Triflic acid adsorbed on silica gel as an efficient and recyclable catalyst for the addition of β-dicarbonyl compounds to alcohols and alkenes†

Pei Nian Liu,*[a,b] Fei Xia,[a] Qing Wei Wang,[a] Yu Jie Ren*[a] and Jun Qin Chen[a]

Received 11th December 2009, Accepted 19th March 2010
First published as an Advance Article on the web 12th May 2010
DOI: 10.1039/b926142g

The silica gel supported triflic acid was readily prepared *via* simple absorption of TfOH onto chromatographic silica gel. This solid acid was applied as an efficient catalyst for the heterogeneous addition of various β-dicarbonyl compounds to a series of alcohols and alkenes, which afforded moderate to excellent yields under solvent-free conditions or in nitromethane. Moreover, this silica gel supported catalyst surprisingly exhibited higher reaction yields in comparison with the homogeneous catalyst and can be readily recovered and reused up to 6 times with almost maintained reactivity and yields.

Introduction

Following the urgent demand of "green chemistry", the search for more environmentally friendly forms of catalysis has created fast-growing interest, and one of the leading contenders for environmentally acceptable alternatives is supported catalysis. The catalyst immobilization provides easy separation of the products from the catalysts without tedious experimental work-up, and enables the efficient recovery of the catalysts, and potentially allows the adaptation of the immobilized catalysts to continuous flow-type processes.[1] Triflic acid (TfOH), which is a superacid, is the strongest protic acid with a large negative H_0 value of −14.1,[2] and has been used as perhaps the most versatile Brønsted acid catalyst in a vast array of organic reactions.[3] Because triflic acid is highly corrosive and is a fuming liquid, difficulties remain in storage, transportation, handling and waste disposal and severely restrict its application in industry. The immobilization of triflic acid onto an inorganic material, such as silica gel, affords solid acids which can be easily handled, as they invariably are low toxicity, non-corrosive, free-flowing powders with superior thermal and mechanical stability under catalytic conditions.[4] In the past several years, some Brønsted acids, such as H_2SO_4,[5] HBF_4,[6] $HClO_4$[7] *etc.* have been successfully supported onto silica gel and applied as solid acids in various catalytic reactions. Although triflic acid supported on functionalized silica has been reported,[8] the study of triflic acid supported on unmodified chromatographic silica gel is still very rare.[9]

Alkylation of β-dicarbonyl compounds is one of the most common methodologies for C–C bond construction. Due to the call of "green chemistry", the direct reaction of alcohols and active methylenes is an ideal transformation because only H_2O is generated as a side product. Besides, the preparation of alkyl halides and the use of bases (as in the traditional protocol) are not required.[10] Although the advantages of enhancing atom efficiency and avoiding waste are notable, successful examples of such "green" transformations have seldom been explored until recent years, due to the low reactivity of alcohol towards the nucleophiles.[11] It has been reported that addition of β-diketones and β-keto esters to benzhydryl alcohols can be promoted by a stoichiometric amount of the Lewis acid $BF_3{\cdot}OEt_2$.[12] Moreover, Pd,[13] Co,[14] Cu[15] with additives, and various Lewis acids such as $InCl_3$,[16] $InBr_3$,[17] $FeCl_3$,[18] $Bi(OTf)_3$,[19] $Ln(OTf)_3$ (Ln = La, Yb, Sc, Hf),[20] and a ruthenium complex[21] have been recently explored as effective catalysts for the addition of β-dicarbonyl compounds to allylic and benzylic alcohols. Additionally, molecular iodine[22] and a series of Brønsted acids, such as H-montmorillonite,[23] dodecylbenzenesulfonic acid,[24] *p*-toluenesulfonic acid,[25] triflic acid[26] and phosphotungstic acid[27] have been disclosed as effective catalysts for the addition of β-diketones to benzylic alcohols. Whereas much progress has been made in the addition of β-dicarbonyl compounds to benzylic alcohols, heterogeneous reactions catalyzed by reusable supported catalysts remain unexplored. Herein, we would like to present a triflic acid catalyst supported on silica gel (TfOH–SiO_2) by simple absorption, which demonstrates high reusability and efficiency for the heterogeneous addition of β-dicarbonyl compounds to alcohols and alkenes.

