Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Cobalt pincer-type complexes demonstrating unique selectivity for hydroboration reaction of olefin under mild conditions

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Spis treści

1. GENERAL INFORMATION

Air- and moisture sensitive reactions were carried out under argon atmosphere using standard Schlenk techniques or a glove box. Solvents used for all experiments were purchased from Honeywell or Sigma Aldrich (Merck), dried over calcium hydride (CaH_2) and purified by distillation. Toluene was additionally dried over sodium, and THF over sodium with benzophenone system. Ligands and Co-complexes were prepared in accordance with previously reported methods,[1] using reagents purchased from Sigma Aldrich (Merck) or ABCR GmBH. Commercially available vinylsilanes (eg. trimethylvinylsilane, triethylvinylsilane, dimethylphenylvinylsilane), olefins (eg. hexene, decene, allyltrimethylsilane, etc.) as well as pinacolborane were purchased from Sigma Aldrich (Merck), ABCR GmBH, Ambeed, Apollo Scientific or Acros Organics, dried over calcium hydride and purified by distillation. Other vinylsilanes (e.g. isopropoxydimethyl(vinyl)silane, (heptyloxy)dimethyl(vinyl)silane, etc.) were synthesized from corresponding chlorovinylsilanes by well-known procedures using alcohols[2] while olefines (e.g. triisopropylallylsilane, ect.) were synthesized from corresponding chlorosilanes by well-known procedures using allylmagnesium bromide solution in THF (Grignard reagent).[3] Cesium carbonate were purchased from Sigma Aldrich (Merck), dried under high vacuum at 70°C and stored in a glove box. Lithium/sodium/potassium triethylborohydride solutions in THF were purchased from Sigma Aldrich (Merck) and used as received. The progress of reactions (conversion of vinylsilane) was monitored by GC chromatography using Agilent 8860 GC and Agilent 5977B GC/MSD with Agilent 8860 GC System. The structures of products were determined by NMR spectroscopy and mass spectrometry. The ^{1}H NMR (300, 400 or 600 MHz), ^{13}C NMR (101 or 151 MHz) and ^{29}Si NMR (79 or 119 MHz) spectra were recorded on Bruker Avance III HD NanoBay spectrometer, using chloroform-d1 ($CDCl_3$), benzene-d6 (C_6D_6) or tetrahydrofuran-d8 (THF-d8) as the solvents. Deuterated solvents were purchased from respectively Deutero GmbH ($CDCl_3$ 99.6 atom% D) and Sigma Aldrich (Merck) (C_6D_6 99.8 atom% D, THF-d8 99.5 atom% D) and used as received.

2. OPTIMIZATION OF REACTION CONDITIONS

Table S1. Structures of obtained complexes.

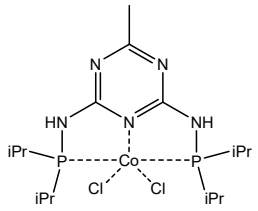
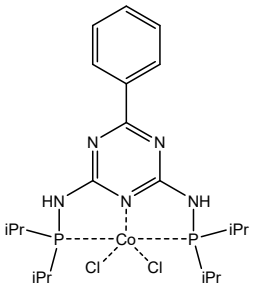
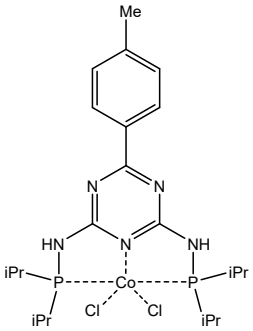
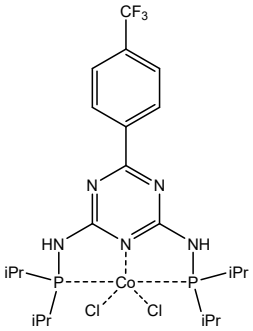
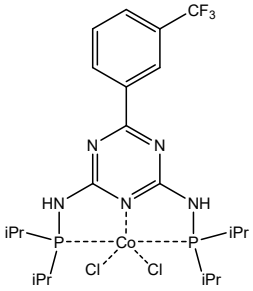
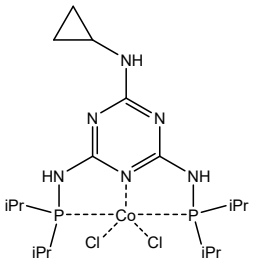
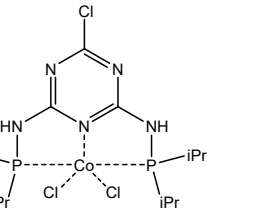
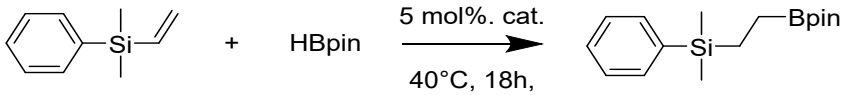
			
precat. A	precat. B	precat. C	precat. D
			
precat. E	precat. F	precat. G	

Table S2. Scope of complexes for cobalt catalyzed hydroboration of vinylsilanes with pinacolborane as activator.

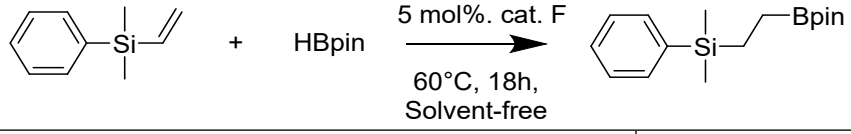


1 eq 1.5 eq

Catalyst	Conversion[a]
-	trace
precat. A	71%
precat. B	8%
precat. C	8%
precat. D	48%
precat. E	11%
precat. F	**78%**
precat. G	trace

a- Conversion of vinylsilane determined by GC with n-dodecane as the internal standard.

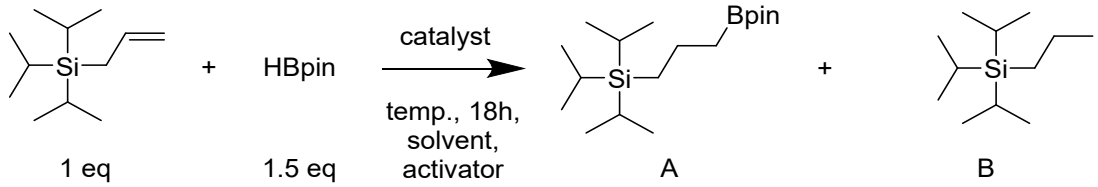
Table S3. Optimization of molar ratio of substrates for hydroboration of vinylsilanes with pinacolborane as activator.



Vinylsilane:borane ratio	Conversion[a]
1:1.5	97%
1:1.4	99%
1:1.3	97%
1:1.2	98%
1:1.1	**96%**

a- Conversion of vinylsilane determined by GC with n-dodecane as the internal standard.

Table S4. Preliminary tests for cobalt catalyzed hydroboration of olefines with additional activator.

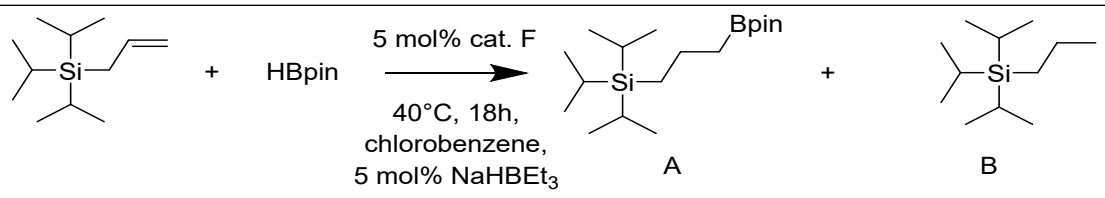


Catalyst	Conc. of cat. [mol %]	Activator	Conc. of activator [mol %]	Temp. [°C]	Solvent	Conversion[a]	Selectivity[b] A:B	
precat. F	5	-	-	60	Solvent-free	8%	50	50
precat. F	5	-	-	80	Solvent-free	58%	95	5
-	-	-	-	60	Chlorobenzene	trace	-	-
precat. F	**5**	**$NaHBEt_3$**	**5**	**40**	**Chlorobenzene**	**99%**	98	2
precat. F	5	$NaHBEt_3$	5	40	Solvent-free	86%	97	3
-	-	$NaHBEt_3$	10	40	Chlorobenzene	8%	41	59
-	-	$NaHBEt_3$	10	40	Solvent-free	34%	80	20
-	-	$NaHBEt_3$	5	40	Chlorobenzene	6%	89	11
-	-	$NaHBEt_3$	5	40	Solvent-free	31%	90	10
-	-	$NaHBEt_3$	2	40	Chlorobenzene	4%	48	52
-	-	$NaHBEt_3$	2	40	Solvent-free	14%	76	24
$CoCl_2$	5	-	-	40	Chlorobenzene	trace	-	-
$CoCl_2$	5	$NaHBEt_3$	5	40	Chlorobenzene	10%	60	40

a- Conversion of olefine determined by GC with n-dodecane as the internal standard.

b- Selectivity of [A]:[B] products determined by GC.

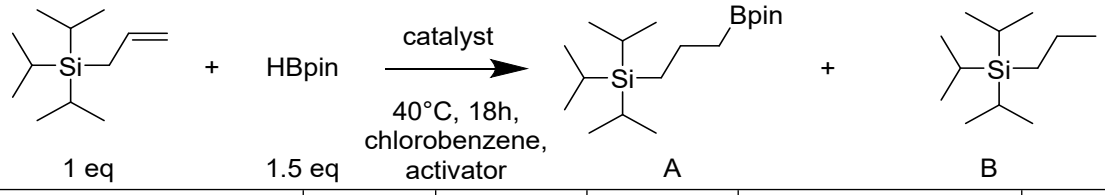
Table S5. Optimization of molar ratio of substrates for hydroboration of olefines with $NaHBEt_3$ as activator.



olefine:borane ratio	Conversion[a]	Selectivity[b] A:B	
1:1.5	**99%**	98	2
1:1.4	90%	98	2
1:1.3	84%	98	2
1:1.2	81%	99	1
1:1.1	80%	99	1

a- Conversion of olefine determined by GC with n-dodecane as the internal standard.

Table S6. Optimization of catalyst and activator concentration for hydroboration of olefines with $NaHBEt_3$ as activator.

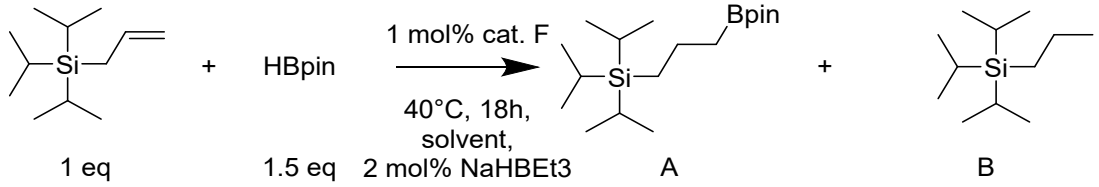


Catalyst	Conc. of cat. [mol %]	Activator	Conc. of activator [mol %]	Conversion[a]	Selectivity[b] A:B	
precat. F	5	$NaHBEt_3$	5	99%	98	2
precat. F	2.5	$NaHBEt_3$	5	99%	98	2
precat. F	**1**	**$NaHBEt_3$**	**2**	**98%**	98	2
precat. F	0.5	$NaHBEt_3$	1	94%	94	6

a- Conversion of olefine determined by GC with n-dodecane as the internal standard.

b- Selectivity of [A]:[B] products determined by GC.

Table S7. Solvent-screening for hydroboration of olefines with $NaHBEt_3$ as activator.



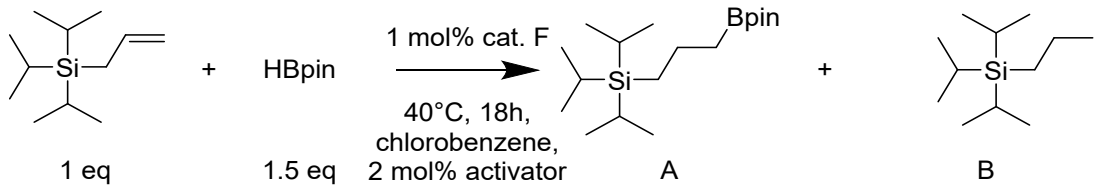
1 eq 1.5 eq 2 mol% NaHBEt3 A B

Solvent	Conversion[a]	Selectivity[b] A:B	
Chlorobenzene	**98%**	98	2
THF	75%	97	3
Toluene	99%	86	14
Dioxane	27%	83	17
$CF_3C_6H_5$	98%	78	22
DMF	33%	82	18
ACN	39%	97	3

a- Conversion of olefine determined by GC with n-dodecane as the internal standard.

b- Selectivity of [A]:[B] products determined by GC.

Table S8. Activator-screening for hydroboration of olefines with additional as activator.



1 eq 1.5 eq 2 mol% activator A B

Activator	Conversion[a]	Selectivity[b] A:B	
$LiHBEt_3$	94%	96	4
$NaHBEt_3$	**98%**	98	2
$KHBEt_3$	95%	95	5
KHMDS	98%	98	2
tBuOK	99%	96	4

a- Conversion of olefine determined by GC with n-dodecane as the internal standard.

b- Selectivity of [A]:[B] products determined by GC.

3. GENERAL SYNTHETIC PROCEDURES

General procedure for ligand preparation (in accordance with previously reported method[1]):

To a 250mL Schlenk flask equipped with a magnetic stirring bar, corresponding triazine diamine (20 mmol, 1 eq.), triethylamine (80 mmol, 4 eq.), and THF (60 mL) were added under an inert gas atmosphere. The solution was cooled to 0 °C and the diisopropylchlorophosphine (42 mmol, 2.1 eq) was added dropwise by syringe. After all the phosphine was added, the reaction mixture was sealed and the reaction was warmed to room temperature and then heated to 60 °C overnight. After cooling, triethyl ammonium chloride was allowed to settle and the organic phase was isolated by filtration. The remaining salt was washed with THF once and the combined organic phases were concentrated and dried under a high vacuum giving the PNP ligand, which was then recrystallized from hot toluene.

General procedure for Co-complex preparation (in accordance with previously reported method[1]):

To a 100mL Schlenk flask equipped with a magnetic stirring bar, $CoCl_2$ (1.4 mmol, 1 eq.), and THF (12 mL) were added under an inert gas atmosphere. The corresponding PNP-ligand (1.4 mmol, 1 eq.) was dissolved in THF (12 mL) and added to the stirred suspension of $CoCl_2$. The Schlenk flask was sealed and heated to 60 °C overnight. After this time, the solvent from the reaction mixture was evaporated giving the Co-complex, which was dried under a high vacuum.

General procedure synthesis of alkoxy(vinyl)silanes (in accordance with previously reported method[2]):

To a 250mL two-neck round-bottom flask equipped with a magnetic stirring bar, corresponding vinylchlorosilane (16.5 mmol, 1 eq.), triethylamine (24.75 mmol, 1.5 eq.), and hexane (50 mL) were added under an inert gas atmosphere. Then, to the stirring reaction mixture corresponding alcohol (17.33 mmol, 1.05 eq) was added drop-wised. The flask was sealed and the reaction was mixed at room temperature overnight. After this time, triethyl ammonium chloride was allowed to settle and the organic phase was isolated by filtration. The remaining salt was washed with hexane once and from the combined organic phases hexane was evaporated using distillation giving alkoxy(vinyl)silane.

General procedure synthesis of allylsilanes (in accordance with previously reported method[3]):

To a 250mL two-neck round-bottom flask equipped with a magnetic stirring bar, corresponding chlorosilane (x mmol, 1 eq.), and THF (50 mL) were added under an inert gas atmosphere. Then, to the stirring reaction mixture allyl magnesium bromide solution in THF was added drop-wised. The flask was sealed and the reaction was mixed at room temperature overnight. After this time, the product and solvent were separated from the remaining salts using trap-to-trap distillation. Allylsilane was purified using simple distillation.

General procedure for cobalt-catalyzed hydroboration of vinylsilanes (1a-1m, 3a)

To a 12mL vial equipped with a magnetic stirring bar, precatalyst F (0.05 eq. per one vinyl group), pinacolborane (0.165 mmol, 1.1 eq.), vinylsilane (0.15 mmol, 1.0 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 60°C for 18 hours. After this time, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. The solvent (volatiles) was evaporated under reduced pressure. The residue mixture was subjected to trap-to-trap distillation or column chromatography using silica gel and with hexane as an eluent which was then evaporated high vacuum giving desired product. The products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

General procedure for cobalt-catalyzed hydroboration of olefines with activator (2a-2s, 3b)

To a 12mL vial equipped with a magnetic stirring bar, 0.03M solution of precatalyst F in chlorobenzene (1.5 µmol, 0.01 eq.), pinacolborane (0.225 mmol, 1.5 eq.), olefine (0.15 mmol, 1.0 eq.) and 1.0M solution of sodium triethylborohydride in THF (3.0 µmol, 0.02 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 40°C for 18 hours. After this time, solvent and volatile residues were evaporated under a high vacuum. In the next step, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. The solvent (volatiles) was evaporated under reduced pressure. The residue mixture was subjected to trap-to-trap distillation or column chromatography using silica gel and with hexane as an eluent which was then evaporated high vacuum giving desired product. The products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Procedure for hydrosililation of allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (4a)

To a 25mL Schlenk flask equipped with a magnetic stirring bar, allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silan (0.4 mmol, 1 eq.), dimethylphenylsilane (0.44 mmol, 1.1 eq.), toluene (300 µL) and Karstedt catalyst (0.8 µmol, 0.002 eq.) were added under inert gas atmosphere. Subsequently, the reaction mixture was stirred at 60°C for 24 hours. After this time, solvent and volatile residues were evaporated under a high vacuum. In the next step, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. The solvent (volatiles) was evaporated under reduced pressure. The residue mixture was subjected to trap-to-trap distillation giving desired product. The products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Procedure for O-sililation of allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (4b)

To a 25 mL one-necked flask equipped with a magnetic stirring bar, allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silan (0.4 mmol, 1 eq.), trimethylsilanol (0.6 mmol, 1.5 eq.), acetonitrile (500 µL) and Amberlyst-15 (30 mg) were added. Subsequently, the reaction mixture was stirred at room temperature for 24 hours. After this time, the catalyst was filtered from the reaction mixture. The solvent (volatiles) was evaporated under reduced pressure. The residue mixture was subjected to trap-to-trap distillation giving desired product. The products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

General procedure for cobalt-catalyzed hydroboration of (methylphenyl(vinyl)silyl)acetylene (5a)

To a 12mL vial equipped with a magnetic stirring bar, precatalyst F (0.05 eq.), pinacolborane (0.165 mmol, 1.1 eq.), (methylphenyl(vinyl)silyl)acetylene (0.15 mmol, 1.0 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 80°C for 18 hours. After this time, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. The solvent (volatiles) was evaporated under reduced pressure. The residue mixture was subjected to trap-to-trap distillation, giving desired product. The product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Gram-scale hydroboration reaction of dimethylphenylvinylsilane

To a 20mL vial equipped with a magnetic stirring bar, precatalyst F (0.5 mmol, 0.05 eq.), pinacolborane (11.0 mmol, 1.1 eq.), and dimethylphenylvinylsilane (10.0 mmol, 1.0 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 60°C for 18 hours. After this time, volatile residues were evaporated under a high vacuum. In the next step, the catalyst was

precipitated by the addition of hexane (5mL) and filtered from the resulting mixture. The solvent (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected to trap-to-trap distillation giving desired product. The product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Gram-scale hydroboration reaction of decene

To a 20mL vial equipped with a magnetic stirring bar, 0.03M solution of precatalyst F (0.1 mmol, 0.01 eq.) in chlorobenzene, pinacolborane (15.0 mmol, 1.5 eq.) decene (10.0 mmol, 1.0 eq.) and 1.0M solution of sodium triethylborohydride in THF (0.2 mmol, 0.02 eq) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 40°C for 18 hours. After this time, solvent and volatile residues were evaporated under a high vacuum. In the next step, the catalyst was precipitated by the addition of pentane or hexane (5mL) and filtered from the resulting mixture. The solvents (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected to trap-to-trap distillation giving desired product. The product was identified by ^{1}H and ^{13}C spectroscopies and mass spectrometry.

Procedure for one-pot hydroboration followed by hydrolysis and condensation reaction of alkoxysilane derivative (6a)

To a 12mL vial equipped with a magnetic stirring bar, precatalyst F (0.04 mmol, 0.05 eq.), pinacolborane (0.88 mmol, 1.1 eq.), ethoxydimethylvinylsilane (0.8 mmol, 1.0 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 60°C for 18 hours. Thereafter, water (8.0 mmol, 10.0 eq) was added to the reaction mixture and it was stirred again for another 18 hours at room temperature. After this time, solvent and volatile residues were evaporated under a high vacuum. In the next step, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. Then, the liquid was dried with magnesium sulfate and filtered again. The solvents (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected to trap-to-trap distillation giving desired product. The product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Procedure for one-pot hydroboration–oxidation reaction (6b)

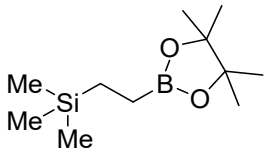
To a 20mL vial equipped with a magnetic stirring bar, precatalyst F (0.04 mmol, 0.05 eq.), pinacolborane (0.88 mmol, 1.1 eq.), triethylvinylsilane (0.8 mmol, 1.0 eq.) were added under inert gas atmosphere (glove box). Subsequently, the reaction mixture was stirred at 60°C for 18 hours. Thereafter, water (1.2mL), methanol (2.4mL), sodium hydroxide (2.4 mmol, 3.0 eq), and hydrogen peroxide (8.0 mmol, 10.0 eq) were added to the reaction mixture and it was stirred again for another 18 hours at room temperature. After this time, solvent and volatile residues were evaporated under a high vacuum. In the next step, the catalyst was precipitated by the addition of pentane or hexane (1mL) and filtered from the resulting mixture. Then, the liquid was dried with magnesium sulfate and filtered again. The solvents (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected to trap-to-trap distillation giving desired product. The product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and mass spectrometry.

Mercury poisoning test

To a 12mL vial equipped with a magnetic stirring bar, 0.03M solution of precatalyst F in chlorobenzene (1.5 µmol, 0.01 eq.), pinacolborane (0.225 mmol, 1.5 eq.), olefine (0.15 mmol, 1.0 eq.) and 1.0M solution of sodium triethylborohydride in THF (3.0 µmol, 0.02 eq.) were added under inert gas atmosphere (glove box). Subsequently, mercury (1.0 mmol, 667 eq. in relation to catalyst) was added and the reaction mixture was stirred at 40°C for 18 hours. After this time, the conversion of substrates was measured using GC-MS.

4. CHARACTERISATION DATA FOR ALL PRODUCTS

trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1a)



trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 73% yield, and is known in the literature. All spectroscopic data are in agreement.[4]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.04 (s, 9H), 0.52-0.57 (m, 2H), 0.71-0.75 (m, 2H), 1.25 (s, 12H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -2.1, 9.3, 24.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 3.1
EI-MS m/z (rel. int.): 213 (7), 171 (17), 131 (42), 117 (12), 113 (22), 100 (21), 83 (100), 73 (59), 69 (17), 59 (15), 55 (22)

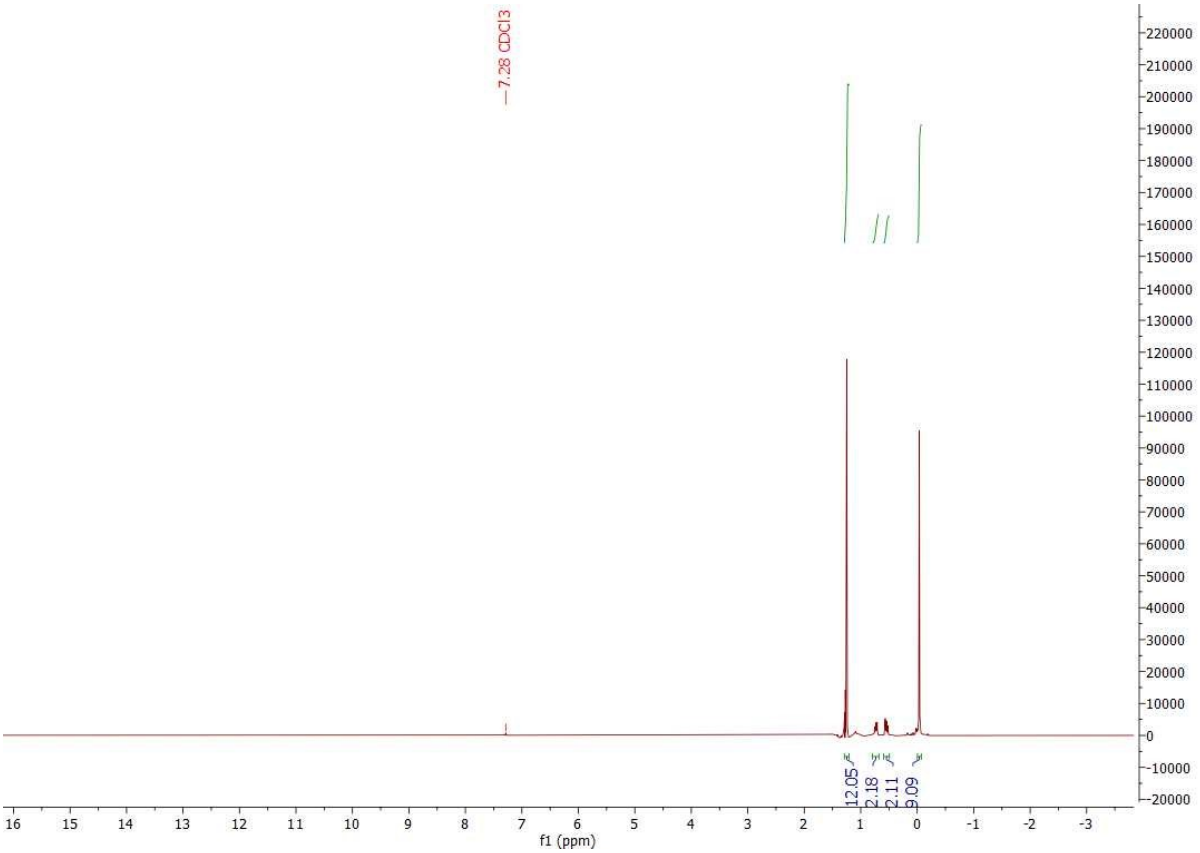


Figure S1. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1a).

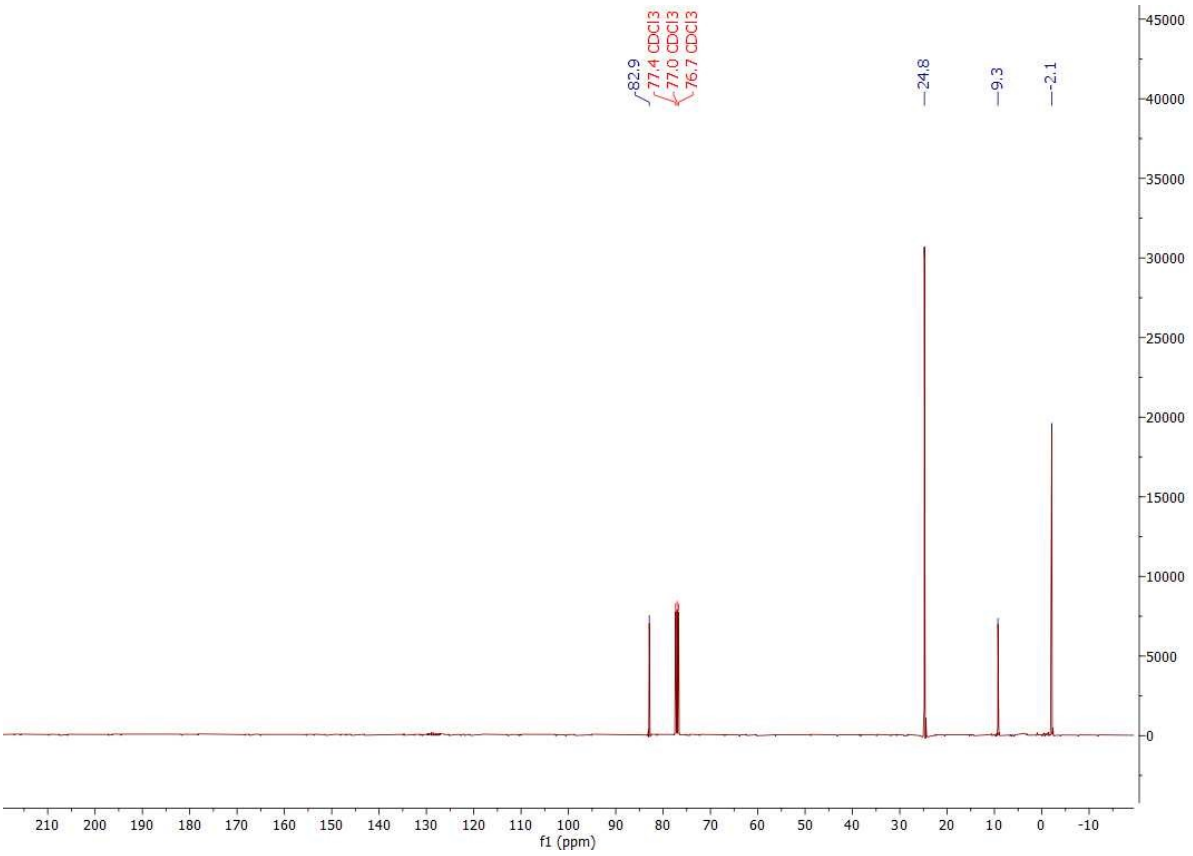


Figure S2. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1a).

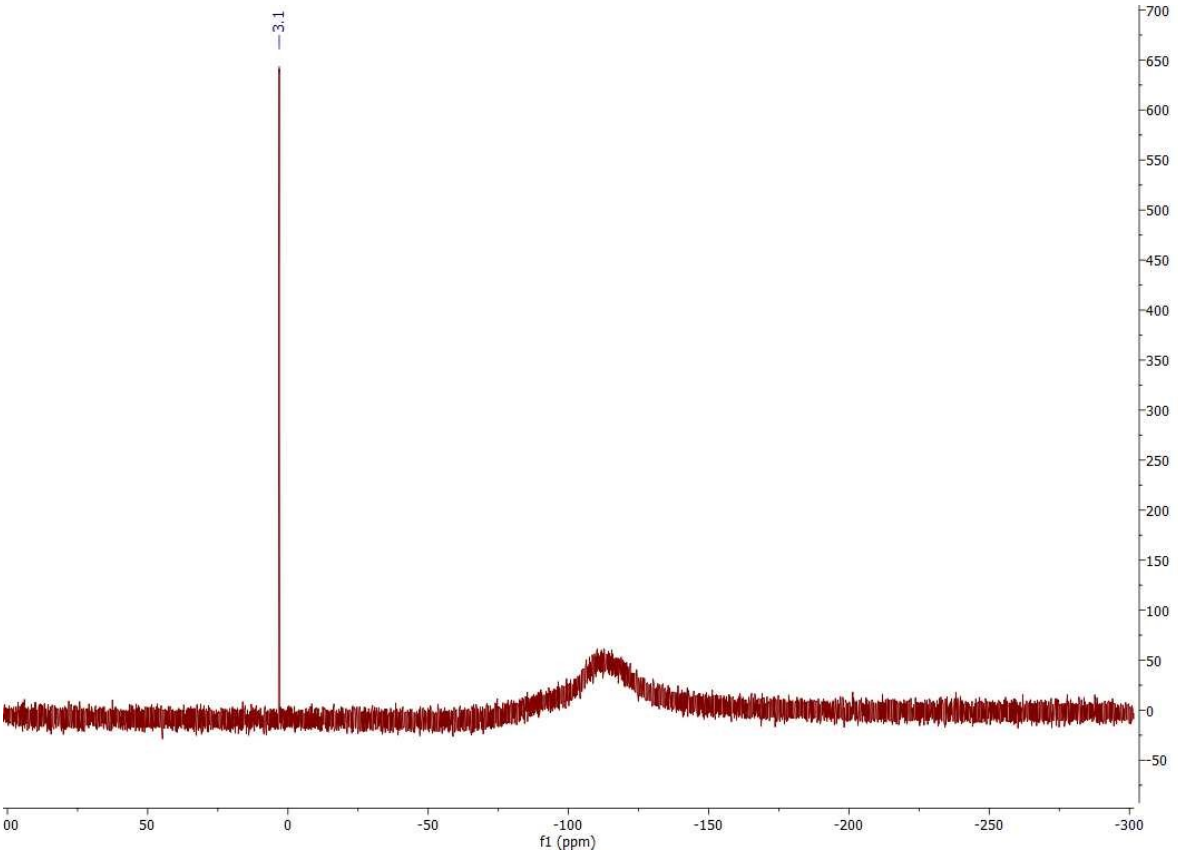
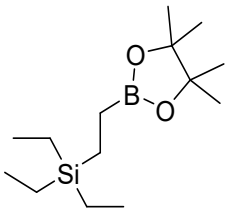


Figure S3. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1a).

triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1b)



triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 81% yield, and is known in the literature. All spectroscopic data are in agreement.[5]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.47 (q, J=7.9 Hz, 6H), 0.52-0.56 (m, 2H), 0.67-0.72 (m, 2H), 0.88 (t, J=7.7 Hz, 9H), 1.23 (s, 12H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 2.8, 3.8, 7.4, 24.7, 82.8, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 8.3
EI-MS m/z (rel. int.): 255 (6), 241 (100), 159 (76), 141 (16), 113 (10), 87 (17), 83 (83), 59 (16), 57 (10), 55 (14)

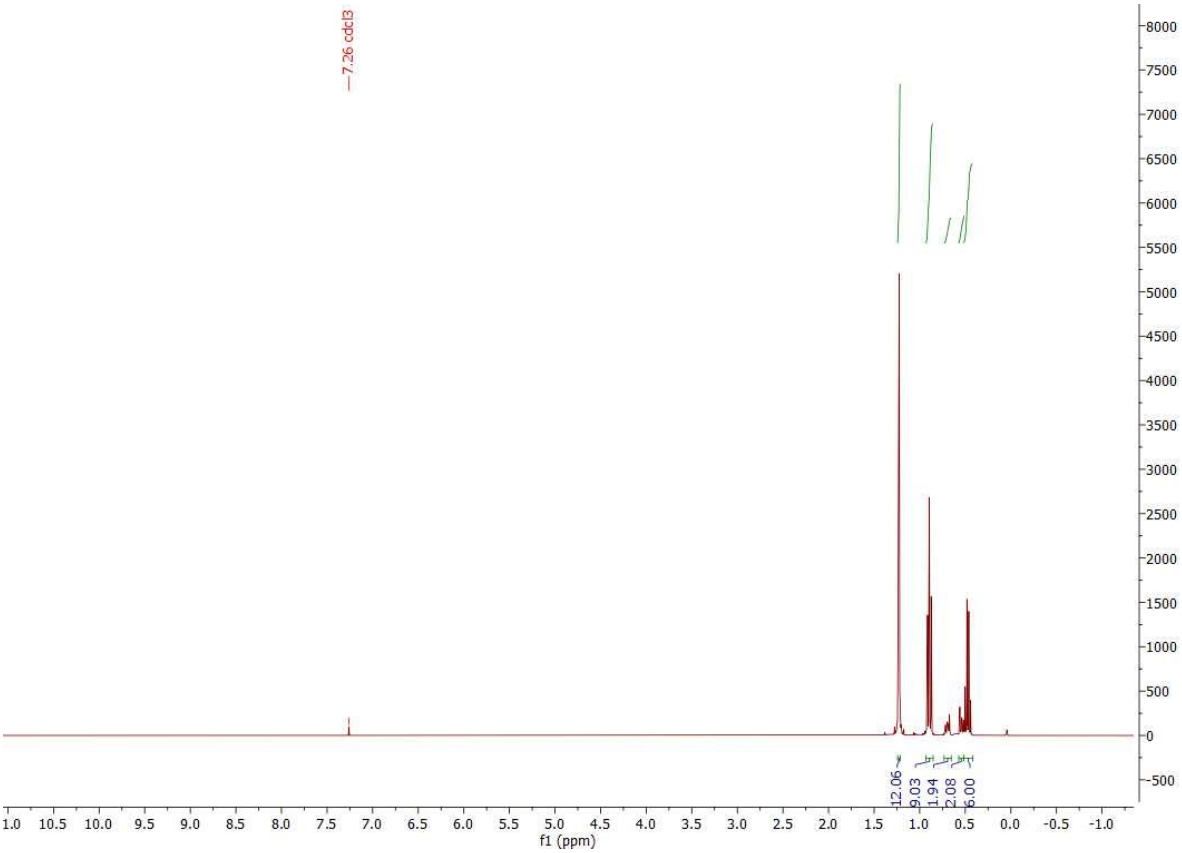


Figure S4. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1b).

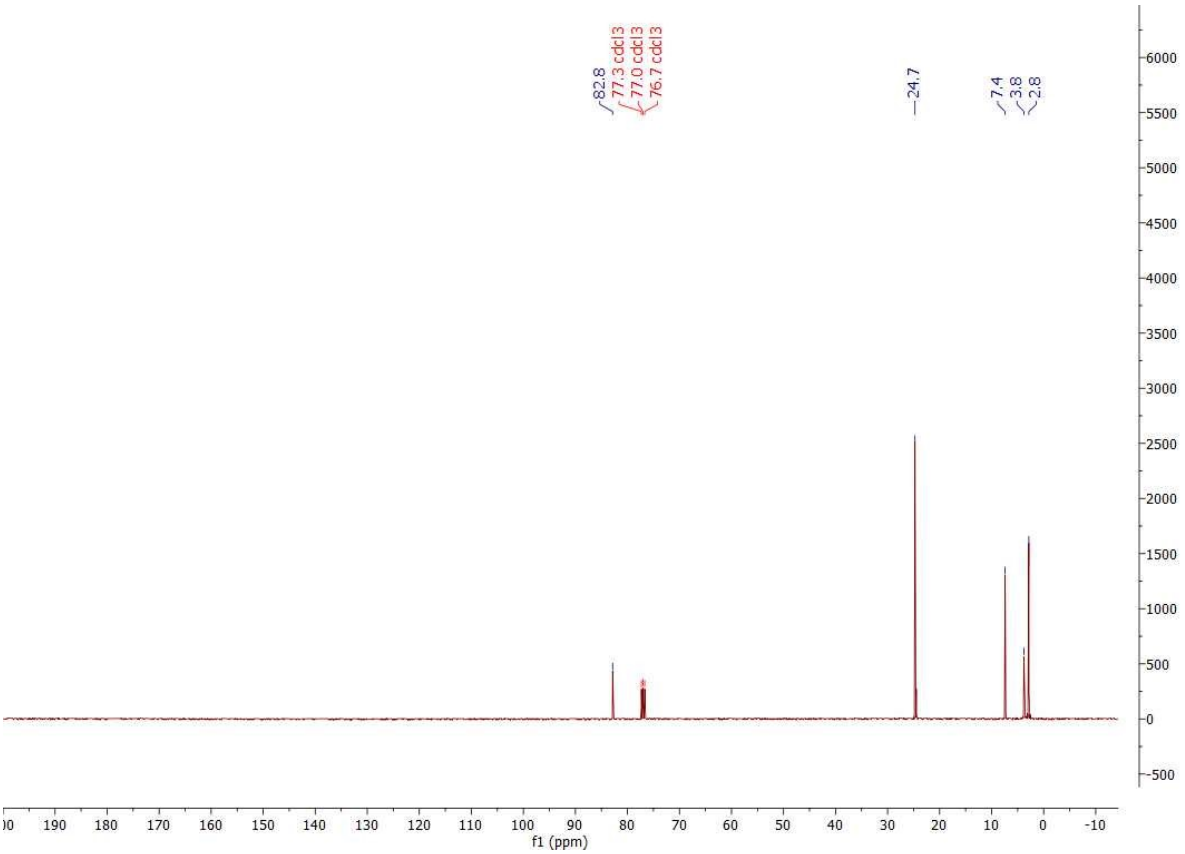


Figure S5. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1b).

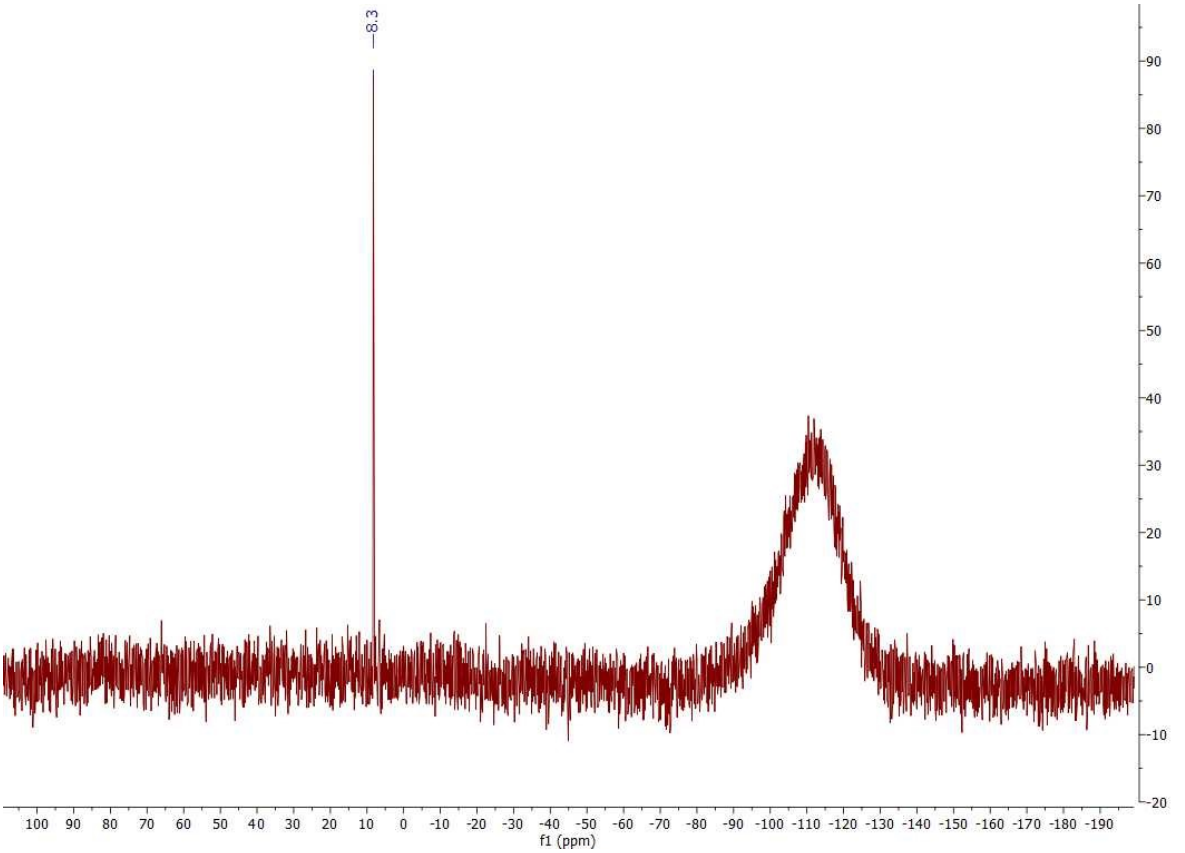
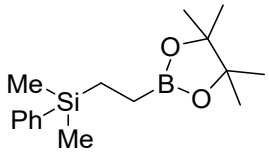


Figure S6. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1b).

dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1c)



dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 94% yield, and is known in the literature. All spectroscopic data are in agreement.[6]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.28 (s, 6H), 0.80-0.82 (m, 4H), 1.26 (s, 12H), 7.35-7.37 (m, 3H), 7.53-7.55 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -3.5, 8.5, 24.8, 83.0, 127.7, 128.7, 133.7, 139.4, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -1.3
EI-MS m/z (rel. int.): 275 (41), 213 (23), 161 (7), 147 (8), 135 (100), 131 (7), 121 (7), 115 (19), 105 (20), 83 (52), 69 (9), 59 (6), 57 (5), 55 (14)

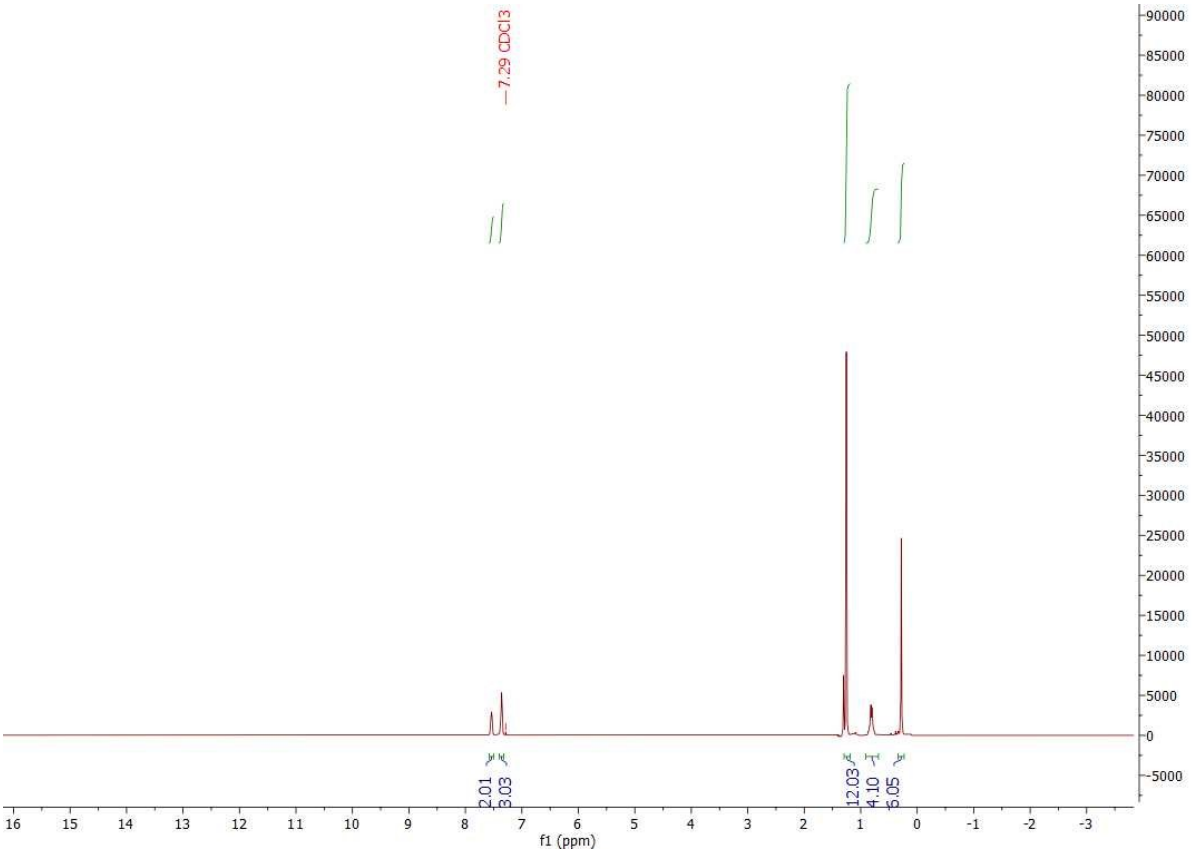


Figure S7. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1c).

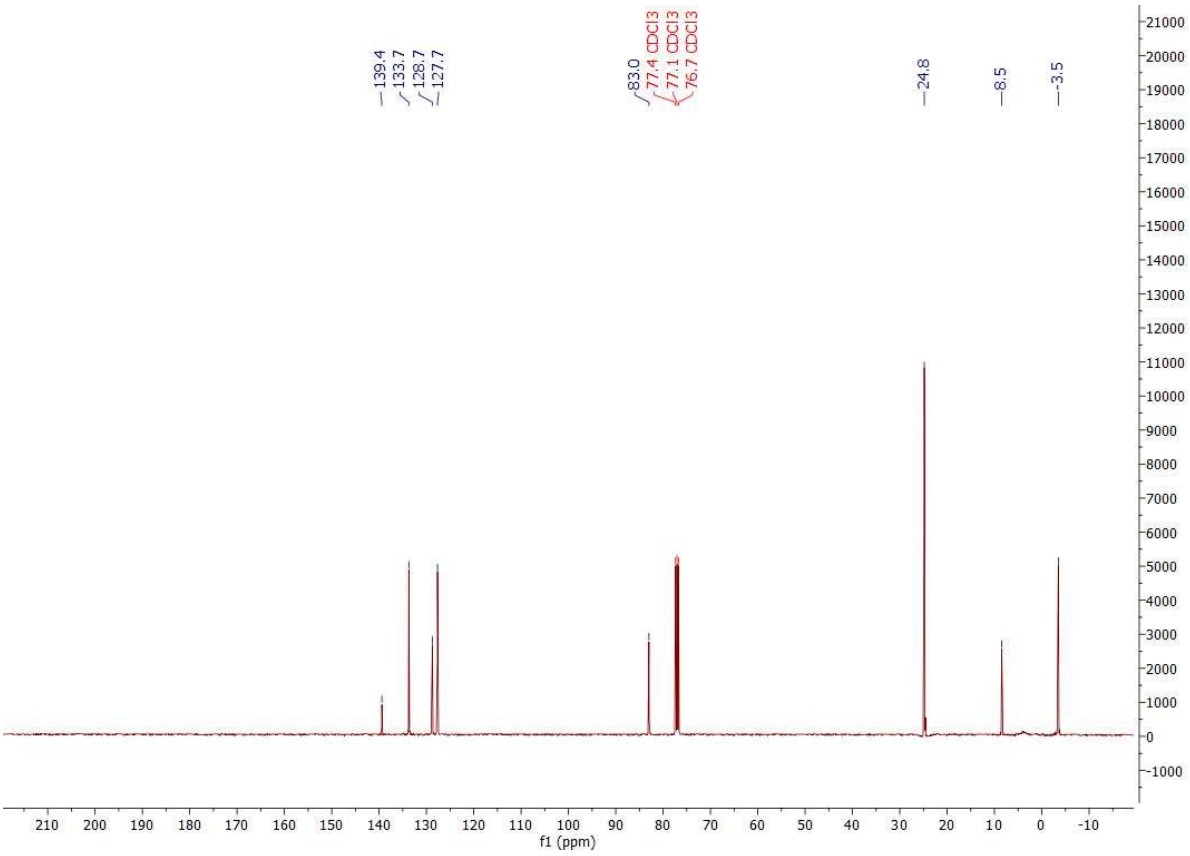


Figure S8. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1c).

