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Solvent-free reactions of alcohols with β-dicarbonyl compounds catalyzed by iron(III) chloride

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The direct substitution of alcohols and β-dicarbonyl compounds was catalyzed with $FeCl_3$ under solvent-free conditions. The catalyst loading could be decreased to 0.01 mol% at high activities. It was shown that the reaction proceeded in two steps via the etherification of the alcohols. This method provided an easy and practical procedure for C–C bond formation. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: alcohols; green chemistry; iron; substitution

INTRODUCTION

Green chemistry has been developed extensively in the methodology of the modern organic synthesis.[1–3] Environment benignity and high efficiency are two important factors for evaluating reactions in green chemistry. Inexpensive, readily available and non-toxic iron salts, which are preferred in green chemistry,[4,5] have been applied to oxidation[6–11] and C–C bond formation[12–17] recently. Meanwhile solvent-free techniques possess several advantages: they can reduce the volume of the reaction system, enhance the efficiency of the reaction and minimize the formation of the other waste. Substitution of the alcohols with nucleophiles catalyzed by Lewis acids under neutral conditions has become a popular topic in recent years because of atom economy, compared with corresponding halids, esters and carbonates. In pioneering work one equivalent of Lewis acids is usually required due to the poor leaving ability of the hydroxyl group.[18–27] Several successful examples have appeared of the modified Trost–Tsuji reaction of the allylic alcohols with catalytic amounts of the palladium complex, whereas a base or acid is usually needed as the cocatalyst or an additive.[28–41] The cobalt species have been utilized in catalytic amounts for the substitution of allylic alcohols with 1,3-dicarbonyl compounds; however, they are not effective for the malonates.[42] Recently, the cross-dehydrogenative-coupling reaction of methylenic sp^3 C–H bond was catalyzed by copper bromide and cobalt chloride, in which the alcohols were generated from the allylic sp^3 C–H *in situ*.[43] Also, C–C bond formation of alcohols with different nucleophiles with indium chloride as the catalyst has been applied in this reaction.[44–47] Shibasaki and Rueping and co-workers developed the direct substitution of alcohol with amide by bismuth in high yields.[48,49] Beller and Jana and co-workers utilized iron as the catalyst in the substitution reactions of alcohol and diketones with high yield.[50,51] Herein, we report iron(III) chloride as a catalyst in the reaction of alcohols with β-dicarbonyl compounds under solvent-free conditions at high activities.

RESULTS AND DISCUSSION

The initial study was focused on screening of the catalytic activity. The reaction of β-ketoester (**1a**) and benzhydrol (**2a**), empolying $FeCl_3$ as a catalyst, was chosen as a model for this direct substitution of alcohols under solvent-free conditions. The donor–acceptor ratio, as well as the catalyst loading, strongly influenced the yield of the desired product (Table 1). The reaction could proceed in a 1 : 1 ratio of **1a** and **2a**, which afforded the expected product (**3a**) at 93% yield within 10 min (entry 1). Furthermore, increasing the ratio of the **2a**, the product of the substitution was obtained quantitatively, maintaining the short reaction time (entries 2 and 3). However, the excess alcohol could not promote

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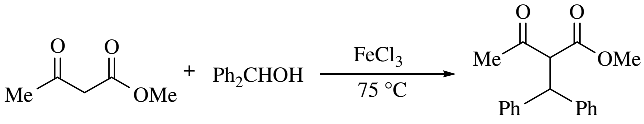
Table 1. $FeCl_3$ catalyzed the reaction of β-ketoester (**1a**) with benzhydrol (**2a**)[a]



1a **2a** **3a**

Entry	$FeCl_3$ (mol %)	**1a**:**2a** (in mmol)	Time	Yield (%)[b]
1	1	1 : 1	10 min	93
2	1	3 : 1	10 min	95
3	1	5 : 1	10 min	99
4	1	1 : 5	12 h	32
5	0.3	5 : 1	60 min	99
6	0.1	5 : 1	12 h	51

[a] Reactions were performed under solvent-free conditions. [b] Isolated yield.

the reaction because most benzhydrol was transformed to the other side products (entry 4). The excess β-ketoester prevented the side reactions of the benzhydrol and favored the direct substitution of alcohol. Decreasing the catalyst loading to 0.3 mol%, the substitution of the benzhydrol was still efficient, completing the reaction in 60 min (entry 5). Moderate yield (51%) could also be obtained using 0.1 mol% $FeCl_3$ after prolonging the reaction time (entry 6).

