

Supplementary Information for

Visible-Light-Mediated Deuteration of Silanes with Deuterium Oxide

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I. General Information

General Experiment Procedure

All reactions were carried out in oven dried (104 °C) glassware unless otherwise indicated. Air or moisture sensitive materials were purchased and stored in a nitrogen filled glove box. Flash column chromatography were performed on Merck 60 (0.040-0.063 mm) mesh silica gel, mixed as a slurry in eluent, packed and run under positive air pressure. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Visualization was by short wave (254 nm) ultraviolet light or by staining with potassium permanganate (KMnO₄) or Phosphomolybdic Acid (PMA), followed by heating.

Materials and Instruments

Chemicals and anhydrous solvents were purchased from commercial suppliers and used as received. Solvents used for column chromatography were of reagent grade and used as received. ¹H NMR and ¹³C NMR spectrum were recorded on Bruker AV-III400 (400 MHz) or AMX500 (500 MHz) spectrometer. Spectra were referenced using CDCl₃ with the residual solvent peak as internal standard (¹H NMR: δ 7.26 ppm). Chemical shifts were reported in parts per million (ppm) and multiplicities were indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet) and brs (broad singlet). Coupling constants (*J*) were reported in Hertz and integration was provided, along with assignments, as indicated. Gas Chromatography-Mass Spectrometry (GC-MS) was performed Agilent 7820A & 5977E GC-MS. GC-MS data are reported in the form of *m/z*. Blue LED strips (2 meter, 18 W, maximum Emission at around 470 nm) were purchased from Inwares Pte Ltd (Singapore). Logato™ 200 series Syringe pumps were purchased from KD Scientific Inc. (Holliston, MA). The flow components: Tefzel shut-off valves, needle gas valve, tee-joints, back pressure regulator (BPR), PFA and HPFA micro tubings were purchased from IDEX Health&Science (Oak Harbor, WA).

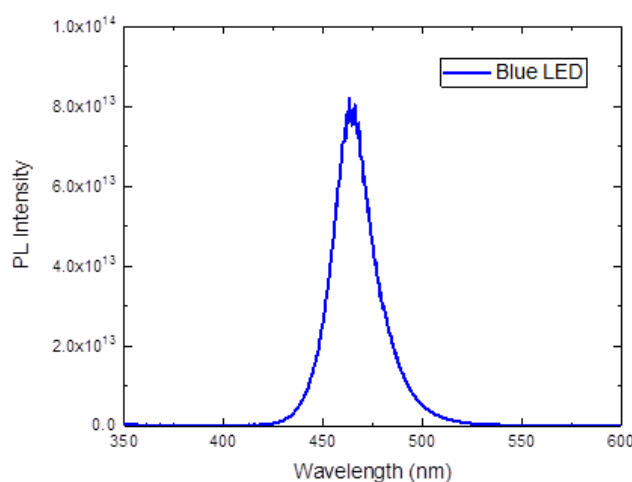
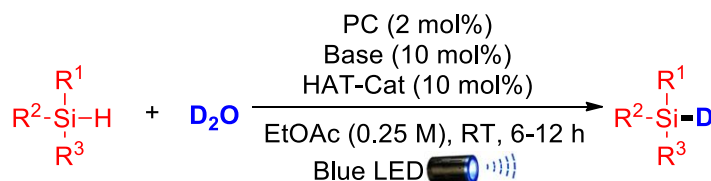


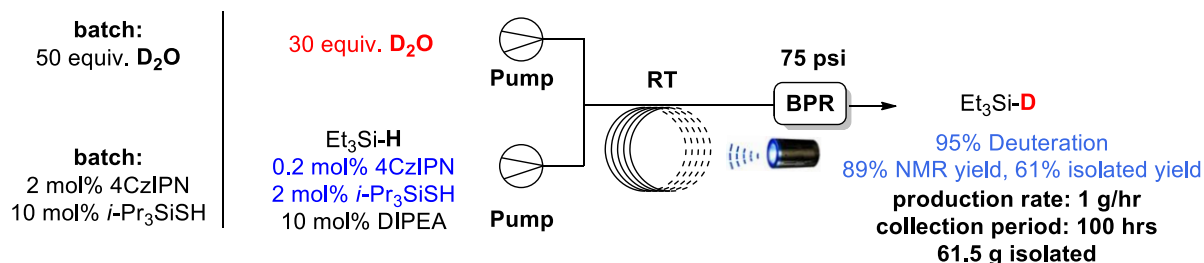
Fig. S1 Emission spectra of 18 W blue LED strips (maximum Emission at around 470 nm)

II. Typical Procedure for Silane Deuteration in Batch



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added photocatalyst **1** 4CzIPN (7.89 mg, 0.01 mmol, 2 mol %). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After which, anhydrous and degassed ethyl acetate (2.0 mL), silane (0.5 mmol, 1 equiv., for solid silane, added together with the photocatalyst), base (0.05 mmol, 10 mol %), and D₂O (0.45 mL, 25 mmol, 50 equiv.) were added sequentially using syringes. The resulting mixture was sealed and irradiated with blue LED (2 meter strip, 18 W), and aliquot of the crude reaction mixture was subjected to GC-MS analysis to determine for reaction completeness. Reaction mixture deemed with acceptable deuteration ratio was added MgSO₄, filtered, and washed with minimum amount of diethyl ether. The combined organic mixture was concentrated and subjected to flash column chromatography (hexane or hexane/ethyl acetate) to yield product as a mixture of Si–D and Si–H (which could not be separated by column chromatography). The ratio of deuteration was determined by ¹H NMR.

III. Large Scale Continuous Flow Synthesis of Et₃Si–D



4CzIPN (2.01 g, 2.54 mmol, 0.2 mol %) was added to a 2.5 L flask equipped with a rubber septum containing 1692 mL EtOAc and sparged with argon for 15 minutes. Then triethylsilane (202.8 mL, 1.27 mol, 1 equiv.), DIPEA (21.0 mL, 0.127 mol, 10 mol %) and triisopropylsilanethiol (5.4 mL, 25.4 mmol, 2 mol %) was added to the flask. D₂O was added to a separate 1.0 L flask and protected under argon atmosphere. A Syrris Asia pump was filled with the combined organic reaction mixture and D₂O and connected to the flow reactor with a 75 psi back-pressure regulator. Flow rate of the combined organic mixture and D₂O were set at 243 μL/min and 87 μL/min, respectively. The reaction mixture would then flow into the micro-tubing reactor (PFA, O.D. = 1/8", I.D. = 0.062", 30.5 m, volume = 59.4 mL) and was irradiated with 207 W blue LED. The temperature of the setup is maintained at room temperature with the usage of a fan for ventilation. The residence time in the reactor was controlled to 3 h, after which the reaction mixture would flow into a flask equipped with an argon balloon. After equilibration for 9 h, the reaction mixture was collected for 100 h (Fig. S2 and S3). The crude organic layer was carefully distilled three times to isolate the pure triethylsilane-D. The first distillation was to remove the bulk of ethyl acetate

using two fractional columns (Fig. S4). The second distillation was performed to collect ethyl acetate and triethylsilane-D from the remaining organic mixture (Fig. S5). The last distillation was performed to isolate triethylsilane-D from the organic mixture (Fig. S6).

