SR2024 - POW11 - Solution

The first step is an intermolecular **Stille**-coupling. The reaction begins with the oxidative addition of the C-I bond. After transmetalation of the stannane, reductive elimination gives the C-C coupling product A.

The reaction rate for oxidative addition is as follows: I > Br > OTf > CI. Therefore the palladium(0)-complex reacts first with the aryl iodide and not the aryl triflate.

$$\begin{array}{c} \text{H-base}^{+}\text{OTf} \\ \text{Base-Mediated} \\ \text{Reduction} \\ \text{base} \\ \end{array}$$

$$\begin{array}{c} \text{TsMeN} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{OTf} \\ \text{H} \\ \text{OTf} \\ \end{array}$$

$$\begin{array}{c} \text{Oxidative} \\ \text{Addition} \\ \text{R}^{1} \\ \text{OTf} \\ \text{H} \\ \text{OTf} \\ \end{array}$$

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$$\begin{array}{c} \text{Oxidative} \\ \text{Addition} \\ \text{R}^{1} \\ \text{OTf} \\ \text{NMeTs} \\ \end{array}$$

$$\begin{array}{c} \text{Oxidative} \\ \text{OTf} \\ \text{H} \\ \text{H} \\ \end{array}$$

$$\begin{array}{c} \text{Oxidative} \\ \text{Addition} \\ \text{NMeTs} \\ \text{OTf} \\ \text{OTf} \\ \text{NMeTs} \\ \end{array}$$

$$\begin{array}{c} \text{Oxidative} \\ \text{Oxidative} \\ \text{Addition} \\ \text{Oxidative} \\ \text{NMeTs} \\ \text{Oxidative} \\$$

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Transmetallation

The second step of the reaction is a **Heck**-reaction. The reaction starts again with an oxidative addition of the triflate. Triflates are only weakly coordinating to the Pd and therefore a cationic intermediate arises and the olefin coordinatively saturates the palladium. After olefin insertion, beta-hydride elimination gives the product with the more stable trans-double bond and a palladium hydride complex. In presence of base, the palladium hydride is reduced back to Pd(0) to close the catalytic cycle.