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Highly chemoselective synthesis of 1,2,3,4,5-pentasubstituted cyclohexanols under solvent-free condition

Xinxiang Luo[b] and Zixing Shan[a,*]

[a]Department of Chemistry, Wuhan University, Wuhan 430072, China
[b]Department of Chemistry and Environment Engineering, Hunan City University, Yiyang 413049, Hunan, China

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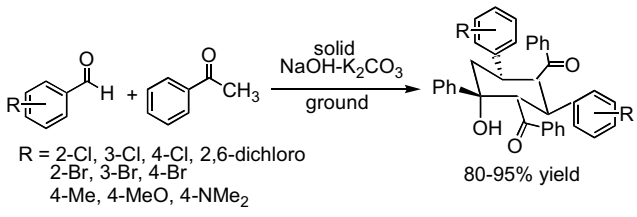
Abstract—Acetophenone reacted with a series of aromatic aldehydes with grinding under catalysis of a double-component solid base system consisting of NaOH and K_2CO_3 to furnish highly chemoselectively 1,2,3,4,5-pentasubstituted cyclohexanols in 80–95% yield, and their composition and structure are identified by spectral technologies and single crystal X-ray diffraction analysis, and a possible mechanism of the formation was suggested.

Polysubstituted cyclohexanol derivatives are of potential application prospect in the synthesis of functional materials (liquid crystal, molecular recognition, fluorescence material, etc.). As far as the 1,2,3,4,5-pentasubstituted cyclohexanols are concerned, only several ones were synthesized and characterized to date. Kostanecki and Rossbach[1] prepared two compounds having the formula $C_{38}H_{32}O_3$ (Kostanecki's triketone) by the reaction of benzaldehyde and acetophenone in a 2:3 molar ratio in a concentrated alcoholic NaOH, about 110 years ago, the two products had different melting points of 198 and 256 °C, respectively. Until 1990, Vasilyer's research group[2] affirmed by single crystal X-ray diffraction analysis that the low-temperature fusion form was 2,4-dibenzoyl-1,3,5-triphenylcycloheaxanol. This is the first structurally proved 1,2,3,4,5-pentasubstituted cyclohexanol, in which only aromatic group was included in the substituents, though its 4-cyano-4-ethoxycarbonyl analogue previously was reported.[3] Later on, Kessler,[4] Raston[5] and their colleague separated its two pyridinyl-containing analogues in moderate yield, in the preparative course of 2,6-disubstituted pyridines. In 2000, Chen and Peng[6] reported that the polysubstituted cyclohexanols were synthesized under microwave irradiation; unfortunately, the evidence for the product authentication was insufficient.[7] Recently, in our attempt to prepare chalcones via an equimolar reaction of acetophenone and aromatic aldehydes under catalysis of a double-component solid base system, unexpectedly, a series of 1,2,3,4,5-pentasubstituted cyclohexanols were obtained in very high yield. In the present letter, we will report the preparative procedure and structure characterization of these new 1,2,3,4,5-pentasubstituted cyclohexanols (Scheme 1).

To a fine-powdery solid mixture of NaOH and K_2CO_3 (2:1 molar ratio) were successively added acetophenone and an aromatic aldehyde, including 4-methylbenzaldehyde, 4-methoxylbenzaldehyde, 4-dimethylaminobenzaldehyde, 4-chlorobenzaldehyde, 2-chlorobenzaldehyde, 2,6-dichlorobenzaldehyde, 2-bromobenzaldehyde, 3-bromobenzaldehyde, and 4-bromobenzaldehyde, in a 1.5:1.0 or 1.1:1.0 molar ratio, followed by grinding at room temperature for 5–20 min till the liquid disappeared, and then worked up with water, and the indissoluble solid was collected and recrystallized from toluene, ethyl acetate or ethanol to furnish a white solid of 1,2,3,4,5-pentasubstituted cyclohexanols in 80–95% yields (Table 1).[8] In fact, all the reactions occurred almost



Scheme 1. One step synthesis of 1,2,3,4,5-pentasubstituted cyclohexanols under catalysis of a double-component solid base system.

* Corresponding author. Tel.: +86 27 87219074; e-mail: zxshan@whu.edu.cn

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quantitatively. The lower isolated yields, in certain cases, were due to more solubility in the solvents for crystallization.

