

# Domino Knoevenagel/Michael synthesis of 2,2'-arylmethylenebis(3hydroxy-5,5-dimethyl-2-cyclohexen-1-one) derivatives catalyzed by silica-diphenic acid and their single crystal X-ray analysis

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Abstract. An efficient and eco-friendly procedure has been developed for the synthesis of various 2,2'arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives which were isolated and characterized by melting point, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectrometric techniques. Out of the fourteen compounds synthesized, four compounds yielded crystals suitable for single crystal X-ray analysis which showed that 2,2'-phenylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) crystallizes in the tetragonal system with space group  $I4_1/a$ , 2,2'-(3-nitrophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) crystallizes in the monoclinic system with space group  $P2_1/n$ , 2,2'-(4-nitrophenyl)methylenebis(3hydroxy-5,5-dimethyl-2-cyclohexene-1-one) crystallizes in the orthorhombic system with space group Pca21and 2,2'-(4-chlorophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) crystallizes in the monoclinic space group P21/c.

**Keywords.** Crystal structure; single crystal X-ray analysis; 5,5-dimethyl-1,3-cyclohexanedione; heterogeneous catalyst.

## 1. Introduction

2,2'-Arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds and their derivatives are biologically important key synthons for the synthesis of various xanthenes and acridinedione derivatives.<sup>1</sup> These compounds also show significant biological and therapeutic activities such as antiviral, antibacterial,<sup>2</sup> antioxidant,<sup>3</sup> lipoxygenase inhibitor, tyrosinase inhibitors against dermatological disorders including hyperpigmentation and skin melanoma<sup>4</sup> and also action against disorders like asthma and inflammatory processes.<sup>5</sup>

For the synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2 cyclohexene-1-one) compounds, various synthetic methods have been reported in the literature which involve the usage of different types of catalysts such as KF/Al<sub>2</sub>O<sub>3</sub>,<sup>6</sup> SmCl<sub>3</sub>,<sup>7</sup> *L*-lysine,<sup>8</sup> CaCl<sub>2</sub>,<sup>9</sup> HClO<sub>4</sub>–SiO<sub>2</sub>,<sup>10</sup> zirconium oxychloride/sodium amide (ZrOCl<sub>2</sub>/NaNH<sub>2</sub>),<sup>11</sup> I<sub>2</sub>,<sup>12</sup> FeCl<sub>3</sub>.6H<sub>2</sub>O/TMSCl/[bmim] [BF<sub>4</sub>]<sup>13</sup> and cetyltrimethyl ammonium bromide (CTMAB).<sup>14</sup> Some of the above mentioned protocols are valuable but suffer from one or more drawbacks

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including long reaction times, poor yield of products, harsh reaction conditions and use of expensive and/or toxic solvents. Due to the biological importance of 2,2'arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds, there is a strong demand for the development of mild and highly efficient procedure for their synthesis. In this regard, we have synthesized 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives via one-pot Knoevenagel/ Michael reaction between various aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) by using silica supported diphenic acid as a recyclable heterogeneous catalyst (scheme 1). The mild and selective action of silica-diphenic acid in the formation of the above mentioned products has been clearly depicted in scheme 1 which shows that the reaction stops after the formation of product 1 and does not undergo cyclization step to form product 2.

## 2. Experimental

## 2.1 Materials and methods

All the chemicals and solvents were purchased from Sigma-Aldrich and Merck and were used without



5,5'-Dimethyl-1,3-cyclohexanedione

Scheme 1. Reaction scheme terminating after formation of product 1.



Scheme 2. Preparation of silica-diphenic acid.

further purification. Silica gel was purchased from ACROSS Organics. All melting points of the products were taken on Perfit melting point apparatus and compared with those reported in the literature. FTIR spectra of the products were recorded on SHIMADZU prestige spectrophotometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the products were recorded in DMSO- $d_6$  on Bruker Avance III 400 MHz spectrometer using TMS as an internal standard (Department of Chemistry, University of Jammu, Jammu). The mass spectra were recorded on Esquire 3000 Bruker Daltonics spectrometer (ESI) (IIIM, Jammu). Suitable crystals of 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds were selected and their single-crystal X-ray data were recorded on a CCD area-detector diffractometer (X'calibur system - Oxford diffraction make, U.K.) (Department of Physics and Electronics, University of Jammu, Jammu).

