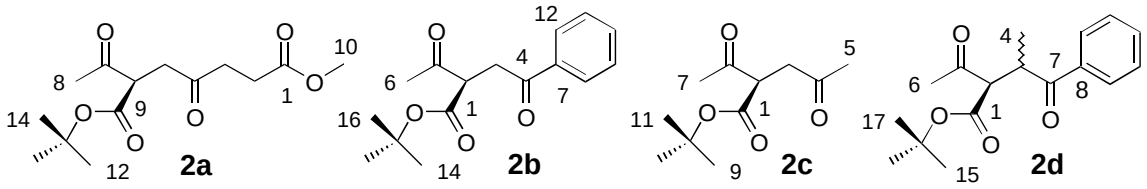
Synthesis of the intermediates **2**.



To a suspension of sodium hydride (1.1 eq.) in tetrahydrofuran (30 ml) cooled at 0°C was added dropwise *tert*-butyl acetoacetate (5-10 mmol). The reaction mixture was stirred 30 min at 0°C before adding the α-bromoketone **1** (1.1 eq) then stirred 2 h at 0°C and overnight at rt. Work-up with HCl 1M (30 ml) and ether (50 ml) followed by extraction of the aqueous layer with ether (2×50 ml), drying of the organic layers over $MgSO_4$, filtration and evaporation of the solvent gave crude product. Subsequent purification by flash chromatography (silica gel; hexane/EtOAc, 5:1→3:1) yielded intermediate **2**.

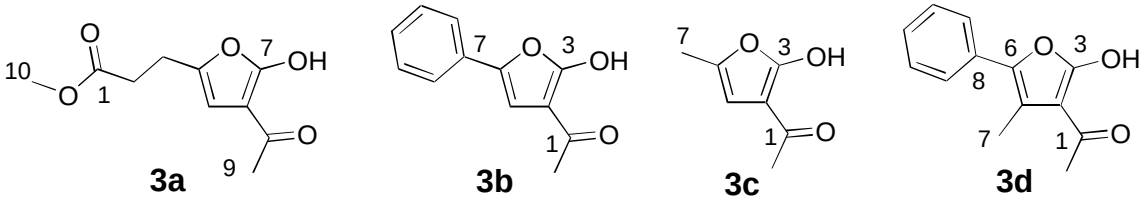
Methyl 6-*tert*-butyloxycarbonyl-4,7-dioxooctanoate (**2a**): liquid (92%); R_f 0.59 (EtOAc/hexane, 3:1, $KMnO_4$); IR (film) 2980*m*, 2955*m*, 2935*m*, 1741*s*, 1718*vs*, 1439*m*, 1408*m*, 1396*m*, 1369*s*, 1259*s*, 1201*s*, 1175*s*, 1147*s*, 1105*m*, 846*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H, H_3-(12-14)); 2.29 (s, 3H, H_3-8); 2.45-2.64 (m, 2H, H_2-2); 2.68-2.81 (m, 2H, H_2-3); 2.88 (dd, J = 18.3, 5.7, 1H, H_A-5); 3.07 (dd, J = 18.2, 8.3, 1H, H_B-5); 3.63 (s, 3H, H_3-10); 3.92 (dd, J = 8.3, 5.7, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (1C, C-2); 27.7 (3C, C-(12-14)); 29.9 (1C, C-8); 36.8 (1C, C-3); 40.5 (1C, C-5); 51.7 (1C, C-10); 54.7 (1C, C-6); 82.3 (1C, C-11); 167.6 (1C, C-9); 172.9 (1C, C-1); 202.5 (1C, C-7), 206.1 (1C, C-4); MS-DCI (relative percentage) *m/z* 305 (17), 304 (100, $[M+18]^+$), 287 (23, $[M+1]^+$), 248 (68, $[M+18-C_4H_8]^+$), 231 (45, $[M+1-C_4H_8]^+$), 213 (21, $[M+1-C_4H_{10}O]^+$), 187 (8, $[M+1-C_5H_8O_2]^+$); HRMS-ESI (positive mode) *m/z* calcd for $C_{14}H_{22}NaO_6$ 309.13085, found 309.13090.

