

Electronic Supplementary Information (ESI) for

**Solvent-Free Copper-Catalyzed Trisilylation of Alkynes: A Practical
and Atom-Economical Approach to Access 1,1,1-trisilylalkanes**

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General Remarks

All the manipulations were performed in an argon-filled glovebox, unless mentioned otherwise. THF, toluene, and hexane were purified by passing the degassed solvents (N₂) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). The following chemicals were purchased and used as received: Cu(OAc)₂ (98%, Sigma-Aldrich), PhSiH₃ (Oakwood Chemicals), phosphine ligand (Oakwood Chemicals, PⁿBu₃ ligand from Sigma-Aldrich), CD₃OD (99.8% atom D, Sigma-Aldrich). Some alkynes (Oakwood Chemicals) were purchased from commercial sources and used without further purification. Other alkynes were prepared by literature report procedure.^[1] All other chemicals were used as received. Neutral aluminum oxide (70-230 mesh ASTM) from Merck and all other chemicals were used as received.

¹H, ²H, and ¹³C{¹H} spectra were recorded using Bruker 300 MHz, 400 MHz, or 500 MHz NMR spectrometers. ¹H NMR and ¹³C NMR spectra were referenced to resonances of the residual signals of the deuterated solvents. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet. GC analysis was acquired on Shimadzu Nexis GC-2030 gas chromatography equipped with a flame-ionization detector. GC-MS analysis was performed on Shimadzu GC-2010 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. HR-MS analyses were performed using Bruker micrOTOFQII (APCI and ESI).

General procedure for evaluating reaction parameters

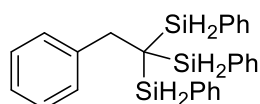
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with copper salt, such as CuOAc, CuTc, Cu(OTf)₂, or Cu(OAc)₂, (30.0 μmol), bisphosphine ligand (30.0 μmol) or monophosphine ligand (60.0 μmol), and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiH₃ (130 mg, 1.20 mmol) was added, stirring for another 10 min before adding alkyne **1a** (30.6 mg, 0.300 mmol) successively. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h and then cooled to room temperature. Tridecane (18.0 mg, 24 μL, 0.100 mmol) and ethyl acetate (1.0 mL) were added before analyzing by GC.

General procedure for copper-catalyzed trisilylation of alkynes

In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with Cu(OAc)₂ (5.5 mg, 30.0 μmol) and PⁿBu₃ (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiH₃ (130 mg, 1.20 mmol) was added, stirring for another 10 min before adding alkynes (0.300 mmol) successively. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h and then cooled to room temperature. Subsequently, the residue was purified by flash chromatography on neutral aluminum oxide using a mixture of ethyl acetate and hexane as eluent. The conditions for chromatography and data for characterization of the 1,1,1-trisilylalkane products are listed below.

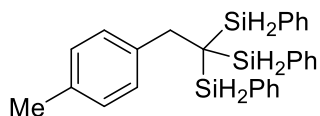
We measured ²⁹Si{¹H} NMR spectra of **2a**, **2b**, **2x**, and **2y**, and only one resonance at around -27 ppm was identified for each trisilylalkane compound.

(2-phenylethane-1,1,1-triyl)tris(phenylsilane) (4a)



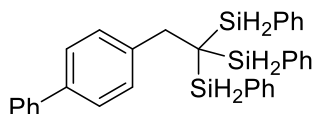
The titled compound was isolated (81.4 mg, 64%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.33 (m, 9H), 7.26 – 7.22 (m, 11H), 4.49 (s, 6H), 3.21 (s, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 139.9, 136.6, 131.0, 130.6, 130.0, 128.3, 127.9, 126.9, 37.2, 0.4. HRMS (EI) m/z: calcd for C₂₆H₂₈Si₃ [M]⁺: 424.1493; Found: 424.1487.

(2-(*p*-tolyl)ethane-1,1,1-triyl)tris(phenylsilane) (4b)



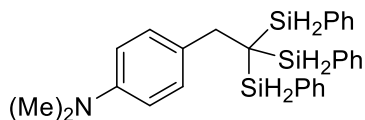
The titled compound was isolated (89.3 mg, 68%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.35 (m, 9H), 7.29 – 7.25 (m, 6H), 7.09 (dd, *J* = 27.3, 8.0 Hz, 4H), 4.50 (s, 6H), 3.19 (s, 2H), 2.35 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.8, 136.6, 136.5, 131.1, 130.5, 129.9, 129.0, 127.8, 36.7, 21.2, 0.5. HRMS (EI) m/z: calcd for C₂₇H₃₀Si₃ [M]⁺: 438.1650; Found: 438.1651.

(2-([1,1'-biphenyl]-4-yl)ethane-1,1,1-triyl)tris(phenylsilane) (4c)



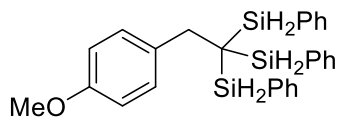
The titled compound was isolated (82.5 mg, 55%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.57 (m, 2H), 7.46 – 7.42 (m, 4H), 7.39 – 7.34 (m, 10H), 7.29 – 7.23 (m, 8H), 4.53 (s, 6H), 3.24 (s, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.1, 139.8, 139.1, 136.6, 130.99, 130.97, 130.0, 128.9, 127.9, 127.3, 127.1, 127.0, 36.8, 0.6. HRMS (EI) m/z: calcd for C₃₂H₃₂Si₃ [M]⁺: 500.1806; Found: 500.1808.

***N,N*-dimethyl-4-(2,2,2-tris(phenylsilyl)ethyl)aniline (4d)**



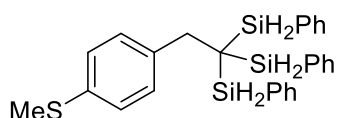
The titled compound was isolated (109 mg, 78%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.40 (m, 9H), 7.33 – 7.29 (m, 6H), 7.18 – 7.14 (m, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 4.55 (s, 6H), 3.21 (s, 2H), 2.98 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.8, 136.6, 135.7, 131.3 (two peaks overlap), 129.9, 127.8, 112.7, 41.0, 36.2, 0.9. HRMS (EI) m/z: calcd for C₂₈H₃₃NSi₃ [M]⁺: 467.1915; Found: 467.1911.

(2-(4-methoxyphenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4e)



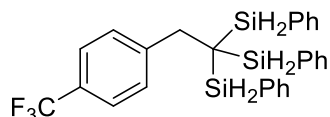
The titled compound was isolated (80.3 mg, 59%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.33 (m, 9H), 7.29 – 7.24 (m, 6H), 7.13 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.50 (s, 6H), 3.80 (s, 3H), 3.18 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 158.7, 136.6, 132.1, 131.6, 131.1, 130.0, 127.9, 113.7, 55.5, 36.3, 0.7. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{30}\text{OSi}_3$ $[\text{M}]^+$: 454.1599; Found: 454.1591.

(2-(4-(methylthio)phenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4f)



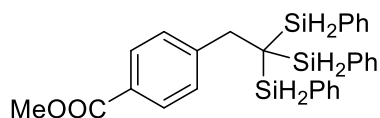
The titled compound was isolated (87.4 mg, 62%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.38 (m, 9H), 7.31 – 7.26 (m, 6H), 7.15 (s, 4H), 4.53 (s, 6H), 3.19 (s, 2H), 2.49 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.9, 136.8, 136.6, 131.0, 130.9, 130.0, 127.9, 126.7, 36.6, 16.2, 0.5. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{30}\text{SSi}_3$ $[\text{M}]^+$: 470.1371; Found: 470.1386.

(2-(4-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4g)



The titled compound was isolated (63.4 mg, 43%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 8.1 Hz, 2H), 7.44 – 7.34 (m, 9H), 7.33 – 7.27 (m, 8H), 4.55 (s, 6H), 3.26 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 144.0, 136.5, 135.6, 130.7, 130.6, 130.2, 128.0, 125.7 (q, J = 273.7 Hz), 125.2 (q, J = 3.7 Hz), 36.9, 0.2. ^{19}F NMR (377 MHz, CDCl_3) δ -62.4. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{27}\text{F}_3\text{Si}_3$ $[\text{M}]^+$: 492.1367; Found: 492.1363.

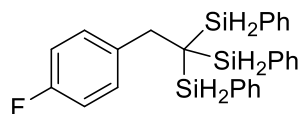
methyl 4-(2,2,2-tris(phenylsilyl)ethyl)benzoate (4h)



The titled compound was isolated (89.6 mg, 62%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.3 Hz, 2H), 7.66 – 7.39 (m, 9H), 7.36 – 7.18 (m, 8H), 4.58 (s, 6H), 3.97 (s, 3H), 3.30 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.1, 145.2, 136.6, 135.6, 130.6, 130.5, 130.1, 129.5, 128.0, 52.2, 37.1, 0.01. HRMS (EI) m/z : calcd for $\text{C}_{28}\text{H}_{30}\text{O}_2\text{Si}_3$ $[\text{M}]^+$:

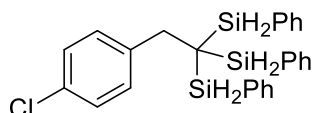
482.1548; Found: 482.1549.

(2-(4-fluorophenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4i)



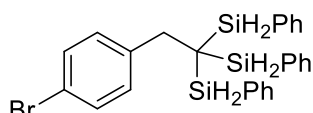
The titled compound was isolated (67.6 mg, 51%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.37 (m, 9H), 7.31 – 7.27 (m, 6H), 7.15 (dd, J = 8.7, 5.4 Hz, 2H), 6.91 (t, J = 8.7 Hz, 2H), 4.51 (s, 6H), 3.20 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 162.0 (d, J = 246.4 Hz), 136.6, 135.6 (d, J = 3.3 Hz), 131.9 (d, J = 7.9 Hz), 130.8, 130.1, 127.9, 115.0 (d, J = 21.2 Hz), 36.4, 0.4. ^{19}F NMR (377 MHz, CDCl_3) δ -116.3. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{27}\text{FSi}_3$ $[\text{M}]^+$: 442.1399; Found: 442.1401.

