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Research Article

An Expeditious and Safe Synthesis of Some Exocyclic α,β-Unsaturated Ketones by Microwave-Assisted Condensation of Cyclic Ketones with Aromatic Aldehydes over Anhydrous Potassium Carbonate

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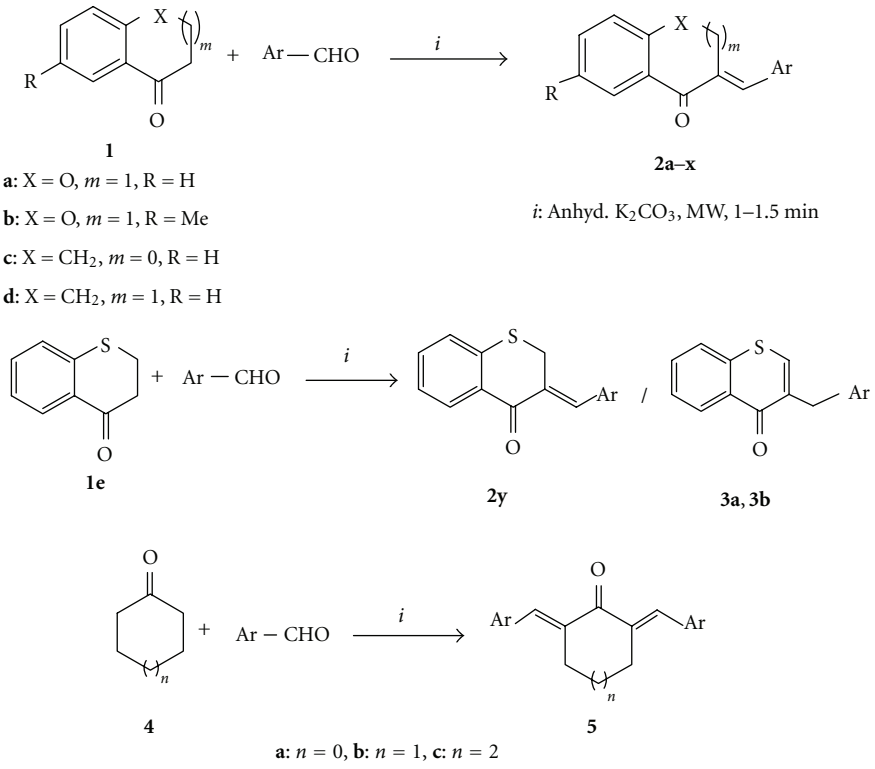
A rapid, efficient, and solvent-free methodology for synthesis of exocyclic α,β-unsaturated ketones of the categories *E*-3-arylidene-4-chromanones, *E*-2-arylidene-1-tetralones, *E*-2-arylidene-1-indanones, *E*-3-cinnamylidene-4-chromanones, *E*-2-cinnamylidene-1-tetralones, *E*-2-cinnamylidene-1-indanones, α,α'-(*E,E*)-bis(arylidene)-cycloalkanones, and α,α'-(*E,E*)-bis(cinnamylidene)-cycloalkanones has been developed through cross-aldol condensation of the constituent cyclic ketones and aldehydes by microwave irradiation over anhydrous potassium carbonate. However, for condensation of 1-thio-4-chromanones with aromatic aldehydes by this method, the initially formed exocyclic α,β-unsaturated ketone has been found to undergo isomerization yielding 3-(arylmethyl)thiochromones.

