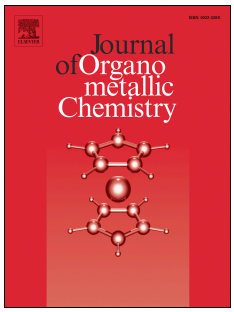

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Yingying Du, Fang Yao, Rongli Zhang, Mingzhong Cai

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A heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates toward α-acyloxy methyl ketones

Yingying Du,[a] Fang Yao,[b] Rongli Zhang,[a] Mingzhong Cai[a]*

[a] *Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China*

[b] *College of Chemical and Material Engineering, Quzhou University, Quzhou 324000, P. R. China*

ABSTRACT

A heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates has been developed that proceeds smoothly in 1,4-dioxane at room temperature in the presence of 1 mol% diphenylphosphine-modified MCM-41-anchored gold(I) complex [Ph_2P-MCM-41-$AuSbF_6$] as catalyst and provides an efficient and practical approach for the synthesis of a variety of α-acyloxy methyl ketones with high atom economy, good to excellent yield, and high functional group tolerance. This new immobilized gold(I) catalyst can readily be obtained by a simple preparative procedure from commercially available reagents, and recovered via a filtration process and reused at least seven times without apparent loss of activity.

Keywords: Gold; Hydration; Propargyl acetate; Methyl ketone; Heterogeneous catalysis

1. Introduction

The hydration of alkynes has provided a straightforward, atom-economical and environmentally friendly method for the construction of diverse ketones and is considered to be one of the most important C–O bond formation reactions in organic

*Corresponding author. Fax: +86 791 88120388.

E-mail address: mzcai@jxnu.edu.cn (M. Cai).

synthesis due to the wide availability of starting alkynes and the incorporation of readily modifiable carbonyl functional moiety in the molecules [1-3]. Traditionally, hydration of alkynes was conducted in the presence of highly toxic mercury salts or more than stoichiometric amount of concentrated sulfuric acid [4-7]. Although some Brønsted acids have also proven to exhibit catalytic activity for this transformation, in most cases stoichiometric or excess amounts of acids were still required to achieve high conversions [8-10]. To overcome the drawbacks of traditional alkyne hydration, a variety of transition-metal complexes such as Fe [11], Co [12], Ag [13], Pt [14], Pd [15], Ir [16], Ru [17], and Au [18-30] have been explored as catalysts for the reaction. Among them, cationic gold catalysts display unique catalytic efficiency and have attracted much attention because they exhibit strong affinity to activate the π bonds of alkynes by nucleophilic attack. Recently, cationic gold(I) complexes have proven to be one of the most promising catalysts for the regioselctive hydration of terminal alkynes owing to their high activity and regioselectivity [21-29]. Cationic gold(I) catalysts are usually prepared in situ by the reaction of neutral gold(I) complexes [LAuCl, L = phosphine or *N*-heterocyclic carbene] with various silver salts [AgOTf, $AgNTf_2$, $AgBF_4$, $AgSbF_6$, etc], which suffers from some drawbacks such as high cost and the light sensitivity of silver salts. In contrast, silver salt-free heterogeneous gold catalysts for the hydration of alkynes have received less attention [31-33].

It was reported that the existence of a neighboring ester group in alkynes, e.g., propargyl carboxylates, would result in regioselective incorporation of the carbonyl functional moiety in the product molecules through gold-catalyzed hydration [34,35].

Recently, Sahoo and coworkers reported gold(I)-catalyzed regioselective hydration of propargyl acetates by using Ph_3PAuCl and $AgSbF_6$ as catalysts, providing α-acyloxy methyl ketones in good to excellent yields under mild conditions [36]. The hydration products could be converted into α-hydroxy methyl ketones in a straightforward manner, and the latter are important synthetic intermediates for various bioactive compounds and are found in many natural products of pharmacological importance [37-39]. Besides, the $Ph_3PAuCl/AgSbF_6$ system has also been applied to regioselective hydration of terminal halo-substituted propargyl carboxylates leading to α-acyloxy α'-halo ketones [40]. Although this homogeneous gold(I) catalytic system is highly efficient for the regioselective hydration of propargyl carboxylates towards various valuable functionalized methyl ketones, the non-recyclability of expensive homogeneous Ph_3PAuCl and the decay of cationic gold as well as the light sensitivity of $AgSbF_6$ make this method of limited synthetic utility. Thus, development of a recyclable heterogeneous gold(I) catalyst having a high catalytic efficiency for the regioselective hydration of propargyl carboxylates is highly desirable from both economical and environmental points of view.

The hexagonally-ordered mesoporous silica MCM-41 has been widely employed as an ideal solid support for anchoring various homogeneous metal catalysts because it possesses ultrahigh surface area, large and uniform pore size, big pore volume and excellent thermal stability [41-43]. To date, some functionalized MCM-41-anchored gold(I) and gold(III) complexes have been successfully utilized in many organic reactions as green and sustainable gold catalysts [44-50]. Recently, we have reported

the preparation of a diphenylphosphine-modified MCM-41-anchored gold(I) complex [Ph_2P-MCM-41-AuCl] and its successful application to regiospecific hydroamination of ynamides and propiolic acid derivatives with anilines [51]. Considering our continued interest in the development of efficient and recyclable gold catalysts for organic transformations [49-51], herein we report a highly efficient, heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates towards α-acyloxy methyl ketones by using the diphenylphosphine-modified MCM-41-anchored gold(I) complex [Ph_2P-MCM-41-$AuSbF_6$] as the catalyst, which could be facilely prepared by treating Ph_2P-MCM-41-AuCl with $AgSbF_6$ in dichloromethane (DCM) at room temperature for 0.5 h (Scheme 1). This supported gold(I) catalyst displays high catalytic efficiency in this transformation and can be readily separated and recovered from the reaction mixture *via* a simple filtration process, and its catalytic activity remains almost unaltered even after being recycled for 8 times.

