

An efficient synthesis of ferrocenyl substituted 1,5-diketone and cyclic α , β -unsaturated ketones under ultrasound irradiation

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Received 13 January 2004; accepted 2 March 2004

Abstract

Michael reactions of deoxybenzoin or dibenzyl ketone with ferrocenyl substituted chalcones catalyzed by sodium hydroxide under ultrasound irradiation can afford the corresponding Michael adducts with excellent yields. It presents a convenient, efficient and simple method for the preparation of ferrocenyl substituted 1,5-diketone compounds in the presence of ultrasound irradiation. In addition, the formation of cyclic, α , β -unsaturated ketones via the reactions of dibenzyl ketone with ferrocenyl substituted chalcones were found, and characterized by X-ray crystal structure analysis.

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Keywords: Ferrocene; Chalcone; 1,5-Diketone; Michael reaction; Ultrasound; Crystal structure

1. Introduction

1,5-Diketone compounds are very important intermediates in organic syntheses due to their applications as fundamental starting materials in the preparation of many heterocyclic [1–3] and polyfunctional compounds [4–7]. These compounds, such as α , β -oligopyridines [4], terpyridylferrocene and bis(terpyridinylferrocene) [5] have potential applications in coordination chemistry, molecular sensing, catalytic reactions, the chemical modification of electrodes, and redox active self-assembly devices. In past reports, one of the methods to prepare 1,5-diketone compounds is via the Michael reactions of deoxybenzoin or dibenzyl ketone with chalcones using conventional heating method and employing strong organic bases such as ethoxide [8] or methoxide [9] as catalyst. However, these methods more or less have the following limitations: the use of strong organic base which is moisture-sensitive and is not

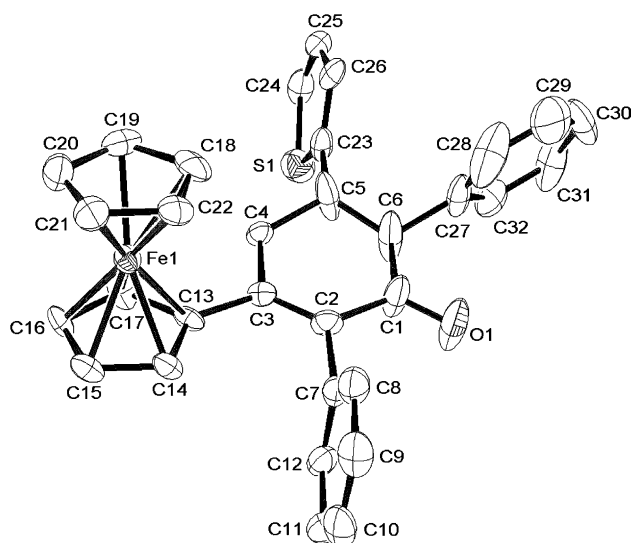
available directly; longer reaction time and complicated manipulation et al.

Recently, ultrasound has been utilized in organic synthesis as a new reaction media. Compared with traditional heating methods, this approach is more convenient, efficient and can be controlled easily. It has been reported that a large number of organic reactions could be facilitated by ultrasound irradiation with higher yields, shorter reaction time and milder conditions [10–21].

The bright prospects of the applications of ultrasound in organic synthesis spurred us to investigate organic reactions which are operated under ultrasound irradiation. In past reports, Ma and co-workers [22] had described the syntheses of 1,5-diketone derivatives such as **1** by Michael reaction of acetophenone with ferrocenylenones. However, to our knowledge, there is no report about the reaction of deoxybenzoin and dibenzyl ketone with ferrocenyl substituted chalcones (**1**). Herein, we wish to report the syntheses of a new series of ferrocenyl substituted 1,5-diketones using deoxybenzoin and dibenzyl ketone as Michael donors and promoted by inorganic base under ultrasound irradiation, and afford the corresponding Michael adducts with excellent yields. At the same time, some cyclic α , β -unsaturated ketones

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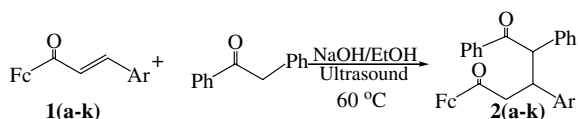
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Fig. 1. X-ray crystal structure of **3a**.

were obtained via the reactions of dibenzyl ketone with **1**, its structure was characterized by X-ray crystal structure analysis (Fig. 1).

