Supporting Information

Ligand-Dependent Controlled Copper-Catalyzed Regio- and Stereoselective Silaboration of Alkynes

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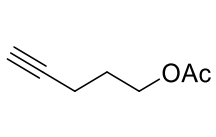
I. General Information

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of argon or glove box. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. Other reagents were commercially purchased and were used as received without further purification for the reactions. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on a Bruker Advance 400M NMR spectrometers ($CDCl_3$ or DMSO-d_6 as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0) and relative to the signal of chloroform-*d* (δ = 7.26, singlet) or DMSO-d_6 (δ = 2.50, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and *etc*. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0) and relative to the signal of chloroform-*d* (δ = 77.16, triplet). High-resolution mass spectral analysis (HRMS) was performed on Water XEVO G2 Q-TOF (Waters Corporation).

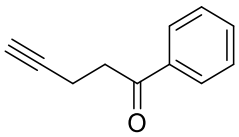
II. Experimental Procedures

2.1 General Procedures for the Synthesis of Starting Materials

Compounds **1f**,[1] **1h-1m**,[2-7] **1u**,[8] **1u′**,[9] **1x**[10] and **1y**[11] were prepared according to the previously reported procedures.



1f



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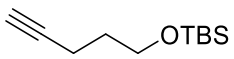
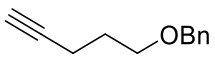
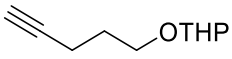


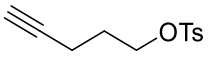
1i



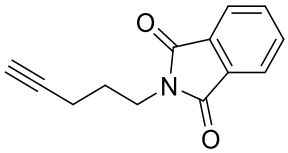
1j



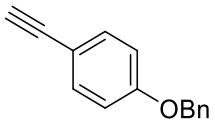
1k



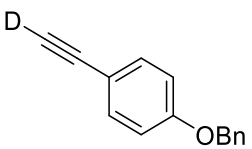
1l



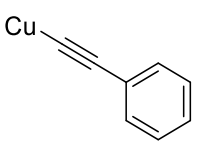
1m



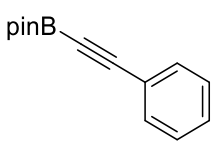
1u



1u'