With these inspiring results in hand, the substitution of various alcohols with different β-dicarbonyl compounds, in the ratio of 1 : 5, catalyzed by $FeCl_3$, was surveyed under solvent-free conditions. The reactions took place smoothly to afford the corresponding products in good to excellent yields (Table 2). It was found that the malonate (**1b**) was the less reactive of three types of dicarbonyl compound [β-ketoester (**1a**), diester (**1b**) and diketone (**1c**)] in this catalytic system, owing to the lower enolizable ability. Moderate and good yields were observed with the 10 mol% $FeCl_3$ and modest yields were obtained with 1 mol% catalyst loading (entries 6–9). Among the results of the substitution of all the alcohols, the allylic alcohol (**2d**) was the most active one, reacting with β-ketoester (**1a**) or diketone (**1c**) completely within 10 min using 1 mol% catalyst. Moreover, it was carried out smoothly in the presence of 0.01 mol% $FeCl_3$ respectively (entries 5 and 15). In the case of the reaction of **1a** with **2d**, 10 times excess **1a** was required in the system to achieve the best result (76%). The alcohol **2b** showed slightly less reactivity than **2c** in these reactions because α-ferrocenylcarbonium ions possess a high degree of stabilization.[52] Particularly when **1b** was used, a large amount of starting material remained, even after increasing the catalyst loading and prolonging the reaction time (entry 7). It has been observed that the ratio of the regioisomeric products **5e** and **5f** was essentially the same regardless of whether one started with the alcohol **2e** or its regioisomer **2f**, which showed that the π-allylic cation existed in the reaction.

Detecting using GC, valuable information for the reaction mechanism was provided by the separate experiments. The time-course of the conversion of **2a** into **3a** in the presence of 0.3 mol% $FeCl_3$ at 75 °C showed that the intermediate (**6**) appeared in the reaction (Fig. 1). The reaction proceeded in two steps via the etherification of benzhydrol. Catalyzed by $FeCl_3$, the benzhydrol was changed to the dimeric ether **6** within a few minutes, which agreed with the result observed by Namboodiri and Varma,[53] and only a small amount of product was detected in the first stage. Then the desired product was generated completely from **1a** and **6** in the presence of $FeCl_3$ as the catalyst in the following step. For the further confirmation of the reaction process, the isolated ether **6** was reacted with **1a** directly catalyzed by $FeCl_3$ under the same conditions in almost quantitative yield. This suggested that the intermediate ether **6** was the mainly active species to obtain the corresponding product in high yield.

CONCLUSION

In this work, we have developed the direct substitution of the hydroxyl group in alcohols and β-dicarbonyl compounds catalyzed with $FeCl_3$ under solvent-free conditions. This method adapted the different types of β-dicarbonyl compounds including diketone, β-ketoester and diester. The readily available $FeCl_3$ could be decreased to 0.01 mol% still retaining the high catalytic efficiency. This allows an easy and practical procedure for the purpose of C–C bond formation because of the inexpensive catalyst and solvent-free condition.

EXPERIMENTAL

General procedure

$FeCl_3$, methyl acetoacetate **1a**, dimethyl malonate **2a**, acetylacetone **3a** and alcohols **2a, 2b** and **2f** were commercially available without further purification. Alcohols **2c, 2d** and **2e** were prepared according to the literature.[55–56] Melting points were recorded on an Electrothermal digital melting point apparatus and uncorrected. ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were obtained with a Bruker Avance 600 spectrometer in $CDCl_3$ with TMS as an internal standard. Infrared spectra were recorded with a Bruker Tensor 27 FT-IR spectrophotometer using KBr pellets. GC-MS was performed on a Finnigan Trace DSQ chromatograph. HRMS was determined on a Kratos Concept instrument.

