Accessing 1*H*-Indenyl and Dihydro-*s*-Indacenyl Magnesium Reagents via Iron-catalyzed C–O Activation/Acetylenic Cyclization with Magnesium Powder

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Carbon-bridged phenylene vinylene structure, previously reported by our group has found to be applicable in prototype organic photovoltaic device regarding its remarkable photophysical properties and stability. The conventional linear synthesis started from commercially available 1-bromo-2-iodobenzene via 3-lithioindene intermediate using lithium naphthalenide, which guarantees high reactivity while severely limits the substrate scope. Transition-metal catalyzed nucleophilic addition and cross-coupling reactions involving functionalized organometallic reagents are of great importance for carbon–heteroatom or carbon–carbon bond formation in a mild manner².

Here we report a mild and effective synthesis of new indenes and indacenes via iron-catalyzed C–O activation and acetylenic cyclization. An arylalkyne substrate possessing methoxy group was successfully cyclized via 1*H*-Indenyl and Dihydro-*s*-Indacenyl magnesium intermediate using magnesium as a reductant, lithium chloride as an additive and catalytic amount of iron(II) chloride and triphenylphosphine ligand. A few examples of indenes trapped with various electrophiles are presented.

$$R^{1} \stackrel{\stackrel{\longleftarrow}{\text{II}}}{ } \stackrel{Ar}{ } \stackrel{Ar$$

1) a). Zhu, X.; Mitsui, C.; Tsuji, H.; Nakamura, E. J. Am. Chem. Soc. **2009**, 131, 13596–13597; b) Zhu, X.; Tsuji, H.; Lopez Navarrete, J. T.; Casado, J.; Nakamura, E. J. Am. Chem. Soc., **2012**, 134, 19254-19259. 2) Liu, Y.; Wang, L.; Deng, L. J. Am. Chem. Soc. **2016**, 138, 112–115.