

Ruthenium nanoparticles stabilized by 1,2,3-triazolylidene ligands in the hydrogen isotope exchange of E-H bonds (E = B, Si, Ge, Sn) using deuterium gas

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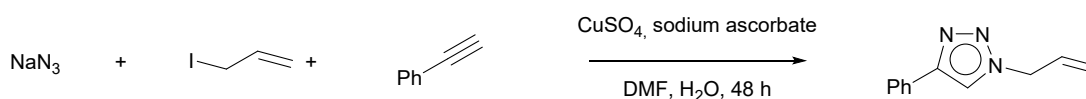
S1. General procedures, materials and characterization techniques.

Liquid phase ^1H and ^2H NMR spectra were recorded on a Bruker DRX-400 spectrometer. Spectra were referenced to SiMe_4 ($\delta = 0$ ppm) using the residual proton solvent peaks as internal standards. All NMR spectra were recorded at 25°C .

HRMS experiments were carried out in a Thermo Scientific-QExactive apparatus by the Mass Spectrometry Service of the Centro de Investigación, Tecnología e Innovación – CITIUS (University of Sevilla).

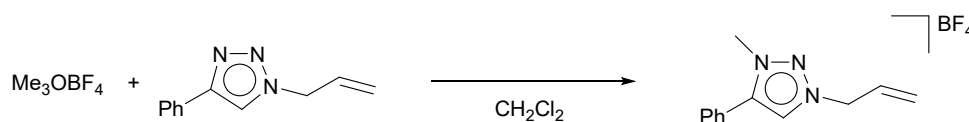
S2. Synthesis of 1,2,3-triazolylidene ligands precursors.

MIC1 precursor



In a round-bottom flask, copper sulphate (0.250 g, 1.1 mmol), sodium ascorbate (0.210 g, 1.1 mmol) and sodium azide (0.806 g, 12.4 mmol) were dissolved in DMF (8 mL) and water (5 mL). Phenylacetylene (1.1 mL, 10 mmol) and allyl iodide (1.64 g, 9.8 mmol) were added, and the reaction mixture was stirred under N_2 for 48 h. After that time, the reaction was quenched using 100 mL of an aqueous basic solution (0.6% NH_4OH), producing the precipitation of a solid. The precipitate was filtered, washed with water (3 x 30 mL), and dried. White solid (1.30 g, 70%). Spectroscopic data for this product agree to those previously reported in the literature.¹

^1H NMR (400 MHz, CD_2Cl_2): δ 7.87 (m, 2H, 2 H_{Ph}), 7.84 (s, 1H, $\text{H}_{\text{triazole}}$), 7.56-7.32 (m, 3H, 3 H_{Ph}), 6.11 (m, 1H, $\text{CH}=\text{CH}_2$), 5.38 (m, 2H, $=\text{CH}_2$), 5.03 (d, $^3J_{\text{HH}} = 6.3$ Hz, 2H, CH_2).



1-allyl-4-phenyl-1H-1,2,3-triazole (0.120 g, 0.65 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was cooled to 0°C , and added to Me_3OBF_4 (0.252 g, 0.85 mmol). The mixture was allowed to reach room temperature, and stirred for 72 h. The solvent was evaporated under vacuum, and MeOH (10 mL) was added producing the formation of a precipitate. The solid was filtered off, and the solution was evaporated to dryness. The residue was washed with diethyl ether (3 x 10 mL) to yield a white solid (0.091 g, 45%). Spectroscopic data for this product agree to those previously reported in the literature.¹

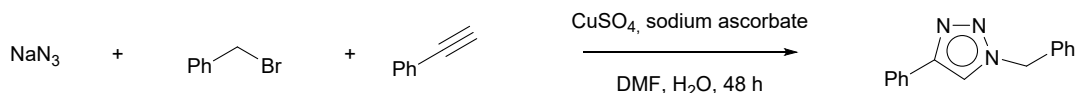
^1H NMR (400 MHz, CD_2Cl_2): δ 8.53 (s, 1H, $\text{H}_{\text{triazolium}}$), 7.65 (m, 5H, 5 H_{Ph}), 6.19 (m, 1H, $\text{CH}=\text{CH}_2$), 5.66 (d, $^3J_{\text{HH}} = 17.1$ Hz, 1H, $=\text{CHH}$), 5.58 (d, $^3J_{\text{HH}} = 10.2$ Hz, 1H, $=\text{CHH}$), 5.26 (d, $^3J_{\text{HH}} = 6.7$ Hz, 2H, CH_2), 4.28 (s, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 143.6, 131.9, 129.7, 129.3, 128.3, 128.1, 124.0, 121.9, 56.2, 38.5.

HRMS (ESI, positive mode): m/z 200.1182 [M^+], exact mass calculated for $C_{12}H_{14}N_3$: 200.1178.

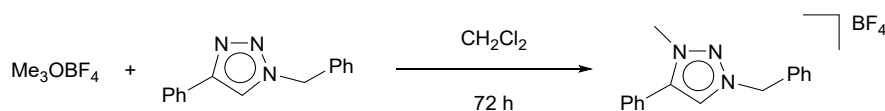
HRMS (ESI, negative mode): m/z 87.0035 [M^-]; exact mass calculated for BF_4 : 87.0034.

MIC2 precursor



In a round-bottom flask, copper sulphate (0.250 g, 1.1 mmol), sodium ascorbate (0.210 g, 1.1 mmol) and sodium azide (0.806 g, 12.4 mmol) were dissolved in DMF (8 mL) and water (5 mL). Phenylacetylene (1.1 mL, 10 mmol) and benzyl bromide (1.67 g, 9.8 mmol) were added and the reaction mixture was stirred under N_2 for 48 h. After that time, the reaction was quenched using 100 mL of an aqueous basic solution (0.6% NH_4OH), producing the precipitation of a solid. The precipitate was filtered, washed with water (3 x 30 mL), and dried. Pale white solid (1.10 g, 46%). Spectroscopic data for this product agree to those previously reported in the literature.²

1H NMR (400 MHz, CD_2Cl_2): δ 7.79 (m, 2H, 2 H_{Ph}), 7.74 (s, 1H, $H_{triazole}$), 7.44-7.28 (m, 8H, 8 H_{Ph}), 5.56 (s, 2H, CH_2).



1-benzyl-4-phenyl-1H-1,2,3-triazole (0.150 g, 0.65 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was cooled to 0 °C, and added to Me_3OBF_4 (0.250 g, 0.85 mmol). The mixture was allowed to reach room temperature, and stirred for 72 h. The solvent was evaporated under vacuum, and MeOH (10 mL) was added producing the formation of a precipitate. The solid was filtered off, and the solution was evaporated to dryness. The residue was washed with diethyl ether (3 x 10 mL) to yield a white solid (0.120 g, 55%). Spectroscopic data for this product agree to those previously reported in the literature.³

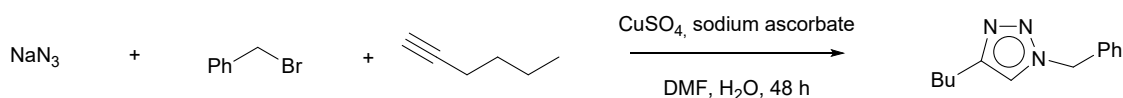
1H NMR (400 MHz, CD_2Cl_2): δ 8.53 (s, 1H, $H_{triazolium}$), 7.57 (m, 10H, 10 H_{Ph}), 5.86 (s, 2H, CH_2), 4.28 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 143.6, 132.0, 131.3, 129.9, 129.7, 129.6, 129.4, 129.2, 128.3, 121.8, 57.6, 38.6.

HRMS (ESI, positive mode): m/z 250.1338 [M^+], exact mass calculated for $C_{16}H_{16}N_3$: 250.1337.

HRMS (ESI, negative mode): m/z 87.0035 [M^-]; exact mass calculated for BF_4 : 87.0034.

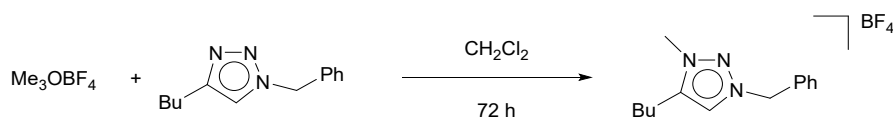
MIC3 precursor



In a round-bottom flask, copper sulphate (0.250 g, 1.1 mmol), sodium ascorbate (0.210 g, 1.1 mmol) and sodium azide (0.806 g, 12.4 mmol) were dissolved in DMF (8 mL) and water (5 mL).

1-Hexyne (1.1 mL, 10.0 mmol) and benzyl bromide (1.67 g, 9.8 mmol) were added and the reaction mixture was stirred under N₂ for 48 h. After that time, the reaction was quenched using 100 mL of an aqueous basic solution (0.6% NH₄OH), producing the precipitation of a solid. The precipitate was filtered, washed with water (3 x 30 mL), and dried. White solid (1.30 g, 60%). Spectroscopic data for this product agree to those previously reported in the literature.¹

¹H NMR (400 MHz, CD₃OD): δ 7.36 (m, 2H, 2 H_{Ph}), 7.31 (s, 1H, H_{triazole}), 7.25 (m, 3H, 3 H_{Ph}), 5.78 (s, 2H, CH₂), 2.66 (t, ³J_{HH} = 7.2 Hz, 2H, CH₂), 1.61 (m, 2H, CH₂), 1.49 (m, 2H, CH₂), 1.00 (t, ³J_{HH} = 8.2 Hz, 3H, CH₃).



1-benzyl-4-butyl-1H-1,2,3-triazole (0.141 g, 0.65 mmol) was dissolved in CH₂Cl₂ (10 mL). The resulting solution was cooled to 0 °C, and added to Me₃OBF₄ (0.250 g, 0.85 mmol). The mixture was allowed to reach room temperature, and stirred for 72 h. The solvent was evaporated under vacuum, and MeOH (10 mL) was added producing the formation of a precipitate. The solid was filtered off, and the solution was evaporated to dryness. The residue was washed with diethyl ether (3 x 10 mL) to yield a white solid (0.112 g, 53%). Spectroscopic data for this product agree to those previously reported in the literature.^{1,4}

¹H NMR (400 MHz, CD₃OD): δ 8.59 (s, 1H, H_{triazolium}), 7.47 (m, 5H, 5 H_{Ph}), 5.78 (s, 2H, CH₂), 4.24 (s, 3H, CH₃), 2.86 (t, ³J_{HH} = 8.4 Hz, 2H, CH₂), 1.74 (m, 2H, CH₂), 1.48 (m, 2H, CH₂), 1.00 (t, ³J_{HH} = 7.8 Hz, 3H, CH₃).

¹³C{¹H} NMR (101 MHz, CD₃OD): δ 145.2, 132.4, 129.2, 128.9, 128.8, 127.5, 56.6, 36.4, 28.4, 22.4, 21.7, 12.5.

HRMS (ESI, positive mode): *m/z* 230.1648 [M⁺], exact mass calculated for C₁₄H₂₀N₃: 230.1652.

HRMS (ESI, negative mode): *m/z* 87.0035 [M⁻]; exact mass calculated for BF₄: 87.0034.

S3. TEM and HRTEM images.

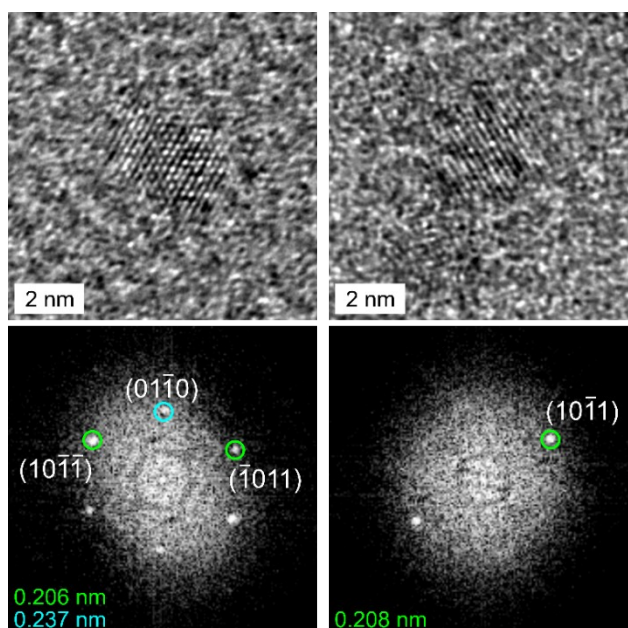


Figure S1. HRTEM images of Ru-MIC3^{0.2} nanoparticles and their corresponding fast Fourier transform analyses.

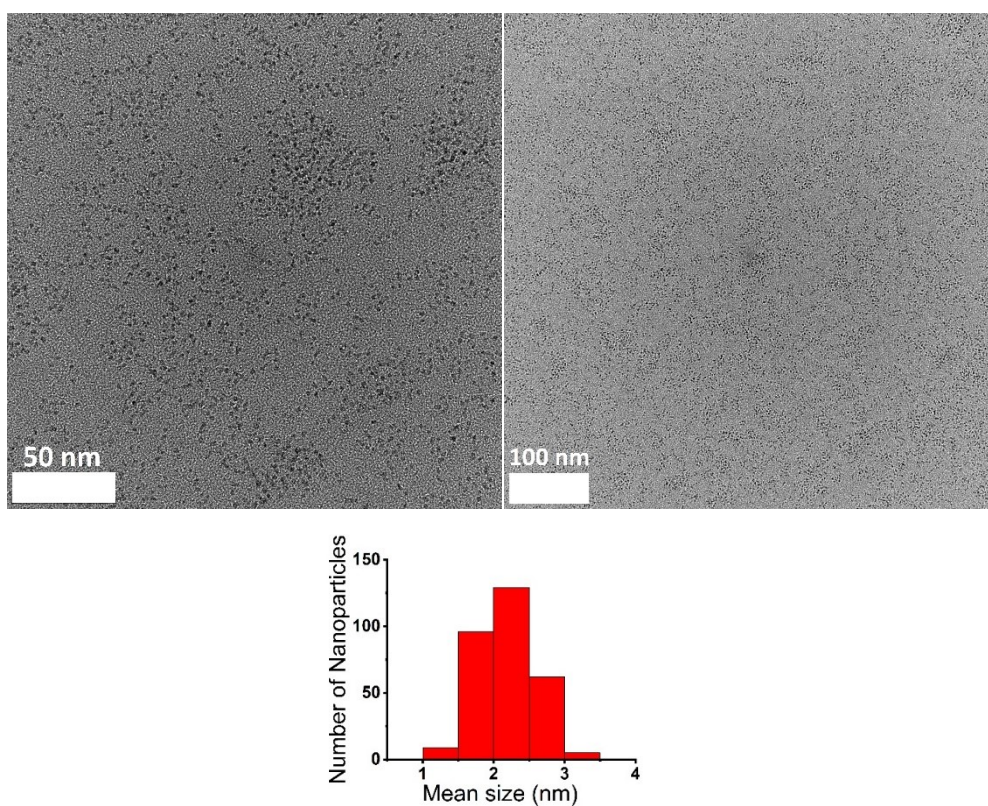


Figure S2. TEM images and size distribution histogram of Ru-MIC1^{0.2} nanoparticles after the catalytic deuteration of Si-5.

