

Electronic Supplementary Information

Selective hydrosilylation of alkynes with nanoporous gold catalyst

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General Information

For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck, 230-400 mesh). GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m x 0.25 mm capillary column, HP-5MS). Scanning electron microscope (SEM) observations were carried out using JEOL JSM-7800F instruments operated at accelerating voltages of 15 kV, respectively. EDX analysis was carried out using Oxford X-max50 with JEOL JSM-7800F operated at an accelerating voltage of 15 kV. The CV measurements were carried out in a conventional three-electrode cell at ambient temperature by using an Iviumstat electrochemical analyzer (Ivium Technology). Nanoporous gold fixed to glassy carbon electrode with nafion was employed as the working electrodes, and a saturated calomel electrode and a Pt plate were used as the reference and counter electrodes, respectively. ICP analysis was performed on Shimadzu ICPS-7510 equipment.

Fabrication of Nanoporous Gold Catalyst

AuNPore-1 (Au₉₆Al₄): Au (99.99%) and Al (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au/Al alloy (20:80, in at. %), which was manufactured to thickness of 40 μm ribbon by melt spinning method. Treatment of the resulting ribbon with 20 wt. % aqueous sodium hydroxide for 3h at room temperature resulted in the formation of the nanoporous structure by selective leaching of aluminum. The material was washed with pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (AuAl) and its composition was found to be Au₉₆Al₄ by EDX analysis.

AuNPore-2 (Au₉₈Ag₂): Au (99.99%) and Ag (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au/Ag alloy (30:70, in at. %), which was rolled down to thickness of 40 μm. The foil was cut into small pieces (2 x 5 mm square). Treatment of the resulting several chips with 70 wt. % nitric acid for 18 hours at room temperature resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with pure water, and

acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (AuAg) and its composition was found to be Au₉₈Ag₂ by EDX analysis.

AuNPore-3 (Au₉₈Al₂): AuNPore-1 was treated with 70 wt. % nitric acid for 1 hour at room temperature. The material was washed with pure water and acetone, successively. The material was dried under reduced pressure and its composition was found to be Au₉₈Al₂.

AuNPore-4 (Au₉₃Ag₃Al₄): Au (99.99%), Ag (99.99%) and Al (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au:Ag:Al alloy (19:1:80, in at. %), which was manufactured to thickness of 40 μm ribbon by melt spinning method. Treatment of the resulting ribbon with 20 wt. % aqueous sodium hydroxide for 3h at room temperature resulted in the formation of the nanoporous structure by selective leaching of aluminum. The material was washed with pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (AuAgAl) and its composition was found to be Au₉₃Ag₃Al₄ by EDX analysis.

AuNPore-5 (Au₉₆Ag₁Al₃): AuNPore-4 was treated with 70 wt. % nitric acid for 1 hour at room temperature. The material was washed with pure water and acetone, successively. The material was dried under reduced pressure and its composition was found to be Au₉₆Ag₁Al₃.