tert-Butyl 2-acetyl-4-oxo-4-phenylbutyrate (**2b**): white solid (95%); R_f 0.61 (EtOAc/hexane, 2:1, $KMnO_4$); IR (KBr) 3006*w*, 2987*m*, 2919*w*, 1729*vs*, 1708*s*, 1648*s*, 1451*m*, 1421*m*, 1401*m*, 1369*m*, 1356*m*, 1333*m*, 1314*m*, 1283*s*, 1260*m*, 1210*m*, 1168*s*, 1136*s*, 844*m*, 756*s*, 691*m*; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46 (s, 9H, H_3-(14-16)); 2.42 (s, 3H, H_3-6); 3.46 (dd, J = 18.4, 5.1, 1H, H_A-3); 3.64 (dd, J = 18.4, 8.2, 1H, H_B-3); 4.13 (dd, J = 8.2, 5.6, 1H, H-2); 7.42-7.46 (m, 2H, H-9, H-11)); 7.53-7.57 (m, 1H, H-10); 7.95-7.98 (m, 2H, H-8, H-12); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) : 27.8 (3C, C-(14-16)); 30.2 (1C, C-6); 37.3 (1C, C-3); 54.9 (1C, C-2); 82.4 (1C, C-13); 128.1, 128.6 (4C, C-8, C-9, C-11, C-12); 133.3 (1C, C-10); 136.1 (1C, C-7); 167.9 (1C, C-1); 197.3, 202.9 (2C, C-4, C-5); MS-ESI (negative mode) *m/z* ms 275 $[M-1]^-$, ms-(275) 201 $[M-1-C_4H_{10}O]^-$, ms-(201) 173 $[M-1-C_4H_{10}O-CO]^-$, 159 $[M-1-C_4H_{10}O-C_2H_2O]^-$, 157, 131 $[M-1-C_4H_{10}O-C_2H_2O-CO]^-$; Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.71; H, 7.56.

tert-Butyl 2-acetyllevulinate (**2c**) [1]: liquid (60%); R_f 0.46 (EtOAc/hexane, 1:1, $KMnO_4$); IR (film) 3004*w*, 2980*m*, 2935*w*, 1739*s*, 1718*vs*, 1396*m*, 1370*s*, 1316*m*, 1259*m*, 1148*s*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 9H, H_3-(9-11)); 2.11 (s, 3H, H_3-5); 2.27 (s, 3H, H_3-7); 2.83 (dd, J = 18.5, 5.7, 1H, H_A-3); 3.01 (dd, J = 18.4, 8.4, 1H, H_B-3); 3.86 (dd, J = 8.1, 5.8, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7 (3C, C-(9-11); 29.5, 29.9 (2C, C-5, C-7); 41.4 (1C, C-3); 54.7 (1C, C-2); 82.2 (1C, C-8); 167.7 (1C, C-1); 202.5 (1C, C-6), 205.7 (1C, C-4); MS-DCI (relative percentage) *m/z* 232 (36, $[M+18]^+$), 215 (60, $[M+1]^+$), 176 (86, $[M+18-C_4H_8]^+$), 159 (100, $[M+1-C_4H_8]^+$).

