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The silica supported $H_3PW_{12}O_{40}$ (a heteropoly acid) as an efficient and reusable catalyst for a one-pot synthesis of β-acetamido ketones by Dakin–West reaction

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Abstract

Heteropoly acid $H_3PW_{12}O_{40}$ (PW) supported on silica (PW/SiO_2) has been used as an effective catalytic system for a four-component coupling process for the synthesis of β-acetamido ketones by Dakin–West reaction. The present methodology offers several advantages, such as high yields, short reaction times, mild condition and a recyclable catalyst with a very easy work up.

Keywords: β-Acetamido ketones; Supported heteropoly acid; Dakin–West reaction; Multi-component reactions (MCR)

1. Introduction

Heteropoly acids (HPAs) have been extensively studied as acid catalysts for many reactions and found industrial applications in several processes [1]. HPAs are promising solid acids to replace environmentally harmful liquid acid catalysts, such as H_2SO_4 [1a,1b]. The Keggin-type HPAs typically represented by the formula $H_{x-8}[XM_{12}O_{40}]$, where X is the heteroatom (e.g. P^{5+} or Si^{4+}), x the oxidation state, and M is the addenda atom (usually Mo^{6+} or W^{6+}), are the most important catalysts, especially $H_3PW_{12}O_{40}$ (PW), $H_3PMo_{12}O_{40}$ (PMo) or $H_4SiW_{12}O_{40}$ (SiW) [2]. Being stronger acids, HPAs generally exhibit higher catalytic activities than conventional catalysts, such as mineral acids, ion-exchange resins, zeolites, SiO_2/Al_2O_3, H_3PO_4/SiO_2 [1a,1b], etc., in both heterogeneous and homogeneous systems [1a]. Furthermore, HPA catalysis lacks side reactions, such as sulfonation, chlorination, etc., that frequently occur with mineral acids.

Supported HPA catalysts are important for applications due to environmental and economic considerations. They also have excellent activity and can be easily recovered from reaction mixtures and reused. Acidic or neutral substances, such as SiO_2, active carbon, acidic ion-exchange resin, etc., are all suitable supports, but SiO_2, which is relatively inert towards HPAs, is the one most often used [3].

The design of multi-component reactions (MCR) is an important field of research from the point of view of combinatorial chemistry [4–7]. In the past decade, there has been tremendous development in three- and four-component reactions involving Passerini- [8], Ugi- [9], and Mannich-type reactions [10] as a result of which, these processes are performed without isolation of any intermediates, thus reducing time and saving both energy and raw materials. Dakin–West reaction is the best known route for the synthesis of β-acetamido ketones [11,12]. These compounds are versatile intermediates, in that their skeletons exist in a number of biologically or pharmacologically important compounds [13,14]. A few catalysts have already been applied to synthesis of β-acetamido ketones, using this method, including $CoCl_2$ [15], montmorillonite K-10 clay [16], H_2SO_4/SiO_2 [17], triflate salts [18]. However, these procedures are not entirely satisfactory and suffer from long reaction time or tedious work up. Hence, the development of new catalysts with more efficiency is of interest.

2. Experimental

2.1. Techniques

Surface area and porosity of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP

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2000 instrument. Thermogravimetric analyses (TGA) were performed using Perkin-Elmer TGA 7 instrument under nitrogen flow. IR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer and FT-IR spectra were performed using Bomem MB 104 spectrophotometer. Tungsten content in the catalysts was measured by inductively coupled plasma (ICP atomic emission spectroscopy) on a Spectro Ciros CCd spectrometer. The products of the catalysis reaction were detected by a Bruker Avance 200 MHz NMR spectrometer.

2.2. Materials and catalysts

All chemical reagents and solvents were analytical grade and used without further purification. $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ hydrate from Aldrich, Merck and Aerosil 300 silica from Degussa were used. Silica-supported PW catalysts (PW/SiO_2) were prepared by impregnating Aerosil 300 silica (S_{BET}, 300 m^2/g) with an aqueous solution of PW. The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator, as described elsewhere [19]. The acidic salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was prepared by the literature method [19]. Catalyst characterisation is given in Table 1.

