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Silver-containing microemulsion as a high-efficient and recyclable catalytic system for hydration of alkynes

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ABSTRACT

A silver-catalyzed highly efficient and regioselective synthesis of ketones from a wide range of alkynes is described. The reaction is dramatically accelerated by its performance in aqueous emulsion, which is self-assembled by the addition of silver perfluorooctanesulfonate (**1**) and perfluorooctanesulfonic acid (PFOS) to water. The reaction is conducted under convenient conditions with broad substrate scope, including a variety of aromatic and aliphatic terminal alkynes and internal alkynes. Furthermore, the air- and light-stable silver catalytic microemulsion can be reused for 4 times with minimal change in catalytic efficiency.

1. Introduction

Microemulsion as micro-heterogeneous systems [1] can solubilize both polar and nonpolar substances, and have been extensively applied in many fields, such as in organic synthesis, material science, separation science [2]. Since water is a clean, safe, readily available and almost free of charge solvent, thus utilizing water in microemulsions for the synthesis of a broad spectrum of organic compounds has been comprehensively realized and proven [3]. For example, Sheng et al. have developed a high efficient silver-catalyzed decarboxylative trifluoromethylthiolation of alkyl carboxylic acid in an aqueous emulsion [4]. Kobayshi et al. reported another high efficient dehydration reactions in water assisted with a surfactant-type catalyst [5]. Wass et al. found the noble metal complex platinum (II) diphosphinamine can be also used as the efficient catalyst for the hydration of alkynes in micellar media [6]. However, performing stereoselective organic synthesis in the microemulsion with water is still very rare [7].

Hydration of alkynes is a simple and efficient method for the preparation of valuable carbonyl compounds (aldehyde and ketone) [8]. Several strong brønated acids, such as TfOH, Tf_2NH, could catalyze hydration of alkynes efficiently [9]. And the efficient hydration of alkynes through acid-assisted brønsted acid catalysis was also described [10]. Besides, a variety of metal based catalysts such as Hg, Au, Pt, Pd, Ir, Co and Ru have been employed [11]. Silver salts for the hydration of alkynes were also explored with limited examples, such as $AgSbF_6$, $AgBF_4$, AgOTf and $AgBAr^F$ [12]. But, these catalysts were moisture-sensitive, light-sensitive and limited for narrow substrates, e.g., lower yield was obtained or no reaction was proceed for internal alkynes, and they can't be recycled. Another silver exchanged silicotungstic acid as heterogeneous catalyst for the hydration of alkynes was developed by Marsella et al. [13]. However, extremely longer reaction time (70 h) was needed. Thus, the development of an highly efficient silver-catalyzed system that free of hydrolysis as well as light-sensitive and can be conveniently applied in hydration of alkynes is highly demanded.

In contrast to AgOTf, we found silver perfluorooctanesulfonate ($AgOSO_2C_8F_{17}\cdot H_2O$, **1**) is air-stable and water-tolerant and suffered no color change in air for at least half a year. Generally, perfluorooctanesulfonic acid (PFOS) is used as a surfactant in industrial production [14]. Herein, we disclose our progress in direct hydration of alkynes in microemulsions self-assembled by adding silver perfluorooctanesulfonate (**1**) and perfluorooctanesulfonic acid to water. Moreover, the high catalytic efficiency for the hydration of alkynes catalyzed by the above microemulsion is successfully achieved (Fig. 1).