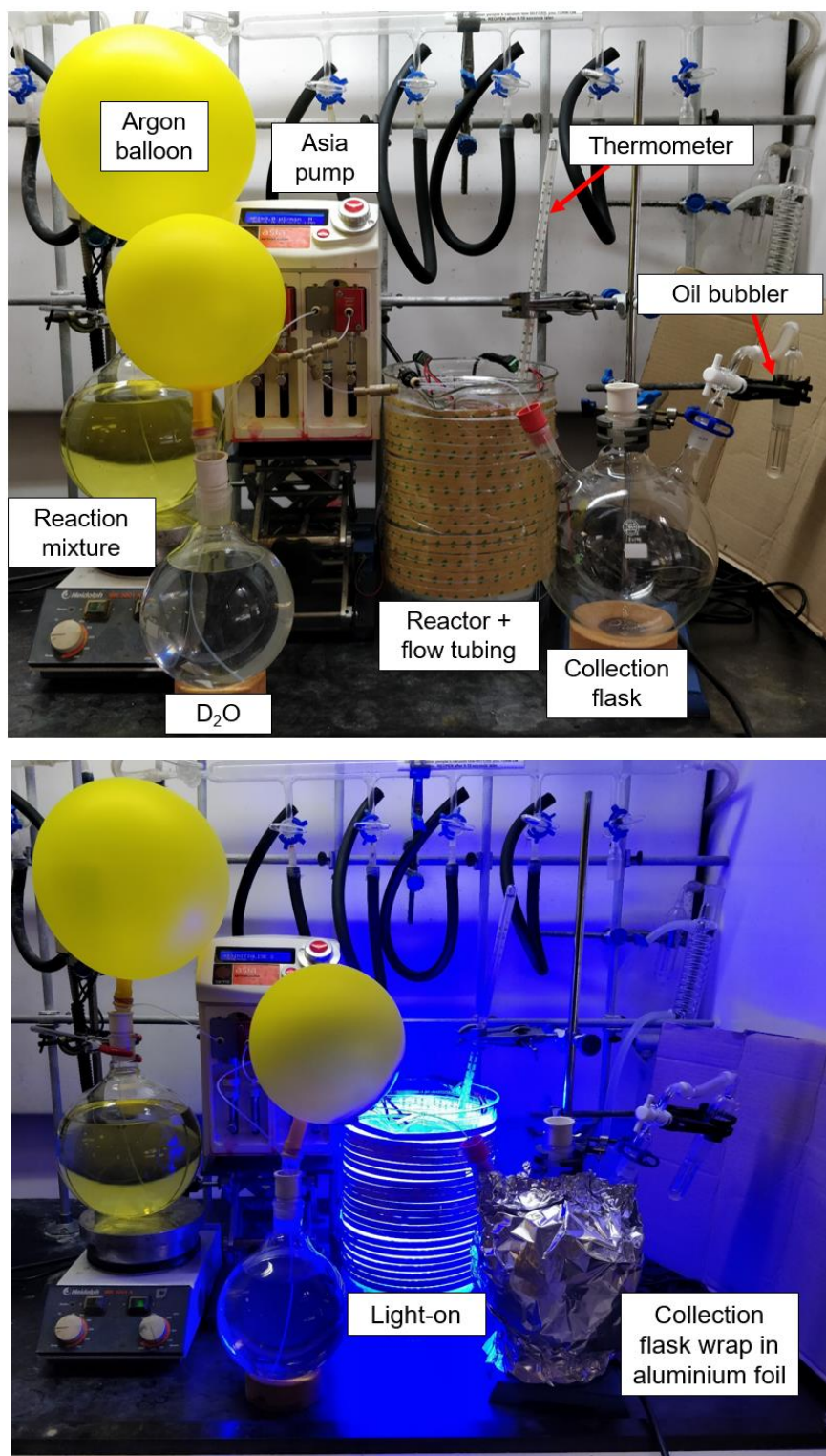


Fig. S2 Continuous flow setup (note: fan omitted for clarity)

