

## Supplementary Information

### **Porous silica nanoparticle with mesoscopic void space for the domino intermolecular aerobic oxidative synthesis of novel $\beta,\beta'$ -diketoenamines**

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## Spectroscopic characterization of 4a-4l

### **2-(amino(4-nitrophenyl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4a):**

Brown solid; Yield: 327 mg, 88 %; m.p. 192-194 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.49; H, 5.59; N, 9.52 %. Found: C, 62.78; H, 5.68; N, 9.52 %; R<sub>f</sub> (50% MeOH/50% EtOAc) 0.31; IR (KBr) cm<sup>-1</sup>: 3267, 2960, 2869, 1644, 1581, 1488, 1442, 1358, 1338; δ<sub>H</sub> ppm (300 MHz; DMSO-D<sub>6</sub>; TMS) 0.95 (6H, s, 2xCH<sub>3</sub>), 2.26 (4H, br s, 2xCH<sub>2</sub>), 7.40 (2H, d, *J* = 7.8 Hz, arom.), 8.14 (2H, d, *J* = 8.7 Hz, arom.), 9.25 (1H, br s, -NH), 11.49 (1H, br s, -NH); δ<sub>C</sub> ppm (75 MHz, DMSO-d<sub>6</sub>, TMS) 28.1, 31.1, 52.3, 112.6, 123.1, 128.1, 139.4, 148.3, 166.0, 196.6.

### **2-(amino(4-chlorophenyl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4b):**

White solid; Yield: 243 mg, 88 %; m.p. 218-220 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for C<sub>15</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 64.87; H, 5.81; N, 5.04 %. Found: C, 64.87; H, 5.90; N, 5.23 %; R<sub>f</sub> (50% MeOH/50% EtOAc) 0.41; IR (KBr) cm<sup>-1</sup>: 3269, 2952, 2870, 1649, 1582, 1498, 1445, 1334, 1324; δ<sub>H</sub> ppm (300 MHz; DMSO-D<sub>6</sub>; TMS) 0.93 (6H, s, 2xCH<sub>3</sub>), 2.21 (4H, br s, 2xCH<sub>2</sub>), 7.10 (2H, d, *J* = 8.1 Hz, arom.), 7.21 (2H, d, *J* = 8.4 Hz, arom.), 9.08 (1H, br s, -NH), 10.55 (1H, br s, -NH); δ<sub>C</sub> ppm (75 MHz, DMSO-d<sub>6</sub>, TMS) 28.1, 31.1, 52.3, 106.9, 127.9, 129.9, 130.1, 132.1, 165.1, 195.6.

### **2-(amino(4-methoxyphenyl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4c):**

White solid; Yield: 210 mg, 77 %; m.p. 176-178 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>: C, 70.31; H, 7.01; N, 5.12 %. Found: C, 70.12; H, 7.10; N, 5.22 %; R<sub>f</sub> (50% MeOH/50% EtOAc) 0.45; IR (KBr) cm<sup>-1</sup>: 3281, 29545, 2882, 1645, 1577, 1485, 1441, 1365, 1342, 1326; δ<sub>H</sub> ppm (300 MHz; DMSO-D<sub>6</sub>; TMS) 0.93 (6H, s, 2xCH<sub>3</sub>), 2.21 (4H, br s, 2xCH<sub>2</sub>), 3.75 (3H, s, -OCH<sub>3</sub>), 6.91 (2H, d, *J* = 9.0 Hz, arom.), 7.39 (2H, d, *J* = 8.7 Hz, arom.), 9.25 (1H, br s, -NH), 10.95 (1H, br s, -NH); δ<sub>C</sub> ppm (75 MHz, DMSO-d<sub>6</sub>, TMS) 27.7, 31.3, 52.3, 55.3, 111.9, 113.9, 127.1, 127.3, 159.6, 166.6, 193.9.

