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A facile synthesis of trisubstituted alkenes from β-diketones and aldehydes with $AlCl_3$ as catalyst

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Abstract Preparation of trisubstituted alkenes from low-activity β-diketones and aldehydes with aluminum chloride as catalyst has been studied. The frequently used catalyst $AlCl_3$ is used for the first time to promote this condensation. The procedure is a convenient, low toxicity, and highly efficient method for industrial synthesis of trisubstituted alkenes in high yield.

Keywords $AlCl_3$ · Knoevenagel condensation · β-Diketones · Aldehydes · Facile reaction conditions

Introduction

Trisubstituted alkenes, for example α,β-unsaturated carbonyl compounds and α,β-unsaturated esters, are good Michael-addition acceptors and can be used directly in the Diels–Alder reaction for further transformations. These important derivatives are used widely in perfume, polymer, and pharmaceutical applications [1, 2], especially as elegant intermediates in the production of anti-hypertensive drugs and calcium antagonists. The Knoevenagel reaction is well-known to produce these

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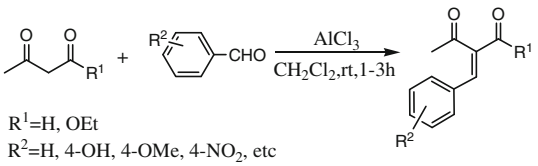
Scheme 1 Knoevenagel condensation of β-diketones and aldehydes



products [3]. Most Knoevenagel condensations are from active methylene compounds carrying two electron-withdrawing groups, for example malononitrile and malonate. Few examples of the use of β-diketones as starting materials have been reported, probably because such compounds are less reactive than the methylene compounds mentioned above, as a result of their tendency to form a stable cyclic enol [2].

The importance of trisubstituted alkenes has led to exploration of several new reagents to promote Knoevenagel condensation. Novel types of catalysts and technologies have been used for Knoevenagel condensations, for example procedures involving amino acids [3–5], azacyclo compounds [6, 7], metallohalides [8–11], inorganic salts [2, 12, 13], solid support catalysts [10, 14–19], hydroxyapatite [6, 19, 20], metals [21], ionic liquids [18, 22–26], supercritical CO_2 technology [27], and high-pressure conditions [28], etc. However, these procedures either require harsh conditions or are expensive as a result of the cost of the energy required, the catalyst used, or environmental protection. Also, some, for example perchlorates, may cause explosions. Although the classic base-promoted condensation is well-known, Lewis acids have attracted our attention. Basic compounds act as catalysts in this condensation because they can abstract a proton from an active methylene group, leading to an increase in the nucleophilicity of the active methylene. Lewis acids with oxophilicity also have this property—they tend to form oxides by hydrolysis or abstraction of oxygen, and so have a similar function to basic compounds in this condensation reaction. $AlCl_3$, a typical Lewis acid containing an oxophilic metal, and a classic catalyst in the Friedel–Crafts reaction, attracted our attention because of its use under facile conditions, with short reaction times, high conversion ratios, low toxicity, and wide commercial availability. Also, compared with the catalysts listed above, $AlCl_3$ is very inexpensive, and the by-product, $Al(OH)_3$, can be used as an inorganic flame retardant additive.

Herein, we report a mild procedure for Knoevenagel condensation with $AlCl_3$ as Lewis acid catalyst (Scheme 1); such reactions have high catalyst efficiency, are of low cost, and are environmentally friendly.

Results and discussion

Optimization of the Lewis acid used for the Knoevenagel condensation

We investigated some common Lewis acids as possible catalysts for the Knoevenagel reaction. To test the reactivity of Lewis acids we chose the reaction of ethyl acetoacetate with benzaldehyde in the presence of different catalytic

Table 1 Optimization of the Lewis acid for the Knoevenagel condensation

Entry	Catalyst	Amount of catalyst/mol%	Time/h	Yield[a]/%
1	$ZnCl_2$	10	12	0
2	$CaCl_2$	10	12	0
3	$AlCl_3$	10	3	88
4	$AlCl_3$	20	2	90
5	$AlCl_3$	5	2	30
6	No	–	12	0

