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Facile Microwave-Assisted Michael Addition of Diphenacyl Sulfides to Chalcones Under Solvent-Free Conditions: Generation of Symmetrical and Unsymmetrical 1,5-Diketones

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FACILE MICROWAVE-ASSISTED MICHAEL ADDITION OF DIPHENACYL SULFIDES TO CHALCONES UNDER SOLVENT-FREE CONDITIONS: GENERATION OF SYMMETRICAL AND UNSYMMETRICAL 1,5-DIKETONES

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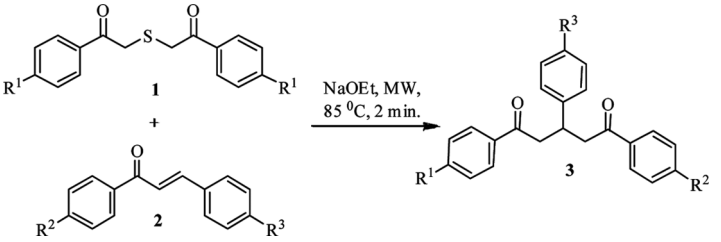
GRAPHICAL ABSTRACT



Abstract *The article describes an efficient and environmentally friendly Michael addition of 2-[(2-oxo-2-phenylethyl)sulfanyl]-1-phenyl-1-ethanones (diphenacyl sulfides) to substituted chalcones using microwave irradiation under solvent-free conditions, affording differently substituted 1,3,5-triarylpentan-1,5-diones in moderate to good yields of 74–83%.*

Keywords 1,5-Diketones; diphenacyl sulphide; Michael addition; microwave reaction

INTRODUCTION

Michael addition of enolates to α,β-unsaturated carbonyl compound is an effective method for the synthesis of 1,5-dicarbonyl compounds through the formation of C-C bond which can be further transformed to multifunctional molecules *via* Robinson annulation.[1] 1,5-Diketones are extremely important synthetic intermediates and are desirable starting materials for generating many heterocyclic and polyfunctional compounds.[2] Many of these compounds have potential applications in coordination chemistry, molecular sensing, catalytic reactions, chemical

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modification of electrodes, and redox active self-assembly devices.[2d,e] Barium hydroxide or barium alkoxide like barium isopropoxide catalysed tandem cross coupling reaction of aryl methyl ketones with aromatic aldehydes,[3] reaction of chalcones with cyclohexanone[4]/trimethyl silyl enol ethers[5]/deoxybenzoin[6] are described in literature for the preparation of 1,5-diones. The conjugate addition of diethyl malonate to chalcones is also an efficient approach.[7] The use of microwave irradiation[8] for carrying out organic reactions is a well-established procedure and has emerged as a promising synthetic technique because the reactions are clean, fast, and economical with easy workup. Microwave irradiation under solvent-free condition[9] enables organic reactions to occur expeditiously at ambient pressure, resulting in accelerated reaction rate, reduced reaction time, and relatively good yields.[10]

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RESULTS AND DISCUSSION

In continuation of our work on the synthesis of novel heterocyclic compounds[11] and the reactions of diphenacyl sulfide with electrophilic reagents,[12] we have explored the reaction of diphenacyl sulfide with α, β-unsaturated carbonyl compounds. Previously, a related reaction of chalcone with the nitrogen analogs of diphenacyl sulfide, diphenacylaniline, has led to the formation of a highly substituted piperidine derivative, (4-benzoyl-5-hydroxy-1,3,5-triphenyl-2-piperidyl)(phenyl)-methanone.[13] In the present case, we expect such a domino reaction, involving a Michael addition–aldol condensation sequence, to take place, yielding (4-benzoyl-5-hydroxy-3,5-diphenyltetrahydro-2*H*-2-thiopyranyl) (phenyl)methanone **4**. Interestingly, the reaction between diphenacyl sulfide and chalcone in the presence of ethoxide has not gone as expected. The products obtained have been found to be symmetrical or unsymmetrical 1,3,5-triarylpentane-1,5-diones. The reaction is also selective as (5-benzoyl-3-phenyl-2-thienyl) (phenyl) methanone **5**, a self-condensation product of diphenacyl sulfide **1** obtained previously in basic medium,[14] has not been obtained in the present case. The influences of different bases on the reaction have also been systematically investigated (Table 1). A 1:1.5 molar ratio of diphenacyl sulfide and chalcone respectively with 1.5 equivalents of sodium ethoxide as base under a microwave power of 120 W at 80–85 °C for 2 min has been found to be the optimized condition for the reaction to yield the diketones. It is observed that the yield of product depends on the molar ratio of the reactants, and a 1:1 molar ratio of diphenacyl sulfide and chalcone has led to a worse yield than a 1:1.5 molar ratio. When the ratio is changed to 1:1.8 or 1:2, there is no appreciable change in the yield of the product. To illustrate the scope of the reaction, different chalcones were allowed to react with differently substituted diphenacyl sulfides, and in almost all the reactions, the yields of diketones were appreciable. The reactions were also performed using the conventional method with diethyl ether as the solvent (Table 2).