Typical procedure for reaction of alcohol 2 with nucleophile 1 catalyzed by $FeCl_3$ (Tables 1 and 2)

The nucleophile **1** (5.0 mmol) was added to a mixture of $FeCl_3$ (0.1–0.0001 mmol) and alcohol **2** (1.0 mmol) under argon. After stirring, the reaction was quenched with water

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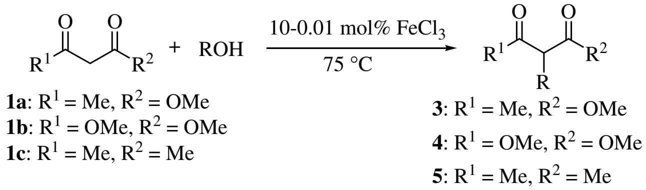
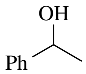
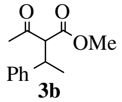
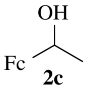
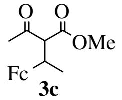
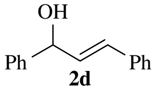
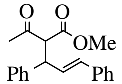
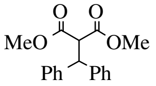
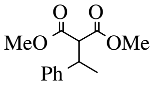
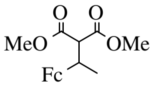
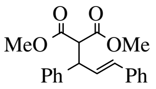
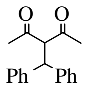
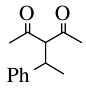
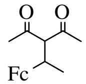
Table 2. Iron-catalyzed substitution of alcohols and β-dicarbonyl compounds[a]



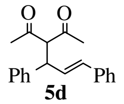
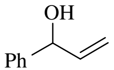
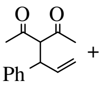
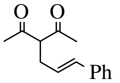
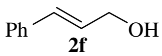
1a: R^1 = Me, R^2 = OMe
1b: R^1 = OMe, R^2 = OMe
1c: R^1 = Me, R^2 = Me

3: R^1 = Me, R^2 = OMe
4: R^1 = OMe, R^2 = OMe
5: R^1 = Me, R^2 = Me

Entry	Nucleophile	Alcohol	$FeCl_3$ (mol%)	Time	Product	Yield (%)[b]
1	**1a**	 **2b**	1	8 h	 **3b**	70
2	**1a**	 **2c**	1	8 h	 **3c**	95[c]
3	**1a**	 **2d**	1	10 min	 **3d**	96
4	**1a**	**2d**	0.1	3 h	**3d**	93
5	**1a**	**2d**	0.01	18 h	**3d**	76[d]
6	**1b**	**2a**	1	12 h	 **4a**	57(82[e])
7	**1b**	**2b**	1	24 h	 **4b**	trace[f]
8	**1b**	**2c**	1	12 h	 **4c**	53
9	**1b**	**2d**	1	12 h	 **4d**	63
10	**1c**	**2a**	1	10 min	 **5a**	99
11	**1c**	**2b**	1	12 h	 **5b**	25(80[e])
12	**1c**	**2c**	1	8 h	 **5c**	61

(*continued overleaf*)

Table 2. (*Continued*)

13	**1c**	**2d**	1	10 min	 **5d**	91
14	**1c**	**2d**	0.1	3 h	**5d**	90
15	**1c**	**2d**	0.01	18 h	**5d**	70
16	**1c**	 **2e**	1	8 h	 +  **5e** **5f**	90 (13 : 87[g])
17	**1c**	 **2f**	1	8 h	**5e** + **5f**	75 (21 : 79[g])

[a] Reactions carried out with alcohols (1 mmol), nucleophiles (5 mmol) at 75 °C under solvent-free conditions unless otherwise indicated. [b] Isolated yield. [c] Fc = Ferrocenyl. [d] Reactant ratio was **1a:2d**, 10 : 1. [e] 10 mol% $FeCl_3$ was used. [f] Detected by GC. [g] The ratio of the regioisomers were determined by GC.

(5 ml). The resulting mixture was extracted with Et_2O, and the organic layer was dried over $MgSO_4$. The crude products were purified by column chromatography on silica gel (petroleum ether–ethyl acetate).

