

Note

An efficient and simple synthesis of tetraketones catalyzed by $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ under solvent free conditions

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A novel and efficient three-component one-pot condensation method has been described for the synthesis of tetraketones or arylmethylene[*bis*(3-hydroxy-2-cyclohexene-1-ones)] using $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ and amine as catalytic system under solvent free conditions. Tetraketones are obtained in high yield (73-88%). The application of an eco-friendly, non-corrosive, and reusable catalytic system makes this method advantageous.

Keywords: Tetraketones, ytterbium triflate, three-component condensation, Knoevenagel condensation, Michael addition

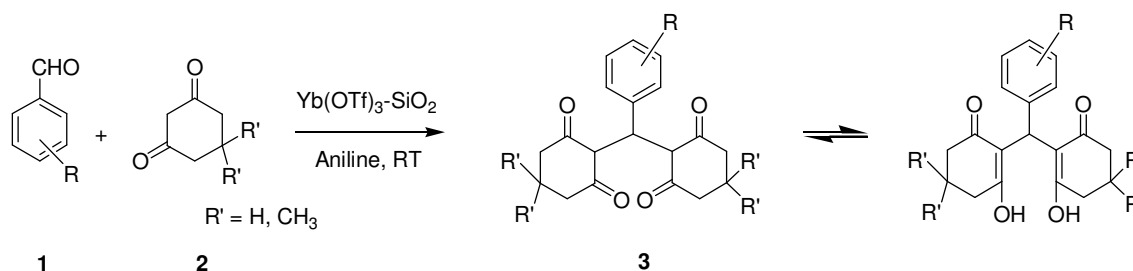
Tetraketones or arylmethylene[*bis*(3-hydroxy-2-cyclohexene-1-ones)] are extensively used as important precursors for the synthesis of various acridinediones, xanthenedione, and thiaxanthenes derivatives, which are structural units in various natural products and synthetic compounds^{1,2}. They have been reported to show lipoxygenase inhibition and antioxidation activities³. Formation of tetraketones by the reaction of 1,3-cyclohexanediones and aldehydes has also been utilized for the identification of aldehydes⁴. These compounds possess phenolic properties and can be coupled with diazonium compounds to give dyestuffs⁵. Due to their importance in synthetic and medicinal chemistry, several methods have appeared employing various catalysts such as I_2 (Ref 6), $\text{HClO}_4\text{-SiO}_2$ (Ref 7), $\text{In}(\text{OTf})_3$ (Ref 8), $\text{FeCl}_3\cdot 6\text{H}_2\text{O}/\text{TMSCl}/[\text{bmim}][\text{BF}_4]$ (Ref 9), sodium *para*-toluene sulfonate (Na-PTS) (Ref 10), CTABr (Ref 11), $\text{Et}_4\text{NBr}/\text{NH}_4\text{Cl}$ (Ref 12), $\text{KF}/\text{Al}_2\text{O}_3$ (Ref 13), SDS (Ref 14), solid state grinding¹⁵ and without catalysts under heating¹⁶ for the synthesis of tetraketones. Many of these methods involve harsh reaction conditions, elevated temperatures and tedious reaction work-up to obtain the products. Moreover, under Lewis acidic

conditions, xanthenedione are also observed along with tetraketones as side products. Recently, it was reported that the reaction of benzaldehyde and dimedone in the presence of 30 mol% $\text{BF}_3\text{-Et}_2\text{O}$ in refluxing THF for 4 hr gave a mixture of 2,2'-phenylmethylene-*bis*(5,5-dimethylcyclohexane-1,3-dione) and corresponding xanthenedione derivative in 56 and 33% yields, respectively⁸. Thus, the development of simple and efficient procedures for the synthesis of tetraketones is highly desirable.

With the increasing environmental concerns and the regulatory constraints, development of easy, expeditious, economical and environmentally benign methods for organic reactions has become a challenging task in organic chemical research. In this regard, rare earth metal triflates have been recognized as unique Lewis acid catalysts in a variety of synthetic reactions^{17,18}. These metal triflates are not only safe alternatives to hazardous and corrosive liquid acids, but also have many advantages, such as simplicity in handling, and environmentally safe disposal. Among rare-earth metal triflates, ytterbium triflate is one of the most frequently used as Lewis acid catalysts for carbon-carbon and carbon-heteroatom bond forming reactions¹⁹. In continuation of the efforts towards development of environment friendly reaction methodologies²⁰, herein is described an expeditious and economical method for the synthesis of tetraketones *via* sequential Knoevenagel condensation-Michael addition reaction catalyzed by $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ in presence of amines under solvent free conditions (**Scheme I**).