2. Results and discussion

2.1. Heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates.

Four diphenylphosphine-modified MCM-41-anchored gold(I) complexes [Ph_2P-MCM-41-AuX, X = OTf, NTf_2, SbF_6, and BF_4] were facilely prepared by the reaction of the known Ph_2P-MCM-41-AuCl complex [51] with various silver salts (AgX = AgOTf, $AgNTf_2$, $AgSbF_6$, and $AgBF_4$) in DCM at room temperature for 0.5 h, as shown in Scheme 2. Their characterization data were given in the Supporting Information. They were then used as the catalysts for regioselective hydration of

propargyl acetates. In our initial screening experiments, 1-phenylprop-2-ynyl acetate **1a** was chosen as the model substrate to optimize reaction conditions, and the results are summarized in Table 1. At first, the effect of various heterogeneous gold catalysts on the model reaction was examined in dioxane at room temperature (entries 1-5). Ph_2P-MCM-41-$AuSbF_6$ was found to be the most effective for this reaction and the use of 2 mol% Ph_2P-MCM-41-$AuSbF_6$ as catalyst afforded the desired product **2a** in 97% isolated yield within 5 h (entry 3), while other heterogeneous gold complexes such as Ph_2P-MCM-41-AuOTf, Ph_2P-MCM-41-$AuNTf_2$, and Ph_2P-MCM-41-$AuBF_4$ provided relatively lower yields on longer reaction times (entries 1, 2 and 4) and Ph_2P-MCM-41-AuCl was ineffective (entry 5). Replacement of dioxane with CH_2Cl_2 or MeOH resulted in a decreased yield of **2a** (entries 6 and 7), whilst the use of DMF or DMSO as solvents did not produce **2a** (entries 8 and 9). Finally, the amount of Ph_2P-MCM-41-$AuSbF_6$ was also screened (entries 10 and 11). To our delight, reducing the catalyst loading from 2 to 1 mol% did not affect the reaction efficiency significantly and led to the hydration product **2a** in 96% isolated yield (entry 10). But, further reducing the amount of the gold catalyst to 0.5 mol% resulted in a slightly decreased yield and a longer reaction time was required (entry 11). When a homogenous Ph_3PAuCl (1 mol%)/$AgSbF_6$ (1 mol%) catalytic system was used in the reaction, the desired **2a** was also isolated in 97% yield, which indicating that the catalytic efficiency of Ph_2P-MCM-41-$AuSbF_6$ was comparable to that of homogenous $Ph_3PAuCl/AgSbF_6$ system (entry 12). Therefore, the optimum conditions for this hydration reaction were the use of Ph_2P-MCM-41-$AuSbF_6$ (1 mol%) in dioxane as

solvent at room temperature under Ar for 12 h (Table 1, entry 10).

Having established the optimized reaction conditions, we started to investigate the generality of this heterogeneous gold(I)-catalyzed hydration of the terminal alkynes of propargyl acetates, and the results are summarized in Table 2. At first, the effect of the electronic nature of substituents on the aryl moiety of 1-arylprop-2-ynyl acetates (**1b-l**) on the hydration reaction was examined. 1-Arylprop-2-ynyl acetates (**1b-e**) bearing various electron-donating groups, such as methyl, *t*-butyl, benzyloxy, and methoxy at the 4- or 3-positions on the benzene ring, showed a similar reactivity with the electronically neutral 1-phenylprop-2-ynyl acetate (**1a**) and underwent hydration smoothly to give the corresponding hydrated products **2b-e** in 89-94% yields. Besides, more electron-rich substrate **1f** provided the target product **2f** in 90% yield. Furthermore, electron-neutral substrate **1g** having a rigid biphenyl group also reacted well to afford **2g** in 90% yield. Electron-withdrawing substituents such as halo and trifluoromethyl groups on the benzene ring did not affect the hydration reaction, and halo groups are inert to the optimized conditions. The hydration reactions of electron-deficient substrates **1h-l** proceeded effectively to afford the desired products **2h-l** in excellent yields. These halo groups in products **2h-k** are expected to be converted into other useful functional groups through the cross-coupling reactions catalyzed by transition metals. It is well known that protecting groups of the hydroxyl moiety are sensitive to the mild acidic and basic conditions. To examine the relative stability of the protecting groups under the optimized conditions, the hydration reaction of the substrate **1m** with a silyl ether unit was performed. To our delight, *t*-butyldimethylsilyl (TBS) as the

bulkier silyl protecting group was tolerated well in the reaction and the expected product **2m** was obtained in 81% yield.

We next examined the effect of *ortho*-substitution on the aryl moiety to hydration reaction, and the results are also shown in Table 2. The *ortho*-allyloxy group did not partake in the hydration reaction and the expected product **2n** was produced in 95% yield; the allyl functionality could undergo further organic transformations. Electron-donating methoxy or acetyloxy groups at the 2-position did not inhibit the hydration and provided the desired products **2o-q** in excellent yields. The hydration of propargyl acetates **1r-u** bearing various electron-withdrawing *ortho* substituents, such as chloro, bromo, and nitro groups, proceeded smoothly under the standard conditions to afford the corresponding ketones **2r-u** in 88-94% yields. Gratifyingly, bulky 1-(naphthalene-1-yl)prop-2-ynyl acetate **1v** also reacted quite well, furnishing the target product **2v** in 93% yield. The above results indicated that electronic and steric effects of substituents on the aromatic ring did not impart the significant effect to hydration of terminal triple bond of propargyl acetates. Notably, thienyl-2-substituted propargyl acetate **1w** could undergo hydration effectively, affording 76% yield of **2w**, but furyl-2-substituted propargyl acetate did not deliver the desired methyl ketone. In addition to aryl- and heteroaryl-substituted propargyl acetates, the hydration of alkyl-, vinyl-, dialkyl-, and aryl/alkyl-substituted propargyl acetates was also investigated. As shown in Table 2, alkyl-, benzyl- and cycloalkyl-substituted propargyl acetates **1x-b'** underwent the regioselective hydration reaction smoothly to give the corresponding methyl ketones **2x-b'** in 84-93% yields. Interestingly, vinyl-substituted propargyl acetates **1c'** and **1d'**

were compatible with the standard conditions and afforded the desired α-acetyloxy-β,γ-unsaturated methyl ketones **2c'** and **2d'**, respectively in high yields. Besides, sterically hindered substrate **1e'** having a quaternary α-carbon center with two alkyl groups also reacted well, thus furnishing the expected ketone **2e'** in 93% yield. Similarly, both aryl- and methyl-substituted propargyl acetates **1f'** and **1g'** did not influence the reaction efficiency and gave the desired products **2f'** and **2g'** in 90-92% yields. Notably, sterically hindered 1-ethynylcyclohexyl acetate **1h'** also underwent the hydration effectively to produce the target product **2h'** in 86% yield.

