Synthesis of BMS-644950

**Significance:** BMS-644950 is a development candidate for the treatment of hypercholesterolemia. The route depicted delivered >70 kg of the API in 35% overall yield. The synthesis is noteworthy for the large-scale TEMPO oxidation (H → I, 83 mol scale) and Julia–Kocienski olefination (A + B → C, 78 mol scale).

**Comment:** The Julia–Kocienski olefination was performed by adding LiHMDS to a mixture of the aldehyde I and the sulfone J in THF at −70 °C (Barbier conditions). In this way the E-alkene product was obtained with high stereoselectivity (E/Z up to 200:1). Note the use of dimethyl carbonate and DABCO for the N-alkylation of G.