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# $HClO_4$–$SiO_2$ and PPA–$SiO_2$ catalyzed efficient one-pot Knoevenagel condensation, Michael addition and cyclo-dehydration of dimedone and aldehydes in acetonitrile, aqueous and solvent free conditions: Scope and limitations

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**Abstract**

Efficient one-pot Knoevenagel condensation, Michael addition and cyclodehydration of dimedone with various aldehydes in acetonitrile and solvent free conditions using PPA–$SiO_2$ catalyst gave 1,8-dioxo-octahydroxanthenes **3** in excellent yields; whereas in the presence of $HClO_4$–$SiO_2$ catalyst the reaction is limited to give only 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4** in very good yields. In aqueous medium both $HClO_4$–$SiO_2$ and PPA–$SiO_2$ catalysts yielded only **4** as the product. The scope and limitations of the two catalysts in various reaction conditions examined were described.
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*Keywords:* 1,8-Dioxo-octahydroxanthene; 5,5-Dimethyl-1,3-cyclohexanedione; Heterogeneous catalyst; β-Diketone; $HClO_4$–$SiO_2$; Polyphosphoric acid–$SiO_2$; Knoevenagel condensation; Michael addition

## 1. Introduction

Solid supported reagents are unique acid catalysts that have become popular over the last two decades. Since the activity and selectivity of a reagent dispersed on the surface of the support, is improved, as the effective surface area of reagent can be increased manifold, they expected to be performed better than the individual reagents [1]. Low toxicity, moisture, air tolerance and low price are other common features make the use of solid supported reagents as attractive alternate to the conventional Lewis acid and triflates. Although, the catalytic applications of silica supported reagents for organic synthesis have been established, to the best of our knowledge relatively only few examples are reported on the use of perchloric acid adsorbed on silica gel ($HClO_4$–$SiO_2$) [2] and very few with polyphosphoric acid supported on silica (PPA–$SiO_2$) [3].

Synthesis of 1,8-dioxo-octahydroxanthene **3** is generally achieved by the condensation of 5,5-dimethyl-1,3-cyclohexadione **1** with aromatic aldehydes **2** using Lewis acid catalysts. Although there are several methods reported, using Lewis acid catalysts for the synthesis of 1,8-dioxo-octahydroxanthene [4], they suffer from one or other drawbacks such as longer reaction times, low yields, ease of availability of catalyst, involves cumbersome preparation of catalysts and lack of selectivity. In continuation of our work [5] on the development of efficient and environmentally benign procedures using silica supported reagents, initially we examined $HClO_4$–$SiO_2$ as heterogeneous catalyst in the condensation of 5,5-dimethyl-1,3-cycloheanedione **1** with benzaldehyde **2a** refluxing in acetonitrile. Surprisingly, contrary to our expectation, only intermediate 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4a** is obtained in 92% yield. Cyclized product **3a** was not obtained. Prolonging the reaction time and increase in catalyst amount $HClO_4$-$SiO_2$ (30 mol%) did not yield the cyclized product **3a**. At 110 °C, under solvent free condition, in the presence of $HClO_4$–$SiO_2$ (30 mol%), after 7 h, yielded only mixture of **4a** (68%) and **3a** (32%). The result led us to examine other silica-supported catalysts for this condensation. Poly phosphoric acid (PPA) being a good acidic dehydrating agent in various organic transformations [6], we have cho-

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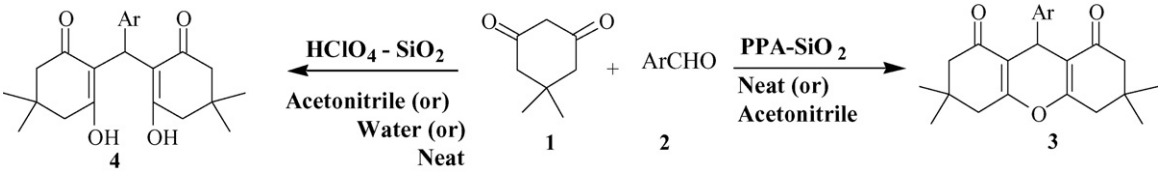
Table 1
Synthesis of 1,8-dioxo-octahydroxanthenes **3a** and 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4a** using different catalysts and reaction conditions