Results and discussion

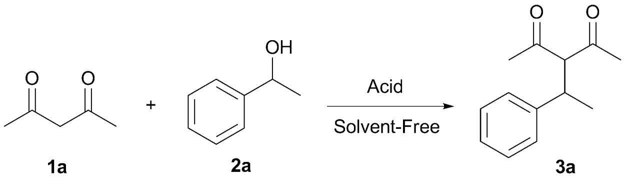
As the first stage of our research, we attempted to immobilize TfOH onto unmodified chromatographic silica gel and neutral or alkaline alumina *via* simple adsorption. As shown in Table 1, the resulting supported TfOH catalysts were used to catalyze the reactions of acetylacetone (**1a**) and 1-phenylethanol (**2a**) in air without solvent at 70 °C. The reaction results revealed

---

[a] *Key Lab for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, P. R. China. E-mail: liupn@ecust.edu.cn; Fax: +86-21-64252758; Tel: +86-21-64250552*
[b] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, P. R. China*

† Electronic supplementary information (ESI) available: Analytical data of the known products (**3a–g**, **3i–t**) and crystallographic data of **3a** in CIF or other electronic format. CCDC reference number 651081. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b926142g

Table 1 Reactions of **1a** and **2a** using acids as catalysts under various conditions[a]



Entry	Catalyst	Loading of TfOH (mmol g^{-1})	Run	Temp. (°C)	Time (h)	Yield (%)[b]
1[c]	TfOH–neutral Al_2O_3	0.5	1	70	17	13
2[c]	TfOH–alkaline Al_2O_3	0.5	1	70	17	55
3[c]	TfOH–SiO_2	0.5	1	70	5	80
4	TfOH–SiO_2	0.5	1	70	5	90
5	TfOH–SiO_2	0.5	2	70	5	89
6	TfOH–SiO_2	0.5	3	70	5	90
7	TfOH–SiO_2	0.5	4	70	5	86
8	TfOH–SiO_2	0.5	5	70	5	85
9	TfOH–SiO_2	0.5	6	70	5	51
10	TfOH	—	1	70	5	84
11	TfOH–SiO_2	0.5	1	90	3	83
12	TfOH–SiO_2	0.5	1	50	10	51
13[d]	TfOH–SiO_2	0.5	1	70	17	76
14	TfOH–SiO_2	0.25	1	70	5	70
15	TfOH–SiO_2	0.25	2	70	5	69
16	TfOH–SiO_2	1.0	1	70	5	85
17	TfOH–SiO_2	1.0	2	70	5	81

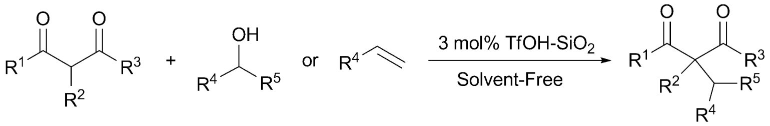
[a] Reaction conditions: supported TfOH (60 mg, containing 0.03 mmol TfOH), **1a** (3.0 mmol), **2a** (1.0 mmol), 70 °C, solvent-free conditions in air, unless noted otherwise. [b] Isolated yield. [c] **1a** (1.0 mmol) and **2a** (2.0 mmol) were used and the yield was determined based on **1a**. [d] TfOH–SiO_2 (20 mg, containing 0.01 mmol TfOH) was used.

that the unmodified chromatographic silica gel was a much better support for TfOH in comparison with neutral or alkaline alumina (Table 1, entries 1–3). When the pure oily product **3a** was placed in a sealed flask at room temperature for several weeks, it was interesting to find that the compound sublimed to form single crystals suitable for X-ray crystallography study.† As the ratio of **1a** to **2a** was changed from 1 : 2 to 3 : 1, the reaction catalyzed by TfOH–SiO_2 gave a further increased yield of 90% (Table 1, entry 4). Moreover, the silica gel supported TfOH exhibited excellent reusability in the reaction of **1a** and **2a** and it could be readily recovered and reused for 6 runs with almost maintained reactivities and yields (Table 1, entries 4-9). It is worth noting that when a different batch of TfOH–SiO_2 was used as the catalyst for the reaction of **1a** and **2a**, similar reaction results were also obtained, which illustrated the good catalytic reproducibility of TfOH–SiO_2. For comparison, a control experiment using liquid TfOH as the homogeneous catalyst was carried out under the same conditions, and only 84% yield was obtained in the reaction of **2a** and **1a**. This result suggested that the supported TfOH was a more effective catalyst than the original homogeneous one (Table 1, entries 4, 10). If the reaction temperature was increased or decreased, the reaction completion time was then shortened or prolonged, but the yields were both affected negatively. (Table 1, entries 11, 12). This reaction was also effective when the catalyst loading was decreased to 1%, but the reaction did not proceeds in the second run (Table 1, entry 13). When the loading of TfOH in TfOH–SiO_2 was varied from 0.5 mmol g^{-1} to 0.25 mmol g^{-1} or 1.0 mmol g^{-1}, worse reaction yields were observed and both the catalysts were ineffective after two runs (Table 1, entries 14-17). Moreover, further investigations of leaching of TfOH in the recycle reactions (Table 1, entries 4-9) were carried out by elemental analysis of fluorine and sulfur in TfOH–SiO_2. The results showed that the amount of TfOH contained in TfOH–SiO_2 before reaction and after six runs was 7.1% and 4.2%, respectively, which meant that approximately 40% of TfOH had leached from the catalyst after six uses. The elemental analysis results of the catalyst after each cycle also suggested that 5–8% of TfOH leached out in one cycle of reaction.

