

**Supporting Information**

**for**

**Hydrodehalogenation of Alkyl Halides Catalyzed by a Trichloroniobium Complex with  
a Redox Active  $\alpha$ -Diimine Ligand**

Haruka Nishiyama,<sup>a</sup> Hiromu Hosoya,<sup>a</sup> Bernard F. Parker,<sup>a,b</sup> John Arnold,<sup>b,\*</sup>

Hayato Tsurugi,<sup>a,\*</sup> and Kazushi Mashima<sup>a,\*</sup>

<sup>a</sup> *Department of Chemistry, Graduate School of Engineering Science, Osaka University*

<sup>b</sup> *Department of Chemistry, University of California, Berkeley*

\*E-mail: [tsurugi@chem.es.osaka-u.ac.jp](mailto:tsurugi@chem.es.osaka-u.ac.jp) (H.T.), [arnold@berkeley.edu](mailto:arnold@berkeley.edu) (J.A.),

[mashima@chem.es.osaka-u.ac.jp](mailto:mashima@chem.es.osaka-u.ac.jp) (K.M.)

## 1. General Procedure

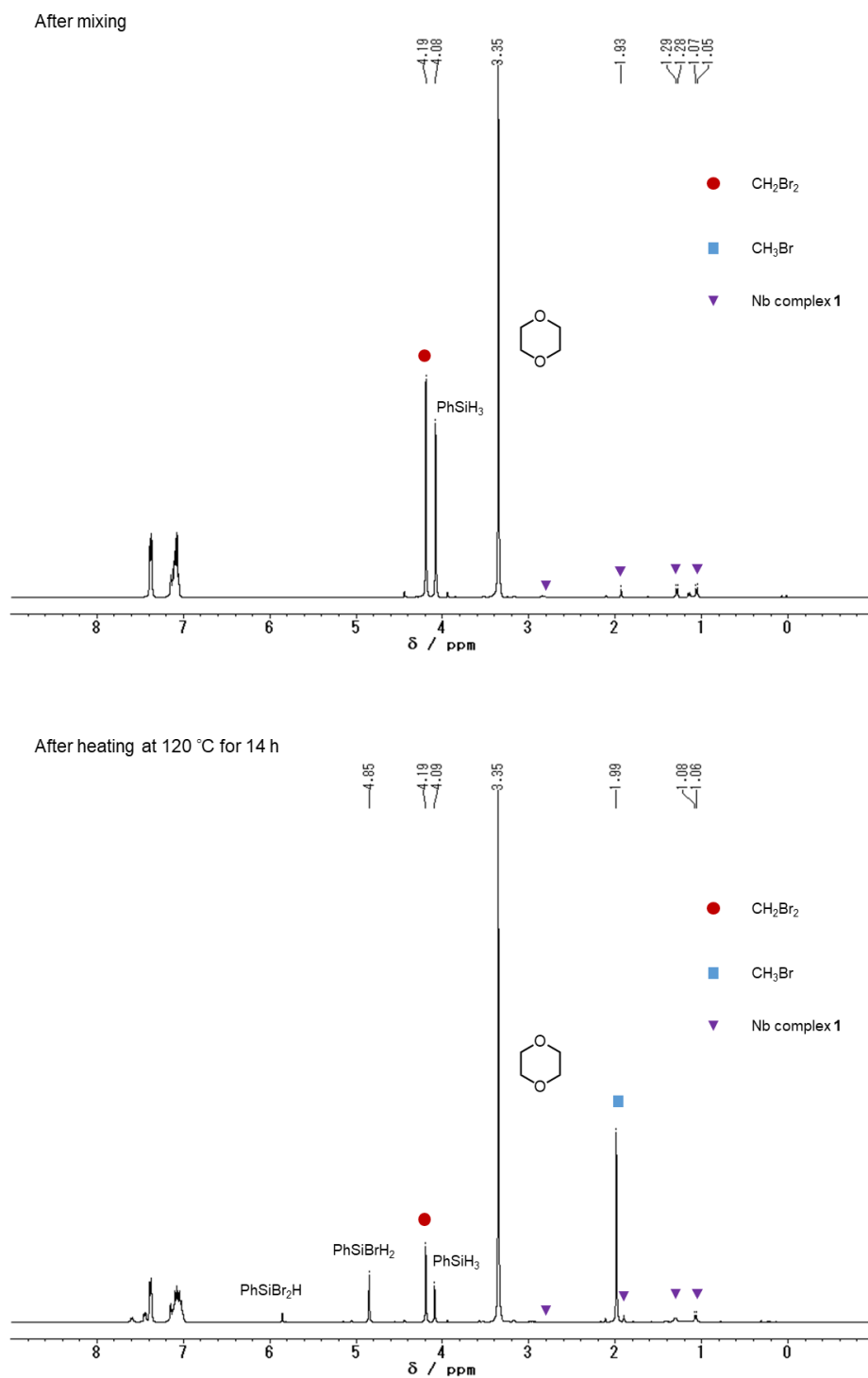
All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. Niobium complexes **1** and **2** were prepared according to the literature procedure.<sup>1</sup> NbCl<sub>3</sub> was prepared by reduction of NbCl<sub>5</sub> with 1 equiv of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene.<sup>1</sup> Anhydrous hexane and toluene were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al.*<sup>2</sup> Alkyl halides and silanes were purchased and, if necessary, purified by distillation over CaH<sub>2</sub>. Benzene-*d*<sub>6</sub> was distilled over CaH<sub>2</sub> and degassed before use. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometers and JEOL JNM-ECS400 (400 MHz) spectrometers.

