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Modular and Regioselective Synthesis of All-Carbon Tetrasubstituted Olefins Enabled by an Alkenyl Catellani Reaction

Regioselective Synthesis of Tetrasubstituted Olefins via an Alkenyl Catellani Reaction

**Significance:** The Dong group reports a general method for the bis-functionalization of alkenes via a Catellani reaction. This method affords unsymmetrical tetrasubstituted alkenes. The use of a functionalized norbornene gave high yields and selectivities.

**Comment:** Utilization of the N-methyl amide-substituted norbornene (N11) was optimal as it gave the highest yield of product and eliminated the formation of the cyclopropane adduct. A mechanism was proposed that was supported with detailed kinetic analysis.

**Equation:**

\[
\text{R}_1\text{OTf} + \text{R}_2 + \text{N}11 \overset{\text{Pd(cod)Cl}_2, \text{N}11 (50 \text{ mol\%})}{\rightarrow} \text{R}_1\text{R}_2\text{H}^1
\]

\[
\text{MeO}_2\text{C} - 2 \overset{\text{Pd(0)}}{\rightarrow} \text{MeO}_2\text{C}
\]

\[
\text{N}11 \overset{\text{Pd(0)}}{\rightarrow} \text{MeO}_2\text{C}
\]

**Scheme:**

- **R**
- **OTf**
- **R1**
- **R2**
- **N11**
- **Ph-DavePhos**
- **Cs_2CO_3, 5-CF_3-2-pyridinol**
- **1,4-dioxane, 100 °C**

- **62% yield**
- **92% yield**
- **62% yield**
- **46% yield**

**Key words:** Catellani reaction, palladium catalysis, C–H functionalization