Subsequently, the reactions of various β-dicarbonyl compounds with a series of alcohols and alkenes were examined in air at 70 °C, using 3 mol% TfOH–SiO_2 as the catalyst. The results of reactions carried out under solvent-free conditions are listed in Table 2. The reactions of acetylacetone **1a** with the benzylic alcohols **2b** and **2c** bearing electron-donating groups on the aromatic ring gave good to excellent yields (Table 2, entries 2, 3). But the reaction of **1a** with 1-(4-chlorophenyl)ethanol **2d** showed only 68% yield, which suggested that the electron-withdrawing substitution on the aromatic ring affected the reaction negatively (Table 2, entry 4). Acetylacetone **1a** could also react with 1-(2-naphthyl)ethanol **2e** and benzhydrol **2f** smoothly to give the products **3e** and **3f** in 93% and 96% yields, respectively (Table 2, entries 5, 6). When the allylic alcohol **2g** was applied to the reaction with **1a**, the reaction produced the product **3g** in 82% yield (Table 2, entry 7).

When the sterically hindered cyclic diketone **1b** was used in the reaction with **2f**, the product **3h** with a quaternary carbon atom was obtained in excellent 96% yield, which illustrates that the steric hindrance of the β-diketone had no obvious effect on the reactivity and yield of this Brønsted acid catalyzed heterogeneous reaction (Table 2, entry 8). With the hope to expand the substrate scope, β-keto esters **1c** and **1d** were used as

Table 2 Reactions of β-dicarbonyl compounds with alcohols or styrene catalyzed by TfOH–SiO$_2$[a]



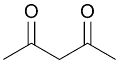
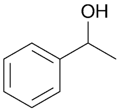
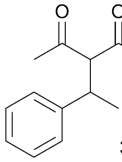
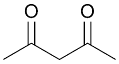
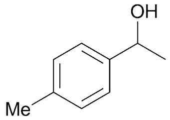
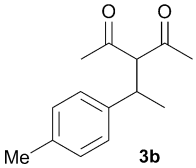
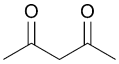
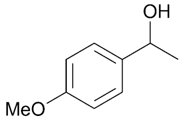
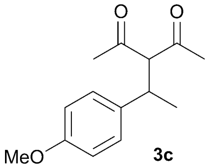
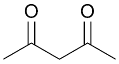
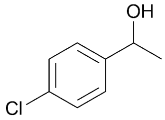
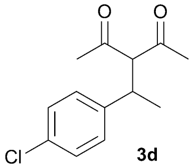
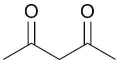
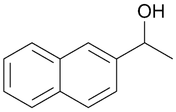
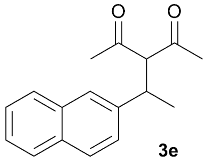
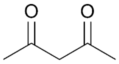
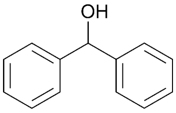
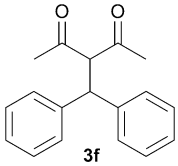
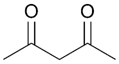
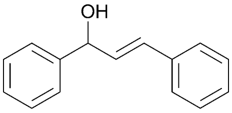
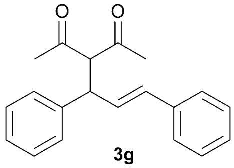
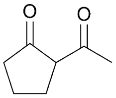
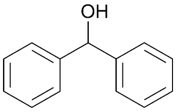
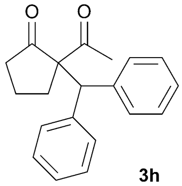
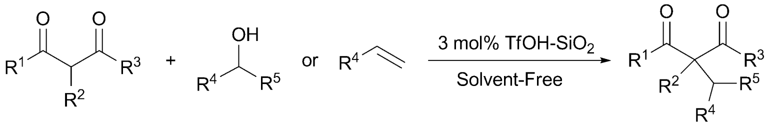
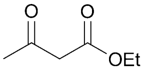
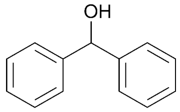
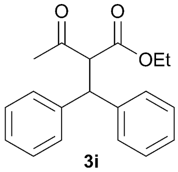
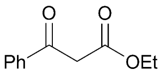
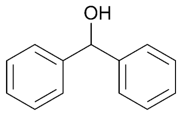
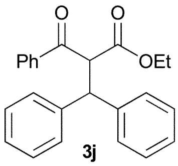
Entry	Dicarbonyl compound	Alcohol	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	90
2	 **1a**	 **2b**	 **3b**	84
3	 **1a**	 **2c**	 **3c**	94
4	 **1a**	 **2d**	 **3d**	68
5	 **1a**	 **2e**	 **3e**	93
6	 **1a**	 **2f**	 **3f**	96
7	 **1a**	 **2g**	 **3g**	82
8	 **1b**	 **2f**	 **3h**	96

