Supplementary Figure 1
HPLC analysis of chemically and enzymatically synthesized S-adenosyl-L-ethionine (AdoEth, 2).

Chemical coupling of S-adenosyl-L-homocysteine (AdoHcy, 6) and ethyltrifluoromethyl sulfonate leads to the formation of (S)- and (R)-AdoEth (diastereomeric mixture at the sulfonium center) (a), while the AdoMet synthetase-catalyzed reaction between ATP and L-ethionine yields only MTase-active (S)-AdoEth (b). Larger methyl group replacements are not well tolerated by AdoMet synthetases making the chemical synthesis of AdoMet analogs with larger methyl replacements obligatory.