2.2. Leaching test for Ph_2P-MCM-41-$AuSbF_6$

To confirm that the observed hydration reaction was due to the Ph_2P-MCM-41-$AuSbF_6$ catalyst and not to a soluble gold species leached from this heterogeneous catalyst, we focused on the hydration of 1-phenylprop-2-ynyl acetate **1a**. After the reaction was carried out for 4 h, the catalyst was removed from the reaction mixture by filtration and the catalyst-free filtrate was stirred at room temperature under Ar for another 10 h. It was found that no increase in conversion of 1-phenylprop-2-ynyl acetate **1a** was observed in the filtrate, indicating that the soluble gold species leached from the catalyst (if any) are not related to the observed reaction. In addition, no gold species could be detected in the filtrate based on ICP-AES analysis. The above results indicated that the Ph_2P-MCM-41-$AuSbF_6$ complex was stable during the hydration and is actually functioning in a heterogeneous manner.

2.3. Possible mechanism for the heterogeneous gold(I)-catalyzed regioselective

hydration reaction.

A possible mechanism for the heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates to α-acyloxy methyl ketones is illustrated in Scheme 3 [36]. Firstly, coordination of the Ph_2P-MCM-41-$AuSbF_6$ complex to alkyne moiety in propargyl acetate **1** produces an MCM-41-bound gold(I)–alkyne–π complex intermediate **A**. Then reactive intermediate **A** undergoes an intramolecular 5-*exo*-*dig* attack of carbonyl oxygen on the acetylenic carbon to generate an MCM-41-bound 5-membered vinylgold cation intermediate **B**. Subsequent nucleophilic addition of H_2O to intermediate **B** forms another MCM-41-bound vinylgold cation intermediate **C**. The latter undergoes the protodeauration to provide intermediate **D** and regenerate the gold(I) catalyst. Finally, the isomerization of intermediate **D** occurs to furnish α-acyloxy methyl ketone **2**.

2.4. Recycling of the gold(I) catalyst

For practical application of a supported precious metal catalyst, its ease of separation, stability and reusability are important factors to be examined. Ph_2P-MCM-41-$AuSbF_6$ can be readily separated and recovered from the reaction product via a simple filtration process. We next examined the recyclability of the Ph_2P-MCM-41-$AuSbF_6$ catalyst in the hydration reaction of 1-phenylprop-2-ynyl acetate **1a**. Upon completion of the first reaction cycle, the Au(I) catalyst was recovered by filtration of the reaction solution and washed with dioxane and acetone. After being air-dried, the recovered gold(I) catalyst was employed in the next cycle using the same substrate under the

identical conditions, and the results are listed in Table 3. As shown in Table 3, the target product **2a** was produced in almost consistent yield for eight consecutive cycles, which indicating that this heterogeneous gold(I) catalyst can be recycled at least eight times without any significant decrease in catalytic efficiency. In order to determine if the supported phosphine ligand was oxidized to the phosphine oxide during the hydration reaction, both the recovered catalyst after eight consecutive cycles and the fresh catalyst were subjected to hydrolysis under basic conditions and the silyl attachments obtained were subjected to ^{31}P NMR determination. ^{31}P NMR spectrum of the fresh catalyst (Fig. 1a) showed a strong signal at δ 33.2 ppm, which corresponding to the phosphine in the diphenylphosphine gold(I) complex [52], whilst ^{31}P NMR spectrum of the recovered catalyst (Fig. 1b) also displayed only one signal at δ 32.5 ppm, which indicating that the oxidation of the phosphine ligand to the phosphine oxide did not occur under the optimized reaction conditions. In addition, the Au content of the recovered gold(I) catalyst after eight consecutive runs was measured to be 0.36 mmol/g by ICP-AES analysis, which revealing negligible gold leaching.

3. Conclusions

In summary, heterogenized homogeneous gold(I) catalyst [Ph_2P-MCM-41-$AuSbF_6$] has been successfully developed for the regioselective hydration reaction of propargyl acetates. It is demonstrated that such a heterogenized diphenylphosphine-gold(I) complex is a highly efficient and recyclable heterogeneous catalyst for the synthesis

of a variety of α-acyloxy methyl ketones. The reaction was applicable to a wide range of propargyl acetates with broad functional group compatibility and tolerance to acid-labile protecting groups. This heterogeneous gold(I)-catalyzed hydration reaction has some attractive features such as readily available starting materials, mild reaction conditions, the absence of acidic promoter, good to excellent yields, and excellent recyclability of the gold(I) catalyst, offering a simple, highly efficient, economic and practical route to α-acyloxy methyl ketones, which would transform to synthetically versatile α-hydroxy methyl ketones in a straightforward manner.

4. Experimental

4.1. General remarks

All starting chemicals were purchased from different commercial sources and utilized as received without further purification. All solvents were purified by drying and distillation before use. The products were isolated by using column chromatography on 230-400 mesh silica gel. A mixture of hexane and EtOAc was generally used as eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 NMR spectrometer in $CDCl_3$ as solvent. ^{31}P NMR spectra (121 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Melting points are uncorrected. The content of gold was determined with a Jarrell-Ash 1100 ICP. HRMS spectra were recorded on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES). Mesoporous MCM-41 material [41] and propargyl acetates **1** [36] were prepared according to

literature methods.

4.2. Preparation of Ph_2P-MCM-41-$AuSbF_6$ complex [51].

A mixture of 2-(diphenylphosphino)ethyltriethoxysilane (0.566 g, 1.5 mmol) and the MCM-41 (2.0 g) in dry toluene (130 mL) was stirred at 100 °C for 24 h under an argon atmosphere. The product was collected by filtration, washed with chloroform (25 mL), and dried *in vacuo* at 130 °C for 6 h. The resulting white powders were then added to a solution of Me_3SiCl (3.0 g) in dry toluene (110 mL) and the mixture was stirred at room temperature under argon for 24 h. The solid product was isolated by filtration, followed by washing with acetone (2 × 25 mL), and drying *in vacuo* at 110 °C for 5 h to provide 2.412 g of modified material Ph_2P-MCM-41. The content of phosphorus was determined to be 0.42 mmol g^{-1} by elemental analysis.

