

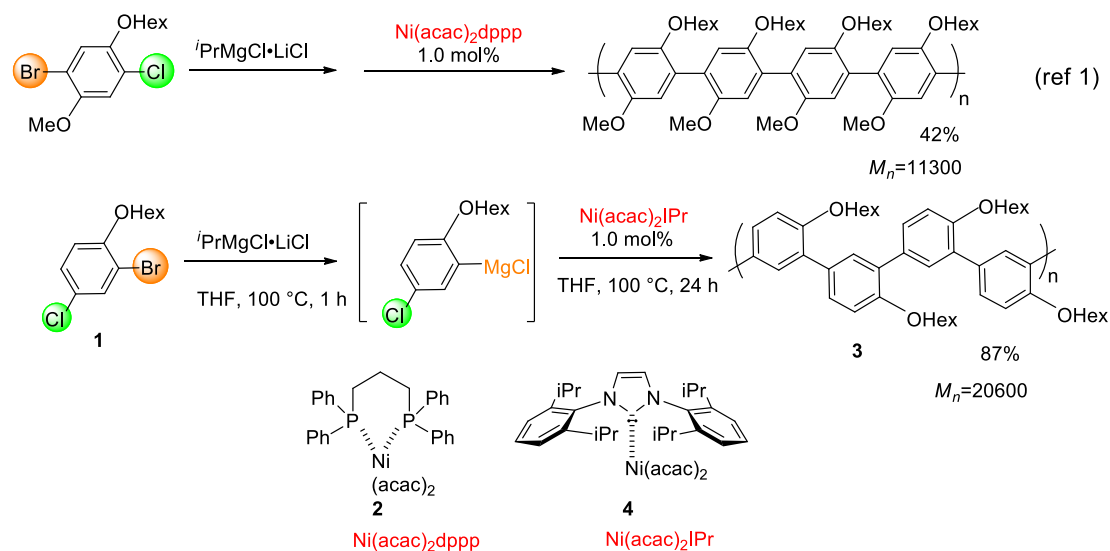
## Nickel-catalyzed synthesis of poly(1,3-phenylene) with controlled regioregularity

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We have recently reported synthesis of regioregular poly(1,4-phenylene) using a nickel catalyst with bidentate phosphine as a ligand.<sup>1</sup> Our next interest has turned to the synthesis of high molecular weight and regioregular poly(1,3-phenylene), which has not been reported so far. We describe herein the synthesis of poly(1,3-phenylene) of high molecular weight with controlled regioregularity catalyzed by nickel(II)-N-heterocyclic carbene (NHC) complex.

When the reaction of 4-bromo-2-chloro-hexyloxybenzene (**1**) with a Grignard reagent was carried out, selective metal-halogen exchange took place at the bromine atom. Following addition of nickel catalyst Ni(acac)<sub>2</sub>(dppp) (**2**), which has been effective for poly(1,4-phenylene) synthesis, only afforded polymer (**3**) with an insufficient molecular weight ( $M_n = 2800$ ), while the use of N-heterocyclic carbene (NHC) **4** revealed to give **3** in 87% yield with a remarkably high molecular weight ( $M_n = 20600$ ). Such a high molecular weight has not been achieved with a conventional synthesis of poly(1,3-phenylene).<sup>2</sup>



- 1) Shibuya, Y.; Nakagawa, N.; Miyagawa, N.; Suzuki, T.; Okano, K.; Mori, A. *Angew. Chem. Int. Ed.* **2019**, 58, 9547.
- 2) Suda, K.; Akagi, K. *Macromolecules* **2011**, 44, 9473.