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Synthetic carbohydrate derivatives often serve as important tools to study the intricate and complex carbohydrate – protein recognition processes. The finding that multivalent interactions are crucial to facilitate a significant carbohydrate – protein recognition has set a paradigm by which to design, synthesize and evaluate newer types of synthetic carbohydrate derivatives to study specific carbohydrate mediated processes. In this communication, we report the synthesis and studies of a series of carbohydrate ligands that are attached to a photoisomerizable azobenzene core unit. These ligands are designed specifically to study the lectin binding properties of their isomers that form as a result of an externally applied stimulus, namely, photochemical or thermal. Upon synthesis of desired mono- to tetravalent galacto- and lactoside ligands, having azobenzenoid core unit, we have evaluated first the physical properties of their isomers, including an assessment of their kinetic constants and activation energies. We have further evaluated the lectin binding properties of these carbohydrate ligands in each of their structural isomeric states, using isothermal calorimetric methods. The results from the calorimetric studies show that these carbohydrate ligands interact with the lectin peanut agglutinin in a co-operative manner, especially in the case of higher affinity lactoside derivatives. This observation of co-operativity is very unique, as it is unknown so far that this phenomenon can be observed for such rather smaller carbohydrate structures.