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Formation of 1,4-diketones via bis-acylation of the conjugated carbon–carbon double bonds in acrylates, acrylamides, methyl vinyl ketone and styrenes with aroyl chlorides promoted by samarium metal in DMF

Yongjun Liu[a] and Yongmin Zhang[a,b,*]

[a]*Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028, People's Republic of China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

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Abstract—Promoted by samarium in DMF, aroyl chlorides react readily with conjugated carbon–carbon double bonds in acrylates, acrylamides, methyl vinyl ketone and styrenes in a bis-acylation manner. These reactions proceed smoothly under mild conditions without the need of pretreating or activating the metallic samarium, affording the corresponding 1,4-diketones in good to excellent yields.

1. Introduction

Organic reactions that involve the addition to carbon–carbon double bond provide one of the most useful methodologies for the synthesis of multi-functionalized intermediates and products. Recently, a few notable examples of addition reactions to conjugated carbon–carbon double bonds which are different from the general 1,4-addition have appeared.[1] In the presence of a chiral diamine, the *cis*-dihydroxylation reaction of carbon–carbon double bonds was realized by enantioface differentiable bis-addition with osmium tetroxide.[1a] Bakers' yeast-catalyzed enantioselective reductions of activated carbon–carbon double bonds were applied in the synthesis of some chiral natural products.[1b] Under specific conditions, a carbon–carbon double bond in homoallylic alcohol disilanyl ethers could undergo an intramolecular bis-silylation to afford (−)-avenaciolide in a highly diastereoselective manner.[1c] Various substituted carbon–carbon double bonds were hydrogenated with catalysis of the palladium/sepiolite system, either using gaseous hydrogen or cyclohexane as the hydrogen donor.[1d] In addition, addition reactions to the C=C group are well documented by several books and reviews.[1e–g]

As a powerful, versatile, and ether-soluble one-electron transfer reducing agent, samarium diiodide (SmI_2) has played an ever-increasing role in organic synthesis since its introduction by Kagan's group.[2] Though SmI_2 is a useful reductive reagent, its application in organic synthesis is limited in some extent. For example, Sm^{2+} only gives one electron in the reaction, which seriously restricts its application in large scale.

However, metallic samarium is stable in air, and its strong reducing power ($Sm^{3+}/Sm=-2.41$ V) is comparable with that of magnesium ($Mg^{2+}/Mg=-2.37$ V), and superior to that of zinc ($Zn^{2+}/Zn=-0.71$ V). Therefore, the direct use of metallic samarium as a reducing agent in organic transformations has attracted considerable attention in recent years.[3] In most cases, reactions promoted by samarium are usually carried out in THF,[4] and metallic samarium has to be activated or pretreated by various methods so as to ensure smooth reactions. Generally, metallic samarium is activated by reagents such as iodine, hydrochloric acid, and alkyl halides.[4,5] Alkyl iodides are reduced to alkanes by Sm in THF.[4a] Iodomethylation of carbonyl compounds can be achieved by treatment with Sm and CH_2I_2 in THF.[4c] Sm with a catalytic amount of I_2 in THF is used in the reductive coupling reactions of *N*-alkylideneanilines, giving vicinal diamines.[4d] Deoxygenative coupling of benzamides to 1,2-diaminostilbenes can be carried out with Sm and a catalytic amount of SmI_2 in THF.[4e] A trace amount of water was found to accelerate the pinacolic coupling of aromatic carbonyl compounds mediated by Sm/Me_3SiCl in THF.[5a] Reductions of nitrobenzene,[5b]

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* Corresponding author. Fax: +86-571-88807077; e-mail: yminzhang@mail.hz.zj.cn

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1,2-dibromoalkanes,[5c,d] benzoic acid derivatives,[5e] and pyridines[5f] have been realized by using Sm/I_2 or Sm/$HCl_{(aq.)}$ in MeOH. Pinacolic coupling reactions of aromatic ketones have been achieved by using Sm in MeOH with alkyl halides as an activator without the formation of Barbier-type addition products.[5g] The reduction coupling of ketones or aldehydes in Sm/$HCl_{(aq.)}$/THF has also been studied.[5h] However, up till now, few reports have appeared in the literature using metallic samarium without any activator or pretreatment.[6] In our investigation, on the direct use of samarium metal in organic synthesis, we found that when *N*,*N*-dimethylformamide (DMF) was used as a solvent instead of THF, metallic samarium exhibited unusual reactivity. Described herein are our findings.

2. Results and discussion

1,4-Dicarbonyl compounds constitute key intermediates in various natural product syntheses, and are important synthetic precursors of cyclopentenones, cyclopenta-1,3-diones, butenolides, and derivatives of furan and pyrrole.[7] A number of methods for their synthesis have been developed.[8] In particular, the syntheses of tricarbonyl compounds of the type 2-alkoxycarbonyl 1,4-diketones have rarely been reported, and only a few methods are available which required unusual substrates and relatively harsh reaction conditions.[9] Here, we wish to report a facile and efficient synthesis of 1,4-dicarbonyl compounds using a new strategy which involves the bis-acylation of conjugated carbon–carbon bonds with aroyl chlorides in the presence of samarium metal in DMF without any pretreatment or activation

2.1. Sm-promoted bis-acylation of the carbon–carbon double bond addition of acrylates with aroyl chlorides in DMF

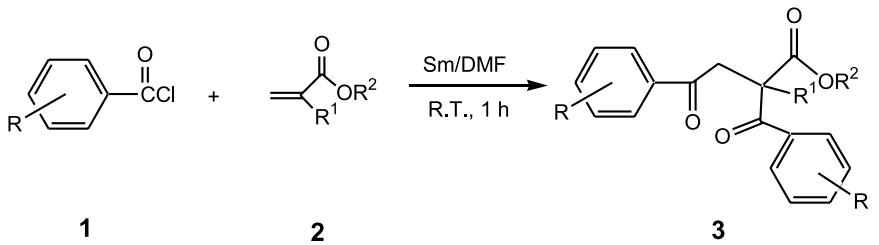
When *N*,*N*-dimethylformamide (DMF) is used as a solvent instead of THF, metallic samarium, without the need to be activated or pretreated, can promote the reactions of acrylates **2** with aroyl chlorides **1**, affording a new strategy for the synthesis of tricarbonyl compounds 2-alkoxycarbonyl 1,4-diketones **3** (Scheme 1).

A variety of 2-alkoxycarbonyl 1,4-diketones **3** were obtained in good to excellent yields in Sm/DMF system, as shown in Table 1. Notably, when α-substituted acrylate was used as substrate (for example, methyl α-methylacrylate, **2c**), the reaction still afforded compounds **3c**, **3f**, **3i**, **3l** and **3m** in good yields. However, the reaction is strongly influenced by the substituent on the β-position of the acrylate, and attempts to extend this reaction to methyl cinnamate (**2f**), ethyl crotonate (**2g**) and methyl β-dimethylacrylate (**2h**) were not successful. Substrate **2e** is an exception, which could react with 4-fluorobenzoyl chloride to afford product **3n** in 46% yield. This may be attributed to the activation of the carbon–carbon double bond in **2e** by two ester groups.

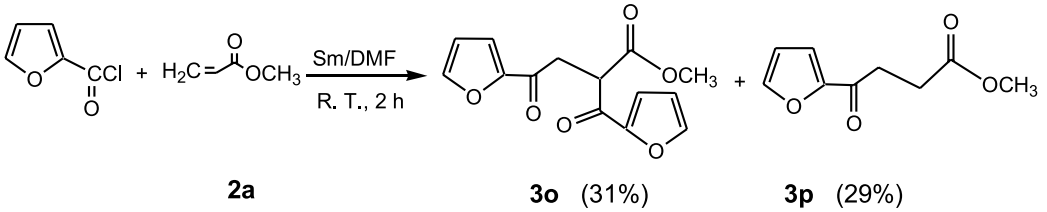
Interestingly, carbon–carbon double bond addition product **3o** and the 1,4-addition product **3p** were obtained with an approximate ratio of 1:1 when 2-furoyl chloride was used as the acylating substrate (Scheme 2). However, when aliphatic acid chlorides (such as phenylacetyl chloride, lauroyl chloride and acetyl chloride) were used instead of aroyl chlorides, the reaction did not occur at all. The temperature also influences the reaction remarkably. Hardly any reaction was observed in such reaction systems after 2 h when the reaction temperature was below −10°C, and, on the other hand, the self-coupling by-products of aroyl chloride noticeably increased when the reaction temperature exceeded 40°C. Generally, according to the results of the experiment, the ideal temperature for this reaction was 15–25°C.