Conditions: benzaldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol); TLC detection

[a] Isolated yield

systems at room temperature. $ZnCl_2$ (10 mol%) was first used as the catalyst in the reaction of ethyl acetoacetate (1 mmol) and benzaldehyde (1 mmol) stirred at room temperature, with product detection by MS. Unfortunately, no target product was formed. Use of $CaCl_2$ was also unsuccessful (Table 1, entry 1–2). Then another Lewis acid, $AlCl_3$, was investigated. Fortunately, it was found that the reaction proceeded well within 3 h, and the system was clean (Table 1, entry 3). The product was isolated and characterized as a trisubstituted alkene. To find the optimum amount of $AlCl_3$, 20 mol% $AlCl_3$ was added under the same conditions; although the yield increased slightly, the duration of the reaction was reduced to 2 h (Table 1, entry 4). When the amount of $AlCl_3$ was reduced to 5 mol% the yield decreased noticeably (Table 1, entry 5). When no catalyst was used no product was obtained (Table 1, entry 6). It is apparent from Table 1 that the best reaction conditions are at least 20 mol% $AlCl_3$ to obtain 90% target product yield without any traces of byproducts. Compared with traditional or novel catalysts reported recently, the amount of $AlCl_3$ required is almost the same, or even less, but the yield is higher.

Optimization of the solvent for the Knoevenagel condensation

The condensation reaction between ethyl acetoacetate and benzaldehyde in the presence of 20 mol% $AlCl_3$ was used to investigate the effect of the solvent used. It was found that strongly polar solvents had a deleterious effect on the reaction. As shown in Table 2, with CH_2Cl_2 as solvent the yield was slightly higher than with THF, and with EtOH, acetonitrile, or DMF as solvent no target product was obtained. Therefore, CH_2Cl_2 was chosen as solvent because of its low cost and ease of use.

Knoevenagel reaction of ethyl acetoacetate with aromatic aldehyde

To test the universality of $AlCl_3$ as catalyst, the procedure was applied in classical Knoevenagel condensation reactions of β-diketones with different aromatic aldehydes. We focused on the reaction of ethyl acetoacetate. Various benzaldehyde

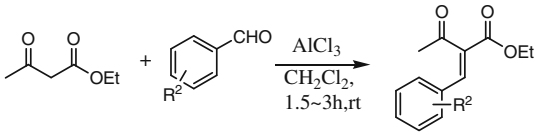
Table 2 Optimization of the solvent for the Knoevenagel reaction

Conditions: benzaldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), catalyst (0.2 mmol); TLC detection

[a] Isolated yield

Entry	Solvent	Yield[a]/%
1	EtOH	0
2	AN	0
3	THF	85
4	DMF	0
5	CH_2Cl_2	90

Scheme 2 Reaction of ethyl acetoacetate with aromatic aldehydes



R^2=H, 4-OH, 4-OMe, 4-NO_2, etc **1-11a**

derivatives carrying electron-withdrawing or electron-donating groups were used for the condensation reactions under the established procedure (Scheme 2). As shown in Table 3, because electron-withdrawing groups increased the electrophilicity of the carbonyl group, benzaldehyde derivatives carrying electron-withdrawing groups afforded slightly higher yields than benzaldehyde derivatives carrying electron-donating groups (Table 3, entries 6–9). In addition, it was found that aromatic aldehyde with large functional groups hindered the reaction more than those with small functional groups, irrespective of whether the groups were electron-donating or electron-withdrawing (Table 3, entries 2–5, 7–11).

Knoevenagel reaction of acetylacetone with aromatic aldehydes

After these encouraging results, the procedure was applied to the reaction of acetylacetone with aromatic aldehydes (Scheme 3). The results are reported in Table 4. Fortunately, we obtained similar results. Higher yields were achieved not only because of the symmetrical structure of acetylacetone, but also less stereospecific hindrance of the reagents (Table 4).

