Supplementary Materials

Synthesis:

1-[2-(2-Methyl-[1,3]dioxolan-2-yl)phenyl]propan-2-ol, 4a: Thin strips of lithium metal was placed in 80 mLdry ether under nitrogen. The ketal **3** (15.05 g, 61.9 mmol) was added to the mixture and heated till the reaction commenced. The mixture was stirred for nearly two hours. Propylene epoxide (25 mL, 357 mmol) was added dropwise to the mixture and the solution was stirred for another 2h. Excess lithium was quenched with slow addition of water. The mixture was stirred overnight. The ether layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The ketal **4a** was purified by column chromatography with ethyl acetate and hexane mixture. The yellow oil was distilled under reduced pressure. Yield 8.86 g (64%), white solid: mp 37-39°C; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, J = 6.1 Hz, 3H), 1.52 (s, 3H), 2.79-2.84 (m, 2H), 3.64-3.70 (m, 2H), 3.85-3.92 (m, 3H), 7.02-7.11 (m, 3H), 7.42-7.44 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.9, 28.1, 42.7, 64.3, 69.5, 109.6, 128.9, 126.2, 128.1, 131.5, 136.6, 141.2.

1-[2-(2-Methyl-[1,3]dioxolan-2-yl)phenyl]butan-2-ol, 4b: Synthetic procedure same as above. Yield 0.607 g (61%) from 1.021 g of **3**, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.5 Hz, 3H), 1.66 (m, 2H), 1.72 (s, 3H), 2.95 (dd, J_1 = 9.1 Hz, J_2 = 13.8 Hz, 1H), 3.03 (dd, J_1 = 3.4 Hz, J_2 = 13.8 Hz, 1H), 3.83-3.89 (m, 3H), 4.04-4.10 (m, 2H), 7.20-7.31 (m, 3H), 7.61-7.63 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.1, 28.0, 30.8, 40.4, 64.3, 74.7, 109.6, 125.7, 126.1, 128.1, 131.4, 136.8, 141.2.

Acetic acid 2-(2-acetylphenyl)-1-methylethyl ester, 5a: Synthetic procedure described in text. Yield 0.187 g (92%) from 0.207 g of **4a**, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, J = 6.3 Hz, 3H), 1.93 (s, 3H), 2.62 (s, 3H), 2.98 (dd, J_1 = 8.5 Hz, J_2 = 13.5 Hz, 1H), 3.36 (dd, J_1 = 7.3 Hz, J_2 = 13.5 Hz, 1H), 5.14-5.18 (m, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.4, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.2, 29.7, 40.1, 71.7, 126.6, 129.6, 131.3, 132.4, 137.9, 138.1, 170.4, 201.8.

Acetic acid 1-(2-acetylbenzyl)propyl ester, 5b: Synthetic procedure described in text. Yield 0.314 g (86%) from 0.376 g of **4b**, colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.57-1.68 (m, 2H), 1.85 (s, 3H), 2.58 (s, 3H), 2.81 (dd, J_1 = 9.2 Hz, J_2 = 13.5 Hz, 1H), 3.44 (dd, J_1 = 3.8 Hz, J_2 = 13.5 Hz, 1H), 5.00-5.06 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.27 (dt, J_1 = 1.3 Hz, J_2 = 7.6 Hz, 1H), 7.36 (dt, J_1 = 1.3 Hz, J_2 = 7.6 Hz, 1H), 7.67 (dd, J_1 = 1.3 Hz, J_2 = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.6, 21.0, 27.5, 29.7, 38.3, 75.9, 126.5, 129.6, 131.2, 132.4, 137.8, 138.3, 170.5, 201.9.

Phenylacetic acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester: Synthetic procedure described in references (see text). Yield 0.226 g (53%) from 0.277 g of **4a**, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, J = 6.2 Hz, 3H), 1.70 (s, 3H), 3.01 (dd, J_1 = 8.9 Hz, J_2 = 13.9 Hz, 1H), 3.18 (dd, J_1 = 4.3 Hz, J_2 = 13.9 Hz, 1H), 3.57 (d, J = 2.7 Hz, 2H), 3.78-3.83 (m, 2H), 4.00-4.05 (m, 2H), 5.25-5.29 (m, 1H), 7.12-7.22 (m, 5H), 7.26-7.35 (m, 3H), 7.58 (d, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.4, 27.8, 39.4, 41.7, 64.0, 64.3, 72.4, 109.3, 126.2, 126.2, 126.8, 127.6, 128.4, 129.2, 131.7, 134.2, 135.4, 141.0, 171.0.