2.2. Sm-promoted bis-acylation of *N*,*N*-dimethylacylamide, methyl vinyl ketone with aroyl chlorides

With the successful bis-acylation of acrylate, further experiments were carried out to extend the reaction to the analogous acrylamides. To our delight, the bis-acylation of *N*,*N*-dimethylacrylamide was realized smoothly under the same reaction conditions (Scheme 3). However, only a



Scheme 1.



Scheme 2.

Table 1. Sm-promoted bis-acylation of the carbon–carbon double bond in acrylates with aroyl chlorides

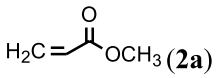
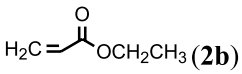
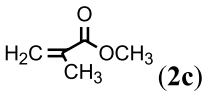
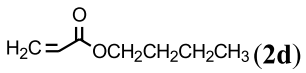
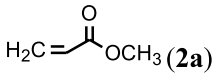
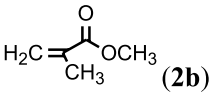
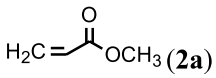
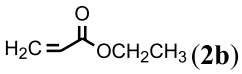
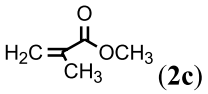
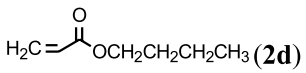
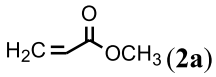
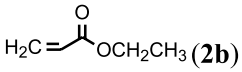
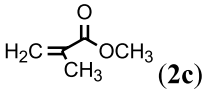
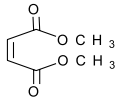
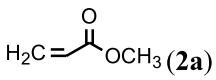
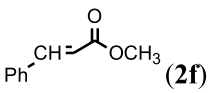
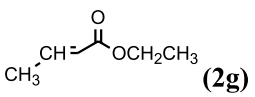
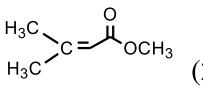
Entry	R in **1**	Substituted acrylate **2**	Isolated yield (%) of **3**[a]
1	H	 (**2a**)	91(**3a**)
2	H	 (**2b**)	93(**3b**)
3	H	 (**2c**)	84(**3c**)
4	H	 (**2d**)	81(**3d**)
5	4-CH_3	 (**2a**)	86(**3e**)
6	4-CH_3	 (**2b**)	79(**3f**)
7	4-Cl	 (**2a**)	78(**3g**)
8	4-Cl	 (**2b**)	77(**3h**)
9	4-Cl	 (**2c**)	72(**3i**)
10	4-Cl	 (**2d**)	90(**3j**)
11	4-F	 (**2a**)	82(**3k**)
12	4-F	 (**2b**)	88(**3l**)
13	3-Cl	 (**2c**)	63(**3m**)
14	4-F	 (**2e**)	46(**3n**)[b]
15	H[c]	 (**2a**)	31(**3o**)
16	H	 (**2f**)	29(**3p**)[d] –[e]
17	4-F	 (**2g**)	–[e]

Table 1 (*continued*)

Entry	R in **1**	Substituted acrylate **2**	Isolated yield (%) of **3**[a]
18	H	 (**2h**)	–[f]

[a] Isolated yields based on aroyl chlorides.
[b] A pair of inseparable diastereoisomers were obtained.
[c] 2-Furoyl chloride was used as substrate.
[d] **3p** is a 1,4-addition product.
[e] The resulting residue was a complicated mixture which defied further separation and identification.
[f] Only self-coupling products of aroyl chloride were obtained.

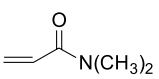
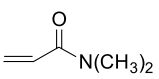
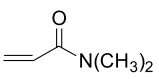
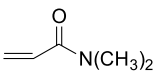
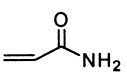
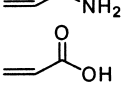
complex mixture was obtained when acrylic acid or *N*-unsubstituted acrylamide (Table 2, entries 7 and 8) was used as the substrate.

As for vinyl ketone **6** (Scheme 4), the bis-acylation reaction occurred only to a slight extent. The 1,4-addition product **7** was the major product while the bis-acylation product **8** was obtained in very low yields (Table 2, entries 5 and 6).

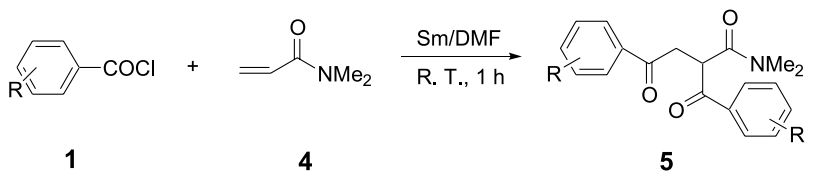
2.3. Sm-promoted bis-acylation of styrenes with aroyl chlorides

The carbon–carbon double bonds in styrenes were reported to be attacked readily by ketyl resulting from the metal-induced reduction of ketones.[10a,b] Furthermore, stilbene and acenaphthylene derivatives could be single-acylated in a cross-coupling procedure with acid anhydrides/TMSCl or acyl chlorides in the presence of

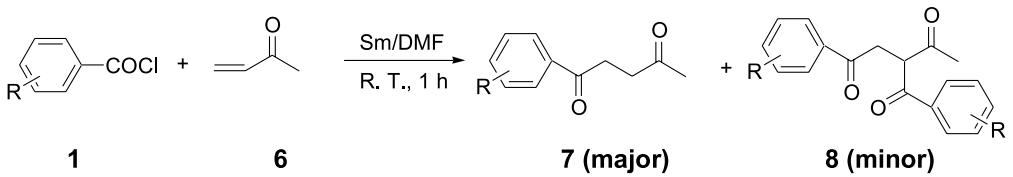
Table 2. Bis-acylation of *N*,*N*-dimethylacylamide, methyl vinyl ketone with aroyl chlorides with Sm/DMF

Entry	R in **1**	Substrate **4** or **6**	Isolated yield[a] (%)
1	H		88(**5a**)
2	4-CH_3		82(**5b**)
3	4-Cl		78(**5c**)
4	4-F		85(**5d**)
5	H		87(**7a**+**8a**) (**7a**:**8a**=82:18)
6	4-F		86(**7b**+**8b**) (**7b**:**8b**=91:9)
7	H		–[b]
8	H		–[b]

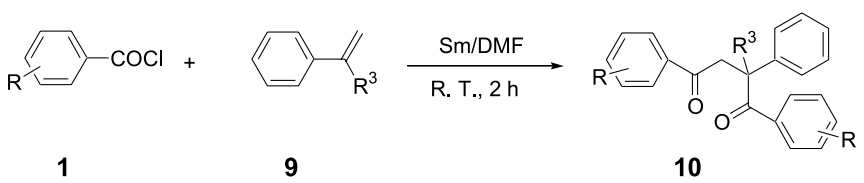
[a] Isolated yields based on aroyl chlorides.
[b] Only a complex mixture was obtained.



Scheme 3.



Scheme 4.



Scheme 5.

metallic magnesium.[10c] Very recently, the double addition of the electrophiles (such as Me_3SiCl and ketones) to each olefinic carbon atom in styrenes was realized with DTBB-catalyzed lithiation.[10d]

It seemed reasonable to further extend the bis-acylation method exploited here to styrenes, since styrenes also contain conjugated carbon–carbon double bonds. It was found that promoted by samarium in DMF, styrene and α-methylstyrene could be bis-acylated smoothly with aroyl chlorides to afford the corresponding 1,2-diaroylethylbenzene in good yields (Scheme 5, Table 3), though completion of the reaction required relatively prolonged time.

