

Supporting Information

General Experimental Methods

¹H NMR were recorded at 400 MHz. ¹³C NMR were recorded at 100 MHz. GLC analyses were performed on a capillary column of fused silica (0.32 mm×25 m), stationary phase SE54. 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. Amberlyst A21 and 15 and the compounds **2b** and **2c** are commercially available. Ketal-functionalized nitroalkanes **1a-g**¹ and α-oxoaldehyde derivatives **2a**, **2d** and **2e**² were prepared using previously reported procedure.

1. a) T. Miyakoshi, S. Saito and J. Kumanotani, *Chem. Lett.* 1981, 1677; b) G. Rosini, R. Ballini and P. Sorrenti, *Tetrahedron* 1981, **39**, 4127.
2. a) Y. -L. Zhong and T. K. M. Shing, *J. Org. Chem.* 1997, **62**, 2622; b) H. C. G. Ottenheijm, R. M. J. Liskamp, S. P. J. M. Van Nispen, H. A. Boots, M. W. Tjihuis *J. Org. Chem.* 1981, **46**, 3273; c) S. S. Bhella, M. Elango and M. P. S. Ishar, *Tetrahedron* 2009, **65**, 240.

Characterization data of compounds 1a-g:

1a. Clear oil. IR (cm⁻¹, neat): 872, 950, 1058, 1153, 1384, 1556. ¹H-NMR (CDCl₃, 400MHz) δ: 1.34 (s, 3H), 2.44 (t, 2H, *J* = 6.8 Hz), 3.89-4.00 (m, 4H), 4.44 (t, 2H, *J* = 6.8 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 24.3, 36.2, 65.1, 71.1, 108.1. GC-MS (70 eV): *m/z*: 146(11), 99(80), 87(100), 55(24), 43(87). Anal. Calcd. for C₆H₁₁NO₄ (161.16): C, 44.72; H, 6.88; N, 8.69. Found: C, 44.75; H, 6.90; N, 8.63.

1b. Clear oil. IR (cm⁻¹, neat): 871, 952, 1051, 1147, 1379, 1557. ¹H-NMR (CDCl₃, 400MHz) δ: 0.89 (t, 3H, *J* = 7.3 Hz), 1.21-1.42 (m, 6H), 1.54-1.62 (m, 2H), 2.41 (t, 2H, *J* = 6.8 Hz), 3.91-3.97 (m, 4H), 4.43 (t, 2H, *J* = 6.8 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.2, 22.8, 23.7, 32.1, 34.3, 37.7, 65.3, 71.2, 110.0. GC-MS (70 eV): *m/z*: 146(29), 143(38), 99(100), 55(21), 43(17). Anal. Calcd. for C₁₀H₁₉NO₄ (217.26): C, 55.28; H, 8.81; N, 6.45. Found: C, 55.31; H, 8.84; N, 6.42.

1c. Yellow waxy solid. IR (cm⁻¹, nujol): 701, 757, 900, 1040, 1379, 1557, 3031. ¹H-NMR (CDCl₃, 400MHz) δ: 2.63 (t, 2H, *J* = 6.8 Hz), 3.75-3.80 (m, 2H), 3.99-4.05 (m, 2H), 4.51 (t, 2H, *J* = 6.8 Hz), 7.30-7.40 (m, 3H), 7.44-7.48 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 37.4, 64.9, 70.9, 108.4, 125.6, 128.7, 128.8, 141.3. GC-MS (70 eV): *m/z*: 149(100), 105(79), 99(18), 77(45), 51(13). Anal. Calcd. for C₁₁H₁₃NO₄ (223.23): C, 59.19; H, 5.87; N, 6.27. Found: C, 59.21; H, 5.85; N, 6.24.

1d. White solid, m.p. 113-115°C. IR (cm⁻¹, nujol): 689, 724, 760, 834, 899, 1041, 1185, 1380, 1569. ¹H-NMR (CDCl₃, 400MHz) δ: 2.67 (t, 2H, *J* = 6.8 Hz), 3.80-3.85 (m, 2H), 4.03-4.08 (m, 2H), 4.54 (t, 2H, *J* = 6.8 Hz), 7.33-7.64 (m, 9H). ¹³C-NMR (CDCl₃, 100MHz) δ: 37.4, 65.0, 70.9, 108.5, 126.2, 127.4, 127.5, 127.8, 129.1, 140.3, 140.8, 141.8. GC-MS (70 eV): *m/z*: 299([M⁺], 3), 225(100), 181(44), 152(32), 76(10). Anal. Calcd. for C₁₇H₁₇NO₄ (299.32): C, 68.21; H, 5.72; N, 4.68. Found: C, 68.25; H, 5.70; N, 4.66.

