Supporting Information for

Highly selective redistribution of primary arylsilanes to secondary arylsilanes catalyzed by $Ln(CH_2C_6H_4\text{-}NMe_2\text{-}o)_3$@SBA-15

Chenjun Guo,[a] Min Li,[a] Jue Chen,*[,b] and Yunjie Luo*[,a]

Contents

EXPERIMETAL SECTION

Materials and procedures. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glovebox. Solvents (toluene, *n*-hexane and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. Phenylsilane and its derivatives were obtained from Acros. $LnCl_3$ were purchased from Strem Chemicals. Periodic mesoporous silica (SBA-15) was purchased from J&K scientific and dehydrated before use under high vacuum (10^{-5} Torr) at 220 °C for 12 h. $Ln(CH_2C_6H_4\text{-}NMe_2\text{-}o)_3$[1] were prepared according to the literature.

Samples of the redistribution reaction for NMR spectroscopic measurements were prepared in the glovebox using J. Young type, PTFE-valved NMR tubes. Rare-earth metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer. ^{1}H NMR spectra were recorded on a Bruker Ascend 500 spectrometer at 25 °C and referenced to internal standard 1,3,5-trimethylbenzene. The FT-IR spectra were recorded on a Nicolet 6700 series spectrometer, samples were prepared in a glovebox and mixed with KBr powder. Nitrogen adsorption-desorption isotherms were measured on a Quantachrome Instruments ASIQM002100-6 volumetric adsorption apparatus (Micromeritics) at 298 K for relative pressures from 10^{-2} to 0.99. The BET specific surface area was obtained from the nitrogen adsorption data in the relative pressure range from 0.05 to 0.25. The pore size distributions were derived from the desorption branches using the BJH method. Powder XRD (PXRD) patterns for samples were collected on a Bruker D8 Advance between $0.6° < 2\theta < 10°$ at ambient temperature. SEM micrographs were obtained with a Hitachi S-4800 scanning electron microscope. The particle size

distribution of the hybrid materials and the raw materials were measured by Helos (H2553) & Cuvette, and the wet test was performed with *n*-hexane as a dispersant. X-ray photoelectron spectroscopy and elemental analyses were performed on Escalab 250xi and Elementar Vario EL III in the microanalytical laboratory at Soochow University. The contents of La in fresh sample and after the cycling were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 2100 DV spectrometer.

Grafting Procedure for La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (2a). In an argon-filled glovebox, SBA-15 (300 mg) was dispersed in about 3 mL of toluene. Then a toluene solution of La($CH_2C_6H_4$-NMe_2-*o*)$_3$ (**1a**) (298 mg, 0.55 mmol) in 5 mL of toluene was added, and the reaction mixture was stirred for 20 h at ambient temperature. The hybrid material **2a** was collected by filtration, washed with toluene for three times, and dried under vacuum as light yellow powder. Elemental analysis, Found: C, 8.53; N, 1.04; La, 18.21.

Grafting Procedure for Y($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (2b). Following the procedure as that for **2a**. Using Y($CH_2C_6H_4$-NMe_2-*o*)$_3$ (**1b**) (270 mg, 0.55 mmol) and SBA-15 (300 mg) to give **2b** as orange powder. Elemental analysis, Found: C, 8.80; N, 1.08; Y, 12.10.

Typical Procedure for the Redistribution of Primary Silanes. In an argon-filled glovebox, phenylsilane (54 mg, 0.5 mmol) and internal standard 1,3,5-trimethylbenzene (20 mg, 0.16 mmol) were combined in 0.5 mL of C_6D_6. The resulting mixture was added to a 1 mL of C_6D_6 suspension of La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2a**) (17 mg, 5 mol%) in a Schlenk flask with a stirring bar. Then the flask was taken out from the glovebox, and heated in an oil bath at 60 ^oC for 6 h. The supernatant was separated and tested for ^1H NMR spectrum.

Gram-Scale Reaction for the Redistribution of $PhSiH_3$ Catalyzed by 2a. In an argon-filled glovebox, phenylsilane (1.08 g, 10 mmol) was dissolved in 4 mL of *n*-hexane. The resulting mixture was added to a 1 mL of hexane suspension of La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2a**) (340 mg, 5 mol%) in a Schlenk flask with a stirring bar. Then the flask was taken out from the glovebox, and heated in an oil bath at 60 ^oC for 8 h. The supernatant was separated by filtration, and the solvents were removed in vacuo to give an oily product (0.92 g, 93%).

Sheldon's Hot Filtration Test for the Redistribution of $PhSiH_3$ Catalyzed by 2a. In an argon-filled glovebox, phenylsilane (108 mg, 1 mmol) and internal standard 1,3,5-trimethylbenzene (40 mg, 0.32 mmol) were combined in 0.5 mL of C_6D_6. The resulting mixture was added to a 1.5 mL of C_6D_6 suspension of La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2a**) (34 mg, 5 mol%) in a Schlenk flask with a stirring bar. Then the flask was taken out from the glovebox, and heated in an oil bath at 60 ^oC. The catalyst was filtered out from the reaction mixture after 2 h during the reaction. The filtrate was then charged into a new Schlenk flask for the continuation of the reaction up to 6 h in the absence of the catalyst. The resulting solution was subjected to ^1H NMR analysis.

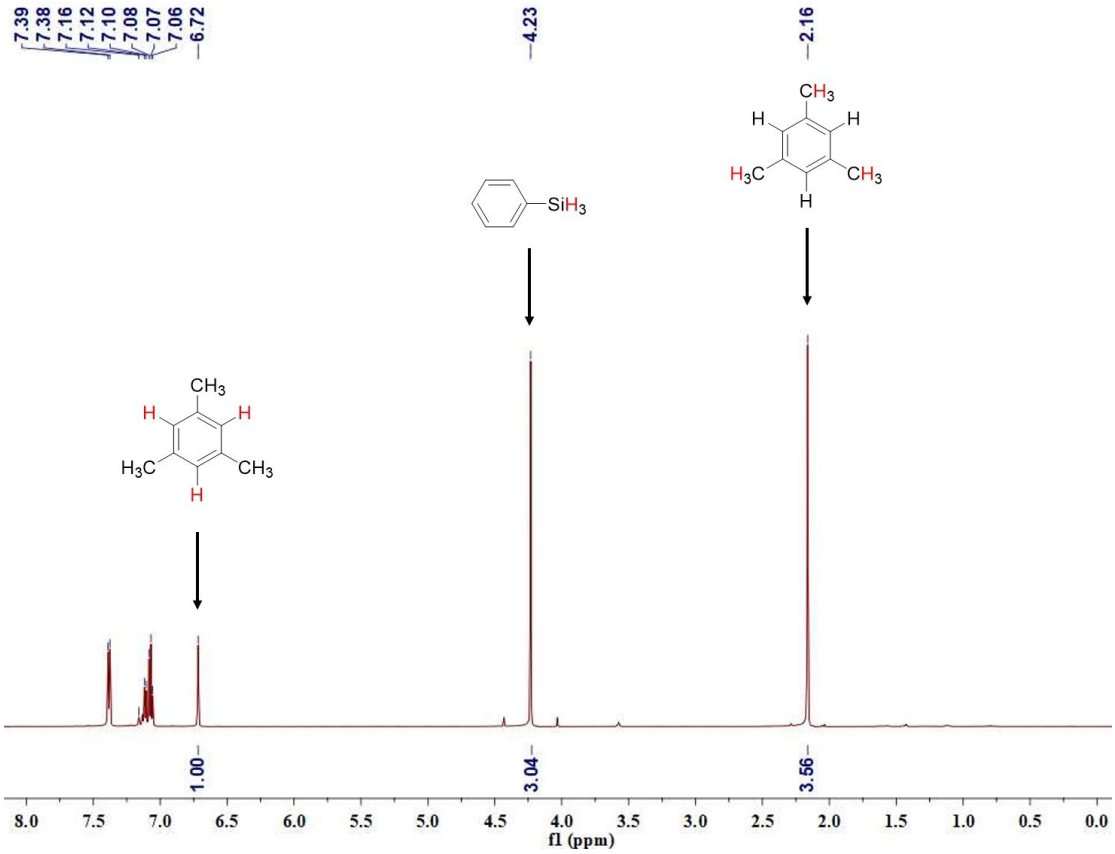


Fig. S1. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of $PhSiH_3$ for the catalytic redistribution with 1,3,5-trimethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

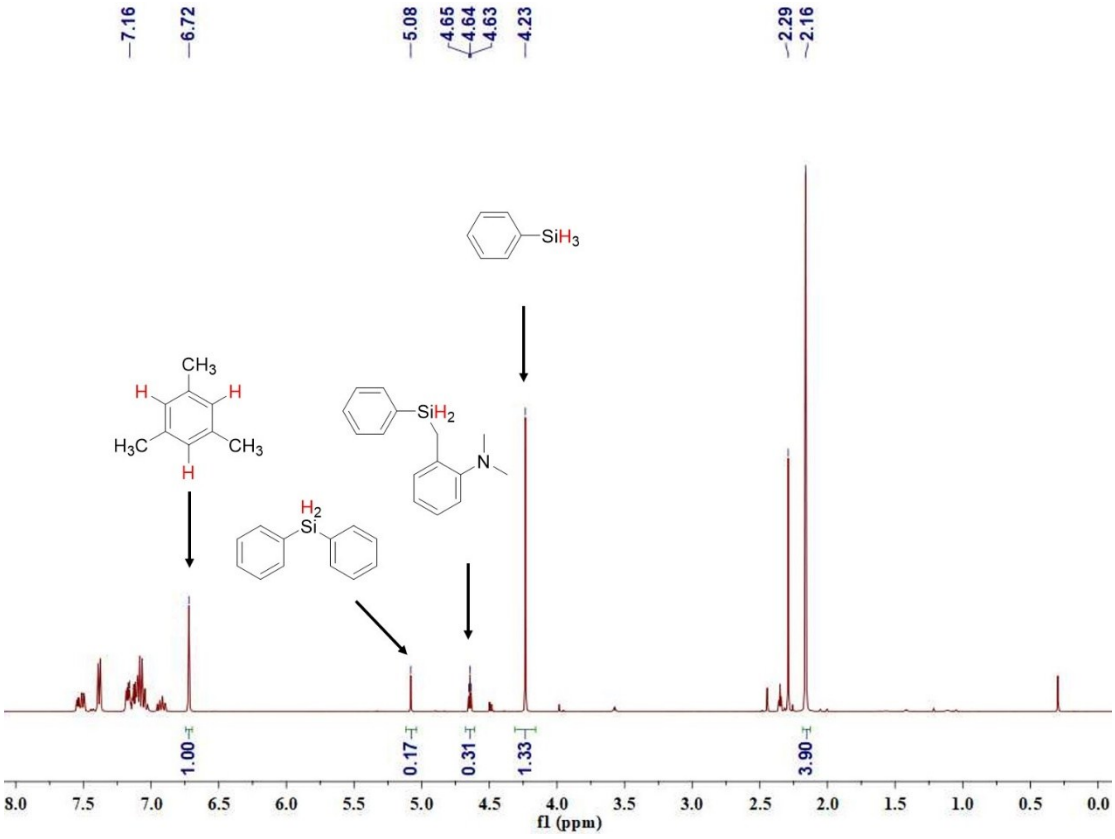


Fig. S2. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **1a** at 25 ^{o}C for 12 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 1, Table 2).