2.4. Possible mechanism

Generally, the bis-acylation reaction works well for substrates with terminal olefinic bonds. To have an understanding of the reaction mechanism, attempts were made to find out if the conjugated C=C groups are reactive towards samarium in the absence of aroyl chlorides. The experimental results showed that acrylates, *N*,*N*-dimethylacylamide, methyl vinyl ketone and styrenes all failed to undergo any reaction under the same Sm/DMF conditions.

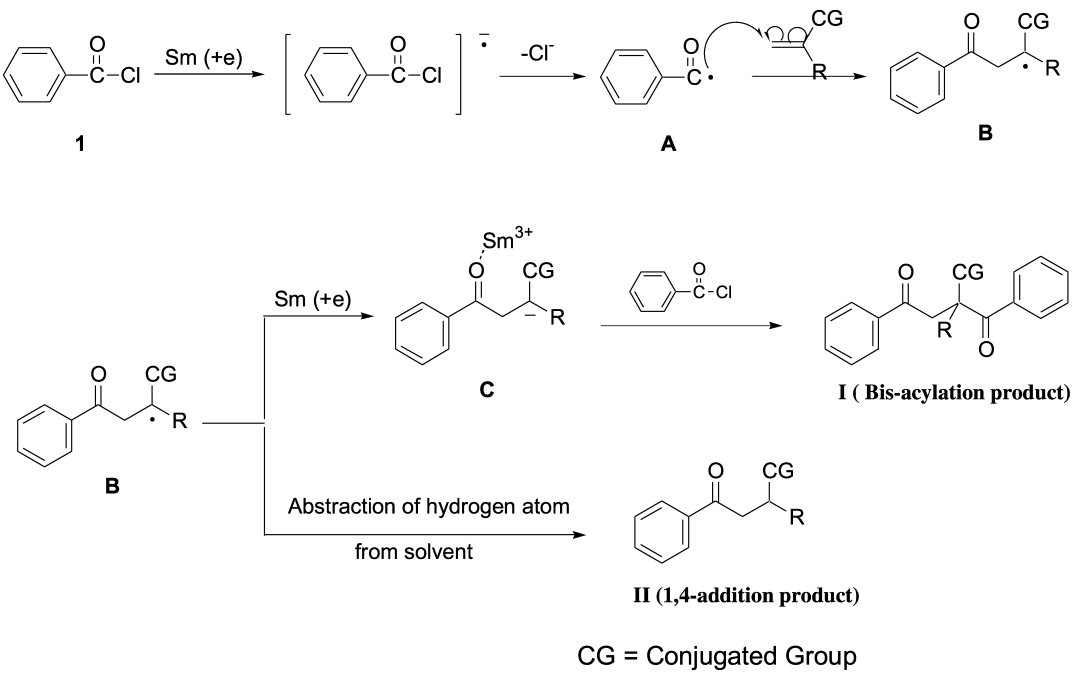
Table 3. Bis-acylation of styrenes with aroyl chlorides in Sm/DMF system

Entry	R in **1**	R^3 in **9** and **10**	Isolated yield of **10**[a] (%)
1	H	H	78(**10a**)
2	H	CH_3	77(**10b**)
3	4-F	H	68(**10c**)
4	4-F	CH_3	75(**10d**)
5	4-CH_3	H	71(**10e**)
6	3-CH_3	H	62(**10f**)

[a] Isolated yields based on aroyl chlorides.

Therefore, the bis-acylation must be initiated by an attack of aroyl intermediates (radical or anion) on the conjugated carbon–carbon double bonds. The successful bis-acylation of styrenes (Scheme 5) indicates that the reaction may involve a radical process since styrenes are not likely attacked by an anion, and there are many reports mentioned above giving evidences that styrenes were readily attacked by radical intermediates formed from metal-induced reduction of ketones.[10] On the other hand, the aroyl radicals resulting from aroyl chlorides are much more stable than the aliphatic acyl radicals from aliphatic acid chlorides in such a reaction system, and therefore, via radical mechanisms, aroyl chlorides react smoothly with various conjugated carbon–carbon double bonds while aliphatic acid chlorides do not. It should be pointed out that, DMF may play an important role in dissolving the intermediate samarium salts while THF cannot. In the latter case even the self-coupling of aroyl chloride rarely occurs.[11]

Although the mechanism of this reaction is not entirely clear yet, we presume that the reaction should involve a radical mechanism.[10a,b] The following reaction pathway is proposed to be operative. An electron transfer from samarium to an aroyl chloride **1** gives the corresponding aroyl radical **A**. **A** attacks the β-position of conjugated carbon–carbon double bond, and a radical intermediate **B** is formed. Intermediate **B** can capture an electron from Sm to form an anion **C**, which is relatively stable due to the strong oxophilicity of samarium.[12] Subsequently, **C** attacks another aroyl chloride to afford the bis-acylation product **I**. On the other hand, if intermediate **B** is much reactive, for example, in the case of methyl vinyl ketone used as substrate, the reaction path will be different. According to our assumption, intermediate **B** will be more sympathetic to abstract a hydrogen atom from solvent to afford 1,4-addition product **II** (Scheme 6).



Scheme 6.

In conclusion, a new bis-acylation method of conjugated carbon–carbon double bonds has been developed with aroyl chlorides in the presence of Sm in DMF. This method offers a facile, efficient and novel method for the synthesis of polycarbonyl compounds in good to excellent yields from very simple starting materials. Furthermore, the direct use of metallic samarium in organic synthesis without any activator is reported here for the first time.

3. Experimental

3.1. General

Melting points were uncorrected. Infrared spectra were recorded on an IR-408 spectrometer in KBr or film with absorption in cm^{-1}. ^1H NMR spectra were determined in a Bruker AC-400 spectrometer as $CDCl_3$ solutions. *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Elemental analyses were performed on an EA-1110 instrument. DMF was redistilled and dried by molecular sieve before use. Metallic samarium and all solvents were purchased from commercial sources, without further purification before use. The reaction was monitored by TLC, and the products were isolated by silica gel column chromatography using ethyl acetate and cyclohexane as eluant.

3.2. Typical procedure for the synthesis of compounds 3

To a mixture of Sm powder (1 mmol), methyl acrylate (4 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL), benzoyl chloride (2 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned yellow-green within 15 min and an exothermic reaction was observed. After completion of the reaction (about 1 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture extracted with diethylether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel with ethyl acetate and cyclohexane (1:6) as eluent to afford the methyl α,β-dibenzoylpropionate **3a** in 91% yield.

3.3. General procedure for the synthesis of compounds 5

To a mixture of Sm powder (1 mmol), *N*,*N*-dimethylacrylamide (4 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL), aroyl chloride (2 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned yellow-green within 15 min and an exothermic reaction was observed. After completion of the reaction (about 1 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture extracted with diethylether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate and cyclohexane (1:1) as eluent to afford the product **5**.

3.4. General procedure for the synthesis of compounds 7 and 8

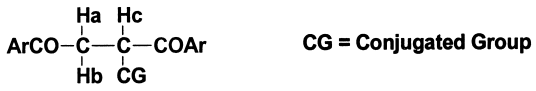
To a mixture of Sm powder (1 mmol), methyl vinyl ketone (4 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL), aroyl chloride (2 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned yellow-green within 15 min and an exothermic reaction was observed. After completion of the reaction (about 1 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture extracted with diethylether (3×20 mL).

The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel with ethyl acetate and cyclohexane (1:8) as eluent to afford the products **7** and **8**.

3.5. Typical procedure for the synthesis of compounds 10

To a mixture of Sm powder (1 mmol), styrene (4 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL), benzoyl chloride (2 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned yellow-green within 30 min and an exothermic reaction was observed. After completion of the reaction (about 2 h), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture extracted with diethylether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel with ethyl acetate and cyclohexane (1:8) as eluent to afford the 1,2,4-triphenyl-1,4-butandione **10a** in 78% yield.