Knoevenagel reaction of β-diketones with nonaromatic aldehydes

We tried to extend the procedure to nonaromatic aldehydes (Scheme 4) but, unfortunately, unsatisfactory results were obtained. In fact, in the reaction of β-diketones with furfural, cinnamaldehyde, and aliphatic aldehydes, the most desired products were not obtained, only a mixture of starting materials and unidentified by-products, except for furfural (Table 5). We suggest this is because active methylene groups are electronegative, and the aliphatic hydrocarbon groups of aliphatic aldehydes usually increase the electronegativity of the carbonyl carbon because of their electron-donating properties, and this becomes a barrier to the reaction. Correspondingly, neither the traditional or novel catalysts reported worked efficiently with aliphatic aldehydes. Further research on the reactions of these substrates might be worthwhile.

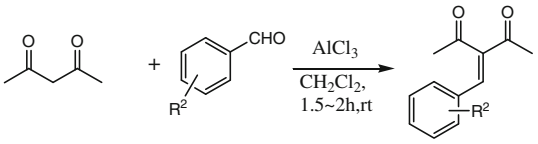
Table 3 Reaction of ethyl acetoacetate with aromatic aldehydes

Entry	R^2	Time/h	Yield[a]/%	Entry	R^2	Time/h	Yield[a]/%
1	H	2	88	7	4-NO_2	3	85
2	4-OH	2	78	8	3-NO_2	3	82
3	4-Me	2	80	9	2-NO_2	3	78
4	4-N(Me)$_2$	3	80	10	3,4-OMe	3	65
5	4-OMe	2	70	11	3-OMe, 4-OH	1.5	68
6	4-F	2	90				

Conditions: aromatic aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), catalyst (0.2 mmol); TLC detection

[a] Isolated yield

Scheme 3 Reaction of acetylacetone with aromatic aldehydes



R^2=H, 4-OH, 4-OMe, 4-NO_2, etc **1-11b**

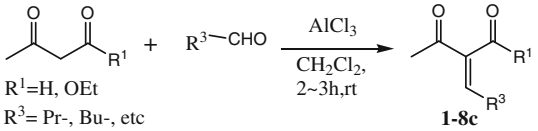
Table 4 Reaction of acetylacetone with aromatic aldehydes

Entry	R^2	Time/h	Yield[a]/%	Entry	R^2	Time/h	Yield[a]/%
1	H	2	90	7	4-NO_2	2	85
2	4-OH	1.5	85	8	3-NO_2	2	85
3	4-Me	2	80	9	2-NO_2	2	80
4	4-N(Me)$_2$	2	84	10	3,4-OMe	2	70
5	4-OMe	1.5	78	11	3-OMe,4-OH	1.5	70
6	4-F	2	90				

Conditions: aromatic aldehyde (1.0 mmol), acetylacetone (1.0 mmol), catalyst (0.2 mmol); TLC detection

[a] Isolated yield

Scheme 4 Reaction of active β-diketones with nonaromatic aldehydes



R^1=H, OEt
R^3= Pr-, Bu-, etc **1-8c**

Conclusions

In summary, we have demonstrated an interesting application of $AlCl_3$ as a Lewis acid catalyst in promoting the synthesis of trisubstituted functionalized alkenes via a Knoevenagel condensation between β-diketones and aromatic aldehydes. The reaction conditions are very mild, and the condensation occurs at room temperature

Table 5 Reaction of active β-diketones with nonaromatic aldehydes

Entry	R^1	R^3	Time/h	Yield[a]/%
1	H		2	70
2	H		3	0
3	H	^{n}Bu-	3	0
4	H	^{n}Pr-	3	0
5	OEt		2	60
6	OEt		3	0
7	OEt	^{n}Bu-	3	0
8	OEt	^{n}Pr-	3	0

Conditions: nonaromatic aldehyde (1.0 mmol), β-diketones (1.0 mmol), catalyst (0.2 mmol); TLC detection

[a] Isolated yield

with CH_2Cl_2 as solvent. Results demonstrated that the simple and highly efficient catalyst $AlCl_3$ can accelerate Knoevenagel condensation of aldehydes with β-diketones, with excellent yields. We found that $AlCl_3$ is efficient in reactions of aromatic aldehydes, and the corresponding trisubstituted alkenes could be synthesized in high yields. The reaction time is reduced to 2–3 h by using $AlCl_3$ as catalyst. Our results suggest that this method may displace most Knoevenagel condensation methods with other catalysts.

