Ferric chloride-catalyzed decarboxylative alkylation of β -keto acids with benzylic alcohols

YANG CuiFeng¹, SHEN Chen¹, LI HaiHua¹ & TIAN ShiKai^{1,2*}

¹ Joint Laboratory of Green Synthetic Chemistry, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China;

² Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

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β -Keto acids are unstable to heat, acids, and bases, and have rarely been employed as carbon nucleophiles for the formation of carbon-carbon bonds. In this context, an efficient decarboxylative alkylation reaction of β -keto acids with benzylic alcohols has been developed, for the first time, through sequential cleavage of carbon-oxygen and carbon-carbon bonds. In the presence of 10 mol% of ferric chloride, a range of β -keto acids smoothly undergo decarboxylative alkylation with benzylic alcohols to give structurally diverse unsymmetric ketones in moderate to excellent yields and with extremely high regioselectivity. Preliminary mechanistic studies indicate that the reaction proceeds through an S_N1 alkylation followed by decarboxylation.

alkylation, benzylic alcohols, decarboxylation, ferric chloride, β -keto acids

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In sharp contrast to β -keto esters, β -keto acids have rarely been employed as carbon nucleophiles in the formation of carbon-carbon bonds. For a long time the synthetic applications of β -keto acids have been hampered by their instability to heat, acids, and bases [1,2]. Nevertheless, a few appropriate conditions have been reported for β -keto acids to undergo decarboxylative carbon-carbon bond-forming reactions with carbon electrophiles such as aldehydes [1–5], imines [6,7], electron-deficient alkenes [8–10], allylic acetates [11], 1,3-diene monoepoxides [12], and *N*-benzylic sulfonamides [13]. These biomimetic reactions have demonstrated that β -keto acids are able to serve as attractive surrogates of ketones for α -alkylation because of high reactivity and regioselectivity.

In the course of investigating sp^3 carbon-nitrogen bond cleavage [13–20], we recently found that *N*-benzylic sulfonamides could serve as carbon electrophiles for the decarboxylative alkylation of β -keto acids [13]. Mechanistic studies show that benzyl cation intermediates are generated

through the acid-catalyzed cleavage of the carbon-nitrogen bonds of *N*-benzylic sulfonamides. Since benzyl cation intermediates can also be generated from benzyl alcohols [21–28], we envisioned that it would be possible to develop a decarboxylative alkylation reaction of β -keto acids with benzyl alcohols under appropriate acidic conditions, which would allow an alkylation/decarboxylation sequence. The proposed reaction would generate water and carbon dioxide as byproducts, which were not expected to accelerate the decomposition of β -keto acids through decarboxylation. Nevertheless, it is a formidable challenge to fine tune reaction conditions to cleave the carbon-oxygen bonds in benzylic alcohols prior to the carbon-carbon bonds in β -keto acids.

1 Experimental

1.1 General information

¹H and ¹³C NMR spectra were recorded using tetramethylsilane as an internal reference. Melting points were un-

*Corresponding author (email: tiansk@ustc.edu.cn)

corrected. Alcohols [26,28] and β -keto acids [1,10,29] were prepared according to known procedures, and the rest of chemicals were purchased and used as received. The solvents were dried over anhydrous magnesium sulfate prior to use.

1.2 General procedure for the decarboxylative alkylation of β -keto acids with benzylic alcohols

To a solution of benzylic alcohol **2** (0.20 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature were added β -keto acid **1** (0.24 mmol) and ferric chloride (3.2 mg, 10 mol%). The resulting mixture was stirred at 60°C for 40 min, and cooled to room temperature. The mixture was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (20:1), to give compound **3**.