1. Introduction

Exocyclic α,β-unsaturated ketones are very suitable starting materials for synthesis of versatile heterocycles having polycyclic skeletons. Their cyclocondensation with dinucleophiles constitutes an important route to polycyclic fused ring systems, for example, tricyclic pyrazolines, tetracyclic benzothiazepines, tetracyclic benzodiazepines, thiazines, pyrimidines, quinazolines, and so forth [1–4]. Again, their 1,3-dipolar cycloaddition with different dipoles provides important nitrogen-containing spiroheterocycles [2]. Moreover, there is scope for performing a Michael addition reaction at the active double bond present in them. Some of the exocyclic α,β-unsaturated ketones, namely, aurones and *E*-3-benzylidenechromanones, are natural compounds [1, 5–7]. It may be mentioned here that several classes of compounds belonging to this category show interesting biological properties, for example, α,α'-(*E,E*)-bis(arylidene)-cycloalkanones show antiangiogenic [8, 9], quinine reductase inducer [10], arginine methyltransferase inhibitor [11], cytotoxic [12, 13], cholesterol-lowering [14], and antitubercular [15] activities, and *E*-3-benzylidenechromanones and related homoisoflavonoids show antioxidant, anti-inflammatory, antifungal, antiviral, antiallergic, antihistaminic, antirhinovirus, antimutagenic, angioproductive, hypocholesterolemic, and cytotoxic activities [7, 16]. Moreover, α,α'-(*E,E*)-bis(arylidene)-cycloalkanones find application as fluorescent materials [17] and in the preparation of nonlinear optical materials and liquid-crystalline polymers [18]. All these aspects have made exocyclic α,β-unsaturated ketones important synthetic targets for organic chemists. The reported methods for their synthesis up to 2003 have been reviewed by Lévai [1]. There has been addition of a good number of other methods in the literature subsequently [7, 9, 17–37]. However, some of the methods available so far suffer from drawbacks like use of toxic or corrosive reagents, expensive catalysts, hazardous solvents, long reaction times, tedious isolation procedure, and so forth, due to which the current literature shows a growing trend for developing environmentally benign methodologies for synthesis of



Scheme 1: Condensation of cyclic ketones with aromatic aldehydes.

different exocyclic α,β-unsaturated ketones [7, 18, 23, 33–35, 37]. Mention of few such recent methods for synthesis of chalcones [38–43], a group of structurally related acyclic compounds, may be done in this connection. Microwave (MW) irradiation, an unconventional energy source, has been used for a variety of applications including organic synthesis, wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules**.** This technology has opened up new opportunities to the synthetic chemists since mid-1980s, in the form of new reactions that are not possible by use of conventional heating. Its important advantages are being improved reaction yields, decreased reaction times, and safe performance of some reactions even under solvent-free reaction conditions. All these advantageous features have resulted in publication of a huge number of original research papers and a good number of reviews and monographs in the area during the last twenty five years [44–57]. A number of environmentally benign methodologies for condensation reactions leading to exocyclic α,β-unsaturated ketones and chalcones are reported to be assisted by microwave [39–43]. Very recently, we have developed a method for synthesis of flavanones directly from 2′-hydroxyacetophenones and benzaldehydes by potassium carbonate catalyzed microwave-assisted condensation [58], the first step of which involves the occurrence of a Claisen-Schmidt reaction. Moreover, the appearance of several papers on utilization of anhydrous potassium carbonate for synthesis of α,β-unsaturated ketones is evident from the recent literature [23, 41, 42]. All these aspects interested us to apply the very simple methodology developed by us [58] for the synthesis of exocyclic α,β-unsaturated ketones. Thus, we took cyclic methyleneketones belonging to the categories 4-chromanone, 1-thio-4-chromanone, 1-tetralone, 1-indanone, and cycloalkanones as starting materials for getting the corresponding exocyclic α,β-unsaturated ketones (Scheme 1). The results of this study have been presented herein.

2. Results and Discussion

By following our recent methodology [58], when an equimolar mixture of an aromatic aldehyde and chromanone (**1a** or **1b**)/1-tetralone (**1c**)/1-indanone (**1d**)/1-thio-4-chromanone (**1e**) was subjected to microwave irradiation over anhydrous potassium carbonate, reaction took place completely within 1–1.5 min yielding only one product in each case. For combinations where liquid aldehydes were used, a mixture of neutral alumina and anhydrous potassium carbonate was taken instead of anhydrous potassium carbonate alone. Some representative examples of microwave irradiation over neutral alumina alone done by us were found to give the condensation products in much lower yields (42%–55%). This observation has analogy with that reported in a recent paper by Kakati and Sarma [43] for synthesis of chalcones. Isolation of the product done by washing the solid obtained after the MW irradiation with dichloromethane followed by chromatography of the concentrate of the washings gave

the desired condensation products from **1a–d** (Table 1). When **1e** was used as substrate and condensation reaction was studied with benzaldehyde, 4-chlorobenzaldehyde, and 4-methoxybenzaldehyde (irradiation time 1.5 min), it was found that the initially formed exocyclic α,β-unsaturated ketone underwent complete isomerization in the first two cases yielding corresponding 3-benzylthiochromones (**3a** and **3b**), while the desired product **2y** was obtained in the last case (Table 2). The role of the electron donating *p*-OMe group in **2y** in inhibiting the double bond isomerization was thus evident. The same reaction done on neutral alumina, however, gave the desired exocyclic α,β-unsaturated ketones (**2y-z1**), *albeit* only in moderate yield (Table 2). Attempted synthesis of *E*-3-benzylideneflavanones by condensation of flavanone and benzaldehydes by the use of this methodology, however, did not meet with success.

