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Tetrahedron
Tetrahedron 60 (2004) 3803–3811

A convenient and selective synthesis of unsymmetrical benzoins via the cyanide ion catalyzed cleavage of benzils

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Received 18 November 2003; revised 10 February 2004; accepted 4 March 2004

Abstract—The cyanide ion-catalyzed cleavage of benzils is used for the generation of various 'masked' acyl intermediates. The reaction of these intermediates with various aldehydes furnishes the corresponding esters of unsymmetrical benzoins in very good yields. A variety of unsymmetrical benzoin derivatives are synthesized in this way, including ferrocene derivatives. The hydrolysis of benzoin esters and their subsequent oxidation affords the corresponding unsymmetrical benzoins and benzils in high yield.

1. Introduction

The cyanide ion-catalyzed condensation of aromatic aldehydes to the corresponding benzoins has great synthetic utility. According to a well documented classical benzoin condensation mechanism, cyanide ion catalyzed generation of acyl anion equivalent **1a** ion is the key step in this transformation.[1] Many improvements have been made for the symmetrical benzoin condensation utilizing thiazolium and triazolium salts,[2] but synthesis of unsymmetrical benzoins, under traditional conditions, have problems associated with the formation of four possible benzoins, two of them being isomeric.[3] Thus, the synthesis of a specific isomer, especially the more energetic one, is accomplished by condensation of an acceptor aldehyde with an acyl anion equivalent of type **1** (Figure 1).

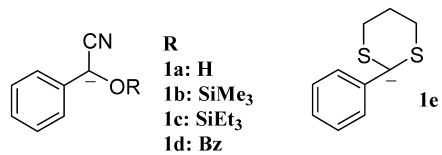

Figure 1.

Common approaches employ LDA deprotonation of the TMS ether of an aromatic cyanohydrin to form **1b** or the BuLi deprotonation of dithianes to form **1e**, which can subsequently be reacted with the acceptor aldehydes to obtain the desired benzoins. Alternatively, aromatic Grignard reagents can be added to OTMS cyanohydrins to form the isomeric benzoin via a common intermediate.[4,5] These methods have certain drawbacks such as use of air sensitive reagents and protection–deprotection steps. Recently, an excellent method was disclosed in which acylsilanes produce **1c** in the cyanide ion-catalyzed reaction. This intermediate reacts with aldehydes to afford the corresponding silyl protected benzoins in high yields.[6] However, the synthesis of acylsilanes are generally accomplished via the corresponding dithianes that also requires the use of air sensitive reagents and some laborious protection–deprotection steps.[7] Although C–C forming enzymes[8] have been shown to provide unsymmetrical benzoins in enantiomerically pure form, its applicability is limited to the use of only a few aldehydes; and enzymes mediating this reaction are not readily available.[8d] Some other methods have also been reported to provide less stable unsymmetrical benzoins, but the versatility of the reaction is limited by low yields (30–50%) and side products.[9]

In 1923, Dakin and Harington showed that the cyanide ion catalyzes the cleavage of benzil to benzaldehyde and the ester of benzoic acid.[10] Later, the mechanism and kinetics of the reaction were investigated by Kwart and Baevsky, demonstrating the intermediacy of **1d**.[11] Trisler and Frye showed that **1d**, in aprotic solvent DMSO where it is highly nucleophilic, reacts with another molecule of benzil present in the reaction solution to form *trans*-α,α′-stilbendiol dibenzoate.[12] This work showed that **1d** is a potent nucleophile and can react with an electrophile in the medium. Later, Kuebrich and Schowen used benzil and cyanide in DMF to generate the intermediate **1d** and examined its reaction with benzaldehyde and furfural.[13]Although **1d** could be generated efficiently under aprotic conditions, utilizing it to unsymmetrical benzoins has only been

Keywords: Benzoin; Benzil; Unsymmetrical; Photolabile.
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doi:10.1016/j.tet.2004.03.016

exemplified with furfural and not well developed and understood as discussed below; otherwise it would be quite useful for benzoin synthesis in both free and protected form. Herein we report our investigation focused on understanding the nature of **1d** and its derivatives together with its possible utilization for the synthesis of unsymmetrical benzoins.

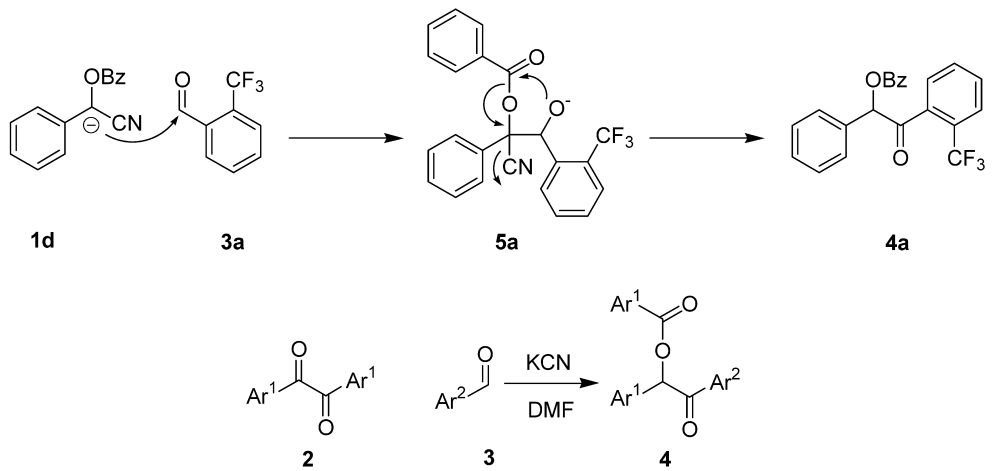
2. Results and discussion

For the synthesis of unsymmetrical benzoins, a solution of benzil **2a** and a potentially competent electrophile, 2-trifluoromethylbenzaldehyde **3a**, in DMF was treated with KCN. Product **4a** was obtained as expected, in agreement with the mechanisms proposed by Kuebrich et al., as shown in Scheme 1. According to this procedure, various aldehydes were reacted in order to understand the scope of the reaction and the effect of the electronic nature of the substituents. We have also shown that 2-naphthil **2b** can be used instead of **2a** (entries 9–12). Protected unsymmetrical benzoins, including interesting ferrocenyl derivatives, were obtained in very good to excellent yields as summarized in Table 1.