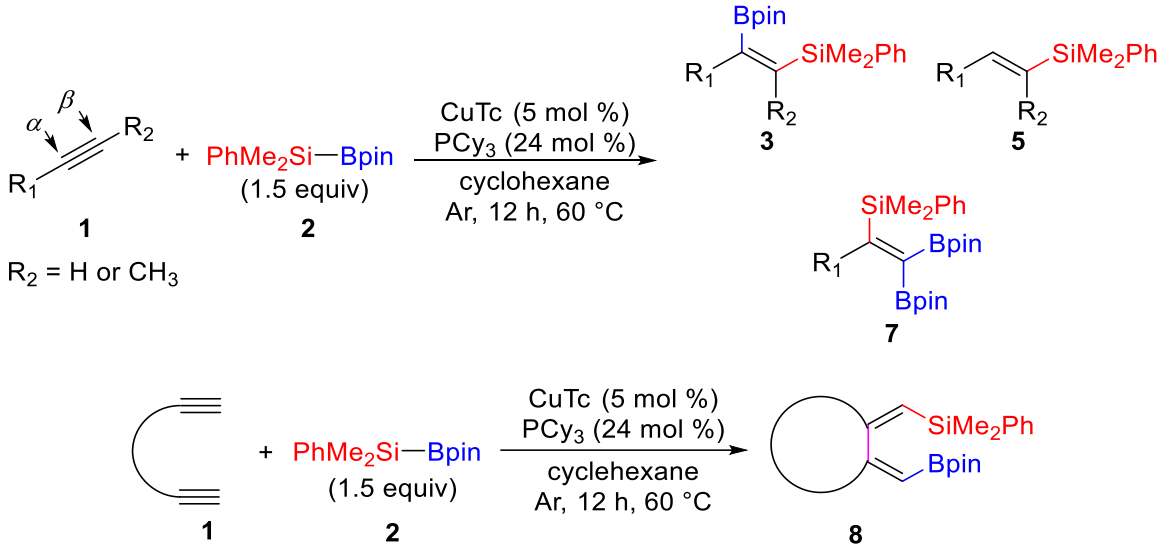
1x



1y

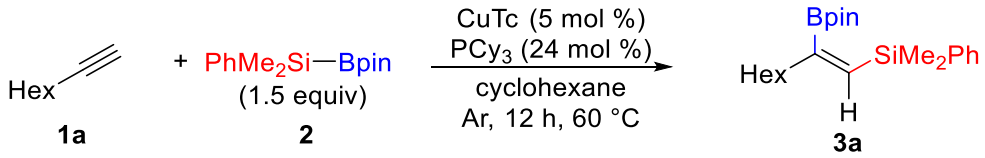
2.2 General Procedures for Copper-Catalyzed Silaboration of Alkynes

A. General Procedure A:



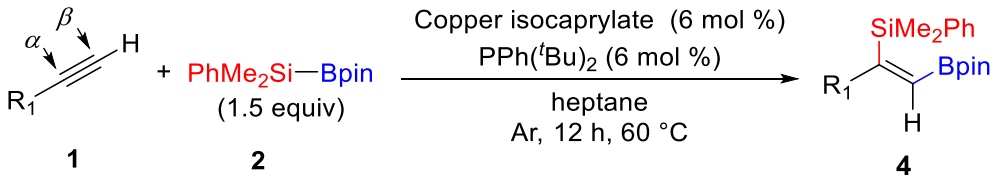
An oven-dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuTc (1.9 mg, 0.010 mmol, 5 mol %) and PCy_3 (13.4 mg, 0.048 mmol, 24 mol %). Then, the tube was sealed with a septum and removed from glove box. The mixture in dry cyclohexane solvent (1 mL, 0.2 M) was stirred for 1h at room temperature. Subsequently, the alkyne (0.2 mmol, 1.0 equiv) and Me_2PhSi-Bpin (78.6 mg, 0.3 mmol, 1.5 equiv) were added by syringe under argon atmosphere. The reaction mixture was stirred at 60 ˚C for another 12 h. After cooling to the room temperature, the reaction mixture was filtered through celite and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the target product.

*5 mmol scale experiment for the preparation of **3a***



An oven-dried 100 mL Schlenk flask equipped with a magnetic stirrer was charged with CuTc (47.7 mg, 0.250 mmol, 5 mol %) and PCy_3 (336.5 mg, 1.250 mmol, 24 mol %). Then, the flask was sealed with a septum and removed from glove box. The mixture in dry cyclohexane solvent (25 mL, 0.2 M) was stirred for 1h at room temperature. Subsequently, substrate 1a (551.0 mg, 5.000 mmol, 1.0 equiv) and Me_2PhSi-Bpin (1966.7 mg, 7.500 mmol, 1.5 equiv) were added by syringe under argon atmosphere. The reaction mixture was stirred at 60 ˚C for another 20 h. After cooling to the room temperature, the reaction mixture was filtered through celite and concentrated in vacuo. The residue was purified by flash column chromatography (PE:EA = 99.7:0.3) on silica gel to give 3a (1.3221 g, 3.550 mmol, 71%).as colorless oil.

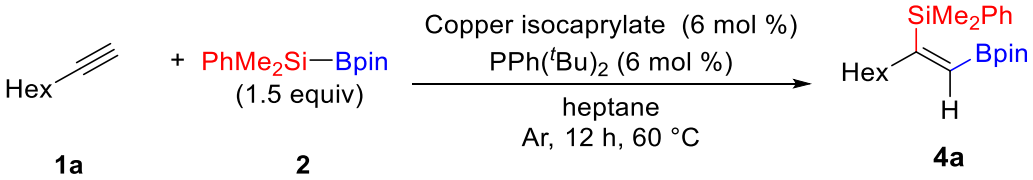
B. General Procedure B:



1 **2** **4**

An oven-dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with copper isocaprylate (4.2 mg, 0.012 mmol, 6 mol %) and $PPh(^tBu)_2$ (2.7 mg, 0.012 mmol 6 mol %). Then the tube was sealed with a septum and removed from glove box. The mixture in dry heptane (1 mL, 0.2 M) was stirred for 1 h. Subsequently, the alkyne (0.2 mmol, 1.0 equiv) and Me_2PhSi-Bpin (78.6 mg, 0.3 mmol, 1.5 equiv) were added by syringe under argon atmosphere. The reaction mixture was stirred at 60 ˚C for another 12 h. After cooling to the room temperature, the reaction mixture was filtered through celite and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the target product.

*5 mmol scale experiment for the preparation of **4a***



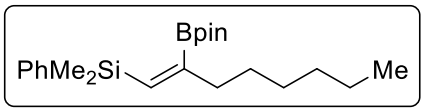
1a **2** **4a**

An oven-dried 100 mL Schlenk flask equipped with a magnetic stirrer was charged with copper isocaprylate (105.0 mg, 0.300 mmol, 6 mol %) and $PPh(^tBu)_2$ (66.7 mg, 0.300 mmol, 6 mol %). Then, the flask was sealed with a septum and removed from glove box. The mixture in dry heptane solvent (25 mL, 0.2 M) was stirred for 1h at room temperature. Subsequently, substrate **1a** (551.0 mg, 5.000 mmol, 1.0 equiv) and Me_2PhSi-Bpin (2622.3 mg, 10.000 mmol, 2.0 equiv) were added by syringe under argon atmosphere. The reaction mixture was stirred at 60 ˚C for another 20 h. After cooling to the room temperature, the reaction mixture was filtered through celite and concentrated in vacuo. The residue was purified by flash column chromatography (PE:EA = 99.7:0.3) on silica gel to give **4a** (1.3983 g, 3.754 mmol, 75%).as colorless oil.

III. Characterization Data and Spectrum of Products

A. Characterization data and spectrum of products 3

(*E*)-dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)silane (3a).



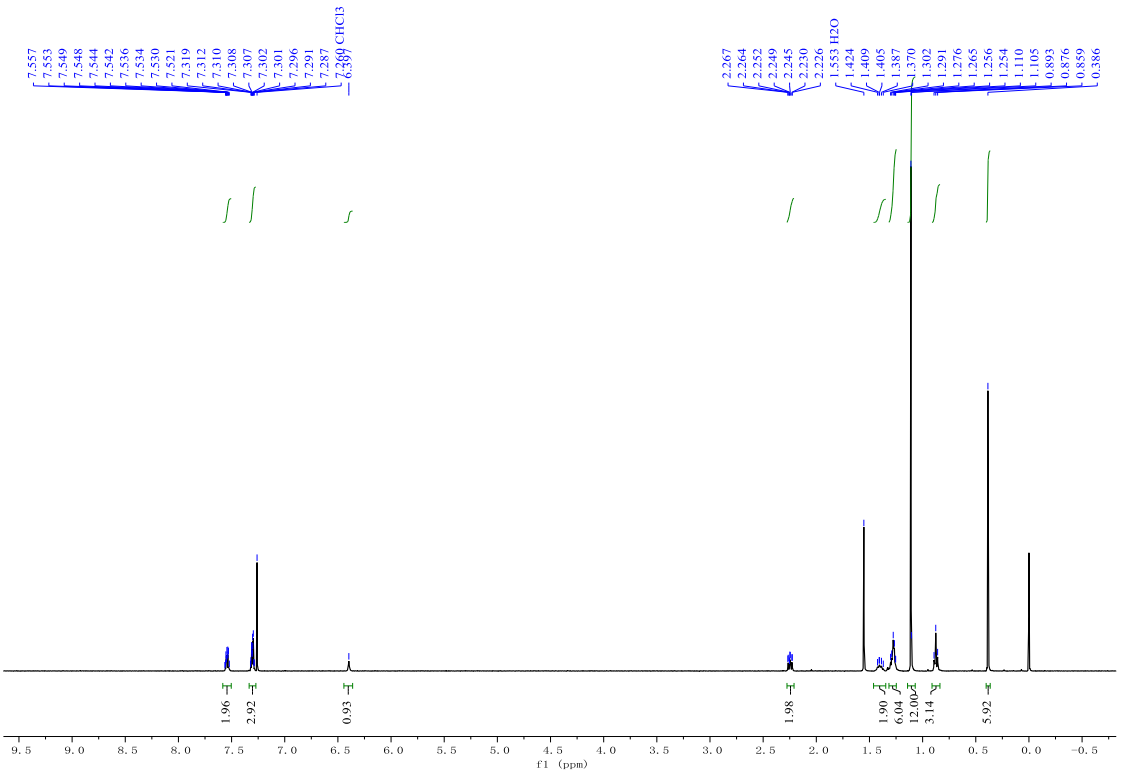
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 90% yield (67.3 mg). R_f = 0.63 (Petroleum ether:EtOAc = 98:2).

