Organic radicals are usually highly reactive and short-lived species. By contrast, tetrathiatriaryl methyl (TAM) radicals, derived from the Gomberg radical, are persistent even under cellular conditions. Their strong EPR intensities, long relaxation times, and lineshape-sensitivity towards local pO₂ facilitated their use for spin-labelling EPR, dynamic nuclear polarization, and magnetic resonance imaging. Therefore, synthesis methods yielding TAM radicals tailored to their desired approaches are required, but rarely reported. Most TAM derivatives reported in literature are based on amidation/esterification of the carboxylated Finland trityl. In this work, an iodinated TAM radical is introduced and its reactivity in C-C cross coupling reactions evaluated. While Suzuki-Miyaura coupling performs well, a carbothiolation competitive to Sonogashira coupling was observed and restrained by proper choice of alkyne, solvent, and catalyst. Versatile TAM building blocks were obtained on gram scale and used modularly to synthesize a TAM-porphyrin, a TAM biradical, and a clickable spin-label. As a consequence of \( \pi \)-conjugation in these compounds, the spin density becomes delocalized which holds implications not only for magnetic resonance spectroscopy, but also for the design of molecular magnets or quantum computing devices.


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