2.3. Typical procedure for the synthesis of β-acetamido ketones

A solution of aryl aldehyde (1 mmol), ketone (1 mmol), acetyl chloride (0.3 mL) and acetonitrile (3 mL) in the presence of appropriate amount of catalyst (Table 2) was stirred at ambient temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the filtrate was poured into 50 mL ice-water. The solid product was filtered, washed with ice-water and recrystallized from ethyl acetate/*n*-heptane to give the pure product. All products were identified by comparing their NMR and IR values with those for authentic samples [16,17,21].

3. Results and discussion

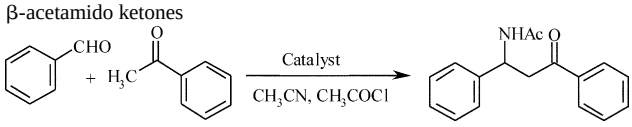
Since, Keggin-type heteropoly acids, e.g. PW, PMo and SiW were previously found to be highly active solid acid catalysts [2,20], the utilization of such HPAs properties in the synthesis of β-acetamido ketones was studied. First the reaction of benzaldehyde and acetophenone was examined in the presence of several HPAs catalysts (Table 2, entries 2–4). The synthesis could not be achieved in the absence of the catalyst (Table 2, entry 1). The reaction was more efficient in the presence of HPAs when compared to the literature procedure [16–18] (Table 2, entries 5–18). It was observed that PW returned a high yield for the coupling of an aldehyde with ketones. Heterogeneous catalysts have gained importance due to environmental and economic considerations. This encouraged the investigation of the efficiency of PW/SiO_2 as a catalyst on such reactions. PW/SiO_2 with different weight percent of PW was examined (Table 2 entries 19–21). FT-IR of the supported Keggin HPA catalysis after catalysis preparation and also after catalytic reaction were checked and characteristic peaks at about 1081, 985, 890 and 814 cm^{-1} were observed. It should be emphasized that both catalyst preparation and reaction conditions are mild, thus it is reasonable that the Keggin unit should be intact under the reaction condition. Acidic heteropoly salts, such as CsPW showed no reactivity in this reaction (Table 2, entry 22). The temperature and the quantity of catalyst used in this reaction were optimized (Table 2, entries 23–25).

Table 1
Catalyst characterisation

Catalyst[a]	S_{BET}	Pore size	Pore volume	H_2O (wt.%)[b]	*W* (wt.%)[c]
60% PW/SiO_2	87	145	0.34	1.8	45.6
40% PW/SiO_2	117	227	0.67	4.8	28.9
20% PW/SiO_2	208	145	0.75	3.5	15.4
CsPW	129	38	0.12	1.8	60.5

[a] Catalysts pre-treated at 150 °C/0.5 Torr for 1.5 h, PW content from preparation stoichiometry in anhydrous catalysts.
[b] From TGA as a weight loss in the range of 30–300 °C.
[c] *W* content in anhydrous catalysts from ICP. Typically, the *W* content from ICP was slightly lower than expected from the preparation stoichiometry.

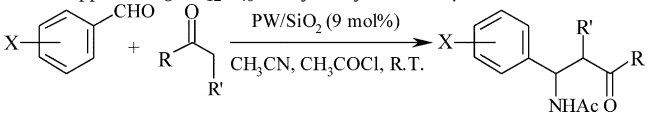
Table 2
Effect of catalysts on the four-component Dakin–West reaction to give β-acetamido ketones



Entry	Catalyst	Temperature (°C)	*T* (h)	Yield (%)[a]
1	–	80	10	0
2	PW (5 mol%)	RT	0.85	95
3	PMo (5 mol%)	RT	0.85	88
4	SiW (5 mol%)	RT	0.85	90
5	$Zn(OTf)_2$ (10 mol%)[18]	RT	30	60
6	$Bi(OTf)_3$ (10 mol%)[18]	RT	30	69
7	$Sn(OTf)_3$ (10 mol%)[18]	RT	30	68
8	$Sc(OTf)_3$ (10 mol%)[18]	RT	30	82
9	$Cu(OTf)_2$ (10 mol%)[18]	RT	30	64
10	$Yb(OTf)_3$ (10 mol%)[18]	RT	30	75
11	$BF_3{\cdot}OEt_2$ (100 mol%)[18]	RT	30	78
12	$CuCl_2$ (100 mol%)[18]	RT	30	79
13	$BiCl_3$ (100 mol%)[18]	RT	30	77
14	$LaCl_3$ (100 mol%)[18]	RT	30	77
15	$LiClO_4$ (100 mol%)[18]	RT	30	59
16	$InCl_3$ (100 mol%)[18]	RT	30	19
17	SiO_2/H_2SO_4 (0.3 g)[17]	80	1.08	91
18	Montmorillonite K-10 (2 g)[16]	70	7	80
19	60% PW/SiO_2 (14 mol%)	RT	1	95
20	40% PW/SiO_2 (9 mol%)	RT	1	90
21	20% PW/SiO_2 (5 mol%)	RT	1	75
22	CsPW (100 mol%)	80	4	0
23	40% PW/SiO_2 (9 mol%)	80	1	92
24	40% PW/SiO_2 (20 mol%)	RT	1	93
25	40% PW/SiO_2 (5 mol%)	RT	1	80
26	40% PW/SiO_2 (9 mol%)[b]	RT	1	80
27	40% PW/SiO_2 (9 mol%)[b]	RT	1	72
28	40% PW/SiO_2 (9 mol%)[b]	RT	1	67