A mixture of Ph_2P-MCM-41 (1.00 g) and Me_2SAuCl (115 mg, 0.39 mmol) in dry CH_2Cl_2 (30 mL) was stirred at room temperature for 8 h under an argon atmosphere. The product was filtered off, washed with CH_2Cl_2 and then treated with $AgSbF_6$ (134 mg, 0.39 mmol) in CH_2Cl_2 (30 mL) at room temperature for 0.5 h. The resulting product was collected by filtration, washed with 25 wt% of $NH_3 \cdot H_2O$ (2 × 20 mL), distilled water (2 × 20 mL) and EtOH (2 × 20 mL), and dried *in vacuo* to afford 1.053 g of a gray gold complex (Ph_2P-MCM-41-$AuSbF_6$). The content of gold was found to be 0.37 mmol g^{-1} based on ICP-AES.

The Ph_2P-MCM-41-AuOTf, Ph_2P-MCM-41-$AuNTf_2$, and Ph_2P-MCM-41-$AuBF_4$ were also prepared by using Ph_2P-MCM-41 (1.00 g), Me_2SAuCl (115 mg, 0.39 mmol),

and AgX (X = OTf, $SbNTf_2$ and BF_4, 0.39 mmol) as the starting materials in the same manner, the contents of gold were determined to be 0.38 mmol g^{-1}, 0.35 mmol g^{-1} and 0.36 mmol g^{-1}, respectively based on ICP-AES analysis.

4.3. General procedure for the heterogeneous gold(I)-catalyzed regioselective hydration of propargyl acetates.

A Schlenk tube was charged with Ph_2P-MCM-41-$AuSbF_6$ (28 mg, 0.01 mmol), propargyl acetate (1.0 mmol), deionized water (3.0 mmol) and 1,4-dioxane (1.5 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction, the mixture was diluted with EtOAc (10 mL) and filtered. The gold(I) catalyst was washed with dioxane (2 × 3 mL) and acetone (2 × 3 mL), and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by using column chromatography on silica gel (eluent: hexane/ethyl acetate) to afford the desired product **2**.

*4.3.1. 2-Oxo-1-phenylpropyl acetate (**2a**) [36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.39 (m, 5H), 5.98 (s, 1H), 2.18 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 170.2, 133.2, 129.4, 129.1, 128.1, 80.9, 26.1, 20.7.

*4.3.2. 2-Oxo-1-(p-tolyl)propyl acetate (**2b**) [36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.86 (s, 1H), 2.28 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.3, 139.4, 130.2, 129.8, 128.1, 80.8, 26.1, 21.2, 20.7.

*4.3.3. 1-(4-(tert-Butyl)phenyl)-2-oxopropyl acetate (**2c**)*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.96 (s, 1H), 2.17

(s, 3H), 2.11 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.3, 152.6, 130.1, 127.9, 126.1, 80.8, 34.7, 31.2, 26.2, 20.7. HRMS calcd for $C_{15}H_{20}O_3^+$ [M^+]: 248.1412, found 248.1419.

4.3.4. 1-(4-(Benzyloxy)phenyl)-2-oxopropyl acetate ***(2d)***. Pale yellow solid. Mp 84.2-84.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.27 (m, 4H), 7.26-7.20 (m, 3H), 6.91 (d, J = 8.8 Hz, 2H), 5.84 (s, 1H), 4.97 (s, 2H), 2.07 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 170.4, 159.7, 136.6, 129.7, 128.7, 128.1, 127.5, 125.4, 115.5, 80.5, 70.1, 26.2, 20.7. HRMS calcd for $C_{18}H_{18}O_4^+$ [M^+]: 298.1205, found 298.1203.

4.3.5. 1-(3-Methoxyphenyl)-2-oxopropyl acetate ***(2e)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.96-6.90 (m, 2H), 5.95 (s, 1H), 3.80 (s, 3H), 2.18 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 170.1, 160.0, 134.6, 130.1, 120.3, 114.9, 113.4, 80.8, 55.3, 26.0, 20.6.

4.3.6. 1-(3,5-Dimethoxyphenyl)-2-oxopropyl acetate ***(2f)***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (d, J = 2.0 Hz, 2H), 6.47 (t, J = 2.2 Hz, 1H), 5.89 (s, 1H), 3.79 (s, 6H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 170.1, 161.2, 135.2, 106.0, 101.2, 80.9, 55.4, 26.0, 20.7. HRMS calcd for $C_{13}H_{16}O_5^+$ [M^+]: 252.0998, found 252.0995.

4.3.7. 1-([1,1'-Biphenyl]-4-yl)-2-oxopropyl acetate ***(2g)***. Pale yellow solid. Mp 94.8-95.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.40-7.32 (m, 4H), 7.28-7.25 (m, 1H), 5.93 (s, 1H), 2.10 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 170.3, 142.4, 140.2, 132.1, 128.9, 128.6, 127.8, 127.7, 127.2, 80.7, 26.2, 20.7. HRMS calcd for $C_{17}H_{16}O_3^+$ [M^+]: 268.1099, found 268.1091.

4.3.8. 1-(4-Fluorophenyl)-2-oxopropyl acetate ***(2h)*** *[36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 8.8, 5.2 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 5.96 (s, 1H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 170.1, 163.3 (d, J = 247.4 Hz), 129.9 (d, J = 8.4 Hz), 129.2 (d, J = 3.1 Hz), 116.1 (d, J = 21.6 Hz), 80.1, 26.1, 20.6.

4.3.9. 1-(4-Chlorophenyl)-2-oxopropyl acetate ***(2i)*** *[36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 5.93 (s, 1H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 170.1, 132.3, 129.6, 123.6, 80.2, 26.1, 20.7.

4.3.10. 1-(4-Bromophenyl)-2-oxopropyl acetate ***(2j)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 5.93 (s, 1H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 170.0, 135.4, 131.8, 129.3, 129.2, 80.1, 26.0, 20.6.

4.3.11. 1-(3,4-Dichlorophenyl)-2-oxopropyl acetate ***(2k)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 8.2, 1.8 Hz, 1H), 5.92 (s, 1H), 2.21 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 169.9, 133.7, 133.4, 133.3, 131.0, 129.7, 127.1, 79.4, 26.1, 20.6.