Some derivatives of benzoins are very useful photolabile protecting group of carboxylic acids. Upon irradiation at ~350 nm they release the acid moiety. The best photosensitive benzoin developed so far can be obtained from **4e** after hydrolysis,[5] and a recent report showed that **4e** itself releases the benzoate moiety almost quantitatively.[4c] Thus, the present method may allow the rapid synthesis of derivatives of **4**, which can then be tested for photolability, such as **4f**.[14] Recently reported synthesis of unprotected form of **4e** in 56% yield (overall 35% yield starting from benzaldehyde) by a dithiane method[4d] compared to 71% of this method (for hydrolysis, see below) is very promising in terms of yield and operational simplicity.

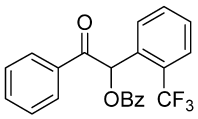
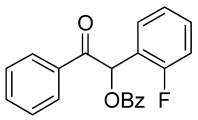
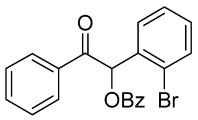
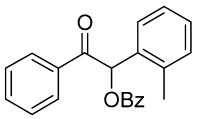
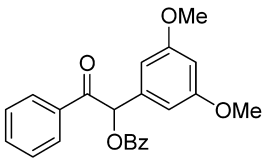
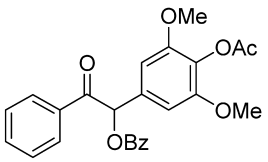
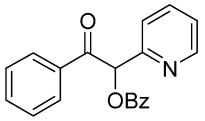
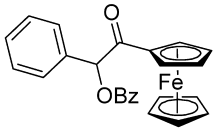
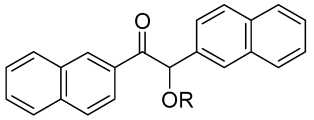
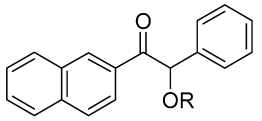
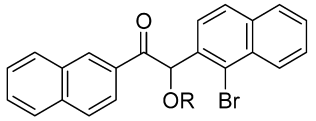
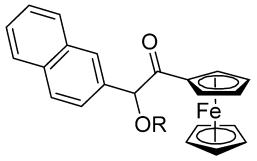
Particular attention to the structural integrity was required, because it was demonstrated by Corrie et al. that carbonyl derivatives of unsymmetrical benzoins may scramble to form isomeric compounds.[15] Taking into account the fact that some unsymmetrical benzoins may also isomerize to the thermodynamically more stable isomer under typical basic hydrolysis conditions, the correct structural assignment of the initial structures gains prime importance. Reported ^{1}H NMR shift values for a series of mono substituted benzoins show that two *ortho*-protons of benzoyl moiety resonate at around δ 7.9.[9] For the compounds listed in Table 1, we observed two doublets at around δ 7.9 and 8.1 that respectively originate from the benzoyl moiety of the benzoin and ester part. However, ferrocenecarboxaldehyde afforded the isomeric products **4h** and **4l** instead of the expected compounds **6** and **7** (Scheme 2). This observation was based on the lack of two *ortho*-protons of benzoyl moiety in benzoin portion of the molecule supported by 2D NMR analysis. All other products have 2D NMR spectra in agreement with the structures depicted in Table 1. The difference in reactivity can be attributed to the electron-rich nature of the ferrocenyl group. Although aldehyde **3e** has two electron-donating groups, methoxy substituent on the *meta*- position has a σ-value with a positive sign and yields the expected product. For a better understanding, 3,4,5-trimethoxybenzaldehyde **9** was reacted in a similar manner and two isomeric products were isolated in a 1:2 ratio (in favor of isomeric product) just after the completion of the reaction. Changing the *p*-methoxy group with an acetoxy group resulted in the formation of the desired isomer **4f**. As mentioned previously, Kuebrich et al. reported the same reaction with electron-rich furfural.[13] Although they reported the formation of **10** according to the mechanism in Scheme 1, their NMR data strongly resembles that of **11** lacking the two *ortho*-benzoyl protons. This supports the idea that electron-rich aldehydes have a propensity to yield isomeric products but it is not clear whether this is a problem of product stability or a different mechanism is operative.

Products **4a-l** are in protected form and their hydrolysis can afford the corresponding unsymmetrical benzoins or benzils upon oxidation. Hydrolysis of the products to the corresponding benzoins **12** was carried out in a basic medium similar to previously reported procedure (Scheme 3).[16] While isomerization was not a problem with most derivatives, the 2-methyl derivative **4d** afforded an isomeric mixture, and 2-Br derivative **4c** exhibited a small amount of isomerization and the product was obtained in a 9:1 ratio.

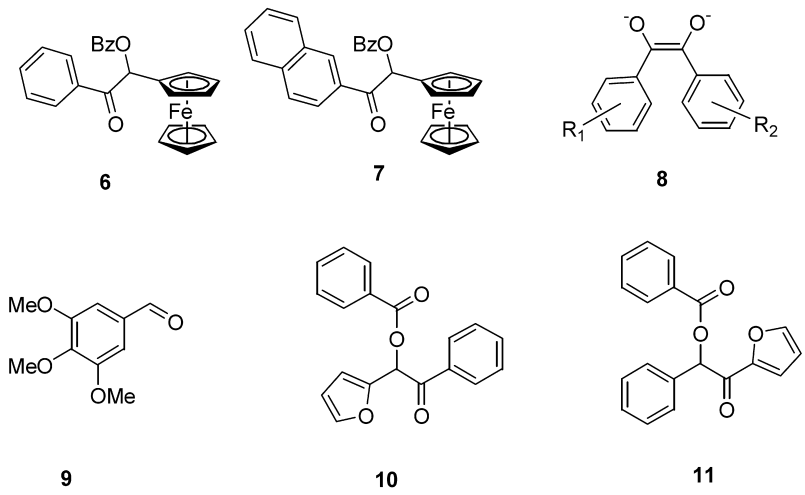


Scheme 1.

