

## Supporting Information

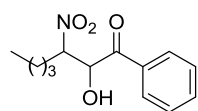
### General Remarks

<sup>1</sup>H-NMR were recorded at 400 MHz on a VarianMercury Plus 400. <sup>13</sup>C-NMR were recorded at 100 MHz. IR spectra were recorded with a PerkinElmer Paragon 500 FT-IR. Microwave irradiations were performed by Biotage® Initiator<sup>+</sup>. Mass spectra were performed on a GC/MS system by means of the EI technique (70 eV). Microanalyses were performed with a CHNS-O analyzer Model EA 1108 from Fisons Instruments. Nitroalkanes **1a**, **1b**, **1h**, **1j** and **1k** are commercially available, while **1c-g** and **1i** were synthesized by reported literature.<sup>1</sup>  $\alpha$ -Oxoaldehydes **2** were synthesized by the oxidation of the corresponding acetophenones.<sup>2</sup>

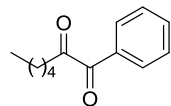
- (a) D. P. Curran and T. A. Heffner, *J. Org. Chem.* 1990, **55**, 4585; (b) R. Ballini, L. Barboni and A. Palmieri, *Green Chem.* 2008, **10**, 1004; c) R. Ballini, M. Petrini and V. Polzonetti, *Synthesis* 1992, 355.
- S. S. Bhella, M. Elango and M. P. S. Ishar, *Tetrahedron* 2009, **65**, 240.

### General Procedure for the preparation of compounds **5**.

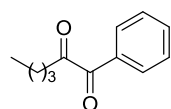
A solution of nitroalkane **1** (0.65 mmol) and aldehyde **2** (0.5 mmol) in 2-MeTHF (11 mL) was treated with Amberlyst A21 (0.250 g) and stirred at room temperature for the appropriate time (see Time<sub>1</sub> in Table 3). At that time, the solution was irradiated by Biotage® Initiator<sup>+</sup> at 110°C for 1 hour, and then, the Amberlyst A21 was filtered off washing with fresh 2-MeTHF (10 mL). After removing the solvent at reduced pressure, the crude product **5** was purified by flash chromatography column (hexanes:EtOAc = 95:5).



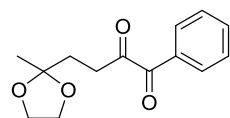
Compound **3aa**. Yield 76% (2:1 distereomeric mixture). Colorless waxy solid. IR (cm<sup>-1</sup>, neat): 997, 1363, 1544, 1597, 1678, 3461. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz)  $\delta$ : 0.77 (t, 1H,  $J = 7.3$  Hz), 0.91 (t, 2H,  $J = 7.3$  Hz), 1.02-1.47 (m, 4H), 1.84-1.98 (m, 1H), 2.11-2.29 (m, 1H), 3.93 (d, 0.66H,  $J = 7.3$  Hz), 3.98 (d, 0.34H,  $J = 6.4$  Hz), 4.70-4.84 (m, 1H), 5.22-5.28 (m, 0.66H), 5.67-5.72 (m, 0.34H), 7.46-7.74 (m, 3H), 7.90 (dd, 1.32H,  $J = 1.3, 8.1$  Hz), 8.02 (dd, 0.68,  $J = 1.3, 8.1$  Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz)  $\delta$ : 13.8, 14.0, 22.3, 22.4, 25.7, 28.0, 28.2, 29.8, 73.3, 74.8, 89.2, 89.8, 126.4, 128.7, 129.0, 129.4, 129.7, 134.0, 134.7, 135.3, 197.2, 197.9. Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>4</sub> (251.28): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.18; H, 6.79; N, 5.53.