Experimental

General procedure for Knoevenagel reactions

Unless otherwise indicated, reagents and solvents were obtained from commercial suppliers. Thin-layer chromatography was performed on E. Merck TLC plates precoated with silica gel 60 F254. Visualization was accomplished by use of a UV lamp then vanillin staining. Flash column chromatography was accomplished with silica gel 60 (300–400 mesh). NMR spectra were obtained at 500 MHz for proton and 125 MHz for carbon in deuterated solvents, using tetramethylsilane as internal standard.

Experimental procedures

$AlCl_3$ (0.2 mmol) was added to a solution of the β-diketone (1.0 mmol) in dichloromethane (2 mL), stirring at room temperature for 5 min, and then the aldehyde (1.0 mmol) was added. The reaction was stirred at room temperature until the reaction was complete (TLC detection), then quenched with saturated $NaHCO_3$

solution. The dichloromethane solution was then washed with the same solution (3 × 10 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude mixture was purified by silica gel column chromatography.

Compound **1a**

Compound **1a** was prepared according to the general procedure using benzaldehyde and ethyl acetoacetate as starting materials. Yield: 88%; yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.336 (t, 3H), 2.357 (s, 3H), 4.283–4.326 (m, 2H), 7.386 (t, 5H), 7.678 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.44, 164.45, 140.52, 134.11, 132.92, 130.43, 129.68, 128.93, 61.57, 31.23, 14.18; ESI–MS *m*/*z* calculated for $C_{13}H_{14}O_3 + H^+$ 219.25, found 219.3.

Compound **2a**

Compound **2a** was prepared according to the general procedure using 4-OH-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 88%; yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.301, 1.316 and 1.330 (t, 3H); 2.405 (s, 3H); 4.339–4.382 (m, 2H); 5.314 (m, 1H); 6.827, 6.844 (m, 2H); 7.372, 7.389 (m, 2H), 7.498 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.78, 158.04, 141.07, 132.41, 131.97, 125.57, 115.97, 61.75, 26.47, 13.95; ESI–MS *m*/*z* calculated for $C_{13}H_{14}O_4 + H^+$ 235.25, found 235.2.

Compound **3a**

Compound **3a** was prepared according to the general procedure using 4-Me-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 80%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.300–1.358 (m, 3H); 2.374, 2.410 (m, 3H); 3.028, 3.036 (m, 6H); 4.245–4.400 (m, 2H), 6,616–6,648 (m, 2H); 7.266–7.377 (m, 2H); 7.466 and 7.571 (d, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.81, 194.69, 169.16, 165.29, 152.07, 142.19, 141.42, 132.23, 129.15, 119.94, 111.62, 61.43, 40.00, 26.30, 14.05.

Compound **4a**

Compound **4a** was prepared according to the general procedure using 4-N(Me)$_2$-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 80%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.300–1.358 (m, 3H); 2.374, 2.410 (m, 3H); 3.028, 3.036 (m, 6H); 4.245–4.400 (m, 2H), 6.616–6.648 (m, 2H); 7.266–7.377 (m, 2H); 7.466 and 7.571 (d, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.81, 194.69, 169.16, 165.29, 152.07, 142.19, 141.42, 132.23, 129.15, 119.94, 111.62, 61.43, 40.00, 26.30, 14.05; ESI–MS *m*/*z* calculated for $C_{15}H_{19}NO_3 + H^+$ 261.32, found 261.1.

Compound **5a**

Compound **5a** was prepared according to the general procedure using 4-MeO-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 70%; white solid;

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.298 (t, 3H); 2.376 (s, 3H); 2.415 (s, 3H); 4.326–4.369 (m, 2H); 7.189 and 7.205 (d, 2H); 7.352,7.368 (d, 2H); 7.536 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.77, 168.08, 141.49, 141.37, 133.67, 129.65, 61.70, 31.24, 26.48, 21.53, 13.92; ESI–MS *m/z* calculated for $C_{14}H_{16}O_4 + H^+$ 249.27, found 249.1.