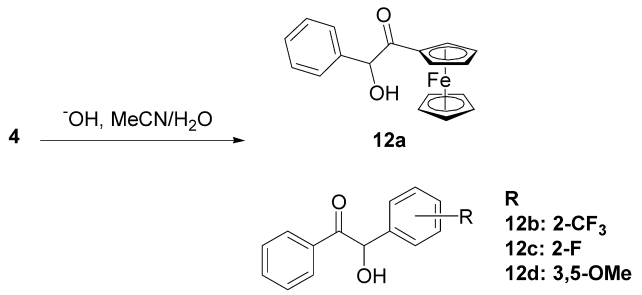
Table 1. Yields and structures of unsymmetrical benzoin derivatives

Entry	Benzil **2** **Ar**[1]	Aldehyde **3** **Ar**[2]	Product **4**		Yield (%)[a]
1	**2a** Ph	**3a** 2-CF_3Ph		**4a**	98
2	**2a** Ph	**3b** 2-FPh		**4b**	99
3	**2a** Ph	**3c** 2-BrPh		**4c**	95
4	**2a** Ph	**3d** 2-MePh		**4d**	93
5	**2a** Ph	**3e** 3,5-$(OMe)_2$Ph		**4e**	83
6	**2a** Ph	**3f** 3,5-$(OMe)_2$-4-OAcPh		**4f**	85
7	**2a** Ph	**3g** 2-pyridyl		**4g**	78
8	**2a** Ph	**3h** ferrocenyl		**4h**	89
9[b]	**2b** 2-naphthyl	**3i** 2-naphthyl		**4i**	77
10[b]	**2b** 2-naphthyl	**3j** Ph		**4j**	79
11[b]	**2b** 2-naphthyl	**3k** 1-Br-2-naphthyl		**4k**	73
12[b]	**2b** 2-naphthyl	**3h** ferrocenyl		**4l**	74

[a] Isolated yields.
[b] R: 2-naphthoyl.



Scheme 2.

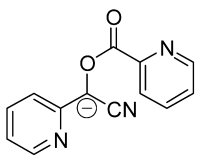


Scheme 3.

Hydrolysis of already isomeric **4h** furnished **12a**. Oxidation was a problem during hydrolysis if the oxygen in the medium was not removed before the reaction, as reported previously.[16] Isomerization possibly occurs via an endiol intermediate like **8** and the yellow color that developed during the reaction was attributed to this intermediate. This intermediate is expected to be easily oxidized during hydrolysis if air is not excluded from the medium. In the hydrolysis of **4e** to the corresponding benzoin **12d**, 4:1 mixture of isomers was obtained under standard conditions. When the same reaction was carried out at lower pH values, a 10:1 mixture of isomers was obtained with prolonged reaction times (6–8 h) in 94% overall yield.

In order to obtain further insights into the scope of the reaction, a series of electronically diverse *ortho*-substituted symmetric α-diketones were reacted with selected aldehydes as depicted earlier in Scheme 1. *ortho*-Position was selected in order to asses the effect of the steric hindrance adjacent to the reacting center. The results are summarized in Table 2. Amongst these α-diketones, *o*-methoxy was unreactive under the reaction conditions. Increasing the temperature did not affect the transformation. This stability of the diketone **2c** can be attributed to the strong electron-donating nature of –OMe, which disfavors cyanide addition. Although this type of group eases the shift of the carbonyl group, Kwart and Baevsky described the failure of an electron-donating group to significantly accelerate the cleavage if the resonance stabilization of the positive charge on the migrating carbonyl was the only important feature. Other *o*-substituted α-diketones were effectively converted into the corresponding benzoins.

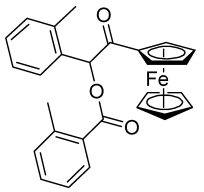
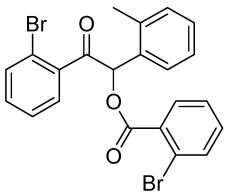
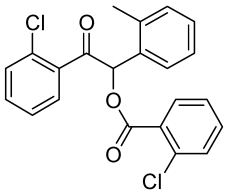
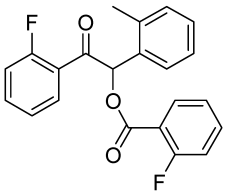
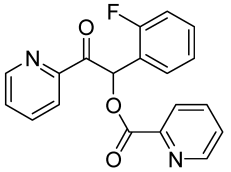
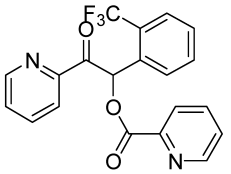
An interesting feature of the reaction was observed with 2,2′-bipyridil **2h**. When the reaction was carried out in the presence of 2-methylbenzaldehyde at 35 °C, the reaction was very slow and only small amounts of product were observed after 5 days. Increasing the temperature resulted in the formation of side products. When 2-fluorobenzaldehyde was used instead of 2-methylbenzaldehyde (Table 2, entry 6), the yield was 65% after 72 h, even though the reaction was not complete. Increasing the temperature also increased the amounts of side products. Changing 2-fluorobenzaldehyde with the more electronegative 2-trifluoromethylbenzaldehyde furnished the product **4r** in 77% yield in 24 h. This behavior of the reaction can be attributed to the rate of formation of intermediate **13** from 2,2′-bipyridil and the rate of its reaction with the aldehyde. Although the cyanide attack should have been favored by the presence of pyridyl moiety, it disfavors the cleavage of the central C–C bond formation and retards the transfer of this group onto oxygen, which results in the slow formation of **13**. The increase in the reaction rate upon the use of an aldehyde substituted with a more electronegative group can be explained on the basis of the increased stability of the intermediate **13** which can rearrange back to the starting material and only reacts with an appreciable rate when the aldehyde is very reactive.



