

General procedure for the synthesis γ -AIBs

To a solution of γ -butenolide (0.3 mmol) and aldehyde or ketone 0.45 ~ 0.9 mmol) in methanol(15mL) was added Na_2CO_3 (0.05 ~ 0.09 mmol) at room temperature. The solution was allowed to reflux, and stirred until complete conversion of the starting material (5 ~ 16 h, monitored by TLC). The reaction mixture was directly filtered and the crude products was purified by crystallization from methanol. Or the reaction mixture was diluted with CHCl_3 and washed subsequently brine and water. The CHCl_3 phase was purified by column chromatography to afford the products. All compounds were characterized (see supplementary information).

Characterization of selected compounds

- 3a mp 127 ~ 129 °C. IR 3393, 2933, 2847, 1750, 1644, 1450, 1036, 942, 894, 758, 690 cm^{-1} . ^1H NMR (400MHz, CDCl_3) 7.77 (2H, d, $J=7.6\text{Hz}$), 7.40(2H,m), 7.32(1H,m), 7.12(1H,s), 6.92 (1H, dd, $J=10.0, 15.7\text{Hz}$), 6.20(1H, d, $J=15.7\text{Hz}$), 5.96(1H, s), 4.80 (1H, s), 4.54 (1H, s), 4.24 (1H, bs), 3.49 (1H, bs), 3.38(1H, bs), 2.46(1H, d, $J=13.4\text{Hz}$), 2.36 (1H, d, $J=10.0\text{Hz}$), 2.27 (2H, bs), 2.05 (1H, t, $J=13.0\text{Hz}$), 1.8 (3H, m), 1.54 (1H, $J=13.0\text{Hz}$), 1.41 (1H, m), 1.38 (3H, s), 1.14 (2H, m), 0.84 (3H, s). ^{13}C NMR (100MHz, CDCl_3) δ 168.8, 148.0, 147.5, 137.6, 135.5, 133.2, 130.4, 128.9, 128.8, 127.0, 121.5, 133.1, 109.3, 80.8, 64.2, 61.9, 54.6, 13.0, 38.7, 38.3, 36.5, 28.1, 22.9, 22.8, 15.9. HR-MS m/z $[\text{M}+\text{Na}]^+$, 443.2187, (calcd.443.2199).
- 3f mp 179.1 ~ 181.4 °C. IR 3337, 3080, 2928, 2855, 1746, 1642, 1445, 1375, 1073, 1034, 896 cm^{-1} . ^1H NMR(400 MHz, CDCl_3) 7.26 (1H, d, $J=3.67\text{Hz}$), 6.83 (1H, dd, $J=10.0, 15.8\text{Hz}$), 6.15 (1H, d, $J=15.8\text{Hz}$), 4.78 (1H, d, $J=1.5\text{Hz}$), 4.54 (1H, d, 1.48 Hz), 4.22 (1H, d, $J=13.1\text{Hz}$), 3.50 (1H, dd, $J=13.4, 4.7\text{Hz}$), 3.35 (1H, d, $J=13.0\text{Hz}$), 2.47 (1H, m), 2.33 (1H, d, $J=9.8\text{Hz}$), 2.05 (1H, m), 2.01(3H, s), 1.93 (3H, s), 1.82 (1H, m), 1.78 (2H, m), 1.53 (1H, m), 1.34 (1H, m), 1.26 (3H, s), 1.25 (1H, m), 1.20 (1H, m), 0.82 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 148.1, 144.8, 136.3, 130.6, 126.9, 122.0, 121.8, 109.2, 80.9, 64.2, 61.9, 54.7, 43.0, 38.7, 38.7, 36.6, 29.7, 28.1, 23.0, 22.6, 18.7, 15.9. HR-MS m/z $[\text{M}+\text{Na}]^+$ 395.2197, (calcd. 395.2198).