SEM micrographs of nanoporous gold

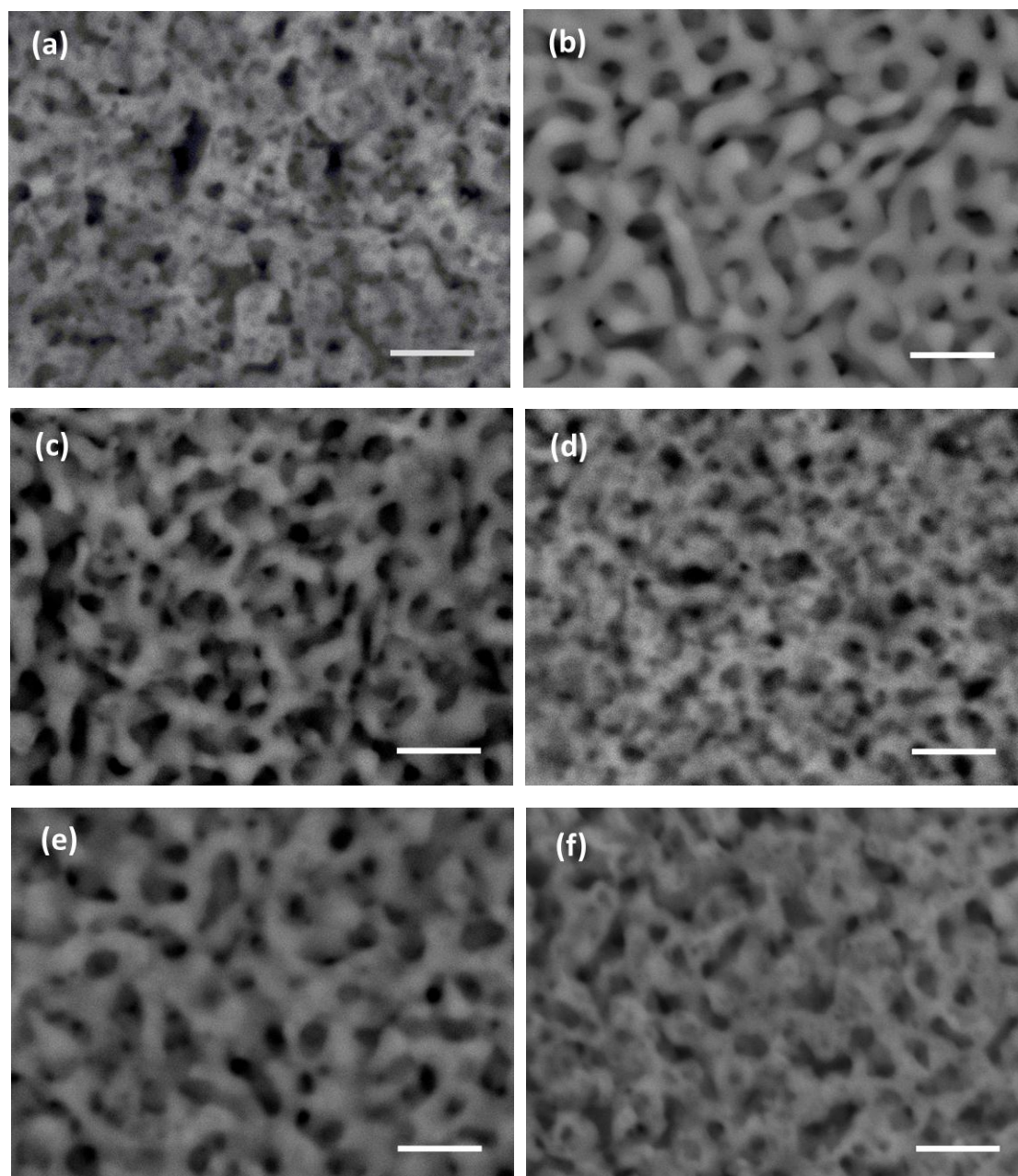


Figure S1. SEM images of AuNPore. The scale bar is 100 nm. (a) AuNPore-1; (b) AuNPore-2; (c) AuNPore-3; (d) AuNPore-4; (e) AuNPore-5; (f) AuNPore-1 after being used five times for hydrosilylation of **1b**.

Cyclic voltammogram for nanoporous gold

The CV analysis of AuNPore-1 is representative; The amount of reduction charge corresponding to the shaded region in Figure S2 was obtained by integrating the charge passed in the surface oxide stripping reaction recorded for AuNPore-1 (1.47 mg), which was marked in the figure.

The electrochemically active surface area of the nanoporous gold is:

$$68400 / 222 \cdot 10^4 / 2 = 1.54 \cdot 10^{-2} \text{ (m}^2\text{)}$$

where $2.22 \cdot 10^4 \mu\text{C m}^{-2}$ is the gold's conversion factor.¹

Hence, the specific surface area was calculated to be $1.54 \cdot 10^{-2} / 1.47 \cdot 10^{-3} = 10.5 \text{ m}^2/\text{g}$.