13

According to the mechanism of cyanide ion cleavage of benzil proposed by Kwart and Baevsky, the phenyl ring having a substituent with a more positive σ-value ends up as aldehyde, while the other phenyl ring ends up in the ester or acid part through the decomposition of intermediate **14** that can be trapped with an aldehyde, thus forming disubstituted unsymmetrical benzoins. In fact, when compound **15** was

Table 2. Yields of disubstituted benzoin derivatives

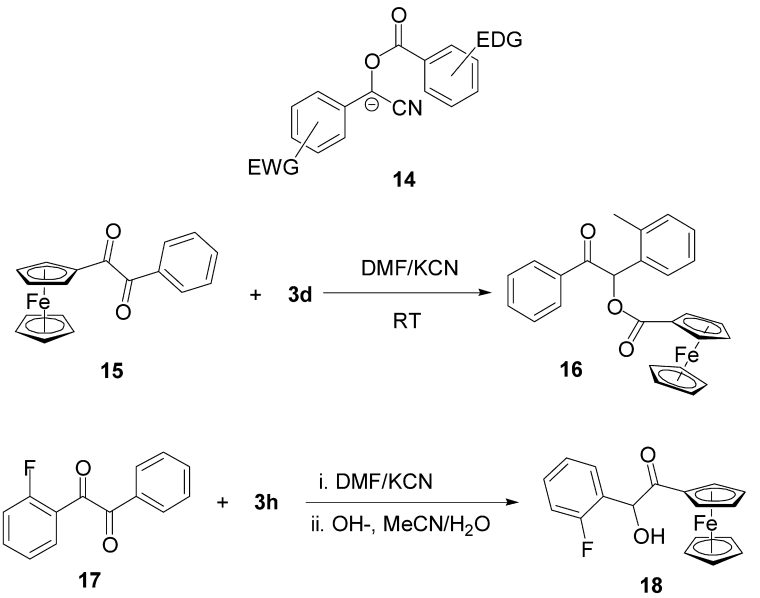
Entry	Benzil **2** **Ar**[1]	Aldehyde **3** **Ar**[2]	Product **4**		Yield[a] (%)
1	**2c** 2-OMePh	**2d**	No reaction		—
2	**2d** 2-MePh	**2h**		**4m**	73
3	**2e** 2-BrPh	**2d**		**4n**	69
4	**2f** 2-ClPh	**2d**		**4o**	82
5	**2g** 2-FPh	**2d**		**4p**	72
6	**2h** 2-pyridyl	**2b**		**4q**	65
7	**2h** 2-pyridyl	**2a**		**4r**	77

[a] Isolated yields.

treated with KCN in the presence of aldehyde **3d** (Scheme 4), we isolated the product **16** where electron rich ferrocene ring occupied the ester part. The hydrolysis of **16** furnished only ferrocene carboxylic acid and corresponding 2-methylbenzil in accordance with the proposed structure. Similarly, reaction of **17** with **3h** and subsequent hydrolysis of the crude product afforded **18** in 69% yield in accordance with these predictions. According to these results, the reaction of unsymmetrical benzils is promising and requires further investigation to find out if this approach is a generally applicable; a subject already under investigation. It is worth mentioning that a comparable result was obtained in an unoptimized reaction between **2a** and **3d** in refluxing MeCN as solvent.

3. Conclusion

In conclusion, we have shown that the cyanide ion-catalyzed cleavage of aromatic α-diketones can be used for the generation of various 'masked' acyl intermediates of type **1d**. These intermediates may be reacted with various aromatic aldehydes to form the corresponding esters of unsymmetrical benzoins in high yields. A variety of different benzoin derivatives can be synthesized in this way. In addition, benzoate ester products may be used as photoprotective groups. This method does not require the handling of air sensitive reagents and protecting groups. It gave either better or at least comparable results for the synthesis of certain unsymmetrical benzoins such as the



Scheme 4.

photolabile protecting group **12d**. Thus, this method generally offers the simplest approach for certain benzoins.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker DPX 400. Chemical shifts δ are reported in ppm relative to C*H*Cl_3 (^{1}H: δ=7.26) and *C*DCl_3 (^{13}C: δ=77.0) as an internal standard; coupling constnats are reported in Hz. Column chromatography was conducted on silica gel 60 (mesh size 40–63 μm). TLC was carried out on aluminum sheets precoated with silica gel 60F_{254} (Merck), and the spots were visualized with UV light (λ=254 nm). MS: ThermoQuest Finnigan multi Mass (EI, 70 eV). Melting points were measured on a capillary tube apparatus and are uncorrected. All aldehydes **3a**-**j** were purchased and used as obtained. **3k** was prepared from 1-bromo-2-methyl-naphthalene (see below). Benzils **2c**-**g** (**2h** commercially available) were synthesized by the oxidation of the corresponding benzoins, prepared by classical benzoin condensation and structure of benzils was confirmed by comparison of the analytical data with published values; **2c** (mp[17a] 128–129 °C), **2d** (mp[17b] 92 °C), **2e** (mp[17c] 128–130 °C), **2f** (mp[17d] 134–135 °C), **2g** (mp[17e] 95.5–96.6 °C) and **15** (mp[17f] 85.5–86 °C) DMF was distilled under vacuum and stored over 4 Å molecular-sieves.

4.1.1. 1-Bromo-2-naphthaldehyde (3k). To a solution of 1-bromo-2-methyl-naphthalene (3.58 ml, 23 mmol) and NBS (12 g, 67 mmol) in CCl_4 (250 ml), benzoyl peroxide (0.75 g, 3 mmol) was added in multiple portions and the resulting solution was heated under reflux for 7 h. The reaction mixture was filtered and evaporated under reduced pressure to obtain waxy brownish solid. Crystallization from hot ethanol gave 5.86 g yellowish crystals of 1-bromo-2-dibromomethyl naphthalene in 85% yield: mp 82.5–83.5 °C; MS(EI), *m*/*z* 378–380 (M^+, 18), 299 (100), 219 (12), 149 (32), 139 (82), 109 (22), 86 (24), 69 (74); ^{1}H NMR ($CDCl_3$) δ 7.38 (1H, s), 7.44–7.48 (1H, m), 7.51–7.54 (1H, m), 7.72 (1H, d, *J*=8 Hz), 7.78 (1H, d, *J*=8.6 Hz), 7.97 (1H, d, *J*=8.6 Hz), 8.2 (1H, d, *J*=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 41.3, 119.9, 127.2, 128.2, 128.5, 128.8, 129.2, 131.6, 135.0, 138.4. Anal. Calcd for $C_{11}H_7Br_3$: C, 34.87; H 1.86 found C, 34.95; H, 1.85.