[a] Isolated yield.
[b] Catalyst reused in four successive runs; the catalyst was filtered off, washed with acetonitrile and dried at 150 °C/0.5 Torr for 1.5 h.

Table 3
Silica-supported $H_3PW_{12}O_{40}$ catalysed synthesis of β-acetamido ketones at room temperature



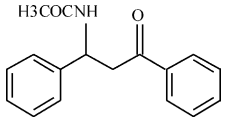
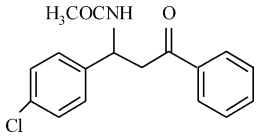
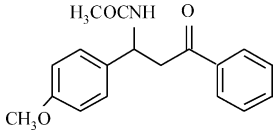
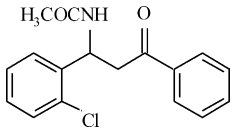
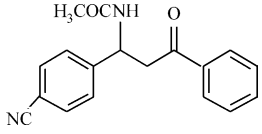
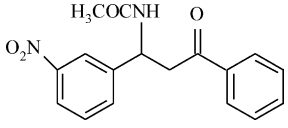
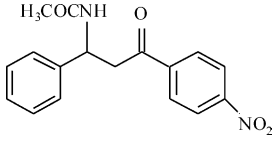
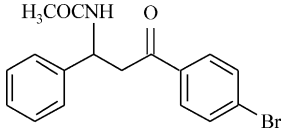
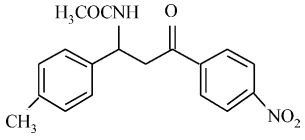
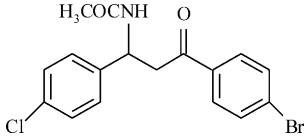
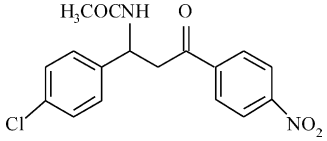
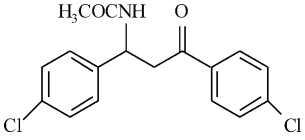
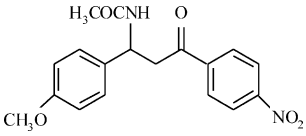
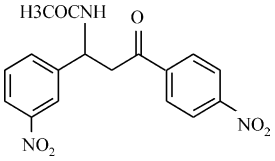
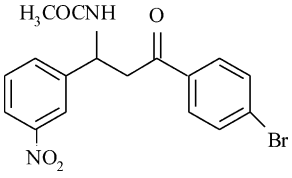
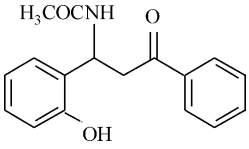
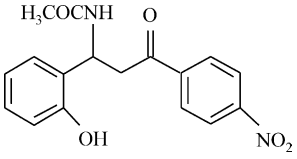
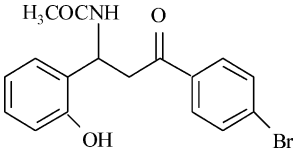
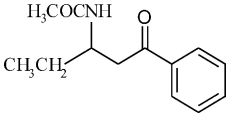
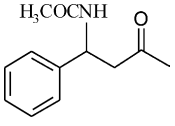
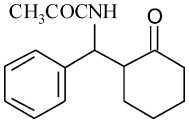
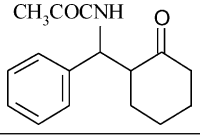
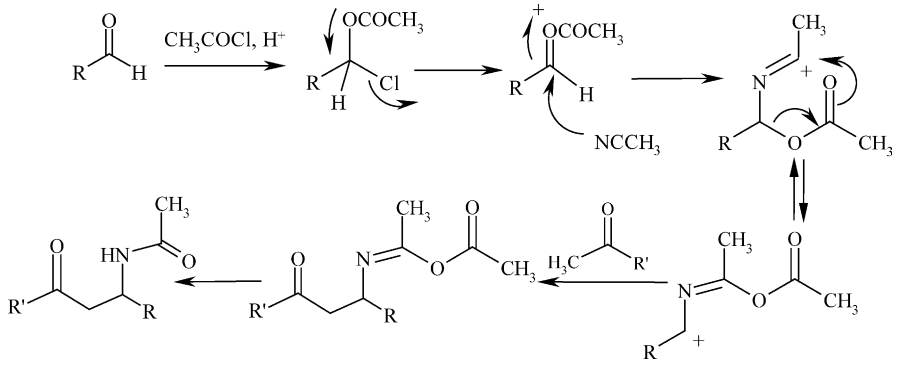
Entry	Ar/R	Ar′/R′	Product	Time (min)	Yield (%)[a]
1	C_6H_5	C_6H_5		60	90
2	4-ClC_6H_4	C_6H_5		40	95
3	4-$CH_3OC_6H_4$	C_6H_5		90	80
4	2-ClC_6H_4	C_6H_5		60	90
5	4-CNC_6H_4	C_6H_5		90	87
6	3-$NO_2C_6H_4$	C_6H_5		70	95
7	C_6H_5	4-NO_2C_6H		90	73
8	C_6H_5	4-BrC_6H_4		60	95
9	4-$CH_3C_6H_4$	4-$NO_2C_6H_4$		60	96
10	4-ClC_6H_4	4-BrC_6H4		70	95
11	4-ClC_6H_4	4-$NO_2C_6H_4$		60	90