3.6. General structure of bis-acylation products



3.6.1. Methyl α,β-dibenzoylpropionate (3a). White solid, mp: 77–78°C. ν_{max}(KBr)/cm^{-1}: 2955, 1736, 1683, 1595, 1581, 1451. δ_H($CDCl_3$): 8.09–8.11 (2H, m), 7.99–8.01 (2H, m), 7.57–7.63 (2H, m), 7.45–7.53 (4H, m), 5.13–5.17 (1H, dd, Hc, J_{cb}=7.5 Hz, J_{ca}=6.1 Hz), 3.80–3.87 (1H, dd, Hb, J_{bc}=7.5 Hz, J_{ba}=18.3 Hz), 3.71–3.77 (1H, dd, Ha, J_{ab}=18.3 Hz, J_{ac}=6.1 Hz), 3.71 (3H, s). ^{13}C NMR δ($CDCl_3$): 196.3, 194.2, 169.3, 135.5, 135.5, 133.1, 133.0, 128.5, 128.2, 128.1, 127.7, 52.3, 48.0, 37.8. *m*/*z* (%): 297 (M^++1, 0.10), 296 (M^+, 0.06), 279 (M^+−17, 0.47), 265 (0.59), 191 (1.58), 105 (100.00), 77 (43.65). Anal. $C_{18}H_{16}O_4$. Calcd C, 72.96; H, 5.44. Found C, 72.83; H, 5.40%.

3.6.2. Ethyl α,β-dibenzoylpropionate (3b). White solid, mp: 40–41°C. ν_{max}(KBr)/cm^{-1}: 2982, 1736, 1684, 1597, 1581, 1449. δ_H($CDCl_3$): 8.09–8.11 (2H, m), 7.99–8.01 (2H, m), 7.58–7.63 (2H, m), 7.45–7.53 (4H, m), 5.11–5.14 (1H, dd, Hc, J_{cb}=7.5 Hz, J_{ca}=6.1 Hz), 4.14–4.19 (2H, q, J=7.1 Hz), 3.79–3.85 (1H, dd, Hb, J_{bc}=7.5 Hz, J_{ba}=18.3 Hz), 3.69–3.76 (1H, dd, Ha, J_{ab}=18.3 Hz, J_{ac}=6.1 Hz), 1.16–1.19 (3H, t, J=7.1 Hz). ^{13}C NMR δ($CDCl_3$): 196.4, 194.3, 168.8, 135.6, 133.2, 133.1, 133.0, 128.4, 128.2, 128.1, 127.7, 61.3, 48.4, 37.6, 13.4. *m*/*z*(%): 311 (M^++1, 0.04), 310 (M^+, 0.04), 293 (M^+−17, 0.13), 265 (1.12), 205 (2.22), 105 (100.00), 77 (44.97). Anal. $C_{19}H_{18}O_4$. Calcd C, 73.53; H, 5.85. Found C, 73.39; H, 5.83%.

3.6.3. Methyl α,β-dibenzoyl-α-methylpropionate (3c). White solid, mp: 69–70°C. ν_{max}(KBr)/cm^{-1}: 2948, 1734, 1692, 1682, 1596, 1580, 1462, 1449. δ_H($CDCl_3$): 7.96–7.98 (2H, m), 7.83–7.85 (2H, m), 7.39–7.59 (6H, m), 3.84 (2H, s), 3.71 (3H, s), 1.73 (3H, s). ^{13}C NMR δ($CDCl_3$): 197.9, 196.9, 173.5, 136.9, 136.5, 133.4, 132.3, 128.7, 128.5, 128.4, 128.1, 56.2, 52.9, 45.6, 21.8. *m*/*z*(%): 293 (M^+−17, 0.20), 279 (0.17), 205 (1.46), 105 (100.00), 77 (44.97). Anal. $C_{19}H_{18}O_4$. Calcd C, 73.53; H, 5.85. Found C, 73.49; H, 5.86%.

3.6.4. Butyl α,β-dibenzoylpropionate (3d). White solid, mp: 51–52°C. ν_{max}(KBr)/cm^{-1}: 2958, 1736, 1689, 1677, 1594, 1446. δ_H($CDCl_3$): 8.07–8.11 (2H, m), 8.00–8.02 (2H, m), 7.56–7.63 (2H, m), 7.45–7.53 (4H, m), 5.12–5.16 (1H, dd, Hc, J_{cb}=7.6 Hz, J_{ca}=6.0 Hz), 4.09–4.12 (2H, t, J=6.8 Hz), 3.81–3.87 (1H, dd, Hb, J_{bc}=7.6 Hz, J_{ba}=18.0 Hz), 3.69–3.75 (1H, dd, Ha, J_{ab}=18.0 Hz, J_{ac}=6.0 Hz), 1.47–1.54 (2H, m), 1.16–1.26 (2H, m), 0.80–0.84 (3H, t, J=7.6 Hz). ^{13}C NMR δ($CDCl_3$): 197.0, 194.8, 169.3, 136.3, 136.2, 133.5, 133.5, 129.0, 128.7, 128.5, 128.3, 65.6, 48.9, 38.1, 30.4, 18.9, 13.6. *m*/*z*(%): 339 (M^++1, 0.31), 338 (M^+, 0.07), 321 (M^+−17, 1.07), 265 (1.37), 233 (1.41), 105 (100.00), 77 (44.97). Anal. $C_{21}H_{22}O_4$. Calcd C, 74.54; H, 6.55. Found C, 74.39; H, 6.54%.

3.6.5. Methyl α,β-di(4-methyl-)benzoylpropionate (3e). White solid, mp: 79–80°C. ν_{max}(KBr)/cm^{-1}: 2953, 1734, 1675, 1606, 1435. δ_H($CDCl_3$): 7.98–8.00 (2H, m), 7.88–7.90 (2H, m),7.25–7.31 (4H, m), 5.10–5.14 (1H, dd, Hc, J_{cb}=7.0 Hz, J_{ca}=6.6 Hz), 3.70–3.75 (2H, m), 3.70 (3H, s), 2.43 (3H, s), 2.41 (3H, s) ^{13}C NMR δ($CDCl_3$): 195.9, 193.8, 169.4, 144.0, 143.8, 133.1, 133.0, 128.9, 128.8, 128.6, 127.8, 52.2, 47.9, 37.7, 21.2, 21.1. *m*/*z*(%): 325 (M^++1, 0.06), 324 (M^+, 0.17), 307 (M^+−17, 0.11), 293 (0.55), 205 (1.66), 119 (100.00), 77 (43.65). Anal. $C_{20}H_{20}O_4$. Calcd C, 74.06; H, 6.21. Found C, 73.89; H, 6.21%.

3.6.6. Methyl α,β-di(4-methyl-)benzoyl-α-methylpropionate (3f). White solid, mp: 88–89°C. ν_{max}(KBr)/cm^{-1}: 3005, 2933, 1744, 1683, 1668, 1606, 1430. δ_H($CDCl_3$): 7.87–7.89 (2H, m), 7.80–7.82 (2H, m), 7.20–7.27 (6H, m), 3.80 (2H, s), 3.70 (3H, s), 2.41 (3H, s), 2.39 (3H, s), 1.73 (3H, s). ^{13}C NMR δ($CDCl_3$): 196.6, 196.0, 173.2, 143.6, 142.7, 133.9, 133.0, 128.7, 128.6, 128.2, 127.7, 55.5, 52.2, 44.9, 21.3, 21.1, 21.0. *m*/*z*(%): 338 (M^+, 0.06), 321 (M^+−17, 0.20), 307 (0.16), 219 (1.14), 119 (100.00), 91 (36.03). Anal. $C_{21}H_{22}O_4$. Calcd C, 74.54; H, 6.55. Found C, 74.389; H, 6.53%.