(2-(4-chlorophenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4j)



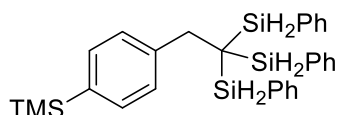
The titled compound was isolated (72.8 mg, 53%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.38 (m, 9H), 7.32 – 7.26 (m, 6H), 7.20 – 7.17 (m, 2H), 7.13 – 7.11 (m, 2H), 4.53 (s, 6H), 3.19 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.2, 136.5, 132.6, 131.7, 130.6, 130.0, 128.2, 127.9, 36.4, 0.2. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{27}\text{ClSi}_3$ $[\text{M}]^+$: 458.1104; Found: 458.1102.

(2-(4-bromophenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4k)



The titled compound was isolated (64.7 mg, 43%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.26 (m, 17H), 7.06 (d, J = 8.2 Hz, 2H), 4.53 (s, 6H), 3.17 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.9, 136.6, 132.2, 131.3, 130.7, 130.1, 128.0, 120.8, 36.5, 0.2. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{27}\text{BrSi}_3$ $[\text{M}]^+$: 502.0598; Found: 502.0607.

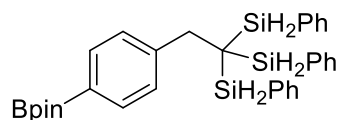
(2-(4-(trimethylsilyl)phenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4l)



The titled compound was isolated (95.2 mg, 64%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.21 (m, 5H), 7.20 – 7.15 (m, 6H), 7.14 – 7.07 (m, 8H), 4.37 (s, 6H), 3.06 (s, 2H), 0.15 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.6, 138.8, 136.6, 133.4, 131.0, 130.0, 129.9, 127.8, 37.1, 0.5, -0.9. HRMS (EI) m/z : calcd for $\text{C}_{29}\text{H}_{36}\text{Si}_4$ $[\text{M}]^+$: 496.1889; Found:

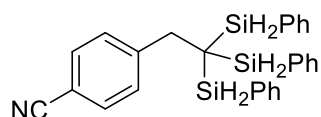
496.1904.

(2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane-1,1,1-triyl)tris(phenylsilane) (4m)



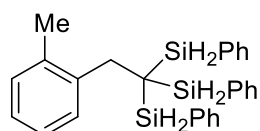
The titled compound was isolated (102 mg, 62%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.1 Hz, 2H), 7.40 – 7.34 (m, 9H), 7.28 – 7.20 (m, 8H), 4.49 (s, 6H), 3.22 (s, 2H), 1.36 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.1, 136.6, 135.7, 134.8, 131.0, 130.0, 129.9, 127.9, 83.9, 37.3, 25.0, 0.2. HRMS (EI) m/z : calcd for $\text{C}_{32}\text{H}_{39}\text{BO}_2\text{Si}_3$ $[\text{M}]^+$: 550.2345; Found: 550.2347.

4-(2,2,2-tris(phenylsilyl)ethyl)benzonitrile (4n)



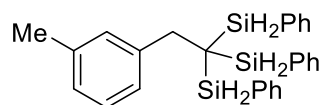
The titled compound was isolated (43.1 mg, 32%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.36 (m, 11H), 7.31 – 7.27 (m, 6H), 7.23 (d, J = 8.4 Hz, 2H), 4.52 (s, 6H), 3.23 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.4, 136.5, 135.5, 131.9, 131.1, 130.3, 128.2, 128.1, 110.7, 37.3, 0.0. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{27}\text{NSi}_3$ $[\text{M}]^+$: 449.1446; Found: 449.1439.

(2-(*o*-tolyl)ethane-1,1,1-triyl)tris(phenylsilane) (4o)



The titled compound was isolated (59.1 mg, 45%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.37 (m, 9H), 7.30 – 7.25 (m, 7H), 7.14 – 7.03 (m, 3H), 4.58 (s, 6H), 3.16 (s, 2H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.9, 136.8, 136.7, 131.1, 130.7, 130.6, 130.0, 127.8, 126.8, 125.9, 31.9, 20.6, -1.1. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{30}\text{Si}_3$ $[\text{M}]^+$: 438.1650; Found: 438.1648.

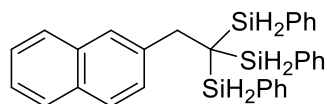
(2-(*m*-tolyl)ethane-1,1,1-triyl)tris(phenylsilane) (4p)



The titled compound was isolated (99.8 mg, 76%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.33 (m, 9H), 7.29 (t, J = 7.3 Hz, 6H), 7.18 – 7.12 (m, 1H), 7.05 (d, J = 7.6 Hz, 2H),

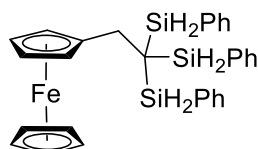
6.97 (s, 1H), 4.52 (s, 6H), 3.20 (s, 2H), 2.26 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.8, 137.9, 136.6, 131.4, 131.1, 130.0, 128.2, 127.9, 127.6, 127.5, 37.0, 21.5, 0.4. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{30}\text{Si}_3$ $[\text{M}]^+$: 438.1650; Found: 438.1647.

(2-(naphthalen-2-yl)ethane-1,1,1-triyl)tris(phenylsilane) (4q)



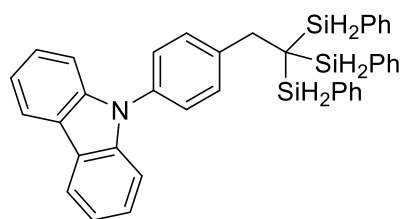
The titled compound was isolated (81.1 mg, 57%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, $J=6.1, 3.4$ Hz, 1H), 7.79 – 7.68 (m, 2H), 7.62 (s, 1H), 7.52 – 7.49 (m, 2H), 7.41 (ddd, $J=10.1, 7.7, 1.5$ Hz, 10H), 7.29 (t, $J=7.5$ Hz, 6H), 4.62 (s, 6H), 3.45 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 137.5, 136.6, 133.4, 132.4, 131.0, 130.0, 129.0, 128.9, 127.9, 127.7, 127.6, 126.1, 125.7, 37.3, 0.7. HRMS (EI) m/z : calcd for $\text{C}_{30}\text{H}_{30}\text{Si}_3$ $[\text{M}]^+$: 474.1650; Found: 474.1648.

(2-ferrocene-1,1,1-triyl)tris(phenylsilane) (4r)



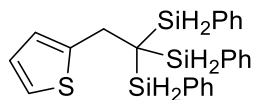
The titled compound was isolated (104 mg, 65%) as pale-yellow solid after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.38 (m, 9H), 7.30 (t, $J=7.3$ Hz, 6H), 4.45 (s, 6H), 4.20 – 4.06 (m, 9H), 3.02 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.7, 131.2, 129.9, 127.8, 71.3, 69.0, 68.0, 32.3, 1.2. HRMS (EI) m/z : calcd for $\text{C}_{30}\text{H}_{32}\text{FeSi}_3$ $[\text{M}]^+$: 532.1156; Found: 532.1169.

9-(4-(2,2,2-tris(phenylsilyl)ethyl)phenyl)-9H-carbazole (4s)



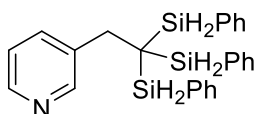
The titled compound was isolated (111 mg, 63%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 8.27 – 8.22 (m, 2H), 7.61 – 7.45 (m, 17H), 7.40 – 7.36 (m, 8H), 4.70 (s, 6H), 3.42 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.9, 139.3, 136.6, 135.6, 132.0, 130.8, 130.1, 128.0, 126.7, 126.0, 123.5, 120.5, 120.1, 109.9, 36.9, 0.6. HRMS (ESI) m/z : calcd for $\text{C}_{38}\text{H}_{37}\text{NSi}_3$ $[\text{M}+\text{H}]^+$: 590.2150; Found: 590.2146.

(2-(thiophen-2-yl)ethane-1,1,1-triyl)tris(phenylsilane) (4t)



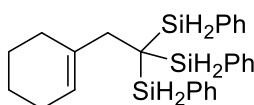
The titled compound was isolated (84.9 mg, 66%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.38 (m, 9H), 7.30 – 7.26 (m, 6H), 7.15 (dd, J = 5.1, 1.1 Hz, 1H), 6.91 (dd, J = 5.1, 3.5 Hz, 1H), 6.86 (d, J = 3.4 Hz, 1H), 4.54 (s, 6H), 3.38 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.5, 136.6, 130.8, 130.1, 127.9, 127.7, 126.7, 124.5, 31.2, 0.3. HRMS (EI) m/z : calcd for $\text{C}_{24}\text{H}_{25}\text{SSi}_3$ $[\text{M}]^+$: 429.0979; Found: 429.0981.

3-(2,2,2-tris(phenylsilyl)ethyl)pyridine (4u)



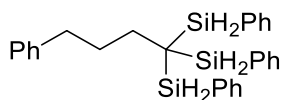
The titled compound was isolated (61.1 mg, 48%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 2H), 7.42 – 7.40 (m, 1H), 7.34 – 7.29 (m, 9H), 7.23 – 7.18 (m, 6H), 7.05 (dd, J = 7.8, 4.9 Hz, 1H), 4.45 (s, 6H), 3.11 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.7, 147.6, 138.2, 136.6, 135.7, 130.4, 130.3, 128.1, 123.2, 34.3, -0.02. HRMS (EI) m/z : calcd for $\text{C}_{25}\text{H}_{26}\text{NSi}_3$ $[\text{M}]^+$: 424.1368; Found: 424.1371.

(2-(cyclohex-1-en-1-yl)ethane-1,1,1-triyl)tris(phenylsilane) (4v)



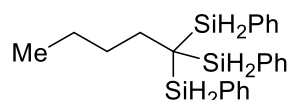
The titled compound was isolated (92.5 mg, 72%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, J = 8.0, 1.4 Hz, 6H), 7.43 – 7.34 (m, 3H), 7.29 (dd, J = 14.3, 7.3 Hz, 6H), 5.58 (s, 1H), 4.57 (s, 6H), 2.50 (s, 2H), 2.04 – 1.90 (m, 2H), 1.84 – 1.80 (m, 2H), 1.53 – 1.41 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 137.1, 136.7, 131.6, 129.9, 127.8, 125.6, 39.4, 30.3, 25.3, 22.8, 22.0, -2.5. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{32}\text{Si}_3$ $[\text{M}]^+$: 428.1806; Found: 428.1788.