4.3.12. 2-Oxo-1-(3-(trifluoromethyl)phenyl)propyl acetate ***(2l)***. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.58-7.53 (m, 2H), 7.46 (t, J = 7.8 Hz, 1H),

5.94 (s, 1H), 2.13 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 170.0, 134.4, 131.5 (q, J = 32.5 Hz), 131.2, 129.6, 126.1 (q, J = 3.6 Hz), 124.6 (q, J = 3.8 Hz), 123.7 (q, J = 270.8 Hz), 80.1, 26.0, 20.5. HRMS calcd for $C_{12}H_{11}F_3O_3^+$ [M^+]: 260.0660, found 260.0665.

*4.3.13. 1-(3-(tert-Butyldimethylsilyloxy)phenyl)-2-oxopropyl acetate (**2m**) [36]*. Pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.89-6.84 (m, 2H), 5.91 (s, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 0.99 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 170.2, 156.2, 134.5, 130.1, 121.0, 120.9, 119.7, 80.7, 26.0, 25.6, 20.7, 18.2, -4.4.

*4.3.14. 1-(2-(Allyloxy)phenyl)-2-oxopropyl acetate **(2n)** [36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 2H), 6.99 (d, J = 7.6 Hz, 1H), 6.95 (dd, J = 8.6, 4.6 Hz, 1H), 6.51 (s, 1H), 6.09-6.00 (m, 1H), 5.43 (dd, J = 17.4, 1.2 Hz, 1H), 5.31 (dd, J = 10.6, 1.0 Hz, 1H), 4.67-4.56 (m, 2H), 2.16 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 170.3, 155.9, 132.7, 130.6, 129.5, 122.3, 121.3, 117.8, 112.4, 75.0, 69.2, 26.3, 20.7.

*4.3.15. 1-(2-Methoxyphenyl)-2-oxopropyl acetate **(2o)***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.18 (m, 2H), 6.91-6.83 (m, 2H), 6.37 (s, 1H), 3.77 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.2, 156.9, 130.7, 129.4, 122.0, 121.0, 111.2, 74.9, 55.6, 26.1, 20.7. HRMS calcd for $C_{12}H_{14}O_4^+$ [M^+]: 222.0892, found 222.0883.

*4.3.16. 1-(2,5-Dimethoxyphenyl)-2-oxopropyl acetate **(2p)***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81-6.77 (m, 3H), 6.36 (s, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.08

(s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 170.2, 153.8, 151.0, 122.7, 115.6, 114.6, 112.4, 74.7, 56.2, 55.7, 26.1, 20.7. HRMS calcd for $C_{13}H_{16}O_5^+$ [M^+]: 252.0998, found 252.0992.

4.3.17. 2-(1-Acetoxy-2-oxopropyl)phenyl acetate ***(2q)***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.25-7.19 (m, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.09 (s, 1H), 2.26 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 170.0, 169.2, 149.0, 130.7, 130.4, 126.7, 126.1, 123.7, 76.1, 26.2, 20.8, 20.6. HRMS calcd for $C_{13}H_{14}O_5^+$ [M^+]: 250.0841, found 250.0844.

4.3.18. 1-(2-Chlorophenyl)-2-oxopropyl acetate ***(2r)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 (dd, J = 7.2, 2.4 Hz, 1H), 7.37-7.29 (m, 2H), 6.52 (s, 1H), 2.19 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 170.0, 134.0, 131.5, 130.6, 130.1, 129.8, 127.5, 76.9, 26.7, 20.6.

4.3.19. 1-(2-Bromophenyl)-2-oxopropyl acetate ***(2s)*** [36]. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 1H), 7.40-7.33 (m, 2H), 7.28-7.23 (m, 1H), 6.51 (s, 1H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 170.0, 133.4, 133.2, 130.9, 129.9, 128.1, 124.4, 79.2, 26.9, 20.6.

4.3.20. 1-(2,4-Dichlorophenyl)-2-oxopropyl acetate ***(2t)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.30 (dd, J = 8.4, 2.0 Hz, 1H), 6.45 (s, 1H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 169.8, 136.0, 134.6, 130.6, 130.2, 129.9, 127.9, 76.3, 26.7, 20.5.

4.3.21. 1-(2-Nitrophenyl)-2-oxopropyl acetate ***(2u)***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.58-7.52 (m, 2H),

6.74 (s, 1H), 2.32 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 169.5, 148.1, 133.8, 130.1, 129.9, 129.7, 125.2, 75.7, 27.1, 20.6. HRMS calcd for $C_{11}H_{11}NO_5^+$ [M^+]: 237.0637, found 237.0632.

4.3.22. 1-(Naphthalen-1-yl)-2-oxopropyl acetate ***(2v)*** *[36]*. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 1H), 7.77-7.73 (m, 2H), 7.48-7.32 (m, 4H), 6.56 (s, 1H), 2.06 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.2, 134.2, 131.3, 130.4, 129.6, 129.0, 128.3, 127.2, 126.3, 125.4, 123.9, 79.5, 26.3, 20.8.

4.3.23. 2-Oxo-1-(thiophen-2-yl)propyl acetate ***(2w)*** *[36]*. Pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 1H), 7.15 (d, J = 3.2 Hz, 1H), 7.05 (dd, J = 4.8, 3.6 Hz, 1H), 6.23 (s, 1H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 170.1, 134.6, 128.4, 127.8, 127.3, 75.9, 26.0, 20.6.

4.3.24. 2-Oxoundecan-3-yl acetate ***(2x)***. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92-4.88 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.71-1.62 (m, 2H), 1.33-1.17 (m, 12H), 0.81 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.4, 170.6, 78.7, 31.8, 30.2, 29.3, 29.2, 29.1, 26.0, 25.1, 22.6, 20.6, 14.0. HRMS calcd for $C_{13}H_{24}O_3^+$ [M^+]: 228.1725, found 228.1729.

4.3.25. 3-Oxo-1-phenylbutan-2-yl acetate ***(2y)*** *[36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, J = 7.2 Hz, 2H), 7.26-7.18 (m, 3H), 5.22-5.18 (m, 1H), 3.13-3.07 (m, 1H), 3.02-2.95 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2, 170.3, 135.9, 129.3, 128.6, 127.1, 79.1, 36.7, 26.8, 20.6.

