



## Amberlyst-15<sup>®</sup> in ionic liquid: an efficient and recyclable reagent for the benzylation and hydroalkylation of $\beta$ -dicarbonyl compounds

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### ABSTRACT

Benylation and hydroalkylation of 1,3-dicarbonyl compounds using Amberlyst-15 immobilized in ionic liquid [Bmim][PF<sub>6</sub>] as an efficient reusable reagent was studied. The reagent was compared with other solid acid reagents along with role of the ionic liquid. The effect of various reaction parameters like type of reagent, solvent, substrate molar ratio, reaction time, and temperature were studied. Present protocol is advantageous due to the ease in handling of reagent, simple work-up procedure, economical and environmentally benign process. The products were obtained in good to excellent yield and applicable to wide variety of substrates.

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The alkylation of  $\beta$ -dicarbonyl compounds represents one of the most important C–C bond formation methodology in organic synthesis.<sup>1</sup> Addition of  $\beta$ -dicarbonyl compounds to olefins results in a highly atom efficient protocol.<sup>2</sup> In general, these transformations were performed by the reaction of alcohols<sup>3</sup> or alkyl halides<sup>4</sup> with  $\beta$ -dicarbonyl compounds. In case of alcohols, hydroxy group is a poor leaving group which necessitates its preactivation and which can be achieved using high temperature or by suitable promoter.<sup>5</sup> This leads to the formation of stoichiometric amount of salt-waste. The substitution with halides also requires a stoichiometric amount of base which limits its application for the larger scale. Recently, many acid catalysts were employed to perform nucleophilic substitution of benzyl alcohols with active methylene compounds,<sup>6</sup> whereas, the alkylation of  $\beta$ -dicarbonyl compounds with alkenes was also explored with different types of acid catalysts.<sup>7</sup>

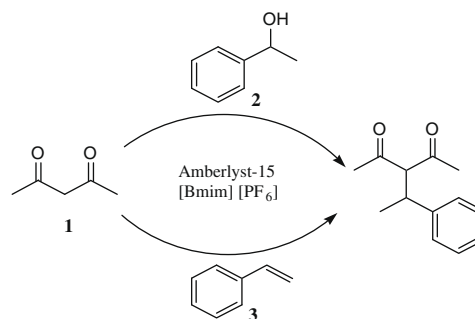
There has been an increasing interest in exploiting the potential of ionic liquids as a reaction media to develop green methodologies; allowing reuse of the catalysts or reagents.<sup>8</sup> Features that make ionic liquids attractive include lack of vapor pressure and the great versatility of their chemical and physical properties. Using a judicious combination of cations and anions, it is possible to tune the solvent properties as per the requirement of the reaction and thus creating an almost indefinite set of 'designer solvents'. Besides the possibility of recycling the catalytic system, potential interest in using ionic liquids result in the unique interactions of these media with the active species and in the possibility to modify the reaction activity and selectivity.<sup>9</sup> Their successful use as solvents has been demonstrated for a wide range of organic reactions including acid-catalyzed reactions and transition metals

catalyzed transformations.<sup>8,10</sup> This prompted us to initiate a systematic exploration on benzylation and hydroalkylation of  $\beta$ -dicarbonyl compounds with the help of ionic liquids (Scheme 1).

In continuation of our research on application of ionic liquids in several organic transformations,<sup>11</sup> we herein report the benzylation and hydroalkylation of  $\beta$ -dicarbonyl compounds by Amberlyst-15 in ionic liquid [Bmim][PF<sub>6</sub>].

The reagent Amberlyst-15 and solvent [Bmim][PF<sub>6</sub>] are air-stable and applicable to the wide range of substrates.

Initially, the coupling reaction of acetylacetone **1** with 1-phenylethanol **2** in the presence [Bmim][PF<sub>6</sub>] as a solvent was chosen as a model reaction<sup>13</sup> (Table 1). Various solid acid reagents such as Amberlite-IR 120, Amberlyst-15, Indion-225H, Montmorillonite K-10, Al<sub>2</sub>O<sub>3</sub> were screened (Table 1, entries 1–5). Amberlyst-15 was found to be most effective reagent providing 66% yield of the desired product (Table 1, entry 5) under screening conditions. The probable reason for its higher activity can be explained on the



Scheme 1. Benzylation and hydroalkylation of  $\beta$ -dicarbonyl compounds.