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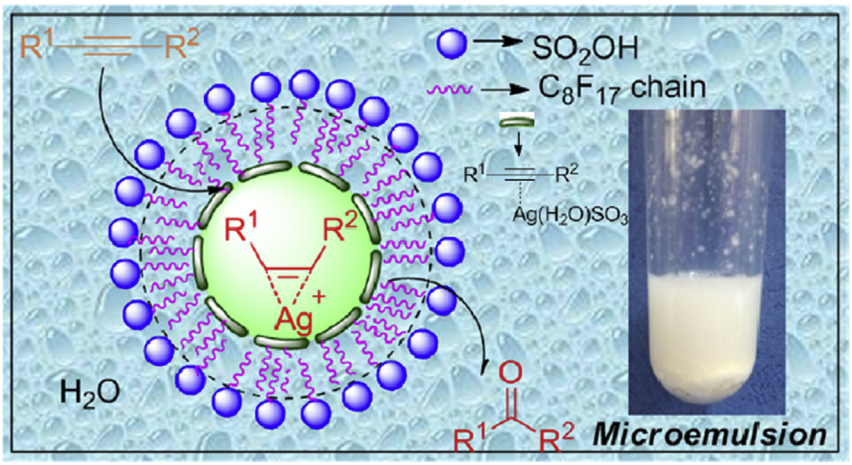


Fig. 1. Hydration of alkynes catalyzed by **1** in the microemulsion.

2. Results and discussion

2.1. Characterization of $AgOSO_2C_8F_{17}·H_2O$

In previous works [15], $C_8F_{17}SO_3^-$ was mainly used as counter anion to overcome the hydrolytic instability of the cationic organometallic species and enhance the Lewis acidity. In order to further reveal its air-stability and hydrophobility, the crystal structure of **1** and thermal behavior were studied. Single crystals of **1** could be obtained by diffusion of hexane into a saturated solution of the product **1** in THF. An ORTEP representation of **1**, and the crystal structure and unit cell are shown in Fig. 2.

The silver ion is coordinated by four O atoms in a distorted tetrahedral coordination environment with the Ag—O distance, from 2.316 to 2.473 Å (Fig. 2a). Corner-sharing connectivity of AgO_4 tetrahedron generated a double-chain coordination polymer, along the *b* direction with the perfluorocarbon chain, regularly extending outside on both sides (Fig. 2b). Double-chains are linked by two O—H(water)···O(sulfonate) hydrogen bonds(H···O = 1.98, 2.10, and 2.49 Å; O···O = 2.781, 2.787, and 2.924 Å; O—H···O = 157.2, 137.8, and 112.3°), as two-dimensional symmetric "head-to-head" bilayer structure with alternating $R_2^1(8)$ and $R_3^2(8)$ motifs (Fig. 2c). Because of the hydrophobic and electron-withdrawing properties of long-chain perfluorooctanesulfonate anion [16], the bilayer structure can stabilize the silver salt against hydrolysis in air.

TG-DSC analysis shows the complex **1** is thermal stable up to 400 °C (Fig. 3). The endothermic step below 150 °C can be assigned to the removal of H_2O molecules. The weight loss of an exothermic nature at 400 °C is plausibly due to the oxidation of counter anion $OSO_2C_8F_{17}$-. The loss of weight is attributed to the fragments of C_8F_{17}.

2.2. Optimization of the reaction conditions for silver-catalyzed hydration of alkynes

Since the high air-stability and thermal stability of the silver complex **1**, we hence estimate its catalytic performance in hydration of phenylacetylene at 100 °C for 8 h in the dark. As shown in Table 1, in the absence of the additive, the reaction is almost not effective (entry 1). The reaction is performed in the presence of PFOS and 35% yield of ketone is obtained (entry 2). When the 2 mol % of PFOS and 5 mol% of **1** are added together, the yield is up to 95% (entry 4). To further demonstrate the advantage of **1** over other silver salts, the different silver catalysts were tested. $AgNO_2$, Ag_2CO_3, Ag_2O, and AgOAc give about 10% yield (entries 6–9), which may be the role of PFOS. $AgBF_4$ and AgOTf give the yields of 53%, 57%, respectively (entries 10–11), while $AgSbF_6$ affords 71% yield (entry 12). We also put the reaction under natural light to reveal the