Considering the importance of α,α'-(*E,E*)-bis (arylidene)-cycloalkanones (**5**) as mentioned in the introduction, our study was then directed to the reactions involving cycloalkanones (**4**) as ketomethylene component. Thus, condensation of each of cyclopentanone (**4a**), cyclohexanone (**4b**), and cycloheptanone (**4c**) with 2 molar proportion of simple aromatic aldehydes was also found to produce exocyclic α,β-unsaturated ketones **5a–j** in very good yield (Table 3). Reactions of these cycloalkanones with 1 molar proportion of aromatic aldehyde under the previously said irradiation condition were found to produce α,α'-(*E,E*)-bis(arylidene)-cycloalkanones (yield: 38%–45%) instead of any monoarylidene product. Our attempts to apply this methodology for condensation of each of the ketones **1a** and **4** with the aliphatic aldehydes heptanal and citral, however, did not meet with success.

3. Conclusion

Microwave irradiation of cyclic ketones and aromatic aldehydes over anhydrous potassium carbonate has been developed as a new methodology for the synthesis of several series of exocyclic α,β-unsaturated ketones. The method is very efficient, simple, and environmentally benign.

4. Experimental

4.1. General. Melting points were recorded on a Köfler block. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer (Spectrum BX II) in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AV-300 (300 MHz) spectrometer. Analytical samples were routinely dried *in vacuo* at room temperature. Microanalytical data were recorded on a Perkin-Elmer 2400 Series II C, H, N analyzer. Mass spectra were measured in the following ways: ESIMS(+) [Waters Micromass Q-Tof micro] and FAB-MS [Jeol the M Station JMS.700]. An unmodified domestic household microwave oven (LG, DMO, Model No.-556P, 900 watt) equipped with inverter technology, which provides a realistic control of the microwave power to the desired level (20%–100%), was used for microwave heating. The MW oven was operated at reduced MW-power level of 60% (540 watt). Column chromatography was performed with silica gel (100–200 mesh), and TLC with silica gel G made of SRL Pvt. Ltd. Petroleum ether had the boiling range 60–80°C.

4.2. General Procedure for Condensation of Ketones with Aldehydes. A solution of a mixture of ketone (**1**) (1 mmol) and aldehyde (1 mmol/2 mmol) in CH_2Cl_2 was added to a mixture of anhyd. K_2CO_3 (1 g) (neutral alumina (1.5 g) was added when liquid aldehyde was used), and the solvent was removed. The solid material thus obtained was subjected to microwave irradiation (2450 MHz) at temperatures 92°C (for 1.5 min) and 82°C (for 1 min), monitoring the progress of reaction by TLC. It was then washed thoroughly with CH_2Cl_2, and the concentrate of the washings was chromatographed over silica gel to obtain pure product. All the exocyclic α,β-unsaturated ketones (**2** (Tables 1 and 2) and **5** (Table 3), all light yellow crystals) as well as the 3-benzylthiochromones (**3** (Table 2), very light yellow crystals) obtained were properly characterized from their physical, analytical, and spectral data (majority of these compounds were known previously). The analytical and spectral data of some selected compounds are given in the following.

*4.2.1. Compound **2i**.* IR (KBr, cm^{-1}): 1669 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.34 (s, 3H, Me), 5.28 (s, 2H, H_2-2), 6.87 (d, 1H, J = 8.4 Hz, H-8), 7.19–7.32 (m, 3H, H-7, H-2′ and H-6′), 7.43 (d, 2H, J = 8.4 Hz, H-3′ and H-5′), 7. 80 (br. s, 2H, H-β and H-5).

