

Figure 1SM. Stereoselective production of γ-oxyfunctionalyzed AAs. Engineered NSAR mutant (G291D/F323Y) from *Amycolatopsis* sp. Ts1-60 (NSAR); L-aminoacylase from *Geobacillus thermoglucosidasius (*L-Acyl). BtDO: stereoselective isoleucine dioxygenase from *Bacillus thuringiensis.* L-methionine-(*S*)-sulfoxide with 97% yield and 95% d.e. was produced (Enoki et al, 2016).



Figure 2SM. Preparation of L-α-ABA starting from L-Thr using Threonine deaminase (ThrD), aromatic aminotransferase (TyrTA), and acetolactate synthase (AceS), together alanine racemase (AlaR)/D-amino acid oxidase (DAOO) for removal of the by product L-Ala produced during the reaction (Zhu et al, 2011). The AceS pyruvate-degrading pathway and the AlaR/DAOO pyruvate-recycling route are marked by dashed lines.



Figure 3SM. One-pot MEC reaction for the production of D- and L‐β‐methyl‐α‐AAs using enantioselective SAM‐dependent α‐keto acid methyltransferases (MT), an halide methyltransferase (HMT) and a D- or L-α‐aminotransferase (D- or L-TA) cooperating in two orthogonal reaction cycles (Liao and Seebeck, 2020).



Figure 4SM. A) Enzymatic synthesis of [2-3H]-L-Tyr starting from chemically synthesised [2-3H]-cinnamic acid using L-phenylalanine ammonia lyase and L-Phe-4'-monooxygenase from rat liver (4MO, EC 1.14.16.1; Pajak et al, 2018). The reaction was carried out in the presence of D,L-6-methyl-5,6,7,8-tetrahydropterine (THP, 4MO cofactor) and D,L-dithiothreitol. B) Theoretical production of L-DOPA coupling the previous system to p-hydroxyphenylacetate 3-hydroxylase (PHAH, Min et al, 2015), also including THP- (Hara and Kino, 2013) and NADH-recycling systems

**References**

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