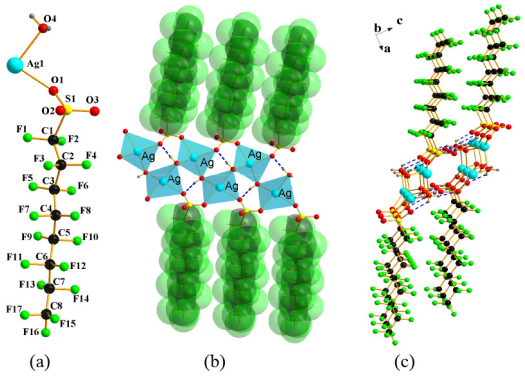


Fig. 2. (a) A perspective view of a single repeating unit of $AgOSO_2C_8F_{17}·H_2O$ (**1**) with the atomic numbering scheme; (b) the coordination environment in the silver salt, and the one-dimensional infinite chain structure along the *b* axis linked by corner-sharing connectivity of AgO_4 tetrahedron; (c) two-dimensional symmetric "head-to-head" bilayer structure in Ag complex guided by hydrogen bond between coordination water and sulfonate. Nonbonded contacts are indicated by dashed lines.

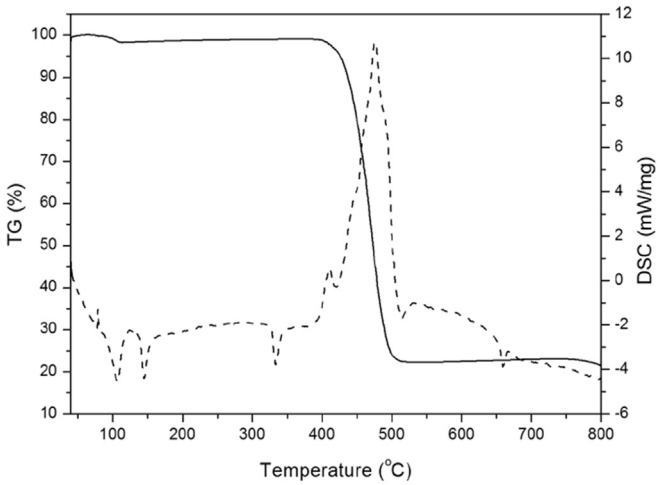
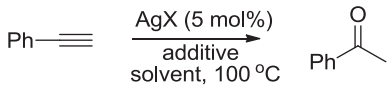


Fig. 3. TG-DSC curves of $AgOSO_2C_8F_{17}·H_2O$ (**1**).

Table 1
Optimization of the reaction conditions for silver-catalyzed hydration of alkynes.[a]



Entry	AgX	Additive	Solvent	Yield (%)
1	**1**	–	H_2O	<5
2	–	PFOS (0.05 mmol)	H_2O	35
3	**1**	PFOS (0.01 mmol)	H_2O	78
4	**1**	PFOS (0.02 mmol)	H_2O	95 (94)[b]
5	**1**	PFOS (0.03 mmol)	H_2O	94
6	$AgNO_2$	PFOS (0.02 mmol)	H_2O	11
7	Ag_2CO_3	PFOS (0.02 mmol)	H_2O	13
8	Ag_2O	PFOS (0.02 mmol)	H_2O	12
9	AgOAc	PFOS (0.02 mmol)	H_2O	15
10	$AgBF_4$	PFOS (0.02 mmol)	H_2O	53 (16)[b]
11	AgOTf	PFOS (0.02 mmol)	H_2O	57 (28)[b]
12	$AgSbF_6$	PFOS (0.02 mmol)	H_2O	71 (34)[b]

[a] Reaction condition: phenylacetylene (1 mmol), AgX (0.05 mmol), additive: PFOS; solvent: 1 mL; 8 h, 100 °C, dark, isolated yield.
[b] Under natural light.

light-stability of the complex **1** over $AgBF_4$, AgOTf and $AgSbF_6$, the yields are shown in parentheses (entries 4, 10–12). The result implies that the counter anion of $C_8F_{17}SO_3^-$ in **1** has a significant protection for the silver core. Finally, the optimum catalytic microemulsion system is **1** (5 mol%)/PFOS (2 mol%)/water (1 mL) mixture.