4.3.26. 4-Oxo-1-phenylpentan-3-yl acetate ***(2z)***. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.4 Hz, 2H), 7.23-7.15 (m, 3H), 5.00-4.95 (m, 1H), 2.75-2.67

(m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.12-2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.1, 170.5, 140.4, 128.6, 128.4, 126.4, 78.1, 31.9, 31.5, 26.1, 20.7. HRMS calcd for $C_{13}H_{16}O_3^+$ [M^+]: 220.1099, found 220.1094.

4.3.27. 2-Oxo-4-phenylpentan-3-yl acetate ***(2a')***. Colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.4 Hz, 2H), 7.27-7.21 (m, 3H), 5.04 (d, J = 6.0 Hz, 1H), 3.30-3.24 (m, 1H), 2.11 (s, 3H), 1.89 (s, 3H), 1.35 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5, 170.5, 141.3, 128.7, 127.8, 127.3, 82.4, 40.8, 27.9, 20.5, 15.9. HRMS calcd for $C_{13}H_{16}O_3^+$ [M^+]: 220.1099, found 220.1097.

4.3.28. 1-Cyclohexyl-2-oxopropyl acetate ***(2b')***. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 (d, J = 4.4 Hz, 1H), 2.07 (s, 6H), 1.85-1.75 (m, 1H), 1.73-1.64 (m, 2H), 1.62-1.48 (m, 3H), 1.24-1.06 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5, 170.7, 82.6, 39.0, 29.3, 27.3, 27.1, 26.1, 25.9, 25.8, 20.6. HRMS calcd for $C_{11}H_{18}O_3^+$ [M^+]: 198.1256, found 198.1259.

4.3.29. (E)-5,9-dimethyl-2-oxodeca-4,8-dien-3-yl acetate ***(2c')***. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (d, J = 10.0 Hz, 1H), 5.15 (d, J =10.0 Hz, 1H), 5.03 (t, J = 5.6 Hz, 1H), 2.16-2.10 (m, 9H), 1.85 (s, 3H), 1.69-1.66 (m, 4H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.6, 170.4, 145.9, 132.2, 123.3, 116.6, 76.5, 39.6, 26.1, 25.9, 25.7, 20.7, 17.7, 17.3. HRMS calcd for $C_{14}H_{22}O_3^+$ [M^+]: 238.1569, found 238.1574.

4.3.30. (E)-4-Oxo-1-phenylpent-1-en-3-yl acetate ***(2d')***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 7.2 Hz, 2H), 7.24-7.14 (m, 3H), 6.71 (d, J = 16.0 Hz, 1H), 6.06 (dd, J = 15.6, 8.0 Hz, 1H), 5.50 (dd, J = 7.6, 0.8 Hz, 1H), 2.10 (s, 3H),

2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 170.0, 136.2, 135.5, 128.8, 128.7, 126.8, 120.5, 79.9, 26.1, 20.7. HRMS calcd for $C_{13}H_{14}O_3^+$ [M^+]: 218.0943, found 218.0945.

4.3.31. 3,5-Dimethyl-2-oxohexan-3-yl acetate ***(2e')*** *[36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 3H), 2.08 (s, 3H), 1.80-1.72 (m, 2H), 1.69-1.63 (m, 1H), 1.52 (s, 3H), 0.95 (dd, J = 6.0, 3.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 170.1, 86.5, 44.4, 24.4, 24.0, 23.9, 23.7, 21.2, 20.5.

4.3.32. 2-(4-Bromophenyl)-3-oxobutan-2-yl acetate ***(2f')***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 2.26 (s, 3H), 1.95 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 169.9, 137.7, 131.9, 126.6, 122.4, 87.1, 23.6, 22.8, 21.3. HRMS calcd for $C_{12}H_{13}BrO_3^+$ [M^+]: 284.0048, found 284.0047.

4.3.33. 2-(3,4-Dimethylphenyl)-3-oxobutan-2-yl acetate ***(2g')***. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.15 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 6H), 1.95 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8, 170.1, 137.0, 136.7, 136.0, 130.0, 125.9, 122.2, 87.5, 23.6, 22.9, 21.4, 20.0, 19.4. HRMS calcd for $C_{14}H_{18}O_3^+$ [M^+]: 234.1256, found 234.1258.

4.3.34. 1-Acetylcyclohexyl acetate ***(2h')*** *[36]*. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14-1.81 (m, 8H), 1.73-1.28 (m, 7H), 1.22-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.1, 170.2, 85.2, 30.8, 25.0, 23.5, 21.1, 20.9.

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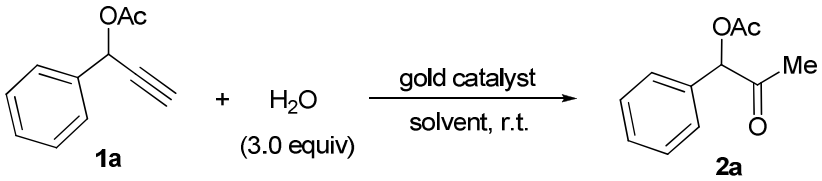
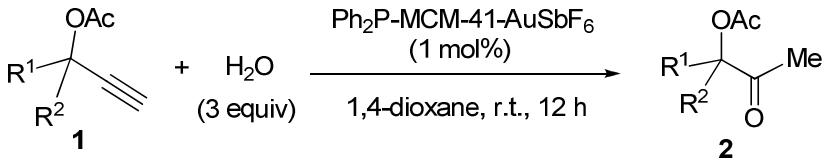
Table 1 Optimization of the reaction conditions.[a]