1.3 Characterization data

Ketone **3o**, white solid; m.p. 74–75°C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.21–7.03 (m, 6H), 6.88–6.78 (m, 2H), 4.92 (t, $J = 7.5$ Hz, 1H), 3.78 (s, 3H), 3.11 (d, $J = 7.5$ Hz, 2H), 2.27 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.4, 156.9, 140.5, 135.7, 132.6, 129.1, 127.9, 127.6, 120.7, 111.0, 55.5, 49.2, 39.3, 30.2, 21.1; IR (film) ν 3020, 1715, 1598, 1491, 1465 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}^+$) 269.1536, found 269.1535.

Ketone **3p**, colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 7.21–7.16 (m, 2H), 7.14–7.06 (m, 6H), 4.78 (t, $J = 6.9$ Hz, 1H), 3.35–3.22 (m, 2H), 3.17 (d, $J = 6.9$ Hz, 2H), 3.11–2.98 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 206.4, 141.2, 139.3, 130.4, 129.3, 126.9, 126.3, 51.5, 46.6, 33.3, 30.6; IR (film) ν 3017, 2933, 1714, 1491, 1448 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{18}\text{O}$ (M) 250.1358, found 250.1345.

Ketone **3r**, white solid; m.p. 79–80°C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40–7.30 (m, 4H), 7.24–7.11 (m, 4H), 4.67 (t, $J = 7.2$ Hz, 1H), 2.86 (d, $J = 7.2$ Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 206.9, 137.6, 137.4, 132.7, 132.3, 130.0, 129.1, 127.1, 126.8, 126.4, 126.0, 45.5, 44.3, 30.9; IR (film) ν 3061, 2923, 1709, 1464, 1438 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{14}\text{OS}$ (M) 254.0765, found 254.0764.

2 Results and discussion

Initially, the acidity of β -keto acid **1a** itself was attempted to catalyze the decarboxylative alkylation of β -keto acid **1a** with alcohol **2a** in 1,2-dichloroethane (DCE) at room temperature (Table 1, entry 1). However, the alkylation reaction did not take place and β -keto acid **1a** decomposed slowly to give acetophenone. Gratifyingly, the addition of 10 mol% of ferric chloride to the reaction mixture resulted in the formation of ketone **3a** in 16% yield (Table 1, entry 2) [30], and moreover, the yield was dramatically improved to 83%

Table 1 Optimization of reaction conditions^{a)}

Entry	Catalyst	Solvent	Temperature (°C)	Yield (%) ^{b)}
1	None	DCE	25	0
2	FeCl_3	DCE	25	16
3	FeCl_3	DCE	60	83
4	BiCl_3	DCE	60	18
5	ZnCl_2	DCE	60	Trace
6	$\text{Cu}(\text{OTf})_2$	DCE	60	27
7	SnCl_2	DCE	60	37
8	HCl	DCE	60	13
9	TsOH	DCE	60	10
10	H_2SO_4	DCE	60	61
11	FeCl_3	CHCl_3	60	31
12	FeCl_3	EtOAc	60	15
13	FeCl_3	THF	60	Trace
14	FeCl_3	MeNO_2	60	63
15	FeCl_3	MeCN	60	21
16 ^{c)}	FeCl_3	DCE	60	73

a) Reaction conditions: β -keto acid **1a** (0.24 mmol), alcohol **2a** (0.20 mmol), catalyst (if any, 10 mol%), solvent (1.0 mL), 40 min. b) Isolated yield. c) 5 mol% of FeCl_3 was used.

by elevating the temperature to 60°C (Table 1, entry 3). Diminished yields were obtained when switching the catalyst to some other Lewis acids or Brønsted acids, replacing 1,2-dichloroethane with a few other organic solvents, or lowering the catalyst loading (Table 1, entries 4–16).

Under the optimized reaction conditions, a range of β -keto acids smoothly underwent decarboxylative alkylation with alcohol **2a** to give structurally diverse unsymmetric ketones in moderate to excellent yields (Table 2). The R^1 group in the β -keto acid could be an alkyl, an aryl, or a heteroaryl group, and the R^2 group could be a hydrogen or an alkyl group. This reaction well tolerated electron-rich aromatic moieties (Table 2, entries 6 and 9), and moreover, no regioisomeric alkylation product was obtained from the reaction with β -keto acids **1b** and **1c** (Table 2, entries 2, 3).

