Title:	Intermolecular CDC amination of remote and proximal unactivated Csp3–H bonds through intrinsic substrate reactivity – expanding towards a traceless directing group
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Abstract:	An intermolecular radical based distal selectivity in appended alkyl chains has been developed. The selectivity is maximum when the distal carbon is γ to the appended group and decreases by moving from γ → δ → ε positions. In –COO– linked alkyl chains, the same distal γ-selectivity is observed irrespective of its origin, either from the alkyl carboxy acid or alkyl alcohol. The appended groups include esters, N–H protected amines, phthaloyl, sulfone, sulfinimide, nitrile, phosphite, phosphate and borate esters. In borate esters, boron serves as a traceless directing group, which is hitherto unprecedented for any remote Csp3–H functionalization. The selectivity order follows the trend: 3° benzylic > 2° benzylic > 3° tertiary > α to keto > distal methylene (γ > δ > ε). Computations predicted the radical stability (thermodynamic factors) and the kinetic barriers as the factors responsible for such trends. Remarkably, this strategy eludes any designer catalysts, and the selectivity is due to the intrinsic substrate reactivity.
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