

Nickel-Catalyzed Decarboxylative C–Si Bond Formation: A Regioselective Cross-Coupling Between Trialkyl Silanes and α,β -Unsaturated Carboxylic Acids

Bharat Kumar Allam*, Sadaf Azeez, Jeyakumar Kandasamy

Department of Chemistry, Faculty of Basic Sciences, Rajiv Gandhi University, Arunachal Pradesh, India

Department of Chemistry, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh, India

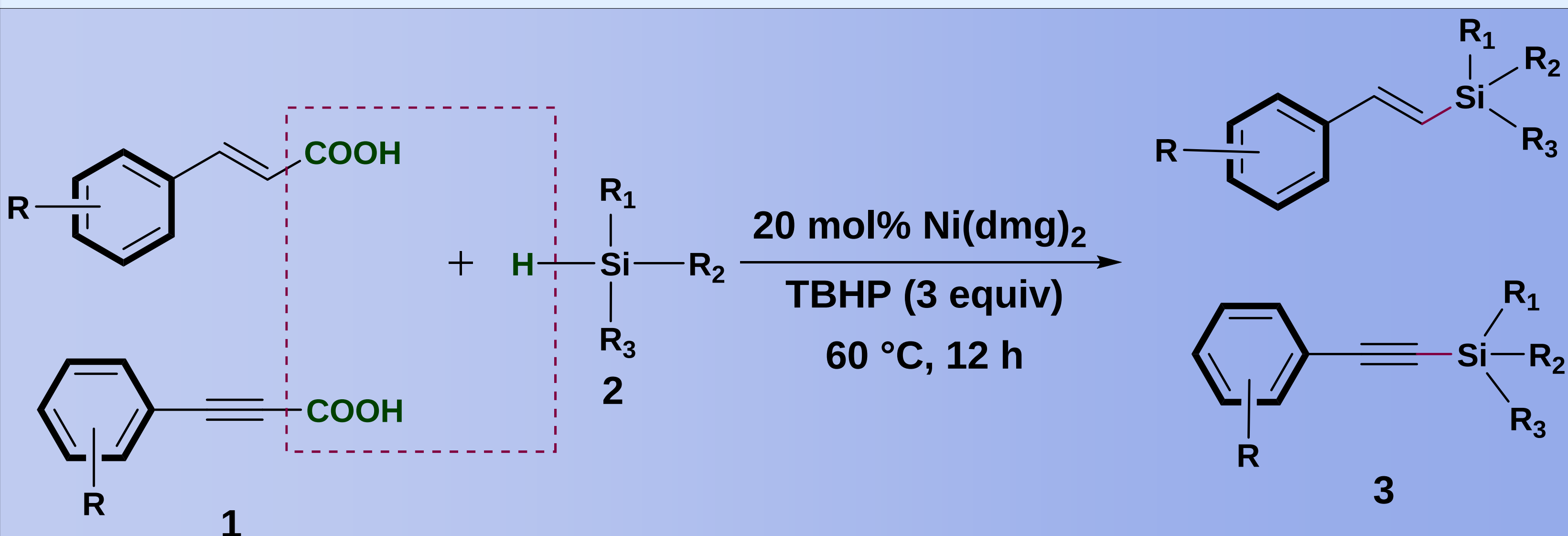
*E-mail: allambharatkumar@gmail.com

Abstract:

This report presents the first example of nickel-catalyzed mild decarboxylative cross-coupling reaction for the regioselective formation of C–Si bond. An easily accessible and significantly stable $\text{Ni}(\text{dmg})_2$ owes the role of key promoter. This reaction is highly functional group tolerant and offers α,β -unsaturated silanes in synthetically useful yields. The reaction gives access to the successful utilization of otherwise difficult trialkyl silanes as coupling partners and operates at a moderate temperature, which is beneficial to deal with highly volatile silanes.