Table 3 (*Continued*)

Entry	Ar/R	Ar′/R′	Product	Time (min)	Yield (%)[a]
12	4-ClC_6H_4	4-ClC_6H_4		70	94
13	4-$CH_3OC_6H_4$	4-$NO_2C_6H_4$		90	90
14	3-$NO_2C_6H_4$	4-$NO_2C_6H_4$		60	96
15	3-$NO_2C_6H_4$	4-BrC_6H_4		60	95
16	2-HOC_6H_4	C_6H_5		100	86
17	2-HOC_6H_4	4-$NO_2C_6H_4$		60	60
18	2-HOC_6H_4	4-BrC_6H_4		90	85
19	CH_3CH_2	C_6H_5		240	10
20	C_6H_5	CH_3		240	40
21	C_6H_5	$C_6H_{10}O$		240	40
22	C_6H_5	$C_6H_{10}O$		60	85[b]

[a] Isolated yield after purification characterised by ^1H NMR and IR spectroscopy [21].
[b] The reaction performed at reflux condition.



Scheme 1.

The reaction was extended to other aryl and alkyl aldehydes and ketones as substrate under the optimum conditions. As shown in Table 3, aromatic aldehydes or acetophenones both with electron withdrawing or donating substitution performed to afford the β-acetamido ketones without the formation of any side products, in excellent yields and in relatively short reaction times at room temperature. Interestingly, it was found that no acetylation of an aromatic hydroxyl group was observed when salicylaldehyde was used, and the corresponding β-acetamido ketones were isolated in an excellent yield (Table 3, entry 16–18). Aliphatic aldehyde and acyclic aliphatic ketone gave unsatisfactory results (Table 3, entry 19–21) but acyclic aliphatic ketone shows good results at reflux condition (Table 3, entry 22). Based on literature [15,17,18], the authors suggested a reaction mechanism that was shown in Scheme 1. The reaction in the absence of catalyst or acethyl chloride gave none of the desired products.

Due to the high porosity of the catalyst (Table 1), the deposited coke built 6–10 wt.% carbon during the reaction. After reaction, PW/SiO_2 can be recovered by filtering, washing with acetonitrile and then with acetone several times. However, the catalyst activity were gradually declined in successive runs (Table 2, entries 26–28), which indicates loss of catalyst activity probably due to the catalyst coking. But this loss was not very significant.