Table 2 *(Contd.)*



Entry	Dicarbonyl compound	Alcohol	Product	Yield (%)[b]
9	 **1c**	 **2f**	 **3i**	96
10	 **1d**	 **2f**	 **3j**	98

[a] Reaction conditions: TfOH–SiO$_2$ (60 mg, containing 0.03 mmol TfOH), dicarbonyl compound (3.0 mmol), alcohol or alkene (1.0 mmol), solvent-free, 70 °C, 5 h. [b] Isolated yield based on alcohol or alkene used.

the nucleophiles to react with benzhydrol **2f**, and the products **3i** and **3j** were obtained in 96% and 98% yields, respectively (Table 2, entries 9 and 10).

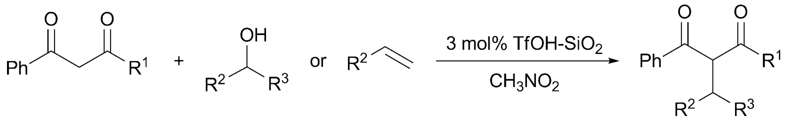
When the solid β-diketones benzoylacetone **1e** and 1,3-diphenyl-1,3-propanedione **1f** were used as the nucleophiles, a small amount of CH_3NO_2 was needed as a solvent to dissolve the solid reactants. The reaction of **1e** and **2a** afforded the product **3k** in 98% yield (Table 3, entry 1), while the homogeneous reaction catalyzed by 5 mol% TfOH gave only an 80% yield.[26] The reaction of **1e** with the alcohol **2d**, which bears an electron-withdrawing chloride on the aromatic ring, generated the product **3l** as two inseparable diastereoisomers in 94% yield (Table 3, entry 2). The reaction of **1e** and benzhydrol **2f** also showed excellent 98% yield (Table 3, entry 3).

When the β-diketone **1f** with two phenyl groups was reacted with the benzylic alcohols **2a**, 99% yield was obtained after 5 h (Table 3, entry 4), whereas the reaction of **1f** and **2a** only afforded 70% yield in the 5 mol% TfOH-catalyzed homogeneous reaction.[26] The reaction of β-diketone **1f** with the benzylic alcohols **2b** and **2d** both gave high yields, although one alcohol bears electron-donating groups and the other bears electron-withdrawing groups on the aromatic ring (Table 3, entries 5, 6). As for the reactions of **1f** with 1-(2-naphthyl)ethanol **2e** and benzhydrol **2f**, the corresponding products **3q** and **3r** were both produced in excellent 98% or 97% yields (Table 3, entries 7, 8). It is noteworthy that the reaction of **1f** with *exo*-norborneol **2h** was accomplished after 5 h in a moderate yield (Table 3, entry 9), whereas a much longer time was needed in the previously reported Brønsted acid-catalyzed reaction due to the rigid structure of norborneol.[21] When the benzyl alcohol **2i** was used as the reactant for this heterogeneous reaction, we were delighted that the addition product **3t** was isolated in 65% yield, which to the best of our knowledge is the first example of the Brønsted acid-catalyzed addition of a β-diketone to a primary alcohol (Table 3, entry 10).[19,20] The TfOH–SiO$_2$ catalyzed addition of β-diesters to the alcohols was, unfortunately, not successful under the present reaction conditions. As a further attempt to expand the versatility of the solid acid TfOH–SiO$_2$, we tried the addition of **1f** to the styrene **2j**. We were delighted that the reaction proceeded well, to afford the addition products **3n** in moderate yield (Table 3, entry 11). Moreover, the addition of **1f** to 2-norbornene **2k** catalyzed by TfOH–SiO$_2$ also smoothly produced the product **3s** in 80% yield just after 5 h, while much longer reaction time is needed in other homogeneous Brønsted acid catalyzed reactions (Table 3, entry 12).[21]

