Tetrahedron 69 (2013) 6116–6120

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Highly efficient $AgBF_4$-catalyzed synthesis of methyl ketones from terminal alkynes☆

Zheng-Wang Chen *, Dong-Nai Ye, Yi-Ping Qian, Min Ye, Liang-Xian Liu *

Key Laboratory of Organo-Pharmaceutical Chemistry of Jiangxi Province, Gannan Normal University, Ganzhou 341000, PR China

ARTICLE INFO

Article history:
Received 9 March 2013
Received in revised form 13 May 2013
Accepted 16 May 2013
Available online 22 May 2013

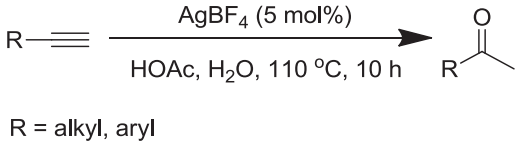
ABSTRACT

A silver-catalyzed highly efficient synthesis of a wide range of methyl ketones from terminal alkynes is described. The reactions are conducted under convenient conditions and provide products with excellent regioselectivity in moderate to excellent yields, with broad substrate scope, including a variety of aromatic and aliphatic terminal alkynes.

1. Introduction

Ketones are unambiguously important building blocks in organic synthesis.[1] The classical synthesis of ketones from hydration of alkynes employed a stoichiometric amount of mercury under acidic conditions. The toxicity of mercury and the requirement of strong acid limited its applications.[2] Over the past decades, alternative catalytic systems for the alkyne hydration reactions have been extensively explored. Among them, the transition-metal-complex containing Ru,[3] Rh,[4] Pd,[5] Pt,[6] Sn–W,[7] Au,[8] Fe,[9] Ir,[10] and Co[11] have proved to be useful for the formation of ketones following the Markovnikov rule. Recently, the additions of water to terminal alkynes affording aldehydes by Ru complexes have also been described with anti-Markovnikov-type regioselectivity.[12] However, only few examples were explored using silver complex as the sole catalyst for the hydration of alkynes.[13]

Very recently, we reported a convenient and expedient method for the synthesis of (*Z*)-β-haloenol acetates from terminal alkynes using silver tetrafluoroborate as the catalyst.[14] In the process of optimizing the reaction conditions for the difunctionalization of phenylacetylene, we found that acetophenone was observed when employing acetic acid as the solvent. Inspired by this observation, here we would like to present a silver tetrafluoroborate catalyzed synthesis of methyl ketones from terminal alkynes with high regioselectivity (Scheme 1).



Scheme 1. Silver-catalyzed synthesis of methyl ketones from terminal alkynes.

2. Results and discussion

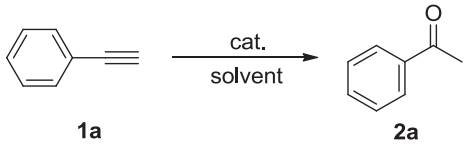
Initial efforts were focused on searching for efficient catalysts and suitable reaction conditions in acetic acid, when phenylacetylene (**1a**) was chosen as the model substrate. As shown in Table 1, the reaction did not proceed without catalyst (Table 1, entry 1). We next examined the effects of using different silver species. To our delight, we found that $AgBF_4$ could afford the corresponding product in 92% yield (Table 1, entry 9). Other silver salts, such as $AgSbF_6$ and AgOTf, were inactive for the transformation (Table 1, entries 2–8). Replacing $AgBF_4$ to KBF_4 failed to generate any product (Table 1, entry 10). We then next screened the solvent effect on this reaction, and showed that solvents played key role in the reaction outcome. Conducting the reaction in other common polar solvents, such as water, dioxane, DMF, DMSO, with or without HOAc as catalyst all led to no product or trace amount of product (Table 1, entries 11–16). Lower temperature and shorter time decreased the reaction yields (Table 1, entries 17–19). Therefore, the optimized reaction conditions are the following: **1a** (1 mmol), water (2 equiv), silver tetrafluoroborate (5 mol %) in acetic acid (2 mL) at 110 °C for 10 h (Table 1, entry 9).