2. Results and discussion

In our initial research, we found that the Michael reactions of deoxybenzoin with **1** (Scheme 1) could be performed easily and the reactions proceeded efficiently simply by irradiating the mixture of substrates in the presence of ultrasound irradiation at 60 °C, and afforded the corresponding Michael adducts with excellent yields of 81–96%. All the results are summarized in Table 1. In the meantime, compound **1** (**a–k**) could transform into compound **2** (**a–k**) almost completely when an excess of deoxybenzoin (two equivalent) was added. However, when we stirred the mixture of 1-ferrocenyl-3-phenylprop-2-ene-1-one (**1d**) (0.5 mmol), deoxybenzoin (1 mmol), sodium hydroxide (2 mmol) and ethanol (30 ml) at 60 °C for 2 h without the involvement of ultrasound irradiation, we could only get 69% yield of compound **2d**. And the yield of the **2d** was not increase greatly even prolonged the reaction time or increased the temperature of the reaction mixture (It can lead the decomposition of **1** at higher temperature in the base conditions). It indicates obviously that the participation of ultrasound irradiation plays a very important role for



Scheme 1.

Table 1

The Michael reactions of deoxybenzoin with ferrocenyl substituted chalcones catalyzed by sodium hydroxide at 60 °C under ultrasound irradiation

Entry	Reactant	Ar	Time (h)	Product	Yield ^a (%)
1	1a	4-NO ₂ -C ₆ H ₄	1	2a	89
2	1b	4-Cl-C ₆ H ₄	1	2b	93
3	1c	2-Cl-C ₆ H ₄	2	2c	86
4	1d	C ₆ H ₅	2	2d	92
5	1e	4-CH ₃ -C ₆ H ₄	2	2e	85
6	1f	4-OCH ₃ -C ₆ H ₄	2	2f	93 ^b
7	1g	3,4-O ₂ CH ₂ -C ₆ H ₃	2	2g	82 ^b
8	1h	2-C ₅ H ₄ N	2	2h	85
9	1i	2-C ₄ H ₃ S	2	2i	81
10	1j	3-C ₄ H ₃ S	1	2j	96 ^b
11	1k	2-C ₄ H ₃ O	1	2k	85 ^b

^a Isolated yields.

^b The amount of solvent-ethanol used is 5 ml (others are 30 ml).

accelerating the reaction rate and improving the yields. In addition, we found that reaction rate could also be accelerated if the amount of solvent (ethanol) has been decreased from 30 to 5 ml, which might be due to the concentration of substrates and catalyst enhanced.

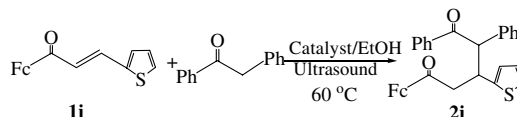
Compared with literature reported methods which are operated under traditional homogeneous conditions catalyzed by ethoxide, current methods have a series of advantages, such as mild conditions, short reaction time, excellent yields, low cost and manipulative simplicity.

Furthermore, we discovered that the Michael reactions could also be promoted effectively by potassium hydroxide and lithium hydroxide since the reaction of chalcone **1i** with deoxybenzoin could afford Michael adduct **2i** with both excellent yields of 88% under ultrasonication (Table 2). At the same time, we can see from Table 2 that strong base can accelerate the reaction rate evidently since potassium hydroxide only takes 0.5 h to drive the above Michael reaction to completion, while under the catalysis of potassium carbonate, only 42% yield of product **2i** was attained even after reacting for 1 h.