1e. Clear oil. IR (cm⁻¹, neat): 896, 950, 1070, 1152, 1385, 1557. ¹H-NMR (CDCl₃, 400MHz) δ: 0.92 (t, 3H, *J* = 7.3 Hz), 1.62 (q, 2H, *J* = 7.3 Hz), 2.40 (t, 2H, *J* = 6.8 Hz), 3.92-3.96 (m, 4H), 4.43 (t, 2H, *J* = 6.8 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 8.3, 30.5, 33.9, 65.4, 71.2, 110.2. GC-MS (70 eV): *m/z*: 146(18), 101(45), 99(100), 57(40), 55(25), 29(14). Anal. Calcd. for C₇H₁₃NO₄ (175.18): C, 47.99; H, 7.48; N, 8.00. Found: C, 48.01; H, 7.50; N, 7.99.

1f. Yellow oil. IR (cm⁻¹, neat): 701, 752, 895, 950, 1048, 1147, 1384, 1556, 3027, 3062. ¹H-NMR (CDCl₃, 400MHz) δ: 1.90-1.96 (m, 2H), 2.47 (t, 2H, *J* = 6.8 Hz), 2.66-2.73 (m, 2H), 3.98-4.01 (m, 4H), 4.54 (t, 2H, *J* = 6.8 Hz), 7.16-7.22 (m, 3H), 7.25-7.32 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 30.2, 34.5, 39.6, 65.5, 71.1, 109.5, 126.2, 128.5, 128.7, 141.6. GC-MS (70 eV): *m/z*: 177(37), 146(34), 99(100), 91(59), 77(9), 55(18). Anal. Calcd. for C₁₃H₁₇NO₄ (251.28): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.11; H, 6.80; N, 5.59.

1g. White solid, m.p. 60-62°C. IR (cm⁻¹, nujol): 751, 826, 863, 892, 951, 1041, 1178, 1377, 1569. ¹H-NMR (CDCl₃, 400MHz) δ: 2.72 (t, 2H, *J* = 6.8 Hz), 3.80-3.85 (m, 2H), 4.05-4.10 (m, 2H), 4.56 (t, 2H, *J* = 6.8 Hz), 7.48-7.58 (m, 3H), 7.82-7.90 (m, 3H), 7.95 (s, 1H). ¹³C-NMR (CDCl₃, 50MHz) δ: 37.3, 65.1, 70.9, 108.6, 123.5, 124.8, 126.6, 126.7, 127.9, 128.5, 128.8, 133.1, 133.5, 138.6. GC-MS (70 eV): *m/z*: 273([M⁺], 9), 199 (100), 155(50), 127(50). Anal. Calcd. for C₁₅H₁₅NO₄ (273.28): C, 65.92; H, 5.53; N, 5.13. Found: C, 65.95; H, 5.55; N, 5.11.

General procedure for the synthesis of compounds 3aa:

To a stirred solution of the nitro compound **1a** (1 mmol) and aldehyde **2a** (1 mmol) in EtOAc (1mL), 500 mg of Amberlyst A21 were added. The resulting heterogeneous mixture was stirred 3 hours at room temperature, then the catalyst was filtered off by washing with EtOAc. After evaporation of the solvent, the crude product **3aa** was purified by flash chromatography column.

