Supporting Information

Directed *cis*-hydrosilylation of borylalkynes to borylsilylalkenes

Kinga Stefanowska[a], Tomasz Sokolnicki[a,b], Jędrzej Walkowiak[a] Agnieszka Czapik[b] and Adrian Franczyk[a,*]

[a]Center for Advanced Technology, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 10, Poznań 61-614, Poland

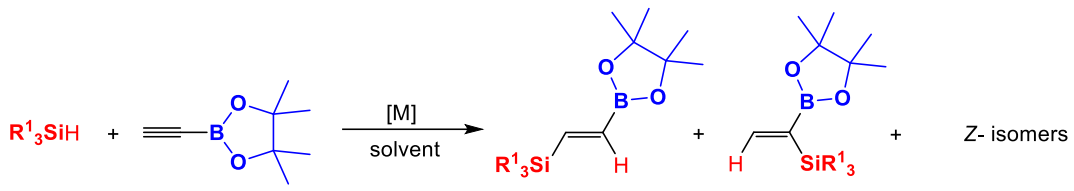
E-mail: adrian.franczyk@amu.edu.pl

[b]Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 8, Poznań 61-614, Poland

Table of Contents

1. Optimization of the reaction conditions

Table S1. Hydrosilylation of 2-ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**) with silanes **1a-f**.



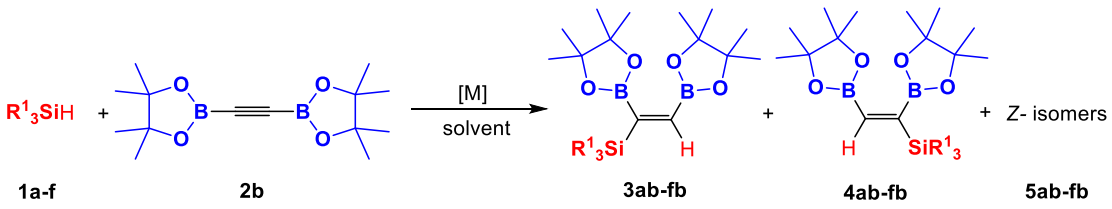
1a-f **2a** **3aa-fa** **4aa-fa** **5aa-fa**

SiR^1_3 = $SiEt_3$ (**1a**), $SiPh_3$ (**1b**), $SiMe_2(OEt)$ (**1d**), $SiMe_2Ph$ (**1e**), $SiMe_2Bn$ (**1f**); Bn= benzyl
[M] = PtO_2/XPhos (1:2) (**I**), [M]= $Pt_2(dvs)_3$ (**II**), $Pt(PPh_3)_4$ (**III**), $[CpRu(CH_3CN)_3][PF_6]$ (**IV**), $Ru(CO)Cl(H)(PCy_3)_2$ (**V**), $Ru{=}CHPh(Cl)_2(PCy_3)_2$ (**VIII**), $RhCl(PPh_3)_3$ (**IX**), [M] = $PtCl_2$/XPhos (1:4) (**X**)

Entry	R_3SiH 1	Alkyne 2	[M]	[1]:[2]:[M]	t [h]	Temp. [°C]	Conversion of 1 [%]	Selectivity of 3/4/5 [%] NMR (GC-MS)
1[THF, Ar]	**1a**	**2a**	**I**	$1:1:10^{-2}$	48	60	100	**aa**, 96/4/0 (97/3/0)
2[THF, Ar]						100	100	**aa**, 100/0/0 (93/7/0)
3[Tol., Air]			**II**	$1:1:10^{-4}$	24	60	100	**aa**, 55/45/0 (51/49/0)
4[Tol., Air]			**III**	$1:1:10^{-2}$	24	60	100	**aa**, 61/39/0 (53/47/0)
5[DCM, Ar,a]			**V**	$1:1:10^{-2}$	24	rt	100	**aa**, 100/0/0 (100/0/0)
6[DCM, Ar, a]				$2:1:10^{-2}$		rt	50	**aa**, 100/0/0 (96/4/0)
7[Ar,b]			**VIII**	$1:1.5:10^{-2}$	24	65	100	**aa**, 100/0/0 (100/0/0)
8[Tol., Ar, c]			**IX**	$1:1:1.1x10^{-2}$	24	rt	100	**aa**, 54/16/30 (60/18/22)
9[Tol., Ar, c]						100	100	**aa**, 64/0/36 (66/0/34)
10[DCM, Ar]			**IV**	$1:1:2x10^{-2}$	48	rt	100	**aa**, 10/81/8 (11/80/9)
11[THF, Ar]	**1b**		**I**	$1:1:10^{-2}$	48	100	100	**ba**, 87/13/0 (88/12/0)
12[Tol., Air]			**II**	$1:1:4x10^{-4}$	48	100	100	**ba**, 92/8/0 (92/8/0)
13[DCM, Ar]			**V**	$1:1:10^{-2}$	48	rt	0	**ba**, -
14[DCM, Ar]						40	0	**ba**, -
15[Tol., Ar, c]			**IX**	$1:1:1.1x10^{-2}$	48	100	47	**ba**, (97/2/1)
16[Tol., Ar, c]						rt	36	**ba**, 100/0/0 (100/0/0)
17[MeCN, Ar]			**IV**	$1:1:2x10^{-2}$	24	rt	100	**ba**, 0/100/0 (0/100/0)*
18[THF, Ar]	**1c**		**I**	$1:1:10^{-2}$	24	100	100	**ca**, 94/6/0 (94/6/0)
19[THF, Ar]	**1d**		**I**	$1:1:10^{-2}$	48	40	50	**da**, *complex mixture*
20[THF, Ar]						100	63	**da**, *complex mixture*
21[THF, Ar]	**1e**		**I**	$1:1:10^{-2}$	48	100	100	**ea**, 78/7/15
22[THF, Ar]						60	100	**ea**, 84/5/11
23[THF, Ar]	**1f**		**I**	$1:1:10^{-2}$	24	100	100	**fa**,95/5/0 (97/3/0)
24[DCM, Ar]			**V**	$1:1:10^{-2}$	24	rt	82	**fa**,94/6/0 (99/1/0)
25[THF, Air, d]			**X**	$1.5:1:2x10^{-2}$	24	50	67	**fa**, 73/27/0**

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m_{1a} = 0.0414g, m_{1b} = 0.0934g, m_{1d} = 0.04g, m_{1e} = 0.05g, m_{1f} = 0.055g, 2 ml of solvent; [a]$m_{1a}/V_{DCM.}$ = 0.116g/ml; [b]without solvent; [c]addition of 5mol% of NaI, $m_{1a}/V_{Tol.}$ = 0.038g/ml, NaI and silane was mixed for 2h at room temperature. Then the mixture was cooled to 0°C and alkyne was added; [d]m_{1f}/V_{THF} = 0.208g/ml; *product precipitated as a white solid during the process. **complex mixture of products observed on ^{29}Si NMR. Dvs= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; XPhos= 2-dicyclohexylphosphino-2′,4′,6′-tri*iso*propylbiphenyl. Conversions of reagents were determined by ^1H NMR spectroscopy and GC-MS. The selectivity was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

Table S2. Hydrosilylation of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyne (**2b**) with silanes **1a-f**.



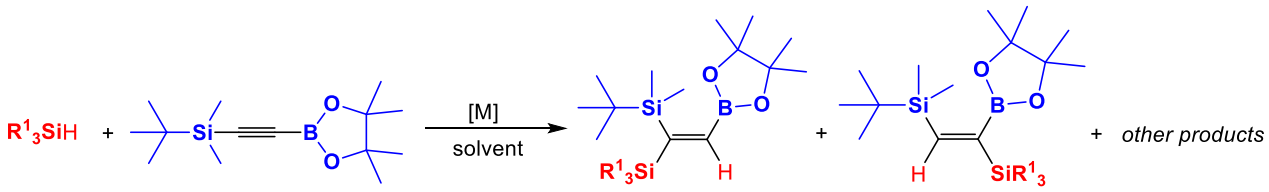
1a-f **2b** **3ab-fb** **4ab-fb** **5ab-fb**

SiR^1_3 = $SiEt_3$ (**1a**), $SiPh_3$ (**1b**), $SiMe(OSiMe_3)_2$ (**1c**), $SiMe_2(OEt)$ (**1d**), $SiMe_2Ph$ (**1e**), $SiMe_2Bn$ (**1f**); Bn= benzyl
[M] = $Pt_2(dvs)_3$ (**II**), $Pt(PPh_3)_4$ (**III**), $PtCl_2$ (**VI**), PtO_2 (**VII**)

Entry	R_3SiH 1	Alkyne 2	[M]	[1]:[2]:[M]	t [h]	Temp. [°C]	Conversion of 1 [%]	Selectivity of 3=4/5 [%] NMR (GC-MS)
1$^{Tol., Air}$	**1a**	**2b**	**II**	$1:1:10^{-4}$	24	rt	62	**ab**, 100/0 (99/1)
2$^{Tol., Air}$				$1:1:10^{-3}$		rt	94	**ab**, 100/0 (99/1)
3$^{Tol., Air}$				$1:1:10^{-2}$		rt	94	**ab**, 100/0 (99/1)
4$^{Tol., Air}$					48	rt	100	**ab**, 100/0 (99/1)
5$^{Tol., Air}$				$1:1:10^{-4}$	24	60	81	**ab**, (95/5)
6$^{Tol., Air}$					48	60	93	**ab**, (96/4)
7$^{Tol., Air}$			**III**	$1:1:10^{-2}$	24	rt	94	**ab**, 100/0 (100/0)
8$^{Tol., Air}$					48	rt	97	**ab**, 100/0 (100/0)
9$^{Tol., Air}$					120	rt	100	**ab**, 100/0 (100/0)
10$^{Tol., Air}$					24	60	94	**ab**, 95/5 (95/5)
11$^{Tol., Air}$					48	60	99	**ab**, 95/5 (94/6)
12$^{Tol., Air}$						100	98	**ab**, 93/7 (94/6)
13$^{Tol., Ar}$			**VI**	$1:1:10^{-2}$	24	rt	100	**ab**, (100/0)
14$^{Tol., Ar}$					48	60	100	**ab**, 95/5
15$^{Tol., Air}$	**1b**		**III**	$1:1:10^{-2}$	24	100	100	**bb**, 95/5
16$^{Tol., Air}$						120	100	**bb**, 100/0 (100/0)
17$^{Tol., Air}$	**1c**		**III**	$1:1:10^{-2}$	24	60	100	**cb**, 96/4 (96/4)
18$^{Tol., Ar}$			**VII**	$1:1:10^{-2}$	24	60	84	**cb**, 100/0
19$^{Tol., Ar}$					48	60	90	**cb**, 100/0
20$^{Tol., Air}$	**1d**		**II**	$1:1:10^{-2}$	48	50	24	**db**, *complex mixture*
21$^{Tol., Air}$						rt	12	**db**, *complex mixture*
22$^{Tol., Air}$			**III**	$1:1:10^{-2}$	48	60	33	**db**, *complex mixture*
23$^{Tol., Ar}$			**VI**	$1:1:10^{-2}$	48	60	8	**db**, *complex mixture*
24$^{Tol., Ar}$			**VII**	$1:1:10^{-2}$	48	60	36	**db**, *complex mixture*
25$^{Tol., Ar}$				$1:1.05:10^{-2}$		60	42	**db**, *complex mixture*
26$^{Tol., Air}$	**1e**		**II**	$1:1:10^{-2}$	48	rt	60	**eb**, 87/13
27$^{Tol., Air}$	**1f**		**III**	$1:1:10^{-2}$	24	100	100	**fb**, 100/0 (93/7)

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m_{1a} = 0.0414g, m_{1b} = 0.0934g, m_{1c} = 0.0802g, $m_{1d.}$ = 0.04g, $m_{1e.}$ = 0.05g/ml, m_{1f} = 0.055g,; 2 ml of toluene. dvs= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were determined by ^1H NMR spectroscopy and GC-MS. The selectivity was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

Table S3. Hydrosilylation of 2-((*tert*-butyldimethylsilanyl)ethynyl)-4,4,5,5-tetramethyl-(1,3,2)dioxaborolane (**2c**) with silanes **1a-f**.



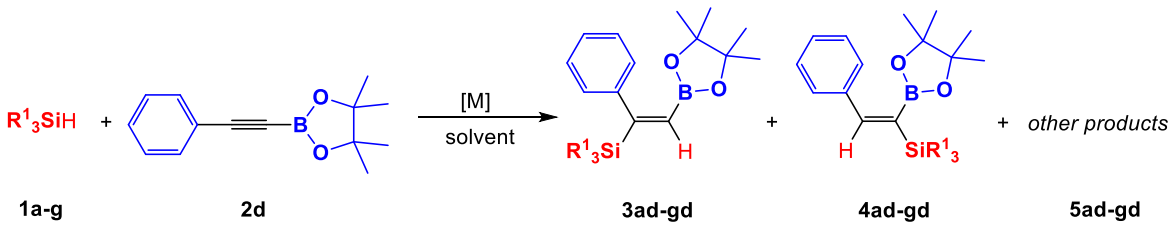
1a-f **2c** **3ac-fc** **4ac-fc** **5ac-fc**

SiR^1_3 = $SiEt_3$ (**1a**), $SiPh_3$ (**1b**), $SiMe(OSiMe_3)_2$ (**1c**), $SiMe_2Ph$ (**1e**), $SiMe_2Bn$ (**1f**); Bn= benzyl
[M] = $Pt_2(dvs)_3$ (**II**), $Pt(PPh_3)_4$ (**III**), $[CpRu(CH_3CN)_3][PF_6]$ (**IV**), $PtCl_2$ (**VI**)

Entry	R_3SiH 1	Alkyne 2	[M]	[1]:[2]:[M]	t [h]	Temp. [°C]	Conversion of 1 [%]	Selectivity of 3/4/5 [%] NMR (GC-MS)
1$^{Tol., Air}$	**1a**	**2c**	**II**	1:1:10^{-4}	168	rt	0	**ac**,-
2$^{Tol., Air}$					48	60	61	**ac**, (41/59/0)
3$^{Tol., Air}$			**III**	1:1:10^{-2}	24	60	100	**ac**, 0/100/0 (3/97/0)
4$^{Tol, Ar}$			**VI**	1:1:10^{-2}	48	60	93	**ac**, 0/100/0 (0/100/0)
5$^{Tol., Ar}$				1.05:1:10^{-2}	48	60	96	**ac**, 0/100/0 (0/100/0)
6$^{Tol., Ar}$					24	100	90	**ac**, 0/100/0 (0/100/0)
7$^{Tol., Air}$	**1b**		**II**	1:1:4x10^{-4}	92	60	0	**bc**, -
8$^{Tol., Air}$					24	100	100	**bc**, 0/100/0
9$^{Tol., Air}$			**III**	1.05:1:10^{-2}	24	60	20	**bc**, *complex mixture*
10$^{Tol., Air}$						100	44	**bc**, *complex mixture*
11$^{Tol., Air}$				1.1:1:10^{-2}	48	120	45	**bc**, *complex mixture*
12$^{Tol., Air}$				1:1:10^{-2}	24	120	82	**bc**, (8/92/0)
13$^{Tol., Air}$						100	52	**bc**, (8/92/0)
14$^{Tol., Air}$	**1c**		**II**	1:1:4x10^{-4}	48	60	0	**cc**, -
15$^{Tol., Air}$			**III**	1:1:10^{-2}	24	60	100	**cc**, 5/95/0
16$^{Tol., Ar}$			**IV**	1:2:10^{-1}	24	rt	0	**cc**, -
17$^{Tol., Ar}$				1:1:10^{-1}	24	100	0	**cc**, -
18$^{Tol., Air}$	**1d**		**III**	1:1:10^{-2}	24	60	100	**dc**, 0/100/0
19$^{Tol., Air}$	**1e**		**II**	1:1:4x10^{-4}	24	100	100	**ec**, 0/100/0
20$^{Tol., Ar}$			**IV**	1:1:10^{-1}	24	rt	93	**ec**, (10/15/75)
21$^{DCM, Ar}$						38	100	**ec**, (3/18/79)
22$^{Tol., Air}$	**1f**		**II**	1:1:4x10^{-4}	24	100	100	**fc**, 0/100/0
23$^{Tol., Ar}$			**III**	1:1:10^{-2}	24	100	100	**fc**, (3/97/0)
24$^{DCM, Ar}$			**IV**	1:1:10^{-1}	96	rt	87	**fc**, (9/45/46)
25$^{DCM, Ar}$						38	86	**fc**, (11/43/46)
26$^{1,4\text{-dioxane, Ar}}$				1:1:2x10^{-1}	24	rt	38	**fc**, *complex mixture*

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m_{1a} = 0.0414g, m_{1b} = 0.0934g, m_{1c} = 0.0802g, m_{1d} = 0.04g, m_{1e} = 0.05g, m_{1f} = 0.055g, 2ml of solvent. Dvs= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were determined by ^1H NMR spectroscopy and GC-MS. The selectivity was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

Table S4. Hydrosilylation of 2-phenyl-1-ethynylboronic acid pinacol ester (**2d**) with silanes **1a-g**.



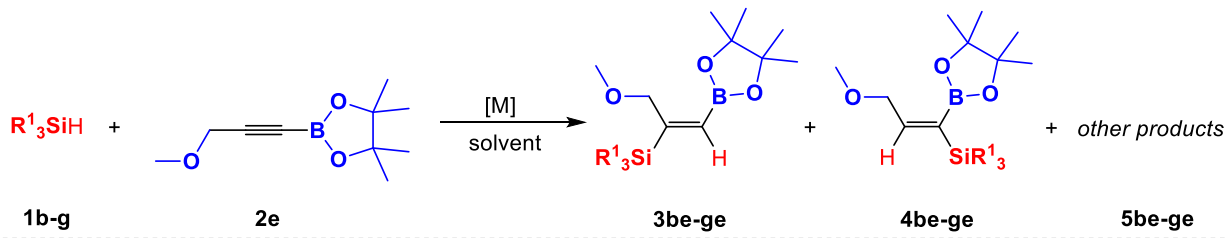
1a-g **2d** **3ad-gd** **4ad-gd** **5ad-gd**

SiR^1_3 = $SiEt_3$ (**1a**), $SiPh_3$ (**1b**), $SiMe(OSiMe_3)_2$ (**1c**), $SiMe_2Ph$ (**1e**), $SiMe_2Bn$ (**1f**); Bn= benzyl, $Si(OSiMe_3)_3$ (**1g**)
[M] = $Pt_2(dvs)_3$ (**II**), $Pt(PPh_3)_4$ (**III**), $[CpRu(CH_3CN)_3][PF_6]$ (**IV**)

Entry	R_3SiH 1	Alkyne 2	[M]	[1]:[2]:[M]	t [h]	Temp. [°C]	Conversion of 1 [%]	Selectivity of 3/4/5 [%] NMR (GC-MS)
1[Tol., Air]	**1a**	**2d**	**II**	1:1:4x10^{-4}	48	rt	100	**ad**, 18/82/0
2[Tol., Air]				1:1:10^{-3}		rt	100	**ad**, 18/82/0
3[Tol., Air]			**III**	1:1:10^{-2}	48	rt	100	**ad**, 35/65/0
4[Tol., Air]	**1b**		**II**	1:1:10^{-2}	48	120	100	**bd**, 0/100/0
5[Tol., Ar]			**IV**	1:1:10^{-2}	24	120	0	**bd**, -
6[1,4-dioxane, Ar]				1:1:2x10^{-1}		120	43	**bd**, 95/5/0
7[Tol., Air]	**1c**		**II**	1:1:4x10^{-4}	48	40	100	**cd**, *complex mixture*
8[Tol., Air]						60	100	**cd**, 9/88/3
9[Tol., Air]			**III**	1:1:10^{-2}	48	40	100	**cd**, *complex mixture*
10[Tol., Air]					24	60	100	**cd**, 8/83/9
11[Tol., Ar]			**IV**	1:1:2x10^{-1}	24	rt	100	**cd**, 84/7/9 (88/7/5)
12[Tol., Air]	**1e**		**II**	1:1:4x10^{-4}	48	40	100	**ed**, (8/85/7)
13[Tol., Air]					24	100	100	**ed**, 40/60/0
14[Tol., Air]			**III**	1:1:10^{-2}	24	60	23	**ed**, 34/66/0
15[Tol., Air]						100	100	**ed**, 30/70/0
16[DCM, Ar]			**IV**	1:1:10^{-1}	24	rt	100	**ed**, (83/17/0)
17[DCM, Ar]						38	100	**ed**, (84/16/0)
18[Tol., Air]	**1f**		**II**	1:1:4x10^{-4}	48	rt	100	**fd**, (3/94/3)
19[Tol., Air]					24	40	100	**fd**, (4/93/3)
20[Tol., Air]			**III**	1:1:10^{-2}	24	100	100	**fd**, (38/62/0)
21[Acetone, Air]			**IV**	1:1:10^{-1}	24	0	79	**fd**, 78/22/0 (78/22/0)
22[Acetone, Air]						50	100	**fd**, 79/21/0 (76/21/3)
23[Tol., Ar]						60	100	**fd**, (76/34/0)
24[THF, Ar]						60	100	**fd**, 82/18/0 (84/16/0)
25[1,4-dioxane, Ar]				1:1:2x10^{-1}		rt	100	**fd**, 89/0/11 (91/0/9)
26[1,4-dioxane, Ar]				1:1:10^{-1}		100	100	**fd**, (84/13/3)
27[1,4-dioxane, Ar]				1:1:10^{-2}		120	39	**fd**, (46/22/31)
28[Tol., Ar]				1:1:2x10^{-1}		rt	100	**fd**, 81/19/0
29[1,4-dioxane, Ar]						120	98	**fd**, 82/10/8 (91/9/0)
30[1,4-dioxane, Ar]				1:1:3x10^{-1}		120	100	**fd**, (87/2/12)
31[Tol., Ar]	**1g**		**IV**	1:1:2x10^{-1}	24	rt	100	**gd**, 91/9/0 (97/0/3)

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m_{1a} = 0.0414g, m_{1c} = 0.0802g, m_{1d} = 0.04g, m_{1e} = 0.05g/ml, m_{1f} = 0.055g, m_{1g} = 0.064g; 2ml of solvent; dvs= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were determined by ^1H NMR spectroscopy and GC-MS. The selectivity was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy.

Table S5. Hydrosilylation of 3-methoxy-1-propyn-1-ylboronic acid pinacol ester (**2e**) with silanes **1b-g**.



1b-g **2e** **3be-ge** **4be-ge** **5be-ge**

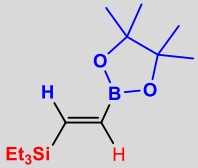
SiR^1_3 = $SiPh_3$ (**1b**), $SiMe(OSiMe_3)_2$ (**1c**), $SiMe_2Bn$ (**1f**); Bn= benzyl, $Si(OSiMe_3)_3$ (**1g**)
[M] = $Pt_2(dvs)_3$ (**II**), $Pt(PPh_3)_4$ (**III**), $[CpRu(CH_3CN)_3][PF_6]$ (**IV**)

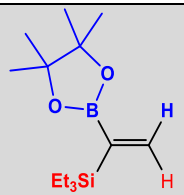
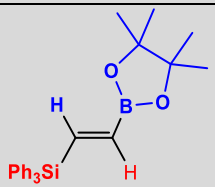
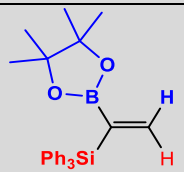
Entry	R_3SiH 1	Alkyne 2	[M]	[1]:[2]:[M]	t [h]	Temp. [°C]	Conversion of 1 [%]	Selectivity of 3/4/5 [%] NMR (GC-MS)
1[Tol., Air]	**1b**	**2e**	**II**	1:1:4x10^{-4}	24	100	100	**be**, (0/52/48)
2[Tol., Air]				1:1:10^{-2}		rt	100	**be**, (0/40/60)
3[Tol., Air]						60	100	**be**, (0/40/60)
4[Tol., Air]						100	100	**be**, (0/67/33)
5[Tol., Air]			**III**	1:1:10^{-2}	24	120	100	**be**, (14/86/0)
6[Tol., Air]	**1c**		**II**	1:1:10^{-2}	24	rt	100	**ce**, (0/55/45)
7[Tol., Air]				1:1:4x10^{-4}		60	100	**ce**, (0/40/60)
8[Tol., Air]				1:1:10^{-2}		60	100	**ce**, 17/51/32 (9/54/37)
9[Tol., Air]			**III**	1:1:10^{-2}	24	rt	0	**ce**, -
10[Tol., Air]			**III**	1:1:10^{-2}	24	60	100	**ce**, (31/79/0)
11[Tol., Ar]			**IV**	1:1:2x10^{-1}	24	rt	100	**ce**, 100/0/0 (96/2/2)
12[DCM, Ar, a]				1:1:10^{-2}		rt	100	**ce**, 71/29/0 (68/25/7)
13[Tol., Air]	**1f**		**II**	1:1:4x10^{-4}	48	rt	100	**fe**, 3/88/9 (7/85/8)
14[Tol., Air]				1:1:10^{-2}	24	rt	100	**fe**, (0/80/20)
15[Tol., Air]			**III**	1:1:10^{-2}	24	rt	100	**fe**, (31/69/0)
16[Tol., Ar]			**IV**	1:1:2x10^{-1}	24	rt	100	**fe**, (80/10/10)
17[DCM, Ar, b]				1.5:1:10^{-2}		rt	67	**fe**, (84/7/9*)
18[Tol., Ar]	**1g**		**IV**	1:1:2x10^{-1}	24	rt	100	**ge**, 100/0/0 (100/0/0)

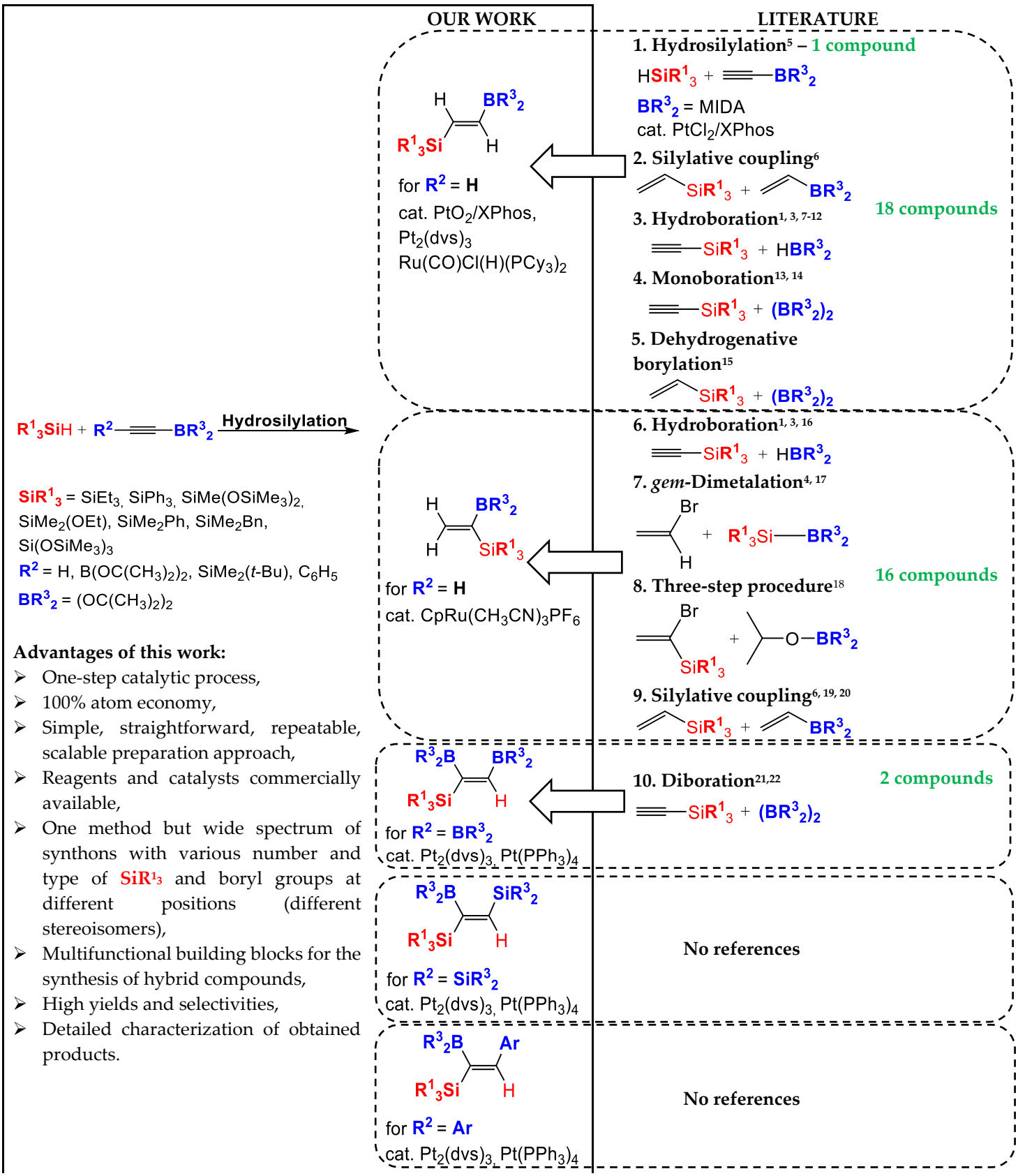
The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m_{1b} = 0.0934g, m_{1c} = 0.0802g, m_{1f} = 0.055g, m_{1g} = 0.064g, 2 ml of solvent; [a]$m_{1f}/V_{DCM.}$ = 0.029g/ml; [b]$m_{1f}/V_{DCM.}$ = 0.022g/ml; * side-products were observed on ^{29}Si NMR. Dvs - 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were complete in each experiment and determined by ^{1}H NMR spectroscopy and for processes with **1b-f** confirmed by GC-MS. The selectivity was determined by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy.

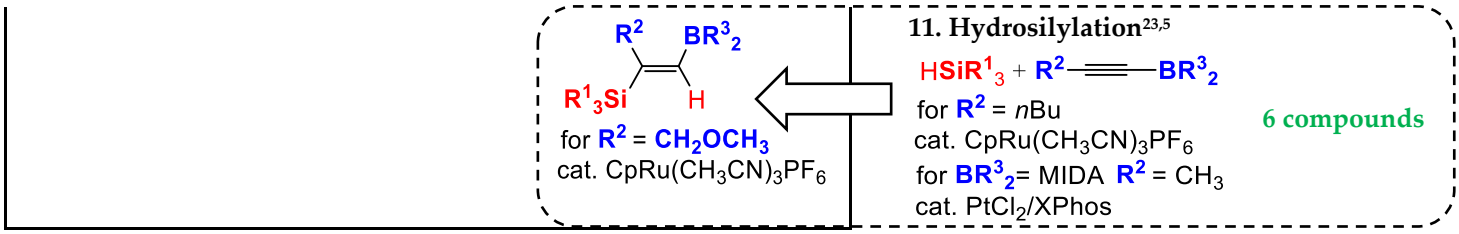
2. Literature screening

Table S6. Synthesis methods of borylsilylalkenes **3aa**, **3ba**, **4ba** and **5ba**, described in the literature.

Entry	Compound	Synthesis method	Catalyst	Reaction yield of product (Isolated yield) [%]	Reaction conditions	Characterization method
1	 **3aa**	Hydroboration of (triethylsilyl)acetylene with pinacolborane[1]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	94 (78)	60°C, 24h, solvent: PEG 10, Argon atmosphere, **20% excess of pinacolborane.**	^{1}H and ^{13}C NMR, MS
2		Hydroboration of (triethylsilyl)acetylene with pinacolborane[2]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	69-91 (82) for IL (([EMPyrr][OTf]) 70-91 (-) for IL ([EMPyrr][NTf_2]) 10 catalytic cycles	100°C, 15 min., solvent: IL/$scCO_2$, Argon atmosphere, **20% excess of pinacolborane.**	^{1}H NMR, MS
3		Hydroboration of (triethylsilyl)acetylene with pinacolborane [3]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	97 (99)	100°C, 3h, solvent: $scCO_2$, Argon atmosphere, **20% excess of pinacolborane.**	^{1}H, ^{13}C, ^{29}Si and ^{11}B NMR, MS, Elemental. Anal.
4				95 (-)	100°C, 3h, without solvent, Argon atmosphere, **20% excess of pinacolborane**	
5				60 (-)	100°C, 3h, solvent: toluene, Argon atmosphere, **20% excess of pinacolborane**	

6	 **4aa**	Hydroboration of (triethylsilyl)acetylene with pinacolborane[3]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	3 (-)	100°C, 3h, solvent: toluene. **Obtained as a side product.**	-
7		Hydroboration of (triethylsilyl)acetylene with pinacolborane[1]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	5 (-)	60°C, 24h, solvent: PEG 10. **Obtained as a side product.**	-
8		Hydroboration of (triethylsilyl)acetylene with pinacolborane[2]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	4 -7 (-)	100°C, 15min – 1.5h, solvent: [EMPyrr][OTf] or [EMPyrr][NTf_2]. **Obtained as a side product.**	-
9	 **3ba**	Hydroboration of (triphenylsilyl)acetylene with pinacolborane[3]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	3 (-)	100°C, 3h, solvent: toluene. **Obtained as a side product.**	IR, ^1H and ^{13}C NMR
10		Hydroboration of (triphenylsilyl)acetylene with pinacolborane[3]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	58 (52)	100°C, 3h, solvent: $scCO_2$; **20% excess of pinacolborane**	^1H, ^{13}C, ^{29}Si and ^{11}B NMR, MS
11				90 (-)	100°C, 3h, without solvent; **20% excess of pinacolborane**	
12				81 (78)	100°C, 3h, solvent: toluene; **20% excess of pinacolborane**	
13	 **4ba**	Gem-silylborylation of 1-bromo-1-lithioethene with (triphenylsilyl)(pinacolato)borane[4]	-	-	-110°C, 10 min., solvent: THF, Et_2O.	^1H and ^{13}C NMR, MS, HRMS
14		Hydroboration of (triphenylsilyl)acetylene with pinacolborane[3]	$Ru(CO)Cl(H)(PPh_3)_3$ (1mol%)	5 (-)	100°C, 3h, solvent: toluene. **Obtained as a side product.**	-


OUR WORK
LITERATURE
1. Hydrosilylation[5] – 1 compound
HSiR13 + BR32
BR32 = MIDA
cat. PtCl2/XPhos
2. Silylative coupling[6]
SiR13 + BR32
3. Hydroboration[1, 3, 7-12]
SiR13 + HBR32
4. Monoboration[13, 14]
SiR13 + (BR32)2
5. Dehydrogenative borylation[15]
SiR13 + (BR32)2
18 compounds
for R2 = H
cat. PtO2/XPhos, Pt2(dvs)3
Ru(CO)Cl(H)(PCy3)2
R13SiH + R2 BR32 Hydrosilylation
SiR13 = SiEt3, SiPh3, SiMe(OSiMe3)2, SiMe2(OEt), SiMe2Ph, SiMe2Bn, Si(OSiMe3)3
R2 = H, B(OC(CH3)2)2, SiMe2(t-Bu), C6H5
BR32 = (OC(CH3)2)2
6. Hydroboration[1, 3, 16]
SiR13 + HBR32
7. gem-Dimetalation[4, 17]
R13Si—BR32
8. Three-step procedure[18]
9. Silylative coupling[6, 19, 20]
SiR13 + BR32
16 compounds
for R2 = H
cat. CpRu(CH3CN)3PF6
10. Diboration[21,22]
SiR13 + (BR32)2
2 compounds
for R2 = BR32
cat. Pt2(dvs)3, Pt(PPh3)4
for R2 = SiR32
cat. Pt2(dvs)3, Pt(PPh3)4
No references
for R2 = Ar
cat. Pt2(dvs)3, Pt(PPh3)4
No references
Advantages of this work:
One-step catalytic process,
100% atom economy,
Simple, straightforward, repeatable, scalable preparation approach,
Reagents and catalysts commercially available,
One method but wide spectrum of synthons with various number and type of SiR13 and boryl groups at different positions (different stereoisomers),
Multifunctional building blocks for the synthesis of hybrid compounds,
High yields and selectivities,
Detailed characterization of obtained products.



Scheme S1. Methods for the synthesis of borylsilylalkenes described in our work.

3. General information

3.1 Materials

2-Ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (90%, Sigma-Aldrich), 1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyne (97%, Sigma-Aldrich), 2-((*tert*-Butyldimethylsilanyl)ethynyl)-4,4,5,5-tetramethyl-(1,3,2)dioxaborolane (97%, Sigma-Aldrich), 2-Phenyl-1-ethynylboronic acid pinacol ester (90%, Sigma-Aldrich), 3-methoxy-1-propyn-1-ylboronic acid pinacol ester (96%, Sigma-Aldrich), (3,3-Dimethyl-1-butynyl)boronic acid diisopropyl ester (97%, Sigma-Aldrich), Triethylsilane (97%, Sigma-Aldrich), Triphenylsilane (97%, Sigma-Aldrich), 1,1,1,3,5,5,5-Heptamethyltrisiloxane (97%, Sigma-Aldrich), Dimethylethoxysilane (94%, Acros Organics), Dimethylphenylsilane (>98%, Sigma-Aldrich), Benzyldimethylsilane (98%, Fluorochem), Tris(trimethylsiloxy)silane (≥98%, Sigma-Aldrich), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst, solution in xylene, Pt 2%, Sigma-Aldrich), platinum (IV) oxide (surface area ≥ 75m^2/g, Sigma-Aldrich), XPhos (97%, Sigma-Aldrich), Tetrakis(triphenylphosphine)platinum(0) (97%, Sigma-Aldrich), platinum(II) chloride (98%, Sigma- Aldrich), Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (98%, Acros Organics), Grubbs catalyst (97%, Sigma-Aldrich), The ruthenium catalyst [Ru(CO)Cl(H)(PCy_3)$_2$] was prepared according to literature procedures.[24] Tris(triphenylphosphine)rhodium(I) chloride (99.9%, Sigma-Aldrich), chloroform-d (99.96 atom% D, Sigma-Aldrich), benzene d^6 (99.6 atom% D, Sigma-Aldrich), dichloromethane (anhydrous, ≥99.8%, contains 40-150 ppm amylene as stabilizer, Sigma-Aldrich), 1,4-dioxane (anhydrous, 99.8%, Sigma-Aldrich), acetone (suitable for HPLC, ≥99.9%, Sigma-Aldrich), *n*-pentane (Lach-Ner). Toluene and tetrahydrofuran were dried using standard procedures, deoxygenated and stored over molecular sieves 4 Å under argon atmosphere (toluene). Argon (99,999%) was purchased from Linde. Silica gel (MN-Kieselgel 60, 0.04-0.063 mm (230-400 mesh ASTM; Sigma-Aldrich)) was used as received.

3.2 NMR analyses

^{1}H, ^{13}C, ^{29}Si and ^{11}B NMR spectra were recorded at 25°C on a Bruker Ultra Shield 300 MHz and Bruker Ascend 400 MHz NANOBAY spectrometers. $CDCl_3$ or C_6D_6 were used as a solvents and for internal deuterium lock. Chemical shifts are reported in ppm with reference to the residual portion solvent peak for ^{1}H and ^{13}C NMR, to TMS for ^{29}Si NMR and to BF_3-Et_2O for ^{11}B NMR. The multiplicities were reported as follow: singlet (s), doublet (d), triplet (t) and multiplet (m). To prove the regioselectivity of the process 2D Heteronuclear single quantum correlation (HSQC) and selective gradient NOE experiments for selected products were performed.

3.3 GC-MS analysis

GC-MS analyses were performed on a Bruker 450-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. Two temperature programs were used a) 80°C (3 min), 10°C/min, 250°C (30 min), b) 150°C (3 min), 10°C/min, 280°C (44.5 min).

3.4 Elemental analyses

Elemental analyses were carried out on a Vario EL III analyzer. The content of hydrogen and carbon was obtained as data in percentage.

3.5 Melting points

Melting points were determined using Buchi Switzerland Melting Point M-565 instrument.

3.6 Electrospray ionization mass spectrometry (ESI MS)

High resolution mass spectra (HRMS) were obtained using Impact HD mass spectrometer (Q-TOF type instrument equipped with electrospray ion source; Bruker Daltonics, Germany). The sample solutions (DCM:MeOH) were infused into the ESI source by a syringe pump (direct inlet) at the flow rate of 3 μL/min. The instrument was operated under the following optimized settings: end plate voltage 500 V;

capillary voltage 4.2 kV; nebulizer pressure 0.3 bar; dry gas (nitrogen) temperature 200°C; dry gas flow rate 4 L/min. The spectrometer was previously calibrated with the standard tune mixture.

3.7 FT-IR analysis

FT-IR spectra were measured on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) equipped with a built-in ATR accessory with ATR diamond unit. In all experiments, 16 scans at a resolution of 2 cm^{-1} were used to record the spectra.

3.8 X-ray crystallography

A colourless single crystals of **3ba**, **4ba, 3bb**, **3fb**, **6dc** suitable for X-ray structural analysis were obtained by slow evaporation of dichloromethane (**3ba**), hexane (**4ba**), hexane (**3bb**), hexane (**3fb**), and chloroform (**6dc**). The diffraction data were collected at 130 K with an Oxford Diffraction SuperNova diffractometer using Cu Kα radiation (λ = 1.54184 Å) equipped with mirror monochromator. The intensity data were collected and processed using CrysAlis PRO software.[25] The structures were solved by direct methods with the program SHELXT 2018/2[26] and refined by full-matrix least-squares method on F^2 with SHELXL 2018/3.[27] The carbon-bound hydrogen atoms were refined as riding on their carriers and their displacement parameters were set equal to 1.5Ueq(C) for the methyl groups and 1.2Ueq(C) for the remaining H atoms. Absolute structures of the compounds were confirmed using Flack parameter.[28] A summary of the crystallographic data is given in Table S7 and selected geometrical data are juxtaposed in Table S8. Molecular graphics were generated with Olex2[29] and Mercury 2021.1.0 software.[30] ORTEP representation of the molecular structures of the reported compounds are presented in Figures S117-121. Asymmetric unit of crystal of compound **3ba** consist six symmetrically independent molecules (Z'=6, Z=12) additionally four of them are disordered. Assuming the phenyl rings remain stationary, the tail of molecule ended with the Bpin may take an alternative orientation as shown in Figure S118. Refined occupancy factors for disordered fragment are 0.88 and 0.12. For lower occupied fragment the reasonable relative motion of atoms was imposed and the anisotropic displacement parameters for atom C1C' was restrained to behave more isotropically. Molecule of compound (**3bb**) is disordered in crystal structure - one of the Bpin group swings around the C1-B1 bond (as showed in the Figure 122) and refined occupancy factors for disordered fragment are 0.82 and 0.12. For lower occupied fragment reasonable relative motion of atoms was imposed (RIGU 0.002 0.002 restrains were used). In crystal of compound **6dc**, the molecule is located on special position (Z'=1/2, Z=4) with O3 atom situated on two-fold axis. X-ray measurement for the compound **3fb** was performed on a twinned crystal and the volume ratio of the domain in crystal is 0.72: 0.28. Assymetric unit consist two independent molecules and both of them are disordered and the Bpin group swings around the C1-B1 bond (as showed in the Figure 123). Refined occupancy factors for disordered fragment are 0.55 and 0.45. For disordered fragment reasonable relative motion of atoms was imposed (RIGU and ISOR restrains were used).

CCDC 2083476, 2107079, 2107080, 2184400 and 2193621 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3.9 Products purification

*Purification of **3aa, 4aa, 3ba, 4ba, 3ca, 3fa, 4ac, 4bc, 4cc, 4dc, 4fc, 4ad, 4bd, 3cd, 4ed, 4fd, 3gd, 4be, 3ce, 4fe, 3fe, 3ge**.*

The UV-absorbing products were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with UV detector (λ_1 = 255 nm, λ_2= 280 nm). Purification details: cartridge 10 g, flow rate: 8 mL/min, length: 10 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100%

by 4 CV, step 2: gradient 10%/CV by 4 CV, step 3: hexane 50% by 2 CV). The non-aromatic products were purified on silica using standard column chromatography using n-hexane/ethyl acetate (97/3–8/2) as eluents. Products were characterized by GC-MS or ESI MS, ^{1}H, ^{13}C, ^{11}B, ^{29}Si NMR, FT-IR analyses. For new compounds in solid state, melting points were estimated as well.

*Purification of **3ab**, **3bb**, **3cb**, **3fb**, **4ea**.*

The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in *n*-pentane and filtered through the syringe filter (0.2 μm). After evaporation of *n*-pentane, the product was heated (approx. 70-130 °C) and condensed at cold-finger trap under vacuum (<10^{-3} mbar). The products were dried for 6 hours under vacuum. Isolated products were characterized by ^{1}H, ^{13}C, ^{29}Si, ^{11}B NMR, GC-MS or ESI MS.

4. General procedures

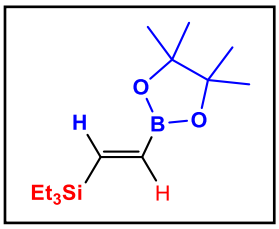
*4.1 Hydrosilylation of alkynes **2a–e** with silanes **1a-g** in the presence of Karstedt's catalyst and $Pt(PPh_3)_4$.*
To a solution of silane **1a-g** (40 – 93.4 mg, 0.298 - 0.358 mmol) and an appropriate borylalkyne (**2a**-**e**) (0.298 - 0.358 mmol) in 2 ml of toluene, Karstedt's catalyst or $Pt(PPh_3)_4$ was added, depending on the experiment in the amount of $4x10^{-4}$–10^{-2} mmol of Pt. Subsequently, the reaction mixture was heated to 60 - 120°C or kept at room temperature and stirred for 24 or 48h. Since the THF boiling point is 65-57°C, the reaction in this solvent at 120°C was performed in a Schlenk flask with a Rotaflo® stopcock. Afterwards, crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyzes and purified according to the procedure in 3.7 subsection.

*4.2 Hydrosilylation of alkyne **2a** with silanes **1a-f** in the presence of PtO_2/XPhos system.*
All reactions were carried out under an argon atmosphere. To a Schlenk flask with a Rotaflo® stopcock equipped with a magnetic stirrer PtO_2 (1mol%) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (2 mol%) (XPhos) were added. The catalyst and XPhos were dried under vacuum for 1 hour. Then the flask was flushed quickly with argon and 1ml of anhydrous and degassed THF was added. The mixture was stirred at 60°C for 30 minutes until the homogeneous system was obtained. After this time 2-ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2a** (0.356 - 0.358 mmol), an appropriate silane (41.4 – 93.4 mg, 0.356 - 0.358 mmol) and 1mL of THF were added. Reactions were carried out at 60°C or 100°C and stirred for 24 or 48h, depending on the experiment. Afterwards, crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyzes and purified according to the procedure in 3.7 subsection.

*4.3 Hydrosilylation of alkynes **2a, 2b, 2c, 2d** and **2e** with silane **1a-g** in the presence of $[CpRu(CH_3CN)_3][PF_6]$.*
All reactions were carried out under an argon atmosphere. To a Schlenk flask with a Rotaflo® stopcock equipped with a magnetic stirrer $[CpRu(CH_3CN)_3][PF_6]$ and 2mL of toluene/THF/DCM/1,4-dioxane, CH_3CN or acetone were added. Than a silane **1a-g** (40 – 93.4 mg, 0.298 - 0.358 mmol) and an appropriate borylalkyne (**2a**-**e**) (0.298 - 0.358 mmol) were added. Subsequently, the reaction mixture was heated to 60 - 120°C or kept at room temperature and stirred for 24 or 48h. Since the THF boiling point is 65-57°C, the reaction in this solvent at 120°C was performed in a Schlenk flask with a Rotaflo® stopcock. Afterwards, crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyzes and purified according to the procedure in 3.7 subsection.

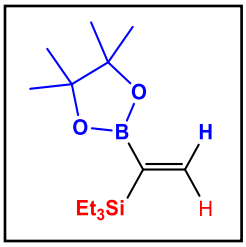
5. Products characterization

(*E*)-Triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3aa)



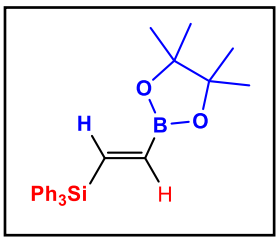
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.58 (q, 6H, $J_{(H,H)}$= 7.45 Hz), 0.93 (t, 9H, $J_{(H,H)}$= 7.88 Hz), 1.28 (s, 12H), 6.26 (d, 1H, $J_{(H,H)}$= 22.04 Hz), 7.06 (d, 1H, $J_{(H,H)}$= 21.98 Hz). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 3.13, 7.45, 24.96, 83.47, 154.83. Signal from carbon atom BC= is not observed.**^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -0.62. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 253.1 (M^+ - 15.18, 2.7), 239.0 (32.7), 210.9 (41.2), 157.0 (15.2), 154.9 (15.7), 110.9 (10.1), 85.0 (20.1), 84.1 (18.1), 83.0 (100.0), 58.9 (18.5), 55.0 (15.5). **FT-IR** (cm^{-1}): 2954, 2911, 2875, 1599, 1493, 1451, 1371, 1354, 1295, 1245, 1206, 1142, 1108, 1071, 1057, 856, 831, 792, 760, 698. **Elem. Anal.** calcd for $C_{14}H_{29}BO_2Si$: C, 62.68; H, 10.90; found C, 62.78; H, 10.95. Isolated yield = 93%, colorless oil.

Triethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4aa)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.63 (q, 6H, $J_{(H,H)}$= 7.88 Hz), 0.91 (t, 9H, $J_{(H,H)}$= 7.82 Hz), 1.24 (s, 12H), 6.22 (d, 1H, $J_{(H,H)}$= 5.34 Hz), 6.67 (d, 1H, $J_{(H,H)}$= 5.63 Hz). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 3.26, 7.55, 24.89, 83.04, 144.91. Signal from carbon atom BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): 2.74. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 30.92. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 253.1 (M^+ - 15.18, 0.7), 239.0 (10.6), 156.9 (22.9), 154.9 (7.6), 85.0 (9.1), 84.1 (9.1), 83.0 (100.0), 58.9 (9.1), 55.0 (24.2). **Elem. Anal.** calcd for $C_{14}H_{29}BO_2Si$: C, 62.68; H, 10.90; found C, 62.83; H, 10.97. Isolated yield = 57%, colorless oil.

(*E*)-Triphenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3ba)

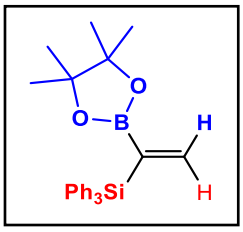


^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 1.29 (s, 12H), 6.39 (d, 1H, $J_{(H,H)}$= 21.64 Hz), 7.59 (d, 1H, $J_{(H,H)}$= 21.62 Hz), 7.33-7.54 (m, 16H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 24.98, 83.67, 127.99, 129.70, 133.87, 136.21, 150.68. Signal from carbon atom BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -17.53. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 29.46. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 397.1 (M^+ - 15.3, 0.9), 355.0 (19.5), 259.0 (13.4), 225.0 (10.3), 206.9 (10.9), 180.9 (17.3), 104.8 (11.7), 83.9 (100.0), 68.9 (30.6). **FT-IR** (cm^{-1}): 3067, 1588, 1484, 1427, 1368, 1324, 1266, 1141, 1111, 1018, 997, 968, 892, 847, 763, 689, 615, 511, 480, 454.

Elem. Anal. calcd for $C_{26}H_{29}BO_2Si$: C, 75.72; H, 7.09; found C, 76.04; H, 7.23. **mp** = 138.5 °C. Isolated yield = 81%, white solid.

X-ray determined for the first time, data presented on page 86.

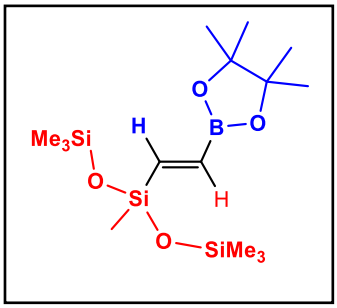
Triphenyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ba)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 1.14 (s, 12H), 6.29 (d, 1H, $J_{(H,H)}$= 5.38 Hz), 6.96 (d, 1H, $J_{(H,H)}$= 5.39 Hz), 7.33-7.60 (m, 15H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 24.72, 83.48, 127.66, 129.30, 134.89, 136.52, 149.99. Signal from carbon atom BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -13.57. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 31.62. **FT-IR** (cm^{-1}): 3067, 3047, 2979, 1588, 1571, 1482, 1380, 1371, 1360, 1356, 1323, 1301, 1217, 1149, 1129, 1108, 992, 970, 850, 735, 698, 625, 547, 516, 490, 468, 433. **Elem. Anal.** calcd for $C_{26}H_{29}BO_2Si$: C, 75.72; H, 7.09; found C, 75.98; H, 7.16. **mp** = 145.0 °C. Isolated yield = 72%, white solid.

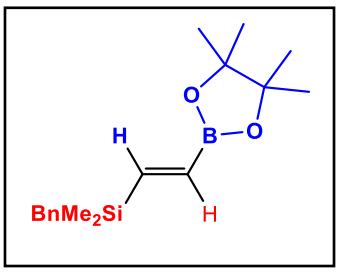
X-ray determined for the first time, data presented on page 86.

(*E*)-1,1,1,3,5,5,5-Heptamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trisiloxane (3ca/4ca = 94/6)



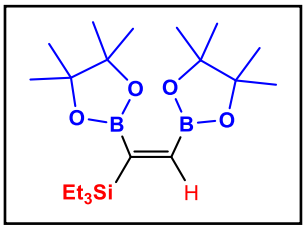
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.08 (s, 21H), 1.27 (s, 12H), 6.28 (d, 1H, $J_{(H,H)}$= 21.76 Hz), 6.36 (d, 1H, $J_{(H,H)}$= 5.92 Hz, **4ca**), 6.61 (d, 1H, $J_{(H,H)}$= 6.13 Hz, **4ca**), 6.89 (d, 1H, $J_{(H,H)}$= 21.87 Hz). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 1.99, 24.72, 24.92, 24.97, 83.51, 154.11. Signal from carbon atom BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -36.02, 8.29. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 29.54. Traces of product **4ca** are visible on spectras. **ESI MS** (m/z) ([M+Na]): 397.2. **FT-IR** (cm^{-1}): 2979, 2958, 1598, 1371, 1328, 1282, 1252, 1146, 1040, 970, 836, 800, 780, 753, 615. **Elem. Anal.** calcd for $C_{15}H_{35}BO_4Si_3$: C, 48.11; H, 9.42; found C, 48.15; H, 9.43. Isolated yield = 91%, colorless oil.

(*E*)-Benzyldimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3fa/4fa = 95/5)



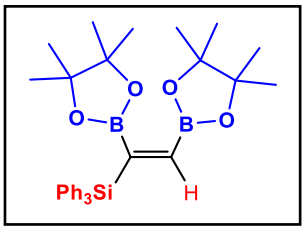
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.05 (s, 6H), 1.29 (s, 12H), 2.16 (s, 2H), 6.28 (d, 1H, $J_{(H,H)}$= 21.87 Hz), 6.99-7.22 (m, 6H, multiplet and dublet overlapped). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -3.82, 24.92, 25.43, 83.53, 124.15, 128.26, 128.36, 139.83, 155.88. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -6.28. Traces of product **4fa** are visible on spectras. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 302.3 (M^+- 15.4, 4.1), 210.9 (68.6), 209.9 (17.7), 126.8 (18.3), 110.8 (17.4), 84.9 (29.4), 82.9 (100.0), 58.9 (18.6), 55.0 (15.6). **Elem. Anal.** calcd for $C_{17}H_{27}BO_2Si$: C, 67.55; H, 9.00; found C, 67.72; H, 9.02. Isolated yield = 86%, colorless oil.

(*E*)-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)triethylsilane (3ab)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.62 (q, 6H, $J_{(H,H)}$= 7.79 Hz), 0.92 (t, 9H, $J_{(H,H)}$= 7.88 Hz), 1.26 (s, 12H), 1.32 (s, 12H), 6.57 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 3.32, 7.52, 24.67, 25.03, 25.36, 83.52, 83.63. Signals from carbon atoms BC= are not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): 3.16. **FT-IR** (cm^{-1}): 2977, 2953, 2911, 2975, 1578, 1445, 1369, 1329, 1298, 1269, 1232, 1139, 1110, 1006, 968, 856, 789, 734, 671, 578. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 368.3 (M^+ - 25.94, 0.3), 365.1 (32.8), 364.0 (14.0), 253.1 (19.3), 182.9 (10.2), 55.0 (22.7), 101.0 (12.0), 84.1 (20.6), 83.0 (100.0), 69.0 (14.4). **Elem. Anal.** calcd for $C_{20}H_{40}B_2O_4Si$: C, 60.93; H, 10.23; found C, 61.17; H, 10,27. Isolated yield = 90%, pale yellow oil. The traces of alkyne **2b** are visible on spectras.

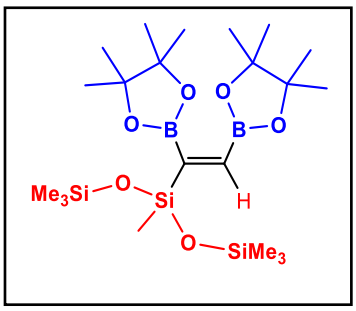
(*E*)-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)triphenylsilane (3bb)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.96 (s, 12H), 1.19 (s, 12H), 6.65 (s, 1H), 7.21 – 7.53 (m, 15H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 25.01, 25.04, 83.69, 83.82, 127.67, 129.35, 134.43, 136.80. Signals from carbon atoms BC= are not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -14.97. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 22.34, 29.11. **FT-IR** (cm^{-1}): 3067, 3049, 2978, 2930, 1568, 1428, 1370, 1305, 1268, 1232, 1188, 1137, 1108, 1028, 969, 909, 846, 831, 786, 732, 698, 673, 646, 572, 498. **ESI MS**- (m/z) ([M+Na]): 561.3. **Elem. Anal.** calcd for $C_{32}H_{40}B_2O_4Si$: C, 71.39; H, 7.49; found C, 71.50; H, 7.50. **mp** = 132.9 °C. Isolated yield = 98%, white solid.

