1.5)	THF	61
22	AgI (2)	Cs_2CO_3 (1.5)	CH_3CN	48[c]
23	AgI (2)	Cs_2CO_3 (1.5)	CH_3CN	78[d]
24	AgI (2)	Cs_2CO_3 (1.5)	CH_3CN	63[e]
25[f]	CuI(10)	Cs_2CO_3 (1.2)	DMF	40
26[g]	Ag-NHC (1)	Cs_2CO_3 (1.5)	CH_3CN	61

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), CO_2 (99.999%, balloon), solvent (5 mL), 40 ^oC, 48 h; [b] Isolated yields; [c] rt; [d] 60 ^oC; [e] 80 ^oC; [f] ref 7a; [g] ref 9.

With the standard condition **A** in hand, we then carefully explored the substrate scope of this reaction. First, the carboxylation of various alkynes with 3-cyanobenzyl bromide **2a** and CO_2 was examined. As shown in Table 2, the reaction can be proceeded for both aryl and alkyl substituted terminal alkynes, affording **3aa-3ma** as the only isolated products. In the case of using aryl alkynes, the electronic effect of substituents on the phenyl ring plays important roles on reactivity. Good yields can be achieved for aryl alkynes bearing electron-donating groups such as CH_3, n-Pr, Ph and OCH_3, giving the corresponding products **3ba-3ea** in 66-73% of isolated yields. Fluoro and chloro substituted aryl alkynes also resulted in satisfactory yields of **3fa-3ha**. Unfortunately, aryl alkynes bearing electron-withdrawing groups such CN or NO_2 on the phenyl ring only led to moderate yields (**3ia**, **3ja**). The reaction also resulted in moderate yields (**3ka**, **3la**, **3ma**) for aliphatic terminal alkynes. Owing to the comparatively low activity, the activation of sp C-H bond of aliphatic and electron-poor aryl terminal alkynes might be more difficult, which may be responsible for the low product yields. It has also been found that the formation of byproduct dibenzyl carbonates could not be hindered for the reactions of **3ia-3ma**.

Table 2 Substrate scope of terminal alkynes[a,b].