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**Table 1**  
Effect of different catalyst on the addition of acetylacetone (**1**) to 1-phenylethanol (**2**)<sup>a</sup>

Entry	Reagent	H <sup>+</sup> capacity	Surface area (m <sup>2</sup> /g)	Particle size (mesh)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	Amberlite-IR 120	4.4 mequiv/g	45	16–50	96	61
2	Indion-225H	1.8 mequiv/mL	–	14–52	97	36
3	Montmorillonite K-10	3–4 mequiv/g	220	<200	96	27
4	Al <sub>2</sub> O <sub>3</sub>	4.5 mequiv/g	200	150–300	44	–
5	Amberlyst-15	4.2 mequiv/g	42	20–50	97	66

<sup>a</sup> Reaction conditions: Catalyst (0.32 g), [Bmim][PF<sub>6</sub>] (2 mL), reaction temperature 80 °C.<sup>b</sup> The conversion was determined by GC with respect to 1-phenyl ethanol.<sup>c</sup> The yield was determined by GC, Reaction time 2 h.

basis of the physical properties like high H<sup>+</sup> exchange capacity (4.2 meq/g) and high surface area (42 m<sup>2</sup>/g).

The influence of various parameters like solvent, substrates molar ratio, reaction temperature, and time were examined (Table 2). The influence of solvents on the coupling reaction of acetylacetone with 1-phenylethanol using Amberlyst-15 as a reagent of choice was studied (Table 2, entries 1–8). The reaction was more favorable in ionic liquids such as [Bmim][PF<sub>6</sub>] and [Bmim][BF<sub>4</sub>] as compared to conventional organic solvents, as the dimerization of 1-phenylethanol to 1,3-diphenylbut-1-ene is observed as major side product. Since better results were obtained in [Bmim][PF<sub>6</sub>], it was used for further studies. Substrate ratio of 1:4 (**2:1**) is found to be best for this transformation (Table 2, entry 10) in order to get **4** as single major product (84% yield) indicating the effect of solvent and the Amberlyst-15 reagent. The self condensation of 1-phenylethanol to give symmetrical ether **5** is one of the side reactions observed. Further, the reaction was carried out at different temperatures (80, 60 °C, and rt) (Table 2, entries 10–12). It was observed that as the temperature decreased from 80 °C to rt the yield of the desired product **4** also decreased. Increase in the reaction time did not offer any significant advantages (Table 2, entry 13). Hence the optimum reaction parameters were reagent: Amberlyst-15, solvent: [Bmim][PF<sub>6</sub>], Substrate ratio of **2:1**: 1:4, temperature: 80 °C, and time: 2 h.

The optimized reaction conditions were used for the coupling reaction of various substituted alcohols with substrates containing active methylene group. This gives moderate to good yields of desired products (Table 3, entries 1–14). The reaction of acetylacetone **1a** with different types of benzyl alcohols **2a–c** proceeded smoothly providing 63–90% yield of the desired products (Table

3, entries 1–3). Benzoylacetone **1b** also undergoes benzylation **2a–b**, which gives a mixture of diastereomers (1.2:0.8) in good yield (Table 3, entries 4 and 5). It was observed that bulky β-diketone **1c** also gives 81% yield of the expected product (Table 3, entry 6). Electron rich *para*-methoxy benzyl alcohol **2d** undergoes smooth conversion to the desired product with excellent yield (Table 3, entry 7). The present protocol works well for the benzylation **2b** of aliphatic, cyclic and aromatic β-ketoesters **1d–g** (Table 3, entries 8–11), as selectively alkylated products are obtained instead of transesterification. Diethyl malonate does not undergo benzylation, which might be due to the inability of diethyl malonate for enolization during the reaction (Table 3, entry 12). Acetyl acetone **1a** also undergoes allylation with **2e** to furnish the allylated product in 81% (Table 3, entry 13). It is observed that aliphatic alcohol **2f** is not favorable for the alkylation with acetyl acetone **1a** (Table 3, entry 14).

