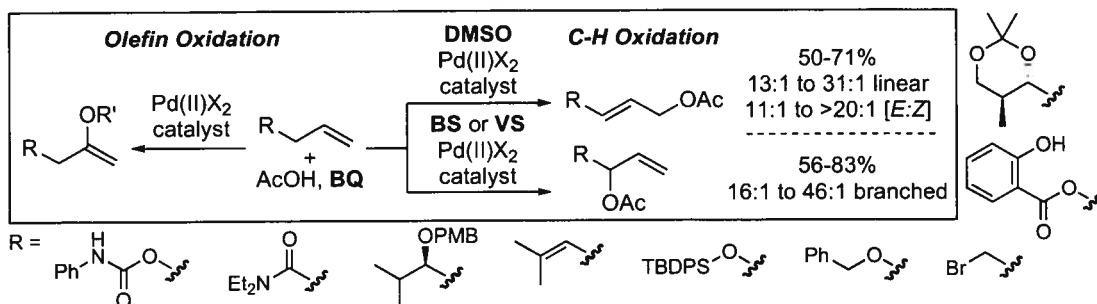


Palladium-Sulfoxide Catalyzed Allylic Oxidations and Serial Ligand Catalysis

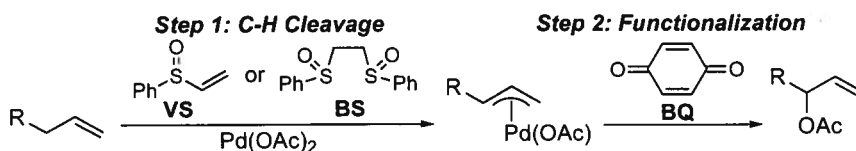
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We have discovered sulfoxide-based palladium catalyzed systems for the highly selective allylic C-H oxidation of α -olefins. In the absence of sulfoxide under identical conditions, olefin oxidation is the major pathway, resulting in vinyl acetate products.

In the presence of DMSO solvent, Pd(II) (10 mol%)/benzoquinone (**BQ**, 2 equiv.)/AcOH (52 equiv.) catalyzes the oxidation of α -olefins to linear (*E*)-allylic acetate products in high regioselectivity (up to 31:1) and stereoselectivities (up to >20:1). Moreover, this reaction showed exceptional functional group compatibility, tolerating basic, acidic and chiral functionality (Figure 1). Overall, these selectivities are unprecedented for an allylic C-H oxidation process.



In the presence of catalytic (10 mol%) bis-sulfoxide (**BS**) or vinyl sulfoxide (**VS**), Pd(II) (10 mol%)/**BQ** (2 equiv.) with alkyl or benzoic acids (1.5 to 4 equiv.) catalyzes the oxidation of α -olefins to branched allylic ester products in exceptionally high regioselectivities (up to 46:1). The **BS/VS** system was equally functional group tolerant (Figure 1) and additionally showed high chemoselectivity for mono- versus di- and tri-substituted olefins.



Preliminary mechanistic studies indicate **VS** (or **BS**) alone is necessary for promoting Pd-mediated C-H cleavage to generate a π -allyl palladium acetate species. This species was observed as a π -allyl palladium acetate dimer free of association with the sulfoxide ligand. Benzoquinone (**BQ**) alone effects and controls functionalization of the π -allyl palladium acetate species. Upon exposure of the dimer (synthesized independently from sulfoxide) to **BQ**, branched allylic acetate was generated with the same high regioselectivities ([B:L] = 32:1) and yields as those observed under the standard reaction conditions. This is the first example of two different ligands working with a single metal ion to promote separate product-forming steps within a catalytic cycle. We term this effect serial ligand catalysis. This data rules out the possibility that a change in the sulfoxide ligand environment of the catalyst is responsible for the divergent regioselectivities between the two allylic oxidation systems.