Conclusions

In summary, we have developed and optimized an easy-to-handle, efficient and recyclable solid acid catalyst through direct absorption of TfOH onto very cheap chromatographic silica gel. This silica gel supported TfOH (TfOH–SiO$_2$) has been applied as the catalyst for the direct addition of various β-dicarbonyl compounds to a series of alcohols or alkenes. The reactions can be conveniently performed in air under solvent-free conditions or in nitromethane, and usually give moderate to excellent yields with H_2O as the only by-product. In comparison with the homogeneous reactions catalyzed by TfOH, the heterogeneous reactions give better reaction yields with lower catalyst loading in many cases. Moreover, the catalyst TfOH–SiO$_2$ can be readily recovered and reused in multiple consecutive catalytic runs (up to 6 runs) with almost maintained reactivity and yields. This TfOH–SiO$_2$ catalyzed addition of β-dicarbonyl compounds to alcohols or alkenes provides an efficient, environmentally friendly protocol, which possesses the potential for application in industry. Further investigations to expand the usage of this readily available TfOH–SiO$_2$ catalyst to more catalytic organic reactions are underway in our lab.

Table 3 Reactions of β-diketones with alcohols or alkenes catalyzed by TfOH–SiO$_2$[a]



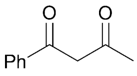
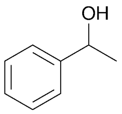
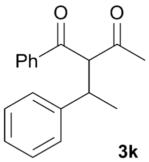
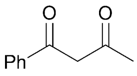
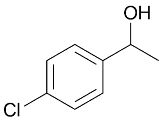
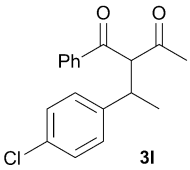
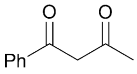
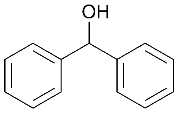
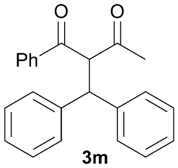
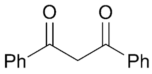
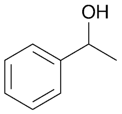
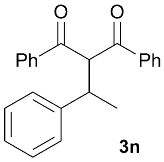
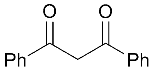
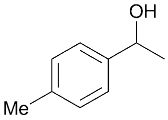
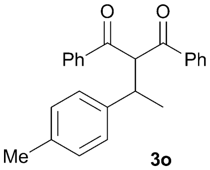
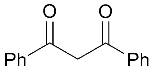
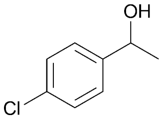
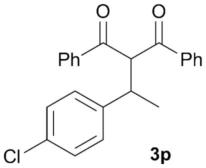
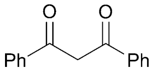
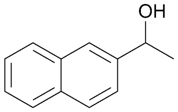
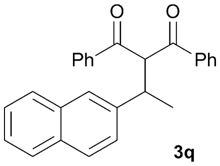
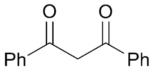
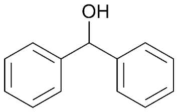
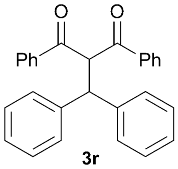
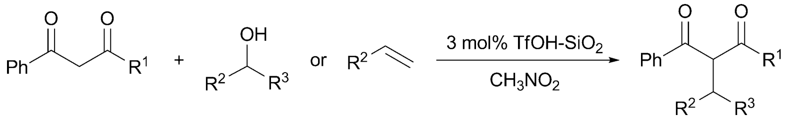
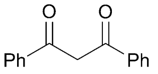
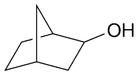
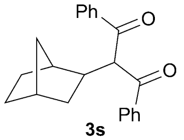
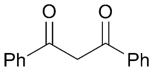
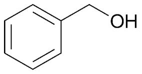
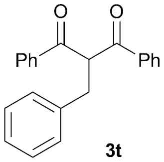
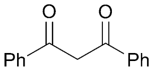
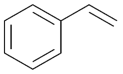
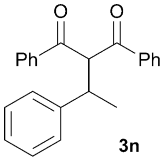
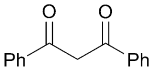
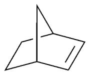
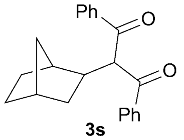
Entry	Dicarbonyl compounds	Alcohol	Product	Yield (%)[b]
1	 **1e**	 **2a**	 **3k**	98 (1 : 0.8)[c]
2	 **1e**	 **2d**	 **3l**	94 (1 : 0.7)[c]
3	 **1e**	 **2f**	 **3m**	98
4	 **1f**	 **2a**	 **3n**	99
5	 **1f**	 **2b**	 **3o**	92
6	 **1f**	 **2d**	 **3p**	99
7	 **1f**	 **2e**	 **3q**	98
8	 **1f**	 **2f**	 **3r**	97