The optimized reaction parameters were extended for a comparative study of 1,3-dicarbonyl compounds with styrene and its derivatives (Table 4). In general we observed that yield of the desired product was lower than the reaction with the subsequent alcohols, which might be due to dimerization of styrene during the reaction.

We explored the scope of the Amberlyst-15 reagent for hydroalkylation by varying styrene and its derivatives as well as 1,3-dicarbonyl compounds in [Bmim][PF<sub>6</sub>] (Table 4). Styrene **3a** was effectively added to acetylacetone **1a** to give the corresponding product **6a** in 79% (Table 4, entry 1), but 1,3-diphenylbut-1-ene **7** was also formed as side product. Various electron-donating and electron-withdrawing groups such as –CH<sub>3</sub>, *t*-butyl, F, Cl, Br on styrene **3b–e** underwent hydroalkylation with smooth conversion to give the desired products **6b–e** in good yields (Table 4, entries 2–6). Hindered 4-*tert*-butyl styrene **3f** smoothly undergoes hydroalkylation with acetylacetone **1a** giving 87% of the expected product **6f** (Table 4, entry 6). When  $\alpha$ -methyl styrene was reacted with acetylacetone, it was observed that instead of expected product **6f**,  $\alpha$ -methyl styrene under acidic conditions, itself undergoes dimerization to form 4-methyl-2,4-diphenyl-2-pentene and 4-methyl-2,4-diphenyl-1-pentene in 69% yield (1:1) (Table 4 entry 7). Previously Shirakawa and co-workers have successfully demonstrated a palladium catalyzed dimerization of vinylarenes using Indium triflate as a co-catalyst.<sup>12</sup> Similarly, **1b** undergoes hydroalkylation with styrene and gave a mixture of diastereomers **6h** in 81% (Table 4, entry 8). The reaction of styrene and its derivatives with bulky β-dicarbonyl compounds proceeded efficiently giving moderate to good yields (Table 4, entries 9–11).

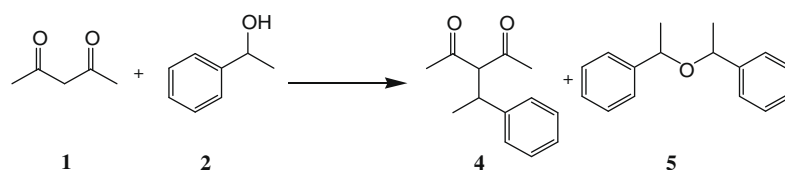
A recyclability study of present protocol was also studied. Reaction of 1-phenyl ethanol and acetylacetone with Amberlyst-15-ionic liquid reagent was recycled up to three cycles (83%, 85%, 82%). There was no significant decrease during the first cycle whereas the yield declined up to 82% after the completion of the third cycle. Thus the Amberlyst-15-ionic liquid system can be successfully recycled and the reusability procedure was tested up to three times and consistent results were obtained.

**Table 2**  
Effect of reaction parameters on the addition of acetylacetone (**1**) to 1-phenylethanol (**2**)<sup>a</sup>

Entry	Molar ratio <b>2:1</b>	Solvent	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	1:1	[Bmim][PF <sub>6</sub> ]	97	66
2	1:1	Toluene	100	16
3	1:1	CH <sub>2</sub> Cl <sub>2</sub>	15	Trace
4	1:1	CH <sub>3</sub> CN	21	10
5	1:1	THF	30	–
6	1:1	CH <sub>3</sub> NO <sub>2</sub>	83	49
7	1:1	[Bmim][BF <sub>4</sub> ]	97	55
8	1:1	Neat	100	35
9	1:2	[Bmim][PF <sub>6</sub> ]	96	70
10	1:4	[Bmim][PF <sub>6</sub> ]	97	84
11 <sup>d</sup>	1:4	[Bmim][PF <sub>6</sub> ]	97	76
12 <sup>e</sup>	1:4	[Bmim][PF <sub>6</sub> ]	94	53
13 <sup>f</sup>	1:4	[Bmim][PF <sub>6</sub> ]	96	85