With the optimized conditions in hand, we next concentrated on the generality of the reaction (Tables 2 and 3). Both electron-rich and electron-deficient alkynes afforded the corresponding products in good to excellent yields (Table 2, entries 1–15). Clearly, the electronic effect played an important role, with electron-rich

* Corresponding authors. E-mail addresses: chenzwang@126.com (Z.-W. Chen), lxliu@mail.xmu.edu.cn (L.-X. Liu).

0040-4020/$ – see front matter © 2013 The Authors. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.05.057

Table 1
Optimization of reaction conditions for the synthesis of acetophenone[a]

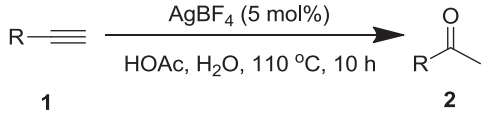


Entry	Catalyst	Solvent	Yield (%)[b]
1		HOAc	n.r.
2	AgCl	HOAc	n.r.
3	Ag_2O	HOAc	Trace
4	Ag_2CO_3	HOAc	n.r.
5	$AgNO_3$	HOAc	n.r.
6	AgF	HOAc	n.r.
7	AgOTf	HOAc	n.r.
8	$AgSbF_6$	HOAc	n.r.
9	$AgBF_4$	**HOAc**	**92**
10	KBF_4	HOAc	n.r.
11	$AgBF_4$	H_2O	n.p.
12[c]	$AgBF_4$	H_2O/HOAc	n.p.
13	$AgBF_4$	DMF/HOAc	n.r.
14	$AgBF_4$	Dioxane/HOAc	15
15	$AgBF_4$	Ac_2O/HOAc	Trace
16	$AgBF_4$	DMSO/HOAc	n.p.
17[d]	$AgBF_4$	HOAc	82
18[e]	$AgBF_4$	HOAc	Trace
19[f]	$AgBF_4$	HOAc	53
20[g]	$AgBF_4$	HOAc	74

[a] Reaction conditions: phenylacetylene (1.0 mmol), solvent (2.0 mL), water (2 equiv), and catalyst (5 mol %) at 110 °C for 10 h.
[b] Isolated yield.
[c] Acetic acid is 5 equiv in entries 12–16.
[d] 80 °C.
[e] Room temperature.
[f] Reacted for 3 h.
[g] 2 mol % $AgBF_4$ was used.

substituents on the benzene ring affording the products in higher yields than the corresponding strong electron-withdrawing groups (Table 2, entries 2–7, 15, 16). Substitution at the 2-position of the aromatic ring slightly lowered the yields (Table 2, entries 9 and 14).

Table 2
$AgBF_4$-catalyzed synthesis of methyl ketones from aromatic alkynes[a]