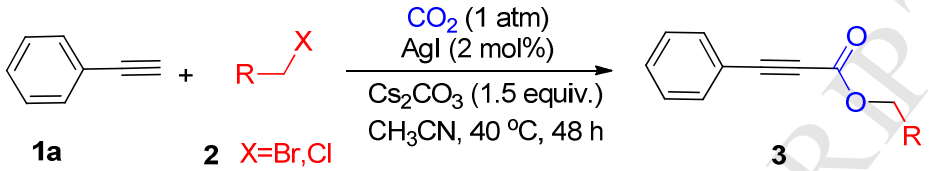


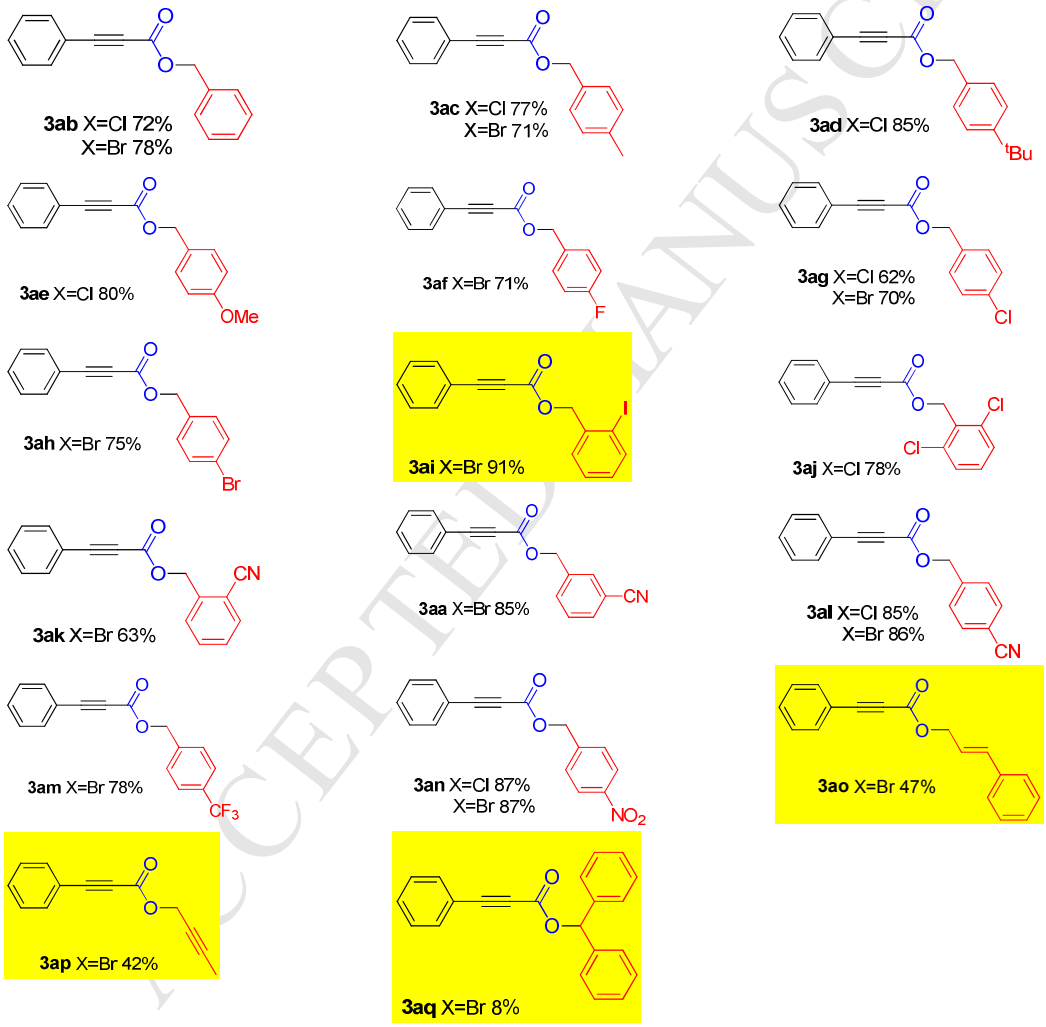
[a] Reaction conditions: **1** (1.0 mmol), **2a** (1.1 mmol), Cs_2CO_3 (1.5 mmol), CO_2 (99.999%, balloon), AgI (0.02 mmol), CH_3CN (5 mL), 40 °C, 48 h; [b] Isolated yields.

Subsequently, the carboxylation of phenylacetylene **1a** with various benzyl bromides or benzyl chlorides was examined under condition **A** (Table 3). The reaction proved to be applicable for both benzyl chlorides and benzyl bromides, and no obvious differences on activity can be observed. Good yields can be achieved for benzyl bromide or chloride with **1a** under standard conditions (**3ab**). Aryl bromides or chlorides bearing electron-donating groups such as CH_3, t-Bu and OCH_3 resulted in 71-85% of **3ac**-**3ae**. Halogen substituted aryl halides led to 62-91% of **3af**-**3aj**. The reaction is also applicable for aryl halides bearing strong electron-withdrawing CN,

CF_3 or NO_2 groups, leading to 63-87% of **3ak-3an**. For allylic / propargylic halides, moderate yields of the corresponding products were also afforded (**3ao-3ap**). Additionally, the reaction using the secondary benzyl halide-(bromomethylene)dibenzene resulted in an inferior yield of **3aq**.

Table 3 Substrate scope of benzyl halides[a,b].

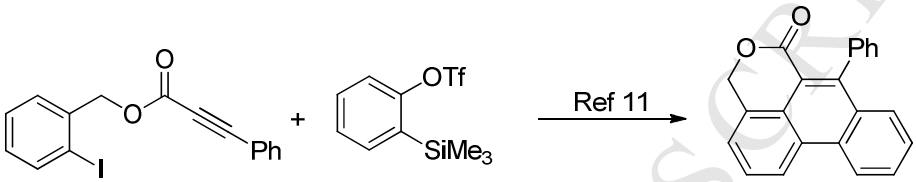




[a] Reaction conditions**:** **1a** (1.0 mmol), **2** (1.1 mmol), Cs_2CO_3 (1.5 mmol), CO_2 (99.999%, balloon), AgI (0.02 mmol), CH_3CN (5 mL), 40 °C, 48 h. [b] Isolated yields.