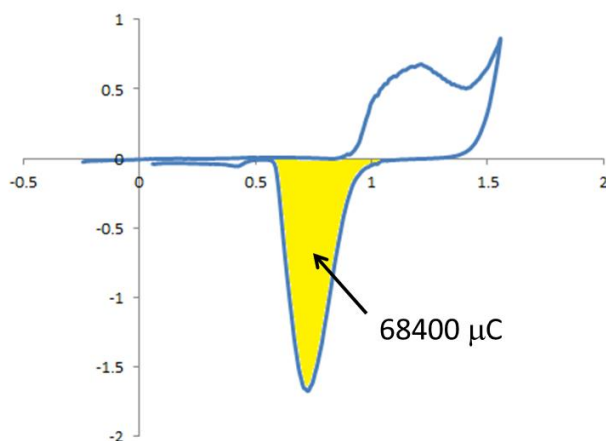


Figure S2. Original cyclic voltammogram for nanoporous gold thin film (1.47 mg) in 0.1 M HClO₄ solutions. Scan rate: 5 mV s⁻¹

Hydrosilylation of alkynes with AuNPore catalyst

The preparation of **3a** is representative; Ethyl acetate (1 mL), **1a** (110 μl, 1 mmol) and **2a** (160 μl, 1.5 mmol) were added successively to the nanoporous gold (4.0 mg, 2 mol %) in a micro reaction vial at room temperature. The mixture was stirred at 70 °C for 3 h under N₂ atmosphere. The catalyst was removed and the reaction mixture was then concentrated under reduced pressure to give a crude material. The chemical yield of product was determined by ¹H NMR analysis with *p*-xylene as an internal standard. The recovered catalyst was washed with ether, dried in vacuo, and reused.

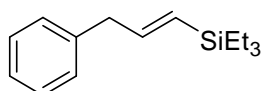
Calculation of TOF²

The AuNPore-1-catalyzed hydrosilylation of **1a** with **2a** is representative; The AuNPore-1 (4.0 mg) catalyzed reaction of **1a** (1 mmol) and gave **2a** in 74% yield with 1 h. The surface area was electrochemically measured to be 10.5 m²/g (Figure S2) and the density of surface atoms for the energetically most stable Au(111) surface is $1.4 \cdot 10^{19} \text{ atoms/m}^2$. Using these values the TOF was calculated to be 757 h⁻¹.

Characterization Data

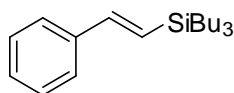
Spectral data of products **3a-d** and **3f-3h** are consistent with the literature data; **3a-c**,³ **3d**,⁴ **3f**,⁵ and **3g-h**.⁶

(*E*)-Triethyl(3-phenylprop-1-enyl)silane (**3e**)



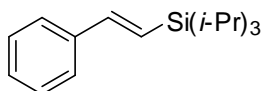
Colorless oil; IR (neat, cm^{-1}): 2941, 2909, 2873; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.18 (m, 5H), 6.19 (dt, $J = 18.4$ Hz, 6.4 Hz, 1H), 5.68 (dt, $J = 18.4$ Hz, 1.6 Hz, 1H), 3.50 (d, $J = 6.4$ Hz, 2H), 0.96 (t, $J = 7.6$ Hz, 9H), 0.59 (q, $J = 7.6$ Hz, 6H) ^{13}C NMR (100 MHz, CDCl_3) δ 146.3, 140.1, 128.6, 128.3, 127.7, 125.9, 43.6, 7.5, 3.6; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{Si}$, 232.1647; found 232.1644. Minor α product was observed: ^1H NMR (300 MHz CDCl_3): δ 5.52-5.54 (m, 1H), 5.43-5.45 (m, 1H)

(*E*)-Tributyl(styryl)silane (**3i**)