Results and Discussion

At the outset of this study, the reaction of benzaldehyde **1a** and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) **2a** was selected as a model reaction to establish the optimum reaction conditions and catalyst loading (**Table I**). The best yields for the reaction of **1a** with **2a** were observed in presence of aniline (1 equiv.) with $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ (30 mol%) to afford 2,2'-phenylmethylene-*bis*(5,5-dimethylcyclohexane-1,3-dione) **3a** (81% isolated yield) under solvent free conditions at RT. Among the various metal triflates used in combination with silica gel, $\text{Yb}(\text{OTf})_3$ was found to give highest yield of **3a**



Scheme I

Table I — Catalysts effect on the synthesis of tetraketone **3a** under solvent free conditions^a

| Entry | Catalyst | Time (min) | Yield ^b (%) |
|-------|----------------------|------------|------------------------|
| 1 | - | 60 | - |
| 2 | SiO ₂ | 120 | 42 |
| 3 | Yb(OTf) ₃ | 2 | 81 ^{c,d,e} |
| 4 | Ce(OTf) ₃ | 5 | 58 |
| 5 | Y(OTf) | 5 | 57 |
| 6 | Zn(OTf) ₃ | 10 | 61 |
| 7 | Ba(OTf) ₃ | 10 | 44 |
| 8 | Sc(OTf) ₃ | 10 | 58 |
| 9 | Er(OTf) ₃ | 15 | 46 |
| 10 | In(OTf) ₃ | 5 | 58 |
| 11 | PTSA | 10 | 58 |

^aReaction condition: **1a** (1 mmol), **2a** (2 mmol), SiO₂ (300 mg) and catalyst (30 mol%). ^bIsolated yield. ^cWith silica gel, yield of **3a** was 40% after 2 hr. ^dYield of **3a** was 80, 81, 79 with 30 mol% Yb(OTf)₃ and 250, 300, 400 and 600 mg of silica gel. ^eIn absence of aniline, yield of **3a** was 30% after 30 min.

(**Table I**, entry 3). The high activity of Yb(OTf)₃ among the metal triflates used may be attributed to its high acidity. Negligible amount of **3a** was observed in the absence of both Yb(OTf)₃ and SiO₂ even after long reaction times (2 hr) at RT whereas, **3a** was formed in 40 and 42% yield using either Yb(OTf)₃ or SiO₂ alone, respectively. It was also found that increasing the amount of silica gel to more than 300 mg/mmol of aldehyde did not improve the yield of **3a** (**Table I**, footnote d).

The model reaction was used to examine both the catalysts loading and solvent effect as shown in **Table II**. A significant increase in yield of **3a** was observed with increasing Yb(OTf)₃ loading on silica gel up to 30 mol% value which has been adopted as optimum loading for this methodology (**Table II**, entries 1-5). Solvent effect was studied by performing model reaction with Yb(OTf)₃-SiO₂ (30 mol%) in different organic solvents (acetonitrile, methanol, ethanol and

Table II — Effect of catalysts loading and different solvents on the synthesis of **3a** catalyzed by Yb(OTf)₃.SiO₂^a

| Entry | Solvent | Catalyst loading (mol%) | Time (min) | Yield ^{b,c} (%) |
|-------|--------------------------|-------------------------|------------|--------------------------|
| 1 | Neat | 5 | 2 | 61 |
| 2 | Neat | 10 | 2 | 67 |
| 3 | Neat | 20 | 2 | 73 |
| 4 | Neat | 30 | 2 | 81 |
| 5 | Neat | 50 | 2 | 80 |
| 6 | [Bmim][BF ₄] | 30 | 30 | 75 |
| 7 | CH ₃ CN | 30 | 30 | 75 |
| 8 | DCM | 30 | 60 | 70 |
| 9 | MeOH | 30 | 60 | 66 |
| 10 | H ₂ O | 30 | 60 | 56 |
| 11 | EtOH | 30 | 60 | 52 |

^aSiO₂ was 300 mg in each case. ^bReaction condition: **1a** (1 mmol), **2a** (2 mmol) at RT. ^cIsolated yield.

dichloromethane), ionic liquid and water (**Table II**, entries 6-11). The reaction in all these solvents was found to be markedly less efficient than under solvent free conditions. It is also worth mentioning that in absence of aniline, yield of **3a** decreased to 30% and it took longer for the reaction (30 min) to complete. However, by replacing aniline with naphthalen-1-amine or 2-iodoaniline in model reaction, **3a** was obtained in 75 and 80% yields, respectively after 2 min.