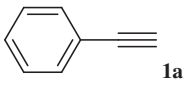
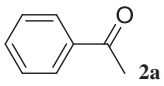
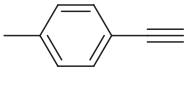
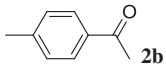
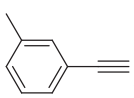
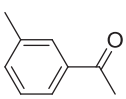
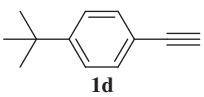
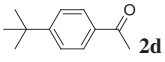
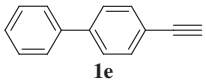
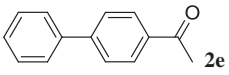
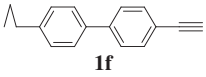
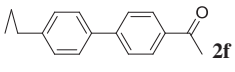
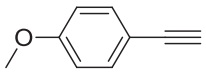
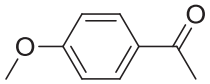
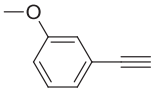
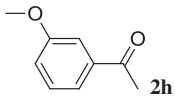
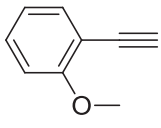
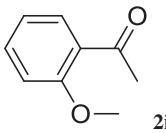
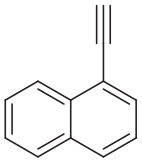
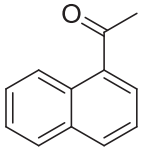
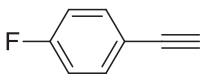
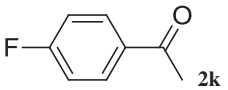
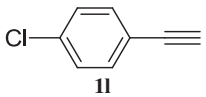
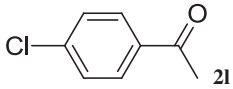
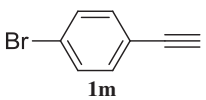
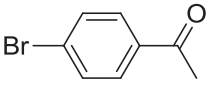
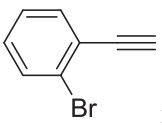
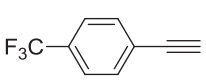
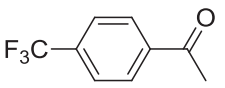
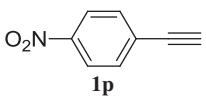
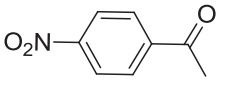
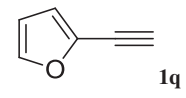
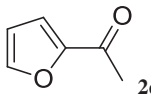
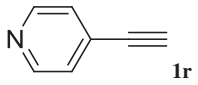
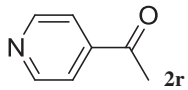
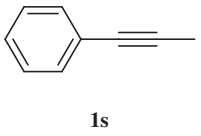
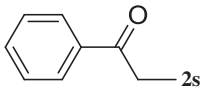
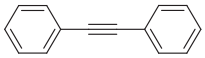
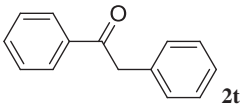
Entry	Substrate	Product	Yield (%)[b]
1	 1a	 2a	92
2	 1b	 2b	99
3	 1c	 2c	98
4	 1d	 2d	92

Table 2 (*continued*)

Entry	Substrate	Product	Yield (%)[b]
5	 1e	 2e	94
6	 1f	 2f	99
7	 1g	 2g	99
8	 1h	 2h	95
9	 1i	 2i	88
10	 1j	 2j	83
11	 1k	 2k	90
12	 1l	 2l	91
13[c]	 1m	 2m	81
14	 1n	 2n	74
15	 1o	 2o	75
16[d]	 1p	 2p	78

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Product	Yield (%)[b]
17	 1q	 2q	76
18	 1r	 2r	58
19	 1s	 2s	84
20[e]	 1t	 2t	35

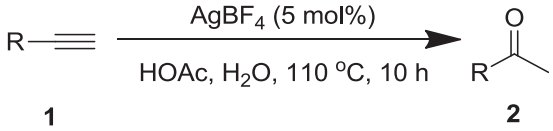
[a] Reaction conditions: aromatic alkyne (1.0 mmol), acetic acid (2.0 mL), water (2 equiv), and silver tetrafluoroborate (5 mol %) at 110 °C for 10 h.
[b] Isolated yield.
[c] 17% enol acetate product was afforded.
[d] Reacted for 20 h and 20% raw material was recovered.
[e] Reacted for 20 h and 60% raw material was recovered.

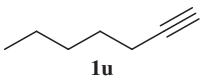
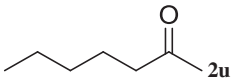
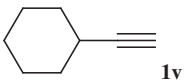
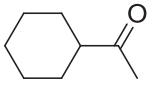
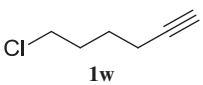
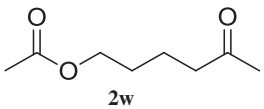
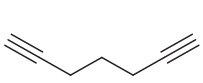
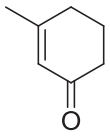
It should be pointed out that the carbon–halogen bonds were well tolerated and the products containing halogen were afforded smoothly. Especially the aryl bromides and chlorides could be further functionalized (Table 2, entries 12–14). Moreover, we were able to separate the enol acetate side product in 17% yield (Table 2, entries 13), which is useful in understanding the reaction mechanism. This reaction was also applicable to heterocycle alkynes, giving the corresponding heterocycle ketones in moderate to good yields (Table 2, entries 17, 18). Furthermore, internal alkynes were reactive under the standard conditions. For example, **1s** afforded propiophenone (**2s**) as the main product in high yield, but diphenylethyne (**1t**) gave corresponding ketone (**2t**) in low yield even with a prolonged time (Table 2, entries 19, 20).