S4. XPS spectra.

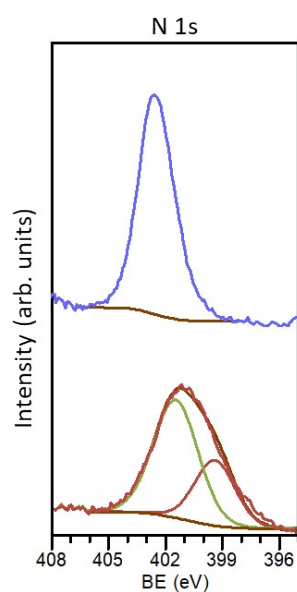


Figure S3. High resolution N 1s photoemission region for **MIC2** ligand precursor (top) and **Ru·MIC2^{0.2}** nanoparticles (bottom).

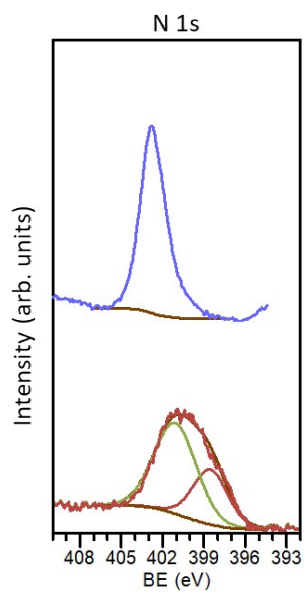


Figure S4. High resolution N 1s photoemission region for **MIC3** ligand precursor (top) and **Ru·MIC3^{0.2}** nanoparticles (bottom).

S5. NMR data of deuterated products.

Me₂PhSiD (Si-1)

Deuterium incorporation: 96%. Spectroscopic data for this product agree to those previously reported in the literature.⁵

¹H NMR (400 MHz, CD₂Cl₂): δ 7.57 (m, 2H, 2 H arom), 7.37 (m, 3H, 3 H arom), 4.45 (hept, ³J_{HH} = 3.8 Hz, SiH), 0.37 (s, 6H, 2 CH₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.45 (SiD).

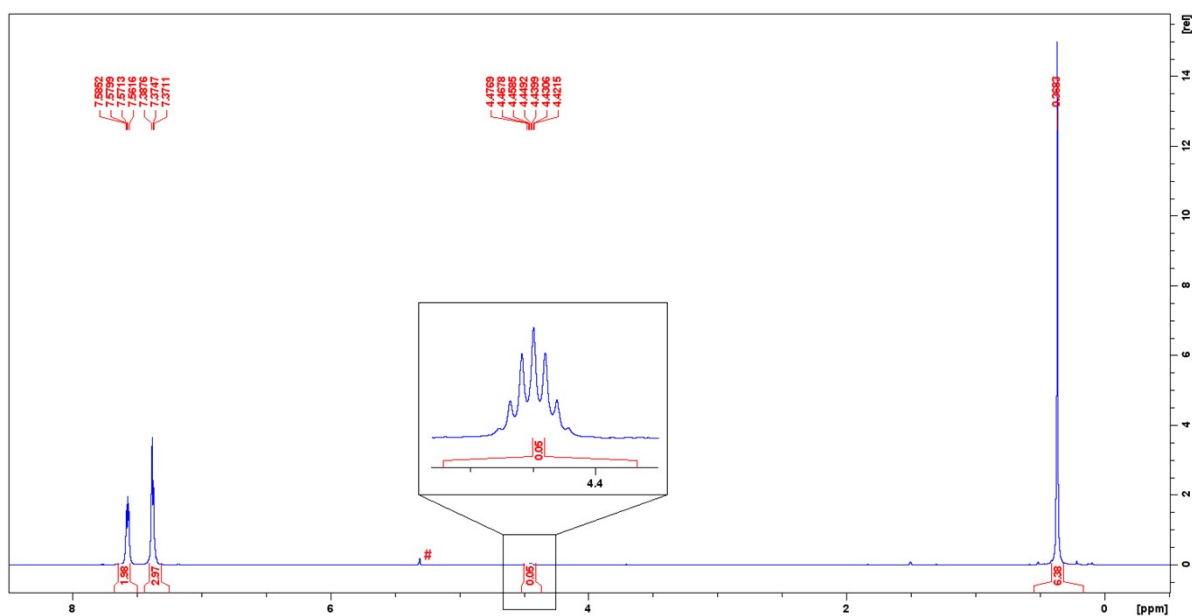


Figure S5. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in Me₂PhSiH (**Si-1**). (# denotes residual CH₂Cl₂ from the deuterated solvent).

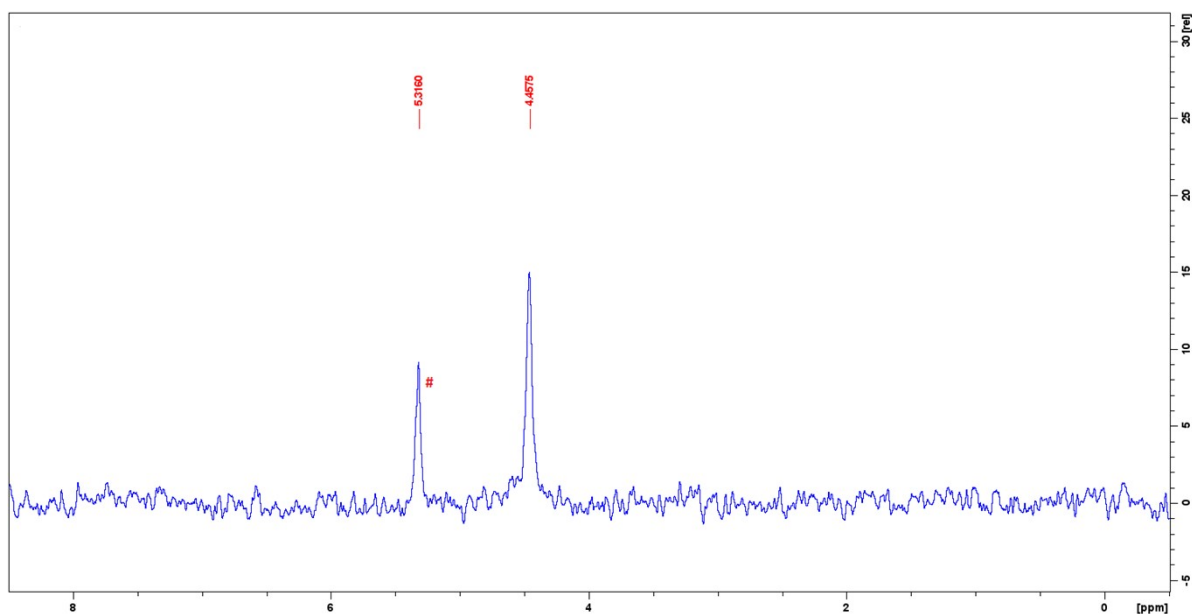


Figure S6. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in Me₂PhSiH (**Si-1**). (# denotes CD₂Cl₂ used as reference).

MePh₂SiD (Si-2)

Deuterium incorporation: 85%. Spectroscopic data for this product agree to those previously reported in the literature.⁶

¹H NMR (400 MHz, CD₂Cl₂): δ 7.62 (m, 4H, 4 H arom), 7.42 (m, 6H, 6 H arom), 4.99 (q, ³J_{HH} = 3.8 Hz, SiH), 0.68 (s, 3H, CH₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.99 (SiD).

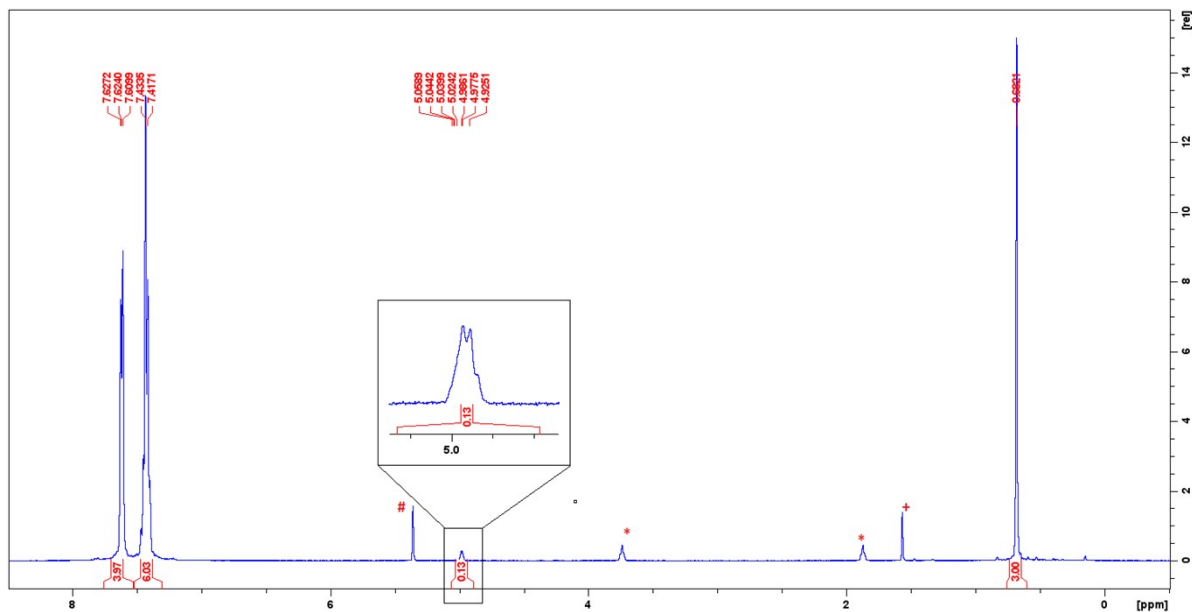


Figure S7. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in MePh₂SiH (Si-2). (# denotes residual CH₂Cl₂ from the deuterated solvent, * denotes residual THF, + denotes H₂O).

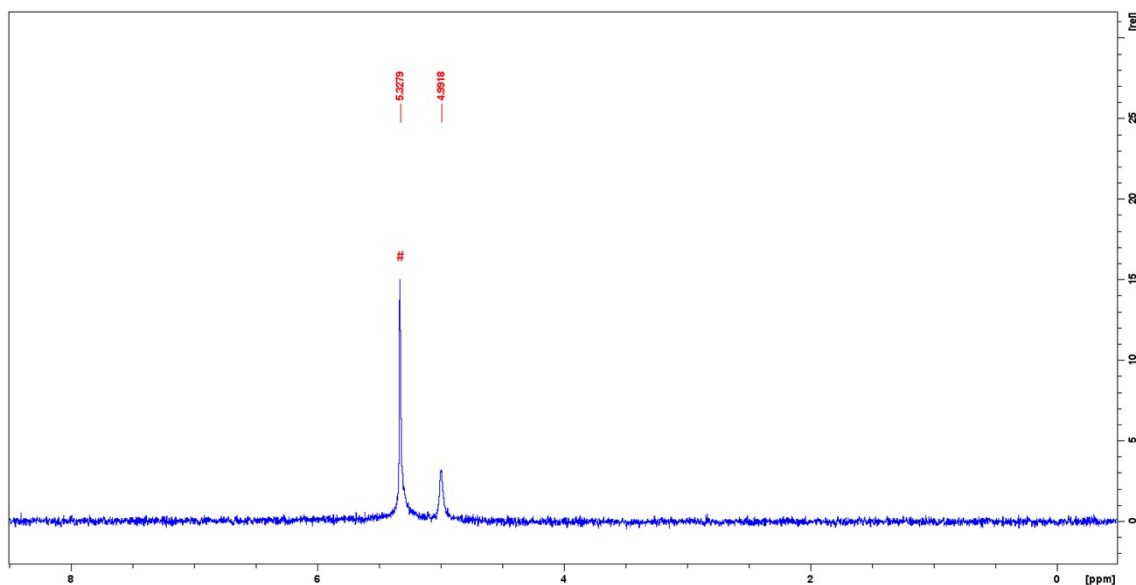


Figure S8. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in MePh₂SiH (Si-2). (# denotes CD₂Cl₂ used as reference).

Ph₃SiD (Si-3)

Deuterium incorporation: 91%. Spectroscopic data for this product agree to those previously reported in the literature.⁷

¹H NMR (400 MHz, CD₂Cl₂): δ 7.66 (m, 6H, 6 H arom), 7.46 (m, 9H, 9 H arom), 5.52 (s, SiH).

²H NMR (60 MHz, CH₂Cl₂): δ 5.53 (SiD).