To a solution of 1-bromo-2-dibromomethyl naphthalene (1.89 g, 5 mmol) in 200 ml EtOH, a solution of $AgNO_3$ (1.7 g, 10 mmol) in 50 ml water was added and resulting solution was refluxed. After 75 min green precipitate was filtered by suction from hot solution. White crystals appeared upon concentration under reduced pressure and crystals were washed with cold EtOH:H_2O (4:1) to obtain 1-bromo-2-naphthaldehyde (**3k**) quantitatively. Analytical data were in agreement with published values.[18]

4.2. General procedure for the synthesis of protected benzoins

To a solution of 5 mmol diketone and 5 mmol of aromatic aldehyde in 3 ml DMF was added 0.2 equiv. of KCN (the course of reaction generally was not affected by the amount and source of DMF). The reaction was monitored by TLC. After completion of reaction, the mixture was directly subjected to chromatography through to a pad of silica to remove DMF and side products and eluted with 1:7 EtOAc:hexane. Evaporation of the solvent with rotary evaporator followed by high vacuum furnished the desired product. For some reactions, the product was pure enough for most purposes. Otherwise, products were purified with a second column chromatography with 1:7 EtOAc:hexane as eluent or crystallized from a mixture of EtOAc:Hexane.

4.2.1. 1-(2-Trifluoromethylphenyl)-2-oxo-2-phenylethyl benzoate (4a). Colorless viscous oil (1.82 g), ^{1}H NMR ($CDCl_3$) δ 7.32–7.38 (4H, m), 7.41–7.53 (6H, m), 7.72 (1H, d, *J*=7.6 Hz), 7.86 (2H, d, *J*=8.2 Hz), 7.98 (2H, d, *J*=8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 73.1 (1.5 Hz long range

coupling is observable), 127.0 (q, J=5.5 Hz), 127.1 (q, J=273 Hz), 129.7 (q, J=30 Hz), 128.7, 129.10, 129.17, 129.8, 130.6, 131.2, 132.7, 132.8, 133.6, 133.9, 135.0, 165.4, 193.2. Anal. Calcd for $C_{22}H_{15}F_3O_3$: C, 68.75; H 3.93 found C, 68.88; H, 4.07.

4.2.2. 1-(2-Fluorophenyl)-2-oxo-2-phenylethyl benzoate (4b). White solid (1.66 g), mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.03–7.11 (2H, m), 7.25–7.31 (1H, m), 7.34–7.38 (5H, m), 7.44–7.54 (3H, m), 7.93 (2H, m), 8.03 (2H, m); ^{13}C NMR ($CDCl_3$) δ 70.7, 116.4 (d, J=22 Hz), 121.8 (d, J=13 Hz), 125.2 (d, J=2.7 Hz), 128.7, 128.9, 129.12, 129.7, 130.4, 130.5 (d, J=1.9 Hz), 131.7 (d, J=8.2 Hz), 133.6, 134.0, 134.7, 160.5 (d, J=250 Hz), 165.9, 192.8. Anal. Calcd for $C_{21}H_{15}FO_3$: C, 75.44; H 4.52 found C, 75.45; H, 4.61.

4.2.3. 1-(2-Bromophenyl)-2-oxo-2-phenylethyl benzoate (4c). White solid (1.88 g), mp 110–111 °C; MS(EI), m/z 394–396 (M^+, <2), 289 (32), 183–185 (100), 155–157 (35), 105 (100), 77 (100); ^{1}H NMR ($CDCl_3$) δ 7.17 (1H, m), 7,25 (1H, m), 7,34–7,48 (8H, m), 7,92 (2H, d, J=7.3 Hz), 8.02 (2H, d, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 76.8, 125.1, 128.5, 128.7, 129.10, 129.17, 129.7, 130.4, 131.0, 131.3, 133.6, 133.90, 133.98, 134.2, 134.9, 165.7, 193.3. Anal. Calcd for $C_{21}H_{15}BrO_3$: C, 63.81; H 3.83 found C, 63.84; H, 3.83.

4.2.4. 1-(2-Methylphenyl)-2-oxo-2-phenylethyl benzoate (4d). White solid (1.54 g), mp 133–134 °C; ^{1}H NMR ($CDCl_3$) δ 2.57 (3H, s, Me), 7.19–7.23 (1H, m), 7.27–7.29 (2H, m), 7.38–7.47 (5H, m), 7.52–7.59 (2H), 7.90 (2H, d, J=7.4 Hz), 8.13 (2H, d, J=7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 19.9, 75.8, 127.1, 128.7, 129.0, 129.8, 129.9, 130.4, 131.6, 132.8, 133.5, 133.6, 135.5, 137.5, 166.1, 194.1. Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49 found C, 79.82; H, 5.45.

4.2.5. 1-(3,5-Dimethoxyphenyl)-2-oxo-2-phenylethyl benzoate (4e). White solid (1.56 g), mp 136–137 °C; ^{1}H NMR ($CDCl_3$) δ 3.70 (6H, s), 6.37 (1H, t, J=2 Hz), 6.63 (2H, d, J=2 Hz), 6.91 (1H, s), 7.31–7.39 (4H, m), 7.44–7.52 (2H, m), 7.93 (2H, d, J=7.4 Hz), 8.05 (2H, d, J=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 55.8, 78.3, 101.5, 107.1, 128.8, 129.1, 129.2, 129.8, 130.4, 133.8, 133.9, 135.1, 136.1, 161.6, 166.3, 193.9. Anal. Calcd for $C_{23}H_{20}O_5$: C, 73.39; H 5.36 found C, 73.27; H, 5.48.

4.2.6. 1-(3,5-Dimethoxy-4-acetoxyphenyl)-2-oxo-2-phenylethyl benzoate (4f). White solid (1.85 g), mp 141.5–142 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (3H, s), 3.75 (6H, s), 6.70 (2H, s), 6.91 (1H, s), 7.92 (2H, d, J=8.4 Hz), 8.04 (2H, 8.3); ^{13}C NMR ($CDCl_3$) δ 20.7, 56.5, 77.9, 105.7, 128.7, 129.0, 129.1, 129.7, 129.9, 130.4, 132.1, 133.6, 133.8, 135.2, 153.0, 166.0, 168.2, 193.5. Anal. Calcd for $C_{25}H_{22}O_7$: C, 69.12; H, 5.10 found C, 69.28; H, 5.15.

4.2.7. 1-(2-Pyridyl)-2-oxo-2-phenylethyl benzoate (4g). White solid (1.24 g), mp 125–126 °C; ^{1}H NMR ($CDCl_3$) δ 7.16–7.2 (1H, m), 7.35–7.39 (4H, m), 7.44–7.55 (2H, m), 7.89 1H, d, J=7.8 Hz), 7.64–7.69 (1H, m), 8.05 (2H, d, J=8.4 Hz), 8.1 (2H, d, J=8.5 Hz), 8.52 (1H, d, J=4.2 Hz). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41 found C, 75.44; H, 5.08; N, 4.35.