3aa. Yield: 81%. Clear oil. IR (cm⁻¹, neat): 1097, 1179, 1369, 1560, 3482. ¹H-NMR (CDCl₃, 400MHz) δ: 0.91-0.97 (m, 3H), 1.32 (s, 1.5H), 1.34-1.45 (m, 2H), 1.36 (s, 1.5H), 1.62-1.72 (m, 2H), 2.17 (dd, 0.5H, *J* = 2.6, 15.8 Hz), 2.37 (dd, 0.5H, *J* = 5.6, 15.8 Hz), 2.73-2.84 (m, 1H), 3.25 (d, 0.5H, *J* = 7.3 Hz), 3.35 (d, 0.5H, *J* = 5.6 Hz), 3.83-4.03 (m, 4H), 4.17-4.33 (m, 2H), 4.49-4.59 (m, 1H), 4.88-5.00 (m, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 13.8, 19.2, 24.2, 24.4, 30.6, 37.2, 27.6, 64.86, 64.93, 65.1, 66.9, 67.2, 71.97, 72.03, 84.4, 85.2, 107.9, 108.1, 171.1, 171.2. Anal. Calcd. for C₁₂H₂₁NO₇ (291.30): C, 49.48; H, 7.27; N, 4.81. Found: C, 49.55; H, 7.31; N, 4.77.

General procedure for the synthesis of compounds 4:

To a stirred solution of the nitro compound **1** (1 mmol) and aldehyde **2** (1 mmol) in EtOAc (1mL), 500 mg of Amberlyst A21 were added. The resulting heterogeneous mixture was stirred for the appropriate time (see Table 3) at room temperature, then the catalyst was filtered off by washing with EtOAc. The solution was concentrated until arrive at a volume of 6 mL, then Amberlyst A15 was added and the

mixture was stirred at 55°C. After completion of the reaction (see Table 3), the catalyst was removed by filtration, washing with EtOAc and, after evaporation of the solvent, the crude product **4** was purified by flash chromatography column.

4aa. Yield: 78%. Clear oil. IR (cm⁻¹, neat): 1726, 1599, 1534, 1299, 1209, 1139, 1021, 799, 760. ¹H-NMR (CDCl₃, 400MHz) δ: 0.94 (t, 3H, *J* = 7.3 Hz), 1.36-1.47 (m, 2H), 1.65-1.75 (m, 2H), 2.36 (s, 3H), 4.26 (t, 2H, *J* = 6.8 Hz), 6.08 (dd, 1H, *J* = 0.9, 3.4 Hz), 7.05 (d, 1H, *J* = 3.4 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 13.9, 14.2, 19.4, 31.0, 64.7, 108.5, 119.3, 143.5, 157.3, 159.2. GC-MS (70 eV): *m/z*: 182([M⁺], 15), 126(100), 109(89), 81(42), 53(49), 41(11), 29(11). Anal. Calcd. for C₁₀H₁₄O₃ (182.22): C, 65.91; H, 7.74. Found: C, 65.99; H, 7.80.

4ab. Yield: 65%. Clear oil. IR (cm⁻¹, neat): 3061, 1641, 1599, 1509, 1320, 1211, 1172, 1024, 880, 803, 725, 697, 651. ¹H-NMR (CDCl₃, 400MHz) δ: 2.44 (s, 3H), 6.20 (dd, 1H, *J* = 0.9, 3.4 Hz), 7.10 (d, 1H, *J* = 3.4 Hz), 7.43-7.50 (m, 2H), 7.53-7.59 (m, 1H), 7.88-7.92 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.4, 109.3, 123.2, 128.6, 129.3, 132.4, 137.9, 151.1, 159.0, 182.5. GC-MS (70 eV): *m/z*: 186([M⁺], 100), 171(37), 157(15), 109(97), 105(51), 77(61), 53(21), 51(29). Anal. Calcd. for C₁₂H₁₀O₂ (186.21): C, 77.40; H, 5.41. Found: C, 77.45; H, 5.45.

4ba. Yield: 61%. Yellow oil. IR (cm⁻¹, neat): 1727, 1595, 1530, 1466, 1299, 1204, 1139, 1016, 799, 761. ¹H-NMR (CDCl₃, 400MHz) δ: 0.86-0.91 (m, 3H), 0.95 (t, 3H, *J* = 7.3 Hz), 1.28-1.36 (m, 4H), 1.37-1.48 (m, 2H), 1.62-1.75 (m, 4H), 2.67 (t, 2H, *J* = 7.7 Hz), 4.27 (t, 2H, *J* = 6.8 Hz), 6.10 (d, 1H, *J* = 3.4 Hz), 7.06 (d, 1H, *J* = 3.4 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.0, 14.2, 19.4, 22.6, 27.6, 28.5, 31.0, 31.5, 64.7, 107.6, 119.1, 143.3, 159.3, 161.8. GC-MS (70 eV): *m/z*: 238([M⁺], 22), 182(48), 181(31), 165(47), 126(44), 109(100), 81(39), 52(15), 41(22), 29(19). Anal. Calcd. for C₁₄H₂₂O₃ (238.32): C, 70.56; H, 9.30. Found: C, 70.65; H, 9.37.

