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$FeCl_3$-Catalyzed Addition of 1,3-Dicarbonyl Compounds to Aromatic Olefins

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Abstract: A direct, intermolecular addition of 1,3-dicarbonyl compounds to styrenes in the presence of $FeCl_3$ as an inexpensive and disposable catalyst has been developed for the straightforward and practical synthesis of arylated diketones and ketoesters. The reactions proceed under mild conditions for most substrates (50–80 °C), and no strong acid or base is required. The synthetic value of the method is demonstrated by 15 examples, including the synthesis of the current pharmaceutical drug warfarin in one step and 42% yield from commercially available substrates.

Keywords: alkenes · C–C coupling · dicarbonyl compounds · iron · styrene

Introduction

The alkylation of 1,3-dicarbonyl compounds is probably one of the most common methods of C–C coupling.[1] Haloalkanes, benzylic halides, or aldehydes (Knoevenagel condensation) are typically used as the electrophilic substrate, and a stoichiometric amount of a base is required.[2] Clearly, such methodology does not fully meet the prevailing need for more environmentally benign synthetic methods. In particular, the aspect of atom economy could be improved for this transformation. A catalytic addition of 1,3-dicarbonyl compounds to olefins would provide an alternative greener reaction pathway.[3]

Widenhoefer and co-workers disclosed recently an elegant palladium-catalyzed intramolecular hydroalkylation of alkenes with carbonyl compounds.[4] The same research group reported the addition of β-diketones to ethylene or propylene under the catalysis of platinum or palladium complexes.[5] Furthermore, Toste and co-workers described a gold(I)-catalyzed carbocyclization of 1,3-dicarbonyl-substituted alkynes,[6] and Yang and co-workers presented a nickel(II)-catalyzed Conia-ene reaction.[7] Only few examples of the intermolecular hydroalkylation of alkenes have been reported to date. Hartwig and co-workers presented a palladium-catalyzed addition of mono- and dicarbonyl compounds to conjugated 1,3-dienes. Interestingly, an enantioselective version of this reaction was also developed.[8] In 2004, Yao and Li described an effective intermolecular addition of activated methylene compounds to alkenes in the presence of $AuCl_3$/AgOTf as a combined catalyst system. Later, they were able to show that silver triflate alone acts as a catalyst for this reaction.[9] Not only catalysts based on late transition metals are suitable for reactions of this type: Nakamura et al. presented an indium-catalyzed addition of activated methylene compounds to 1-alkynes.[10]

Recently, we reported a 100% atom efficient addition of olefins with aromatic substituents to arenes under mild conditions.[11] In these reactions, $FeCl_3 \cdot 6H_2O$ catalyzed the formation of the corresponding unsymmetrical diarylethanes in good to excellent yield and with good to excellent regioselectivity. Furthermore, we described a novel $FeCl_3$-catalyzed benzylation of 1,3-dicarbonyl compounds with benzylic alcohols.[12] This research led to our interest in the direct alkylation of 1,3-dicarbonyl compounds with aromatic olefins. The resulting structural motif is found in a number of biologically active compounds (Scheme 1). For example, 4-hydroxy-3-(1-phenylbutan-3-one)-2*H*-chromen-2-one (warfarin) is a known antagonist of vitamin K and is employed as an oral anticoagulant. Tipranavir,[13] an HIV-protease inhibitor, 2,4,6-trioxo-5-(1-phenylethyl)hexahydropyrimidin-5-yl pivalate (A),[14] an analgetic agent, and 4-(5-acetyl-6-methyl-2-oxo-3-(4-phenylpiperazine-1-carbonyl)-1-(3-(trifluoromethyl)-phenyl)-1,2,3,4-tetrahydropyridin-4-yl)benzonitrile (B),[15] which is used for the treatment of heart and lung disease, also include this motif. Herein, we report a convenient $FeCl_3 \cdot 6H_2O$-catalyzed addition of styrenes to various 1,3-dicarbonyl compounds.

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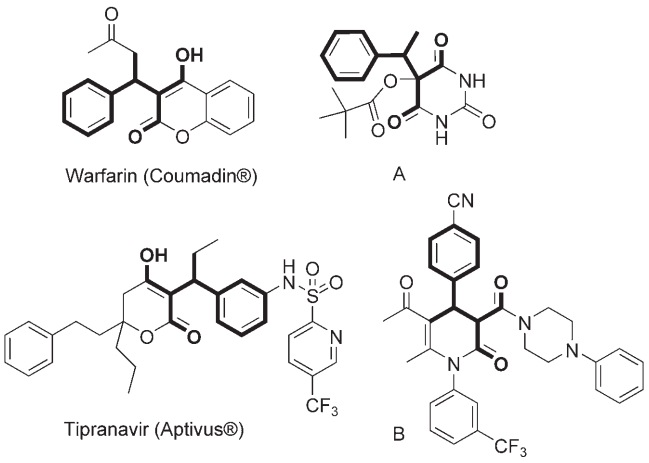
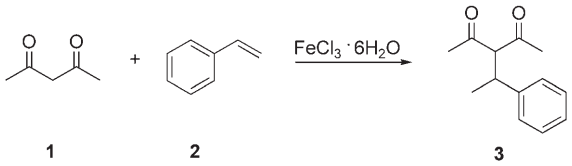


Scheme 1. Selected examples of biologically active compounds with the structural motif that results from the direct alkylation of 1,3-dicarbonyl compounds with aromatic olefins.