4. Conclusion

Silica-supported heteropoly acid, PW/SiO_2, is an active and solid acid catalyst for synthesis of β-acetamido ketones in heterogeneous systems. To the best of our knowledge, this is the first report on HPAs mediated for Dakin–West reactions. The present methodology offers several advantages, such as high yields, short reaction times, mild condition and recyclable catalyst with very easy work up.

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[21] Spectroscopic data of products:

β-acetamido-β-(phenyl)propiophenone (Table 3, entry 1): 1H NMR ($CDCl_3$, 200 MHz) δ 2.03 (s, 3H), 3.34 (dd, J = 6.6 and 9.7 Hz, 1H), 3.67 (dd, J = 6.6 and 9.7 Hz, 1H), 5.60 (m, 1H), 7.32 (s, 1H), 7.58 (d, J = 9.1 Hz, 5H), 7.76 (d, J = 9.1 Hz, 5H); IR (KBr, cm^{-1}) 3252, 3046, 1667, 1624, 1574, 1288, 1082, 878, 819;

β-acetamido-β-(4-chlorophenyl)propiophenone (Table 3, entry 2): M 144–146 °C; 1H NMR ($CDCl_3$, 200 MHz) δ 2.00 (s, 3H), 3.40 (dd, J = 6.9 and 9.9 Hz, 1H), 3.71 (dd, J = 6.9 and 9.9 Hz, 1H), 5.54 (m, 1H), 7.02 (m, 5H), 7.45 (m, 3H), 7.84 (d, J = 9.1 Hz, 2H); IR (KBr, cm^{-1}) 3270, 3082,1668, 1635, 1556, 1255, 1104, 887, 823, 687;

β-acetamido-β-(4-methoxyphenyl)propiophenone (Table 3, entry 3): 1H NMR ($CDCl_3$, 200 MHz) δ 2.09 (s, 3H), 2.47 (s, 3H), 3.51 (dd, J = 7.1 and 10.0 Hz, 1H), 3.84 (dd, J = 7.1 and 10.0 Hz, 1H), 5.58 (m,1H), 7.39 (s, 1H), 7.52 (m, 5H), 7.96 (m, 4H); IR (KBr, cm^{-1}) 3263, 3051, 1672, 1630, 1581, 1290, 1081. 878, 817;

β-acetamido-β-(2-chlorophenyl)propiophenone (Table 3, entry 4): M 149–151 °C; 1H NMR ($CDCl_3$, 200 MHz) δ 2.06 (s, 3H), 3.43 (dd, J = 7.1 and 10.0 Hz, 1H), 3.71 (dd, J = 7.1 and 10.0 Hz, 1H), 5.60 (m, 1H), 7.12 (m, 5H),7.52 (m, 3H), 7.90 (d, J = 9.3 Hz, 2H); IR (KBr, cm^{-1}) 3250, 3062,1660, 1640, 1563, 1261, 1109, 890, 833, 682;

β-acetamido-β-(4-cyanophenyl)propiophenone (Table 3, entry 5): M 85–88 °C; 1H NMR (200 MHz, $CDCl_3$) δ 1.92 (s, 3H), 3.34 (dd, J = 5.1 and 16.07 Hz, 1H), 3.62 (dd, J = 5.9 and 16.1 Hz, 1H), 5.65 (d, J = 7.03, 1H), 7.45 (m, 4H), 7.80 (m, 3H), 8.02 (s,1H); IR (KBr, cm^{-1}) 3294, 3035, 2250, 1690, 1650, 1541, 1439, 1225, 978, 752, 677, 548;

β-acetamido-β-(3-nitrophenyl)propiophenone (Table 3, entry 6): M 110–112 °C; 1H NMR (200 MHz, $CDCl_3$) δ 1.87 (s, 3H), 3.11 (d, J = 15.9 Hz, 1H), 3.52 (d, J = 12.1 Hz, 1H), 5.50 (s, 1H), 7.30 (m, 5H), 7.80 (d, J = 6.2 Hz, 2H), 8.00 (d, J = 6.2 Hz, 2H); IR (KBr, cm^{-1}) 3290, 3024, 2245, 1680, 1649, 1542, 1440, 1215, 987, 750, 680, 545;

