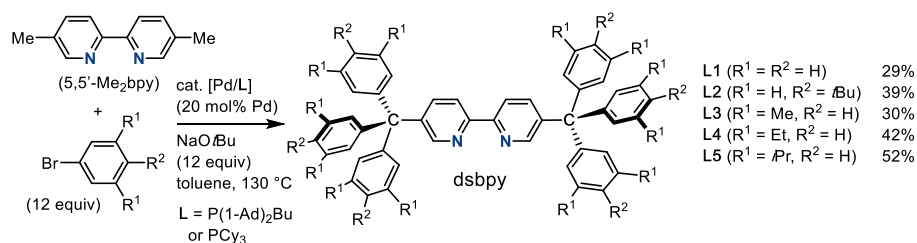


Dumbbell-Shaped 2,2'-Bipyridines: Controlled Metal Monochelation and Application to Ni-catalyzed Cross-Couplings

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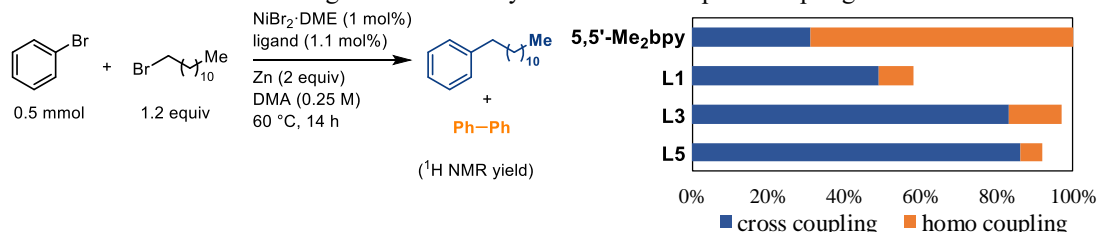
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2,2'-Bipyridine (bpy) ligands have been widely used in transition metal catalysis as N,N'-bidentate ligands, especially in recent Ni catalysis.¹ Despite their great success in many catalysis, traditional bpy ligands have two major problems: formation of multi-ligated complexes, [ML₂] and [ML₃],² and undesired bimetallic pathways.³ In this research, we aimed to address those problems by introducing bulky substituents at N-β-positions of bpy, which do not hamper the catalytic reactions by steric hindrance in the vicinity of the metal but develop outside the boundary of the catalytic space. Thus, we designed and synthesized dumbbell-shaped bipyridine (dsbpy) ligands bearing bulky triarylmethane substituents (Scheme 1, **L1–L5**). The dsbpy and Ni^{II} titration study clearly showed the monochelation properties of dsbpys (**L3–L5**). The ligands highly outperformed traditional bpy ligands in the representative Ni catalysis such as the Ni-catalyzed cross-electrophile coupling reaction⁴ (Scheme 2) and Ni/photoredox dual catalytic decarboxylative coupling reaction.



Scheme 1. The design and synthesis of the dumbbell-shaped bipyridine and phenanthroline ligands

Scheme 2. The effect of the ligands in Ni-catalyzed cross-electrophile coupling reaction



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