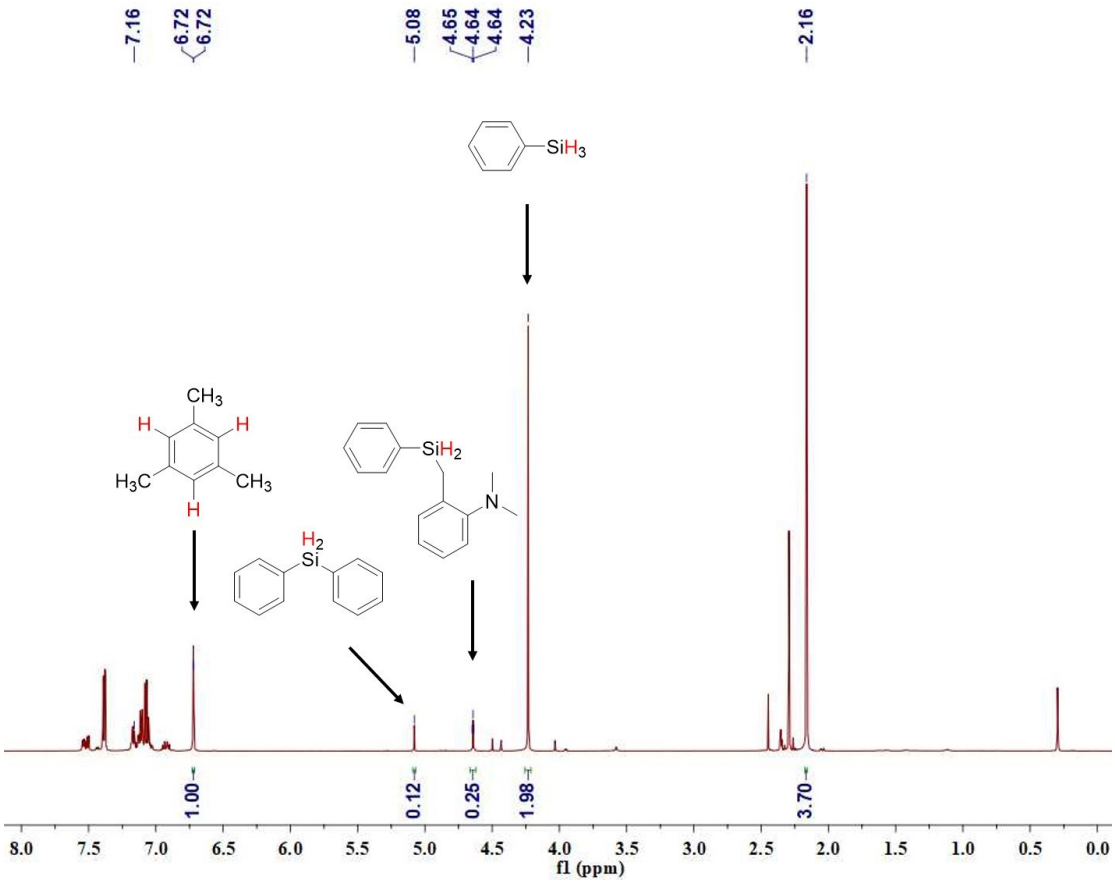


Fig. S3. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **1b** at 25 °C for 12 h (500 MHz, C_6D_6, 25 °C, Entry 2, Table 2).

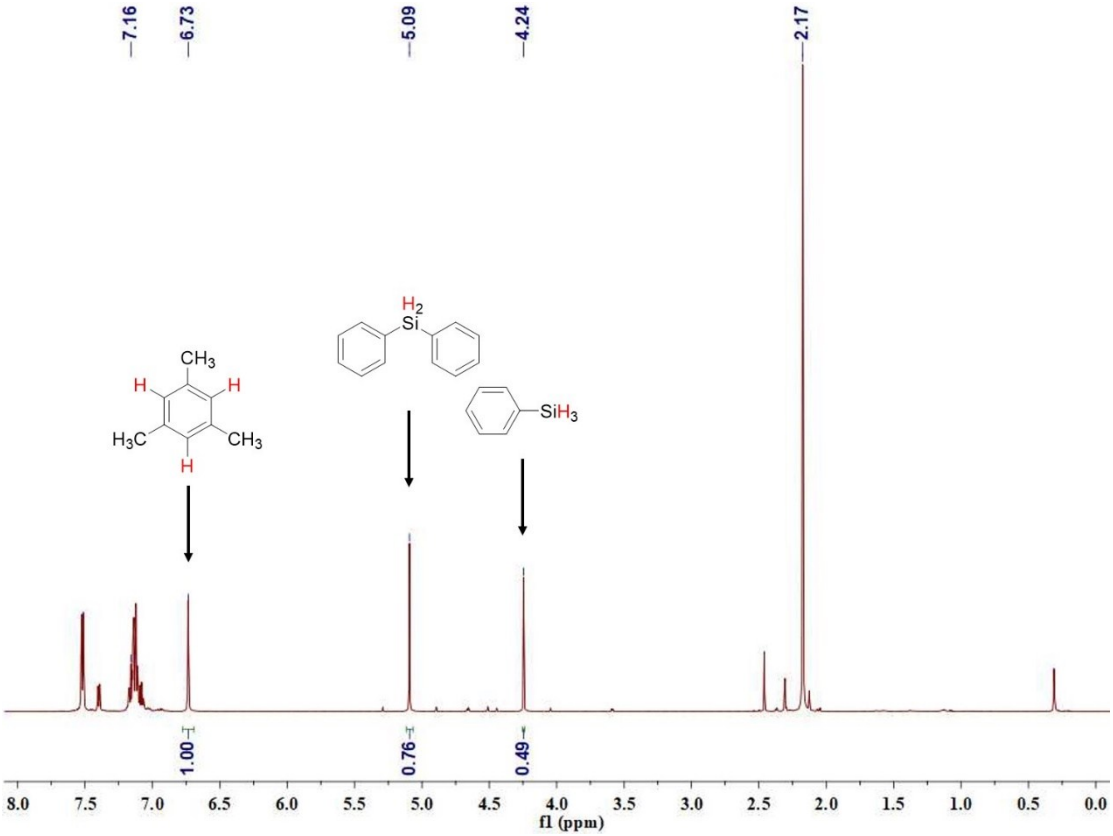


Fig. S4. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2a** at 25 ^{o}C for 6 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 3, Table 2).

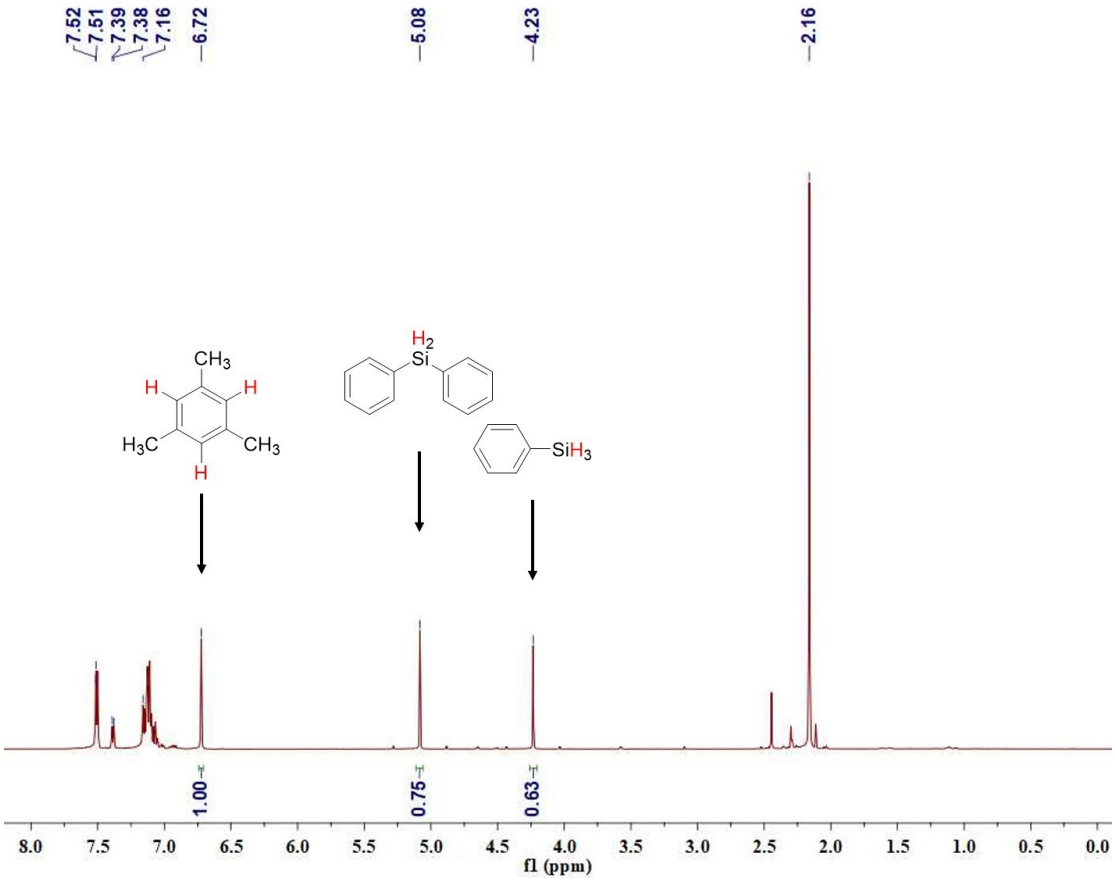


Fig. S5. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2b** at 25 ^{o}C for 6 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 4, Table 2).

