The site-specific oxidation of strong C(sp^3)-H bonds is of uncontested utility in organic synthesis. In both academic and industrial circles there is a growing demand for such a transformation since it allows simplifying access to metabolites, late-stage diversification of lead compounds and truncating retrosynthetic plans. One main drawback of chemical reagents used in current C(sp^3)-H oxidations is the lack of diversity with regards to structure and reactivity that prevent a combinatorial approach for rapid screening to be employed. In that regard, directed evolution still holds the greatest promise for achieving complex C–H oxidations in a variety of complex settings. Herein we present a rationally designed platform that provides a step towards this challenge using *N*-ammonium ylides as electrochemically driven oxidants for site-specific, chemoselective C(sp^3)–H oxidation. By taking a first-principles approach guided by computation, these new mediators were identified and rapidly expanded into a library using ubiquitous building blocks and trivial synthesis techniques. The ylide-based approach to C–H oxidation exhibits tunable selectivity that is often exclusive to this class of oxidants and can be applied to real world problems in the agricultural and pharmaceutical sectors.