Results and Discussion

We chose the addition of acetylacetone (**1**) to styrene (**2**) to give 3-(1-phenylethyl)pentane-2,4-dione (**3**) as a model reaction for our investigation (Scheme 2). An initial comparison



Scheme 2. $FeCl_3$-catalyzed reaction of acetylacetone with styrene.

of $FeCl_3{\cdot}6H_2O$ (10 mol%) with Brønsted acids (HCl, TsOH) revealed that **3** was not formed or was only formed in low yield (<5%) in the presence of the latter (Table 1). Next, various parameters, including the solvent, substrate ratio, catalyst concentration, temperature, and reaction time, were examined for the $FeCl_3{\cdot}6H_2O$-catalyzed reaction. Selected results of this study are summarized in Table 1. To obtain **3** in significant yield, the choice of solvent is crucial (Table 1, entries 6 and 7). The best result was observed with 1,2-dichloroethane (DCE), in which the desired product **3** was produced in 83% yield (Table 1, entry 8). Temperatures of 80–100°C are required for smooth conversion (Table 1, entries 8–11). When the reaction was carried out at 50°C, the yield of the product dropped significantly to 34% (Table 1, entry 10). An excess of acetylacetone relative to styrene (10:1) is necessary to obtain **3** in good yield. The requirement of an excess of the diketone is not a problem in the case of cheap and readily available substrates such as **1**; however, in other cases the starting 1,3-dicarbonyl compound has to be recycled. In general, the reaction also proceeds well in the presence of 5 mol% of $FeCl_3{\cdot}6H_2O$ (Table 1, entry 18). In a number of reactions, complete conversion of styrene was observed; however, the chemoselectivity was low (Table 1, entries 3–5 and 14–16). In these experiments, the oligomerization of styrene occurred as a major side reaction. When the model reaction was carried out on a preparative (2-g) scale, a similarly successful result was obtained.[16]

Table 1. Optimization of the reaction parameters for the addition of acetylacetone (**1**) to styrene (**2**).[a]

Entry	**2**/**1**	*T* [°C]	Conv. [%][b]	Yield [%][c]
1[d]	1:40	RT	0	0
2[d]	1:40	50	8	4
3[d]	1:40	80	57	30
4[d]	1:40	100	79	45
5[d]	1:40	120	86	54
6[e]	1:10	80	3	5
7[f]	1:10	80	99	78
8	1:10	80	**99**	**83**
9	1:10	100	99	83
10	1:10	50	46	34
11	1:10	RT	0	2
12[g]	1:10	80	58	44
13[h]	1:10	80	77	62
14	1:4	80	99	66
15	1:2	80	100	47
16	1:1	80	100	20
17[i]	1:10	80	**99**	**81**
18[j]	1:10	80	**99**	**82**
19[k]	1:10	80	0	2

[a] Reaction conditions: **2** (0.5 mmol), $FeCl_3{\cdot}6H_2O$ (0.05 mmol), DCE (5 mL), 20 h. [b] The conversion was calculated with respect to styrene and determined by GC. [c] The yield was determined by GC. [d] Compound **1**: 5 mL; no DCE was used. [e] The reaction was carried out in dichloromethane (5 mL). [f] The reaction was carried out in nitromethane (5 mL). [g] Reaction time: 6 h. [h] Reaction time: 4 h. [i] $FeCl_3{\cdot}6H_2O$: 20 mol%. [j] $FeCl_3{\cdot}6H_2O$: 5 mol%. [k] $FeCl_3{\cdot}6H_2O$: 1 mol%.

A variety of 1,3-dicarbonyl compounds and alkenes were then subjected to the optimized reaction conditions ($FeCl_3{\cdot}6H_2O$ (5 mol%), excess acetylacetone (10:1), 80°C, 20 h; Table 2). In general, we found that aliphatic and aromatic 1,3-diketones (acetylacetone and dibenzoylmethane), as well as ß-ketoesters, react smoothly with styrene. The substituted styrene derivatives 4- and 2-chlorostyrene, 4-bromostyrene, and 2-, 3-, and 4-methylstyrene were also found to be suitable substrates, with the corresponding products formed in moderate to good yields (58–88%; Table 2, entries 2–8, 13, and 14). In the presence of an increased amount of the catalyst (20 mol%), the yield of the product was improved significantly in the case of 4-bromostyrene (**3e** was formed in up to 88% yield) and 4-chlorostyrene (**3d** was formed in up to 69% yield; Table 2, entries 5–8). The reaction of methyl-3-oxobutanoate with benzylideneacetone gave the cyclohexenone derivative **3h** in 78% yield by a sequential alkylation–intramolecular aldol condensation (Table 2, entry 11). The two diastereomers of **3h** were formed in a 3:1 ratio. Interestingly, the addition of **1** to indene under the catalysis of $FeCl_3$ is also possible (Table 2, entry 9). Several dicarbonyl compounds were tested for their suitability as substrates in this reaction. Dibenzoylmethane, in particular, was found to be highly reactive. The desired products were formed in yields of 75% or more in

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Table 2. $FeCl_3$-catalyzed reaction of alkenes with 1,3-dicarbonyl compounds.[a]