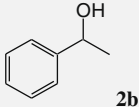
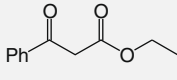
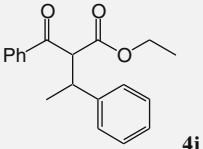
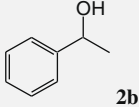
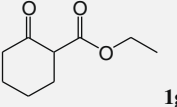
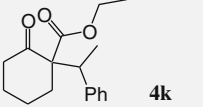
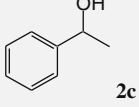
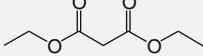
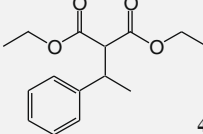
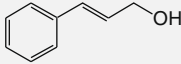
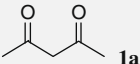
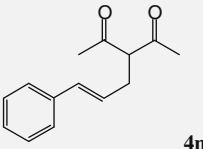
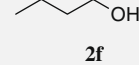
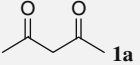
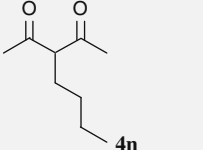
<sup>a</sup> Reaction conditions: Amberlyst-15 (0.32 g), solvent (2 mL), reaction temperature 80 °C.<sup>b</sup> The conversion was determined by GC with respect to 1-phenylethanol.<sup>c</sup> The yield was determined by GC, Reaction time 2 h.<sup>d</sup> Reaction at 60 °C for 5 h.<sup>e</sup> Reaction at room temperature for 5 h.<sup>f</sup> Reaction at 80 °C for 4 h.

**Table 3**  
Amberlyst-15 reagent for the addition of  $\beta$ -dicarbonyl compounds with benzylic alcohols<sup>a</sup>



Entry	Alcohol (2)	Nucleophile (1)	Time (h)	Product	Yield <sup>b,(Ref.)</sup> (%)
1			3		63 <sup>6f</sup>
2			2		84 <sup>6f</sup>
3			3		90 <sup>4</sup>
4 <sup>c</sup>			5		65 <sup>6f</sup>
5 <sup>c</sup>			5		88 <sup>6f</sup>
6			6		81 <sup>6f</sup>
7			3.5		91 <sup>4</sup>
8 <sup>c</sup>			5		77 <sup>4</sup>
9 <sup>c</sup>			5		85 <sup>4</sup>

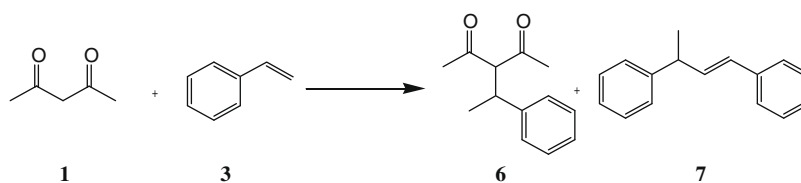
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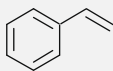
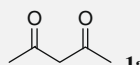
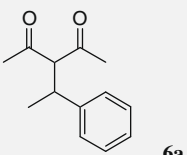
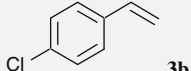
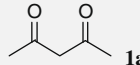
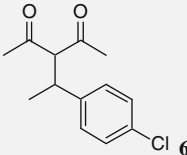
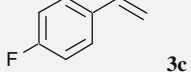
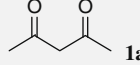
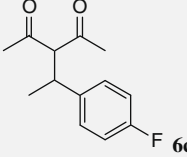
Entry	Alcohol (2)	Nucleophile (1)	Time (h)	Product	Yield <sup>b,(Ref.)</sup> (%)
10 <sup>c</sup>	 <b>2b</b>	 <b>1f</b>	6	 <b>4j</b>	60 <sup>4</sup>
11 <sup>c</sup>	 <b>2b</b>	 <b>1g</b>	6	 <b>4k</b>	86 <sup>6e</sup>
12	 <b>2c</b>	 <b>1h</b>	6	 <b>4l</b>	—
13	 <b>2e</b>	 <b>1a</b>	5	 <b>4m</b>	81 <sup>6f</sup>
14	 <b>2f</b>	 <b>1a</b>	5	 <b>4n</b>	—

See Ref. 13 for experimental procedure.