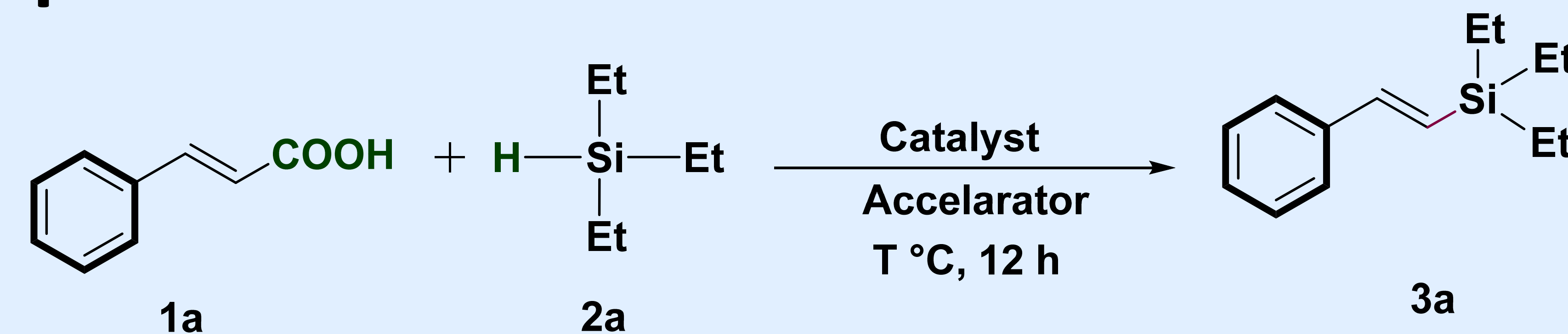
Objectives:

To develop nickel catalyzed decarboxylative silyl functionalization strategy via the reaction of trialkyl silanes with (*E*)-cinnamic acids/alkynoic acids, to deliver trialkyl(alkenyl/alkynyl)silanes.