Colorless oil; IR (neat, cm^{-1}): 2955, 2918, 2870, 2855; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.22 (m, 5H), 6.89 (d, $J = 19.2$ Hz, 1H), 6.45 (d, $J = 19.2$, 1H), 1.40-1.29 (m, 12H), 0.92 (t, $J = 2.8$, 9H), 0.72-0.64 (m, 6H) ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 138.5, 128.4, 127.8, 126.9, 126.2, 26.8, 26.2, 13.9, 12.4; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{34}\text{Si}$, 302.2430; found 302.2426. Minor α product was observed: ^1H NMR (300 MHz CDCl_3): δ 5.86 (d, $J = 2.8$ Hz, 1H), 5.58 (d, $J = 2.8$ Hz, 1H)

(*E*)-Triisopropyl(styryl)silane (**3j**)

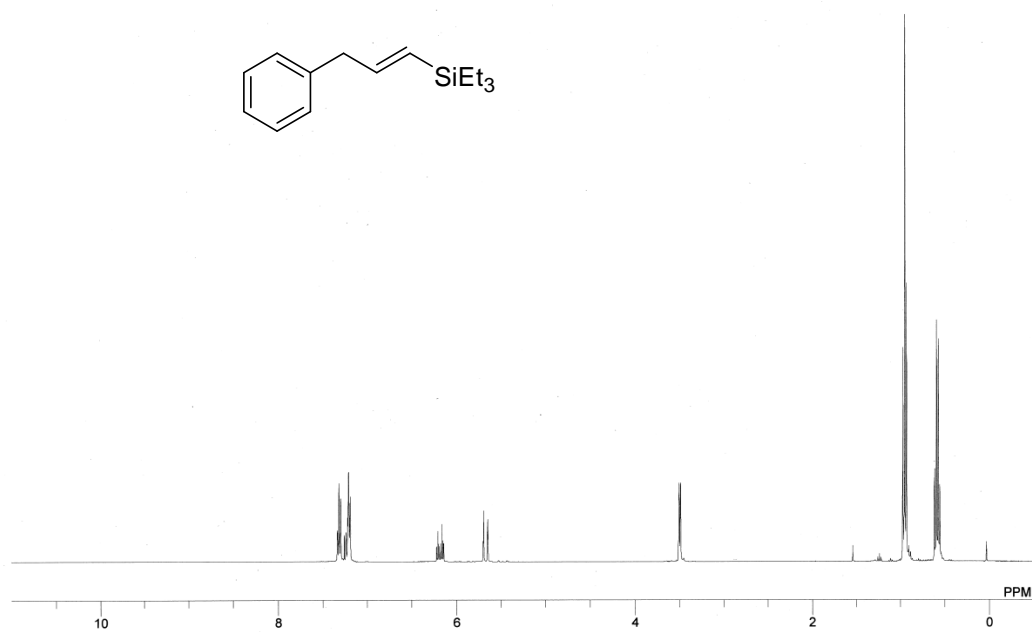


Colorless oil; IR (neat, cm^{-1}): 3060, 3027, 2952, 2909, 2873; ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.22 (m, 5H), 6.95 (d, $J = 19.2$ Hz, 1H), 6.41 (d, $J = 19.2$), 1.14-1.09 (m, 21H) ^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 138.6, 128.4, 127.8, 126.2, 123.9, 18.8, 11.1; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{28}\text{Si}$, 260.1960; found 360.1963. Minor α product was observed: ^1H NMR (300 MHz CDCl_3): δ 5.89 (d, $J = 2.8$ Hz, 1H), 5.66 (d, $J = 2.8$ Hz, 1H)