It is interesting that the reaction has led to the formation of a simple diketone instead of the routine Michael addition or subsequent intramolecular–aldol ring formation through **6**. The formation of the product can be explained by an elimination involving ArCOCHS, with the acidity of methylene hydrogen being increased by the sodium ethoxide (Scheme 2). A six-membered cyclic transition state, **7**, can be visualized like other popular *cis* elimination reactions. It must be mentioned that our attempt to identify the by-product ArCOCHS in the reaction mixture in support

Table 1. Screening of bases and chalcone mole ratio in the formation of **3a**

Entry	Catalyst	MW power (W)	Time (min)	Base equiv.	Chalcone equiv.	Yield (%)
1	K_2CO_3	120	15	5	2	—[a]
2	NaOH	120	3	1.5	1.5	65[b]
3	KOH	100	3	1.5	1.5	69[c]
4	NaOEt	80	2	1.5	1.5	76[c]
5	NaOEt	120	3	1	1.5	43[b]
6	NaOEt	120	2	1.5	1	67[c]
7	NaOEt	120	2	1.5	1.5	80[c]
8	NaOEt	120	3	1.5	1.8	78[c]
9	NaOEt	150	3	2	2	78[c]
10	*t*-BuOK	120	3	2	1.5	64[b]
11	$Ba(OH)_2$	80	6	2	1.7	58[b]
12	$N(Et)_3$	100	6	2	2	—[a]
13	Pyridine	110	15	4	2	—[a]
14	Morpholine	110	15	3	1.5	—[a]
15	Pyrrolidine	110	15	6	2	—[a]

[a]No recognizable product was isolated.
[b]Separation through wash column.
[c]After recrystallization from ethanol-ethyl acetate mixture.

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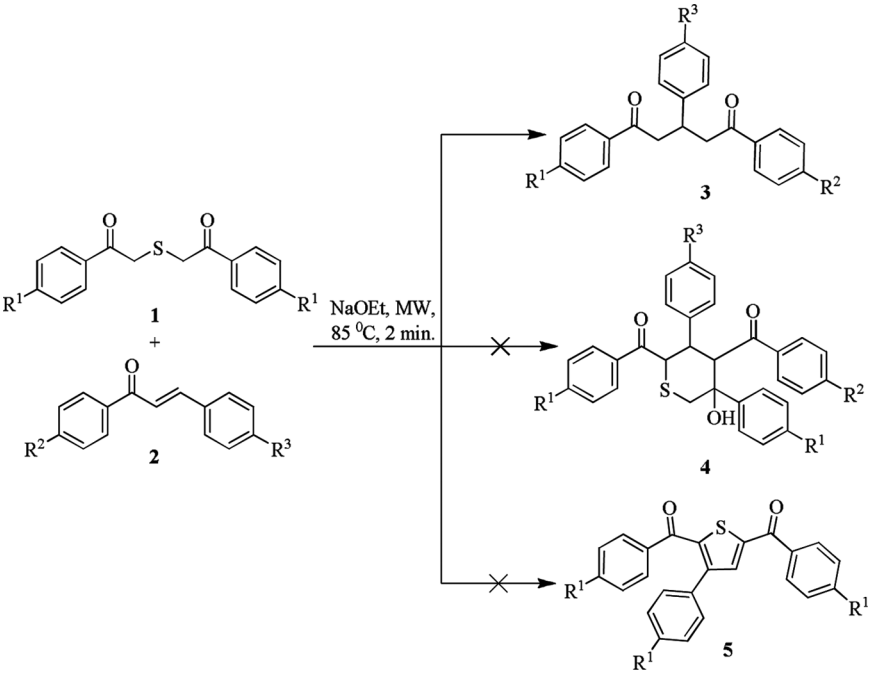
of the proposed mechanism (either by trapping the proposed intermediate, 2-oxo-2-phenylethanethial, with diene or by preparing its derivatives) was not successful, though an awful smell characteristic of thio compounds was noticed during the workup. 2-Oxo-phenylethanethial had been previously obtained in situ by