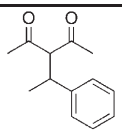
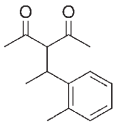
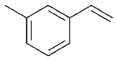
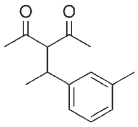
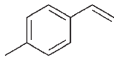
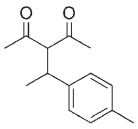
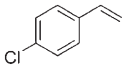
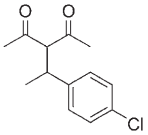
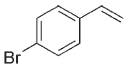
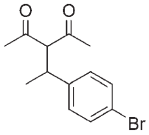
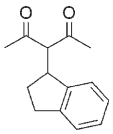
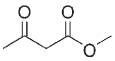
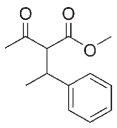
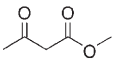
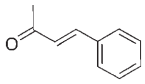
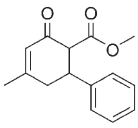
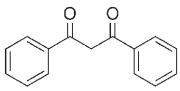
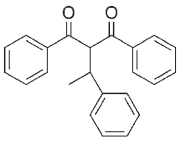
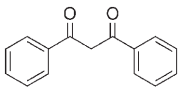
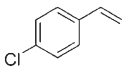
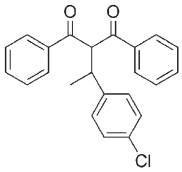
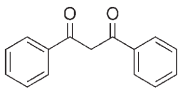
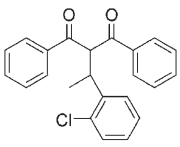
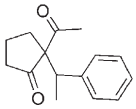
Entry	β-Diketone	Styrene	Product		Conv. [%][b]	Yield [%][c]
1				**3**	99	82
2				**3a**	100	68
3				**3b**	100	66
4				**3c**	100	58
5[d] 6[e]				**3d**	100 100	58 69
7[d] 8[e]				**3e**	100 100	48 88
9[d,f]				**3f**	96	41
10[d,g]				**3g**	88	69 (48:52)
11[d]				**3h**	100	78 (75:25)
12[f,h]				**3i**	89	76
13[d,h]				**3j**	100	75
14[d]				**3k**	90	83

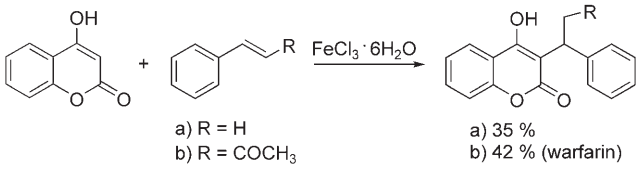
Table 2. (Continued)

Entry	β-Diketone	Styrene	Product		Conv. [%][b]	Yield [%][c]
15[d]				**31**	99	56 (46:54)

[a] Reaction conditions: styrene derivative (0.5 mmol), $FeCl_3{\cdot}6H_2O$ (5 mol%), dicarbonyl compound (5 mmol), DCE (5 mL), 80°C, 20 h. [b] The conversion was calculated with respect to the styrene derivative and determined by GC. [c] The yield was determined by GC. The ratio of diastereomers is given in parentheses. [d] $FeCl_3{\cdot}6H_2O$: 10 mol%. [e] $FeCl_3{\cdot}6H_2O$: 20 mol%. [f] Reaction time: 4 h. [g] The dicarbonyl compound (5 mL) was used as the solvent. The reaction was carried out at 120°C. [h] Temperature: 50°C.

the addition of dibenzoylmethane to styrene and 2- or 4-chlorostyrene (Table 2, entries 12–14). Furthermore, the treatment of 2-acetylcyclopentanone, an example of a cyclic dicarbonyl compound, with styrene gave the desired product in 56% yield (Table 2, entry 15).

To demonstrate the synthetic usefulness of our reaction protocol, we synthesized warfarin (coumadin), an anticoagulant drug, by the addition of 4-hydroxycoumarine to benzylideneacetone (Scheme 3). In the presence of $FeCl_3{\cdot}6H_2O$ (10 mol%) as the catalyst, the reaction gave the desired product in 42% yield, whereas the addition of 4-hydroxycoumarine to styrene was not particularly effective.



Scheme 3. Synthesis of warfarin by the $FeCl_3{\cdot}6H_2O$-catalyzed addition of 4-hydroxycoumarine to benzylideneacetone.

Conclusions

In summary, we have developed an iron-catalyzed direct addition of 1,3-dicarbonyl compounds to aromatic alkenes. This methodology is particularly attractive because of its high atom efficiency and the cheap and environmentally benign catalyst system. Typically, the reactions proceed under mild conditions (50–80°C, no strong acid or base) in good yield. The synthesis of the current drug warfarin serves as an illustration of the practical utility of our reaction protocol.

Experimental Section

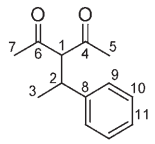
General

All reactions were performed in ACE pressure tubes. Commercial solvents were used directly without further purification. Column chromatography was carried out with silica gel (230–400 mesh ASTM) from Merck. ^{1}H NMR spectra (300.13 and 500.13 MHz) and ^{13}C NMR spectra (75.5 and 125.8 MHz) were recorded on AVANCE 300 and AVANCE 500 Bruker spectrometers. Spectra were calibrated with respect to the solvent signal ($CDCl_3$: $\delta_H=7.25$, $\delta_C=77.0$ ppm; CD_2Cl_2: $\delta_H=5.31$, $\delta_C=53.8$ ppm; [D$_6$]acetone: $\delta_H=2.05$, $\delta_C=29.8$ ppm). IR spectra were recorded of samples as nujol mulls (with KBr plates), KBr pellets, or capillary films (cap.). Mass spectra were obtained with an AMD 402/3 spectrometer (EI, 70 eV). HRMS analysis was carried out on a high-resolution magnetic-sector spectrometer. GC analysis was performed on an HP 6890 instrument equipped with an HP-5 capillary column ($L=30$ m, $d=250$ μm) and an FID detector. Quantitative GC analyses were referenced to decane as an internal standard.