3.6.7. Methyl α,β-di(4-chloro-)benzoylpropionate (3g). White solid, mp: 85–86°C. ν_{max}(KBr)/cm^{-1}: 3089, 2953, 1743, 1683, 1589, 1570, 1488. δ_H($CDCl_3$): 8.04–8.06 (2H, m), 7.93–7.95 (2H, m), 7.45–7.51 (4H, m), 5.05–5.09 (1H, dd, Hc, J_{cb}=8.3 Hz, J_{ca}=5.5 Hz), 3.82–3.89 (1H, dd, Hb, J_{bc}=8.3 Hz, J_{ba}=18.3 Hz), 3.65–3.71 (1H, dd, Ha, J_{ab}=18.3 Hz, J_{ac}=5.5 Hz), 3.71 (3H, s). ^{13}C NMR δ($CDCl_3$): 195.2, 192.8, 168.8, 139.8, 139.6, 133.8, 133.8, 129.9, 129.1, 128.6, 128.5, 52.4, 47.9, 37.7. *m*/*z*(%): 364 (M^+, 0.07), 333 (0.59), 225 (1.96), 139 (100.00), 111 (34.28). Anal. $C_{18}H_{14}Cl_2O_4$. Calcd C, 59.20; H, 3.86. Found C, 59.32; H, 3.87%.

3.6.8. Ethyl α,β-di(4-chloro-)benzoylpropionate (3h). White solid, mp: 62–63°C. ν_{max}(KBr)/cm^{-1}: 3086, 2986, 1738, 1683, 1588, 1569, 1488. δ_H($CDCl_3$): 8.04–8.06 (2H, m), 7.93–7.96 (2H, m), 7.44–7.51 (4H, m), 5.03–5.06 (1H, dd, Hc, J_{cb}=8.2 Hz, J_{ca}=5.5 Hz), 4.14–4.20 (2H, q,

J=7.2 Hz), 3.80–3.87 (1H, dd, Hb, J_{bc}=8.2 Hz, J_{ba}=18.2 Hz), 3.64–3.70 (1H, dd, Ha, J_{ab}=18.2 Hz, J_{ac}=5.5 Hz), 1.16–1.20 (3H, t, J=7.2 Hz). ^{13}C NMR δ($CDCl_3$): 195.2, 192.9, 168.3, 139.7, 139.6, 134.0, 133.8, 129.9, 129.1, 128.5, 128.5, 61.5, 48.2, 37.6, 13.4. m/z(%): 361 (M^+-17, 0.17), 333 (0.60), 239 (1.87), 139 (100.00), 111 (26.59). Anal. $C_{19}H_{16}Cl_2O_4$. Calcd C, 60.18; H, 4.25. Found C, 60.22; H, 4.24%.

3.6.9. Methyl α,β-di(4-chloro-)benzoyl-α-methylpropionate (3i). White solid, mp: 133–135°C. ν_{max}(KBr)/cm^{-1}: 3106, 2951, 1745, 1686, 1671, 1591, 1571, 1488, 1432. δ_H($CDCl_3$): 7.90–7.93 (2H, m), 7.79–7.81 (2H, m), 7.39–7.46 (4H, m), 3.78 (2H, s), 3.72 (3H, s), 1.72 (3H, s). ^{13}C NMR δ($CDCl_3$): 196.2, 195.0, 172.7, 139.5, 138.3, 134.4, 134.1, 129.5, 129.0, 128.5, 128.2, 55.6, 52.5, 45.1, 21.4. m/z(%): 361 (M^+-17, 1.93), 347 (0.15), 239 (0.74), 139 (100.00), 111 (26.14). Anal. $C_{19}H_{16}Cl_2O_4$. Calcd C, 60.18; H, 4.25. Found C, 60.31; H, 4.26%.

3.6.10. Butyl α,β-di(4-chloro-)benzoylpropionate (3j). White solid, mp: 93–94°C. ν_{max}(KBr)/cm^{-1}: 2958, 1738, 1690, 1678, 1591, 1571, 1488. δ_H($CDCl_3$): 8.04–8.06 (2H, m), 7.94–7.96 (2H, m), 7.45–7.51 (4H, m), 5.04–5.07 (1H, dd, Hc, J_{cb}=8.3 Hz, J_{ca}=5.4 Hz), 4.09–4.12 (2H, t, J=6.6 Hz), 3.81–3.88 (1H, dd, Hb, J_{bc}=8.3 Hz, J_{ba}=18.3 Hz), 3.65–3.70 (1H, dd, Ha, J_{ab}=18.3 Hz, J_{ac}=5.4 Hz), 1.49–1.53 (2H, m), 1.18–1.24 (2H, m), 0.82–0.86 (3H, t, J=7.4 Hz). ^{13}C NMR δ($CDCl_3$): 195.3, 193.0, 168.3, 139.6, 139.6, 134.1, 133.8, 129.8, 129.1, 128.5, 128.5, 65.3, 48.2, 37.5, 29.8, 18.4, 13.0. m/z(%): 389 (M^+-17, 0.08), 333 (0.47), 267 (1.42), 139 (100.00), 111 (22.70). Anal. $C_{21}H_{20}Cl_2O_4$. Calcd C, 61.93; H, 4.95. Found C, 61.93; H, 5.01%.

3.6.11. Methyl α,β-di(4-fluoro-)benzoylpropionate (3k). White solid, mp: 92–94°C. ν_{max}(KBr)/cm^{-1}: 3079, 2962, 1737, 1684, 1595, 1507, 1437. δ_H($CDCl_3$): 8.09–8.13 (2H, m), 8.00–8.02 (2H, m), 7.09–7.18 (4H, m), 5.04–5.07 (1H, dd, Hc, J_{cb}=8.2 Hz, J_{ca}=5.6 Hz), 3.63–3.68 (1H, dd, Hb, J_{bc}=8.2 Hz, J_{ba}=18.4 Hz), 3.78–3.85 (1H, dd, Ha, J_{ab}=18.4 Hz, J_{ac}=5.6 Hz), 3.64 (3H, s). ^{13}C NMR δ($CDCl_3$): 196.4, 195.3, 173.3, 169.5, 167.4, 167.3, 164.8, 132.5, 131.8, 131.7, 130.9, 130.8, 130.7, 130.6, 115.9, 115.8, 115.7, 52.9, 48.5, 38.2. m/z(%): 333 (M^++1, 0.18), 332 (M^+, 0.18), 315 (M^+-17, 0.90), 301 (0.58), 209 (1.13), 123 (100.00), 95 (35.27). Anal. $C_{18}H_{14}F_2O_4$. Calcd C, 65.06; H, 4.25. Found C, 64.98; H, 4.23%.

3.6.12. Methyl α,β-di(4-fluoro-)benzoyl-α-methylpropionate (3l). White solid, mp: 84–85°C. ν_{max}(KBr)/cm^{-1}: 3075, 2956, 1743, 1683, 1671, 1597, 1506, 1460, 1434. δ_H($CDCl_3$): 7.95–7.98 (2H, m), 7.86–7.89 (2H, m), 7.04–7.12 (4H, m), 3.75 (2H, s), 3.70 (3H, s), 1.70 (3H, s). ^{13}C NMR δ($CDCl_3$): 196.2, 195.3, 173.4, 168.0, 166.4, 164.7, 163.9, 133.2, 133.2, 132.5, 131.3, 131.2, 130.8, 130.7, 115.8, 115.6, 115.4, 56.1, 52.9, 45.6, 21.9. m/z(%): 329 (M^+-17, 0.13), 315 (0.12), 223 (0.70), 123 (100.00), 95 (38.97). Anal. $C_{19}H_{16}F_2O_4$. Calcd C, 65.89; H, 4.66. Found C, 65.91; H, 4.63%.

3.6.13. Methyl α,β-di(3-chloro-)benzoyl-α-methylpropionate (3m). Oil. ν_{max}(film)/cm^{-1}: 2952, 1735, 1691, 1571, 1459, 1423. δ_H($CDCl_3$): 7.93 (2H, s), 7.83–7.85 (2H, m), 7.35–7.43 (4H, m), 3.73 (2H, s), 3.70 (3H, s), 1.71 (3H, s). m/z(%): 379 (M^++1, 4.47), 361 (M^+-17, 19.25), 347 (0.70), 239 (2.41), 139 (100.00), 111 (9.64). Anal. $C_{19}H_{16}Cl_2O_4$. Calcd C, 60.18; H, 4.25. Found C, 60.01; H, 4.28%.