4cc. Yield: 80%. Clear oil. IR (cm⁻¹, neat): 1714, 1573, 1531, 1481, 1302, 1272, 1140, 1019, 959, 922, 804, 763, 691, 671. ¹H-NMR (CDCl₃, 400MHz) δ: 1.40 (t, 3H, *J* = 7.3 Hz), 4.38 (q, 2H, *J* = 7.3 Hz), 6.73 (d, 1H, *J* = 3.8 Hz), 7.24 (d, 1H, *J* = 3.8 Hz), 7.31-7.37 (m, 1H), 7.38-7.45 (m, 2H), 7.76-7.81 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.6, 61.1, 107.0, 120.0, 125.1, 129.0, 129.1, 129.8, 144.1, 157.7, 159.1. GC-MS (70 eV): *m/z*: 216([M⁺], 73), 188(56), 171(40), 144(61), 131(16), 115(100), 89(21), 63(16). Anal. Calcd. for C₁₃H₁₂O₃ (216.23): C, 72.21; H, 5.59. Found: C, 72.24; H, 5.64.

4dc. Yield: 60%. White solid, m.p. 99-101°C. IR (cm⁻¹, nujol): 1721, 1377, 1304, 1157, 1021, 840, 800, 762, 720. ¹H-NMR (CDCl₃, 400MHz) δ: 1.41 (t, 3H, *J* = 7.3 Hz), 4.40 (q, 2H, *J* = 7.3 Hz), 6.77 (d, 1H, *J* = 3.4 Hz), 7.26 (d, 1H, *J* = 3.4 Hz), 7.34-7.40 (m, 1H), 7.43-7.49 (m, 2H), 7.60-7.68 (m, 4H), 7.86 (d, 2H, *J* = 8.5 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.7, 61.2, 107.2, 120.1, 125.5, 127.2, 127.7, 127.9, 128.7, 129.1, 140.5, 141.8, 144.2, 157.5, 159.1. GC-MS (70 eV): *m/z*: 292([M⁺], 100), 264(49), 220(38), 191(61), 190(44), 165(17), 95(16). Anal. Calcd. for C₁₉H₁₆O₃ (292.33): C, 78.06; H, 5.52. Found: C, 77.99; H, 5.49.

4ed. Yield: 56%. Yellow waxy solid. IR (cm⁻¹, nujol): 1634, 1607, 1513, 1316, 1210, 1170, 1111, 1036, 977, 943, 883, 831, 811, 790, 754. ¹H-NMR (CDCl₃, 400MHz) δ: 1.31 (t, 3H, *J* = 7.7 Hz), 2.42 (s, 3H), 2.78 (q, 2H, *J* = 7.7 Hz), 6.20 (dt, 1H, *J* = 0.9, 3.4 Hz), 7.11 (d, 1H, *J* = 3.4 Hz), 7.27 (d, 2H, *J* = 8.1 Hz), 7.83 (d, 2H, *J* = 8.1 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 12.0, 21.8, 22.0, 107.5, 122.4, 129.2, 129.5, 135.2, 143.1, 151.1, 164.0, 182.2. GC-MS (70 eV): *m/z*: 214([M⁺], 74), 199(45), 185(42), 171(40), 123(31), 119(100), 91(60), 65(31), 39(14). Anal. Calcd. for C₁₄H₁₄O₂ (214.26): C, 78.48; H, 6.59. Found: C, 78.53; H, 6.64.