Compound **7a**

Compound **7a** was prepared according to the general procedure using 4-NO_2-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 85%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.345–1.371 (m, 3H); 2.367, 2.370 (s, 3H); 4.322–4.361 (m, 2H); 7.553, 7.568 (m, 2H); 7.687 (m, 1H); 8.226 and 8.240 (m, 2H).

Compound **9a**

Compound **9a** was prepared according to the general procedure using benzaldehyde and ethyl acetoacetate as starting materials. Yield: 78%; yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.352, 1.366 and 1.381 (t, 3H); 2.213 (s, 3H); 4.326–4.369 (m, 2H); 7.360 and 7.375 (t, 1H); 7.555–7.586 (m, 1H); 7.627–7.657 (m, 1H); 8.197 and 8.214 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.60, 163.87, 147.21, 139.17, 136.20, 133.88, 131.10, 130.22, 130.12, 125.07.

Compound **10a**

Compound **10a** was prepared according to the general procedure using benzaldehyde and ethyl acetoacetate as starting materials. Yield: 65%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.312–1.340 (t, 3H); 2.413 (s, 3H); 3.830–3.926 (m, 9H); 4.340–4.383 (m, 2H); 6.872 and 6.889 (m, 1H); 7.032 (d, 1H); 7.098 and 7.115 (m, 1H); 7.501 (d, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.65, 168.41, 151.52, 149.02, 141.25, 132.52, 125.58, 124.53, 111.75, 111.03, 61.70, 55.99, 55.84, 26.45, 14.03.

Compound **11a**

Compound **11a** was prepared according to the general procedure using 3-OMe,4-OH-benzaldehyde and ethyl acetoacetate as starting materials. Yield: 68%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.310–1.338 (t, 3H); 2.407 (s, 3H); 3.886 (s, 3H); 4.335–4.378 (m, 2H); 6.075 (d, 1H); 6.916 and 6.933 (m, 1H); 7.022–7.060 (m, 2H); 7.485 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.74, 168.47, 148.52, 146.66, 141.46, 132.24, 125.26, 114.87, 111.40, 61.72, 55.94, 26.42, 14.02; ESI–MS *m/z* calculated for $C_{14}H_{16}O_5 + H^+$ 265.27, found 265.3.

Compound **1b**

Compound **1b** was prepared according to the general procedure using benzaldehyde and acetylacetone as starting materials. Yield: 90%; white solid; ^{1}H NMR ($CDCl_3$,

500 MHz): δ 2.289 (s, 3H), 2.430 (s, 3H), 7.401 (s, 4.96H), 7.501 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 205.59, 196.47, 142.82, 139.80, 132.91, 130.67, 129.71, 129.05, 31.66, 26.54; ESI–MS *m*/*z* calculated for $C_{12}H_{12}O_2 + H^+$ 189.22, found 189.5.

Compound **2b**

Compound **2b** was prepared according to the general procedure using 4-OH-benzaldehyde and acetylacetone as starting materials. Yield: 85%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.361 and 2.423 (d, 6H), 6.278 (s,1H), 6.827 and 6.844 (d,2H), 7.265 and 7.279 and 7.297 (t, 2H), 7.424 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 26.33, 31.77, 116.25, 125.09, 132.10, 140.35, 158.48, 196.94, 207.18; ESI–MS *m*/*z* calculated for $C_{12}H_{12}O_3 + H^+$ 205.22, found 205.2.

Compound **3b**

Compound **3b** was prepared according to the general procedure using 4-Me-benzaldehyde and acetylacetone as starting materials. Yield: 80%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.303 (s, 3H), 2.382 (s, 3H), 2.420 (s, 3H), 7.194, 7.210 (d, 2H), 7.289, 7.306 (d, 2H), 7.460 (s, 1H).

Compound **4b**

Compound **4b** was prepared according to the general procedure using 4-N$(Me)_2$-benzaldehyde and acetylacetone as starting materials. Yield: 84%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.365, 2.385 (d, 6H); 3.042 (s, 6H); 6,635, 6.653 (d, 2H); 7.292, 7.309 (d, 2H), 7.388 (s, 1H).

