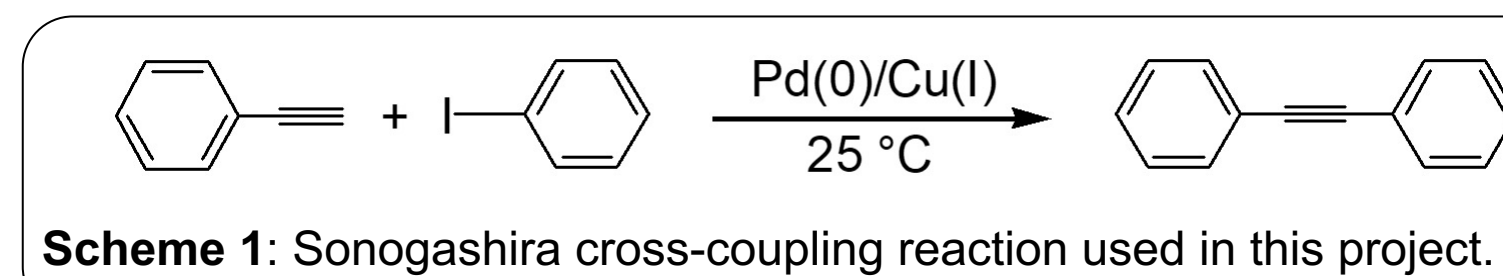


Introduction

Transition metal catalysts enable attractive synthetic pathways but some are expensive or require sophisticated syntheses. Traditional homogeneous catalysts are difficult to separate and reuse but are typically favored due to their high activity and selectivity. The difficulty of reuse and cost of replacement hinder further adoption of transition metal catalysts. Immobilized catalysts provide a possible solution by providing the advantages of homogeneous catalysts in a heterogeneous system. These immobilized catalysts^{1,2} are bound to insoluble supports, such as silica, and can be easily separated from reaction mixtures and recycled numerous times. Previous immobilized Sonogashira catalyst systems³ consist of palladium and copper immobilized as separate components. These immobilized catalysts create an active and recyclable system but may be improved by bringing the metal centers closer together as an immobilized heterobimetallic complex.