tert-Butyl 2-acetyl-3-benzoyl-butyrate (**2d**): liquid (94%, mixture of diastereoisomers 61:39); R_f 0.65 (EtOAc/hexane, 2:1, $KMnO_4$); IR (KBr) minor diastereoisomer 3093*w*, 3066*w*, 3045*w*, 3031*w*, 3005*m*, 2982*m*, 2960*w*, 2936*w*, 2888*w*, 1732*vs*, 1716*s*, 1682*vs*, 1596*m*, 1579*m*, 1459*m*, 1451*m*, 1417*m*, 1394*m*, 1381*m*, 1366*m*, 1357*m*, 1279*vs*, 1235*m*, 1201*m*, 1157*s*, 1142*s*, 978*s*, 842*m*, 782*m*, 708*s*, 685*m*, 658*m*, 566*m*; ^{1}H NMR (400 MHz, $CDCl_3$) major diastereoisomer (61%) δ 1.17 (d, *J* = 7.2, 3H, H_3-4); 1.49 (s, 9H, H_3-(15-17)); 2.26 (s, 3H, H_3-6); 4.04 (d, *J* = 10.6, 1H, H-2); 4.16 (dq, *J* = 10.6, 7.1, 1H, H-3); 7.42-7.47 (m, 2H, H-10, H-12); 7.52-7.54 (m, 1H, H-11); 7.95-8.00 (m, 2H, H-9, H-13)); minor diastereoisomer (39%) δ 1.08 (d, *J* = 7.1, 3H, H_3-4); 1.30 (s, 9H, H_3-(15-17)); 2.36 (d, *J* = 0.2, 3H, H_3-6); 4.08 (d, *J* = 10.7, 1H, H-2); 4.21 (dq, *J* = 10.7, 7.1, 1H, H-3); 7.42-7.47 (m, 2H, H-10, H-12); 7.52-7.54 (m, 1H, H-11); 7.95-8.00 (m, 2H, H-9, H-13)); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereoisomer δ 15.7 (1C, C-4); 27.7 (3C, C-(15-17)); 29.2 (1C, C-6); 40.3 (1C, C-3); 63.8 (1C, C-2); 82.3 (1C, C-14); 128.4, 128.5 (4C, C-9, C-10, C-12, C-13); 133.0 (1C, C-11); 135.5 (1C, C-8); 167.5 (1C, C-1); 201.7 (1C, C-5); 202.2 (1C, C-7); minor diastereoisomer δ 15.8 (1C, C-4); 27.5 (3C, C-(15-17)); 31.1 (1C, C-6); 39.8 (1C, C-3); 62.9 (1C, C-2); 82.1 (1C, C-14); 128.5, 128.5 (4C, C-9, C-10, C-12, C-13); 133.0 (1C, C-11); 135.6 (1C, C-8); 167.0 (1C, C-1); 202.0 (1C, C-7); 203.0 (1C, C-5); ESI-MS (negative mode) *m/z* 289 $[M-1]^-$, ms-(289) 215 $[M-1-C_4H_{10}O]^-$, ms-(215) 187 $[M-1-C_4H_{10}O-CO]^-$, 173 $[M-1-C_4H_{10}O-C_2H_2O]^-$, 145 $[M-1-C_4H_{10}O-CO-C_2H_2O]^-$; Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.60; H, 7.93.

Syntheses of the furans **3**.



3a **3b** **3c** **3d**

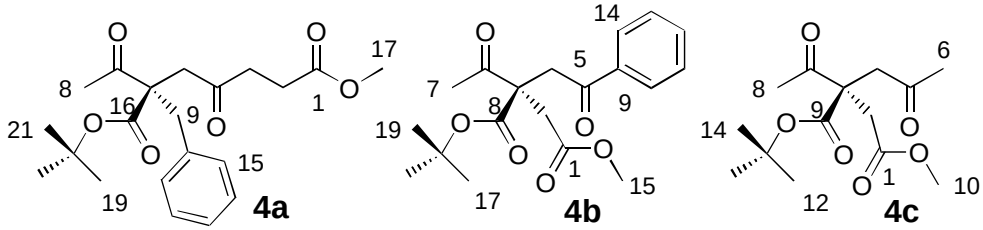
A solution of **2** in TFA (97%, puriss, Fluka (Buchs)) (5-10 ml) was stirred 1 h at rt. The reaction mixture was evaporated and the brown residue was absorbed on silica gel and purified by flash chromatography (hexane/EtOAc 4:1→1:1) to yield **3**. As an alternative procedure, the procedure used to synthesis the furans **5** gave similar yields of **3**.