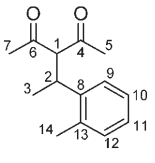
Representative Procedure

$FeCl_3{\cdot}6H_2O$ (5 mol%, 0.025 mmol), styrene (0.5 mmol), and pentane-2,4-dione (5 mmol) were dissolved in 1,2-dichloroethane (5 mL) in a pressure tube, and the resulting mixture was stirred for 20 h at 80°C. Decane (50 μL) was then added as an internal standard for GC analysis. Aliquots were taken from the reaction mixture and subjected to GC analysis (sample heated at 60°C for 3 min, then temperature increased at 12 K min^{-1} to 260°C and kept there for 10 min) to determine the yield and conversion. To isolate the product, the reaction was quenched with water, and the mixture was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the solvents were removed by distillation. The product was purified by column chromatography (*n*-hexane/ethyl acetate = 2:1).

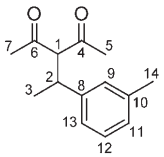
3: 3-(1-Phenylethyl)pentane-2,4-dione: IR (cap.): $\tilde{\nu}=2971$ (m), 1724 (vs), 1699 (vs), 1452 (m), 1363 (s), 1294 (m), 1148 (s), 759 (s), 701 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.19$ (d, $^3J_{3\text{-H},2\text{-H}}=6.8$ Hz, 3H, CH_3CH), 1.81 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.52–3.62 (dq, $^3J_{2\text{-H},3\text{-H}}=6.8$ Hz, $^3J_{2\text{-H},1\text{-H}}=11.3$ Hz, 1H, 2-H), 4.02 (d, $^3J_{1\text{-H},2\text{-H}}=11.3$ Hz, 1H, 1-H), 7.15–7.30 ppm (m, 5H, 9-H, 10-H, 11-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.8$ (C3), 29.7 (CH_3), 29.8 (CH_3), 40.4 (C2), 76.6 (C1), 126.9 (C11), 127.2 (C9), 128.8 (C10), 142.9 (C8), 203.4, 203.5 ppm (C4, C6); MS (EI): *m*/*z* (%) = 161 (100) $[M-COCH_3]^+$, 147 (34), 129 (10), 105 (31), 91 (10), 77 (17) $[C_6H_5]^+$; GC: $t_R=15.47$ min.



3a: 3-(1-*o*-Tolylethyl)pentane-2,4-dione: $R_f=0.41$ (*n*-hexane/EtOAc = 2:1); IR (cap.): $\tilde{\nu}=2970$ (s), 1698 (vs), 1492 (s), 1461 (s), 1421 (s), 1357 (vs), 1285 (m), 1266 (m), 1183 (s), 1158 (s), 762 (vs), 729 (s), 458 cm^{-1} (m); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=1.12$ (d, $^3J_{3\text{-H},2\text{-H}}=6.8$ Hz, 3H, CH_3CH), 1.82 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.39 (s, 3H, CH_3Ph), 3.87 (dq, $^3J_{2\text{-H},3\text{-H}}=6.8$ Hz, $^3J_{2\text{-H},1\text{-H}}=11.4$ Hz, 1H, 2-H), 4.19 (d, $^3J_{1\text{-H},2\text{-H}}=11.4$ Hz, 1H, 1-H), 7.07–7.18 ppm (m, 4H, 9-H, 10-H, 11-H, 12-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta=19.7$ (C14), 20.7 (C3), 29.9, 30.2 (C7, C5), 35.3 (C2), 76.0 (C1), 126.0 (C9), 126.8 (C10, C11), 131.2 (C12), 136.0 (C13), 142.2 (C8), 203.3, 203.4 ppm (C4, C6); MS (EI): *m*/*z* (%) = 218 (1) $[M]^+$, 200 (3), 185 (1), 175 (54), 157 (83), 143 (25), 128 (9), 119 (100), 91 (31), 77 (10) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{14}H_{18}O_2$: 218.1301 $[M]^+$; found: 218.1303; GC: $t_R=14.52$ min.

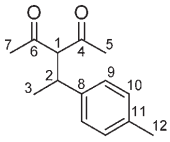


3b: 3-(1-*m*-Tolylethyl)pentane-2,4-dione: $R_f=0.39$ (*n*-hexane/EtOAc = 2:1); IR (cap.): $\tilde{\nu}=2970$ (s), 1698 (vs), 1492 (s), 1461 (s), 1421 (s), 1357 (vs), 1285 (m), 1266 (m), 1183 (s), 1158 (s), 762 (vs), 729 (s), 458 cm^{-1}

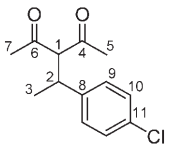


(m); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=1.17 (d, $^3J_{3\text{-H},2\text{-H}}$=6.9 Hz, 3H, C$H_3$CH), 1.83 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.31 (s, 3H, CH_3Ph), 3.51 (dq, $^3J_{2\text{-H},3\text{-H}}$=6.9 Hz, $^3J_{2\text{-H},1\text{-H}}$=11.4 Hz, 1H, 2-H), 4.05 (d, $^3J_{1\text{-H},2\text{-H}}$=11.4 Hz, 1H, 1-H), 6.97–7.03 (m, 3H, 9-H, 11-H, 13-H), 7.17 ppm (app. t, $^3J_{12\text{-H},11\text{-H}}$= 7.6 Hz, $^3J_{12\text{-H},13\text{-H}}$=7.6 Hz, 1H, 12-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ=21.1 (C3), 21.5 (C14), 30.1, 30.2 (C7, C5), 40.7 (C2), 76.5 (C1), 124.6 (C13), 127.9 (C11), 128.4 (C9), 128.9 (C12), 138.8 (C10), 143.7 (C8), 203.50, 203.53 ppm (C4, C6); MS (EI): *m*/*z* (%)=218 (1) $[M]^+$, 200 (3), 185 (1), 175 (54), 157 (83), 143 (25), 128 (9), 119 (100), 91 (31), 77 (10) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{14}H_{18}O_2$: 218.1301 $[M]^+$; found: 218.1298; elemental analysis: calcd (%) for $C_{14}H_{18}O_2$: C 77.03, H 8.31; found: C 77.10, H 8.37; GC: t_R=16.34 min.