| S. no. | Catalyst | Solvent | Temperature (°C) | Time (h) | Yield (%) | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | | **3a** | **4a** | |
| 1 | No catalyst | DMF | 80 | 1 | 80–90 | – | [4a] |
| 2 | $TiO_2/SO_4^{2-}$ | Solvent free | RT | 24 | – | 85–90 | [4b] |
| 3 | $HClO_4$–$SiO_2$ (50 mg, 0.025 mmol) | Acetonitrile | Reflux | 6 | – | 54.1 | – |
| | | Aqueous | 100 | 0.5 | – | 91 | – |
| | | Solvent free | 140 | 3 | 32 | 68 | – |
| 4 | PPA–$SiO_2$ (50 mg, 0.025 mmol) | Acetonitrile | Reflux | 10 | 52 | – | – |
| | | Aqueous | 100 | 0.5 | – | 78.1 | – |
| | | Solvent free | 140 | 0.5 | 92.8 | – | – |
| 5 | $NaHSO_4$–$SiO_2$ | Solvent free | Reflux | 6.5 | 90 | – | [4d] |
| 6 | DBSA | Water | Reflux | 6 | 89–90 | – | [4e] |
| 7 | SDS | Water | Reflux | 3 | – | 67–92 | [4f] |
| 8 | Ultrasound | Water | 25–30 | 1 | 72–90 | – | [4c] |

sen silica supported poly phosphoric acid for further study. When polyphosphoric acid supported on silica (PPA–$SiO_2$) is used, the condensation of dimedone **1** with benzaldehyde **2a** proceeds smoothly to give 1,8-dioxo-octahydroxanthene **3a** in excellent yield in acetonitrile as well as under solvent free conditions (Table 1). It is also noticed that the condensation using PPA–$SiO_2$ proceeds rapidly and is superior to the reported procedures with respect to reaction time and temperature, yield, amount of the catalyst and solvent free conditions employed. This claim is justified through the representative examples, illustrated in Table 1, in which the efficiency of the catalysts has been compared with those of recently reported supported Lewis/protic acid catalysts (Table 1).




In aqueous media, both the catalysts $HClO_4$–$SiO_2$ and PPA–$SiO_2$ on condensation of dimedone **1** and aromatic aldehydes **2** gave only 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4a** as lone product (Table 1). Blank experiments with out catalyst cannot bring about this transformation efficiently even after longer hours.

In order to evaluate the generality of the process, scope and limitations of the catalysts, several diversified examples illustrating the present method for the synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives **3** and 2,2′-aryl-methylene bis(3-hydroxy-2-cyclohexene-1-one) derivatives **4** was examined (Table 2). The reaction of dimedone **1** with various aromatic aldehydes bearing electron withdrawing groups (such as nitro, halide) or electron releasing groups (such as *N*,*N*-dimethylamino, methyl, hydroxyl; mono, di, or trimethoxy groups), was carried out in the presence of $HClO_4$–$SiO_2$ and PPA–$SiO_2$ as catalyst. The yields obtained were good to excellent, which are normally observed under the influence of strong acids. The reaction of aromatic aldehydes having electron-withdrawing groups reacted very well at faster rate compared with aromatics aldehydes substituted with electron releasing groups. The results obtained in the current method are illustrated in Table 2.

From these results, it is evident that the catalyst plays crucial role in limiting the reaction to the desired level, to yield products **3** or **4**. The hypothesis supported the fact that reaction proceeds via one-pot Knoevenagel condensation, Michael addition and cyclodehydration (Fig. 1). Use of just 10 mol% PPA–$SiO_2$ in solvent free conditions at 140 °C is sufficient to push the reaction forward from **4** to **3**. Higher amounts of the catalyst did not improve the results to a greater extent. Thus, PPA–$SiO_2$ 10 mol% was chosen as a quantitative catalyst for these reactions. In the presence of $HClO_4$–$SiO_2$, the reaction limits to the one-pot Knoevenagel condensation and Michael addition to obtain **4** in excellent yields. It was envisaged that the formation **4** takes place through the enolization of **5** with out undergoing cyclodehydration.

For our investigations, $HClO_4$–$SiO_2$ [2a] and PPA–$SiO_2$ [3] were conveniently prepared from readily available 70% aq. perchloric acid and polyphosphoric acid respectively, according to the literature procedures. All the products obtained were fully characterized by spectroscopic methods such as IR, $^1$H NMR, $^{13}$C NMR and mass spectroscopy and also by comparison of the spectral data with that reported.