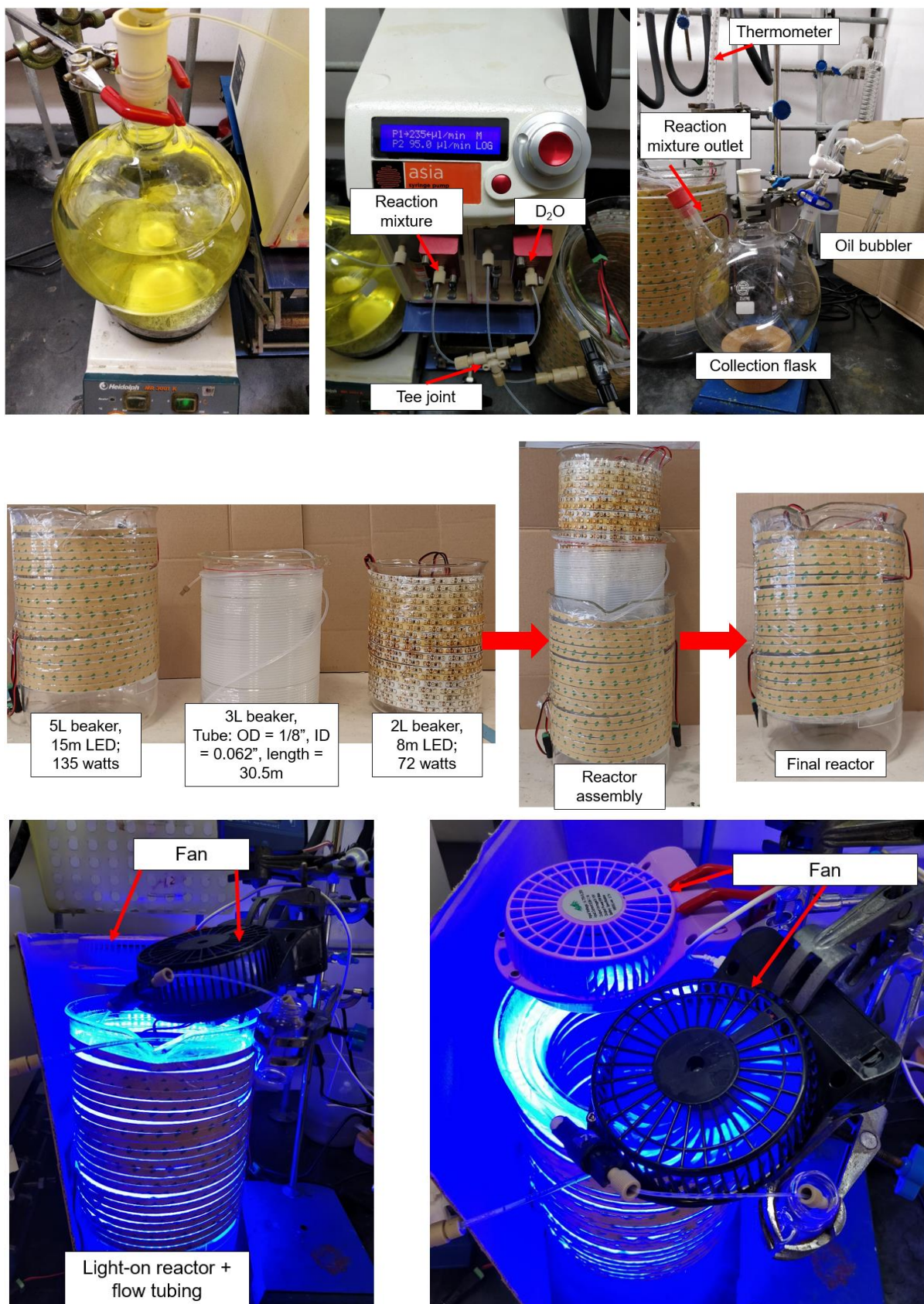


Fig. S3 Components of continuous flow setup

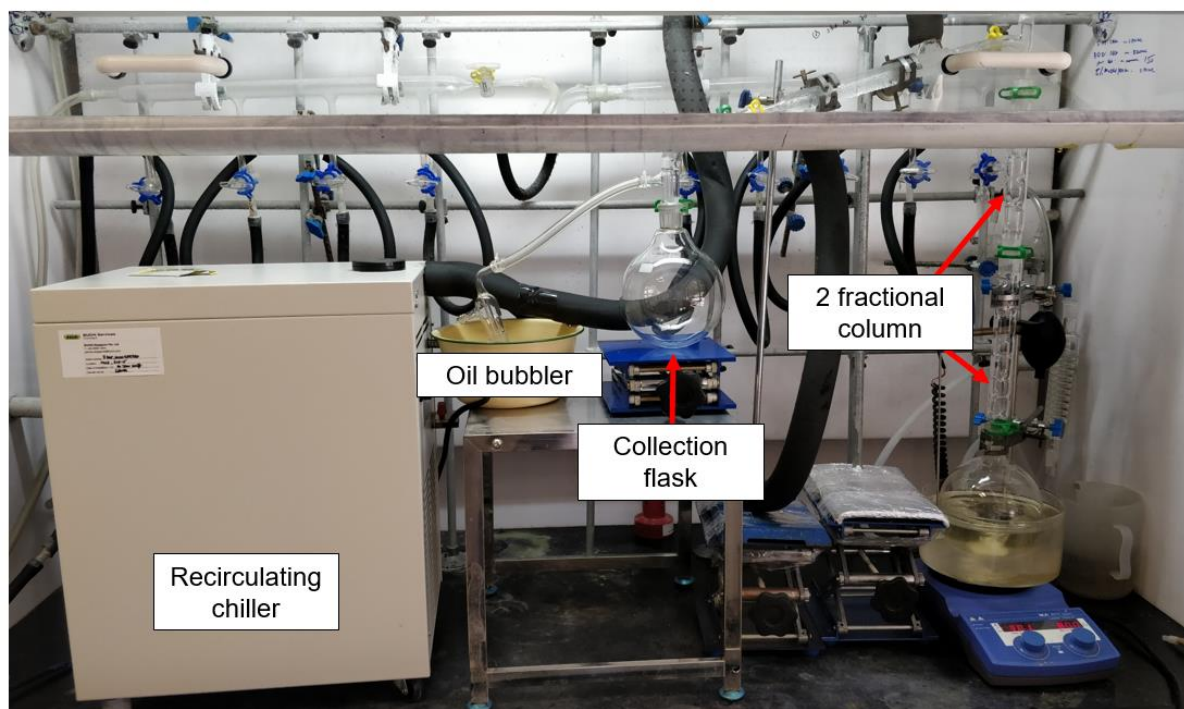


Fig. S4 First distillation setup

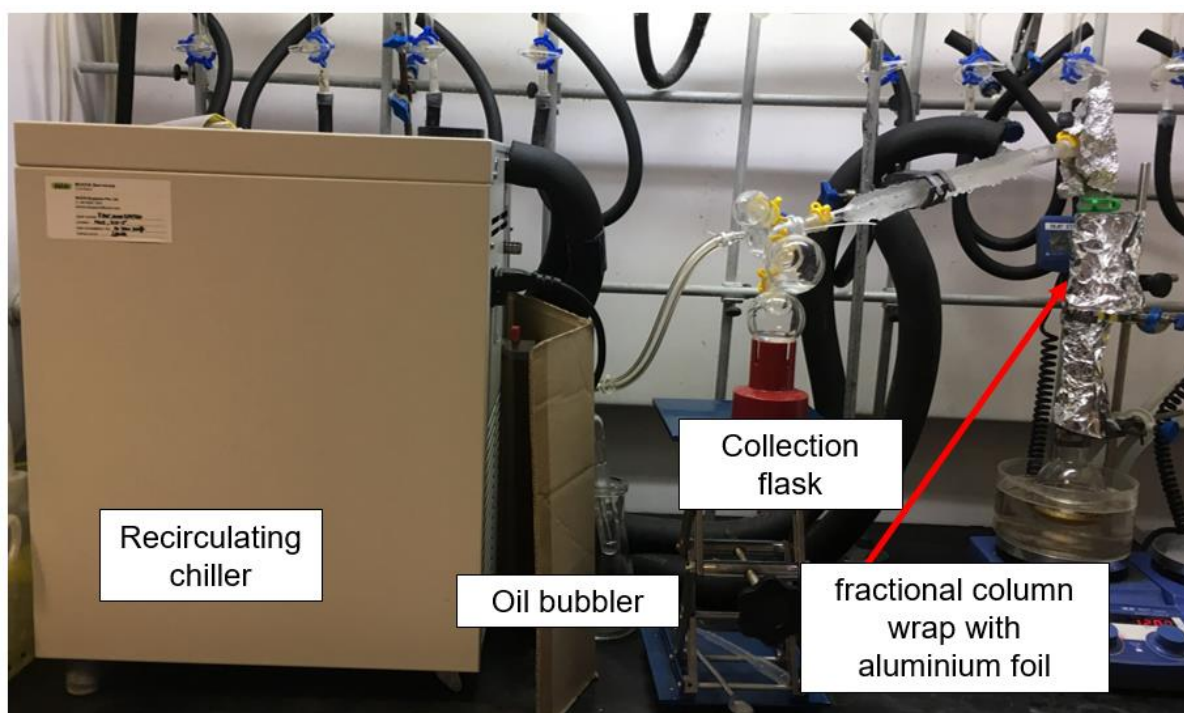


Fig. S5 Second distillation setup

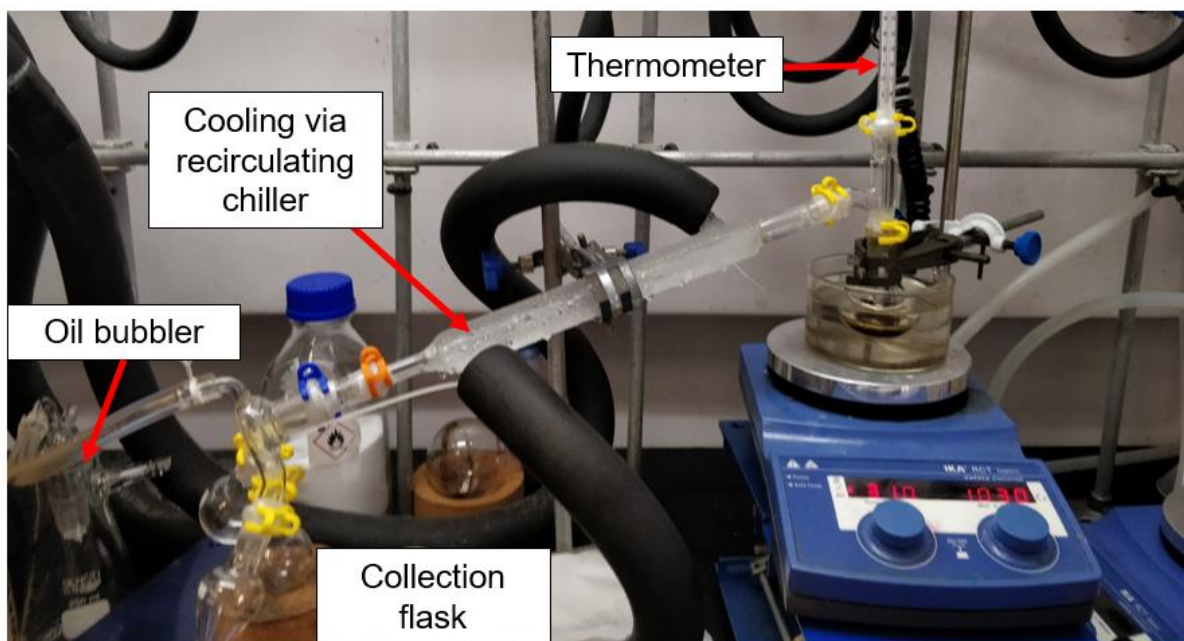


Fig. S6 Final distillation setup