## 2. Screening of hydrogen sources for catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane (Table 1)

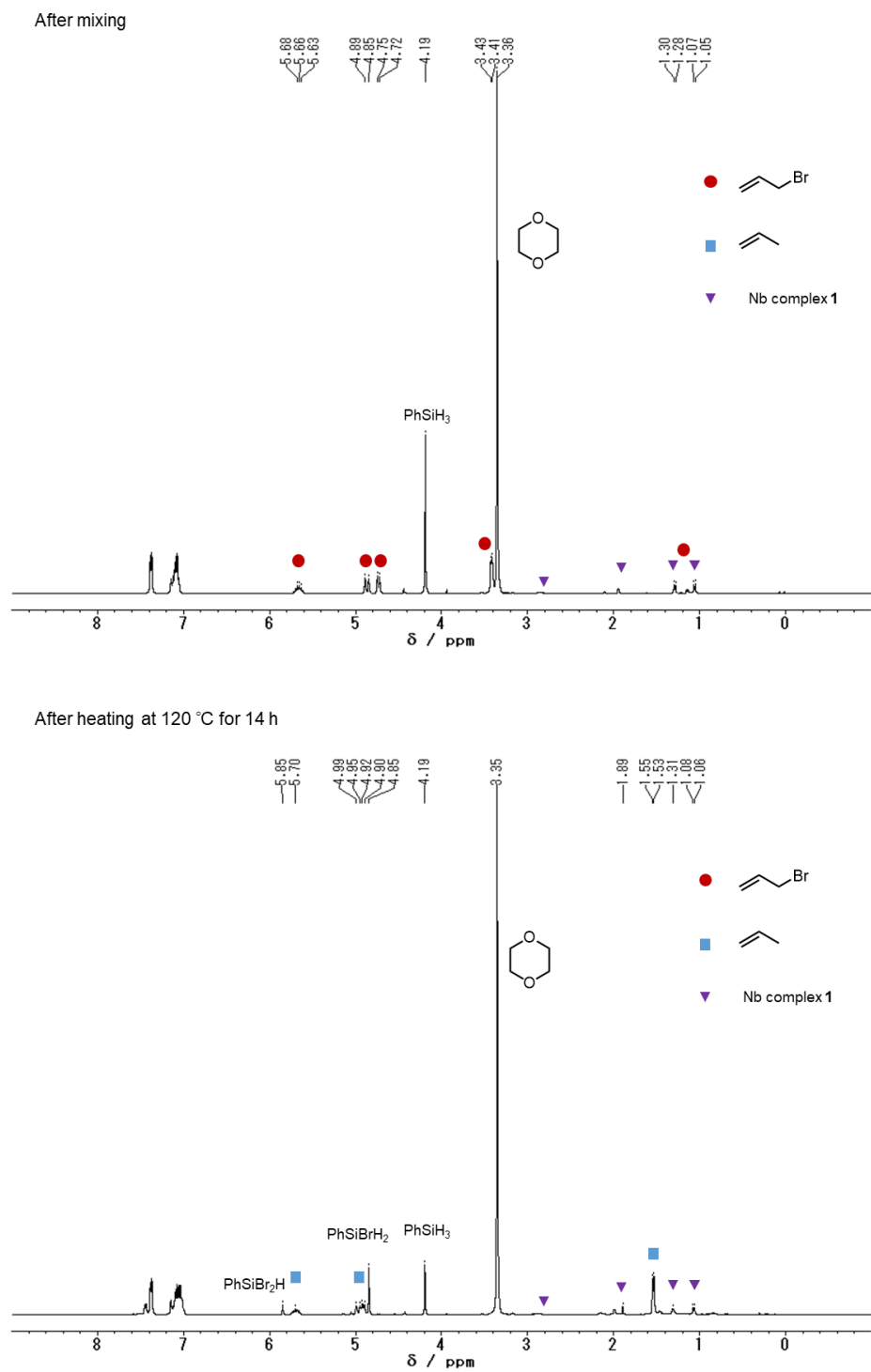
To a solution of 1,1,1,3-tetrachloropropane (0.300 mmol), hydrogen source (0.300 mmol), and hexamethylbenzene (2.4 mg, 15.0 μmol) in C<sub>6</sub>D<sub>6</sub> (0.10 mL) as an internal standard in C<sub>6</sub>D<sub>6</sub> (0.20 mL) was added catalyst **1** (9.00 μmol) in C<sub>6</sub>D<sub>6</sub> (0.10 mL) in a J-Young NMR tube. The NMR sample of the reaction mixture was kept in 120 °C oil bath. After the reaction time, the sample was measured by <sup>1</sup>H NMR.