*Methyl 3-oxo-2-(1,1-diphenylmethyl)butanoate (**3a**)*

This compound was prepared from **1a, 2a** and $FeCl_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 104.5–106.0 °C. IR (KBr): 3027, 2957, 1745, 1741, 1595, 1495, 1451, 1360, 1266, 1175, 1141, 1027, 751, 703, 628, 595, 542 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.30$–7.27 (m, 8 H), 7.19–7.18 (m, 2 H), 4.79 (d, $J = 12.6$ Hz, 1 H), 4.55 (d, $J = 12.0$ Hz, 1 H), 3.55 (s, 3 H), 2.10 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 201.73$, 168.21, 141.58, 141.17, 128.92, 128.73, 127.92, 127.64, 127.06, 126.93, 65.06, 52.57, 50.95, 30.11. MS (EI, 70 eV): m/z (%) = 282 (M^+, 0.2), 264 (43), 239 (15), 223 (14), 207 (68), 178 (31), 167 (100), 152 (36), 103 (13), 77 (6). Anal. calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.39.

*Methyl 3-oxo-2-(1-phenylethyl)butanoate (**3b**)*[57]

This compound was prepared from **1a, 2b** and $FeCl_3$ to give the product as colorless oil after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

IR (KBr): 3027, 2962, 1745, 1716, 1595, 1495, 1434, 1359, 1288, 1202, 1165, 1025, 897, 765, 702, 539 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 7.29$–7.26 (m, 4 H), 7.21–7.18 (m, 6 H), 3.80 (d, $J = 10.8$ Hz, 1 H), 3.76 (s, 3 H), 3.74 (d, $J = 10.8$ Hz, 1 H), 3.57–3.52 (m, 2 H), 3.43 (s, 3 H), 2.28 (s, 3 H), 1.92 (s, 3 H), 1.30 (d, $J = 6.6$ Hz, 3 H), 1.24 (d, $J = 6.6$ Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 202.37$, 202.36, 169.11, 168.69, 143.28, 143.02, 128.80, 128.57, 127.42, 127.37, 127.04, 126.92, 67.50, 66.90, 52.54, 52.22, 40.21, 39.83, 30.04, 29.69, 20.66, 20.16. GC-MS gave two signals corresponding to the diasteromers. MS (EI, 70 eV): m/z (%) = 220 (M^+, 0.2), 202 (78), 177 (26), 161 (15), 159 (27), 145 (100), 131 (30), 105 (96), 77 (8). MS (EI, 70 eV): m/z (%) = 220 (M^+, 0.2), 202 (78), 177 (27), 161 (20), 159 (28), 145 (100), 131 (36), 105 (97), 77 (11).

*Methyl 3-oxo-2-(1-ferrocenylethyl)butanoate (**3b**)*

This compound was prepared from **1a, 2c** and $FeCl_3$ to give the product as viscous slightly brown oil after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

IR (KBr): 2958, 2924, 1744, 1715, 1435, 1357, 1259, 1204, 1161, 1106, 1027, 820, 485 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 4.07$–3.97 (m, 18 H), 3.63 (s, 3 H), 3.50 (s, 3 H), 3.41 (d, $J = 9.6$ Hz, 1 H), 3.36 (d, $J = 9.6$ Hz, 1 H), 3.32–3.29 (m, 1 H), 3.27–3.24 (m, 1 H), 2.09 (s, 3 H), 1.85 (s, 3 H), 1.32 (br, 3 H), 1.29 (br, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 203.48$, 202.58, 169.32, 168.99, 91.39, 91.21, 68.70, 67.62, 67.58, 67.51, 67.36, 65.67, 65.55, 52.28, 52.18, 34.11, 33.92, 30.01, 29.75, 18.52, 17.91. MS (EI, 70 eV): m/z (%) = 328 (M^+, 33), 236 (100), 213 (25), 204 (42), 171 (15), 152 (45), 121 (36). HRMS (EI): calcd for $C_{17}H_{20}FeO_3$ 328.0762; found: 328.0771 (M^+).