In the following work, the reactions of dibenzyl ketone with various ferrocenyl enones (**1b**, **1d**, **1e**, **1g**, **1i**) in

Table 2

The Michael reaction of deoxybenzoin with chalcone (**1i**) promoted by different bases at 60 °C under ultrasound irradiation



Entry	Catalyst	Time (h)	Yield ^a (%)
1	K ₂ CO ₃	1	42
2	LiOH	1	88
3	KOH	0.5	88

^a Isolated yields.

the presence of sodium hydroxide have been investigated. For example, when the mixture of chalcone **1b** (0.5 mmol), dibenzyl ketone (1.2 mmol), sodium hydroxide (2 mmol) and ethanol (5 ml) were irradiated at 60 °C for 1 h, the red solid turned orange–yellow eventually and obtained the corresponding Michael adduct **2l** with excellent yield of 89% after subsequent simple manipulation. And the results are listed in Table 3.

Nevertheless, when we conducted the reactions of dibenzyl ketone with some ferrocene-containing chalcones using sodium hydroxide as catalyst (Table 4), we discovered the formation of cyclic α, β -unsaturated ketones which formed by base-induced further Aldol condensation after the first-step Michael addition. In other words, the formed Michael adducts could undergo further Aldol condensation and closed-ring products generated eventually. A case in point is the reaction of 1-ferrocenyl-3-(α -thienyl)prop-2-ene-1-one (**1i**) with dibenzyl ketone catalyzed by sodium hydroxide in the presence of ultrasound irradiation at 60 °C, we observed that the red color of the solution turned orange–yellow gradually (explain: the formation of Michael adduct requires the transformation of double-bond of chalcone into single-bond and the process leads to blue shift of absorption wavelength, which thus causes the color of mixture turn orange–yellow). However, with the prolongation of time, the color became red again (explain:

the subsequent occurrence of Aldol condensation which takes place in situ under the additive of sodium hydroxide effects a cyclic α, β -unsaturated ketone **3a** and the formation of the new cyclic compound (a new cyclic conjugate system) results in red shift of absorption wavelength and consequently explains the change of color reasonably).

At the present stage of experiments, we really was puzzled by the results we had obtained, for it was very much difficult for us to present a rational explanation for following truth: why for these chalcones bearing a five-membered heteroatomic ring (entries 1–4, Table 4) favor the formation of cyclic compounds while for other chalcones (entries 1–5, Table 3) only Michael adducts have been furnished? When we compare with the facts that two different types of products have been got for two similar substrates–chalcone **1i** (entry 5, Table 3) and chalcone **1i** (entry 1, Table 4), we could make sure that the electronic nature of the chalcone plays a dominant influence on the type of the final product.

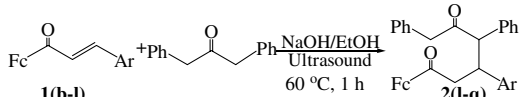
Further investigations reveal that the basicity of base used also plays a very important role for the formation of final products as well as the electronic nature of chalcone itself.

To examine the effects of different bases on the reaction, several other bases, including potassium hydroxide, lithium hydroxide and potassium carbonate, were applied to the reaction of chalcone **1 (b, i)** with dibenzyl ketone under ultrasonication. And the results are outlined in Table 5 below.

From entries 1–2 (Table 5), we can see that lithium hydroxide can also promote the cyclization of chalcone **1i** with dibenzyl ketone, although the yield (76%) is a bitter lower in contrast with the yields obtained using sodium hydroxide or potassium hydroxide as additive. In the meantime, we also found in our experiments that only Michael adduct has been yielded when we carried out the reaction of chalcone **1i** with dibenzyl ketone under the additive of potassium carbonate, and the yield

Table 3

The Michael reactions of dibenzyl ketone with ferrocenyl substituted chalcones **1** under ultrasound irradiation

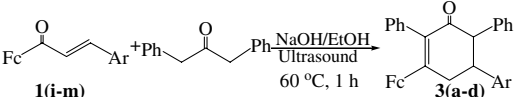


Entry	Reactant	Ar	Product	Yield ^a (%)
1	1b	4-Cl-C ₆ H ₄	2l	89
2	1d	C ₆ H ₅	2m	92
3	1e	4-CH ₃ -C ₆ H ₄	2n	81
4	1g	3,4-O ₂ CH ₂ -C ₆ H ₃	2o	91
5	1i	4-Br-2-C ₄ H ₂ S	2p	92

^a Isolated yields.