The structure of **3a** was analyzed by IR, ¹H NMR, and mass spectroscopic data. IR spectrum showed characteristic stretching band at ~1646 cm⁻¹ due to C=O bond. In the ¹H NMR spectrum, the C-5 and C-5' methyl protons appeared at δ 1.03 as a singlet; the C-4, C-6, C-4' and C-6' methylene protons appeared at δ 2.25 as a singlet; the benzylic methine proton appeared at δ 5.52; and the phenyl protons resonated at δ 7.12–7.27 as a multiplet. In ESI-MS a peak appeared at *m/z* 369.1088 which corresponds to [M + H]⁺ ion of **3a**.

To determine the substrate scope of the present method, structurally diverse aldehydes and 1,3-cyclohexadione were subjected to the standardized reaction conditions. All the aldehydes and 1,3-cyclohexadione produced corresponding tetraketones

in good to excellent yields (**Table III**). It was found that aldehydes possessing both electron-withdrawing and electron-donating groups, afforded the corresponding products in satisfactory yield without much difference. All the tetraketones **3a-r** showed

Table III — Synthesis of different tetraketones **3a-r** catalyzed by Yb(OTf)₃-SiO₂ (30 mol%) and aniline (1 equivalent)

| Entry | R | R' | Product 3 ^a | Time (min) | Yield ^b | m.p. (Lit. m.p.) (°C) |
|----------|-------------------|-----------------|-------------------------------|------------|--------------------|-----------------------------|
| a | H | CH ₃ | | 2 | 81 | 183-85 (184-86) (Ref 6) |
| b | 4-Cl | CH ₃ | | 2 | 80 | 136-38 (140-42) (Ref 7) |
| c | 4-NO ₂ | CH ₃ | | 4 | 76 | 177-79 (188-90) (Ref 16) |
| d | 3-NO ₂ | CH ₃ | | 4 | 83 | 189-91 (196-98) (Ref 7) |
| e | 3-Cl | CH ₃ | | 4 | 83 | 139-40 (185-87) (Ref 7) |
| f | 4-OH | CH ₃ | | 2 | 87 | 187-89 (188-90) (Ref 4a) |
| g | 4-OMe | CH ₃ | | 2 | 83 | 136-39 (142-43) (Ref 4a) |

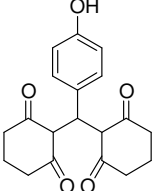
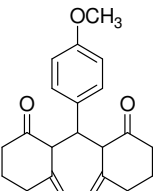
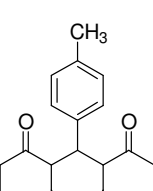
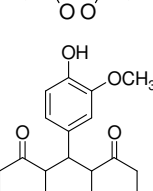
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Table III — Synthesis of different tetraketones **3a-r** catalyzed by Yb(OTf)₃-SiO₂ (30 mol%) and aniline (1 equivalent)—*Contd*

| Entry | R | R' | Product 3 ^a | Time (min) | Yield ^b | m.p. (Lit. m.p.) (°C) |
|----------|-------------------|-----------------|-------------------------------|------------|--------------------|-----------------------------|
| h | 4-CH ₃ | CH ₃ | | 2 | 78 | 123-26 (126-28) (Ref 16) |
| i | 4-OH, 3-OMe | CH ₃ | | 2 | 88 | 189-91 (195-96) (Ref 4a) |
| j | H | H | | 4 | 73 | 208-10 (217-18) (Ref 3) |
| k | 4-Cl | H | | 4 | 83 | 202-04 |
| l | 4-NO ₂ | H | | 4 | 88 | 193-94 (219-21) (Ref 3) |
| m | 3-NO ₂ | H | | 4 | 87 | 207-09 (209-10) (Ref 4b) |
| n | 3-Cl | H | | 2 | 87 | 203-05 (199-00) (Ref 3) |

