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Synthesis and studies of poly(alkyl aryl ether) dendrimers of up to three generations, consisting of up to 24 triphenyl phosphine units, at the peripheries of these dendrimers, are reported. Triphenyl phosphine attracts immediate interest, in view of its ability to mediate several organic reactions, as well as, organometallic reactions upon complexation with suitable metal ions. Triphenyl phosphine unit is completely retained in the dendrimer framework in this work. Upon synthesis, the reactivity profiles of the triphenyl phosphine containing dendrimers were tested in an etherification reaction, namely, the Mitsunobu reaction. Several alkyl aryl ethers were prepared using the dendritic phosphines as one of the reagents. Excellent conversions, facile separation of the products and reusability of the reagent are studied with the new dendritic phosphines.