Table 4

The reactions of dibenzyl ketone with **1i–m** promoted by sodium hydroxide at 60 °C under ultrasound irradiation

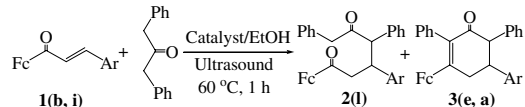


Entry	Reactant	Ar	Product	Yield ^a (%)
1	1i	2-C ₄ H ₃ S	3a	85
2	1j	3-C ₄ H ₃ S	3b	96
3	1k	2-C ₄ H ₃ O	3c	92
4	1m	3-CH ₃ -2-C ₄ H ₂ S	3d	78

^a Isolated yields.

Table 5

The reactions of chalcone **1(b, i)** with dibenzyl ketone promoted by different bases under ultrasound irradiation



Entry	Ar	Catalyst	Yield ^a (%)
1	2-C ₄ H ₃ S	LiOH	3a (76)
2	2-C ₄ H ₃ S	KOH	3a (92)
3	4-Cl-C ₆ H ₄	K ₂ CO ₃	2l (28) ^b
4	4-Cl-C ₆ H ₄	LiOH	2l (61) ^b
5	4-Cl-C ₆ H ₄	KOH	2l (46) 3e (47)

^a Isolated yields.

^b The reaction proceeded incompletely, and the existence of chalcone has been tested by TLC.

was too much lower. We can infer from it that the basicity of base is also an important factor influencing the progress of the reaction and the type of final product. Results obtained in entries 3–5 demonstrate it further that when the reaction of chalcone **1b** with dibenzyl ketone was operated under ultrasound irradiation employing potassium carbonate and lithium hydroxide as catalyst, we could achieve the corresponding Michael adduct **2l** with the yields of 28% and 61%, respectively. While when the mixture of substrates were subjected to the catalysis of potassium hydroxide, 47% yield of cyclic α , β -unsaturated ketone **3e** has been afforded apart from giving 46% yield of Michael adduct **2l**, that is to say, the formed Michael adduct **2l** could transform into cyclized ketone partially in the presence of strong base potassium hydroxide.

In summary, all the results above indicate that the basicity of the catalysts also have significant influence for determining the occurrence of the reaction and especially the final products and their ratios, which is also an equally important factor for the reactions in contrast with the electronic nature of chalcone itself. At the same time, the effects of time, temperature and ultrasound on the reaction cannot be ignored too.

3. Conclusions

In conclusion, we have developed an convenient, efficient and economical approach for the preparation of a series of new ferrocenyl substituted 1,5-diketone compounds **1** and cyclic α , β -unsaturated ketones under ultrasound irradiation. And the final products for the reactions of dibenzyl ketone with **1** are largely dependent on the following factors: the electronic nature of chalcone itself, the basicity of the base used, reaction time and temperature et al. And the influence of electronic nature of chalcone is well under way. This method proved to be an attractive alternative to existing methodologies under conventional and moisture-sensitive homogeneous base catalysis with the frequent troublesome manipulation and work-up. The one pot synthesis of the ferrocenyl substituted cyclic α , β -unsaturated ketones are underway in our laboratory, which to be continued.

4. Experimental

Melting points were determined on a XT-5A digital melting points apparatus and uncorrected. IR spectra were obtained on a Nicolet FT-IR500 spectrophotometer using KBr pellets. Elemental analyses were performed on a Carlo-Erba 1110 Elemental analysis instrument. ^1H NMR spectra were recorded on Varian Inova 400 MHz NMR spectrometer in CDCl_3 . Ultra-

sonication was performed in a KQ-250E ultrasonic cleaner with a frequency of 40 KHz and a normal power of 250 W. The reaction flask was located in the water bath of the ultrasonic cleaner, and the temperature of the water bath was controlled by inherently heating. Ferrocenyl substituted chalcones **1** are prepared as previously reported [23].