4ee. Yield: 69%. Clear oil. IR (cm⁻¹, neat): 3065, 3033, 1719, 1594, 1529, 1379, 1297, 1212, 1132, 1019, 968, 783, 758, 698. ¹H-NMR (CDCl₃, 400MHz) δ: 1.27 (t, 3H, *J* = 7.7 Hz), 2.72 (q, 2H, *J* = 7.7 Hz), 5.32 (s, 2H), 6.12 (d, 1H, *J* = 3.4 Hz), 7.13 (d, 1H, *J* = 3.4 Hz), 7.33-7.46 (m, 5H). ¹³C-NMR (CDCl₃, 100MHz) δ: 12.0, 21.9, 66.4, 107.0, 119.7, 128.5, 128.5, 128.7, 136.1, 142.9, 158.9, 163.2. GC-MS (70 eV): *m/z*: 230([M⁺], 36), 123(90), 107(15), 96(29), 91(100), 65(24), 39(13). Anal. Calcd. for C₁₄H₁₄O₃ (230.26): C, 73.03; H, 6.13. Found: C, 72.97; H, 6.07.

4fc. Yield: 84%. Clear oil. IR (cm⁻¹, neat): 3063, 3028, 1720, 1595, 1530, 1454, 1368, 1301, 1204, 1127, 1019, 955, 864, 801, 760, 698. ¹H-NMR (CDCl₃, 400MHz) δ: 1.37 (t, 3H, *J* = 7.3 Hz), 3.00 (s, 4H), 4.35 (q, 2H, *J* = 7.3 Hz), 6.07 (d, 1H, *J* = 3.4 Hz), 7.07 (d, 1H, *J* = 3.4 Hz), 7.15-7.23 (m, 3H), 7.25-7.31 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.6, 30.3, 34.1, 60.9, 108.3, 119.1, 126.4, 128.5, 128.6, 140.7, 143.5, 159.1, 160.3. GC-MS (70 eV): *m/z*: 244([M⁺], 29), 171(22), 153(100), 125(46), 91(72), 79(16), 65(15), 52(13). Anal. Calcd. for C₁₅H₁₆O₃ (244.29): C, 73.75; H, 6.60. Found: C, 73.80; H, 6.63.

4fd. Yield: 61%. Clear oil. IR (cm⁻¹, neat): 3061, 3027, 1639, 1599, 1508, 1320, 1302, 1212, 1171, 1023, 978, 962, 930, 880, 804, 789, 750, 722, 697, 676. ¹H-NMR (CDCl₃, 400MHz) δ: 3.01-3.14 (m, 4H), 6.19 (d, 1H, *J* = 3.4 Hz), 7.11 (d, 1H, *J* = 3.4 Hz), 7.17-7.25 (m, 3H), 7.27-7.33 (m, 2H), 7.45-7.51 (m, 2H), 7.54-7.60 (m, 1H), 7.88-7.92 (m, 2H). ¹³C-NMR (CDCl₃, 100MHz) δ: 30.4, 34.1, 109.0, 122.8, 126.5, 128.5, 128.5, 128.7, 129.3, 132.4, 137.8, 140.5, 151.1, 161.8, 182.5. GC-MS (70 eV): *m/z*: 276([M⁺], 26), 185(100), 171(17), 157(28), 105(87), 91(50), 77(51), 65(13), 51(15). Anal. Calcd. for C₁₉H₁₆O₂ (276.33): C, 82.58; H, 5.84. Found: C, 82.63; H, 5.79.

4gb. Yield: 68%. White solid, m.p. 112-114°C. IR (cm⁻¹, nujol): 3052, 1666, 1631, 1598, 1516, 1377, 1323, 1268, 1177, 1026, 989, 958, 881, 864, 801, 786, 747, 723, 697, 677. ¹H-NMR (CDCl₃, 400MHz) δ: 6.94 (d, 1H, *J* = 3.8 Hz), 7.32 (d, 1H, *J* = 3.8 Hz), 7.47-7.55 (m, 4H), 7.57-7.63 (m, 1H), 7.79-7.92 (m, 4H), 7.98-8.03 (m, 2H), 8.33 (s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 108.1, 122.7, 123.4, 124.6, 126.7, 127.0, 127.1, 128.0, 128.6, 128.7, 128.9, 129.4, 132.6, 133.4, 133.7, 137.8, 151.6, 158.7, 182.4. GC-MS (70 eV): *m/z*: 298([M⁺], 100), 270(10), 241(8), 221(20), 165(48), 105(19), 77(25). Anal. Calcd. for C₂₁H₁₄O₂ (298.33): C, 84.54; H, 4.73. Found: C, 84.58; H, 4.69.