Table 2. Yield of 1,3,5-triaryl-1,5-pentanediones **3**

						Yield (%)	
Entry	R^2	R^3	R^1	Compound obtained	MW time (min)	MW	Conventional[c]
1	H	H	H	**3a**	2	80[a]	57
2	Cl	H	H	**3b**	1.5	83[a]	60
3	H	H	Ph	**3c**	1.5	81[a]	57
4	H	H	Cl	**3b**	2	79[a]	53
5	Me	H	Me	**3d**	2	74[b]	50
6	H	Me	H	**3e**	2	78[a]	52
7	H	OMe	H	**3f**	1.5	76[b]	51
8	H	Me	Cl	**3g**	1.5	78[a]	57
9	Ph	H	H	**3c**	2	79[a]	56
10	Me	Cl	H	**3h**	2	74[b]	48
11	Me	Cl	Me	**3i**	2	75[a]	50
12	Cl	Cl	Me	**3j**	2	82[a]	59
13	H	Cl	Me	**3h**	1.5	76[a]	55
14	Cl	Me	H	**3g**	1.5	83[a]	62
15	Me	Cl	Cl	**3j**	2	75[a]	49

[a]Recrystallization from ethanol–ethyl acetate mixture.
[b]Separation through wash column.
[c]Purified through column chromatography.



Scheme 1. Synthesis of 1,3,5-triaryl-1,5-pentanediones **3**.

thermolysis of a heteroaryl phenacyl sulfoxide and trapped by Diels–Alder reaction.[15] The acidity of methylene hydrogens adjacent to the sulfur is more than that of the other methylene hydrogens, and hence the cyclization yielding **4** has not occurred.

In the NMR spectrum of 1,5-diketones **3** (Fig. 1), when $R^1 = R^2$, the methylene protons H_a and H_c (and H_b and H_d) are diastereotopic in nature. Thus H_a and H_c give a 2H doublet of doublet and same is the case with H_b and H_d. H_e appears as a quintet. When $R^1 \neq R^2$, it is observed that H_a, H_b, H_c, and H_d all appear as separate doublets of doublets. In some cases (for example, **3j**), even though $R^1 \neq R^2$, the chemical shift differences between H_a and H_c and between H_b and H_d are so close that in the former case a single doublet of doublet is noticed and in the latter case the middle peaks merge together and appear as a deceptive triplet.

This article describes the reaction of diphenacyl sulfides with substituted chalcones using sodium ethoxide as the base under solvent-free microwave radiation, yielding symmetrically and unsymmetrically substituted 1,3,5-pentane-1,5-diones by Michael addition, an alternate efficient route for this class of compounds.

EXPERIMENTAL

Melting points were measured in open capillary tubes and are uncorrected. A CEM Discover microwave synthesizer (Model No. 908010) operating at 180/264 V and 50/60 Hz with microwave power maximum level of 300 W and microwave

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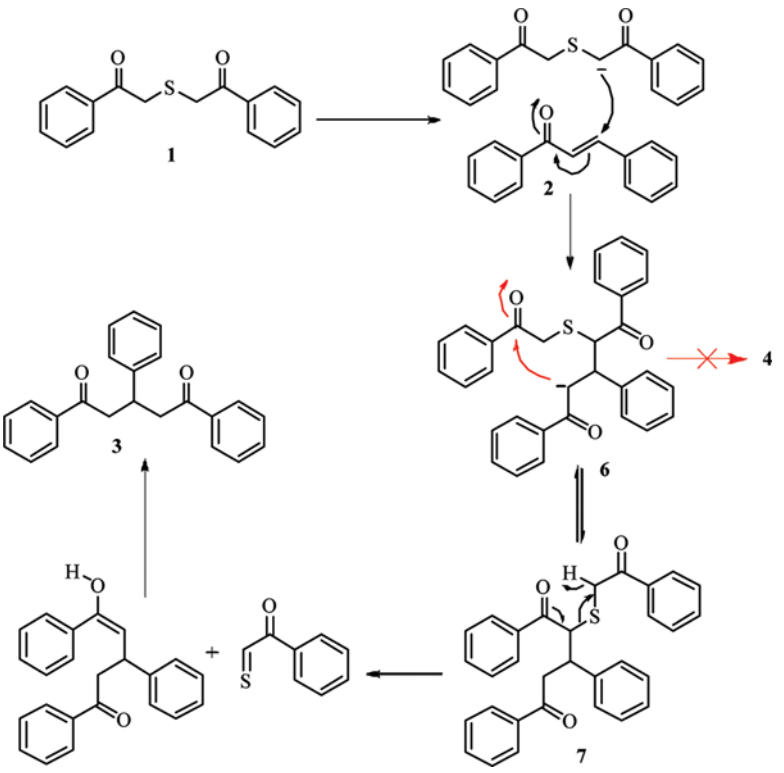