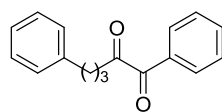
Compound **5aa**. Yield 75%. Yellow oil. IR (cm<sup>-1</sup>, neat): 689, 1597, 1672, 1710. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz)  $\delta$ : 0.91 (t, 3H,  $J = 7.3$  Hz), 1.21-1.47 (m, 4H), 1.59-1.82 (m, 2H), 2.88 (t, 2H,  $J = 7.3$  Hz), 7.43-7.56 (m, 2H), 7.58-7.70 (m, 1H), 7.94-8.02 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz)  $\delta$ : 14.1, 22.6, 22.7, 31.5, 38.9, 129.0, 130.3, 132.2, 134.7, 192.8, 203.7. GC-MS (70 eV):  $m/z$ : 204 ([M<sup>+</sup>], 2), 106 (8), 105 (100), 99 (7), 77 (32), 71 (7), 51 (10), 43 (11), 29 (3). Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> (204.27): C, 76.44; H, 7.90. Found: C, 76.51; H, 7.93.



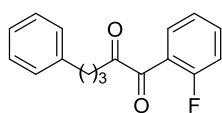
Compound **5ba**. Yield 72%. Yellow oil. IR (cm<sup>-1</sup>, neat): 688, 1671, 1708. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz)  $\delta$ : 0.93 (t, 3H,  $J = 7.3$  Hz), 1.34-1.45 (m, 2H), 1.63-1.72 (m, 2H), 2.87 (t, 2H,  $J = 7.3$  Hz), 7.45-7.52 (m, 2H), 7.60-7.66 (m, 1H), 7.93-7.99 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz)  $\delta$ : 14.1, 22.5, 25.1, 38.7, 129.1, 130.4, 132.2, 134.8, 192.8, 203.8. GC-MS (70 eV):  $m/z$ : 190 ([M<sup>+</sup>], 2), 106 (9), 105 (100), 85 (7), 77 (38), 57 (13), 51 (14), 41 (8), 29 (7). Anal. Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> (190.24): C, 75.76; H, 7.42. Found: C, 75.80; H, 7.45.



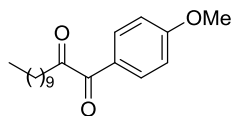
Compound **5ca**. Yield 70%. Yellow oil. IR (cm<sup>-1</sup>, neat): 699, 1044, 1256, 1597, 1671, 1710. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz)  $\delta$ : 1.32 (s, 3H), 2.17 (t, 2H,  $J = 6.8$  Hz), 2.92 (t, 2H,  $J = 6.8$  Hz), 3.75-3.94 (m, 4H), 7.47 (t, 2H,  $J = 7.7$  Hz), 7.61 (t, 1H,  $J = 7.7$  Hz), 8.01 (d, 2H,  $J = 7.7$  Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz)  $\delta$ : 24.2, 33.3, 33.5, 64.9, 109.3, 128.9, 130.6, 132.4, 134.5, 191.7, 202.2. GC-MS (70 eV):  $m/z$ : 233 (9), 143 (100), 105 (68), 99 (66), 87 (28), 77 (39), 71 (9), 51 (10), 43 (27). Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub> (248.28): C, 67.73; H, 6.50. Found: C, 67.79; H, 6.55.



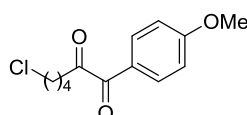
Compound **5da**. Yield 76%. Yellow oil. IR (cm<sup>-1</sup>, neat): 697, 731, 908, 1596, 1671, 1711. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz)  $\delta$ : 1.97-2.17 (m, 2H), 2.74 (t, 2H,  $J = 7.6$  Hz), 2.93 (t, 2H,  $J = 7.3$  Hz), 7.16-7.38 (m, 5H), 7.44-7.57 (m, 2H), 7.60-7.71 (m, 1H), 7.94-8.02 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz)  $\delta$ : 24.7, 35.3, 38.3, 126.3, 128.7, 129.1, 130.4, 132.1, 134.8, 141.4, 192.5, 203.2. GC-MS (70 eV):  $m/z$ : 252 ([M<sup>+</sup>], 14), 147 (77), 129 (10), 105 (100), 91 (58), 77 (49), 65 (9), 51 (12). Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> (252.31): C, 80.93; H, 6.39. Found: C, 80.97; H, 6.41.