β-acetamido-β-(phenyl)-4-nitropropiophenone (Table 3,entry 7): 1H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 3H), 3.32 (d, J = 13.8 Hz, 1H), 3.52 (d, J = 13.8 Hz, 1H), 5.70 (s, 1H), 7.32 (m, 4H), 7.88 (m, 3H), 8.08 (m, 2H); IR (KBr, cm^{-1}) 3260, 3027, 2270, 1676, 1637, 1557, 1397, 1222, 969, 817, 667, 556;

β-acetamido-β-(phenyl)-4-bromopropiophenone (Table 3, entry 8): M 98–100 °C; 1H NMR (200 MHz, $CDCl_3$) δ 2.1 (s, 3H), 3.40 (dd, J = 8.1 and 10.07 Hz, 1H), 3.81 (dd, J = 8.1 and 10.07 Hz, 1H), 5.6 (s, 1H), 6.8 (d, 1H), 7.2–7.5 (m, 5H), 7.6 (d, 2H), 7.8 (d, 2H); IR (KBr, cm^{-1}) 3296, 1690, 1685, 1644, 1545, 1395, 1372, 1070. 995, 816, 759, 705;

β-acetamido-β-(4-methylphenyl)-4-nitropropiophenone (Table 3, entry 9): 1H NMR (200 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.33 (s, 3H), 3.44 (d, J = 14.5 Hz, 1H), 3.73 (d, J = 14.5 Hz, 1H), 6.01 (s, 1H), 7.54 (m, 4H), 7.97 (m, 3H), 8.10 (m, 2H); IR (KBr, cm^{-1}) 3256, 3034, 2276, 1668, 1629, 1601, 1386, 1231, 974, 823, 674, 561;

β-acetamido-β-(4-chlorophenyl)-4-bromopropiophenone (Table 3, entry 10): 1H NMR (200 MHz, $CDCl_3$) δ 2.08 (s, 3H), 3.34 (dd, J = 7.1 and 10.1 Hz, 1H), 3.75 (dd, J = 7.1 and 10.1 Hz, 1H), 5.70 (m,1H), 7.36 (s, 1H), 7.65 (d, J = 9.1 Hz, 4H), 7.96 (d, J = 9.1 Hz, 4H); IR (KBr, cm^{-1}) 3263, 3053, 1680, 1632, 1585, 1293, 1085, 887, 827;

β-acetamido-β-(4-chlorophenyl)-4-nitropropiophenone (Table 3, entry 11): M 116–118 °C; 1H NMR (200 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.50 (dd, J = 6.8 and 9.9 Hz, 1H), 3.90 (dd, J = 6.8 and 9.9 Hz, 1H), 5.69 (s, 1H), 7.10 (s, 1H), 7.30–7.82 (m, 6H), 8.12 (m, 3H); IR (KBr, cm^{-1}) 3264, 1690, 1644, 1585, 1542, 1510, 1353, 1077, 1000, 820, 670, 573;

β-acetamido-β-(4-chlorophenyl)-4-chloropropiophenone (Table 3, entry 12): M 143–145 °C; 1H NMR ($CDCl_3$, 200 MHz) δ 2.11 (s, 3H), 3.45 (dd, J = 6.8 and 9.9 Hz, 1H), 3.84 (dd, J = 6.8 and 9.9 Hz, 1H), 5.61 (m, 1H), 7.42 (s, 1H), 7.54 (d, J = 8.9 Hz, 4H), 7.96 (d, J = 8.9 Hz, 4H); IR (KBr, cm^{-1}) 3259, 3048, 1671, 1627, 1578, 1289, 1080, 881, 820;

β-acetamido-β-(4-methoxyphenyl)-4-nitropropiophenone (Table 3, entry 13): 1H NMR (200 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.12 (s, 3H), 3.52 (d, J = 15.2 Hz, 1H), 3.77 (d, J = 15.2 Hz, 1H), 5.97 (s, 1H), 7.32 (m, 4H), 7.69 (m, 3H), 8.02 (m, 2H); IR (KBr, cm^{-1}) 3243, 3023, 2265, 1667, 1634, 1589, 1379, 1227, 969, 819, 676, 568;

β-acetamido-β-(4-methoxyphenyl)-4-nitropropiophenone (Table 3, entry 14): 1H NMR (200 MHz, $CDCl_3$) δ 2.02 (s, 3H), 3.43 (d, J = 13.1 Hz, 1H), 3.65 (d, J = 13.1 Hz, 1H), 5.86 (s, 1H), 7.32 (m, 4H), 7.69–7.89 (m, 5H); IR (KBr, cm^{-1}) 3236, 3030, 2273, 1675, 1620, 1556, 1358, 1347, 1286, 945, 830, 670, 557;