A variety of benzylic alcohols smoothly reacted with β -keto acid **1a** in the presence of 10 mol% of ferric chloride to give the corresponding alkyl methyl ketones in good to excellent yields (Table 3). It is noteworthy that a few electron-donating groups were successfully introduced into the ketone products by employing the alcohols bearing such groups on the aromatic rings. Moreover, no rearrangement was observed for the carbon-carbon multiple bonds during the reaction (Table 3, entries 8–10). Nevertheless, this reaction was not applicable to less reactive benzylic alcohols such as benzyl alcohol and 1-phenylethanol. In addition, no decarboxylative alkylation product was obtained from the reaction of β -keto acid **1a** with 2-cyclohexenol or cyclohexanol. It could be attributable to the relatively low stability

Table 2 Decarboxylative alkylation of β -keto acids with alcohol **2a**^{a)}

$ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}^1-\text{C}-\text{CH}(\text{R}^2)-\text{C}-\text{OH} \\ \mathbf{1} \end{array} \xrightarrow[\text{DCE, 60}^\circ\text{C, 40 min}]{\mathbf{2a, FeCl}_3 (10 \text{ mol}\%)} \begin{array}{c} \text{O} \quad \text{Ph} \\ \parallel \quad \\ \text{R}^1-\text{C}-\text{CH}(\text{R}^2)-\text{C}-\text{Ph} \\ \mathbf{3a-k} \end{array} $			
Entry	β -Keto acid	Product	Yield (%) ^{b)}
	$ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}^1-\text{C}-\text{CH}_2-\text{C}-\text{OH} \end{array} $	$ \begin{array}{c} \text{O} \quad \text{Ph} \\ \parallel \quad \\ \text{R}^1-\text{C}-\text{CH}_2-\text{C}-\text{Ph} \end{array} $	
1	1a , R ¹ = Me	3a , R ¹ = Me	83
2	1b , R ¹ = (CH ₂) ₂ Me	3b , R ¹ = (CH ₂) ₂ Me	98
3	1c , R ¹ = CHMe ₂	3c , R ¹ = CHMe ₂	94
4	1d , R ¹ = CMe ₃	3d , R ¹ = CMe ₃	83
5	1e , R ¹ = Ph	3e , R ¹ = Ph	87
6	1f , R ¹ = 4-MeOC ₆ H ₄	3f , R ¹ = 4-MeOC ₆ H ₄	95
7	1g , R ¹ = 4-ClC ₆ H ₄	3g , R ¹ = 4-ClC ₆ H ₄	71
8	1h , R ¹ = 4-O ₂ NC ₆ H ₄	3h , R ¹ = 4-O ₂ NC ₆ H ₄	58
9	1i , R ¹ = 2-thienyl	3i , R ¹ = 2-thienyl	78
10	$ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}_6\text{H}_{10}-\text{C}-\text{CH}_2-\text{C}-\text{OH} \\ \mathbf{1j} \end{array} $	$ \begin{array}{c} \text{O} \quad \text{Ph} \\ \parallel \quad \\ \text{C}_6\text{H}_{10}-\text{C}-\text{CH}_2-\text{C}-\text{Ph} \\ \mathbf{3j} \end{array} $	65
11	$ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}_6\text{H}_4-\text{C}-\text{CH}_2-\text{C}-\text{OH} \\ \mathbf{1k} \end{array} $	$ \begin{array}{c} \text{O} \quad \text{Ph} \\ \parallel \quad \\ \text{C}_6\text{H}_4-\text{C}-\text{CH}_2-\text{C}-\text{Ph} \\ \mathbf{3k} \end{array} $	53

a) Reaction conditions: β -keto acid **1** (0.24 mmol), alcohol **2a** (0.20 mmol), FeCl₃ (10 mol%), 1,2-dichloroethane (1.0 mL), 60°C, 40 min.
b) Isolated yield.

of the corresponding carbocations generated via carbon-oxygen bond cleavage.