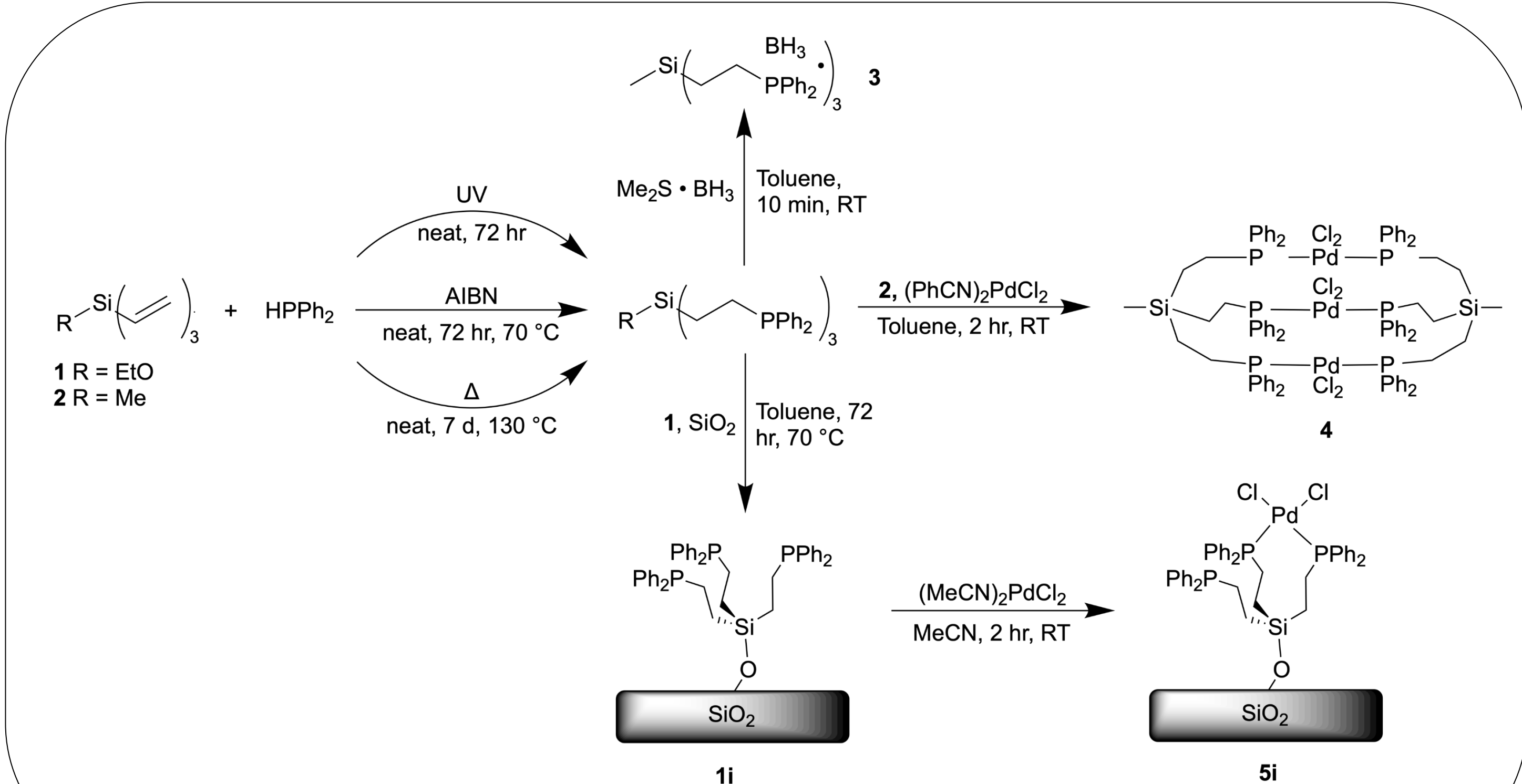
Sonogashira Catalyst Systems



The Sonogashira reaction is a prominent cross-coupling reaction for aryl halides and acetylenes. Under mild conditions, the Sonogashira reaction is catalyzed by Pd(0) and Cu(I).

Synthesis and Immobilization

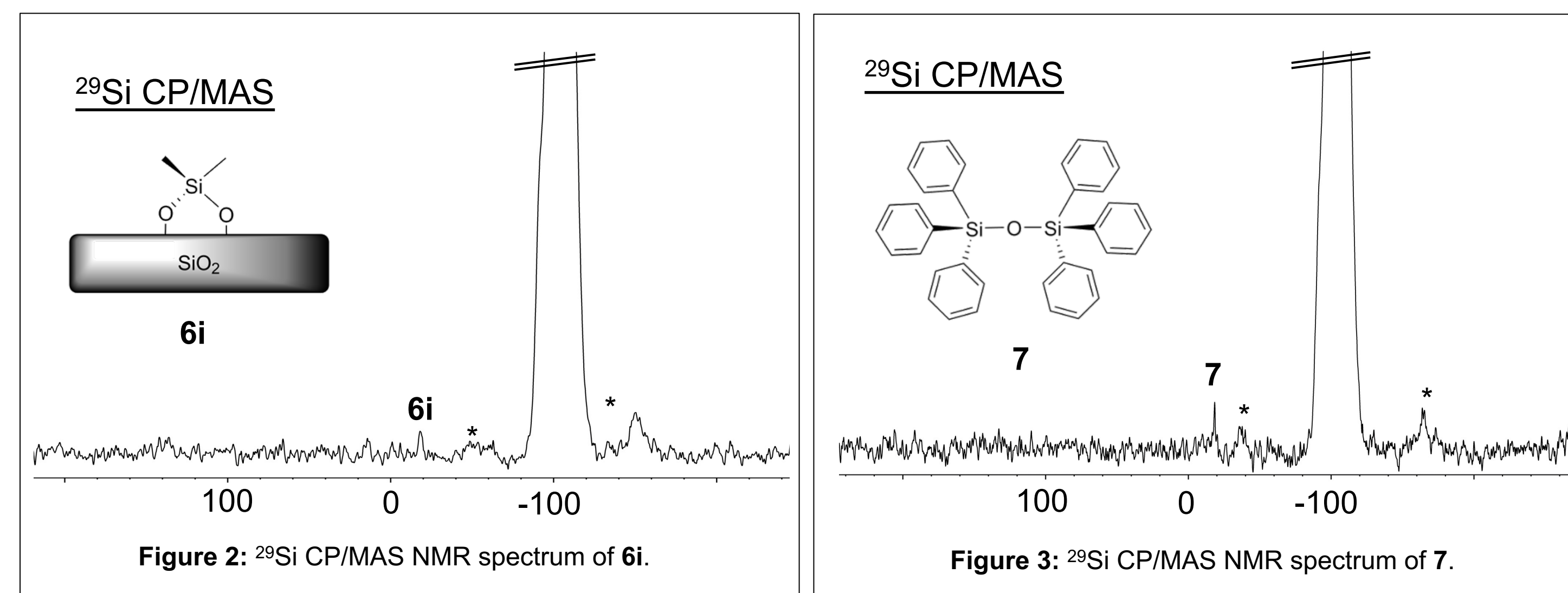
Ligand **1** has been synthesized using radical initiated hydrophosphination. Unactivated and UV driven hydrophosphination have been performed but result in lower yields and long reaction times. Functionalized silica, **1i**, was synthesized by reacting an excess (1.8 times) of ligand **1** in a suspension of rigorously dried silica with toluene at 70 °C. Reaction of ligand **2** with a PdCl₂ source or reaction of benzonitrile palladium chloride with ligand **2** results in complex **4**. Air-stable borane adducts of ligand **2** can be formed by reaction with Me₂S·BH₃ in toluene to form **3**. Literature suggests reaction of ligand **1** in solution forms a similar complex to **4**.⁴ The immobilized ligand **1i** readily coordinates to a soluble PdCl₂ source, forming complex **5i**.