IV. Mechanistic Investigations

Control experiments:

H/D exchange of thiol HAT catalyst with D₂O

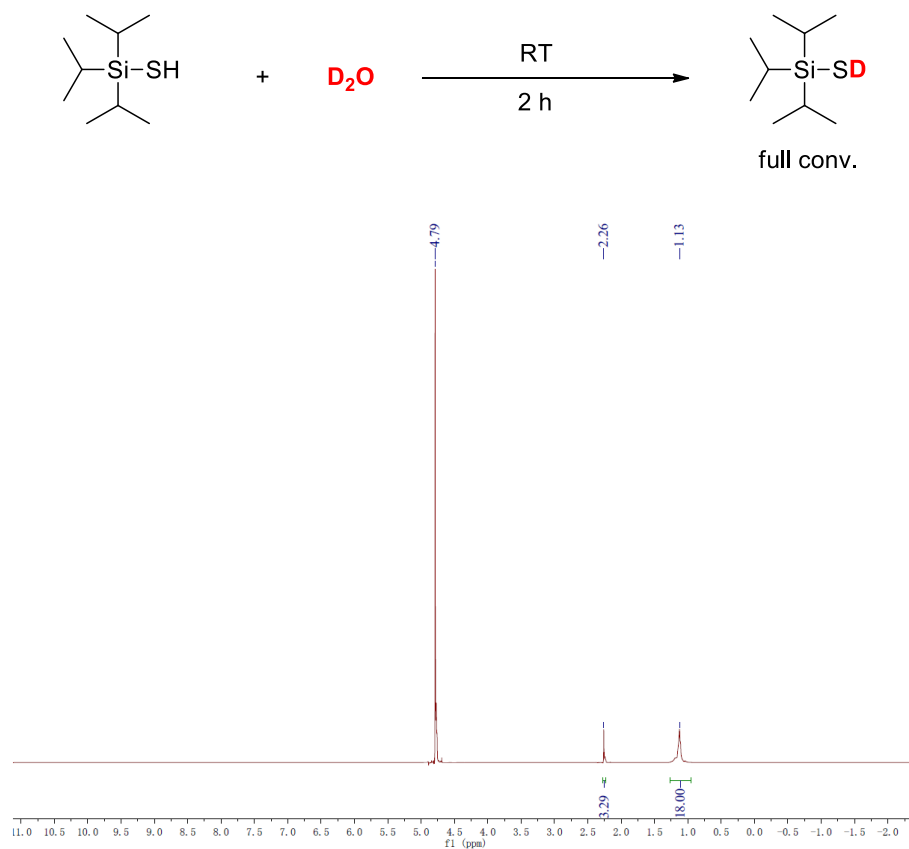


Fig. S7 ¹H NMR spectrum of *t*Pr₃SiSH in D₂O

The S–H peak from thiol disappeared in D₂O, which indicated the hydrogen deuterium exchange of the thiol catalyst with D₂O.