(4-phenylbutane-1,1,1-triyl)tris(phenylsilane) (4w)



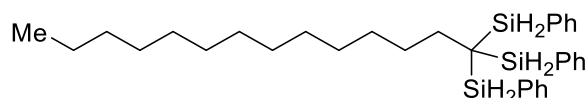
The titled compound was isolated (78.6 mg, 58%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.40 (m, 9H), 7.33 – 7.20 (m, 9H), 7.05 – 7.03 (m, 2H), 4.52 (s, 6H), 2.45 (t, J = 7.1 Hz, 2H), 1.93 – 1.81 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.8, 136.5, 131.2, 130.0, 128.6, 128.4, 128.0, 125.9, 36.6, 31.0, 30.7, -2.1. HRMS (EI) m/z : calcd for $\text{C}_{28}\text{H}_{32}\text{Si}_3$ $[\text{M}]^+$: 452.1806; Found: 452.1800.

pentane-1,1,1-triyltris(phenylsilane) (4x)



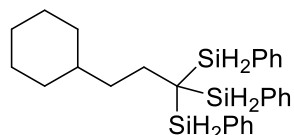
The titled compound was isolated (66.7 mg, 57%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.44 – 7.38 (m, 3H), 7.33 (t, $J = 7.2$ Hz, 6H), 4.54 (s, 6H), 1.85 – 1.77 (m, 2H), 1.63 – 1.54 (m, 2H), 1.24 – 1.12 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.3, 129.9, 127.9, 31.6, 30.9, 23.5, 13.8, -1.9. HRMS (EI) m/z : calcd for $\text{C}_{23}\text{H}_{30}\text{Si}_3$ $[\text{M}]^+$: 390.1650; Found: 390.1658.

tetradecane-1,1,1-triyltris(phenylsilane) (4y)



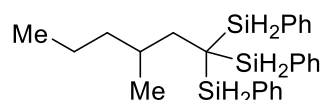
The titled compound was isolated (77.4 mg, 50%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.43 – 7.35 (m, 3H), 7.30 (t, $J = 7.2$ Hz, 6H), 4.51 (s, 6H), 1.83 – 1.70 (m, 2H), 1.57 – 1.11 (m, 2H), 1.34 – 1.11 (m, 20H), 0.90 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.4, 129.9, 127.9, 32.1, 31.3, 30.4, 29.9, 29.8 (two peaks overlap), 29.7, 29.6, 29.5 (two peaks overlap), 29.3, 22.9, 14.3, -1.8. HRMS (EI) m/z : calcd for $\text{C}_{32}\text{H}_{48}\text{Si}_3$ $[\text{M}]^+$: 516.3058; Found: 516.3065.

(3-cyclohexylpropane-1,1,1-triyl)tris(phenylsilane) (4z)



The titled compound was isolated (77.3 mg, 58%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.44 – 7.34 (m, 3H), 7.31 (t, $J = 7.2$ Hz, 6H), 4.50 (s, 6H), 1.86 – 1.77 (m, 2H), 1.65 – 1.45 (m, 7H), 1.21 – 1.11 (m, 3H), 1.02 – 0.96 (m, 1H), 0.76 (t, $J = 12$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.4, 129.9, 127.9, 38.7, 36.9, 33.2, 28.8, 26.7, 26.4, -2.1. HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{36}\text{Si}_3$ $[\text{M}]^+$: 444.2119; Found: 444.2121.

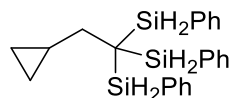
(3-methylhexane-1,1,1-triyl)tris(phenylsilane) (4aa)



The titled compound was isolated (66.5 mg, 53%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.48 (m, 6H), 7.42 – 7.38 (m, 3H), 7.32 – 7.28 (m, 6H), 4.57 (s, 6H), 1.94 – 1.75 (m, 3H), 1.30 – 0.98 (m, 4H), 0.87 (d, $J = 6.3$ Hz, 3H), 0.80 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR

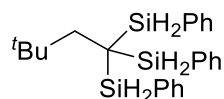
(101 MHz, CDCl₃) δ 136.6, 131.6, 129.9, 127.9, 40.9, 39.2, 34.3, 21.4, 20.3, 14.4, -1.7. HRMS (EI) m/z: calcd for C₂₅H₃₄Si₃ [M]⁺: 418.1963; Found: 418.1958.

(2-cyclopropylethane-1,1,1-triyl)tris(phenylsilane) (4ab)



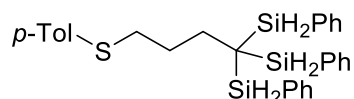
The titled compound was isolated (89.6 mg, 77%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.42 (m, 6H), 7.33 – 7.29 (m, 3H), 7.23 – 7.20 (m, 6H), 4.50 (s, 6H), 1.72 (d, *J* = 6.4 Hz, 2H), 0.91 – 0.81 (m, 1H), 0.40 (ddd, *J* = 7.9, 5.8, 4.3 Hz, 2H), 0.01 (q, *J* = 4.6 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.6, 131.5, 129.9, 127.9, 36.9, 11.0, 7.1, 0.14. HRMS (EI) m/z: calcd for C₂₃H₂₈Si₃ [M]⁺: 388.1493; Found: 388.1484.

(3,3-dimethylbutane-1,1,1-triyl)tris(phenylsilane) (4ac)



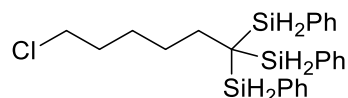
The titled compound was isolated (75.2 mg, 62%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.47 – 7.36 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 6H), 4.71 (s, 6H), 2.10 (s, 2H), 1.05 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.8, 131.8, 129.9, 127.9, 45.4, 35.3, 31.7, -1.5. HRMS (EI) m/z: calcd for C₂₄H₃₂Si₃ [M]⁺: 404.1806; Found: 404.1808.

(4-(*p*-tolylthio)butane-1,1,1-triyl)tris(phenylsilane) (4ad)



The titled compound was isolated (93.9 mg, 63%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.44 (m, 9H), 7.33 – 7.29 (m, 6H), 7.23 – 7.21 (m, 2H), 7.13 – 7.10 (m, 2H), 4.51 (s, 6H), 2.80 – 2.64 (m, 2H), 2.36 (s, 3H), 1.95 – 1.88 (m, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.5, 135.6, 132.7, 130.9, 130.4, 130.0, 129.8, 128.0, 35.0, 30.4, 29.3, 21.2, -1.8. HRMS (EI) m/z: calcd for C₂₉H₃₃SSi₃ [M]⁺: 497.1605; Found: 497.1622.

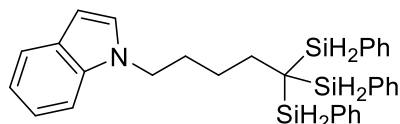
(6-chlorohexane-1,1,1-triyl)tris(phenylsilane) (4ae)



The titled compound was isolated (80.2 mg, 61%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.49 (m, 6H), 7.45 – 7.40 (m, 3H), 7.35 – 7.31 (m, 6H), 4.55 (s, 6H), 3.42 (t, *J* = 6.7

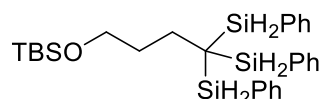
Hz, 2H), 1.82 – 1.78 (m, 2H), 1.67 – 1.53 (m, 4H), 1.31 – 1.23 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.2, 130.0, 128.0, 45.0, 32.2, 31.1, 28.7, 27.5, -1.9. HRMS (EI) m/z : calcd for $\text{C}_{24}\text{H}_{31}\text{ClSi}_3$ $[\text{M}]^+$: 438.1417; Found: 438.1397.

1-(5,5,5-tris(phenylsilyl)pentyl)-1*H*-indole (4af)



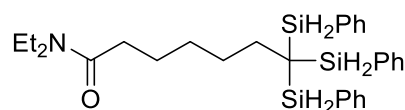
The titled compound was isolated (77.3 mg, 51%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 7.8 Hz, 1H), 7.30 – 7.26 (m, 9H), 7.17 – 7.10 (m, 8H), 7.04 – 6.99 (m, 1H), 6.84 (d, J = 3.1 Hz, 1H), 6.38 (d, J = 3.1 Hz, 1H), 4.39 (s, 6H), 3.81 (t, J = 6.6 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.49 – 1.40 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.4, 135.9, 130.9, 130.0, 128.8, 128.0, 127.8, 121.5, 121.1, 119.4, 109.4, 101.1, 46.0, 30.9, 30.8, 27.2, 27.5, -1.9. HRMS (EI) m/z : calcd for $\text{C}_{31}\text{H}_{35}\text{NSi}_3$ $[\text{M}]^+$: 505.2072; Found: 505.2047.

4-((*tert*-butyldimethylsilyl)oxy)butane-1,1,1-triyltris(phenylsilane) (4ag)



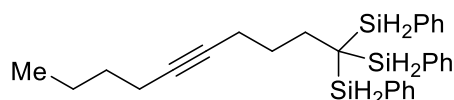
The titled compound was isolated (92.6 mg, 61%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.46 (m, 6H), 7.42 – 7.36 (m, 3H), 7.29 (t, J = 7.2 Hz, 6H), 4.51 (s, 6H), 3.46 (t, J = 5.7 Hz, 2H), 1.90 – 1.78 (m, 4H), 0.86 (s, 9H), -0.02 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.2, 130.0, 128.0, 63.3, 32.3, 27.6, 26.1, 18.4, -2.4, -5.2. HRMS (EI) m/z : calcd for $\text{C}_{28}\text{H}_{42}\text{OSi}_4$ $[\text{M}]^+$: 506.2307; Found: 506.2292.

