Supporting Information

Kinetic Resolution and Unusual Regioselectivity in Palladium-Catalyzed Allylic Alkylations with a Chiral P,S Ligand

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Experimental methods: All synthetic manipulations were carried out using standard Schlenk techniques under inert atmosphere. Dichloromethane and THF were distilled over appropriate drying agents prior to use. Allylic substrates were prepared by stirring the racemic alcohol with the appropriate acid chloride in Et₂O in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine at room temperature for 12 h. Allylpalladium chloride dimer was prepared according to a published procedure¹. (*S*)-BINAP and NaSbF₆ (Strem) were used without further purification. All spectra were recorded on either a Bruker 400 or 500 MHz spectrometer. Enantiomeric excesses were determined by ¹H NMR chiral shift experiments using (+)-Eu(hfc)₃. Absolute configurations were assigned based on comparison of the sign of their optical rotations to their literature values (See Table S1). Optical rotations were measured on a Perkin-Elmer model 341 polarimeter at 589 nm and 25 °C, using a 1 dm path length.

Preparation of (*S*)-BINAP(S) (1). A flame-dried flask was charged with (*S*)-BINAP (2.08 g, 33.4 mmol) and sulfur (107 mg, 33.4 mmol). The solids were placed under inert atmosphere, and THF was added (40 mL). The resulting suspension was stirred at RT until the solution became clear. The solvent was removed under reduced pressure to leave a mixture of (*S*)-BINAP, (*S*)-BINAP(S), and (*S*)-BINAP(S)₂. Column

chromatography over silica gel with 4:1 CH₂Cl₂: hexanes as eluent provided **1** as a white powder (554 mg, 25%). Spectral characteristics of this compound were consistent with a published report.²

Preparation of (S)-[(η^3 -allyl)Pd(BINAP(S))SbF₆] (2). To a flame-dried flask was added [(η^3 -allyl)PdCl]₂ (14 mg, 0.038 mmol), (S)-BINAP(S) (50 mg, 0.076 mmol), and NaSbF₆ (40 mg, 0.154 mmol). The solids were placed under inert atmosphere, and CH₂Cl₂ (5 mL) was added. The resulting yellow suspension was stirred at room temperature for 12 h, filtered through a pad of Celite, and concentrated under reduced pressure to leave the product as a yellow powder (68 mg, 86%) which was dried under vacuum (68 mg, 86%). Anal. Calcd for C₄₇H₃₇F₆ P₂PdS₂Sb.0.5 CH₂Cl₂: C, 52.80; H, 3.54. Found: C, 52.54; H 3.82. Prolonged heating under vacuum yields a product with no remaining methylene incorporation, as indicated by ¹H NMR. This compound exists as a 52:48 mixture of diastereomers in chloroform-*d* solution. **Major Diastereomer:** ¹H NMR (400 MHz, CDCl₃): δ 8.2-6.0 (32 H); 5.54 (1 H, dddd, *J* = 6.9, 7.3, 12.6, 13.6 Hz); 4.33 (1 H, ddd, *J*_{P-H} = 7.3 Hz, *J* = 7.3, 2.3 Hz); 4.25 (1 H, d, *J* = 6.9 Hz); 3.34 (1 H, dd, *J*_{P-H} = 10.5 Hz, *J* = 13.6 Hz); 2.32 (1 H, d, *J* = 12.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 43.76 (*P*=*S*, *J* = 4 Hz); 27.81 (*P*, *J* = 4 Hz); ¹³C NMR (125 MHz, CDCl₃, allyl resonances only): δ 120.1 (central, *J*_{P-C} = 6 Hz); 76.4 (*trans* to *P*, *J*_{P-C} = 30 Hz); 67.7 (*trans* to *S*). **Minor Diastereomer:** ¹H NMR (400 MHz, CDCl₃): δ 8.2-6.0 (32 H); 5.18 (1 H, dddd, *J* = 6.9, 7.3, 12.3, 13.6 Hz); 4.79 (1 H, ddd, *J*_{P-H} = 7.3 Hz, *J* = 7.3 Hz, 2.3); 3.67 (1 H, d, *J* = 6.9 Hz); 3.20 (1 H, dd, *J*_{P-H} = 10.5 Hz, *J* = 13.6 Hz); 2.67 (1 H, d, *J* = 12.3 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 42.90 (*P*=*S*, *J* = 4 Hz); 24.88 (*P*, *J* = 4 Hz); ¹³C NMR (125

MHz, CDCl₃, allyl resonances only): δ 118.0 (central, J_{P-C} = 6 Hz); 80.4 (*trans* to P, J_{P-C} = 30 Hz); 64.0 (*trans* to S).

Typical procedure for allylic alkylation. A flame-dried flask was charged with **2** (90 mg, 0.086 mmol) and THF (35 mL) and placed under inert atmosphere. *Rac*-3-buten-2-yl benzoate **5a** (300 mg, 1.7 mmol) was added as a solution in 5 mL THF and the mixture was cooled to -30 °C. A precooled solution of sodium dimethylmalonate (mg, mmol) in 5 mL THF was then added. All reactions were generally complete in <5 min. The reaction mixture was then poured into an excess of pentane (150 mL), filtered through a pad of Celite, and the solvent removed under reduced pressure to leave the enantiomerically enriched **5a** and its corresponding alkylated products **5b** and **5c**. The products and reactant were separated via flash column chromatography over silica gel with 5:1 pentane: Et₂O as eluent, providing first pure **5a** (86 mg), followed by isomers **5b/5c** (193 mg), which were not separated from each other.

Table S1. Absolute Configuration Data for Compounds 3-5.

Compound	Sign of Optical Rotation, 589 nm	Enantiomer that Shifted Further Downfield with (+)-Eu(hfc) ₃ , Solvent
(<i>R</i>)- 3a ³	+	(<i>S</i>), CDCl ₃
(<i>S</i>)- 3b ⁴	-	(<i>R</i>), CDCl ₃
(<i>R</i>)- 4a ⁵	-	(<i>R</i>), C ₆ D ₆
(<i>R</i>)- 4b [*]	-	(<i>R</i>), C ₆ D ₆
(<i>R</i>)- 5a ⁶	-	(<i>S</i>), C ₆ D ₆
(<i>R</i>)- 5b ⁷	-	(<i>S</i>), C ₆ D ₆

^{*} Assignment made by comparison to (*R*)-**5b**.

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