Immobilization of Disiloxanes

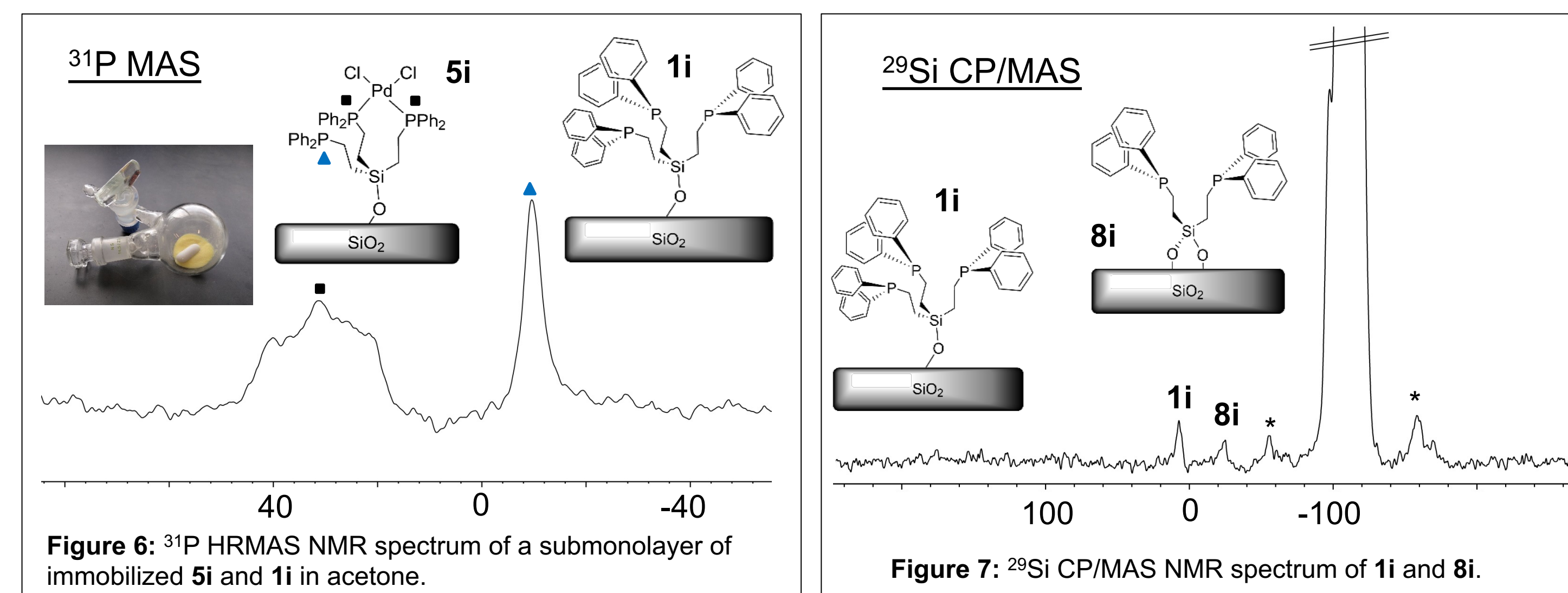
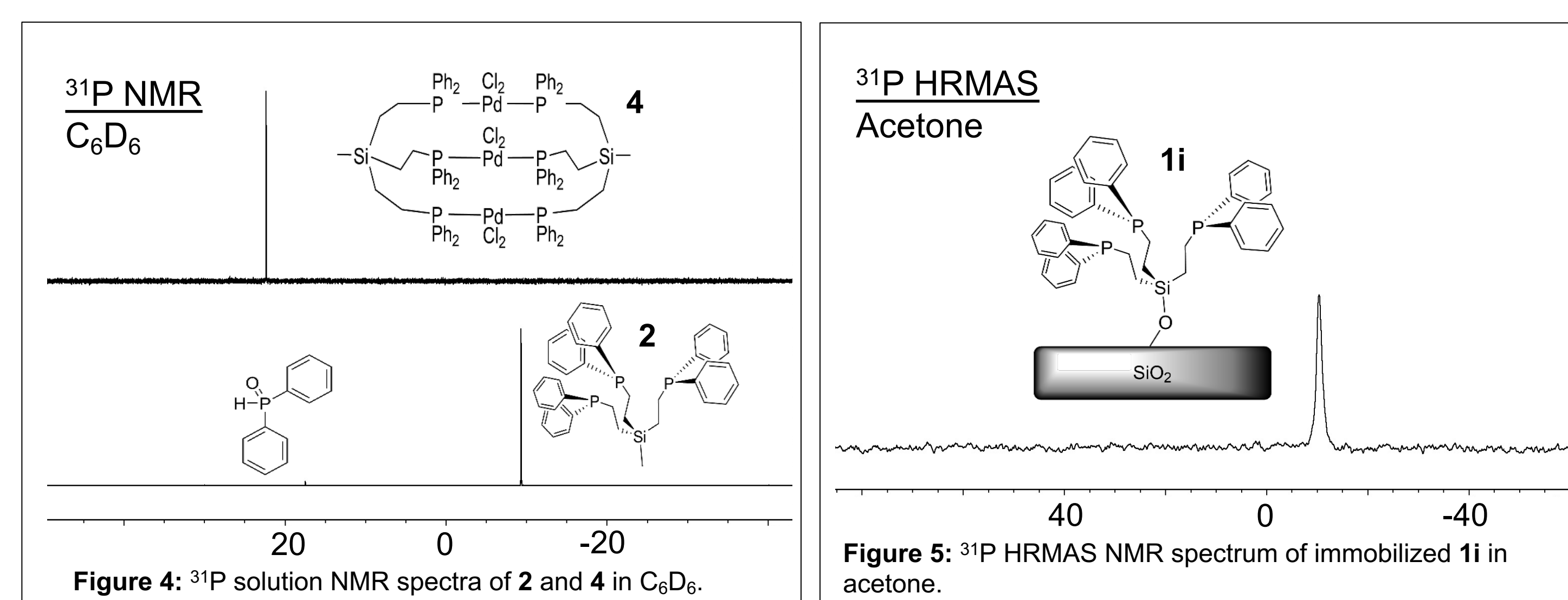
Immobilization of long-chain tripodal disiloxanes was observed by Guenther.¹ This reaction would be preferable to ethoxysilane immobilization since disiloxanes are water tolerant, have higher atom economy, and in principle result in higher surface coverage than their ethoxysilane counterparts.

Silica was dried *in vacuo* at room temperature or rigorously dried *in vacuo* at 300 °C. Hexamethyldisiloxane and hexaphenyldisiloxane were added in an amount to form a monolayer. The mixture was stirred in toluene at 90 °C overnight. The supernatant was decanted, and the silica was washed with pentane and dried *in vacuo*. Disiloxanes immobilized on room temperature dried silica did not produce measurable signals in ²⁹Si NMR. Hexamethyldisiloxane on dry silica yielded **6i** (Fig. 2), while hexaphenyldisiloxane did not react with the surface and remained crystalline (Fig. 3).