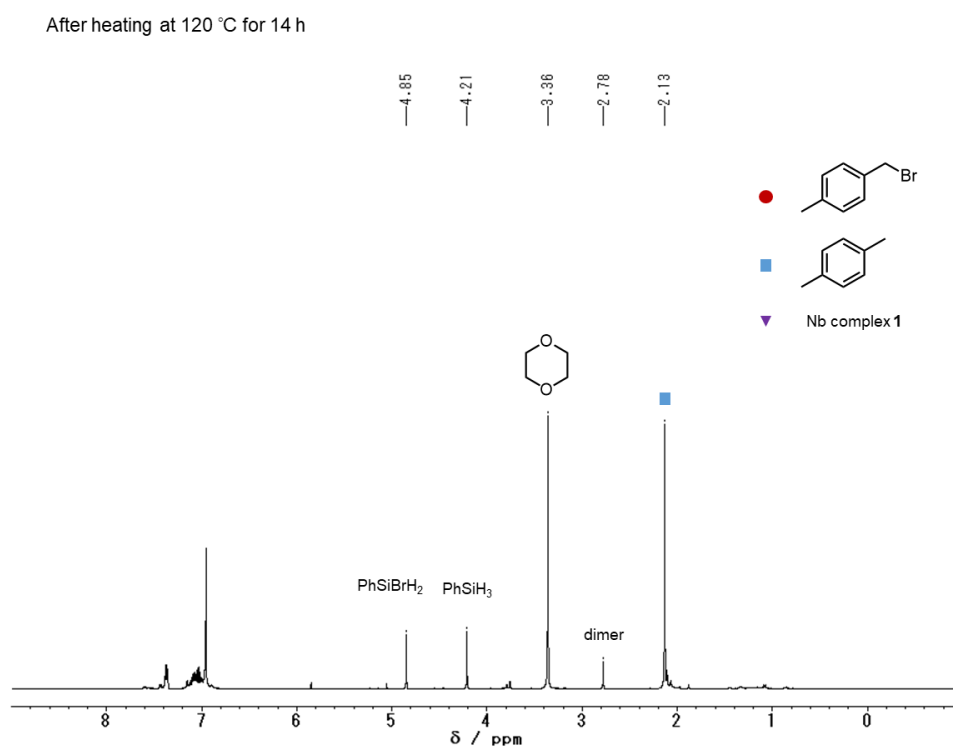
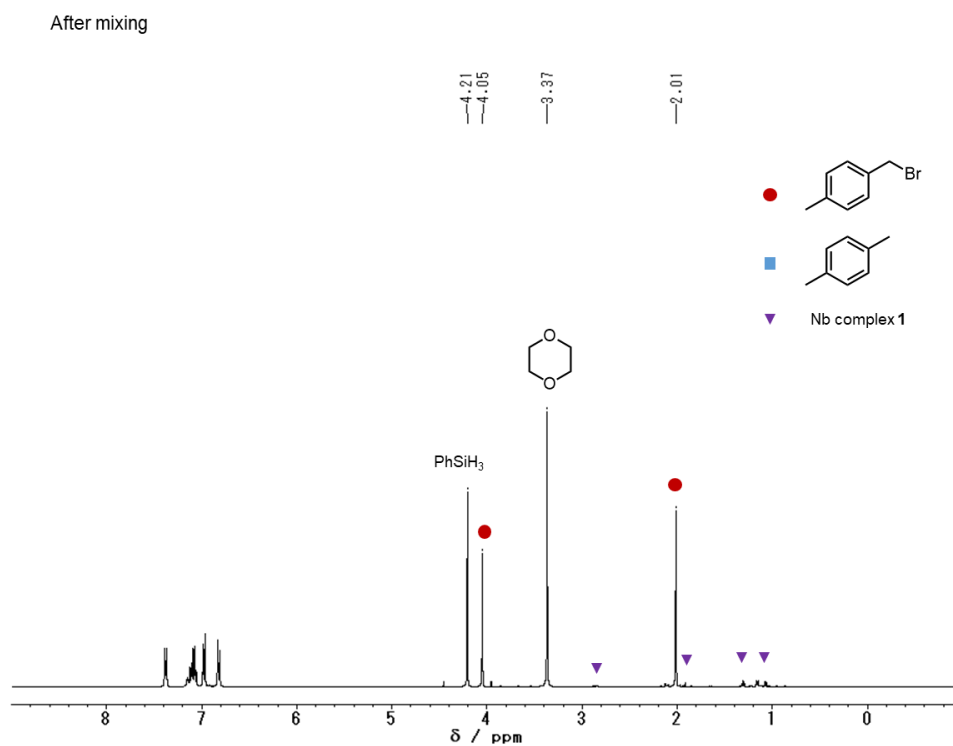
### 3. Substrate scope for catalytic hydrodehalogenation of alkyl halides with $\text{PhSiH}_3$ in Table 2.



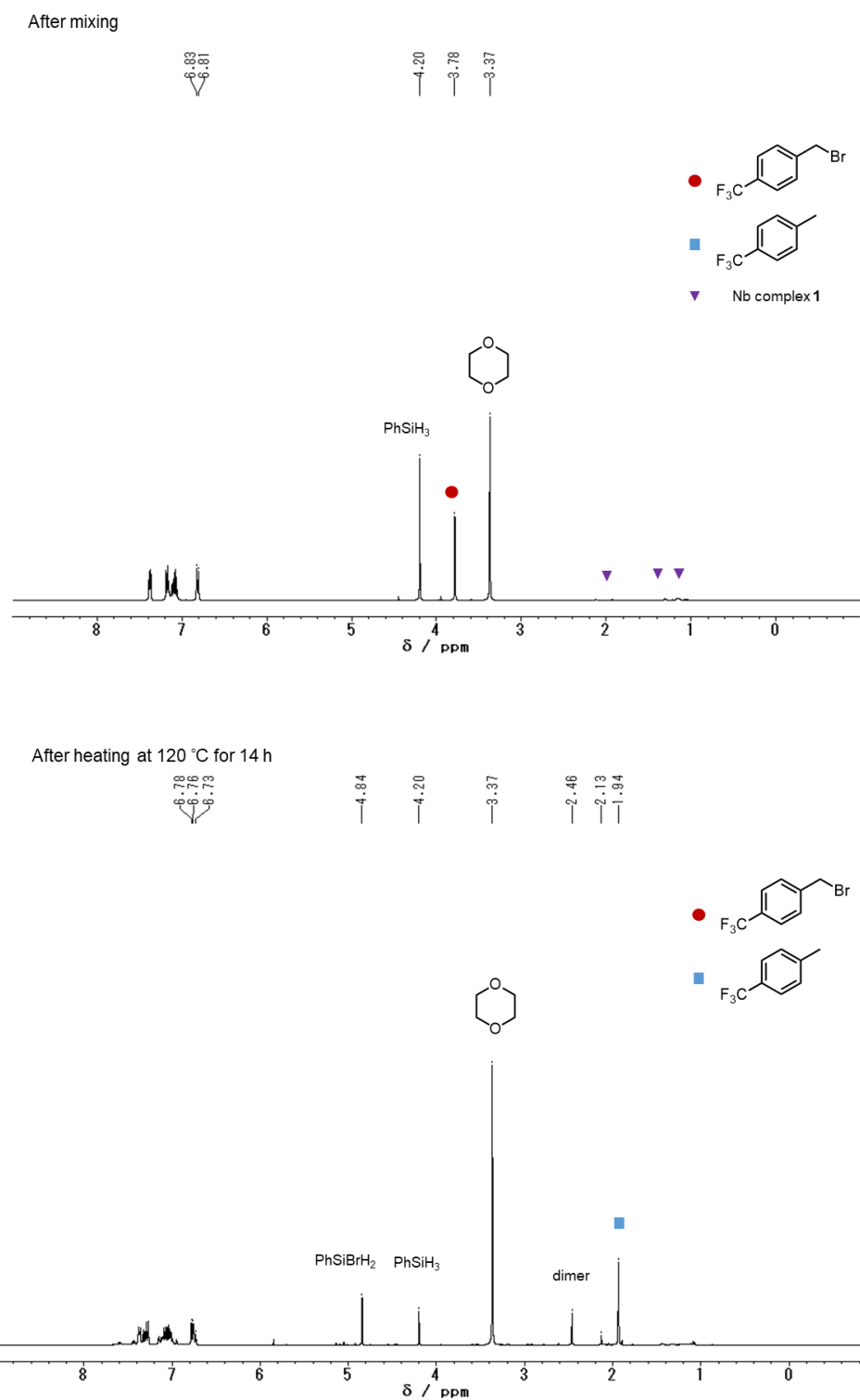
**Figure S2.**  $^1\text{H}$  NMR spectrum for hydrodehalogenation reaction of dibromomethane.