Methyl 3-[2-(4-acetyl-5-hydroxyfuranyl)]propionate (**3a**): white solid (87%); R_f 0.35 (EtOAc/hexane, 3:1, $KMnO_4$); IR (KBr) 3600-2200*m(br)*, 3119*m*, 3031*m*, 2957*m*, 2928*m*, 2624*m*, 1728*vs*, 1697*s*, 1679*vs*, 1616*m*, 1590*s*, 1467*m*, 1440*s*, 1393*m*, 1362*m*, 1322*s*, 1286*s*, 1237*s*, 1200*s*, 1167*s*, 1089*s*, 992*m*, 951*m*, 928*m*, 895*m*, 853*m*, 787*m*, 744*m*, 568*m*, 478*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H, H_3-9); 2.64 ("t", *J* = 7.6, 2H, H_2-2); 2.90 (t, *J* = 7.6, 2H, H_2-3); 3.68 (s, 3H, H_3-10); 6.29 (s, 1H, H-5); 10.8-12.4 (s(l), 1H, HO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (1C, C-9); 23.0 (1C, C-3); 32.1 (1C, C-2); 51.8 (1C, C-10); 106.2 (1C, C-5); 113.3 (1C, C-6); 152.3 (1C, C-4); 159.7 (1C, C-8); 169.9 (1C, C-7); 172.7 (1C, C-1); EI-MS (relative percentage) *m/z* 212 (23, $[M]^{+\bullet}$), 195 (3, $[M-OH]^+$), 181 (2, $[M-CH_3O]^+$), 152 (66, $[M-C_2H_4O_2]^{+\bullet}$), 140 (11), 139 (100, $[M-C_3H_5O_2]^+$), 121 (29, $[M-C_3H_7O_3]^+$), 107 (10), 106 (12), 93 (11), 92 (18), 91 (26), 90 (14), 88 (19), 87 (15), 79 (20), 78 (12), 77 (12), 76 (10), 73 (20), 70 (49), 69 (15), 65 (10), 61 (66), 59 (12), 55 (22); HRMS-ESI (positive mode) *m/z* calcd for $C_{10}H_{13}O_5$ 213.07575, found 213.07581.

1-[3-(2-Hydroxy-5-phenyl)furanyl]ethanone (**3b**): white solid (67%); R_f 0.49 (EtOAc/hexane, 3:1, $KMnO_4$); mp = 176°C (lit. [2] 111°C); IR (KBr) 3400-2200*m(br)*, 3058*m*, 3038*m*, 2863*m*, 2619*m*, 1685*vs*, 1615*s*, 1605*m*, 1587*m*, 1563*m*, 1491*m*, 1471*m*, 1446*m*, 1312*m*, 1296*m*, 1275*m*, 1238*m*, 1104*m*, 1027*m*, 944*m*, 929*m*, 777*m*, 758*s*, 714*m*, 687*m*, 660*m*, 577*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H, H_3-2); 6.93 (s, 1H, H-5); 7.27-7.31 (m, 1H, H-10); 7.37-7.42 (m, 2H, H-9, H-11)); 7.64-7.67 (m, 2H, H-8, H-12); 9.5-11.3 (s(l), 1H, HO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (1C, C-2); 105.4 (1C, C-5); 114.7 (1C, C-4); 123.7 (2C, C-8, C-12); 127.7 (1C, C-10); 128.7 (2C, C-9, C-11); 129.8 (1C, C-7); 152.1 (1C, C-6); 160.3 (1C, C-1); 169.9 (1C, C-3); ESI-MS (negative mode) *m/z* 201 (23, $[M-1]^-$), ms-(201) 157 $[M-1-CO_2]^-$.