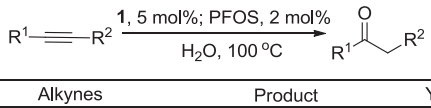
2.3. The scope with different alkynes

With an efficient protocol for the hydration of alkynes in hand, we next investigate its scope with different alkynes. As shown in Table 2, both electron-donating and electron-withdrawing alkynes afford the corresponding products in good to excellent yields. Clearly, the electronic effect plays an important role, the electron-donating groups attached in the phenyl ring of alkynes exhibit in higher yields than that of the electron-withdrawing groups (entries 2–7). Substitution at the 2-position of the aromatic ring is slightly lowered the yields (entries 3, 4). It should be noted that the carbon-halogen bonds are well tolerated (entry 4), which could be easily further functionalized. Gratifyingly, other acid-sensitive functionalities such as –CN, –CHO, $-C(O)CH_3$ and alkene are also unaffected under the present reaction conditions (entries 5–8). For heterocycle alkyne, it still gives the corresponding heterocycle ketone in 80% yield (entry 9). The catalytic system can be easily extending to the aliphatic alkyne, in 78% yield (entry 10). The internal alkynes, such as 5-decyne and diphenylacetylene, can afford the corresponding products in good yields (entries 11–12). Interestingly, asymmetric internal alkynes also show good reactivity in this catalytic system with 74% and 58%, respectively (entry 13–14).

2.4. Cycles of catalyst *1*

To test the reusability and reproducibility, the catalytic microemulsion is subject to cycles of hydration of phenylacetylene as the model reaction. After completion of reaction, *n*-hexane is added to the reaction mixture, which is automatic layering. After separating, the lower microemulsion is used for next cycle of the reaction. The decline in product yield is minimal in a run of 4 cycles (95%–92%), indicating that the microemulsion is stable and suitable for reuse (Table 3).

Table 2
The hydration of alkynes catalyzed by **1** (5 mol%)/PFOS (2 mol%) in water.[a]



Entry	Alkynes	Product	Yield (%)
1	(**2a**)	(**3a**)	95%
2	R (**2b-2f**)	R	***R*** = CH_3, **3b**: 94% C_2H_5, **3c**: 92% *n*-C_3H_7, **3d**: 88% *n*-C_4H_9, **3e**: 82% *n*-C_5H_{11}, **3f**: 80%
3	G (**2g-2j**)	G	***G*** = *p*-OMe, **3g**: 95% *m*-OMe, **3h**: 93% *o*-OMe, **3i**: 90% 3.4-diOMe, **3j**: 97%
4	X (**2k-2n**)	X	***X*** = 2-Cl, **3k**: 81% 3-Cl, **3l**: 83% 4-Br, **3m**: 84% 2-Br, **3n**: 81%
5	Q (**2o-2r**)	Q	***Q*** = 4-CN, **3o**: 88% 4-CF_3, **3p**: 81% 3-NO_2, **3q**: 83% 4-$C(O)CH_3$,**3r**: 86%
6	O_2N (**2s**)	O_2N (**3s**)	83%
7	H (**2t**)	H (**3t**)	82%
8	(**2u**)	(**3u**)	81%
9	(**2v**)	(**3v**)	80%
10	C_8H_{17} (**2w**)	C_8H_{17} (**3w**)	78%
11	(**2x**)	(**3x**)	72%
12	(**2y**)	(**3y**)	54%[b]
13	(**2z**)	(**3z**)	74%
14	OMe (**2aa'**)	OMe (**3aa'**)	58%[c]

[a] Reaction conditions: alkynes (1 mmol), **1** (0.05 mmol), PFOS (0.02 mmol), H_2O: 1 ml, 100 °C, 8 hours, isolated yield. [b] 15 hours, [c] 20 hours

2.5. The possible mechanism

The possible mechanism was proposed in Scheme 1 on the basis of the previous reports [12b]. First, the silver center coordinates with the triple bond of the terminal alkyne and forms a π-complex **A**. the nucleophile $C_8F_{17}SO_3$- anion attacks the complex to provide intermediate **B**, and then protonation to form enol perfluorooctanesulfonate **C**, which subsequently undergoes successive hydrolysis and keto–enol tautomerism to generate methyl ketone. The possible catalytic performance in the microemulsion is proposed as shown in Fig. S1.