The simplicity, together with the use of inexpensive, non-toxic and environmentally benign nature of PPA–$SiO_2$ and $HClO_4$–$SiO_2$ catalyst under solvent free condition is other remarkable feature of the procedure. Ethyl acetate was added to the reaction mixture, the catalyst was filtered and the filtrate was concentrated to give crude residue, which was crystallized in

Table 2
Synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives **3** and 2,2′-aryl-methylene bis(3-hydroxy-2-cyclohexene-1-one) derivatives **4** in acetonitrile, aqueous media and solvent free conditions

| Entry | Aldehyde | Solvent | Temperature (°C) | $HClO_4$–$SiO_2$ | | | PPA–$SiO_2$ | | | m.p. (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Time (h) | **4** yield (%) | **3** yield (%) | Time (h) | **4** yield (%) | **3** yield (%) | |
| a | $C_6H_5$ | Acetonitrile | Reflux | 6.0 | 54.1 | – | 10.0 | – | 52.0 | – |
| | | Water | 100 | 0.5 | 91.0 | – | 0.5 | 78.1 | – | 192–194 |
| | | Neat | 140 | 3.0 | 68.0 | 32.0 | 0.5 | – | 92.8 | 201–202 |
| b | 4-$ClC_6H_4$ | Acetonitrile | Reflux | 6.0 | 52.2 | – | 12 | 72.5 | 48.1 | – |
| | | Water | 100 | 0.5 | 89.0 | – | 0.8 | – | – | 140–142 |
| | | Neat | 140 | 3 | 62.1 | 30.8 | 0.5 | – | 84.6 | 230–232 |
| c | 4-$NMe_2$ $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 54.2 | – | 12.0 | – | 42.0 | – |
| | | Water | 100 | 0.8 | 86.5 | – | 0.8 | 68.0 | – | 186–188 |
| | | Neat | 140 | 3 | 61.2 | 28.9 | 0.5 | – | 68.7 | 222–225 |
| d | 3,4,5-$(OMe)_3$ $C_6H_2$ | Acetonitrile | Reflux | 6.0 | 53.9 | – | 12.0 | – | 41.5 | – |
| | | Water | 100 | 0.8 | 72.1 | – | 0.8 | 64.8 | – | |
| | | Neat | 140 | 3 | 60.9 | 28.2 | 0.5 | – | 80.3 | 205–208 |
| e | 4-OMe $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 52.3 | – | 12.0 | – | 38.5 | – |
| | | Water | 100 | 0.8 | 74.2 | – | 1.0 | 56.2 | – | 146–148 |
| | | Neat | 140 | 3 | 68.8 | 29.4 | 0.5 | – | 74.6 | 242–245 |
| f | 4-$BrC_6H_4$ | Acetonitrile | Reflux | 6.0 | 58.2 | – | 12 | – | 52.1 | – |
| | | Water | 100 | 0.8 | 84.2 | – | 0.8 | 68.5 | – | – |
| | | Neat | 140 | 3 | 69.0 | 25.7 | 0.5 | – | 84.5 | 240–242 |
| g | 3-OMe $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 54.1 | – | 12 | – | 51.0 | – |
| | | Water | 100 | 0.8 | 68.2 | – | 1.0 | 50.1 | – | – |
| | | Neat | 140 | 3 | 64.1 | 26.2 | 0.5 | – | 75.3 | 162–165 |
| h | 4-$NO_2$ $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 49.4 | – | 12 | – | 47.0 | – |
| | | Water | 100 | 1.0 | 68.2 | – | 0.8 | 51.5 | – | 188–190 |
| | | Neat | 140 | 3 | 66.8 | 25.3 | 0.5 | – | 70.7 | 225–227 |
| i | 2-$NO_2$ $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 44.3 | – | 12 | – | 41.4 | – |
| | | Water | 100 | 1.0 | 61.1 | – | 0.8 | 54.5 | – | 248–252 |
| | | Neat | 140 | 3 | 61.4 | 22.9 | 0.5 | – | 74.2 | 258–262 |
| j | 4-OH $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 48.2 | – | 12 | – | 38.1 | – |
| | | Water | 100 | 1.0 | 44.5 | – | 0.8 | 41.1 | – | 202–205 |
| | | Neat | 140 | 3 | 65.2 | 25.4 | 0.5 | – | 66.2 | 245–250 |
| k | 3-Cl $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 51.2 | – | 12 | – | 45.9 | – |
| | | Water | 100 | 0.8 | 74.2 | – | 0.8 | 50.1 | – | 185–187 |
| | | Neat | 140 | 3 | 68.5 | 31.1 | 0.5 | – | 84.6 | 190–192 |
| l | 2,4-$Cl_2$ $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 52.2 | – | 12 | – | 42.2 | – |
| | | Water | 100 | 0.8 | 71.3 | – | 1.0 | 51.2 | – | 203–205 |
| | | Neat | 140 | 3 | 63.5 | 27.2 | 0.5 | – | 82.7 | 248–250 |
| m | 3-OH $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 43. 8 | – | 12 | – | 38.2 | – |
| | | Water | 100 | 0.8 | 69.9 | – | 1.0 | 48.2 | – | – |
| | | Neat | 140 | 3 | 58.9 | 28.0 | 0.5 | – | 70.5 | 215–218 |
| n | 4-$CH_3$ $C_6H_4$ | Acetonitrile | Reflux | 6.0 | 56.8 | – | 12 | – | 41.4 | – |
| | | Water | 100 | 0.8 | 61.2 | – | 0.8 | 44.1 | – | 128–130 |
| | | Neat | 140 | 3 | 66.4 | 27.1 | 0.5 | – | 82.8 | 222–225 |