**Figure S3.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of allyl bromide.



**Figure S4.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of 4-methylbenzyl bromide.

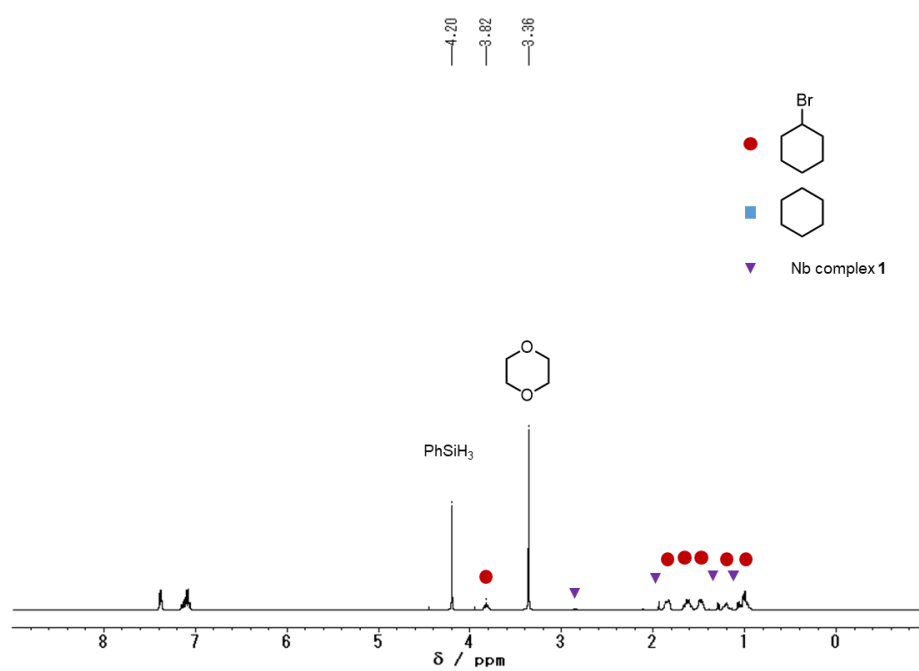


**Figure S5.