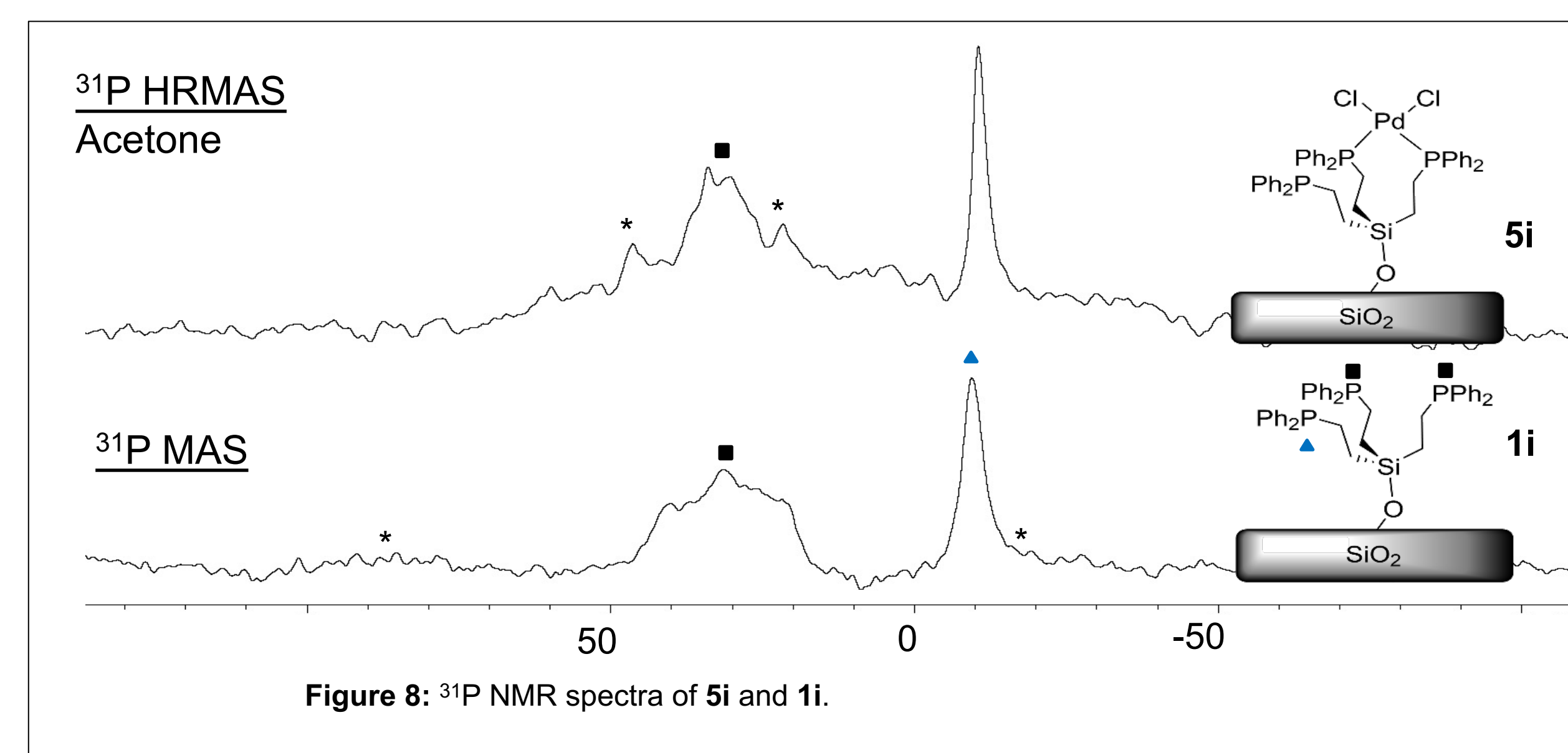
NMR of the Tripodal Pd Complex

Immobilization of **1** results in a ³¹P chemical shift of 0.55 ppm upfield and a signal halfwidth change from 5 Hz to 204 Hz, indicating that **1i** is covalently bound to the surface. Palladium complexes **4** and **5i** show a large chemical shift difference, 21.7 ppm vs. 32.9 ppm, indicating different coordination. This chemical shift change may be due a *trans* to *cis* coordination change.