N,N-diethyl-7,7,7-tris(phenylsilyl)heptanamide (4ah)



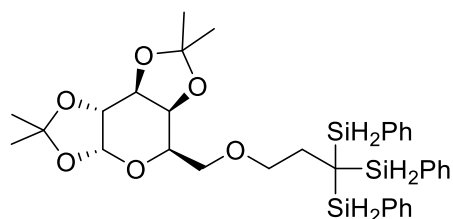
The titled compound was isolated (84.4 mg, 56%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, J = 8.0, 1.4 Hz, 6H), 7.42 – 7.36 (m, 3H), 7.30 (t, J = 7.2 Hz, 6H), 4.52 (s, 6H), 3.37 (dd, J = 13.5, 6.6 Hz, 2H), 3.25 (dd, J = 13.6, 6.6 Hz, 2H), 2.18 (t, J = 8.0 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.62 – 1.51 (m, 4H), 1.22 – 1.10 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.2, 136.4, 131.2, 129.9, 127.9, 42.0, 40.1, 33.0, 31.1, 30.2, 29.3, 25.1, 14.5, 13.2, -1.9. HRMS (EI) m/z : calcd for $\text{C}_{29}\text{H}_{40}\text{NOSi}_3$ $[\text{M}]^+$: 502.2412; Found: 502.2427.

dec-5-yne-1,1,1-triyltris(phenylsilane) (4ai)



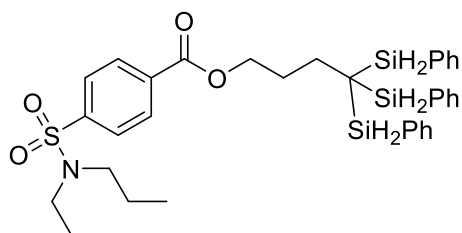
The titled compound was isolated (96.5 mg, 71%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.44 – 7.37 (m, 3H), 7.30 (t, $J = 7.2$ Hz, 6H), 4.51 (s, 6H), 2.14 – 2.11 (m, 2H), 2.06 – 2.01 (m, 2H), 1.98 – 1.89 (m, 2H), 1.82 – 1.73 (m, 2H), 1.47 – 1.36 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.5, 131.1, 130.0, 127.9, 81.1, 79.2, 31.3, 30.5, 28.6, 22.1, 19.5, 18.6, 13.8, -2.0. HRMS (EI) m/z : calcd for $\text{C}_{28}\text{H}_{33}\text{Si}_3$ $[\text{M}]^+$: 453.1885; Found: 453.1890.

(3-(((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methoxy)propane-1,1,1-triyl)tris(phenylsilane) (4aj)



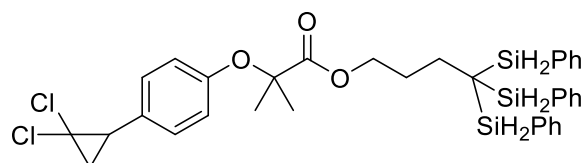
The titled compound was isolated (114 mg, 61%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 30:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 8.0, 1.4$ Hz, 6H), 7.38 (ddd, $J = 6.8, 4.0, 1.4$ Hz, 3H), 7.28 (t, $J = 7.3$ Hz, 6H), 5.52 (d, $J = 5.0$ Hz, 1H), 4.57 – 4.52 (m, 1H), 4.51 (s, 6H), 4.28 (dd, $J = 5.0, 2.4$ Hz, 1H), 4.12 (dd, $J = 7.9, 1.9$ Hz, 1H), 3.90 (td, $J = 6.3, 1.8$ Hz, 1H), 3.65 (td, $J = 6.8, 1.4$ Hz, 2H), 3.50 (ddd, $J = 30.1, 10.1, 6.3$ Hz, 2H), 2.10 (t, $J = 6.8$ Hz, 2H), 1.44 (d, $J = 3.5$ Hz, 6H), 1.31 (d, $J = 5.5$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.6, 131.2, 130.0, 127.9, 109.3, 108.7, 96.5, 71.2, 71.0, 70.75, 70.7, 69.6, 66.6, 30.7, 26.17, 26.13, 25.1, 24.6, -4.0. HRMS (ESI) m/z : calcd for $\text{C}_{33}\text{H}_{45}\text{O}_6\text{Si}_3$ $[\text{M}+\text{H}]^+$: 621.2520; Found: 621.2516.

4,4,4-tris(phenylsilyl)butyl-4-(*N,N*-dipropylsulfamoyl)benzoate (4ak)



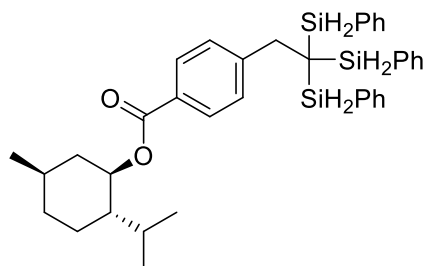
The titled compound was isolated (111 mg, 56%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.7$ Hz, 2H), 7.77 (d, $J = 8.7$ Hz, 2H), 7.56 – 7.34 (m, 6H), 7.30 (dd, $J = 8.5, 6.4$ Hz, 3H), 7.18 (t, $J = 7.3$ Hz, 6H), 4.46 (s, 6H), 4.08 (t, $J = 5.9$ Hz, 2H), 3.08 – 3.00 (m, 4H), 2.03 – 1.69 (m, 4H), 1.54 – 1.43 (m, 4H), 0.80 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 165.2, 144.4, 136.4, 135.6, 130.7, 130.3, 130.1, 128.0, 127.1, 65.6, 50.1, 28.2, 27.7, 22.1, 11.3, -2.4. HRMS (ESI) m/z : calcd for $\text{C}_{35}\text{H}_{46}\text{NO}_4\text{SSi}_3$ $[\text{M}+\text{H}]^+$: 660.2450; Found: 660.2447.

4,4,4-tris(phenylsilyl)butyl-2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (4al)



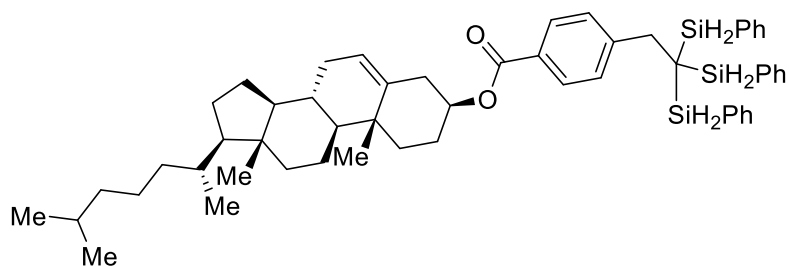
The titled compound was isolated (133 mg, 67%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.44 (m, 6H), 7.40 (dt, $J = 2.9, 1.8$ Hz, 3H), 7.31 (t, $J = 7.2$ Hz, 6H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 4.50 (s, 6H), 3.98 (t, $J = 6.0$ Hz, 2H), 2.81 (dd, $J = 10.7, 8.4$ Hz, 1H), 1.96 – 1.85 (m, 3H), 1.82 – 1.74 (m, 3H), 1.55 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 174.2, 155.0, 136.4, 135.6, 130.8, 130.1, 129.8, 128.1, 118.8, 79.3, 65.5, 61.0, 35.0, 28.1, 27.7, 26.0, 25.50, -2.4. HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{28}\text{Si}_3$ $[\text{M}+\text{H}]^+$: 663.1735; Found: 663.1725.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-(2,2,2-tris(phenylsilyl)ethyl)benzoate (4am)



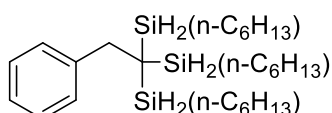
The titled compound was isolated (138 mg, 76%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 50:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.27 – 7.23 (m, 9H), 7.16 – 7.12 (m, 8H), 4.86 – 4.79 (m, 1H), 4.40 (s, 6H), 3.12 (s, 2H), 2.02 (dd, $J = 6.6, 5.1$ Hz, 1H), 1.89 – 1.84 (m, 1H), 1.63 – 1.60 (m, 2H), 1.47 – 1.40 (m, 2H), 1.04 – 0.95 (m, 3H), 0.83 – 0.81 (m, 6H), 0.71 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.1, 145.0, 136.6, 135.6, 130.7, 130.4, 130.1, 129.5, 127.9, 74.9, 47.4, 41.1, 37.1, 34.5, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7, 0.2. HRMS (ESI) m/z : calcd for $\text{C}_{37}\text{H}_{46}\text{O}_2\text{Si}_3$ $[\text{M}+\text{Na}]^+$: 629.2698; Found: 629.2693.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl-4-(2,2,2-tris(phenylsilyl)ethyl)benzoate (4an)



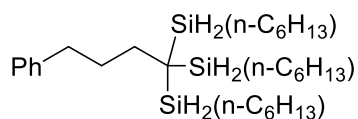
The titled compound was isolated (47.7 mg, 57%) as colorless oil after chromatography on neutral aluminum oxide (100:1 to 30:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.48 – 7.34 (m, 9H), 7.33 – 7.22 (m, 8H), 5.44 (d, $J = 3.4$ Hz, 1H), 4.93 – 4.81 (m, 1H), 4.51 (s, 6H), 3.24 (s, 2H), 2.48 (d, $J = 7.4$ Hz, 2H), 2.11 – 1.99 (m, 3H), 1.96 – 1.82 (m, 2H), 1.61 – 1.46 (m, 7H), 1.44 – 1.28 (m, 5H), 1.08 (s, 12H), 0.94 (d, $J = 6.5$ Hz, 3H), 0.88 (dd, $J = 6.6, 1.8$ Hz, 6H), 0.70 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.0, 145.0, 139.8, 136.6, 135.6, 130.7, 130.4, 130.1, 129.6, 128.0, 122.9, 74.7, 56.9, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.1, 24.5, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0, 0.1. HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{28}\text{Si}_3$ $[\text{M}+\text{H}]^+$: 837.4913; Found: 837.4914.

(2-phenylethane-1,1,1-triyl)tris(hexylsilane) (4a')



The titled compound was isolated (27.0 mg, 20%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, $J = 4.3$ Hz, 1H), 7.27 – 7.20 (m, 4H), 3.77 (t, $J = 4.2$ Hz, 6H), 3.02 (s, 2H), 1.36 – 1.24 (m, 24H), 0.89 (t, $J = 7.0$ Hz, 9H), 0.67 – 0.61 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.2, 130.0, 128.1, 126.7, 38.1, 32.6, 31.6, 25.9, 22.7, 14.3, 8.8, -0.9. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{52}\text{Si}_3$ $[\text{M}]^+$: 448.3371; Found: 448.3372.

