Synthesis of the macrocyclic core of (-)-pladienolide B
An efficient synthesis of the macrocyclic core of (-)-pladienolide B is disclosed. The concise route relies on a chiral auxiliary-mediated asymmetric aldol addition and an osmium-catalyzed asymmetric dihydroxylation to install the three oxygenated stereocenters of the macrocycle. This purely reagent-controlled and flexible strategy sets the stage for future analogue syntheses and structure-activity relationship plotting of the appealing anticancer lead structure pladienolide B.

Synthesis of the Calystegine Alkaloids, Calystegine A3
An efficient strategy is described for the synthesis of enantiopure calystegine alkaloids. The key step employs a zinc-mediated fragmentation of benzyl-protected methyl 6-iodo-glycosides followed by in situ formation of the benzyl imine and Barbier-type alkylation with zinc, magnesium, or indium metal. Stereochemistry in the pivotal allylation is controlled by the choice of the metal. The functionalized 1,8-nonadienes, thus formed, are converted into cycloheptenes by ring-closing metathesis. Regioselective hydroboration and oxidation give the corresponding cycloheptanones, which are deprotected to afford the desired calystegines. Hereby, calystegine B2, B3, and B4 are prepared from D-glucose, D-galactose, and D-mannose, respectively. This route constitutes the shortest synthesis of calystegine B2 and gives rise to the first total syntheses of calystegine B3 and B4.
Regioselective conversion of primary alcohols into iodides in unprotected methyl furanosides and pyranosides
Two methods are described for the regioselective displacement of the primary hydroxy group in methyl glycosides with iodide. The first method is a modification of a literature procedure employing triphenylphosphine and iodine, where purification has been carried out on a reverse phase column in order to efficiently separate the desired iodoglycosides from triphenylphosphine oxide. The second method employs a new procedure using sulfonylation in pyridine with sterically hindered 2,4,6-trichloro- and 2,4,6-tribromobenzenesulfonyl chloride. The sulfonates thus formed are effective leaving groups and substitution with iodide can be carried out in a one-pot process. Protection of the iodoglycosides is also described either by benzylation with benzyl trichloroacetimidate or silylation with triethylsilyl chloride.

Zinc-mediated fragmentation of methyl 6-deoxy-6-iodo-hexopyranosides
An improved procedure was developed for the zinc-mediated fragmentation of protected and unprotected methyl 6-deoxy-6-iodo-hexopyranosides. The method employs sonication of the iodoglycoside with zinc dust in a THF/H₂O mixture.

Short syntheses of enantiopure calystegine B-2, B-3, and B-4
Calystegine B-2 B-3, and B-4 have been prepared in 5 steps from the benzyl protected methyl 6-iodoglycopyranosides of glucose, galactose and mannose, respectively, by using a zinc-mediated domino reaction followed by ring-closing olefin metathesis as the key steps.

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Platinum-Catalyzed Ring Opening of 1,2-Cyclopropanated Sugars with O-Nucleophiles. Convenient Synthesis of 2-C-Branched Carbohydrates

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