Reaction with TEMPO



Light on/off experiments:

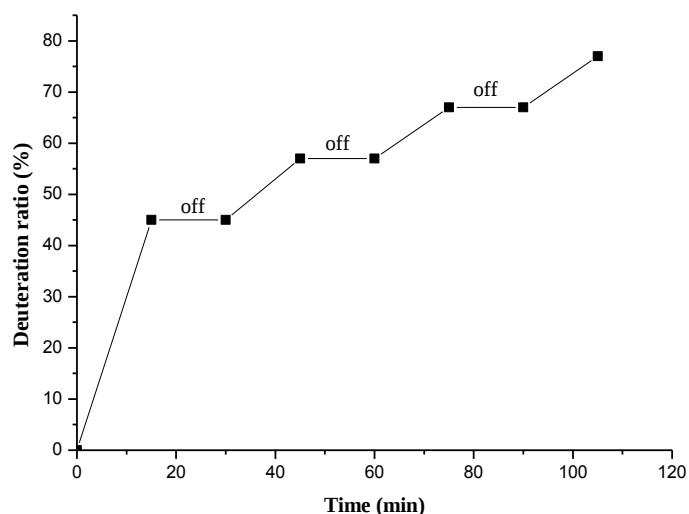
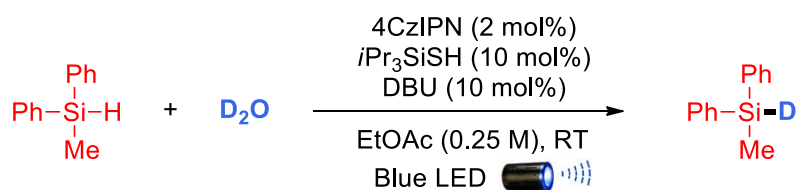
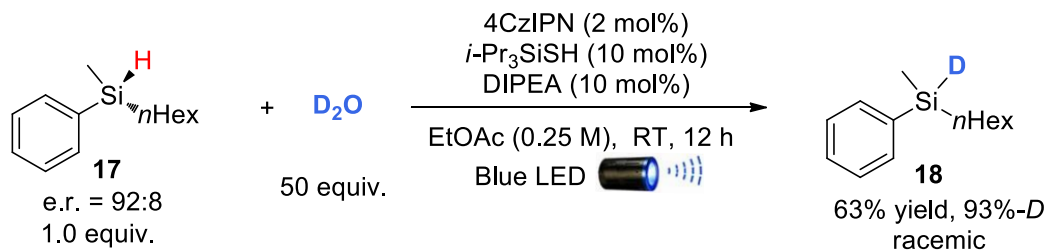
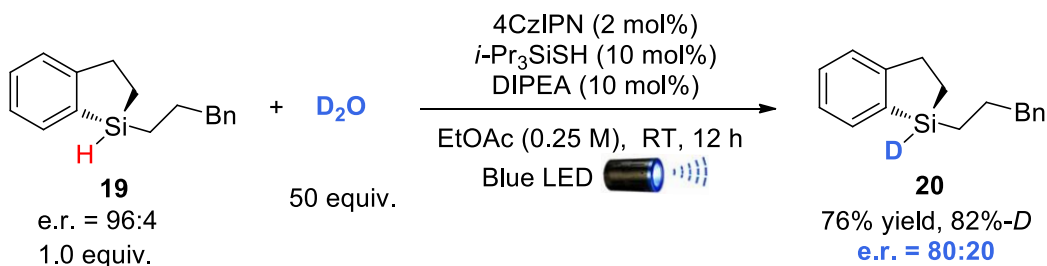


Fig. S8 Light on-off experiments for deuteration of methylphenylsilane

V. Synthesis of Chiral Deuterated Silanes

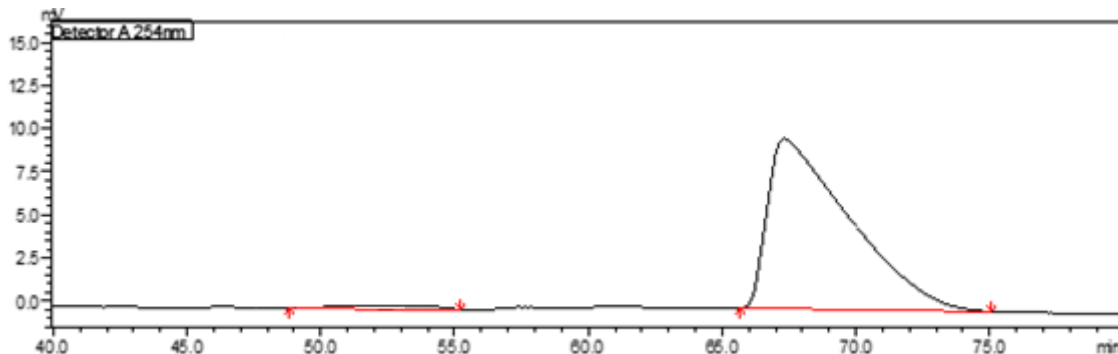




To a 25 mL Schlenk tube equipped with a magnetic stir bar was added photocatalyst **1** 4CzIPN (7.89 mg, 0.01 mmol, 2 mol %). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After which, anhydrous and degassed ethyl acetate (2.0 mL), chiral silane (0.5 mmol, 1 equiv.), DIPEA (8.2 μ L, 0.05 mmol, 10 mol %), and D₂O (0.45 mL, 25 mmol, 50 equiv.) were added sequentially by means of syringe. This resulting mixture was sealed and irradiated with blue LED (2 meter strip, 18 W), and aliquot of the crude reaction mixture was subjected to GC-MS analysis to determine for reaction completeness. After that MgSO₄ was added, filtered, and washed with minimum amount of diethyl ether. The combined organic mixture was carefully concentrated and subjected to chromatography to yield product as a mixture of Si-D and Si-H (which could not be separated by column chromatography).