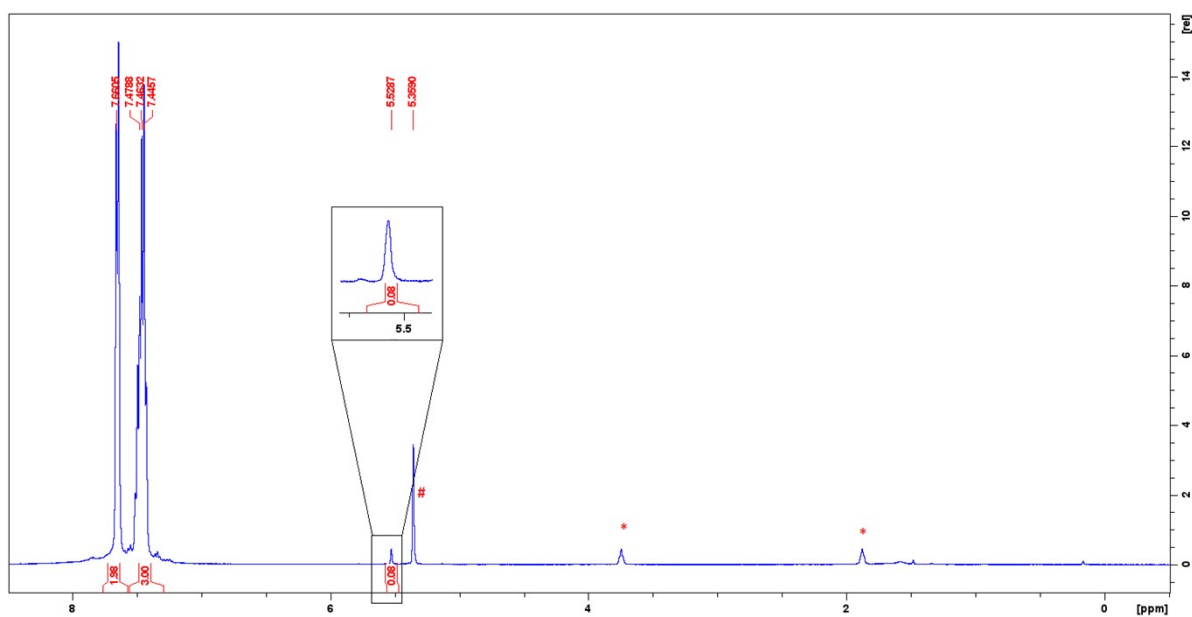


Figure S9. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in Ph₃SiH (Si-3). (# denotes residual CH₂Cl₂ from the deuterated solvent, * denotes residual THF)

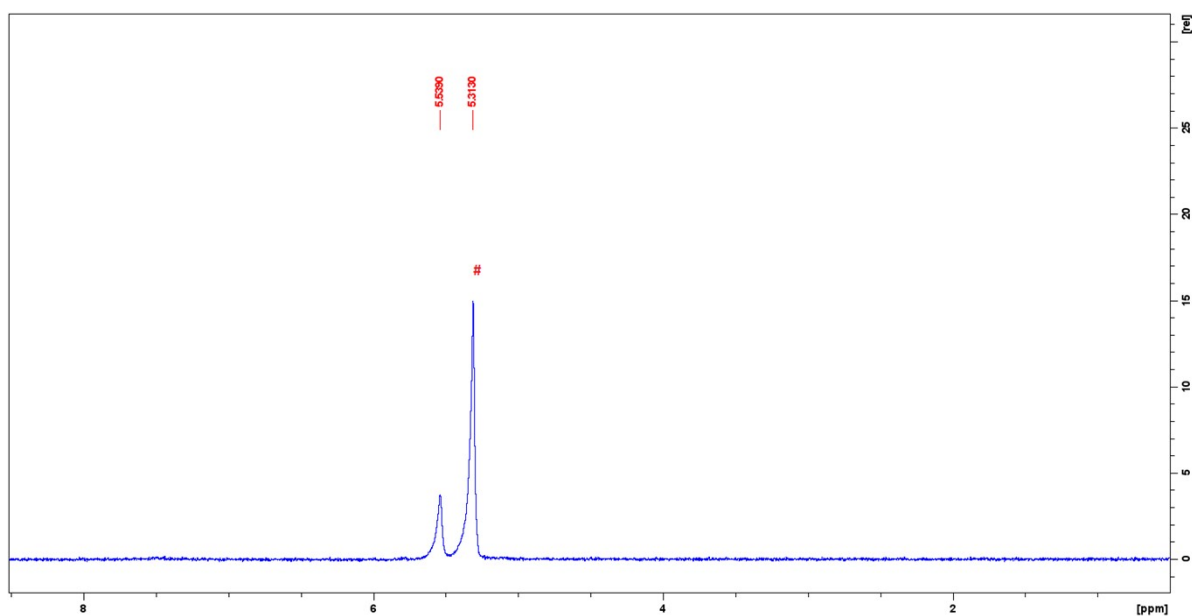


Figure S10. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in Ph₃SiH (Si-3). (# denotes CD₂Cl₂ used as reference).

^tBuMe₂SiD (Si-4)

Deuterium incorporation: 95%. Spectroscopic data for this product agree to those previously reported in the literature.⁷

¹H NMR (400 MHz, THF-*d*₈): δ 3.72 (hept, ³J_{HH} = 3.8 Hz, SiH), 0.95 (s, 9H, SiC(CH₃)₃), 0.07 (m, 6H, 2 CH₃).

²H NMR (60 MHz, THF-*d*₈): δ 3.71 (SiD).

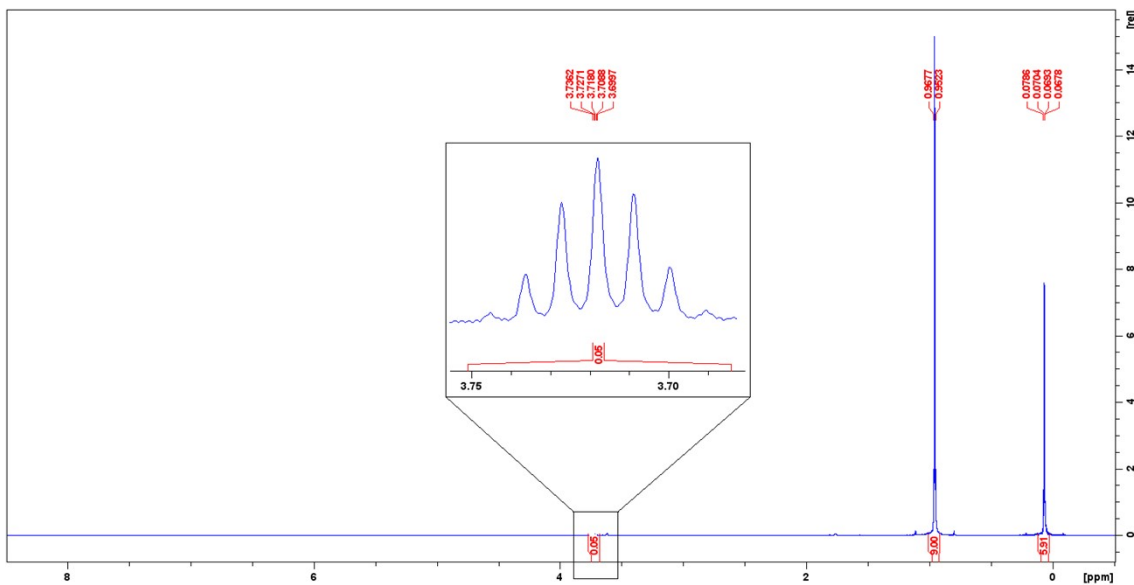


Figure S11. ¹H NMR spectrum (THF-*d*₈, 400 MHz) of the H/D exchange in ^tBuMe₂SiH (Si-4).

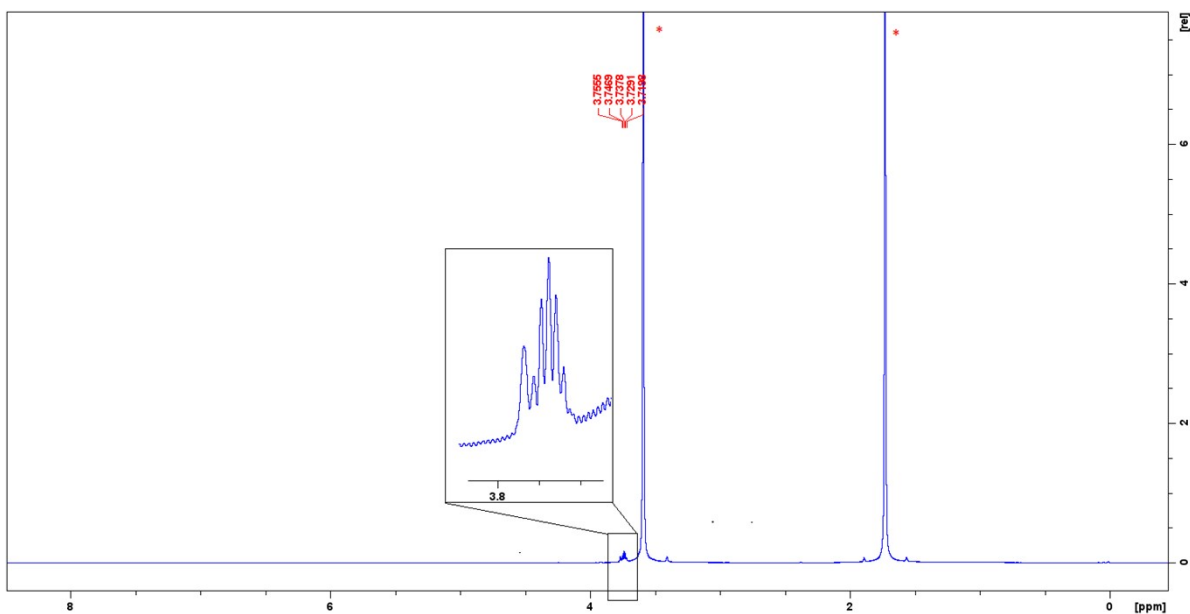


Figure S12. ²H NMR spectrum (THF-*d*₈, 400 MHz) of the H/D exchange in ^tBuMe₂SiH (Si-4). (* denotes residual THF from the deuterated solvent).

$^n\text{Pr}_3\text{SiD}$ (Si-5)

Deuterium incorporation: 92% (SiD), 5% (SiCD₂). Spectroscopic data for this product agree to those previously reported in the literature.⁸

¹H NMR (400 MHz, CD₂Cl₂): δ 3.69 (hept, ³J_{HH} = 3.2 Hz, SiH), 1.40 (m, ³J_{HH} = 7.2 Hz, 6H, 3 CH₂), 0.96 (t, ³J_{HH} = 7.2 Hz, 9H, 3 CH₃), 0.60 (t, ³J_{HH} = 8.1 Hz, 6H, 3 SiCH₂).

²H NMR (60 MHz, CH₂Cl₂): δ 3.76 (SiD), 0.63 (SiCD₂).

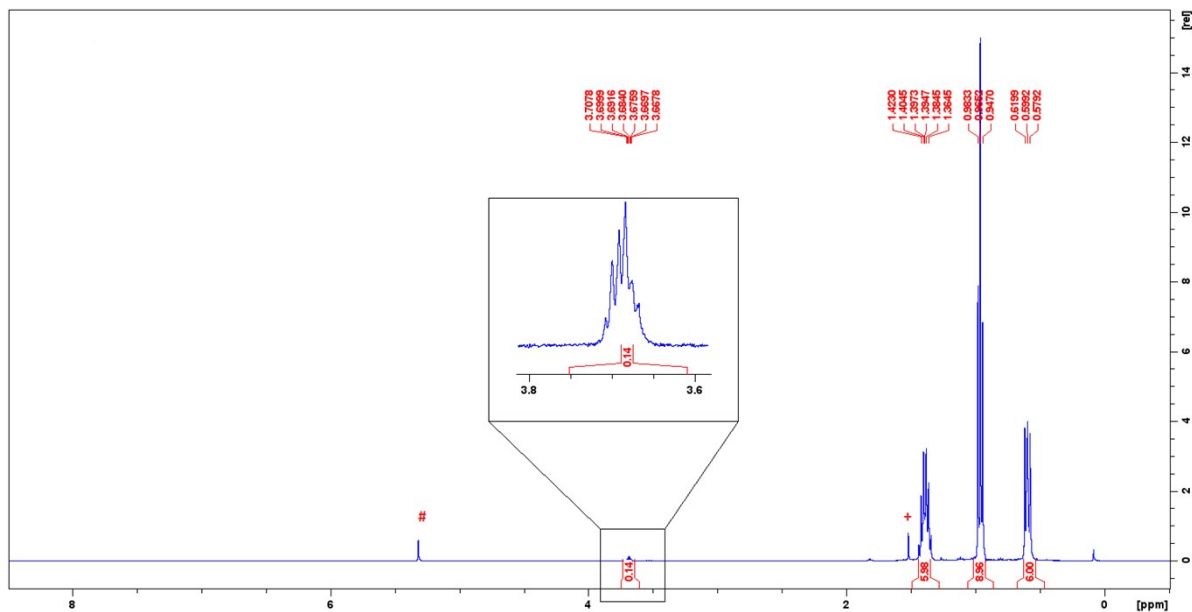


Figure S13. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in $^n\text{Pr}_3\text{SiH}$ (Si-5). (# denotes residual CH₂Cl₂ from the deuterated solvent, + denotes H₂O).