(4-phenylbutane-1,1,1-triyl)tris(hexylsilane) (4w')



The titled compound was isolated (40.1 mg, 28%) as colorless oil after chromatography on neutral aluminum oxide (200:1 to 100:1 hexane/EtOAc). ^1H NMR (400 MHz, CDCl_3) δ 7.15 – 7.10 (m, 2H), 7.05 – 6.98 (m, 3H), 3.59 (t, $J = 4.2$ Hz, 6H), 2.46 – 2.41 (m, 2H), 1.68 – 1.53 (m, 4H), 1.28 – 1.06 (m, 24H), 0.73 (t, $J = 7.0$ Hz, 9H), 0.59 – 0.52 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.1, 128.5 (two peaks overlap), 126.0, 36.8, 32.6, 31.7, 26.0, 25.7, 22.7, 14.3, 9.4, 8.9, -4.1. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{28}\text{Si}_3$ $[\text{M}]^+$: 476.3684; Found: 476.3675.

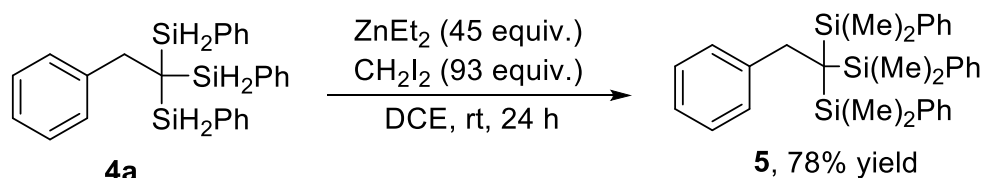
Gram scale reaction

(A)

In an Ar-filled glovebox, a flame-dried 100-mL Schlenk tube was charged with $\text{Cu}(\text{OAc})_2$ (182 mg, 1.00 mmol) and P^tBu_3 (404 mg, 2.00 mmol) and a magnetic stirring bar. The resulting mixture was stirred for 5 min, then PhSiH_3 (4.32 g, 40.0 mmol) was added, stirring for another 10 min before slowly adding phenylacetylene (1.02 g, 10.0 mmol) successively. The tube was sealed and removed from the glove box, and the mixture was stirred at 40 °C for 12 h. Subsequently, the residue was purified by flash chromatography on neutral aluminium oxide using hexane as eluent, yielding the product **4a** (2.46 g, 59% yield) as a colorless oil which solidified upon storage at room temperature overnight.

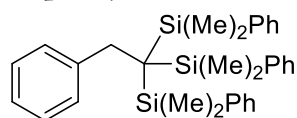
Transformations of compound 4a

(B)



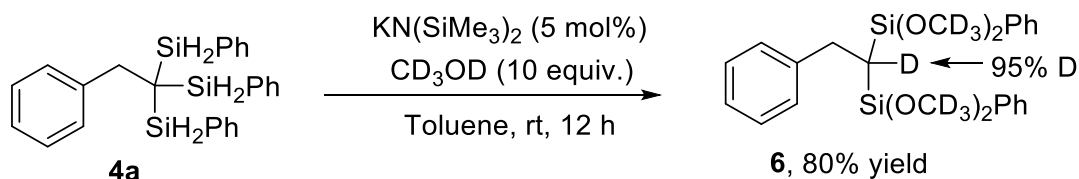
Prepared according to a previously reported procedure.^[2] To a 50 mL Schlenk tube, **4a** (84.8 mg, 0.200 mmol) and 10 mL of dry DCE were added. The solution was stirred at 0 °C. Then 1.5 mL (18.6 mmol) of CH_2I_2 and 9.0 mL (1.0 M in hexane, 9.00 mmol) of ZnEt_2 were added at 0 °C in sequence. After being stirred at 0 °C for 10 min, the reaction was allowed to stir at ambient temperature for 24 h. After completion of the reaction, the reaction mixture was quenched with saturated solution of NH_4Cl (10 mL) under ice bath and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by flash column chromatography to give the title compound **5** as a colorless oil (79.2 mg, 78% yield).

(2-phenylethane-1,1,1-triyl)tris(dimethyl(phenyl)silane) (**5**)



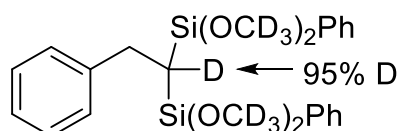
^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.48 (m, 2H), 7.48 – 7.42 (m, 6H), 7.38 – 7.29 (m, 12H), 3.70 (s, 2H), 0.29 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.7, 141.0, 135.5, 131.9, 128.8, 128.1, 127.6, 126.7, 36.6, 13.6, 2.6. HRMS (EI) m/z : calcd for $\text{C}_{32}\text{H}_{40}\text{Si}_3$ $[\text{M}]^+$: 508.2432; Found: 508.2428.

(C)