Compound **5b**

Compound **5b** was prepared according to the general procedure using 4-OMe-benzaldehyde and acetylacetone as starting materials. Yield: 78%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.306, 2.320 (d, 3H); 2.338, 2.402 (d, 3H); 3.819, 3.835 (m, 3H); 6.893–6.910 (m, 2H), 7.342–7.369 (m, 2H); 7.415–7.426 (m, 1H).

Compound **6b**

Compound **6b** was prepared according to the general procedure using 4-F-benzaldehyde and acetylacetone as starting materials. Yield: 90%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.371 (s, 3H), 2.428 (s, 3H), 6.831 and 6.848 (d, 2H), 7.015 (s, 1H), 7.270 and 7.284 (d, 1H), 7.434 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 205.52, 196.42, 164.91, 162.90, 142.58, 138.47, 131.87, 131.80, 129.08, 116.37, 116.20, 77.35, 77.10, 76.84; ESI–MS *m*/*z* calculated for $C_{12}H_{11}FO_2 + H^+$ 207.11, found 207.0.

Compound **7b**

Compound **7b** was prepared according to the general procedure using 4-NO_2-benzaldehyde and acetylacetone as starting materials. Yield: 85%; yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.295, 2.337 (m, 3H); 2.469 (m, 2H); 3.166 (s, 1H); 7.503–7.579 (m, 3H); 8.214–8.262 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.42, 200.64, 195.96, 148.50, 145.63, 139.26, 136.47, 130.24, 128.54, 124.14, 81.16, 75.83, 57.03, 31.75, 29.16, 24.04.

Compound **8b**

Compound **8b** was prepared according to the general procedure using 3-NO_2-benzaldehyde and acetylacetone as starting materials. Yield: 85%; Yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.326 (s, 3H); 2.478 (s, 3H); 7.503 (s, 1H); 7.589–7.622 (m, 1H); 7.722 and 7.737 (m, 1H); 8.260 and 8.273 (d, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.27, 200.37, 195.96, 148.50, 145.95, 139.26, 136.47, 130.24, 128.54, 127.33, 126.66, 124.14, 123.59, 81.16, 75.83, 57.03, 31.75, 29.16, 26.70.

Compound **10b**

Compound **10b** was prepared according to the general procedure using 3,4-OMe-benzaldehyde and acetylacetone as starting materials. Yield: 70%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.331 (m, 3H); 2.418 (s, 3H); 3,872 (m, 3H); 3.926 (m, 3H); 6.869–6.930 (m, 2H); 7.026–7.045 (m, 1H); 7.422 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.40, 151.37, 149.11, 139.89, 124.27, 112.00, 111.15, 55.99, 55.89, 31.75, 26.40; ESI–MS *m*/*z* calculated for $C_{14}H_{16}O_4 + H^+$ 249.27, found 249.4.

Compound **1c**

Compound **1c** was prepared according to the general procedure using furfural and acetylacetone as starting materials. Yield: 70%; yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.367–1.395 (m, 3H); 2.379 (s, 3H); 6.523–6.529 (m, 1H); 6.822 and 6.829 (t, 1H); 7.308 (s, 1H); 7.544 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.94, 167.58, 148.98, 146.39, 129.98, 126.43, 118.79, 112.92, 61.69, 26.54, 14.14; ESI–MS *m*/*z* calculated for $C_{10}H_{10}O_3 + H^+$ 179.18, found 179.3.

Compound **5c**

Compound **5c** was prepared according to the general procedure using benzaldehyde and acetylacetone as starting materials. Yield: 60%; yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.378 (m, 3H); 2.449 (m, 3H); 6.521–6.527 (m, 1H); 6.784 and 6.791 (m, 1H); 7.169 (s, 1H); 7.559 (t, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.47, 195.90, 148.82, 146.58, 138.31, 124.98, 118.37, 112.99, 50.81, 31.50, 26.13; ESI–MS *m*/*z* calculated for $C_{11}H_{12}O_4 + H^+$ 208.21, found 209.3.