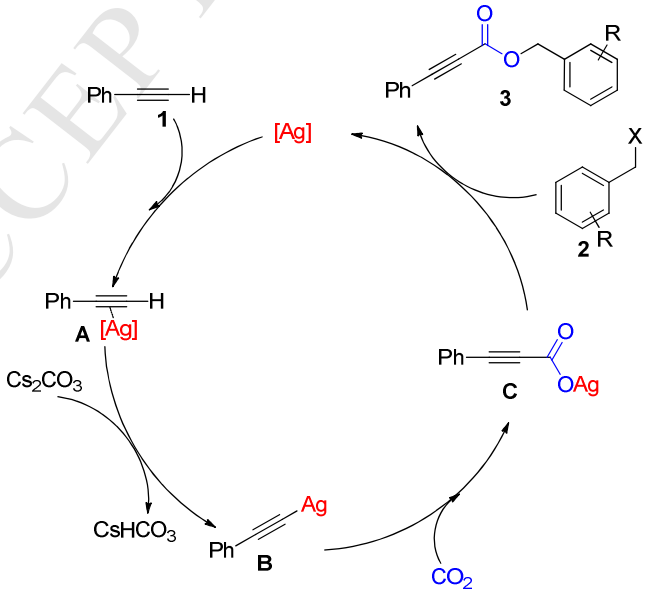
In general, this reaction protocol shows a wide substrate scope and high functional group tolerance ability for benzyl halides. This one-pot, ligand-free and CH_3CN

mediated synthetic route is also easy to handle, as the low boiling point CH_3CN can be simply evaporated in vacuo and the isolation of benzyl 2-alkynoates and the ligand can be avoided. It is noteworthy that an important synthetic intermediate - 2-iodobenzyl 3-phenylpropiolate can be also successfully synthesized in satisfactory yield using our reaction protocol (**3ai)**. 2-iodobenzyl 3-phenylpropiolate can be used to synthesis isochromenone, which is a major fragment containing in various natural products and biologically active compounds (Scheme 1) [11].



Scheme 1 Synthesis of isochromenone

Based on the literature precedents [1e, 3a, 3b, 7b, 9, 12] and experimental observations, the possible reaction mechanism is proposed as shown in Scheme 2. Firstly, terminal alkynes **1** coordinates with silver (I) species to form a species **A**. Subsequent deprotonation of **A** by Cs_2CO_3 leads to the formation of the silver(I) acetylide **B**. Then, the insertion of CO_2 to C-Ag bond of **B** gives a silver propiolate intermediate **C**. Finally, the coupling of **C** with benzyl halide **2** affords the desired product **3**, releasing Ag (I) species to fulfill a catalytic cycle.



Scheme 2 The proposed mechanism

3 Conclusions

In summary, we have successfully developed a simple and easy method for the synthesis of benzyl 2-alkynoates via one-pot carboxylative coupling of terminal alkynes, benzyl halides and CO_2 using silver iodide as the catalyst and Cs_2CO_3 as the base. By using this three-component carboxylative coupling reaction, benzyl 2-alkynoates with various functional groups can be achieved in good yields under ambient pressure of CO_2.

4 Experimental Section

General Information

All manipulations were performed using standard Schlenk techniques under a dry nitrogen or CO_2 atmosphere. All the experiments were performed in flame-dried Schlenk tubes. NMR spectra were determined on a Bruker Ascend HD 500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz) spectrometer using $CDCl_3$ as solvents. IR spectra were recorded on a Spectrum GX FT-IR spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics McriOTOF II spectrometer. HRMS (EI) were measured with a Agilent Technologies 5973N. The cesium carbonate was dried for 12 h in vacuo at 120 °C, and CO_2 (99.999%, balloon) was dried by 4Å molecular sieves prior to use. Silver (I) salts and other reagents of analytic grades were used as received.