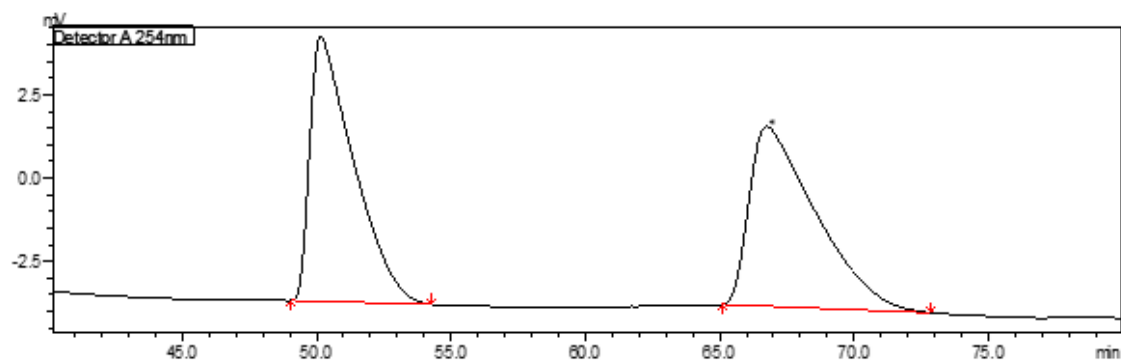
HPLC result for enantiomeric ratio

1. Pure chiral silane **19**



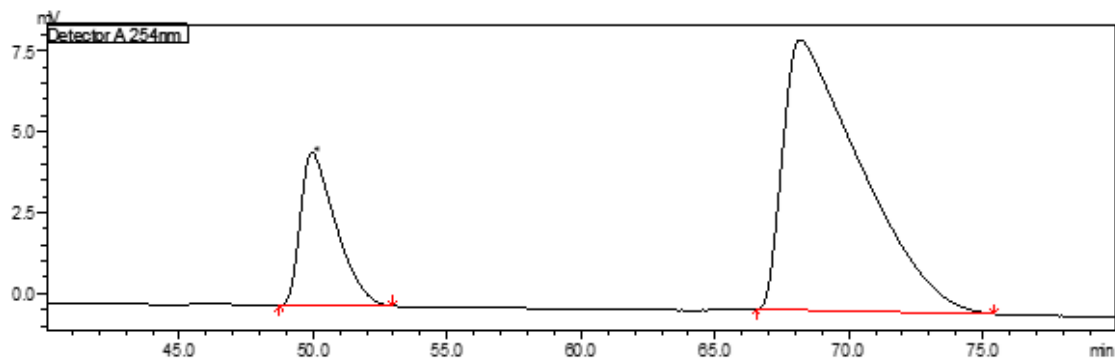
Peak#	Ret. Time	Area	Area%
1	52.211	73465.56	3.382
2	67.318	2099016	96.618
Total		2099016	100.000

2. Pure racemic counterpart of silane **19**



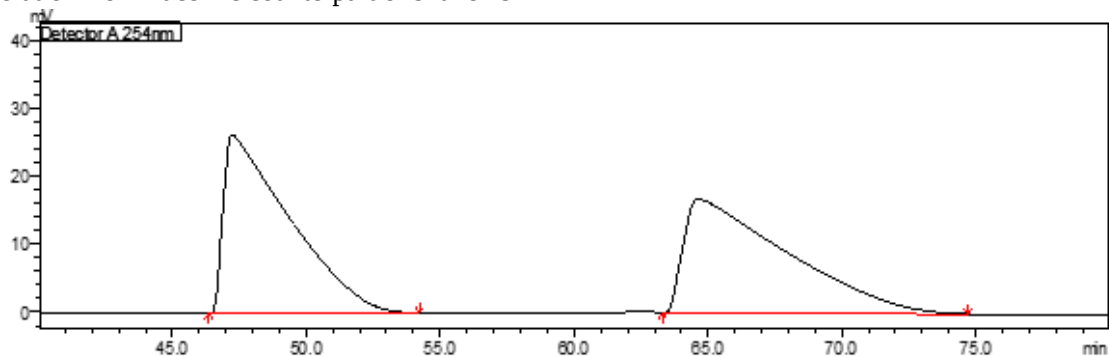
Peak#	Ret. Time	Area	Area%
1	50.150	902738	49.227
2	66.746	931103	50.773
Total		1833841	100.000

3. Deuterated chiral silane **20**



Peak#	Ret. Time	Area	Area%
1	49.951	435940	20.486
2	68.189	1692081	79.514
Total		2128021	100.000

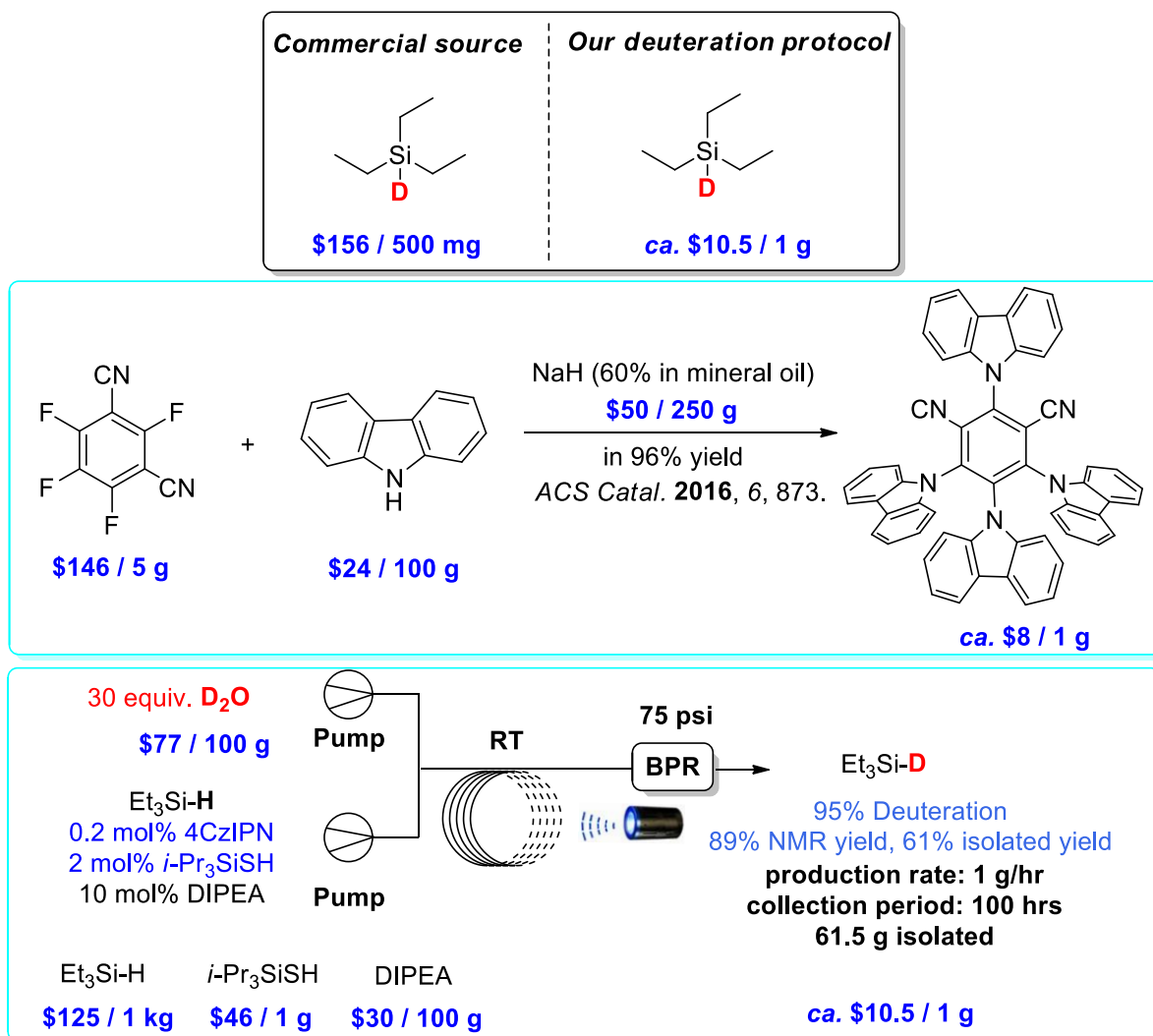
4. Deuteration from racemic counterpart of silane **19**