*Methyl 3-oxo-2-(1,3-diphenyl-2-propenyl)butanoate (**3d**)*[58,59]

This compound was prepared from **1a, 2d** and $FeCl_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 63.5–64.5 °C. IR (KBr): 3029, 2954, 1746, 1717, 1494, 1446, 1357, 1248, 1214, 1161, 1027, 969, 747, 698, 538 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 7.35$–7.21 (m, 20 H), 6.48 (d, $J = 16.6$ Hz, 1 H), 6.48 (d, $J = 16.6$ Hz, 1 H), 6.32 (dd, $J = 15.7$, 8.4 Hz, 1 H), 6.27 (dd, $J = 15.7$, 8.4 Hz, 1 H), 4.32 (dd, $J = 8.6$, 4.9 Hz, 1 H), 4.30 (dd, $J = 8.6$, 4.9 Hz, 1 H), 4.15 (d, $J = 11.1$ Hz, 1 H), 4.12 (d, $J = 11.1$ Hz, 1 H), 3.73 (s, 3 H), 3.51 (s, 3 H), 2.32 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): diastereomixture (ca. 1 : 1) $\delta = 201.64$, 201.41, 168.44, 168.11, 140.43, 140.11, 136.90, 136.69, 132.02, 131.62, 129.53, 129.14, 128.99, 128.80, 128.55,

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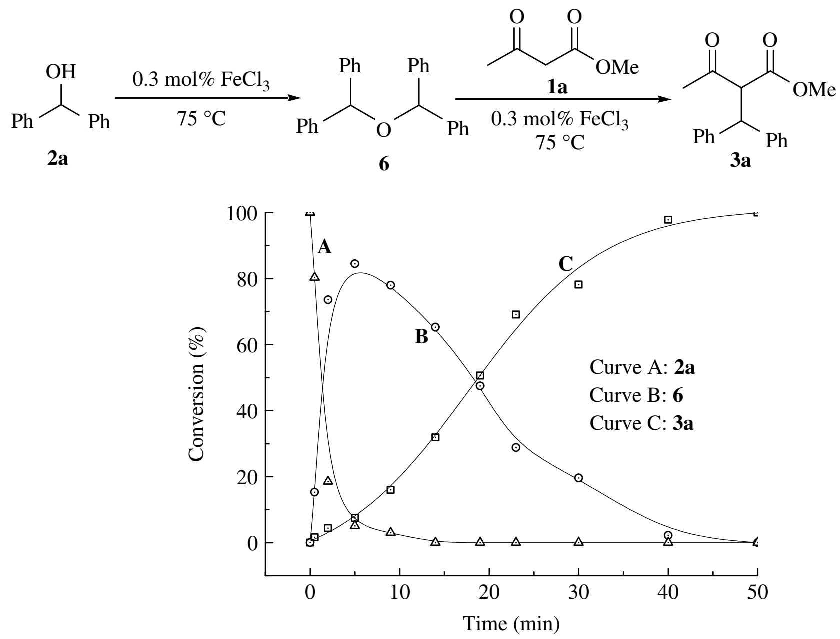

Figure 1. Time curves for conversion of **2a** into **3a**. All reactions were performed with **1a** (5 mmol) and **2a** (1 mmol) at 75 °C using 0.3 mol% $FeCl_3$ under solvent-free conditions and the conversions were detected by GC.

128.03, 127.93, 127.71, 127.63, 127.29, 127.18, 126.43, 65.50, 65.20, 52.64, 52.42, 49.05, 48.83, 30.13, 29.99. MS (EI, 70 eV): m/z (%) = 308 (M^+, 0.1), 290 (100), 265 (14), 249 (12), 233 (43), 205 (45), 193 (75), 115 (71), 91 (30).

*Dimethyl 2-(1,1-diphenylmethyl)malonate (**4a**)*[60]

This compound was prepared from **1b,2a** and $FeCl_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 88.0–89.0 °C. IR (KBr): 3030, 2958, 1761, 1733, 1500, 1436, 1269, 1144, 1022, 754, 706, 609 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.30–7.26$ (m, 8 H), 7.20–7.18 (m, 2 H), 4.79 (d, $J = 12.1$ Hz, 1 H), 4.35 (d, $J = 12.1$ Hz, 1 H), 3.56 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 168.12$, 141.23, 128.71, 127.79, 127.00, 57.31, 52.65, 51.18. MS (EI, 70 eV): m/z 298 (M^+, 17), 266 (8), 239 (18), 238 (52), 207 (53), 179 (34), 167 (100), 152 (29), 77 (7).

*Dimethyl 2-(1-ferrocenylmethyl)malonate (**4c**)*

This compound was prepared from **1b,2c** and $FeCl_3$ to give the product as viscous slightly brown oil after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

IR (KBr): 2959, 2924, 1756, 1736, 1435, 1383, 1262, 1208, 1156, 1103, 1025, 807, 485 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 4.06–3.92$ (m, 9 H), 3.64 (s, 3 H), 3.53 (s, 3 H), 3.41(d, $J = 9.6$ Hz, 1 H), 3.24 (m, 1 H), 1.35 (br, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 168.96$, 168.72, 91.03, 68.66, 67.54, 67.46, 65.82, 60.14, 52.30, 34.17, 18.04. MS (EI, 70 eV): m/z (%) = 344 (M^+, 39), 252 (53), 213 (28), 157 (33), 152 (86), 121 (100), 91 (17). HRMS (EI): calcd for $C_{17}H_{20}FeO_4$ 344.0711; found: 344.0707 (M^+).

*Dimethyl 2-(1,3-diphenyl-2-propenyl)malonate (**4d**)*[61,62]

This compound was prepared from **1b,2d** and $FeCl_3$ to give the product as a white solid after after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 93.0–95.0 °C. IR (KBr): 3032, 2950, 1754, 1599, 1494, 1435, 1322, 1264, 1228, 1178, 1143, 1020, 970, 919, 747, 696, 533 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.30–7.17$ (m, 10 H), 6.46 (d, $J = 15.7$ Hz, 1 H), 6.31 (dd, $J = 15.7$, 8.7 Hz, 1 H), 4.26 (t, $J = 10.6$ Hz 1 H), 3.94 (d, $J = 10.9$ Hz, 1 H), 3.68 (s, 3H), 3.50 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 168.26$, 167.84, 140.25, 136.91, 131.91, 129.20, 128.79, 128.54, 127.94, 127.64, 127.24, 126.46, 57.72, 52.68, 52.50, 49.25. MS (EI, 70 eV): m/z (%) = 324 (M^+, 10), 292 (12), 265 (7), 232 (22), 205 (90), 193 (100), 115 (98), 91 (26), 77 (7).

*3-(1,1-Diphenylmethyl)pentane-2,4-dione (**5a**)*[63,64]

This compound was prepared from **1c,2a** and $FeCl_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 115.0–117.0 °C. IR (KBr): 3027, 2955, 1693, 1494, 1451, 1418, 1356, 1264, 1184, 1153, 1027, 747, 702, 622, 542, 475 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.29–7.25$ (m, 8 H), 7.19–7.16 (m, 2 H), 4.82 (d, $J = 12.6$ Hz, 1 H), 4.74 (d, $J = 12.6$ Hz, 1 H), 2.01 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 203.03$, 141.34, 129.01, 127.81, 127.10, 74.62, 51.32, 29.75. MS (EI, 70 eV): m/z (%) = 266 (M^+, 0.1), 248 (4), 223 100), 205 (32), 167 (50), 165 (33), 152 (15), 103 (7), 77 (4).

3-(1-Phenylethyl)pentane-2,4-dione (**5b**)[65,66]

This compound was prepared from **1c,2b** and FeCl$_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 48.0–49.0 °C. IR (KBr): 3027, 2962, 1692, 1492, 1418, 1185, 1358, 1292, 1186, 1158, 1023, 761, 701, 533 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 7.33$–7.28 (m, 2 H), 7.24–7.20 (m, 3 H), 4.05 (d, $J = 11.4$ Hz, 1 H), 3.60 (dq, $J = 11.4$, 6.6 Hz, 1 H), 2.29 (s, 3 H), 1.86 (s, 3 H), 1.24 (d, $J = 7.2$ Hz, 3 H). ^{13}C NMR (150 MHz, CDCl$_3$): $\delta = 203.53$, 203.49, 143.10, 128.87, 127.32, 127.04, 76.76, 40.49, 29.84, 29.74, 20.90. MS (EI, 70 eV): m/z (%) = 204 (M$^+$, 0.1), 186 (6), 161 (100), 147 (32), 143 (25), 105 (44), 77 (8).