General procedure of Ag (I)-catalyzed carboxylation

In a typical procedure, a 50 mL Schlenk tube was charged with alkyne **1** (1.0 mmol), benzyl halide **2** (1.1 mmol), AgI (0.02 mmol), Cs_2CO_3 (1.5 mmol) and anhydrous CH_3CN (5 mL). CO_2 (99.999%, balloon) were then introduced into the reaction mixture under stirring. After stirring at 40 ºC for 48 hours, the reaction mixture was cooled to room temperature, filtered and evaporated in vacuo. The resulting residue was then purified by column chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 20:1) to afford the corresponding products **3aa-3aq.**

3-Cyanobenzyl 3-phenylpropiolate (3aa): White solid (223 mg, 85%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (s, 1 H), 7.64 (t, *J* = 8.0 Hz, 2 H), 7.60-7.56 (m, 2 H), 7.52-7.42 (m, 2 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 5.27 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125

MHz) δ 153.47, 136.52, 133.03, 132.52, 132.09, 131.70, 130.90, 129.50, 128.60, 119.17, 118.33, 112.87, 87.52, 79.98, 66.04; IR (cm^{-1}) (KBr) 2226, 1710, 1486, 1445, 1288; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{12}NO_2$ $[M+H]^+$: 262.0863, found: 262.0869.

3-Cyanobenzyl 3-(*p*-tolyl)propiolate (3ba): White solid (202 mg, 73%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.73 (s, 1 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.54-7.46 (m, 3 H), 7.19 (d, *J* = 7.5 Hz, 2 H), 5.27 (s, 2 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.74, 141.68, 136.65, 133.11, 132.56, 132.12, 131.75, 129.51, 129.42, 116.10, 112.93, 88.20, 79.71, 66.01, 21.73; IR (cm^{-1}) (KBr) 2226, 2213, 1710, 754, 685; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1019, found: 276.1036.

3-Cyanobenzyl 3-(4-propylphenyl)propiolate (3ca): Yellow solid (200 mg, 66%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.72 (s, 1 H), 7.63 (t, *J* = 9.0 Hz, 2 H), 7.52-7.46 (m, 3 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 5.27 (s, 2 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 1.67-1.59 (m, 2 H), 0.94-0.91 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.48, 146.22, 136.56, 132.96, 132.41, 131.93, 131.56, 129.39, 128.69, 118.23, 116.18, 112.74, 88.02, 79.65, 65.86, 37.90, 23.97, 13.55; IR (cm^{-1}) (KBr) 2228, 1711, 1605, 1485, 1290; HRMS (ESI, *m*/*z*) calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1332, found: 304.1338.

3-Cyanobenzyl 3-([1,1'-biphenyl]-4-yl)propiolate (3da): Yellow solid (243 mg, 72%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.75 (s, 1 H), 7.69-7.63 (m, 4 H), 7.63-7.57 (m, 4 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 5.29 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.55, 143.75, 139.68, 136.58, 133.60, 132.56, 132.14, 131.76, 129.53, 128.97, 128.22, 127.28, 127.12, 118.37, 117.90, 112.95, 87.66, 80.60, 66.09; IR (cm^{-1}) (KBr) 2214, 1708, 1601, 1477, 1283; HRMS (ESI, *m*/*z*) calcd. for $C_{23}H_{16}NO_2$ $[M+H]^+$: 338.1176, found: 338.1183.

3-Cyanobenzyl 3-(4-methoxyphenyl)propiolate (3ea): White solid (198 mg, 68%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.72 (s, 1 H), 7.66-7.62 (m, 2 H), 7.54 (d, *J* = 9.0 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 5.26 (s, 2 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.70, 153.68, 136.69, 135.01, 132.47, 131.99, 131.64, 129.44, 118.33, 114.30, 112.82, 110.89, 88.46, 79.51, 65.85, 55.34; IR (cm^{-1}) (KBr) 2222, 1706, 1607, 1510, 1292, 1251; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0968, found: 292.0978.