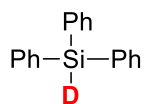
Peak#	Ret. Time	Area	Area%
1	47.232	4480957	50.011
2	64.653	4478936	49.989
Total		8959894	100.000

VI. Estimated Cost of Our Protocol for Preparation of 1.0 Gram of Et₃Si-D

Note: the prices of commercially available chemicals are based on MOLBASE reference prices.

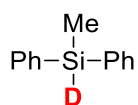


VII. Analytical Data of the Products



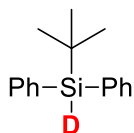
Triphenylsilane-*d* (2)

The above compound was synthesized according to general procedure from triphenylsilane (130 mg, 0.5 mmol) to give product **2** in 78% yield and 95%-*D* ratio. ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.61 (m, 6H), 7.54 – 7.37 (m, 9H), 5.56 (s, 0.05H); GC-MS (EI) [M]⁺ Calcd for C₁₈H₁₅DSi 261.1, found 261.1.



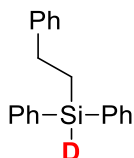
Methylphenylsilane-*d* (3)

The above compound was synthesized according to general procedure from methyldiphenylsilane (99 mg, 0.5 mmol) to give product **3** in 82% yield and 95%-*D* ratio. ^1H NMR (500 MHz, CDCl_3) δ 7.63 (dd, J = 7.7, 1.7 Hz, 4H), 7.48 – 7.39 (m, 6H), 5.02 (q, J = 3.8 Hz, 0.05H), 0.69 (s, 3H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{13}\text{DSi}$ 199.1, found 199.1.



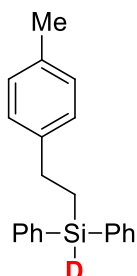
***tert*-Butyldiphenylsilane-*d* (4)**

The above compound was synthesized according to general procedure from *tert*-butyldiphenylsilane (120 mg, 0.5 mmol) to give product **4** in 72% yield and 94%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.69 - 7.72 (m, 4H), 7.39 - 7.42 (m, 6H), 4.68 (m, 0.06H), 1.11 (s, 9H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{DSi}$ 241.1, found 241.1.



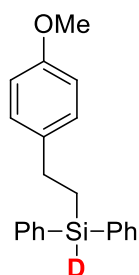
Phenethyldiphenylsilane-*d* (5)

The above compound was synthesized according to general procedure from phenethyldiphenylsilane (144 mg, 0.5 mmol) to give product **5** in 78% yield and 93%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.42 (m, 4H), 7.34 – 7.21 (m, 6H), 7.18 – 7.11 (m, 2H), 7.10 – 7.02 (m, 3H), 4.81 (t, J = 3.7 Hz, 0.07H), 2.72 – 2.61 (m, 2H), 1.46 – 1.36 (m, 2H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{DSi}$ 289.1, found 289.1.



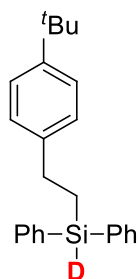
(4-Methylphenethyl)diphenylsilane-*d* (6)

The above compound was synthesized according to general procedure from (4-methylphenethyl)diphenylsilane (151 mg, 0.5 mmol) to give product **6** in 80% yield and 90%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.62 (m, 4H), 7.52 – 7.40 (m, 6H), 7.16 (s, 4H), 5.00 (t, J = 3.7 Hz, 0.1H), 2.87 – 2.78 (m, 2H), 2.39 (s, 3H), 1.63 – 1.54 (m, 2H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{DSi}$ 303.2, found 303.1.



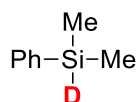
(4-Methoxyphenethyl)diphenylsilane-*d* (7)

The above compound was synthesized according to general procedure from (4-methylphenethyl)diphenylsilane (159 mg, 0.5 mmol) to give product **7** in 70% yield and 84%-*D* ratio. ^1H NMR (500 MHz, CDCl_3) δ 7.77 – 7.64 (m, 4H), 7.55 – 7.39 (m, 6H), 7.27 – 7.14 (m, 2H), 7.01 – 6.84 (m, 2H), 5.02 (q, J = 3.8 Hz, 0.16H), 3.86 (d, J = 2.2 Hz, 3H), 2.83 (td, J = 8.7, 3.9 Hz, 2H), 1.70 – 1.56 (m, 2H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{DOSi}$ 319.1, found 319.2.



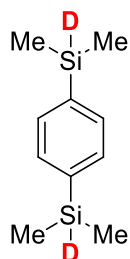
(4-(*tert*-Butyl)phenethyl)diphenylsilane-*d* (8)

The above compound was synthesized according to general procedure from (4-(*tert*-butyl)phenethyl)diphenylsilane (173 mg, 0.5 mmol) to give product **8** in 80% yield and 92%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.60 (m, 4H), 7.49 – 7.38 (m, 6H), 7.38 – 7.32 (m, 2H), 7.22 – 7.15 (m, 2H), 4.98 (t, J = 3.7 Hz, 0.08H), 2.86 – 2.77 (m, 2H), 1.62 – 1.54 (m, 2H), 1.37 (s, 9H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{24}\text{H}_{27}\text{DSi}$ 345.2, found 345.3.