3-(1-Ferrocenylethyl)pentane-2,4-dione (**5c**)

This compound was prepared from **1c,2c** and FeCl$_3$ to give the product as a brown solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 78.0–81.0 °C. IR (KBr): 2977, 2949, 1722, 1700, 1419, 1355, 1257, 1201, 1166, 1147, 1104, 1029, 821, 483 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 4.07$–3.92 (m, 9 H), 3.51 (d, $J = 10.2$ Hz, 1 H), 3.26 (dq, J = 14.4, 7.2 Hz, 1 H), 2.08 (s, 3H), 1.79 (s, 3 H), 1.25 (d, $J = 6.6$ Hz, 3 H). ^{13}C NMR (150 MHz, CDCl$_3$): $\delta = 204.54$, 203.48, 91.55, 68.70, 67.69, 67.55, 65.25, 34.70, 32.02, 29.42, 18.36. MS (EI, 70 eV): m/z (%) = 312 (M$^+$, 8), 247 (5), 220 (100), 212 (12), 155 (43), 121 (16). Anal. calcd for C$_{17}$H$_{20}$FeO$_2$: C, 65.40; H, 6.46. Found: C, 65.15; H, 6.39.

3-(1,3-Diphenyl-2-propenyl)pentane-2,4-dione (**5d**)[67]

This compound was prepared from **1c,2d** and FeCl$_3$ to give the product as a white solid after column chromatography (petroleum ether–ethyl acetate = 10 : 1).

M.p.: 84.5–85.5 °C. IR (KBr): 3026, 2955, 1725, 1493, 1449, 1419, 1360, 1273, 1217, 1173, 1139, 1026, 971, 919, 743, 697, 530, 491 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 7.35$–7.21 (m, 10 H), 6.44 (d, $J = 16.2$ Hz, 1 H), 6.25–6.18 (m, 1 H), 4.36 (d, $J = 3.6$ Hz, 2 H), 2.27 (s, 3 H), 1.94 (s, 3 H). ^{13}C NMR (150 MHz, CDCl$_3$): $\delta = 202.89$, 202.73, 140.16, 136.62, 131.74, 129.33, 129.08, 128.54, 127.98, 127.78, 127.33, 126.42, 74.58, 49.22, 30.07, 29.79. MS (EI, 70 eV): m/z (%) = 292 (M$^+$, 4), 274 (21), 249 (3), 232 (26), 187 (20), 104 (100), 91 (9).

3-(1-Phenylallyl)pentane-2,4-dione (**5e**)[68] *and 3-cinnamylpentane-2,4-dione* (**5f**)[69]

The two compounds were prepared from **1c,2e** and FeCl$_3$ to give the mixed product after column chromatography (petroleum ether–ethyl acetate = 10 : 1). GC-MS gave two signals corresponding to the regioisomers.

3-(1-Phenylallyl)pentane-2,4-dione (**5e**)

^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 7.15$–7.11 (m, 5 H), 5.83–5.76 (m, 1 H), 5.03–4.98 (m, 2 H), 4.18 (d, $J = 12.0$ Hz, 1 H), 4.11 (dd, $J = 7.2$, 13.2 Hz, 1 H), 2.17 (s, 3 H), 1.81 (s, 3 H). MS (EI, 70 eV): m/z 216 (M$^+$, 0.1), 198 (8), 173 (100), 156 (22), 117 (43), 91 (12).

3-Cinnamylpentane-2,4-dione (**5f**)

^{1}H NMR: diastereomixture (600 MHz, CDCl$_3$) $\delta = 7.27$–7.14 (m, 10 H), 6.37 (d, $J = 15.6$ Hz, 1 H), 6.26 (d, $J = 15.6$ Hz, 1 H), 6.17–6.11 (m, 1 H), 6.03–5.97 (m, 1 H), 3.73 (t, $J = 6.6$ Hz, 1 H), 3.40 (t, $J = 6.6$ Hz, 1 H), 3.08 (t, $J = 7.8$ Hz, 2 H), 2.68 (t, $J = 7.8$ Hz, 2 H), 2.13 (s, 6 H), 2.08 (s, 6 H). MS (EI, 70 eV): m/z (%) = 216 (M$^+$, 3), 198 (10), 173 (100), 156 (13), 117 (11), 115 (23), 91 (42).

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