3-Cyanobenzyl 3-(4-fluorophenyl)propiolate (3fa): White solid (210 mg, 75%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (s, 1 H), 7.67-7.64 (m, 2 H), 7.62-7.57 (m, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.11-7.06 (m, 2 H), 5.28 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.97 (d, *J* = 252.0 Hz), 153.27, 136.43, 135.31 (d, *J* = 9.12 Hz,) 132.48, 132.07, 131.65, 129.46, 118.28, 116.13 (d, *J* = 22.5 Hz), 115.26 (d, *J* = 3.62 Hz), 112.84, 86.40, 79.89 (d, *J* = 1.75 Hz), 66.04; IR (cm^{-1}) (KBr) 2222, 1706, 1601, 1506, 1460, 1381, 1280; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}FNO_2$ $[M+H]^+$: 280.0768, found: 280.0775.

3-Cyanobenzyl 3-(3-fluorophenyl)propiolate (3ga): White solid (196 mg, 70%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (s, 1 H), 7.67-7.65 (m, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.40-7.33 (m, 2 H), 7.29-7.25 (m, 1 H), 7.20-7.14 (m, 1 H), 5.29 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.10 (d, *J*=247.3 Hz), 153.09, 136.36, 132.50, 132.10, 131.68, 130.35 (d, *J*=8.1 Hz) 129.49, 128.87 (d, *J* = 3.6 Hz). 120.94 (d, *J* = 9.0 Hz), 119.62 (d, *J* = 9.0 Hz), 118.44, 118.26 (d, *J* = 3.6 Hz), 112.87, 85.59 (d, *J* = 3.6 Hz), 80.42, 66.15; IR (cm^{-1}) (KBr) 2225, 1706, 1582, 1431, 1311, 1216; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}FNO_2$ $[M+H]^+$: 280.0768, found: 280.0769.

3-Cyanobenzyl 3-(4-chlorophenyl)propiolate (3ha): Yellow solid (193 mg, 65%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (s, 1 H), 7.65 (d, *J* = 7.5 Hz, 2 H), 7.54-7.50 (m, 3 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 5.28 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.26, 137.36, 136.43, 134.22, 132.52, 132.14, 131.72, 129.52, 129.10, 118.29, 117.66, 113.94, 86.17, 80.78, 66.15; IR (cm^{-1}) (KBr) 2222, 1699, 1587, 1479, 1379, 1298; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}ClNO_2$ $[M+H]^+$: 296.0473, found: 296.0481.

3-Cyanobenzyl 3-(4-cyanophenyl)propiolate (3ia): Yellow solid (130 mg, 45%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (s, 1 H), 7.69 (s, 4 H), 7.66 (t, *J* = 7.5 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 5.30 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.82, 136.19, 133.34, 132.56, 132.26, 132.25, 131.77, 129.59, 124.01, 118.26, 117.71, 114.30, 113.02, 84.47, 82.89, 66.42; IR (cm^{-1}) (KBr) 2226, 1705, 1498, 1405, 1375, 1292; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{11}N_2O_2$ $[M+H]^+$: 287.0815, found: 287.0812.

3-Cyanobenzyl 3-(4-nitrophenyl)propiolate (3ja): Yellow solid (102 mg, 33%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.27 (d, *J* = 8.5 Hz, 2 H), 7.78-7.74 (m, 3 H), 7.67 (t, *J* =

7.5 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 5.31 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.74, 148.63, 136.12, 133.77, 132.59, 132.28, 131.78, 129.59, 125.82, 123.76, 118.26, 112.99, 84.06, 83.37, 66.48; IR (cm^{-1}) (KBr) 2229, 1709, 1514, 1403, 1344,1291; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}N_2O_4Na$ $[M+H]^+$: 307.0713, found: 307.0707.

3-Cyanobenzyl 3-cyclopropylpropiolate (3ka): Yellow oil (113 mg, 50%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (s, 1 H), 7.64-7.58 (m, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 5.19 (s, 2 H), 1.43-1.36 (m, 1 H), 1.00-0.91 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.10, 136.69, 132.38, 131.92, 131.55, 129.39, 118.31, 112.77, 94.75, 67.86, 65.63, 9.26, -0.67; IR (cm^{-1}) (neat) 2223, 1699, 1451, 1370, 1265; HRMS (ESI, *m*/*z*) calcd. for $C_{14}H_{12}NO_2$ $[M+H]^+$: 226.0863, found: 226.0876.