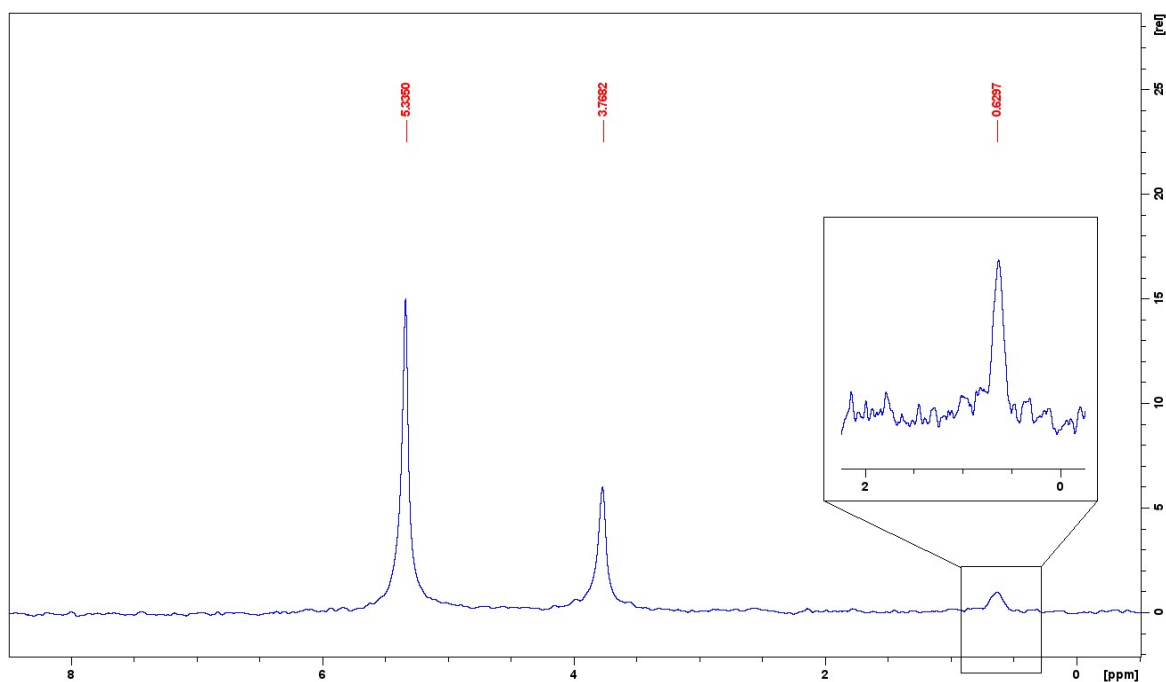


Figure S14. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in $^n\text{Pr}_3\text{SiH}$ (Si-5). (# denotes CD₂Cl₂ used as reference).

$i\text{Pr}_3\text{SiD}$ (Si-6)

Deuterium incorporation: 94%. Spectroscopic data for this product agree to those previously reported in the literature.⁹

^1H NMR (400 MHz, CD_2Cl_2): δ 3.35 (s, SiH), 1.10 (m, 21H, 3 CH + 6 CH_3).

^2H NMR (60 MHz, CH_2Cl_2): δ 3.36 (SiD).

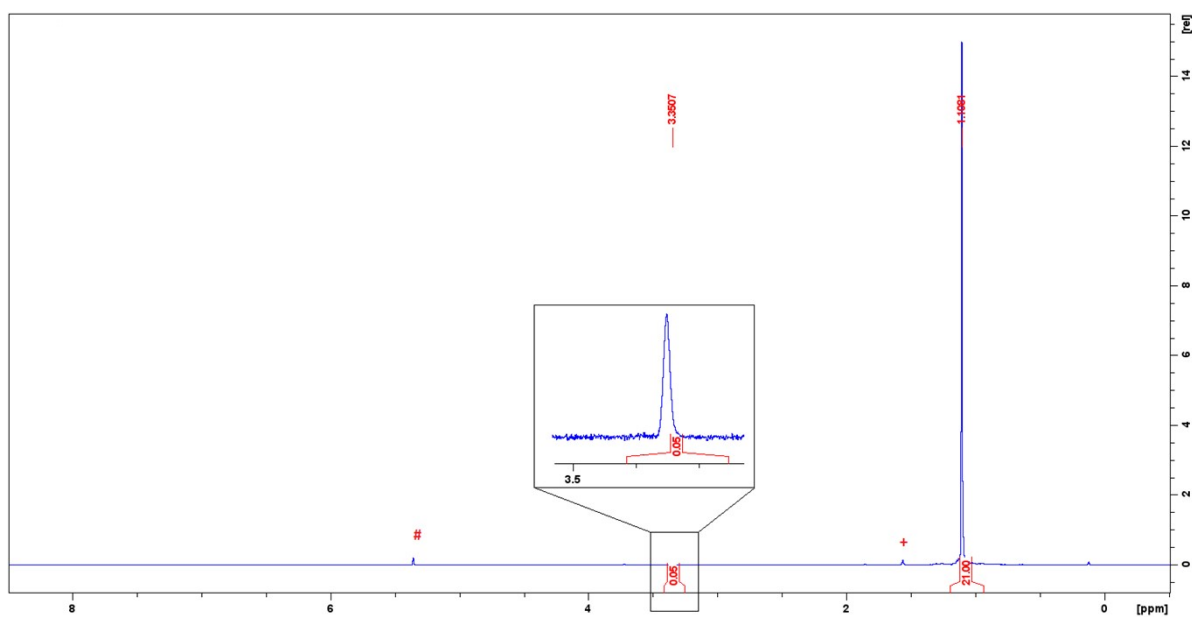


Figure S15. ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of the H/D exchange in $i\text{Pr}_3\text{SiH}$ (Si-6). (# denotes residual CH_2Cl_2 from the deuterated solvent, + denotes H_2O).

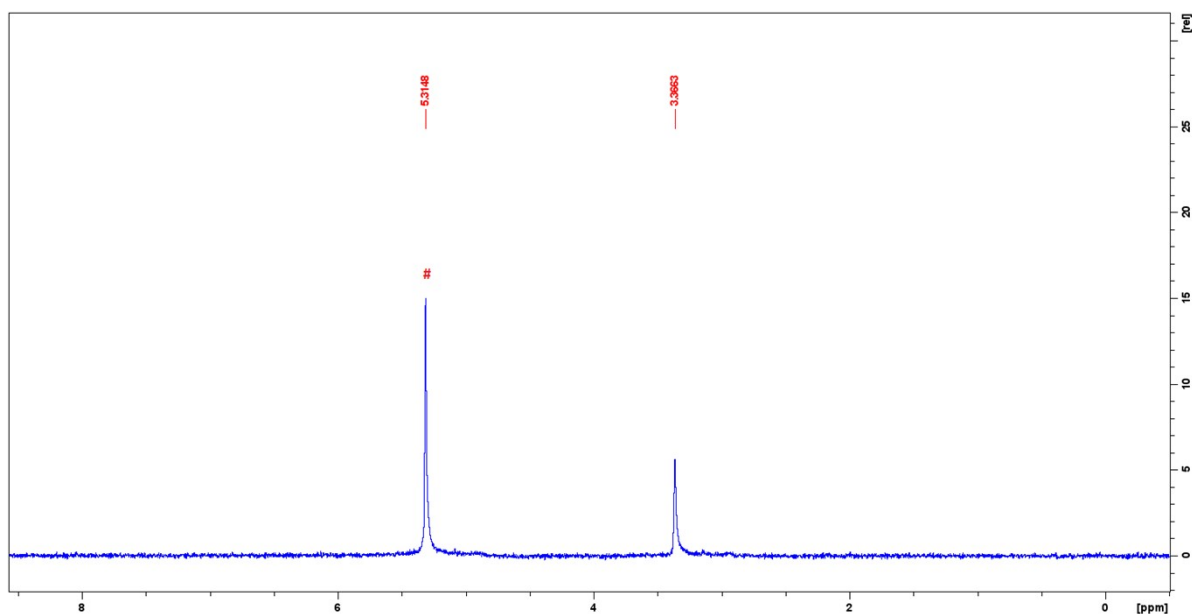


Figure S16. ^2H NMR spectrum (CH_2Cl_2 , 60 MHz) of the H/D exchange in $i\text{Pr}_3\text{SiH}$ (Si-6). (# denotes CD_2Cl_2 used as reference).

(Me)₂DSiPhSiD(Me)₂ (Si-7)

Deuterium incorporation: 85%. Spectroscopic data for this product agree to those previously reported in the literature.¹⁰

¹H NMR (400 MHz, CD₂Cl₂): δ 7.63-7.61 (m, 2H, 2 H arom), 7.41-7.38 (m, 2H, 2 H arom), 4.72 (hept, ³J_{HH} = 3.6 Hz, SiH), 0.41 (s, 12H, 4CH₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.82 (s, 1D, SiD).

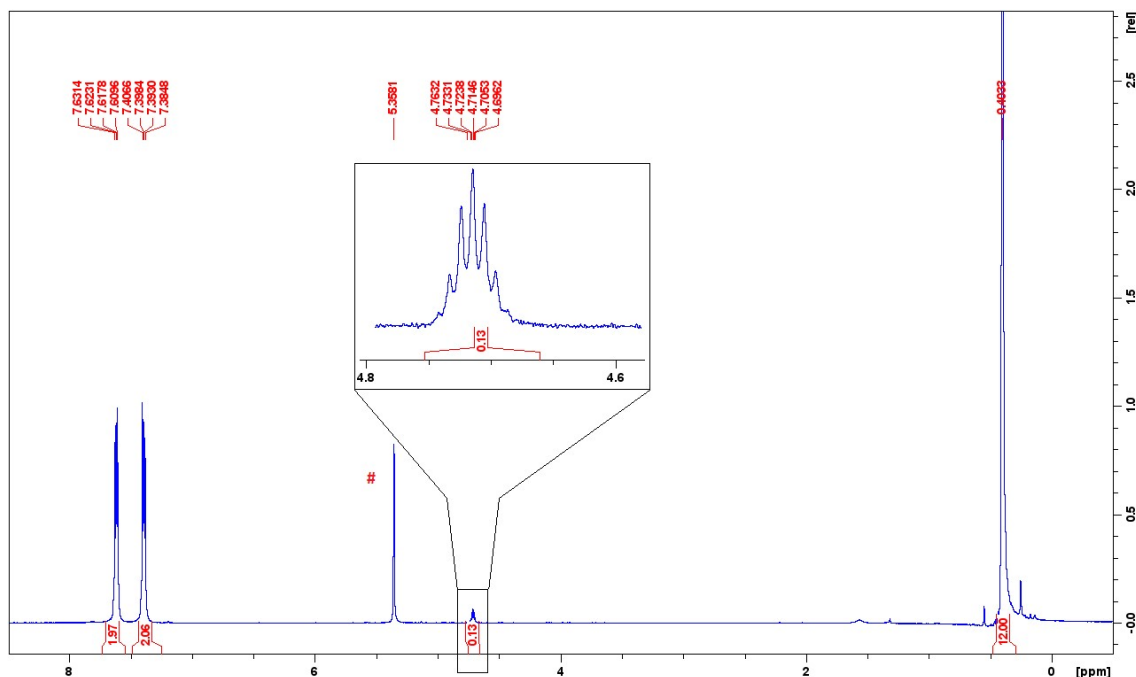


Figure S17. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in (Me)₂DSiPhSiD(Me)₂ (Si-7). (# denotes residual CH₂Cl₂ from the deuterated solvent).

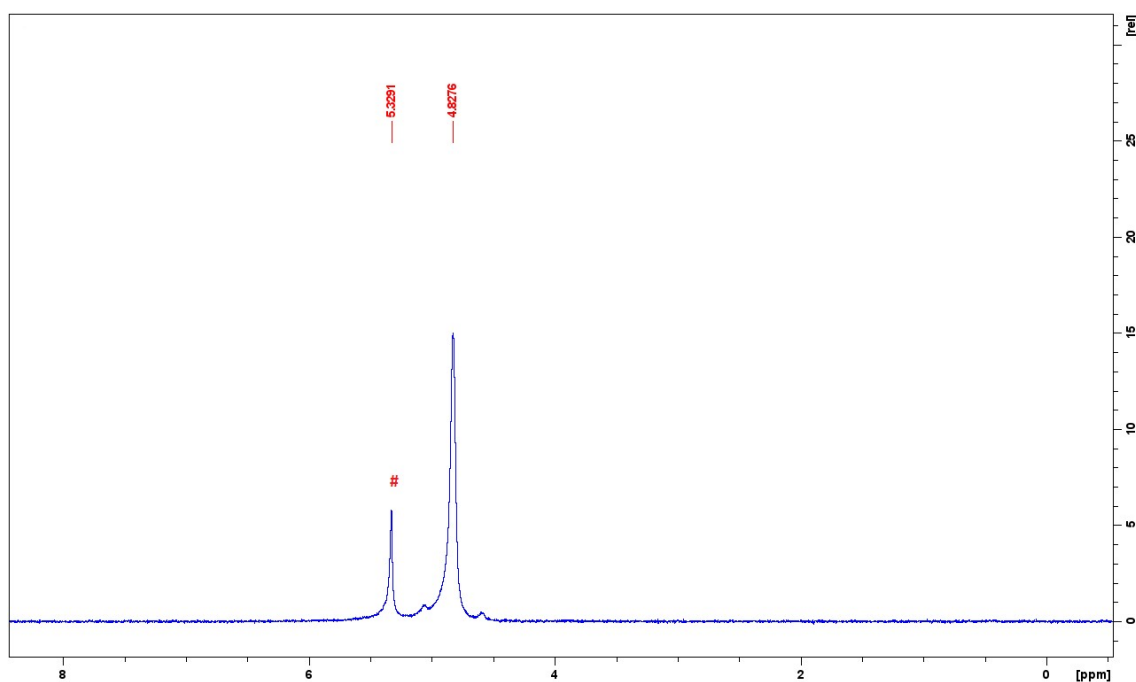


Figure S18. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in (Me)₂DSiPhSiD(Me)₂ (Si-7). (# denotes CD₂Cl₂ used as reference).

(EtO)₃SiD (Si-8)

Deuterium incorporation: >99%. Spectroscopic data for this product agree to those previously reported in the literature.¹¹

¹H NMR (400 MHz, CD₂Cl₂): δ 3.85 (q, ³J_{HH} = 7.0 Hz, 6H, 3 CH₂), 1.23 (t, ³J_{HH} = 7.0 Hz, 9H, 3 CH₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.28 (SiD).