Table 3 *(Contd.)*



Entry	Dicarbonyl compounds	Alcohol	Product	Yield (%)[b]
9	 **1f**	 **2h**	 **3s**	70
10	 **1f**	 **2i**	 **3t**	65
11[d]	 **1f**	 **2j**	 **3n**	65
12	 **1f**	 **2k**	 **3s**	80

[a] Reaction conditions: TfOH–SiO$_2$ (60 mg, containing 0.03 mmol TfOH), dicarbonyl compound (3.0 mmol), alcohol or alkene (1.0 mmol), 2 mL CH$_3$NO$_2$, 70 °C, 5 h unless noted. [b] Isolated yield based on alcohol or alkene used. [c] The ratio of the diastereoisomers was determined by ^{1}H NMR. [d] The reaction time was 10 h.

Experimental

1-(4-Methylphenyl)ethanol **2b**, 1-(4-methoxyphenyl)ethanol **2c**, 1-(4-chlorophenyl)ethanol **2d**, 1-(2-naphthyl)ethanol **2e** and 1,3-diphenyl-2-propenol **2g** were prepared by reduction of the corresponding ketone precursors with NaBH$_4$ in methanol. Chromatographic silica gel used as the support for TfOH was obtained from Qingdao Haiyang Chemical Co. Ltd. The other reagents were obtained from Aldrich and were used without further purification. ^{1}H NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts (δ, ppm) were reported using TMS as the internal standard. ^{13}C{^{1}H} NMR spectra were recorded with a Bruker DPX-400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to CHCl$_3$ ($\delta = 77.0$ ppm). Mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer and HRMS was carried out using a Waters Micromass Q-Tof-2 instrument. Melting points were determined on a Barnstead Electrothermal 9100 apparatus and are uncorrected.

Preparation of the silica gel supported triflic acid (TfOH–SiO$_2$)

To a suspension of silica gel (10.0 g, 200–300 mesh) in Et$_2$O (35 mL), TfOH (0.765 g, 5 mmol) was added. The mixture was stirred magnetically for 60 min at r.t. The Et$_2$O was removed under reduced pressure and the residue was dried at 110 °C for 2 h to afford TfOH–SiO$_2$ (0.5 mmol g^{-1}) as a white powder.

Typical procedure for the catalytic reaction of β-dicarbonyl compounds with alcohols (or alkenes)

A mixture of the β-dicarbonyl compound (3.0 mmol) and alcohol (or alkene, 1.0 mmol) was combined and TfOH–SiO$_2$ (60 mg, containing 0.03 mmol TfOH) was added. The mixture was stirred at 70 °C and monitored by TLC. After the completion of the reaction, CH$_2$Cl$_2$ (1 mL) was added and the mixture was stirred for 1 min, then the reaction was centrifuged (2000 rpm) for 1–2 min and the solution removed with a syringe. The catalyst was then washed with CH$_2$Cl$_2$ (1 mL) twice and the solution was removed; a new reaction could be conducted by adding a new batch of β-dicarbonyl compound (3.0 mmol) and alcohol (or alkene, 1.0 mmol) to the recovered catalyst. The solution containing the product was passed through a flash chromatography column on silica gel to afford the product.

2-Acetyl-2-benzhydrylcyclopentanone (3h). White solid, Mp: 156–158 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.31-1.40 (m, 1H), 1.63-1.76 (m, 2H), 2.05-2.22 (m, 5H), 3.12-3.17 (m, 1H), 5.34

(s, 1H), 7.00-7.02 (m, 2H), 7.16-7.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 25.9, 27.4, 38.9, 55.1, 74.3, 126.9, 128.3, 128.8, 128.9, 129.8, 140.4, 202.6, 215.2; HRMS (+ESI) calcd for $C_{20}H_{20}O_2^+$ (M^+): 292.1458, found: 292.1460.

Acknowledgements

This work was supported financially by NSFC (Project No. 20902020), the Shanghai Pujiang Talent Program (Project No. 09PJ1403500) and the Fundamental Research Funds for the Central Universities.

References

1 M. R. Buchmeiser, *Chem. Rev.*, 2009, **109**, 303–321; J. M. Fraile, J. I. García and J. A. Mayoral, *Chem. Rev.*, 2009, **109**, 360–417; M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev.*, 2003, **103**, 3401–3430; C. Aprile, F. Giacalone, M. Gruttadauria, A. M. Marculescu, R. Noto, J. D. Revellc and H. Wennemers, *Green Chem.*, 2007, **9**, 1328–1334; B. Basu, S. Paul and A. K. Nanda, *Green Chem.*, 2009, **11**, 1115–1120.