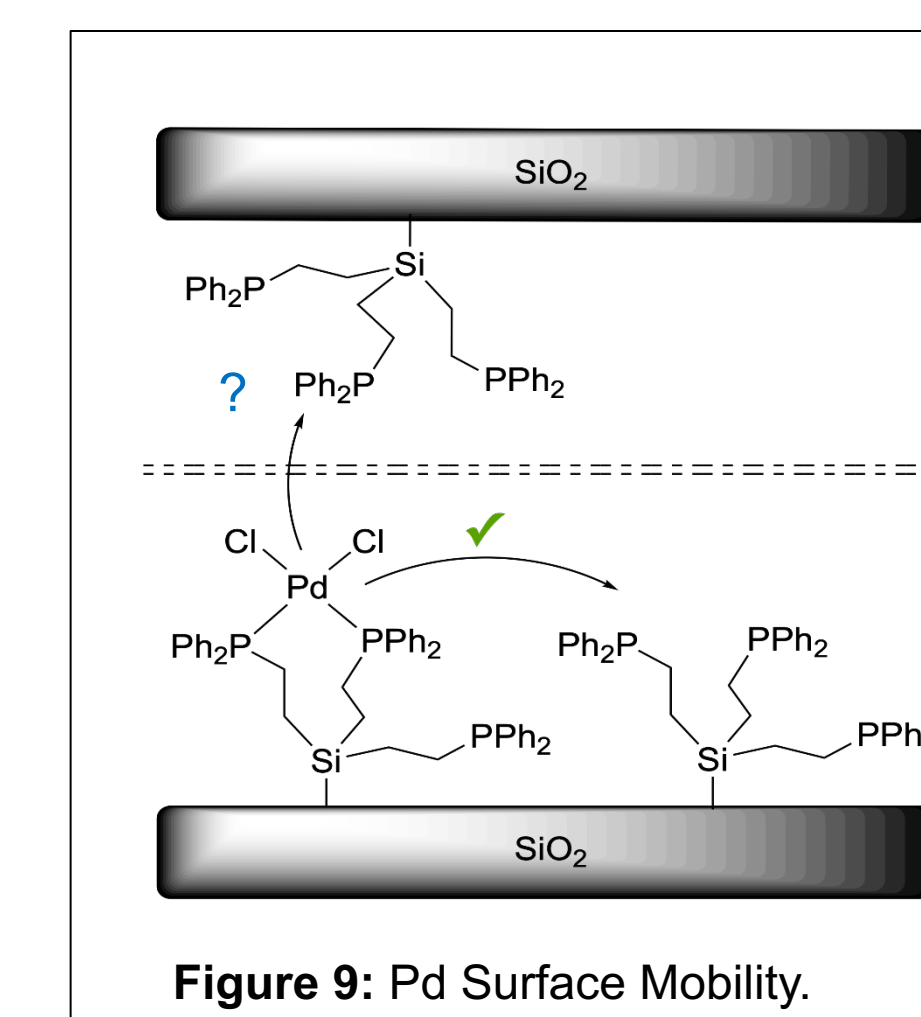
In **Figure 7** the peak at -18 ppm suggests degradation of **1i**, forming **8i**. Sharper peaks occur in the presence of a solvent (HRMAS) compared to broader peaks solely with magic angle spinning (MAS).

Surface Mobility of Palladium



In agreement with previously synthesized phosphine Pd complexes,⁵⁻⁷ the tripodal linker allows Pd mobility on the surface in solution and in the presence of uncoordinated phosphine groups. **Figure 8** shows the formation of a very broad signal with addition of solvent, with a halfwidth of 15.8 kHz and a chemical shift of 22.8 ppm.

This result is interpreted as Pd mobility on the surface, since such broadening and chemical shift change is not typically associated with HRMAS signals. The observed broadening and chemical shift change is associated with kinetics on the NMR timescale, producing a weighted average chemical shift and extremely broad signals.