—*Contd*

Table III — Synthesis of different tetraketones **3a-r** catalyzed by Yb(OTf)₃-SiO₂ (30 mol%) and aniline (1 equivalent)—

| Entry | R | R' | Product 3 ^a | Time (min) | Yield ^b | m.p. (Lit. m.p.) (°C) |
|----------|---------------------------|----|---|------------|--------------------|-----------------------------|
| o | 4-OH | H |  | 2 | 88 | 197-99 (196-97) (Ref 3) |
| p | 4-OMe | H |  | 2 | 85 | 195-97 (196) (Ref 4b) |
| q | 4-CH ₃ | H |  | 2 | 76 | 190-91 (187) (Ref 4b) |
| r | 3-OCH ₃ , 4-OH | H |  | 5 | 82 | 203-05 (204-05) (Ref 4b) |

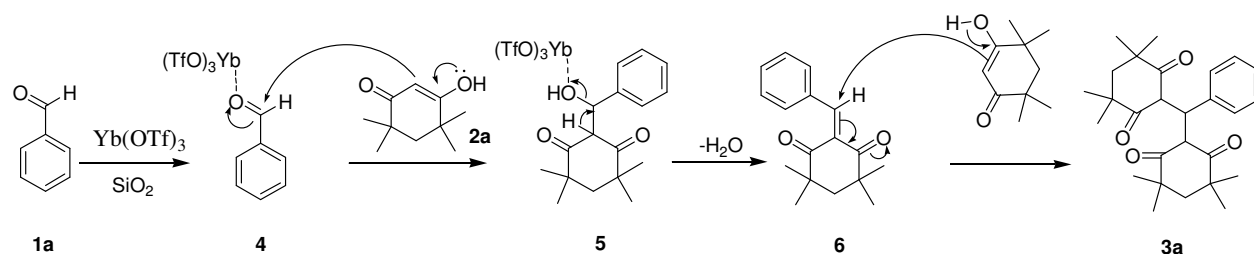
^aAll products were characterized by IR, MS, ¹H and ¹³C NMR. ^bIsolated yield by column chromatography over silica gel.

satisfactory results for their analysis by IR, ¹H NMR and mass spectroscopic data.

To make this method more suitable, the reusability of the catalytic system Yb(OTf)₃-SiO₂ was examined using **1a** and **2a** as model substrates. Towards this aim, after completion of the reaction (monitored by TLC), the catalyst was easily regenerated by filtering the reaction mixture, washing it with ethyl acetate and drying it under vacuum for 15 min. The dried Yb(OTf)₃-SiO₂ was reused for reaction of **1a** with **2a** in presence of aniline and it was found that the catalyst can be reused without much change in activity even after five consecutive runs (**Table IV**).

Based on the experimental results a possible mechanistic pathway for the reaction has been tentatively proposed. It is likely to proceed *via* sequential Knoevenagel condensation-Michael

addition reactions (**Scheme II**). It is expected that Yb(OTf)₃ coordinates with oxygen of carbonyl group of benzaldehyde **1a** to form a complex **4** and thus activates it for nucleophilic attack. The complex **4** is attacked by dimedone **2a** to give an intermediate alcohol **5**. Such intermediate alcohols have been observed to undergo nucleophilic attack in the Lewis acid catalyzed condensation of indoles with arylaldehydes to afford *bis*(indolyl)methanes²¹. Dehydration of **5** catalyzed by Yb(OTf)₃ on silica gel gives enone **6**, which undergoes Michael addition reaction with **2a** to yield tetraketone **3a**. It is expected that presence of silica gel affects this dehydration step. Although, the role of amine is not clear, it appears that in the presence of aniline, Yb(OTf)₃-SiO₂ behaves as acid-base catalyst and the rate of last step *i.e.* Michael addition is enhanced resulting in overall higher yield.



Scheme II — Plausible mechanism for the synthesis of tetraketones catalyzed by $\text{Yb}(\text{OTf})_3$

Table IV — Recycling of catalyst $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ for the synthesis of **3a**

| Entry | 1 | 2 | 3 | 4 | 5 |
|------------------------|----|----|----|----|----|
| Yield (%) ^a | 81 | 79 | 77 | 78 | 75 |

^aIsolated yield

In conclusion, a novel and efficient method has been developed for the synthesis of tetraketones in high yields employing $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ and amine as catalyst under solvent free conditions. The application of an inexpensive, easily available and reusable catalytic system makes this method advantageous and economically viable.

