Reactions that allow complex molecular fragments to be combined in high yield occupy an exalted position in organic synthesis because they are fundamental to convergent synthesis strategies. Recent discoveries from our laboratories show that bimolecular reactions of structurally elaborate tertiary carbon radicals and electron-deficient alkenes can unite complex fragments by forming a new $sp^3-sp^3$ C–C bond using equimolar amounts of the two coupling partners. Reflecting the large steric bulk of tertiary carbon radicals, these reactions can take place with high stereoselectivity to form new quaternary and secondary carbon stereocenters. Tertiary carbon radicals can be generated conveniently using visible-light photocatalysis, which offers distinct advantages over older less-green methods for forming carbon radicals.