The spectra of all the compounds prepared above are similar to each other. Their IR spectra show stronger absorption of hydroxy group at 3450 ± 50 cm^{-1} and two carbonyl groups at ca. 1660 ± 20 and 1615 ± 5 cm^{-1}. It is obvious that one of the carbonyl groups is in H bonding environment. Their ^{1}H NMR spectra display the chemical shifts of seven non-aromatic protons (except those of the methylic protons in the substituents of **A**, **B**, and **C**) in the 6.00–1.90 ppm region as well as of the aryl protons (for the three phenyl groups and two substituted phenyl groups) in the region of 7.80–6.40 ppm. The ^{13}C NMR spectra of them show six aliphatic carbons in the region of 76–34 ppm (except the methylic carbon(s) in the substitutents of **A**, **B**, and **C**) as well as the aromatic ring carbon resonances in the 158–112 ppm region (most in the 147–121 ppm region). It is obvious that six of the seven non-aromatic protons correlate with the six aliphatic ring carbons, and bigger chemical shift values of the aliphatic carbons imply that the compounds can be polysubstituted cyclohexane derivatives. For all the compounds, one singlet corresponding to one proton appears in the region of 5.60–5.00 ppm. Without doubt, the singlet belongs to the hydroxy proton. Unfortunately, an attempt to designate the ownership of the singlet by adding heavy water did not meet with success. This is most likely due to the strong intramolecular hydrogen bond. Analysis of the reaction process indicates that each ring carbon is merely able to connect with an aromatic group. Thus, it is easily concluded that there at least is one methylene group in the cyclohexane ring, and one of the ring carbons must be a quaternary carbon [δ_C (76.1–72.2 ppm), C(1)], which connects directly with the hydroxy group. Therefore, it can be thought that the products obtained are 1,2,3,4,5-pentasubstituted cyclohexanol derivatives.

Table 1. Solvent-free synthesis of 1,2,3,4,5-pentasubstituted cyclo hexanols[a]

Entry	Cyclohexanol	R	Mp (°C)	Yield[b] (%)
1	**A**	4-Me	197–198	92 (88)
2	**B**	4-MeO	180–182	93 (92)
3	**C**	4-Me_2N	228–230	86 (82)
4	**D**	4-Br	176–178	85 (80)
5	**E**	2-Br	219–221	94 (89)
6	**F**	3-Br	140–142	82 (80)
7	**G**	4-Cl	187–189	88 (85)
8	**H**	2-Cl	208–210	95 (95)
9	**I**	2,6-Cl_2	218–219	92 (90)

[a] All the reactions were performed in 50 mmol scale in the presence of a 1.0:0.5 molar ratio of NaOH and K_2CO_3.

[b] All are the isolated yields after recrystallization; the figures before brackets are for the reactions in a 1.0:1.5 molar ratio of the aromatic aldehyde and acetophenone, and those between brackets are for the reactions in a 1.0:1.1 molar ratio.

The C, H gHSQC and H, H COSY spectra of product **B**, as a representative of the new compounds, were examined (Figs. 1 and 2). Figures 1 and 2 provide unambiguous evidence for the authentication of the 1,2,3,4,5-pentasubstituted cyclohexanol. It can be seen in Figure 1 that six of the seven non-aromatic protons (the protons in the two methoxyl groups at 3.64 and 3.51 ppm are not included) are connected with five carbons of the cyclohexane ring, and the ring carbon at 39.0 ppm has two protons. It is noteworthy that the proton at 5.22 ppm is not correlative to any carbon; without doubt, it is the hydroxylic proton connected to the ring carbon (δ_C 76.2 ppm) through oxygen. Figure 2 showed the correlation between different protons. It can be seen