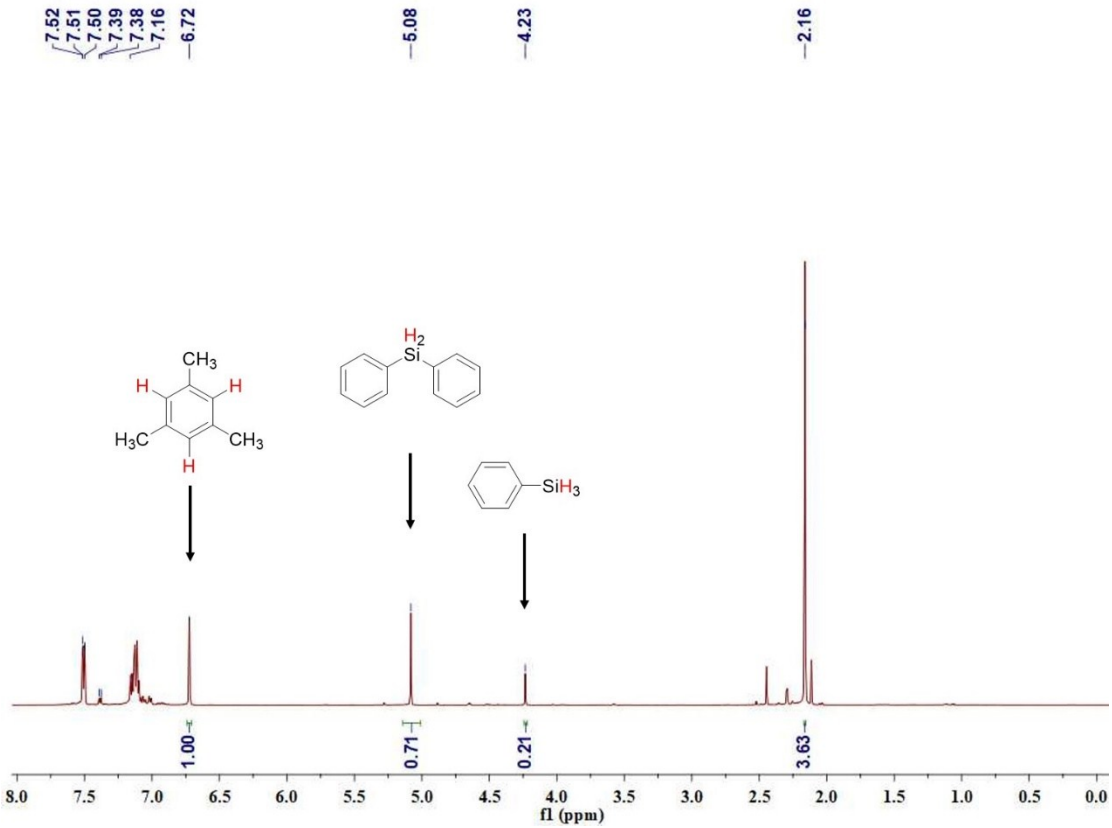


Fig. S6. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2a** at 60 ^{o}C for 6 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 7, Table 2).

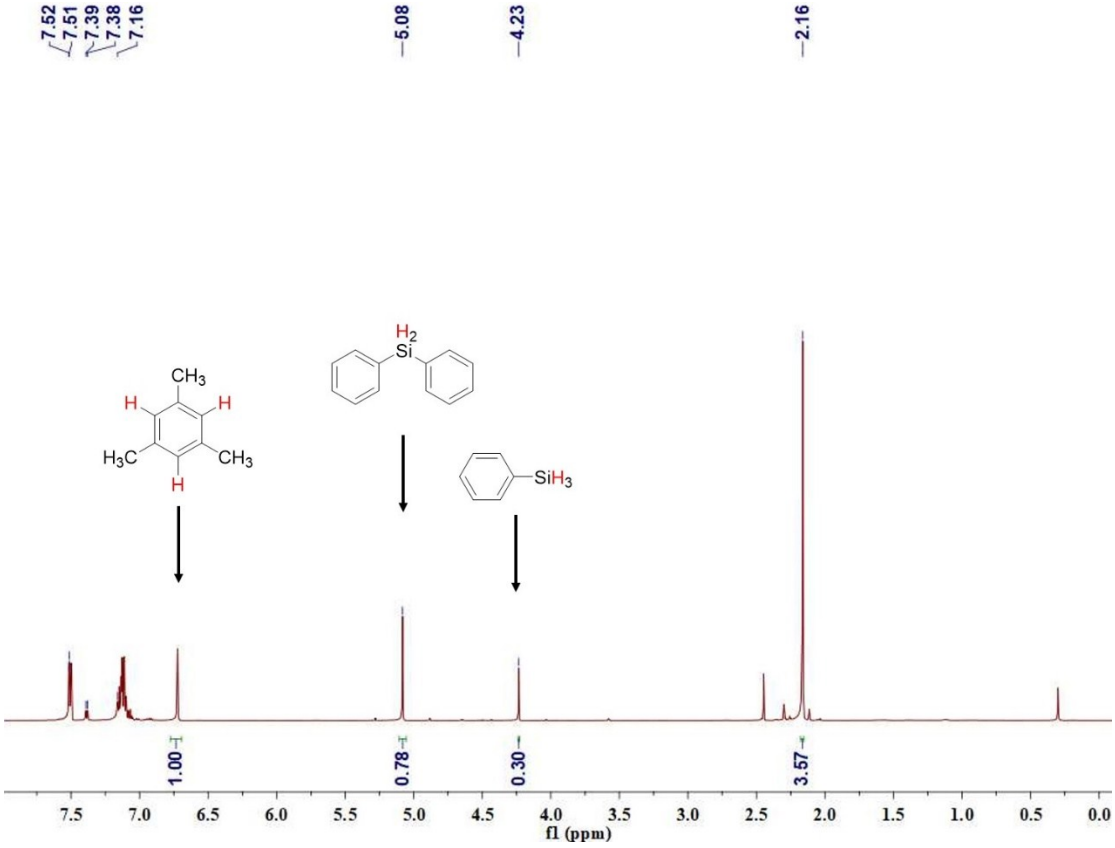


Fig. S7. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2b** at 60 ^{o}C for 6 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 8, Table 2).

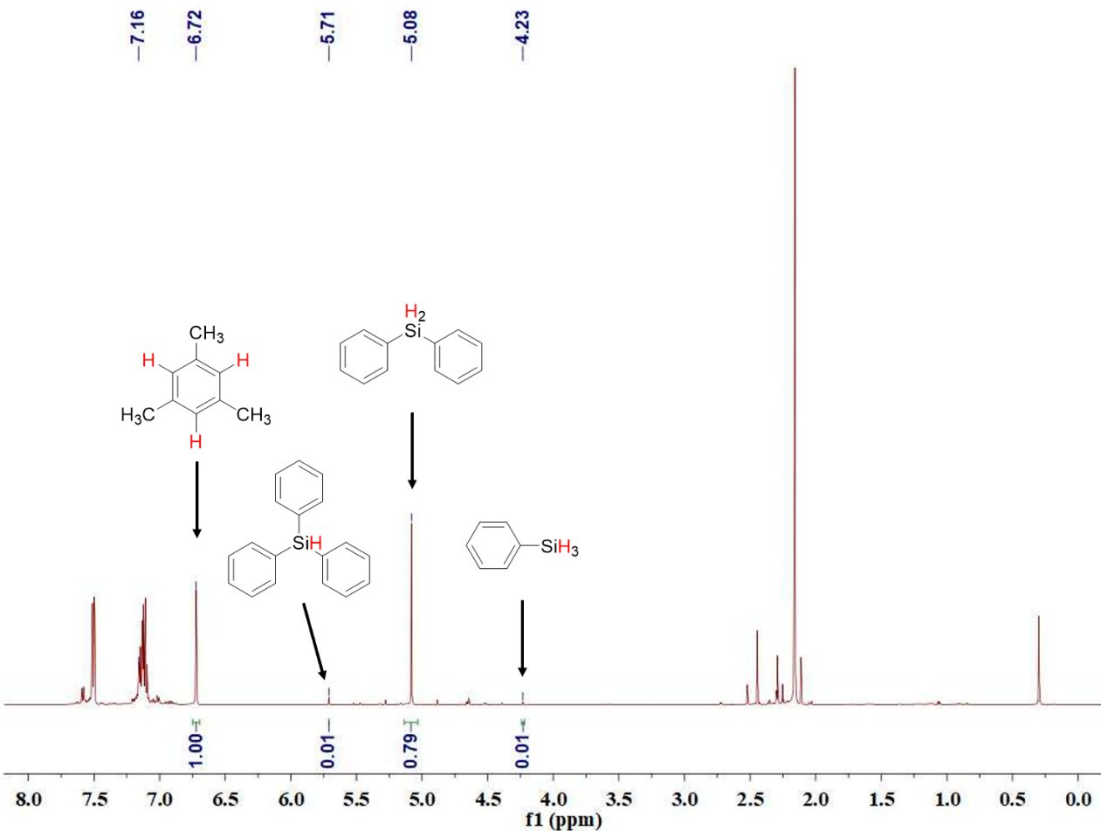


Fig. S8. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2a** at 120 °C for 12 h (500 MHz, C_6D_6, 25 °C, Entry 11, Table 2).

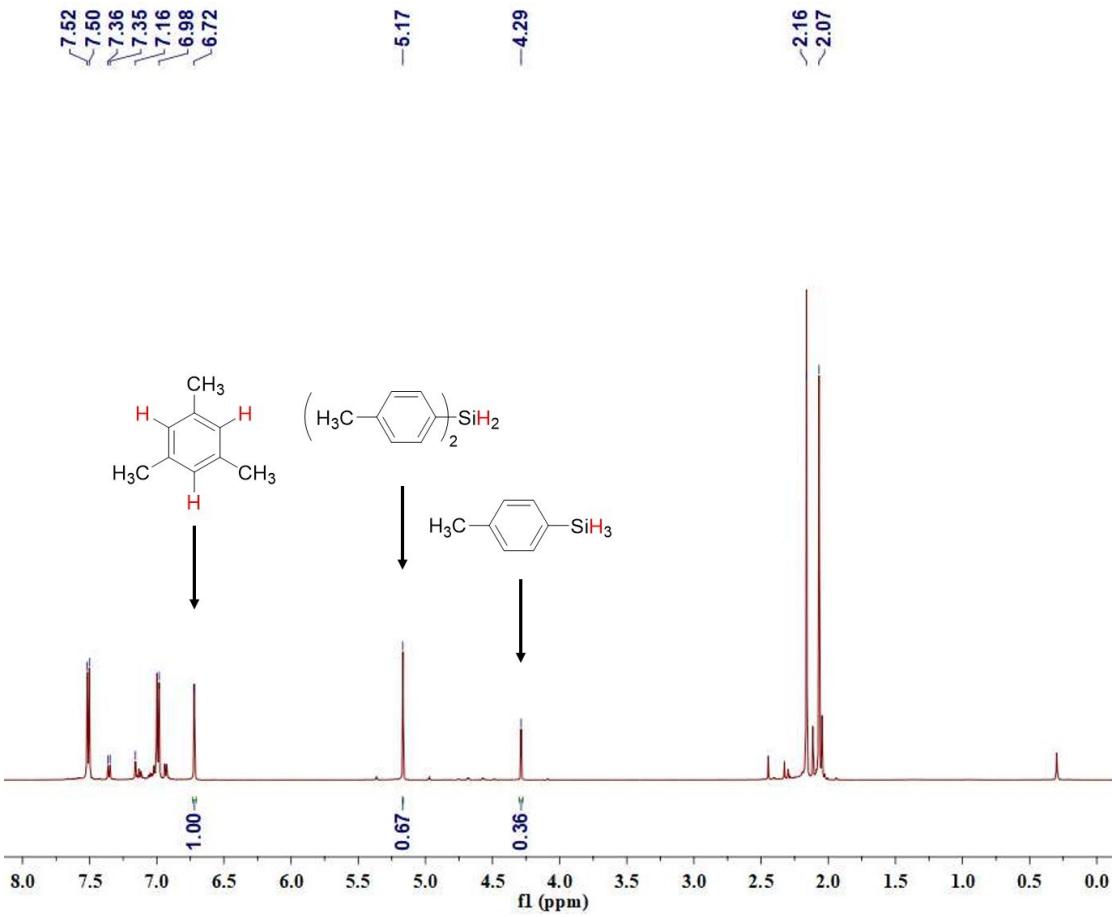


Fig. S9. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-Me-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C in 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 12, Table 2).