1-[3-(2-Hydroxy-5-methyl)furanyl]ethanone (**3c**): white solid (77%); R_f 0.50 (EtOAc/hexane, 3:1, $KMnO_4$); IR (KBr) 3400-2100*m(br)*, 3130*m*, 3036*m*, 2954*m*, 2925*m*, 2714*m*, 2637*m*, 1685*vs*, 1619*m*, 1586*s*, 1437*s*, 1389*m*, 1365*m*, 1304*s*, 1239*s*, 1220*s*, 1134*m*, 1087*s*, 1004*m*, 983*m*, 928*s*, 829*m*, 784*s*, 717*m*, 555*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (d, J = 0.5, 3H, H_3-7); 2.55 (s, 3H, H_3-2); 6.24 (d, J = 1.0, 1H, H-5); 10.8-12.2 (s(l), 1H, HO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1 (1C, C-7); 13.8 (1C, C-2); 106.3 (1C, C-5); 113.4 (1C, C-4); 150.3 (1C, C-6); 159.4 (1C, C-1); 170.3 (1C, C-3); EI-MS (relative percentage) *m/z* 141 (10), 140 (100, $[M]^{+\bullet}$), 125 (10, $[M-CH_3]^+$), 123 (20), 122 (27, $[M-H_2O]^{+\bullet}$), 121 (17), 97 (10), 96 (13), 95 (27, $[C_6H_7O]^+$), 81 (10), 80 (11), 74 (11), 72 (11), 71 (17), 70 (26), 68 (12), 67 (11), 66 (14), 62 (47), 61 (10), 58 (13), 56 (19).

1-[3-(2-Hydroxy-4-methyl-5-phenyl)furanyl]ethanone (**3d**): white solid (75%); R_f 0.54 (EtOAc/hexane, 2:1, UV+$KMnO_4$); IR (KBr) 3300-2100*m(br)*, 2966*m*, 2920*m*, 2870*m*, 2678*m*, 2613*m*, 2555*m*, 1677*vs*, 1612*m*, 1578*m*, 1562*m*, 1496*m*, 1464*m*, 1447*s*, 1378*m*, 1324*m*, 1312*m*, 1255*m*, 1118*s*, 1072*m*, 1016*m*, 939*m*, 764*s*, 694*m*, 669*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H, H_3-7); 2.55 (s, 3H, H_3-2); 7.20-7.33 (m, 1H, H-11); 7.42-7.46 (m, 2H, H-10, H-12); 7.54-7.66 (m, 2H, H-9, H-13)); 12.62 (s, 1H, HO); ^{13}C NMR (100 MHz, d_6-DMSO) δ 10.8 (1C, C-7); 14.3 (1C, C-2); 115.7 (1C, C-4); 117.0 (1C, C-5); 125.8 (2C, C-9, C-13); 127.5 (1C, C-11); 128.9 (2C, C-10, C-12); 130.5 (1C, C-8); 147.1 (1C, C-6); 158.0 (1C, C-1); 165.5 (1C, C-3); ESI-MS (negative mode) *m/z* 215 $[M-H]^-$, ms-(215) 171 $[M-H-CO_2]^-$, ms-(171) 156 $[M-H-CO_2-CH_3]^-$; Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.72. Found C, 72.30; H, 5.72.



Synthesis of methyl 6-benzyle-6-*tert*-butyloxycarbonyl-4,7-dioxooctanoate (**4a**).

To a suspension of sodium hydride (4.4 mmol) in tetrahydrofuran (30 ml) cooled at 0°C was added dropwise **2a** (4 mmol). The reaction mixture was stirred 1 h at 0°C before adding dropwise benzyl bromide (4.4 mmol) then stirred 2 h at 0°C, overnight at rt and refluxed 2 h. Work-up with H_2O (30 ml) and ether (50 ml) followed by extraction of the aqueous layer with ether (2×50 ml), drying of the organic layers over $MgSO_4$, filtration and evaporation of the solvent gave crude product as a liquid. Subsequent purification by flash chromatography