3c: 3-(1-*p*-Tolylethyl)pentane-2,4-dione: R_f=0.51 (*n*-hexane/EtOAc= 5:1); IR (cap.): $\tilde{\nu}$=2967 (s), 1700 (vs), 1515 (s), 1419 (m), 1357 (s), 1187 (m), 1157 (s), 818 cm^{-1} (s); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=1.17 (d, $^3J_{3\text{-H},2\text{-H}}$=6.9 Hz, 3H, C$H_3$CH), 1.83 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.29 (s, 3H, CH_3Ph), 3.52 (dq, $^3J_{2\text{-H},3\text{-H}}$=6.9 Hz, $^3J_{2\text{-H},1\text{-H}}$= 11.4 Hz, 1H, 2-H), 4.04 (d, $^3J_{1\text{-H},2\text{-H}}$=11.4 Hz, 1H, 1-H), 7.07–7.11 ppm (m, 4H, 9-H, 10-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ=21.08 (C12), 21.11 (C3), 30.0 (CH_3), 30.2 (CH_3), 40.3 (C2), 76.7 (C1), 127.5 (C9), 129.7 (C10), 136.8 (C11), 140.7 (C8), 203.5, 203.6 ppm (C4, C6); MS (EI): *m*/*z* (%)=218 (1) $[M]^+$, 175 (100), 157 (31), 142 (8), 119 (56), 91 (17), 77 (6) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{14}H_{18}O_2$: 218.1301 $[M]^+$; found: 218.1299; elemental analysis: calcd (%) for $C_{14}H_{18}O_2$: C 77.03, H 8.31; found: C 77.14, H 8.83; GC: t_R=16.71 min.

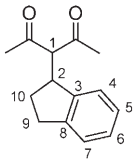


3d: 3-(1-(4-Chlorophenyl)ethyl)pentane-2,4-dione: R_f=0.17 (*n*-hexane/ EtOAc=5:1); IR (KBr): $\tilde{\nu}$=2968 (m), 1724 (vs), 1698 (s), 1495 (m), 1363 (s), 1288 (m), 1177 (m), 1146 (m), 1012 (m), 825 cm^{-1} (s); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=1.16 (d, $^3J_{3\text{-H},2\text{-H}}$=6.9 Hz, 3H, C$H_3$CH), 1.84 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.55 (dq, $^3J_{2\text{-H},3\text{-H}}$= 6.9 Hz, $^3J_{2\text{-H},1\text{-H}}$=11.4 Hz, 1H, 2-H), 4.00 (d, $^3J_{1\text{-H},2\text{-H}}$=11.4 Hz, 1H, 1-H), 7.14 (m, 2H, 9-H), 7.27 ppm (m, 2H, 10-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ=20.8 (C3), 30.1 (C7), 30.2 (C5), 40.0 (C2), 76.5 (C1), 129.1 (C10), 129.2 (C9), 132.8 (C11), 142.4 (C8), 203.0, 203.1 ppm (C4, C6); MS (70 eV): *m*/*z* (%)=220 (5), 195 (100) $[M-Ac]^+$, 181 (19), 165 (5), 153 (1), 139 (31), 127 (4), 115 (10), 103 (18), 89 (4), 77 (11) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{13}H_{15}ClO_2$: 238.0755 $[M]^+$; found: 238.0749; elemental analysis: calcd (%) for $C_{13}H_{15}ClO_2$: C 65.41, H 6.33; found: C 65.40, H 5.58; GC: t_R=17.84 min.

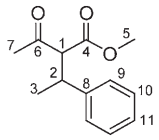


3e: 3-(1-(4-Bromophenyl)ethyl)pentane-2,4-dione: R_f=0.44 (*n*-hexane/ EtOAc=2:1); IR (KBr): $\tilde{\nu}$=2975 (m), 2965 (m), 1723 (vs), 1697 (vs), 1492 (s), 1406 (m), 1363 (vs), 1285 (s), 1177 (s), 1145 (s), 1010 (s), 822 (vs), 534 cm^{-1} (s); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=1.16 (d, $^3J_{3\text{-H},2\text{-H}}$= 6.9 Hz, 3H, C$H_3$CH), 1.84 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.53 (dq, $^3J_{2\text{-H},3\text{-H}}$=6.9 Hz, $^3J_{2\text{-H},1\text{-H}}$=11.2 Hz, 1H, 2-H), 4.00 (d, $^3J_{1\text{-H},2\text{-H}}$=11.2 Hz, 1H, 1-H), 7.08 (m, 2H, 9-H), 7.42 ppm (m, 2H, 10-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ=20.8 (C3), 30.2 (CH_3), 30.2 (CH_3), 40.0 (C2), 76.4 (C1), 120.8 (C11), 129.6 (C9), 132.1 (C10), 143.0 (C8), 203.0, 203.1 ppm (C4, C6); MS (70 eV): *m*/*z* (%)=284 (1) $[M]^+$, 241 (98), 239 (100), 225 (15), 185 (35), 159 (11), 104 (28), 77 (9) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{13}H_{15}BrO_2$: 282.0250 $[M]^+$; found: 282,0244; elemental analysis: calcd (%) for $C_{13}H_{15}BrO_2$: C 55.14, H 5.34, Br 28.22; found: C 55.13, H 4.98, Br 28.30; GC: t_R=18.74 min.