## 2.2 *Preparation and characterization of silica supported diphenic acid*

The detailed preparation scheme and characterization (FTIR, TGA, SEM and TEM) of silica-diphenic acid has already been reported.<sup>15</sup> Scheme 2 shows the preparation of silica-diphenic acid

#### 2.3 Determination of Acidity of silica-diphenic acid

In the reported characterization of silica-diphenic acid,<sup>15</sup> the nature of bonding of diphenic acid with activated silica was well explained by FTIR spectroscopy which concluded that out of the two carboxylic groups of diphenic acid, one carboxylic group remains free and becomes responsible for catalyzing the reactions. Further, to explain the nature of bonding of diphenic acid over activated silica, we have performed the acid-base

titrations which gave a quantitative knowledge of availability of free carboxylic groups for catalysis per silica support. The detailed procedure and conclusions related to the acid-base titration are reported in the Supplementary Information.

## 2.4 General procedure for the synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one)

2.4a *Grinding method*: In a pre-weighed agate mortar, an aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) and silica supported diphenic acid (0.05 g) as a heterogeneous catalyst were subjected to mechanical grinding with the help of pestle for appropriate time at room temperature. On completion of the reaction (monitored by TLC), ethyl acetate was added to the reaction mixture and the mixture filtered to separate the catalyst, followed by washing of the filtrate with distilled water and dried over anhydrous  $Na_2SO_4$ . Finally, the solvent was allowed to evaporate over water-bath and the crude product obtained was finally recrystallized from ethanol to isolate pure products.

2.4b *Thermal heating method*: To a solution of ethanol (2 mL) and water (0.4 mL) in a round bottom flask (50 mL), aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) and the heterogeneous catalyst silica supported diphenic acid (0.05 g) were added and the reaction mixture was allowed to be refluxed at 80°C in an oil-bath for an appropriate duration. On completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and

diluted with EtOAc (20 mL). After dilution, the reaction mixture was filtered to separate the catalyst followed by washing of filtrate with distilled water and dried over anhydrous  $Na_2SO_4$ . Finally, the solvent was allowed to evaporate over water bath and crude product was obtained. The crude product was further recrystallized from ethanol at room temperature to isolate pure product.

The pure products were characterized by melting point, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectrometry. Table 1 shows the calculated and experimental mass (ESI) values (g/mol) for all compounds along with their molecular formula. Some compounds were also characterized by single-crystal X-ray analysis.

## 2.5 X-ray data collection and structure refinement

Several attempts have been made to grow crystals of all the compounds 1-16, but only four compounds formed crystals suitable for single crystal X-ray analysis. These crystals were obtained by very slow evaporation of their ethanol solution at room temperature. The structures of the four compounds were determined by single-crystal X-ray diffraction analysis. X-ray intensity data of these compounds were collected on a CCD area-detector diffractometer (X'calibur system - Oxford diffraction make, U.K.) equipped with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The crystal used for data collection was of dimensions 0.30 x 0.20 x 0.20 mm. The data were corrected for Lorentz and polarisation factors. The structures were solved by direct methods using SHELXS97.<sup>16</sup> All nonhydrogen atoms of the molecule were located in the

 Table 1.
 Calculated and experimental mass (ESI) values for all compounds along with their molecular formula.

S.No.	Molecular Formula	Calculated Mass	Experimental Mass (+ESI)
1	C <sub>23</sub> H <sub>28</sub> O <sub>4</sub>	368	368.96
2	$C_{23}H_{27}NO_6$	413	414.02
3	$C_{23}H_{27}NO_6$	413	414.16
4	$C_{23}H_{27}NO_6$	413	414.19
5	$C_{23}H_{27}O_4Cl$	402	403.11
6	$C_{23}H_{27}O_4Cl$	402	403.16
7	$C_{23}H_{27}O_4Br$	449	450.11
8	$C_{23}H_{27}O_4Br$	449	450.09
9	$\tilde{C}_{24}H_{30}O_4$	382	383.03
10	$C_{24}H_{30}O_5$	398	382.97
11	$C_{25}H_{32}O_{6}$	428	429.22
12	$C_{25}H_{31}NO_4$	411	412.05
13	$\tilde{C}_{24}H_{30}O_6$	414	415.09
14	$C_{27}H_{30}O_4$	419	420.13
15	$C_{21}H_{26}O_5$	358	359.11
16	$C_{25}H_{30}O_4$	394	395.02