3-Cyanobenzyl non-2-ynoate (3la): Yellow oil (100 mg, 38%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (s, 1 H), 7.62 (t, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 5.20 (s, 2 H), 2.35 (t, *J* = 7.5 Hz, 2 H), 1.62-1.54 (m, 2 H), 1.44-1.36 (m, 2 H), 1.34-1.24 (m, 4 H), 0.89 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.13, 136.61, 132.36, 131.89, 131.51, 129.36, 118.26, 112.72, 91.06, 72.42 65.67, 31.01, 28.35, 27.26, 22.28, 18.56, 13.85; IR (cm^{-1}) (neat) 2230, 1715, 1455, 1380, 1240; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{19}NO_2$ $[M+H]^+$: 270.1489, found:270.1490.

3-Cyanobenzyl 4-methylpent-2-ynoate (3ma): Yellow oil (90 mg, 40%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (s, 1 H), 7.63 (t, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 8.0 Hz, 1 H), 5.21 (s, 2 H), 2.76-2.66 (m, 1 H), 1.24 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.20, 136.56, 132.38, 131.86, 131.50, 129.33, 118.22, 112.64, 95.38, 71.62, 65.64, 21.47, 20.32; IR (cm^{-1}) (neat) 2229, 1706, 1468, 1373, 1259; HRMS (EI, *m*/*z*) calcd. for $C_{17}H_{19}NO_2$ $[M]^+$: 227.0946, found: 227.0950.

Benzyl 3-phenylpropiolate (3ab)[3a**]:** Yellow solid (185 mg, 78%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55-7.53 (m, 2 H), 7.42-7.30 (m, 8 H), 7.42-7.31 (m, 8 H), 5.24 (s, 2 H).

4-Methylbenzyl 3-phenylpropiolate (3ac): Yellow solid (164 mg, 71%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56-7.52 (m, 1 H), 7.44-7.40 (m, 1 H), 7.36-7.28 (m, 4 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 5.21 (s, 2 H), 2.35 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.86, 138.46, 132.91, 131.86, 130.58, 129.27, 128.73, 128.48, 119.50, 86.48, 80.52,

67.60, 21.15; IR (cm^{-1}) (KBr) 2215, 1702, 1488, 1445, 1376, 1280; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{14}O_2$ $[M+H]^+$: 251.1067, found: 251.1078.

4-(*tert*-Butyl)benzyl 3-phenylpropiolate (3ad): Yellow solid (247 mg, 85%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.54 (m, 2 H), 7.46-7.40 (m, 3 H), 7.38-7.32 (m, 4 H), 5.23 (s, 2 H), 1.32 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.94, 151.75, 132.97, 131.86, 130.61, 128.61, 128.53, 125.59, 119.56, 86.53, 80.55, 67.59, 34.60, 31.25; IR (cm^{-1}) (KBr) 2212, 1705, 1485, 1368, 1283; HRMS (ESI, *m*/*z*) calcd. for $C_{20}H_{20}O_2$ $[M+H]^+$: 293.1536, found: 293.1543.

4-Methoxybenzyl 3-phenylpropiolate (3ae) [3a]**:** Yellow solid (230 mg, 80%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56-7.52 (m, 2 H), 7.44-7.38 (m, 1 H), 7.36-7.30 (m, 4 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 5.19 (s, 2 H), 3.79 (s, 3 H).

4-Fluorobenzyl 3-phenylpropiolate (3af) [3a]**:** Yellow solid (181 mg, 71%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.54 (m, 2 H), 7.46-7.32 (m, 5 H), 7.07 (t, *J* = 8.5 Hz, 2 H), 5.22 (s, 2 H).

4-Chlorobenzyl 3-phenylpropiolate (3ag): Yellow solid (190 mg, 70%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56-7.52 (m, 2 H), 7.44-7.38 (m, 1 H), 7.36-7.22 (m, 6 H), 5.20 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.57, 134.40, 133.34, 132.89, 130.67, 129.85, 128.72, 128.48, 119.26, 86.87, 80.26, 66.64; IR (cm^{-1}) (KBr) 2217, 1698, 1595, 1488, 1459, 1439, 1405, 1367, 1284; HRMS (ESI, *m*/*z*) calcd. for $C_{16}H_{11}ClO_2$ $[M+H]^+$: 271.0520, found: 271.0527.