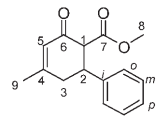
3f: 3-(2,3-Dihydro-1*H*-inden-1-yl)pentane-2,4-dione: R_f=0.42 (*n*-hexane/ EtOAc=2:1); IR (cap.): $\tilde{\nu}$=2947 (m), 1725 (s), 1698 (vs), 1478 (m), 1358 (s), 1159 (m), 753 cm^{-1} (m); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=1.71 (m, 1H, 10-H), 2.14 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.24 (m, 1H, 10-H), 2.81–2.95 (m, 2H, 9-H), 3.91 (d, $^3J_{1\text{-H},2\text{-H}}$=9.8 Hz, 1H, 1-H), 3.94–3.99 (m, 1H, 2-H), 7.00 (br d, $^3J_{4\text{-H},5\text{-H}}$=7.5 Hz, 1H, 4-H), 7.10 (m, 1H, 5-H), 7.16 (m, 1H, 6-H), 7.22 ppm (br d, $^3J_{7\text{-H},6\text{-H}}$=7.5 Hz, 1H, 7-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ=29.9 (CH_3), 30.3 (C10), 31.2 (CH_3), 31.2 (C9), 44.8 (C2), 73.5 (C1), 124.4 (C4), 125.2 (C7), 126.6 (C5), 127.5 (C6), 144.1, 144.4 (C3, C8), 203.6 (CO), 204.1 ppm (CO); MS (70 eV): *m*/*z* (%)=216 (2) $[M]^+$, 173 (100), 155 (8), 128 (11), 116 (45), 91 (11), 77 (3) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{14}H_{16}O_2$: 216.1145 $[M]^+$; found: 216.1144; elemental analysis: calcd (%) for $C_{14}H_{16}O_2$: C 77.75, H 7.46; found: C 77.94, H 7.44; GC: t_R=17.82 min.



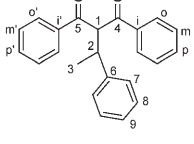
3g: Methyl 2-acetyl-3-phenylbutanoate: R_f=0.5 (*n*-heptane/EtOAc= 1:1); IR (cap.): $\tilde{\nu}$=2968 (m), 1747 (vs), 1718 (vs), 1494 (s), 1163 (m), 1014 (m), 830 cm^{-1} (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.24 (d, $^3J_{3\text{-H},2\text{-H}}$= 6.9 Hz, 3H, C$H_3$CH (II)), 1.29 (d, $^3J_{3\text{-H},2\text{-H}}$=6.9 Hz, 3H, C$H_3$CH (I)), 1.92 (s, 3H, CH_3 (I)), 2.29 (s, 3H, CH_3 (II)), 3.43 (s, 3H, OCH_3 (II)), 3.49–3.59 (m, 1H (I), 1H (II), CH_3CH), 3.74 (d, $^3J_{1\text{-H},2\text{-H}}$=11.0 Hz, 1H, 1-H (II)), 3.75 (s, 3H, OCH_3 (I)), 3.80 (d, $^3J_{1\text{-H},2\text{-H}}$=11.0 Hz, 1H, 1-H (I)), 7.18–7.31 ppm (m, 5H (I), 5H (II), 9-H, 10-H, 11-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.1, 20.6 (C3), 29.6, 29.9 (C7), 39.7, 40.1 (C2), 52.1, 52.5 (OCH_3), 66.8, 67.4 (C1), 126.8, 126.9 (C11), 127.25, 127.31 (C9), 128.5, 128.7 (C10), 142.9, 143.2 (C8), 168.6, 169.0 (C4), 202.3, 202.3 ppm (C6); MS (EI): *m*/*z* (%)=220 (1) $[M]^+$, 202 (100), 189 (9), 177 (44), 159 (18), 145 (97), 131 (47), 117 (16), 105 (94), 91 (13), 77 (18) $[C_6H_5]^+$; HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O_3$: 220.1094; found: 220.1096; GC: t_R(diastereomer I)=15.86 min, t_R(diastereomer II)=16.16 min.



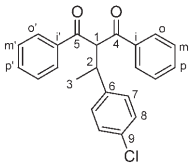
3h: Methyl 4-methyl-2-oxo-6-phenylcyclohex-3-enecarboxylate: R_f=0.31 (*n*-hexane/EtOAc=2:1); IR (cap.): $\tilde{\nu}$=2953 (s), 1732 (vs), 1669 (vs), 1436 (vs), 1162 (vs), 1086 (s), 1032 (s), 765 (s), 702 cm^{-1} (vs); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.95 (m, 3H, CH_3 (I)), 1.99 (m, 3H, CH_3 (II)), 2.47 (dd, $^2J_{H,H}$=16.4 Hz, $^3J_{H,H}$=4.5 Hz, 1H, 3-H (II)), 2.59–2.68 (m, 2H, 3-H (I)), 3.33 (dd, $^2J_{H,H}$=16.4 Hz, $^3J_{H,H}$=14.5 Hz, 1H, 3-H (II)), 3.43 (s, 3H, OCH_3 (II)), 3.49 (d, $^3J_{1\text{-H},2\text{-H}}$=5.5 Hz, 1H, 1-H (II)), 3.57 (s, 3H, OCH_3 (I)), 3.58–3.66 (m, 2H (I), 1H (II), 1-H (I), 2-H (I), 2-H (II)), 6.01 (m, 1H, 5-H (I)), 6.02 (br, 1H, 5-H (II)), 7.20–7.35 (m, 5H (I), 5H (II), Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=22.5 (CH_3 (I)), 23.3 (CH_3 (II)), 37.7 (C3 (II)), 42.7 (C2 (II)), 43.0 (C3 (I)), 44.3 (C2 (I)), 52.3 (OCH_3 (II)), 52.4 (OCH_3 (I)), 54.0 (C1 (II)), 54.6 (C1 (I)), 127.5 (*o*-C (I)), 127.5 (*o*-C (II)), 127.7 (*p*-C (I)), 127.7 (*p*-C (II)), 128.6 (C5 (I)), 128.6 (C5 (II)), 128.9 (*m*-C (II)), 129.1 (*m*-C (I)), 140.6 (*i*-C (II)), 141.7 (*i*-C (I)), 156.3 (C4 (I)), 156.4 (C4 (II)), 170.5 (COO (II)), 172.1 (COO (I)), 197.1 (CO (I)), 198.6 (CO (II)); MS (70 eV): *m*/*z* (%)=244 (11) $[M]^+$, 212 (3), 185 (100), 167 (3), 157 (10), 140 (20), 129 (3), 112 (73), 97 (9); HRMS (70 eV): *m*/*z* calcd for $C_{15}H_{16}O_3$: 244.1094 $[M]^+$; found: 244.1094; elemental analysis: calcd (%) for $C_{15}H_{16}O_3$: C 73.75, H 6.60; found: C 72.70, H 6.57; GC: t_R(diastereomer I)=20.30 min, t_R(diastereomer II)= 20.54 min (I/II 75:25).