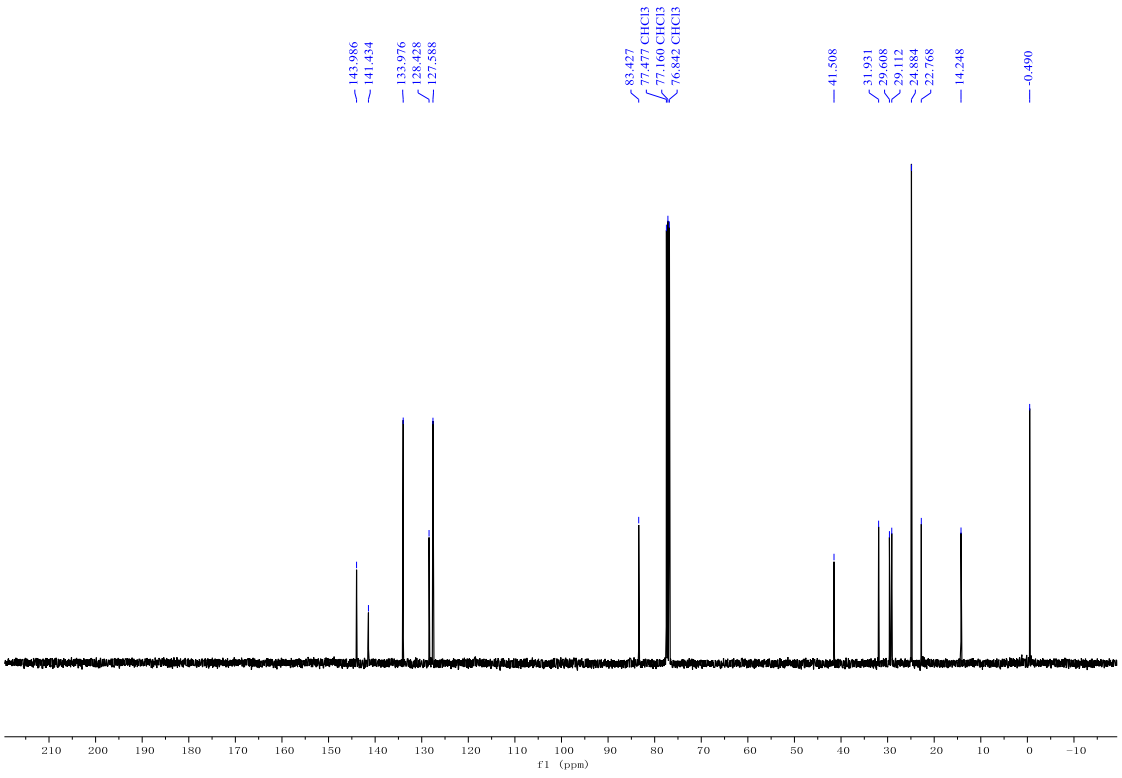
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.33 – 7.28 (m, 3H), 6.40 (s, 1H), 2.25 (td, *J* = 7.5, 1.4 Hz, 2H), 1.49 – 1.35 (m, 2H), 1.32 – 1.24 (m, 6H), 1.11 (s, 12H), 0.90 – 0.85 (m, 3H), 0.39 (s, 6H).