Synthetic procedure of ester **6**:

To a stirred solution of **5** (6 mmol) in MeOH (20 mL), conc. H₂SO₄ (2 mL) was added and the resulting mixture was refluxed for 2 hours. Then, water (40 mL) was added to the reaction mixture and methanol was evaporated under vacuum. The resulting aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL), the combined organic layer was dried over dry Na₂SO₄ and, after filtration and evaporation of the solvent, the crude product **6** was isolated. The resulted ester **6** was pure enough to be, directly, involved in the following reaction without

any further purification. The compound **6** was characterized by m.p. and ^1H NMR, compared to those reported in literature (Ref. Z. Liu, F. Shi, P. D. G. Martinez, C. Raminelli, R. Larock, *J. Org. Chem.* **2008**, *73*, 219-226).

Yield: 95%. White solid, m.p. 160-162 °C. ^1H -NMR (CDCl_3 , 400MHz) δ : 4.00 (s, 3H), 7.22-7.27 (m, 1H), 7.34-7.39 (m, 1H), 7.57 (dt, 1H, $J = 0.9, 8.5$ Hz), 8.16 (dt, 1H, $J = 0.9, 8.1$ Hz), 12.91 (bs, 1H).

Synthetic procedure of ester 7:

To a stirred heterogeneous mixture of compounds **6** (3 mmol) and CsF-Celite system (4.5 mmol), in 70 mL of acetonitrile, the benzylbromide (6 mmol) was added and the mixture was refluxed 48 hours. Then, the solvent was evaporated and the residue was dissolved in ethyl acetate (40 mL). The promoter was filtered off by a short pad of celite and, the filtrate was evaporated under reduced pressure affording the crude **7**, which was purified by flash chromatography column.

Yield: 79%. White solid, m.p. 80-82°C. IR (cm^{-1} , nujol): 751, 788, 1068, 1183, 1608, 1681. ^1H -NMR (CDCl_3 , 400MHz) δ : 4.05 (s, 3H), 5.71 (s, 2H), 7.18-7.39 (m, 8H), 8.24 (dt, 1H, $J = 1.3, 8.1$ Hz). ^{13}C -NMR (CDCl_3 , 100MHz) δ : 52.3, 54.3, 116.3, 122.4, 123.5, 124.3, 127.3, 127.4, 128.3, 129.0, 135.1, 135.8, 140.7, 163.3. GC-MS (70 eV): m/z : 266($[\text{M}^+$], 57), 235(11), 207(56), 205(20), 102(11), 91(100), 65(30). Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$ (266.29): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.04; H, 5.33; N, 10.48.

Synthetic procedure of aldehyde 8:

To a stirred solution of ester **7** (3 mmol), in dry THF (25 mL) and under inert atmosphere at -10 °C, a 1 M hexanes solution of DIBAL-H (9 mmol) was added dropwise. The resulting mixture was stirred at the same temperature for 1 hour, after that additional 9 mmol of the DIBAL-H solution were added. Finally the reaction was stirred at room temperature for 6 hours (the reaction was monitored by TLC), then it was quenched initially, by slowly addition of water (10 mL), and successively by 1M aq. HCl (20 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3 x 20 mL), then the combined organic layer was dried over dry Na_2SO_4 and the solvent was evaporated under vacuum affording the crude intermediate alcohol, which was solubilized in CH_2Cl_2 (50 mL) and activated MnO_2 (21 mmol) was added. The resulting heterogeneous mixture was stirred at room temperature 24 hours, after that, MnO_2 was filtered off by short pad of celite, and the filtrate was evaporated under reduced pressure affording the crude **8**, which was purified by flash chromatography column.

Yield: 90%. White solid, m.p. 68-70°C. IR (cm^{-1} , nujol): 699, 751, 789, 1670. ^1H -NMR (CDCl_3 , 400MHz) δ : 5.69 (s, 2H), 7.22-7.27 (m, 2H), 7.29-7.37 (m, 4H), 7.40-7.44 (m, 2H), 8.32 (dt, 1H, $J = 1.3, 8.1$ Hz), 10.27 (s, 1H). ^{13}C -NMR (CDCl_3 , 100MHz) δ : 54.3, 110.1, 122.5, 124.3, 127.5, 127.8, 128.5, 129.2, 135.5, 141.1, 143.4, 187.2. GC-MS (70 eV): m/z : 236($[\text{M}^+$], 78), 207(44), 159(9), 91(100), 65(20). Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$ (236.27): C, 76.25; H, 5.12; N, 11.86. Found: C, 76.15; H, 5.14; N, 11.93.