Having defined the broad scope of aromatic alkynes, this reaction was then extended to aliphatic terminal alkynes as shown in Table 3. Both the terminal alkynes (**1u** and **1v**) were smoothly converted into the ketone products in good to excellent yields (Table 3, entries 1, 2). Aliphatic alkyne bearing chloro group is well tolerated, providing the product in excellent yield (Table 3, entry 3). Interestingly, the conjugated enone (**2x**) was formed in high yield from the diyne (**1x**). Presumably, enone (**2x**) was generated from the aldol condensation reaction of diketone intermediate, which is formed by the double hydration of diyne (**1x**) (Table 3, entry 4).[15]

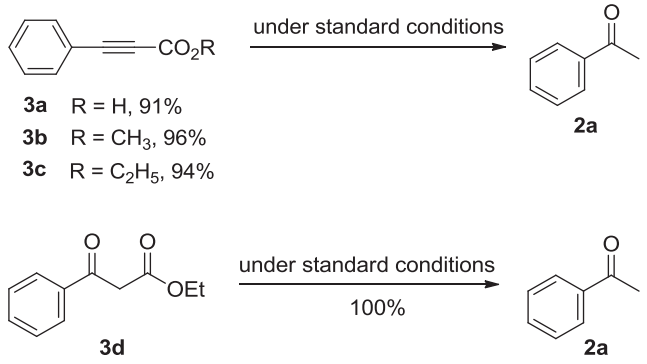
An unexpected cascade reaction was observed when extended the reaction to the phenylpropiolic acid and esters (**3a**–**c**). Under the standard conditions, we were surprised to find that the acetophenone was formed in excellent yields instead of the corresponding β-dicarbonyl compounds. We suspected that acetophenone was produced through a silver-catalyzed decarboxylation of the β-dicarbonyl compounds, which is generated from hydration of alkynes. To prove this concept, the β-dicarbonyl compound (**3d**) was subjected to the reaction condition and acetophenone was obtained in quantitative yield (Scheme 2).

Table 3
$AgBF_4$-catalyzed synthesis of methyl ketones from aliphatic alkynes[a]



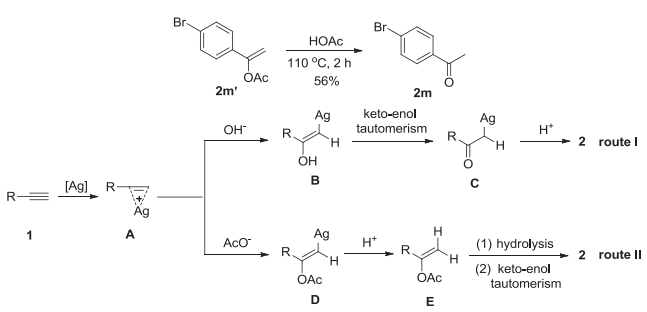
Entry	Substrate	Product	Yield (%)[b]
1	 1u	 2u	74
2	 1v	 2v	92
3	 1w	 2w	96
4	 1x	 2x	87

[a] Reaction conditions: aliphatic alkyne (1.0 mmol), acetic acid (2.0 mL), water (2 equiv), and silver tetrafluoroborate (5 mol %) at 110 °C for 10 h.
[b] Isolated yield.



Scheme 2. $AgBF_4$-catalyzed synthesis of acetophenone from alkyne derivatives and β-dicarbonyl compound.