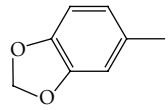
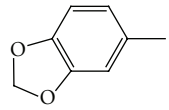
*4.2.2. Compound **2l**.* IR (KBr, cm^{-1}): 1670 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.33 (s, 3H, Me), 5.31 (s, 2H, H_2-2), 6.03 (s, 2H, –OCH_2O–), 6.79–6.90 (m, 4H, Ar–H), 7.25–7.30 (m, 1H, H-7), 7.77 (br. s, 1H, H-β/H-5), 7. 80 (br. s, 1H, H-5/H-β).

*4.2.3. Compound **2n**.* IR (KBr, cm^{-1}): 1662 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.34 (s, 3H, Me), 3.86 (s, 3H, OMe), 5.34 (br. s, 2H, H_2-2), 6.87 (d, 1H, J = 8.9 Hz, H-8), 6.97 (d, 2H, J = 8.9 Hz, H-3′,5′), 7.27–7.31 (m, 3H, H-7 and H-2′,6′), 7.80 (br. s, 1H, H-β/H-5), 7. 83 (br. s, 1H, H-5/H-β).

*4.2.4. Compound **2r**.* IR (KBr, cm^{-1}): 1669 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.96 (t, 2H, J = 6.9 Hz, H_2-3/H_2-4), 3.17 (t, 2H, J = 6.0 Hz, H_2-4/H_2-3), 3.87 (s, 3H, OMe), 6.97 (d, 2H, J = 8.7 Hz, H-3′,5′), 7.27 (d, 1H, J = 7.8 Hz, H-5), 7.38 (t, 1H, J = 7.5 Hz, H-7), 7.45 (d, 2H, J = 8.7 Hz, H-2′,6′), 7.50 (dt, 1H, J = 7.5 and 1.0 Hz, H-6), 7.87 (br. s, 1H, H-β), 8.14 (br. d, 1H, J = 7.8 Hz, H-8).

*4.2.5. Compound **2s**.* IR (KBr, cm^{-1}): 1666 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.96 (t, 2H, J = 6.3 Hz, H_2-3/H_2-4), 3.09 (t, 2H, J = 6.1 Hz, H_2-4/H_2-3), 7.25 (br. d, 1H, J = 7.5 Hz), 7.30 (br. d, 2H, J = 8.1 Hz, H-3′,5′), 7.37 (br. t, 1H, J = 7.6 Hz), 7.50 (br. t, 1H, J = 7.4 Hz, H-6), 7.55 (d, 2H, J = 8.4 Hz, H-2′,6′), 7.77 (br. s, 1H, H-β), 8.13 (br. d, 1H, J = 7.7 Hz, H-8).

Table 1: Microwave-assisted condensation of chromanones/1-tetralone/1-indanone with aromatic aldehydes.

Entry	Ketone (**1**)	Ar of aldehyde	Time (min)	Product (**2**)	Yield (%)	M.P. (°C) Obs. (Lit.) [Reference]
(1)	**1a**	C_6H_5–	1.5	**2a**	82[a] 45[b]	111 (110) [59]
(2)	**1a**	4-Cl–C_6H_4–	1.5	**2b**	88[a] 49[b]	169-170 (168) [59]
(3)	**1a**	4-MeO–C_6H_4–	1.0	**2c**	79[a] 43[b]	131 (132) [59]
(4)	**1a**	4-Br–C_6H_4–	1.0	**2d**	86[a] 55[b]	175 (174) [59]
(5)	**1a**	4-Me–C_6H_4–	1.0	**2e**	77[a] 51[b]	117 (118) [59]
(6)	**1a**		1.5	**2f**	74[a]	115 (115) [59]
(7)	**1a**	*E*-C_6H_5CH=CH–	1.5	**2g**	87[a] 42[b]	135-136 (136) [59]
(8)	**1b**	C_6H_5–	1.0	**2h**	84[a]	132 (133) [59]
(9)	**1b**	4-Cl–C_6H_4–	1.5	**2i**	89[a]	143-144 (144) [59]
(10)	**1b**	4-Me–C_6H_4–	1.5	**2j**	76[a]	120 (120) [59]
(11)	**1b**	4-Me_2N–C_6H_4–	1.0	**2k**	81[a]	140 (140) [59]
(12)	**1b**		1.5	**2l**	73[a]	134-135 (135) [59]
(13)	**1b**	2-Furanyl	1.5	**2m**	80[a]	101 (101) [42]
(14)	**1b**	4-MeO–C_6H_4–	1.5	**2n**	72[a]	104
(15)	**1b**	*E*-C_6H_5CH=CH–	1.5	**2o**	85[a]	148 (148) [59]
(16)	**1c**	C_6H_5–	1.5	**2p**	74[a]	120 (120-121) [60]
(17)	**1c**	4-Cl–C_6H_4–	1.5	**2q**	84[a] 51[b]	133-134 (132-133) [60]
(18)	**1c**	4-MeO–C_6H_4–	1.5	**2r**	75[a] 46[b]	88 (87-88) [60]
(19)	**1c**	4-Br–C_6H_4–	1.5	**2s**	82[a]	158
(20)	**1c**	*E*-C_6H_5CH=CH–	1.5	**2t**	82[a] 48[b]	134 (133-134) [61]
(21)	**1d**	4-Me–C_6H_4–	1.5	**2u**	76[a]	139-140 (137-138) [62]
(22)	**1d**	4-MeO–C_6H_4–	1.5	**2v**	71[a]	139-140 (138-139) [62]
(23)	**1d**	4-Br–C_6H_4–	1.5	**2w**	83[a] 53[b]	188-189
(24)	**1d**	*E*-C_6H_5CH=CH–	1.5	**2x**	88[a] 45[b]	125 (124-125) [61]