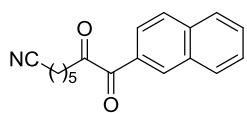
Compound **5db**. Yield 68%. Yellow oil. IR (cm<sup>-1</sup>, neat): 699, 751, 1609, 1675, 1716. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 2.01-2.18 (m, 2H), 2.76 (t, 2H, *J* = 7.6 Hz), 2.92 (t, 2H, *J* = 7.3 Hz), 7.09-7.39 (m, 7H), 7.56-7.71 (m, 1H), 7.81-7.92 (m, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 24.5, 35.2, 37.0, 116.4, 116.8, 125.0, 125.1, 126.3, 128.6, 128.7, 131.1, 131.2, 136.3, 136.5, 141.5, 160.1, 165.2, 191.8, 201.8. GC-MS (70 eV): *m/z*: 270 ([M<sup>+</sup>], 11), 148 (12), 147 (100), 129 (18), 123 (78), 95 (22), 91(87), 75 (10), 65 (10). Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>FO<sub>2</sub> (270.30): C, 75.54; H, 5.59. Found: C, 75.50; H, 5.57.



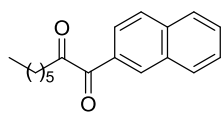
Compound **5ec**. Yield 62%. Yellow oil. IR (cm<sup>-1</sup>, neat): 1254, 1598, 1663, 1775. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 0.86 (t, 3H, *J* = 6.8 Hz), 1.18-1.41 (m, 14H), 1.61-1.71 (m, 2H), 2.84 (t, 2H, *J* = 7.3 Hz), 3.87 (s, 3H), 6.94 (d, 2H, *J* = 8.7 Hz), 7.95 (d, 2H, *J* = 8.7 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 14.4, 22.9, 23.1, 29.4, 29.5, 29.6, 29.7, 29.8, 32.1, 39.1, 55.8, 114.4, 125.1, 132.9, 165.0, 191.5, 204.4. GC-MS (70 eV): *m/z*: 304([M<sup>+</sup>], 1), 136 (25), 135 (100), 107 (11), 92 (12), 77 (19), 43 (7), 41 (7). Anal. Calcd. for C<sub>19</sub>H<sub>28</sub>O<sub>3</sub> (304.43): C, 74.96; H, 9.27. Found: C, 75.01; H, 9.32.



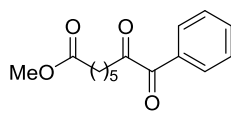
Compound **5fc**. Yield 52%. Yellow oil. IR (cm<sup>-1</sup>, neat): 1257, 1595, 1660, 1709. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 1.82-1.87 (m, 4H), 2.87-2.93 (m, 2H), 3.54-3.58 (m, 2H), 3.88 (s, 3H), 6.96 (d, 2H, *J* = 8.7 Hz), 7.97 (d, 2H, *J* = 8.7 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 20.5, 32.0, 38.0, 44.7, 55.9, 114.5, 125.0, 133.0, 165.1, 190.9, 203.3. GC-MS (70 eV): *m/z*: 254 ([M<sup>+</sup>], 1), 136 (24), 135 (100), 107 (18), 92 (23), 77 (31), 64 (10), 55 (9). Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>ClO<sub>3</sub> (254.71): C, 61.30; H, 5.94. Found: C, 61.35; H, 5.97.



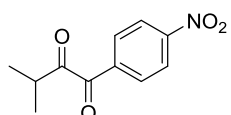
Compound **5gd**. Yield 74%. Yellow oil. IR (cm<sup>-1</sup>, neat): 730, 1625, 1664, 1710, 2250. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 1.52-1.61 (m, 2H), 1.68-1.83 (m, 4H), 2.38 (t, 2H, *J* = 6.8 Hz), 2.97 (t, 2H, *J* = 7.3 Hz), 7.54-7.59 (m, 1H), 7.62-7.67 (m, 1H), 7.85-8.03 (m, 4H), 8.52 (s, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 17.3, 22.3, 25.4, 28.4, 38.6, 119.8, 124.4, 127.4, 128.1, 129.3, 129.8, 130.3, 132.5, 133.9, 136.5, 192.3, 203.1. GC-MS (70 eV): *m/z*: 279([M<sup>+</sup>], 7), 156 (13), 155 (100), 127 (58), 101 (6), 77 (7), 55 (6), 41 (5). Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub> (279.34): C, 77.40; N, 5.01; H, 6.13. Found: C, 77.46; N, 4.998; H, 6.16.