Table 2.	Reaction bet	ween various a	ldehydes and	5,5-dimethyl-	1,3-cyclohexanedior	le in presence c	of silica-dipher	nic acid as a h	leterogeneous cataly	st.
			Grindir	ig condition <sup>a</sup>			Therma	l condition <sup>b</sup>		
Entry	Aldehydes	Time (min)	Yield <sup>c</sup> (%)	TON	TOF (TON/min)	Time (min)	Yield <sup>c</sup> (%)	NOT	TOF (TON/min)	M.P. (°C) (Lit. M.p.)
-	ef and the second secon	15	95	$2.50 \times 10^4$	1.67×10 <sup>3</sup>	30	06	$2.36 \times 10^{4}$	$7.86 \times 10^{2}$	191-192/193-195 <sup>18</sup>
7	CHO	10	92	2.42×10 <sup>4</sup>	$2.42 \times 10^{3}$	25	95	2.50×10 <sup>4</sup>	$1.00 \times 10^{3}$	245-247/249-251 <sup>18</sup>
<del>ر</del>	CHO NO2	Ś	8	2.57×10 <sup>4</sup>	$5.14 \times 10^{3}$	15	86	$2.57 \times 10^4$	$1.71 \times 10^{3}$	199/201-203 <sup>7</sup>
4	Q Q Q	10	95	2.50×10 <sup>4</sup>	2.50×10 <sup>3</sup>	15	95	2.50×10 <sup>4</sup>	$1.66 \times 10^{3}$	186-188/188-190 <sup>18</sup>
Ś	CHO	10	06	2.36×10 <sup>4</sup>	$2.36 \times 10^{3}$	15	06	2.36×10 <sup>4</sup>	$1.57 \times 10^{3}$	145/140-142 <sup>19</sup>
Q	ġō	∞	95	$2.50 \times 10^4$	3.12×10 <sup>3</sup>	20	95	$2.50 \times 10^{4}$	$1.25 \times 10^{3}$	145/140-142 <sup>18</sup>

Table 2	. (continued)									
			Grindin	g condition <sup>a</sup>			Therma	ll condition <sup>b</sup>		
Entry	Aldehydes	Time (min)	Yield <sup>c</sup> (%)	TON	TOF (TON/min)	Time (min)	Yield <sup>c</sup> (%)	NOT	TOF (TON/min)	M.P. (°C) (Lit. M.p.)
٢	et e	12	92	2.42×10 <sup>4</sup>	$2.01 \times 10^{3}$	25	95	$2.50 \times 10^{4}$	$1.00 \times 10^{3}$	152-154/155 <sup>19</sup>
œ	ġ ġ ġ ġ ġ ġ ġ	10	95	$2.50 \times 10^4$	$2.50 \times 10^{3}$	25	76	$2.55 \times 10^{4}$	$1.02 \times 10^{3}$	152-154/155 <sup>20</sup>
Q	Ğ	15	60	2.36×10 <sup>4</sup>	$1.57 \times 10^{3}$	35	95	$2.50 \times 10^4$	7.14× 10 <sup>2</sup>	135-137/139-141 <sup>7</sup>
10	oct	12	95	2.50×10 <sup>4</sup>	2.08×10 <sup>3</sup>	35	06	$2.36 \times 10^{4}$	6.74× 10 <sup>2</sup>	143-145/146-148 <sup>18</sup>
11	осн <sub>3</sub>	20	95	2.50×10 <sup>4</sup>	1.25×10 <sup>3</sup>	40	95	2.50×10 <sup>4</sup>	$6.74 \times 10^{2}$	170-171/173-175 <sup>18</sup>

# Application of silica-diphenic acid catalyst

Table 2.	. (continued)									
			Grindin	g condition <sup>a</sup>			Therma	l condition <sup>b</sup>		
Entry	Aldehydes	Time (min)	Yield <sup>c</sup> (%)	TON	TOF (TON/min)	Time (min)	Yield <sup>c</sup> (%)	TON	TOF (TON/min)	M.P. (°C) (Lit. M.p.)
12	СНО	18	06	$2.36 \times 10^{4}$	$1.31 \times 10^{3}$	30	85	$2.23 \times 10^{4}$	$6.25 \times 10^{2}$	189-190/191-193 <sup>2</sup>
	-									
	н <sub>а</sub> с сн									
13	, cHO	25	06	$2.36 \times 10^{4}$	$9.44 \times 10^{2}$	42	80	$2.10 \times 10^4$	$5.00  imes 10^{2}$	191-193/193-195 <sup>7</sup>
	$\langle$									
	OCH <sub>3</sub>									
14	СНО	30	80	$2.10 \times 10^{4}$	$7.00 \times 10^{2}$	45	75	$1.97 \times 10^{4}$	$4.37 \times 10^2$	229-231/233-235 <sup>18</sup>
15	CHO	45	75	$1.97 \times 10^{4}$	$4.37 \times 10^{2}$	60	70	$1.84 \times 10^{4}$	$3.06 \times 10^{2}$	141-143/139-141 <sup>7</sup>
16	о опо	40	82	$2.16 \times 10^{4}$	$5.40 \times 10^{2}$	55	75	$1.97 \times 10^{4}$	$3.58 \times 10^{2}$	214-217/213-215 <sup>7</sup>
		1				1	1			
t T	, ,									
17	⊳=<	I	I	I	I	I	I	I	I	I
0	= c									
18	)⇒≪ >	I	I	I	I	I	I	I	I	I
	۲ >									
Optimiz	ed Reaction cond	itions: <sup>a</sup> Aldehy	/de (1 mmol),	5,5-dimethyl	-1,3-cyclohexanedi	one $(2 \text{ mmol})$ ,	silica-dipheni	c acid (0.05	g) were grinded in :	a motar and pestle for