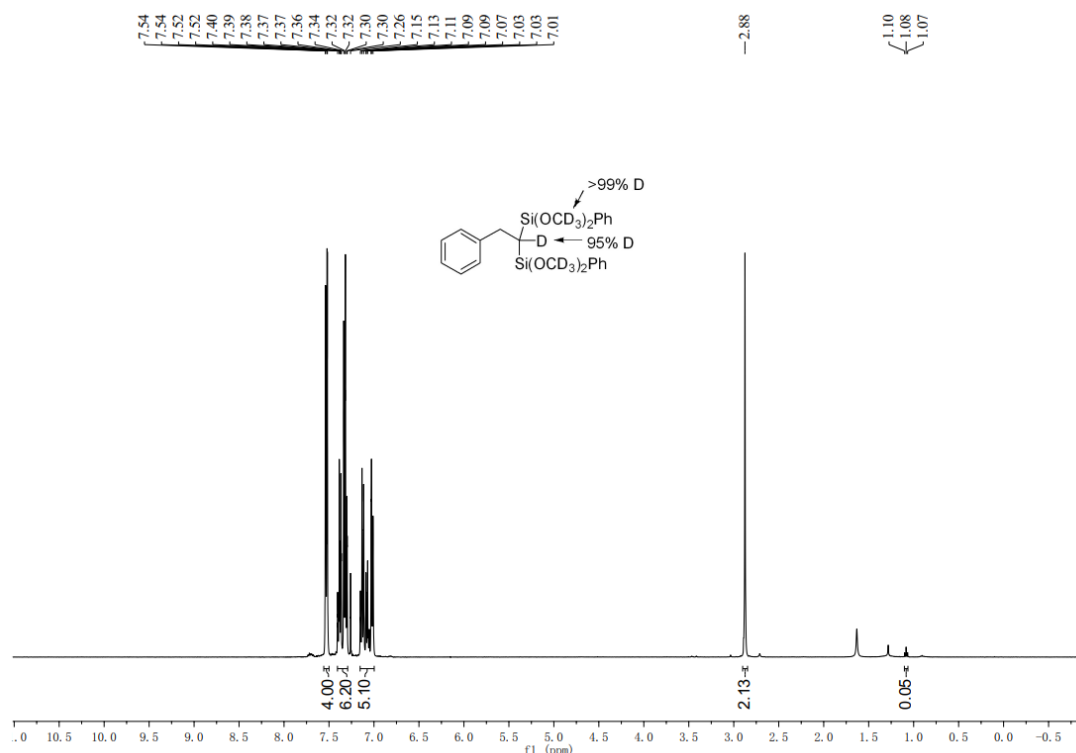


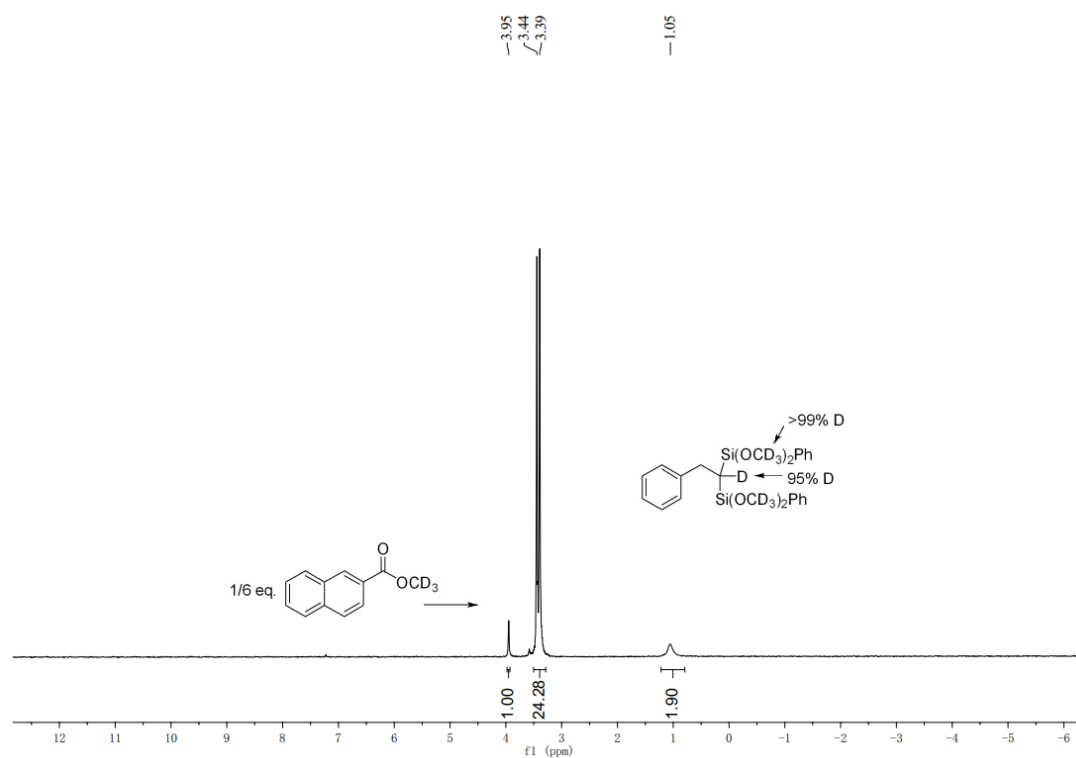
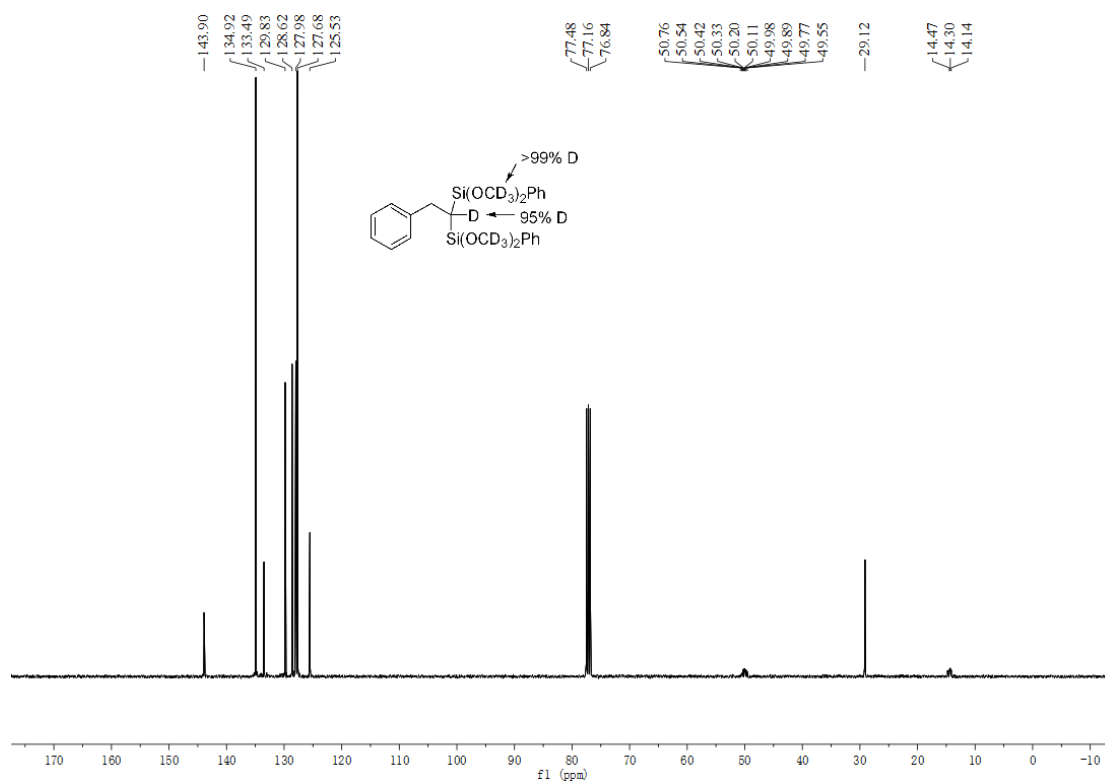
To a mixture toluene (2 mL) solution of $\text{KN(SiMe}_3)_2$ (0.010 mmol, 5 mol %) and **4a** (84.8 mg, 0.200 mmol) was added CD_3OD (10 equiv., 2.00 mmol) at room temperature under argon atmosphere. The reaction mixture was stirred for 12 hours. Then reaction mixture was purified by flash chromatography on silica gel. The desired product **6** (72.2 mg, 80%) was obtained as a colorless oil. The ^2H NMR spectroscopy was measured with methyl- d_3 -2-naphthoate (1/6 equiv.) as an internal standard.

4-benzyl-3,5-bis(methoxy- d_3)-3,5-diphenyl-2,6-dioxane-1,1,1,4,7,7,7- d_7 (**6**)

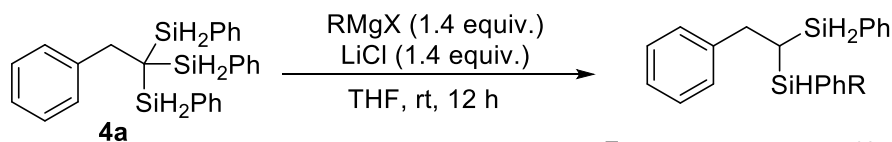


^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 8.0, 1.4$ Hz, 4H), 7.41 – 7.29 (m, 6H), 7.15 – 7.00 (m, 5H), 2.88 (s, 2H), 1.08 (t, $J = 6.6$ Hz, 0.05H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.9, 134.9, 133.5, 129.8, 128.6, 128.0, 127.7, 125.5, 50.8 – 49.6 (m), 29.1, 14.3 (t, $J = 16.2$ Hz). HRMS (EI) m/z : calcd for $\text{C}_{24}\text{H}_{17}\text{D}_{13}\text{O}_4\text{Si}_2$ $[\text{M}]^+$: 451.2493; Found: 451.2487.





(D) and (F)



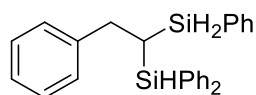
7, R = Ph, X = Br, 68% yield

9, R = ⁿPropyl, X = Cl, 65% yield, dr = 1.1

Synthesis of compounds 7 and 9: prepared according to a previously reported procedure.^[3]

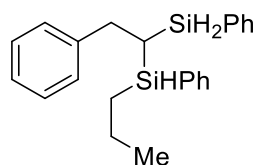
The general procedure for this conversion is as follows: Phenylmagnesium Bromide (280 μL , 0.280 mmol, 1.0 M in THF) for compound **7** or *n*-propylmagnesium chloride (280 μL , 0.280 mmol, 1.0 M in 2-methyltetrahydrofuran) for compound **9** was added to a suspension of compound **4a** (84.8 mg, 0.200 mmol) and lithium chloride (11.8 mg, 0.280 mmol, 1.4 equiv.) in THF (1.0 mL) under argon. The reaction was stirred at room temperature for 12 h and quenched by adding saturated NH_4Cl solution (0.5 mL). The resulting solution was extracted with Et_2O (2 x 10 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified using silica gel flash column chromatography with hexanes as eluent. Compound **7** was isolated as colorless oil (53.7 mg, 68%) and compound **9** was also isolated as colorless oil (46.8 mg, 65%), respectively.

diphenyl(2-phenyl-1-(phenylsilyl)ethyl)silane (7)

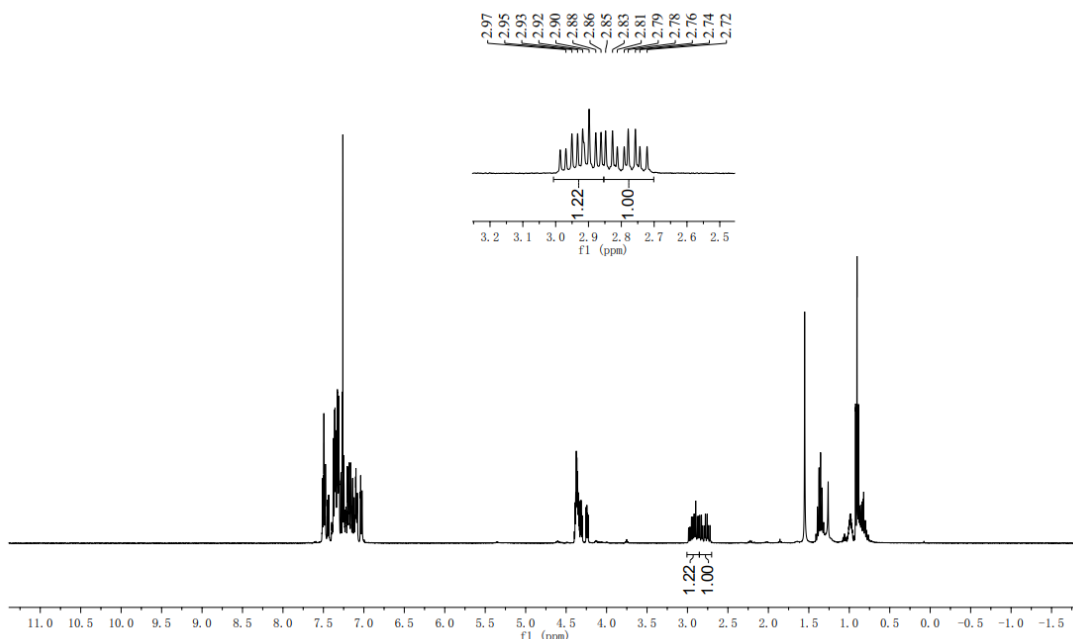


^1H NMR (400 MHz, CDCl_3) δ 7.56 (dd, $J = 3.9, 3.5$ Hz, 4H), 7.42 – 7.31 (m, 7H), 7.24 – 7.12 (m, 7H), 7.08 – 7.03 (m, 2H), 4.97 (d, $J = 3.5$ Hz, 1H), 4.34 (ddd, $J = 26.2, 5.9, 3.2$ Hz, 2H), 2.95 (ddd, $J = 23.5, 14.2, 7.5$ Hz, 2H), 1.34 – 1.29 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.6, 135.7, 135.6, 133.8, 133.7, 132.3, 129.8 (two peaks overlap), 129.5, 128.8, 128.4, 128.1, 127.9, 126.1, 33.3, 8.7. HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{26}\text{Si}_2$ $[\text{M}]^+$: 394.1568; Found: 394.1561.

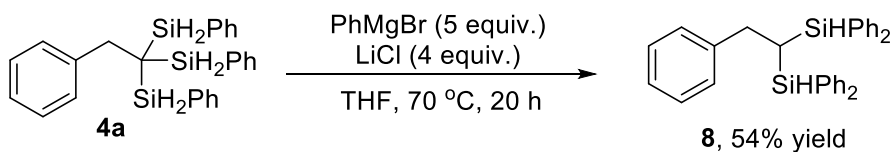
phenyl(2-phenyl-1-(phenylsilyl)ethyl)(propyl)silane (9)



^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.43 (m, 2H), 7.41 – 7.28 (m, 6H), 7.29 – 7.25 (m, 2H), 7.23 – 7.02 (m, 5H), 4.41 – 4.16 (m, 3H), 2.99 – 2.72 (m, 2H), 1.41 – 1.31 (m, 2H), 1.03 – 0.94 (m, 1H), 0.90 (td, $J = 7.2, 0.6$ Hz, 3H), 0.88 – 0.75 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.8, 135.7, 135.6, 135.5, 135.3, 135.2, 129.8, 129.6 (two peaks overlap), 129.5, 128.7 (two peaks overlap), 128.4, 128.3, 128.1, 128.0, 127.9, 126.1, 126.0, 33.4, 33.3, 18.4, 18.3, 17.9 (two peaks overlap), 14.5, 14.1, 8.8, 8.6. HRMS (EI) m/z : calcd for $\text{C}_{23}\text{H}_{28}\text{Si}_2$ $[\text{M}]^+$: 360.1728; Found: 360.1724. This spectra consists of two diastereomers, and diastereoselectivity is confirmed by ^1H NMR.