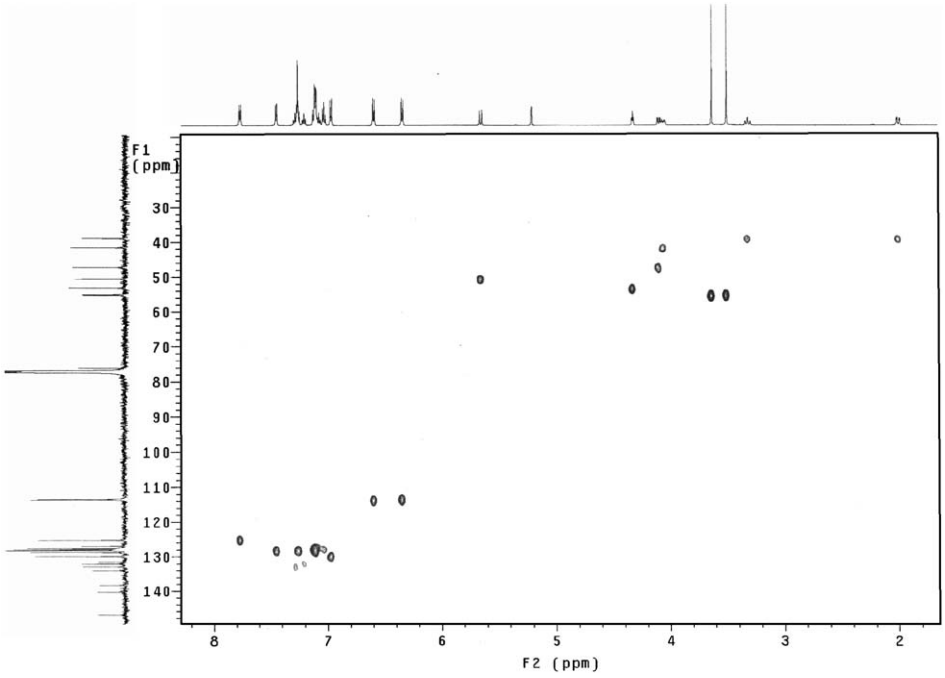


Figure 1. The C, H gHSQC spectra of the product **B**.

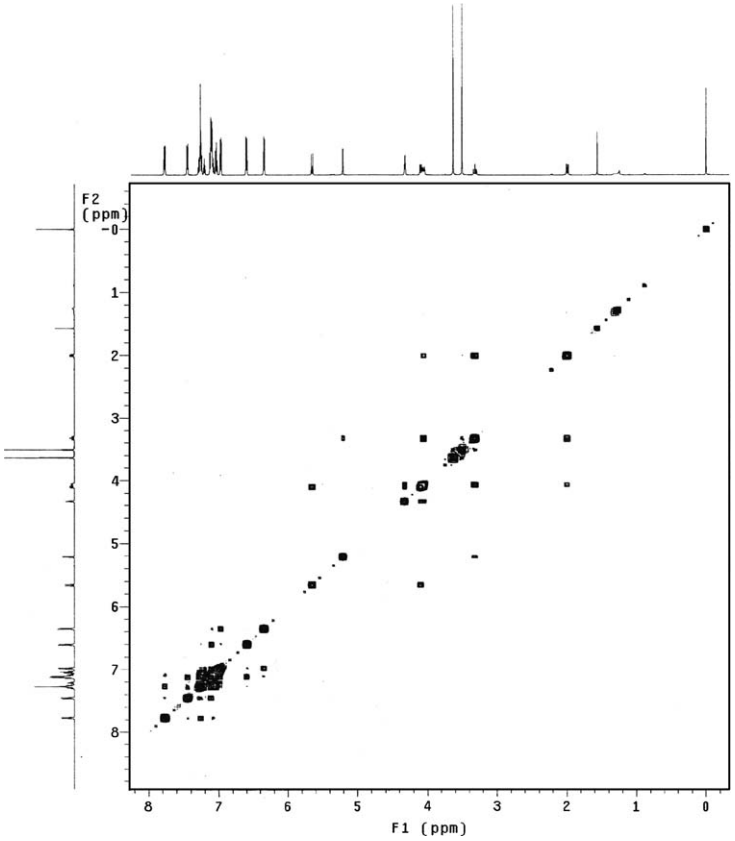


Figure 2. The H, H COSY spectra of the product **B**.

that the C(2)–H, the C(3)–H, the C(4)–H, and the C(5)–H are correlated with the adjacent protons, respectively, and the C(6)–H_{eq} correlates to the C(5)–H, and the C(6)–H_{ax} is correlated with C(3)–H and C(1)–OH as well as the coupling between the germinal protons.