4.2.8. 1-Phenyl-2-oxo-2-ferrocenylethyl benzoate (4h). Red solid (1.89 g), mp 146.5–147 °C; MS(EI), m/z 423 (M^+, 100), 213 (100), 185 (46), 153 (26), 129 (34), 105 (60), 77 (36); ^{1}H NMR ($CDCl_3$) δ 4.1 (5H, s), 4.34 (1H, s), 4.41 (1H, s), 4.58 (1H, s), 4.82 (1H,m), 6.58 (1H, s), 7.19–7.37 (5H, m), 7.46–7.51 (3H, m), 8.06 (2H, d, J=7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 70.0, 70.1, 72.5, 72.6, 76.4, 79.2, 128.6, 129.1, 129.3, 129.5, 130.1, 130.4, 133.4, 135.6, 165.9, 197.7. Anal. Calcd for $C_{25}H_{20}FeO_3$: C, 70.77; H, 4.75 found C, 70.62; H, 4.78; HRMS Calcd: 424.0761, found: 424.0762.

4.2.9. 2-(2-Naphthyl)-2-oxo-1-(2-naphthyl)ethyl 2-naphthoate (4i). White solid (1.79 g), mp 150–151 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.43 (6H, m), 7.61–7.79 (9H, m), 7.94–7.96 (1H, m), 7.56–8.05 (2H, m), 8.50 (1H, s), 8.60 (1H, s); ^{13}C NMR ($CDCl_3$) δ 78.5, 124.8, 125.9, 126.1, 126.8, 126.9, 127.0, 127.2, 128.11, 128.17, 128.5, 128.6, 128.7, 128.9, 129.2, 129.5, 129.9, 130.1, 131.17, 131.91, 132.1, 132.6, 132.8, 132.9, 133.8, 134.0, 136.0, 136.1, 166.3, 193.6. Anal. Calcd for $C_{33}H_{22}O_3$: C, 84.96; H, 4.75 found C, 84.91; H, 4.88.

4.2.10. 2-(2-Naphthyl)-2-oxo-1-phenylethyl 2-naphthoate (4j). White solid (1.66 g), mp 169–171 °C (decompose); ^{1}H NMR ($CDCl_3$) δ 7.21 (1H, s), 7.28–7.38 (3H, m), 7.43–7.50 (4H, m), 7.57–7.59 (2H, m), 7.72–7.80 (4H, m), 7.84–7.88 (2H, m), 7.94–7.97 (1H, m), 8.04–8.07 (1H, m), 8.49 (1H, s), 8.62 (1H, s); ^{13}C NMR ($CDCl_3$) δ 78.3, 124.7, 125.9, 126.9, 127.10, 127.18, 128.12, 128.14, 128.5, 128.6, 128.94, 128.98, 129.1, 129.5, 129.6, 129.8, 130.1, 131.0, 132.0, 132.6, 132.8, 132.9, 134.5, 136.0, 136.1, 166.3, 193.6. Anal. Calcd for $C_{29}H_{20}O_3$: C, 83.63; H, 4.84 found C, 83.37; H, 4.74.

4.2.11. 2-(2-Naphthyl)-2-oxo-1-(1-bromo-2-naphthyl)-ethyl 2-naphthoate (4k). White solid (1.99 g), mp 153.5–154 °C; ^{1}H NMR ($CDCl_3$) δ 7.39–7.55 (6H, m), 7.61 (1H, d, J=8.6 Hz), 7.70–7.98 (8H, m), 7.99–8.06 (3H(2H+CH), m), 8.33 (1H, d, J=8.5 Hz), 8.62 (1H, s), 8.64 (1H, s); ^{13}C NMR ($CDCl_3$) δ 78.4, 124.5, 125.8, 126.1, 126.4, 126.9, 127.0, 127.2, 128.10, 128.14, 128.19, 128.4, 128.61, 128.66, 128.7, 128.8, 129.0, 129.1, 129.2, 129.8, 130.2, 131.3, 132.1, 132.2, 132.7, 132.8, 132.9, 135.1, 136.1, 136.3, 166.3, 194.0. Anal. Calcd for $C_{33}H_{21}BrO_3$: C, 72.67; H 3.88 found C, 72.41; H, 3.93.

4.2.12. 2-(Ferrocenyl)-2-oxo-1-(1-bromo-2-naphthyl)-ethyl 2-naphthoate (4l). Red solid (1.94 g), mp decompose >190 °C; ^{1}H NMR ($CDCl_3$) δ 4.13 (5H, s), 4.33 (1H, s), 4.41 (1H, s), 4.63 (1H, s), 4.88 (1H, s), 6.83 (1H, s), 7.35–7.51 (4H, m), 7.62–7.64 (1H, m), 7.77–7.88 (6H, m), 7.97 (1H, br s), 8.06–8.09 (1H, m), 8.63 (1H, s); ^{13}C NMR ($CDCl_3$) δ 70.0, 70.2, 70.65, 72.5, 72.6, 76.5, 79.5, 125.9, 126.3, 126.8, 126.9, 127.1, 127.3, 128.12, 128.18, 128.4, 128.5, 128.6, 129.1, 129.3, 129.8, 132.0, 132.92, 132.96, 133.6, 133.9, 136.1, 166.1, 197.7. Anal. Calcd for $C_{33}H_{24}FeO_3$: C, 75.58; H, 4.61 found C, 75.30; H, 4.79. HRMS Calcd: 524.1074, found: 524.1066.

4.2.13. 2-(2-Methylphenyl)-1-ferrocenyl-2-oxoethyl 2-methylbenzoate (4m). Red solid (1.65 g), mp 101–102 °C; MS(EI), m/z 452 (M^+, 50), 213 (100), 185 (28),

119 (48), 91 (46); ^{1}H NMR ($CDCl_3$) δ 2.61 (3H, s, Me), 2.68 (3H, s, Me), 4.30 (5H, s), 4.40 (2H, s), 4.50 (1H, s), 4.94 (1H, s), 7.01 (1H, s), 7.2–7.32 (5H, m), 7.36–7.43 (2H, m), 8.06 (1H, m); ^{13}C NMR ($CDCl_3$) δ 19.9, 22.1, 69.8, 69.9, 70.6, 72.3, 72.6, 76.5, 76.6, 126.0, 127.0, 129.6, 130.1, 131.4, 131.5, 131.8, 132.3, 134.1, 137.3, 140.8, 167.1, 198.1. Anal. Calcd for $C_{27}H_{24}FeO_3$: C, 71.69; H, 5.35 found C, 71,51; H, 5,16. HRMS Calcd: 452.1075, found: 452.1076.