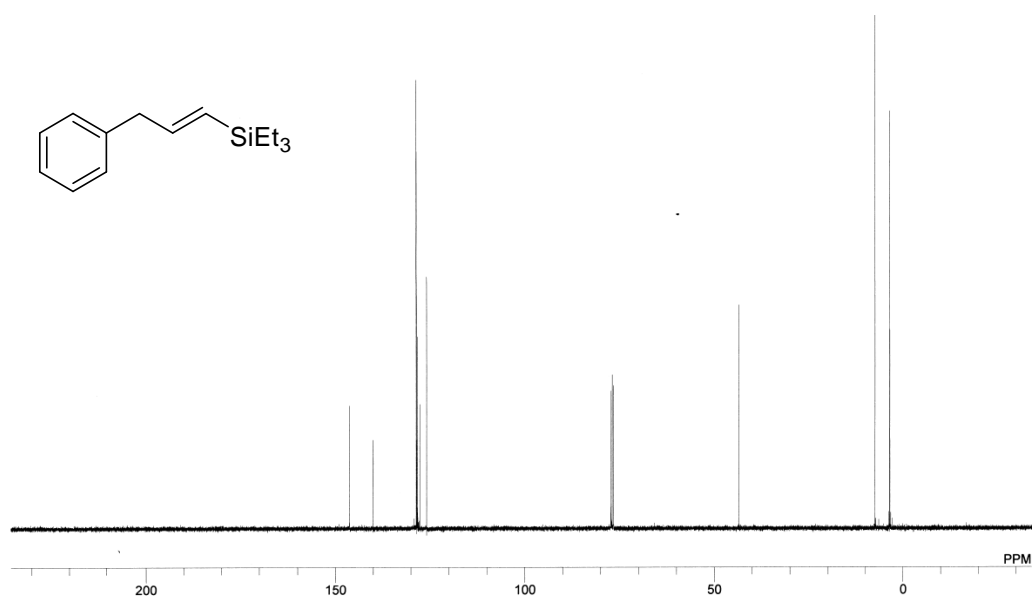
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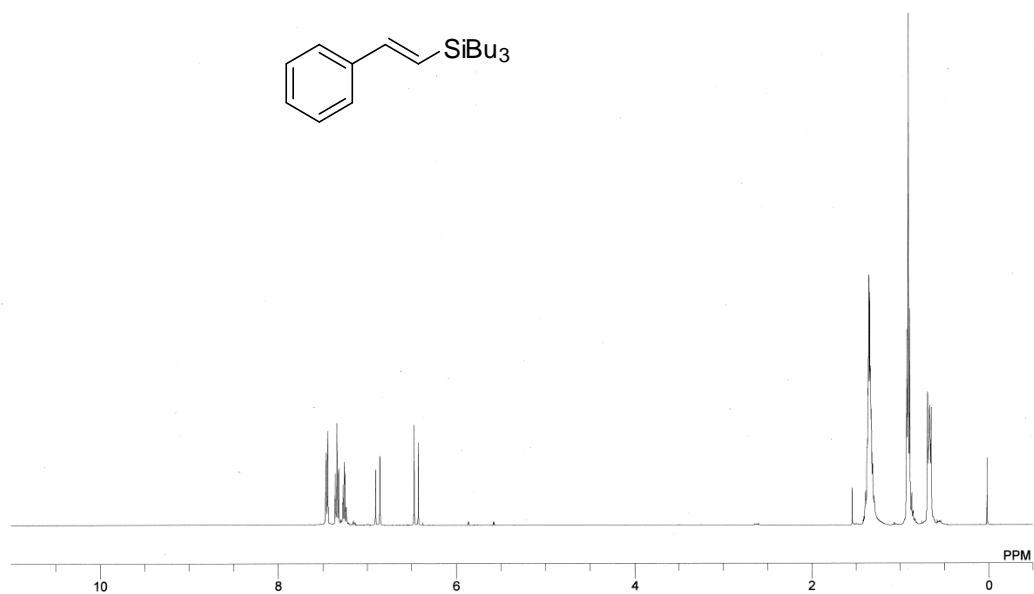
^1H NMR of 3e