4.1. General procedure for the reactions of deoxybenzoin with ferrocenyl substituted chalcones

The mixture of ferrocenyl substituted chalcones **1** (0.5 mmol), deoxybenzoin (1 mmol), sodium hydroxide (2 mmol) and ethanol was added to a flask. Then it was immersed into the water bath of an ultrasonic cleaner at 60 °C for a special time as shown in Table 1. And the progress of the reaction is monitored by TLC. After the completion of the reaction, 30 ml water is added to the final products and stirred for a while, then it was filtered under reduced pressure and the solid was washed with water and aqueous ethanol (1:1). Further purification was accomplished by crystallization from 95% ethanol and yield product **2**.

1,2-Diphenyl-3-(4-nitrophenyl)-5-ferrocenyl-pentane-1,5-dione (2a): m.p.: 215–217 °C; IR (KBr): ν 1676, 1664 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.95 (q, 2H); 3.81 (s, 5H); 4.40 (s, 2H); 4.46 (m, 1H); 4.57 (s, 2H); 5.25 (d, $J = 11.2$ Hz, 1H); 7.26–8.11 (m, 14H); HRMS [Found: m/z , 557.1266 (M^+); Calc. for $\text{C}_{33}\text{H}_{27}\text{FeNO}_4$: M, 557.1289].

1,2-Diphenyl-3-(4-chlorophenyl)-5-ferrocenyl-pentane-1,5-dione (2b): m.p.: 190–192 °C; IR (KBr): ν 1677, 1655 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.20 (d, $J = 4.8$ Hz, 2H); 4.01 (s, 5H); 4.24 (s, 1H); 4.44 (s, 2H); 4.72 (d, $J = 10$ Hz, 2H); 5.03 (d, $J = 10$ Hz, 1H); 7.09–8.05 (m, 14H); HRMS [Found: m/z , 546.1019 (M^+); Calc. for $\text{C}_{33}\text{H}_{27}\text{ClFeO}_2$: M, 546.1049].

1,2-Diphenyl-3-(2-chlorophenyl)-5-ferrocenyl-pentane-1,5-dione (2c): m.p.: 191–193 °C; IR (KBr): ν 1674 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.16 (d, $J = 14.4$ Hz, 1H); 3.56 (s, 1H); 4.00 (s, 5H); 4.44 (s, 2H); 4.74 (s, 3H); 5.55 (d, $J = 8.4$ Hz, 1H); 6.98–7.51 (m, 11H); 8.04 (d, $J = 7.2$ Hz, 2H); HRMS [Found: m/z , 546.1011 (M^+); Calc. for $\text{C}_{33}\text{H}_{27}\text{ClFeO}_2$: M, 546.1049].

1,2,3-Triphenyl-5-ferrocenyl-pentane-1,5-dione (2d): m.p.: 198–201 °C; IR (KBr): ν 1669, 1652 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.76 (q, 1H); 2.97 (q, 1H); 3.76 (s, 5H); 4.27 (t, $J = 9$ Hz, 1H); 4.36 (s, 2H); 4.57 (d, $J = 26.4$ Hz, 2H); 5.10 (d, $J = 10.8$ Hz, 1H); 7.00–7.56 (m, 13H); 7.85 (d, $J = 8$ Hz, 2H); HRMS [Found: m/z , 512.1440 (M^+); Calc. for $\text{C}_{33}\text{H}_{28}\text{FeO}_2$: M, 512.1439].

1,2-Diphenyl-3-(4-methylphenyl)-5-ferrocenyl-pentane-1,5-dione (2e): m.p.: 203–206 °C; IR (KBr): ν 1671, 1655 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.18 (s, 3H); 2.75 (t, $J = 8.6$ Hz, 1H); 2.94 (q, 1H); 3.78 (s, 5H); 4.37 (d, $J = 10$ Hz, 3H); 4.57 (d, $J = 25.6$ Hz, 2H); 5.27 (d,

$J = 11.6$ Hz, 2H); 7.00–7.87 (m, 14H); HRMS [Found: m/z , 526.1554 (M^+); Calc. for $C_{34}H_{30}FeO_2$: M, 526.1595].