We carried out ¹H NMR spectroscopic analysis of the mixture of β -keto acid **1e**, alcohol **2a**, and sulfuric acid (10 mol%) in deuterated chloroform at room temperature and identified three intermediates: ether **4a**, β -keto acid **5a**, and β -keto ester **6a** (Figure 1). These intermediates were confirmed by ESI-MS spectroscopic analysis (Table 4). Nevertheless, the isolation of β -keto acid **5a** and β -keto ester **6a** was not successful by chromatography on silica gel due to rapid decomposition. The ¹H NMR (400 M) spectra shown in Figure 1 clearly indicate the formation and the disappearance of these intermediates as the reaction progressed. Although acetophenone was detected in a significant amount in the reaction mixture, it could hardly be alkylated with alcohol **2a** under our standard reaction conditions.

Based on our experimental results, we propose the following reaction pathways for the catalytic decarboxylative alkylation of β -keto acids with benzylic alcohols (Scheme 1). Alcohol **2** is subjected to iron-catalyzed carbon-oxygen bond cleavage to give benzyl cation **7** [31–34], which reversibly reacts with alcohol **2** to generate ether **4** as an intermediate [21,35,36]. Benzyl cation **7** couples with β -keto acid **1** to give β -keto acid **5** via carbon-carbon bond-formation and

Table 3 Decarboxylative alkylation of β -keto acid **1a** with benzylic alcohols^{a)}

$ \begin{array}{c} \text{OH} \\ \\ \text{R}^3-\text{C}-\text{R}^4 \\ \mathbf{2} \end{array} \xrightarrow[\text{DCE, 60}^\circ\text{C, 40 min}]{\mathbf{1a, FeCl}_3 (10 \text{ mol}\%)} \begin{array}{c} \text{O} \quad \text{R}^4 \\ \parallel \quad \\ \text{Me}-\text{C}-\text{CH}_2-\text{C}-\text{R}^3 \\ \mathbf{3l-u} \end{array} $			
Entry	Alcohol	Product	Yield (%) ^{b)}
	$ \begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_4-\text{R} \end{array} $	$ \begin{array}{c} \text{COMe} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_4-\text{R} \end{array} $	
1	2b , R = OMe	3l , R = OMe	98
2	2c , R = OH	3m , R = OH	81
3	2d , R = NMe ₂	3n , R = NMe ₂	80
	$ \begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3(\text{R})-\text{C}-\text{C}_6\text{H}_4-\text{Me} \end{array} $	$ \begin{array}{c} \text{COMe} \\ \\ \text{C}_6\text{H}_3(\text{R})-\text{C}-\text{C}_6\text{H}_4-\text{Me} \end{array} $	
4	2e , R = OMe	3o , R = OMe	73
	$ \begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_3(\text{X})-\text{C}_6\text{H}_4 \end{array} $	$ \begin{array}{c} \text{COMe} \\ \\ \text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_3(\text{X})-\text{C}_6\text{H}_4 \end{array} $	
5	2f , X = CH ₂ CH ₂	3p , X = CH ₂ CH ₂	83
6	2f , X = O	3q , X = O	81
7	2f , X = S	3r , X = S	73
	$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\ \mathbf{2i} \end{array} $	$ \begin{array}{c} \text{COMe} \\ \\ \text{Ph}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\ \mathbf{3s} \end{array} $	81
	$ \begin{array}{c} \text{HO} \\ \\ \text{Ph}-\text{C}-\text{C}\equiv\text{C}-\text{R} \end{array} $	$ \begin{array}{c} \text{COMe} \\ \\ \text{Ph}-\text{C}-\text{C}\equiv\text{C}-\text{R} \end{array} $	
9	2j , R = Ph	3t , R = Ph	90
10	2k , R = (CH ₂) ₃ Me	3u , R = (CH ₂) ₃ Me	71

a) Reaction conditions: β -keto acid **1a** (0.24 mmol), alcohol **2** (0.20 mmol), FeCl₃ (10 mol%), 1,2-dichloroethane (1.0 mL), 60°C, 40 min.
b) Isolated yield.