3.6.14. Methyl α,β-di(4-fluoro-)benzoyl-β-methoxycarbonylpropionate (3n). Light yellow solid, a pair of inseparable diastereoisomers. ν_{max}(KBr)/cm^{-1}: 3079, 2960, 1737, 1685, 1605, 1509, 1432. δ_H($CDCl_3$): 8.20–8.24 (2H, m), 8.07–8.11 (2H, m), 7.14–7.22 (4H, m), 5.59 (2H, s), 3.55 (6H, s). m/z(%): 373 (M^+-17, 0.08), 372 (M^+-18, 0.14), 359 (0.09), 267 (0.48), 250 (5.09), 123 (100.00), 95 (31.04). Anal. $C_{20}H_{16}F_2O_6$. Calcd C, 61.54; H, 4.13. Found C, 61.32; H, 4.15%.

3.6.15. Methyl α,β-difuroylpropionate (3o). Oil. ν_{max}(film)/cm^{-1}: 3135, 2956, 2925, 1741, 1674, 1569, 1467, 1261. δ_H($CDCl_3$): 7.62–7.64 (1H, m), 7.57–7.59 (1H, m), 7.38–7.39 (1H, m), 7.24–7.26 (1H, m), 6.56–6.59 (1H, m), 6.53–6.55 (1H, m), 4.86–4.89 (1H, q), 3.73 (3H, s), 3.57–3.71 (2H, m). m/z(%): 277 (M^++1, 65.94), 259 (M^+-17, 13.91), 245 (21.01), 244 (2.13), 181 (13.59), 95 (100.00), 67 (5.24). Anal. $C_{14}H_{12}O_6$. Calcd C, 60.87; H, 4.38. Found C, 60.93; H, 4.40%.

3.6.16. Methyl β-furoylpropionate (3p). White solid, mp: 55–57°C. ν_{max}(KBr)/cm^{-1}: 3135, 2955, 2925, 2851, 1741, 1667, 1569, 1465, 1261. δ_H($CDCl_3$): 7.57 (1H, s), 6.52–6.53 (1H, m), 3.68 (3H, s), 3.15–3.18 (2H, t, J=6.8 Hz), 2.72–2.75 (2H, t, J=6.8 Hz). m/z(%): 183 (M^++1, 2.39), 182 (M^+, 20.98), 151 (12.40), 150 (9.00), 95 (100.00), 87 (5.95), 67 (3.47). Anal. $C_9H_{10}O_4$. Calcd C, 59.34; H, 5.53. Found C, 59.28; H, 5.55%.

3.6.17. α,β-Dibenzoyl-*N*,*N*-dimethylpropionamide (5a). Oil. ν_{max}(film)/cm^{-1}: 3061, 2926, 1683, 1642, 1597, 1581, 1493, 1448. δ_H($CDCl_3$): 8.01–8.05 (4H, m), 7.57–7.62 (2H, m), 7.46–7.53 (4H, m), 5.33–5.36 (1H, dd, Hc, J_{cb}=7.2 Hz, J_{ca}=5.2 Hz), 3.81–3.86 (1H, dd, Hb, J_{bc}=7.2 Hz, J_{ba}=18.0 Hz), 3.52–3.57 (1H, dd, Ha, J_{ab}=18.0 Hz, J_{ac}=5.2 Hz), 3.12 (3H, s), 3.01 (3H, s). m/z(%): 311 (M^++2, 2.44), 310 (M^++1, 11.58), 292 (M^+-17, 6.27), 291 (M^+-18, 4.74), 265 (4.05), 204 (13.04), 186 (3.07), 159 (5.32), 105 (100.00), 77 (53.06), 72 (61.15). Anal. $C_{19}H_{19}NO_3$. Calcd C, 73.77; H, 6.19; N, 4.53. Found C, 73.45; H, 6.17; N, 4.51%.

3.6.18. α,β-Di(4-methyl-)benzoyl-*N*,*N*-dimethylpropionamide (5b). White solid, mp: 112–114°C. ν_{max}(KBr)/cm^{-1}: 2922, 1680, 1641, 1609, 1576, 1492, 1448. δ_H($CDCl_3$): 8.00–8.02 (2H, m), 7.90–7.93 (2H, m), 7.25–7.30 (4H, m), 5.29–5.33 (1H, dd, Hc, J_{cb}=8.0 Hz, J_{ca}=4.8 Hz), 3.82–3.87 (1H, dd, Hb, J_{bc}=8.0 Hz, J_{ba}=17.6 Hz), 3.43–3.48 (1H, dd, Ha, J_{ab}=17.6 Hz, J_{ac}=4.8 Hz), 3.09 (3H, s), 3.00 (3H, s), 2.45 (3H, s), 2.43 (3H, s). m/z(%): 339 (M^++2, 0.24), 338 (M^++1, 1.00), 320 (M^+-17, 2.28), 319 (M^+-18, 6.08), 293 (2.62), 218 (11.76), 200 (2.72), 173 (4.84), 119 (100.00), 91 (44.98), 72 (17.09). Anal. $C_{21}H_{23}NO_3$. Calcd C, 74.75; H, 6.87; N, 4.15. Found C, 74.63; H, 6.89; N, 4.14%.

3.6.19. α,β-Di(4-chloro-)benzoyl-*N*,*N*-dimethylpropionamide (5c). Light yellow solid, mp: 89–91°C. ν_{max}(KBr)/

cm^{-1}: 3063, 2930, 1684, 1641, 1589, 1488. δ_H($CDCl_3$): 7.92–7.98 (4H, m), 7.43–7.49 (4H, m), 5.23–5.26 (1H, dd, Hc, J_{cb}=6.8 Hz, J_{ca}=6.0 Hz), 3.68–3.74 (1H, dd, Hb, J_{bc}=6.8 Hz, J_{ba}=17.6 Hz), 3.52–3.58 (1H, dd, Ha, J_{ab}=17.6 Hz, J_{ac}=6.0 Hz), 3.12 (3H, s), 3.00 (3H, s). *m/z*(%): 381 (M^++4, 2.00), 380 (M^++3, 9.75), 379 (M^++2, 3.44), 378 (M^++1, 15.30), 360 (M^+−17, 4.41), 359 (M^+−18, 1.40), 333 (1.74), 238 (7.53), 220 (1.02), 193 (4.09), 141 (15.71), 139 (49.95), 111 (17.97), 72 (100.00). Anal. $C_{19}H_{17}Cl_2NO_3$. Calcd C, 60.33; H, 4.53; N, 3.70. Found C, 60.46; H, 4.55; N, 3.67%.

3.6.20. α,β-Di(4-fluoro-)benzoyl-*N*,*N*-dimethylpropionamide (5d). Oil. ν_{max}(film)/cm^{-1}: 3075, 2939, 1685, 1643, 1601, 1508, 1431. δ_H($CDCl_3$): 8.12–8.16 (2H, m), 8.04–8.07 (2H, m), 7.13–7.20 (4H, m), 5.25–5.28 (1H, dd, Hc, J_{cb}=6.8 Hz, J_{ca}=6.0 Hz), 3.71–3.77 (1H, dd, Hb, J_{bc}=6.8 Hz, J_{ba}=17.6 Hz), 3.52–3.57 (1H, dd, Ha, J_{ab}=17.6 Hz, J_{ac}=6.0 Hz), 3.12 (3H, s), 3.00 (3H, s). *m/z*(%): 347 (M^++2, 8.15), 346 (M^++1, 38.32), 328 (M^+−17, 10.48), 327 (M^+−18, 2.98), 301 (4.78), 222 (9.68), 204 (1.32), 177 (5.57), 123 (70.27), 95 (25.37), 72 (100.00). Anal. $C_{19}H_{17}F_2NO_3$. Calcd C, 66.08; H, 4.96; N, 4.06. Found C, 66.26; H, 4.95; N, 4.07%.