<sup>a</sup> Reaction conditions: alcohol **2** (1 mmol), 1,3-dicarbonyl compounds **1** (4 equiv), Amberlyst-15 (0.32 g), [Bmim][PF<sub>6</sub>] (2 mL) at 80 °C.<sup>b</sup> Isolated yield.<sup>c</sup> Mixture of diastereomers (1.2:0.8).

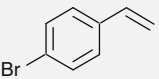
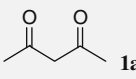
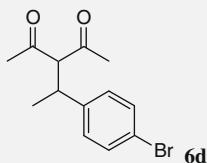
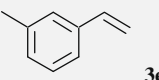
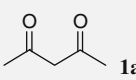
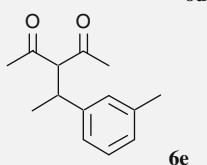
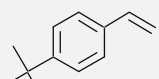
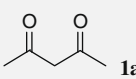
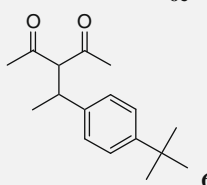
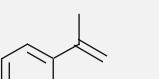
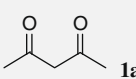
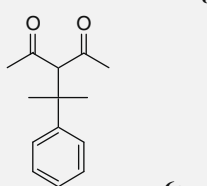
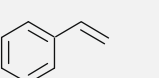
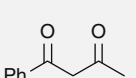
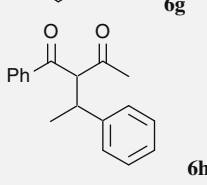
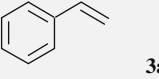
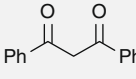
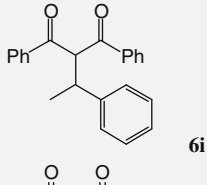
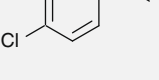
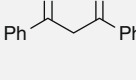
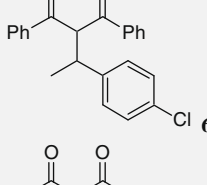
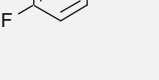
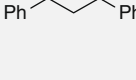
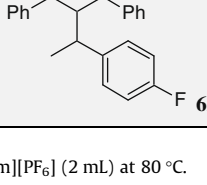
Table 4

Amberlyst-15 reagent for the addition of β-dicarbonyl compounds with alkenes<sup>a</sup>

Entry	Alkene (3)	Nucleophile (1)	Time (h)	Product	Yield <sup>b,(Ref.)</sup> (%)
1	 <b>3a</b>	 <b>1a</b>	5	 <b>6a</b>	79 <sup>7d</sup>
2	 <b>3b</b>	 <b>1a</b>	5	 <b>6b</b>	77 <sup>7d</sup>
3	 <b>3c</b>	 <b>1a</b>	5	 <b>6c</b>	81 <sup>6g</sup>

(continued on next page)

Table 4 (continued)

Entry	Alkene ( <b>3</b> )	Nucleophile ( <b>1</b> )	Time (h)	Product	Yield <sup>b,(Ref.)</sup> (%)
4	 <b>3d</b>	 <b>1a</b>	5	 <b>6d</b>	72 <sup>7d</sup>
5	 <b>3e</b>	 <b>1a</b>	5	 <b>6e</b>	77 <sup>7d</sup>
6	 <b>3f</b>	 <b>1a</b>	5	 <b>6f</b>	87
7	 <b>3g</b>	 <b>1a</b>	5	 <b>6g</b>	—
8 <sup>c</sup>	 <b>3a</b>	 <b>1b</b>	6	 <b>6h</b>	81 <sup>6g</sup>
9	 <b>3a</b>	 <b>1c</b>	6	 <b>6i</b>	65 <sup>7d</sup>
10	 <b>3b</b>	 <b>1c</b>	6	 <b>6j</b>	61 <sup>7d</sup>
11	 <b>3c</b>	 <b>1c</b>	6	 <b>6k</b>	55 <sup>6g</sup>

See Ref. 13 for experimental procedure.

