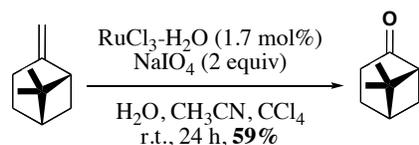


Excerpts of Dr. B's dissertation: "Novel (-)- β -Pinene-Derived Amino Alcohols as Asymmetric Directors for the Addition of Organozinc Reagents to Aldehydes" *UC Santa Cruz, 2010.*

EXPERIMENTAL METHODS AND COMPOUND CHARACTERIZATION

General Methods.

All reagents were commercially available, unless otherwise stated. All air and moisture sensitive reactions were carried out under argon atmosphere using flame- or oven-dried glassware and standard syringe technique. Tetrahydrofuran (THF), dichloromethane (DCM), cyclohexane, triethylamine (Et₃N), morpholine, *tert*-butanol (*t*-BuOH), and dimethyl sulfoxide (DMSO) were distilled over CaH₂. Oxalyl chloride was distilled without drying agent prior to use. Column chromatography was carried out with Silica Gel 60. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were carried out at 300, 500, or 600 MHz. Chemical shifts are reported relative to TMS ($\delta=0$ ppm), CHCl₃ ($\delta=7.27$ ppm) or DMSO ($\delta=2.54$ ppm) for ¹H NMR and CHCl₃ ($\delta=77$ ppm) for ¹³C NMR. The following abbreviations were used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, app=apparent, sep=septet, and m=multiplet. IR spectra were carried out on NaCl plates with ν_{\max} in inverse centimeters. Optical rotations were obtained on a digital polarimeter at 20 °C. High resolution mass measurements were obtained on a benchtop ESITOF mass spectrometer.



(+)-Nopinone. NaIO₄ (44.96 g, 210 mmol) was added to a 2-L round-bottom flask equipped with a magnetic stir bar and dissolved in water (300 mL), CCl₄ (200 mL), and CH₃CN (200 mL). (-)- β -Pinene (13.88 g, 102.0 mmol) was added followed by RuCl₃·3H₂O (457 mg, 1.7 mmol). The reaction was stirred overnight while open to the atmosphere (24 h). The crude reaction mixture was filtered through a pad of celite and rinsed with DCM, creating two distinct layers. The aqueous layer was extracted with DCM (3 x 100 mL). The combined organic extracts were washed with water (2 x 30 mL), dried (MgSO₄), filtered, and concentrated *in vacuo* to a black liquid. This was purified by column chromatography (500 mL SiO₂, 100% hexane to elute β -pinene, 4:1 Hexane/EtOAc to elute nopinone) and the nopinone fractions were concentrated to a clear oil (8.3 g, 59% yield). ¹H NMR (CDCl₃, 600 MHz) δ (ppm): 2.60 (m, 1H), 2.57 (m, 1H), 2.53 (m, 1H), 2.35 (ddd, *J*=19.2 Hz, *J*=9.6 Hz, *J*=1.8 Hz, 1H), 2.24 (tt, *J*=6.6 Hz, *J*=1.8 Hz, 1H), 2.05 (dddd, *J*=13.2 Hz, *J*=9.0 Hz, *J*=3.6 Hz, *J*=1.8 Hz, 1H), 1.95 (m, 1H), 1.58 (d, *J*=10.2 Hz, 1H), 1.33 (s, 3H), 0.86 (s, 3H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm): 215.3, 58.0, 41.3, 40.4, 32.8, 25.9, 25.3, 22.2, 21.4. bp 74-76 °C (2 mm Hg), $[\alpha]_D^{22} +34.43^\circ$ (c 4, MeOH), IR (neat) 1714 cm⁻¹.