4.2.14. 2-(2-Bromophenyl)-1-(2-methylphenyl)-2-oxoethyl 2-bromobenzoate (4n). White solid (1.68 g), mp 115–116 °C; ^{1}H NMR ($CDCl_3$) δ 7.19–7.27 (3H, m), 7.3–7.5 (5H, m), 7.56–7.60 (2H, m), 7.68 (1H, d, J=7.5 Hz), 7.83 (1H, d, J=7.5 Hz), 8.04 (1H, d, J=6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.0, 78.6, 122.7, 125.1, 126.0, 127.4, 128.2, 129.2, 130.7, 131.1, 131.5, 132.02, 132.1, 132.4, 133.1, 133.2, 133.8, 134.7, 135.7, 139.0, 165.1, 196.2. Anal. Calcd for $C_{22}H_{16}Br_2O_3$: C, 54.13; H, 3.30 found C, 54.44; H, 3.68.

4.2.15. 2-(2-Chlorophenyl)-1-(2-methylphenyl)-2-oxoethyl 2-chlorobenzoate (4o). White solid (1.64 g), mp 95 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (3H, s, Me), 7.04–7.39 (10H, m), 7.49–7.52 (1H, m), 7.73 (1H, d, J=1.9 Hz), 7.96 (1H, dd, J=7.6, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 20.9, 76.2, 126.0, 126.8, 127.6, 129.0, 129.5, 130.4, 130.5, 130.9, 131.50, 131.52, 132.0, 132.1, 132.4, 133.1, 134.6, 134.8, 135.7, 139.0, 164.7, 196.1. Anal. Calcd for $C_{22}H_{16}Cl_2O_3$: C, 66.18; H, 4.04 found C, 66.07; H, 4.25.

4.2.16. 2-(2-Fluorophenyl)-1-(2-methylphenyl)-2-oxoethyl 2-fluorobenzoate (4p). White solid (1.32 g), mp 94 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (3H, s, Me), 6.92–6.97 (1H, m), 7.04–7.27 (8H, m), 7.43–7.54 (2H, m), 7.72–7.74 (1H, m), 7.96–7.99 (1H, m); ^{13}C NMR ($CDCl_3$) δ 20.8, 72.8, 116.2 (d, J=22 Hz), 117.4 (d, J=22 Hz), 118.4 (d, J=9.5 Hz), 121.1 (d, J=14.1 Hz), 124.2 (d, J=3.6 Hz), 125.0 (J=3.6 Hz), 125.9, 128.7, 130.1, 130.2, 131.4 (d, J=8.3 Hz), 131.9, 132.0, 132.9, 135.1 (d, J=9 Hz), 135.6, 160.4 (d, J=248 Hz), 162.7 (d, J=260 Hz), 163.5 (d, J=3.7 Hz), 195.8. Anal. Calcd for $C_{22}H_{16}F_2O_3$: C, 72.13; H, 4.40 found C, 71.99; H, 4.58.

4.2.17. 2-(2-Pyridyl)-1-(2-fluorophenyl)-2-oxoethyl 2-pyridoate (4q). White solid (1.09 g), mp 121–122 °C; ^{1}H NMR ($CDCl_3$) δ 6.94–7.04 (2H, m), 7.12–7.25 (1H, m), 7.31–7.45 (3H, m), 7.65–7.76 (2H, m), 7.85 (1H, s), 7.98 (1H, d, J=7.8 Hz), 8.09 (1H, d, J=7.7 Hz), 7.86 (1H, d, J=4.4 Hz), 8.70 (1H, s); ^{13}C NMR ($CDCl_3$) δ 74.8, 118.5 (d, J=21 Hz), 123.8 (d, J=14 Hz), 125.2, 126.8 (d, J=3.6 Hz), 128.0, 129.5, 130.0, 133.0 (d, J=2.7 Hz), 133.5 (d, J=8.3 Hz), 139.3, 139.4, 149.9, 151.4, 152.5, 153.6, 163.3 (d, J=250 Hz), 166.8, 195.6. Anal. Calcd for $C_{19}H_{13}FN_2O_3$: C, 67.85; H, 3.90; N, 8.33 found C, 67.95; H, 4.01; N, 8.17.

4.2.18. 2-(2-Pyridyl)-1-(2-trifluoromethylphenyl)-2-oxoethyl 2-pyridoate (4r). White solid (1.49 g), mp 113–114.5°C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.34 (1H, m), 7.34–7.47 (4H, m), 7.69–7.75 (3H, m), 7.93 (1H, s), 8.0–8.06 (2H, m), 8.47 (1H, d, J=4 Hz), 8.68 (1H, d, J=3 Hz); ^{13}C NMR ($CDCl_3$) δ 73.3 (1.7 Hz long range coupling is observable), 123.0 (q, J=272 Hz), 121.8, 124.5, 125.9 (q, J=5.5 Hz), 126.0, 126.5, 128.1, 128.7 (q, J=30 Hz), 129.3, 131.11, 131.29, 135.8, 135.9, 146.4, 148.0, 149.0, 150.0, 163.0, 192.7. Anal. Calcd for $C_{20}H_{13}F_3N_2O_3$: C, 62.18; H, 3.39; N, 7.25 found C, 61.71; H, 3.62; N, 7.15.

4.2.19. 1-(2-Methylphenyl)-2-oxo-2-phenylethyl ferrocenecarboxylate (16). Red solid (1.60 g, 73%), MS(EI), m/z 438 ($M^{+\cdot}$, 5), 230 (82), 213 (100), 185 (23), 166 (28), 129 (37), 104 (32), 76 (44); ^{1}H NMR ($CDCl_3$) δ 2.48 (3H, s), 4.24 (5H, s), 4.33 (2H, s), 4.78 (1H, s), 4.82 (1H, s), 7.10–7.25 (4H, m), 7.28–7.5 (4H, m), 7.86 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.0, 70.8, 71.1, 71.20, 71.26, 72.0, 72.1, 75.4, 127.7, 129.73, 129.79, 130.4, 130.6, 132.39, 133.9, 134.2, 136.7, 138.3, 172.3, 195.8. Anal. Calcd for $C_{26}H_{22}FeO_3$: C, 71.07; 5.01 found C, 71.36; H, 5.17.