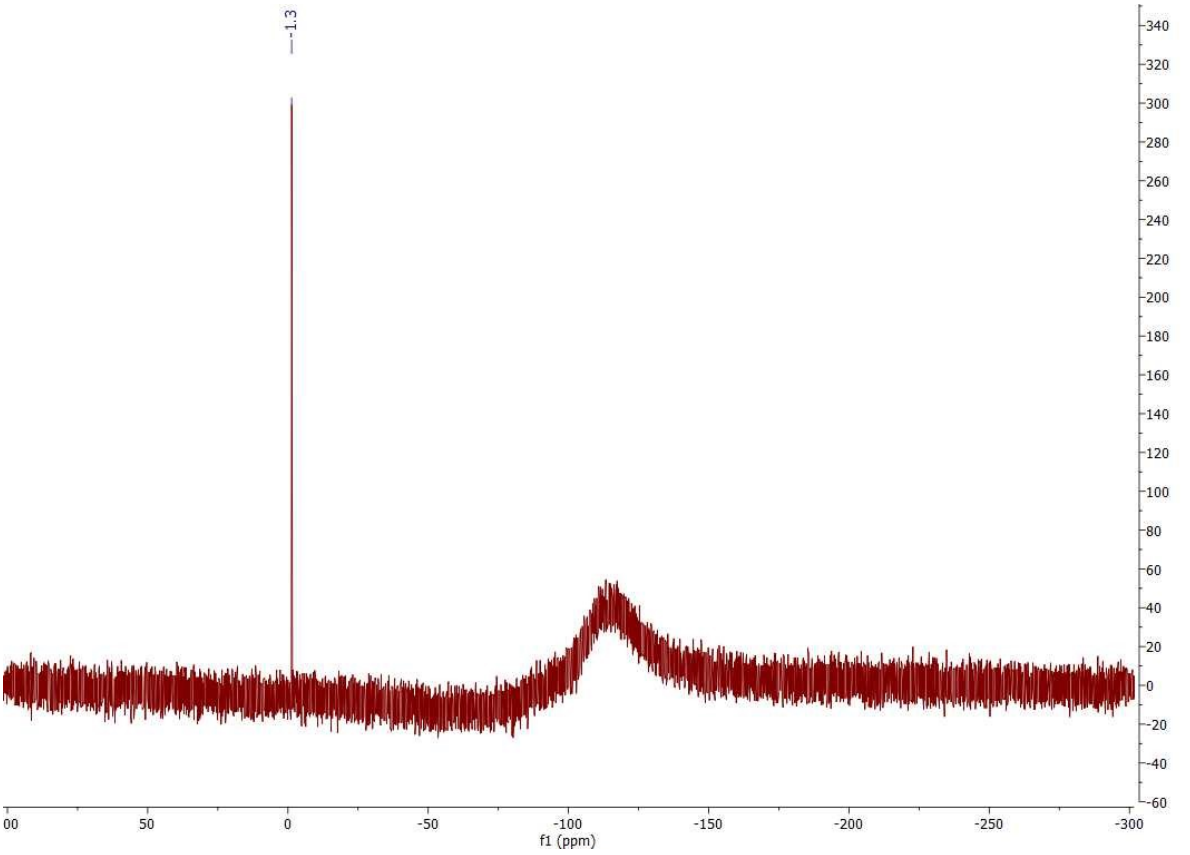
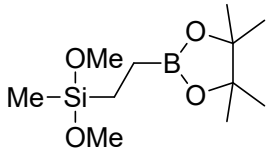


Figure S9. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1c).

methoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1d)



methoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 83% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.07 (s, 3H), 0.64-0.68 (m ,2H), 0.76-0.80 (m, 2H), 1.21 (s, 12H), 3.48 (s, 6H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -6.3, 5.5, 24.8, 50.1, 83.0, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -1.6
EI-MS m/z (rel. int.): 245 (18), 202 (30), 187 (21), 163 (24), 161 (14), 160 (18), 149 (15), 145 (12), 132 (27), 129 (24), 117 (14), 105 (100), 101 (16), 83 (40), 75 (37), 69 (17), 59 (24), 55 (18)

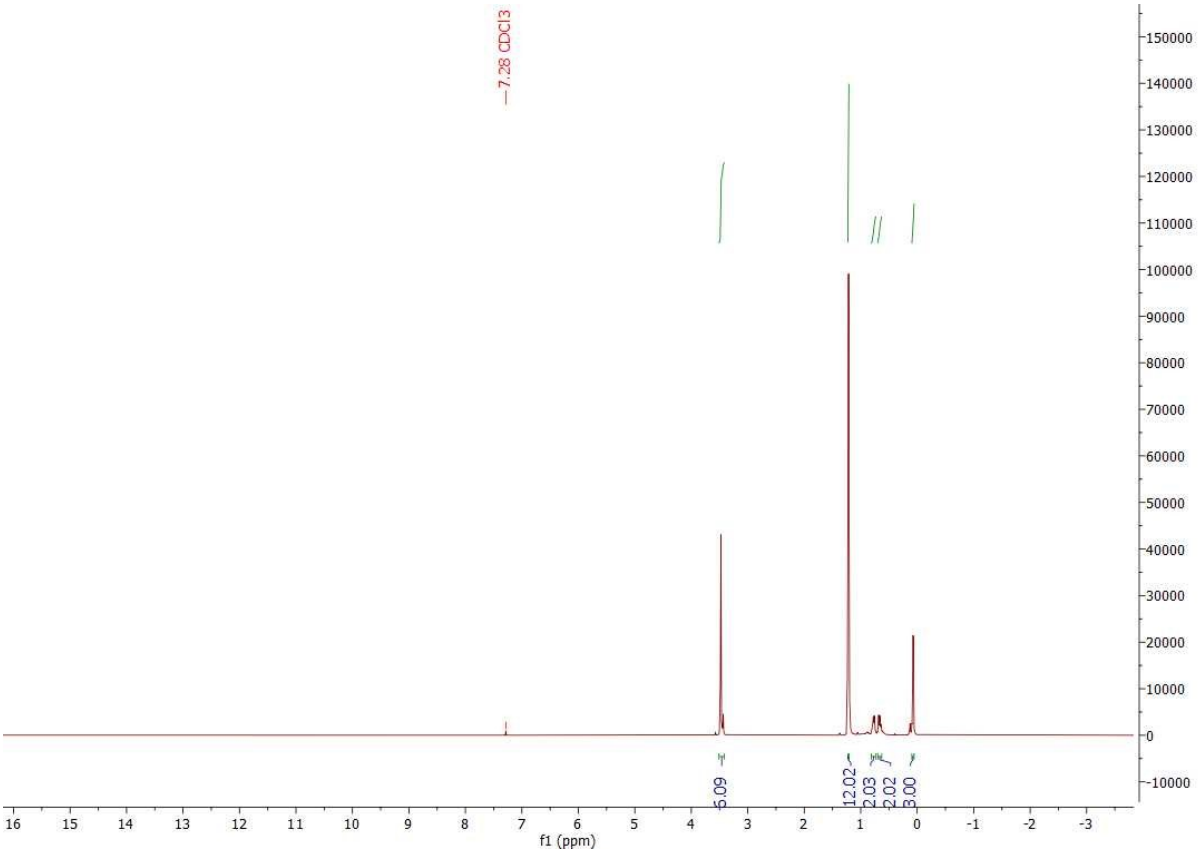


Figure S10. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of methoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1d).

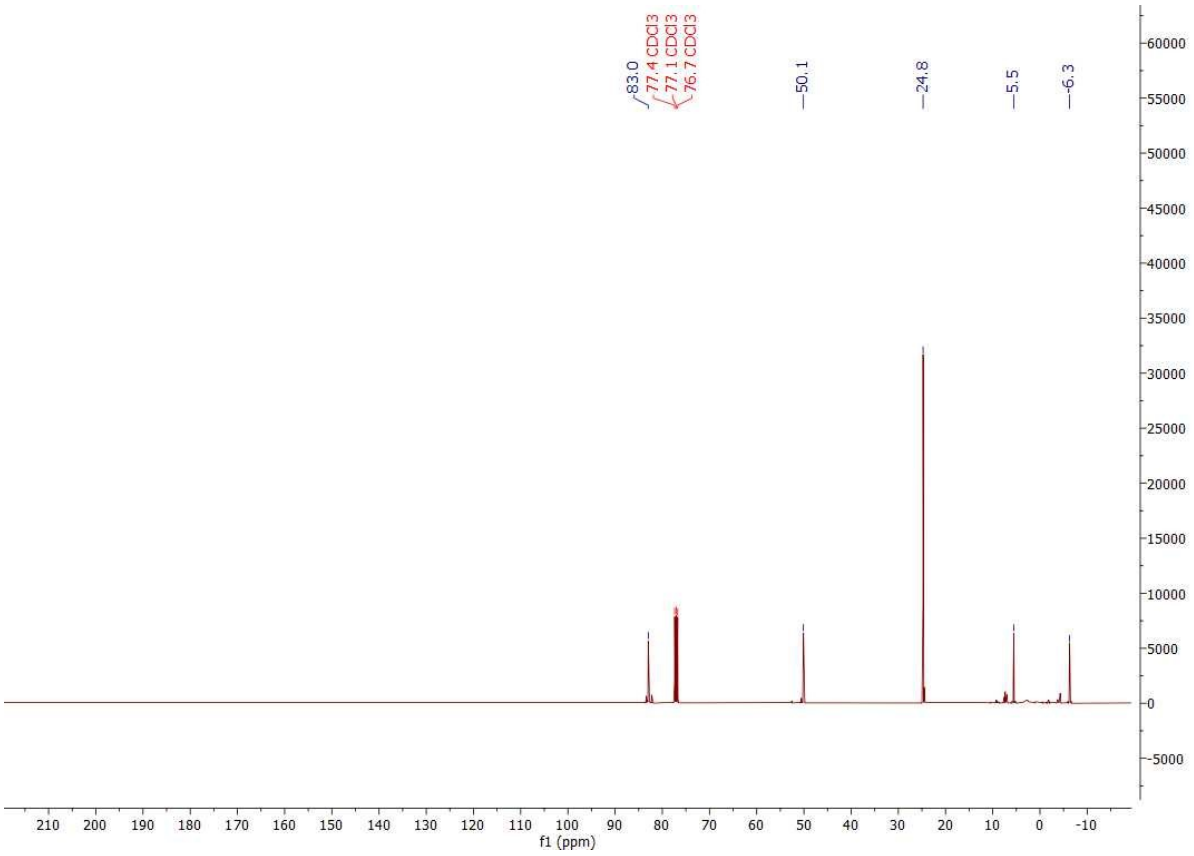


Figure S11. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of methoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1d).

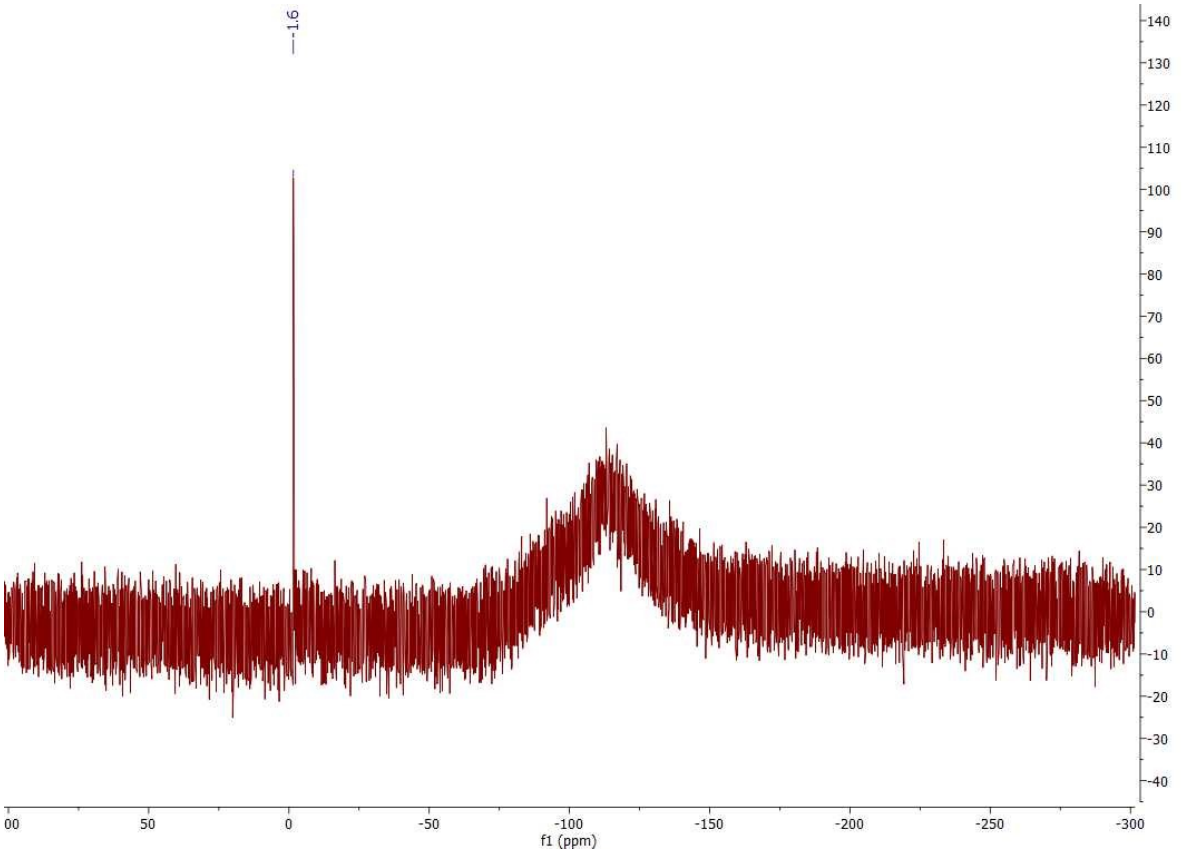
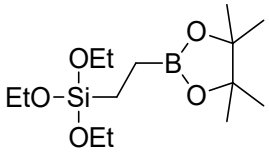


Figure S12. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of methoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1d).

triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1e)



triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 95% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 3.77 (q, J=7.0 Hz, 6H), 1.21-1.16 (m, 21H), 0.83-0.79 (m, 2H), 0.68-0.63 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 2.9, 18.2, 24.7, 58.2, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -44.4
EI-MS m/z (rel. int.): 303 (2), 273 (16), 260 (17), 231 (32), 190 (14), 163 (100), 145 (10), 135 (24), 119 (27), 117 (15), 89 (14), 84 (18), 83 (14), 79 (13), 55 (7)

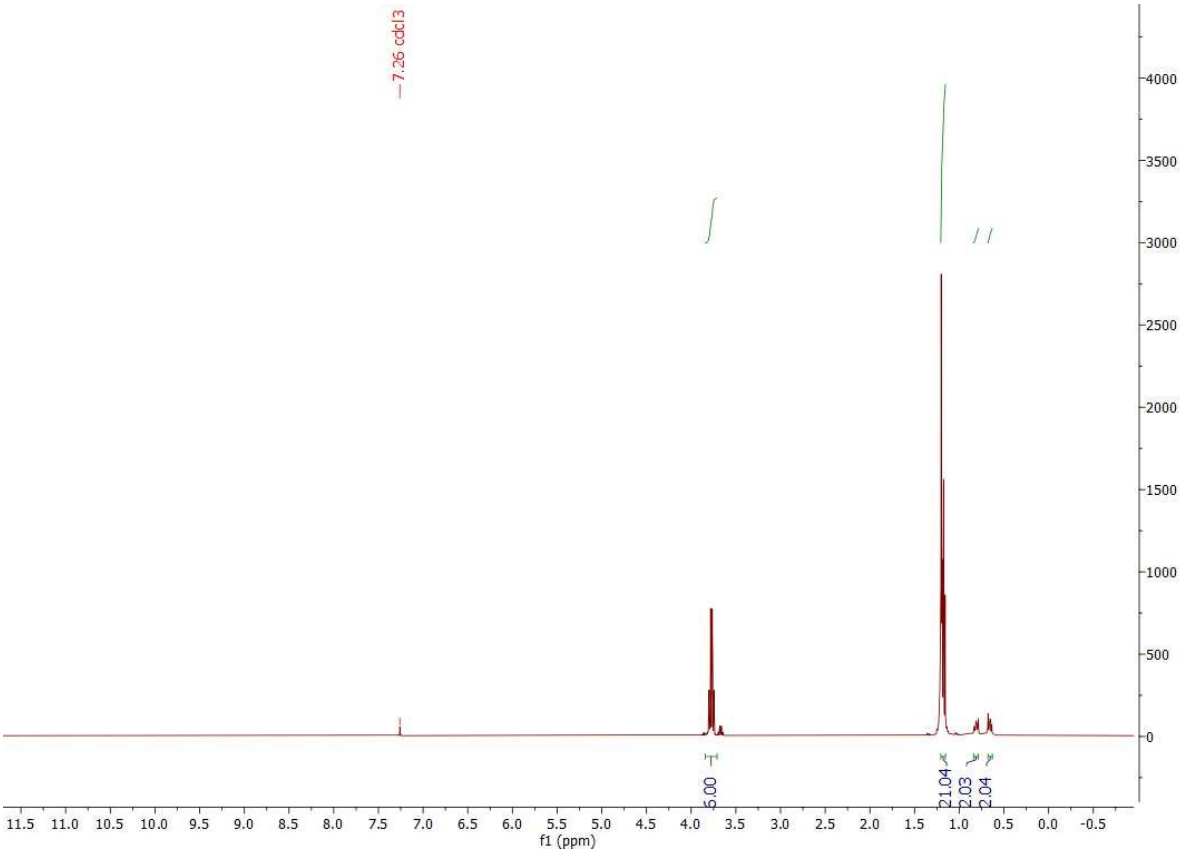


Figure S13. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1e).

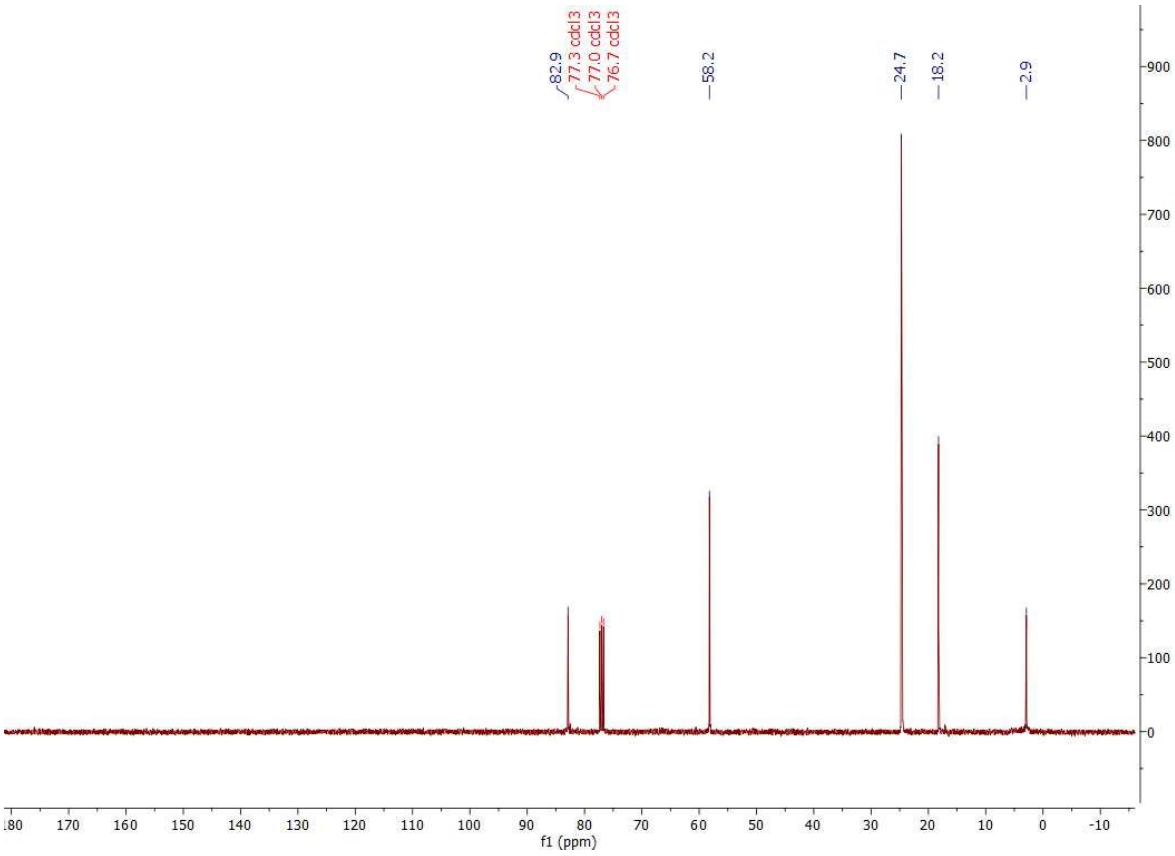


Figure S14. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1e).

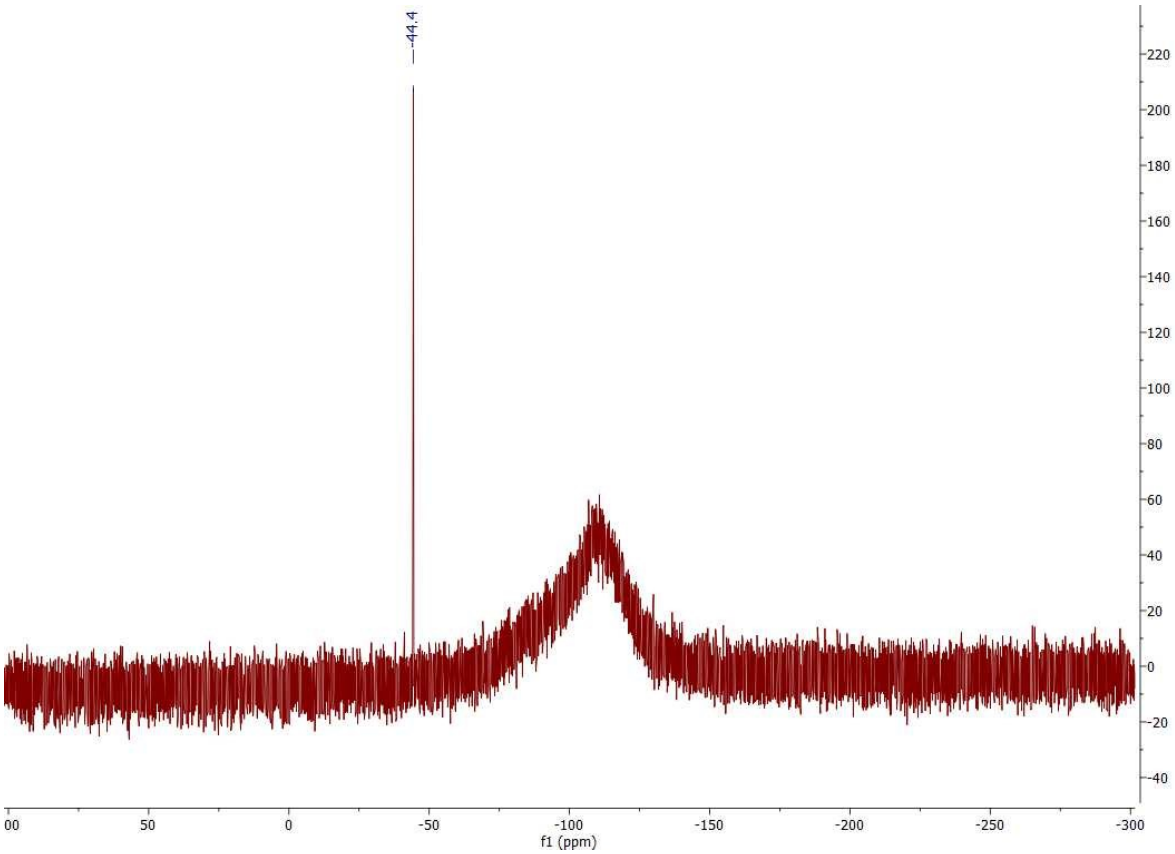
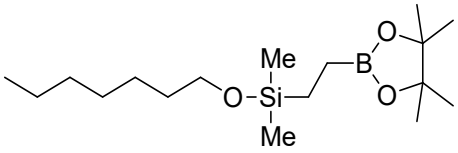


Figure S15. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1e).

(heptyloxy)dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1f)



(heptyloxy)dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 75% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.08 (s, 6H), 0.63-0.67 (m, 2H), 0.75-0.79 (m, 2H), 0.89 (t, J=6.2Hz, 3H), 1.23-1.28 (m, 20H), 1.50-1.57 (m, 2H), 3.57 (t, J=6.8 Hz, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -2.6, 8.8, 14.1, 22.6, 24.8, 25.8, 29.1, 31.9, 32.8, 62.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 18.0
EI-MS m/z (rel. int.): 313 (52), 271 (16), 213 (21), 173 (71), 171 (65), 157 (9), 133 (39), 131 (69), 119 (26), 115 (31), 113 (19), 101 (13), 97 (19), 89 (16), 87 (13), 83 (100), 75 (75), 69 (20), 59 (14), 57 (38), 55 (41)

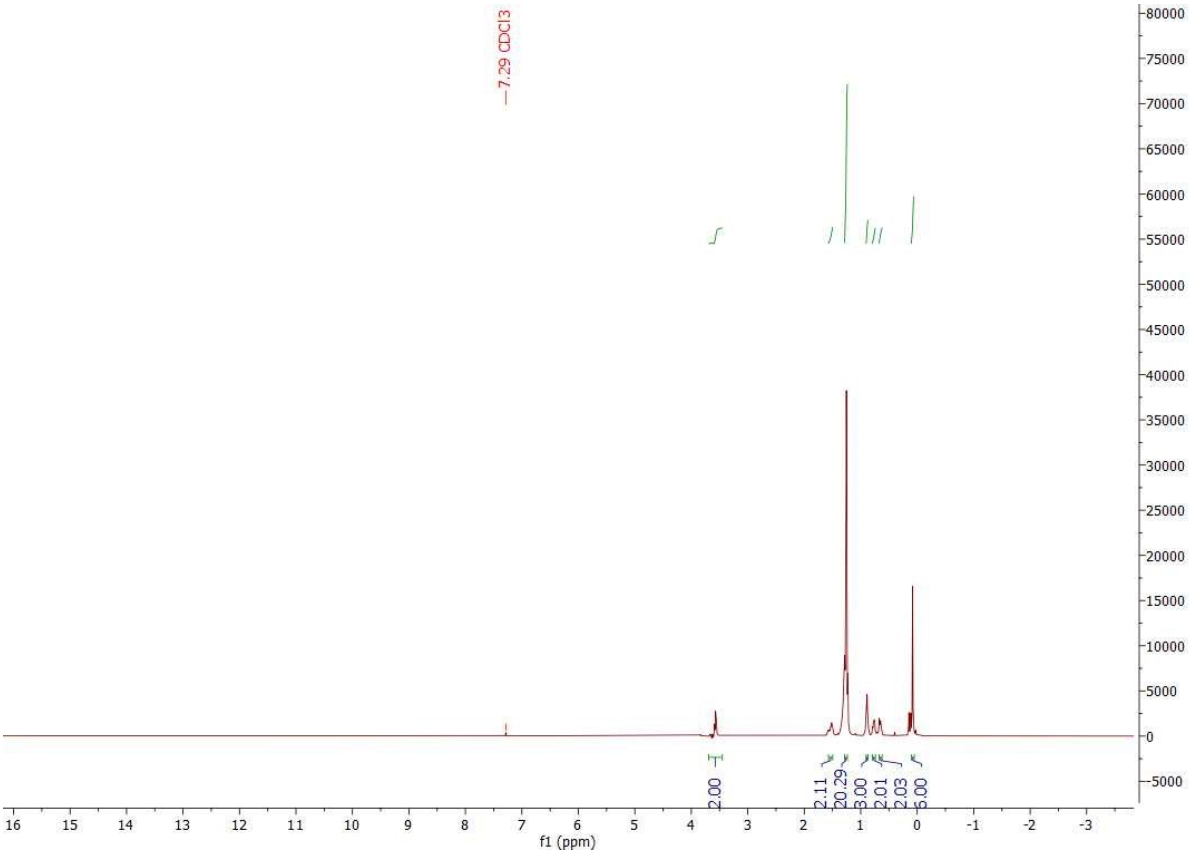


Figure S16. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of (heptyloxy)dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1f).

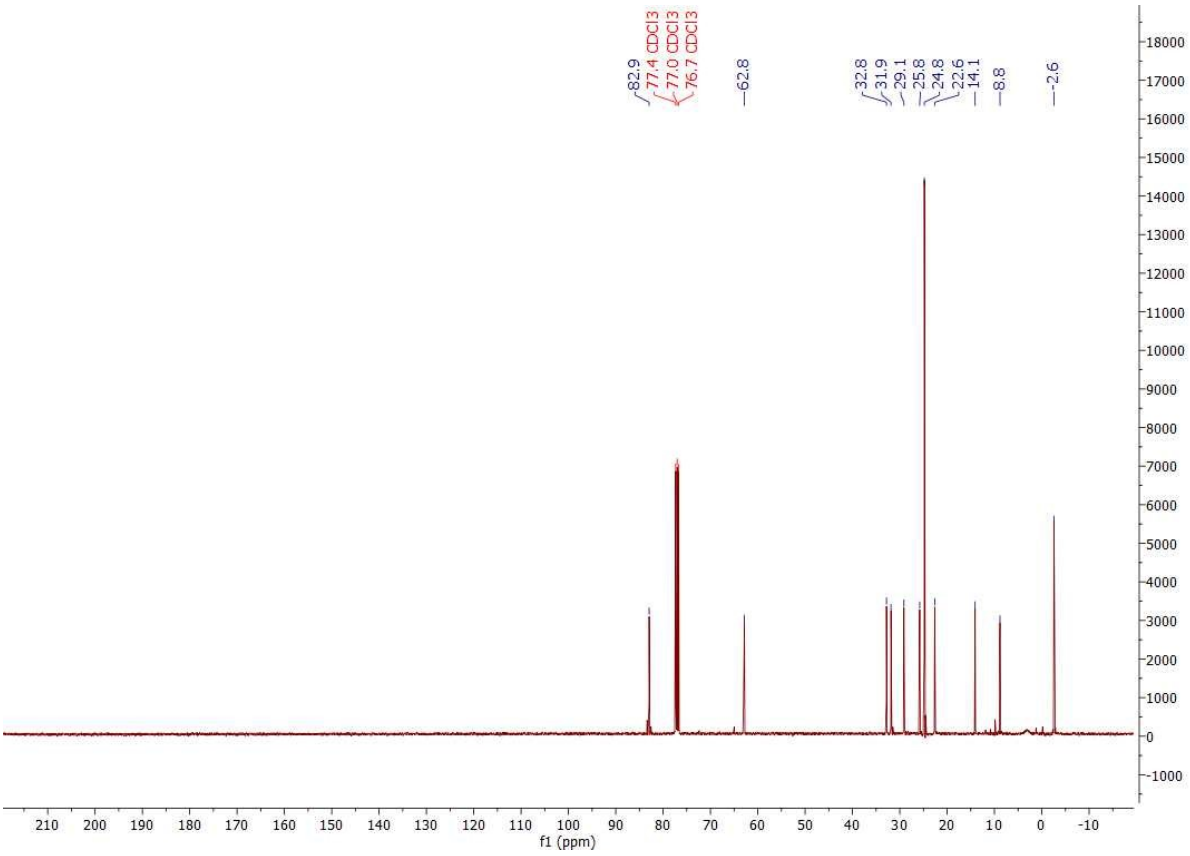


Figure S17. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of (heptyloxy)dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1f).

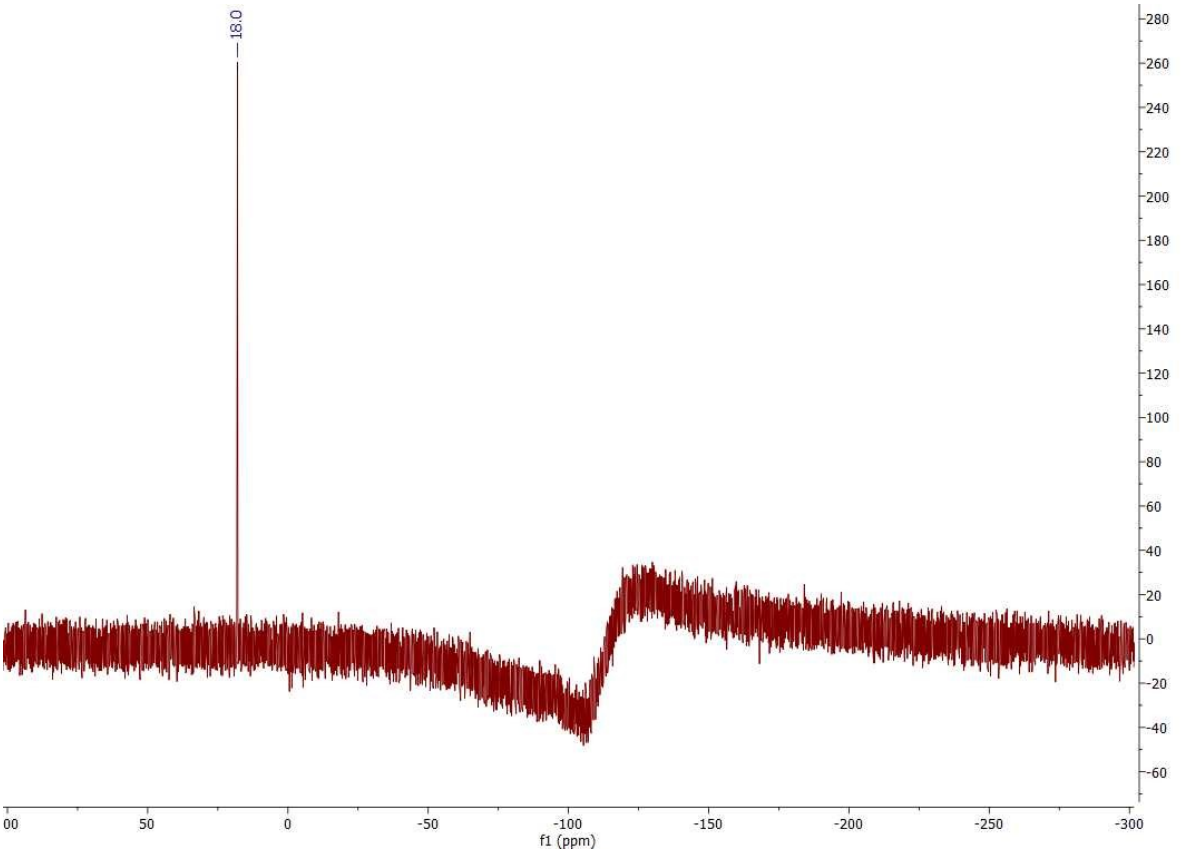
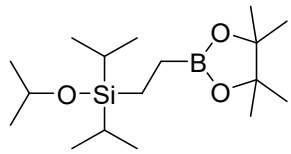


Figure S18. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of (heptyloxy)dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1f).

isopropoxydiisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1g)



isopropoxydiisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 82% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.68-0.74 (m, 2H), 0.78-0.84 (m, 2H), 0.99-1.05 (m, 14H), 1.16 (d, J = 6.0 Hz, 6H), 1.26 (s, 12H), 4.05 (p, J = 6.0 Hz, 1H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 3.2, 12.5, 17.7, 17.8, 24.8, 26.0, 64.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 13.1
EI-MS m/z (rel. int.): 285 (39), 243 (14), 227 (34), 187 (11), 161 (50), 143 (34), 115 (17), 101 (10), 99 (10), 87 (19), 85 (12), 83 (100), 75 (19), 69 (9), 61 (14), 57 (20), 55 (23)

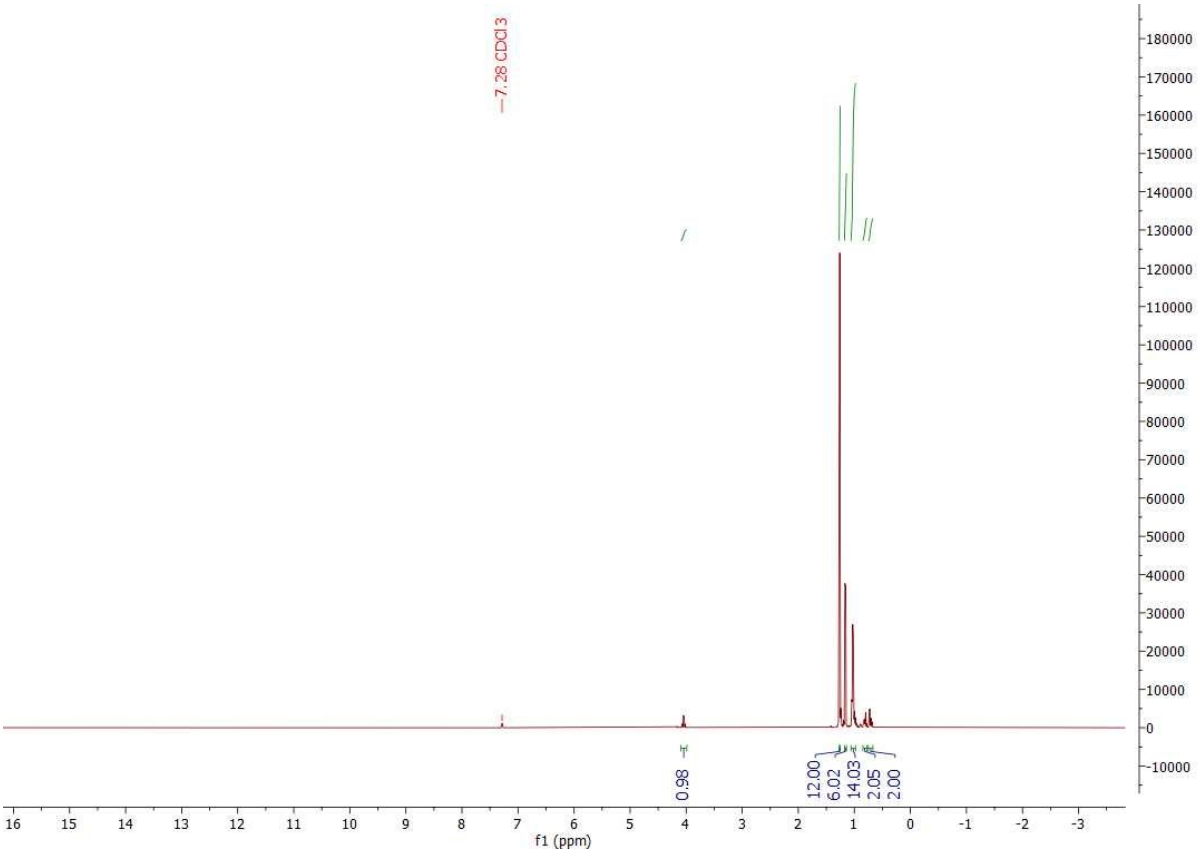


Figure S19. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of isopropoxydiisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1g).

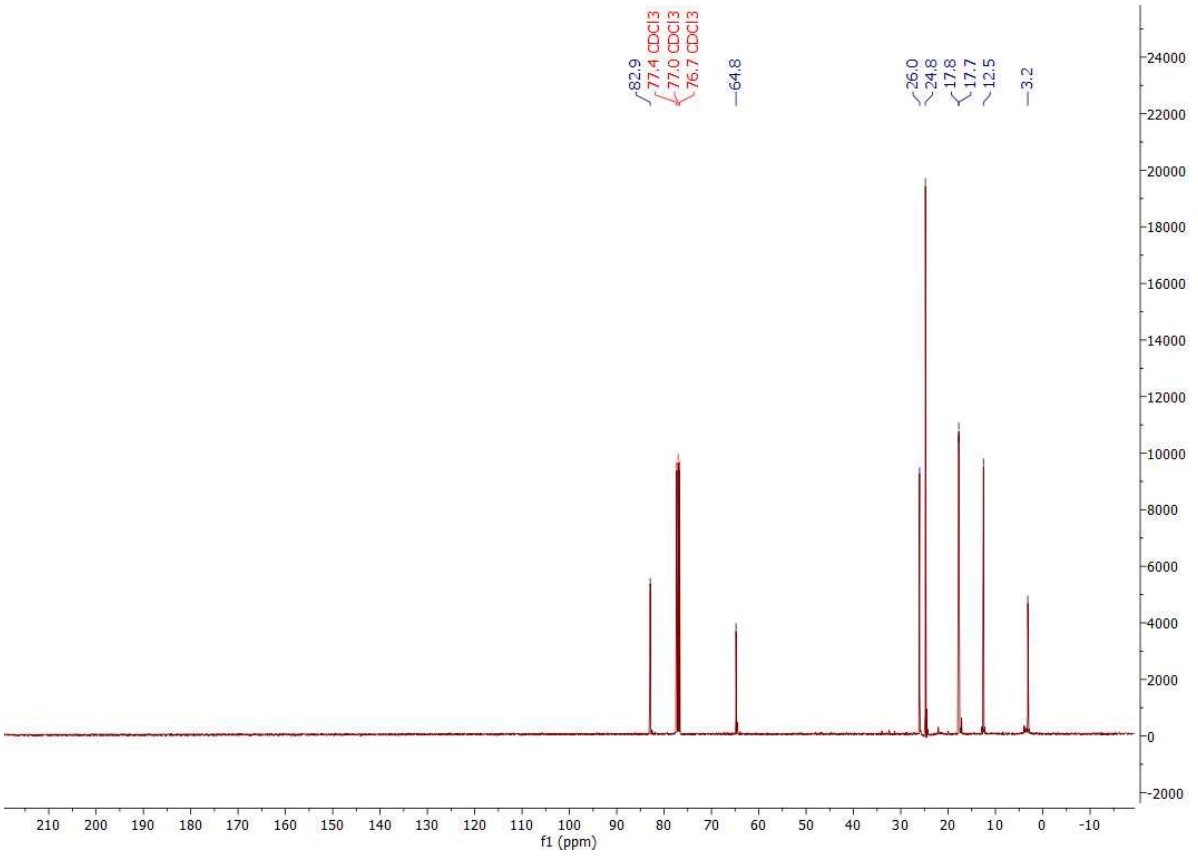


Figure S20. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of isopropoxydiisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1g).

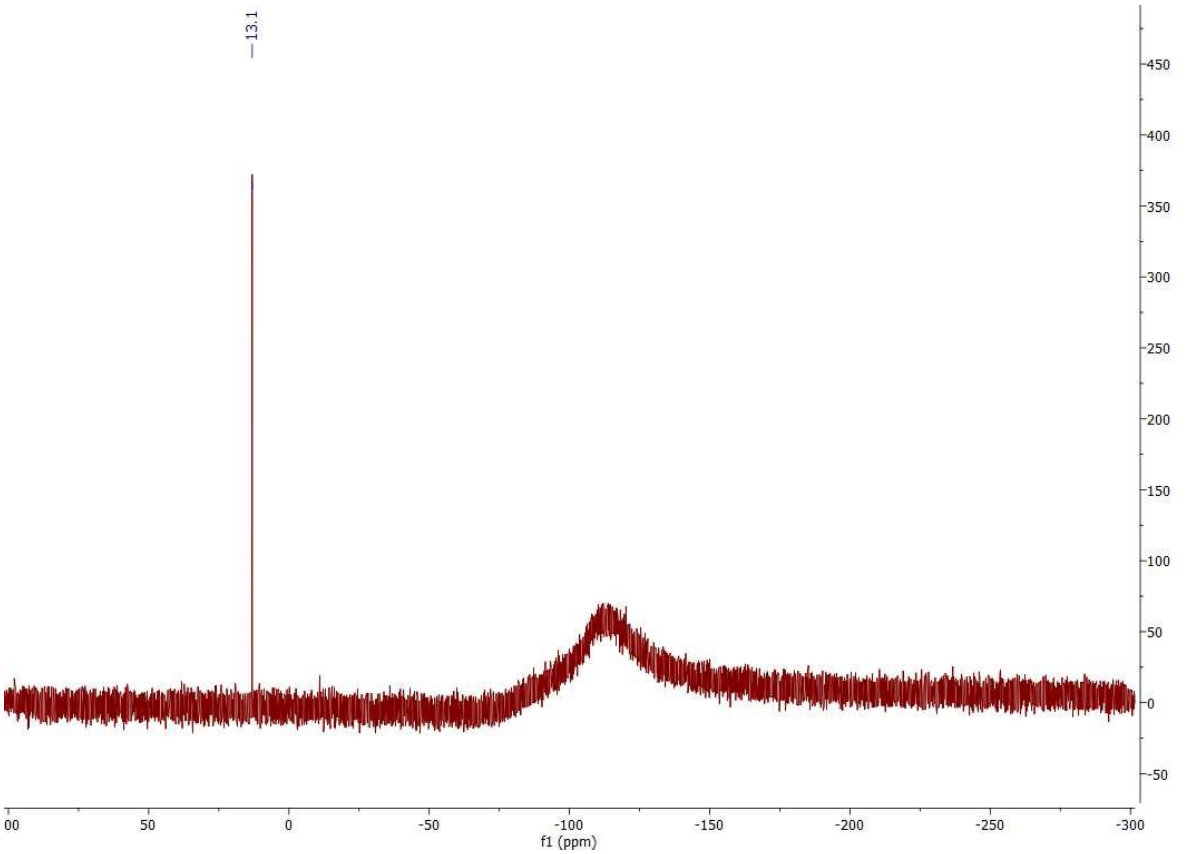
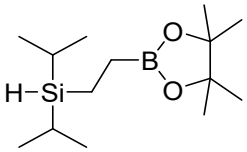


Figure S21. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of isopropoxydiisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1g).

diisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1h)



diisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 93% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.65-0.70 (m, 2H), 0.82-0.86 (m, 2H), 1.00-1.04 (m, 14H), 1.25 (s, 12H), 3.40 (s, 1H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 1.1, 10.5, 18.8, 19.1, 24.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 9.9
EI-MS m/z (rel. int.): 227 (47), 145 (24), 127 (11), 99 (16), 83 (100), 71 (14), 69 (12), 59 (18), 57 (13), 55 (23)

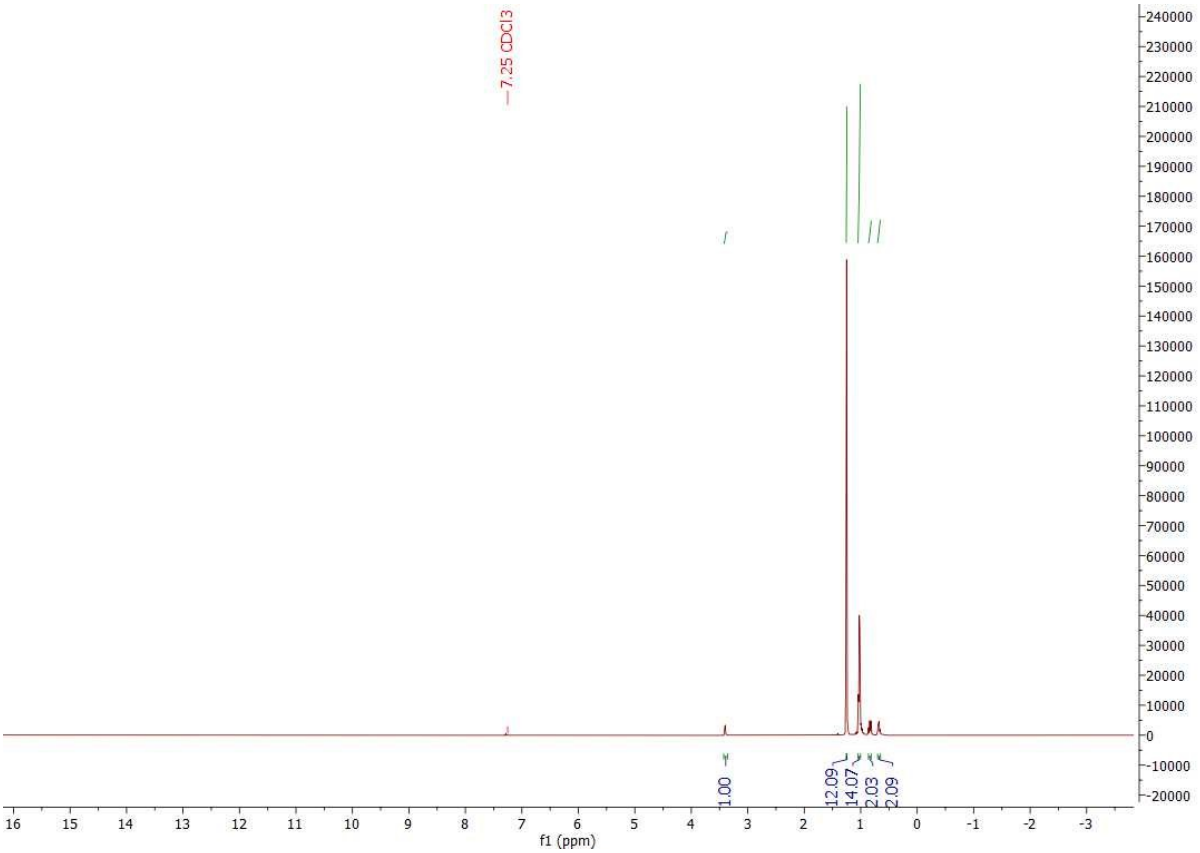


Figure S22. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of diisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1h).

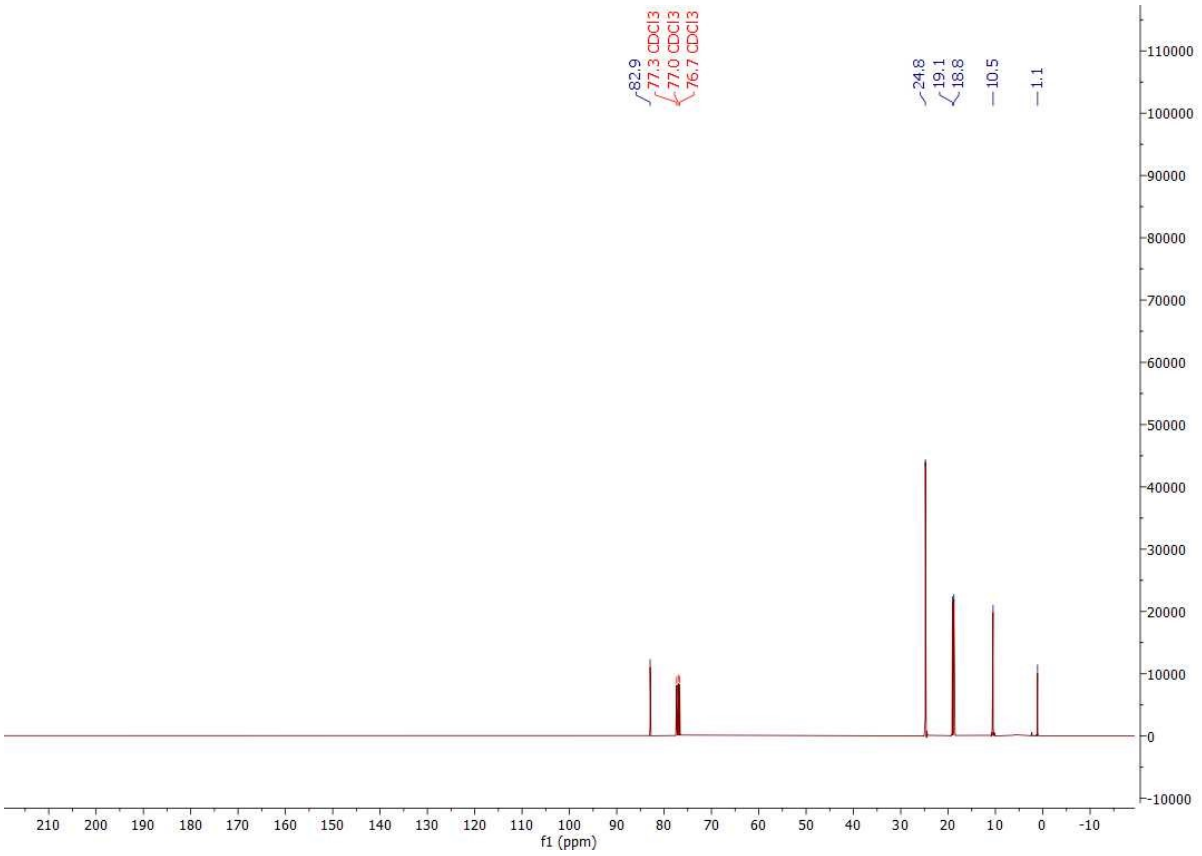


Figure S23. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of diisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1h).

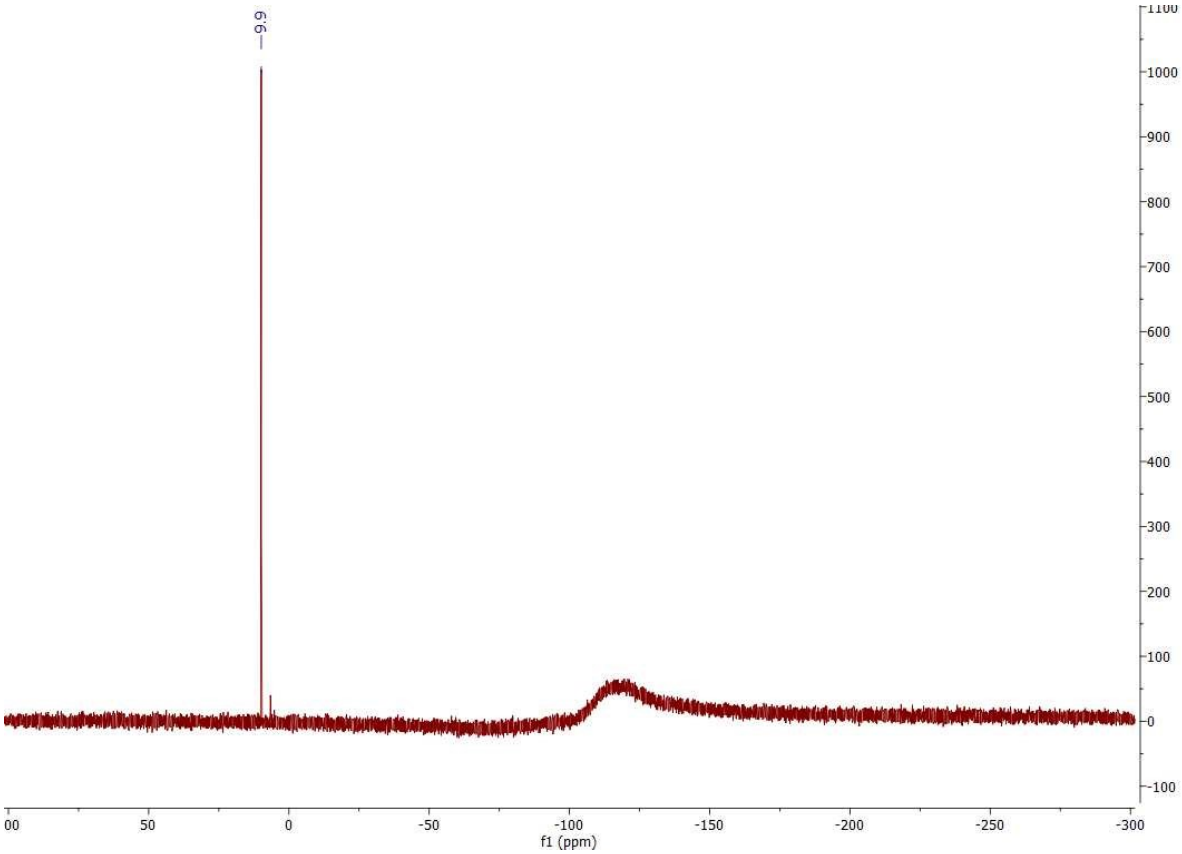
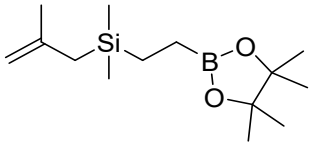


Figure S24. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of diisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1h).

dimethyl(2-methylallyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1i)



dimethyl(2-methylallyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 72% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, C_6D_6, 25°C) δ (ppm): 0.00 (s, 6H), 0.76-0.82 (m, 2H), 0.91-0.97 (m, 2H), 1.04 (s, 12H), 1.50 (s, 2H), 1.64 (s, 3H), 4.63 (d, J=37.1, 2H)
^{13}C NMR (101 MHz, C_6D_6, 25°C) δ (ppm): -3.2, 8.5, 25.1, 25.5, 27.1, 82.9, 108.8, 143.8, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 2.5
EI-MS m/z (rel. int.): 213 (100), 131 (58), 115 (12), 113 (18), 85 (22), 83 (97), 59 (16), 55 (18)

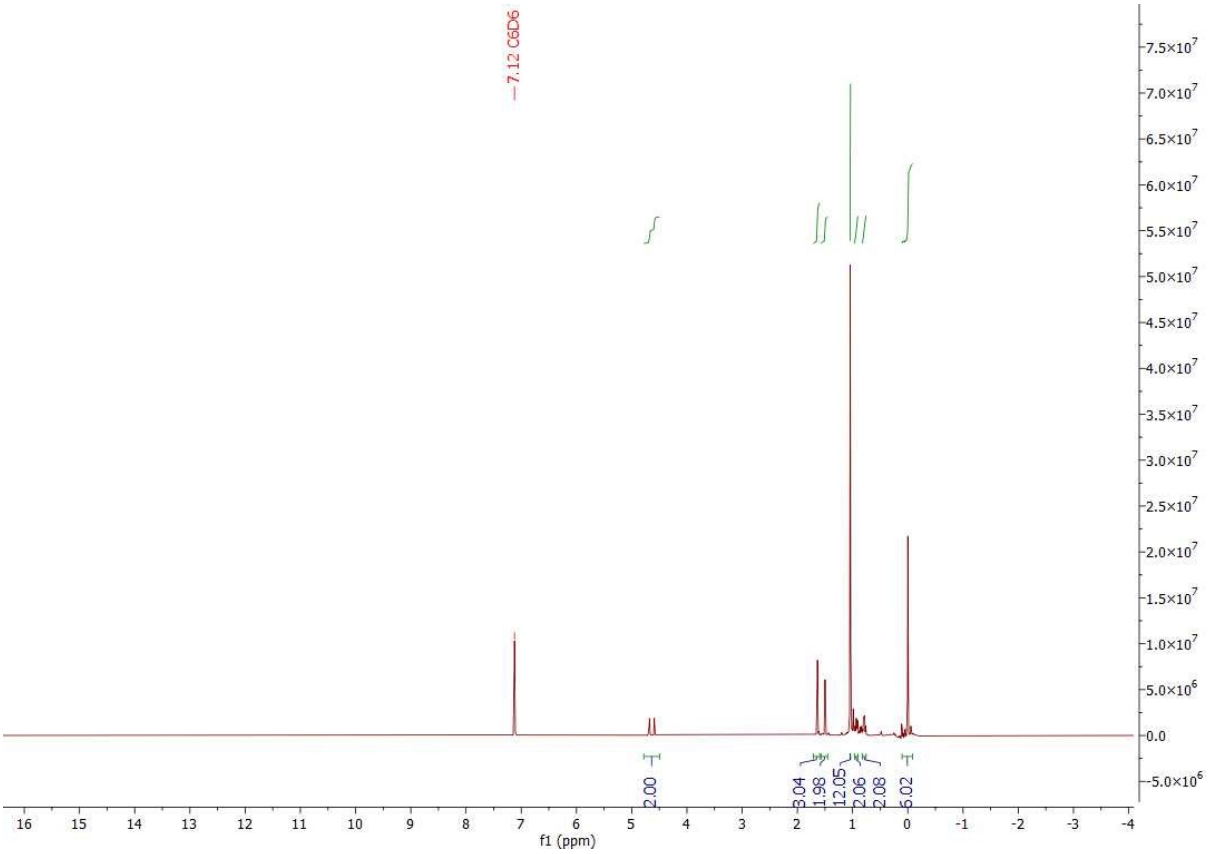


Figure S25. ^{1}H NMR (400 MHz, C_6D_6, 25°C) of dimethyl(2-methylallyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1i).

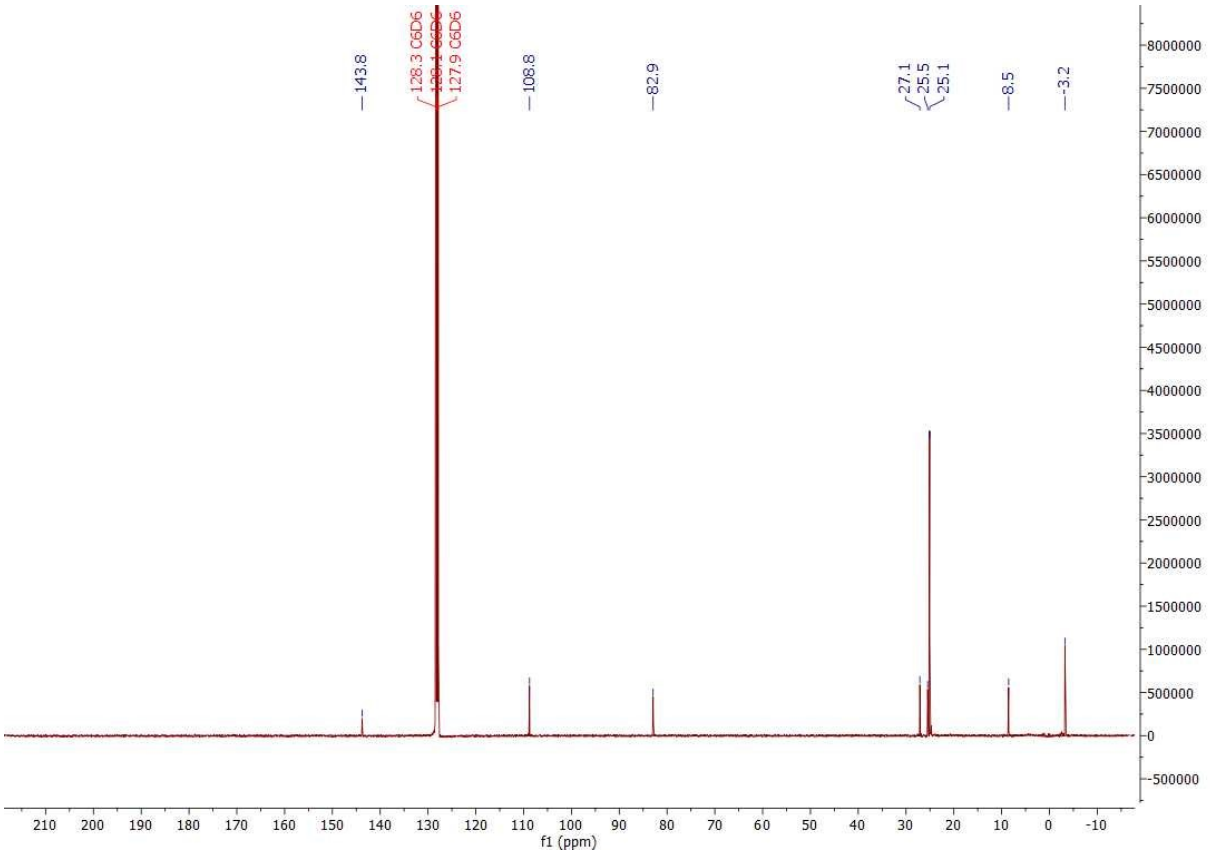


Figure S26. ^{13}C NMR (101 MHz, C_6D_6, 25°C) of dimethyl(2-methylallyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1i).

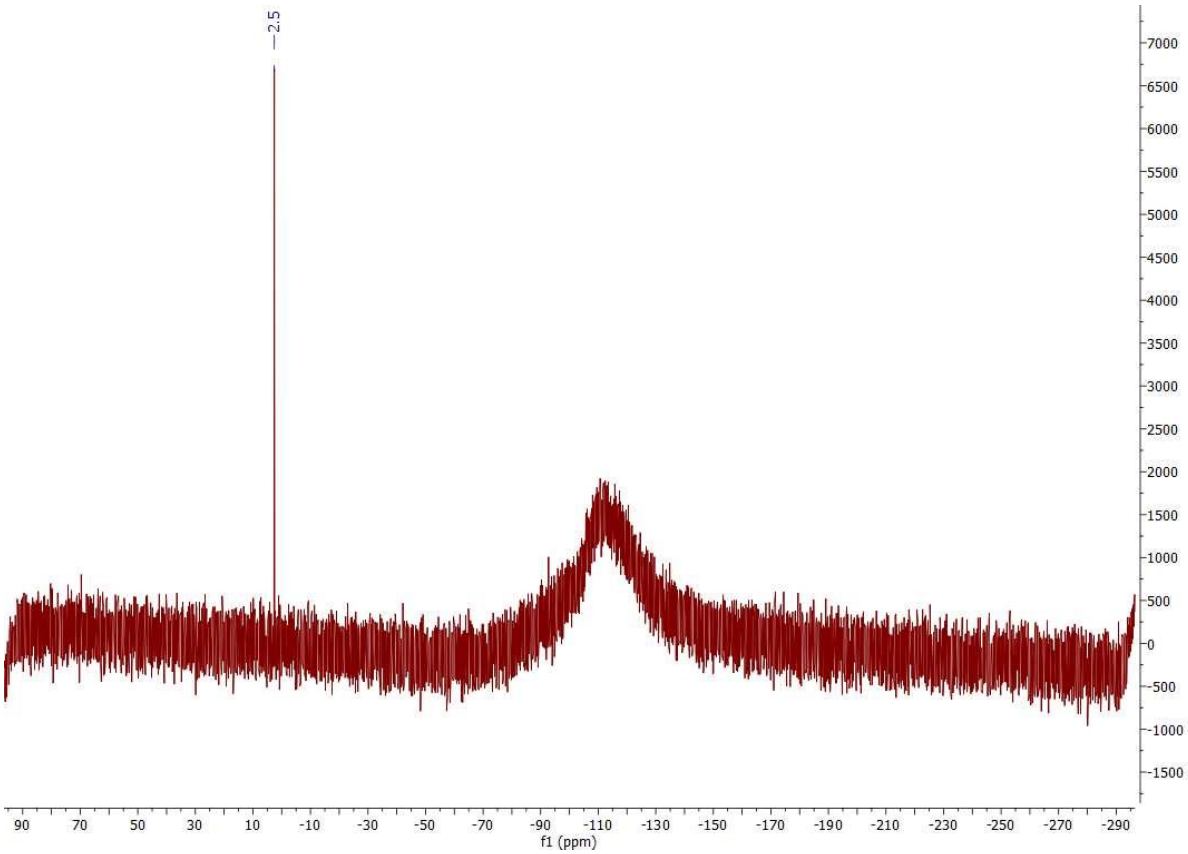
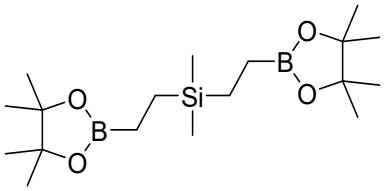


Figure S27. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of dimethyl(2-methylallyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1i).

dimethylbis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1j)



dimethylbis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 87% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.11 (s, 6H), 0.49-0.53 (m, 4H), 0.66-0.70 (m, 4H), 1.21 (s, 24H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -4.3, 7.4, 24.8, 82.8, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 6.0
EI-MS m/z (rel. int.): 253 (8), 213 (100), 169 (8), 131 (31), 113 (5), 83 (53), 69 (6), 59 (5), 55 (10)

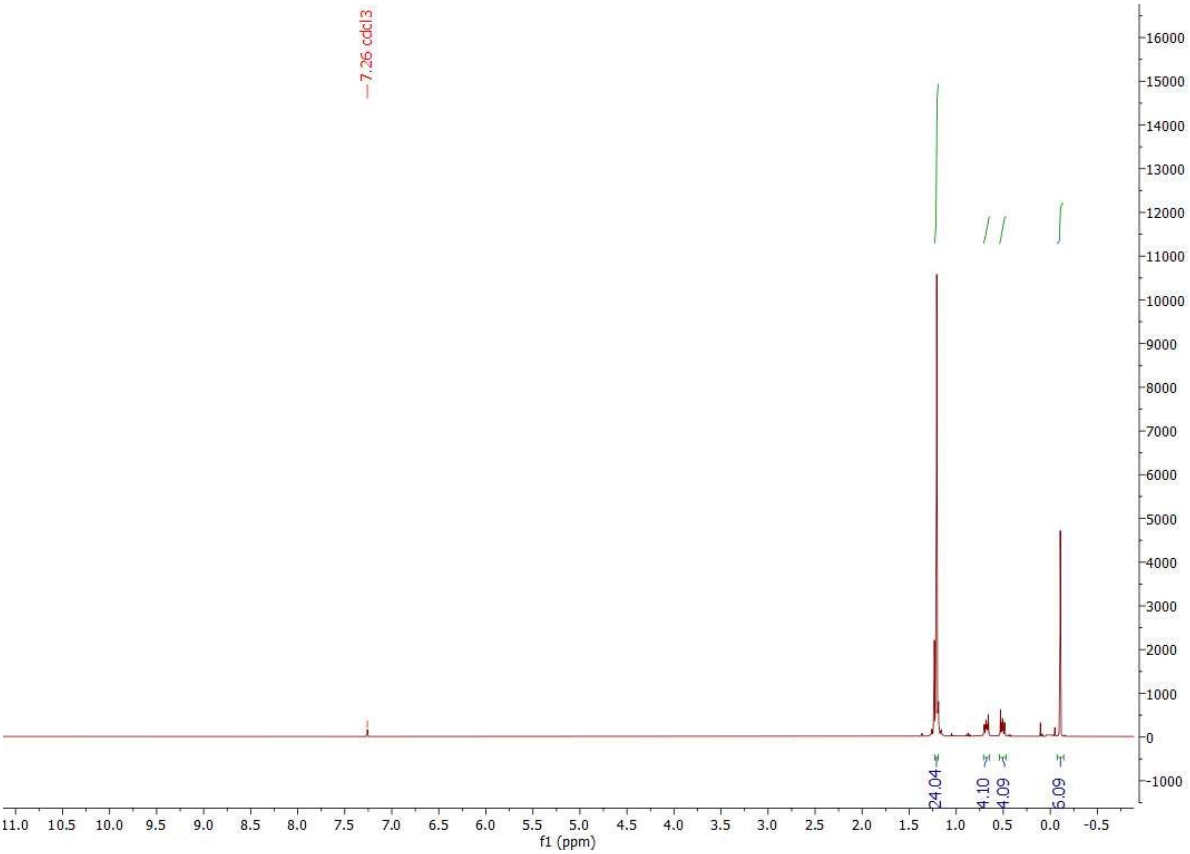


Figure S28. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of dimethylbis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1j).

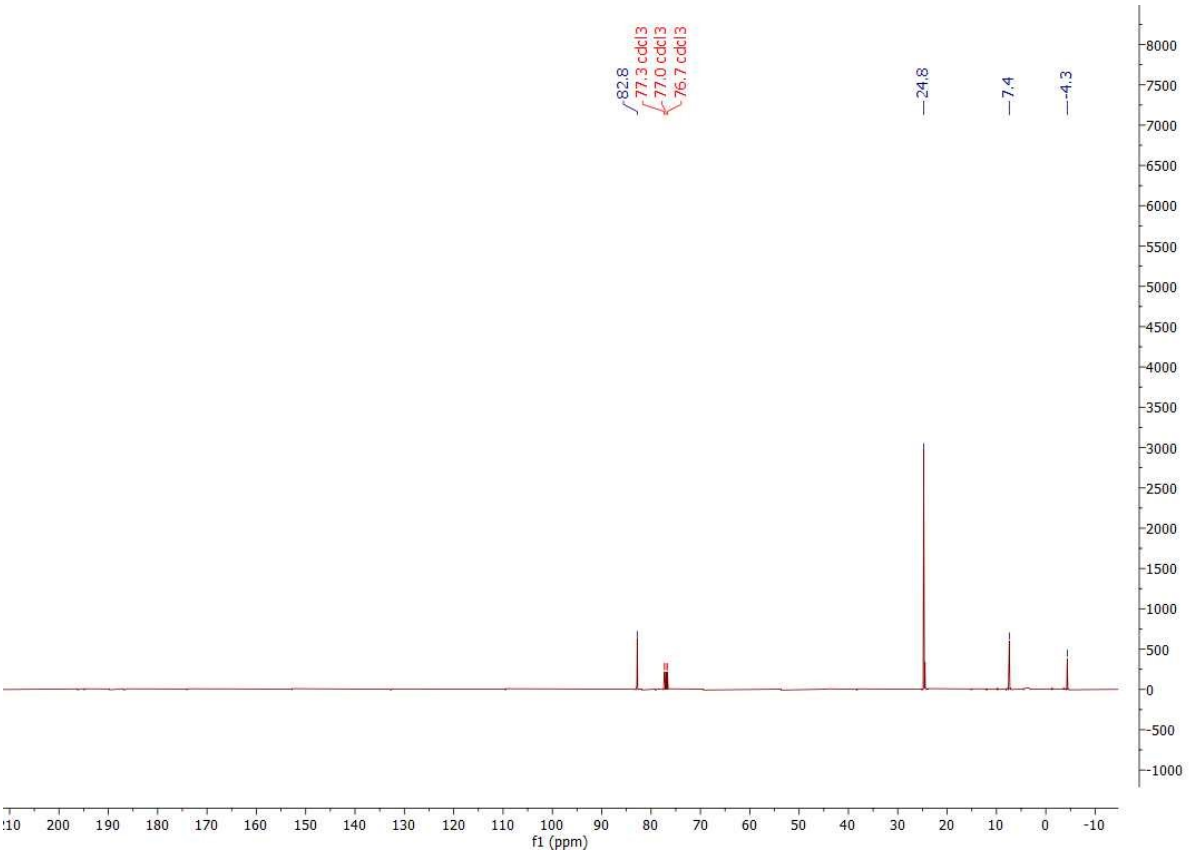


Figure S29. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of dimethylbis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1j).

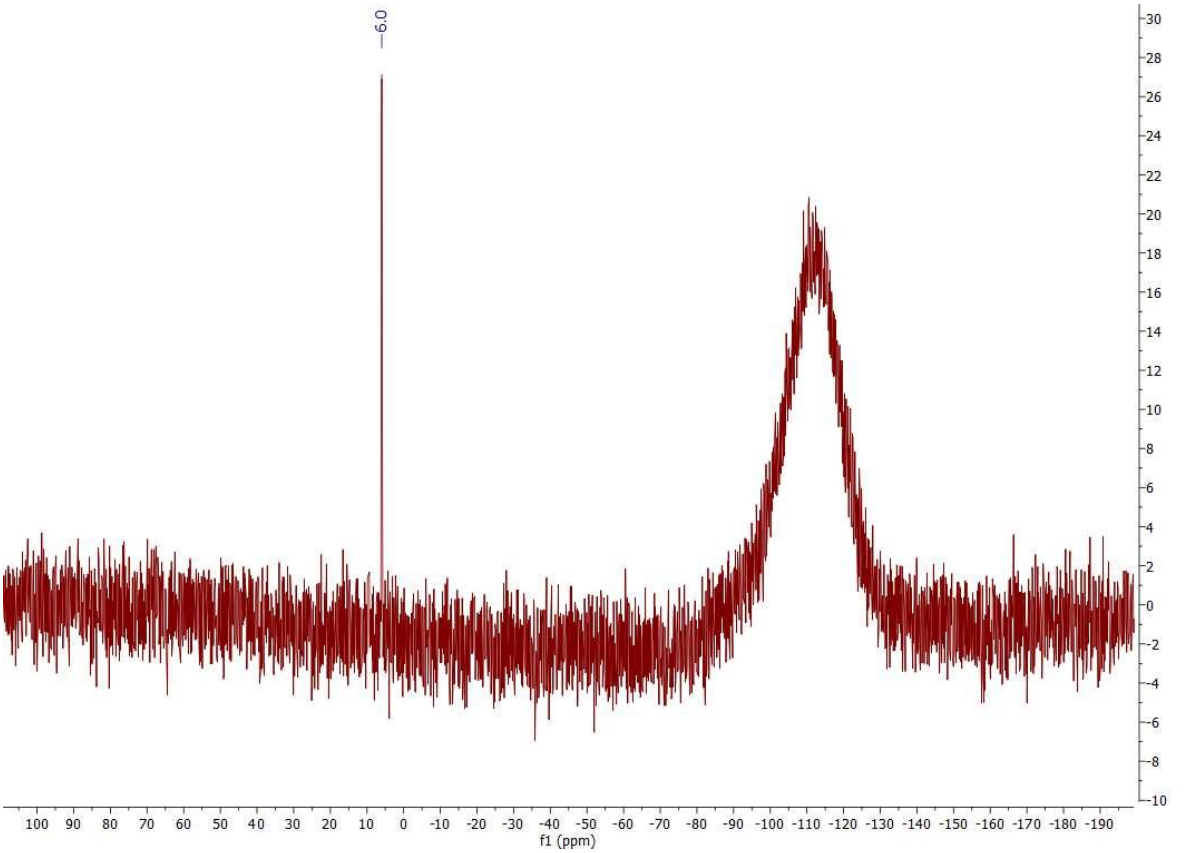
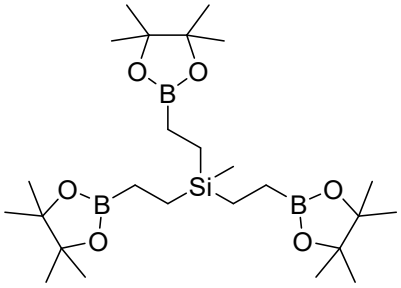


Figure S30. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of dimethylbis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1j).

methyltris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1k)



methyltris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 95% yield, and is known in the literature. All spectroscopic data are in agreement.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.14 (s, 3H), 0.49-0.53 (m, 6H), 0.65-0.70 (m, 6H), 1.20 (s, 36H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -6.6, 5.6, 24.8, 82.8, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 8.1

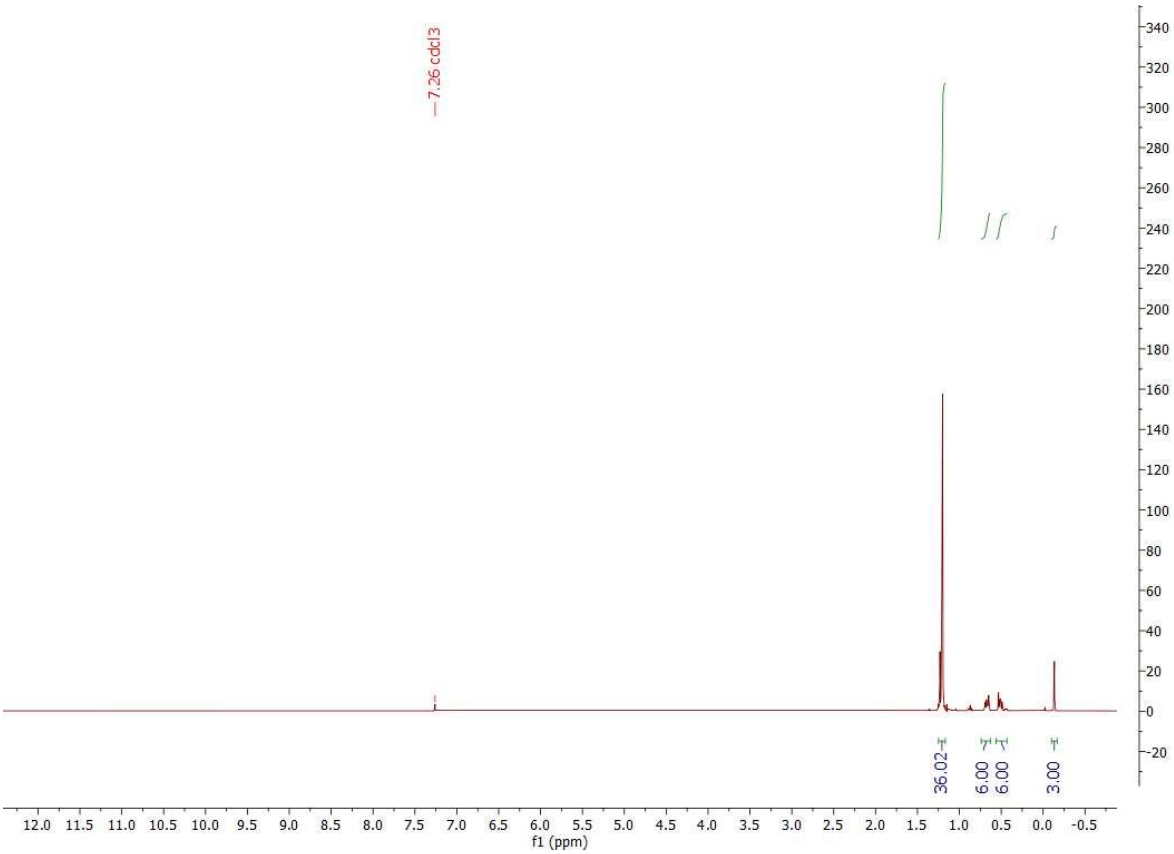


Figure S31. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of methyltris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1k).

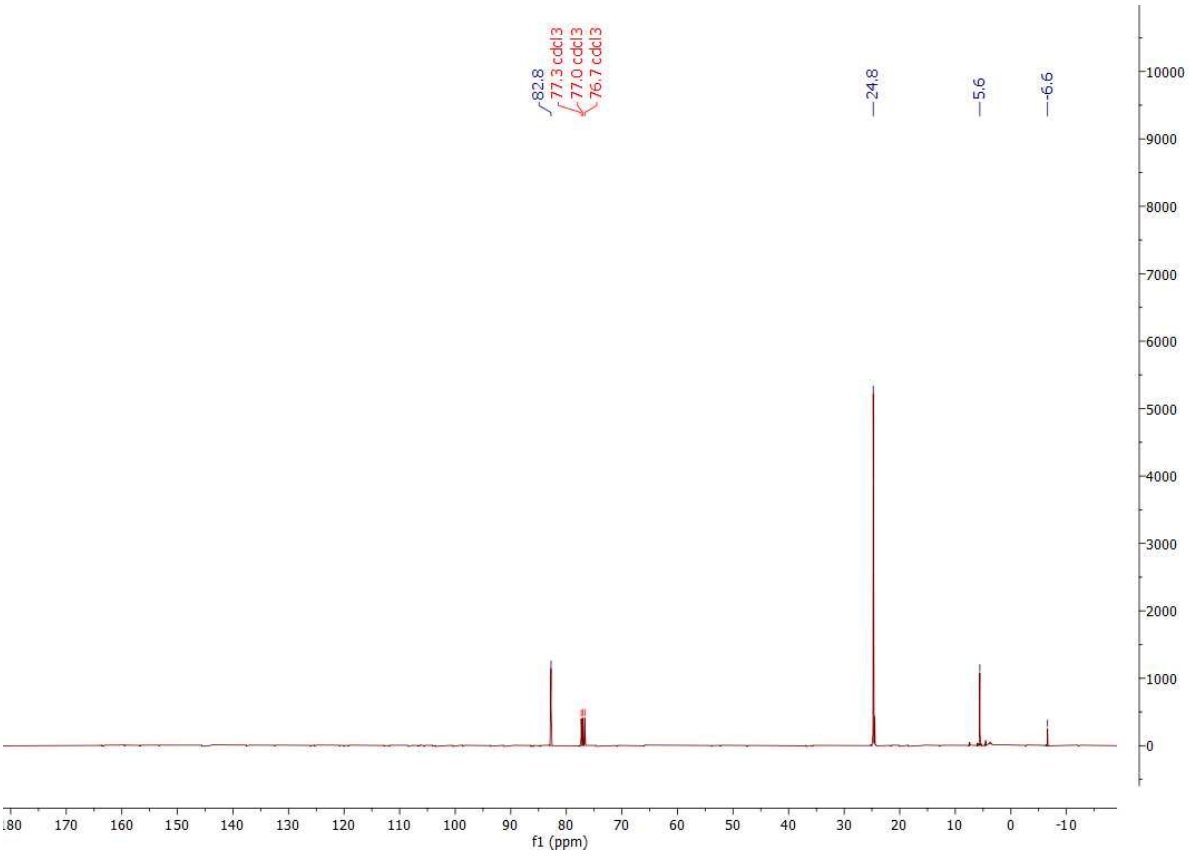


Figure S32. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of methyltris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1k).

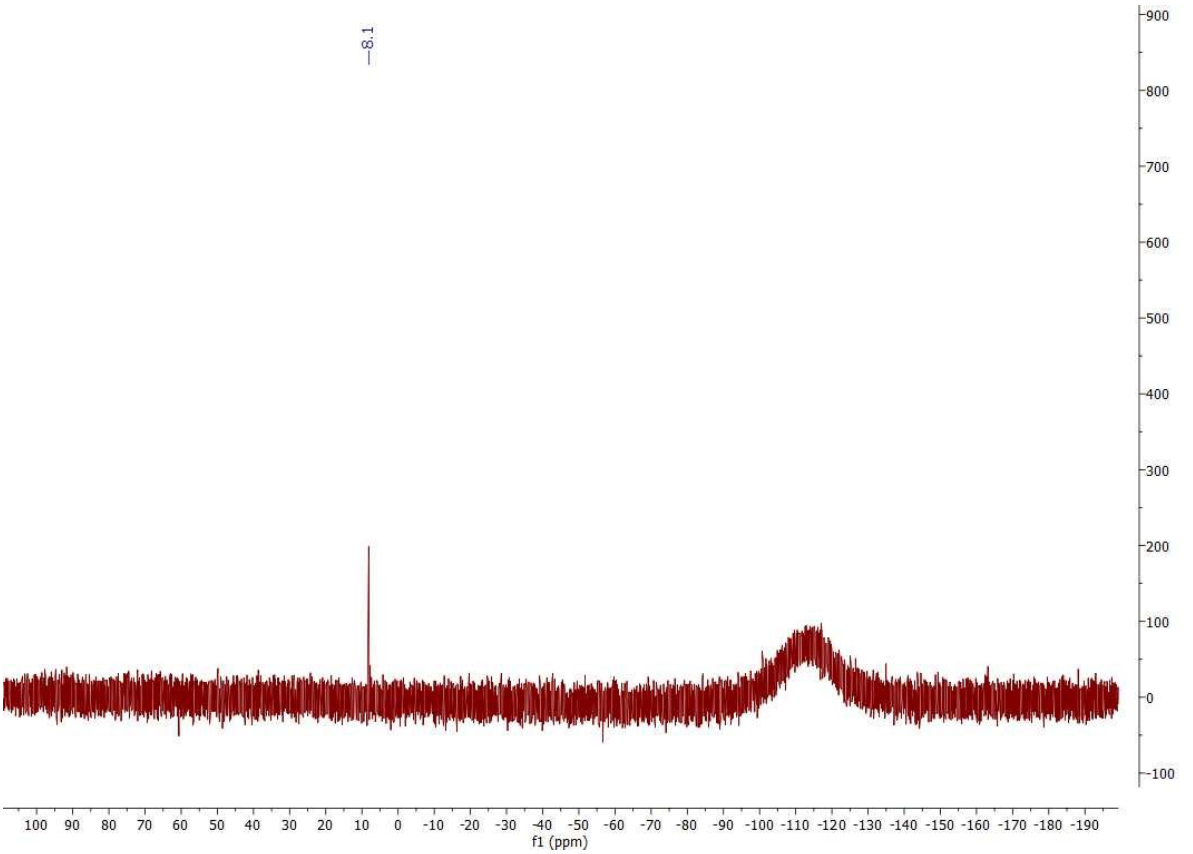
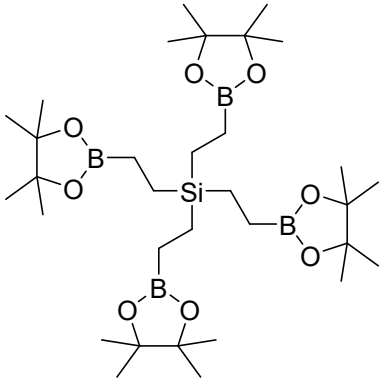


Figure S33. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of methyltris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1k).

tetrakis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1l)



tetrakis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 98% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.52-0.56 (m, 8H), 0.67-0.71 (m, 8H), 1.21 (s, 48H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 3.9, 24.8, 82.7, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 10.1

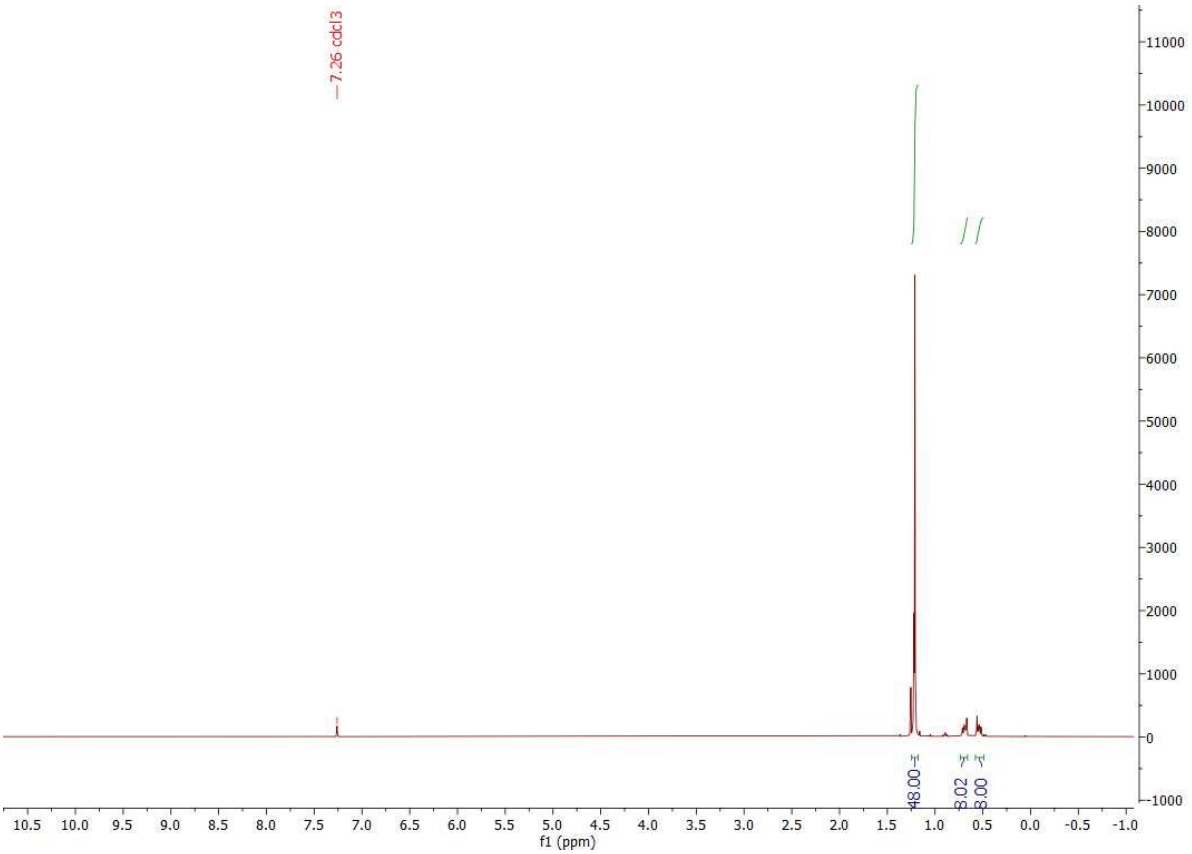


Figure S34. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of tetrakis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1l).

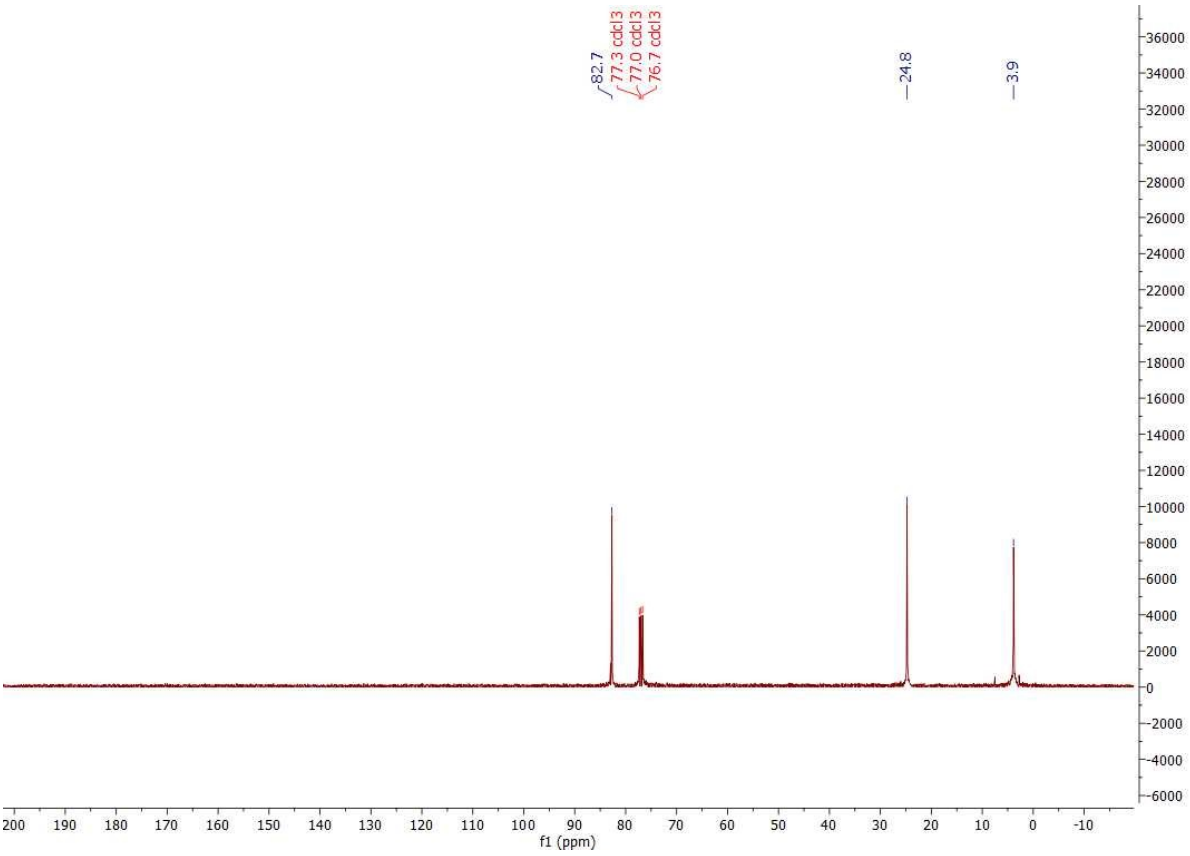


Figure S35. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of tetrakis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1l).

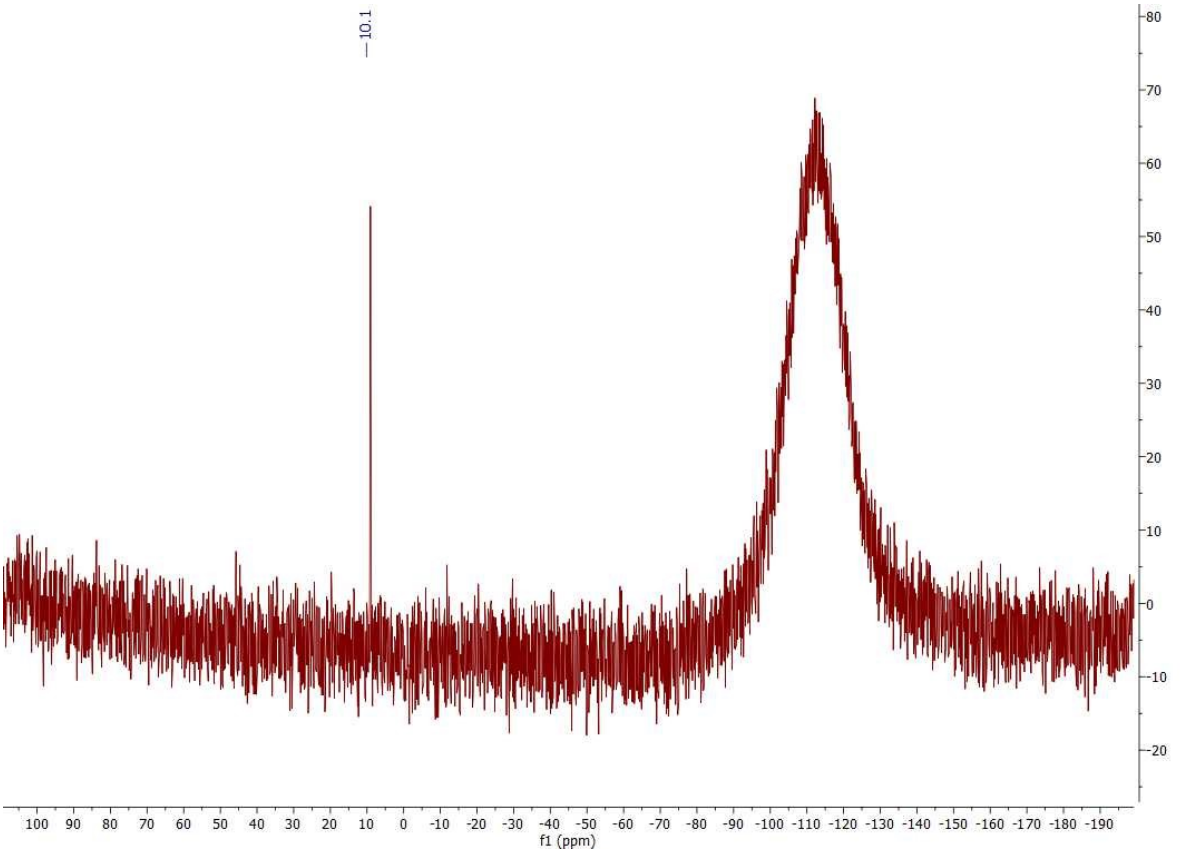
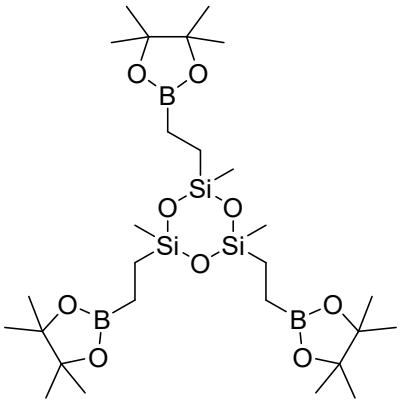


Figure S36. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of tetrakis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (1l).

2,4,6-trimethyl-2,4,6-tris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,5,2,4,6-trioxatrisilinane (1m)



2,4,6-trimethyl-2,4,6-tris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,5,2,4,6-trioxatrisilinane was obtained with 82% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.10 (s, 9H), 0.57-0.62 (m, 6H), 0.74-0.79 (m, 6H), 1.22 (s, 36H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -0.9, 9.9, 24.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -9.0

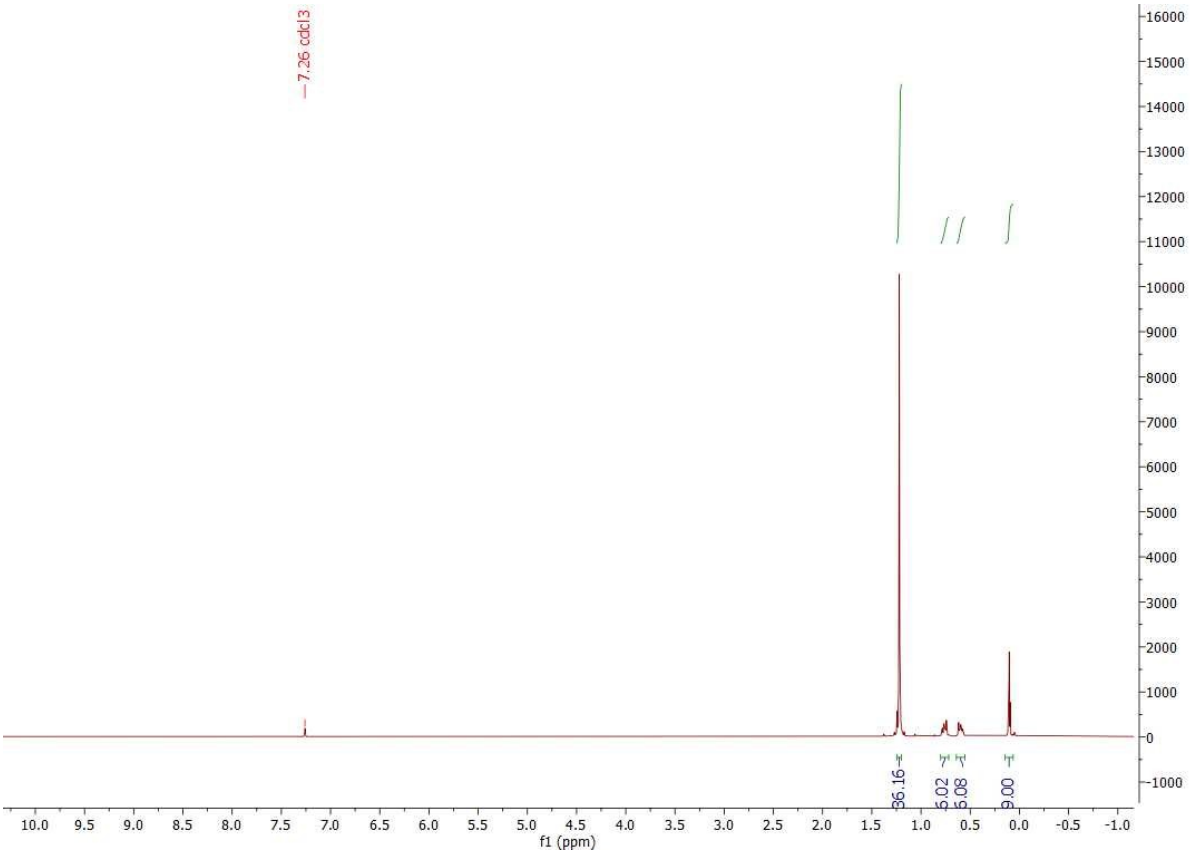


Figure S37. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2,4,6-trimethyl-2,4,6-tris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,5,2,4,6-trioxatrisilinane (1m).

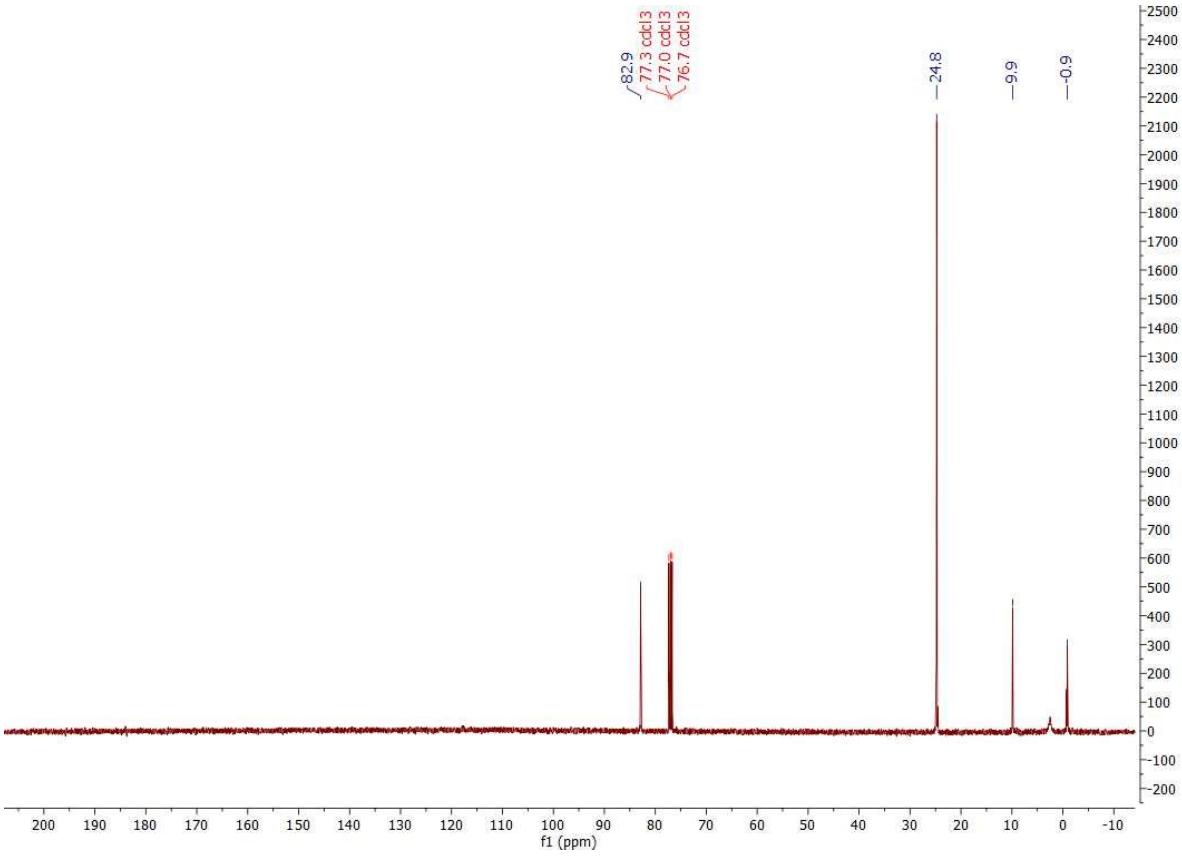


Figure S38. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2,4,6-trimethyl-2,4,6-tris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,5,2,4,6-trioxatrisilinane (1m).

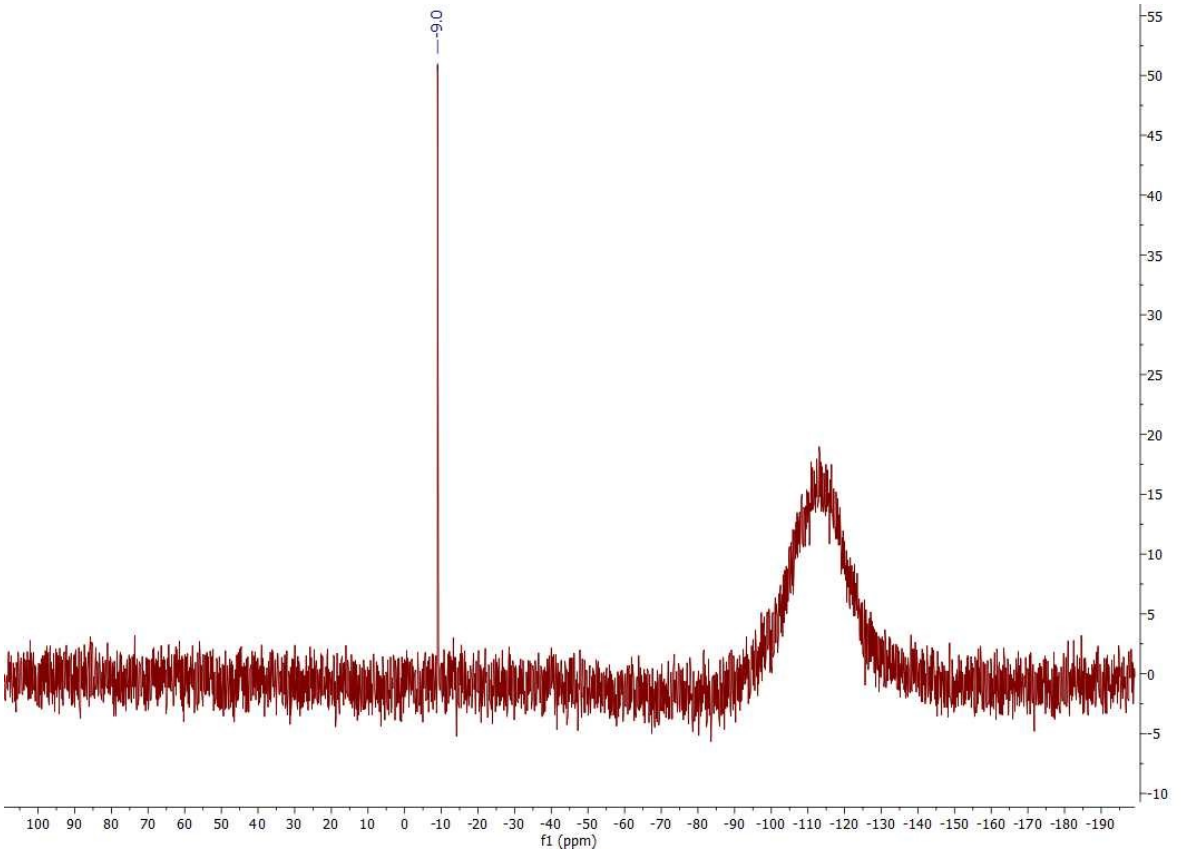
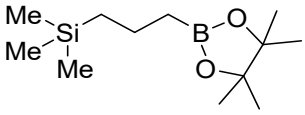


Figure S39. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of 2,4,6-trimethyl-2,4,6-tris(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,5,2,4,6-trioxatrisilinane (1m).

trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2a)



trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane was obtained with 62% yield, and is known in the literature. All spectroscopic data are in agreement.[6]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.04 (s, 9H), 0.49-0.54 (m, 2H), 0.80-0.84 (m, 2H), 1.24 (s, 12H), 1.39-1.45 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -1.6, 18.5, 20.1, 24.5, 83.1, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 0.7
EI-MS m/z (rel. int.): 227 (94), 185 (16), 157 (7), 145 (7), 127 (80), 117 (22), 114 (37), 99 (30), 83 (70), 73 (100), 69 (13), 59 (21), 55 (14)

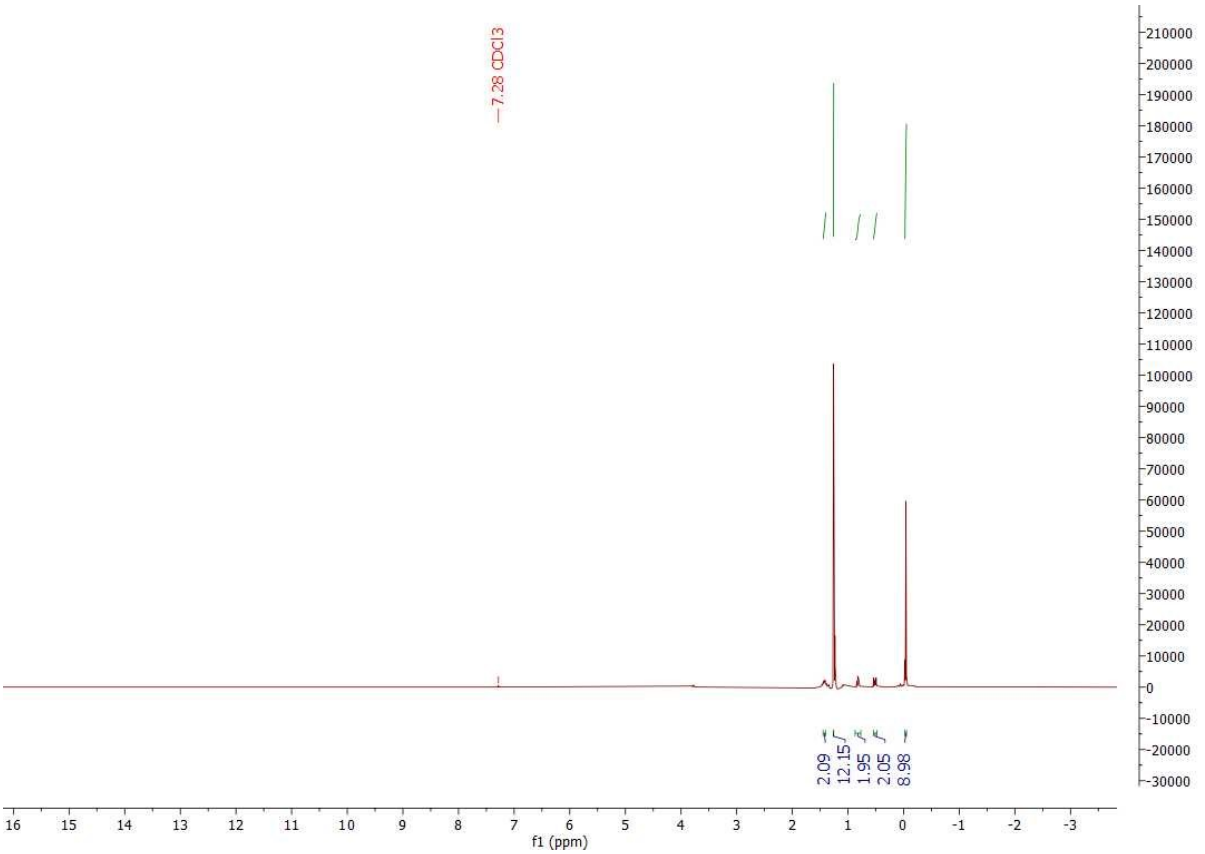


Figure S40. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2a).

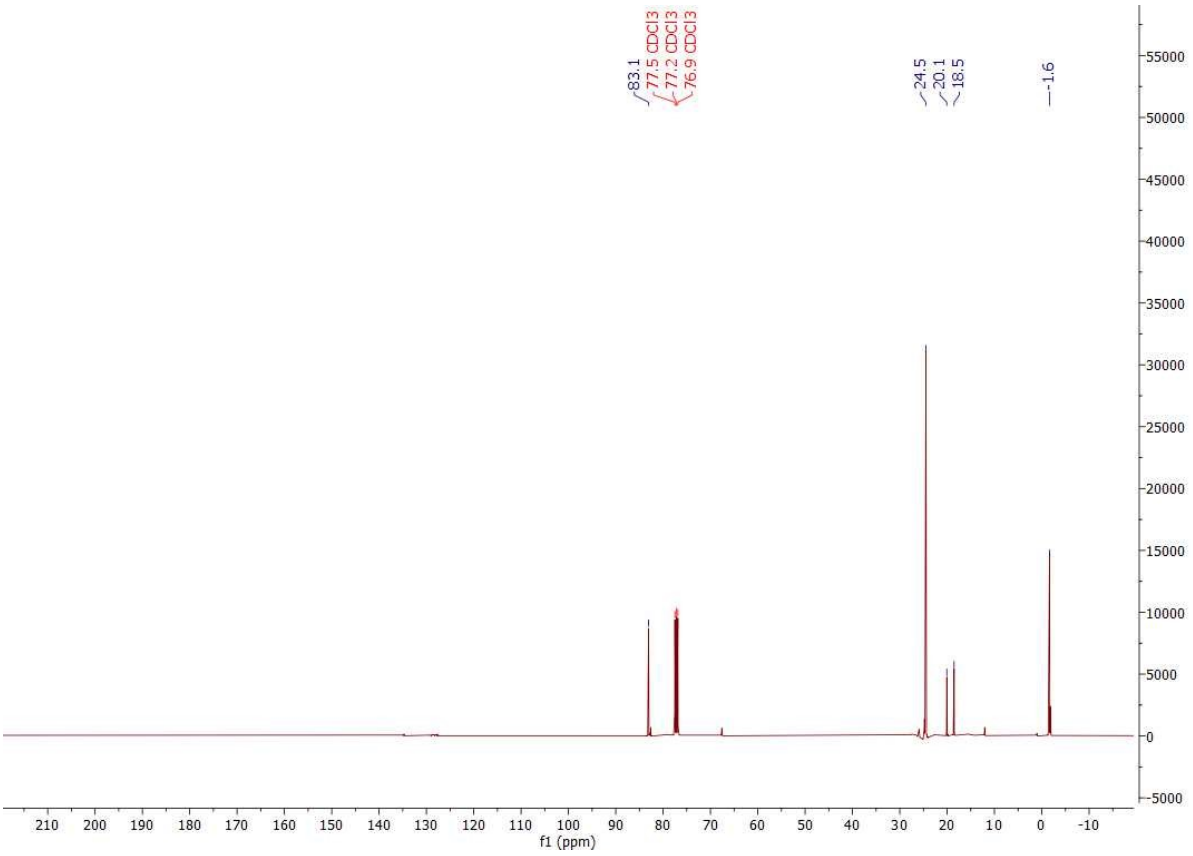


Figure S41. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2a).

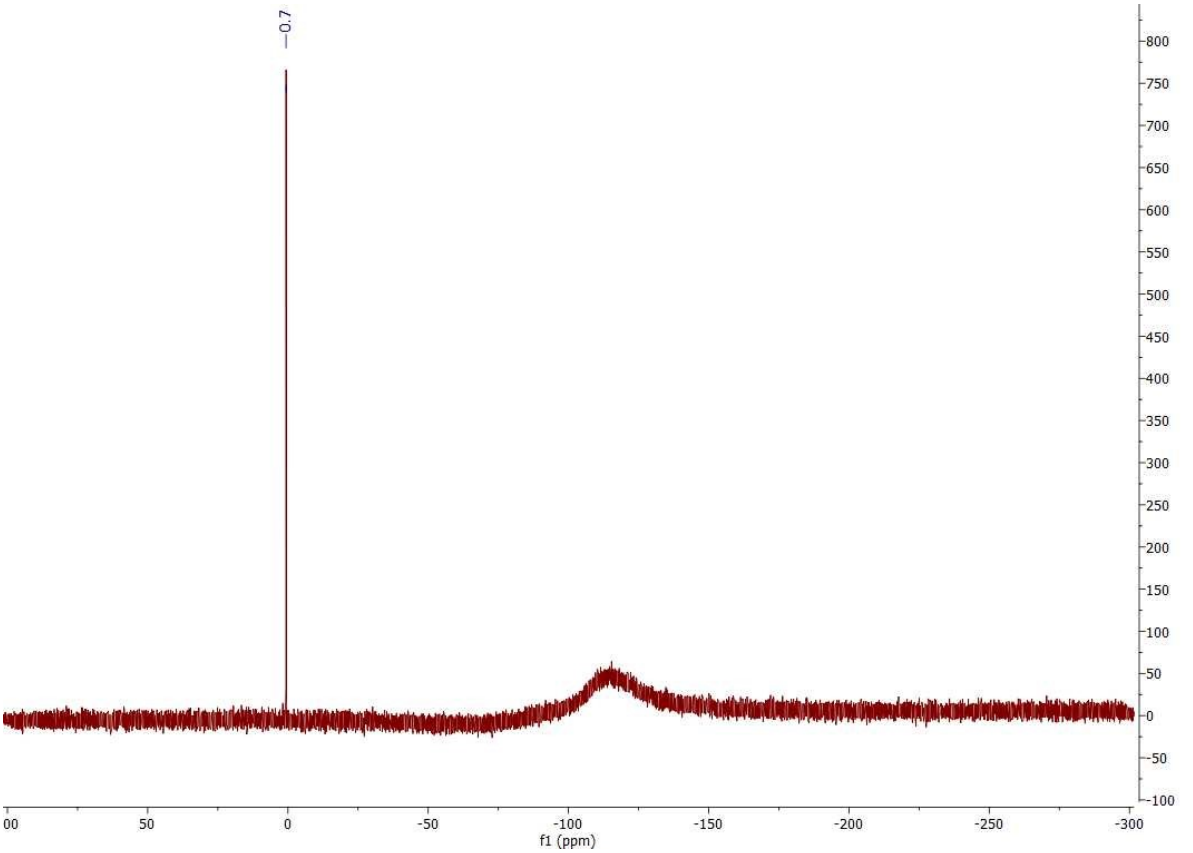
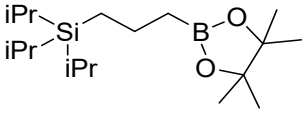


Figure S42. ^{1}H NMR (79 MHz, Chloroform-d, 25°C) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2a).

triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2b)



triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane was obtained with 97% yield, and is known in the literature. All spectroscopic data are in agreement.[6]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.60-0.64 (m, 2H), 0.85-0.88 (m, 2H), 1.04 (s, 21H), 1.26 (s, 12H), 1.45-1.53 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 11.0, 12.7, 18.9, 19.1, 24.8, 82.8
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 5.7
EI-MS m/z (rel. int.): 283 (100), 201 (7), 183 (97), 155 (43), 141 (9), 127 (12), 115 (12), 113 (32), 99 (20), 87 (14), 85 (43), 83 (66), 73 (17), 71 (12), 69 (13), 59 (40), 55 (12)

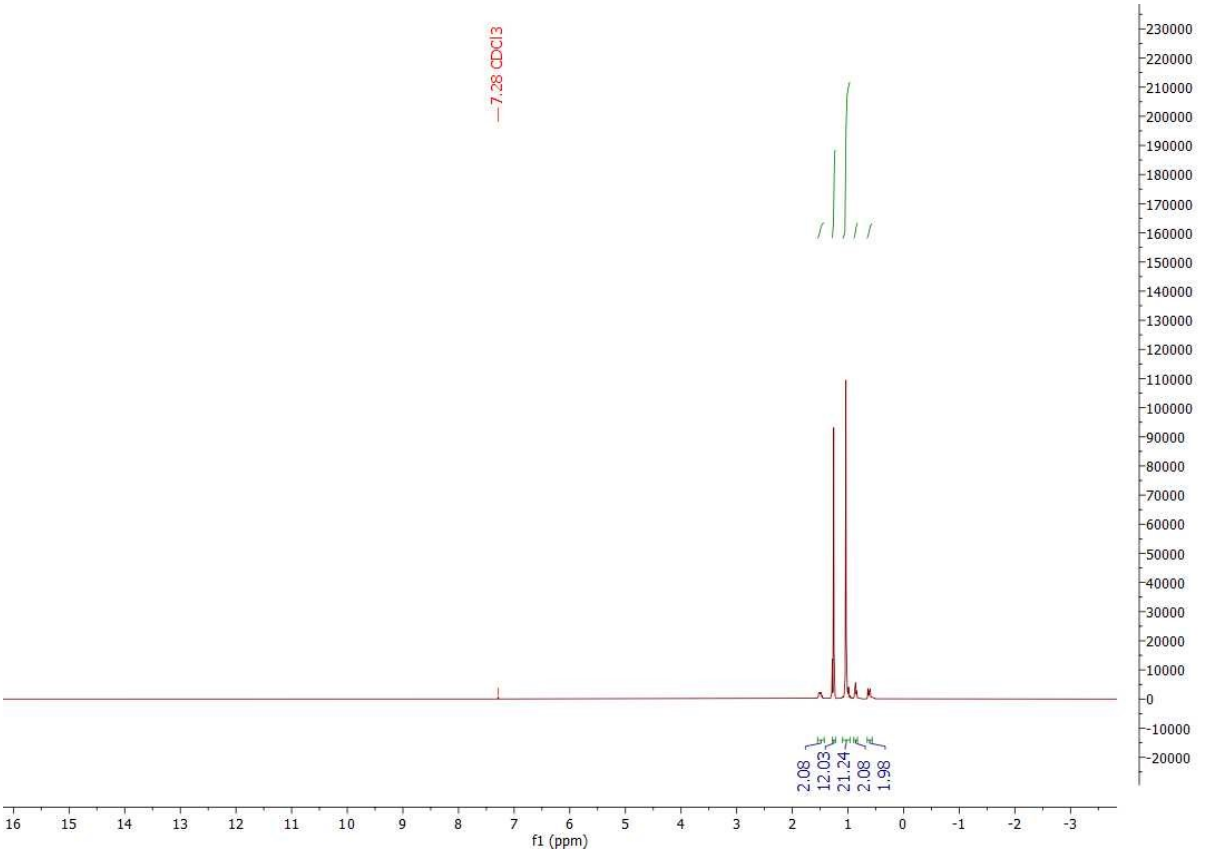


Figure S43. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2b).

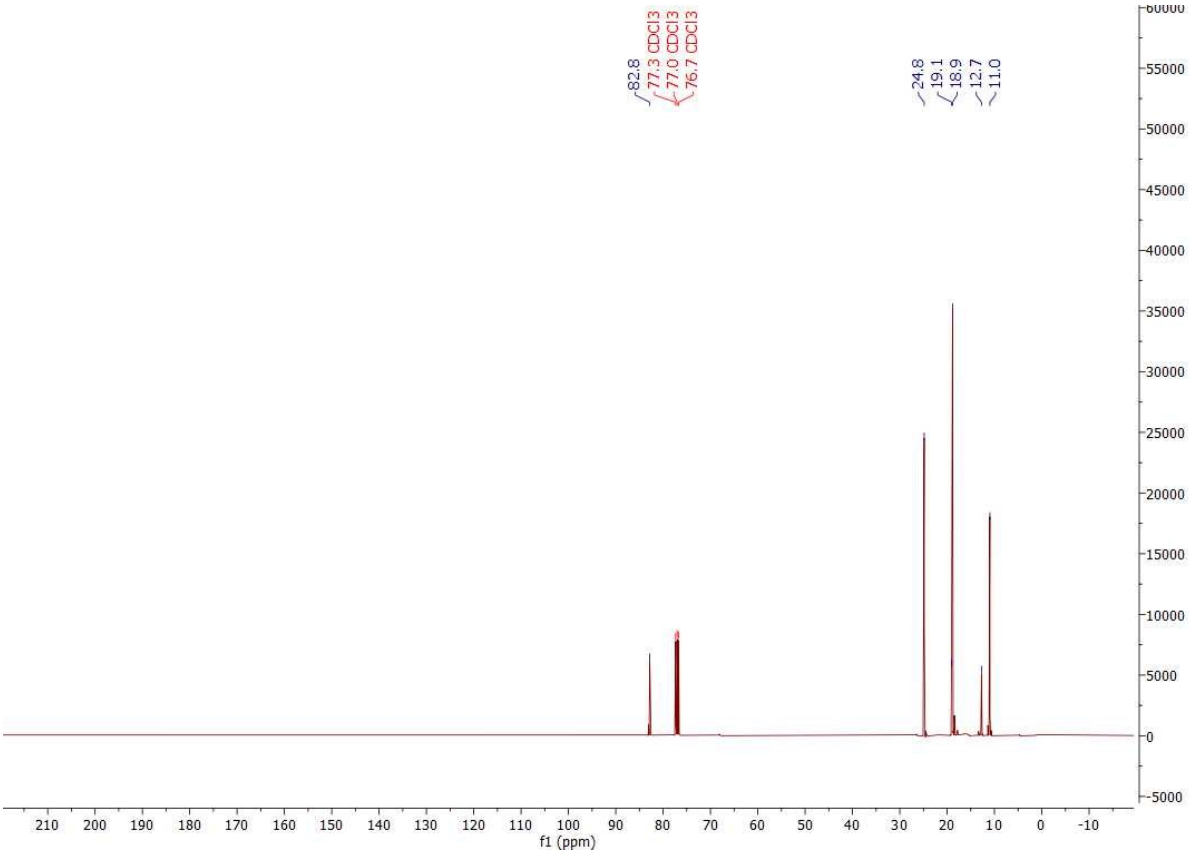


Figure S44. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2b).

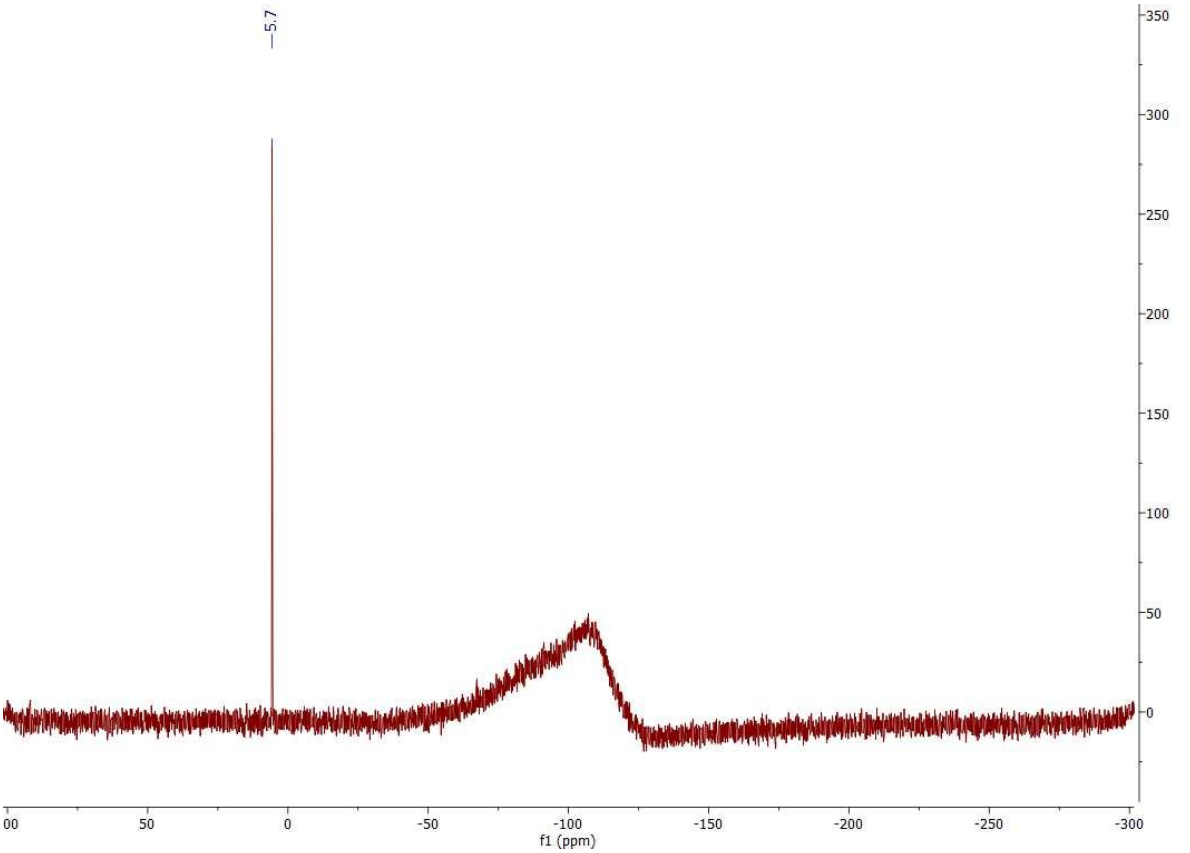
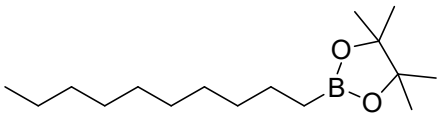


Figure S45. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (2b).

2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 92% yield, and is known in the literature. All spectroscopic data are in agreement.[7]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.77 (t, J=7.8, 2H), 0.88 (t, J=6.6 Hz, 3H), 1.25-1.28 (m, 26H), 1.35-1.43 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 14.1, 22.7, 24.0, 24.8, 29.3, 29.4, 29.6, 29.6, 31.9, 32.4, 82.8
EI-MS m/z (rel. int.): 253 (53), 211 (10), 182 (9), 168 (9), 129 (100), 111 (14), 101 (19), 97 (37), 87 (34), 85 (67), 83 (29), 71 (11), 69 (28), 59 (23), 57 (22), 55 (24)

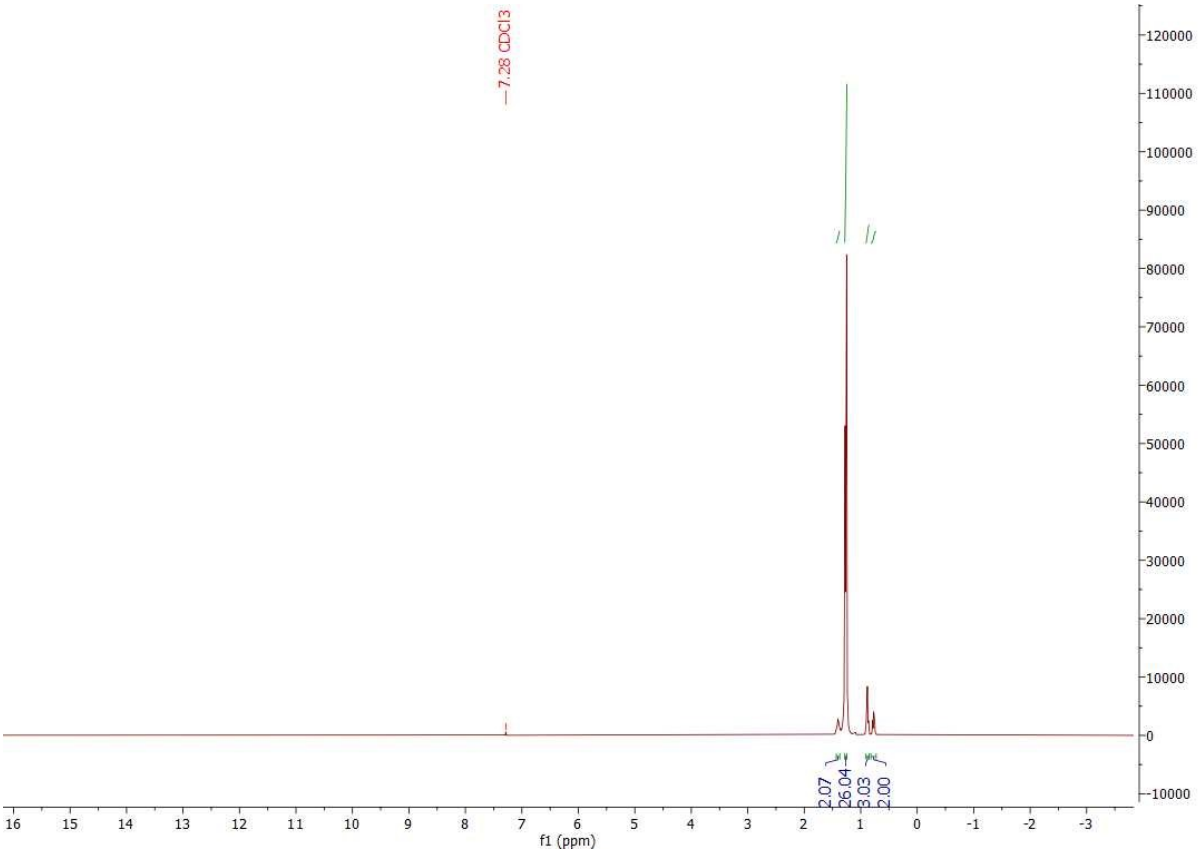


Figure S46. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d).

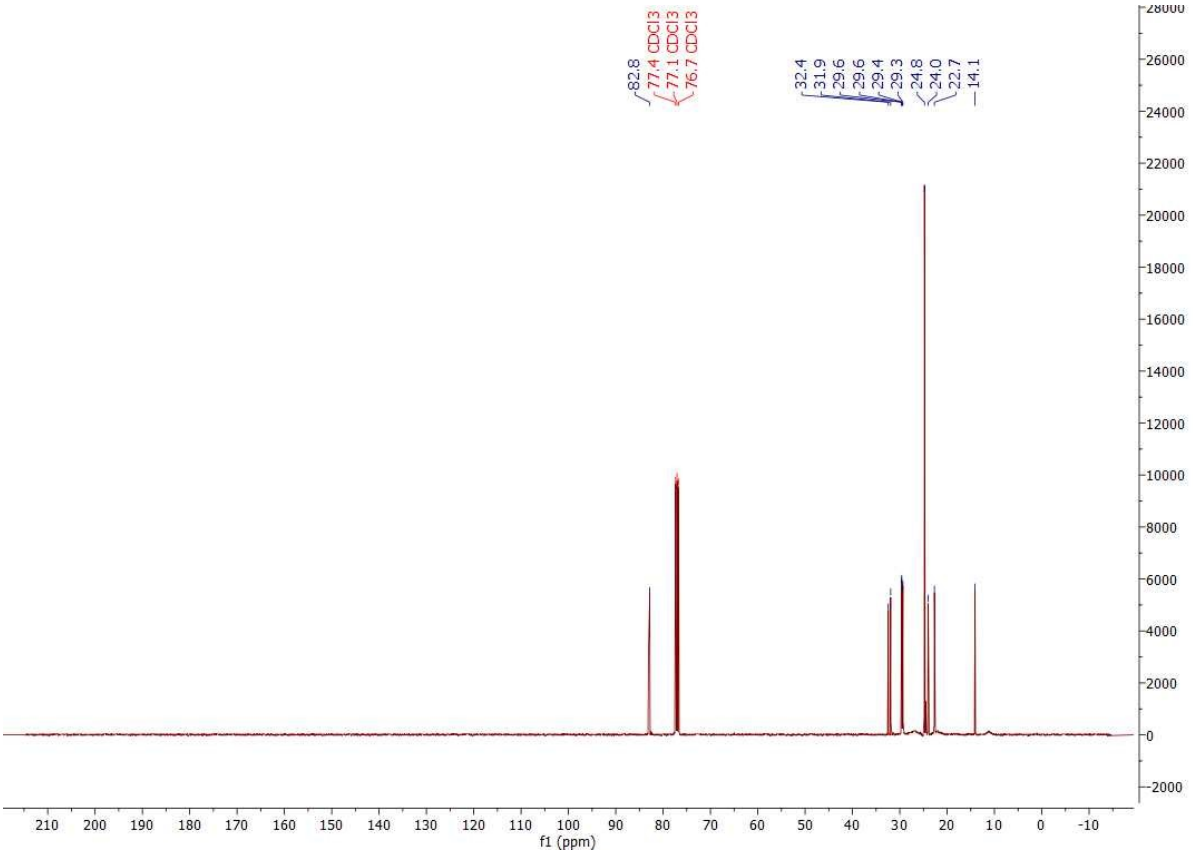
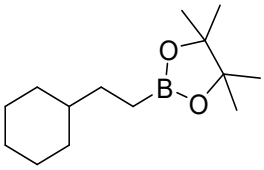


Figure S47. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-decyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d).

2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 74% yield, and is known in the literature. All spectroscopic data are in agreement.[7]

^{1}H NMR (400 MHz, Benzene-d6, 25°C) δ (ppm): 0.80-0.90 (m, 2H), 0.97 (t, J = 8.3 Hz, 2H), 1.06 (s, 12H), 1.10-1.24 (m, 4H), 1.49 (q, J = 6.7 Hz, 2H), 1.56-1.69 (m, 3H), 1.69-1.79 (m, 2H)
^{13}C NMR (101 MHz, Benzene-d6, 25°C) δ (ppm): 24.6, 26.5, 26.8, 31.7, 33.1, 39.9, 82.3
EI-MS m/z (rel. int.): 238 (4), 223 (36), 154 (41), 138 (12), 129 (82), 110 (41), 101 (23), 97 (26), 87 (48), 84 (100), 69 (32), 67 (27), 59 (25), 57 (19), 55 (58)

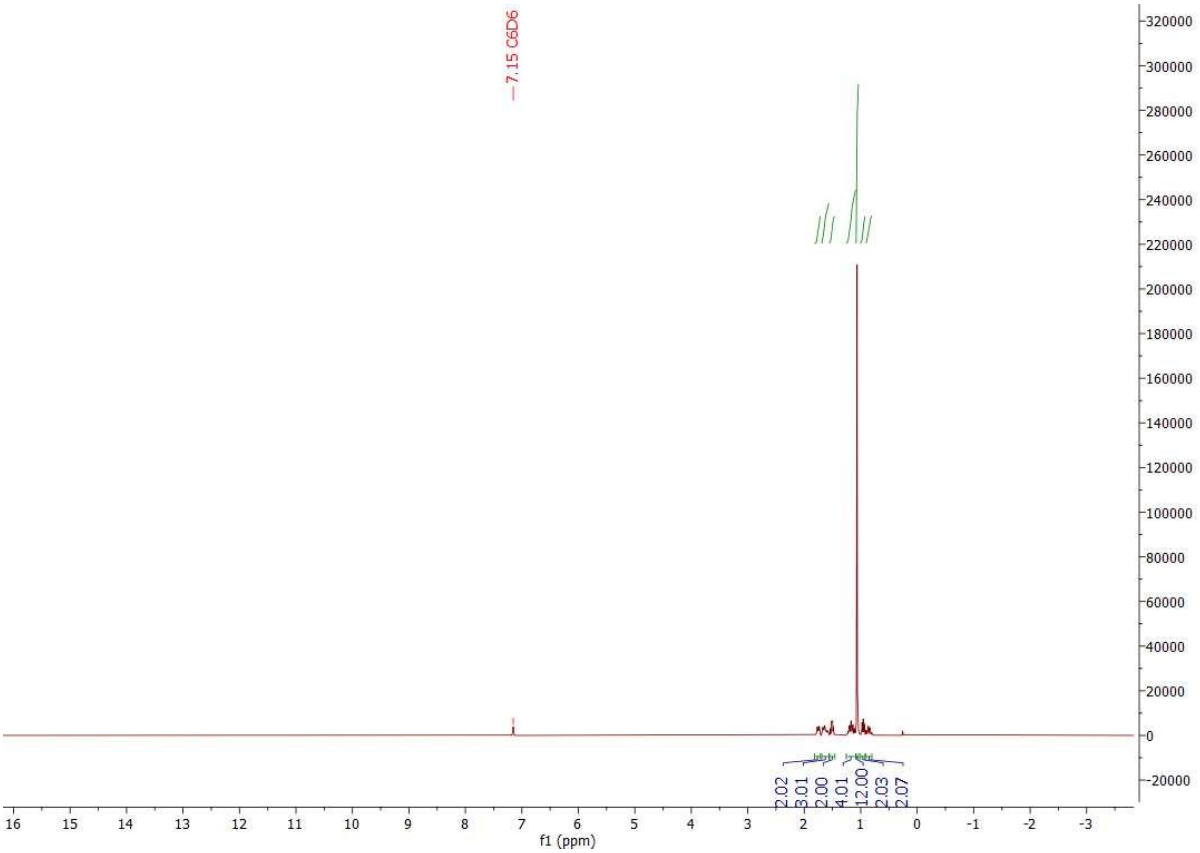


Figure S48. ^{1}H NMR (400 MHz, Benzene-d6, 25°C) of 2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e).

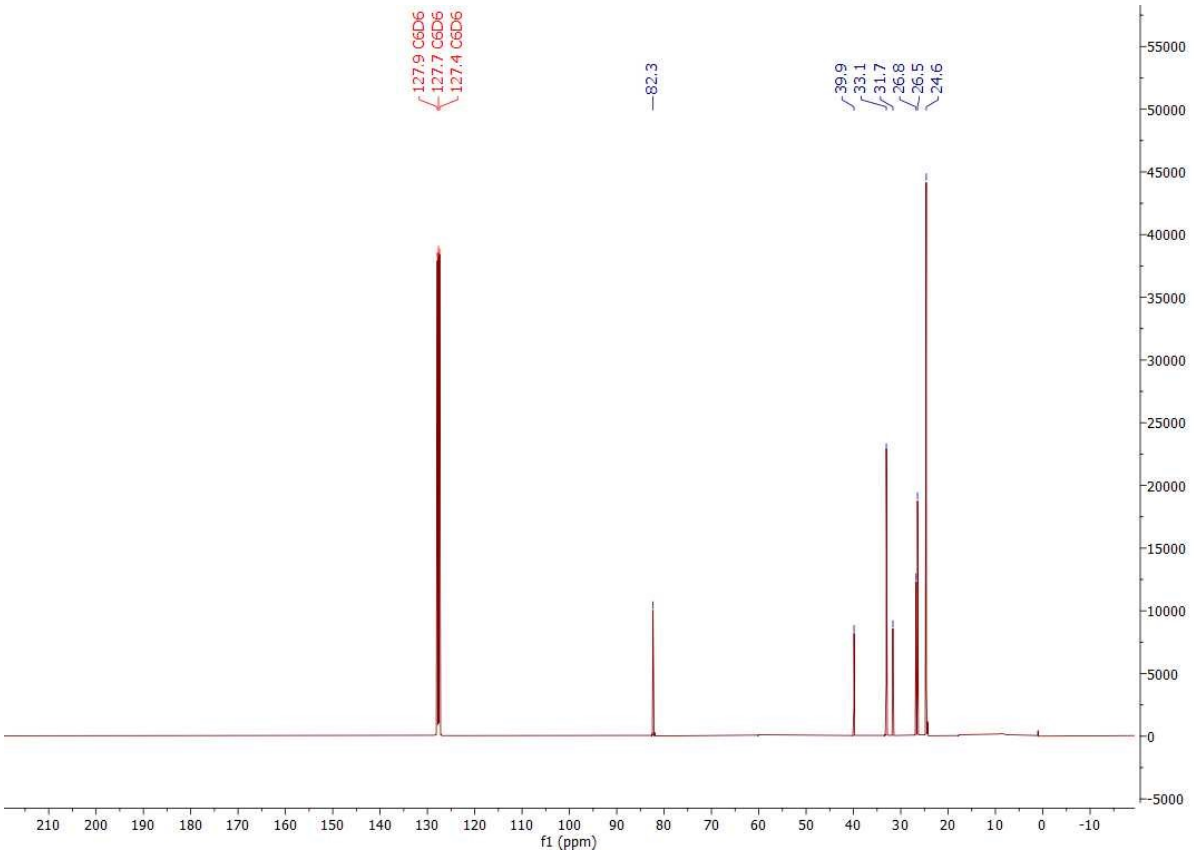
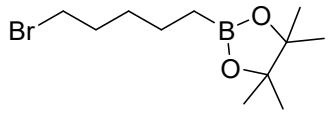


Figure S49. ^{13}C NMR (101 MHz, Benzene-d6, 25°C) of 2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e).

2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 81% yield, and is known in the literature. All spectroscopic data are in agreement.[8]

^{1}H NMR (400 MHz, Benzene-d6, 25°C) δ (ppm): 0.83 (t, J = 7.6 Hz, 2H), 1.06 (s, 12H), 1.25 (p, J = 7.2 Hz, 2H), 1.39 (p, J = 7.6 Hz, 2H), 1.53 (p, J = 6.9 Hz, 2H), 2.95 (t, J = 6.8 Hz, 2H)
^{13}C NMR (101 MHz, Benzene-d6, 25°C) δ (ppm): 23.2, 24.6, 30.6, 32.6, 33.4, 82.5
EI-MS m/z (rel. int.): 263 (85), 261 (87), 197 (27), 192 (14), 190 (14), 177 (35), 175 (24), 150 (10), 148 (10), 139 (29), 129 (99), 113 (20), 111 (23), 109 (12), 107 (11), 101 (21), 97 (61), 85 (84), 83 (68), 68 (100), 59 (60), 57 (34), 55 (56)

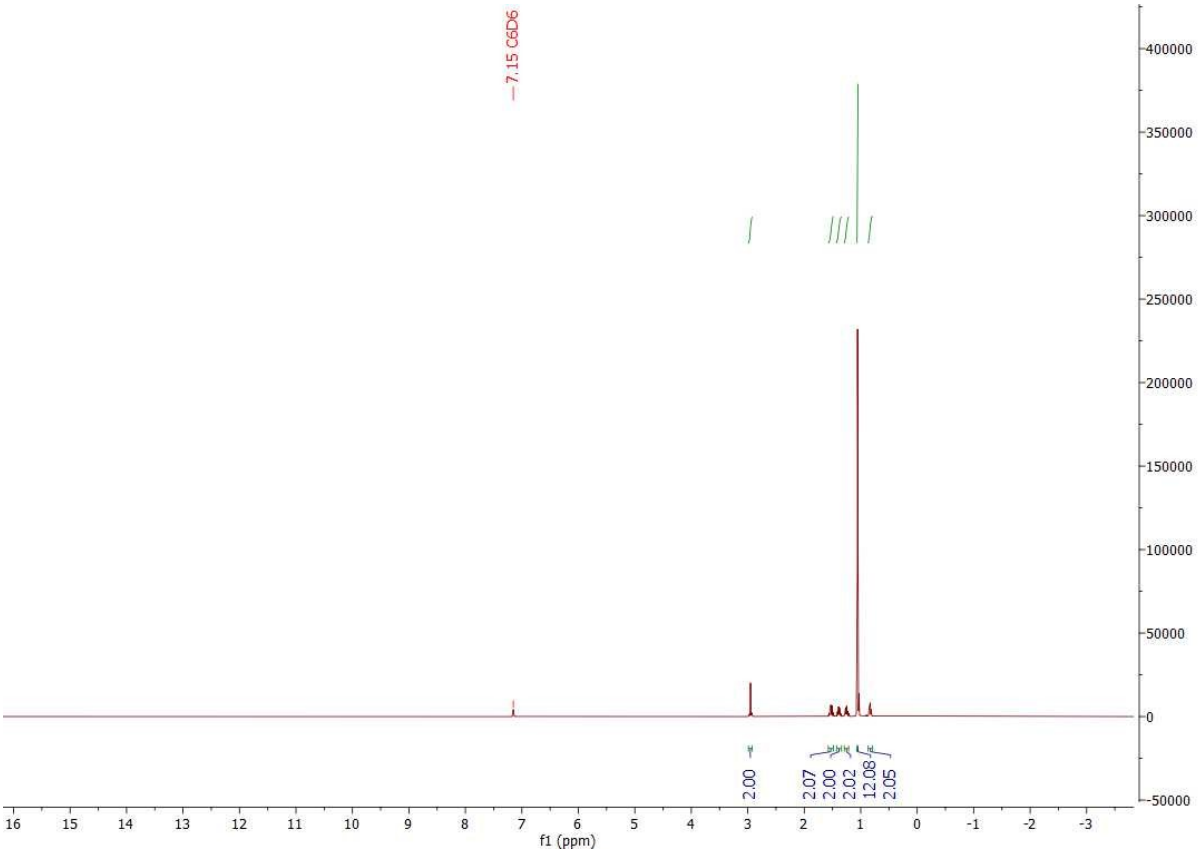


Figure S50. ^{1}H NMR (400 MHz, Benzene-d6, 25°C) of 2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f).

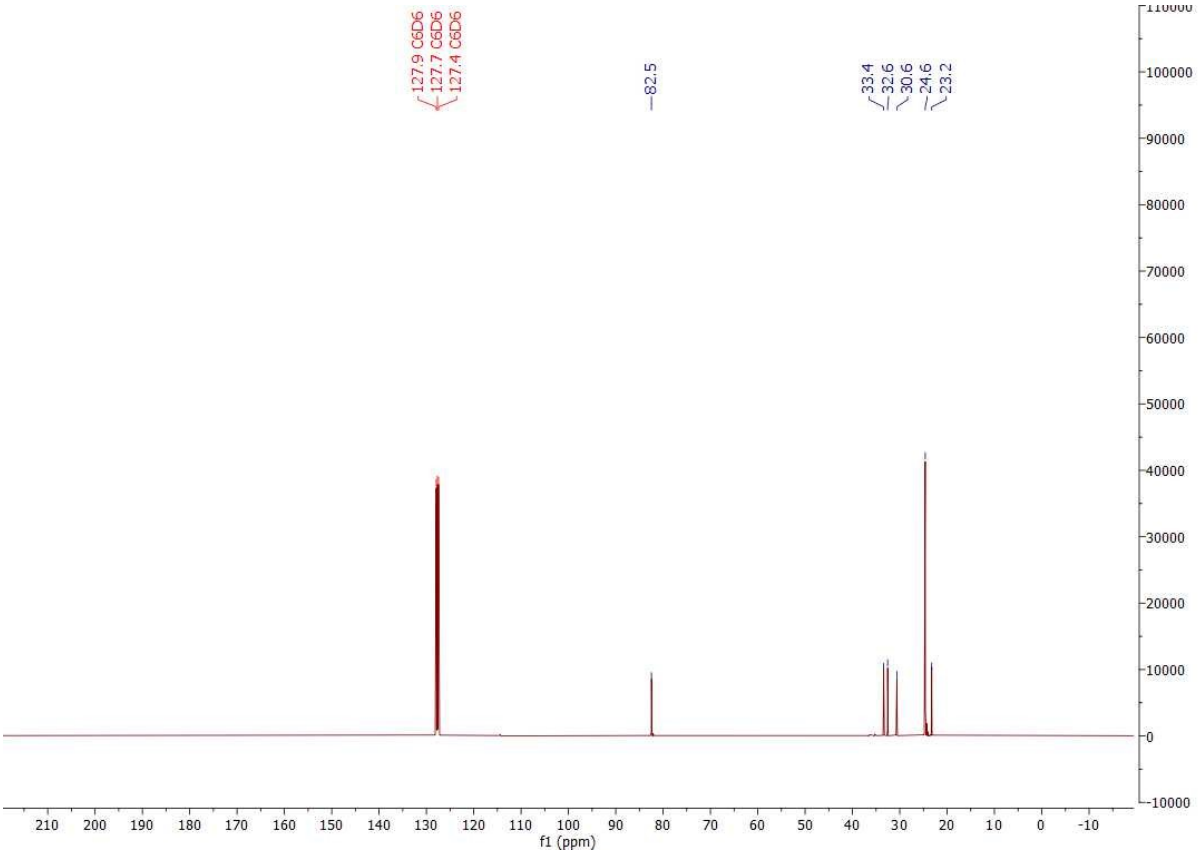
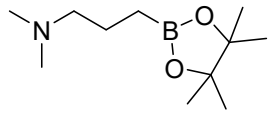


Figure S51. ^{13}C NMR (101 MHz, Benzene-d6, 25°C) of 2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f).

N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (2g)



N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine was obtained with 72% yield, and is known in the literature. All spectroscopic data are in agreement.[9]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.69 (t, J=7.8 Hz, 2H), 1.20 (s, 12H), 1.55 (p, J=7.7, 2H), 2.20 (s, 6H), 2.26 (t, J=7.5, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 21.6, 24.9, 45.2, 62.0, 82.4
EI-MS m/z (rel. int.): 213 (15), 198 (6), 154 (22), 140 (15), 112 (11), 83 (4), 69 (3), 58 (100), 55 (4)

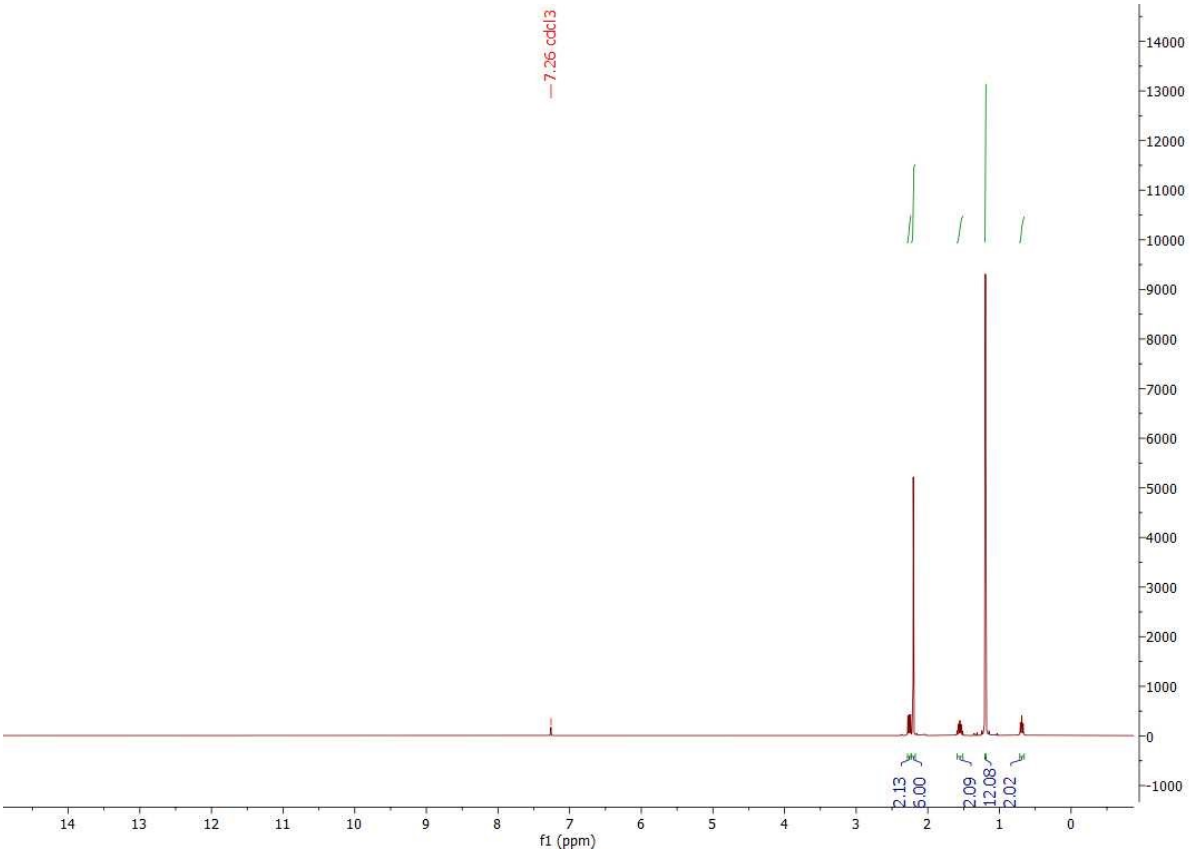


Figure S52. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (2g).

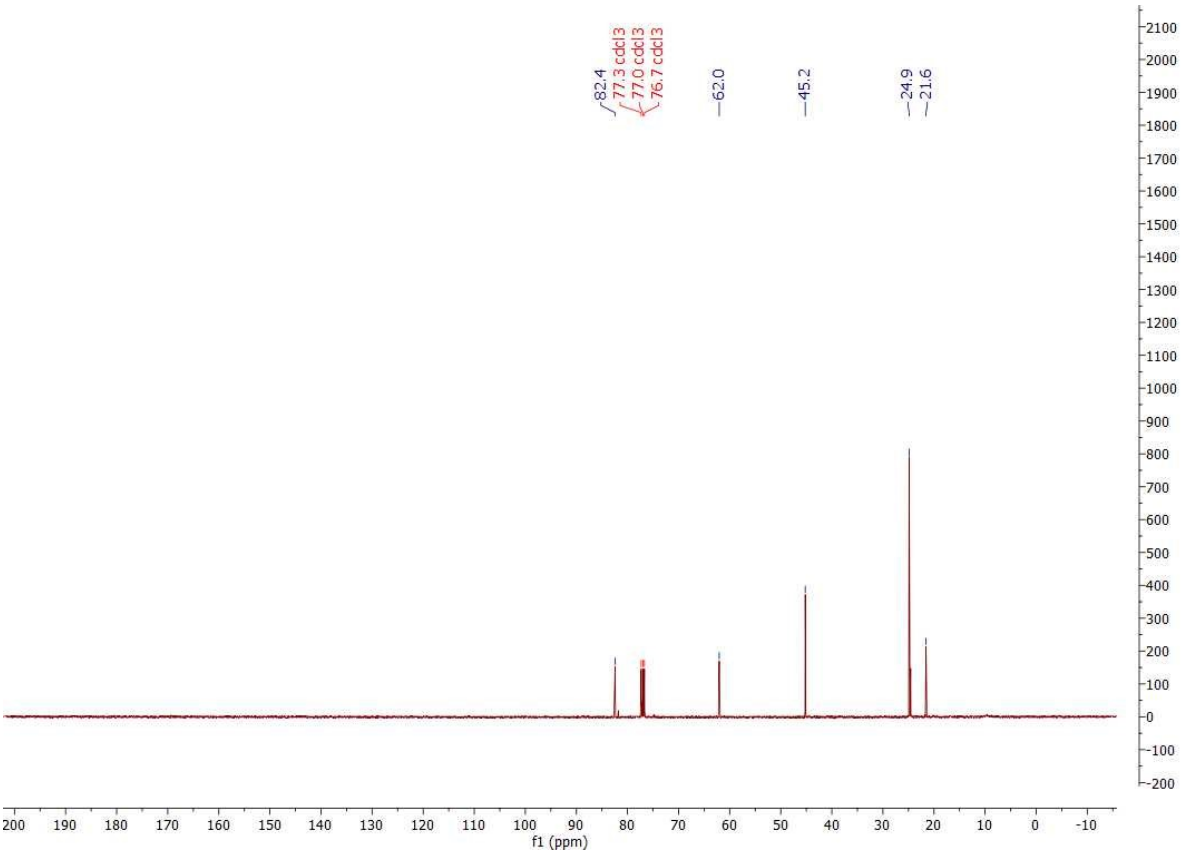
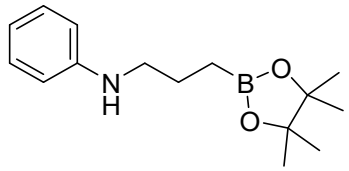


Figure S53. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (2g).

N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline (2h)



N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline was obtained with 65% yield, and is known in the literature. All spectroscopic data are in agreement.[10]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.89 (t, J=7.6 Hz, 2H), 1.27 (s, 12H), 1.75 (p, J=7.4 Hz, 2H), 3.11 (t, J=7.1 Hz, 2H), 6.60-6.62 (m, 2H), 6.66-6.70 (m, 1H), 7.15-7.19 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 23.7, 24.7, 45.9, 83.0, 112.5, 116.7, 129.0, 148.4
EI-MS m/z (rel. int.): 261 (14), 188 (8), 160 (7), 119 (16), 106 (100), 77 (12), 59 (2), 55 (3)

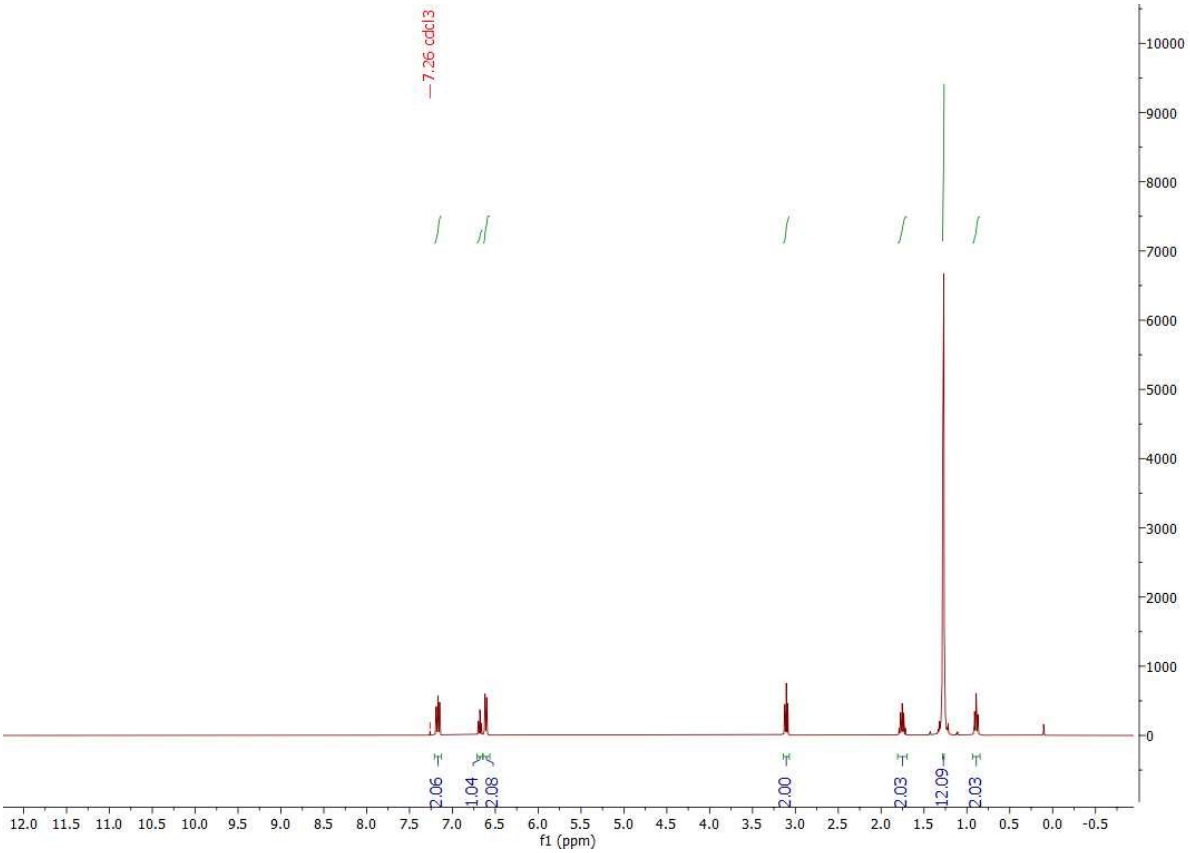


Figure S54. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline (2h).

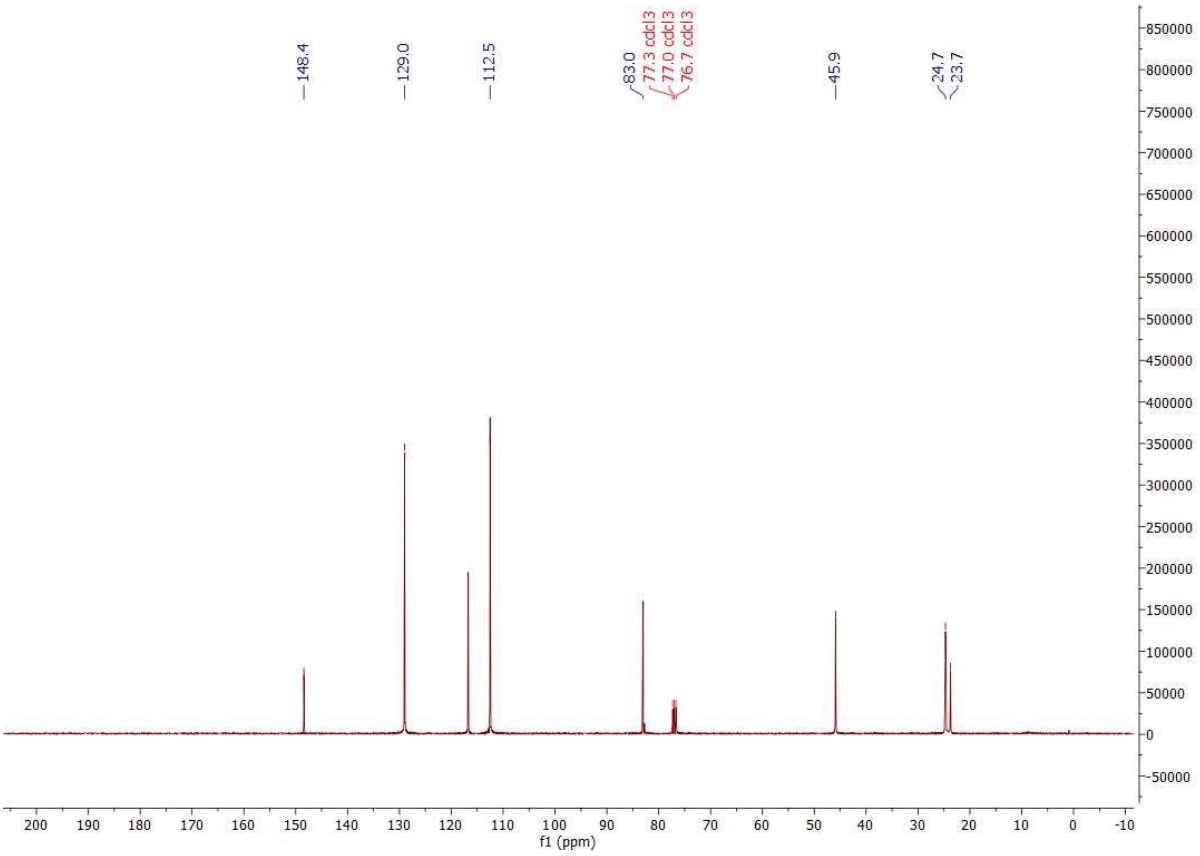
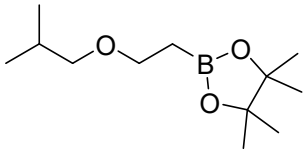


Figure S55. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline (2h).

2-(2-isobutoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)



2-(2-isobutoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 89% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.83 (d, J=6.7 Hz, 6H), 1.11 (t, J=7.9 Hz, 2H), 1.19 (s, 12H), 1.74-1.84 (m, 1H), 3.11 (d, J=6.7 Hz, 2H), 3.49 (t, J=7.8 Hz, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 19.3, 24.7, 28.2, 67.3, 77.4, 83.0
EI-MS m/z (rel. int.): 185 (29), 155 (81), 129 (12), 127 (24), 101 (15), 99 (27), 83 (100), 69 (11), 59 (20), 57 (41), 55 (22)

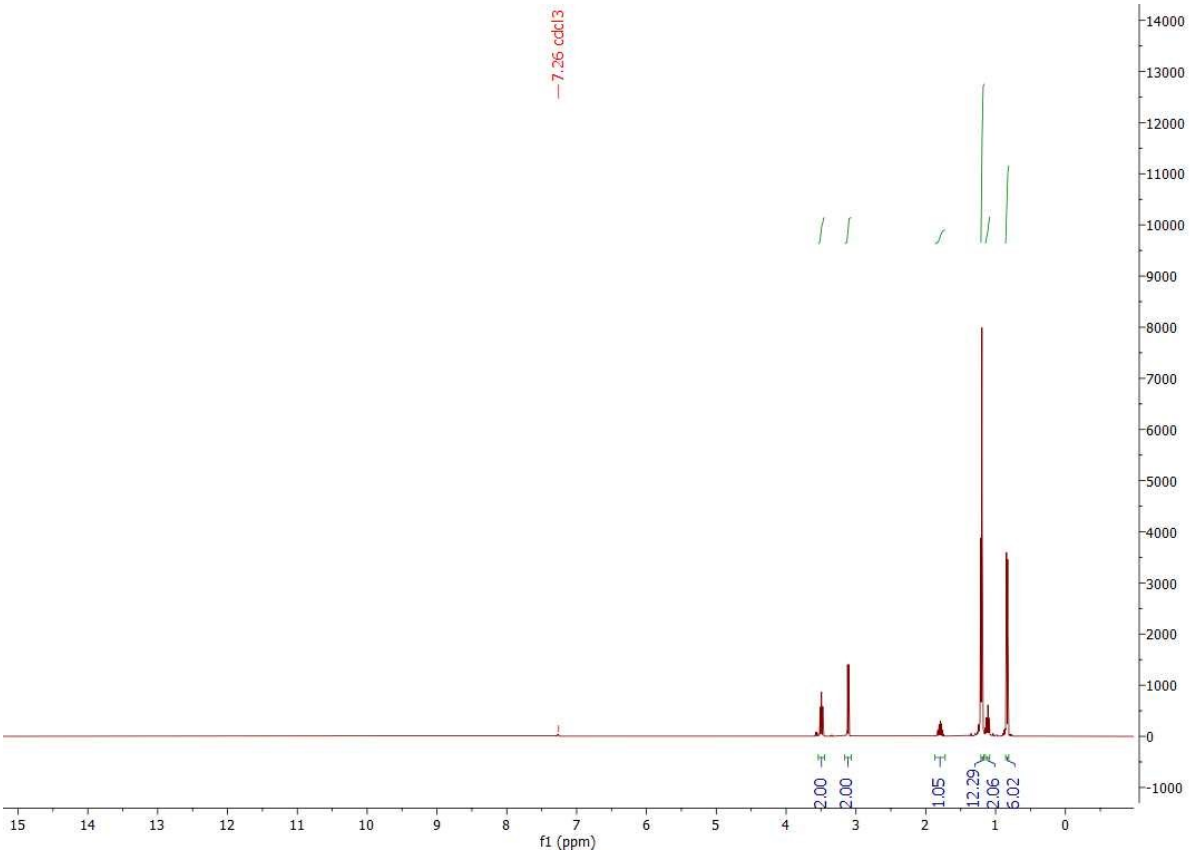


Figure S56. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-(2-isobutoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i).

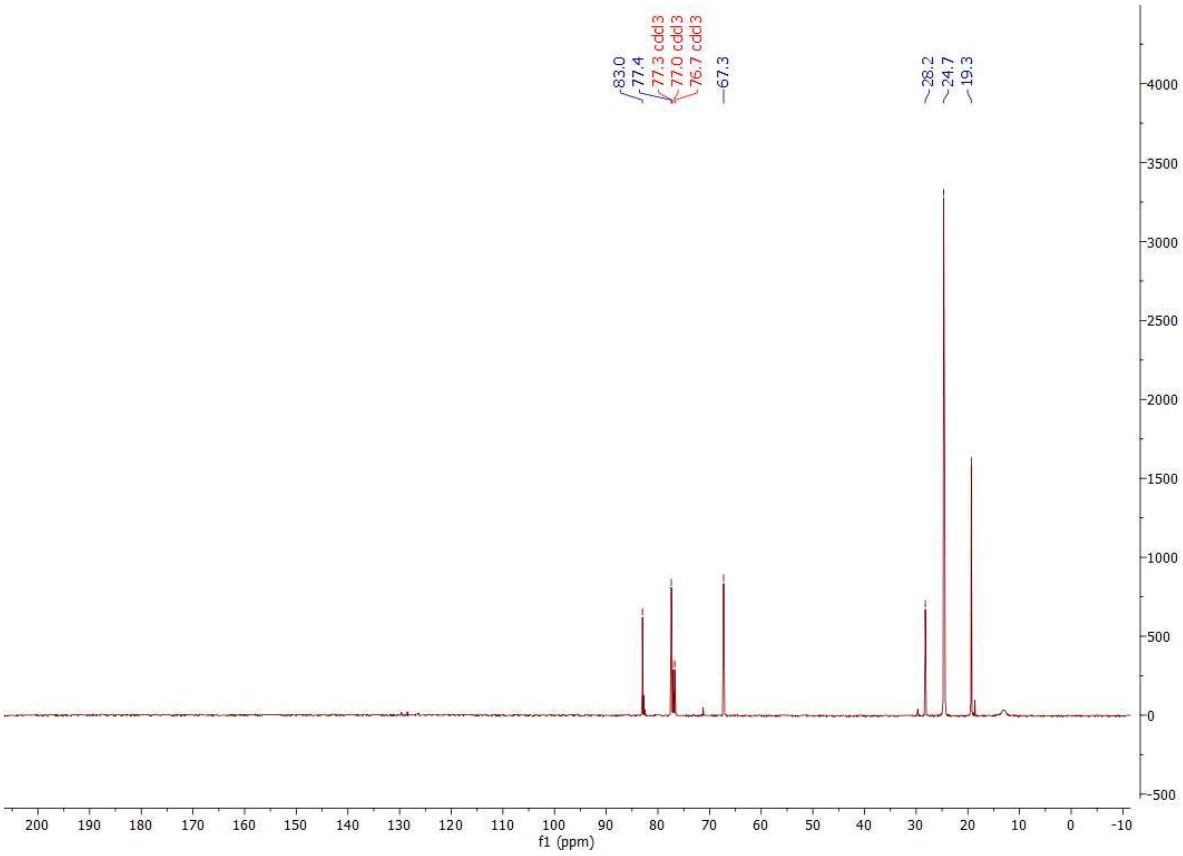
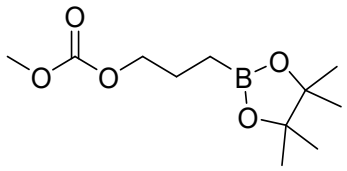


Figure S57. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-(2-isobutoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i).

methyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) carbonate (2j)



methyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) carbonate was obtained with 89% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Benzene-d6, 25°C) δ (ppm): 0.84 (t, J = 7.7 Hz, 2H), 1.02 (s, 12H), 1.76 (p, J = 7.7 Hz, 2H), 3.33 (s, 3H), 4.07 (t, J = 6.7 Hz, 2H)
^{13}C NMR (101 MHz, Benzene-d6, 25°C) δ (ppm): 23.4, 24.5, 53.7, 69.3, 82.7, 156.0
EI-MS m/z (rel. int.): 229 (2), 186 (38), 185 (10), 145 (10), 144 (10), 127 (100), 101 (10), 99 (21), 85 (34), 83 (26), 69 (25), 59 (49), 57 (28), 55 (21)

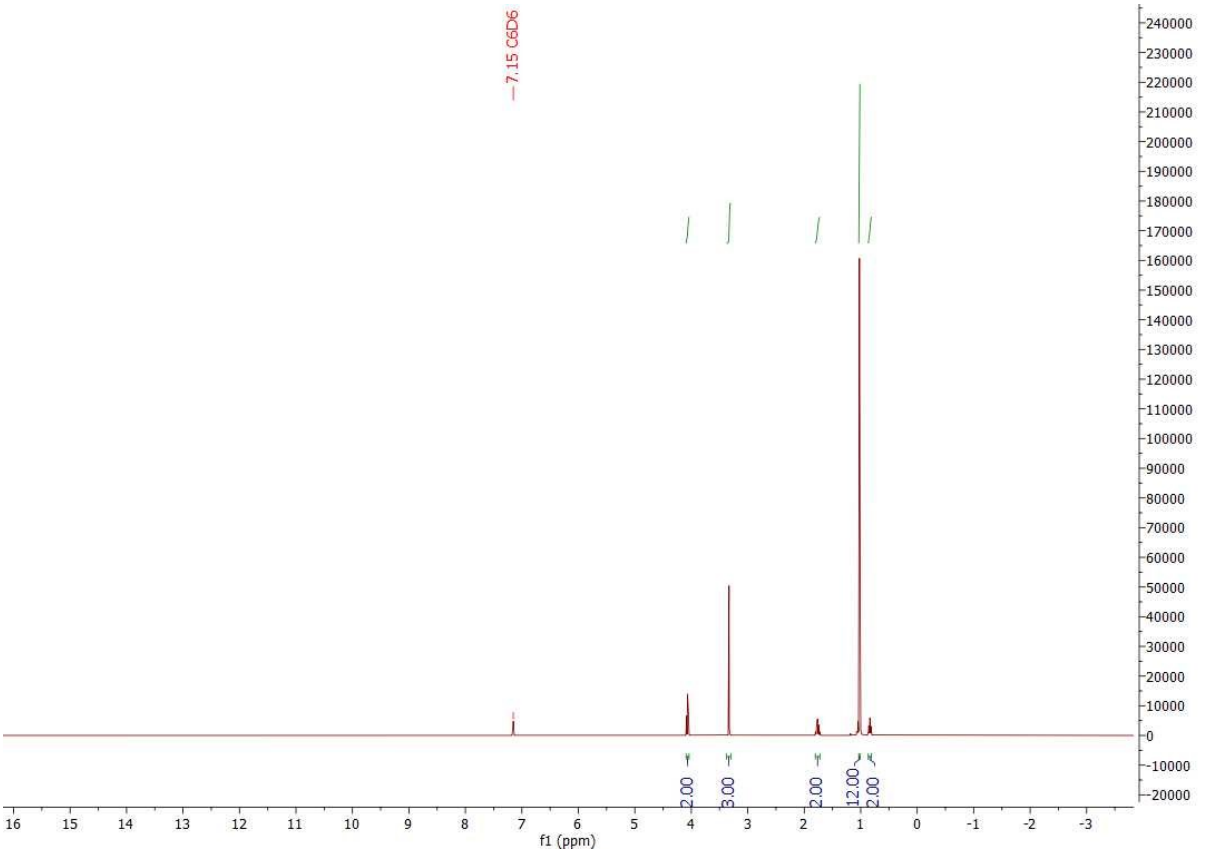


Figure S58. ^{1}H NMR (400 MHz, Benzene-d6, 25°C) of methyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) carbonate (2j).

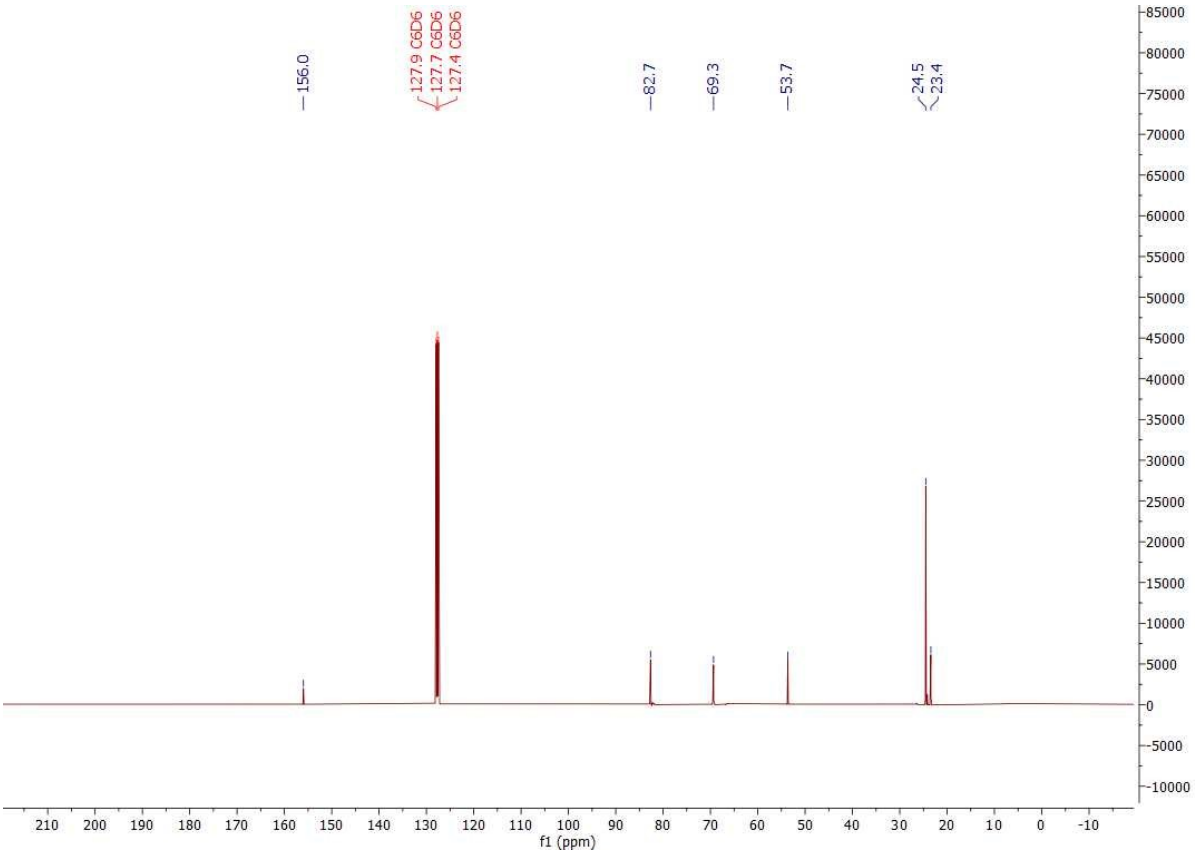
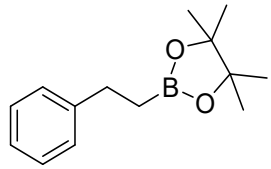


Figure S59. ^{13}C NMR (101 MHz, Benzene-d6, 25°C) of methyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) carbonate (2j).

4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2k)



4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane was obtained with 90% yield, and is known in the literature. All spectroscopic data are in agreement.[8]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 1.14 (t, J=8.0 Hz, 2H), 1.22 (s, 12H), 2.75 (t, J=8.3 Hz, 2H), 7.10-7.25 (m, 4H), 7.26-7.28 (m, 1H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 24.7, 29.9, 83.0, 125.4, 127.9, 128.1, 144.3
EI-MS m/z (rel. int.): 232 (10), 217 (12), 175 (43), 146 (10), 132 (68), 105 (45), 91 (69), 84 (100), 77 (9), 69 (11), 59 (12), 57 (5), 55 (5)

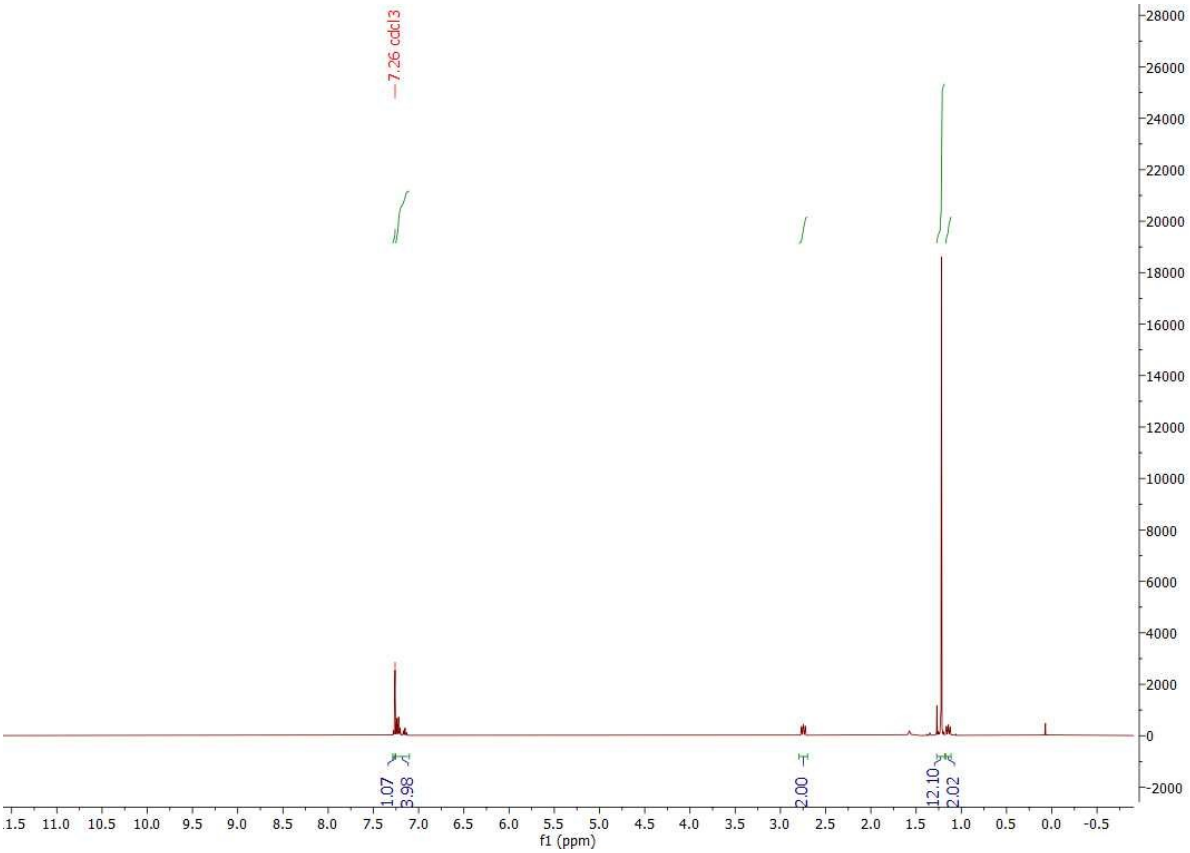


Figure S60. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2k).

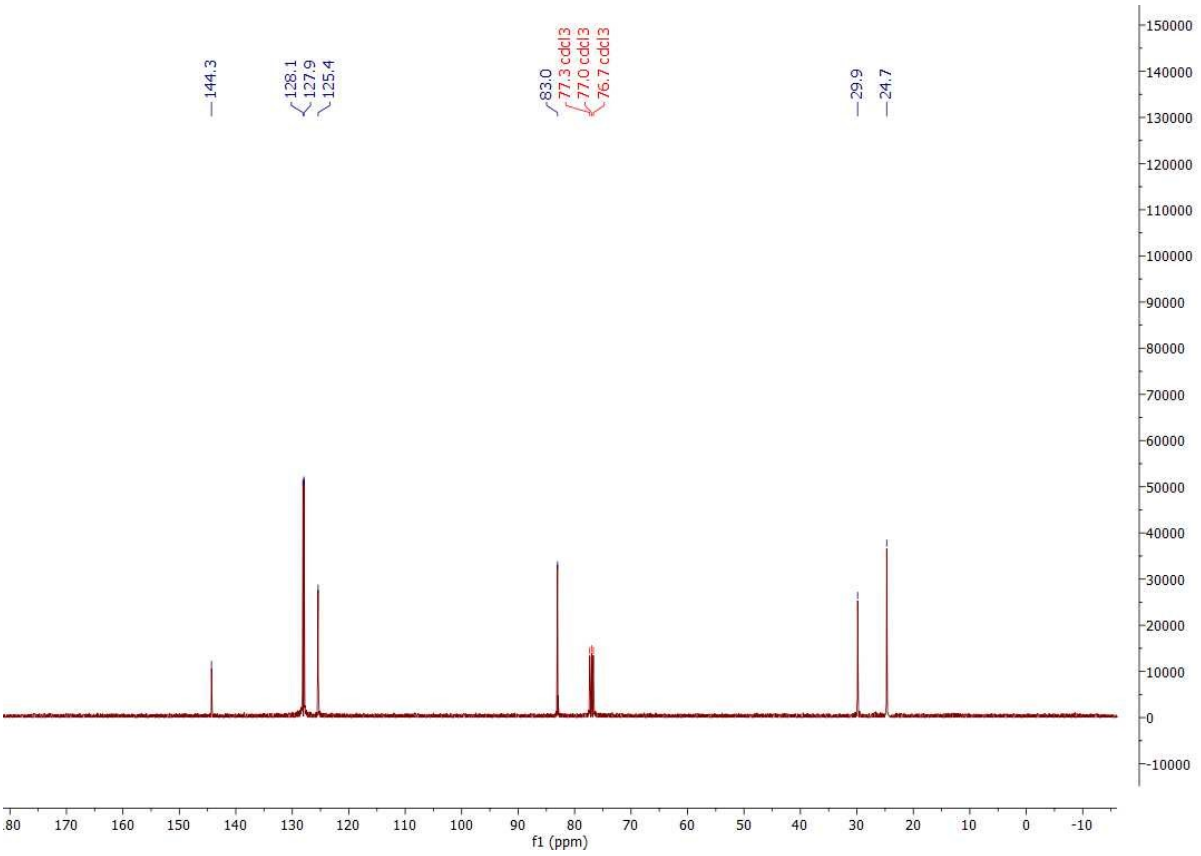
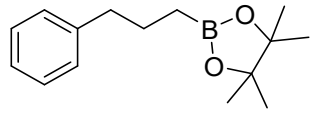


Figure S61. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2k).

4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2l)



4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane was obtained with 97% yield, and is known in the literature. All spectroscopic data are in agreement.[11]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.85 (t, J = 7.9 Hz, 2H), 1.26 (s, 12H), 1.76 (p, J = 7.9 Hz, 2H), 2.62 (t, J = 8.2 Hz, 2H), 7.14-7.36 (m, 5H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 24.8, 26.1, 38.6, 82.9, 125.6, 128.2, 128.5, 142.7
EI-MS m/z (rel. int.): 246 (20), 231 (10), 189 (10), 173 (15), 146 (12), 129 (8), 127 (27), 118 (100), 105 (15), 91 (66), 85 (83), 69 (7), 65 (9), 59 (7), 57 (6), 55 (8)

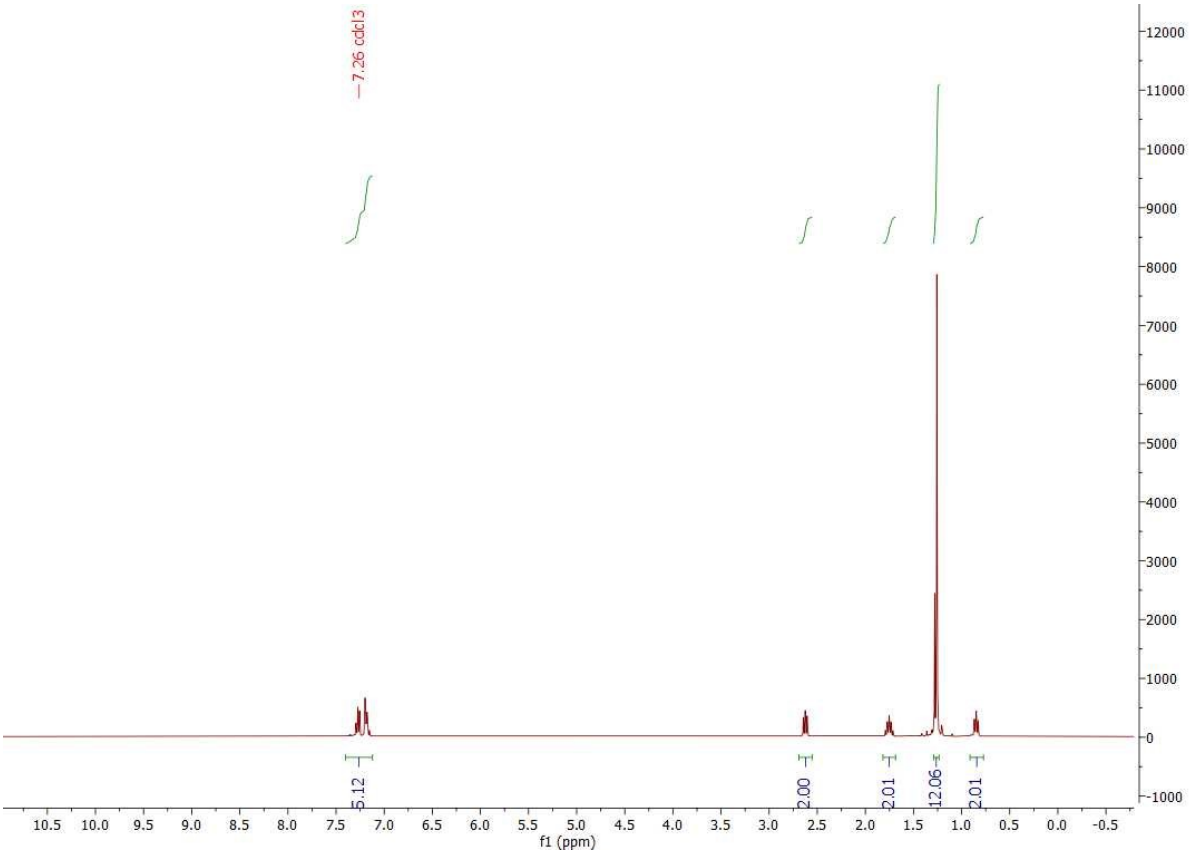


Figure S62. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2l).

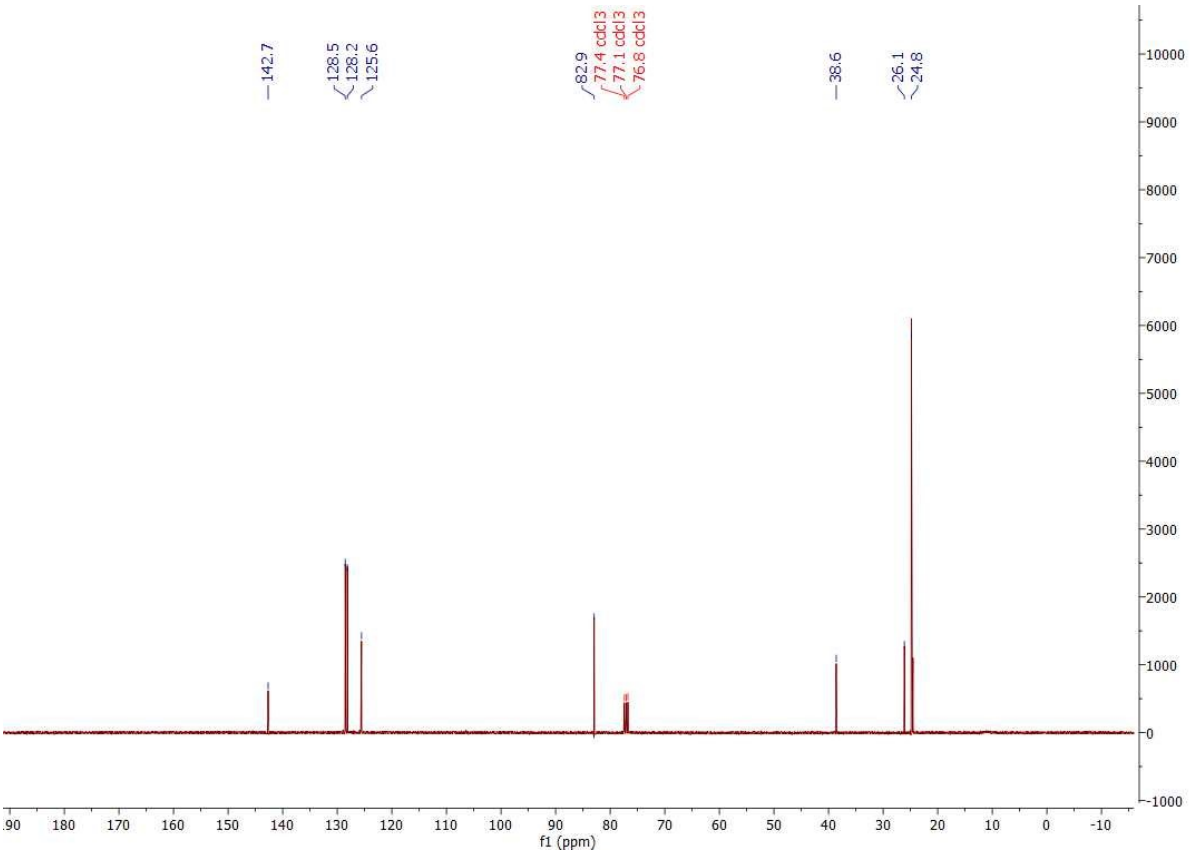
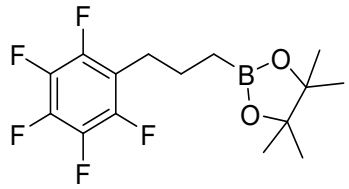


Figure S63. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2l).

4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane (2m)



4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane was obtained with 98% yield, and is known in the literature. All spectroscopic data are in agreement.[12]

^{1}H NMR (600 MHz, Chloroform-d, 25°C) δ (ppm): 0.74 (t, J = 7.9 Hz, 2H), 1.17 (s, 12H), 1.62 (p, J = 7.8 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H)
^{13}C NMR (151 MHz, Chloroform-d, 25°C) δ (ppm): 23.8, 24.7, 83.1, 115.32 (t, J = 19.0 Hz), 137.32 (d, J = 249.7 Hz), 139.35 (d, J = 250.8 Hz), 145.05 (d, J = 245.7 Hz)
EI-MS m/z (rel. int.): 336 (5), 321 (36), 279 (5), 237 (9), 208 (9), 192 (5), 181 (77), 169 (26), 163 (23), 155 (12), 151 (27), 145 (8), 129 (36), 127 (24), 113 (10), 101 (10), 85 (100), 83 (38), 69 (17), 59 (39), 57 (19), 55 (17)

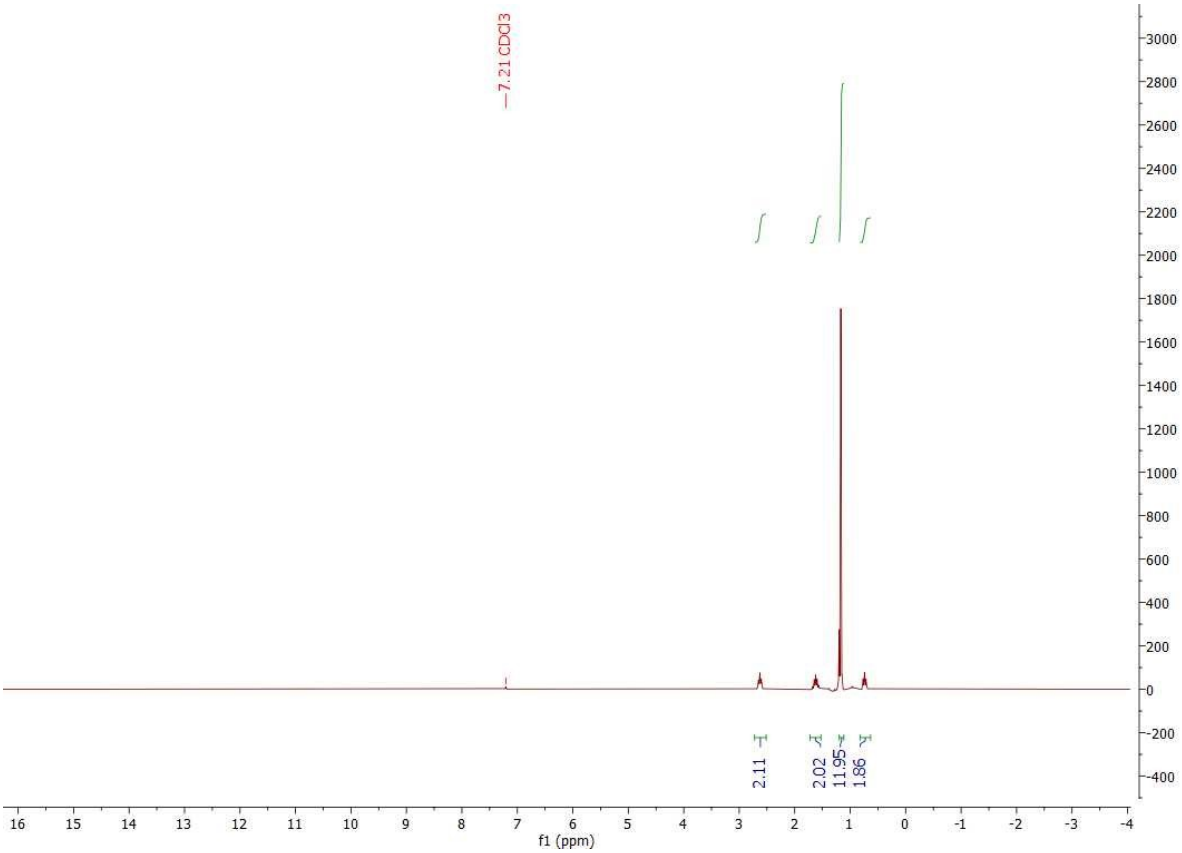


Figure S64. ^{1}H NMR (600 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane (2m).

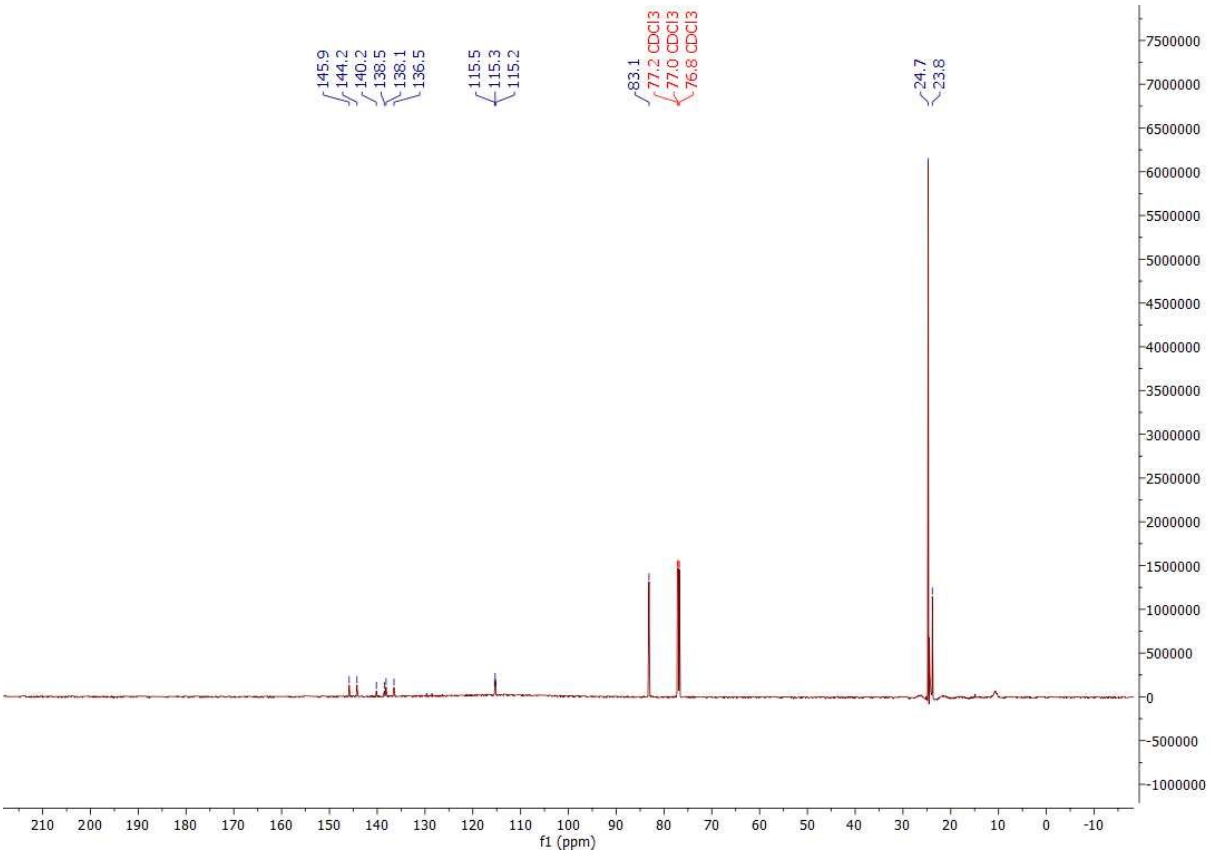
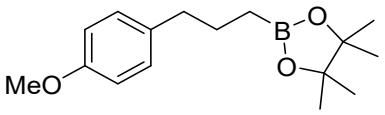


Figure S65. ^{13}C NMR (151 MHz, Chloroform-d, 25°C) of 4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane (2m).

2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 73% yield, and is known in the literature. All spectroscopic data are in agreement.[13]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.82 (t, J = 8.0 Hz, 2H), 1.24 (s, 12H), 1.70 (p, J = 7.8 Hz, 2H), 2.54 (t, J = 8.0 Hz, 2H), 3.78 (s, 3H), 6.81 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 24.8, 26.3, 37.6, 55.2, 82.9, 113.5, 129.3, 134.7, 157.5
EI-MS m/z (rel. int.): 276 (27), 192 (15), 160 (14), 148 (38), 121 (100), 91 (7), 85 (14), 77 (6), 59 (3), 55 (3)

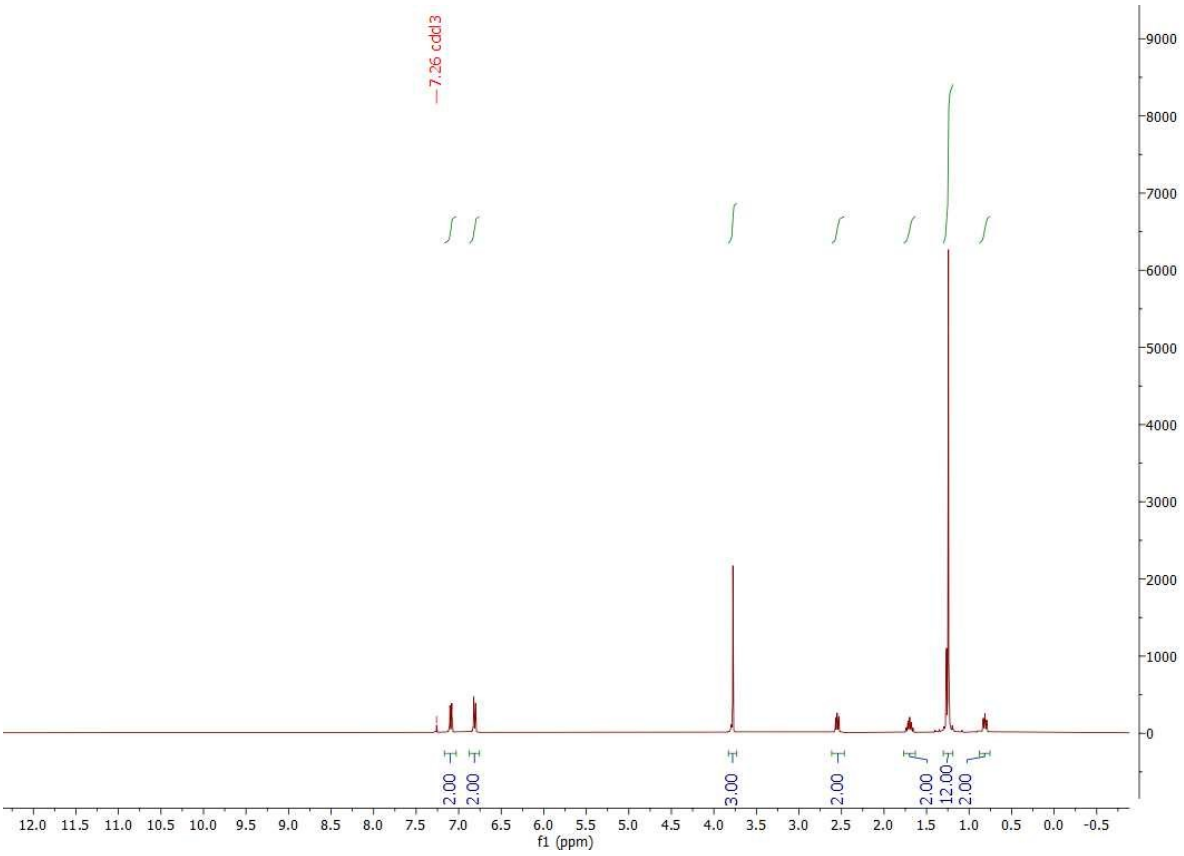


Figure S66. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n).

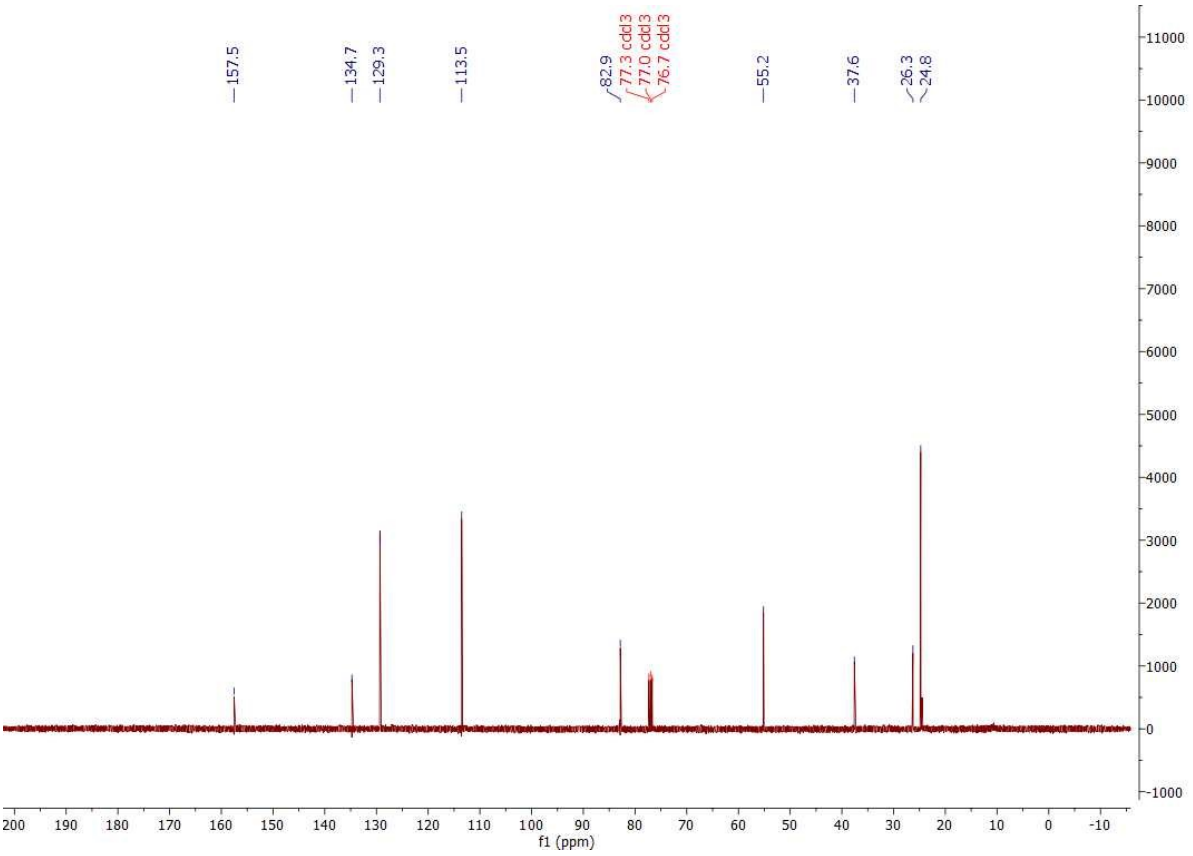
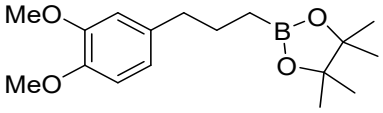


Figure S67. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n).

2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)



2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 68% yield, and is known in the literature. All spectroscopic data are in agreement.[13]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.81 (t, J = 7.9 Hz, 2H), 1.23 (s, 12H), 1.70 (p, J = 7.8 Hz, 2H), 2.55 (t, J = 7.4 Hz, 2H), 3.83 (s, 3H), 3.85 (s, 3H), 6.65-6.77 (m, 3H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 24.7, 26.2, 38.1, 55.6, 55.8, 82.8, 111.0, 111.8, 120.2, 135.3, 146.9, 148.5
EI-MS m/z (rel. int.): 306 (48), 206 (8), 190 (16), 178 (18), 151 (100), 137 (4), 107 (7), 83 (3), 59 (3), 55 (3)

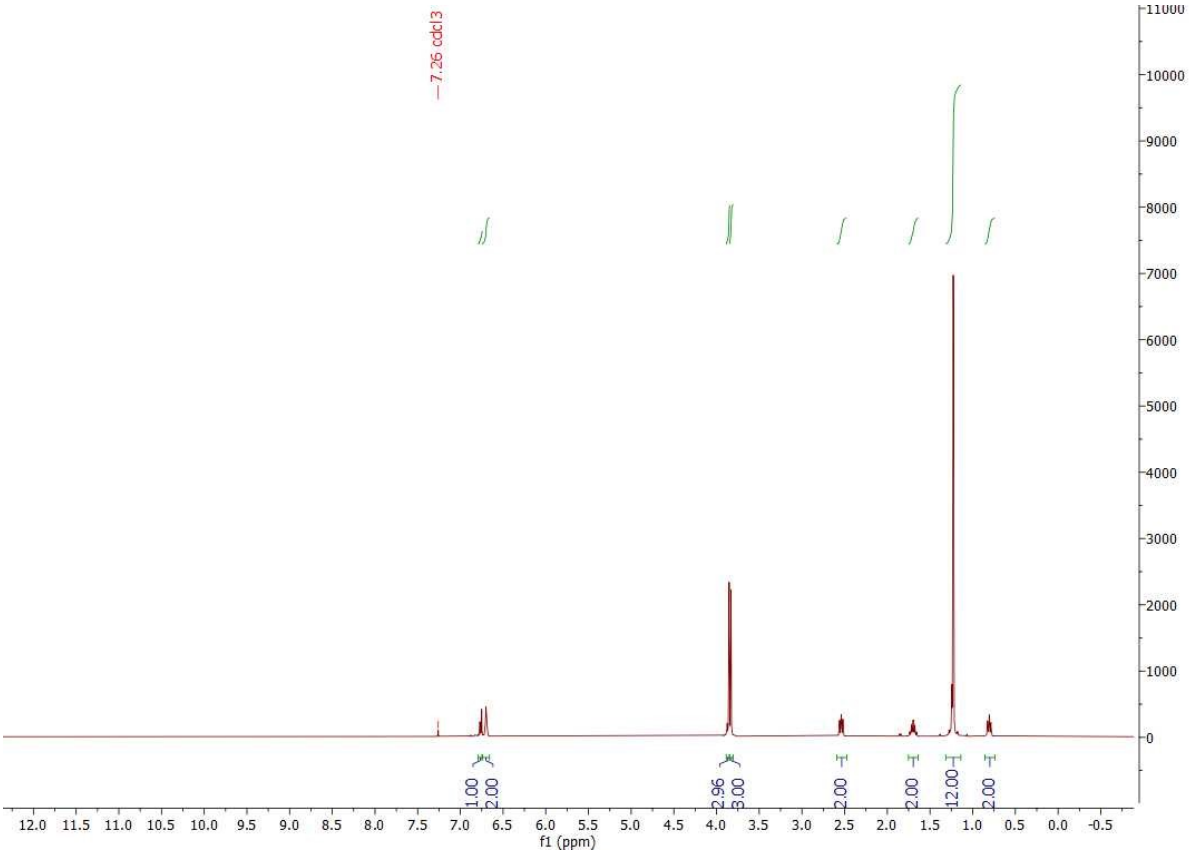


Figure S68. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o).

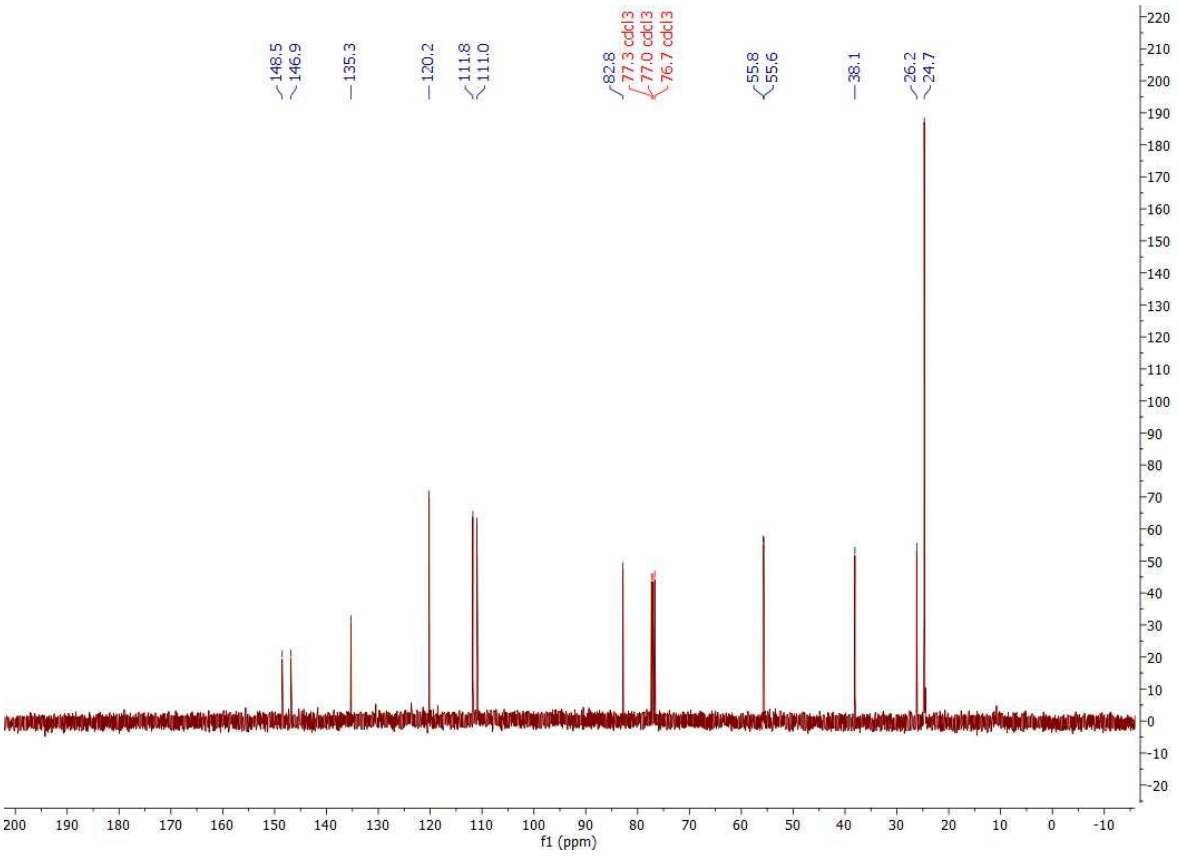
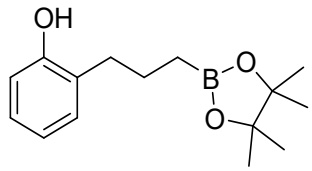


Figure S69. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o).

2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol (2p)



2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol was obtained with 85% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.95 (t, J = 7.1 Hz, 2H), 1.32 (s, 12H), 1.72 (p, J = 7.2 Hz, 2H), 2.60 (t, J = 8.0 Hz, 2H), 6.62 (s, 1H), 6.81-6.88 (m, 2H), 7.07-7.13 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 24.6, 24.7, 32.3, 83.6, 115.7, 120.0, 127.3, 127.9, 129.9, 154.4
EI-MS m/z (rel. int.): 213 (12), 154 (19), 140 (13), 112 (10), 98 (6), 83 (2), 72 (4), 58 (100)
IR (cm^{-1}): 3403, 2978, 2932, 1592, 1455, 1371, 1316, 1230, 1254, 1167, 966, 846, 751

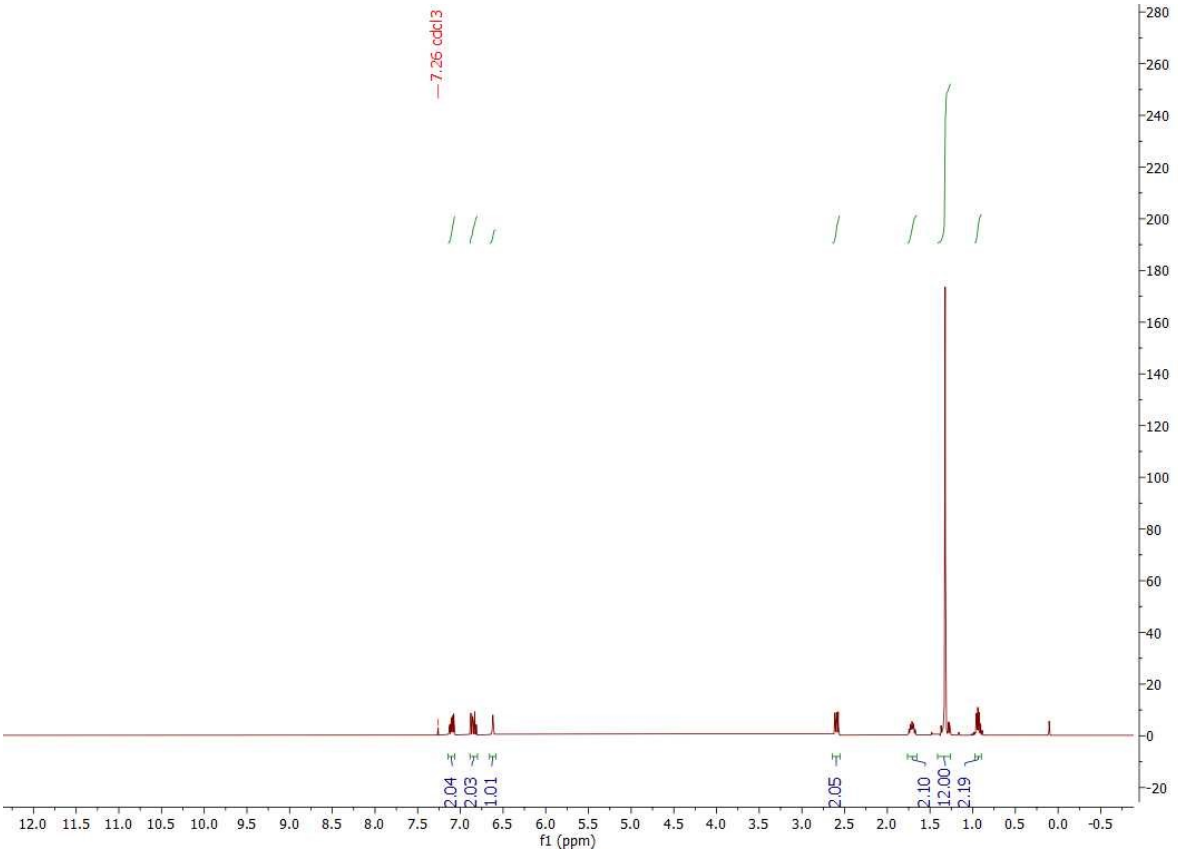


Figure S70. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol (2p).

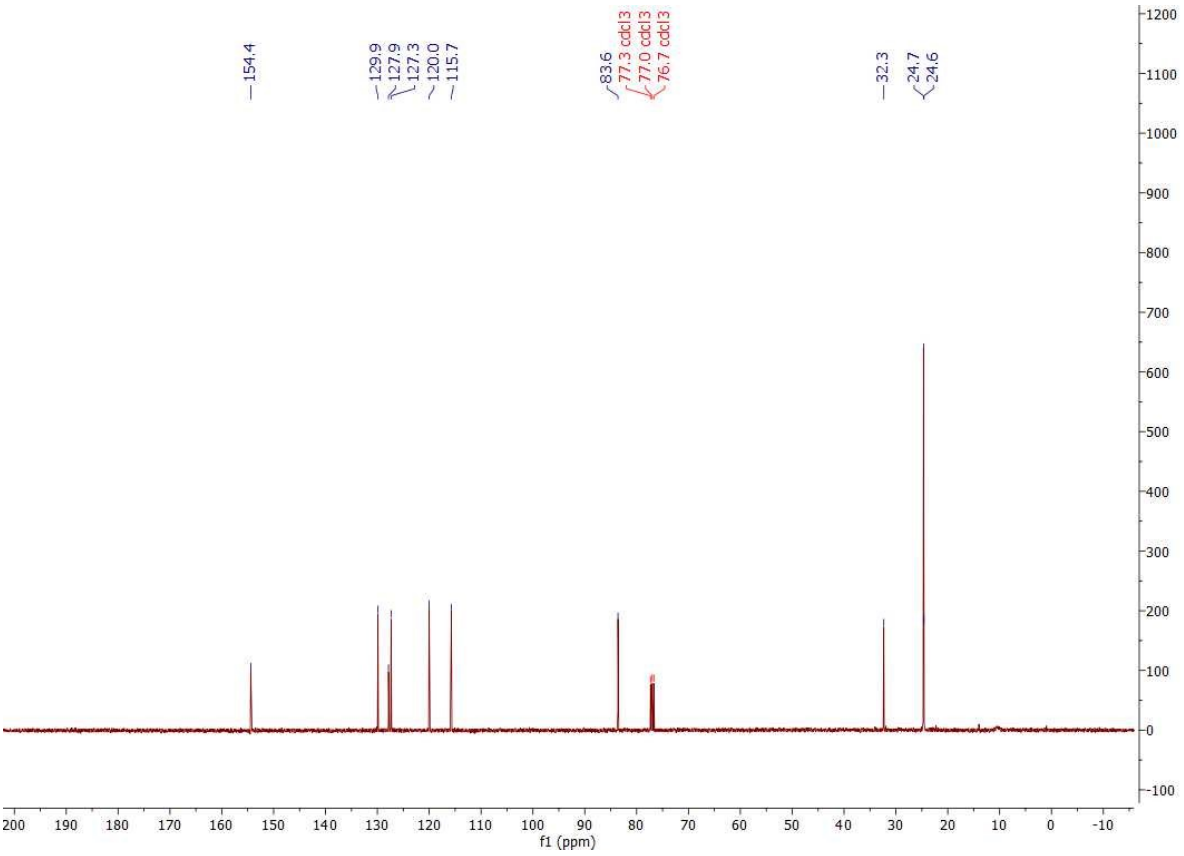


Figure S71. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol (2p).

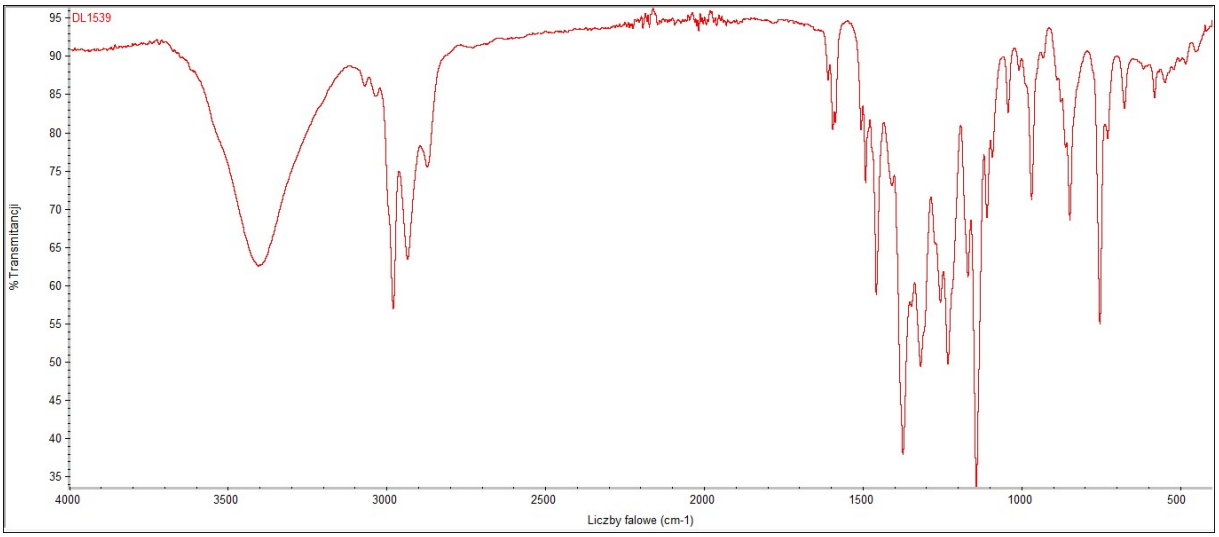
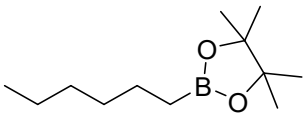


Figure S72. IR spectrum of 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol (2p).

2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)



2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 97% yield, and is known in the literature. All spectroscopic data are in agreement.[14]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.71 (t, J = 7.8 Hz, 2H), 0.82 (t, J = 7.1 Hz, 3H), 1.20 (s, 12H), 1.22 (s, 6H), 1.32-1.38 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 14.0, 22.5, 23.9, 24.7, 31.6, 32.1, 82.8
EI-MS m/z (rel. int.): 197 (67), 155 (8), 129 (100), 127 (28), 113 (33), 101 (15), 97 (15), 85 (89), 71 (49), 67 (15), 59 (59), 57 (48), 55 (55), 53 (10)

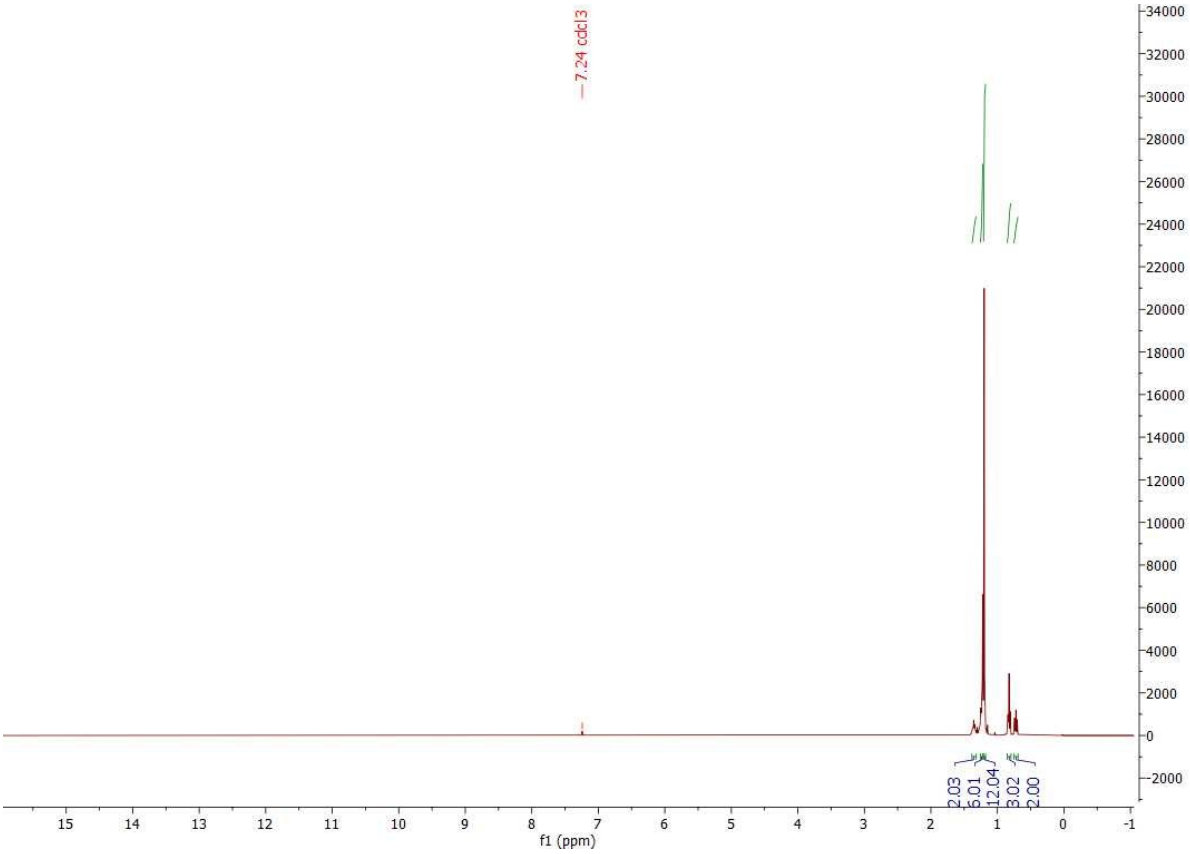


Figure S73. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r).

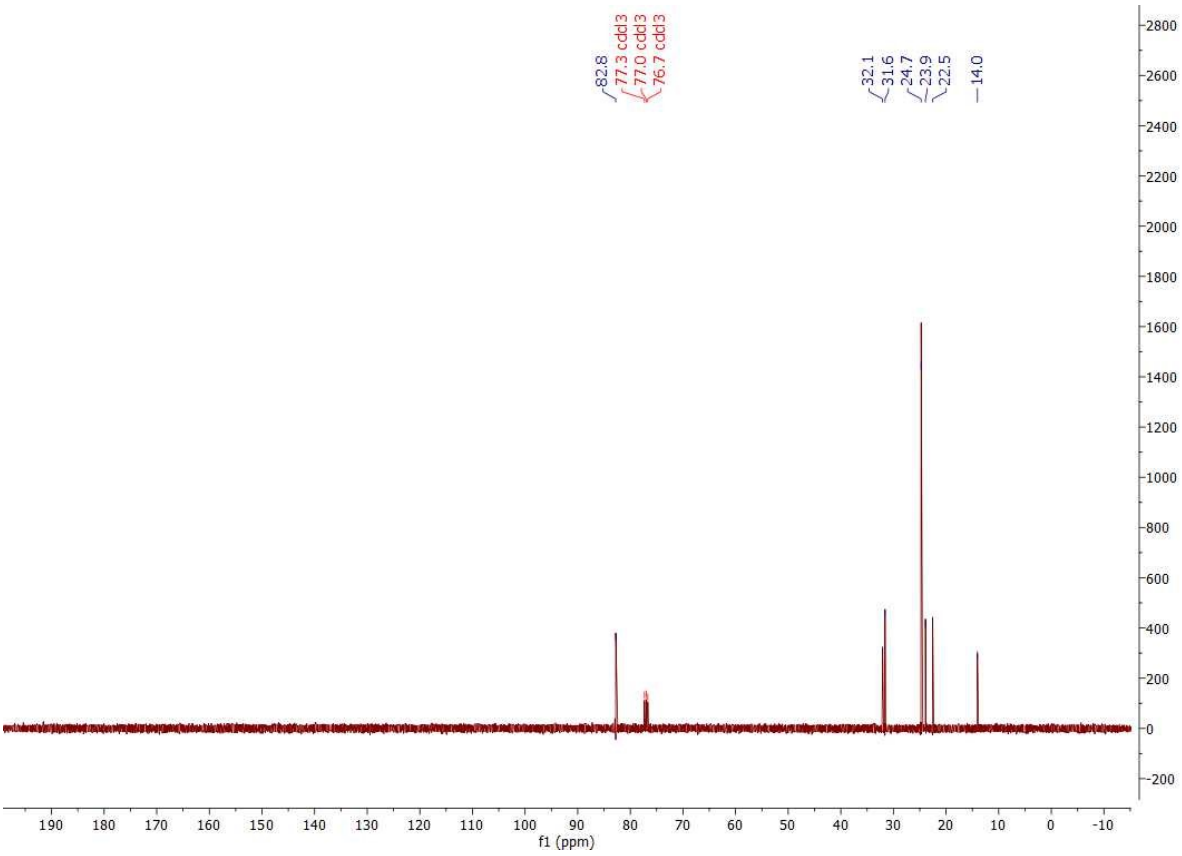
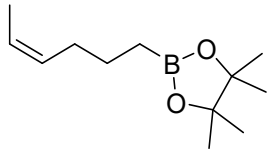


Figure S74. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r).

(Z)-2-(hex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s)



(Z)-2-(hex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was obtained with 87% yield, and is known in the literature. All spectroscopic data are in agreement.[14]

^{1}H NMR (300 MHz, Chloroform-d, 25°C) δ (ppm): 0.72 (t, J=7.8 Hz, 2H), 1.17 (s, 12H), 1.35-1.45 (m, 3H), 1.52 (d, J=4.9 Hz, 2H), 1.93-2.00 (m, 2H), 5.26-5.39 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 12.7, 23.9, 24.7, 29.3, 82.3, 123.8, 130.5
EI-MS m/z (rel. int.): 210 (3), 195 (8), 153 (10), 127 (18), 109 (10), 101 (21), 85 (100), 83 (61), 82 (84), 69 (33), 67 (20), 59 (17), 57 (19), 55 (46), 53 (11)

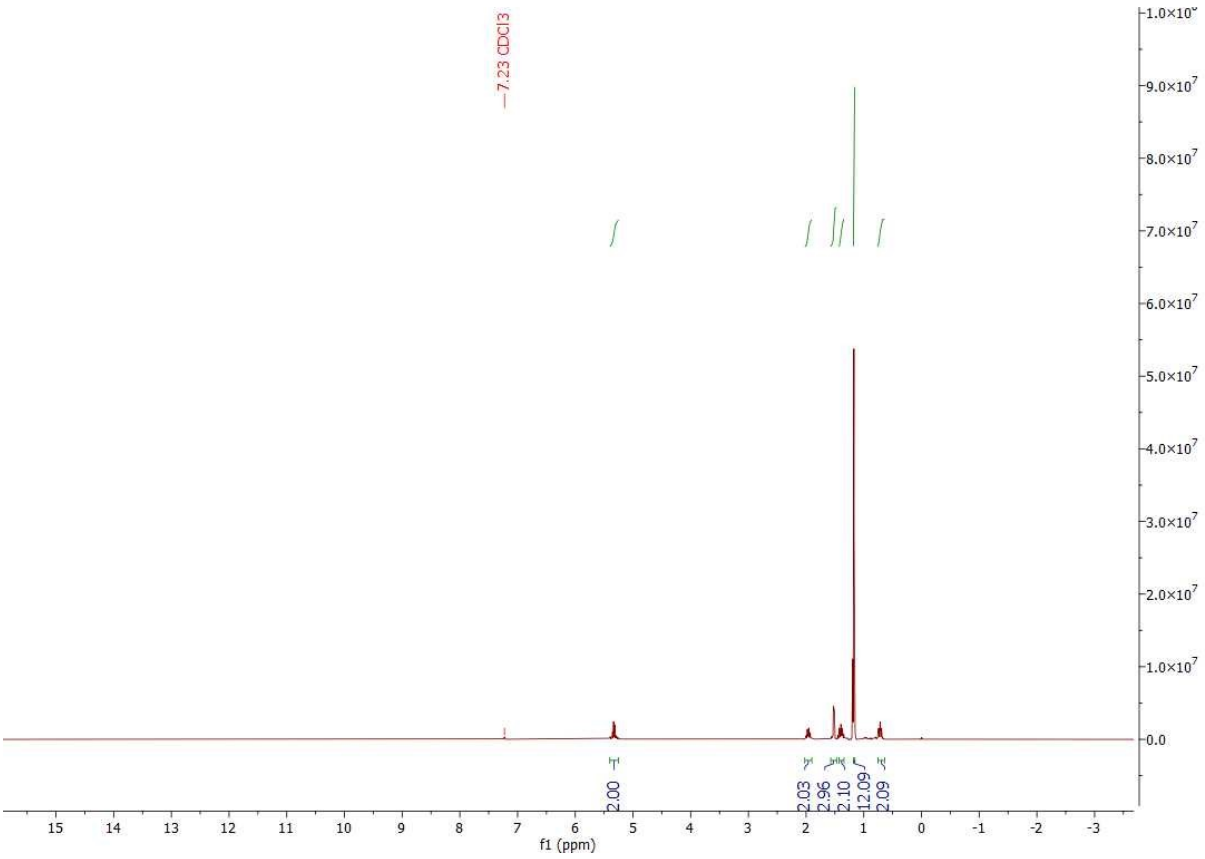


Figure S75. ^{1}H NMR (300 MHz, Chloroform-d, 25°C) of (Z)-2-(hex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s).

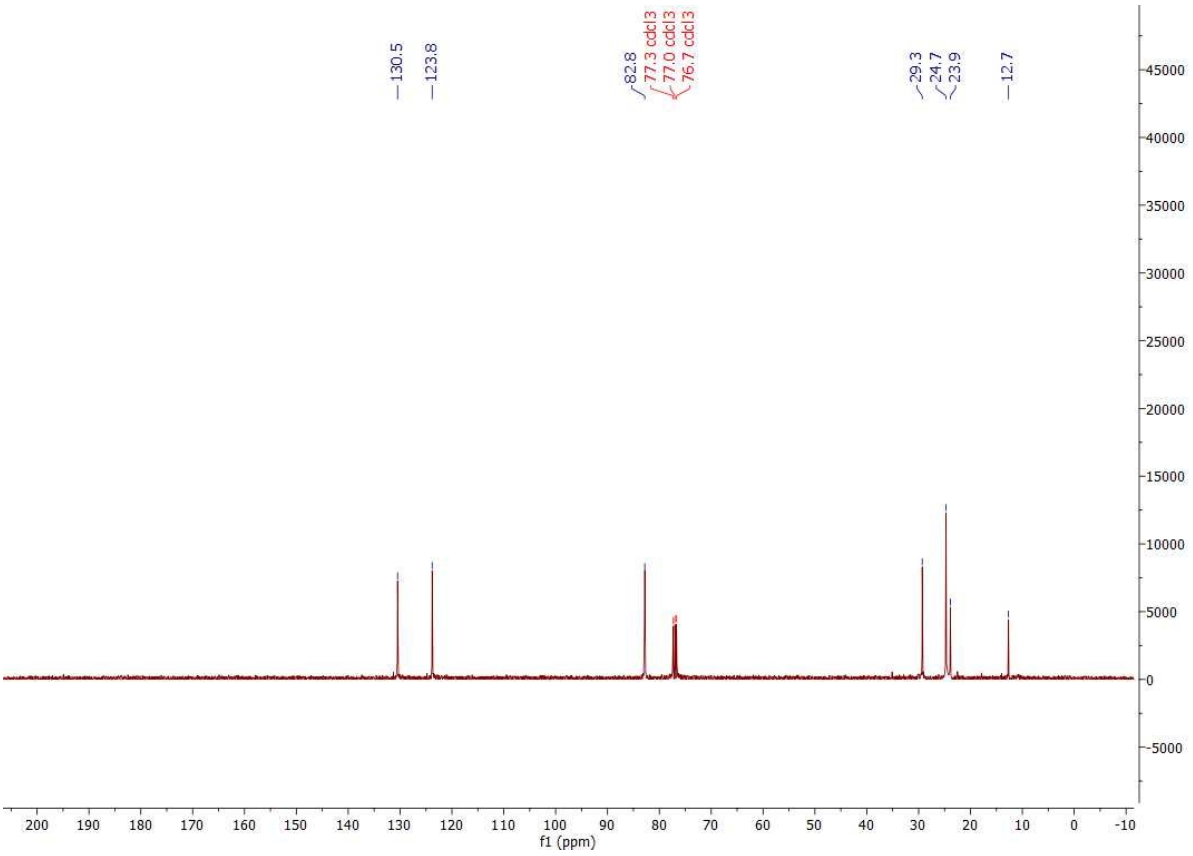
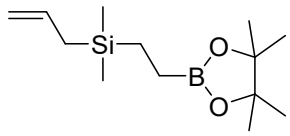


Figure S76. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of (Z)-2-(hex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s).

allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (3a)



allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was obtained with 79% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.02 (s, 6H), 0.57-0.62 (m, 2H), 0.73-0.77 (m, 2H), 1.26 (s, 12H), 1.52 (dt, J = 8.0, 1.2 Hz, 2H), 4.78-4.86 (m, 2H), 5.73-5.84 (m, 1H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -4.2, 7.5, 22.9, 24.8, 83.0, 112.5, 135.3, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 3.2
EI-MS m/z (rel. int.): 213 (56), 131 (50), 115 (10), 113 (19), 99 (10), 85 (23), 83 (100), 71 (10), 69 (10), 59 (24), 57 (15), 55 (24)

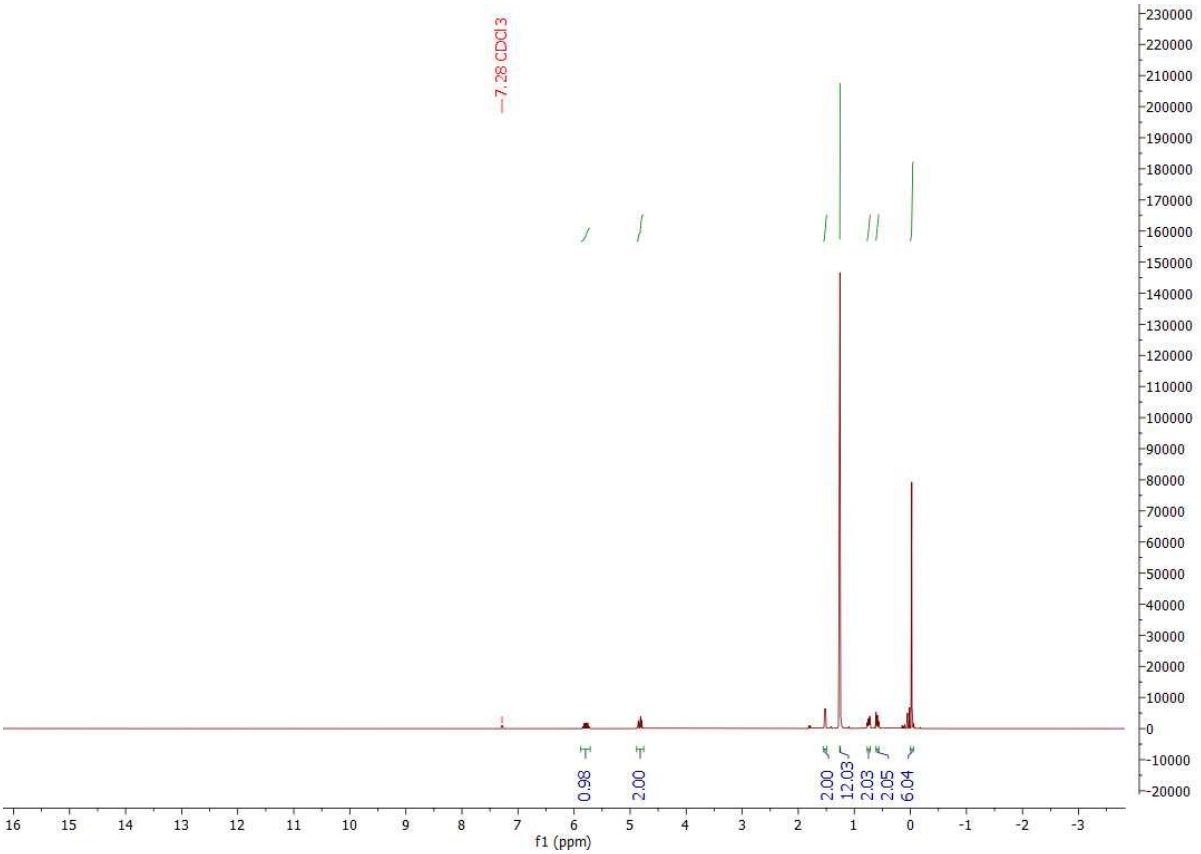


Figure S77. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (3a).

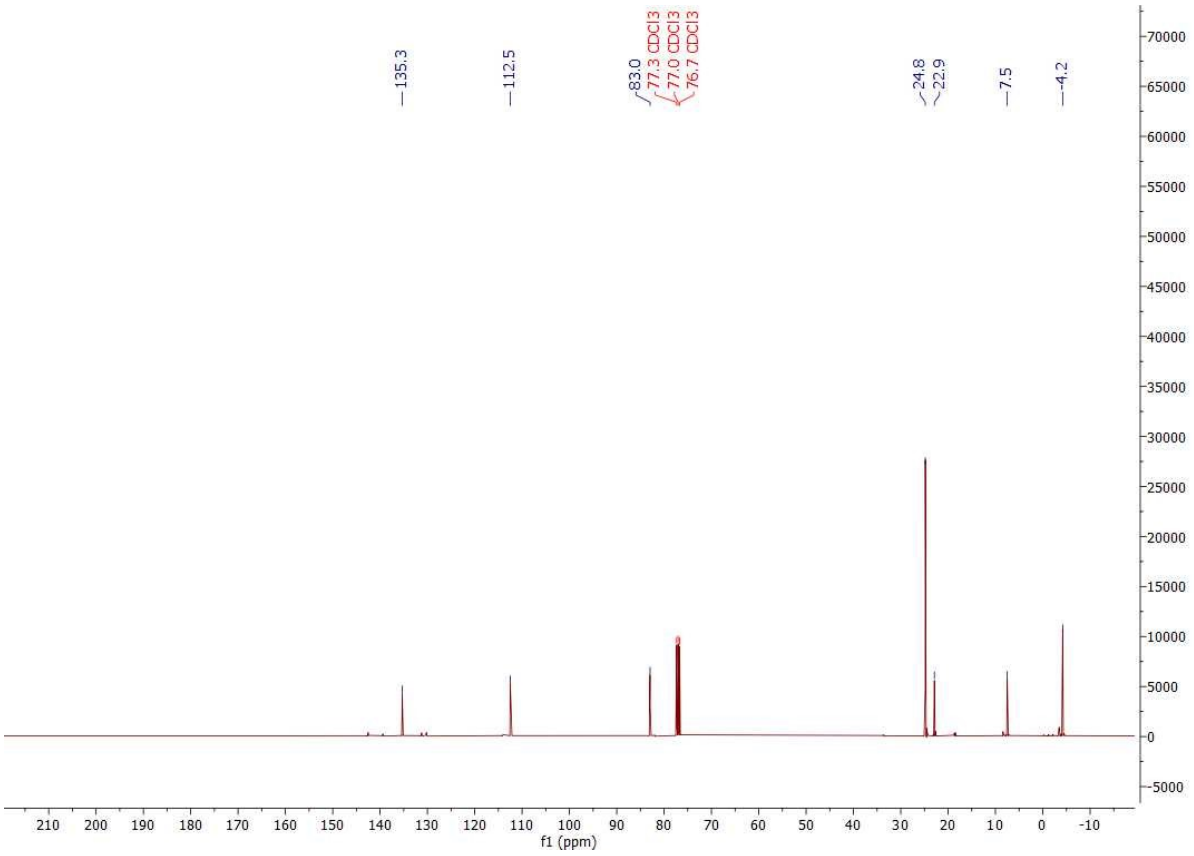


Figure S78. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (3a).

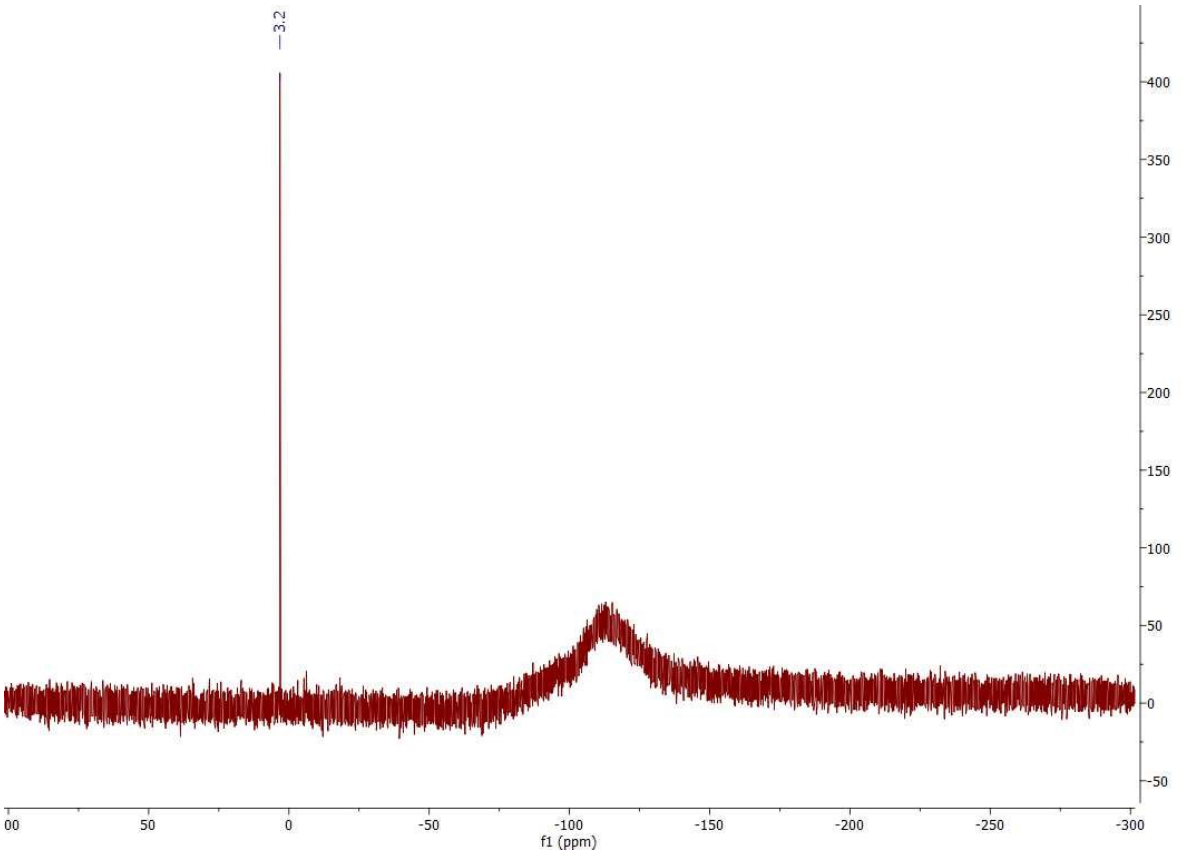
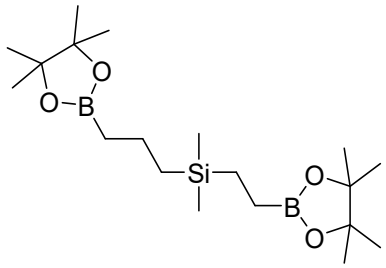


Figure S79. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (3a).

dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (3b)



dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane was obtained with 90% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.06 (s, 6H), 0.51-0.55 (m, 4H), 0.70-0.74 (m, 2H), 0.82 (t, J = 7.7 Hz, 2H), 1.25 (s, 24H), 1.40-1.45 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -3.8, 7.9, 18.3, 18.5, 24.8, 82.8, 82.9, Carbon adjacent to boron not observed.
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 3.7
EI-MS m/z (rel. int.): 227 (85), 213 (100), 167 (15), 145 (6), 131 (38), 127 (35), 113 (11), 99 (16), 83 (95), 69 (16), 59 (18), 57 (31), 55 (24)

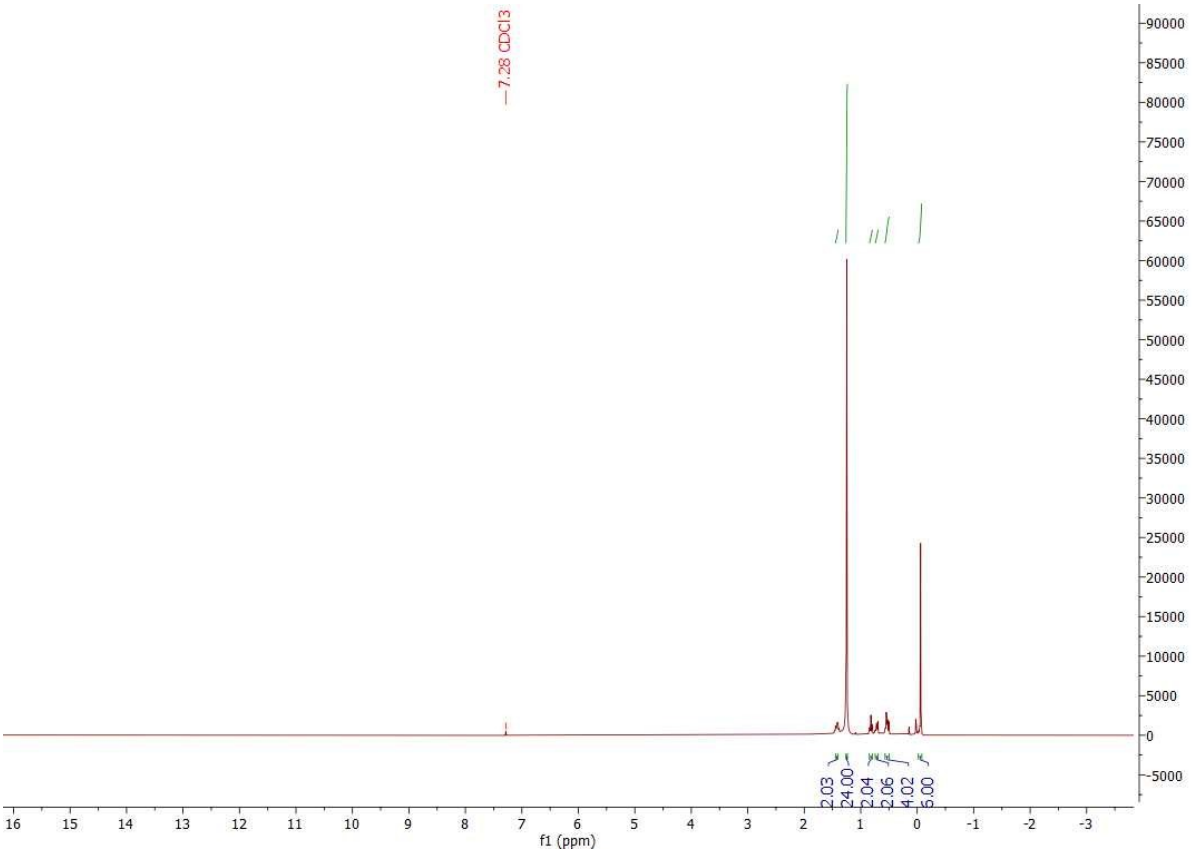


Figure S80. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (3b).

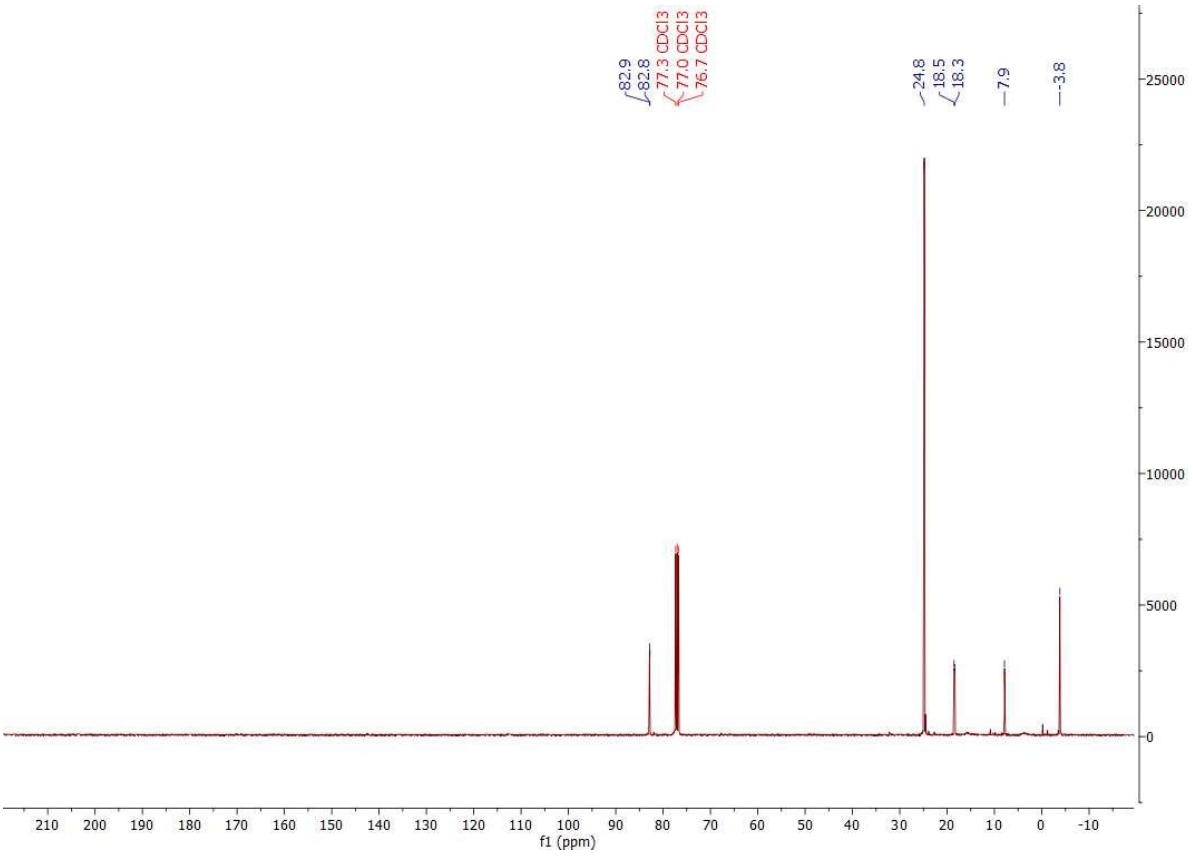


Figure S81. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (3b).

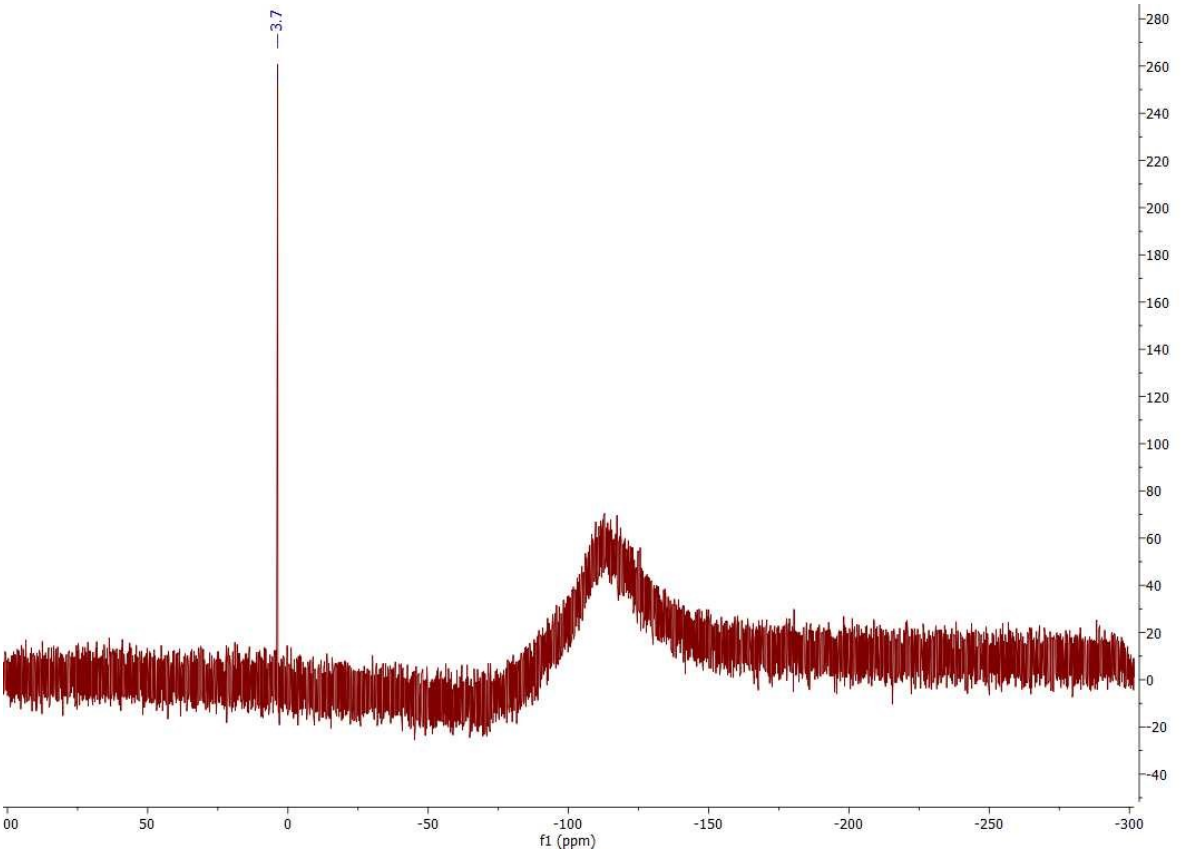
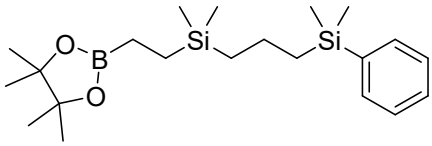


Figure S82. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (3b).

(3-(dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silyl)propyl)dimethyl(phenyl)silane (4a)



(3-(dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silyl)propyl)dimethyl(phenyl)silane was obtained with 85% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.00 (s, 6H), 0.33 (s, 6H), 0.55-0.66 (m, 4H), 0.76-0.81 (m, 2H), 0.86-0.92 (m, 2H), 1.33 (s, 12H), 1.41-1.49 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -3.5, -2.7, 8.2, 18.6, 19.7, 20.5, 25.0, 83.1, 127.9, 128.9, 133.8, 140.1
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -3.8, 3.5
EI-MS m/z (rel. int.): 275 (1), 235 (1), 213 (100), 135 (58), 131 (28), 121 (5), 113 (4), 105 (5), 83 (45), 78 (5), 59 (6), 57 (7), 55 (10)

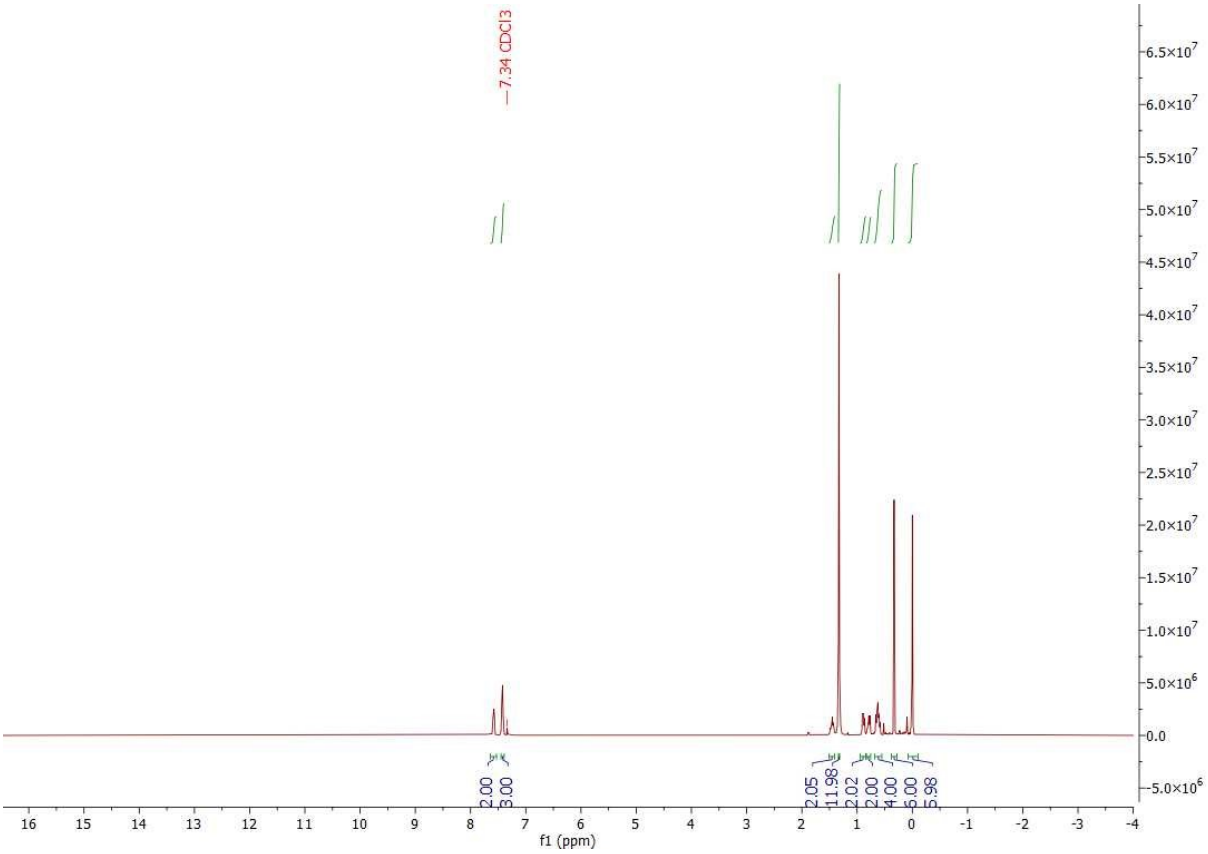


Figure S83. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of (3-(dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silyl)propyl)dimethyl(phenyl)silane (4a)

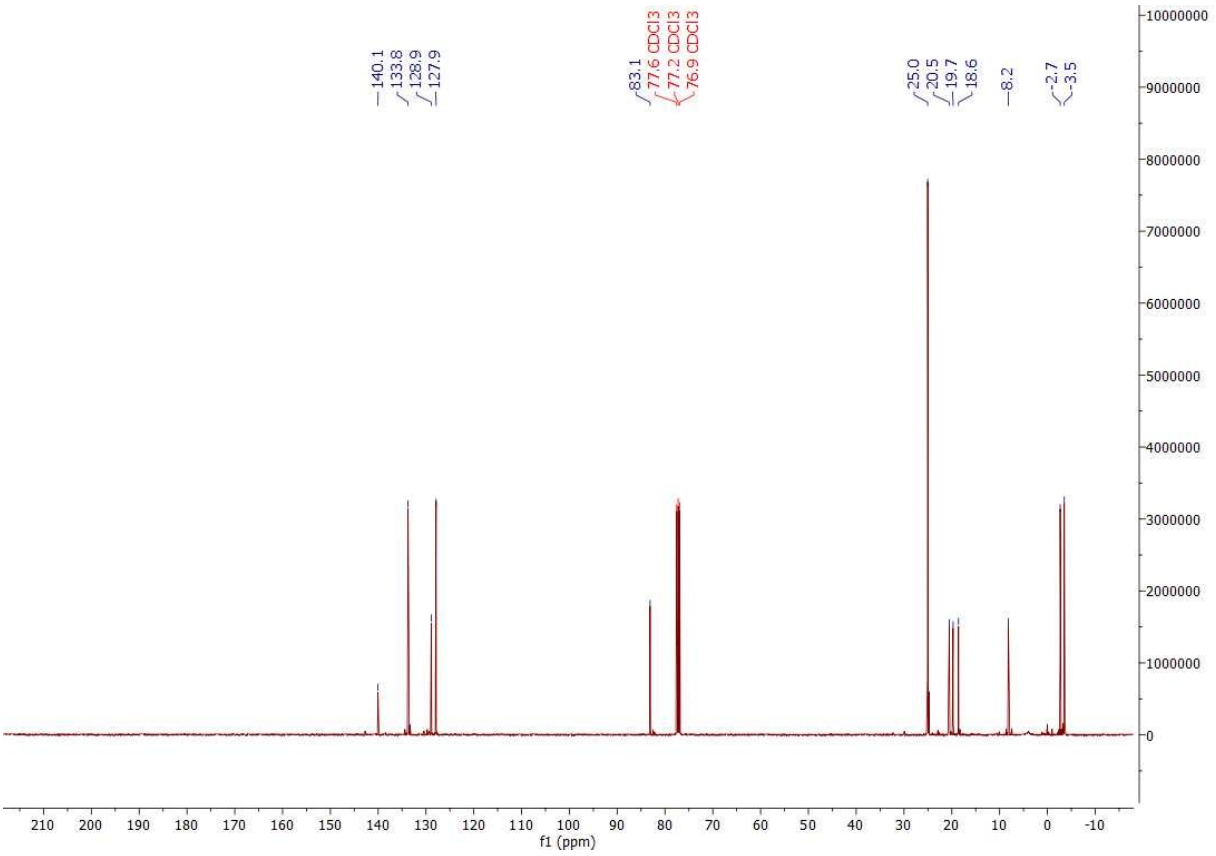


Figure S84. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of (3-(dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silyl)propyl)dimethyl(phenyl)silane (4a)

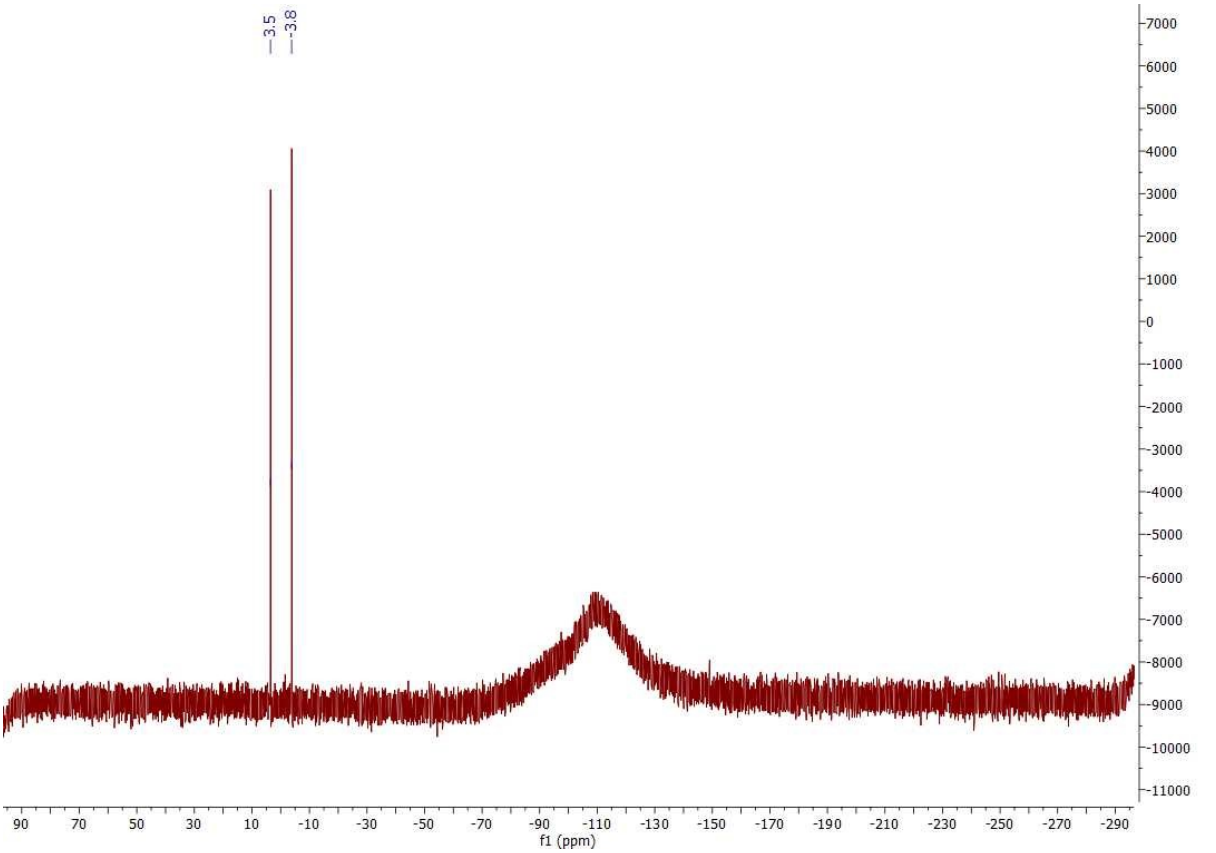
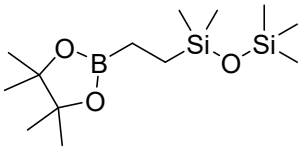


Figure S85. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of (3-(dimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silyl)propyl)dimethyl(phenyl)silane (4a)

1,1,1,3,3-pentamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (4b)



1,1,1,3,3-pentamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane was obtained with 82% yield, and is known in the literature. All spectroscopic data are in agreement.[15]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.02 (s, 6H), 0.00 (s, 9H), 0.48-0.53 (m, 2H), 0.66-0.70 (m, 2H), 1.20 (s, 12H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -2.2, 0.0, 8.9, 22.8, 80.9
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 7.1, 8.5
EI-MS m/z (rel. int.): 287 (46), 245 (22), 187 (70), 173 (19), 147 (100), 131 (11), 117 (10), 83 (27), 73 (21), 59 (7), 55 (7)

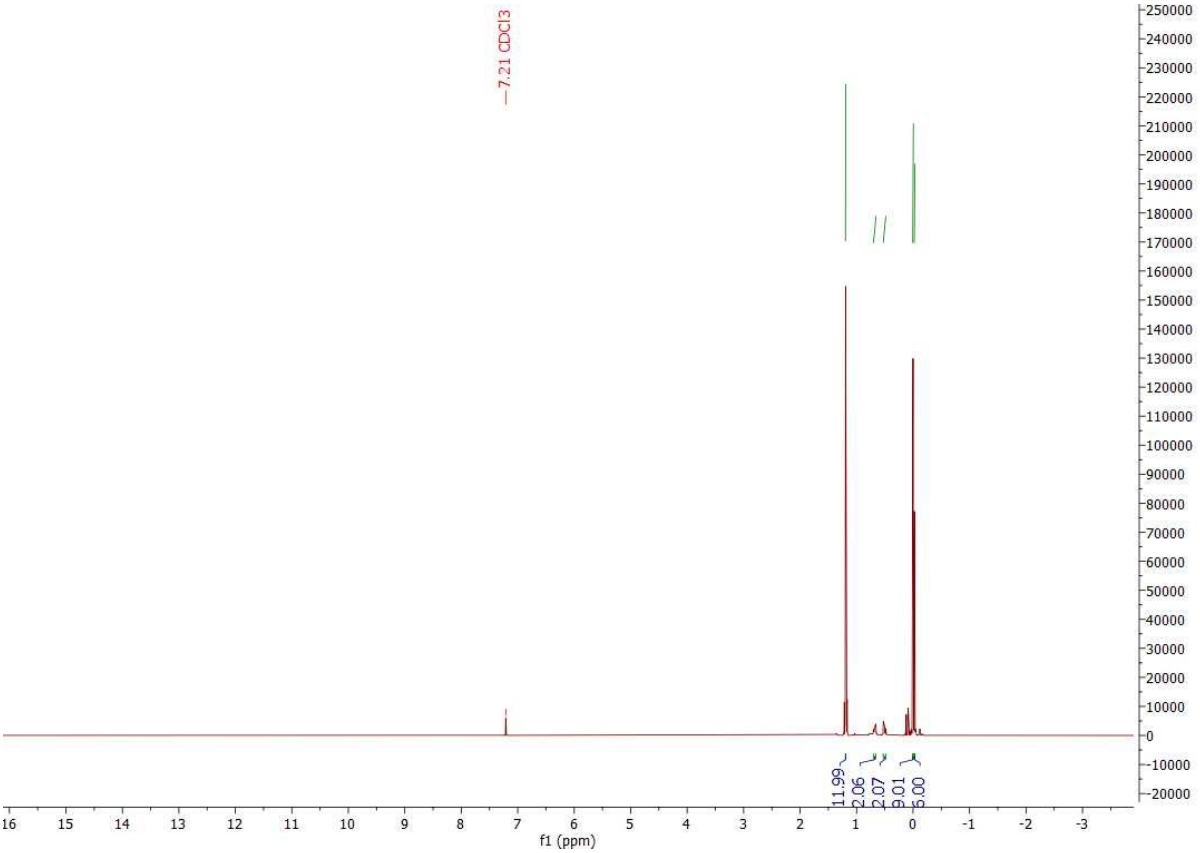


Figure S86. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (4b)

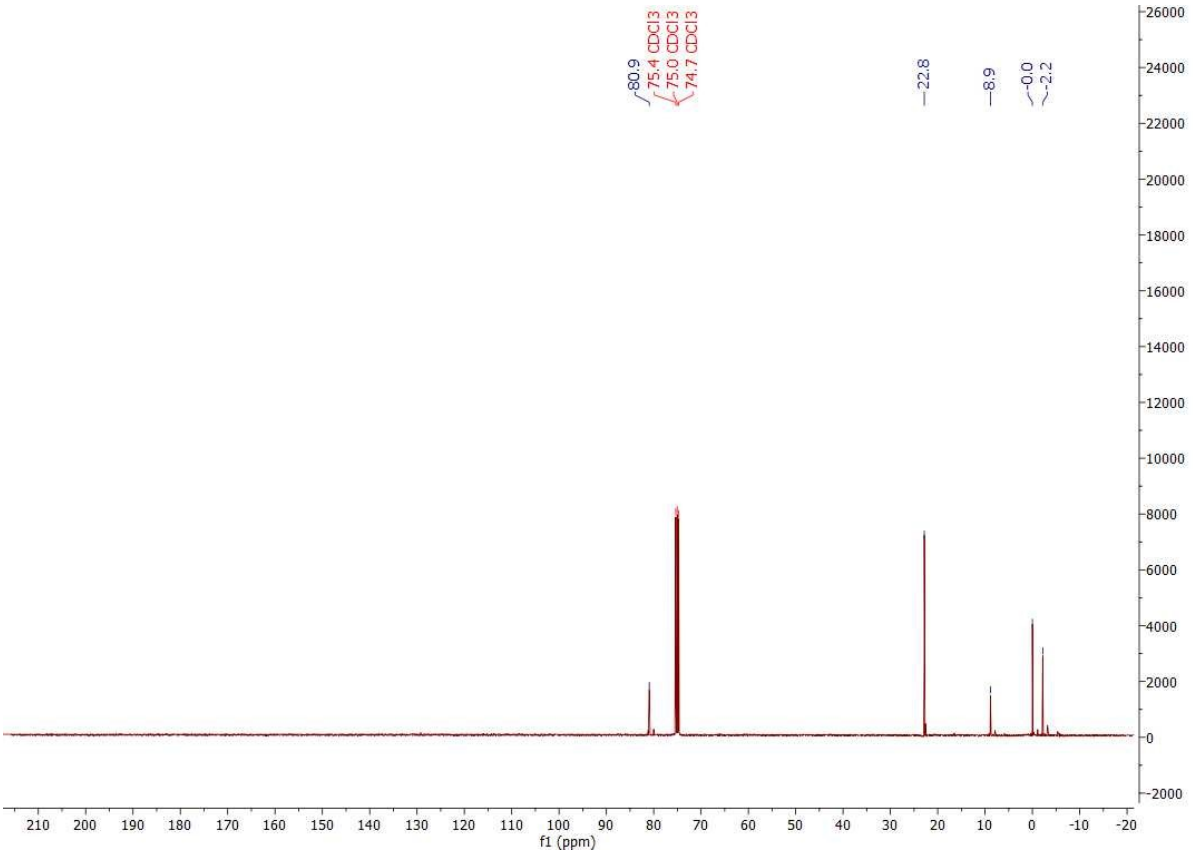


Figure S87. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (4b)

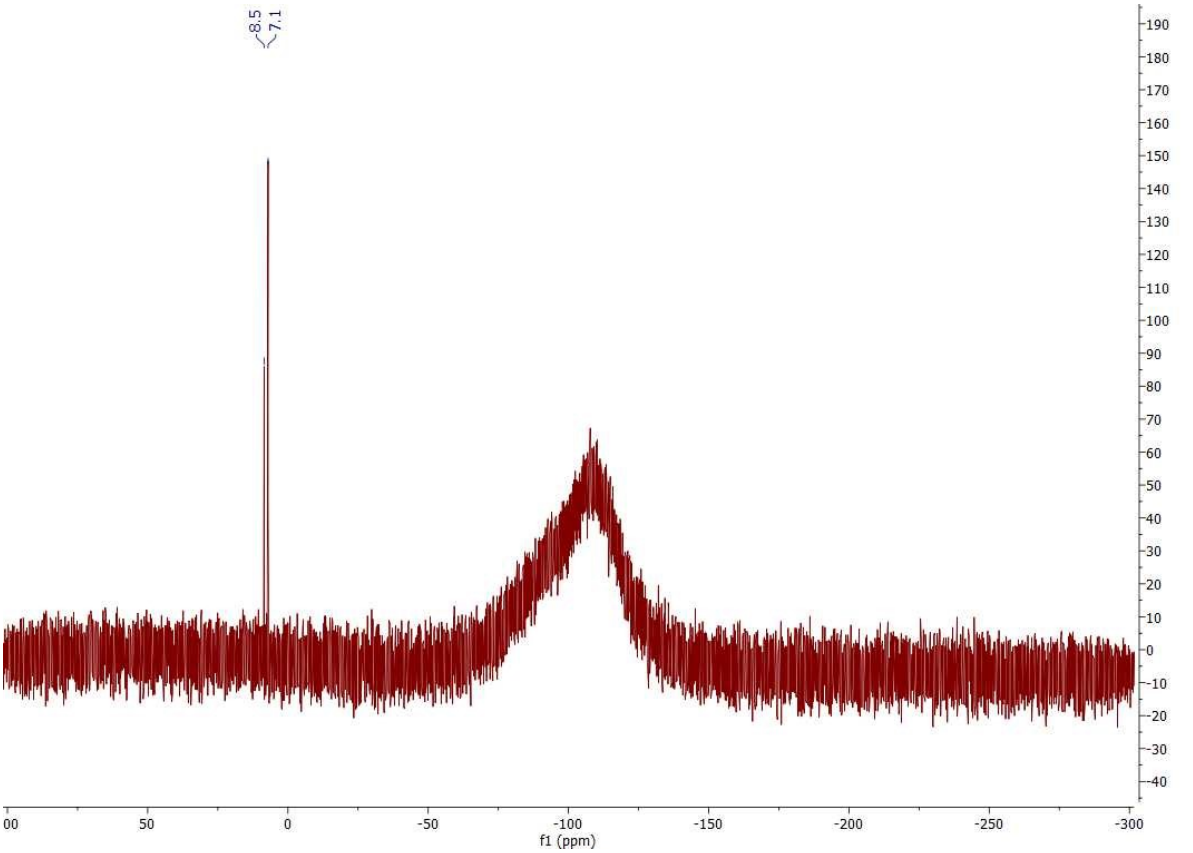
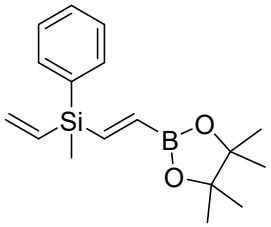


Figure S88. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of 1,1,1,3,3-pentamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (4b)

(E)-methyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(vinyl)silane (5a)



(E)-methyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(vinyl)silane was obtained with 77% yield. It was unknown in the literature and was characterized for the first time.

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.36 (s, 3H), 1.20 (s, 12H), 5.71 (dd, J = 20.2, 3.8 Hz, 1H), 6.05 (dd, J = 14.6, 3.8 Hz, 1H), 6.32 – 6.17 (m, 2H), 7.15 (d, J = 21.8 Hz, 1H), 7.25-7.46 (m, 5H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -4.9, 24.8, 83.5, 127.8, 129.3, 134.5, 134.6, 135.4, 135.9, 152.9
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): -17.9
EI-MS m/z (rel. int.): 285 (9), 243 (41), 201 (7), 189 (7), 175 (8), 158 (21), 137 (10), 131 (13), 121 (47), 113 (9), 107 (10), 105 (27), 84 (100), 69 (41), 57 (12), 55 (12)

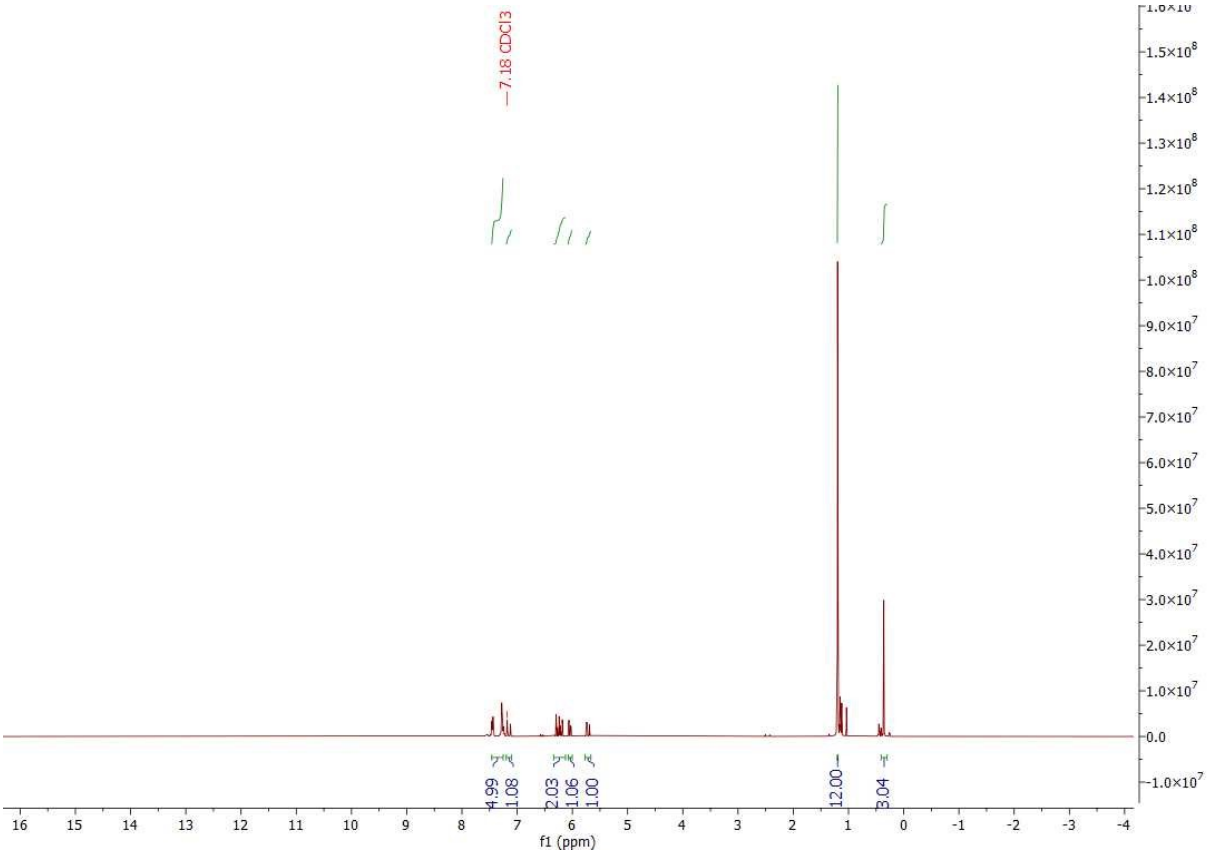


Figure S89. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of (E)-methyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(vinyl)silane (5a)

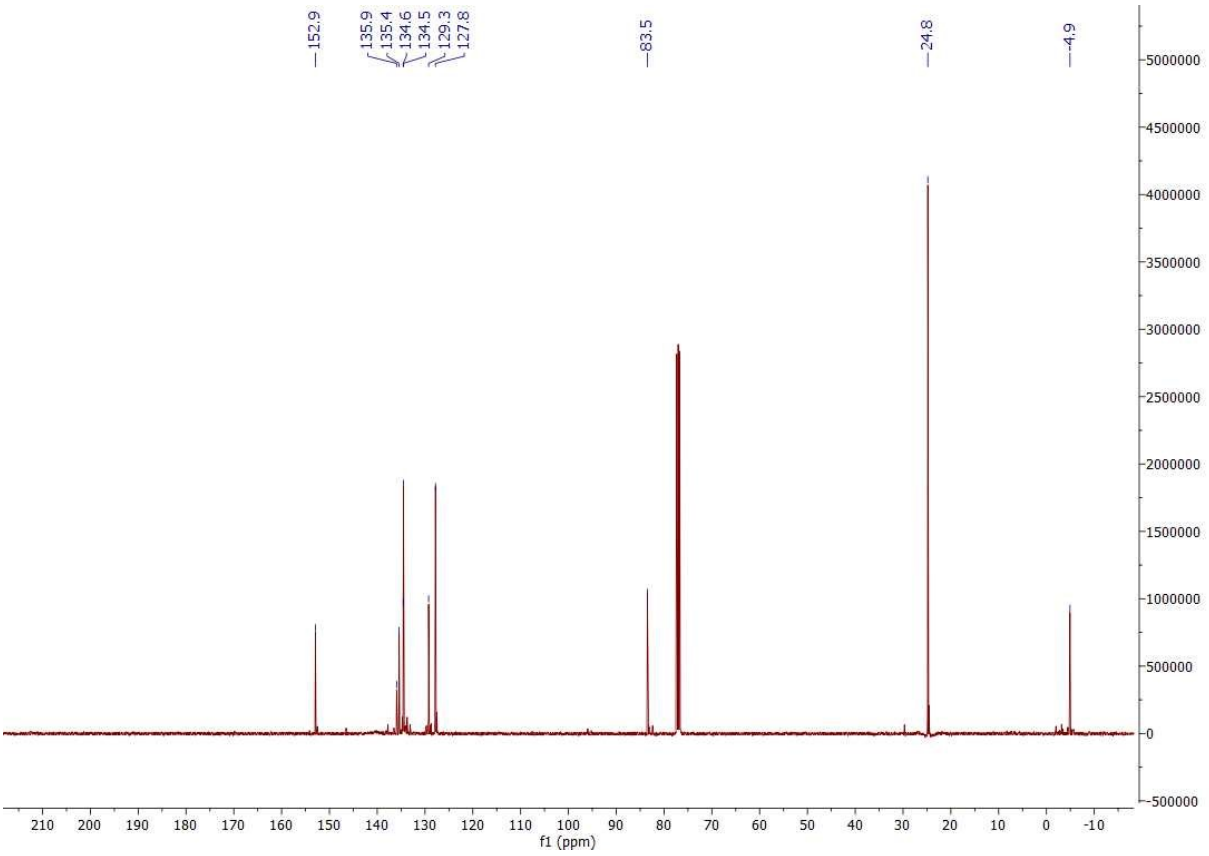


Figure S90. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of (E)-methyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(vinyl)silane (5a)

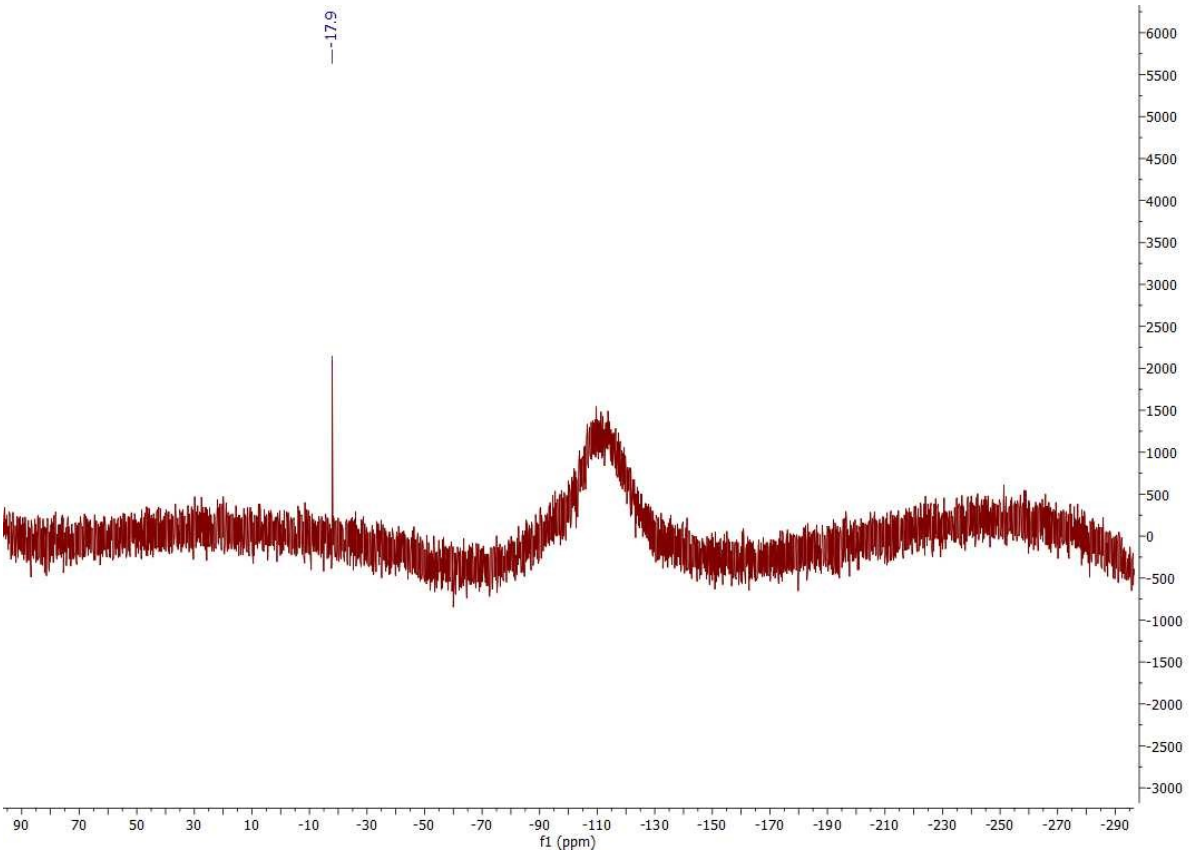
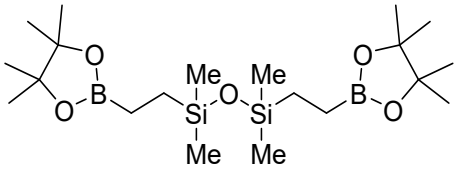


Figure S91. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of (E)-methyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)(vinyl)silane (5a)

1,1,3,3-tetramethyl-1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (6a)



1,1,3,3-tetramethyl-1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane was obtained with 85% yield, and is known in the literature. All spectroscopic data are in agreement.[16]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): -0.01 (s, 12H), 0.49-0.54 (m, 4H), 0.67-0.71 (m, 4H), 1.21 (s, 24H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): -0.2, 10.8, 24.8, 82.8
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 8.3
EI-MS m/z (rel. int.): 287 (11), 227 (9), 213 (51), 187 (100), 145 (26), 131 (7), 83 (17), 69 (3), 59 (3), 55 (5)

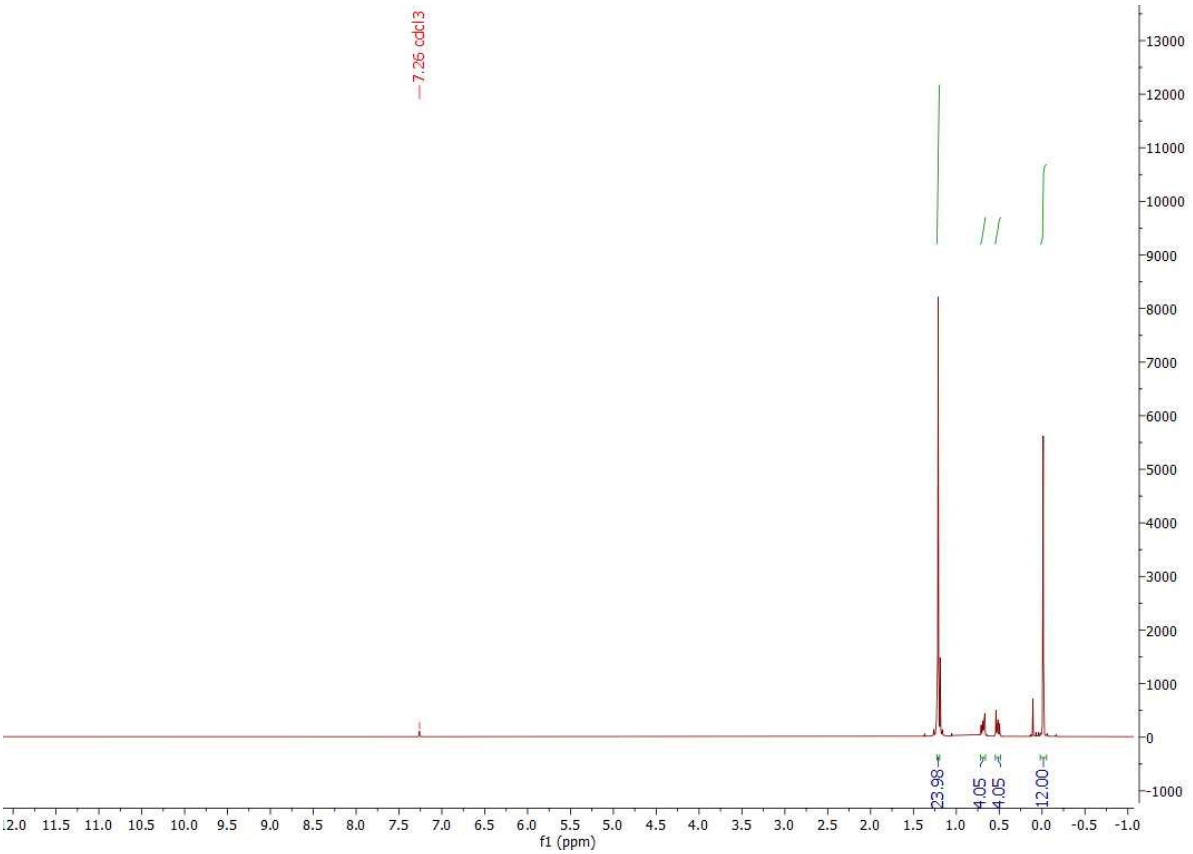


Figure S92. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 1,1,3,3-tetramethyl-1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (6a).

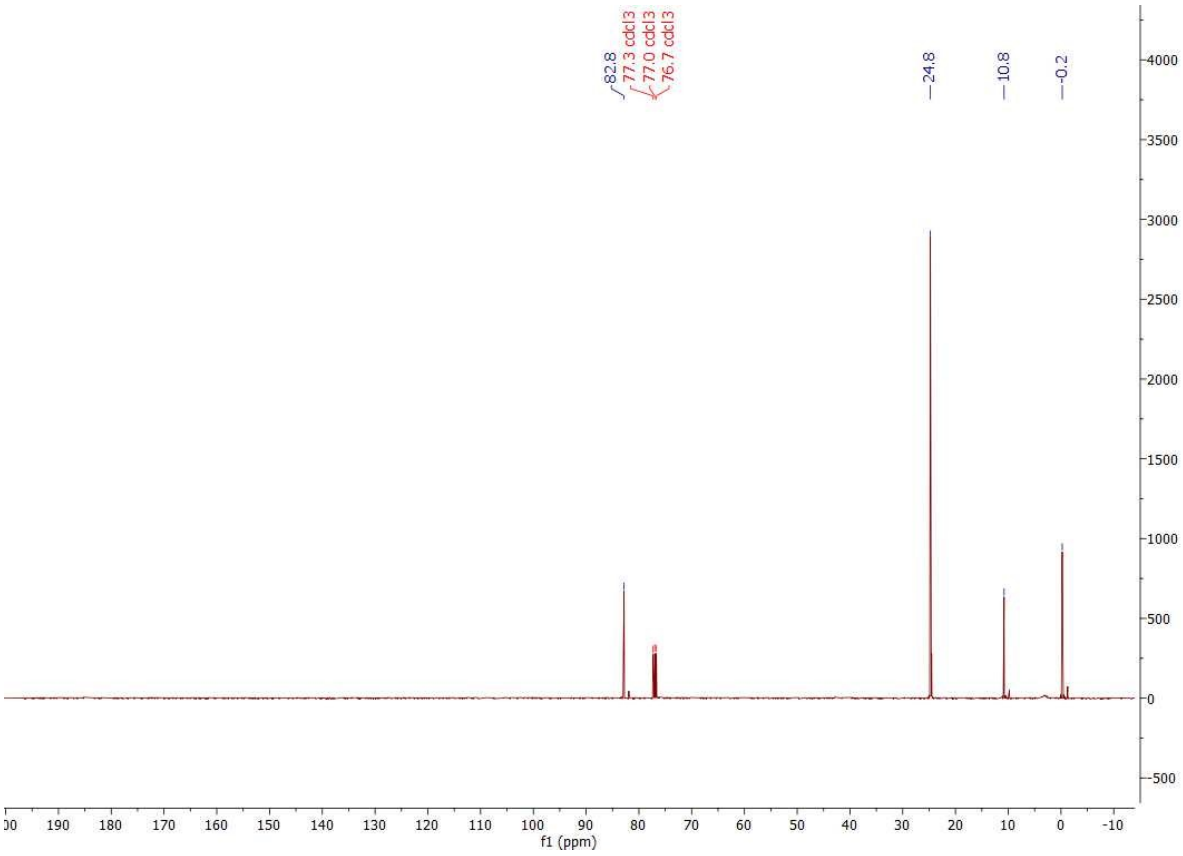


Figure S93. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 1,1,3,3-tetramethyl-1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (6a).

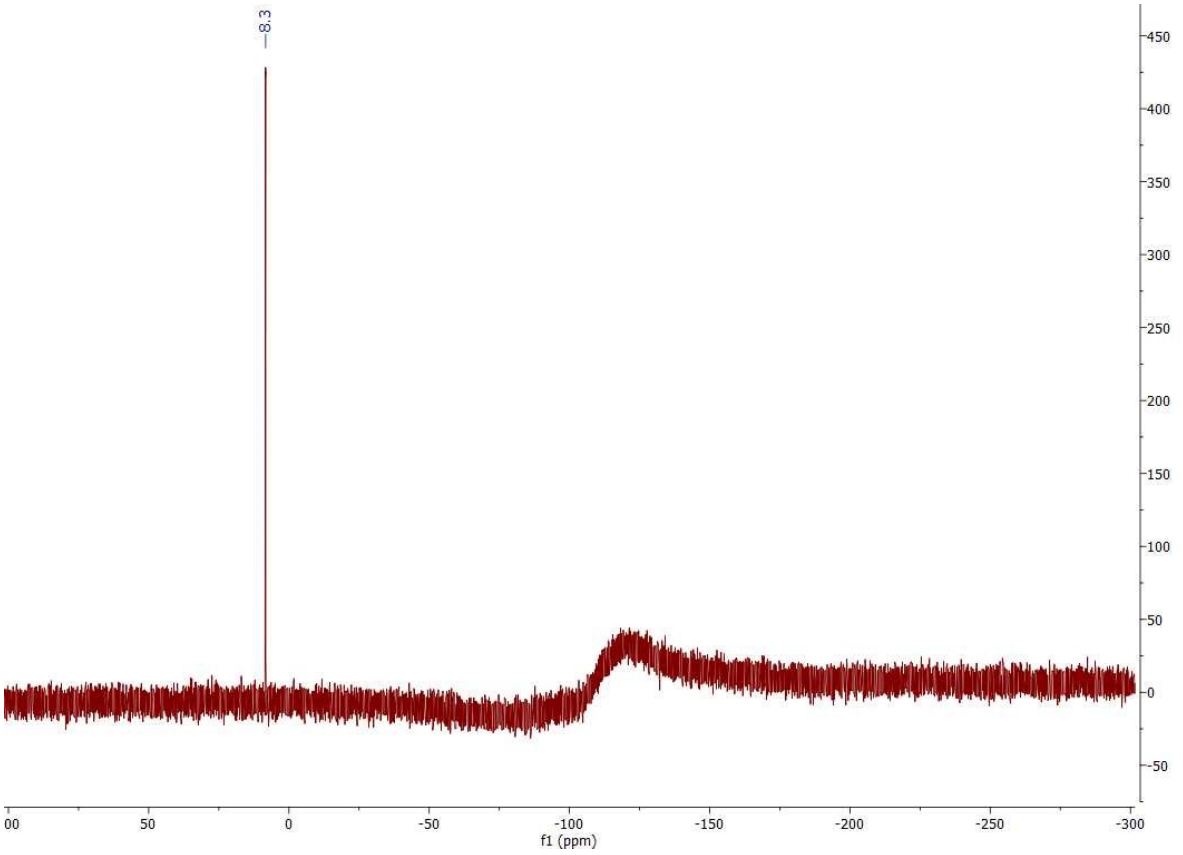
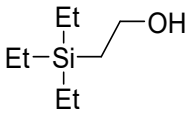


Figure S94. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of 1,1,3,3-tetramethyl-1,3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)disiloxane (6a).

2-(triethylsilyl)ethan-1-ol (6b)



2-(triethylsilyl)ethan-1-ol was obtained with 71% yield, and is known in the literature. All spectroscopic data are in agreement.[17]

^{1}H NMR (400 MHz, Chloroform-d, 25°C) δ (ppm): 0.52 (q, J = 7.9 Hz, 6H), 0.93 (t, J = 7.9 Hz, 9H), 0.97-1.01 (m, 2H), 3.71-3.75 (m, 2H)
^{13}C NMR (101 MHz, Chloroform-d, 25°C) δ (ppm): 3.4, 7.3, 17.4, 60.1
^{29}Si NMR (79 MHz, Chloroform-d, 25°C) δ (ppm): 5.0
EI-MS m/z (rel. int.): 103 (100), 87 (7), 75 (90), 59 (6), 57 (6), 55 (4)

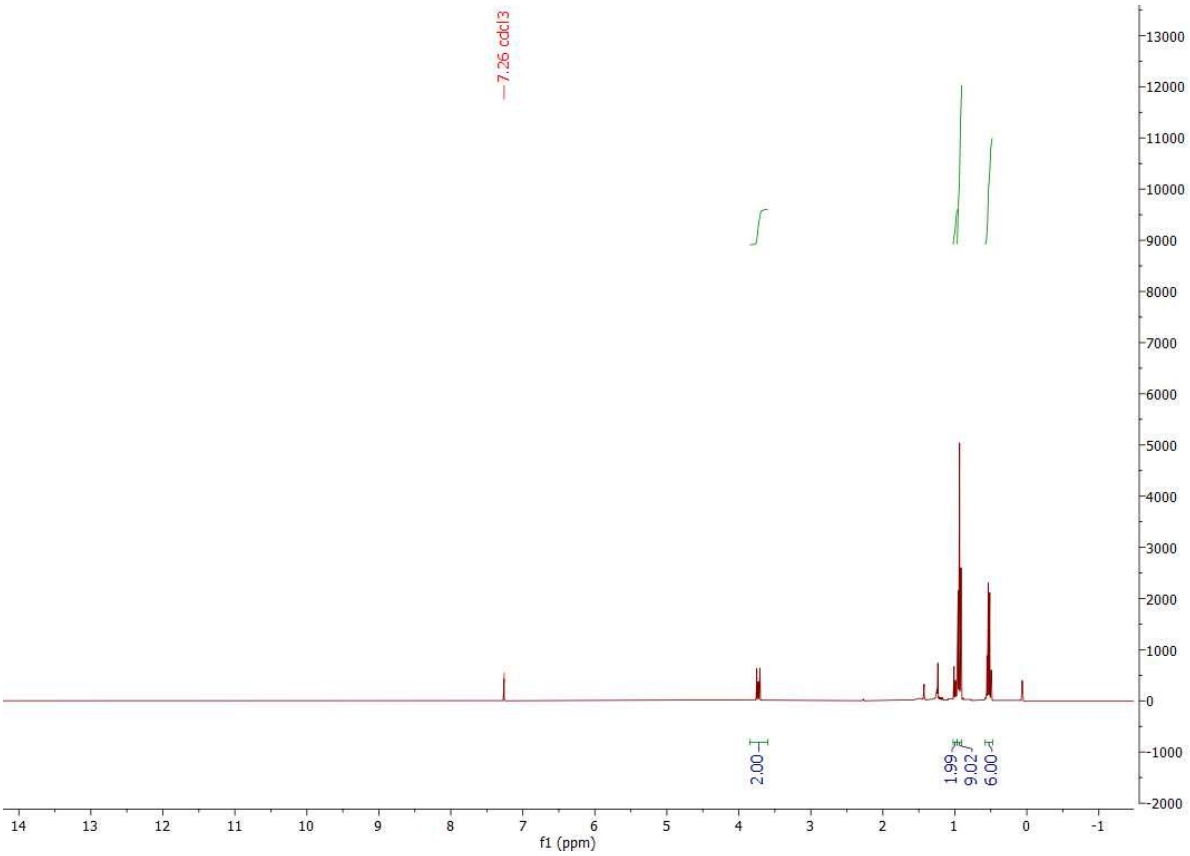


Figure S95. ^{1}H NMR (400 MHz, Chloroform-d, 25°C) of 2-(triethylsilyl)ethan-1-ol (6b).

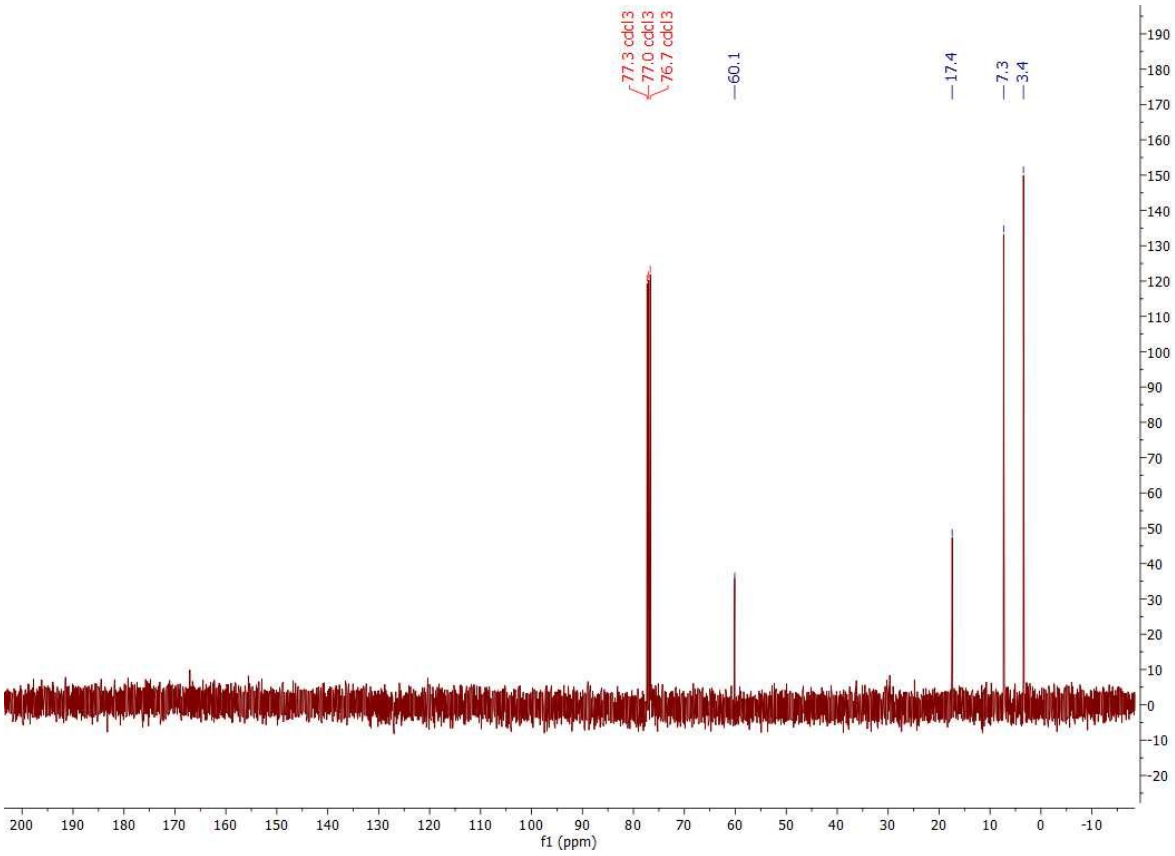


Figure S96. ^{13}C NMR (101 MHz, Chloroform-d, 25°C) of 2-(triethylsilyl)ethan-1-ol (6b).

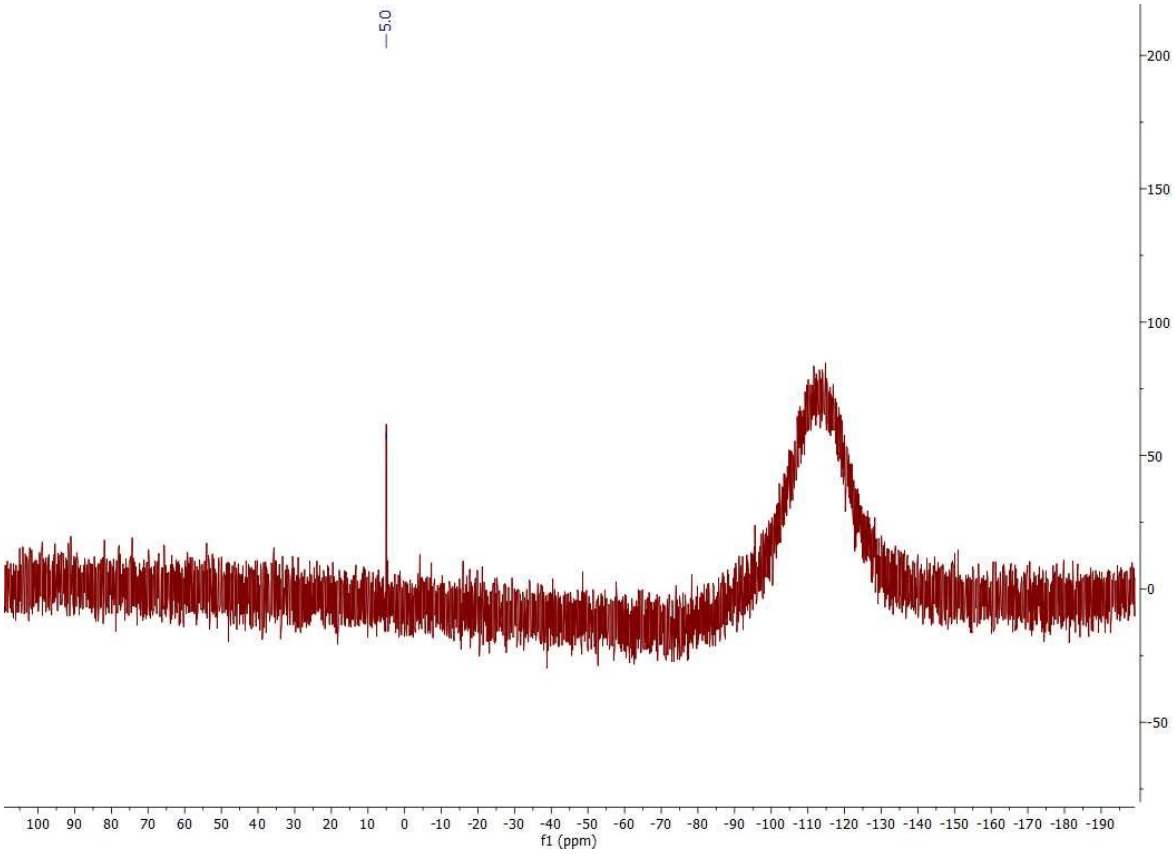
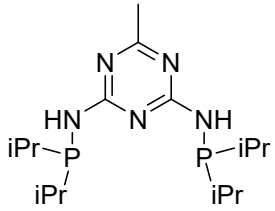


Figure S97. ^{29}Si NMR (79 MHz, Chloroform-d, 25°C) of 2-(triethylsilyl)ethan-1-ol (6b).

5. MECHANISTIC STUDIES

N^2 ,N^4 -bis(diisopropylphosphino)-6-methyl-1,3,5-triazine-2,4-diamine



N^2,N^4-bis(diisopropylphosphino)-6-methyl-1,3,5-triazine-2,4-diamine was obtained in 74% yield, and is known in the literature. All spectroscopic data are in agreement.[18]

^{1}H NMR (400 MHz, C_6D_6, 25°C) δ (ppm) = 0.94 (m, 24H), 1.71 (s, 4H), 2.38 (s, 3H), 5.45 (s, 2H)

^{31}P NMR (162 MHz, C_6D_6, 25°C) δ (ppm) = 51.5

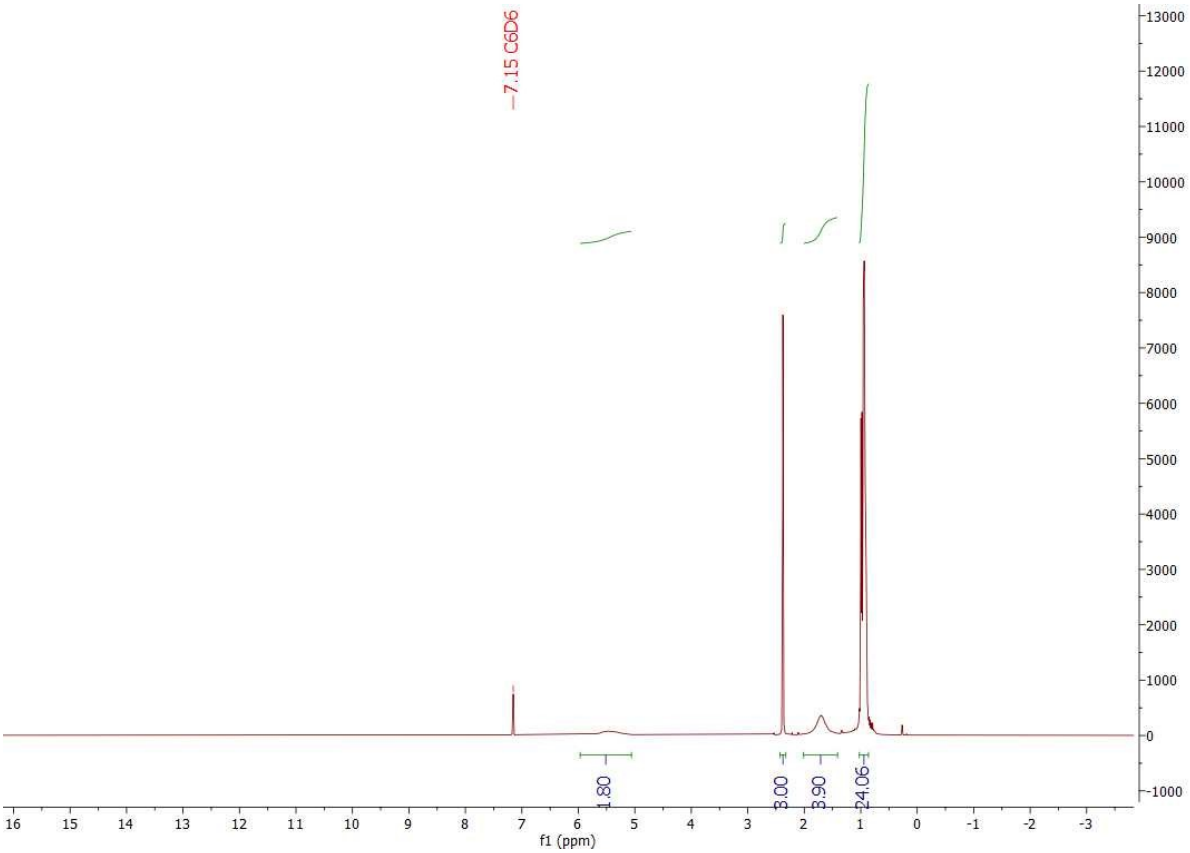


Figure S98. ^{1}H NMR (400 MHz, C_6D_6, 25°C) spectrum of N^2 ,N^4 -bis(diisopropylphosphino)-6-methyl-1,3,5-triazine-2,4-diamine.

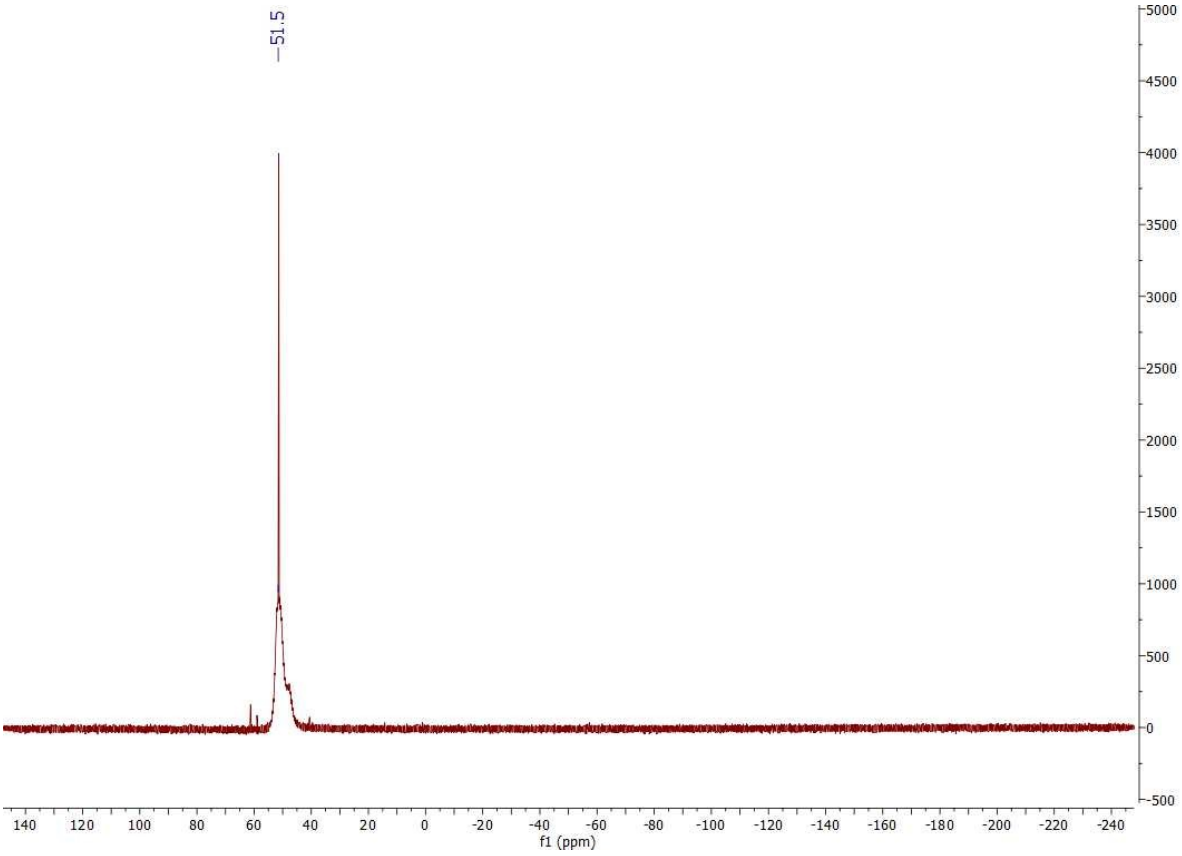
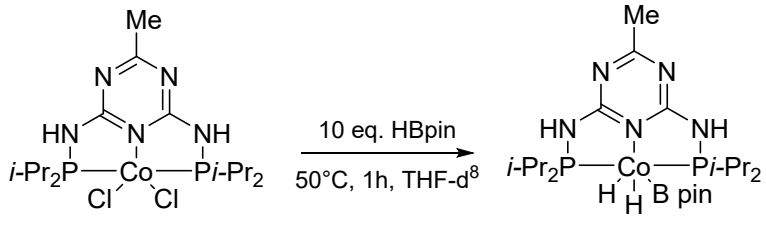


Figure S99. ^{31}P NMR (162 MHz, C_6D_6, 25°C) spectrum of N2 ,N4 -bis(diisopropylphosphino)-6-methyl-1,3,5-triazine-2,4-diamine.

Reaction of 1 eq. precat. A with 10 eq. HBpin in THF-d^8 stirred for 1h at 50°C.



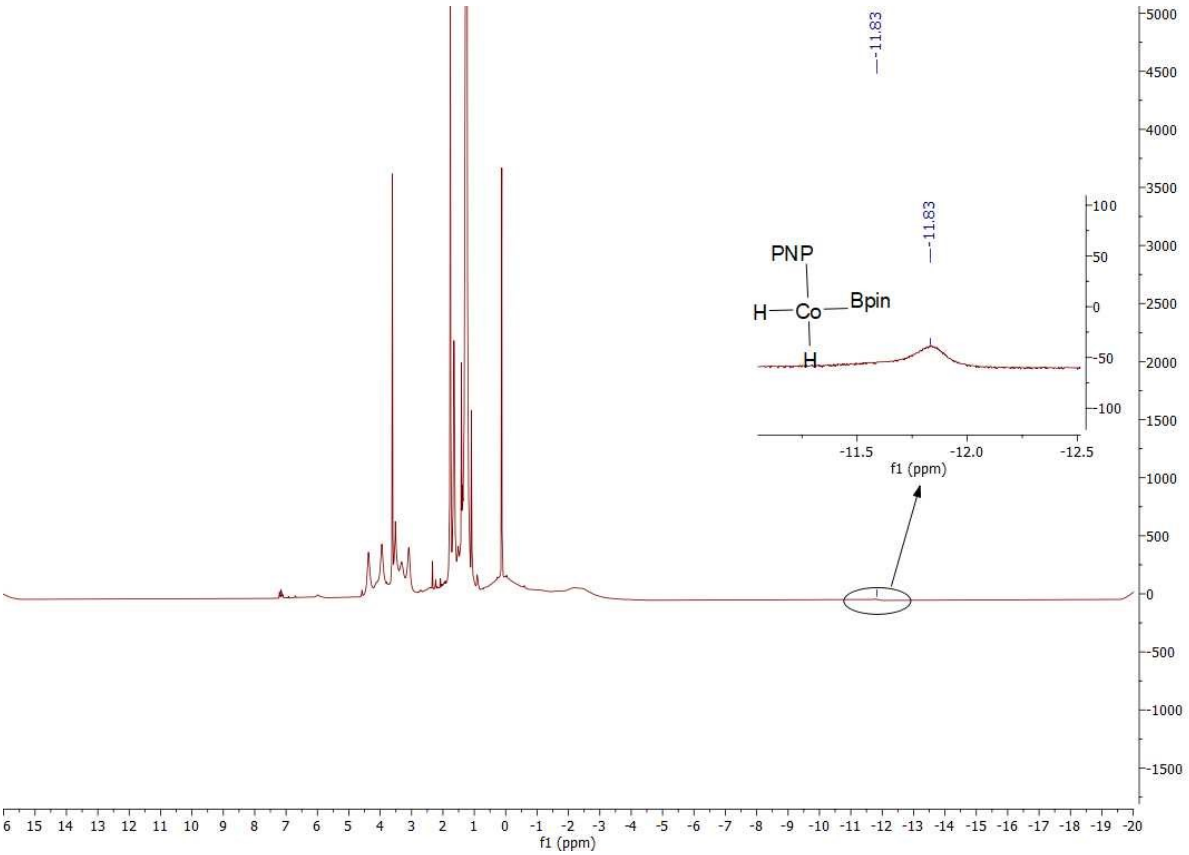


Figure S100. ^{1}H NMR (400 MHz, THF-d^8, 25°C) spectrum of precatalyst A activation.

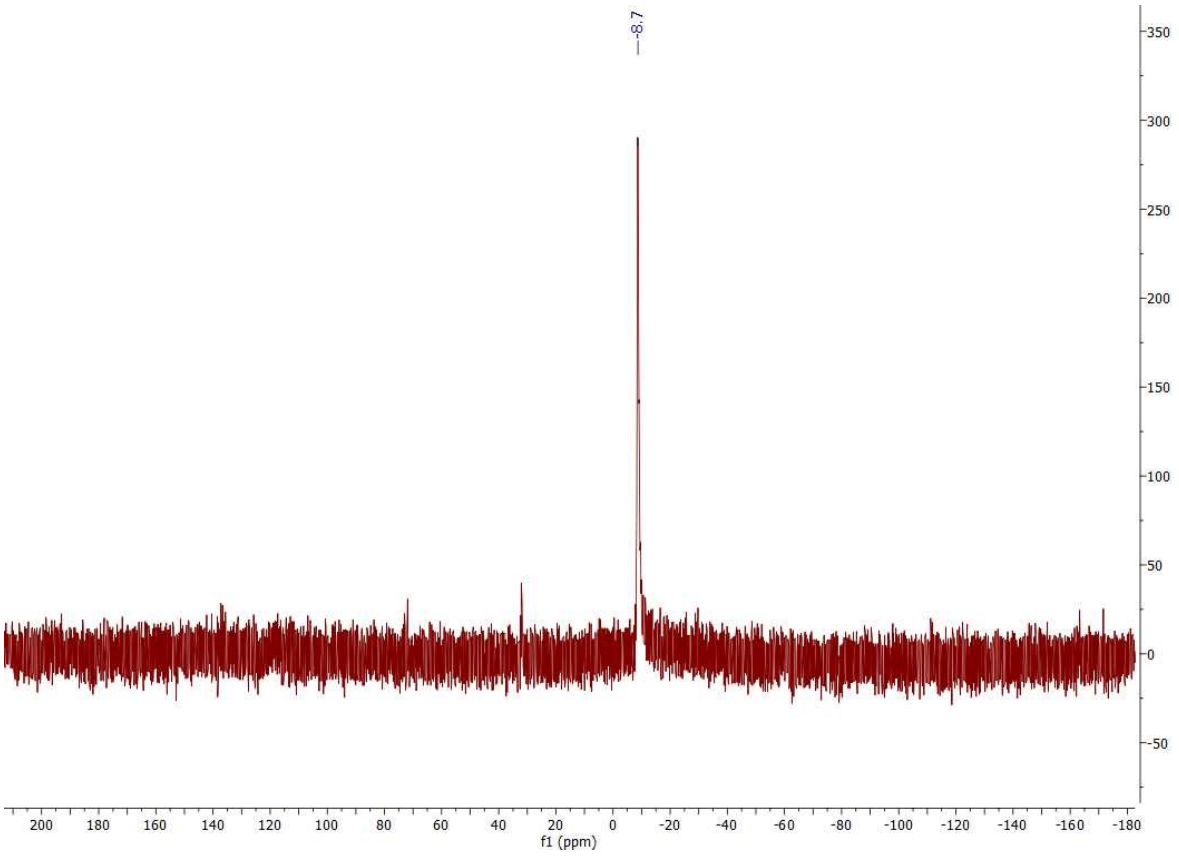


Figure S101. ^{31}P (243 MHz, C^6D^6, 25°C) NMR spectrum of precatalyst A activation.

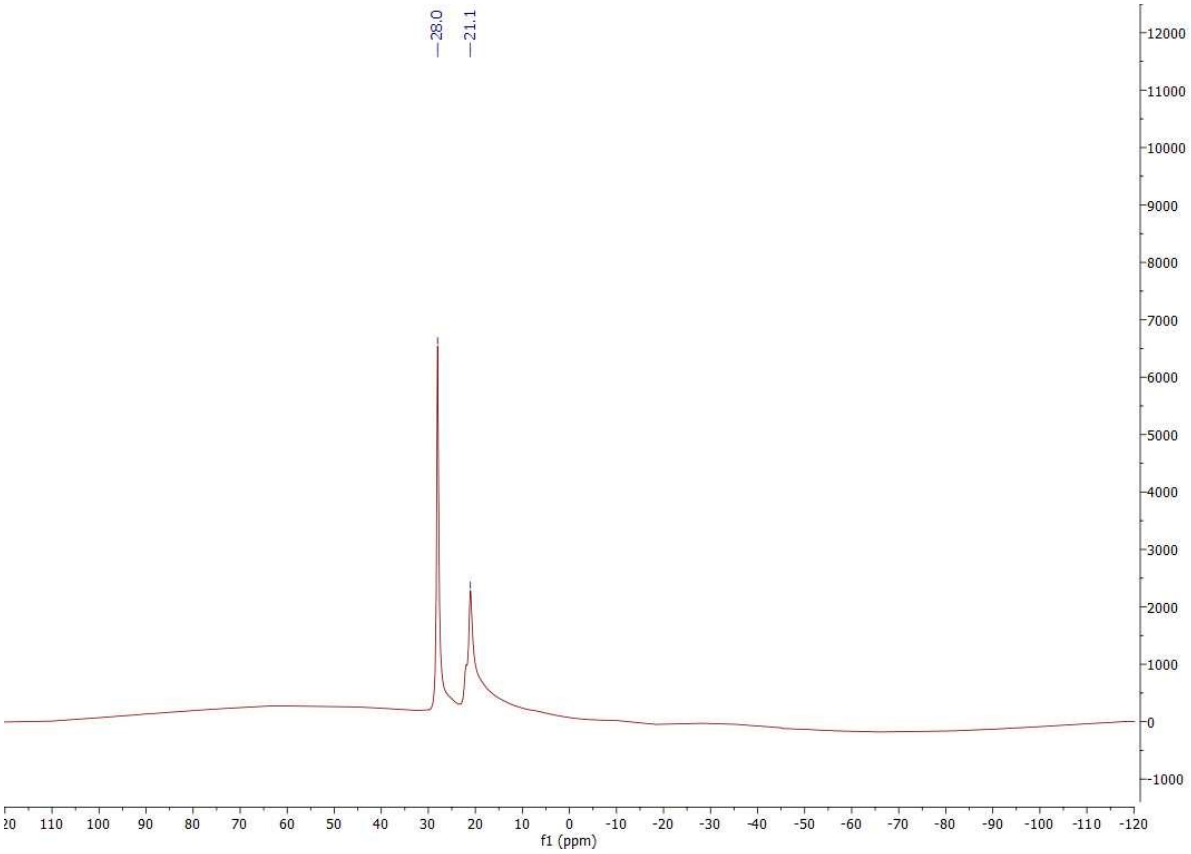


Figure S102. ^{11}B NMR (128 MHz, THF-d^8, 25°C) spectrum of precatalyst A activation. Based on literature data, we assign the signal at 28.0 ppm to the HBpin excess,[19] while the signal at 21.1 ppm is attributed to the Co-B complex.[20,21]

Reaction of 1 eq. precat. F with 3 eq. NaHBEt3 and 4 eq. HBpin in chlorobenzene-d^5 stirred for 20h at 60°C.

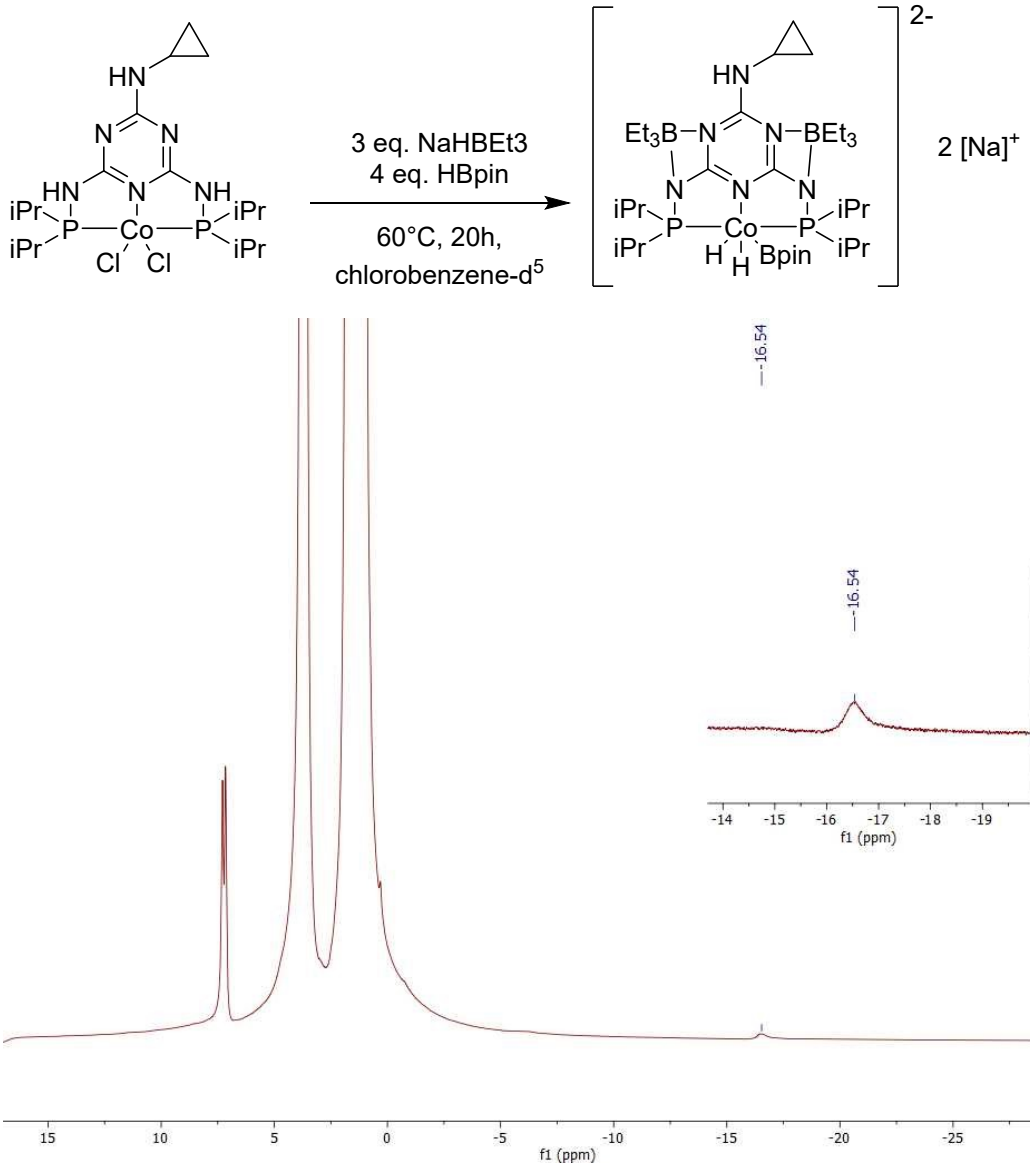


Figure S103. ^{1}H NMR (400 MHz, chlorobenzene-d^5, 25°C) spectrum of precatalyst F activation.

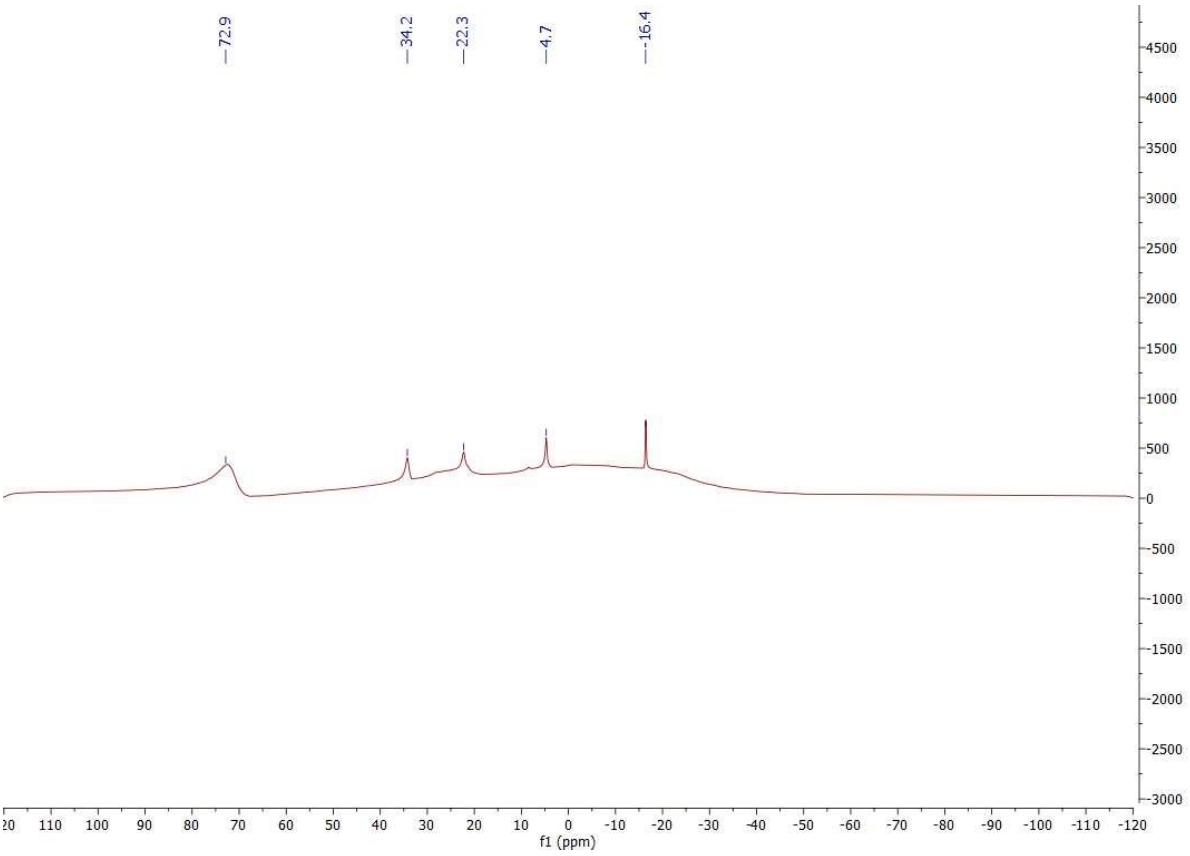


Figure S104. ^{11}B NMR (128 MHz, THF-d^8, 25°C) spectrum of precatalyst F activation. Based on literature data, the broad signal at 72.9 ppm probably comes from the adduct of BEt_2 with the ligand,[22] 22.3 ppm from the Co-B complex,[20,21] 4.7 ppm from the adduct of BEt_3 with the ligand,[22] while -16.4 ppm from $[HBEt_3]^-$.[22] The remaining signal may come from side reactions of the redistribution of triethylboronhydride substituents (L-BEt_2, $[BEt_4]^-$) or bridge complexes (Et_3B-H-BEt_3).[22]

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