1,2-Diphenyl-3-(4-methoxyphenyl)-5-ferrocenyl-pentane-1,5-dione (2f): m.p.: 192–194 °C; IR (KBr): ν 1673, 1655 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.75 (t, $J = 10$ Hz, 1H); 2.93 (q, 1H); 3.67 (s, 3H); 3.80 (s, 5H); 4.32 (d, $J = 2.8$ Hz, 1H); 4.36 (s, 2H); 4.57 (d, $J = 24.8$ Hz, 2H); 5.24 (d, $J = 10.8$ Hz, 1H); 6.74–7.86 (m, 14H); HRMS [Found: m/z , 542.1545 (M^+); Calc. for $C_{34}H_{30}FeO_3$: M, 542.1544].

1,2-Diphenyl-3-(3,4-methylenedioxyphenyl)-5-ferrocenyl-pentane-1,5-dione (2g): m.p.: 190–193 °C; IR (KBr): ν 1672 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.73 (t, $J = 8.4$ Hz, 1H); 2.91 (q, 1H); 3.83 (s, 5H); 4.31 (d, $J = 10.4$ Hz, 1H); 4.38 (s, 2H); 4.58 (d, $J = 25.6$ Hz, 2H); 5.19 (d, $J = 10.8$ Hz, 1H); 5.81 (s, 2H); 6.64–7.88 (m, 13H); HRMS [Found: m/z , 556.1323 (M^+); Calc. for $C_{34}H_{28}FeO_4$: M, 556.1337].

1,2-Diphenyl-3-(2-pyridinyl)-5-ferrocenyl-pentane-1,5-dione (2h): m.p.: 188–190.5 °C; IR (KBr): ν 1673, 1660 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.72 (d, $J = 15.6$ Hz, 1H); 3.48 (s, 1H); 3.80 (s, 5H); 4.38 (s, 2H); 4.59 (s, 2H); 4.65 (s, 1H); 5.45 (s, 1H); 7.07–7.90 (m, 13H); 8.44 (s, 1H); HRMS [Found: m/z , 513.1359 (M^+); Calc. for $C_{32}H_{27}FeNO_2$: M, 513.1391].

1,2-Diphenyl-3-(2-thienyl)-5-ferrocenyl-pentane-1,5-dione (2i): m.p.: 223.5–225 °C; IR (KBr): ν 1674, 1652 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.82 (t, $J = 8.8$ Hz, 1H); 2.93 (q, 1H); 3.84 (s, 5H); 4.39 (s, 2H); 4.60 (d, $J = 18.4$ Hz, 2H); 4.74 (t, $J = 8.4$ Hz, 1H); 5.33 (d, $J = 11.2$ Hz, 1H); 6.79–7.93 (m, 13H); HRMS [Found: m/z , 518.0997 (M^+); Calc. for $C_{31}H_{26}FeO_2S$: M, 518.1003].

1,2-Diphenyl-3-(3-thienyl)-5-ferrocenyl-pentane-1,5-dione (2j): m.p.: 224–225.5 °C; IR (KBr): ν 1674, 1651 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.83 (t, $J = 7.2$ Hz, 2H); 3.83 (s, 5H); 4.39 (s, 2H); 4.51 (t, $J = 8.2$ Hz, 1H); 4.59 (d, $J = 14.8$ Hz, 2H); 5.32 (d, $J = 11.2$ Hz, 1H); 7.14–7.89 (m, 13H); HRMS [Found: m/z , 518.0986 (M^+); Calc. for $C_{31}H_{26}FeO_2S$: M, 518.1003].

1,2-Diphenyl-3-(2-furyl)-5-ferrocenyl-pentane-1,5-dione (2k): m.p.: 180.5–182 °C; IR (KBr): ν 1676, 1655 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.77 (d, $J = 14.8$ Hz, 1H); 2.98 (d, $J = 9.6$ Hz, 1H); 3.92 (s, 5H); 4.40 (s, 2H); 4.52 (s, 1H); 4.62 (d, $J = 15.6$ Hz, 2H); 5.32 (d, $J = 10.8$ Hz, 1H); 6.17 (d, $J = 3.2$ Hz, 2H); 7.20–7.94 (m, 11H); HRMS [Found: m/z , 502.1215 (M^+); Calc. for $C_{31}H_{26}FeO_3$: M, 502.1231].