To elucidate the mechanism, the enol acetate (**2m′**) was performed in acetic acid (Scheme 3). The successful formation of ketone (**2m**) suggested that the enol acetate might be the intermediate in this transformation. Two possible mechanisms were proposed and outlined in Scheme 3 on the basis of the previous reports and our observation.[8a,10a,14,16] First, the silver center



Scheme 3. Controlled experiment and possible reaction mechanism.

coordinates with the triple bond of the terminal alkyne and forms a π-complex **A**. In route I, the nucleophile $^{-}$OH attacks the complex to generate enol intermediate **B**, which subsequently undergoes keto–enol tautomerism to produce **C**, and the intermediate **C** would generate methyl ketone **2** by protonation. In route II, the nucleophile acetic anion attacks the complex to provide intermediate **D**, and then protonation to form enol acetate **E**, which subsequently undergoes successive hydrolysis and keto–enol tautomerism to generate methyl ketone **2**.

3. Conclusions

In conclusion, we have presented a general and facile method for the synthesis of methyl ketones from the simple terminal alkynes in high yields with excellent regioselectivity. The silver-catalyzed functionalization reaction tolerated a variety of functional groups. The proposed mechanism indicates that enol acetate may be the intermediate in this transformation. Further utilization of this procedure and understanding the mechanism will continue in our laboratory.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a GC–MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). All the other chemicals were purchased from Aldrich Chemicals.

4.2. General procedure for the synthesis of methyl ketones (2a–x)

To the mixture of terminal alkyne (1 mmol), water (2.0 equiv), and acetic acid (2 mL), silver tetrafluoroborate (5 mol %) was added. The mixture was stirred at 110 °C for 10 h. Water (10 mL) was added and the solution was extracted with ethyl acetate (3×8 mL), the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography to give the pure sample.

*4.2.1. Acetophenone (**2a**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.94–7.96 (m, 2H), 7.53–7.58 (m, 1H), 7.44–7.47 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.1, 137.1, 133.1, 128.5, 128.3, 26.6. MS (EI) *m*/*z*: 120, 105, 71, 51.

*4.2.2. 1-(p-Tolyl)ethanone (**2b**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84 (d, *J*=8.0 Hz, 2H), 7.24 (d, *J*=8.0 Hz, 2H), 2.56 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.8, 143.8, 134.7, 129.2, 128.4, 26.4, 21.5. MS (EI) *m*/*z*: 134, 119, 91, 65.

*4.2.3. 1-(m-Tolyl)ethanone (**2c**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.75 (d, *J*=10.8 Hz, 2H), 7.33 (t, *J*=8.0 Hz, 2H), 2.58 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.4, 138.3, 137.4, 133.8, 128.7, 128.4, 125.5, 26.6, 21.3. MS (EI) *m*/*z*: 134, 119, 91, 65, 51.

*4.2.4. 1-(4-(tert-Butyl)phenyl)ethanone (**2d**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91 (t, *J*=3.0 Hz, 1H), 7.89 (t, *J*=3.0 Hz, 1H), 7.49 (t, *J*=3.0 Hz, 1H), 7.46 (t, *J*=3.0 Hz, 1H), 2.58 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.9, 156.8, 134.6, 128.2, 125.5, 35.1, 31.0, 26.5. MS (EI) *m*/*z*: 176, 161, 133, 118, 91, 77.

*4.2.5. 1-([1,1′-Biphenyl]-4-yl)ethanone (**2e**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.02–8.05 (m, 2H), 7.67–7.70 (m, 2H), 7.61–7.64 (m, 2H), 7.45–7.49 (m, 2H), 7.38–7.42 (m, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.8, 145.7, 139.8, 135.8, 128.9, 128.9, 128.2, 127.2, 127.2, 26.6. MS (EI) *m*/*z*: 196, 181, 152, 76, 43.

*4.2.6. 1-(4′-Propyl-[1,1′-biphenyl]-4-yl)ethanone (**2f**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.00–8.03 (m, 2H), 7.66–7.69 (m, 2H), 7.54–7.56 (m, 2H), 7.28 (d, *J*=8.4 Hz, 2H), 2.64 (t, *J*=7.6 Hz, 2H), 2.63 (s, 3H), 1.64–1.73 (m, 2H), 0.98 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.7, 145.7, 143.0, 137.1, 135.5, 129.1, 128.9, 127.1, 126.9, 37.7, 26.6, 24.5, 13.8. MS (EI) *m*/*z*: 238, 223, 209, 165, 152, 115, 76, 43.