3.6.21. Benzene-1,4-pentandione (7a). Oil. ν_{max}(film)/cm^{-1}: 3049, 2942, 1717, 1685, 1617, 1581, 1449. δ_H($CDCl_3$): 7.97–7.99 (2H, m), 7.54–7.56 (1H, m), 7.44–7.47 (2H, m), 3.26–3.29 (2H, t, *J*=6.4 Hz), 2.87–2.90 (2H, t, *J*=6.4 Hz). *m/z*(%): 177 (M^++1, 6.79), 176 (M^+ 2.03), 161 (9.20), 159 (M^+−17, 5.92), 158 (3.44), 133 (5.81), 105 (100.00), 77 (48.22). Anal. $C_{11}H_{12}O_2$. Calcd C, 74.98; H, 6.86. Found C, 74.78; H, 6.84%.

3.6.22. (4-Fluoro-)benzene-1,4-pentandione (7b). White solid, mp: 48–50°C. ν_{max}(KBr)/cm^{-1}: 3076, 2912, 1716, 1676, 1616, 1508, 1409. δ_H($CDCl_3$): 8.01–8.05 (2H, m), 7.13–7.17 (2H, m), 3.25–3.28 (2H, t, *J*=6.4 Hz), 2.90–2.93 (2H, t, *J*=6.4 Hz). *m/z*(%): 179 (M^+−15, 0.45), 177 (M^+−17, 0.92), 176 (5.60), 151 (6.06), 123 (100.00), 95 (63.54). Anal. $C_{11}H_{11}FO_2$. Calcd C, 68.03; H, 5.71. Found C, 68.18; H, 5.74%.

3.6.23. 1,2-Dibenzoyl-3-butanone (8a). Oil. ν_{max}(film)/cm^{-1}: 3045, 2935, 1717, 1685, 1597, 1449. δ_H($CDCl_3$): 8.06–8.09 (2H, m), 7.89–7.92 (2H, m), 7.54–7.56 (2H, m), 7.35–7.43 (4H, m), 5.25–5.28 (1H, dd, Hc, J_{cb}=6.8 Hz, J_{ca}=6.4 Hz), 3.70–3.77 (1H, dd, Hb, J_{bc}=6.8 Hz, J_{ba}=18.4 Hz), 3.55–3.62 (1H, dd, Ha, J_{ab}=18.4 Hz, J_{ac}=6.4 Hz), 2.25 (3H, s). *m/z*(%): 280 (M^+, 1.20), 263 (M^+−17, 1.32), 238 (0.66), 175 (2.25), 105 (100.00), 77 (24.11). Anal. $C_{18}H_{16}O_3$. Calcd C, 77.12; H, 5.75. Found C, 77.34; H, 5.76%.

3.6.24. 1,2-Di(4-fluoro-)benzoyl-3-butanone (8b). Oil. ν_{max}(film)/cm^{-1}: 3077, 2916, 1717, 1680, 1597, 1508, 1409. δ_H($CDCl_3$): 8.13–8.16 (2H, m), 8.01–8.05 (2H, m), 7.12–7.25 (4H, m), 5.23–5.26 (1H, dd, Hc, J_{cb}=6.4 Hz, J_{ca}=6.4 Hz), 3.72–3.78 (1H, dd, Hb, J_{bc}=6.4 Hz, J_{ba}=18.4 Hz), 3.60–3.66 (1H, dd, Ha, J_{ab}=18.4 Hz, J_{ac}=6.4 Hz), 2.25 (3H, s). *m/z*(%): 317 (M^++1, 0.34), 299 (M^+−17, 0.32), 274 (2.72), 193 (5.70), 123 (100.00), 95 (45.36). Anal. $C_{18}H_{14}F_2O_3$. Calcd C, 68.35; H, 4.46. Found C, 68.29; H, 4.46%.

3.6.25. 1,2,4-Triphenyl-1,4-butandione (10a). White solid, mp: 124–126°C. ν_{max}(KBr)/cm^{-1}: 3037, 2986, 1681, 1617, 1598, 1569, 1507, 1454. δ_H($CDCl_3$): 8.06–8.08 (2H, m), 8.00–8.02 (2H, m), 7.56–7.58 (1H, m), 7.39–7.52 (7H, m), 7.32–7.36 (2H, m), 7.25–7.28 (1H, m), 5.25–5.38 (1H, dd, Hc, J_{cb}=10.0 Hz, J_{ca}=3.6 Hz), 4.22–4.29 (1H, dd, Hb, J_{bc}=10.0 Hz, J_{ba}=18.0 Hz), 3.31–3.36 (1H, dd, Ha, J_{ab}=18.0 Hz, J_{ac}=3.6 Hz). *m/z*(%): 315 (M^++1, 0.95), 314 (M^+, 3.42), 297 (M^+−17, 0.18), 209 (8.39), 192 (1.73), 105 (100.00), 77 (53.92). Anal. $C_{22}H_{18}O_2$. Calcd C, 84.05; H, 5.77. Found C, 83.84; H, 5.76%.

3.6.26. 1,2,4-Triphenyl-2-methyl-1,4-butandione (10b). White solid, mp: 110–112°C. ν_{max}(KBr)/cm^{-1}: 3088, 3034, 2981, 1683, 1597, 1580, 1496. δ_H($CDCl_3$): 7.77–7.79 (3H, m), 7.50–7.53 (2H, m), 7.39–7.43 (3H, m), 7.21–7.26 (5H, m), 7.03–7.05 (2H, m), 3.89–3.94 (1H, d, *J*=17.6 Hz), 3.29–3.33 (1H, d, *J*=17.6 Hz), 1.75 (3H, s). *m/z*(%): 328 (M^+, 0.59), 327 (2.15), 311 (M^+−17, 0.63), 310 (1.63), 223 (5.24), 105 (100.00), 77 (29.11). Anal. $C_{23}H_{20}O_2$. Calcd C, 84.12; H, 6.14. Found C, 84.37; H, 6.12%.

3.6.27. 1,4-Di(4-fluoro-)phenyl-2-phenyl-1,4-butandione (10c). Oil. ν_{max}(film)/cm^{-1}: 3067, 2985, 1679, 1617, 1494, 1448. δ_H($CDCl_3$): 8.01–8.09 (4H, m), 7.28–7.35 (4H, m), 7.17–7.25 (1H, m), 7.06–7.13 (4H, m), 5.27–5.30 (1H, dd, Hc, J_{cb}=10.0 Hz, J_{ca}=3.2 Hz), 4.22–4.29 (1H, dd, Hb, J_{bc}=10.0 Hz, J_{ba}=18.0 Hz), 3.31–3.36 (1H, dd, Ha, J_{ab}=18.0 Hz, J_{ac}=3.2 Hz). *m/z*(%): 351 (M^++1, 1.20), 350 (M^+, 2.52), 333 (M^+−17, 0.89), 227 (6.53), 210 (1.78), 123 (100.00), 95 (32.74). Anal. $C_{22}H_{16}F_2O_2$. Calcd C, 75.42; H, 4.60. Found C, 75.26; H, 4.63%.

3.6.28. 1,4-Di(4-fluoro-)phenyl-2-phenyl-2-methyl-1,4-butandione (10d). White solid, mp: 154–156°C. ν_{max}(KBr)/cm^{-1}: 3058, 3021, 2987, 1685, 1692, 1597, 1505, 1445. δ_H($CDCl_3$): 7.79–7.83 (3H, m), 7.24–7.29 (5H, m), 7.03–7.11 (5H, m), 3.84–3.88 (1H, d, *J*=17.6 Hz), 3.26–3.30 (1H, d, *J*=17.6 Hz), 1.76 (3H, s). *m/z*(%): 364 (M^+, 0.07), 363 (0.12), 347 (M^+−17, 0.22), 346 (0.40), 345 (1.27), 241 (6.43), 123 (100.00), 95 (22.67). Anal. $C_{23}H_{20}O_2$. Calcd C, 75.81; H, 4.98. Found C, 75.74; H, 4.96%.