ethanol to give pure **3a–n** in excellent yields. In aqueous media, the catalyst was filtered in hot condition and the filtrate was cooled to RT, the precipitate formed was filtered, dried under vacuum to give **4a** as solid precipitate.

From these results, it is clear that, $HClO_4$–$SiO_2$ catalyst limits to the synthesis of **4a** with out formation of any cyclized product. Where as with PPA–$SiO_2$ the reaction proceeds completely to give cyclized product. The catalyst can be recovered, regenerated and reused without loss of its activity.

In conclusion, we have reported herein PPA adsorbed on silica gel (PPA–$SiO_2$) catalyzed highly efficient, one-pot Knoevenagel condensation Michael addition and cyclodehydration synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives (**3a–n)** by the condensation of an aromatic aldehydes and dimedone under solvent free conditions in excellent yields. When $HClO_4$–$SiO_2$ catalyst used the reaction is limited to give only 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) in very good yields with out under-

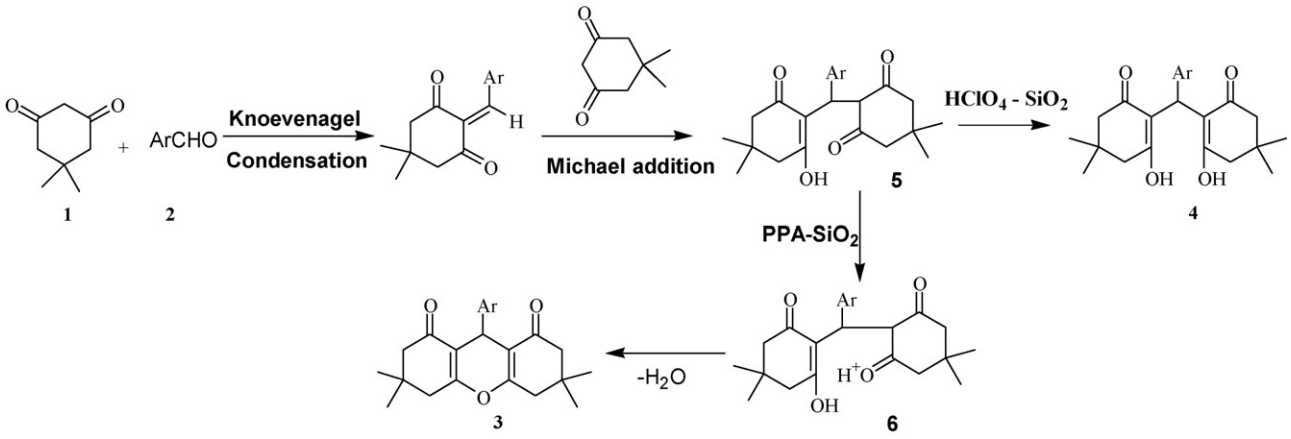



Fig. 1.

going cyclodehydration. The remarkable catalytic activity of $HClO_4$–$SiO_2$, PPA–$SiO_2$ exhibited is convincingly superior to the recently reported other catalytic methods with respect reaction time, amount of catalyst and the pure products were obtained by simple crystallization. Easy work up; inexpensive, easy preparation of the catalyst make the procedure an attractive alternative to the existing methods for the synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives **3a**–**n**.

