Supporting Information:

Synthesis of New Chiral 2,2'-Bipyridine Ligands and their Application in the Copper-Catalyzed Asymmetric Allylic Oxidation and Cyclopropanation

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Contents

1. Experimental procedure for the preparation of (+)-Nopinone (**10**).
2. ¹H and ¹³C NMR spectra of compounds **3-5**, **12**, **13**, **34**, **42**, and **46**.

(+)-Nopinone (+)-11. A solution of (–)-β-pinene (–)-**10** (40.0 g, 293.6 mmol) in a mixture of methanol (80 mL) and dichloromethane (80 mL) was cooled to -78°C in a three-neck, round-bottomed flask. While the mixture was stirred at the same temperature, ozone was bubbled through the solution by means of a sinter-glass-ended tube for 20 h, until the blue color persisted. The reaction progress was monitored by TLC (petroleum ether-AcOEt, 95:5). Nitrogen was then bubbled through the reaction mixture for 30 min, which was then allowed to warm to room temperature. Zinc powder (57.6 g, 880 mmol, 3 equiv) and acetic acid (84 mL, 1.468 mol, 5 equiv) were then added carefully, portionwise, over 1 h period. (**CAUTION!** The reaction mixture tends to bubble off. Effective stirring and a 2L beaker recommended). The resulting suspension was filtered and the solid material was washed with dichloromethane repeatedly. The organic layer was carefully washed with saturated aqueous NaHCO₃ solution. The aqueous layer was extracted with dichloromethane (3 × 60 mL), the combined organic layers were washed with water (3 × 100 mL), dried over Na₂SO₄ and the solvent was evaporated *in vacuo* to give the crude nopinone (32 g, 80%), which was of sufficient purity for the subsequent reactions. The latter product was further purified by vacuum distillation (bp 92-94 °C, 17 mm Hg) to afford (+)-nopinone (+)-**11** (26 g, 65%) as a colorless liquid, identical with an authentic sample: ¹H NMR δ 0.79 (s, 3 H), 1.26 (s, 3 H), 1.51 (d, *J* = 10.2 Hz, 1 H), 1.87-1.99 (m, 2 H), 2.15-2.19 (m, 1 H), 2.24-2.31 (m, 1 H), 2.44-2.54 (m, 3 H).

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