The ethanol solution of the product (**B**) was allowed to stand at room temperature for several days to isolate a single crystal suitable for X-ray diffraction structure analysis. The crystal data clearly indicated that the product is 2,4-dibenzoyl-3,5-di(4-methoxylphenyl)-1-phenylcyclohexanol (Fig. 3), in which all the aromatic side groups except the phenyl group of the benzoyl group bound to C(31) are located in equatorial positions relative to the central six-membered ring, and the cyclohexane ring is in chair conformation. It is also clearly indicated that there is a hydrogen bonding between C(34)–OH and C(37)═O(5).

The above facts reveal that the compound shows identical stereochemistry in the crystalline state and in the solution.

A possible mechanism for the formation of 1,2,3,4,5-pentasubstituted cyclohexanols has been suggested (Scheme 2). In this class of reactions, chalcones and 3-aryl-1,5-diphenyl-1,5-dione are key intermediates, which have been separated in the reactions using lower ratio of NaOH. Both the intermediates were ground in a 2:1 mixture of NaOH and K_2CO_3 to furnish almost quantitatively the desired pentasubstituted cyclohexanols. It appears that under the experimental condition, aldol condensation between acetophenone and an aromatic aldehyde and sequential Michael addition occur highly chemoselectively and fleetly, and result in high yield of the 1,2,3,4,5-pentasubstituted cyclohexanols.

Utilization of the double-component solid base system consisting of NaOH and K_2CO_3 in the reaction possesses some obvious advantages compared with using only NaOH, where the reaction mixture formed a syrupy dope and led to a difficult operation. Under our experiment conditions, no tacky material formed in the whole course of reaction, and the solid mixture always was in an incompact state. Thus, it is convenient for operation and treatment. It is a blemish in an otherwise perfect thing that the products thus obtained are with yellow, recrystallization is necessary for obtaining pure, white crystals. Even so, this preparing procedure still is very simple, and the level of greenization is quite high.

In summary, we accomplished for the first time high-yielding, seriation synthesis of 1,2,3,4,5-pentasubstituted cyclohexanols via a solvent-free reaction. Under catalysis of a double-component solid base system consisting of NaOH and K_2CO_3, acetophenone reacted with aromatic aldehydes with grinding at room temperature for 5–20 min to furnish highly chemoselectively the polysubstituted cyclohexane derivatives.

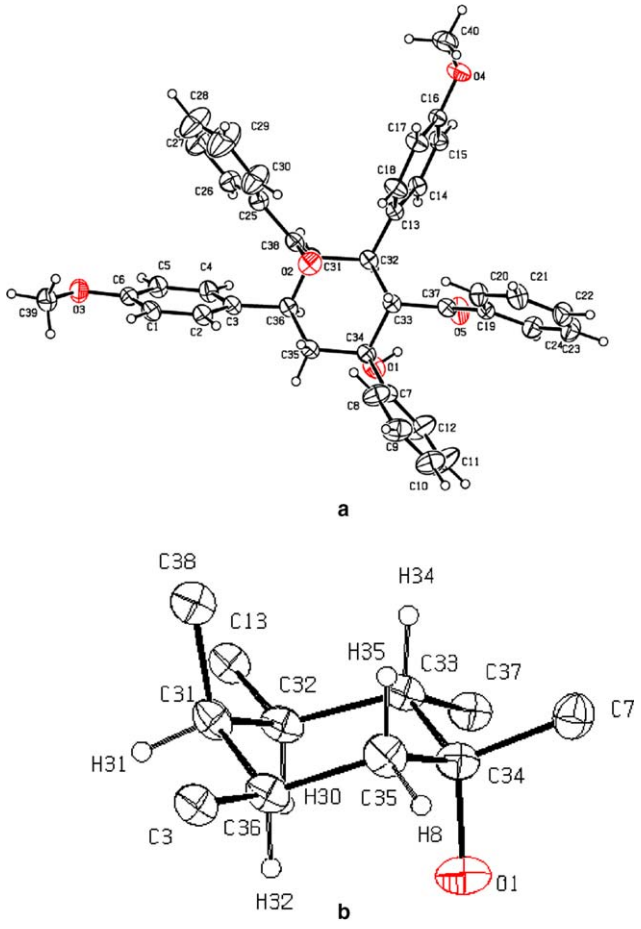
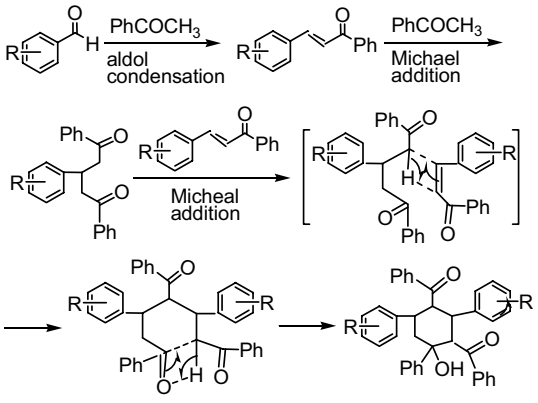