## 2. Experimental

### 2.1. General

Perchloric acid ($HClO_4$) aqueous solution (70%) was purchased from Loba Chemie, India and silicagel (230–400 mesh) from spectrochem India Pvt. Ltd. India. All the commercial reagents and solvents used without further purification unless otherwise stated. Melting points were recorded on Buchi 535 melting point apparatus and are uncorrected. All the reactions were monitored by thin layer chromatography performed on precoated silica gel $60F_{254}$ plates (Merck). Compounds were visualized with UV light at 254 and 365 nm, iodine and heating plates after dipping in 2% phosphomolybdic acid in 15% aq. $H_2SO_4$ solution. IR spectra were recorded on Perkin-Elmer 683 or 1310 FT-IR spectrometer with KBr pellets. NMR spectra were recorded on Varian Unity-400 MHz and BRUKER AMX 300 MHz spectrometers using tetra methyl silane as an internal standard. $^{13}C$ NMR was recorded on Varian Unity 100 MHz using $CDCl_3$ as internal standard. Mass spectra were recorded on a VG Micromass 7070H and Finnigan Mat 1020B mass spectrometers operating at 70 eV.

#### 2.1.1. Preparation of $HClO_4/SiO_2$ catalyst

A 70% aqueous perchloric acid (1.8 g, 12.5 mmol) was added to a suspension of $SiO_2$ (230–400 mesh, 23.7 g) in ether (70 ml). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to give $HClO_4$–$SiO_2$ (0.5 mmol/g) as free flowing powder (50 mg = 0.025 mmol of $HClO_4$).

#### 2.1.2. Preparation of PPA/$SiO_2$ catalyst

PPA (2.1 g) was charged in the round-bottom flask, and $CHCl_3$ (100 mL) was added. After the mixture was stirred at 50 °C for 1 h, $SiO_2$ [(100–200 mesh), 4.91 g] was added to the solution, and the mixture was stirred for another 1 h. The $CHCl_3$ was removed with rotary evaporator and the resulting solid was dried in vacuum at r.t. for 3 h.

Used PPA/$SiO_2$ was regenerated as follows: PPA/$SiO_2$ was recovered by filtration from the reaction mixture, and then it was put in the 50 mL round-bottom flask and dried in vacuum at 100 °C for 2 h.

#### 2.1.3. General experimental procedure for the preparation of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one)

A mixture of dimedone (2 mmol), aldehyde (1 mmol) in water (10 ml) catalyst PPA–$SiO_2$ or $HClO_4$–$SiO_2$ (10 mol%) was added. The mixture was heated to reflux and the reaction was monitored by TLC. After completion, The catalyst was filtered under hot condition, the filtrate was cooled to RT, the solid separated filtered and dried under vacuum to obtain 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4** as crystalline solid. The products were fully characterized by IR, $^1H$ NMR, $^{13}C$ NMR and mass spectroscopy and also by comparison of the spectral data with that reported.

#### 2.1.4. General experimental procedure for the preparation of 9-aryl-1,8-dioxooctahydroxanthene

A mixture of dimedone (2 mmol), aldehyde (1 mmol) and catalyst PPA/$SiO_2$ (10 mol%) was heated at 140 °C. After completion (monitored by TLC) the reaction mixture was cooled to RT, extracted with EtOAc (3× 15 ml), filtered the catalyst and the filtrate was concentrated to obtain crude product. The residue was crystallized by ethanol to obtain pure 9-aryl-1,8-dioxooctahydroxanthene **3** as crystalline solid.

All the products obtained were fully characterized by spectroscopic methods such as IR, $^1H$ NMR, $^{13}C$ NMR and mass spectroscopy and also by comparison of the spectral data with that reported.

The representative spectral ($^1$H NMR) data of 9-aryl-1, 8-dioxooctahydroxanthene derivatives (**3a–n)** and 2,2′-aryl-methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **4a** and **4k** are given below.

Compound **3a**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 0.99 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.14–2.23 (q, $J$ = 15.86 Hz, 4H, 2× $CH_2$); 2.43 (s, 4H, 2× $CH_2$); 4.68 (s, 1H, CH); 7.04–7.25 (m, 5H, Ar).

Compound **3b**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 0.99 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.10–2.23 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.42 (s, 4H, 2× $CH_2$); 4.63 (s, 1H, CH); 7.14–7.20 (m, 4H, Ar).

Compound **3c**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.01 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.11–2.22 (q, $J$ = 16.05 Hz, 4H, 2× $CH_2$); 2.42 (s, 4H, 2× $CH_2$); 2.93 (s, 6H, $NMe_2$); 4.61 (s, 1H, CH); 7.13–7.25 (m, 4H, Ar).