2 G. A. Olah and G. K. S. Prakash, *Superacids*, Wiley, New York. 1985.

3 S. R. Mothe and P. W. H. Chan, *J. Org. Chem.*, 2009, **74**, 5887–5893; T. Jin, M. Himuro and Y. Yamamoto, *Angew. Chem., Int. Ed.*, 2009, **48**, 5893–5896; M. Abid, L. Teixeira and B. Török, *Org. Lett.*, 2008, **10**, 933–935; A. Puglisi, A.-L. Lee, R. R. Schrock and A. H. Hoveyda, *Org. Lett.*, 2006, **8**, 1871–1874; T. G. Elford, Y. Arimura, S. H. Yu and D. G. Hall, *J. Org. Chem.*, 2007, **72**, 1276–1284.

4 A. Corma and H. Garcia, *Adv. Synth. Catal.*, 2006, **348**, 1391–1412; C. E. Song and S.-g. Lee, *Chem. Rev.*, 2002, **102**, 3495–3524; D. E. D. Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, **102**, 3615; P. N. Liu, P. M. Gu, F. Wang and Y. Q. Tu, *Org. Lett.*, 2004, **6**, 169–172; P. N. Liu, J. G. Deng, Y. Q. Tu and S. H. Wang, *Chem. Commun.*, 2004, 2070–2071; P.-N. Liu, P.-M. Gu, J.-G. Deng, Y.-Q. Tu and Y.-P. Ma, *Eur. J. Org. Chem.*, 2005, 3221–3227.

5 B. Roy, P. Verma and B. Mukhopadhyay, *Carbohydr. Res.*, 2009, **344**, 145; B. Mukhopadhyay, *Tetrahedron Lett.*, 2006, **47**, 4337–4341; V. K. Rajput and B. Mukhopadhyay, *Tetrahedron Lett.*, 2006, **47**, 5939–5941; V. K. Rajput, B. Roy and B. Mukhopadhyay, *Tetrahedron Lett.*, 2006, **47**, 6987–6991; S. Dasgupta, B. Roy and B. Mukhopadhyay, *Carbohydr. Res.*, 2006, **341**, 2708–2713; B. Roy and B. Mukhopadhyay, *Tetrahedron Lett.*, 2007, **48**, 3783–3787; S. Mandal and B. Mukhopadhyay, *Tetrahedron*, 2007, **63**, 11363–11370; S. Dasgupta, K. Pramanik and B. Mukhopadhyay, *Tetrahedron*, 2007, **63**, 12310–12316; B. Roy, K. Pramanik and B. Mukhopadhyay, *Glycoconjugate J.*, 2008, **25**, 157–166; V. K. Rajput and B. Mukhopadhyay, *J. Org. Chem.*, 2008, **73**, 6924–6927.

6 G. Sharma, R. Kumar and A. K. Chakraborti, *Tetrahedron Lett.*, 2008, **49**, 4272; B. P. Bandgar and A. V. Patil, *Tetrahedron Lett.*, 2007, **48**, 7552; B. P. Bandgar, A. V. Patil, V. T. Kamble and J. V. Totre, *J. Mol. Catal. A: Chem.*, 2007, **273**, 114; B. P. Bandgar and A. V. Patil, *Tetrahedron Lett.*, 2007, **48**, 173; B. P. Bandgar, A. V. Patil and O. S. Chavan, *J. Mol. Catal. A: Chem.*, 2006, **256**, 99; A. K. Chakraborti and R. Gulhane, *Tetrahedron Lett.*, 2003, **44**, 3521.

