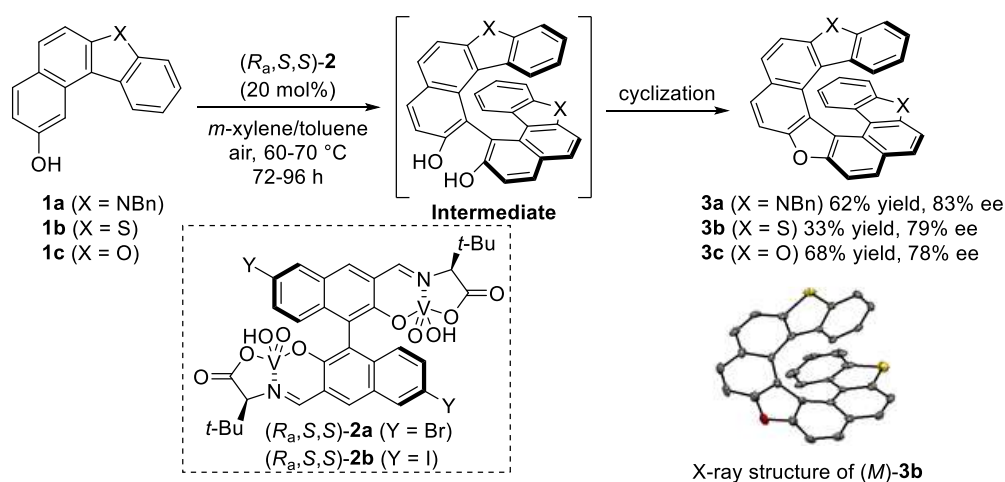


Enantioselective Synthesis of Hetero[9]helicenes Using a Chiral Dinuclear Vanadium(V) Catalyst

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Optically active helicenes and other related helical molecules have received considerable attention due to their enormous potential as catalysts, liquid crystals and molecular electronics.^{1,2} Our group has reported chiral vanadium complex-mediated oxidative coupling of polycyclic phenols,³ followed by Lewis acid-promoted cyclization,⁴ leading to a formation of enantioenriched oxa[9]helicenes in up to 94% ee.⁵ In extension of our interest in the development of novel protocols for the synthesis of other hetero[9]helicenes with extraordinary chiroptical properties, here we report a facile one-pot synthesis of enantioenriched aza, oxa, and thia[9]helicenes from hydroxycarbazols, furans and thiophenes as starting materials. Among the chiral vanadium catalysts we screened, halogenated dinuclear vanadium(V) catalysts **2** (**2a**: Y = Br; **2b**: Y = I) promoted the sequential reaction to afford diazaoxa[9]helicene **3a** (X = NBn), dithiaoxa[9]helicene **3b** (X = S) and trioxa[9]helicene **3c** (X = O) in moderate yields with good enantioselectivities. Optically pure **3b** was readily accessible by a single recrystallization of the enantioenriched product. The helical structure of **3b** was unambiguously demonstrated by X-ray crystallography, and the absolute configuration of **3b** was determined to be *M* on the basis of the Flack parameter.



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