Synthetic procedure of unsaturated ketone 9:

To a stirred solution of aldehyde **8** (3 mmol), in dry Et_2O (30 mL) and under inert atmosphere at -10 °C, a 1.6 M solution in THF of vinylmagnesium chloride (3.6 mmol) was slowly added. The resulting mixture was stirred at the same temperature for 1.5 hours, then it was initially quenched by slowly addition of water (10 mL) and, successively, by 1M aq. HCl (20 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3 x 20 mL), then the organic layer was dried over dry Na_2SO_4 and the solvent was evaporated under vacuum, affording the crude allylic alcohol. The latter, was solubilized in CH_2Cl_2 (50 mL), following by addition of activated MnO_2 (21 mmol). The resulting heterogeneous mixture was stirred at room temperature 24 hours, after that, MnO_2 was filtered off by short pad of celite, and the filtrate was evaporated under reduced pressure affording the crude **9**, which was purified by flash chromatography column.

Yield: 85%. White solid, m.p. 69-71°C. IR (cm^{-1} , nujol): 712, 744, 954, 1065, 1147, 1377, 1604, 1658. ^1H -NMR (CDCl_3 , 400MHz) δ : 5.68 (s, 2H), 5.88 (dd, 1H, $J = 2.1, 10.3$ Hz), 6.63 (dd, 1H, $J = 2.1, 17.5$ Hz), 7.20-7.41 (m, 8H), 7.69 (dd, 1H, $J = 10.3, 17.5$ Hz), 8.45 (dt, 1H, $J = 1.3, 8.1$ Hz). ^{13}C -NMR (CDCl_3 , 100MHz) δ : 54.2, 110.0, 123.4, 124.0, 127.4, 128.3, 128.4, 129.1, 132.9, 135.9, 141.0, 142.7, 185.3. GC-MS (70 eV): m/z : 262($[\text{M}^+$], 75), 235(11), 207(22), 171(15), 145(13), 91(100), 65(18), 55(10). Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ (262.31): C, 77.84; H, 5.38; N, 10.68. Found: C, 77.94; H, 5.43; N, 10.59.

Synthetic procedure of nitro compound 10:

To a stirred solution of unsaturated ketone **9** (3 mmol), in THF (2 mL), NaNO_2 (6 mmol) and AcOH (6 mmol) were added and the resulting mixture was stirred at room temperature for 24 hours. After completion of the reaction (monitored by TLC), the system was diluted with water (10 mL) and extracted with ethyl acetate (3 x 20 mL). Then, the organic layer was dried over dry Na_2SO_4 and the solvent was evaporated under vacuum affording the crude β -nitro ketone. The so obtained β -nitro ketone was placed in a dried nitrogen flushed flask, equipped with a Den-Stark apparatus and condenser, after that, benzene (7 mL), ethylene glycol (18 mmol) and *p*-toluenesulfonic acid (0.15 mmol) were added and the solution was refluxed for 24 hours. The mixture was cooled and NaHCO_3 saturated aqueous solution (10 mL) was added. The organic layer was separated and the aqueous phase was extracted with CHCl_3 (3 x 20 mL). The organic layer was dried over dry Na_2SO_4 and the solvent was evaporated under vacuum affording the crude product **10**, which was purified by flash chromatography column.

Yield: 67%. Yellow solid, m.p. 85-87°C. IR (cm^{-1} , nujol): 728, 914, 1027, 1378, 1551, 1615. ^1H -NMR (CDCl_3 , 400MHz) δ : 2.94 (t, 2H, $J = 6.8$ Hz), 3.95-4.05 (m, 2H), 4.10-4.20 (m, 2H), 4.63 (t, 2H, $J = 6.8$ Hz), 5.60 (s, 2H), 7.13-7.21 (m, 3H), 7.23-7.37 (m, 5H), 7.90 (d, 1H, $J = 8.1$ Hz). ^{13}C -NMR (CDCl_3 , 100MHz) δ : 36.0, 53.4, 65.5, 70.9, 106.8, 109.8, 121.5, 121.7, 121.8, 126.9, 127.3, 128.0, 128.9, 136.7, 140.8, 143.8. GC-MS (70 eV): m/z : 353($[\text{M}^+$], 3), 180 (22), 279(100), 235(16), 91(58), 65(6). Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_4$ (353.37): C, 64.58; H, 5.42; N, 11.89. Found: C, 64.63; H, 5.45; N, 11.70.