7 H. R. Shaterian, H. Yarahmadi and M. Ghashang, *Tetrahedron*, 2008, **64**, 1263; A. K. Chakraborti and R. Gulhane, *Chem. Commun.*, 2003, 1896; H. R. Shaterian, F. Shahrekipoor and M. Ghashang, *J. Mol. Catal. A: Chem.*, 2007, **272**, 142; B. Das, K. Laxminarayana and B. Ravikanth, *J. Mol. Catal. A: Chem.*, 2007, **271**, 131; S. Kantevari, R. Bantu and L. Nagarapu, *J. Mol. Catal. A: Chem.*, 2007, **269**, 53; M. A. Bigdeli, M. M. Heravi and G. H. Mahdavinia, *J. Mol. Catal. A: Chem.*, 2007, **275**, 25; B. Das, K. Damodar, N. Chowdhury and R. A. Kumar, *J. Mol. Catal. A: Chem.*, 2007, **274**, 148; V. T. Kamble, V. S. Jamode, N. S. Joshi, A. V. Biradara and R. Y. Deshmukh, *Tetrahedron Lett.*, 2006, **47**, 5573; B. Das, K. Venkateswarlu, A. Majhi, M. R. Reddy, K. N. Reddy, Y. K. Rao, K. Ravikumar and B. Sridhar, *J. Mol. Catal. A: Chem.*, 2006, **246**, 276; B. Das, K. Venkateswarlu, K. Suneel and A. Majhi, *Tetrahedron Lett.*, 2007, **48**, 5371; G. L. Khatik, G. Sharma, R. Kumar and A. K. Chakraborti, *Tetrahedron*, 2007, **63**, 1200.

8 A. N. Pârvulescu, B. C. Gagea, V. I. Pârvulescu, D. D. Vos and P. A. Jacobs, *Appl. Catal., A*, 2006, **306**, 159–164; A. N. Pârvulescu, B. C. Gagea, G. Poncelet and V. I. Pârvulescu, *Appl. Catal., A*, 2006, **301**, 133–137; B. C. Gageaa, A. N. Pârvulescua, G. Ponceletb and V. I. Pârvulescu, *Catal. Lett.*, 2005, **105**, 219–222; B. C. Gagea, A. N. Parvulescu, V. I. Parvulescu, A. Auroux, P. Grange and G. Poncelet, *Catal. Lett.*, 2003, **91**, 141–144.

9 A. de Angelis, C. Flego, P. Ingallina, L. Montanari, M. G. Clerici, C. Carati and C. Perego, *Catal. Today*, 2001, **65**, 363–371.

10 *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 3.

11 G. Guillena, D. J. Ramón and M. Yus, *Angew. Chem., Int. Ed.*, 2007, **46**, 2358–2364.

12 F. Bisaro, G. Prestat, M. Vitale and G. Poli, *Synlett*, 2002, 1823–1826.

13 For a recent review, see:J. Muzart, *Tetrahedron*, 2005, **61**, 4179–4212.

14 M. Mukhopadhyay and J. Iqbal, *Tetrahedron Lett.*, 1995, **36**, 6761–6764.

15 J. B. Baruah and A. G. Samuelson, *J. Organomet. Chem.*, 1989, **361**, 57–60.

16 M. Yasuda, T. Somyo and A. Baba, *Angew. Chem., Int. Ed.*, 2006, **45**, 793–796.

17 P. Vicennati and P. G. Cozzi, *Eur.J.Org. Chem.*, 2007, 2248–2253.

18 J. Kischel, K. Mertins, D. Michalik, A. Zapf and M. Beller, *Adv. Synth. Catal.*, 2007, **349**, 865–870; Y. Yuan, Z. Shi, X. Feng and X. Liu, *Appl. Organomet. Chem.*, 2007, **21**, 958–964; U. Jana, S. Biswas and S. Maiti, *Tetrahedron Lett.*, 2007, **48**, 4065–4069.

19 M. Rueping, B. J. Nachtsheim and A. Kuenkel, *Org. Lett.*, 2007, **9**, 825–828.

20 M. Noji, Y. Konno and K. Ishii, *J. Org. Chem.*, 2007, **72**, 5161–5167; W. Huang, J. Wang, Q. Shen and X. Zhou, *Tetrahedron Lett.*, 2007, **48**, 3969–3973.

21 P. N. Liu, Z. Y. Zhou and C. P. Lau, *Chem.–Eur. J.*, 2007, **13**, 8610–8619.

22 W. Rao, A. H. L. Tay, P. J. Goh, J. M. L. Choy, J. K. Ke and P. W. H. Chan, *Tetrahedron Lett.*, 2008, **49**, 122–126.

23 K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *Angew. Chem., Int. Ed.*, 2006, **45**, 2605–2609; K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Org. Chem.*, 2007, **72**, 6006–6015.

24 S. Shirakawa and S. Kobayashi, *Org. Lett.*, 2007, **9**, 311–314.

25 R. Sanz, A. Martínez, D. Miguel, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Adv. Synth. Catal.*, 2006, **348**, 1841–1845; R. Sanz, D. Miguel, A. Martínez, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Org. Lett.*, 2007, **9**, 727–730.

26 R. Sanz, D. Miguel, A. Martínez, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Org. Lett.*, 2007, **9**, 2027–2030.

27 G. W. Wang, Y. B. Shen and X. L. Wu, *Eur. J. Org. Chem.*, 2008, 4999–5004.