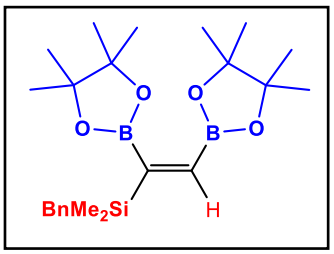
X-ray determined for the first time, data presented on page 87.

(*E*)-3-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (3cb/4cb = 96/4)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.09 (s, 21H), 1.26 (s, 12H), 1.30 (s, 12H), 6.67 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 0.14, 2.08, 25.01, 25.20, 83.44, 83.64. Signals from carbon atoms BC= are not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -35.11, 7.83. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 28.69. Traces of product **4cb** are visible on spectras. **FT-IR** (cm^{-1}): 2978, 2958, 1585, 1370, 1331, 1302, 1250, 1232, 1140, 1039, 836, 801, 785, 753, 688, 578, 542. **ESI MS**- (m/z) ([M+Na]): 523.3. **Elem. Anal.** calcd for $C_{21}H_{46}B_2O_6Si_3$: C, 50.40; H, 9.26; found C, 50.51; H, 9.27. Isolated yield = 90%, colorless oil. MALDI TOF MS analysis from this sample was unsuccessful.

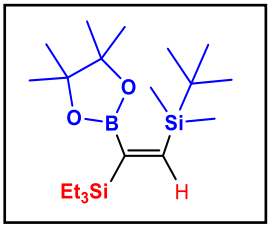
(*E*)-Benzyl(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (3fb)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.03 (s, 6H), 1.28 (s, 12H), 1.35 (s, 12H), 2.20 (s, 2H), 6.62 (s, 1H), 6.99 – 7.21 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -3.65, 25.04, 25.37, 25.56, 83.78, 83.79, 124.02, 128.21, 128.48, 140.26. Signals from carbon atoms BC= are not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -2.46. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 28.31. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 370.4 (M^+ - 57.86, 1.2), 337.4 (8.9), 237.3 (8.1), 83.2 (100.0), 55.1 (23.9). **FT-IR** (cm^{-1}): 2978, 1597, 1492, 1449, 1368, 1334, 1302, 1270, 1233, 1202, 1136, 1054, 970, 848, 814, 763, 700, 671, 579, 482. **Elem. Anal.** calcd for $C_{23}H_{38}B_2O_4Si$: C, 64.51; H, 8.94; found C, 64.68; H, 8.97. **mp** = 95.1 °C. Isolated yield = 91%, white solid.

X-ray determined for the first time, data presented on page 87.

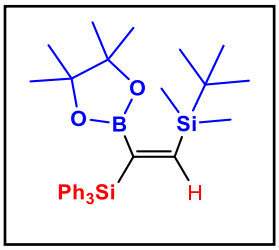
(*E*)-*Tert*-butyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(triethylsilyl)vinyl)silane (4ac)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.10 (s, 6H), 0.62 (q, 6H, $J_{(H,H)}$= 7.34 Hz), 0.89 – 0.94 (m, 18H), 1.28 (s, 12H), 7.07 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -4.84, 3.53, 7.63, 16.94, 25.64, 26.69, 83.24, 160.01.

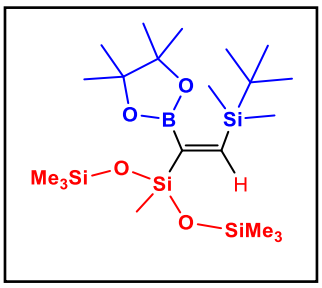
Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -2.40, 3.58. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 31.39. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 369.3 (M^+ - 13.24, 0.2), 326.2 (27.0), 325.1 (100.0), 324.0 (22.7), 243.0 (41.2), 184.9 (45.2), 183.8 (11.0), 86.9 (11.1), 84.1 (10.1), 83.0 (70.9), 72.9 (29.2), 68.9 (10.5), 58.9 (17.2), 55.0 (18.7). **FT-IR** (cm^{-1}): 2978, 2951, 2875, 2856, 1540, 1462, 1415, 1371, 1295, 1245, 1142, 1110, 1005, 972, 855, 836, 823, 808, 792, 736, 717. **Elem. Anal.** calcd for $C_{20}H_{43}BO_2Si_2$: C, 62.80; H, 11.33; found C, 63.04; H, 11.37. Isolated yield = 89%, pale yellow oil.

(*E*)-*Tert*-butyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(triphenylsilyl)vinyl)silane (4bc)



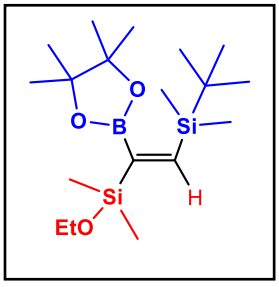
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.00 (s, 6H), 0.69 (s, 9H), 0.87 (s, 12H), 7.10-7.48 (m, 16H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -4.91, 16.94, 25.30, 26.59, 83.47, 127.59, 129.24, 135.30, 136.77, 167.08. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -14.53, -1.41. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 511.4 (M^+ - 15.27, 0.9), 471.4 (15.9), 470.4 (40.1), 469.3 (100.0), 309.2 (40.9), 291.2 (25.0), 259.2 (50.2), 197.2 (26.6), 181.2 (23.2), 135.1 (45.9), 105.1 (32.6), 83.2 (93.1), 84.2 (49.9), 73.2 (64.2), 69.3 (56.4), 68.3 (21.3). **FT-IR** (cm^{-1}): 3049, 2852, 1528, 1467, 1428, 1349, 1300, 1244, 1139, 1107, 972, 853, 823, 738, 504. **Elem. Anal.** calcd for $C_{32}H_{43}BO_2Si_2$: C, 72.98; H, 8.23; found C, 72.78; H, 8.21. **mp** = 87.2 °C. Isolated yield = 93%, white solid.

(*E*)-3-(2-(*Tert*-butyldimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (4cc)



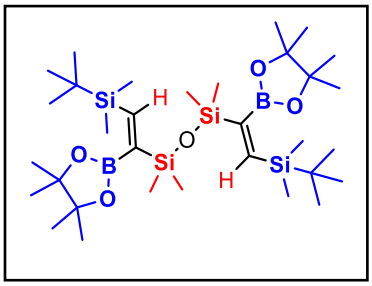
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.09, 0.10 (s, 27H), 0.91 (s, 9H), 1.27 (s, 12H), 7.33 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -4.95, 0.27, 2.09, 16.92, 25.39, 26.65, 83.21, 161.67. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -35.46, -2.10, 7.40. **Elem. Anal.** calcd for $C_{21}H_{49}BO_4Si_4$: C, 51.61; H, 10.11; found C, 51.72; H, 10.13. Isolated yield = 87%, colorless oil.

(*E*)-*Tert*-butyl(2-(ethoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (4dc)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.10 (s, 6H), 0.20 (s, 6H), 0.89 (s, 9H), 1.17 (t, 3H, $J_{(H,H)}$= 6.98 Hz), 1.29 (s, 12H), 3.64 (q, 2H, $J_{(H,H)}$= 6.99 Hz), 7.23 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -4.97, -1.42, 16.87, 18.58, 25.48, 26.67, 58.60, 83.43, 160.59. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -1.62, 6.67. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 313.1 (M^+- 57.5, 24.2), 231.0 (100.0), 214.1 (19.8), 212.0 (24.5), 185.0 (46.3), 183.9 (12.0), 142.9 (16.5), 84.0 (12.3), 83.0 (30.0), 74.9 (29.7), 73.0 (48.6), 69.0 (20.4), 59.0 (16.3), 55.0 (21.0). **FT-IR** (cm^{-1}): 2978, 2953, 2927, 2856, 1541, 1438, 1371, 1297, 1244, 1142, 1054, 975, 857, 821, 785, 677. **Elem. Anal.** calcd for $C_{18}H_{39}BO_3Si_2$: C, 58.36; H, 10.61; found C, 58.34; H, 10.61. Isolated yield = 91%, colorless oil.

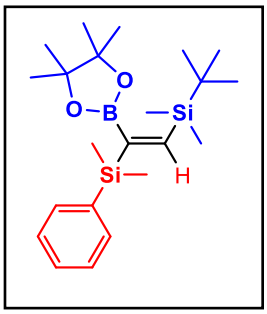
1,3-Bis((*E*)-2-(tert-butyldimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1,3,3-tetramethyldisiloxane (6dc)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.09 (s, 12H), 0.16 (s, 12H), 0.90 (s, 18H), 1.27 (s, 24H), 7.25 (s, 2H). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -4.86, 1.34, 16.92, 25.47, 26.72, 83.24, 159.63. Signals from carbon atoms BC= are not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -3.24, -2.14. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 31.86. **FT-IR** (cm^{-1}): 2983, 2953, 2933, 2922, 2849, 1536, 1470, 1381, 1369, 1352, 11330, 1296, 1242, 1145, 1086, 978, 933, 872, 858, 824, 800, 780, 760, 723, 659. **Elem. Anal.** calcd for $C_{32}H_{68}B_2O_5Si_4$: C, 57.64; H, 10.28; found C, 57.62; H, 10.28. Isolated yield = 85%, colorless oil.

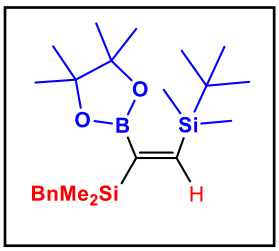
X-ray determined for the first time, data presented on page 88.

(*E*)-*Tert*-butyl(2-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (4ec)



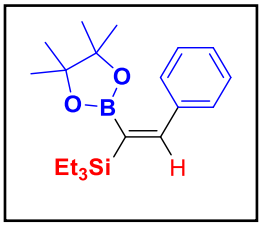
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.03 (s, 6H), 0.32 (s, 6H), 0.80 (s, 9H), 1.09 (s, 12H), 7.06 (s, 1H), 7.24-7.47 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -4.95, -2.10, 16.94, 25.44, 26.66, 83.36, 127.59, 128.81, 134.52, 139.11, 160.99. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -7.10, -1.93. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 31.38. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 345.0 (M^+- 57.3, 48.7), 185.0 (100.0), 186.0 (17.6), 183.9 (25.9), 142.9 (20.3), 134.9 (47.5), 104.9 (16.3), 82.9 (52.3), 72.9 (35.3), 55.0 (17.5). **FT-IR** (cm^{-1}): 2978, 2952, 2926, 2882, 2855, 1541, 1470, 1346, 1297, 1242, 1141, 1112, 974, 812, 772, 730, 698. **Elem. Anal.** calcd for $C_{22}H_{39}BO_2Si_2$: C, 65.64; H, 9.77; found C, 65.97; H, 9.91. Isolated yield = 89%, colorless oil.

(*E*)-Benzyl(2-(tert-butyldimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (4fc)



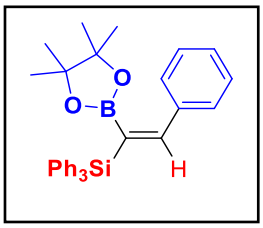
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.05 (s, 6H), 0.10 (s, 6H), 0.86 (s, 9H), 1.32 (s, 12H), 2.20 (s, 2H), 6.97-7.17 (m, 6H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 Hz, δ, ppm): -4.89, -3.25, 16.94, 25.62, 26.18, 26.64, 83.45, 123.83, 128.07, 128.51, 140.59, 160.90. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -2.30, -2.29. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 31.55. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 359.5 (M^+- 56.8, 31.9), 260.4 (23.7), 259.3 (100.0), 258.3 (23.6), 243.3 (25.4), 149.2 (17.9), 83.2 (82.0), 73.2 (81.0), 69.3 (20.6), 55.2 (31.5). **FT-IR** (cm^{-1}): 2951, 2856, 1597, 1469, 1335, 1298, 1239, 1155, 1057, 972, 854, 763, 698, 645, 477. **Elem. Anal.** calcd for $C_{23}H_{41}BO_2Si_2$: C, 66.32; H, 9.92; found C, 66.45; H, 9.95. **mp** = 62.1 °C. Isolated yield = 91%, white solid.

(*E*)-Triethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ad)



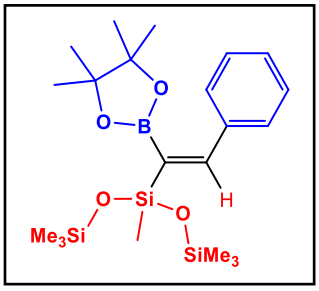
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.77 (q, 6H, $J_{(H,H)}$= 7.91 Hz), 1.04 (t, 9H, $J_{(H,H)}$= 7.87 Hz), 1.32 (s, 12H), 7.25 – 7.47 (m, 6H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 3.76, 7.56, 25.26, 83.49, 127.77, 127.95, 128.10, 140.75, 151.30. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): 4.00. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 32.53. **FT-IR** (cm^{-1}): 2978, 2952, 2910, 2874, 1591, 1568, 1493, 1459, 1371, 1292, 1252, 1210, 1140, 1109, 1005, 976, 940, 856, 797, 747, 695. **Elem. Anal.** calcd for $C_{20}H_{33}BO_2Si$: C, 69.75; H, 9.66; found C, 69.86; H, 9,68. Isolated yield = 76%, colorless oil.

(*E*)-Triphenyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4bd)



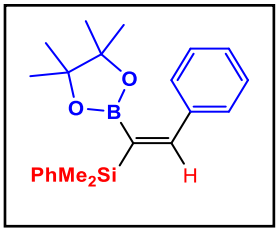
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.96 (s, 12H), 7.26-7.70 (m, 21H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 24.89, 83.69, 127.76, 128.17, 128.27, 128.35, 129.47, 134.85, 136.82, 140.25, 156.79. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -14.24. **FT-IR** (cm^{-1}): 3068, 2984, 2926, 1591, 1568, 1481, 1427, 1387, 1371, 1343, 1304, 1251, 1206, 1137, 1107, 978, 947, 854, 800, 740, 697, 592, 574, 493. **Elem. Anal.** calcd for $C_{32}H_{33}BO_2Si$: C, 78.68; H, 6.81; found C, 78.92; H, 6.83. Isolated yield = 85%, white solid.

(*E*)-1,1,1,3,5,5,5-Heptamethyl-3-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trisiloxane (4cd)



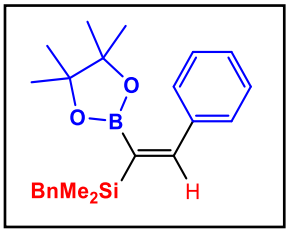
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.01 (s, 18H), 0.14 (s, 3H), 1.09 (s, 12H), 6.20 (s, 1H), 7.12-7.23 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -0.43, 1.86, 24.73, 83.35, 126.17, 127.52, 127.87, 143.92, 164.19. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -38.13, 8.16. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 450.6 (M^+, 3.5), 335.0 (12.2), 293.0 (7.7), 223.0 (7.4), 222.1 (12.6), 221.0 (57.2), 206.9 (19.8), 84.0 (100.0), 82.9 (7.9), 73.0 (53.4), 69.0 (10.9). **FT-IR** (cm^{-1}): 2958, 1725, 1588, 1499, 1371, 1346, 1252, 1144, 1046, 838, 783, 754, 698, 540. **Elem. Anal.** calcd for $C_{21}H_{39}BO_4Si_3$: C, 55.98; H, 8.72; found C, 55.78; H, 8.69. Isolated yield = 79%, colorless oil.

(*E*)-Dimethyl(phenyl)(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ed)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.38 (s, 6H), 1.05 (s, 12H), 7.12-7.52 (m, 11H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -1.91, 25.06, 83.59, 127.76, 128.05, 128.08, 128.12, 129.08, 134.58, 138.53, 140.34, 152.25. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -6.29. **FT-IR** (cm^{-1}): 3068, 2978, 1624, 1592, 1569, 1494, 1449, 1427, 1378, 1371, 1351, 1246, 1210, 1140, 1111, 998, 974, 944, 856, 820, 790, 771, 748, 695, 643, 577, 469. **Elem. Anal.** calcd for $C_{22}H_{29}BO_2Si$: C, 72.52; H, 8.02; found C, 72.65; H, 8.04. Isolated yield = 88%, colorless oil.

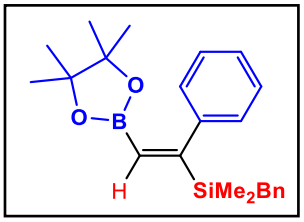
(*E*)-Benzyldimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4fd)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.21 (s, 6H), 1.36 (s, 12H), 2.36 (s, 2H), 7.11-7.47 (m, 11H, overlapped singlet and multiplet). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -3.07, 25.22, 26.22, 83.63, 124.01, 127.95, 127.97, 128.10, 128.15, 128.54, 140.15, 140.45, 151.51. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -1.74. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 32.45. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 363.1 (M^+, -15.3, 1.5), 288.2 (17.3), 287.0 (81.6), 285.9 (18.7), 205.0 (77.7), 203.8 (19.1), 188.9 (45.8), 186.9 (39.1), 158.9 (26.5), 144.9 (36.9), 134.9 (42.8), 120.9 (35.4), 84.1 (18.3), 83.0 (100.0), 68.9 (15.3), 55.0 (51.7). **FT-IR** (cm^{-1}): 2960, 2865, 1592, 1570, 1493, 1451, 1371, 1294, 1251, 1206, 1140, 1086, 945, 908, 827,

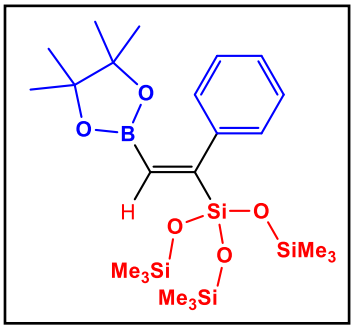
791, 733, 697, 603, 558. **Elem. Anal.** calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26; found C, 73.36; H, 8.28. Isolated yield = 83%, yellow oil.

(*E*)-Benzyldimethyl(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3fd/5fd = 89/11)



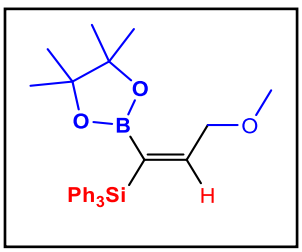
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.01 (s, 6H), 1.04 (s, 12H), 2.12 (s, 2H), 6.16 (s, 1H), 6.19-7.23 (m, 10H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -3.48, 24.67, 24.99, 83.35, 124.14, 126.05, 127.28, 127.73, 128.23, 128.43, 139.81, 144.90, 166.16. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -3.68. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 363.1 (M^+, -15.3, 1.5), 288.2 (17.3), 287.0 (81.6), 285.9 (18.7), 205.0 (77.7), 203.8 (19.1), 188.9 (45.8), 186.9 (39.1), 158.9 (26.5), 144.9 (36.9), 134.9 (42.8), 120.9 (35.4), 84.1 (18.3), 83.0 (100.0), 68.9 (15.3), 55.0 (51.7). **FT-IR** (cm^{-1}): 3059, 3024, 2978, 1623, 1599, 1570, 1493, 1450, 1378, 1352, 1294, 1246, 1140, 1108, 1056, 1001, 975, 945, 903, 833, 749, 696, 623, 555, 474. **Elem. Anal.** calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26; found C, 72.81; H, 8.24. Isolated yield = 86%, traces of product **5fd** are visible on spectras, colorless oil.

(*E*)-1,1,1,5,5,5-Hexamethyl-3-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-3-((trimethylsilyl)oxy)trisiloxane (3gd)



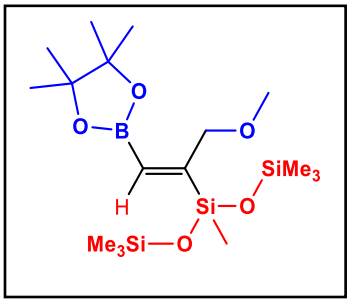
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.03 (s, 27H), 1.10 (s, 12H), 6.27 (s, 1H), 7.17-7.23 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 1.79, 24.72, 83.30, 126.27, 127.45, 128.13, 143.84, 160.38. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -82.67, 8.49. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 524.1 (M^+, 9.6), 410.2 (11.4), 409.0 (29.0), 367.0 (10.5), 282.1 (13.9), 281.0 (49.9), 209.0 (12.5), 208.1 (20.2), 206.9 (100.0), 84.0 (42.5), 83.0 (23.4), 72.9 (95.3), 69.0 (16.7). **FT-IR** (cm^{-1}): 2959, 1590, 1443, 1371, 1348, 1251, 1051, 968, 837, 754, 734, 698, 602, 545. **Elem. Anal.** calcd for $C_{23}H_{45}BO_5Si_4$: C, 52.64; H, 8.64; found C, 52.60; H, 8.63. Isolated yield = 91%, colorless oil.

(*E*)-(3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)triphenylsilane (4be)



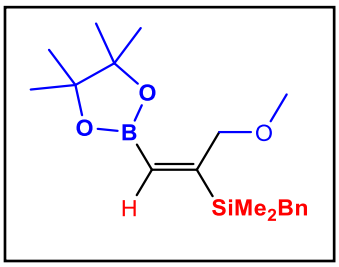
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.93 (s, 12H), 3.26 (s, 3H), 4.07 (d, 2H, $J_{(H,H)}$= 4.37 Hz), 6.42 (t, 1H, $J_{(H,H)}$= 4.35 Hz), 7.21-7.54 (m, 15H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 24.87, 58.41, 74.60, 83.37, 127.65, 129.32, 134.88, 136.67, 156.91. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -14.34. **FT-IR** (cm^{-1}): 3068, 3048, 2979, 2927, 2821, 1597, 1483, 1428, 1371, 1299, 1256, 1190, 1141, 1107, 1030, 972, 910, 853, 737, 698, 491. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 441.2 (M^+- 15.3, 1.2), 380.2 (22.0), 379.0 (74.3), 377.9 (16.3), 260.1 (23.1), 259.0 (100.0), 219.0 (19.8), 212.9 (35.4), 183.0 (25.8), 180.9 (57.7), 179.0 (21.1), 174.9 (22.5), 104.9 (37.3), 82.9 (76.3), 58.9 (19.8), 55.0 (30.4). **Elem. Anal.** calcd for $C_{28}H_{33}BO_3Si$: C, 73.68; H, 7.29; found C, 73.83; H, 7.30. Isolated yield = 71%, colorless oil.

(*E*)-3-(3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (3ce)



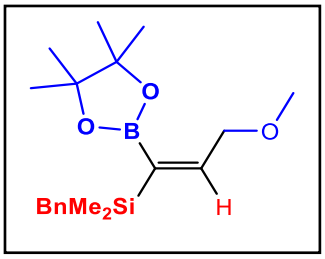
^{1}H NMR (C_6D_6, 300 MHz, δ, ppm): 0.20 (s, 18H), 0.37 (s, 3H), 1.05 (s, 12H), 3.24 (s, 3H), 4.66 (s, 2H), 6.57 (s, 1H). **^{13}C NMR** (C_6D_6, 75 MHz, δ, ppm): 1.19, 2.05, 24.94, 57.94, 75.32, 83.12, 164.28. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** (C_6D_6, 79 MHz, δ, ppm): -36.55, 7.39. **FT-IR** (cm^{-1}): 2978, 2958, 2819, 1601, 1449, 1371, 1251, 1146, 1046, 837, 785, 753. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 403.1 (M^+-15.5, 4.4), 303.0 (14.0), 238.2 (15.8), 237.0 (73.8), 223.1 (11.2), 222.2 (16.4), 221.0 (76.3), 207.0 (40.0), 190.9 (10.4), 84.1 (12.3), 83.0 (11.6), 72.9 (100.0). **Elem. Anal.** calcd for $C_{17}H_{39}BO_5Si_3$: C, 48.78; H, 9.39; found C, 48.83; H, 9.40. Isolated yield = 89%, colorless oil.

(*E*)-Benzyl(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)dimethylsilane (3fe)



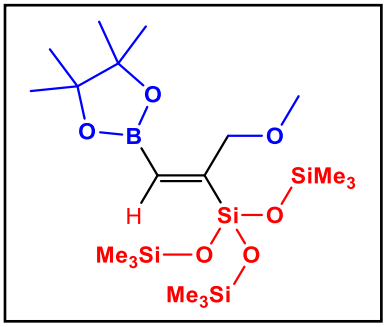
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.05 (s, 6H), 1.29 (s, 12H), 2.22 (s, 2H), 3.33 (s, 3H), 4.31 (d, 2H, $J_{(H,H)}$= 1.60 Hz), 5.95 (t, 1H, $J_{(H,H)}$= 1.57 Hz), 5.96-7.22 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -3.43, 25.02, 25.56, 58.07, 75.24, 83.36, 124.05, 128.19, 128.43, 140.25, 163.49. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -3.46. **FT-IR** (cm^{-1}): 3024, 2977, 2927, 2817, 1598, 1493, 1451, 1370, 1325, 1245, 1206, 1142, 1106, 1066, 989, 966, 824, 792, 761, 698, 476. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 255.0 (M^+- 91.4, 30.3), 156.1 (11.9), 154.9 (94.2), 153.8 (22.1), 148.9 (11.0), 132.8 (28.6), 123.0 (16.9), 120.9 (25.2), 112.9 (60.7), 90.9 (15.0), 88.9 (100.0), 83.0 (52.7), 81.0 (16.1), 59.0 (28.6), 55.0 (15.6). **Elem. Anal.** calcd for $C_{19}H_{31}BO_3Si$: C, 65.89; H, 9.02; found C, 65.80; H, 9.00. Isolated yield = 70%, colorless oil.

(*E*)-Benzyl(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)dimethylsilane (4fe)



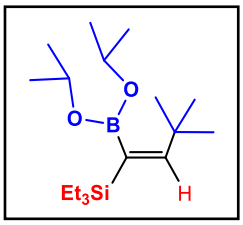
^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.05 (s, 6H), 1.31 (s, 12H), 2.21 (s, 2H), 3.33 (s, 3H), 4.11 (d, 2H, $J_{(H,H)}$= 4.67 Hz), 6.43 (t, 1H, $J_{(H,H)}$= 4.64 Hz), 6.66-7.21 (m, 5H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): -3.25, 25.20, 26.06, 58.28, 74.38, 83.31, 123.92, 128.12, 128.43, 128.46, 140.45, 152.73. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -2.32. **FT-IR** (cm^{-1}): 2977, 2928, 2818, 1599, 1493, 1451, 1371, 1354, 1295, 1245, 1206, 1142, 1108, 1071, 1056, 856, 831, 761, 698. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 332.2 (M^+- 14.1, 0.2), 255.0 (17.8), 172.9 (15.2), 154.9 (34.2), 120.9 (10.3), 114.1 (10.2), 112.9 (100.0), 90.9 (16.3), 88.9 (15.3), 83.0 (23.8), 58.9 (13.1), 55.0 (20.2). **Elem. Anal.** calcd for $C_{19}H_{31}BO_3Si$: C, 65.89; H, 9.02; found C, 65.90; H, 9.02. Isolated yield = 73%, colorless oil.

(*E*)-3-(3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (3ge)



^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.10 (s, 27H), 1.27 (s, 12H), 3.29 (s, 3H), 4.18 (d, 2H, $J_{(H,H)}$= 1.73 Hz), 6.04 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ, ppm): 1.92, 25.02, 58.01, 74.20, 83.19, 156.78. Signal from carbon atom SiBC= is not observed. **^{29}Si NMR** ($CDCl_3$, 79 MHz, δ, ppm): -81.59, 8.05. **FT-IR** (cm^{-1}): 2958, 1603, 1448, 1371, 1338, 1250, 1050, 836, 754, 686, 595. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 477.1 (M^+- 15.6, 7.8), 311.0 (35.5), 281.0 (13.0), 276.0 (11.3), 261.0 (13.3), 223.0 (13.9), 209.0 (12.6), 208.0 (19.9), 206.9 (100.0), 192.9 (10.9), 88.9 (13.9), 83.0 (11.7), 73.0 (99.5). **Elem. Anal.** calcd for $C_{19}H_{45}BO_6Si_4$: C, 46.32; H, 9.21; found C, 46.40; H, 9.22. Isolated yield = 92%, colorless oil.

Di*iso*propyl (*E*)-(3,3-dimethyl-1-(triethylsilyl)but-1-en-1-yl)boronate (4af)



^{1}H NMR (C_6D_6, 300 MHz, δ, ppm): 0.74-0.81 (q, 6H, $J_{(H,H)}$= 7.63 Hz), 1.07-1.20 (m, 30H, overlapped singlet, dublet and triplet), 4.45-4.53 (m, 2H), 6.24 (s, 1H). **^{13}C NMR** (C_6D_6, 75 MHz, δ, ppm): 4.72, 7.87, 24.71, 29.45, 37.75, 65.72, 160.43. Signal from carbon atoms BC= is not observed. **^{29}Si NMR** (C_6D_6, 79 MHz, δ, ppm): 0.97. **^{11}B NMR** ($CDCl_3$, 96 MHz, δ, ppm): 29.92. **GC-MS** (EI, 70 eV) m/z (rel. int., %): 297.4 (M^+- 29,

30.9), 214.4 (16.9), 213.3 (100), 212.3 (24.9), 87.2 (22.5), 75.2 (8.6), 59.1 (26.3), 57.1 (10.1). **FT-IR** (cm^{-1}): 3182, 2261, 1410, 1192, 712, 631, 544. **Elem. Anal.** calcd for $C_{18}H_{39}BO_2Si$: C, 66.24; H, 12.04; found C, 66.38; H, 12.06. Isolated yield = 75%, colorless oil.

6. NMR spectra

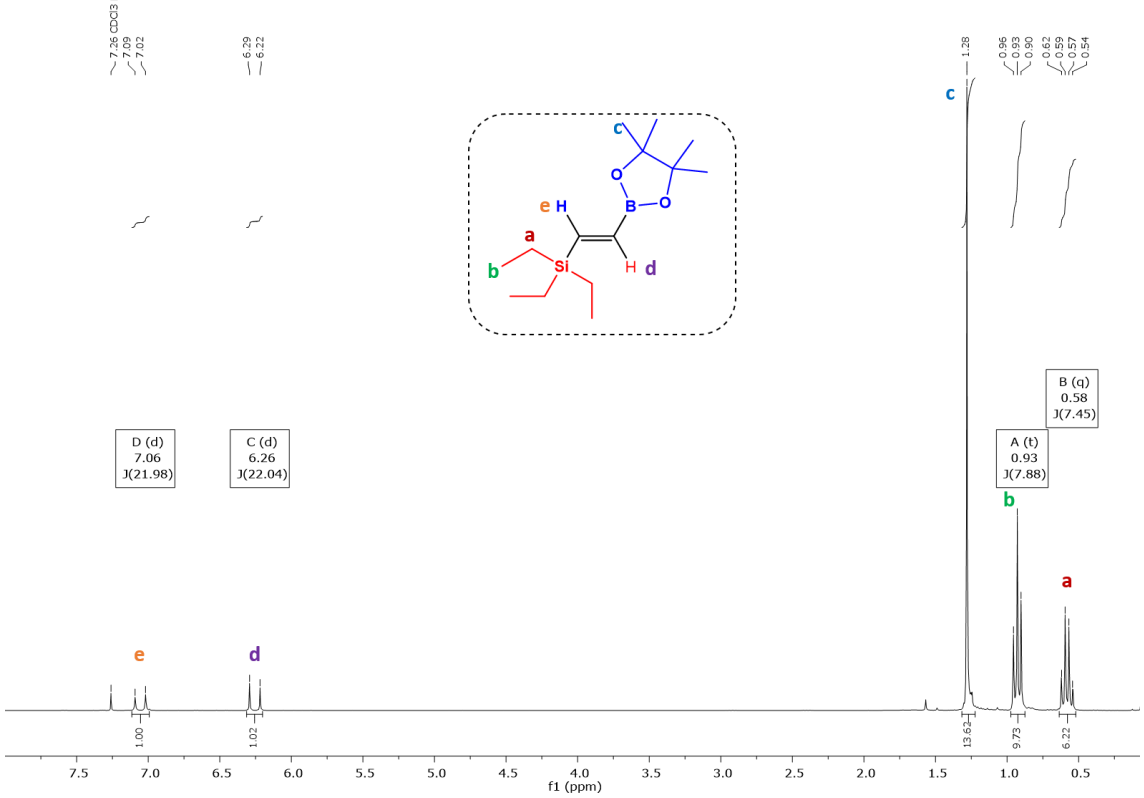


Figure S1. [1]H NMR of compound **3aa**.

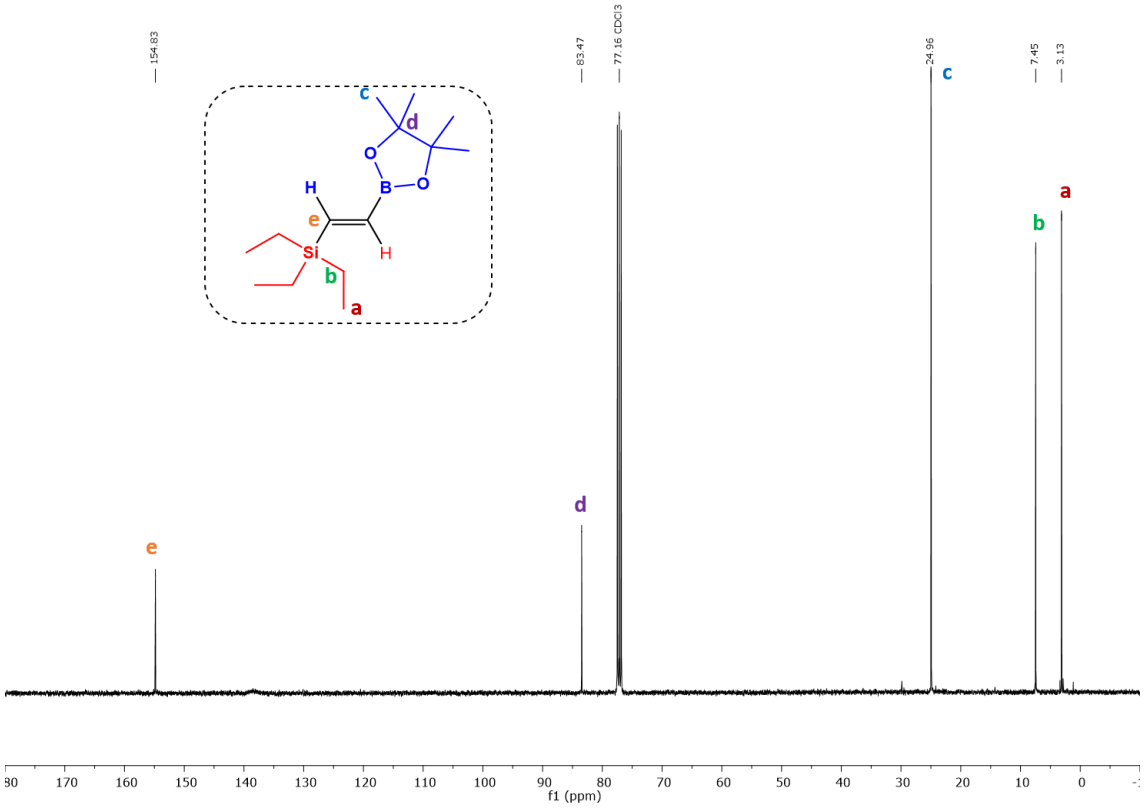


Figure S2. [13]C NMR of compound **3aa**.

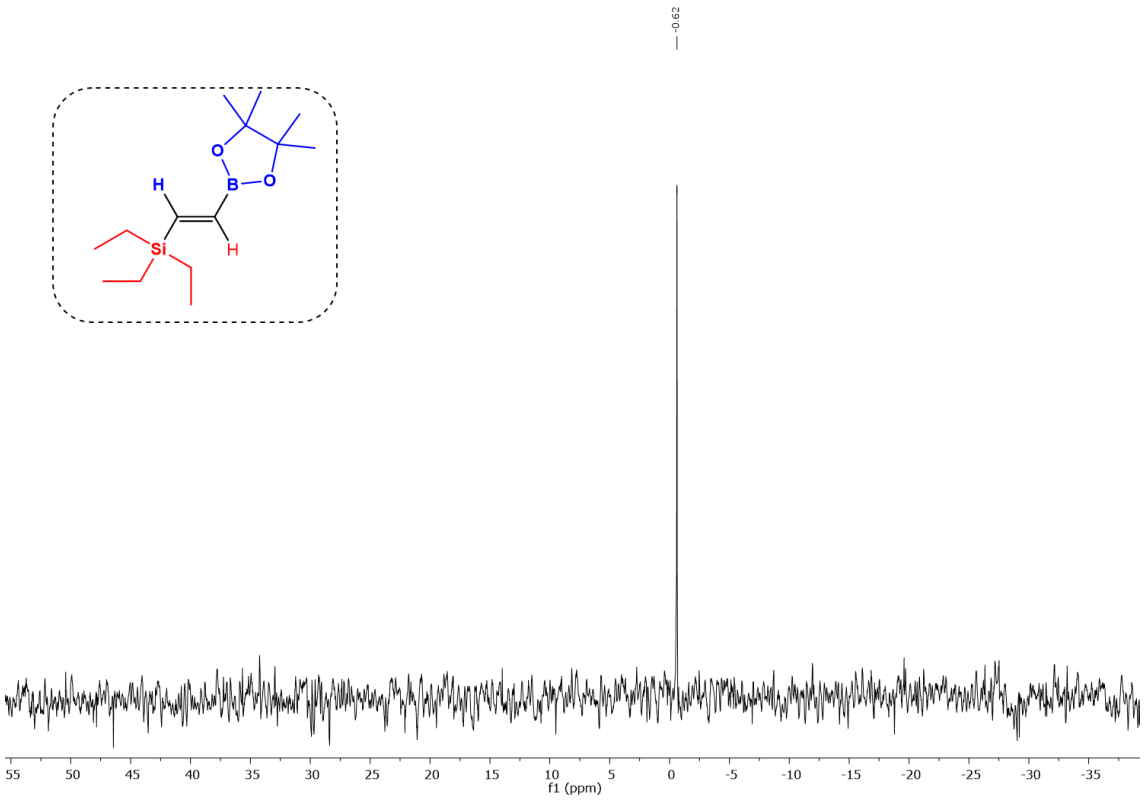


Figure S3. ^{29}Si NMR of compound **3aa**.

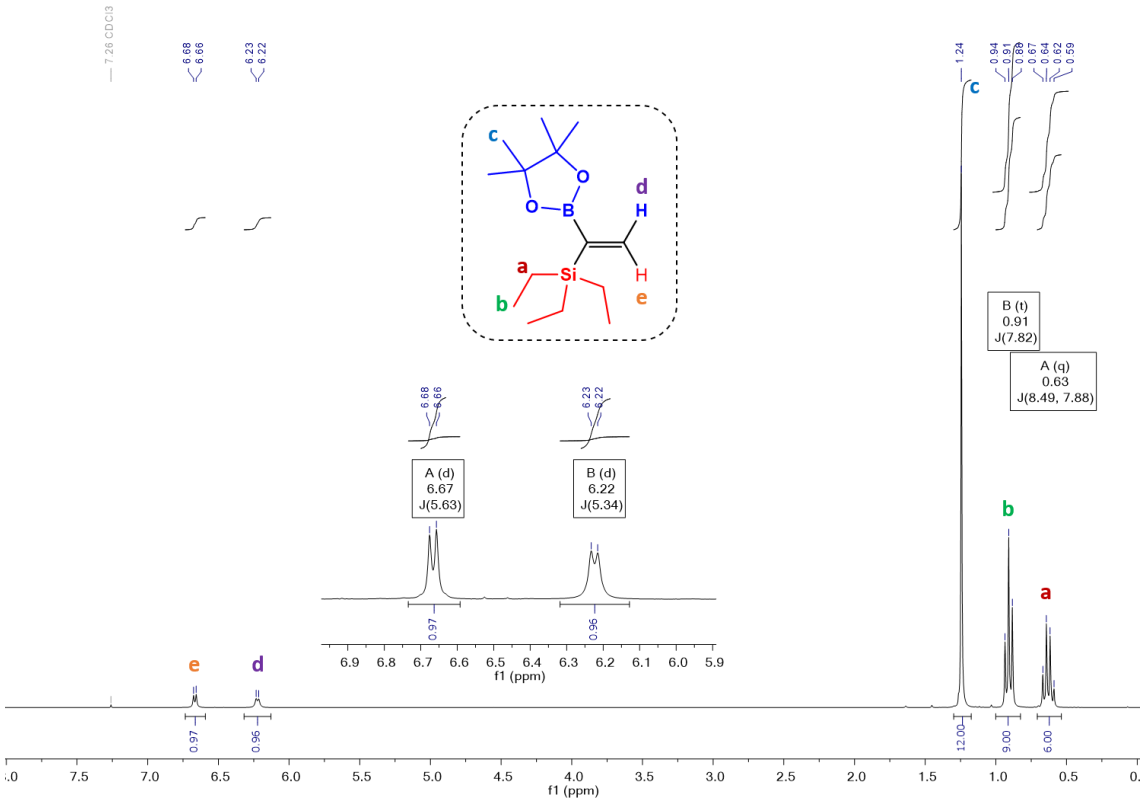


Figure S4. ^{1}H NMR of compound **4aa**.

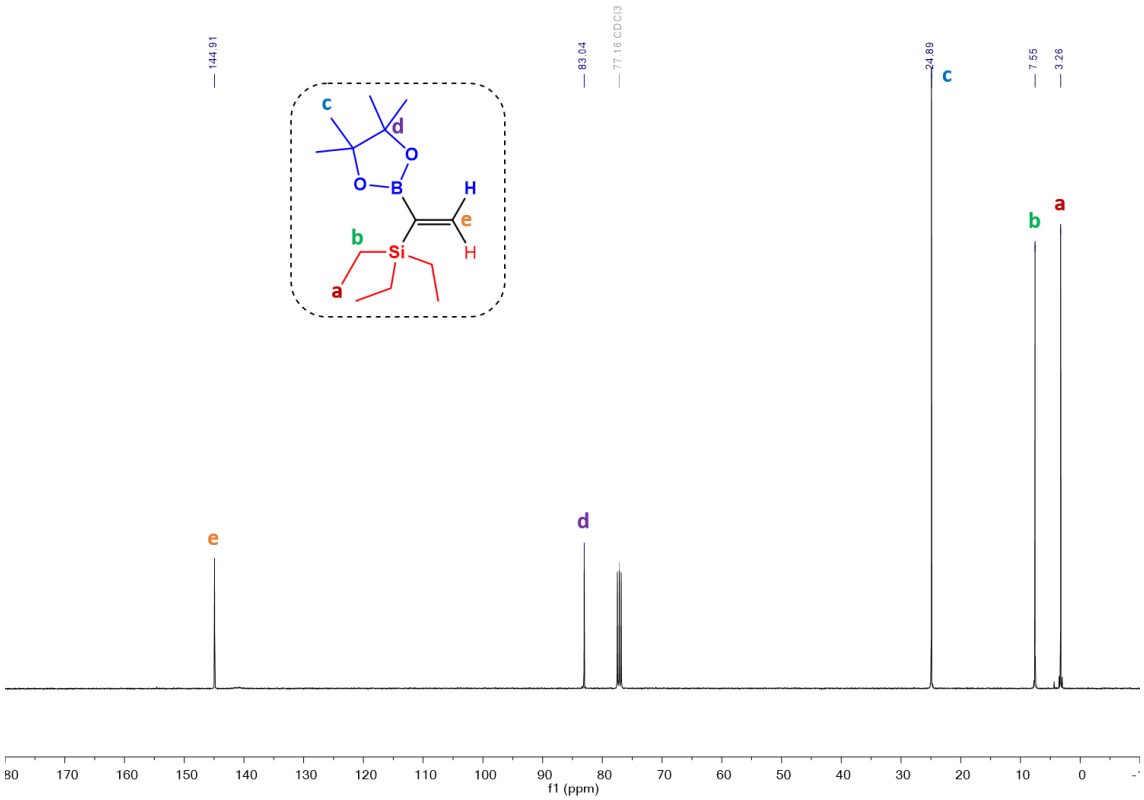


Figure S5. ^{13}C NMR of compound **4aa**.

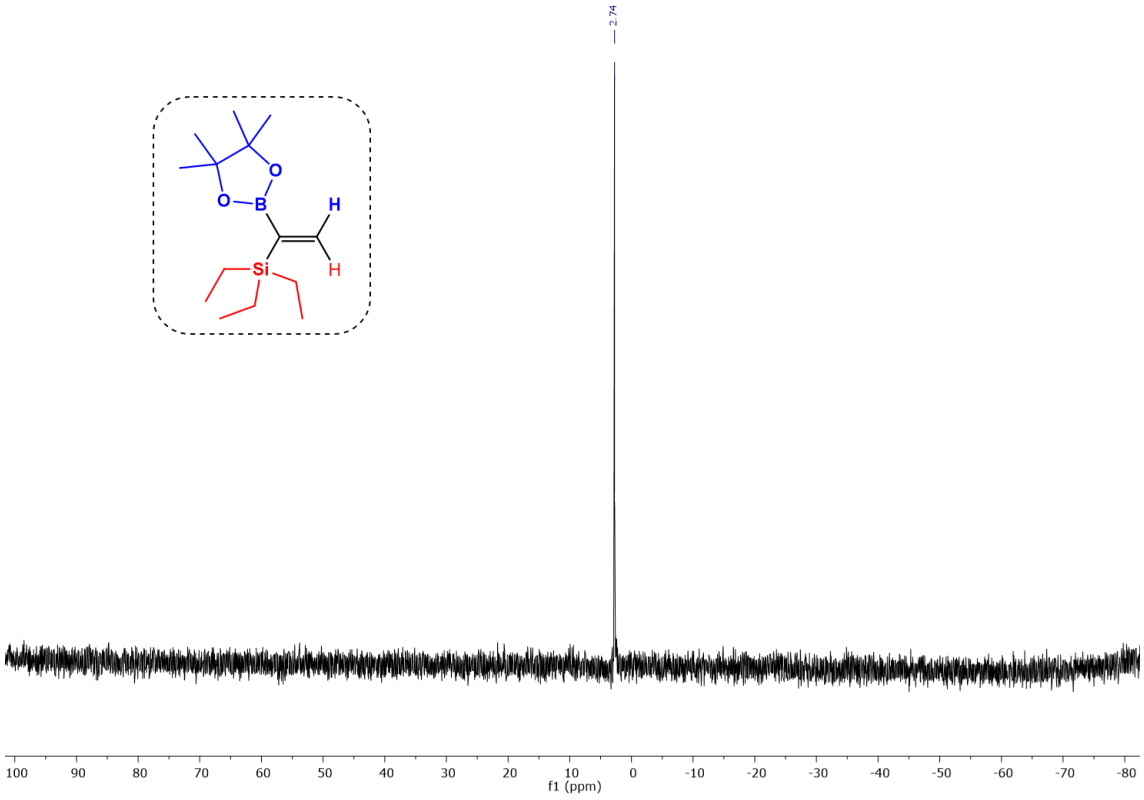


Figure S6. ^{29}Si NMR of compound **4aa**.

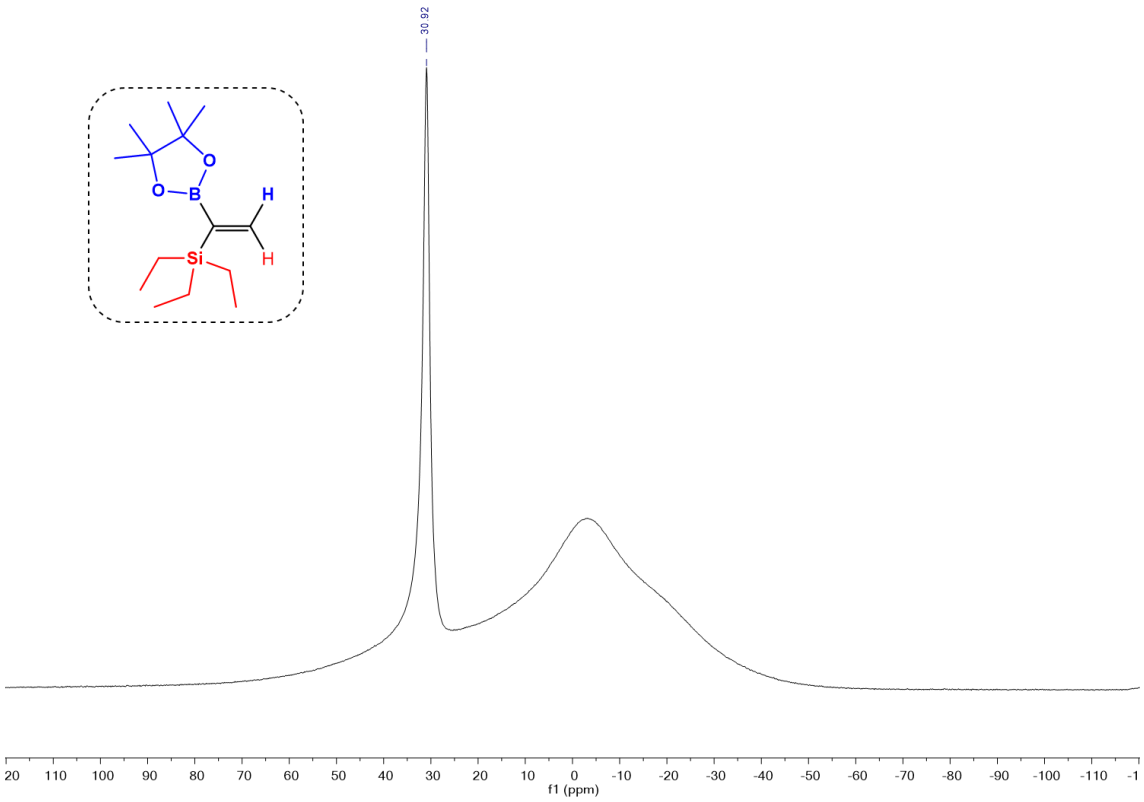


Figure S7. [11]B NMR of compound **4aa**.

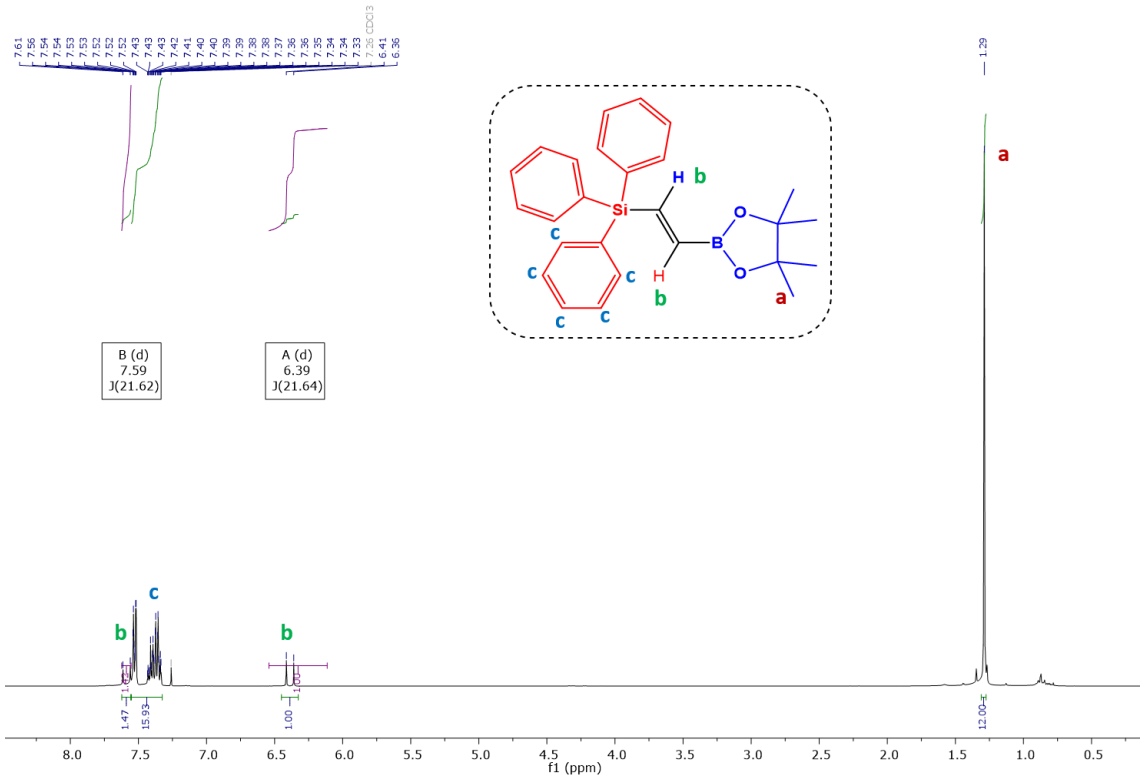


Figure S8. [1]H NMR of compound **3ba**.

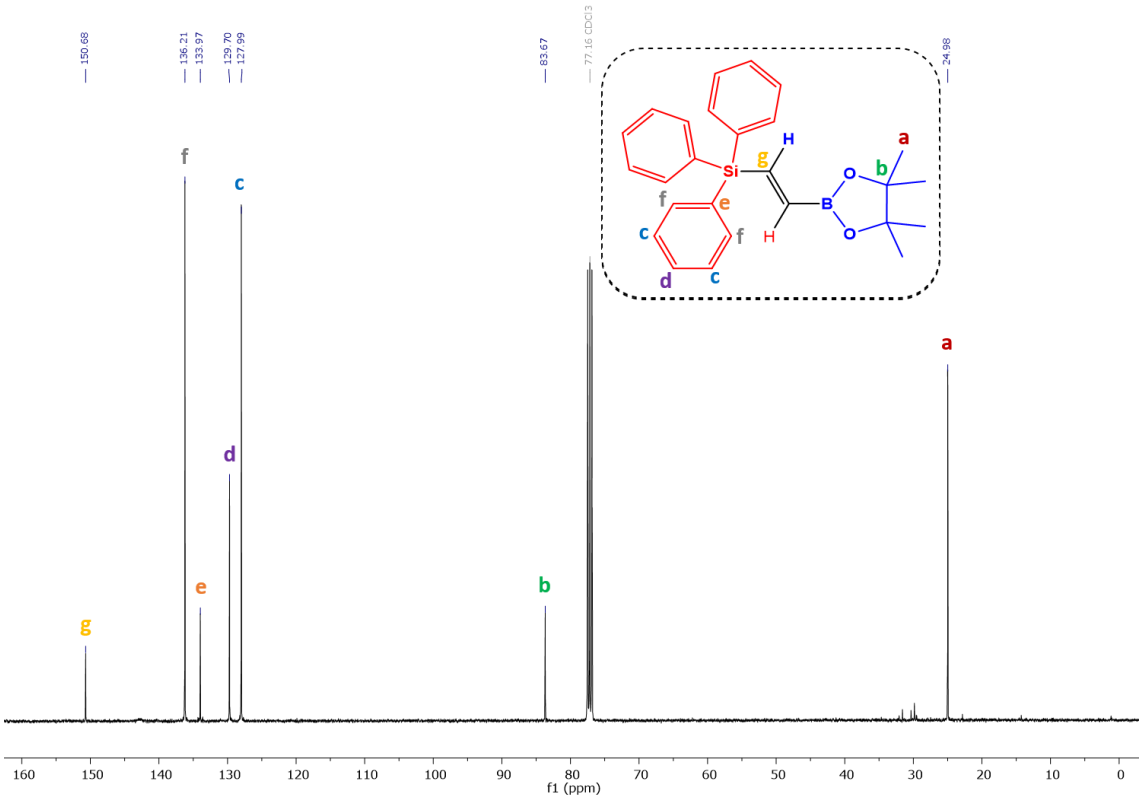


Figure S9. ^{13}C NMR of compound **3ba**.

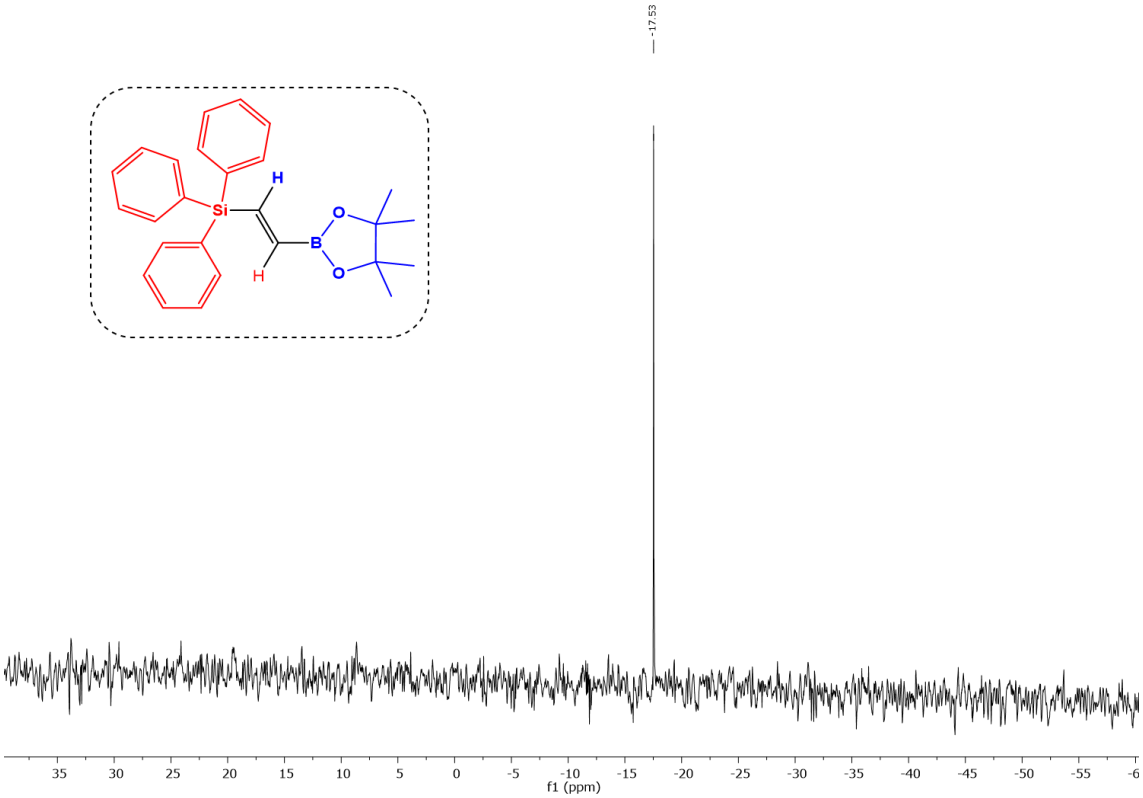


Figure S10. ^{29}Si NMR of compound **3ba**.