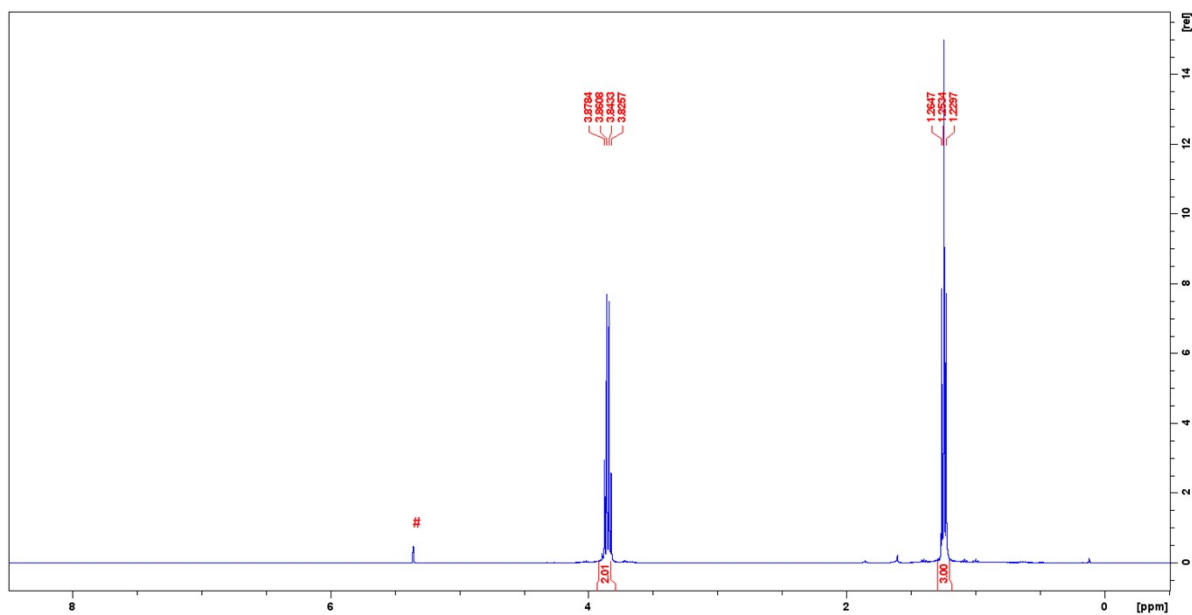


Figure S19. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in (EtO)₃SiH (Si-8). (# denotes residual CH₂Cl₂ from the deuterated solvent).

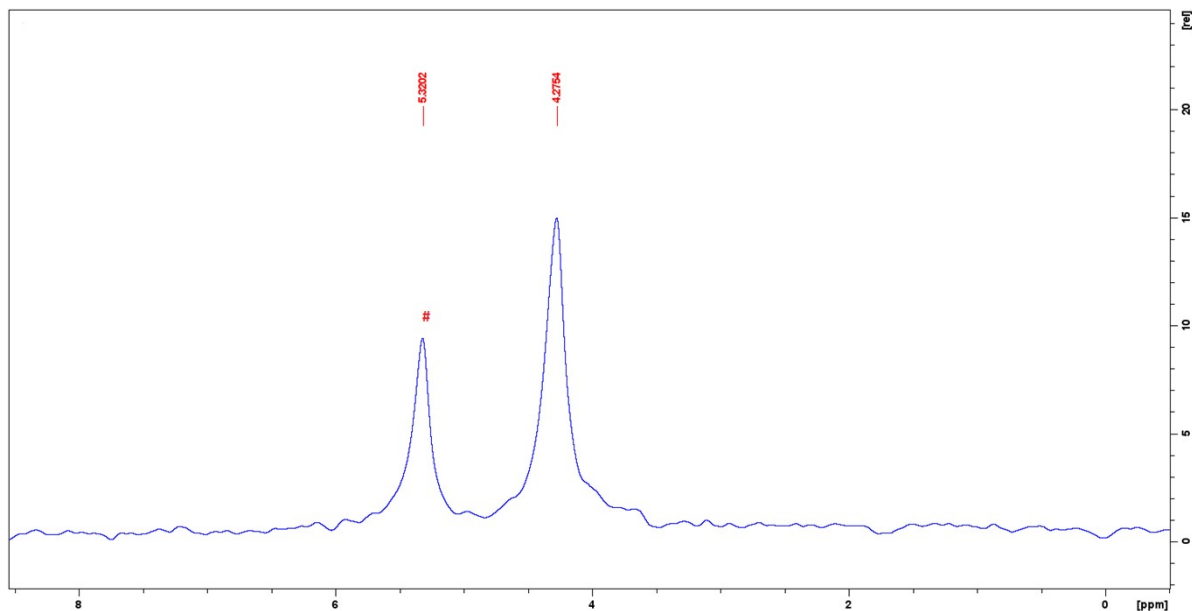


Figure S20. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in (EtO)₃SiH (Si-8). (# denotes CD₂Cl₂ used as reference).

CIMe₂SiD (Si-9)

Deuterium incorporation: 73%. Spectroscopic data for this product agree to those previously reported in the literature.¹¹

¹H NMR (400 MHz, THF-*d*₈): δ 4.87 (hept, ³J_{HH} = 3.2 Hz, SiH), 0.52 (s, 6H, 2 CH₃).

²H NMR (60 MHz, THF-*d*₈): δ 4.88 (SiD).

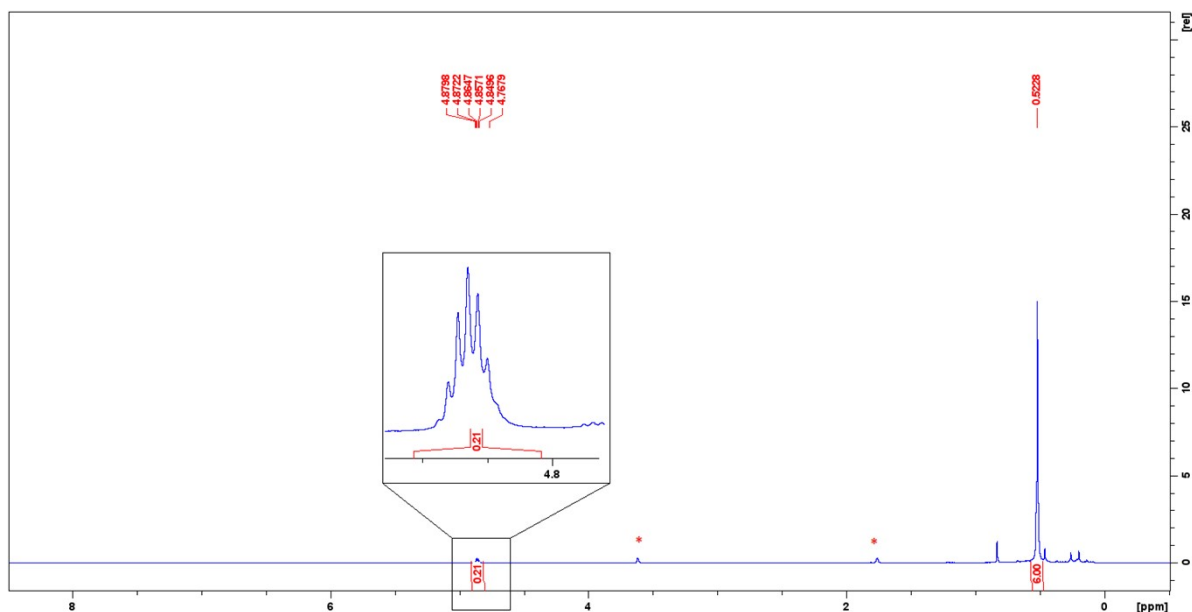


Figure S21. ¹H NMR spectrum (THF-*d*₈, 400 MHz) of the H/D exchange in CIMe₂SiH (Si-9). (* denotes residual THF from the deuterated solvent)

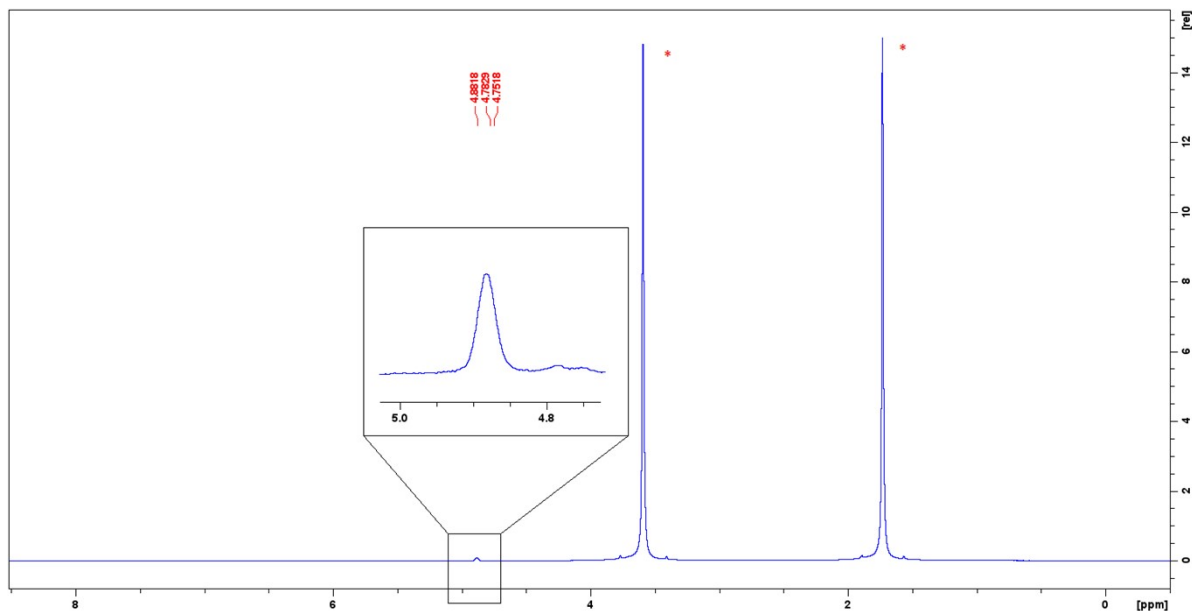


Figure S22. ²H NMR spectrum (THF-*d*₈, 60 MHz) of the H/D exchange in CIMe₂SiH (Si-9).

Ph₂SiD₂ (Si-10)

Deuterium incorporation: 72%. Spectroscopic data for this product agree to those previously reported in the literature.¹²

¹H NMR (400 MHz, CD₂Cl₂): δ 7.69-7.66 (m, 4H, 4 H arom), 7.49-7.42 (m, 6H, 6 H arom), 4.99 (SiH₂).

²H NMR (60 MHz, CH₂Cl₂): δ 5.11 (SiD₂).

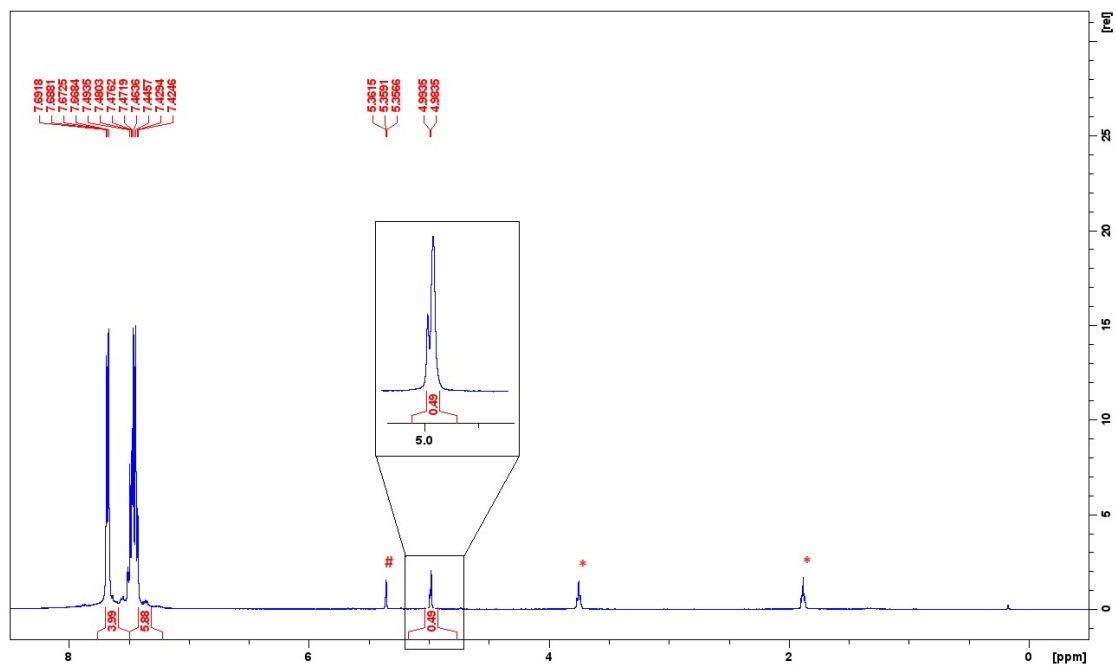


Figure S23. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in Ph₂SiH₂ (Si-10). (# denotes residual CH₂Cl₂ from the deuterated solvent).