Table 3
Yields of Hydration of alkynes by recover catalyst.[a]

Cycle	Yield (%)[b]
1	95
2	94
3	94
4	92
5	81

[a] Reaction conditions: phenylacetylene (1.0 mmol), solvent: water (1.0 mL), and 1 (5.0 mmol%), PFOS (2.0 mmol%), at 100 °C for 8 h.
[b] Isolated yield.

3. Experimental

3.1. General

All chemicals were purchased from Aldrich. Co. Ltd and used as received unless otherwise indicated. The NMR spectra were recorded at 25 °C on INOVA-400M (USA) calibrated with tetramethylsilane (TMS) as an internal reference. TG-DSC analysis was performed on a HCT-1 (HENVEN, Beijing, China) instrument. X-ray single crystal diffraction analysis was performed with SMART-APEX and RASA-7A by Shanghai Institute Organic Chemistry, China Academy of Science.

3.2. Synthesis of $AgOSO_2C_8F_{17}$ (1) [16].

To a solution of $C_8F_{17}SO_3H$ (5 g, 10 mmol) which was prepared according to literature in 15 ml of H_2O was added Ag_2CO_3 (1.656 g, 6 mmol) in ice water and stirred for an hour then was rise the temperature to 100 °C for 1 h, and then at RT for 1 h. After filtration, the solids obtained were washed with ice-water till the filtrate turned neutral. The solids were dissolved in acetone and filtered. After the filtrate had been evaporated, the crude solids were subjected to recrystallization from THF/Et_2O to afford $C_8F_{17}SO_3Ag$ in a pure form (2.42 g, 40%). ^{19}F NMR (376 M, [d_6] acetone): δ = −78.95−−79.00 (t, 3F, CF_3-), −112.91−−112.99 (m, 2F, $-CF_2$-), −118.72 (s, 2F, $-CF_2$-), −119.61−−119.80 (m, 6F, $-(CF_2)_3$-), −120.65(s, 2F, $-CF_2$-), −124.03−−124.11 (m, 2F, $-CF_2$-).

Crystal data for **1**: $C_8H_2F_{17}AgO_4S$; *Mr* = 625.03, Monoclinic, space group *P21/c*, *a* = 26.001(7) Å, *b* = 5.6450(14) Å, *c* = 11.469(3) Å; *V* = 1678.5(7) Å^3; *T* = 298(2) K; *Z* = 4; Reflections collected/unique, 9858/3104, R_{int} = 0.0415, Final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0734, wR_2 = 0.2167; *R* indices (all data), R_1 = 0.0848, wR_2 = 0.2282. *GOF* = 1.071; CCDC No. 895177.

3.3. Typical procedure for synthesis of ketones

To the mixture of phenylacetylene (1 mmol), water (3.0 mL), silver perfluorooctanesulfonate (5 mol%) and perfluorooctane sulfonate acid (2 mol%) was added. The mixture was stirred at 100 °C for 8 h. The solution was extracted with *n*-hexane (diethyl ether) (3 × 5 mL), the combined extract was dried with anhydrous $MgSO_4$. The rest of the solution was used for the next cycle of reaction. The extraction solvent was removed and the crude product was separated by column chromatography to give the pure sample.

Acetophenone (***3a***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.96−7.94 (m, 2H, ArH), 7.57−7.52 (m, 1H, ArH), 7.47−7.43 (m, 2H, ArH), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.15, 137.10, 133.10, 128.56, 128.29, 26.60; MS(70 ev): *m*/*z* = 120.1 [M^+].