3.6.29. 1,4-Di(4-methyl-)phenyl-2-phenyl-1,4-butandione (10e). Oil. ν_{max}(film)/cm^{-1}: 3029, 2920, 1677, 1607, 1494. δ_H($CDCl_3$): 7.97–7.99 (2H, m), 7.91–7.93 (2H, m), 7.21–7.41 (9H, m), 5.33–5.37 (1H, dd, Hc, J_{cb}=10.0 Hz, J_{ca}=4.0 Hz), 4.18–4.25 (1H, dd, Hb, J_{bc}=10.0 Hz, J_{ba}=18.0 Hz), 3.28–3.34 (1H, dd, Ha, J_{ab}=18.0 Hz, J_{ac}=4.0 Hz), 2.42 (3H, s), 2.38 (3H, s). *m/z*(%): 343 (M^++1, 0.92), 342 (M^+, 2.35), 325 (M^+−17, 0.92), 223 (6.68), 206 (1.33), 119 (100.00), 91 (39.70). Anal. $C_{22}H_{18}O_2$. Calcd C, 84.18; H, 6.48. Found C, 84.34; H, 6.50%.

3.6.30. 1,4-Di(3-methyl-)phenyl-2-phenyl-1,4-butandione (10f). Oil. ν_{max}(film)/cm^{-1}: 3028, 2920, 1679, 1602, 1585, 1493. δ_H($CDCl_3$): 7.87–7.89 (2H, m), 7.81–7.83 (2H, m), 7.25–7.42 (9H, m), 5.34–5.38 (1H, dd, Hc, J_{cb}=10.0 Hz, J_{ca}=4.0 Hz), 4.20–4.27 (1H, dd, Hb, J_{bc}=10.0 Hz, J_{ba}=18.0 Hz), 3.31–3.36 (1H, dd, Ha, J_{ab}=

18.0 Hz, J_{ac}=4.0 Hz), 2.42 (3H, s), 2.39 (3H, s). *m/z*(%): 343 (M^++1, 66.58), 342 (M^+, 7.15), 325 (M^+−17, 67.85), 223 (6.20), 206 (2.46), 119 (100.00), 91 (68.18). Anal. $C_{22}H_{18}O_2$. Calcd C, 84.18; H, 6.48. Found C, 84.07; H, 6.46%.

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References

1. (a) Roush, W. R. *Chemtracts: Org. Chem.* **1988**, *1*, 37–39. (b) Gramatica, P. *Chim. Oggi.* **1988**, *6*, 17–20. (c) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608–9609. (d) Aramendia, M. A.; Borau, V.; Castellanos, F.; Jimenez, C.; Marinas, J. M. *React. Kinet. Catal. Lett.* **1988**, *36*, 251–256. (e) Oda, R. *Kagaku (Kyoto)* **1986**, *41*, 760–761. (f) Schmid, H. *Chemistry of Double-bonded Functional Groups*; Patal, S., Ed.; Wiley: Chichester, UK, 1989; Vol. 2(pt. 1), pp 679–731. (g) Marko, I. E.; Svendsen, J. S. *Comprehensive Asymmetric Catalysis I–III*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Germany, 1999; Vol. 2, pp 713–787.
2. (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698. (b) Krief, A.; Laval, A. M. *Chem. Rev.* **1999**, *99*, 745–777. (c) Molander, G. A. *Acc. Chem. Res.* **1998**, *31*, 603–609. (d) Molander, G. A.; Harris, C. R. *Tetrahedron* **1998**, *54*, 3321–3354. (e) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307–338. (f) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29–68.
3. Reviews: Banik, B. K. *Eur. J. Org. Chem.* **2002**, 2431–2444.
4. (a) Ogawa, A.; Nanke, T.; Takami, N.; Sumino, Y.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1994**, 379–380. (b) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778–1786. (c) Imamoto, T.; Takeyama, T.; Koto, H. *Tetrahedron Lett.* **1986**, *27*, 3243–3246. (d) Yanada, R.; Negoro, N.; Okaniwa, M.; Miwa, Y.; Taga, T.; Yanada, K.; Fujita, T. *Synlett* **1999**, 537–540. (e) Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 8729–8730. (f) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1987**, *52*, 3942–3944.
5. (a) Wang, L.; Zhang, Y. *Tetrahedron* **1998**, *54*, 11129–11140. (b) Banik, B. K.; Mukhopadhyay, C.; Venkatraman, M. S.; Becker, F. F. *Tetrahedron Lett.* **1998**, *39*, 7243–7246. (c) Yanada, R.; Negora, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271–3274. (d) Yanada, R.; Bessho, K.; Yanada, K. *Chem. Lett.* **1994**, 1279–1282. (e) Komachi, Y.; Kudo, T. *Chem. Pharm. Bull.* **1994**, *42*, 402–404. (f) Komachi, Y.; Kudo, T. *Chem. Pharm. Bull.* **1995**, *43*, 1422–1424. (g) Ghatak, A.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2000**, *41*, 3793–3796. (h) Talukdar, S.; Fang, J.-M. *J. Org. Chem.* **2001**, *66*, 330–333.
6. (a) Hou, Z.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 3118–3120. (b) Yanada, R.; Negoro, N. *Tetrahedron Lett.* **1996**, *37*, 9313–9316. (c) Wang, L.; Li, P.; Zhou, L. *Tetrahedron Lett.* **2002**, *43*, 8103–8105.
7. (a) Hassner, A. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 1, pp 541–577. (b) Herrmann, J. L.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3275–3278. (c) Cregge, R. J.; Hermann, J. L.; Richman, J. E.; Romanet, R. F.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2595–2598. (d) Hermann, J. L.; Richman, J. E.; Romanet, R. F.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2599–2602. (e) Jonsson, E. U.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5309–5311. (f) Schneider, P. W.; Bravard, D. C.; Mcdonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8641–8642. (g) Chavdarian, C. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 3822–3823. (h) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679–4681. (i) Chiu, P.-K.; Sammes, M. P. *Tetrahedron* **1990**, *46*, 3439. (j) Nagarajan, G.; Shechter, H. *J. Org. Chem.* **1984**, *49*, 62–74.
8. (a) Reviews: Ellison, R. A. *Synthesis* **1973**, 397–412. (b) Ho, T.-L. *Synth. Commun.* **1974**, *4*, 265–272. (c) Rio, G.; Lecas-Nawracka, A. *Bull. Soc. Chim. Fr.* **1976**, 317–326. (d) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926–4928. (e) Stetter, H. *Angew. Chem.* **1976**, *88*, 695–704. (f) Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551–4553. (g) Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551–2552. (h) Ohno, T.; Sakai, M.; Ishino, Y.; Shibata, T.; Maekawa, H.; Nishiguchi, I. *Org. Lett.* **2001**, *3*, 3439–3442.
9. (a) Miyashita, A.; Matsuoka, Y.; Numata, A.; Higashino, T. *Chem. Pharm. Bull.* **1996**, *44*, 448–450. (b) Miyashita, A.; Numata, A.; Suzuki, Y.; Iwamoto, K.-I. *Chem. Lett.* **1997**, 697–698.
10. (a) Ujikawa, O.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1989**, *30*, 2837–2840. (b) Inanaga, J.; Katsuki, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 4921–4924. (c) Nishiguchi, I.; Yamamoto, Y.; Sakai, M.; Ohno, T.; Ishino, Y.; Maekawa, H. *Synlett* **2002**, 759–762. (d) Yus, M.; Martínez, P.; Guijarro, D. *Tetrahedron* **2001**, *57*, 10119–10124.
11. Liu, Y. S.; Jiang, T.; Bei, M. Z. *Chem. J. Chin. Univer.* **1993**, *14*, 54–55.
12. (a) Yu, Y. P.; Lin, R. H.; Zhang, Y. M. *Tetrahedron Lett.* **1993**, *34*, 4547–4550. (b) Bao, W. L.; Zhang, Y. M.; Ying, T. K. *Synth. Commun.* **1996**, *26*, 503–507. (c) Ying, T. K.; Bao, W. L.; Zhang, Y. M.; Wang, J. Q. *Synth. Commun.* **1996**, *26*, 3025–3028.