(silica gel; hexane/EtOAc 5:1→3:1) yielded intermediate **4a** (840 mg, 56%): R_f 0.58 (EtOAc/hexane, 2:1, $KMnO_4$); IR (film) 3088*w*, 3064*w*, 3030*w*, 2978*m*, 2953*w*, 2932*w*, 1739*s*, 1714*vs*, 1455*m*, 1438*m*, 1407*m*, 1395*m*, 1369*s*, 1277*m*, 1252*m*, 1208*m*, 1149*s*, 1101*m*, 1081*m*, 849*m*, 704*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H, H_3-(19-21)); 2.37 (s, 3H, H_3-8)); 2.51-2.57 (m, 2H, H_2-2)); 2.59-2.69 (m, 2H, H_2-3)); 2.90 (d, J = 18.6, 1H, H_A-5)); 2.97 (d, J = 18.6, 1H, H_B-5)); 3.22 (d, J = 13.9, 1H, H_A-9); 3.43 (d, J = 13.9, 1H, H_B-9); 3.67 (s, 3H, H_3-17); 6.99-7.02 (m, 2H, H-11, H-15)); 7.21-7.29 (m, 3H, H-(12-14)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1 (1C, C-8); 27.4 (1C, C-2); 27.6 (3C, C-(19-21)); 36.9 (1C, C-3); 38.8 (1C, C-9); 45.0 (1C, C-5); 51.7 (1C, C-17); 62.7 (1C, C-6); 82.3 (1C, C-18); 127.0 (1C, C-13); 128.4 (2C, C-12, C-14); 129.8 (2C, C-11, C-15); 136.2 (1C, C-10); 169.9 (1C, C-16); 172.8 (1C, C-1); 205.0 (1C, C-7), 206.3 (1C, C-4); ESI-MS (positive mode) *m/z* 399 $[M+Na]^+$, ms-(399) 243 $[M+Na-C_4H_8]^+$, ms-(343) 299 $[M+Na-C_4H_8-CO_2]^+$; HRMS-ESI (positive mode) *m/z* calcd for $C_{21}H_{28}NaO_6$ 399.17780, found 399.17799.

Synthesis of the intermediates **4b** and **4c**.

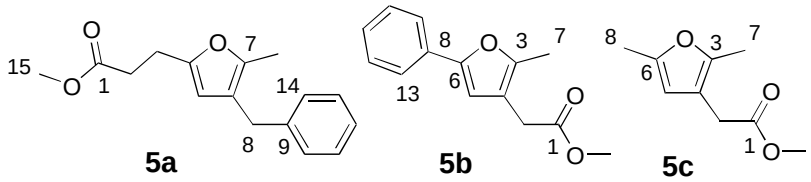
To a suspension of sodium hydride (1.1 eq.) in tetrahydrofuran (30 ml) cooled at 0°C was added dropwise **2b** or **2c** (4 mmol). The reaction mixture was stirred 1 h at 0°C before adding dropwise methyl bromoacetate (4.4 mmol) then stirred 2 h at 0°C, overnight at rt. Work-up with H_2O (30 ml) and ether (50 ml) followed by extraction of the aqueous layer with ether (2×50 ml), drying of the organic layers over $MgSO_4$, filtration and evaporation of the solvent gave crude product as a liquid. Subsequent purification by flash chromatography (silica gel; hexane/EtOAc 5:1→3:1) yielded intermediate **4b** or **4c.**

Methyl 3-acetyl-3-*tert*-butyloxycarbonyl-5-oxo-5-phenylpentanoate (**4b**): liquid (89%); R_f 0.65 (EtOAc/hexane, 2:1, UV+$KMnO_4$); IR (film) 3062*m*, 2979*s*, 2954*m*, 1733*vs*, 1687*s*, 1598*m*, 1450*s*, 1438*s*, 1413*m*, 1395*s*, 1370*s*, 1354*s*, 1319*s*, 1289*s*, 1219*s*, 1153*s*, 1100*m*, 1076*m*, 1043*m*, 1004*m*, 847*s*, 756*s*, 691*s*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 9H, H_3-(17-19)); 2.29 (s, 3H, H_3-7); 3.13 (d, J = 16.9, 1H, H_A-2); 3.23 (d, J = 16.9, 1H, H_B-2); 3.59 (s, 3H, H_3-15); 3.79 (d, J = 18.6, 1H, H_A-4); 3.86 (d, J = 18.6, 1H, H_B-4); 7.40-7.45 (m, 2H, H-11, H-13); 7.52-7.56 (m, 1H, H-12); 7.92-7.95 (m, 2H, H-10, H-14); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0 (1C, C-7); 27.1 (3C, C-(17-19)); 37.0 (1C, C-2); 41.7 (1C, C-4); 51.3 (1C, C-15); 59.6 (1C, C-3); 127.7 (2C, C-10, C-14); 128.2 (2C, C-11, C-13); 133.0 (1C, C-12); 136.0 (1C, C-9); 168.5 (1C, C-8); 171.2 (1C, C-1); 196.8 (1C, C-5), 202.8 (1C, C-6); ESI-MS (negative mode) *m/z* 347 $[M-1]^-$, 275 $[M-C_4H_9O]^-$, ms-(347) 273 $[M-1-C_4H_{10}O]^-$, ms-(273) 241 $[M-1-C_4H_{10}O-CH_4O]^-$, ms-(241) 197 $[M-1-C_4H_{10}O-CH_4O-C_2H_4O]^-$; HRMS-ESI (positive mode) *m/z* calcd for $C_{19}H_{24}NaO_6$: 371.146502, found 371.146597.