1-(4-methphenyl)ethanone(***3b***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.4 Hz, 2H, ArH), 7.27 (t, *J* = 4.0 Hz, 2H, ArH), 2.58 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.84, 143.84, 134.66, 129.19, 128.40, 26.50, 21.60; MS(70 ev): *m*/*z* = 134.1 [M^+].

1-(4-ethylphenyl)ethanone(***3c***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 4.0 Hz, 2H, ArH), 7.28 (d, *J* = 7.6 Hz, 2H, ArH), 2.72−2.70 (m, 2H, CH_2), 2.59 (s, 3H, CH_3), 1.29−1.24 (m, 2H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.90, 150.05, 134.92, 128.54, 128.05, 28.93, 26.55, 15.20; MS(70 ev): *m*/*z* = 148.1 [M^+].

1-(4-n-propylphenyl)ethanone(***3d***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H, ArH), 7.28 (d, *J* = 7.6 Hz, 2H, ArH), 2.66−2.63 (m, 2H, CH_2), 2.58 (s, 3H, CH_3), 1.69−1.62 (m, 2H, CH_3), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.96, 148.58, 134.94, 128.67, 128.46, 38.03, 26.57, 24.24, 13.77; MS(70 ev): *m*/*z* = 162.1 [M^+].

1-(4-n-butylphenyl)ethanone(***3e***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH), 2.70−2.66 (m, 2H, CH_2), 2.59 (s, 3H, CH_3), 1.65−1.59 (m, 2H, CH_3), 1.37−1.33 (m, 2H, CH_3), 0.97−0.93 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.89, 148.80, 134.88, 128.60, 128.46, 35.68, 35.25, 26.53, 22.32, 13.91; MS(70 ev): *m*/*z* = 176.1 [M^+].

1-(4-n-amylphenyl)ethanone(***3f***): ^1H NMR (400 MHz, d_6-DMSO): δ 7.87 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.4 Hz, 2H, ArH), 2.65−2.62 (m, 2H, CH_2), 2.55 (s, 3H, CH_3), 1.62−1.54 (m, 2H, CH_3), 1.32−1.23 (m, 4H, CH_3), 0.87−0.83 (m, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO): δ 197.91, 148.66, 135.08, 129.00, 128.76, 35.48, 31.26, 30.72, 27.05, 22.36, 14.33; MS(70 ev): *m*/*z* = 190.1 [M^+].

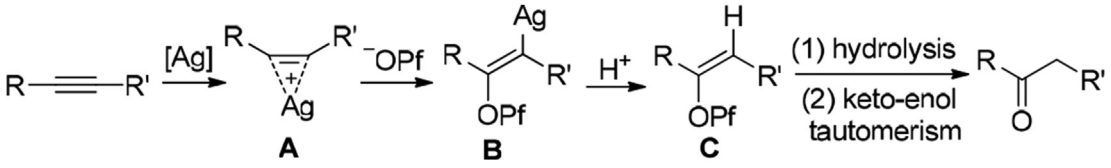
1-(4-methoxyphenyl)ethanone(***3g***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H, ArH), 6.93 (d, *J* = 9.2 Hz, 2H, ArH), 3.87 (s, 3H, OCH_3), 2.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.75, 163.42, 130.53, 130.27, 113.62, 55.43, 26.30; MS(70 ev): *m*/*z* = 150.1 [M^+].

1-(3-methoxyphenyl)ethanone(***3h***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.2 Hz, 1H, ArH), 7.49 (s, 1H, ArH), 7.37 (t, *J* = 7.8 Hz, 1H, ArH), 7.11 (d, *J* = 8.0 Hz, 1H, ArH), 3.85 (s, 3H, OCH_3), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.07, 159.78, 138.43, 129.59, 121.16, 119.65, 112.29, 55.43, 26.77; MS(70 ev): *m*/*z* = 150.1 [M^+].

1-(2-methoxyphenyl)ethanone(***3i***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 1H, ArH), 7.46 (t, *J* = 7.6 Hz, 1H, ArH), 7.00−6.95 (m, 1H, ArH), 3.90 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.94, 158.93, 133.74, 130.34, 128.14, 120.52, 111.57, 55.47, 31.90; MS(70 ev): *m*/*z* = 150.1 [M^+].