Figure 3. Molecular structure of the product (**B**) obtained from the reaction of acetophenone and 4-methoxylbenzaldehyde: (a) perspective view of the molecular structure of **B** showing the numbering scheme, (b) chair conformation of the cyclohexane ring of **B** (only the atoms connected directly to the cyclohexane ring were drawn for clarity).



Scheme 2. A possible mechanism for the formation of 1,2,3,4,5-pentasubstituted cyclohexanols.

Acknowledgments

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7. There is great difference between our and Chen's products in melting point and ^{1}H NMR spectra for the compounds. For example, the melting points for product **B** were 180–182 °C (by us) and 232–234 °C (by Chen), respectively. For product **H**, the melting points were 208–210 °C (by us) and 254–256 °C (by Chen), respectively. For their ^{1}H NMR spectra, see the present note and Ref. 6. It is obvious that the two groups obtained different class of compounds.
8. *Representative experimental procedure:* NaOH (50 mmol) was allowed to mix with K_2CO_3 (25 mmol) and grinded finely. To the fine powder was added a mixture of 2-chlorobenzaldehyde (50 mmol) and acetophenone (0.55 mmol) and ground at room temperature till the liquid disappeared (over 15 min) to furnish an incompact, white solid powder. After treatment with water and recrystallization in toluene, a white solid of 2,4-dibenzoyl-3,5-di(2-chlorophenyl)-1-phenylcyclohexanol (**H**) was obtained, mp 208–210 °C, 95% yields. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (d, $J = 7.2$ Hz, 2H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.32–6.83 (m, 17H), 6.71 (t, $J = 7.2$ Hz, 1H), 6.45 (t, $J = 7.5$ Hz, 1H), 5.70 (d, $J = 8.4$ Hz, 1H), 4.99 (s, 1H), 4.89–4.81 (m, 2H), 4.63 (d, J=12.3 Hz, 1H), 3.42 (t, $J = 12.9$ Hz, 1H). 1.99 (d, $J = 13.5$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 207.2, 205.6, 146.8, 139.4, 138.8, 138.1, 136.6, 134.6, 134.5, 133.3, 132.6, 129.7, 129.4, 128.5, 128.4, 128.2, 128.1, 127.9, 127.4, 127.3, 126.9, 126.2, 125.4, 76.1, 49.5, 45.5, 42.6, 37.9, 37.8. IR (KBr, cm^{-1}): 3428 versus (O–H), 1660 s, 1644 s (C=O). Anal. Calcd. for $C_{38}H_{30}Cl_2O_3$ (FW: 605.52): C 75.37, H 4.99; Found: C 75.14, H 4.86.
The characteristic data of the other products. *2,4-Dibenzoyl-3,5-di(4-methylphenyl)-1-phenylcyclohexanol* (**A**), mp 197–198 °C, 88% yields. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, $J = 7.2$ Hz, 2H), 7.43 (d, $J = 7.2$ Hz, 2H), 7.33–6.95 (m, 13H), 6.91 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 7.5$ Hz, 2H), 6.59 (d $J = 7.5$ Hz, 2H), 5.66 (d, $J = 8.7$ Hz, 1H), 5.14 (s, 1H), 4.31 (t, $J = 4.5$ Hz, 1H), 4.13–4.04 (m 2H), 3.34 (t, $J = 7.8$ Hz, 1H), 2.10 (s, 3H), 2.01 (d, $J = 13.5$ Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 204.7, 203.4, 143.2, 136.6, 134.9, 134.5, 132.6, 132.5, 132.2, 129.1, 128.0, 125.1, 125.0, 124.8, 124.6, 124.5, 124.4, 124.2, 124.0, 123.9, 123.8, 123.7, 123.6, 123.1, 121.4, 72.2, 49.3, 46.5, 43.8, 38.1, 34.8. IR (KBr, cm^{-1}): 3449 s (O–H), 1666 s, 1651 s (C=O). *2,4-Dibenzoyl-3,5-di(4-methoxyphenyl)-1-phenyl-*

