A Novel General Phosphine Ligand for Suzuki–Miyaura Cross-Coupling

**Significance:** A new class of biaryl monophosphorous ligands with outstanding properties was developed. The ligand BI-DIME is highly air-stable and readily accessible in kilogram scale.

**Comment:** BI-DIME was tested as ligand in the palladium-catalyzed Suzuki–Miyaura reaction allowing for the first time the high-yielding cross-coupling of 2,4,6-tri-isopropylboronic acid with ortho-substituted aryl bromides.