### **2-(amino(4-bromophenyl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4d):**

White solid; Yield: 269 mg, 84 %; m.p. 188-190 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for C<sub>15</sub>H<sub>16</sub>BrNO<sub>2</sub>: C, 55.92; H, 5.01; Br, N, 4.35 %. Found: C, 55.92; H, 5.01; N, 4.35 %; R<sub>f</sub> (50% MeOH/50% EtOAc) 0.41; IR (KBr) cm<sup>-1</sup>: 3271, 2949, 2876, 1641, 1481, 1448, 1367, 1338; δ<sub>H</sub> ppm (300 MHz; DMSO-D<sub>6</sub>; TMS) 0.93 (6H, s, 2xCH<sub>3</sub>), 2.21 (4H, br s, 2xCH<sub>2</sub>), 7.00 (2H, d, *J* = 8.1 Hz, arom.), 7.12 (2H, d, *J* = 8.4 Hz, arom.), 9.05 (1H,

br s, -NH), 10.51 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $d_6$ , TMS) 28.0, 31.1, 52.0, 110.6, 123.9, 126.9, 128.9, 129.1, 132.0, 165.0, 195.6, 196.1.

**2-(amino(pyridin-4-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4e):**

Yellow solid; Yield: 200 mg, 82 %; m.p. 226-228 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 68.83; H, 6.60; N, 11.47 %. Found: C, 68.63; H, 6.68; N, 11.27 %;  $R_f$  (50% MeOH/50% EtOAc) 0.22; IR (KBr)  $\text{cm}^{-1}$ : 3271, 2955, 2874, 1645, 1587, 1498, 1448, 1368, 1338, 1324;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $D_6$ ; TMS) 0.95 (6H, s,  $2\times\text{CH}_3$ ), 2.26 (4H, br s,  $2\times\text{CH}_2$ ), 7.18 (2H, d,  $J = 5.7$  Hz, arom.), 8.56 (2H, d,  $J = 5.7$  Hz, arom.), 9.25 (1H, br s, -NH), 11.49 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $d_6$ , TMS) 28.1, 30.0, 52.1, 106.1, 121.6, 121.7, 145.7, 149.1, 149.4, 168.9, 196.5.

**2-(amino(4-methoxyphenyl)methylene)-2H-indene-1,3-dione (4f):**

Yellow solid; Yield: 217 mg, 78 %; m.p. 142-144 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{NO}_3$ : C, 73.11; H, 4.69; N, 5.02 %. Found: C, 73.40; H, 4.60; N, 5.20 %;  $R_f$  (50% MeOH/50% EtOAc) 0.55; IR (KBr)  $\text{cm}^{-1}$ : 3271, 2955, 1665, 1597, 1500, 1424, 1350, 1326, 1276, 1241;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $D_6$ ; TMS) 3.83 (3H, br s,  $-\text{OCH}_3$ ), 6.92-6.94 (2H, m, arom.), 7.71-7.90 (4H, m, arom.), 8.47-8.44 (2H, m, arom.), 9.25 (1H, br s, -NH), 11.45 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $d_6$ , TMS) 55.8, 110.1, 122.8, 122.9, 125.9, 126.3, 135.5, 135.7, 137.0, 139.3, 141.8, 145.7, 163.8, 188.9, 189.8.

**2-(amino(pyridin-4-yl)methylene)cyclohexane-1,3-dione (4g):**

Yellow solid; Yield: 200 mg, 80 %; m.p. 224-226 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 66.65; H, 5.59; N, 12.96 %. Found: C, 66.50; H, 5.69; N, 13.10 %;  $R_f$  (50% MeOH/50% EtOAc) 0.18; IR (KBr)  $\text{cm}^{-1}$ : 3270, 2954, 2875, 1651, 1590, 1495, 1448, 1368, 1324;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $D_6$ ; TMS) 1.74-1.84 (2H, m,  $\text{CH}_2$ ), 2.19 (4H, t,  $J = 6.6$  Hz,  $2\times\text{CH}_2$ ), 7.18 (2H, d,  $J = 5.7$  Hz, arom.), 8.55 (2H, d,  $J = 4.2$  Hz, arom.), 9.25 (1H, br s, -NH), 11.45 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $d_6$ , TMS) 17.19, 39.1, 105.1, 121.1, 121.2, 145.5, 149.0, 149.2, 168.0, 198.5.