Methyl 3-acetyl-3-*tert*-butyloxycarbonyl-5-oxo-hexanoate (**4c**): liquid (88%); R_f 0.43 (EtOAc/hexane, 1:1, $KMnO_4$); IR (film) 2980*s*, 2955*s*, 2935*m*, 1737*s*, 1718*vs*, 1438*s*, 1369*s*, 1317*s*, 1288*s*, 1251*s*, 1156*s*, 1106*s*, 1088*s*, 1046*m*, 1019*s*, 895*m*, 847*s*, 508*s*, 493*s*, 418*s*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H, H_3-(12-14)); 2.12 (s, 3H, H_3-6)); 2.22 (s, 3H, H_3-8)); 3.01 (d, J = 16.7, 1H, H_A-2); 3.07 (d, J = 16.6, 1H, H_B-2)); 3.19 (d, J = 18.6, 1H, H_A-4); 3.25 (d, J = 18.6, 1H, H_B-4); 3.61 (s, 3H, H_3-10); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5 (1C, C-8); 27.5 (3C, C-(12-14)); 30.0 (1C, C-6); 37.4 (1C, C-2); 46.4 (1C, C-4); 51.7 (1C, C-10); 59.7 (1C, C-3); 82.6 (1C, C-11); 168.8 (1C, C-9); 171.4 (1C, C-1); 203.3 (1C, C-7), 205.7 (1C, C-5); EI-MS (relative percentage) *m/z* 304 (46, $[M+18]^+$), 287 (48, $[M+1]^+$), 248 (86, $[M+18-C_4H_8]^+$), 231 (100, $[M+1-C_4H_8]^+$), 213 (43, $[M-C_4H_9O]^+$), 187 (28, $[M+1-C_5H_8O_2]^+$), 171

(11), 170 (96, $[C_9H_{14}O_3]^{+\bullet}$), 169 (56), 155 (22, $[C_8H_{11}O_3]^+$), 142 (21), 138 (11), 127 (56, $[C_7H_{11}O_2]^+$), 112 (11), 111 (18), 110 (23), 59 (10), 58 (25), 57 (78), 56 (17), 55 (15); HRMS-ESI (positive mode) *m/z* calcd for $C_{14}H_{22}NaO_6$: 309.13085, found 309.13076.

Syntheses of the furans **5**.



5a **5b** **5c**

A solution of **4** (2-3.5 mmol) in CH_2Cl_2 (10 ml) was cooled at 0°C and TFA (97%) (1 ml) was added. The reaction mixture stirred 1 h at 0°C and overnight at rt then evaporated and the brown residue was purified by flash chromatography (hexane/EtOAc 5:1) to yield **5**.