Scheme 2. Mechanism for the formation of 1,3,5-triaryl-1,5-pentanediones **3**. (Figure is provided in color online.)

frequency of 2455 MHz was employed for the microwave-assisted experiments done in this work. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300-MHz NMR instrument using tetramethylsilane (TMS) as internal standard and $CDCl_3$ as solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ scale), and the coupling constants are given in hertz. Silica-gel G plates (Merck) were used for thin-layer chromatographic

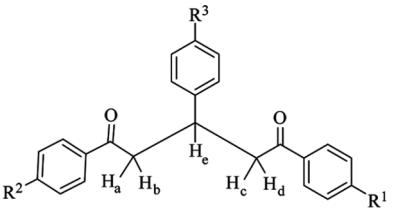

Figure 1. Structure of 1,3,5-triaryl-1,5-pentanedione. (a) $R^1 = R^2 = R^3 = H$; (b)$R^1 = R^3 = H$, $R^2 = Cl$; (c) $R^1 = Ph$, $R^2 = R^3 = H$; (d) $R^1 = R^2 = CH_3$, $R^3 = H$; (e) $R^1 = R^2 = H$, $R^3 = CH_3$; (f) $R^1 = R^2 = H$, $R^3 = OCH_3$; (g) $R^1 = Cl$, $R^2 = H$, $R^3 = CH_3$; (h) $R^1 = H$, $R^2 = CH_3$, $R^3 = Cl$; (i) $R^1 = R^2 = CH_3$, $R^3 = Cl$; and (j) $R^1 = CH_3$, $R^2 = R^3 = Cl$.

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(TLC) analysis with a mixture of petroleum ether (60–80 °C) and ethyl acetate as eluent. Elemental analyses were performed on a Perkin-Elmer 2400 Series II Elemental CHNS analyzer. Infrared (IR) spectra were recorded on a Jasco Fourier transform (FT)–IR instrument (KBr pellet method).

General Procedure for the Synthesis of 1,5-Diketones (3)

Microwave method. A well-ground mixture of diphenacyl sulfide **1** (1 mmol), chalcone **2** (1.5 mmol), and NaOEt (1.5 mmol), were taken in a 10-mL microwave tube and was irradiated in a CEM Discover microwave synthesizer according to the time and power shown in Table 1, and the progress of the reaction was monitored TLC. At the end of the reaction, water was added to the mixture and stirred for a while, and the product was collected by filtration and washed with cold water. The pure products were obtained by crystallization from ethanol–ethyl acetate (4:1) except for **3d, 3f**, and **3h**, which were purified by a wash column.

Conventional method. A mixture of diphenacyl sulfide **1** (1 mmol) and chalcone **2** (1.5 mmol) were taken in a 50-mL conical flask and dissolved in 10-mL ether. Freshly prepared sodium ethoxide (1.5 mmol) was added to this solution and stirred for 30 min. After completion of the reaction (monitored by TLC), the mixture was concentrated under vacuum, and the residue was subjected to column chromatography using a petroleum ether / ethyl acetate mixture (3:1; v/v) as eluent to afford the pure products **3**.