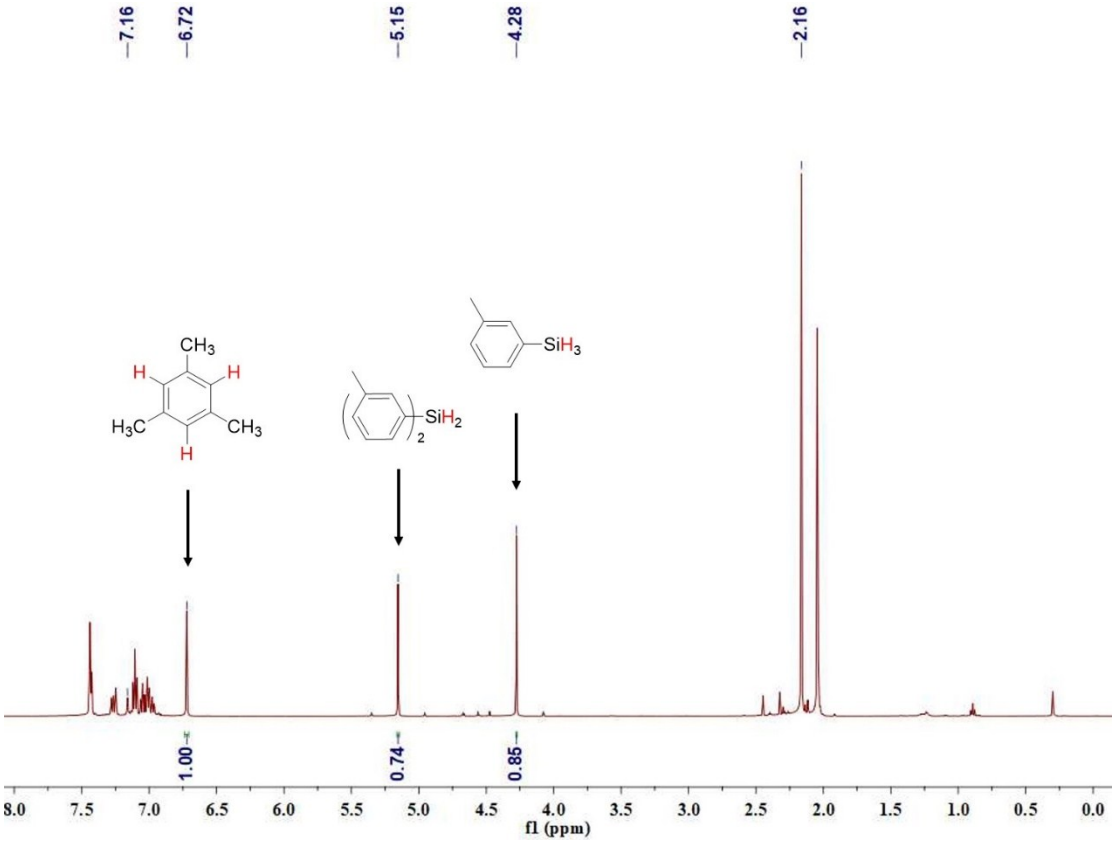


Fig. S10. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*m*-Me-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C in 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 13, Table 2).

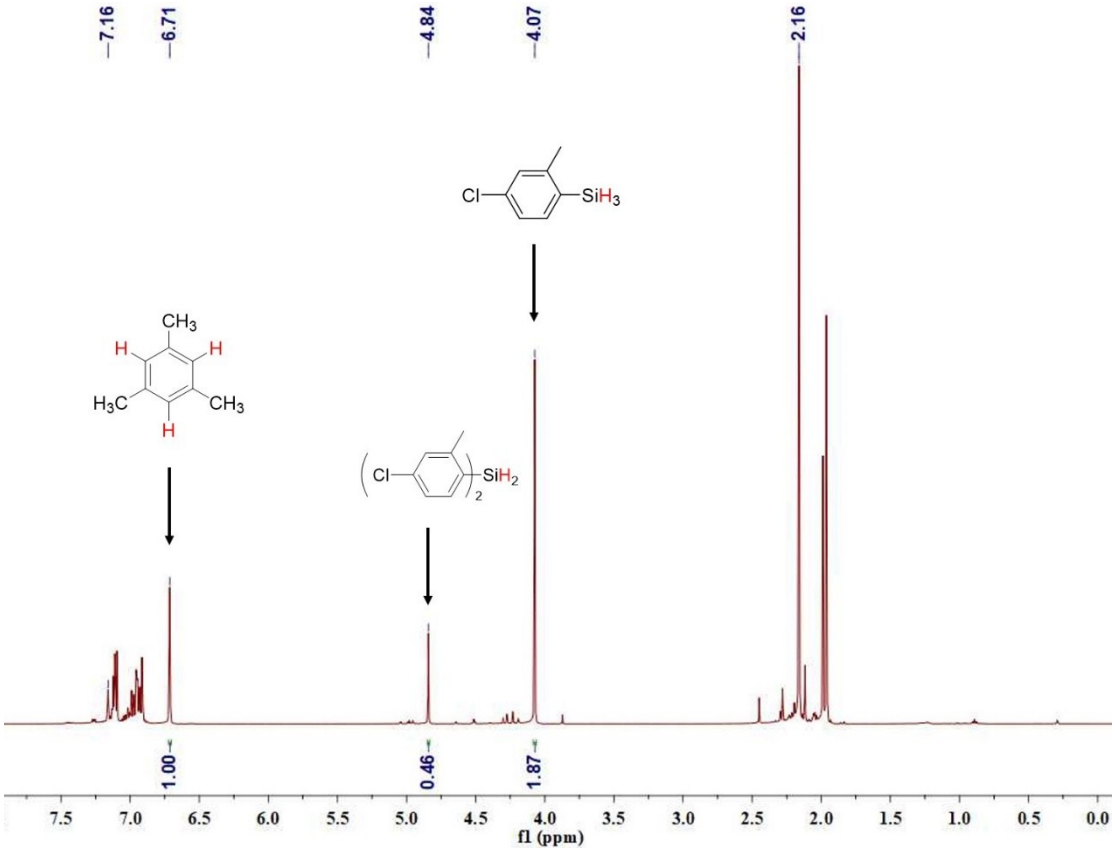


Fig. S11. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-Cl-*o*-Me-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C in 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 14, Table 2).

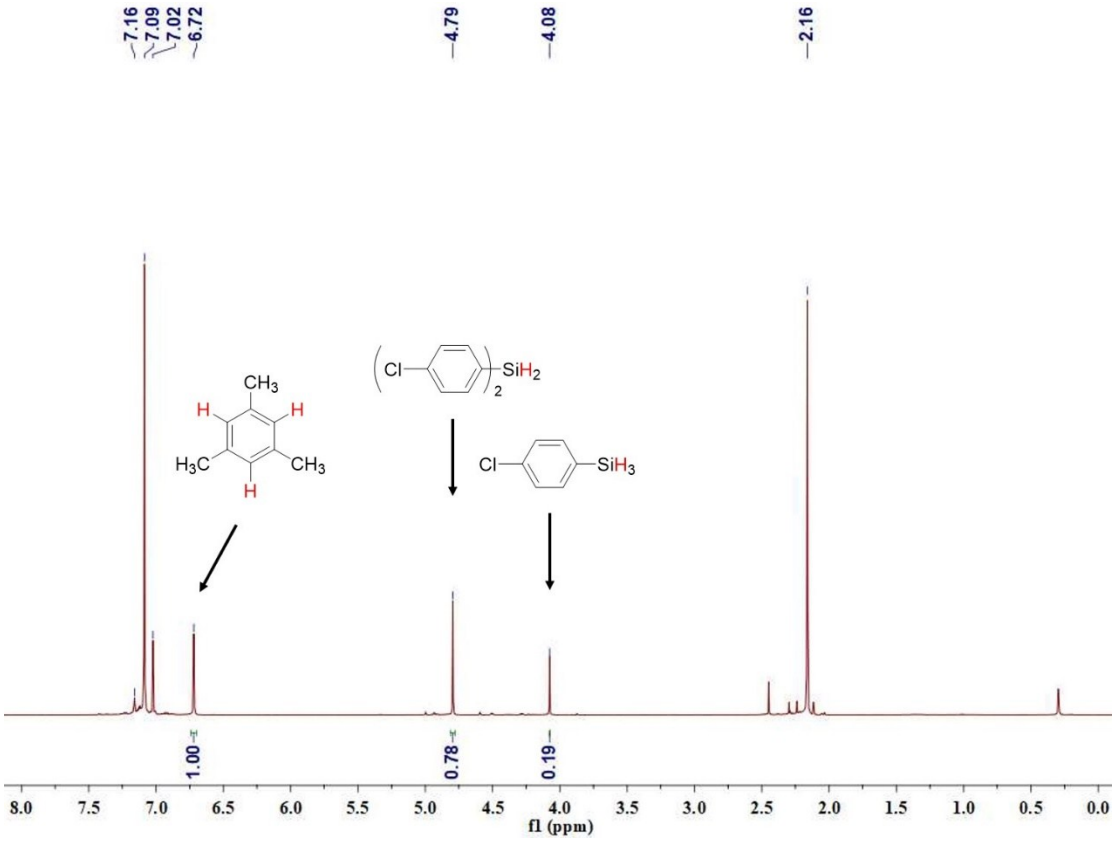


Fig. S12. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-Cl-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C for 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 15, Table 2).