[a]Over anhy. K_2CO_3; [b]over neutral alumina.

Table 2: Microwave-assisted condensation of 1-thiochroman-4-one (**1e**) with aromatic aldehydes.

Entry	Catalyst	Ar of aldehyde	Time (min.)	Product	Yield (%)	M.P Obs. (Lit.) [Reference]
(1)	Anhy. K_2CO_3	C_6H_5–	1.5	**3a**	72	60 (59–61) [63]
(2)	Anhy. K_2CO_3	4-Cl–C_6H_4–	1.5	**3b**	78	110
(3)	Anhy. K_2CO_3	4-MeO–C_6H_4–	1.5	**2y**	69	112-113 (113) [59]
(4)	Neutral alumina	C_6H_5–	1.5	**2z**	55	104-105 (105) [59]
(5)	Neutral alumina	4-Cl–C_6H_4–	1.5	**2z1**	59	138-139 (138-139) [59]
(6)	Neutral alumina	4-MeO–C_6H_4–	1.5	**2y**	52	112-113 (113) [59]

Table 3: Microwave-assisted condensation of cycloalkanones with aromatic aldehydes and cinnamaldehyde over anhy. K_2CO_3.

Entry	Ketone (**1**)	Ar of aldehyde	Time (min.)	Product (**5**)	Yield (%)	M.P Obs. (Lit.) [Reference]
(1)	**4a**	C_6H_5–	1.5	**5a**	85	190 (190) [64]
(2)	**4a**	4-MeO–C_6H_4–	1.5	**5b**	78	215 (215) [64]
(3)	**4a**	4-Cl–C_6H_4–	1.5	**5c**	86	228-229 (229-230) [64]
(4)	**4a**	*E*-C_6H_5CH=CH–	1.5	**5d**	87	220 (220-221) [64]
(5)	**4b**	C_6H_5–	1.5	**5e**	82	155 (155) [64]
(6)	**4b**	4-MeO–C_6H_4–	1.5	**5f**	78	213 (213) [64]
(7)	**4b**	4-Cl–C_6H_4–	1.5	**5g**	88	141-142 (138) [64]
(8)	**4b**	*E*-C_6H_5CH=CH–	1.5	**5h**	82	176-177 (178) [64]
(9)	**4c**	C_6H_5–	1.5	**5i**	85	108 106.5–108 [65]
(10)	**4c**	*E*-C_6H_5CH=CH–	1.5	**5j**	81	204–206 207-208 [65]

*4.2.6. Compound **2v**.* IR (KBr, cm^{-1}): 1688 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.87 (s, 3H, OMe), 4.02 (s, 2H, H_2-3), 6.98 (d, 2H, J = 8.7 Hz, H-3′,5′), 7.42 (br. t, 1H, J = 7.2 Hz, H-6), 7.54–7.66 (m, 5H, Ar–H and H-β), 7.91 (br. d, 1H, J = 7.5 Hz, H-7); ^{13}C NMR (75 MHz) δ 32.47, 55.40, 114.48, 124.30, 126.11, 127.58, 128.15, 132.41, 132.57, 133.81, 134.34, 138.25, 149.50, 160.87, 194.39.