Spectral and Analytical Data

1,3,5-Triphenyl-1,5-pentanedione (3a). Isolated as colorless solid. Spectroscopic data are in the literature.[16]

1-(4-Chlorophenyl)-3,5-diphenyl-1,5-pentanedione (3b). Isolated as colorless solid; mp 96–97 °C; IR (KBr): 3062, 3026, 2890, 1674, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 3.30 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 3.35 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 3.48 (dd, 2H, $J = 16.8$, 6.9 Hz, CH_2), 4.04 (qnt, 1H, $J = 6.9$ Hz, CH), 7.15–7.31 (m, 5H, Ar-H), 7.36–7.47 (m, 4H, Ar-H), 7.53–7.58 (m, 1H, Ar-H), 7.89 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.94 (d, 2H, $J = 8.7$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 37.1, 44.7, 44.8, 126.8, 127.4, 128.1, 128.5, 128.6, 128.9, 129.6, 133.1, 135.1, 136.8, 139.5, 143.5, 197.4, 198.5. Anal. calcd. for $C_{23}H_{19}ClO_2$: C, 76.13; H, 5.28%. Found: C, 76.09; H, 5.24%.

1-(Biphenyl-4-yl)-3,5-diphenyl-1,5-pentanedione (3c). Isolated as colorless solid; mp 98–99 °C; IR (KBr): 3058, 3029, 2882, 1676, 1683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 3.37 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 3.38 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 3.51 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 3.53 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 4.10 (qnt, 1H, $J = 6.9$ Hz, CH), 7.19–7.21 (m, 1H, Ar-H), 7.28–7.35 (m, 3H, Ar-H), 7.37–7.55 (m, 7H, Ar-H), 7.62 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.66 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.96 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.02 (d, 2H, $J = 8.4$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 37.2, 44.8, 44.9, 126.7, 127.2, 127.3, 127.4, 128.1,

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128.2, 128.5, 128.6, 128.7, 128.9, 133.1, 135.5, 136.8, 139.8, 143.8, 145.7, 198.2, 198.6. Anal. calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98%. Found: C, 86.06; H, 5.95%.

1,5-Di(4-methylphenyl)-3-phenyl-1,5-pentanedione (3d). Isolated as colorless solid; mp 110–111 °C; IR (KBr): 3061, 3026, 2890, 1678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.40 (s, 6H, $2CH_3$), 3.31 (dd, 2H, $J = 16.2$, 6.9 Hz, CH_2), 3.46 (dd, 2H, $J = 16.2$, 6.9 Hz, CH_2), 4.05 (qnt, 1H, $J = 6.9$ Hz, CH), 7.25–7.28 (m, 9H, Ar-H), 7.83–7.90 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.6, 37.3, 44.8, 126.6, 127.4, 128.2, 128.6, 129.2, 129.6, 134.4, 143.8, 198.2. Anal. calcd. for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%. Found C, 84.21; H, 6.76%.

3-(4-Methylphenyl)-1,5-diphenyl-1,5-pentanedione (3e)[3b]. Isolated as colorless solid; mp 106–107 °C; IR (KBr): 3059, 3027, 2894, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.28 (s, 3H, CH_3), 3.32 (dd, 2H, $J = 16.5$, 7.2 Hz, CH_2), 3.48 (dd, 2H, $J = 16.5$, 7.2 Hz, CH_2), 4.03 (qnt, 1H, $J = 7.2$ Hz, CH), 7.08 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.17 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.41–7.46 (m, 4H, Ar-H), 7.51–7.57 (m, 2H, Ar-H), 7.93–7.97 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.0, 36.7, 45.0, 127.2, 128.1, 128.5, 129.3, 133.0, 136.1, 136.8, 140.7, 198.7.

3-(4-Methoxyphenyl)-1,5-diphenyl-1,5-pentanedione (3f)[3b]. Isolated as colorless solid; mp 89–90 °C; IR (KBr): 3056, 3025, 2895, 1676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 3.31 (dd, 2H, $J = 16.5$, 7.2 Hz, CH_2), 3.47 (dd, 2H, $J = 16.5$, 7.2 Hz, CH_2), 3.75 (s, 3H, OCH_3), 4.02 (qnt, 1H, $J = 7.2$ Hz, CH), 6.81 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.20 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.41–7.46 (m, 4H, Ar-H), 7.51–7.57 (m, 2H, Ar-H), 7.93–7.96 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 36.4, 45.1, 55.1, 113.9, 128.1, 128.4, 128.6, 133.0, 135.7, 136.8, 158.1, 198.7.