β -keto ester **8** via carbon-oxygen bond-formation. Decarboxylation of β -keto acid **5** leads to the formation of ketone product **3**. Such an alkylation/decarboxylation sequence should account for the extremely high regioselectivity observed in the reaction (Table 2, entries 2 and 3). Alternatively, β -keto ester **6** is generated through S_N1 alkylation of β -keto ester **8** with alcohol **2**, and is subsequently subjected to carbon-oxygen bond cleavage followed by decarboxylation to give ketone product **3**.

3 Conclusion

We have developed an unprecedented decarboxylative alkylation of β -keto acids with benzylic alcohols via catalytic cleavage of carbon-oxygen and carbon-carbon bonds. In the

Figure 1 ^1H NMR (400 M) spectra recorded for the sulfuric acid-catalyzed reaction mixture of β -keto acid **1e** and alcohol **2a** in CDCl_3 at room temperature for 5 min, 1 h, 5 h, and 24 h (from top to bottom). Chemical shifts (δ) assigned for the protons of positions a: 4.06 (s), b: 5.70 (s), c: 5.40 (s), d: 3.74 (d, J = 7.2 Hz), e: 4.83 (t, J = 7.2 Hz), f: 2.61 (s), g: 5.84 (s), h: 5.45 (d, J = 11.6 Hz), i: 5.04 (d, J = 11.6 Hz), j: 5.51 (d, J = 12.0 Hz), k: 5.11 (d, J = 12.0 Hz), and l: 6.61 (s).

Table 4 High resolution mass data of some intermediates

Entry	Species	Mass (calcd.)	Mass (found)	Formula	Error (ppm)
1	$[\mathbf{4a} + \text{H}]^+$	351.17434	351.17395	$\text{C}_{26}\text{H}_{23}\text{O}^+$	1.1
2	$[\mathbf{5a} + \text{Na}]^+$	353.11482	353.11514	$\text{C}_{22}\text{H}_{18}\text{NaO}_3^+$	0.9
3	$[\mathbf{6a} + \text{H}]^+$	497.21112	497.21136	$\text{C}_{35}\text{H}_{29}\text{O}_3^+$	0.5

Scheme 1 Proposed reaction pathways.

presence of 10 mol% of ferric chloride, a range of β -keto acids smoothly undergo decarboxylative alkylation with benzylic alcohols to give structurally diverse unsymmetric ketones in moderate to excellent yields and with extremely high regioselectivity. Preliminary mechanistic studies indicate that the reaction proceeds through an $\text{S}_{\text{N}}1$ alkylation followed by decarboxylation.