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References

1. C.F. Linares, M.R. Goldwasser, F.J. Machado, A. Rivera, G. Rodriguez-Fuentes, J. Barrault, Microporous Mesoporous Mater. **41**, 69 (2000)
2. G. Bartoli, M. Bosco, A. Carlone, R. Dalpozzo, P. Galzerano, P. Melchiorre, L. Sambri, Tetrahedron Lett. **49**, 2555 (2008)
3. K.M. Parida, D. Rath, J. Mol. A Catal. Chem. **310**, 93 (2009)
4. F. Santamarta, P. Verdía, E. Tojo, Catal. Commun. **9**, 1779 (2008)
5. Y. Wang, Z.C. Shang, T.X. Wu, J.C. Fan, X. Chen, J. Mol. Catal. A: Chem. **253**, 212 (2006)
6. G. Yang, Z. Chen, G. Xu, X. Nie, Catal. Commun. **5**, 75 (2004)
7. J. Benites, J.A. Valderrama, F. Rivera, L. Rojo, N. Campos, M. Pedro, M.S.J. Nascimento, Bioorg. Med. Chem. **16**, 862 (2008)
8. R.M. Kumbhare, M. Sridhar, Catal. Commun. **9**, 403 (2008)
9. L. Wang, Y.M. Zhang, Chin. Chem. Lett. **9**, 123 (1998)
10. S. Sebti, R. Nazih, R. Tahir, L. Salhi, A. Saber, Appl. Catal. A **197**, 187 (2000)
11. W.B. Yi, C. Cai, Catal. Commun. **9**, 1291 (2008)
12. J. Bennazha, M. Zahouily, S. Sebti, A. Boukhari, E.M. Holt, Catal. Commun. **2**, 101 (2001)
13. Y. Zhang, Y. Zhao, C. Xia, J. Mol. Catal. A: Chem. **306**, 107 (2009)
14. X. Zhang, E.S. Lai, M.R. Martin-Aranda, K.L. Yeung, Appl. Catal. A **261**, 109 (2004)
15. V. Calvino-Casilda, R.M. Martín-Aranda, A.J. López-Peinado, I. Sobczak, M. Ziolek, Catal. Today **142**, 278 (2009)
16. F. Dong, Y.Q. Li, R.F. Dai, Chin. Chem. Lett. **18**, 266 (2007)
17. Y. Kubota, Y. Nishizaki, H. Ikeya, M. Saeki, T. Hida, S. Kawazu, M. Yoshida, H. Fujii, Y. Sugi, Microporous Mesoporous Mater. **70**, 135 (2004)
18. L. Martins, K.M. Vieira, L.M. Rios, D. Cardoso, Catal. Today **133–135**, 706 (2008)
19. V.S.R. Rajasekhar Pullabhotla, A. Rahman, S.B. Jonnalagadda, Catal. Commun. **10**, 365 (2009)
20. S. Sebti, R. Tahir, R. Nazih, A. Saber, S. Boulaajaj, Appl. Catal. A **228**, 155 (2002)
21. Y. Goa, P. Wu, T. Tatsumi, J. Catal. **224**, 107 (2004)
22. C. Yue, A. Mao, Y. Wei, M. Lu, Catal. Commun. **9**, 1571 (2008)
23. C. Paun, J. Barklie, P. Goodrich, H.Q.N. Gunaratne, A. McKeowna, V.I. Pârvulescu, C. Hardacre, J. Mol A: Catal. Chem. **269**, 64 (2007)
24. D.J. Macquarrie, J.H. Clark, A. Lambert, J.E.G. Mdoe, A. Priest, React. Funct. Polym. **35**, 153 (1997)
25. Y. Moussaoui, R.B. Salem, J. Comptes Rendus Chimie **10**, 1162 (2007)
26. K. Yamashita, T. Tanaka, M. Hayashi, Tetrahedron **61**, 7981 (2005)
27. T. Seki, M. Onaka, J. Mol. Catal. A: Chem. **263**, 115 (2007)
28. G. Jenner, Tetrahedron Lett. **42**, 243 (2001)