Phenylacetic acid 2-(2-acetylphenyl)-1-methylethyl ester (HAPE phenylacetate): Synthetic procedure same as that of ketal removal from acetate described in the text. Yield 0.184 g (96%) from 0.221 g of phenylacetic acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester, colorless oil; ^{1}H NMR (CD_3CN) δ 1.26 (d, J = 6.3 Hz, 3H), 2.56 (s, 3H), 2.95 (dd, J_1 = 8.8 Hz, J_2 = 13.5 Hz, 1H), 3.25 (dd, J_1 = 4.0 Hz, J_2 = 13.5 Hz, 1H), 3.51 (s, 2H), 5.12-5.18 (m, 1H), 7.14-7.42 (m, 8H), 7.78 (dd, J_1 = 1.5 Hz, J_2 = 7.5 Hz, 1H); ^{13}C NMR (CD_3CN) δ 20.9, 30.6, 41.0, 42.3, 73.2, 128.0, 128.2, 129.8, 130.7, 130.9, 132.6, 133.8, 136.1, 138.9, 139.6, 172.2, 203.6.

Benzoic acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester: Synthetic procedure described in references (see text). Yield 0.384 g (86%) from 0.303 g of **4a**, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, J = 6.3 Hz, 3H), 1.70 (s, 3H), 3.14 (dd, J_1 = 8.4 Hz, J_2 = 13.9 Hz, 1H), 3.29 (dd, J_1 = 4.8 Hz, J_2 = 13.9 Hz, 1H), 3.78-3.83 (m, 2H), 4.01-4.07 (m, 2H), 5.45-5.48 (m, 1H), 7.12-7.15 (m, 2H), 7.28-7.30 (m, 1H), 7.40-7.43 (m, 2H), 7.50-7.57 (m, 2H), 8.00-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5, 27.9, 39.6, 64.1, 64.4, 72.6, 109.3, 126.3, 126.3, 127.7, 128.2, 129.4, 130.9, 131.8, 132.6, 135.4, 141.1, 166.0.

Benzoic acid 2-(2-acetylphenyl)-1-methylethyl ester (HAPE benzoate): Synthetic procedure described in references (see text). Yield 0.171 g (95%) from 0.208 g of benzoic acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.32 (d, J = 6.3 Hz, 3H), 2.49 (s, 3H), 3.09 (dd, J_1 = 8.5 Hz, J_2 = 13.5 Hz, 1H), 3.64 (dd, J_1 = 4.3 Hz, J_2 = 13.5 Hz, 1H), 5.30-5.34 (m, 1H), 7.16-7.44 (m, 6H), 7.61 (d, J = 7.4 Hz, 1H), 7.86-7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.2, 29.6, 40.1, 72.5, 126.5, 128.1, 129.4, 129.7, 130.7, 131.4, 132.5, 132.6, 137.5, 138.2, 165.8, 201.7.

***N*-*t*-BOC-glycine 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester:** Synthetic procedure described in references (see text). Yield 0.308 g (87%) from 0.207 g of **4a**, White solid: mp 108-108.5°C; ^{1}H NMR ($CDCl_3$) δ 1.31 (d, J = 6.2 Hz, 3H), 1.42 (s, 9H), 1.65 (s, 3H), 2.97 (dd, J_1 = 8.7 Hz, J_2 = 13.8 Hz, 1H), 3.14 (dd, J_1 = 4.6 Hz, J_2 = 13.8 Hz, 1H), 3.72-3.89 (m, 4H), 3.99-4.03 (m, 2H), 4.88 (s, 1H), 5.22-5.26 (m, 1H), 7.14-7.20 (m, 3H), 7.53-7.55 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 27.9, 28.3, 39.5, 42.6, 64.1, 64.4, 73.3, 79.8, 109.3, 126.4, 126.5, 127.7, 131.7, 135.1, 141.2, 155.5, 169.7.

***N*-*t*-BOC-glycine 2-(2-acetylphenyl)-1-methylethyl ester (HAPE *N*-*t*-BOC-glycine)**: Synthetic procedure described in references (see text). Yield 0.205 g (97%) from 0.239 g of *N*-*t*-BOC-glycine 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, J = 6.2 Hz, 3H), 1.39 (s, 9H), 2.56 (s, 3H), 2.91 (dd, J_1 = 8.6 Hz, J_2 = 13.4 Hz, 1H), 3.32 (dd, J_1 = 4.2 Hz, J_2 = 13.5 Hz, 1H), 3.67 (dd, J_1 = 4.8 Hz, J_2 = 18.0, Hz, 1H), 3.78 (dd, J_1 = 5.0 Hz, J_2 = 18.2 Hz, 1H), 4.89 (s, 1H), 5.16-5.20 (m, 1H), 7.20 (d, J = 7.4 Hz, 1H), 7.28 (dt, J_1 = 0.9 Hz, J_2 = 7.5 Hz, 1H), 7.37 (dt, J_1 = 1.2 Hz, J_2 = 7.5 Hz, 1H), 7.68-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.1, 28.3, 29.5, 40.2, 42.4, 73.0, 79.7, 126.7, 129.8, 131.4, 132.5, 137.5, 137.8, 155.5, 169.5, 201.6.