<sup>a</sup> Reaction conditions: styrene **3** (1 mmol), 1,3-dicarbonyl compounds **1** (3 equiv), Amberlyst-15 (0.32 g), [Bmim][PF<sub>6</sub>] (2 mL) at 80 °C.

<sup>b</sup> Isolated yield.

<sup>c</sup> Mixture of diastereomers (1.2:0.8).

In conclusion, we have demonstrated an efficient methodology for both benzylation and hydroalkylation with 1,3-dicarbonyl compounds using Amberlyst-15 as reagent in [Bmim][PF<sub>6</sub>] ionic liquid. The reaction was optimized with respect to various parameters and enabled coupling reactions of various electron rich, electron deficient and sterically hindered alcohols and alkenes with different 1,3-dicarbonyl compounds affording excellent yield of the desired products. The reaction system employs use of ionic liquids as green-

er solvent, simple of operation, mild reaction conditions, and reusability of system.

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## References and notes

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- General procedure:** To a well-stirred mixture of Amberlyst-15 (0.32 g) in [Bmim][PF<sub>6</sub>] (2 mL), nucleophile **1a–h** (4 equiv) an alcohol **2a–e** or styrene **3a–g** was added. The reaction mixture was stirred at 80 °C and the completion of the reaction was monitored by GC/TLC. The products were confirmed by NMR (Mercury Plus 300 MHz spectrometer), GC–MS (Shimadzu GC–MS QP 2010), IR Perkin–Elmer FT-IR, and also using authentic samples. After completion, 5 mL of di-iso propyl ether was added and vigorously shaken to extract all the reactants and products in the ether phase. The extraction procedure was repeated for about 3–4 times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated in vacuo. The residue obtained was purified using column chromatography (silica gel, mesh size 60–120) using pet ether/ethyl acetate (90:10) as eluent to afford the pure products. After extraction the reactor containing the recovered Amberlyst-15 in ionic liquid was dried in vacuo for an hour and then charged with alcohol and nucleophile again.  
Physical and spectral data of selected compounds: **3-(1-Phenyl-ethyl)-pentane-2,4-dione (4b)**: White solid, mp: 42–44 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  2926, 1727, 1678, 1452, 1360, 1148, 759, 701; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)  $\delta$  = 1.20 (d, 3H, *J* = 6.9 Hz), 1.83 (s, 3 H), 2.27 (s, 3H), 3.54–3.64 (m, 1H), 4.02 (d, 1H, *J* = 11.3 Hz), 7.17–7.32 (m, 5H); <sup>13</sup>C NMR (75.43 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20.76, 29.64, 29.72, 40.34, 76.53, 126.89, 127.20, 128.73, 142.99, 203.29, 203.34 ppm; (EI) *m/z* (%) 204 (M<sup>+</sup>, 1), 186 (10), 161 (100), 147 (33), 143 (14), 105 (33), 43 (26).  