β-acetamido-β-(3-nitrophenyl)-4-bromopropiophenone (Table 3, entry 15): M 115–118 °C; 1H NMR ($CDCl_3$, 200 MHz) δ 2.13 (s, 3H), 3.50 (dd, J = 6.5 and 9.6 Hz, 1H), 3.85 (dd, J = 6.5 and 9.6 Hz, 1H), 5.70 (m, 1H), 7.24 (s, 1H), 7.54–7.87 (m, 4H), 7.96 (m, 4H); IR (KBr, cm^{-1}) 3264, 3035, 1690, 1637, 1585, 1510, 1353, 1285, 1077, 998, 824, 658, 576;

β-acetamido-β-(2-hydroxyphenyl)propiophenone (Table 3, entry 16): M 130–132 °C; 1H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 3H), 3.49 (d, J = 7.2 Hz, 1H), 3.68 (d, J = 7.1 Hz, 1H), 6.87 (s, 1H), 7.50–7.72 (m, 5H), 7.95 (d, J = 5.9 Hz, 2H), 8.23 (d, J = 5.2 Hz, 2H); IR (KBr, cm^{-1}) 3286, 2845, 1679, 1638, 1595, 1501, 1446, 1341, 1289, 851, 747, 681, 588;

β-acetamido-β-(2-hydroxyphenyl)-4-nitropropiophenone (Table 3, entry 17): 1H NMR (200 MHz, $CDCl_3$) δ 2.01 (s, 3H), 3.38 (d, J = 7.1 Hz, 1H), 3.65 (d, J = 7.1 Hz, 1H), 5.98 (s, 1H), 6.79 (s, 1H), 7.44–7.69 (m, 4H), 7.95–8.25 (m, 5H); IR (KBr, cm^{-1}) 3275, 3025, 2843, 1665, 1634, 1595, 1536, 1511, 1341, 1275, 847, 739, 677, 580;

β-acetamido-β-(2-hydroxyphenyl)-4-bromopropiophenone (Table 3, entry 18): 1H NMR (200 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.33 (d, J = 7.3 Hz, 1H), 3.68 (d, J = 7.3 Hz, 1H), 5.38 (s, 1H), 6.68 (s,1H), 7.34–7.80 (m, 5H), 8.02–8.26 (m, 4H); IR (KBr, cm^{-1}) 3250, 3026, 2855, 1658, 1629, 1577, 1515, 1459, 1350, 1278, 860, 745, 679, 593;

β-acetamidopentaniophenone (Table 3, entry 19): 1H NMR ($CDCl_3$, 200 MHz) δ 1.11 (t, J = 10.1, 3H), 1.55 (m, 2H), 2.00 (s, 3H), 3.21 (dd, J = 5.9 and 9.5 Hz, 1H), 3.60 (dd, J = 5.9 and 9.5 Hz, 1H), 5.51 (m, 1H), 7.29 (s, 1H), 7.62–7.70 (m, 5H); IR (KBr, cm^{-1}) 3246, 3030, 2868, 1659, 1631, 1275, 1077, 884, 827;

N-[3-oxo-1-phenylbutyl]acetamide (Table 3, entry 20): 1H NMR ($CDCl_3$, 200 MHz) δ 1.18 (s, 3H), 2.04 (s, 3H), 3.11 (dd, J = 5.8 and 9.0 Hz, 1H), 4.13 (dd, J = 5.8 and 9.0 Hz, 1H), 5.16 (m, 1H), 7.12 (s, 1H), 7.32–7.44 (m, 5H); IR (KBr, cm^{-1}) 3290, 1710, 1652, 1554, 1370, 1308, 1129, 878, 758, 704;

N-{1-phenyl-1-[2-oxocyclohexyl]}acetamide (Table 3, entry 21 or 22): 1H NMR ($CDCl_3$, 200 MHz) δ 1.80 (s, 3H), 2.22–2.24 (m, 8H), 5.49 (s, 1H), 7.12 (s, 1H), 7.60–7.74 (m, 3H), 8.25–8.32 (m, 2H); IR (KBr, cm^{-1}) 3384, 2932, 1650, 1602, 1524, 1227, 858, 758, 694.