- 5a mp 194~196 °C. IR 3312, 2933, 2883, 1760, 1746, 1646, 1484, 1442, 1368, 1344, 1210, 1161, 1081, 1021, 930 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) 7.75 (2H, d, $J=7.6\text{Hz}$), 7.34 (2H, m), 7.32 (1H, d, $J=7.3\text{Hz}$), 7.28 (1H, d, $J=1.6\text{Hz}$), 5.97 (1H, s), 4.83 (1H, t, $J=8.4\text{Hz}$), 4.27 (1H, d, $J=11.1\text{Hz}$), 3.47 (1H, m), 3.38 (1H, d, $J=11.0\text{Hz}$), 2.47(1H, dd, $J=8.1\text{Hz}, 13.8\text{Hz}$), 2.2 (3H, br), 2.10 (1H, m), 1.78~1.72 (5H, om (overlap multiple)), 1.56~1.50 (3H, om), 1.47 (3H, s), 1.13 (3H, s), 1.03~0.99 (2H, om), 0.96 (3H, s). ^{13}C NMR (100.6 MHz, CDCl_3) δ 169.0, 147.4, 137.3, 136.9, 133.1, 130.4, 128.9, 128.8, 113.2, 82.9, 80.9, 72.9, 64.2, 57.9, 52.8, 42.6, 39.0, 36.3, 35.7, 33.3, 31.5, 27.5, 22.7, 18.2, 16.5. HRMS m/z $[\text{M}+\text{Na}]^+$ 461.2299 (calcd. 461.2304).
- 11a mp 208.5 ~210.0 °C. IR 3444, 3082, 2934, 2857, 1744, 1634, 1447, 1388, 1080, 1037 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) 7.24(1H, s), 6.48(1H, dd, $J=10.0, 15.6$ Hz), 6.18(1H, d, $J=15.2$ Hz), 4.23(1H, d, $J=10.8$ Hz), 3.49(1H, m), 3.38 (1H, d, $J=11.2$ Hz), 3.01(1H, br), 2.82(1H, d, $J=3.6$ Hz), 2.75(1H, br), 2.56(1H, d, $J=4.4$ Hz), 2.50 (2H, s), 2.31 (2H, s), 2.17(1H, d, $J=9.6$ Hz), 1.90(2H, om), 1.87(1H, m), 1.72(1H, m), 1.62(6H, br), 1.57~1.45(4H,m), 1.28(3H, s), 1.16~1.17 (2H, m), 0.97 (3H, s). ^{13}C NMR (100.6 MHz, CDCl_3) δ 169.1, 142.2, 131.3, 131.1, 131.0, 126.3, 124.9, 80.6, 64.0, 59.3, 58.2, 54.2, 51.0, 42.8, 39.0, 37.9, 35.5, 29.4, 28.8, 28.2, 27.6, 27.4, 26.2, 22.7, 21.2, 16.1. HR-MS m/z $[\text{M}+\text{Na}]^+$ 451.2457, (calcd. 451.2460).
- 13a mp 172.8 ~ 173.8 °C. IR 3462, 2933, 2880, 1742, 1645,1472, 1449, 1405, 1380, 1274, 1163, 1128, 1068, 1015, 953, 869 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) 7.74 (1H, d, $J=1.3$ Hz), 7.01 (1H, d, $J=3.2\text{Hz}$), 6.64 (1H, s), 6.51 (1H, dd, $J=1.6, 3.2\text{Hz}$), 6.17(1H, s), 4.87~4.92 (3H, om), 4.2 (2H, t, $J=3.7\text{Hz}$), 4.1 (2H, m), 4.03 (1, s), 3.75~3.78 (4H, om), 3.48 (1H, m), 3.75 (1H, m), 3.2~3.3 (4H, m), 2.25~1.65 (20H, om), 1.27 (6H, om), 1.23 (9H, om), 0.91(3H, s), 0.77(3H, s). ^{13}C NMR (100.6 MHz, CDCl_3) δ 170.2, 164.4, 149.5, 148.4, 143.8, 115.6, 114.9, 112.9, 100.1, 98.4, 98.3, 95.5, 86.5, 82.6, 28.2, 75.7, 72.7, 72.6, 69.6, 68.3, 68.1, 66.5, 66.4, 55.5, 42.1, 41.5, 37.8, 37.1, 36.7, 36.3, 35.0, 32.9, 32.6,30.6, 29.8, 29.5, 26.6, 26.5, 23.6, 21.7, 18.2, 8.8. HRMS m/z $[\text{M}+\text{Na}]^+$ 881.4330 (calcd.881.4300).