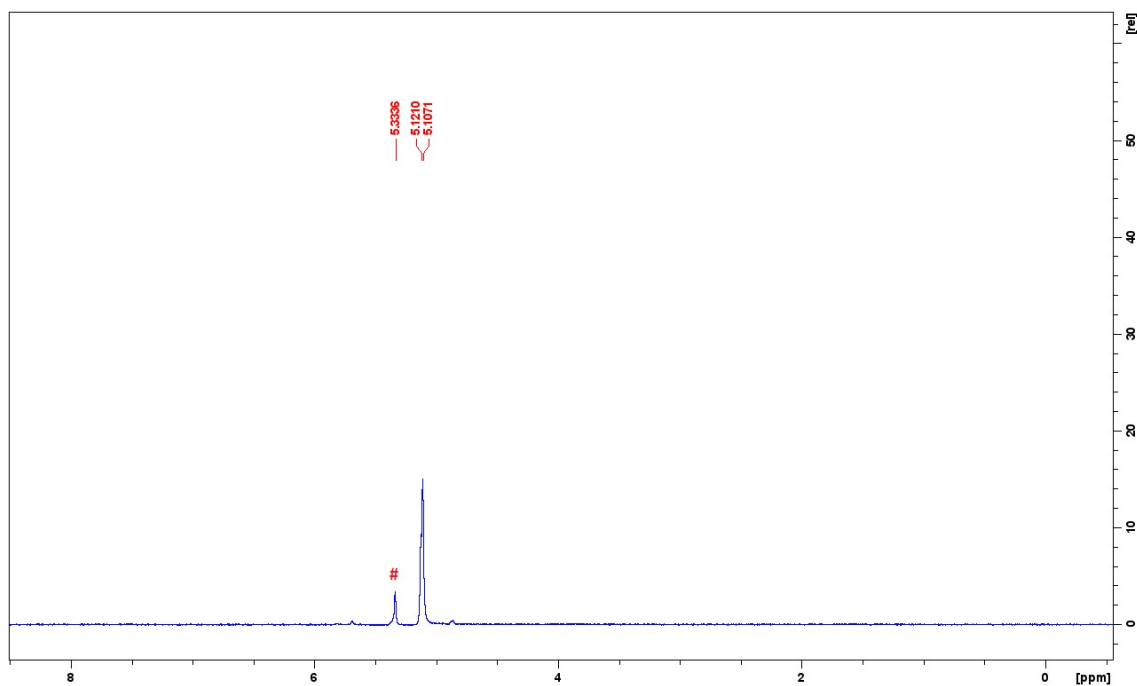


Figure S24. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in Ph₂SiH₂ (Si-10). (# denotes CD₂Cl₂ used as reference).

PhSiD₃ (Si-11)

Deuterium incorporation: 42%. Spectroscopic data for this product agree to those previously reported in the literature.¹³

¹H NMR (400 MHz, CD₂Cl₂): δ 7.65-7.40 (m, 2H, 2 H arom), 7.42-7.40 (m, 3H, 3 H arom), 4.23 (SiD₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.31 (s, 3D, SiD₃).

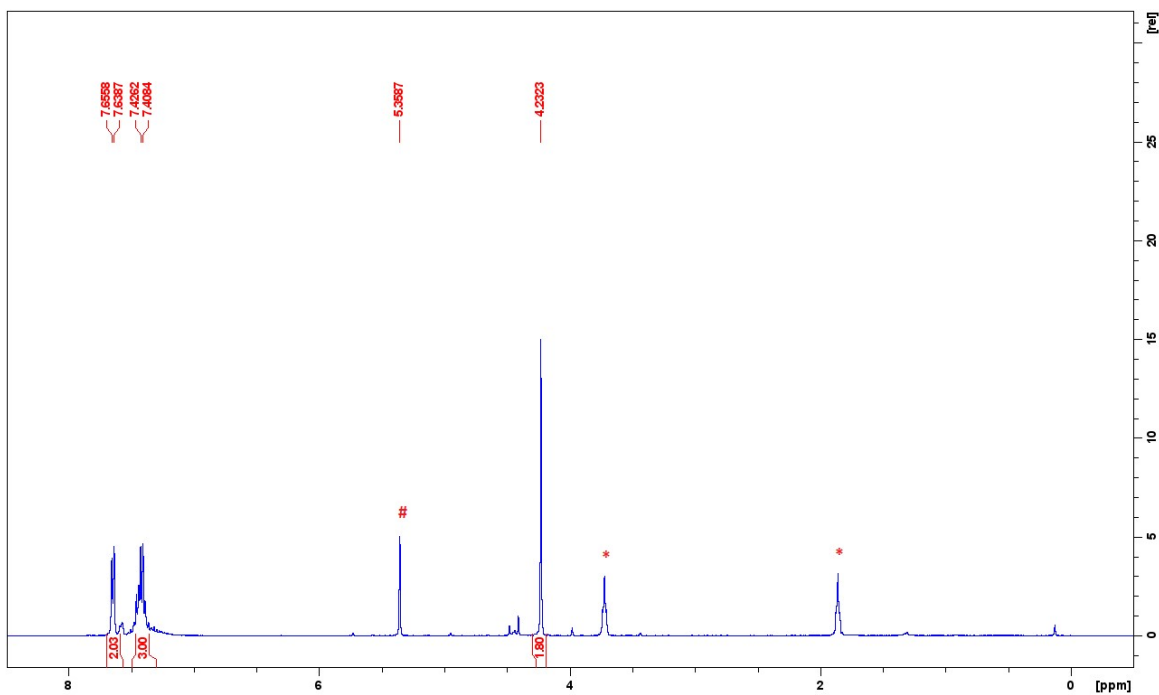


Figure S25. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in PhSiD₃ (**Si-11**). (# denotes residual CH₂Cl₂ from the deuterated solvent).

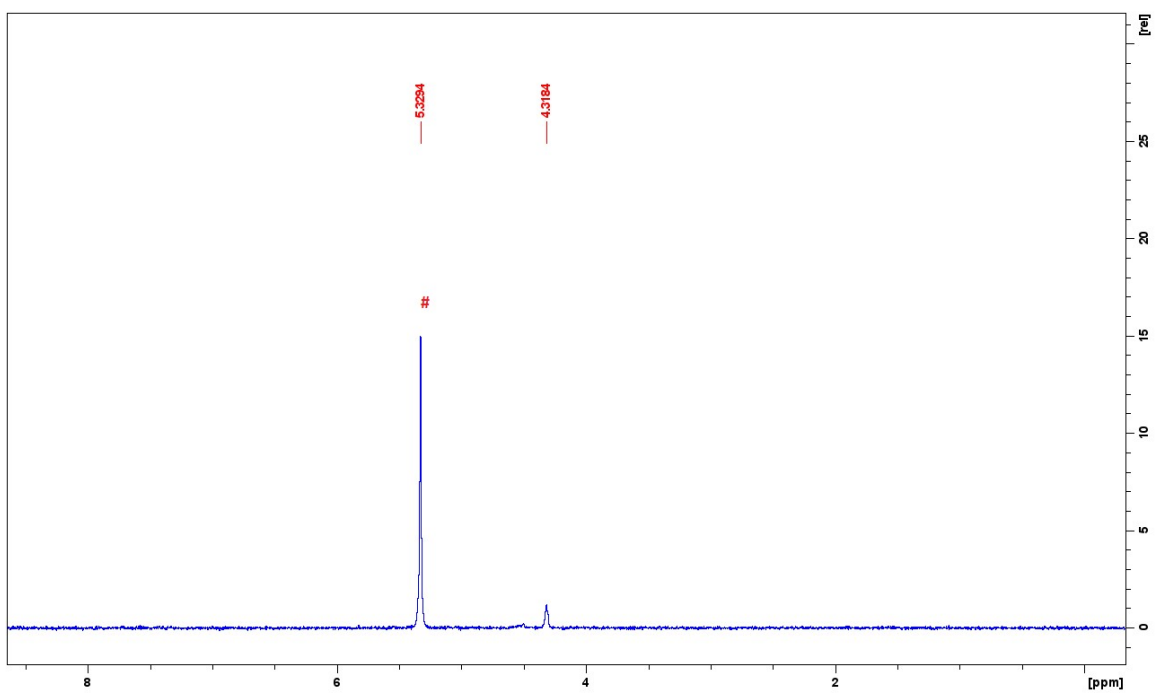


Figure S26. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in PhSiD₃ (**Si-11**). (# denotes CD₂Cl₂ used as reference).

Et₃GeD (Ge-1)

Deuterium incorporation: >99%. Spectroscopic data for this product agree to those previously reported in the literature.¹³

¹H NMR (400 MHz, CD₂Cl₂): δ 1.08 (t, ³J_{HH} = 7.6 Hz, 9H, 3 CH₃), 0.88 (q, ³J_{HH} = 7.6 Hz, 6H, 3 CH₂).

²H NMR (60 MHz, CH₂Cl₂): δ 3.75 (GeD).

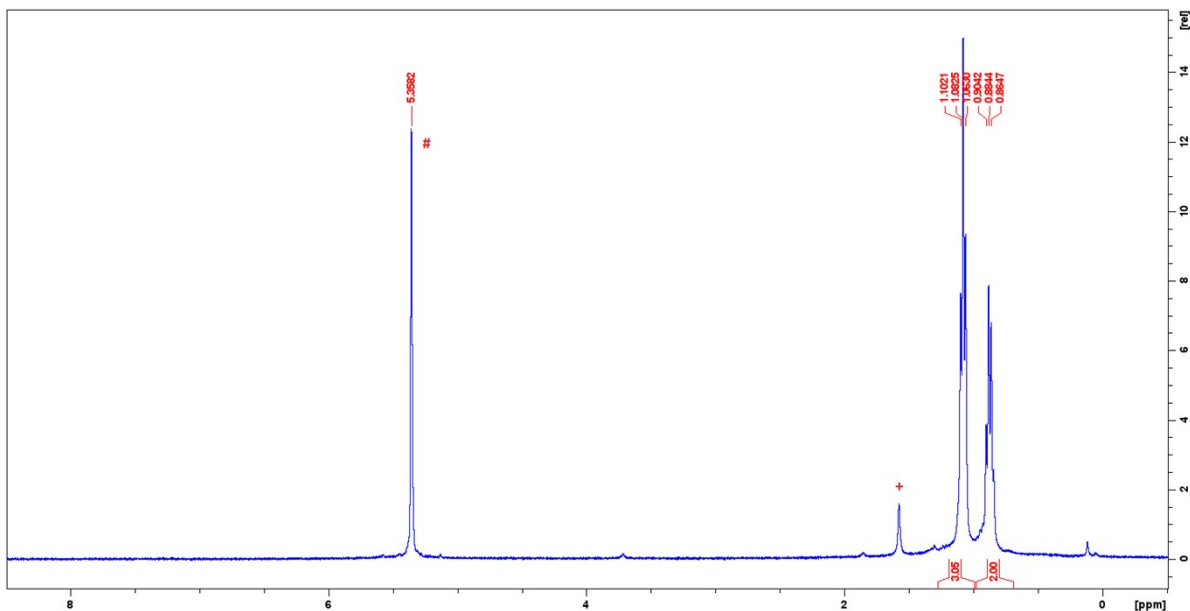


Figure S27. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in Et₃GeH (**Ge-1**). (# denotes residual CH₂Cl₂ from the deuterated solvent, + denotes H₂O)

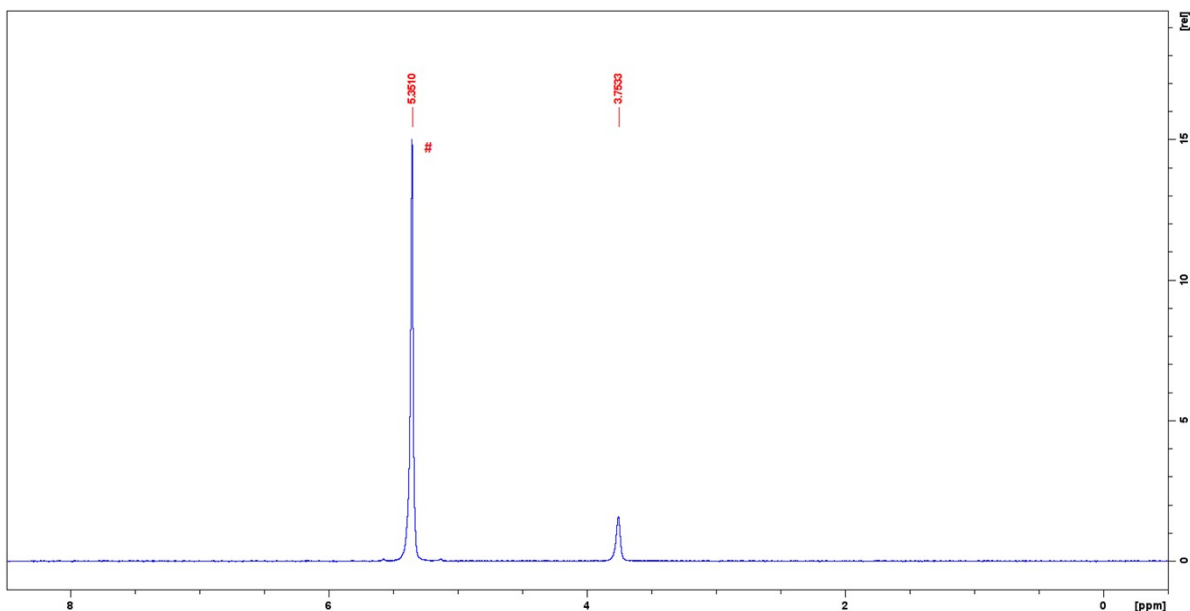


Figure S28. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in Et₃GeH (**Ge-1**). (# denotes CD₂Cl₂ used as reference).

Ph₃GeD (**Ge-2**)

Deuterium incorporation: 70%. Spectroscopic data for this product agree to those previously reported in the literature.¹³

¹H NMR (400 MHz, CD₂Cl₂): δ 7.58 (m, 6H, 6 H arom), 7.43 (m, 9H, H arom), 5.75 (GeH).

²H NMR (60 MHz, CH₂Cl₂): δ 5.99 (GeD).