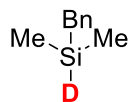
Dimethyl(phenyl)silane-*d* (9)

The above compound was synthesized according to general procedure from dimethyl(phenyl)silane (68 mg, 0.5 mmol) to give product **9** in 76% yield and 94%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.50 (m, 2H), 7.43 – 7.31 (m, 3H), 4.48 – 4.40 (m, 0.06H), 0.35 (s, 6H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_8\text{H}_{11}\text{DSi}$ 137.1, found 137.1.



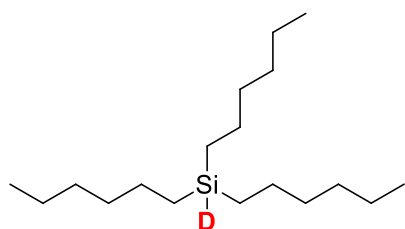
1,4-Bis(dimethylsilyl)benzene-*d*₂ (10)

The above compound was synthesized according to general procedure from 1,4-bis(dimethylsilyl)benzene (97 mg, 0.5 mmol) to give product **10** in 72% yield and 88%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 4H), 4.48 (hept, $J = 3.7$ Hz, 0.25H), 0.39 (s, 12H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_{16}\text{D}_2\text{Si}_2$ 196.1, found 196.2.



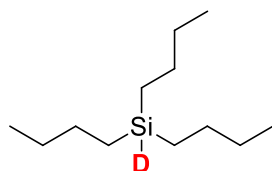
Benzyldimethylsilane-*d* (11)

The above compound was synthesized according to general procedure from benzyldimethylsilane (75 mg, 0.5 mmol) to give product **11** in 70% yield and 94%-*D* ratio. ^1H NMR (500 MHz, CDCl_3) δ 7.22 (t, $J = 7.6$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 7.2$ Hz, 2H), 3.95 (dt, $J = 7.0, 3.5$ Hz, 0.06H), 2.15 (s, 2H), 0.06 (s, 6H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_{13}\text{D}_2\text{Si}_2$ 151.1, found 151.1.



Trihexylsilane-*d* (12)

The above compound was synthesized according to general procedure from trihexylsilane (142.5 mg, 0.5 mmol) to give product **12** in 95% yield and 95%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 3.72 – 3.66 (m, 0.05H), 1.43 – 1.19 (m, 24H), 0.98 – 0.82 (m, 9H), 0.66 – 0.50 (m, 6H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{39}\text{DSi}$ 285.3, found 285.3.



Tributylsilane-*d* (13)

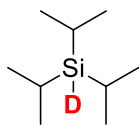
The above compound was synthesized according to general procedure from tributylsilane (100 mg, 0.5 mmol) to give product **13** in 99% yield and 92%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 3.71 – 3.65 (m, 0.08H), 1.43 – 1.22 (m, 12H), 0.97 – 0.81 (m, 9H), 0.66 – 0.52 (m, 6H); GC-MS (EI) $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{27}\text{DSi}$ 201.2, found 201.2.



Tripropylsilane-*d* (14)

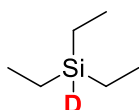
The above compound was synthesized according to general procedure from tripropylsilane (79 mg, 0.5 mmol) to give product **14** in 85% yield and 97%-*D* ratio. ^1H NMR (400 MHz, CDCl_3) δ 3.69 - 3.72 (m,

0.03H), 1.36 - 1.42 (m, 6H), 0.97 (t, $J = 7.6$ Hz, 9H), 0.57 - 0.62 (m, 6H); GC-MS (EI) $[M]^+$ Calcd for $C_9H_{21}DSi$ 159.2, found 159.2.



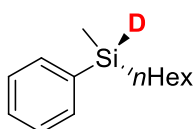
Triisopropylsilane-*d* (15)

The above compound was synthesized according to general procedure from triisopropylsilane (79 mg, 0.5 mmol) to give product **15** in 85% yield and 95%-*D* ratio. 1H NMR (400 MHz, $CDCl_3$) δ 3.31 (s, 0.05H), 1.06 (m, 6H), 0.97 (s, 21H); GC-MS (EI) $[M]^+$ Calcd for $C_9H_{21}DSi$ 159.2, found 159.2.



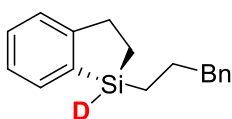
Triethylsilane-*d* (16)

The above compound was synthesized according to general procedure from triethylsilane (58 mg, 0.5 mmol) to give product **16** in 86% yield and 98%-*D* ratio. 1H NMR (400 MHz, $CDCl_3$) δ 3.57 - 3.60 (m, 0.02H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.56 (q, $J = 8.0$ Hz, 6H); GC-MS (EI) $[M]^+$ Calcd for $C_6H_{15}DSi$ 117.1, found 117.2.



(*R*)-hexyl(methyl)(phenyl)silane-*d* (18)

The above compound was synthesized according to general procedure from (*R*)-hexyl(methyl)(phenyl)silane (104 mg, 0.5 mmol) to give product **17** in 63% yield and 93%-*D* ratio. 1H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.57 (m, 2H), 7.36 - 7.38 (m, 3H), 4.35 - 4.38 (m, 0.07H), 1.30 - 1.39 (m, 8H), 0.89 (m, 5H), 0.34 (s, 3H). The enantiomeric ratio was determined to be racemic by HPLC analysis on Chiralpak OJ-H (n-hexane, 0.25 mL/min), $\lambda = UV$ 220 nm. GC-MS (EI) $[M]^+$ Calcd for $C_{13}H_{21}DSi$ 207.2, found 207.2.



(*S*)-1-(3-phenylpropyl)-2,3-dihydro-1*H*-benzo[*b*]silole-*d* (20)

The above compound was synthesized according to general procedure from (*S*)-1-(3-phenylpropyl)-2,3-dihydro-1*H*-benzo[*b*]silole (127 mg, 0.5 mmol) to give product **18** in 76% yield and 82%-*D* ratio. 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 1H), 7.23 - 7.31 (m, 4H), 7.13 - 7.20 (m, 4H), 4.64 (m, 0.18H), 3.11 - 3.12 (m, 2H), 2.63 - 2.67 (m, 2H), 1.78 (m, 2H), 1.19 - 1.23 (m, 1H), 0.92 - 1.09 (m, 3H). The enantiomeric ratio was determined to be racemic by HPLC analysis on Chiralpak OJ-H (n-hexane, 0.5 mL/min), $\lambda = UV$ 254 nm, $t_{minor} = 49.95$ min, $t_{major} = 68.19$ min; GC-MS (EI) $[M]^+$ Calcd for $C_{17}H_{19}DSi$ 253.1, found 253.1.

VIII. ^1H NMR Spectra of Deuterated Silanes