cyclohexanol (**B**), mp 180–182 °C, 92% yields. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (d, $J = 7.8$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.28–7.16 (m, 5H), 7.11–7.06 (m, 6H), 7.02 (d, $J = 7.2$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.57 (d, $J = 8.1$ Hz,2H), 6.32 (d, $J = 8.4$ Hz, 2H), 5.63 (d, $J = 12$ Hz, 1H), 5.20 (s, 1H), 4.13 (t, $J = 4.5$ Hz, 1H), 4.12–4.02 (m, 2H), 3.62 (s, 3H), 3.49 (s, 3H), 3.31 (t, $J = 13.5$ Hz 1H), 2.00 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 208.6, 207.3, 158.1, 158.0, 146.9, 140.2, 138.2, 133.9, 132.8, 131.9, 131.4, 129.8, 128.6, 128.1, 127.8, 127.7, 127.5, 126.8, 125.1, 113.6, 113.4, 75.9, 55.1, 55.0, 53.0, 50.4, 47.1, 41.4, 38.7. IR (KBr, cm^{-1}): 3452 m (O–H), 1660 s, 1611 m (C═O). Anal. Calcd for $C_{40}H_{36}O_5$: C 80.65, H 5.92; Found C 80.34, H 5.86. *2,4-Dibenzoyl-3,5-di(4-dimethylaminophenyl)-1-phenylcyclohexanol* (**C**), mp 228–230 °C, 82% yields. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.23–6.96 (m, 13H), 6.87 (d, $J = 8.7$ Hz, 2H), 6.43 (d, $J = 8.7$ Hz, 2H), 6.16 (d, $J = 9.0$ Hz, 1H), 5.63 (d, $J = 12.3$ Hz, 1H), 5.19 (s, 1H), 4.30 (t, $J = 4.2$ Hz, 1H), 4.05–3.96 (m, 2 H), 3.28 (t, $J = 12.6$ Hz, 1H), 2.74 (s, 3H), 2.62 (s, 3H), 2.00–1.94 (dd, $J = 13.2$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 208.9, 207.9, 149.3, 147.2, 140.6, 138.4, 137.9, 132.5, 131.5, 130.2, 129.4, 129.0, 128.2, 128.1, 128.0, 127.7, 127.6, 126.7, 125.3, 125.2, 112.9, 112.4, 76.0, 53.5, 50.6, 47.0, 41.4, 40.8, 40.5, 38.8. IR (KBr, cm^{-1}): 3458 s (O–H), 1651 s, 1615 s (C═O). *2,4-Dibenzoyl-3,5-di(4-bromophenyl)-1-phenylcyclohexanol* (**D**), 176–178°C, 80% yields, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70 (d, $J = 7.5$ Hz, 2H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.32–7.01 (m, 17 H), 6.92 (s, 2H), 5.62 (d, $J = 12.3$ Hz, 1H), 5.11 (s, 1H), 4.30 (t, $J = 4.8$ Hz, 1H), 4.14–4.05 (m, 2H), 3.29 (t, $J = 11.1$ Hz, 1H). 1.99 (d, $J = 10.5$ Hz, 1H). IR (KBr, cm^{-1}): 3440 versus br (O–H), 1656 s, 1644 s (C═O). *2,4-Dibenzoyl-3,5-di(2-bromophenyl)-1-phenylcyclohexanol* (**E**), 219–221 °C, 89% yields, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (d, $J = 6.9$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.37–6.92 (m, 16H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.62 (t, $J = 7.5$ Hz, 1H), 6.49 (t, $J = 7.2$ Hz, 1H), 5.69 (d, $J = 12.3$ Hz, 1H), 5.00 (s, 1H), 4.89 (d, $J = 3.9$ Hz, 1H), 4.81 (d, $J = 11.7$ Hz, 1H), 4.58 ($J = 13.5$ Hz,), 3.42 (t, $J = 12$ Hz, 1H). 