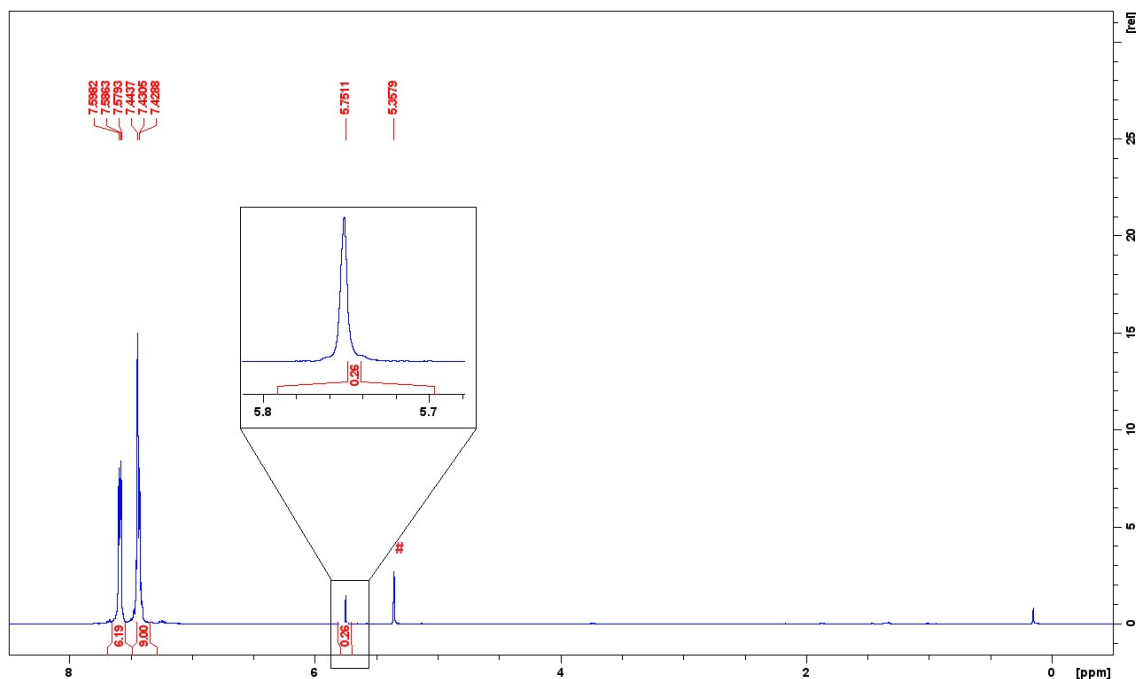


Figure S29. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in Ph₃GeD (**Ge-2**). (# denotes residual CH₂Cl₂ from the deuterated solvent).

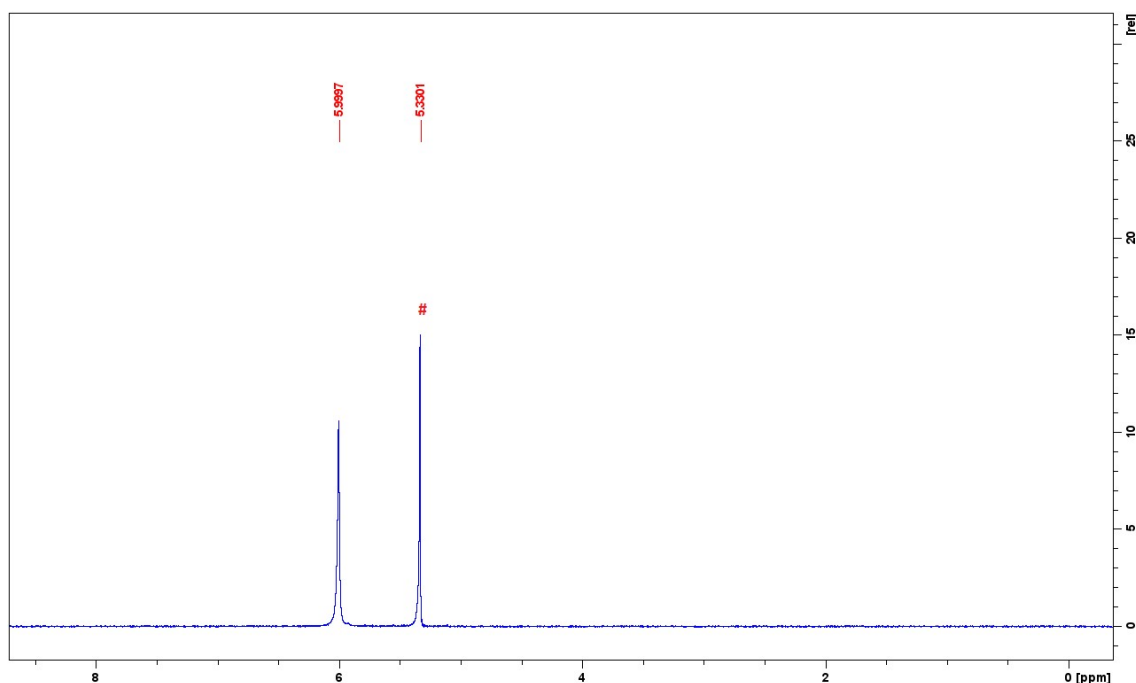


Figure S30. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in Ph₃GeD (**Ge-2**). (# denotes CD₂Cl₂ used as reference).

¹¹⁹Bu₃SnD (Sn-1)

Deuterium incorporation: >99%. Spectroscopic data for this product agree to those previously reported in the literature.¹⁴

¹H NMR (400 MHz, CD₂Cl₂): δ 1.55 (m, 6H, 3 CH₂), 1.35 (m, 6H, 3 CH₂), 1.00 (t, ³J_{HH} = 8.3 Hz, 6H, 3 CH₂), 0.93 (t, ³J_{HH} = 7.5 Hz, 9H, 3 CH₃).

²H NMR (60 MHz, CH₂Cl₂): δ 4.84 (SnD).

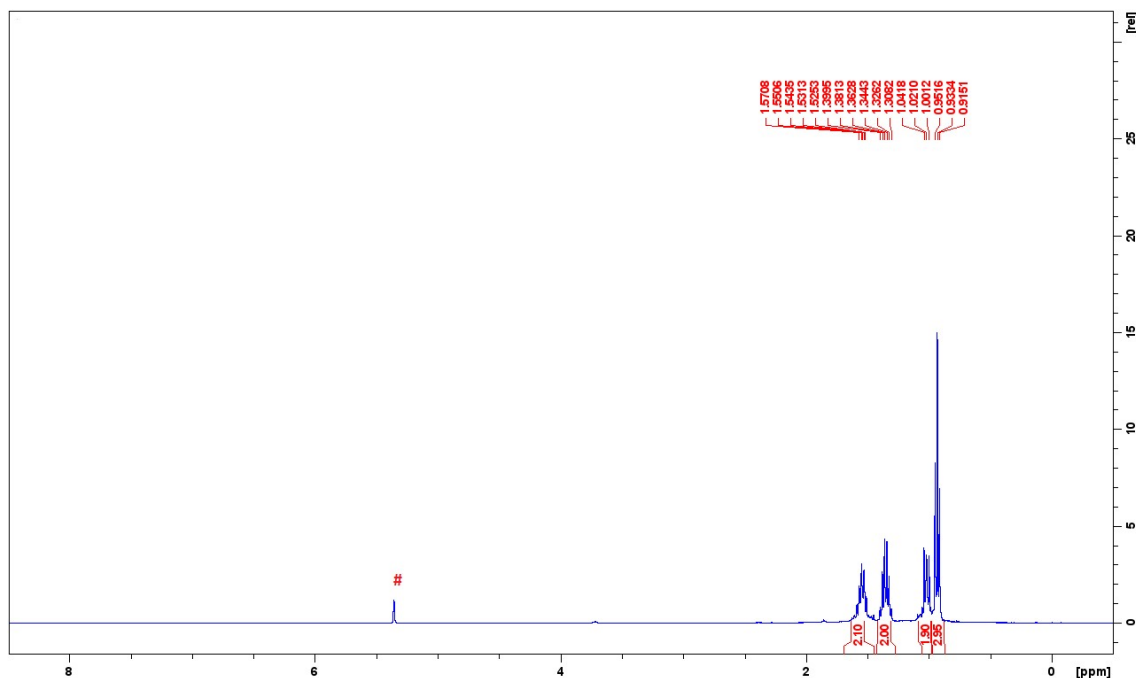


Figure S31. ¹H NMR spectrum (CD₂Cl₂, 400 MHz) of the H/D exchange in ⁿBu)SnD (**Sn-1**). (# denotes residual CH₂Cl₂ from the deuterated solvent).

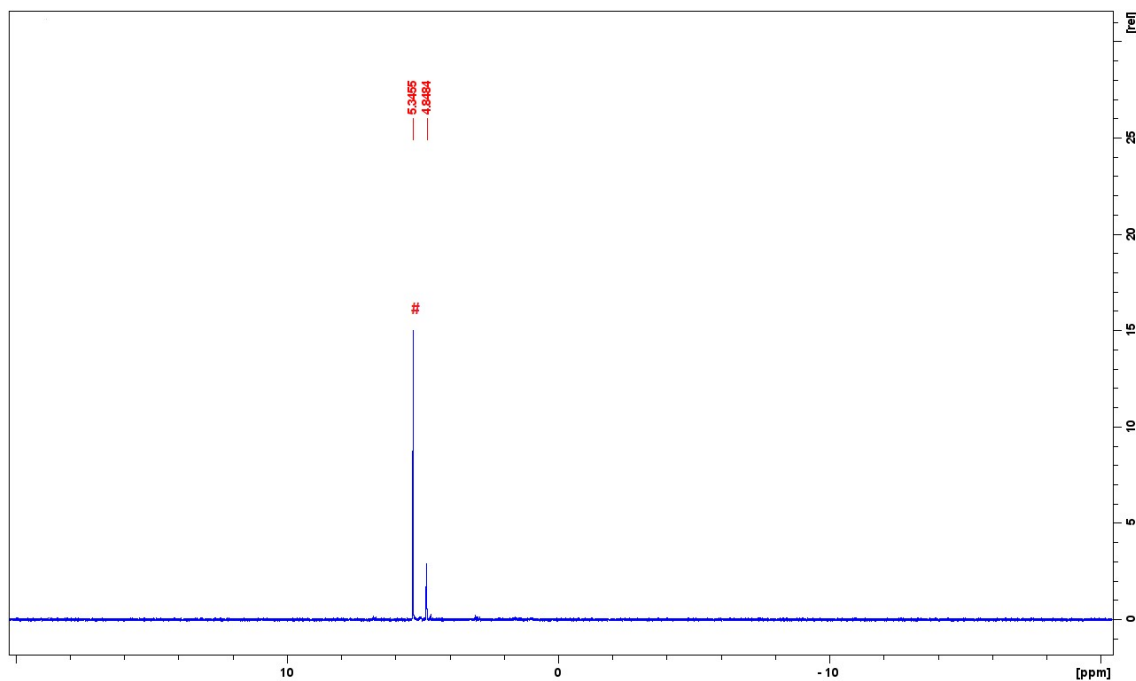


Figure S32. ²H NMR spectrum (CH₂Cl₂, 60 MHz) of the H/D exchange in ⁿBu₃SnD (**Sn-1**). (# denotes CD₂Cl₂ used as reference).

pinBD (**B-1**)

Deuterium incorporation: >99%. Spectroscopic data for this product agree to those previously reported in the literature.¹³

¹H NMR (400 MHz, C₆D₆): δ 1.02 (s, 12H, 4 CH₃).

²H NMR (60 MHz, C₆D₆): δ 4.11 (m, BD).

¹¹B NMR (128 MHz, C₆D₆): δ 28.5 (t, J_{BD} = 20 Hz, BD).

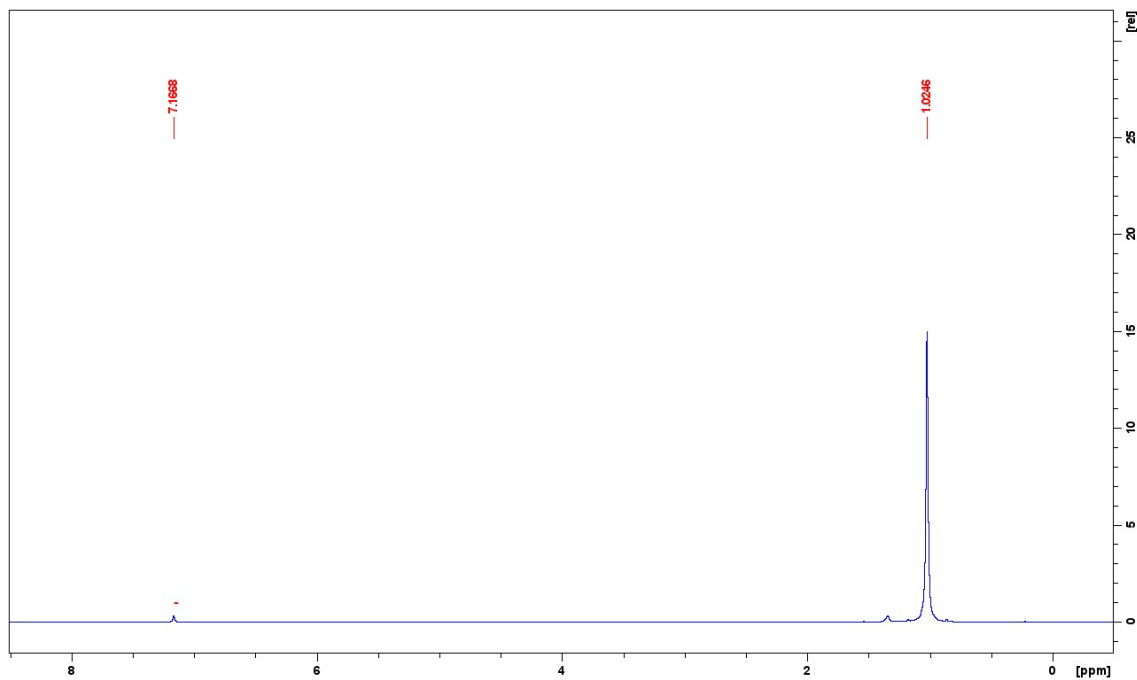


Figure S33. ¹H NMR spectrum (C₆D₆, 400 MHz) of the H/D exchange in pinBD (**B-1**).

