

Supporting Information

Ligand-controlled cobalt-catalyzed remote hydroboration and alkene isomerization of allylic siloxanes

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I. General Information

Unless otherwise noted, all reactions were conducted in an oven-dried vial with a magnetic stirrer under nitrogen atmosphere. Solvents were purified under nitrogen using a solvent purification system. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualisation was by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or KMnO_4 . Flash column chromatography was performed using EM Science (200-300 mesh) silica gel.

^1H -Nuclear Magnetic Resonance (^1H -NMR) and ^{13}C Nuclear Magnetic Resonance (^{13}C -NMR) spectra were recorded on Bruker 400 MHz at 20 °C with CDCl_3 as solvent, tetramethylsilane ($\delta = 0$ ppm for ^1H -NMR) and CHCl_3 ($\delta = 77.0$ ppm for ^{13}C -NMR) as an internal standard. The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant $J(\text{Hz})$, and integration. High resolution mass spectra were recorded on a Bruker Maxis System. IR spectra were collected on a Spectrum BX FTIR from Perkin-Elmer and reported in unit of cm^{-1} .

II. Optimization of Reaction Conditions and Substrate Scope

Table S1 Optimization of reaction conditions^a

entry	ligand	x	base	solvent	T (°C)	time (h)	yield of 2a (%) ^b	yield of 3 (%) ^c	Z/E ^c
1	dcype	1.5	-	THF	rt	3	82	<5	-
2	dcype	1.5	-	toluene	rt	3	<5	<5	-
3	dcype	1.5	-	DCE	rt	3	85	<5	-
4	dcype	1.5	-	1,4-dioxane	rt	3	85	<5	-
5	dcype	1.5	-	octane	rt	3	97	<5	-
6	dcype	1.0	-	octane	rt	4	85	<5	-
7	dppm	1.5	-	octane	rt	3	<5	8	0.1/1
8	dppe	1.5	-	octane	rt	3	16	20	1.2/1
9	dppp	1.5	-	octane	rt	3	10	15	1.7/1
10	dppb	1.5	-	octane	rt	3	5	<5	1/1
11	dppf	1.5	-	octane	rt	3	69	8	2/1
12	dpephos	1.5	-	octane	rt	3	13	25	1.1/1
13	xantphos	1.5	-	octane	rt	3	12	46	1.9/1
14	xantphos	0.2	-	octane	60	12	<5	56	1.4/1
15	xantphos	0	-	octane	60	12	0	0	-
16	xantphos	0.2	NaPF ₆	octane	60	12	<5	68	0.8/1
17	xantphos	0.2	CF ₃ SO ₃ Na	octane	60	12	<5	78	1.4/1
18	xantphos	0.2	CF ₃ CO ₂ Na	octane	60	12	<5	86	1.5/1
19	xantphos	0.2	CF ₃ CO ₂ Na	CyH	60	12	<5	56	0.9/1
20	xantphos	0.2	CF ₃ CO ₂ Na	<i>i</i> Pr ₂ O	60	12	<5	84	1.1/1
21	xantphos	0.2	CF ₃ CO ₂ Na	DME	60	12	<5	90	2.2/1

$\text{Cy}_2\text{R}-\text{CH}_2-\text{CH}_2-\text{PCy}_2$
 dcype
 $\text{Ph}_2\text{R}-\text{CH}_2-\text{CH}_2-\text{PPh}_2$
 n = 1, dppm
 n = 2, dppe
 n = 3, dppp
 n = 4, dppb

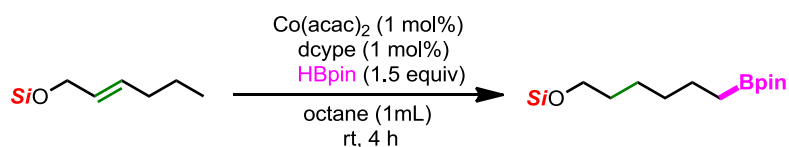
 dppf

 dpephos

 xantphos

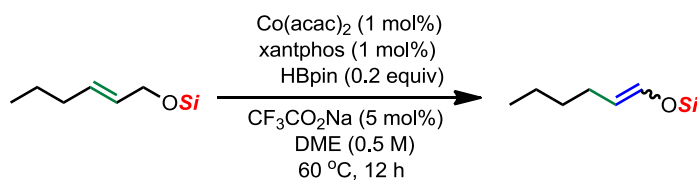
^a Reactions were performed with **1a** (0.50 mmol) and HBpin under N₂. ^b Yields were determined by GC analysis using dodecane as the internal standard. ^c Determined by ¹H NMR analysis of crude product using dibromomethane as the internal standard.

Table S2 Cobalt-catalyzed remote hydroboration of allylic siloxanes^a



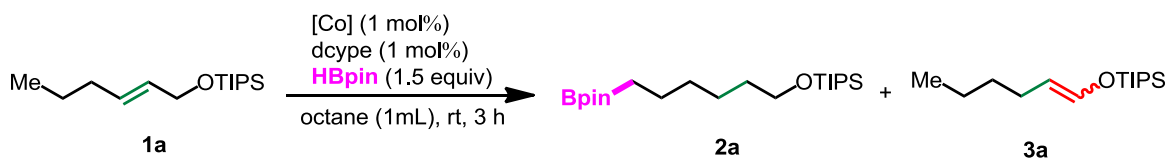
entry	Si	yield (%)
1	TIPS	97
2	TES	88
3	TBS	95

^a Yields were determined by ¹H NMR with CH₂Br₂ as the internal standard.

Table S3 Cobalt-catalyzed alkene isomerization of allylic siloxanes^a

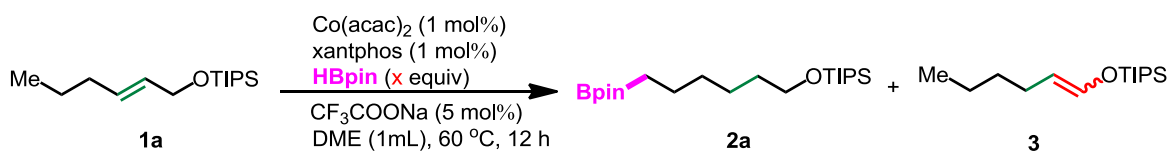
entry	Si	yield (%)	Z/E
1	TIPS	92	1.7/1
2	TES	83	1.8/1
3	TBS	95	1.6/1

^a Yields and ratio of Z/E were determined by ¹H NMR with CH₂Br₂ as the internal standard.

Table S4 Screening of simple cobalt salts^a

entry	[Co]	yield of 2a (%)	yield of 3 (%)
1	Co(OAc) ₂	<5	<5
2	Co ₂ CO ₃	<5	no
3	CoCl ₂	no	no

^a Yields were determined by ¹H NMR with CH₂Br₂ as the internal standard.

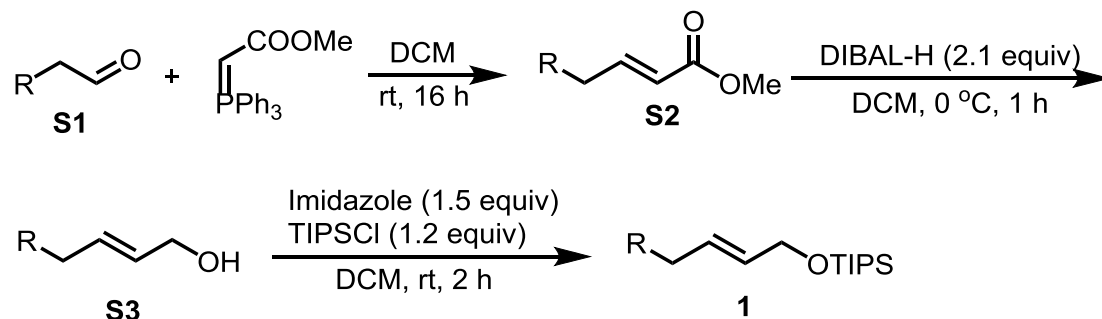
Table S5 Screening of the amount of HBpin^a

entry	x (equiv)	yield of 2a (%)	yield of 3 (%)	Z/E
1	0	0	0	-
2	0.05	<5	28	1.3/1
3	0.10	<5	33	1/1

^a Yields and ratio of Z/E were determined by ¹H NMR with CH₂Br₂ as the internal standard.

III. Synthesis of Substrates

General Procedure A:



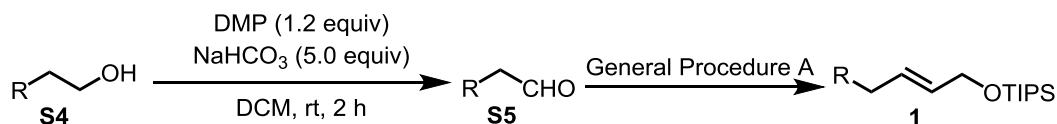
Synthesis of α,β -unsaturated esters^[1]: To a stirred solution of Methyl (triphenylphosphoranylidene)acetate (1.1 equiv) in DCM at room temperature was added **S1**, and the reaction mixture was stirred at room temperature for 16 h. After complete conversion (TLC analysis), the solvent was evaporated under reduced pressure. The resulting residue was purified by column chromatography to give α,β -unsaturated ester **S2**.

Synthesis of allylic alcohols^[2]: To a solution of **S2** in DCM at 0 °C was added DIBAL-H (1 M in hexane, 2.1 equiv) dropwise. The solution was maintained at 0 °C for 1 hour, and gradually warmed to room temperature. After complete conversion (TLC analysis), the reaction was quenched carefully with potassium sodium tartrate aqueous and stirring vigorously for 2 h, the mixture was extracted with DCM, washed with brine, dried over MgSO₄, filtered, concentrated and purified by column chromatography to afford allylic alcohol **S3**.

Synthesis of silicon-protected allyl alcohols^[3]: A flask was charged with allylic alcohol **S3** and imidazole (1.5 equiv). The contents were then dissolved in DCM and triisopropylchlorosilane (TIPSCl) (1.2 equiv) was added dropwise at room temperature over 2 h. After complete conversion (TLC analysis), water was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, concentrated and purified by column chromatography to afford silicon-protected allyl alcohol **1**.

1a, **1b**, **1c**, **1d**, **1e**, **1h**, **1i**, **1j**, **1m**, **1an**, **1ao**, **1ap**, **1aq**, and **1ar** were prepared according to **General Procedure A**.

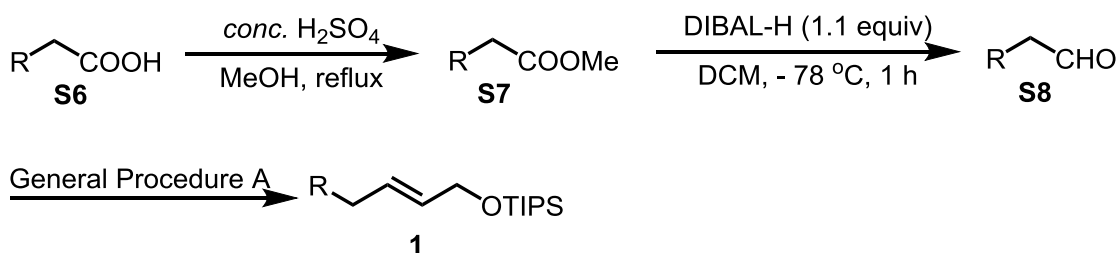
General Procedure B:



Following the literature procedure^[17], to a suspension of Dess-Martin reagent (DMP) (1.2 equiv) and NaHCO₃ (5.0 equiv) in DCM was added **S4** (1.0 equiv) dropwise. The reaction mixture was stirred at room temperature for 2 h. The resulting suspension was filtered through a celite pad with DCM and concentrated under vacuo. The residue was purified by silica gel column chromatography to afford **S5**.

1f, **1g**, **1k**, and **1l** were prepared according to **General Procedure B**.

General Procedure C:



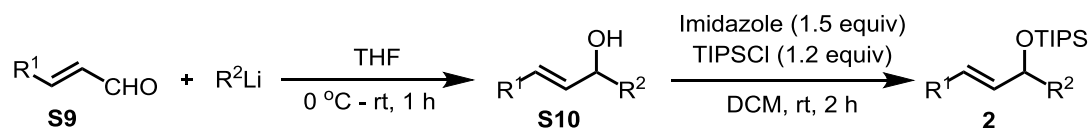
Following the literature procedure, **S6** (1.0 equiv) in MeOH and catalytic amount of *conc.* H₂SO₄ were refluxed for 3 h. After evaporation of the solvent, the residue was extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography to afford **S7**.

DIBAL-H (1 M in hexane, 1.1 equiv) was added dropwise to a solution of **S7** (1.0 equiv) in anhydrous DCM at -78 °C. The resulting solution was stirred at -78 °C for 1 h and quenched carefully with MeOH. The reaction mixture was then poured into DCM and potassium sodium tartrate aqueous. And stirred vigorously for 2 h, the mixture was extracted with DCM, washed with brine,

dried over MgSO_4 , filtered, concentrated and purified by column chromatography to afford **S8**.

1n, **1al**, **1am**, and **1as** were prepared according to **General Procedure C**.

General Procedure D:

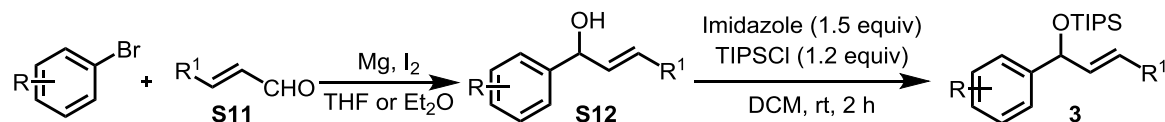


Following the literature procedure^[5], under nitrogen atmosphere, to a solution of **S9** in dry THF at 0 °C was added dropwise R^2Li over a period of 5 min, then the reaction mixture was moved to ambient temperature and stirred for 1 h, the resulting suspension was diluted with ethyl acetate and quenched by NH_4Cl (aq). The mixture was extracted by ethyl acetate, dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to obtaining **S10**.

The **S10** and imidazole (1.5 equiv) was dissolved in DCM, then TIPSCl (1.2 equiv) was added dropwise and the reaction mixture at room temperature over 2 h. After complete conversion (TLC analysis), water was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, washed with brine, dried over MgSO_4 , filtered, concentrated and purified by column chromatography to afford silicon-protected allyl alcohol **2**.

1ac, **1ad**, **1ae**, and **1af** were prepared according to **General Procedure D**.

General Procedure E:



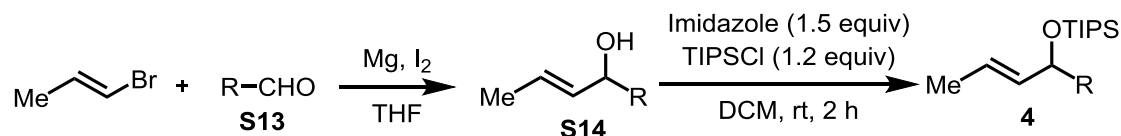
Following the literature procedure^[6,7], a dried round-bottom flask containing stir bar was charged with magnesium (1.2 equiv.), small piece of iodine and the solvent THF under nitrogen atmosphere. To the solution, aryl bromides (1.0 equiv) was dropped slowly and stirred for 30 min. After the formation of the Grignard reagent is completed, the reaction mixture is cooled to 0 °C, then 1.5 equiv of

corresponding **S11** was added. The resulting mixture was stirred for 2 h. After the completion of the reaction, the reaction mixture was washed with saturated NH_4Cl solution and extracted with ethyl acetate for several times. The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . The organic layer was then concentrated under vacuum, and the crude residue was purified by silica gel column chromatography to afford the secondary alcohols **S12**.

The **S12** and imidazole (1.5 equiv) was dissolved in DCM, then TIPSCl (1.2 equiv) was added dropwise and the reaction mixture at room temperature over 2 h. After complete conversion (TLC analysis), water was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, washed with brine, dried over MgSO_4 , filtered, concentrated and purified by column chromatography to afford silicon-protected allyl alcohol **3**.

1o, **1p**^[7], **1q**^[7], **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x**, **1y**, **1z**, **1aa**, **1ab**, **1ag**, and **1ak** were prepared according to **General Procedure E**.

General Procedure F:



Following the literature procedure^[6], A dried round-bottom flask containing stir bar was charged with magnesium (1.2 equiv.), small piece of iodine and the solvent THF under nitrogen atmosphere. To the solution, 1-bromo-1-propene (1.0 equiv) was dropped slowly and stirred for 30 min. After the formation of the Grignard reagent is completed, the reaction mixture is cooled to 0 °C, then 1.5 equiv of corresponding **S13** was added. The resulting mixture was stirred for 2 h. After the completion of the reaction, the reaction mixture was washed with saturated NH_4Cl solution and extracted with ethyl acetate for several times. The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . The organic layer was then concentrated under vacuum, and the crude residue was purified by silica gel column chromatography to afford the

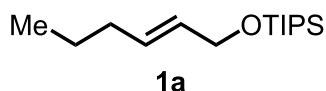
secondary alcohols **S14**.

The **S14** and imidazole (1.5 equiv) was dissolved in DCM, then TIPSCl (1.2 equiv) was added dropwise and the reaction mixture at room temperature over 2 h. After complete conversion (TLC analysis), water was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, washed with brine, dried over MgSO_4 , filtered, concentrated and purified by column chromatography to afford silicon-protected allyl alcohol **4**.

1ah and **1ai** were prepared according to **General Procedure F**.

The yields are the last step of the following substrates.

(E)-(Hex-2-en-1-yloxy)triisopropylsilane (1a)^[11]



1a was prepared as a colorless oil in 99% yield (2.53 g, eluent: petroleum ether) following the general procedure A.

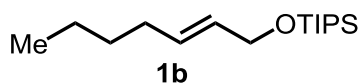
R_f = 0.62 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.73 – 5.63 (m, 1H), 5.61 – 5.48 (m, 1H), 4.22 – 4.16 (m, 2H), 2.06 – 1.98 (m, 2H), 1.48 – 1.32 (m, 2H), 1.18 – 1.01 (m, 21H), 0.90 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 130.9, 129.5, 64.2, 34.4, 22.5, 18.2, 13.8, 12.2.

^{29}Si NMR (79.5 MHz, CDCl_3) δ 13.53.

(E)-(Hept-2-en-1-yloxy)triisopropylsilane (1b)



1b was prepared as a colorless oil in 68% yield (477 mg, eluent: petroleum ether) following the general procedure A.

R_f = 0.72 (petroleum ether)

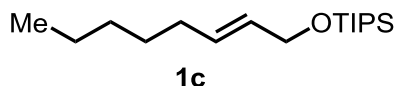
^1H NMR (400 MHz, CDCl_3) δ 5.73 – 5.61 (m, 1H), 5.60 – 5.49 (m, 1H), 4.22 – 4.16 (m, 2H), 2.08 – 1.99 (m, 2H), 1.42 – 1.26 (m, 4H), 1.19 – 1.01 (m, 21H), 0.89 (t, J = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 131.2, 129.3, 64.2, 32.0, 31.6, 22.4, 18.1, 14.1, 12.2.

HRMS (ESI⁺) calcd for C₁₈H₃₉OSi⁺ [M+H]⁺: 299.2770, found: 299.2762.

IR (neat, cm⁻¹): 2958, 2943, 2893, 2866, 1464, 1107, 1060, 969, 882, 681, 658.

(E)-Triisopropyl(oct-2-en-1-yloxy)silane (1c)^[8]



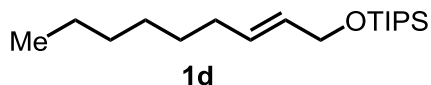
1c was prepared as a colorless oil in 99% yield (1.69 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.62 (petroleum ether)

¹H NMR (400 MHz, CDCl₃) δ 5.73 – 5.61 (m, 1H), 5.59 – 5.49 (m, 1H), 4.22 – 4.16 (m, 2H), 2.07 – 1.98 (m, 2H), 1.43 – 1.24 (m, 6H), 1.10 – 0.99 (m, 21H), 0.88 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 131.2, 129.3, 64.2, 32.3, 31.6, 29.1, 22.7, 18.1, 14.2, 12.2.

(E)-Triisopropyl(non-2-en-1-yloxy)silane (1d)



1d was prepared as a colorless oil in 99% yield (4.85 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.77 (petroleum ether)

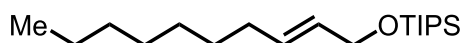
¹H NMR (400 MHz, CDCl₃) δ 5.72 – 5.61 (m, 1H), 5.60 – 5.49 (m, 1H), 4.23 – 4.14 (m, 2H), 2.08 – 1.95 (m, 2H), 1.40 – 1.21 (m, 8H), 1.17 – 1.00 (m, 21H), 0.87 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 131.2, 129.3, 64.3, 32.3, 31.9, 29.4, 29.0, 22.8, 18.2, 14.2, 12.2.

HRMS (APCI⁺) calcd for C₂₀H₄₃OSi⁺ [M+H]⁺: 327.3078, found: 327.3085.

IR (neat, cm⁻¹): 2958, 2926, 2866, 1464, 1104, 1059, 883, 681.

(E)-(Dec-2-en-1-yloxy)triisopropylsilane (1e)



1e

1e was prepared as a colorless oil in 98% yield (1.83 g, eluent: petroleum ether) following the general procedure A.

$R_f = 0.73$ (petroleum ether)

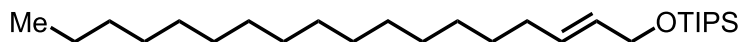
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.71 – 5.62 (m, 1H), 5.58 – 5.50 (m, 1H), 4.22 – 4.16 (m, 2H), 2.07 – 1.98 (m, 2H), 1.41 – 1.21 (m, 10H), 1.16 – 1.02 (m, 21H), 0.88 (t, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 131.2, 129.3, 64.2, 32.3, 32.0, 29.4, 29.3, 29.3, 22.8, 18.2, 14.2, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{19}\text{H}_{40}\text{OSiNa}^+$ [$\text{M}+\text{Na}$] $^+$: 335.2741, found: 335.2748.

IR (neat, cm^{-1}): 2924, 2865, 1463, 1105, 1059, 968, 882, 681, 658.

(E)-Triisopropyl(octadec-2-en-1-yloxy)silane (1f)



1f

1f was prepared as a colorless oil in 86% yield (2.18 g, eluent: petroleum ether) following the general procedure B.

$R_f = 0.64$ (petroleum ether)

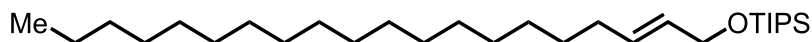
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.73 – 5.61 (m, 1H), 5.59 – 5.48 (m, 1H), 4.22 – 4.16 (m, 2H), 2.07 – 1.98 (m, 2H), 1.43 – 1.20 (m, 26H), 1.17 – 1.01 (m, 21H), 0.91 – 0.86 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 131.2, 129.3, 64.2, 32.3, 32.1, 29.9 – 29.7 (m, 7C), 29.7, 29.5, 29.4, 29.3, 22.8, 18.2, 14.3, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{27}\text{H}_{56}\text{OSiNa}^+$ [$\text{M}+\text{Na}$] $^+$: 447.3993, found: 447.3994.

IR (neat, cm^{-1}): 2922, 2857, 1470, 1115, 1060, 968, 884, 688.

(E)-(Icos-2-en-1-yloxy) triisopropylsilane (1g)



1g

1g was prepared as a colorless oil in 88% yield (3.78 g, eluent: petroleum ether) following the general procedure B.

R_f = 0.65 (petroleum ether)

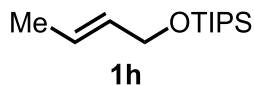
^1H NMR (400 MHz, CDCl_3) δ 5.73 – 5.62 (m, 1H), 5.60 – 5.50 (m, 1H), 4.22 – 4.17 (m, 2H), 2.08 – 1.97 (m, 2H), 1.26 (s, 30H), 1.15 – 0.98 (m, 21H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 131.2, 129.3, 64.3, 32.4, 32.1, 30.0 – 29.8 (m, 9C), 29.7, 29.5, 29.4, 29.3, 22.9, 18.2, 14.3, 12.2.

HRMS (ESI⁺) calcd for $\text{C}_{29}\text{H}_{60}\text{OSiNa}^+$ [M+Na]⁺: 475.4306, found: 475.4309.

IR (neat, cm^{-1}): 2922, 2853, 1460, 1112, 882, 681.

(E)-(But-2-en-1-yloxy)triisopropylsilane (1h)^[12]



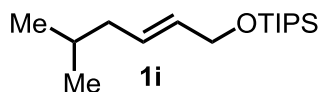
1h was prepared as a colorless oil in 95% yield (1.26 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.64 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.76 – 5.64 (m, 1H), 5.63 – 5.53 (m, 1H), 4.17 (d, J = 5.2 Hz, 2H), 1.69 (d, J = 6.4 Hz, 3H), 1.15 – 1.02 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 130.6, 125.7, 64.1, 18.1, 17.8, 12.1.

(E)-Triisopropyl((5-methylhex-2-en-1-yl)oxy)silane (1i)



1i was prepared as a colourless solid in 94% yield (1.78 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.42 (petroleum ether)

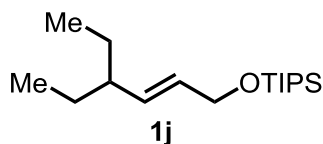
^1H NMR (400 MHz, CDCl_3) δ 5.73 – 5.61 (m, 1H), 5.60 – 5.48 (m, 1H), 4.24 – 4.17 (m, 2H), 1.97 – 1.89 (m, 2H), 1.69 – 1.55 (m, 1H), 1.17 – 1.04 (m, 21H), 0.89 (d, J = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 130.5, 129.7, 64.2, 41.7, 28.5, 22.4, 18.2, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{16}\text{H}_{35}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 271.2457, found: 271.2458.

IR (neat, cm^{-1}): 2958, 2945, 2894, 2867, 1104, 882, 681.

(*E*)-((4-Ethylhex-2-en-1-yl)oxy)triisopropylsilane (1j)



1j was prepared as a colourless solid in 99% yield (1.49 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.80 (petroleum ether)

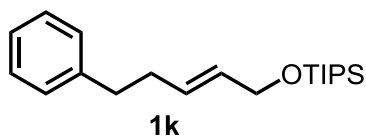
^1H NMR (400 MHz, CDCl_3) δ 5.56 – 5.46 (m, 1H), 5.44 – 5.34 (m, 1H), 4.25 – 4.19 (m, 2H), 1.84 – 1.72 (m, 1H), 1.48 – 1.32 (m, 2H), 1.32 – 1.18 (m, 2H), 1.21 – 1.02 (m, 21H), 0.84 (t, J = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 134.8, 129.6, 64.2, 45.9, 27.7, 18.2, 12.2, 11.8.

HRMS (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 285.2614, found: 285.2614.

IR (neat, cm^{-1}): 2959, 2943, 2866, 1463, 1101, 1056, 970, 882, 680, 658.

(*E*)-Triisopropyl((5-phenylpent-2-en-1-yl)oxy)silane (1k)



1k was prepared as a colorless oil in 97% yield (2.02 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure B.

R_f = 0.42 (petroleum ether)

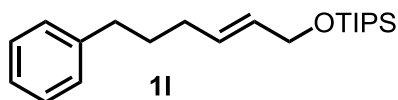
^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 5.84 – 5.66 (m, 1H), 5.69 – 5.58 (m, 1H), 4.27 – 4.21 (m, 2H), 2.79 – 2.70 (m, 2H), 2.46 – 2.36 (m, 2H), 1.34 – 1.02 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.1, 130.0, 129.8, 128.6, 128.4, 125.9, 64.0, 35.9, 34.2, 18.2, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{35}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 319.2457, found: 319.2454.

IR (neat, cm⁻¹): 2941, 2865, 1462, 1117, 1058, 968, 882, 745, 698, 680, 658.

(E)-Triisopropyl((6-phenylhex-2-en-1-yl)oxy)silane (1l)^[10]



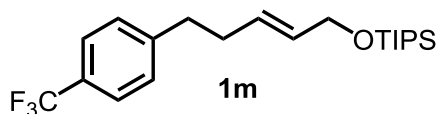
1l was prepared as a colorless oil in 88% yield (2.63 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure B.

R_f = 0.40 (petroleum ether)

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.76 – 5.65 (m, 1H), 5.63 – 5.52 (m, 1H), 4.24 – 4.18 (m, 2H), 2.68 – 2.58 (m, 2H), 2.14 – 2.04 (m, 2H), 1.78 – 1.64 (m, 2H), 1.16 – 1.04 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 142.7, 130.4, 129.9, 128.6, 128.4, 125.8, 64.1, 35.5, 31.9, 31.1, 18.2, 12.2.

(E)-Triisopropyl((5-(4-(trifluoromethyl)phenyl)pent-2-en-1-yl)oxy)silane (1m)



1m was prepared as a colorless oil in 92% yield (912 mg, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure A.

R_f = 0.42 (petroleum ether)

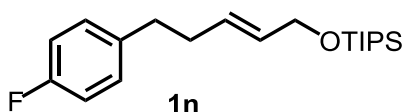
¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.50 (m, 2H), 7.33 – 7.26 (m, 2H), 5.76 – 5.68 (m, 1H), 5.65 – 5.57 (m, 1H), 4.21 (d, *J* = 4.7 Hz, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.44 – 2.32 (m, 2H), 1.18 – 0.99 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 146.1, 130.7, 128.9, 128.4 (q, *J* = 32.0 Hz), 125.3 (q, *J* = 3.8 Hz), 128.1, 124.6 (q, *J* = 270.0 Hz), 63.9, 35.7, 33.7, 18.1, 12.1.

HRMS (ESI⁺) calcd for C₂₁H₃₄OF₃Si⁺ [*M*+*H*]⁺: 387.2331, found: 387.2336.

IR (neat, cm⁻¹): 1324, 1164, 1124, 1067, 681.

(E)-((5-(4-Fluorophenyl)pent-2-en-1-yl)oxy)triisopropylsilane (1n)



1n was prepared as colorless oil in 94% yield (1.33 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure C.

R_f = 0.45 (petroleum ether)

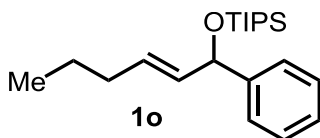
^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.09 (m, 2H), 7.00 – 6.91 (m, 2H), 5.78 – 5.65 (m, 1H), 5.64 – 5.53 (m, 1H), 4.27 – 4.12 (m, 2H), 2.68 (t, J = 7.8 Hz, 2H), 2.41 – 2.30 (m, 2H), 1.19 – 1.00 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.4 (d, J = 243.2 Hz), 137.6 (d, J = 3.3 Hz), 130.3, 129.9 (d, J = 7.8 Hz), 129.5, 115.1 (d, J = 21.0 Hz), 64.0, 35.0, 34.2, 18.2, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{34}\text{OFSi}^+$ $[\text{M}+\text{H}]^+$: 337.2363, found: 337.2366.

IR (neat, cm^{-1}): 2865, 1222, 1117, 1098, 1053, 969, 882, 824, 680, 658.

(E)-Triisopropyl((1-phenylhex-2-en-1-yl)oxy)silane (1o)



1o was prepared as a colorless oil in 98% yield (2.80 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure E.

R_f = 0.85 (petroleum ether)

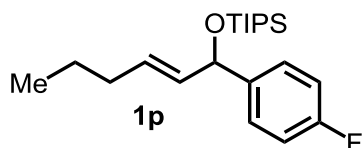
^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.24 (m, 1H), 5.81 – 5.69 (m, 1H), 5.68 – 5.58 (m, 1H), 5.31 (d, J = 6.4 Hz, 1H), 2.12 – 2.02 (m, 2H), 1.55 – 1.41 (m, 2H), 1.31 – 1.06 (m, 21H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 134.7, 129.9, 128.2, 126.9, 126.0, 76.2, 34.4, 22.6, 18.22, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{21}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 333.2614, found: 333.2619.

IR (neat, cm^{-1}): 2943, 2866, 1102, 1056, 964, 882, 697, 680, 659.

(E)-((1-(4-Fluorophenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1p)



1p was prepared as a colorless oil in 88% yield (2.16 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.82 (petroleum ether)

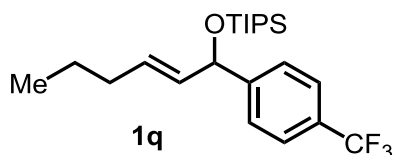
^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.26 (m, 2H), 7.04 – 6.93 (m, 2H), 5.70 – 5.58 (m, 1H), 5.56 – 5.45 (m, 1H), 5.19 (d, J = 6.5 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.44 – 1.33 (m, 2H), 1.14 – 0.97 (m, 21H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.9 (d, J = 244.1 Hz), 141.0 (d, J = 3.0 Hz), 134.4, 130.1, 127.5 (d, J = 8.0 Hz), 115.0 (d, J = 21.3 Hz), 75.5, 34.3, 22.5, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{21}\text{H}_{36}\text{FOSi}^+$ $[\text{M}+\text{H}]^+$: 351.2519, found: 351.2524.

IR (neat, cm^{-1}): 2959, 2944, 2867, 1508, 1222, 1107, 1091, 1058, 966, 882, 832, 681.

(E)-Triisopropyl((1-(4-(trifluoromethyl)phenyl)hex-2-en-1-yl)oxy)silane (1q)



1q was prepared as a colorless oil in 95% yield (2.20 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure E.

R_f = 0.87 (petroleum ether)

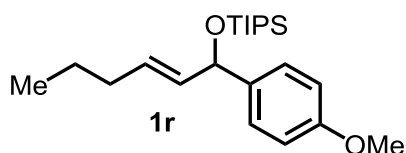
^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.55 (m, 2H), 7.54 – 7.46 (m, 2H), 5.80 – 5.66 (m, 1H), 5.58 – 5.47 (m, 1H), 5.29 (d, J = 6.9 Hz, 1H), 2.10 – 1.94 (m, 2H), 1.48 – 1.34 (m, 2H), 1.23 – 1.01 (m, 21H), 0.90 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 133.9, 131.0, 129.2 (q, J = 32.1 Hz), 126.2, 124.5 (q, J = 270.0 Hz), 125.2 (q, J = 3.9 Hz), 75.7, 34.3, 22.5, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{22}\text{H}_{36}\text{F}_3\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 401.2488, found: 401.2488.

IR (neat, cm^{-1}): 1323, 1164, 1125, 1100, 1066, 1017, 882, 681.

(E)-Triisopropyl((1-(4-methoxyphenyl)hex-2-en-1-yl)oxy)silane (1r)



1r was prepared as a colorless oil in 92% yield (1.67 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure E.

R_f = 0.79 (petroleum ether)

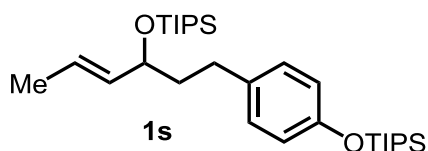
^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.24 (m, 2H), 6.91 – 6.83 (m, 2H), 5.71 – 5.59 (m, 1H), 5.60 – 5.49 (m, 1H), 5.20 (d, J = 6.4 Hz, 1H), 3.81 (s, 3H), 2.07 – 1.93 (m, 2H), 1.47 – 1.35 (m, 2H), 1.18 – 1.00 (m, 21H), 0.90 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 137.5, 134.8, 129.6, 127.1, 113.6, 75.6, 55.3, 34.3, 22.6, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{22}\text{H}_{39}\text{O}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$: 363.2719, found: 363.2721.

IR (neat, cm^{-1}): 2943, 2866, 1510, 1464, 1246, 1099, 1039, 965, 882, 843, 680.

(E)-Triisopropyl(4-(1-((triisopropylsilyl)oxy)hex-2-en-1-yl)phenoxy)silane (1s)



1s was prepared as a colorless oil in 73% yield (3.68 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.58 (petroleum ether)

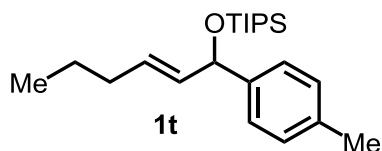
^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.13 (m, 2H), 6.87 – 6.77 (m, 2H), 5.66 – 5.48 (m, 2H), 5.14 (d, J = 5.7 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.45 – 1.32 (m, 2H), 1.32 – 1.19 (m, 3H), 1.16 – 0.94 (m, 39H), 0.87 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 137.8, 134.7, 129.5, 127.1, 119.6, 75.6, 34.3, 22.6, 18.2, 18.0, 13.8, 12.8, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{30}\text{H}_{57}\text{O}_2\text{Si}_2^+$ $[\text{M}+\text{H}]^+$: 505.3897, found: 505.3899.

IR (neat, cm^{-1}): 2944, 2867, 1508, 1464, 1262, 1058, 1012, 913, 882, 680, 659.

(E)-Triisopropyl((1-(p-tolyl)hex-2-en-1-yl)oxy)silane (1t)



1t was prepared as a colorless oil in 91% yield (1.77 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.78 (petroleum ether)

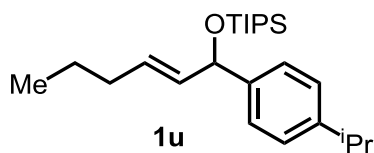
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.31 (m, 2H), 7.23 – 7.17 (m, 2H), 5.81 – 5.69 (m, 1H), 5.69 – 5.59 (m, 1H), 5.29 (d, J = 6.5 Hz, 1H), 2.41 (s, 3H), 2.12 – 2.03 (m, 2H), 1.58 – 1.43 (m, 2H), 1.28 – 1.07 (m, 21H), 0.98 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 136.3, 134.8, 129.6, 128.9, 125.9, 76.0, 34.4, 22.6, 21.2, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{22}\text{H}_{39}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 347.2770, found: 347.2771.

IR (neat, cm^{-1}): 2959, 2943, 2892, 2866, 1464, 1101, 1058, 965, 882, 681, 659.

(E)-Triisopropyl((1-(4-isopropylphenyl)hex-2-en-1-yl)oxy)silane (1u)



1u was prepared as a colorless oil in 7% yield (126 mg, eluent: petroleum ether) following the general procedure E.

R_f = 0.75 (petroleum ether)

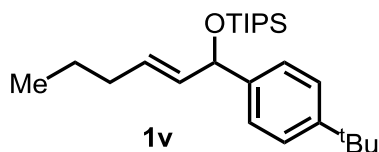
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 2H), 7.27 – 7.16 (m, 2H), 5.78 – 5.66 (m, 1H), 5.66 – 5.53 (m, 1H), 5.25 (d, J = 6.7 Hz, 1H), 3.01 – 2.86 (m, 1H), 2.09 – 1.97 (m, 2H), 1.52 – 1.39 (m, 2H), 1.30 (d, J = 6.9 Hz, 6H), 1.21 – 1.02 (m, 21H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 142.5, 134.7, 129.8, 126.2, 125.9, 76.0, 34.4, 33.9, 24.2, 22.6, 18.2, 13.9, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{24}\text{H}_{43}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 375.3083, found: 375.3085.

IR (neat, cm^{-1}): 2959, 2944, 2892, 2866, 1463, 1100, 1055, 1015, 997, 985, 965, 883, 843, 681, 660.

(E)-((1-(4-(Tert-butyl)phenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1v)



1v was prepared as a colorless oil in 67% yield (1.68 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.73 (petroleum ether)

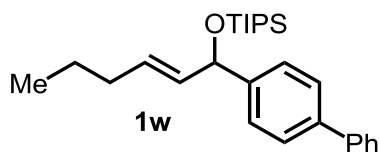
¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 4H), 5.78 – 5.66 (m, 1H), 5.64 – 5.53 (m, 1H), 5.25 (d, *J* = 6.8 Hz, 1H), 2.08 – 2.00 (m, 2H), 1.49 – 1.40 (m, 2H), 1.35 (s, 9H), 1.18 – 1.04 (m, 21H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 149.6, 142.1, 134.7, 129.9, 125.7, 125.0, 76.0, 34.6, 34.4, 31.6, 22.6, 18.3, 13.9, 12.6.

HRMS (ESI⁺) calcd for C₂₅H₄₅OSi⁺ [M+H]⁺: 389.3240, found: 389.3246.

IR (neat, cm⁻¹): 2959, 2866, 1463, 1102, 1058, 965, 882, 834, 680, 658, 578.

(E)-((1-([1,1'-Biphenyl]-4-yl)hex-2-en-1-yl)oxy)triisopropylsilane (1w)



1w was prepared as a colorless oil in 92% yield (6.08 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.66 (petroleum ether)

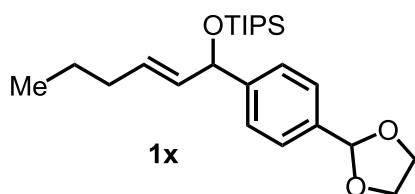
¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.56 (m, 5H), 7.48 – 7.42 (m, 3H), 7.38 – 7.32 (m, 1H), 5.79 – 5.70 (m, 1H), 5.65 – 5.58 (m, 1H), 5.31 (d, *J* = 6.5 Hz, 1H), 2.11 – 1.97 (m, 2H), 1.50 – 1.38 (m, 2H), 1.19 – 1.05 (m, 21H), 0.94 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 144.3, 141.3, 139.7, 134.5, 130.1, 128.9, 128.8, 127.2, 127.0, 126.4, 75.9, 34.4, 22.5, 18.2, 13.9, 12.5.

HRMS (ESI⁺) calcd for C₂₇H₄₁OSi⁺ [M+H]⁺: 409.2927, found: 409.2921.

IR (neat, cm⁻¹): 2958, 2943, 2865, 1486, 1464, 1100, 1058, 1008, 966, 882, 761, 696, 681.

(E)-((1-(4-(1,3-Dioxolan-2-yl)phenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1x)



1x was prepared as a colorless oil in 65% yield (2.63 g, eluent: petroleum ether: ethyl acetate = 50:1) following the general procedure E.

R_f = 0.20 (petroleum ether: ethyl acetate = 10:1)

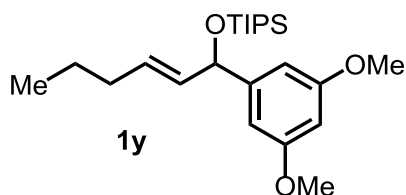
^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.40 (m, 2H), 7.44 – 7.29 (m, 2H), 5.80 (s, 1H), 5.72 – 5.59 (m, 1H), 5.56 – 5.46 (m, 1H), 5.23 (d, J = 6.6 Hz, 1H), 4.20 – 4.07 (m, 2H), 4.11 – 3.97 (m, 2H), 2.02 – 1.93 (m, 2H), 1.48 – 1.23 (m, 2H), 1.15 – 0.98 (m, 21H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 136.5, 134.7, 130.3, 126.6, 126.3, 104.2, 76.1, 65.7, 34.6, 22.7, 18.4, 18.1, 14.1, 12.7.

HRMS (ESI $^+$) calcd for $\text{C}_{24}\text{H}_{41}\text{O}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 405.2825, found: 405.2826.

IR (neat, cm^{-1}): 2958, 2942, 2866, 1699, 1604, 1464, 1209., 1015, 968, 882, 810, 679.

(E)-((1-(3,5-Dimethoxyphenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1y)



1y was prepared as a colorless oil in 54% yield (994 mg, eluent: petroleum ether) following the general procedure E.

R_f = 0.35 (petroleum ether)

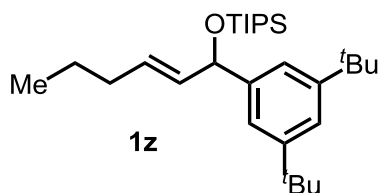
^1H NMR (400 MHz, CDCl_3) δ 6.61 – 6.53 (m, 2H), 6.37 – 6.31 (m, 1H), 5.74 – 5.62 (m, 1H), 5.60 – 5.49 (m, 1H), 5.16 (d, J = 6.7 Hz, 1H), 3.79 (s, 6H), 2.05 – 1.95 (m, 2H), 1.48 – 1.34 (m, 2H), 1.19 – 0.99 (m, 21H), 0.90 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 147.7, 134.1, 130.1, 103.8, 98.8, 75.9, 55.2, 34.2, 22.4, 18.1, 13.7, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{23}\text{H}_{41}\text{O}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 393.2825, found: 393.2826.

IR (neat, cm^{-1}): 2866, 1597, 1463, 1204, 1154, 1064, 882, 681.

(E)-((1-(3,5-Di-tert-butylphenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1z)



1z was prepared as a colorless oil in 87% yield (2.33 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.64 (petroleum ether)

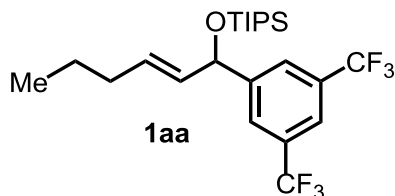
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 1H), 7.33 – 7.28 (m, 2H), 5.83 – 5.71 (m, 1H), 5.71 – 5.61 (m, 1H), 5.28 (d, J = 6.6 Hz, 1H), 2.16 – 2.02 (m, 2H), 1.54 – 1.43 (m, 2H), 1.40 (s, 18H), 1.25 – 1.06 (m, 21H), 0.98 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 144.1, 134.8, 129.9, 120.6, 120.5, 76.6, 35.0, 34.4, 31.7, 22.6, 18.3, 13.9, 12.6.

HRMS (ESI $^+$) calcd for $\text{C}_{29}\text{H}_{53}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 445.3866, found: 445.3861.

IR (neat, cm^{-1}): 2958, 2866, 1464, 1362, 1104, 1060, 965, 881, 714, 680, 656.

(E)-((1-(3,5-Bis(trifluoromethyl)phenyl)hex-2-en-1-yl)oxy)triisopropylsilane (1aa)



1aa was prepared as a colorless oil in 40% yield (1.04 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.87 (petroleum ether)

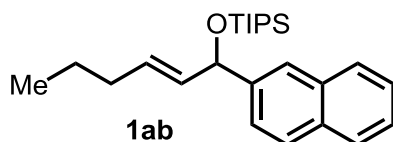
^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.83 (m, 2H), 7.77 – 7.73 (m, 1H), 5.84 – 5.72 (m, 1H), 5.56 – 5.45 (m, 1H), 5.34 (d, J = 7.2 Hz, 1H), 2.13 – 1.94 (m, 2H), 1.51 – 1.34 (m, 2H), 1.22 – 1.00 (m, 21H), 0.90 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 133.1, 132.3, 131.5 (q, J = 33.1 Hz), 126.2 (q, J = 4.0 Hz), 123.7 (q, J = 270.0 Hz), 120.9 (m), 75.3, 34.3, 22.4, 18.1, 18.0, 13.7, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{23}\text{H}_{35}\text{OF}_6\text{Si}^+$ $[\text{M}+\text{H}]^+$: 469.2361, found: 469.2361.

IR (neat, cm^{-1}): 1276, 1170, 1131, 882, 682.

(E)-Triisopropyl((1-(naphthalen-2-yl)hex-2-en-1-yl)oxy)silane (1ab)



1ab was prepared as a colorless oil in 70% yield (1.28 g, eluent: petroleum ether) following the general procedure E.

R_f = 0.68 (petroleum ether)

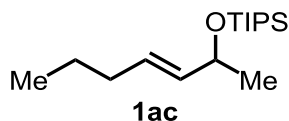
^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.80 (m, 4H), 7.57 – 7.42 (m, 3H), 5.83 – 5.71 (m, 1H), 5.70 – 5.60 (m, 1H), 5.46 – 5.40 (m, 1H), 2.11 – 1.99 (m, 2H), 1.49 – 1.38 (m, 2H), 1.24 – 1.04 (m, 21H), 0.93 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 134.5, 133.5, 132.9, 130.2, 128.1, 127.9, 127.8, 125.9, 125.5, 124.9, 124.2, 76.2, 34.4, 22.5, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{25}\text{H}_{39}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 383.2770, found: 383.2773.

IR (neat, cm^{-1}): 2943, 2865, 1463, 1102, 1057, 882, 856, 743, 680, 656, 477.

(E)-(Hept-3-en-2-yloxy)triisopropylsilane (1ac)



1ac was prepared as a colorless oil in 95% yield (2.38 g, eluent: petroleum ether) following the general procedure D.

R_f = 0.77 (petroleum ether)

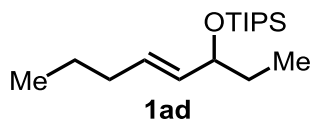
^1H NMR (400 MHz, CDCl_3) δ 5.60 – 5.41 (m, 2H), 4.38 – 4.28 (m, 1H), 2.06 – 1.91 (m, 2H), 1.45 – 1.31 (m, 2H), 1.22 (d, J = 6.3 Hz, 3H), 1.15 – 0.98 (m, 21H), 0.89 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 135.5, 128.9, 69.6, 34.4, 25.3, 22.6, 18.2, 13.8, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{16}\text{H}_{35}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 271.2457, found: 271.2449.

IR (neat, cm^{-1}): 2960, 2943, 2866, 1464, 1088, 1065, 1000, 966, 882, 677, 656.

(E)-Triisopropyl(oct-4-en-3-yloxy)silane (1ad)



1ad was prepared as a colorless oil in 93% yield (1.58 g, eluent: petroleum ether) following the general procedure D.

R_f = 0.67 (petroleum ether)

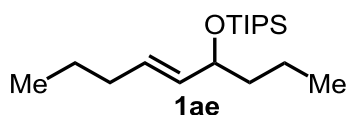
^1H NMR (400 MHz, CDCl_3) δ 5.58 – 5.46 (m, 1H), 5.44 – 5.34 (m, 1H), 4.14 – 4.02 (m, 1H), 2.09 – 1.92 (m, 2H), 1.68 – 1.46 (m, 2H), 1.45 – 1.31 (m, 2H), 1.18 – 0.98 (m, 21H), 0.97 – 0.78 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 133.8, 130.5, 75.3, 34.5, 31.6, 22.7, 18.3, 13.8, 12.6, 9.4.

HRMS (ESI $^+$) calcd for $\text{C}_{17}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 285.2614, found: 285.2608.

IR (neat, cm^{-1}): 2960, 2942, 2866, 1464, 1100, 1081, 1061, 1012, 969, 882, 678, 657.

(E)-Triisopropyl(non-5-en-4-yloxy)silane (1ae)



1ae was prepared as a colorless oil in 92% yield (2.60 g, eluent: petroleum ether) following the general procedure D.

R_f = 0.73 (petroleum ether)

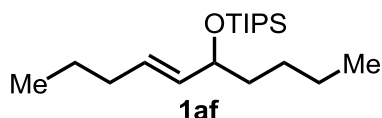
^1H NMR (400 MHz, CDCl_3) δ 5.57 – 5.46 (m, 1H), 5.45 – 5.35 (m, 1H), 4.19 – 4.10 (m, 1H), 2.07 – 1.92 (m, 2H), 1.63 – 1.50 (m, 1H), 1.49 – 1.26 (m, 5H), 1.14 – 1.00 (m, 21H), 0.90 (t, J = 7.5 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 134.2, 130.3, 74.0, 41.3, 34.5, 22.6, 18.4, 18.3, 14.4, 13.8, 12.6.

HRMS (ESI $^+$) calcd for $\text{C}_{18}\text{H}_{39}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 299.2770, found: 299.2767.

IR (neat, cm^{-1}): 2958, 2931, 2866, 1464, 1100, 1082, 1062, 1039, 968, 882, 677, 656.

(E)-(Dec-6-en-5-yloxy)triisopropylsilane (1af)



1af was prepared as a colorless oil in 85% yield (1.48 g, eluent: petroleum ether) following the general procedure D.

R_f = 0.63 (petroleum ether)

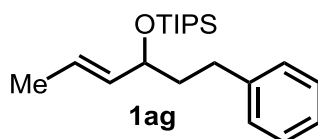
^1H NMR (400 MHz, CDCl_3) δ 5.56 – 5.45 (m, 1H), 5.44 – 5.34 (m, 1H), 4.20 – 4.03 (m, 1H), 2.08 – 1.91 (m, 2H), 1.65 – 1.52 (m, 1H), 1.51 – 1.35 (m, 3H), 1.34 – 1.21 (m, 4H), 1.15 – 0.97 (m, 21H), 0.94 – 0.81 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 134.2, 130.3, 74.2, 38.7, 34.5, 27.4, 23.0, 22.6, 18.3, 14.3, 13.9, 12.6.

HRMS (APCI⁺) calcd for $\text{C}_{19}\text{H}_{41}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 313.2927, found: 313.2922.

IR (neat, cm^{-1}): 2958, 2930, 2865, 1464, 1102, 1084, 1056, 969, 882, 677, 656.

(E)-Triisopropyl((1-phenylhex-4-en-3-yl)oxy)silane (1ag)



1ag was prepared as a colorless oil in 72% yield (920 mg, eluent: petroleum ether) following the general procedure E.

R_f = 0.82 (petroleum ether)

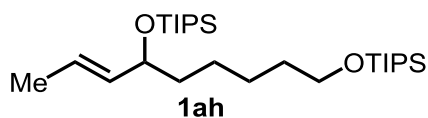
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.26 (m, 2H), 7.28 – 7.16 (m, 3H), 5.59 – 5.43 (m, 2H), 4.71 – 4.61 (m, 1H), 2.78 – 2.61 (m, 2H), 2.03 – 1.76 (m, 2H), 1.65 (d, J = 5.2 Hz, 3H), 1.17 – 1.03 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 135.0, 128.5, 128.4, 125.7, 123.4, 68.2, 40.7, 31.4, 18.2, 13.7, 12.5.

HRMS (ESI⁺) calcd for $\text{C}_{21}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 333.2614, found: 333.2611.

IR (neat, cm^{-1}): 2943, 2866, 1463, 1089, 1064, 882, 717, 698, 680, 658.

(E)-3,3,12,12-Tetraisopropyl-2,13-dimethyl-5-(prop-1-en-1-yl)-4,11-dioxa-3,12-disilatetradecane (1ah)



1ah was prepared as a colorless oil in 64% yield (827 mg, eluent: petroleum ether)

following general procedure B and the general procedure F.

$R_f = 0.84$ (petroleum ether)

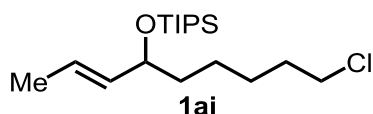
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.49 – 5.33 (m, 2H), 4.58 – 4.49 (m, 1H), 3.66 (t, $J = 6.6$ Hz, 2H), 1.69 – 1.50 (m, 7H), 1.39 – 1.25 (m, 4H), 1.05 (d, $J = 4.8$ Hz, 42H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.5, 122.8, 68.5, 63.6, 39.0, 33.2, 26.2, 24.9, 18.2, 18.1, 13.6, 12.5, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{27}\text{H}_{59}\text{O}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$: 471.4054, found: 471.4049.

IR (neat, cm^{-1}): 2941, 2893, 2866, 1463, 1100, 1066, 882, 679, 657.

(*E*)-((9-Chloronon-2-en-4-yl)oxy)triisopropylsilane (**1ai**)



1ai was prepared as a colorless oil in 43% yield (419 mg, eluent: petroleum ether) following the general procedure F.

$R_f = 0.73$ (petroleum ether)

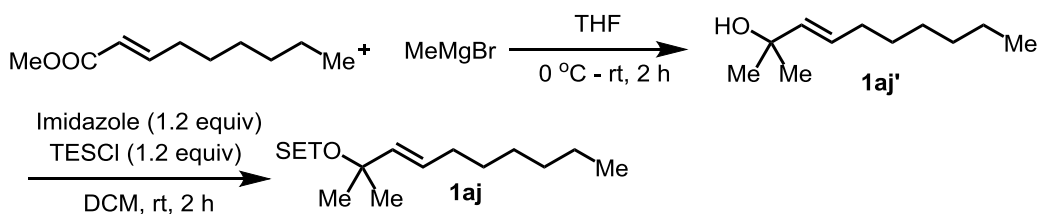
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.48 – 5.33 (m, 2H), 4.60 – 4.48 (m, 1H), 3.52 (t, $J = 6.7$ Hz, 2H), 1.83 – 1.73 (m, 2H), 1.63 – 1.55 (m, 4H), 1.51 – 1.39 (m, 3H), 1.38 – 1.29 (m, 2H), 1.11 – 1.00 (m, 21H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.3, 123.0, 68.4, 45.2, 38.7, 32.8, 27.2, 24.3, 18.2, 13.6, 12.5.

HRMS (ESI $^+$) calcd for $\text{C}_{18}\text{H}_{38}\text{ClOSi}^+$ $[\text{M}+\text{H}]^+$: 333.2380, found: 333.2373.

IR (neat, cm^{-1}): 2941, 2866, 1090, 1065, 883, 681.

(*E*)-Triethyl((2-methyldec-3-en-2-yl)oxy)silane (**1aj**)



A dried round-bottom flask containing stir bar was charged with methyl trans-2-nonenoate (1.70 g, 10.0 mmol) and the solvent THF under nitrogen

atmosphere. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and MeMgBr (3 equiv, 3 M solution in Et₂O) was added dropwise. The flask was then sealed and heated to $60\text{ }^{\circ}\text{C}$ in an oil bath for 3 hours. The reaction was then poured into an ice/water mixture and extracted three times with 50 mL of ethyl acetate. The combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **1aj'** (1.34 g, 79%) as colorless oil.

Following the literature procedure^[3], a flask was charged with allylic alcohol and imidazole (1.2 equiv). The contents were then dissolved in DCM and chlorotriethylsilane (TESCl) (1.2 equiv) was added dropwise at room temperature over 2 h. After complete conversion (TLC analysis), water was added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, concentrated, the residue purified by column chromatography to afford silicon-protected allyl alcohol **1aj**.

1aj was prepared as a colorless oil in 89% yield (1.08 g, eluent: petroleum ether)

$R_f = 0.69$ (petroleum ether)

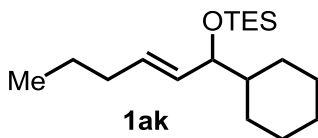
¹H NMR (400 MHz, CDCl₃) δ 5.57 – 5.51 (m, 2H), 2.03 – 1.96 (m, 2H), 1.42 – 1.22 (m, 15H), 1.01 – 0.83 (m, 11H), 0.62 – 0.52 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 138.6, 126.7, 72.8, 32.3, 31.8, 30.6, 29.3, 28.9, 22.6, 14.0, 7.0, 6.7.

HRMS (ESI⁺) calcd for C₁₇H₃₇OSi⁺ [M+H]⁺: 285.2608, found: 285.5102.

IR (neat, cm⁻¹): 2956, 2925, 1150, 1039, 1016, 968, 742, 723.

(E)-((1-Cyclohexylhex-2-en-1-yl)oxy)triethylsilane (**1ak**)



1ak was prepared as a colorless oil in 95% yield (744 mg, eluent: petroleum ether) following the general procedure E.

$R_f = 0.66$ (petroleum ether)

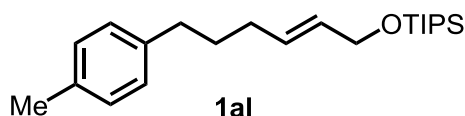
¹H NMR (400 MHz, CDCl₃) δ 5.53 – 5.41 (m, 1H), 5.42 – 5.31 (m, 1H), 3.70 (m, 1H), 2.06 – 1.92 (m, 2H), 1.91 – 1.80 (m, 1H), 1.78 – 1.59 (m, 4H), 1.45 – 1.06 (m, 6H), 1.00 – 0.85 (m, 14H), 0.63 – 0.49 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 132.6, 131.4, 78.7, 44.7, 34.5, 29.2, 26.9, 26.5, 22.6, 13.9, 7.0, 5.2.

HRMS (ESI⁺) calcd for C₁₈H₃₇OSi⁺ [M+H]⁺: 297.2614, found: 297.2619.

IR (neat, cm⁻¹): 2954, 2924, 2875, 2853, 1092, 1051, 1005, 969, 740, 724.

(E)-Triisopropyl((6-(*p*-tolyl)hex-2-en-1-yl)oxy)silane (1aI)



1aI was prepared as a colourless solid in 93% yield (1.71 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure C.

R_f = 0.68 (petroleum ether: ethyl acetate = 20:1)

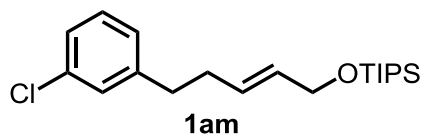
¹H NMR (400 MHz, CDCl₃) δ 7.13 – 7.04 (m, 4H), 5.76 – 5.65 (m, 1H), 5.63 – 5.53 (m, 1H), 4.24 – 4.18 (m, 2H), 2.63 – 2.55 (m, 2H), 2.33 (s, 3H), 2.14 – 2.04 (m, 2H), 1.76 – 1.62 (m, 2H), 1.19 – 1.03 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 139.6, 135.2, 130.5, 129.88, 129.1, 128.5, 64.2, 35.1, 31.9, 31.3, 21.1, 18.2, 18.1, 12.2.

HRMS (ESI⁺) calcd for C₂₂H₃₈OSiNa⁺ [M+Na]⁺: 369.2584, found: 369.2587.

IR (neat, cm⁻¹): 2939, 2864, 1462, 1122, 1058, 1013, 968, 882, 802, 680, 658.

(E)-((5-(3-Chlorophenyl)pent-2-en-1-yl)oxy)triisopropylsilane (1aM)



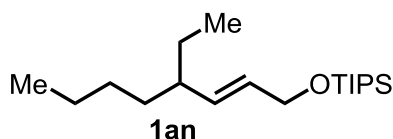
1aM was prepared as a colorless oil in 72% yield (1.29 g, eluent: petroleum ether: ethyl acetate = 100:1) following the general procedure C.

R_f = 0.23 (petroleum ether)

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 1H), 7.27 – 7.09 (m, 3H), 5.82 – 5.70 (m, 1H), 5.66 – 5.57 (m, 1H), 4.27 – 4.19 (m, 2H), 2.90 – 2.78 (m, 2H), 2.44 – 2.33 (m, 2H), 1.30 – 0.98 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 138.6, 133.1, 129.5, 129.3, 128.5, 128.4, 126.4, 125.8, 63.0, 32.5, 31.3, 17.2, 11.2.

(E)-((4-Ethyl-2-en-1-yl)oxy)triisopropylsilane (1an)



1an was prepared as a colorless oil in 92% yield (1.43 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.72 (petroleum ether)

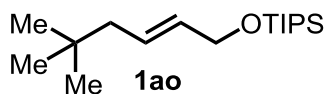
¹H NMR (400 MHz, CDCl₃) δ 5.56 – 5.46 (m, 1H), 5.45 – 5.34 (m, 1H), 4.25 – 4.19 (m, 2H), 1.92 – 1.79 (m, 1H), 1.47 – 1.33 (m, 2H), 1.33 – 1.18 (m, 6H), 1.18 – 0.96 (m, 21H), 0.96 – 0.78 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 135.2, 129.4, 64.2, 44.2, 34.8, 29.6, 28.1, 23.0, 18.2, 14.2, 12.3, 11.8.

HRMS (ESI⁺) calcd for C₁₉H₄₁OSi⁺ [M+H]⁺: 313.2927, found: 313.2927.

IR (neat, cm⁻¹): 2959, 2928, 2866, 1464, 1103, 1060, 882, 681.

(E)-((5,5-Dimethylhex-2-en-1-yl)oxy)triisopropylsilane (1ao)



1ao was prepared as a colorless oil in 95% yield (1.56 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.75 (petroleum ether)

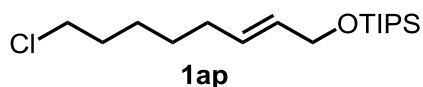
¹H NMR (400 MHz, CDCl₃) δ 5.76 – 5.66 (m, 1H), 5.59 – 5.48 (m, 1H), 4.25 – 4.19 (m, 2H), 1.96 – 1.88 (m, 2H), 1.20 – 1.00 (m, 21H), 0.88 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 131.6, 127.8, 64.1, 46.9, 31.0, 29.4, 18.2, 12.2.

HRMS (ESI⁺) calcd for C₁₇H₃₇OSi⁺ [M+H]⁺: 285.2614, found: 285.2608.

IR (neat, cm⁻¹): 2944, 2893, 2866, 1464, 1365, 1112, 1057, 972, 882, 680, 658.

(E)-((8-Chlorooct-2-en-1-yl)oxy)triisopropylsilane (1ap)



1ap was prepared as a colorless oil in 87% yield (1.43 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.45 (petroleum ether)

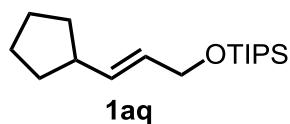
¹H NMR (400 MHz, CDCl₃) δ 5.72 – 5.61 (m, 1H), 5.59 – 5.50 (m, 1H), 4.22 – 4.16 (m, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.84 – 1.73 (m, 2H), 1.50 – 1.32 (m, 4H), 1.17 – 1.00 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 130.5, 129.8, 64.1, 45.2, 32.6, 32.1, 28.6, 26.5, 18.2, 12.2.

HRMS (ESI⁺) calcd for C₁₇H₃₆ClOSi⁺ [*M*+H]⁺: 319.2224, found: 319.2230.

IR (neat, cm⁻¹): 2941, 2893, 2865, 1463, 1101, 1059, 1013, 969, 882, 681, 657.

(E)-((3-Cyclopentylallyl)oxy)triisopropylsilane (1aq)



1aq was prepared as a colorless oil in 74% yield (1.42 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.46 (petroleum ether)

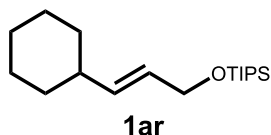
¹H NMR (400 MHz, CDCl₃) δ 5.68 – 5.61 (m, 1H), 5.58 – 5.49 (m, 1H), 4.22 – 4.16 (m, 2H), 2.49 – 2.39 (m, 1H), 1.83 – 1.71 (m, 2H), 1.69 – 1.51 (m, 4H), 1.37 – 1.22 (m, 2H), 1.20 – 0.98 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 135.7, 127.5, 64.3, 43.2, 33.1, 25.2, 18.2, 12.2.

HRMS (ESI⁺) calcd for C₁₇H₃₅OSi⁺ [*M*+H]⁺: 283.2457, found: 283.2456.

IR (neat, cm⁻¹): 2944, 2892, 2866, 1128, 1110, 1060, 969, 882, 681.

(E)-((3-Cyclohexylallyl)oxy)triisopropylsilane (1ar)



1ar was prepared as a colorless oil in 79% yield (1.51 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.63 (petroleum ether)

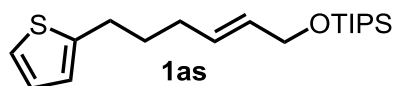
^1H NMR (400 MHz, CDCl_3) δ 5.67 – 5.56 (m, 1H), 5.55 – 5.42 (m, 1H), 4.23 – 4.16 (m, 2H), 2.01 – 1.90 (m, 1H), 1.76 – 1.61 (m, 4H), 1.32 – 1.11 (m, 6H), 1.10 – 0.98 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 126.8, 64.4, 40.4, 33.0, 26.4, 26.2, 18.2, 12.2.

HRMS (ESI⁺) calcd for $\text{C}_{18}\text{H}_{37}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 297.2614, found: 297.2608.

IR (neat, cm^{-1}): 2924, 2865, 2852, 1463, 1115, 1099, 1059, 968, 882, 680, 657.

(E)-Triisopropyl((6-(thiophen-2-yl)hex-2-en-1-yl)oxy)silane (1as)



1as was prepared as a colorless oil in 68% yield (244 mg, eluent: petroleum ether: ethyl acetate=20:1) following the general procedure C.

R_f = 0.72 (petroleum ether: ethyl acetate = 5:1)

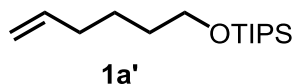
^1H NMR (400 MHz, CDCl_3) δ 7.15 – 7.09 (m, 1H), 6.97 – 6.90 (m, 1H), 6.83 – 6.77 (m, 1H), 5.78 – 5.66 (m, 1H), 5.66 – 5.55 (m, 1H), 4.26 – 4.20 (m, 2H), 2.90 – 2.82 (m, 2H), 2.19 – 2.10 (m, 2H), 1.86 – 1.74 (m, 2H), 1.23 – 1.00 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 130.2, 130.0, 126.8, 124.2, 123.0, 64.1, 31.6, 31.4, 29.4, 18.2, 12.2.

HRMS (ESI⁺) calcd for $\text{C}_{19}\text{H}_{35}\text{OSSi}^+$ $[\text{M}+\text{H}]^+$: 339.2178, found: 339.2175.

IR (neat, cm^{-1}): 2941, 2893, 2866, 1058, 882, 689.

(Hex-5-en-1-yloxy)triisopropylsilane (1a')^[4]



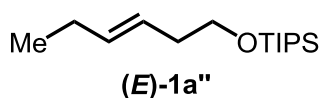
1a' was prepared as a colorless oil in 93% yield (1.19 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.84 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.92 – 5.77 (m, 1H), 5.06 – 4.93 (m, 2H), 3.71 (t, J = 6.4 Hz, 2H), 2.15 – 2.03 (m, 2H), 1.63 – 1.42 (m, 4H), 1.18 – 1.01 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 114.5, 63.4, 33.7, 32.6, 25.3, 18.2, 12.2.

(E)-(Hex-3-en-1-yloxy)triisopropylsilane ((E)-1a'')^[14]



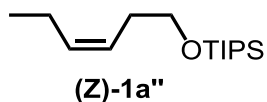
(E)-1a'' was prepared as a colorless oil in 56% yield (736 mg, eluent: petroleum ether) following the general procedure A.

R_f = 0.80 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.56 – 5.48 (m, 1H), 5.46 – 5.37 (m, 1H), 3.68 (t, J = 6.9 Hz, 2H), 2.29 – 2.19 (m, 2H), 2.06 – 1.94 (m, 2H), 1.16 – 1.01 (m, 21H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 134.2, 125.7, 63.8, 36.6, 25.8, 18.2, 13.9, 12.2.

(Z)-(Hex-3-en-1-yloxy)triisopropylsilane ((Z)-1a'')^[4]



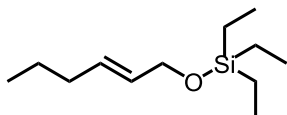
(Z)-1a'' was prepared as a colorless oil in 92% yield (2.35 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.82 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.51 – 5.41 (m, 1H), 5.40 – 5.29 (m, 1H), 3.67 (t, J = 7.1 Hz, 2H), 2.35 – 2.26 (m, 2H), 2.12 – 2.00 (m, 2H), 1.14 – 1.02 (m, 21H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 133.5, 125.2, 63.4, 31.3, 20.8, 18.2, 14.5, 12.2.

(E)-Triethyl(hex-2-en-1-yloxy)silane^[15]



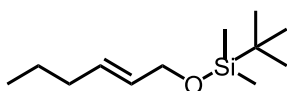
The compound was prepared as a colorless oil in 90% yield (0.96 g, eluent: petroleum ether) following the general procedure A.

R_f = 0.75 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.70 – 5.57 (m, 1H), 5.58 – 5.49 (m, 1H), 4.15 – 4.09 (m, 2H), 2.06 – 1.96 (m, 2H), 1.47 – 1.35 (m, 2H), 0.94 – 0.86 (m, 12H), 0.14 – 0.03 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 131.4, 129.4, 64.3, 34.4, 26.1, 22.5, 18.6, 13.8.

(E)-tert-Butyl(hex-2-en-1-yloxy)dimethylsilane^[16]



The compound was prepared as a colorless oil in 93% yield (0.99 g, eluent: petroleum ether) following the general procedure A.

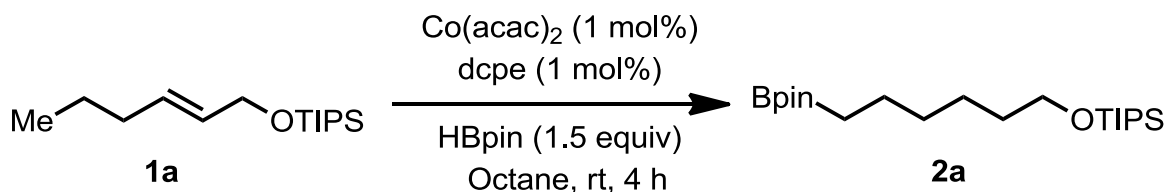
R_f = 0.80 (petroleum ether)

^1H NMR (400 MHz, CDCl_3) δ 5.69 – 5.60 (m, 1H), 5.59 – 5.50 (m, 1H), 4.14 – 4.08 (m, 2H), 2.05 – 1.97 (m, 2H), 1.46 – 1.31 (m, 2H), 1.01 – 0.93 (m, 9H), 0.90 (t, J = 7.4 Hz, 3H), 0.66 – 0.54 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 131.9, 129.3, 63.9, 34.5, 22.5, 13.8, 6.9, 4.7.

IV. Remote Hydroboration and Alkene Isomerization of Allylic Siloxanes

Typical procedure A of remote hydroboration of allylic siloxanes



Triisopropyl((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (**2a**)^[4]

In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (2.6 mg, 0.01 mmol, 1 mol%), dcype (4.3 mg, 0.01 mmol, 1 mol%), and anhydrous octane (1 mL). The resulting solution was stirred for 5 min at room temperature, then HBpin (192 mg, 1.5 mmol, 1.5 equiv) was added and the reaction mixture was stirred for 5 min, followed by the addition of **1a** (256 mg, 1.0 mmol, 1.0 equiv) and octane (1 mL). The reaction mixture was sealed, removed from the glovebox and stirred at room temperature for 4 h. After completion, the reaction was filtered through a silica gel pad, washed with ethyl acetate, and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to give the desired product **2a** as colorless oil (315 mg, 82% yield).

R_f = 0.63 (petroleum ether/ethyl acetate = 20/1)

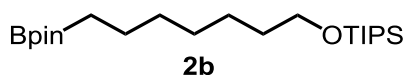
^1H NMR (400 MHz, CDCl_3) δ 3.63 (t, J = 6.7 Hz, 2H), 1.55 – 1.45 (m, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.25 (m, 4H), 1.21 (s, 12H), 1.12 – 0.98 (m, 21H), 0.74 (t, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 82.7, 63.5, 33.0, 32.2, 25.6, 24.8, 24.0, 18.0, 12.0.

^{29}Si NMR (79.5 MHz, CDCl_3) δ 11.88.

^{11}B NMR (128.4 MHz, CDCl_3) δ 34.09.

Triisopropyl((7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)silane (**2b**)



2b was prepared as a colorless oil in 72% yield (287 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1b** (135 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), dcype (2.2 mg, 0.005 mmol, 1 mol%), and HBpin (96 mg, 0.75 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.63 (petroleum ether/ethyl acetate = 20/1)

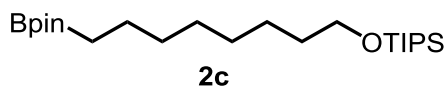
¹H NMR (400 MHz, CDCl₃) δ 3.66 (t, J = 6.8 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.46 – 1.36 (m, 2H), 1.36 – 1.27 (m, 6H), 1.24 (s, 12H), 1.12 – 1.02 (m, 21H), 0.77 (t, J = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.8, 63.5, 33.0, 32.4, 29.2, 25.7, 24.8, 23.9, 18.0, 12.0.

HRMS (ESI⁺) calcd for C₂₄H₅₂BO₃Si⁺ [M+H]⁺: 427.3779, found: 427.3786.

IR (neat, cm⁻¹): 2928, 2865, 1378, 1371, 1317, 1146, 1106, 882, 679.

Triisopropyl((8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)silane (2c)^[8]



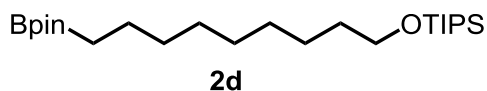
2c was prepared as a colorless oil in 78% yield (317 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1c** (284 mg, 1.0 mmol, 1.0 equiv), Co(acac)₂ (2.6 mg, 0.01 mmol, 1 mol%), dcype (4.3 mg, 0.01 mmol, 1 mol%), and HBpin (192 mg, 1.5 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.64 (petroleum ether/ethyl acetate = 20/1)

¹H NMR (400 MHz, CDCl₃) δ 3.62 (t, J = 6.7 Hz, 2H), 1.54 – 1.44 (m, 2H), 1.37 (d, J = 8.2 Hz, 2H), 1.29 – 1.22 (m, 8H), 1.20 (s, 12H), 1.11 – 0.98 (m, 21H), 0.72 (t, J = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.7, 63.5, 33.0, 32.3, 29.4, 29.3, 25.8, 24.7, 23.9, 18.0, 12.0.

Triisopropyl((9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)silane (2d)



2d was prepared as a colorless oil in 66% yield (288 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1d** (228 mg, 1.0 mmol, 1.0 equiv), Co(acac)₂ (2.6 mg, 0.01 mmol, 1 mol%), dcype (4.3 mg, 0.01 mmol, 1 mol%), and HBpin (192 mg, 1.5 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.67 (petroleum ether/ethyl acetate = 20/1)

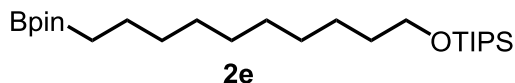
¹H NMR (400 MHz, CDCl₃) δ 3.66 (t, J = 6.7 Hz, 2H), 1.59 – 1.47 (m, 2H), 1.44 – 1.35 (m, 2H), 1.35 – 1.25 (m, 10H), 1.23 (s, 12H), 1.12 – 1.00 (m, 21H), 0.76 (t, J = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.7, 63.5, 33.0, 32.4, 29.6, 29.5, 29.4, 25.8, 24.8, 24.0, 18.0, 12.0.

HRMS (ESI⁺) calcd for C₂₆H₅₆BO₃Si⁺ [M+H]⁺: 455.4092, found: 455.4100.

IR (neat, cm⁻¹): 926, 2865, 1464, 1378, 1371, 1317, 1146, 1106, 882, 680.

Triisopropyl((10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decyl)oxy)silane (2e)



2e was prepared as a colorless oil in 79% yield (347 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1e** (312 mg, 1.0 mmol, 1.0 equiv), Co(acac)₂ (2.6 mg, 0.01 mmol, 1 mol%), dcype (4.3 mg, 0.01 mmol, 1 mol%), and HBpin (192 mg, 1.5 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.65 (petroleum ether/ethyl acetate = 20/1)

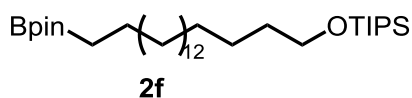
¹H NMR (400 MHz, CDCl₃) δ 3.64 (t, J = 6.6 Hz, 2H), 1.59 – 1.46 (m, 2H), 1.43 – 1.34 (m, 2H), 1.29 – 1.23 (m, 12H), 1.21 (s, 12H), 1.19 – 0.97 (m, 21H), 0.73 (t, J = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.7, 63.4, 33.0, 32.4, 29.6, 29.5, 29.4, 29.3, 25.8, 24.7, 23.9, 17.8, 12.0.

HRMS (ESI⁺) calcd for C₂₅H₅₃BO₃SiNa⁺ [M+Na]⁺: 463.3749, found: 463.3754.

IR (neat, cm⁻¹): 2925, 2865, 1464, 1378, 1371, 1317, 1146, 1106, 882, 680.

Triisopropyl((18-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octadecyl)oxy)silane (2f)



2f was prepared as a colorless oil in 75% yield (122 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1f** (127 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.65 (petroleum ether/ethyl acetate = 20/1)

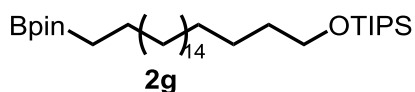
¹H NMR (400 MHz, CDCl₃) δ 3.68 (t, J = 6.7 Hz, 2H), 1.61 – 1.49 (m, 2H), 1.46 – 1.38 (m, 2H), 1.37 – 1.20 (m, 40H), 1.14 – 1.01 (m, 21H), 0.77 (t, J = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.8, 63.5, 33.1, 32.4, 29.8 – 29.6 (m, 10C), 29.5, 29.4, 25.8, 24.8, 24.0, 18.0, 12.0.

HRMS (ESI⁺) calcd for C₃₃H₆₈BO₃Si⁺ [M+H]⁺: 553.5182, found: 553.5194.

IR (neat, cm⁻¹): 2923, 2853, 1378, 1371, 1317, 1146, 1105, 882, 680.

Triisopropyl((20-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)icosyl)oxy)silane (2g)



2g was prepared as a colorless oil in 67% yield (115 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1g** (135 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.65 (petroleum ether/ethyl acetate = 20/1)

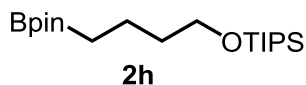
¹H NMR (400 MHz, CDCl₃) δ 3.69 (t, J = 6.7 Hz, 2H), 1.60 – 1.50 (m, 2H), 1.47 – 1.38 (m, 2H), 1.36 – 1.22 (m, 44H), 1.13 – 1.02 (m, 21H), 0.78 (t, J = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.8, 63.5, 33.1, 32.5, 29.8 – 29.6 (m, 12C), 29.5, 29.4, 25.8, 24.8, 24.0, 18.0, 12.0.

HRMS (ESI⁺) calcd for C₃₅H₇₁BO₃SiNa⁺ [M+Na]⁺: 603.5314, found: 603.5315.

IR (neat, cm⁻¹): 2922, 2853, 1378, 1371, 1317, 1146, 1104, 882, 679.

Triisopropyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane (2h)^[9]



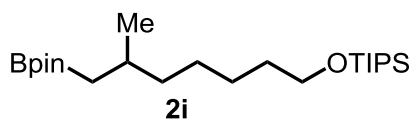
2h was prepared as a colorless oil in 92% yield (325 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1h** (228 mg, 1.0 mmol, 1.0 equiv), Co(acac)₂ (2.6 mg, 0.01 mmol, 1 mol%), dcype (4.3 mg, 0.01 mmol, 1 mol%), and HBpin (192 mg, 1.5 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.66 (petroleum ether/ethyl acetate = 20/1)

¹H NMR (400 MHz, CDCl₃) δ 3.63 (t, *J* = 6.7 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.47 – 1.38 (m, 2H), 1.20 (s, 12H), 1.06 – 0.98 (m, 21H), 0.75 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.7, 63.2, 35.5, 24.7, 20.2, 18.0, 12.0.

Triisopropyl((6-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)silane (2i)



2i was prepared as a colorless oil in 66% yield (131 mg, eluent: petroleum ether /ethyl acetate = 100/1) from **1i** (135 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (6.4 mg, 0.025 mmol, 5 mol%), dcype (10.5 mg, 0.025 mmol, 5 mol%), and HBpin (96 mg, 0.75 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.45 (petroleum ether/ethyl acetate = 40/1)

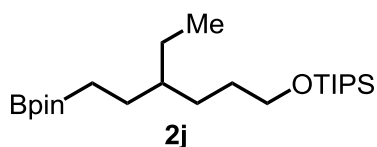
¹H NMR (400 MHz, CDCl₃) δ 3.66 (t, *J* = 6.6 Hz, 2H), 1.73 – 1.64 (m, 1H), 1.57 – 1.45 (m, 2H), 1.36 – 1.26 (m, 4H), 1.28 – 1.20 (m, 14H), 1.10 – 1.01 (m, 21H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 – 0.78 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.9, 77.5, 77.2, 76.8, 63.7, 39.6, 33.5, 29.6, 25.0, 24.9, 23.7, 22.4, 18.2, 12.2.

HRMS (ESI⁺) calcd for C₂₃H₅₀BO₃Si⁺ [*M*+*H*]⁺: 413.3622, found: 413.3629.

IR (neat, cm⁻¹): 2942, 2866, 1462, 1370, 1314, 1145, 1103, 969, 882, 678.

((4-Ethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane(2j)



2j was prepared as a colorless oil in 69% yield (142 mg, eluent: petroleum ether /ethyl acetate = 100/1) from **1j** (142 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (6.4 mg, 0.025 mmol, 5 mol%), dcype (10.5 mg, 0.025 mmol, 5 mol%), and HBpin (96 mg, 0.75 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.5 (petroleum ether/ethyl acetate = 40/1)

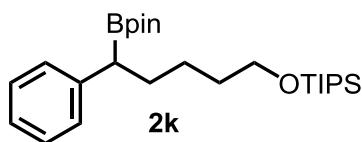
¹H NMR (400 MHz, CDCl₃) δ 3.63 (t, J = 6.7 Hz, 2H), 1.55 – 1.45 (m, 2H), 1.41 – 1.30 (m, 5H), 1.25 – 1.18 (m, 14H), 1.12 – 0.98 (m, 21H), 0.82 (t, J = 7.4 Hz, 3H), 0.76 – 0.67 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.8, 77.3, 77.0, 76.7, 64.0, 40.7, 30.2, 28.6, 27.1, 25.3, 24.8, 18.0, 12.0, 10.8.

HRMS (ESI⁺) calcd for C₂₃H₅₀BO₃Si⁺ [M+H]⁺: 413.3622, found: 413.3624.

IR (neat, cm⁻¹): 2939, 2865, 1462, 1370, 1318, 1145, 1102, 968, 882, 679, 657.

Triisopropyl((5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane (2k)



2k was prepared as a colorless oil in 86% yield (114 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1k** (95 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.48 (petroleum ether/ethyl acetate = 20/1)

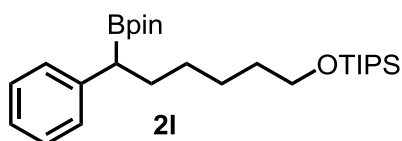
¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.14 (m, 4H), 7.13 – 7.04 (m, 1H), 3.61 (t, J = 6.5, 0.9 Hz, 2H), 2.28 (t, J = 7.9 Hz, 1H), 1.92 – 1.75 (m, 1H), 1.71 – 1.60 (m, 1H), 1.59 – 1.44 (m, 2H), 1.35 – 1.28 (m, 2H), 1.17 (d, J = 7.3 Hz, 12H), 1.08 – 0.97 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 128.4, 128.2, 125.1, 83.2, 63.4, 33.1, 32.6, 25.6, 24.7, 18.1, 12.1.

HRMS (ESI $^+$) calcd for $\text{C}_{26}\text{H}_{48}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 447.3466, found: 447.3473.

IR (neat, cm^{-1}): 2941, 2866, 1462, 1371, 1144, 883, 701, 686, 680, 468, 456.

Triisopropyl((6-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (2l)



2l was prepared as a colorless oil in 84% yield (116 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1l** (100 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following the typical procedure A.

R_f = 0.48 (petroleum ether/ethyl acetate = 20/1)

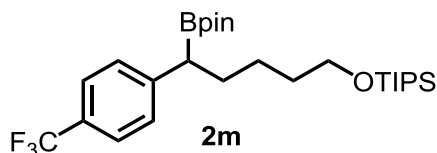
^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.19 (m, 4H), 7.17 – 7.10 (m, 1H), 3.66 (t, J = 6.7 Hz, 2H), 2.32 (t, J = 8.0 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.76 – 1.61 (m, 1H), 1.59 – 1.48 (m, 2H), 1.42 – 1.28 (m, 4H), 1.21 (d, J = 7.8 Hz, 12H), 1.14 – 1.00 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 128.5, 128.3, 125.2, 83.3, 63.6, 33.1, 32.7, 29.3, 26.0, 24.8, 18.2, 12.2.

HRMS (ESI $^+$) calcd for $\text{C}_{27}\text{H}_{50}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 461.3622, found: 461.3629.

IR (neat, cm^{-1}): 2940, 2865, 1379, 1371, 1320, 1143, 1106, 882, 700, 680, 658.

Triisopropyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(4-(trifluoromethyl)phenyl)pentyl)oxy)silane (2m)



2m was prepared as a colorless oil in 72% yield (112 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1m** (116 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg,

0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.43 (petroleum ether/ethyl acetate = 20/1)

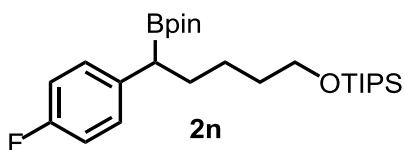
^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.46 (m, 2H), 7.34 – 7.28 (m, 2H), 3.64 (t, J = 6.5 Hz, 2H), 2.38 (t, J = 7.9 Hz, 1H), 1.96 – 1.82 (m, 1H), 1.75 – 1.62 (m, 1H), 1.62 – 1.46 (m, 2H), 1.37 – 1.29 (m, 2H), 1.20 (d, J = 5.2 Hz, 12H), 1.11 – 0.98 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 127.7, 126.6 (q, J = 32.4 Hz), 124.3 (q, J = 3.7 Hz), 123.7 (q, J = 269.8 Hz), 82.7, 62.4, 32.1, 31.4, 24.7, 23.7, 17.2, 11.2.

HRMS (ESI⁺) calcd for $\text{C}_{27}\text{H}_{47}\text{BF}_3\text{O}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 515.3340, found: 515.3340.

IR (neat, cm^{-1}): 2943, 2863, 1445, 1324, 1125, 1073, 882, 677.

((5-(4-Fluorophenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)triisopropylsilane (2n)



2n was prepared as a colorless oil in 65% yield (90 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1n** (101 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.45 (petroleum ether/ethyl acetate = 20/1)

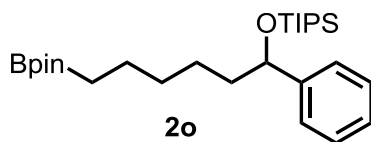
^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.07 (m, 2H), 6.97 – 6.88 (m, 2H), 3.64 (t, J = 6.6 Hz, 2H), 2.29 (t, J = 7.9 Hz, 1H), 1.91 – 1.77 (m, 1H), 1.70 – 1.45 (m, 3H), 1.39 – 1.28 (m, 2H), 1.20 (d, J = 6.2 Hz, 12H), 1.13 – 0.96 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.1 (d, J = 242.2 Hz), 139.1 (d, J = 3.1 Hz), 129.7 (d, J = 7.5 Hz), 115.0 (d, J = 20.9 Hz), 83.4, 63.5, 33.2, 32.8, 25.7, 24.7, 18.2, 12.1.

HRMS (ESI⁺) calcd for $\text{C}_{26}\text{H}_{47}\text{BFO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 465.3372, found: 465.3379.

IR (neat, cm^{-1}): 2942, 2866, 1510, 1463, 1224, 1105, 883, 836, 680.

Triisopropyl((1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (2o)



2o was prepared as a colorless oil in 91% yield (126 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1o** (100 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.36 (petroleum ether/ethyl acetate = 20/1)

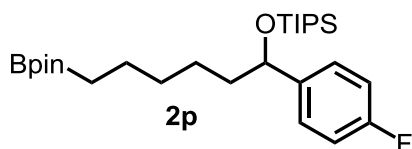
¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 4H), 7.23 – 7.18 (m, 1H), 4.74 (t, J = 6.2 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.59 (m, 1H), 1.40 – 1.31 (m, 2H), 1.23 (m, 16H), 1.06 – 0.92 (m, 21H), 0.72 (t, J = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 145.9, 127.9, 126.8, 126.3, 82.9, 75.3, 41.8, 32.7, 24.9, 24.8, 24.1, 18.2, 12.5.

HRMS (ESI⁺) calcd for C₂₇H₅₀BO₃Si⁺ [M+H]⁺: 461.3622, found: 461.3626.

IR (neat, cm⁻¹): 2932, 2866, 1378, 1371, 1317, 1145, 1093, 1062, 882, 700, 679.

((1-(4-Fluorophenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2p)



2p was prepared as a colorless oil in 88% yield (126 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1p** (105 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.42 (petroleum ether/ethyl acetate = 20/1)

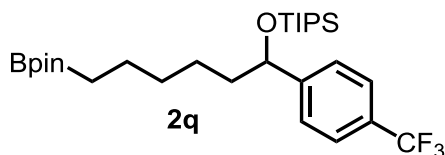
¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.20 (m, 2H), 7.00 – 6.91 (m, 2H), 4.72 (t, J = 6.5 Hz, 1H), 1.80 – 1.56 (m, 2H), 1.41 – 1.28 (m, 2H), 1.25 – 1.20 (m, 16H), 1.08 – 0.88 (m, 21H), 0.71 (t, J = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 161.9 (d, J = 244.1 Hz), 141.6 (d, J = 3.2 Hz), 127.7 (d, J = 7.9 Hz), 114.7 (d, J = 21.1 Hz), 82.9, 74.7, 41.1, 32.6, 24.9, 24.7, 24.1, 18.2, 12.4.

HRMS (ESI⁺) calcd for C₂₇H₄₉BFO₃Si⁺ [M+H]⁺: 479.3528, found: 479.3523.

IR (neat, cm⁻¹): 2935, 2867, 1509, 1464, 1379, 1222, 1146, 1088, 882, 845, 680.

Triisopropyl((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)hexyl)oxy)silane (2q)



2q was prepared as a colorless oil in 82% yield (130 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1q** (120 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.38 (petroleum ether/ethyl acetate = 20/1)

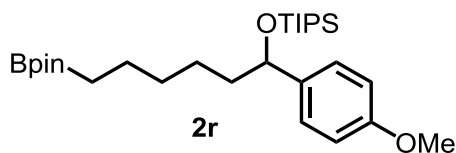
¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.51 (m, 2H), 7.44 – 7.38 (m, 2H), 4.82 (t, *J* = 6.1 Hz, 1H), 1.82 – 1.62 (m, 2H), 1.43 – 1.29 (m, 2H), 1.28 – 1.13 (m, 16H), 1.08 – 0.92 (m, 21H), 0.71 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 149.9, 129.1 (q, *J* = 30.9 Hz), 126.5, 125.0 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.0 Hz), 83.0, 74.7, 40.8, 32.6, 24.9, 24.4, 24.1, 18.1, 12.4.

HRMS (ESI⁺) calcd for C₂₈H₄₉BF₃O₃Si⁺ [M+H]⁺: 529.3496, found: 529.3497.

IR (neat, cm⁻¹): 1325, 1165, 1146, 1127, 1067.

Triisopropyl((1-(4-methoxyphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (2r)



2r was prepared as a colorless oil in 85% yield (126 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1r** (109 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.35 (petroleum ether/ethyl acetate = 20/1)

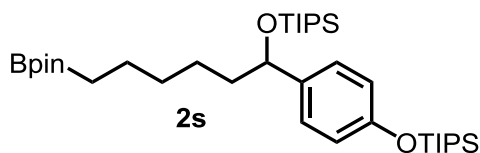
^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.16 (m, 2H), 6.86 – 6.77 (m, 2H), 4.72 – 4.64 (m, 1H), 3.79 (s, 3H), 1.80 – 1.57 (m, 2H), 1.39 – 1.28 (m, 2H), 1.26 – 1.16 (m, 16H), 1.04 – 0.90 (m, 21H), 0.71 (t, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 138.0, 127.2, 113.1, 82.8, 74.7, 55.1, 41.0, 32.6, 24.8, 24.0, 18.1, 18.0, 12.3.

HRMS (ESI $^+$) calcd for $\text{C}_{28}\text{H}_{52}\text{BO}_4\text{Si}^+$ $[\text{M}+\text{H}]^+$: 491.3728, found: 491.3731.

IR (neat, cm^{-1}): 2932, 2865, 1512, 1464, 1378, 1317, 1171, 1145, 1089, 882, 841, 679.

Triisopropyl(4-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-((triisopropylsilyl)oxy)hexyl)phenoxy)silane (2s)



2s was prepared as a colorless oil in 88% yield (166 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1s** (151 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following the typical procedure A.

R_f = 0.35 (petroleum ether/ethyl acetate = 20/1)

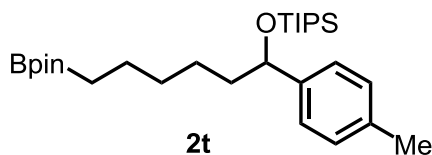
^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.11 (m, 2H), 6.85 – 6.79 (m, 2H), 4.66 (t, J = 6.2 Hz, 1H), 1.84 – 1.71 (m, 1H), 1.71 – 1.57 (m, 1H), 1.43 – 1.26 (m, 2H), 1.29 – 1.20 (m, 19H), 1.10 (d, J = 7.5 Hz, 18H), 1.06 – 0.90 (m, 21H), 0.73 (t, J = 7.7 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 138.6, 127.3, 119.5, 82.9, 75.0, 41.1, 32.7, 24.9, 24.1, 18.2, 18.1, 18.0, 12.7, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{36}\text{H}_{70}\text{BO}_4\text{Si}_2^+$ $[\text{M}+\text{H}]^+$: 633.4906, found: 633.4902.

IR (neat, cm^{-1}): 2942, 2866, 1509, 1379, 1261, 1146, 1089, 914, 882, 846, 679.

Triisopropyl((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)hexyl)oxy)silane (2t)



2t was prepared as a colorless oil in 88% yield (126 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1t** (104 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.35 (petroleum ether/ethyl acetate = 20/1)

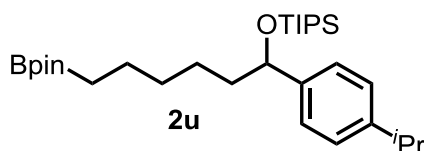
¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.74 (t, *J* = 6.2 Hz, 1H), 2.35 (s, 3H), 1.85 – 1.63 (m, 2H), 1.43 – 1.33 (m, 2H), 1.32 – 1.17 (m, 16H), 1.09 – 0.96 (m, 21H) 0.75 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 142.9, 136.2, 128.6, 126.2, 82.9, 75.1, 41.1, 32.7, 24.9, 24.8, 24.1, 21.3, 18.2, 12.5.

HRMS (ESI⁺) calcd for C₂₈H₅₂BO₃Si⁺ [M+H]⁺: 475.3779, found: 475.3770.

IR (neat, cm⁻¹): 2939, 2865, 1372, 1324, 1148, 1105, 882, 852, 816, 676, 658.

Triisopropyl((1-(4-isopropylphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (2u**)**



2u was prepared as a colorless oil in 81% yield (122 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1u** (112 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.42 (petroleum ether/ethyl acetate = 20/1)

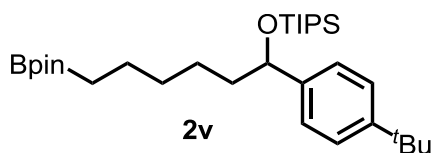
¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 4.71 (t, *J* = 6.1 Hz, 1H), 2.95 – 2.79 (m, 1H), 1.85 – 1.71 (m, 1H), 1.70 – 1.57 (m, 1H), 1.45 – 1.31 (m, 2H), 1.25 (s, 6H), 1.24 – 1.21 (m, 16H), 1.09 – 0.84 (m, 21H), 0.73 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 147.3, 143.2, 126.2, 125.9, 82.9, 75.2, 41.1, 33.9, 32.7, 24.9, 24.2, 24.1, 18.2, 18.1, 12.5.

HRMS (ESI⁺) calcd for C₃₀H₅₆BO₃Si⁺ [M+H]⁺: 503.4092, found: 503.4086.

IR (neat, cm⁻¹): 2960, 2933, 2866, 1464, 1379, 1371, 1318, 1146, 1090, 1065, 1014, 882, 845, 679.

((1-(4-(*tert*-Butyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2v)



2v was prepared as a colorless oil in 80% yield (125 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1v** (117 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.48 (petroleum ether/ethyl acetate = 20/1)

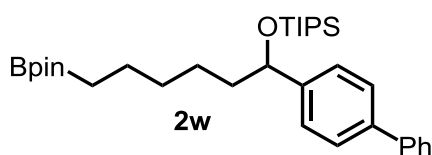
¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.24 – 7.17 (m, 2H), 4.73 (t, *J* = 6.2 Hz, 1H), 1.84 – 1.60 (m, 2H), 1.45 – 1.34 (m, 2H), 1.33 – 1.29 (s, 9H), 1.28 – 1.19 (m, 16H), 1.05 – 0.92 (m, 21H), 0.73 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 149.6, 142.7, 125.9, 124.7, 82.9, 75.1, 41.0, 34.5, 32.7, 31.6, 24.9, 24.1, 18.2, 18.1, 12.5.

HRMS (ESI⁺) calcd for C₃₁H₅₈BO₃Si⁺ [M+H]⁺: 517.4248, found: 517.4250.

IR (neat, cm⁻¹): 2939, 2866, 1464, 1378, 1371, 1318, 1146, 1091, 1065, 883, 846, 680.

((1-([1,1'-Biphenyl]-4-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2w)



2w was prepared as a colorless oil in 82% yield (132 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1w** (122 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.48 (petroleum ether/ethyl acetate = 20/1)

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.52 (m, 2H), 7.48 – 7.31 (m, 5H), 4.86 – 4.79 (t, *J* = 5.88 Hz, 1H), 1.90 – 1.68 (m, 2H), 1.46 – 1.35 (m, 2H), 1.34

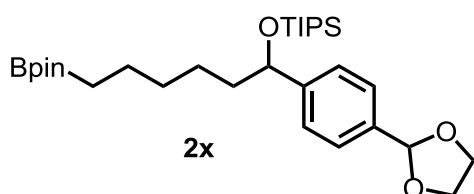
– 1.18 (m, 16H), 1.14 – 0.94 (m, 21H), 0.76 (t, $J = 7.7$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 141.2, 139.6, 128.8, 127.1, 126.7, 126.6, 82.9, 75.0, 41.0, 32.7, 24.9, 24.8, 24.1, 18.2, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{33}\text{H}_{54}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 537.3935, found: 537.3936.

IR (neat, cm^{-1}): 2935, 2865, 1464, 1371, 1318, 1146, 1091, 882, 847, 697, 680.

((1-(4-(1,3-Dioxolan-2-yl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2x)



2x was prepared as a colorless oil in 64% yield (91 mg, eluent: petroleum ether /ethyl acetate = 50:1) from **1x** (105 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

$R_f = 0.28$ (petroleum ether/ethyl acetate = 10/1)

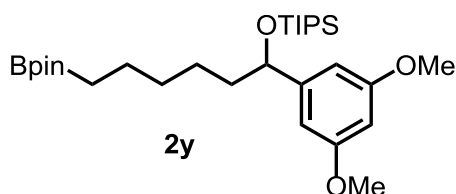
^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 5.78 (s, 1H), 4.76 (m, 1H), 4.18 – 3.96 (m, 4H), 1.79 – 1.59 (m, 2H), 1.38 – 1.26 (m, 2H), 1.25 – 1.11 (m, 16H), 1.07 – 0.89 (m, 21H), 0.71 (t, $J = 7.7$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 136.2, 126.3, 126.2, 104.0, 82.9, 75.0, 65.4, 41.0, 32.7, 24.9, 24.6, 24.1, 18.2, 12.4.

HRMS (ESI $^+$) calcd for $\text{C}_{30}\text{H}_{54}\text{BO}_5\text{Si}^+$ $[\text{M}+\text{H}]^+$: 533.3834, found: 533.3841.

IR (neat, cm^{-1}): 2938, 2866, 1379, 1371, 1318, 1146, 1084, 968, 882, 846, 680.

((1-(3,5-Dimethoxyphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2y)



2y was prepared as a colorless oil in 64% yield (100 mg, eluent: petroleum ether /ethyl acetate = 50:1) from **1y** (118 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.52 (petroleum ether/ethyl acetate = 10/1)

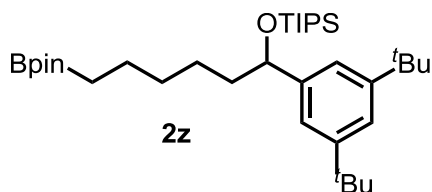
¹H NMR (400 MHz, CDCl₃) δ 6.50 – 6.45 (m, 2H), 6.33 – 6.29 (m, 1H), 4.68 (t, *J* = 6.0 Hz, 1H), 3.78 (s, 6H), 1.78 – 1.58 (m, 2H), 1.41 – 1.29 (m, 2H), 1.25 – 1.21 (s, 16H), 1.11 – 0.91 (m, 21H), 0.72 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 160.4, 148.5, 104.2, 98.8, 82.9, 75.3, 55.4, 40.9, 32.8, 24.9, 24.7, 24.1, 18.2, 12.5.

HRMS (ESI⁺) calcd for C₂₉H₅₄BO₅Si⁺ [M+H]⁺: 521.3834, found: 521.3837.

IR (neat, cm⁻¹): 2935, 2866, 1598, 1463, 1371, 1205, 1152, 1064, 883, 681.

((1-(3,5-Di-*tert*-butylphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl oxy)triisopropylsilane (2z)



2z was prepared as a colorless oil in 68% yield (117 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1z** (133 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.46 (petroleum ether/ethyl acetate = 20/1)

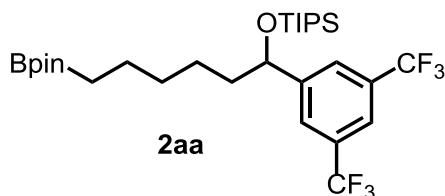
¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.21 (m, 1H), 7.15 – 7.08 (m, 2H), 4.69 (t, *J* = 6.2 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.73 – 1.59 (m, 1H), 1.43 – 1.34 (m, 2H), 1.31 (s, 18H), 1.29 – 1.25 (m, 4H), 1.23 (s, 12H), 1.07 – 0.84 (m, 21H), 0.74 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 150.0, 145.1, 120.8, 120.5, 82.9, 76.2, 41.1, 34.9, 32.7, 31.6, 25.4, 24.9, 24.1, 18.2, 12.5.

HRMS (ESI⁺) calcd for C₃₅H₆₆BO₃Si⁺ [M+H]⁺: 573.4874, found: 573.4880.

IR (neat, cm⁻¹): 2943, 2866, 1464, 1379, 1317, 1248, 1147, 1092, 1065, 882, 680.

((1-(3,5-Bis(trifluoromethyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triisopropylsilane (2aa)



2aa was prepared as a colorless oil in 86% yield (154 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1aa** (146 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.50 (petroleum ether/ethyl acetate = 20/1)

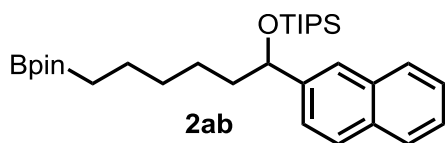
¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.72 (m, 3H), 4.90 (t, J = 5.8 Hz, 1H), 1.83 – 1.64 (m, 2H), 1.42 – 1.31 (m, 2H), 1.31 – 1.11 (m, 16H), 1.11 – 0.91 (m, 21H), 0.72 (t, J = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 148.4, 131.2 (q, J = 33.1 Hz), 126.2 (q, J = 3.9 Hz), 123.4 (q, J = 272.5 Hz), 121.0 – 120.5 (m), 82.9, 74.1, 40.5, 32.4, 24.8, 24.0, 23.9, 17.9, 17.8, 12.2.

HRMS (ESI⁺) calcd for C₂₉H₄₈BF₆O₃Si⁺ [M+H]⁺: 597.3370, found: 597.3372.

IR (neat, cm⁻¹): 1276, 1171, 1133, 1110, 682.

Triisopropyl((1-(naphthalen-2-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (2ab)



2ab was prepared as a colorless oil in 73% yield (112 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ab** (115 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.38 (petroleum ether/ethyl acetate = 20/1)

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.77 (m, 3H), 7.74 – 7.68 (m, 1H), 7.55 – 7.40

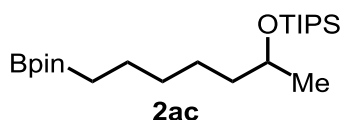
(m, 3H), 4.94 (t, $J = 6.9$ Hz, 1H), 1.93 – 1.71 (m, 2H), 1.42 – 1.28 (m, 2H), 1.28 – 1.18 (m, 16H), 1.13 – 0.93 (m, 21H), 0.73 (t, $J = 7.6$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 133.3, 132.9, 128.0, 127.8, 127.7, 125.8, 125.4, 124.9, 124.7, 82.9, 75.4, 40.9, 32.7, 24.9, 24.8, 24.1, 18.2, 12.5.

HRMS (ESI⁺) calcd for $\text{C}_{31}\text{H}_{52}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 511.3779, found: 511.3776.

IR (neat, cm^{-1}): 2932, 2865, 1378, 1371, 1145, 1091, 1064, 882, 744, 679, 478

Triisopropyl((7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-yl)oxy)silane (2ac)



2ac was prepared as a colorless oil in 81% yield (174 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ac** (153 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (6.4 mg, 0.025 mmol, 5 mol%), dcype (10.5 mg, 0.025 mmol, 5 mol%), and HBpin (96 mg, 0.75 mmol, 1.5 equiv) following **the typical procedure A**.

$R_f = 0.65$ (petroleum ether/ethyl acetate = 20/1)

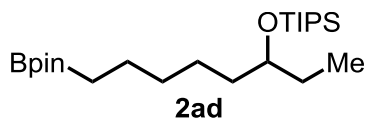
^1H NMR (400 MHz, CDCl_3) δ 3.96 – 3.84 (m, 1H), 1.56 – 1.36 (m, 4H), 1.35 – 1.26 (m, 4H), 1.24 (s, 12H), 1.13 (d, $J = 6.1$ Hz, 3H), 1.08 – 1.03 (m, 21H), 0.76 (t, $J = 7.8$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 83.2, 69.1, 40.4, 33.1, 25.6, 25.2, 24.5, 23.9, 18.6, 12.9.

HRMS (ESI⁺) calcd for $\text{C}_{22}\text{H}_{48}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 399.3466, found: 399.3466.

IR (neat, cm^{-1}): 2931, 2866, 1371, 1317, 1146, 1044, 882, 675.

Triisopropyl((8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-3-yl)oxy)silane (2ad)



2ad was prepared as a colorless oil in 90% yield (200 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ad** (160 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (6.4 mg, 0.025 mmol, 5 mol%), dcype (10.5 mg, 0.025 mmol, 5 mol%), and HBpin (96 mg, 0.75 mmol, 1.5 equiv) following **the typical procedure A**.

$R_f = 0.65$ (petroleum ether/ethyl acetate = 20/1)

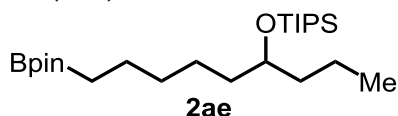
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.82 – 3.71 (m, 1H), 1.59 – 1.36 (m, 6H), 1.33 – 1.27 (m, 4H), 1.25 (s, 12H), 1.10 – 0.99 (m, 21H), 0.87 (t, $J = 7.5$ Hz, 3H), 0.78 (t, $J = 7.8$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 82.8, 73.3, 36.0, 32.8, 29.0, 24.8, 24.7, 24.0, 18.2, 12.7, 9.0.

HRMS (ESI⁺) calcd for $\text{C}_{23}\text{H}_{50}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 413.3622, found: 413.3622.

IR (neat, cm^{-1}): 2931, 2866, 1464, 1378, 1371, 1318, 1146, 1055, 1014, 882, 675.

Triisopropyl((9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-4-yl)oxy)silane (2ae)



2ae was prepared as a colorless oil in 81% yield (103 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ae** (90 mg, 0.3 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

$R_f = 0.60$ (petroleum ether/ethyl acetate = 20/1)

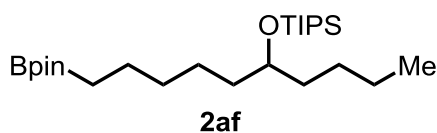
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.85 – 3.77 (m, 1H), 1.52 – 1.37 (m, 6H), 1.37 – 1.27 (m, 6H), 1.25 (s, 12H), 1.06 (d, $J = 2.1$ Hz, 21H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.78 (t, $J = 7.8$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 82.8, 72.2, 38.9, 36.7, 32.8, 24.8, 24.7, 24.1, 18.2, 18.1, 14.4, 12.7.

HRMS (ESI⁺) calcd for $\text{C}_{24}\text{H}_{52}\text{BO}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 427.3779, found: 427.3795.

IR (neat, cm^{-1}): 2958, 2932, 2866, 1379, 1371, 1318, 1147, 883, 675.

Triisopropyl((10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-5-yl)oxy)silane (2af)



2af was prepared as a colorless oil in 66% yield (87 mg, eluent: petroleum ether

/ethyl acetate = 100:1) from **1af** (132 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.60 (petroleum ether/ethyl acetate = 20/1)

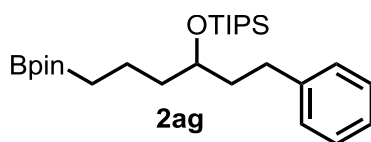
¹H NMR (400 MHz, CDCl₃) δ 3.86 – 3.75 (m, 1H), 1.52 – 1.38 (m, 6H), 1.36 – 1.27 (m, 8H), 1.25 (s, 12H), 1.11 – 1.02 (m, 21H), 0.89 (t, 3H), 0.78 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 82.8, 72.3, 36.6, 36.2, 32.8, 27.0, 24.8, 24.7, 24.1, 23.0, 18.2, 14.2, 12.7.

HRMS (ESI⁺) calcd for C₂₅H₅₄BO₃Si⁺ [M+H]⁺: 441.3930, found: 441.3933.

IR (neat, cm⁻¹): 2933, 2866, 1379, 1319, 1147, 1058, 883.

Triisopropyl((1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-yl)oxy)silane (2ag)



2ag was prepared as a colorless oil in 84% yield (115 mg, eluent: petroleum ether /ethyl acetate = 50:1) from **1ag** (99 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.50 (petroleum ether/ethyl acetate = 10/1)

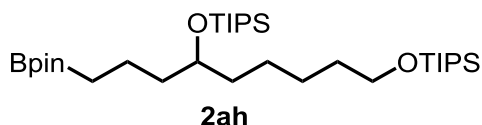
¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 3.94 – 3.84 (m, 1H), 2.76 – 2.60 (m, 2H), 1.92 – 1.70 (m, 2H), 1.65 – 1.53 (m, 2H), 1.53 – 1.38 (m, 2H), 1.25 (d, *J* = 1.0 Hz, 12H), 1.16 – 0.99 (m, 21H), 0.81 (t, *J* = 7.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 143.1, 128.5, 128.4, 125.7, 83.0, 71.9, 39.3, 38.4, 31.1, 25.0, 19.7, 18.4, 12.8.

HRMS (ESI⁺) calcd for C₂₇H₅₀BO₃Si⁺ [M+H]⁺: 461.3622, found: 461.3627.

IR (neat, cm⁻¹): 2942, 2866, 1464, 1379, 1318, 1146, 1092, 1062, 883, 699, 677.

3,3,12,12-Tetraisopropyl-2,13-dimethyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4,11-dioxo-3,12-disilatetradecane (2ah)



2ah was prepared as a colorless oil in 85% yield (153 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ah** (140 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.43 (petroleum ether/ethyl acetate = 20/1)

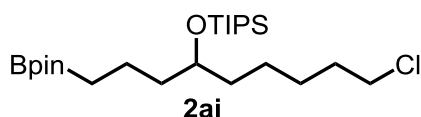
¹H NMR (400 MHz, CDCl₃) δ 3.83 – 3.75 (m, 1H), 3.66 (t, J = 6.7 Hz, 2H), 1.59 – 1.51 (m, 2H), 1.50 – 1.37 (m, 6H), 1.36 – 1.28 (m, 4H), 1.23 (s, 12H), 1.09 – 1.01 (m, 42H), 0.76 (t, J = 6.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 83.0, 72.3, 63.6, 39.5, 36.6, 33.3, 26.3, 25.0, 24.7, 19.6, 18.4, 18.2, 12.8, 12.1, 1.2.

HRMS (ESI⁺) calcd for C₃₃H₇₂BO₄Si₂⁺ [M+H]⁺: 599.5062, found: 599.5069.

IR (neat, cm⁻¹): 2941, 2866, 1379, 1146, 1100, 1059, 1013, 881, 797, 676, 657.

((9-Chloro-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-4-yl)oxy)triisopropylsilane (2ai)



2ai was prepared as a colorless oil in 71% yield (98 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ai** (100 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.40 (petroleum ether/ethyl acetate = 20/1)

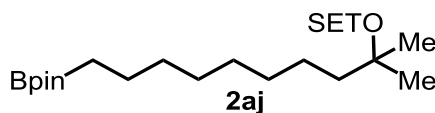
¹H NMR (400 MHz, CDCl₃) δ 3.83 – 3.75 (m, 1H), 3.52 (t, J = 6.8 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.55 – 1.30 (m, 10H), 1.23 (s, 12H), 1.10 – 0.97 (m, 21H), 0.81 – 0.72 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 83.0, 72.1, 45.3, 39.4, 36.3, 32.9, 27.4, 25.0, 24.0, 19.6, 18.4, 12.8.

HRMS (ESI⁺) calcd for C₂₄H₅₁BClO₃Si⁺ [M+H]⁺: 461.3389, found: 461.3386.

IR (neat, cm⁻¹): 2942, 2866, 1379, 1371, 1318, 1146, 886, 675.

Triethyl((2-methyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-2-yl)oxy)silane (2aj)



2aj was prepared as a colorless oil in 65% yield (80 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1aj** (85 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.52 (petroleum ether/ethyl acetate = 20/1)

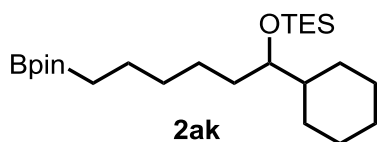
¹H NMR (400 MHz, CDCl₃) δ 1.43 – 1.36 (m, 4H), 1.33 – 1.21 (m, 22H), 1.17 (s, 6H), 0.93 (t, J = 7.9 Hz, 9H), 0.76 (t, J = 7.7 Hz, 2H), 0.55 (q, J = 7.9 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 83.0, 73.6, 45.3, 32.6, 30.4, 30.0, 29.8, 29.6, 25.0, 24.6, 24.2, 7.3, 7.0.

HRMS (ESI⁺) calcd for C₂₃H₅₀BO₃Si⁺ [M+H]⁺: 413.3622, found: 413.3620.

IR (neat, cm⁻¹): 2927, 2876, 1379, 1371, 1317, 1147, 1041, 743, 723.

((1-Cyclohexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)triethylsilane (2ak)



2ak was prepared as a colorless oil in 66% yield (84 mg, eluent: petroleum ether /ethyl acetate = 100:1) from **1ak** (89 mg, 0.3 mmol, 1.0 equiv), Co(acac)₂ (4.0 mg, 0.015 mmol, 5 mol%), dcype (6.3 mg, 0.015 mmol, 5 mol%), and HBpin (58 mg, 0.45 mmol, 1.5 equiv) following **the typical procedure A**.

R_f = 0.60 (petroleum ether/ethyl acetate = 20/1)

¹H NMR (400 MHz, CDCl₃) δ 3.46 – 3.40 (m, 1H), 1.79 – 1.60 (m, 6H), 1.47 – 1.33 (m, 6H), 1.33 – 1.21 (m, 16H), 1.20 – 1.01 (m, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.78 (t, J = 7.9 Hz, 2H), 0.60 (q, J = 7.9 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 83.0, 76.8, 43.4, 33.9, 33.0, 29.0, 28.5, 26.9, 26.7, 25.4,

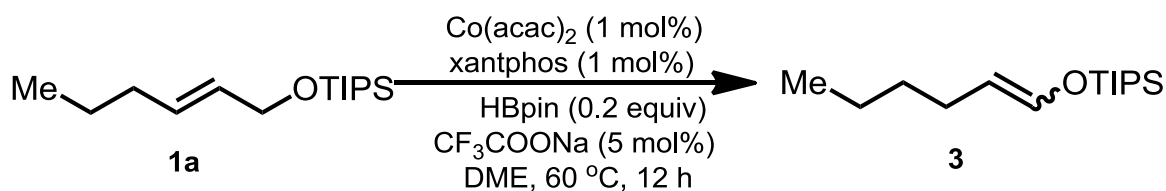
24.9, 24.2, 7.2, 5.4.

HRMS (ESI⁺) calcd for C₂₄H₅₀BO₃Si⁺ [M+H]⁺: 425.3622, found: 425.3618.

IR (neat, cm⁻¹): 2926, 2853, 1378, 1317, 1146, 1072, 1005, 969, 723.

V. Cobalt-Catalyzed Alkene Isomerization of Allylic Siloxanes

Typical procedure B of alkene isomerization of allylic siloxanes



(Hex-1-en-1-yloxy)triisopropylsilane (3)^[4]

In a glovebox, to an oven-dried 10-mL vial were added Co(acac)₂ (1.3 mg, 0.005mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), and anhydrous 1,2-dimethoxyethane (DME) (0.5 mL). The resulting solution was stirred for 10 min at room temperature, then HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) was added. The reaction mixture was stirred for 10 min, and CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%) was added. The reaction mixture was stirred for 10 min, followed by the addition of **1a** (128 mg, 0.5 mmol, 1.0 equiv) and DME (0.5 mL). The reaction mixture was sealed, removed from the glovebox, and stirred for 12 h at 60 °C in an oil bath. After completion, the reaction mixture was concentrated under vacuo, then filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to give the desired product **3** as colorless oil (110 mg, 86% yield).

R_f = 0.83 (petroleum ether)

Z/E = 2.1/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.29 – 6.24 (m, 1H), 4.45 – 4.32 (m, 1H), 1.93 – 1.84 (m, 2H), 1.40 – 1.25 (m, 4H), 1.15 – 1.07 (m, 21H), 0.94 – 0.86 (m, 3H).

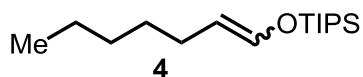
E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.34 – 6.29 (m, 1H), 5.0 – 4.96 (m, 1H), 2.19 – 2.05 (m, 2H), 1.40 – 1.25 (m, 4H), 1.15 – 1.07 (m, 21H), 0.94 – 0.86 (m, 3H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 139.0, 111.4, 110.2, 32.8, 32.1,

27.1, 23.4, 22.5, 22.3, 17.9, 17.8, 14.1, 14.0, 12.2, 12.1.

^{29}Si NMR (79.5 MHz, CDCl_3) δ 14.65, 14.47.

(Hept-1-en-1-yloxy)triisopropylsilane (4)^[4]



4 was prepared as a colorless oil in 77% yield (104 mg, eluent: petroleum ether) from **1b** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.83 (petroleum ether)

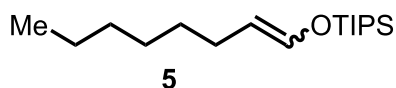
Z/E = 1.3/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.28 – 6.26 (m, 1H), 4.46 – 4.36 (m, 1H), 2.14 – 2.07 (m, 2H), 1.41 – 1.24 (m, 6H), 1.20 – 1.04 (m, 21H), 0.93 – 0.85 (m, 3H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.33 – 6.28 (m, 1H), 5.06 – 4.96 (m, 1H), 1.92 – 1.81 (m, 2H), 1.41 – 1.24 (m, 6H), 1.20 – 1.04 (m, 21H), 0.93 – 0.85 (m, 3H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 138.9, 111.3, 110.0, 31.6, 31.2, 30.1, 29.3, 27.2, 23.5, 22.6, 22.5, 17.8, 17.7, 14.0, 12.0, 11.9.

Triisopropyl(oct-1-en-1-yloxy)silane (5)^[4]



5 was prepared as a colorless oil in 77% yield (109 mg, eluent: petroleum ether) from **1c** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.65 (petroleum ether)

Z/E = 2.3/1

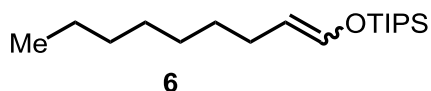
Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.28 – 6.26 (m, 1H), 4.44 – 4.35 (m, 1H), 2.15 – 2.06 (m, 2H), 1.39 – 1.23 (m, 8H), 1.20 – 1.03 (m, 21H), 0.93 – 0.84 (m, 3H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.33–6.29 (m, 1H), 5.05–4.96 (m, 1H),

1.93–1.82 (m, 2H), 1.39–1.23 (m, 8H), 1.20–1.03 (m, 21H), 0.93–0.84 (m, 3H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 139.0, 111.5, 110.2, 32.0, 31.9, 30.6, 29.8, 29.2, 28.9, 27.4, 23.7, 22.9, 17.9, 17.8, 14.3, 12.2, 12.1.

Triisopropyl(non-1-en-1-yloxy)silane (**6**)^[4]



6 was prepared as a colorless oil in 81% yield (121 mg, eluent: petroleum ether) from **1d** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following the typical procedure B.

R_f = 0.90 (petroleum ether)

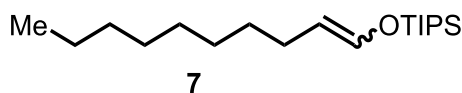
E/Z = 3.2/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.31 – 6.28 (m, 1H), 4.47 – 4.37 (m, 1H), 2.17 – 2.09 (m, 2H), 1.41 – 1.25 (m, 10H), 1.21 – 1.07 (m, 21H), 0.91 (t, J = 6.8 Hz, 3H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.35 – 6.31 (m, 1H), 5.09 – 4.97 (m, 1H), 1.94 – 1.87 (m, 2H), 1.41– 1.25 (m, 10H), 1.21 – 1.07 (m, 21H), 0.91 (t, J = 6.8 Hz, 3H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 139.0, 111.5, 110.2, 32.1, 30.7, 29.9, 29.5, 29.4, 29.3, 29.2, 27.4, 23.7, 22.9, 22.8, 17.9, 17.8, 14.3, 12.2, 12.1.

(Dec-1-en-1-yloxy)triisopropylsilane (**7**)^[4]



7 was prepared as a colorless oil in 68% yield (103 mg, eluent: petroleum ether) from **1e** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following the typical procedure B.

R_f = 0.85 (petroleum ether)

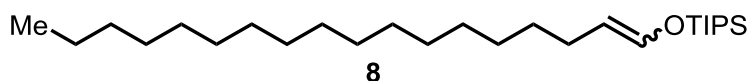
Z/E = 2.8/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.28 – 6.26 (m, 1H), 4.43 – 4.36 (m, 1H), 2.15 – 2.06 (m, 2H), 1.39 – 1.22 (m, 12H), 1.21 – 1.04 (m, 21H), 0.91 – 0.86 (m, 3H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.33 – 6.28 (m, 1H), 5.05 – 4.95 (m, 1H), 1.92 – 1.82 (m, 2H), 1.39 – 1.22 (m, 12H), 1.21 – 1.04 (m, 21H), 0.91 – 0.86 (m, 3H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 139.0, 111.5, 110.2, 32.1, 32.0, 30.7, 29.9, 29.7, 29.6, 29.2, 29.6, 29.5, 27.4, 23.7, 22.9, 22.8, 17.9, 17.8, 14.2, 12.2, 12.1.

Triisopropyl(octadec-1-en-1-yloxy)silane (**8**)^[4]



8 was prepared as a colorless oil in 71% yield (154 mg, eluent: petroleum ether) from **1f** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.89 (petroleum ether)

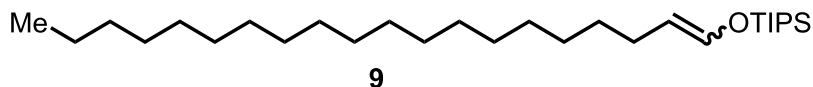
Z/E = 1.7/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.28 – 6.26 (m, 1H), 4.43 – 4.36 (m, 1H), 2.15 – 2.06 (m, 2H), 1.38 – 1.22 (m, 28H), 1.20 – 1.04 (m, 21H), 0.89 (t, J = 6.7 Hz, 3H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.32 – 6.28 (m, 1H), 5.05 – 4.96 (m, 1H), 1.92 – 1.84 (m, 2H), 1.38 – 1.22 (m, 28H), 1.20 – 1.04 (m, 21H), 0.89 (t, J = 6.7 Hz, 3H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 138.9, 111.3, 110.1, 32.0, 30.5, 29.8 – 29.7 (m, 19C), 29.6, 29.5 – 29.4 (m, 3C), 29.1, 27.3, 23.6, 22.7, 17.8, 17.7, 14.1, 12.1, 12.0.

(Icos-1-en-1-yloxy)triisopropylsilane (**9**)^[4]



9 was prepared as a colorless oil in 67% yield (151 mg, eluent: petroleum ether) from **1g** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%),

xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.90 (petroleum ether)

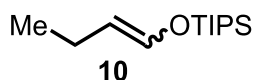
Z/E = 3.2/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.28 – 6.26 (m, 1H), 4.45 – 4.35 (m, 1H), 2.15 – 2.06 (m, 2H), 1.37 – 1.22 (m, 32H), 1.19 – 1.05 (m, 21H), 0.89 (t, *J* = 6.7 Hz, 3H).

E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.33 – 6.28 (m, 1H), 5.06 – 4.95 (m, 1H), 1.93 – 1.83 (m, 2H), 1.37 – 1.22 (m, 32H), 1.19 – 1.05 (m, 21H), 0.89 (t, *J* = 6.7 Hz, 3H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 139.0, 111.5, 110.2, 32.1, 30.7, 30.0 – 29.9 (m, 22C), 29.8, 29.7, 29.6 – 29.5 (m, 3C), 29.2, 27.4, 23.7, 22.9, 17.9, 17.8, 14.3, 12.2, 12.1.

(But-1-en-1-yloxy)triisopropylsilane (10)^[4]



10 was prepared as a colorless oil in 79% yield (106 mg, eluent: petroleum ether) from **1h** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.79 (petroleum ether)

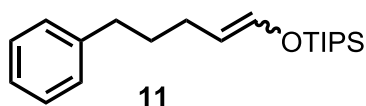
Z/E = 1/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.26 – 6.22 (m, 1H), 4.49 – 4.32 (m, 1H), 2.18 – 2.06 (m, 2H), 1.21 – 1.03 (m, 21H), 0.99 – 0.93 (m, 3H).

E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.35 – 6.29 (m, 1H), 5.11 – 4.96 (m, 1H), 1.97 – 1.85 (m, 2H), 1.21 – 1.03 (m, 21H), 0.99 – 0.93 (m, 3H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 138.4, 113.0, 111.8, 20.6, 17.8, 17.7, 17.0, 15.1, 14.2, 12.1, 12.0.

Triisopropyl((5-phenylpent-1-en-1-yl)oxy)silane (11)



11 was prepared as a colorless oil in 58% yield (92 mg, eluent: petroleum ether: ethyl acetate = 100:1) from **1k** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.73 (petroleum ether)

Z/E = 1.9/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 6.35 – 6.33 (m, 1H), 4.51 – 4.43 (m, 1H), 2.66 (m, 2H), 2.24 – 2.17 (m, 2H), 1.75 – 1.63 (m, 2H), 1.19 – 1.08 (m, 21H).

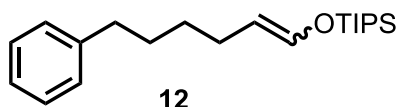
E isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 6.39 – 6.35 (m, 1H), 5.11 – 5.03 (m, 1H), 2.66 (m, 2H), 2.02 – 1.92 (m, 2H), 1.75 – 1.63 (m, 2H), 1.19 – 1.08 (m, 21H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 143.1, 142.8, 141.1, 139.5, 128.6, 128.4, 128.3, 125.7, 125.6, 110.8, 109.5, 35.8, 35.4, 32.4, 31.7, 27.1, 23.5, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for C₂₀H₃₅OSi⁺ [M+H]⁺: 319.2457, found: 319.2460.

IR (neat, cm⁻¹): 2942, 2866, 1656, 1173, 1114, 882, 795, 743, 697, 684, 664.

Triisopropyl((6-phenylhex-1-en-1-yl)oxy)silane (**12**)^[4]



12 was prepared as a colorless oil in 56% yield (92 mg, eluent: petroleum ether: ethyl acetate = 100:1) from **11** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.42 (petroleum ether)

Z/E = 1/1

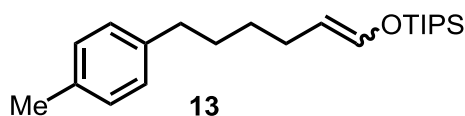
Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.16 (m, 5H), 6.36 – 6.32 (m, 1H),

4.45 – 4.38 (m, 1H), 2.64 (m, 2H), 2.23 – 2.13 (m, 2H), 1.74 – 1.59 (m, 2H), 1.48 – 1.36 (m, 2H), 1.20 – 1.09 (m, 21H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.16 (m, 5H), 6.32 – 6.28 (m, 1H), 5.08 – 4.99 (m, 1H), 2.64 (m, 2H), 2.00 – 1.89 (m, 2H), 1.74 – 1.59 (m, 2H), 1.48 – 1.36 (m, 2H), 1.20 – 1.09 (m, 21H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 142.9, 140.8, 139.3, 128.6, 128.5, 128.3, 128.2, 125.7, 125.6, 111.1, 109.8, 36.0, 35.9, 31.3, 31.0, 30.3, 29.4, 27.2, 23.5, 17.9, 17.8, 12.2, 12.1.

Triisopropyl((6-(*p*-tolyl)hex-1-en-1-yl)oxy)silane (13**)^[4]**



13 was prepared as a colorless oil in 50% yield (86 mg, eluent: petroleum ether: ethyl acetate = 100:1) from **1aI** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following the typical procedure B.

R_f = 0.39 (petroleum ether)

E/Z = 1/1

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.16 – 7.07 (m, 4H), 6.33 – 6.30 (m, 1H), 4.51 – 4.37 (m, 1H), 2.61 (m, 2H), 2.36 (s, 3H), 2.24 – 2.13 (m, 2H), 1.73 – 1.58 (m, 2H), 1.51 – 1.37 (m, 2H), 1.25 – 1.02 (m, 21H).

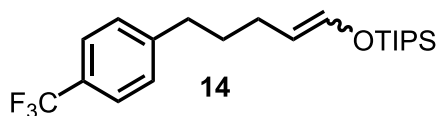
E isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.16 – 7.07 (m, 4H), 6.38 – 6.33 (m, 1H), 5.08 – 4.99 (m, 1H), 2.61 (m, 2H), 2.36 (s, 3H), 2.01 – 1.90 (m, 2H), 1.73 – 1.58 (m, 2H), 1.51 – 1.37 (m, 2H), 1.25 – 1.02 (m, 21H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 140.0, 139.9, 139.2, 135.1, 135.0, 129.1, 129.0, 128.4, 128.4, 111.2, 109.9, 35.5, 35.4, 31.4, 31.2, 30.3, 29.4, 27.3, 23.5, 21.1, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for $\text{C}_{22}\text{H}_{39}\text{OSi}^+$ [$\text{M}+\text{H}$]⁺: 347.2770, found: 347.2769.

IR (neat, cm^{-1}): 2927, 2866, 1660, 1463, 1170, 1115, 1065, 883, 805, 684, 664.

Triisopropyl((5-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)oxy)silane (14)^[4]



14 was prepared as a colorless oil in 62% yield (116 mg, eluent: petroleum ether: ethyl acetate = 100:1) from **1m** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.51 (petroleum ether)

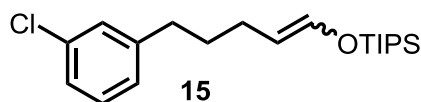
Z/E = 2.5/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.49 (m, 2H), 7.32 – 7.25 (m, 2H), 6.33 – 6.30 (m, 1H), 4.47 – 4.39 (m, 1H), 2.73 – 2.63 (m, 2H), 2.21 – 2.11 (m, 2H), 1.75 – 1.63 (m, 2H), 1.14 – 1.03 (m, 21H).

E isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.49 (m, 2H), 7.32 – 7.25 (m, 2H), 6.37 – 6.33 (m, 1H), 5.10 – 4.95 (m, 1H), 2.73 – 2.63 (m, 2H), 1.99 – 1.89 (m, 2H), 1.75 – 1.63 (m, 2H), 1.22 – 0.98 (m, 21H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 147.0, 146.7, 141.2, 139.6, 128.8, 128.7, 128.0 (dd, *J* = 32.2, 10.6 Hz), 125.2 – 125.0 (m), 124.4 (q, *J* = 270.0 Hz), 124.4 (q, *J* = 270.0 Hz), 110.3, 108.9, 35.4, 35.1, 31.9, 31.2, 26.8, 23.1, 17.8, 17.7, 12.0, 11.9.

((5-(3-Chlorophenyl)pent-1-en-1-yl)oxy)triisopropylsilane (15)



15 was prepared as a colorless oil in 73% yield (154 mg, eluent: petroleum ether: ethyl acetate = 100:1) from **1am** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.52 (petroleum ether)

Z/E = 1.3/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.31 (m, 1H), 7.25 – 7.09 (m, 3H),

6.36 – 6.32 (m, 1H), 4.53 – 4.43 (m, 1H), 2.82 – 2.71 (m, 2H), 2.28 – 2.17 (m, 2H), 1.76 – 1.62 (m, 2H), 1.22 – 1.07 (m, 21H).

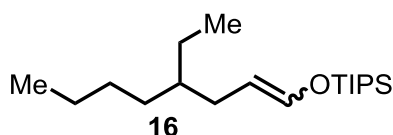
E isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.31 (m, 1H), 7.25 – 7.09 (m, 3H), 6.42 – 6.36 (m, 1H), 5.13 – 5.02 (m, 1H), 2.82 – 2.71 (m, 2H), 2.08 – 1.95 (m, 2H), 1.76 – 1.62 (m, 2H), 1.22 – 1.07 (m, 21H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 140.5, 140.3, 139.6, 134.1, 130.5, 130.5, 129.5, 129.4, 127.2, 127.1, 126.8, 126.7, 110.7, 109.3, 33.5, 33.2, 30.6, 29.8, 27.2, 23.5, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for $\text{C}_{20}\text{H}_{34}\text{ClOSi}^+$ $[\text{M}+\text{H}]^+$: 353.2067, found: 353.2063.

IR (neat, cm^{-1}): 2943, 2866, 1474, 1463, 1176, 1056, 883, 750, 681.

((4-Ethyl-oct-1-en-1-yl)oxy)triisopropylsilane (**16**)



16 was prepared as a colorless oil in 72% yield (113 mg, eluent: petroleum ether) from **1an** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following the typical procedure B.

R_f = 0.87 (petroleum ether)

Z/E = 2.3/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.35 – 6.33 (m, 1H), 4.44 – 4.35 (m, 1H), 2.16 – 2.08 (m, 2H), 1.36 – 1.15 (m, 9H), 1.14 – 1.07 (m, 21H), 0.95 – 0.83 (m, 6H).

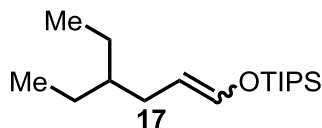
E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.32 – 6.29 (m, 1H), 5.03 – 4.93 (m, 1H), 1.91 – 1.84 (m, 2H), 1.36 – 1.15 (m, 9H), 1.14 – 1.07 (m, 21H), 0.95 – 0.83 (m, 6H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 139.6, 109.2, 108.1, 39.8, 39.7, 33.2, 32.7, 30.7, 29.4, 29.2, 27.1, 26.2, 25.8, 23.3, 23.2, 18.2, 17.9, 14.3, 14.2, 12.2, 12.1, 11.3, 11.1.

HRMS (ESI⁺) calcd for $\text{C}_{19}\text{H}_{41}\text{OSi}^+$ $[\text{M}+\text{H}]^+$: 313.2927, found: 313.2925.

IR (neat, cm^{-1}): 2958, 2926, 2867, 1655, 1463, 1168, 1095, 996, 882, 684, 663.

((4-Ethylhex-1-en-1-yl)oxy)triisopropylsilane (17)



17 was prepared as a colorless oil in 65% yield (93 mg, eluent: petroleum ether) from **1j** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.89 (petroleum ether)

Z/E = 2.5/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.33 – 6.30 (m, 1H), 4.42 – 4.32 (m, 1H), 2.16 – 2.04 (m, 2H), 1.36 – 1.22 (m, 4H), 1.20 – 1.17 (m, 1H), 1.17 – 1.05 (m, 21H), 0.89 – 0.82 (m, 6H).

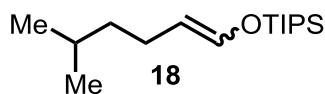
E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.30 – 6.26 (m, 1H), 5.03 – 4.90 (m, 1H), 1.89 – 1.82 (m, 2H), 1.36 – 1.22 (m, 4H), 1.20 – 1.17 (m, 1H), 1.17 – 1.05 (m, 21H), 0.89 – 0.82 (m, 6H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.6, 109.3, 108.1, 41.4, 41.3, 30.3, 26.7, 25.8, 25.3, 17.9, 17.8, 12.2, 12.1, 11.4, 11.2.

HRMS (ESI⁺) calcd for C₁₇H₃₇OSi⁺ [M+H]⁺: 285.2614, found: 285.2618.

IR (neat, cm⁻¹): 2960, 2944, 2868, 1656, 1463, 1170, 1091, 997, 882, 684, 664.

Triisopropyl((5-methylhex-1-en-1-yl)oxy)silane (18)^[13]



18 was prepared as a colorless oil in 78% yield (106 mg, eluent: petroleum ether) from **1i** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.92 (petroleum ether)

Z/E = 2.4/1

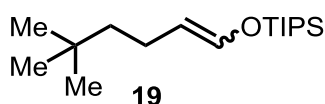
Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.28 – 6.24 (m, 1H), 4.43 – 4.34 (m, 1H),

2.17 – 2.07 (m, 2H), 1.63 – 1.49 (m, 1H), 1.29 – 1.21 (m, 2H), 1.21 – 1.00 (m, 21H), 0.92 – 0.85 (m, 6H).

E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.34 – 6.29 (m, 1H), 5.05 – 4.95 (m, 1H), 1.93 – 1.85 (m, 2H), 1.63 – 1.49 (m, 1H), 1.29 – 1.21 (m, 2H), 1.21 – 1.00 (m, 21H), 0.92 – 0.85 (m, 6H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 138.9, 111.6, 110.3, 39.9, 39.1, 27.8, 27.5, 25.3, 22.7, 22.6, 21.7, 17.9, 17.8, 12.2, 12.1.

((5,5-Dimethylhex-1-en-1-yl)oxy)triisopropylsilane (19)



19 was prepared as a colorless oil in 84% yield (119 mg, eluent: petroleum ether) from **1ao** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF_3COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.85 (petroleum ether)

Z/E = 3.9/1

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.28 – 6.22 (m, 1H), 4.45 – 4.36 (m, 1H), 2.13 – 2.03 (m, 2H), 1.28 – 1.20 (m, 2H), 1.18 – 1.04 (m, 21H), 0.89 (s, 9H).

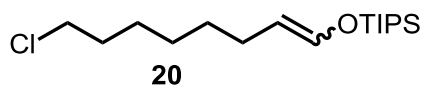
E isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.34 – 6.29 (m, 1H), 5.04 – 4.95 (m, 1H), 1.92 – 1.79 (m, 2H), 1.28 – 1.20 (m, 2H), 1.18 – 1.04 (m, 21H), 0.89 (s, 9H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 138.8, 112.2, 110.9, 45.3, 44.2, 30.6, 30.5, 29.5, 29.4, 22.8, 19.2, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for $\text{C}_{17}\text{H}_{37}\text{OSi}^+$ [$\text{M}+\text{H}$]⁺: 285.2614, found: 285.2613.

IR (neat, cm^{-1}): 2946, 2867, 1655, 1465, 1173, 1108, 1061, 996, 882, 683, 664.

((9-Chloronon-1-en-1-yl)oxy)triisopropylsilane (20)



20 was prepared as a colorless oil in 53% yield (85 mg, eluent: petroleum ether) from **1ap** (128 mg, 0.5 mmol, 1.0 equiv), $\text{Co}(\text{acac})_2$ (1.3 mg, 0.005 mmol, 1 mol%),

xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.62 (petroleum ether)

Z/E = 1/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.28 – 6.25 (m, 1H), 4.43 – 4.33 (m, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.15 – 2.05 (m, 2H), 1.82 – 1.70 (m, 2H), 1.49 – 1.24 (m, 6H), 1.21 – 1.02 (m, 21H).

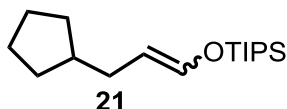
E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.34 – 6.28 (m, 1H), 5.02 – 4.94 (m, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.82 – 1.70 (m, 2H), 1.49 – 1.24 (m, 6H), 1.21 – 1.02 (m, 21H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 139.3, 111.1, 109.8, 45.3, 45.2, 32.8, 32.7, 30.4, 29.6, 28.7, 28.4, 27.3, 26.9, 26.8, 23.5, 17.9, 17.8, 12.1, 12.0.

HRMS (ESI⁺) calcd for C₁₇H₃₆ClOSi⁺ [M+H]⁺: 319.2224, found: 319.2216.

IR (neat, cm⁻¹): 2931, 2866, 1660, 1464, 1169, 1113, 1069, 882, 800, 683, 656.

((3-Cyclopentylprop-1-en-1-yl)oxy)triisopropylsilane (**21**)



21 was prepared as a colorless oil in 58% yield (82 mg, eluent: petroleum ether) from **1aq** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.92 (petroleum ether)

Z/E = 2.2/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.29 – 6.26 (m, 1H), 4.46 – 4.38 (m, 1H), 2.15 – 2.07 (m, 2H), 1.85 – 1.76 (m, 1H), 1.76 – 1.67 (m, 2H), 1.65 – 1.55 (m, 2H), 1.55 – 1.45 (m, 2H), 1.20 – 1.05 (m, 23H).

E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.33 – 6.29 (m, 1H), 5.06 – 4.97 (m, 1H), 1.91 – 1.86 (m, 2H), 1.85 – 1.76 (m, 1H), 1.76 – 1.67 (m, 2H), 1.65 – 1.55 (m, 2H), 1.55 – 1.45 (m, 2H), 1.20 – 1.05 (m, 23H).

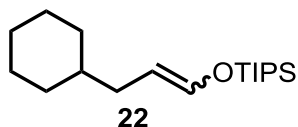
Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 139.1, 110.8, 109.3, 40.9, 40.4,

33.7, 32.4, 32.3, 29.7, 25.4, 25.3, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for C₁₇H₃₅OSi⁺ [M+H]⁺: 283.2457, found: 283.2450.

IR (neat, cm⁻¹): 2944, 2867, 1656, 1464, 1172, 1105, 1070, 1014, 882, 684, 664.

((3-Cyclohexylprop-1-en-1-yl)oxy)triisopropylsilane (22)



22 was prepared as a colorless oil in 77% yield (115 mg, eluent: petroleum ether) from **1ar** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg, 0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

R_f = 0.86 (petroleum ether)

Z/E = 2.1/1

Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.31 – 6.29 (m, 1H), 4.45 – 4.33 (m, 1H), 2.04 – 1.95 (m, 2H), 1.75 – 1.60 (m, 5H), 1.29 – 1.17 (m, 4H), 1.16 – 1.02 (m, 21H), 0.96 – 0.84 (m, 2H).

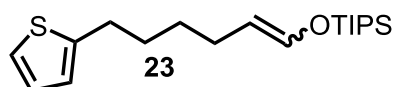
E isomer: ¹H NMR (400 MHz, CDCl₃) δ 6.29 – 6.24 (m, 1H), 5.04 – 4.95 (m, 1H), 1.81 – 1.75 (m, 2H), 1.75 – 1.60 (m, 5H), 1.29 – 1.17 (m, 4H), 1.16 – 1.02 (m, 21H), 0.96 – 0.84 (m, 2H).

Z/E mixture: ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 139.4, 109.7, 108.4, 38.8, 38.5, 35.3, 33.4, 33.2, 31.5, 26.9, 26.8, 26.6, 26.5, 17.9, 17.8, 12.2, 12.1.

HRMS (ESI⁺) calcd for C₁₈H₃₇OSi⁺ [M+H]⁺: 297.2614, found: 297.2616.

IR (neat, cm⁻¹): 2922, 2867, 2852, 1655, 1107, 1069, 882, 684, 665.

Triisopropyl((6-(thiophen-2-yl)hex-1-en-1-yl)oxy)silane (23)



23 was prepared as a yellow oil in 56% yield (95 mg, eluent: petroleum ether: *ethyl acetate*=100:1) from **1as** (128 mg, 0.5 mmol, 1.0 equiv), Co(acac)₂ (1.3 mg, 0.005 mmol, 1 mol%), xantphos (2.8 mg, 0.005 mmol, 1 mol%), CF₃COONa (3.4 mg,

0.025 mmol, 5 mol%), and HBpin (12.8 mg, 0.1 mmol, 0.2 equiv) following **the typical procedure B**.

$R_f = 0.60$ (petroleum ether)

$Z/E = 1.9/1$

Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.15 – 7.06 (m, 1H), 6.96 – 6.88 (m, 1H), 6.81 – 6.75 (m, 1H), 6.31 – 6.28 (m, 1H), 4.45 – 4.35 (m, 1H), 2.89 – 2.79 (m, 2H), 2.22 – 2.11 (m, 2H), 1.78 – 1.62 (m, 2H), 1.50 – 1.38 (m, 2H), 1.22 – 1.01 (m, 21H).

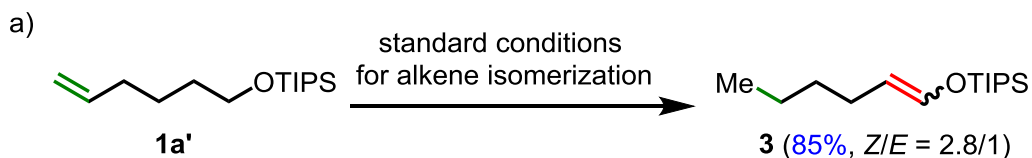
E isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.15 – 7.06 (m, 1H), 6.96 – 6.88 (m, 1H), 6.81 – 6.75 (m, 1H), 6.36 – 6.31 (m, 1H), 5.05 – 4.97 (m, 1H), 2.89 – 2.79 (m, 2H), 1.99 – 1.89 (m, 2H), 1.78 – 1.62 (m, 2H), 1.50 – 1.38 (m, 2H), 1.22 – 1.01 (m, 21H).

Z/E mixture: ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 145.8, 140.9, 139.4, 126.7, 126.6, 124.1, 124.0, 122.9, 122.8, 110.9, 109.6, 31.5, 31.3, 30.1, 29.9, 29.2, 27.1, 23.4, 17.9, 17.8, 17.7, 12.2, 12.1.

HRMS (ESI⁺) calcd for $\text{C}_{19}\text{H}_{35}\text{OSSi}^+$ $[\text{M}+\text{H}]^+$: 339.2172, found: 339.2181.

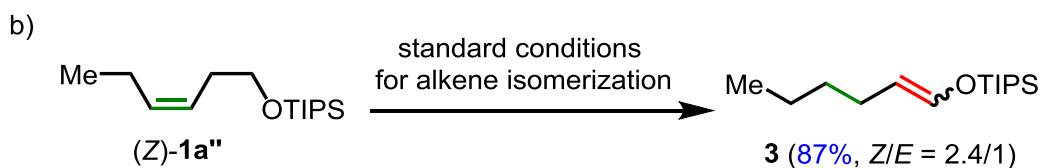
IR (neat, cm^{-1}): 2937, 2868, 1654, 1462, 1108, 884, 688.

Further investigation of substrate scope of alkene isomerization

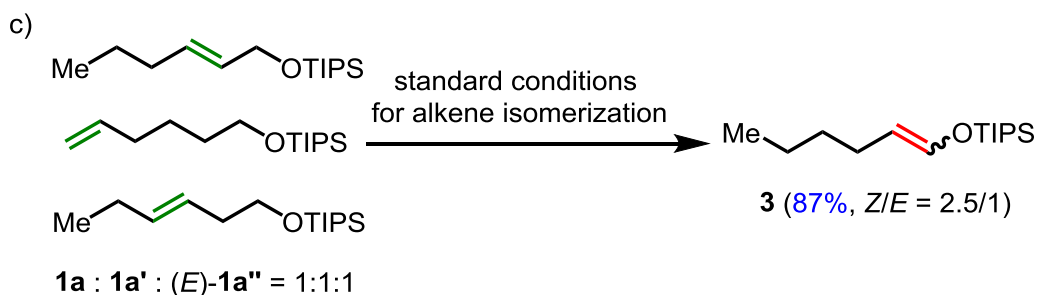


In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (0.8 mg, 0.003 mmol, 1 mol%), xantphos (1.7 mg, 0.003 mmol, 1 mol%) and anhydrous 1,2-dimethoxyethane (DME) (0.5 mL). The resulting solution was stirred for 10 min at room temperature, then HBpin (7.7 mg, 0.06 mmol, 0.2 equiv) was added and the reaction mixture was stirred for 10 min. and $\text{CF}_3\text{CO}_2\text{Na}$ (2.1 mg, 0.015 mmol, 5 mol%) was added and the reaction mixture was stirred for 10 min. followed by the addition of **1a'** (76.8 mg, 0.3 mmol) and 1,2-dimethoxyethane (DME) (0.5 mL). The reaction mixture was sealed, removed from the glovebox and stirred for 12 h at 60 °C in an oil bath. After completion, the reaction mixture was concentrated under vacuo, then filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to give the desired product **3** (85%

yield, Z/E = 2.8/1) as a colorless oil. The ratio of Z/E were determined by ^1H NMR using dibromomethane as the internal standard.



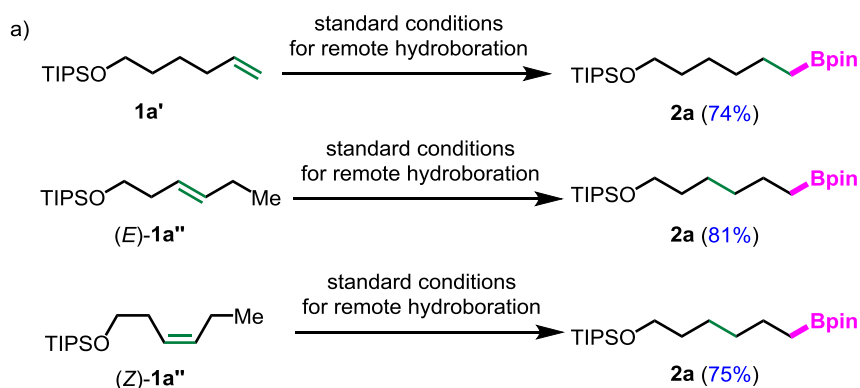
In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (0.8 mg, 0.003 mmol, 1 mol%), xantphos (1.7 mg, 0.003 mmol, 1 mol%) and anhydrous 1,2-dimethoxyethane (DME) (0.5 mL). The resulting solution was stirred for 10 min at ambient temperature, then HBpin (7.7 mg, 0.06 mmol, 0.2 equiv) was added and the reaction mixture was stirred for 10 min. and CF_3COONa (2.1 mg, 0.015 mmol, 5 mol%) was added and the reaction mixture was stirred for 10 min. followed by the addition of **(Z)-1a''** (76.8 mg, 0.3 mmol) and 1,2-dimethoxyethane (DME) (0.5 mL). The reaction mixture was sealed, removed from the glovebox and stirred for 12 h at 60 °C in an oil bath. After completion, the reaction mixture was concentrated under vacuo, then filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to give the desired product **3** (87% yield, Z/E = 2.4/1) as a colorless oil. The ratio of Z/E were determined by ^1H NMR using dibromomethane as the internal standard.



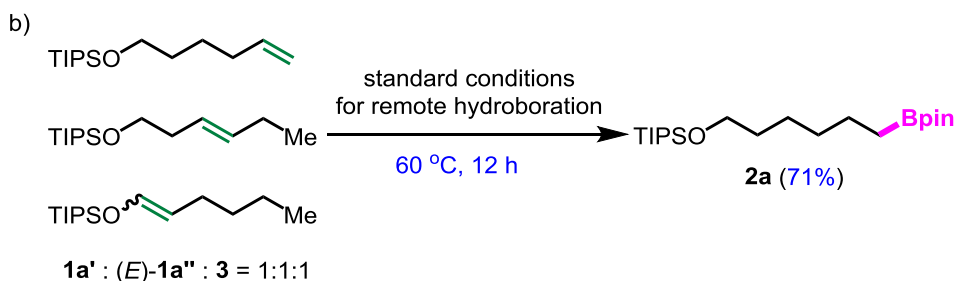
In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (0.8 mg, 0.003 mmol, 1 mol%), xantphos (1.7 mg, 0.003 mmol, 1 mol%) and anhydrous 1,2-dimethoxyethane (DME) (0.5 mL). The resulting solution was stirred for 10

min at ambient temperature, then HBpin (7.7 mg, 0.06 mmol, 0.2 equiv) was added and the reaction mixture was stirred for 10 min. and CF₃CO₂Na (2.1 mg, 0.015 mmol, 5 mol%) was added and the reaction mixture was stirred for 10 min. followed by the addition of **1a** (25.6 mg, 0.1 mmol), **1a'** (25.6 mg, 0.1 mmol), (*E*)-**1a''** (25.6 mg, 0.1 mmol) and 1,2-dimethoxyethane (DME) (0.5 mL). The reaction mixture was sealed, removed from the glovebox and stirred for 12 h at 60 °C in an oil bath. After completion, the reaction mixture was concentrated under vacuo, then filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to give the desired product **3** (87% yield, Z/E = 2.5/1) as colorless oil. The ratio of Z/E were determined by ¹H NMR using dibromomethane as the internal standard.

VI. Control Experiments and Plausible Catalytic Cycle



In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (0.8 mg, 0.003 mmol, 1 mol%), dcype (1.3 mg, 0.003 mmol, 1 mol%), and anhydrous octane (0.5 mL). The resulting solution was stirred for 5 min at room temperature, then HBpin (57.6 mg, 0.45 mmol, 1.5 equiv) was added. The reaction mixture was stirred for 5 min, followed by the addition of **1a'** or **(E)-1a''** or **(Z)-1a''** (76.8 mg, 0.3 mmol, 1.0 equiv) and octane (0.5 mL). The reaction mixture was sealed, removed from the glovebox, and stirred at room temperature for 4 h. After completion, the reaction was filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether: ethyl acetate = 100:1) to give the desired product **2a**.



In a glovebox, to an oven-dried 10-mL vial were added $\text{Co}(\text{acac})_2$ (0.8 mg, 0.003 mmol, 1 mol%), dcype (1.3 mg, 0.003 mmol, 1 mol%) and anhydrous octane (0.5 mL). The resulting solution was stirred for 5 min at room temperature, then HBpin (57.6 mg, 0.45 mmol, 1.5 equiv) was added and the reaction mixture was stirred for 5 min. followed by the addition of **1a'** (25.6 mg, 0.1 mmol), **(E)-1a''** (25.6 mg, 0.1 mmol), **3** (25.6 mg, 0.1 mmol) and octane (0.5 mL). The reaction mixture was sealed, removed from the glovebox and stirred for 12 h at 60 °C in an oil bath.

After completion, the reaction was filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to give the **2a** (82 mg, 71% yield).

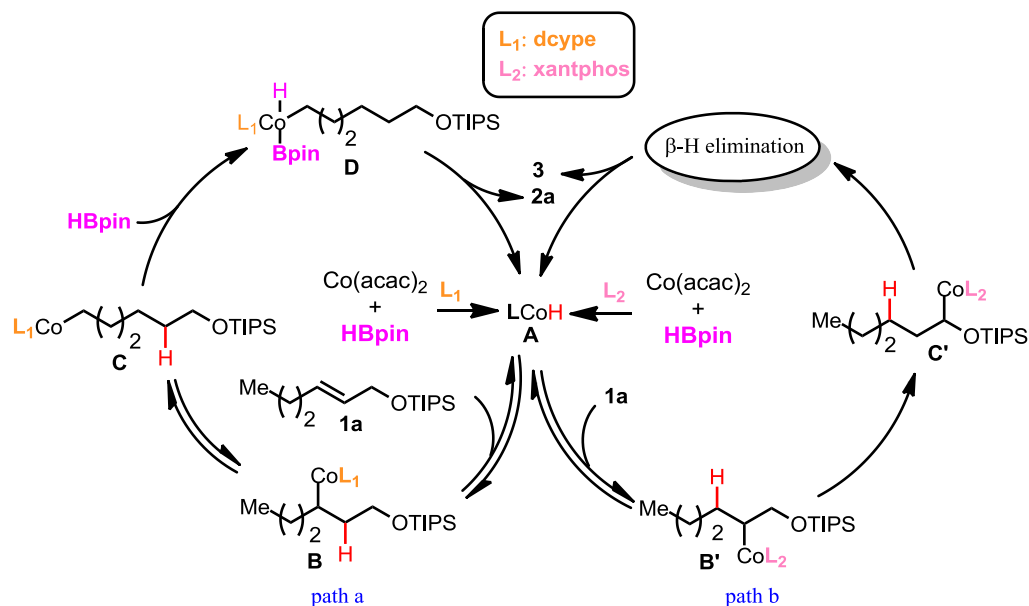
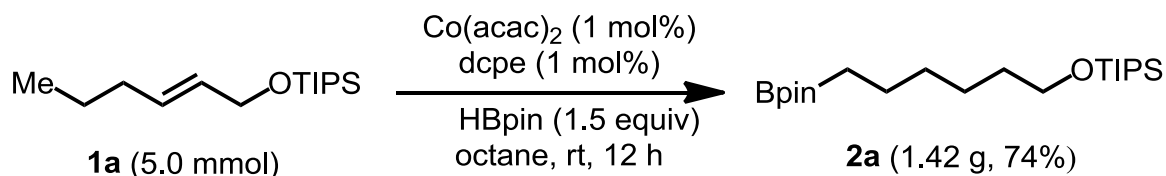


Figure S1 Plausible catalytic cycle.

Based on the observed results and previous reports, we proposed a plausible catalytic cycle. (Figure S1). For the remote hydroboration, the activation of $\text{Co}(\text{acac})_2$ with HBpin in the presence of dcype (L_1) generates a cobalt hydride species $\text{L}_1\text{Co-H}$ (**A**). Then allylic siloxane **1a** undergoes insertion into $\text{L}_1\text{Co-H}$ to form an alkyl cobalt species (**B**). The following β -H elimination and reinsertion result in the formation of species **C**. Finally, species **C** undergoes metathesis with HBpin to release the borylated product **2a** and regenerates cobalt hydride species **A**. For the alkene isomerization, cobalt hydride species $\text{L}_2\text{Co-H}$ (**A**) reacted with **1a** to afford cobalt species (**B'**), which then follows β -H elimination and reinsertion to give the intermediate species **C'**. Final β -H elimination affords silyl enol ethers **3** and regenerates cobalt hydride species **A**.

VII. Gram-Sale Catalytic Reaction and Product Transformations

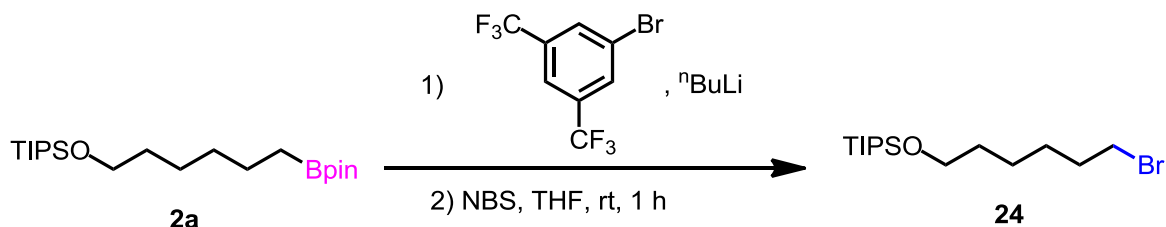
Gram-Sale Catalytic Reaction



In a glovebox, to an oven-dried round-bottom flask were added $\text{Co}(\text{acac})_2$ (13.0 mg, 0.05 mmol, 1 mol%), dcpe (22.0 mg, 0.05 mmol, 1 mol%) and anhydrous octane (5 mL). The resulting solution was stirred for 5 min at room temperature, then HBpin (960 mg, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was stirred for 5 min, followed by the addition of **1a** (1.28 g, 5.0 mmol, 1.0 equiv) and octane (5 mL). The reaction mixture was sealed, removed from the glovebox, and stirred at room temperature for 4 h. After completion, the reaction was filtered through a silica gel pad with ethyl acetate and concentrated under vacuo. The residue was purified by silica gel flash chromatography (eluent: petroleum ether: ethyl acetate = 100:1) to give the desired product **2a** (1.42 g, 74%) as colorless oil.

Product Transformations

Synthesis of Compound **24**^[4,18]



To a solution of 3,5-bis(trifluoromethyl)-1-bromobenzene (132 mg, 0.45 mmol, 1.5 equiv) in THF (1.5 mL) at -78°C was dropwise added $n\text{BuLi}$ (0.18 mL, 2.5 M in hexanes, 0.45 mmol). The mixture was stirred at -78°C for 1 h, and then a solution of compound **2a** (115.2 mg, 0.3 mmol, 1.0 equiv) in THF (1.5 mL) was added. The reaction mixture was allowed to stir at -78°C for 30 min and at room temperature for 30 min. The resulting solution was added a solution of NBS (82 mg, 0.45 mmol, 1.5 equiv) in THF (1.5 mL) dropwise. Upon completion of the reaction, the reaction mixture was quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ (aq.), extracted with ethyl

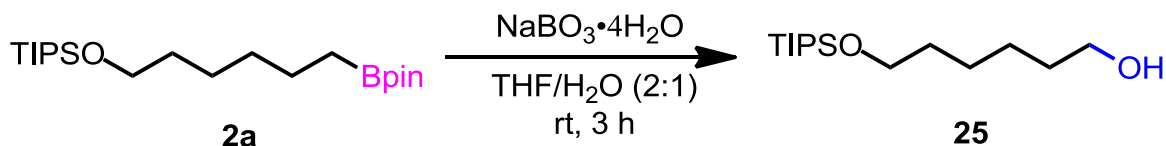
acetate, dried over MgSO_4 , filtered, and concentrated under vacuo. The resulting residue was purified by silica gel flash column chromatography (eluent: petroleum ether / dichloromethane = 20:1) to give the desired product **24** (84 mg, 83% yield) as colorless oil.

R_f = 0.33 (petroleum ether).

^1H NMR (400 MHz, CDCl_3) δ 3.68 (t, J = 6.4 Hz, 2H), 3.40 (t, J = 6.9 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.61 – 1.49 (m, 2H), 1.49 – 1.33 (m, 4H), 1.13 – 1.00 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 63.4, 34.0, 33.0, 32.9, 28.1, 25.2, 18.2, 12.1.

Synthesis of Compound **25**^[4,19]

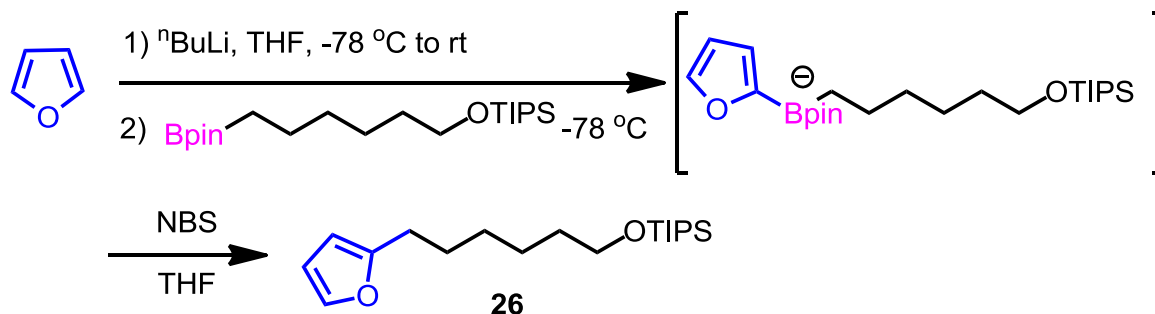


To a solution of **2a** (115 mg, 0.3 mmol, 1.0 equiv) in THF/ H_2O (4.5 mL, 2:1(v/v)) was added sodium perborate (238 mg, 1.5 mmol, 5.0 equiv). The reaction mixture was stirred vigorously for 3 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 20:1) to give the desired product **25** (82 mg, 99% yield) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 3.70 – 3.58 (m, 4H), 1.63 (br, 1H), 1.60 – 1.49 (m, 4H), 1.44 – 1.30 (m, 4H), 1.18 – 0.93 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 63.3, 62.9, 32.9, 32.7, 25.6, 25.5, 18.0, 12.0.

Synthesis of Compound **26**^[20]



A solution of furan (22 μ L, 0.36 mmol, 1.2 equiv) in THF (1.0 mL) was cooled to -78 $^{\circ}$ C and treated with n BuLi (0.15 mL, 0.36 mmol, 1.2 equiv, 1.6 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 $^{\circ}$ C and **2a** (115 mg, 0.3 mmol, 1.0 equiv) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred at -78 $^{\circ}$ C for 1 h. A solution of NBS (0.36 mmol, 1.2 equiv) in THF (1.0 mL) was added dropwise. After 1 h at -78 $^{\circ}$ C, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with n-hexane to give the desired product **26** (88 mg, 91% yield) as a colorless oil.

R_f = 0.37 (petroleum ether).

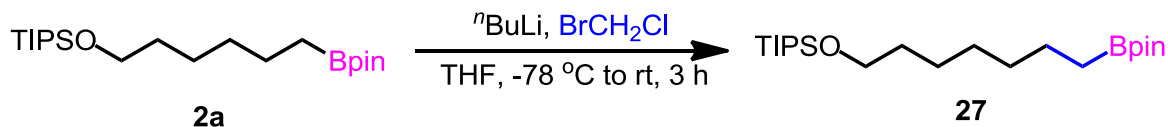
^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 1.8 Hz, 1H), 6.31 – 6.25 (m, 1H), 5.98 (d, J = 3.2 Hz, 1H), 3.69 (t, J = 6.5 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 1.72 – 1.50 (m, 4H), 1.46 – 1.34 (m, 4H), 1.13 – 1.02 (m, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 156.6, 140.7, 110.1, 104.6, 63.5, 33.0, 29.1, 28.2, 28.0, 25.7, 18.1, 12.1.

HRMS (ESI $^+$) calcd for $\text{C}_{19}\text{H}_{37}\text{O}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$: 325.2563, found: 325.2561.

IR (neat, cm^{-1}): 2940, 2865, 1464, 1108, 883, 725, 680.

Synthesis of Compound **27**^[4,21]



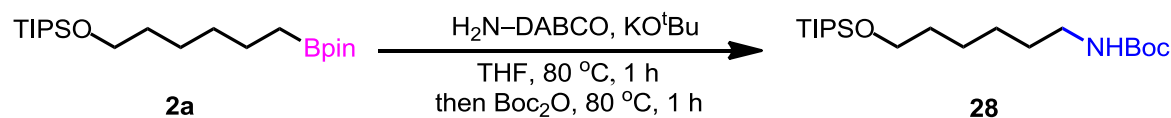
To an oven-dried round-bottom flask were added **2a** (76.8 mg, 0.2 mmol, 1.0 equiv), BrCH_2Cl (26 μ L, 0.4 mmol, 2.0 equiv), and THF (1.5 mL), and then n BuLi (0.12 mL, 2.5 M in hexanes, 0.3 mmol) was added at -78 $^{\circ}$ C under N_2 atmosphere. The resulting mixture was allowed to stir at the same temperature for 10 min and

then allowed to stir at room temperature for 3 h. The mixture was then diluted by H₂O (5 mL). The biphasic mixture was then extracted by ethyl acetate three times (3 x 5 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to give the desired product **27** (53 mg, 67% yield) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.65 (t, *J* = 6.7 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.45 – 1.36 (m, 2H), 1.34 – 1.26 (m, 6H), 1.24 (s, 12H), 1.11 – 1.01 (m, 21H), 0.76 (t, *J* = 7.8, 1.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 83.0, 63.7, 33.2, 32.4, 29.4, 25.9, 25.0, 24.0, 18.2, 12.2.

Synthesis of Compound **28**^[4,22]

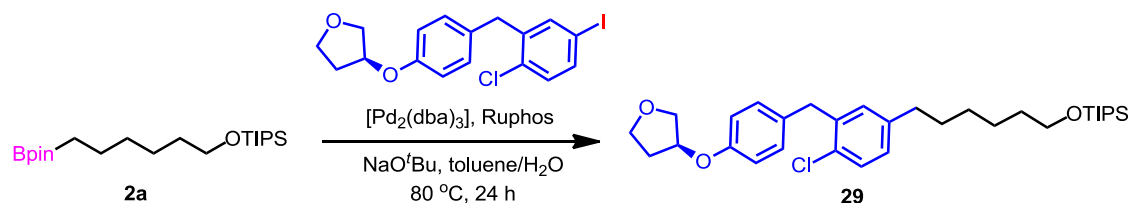


In a glovebox, to an oven-dried round-bottom flask with **2a** (76.8 mg, 0.2 mmol, 1.0 equiv) and THF (1 mL) were added H₂N-DABCO (76.8 mg, 0.2 mmol, 1.0 equiv) and ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv) at room temperature. The reaction mixture was sealed, removed from the glovebox and stirred for 1 h at 80 °C in an oil bath. After completion of the amination, the reaction mixture was cooled to room temperature and bis(1,1-dimethylethyl)este (Boc₂O) (87.3 mg, 0.4 mmol, 2.0 equiv) was added. The mixture was continued to stir for 1 h at 80 °C in an oil bath. The reaction was then cooled to room temperature and diluted with H₂O (5 mL) and extracted with ethyl acetate (20 mL) three times. The combined organic phase was then dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (50:1) as the eluent to afford the desired product **28** as yellow oil (101 mg, 71% yield).

¹H NMR (400 MHz, CDCl₃) δ 4.51 (s, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.14 – 3.03 (m, 2H), 1.54 – 1.42 (m, 13H), 1.38 – 1.29 (m, 4H), 1.16 – 0.97 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 156.1, 79.1, 63.4, 40.7, 33.0, 30.2, 28.6, 26.8, 25.7, 18.2, 12.1.

Synthesis of Compound 29^[23]



[Pd₂(dba)₃] (3.7 mg, 2 mol%), NaO^tBu (57.6 mg, 3.0 equiv), Ruphos (3.7 mg, 4 mol%), and iodide (61.4 mg, 0.2 mmol, 1.0 equiv) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with N₂ (three cycles). Toluene/H₂O (*v/v*, 10:1) and **2a** (92.2 mg, 0.24 mmol, 1.2 equiv) were added in turn by syringe under an N₂ atmosphere. The resulting reaction mixture was stirred vigorously for 24 h at 80 °C in an oil bath. At this time, the reaction was cooled to room temperature and was filtered through a celite pad. Then the mixture was extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography to afford **29** as a yellow oil (50 mg, 59% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.23 (m, 1H), 7.15 – 7.06 (m, 2H), 7.01 – 6.95 (m, 2H), 6.83 – 6.75 (m, 2H), 4.94 – 4.85 (m, 1H), 4.02 – 3.83 (m, 6H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.57 – 2.49 (m, 2H), 2.24 – 2.12 (m, 2H), 1.61 – 1.48 (m, 4H), 1.45 – 1.19 (m, 4H), 1.14 – 0.99 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 155.8, 141.7, 138.5, 132.2, 131.2, 131.0, 129.9, 129.3, 127.7, 115.3, 77.3, 73.2, 67.2, 63.4, 38.4, 35.3, 33.0, 32.9, 31.4, 29.1, 25.7, 18.1, 12.0.

HRMS (ESI⁺) calcd for C₃₂H₅₀ClO₃Si⁺ [M+H]⁺: 545.3212, found: 545.3218.

IR (neat, cm⁻¹): 2935, 2864, 1508, 1241, 1107, 882, 680.

VIII. References

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¹H NMR and ¹³C NMR Spectra