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of 4-trifluoromethylbenzyl bromide.

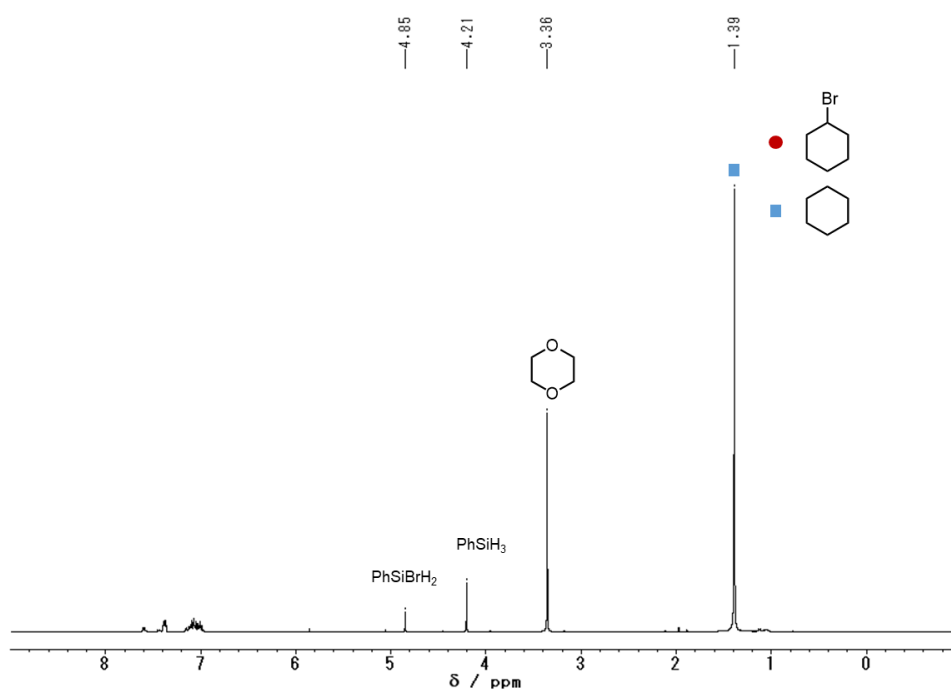




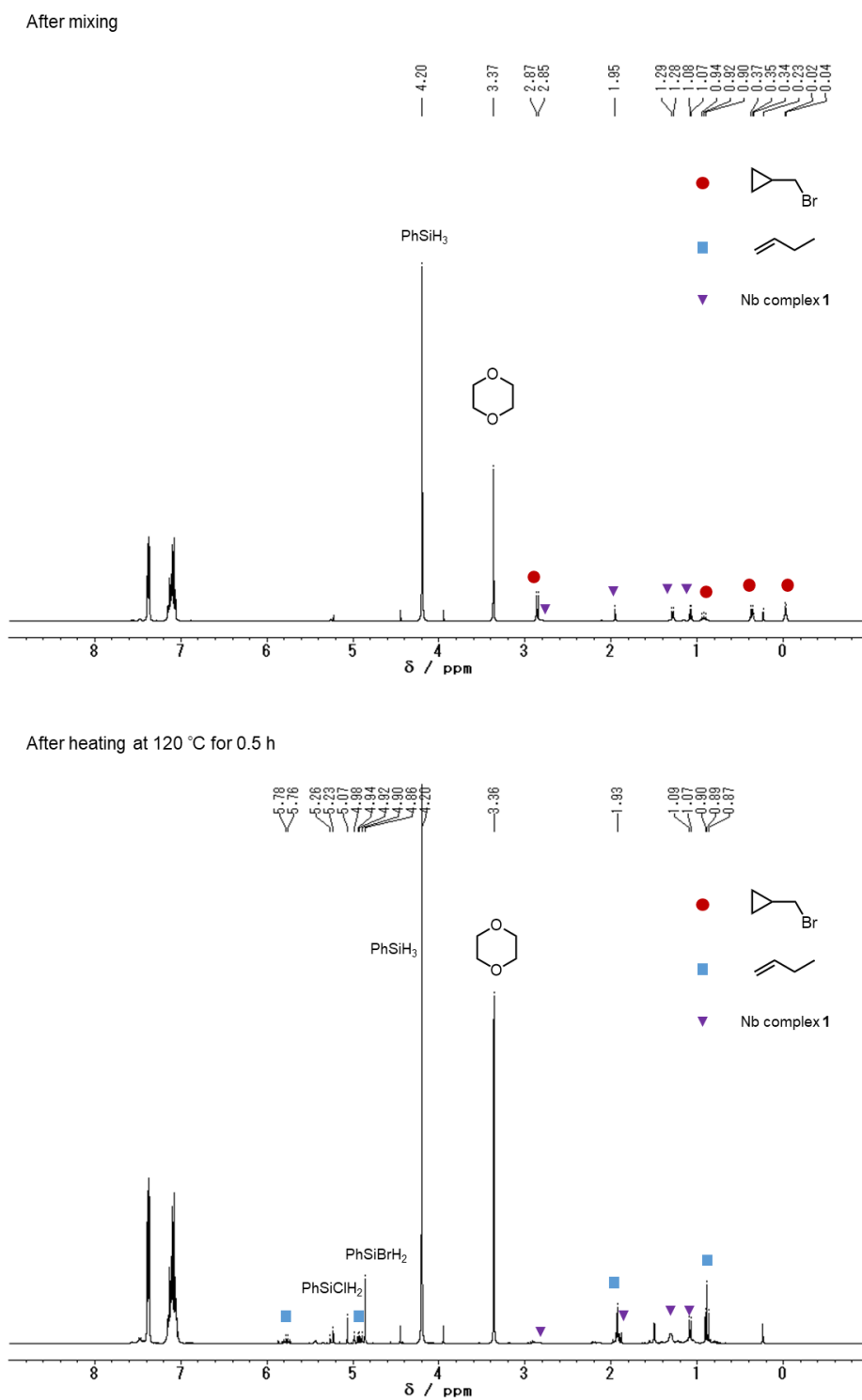
After mixing



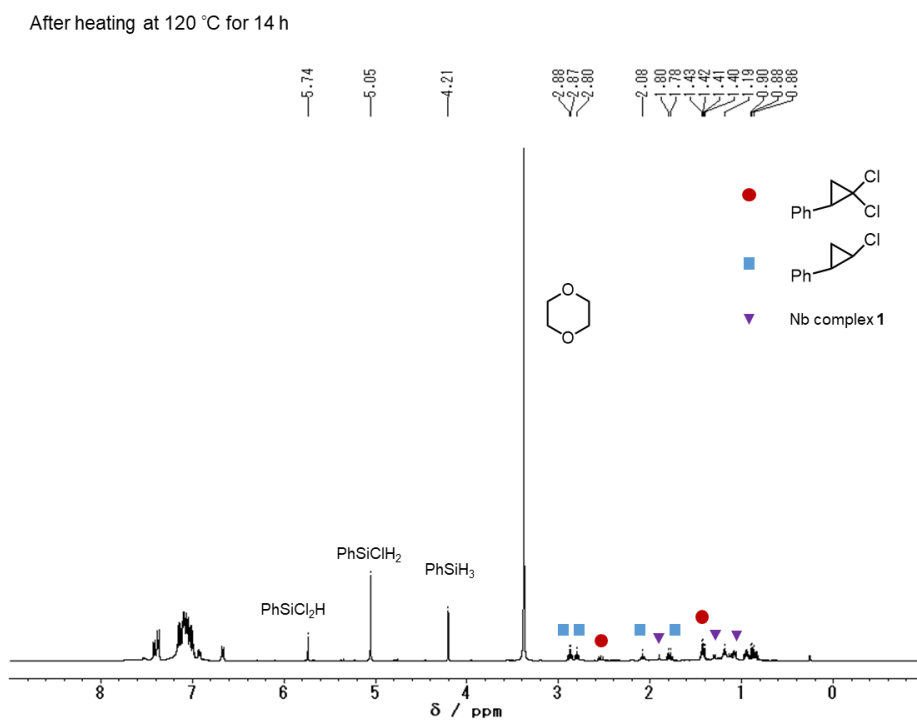
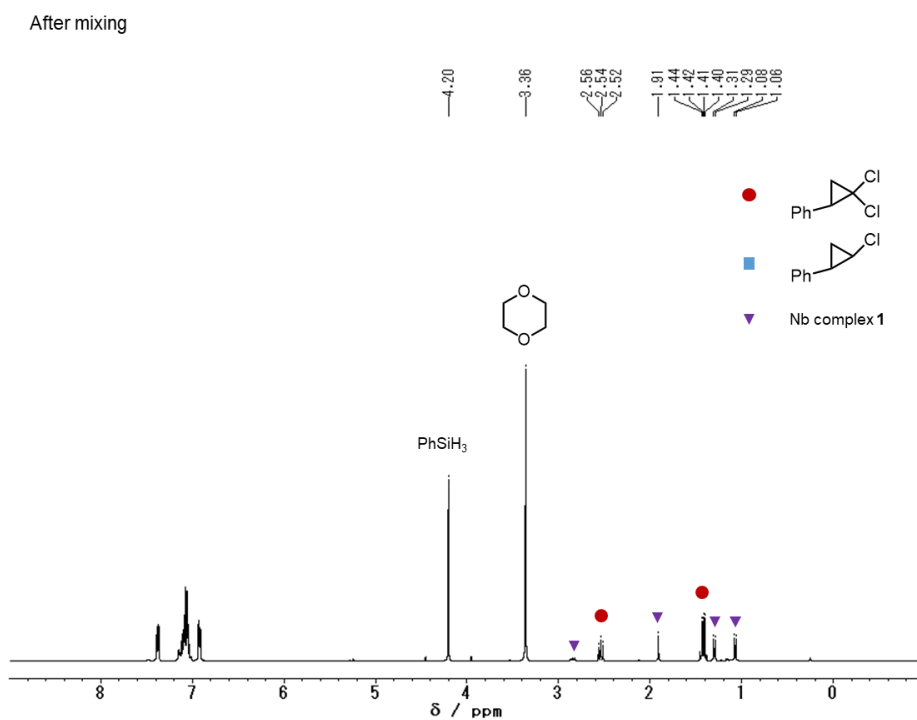
After heating at 120 °C for 14 h



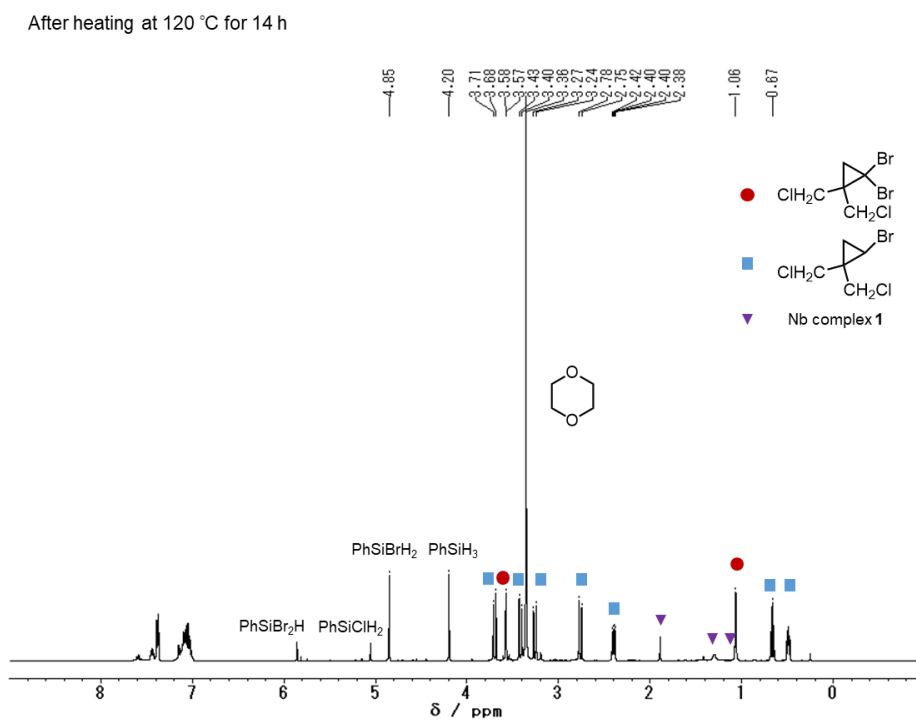
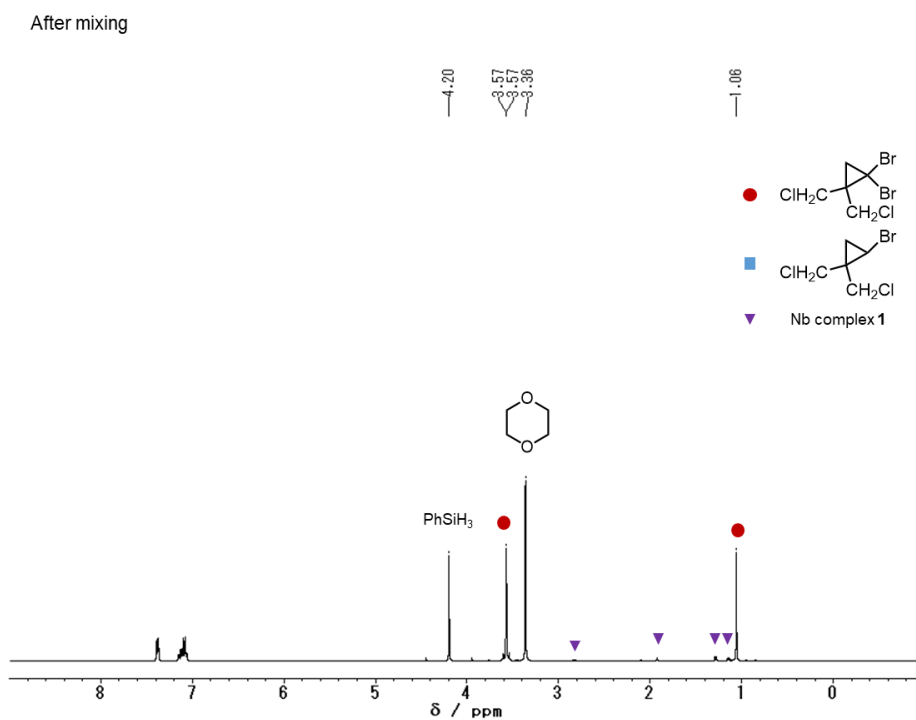
**Figure S7.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of cyclohexyl bromide.



**Figure S8.**  $^1\text{H}$  NMR spectrum for hydrodehalogenation reaction of cyclopropylmethyl bromide.

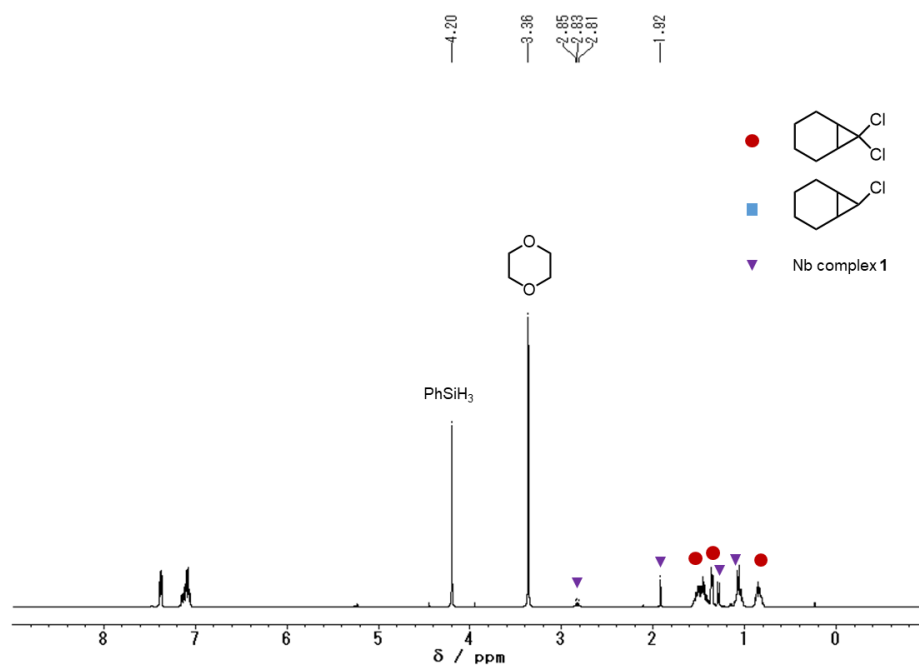


**Figure S9.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of (2,2-dichlorocyclopropyl)benzene.

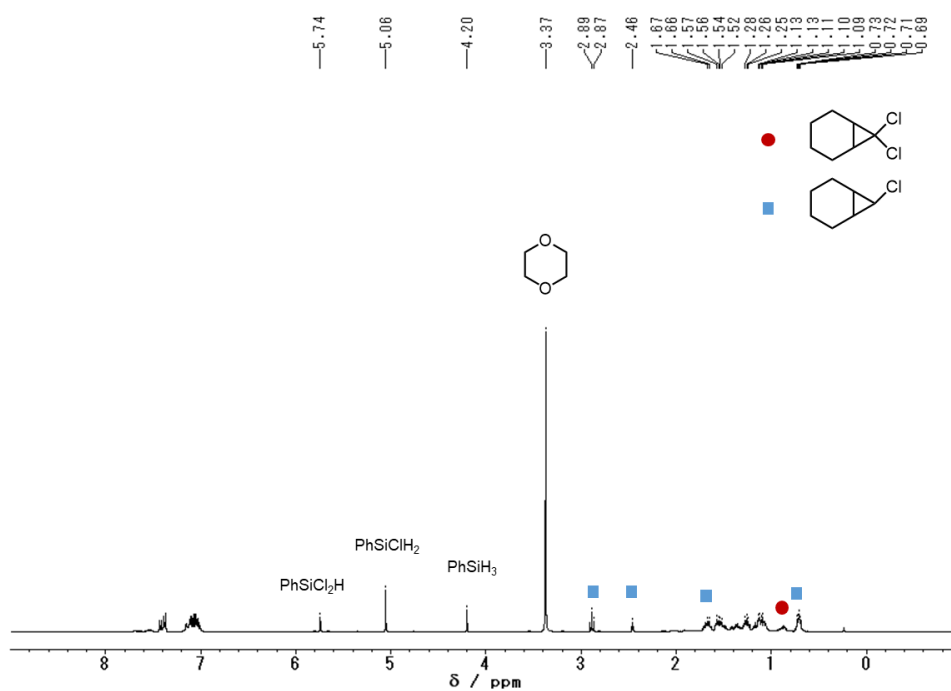


**Figure S10.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.

After mixing

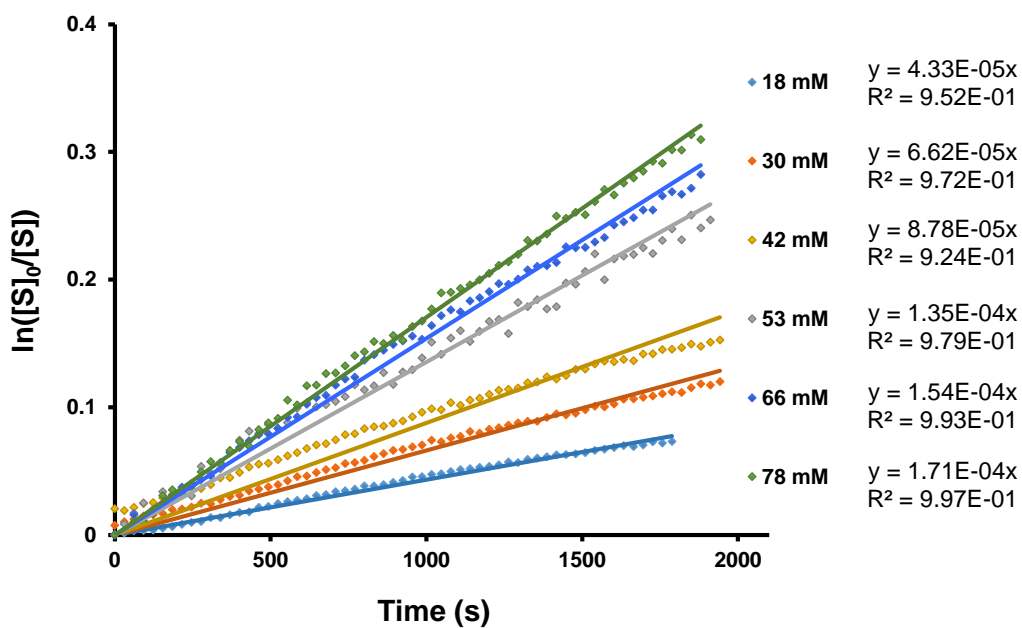


After heating at 120 °C for 14 h

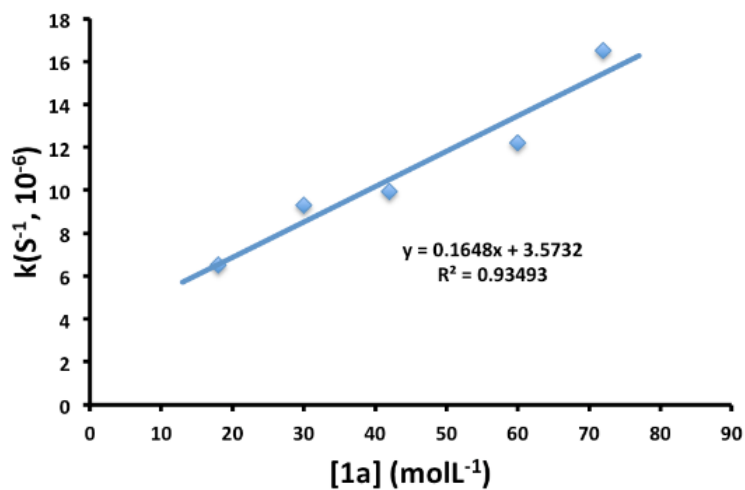


**Figure S11.** <sup>1</sup>H NMR spectrum for hydrodehalogenation reaction of 7,7-dichlorobicyclo[4.1.0]heptane.

#### 4. Kinetic Study for Hydrodehalogenation

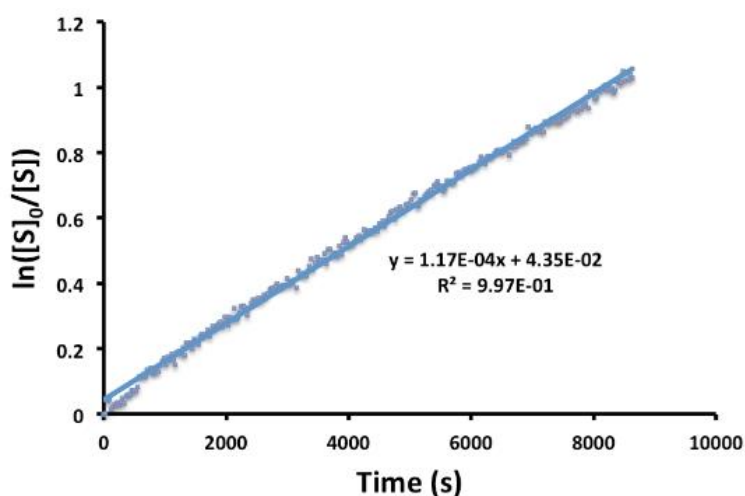


**Figure S12.** Reaction progress with different concentration of **1** as the catalyst for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH<sub>3</sub>



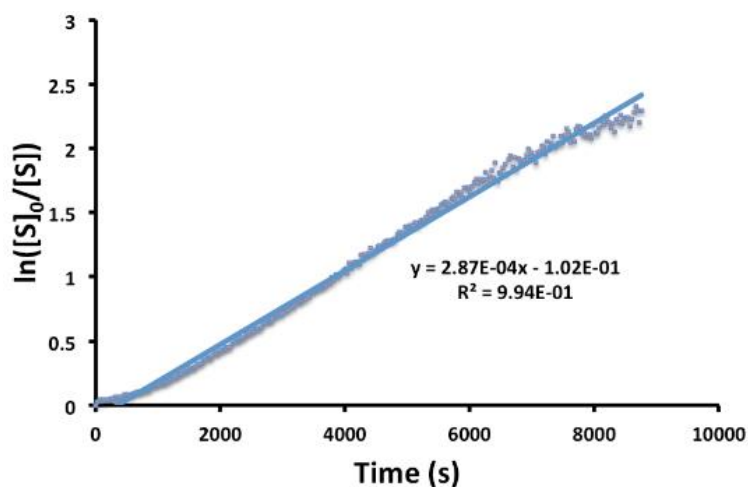
**Figure S13.** Dependence of  $k_{\text{obs}}$  with the concentration of **1** as the catalyst for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH<sub>3</sub>

Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex **1** (3 mol%) and excess PhSiH<sub>3</sub> (10 equiv) in C<sub>6</sub>D<sub>6</sub> at 100 °C. The amount of the product was determined by integral ratios of signals for 1,1,3-trichloropropane and the internal standard, and the time dependence for the product formation was fitted to the first-order plot.



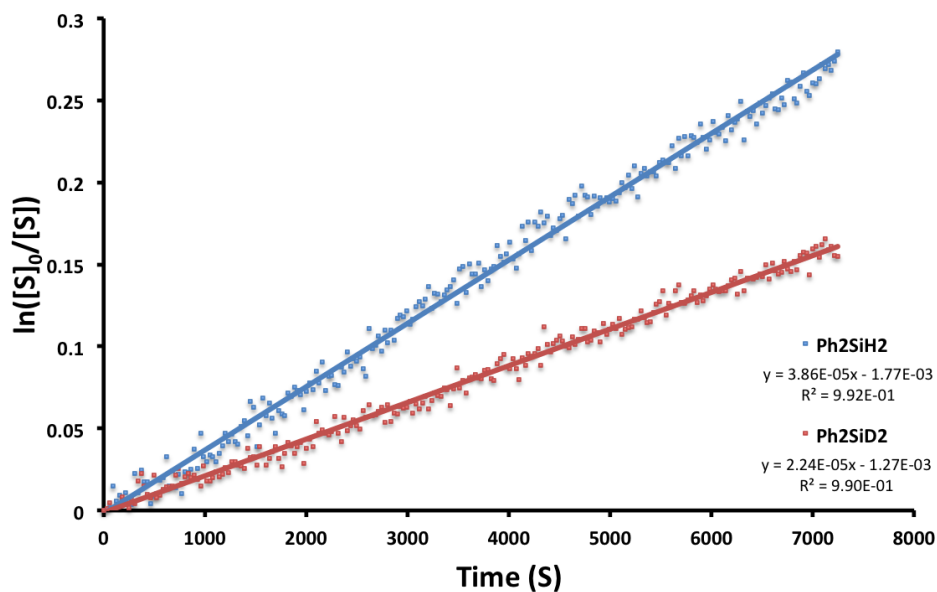