1-(3,4-dimethoxyphenyl)ethanone(***3j***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 1H, ArH), 7.53 (s, 1H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 3.95 (s, 6H, OCH_3), 2.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.84, 153.22, 148.91, 130.40, 123.31, 109.92, 109.88, 56.05, 55.94, 26.23; MS(70 ev): *m*/*z* = 180.1 [M^+].

1-(2-chlorophenyl)ethanone(***3k***): ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H, ArH), 7.43−7.37 (m, 2H, ArH), 7.34−7.28 (m,



Scheme 1. The possible reaction mechanism.

1H, ArH), 2.65 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.57, 139.08, 132.05, 131.30, 130.66, 129.43, 126.96, 30.75; MS(70 ev): *m*/*z* = 154.0 [M^+].

*1-(3-chlorophenyl)ethanone(**3l**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H, ArH), 7.85–7.83 (m, 1H, ArH), 7.56–7.54 (m, 1H, ArH), 7.44–7.40 (m, 1H, ArH), 2.61 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.76, 134.51, 133.08, 129.96, 128.45, 126.43, 125.30, 26.70; MS(70 ev): *m*/*z* = 154.0 [M^+].

*1-(4-bromophenyl)ethanone(**3m**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.61 (d, *J* = 7.6 Hz, 2H, ArH), 2.59 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.08, 135.82, 131.92, 129.86, 128.34, 26.58; MS(70 ev): *m*/*z* = 198.0 [M^+].

*1-(2-bromophenyl)ethanone(**3n**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H, ArH), 7.47 (d, *J* = 7.2 Hz, 1H, ArH), 7.37 (t, *J* = 7.2 Hz, 1H, ArH), 7.30 (t, *J* = 6.8 Hz, 1H, ArH), 2.6 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.44, 141.38, 133.85, 131.86, 128.95, 127.49, 118.90, 30.37; MS(70 ev): *m*/*z* = 198.0 [M^+].

*1-(4-cyanphenyl)ethanone(**3o**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 2H, ArH), 2.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.64, 139.89, 132.55, 128.733, 117.98, 116.39, 26.84; MS(70 ev): *m*/*z* = 145.1 [M^+].

*1-(4-(trifluoromethyl)phenyl)ethanone(**3p**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.6 Hz, 2H, ArH), 7.74 (d, *J* = 7.6 Hz, 2H, ArH), 2.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.07, 139.62, 134.25, 128.64, 125.74, 125.71, 125.67, 124.95, 122.24, 26.83; ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm 63.11; MS(70 ev): *m*/*z* = 188.0 [M^+].

*1-(3-nitrophenyl)ethanone(**3q**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H, ArH), 8.44 (s, 1H, ArH), 8.31 (s, 1H, ArH), 7.72 (s, 1H, ArH), 2.72 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.77, 148.40, 138.19, 133.85, 129.97, 127.44, 123.22, 26.79; MS(70 ev): *m*/*z* = 165.0 [M^+].

*1-(4-acetylphenyl)ethanone(**3r**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 2H, ArH), 2.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.64, 139.89, 132.55, 128.73, 117.98, 116.39, 26.84; MS(70 ev): *m*/*z* = 162.1 [M^+].

*1-(4-nitrophenoxy)propan-2-one(**3s**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.0 Hz, 2H, ArH), 4.69 (s, 2H, CH_2), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.19, 162.50, 142.25, 126.06, 114.64, 72.97, 26.58; MS(70 ev): *m*/*z* = 195.1 [M^+].

*4-(2-oxopropoxy)benzaldehyde(**3t**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H, CHO), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 6.93 (d, *J* = 8.4 Hz, 2H, ArH), 4.59 (s, 2H, CH_2), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.78, 190.77, 132.09, 114.86, 72.82, 26.67; MS(70 ev): *m*/*z* = 178.1 [M^+].