**2-(amino(4-nitrophenyl)methylene)cyclohexane-1,3-dione (4h):**

Yellow solid; Yield: 200 mg, 88 %; m.p. 190-192 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 60.00; H, 4.65; N, 10.76 %. Found: C, 60.29; H, 4.60; N, 10.95 %;  $R_f$  (50% MeOH/50% EtOAc) 0.25; IR (KBr)  $\text{cm}^{-1}$ : 3277, 2961, 1647, 1590, 1490, 1424, 1350, 1332, 1211;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $D_6$ ; TMS)

1.73-1.80 (2H, m,  $\text{CH}_2$ ), 2.18 (4H, t,  $J = 4.2$  Hz,  $2\times\text{CH}_2$ ), 7.30 (2H, d,  $J = 8.4$  Hz, arom.), 8.22 (2H, d,  $J = 8.4$  Hz, arom.), 9.25 (1H, br s, -NH), 11.46 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $\text{d}_6$ , TMS) 18.19, 39.7, 112.6, 123.1, 128.1, 139.4, 148.3, 166.0, 196.6.

**3-(amino(pyridin-4-yl)methylene)pentane-2,4-dione(4i):**

Brown liquid; Yield: 265 mg, 71 %; Anal. Calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 64.69; H, 5.92; N, 13.72 %. Found: C, 64.90; H, 6.01; N, 13.71 %;  $R_{\text{f}}$ (50% MeOH/50% EtOAc) 0.31; IR (Neat)  $\text{cm}^{-1}$ : 3269, 2955, 2874, 1660, 1587, 1499, 1440, 1368, 1338, 1324;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $\text{D}_6$ ; TMS) 2.56 (6H, s,  $2\times\text{CH}_3$ ), 7.18 (2H, d,  $J = 6.3$  Hz, arom.), 8.56 (2H, d,  $J = 5.7$  Hz, arom.), 9.26 (1H, br s, -NH), 11.57 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $\text{d}_6$ , TMS) 28.1, 105.1, 121.7, 121.9, 145.9, 149.3, 149.5, 168.0, 194.5.

**2-((cyclohexylamino)(pyridin-4-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4j):**

Yellow solid; Yield: 200 mg, 89 %; m.p. 220-222 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ : C, 73.59; H, 8.03; N, 8.58 %. Found: C, 73.59; H, 8.13; N, 8.77 %;  $R_{\text{f}}$ (50% MeOH/50% EtOAc) 0.31; IR (KBr)  $\text{cm}^{-1}$ : 3271, 2955, 2874, 1645, 1587, 1498, 1448, 1368, 1338, 1324;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $\text{D}_6$ ; TMS) 0.65-0.80 (1H, m), 0.96-1.09 (8H, m), 1.43-1.65 (5H, m), 1.80-1.84 (2H, m), 2.21 (4H, br s), 3.89-3.98 (1H, m), 7.19 (2H, d,  $J = 4.8$  Hz, arom.), 8.54 (2H, d,  $J = 4.5$  Hz, arom.), 11.01 (1H, br s, -NH);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO- $\text{d}_6$ , TMS) 24.9, 26.1, 28.1, 30.0, 33.5, 52.0, 58.7, 105.2, 121.1, 121.8, 145.3, 149.1, 149.9, 168.6, 195.7.

