Peptide isosteres have emerged as important peptidomimetics for chemical biology and medicinal chemistry. In particular, alkene-type dipeptide isosteres are one of the ideal ground state mimetics of peptide bonds. Recently, we have designed a novel peptide isostere possessing an E/Z-chloroalkene unit for the surrogate functionality of a peptide bond, which is termed chloroalkene dipeptide isostere(s). In this study, practical and divergent methodologies for the synthesis of chloroalkenes dipeptide isosteres have been developed. A Key to our approach is the use of organocopper-mediated SET reduction of allylic gem-dichlorides, which allows the gram-scale synthesis of Xaa-Gly-type chloroalkene dipeptide isostere. In complementary work for the preparation of Xaa-Yaa-type isostere, we have found that the stereogenic center corresponding to the side chain of Yaa can be controlled by 1,4-asymmetric induction derived from tert-butylsulfonylamide group, which enables the stereospecific construction of (L,D)-type isostere framework in high to excellent yields. Design concept, synthetic methods, structural information of chloroalkene dipeptide isosteres and the unique reactivity of allylic gem-dichlorides will be discussed.