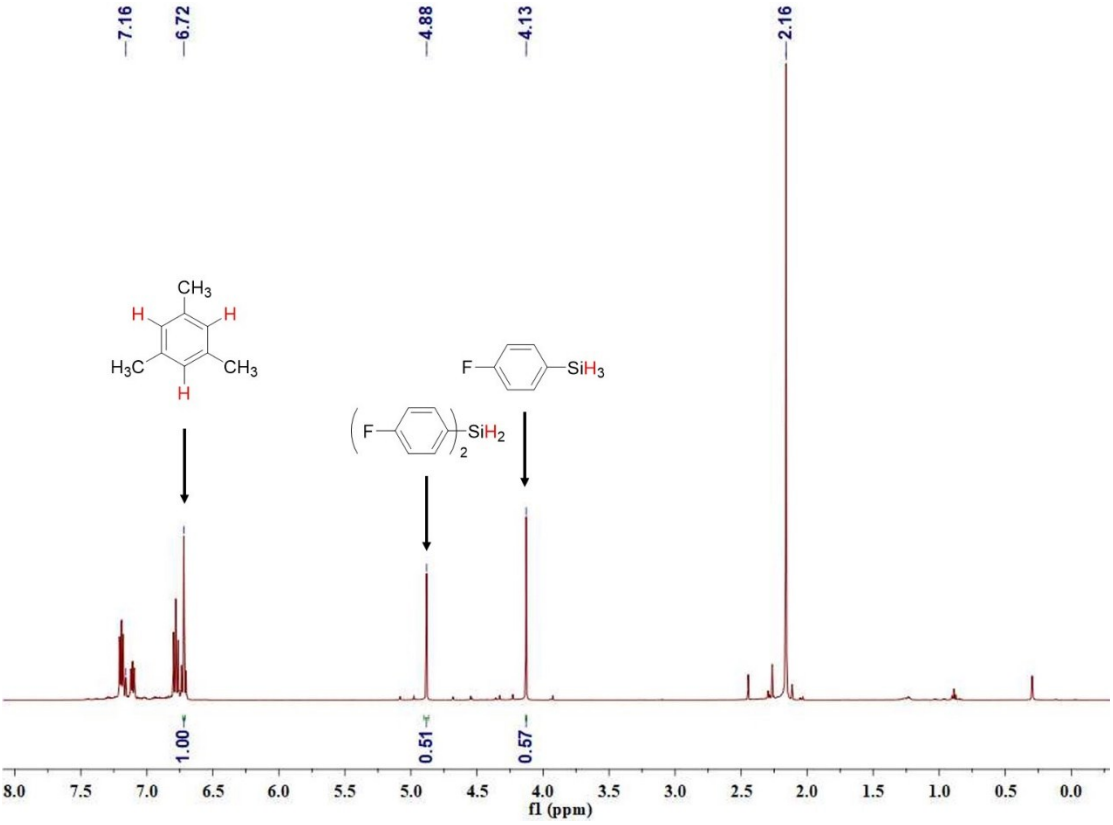


Fig. S13. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-F-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C for 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 16, Table 2).

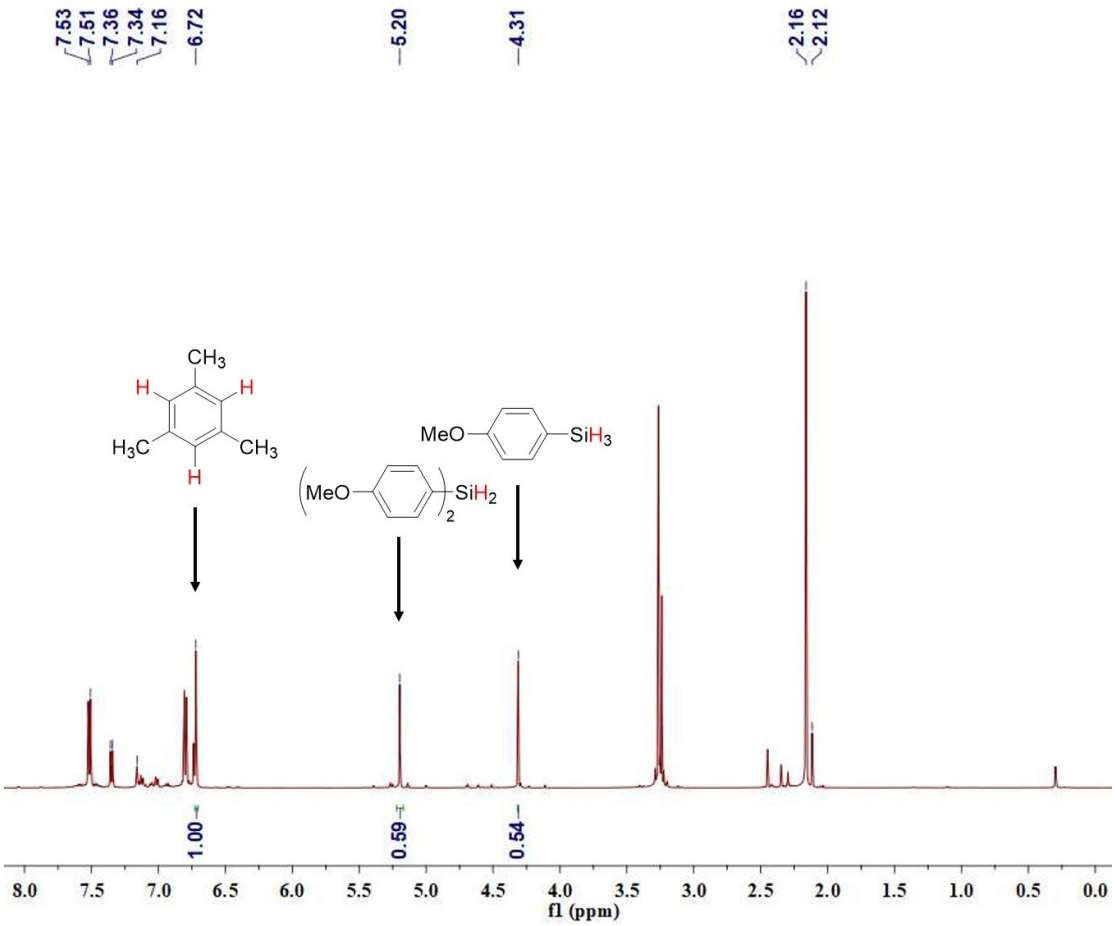


Fig. S14. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-MeO-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C for 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 17, Table 2).

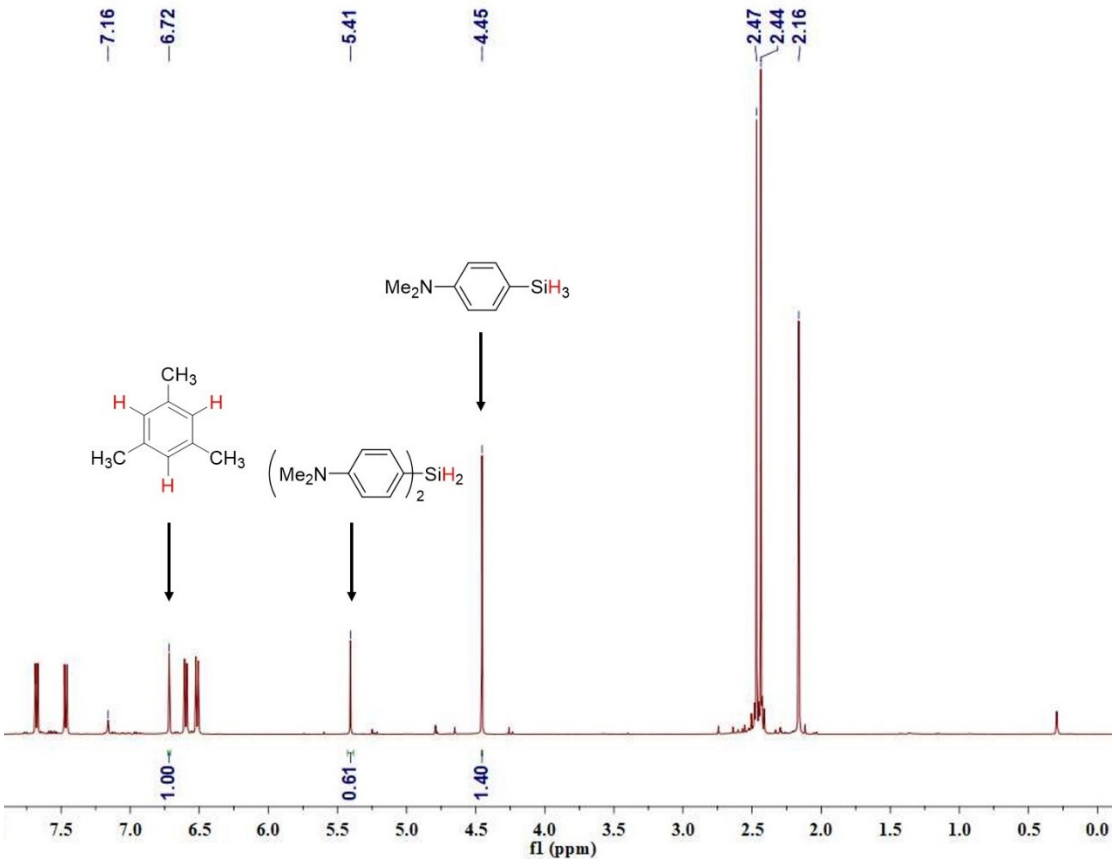


Fig. S15. Quantitative ^{1}H NMR spectrum of the products of redistribution of (*p*-Me_2N-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C for 4 h (500 MHz, C_6D_6, 25 ^{o}C, Entry 18, Table 2).