*1-(cyclohex-2-en-1-yl)ethanone(**3u**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H,CH=), 2.28 (s, 3H, CH_3), 2.24 (d, *J* = 14.0 Hz, 4H, CH_2), 1.62 (s, 4H,CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.52, 141.10, 139.65, 26.12, 25.22, 22.93, 21.91, 21.52; MS(70 ev): *m*/*z* = 124.1 [M^+].

*1-(furan-2-yl)ethanone(**3v**)*: ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H, ArH), 7.20 (s, 1H, ArH), 6.55 (s, 1H, ArH), 2.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.89, 152.76, 146.51, 117.40, 112.28, 26.02; MS(70 ev): *m*/*z* = 110.1 [M^+].

Decanone (**3w**): ^1H NMR (400 MHz, $CDCl_3$): δ 2.33 (t, *J* = 7.4 Hz, 2H, CH_2), 2.04 (s, 3H, CH_3), 1.53–1.43 (m, 2H, CH_2), 1.19 (bs, 10H, CH_2), 0.79 (t, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.10, 43.67, 31.75, 29.68, 29.30, 29.10, 29.06, 23.77, 22.56, 13.97; MS(70 ev): *m*/*z* = 156.1 [M^+].

Decan-5-one (**3x**): ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (t, *J* = 7.4 Hz, 4H, CH_2), 1.53–1.44 (m, 2H, CH_2), 1.28–1.15 (m, 6H, CH_2), 0.85–0.80 (m, 6H, CH_3),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.70, 41.76, 41.51, 30.46, 25.00, 22.58, 21.48, 21.38, 12.90, 12.85; MS(70 ev): *m*/*z* = 156.1 [M^+].

1,2-Diphenylethanone (**3y**). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–8.02 (m, 2H), 7.56–7.51 (m, 1H), 7.49–7.45 (m, 2H), 7.37–7.30 (m, 2H), 7.29–7.25 (m, 3H), 4.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.95, 136.82, 134.77, 133.93, 133.42, 130.41, 129.71, 128.91, 128.88, 128.86, 128.71, 127.13, 45.74; MS(70 ev): *m*/*z* = 196.1 [M^+].

Propiophenone (**3z**): ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.56–7.52 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 3.02–2.96 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.05, 137.11, 133.09, 128.75, 128.17, 31.98, 8.44; MS(70 ev): *m*/*z* = 134.1 [M^+].

1-(4-methoxyphenyl)-2-(4-propylphenyl)ethanone(**3aa′**): White solid, Mp. 59–60 °C; [Lit. [17], Mp. 59–61 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.6 Hz, 2H, ArH), 7.17 (d, *J* = 7.2 Hz, 2H, ArH), 7.12 (d, *J* = 7.2 Hz, 2H, ArH), 6.91 (d, *J* = 7.6 Hz, 2H, ArH), 4.19 (s, 2H, CH_2), 3.84 (s, 3H, CH_3), 2.54 (t, *J* = 7.4 Hz, 2H, CH_2), 1.68–1.56 (m, 2H, CH_2), 0.92 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.53, 163.49, 141.19, 132.12, 131.00, 129.68, 129.23, 128.79, 113.78, 55.49, 44.92, 37.71, 24.56, 13.93; MS(70 ev): *m*/*z* = 268.1 [M^+].

4. Conclusions

In summary, we have developed a simple and efficient method for the selective hydration of alkynes in the microemulsion containing Ag catalyst. Both of the terminal alkynes and internal alkynes can proceed smoothly and afford good to excellent yields, and a variety of functional groups are well tolerated. Furthermore, the catalytic microemulsion system [$AgOSO_2C_8F_{17}\cdot H_2O$ (5 mol %)/$HOSO_2C_8F_{17}$ (2 mol%)/H_2O] can be reused for four times. On account of the stability and high catalytic efficiency, the silver-containing microemulsion should find a broad range of utility in organic synthesis.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.09.014.

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