Methyl 3-[2-(4-benzyl-5-methyl)furanyl]propionate (**5a**): liquid orange (71%); R_f 0.65 (EtOAc/hexane, 2:1, UV+$KMnO_4$); IR (film) 3085*w*, 3063*w*, 3028*w*, 2952*w*, 2921*m*, 2852*w*, 1741*vs*, 1580*m*, 1495*m*, 1454*m*, 1438*s*, 1367*m*, 1202*s*, 1172*s*, 1101*m*, 1072*m*, 1030*m*, 994*m*, 729*m*, 701*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H, H_3-15); 2.66 (t, J = 7.7, 2H, H_2-2); 2.91 (t, J = 7.6, 2H, H_2-3); 3.67 (s, 2H, H_2-8); 3.71 (s, 3H, H_3C-16); 5.80 (s, 1H, H-5); 7.19-7.24 (m, 3H, H-10, H-12, H-14); 7.28-7.39 (m, 2H, H-11, H-13)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4 (1C, C-15); 23.4 (1C, C-3); 31.1 (1C, C-8); 32.6 (1C, C-2); 51.7 (1C, C-16); 107.6 (1C, C-5); 118.2 (1C, C-6); 125.9 (1C, C-12); 128.3, 128.3 (4C, C-10, C-11, C-13, C-14); 140.9 (1C, C-9); 146.2 (1C, C-7), 151.2 (1C, C-4); 173.6 (1C, C-1); HRMS-ESI (positive mode) *m/z* calcd for $C_{16}H_{19}O_3$: 259.13287, found 259.13294.

Methyl 3-(2-methyl-5-phenyl)furanylacetate (**5b**): liquid (67%); R_f 0.62 (EtOAc/hexane, 2:1, UV+$KMnO_4$); IR (film) 3060*w*, 3030*w*, 2997*w*, 2952*m*, 2920*w*, 2847*w*, 1741*vs*, 1602*m*, 1556*m*, 1488*m*, 1436*m*, 1336*m*, 1267*m*, 1231*m*, 1196*s*, 1164*s*, 1104*m*, 1012*m*, 932*m*, 761*s*, 693*m*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H, H_3-7); 3.41 (s, 2H, H_2-2); 3.72 (s, 3H, H_3-14); 6.61 (s, 1H, H-5); 7.23 ("t", $J \cong$ 7.4, 1H, H-11); 7.37 (t, J = 7.7, 2H, H-10, H-12); 7.65 (d, J = 7.6, 2H, H-9, H-13);^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4 (1C, C-7); 30.7 (1C, C-2); 51.8 (1C, C-14); 107.3 (1C, C-5); 113.7 (1C, C-4); 123.1 (2C, C-9, C-13); 126.7 (1C, C-11); 128.4 (2C, C-10, C-12); 130.7 (1C, C-8); 148.5, 151.3 (2C, C-3, C-6); 171.6 (1C, C-1); HRMS-EI *m/z* calcd for $C_{14}H_{14}O_3$: 230.0937, found 230.0933.

Methyl 3-(2,5-dimethyl)furanylacetate (**5c**): liquid (71%); **$C_9H_{12}O_3$** (168.19); R_f 0.65 (EtOAc/hexane, 2:1, $KMnO_4$); IR (film) 2953*m*, 2925*s*, 2856*m*, 1742*vs*, 1586*m*, 1437*s*, 1333*m*, 1271*s*, 1229*s*, 1174*s*, 1100*m*, 1009*s*, 933*m*, 927*m*, 799*m*; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.19, 2.22 (2×s, 6H, H_3-7, H_3-8); 3.30 (s, 2H, H_2-2); 3.69 (s, 3H, H_3-9); 5.87 (s, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 13.3 (2C, C-7, C-8); 30.9 (1C, C-2); 51.9 (1C, C-9); 107.7 (1C, C-5); 112.0 (1C, C-4); 146.8, 149.5 (2C, C-3, C-6); 172.1 (1C, C-1).
Hydrolysis with PLE in phosphate buffer (0.1 M, pH 7.8) followed by flash chromatography purification gave the 3-(2,5-dimethyl)furanylacetic acid (CH_2Cl_2-MeOH 95 : 5) [3]: liquid (55%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.19, 2.22 (2×s, 6H, H_3-7, H_3-8); 3.34 (s, 2H, H_2-2); 5.88 (s, 1H, H-5).

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