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Multiplicity Control in Carbenes Aided by the Trifluoromethyl Group

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Aryl(trifluoromethyl)carbenes are among the most widely utilized reactive intermediates in photoaffinity labeling of biological systems. But, only a handful of studies have probed their chemistry, reactivity, and electronic structures. We have been studying these important systems at cryogenic temperatures with matrix isolation spectroscopy, and have found that we can tune the spin states of the carbenes depending on aryl substituent. We have discovered that a CF_3 group stabilizes singlet carbenes compared to H through its strongly electron withdrawing character. This inductive effect causes rehybridization of the carbenes to favor singlet over triplet. We believe that the small ST gap in these carbenes is also relevant to photoaffinity labeling.