*4.2.7. Compound **2w**.* IR (KBr, cm^{-1}): 1692 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 4.02 (s, 2H, H_2-2), 7.44 (br. t, 1H, J = 7.5 Hz, H-6), 7.51–7.66 (m, 7H, Ar–H and H-β), 7.91 (br. d, 1H, J = 7.5 Hz, H-7).

*4.2.8. Compound **2t**.* IR (KBr, cm^{-1}): 1659 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.02 (s, 4H, H_2-3 and H_2-4), 7.04 (d, 1H, J = 15.3 Hz, H-δ), 7.17 (dd, 1H, J = 15.3 and 11.2 Hz, H-γ), 7.28–7.40 (m, 5H, Ar–H), 7.45–7.58 (m, 4H, H-6, H-2′,6′ and H-β), 8.11 (dd, 1H, J = 7.5 and 1.2 Hz, H-8); ^{13}C NMR (75 MHz) δ: 25.97, 28.72, 123.40, 126.95, 127.14, 128.07, 128.15, 128.77, 128.86, 133.00, 133.78, 134.39, 135.89, 136.62, 140.93, 143.37, 187.27. TOF MS^+: m/z 283 $(M + Na)^+$; Anal. Calcd for $C_{19}H_{16}O$ (260.12): C, 87.66; H, 6.19%. Found C, 87.48; H 6.34%.

*4.2.9. Compound **2x**.* IR (KBr, cm^{-1}): 1693 cm^{-1} (C=O), ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.87 (s, 2H, H_2-3), 7.00–7.10 (m, 2H, H-γ and H-δ), 7.32–7.44 (m, 5H, Ar–H), 7.52–7.63 (m, 4H, H-2′,6′, H-5 and H-β), 7.87 (br. d, 1H, J = 7.8 Hz, H-7).

*4.2.10. Compound **2y**.* IR (KBr, cm^{-1}): 1661 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.86 (s, 3H), 4.16

(s, 2H, H_2-2), 6.96 (d, 2H, J = 8.7 Hz, H-3′,5′), 7.23–7.41 (m, 3H, H-6,7,8), 7.37 (d, 2H, J = 8.7 Hz, H-2′,6′), 7.75 (br. s, 1H, H-β), 8.19 (dd, 1H, J = 7.8 Hz and 1.5 Hz, H-5).

4.2.11. Compound ***3b***. IR (KBr, cm^{-1}): 1673 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 3.96 (br. s, 2H, –CH_2–), 7.21 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.43 (br. s, 1H, H-2), 7.50–7.62 (m, 3H, Ar–H), 8.57 (br. d, 1H, J = 7.8 Hz).

4.2.12. Compound ***5d***. IR (KBr, cm^{-1}): 1674 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.91 (s, 4H, H_2-3 and H_2-4), 6.90–7.00 (m, 4H, 2 × H-γ and 2 × H-δ), 7.24–7.52 (m, 12H, Ar–H and 2 × H-β).

4.2.13. Compound ***5j***. IR (KBr, cm^{-1}): 1658 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.83 (br. s, 4H, H_2-4 and H_2-5), 2.62 (br. s, 4H, H_2-3 and H_2-6), 6.88–7.09 (m, 5H, Ar–H and olefinic H), 7.26–7.38 (m, 7H, Ar–H and olefinic H), 7.48 (br. d, 4H, J = 7.2 Hz, 2 × H-2′,6′); ^{13}C NMR (75 MHz) δ: 27.15, 27.80, 123.27, 126.95, 128.55, 128.70, 135.27, 136.78, 139.40, 140.93, 194.00. FABMS: *m/z* 341.4 $(M + H)^+$; Anal. Calcd for $C_{25}H_{24}O$ (340.18): C, 88.20; H, 7.11%. Found C, 87.91; H 6.98%. ^{1}H and ^{13}C NMR and mass spectral data of some selected compounds are supplied in a separate file. See Supplementary Material available online at doi: 10.1155/2012/456097 online.

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