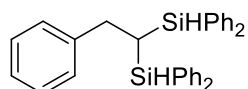


(E)



Prepared according to a previously reported procedure.^[3] The general procedure for this conversion is as follows: Phenylmagnesium Bromide (1.0 mL, 1.00 mmol, 1.0 M in THF) was added to a suspension of compound **4a** (84.8 mg, 0.200 mmol) and lithium chloride (33.6 mg, 0.800 mmol, 4.0 equiv.) in THF (1.0 mL) under argon. The reaction was stirred at 70 °C for 20 h and quenched by adding saturated NH_4Cl solution (0.5 mL). The resulting solution was extracted with Et_2O (2 x 10 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified using silica gel flash column chromatography with hexanes as eluent. Compound **8** was obtained as colorless oil (50.8 mg, 54%).

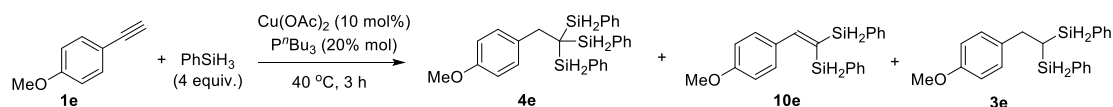
diphenyl(2-phenyl-1-(phenylsilyl)ethyl)silane (**8**)



^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.33 (m, 12H), 7.28 – 7.24 (m, 8H), 7.10 – 7.08 (m, 3H), 6.87 – 6.80 (m, 2H), 4.97 (d, $J = 3.0$ Hz, 2H), 2.94 (d, $J = 7.0$ Hz, 2H), 1.60 – 1.56 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.0, 136.6, 135.8, 135.6, 134.2, 133.7, 129.6, 128.8, 128.2, 128.0, 127.9, 125.9, 32.3, 10.3. HRMS (EI) m/z : calcd for $\text{C}_{32}\text{H}_{30}\text{Si}_2$ [M] $^+$: 470.1884; Found: 470.1876.

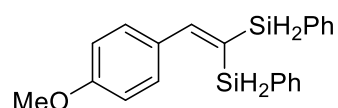
Mechanism studies

For the reaction in Scheme 4A: monitoring the reaction process



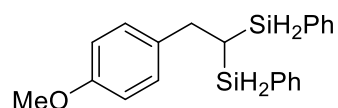
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with $\text{Cu}(\text{OAc})_2$ (5.5 mg, 30.0 μmol) and P^tBu_3 (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiH_3 (130 mg, 1.20 mmol) and tridecane (9.2 mg, 0.050 mmol) as internal standard were added, stirring for another 10 min before adding alkyne **1e** (39.6 mg, 0.300 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C. An aliquot was taken from the reaction mixture with a syringe as indicated time and the yields of compounds **4e**, **10e**, and **3e** were analyzed by GC.

(2-(4-methoxyphenyl)ethene-1,1-diyl)bis(phenylsilane) (**10e**)



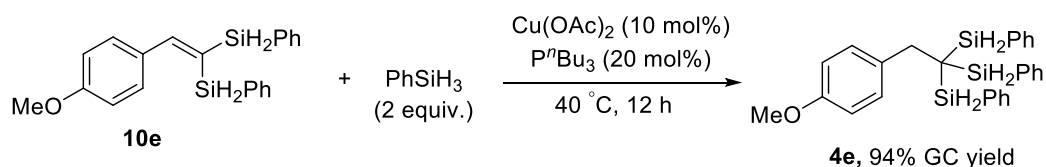
^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.57–7.54 (m, 2H), 7.45–7.24 (m, 10H), 6.83 (d, J = 8.8 Hz, 2H), 4.76 (d, J = 2.1 Hz, 4H), 3.80 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 161.6, 135.9, 135.6, 131.9, 130.6, 129.9, 129.7, 128.2, 128.1, 113.7, 55.4. HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{22}\text{OSi}_2$ [M] $^+$: 346.1204; Found: 346.1196.

(2-(4-methoxyphenyl)ethane-1,1-diyl)bis(phenylsilane) (**3e**)



The titled compound was isolated as colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.48–7.47 (m, 4H), 7.41–7.38 (m, 2H), 7.35–7.31 (m, 4H), 7.03 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 4.42 (dd, J = 6.2, 3.3 Hz, 2H), 4.37 (dd, J = 6.2, 3.7 Hz, 2H), 3.79 (s, 3H), 2.89 (d, J = 7.8 Hz, 2H), 1.09–1.03 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 158.1, 135.7, 134.4, 131.9, 129.8, 129.7, 128.0, 113.8, 55.3, 33.0, 7.2. HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{24}\text{OSi}_2$ [M] $^+$: 348.1360; Found: 348.1371.

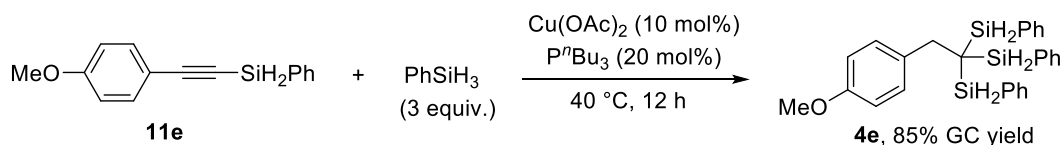
For the reaction in Scheme 4B



In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with $\text{Cu}(\text{OAc})_2$ (5.5 mg, 30.0 μmol) and P^tBu_3 (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiH_3 (64.9 mg, 0.600 mmol) was added, stirring for another 10 min before adding compound **10e** (104 mg, 0.300 mmol). The vial was sealed

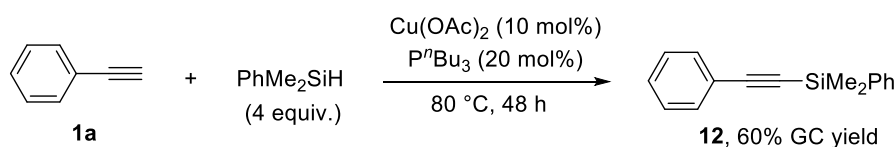
with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h. The mixture was then cooled to room temperature and analyzed by GC.

For the reaction in Scheme 4C



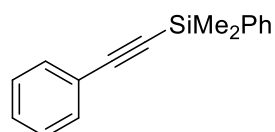
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with $\text{Cu}(\text{OAc})_2$ (5.5 mg, 30.0 μmol) and P^nBu_3 (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiH_3 (97.4 mg, 0.900 mmol) was added, stirring for another 10 min before adding alkynylsilane **11e**^[6a] (71.5 mg, 0.300 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h. The mixture was then cooled to room temperature and analyzed by GC.

For the reaction in Scheme 4D



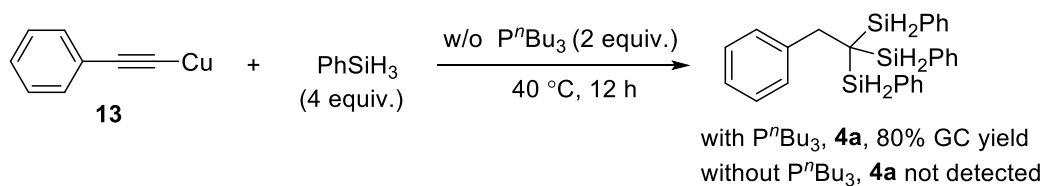
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with $\text{Cu}(\text{OAc})_2$ (5.5 mg, 30.0 μmol) and P^nBu_3 (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhMe_2SiH (163 mg, 1.20 mmol) was added, stirring for another 10 min before adding phenylacetylene **1a** (30.6 mg, 0.300 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 80 °C for 48 h. The mixture was then cooled to room temperature and analyzed by GC.

dimethyl(phenyl)(phenylethynyl)silane (**12**)



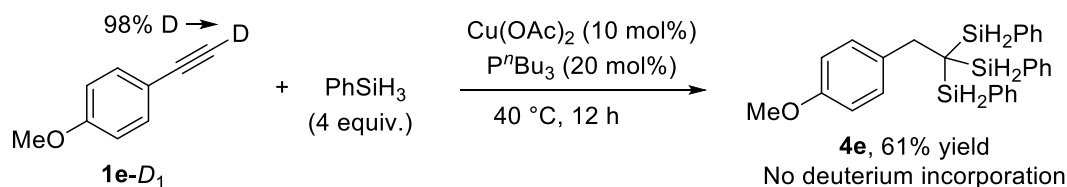
^1H NMR (400 MHz, $\text{THF}-d_8$) δ 7.71 – 7.65 (m, 2H), 7.50 – 7.44 (m, 2H), 7.36 – 7.30 (m, 6H), 0.45 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF}-d_8$) δ 137.9, 134.7, 134.0, 132.9, 130.4, 129.8, 129.3, 128.8, 107.8, 92.6, -0.5. GC-MS (EI) m/z : calcd for $\text{C}_{16}\text{H}_{16}\text{Si}$ $[\text{M}]^+$: 236.10; Found: 236.10. The spectroscopic data of this compound are in accordance with the reported data.^[6b]

For the reaction in Scheme 4E



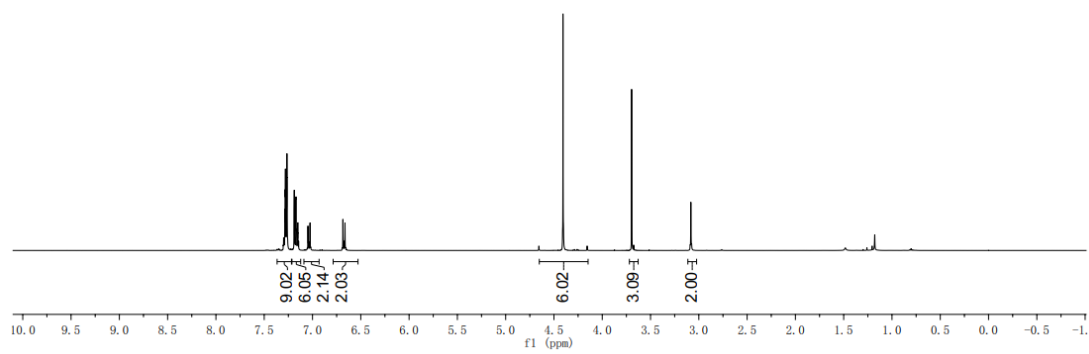
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with copper phenylacetylide **13**^[5] (49.4 mg, 0.300 mmol), P^nBu_3 (121 mg, 0.600 mmol) or without P^nBu_3 , and a magnetic stirring bar. The resulting mixture was stirred for 2 min, and then $PhSiH_3$ (130 mg, 1.20 mmol) was added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h and then cooled to room temperature and filtered through a short plate of neutral aluminum oxide before analyzing by GC.