Compound **3d**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.04 (s, 6H, $CMe_2$); 1.12 (s, 6H, $CMe_2$); 2.20 (s, 4H, 2× $CH_2$); 2.43 (s, 4H, 2× $CH_2$); 3.75 (s, 3H, OMe); 3.75 (s, 6H, $OMe_2$); 4.63 (s, 1H, CH); 6.44 (s, 2H, Ar).

Compound **3e**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.01 (s, 6H, $CMe_2$); 1.12 (s, 6H, $CMe_2$); 2.09–2.26 (q, $J$ = 16.52 Hz, 4H, 2× $CH_2$); 2.43 (s, 4H, 2× $CH_2$); 3.37 (s, 3H, OMe); 4.63 (s, 1H, CH); 6.69 (d, $J$ = 8.62 Hz, 2H, Ar) 7.13 (d, $J$ = 8.62 Hz, 2H, Ar).

Compound **3f**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 0.99 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.10–2.23 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.42 (s, 4H, 2× $CH_2$); 4.63 (s, 1H, CH); 7.12 (d, $J$ = 8.30 Hz, 2H, Ar) 7.29 (d, $J$ = 8.30 Hz, 2H, Ar).

Compound **3g**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.01 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.12–2.23 (q, $J$ = 15.86 Hz, 4H, 2× $CH_2$); 2.43 (s, 4H, 2× $CH_2$); 3.37 (s, 3H, OMe); 4.66 (s, 1H, CH); 6.58–7.10 (m, 4H, Ar).

Compound **3h**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 0.99 (s, 6H, $CMe_2$); 1.13 (s, 6H, $CMe_2$); 2.10–2.24 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.46 (s, 4H, 2× $CH_2$); 4.75 (s, 1H, CH); 7.43 (d, $J$ = 8.30 Hz, 2H, Ar) 8.09 (d, $J$ = 8.30 Hz, 2H, Ar).

Compound **3i**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.00 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.05–2.25 (q, $J$ = 16.23 Hz, 4H, 2× $CH_2$); 2.47 (s, 4H, 2× $CH_2$); 5.48 (s, 1H, CH); 7.27–7.78 (m, 4H, Ar).

Compound **3j**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.00 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.12–2.24 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.42 (s, 4H, 2× $CH_2$); 4.60 (s, 1H, CH); 6.53 (d, $J$ = 8.30 Hz, 2H, Ar) 7.05 (d, $J$ = 8.30 Hz, 2H, Ar).

Compound **3k**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.01 (s, 6H, $CMe_2$); 1.12 (s, 6H, $CMe_2$); 2.12–2.24 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.45 (s, 4H, 2× $CH_2$); 4.61 (s, 1H, CH); 7.05–7.25 (m, 4H, Ar).

Compound **3l**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.03 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.10–2.22 (q, $J$ = 16.61 Hz, 4H, 2× $CH_2$); 2.40 (s, 4H, 2× $CH_2$); 4.85 (s, 1H, CH); 7.13–7.43 (m, 3H, Ar).

Compound **3m**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.02 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.20 (s, 4H, 2× $CH_2$); 2.43 (s, 4H, 2× $CH_2$); 4.67 (s, 1H, CH); 6.52–7.02 (m, 4H, Ar).

Compound **3n**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.00 (s, 6H, $CMe_2$); 1.11 (s, 6H, $CMe_2$); 2.10–2.22 (q, $J$ = 16.24 Hz, 4H, 2× $CH_2$); 2.42 (s, 4H, 2× $CH_2$); 4.62 (s, 1H, CH); 6.69 (d, $J$ = 8.68 Hz, 2H, Ar) 7.13 (d, $J$ = 8.68 Hz, 2H, Ar).

Compound **4a**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.11 (s, 6H, $CMe_2$); 1.25 (s, 6H, $CMe_2$); 2.25–2.47 (m, 8H 4× $CH_2$); 5.46(s, 1H, CH); 7.01–7.24 (m, 5H, Ar); 11.78 (s, 1H).

Compound **4k**: $^1$H NMR (300 MHz, CDCl3), $\delta$ 1.11 (s, 6H, $CMe_2$); 1.25 (s, 6H, $CMe_2$); 2.27–2.46 (m, 8H 4× $CH_2$); 5.41 (s, 1H, CH); 6.92–7.24 (m, 4H, Ar); 11.79 (s, 1H).

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