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SUPPLEMENTARY INFORMATION

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Highly enantioselective rhodium-catalyzed cross-coupling of boronic acids and racemic allyl halides

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Highly Enantioselective Rhodium-Catalyzed Cross-Coupling of Boronic Acids and Racemic Allyl Halides

Supplementary Methods

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Synthesis and recrystallization of $[Rh(cod)OH]_2$

Supplementary reagents

- $[Rh(cod)Cl]_2$ (prepared according to the procedure of Schenck *et al.*)[1]
- KOH (Fisher Scientific, reagent grade)
- Distilled H_2O
- Acetone (Sigma Aldrich, CHROMASOLV®, for HPLC, ≥99.8%, degassed by bubbling through with argon)
- Dichloromethane (collected fresh from a mBraun SPS-800 solvent purification system)
- Hexane (Merck, for HPLC, ≥97.0%, degassed by bubbling through with argon)

Supplementary procedure

$[Rh(cod)(Cl)]_2$ (493 mg, 1.0 mmol, 1 equiv.) was placed in a 50 mL flame dried round bottom flask containing a Teflon-coated magnetic stir bar and the flask was fitted with a rubber septum. The flask was then connected to a vacuum-argon manifold, put under reduced pressure and then carefully back-filled with argon. The reaction flask remained connected to the argon line with a flow of inert gas for the remainder of the experiment. Degassed acetone (20 mL) was added using a syringe. A freshly prepared aqueous solution of KOH (1.5 M, 6.8 mL, 10.0 mmol, 10 equiv.) was then added to the stirred suspension via a syringe. The mixture was allowed to stir at room temperature for 4 hours before approximately half of the volume of solvent was removed under reduced pressure at 30 ^{o}C using a rotary evaporator. Water (6 mL) was then added and the resulting yellow suspension was stirred for 5 min. The yellow solid was filtered off from the suspension using a sintered funnel under a flow of argon. The collected yellow solid was washed with water (3 x 2 mL) and then dried under high vacuum for 3 hours.

Recrystallization: $[Rh(cod)OH]_2$ was placed in a flame dried round bottom flask containing a Teflon-coated magnetic stir bar and fitted with a reflux condenser. Approximately 20 mL of dichloromethane per 300 mg of $[Rh(cod)OH]_2$ was added. The mixture was heated to reflux for 10-20 minutes until a transparent yellow solution was formed (if the solution remains opaque, add more dichloromethane). After the yellow solution had become transparent, hexane (approximately 20 mL per 300 mg of $[Rh(cod)OH]_2$) was added while still heating until a precipitate began to form. The flask was then cooled in an ice bath and more hexane (10-20 mL per 300 mg of $[Rh(cod)OH]_2$) was added. The precipitate was filtered off using a sintered funnel under a flow of argon and dried under high vacuum for 1 hour. The resulting

yellow $[Rh(cod)OH]_2$ powder (250 mg, 0.55 mmol, 55 % yield) was stored in a screw-cap vial under argon in the dark.

We recommend that $[Rh(cod)OH]_2$ should be tested using a known reaction before new reactions are attempted.

Physical data as previously described by Uson *et. al.*[2]

Synthesis of 4-bromophenylboronic acid pinacol ester

Supplementary reagents

- 4-bromophenylboronic acid (Fluorochem, cat. no. 010981)
- Pinacol (Sigma-Aldrich, cat. no. 221171)
- Acetonitrile (Merck, for HPLC, gradient grade, ≥99.9%)

4-bromophenylboronic acid (2.53 g, 12.4 mmol) and pinacol (1.50 g, 12.7 mmol) were added to a 50 mL round bottomed flask containing a Teflon-coated magnetic stir bar under an open air atmosphere at room temperature. Acetonitrile (10 mL) was added using a syringe, and upon stirring the initially formed white suspension turned clear after about 30 minutes. The solvent was then removed using a rotary evaporator under reduced pressure to afford the corresponding boronic ester as a white solid (3.51 g, 12.4 mmol, quantitative yield) which was used without further purification.

Physical data as previously described by Zimmer *et. al.*[3]

References

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2. Uson, R., Oro, L. A., Cabeza, J. A., Bryndza, H. E. & Stepro, M. P. in *Inorganic Syntheses*, *Volume 23;* Kirschner, S., (Ed); pp 126–130 (John Wiley & Sons, Ltd, 2007).
3. Zimmer, D. P., Talley, J. J., Microbia, Inc., WO2006/122117 (2006).