*4.2.7. 1-(4-Methoxyphenyl)ethanone (**2g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91 (d, *J*=8.8 Hz, 2H), 6.90 (d, *J*=8.8 Hz, 2H), 3.84 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.7, 163.4, 130.5, 130.3, 113.6, 55.4, 26.3. MS (EI) *m*/*z*: 150, 135, 107, 92, 77, 63.

*4.2.8. 1-(3-Methoxyphenyl)ethanone (**2h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41–7.47 (m, 2H), 7.26–7.31 (m, 1H), 7.02–7.04 (m, 1H), 3.77 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.7, 159.7, 138.4, 129.5, 121.0, 119.4, 112.3, 55.3, 26.6. MS (EI) *m*/*z*: 150, 135, 107, 92, 77, 63.

*4.2.9. 1-(2-Methoxyphenyl)ethanone (**2i**).* x^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69–7.72 (m, 1H), 7.41 (m, 1H), 6.93–6.98 (m, 2H), 3.88 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.8, 158.9, 133.6, 130.3, 128.2, 120.5, 111.6, 55.4, 31.8. MS (EI) *m*/*z*: 150, 135, 105, 92, 77, 63.

*4.2.10. 1-(Naphthalen-1-yl)ethanone (**2j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.78 (d, *J*=8.4 Hz, 1H), 7.97 (d, *J*=8.0 Hz, 1H), 7.91 (d, *J*=7.2 Hz, 1H), 7.86 (d, *J*=7.6 Hz, 1H), 7.58–7.62 (m, 1H), 7.45–7.54 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=201.8, 135.4, 134.0, 133.0, 130.1, 128.7, 128.4, 128.0, 126.4, 126.0, 124.3, 29.9. MS (EI) *m*/*z*: 170, 155, 127, 101, 77, 51.

*4.2.11. 1-(4-Fluorophenyl)ethanone (**2k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.92–7.95 (m, 2H), 7.06–7.10 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.4, 166.9, 164.4, 133.6, 133.5, 130.9, 130.8, 115.7, 115.4, 26.4. MS (EI) *m*/*z*: 138, 123, 95, 75.

*4.2.12. 1-(4-Chlorophenyl)ethanone (**2l**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J*=8.4 Hz, 2H), 7.36 (d, *J*=8.4 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.7, 139.4, 135.4, 129.6, 128.8, 26.4. MS (EI) *m*/*z*: 154, 139, 111, 74.

*4.2.13. 1-(4-Bromophenyl)ethanone (**2m**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.80 (d, *J*=8.4 Hz, 2H), 7.58 (d, *J*=8.4 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.9, 135.8, 131.8, 129.8, 128.2, 26.5. MS (EI) *m*/*z*: 198, 183, 155, 104, 75.

*4.2.14. 1-(2-Bromophenyl)ethanone (**2n**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59–7.61 (m, 1H), 7.44–7.46 (m, 1H), 7.34–7.38 (m, 1H), 7.26–7.30 (m, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=201.3, 141.5, 133.8, 131.7, 128.9, 127.4, 118.9, 30.3. MS (EI) *m*/*z*: 198, 183, 155, 104, 75, 51.

*4.2.15. 1-(4-(Trifluoromethyl)phenyl)ethanone (**2o**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.06 (d, *J*=8.0 Hz, 2H), 7.73 (d, *J*=8.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.9, 139.6, 134.2, 134.2, 128.6,

125.7, 125.7, 125.6, 125.6, 124.9, 26.7. MS (EI) *m*/*z*: 188, 173, 145, 125, 95, 75, 50.

*4.2.16. 1-(4-Nitrophenyl)ethanone (**2p**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22 (d, *J*=8.4 Hz, 2H), 8.05 (d, *J*=8.4 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.3, 150.2, 141.3, 129.2, 123.7, 26.9. MS (EI) *m*/*z*: 165, 150, 120, 104, 92, 76, 75, 63.

