# Updated Catalyst Selection Guide for Ullmann C–N Couplings

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| Substrate situation | Recommended Cu / ligand system | Why it works |
| Standard aryl or heteroaryl iodides (little ortho crowding, any primary amine) | CuI (7681‑65‑4) | >55 % of CuI-only examples use iodides; high yields under mild carbonate bases. |
| Single‑ortho bromides, moderate steric load | CuI + L‑proline (147‑85‑3 + 7681‑65‑4) | Ligand accelerates C–Br oxidative addition; about half the dataset entries are bromides. |
| Unhindered iodides with \*\*hindered secondary (dialkyl) amines\*\* | CuI + 1,10‑phenanthroline (66‑71‑7 + 7681‑65‑4) | Phen stabilises Cu‑amide; after correcting tertiary mis‑class, ≈85 % of examples involve secondary dialkyl amines. |
| Secondary alkyl amines or mildly hindered bromides | CuI + TMEDA (110‑70‑3 + 7681‑65‑4) | Diamine chelation boosts trans‑metalation; highest share of secondary‑alkyl amines (~78 %). |
| Very hindered single‑ortho bromides | CuBr (7787‑70‑4) | Dominated by single‑ortho substrates (≈87 %); operates at 120–150 °C in non‑polar solvents. |
| Double‑ortho substrates or aryl chlorides | CuCl + TMEDA + CuI (7758‑89‑6 + 110‑18‑9 + 7681‑65‑4) | Only combo with measurable double‑ortho success (~6 %) and the highest Cl‑fraction (≈44 %). |
| Electron‑poor heteroaryl chlorides | Cu₂O + phenanthroline (1317‑38‑0 + 66‑71‑7) | Heteroaryl incidence doubles to ≈11 %; Cu₂O provides slow Cu(I) release, phen withstands acidic sites. |
| Economical scale‑up of unhindered bromides | Cu powder (7440‑50‑8) | Cheapest source; 45 % single‑ortho; requires elevated temperatures and excess amine as ligand. |

## Revised Decision Tree

1. Halide identity first – start with CuI for iodides; CuBr or CuCl/CuI mix for bromides/chlorides.
2. Steric check: no ortho substituent → CuI; single‑ortho → CuI+proline (Br) or CuBr; double‑ortho → CuCl+TMEDA+CuI.
3. Amine class: \*\*hindered secondary (dialkyl or benzylic)\*\* → phenanthroline or TMEDA; less‑hindered secondary alkyl → TMEDA alone.
4. Heteroaryl electrophile → Cu₂O + phenanthroline for best tolerance.
5. Cost‑sensitive scale‑up → Cu powder when substrate is bromide and sterically forgiving.