1.98 (d, $J = 11.4$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 206.9 205.2, 163.9, 146.6, 140.1, 139.3, 138.0, 133.2, 133.1, 133.0, 132.5, 129.5, 128.8, 128.4, 128.2, 128.1, 127.5, 127.4, 127.2, 126.8, 125.4, 76.1, 49.9, 45.8, 45.6, 40.7, 38.2. IR (KBr, cm^{-1}): 3428 versus (O–H), 1660 s, 1644 s (C═O). *2,4-Dibenzoyl-3,5-di(3-bromophenyl)-1-phenylcyclohexanol* (**F**), 140–142 °C, 80% yields, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, $J = 7.2$ Hz, 2H), 7.44 (d, $J = 6.9$ Hz, 2H), 7.32–7.23 (m, 7H), 7.16–7.04 (m, 8H), 6.95–6.87 (m, 3H), 6.64 (t, $J = 7.8$ Hz, 1H), 5.64 (d, $J = 12.0$ Hz, 1H), 5.17 (s, 1H), 4.31 (t, $J = 3.9$ Hz, 1H), 4.12–4.06 (m, 2H), 3.28 (t, $J = 12$ Hz, 1H), 2.03–1.98 (dd, $J = 13.2$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 207.9, 205.9, 146.5, 144.0, 141.5, 139.8, 138.2, 133.4, 132.7, 132.3, 131.1, 130.4, 130.0, 129.8, 128.5, 128.3, 128.2, 127.6, 127.4, 127.3, 126.5, 125.3, 122.6, 122.4, 76.0, 53.4, 52.2, 50.1, 47.9, 42.2, 38.5. IR (KBr, cm^{-1}): 3442 versus (O–H), 1675 s, 1658 s (C═O). *2,4-Dibenzoyl-3,5-di(4-chlorophenyl)-1-phenylcyclohexanol* (**G**), mp 187–189 °C, 85% yields. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, $J = 7.8$ Hz, 2H), 7.41 (d, $J = 7.5$, 2H), 7.31–7.21 (m, 4H), 7.13–6.96 (m, 13H), 6.77 (d, $J = 8.7$ Hz, 2H), 5.62 (d, $J = 8.7$ Hz, 1H), 5.13 (s, 1H), 4.31 (t, $J = 4.5$ Hz, 1H), 4.16–4.05 (m, 2H), 3.30 (t, $J = 13.2$ Hz, 1H), 3.45 (t, $J = 12.9$ Hz, 1H). 2.00 (d, $J = 13.5$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 207.9, 206.2, 146.5, 140.2, 139.8, 138.1, 137.9, 133.5, 132.9, 132.7, 132.6, 130.2, 129.3, 128.6, 128.4, 128.3, 128.2, 127.6, 127.3, 125.3, 76.1, 52.4, 50.3, 47.6, 41.9, 38.6. IR (KBr, cm^{-1}): 3503 s (O–H), 1660 versus, (C═O). *2,4-Dibenzoyl-3,5-di(2,4-dichlorophenyl)-1-phenylcyclohexanol* (**I**), mp 218–219 °C, 90% yields, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, $J = 7.2$ Hz, 4H), 7.38 (d, $J = 7.5$, 2H), 7.23–6.93 (m, 14H), 6.80 (t, $J = 8.1$ Hz, 2H), 6.63 (t, $J = 7.8$ Hz, 1H), 6.54 (t, $J = 7.8$ Hz, 1H), 5.97 (t, $J = 9.6$ Hz, 1H), 5.60 (s, 1H), 5.22–5.07 (m, 3H), 3.26 (t, $J = 13.2$ Hz, 1H), 1.97 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 206.7, 202.5, 146.0, 138.9, 137.9, 137.3, 137.0, 136.3, 134.9, 134.7, 133.7, 132.9, 132.2, 129.8, 129.6, 129.1, 129.0, 128.7, 128.2, 127.8, 127.4, 127.1, 127.0, 124.9, 124.7, 75.2, 50.6, 45.4, 42.4, 40.0,38.8. IR (KBr, cm^{-1}): 3418 s (O–H), 1676 s, 1645 s, (C═O).