**1-Phenyl-2-(1-phenyl-ethyl)-butane-1,3-dione (4e)**: Mixture of diastereomers, colorless oil, IR (neat)  $\nu_{\max}/\text{cm}^{-1}$  2926, 2854, 1727, 1678, 1454, 762, 699; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)  $\delta$  = 1.22 (d, 3H, *J* = 6.6 Hz), 1.32 (d, 3H, *J* = 7.3 Hz), 1.90 (s, 3H), 2.24 (s, 3H), 3.81–3.92 (m, 2H), 4.87 (d, 1H, *J* = 10.9 Hz), 4.91 (d, 1H, *J* = 10.9 Hz), 7.01–7.07 (m, 1H), 7.08–7.25 (m, 6H), 7.28–7.34 (m, 6H), 7.37–7.52 (m, 2H), 7.58–7.60 (m, 1H), 7.77–7.80 (m, 2H), 8.07–8.10 (m, 2H); <sup>13</sup>C NMR (75.43 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 21.67, 22.77, 27.94, 29.78, 40.42, 41.01, 70.95, 71.59, 126.7, 127.08, 127.43, 127.57, 128.53, 128.66, 128.89, 128.95, 133.5, 133.9, 137.26, 143.22, 195.27, 203.3 ppm; (EI) *m/z* (%) 266 (M<sup>+</sup>, 1), 223 (100), 161 (28), 105 (83).  
**3-Oxo-2-(1-phenyl-ethyl)-butyric acid methyl ester (4h)**: Mixture of diastereomers, colorless oil, IR (neat)  $\nu_{\max}/\text{cm}^{-1}$  2955, 1748, 1715, 1494, 1454, 1434, 1275, 1206, 1163, 765, 701; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)  $\delta$  = 1.24 (d, 3H, *J* = 6.9 Hz), 1.30 (d, 3H, *J* = 6.95 Hz), 1.88 (s, 3H), 2.25 (s, 3H), 3.35 (s, 1H), 3.52–3.57 (m, 1H), 3.52–3.57 (m, 1H), 3.69 (s, 1H), 3.76 (d, 1H, *J* = 10.63 Hz), 3.81 (d, 1H, *J* = 10.63 Hz), 7.51–7.27 (m, 5H), 7.51–7.27 (m, 5H); <sup>13</sup>C NMR (75.43 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 19.72, 20.22, 29.24, 29.56, 39.36, 39.47, 51.67, 52.01, 66.25, 66.88, 126.48, 126.59, 126.99, 127.04, 128.13, 128.35, 142.68, 142.97, 168.21, 168.63, 201.74, 201.74 ppm; (EI) *m/z* (%) 220 (M<sup>+</sup>, 1), 202 (100), 177 (41), 77 (145), 131 (33), 105 (82), 43 (23).  
**3-[1-(4-tert-Butyl-phenyl)-ethyl]-pentane-2,4-dione (6f)**: White solid, mp: 45–47 °C, IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  2962, 1696, 1511, 1356, 1260, 1189, 972, 827, 702, 578; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)  $\delta$  = 1.18 (d, 3H, *J* = 6.59 Hz), 1.28 (s, 9H), 1.83 (s, 3H), 2.26 (s, 3H), 3.54–3.6 (m, 1H), 4.01–4.05 (d, 1H, *J* = 11.36 Hz), 7.09–7.11 (d, 2H, *J* = 8.43 Hz), 7.28–7.31 (d, 2H, *J* = 8.43 Hz); <sup>13</sup>C NMR (75.43 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20.92, 29.75, 29.8, 31.33, 34.41, 39.99, 40.45, 76.67, 76.75, 77.1, 77.52, 125.66, 126.87, 127.28, 128.83, 139.84, 149.75, 203.67, 203.77 ppm; (EI) *m/z* (%) 260 (M<sup>+</sup>, 1), 242 (15), 217 (85), 161 (100), 143 (94), 131 (30), 127 (11), 99 (33), 77 (5), 43 (99); Ms–Ms (ESI<sup>+</sup>) *m/z* calcd for (M<sup>+</sup> Na<sup>+</sup>) 283.18; found: 283.20.  
**2-[1-(4-Chloro-phenyl)-ethyl]-1,3-diphenyl-propane-1,3-dione (6j)**: White solid, mp: 110–111 °C, IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  2926, 2853, 1697, 1665, 1596, 1492, 1448, 1260, 1193, 1094, 1014, 932, 797, 688; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)  $\delta$  = 1.30 (d, 3H, *J* = 6.96 Hz), 4.04 (dq, 1H, *J* = 10.26 Hz, 6.96 Hz), 5.58 (d, 1H, *J* = 10.26 Hz), 7.13–7.58 (m, 10H), 7.69–7.77 (m, 2H), 7.96–8.06 (m, 2H); <sup>13</sup>C NMR (75.43 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 20.25, 40.57, 64.56, 128.48, 128.56, 128.8, 129.13, 132.23, 133.26, 133.69, 136.67, 136.96, 142.37, 194.36, 194.69 ppm; (EI) *m/z* (%) 362 (M<sup>+</sup>, 1), 257 (100), 223 (3), 179 (3), 139 (8), 105 (75), 77 (49).