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- 1 Grayson D H, Tuite M R J. Knoevenagel reactions with β -oxo acids. Regiospecific enol equivalents for syntheses of α,β -unsaturated ketones and of some β -ketols. *J Chem Soc, Perkin Trans 1*, 1986, 2137–2142
- 2 Kourouli T, Kefalas P, Ragoussis N, et al. A new protocol for a regioselective aldol condensation as an alternative convenient synthesis of β -ketols and α,β -unsaturated ketones. *J Org Chem*, 2002, 67: 4615–4618
- 3 Schöpf C, Thierfelder K. Die aldolkondensation zwischen aldehyden und β -ketosäuren und ihre bedeutung für die biogenese einiger naturstoffe. *Justus Liebigs Ann Chem*, 1935, 518: 127–155
- 4 Stiles M, Wolf D, Hudson G V. Catalyst selectivity in the reactions of unsymmetrical ketones; Reaction of butanone with benzaldehyde and *p*-nitrobenzaldehyde. *J Am Chem Soc*, 1959, 81: 628–632
- 5 Rohr K, Mahrwald R. Stereoselective direct amine-catalyzed decarboxylative aldol addition. *Org Lett*, 2011, 13: 1878–1880
- 6 Baxter G, Melville J, Robins D J. Stabilisation of 3,4-dihydro-2H-pyrrole (1-pyrroline) by complexation with zinc iodide. *Synlett*, 1991, 359–360
- 7 Kimball F S, Tunoori A R, Victory S F, et al. Synthesis, *in vitro* and *in vivo* cytotoxicity of 6,7-diaryl-2,3,8,8a-tetrahydroindolizin-5(1H)-ones. *Bioorg Med Chem Lett*, 2007, 17: 4703–4707
- 8 Fujii M, Terao Y, Sekiya M. Decarboxylation reactions. Reaction of conjugated unsaturated ketones and nitriles with carboxylic acids. *Chem Pharm Bull*, 1974, 22: 2675–2679
- 9 Yasuda M. A novel decarboxylative condensation of β -keto acids with 2-cyclohexen-1-one. *Chem Lett*, 1975, 89–90
- 10 Evans D A, Mito S, Seidel D. Scope and mechanism of enantioselective Michael additions of 1,3-dicarbonyl compounds to nitroalkenes catalyzed by nickel(II)-diamine complexes. *J Am Chem Soc*, 2007, 129: 11583–11592
- 11 Tsuda T, Okada M, Nishi S, et al. Palladium-catalyzed decarboxylative allylic alkylation of allylic acetates with β -keto acids. *J Org Chem*, 1986, 51: 421–426
- 12 Tsuda T, Tokai M, Ishida T, et al. Palladium-catalyzed reaction of 1,3-diene monoepoxides with β -keto acids. Allylic alkylation and isomerization of 1,3-diene monoepoxides. *J Org Chem*, 1986, 51: 5216–5221
- 13 Yang C F, Wang J Y, Tian S K. Catalytic decarboxylative alkylation of β -keto acids with sulfonamides via the cleavage of carbon-nitrogen and carbon-carbon bonds. *Chem Commun*, 2011, 47: 8343–8345
- 14 Liu C R, Li M B, Yang C F, et al. Selective benzylic and allylic alkylation of protic nucleophiles with sulfonamides through double lewis acid catalyzed cleavage of sp^3 carbon-nitrogen bonds. *Chem Eur J*, 2009, 15: 793–797
- 15 Liu C R, Li M B, Cheng D J, et al. Catalyst-free alkylation of sulfinic acids with sulfonamides via sp^3 C–N bond cleavage at room temperature. *Org Lett*, 2009, 11: 2543–2545
- 16 Liu C R, Yang F L, Jin Y Z, et al. Catalytic regioselective synthesis of structurally diverse indene derivatives from *N*-benzylic sulfonamides and disubstituted alkynes. *Org Lett*, 2010, 12: 3832–3835
- 17 Yang B L, Tian S K. Catalytic coupling of *N*-benzylic sulfonamides with silylated nucleophiles at room temperature. *Chem Commun*, 2010, 46: 6180–6182
- 18 Li M B, Tang X L, Tian S K. Cross-coupling of Grignard Reagents with sulfonyl-activated sp^3 carbon-nitrogen bonds. *Adv Synth Catal*, 2011, 353: 1980–1984