4-Bromobenzyl 3-phenylpropiolate (3ah) [4d]**:** Yellow solid (237 mg, 75%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.59 (s, 1 H), 7.57 (d, *J* = 7.5 Hz, 1 H), 7.53-7.51 (m, 2 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 5.21 (s, 2 H).

2-Iodobenzyl 3-phenylpropiolate (3ai): Yellow oil (330 mg, 91%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.84-7.78 (m, 1 H), 7.56-7.50 (m, 2 H), 7.44-7.37 (m, 2 H), 7.36-7.28 (m, 3 H), 7.10-6.96 (m, 1 H), 5.25 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.54, 139.54, 137.37, 133.03, 130.72, 130.11, 129.65, 129.36, 128.54, 128.42, 119.43, 87.04, 80.29, 71.30; IR (cm^{-1}) (neat) 2218, 1709, 1590, 1565, 1374, 1280; HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{11}BrIO_2$ $[M]^+$: 361.9804, found: 361.9808.

2,6-Dichlorobenzyl 3-phenylpropiolate (3aj) [13]**:** Yellow solid (239 mg, 78%); ^{1}H NMR($CDCl_3$, 500 MHz) δ 7.58-7.54 (m, 2 H), 7.46-7.40 (m, 1 H), 7.38-7.32 (m, 4 H), 7.26 (t, *J* = 7.5 Hz, 1 H), 5.54 (s, 2 H).

2-Cyanobenzyl 3-phenylpropiolate (3ak): White solid (165 mg, 63%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 8.0 Hz, 1 H), 7.68-7.56 (m, 4 H), 7.50-7.43 (m, 2 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 5.45 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.36, 138.25, 133.05, 130.84, 129.58, 129.05, 128.56, 119.24, 116.75, 112.41, 87.56, 79.94, 64.82; IR (cm^{-1}) (KBr) 2221, 1718, 1491, 1454, 1368, 1281; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}NO_2$ $[M+H]^+$: 262.0863, found: 262.0878.

4-Cyanobenzyl 3-phenylpropiolate (3al): Yellow solid (225 mg, 86%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 8.0 Hz, 2 H), 7.61-7.57 (m, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.50-7.44 (m, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 5.31 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.49, 140.18, 133.06, 132.46, 130.94, 128.63, 128.57, 119.20, 118.44, 112.36, 87.58, 79.99, 66.25; IR (cm^{-1}) (KBr) 2228, 1702, 1488, 1377, 1284; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{11}NO_2$ $[M+H]^+$: 262.0863, found: 262.0875.

4-(Trifluoromethyl)benzyl 3-phenylpropiolate (3am) [13]**:** Yellow solid (240 mg, 78%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (d, *J* = 8.5 Hz, 2 H), 7.59-7.56 (m, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.47-7.42 (m, 1 H), 7.37 (t, *J* = 7.5 Hz, 2 H), 5.30 (s, 2 H).

4-Nitrobenzyl 3-phenylpropiolate (3an) [3a]**:** Yellow solid (246 mg, 87%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.26-8.22 (m, 2 H), 7.62-7.56 (m, 4 H), 7.49-7.44 (m, 1 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 5.35 (s, 2 H).

Cinnamyl 3-phenylpropiolate (3ao) [4d]**:** White solid (103 mg, 47%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.54 (m, 2 H), 7.45-7.22 (m, 8 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.31 (dt, *J* = 16.0, 6.5 Hz, 1 H), 4.87 (dd, *J* = 6.5, 1.5 Hz, 2 H).

But-2-yn-1-yl 3-phenylpropiolate (3ap) [4d]**:** Yellow solid (85 mg, 42%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.55 (m, 2 H), 7.48-7.42 (m, 1H), 7.39-7.34 (m, 2 H), 4.79 (q, *J* = 7.5 Hz, 2 H), 1.87 (t, *J* = 7.5 Hz, 3 H).

Benzhydryl 3-phenylpropiolate (3aq) [14]**:** White solid (22 mg, 8%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62-7.56 (m, 2 H), 7.46-7.28 (m, 13 H), 7.01 (s, 1 H).

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