Experimental Section

All chemicals were purchased from Sigma-Aldrich and SD Fine Chemicals (India) and were used as such. All the reactions and homogeneity of synthesized tetraketones were monitored by thin layer chromatography (TLC) using aluminium plates coated with silica gel (E. Merck) using 90% ethyl acetate in petroleum ether as eluent. Melting points were determined in open capillary tubes on a MPA120-automated melting point apparatus and are uncorrected. The IR spectra were recorded using KBr pellets on Shimadzu Prestige-21 FTIR spectrophotometer and ν_{max} was expressed in cm^{-1} . ^1H NMR were recorded on Bruker Heaven Avance 11 400 spectrometer using TMS as internal standard and CDCl_3 as solvent. The chemical shifts are expressed in δ , ppm. Mass spectra were recorded on a Qstar[®] Elite LX/MS/MS mass spectrometer from Applied Biosystem.

Representative procedure for the synthesis of tetraketones

A mixture of an aromatic aldehyde (1.0 mmol), 1,3-cyclohexanone (2.0 mmol), aniline (1.0 mmol)

and $\text{Yb}(\text{OTf})_3\text{-SiO}_2$ (300 mg, 30 mol%) was ground for 2-5 min (as shown in **Table III**). After completion of reaction, the solid mixture was extracted with ethyl acetate and resulting mixture was filtered. The filtrate was dried with anhydrous sodium sulphate and concentrated to give crude product which was purified by column chromatography using hexane and ethyl acetate as eluent.

Spectroscopic data for selected tetraketones

2,2'-(Phenylmethylene)-bis(5,5-dimethylcyclohexane-1,3-dione), 3a: White solid; m.p. 183-85°C; IR (KBr): 2969, 1608, 1496, 1448, 1368, 1300, 1246, 1169, 1128, 1034 and 872 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.03 (s, 12H, CH_3), 2.25 (s, 8H, CH_2), 5.91 (s, 1H, CH), 6.91 (d, $J = 7.81$ Hz, 2H), 7.12–7.27 (m, 5H, Ph); ESI-MS: m/z Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_4$ 368.1988. Found 369.1088 [$\text{M} + \text{H}$]⁺.

2,2'-(4'-Chlorophenyl)methylene-bis(5,5-dimethylcyclohexane-1,3-dione), 3b: White solid; m.p. 136-38°C; IR (KBr): 2965, 2903, 1604, 1498, 1378, 1310, 1252, 1186, 1132, 1029 and 882 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.00 (s, 12H, CH_3), 2.25 (s, 8H, CH_2), 5.92 (s, 1H, CH), 6.94 (d, $J = 7.84$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H); ESI-MS: m/z Calcd for $\text{C}_{23}\text{H}_{27}\text{ClO}_4$ 402.1598. Found 403.0611 [$\text{M} + \text{H}$]⁺.

2,2'-(4'-Nitrophenyl)methylene-bis(5,5-dimethylcyclohexane-1,3-dione), 3c: White solid; m.p. 177-79°C; IR (KBr): 2961, 2901, 1593, 1508, 1374, 1303, 1243, 1194, 1139, 1039 and 852 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.01 (s, 12H, CH_3), 2.24 (s, 8H, CH_2), 6.07 (s, 1H, CH), 7.18 (d, $J = 8.0$ Hz, 2H), 8.01 (m, 2H), 8.06 (d, $J = 8.0$ Hz, 2H); ESI-MS: m/z Calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_6$ 413.1838. Found 414.0822 [$\text{M} + \text{H}$]⁺.

2,2'-(3'-Chlorophenyl)methylene-bis(5,5-dimethylcyclohexane-1,3-dione), 3e: White solid; m.p. 139-40°C; IR (KBr): 2972, 1609, 1510, 1318, 846 and 612 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.59 (s,

12H, CH₃), 2.87 (s, 8H, CH₂), 5.97 (s, 1H, CH), 7.48-7.54 (m, 3H), 7.57-7.63 (m, 1H), 7.65-7.72 (m, 2H); ESI-MS: *m/z* Calcd for C₂₃H₂₇ClO₄ 402.1598. Found 403.0617 [M + H]⁺.