For the reaction in Scheme 5A

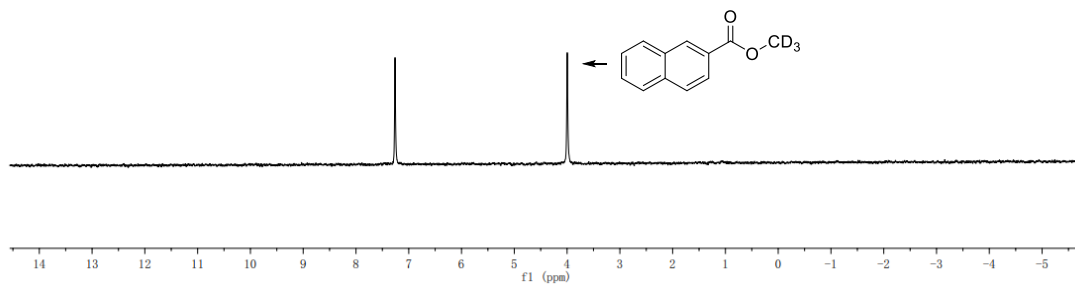


In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with $Cu(OAc)_2$ (5.5 mg, 30.0 μ mol) and P^nBu_3 (12.1 mg, 60.0 μ mol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then $PhSiH_3$ (130 mg, 1.20 mmol) was added, stirring for another 10 min before adding alkyne **1e-D**^[7] (39.9 mg, 0.300 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h. The mixture was then cooled to room temperature and the residue was purified by column chromatography on neutral aluminum oxide with a mixture of ethyl acetate and hexane as eluent. Compound **4e** (83.1 mg, 61%) was obtained as a colorless oil. The analysis of 2H NMR testing with methyl- d_3 2-naphthoate (1/6 equiv.) as an internal standard has shown that there was no deuterium in the compound **4e**.

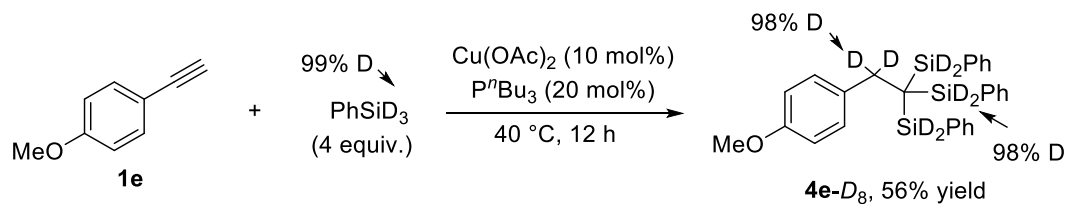
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.19
7.17
7.17
7.15
7.15
7.05
7.03
6.66
-4.41
-3.70
-3.08



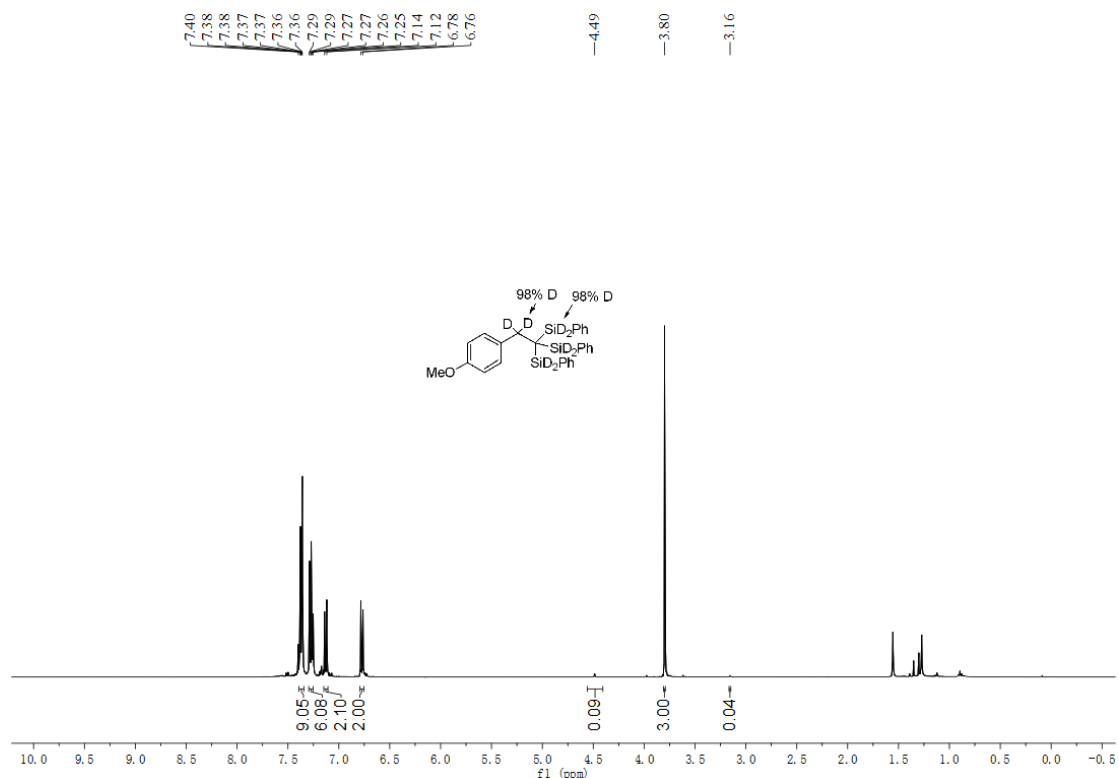
-7.26
-4.00

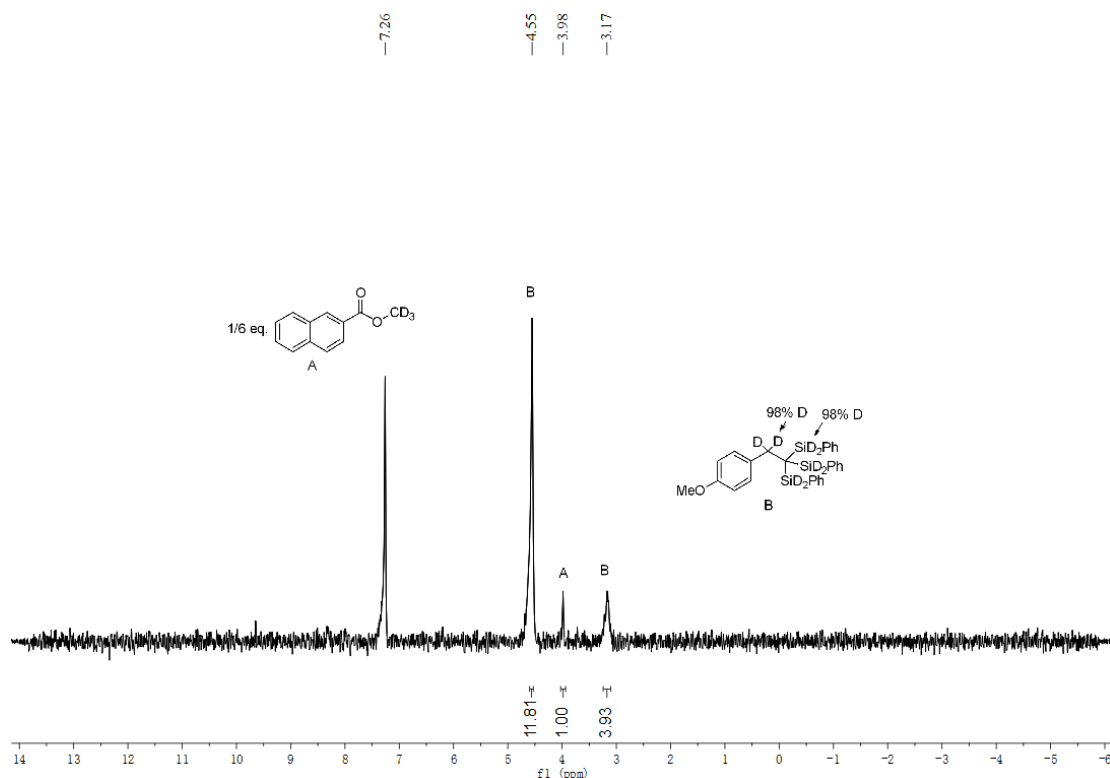


For the reaction in Scheme 5B



In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with Cu(OAc)₂ (5.5 mg, 30.0 μmol) and PⁿBu₃ (12.1 mg, 60.0 μmol) and a magnetic stirring bar. The resulting mixture was stirred for 1 min, and then PhSiD₃^[8] (133 mg, 1.20 mmol) was added, stirring for another 10 min before adding alkyne **1e** (39.6 mg, 0.300 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at 40 °C for 12 h. The mixture was then cooled to room temperature and the residue was purified by column chromatography on neutral aluminum oxide with a mixture of ethyl acetate and hexane as eluent. Compound **4e-D₈** (77.8 mg, 56%) was obtained as a colorless oil. The ²H NMR spectroscopy was measured with methyl-*d*₃ 2-naphthoate (1/6 equiv.) as an internal standard.





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Copies of NMR spectra