required time in solvent-free condition. <sup>b</sup>Aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), silica-diphenic acid (0.05 g) were taken in round bottom flask and refluxed for required time in ethanol: water solvent mixture. <sup>c</sup>Yield of pure products.

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best E-map. Full-matrix least-squares refinement was carried out using SHELXL97. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, tables 4.2.6.8 and 6.1.1.4). Molecular drawings were obtained using DIAMOND, Version 2.1 (table 1).<sup>17</sup>

#### 3. Results and Discussions

The domino synthesis of 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2- cyclohexene-1-one) derivatives *via* Knoevenagel/Michael reaction is an important synthesis as they are key synthons for the preparation of various biologically important organic molecules. In this regard, we have synthesized these derivatives in the presence of silica supported diphenic acid as a heterogeneous catalyst.

#### 3.1 Optimization of reaction conditions

To optimize the reaction conditions, benzaldehyde (1 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) were selected as test substrates. Initially, the reaction of benzaldehyde with 5,5-dimethyl-1,3-cyclohexanedione was carried out by mechanochemical grinding method, in which reactants and catalyst were taken in a pre-weighed mortar and mixed thoroughly with pestle for few minutes in the absence of solvent. The reaction of test substrates was also carried out under thermal conditions, using a conventional pre-heated oil bath.

Firstly, the reaction between test substrates has been carried out without as well as with different types of catalysts such as silica, diphenic acid and silica-diphenic acid and it has been found that of the various catalysts, silica-diphenic acid gave the best yield of products. The reaction of test substrates was also carried out using different amounts of silica-diphenic acid and it has been observed that in mechanochemical activation as well as in thermal activation of reaction, 0.05 g of the catalyst was sufficient to catalyze the reaction and provide excellent yield of the resulting product. In case of mechanochemical grinding method, initially, there was no need of solvent for the reaction to take place but on completion of the reaction, ethyl acetate was added in the reaction mixture to isolate the product. Whereas, in the case of thermal method, solvent was essential and for this different types of solvent mixtures were tried and it has been found that ethanol (2 mL): water (0.4 mL) solution was best for the reaction to take place efficiently. The reasons for the positive effects of ethanol: water solvent mixture was that ethanol is miscible with water and their mixture has less volume than the sum of their individual components at the given fractions. Their mixing is an exothermic reaction by which sufficient amount of energy was released which helps the reactant molecules to condense and form the desired product. Finally, the reaction of test substrates was also carried out at different temperatures in case of thermal method and it has been observed that 80°C was the optimum temperature for the reaction to give products in excellent yield.

The biological importance of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds and their use as starting materials for the design and synthesis of new biologically active agents, has inspired us to extend the scope of the newly developed protocols. Hence, to evaluate the generality of the present protocols, different aromatic aldehydes substituted with electron-donating and electron-withdrawing substituents were selected and reacted with 5,5-dimethyl-1,3-cyclohexanedione under optimized reaction conditions as shown in scheme 1 and the experimental details are summarized in table 2.

The structure-activity relationship has been inferred from the above table which explains that aromatic aldehydes substituted with electron-withdrawing groups undergo faster reactions than aromatic aldehydes substituted with electron-donating groups and heteroaromatic aldehydes. Among sixteen different 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds which were synthesized by above mentioned protocols, four compounds were grown as good crystals and their structures were confirmed by single-crystal X-ray data analysis, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectroscopy.



**Figure 1.** Recyclability graph of silica-diphenic acid in case of (Entry 3, table 2).

#### 3.2 Recyclability of Silica-diphenic acid

In order to classify silica-diphenic acid as a heterogeneous catalyst, recyclability of the catalyst needs to be examined. Hence a series of five consecutive runs were carried out in case of 3-nitrobenzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione (entry 3, table 2) by both mechanochemical grinding and thermal heating method. After examining the five runs in both cases, a slight drop in the activity of the catalyst was observed.

**Table 3.** Recyclability of silica-diphenic acid in case of 3-nitrobenzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione (entry 3, table 2).

		Grinding con	dition <sup>a</sup>		Thermal cond	dition <sup>b</sup>
Entry	Yield (%) <sup>c</sup>	TON	TOF (TON/min)	Yield (%) <sup>c</sup>	TON	TOF (TON/min)
1	98	$2.57 \times 10^{4}$	$5.14 \times 10^{3}$	98	$2.57 \times 10^{4}$	$5.14 \times 10^{3}$
2	98	$2.57 \times 10^{4}$	$5.14 \times 10^{3}$	96	$2.52 \times 10^{4}$	$5.04 \times 10^{3}$
3	97	$2.52 \times 10^{4}$	$5.04 \times 10^{3}$	95	$2.50 \times 10^{4}$	$5.00 \times 10^{3}$
4	95	$2.50 \times 10^{4}$	$5.00 \times 10^{3}$	94	$2.47 \times 10^{4}$	$4.94 \times 10^{3}$
5	94	$2.47 \times 10^{4}$	$4.94 \times 10^{3}$	92	$2.42 \times 10^{4}$	$4.84 \times 10^{3}$

<sup>a</sup>3-Nitrobenzaldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), silica-diphenic acid (0.05 g) were grind in motar and pestle for required time in solvent free conditions. <sup>b</sup>3-Nitrobenzaldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), silica-diphenic acid (0.05 g) were taken in round bottom flask and refluxed for required time in ethanol: water solvent mixture. <sup>c</sup>Yield of pure products.



**Scheme 3.** Plausible mechanism for the silica-diphenic acid-catalyzed synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one).

Further, to explain the lifetime and stability of the catalyst, turnover number (TON) must be calculated as the total moles of product synthesized per mole of the catalyst. The cumulative turnover number (TON) is also calculated as the total moles of product synthesized over repeated reaction cycles per mole of active catalyst initially added in the first run.<sup>21</sup> The calculations were carried out in case of silica-diphenic acid and results are shown in table 2 and graphically represented in figure 1.

The efficiency of recyclable catalyst and the absence of significant catalyst decomposition during the experiment are convincingly explained by determining the turnover frequencies (TOF) of the catalyst over the consecutive five runs. This has been calculated in case of silica-diphenic acid as shown in the above table which concluded that TON and TOF values were almost constant, indicating the excellent recyclability of the silicadiphenic acid in both grinding as well as under thermal conditions (table 3).

#### 3.3 Mechanism

A plausible mechanism for the reaction between aldehydes (1 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) in presence of silica-diphenic acid as a mild, efficient and heterogeneous catalyst has been proposed (scheme 3). In the first step of the proposed mechanism, aldehyde molecule (2) was protonated and activated by the catalyst and undergoes Knoevenagel condensation with 5,5-dimethyl-1,3-cyclohexanedione (1) to form intermediate product (4) which was further activated by catalyst, so that it undergoes Michael reaction with another molecule of 5,5-dimethyl-1,3cyclohexanedione (5) to form final desired product (6).

#### 4. Conclusion

Domino synthesis of 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) compounds has been carried out successfully in presence of silica supported diphenic acid as a heterogeneous catalyst in comparison to homogeneous catalyst, diphenic acid. The heterogeneity of the catalyst as compared to homogeneity provides advantages like easy work-up procedure and better isolation of the synthesized derivatives which leads to their good to excellent yields. The respective synthesized derivatives were then characterized by melting point, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectrometry. The derivatives **1**, **3**, **4** and **6** (table 2) were also characterized by single crystal X-ray analysis. The X-ray structural aspects of these compounds help in understanding their pharmacological properties as they are important starting materials for the synthesis of various biologically active compounds.

## **Supplementary Information (SI)**

The supplementary information includes the following: Procedure of acid-base titration with conclusion, spectral data of synthesized products, mass spectra of three products as figures S1, S2 and S3, ORTEPs of compounds 1, 3, 4 and 6 (table 2) with figures showing packing arrangements as figures S4, S5, S6, S7, S8, S9, S10 and S11, figures S12 to S15 showing intramolecular hydrogen bondings in compounds 3 and 6, optimization tables as table S1, S2, S3 and S4, crystal discussion, table S5 explaining the summary of the crystal structure, data collection and structure refinement parameters for compounds 1, 3, 4 and 6, tables S6 and S7 showing geometry of intramolecular interactions for compounds 3 and 6 (table 2) and tables S8, S9, S10 and S11 showing bond lengths and bond angles of compounds 1, 3, 4 and 6. Supplementary Information is available at www.ias.ac.in/chemsci.

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