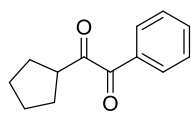
Compound **5hd**. Yield 71%. Yellow oil. IR (cm<sup>-1</sup>, neat): 732, 1626, 1665, 1710. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 0.89 (t, 3H, *J* = 6.8 Hz), 1.25-1.47 (m, 6H), 1.68-1.80 (m, 2H), 2.94 (t, 2H, *J* = 7.3 Hz), 7.54-7.60 (m, 1H), 7.62-7.66 (m, 1H), 7.85-8.05 (m, 4H), 8.51 (s, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 14.3, 22.7, 23.1, 29.1, 31.8, 39.2, 124.4, 127.3, 128.1, 129.2, 129.5, 129.6, 130.2, 132.6, 133.8, 136.4, 192.8, 204.0. GC-MS (70 eV): *m/z*: 268([M<sup>+</sup>], 7), 156 (23), 155 (100), 127 (84), 101 (5), 77 (6), 43 (7). Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub> (268.36): C, 80.56; H, 7.51. Found: C, 80.61; H, 7.54.



Compound **5ia**. Yield 70%. Yellow oil. IR (cm<sup>-1</sup>, neat): 693, 1170, 1671, 1709, 1733. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 1.35-1.45 (m, 2H), 1.61-1.76 (4H), 2.32 (t, 2H, *J* = 7.3 Hz), 2.88 (t, 2H, *J* = 7.3 Hz), 3.65 (s, 3H), 7.45-7.52 (m, 2H), 7.60-7.66 (m, 1H), 7.94-7.98 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 22.7, 24.8, 28.8, 34.0, 38.7, 51.8, 129.1, 130.4, 132.1, 134.8, 174.2, 192.6, 203.4. GC-MS (70 eV): *m/z*: 262 ([M<sup>+</sup>], 1), 157 (27), 125 (18), 105 (100), 97 (8), 77 (37), 69 (16), 55 (10), 51 (8), 41 (5). Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> (262.31): C, 68.69; H, 6.92. Found: C, 68.65; H, 6.89.



Compound **5je**. Yield 42%. Yellow solid, m.p. = 217-220°C. IR (cm<sup>-1</sup>, neat): 714, 1278, 1538, 1604, 1684. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 1.20 (s, 3H), 1.21 (s, 3H), 3.36-3.48 (m, 1H), 8.13 (dd, 2H, *J* = 9.0, 0.8 Hz), 8.33 (dd, 2H, *J* = 9.0, 0.8 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 17.1, 36.4, 124.2, 131.3, 137.3, 151.2, 191.3, 205.0. GC-MS (70 eV): *m/z*: 221 ([M<sup>+</sup>], 1), 151 (22), 150 (50), 134 (19), 104 (32), 92 (12), 76 (34), 71 (92), 50 (15), 43 (100), 41 (17). Anal. Calcd. for C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub> (221.21): C, 59.73; N, 6.33; H, 5.01. Found: C, 59.77; N, 6.30; H, 5.03.



Compound **5ka**. Yield 51%. Yellow oil. IR (cm<sup>-1</sup>, neat): 686, 714, 1671, 1705. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ: 1.59-1.75 (m, 4H), 1.84-1.94 (m, 4H), 3.52-3.61 (m, 1H), 7.49 (t, 2H, *J* = 8.1 Hz), 7.60-7.66 (m, 1H), 7.91-7.96 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ: 26.2, 28.2, 47.2, 129.1, 130.2, 132.7, 134.8, 194.1, 205.4. GC-MS (70 eV): *m/z*: 202 ([M<sup>+</sup>], 2), 105 (100), 97 (33), 77 (50), 69 (71), 51 (15), 41 (20). Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> (202.25): C, 77.20; H, 6.98. Found: C, 77.24; H, 7.01.