4.2. General procedure for the reactions of dibenzyl ketone with ferrocenyl substituted chalcones

The mixture of ferrocenyl substituted chalcones **1** (0.5 mmol), dibenzyl ketone (1.2 mmol), sodium hydroxide (2 mmol) and ethanol (5 ml) was added to a flask. Then

it was immersed into the water bath of an ultrasonic cleaner at 60 °C for a special time as shown in Tables 3 and 4. And the progress of the reaction is monitored by TLC. After the completion of the reaction, 30 ml aqueous ethanol (50%) was added to the final products and stirred for a while, then it was filtered under reduced pressure and the solid was washed with water and aqueous ethanol (1:1). Further purification was accomplished by crystallization from 95% ethanol and yielded products **2 (l–p)** and **3 (a–d)**.

3-(4-Thlorophenyl)-4,6-diphenyl-1-ferrocenyl-hexane-1,5-dione (2l): m.p.: 204–206 °C; IR (KBr): ν 1718, 1652 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.58 (d, 1H); 2.80 (t, 1H); 3.43 (s, 2H); 3.77 (s, 5H); 4.23 (s, q, 2H); 4.35 (s, 2H); 4.51 (d, $J = 25.6$ Hz, 2H); 6.79 (d, $J = 5.2$ Hz, 2H); 7.15–7.38 (m, 12H); HRMS [Found: m/z , 560.1209 (M^+); Calc. for $C_{34}H_{29}ClFeO_2$: M, 560.1205]; Anal. Calc. for $C_{34}H_{29}ClFeO_2$: C, 72.81; H, 5.21; Found: C, 72.70; H, 5.18%.

3,4,6-Triphenyl-1-ferrocenyl-hexane-1,5-dione (2m): m.p.: 201.5–203 °C; IR (KBr): ν 1718, 1658 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.56 (t, $J = 9.8$ Hz, 1H); 2.91 (q, 1H); 3.43 (s, 2H); 3.74 (s, 5H); 4.25–4.35 (m, 4H); 4.49 (s, 1H); 4.59 (s, 1H); 6.73–7.42 (m, 15H); HRMS [Found: m/z , 526.1547 (M^+); Calc. for $C_{34}H_3FeO_2$: M, 526.1595].

3-(4-Methylphenyl)-4,6-diphenyl-1-ferrocenyl-hexane-1,5-dione (2n): m.p.: 209–211 °C; IR (KBr): ν 1719, 1656 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H); 2.56 (d, $J = 14.8$ Hz, 1H); 2.88 (m, 1H); 3.42 (s, 2H); 3.76 (s, 5H); 4.22 (d, $J = 10.4$ Hz, 1H); 4.33 (q, 3H); 4.49 (s, 1H); 4.58 (s, 1H); 6.74–7.40 (m, 14H); HRMS [Found: m/z , 540.1725 (M^+); Calc. for $C_{35}H_{32}ClFeO_2$: M, 540.1752].

3-(3,4-Methylenedioxyphenyl)-4,6-diphenyl-1-ferrocenyl-hexane-1,5-dione (2o): m.p.: 210–212 °C; IR (KBr): ν 1718, 1655 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.51 (d, $J = 16.4$ Hz, 1H); 2.81 (m, 1H); 3.45 (s, 2H); 3.76 (s, 5H); 4.14–4.25 (m, 2H); 4.35 (d, $J = 6.4$ Hz, 2H); 4.53 (d, $J = 38$ Hz, 2H); 5.88 (d, $J = 9.2$ Hz, 2H); 6.65–7.37 (m, 13H); HRMS [Found: m/z , 570.1494 (M^+); Calc. for $C_{35}H_{30}FeO_4$: M, 570.1493].