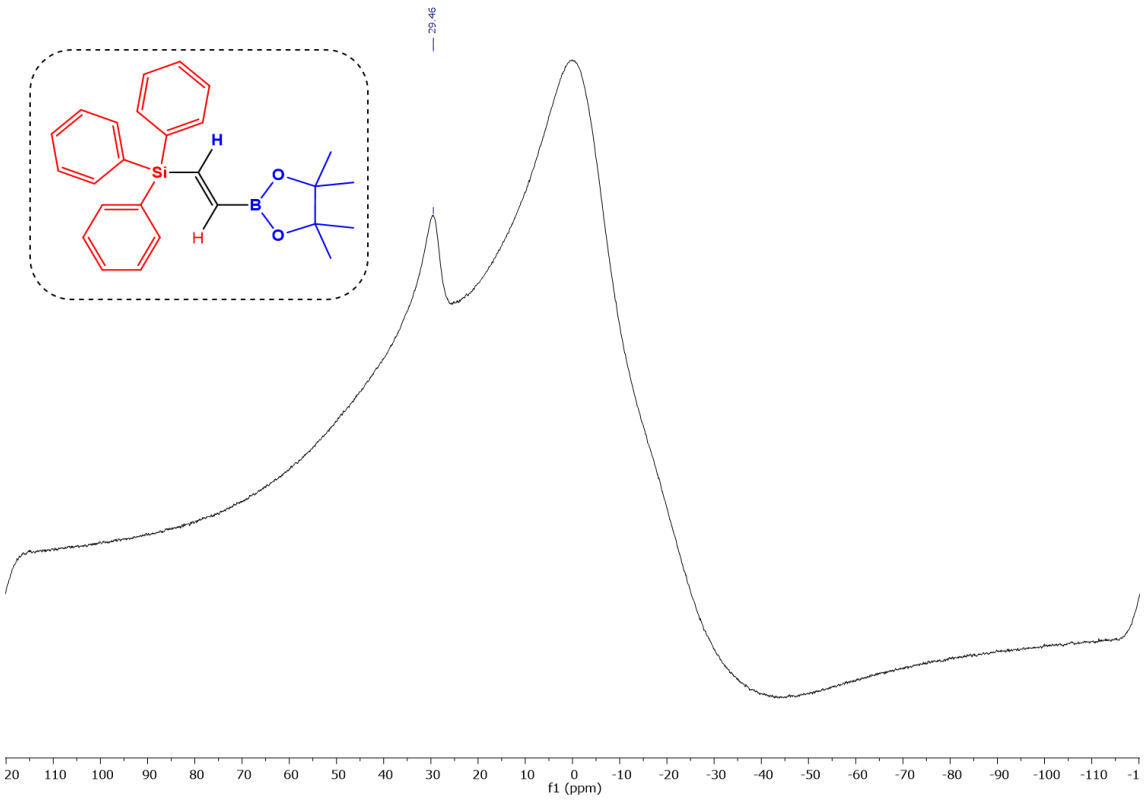


Figure S11. ^{11}B NMR of compound **3ba**.

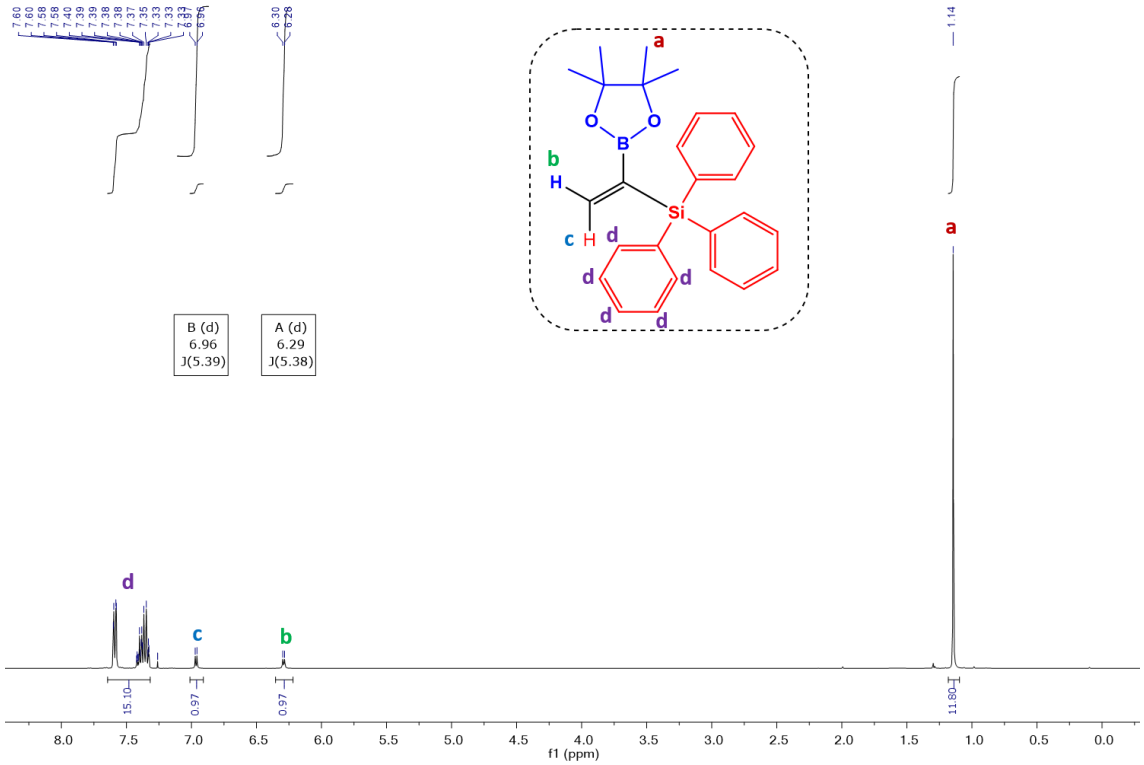


Figure S12. ^{1}H NMR of compound **4ba**.

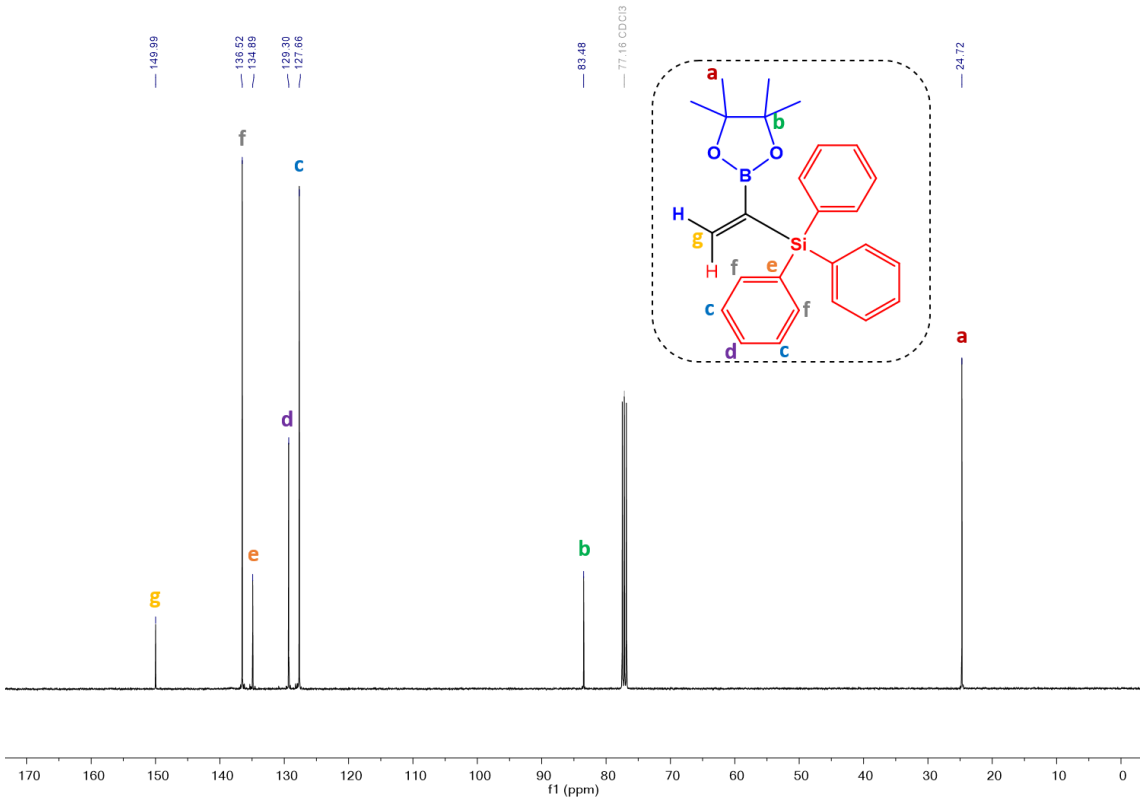


Figure S13. ^{13}C NMR of compound **4ba**.

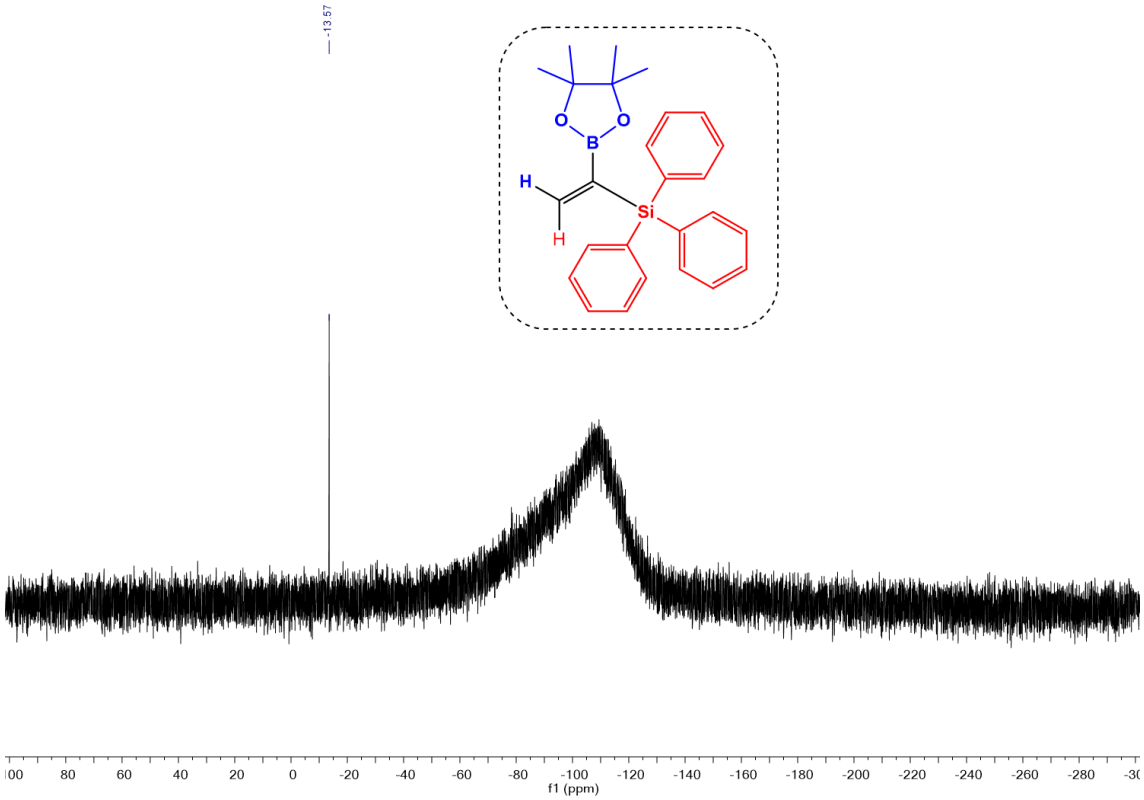


Figure S14. ^{29}Si NMR of compound **4ba**.

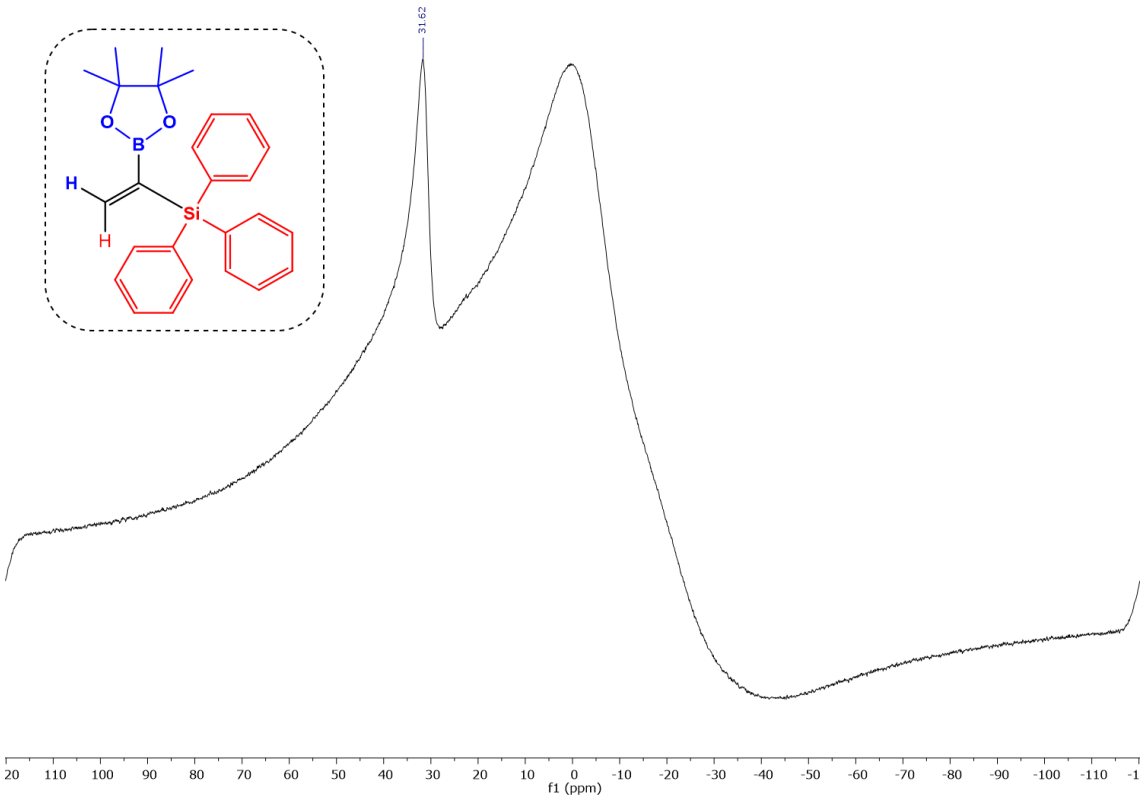


Figure S15. ^{11}B NMR of compound **4ba**.

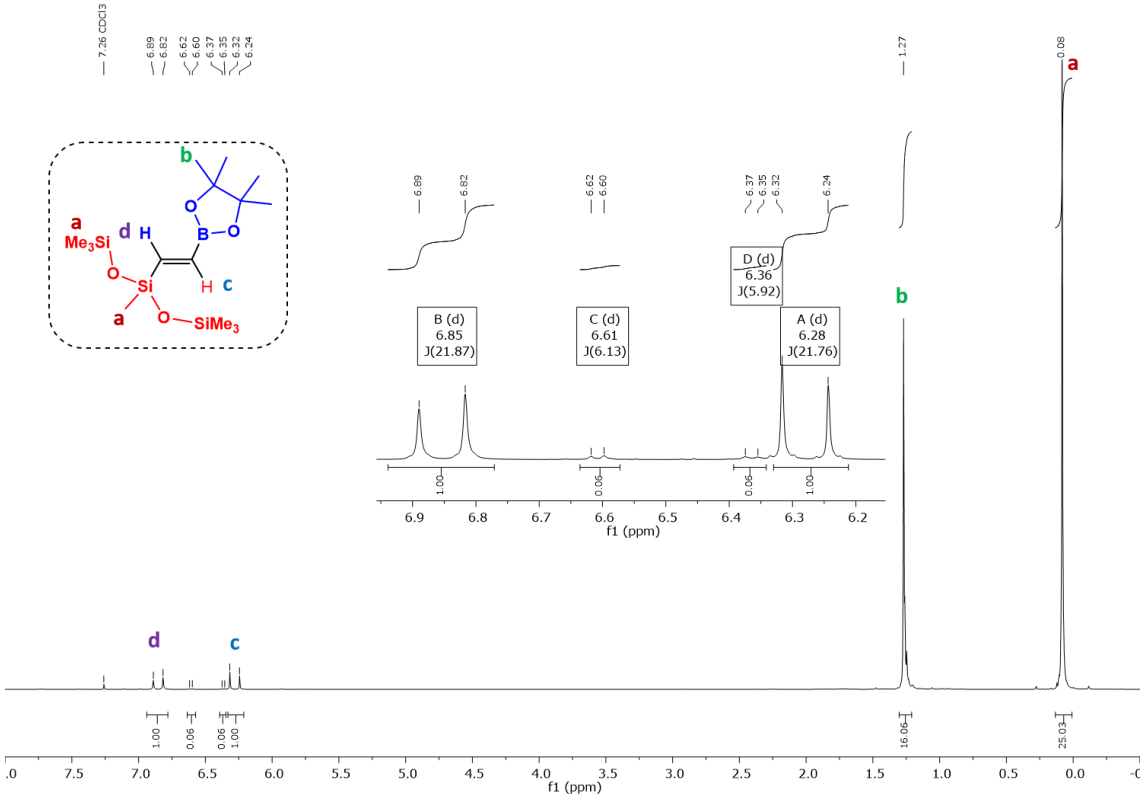


Figure S16. ^{1}H NMR of **3ca/4ca** mixture 94/6.

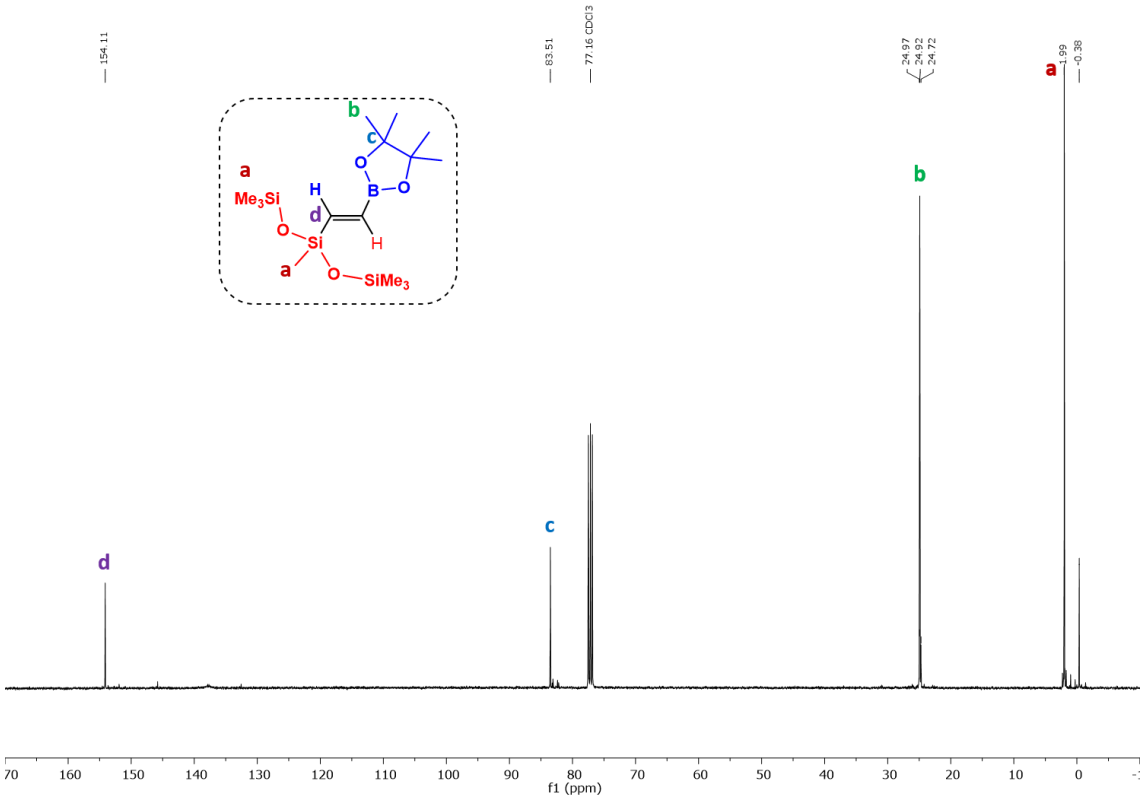


Figure S17. ^{13}C NMR of **3ca/4ca** mixture 94/6.

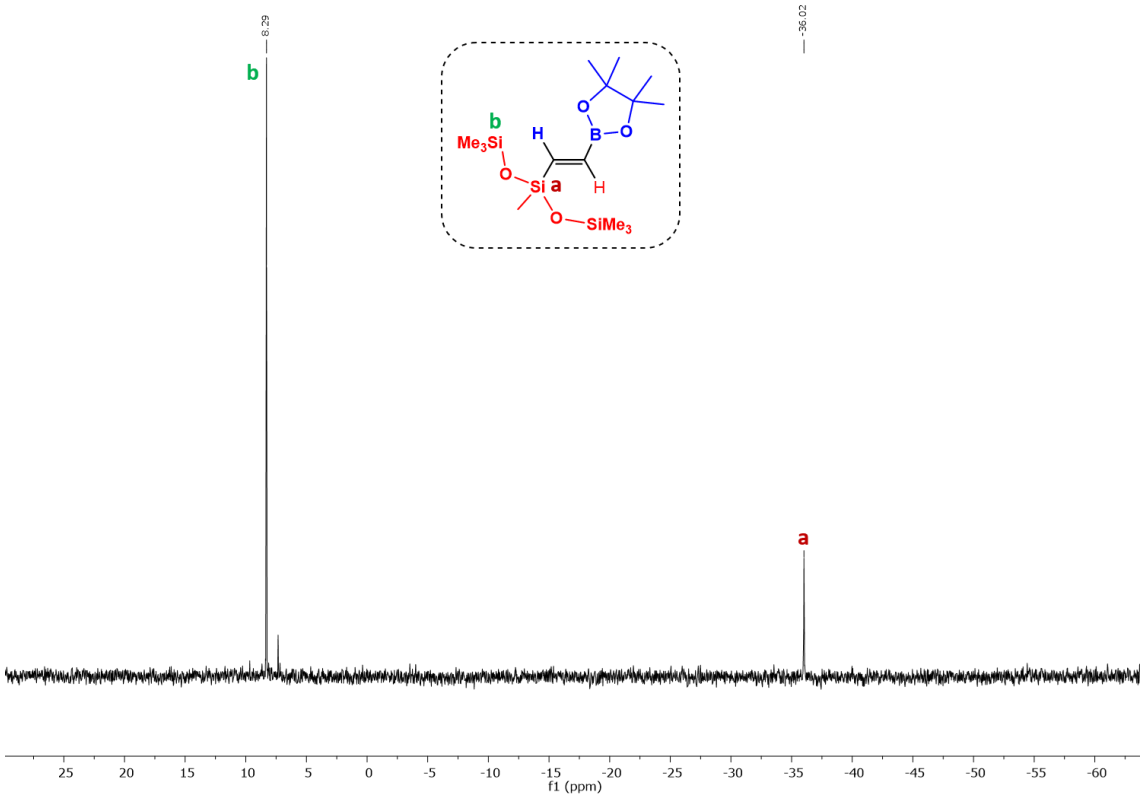


Figure S18. ^{29}Si NMR of **3ca/4ca** mixture 94/6.

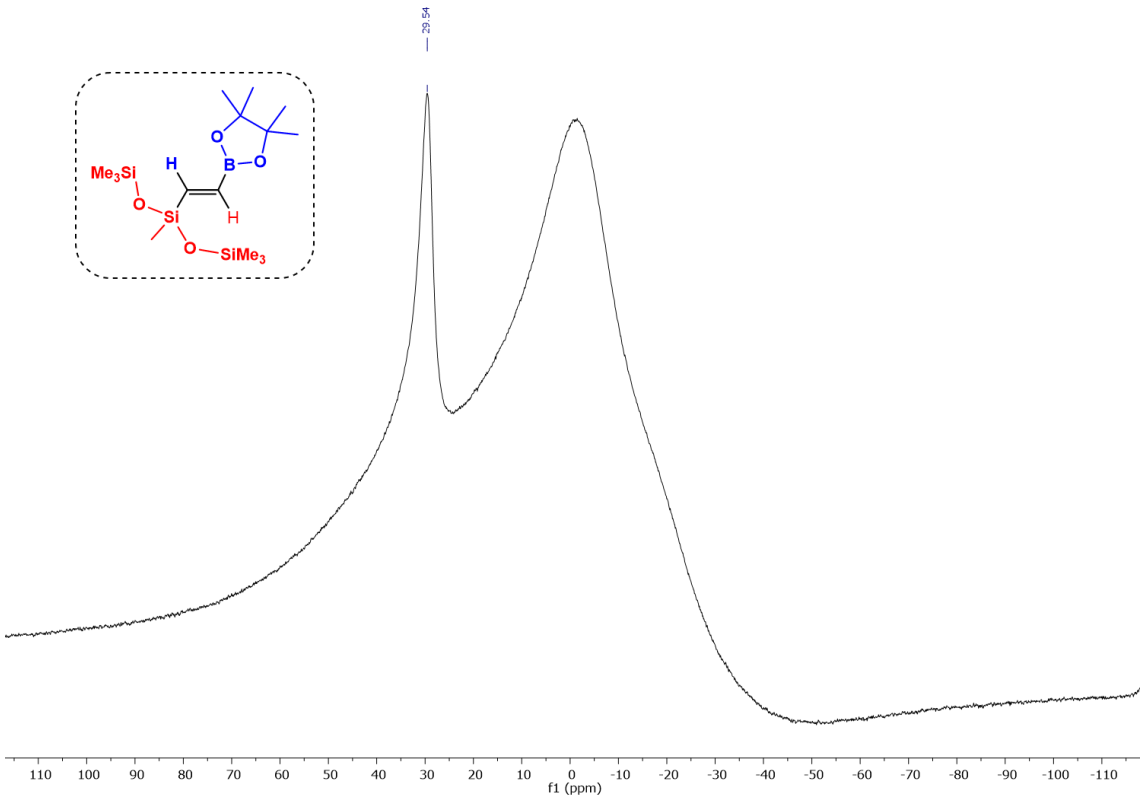


Figure S19. [11]B NMR of **3ca/4ca** mixture 94/6.

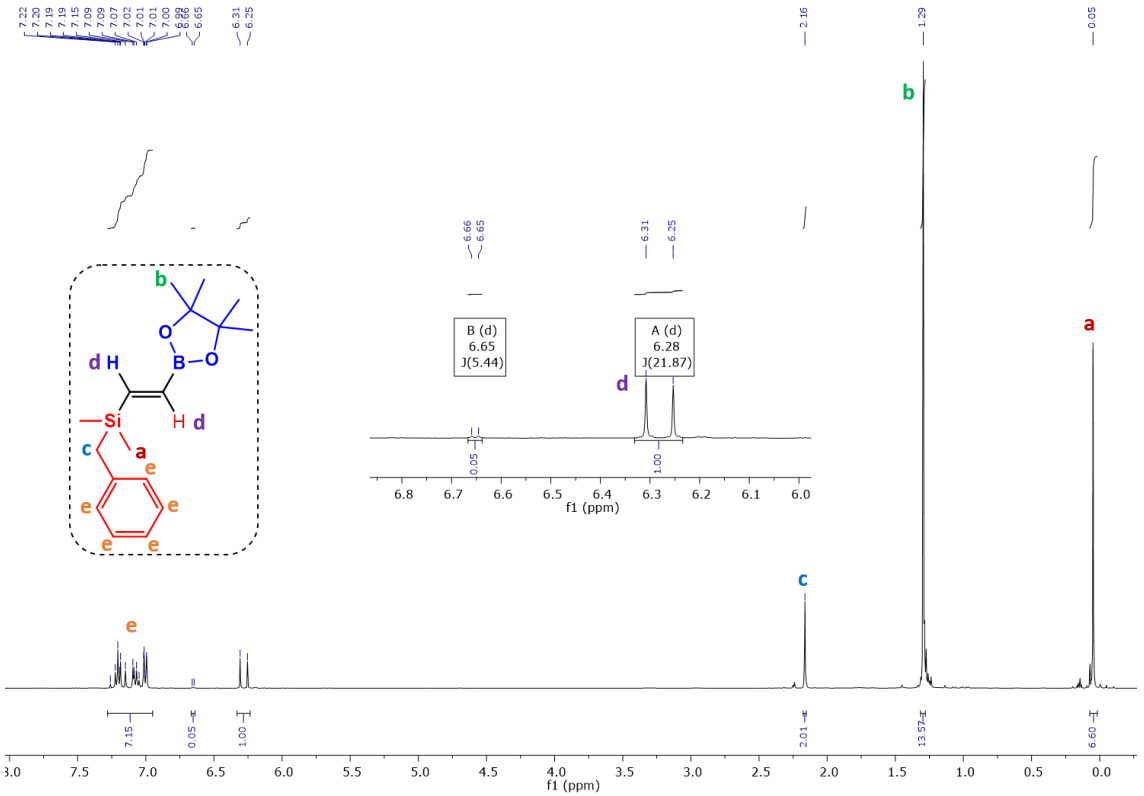


Figure S20. [1]H NMR of **3fa/4fa** mixture 95/5.

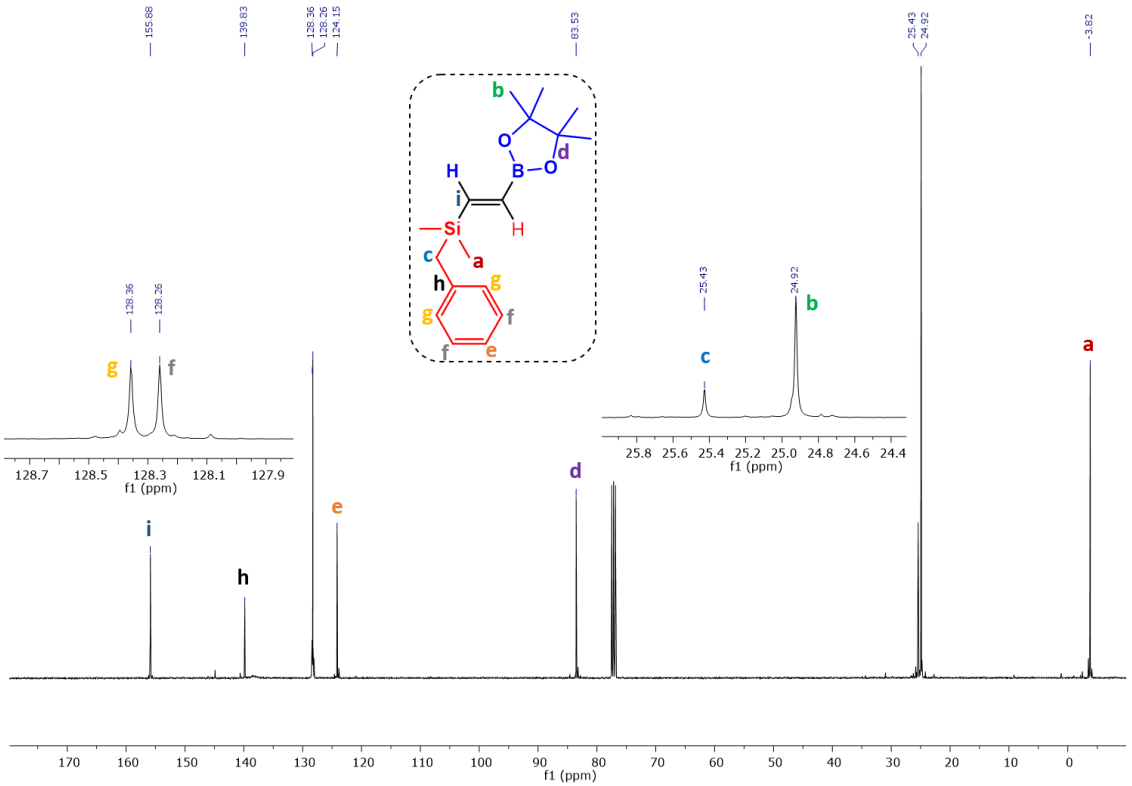


Figure S21. ^{13}C NMR of **3fa/4fa** mixture 95/5.

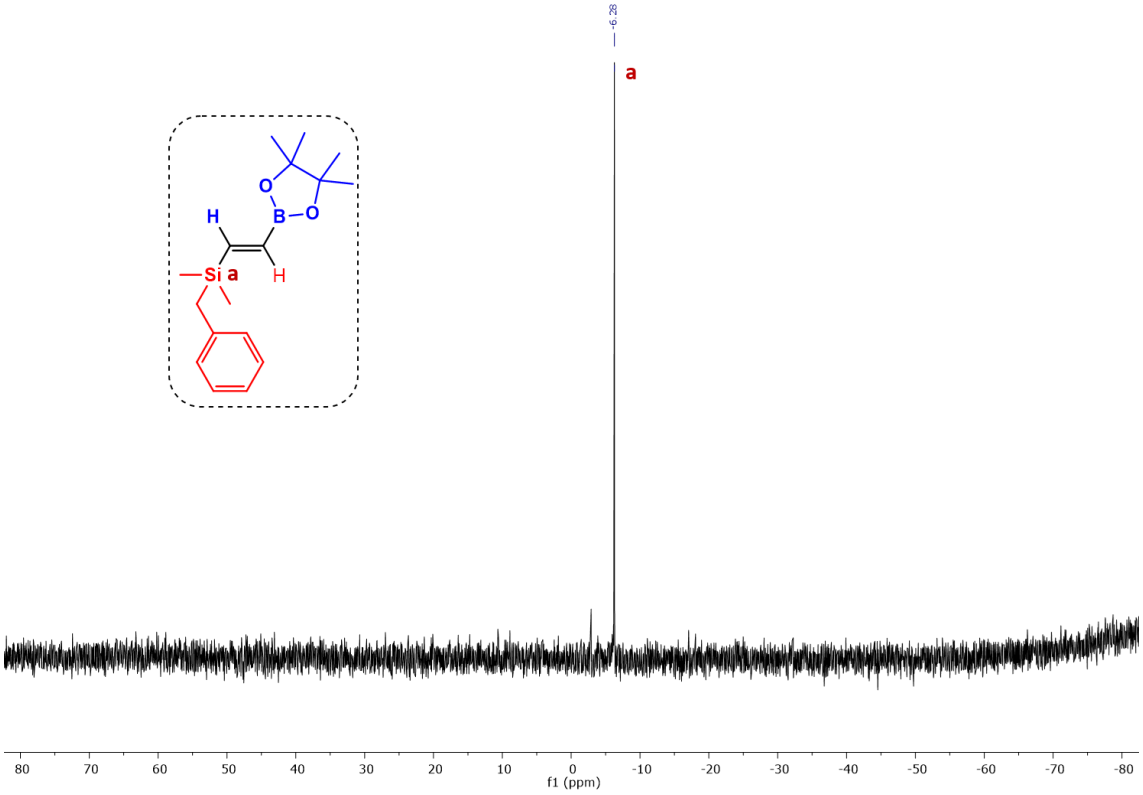


Figure S22. ^{29}Si NMR of **3fa/4fa** mixture 95/5.

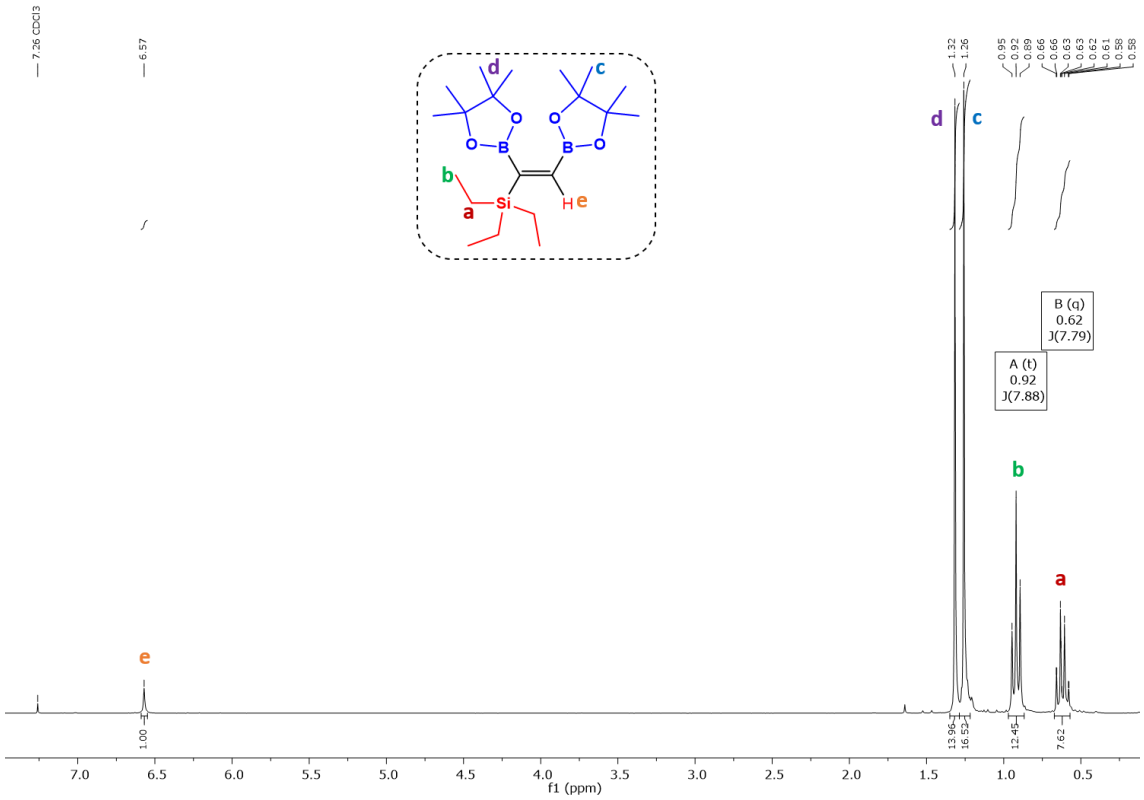


Figure S23. ^{1}H NMR of compound **3ab**.

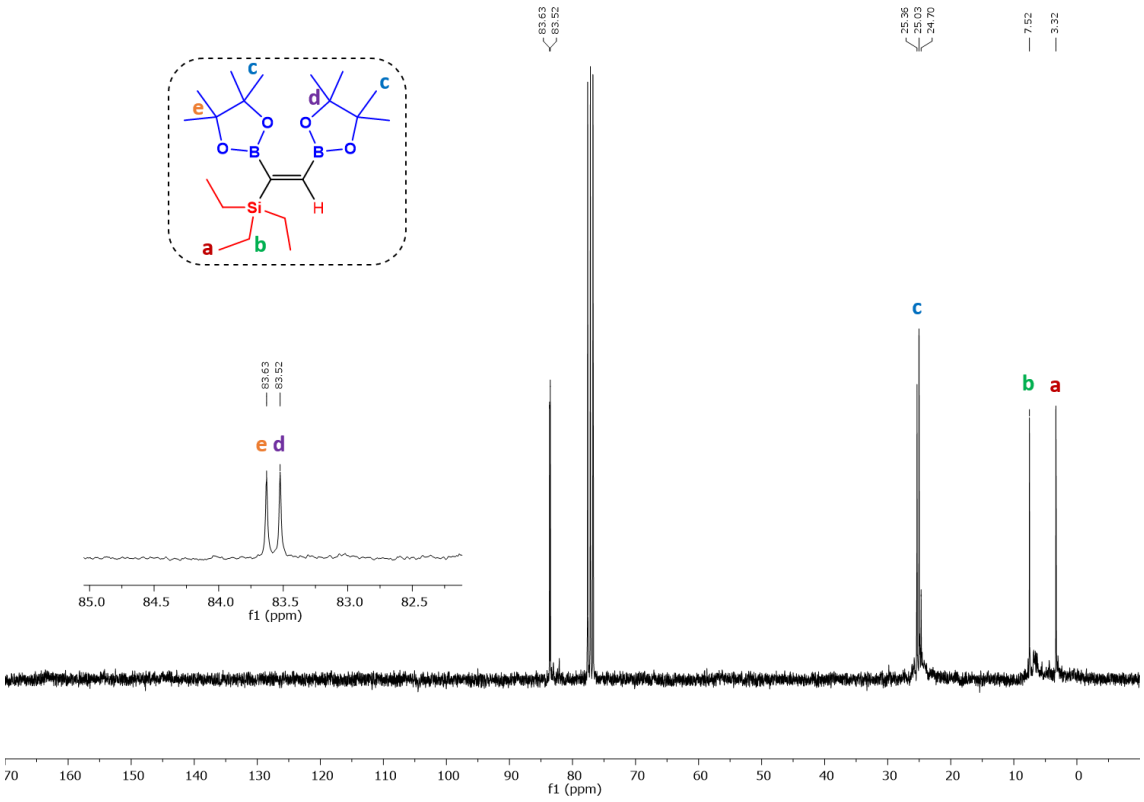


Figure S24. ^{13}C NMR of compound **3ab**.

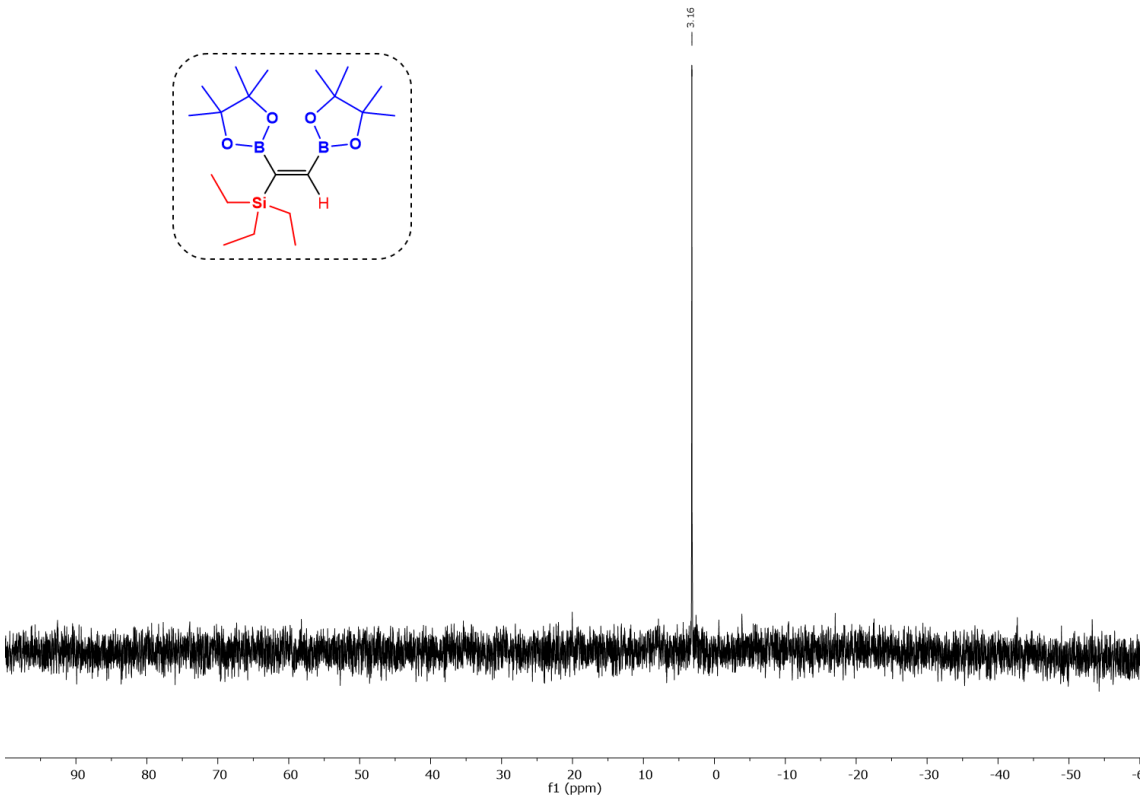


Figure S25. ^{29}Si NMR of compound **3ab**.

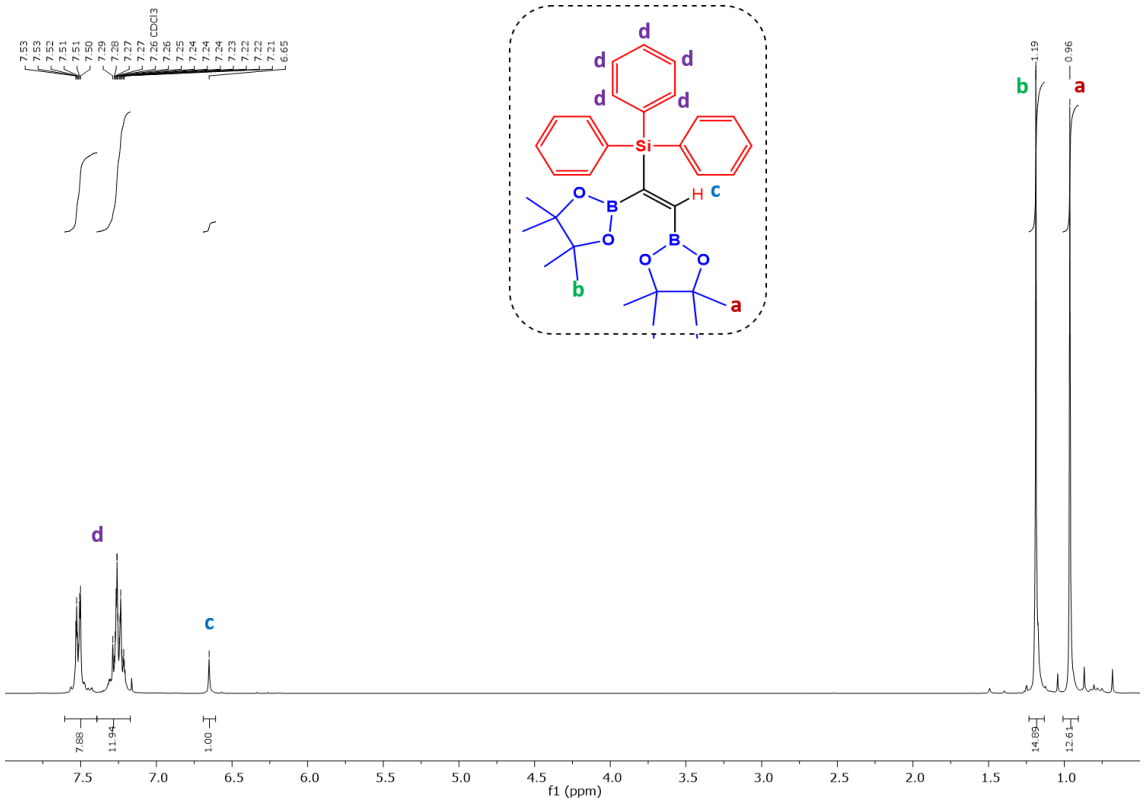


Figure S26. ^{1}H NMR of compound **3bb**.

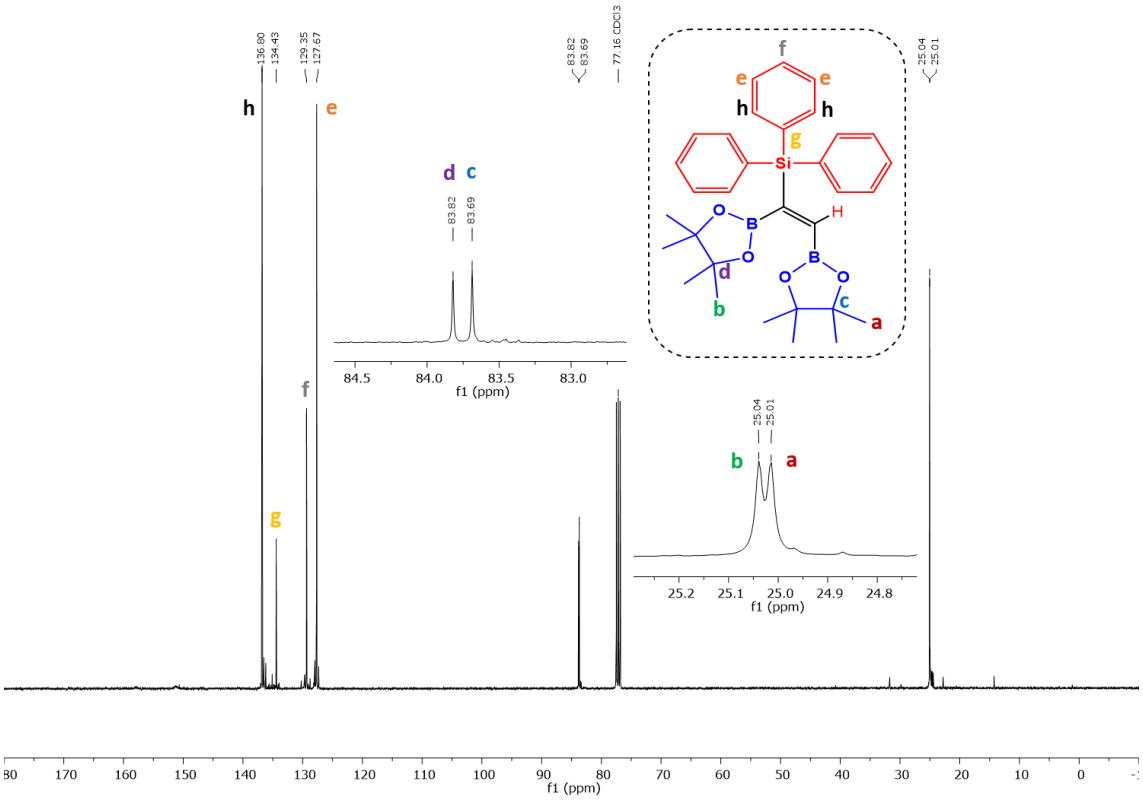


Figure S27. ^{13}C NMR of compound **3bb**.

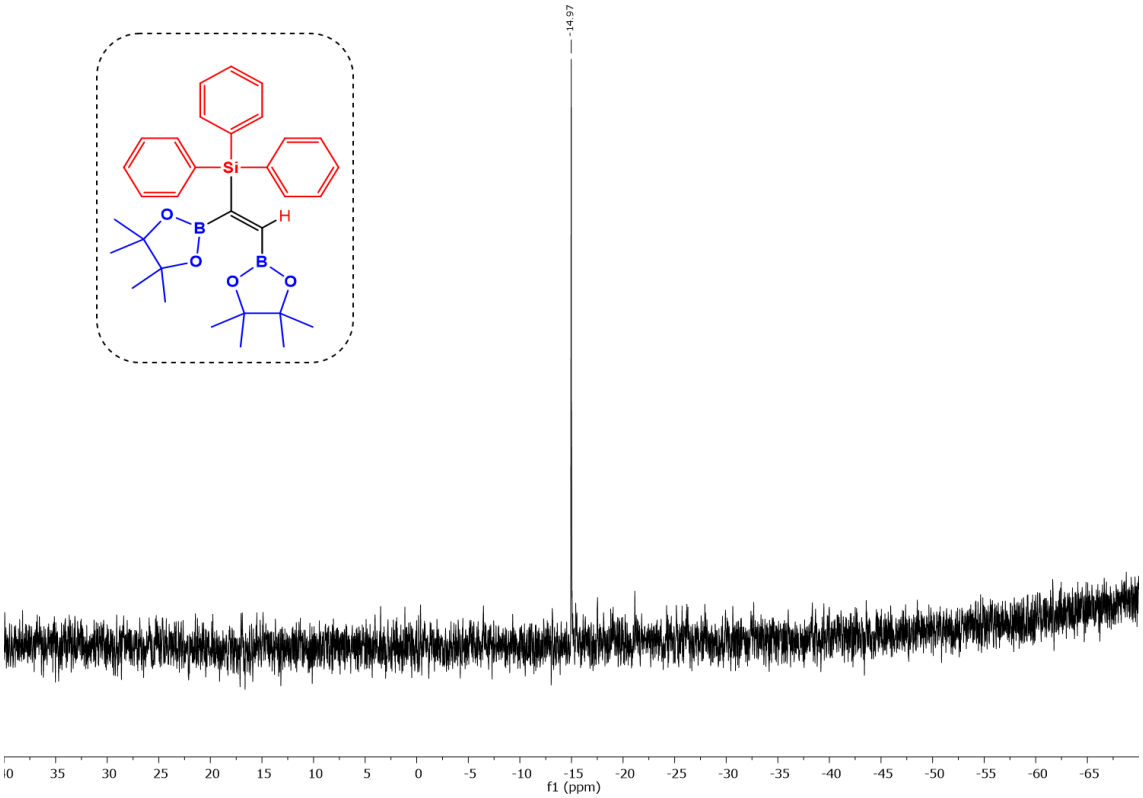


Figure S28. ^{29}Si NMR of compound **3bb**.

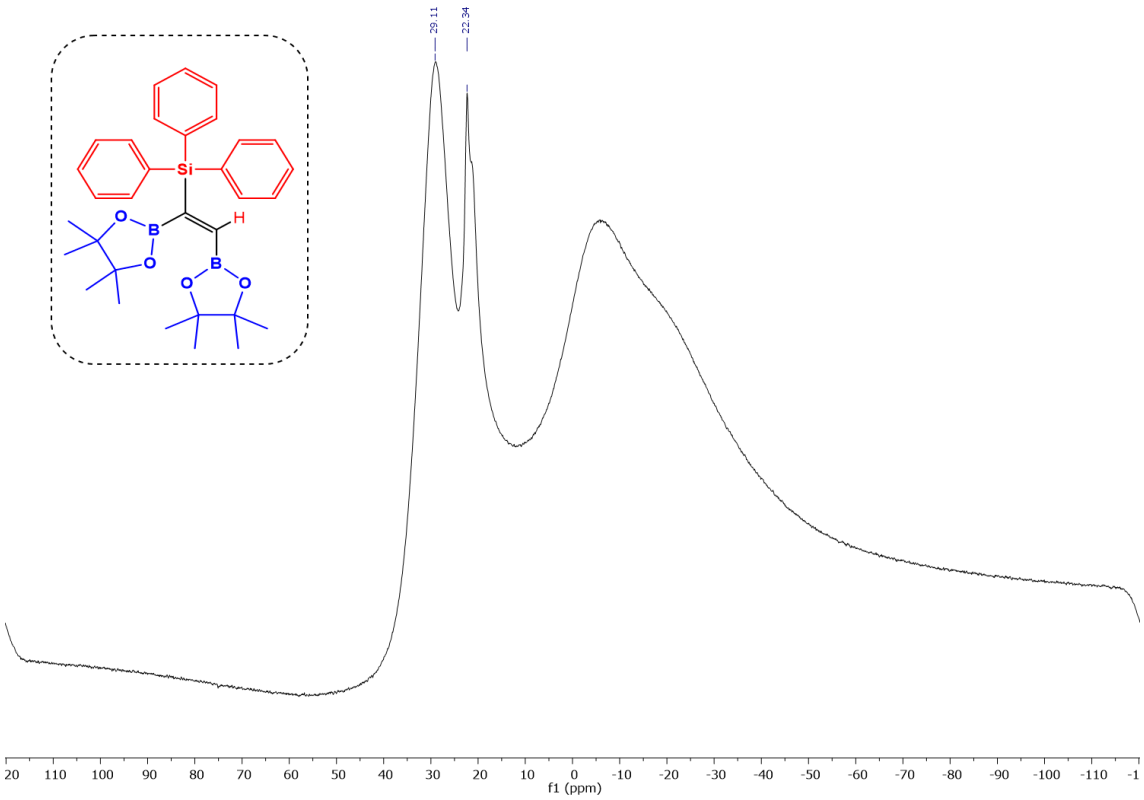


Figure S29. ^{11}B NMR of compound **3bb**.

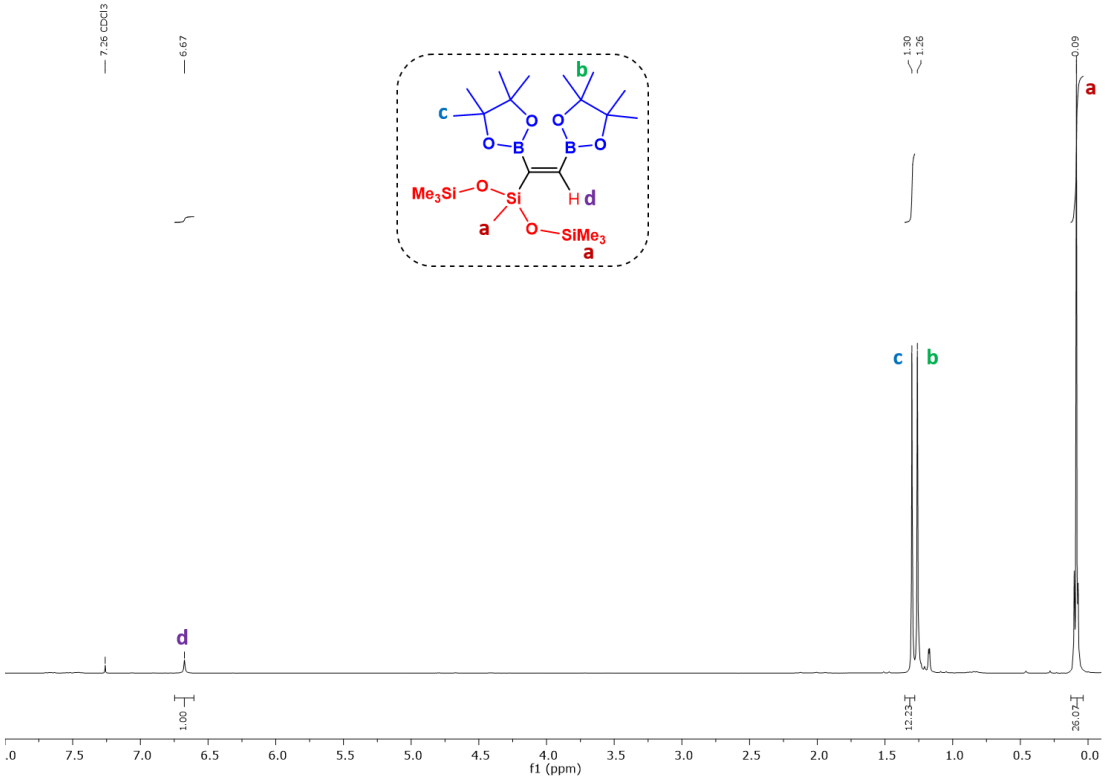


Figure S30. ^{1}H NMR of **3cb/4cb** mixture 96/4.

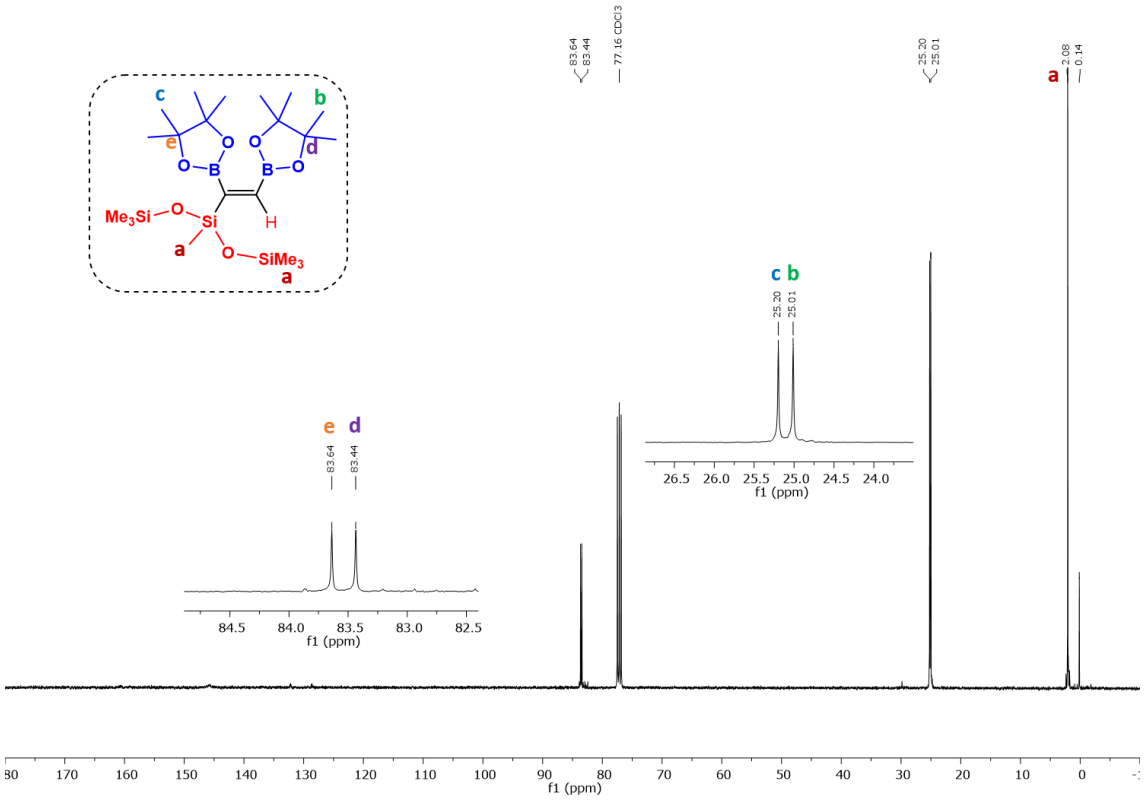


Figure S31. ^{13}C NMR of **3cb/4cb** mixture 96/4.

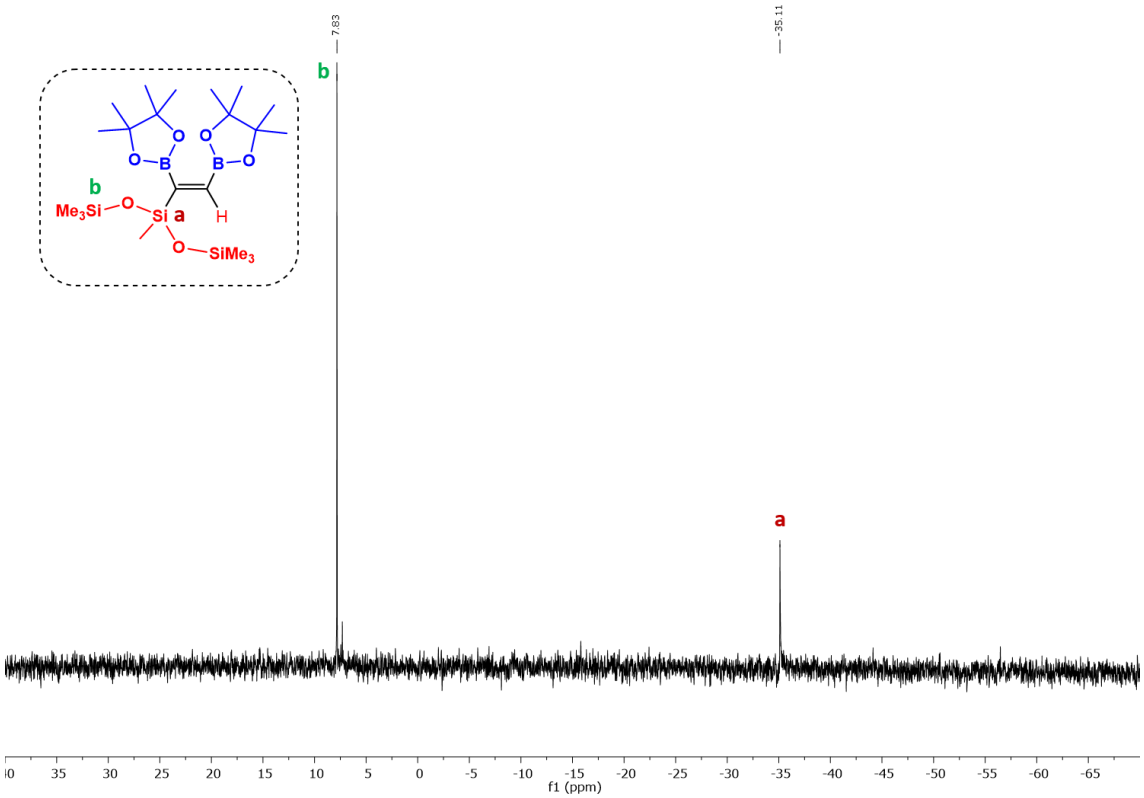


Figure S32. ^{29}Si NMR of **3cb/4cb** mixture 96/4.

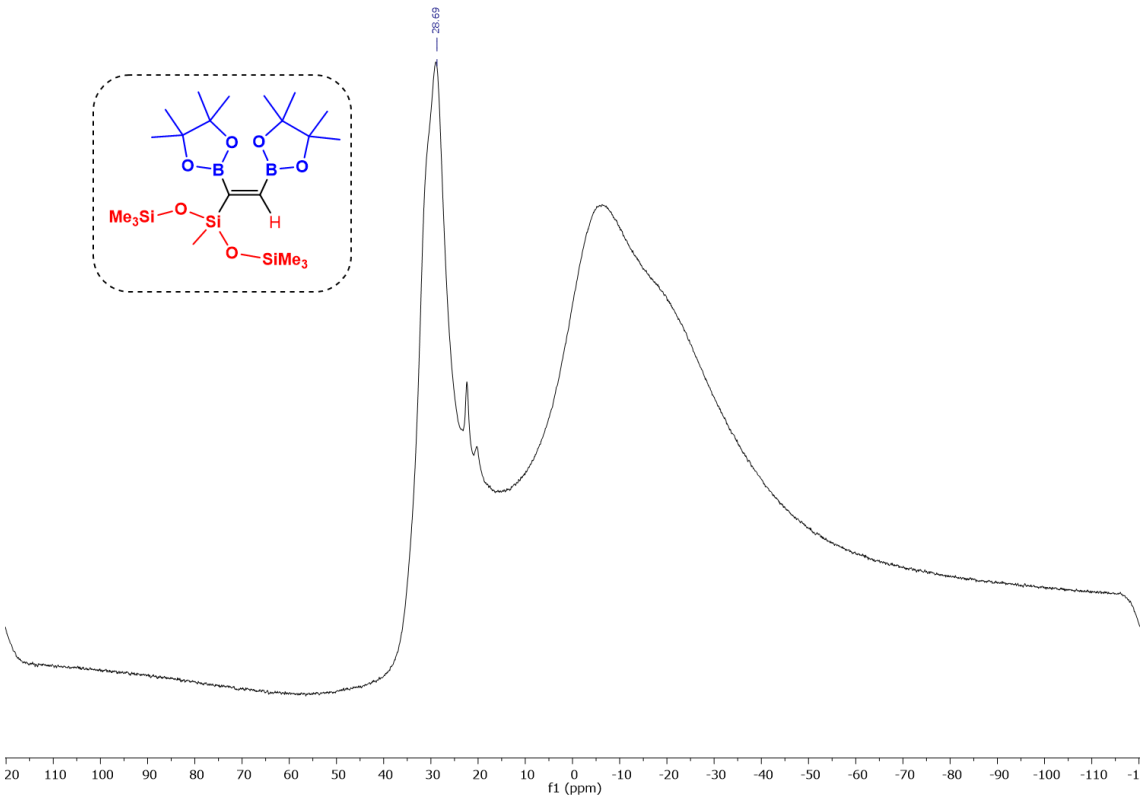


Figure S33. ^{11}B NMR of **3cb/4cb** mixture 96/4.

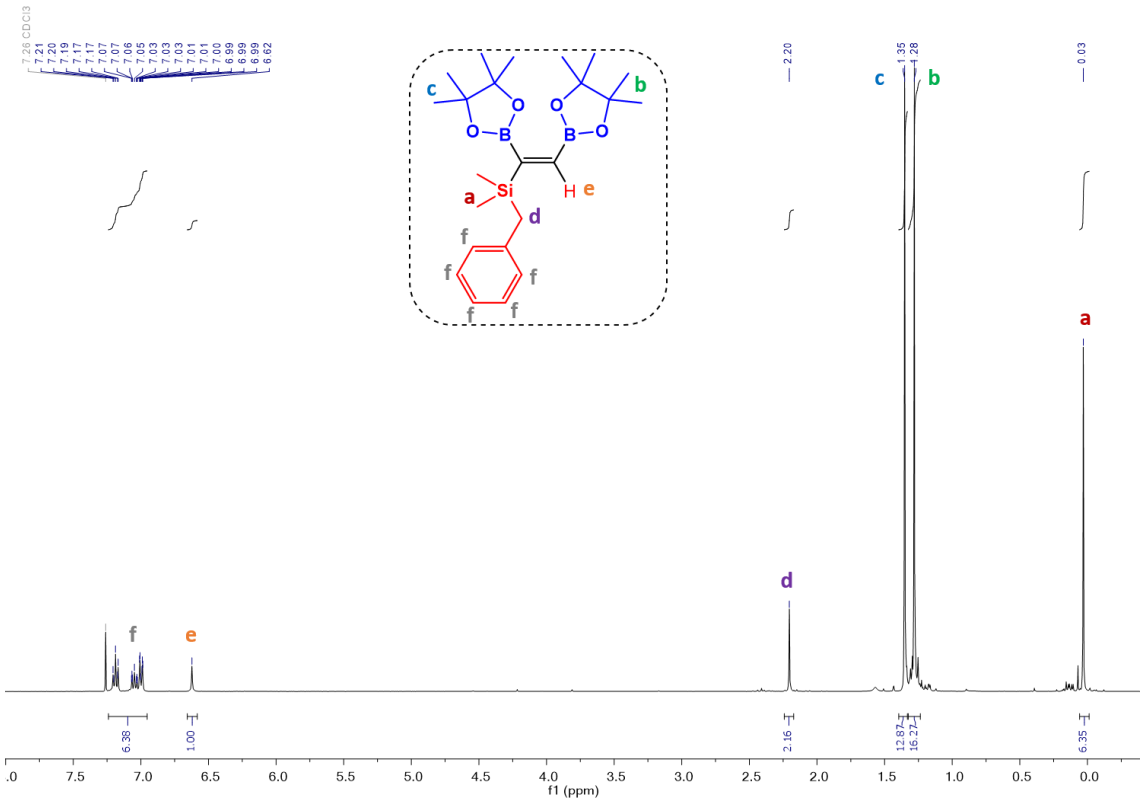


Figure S34. ^{1}H NMR of compound **3fb**.

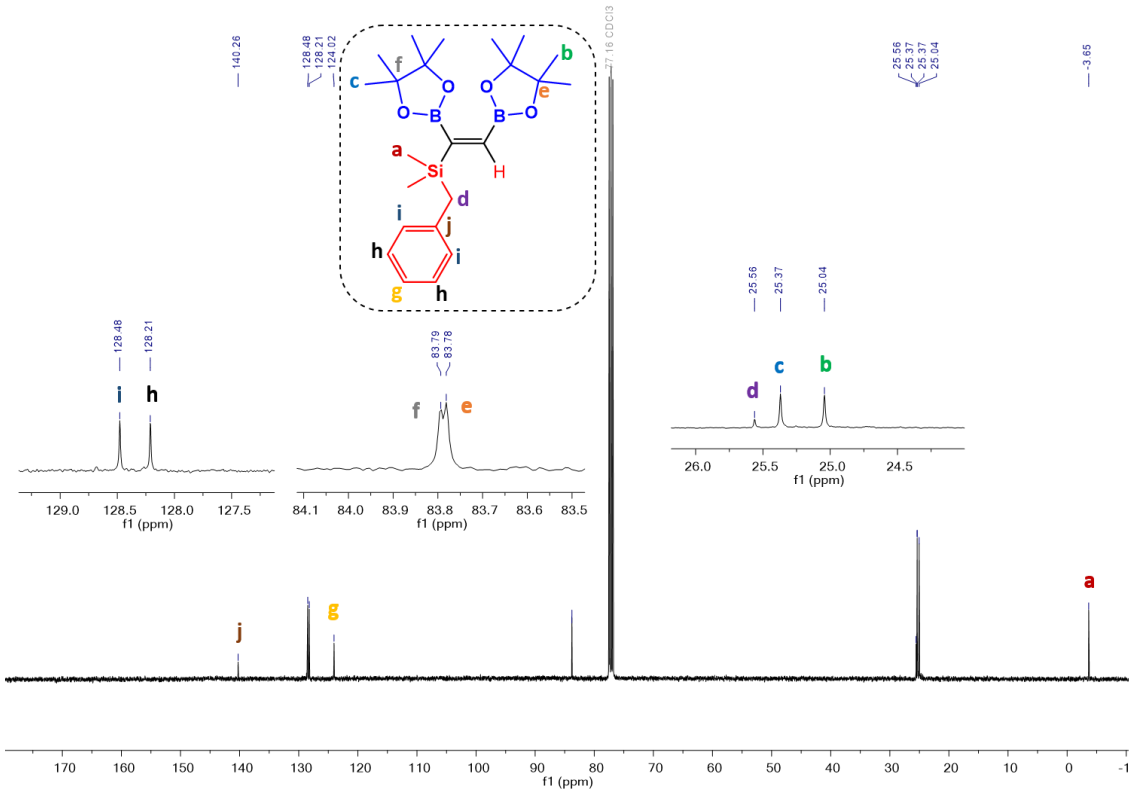


Figure S35. ^{12}C NMR of compound **3fb**.

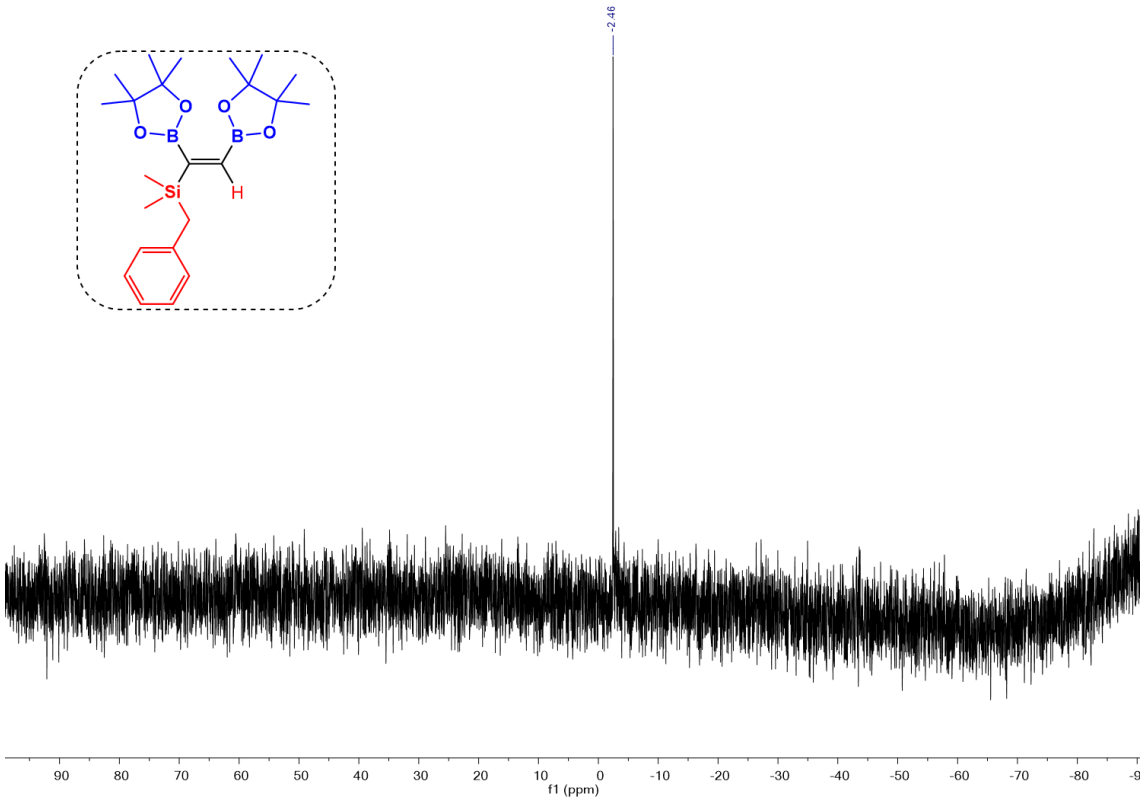


Figure S36. ^{29}Si NMR of compound **3fb**.

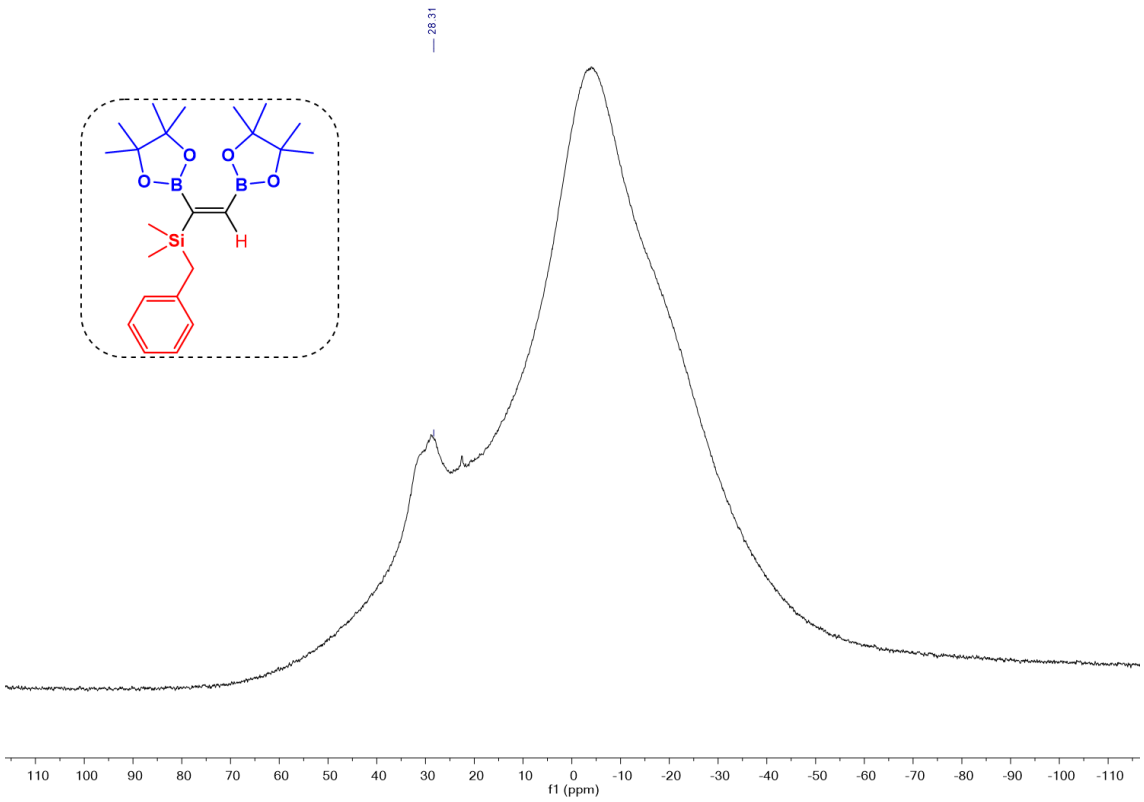


Figure S37. ^{11}B NMR of compound **3fb**.

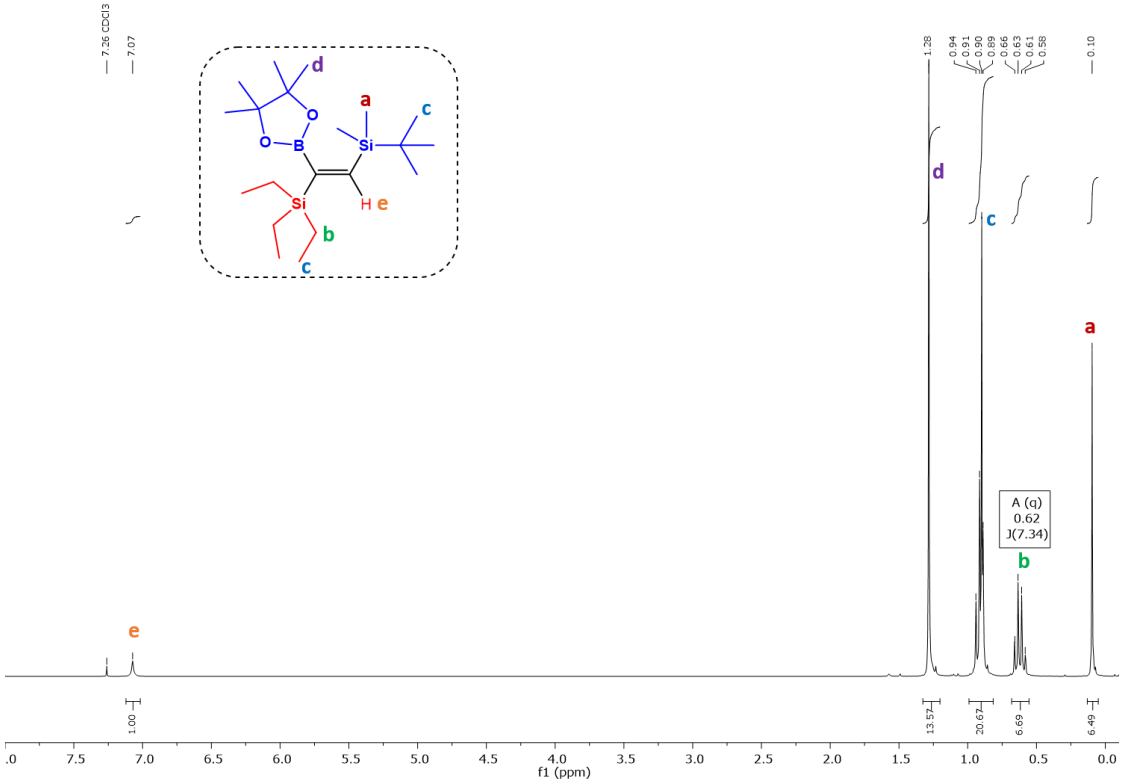


Figure S38. ^{1}H NMR of compound **4ac**.

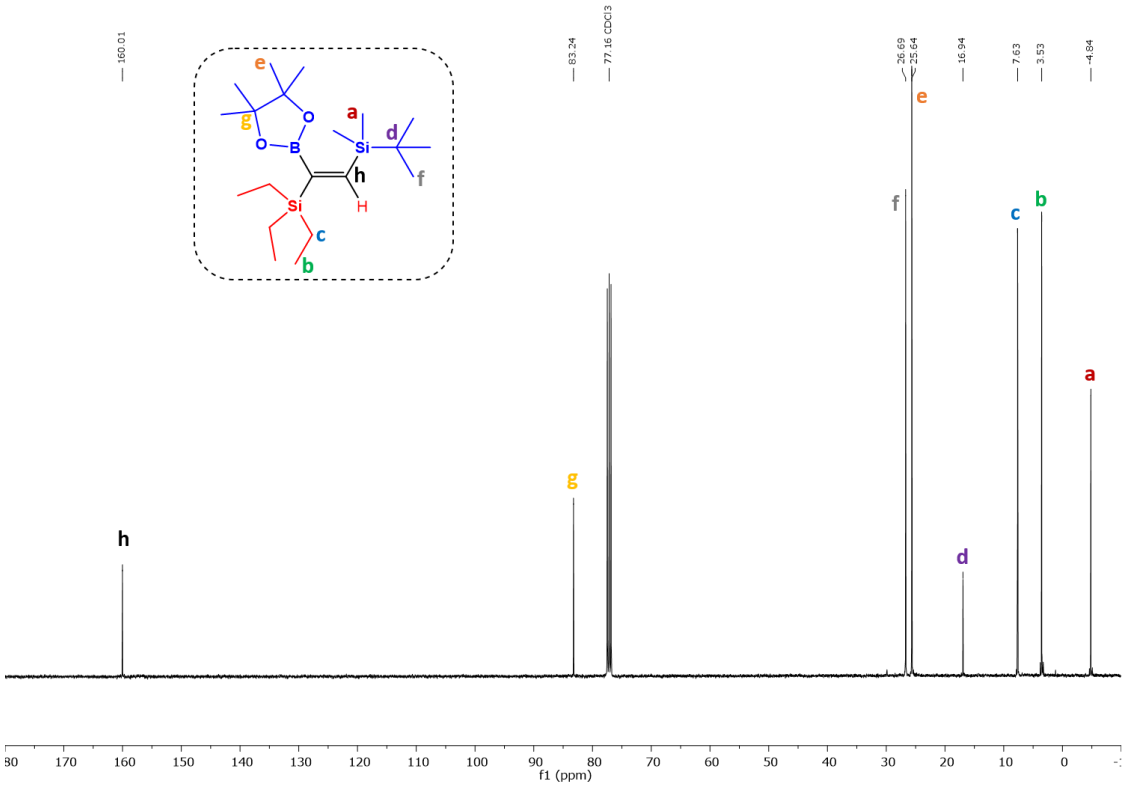


Figure S39. ^{13}C NMR of compound **4ac**.

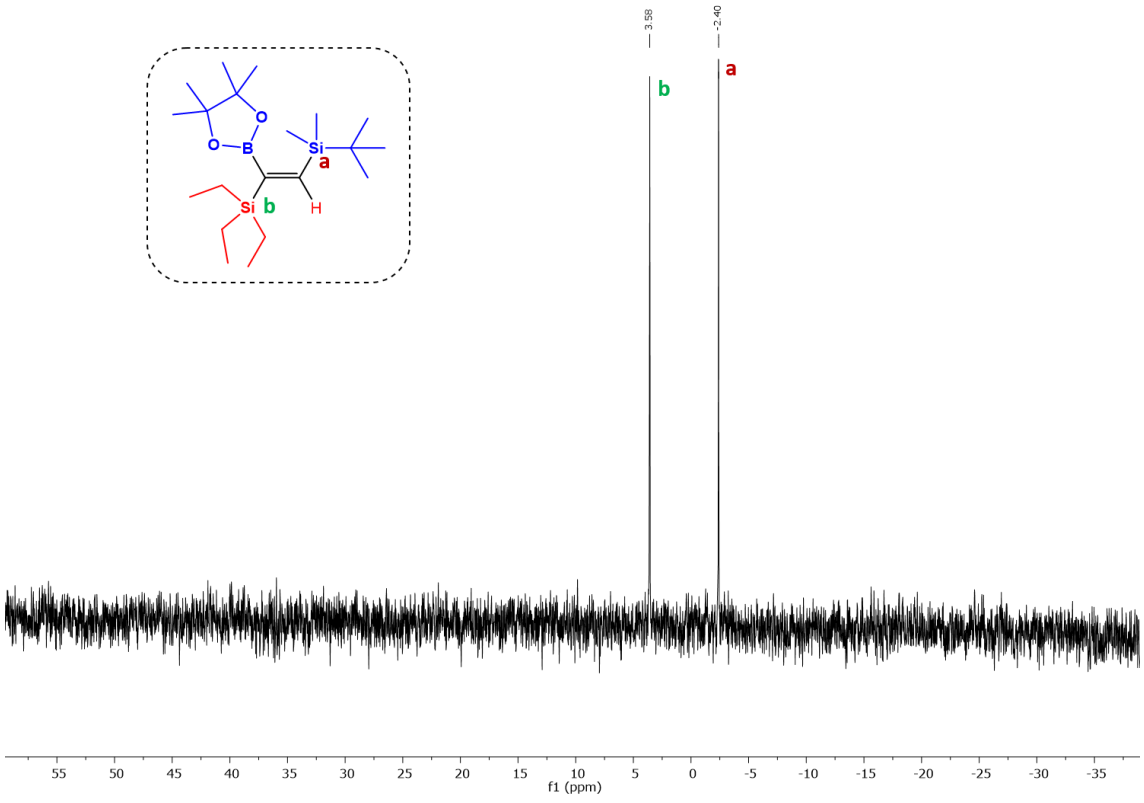


Figure S40. ^{29}Si NMR of compound **4ac**.

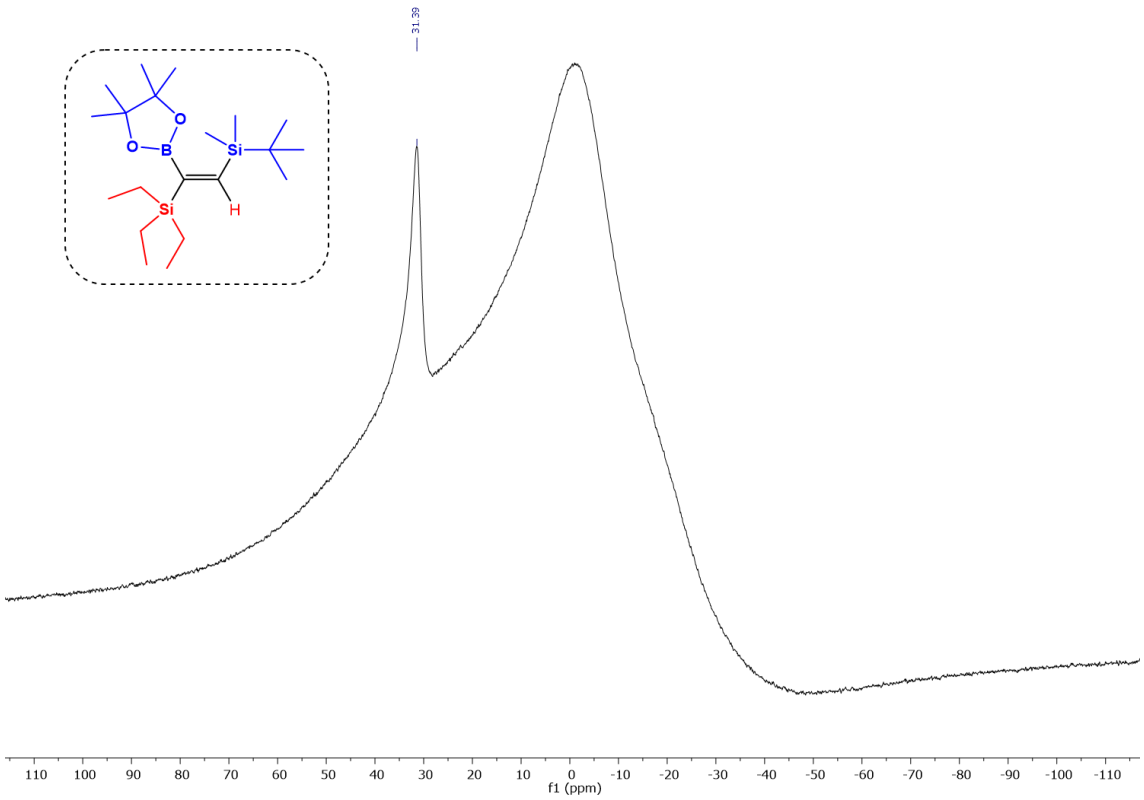


Figure S41. ^{11}B NMR of compound **4ac**.

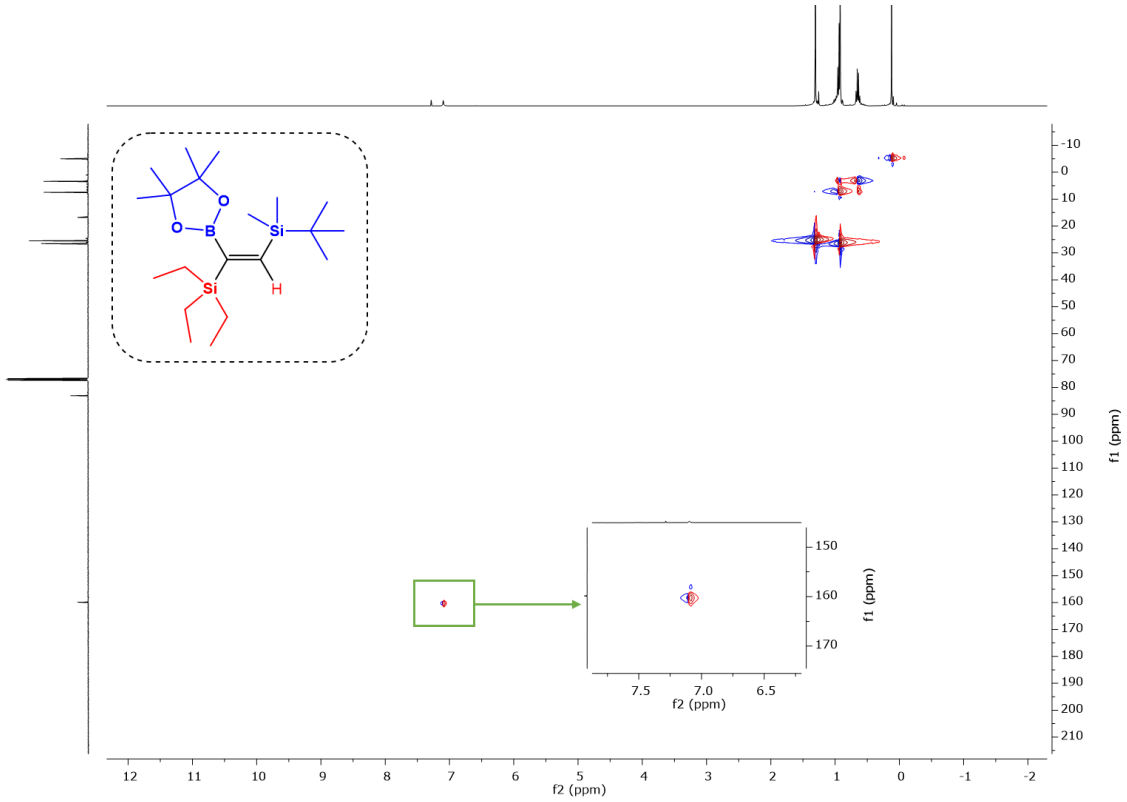


Figure S42. ^{1}H - ^{13}C HSQC of compound **4ac**.

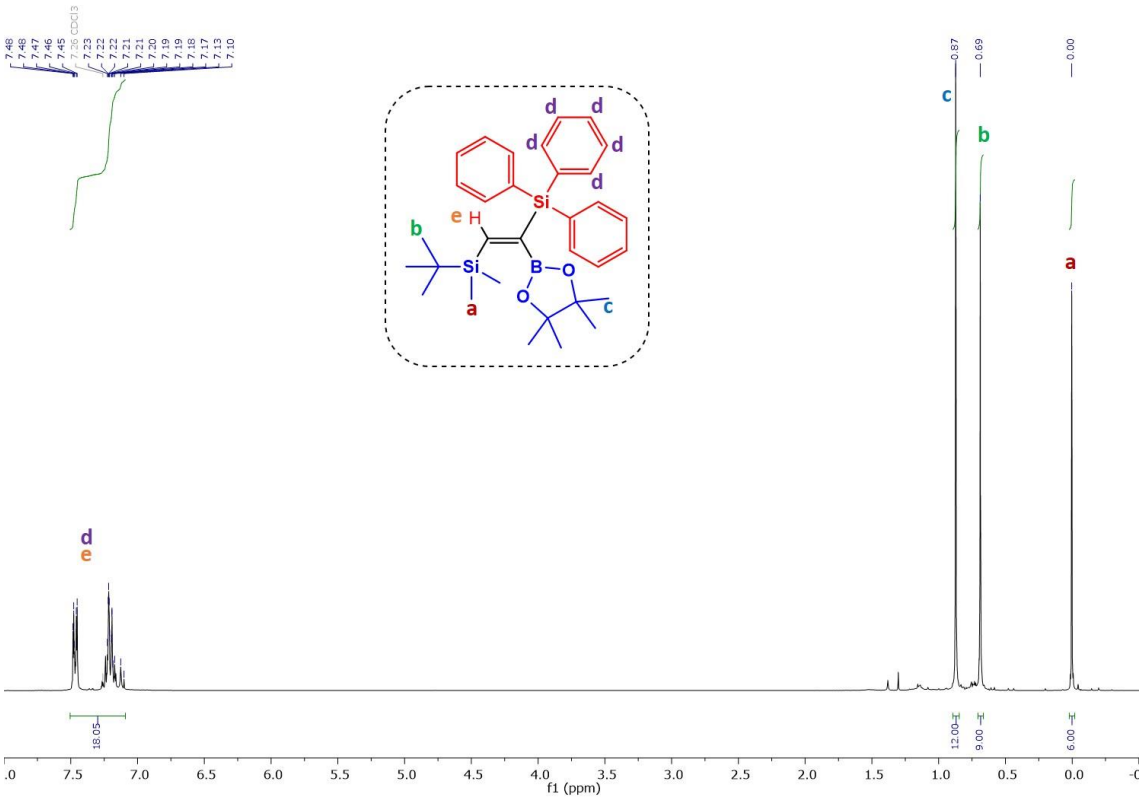


Figure S43. ^{1}H NMR of compound **4bc**.

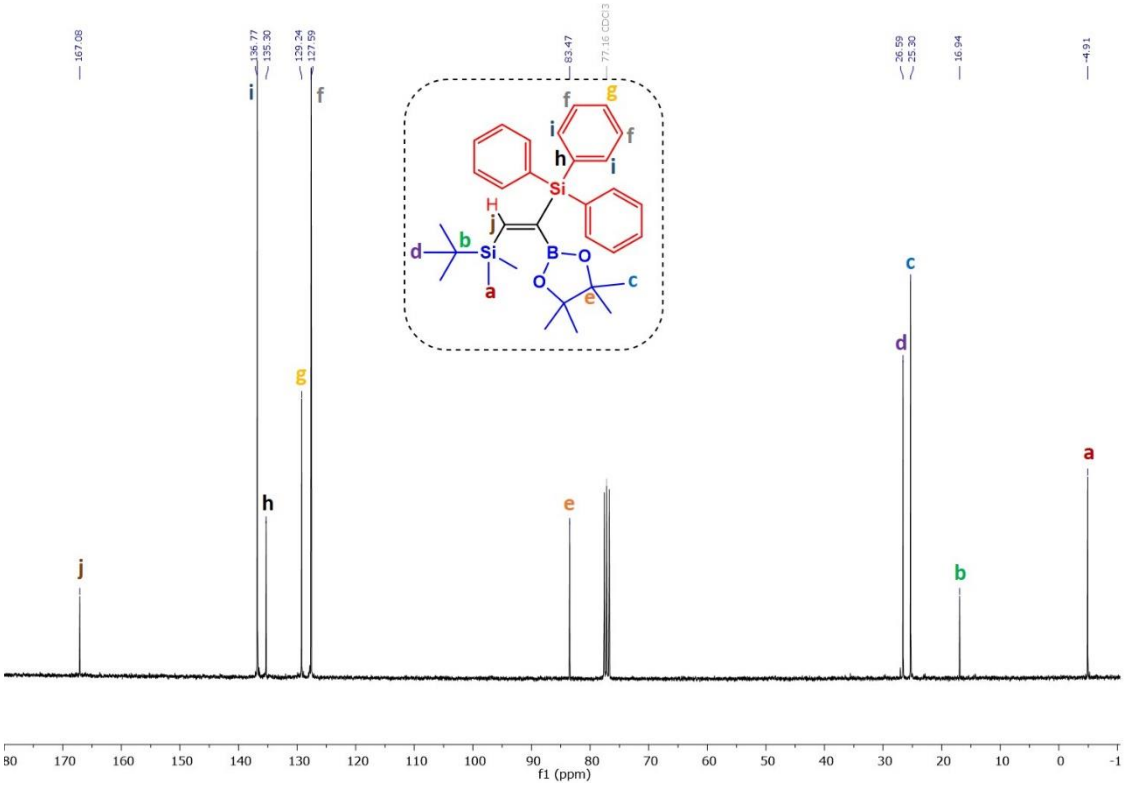


Figure S44.^{13}C NMR of compound **4bc**.

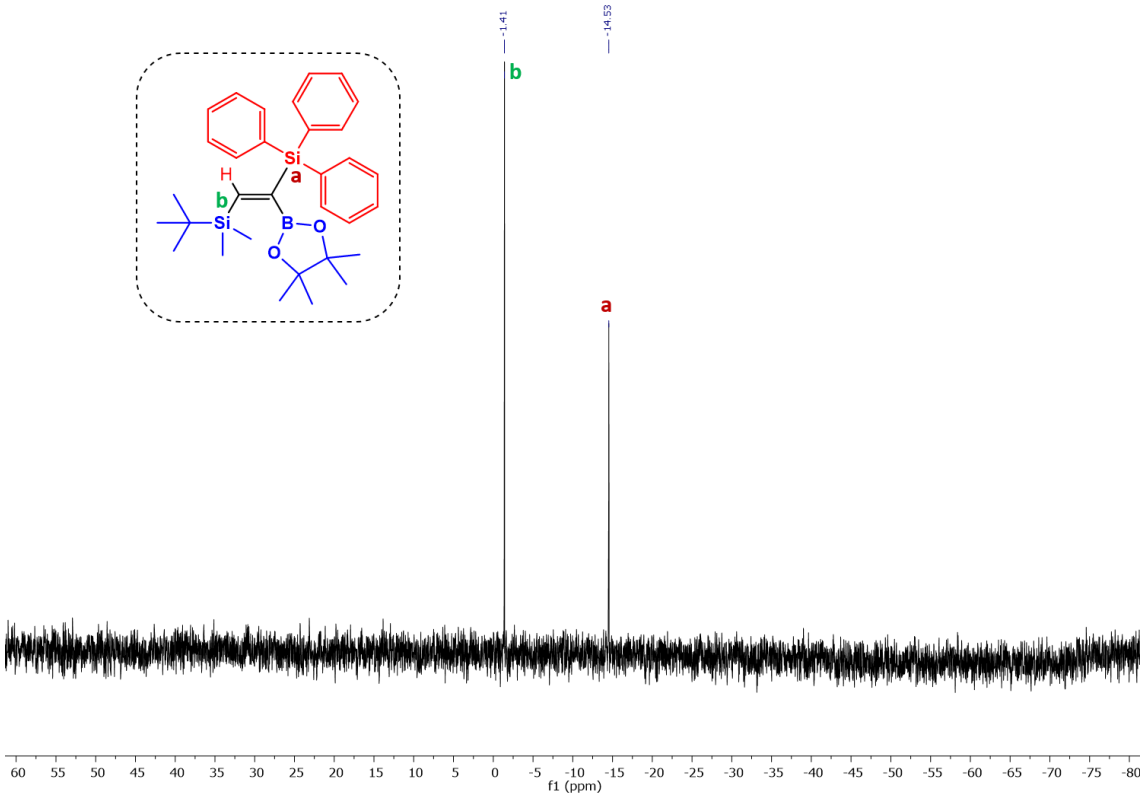


Figure S45. ^{29}Si NMR of compound **4bc**.

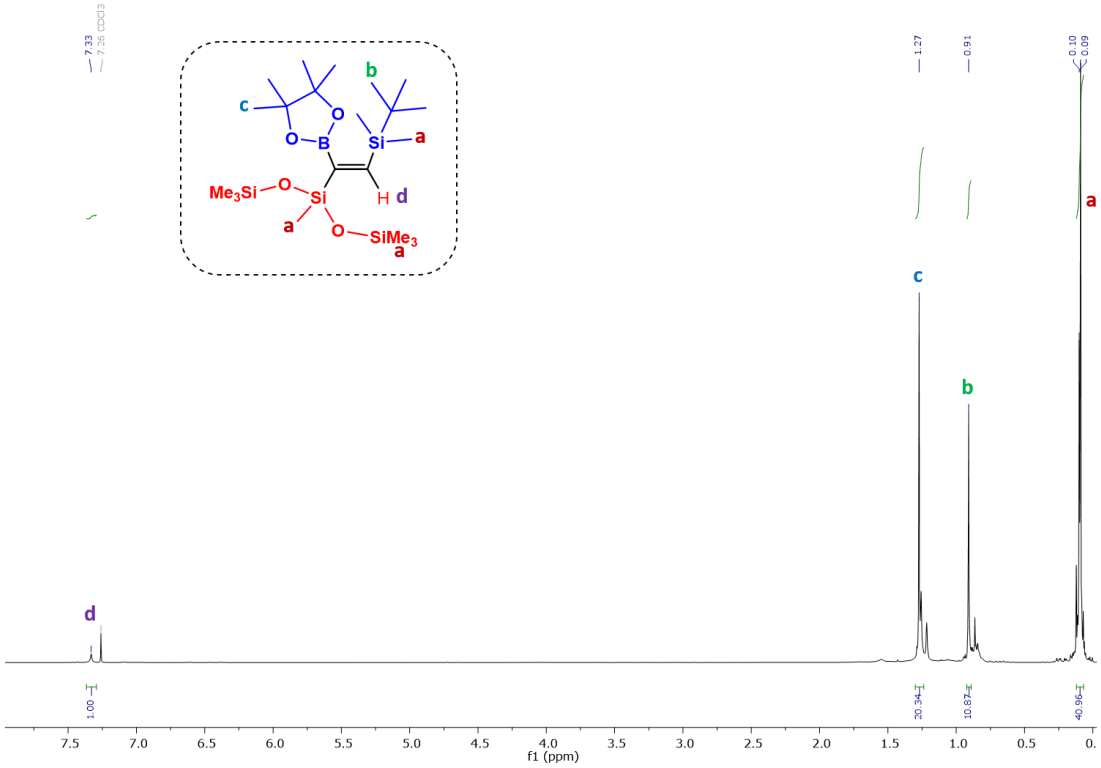


Figure S46. ^{1}H NMR of **3cc**/**4cc** mixture 5/95.

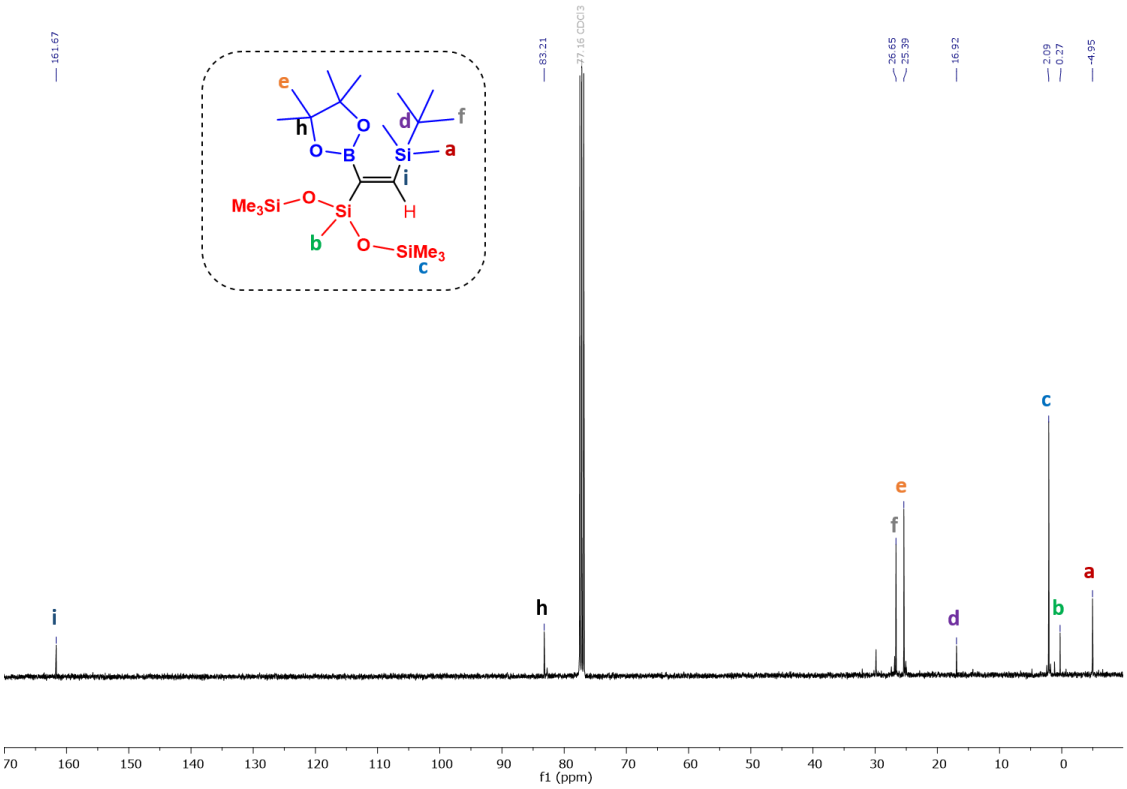


Figure S47. ^{13}C NMR of **3cc**/**4cc** mixture 5/95.

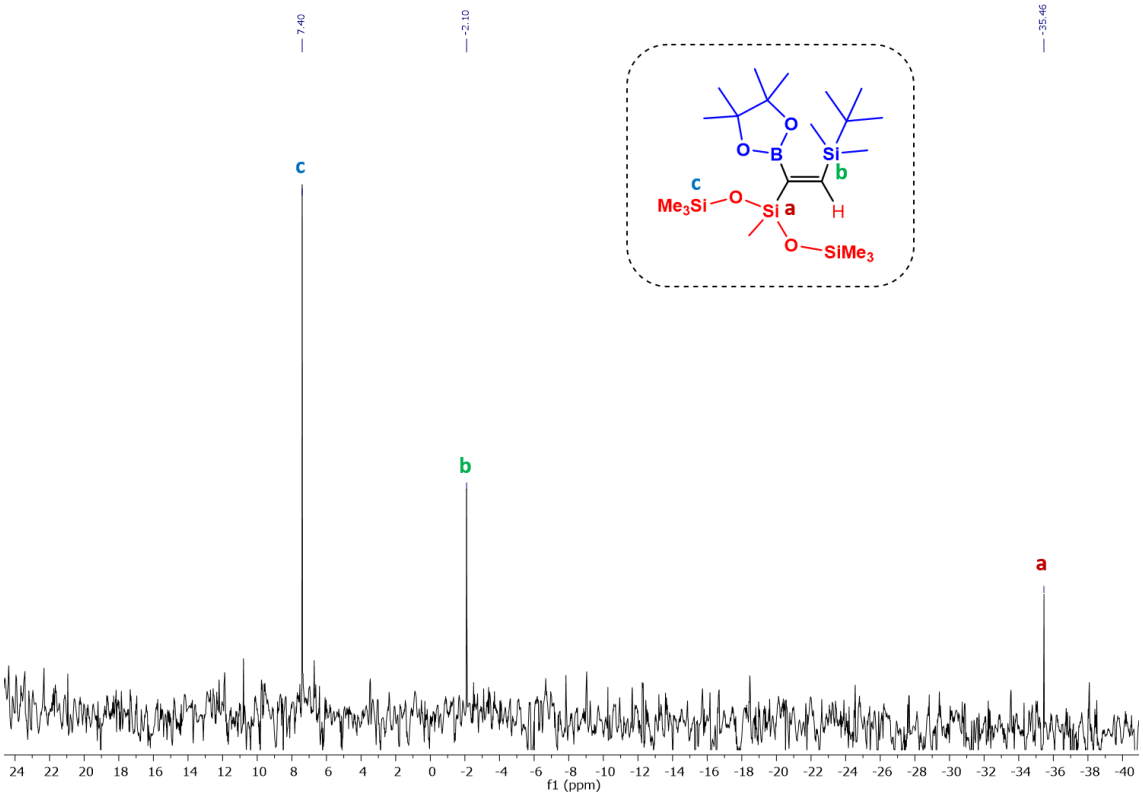


Figure S48. ^{29}Si NMR of **3cc**/**4cc** mixture 5/95.

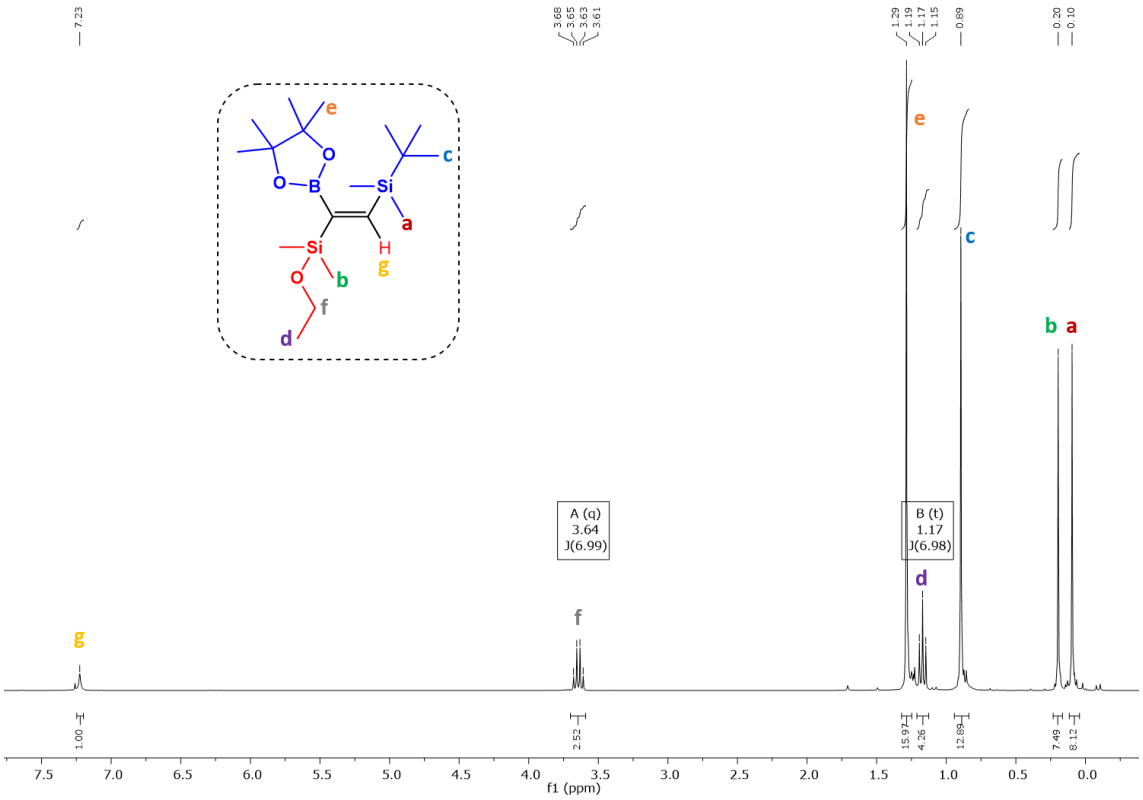


Figure S49. ^{1}H NMR of compound **4dc**.

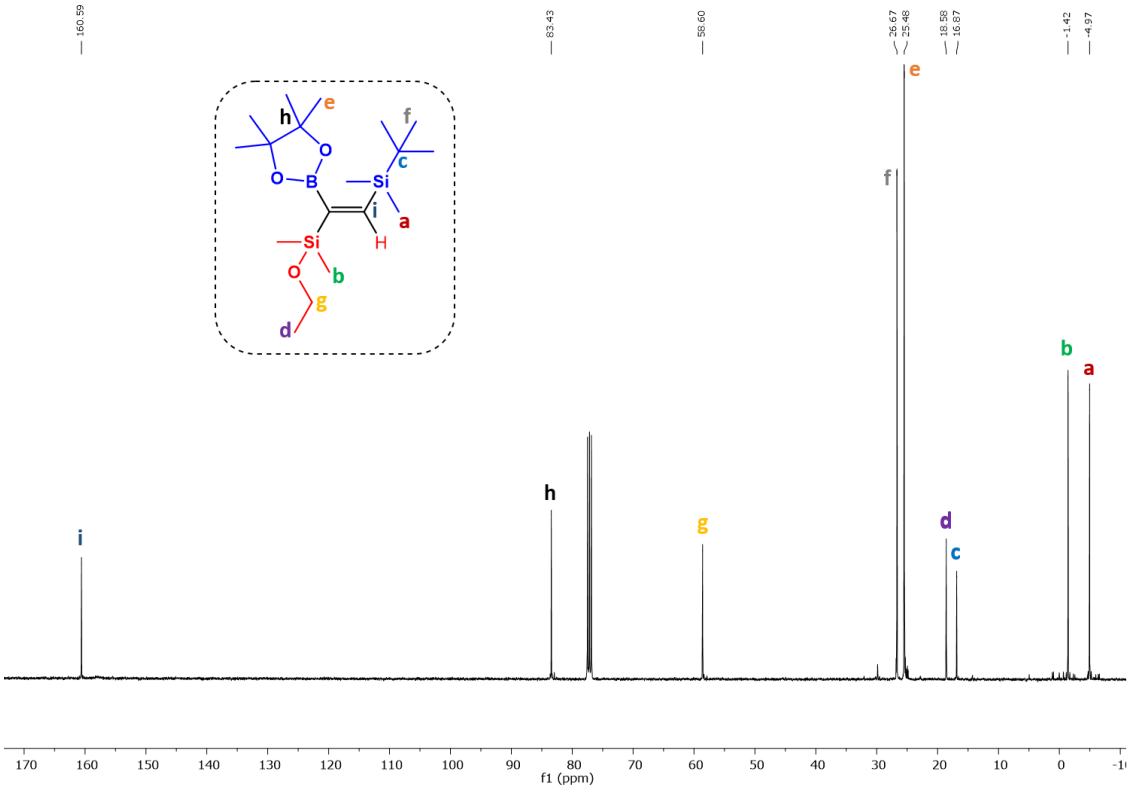


Figure S50. ^{13}C NMR of compound **4dc**.

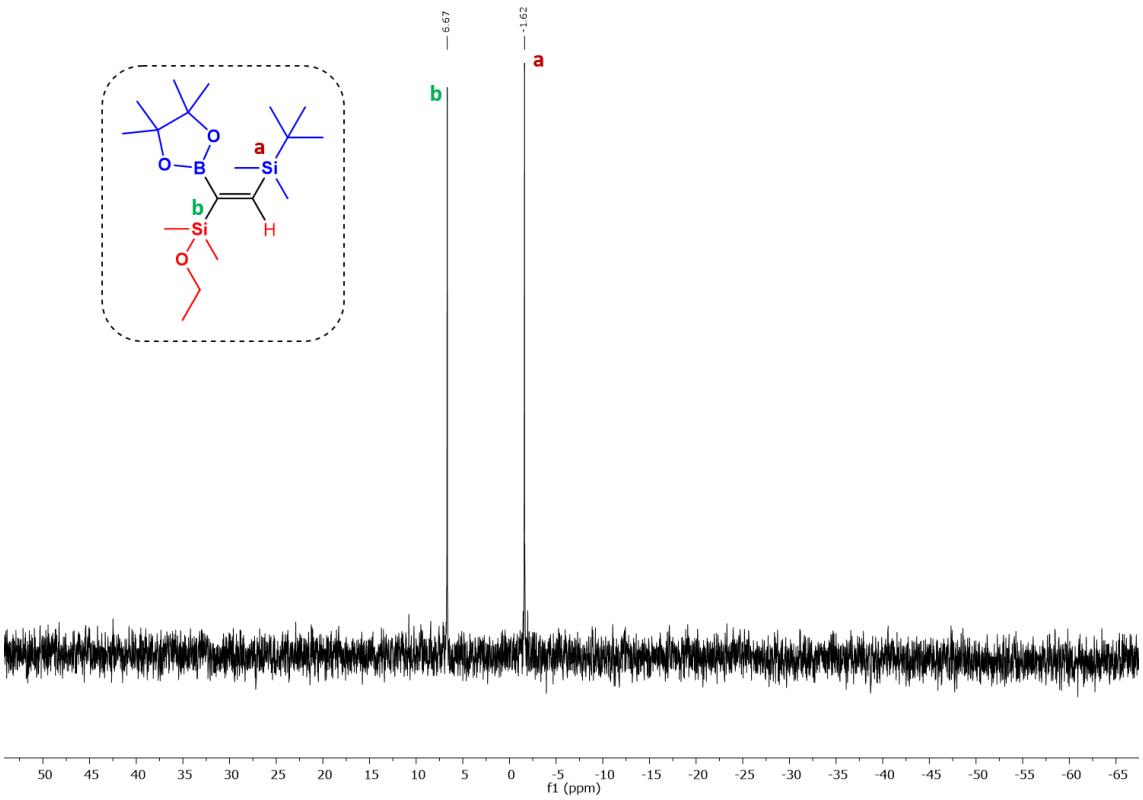


Figure S51. ^{29}Si NMR of compound **4dc**.

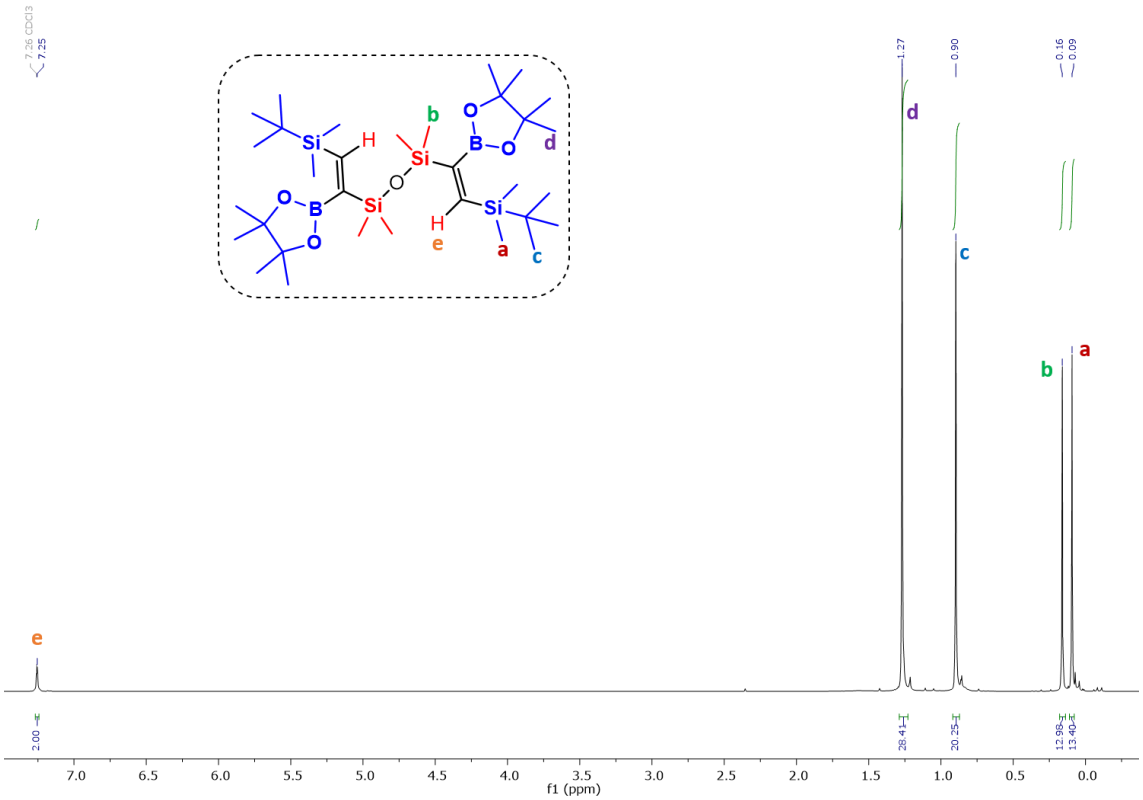


Figure S52. ^{1}H NMR of compound **6dc**.

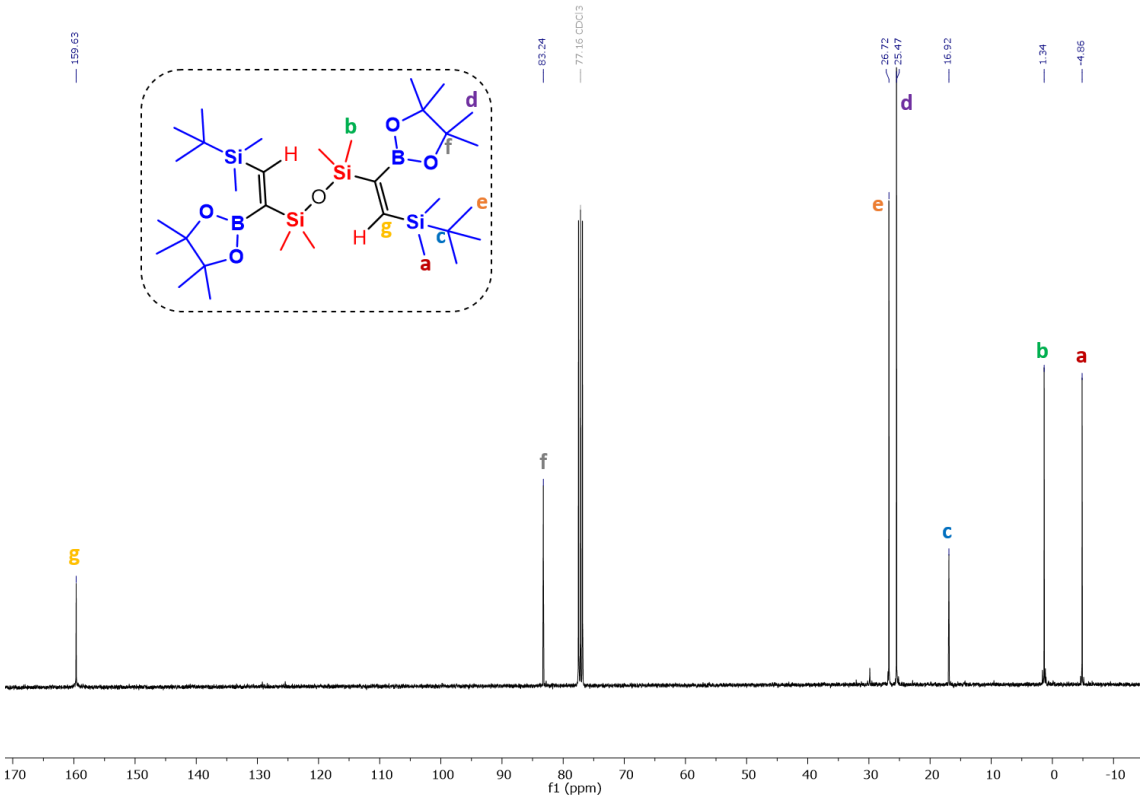


Figure S53. ^{13}C NMR of compound **6dc**.

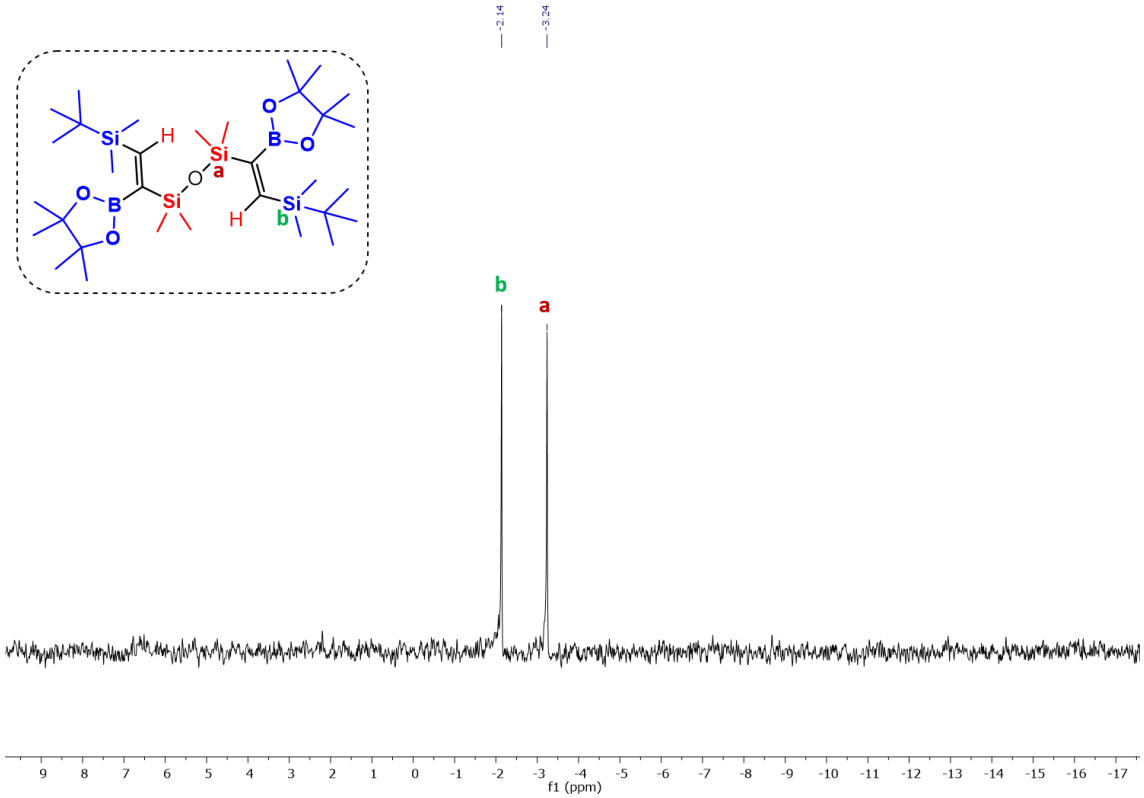


Figure S54. ^{29}Si NMR of compound **6dc**.

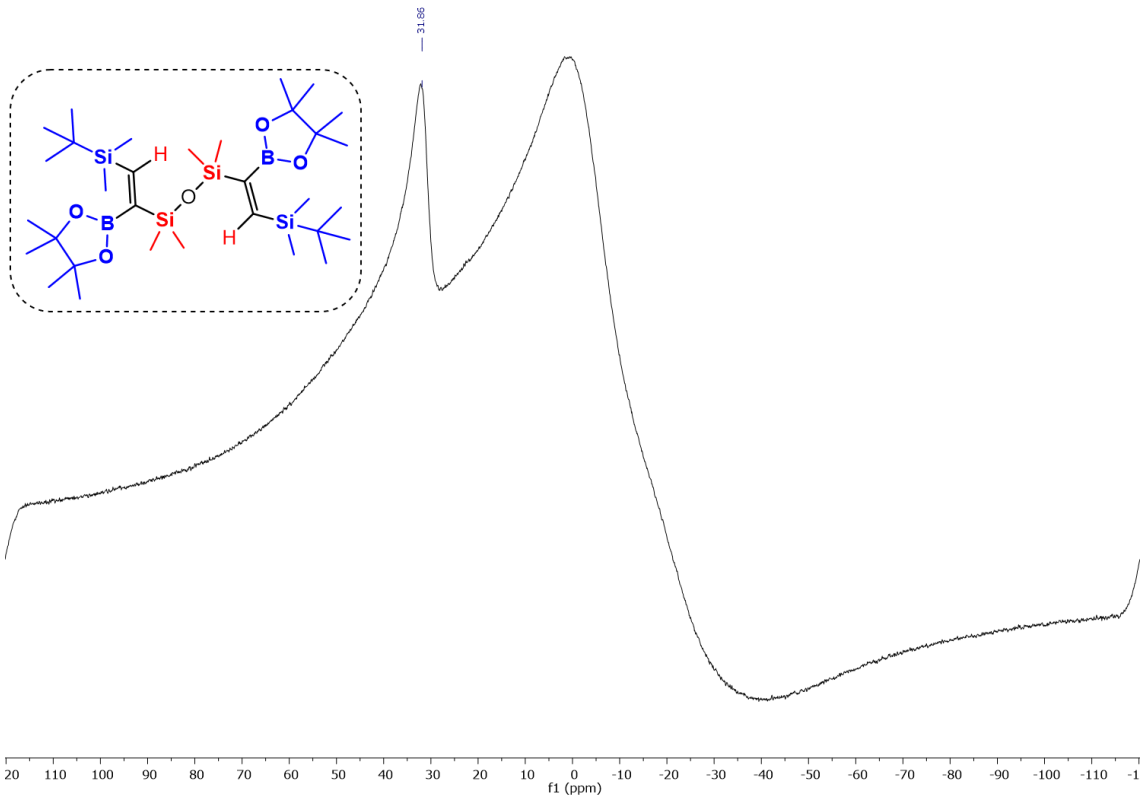


Figure S55. ^{11}B NMR of compound **6dc**.

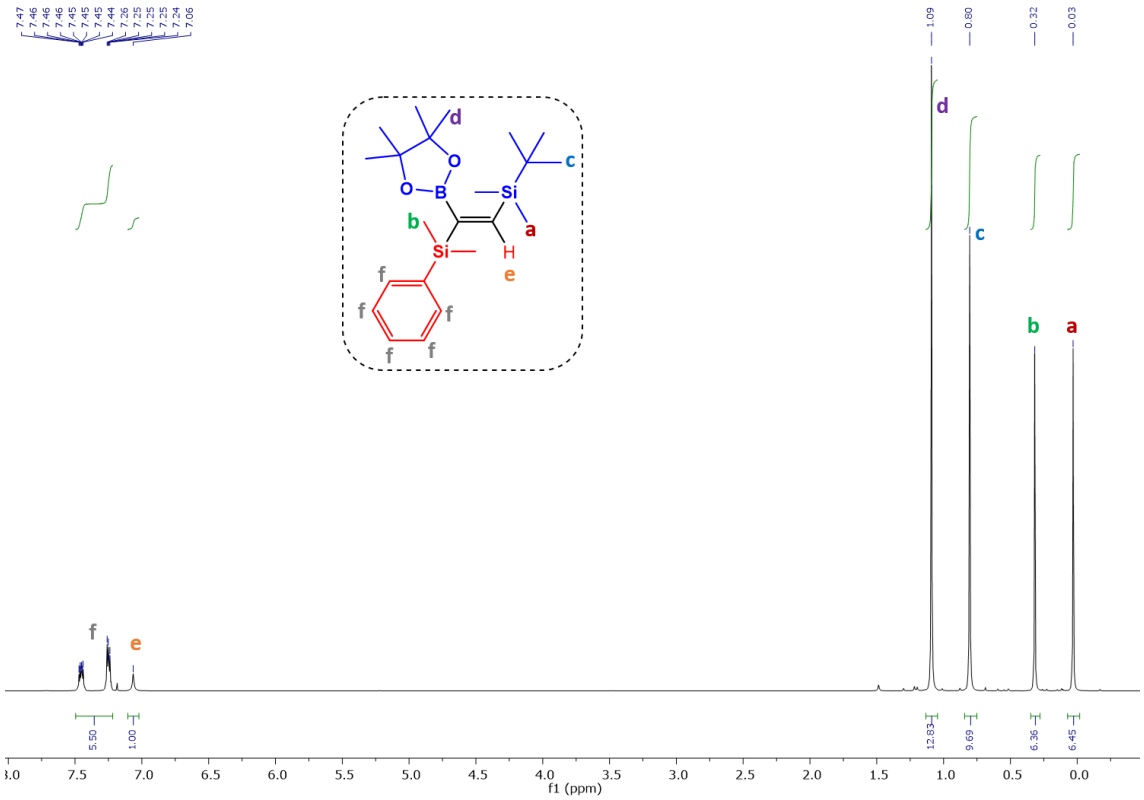


Figure S56. ^{1}H NMR of compound **4ec**.

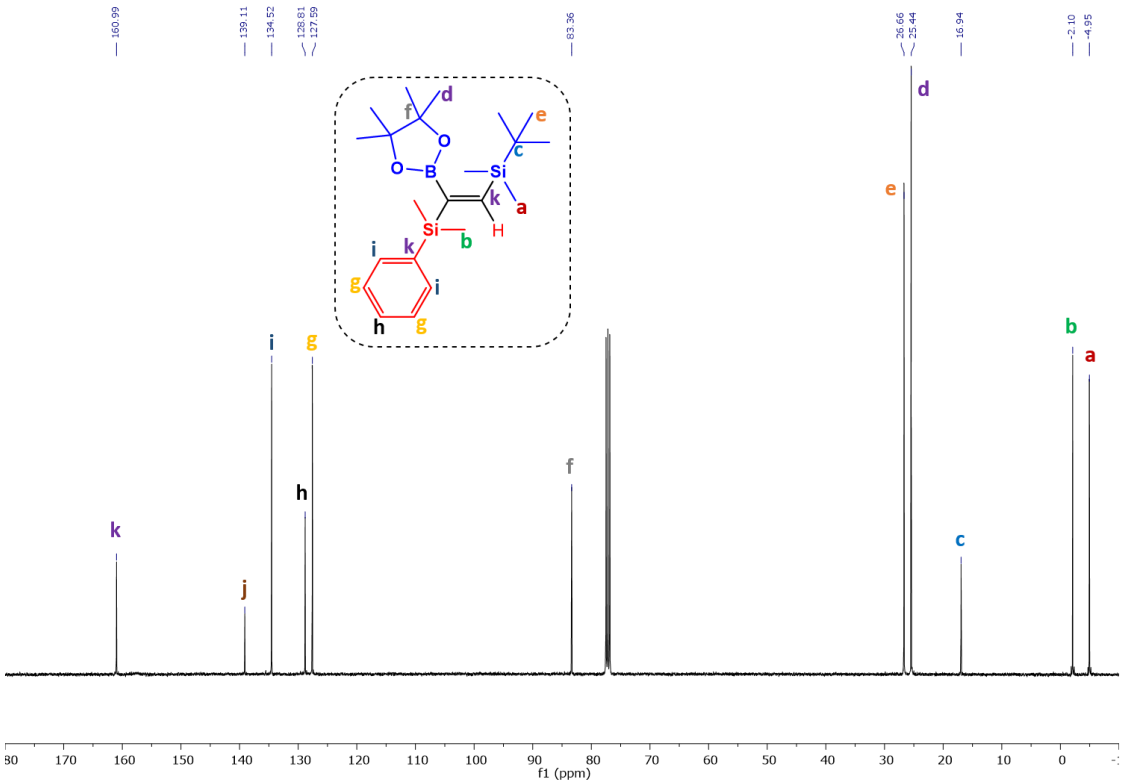


Figure S57. ^{13}C NMR of compound **4ec**.

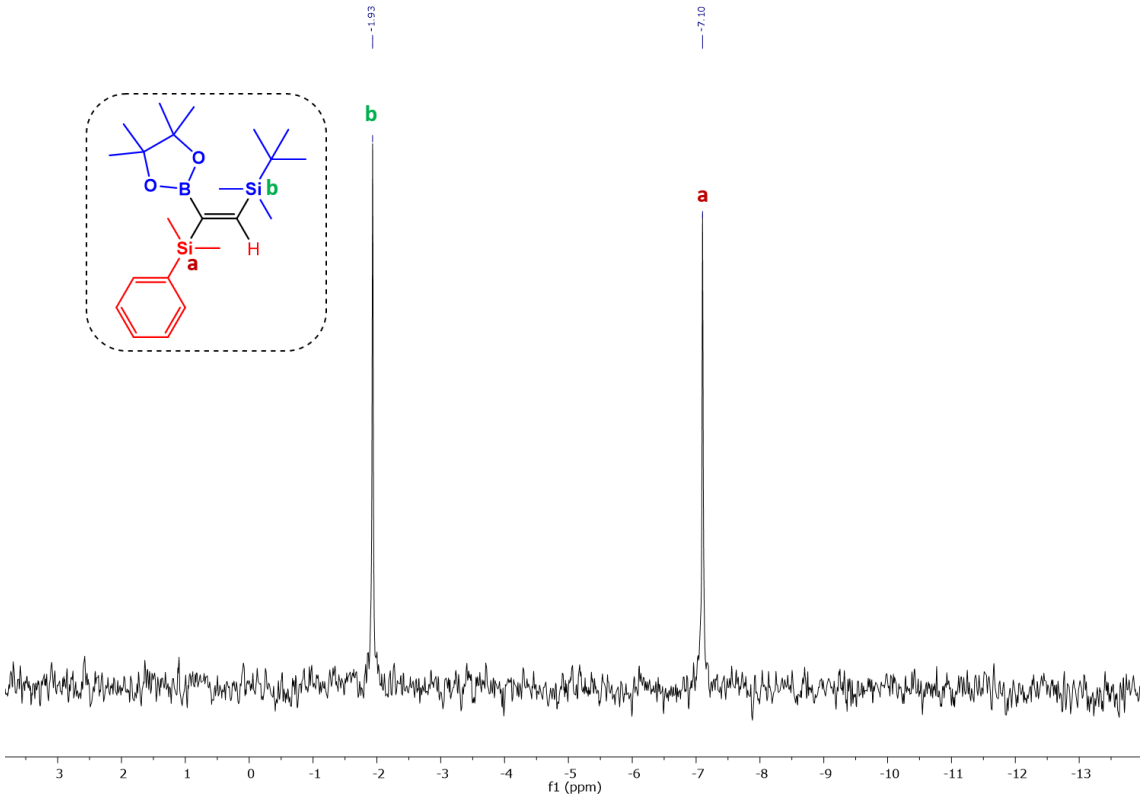


Figure S58. ^{29}Si NMR of compound **4ec**.

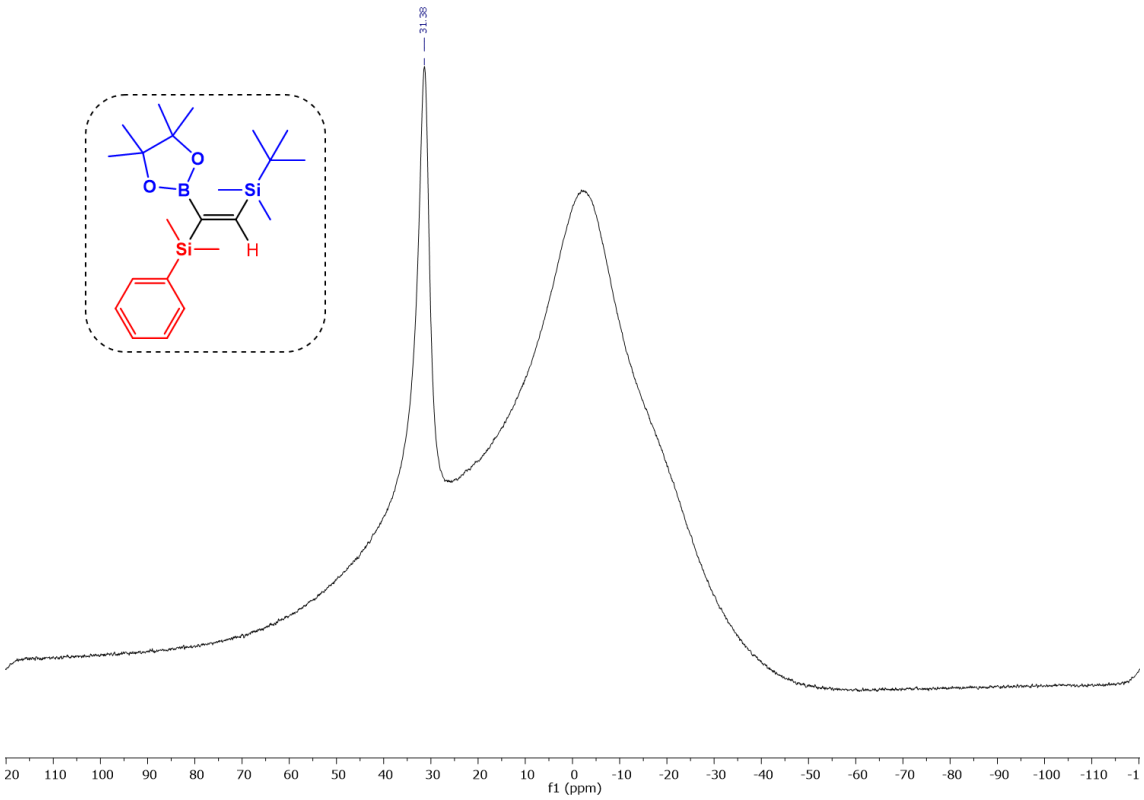


Figure S59. ^{11}B NMR of compound **4ec**.

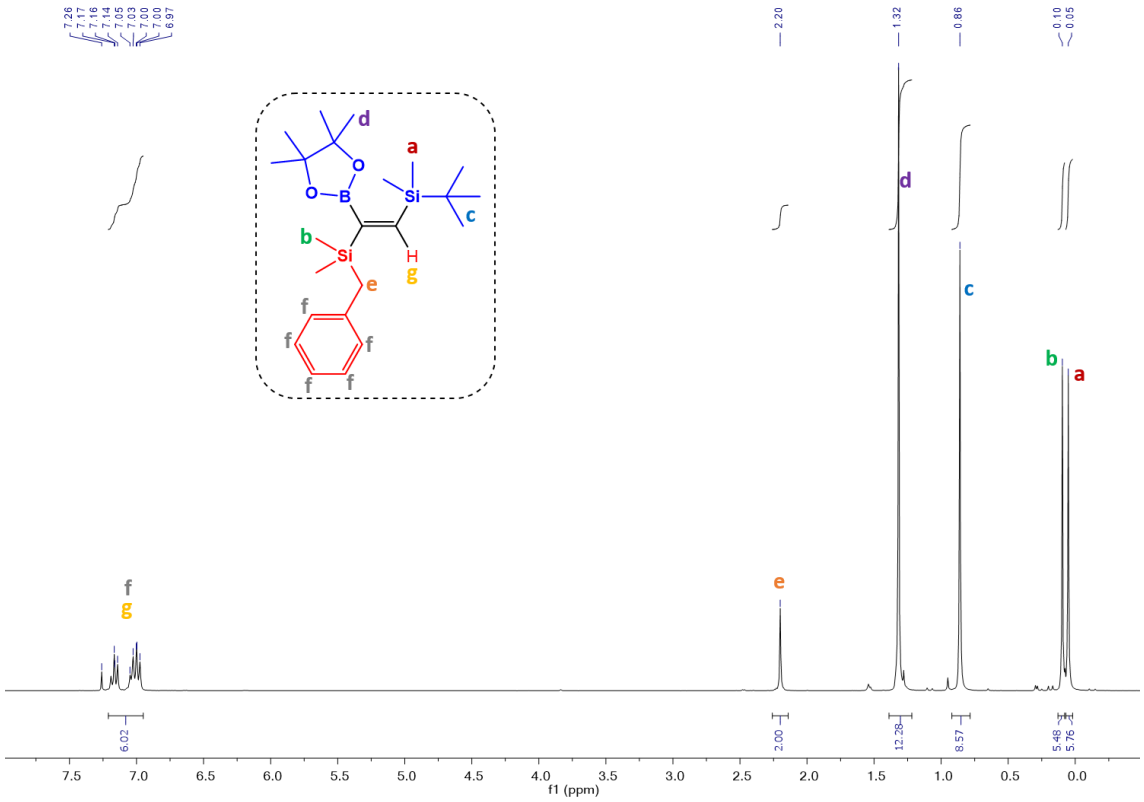


Figure S60. ^{1}H NMR of compound **4fc**.

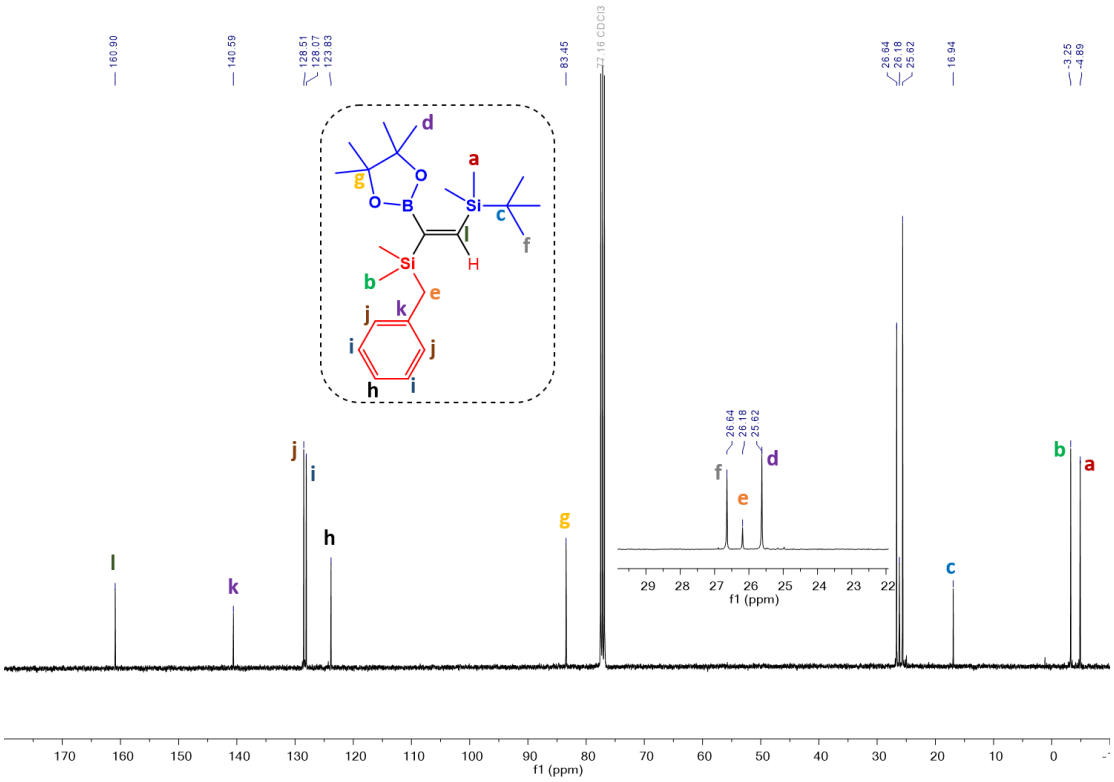


Figure S61. ^{13}C NMR of compound **4fc**.

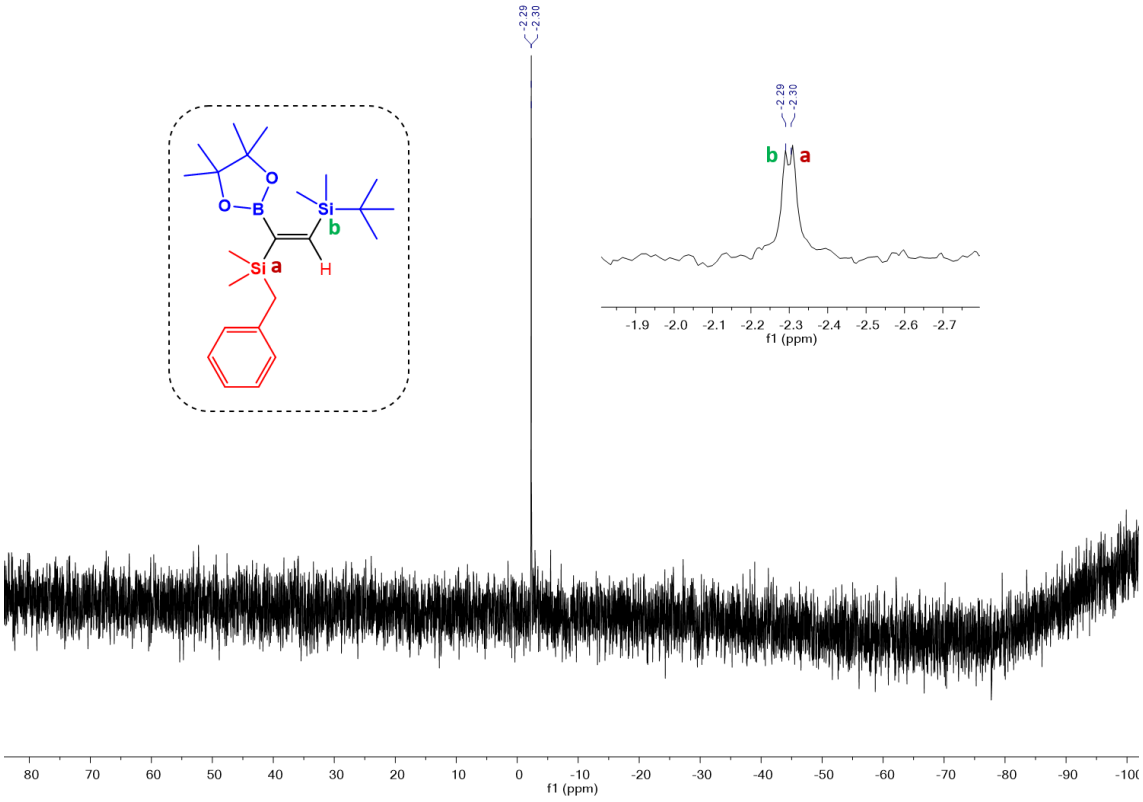


Figure S62. ^{29}Si NMR of compound **4fc**.

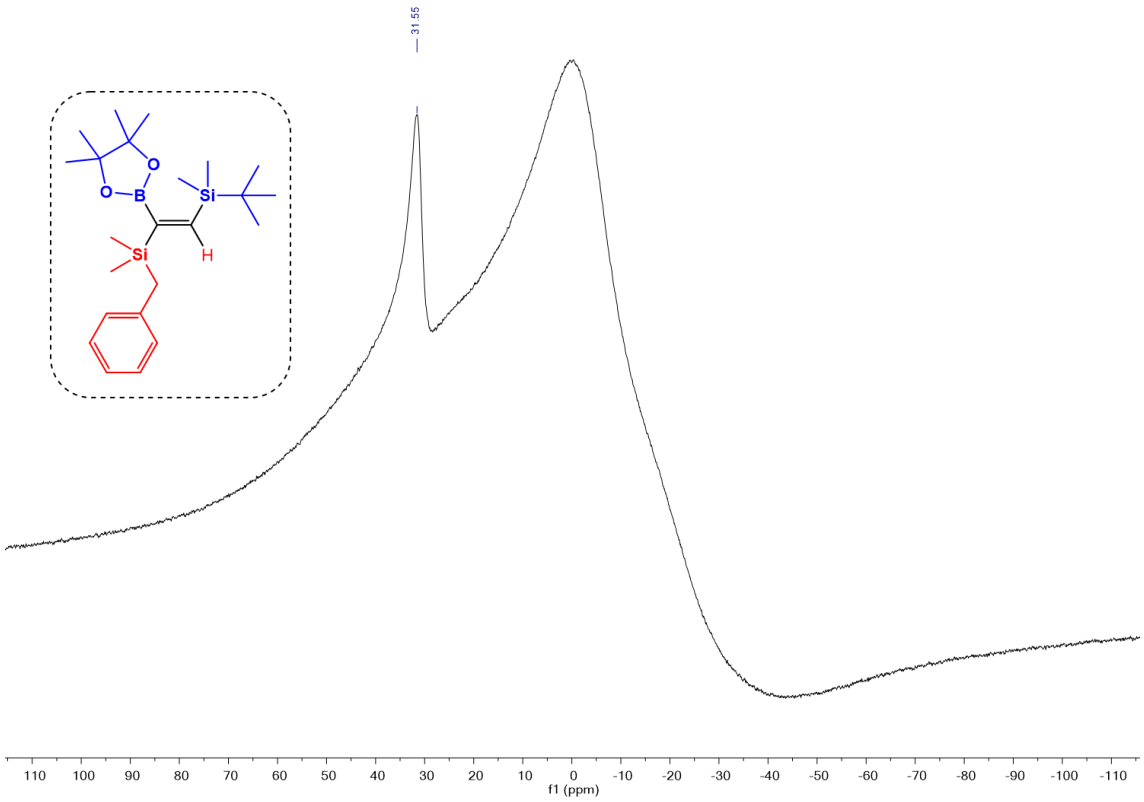


Figure S63. ^{11}B NMR of compound **4fc**.

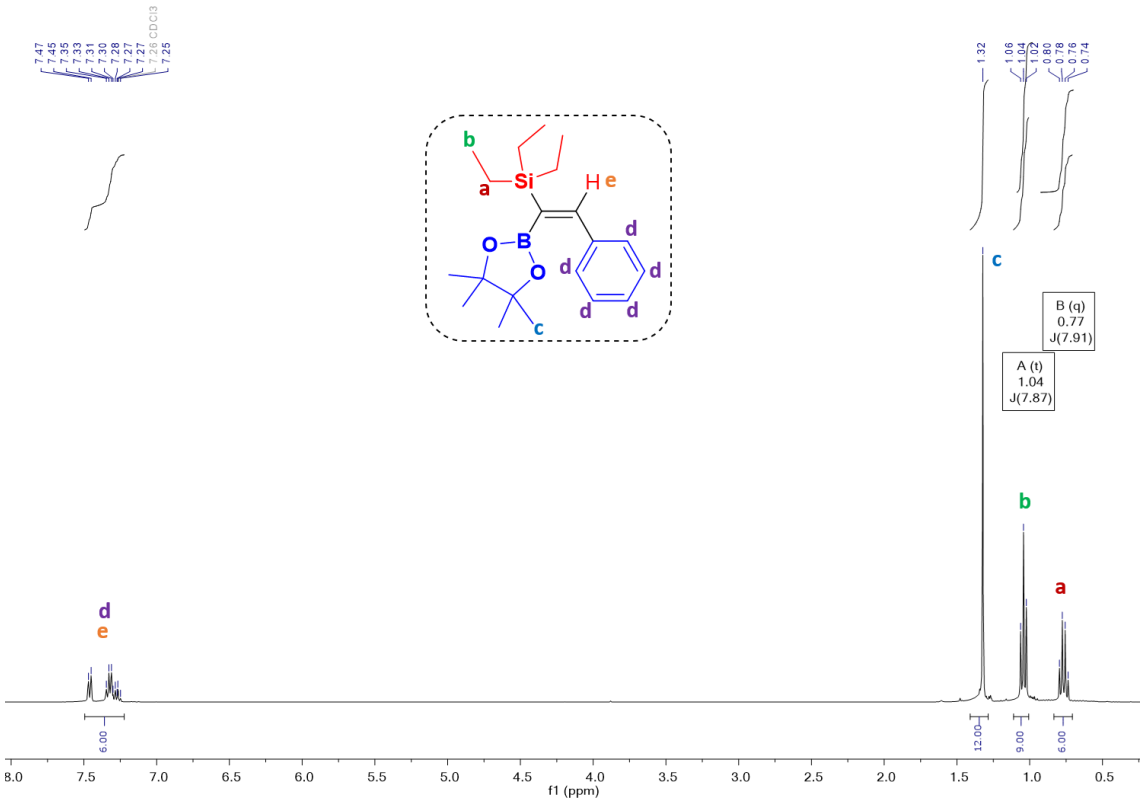


Figure S64.^{1}H NMR of compound **4ad**.

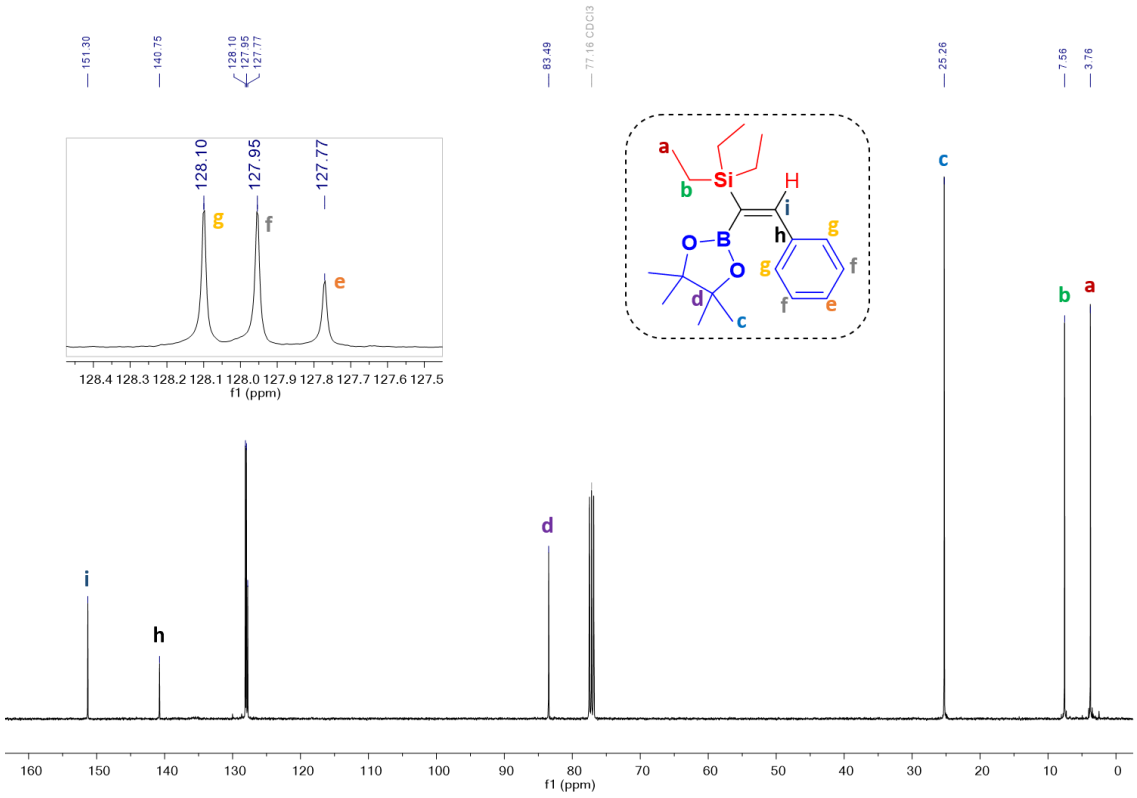


Figure S65.[13]C NMR of compound **4ad**.

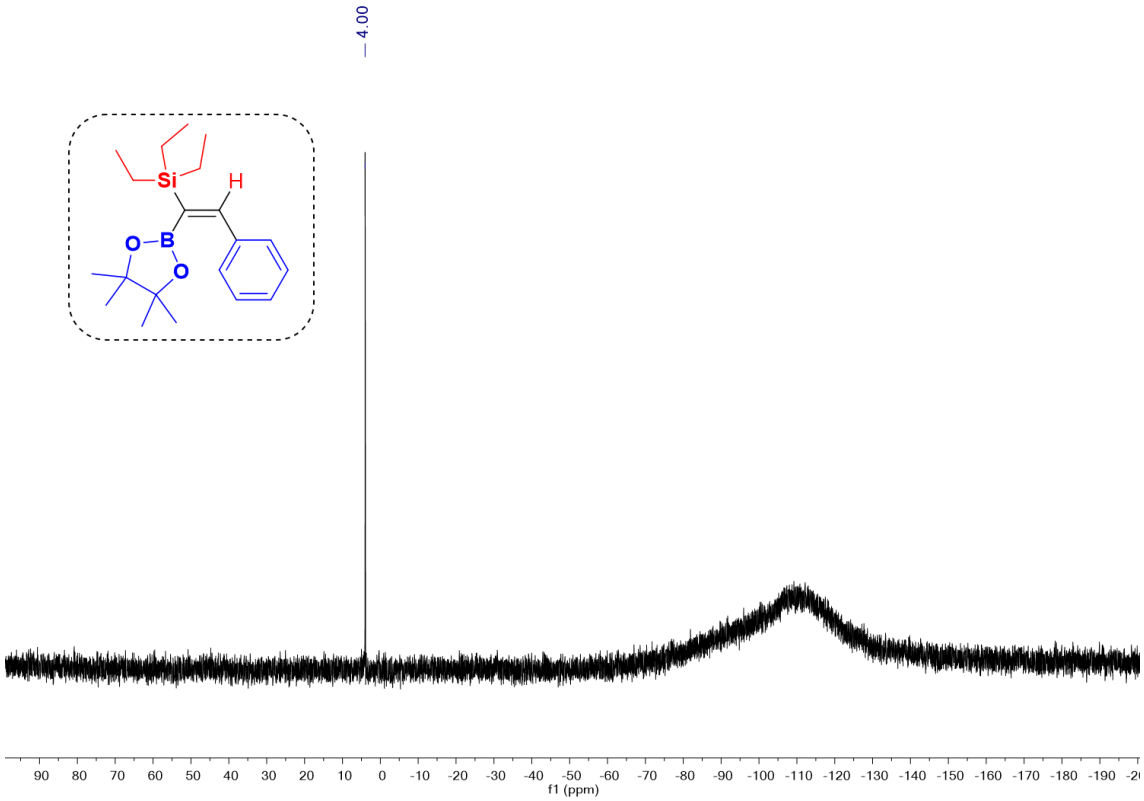


Figure S66.[29]Si NMR of compound **4ad**.

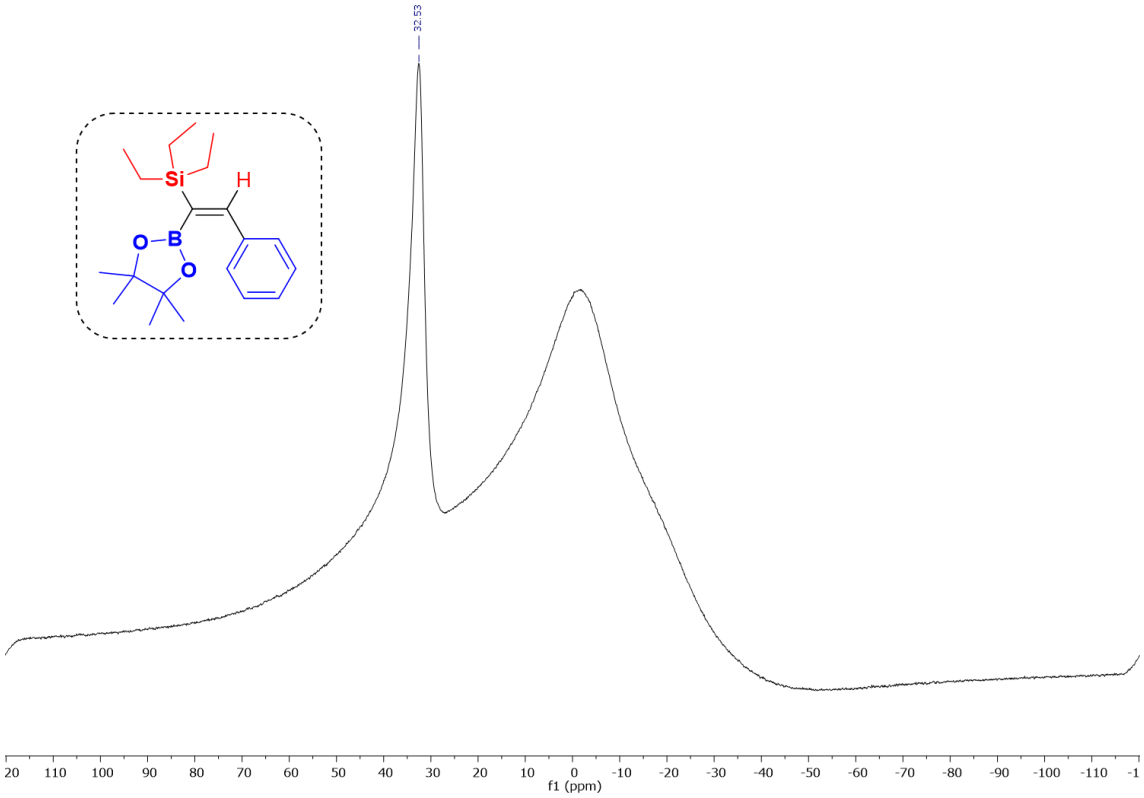


Figure S67. ^{11}B NMR of compound **4ad**.

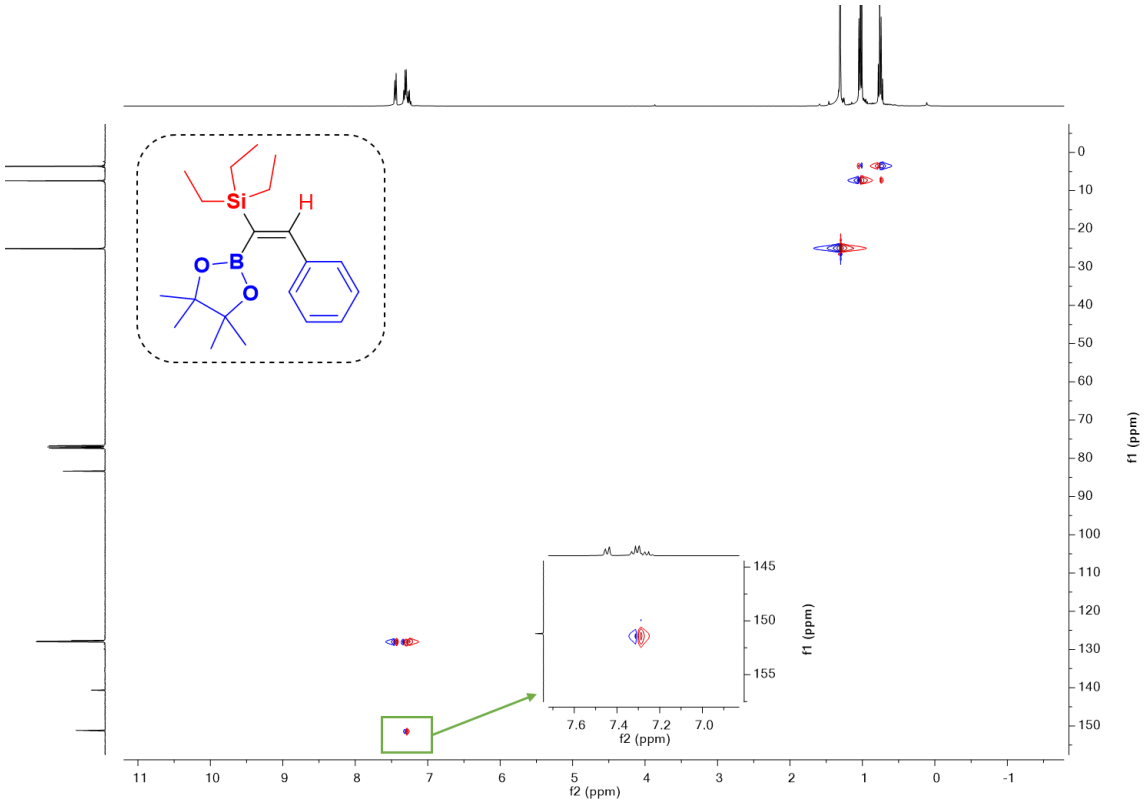


Figure S68. ^{1}H – ^{13}C HSQC of compound **4ad**.

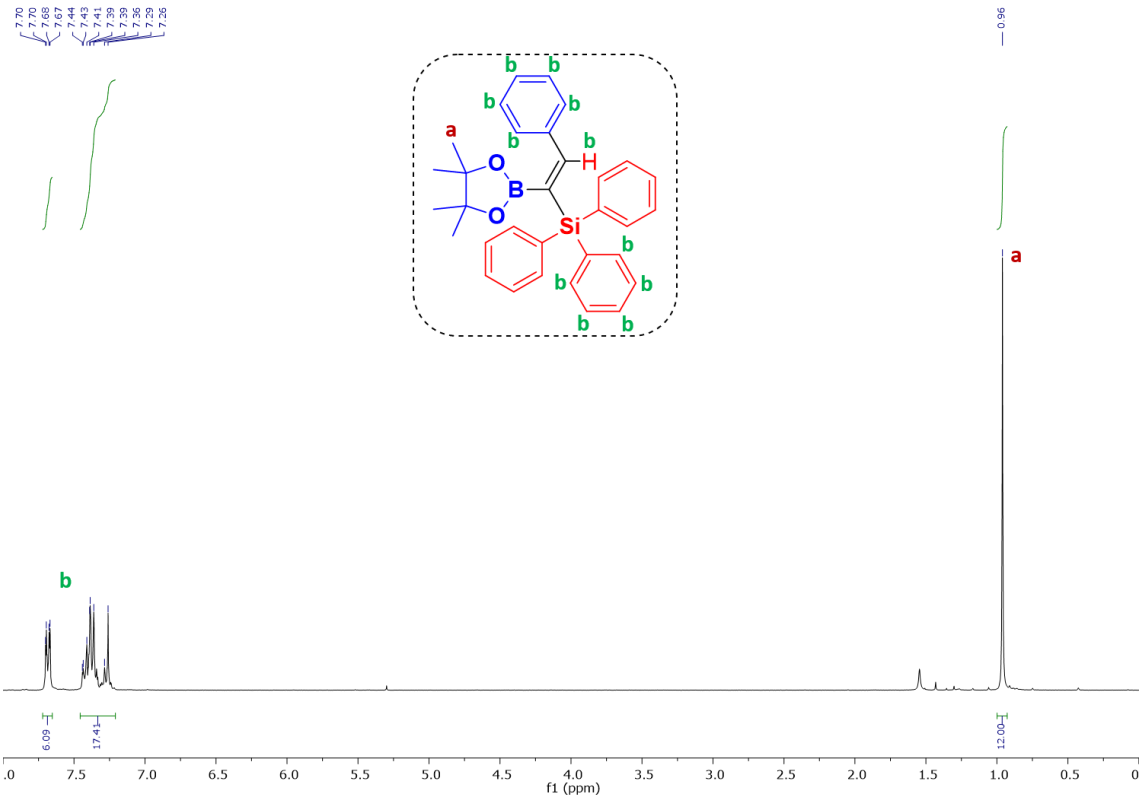


Figure S69. ^{1}H NMR of compound **4bd**.

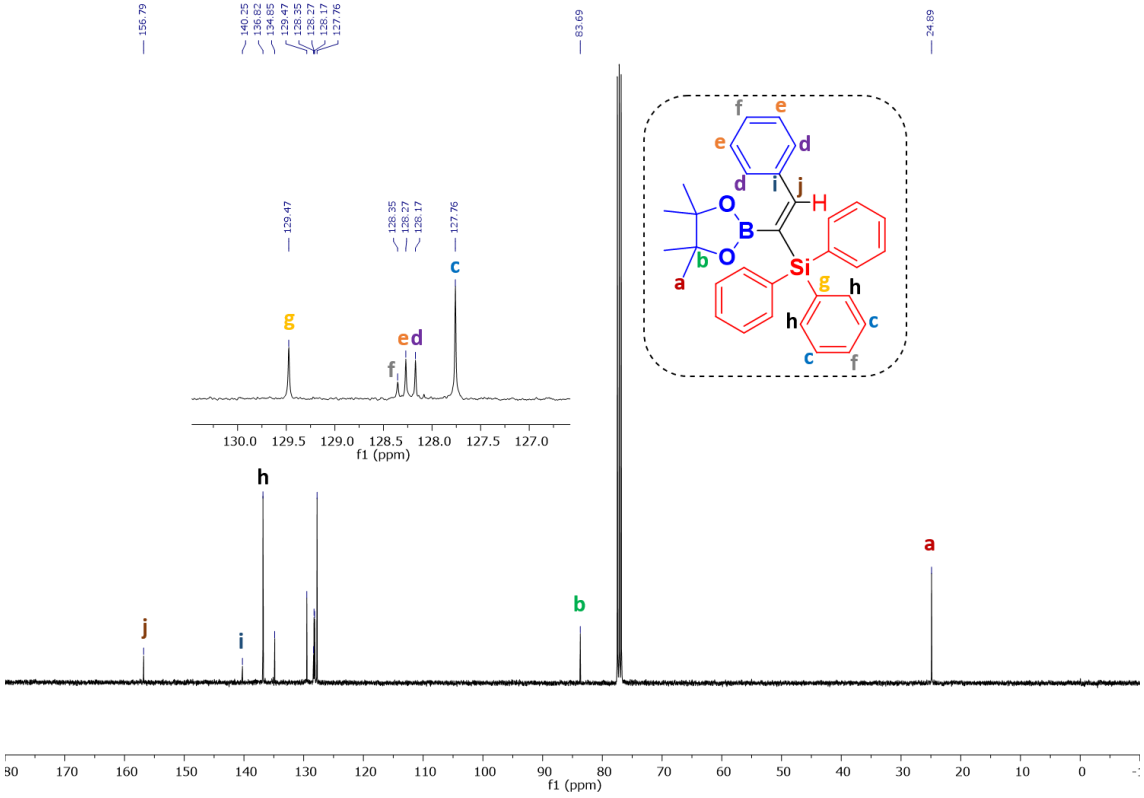


Figure S70. ^{13}C NMR of compound **4bd**.

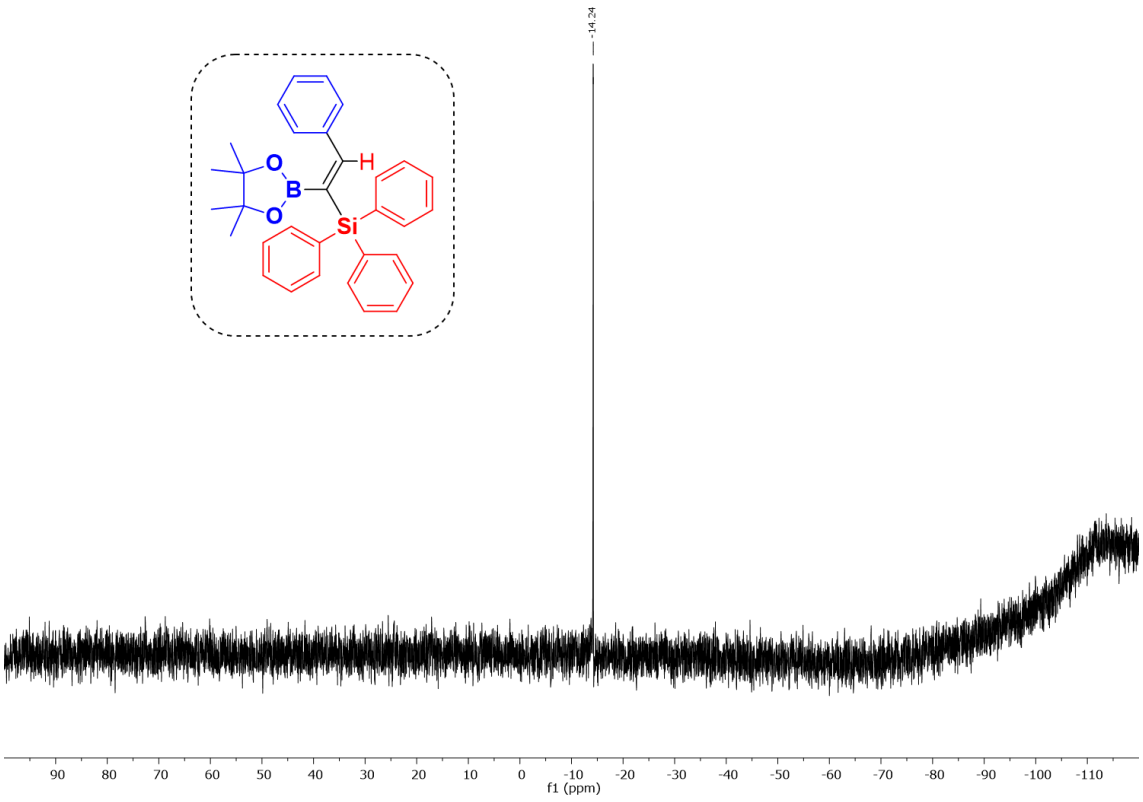


Figure S71.[29]Si NMR of compound **4bd**.

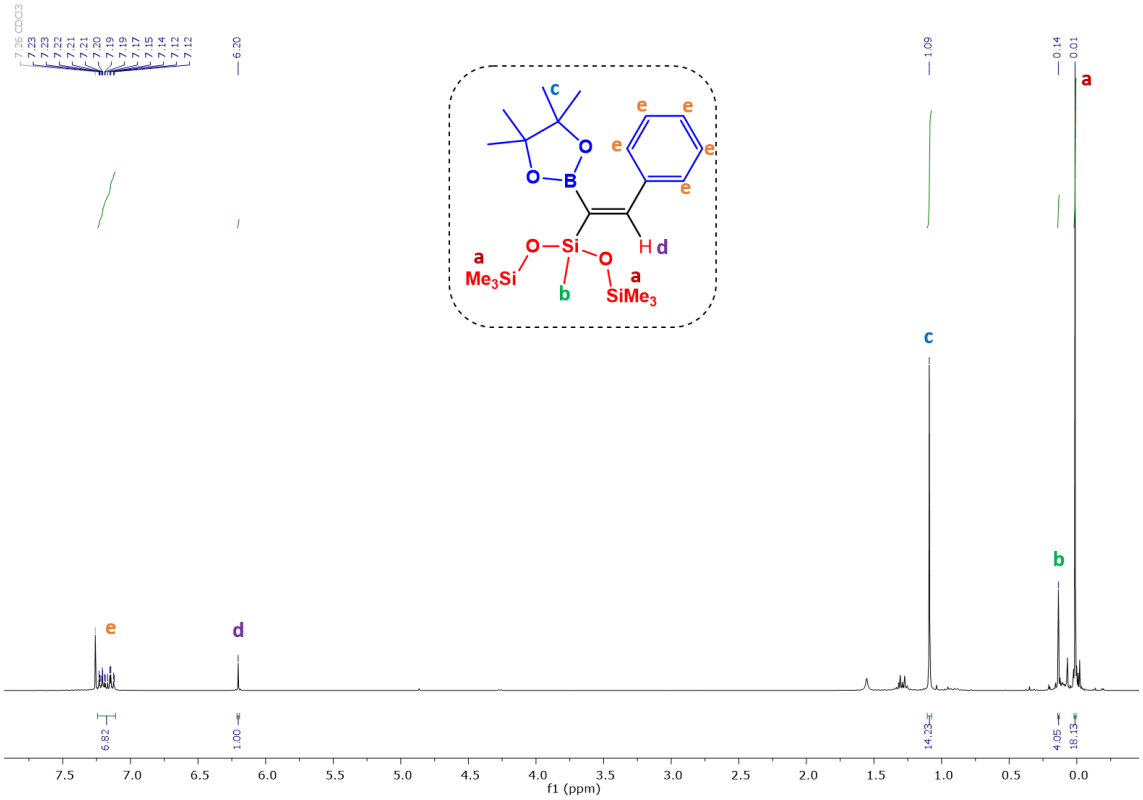


Figure S72.[1]H NMR of compound **4cd**.

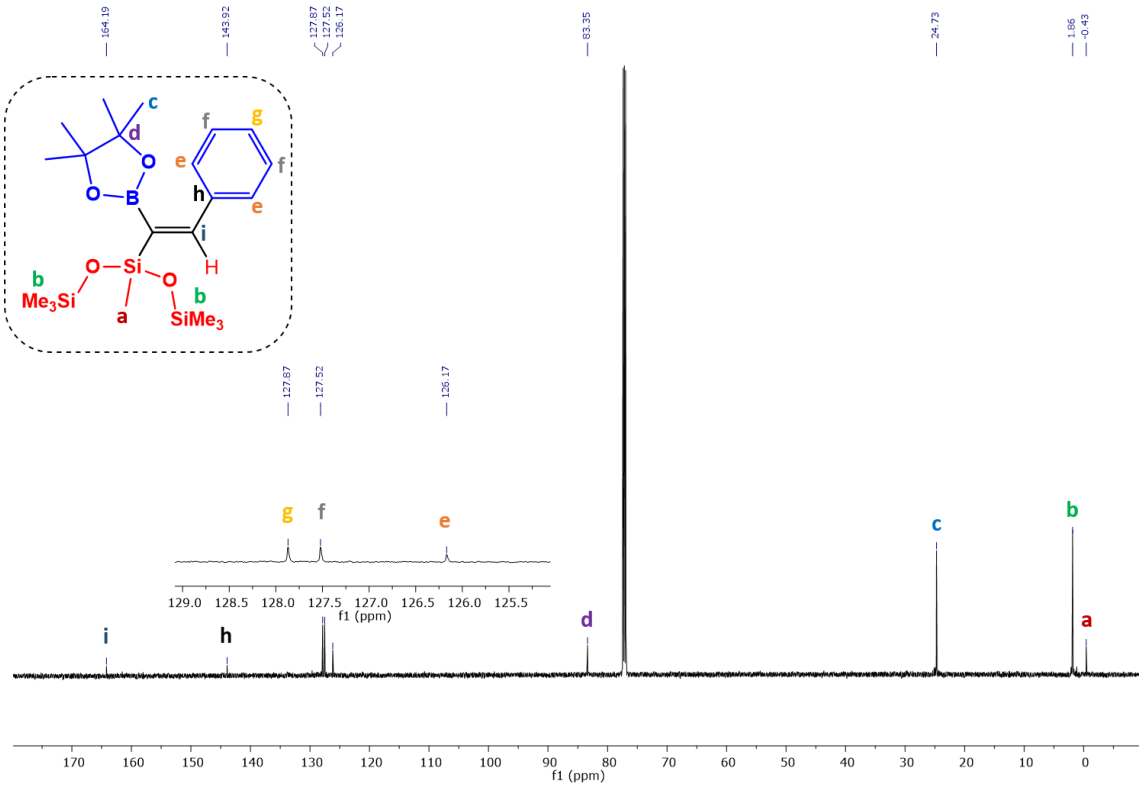


Figure S73.[13]C NMR of compound **4cd**.

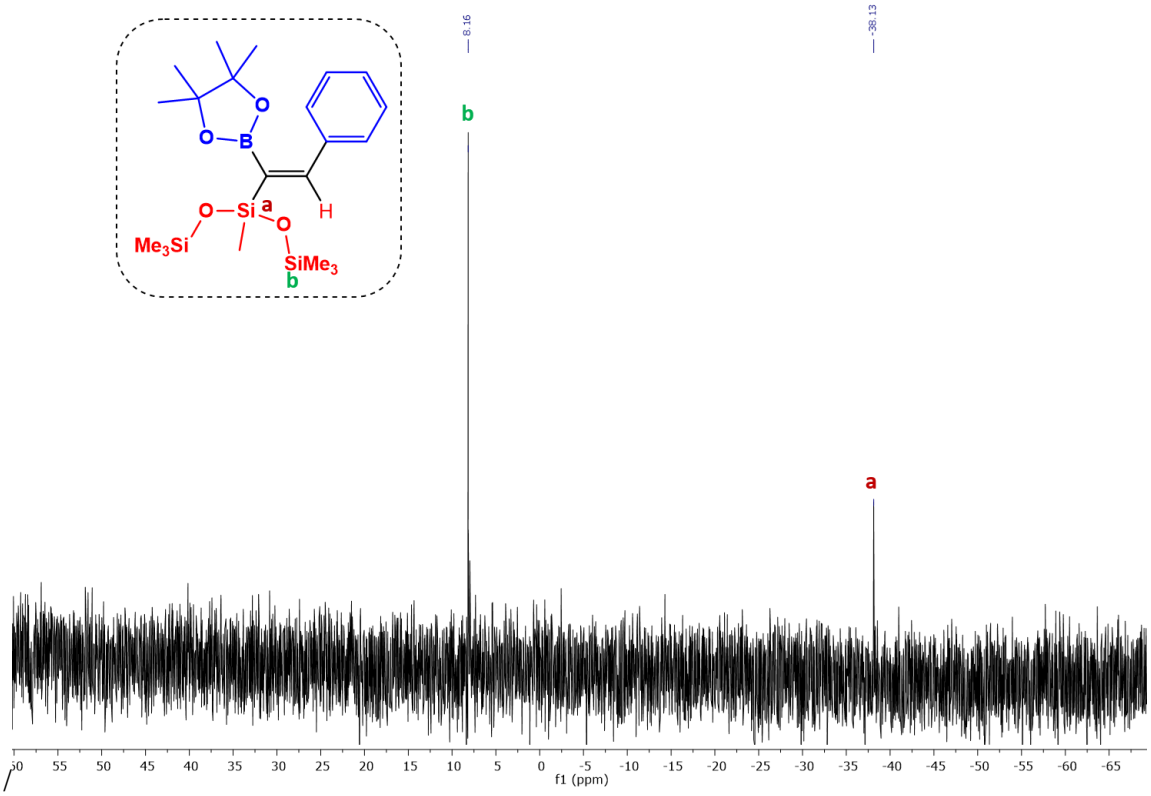


Figure S74.[29]Si NMR of compound **4cd**.

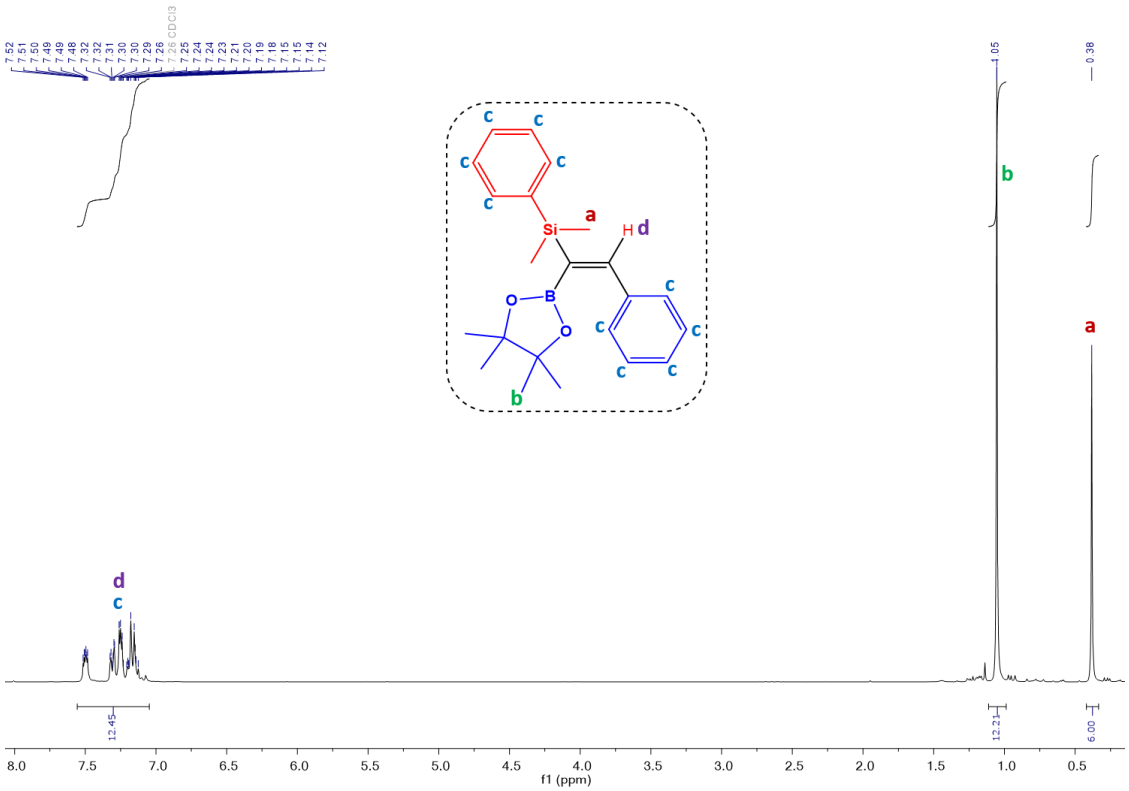


Figure S75.[1]H NMR of compound **4ed**.

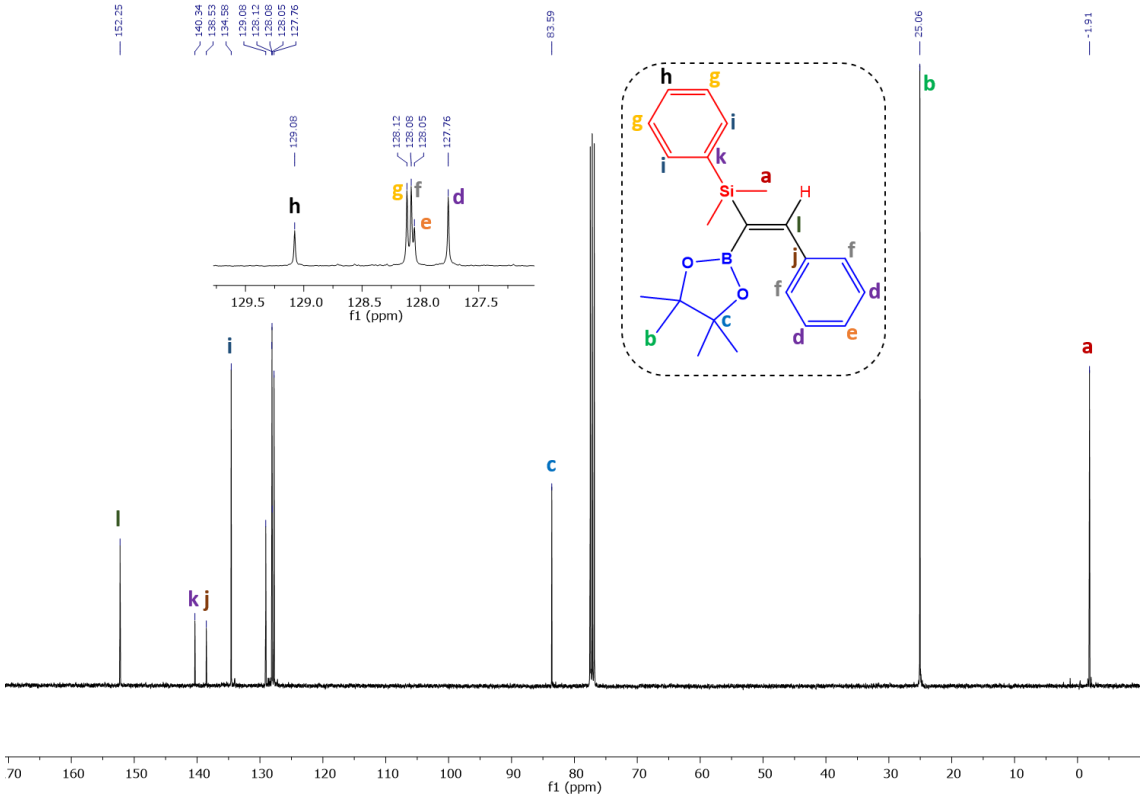


Figure S76.[13]C NMR of compound **4ed**.

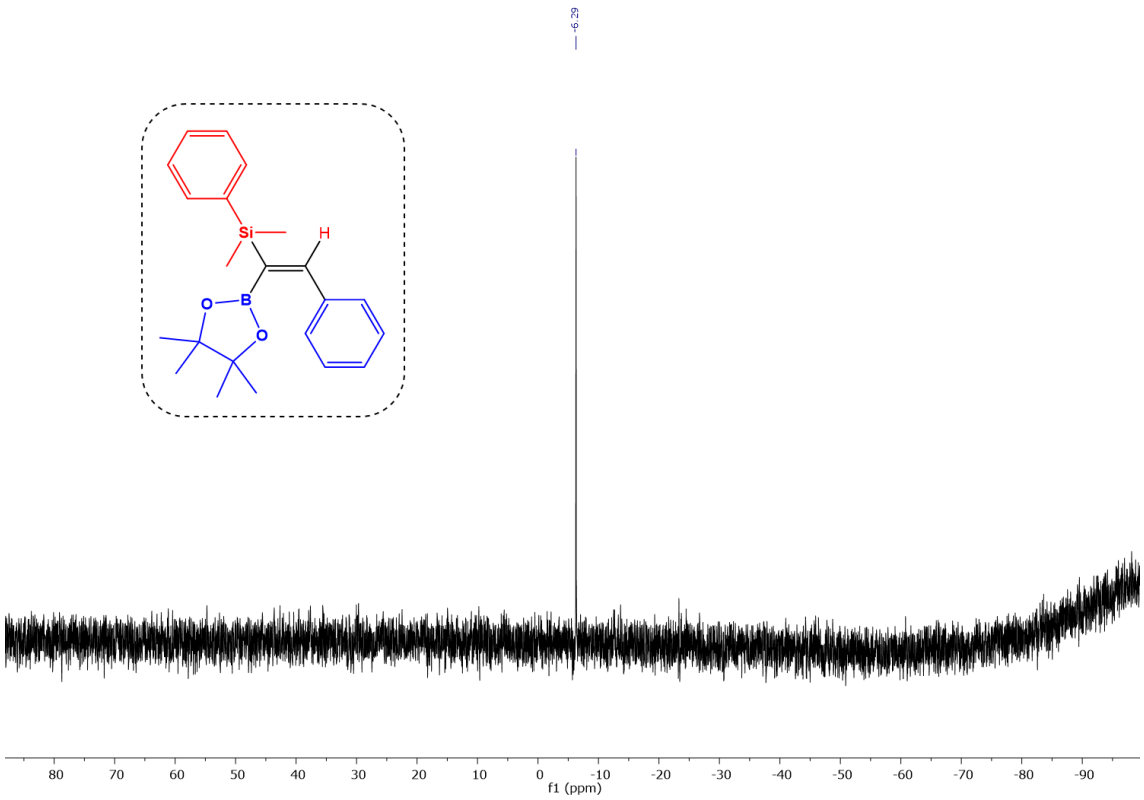


Figure S77.[29]Si NMR of compound **4ed**.

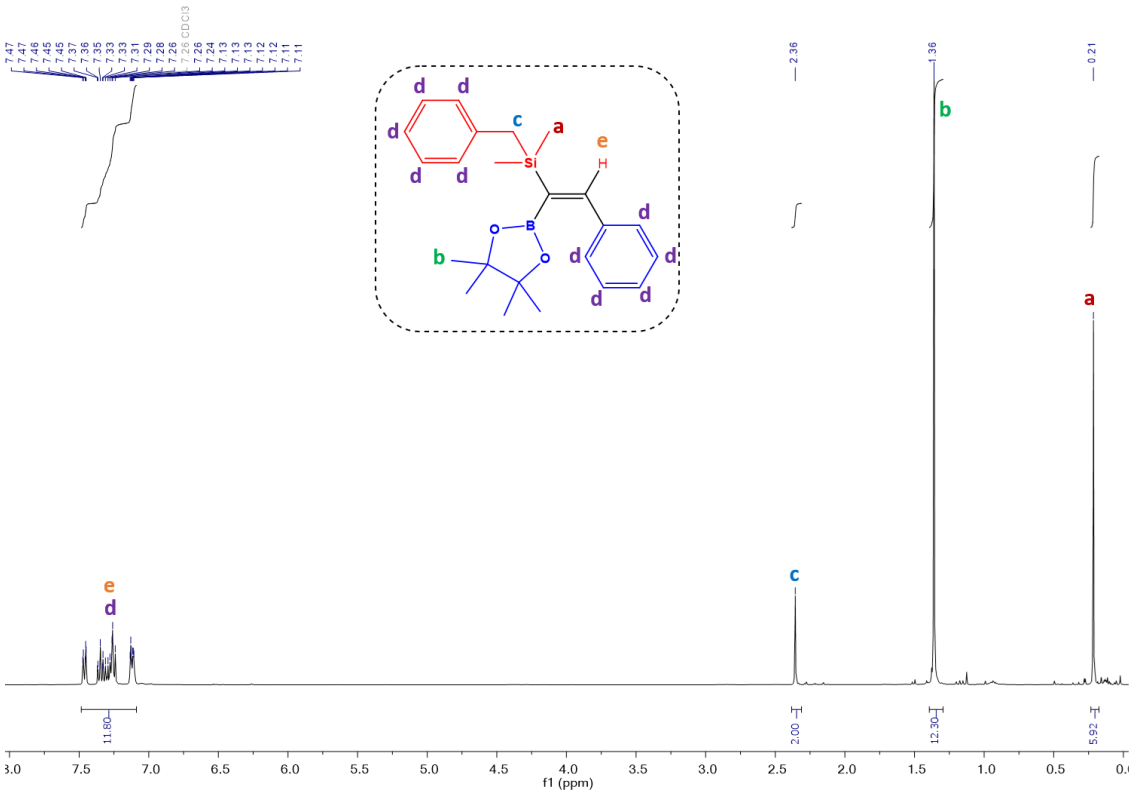


Figure S78.[1]H NMR of compound **4fd**.

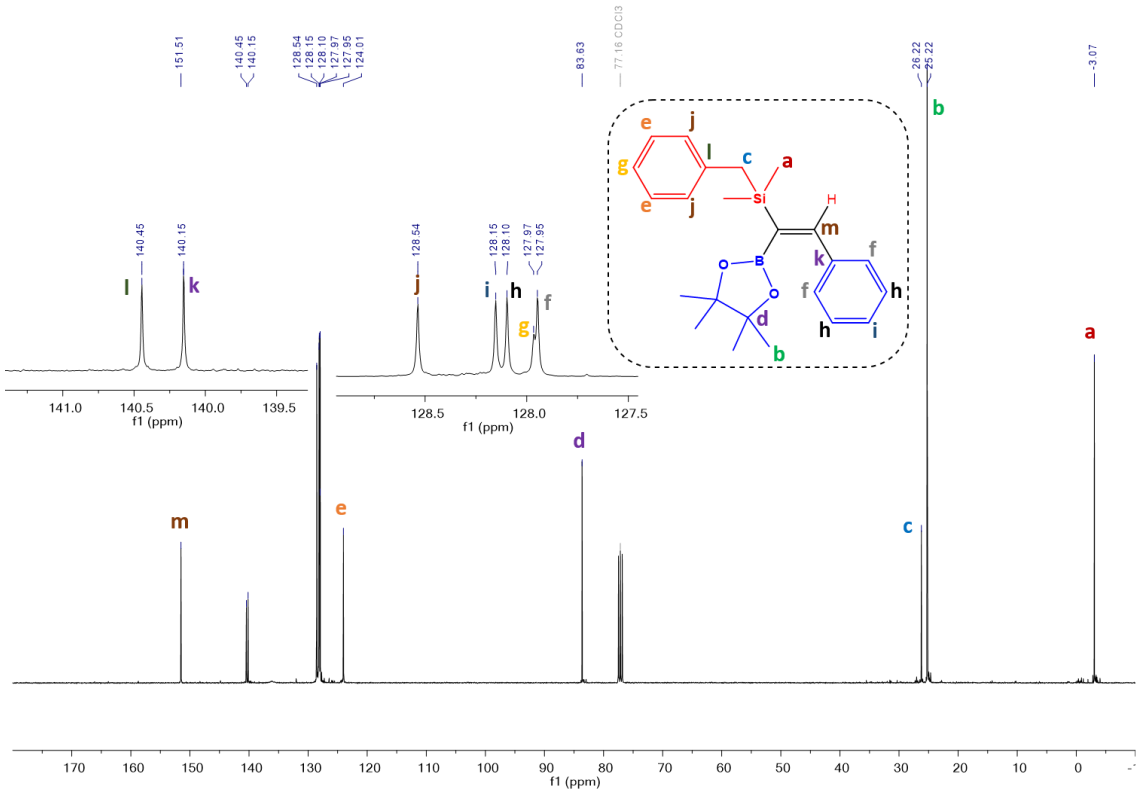


Figure S79.^{13}C NMR of compound **4fd**.

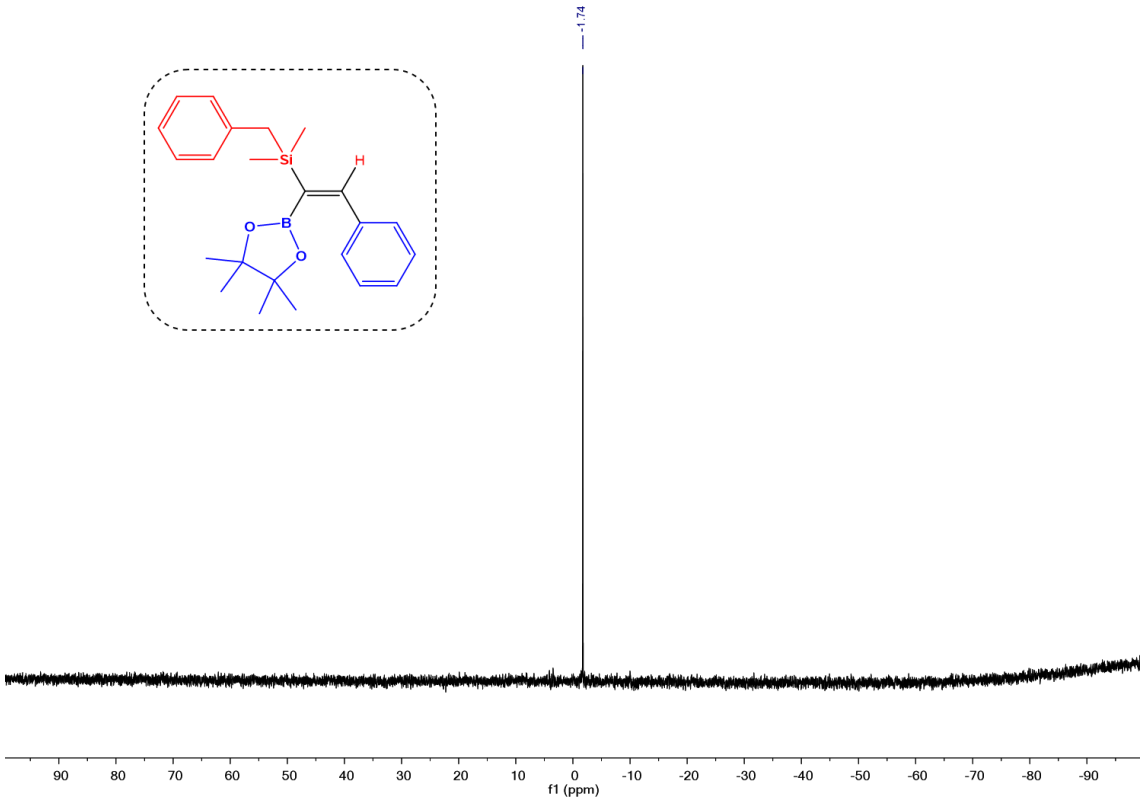


Figure S80.^{29}Si NMR of compound **4fd**.

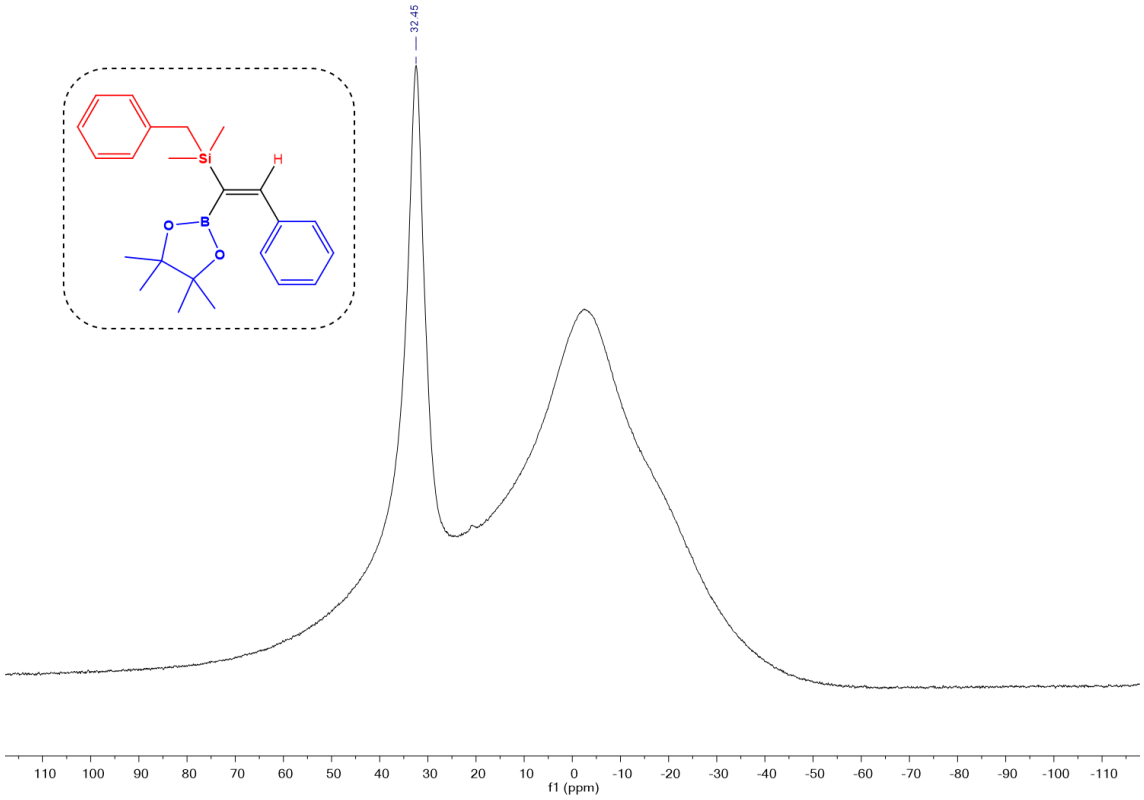


Figure S81.[11]B NMR of compound **4fd**.

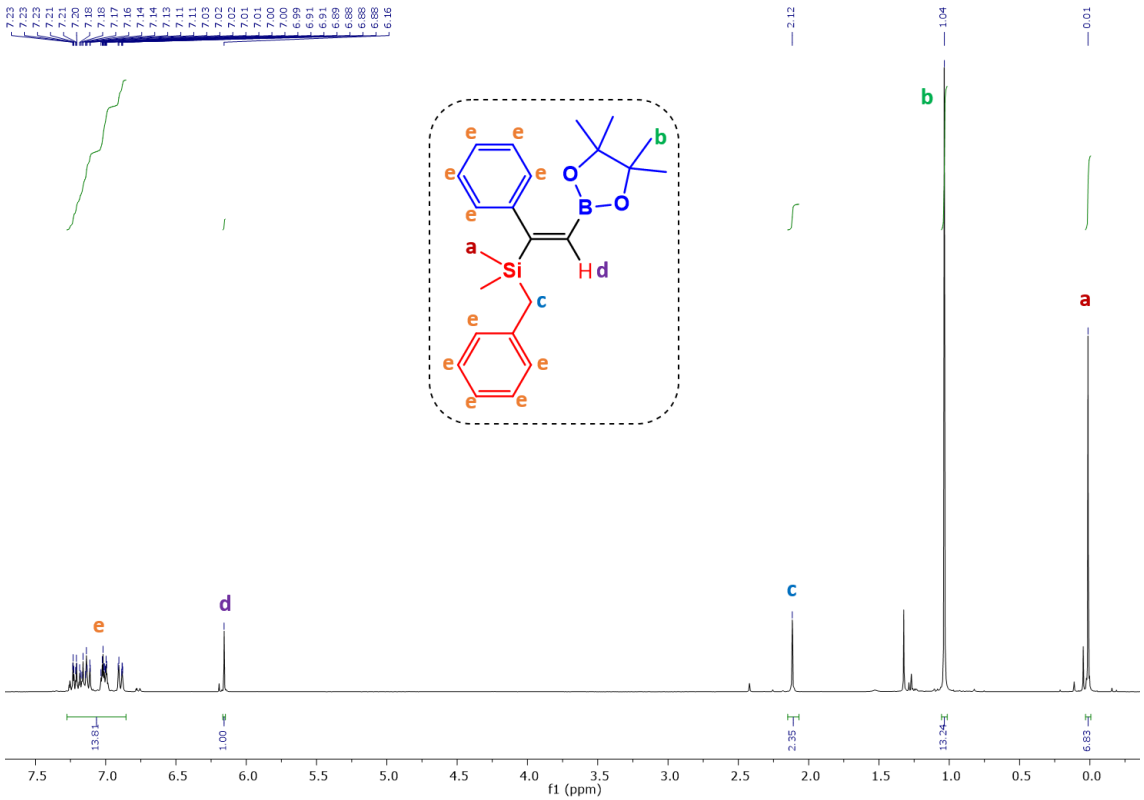


Figure S82.[1]H NMR of **3fd/5fd** mixture 89/11.

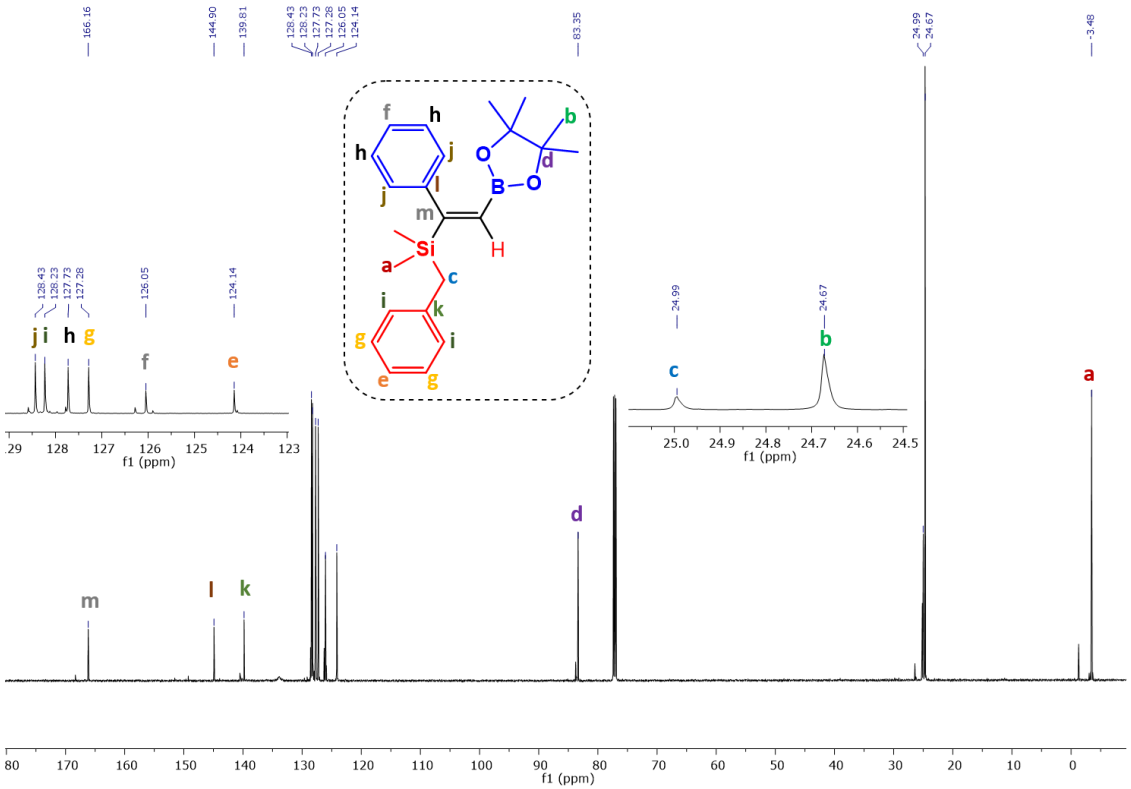


Figure S83. ^{13}C NMR of **3fd/5fd** mixture 89/11.

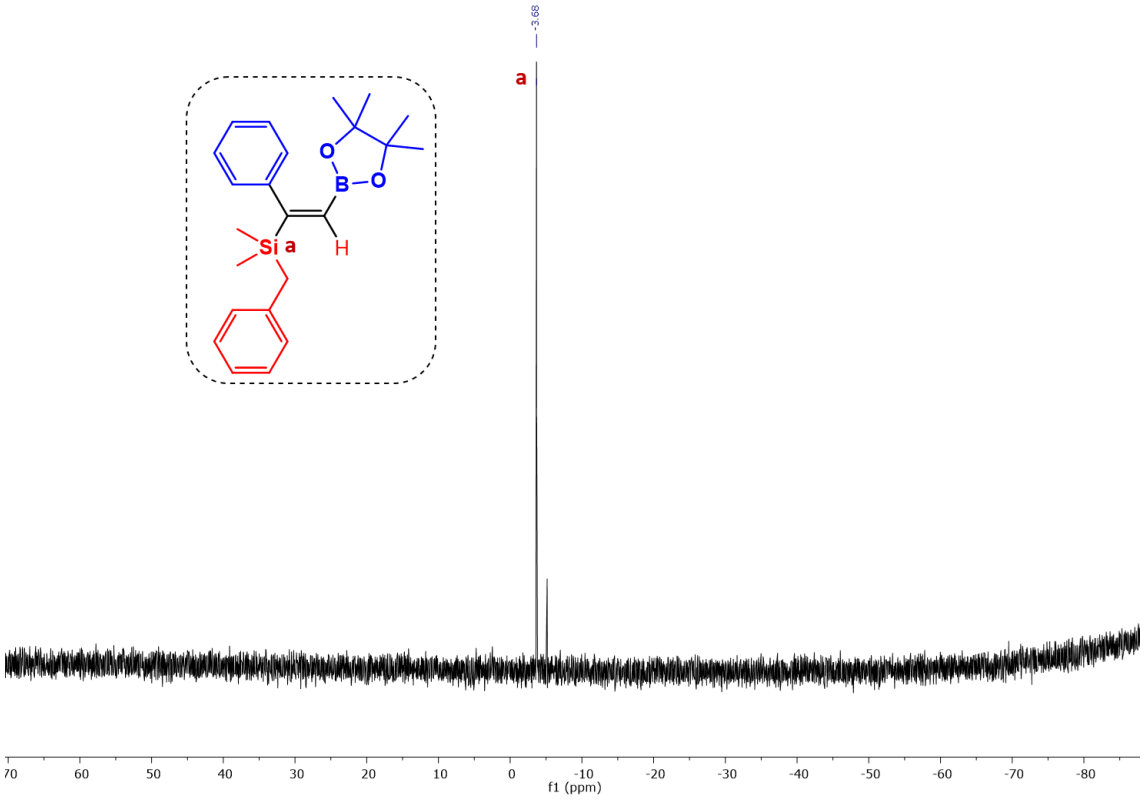


Figure S84. ^{29}Si NMR of **3fd/5fd** mixture 89/11.

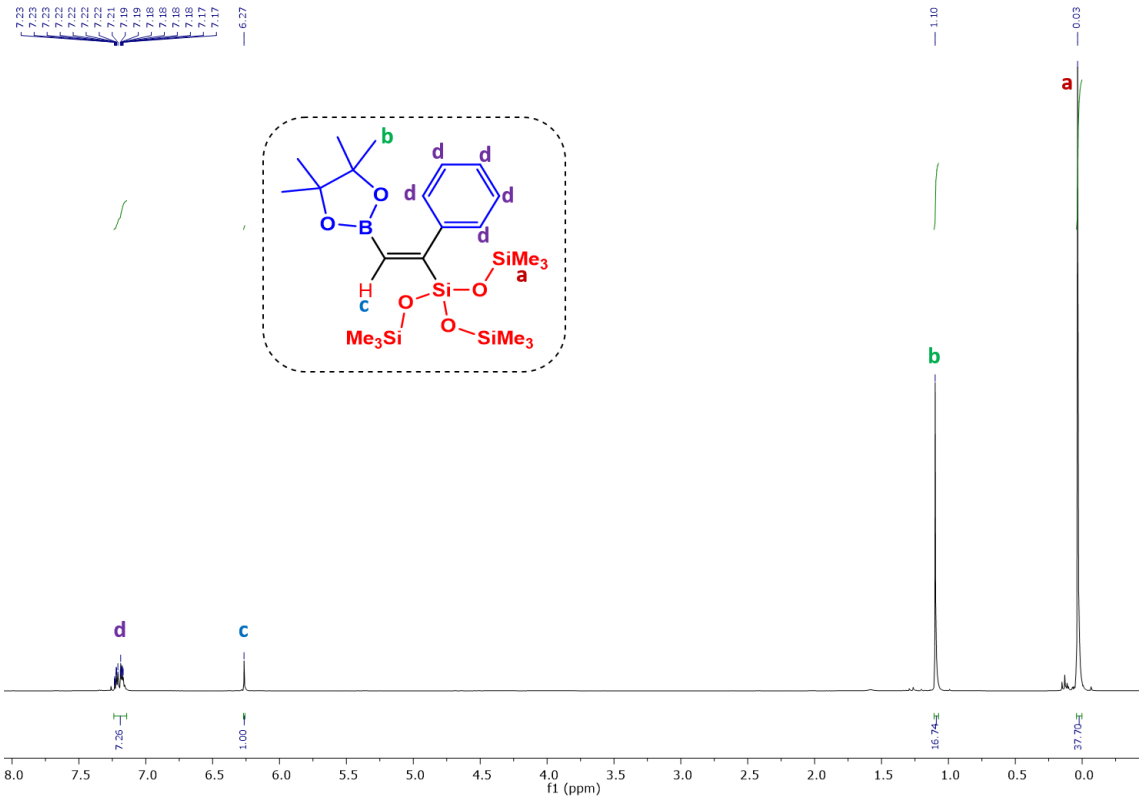


Figure S85.^{1}H NMR of compound **3gd**.

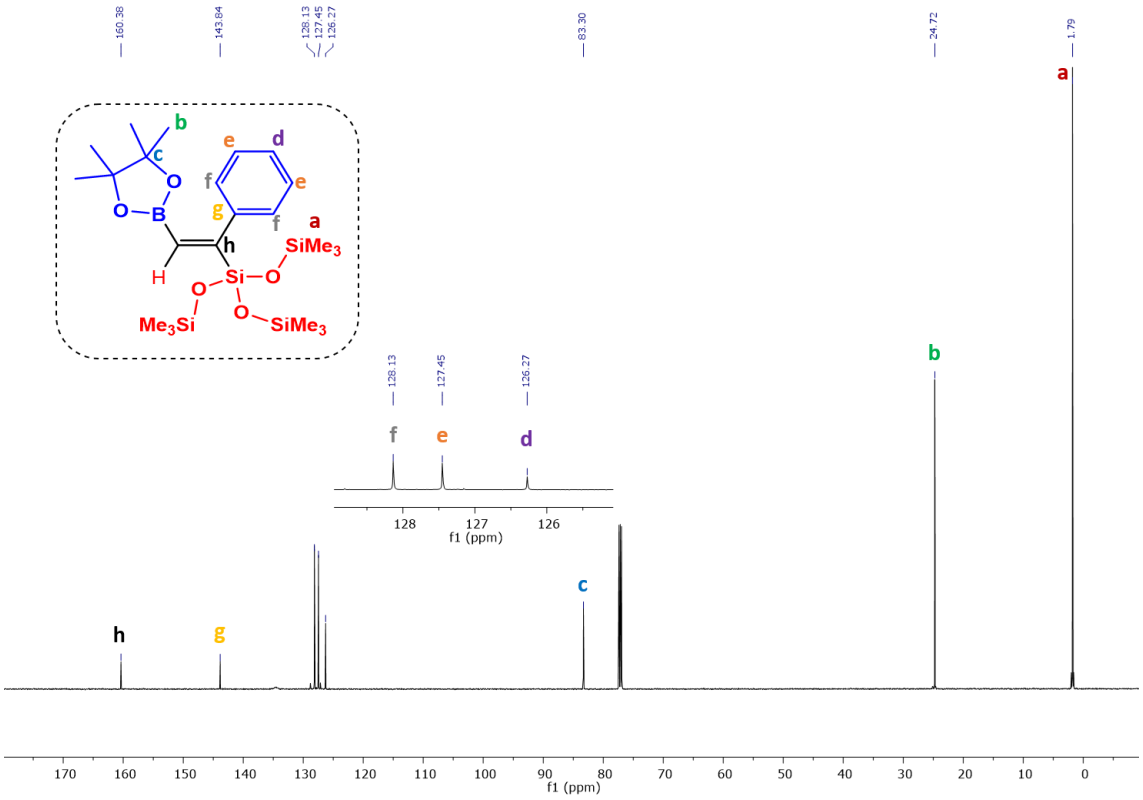


Figure S86.[13]C NMR of compound **3gd**.

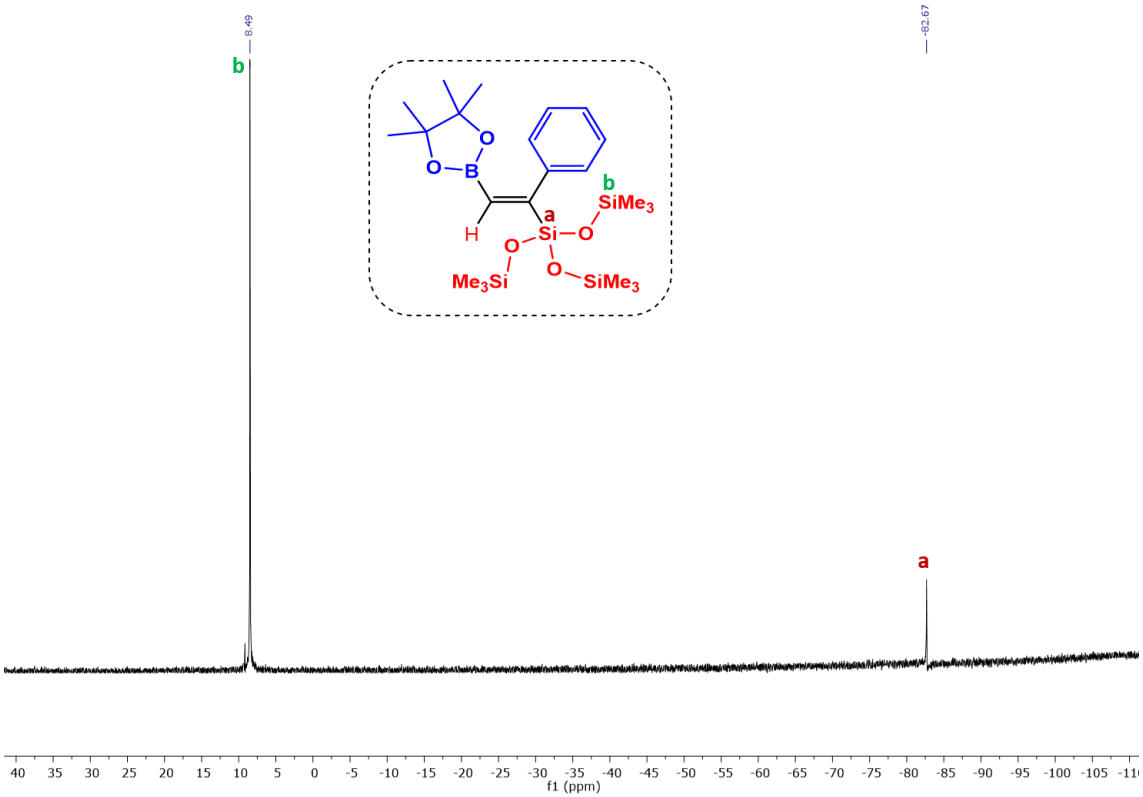


Figure S87.[29]Si NMR of compound **3gd**.

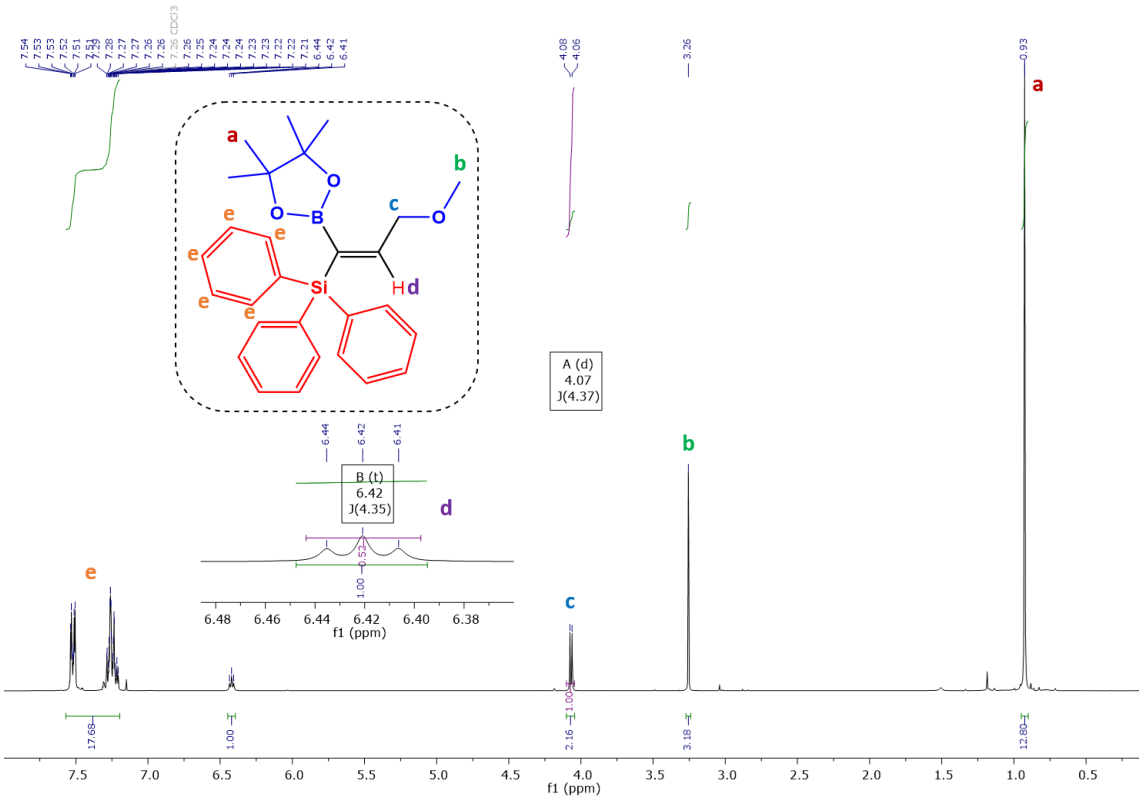


Figure S88. ^{1}H NMR of compound **4be**.

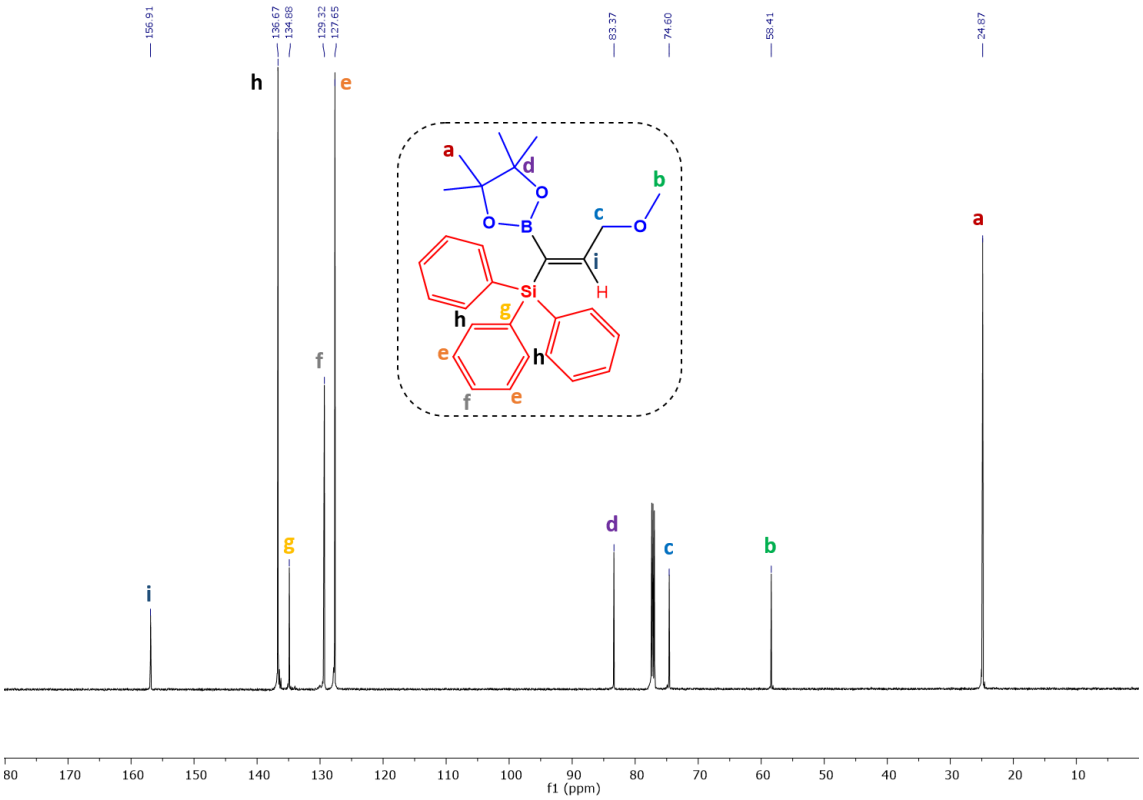


Figure S89. ^{13}C NMR of compound **4be**.

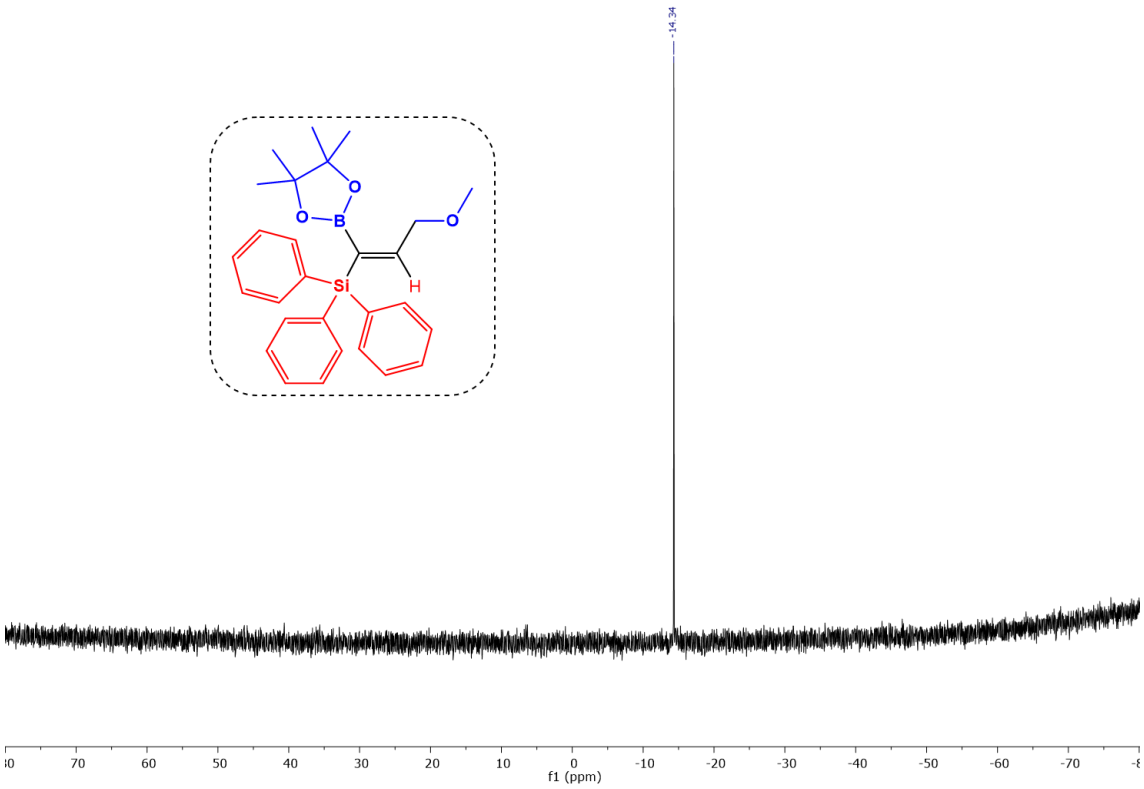


Figure S90. ^{29}Si NMR of compound **4be**.

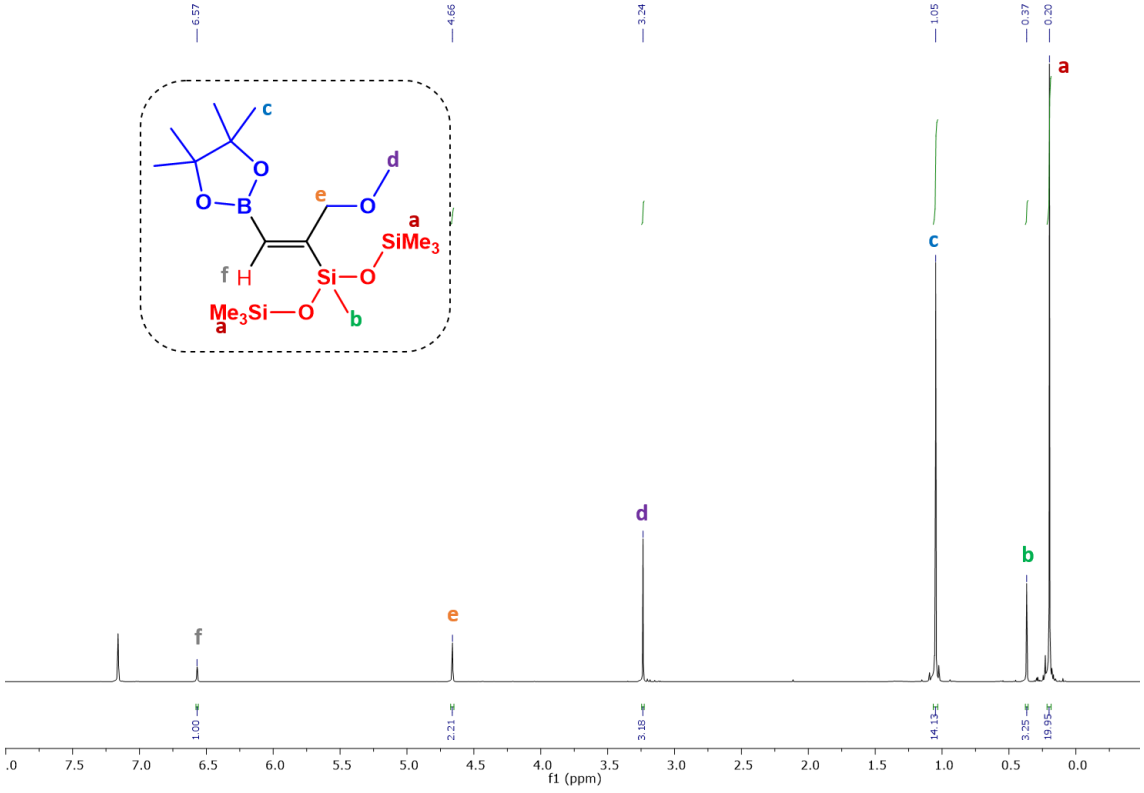


Figure S91. ^{1}H NMR of compound **3ce**.

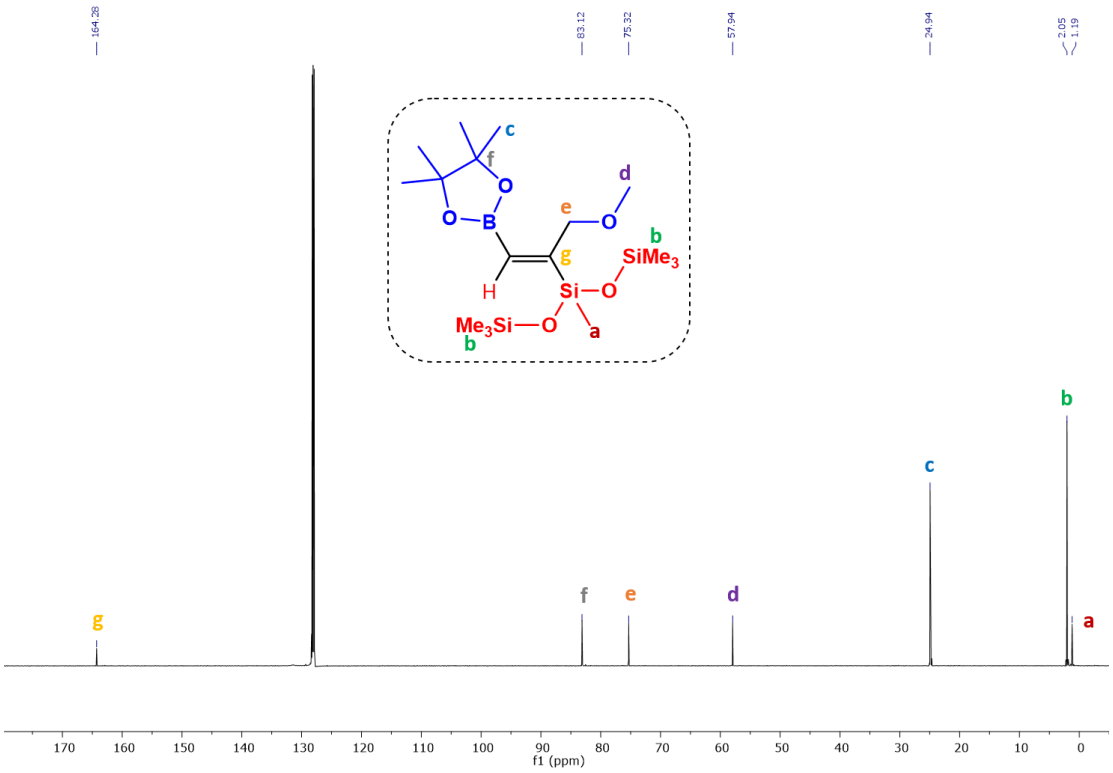


Figure S92. ^{13}C NMR of compound **3ce**.

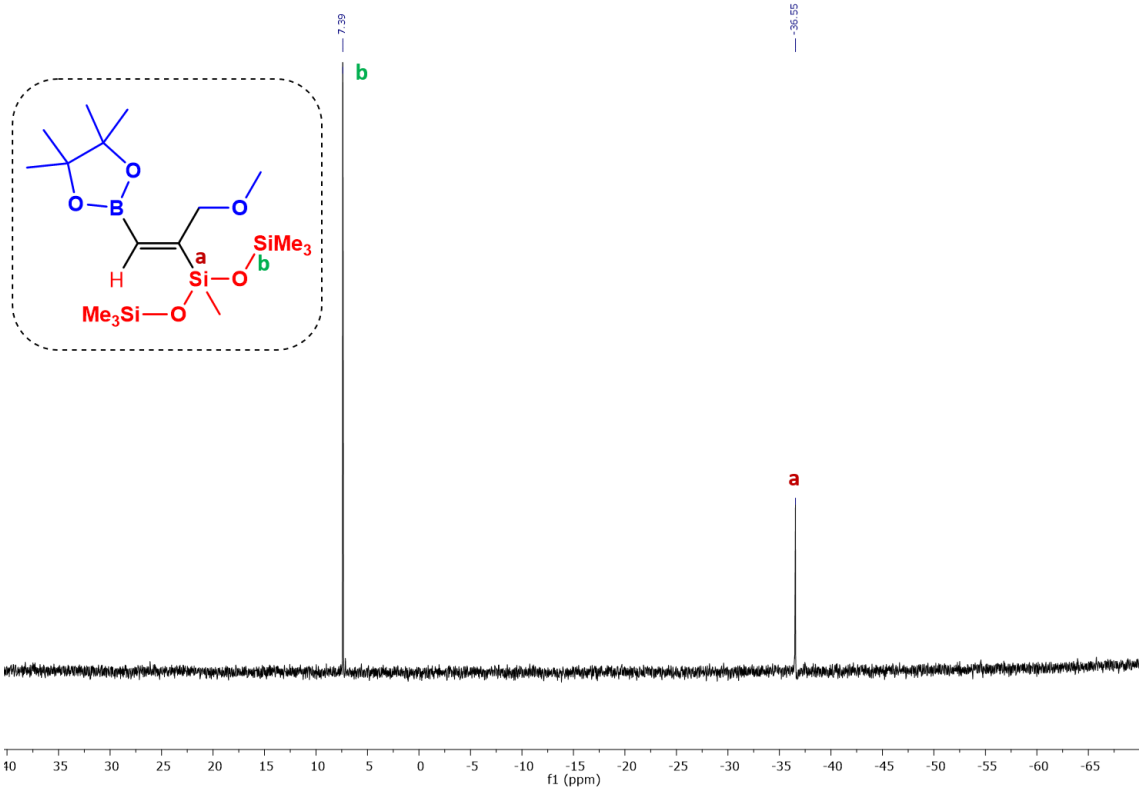


Figure S93. ^{29}Si NMR of compound **3ce**.

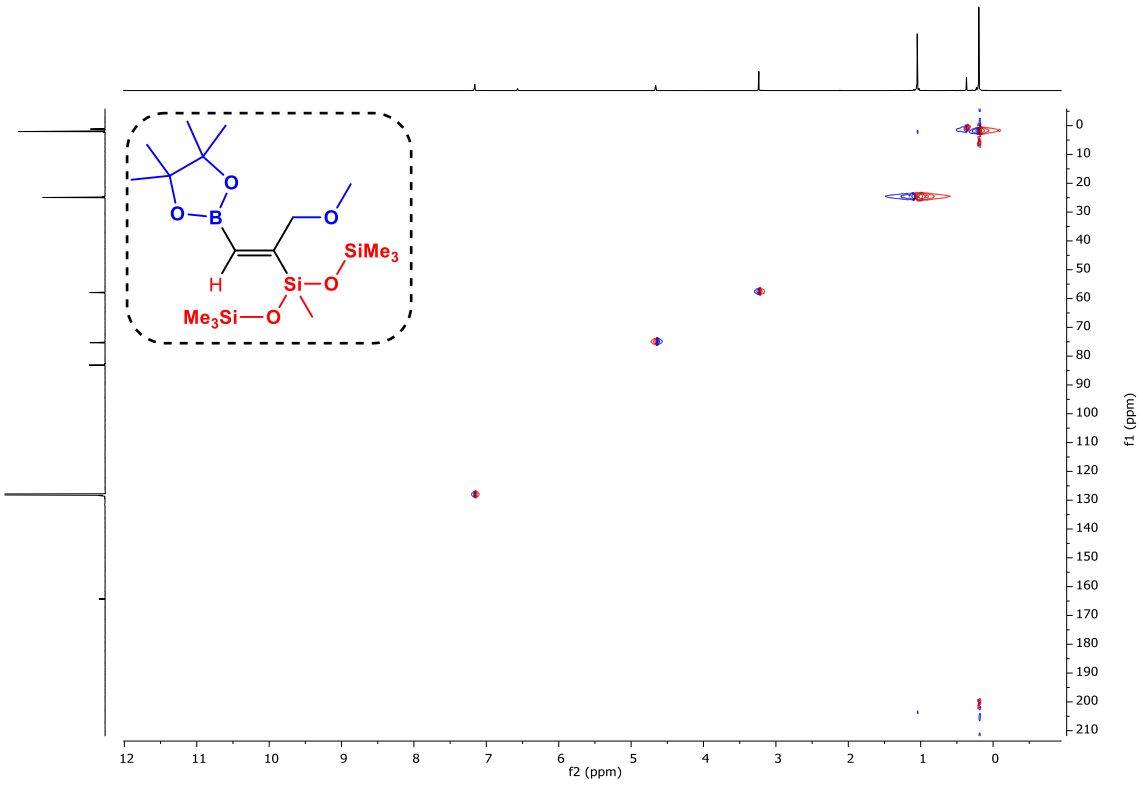


Figure S94. ^{1}H - ^{13}C HSQC of compound **3ce**.

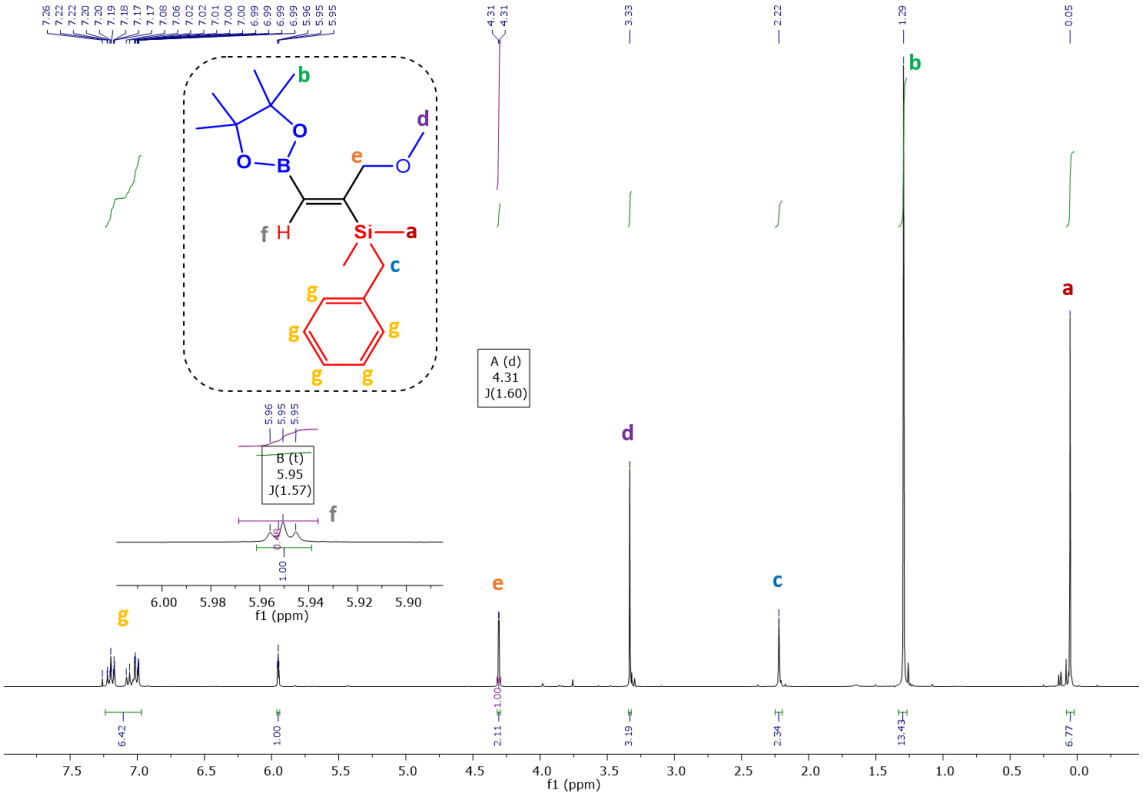


Figure S95. ^{1}H NMR of compound **3fe**.

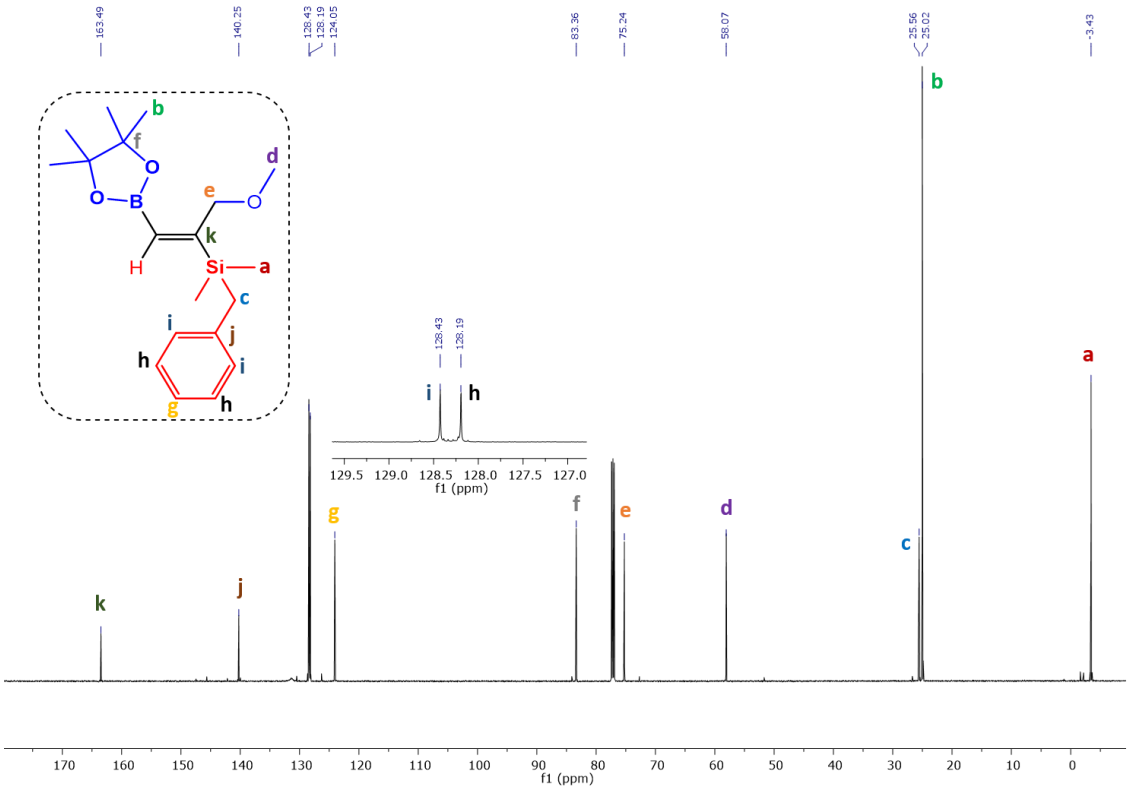


Figure S96. ^{13}C NMR of compound **3fe**.

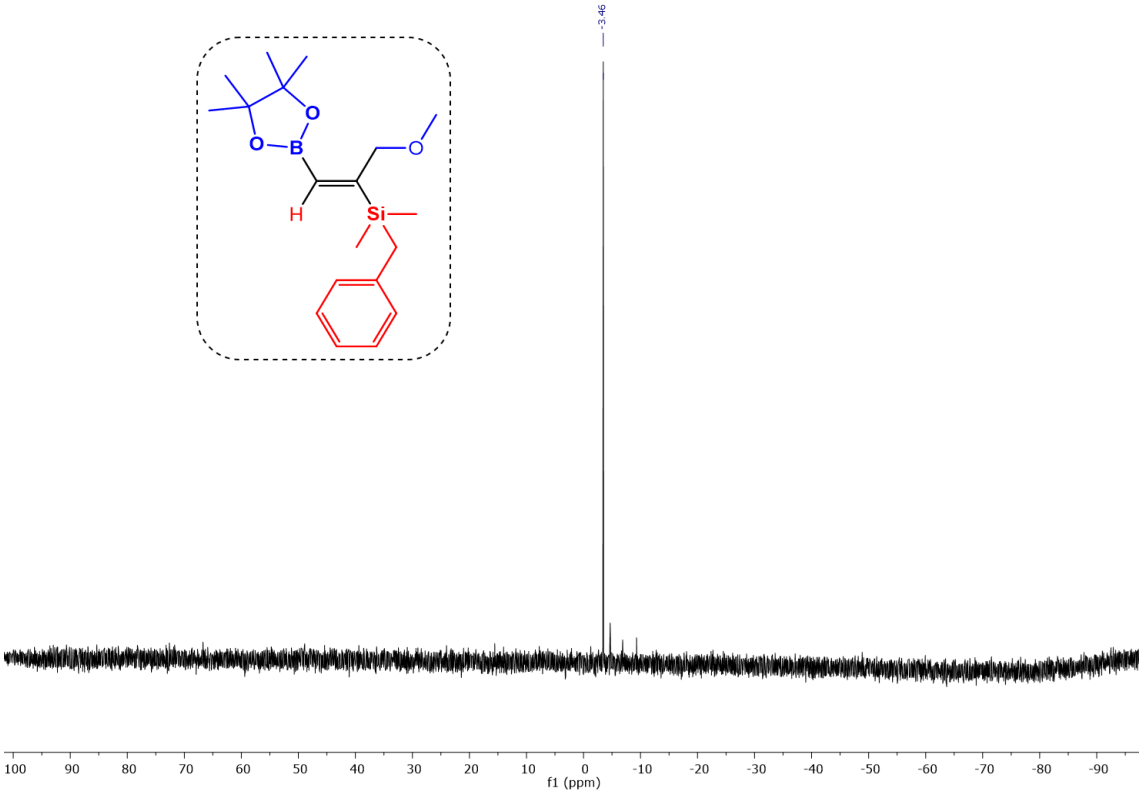


Figure S97. ^{29}Si NMR of compound **3fe**.

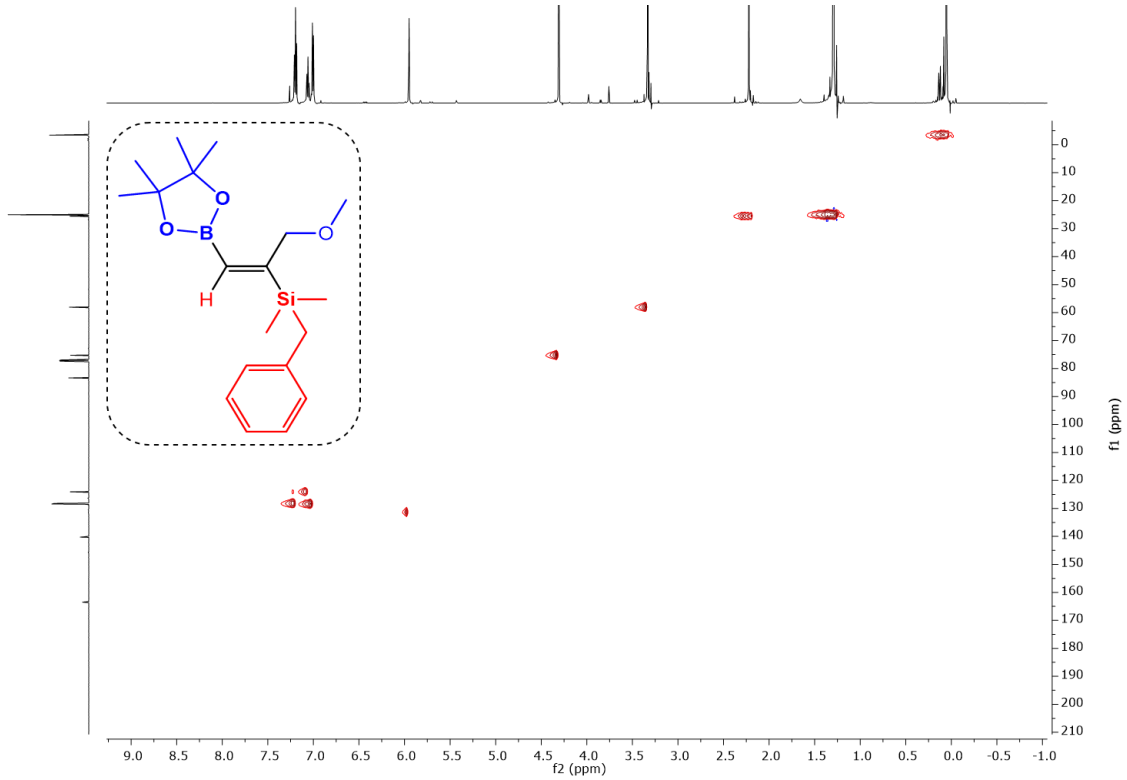


Figure S98. ^{1}H – ^{13}C HSQC of compound **3fe**.

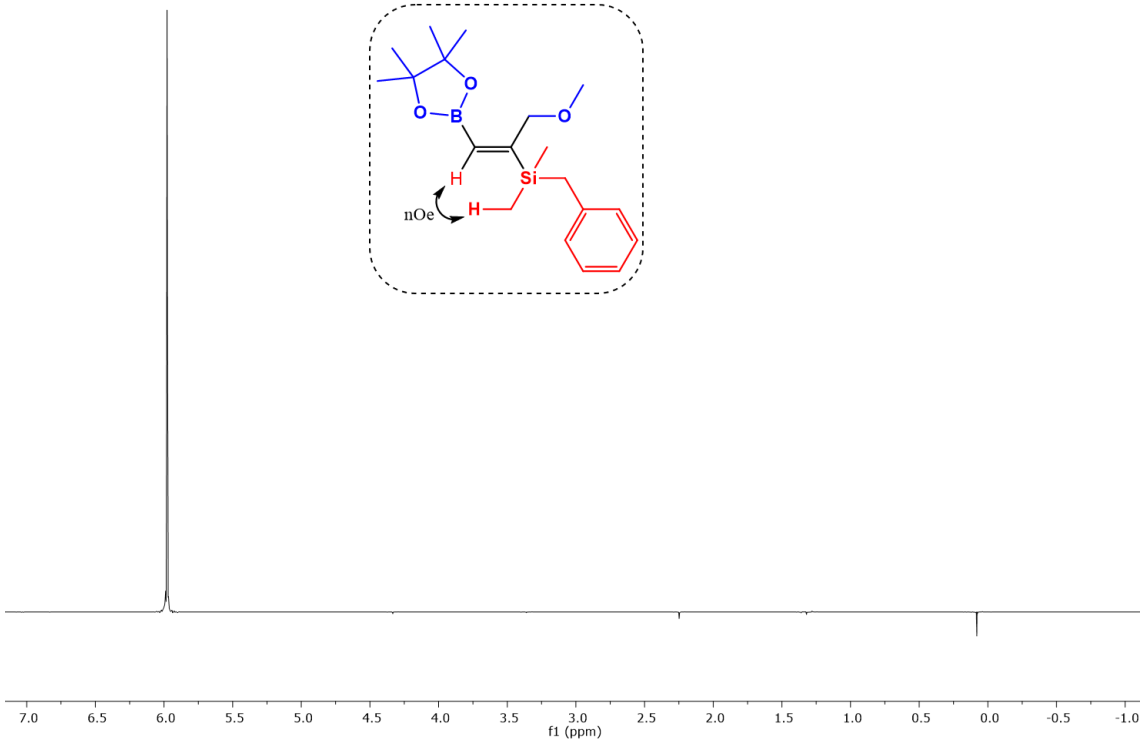


Figure S99. 1D NOE NMR of compound **3fe**.

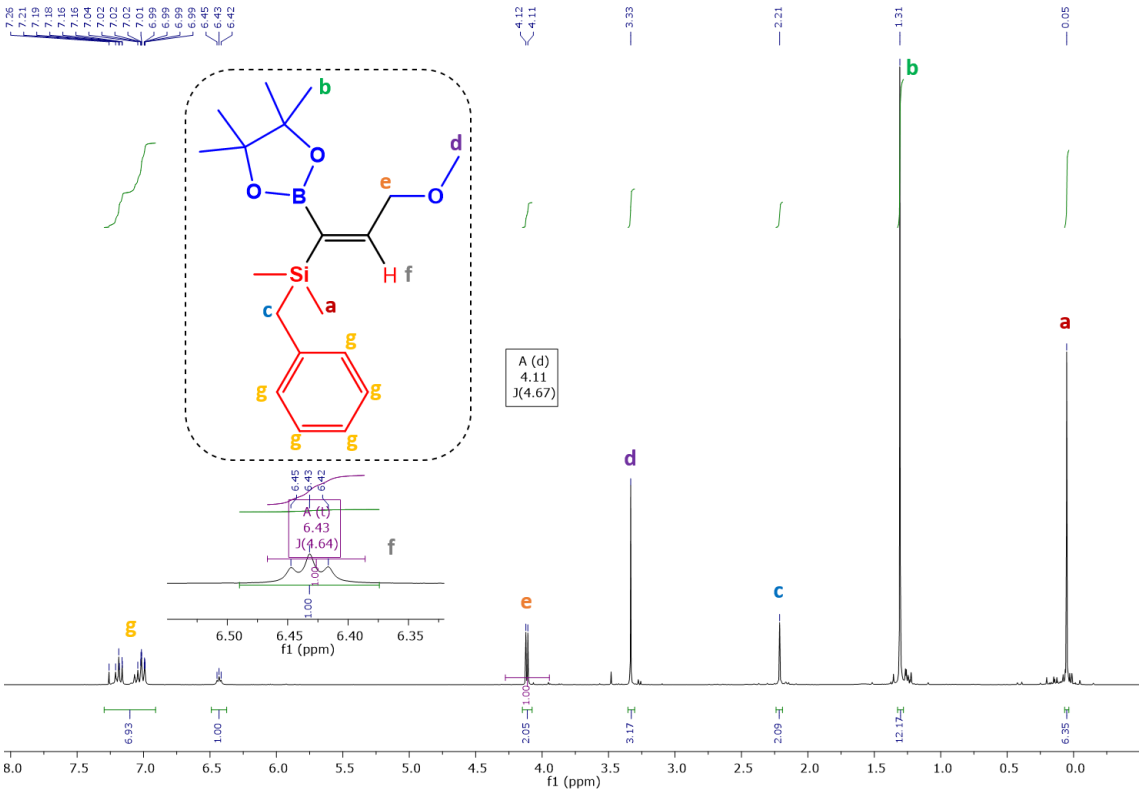


Figure S100. ^{1}H NMR of compound **4fe**.

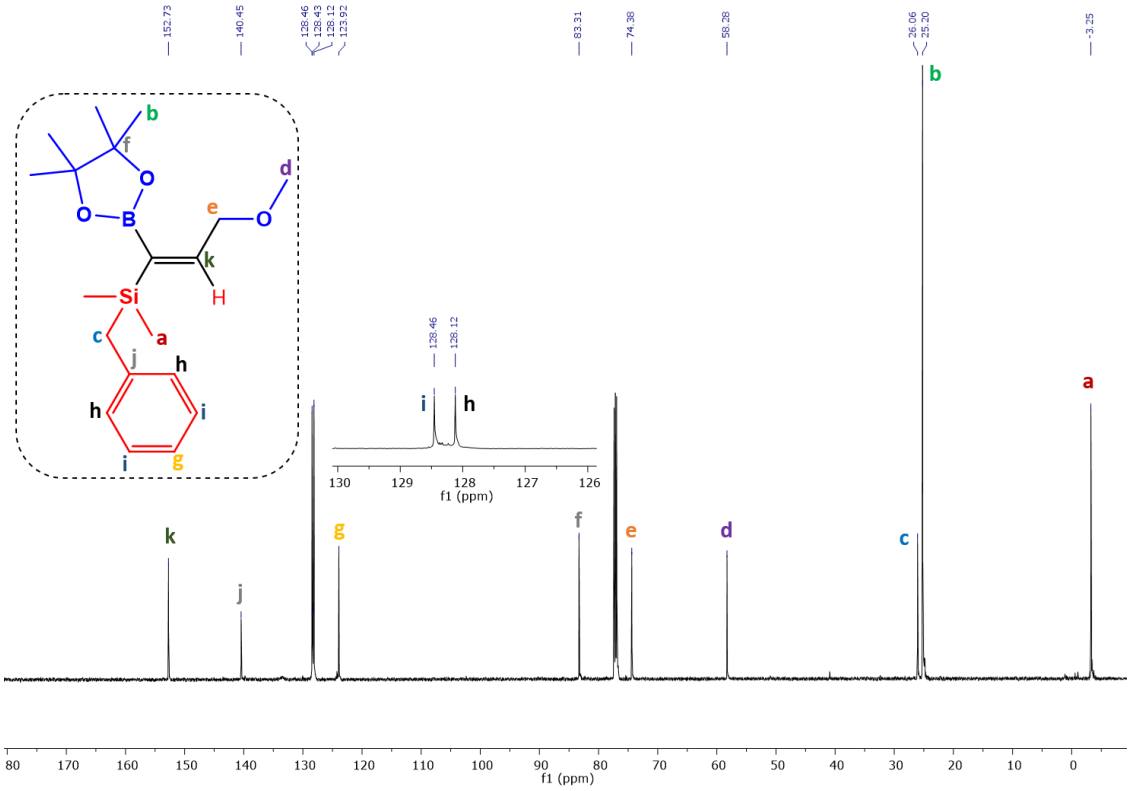


Figure S101. ^{13}C NMR of compound **4fe**.

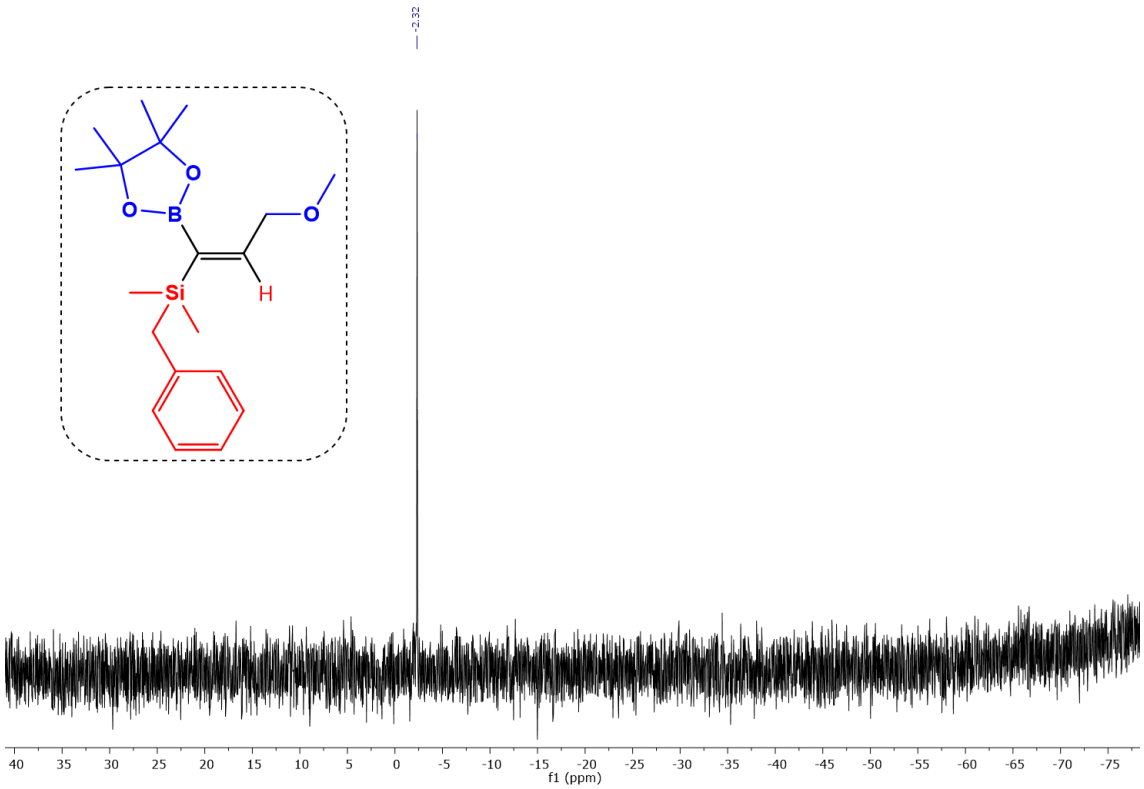


Figure S102. ^{29}Si NMR of compound **4fe**.

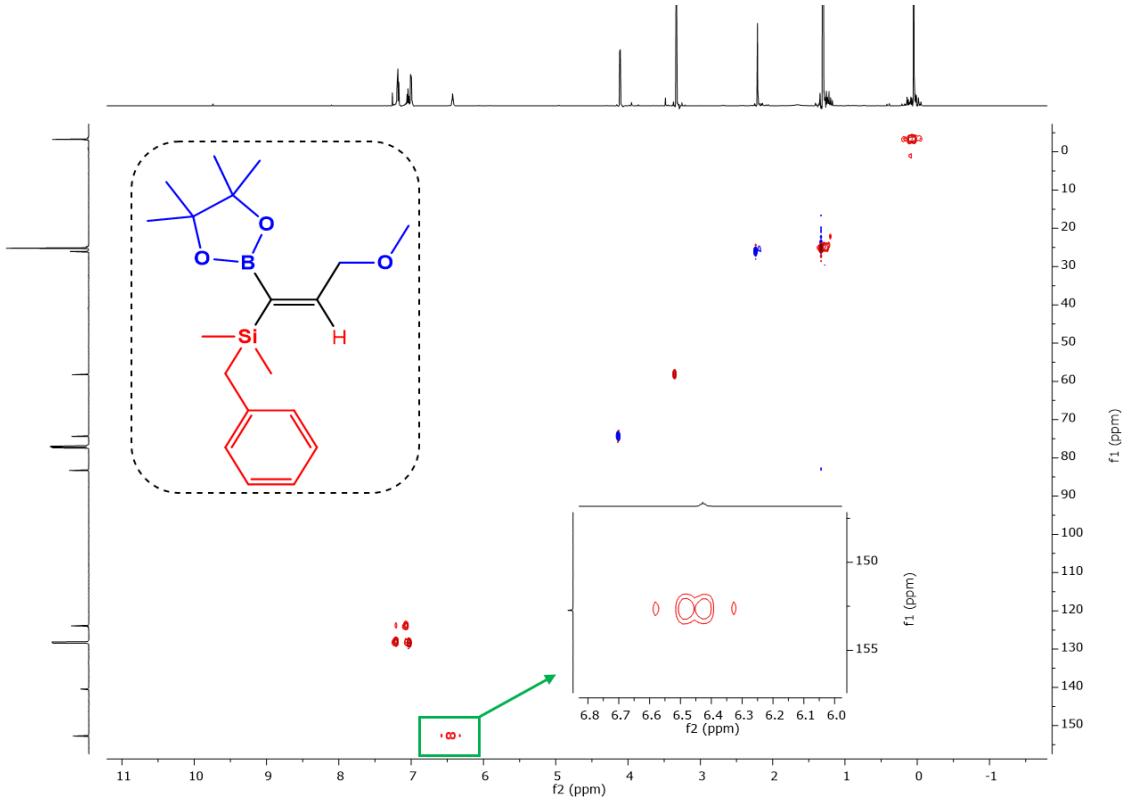


Figure S103. ^{1}H – ^{13}C HSQC of compound **4fe**.

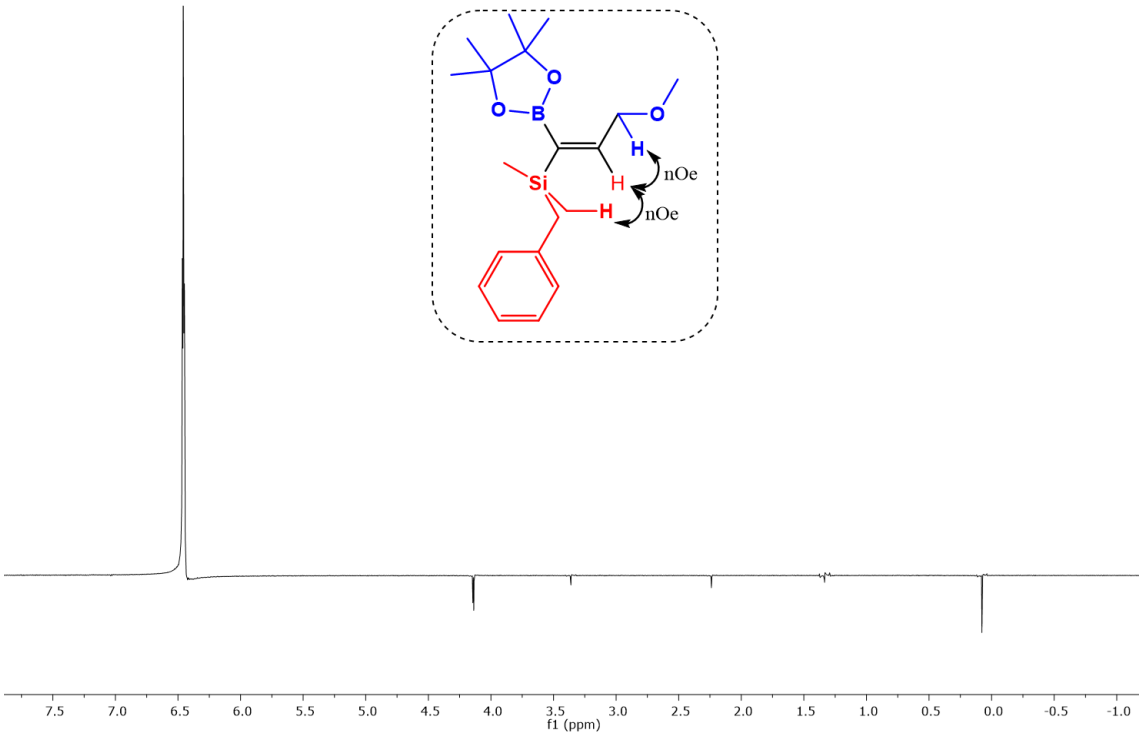


Figure S104. 1D NOE of compound **4fe**.

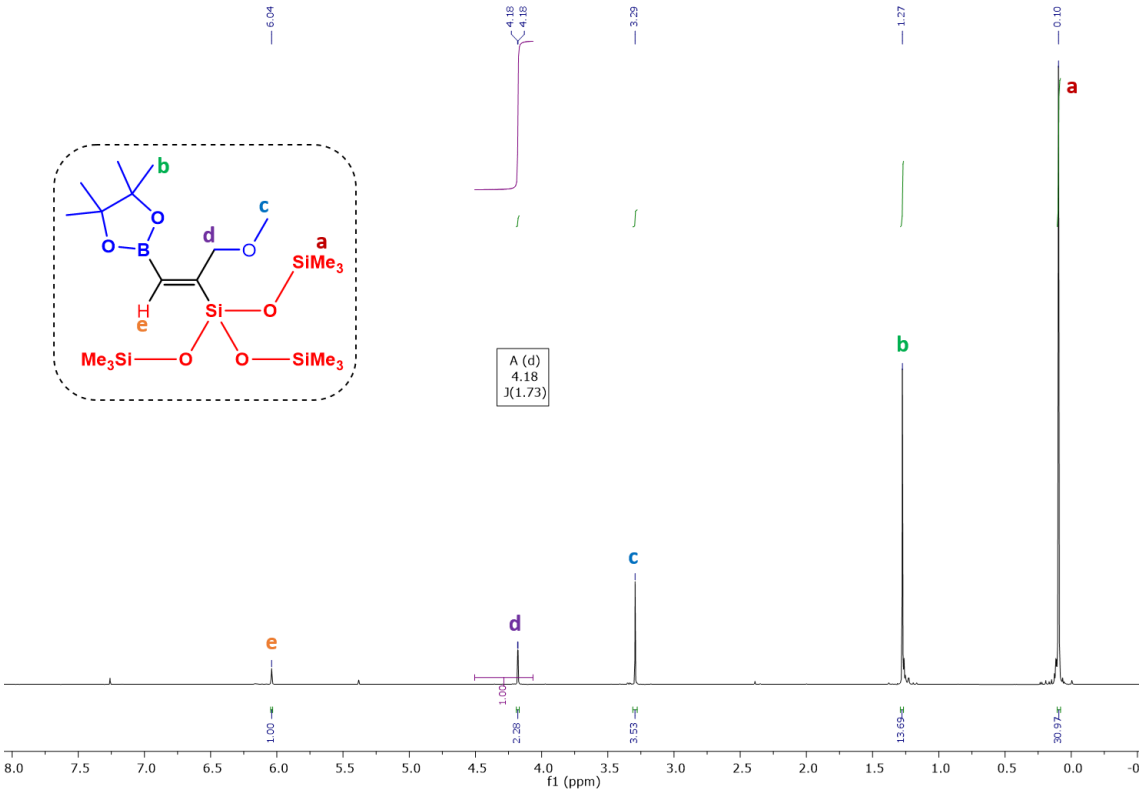


Figure S105. ^{1}H NMR of compound **3ge**.

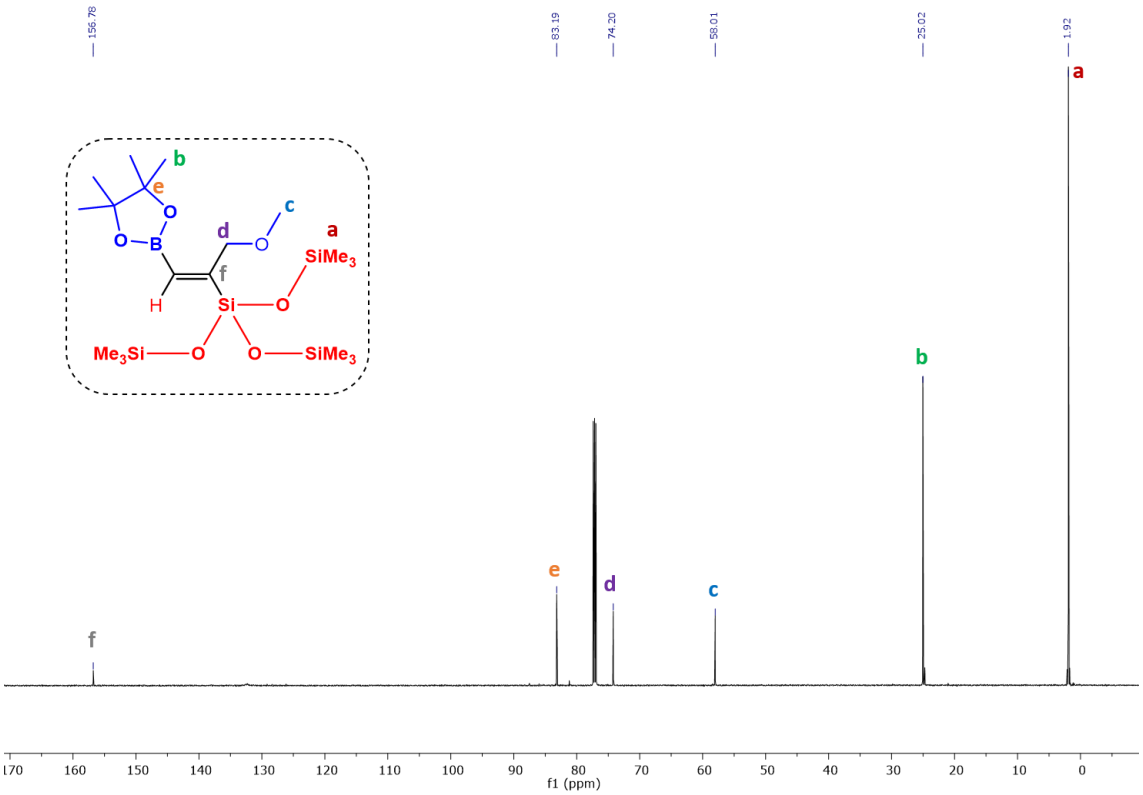


Figure S106. ^{13}C NMR of compound **3ge**.

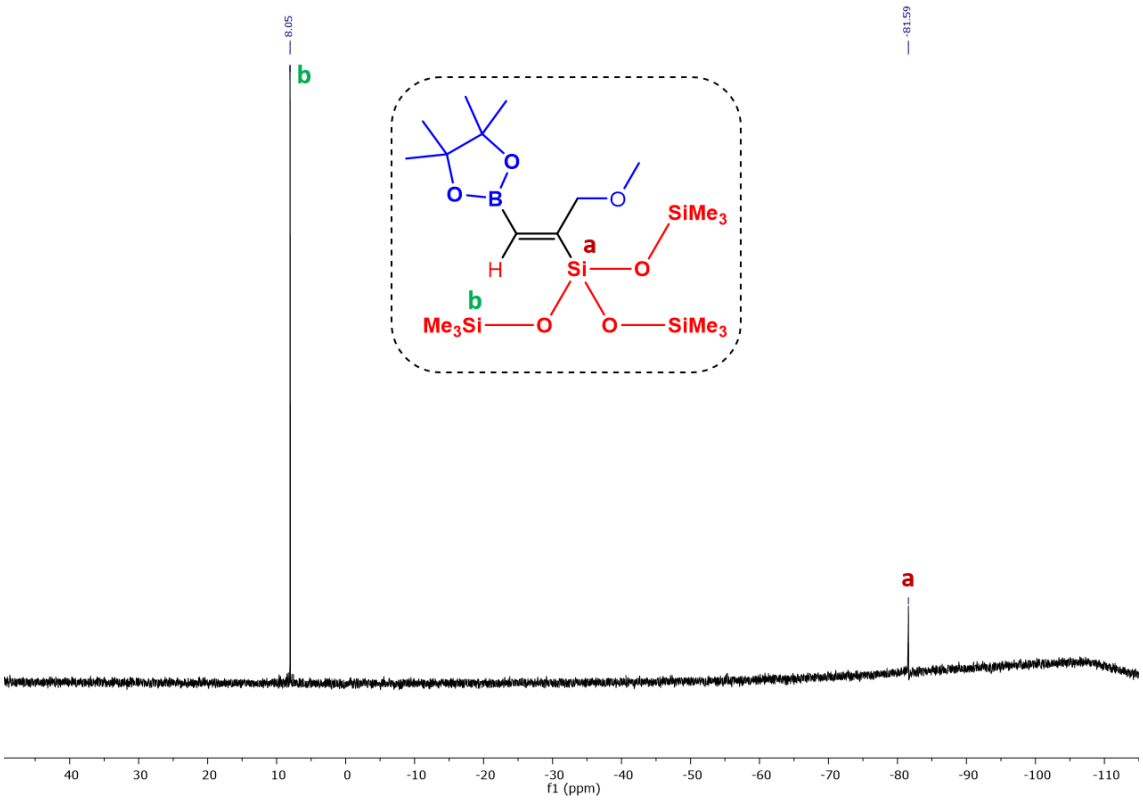


Figure S107. ^{29}Si NMR of compound **3ge**.

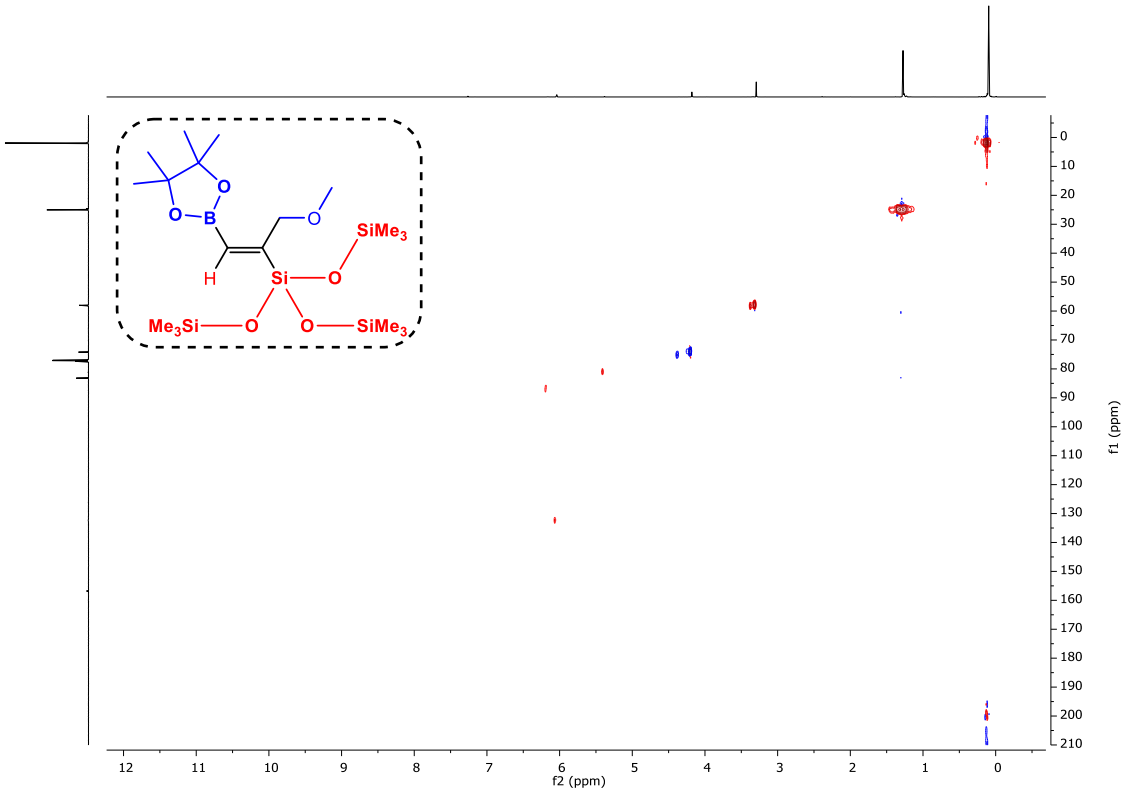


Figure S108. ^{1}H – ^{13}C HSQC of compound **3ge**.

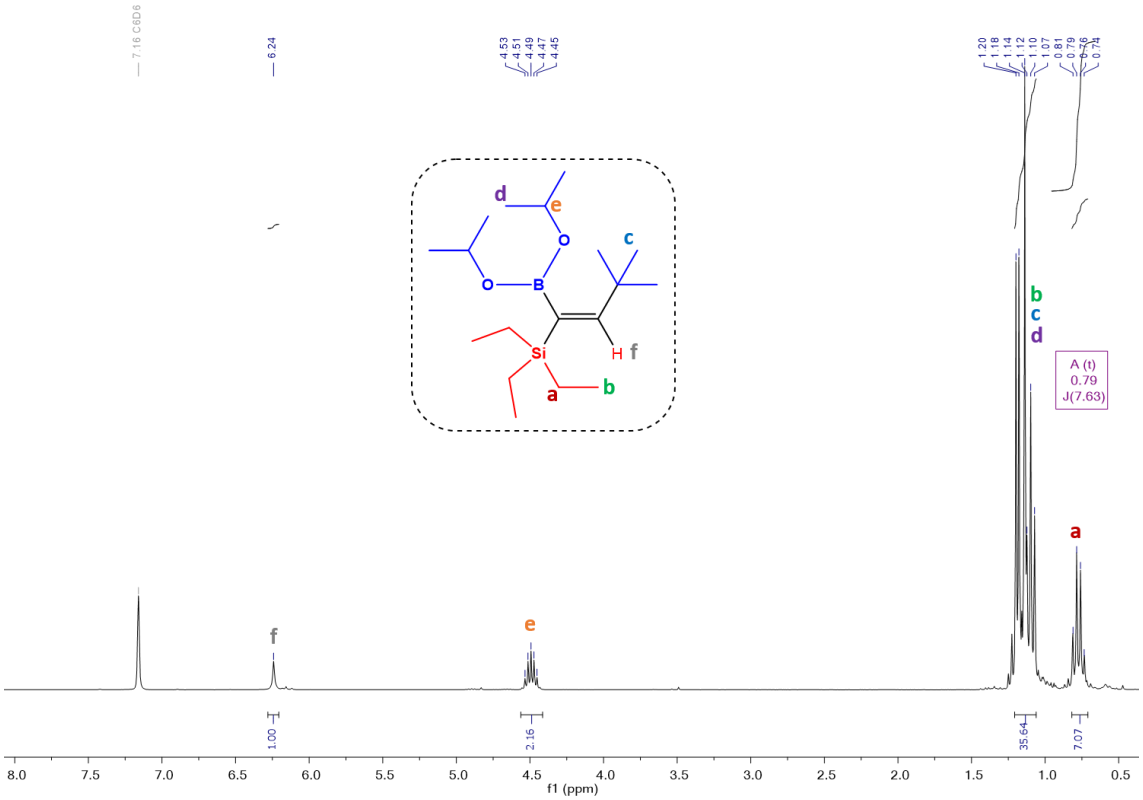


Figure S109. ^{1}H NMR of compound **4af**.

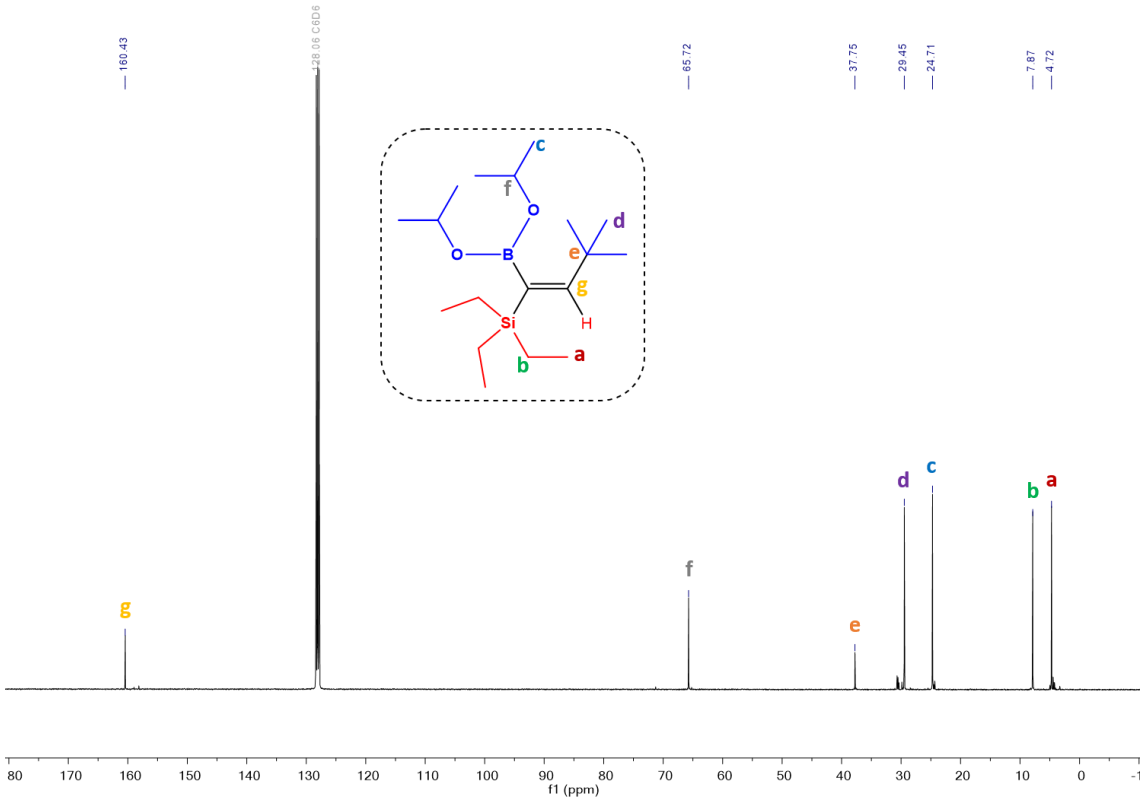


Figure S110. ^{13}C NMR of compound **4af**.

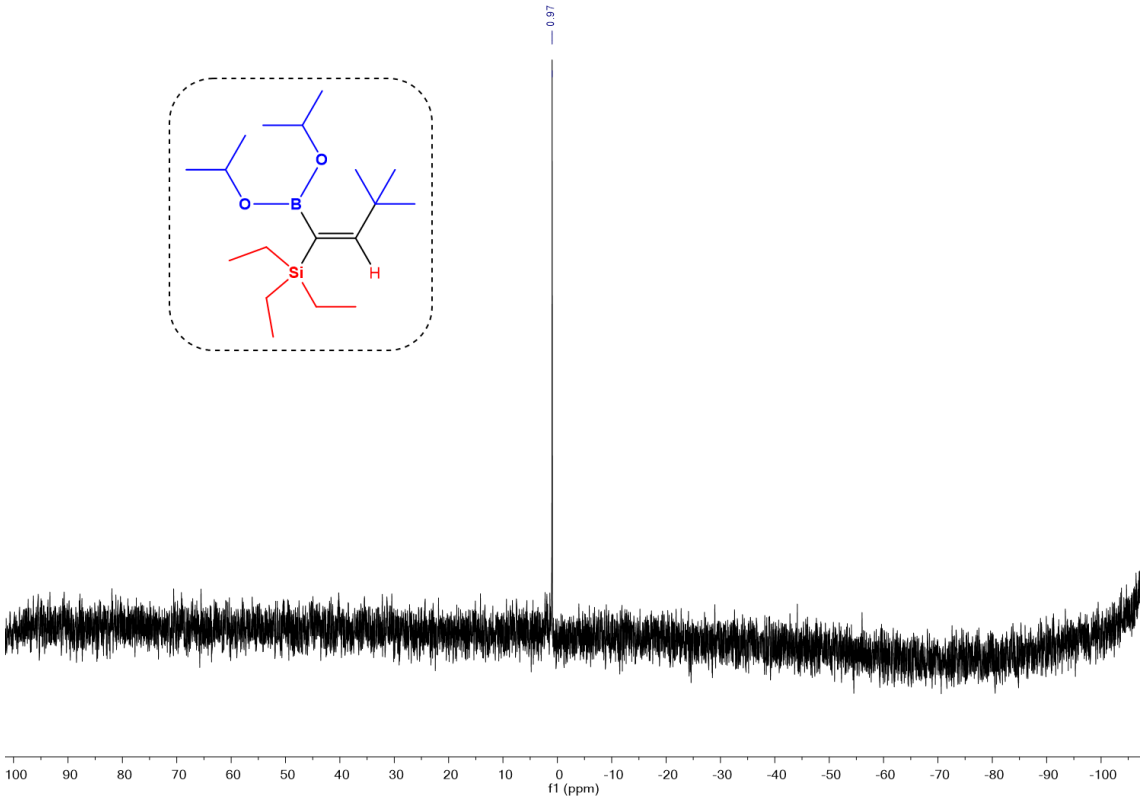


Figure S111. ^{29}Si NMR of compound **4af**.

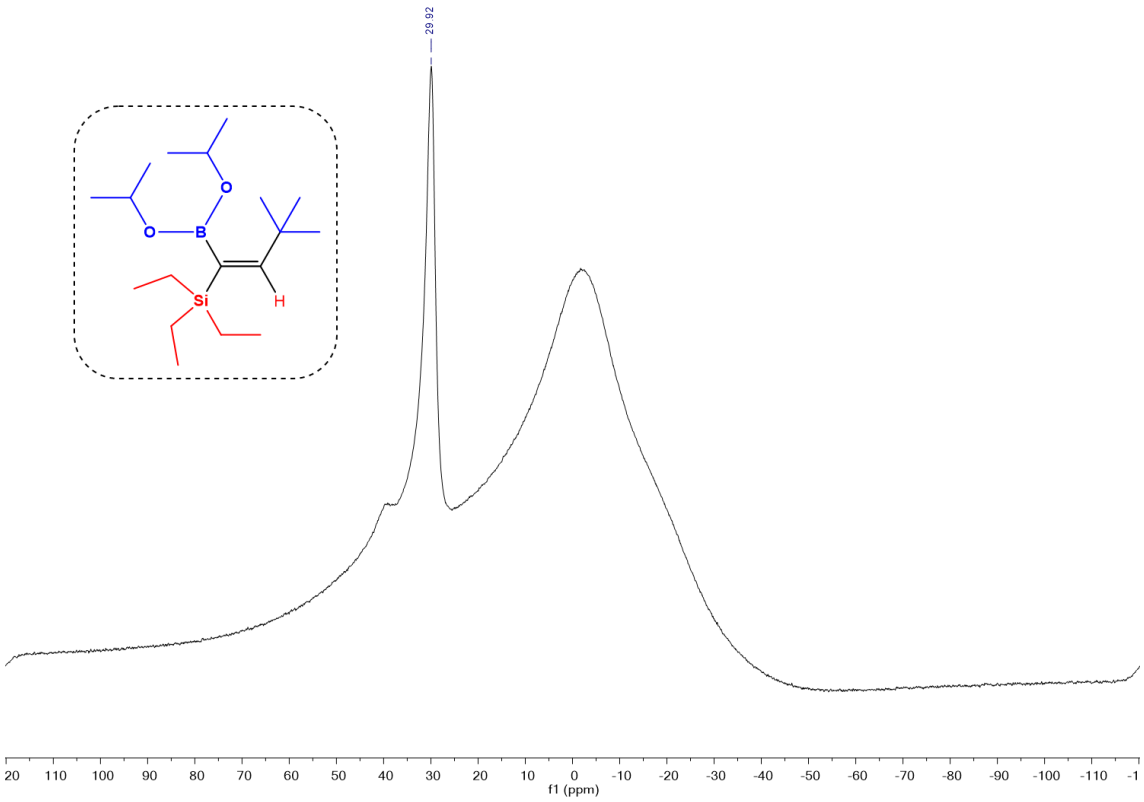


Figure S112. ^{11}B NMR of compound **4af**.

7. ESI spectra

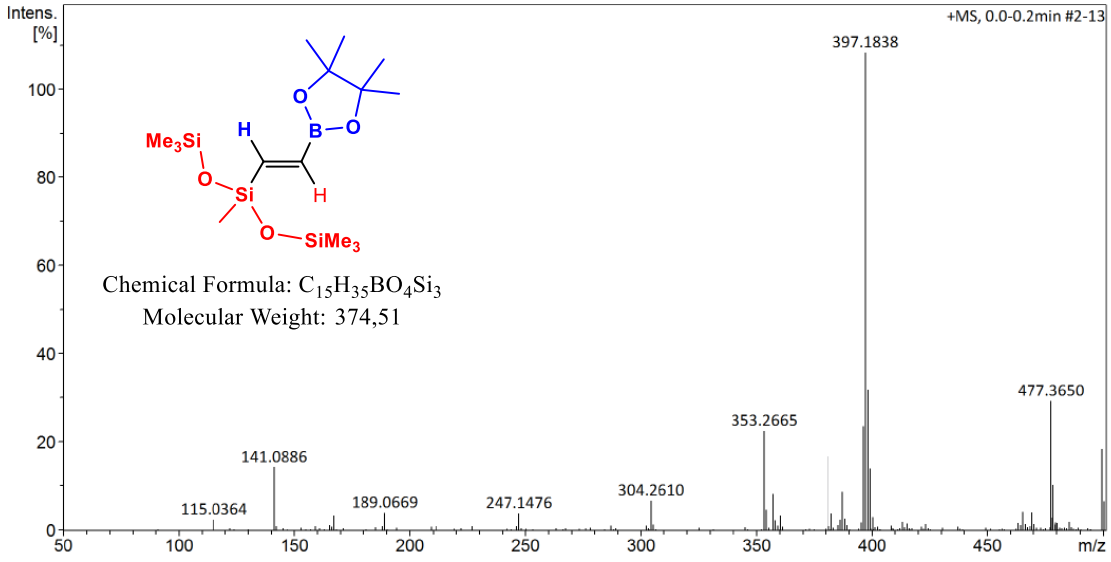


Figure S113. ESI MS spectra of **3ca/4ca** mixture 94/6.

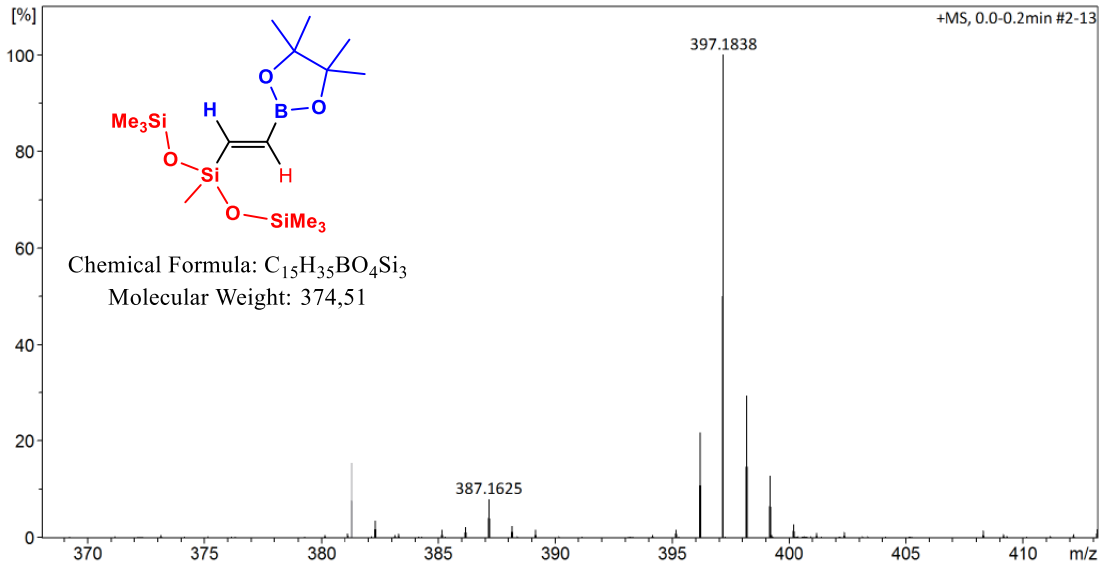


Figure S114. ESI MS spectra of **3ca/4ca** mixture 94/6.

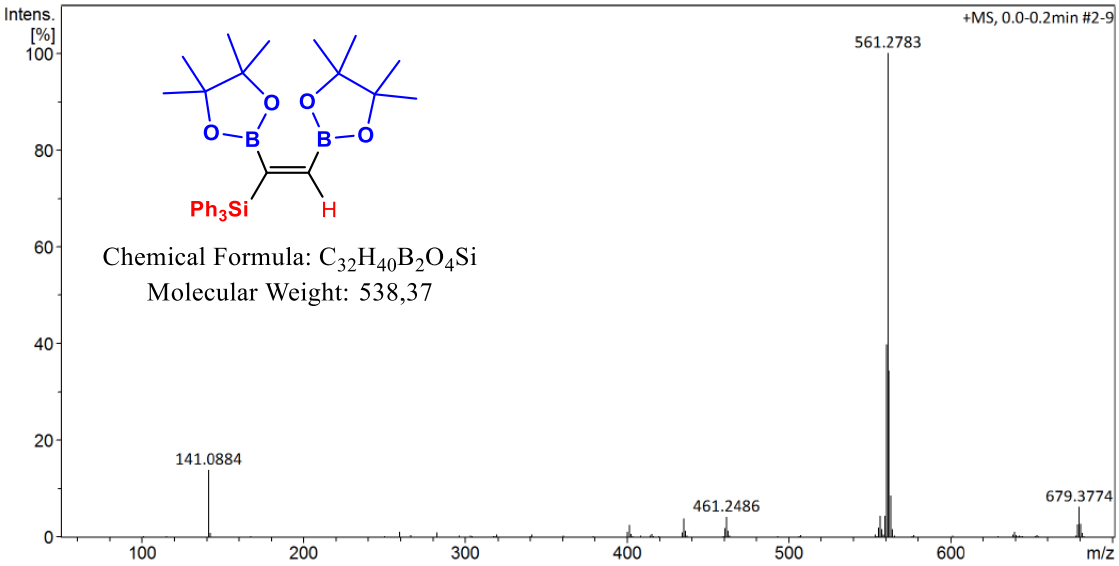


Figure S115. ESI MS spectra of compound **3bb**.

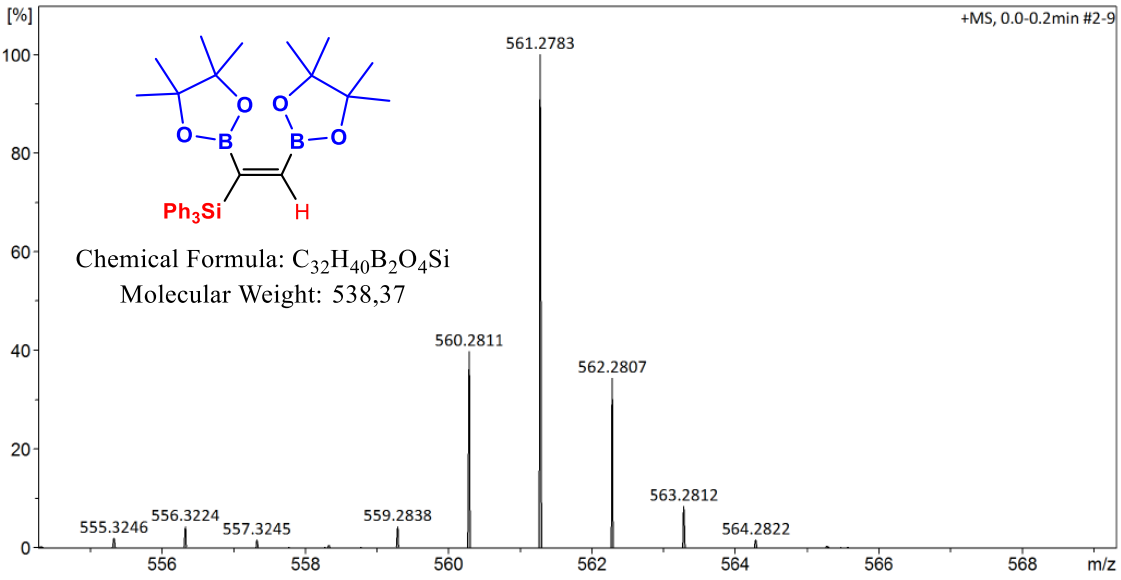


Figure S116. ESI MS spectra of compound **3bb**.

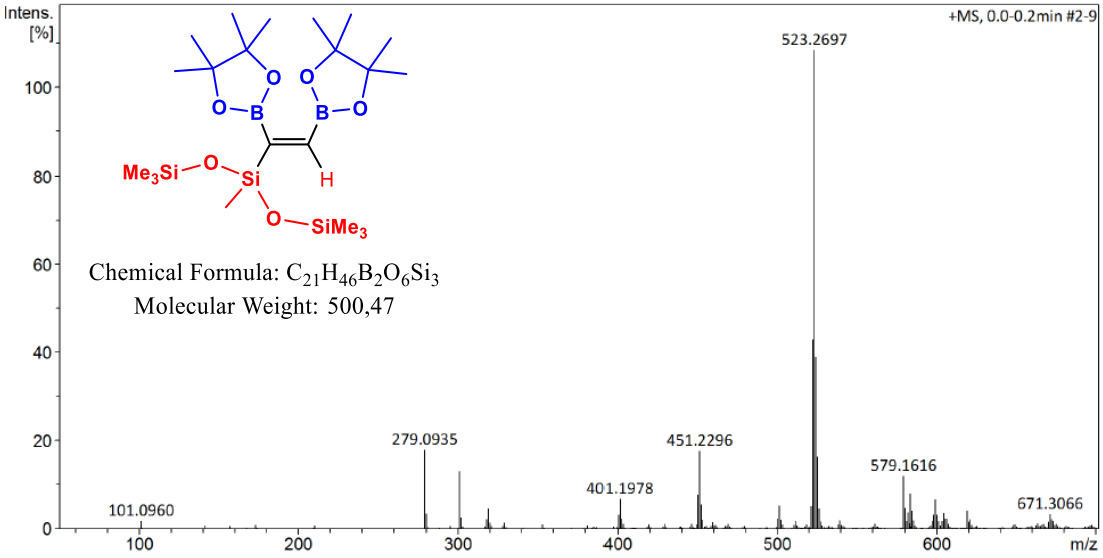


Figure S117. ESI MS spectra of **3cb/5cb** mixture 96/4.

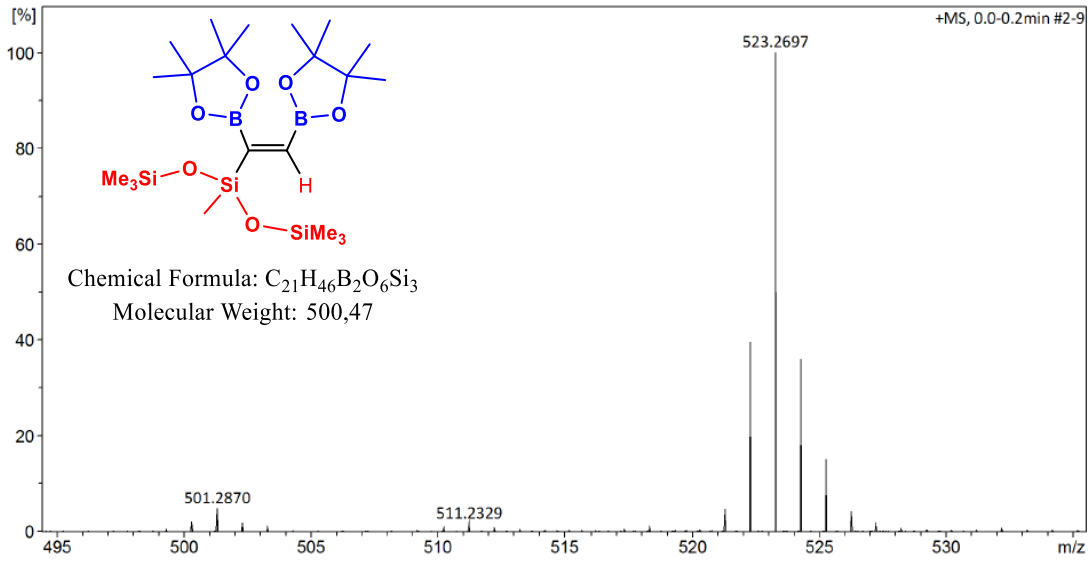


Figure S118. ESI MS spectra of **3cb/5cb** mixture 96/4.

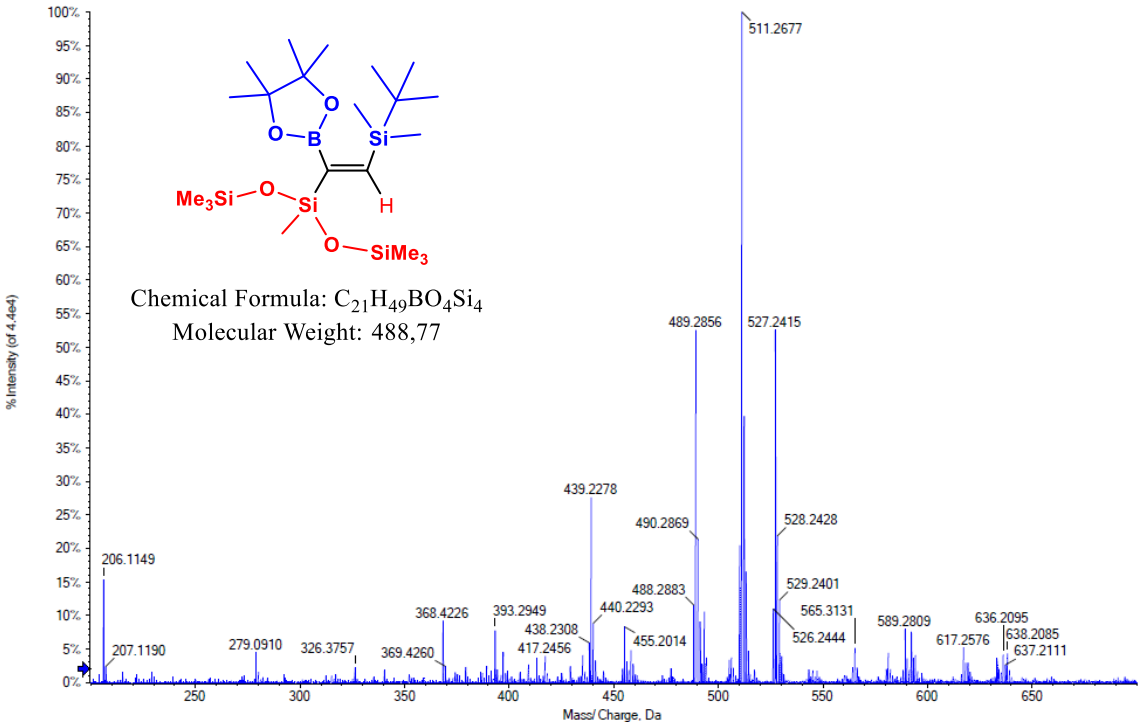


Figure S119. ESI MS spectra of compound **4cc**.

8. X-Ray crystallography

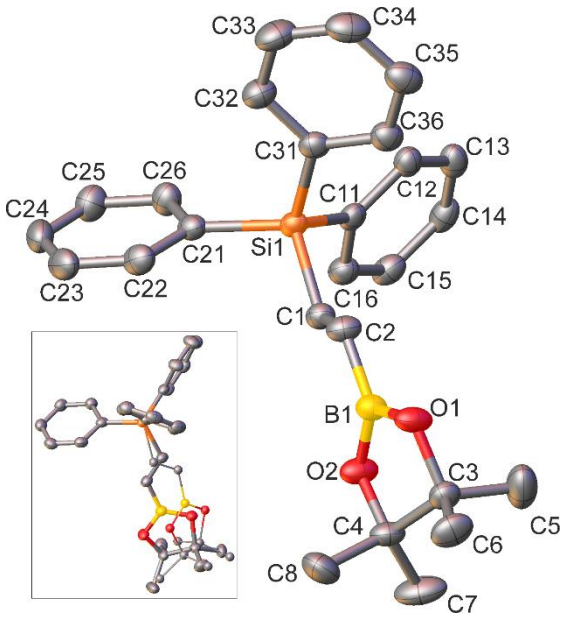


Figure S120. Molecular structure of compound **3ba** and atoms numbering scheme (one of the six symmetrically independent molecules). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The box shows an exemplary model of the disorder of four symmetrically independent molecules.

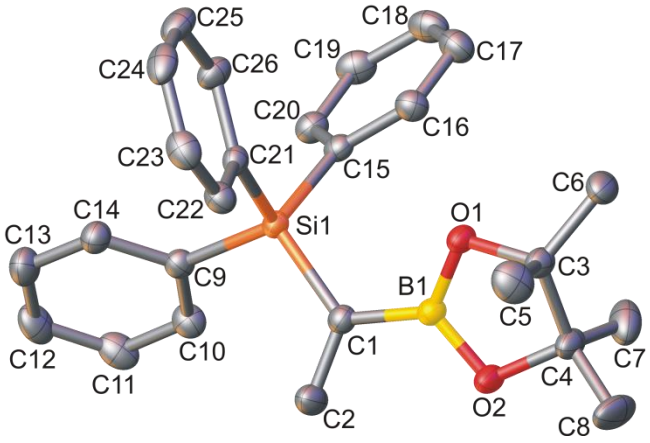


Figure S121. Molecular structure of compound **4ba** and atoms numbering scheme. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

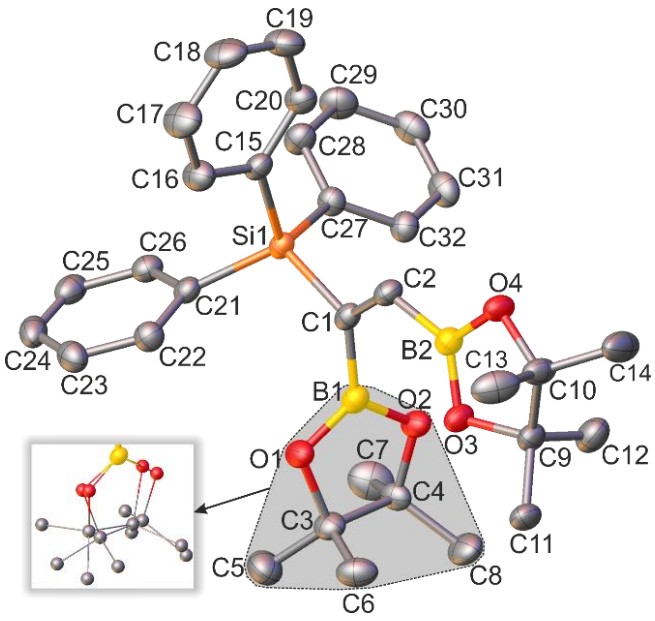


Figure S122. Molecular structure of compound **3bb** and atoms numbering scheme. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The disorder model is highlighted in the box.

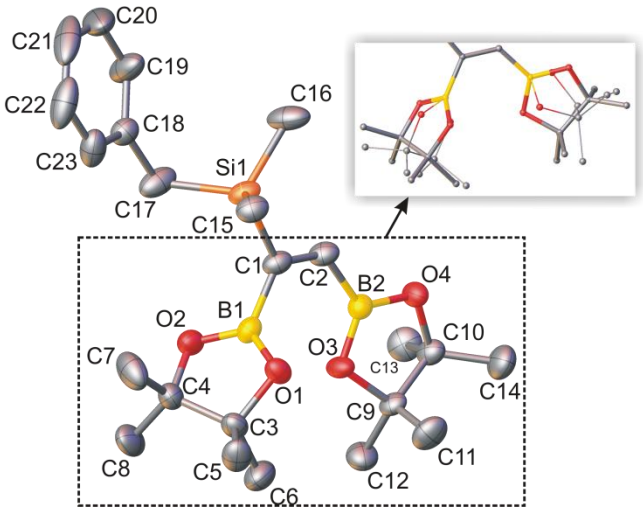


Figure S123. Molecular structure of compound **3fb** and atoms numbering scheme (one of the two symmetrically independent molecules). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The disorder model is highlighted in the box.

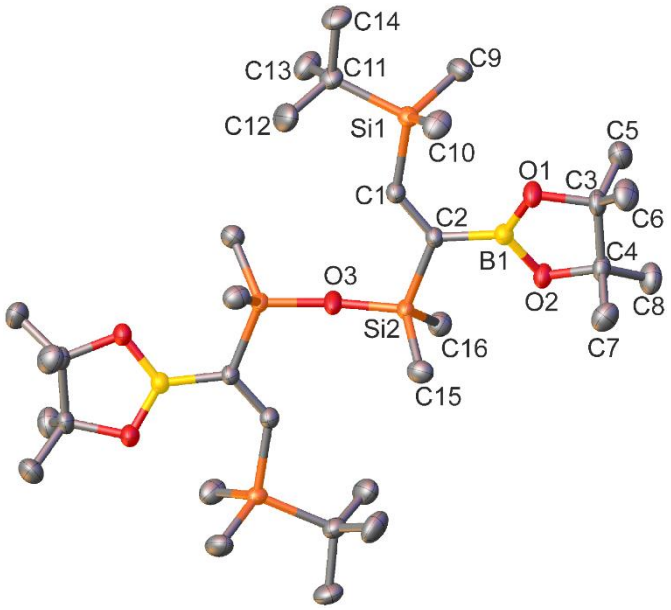


Figure S124. Molecular structure of compound **6dc** and atoms numbering scheme (shown only for asymmetric part of molecule). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

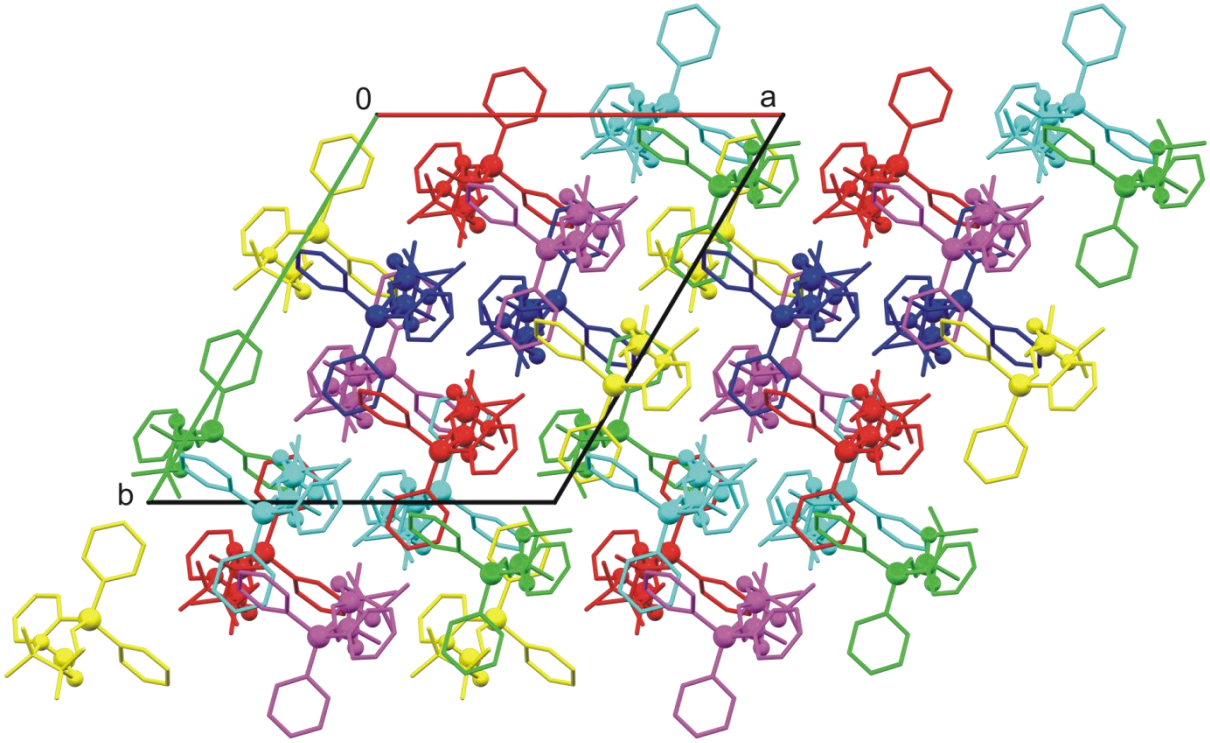


Figure S125. Molecular packing in crystal of **3bb** (view along c-axis). Symmetrically independent molecules are shown in different colour. Atoms of Si, B and O are showed as balls.

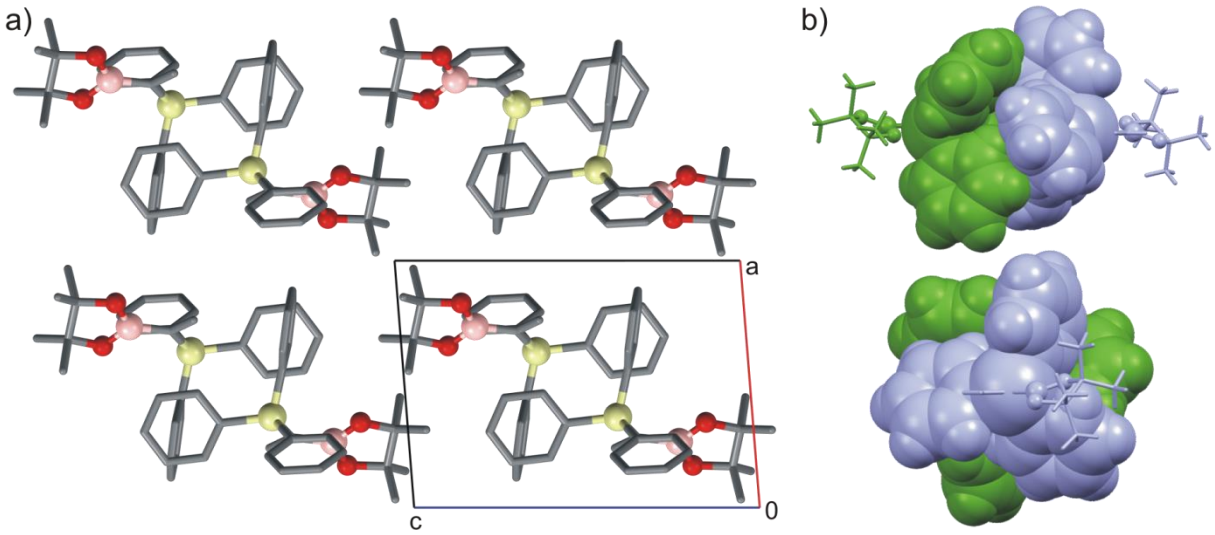


Figure S126. a) Molecular packing in crystal of **4ba** viewed along b axis (atoms of Si, B and O are showed as balls) and b) centrosymmetric sixfold phenyl embrace (6PE) supramolecular synthons (shown as space-fill models).

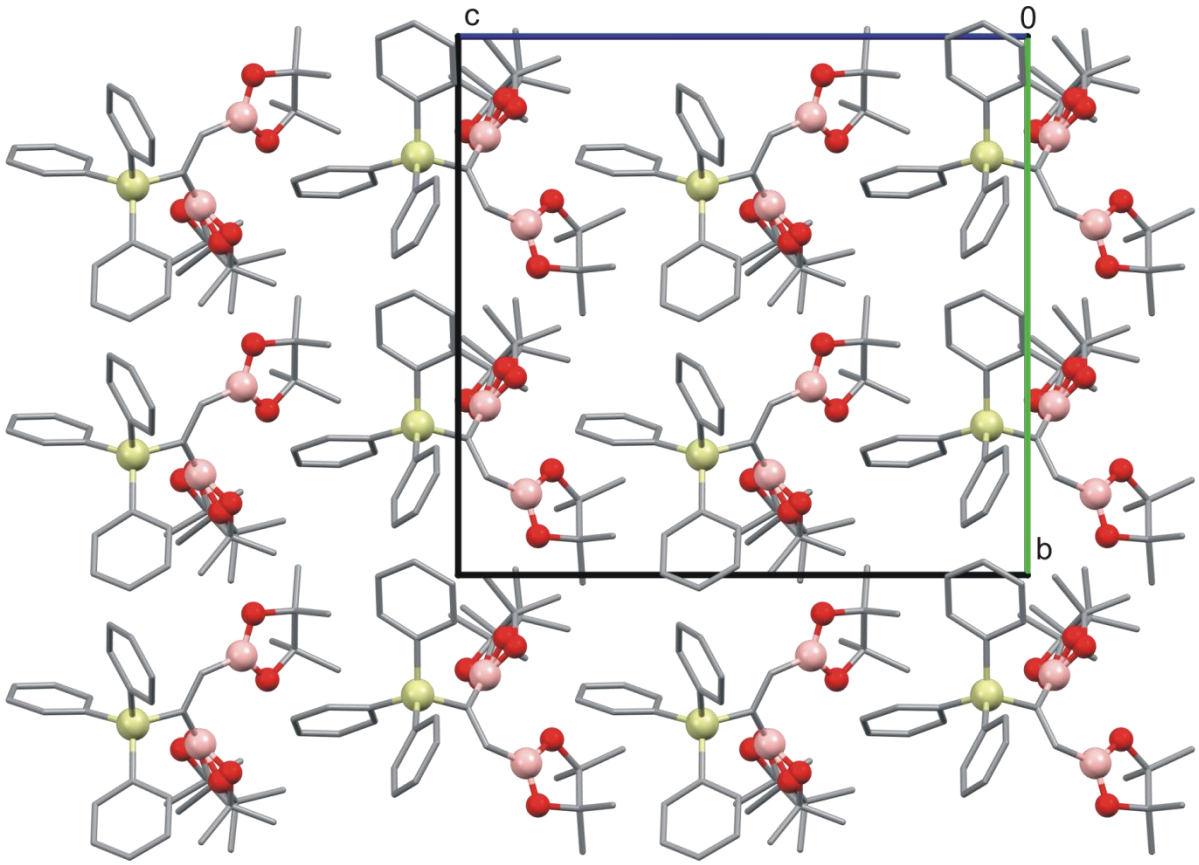


Figure S127. Molecular packing in crystal of **3bb** (view along a-axis). Atoms of Si, B and O are showed as balls.

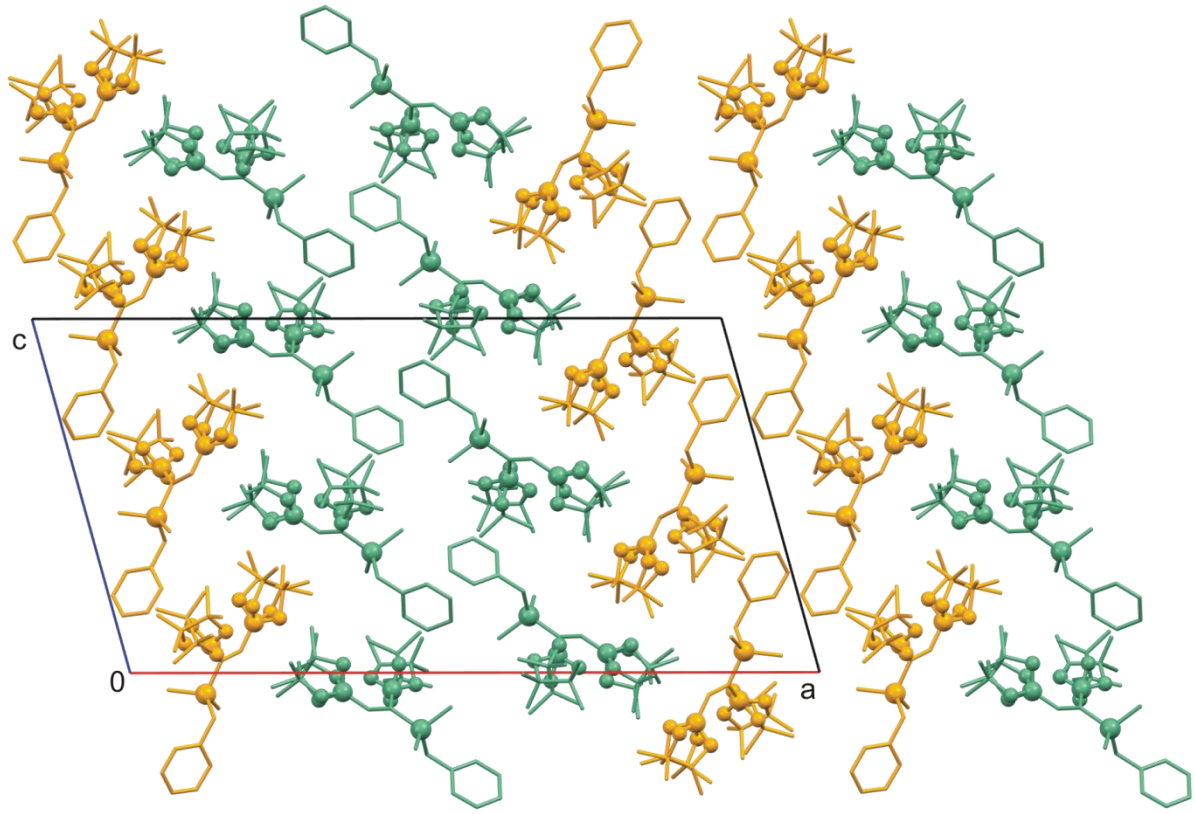


Figure S128. Molecular packing in crystal of **3fb** view along a-axis). Atoms of Si, B and O are showed as balls. Symmetrically independent molecules are shown with different colors.

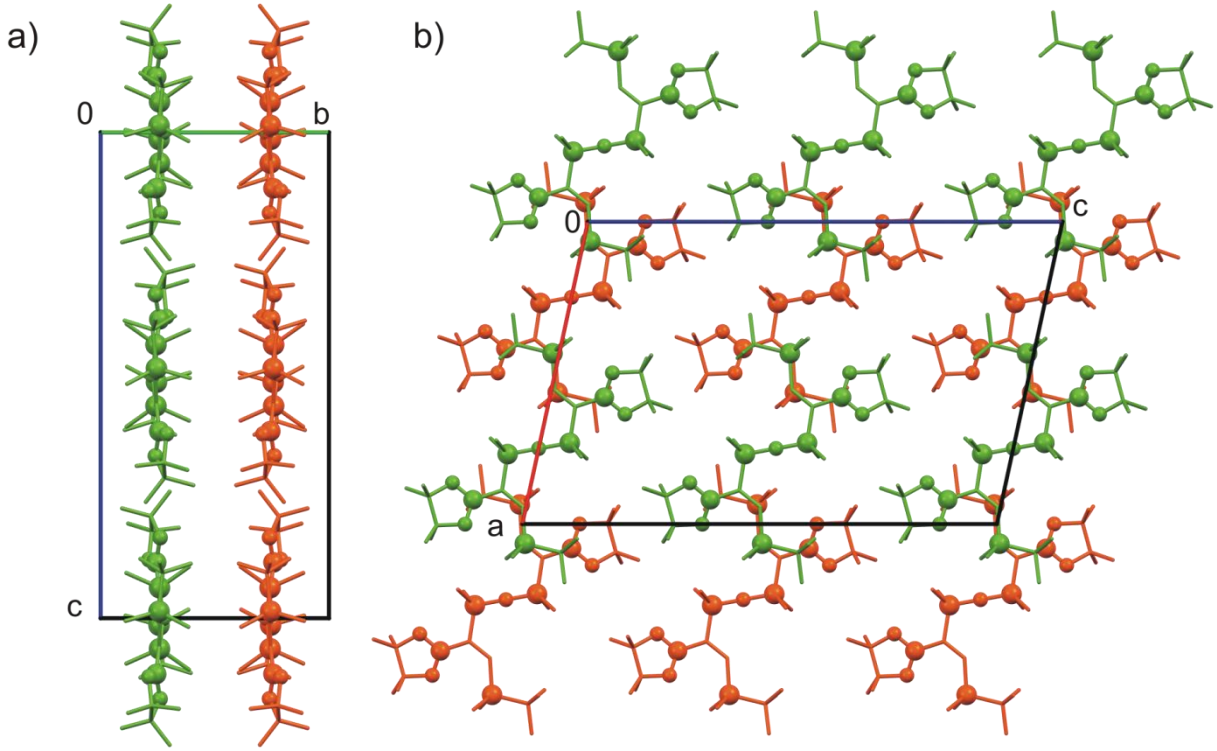


Figure S129. Molecular packing in crystal of **6dc** a) viewed along a-axis and b) viewed along b-axis. Atoms of Si, B and O are showed as balls. Symmetrically independent molecules are shown with different colors.

Table S7. Selected crystal data and structure refinement details.

	3ba	**4ba**	**3bb**	**3fb**	**6dc**
CCDC number	2107080	2184400	2083476	2193621	2107079
Chemical formula	$C_{26}H_{29}BO_2Si$	$C_{26}H_{29}BO_2Si$	$C_{32}H_{40}B_2O_4Si$	$C_{23}H_{38}B_2O_4Si$	$C_{32}H_{68}B_2O_5Si_4$
Mr	412.41	412.4	538.35	428.2	666.84
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, *Cc*	Monoclinic $P2_1/c$	Monoclinic, $I2/a$
Temperature (K)	130	130	130	130	130
a, *b*, *c* (Å)	19.7542 (4), 20.3725 (3), 21.9182 (5)	9.0492 (2), 10.2286 (3), 13.2850 (3)	10.11404 (9), 16.90606 (14), 18.29331 (16)	34.3594 (3), 8.4664 (1), 18.3153 (2)	15.82548 (14), 11.13928 (10), 24.2701 (2)
α,β,γ(°)	96.7187 (14), 112.3612 (19), 114.9700 (17)	71.204 (2), 84.767 (2), 87.048 (2)	90 102.3870 (9) 90	90 105.437 (1) 90	90 102.2310 (9) 90
V (Å^3)	6977.9 (3)	1158.91 (5)	3055.13 (5)	5135.71 (10)	4181.33 (7)
Z	12	2	4	8	4
D_x (Mg m^{-3})	1.178	1.182	1.170	1.108	1.059
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ(mm^{-1})	1.03	1.03	0.94	0.99	1.57
Crystal size (mm)	0.2 × 0.15 × 0.05	0.25 × 0.08 × 0.08	0.4 × 0.3 × 0.28	0.4 × 0.3 × 0.08	0.30 × 0.20 × 0.07
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	106159, 28031, 21060	29645, 4823, 4398	17756, 5832, 5799	78859, 10722, 10363	16793, 4300, 3670
R_{int}	0.027	0.028	0.018	0.035	0.027
Range of *h*, *k*, *l*	h = -24→24, k = -25→22, l = -27→27	h = -11→11, k = -12→12, l = -16→16	h = -12→12, k = -20→20, l = -22→22	h = -43→43, k = -10→9, l = -22→22	h = -19→19, k = -13→13, l = -30→27
$R[F^2 > 2\sigma F^2)]$, $wR(F^2)$, *S*	0.044, 0.143, 1.07	0.033, 0.087, 1.05	0.027, 0.076, 1.08	0.058, 0.159, 1.03	0.038, 0.111, 1.05
No. of parameters	2059	275	437	868	206
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.34, -0.37	0.33, -0.27	0.24, -0.16	0.57, -0.26	0.55, -0.31
Absolute structure parameter	-	-	-0.016 (13)	-	

Table S8. Selected geometric parameters [°] for **3ba, 3bb** and **6dc**.

		3ba	
C1A—C2A—B1A—O2A	6.8 (2)	C1D—C2D—B1D—O2D	-13.9 (2)
C1B—C2B—B1B—O2B	13.3 (3)	C1E—C2E—B1E—O2E	-7.5 (3)
C1B'—C2B'—B1B'—O2B'	16 (2)	C1E'—C2E'—B1E'—O2E'	-10 (3)
C1C—C2C—B1C—O2C	13.4 (3)	C1F—C2F—B1F—O2F	-6.9 (3)
C1C'—C2C'—B1C'—O2C'	14 (2)	C1F'—C2F'—B1F'—O2F'	-15 (2)
O2A—B1A—O1A	113.57 (12)	O1D—B1D—O2D	113.47 (12)
O2B—B1B—O1B	113.01 (16)	O2E—B1E—O1E	113.81 (13)
O1B'—B1B'—O2B'	118.9 (13)	O1E'—B1E'—O2E'	113.1 (15)
O2C—B1C—O1C	113.46 (16)	O2F—B1F—O1F	113.60 (13)
O1C'—B1C'—O2C'	116.7 (12)	O1F'—B1F'—O2F'	114.4 (13)
		4ba	
C2—C1—B1—O2	21.54 (18)		
O1—B1—O2	112.90 (10)		
		3bb	
B1—C1—C2—B2	2.0 (3)	C2—C1—B1—O1	107.8 (3)
C1—C2—B2—O3	-12.8 (3)	C2—C1—B1—O1A	88.2 (9)
O1A—B1—O2A	119.1 (11)		
O1—B1—O2	112.4 (3)	O3—B2—O4	113.9 (2)
		3fb	
B1A—C1A—C2A—B2A	-4.3 (4)	B1C—C1C—C2C—B2C	3.9 (4)
C1A—C2A—B2A—O3A	-57.1 (5)	C1C—C2C—B2C—O4C	71.8 (4)
C2A—C1A—B1A—O1A	82.0 (3)	C2C—C1C—B1C—O1C	16.6 (4)
C1A—C2A—B2A—O3B	16.2 (4)	C1C—C2C—B2C—O3D	-9.9 (6)
C2A—C1A—B1A—O2B	-43.7 (5)	C2C—C1C—B1C—O1D	-84.0 (4)
O2A—B1A—O1A	117.8 (2)	O1C—B1C—O2C	109.0 (3)
O4A—B2A—O3A	114.2 (3)	O3C—B2C—O4C	112.0 (3)
O1B—B1A—O2B	107.2 (3)	O2D—B1C—O1D	117.8 (3)
O3B—B2A—O4B	112.8 (2)	O3D—B2C—O4D	111.9 (3)
		6dc	
C1—C2—B1—O1	14.1 (2)	Si1—C1—C2—Si2	177.55 (8)

O1—B1—O2	112.6 (1)

9. References

1. J. Szyling, A. Franczyk, K. Stefanowska and J. Walkowiak, *Adv. Synth. Catal.*, 2018, **360**, 2966-2974.
2. J. Szyling, A. Franczyk, K. Stefanowska, H. Maciejewski and J. Walkowiak, *ACS Sustainable Chem. Eng.*, 2018, **6**, 10980-10988.
3. J. Szyling, A. Franczyk, K. Stefanowska, M. Klarek, H. Maciejewski and J. Walkowiak, *ChemCatChem*, 2018, **10**, 531-539.
4. T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu and T. Hiyama, *Tetrahedron*, 2002, **58**, 6381-6395.
5. M. G. McLaughlin, C. A. McAdam and M. J. Cook, *Org. Lett.*, 2015, **17**, 10-13.
6. M. Ludwiczak, J. Szyling, A. Garbicz, T. Sokolnicki, J. Pyziak and J. Walkowiak, *Inorg. Chem.*, 2020, **59**, 17555-17564.
7. J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. - Eur. J.*, 2017, **23**, 10997-11000.
8. Y. Meng, Z. Kong and J. P. Morken, *Angew. Chem. Int. Ed.*, 2020, **59**, 8456-8459.
9. N. Sarkar, S. Bera and S. Nembenna, *J. Org. Chem.*, 2020, **85**, 4999-5009.
10. M. Fleige, J. Mobus, T. vom Stein, F. Glorius and D. W. Stephan, *Chem. Commun.*, 2016, **52**, 10830-10833.
11. A. Harinath, I. Banerjee, J. Bhattacharjee and T. K. Panda, *New J. Chem.*, 2019, **43**, 10531-10536.
12. M. Magre, B. Maity, A. Falconnet, L. Cavallo and M. Rueping, *Angew. Chem. Int. Ed.*, 2019, **58**, 7025-7029.
13. K. Wen, J. Chen, F. Gao, P. S. Bhadury, E. Fan and Z. Sun, *Org. Biomol. Chem.*, 2013, **11**, 6350-6356.
14. Y. M. Chae, J. S. Bae, J. H. Moon, J. Y. Lee and J. Yun, *Adv. Synth. Catal.*, 2014, **356**, 843-849.
15. N. Kirai, S. Iguchi, T. Ito, J. Takaya and N. Iwasawa, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 784-799.
16. C. K. Blasius, V. Vasilenko, R. Matveeva, H. Wadepohl and L. H. Gade, *Angew. Chem. Int. Ed.*, 2020, **59**, 23010-23014.
17. T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu and T. Hiyama, *Angew. Chem. Int. Ed.*, 2001, **40**, 790-792.
18. E. K. Edelstein, S. Namirembe and J. P. Morken, *J. Am. Chem. Soc.*, 2017, **139**, 5027-5030.
19. M. Jankowska, B. Marciniec, C. Pietraszuk, J. Cytarska and M. Zaidlewicz, *Tetrahedron Lett.*, 2004, **45**, 6615-6618.
20. J. Walkowiak, B. Marciniec and M. Jankowska–Wajda, *J. Organomet. Chem.*, 2010, **695**, 1287-1292.
21. M. Kidonakis and M. Stratakis, *Eur. J. Org. Chem.*, 2017, **2017**, 4265-4271.
22. F. Alonso, Y. Moglie, L. Pastor-Perez and A. Sepulveda-Escribano, *ChemCatChem*, 2014, **6**, 857-865.
23. Q. Feng, H. Wu, X. Li, L. Song, L. W. Chung, Y-D. Wu, J. Sun, *J. Am. Chem. Soc.*, 2020, **142**, 13867-13877.
24. C.S. Yi, D. W. Lee, Y. Chen, *Organometallics,* 1999, **18**, 2043–2045.
25. CrysAlis PRO 1.171.41.94a, Rigaku Oxford Diffraction, 2021.
26. G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.
27. G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.
28. S. Parsons, H. D. Flack and T. Wagner, *Acta Cryst. B*, 2013, **69**, 249-259.
29. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
30. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.*, 2020, **53**, 226-235.