*4.2.17. 1-(Furan-2-yl)ethanone (**2q**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55 (s, 1H), 7.14 (d, *J*=3.2 Hz, 1H), 6.49–6.50 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=186.7, 152.8, 146.4, 117.2, 112.2, 25.9. MS (EI) *m*/*z*: 110, 95, 67.

*4.2.18. 1-(Pyridin-4-yl)ethanone (**2r**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.73–8.75 (m, 2H), 7.65–7.66 (m, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.2, 150.9, 142.6, 121.1, 26.5. MS (EI) *m*/*z*: 121, 106, 78, 51.

*4.2.19. Propiophenone (**2s**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.93 (d, *J*=7.6 Hz, 2H), 7.49–7.52 (m, 1H), 7.41 (t, *J*=7.6 Hz, 2H), 2.13–2.98 (m, 2H), 1.19 (t, *J*=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=200.7, 136.9, 132.8, 128.5, 127.9, 31.7, 8.2. MS (EI) *m*/*z*: 134, 105, 77, 51.

*4.2.20. 1,2-Diphenylethanone (**2t**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03–8.06 (m, 2H), 7.56–7.60 (m, 1H), 7.46–7.50 (m, 2H), 7.34–7.38 (m, 2H), 7.28–7.31 (m, 3H), 4.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.6, 136.5, 134.5, 133.1, 129.4, 128.6, 128.6, 128.6, 126.9, 45.5. MS (EI) *m*/*z*: 196, 105, 77, 51.

*4.2.21. Heptan-2-one (**2u**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.35 (t, *J*=7.6 Hz, 2H), 2.07 (s, 3H), 1.48–1.55 (m, 2H), 1.19–1.29 (m, 4H), 0.83 (t, *J*=6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=209.1, 43.6, 31.2, 29.7, 23.4, 22.3, 13.8. MS (EI) *m*/*z*: 114, 71, 58.

*4.2.22. 1-Cyclohexylethanone (**2v**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.27–2.34 (m, 1H), 2.11 (s, 3H), 1.63–1.78 (m, 4H), 1.13–1.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=212.2, 51.4, 28.4, 27.8, 25.8, 25.6. MS (EI) *m*/*z*: 126, 111, 71, 55.

*4.2.23. 5-Oxohexyl acetate (**2w**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.05 (t, *J*=6.0 Hz, 2H), 2.46 (t, *J*=6.8 Hz, 2H), 2.14 (s, 3H), 2.04 (s, 3H), 1.60–1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=208.3, 171.1, 64.0, 42.9, 29.8, 28.0, 20.9, 20.1. MS (EI) *m*/*z*: 158, 115, 98, 83, 71, 55.

*4.2.24. 3-Methylcyclohex-2-enone (**2x**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.88 (s, 1H), 2.34 (t, *J*=6.8 Hz, 2H), 2.28 (t, *J*=6.4 Hz, 2H), 1.97–2.05 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.9, 162.9, 126.6, 36.9, 30.9, 24.5, 22.5.

Acknowledgements

The authors thank the NSFC (21202023 and 21162001), NSF of Jiangxi Province (20114BAB213006 and 20114BAB213021) and the NSF of Jiangxi Provincial Education Department (GJJ12579) for financial support.