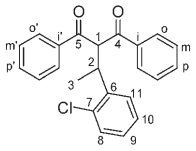
3i: 1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione: R_f=0.39 (CH_2Cl_2); IR (cap.): $\tilde{\nu}$=3442 (m), 1692 (vs), 1595 (m), 1447 (s), 1277 (vs), 1268 (vs), 1198 (m), 973 (m), 756 (s), 703 (s), 544 cm^{-1} (m); ^{1}H NMR (500 MHz, [D$_6$]acetone): δ=1.33 (d, $^3J_{3\text{-H},2\text{-H}}$=7.2 Hz, 3H, CH_3), 3.96 (dq, $^3J_{2\text{-H},3\text{-H}}$= 7.2 Hz, $^3J_{2\text{-H},1\text{-H}}$=10.0 Hz, 1H, 2-H), 6.15 (d, $^3J_{1\text{-H},2\text{-H}}$=10.0 Hz, 1H, 1-H), 7.04 (m, 1H, 9-H), 7.16 (m, 2H, 8-H), 7.34, 7.51 (2×m, 2×2H, *m*-H, *m*′-H), 7.40 (m, 2H, 7-H), 7.48, 7.63 (2×m, 2×1H, *p*-H, *p*′-H), 7.87, 8.16 ppm (2×m, 2× 2H, *o*-H, *o*′-H); ^{13}C NMR (125.8 MHz, [D$_6$]acetone): δ=20.7 (C3), 42.3 (C2), 63.4 (C1), 127.2 (C9), 128.8 (C8), 129.1 (C7), 129.3, 129.6 (*o*-C, *o*′-C), 129.3, 129.7 (*m*-C, *m*′-C), 133.9, 134.3 (*p*-C, *p*′-C), 137.9, 138.4 (*i*-C, *i*′-C), 145.2 (C6), 195.0, 195.7 ppm (C4, C5); MS (EI): *m*/*z* (%)=223 (95), 205 (8), 185 (4), 145 (10), 105 (100), 77 (87) $[C_6H_5]^+$; HRMS (EI): *m*/*z* calcd for $C_{23}H_{20}O_2$: 328.1458 $[M]^+$; found: 328.1451; GC: t_R=30.68 min.



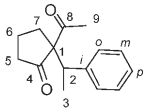
3j: 2-(1-(4-Chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione: $R_f = 0.58$ (CH_2Cl_2); IR (KBr): $\tilde{\nu} = 1692$ (vs), 1446 (m), 1280 (s), 1202 (m), 974 (m), 682 cm^{-1} (m); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 1.31$ (d, $^3J_{3\text{-H},2\text{-H}} = 7.0$ Hz, 3H, CH_3), 4.01 (dq, $^3J_{2\text{-H},3\text{-H}} = 7.0$ Hz, $^3J_{2\text{-H},1\text{-H}} = 10.0$ Hz, 1H, 2-H), 5.64 (d, $^3J_{1\text{-H},2\text{-H}} = 10.0$ Hz, 1H, 1-H), 7.16 (m, 2H, 8-H), 7.23 (m, 2H, 7-H), 7.32 (m, 2H), 7.47 (m, 3H), 7.59 (m, 1H), 7.74, 8.02 ppm (2×m, 2×2H, *o*-H, *o*′-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = 20.4$ (C3), 41.0 (C2), 64.3 (C1), 128.7 (C8), 128.8, 129.0 (*o*-C, *o*′-C), 129.0, 129.3 (*m*-C, *m*′-C), 129.7 (C7), 132.5 (C9), 133.6, 134.0 (*p*-C, *p*′-C), 137.1, 137.5 (*i*-C, *i*′-C), 143.0 (C6), 194.7, 195.0 ppm (C4, C5); MS (70 eV): *m*/*z* (%) = 362 (1) $[M]^+$, 257 (100), 223 (3), 179 (3), 139 (8), 105 (75), 77 (49) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{23}H_{19}ClO_2$: 362.1068 $[M]^+$; found: 362.1057; elemental analysis: calcd (%) for $C_{23}H_{19}ClO_2$: C 76.13, H 5.28, Cl 9.77; found: C 76.48, H 5.80, Cl 10.24; GC: $t_R = 17.84$ min.