***N*-fmoc-glycine 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester:** Synthetic procedure described in references (see text). Yield 0.5863 g (28%) from 0.9103 g of **4a**, White solid: mp 122-126°C; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 6.2 Hz, 3H), 1.65 (s, 3H), 2.97 (dd, J_1 = 8.8 Hz, J_2 = 13.8 Hz, 1H), 3.16 (dd, J_1 = 4.6 Hz, J_2 = 13.8 Hz, 1H), 3.76-3.85 (m, 3H), 3.94-4.03

(m, 3H), 4.20 (t, J = 7.1 Hz, 1H), 4.37 (d, J = 7.0 Hz, 2H), 5.16 (s, 1H), 5.25-5.29 (m, 1H), 7.14-7.18 (m, 3H), 7.27-7.30 (m, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.54-7.57 (m, 3H), 7.74 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.4, 27.9, 39.6, 43.0, 47.1, 64.1, 64.4, 67.1 73.6, 109.3, 120.0, 125.1, 126.4, 126.6, 127.1, 127.7, 127.7, 131.7, 135.1, 141.2, 141.3, 143.8, 156.1, 169.4.

***N*-fmoc-glycine 2-(2-acetylphenyl)-1-methylethyl ester (HAPE *N*-Fmoc-glycine)**: Synthetic procedure described in references (see text). Yield 0.1577 g (85%) from 0.203 g of *N*-Fmoc-glycine 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester, colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.22 (d, J = 6.2 Hz, 3H), 2.48 (s, 3H), 2.86 (dd, J_1 = 8.6 Hz, J_2 = 13.4 Hz, 1H), 3.25 (dd, J_1 = 4.1 Hz, J_2 = 13.5 Hz, 1H), 3.70 (dd, J_1 = 5.1 Hz, J_2 = 18.1, Hz, 1H), 3.80 (dd, J_1 = 5.3 Hz, J_2 = 18.2 Hz, 1H), 4.10 (t, J = 6.9 Hz, 1H), 4.27 (d, J = 7.3 Hz, 2H), 5.13-5.18 (m, 1H), 5.21 (s, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.14-7.30 (m, 6H), 7.48 (d, J = 7.4 Hz, 2H), 7.59-7.65 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 20.0, 29.5, 40.2, 42.7, 47.0, 67.0, 73.2, 119.9, 125.0, 126.7, 127.0, 127.6, 129.8, 131.4, 132.4, 137.4, 137.7, 141.2, 143.7, 156.0, 169.2, 201.6.

***N*-*t*-BOC-4-aminobutyric acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester:** Synthetic procedure described in references (see text). Yield 0.249 g (44%) from 0.310 g of **4a**, Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, J = 6.2 Hz, 3H), 1.40 (s, 9H), 1.64 (s, 3H), 1.65-1.70 (m, 2H), 2.15-2.26 (m, 2H), 2.92-3.12 (m, 4H), 3.73-3.76 (m, 2H), 3.95-4.00 (m, 2H), 4.57 (s, 1H), 5.17-5.21 (m, 1H), 7.12-7.17 (m, 3H), 7.52 (dd, J_1 = 1.7 Hz, J_2 = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.4, 25.1, 27.8, 28.3, 31.8, 39.4, 39.8, 64.0, 64.3, 71.8, 79.0, 109.3, 126.2, 126.3, 127.5, 131.6, 135.4, 141.1, 155.8, 172.6.

***N*-*t*-BOC-4-aminobutyric acid 2-(2-acetylphenyl)-1-methylethyl ester (HAPE *N*-*t*-BOC-GABA)**: Synthetic procedure described in references (see text). Yield 0.087 g (85%) from 0.114 g of *N*-*t*-BOC-4-aminobutyric acid 1-methyl-2-[2-(2-methyl-[1,3]dioxolan-2-yl)-phenyl]-ethyl ester, colorless oil; ^{1}H NMR (CD_3CN) δ 1.21 (d, J = 6.3 Hz, 3H), 1.39 (s, 9H), 1.56 (q, J = 7.2 Hz, 2H), 2.08-2.20 (m, 2H), 2.55 (s, 3H), 2.90-2.96 (m, 3H), 3.33 (dd, J_1 = 4.2 Hz, J_2 = 13.5 Hz, 1H), 5.08-5.12 (m, 1H), 5.22 (s, 1H), 7.29 (dd, J = 7.6 Hz, 1H), 7.34 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.43 (dt, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 7.75 (dd, J_1 = 1.2 Hz, J_2 = 7.7 Hz, 1H); ^{13}C NMR (CD_3CN) δ 20.9, 26.5, 29.0, 30.6, 32.7, 40.8, 41.0, 72.6, 79.5, 128.0, 130.8, 132.6, 133.8, 139.0, 139.8, 157.3, 173.7, 203.7.