**Figure S14.** A pseudo first-order kinetic behavior on the concentration of 1,1,1,3-tetrachloropropane (S) for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH<sub>3</sub>

Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex **1** (3 mol%) and excess 1,1,1,3-tetrachloropropane (10 equiv) with PhSiH<sub>3</sub> (1 equiv) in C<sub>6</sub>D<sub>6</sub> at 100 °C. The reaction progress was followed by integral ratios of signals for PhSiH<sub>3</sub> and the internal standard, and the time dependence for the consumption of PhSiH<sub>3</sub> was fitted to the first-order plot.



**Figure S15.** A pseudo first-order kinetic behavior on the concentration of PhSiH<sub>3</sub> (S) for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH<sub>3</sub>

Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex **1** (3 mol%) and Ph<sub>2</sub>SiH<sub>2</sub> or Ph<sub>2</sub>SiD<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 100 °C. The  $k_{\text{obs}}$  for two reactions were  $k_{\text{obs}}(\text{H}) = 3.77$  and  $k_{\text{obs}}(\text{D}) = 2.00$ , and the KIE value was 1.89, suggesting that the H-abstraction was involved in the rate-determining step.



**Figure S16.** Kinetic isotope effect for hydrodehalogenation reaction



## 5. References

(S1) H. Nishiyama, H. Ikeda, T. Saito, B. M. Kriegel, H. Tsurugi, J. Arnold and K. Mashima, *J. Am. Chem. Soc.* 2017, **139**, 6494.

(S2) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 1518.