4.3. General procedure for the hydrolysis of protected benzoins

Benzoins were obtained according to following procedure. Compound **12d** was isolated in 85% yield and data was in agreement with the published values.[13]

4.3.1. 2-Hydroxy-2-ferrocenyl-1-phenylethan-1-one (12a). 0.5 g (1.18 mmol) **3h** was dissolved in 50 ml MeCN and argon was bubbled through the solution for 15 min to remove the oxygen from medium. While refluxing the solution, 0.06 g NaOH in 20 ml of water was added dropwise in 15 min. Resulting solution was refluxed for an additional 30 min and concentrated under reduced pressure to get slurry, which was then extracted with EtOAc. Organic phase was dried over $MgSO_4$ and concentrated to obtain brownish-red solid **12a** with 87% yield. During reaction or work up some contamination of the product with **15** might occur. This oxidation product can easily be separated by flash column chromatography. Red solid (0.32 g), mp 107 °C; MS(EI), m/z 318 ($M^{+\cdot}$, 100), 213 (92), 185 (55), 129 (52), 121 (16), 105 (16), 77 (24); ^{1}H NMR ($CDCl_3$) δ 4.09 (5H, s), 4.47 (1H, s), 4.54 (2H, s, 1H exchangeable with D_2O), 4.66 (1H, s), 4.86 (1H, s), 5.47 (1H, s), 7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ 68.9, 69.2, 69.4, 71.6, 71.7, 76.2, 126.8, 127.2, 127.7, 139.8, 202.3. Anal. Calcd For $C_{18}H_{16}FeO_2$: C, 67,52; H, 5.03 found C, 67.62; H, 5.02.

4.3.2. 2-(2-Trifluoromethylphenyl)-2-hydroxy-1-phenylethan-1-one (12b). Hydrolysis was carried out as for **3h** except that the reaction was carried out at RT. Reaction was monitored by TLC and after all of the starting material has been consumed, mixture was worked up as above; 94% yield, white solid (0.22 g), mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 4.23 (1H, br s), 6.12 (1H, s), 6.98 (1H, d, d=6.4), 7.12–7.35 (4H, m), 7.4–7.43 (1H, m), 7.68 (1H, m), 7.76 (2H, d, J=7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 72.1, 124.6 (q, J=272 Hz), 127.0 (q, J=5.5 Hz), 129.02, 129.08 (q, J=30 Hz), 129.1, 129.4, 129.5, 133.0, 133.5, 134.3, 137.9, 198. Anal. Calcd for $C_{15}H_{11}F_3O_2$: C, 64.29; H 3.96 found C, 64.45; H, 4.13.

4.3.3. 2-(2-Fluorophenyl)-2-hydroxy-1-phenylethan-1-one (12c). 95% yield, white solid (0.26 g), mp 87 °C; ^{1}H NMR ($CDCl_3$) δ 4.44 (br s, 1H), 6.13 (s, 1H), 6.90–7.00 (2H, m), 7.08–7.19 (2H, m), 7.29–7.33 (2H, m), 7.41–7.45 (1H, m), 7.84 (2H, m); ^{13}C NMR ($CDCl_3$) δ 69.6, 116.4 (d, J=22 Hz), 125.1 (d, J=3.4 Hz), 127.0 (d, J=14.1 Hz), 129.0, 129.1, 129.5 (d, J=3.6 Hz), 130.7 (d, J=8.5 Hz),

133.5, 134.3. 160.4 (d, J=246 Hz), 198.4. Anal. Calcd for $C_{14}H_{11}FO_2$: C, 73.03; H 4.82 found C, 73.09; H, 4.91.

4.3.4. 2-(2-Fluorophenyl)-2-hydroxy-1-ferrocenylethan-1-one (18). 69% yield from **25** (two steps), mp 126.5–127.5 °C; ^{1}H NMR ($CDCl_3$) 4.01 (5H, s), 4.4 (1H, s), 4.48 (2H, m, 1H from OH), 4.63 (1H, s), 4.82 (1H, s), 5.73 (1H, d, d=5.9), 7.02–7.08 (2H, m), 7.17–7.24 (2H, m), 7.29 (1H, m); ^{13}C NMR ($CDCl_3$) δ 70.1, 70.5, 73.1, 73.2, 73.3, 74.5, 116.2 (d, J=22 Hz), 125.0 (d, J=3.3 Hz), 128.1, 129.4 (d, J=3.7 Hz), 130.5 (d, J=8.3 Hz), 160.5 (d, J=245 Hz), 202.6. Anal. Calcd for $C_{18}H_{15}FFeO_2$: C, 63.89; H 4.47 found C, 63.64; H, 4.24; HRMS Calcd: 338.0405, found: 338.0396.

4.4. General procedure for the oxidation of benzoins

12a was oxidized according to a known procedure[17] with 81% yield to obtain **15**. All analytical results were in agreement with published data.[17f,19]

4.4.1. 1-(2-Fluorophenyl)-2-phenylethane-1,2-dione (17). (87% yield); yellowish-white solid; MS(EI), m/z 228 (M^+, 4), 123 (44), 105 (100), 95 (24), 77 (59); ^{1}H NMR ($CDCl_3$) δ 7.02–7.07 (1H, m), 7.25–7.29 (1H, m), 7.42–7.46 (2H, m), 7.53–7.59 (2H, m), 7.89 (2H, m), 7.95–7.99 (1H, m); ^{13}C NMR ($CDCl_3$) δ 116.9 (d, J=21.6 Hz), 122.9 (d, J=10.8 Hz), 125.2 (d, J=3.4 Hz), 129.2, 130.2, 131.2, 132.5, 134.7, 136.83 (d, J=8.7 Hz), 163.2 (d, J=257 Hz), 191.7, 192.7. Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97 found C, 73.71; H, 4.19.

Acknowledgements

Financial support from Middle East Technical University (BAP-2003), the Scientific and Technical Research Council of Turkey (TUBITAK), Turkish Academy of Science (TÜBA) and Turkish State Planning Organization (DPT) is gratefully acknowledged.

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