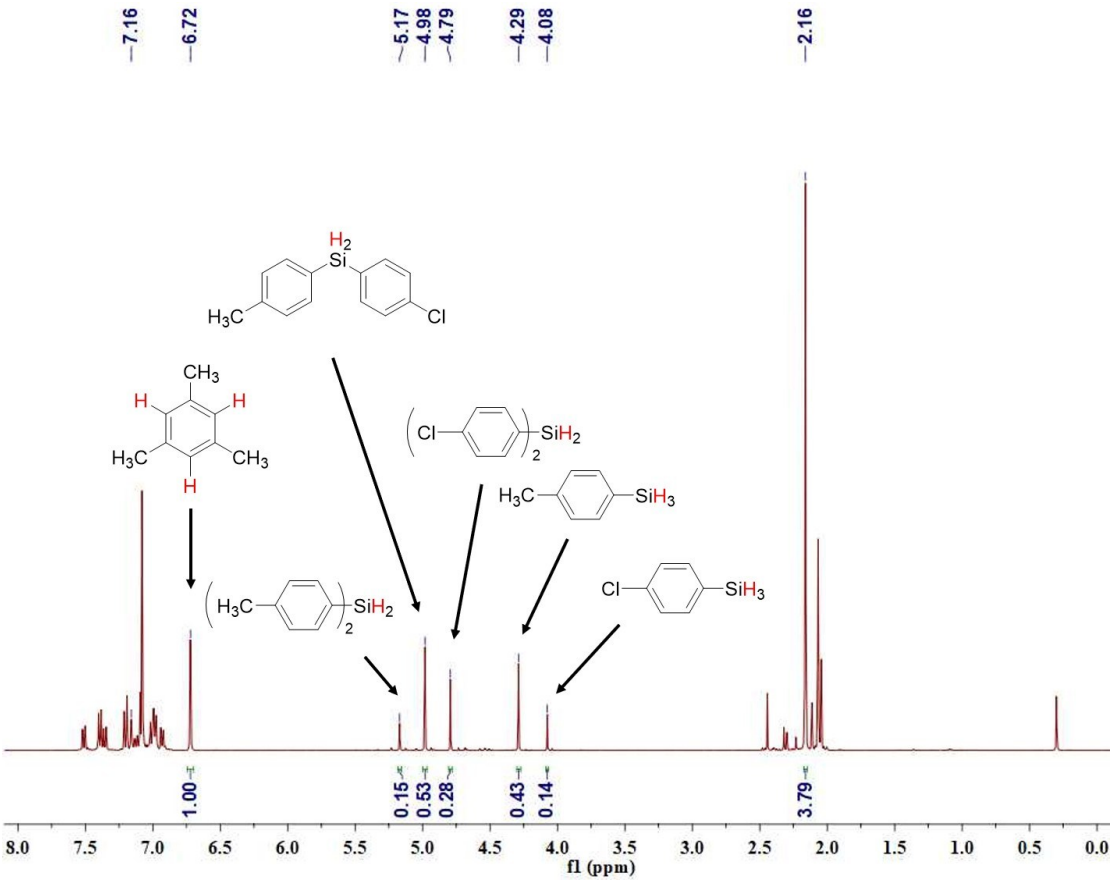


Fig. S16. Quantitative ^{1}H NMR spectrum of the products of the cross-coupling of (*p*-Me-C_6H_4)SiH_3 and (*p*-Cl-C_6H_4)SiH_3 catalyzed by 5 mol% **2a** at 60 ^{o}C for 6 h (500 MHz, C_6D_6, 25 ^{o}C).

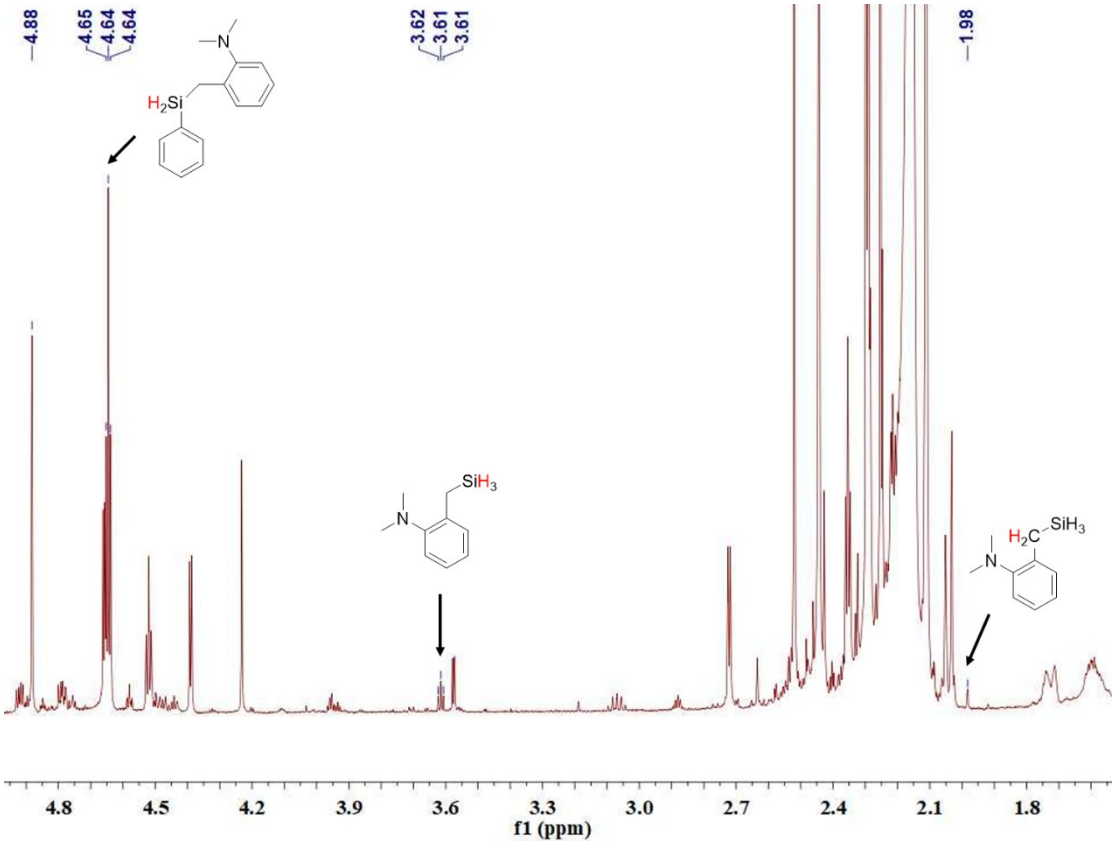


Fig. S17. ^{1}H NMR monitoring of redistribution of $PhSiH_3$ catalyzed by 5 mol% **2a** at 120 ^{o}C for 12 h (500 MHz, C_6D_6, 25 ^{o}C).

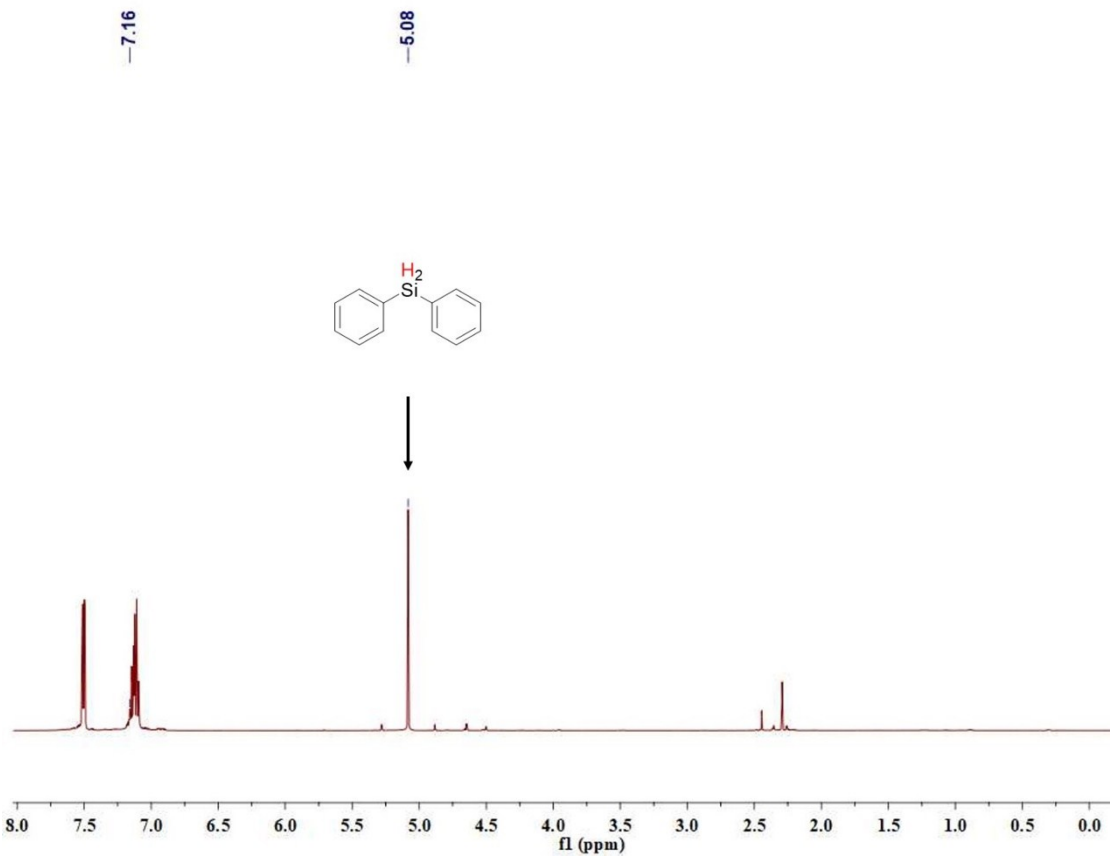


Fig. S18. ^{1}H NMR monitoring of the product of the Gram scale reaction (500 MHz, C_6D_6, 25 ^{o}C).

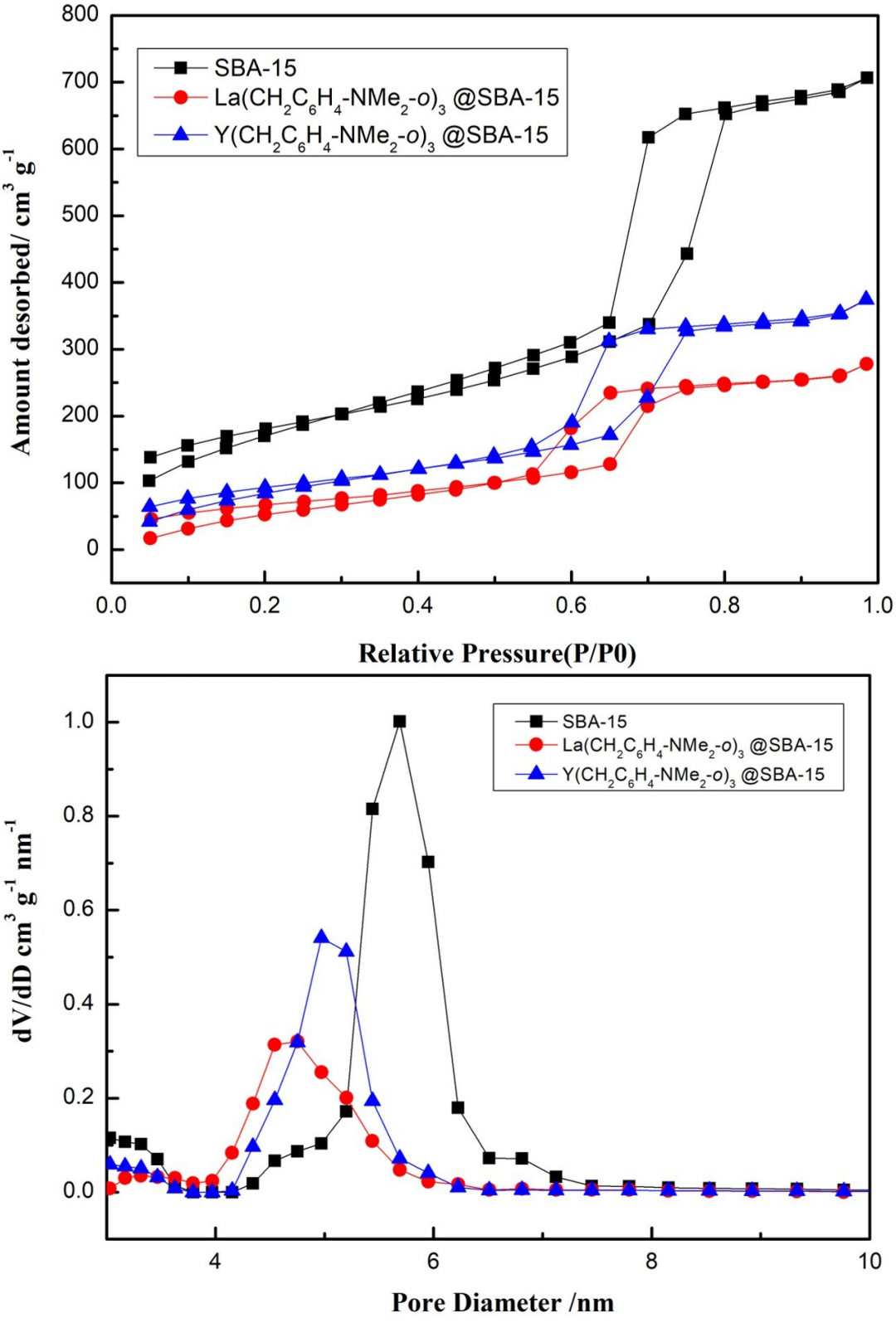


Fig. S19. Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of parent SBA-15, $Ln(CH_2C_6H_4\text{-}NMe_2\text{-}o)_3$@SBA-15 (Ln = La (**2a**), Y (**2b**)).

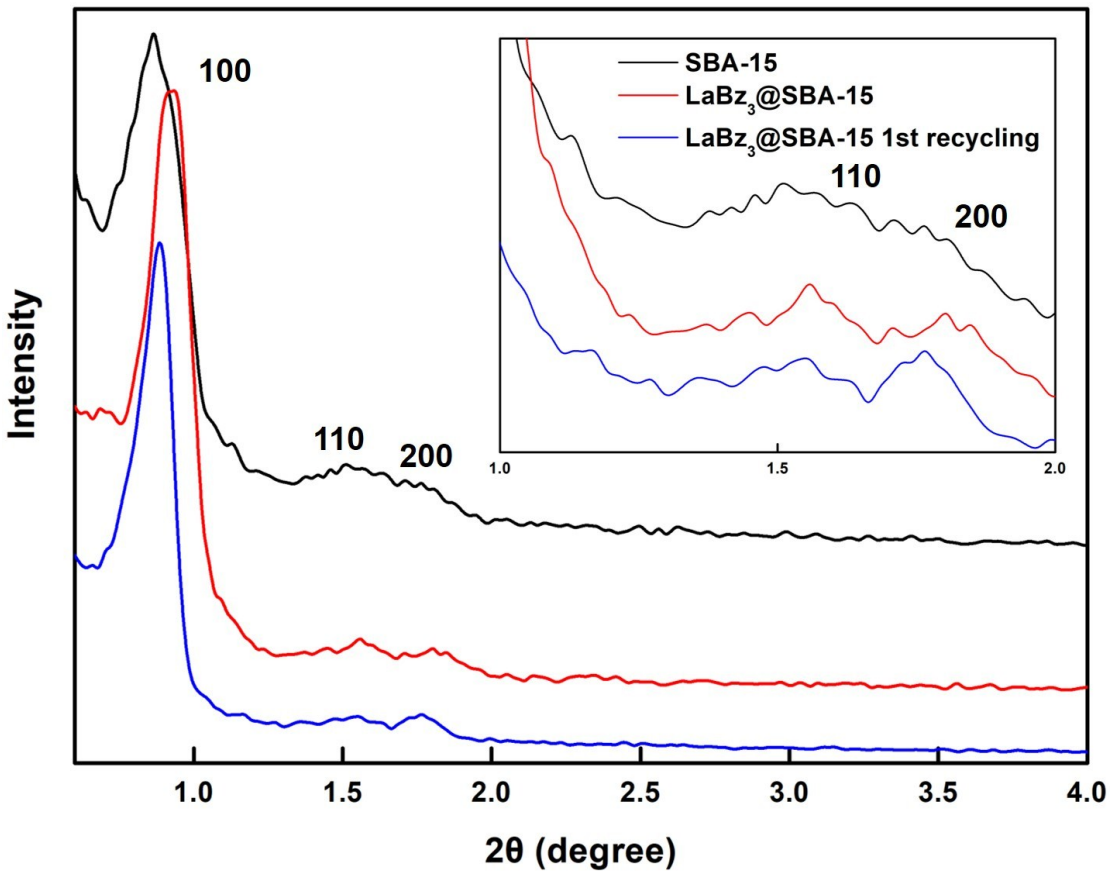


Fig. S20 PXRD patterns of SBA-15, La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2a**) and La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 1st recycling.

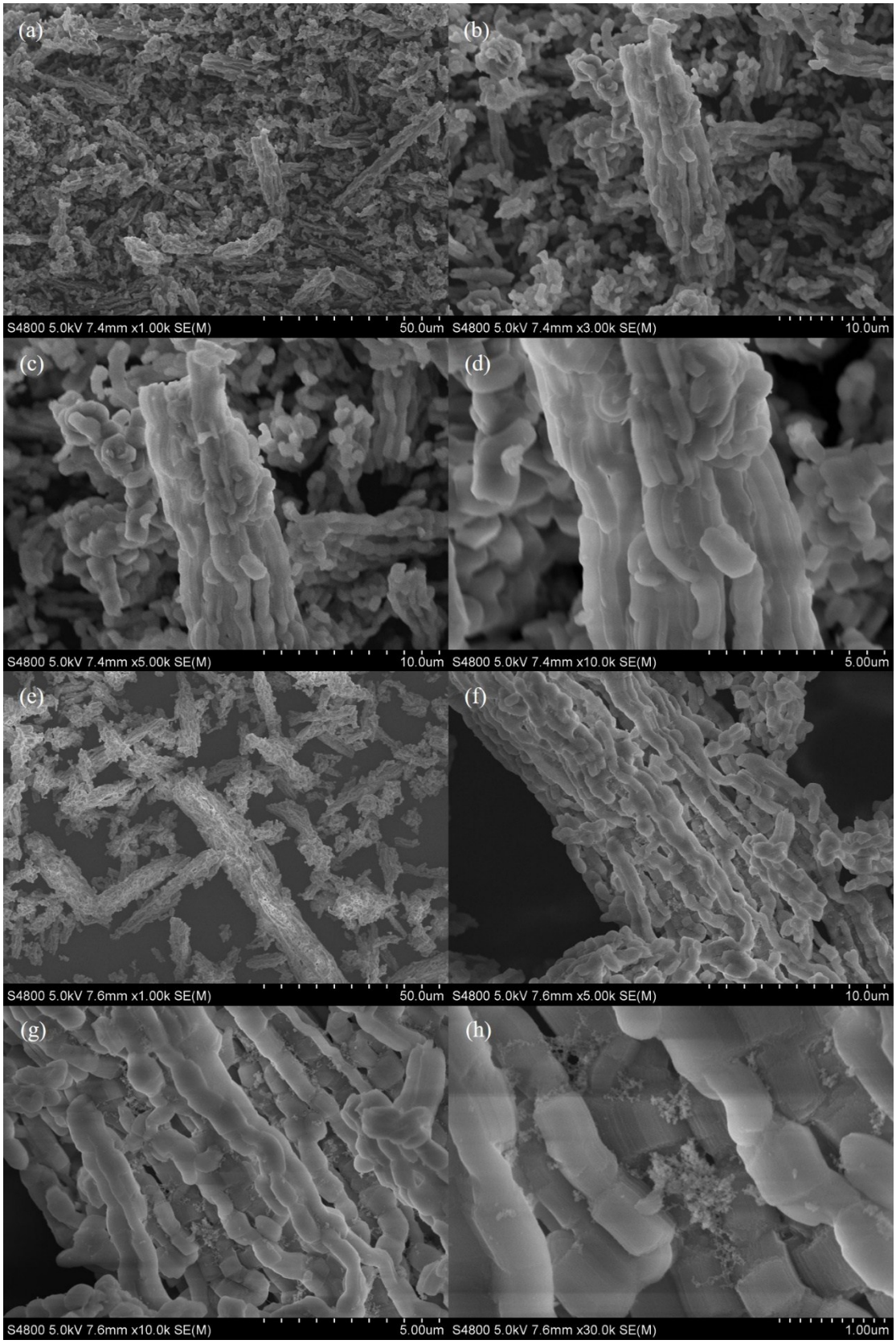


Fig. S21 External surface of particles depicted by SEM images of (a-d) SBA-15 and (e-h) hybrid materials Ln($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15.

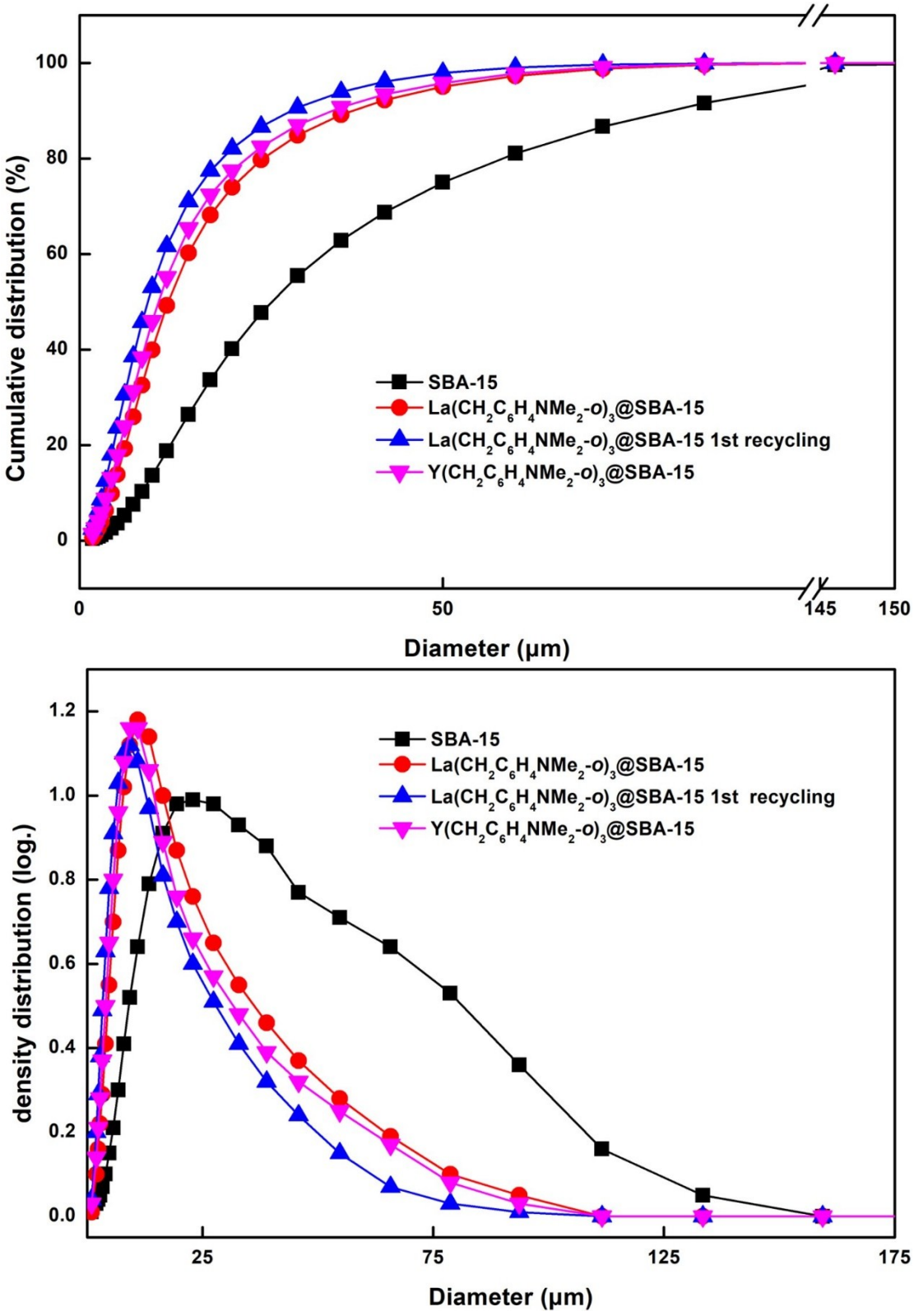


Fig. S22 Particle size distribution of SBA-15, Ln($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (Ln = La (**2a**), Y (**2b**)) and La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 1st recycling in *n*-hexane.

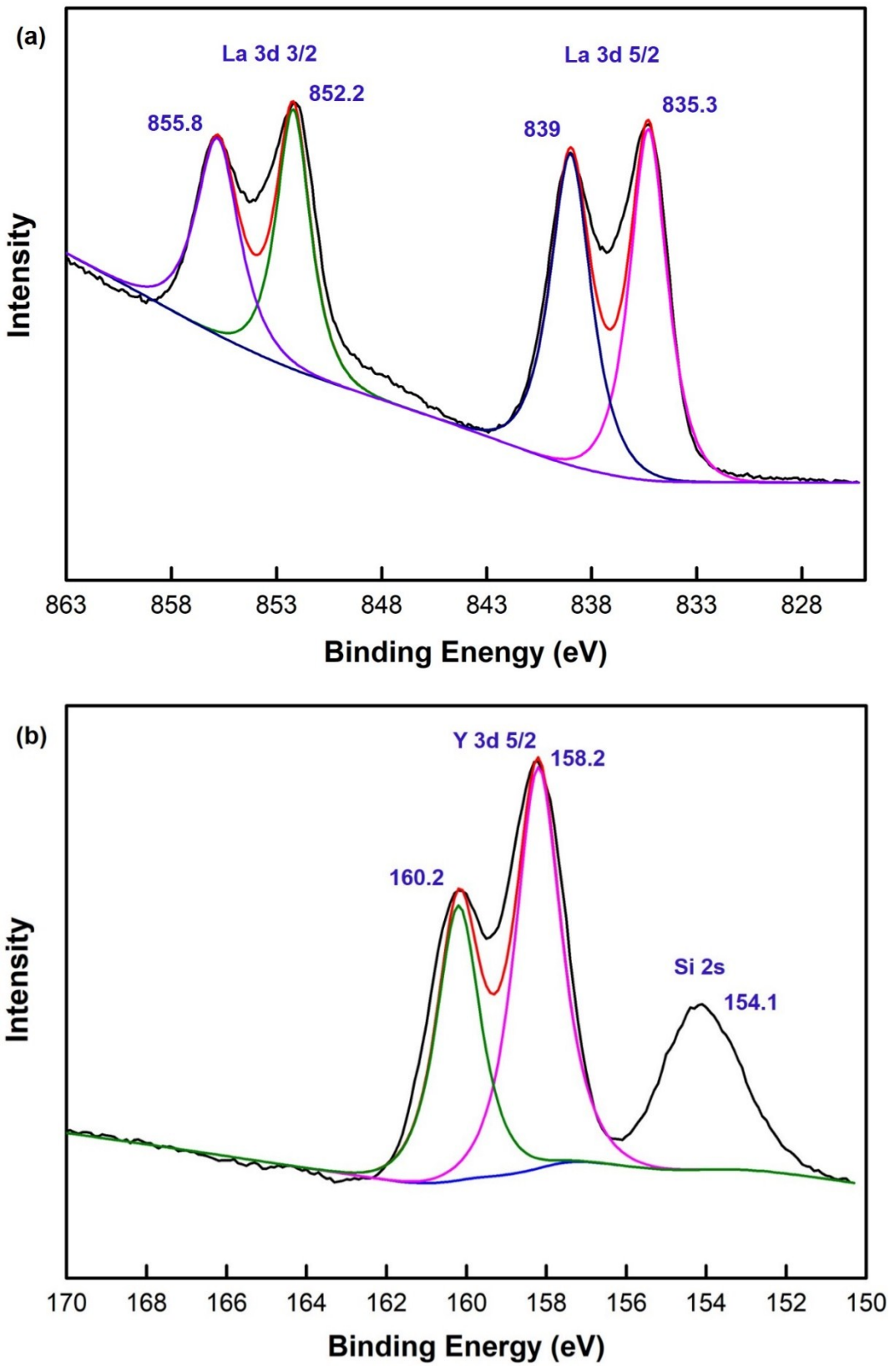


Fig. S23 XPS Narrow scan spectra of (a) La($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2a**) and (b) Y($CH_2C_6H_4$-NMe_2-*o*)$_3$@SBA-15 (**2b**).

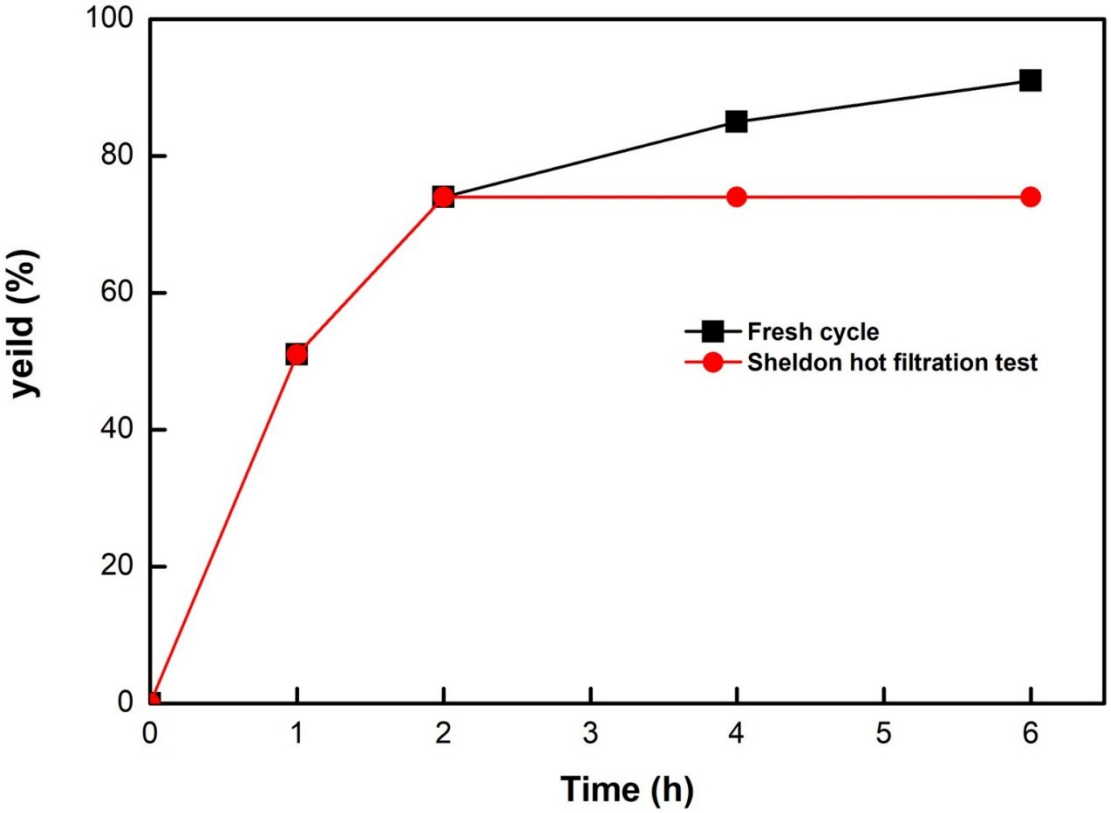
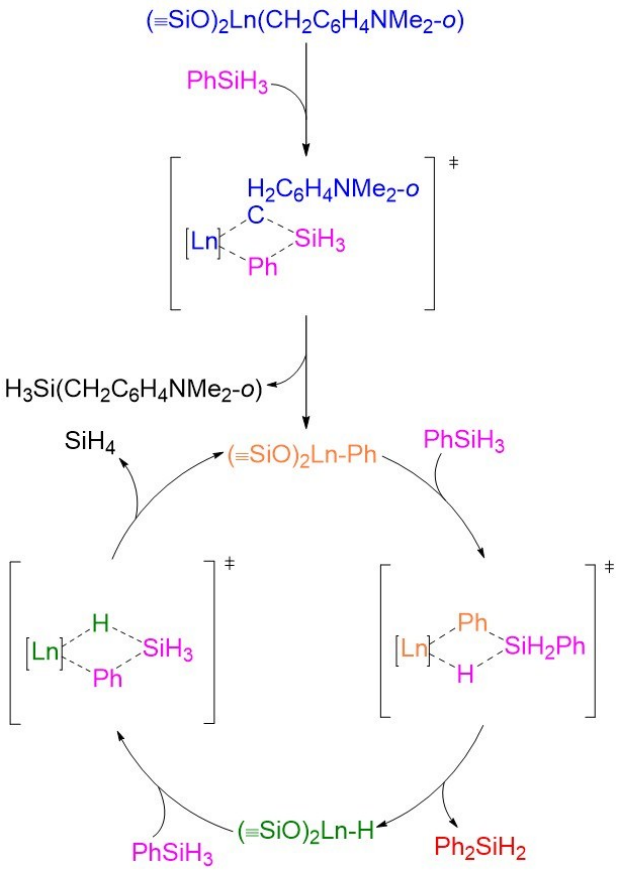


Fig. S24. Sheldon's hot filtration test in redistribution of $PhSiH_3$.



Scheme S1. Proposed mechanism for the redistribution reaction of $PhSiH_3$.

Table S1 ICP-AES for La loss per cycle.

$La(CH_2C_6H_4\text{-}NMe_2\text{-}o)_3$@SBA-15 [a]	1st cycling	2nd cycling
Loss of La	0.38 mmol/g	0.51 mmol/g

[a] The catalyst was dissolved in a mixture solution of hydrofluoric acid and nitric acid.

Reference

1. S. Harder, *Organometallics*, 2005, **24**, 373-379.