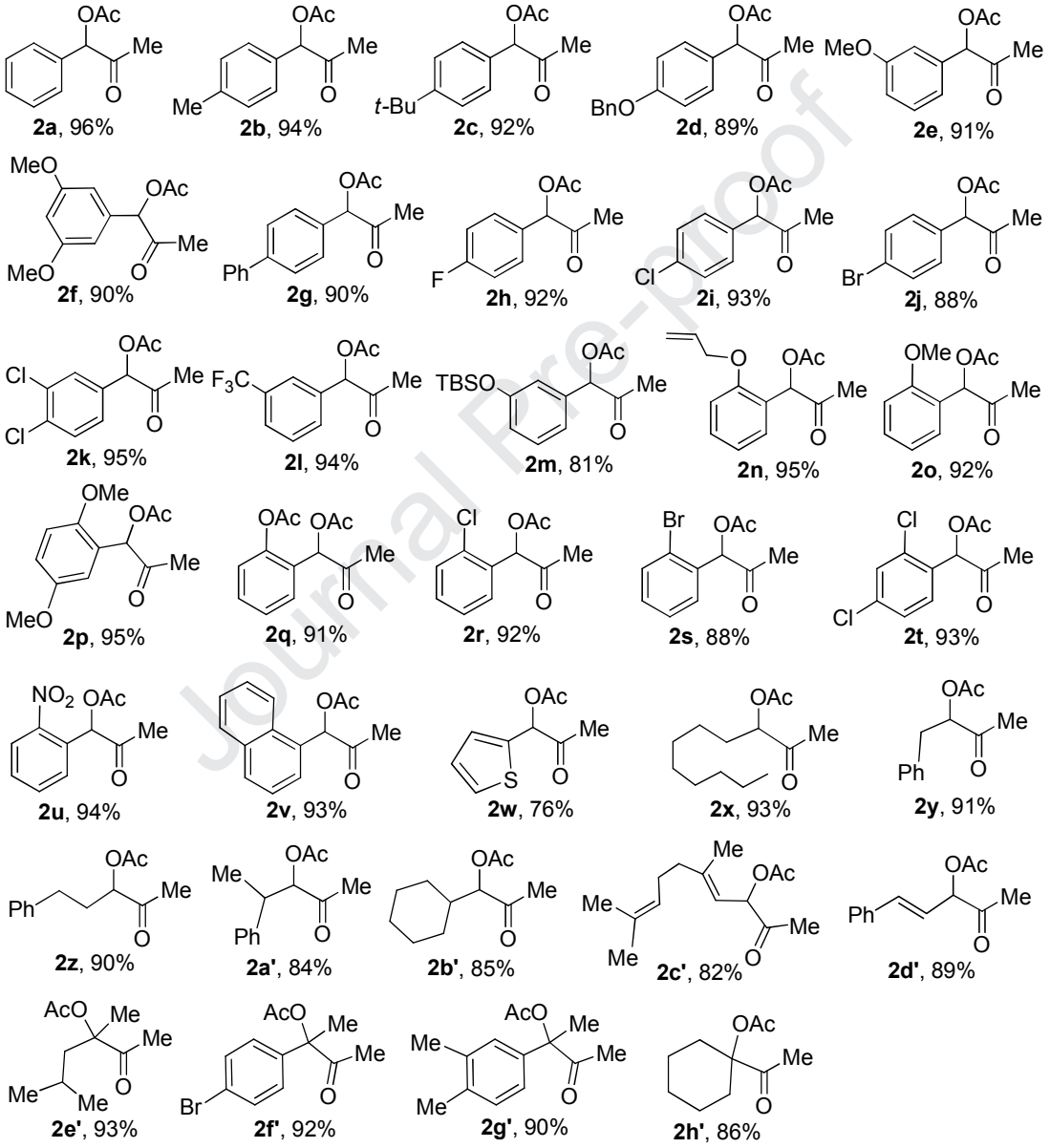


Entry	Gold catalyst (mol%)	Solvent	Time (h)	Yield (%)[b]
1	Ph_2P-MCM-41-AuOTf (2)	dioxane	24	85
2	Ph_2P-MCM-41-$AuNTf_2$ (2)	dioxane	24	74
3	Ph_2P-MCM-41-$AuSbF_6$ (2)	dioxane	5	97
4	Ph_2P-MCM-41-$AuBF_4$ (2)	dioxane	24	80
5	Ph_2P-MCM-41-AuCl (2)	dioxane	36	0
6	Ph_2P-MCM-41-$AuSbF_6$ (2)	CH_2Cl_2	24	68
7	Ph_2P-MCM-41-$AuSbF_6$ (2)	MeOH	24	42
8	Ph_2P-MCM-41-$AuSbF_6$ (2)	DMF	36	0
9	Ph_2P-MCM-41-$AuSbF_6$ (2)	DMSO	36	0
10	Ph_2P-MCM-41-$AuSbF_6$ (1)	dioxane	12	96
11	Ph_2P-MCM-41-$AuSbF_6$ (0.5)	dioxane	24	91
12	Ph_3PAuCl (1)/$AgSbF_6$ (1)	dioxane	8	97

[a] Reactions were carried out with **1a** (1.0 mmol), H_2O (3.0 mmol) in solvent (1.5 mL) at room temperature under Ar. [b] Isolated yield.

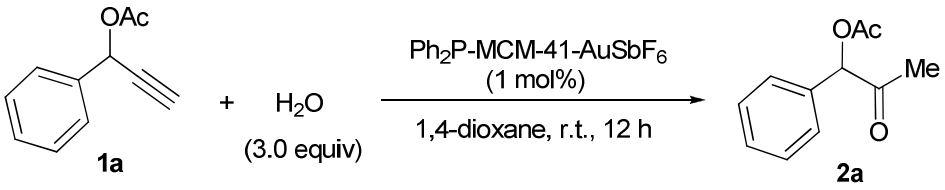
Table 2 Heterogeneous gold(I)-catalyzed synthesis of α-acyloxy methyl ketones.[a,b]





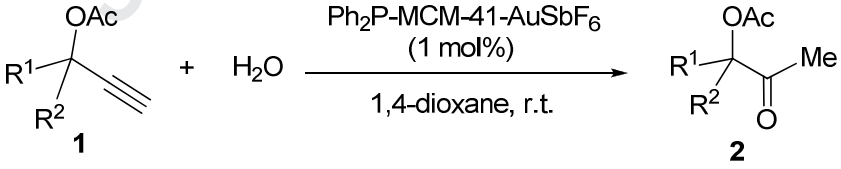
[a] Reactions were conducted with **1** (1.0 mmol), H_2O (3.0 mmol), Ph_2P-MCM-41-$AuSb_6$ (1 mol%) in 1,4-dioxane (1.5 mL) at room temperature under Ar for 12 h. [b] Isolated yield.