Synthetic procedure of furan 11:

To a stirred solution of the nitro compound **10** (3 mmol) and ethyl glyoxalate **2a** (3 mmol) in EtOAc (3mL), Amberlyst A21 (1.5 g) was added. The resulting heterogeneous mixture was stirred for 18 hours at room temperature, then the catalyst was filtrated off by washing with EtOAc (20 mL). The solution was concentrated until arrive at a volume of 18 mL, then Amberlyst A15 (2.1 g) was added and the mixture was stirred at 55°C for 4 hours. Then, the catalyst was removed by filtration, washing with EtOAc (10 mL), and, after evaporation of the solvent, the crude product **11** was purified by flash chromatography column.

Yield: 70%. White solid, m.p. 88-90°C. IR (cm⁻¹, nujol): 728, 746, 1139, 1376, 1594, 1617, 1720. ¹H-NMR (CDCl₃, 400MHz) δ: 1.43 (t, 3H, *J* = 7.3 Hz), 4.42 (q, 2H, *J* = 7.3 Hz), 5.65 (s, 2H), 7.01 (d, 1H, *J* = 3.4 Hz), 1.19-7.40 (m, 9H), 8.27 (d, 1H, *J* = 8.1 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.6, 53.6, 61.1, 108.2, 109.8, 119.8, 121.9, 122.2, 122.3, 127.26, 127.28, 128.1, 129.0, 135.6, 136.5, 140.7, 144.1, 153.0, 159.0. GC-MS (70 eV): *m/z*: 346([M⁺], 89), 126(16), 91(100), 65(9). Anal. Calcd. for C₂₁H₁₈N₂O₃ (346.38): C, 72.82; H, 5.24; N, 8.09. Found: C, 72.86; H, 5.29; N, 8.04.

Synthetic procedure of furan **12**:

To a stirred solution of ester **11** (3 mmol), in dry THF (25 mL) and under inert atmosphere at -10 °C, a 1 M hexanes solution of DIBAL-H (9 mmol) was added dropwise. The resulting mixture was stirred at the same temperature for 1 hour, after that additional 9 mmol of DIBAL-H solution were added. Finally the reaction was stirred at room temperature for 6 hours (the reaction was monitored by TLC), then it was initially quenched by slowly addition of water (10 mL), and successively by 1M aq. HCl (20 mL). The organic phase was separated and the aqueous phase was extracted with Et₂O (3 x 20 mL). The resulting organic layer was dried over dry Na₂SO₄, and the solvent was evaporated under vacuum, affording the crude product **12** which was purified by flash chromatography column.

Yield: 93%. White solid, m.p. 110-112°C. IR (cm⁻¹, nujol): 727, 742, 769, 1015, 1030, 1377, 1495, 1615, 3310. ¹H-NMR (CDCl₃, 400MHz) δ: 2.28 (bs, 1H), 4.74 (s, 2H), 5.65 (s, 2H), 6.47 (d, 1H, *J* = 3.4 Hz), 6.87 (d, 1H, *J* = 3.4 Hz), 7.17-7.38 (m, 8H), 8.05 (d, 1H, *J* = 8.1 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 53.4, 57.8, 108.1, 109.8, 109.9, 121.5, 121.6, 121.7, 127.1, 127.2, 128.0, 128.9, 136.4, 136.8, 140.7, 148.8, 154.1. GC-MS (70 eV): *m/z*: 304([M⁺], 100), 287(40), 213(10), 128(20), 91(76), 65(11). Anal. Calcd. for C₁₉H₁₆N₂O₂ (304.34): C, 74.98; H, 5.30; N, 9.20. Found: C, 75.01; H, 5.33; N, 9.16.