3-(4-Bromo-2-thienyl)-4,6-diphenyl-1-ferrocenyl-hexane-1,5-dione (2p): m.p.: 218–220 °C; IR (KBr): ν 1719, 1654 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.62 (t, $J = 1.6$ Hz, 1H); 2.79 (q, 1H); 3.54 (s, 2H); 3.84 (s, 5H); 4.36 (t, $J = 8$ Hz, 3H); 4.46 (t, $J = 9.2$ Hz, 1H); 4.56 (d, $J = 26.4$ Hz, 2H); 6.73–7.38 (m, 13H); HRMS [Found: m/z , 610.0259 (M^+); Calc. for $C_{32}H_{27}FeO_2S$: M, 610.0265].

2,6-Diphenyl-3-ferrocenyl-5-(2-thienyl)-cyclohex-2-enone (3a): m.p.: 235–238 °C; IR (KBr): ν 1655 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.23 (q, 1H); 3.38 (q, 1H); 3.88 (d, $J = 5.2$ Hz, 2H); 4.05 (q, 7H); 4.27 (s, 2H); 6.85–7.41 (m, 13H); HRMS [Found: m/z , 514.0988 (M^+); Calc. for $C_{32}H_{26}FeOS$: M, 514.1054]; Anal. Calc.

for $C_{32}H_{26}FeOS$: C, 74.94; H, 5.03; Found: C, 74.71; H, 5.09%.

2,6-Diphenyl-3-ferrocenyl-5-(3-thienyl)-cyclohex-2-enone (3b): m.p.: 212–214 °C; IR (KBr): ν 1657 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.17 (q, 1H); 3.28 (q, 1H); 3.82 (s, 1H); 3.90 (s, 2H); 4.03 (d, 6H); 4.26 (s, 2H); 7.05–7.40 (m, 13H); HRMS [Found: m/z , 514.1047 (M^+); Calc. for $C_{32}H_{26}FeOS$: M, 514.1054].

2,6-Diphenyl-3-ferrocenyl-5-(2-furyl)-cyclohex-2-enone (3c): m.p.: 234.5–237 °C; IR (KBr): ν 1655 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.17 (q, 1H); 3.29 (s, 1H); 3.69 (s, 1H); 3.85 (q, 1H); 3.98–4.15 (m, 7H); 4.26 (d, $J = 11.2$ Hz, 2H); 6.12 (d, $J = 3.2$ Hz, 1H); 6.31 (s, 1H); 7.08–7.42 (m, 11H); HRMS [Found: m/z , 498.1249 (M^+); Calc. for $C_{32}H_{26}FeO_2$: M, 498.1282]; Anal. Calc. For $C_{32}H_{26}FeO_2$: C, 77.12; H, 5.26; Found: C, 77.08; H, 5.25%.

2,6-Diphenyl-3-ferrocenyl-5-(3-methyl-2-thienyl)-cyclohex-2-enone (3d): m.p.: 208–210 °C; IR (KBr): ν 1645 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3H); 3.20 (q, 1H); 3.32 (q, 1H); 3.90 (t, 3H); 4.07 (d, 6H); 4.27 (s, 2H); 6.69–7.39 (m, 12H); HRMS [Found: m/z , 528.1183 (M^+); Calc. for $C_{32}H_{28}FeOS$: M, 528.1210].

2,6-Diphenyl-3-ferrocenyl-5-(4-chlorophenyl)-cyclohex-2-enone (3e): m.p.: 254–256 °C; IR (KBr): ν 1666 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.15 (d, 2H); 3.71 (d, 1H); 3.95 (t, 3H); 4.11 (s, 5H); 4.30 (s, 2H); 7.09–7.37 (m, 14H); Anal. Calc. for $C_{34}H_{27}ClFeO$: C, 75.22; H, 5.01; Found: C, 74.94; H, 5.06%.

4.3. X-ray crystallography

X-Ray diffraction data were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo- $K\alpha$ radiation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, and allocated the deposition numbers CCDC No. 223353 for compound **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was supported by the National Nature Science Foundation of China (No. 20172039).

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