Table 3 Recycle of the Ph_2P-MCM-41-$AuSbF_6$ catalyst.[a]

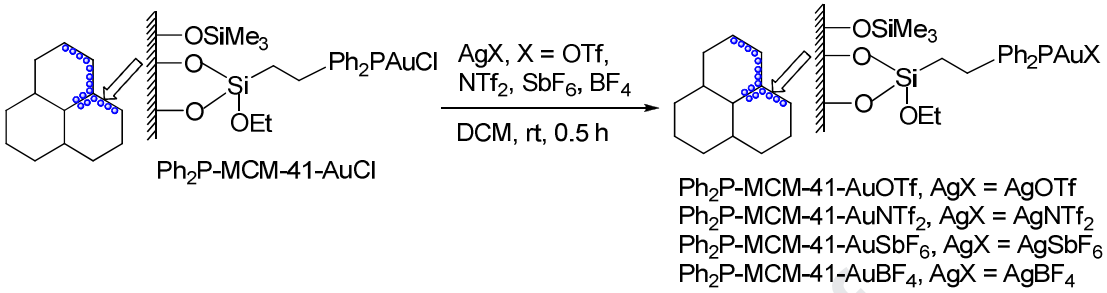


Entry	Au Catalyst	Yield (%)[b]	Entry	Au Catalyst	Yield (%)[b]
1	Fresh	96	5	Recycle 4	95
2	Recycle 1	96	6	Recycle 5	95
3	Recycle 2	95	7	Recycle 6	94
4	Recycle 3	94	8	Recycle 7	93

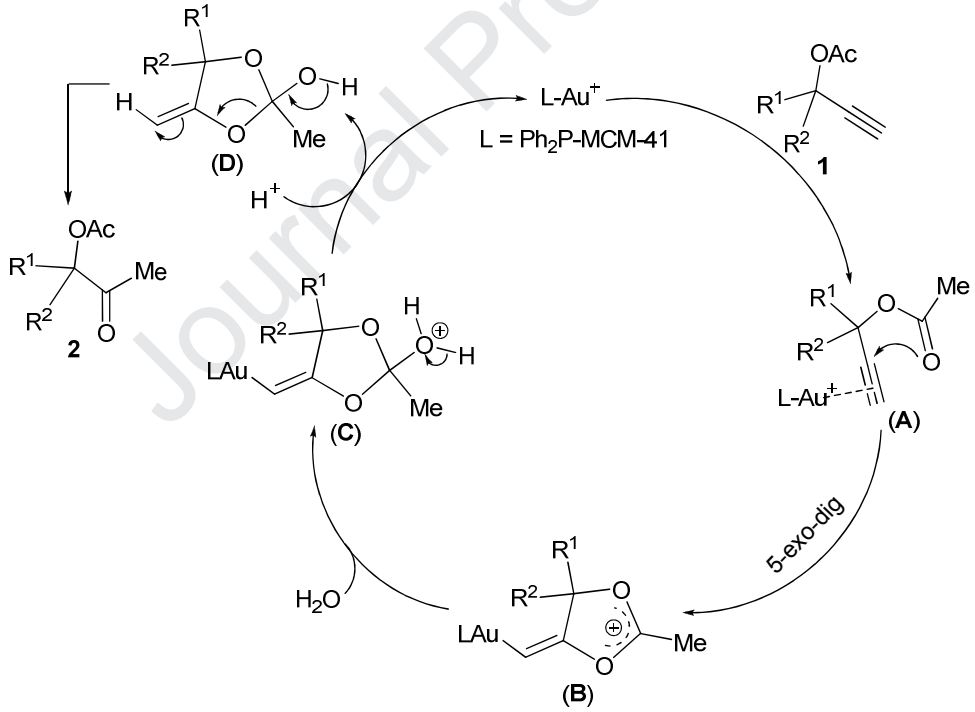
[a] Reactions were conducted with **1a** (1.0 mmol), H_2O (3.0 mmol), Ph_2P-MCM-41-$AuSbF_6$ (1 mol%) in 1,4-dioxane (1.5 mL) at room temperature under Ar for 12 h. [b] Isolated yield.



Scheme 1. Heterogeneous gold(I)-catalyzed hydration of propargyl acetates.



Scheme 2. Synthesis of the Ph_2P-MCM-41-AuX complexes.



Scheme 3. Proposed catalytic cycle.

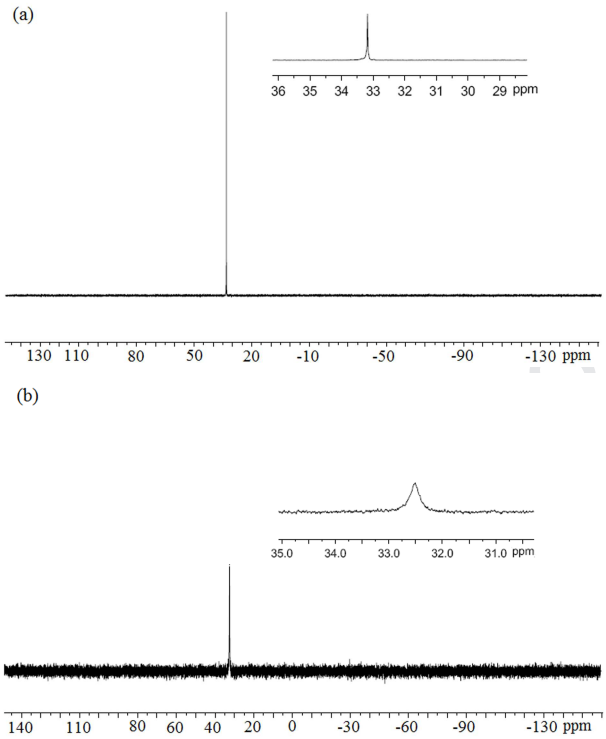


Fig. 1. ^{31}P NMR spectra of fresh gold catalyst (a) and the recycled gold catalyst (b) in $CDCl_3$.

Research Highlights

► The heterogeneous Ph_2P-MCM-41-$AuSbF_6$ complex was first prepared.

► This gold(I) catalyst showed the same catalytic activity as $Ph_3PAuCl/AgSbF_6$ system.

► The reaction generated a variety of α-acyloxy methyl ketones in high yields.

► The gold(I) catalyst can be recycled up to 8 times with almost consistent activity.

► Our catalytic system provides a new and practical route to α-acyloxy methyl ketones.

Declaration of interests

☐√ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: