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An efficient simple one-pot synthesis, characterization and structural studies of some 1,2,3,5-tetraarylpentane-1,5-diones

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HIGHLIGHTS

- The main advantages are time saving, easy workup and high yield of product.
- The one-pot method is economy and reduces the usage of solvent.
- Single crystal X-ray diffraction analysis, FTIR, ^{1}H NMR, ^{13}C NMR and mass spectral techniques.

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ABSTRACT

A series of 1,2,3,5-tetraarylpentane-1,5-diones **(9–23)** were synthesised by simple one-pot method and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectral techniques. The structure of 3-(4-fluorophenyl)-1,2,5-triphenylpentane-1,5-dione **(10)** was determined by single crystal X-ray diffraction analysis. The compound **10** crystallize in monoclinic crystal system, in *C*2/*c* space group. The torsional angle between the two keto groups was found to be −29.50°. The C(23)—C(22)—C(15)—C(8)—C(7) chain is almost planar with “W” conformation and observed maximum deviation is 0.122 Å for C(15) from the C(23)/C(22)/C(15)/C(8)/C(7) plane.

1. Introduction

Multi component reactions (MCRs) continue to attract synthetic organic chemist due to several merits. Significantly complex organic molecules can be synthesized from relatively simpler starting materials in a single step. This makes them more economical and green as compared with conventional multistep synthesis. MCRs have been successfully used to synthesize different classes of compounds or scaffolds [1]. Diketones are one of the important synthetic intermediates and desirable starting materials for synthesis of numerous heterocycles [2–4] and poly functional compounds [5–8]. 1,5-Dicarbonyl compounds can be further transformed into useful multifunctional molecules. The potential of 1,5-diketones to yield heterocycles upon cyclization in presence of nucleophiles makes them key intermediates for the synthesis of various heterocyclic compounds. The reaction between 1,5-diketones and hydrogen sulphide gives thiopyrans [9], whereas use of ammonia and its derivatives result in synthesis of pyridine, dihydropyridine, diazapine and pipridine [10] as product. The heterocyclization of 1,5-diketones under acidic conditions yields pyrans, pyrylium salts and di or tetrahydropyrans [11].

The reactions of an alkanone with an aldehyde are one of the most extensively applied reactions in synthetic organic chemistry. The alkanone undergoes a two component bimolecular reaction with the aldehyde to form an α,β-unsaturated ketone [12] or a β-hydroxy ketones [13]. Conjugate addition of active enolates and other nucleophiles to α,β-unsaturated enones is an efficient method of C—C bond formation and has wide application in organic synthesis [14]. According to the reports in literatures, there are four procedures for synthesizing 1,5-diketones: (i) by the aldol–Michael addition strategy [15–18]; (ii) the addition of activated methylene compounds to α,β-unsaturated ketones [19]; (iii) the condensation of ketone enolate and the Mannich base derived from methyl ketones [20]; and (iv) the conjugate addition of the enones to trimethylsilylenol ethers as donor [21]. These methods can be used for suitable reactive substrates, but there are some limitations, such as the reaction between aldehyde and acetophenone is only performed in alkaline alcohols and under refluxing condition. The aldehyde should have an electron withdrawing group and needs a large amount of solvent. In addition, these methods need to use more expensive reagents and have longer synthetic

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routes. The fourth method is considered to be a better one, but it should be carried under moisture and oxygen-free conditions.

Considering the utility of the 1,5-diones and demerits in the existing methods to synthesize them, there is a need to develop protocols which would yield structurally complex 1,5-diones using simpler and greener procedures. The present communication describes two such methods for synthesis of 1,5-diones, which to an extent overcome demerits of the reported methods.

2. Experimental

2.1. General

The purity and completion of reaction was monitored by TLC. The melting points were recorded in open capillaries and are uncorrected. The FT-IR spectra were recorded on a AVATAR-330FT-IR spectrophotometer. The sample was mixed with KBr and pellet technique was adopted to record the spectra in cm^{-1}. ^{1}H NMR spectra were recorded at 500 or 400 MHz on BRUKER AV-III or Varian 400 MHz spectrometer using CDCl$_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded at 125 or 100 or 75 MHz on BRUKER AV-III spectrometer in CDCl$_3$. For recording ^{1}H NMR spectra, solution were prepared by dissolving about 10 mg of the compound in 0.5 mL of CDCl$_3$. While for recording ^{13}C NMR spectra, about 50 mg of the compound was dissolved in the same volume of the solvent. Mass spectra were recorded on SCIEX-API 2000.

*2.2. General procedure for preparing 2-phenylacetophenone (**4,5 & 6**)*

Benzyl phenyl ketone was prepared by Friedel Craft reaction. To a solution of phenyl acetic acid (0.01 mol) in chloroform (25 mL), thionyl chloride 97.3 mL, (0.01 mol) was added. This was refluxed on a water bath for 30 min. Finely powdered anhydrous aluminium chloride, (0.01 mol) was added in small portions to a mixture of acid chloride and electron rich arenes (0.01 mol) at 0 °C. The mixture was stirred for 1 h at 0 °C and poured over chopped ice. It was extracted with chloroform and dried over anhydrous sodium sulphate. Removal of solvent by distillation gave the desired product in 75–81% yield.

*2.3. General procedure for preparing 1,2,3,5-tetraphenylpentan-1,5-diones (**9–23**)*

A mixture of 2-phenylacetophenone (**4/5/6**) (0.01 mol), acetophenones (**7**) (0.01 mol), bezaldehydes (**8**) (0.01 mol) and sodium hydroxide solution (10 mL, 10%) in ethanol (50 mL) was stirred for 60 min at room temperature. The solid that separated was filtered and was recrystallized from ethanol.

2.4. Spectral data of synthesized compounds

*2.4.1. 1,2-Diphenylethanone (**4**)*

Yield: 75%; MP: 55–57 °C; FT-IR (KBr, cm^{-1}): 1684 (C=O), 3084–3031 (C—H), 2902–2805 (C—H); ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ = 4.28 (s, 2H, CH$_2$), 6.99–8.10 (m, 10H); Mass (*m/z*): 219 [M + Na]$^+$, 197 [M + 1]$^+$ and 105.

*2.4.2. 2-phenyl-1-p-tolylethanone (**5**)*

Yield: 79%; MP:104–106 °C; FT-IR (KBr, cm^{-1}): 1691 (C=O), 3064–3042 (C—H), 2952–2131 (C—H); ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ = 2.39 (s, 3H, CH$_3$), 4.25 (s, 2H, CH$_2$), 7.21–7.92 (m, 9H); Mass (*m/z*): 233 [M + Na]$^+$, 211 [M + 1]$^+$ and 119.

*2.4.3. 1-(4-Methoxyphenyl)-2-phenylethanone (**6**)*

Yield: 81%; MP: 73–75 °C; FT-IR (KBr, cm^{-1}): 1686 (C=O), 3095–3057 (C—H), 2985–2862 (C—H); ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ = 3.85 (s, 3H, OCH$_3$), 4.22 (s, 2H, CH$_2$), 6.91–8.00 (m, 9H); Mass (*m/z*): 249 [M + Na]$^+$, 227 [M + 1]$^+$ and 135.

*2.4.4. 1,2,3,5-Tetraphenylpentane-1,5-dione **9***

FT-IR (KBr, cm^{-1}): 1686 (C=O), 3079–3028 (C—H), 2913–2849 (C—H); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ = 5.51 (d, 1H, H-2), 4.20 (m, 1H, H-3), 3.48 (dd, 1H, H-4a), 2.78 (dd, 1H, H-4b), 7.62–7.89 (m, 20H); ^{13}C NMR (DMSO-d_6, 400 MHz, ppm): δ = 198.7 (C-1, C-5), 58.6 (C-2), 44.6 (C-3), 42.8 (C-4), 126.5–142.5; Mass (*m/z*): 427 [M + Na]$^+$, 405 [M + 1]$^+$ and 209.

*2.4.5. 3-(4-Fluorophenyl)-1,2,5-triphenylpentane-1,5-dione **10***

FT-IR (KBr, cm^{-1}): 1671 (C=O), 3063–3026 (C—H), 2923–2851 (C—H); ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ = 5.11 (d, 1H, H-2), 4.37 (m, 1H, H-3), 3.18 (dd, 1H, H-4a), 3.06 (dd, 1H, H-4b), 6.85–7.80 (m, 19H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ = 198.6 (C-1, C-5), 58.6 (C-2), 44.6 (C-3), 42.8 (C-4), 126.5–142.5; Mass (*m/z*): 445 [M + Na]$^+$, 423 [M + 1]$^+$ and 227.

*2.4.6. 3-(4-Chlorophenyl)-1,2,5-triphenylpentane-1,5-dione **11***

FT-IR (KBr, cm^{-1}): 1682, 1671 (C=O), 3059–3019 (C—H), 2904 (C—H); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ = 5.13 (d, 1H, H-2), 4.38 (m, 1H, H-3), 3.19 (dd, 1H, H-4a), 3.09 (dd, 1H, H-4b), 7.15–7.83 (m, 19H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ = 198.4 (C-1), 198.3 (C-5), 58.5 (C-2), 43.9 (C-3), 42.6 (C-4), 127.9–132.9.

*2.4.7. 3-(4-Bromophenyl)-1,2,5-triphenylpentane-1,5-dione **12***

FT-IR (KBr, cm^{-1}): 1659 (C=O), 3079–3061 (C—H), 2996–2836 (C—H); ^{1}H NMR(CDCl$_3$, 500 MHz, ppm): δ = 5.13 (d, 1H, H-2), 4.37 (m, 1H, H-3), 3.19 (dd, 1H, H-4a), 3.09 (dd, 1H, H-4b), 7.25–7.83 (m, 19H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ = 198.3 (C-1, C-5), 58.4 (C-2), 44.0 (C-3), 42.5 (C-4), 120.4–141.7.Mass (*m/z*): 507 [(M + 2)+Na]$^+$, 505 [M + Na]$^+$, 485 [M + 1]$^+$, 289 and 287.

*2.4.8. 3-(4-Methoxyphenyl)-1,2,5-triphenylpentane-1,5-dione **13***

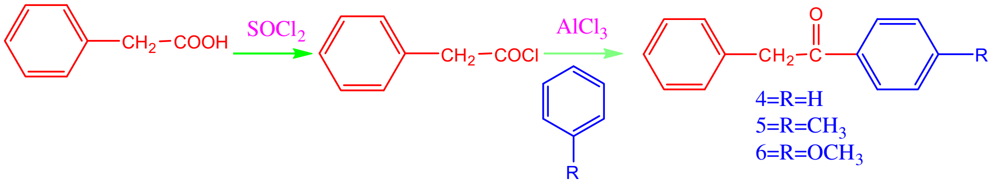
FT-IR (KBr, cm^{-1}): 1677 (C=O), 3060–3019 (C—H), 2964–2827 (C—H); ^{1}H NMR(CDCl$_3$, 400 MHz, ppm): δ = 4.96 (d, 1H, H-2), 4.20 (m, 1H, H-3), 3.49 (dd, 1H, H-4a), 3.37 (dd, 1H, H-4b), 3.65(s,3H, OCH$_3$), 6.53–8.02 (m, 19H); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ = 199.6 (C-1), 198.7 (C-5), 59.5 (C-2), 45.0 (C-3), 43.6 (C-4), 54.9 ($\mathrm{O}\mathbf{C}\mathrm{H_3}$), 113.4–157.8; Mass (*m/z*): 457 [M + Na]$^+$, 435 [M + 1]$^+$ and 239.

*2.4.9. 3-(3-Methoxyphenyl)-1,2,5-triphenylpentane-1,5-dione **14***

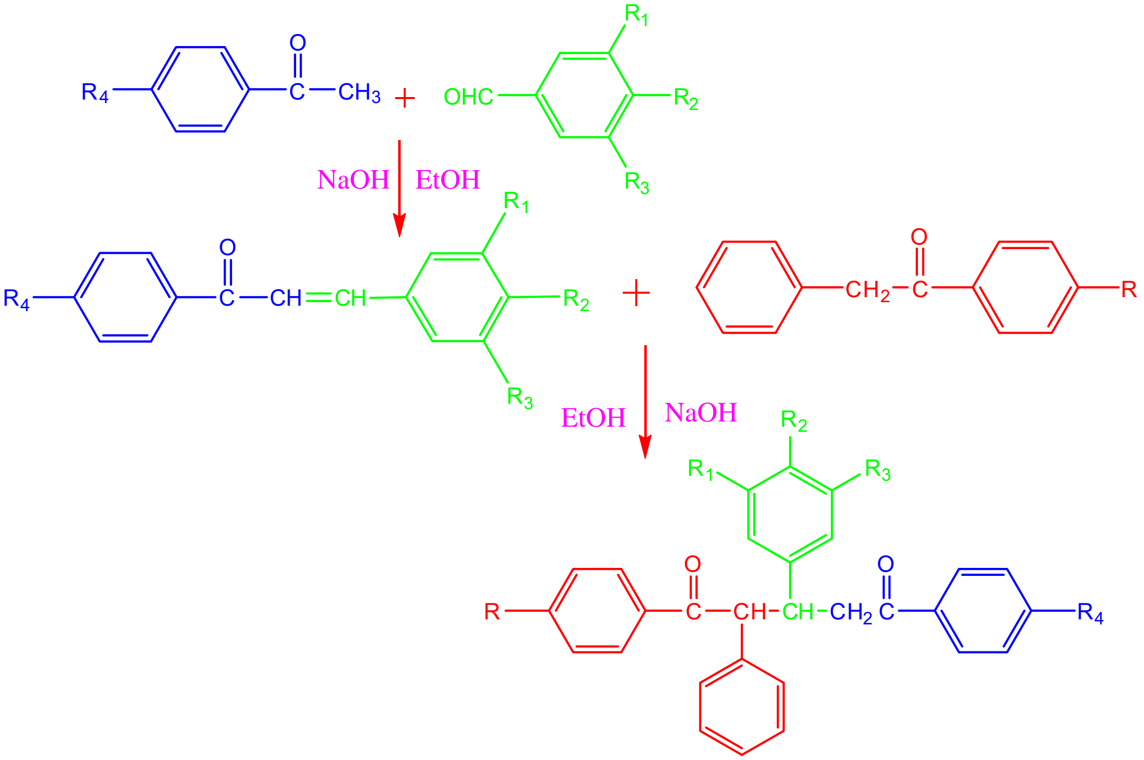
FT-IR (KBr, cm^{-1}): 1681 (C=O), 3059–3003 (C—H), 2964–2842 (C—H); ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ = 5.15 (d, 1H, H-2), 4.36 (m, 1H, H-3), 3.83 (dd, 1H, H-4a), 3.07 (dd, 1H, H-4b), 3.68 (s, 3H, $\mathrm{OC}\mathbf{H_3}$), 6.59–7.81 (m, 19H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ = 198.7 (C-1), 198.6(C-5), 58.5 (C-2), 44.7 (C-3), 42.9 (C-4), 55.1(OCH$_3$), 112.0–159.4; Mass (*m/z*): 457 [M + Na]$^+$, 435 [M + 1]$^+$ and 239.

*2.4.10. 1,2,5-Triphenyl-3-(3,4,5-trimethoxyphenyl)pentane-1,5-dione **15***

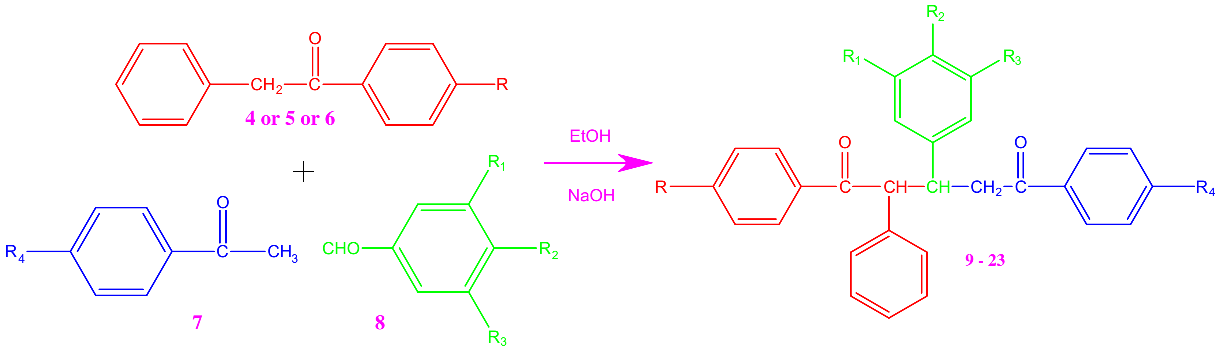
FT-IR (KBr, cm^{-1}): 1679 (C=O), 3059–3030 (C—H), 2997–2835 (C—H); ^{1}H NMR(CDCl$_3$, 300 MHz, ppm): δ = 5.19 (d, 1H, H-2), 3.12 (dd, 1H, H-4b), 3.70 (s, 3H, $\mathrm{OC}\mathbf{H_3}$), 3.68 (s, 6H, $\mathrm{OC}\mathbf{H_3}$), 6.46–8.03 (m, 17H); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ = 198.7 (C-1), 198.6(C-5), 58.5 (C-2), 44.7 (C-3), 42.9 (C-4), 55.1($\mathrm{O}\mathbf{C}\mathrm{H_3}$), 112.0–159.4; Mass (*m/z*): 517 [M + Na]$^+$, 495 [M + 1]$^+$, 477 and 299.



Scheme 1. Synthetic route for 2-phenylacetophenone.



Scheme 2. Double step synthesis of 1,2,3,5-tetraphenylpentane-1,5-diones.



Scheme 3. One-pot synthesis of 1,2,3,5-tetraphenylpentane-1,5-diones.

*2.4.11. 1,2,5-Triphenyl-3-p-tolylpentane-1,5-dione **16***

FT-IR (KBr, cm^{-1}): 1673 (C=O), 3057–3027 (C—H), 2923–2855 (C—H); ^1H NMR($CDCl_3$, 300 MHz, ppm): $\delta = 5.15$ (d, 1H, H-2), 4.35 (m, 1H, H-3), 3.17 (dd, 1H, H-4a), 3.05 (dd, 1H, H-4b), 2.18 (s,3H, $\mathbf{CH_3}$), 6.96–7.81 (m, 19H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 198.8$ (C-1), 198.6 (C-5), 58.6 (C-2), 44.1 (C-3), 43.0 (C-4), 20.9 ($\mathbf{C}H_3$), 127.7–139.4; Mass (*m/z*): 441 $[M + Na]^+$, 419 $[M + 1]^+$ and 223.

*2.4.12. 3-(3-Nitrophenyl)-1,2,5-triphenylpentane-1,5-dione **17***

FT-IR (KBr, cm^{-1}): 1678 (C=O), 3063–3024 (C—H), 2923–2853 (C—H); ^1H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 5.15$ (d, 1H, H-2),

Table 1
Analytical data for compounds 9–23.

Entry	R	R1	R2	R3	R4	Yield (%)	M.P. (°C)	*m/z* [M + Na]$^+$
9	H	H	H	H	H	93	184–186	427
10	H	H	F	H	H	95	201–203	445
11	H	H	Cl	H	H	96	194–196	–
12	H	H	Br	H	H	92	188–190	507
13	H	H	OCH_3	H	H	97	141–143	457
14	H	OCH_3	H	H	H	96	173–175	457
15	H	OCH_3	OCH_3	OCH_3	H	93	100–102	517
16	H	H	CH_3	H	H	92	154–156	441
17	H	NO_2	H	H	H	94	188–190	472
18	CH_3	H	H	H	H	96	168–170	441
19	OCH_3	H	OCH_3	H	H	95	136–138	487
20	OCH_3	H	H	H	H	93	182–184	457
21	CH_3	H	F	H	H	94	168–170	459
22	H	H	F	H	F	96	182–184	463
23	H	H	Cl	H	Cl	97	158–160	495

Table 2
^{1}H chemical shifts of 1,2,3,5-tetraarylpentane-1,-5-diones (ppm).

Entry	H-2	H-3	H-4		Aromatic	Others
			H_{4a}	H_{4b}		
9	5.51	4.20	3.48	2.78	7.62–7.89	–
10	5.11	4.37	3.18	3.06	6.85–7.80	–
11	5.13	4.38	3.19	3.09	7.15–7.83	–
12	5.13	4.37	3.19	3.09	7.25–7.83	–
13	4.96	4.20	3.49	3.37	6.53–8.02	OCH_3-3.65
14	5.15	4.36	3.83	3.07	6.59–7.81	OCH_3-3.68
15	5.19	[a]	[a]	3.12	6.46–8.03	OCH_3-3.70, 3.68
16	5.15	4.35	3.17	3.05	6.96–7.81	CH_3-2.18
17	5.17	4.50	3.29	3.12	6.96–7.81	–
18	5.17	4.41	3.21	3.10	7.05–7.74	CH_3-2.32
19	5.06	4.32	3.13	3.06	6.68–7.83	OCH_3-3.65
20	5.11	4.37	3.17	3.08	6.77–8.00	OCH_3-3.77
21	5.08	4.35	3.16	3.06	6.81–7.72	CH_3-3.65
22	5.02	4.28	3.06	2.96	6.76–7.72	–
23	5.08	4.32	3.12	3.03	7.13–7.97	–

[a] Peaks merged.

Table 4
Coupling constants of 1,2,3,5-tetraarylpentane-1,-5-diones (Hz).

Entry	H-2	H-3		H-4a		H-4b	
	$J_{2,3}$	$J_{3,4}$	$J_{3,2}$	$J_{2,3}$	$J_{2,3}$	$J_{2,3}$	$J_{2,3}$
9	11.28	3.61	10.87	10.50	16.47	3.66	16.43
10	10.80	3.90	10.50	10.50	16.50	3.90	16.81
11	11.00	3.00	11.0	10.00	16.50	3.50	16.50
12	10.50	3.00	[a]	10.25	16.50	3.00	17.00
13	10.20	3.90	10.05	10.20	15.61	3.90	15.61
14	10.76	3.85	10.23	9.74	16.23	3.87	16.19
15	10.80	[a]	[a]	[a]	[a]	[a]	[a]
16	11.10	3.70	10.35	9.90	15.91	3.70	10.35
17	10.80	3.30	10.50	10.05	17.70	3.45	17.11
18	10.50	3.50	10.25	10.00	16.00	3.50	16.51
19	10.75	3.92	10.31	9.91	16.07	3.95	16.03
20	10.75	3.92	10.27	9.83	17.39	3.91	16.19
21	10.83	3.84	10.35	10.03	16.31	3.84	16.31
22	10.80	2.80	10.40	10.40	16.40	3.20	16.40
23	10.40	[a]	[a]	[a]	[a]	[a]	[a]

[a] Peaks merged.

Table 3
^{13}C chemical shifts of 1,2,3,5-tetraarylpentane-1,-5-diones (ppm).

Entry	C-1	C-5	C-2	C-3	C-4	Aromatic	Others
9	198.7	198.7	58.6	44.6	42.8	126.5–142.5	–
10	198.6	198.6	58.8	44.0	42.8	115.1–161.4	–
11	198.4	198.3	58.5	43.9	42.6	127.9–132.9	–
12	198.3	198.3	58.4	44.0	42.5	120.4–141.7	–
13	199.6	198.7	59.5	45.0	43.6	113.4–157.8	OCH_3-54.9
14	198.7	199.6	58.5	44.7	42.9	112.0–159.4	OCH_3-55.1
15	199.0	199.0	58.0	45.2	42.8	127.9–152.8	OCH_3-56.0,60.7
16	198.8	198.6	58.6	44.1	43.0	127.7–139.4	CH_3-20.9
17	197.8	197.7	58.2	43.8	42.2	121.7–148.1	–
18	198.8	198.2	58.4	44.6	42.9	126.5–143.5	CH_3-21.5
19	199.1	197.2	58.35	43.9	43.1	163.3–113.6	OCH_3-55.4,55.1
20	198.9	197.0	58.1	44.6	43.0	163.3–113.6	OCH_3-55.4
21	198.7	198.1	58.5	43.9	42.8	162.5–115.0	CH_3-21.6
22	198.5	197.0	58.7	44.0	42.7	115.1–166.9	–
23	198.2	197.2	58.5	43.9	42.6	121.9–143.9	–

4.50 (m, 1H, H-3), 3.29 (dd,1H, H-4a), 3.12 (dd, 1H, H-4b), 6.96–7.81 (m, 19H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 197.8$ (C-1), 197.7 (C-5), 58.2 (C-2), 43.8 (C-3), 42.2 (C-4), 121.7–148.1; Mass (*m/z*): 472 [M + Na]$^+$, 450 [M + 1]$^+$, 254 and 197.

2.4.13. 2,3,5-Triphenyl-1-p-tolylpentane-1,5-dione ***18***

FT-IR (KBr, cm^{-1}): 1682, 1671 (C=O), 3073–3028 (C—H), 2922–2849 (C—H); ^{1}H NMR($CDCl_3$, 500 MHz, ppm): $\delta = 5.17$ (d, 1H, H-2), 4.41 (m, 1H, H-3), 3.21 (dd, 1H, H-4a), 3.10 (dd, 1H, H-4b), 2.32 (s,3H, C**H_3**), 7.05–7.74 (m, 19H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): $\delta = 198.8$ (C-1), 198.2 (C-5), 58.4 (C-2), 44.6 (C-3), 42.9

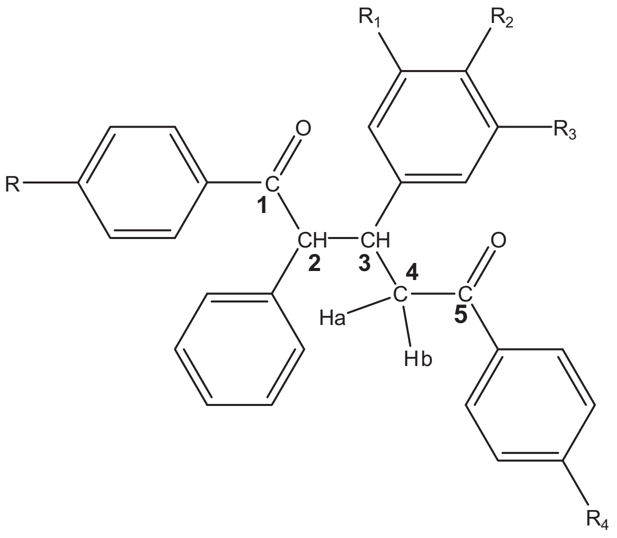


Fig. 1. Representative structure of compound.

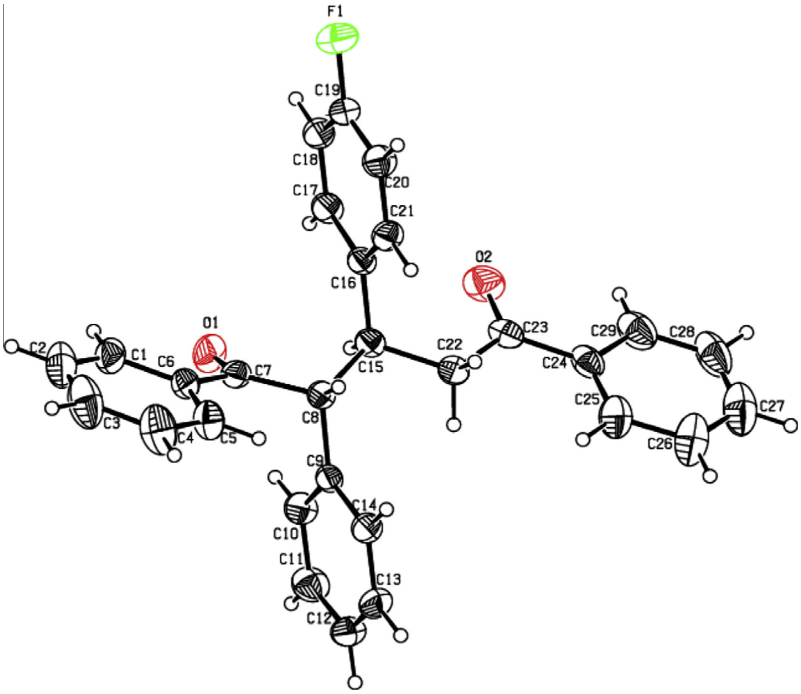


Fig. 2. ORTEP of compound 10.

(C-4), 21.5 (**C**H_3), 126.5–143.5; Mass (*m/z*): 441 $[M + Na]^+$, 419 $[M + 1]^+$ and 209.

2.4.14. 1,3-Bis(4-methoxyphenyl)-2,5-diphenylpentane-1,5-dione **19**

FT-IR (KBr, cm^{-1}): 1682, 1668 (C═O), 3052 (C—H), 2928–2839 (C—H); ^1H NMR ($CDCl_3$, 400 MHz, ppm): $\delta = 5.06$ (d, 1H, H-2), 4.32 (m, 1H, H-3), 3.13 (dd, 1H, H-4a), 3.05 (dd, 1H, H-4b), 3.67 (s, 3H, O**C**$\mathbf{H_3}$), 3.77 (s, 3H, O**C**$\mathbf{H_3}$), 6.68–7.83 (m, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): $\delta = 199.1$ (C-1), 197.2 (C-5), 58.4 (C-2), 43.9 (C-3), 43.1(C-4), 55.4 (O**C**H_3), 55.1 (O**C**H_3), 113.6–1633; Mass (*m/z*): 487 $[M + Na]^+$, 465 $[M + 1]^+$, 301 and 239.

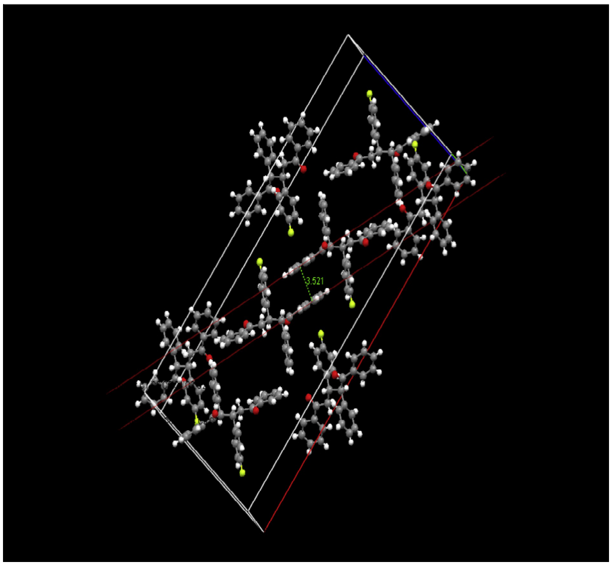


Fig. 3. Packing diagram of compound 10.

2.4.15. 1-(4-Methoxyphenyl)-2,3,5-triphenylpentane-1,5-dione **20**

FT-IR (KBr, cm^{-1}): 1684, 1664 (C═O), 3059–3029 (C—H), 2961–2838 (C—H); ^1H NMR ($CDCl_3$, 400 MHz, ppm): $\delta = 5.11$ (d, 1H, H-2), 4.37 (m, 1H, H-3), 3.17 (dd, 1H, H-4a), 3.08 (dd, 1H, H-4b), 3.77 (s, 3H, O**C**$\mathbf{H_3}$), 6.77–8.00 (m, 19H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): $\delta = 198.9$ (C-1), 197.0 (C-5), 58.1 (C-2), 44.6 (C-3), 43.0 (C-4), 55.4 (O**C**H_3), 113.6–163.3; Mass (*m/z*): 457 $[M + Na]^+$, 435 $[M + 1]^+$, 227, 209 and 174.

2.4.16. 3-(4-Fluorophenyl)-2,5-diphenyl-1-p-tolylpentane-1,5-dione **21**

FT-IR (KBr, cm^{-1}): 1685, 1669 (C═O), 3058–3030 (C—H), 2921–2851 (C—H); ^1H NMR($CDCl_3$, 400 MHz, ppm): $\delta = 5.08$ (d, 1H, H-2),

Table 5
Crystal data and structure refinement detail for10.

Compound	10
Empirical formula	$C_{29}H_{23}FO_2$
Formula weight	422.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C2/c*
Unit cell dimensions	$a = 40.405(4)$ Å $\alpha = 90°$
	$b = 5.9216(6)$ Å $\beta = 93.909°(12)$
	$c = 18.431(12)$ Å $\gamma = 90°$
Volume	4399.5(8) $Å^3$
Z, Calculated density	8, 1.276 mg/m^3
Absorption coefficient	0.105 mm^{-1}
$F_{(000)}$	1776
Crystal size	0.25 × 0.23 × 0.20 mm
Theta range for data collection	2.02–28.60°
Limiting indices	$-53 \leqslant h \leqslant 54$, $-7 \leqslant k \leqslant 7$, $-24 \leqslant l \leqslant 24$
Reflections collected/unique	36473/5536[*R*(int) = 0.09191]
Completeness to theta = 30.87	99.9%
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5539/0/289
Goodness-of-fit on *F*2	1.059
Final *R*, *Rw* (obs, data)	0.0781, 0.1360

4.35 (m, 1H, H-3), 3.16 (dd, 1H, H-4a), 3.06 (dd, 1H, H-4b), 2730 (s, 3H, C**H$_3$**), 6.81–7.72 (m, 18H); ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ = 198.7 (C-1), 198.1 (C-5), 58.5 (C-2), 43.9 (C-3), 42.8 (C-4), 21.6 (**C**H$_3$), 115.0–162.5; Mass (*m/z*): 459 [M + Na]$^+$, 437 [M + 1]$^+$ and 227.

2.4.17. 3,5-Bis(4-fluorophenyl)-1,2-diphenylpentane-1,5-dione *22*

FT-IR (KBr, cm^{-1}): 1677 (C═O), 3061–3024 (C—H), 2933–2904 (C—H); ^{1}H NMR(CDCl$_3$, 400 MHz, ppm): δ = 5.02 (d, 1H, H-2), 4.28 (m, 1H, H-3), 3.06 (dd, 1H, H-4a), 2.96 (dd, 1H, H-4b), 6.76–7.72 (m, 18H); ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ = 198.5 (C-1), 197.0 (C-5), 58.7 (C-2), 43.7 (C-3), 42.7 (C-4), 115.1–166.9; Mass (*m/z*): 463 [M + Na]$^+$, 441 [M + 1]$^+$ and 245.

2.4.18. 3,5-Bis(4-chlorophenyl)-1,2-diphenylpentane-1,5-dione *23*

FT-IR (KBr, cm^{-1}): 1684, 1660 (C═O), 3057–3019 (C—H), 2924–2843 (C—H); ^{1}H NMR(CDCl$_3$, 400 MHz, ppm): δ = 5.08 (d, 1H, H-2), 4.32 (m, 1H, H-3), 3.12 (dd, 1H, H-4a), 3.03 (dd, 1H, H-4b), 7.13–7.97 (m, 18H); ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ = 198.2 (C-1), 197.2 (C-5), 58.5 (C-2), 43.9 (C-3), 42.6 (C-4), 121.9–143.9; Mass (*m/z*): 495 [M + Na]$^+$, 473 [M + 1]$^+$ and 277.

2.5. X-ray data collection, structure solution and refinement

Crystal was grown by slow evaporation technique using acetone as solvent. Determination of the unit cell and data collection were performed on a (Bruker, 2008) APEX2 diffractometer using graphite-monochromated M$_0$ Kα radiation (λ = 0.71073 Å) at 293 K with crystal size of 0.25 × 0.20 × 0.20 mm. Multi-scan absorption correction were applied using the SADABAS program. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full matrix least square procedure on F^2 with anisotropic thermal parameters. All non hydrogen atoms were refined (SHELXL-97) and placed at chemically acceptable position. A total of 289 parameters were refined with 5539 unique reflections which covered the residuals to R_1 = 0.0781. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications number CCDC 853753 for **10**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033: or e-mail: deposit@ccdc.cam.ac.uk (see Scheme 1).

Table 6
Selected bond lengths [Å] for 10.

Atoms	Distance
C(1)—C(2)	1.369(5)
C(3)—C(2)	1.374(6)
C(3)—C(4)	1.365(6)
C(5)—C(4)	1.373(4)
C(6)—C(1)	1.397(4)
C(6)—C(5)	1.389(4)
C(7)—C(6)	1.480(4)
C(7)—O(1)	1.221(3)
C(8)—C(7)	1.530(3)
C(8)—C(9)	1.514(3)
C(8)—C(15)	1.559(3)
C(9)—C(10)	1.387(4)
C(9)—C(14)	1.394(3)
C(10)—C(11)	1.381(4)
C(11)—C(12)	1.368(5)
C(13)—C(12)	1.365(5)
C(14)—C(13)	1.374(4)
C(15)—C(16)	1.510(3)
C(15)—C(22)	1.31(4)
C(16)—C(17)	1.384(3)
C(16)—C(21)	1.394(3)
C(17)—C(18)	1.373(4)
C(19)—C(18)	1.362(4)
C(20)—C(19)	1.370(4)
C(21)—C(20)	1.372(4)
C(22)—C(23)	1.508(3)
C(23)—C(24)	1.502(4)
C(23)—O(2)	1.210(3)
C(24)—C(25)	1.379(5)
C(24)—C(29)	1.392(4)
C(26)—C(25)	1.385(5)
C(26)—C(27)	1.359(6)
C(27)—C(28)	1.369(6)
C(29)—C(28)	1.389(6)
F(1)—C(19)	1.353(3)

3. Results and discussion

The 1,2,3,5-tetraarylpentane-1,5-diones were prepared in two steps. The aryl aldehydes were subjected to Claisen–Schmidt reaction with acetophenone to give corresponding α,β-unsaturated ketones (chalcones). The chalcones were then subjected to Michael addition with 2-aryl acetophenone to yield the 1,2,3,5-tetraarylpentane-1,5-diones. Sodium hydroxide was used as catalyst and the process avoids the use of hazardous chemicals and harsh con-

Table 7
Selected bond Angles [°] for 10.

Atoms	Angles
C(27)—C(26)—C(25)	120.6(4)
C(9)—C(8)—C(7)	108.01(18)
C(9)—C(8)—C(15)	113.3(2)
C(7)—C(8)—C(15)	110.73(19)
C(16)—C(15)—C(22)	113.2(2)
C(16)—C(15)—C(8)	110.3(2)
C(22)—C(15)—C(8)	109.27(19)
C(17)—C(16)—C(21)	117.3(2)
C(13)—C(14)—C(9)	121.0(3)
C(18)—C(17)—C(16)	122.2(3)
C(11)—C(10)—C(9)	120.7(3)
C(19)—C(20)—C(21)	119.0(3)
O(2)—C(23)—C(24)	121.2(2)
O(2)—C(23)—C(22)	121.5(3)
C(24)—C(23)—C(22)	117.3(2)
C(12)—C(13)—C(14)	120.5(3)
C(2)—C(1)—C(6)	120.4(3)
C(4)—C(5)—C(6)	120.3(3)
C(26)—C(27)—C(28)	119.3(4)
C(24)—C(25)—C(26)	120.8(3)
C(28)—C(29)—C(24)	119.7(4)
C(17)—C(16)—C(15)	121.5(2)
C(21)—C(16)—C(15)	121.2(2)
O(1)—C(7)—C(6)	120.3(2)
O(1)—C(7)—C(8)	119.2(2)
C(7)—C(6)—C(8)	120.4(2)
C(10)—C(9)—C(14)	117.6(2)
C(10)—C(9)—C(8)	121.3(2)
C(14)—C(9)—C(8)	121.1(2)
C(23)—C(22)—C(15)	116.1(2)
C(20)—C(21)—C(16)	121.2(2)
C(5)—C(6)—C(1)	118.5(3)
C(5)—C(6)—C(7)	122.7(2)
C(1)—C(6)—C(7)	118.7(3)
F(1)—C(19)—C(18))	119.6(3)
F(1)—C(19)—C(20))	118.5(3)
C(18)—C(19)—C(20)	121.9(3)
C(19)—C(18)—C(17)	118.5(2)
C(25)—C(24)—C(29)	118.4(3)
C(25)—C(24)—C(23)	122.8(2)
C(29)—C(24)—C(23)	118.9(3)
C(12)—C(11)—C(10)	120.6(3)
C(13)—C(12)—C(11)	119.6(3)
C(4)—C(3)—C(2)	120.4(3)
C(27)—C(28)—C(29)	121.0(3)
C(1)—C(2)—C(3)	120.1(3)
C(3)—C(4)—C(5)	120.3(4)

dition like heating. After having success in the synthesis of 1,5-diones using relatively moderate conditions in two steps (Scheme 2), we pondered whether we can make this protocol even more attractive by carrying out the synthesis in a one-step multi component reaction. This would avoid isolation of chalcones, decrease No. of operations and would in essence be easy to execute and more green in terms of solvent usage etc. An experiment was designed and executed wherein equi-molar mixture of 2-phenylacetophenone, acetophenone, benzaldehyde and sodium hydroxide solution in ethanol was stirred at room temperature. To our gratification reaction worked well to yield corresponding 1,2,3,5-tetraarylpentane-1,5-dione (Scheme 3). After having success with one of the substrates, the reactions were carried out using all other substrates and were found to be successful.

Here, we have disclosed an efficient, simple one-pot process for the synthesis of 1,2,3,5-tetraphenylpentan-1,5-diones, wherein sodium hydroxide is used as catalyst and the process avoids the use of hazardous chemicals and harsh condition like heating. An overall yield of 95% is claimed for this one-pot synthetic procedure.

3.1. IR spectral analysis of compound *9*

In IR spectra, the presence of carbonyl stretching frequency around 1686 cm^{-1} confirms the diketone formation. A collection of bands observed in the region of 3079–3028 cm^{-1} are due to aromatic C—H stretching frequency. The absorption bands appeared in the region of 2913–2849 cm^{-1} is assigned to aliphatic C—H stretching frequencies. The C═C stretching frequency observed at 1597 cm^{-1}.

3.2. Mass spectral analysis of compound *9*

The mass spectrum of the compound yields a peak at *m/z* 427 which corresponds to $[M + Na]^+$. The peak absorbed at *m/z* 405 $[M + 1]^+$ is consistent with proposed molecular formula of the compound. The other prominent peak is observed at *m/z* 209 (see Tables 1–3).

Table 8
Atomic coordinates and equivalent isotopic displacement parameters for compound 10.

Atom	x	y	z	U(eq)
C(1)	343(1)	−1402(5)	4472(2)	67(1)
C(2)	35(1)	−1424(7)	4114(2)	87(1)
C(3)	−68(1)	369(8)	3684(3)	101(1)
C(4)	135(1)	2185(7)	3610(2)	90(1)
C(5)	443(1)	2247(5)	3971(2)	63(1)
C(6)	554(1)	446(4)	4405(1)	50(1)
C(7)	888(1)	381(4)	4785(1)	47(1)
C(8)	1111(1)	2471(4)	4802(1)	41(1)
C(9)	1304(1)	2442(4)	4127(1)	41(1)
C(10)	1497(1)	598(5)	3960(2)	55(1)
C(11)	1679(1)	620(6)	3353(2)	68(1)
C(12)	1673(1)	2462(6)	2904(2)	67(1)
C(13)	1482(1)	4282(5)	3054(2)	61(1)
C(14)	1300(1)	4291(4)	3658(1)	51(1)
C(15)	1337(1)	2558(4)	5522(1)	45(1)
C(16)	1128(1)	2675(4)	6169(1)	44(1)
C(17)	1127(1)	941(4)	6673(1)	53(1)
C(18)	936(1)	1015(5)	7261(1)	61(1)
C(19)	741(1)	2859(5)	7345(1)	57(1)
C(20)	733(1)	4629(5)	6865(2)	58(1)
C(21)	924(1)	4529(4)	6279(1)	51(1)
C(22)	1581(1)	4530(5)	5488(1)	50(1)
C(23)	1852(1)	4641(5)	6091(1)	54(1)
C(24)	2103(1)	6503(5)	6056(2)	57(1)
C(25)	2088(1)	8107(6)	5512(2)	75(1)
C(26)	2320(1)	9832(7)	5512(3)	99(1)
C(27)	2572(1)	9943(8)	6037(3)	103(1)
C(28)	2591(1)	8362(8)	6580(2)	92(1)
C(29)	2362(1)	6619(7)	6592(2)	79(1)
O(1)	996(1)	−1374(3)	5058(1)	67(1)
O(2)	1867(1)	3292(4)	6585(1)	77(1)
F(1)	552(1)	2980(4)	7922(1)	91(1)

3.3. NMR spectral analysis of compound *9*

3.3.1. ^1H NMR

The ^1H NMR showed a doublet observed at 5.51 ppm, corresponding to one proton is assigned to H-2. A multiplet centred at 4.20 ppm due to H-3. The compounds also exhibited the presence of two magnetically non-equivalent protons of a methelene group (H_a/H_b at C-4), at 3.48 ppm and 2.78 ppm, respectively, coupled with each other and inturn with vicinal methane proton H-3 and produce two double doublets. The coupling constant values are given in Table 4. The aromatic protons appear in the range 6.46–8.03 ppm.

3.3.2. ^{13}C NMR

The ^{13}C NMR showed weak signals at around 198 ppm, due to carbonyl carbons at C-1 and C-5. The chemical shifts of aromatic carbon appear in the range 112.0–161.4 ppm. The signal observed at 58.0–59.5 ppm corresponding to C-2. The signal appeared at 43.0–45.2 ppm is assigned to C-3. The signal observed at 42.2–43.6 ppm is due to C-4 (see Fig. 1).

3.4. X-ray structure determination of 3-(4-fluorophenyl)-1,2,5-triphenylpentane-1,5-dione*(10)*

The single crystal X-ray structural analysis reveals the structure and geometry of **10** in the solid state. The compound **10** crystallizes in a monoclinic system with C2/c space group. The ORTEP (Oak Ridge Thermal Ellipsoids Plot) of the compound is shown in Fig. 2 and the packing diagram is given in Fig. 3. Crystal data, data collection parameters, selected bond distances and angles are given in Tables 5–9.

Table 9
Anisotropic displacement parameters for compound 10.

	U11	U22	U33	U23	U13	U12
C(1)	72(2)	49(2)	81(2)	−16(2)	23(2)	10(2)
C(2)	64(2)	73(2)	127(3)	−38(2)	17(2)	−16(2)
C(3)	63(2)	94(3)	141(4)	−35(3)	−21(2)	−3(2)
C(4)	78(2)	74(2)	115(3)	−8(2)	−29(2)	8(2)
C(5)	63(2)	50(2)	76(2)	−2(1)	−8(2)	−2(1)
C(6)	57(2)	40(1)	53(1)	−9(1)	10(1)	−18(1)
C(7)	64(2)	36(1)	42(1)	3(1)	10(1)	1(1)
C(8)	53(1)	32(1)	40(1)	3(1)	1(1)	2(1)
C(9)	50(1)	36(1)	37(1)	0(1)	−1(1)	−2(1)
C(10)	65(2)	46(2)	55(2)	2(1)	5(1)	7(1)
C(11)	68(2)	68(2)	70(2)	−12(2)	13(2)	10(2)
C(12)	65(2)	87(2)	51(2)	−3(2)	14(1)	−15(2)
C(13)	71(2)	65(2)	48(2)	12(1)	5(1)	−14(2)
C(14)	66(2)	41(1)	46(1)	7(1)	2(1)	−1(1)
C(15)	55(1)	40(1)	39(1)	4(1)	−2(1)	4(1)
C(16)	59(2)	36(1)	35(1)	4(1)	0(1)	1(1)
C(17)	78(2)	38(1)	43(1)	6(1)	−2(1)	1(1)
C(18)	89(2)	48(2)	44(1)	9(1)	1(1)	−14(2)
C(19)	67(2)	63(2)	44(1)	−4(1)	14(1)	−18(2)
C(20)	67(2)	50(2)	58(2)	0(1)	10(1)	5(1)
C(21)	64(2)	40(1)	49(1)	8(1)	6(1)	2(1)
C(22)	53(2)	54(2)	41(1)	1(1)	0(1)	−1(1)
C(23)	53(2)	69(2)	41(1)	−8(1)	2(1)	8(1)
C(24)	46(1)	69(2)	56(2)	−20(1)	3(1)	5(2)
C(25)	61(2)	69(2)	94(2)	−5(2)	−7(2)	−6(2)
C(26)	75(2)	71(2)	150(4)	−4(2)	−4(2)	−14(2)
C(27)	69(2)	85(3)	153(4)	−34(3)	−1(3)	−12(2)
C(28)	55(2)	117(3)	101(3)	−50(3)	−9(2)	−3(2)
C(29)	58(2)	107(3)	70(2)	−25(2)	−4(2)	4(2)
O(1)	89(1)	39(1)	73(1)	17(1)	−4(1)	−3(1)
O(2)	77(1)	96(2)	56(1)	12(1)	−10(1)	4(1)
F(1)	110(2)	99(2)	70(1)	−3(1)	41(1)	−18(1)

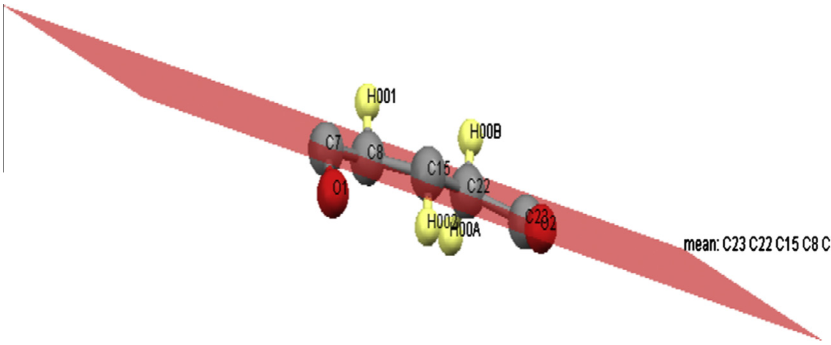


Fig. 4. The 'W' conformation view.

Unit cell contains eight molecules with insignificant intermolecular interactions. From the ORTEP it is observed that the aryl groups attached at C-8 and C-15 are exactly opposite to each other [C(16)—C(15)—C(8)—C(9) = 177.79°]. The two keto group distances are almost similar [C(7)—O(1) = 1.221 Å and C(23)—O(2) = 1.220 Å] and the observed short distances indicate the double bonded nature of these bonds. The torsional angle between the two keto groups was found to be −29.5°.

From the packing diagram it is observed that there are some effective π–π stacking interactions between the aryl groups. Particularly, the π–π stacking interaction between the terminal aryl rings of two adjacent molecules (in chain) was found to be 3.52 Å as shown in Fig. 3 (π–π). The C(23)—C(22)—C(15)—C(8)—C(7) chain is almost planar with "W" conformation (Fig. 4) and the observed maximum deviation is 0.122 Å for C(15) from the C(23)/C(22)/C(15)/C(8)/C(7) plane.

6. Conclusions

In conclusion, we have reported an efficient synthesis of 1,2,3,5-tetraphenylpentan-1,5-diones by the three-component one pot reactions of aromatic aldehydes, acetophenone and 2-phenylacetophenone catalysed by sodium hydroxide. This method is scalable and has the advantages of easy work up, mild reaction conditions, and high yields. Single crystal X-ray structural analysis of **10,** has also been performed and the results reveals that the torsional angle between the two keto groups was found to be −29.5° and the C(23)—C(22)—C(15)—C(8)—C(7) chain is almost planar with "W" conformation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.10.037.

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