2,2'-(4''-Methoxyphenyl)methylene-bis(5,5-dimethylcyclohexane-1,3-dione), 3g: White solid; m.p. 136-39°C; IR (KBr): 2946, 1598, 1508, 1456, 1368, 1296, 1195, 1138, 1039 and 841 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.01 (s, 12H, CH₃), 2.29 (s, 8H, CH₂), 3.67 (s, 3H), 5.82 (s, 1H, CH), 6.70-6.74 (m, 2H), 6.74-6.76 (m, 2H), 6.83-6.86 (m, 2H); ESI-MS: *m/z* Calcd for C₂₄H₃₀O₅ 398.2093. Found 399.1115 [M + H]⁺.

2,2'-(4''-Nitrophenyl)methylene-bis(cyclohexane-1,3-dione), 3l: White solid; m.p. 193-94°C; IR (KBr): 3149, 3023, 2989, 1593, 1511, 1496, 1370, 1345, 1256, 1048 and 713 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.85-1.83 (m, 4H, CH₂), 2.12-2.08 (m, 4H, CH₂), 2.40-2.35 (m, 4H), 7.04 (s, 1H), 7.30 (d, *J* = 7.84 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H); ESI-MS: *m/z* Calcd for C₁₉H₁₉NO₆ 357.1212. Found 380.0013 [M + Na]⁺, 395.9665 [M + K]⁺ and 737.0043 [2M + Na]⁺.

2,2'-(3''-Chlorophenyl)methylene-bis(cyclohexane-1,3-dione), 3n: White solid; m.p. 203-05°C; IR (KBr): 3141, 2956, 1678, 1519, 1346, 1293, 843 and 713 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.85-1.83 (m, 4H, CH₂), 2.04-2.06 (m, 4H, CH₂), 2.48-2.38 (m, 4H), 5.88 (s, 1H), 6.93-6.90 (m, 2H), 7.09-7.18 (m, 4H); ESI-MS: *m/z* Calcd for C₁₉H₁₉ClO₄ 346.0972. Found 368.9809 [M + Na]⁺, 384.9457 [M + K]⁺ and 714.9641 [2M + Na]⁺.

2,2'-(4''-Methoxyphenyl)methylene-bis(cyclohexane-1,3-dione), 3p: White solid; m.p. 195-97°C; IR (KBr): 3145, 2951, 1570, 1515, 1343, 1339, 1211, 1124, 1056 and 845 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.85 (m, 4H, CH₂), 2.24-2.07 (m, 4H, CH₂), 2.35-2.38 (m, 4H), 3.65 (s, 3H), 6.68 (d, *J* = 7.84 Hz, 2H), 6.73 (t, *J* = 6.4 Hz, 1H), 6.81 (s, 1H), 6.91 (t, *J* = 6.38 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H); ESI-MS: *m/z* Calcd for C₂₀H₂₂O₅ 342.1467. Found 365.0282 [M + Na]⁺, 380.9959 [M + K]⁺, 707.0652 [2M + Na]⁺ and 723.0341 [2M + K]⁺.

2,2'-(4''-Methylphenyl)methylene-bis(cyclohexane-1,3-dione), 3q: White solid; m.p. 190-91°C; IR (KBr): 3138, 3048, 2996, 1591, 1487, 1368, 1302, 1250 and 716 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 2.34-2.38 (m, 4H, CH₂), 2.45-2.47 (m, 8H, CH₂), 2.69 (s, 3H, CH₃), 5.82 (s, 1H, CH), 7.38-7.36 (m, 1H), 7.46-7.49 (m, 4H), 7.60-7.58 (m, 1H); ESI-MS: *m/z* Calcd for C₂₀H₂₂O₄ 326.1518. Found 349.0422 [M +

Na]⁺, 365.0097 [M + K]⁺, 675.0890 [2M + Na]⁺ and 691.0603 [2M + K]⁺.

2,2'-(4''-Hydroxy-3''-methoxyphenyl)methylene-bis(cyclohexane-1,3-dione), 3r: White solid; m.p. 203-05°C; IR (KBr): 3267, 3143, 2942, 1568, 1503, 1352, 1338, 1208, 1121, 1066 and 841 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.83-1.85 (m, 4H), 2.05-2.10 (m, 4H), 2.48-2.39 (m, 4H), 3.67 (s, 3H), 6.48-6.54 (m, 3H), 6.68 (s, 1H), 6.77 (s, 1H), 8.50 (s, 1H); ESI-MS: *m/z* Calcd for C₂₀H₂₂O₆ 358.1416. Found 381.0161 [M + Na]⁺, 396.9823 [M + K]⁺ and 739.0393 [2M + Na]⁺.

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