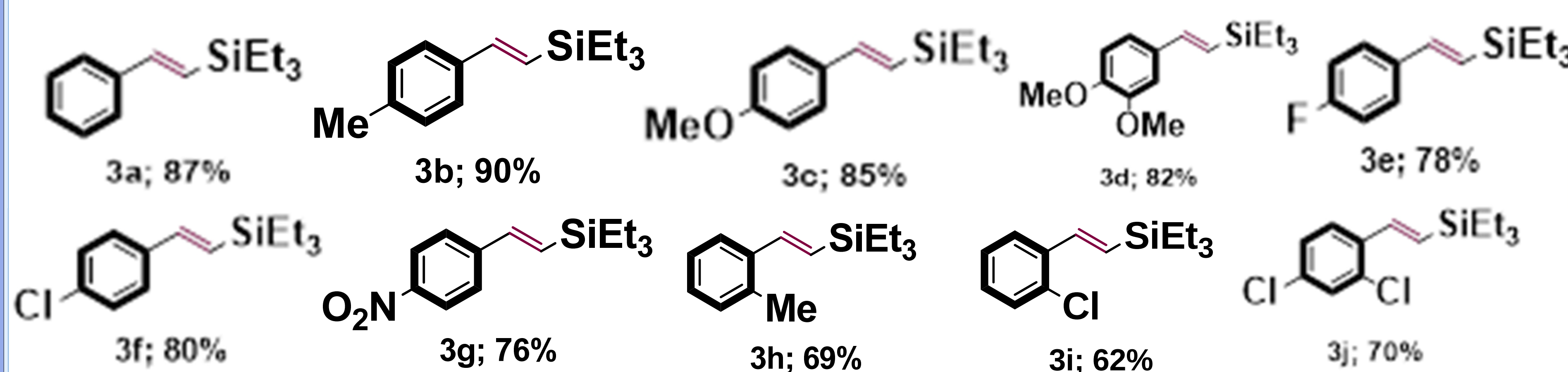
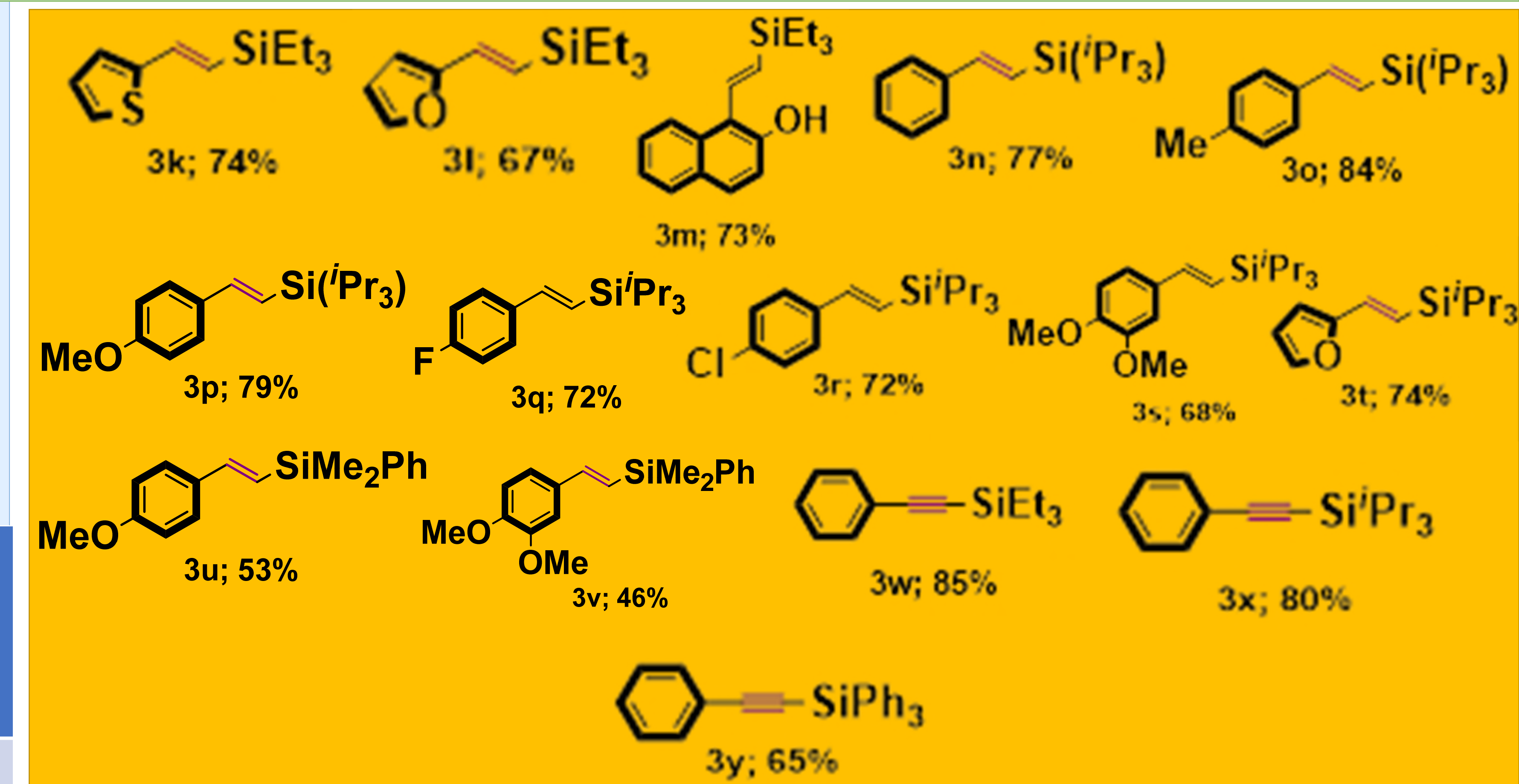
Results:

Optimization:



S. No.	Catalyst	Accelerator	T (°C)	Solvent	Yield (%)
1.	$\text{Ni}(\text{dmg})_2$ (10)	TBHP (100)	60	—	45
2.	$\text{Ni}(\text{dmg})_2$ (10)	TBHP (200)	60	—	53
3.	$\text{Ni}(\text{dmg})_2$ (10)	TBHP (300)	60	—	60
4.	$\text{Ni}(\text{dmg})_2$ (10)	TBHP (400)	60	—	40
5.	$\text{Ni}(\text{dmg})_2$ (20)	TBHP (300)	60	—	87
6.	$\text{Ni}(\text{dmg})_2$ (30)	TBHP (300)	60	—	82

The substrate scope for the decarboxylative C–Si bond formation



Conclusions:

In conclusion, we have developed a mild, selective, economical and high yielding methods for the C–Si bond formation using sustainable and cheap silane feed stocks. The application of *dmg* as a ligand tunes the Lewis acidity of the nickel and safeguard the α,β -unsaturated silanes from further nickel catalyzed C–Si bond cleavage/decomposition.

Reference:

B. K. Allam et al. Appl Organometal Chem; 2019, e5192.