3k: 2-(1-(2-Chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione: $R_f = 0.55$ (CH_2Cl_2); IR (KBr): $\tilde{\nu} = 3443$ (w), 1696 (vs), 1658 (s), 1594 (m), 1447 (m), 1290 (s), 1280 (s), 1215 (m), 989 (m), 752 (s), 688 cm^{-1} (s); ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 1.36$ (d, $^3J_{3\text{-H},2\text{-H}} = 7.0$ Hz, 3H, CH_3), 4.49 (dq, $^3J_{2\text{-H},3\text{-H}} = 7.0$ Hz, $^3J_{2\text{-H},1\text{-H}} = 8.8$ Hz, 1H, 2-H), 5.98 (d, $^3J_{1\text{-H},2\text{-H}} = 8.8$ Hz, 1H, 1-H), 7.05–7.11 (m, 2H, 9-H, 10-H), 7.25 (m, 1H, 11-H), 7.30 (m, 1H, 8-H), 7.34, 7.44 (2×m, 2×2H, *m*-H, *m*′-H), 7.47, 7.57 (2×m, 2×1H, *p*-H, *p*′-H), 7.83, 7.95 ppm (2×m, 2×2H, *o*-H, *o*′-H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = 18.7$ (C3), 37.7 (C2), 61.6 (C1), 127.3, 127.5 (C9, C10), 128.7, 129.1 (*o*-C, *o*′-C), 129.0, 129.2 (*m*-C, *m*′-C), 129.2 (C11), 130.2 (C8), 133.9 (C7), 133.6, 134.0 (*p*-C, *p*′-C), 137.0, 137.5 (*i*-C, *i*′-C), 141.7 (C6), 194.7, 195.6 ppm (C4, C5); MS (70 eV): *m*/*z* (%) = 327 (29), 257 (23), 223 (5), 205 (4), 178 (1), 139 (3), 105 (100), 77 (43) $[C_6H_5]^+$; HRMS (70 eV): *m*/*z* calcd for $C_{23}H_{19}ClO_2$: 362.1068 $[M]^+$; found: 362.1083; elemental analysis: calcd (%) for $C_{23}H_{19}ClO_2$: C 76.13, H 5.28, Cl 9.77; found: C 75.50, H 5.00, Cl 9.69; GC: $t_R = 35.95$ min.



3l: 2-Acetyl-2-(1-phenylethyl)cyclopentanone: $R_f = 0.31$ (*n*-hexane/EtOAc = 5:1); IR (cap.): $\tilde{\nu} = 2970$ (m), 1736 (s), 1703 (vs), 1453 (m), 1358 (m), 1197 (m),1143 (s), 1119 (m), 704 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): diastereomer I: $\delta = 1.19$ (d, $^3J_{3\text{-H},2\text{-H}} = 7.2$ Hz, 3H, CH_3CH), 1.36–1.43 (m, 1H, 6-H), 1.49–1.60 (m, 2H, 5-H, 6-H), 1.82 (m, 1H, 7-H), 2.08 (m, 1H, 5-H), 2.41 (s, 3H, $COCH_3$), 2.72 (m, 1H, 7-H), 3.96 (q, $^3J_{3\text{-H},2\text{-H}} = 7.2$ Hz, 1H, 2-H), 7.22–7.25 (m, 3H, *o*-H, *p*-H), 7.30 ppm (m, 2H, *m*-H); diastereomer II: $\delta = 1.23$ (d, $^3J_{3\text{-H},2\text{-H}} = 7.2$ Hz, 3H, CH_3CH), 1.69–1.91 (m, 2H, 6-H), 2.10 (s, 3H, $COCH_3$), 2.12–2.21 (m, 2H, 5-H, 7-H), 2.36 (m, 1H, 5-H), 2.76 (m, 1H, 7-H), 3.82 (q, $^3J_{3\text{-H},2\text{-H}} = 7.2$ Hz, 1H, CH_3CH), 7.16 (m, 2H, *o*-H), 7.21 (m, 1H, *p*-H), 7.27 ppm (m, 2H, *m*-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): diastereomer I: $\delta = 15.9$ (CH_3), 19.2 (C6), 24.5 (C7), 25.4 ($COCH_3$), 39.7 (C5), 42.8 (CH_3CH), 74.7 (C1), 126.9 (*p*-C), 128.1 (*m*-C), 129.0 (*o*-C), 140.6 (*i*-C), 203.0 (CH_3CO), 215.3 ppm (CO); diastereomer II: $\delta = 18.6$ (CH_3), 19.4 (C6), 26.0 ($COCH_3$), 27.0 (C7), 39.3 (C5), 44.0 (CH_3CH), 74.3 (C1), 126.9 (*p*-C), 127.7 (*o*-C), 128.5 (*m*-C), 142.1 (*i*-C), 202.8 ($COCH_3$), 215.8 ppm (CO); MS (EI): *m*/*z* (%): 187 (58), 173 (46), 145 (3), 128 (10), 115 (20), 105 (100), 91 (22), 77 (25) $[C_6H_5]^+$; HRMS (EI): *m*/*z* calcd for $C_{15}H_{18}O_2$: 230.13013 $[M]^+$; found: 230.13048; elemental analysis: calcd (%) for $C_{15}H_{18}O_2$: C 78.23, H 7.88; found: C 77.34, H 7.83; GC: t_R(diastereomer I) = 18.33 min, t_R(diastereomer II) = 18.69 min.



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[16] The preparative-scale experiment was carried out under the following conditions: styrene (10 mmol), $FeCl_3 \cdot 6H_2O$ (5 mol%), acetylacetone (100 mmol), DCE (100 mL), 80 °C, 20 h.

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