1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenyl-1,5-pentanedione (3g). Isolated as colorless solid; mp 59–60 °C; IR (KBr): 3058, 3026, 2891, 1676, 1680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.27 (s, 3H, CH_3), 3.26 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 3.32 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 3.46 (dd, 2H, $J = 16.5$, 6.9 Hz, CH_2), 4.00 (qnt, 1H, $J = 6.9$ Hz, CH), 7.07 (d, 2H, $J = 7.8$ Hz, Ar-H), 7.15 (d, 2H, $J = 7.8$ Hz, Ar-H), 7.37–7.45 (m, 4H, Ar-H), 7.53 (t, 1H, $J = 7.2$ Hz), 7.88 (d, 2H, $J = 7.5$ Hz, Ar-H), 7.94 (d, 2H, $J = 7.5$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.0, 36.7, 44.8, 44.9, 127.2, 128.0, 128.5, 128.8, 129.3, 129.5, 133.1, 135.1, 136.2, 136.7, 139.4, 140.5, 197.4, 198.5. Anal. calcd. for $C_{24}H_{21}ClO_2$: C, 76.49; H, 5.62%. Found: C, 76.43; H, 5.56%.

3-(4-Chlorophenyl)-1-(4-methylphenyl)-5-phenyl-1,5-pentanedione (3h). Isolated as colorless solid; mp 112–113 °C; IR (KBr): 3062, 3027, 2894, 1674, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.38 (s, 3H, CH_3), 3.25 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 3.33 (dd, 1H, $J = 16.5$, 6.9 Hz, CH), 3.42 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 3.48 (dd, 1H, $J = 16.8$, 6.9 Hz, CH), 4.05 (qnt, 1H, $J = 6.9$ Hz, CH), 7.21 (s, 6H, Ar-H), 7.39–7.55 (m, 3H, Ar-H), 7.83 (d, 2H, $J = 7.2$ Hz, Ar-H), 7.92 (d, 2H, $J = 7.2$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.3, 36.4, 44.3, 44.4, 127.8, 128.0, 128.4(2C), 128.7, 129.0, 131.9, 132.9, 134.1, 136.6, 142.3, 143.7, 197.5, 197.9. Anal. calcd. for $C_{24}H_{21}ClO_2$: C, 76.49; H, 5.62%. Found: C, 76.44; H, 5.57%.

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3-(4-Chlorophenyl)-1,5-di(4-methylphenyl)-1,5-pentanedione (3i). Isolated as colorless solid; mp 108–109 °C; IR (KBr): 3063, 3024, 2897, 1675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.40 (s, 6H, $2CH_3$), 3.28 (dd, 2H, $J = 16.5$, 6.9 Hz, CH_2), 3.44 (dd, 2H, $J = 16.5$, 6.9 Hz, CH_2), 4.03 (qnt, 1H, $J = 6.9$ Hz, CH), 7.22–7.26 (m, 8H, Ar-H), 7.84 (d, 4H, $J = 7.8$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.6, 36.6, 44.6, 128.2, 128.6, 128.9, 129.3, 132.2, 134.2, 142.4, 144.0, 197.9. Anal. calcd. for $C_{25}H_{23}ClO_2$: C, 76.81; H, 5.93%. Found: C, 76.75; H, 5.91%.

1,3-Di(4-chlorophenyl)-5-(4-methylphenyl)-1,5-pentanedione (3j). Isolated as colorless solid; mp 101–102 °C; IR (KBr): 3060, 3026, 2890, 1675, 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.40 (s, 3H, CH_3), 3.25 (dd, 1H, $J = 16.5$, 7.2 Hz, CH), 3.29 (dd, 1H, $J = 16.5$, 7.2 Hz, CH), 3.43 (dd, 1H, $J = 16.5$, 7.2 Hz, CH), 3.48 (dd, 1H, $J = 16.5$, 7.2 Hz, CH), 4.02 (qnt, 1H, $J = 7.2$ Hz, CH), 7.19–7.26 (m, 6H, Ar-H), 7.42 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.83 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.88 (d, 2H, $J = 8.1$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 21.6, 36.5, 44.5, 44.6, 128.2, 128.7, 128.8, 128.9, 129.3, 129.5, 132.3, 134.2, 134.9, 139.6, 142.1, 144.1, 197.1, 197.8. Anal. calcd. for $C_{24}H_{20}Cl_2O_2$: C, 70.08; H, 4.90%. Found C, 70.06; H, 4.85%.

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