Future Work

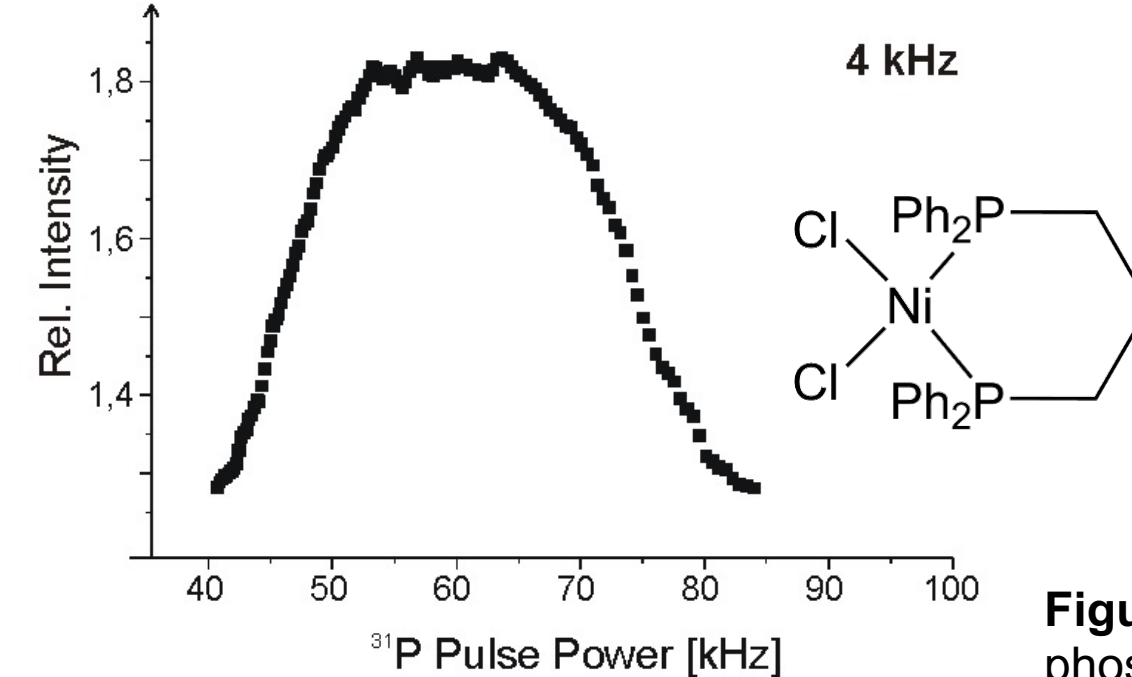
The possibility of inter-molecular palladium hopping on the surface occurring will be investigated. The solvent effects on palladium mobility will be investigated by performing HRMAS with a selection of coordinating solvents. Additionally, mobilities of the linkers can be ascertained in these solvents by comparison of linewidths, which may correlate with catalytic activity. For this purpose, the model Sonogashira reaction (Scheme 1) will be employed.

Immobilization of hexa-*n*-butyldisiloxane and the disiloxane congener of **1** will be attempted. Homogeneous and immobilized Sonogashira catalysts will be synthesized with the addition of (ACN)₄CuBF₄, and the catalytic activity will be compared with other homogeneous and immobilized catalyst systems. Single crystal X-ray diffraction structures of the ethoxysilane congener of **4** will be obtained. ³¹P-³¹P COSY and TOCSY HRMAS NMR spectra will be measured to confirm the signal assignments in **Figures 6** and **8**.

Finally, after catalytic runs the formation of Pd or mixed Pd/Cu nanoparticles will be investigated by electron microscopy.

HRMAS and CP/MAS NMR Spectroscopy

Solid-state NMR spectroscopy is a powerful technique for the characterization of surface-modified silica. High-Resolution Magic Angle Spinning (HRMAS) utilizes a slurry of solids in a solvent. An HRMAS rotor is packed with functionalized silica, then wetted with a drop of solvent. Covalently bound species are granted some mobility by the solvent, like grass blowing in the breeze, leading to solution-like line widths. This mobility allows for shorter relaxation delays, shorter measurement times, and higher resolution. Solvent-mediated kinetics can be studied using HRMAS.^{1,5-7}



Cross-Polarization Magic Angle Spinning (CP/MAS) allows measurement of surface species by transferring magnetization from easily polarized nuclei, such as ¹H, to less abundant, less receptive, or spatially close and desirable nuclei, such as ²⁹Si.²

References

- Guenther, J.; Reibenspies, J.; Blümel, J. *Mol. Catal.* **2019**, 479, 110629.
- Reinhard S., Blümel, J. *Magn. Reson. Chem.* **2003**, 41, 406-416.
- Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, 16, 2776-2786.
- Aizawa, S.-i.; Kawamoto, T.; Nishigaki, S.; Sasaki, A. *Journal of Organometallic Chemistry* **2011**, 696 (11), 2471-2476.
- Posset, T.; Blümel, J. *J. Am. Chem. Soc.* **2006**, 128, 8394-8395.
- Pope, J. C.; Posset, T.; Bhuvanesh, N.; Blümel, J. *Organometallics* **2014**, 33, 6750-6753.
- Posset, T.; Guenther, J.; Pope, J.; Oeser, T.; Blümel, J. *Chem. Commun.* **2011**, 47, 2059-2061.

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