- 19 Weng Z T, Li Y, Tian S K. Catalytic asymmetric α -alkylation of ketones and aldehydes with *N*-benzylic sulfonamides through carbon-nitrogen bond cleavage. *J Org Chem*, 2011, 76: 8095–8099
- 20 Wu X S, Tian S K. Catalytic asymmetric cleavage of sp^3 C–N bonds for access to highly enantioenriched *N*-benzylic sulfonamides. *Chem Commun*, 2012, 48: 898–900
- 21 Emer E, Sinisi R, Capdevila M G, et al. Direct nucleophilic S_N1 -type reactions of alcohols. *Eur J Org Chem*, 2011, 647–666
- 22 Zhang X, Rao W, Chan P W H. Iron(III) chloride-catalysed direct nucleophilic α -substitution of Morita-Baylis-Hillman alcohols with alcohols, arenes, 1,3-dicarbonyl compounds, and thiols. *Org Biomol Chem*, 2009, 7: 4186–4193
- 23 Chen G, Wang Z, Wu J, et al. Facile preparation of α -aryl nitriles by direct cyanation of alcohols with TMS-CN under the catalysis of InX_3 . *Org Lett*, 2008, 10: 4573–4576
- 24 Kabalka W G, Yao M L, Borella S, et al. Substitution of benzylic hydroxyl groups with vinyl moieties using vinylboron dihalides. *Org Lett*, 2005, 7: 2865–2867
- 25 Qin H, Yamagiwa N, Matsunaga S, et al. Bismuth-catalyzed direct substitution of the hydroxy group in alcohols with sulfonamides, carbamates, and carboxamides. *Angew Chem Int Ed*, 2007, 46: 409–413
- 26 Li H H, Dong D J, Tian S K. Three-component synthesis of amine derivatives using benzylic and allylic alcohols as *N*-alkylating agents in the absence of external catalysts and additives. *Eur J Org Chem*, 2008, 3623–3626
- 27 Li H H, Jin Y H, Wang J Q, et al. Controllable stereoselective synthesis of trisubstituted alkenes by a catalytic three-component reaction of terminal alkynes, benzylic alcohols, and simple arenes. *Org Bio Chem*, 2009, 7: 3219–3221
- 28 Li H H, Dong D J, Jin Y H, et al. An expeditious entry to benzylic and allylic sulfones through byproduct-catalyzed reaction of alcohols with sulfinyl chlorides. *J Org Chem*, 2009, 74: 9501–9504
- 29 Hogenkamp D J, Johnstone T B C, Huang J C, et al. Enaminone amides as novel orally active GABA_A receptor modulators. *J Med Chem*, 2007, 50: 3369–3379
- 30 Bolm C, Legros J, Le Paih J, et al. Iron-catalyzed reactions in organic synthesis. *Chem Rev*, 2004, 104: 6217–6254
- 31 Jana U, Biswas S, Maiti S. Iron(III)-catalyzed addition of benzylic alcohols to aryl alkynes—A new synthesis of substituted aryl ketones. *Eur J Org Chem*, 2008, 5798–5804
- 32 Ji W H, Pan Y M, Zhao S Y, et al. $FeCl_3$ -catalyzed propargylation-cycloisomerization tandem reaction: A facile one-pot synthesis of substituted furans. *Synlett*, 2008, 3046–3052
- 33 Anxionnat B, Guérinot A, Reymond S, et al. $FeCl_3$ -catalyzed Ritter reaction. Synthesis of amides. *Tetrahedron Lett*, 2009, 50: 3470–3473
- 34 Wang J, Zhang L, Jing Y, et al. Efficient synthesis of indenenes by $FeCl_3 \cdot 6H_2O$ -catalyzed intramolecular Friedel-Crafts reaction of aryl-substituted allylic alcohols. *Tetrahedron Lett*, 2009, 50: 4978–4982
- 35 Yasuda M, Somyo T, Baba A. Direct carbon-carbon bond formation from alcohols and active methylenes, alkoxyketones, or indoles catalyzed by indium trichloride. *Angew Chem Int Ed*, 2006, 45: 793–796
- 36 Jana U, Maiti S, Biswas S. An efficient $FeCl_3$ -catalyzed amidation reaction of secondary benzylic and allylic alcohols with carboxamides or *p*-toluenesulfonamide. *Tetrahedron Lett*, 2008, 49: 858–862

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