References and notes

1. (a) Lukas, H.; Aurélie, L. *Synthesis* **2007**, 1121; (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079; (c) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368; (d) Brenzovich, W. E. *Angew. Chem., Int. Ed.* **2012**, *51*, 8933.
2. (a) Kutscheroff, M. *Chem. Ber.* **1881**, *14*, 1540; (b) Kutscheroff, M. *Chem. Ber.* **1884**, *17*, 13; (c) Neumann, B.; Schneider, H. *Angew. Chem.* **1920**, *33*, 189; (d) Budde, W. L.; Dessy, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3964; (e) Janout, V.; Regen, S. L. *J. Org. Chem.* **1982**, *47*, 3331.
3. (a) Halpern, J.; James, B. R.; Kemp, A. L. W. *J. Am. Chem. Soc.* **1961**, *83*, 4097; (b) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *J. Mol. Catal.* **1990**, *58*, 299; (c) Almássy, A.; Nagy, C. E.; Bényei, A. C.; Joó, F. *Organometallics* **2010**, *29*, 2484.
4. (a) James, B. R.; Rempel, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 863; (b) Blum, J.; Huminer, H.; Alper, H. *J. Mol. Catal.* **1992**, *75*, 153.
5. Imi, K.; Imai, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3127.
6. (a) Hiscox, W.; Jennings, P. W. *Organometallics* **1990**, *9*, 1997; (b) Hartman, J. W.; Hiscox, W. C.; Jennings, P. W. *J. Org. Chem.* **1993**, *58*, 7613; (c) Baidossi, W.; Lahav, M.; Blum, J. *J. Org. Chem.* **1997**, *62*, 669.
7. Jin, X.; Oishi, T.; Yamaguchi, K.; Mizuno, N. *Chem.—Eur. J.* **2011**, *17*, 1261.
8. (a) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925; (b) Marion, N.; Ramón, R. S.; Nolan, S. P. *J. Am. Chem. Soc.* **2009**, *131*, 448; (c) Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012; (d) Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729; (e) Leyva, A.; Corma, A. *J. Org. Chem.* **2009**, *74*, 2067; (f) Ghosh, N.; Nayak, S.; Sahoo, A. K. *J. Org. Chem.* **2011**, *76*, 500; (g) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563; (h) Hashmi, A. S. K.; Hengst, T.; Lothschütz, C.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 1315; (i) Nun, P.; Ramon, R. S.; Gaillard, S.; Nolan, S. P. *J. Organomet. Chem.* **2011**, *696*, 7.
9. (a) Wu, X.-F.; Bezier, D.; Darcel, C. *Adv. Synth. Catal.* **2009**, *351*, 367; (b) Cabrero-Antonino, J. R.; Leyva-Pérez, A.; Corma, A. *Chem.—Eur. J.* **2012**, *18*, 11107; (c) Damiano, J. P.; Postel, M. *J. Organomet. Chem.* **1996**, *522*, 303.
10. (a) Kanemitsu, H.; Uehara, K.; Fukuzumi, S.; Ogo, S. *J. Am. Chem. Soc.* **2008**, *130*, 17141; (b) Hirabayashi, T.; Okimoto, Y.; Saito, A.; Morita, M.; Sakaguchi, S.; Ishii, Y. *Tetrahedron* **2006**, *62*, 2231.
11. Tachinami, T.; Nishimura, T.; Ushimaru, R.; Noyori, R.; Naka, H. *J. Am. Chem. Soc.* **2013**, *135*, 50.
12. (a) Tokunaga, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2867; (b) Labonne, A.; Kribber, T.; Hintermann, L. *Org. Lett.* **2006**, *8*, 5853; (c) Grotjahn, D. B.; Incarvito, C. D.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3884; (d) Chevallier, F.; Breit, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 1599; (e) Grotjahn, D. B.; Lev, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 12232; (f) Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. *Org. Lett.* **2001**, *3*, 735; (g) Boeck, F.; Kribber, T.; Xiao, L.; Hintermann, L. *J. Am. Chem. Soc.* **2011**, *133*, 8138; (h) Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 11917; (i) Alvarez, P.; Bassetti, M.; Gimeno, J.; Mancini, G. *Tetrahedron Lett.* **2001**, *42*, 8467.
13. (a) Thuong, M. B. T.; Mann, A.; Wagner, A. *Chem. Commun.* **2012**, 434; (b) Rao, K. T. V.; Prasad, P. S. S.; Lingaiah, N. *Green Chem.* **2012**, *14*, 1507; (c) Das, R.; Chakraborty, D. *Appl. Organomet. Chem.* **2012**, *26*, 722.
14. Chen, Z.; Li, J.; Jiang, H.; Zhu, S.; Li, Y.; Qi, C. *Org. Lett.* **2010**, *12*, 3262.
15. Gogoi, S.; Zhao, C.-G.; Ding, D. *Org. Lett.* **2009**, *11*, 2249.
16. Ogo, S.; Uehara, K.; Abura, T.; Watanabe, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 16520.