**2-((3,4-dimethylphenylamino)(pyridin-4-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4k):**

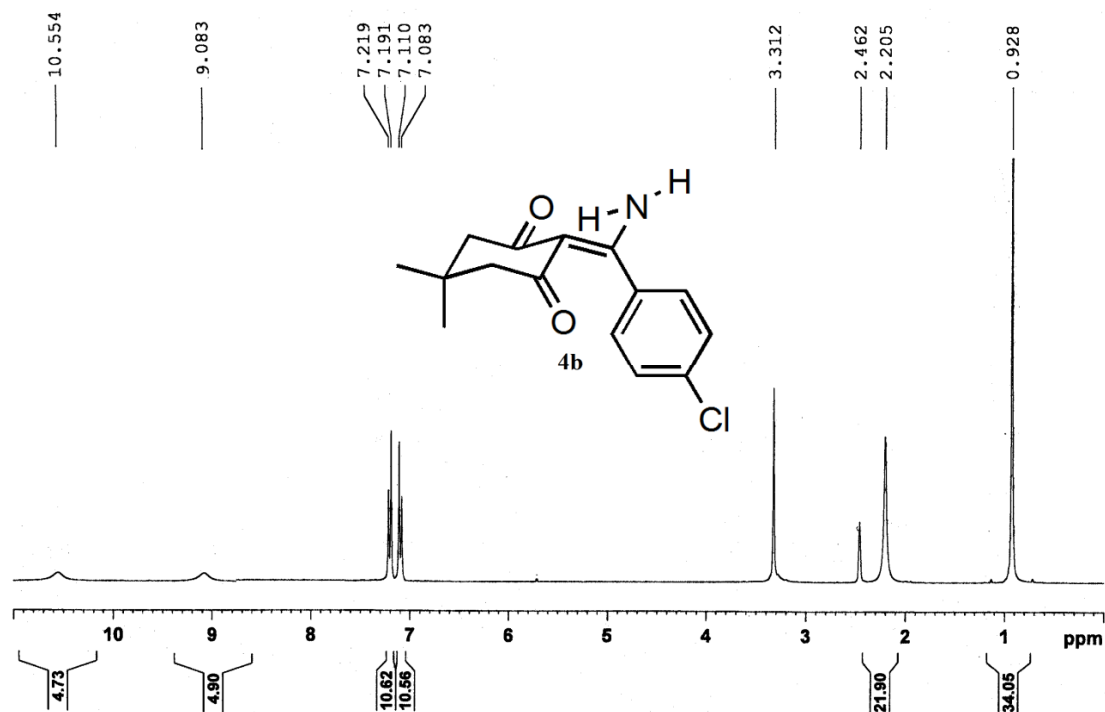
Yellow solid; Yield: 200 mg, 51 %; m.p. 170-172 °C (recrystallized from EtOAc/MeOH); Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ : C, 75.83; H, 6.94; N, 8.04 %. Found: C, 75.81; H, 7.00; N, 8.23 %;  $R_{\text{f}}$ (50% MeOH/50% EtOAc) 0.41; IR (KBr)  $\text{cm}^{-1}$ : 3271, 2955, 1645, 1597, 1500, 1424, 1350, 1326, 1276, 1241;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $\text{D}_6$ ; TMS) 0.96 (6H, s,  $2\times\text{CH}_3$ ), 2.14 (3H, s,  $\text{CH}_3$ ), 2.26 (7H, br s,  $2\times\text{CH}_2$ ,  $\text{CH}_3$ ), 6.79-6.82 (2H, m, arom.), 7.5 (1H, d,  $J = 7.8$  Hz, arom.), 7.18 (2H, d,  $J = 6.0$  Hz, arom.), 8.56 (2H, d,  $J = 5.7$  Hz, arom.), 11.09 (1H, br s, -NH).

**2-((dimethylamino)(pyridin-4-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (4l):**

Brown liquid; Yield: 122.4 mg, 41 %; Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 70.56; H, 7.40; N, 10.29 %. Found: C, 70.80; H, 7.41; N, 10.38 %;  $R_{\text{f}}$ (50% MeOH/50% EtOAc) 0.28; IR (Neat)  $\text{cm}^{-1}$ : 2940, 2873, 1656, 1586, 1498, 1442, 1365, 1311, 1322;  $\delta_{\text{H}}$  ppm (300 MHz; DMSO- $\text{D}_6$ ; TMS) 0.95 (6H, s,  $2\times\text{CH}_3$ ), 2.21 (4H, br s,  $2\times\text{CH}_2$ ), 3.05 (3H, s, - $\text{NCH}_3$ ),

3.32 (3H, s, -NCH<sub>3</sub>), 7.19 (2H, d, *J* = 4.8 Hz, arom.), 8.54 (2H, d, *J* = 4.7 Hz, arom.);  $\delta_{\text{C}}$  ppm (75 MHz, DMSO-d<sub>6</sub>, TMS) 28.1, 30.0, 39.2, 39.9, 52.0, 105.1, 121.5, 121.7, 145.5, 149.0, 149.1, 167.5, 195.5.

Copy of  $^1\text{H}$  NMR of 4b



Copy of  $^{13}\text{C}$  NMR of 4b