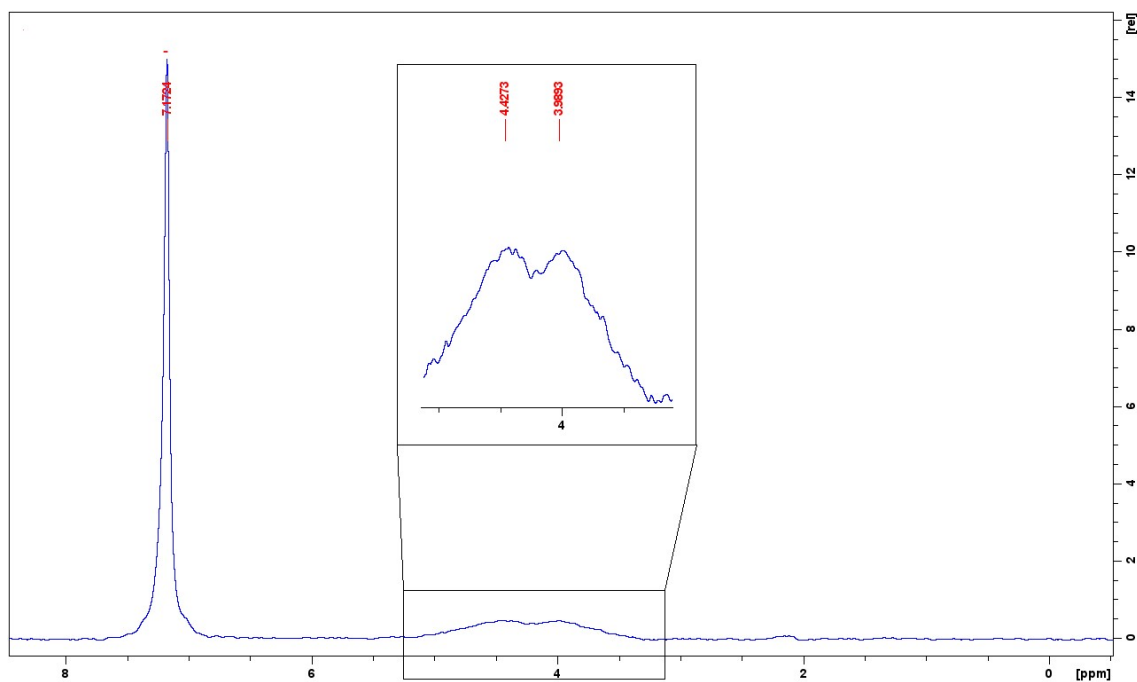


Figure S34. ²H NMR spectrum (C₆D₆, 60 MHz) of the H/D exchange in pinBD (**B-1**). (- denotes C₆D₆).

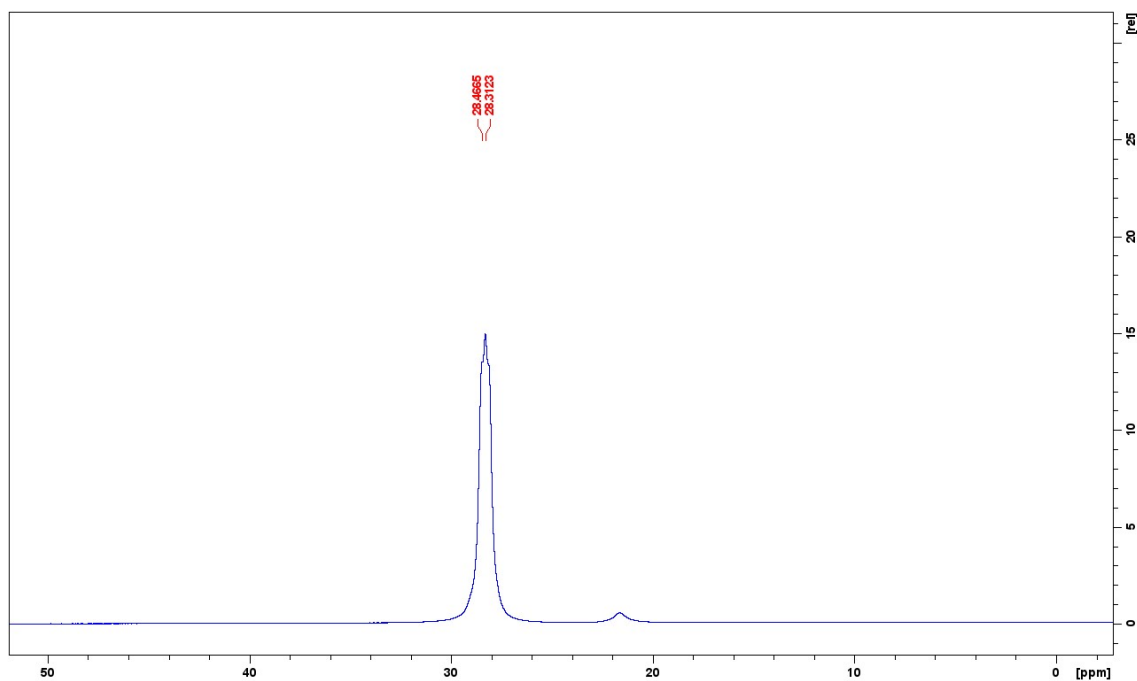


Figure S35. ^{11}B NMR spectrum (C_6D_6 , 128 MHz) of the H/D exchange in pinBD (**B-1**).

catBD (**B-2**)

Deuterium incorporation: >99%. Spectroscopic data for this product agree to those previously reported in the literature.¹³

^1H NMR (400 MHz, C_6D_6): δ 6.96 (m, 2H, 2 H arom), 6.76 (m, 2 H arom)

^2H NMR (60 MHz, C_6D_6): δ 4.72 (m, BD).

^{11}B NMR (128 MHz, C_6D_6): δ 28.7 (t, $J_{\text{BD}} = 159$ Hz, BD).

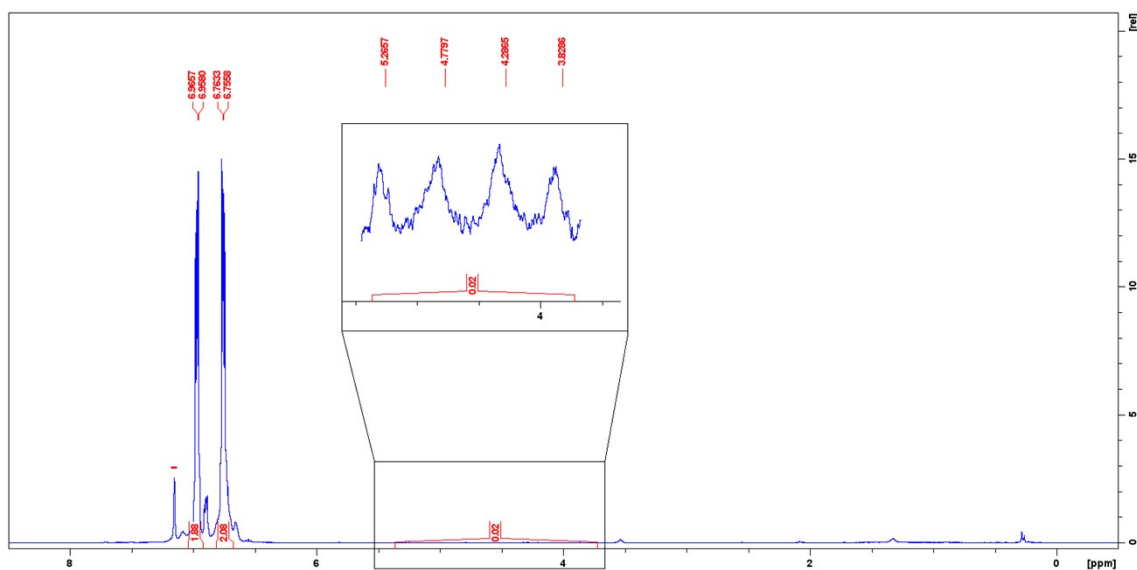


Figure S36. ^1H NMR spectrum (C_6D_6 , 400 MHz) of the H/D exchange in catBD (**B-2**).

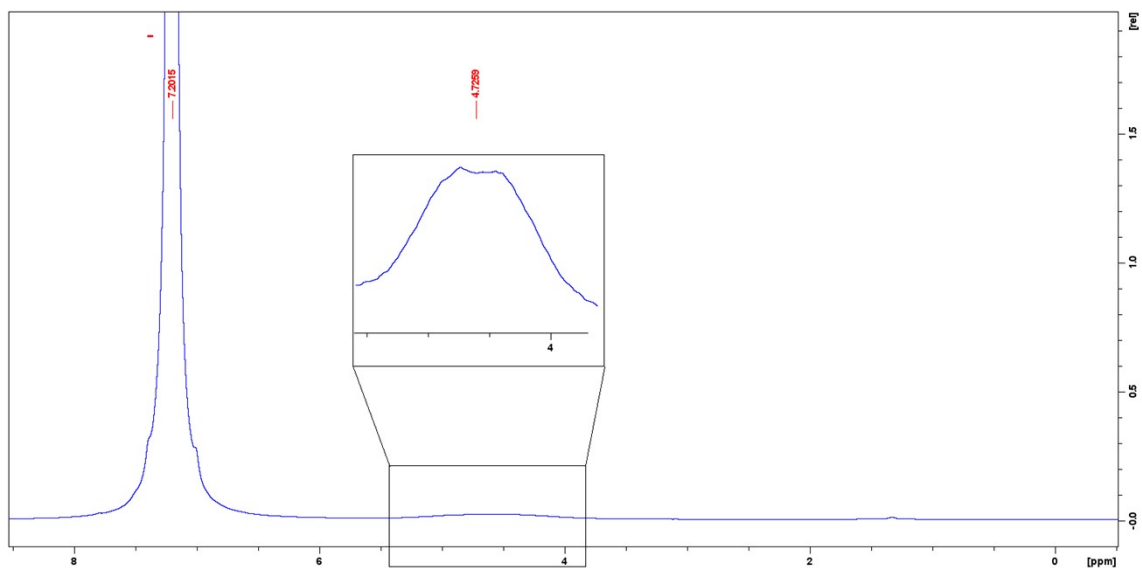


Figure S37. ^2H NMR spectrum (C_6D_6 , 60 MHz) of the H/D exchange in catBD (B-2).

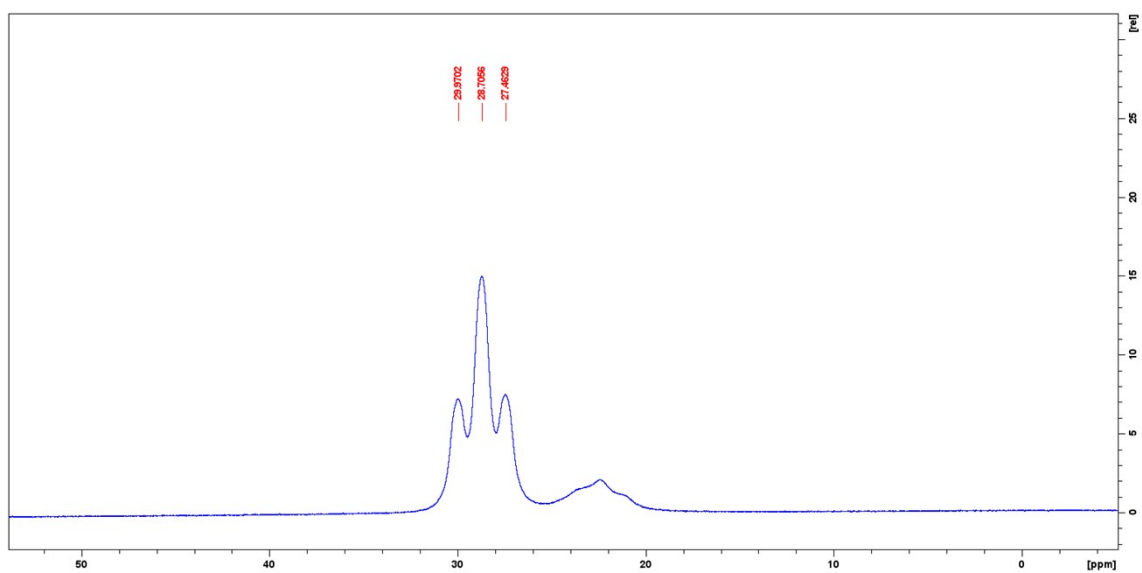


Figure S38. ^{11}B NMR spectrum (C_6D_6 , 128 MHz) of the H/D exchange in catBD (B-2).

S6. References.

- ¹ J. T. Fletcher, M. E. Keeney and S. E. Walz, *Synthesis*, 2010, **19**, 3339-3345.
- ² M. L. Gower and J. D. Crowley, *Dalton Trans.*, 2010, **39**, 2371-2378.
- ³ K. J. Kilpin, U. Paul, L. Ai-Lan and J. Crowley, *Chem. Commun*, 2011, **47**, 328-330.
- ⁴ S. S. Khan, S. Hanelt and J. Liebscher, *Arkivoc*, 2009, **12**, 193-208.
- ⁵ M. Wissing and A. Studer, *Chem. Eur. J.*, 2019, **25**, 5870-5874.
- ⁶ L. Greb, S. Tamke and J. Paradies, *Chem. Commun*, 2014, **50**, 2318-2320.
- ⁷ S. Zhang, H. Fallah, E. J. Gardner, S. Subrata, J. A. Bertke and T. Cundari, *Angew. Chem. Int. Ed.*, 2016, **54**, 9927-9931.
- ⁸ T. Komuro, T. Osawa, R. Suzuki, D. Mochizuki, H. Higashi and H. Tobita, *Chem. Commun.*, 2019, **55**, 957-960.
- ⁹ M. Mato and A. Echavarren, *Angew. Chem. Int. Ed.*, 2019, **58**, 2088-2092.
- ¹⁰ J. Campos, A. Esqueda, J. López-Serrano, L. Sánchez, F. P. Cossio, A. de Cozar, E. Álvarez, C. Maya and E. Carmona, *J. Am. Chem. Soc.*, 2010, **47**, 16765-16767.
- ¹¹ K. Smart, E. Mothes-Martin, T. Annaka and M. Grellier, *Adv. Synth. Catal.*, 2014, **354**, 759-764.
- ¹² N. Gandhamsetty, S. Park and S. Chang, *J. Am. Chem. Soc.*, 2015, **48**, 15176-15184.
- ¹³ M. Esteruelas, A. Martínez, M. Oliván and A. Vélez, *J. Org. Chem.*, 2020, **85**, 15693-15698.
- ¹⁴ Y. Lu and S. Yamago, *Angew. Chem. Int. Ed.*, 2019, **58**, 3952-3956.