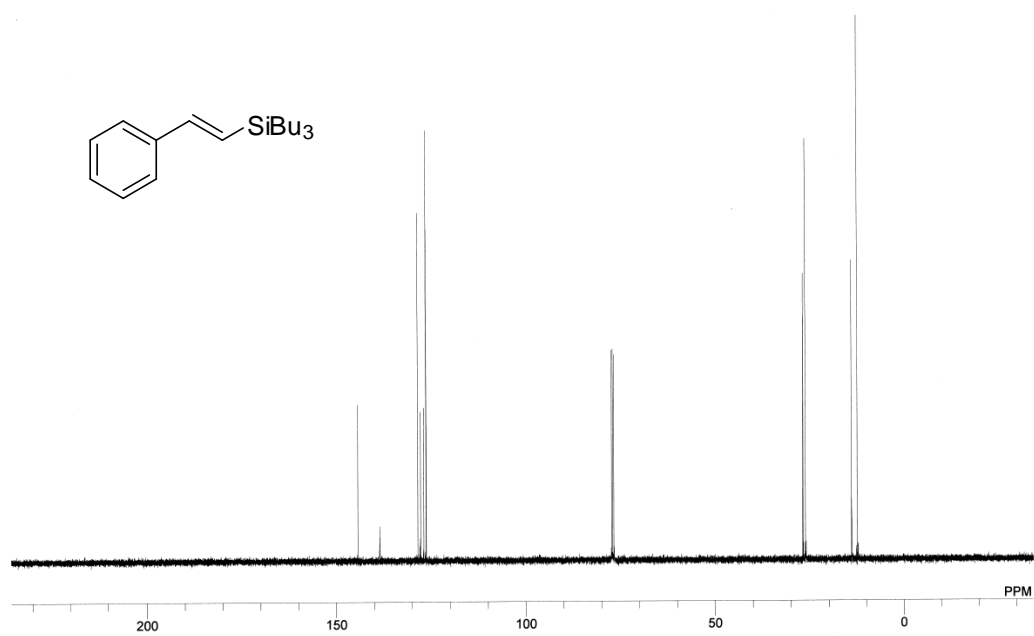
^{13}C NMR of 3e



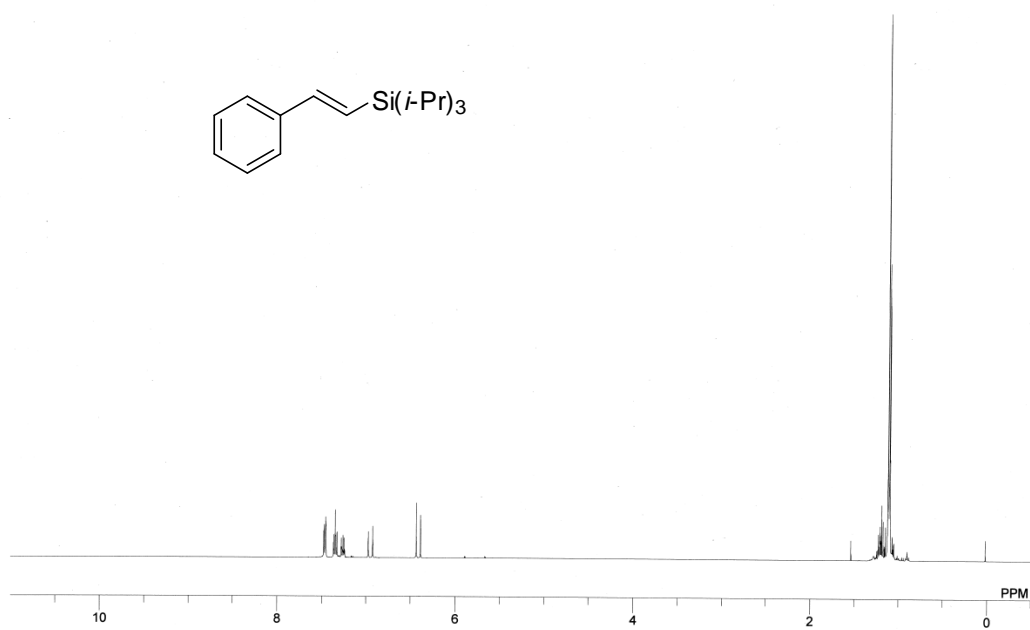
¹H NMR of 3i



¹³C NMR of 3i



^1H NMR of 3j



^{13}C NMR of 3j