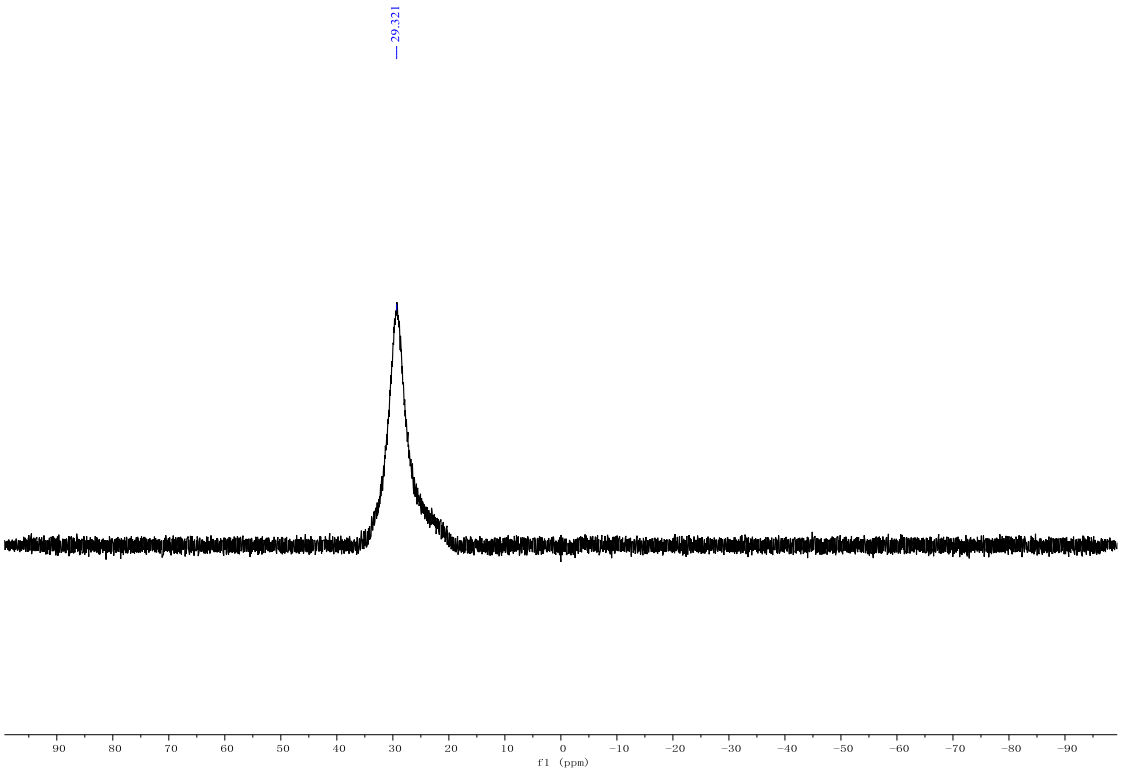
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.83, 141.27, 133.82, 128.27, 127.43, 83.27, 41.35, 31.77, 29.45, 28.95, 24.72, 22.61, 14.09, -0.65.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.32.

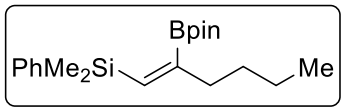
HRMS (ESI) m/z calculated for $C_{22}H_{37}BO_2SiNa$ $[M+Na]^+$: 395.2554, found: 395.2563.




143.986
141.434
133.976
128.428
127.588
83.427
77.477 CHCl3
77.160 CHCl3
76.842 CHCl3
41.508
31.931
29.608
29.112
24.884
22.768
14.248
-0.490
f1 (ppm)


29.321
f1 (ppm)

(*E*)-dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)silane (3b).



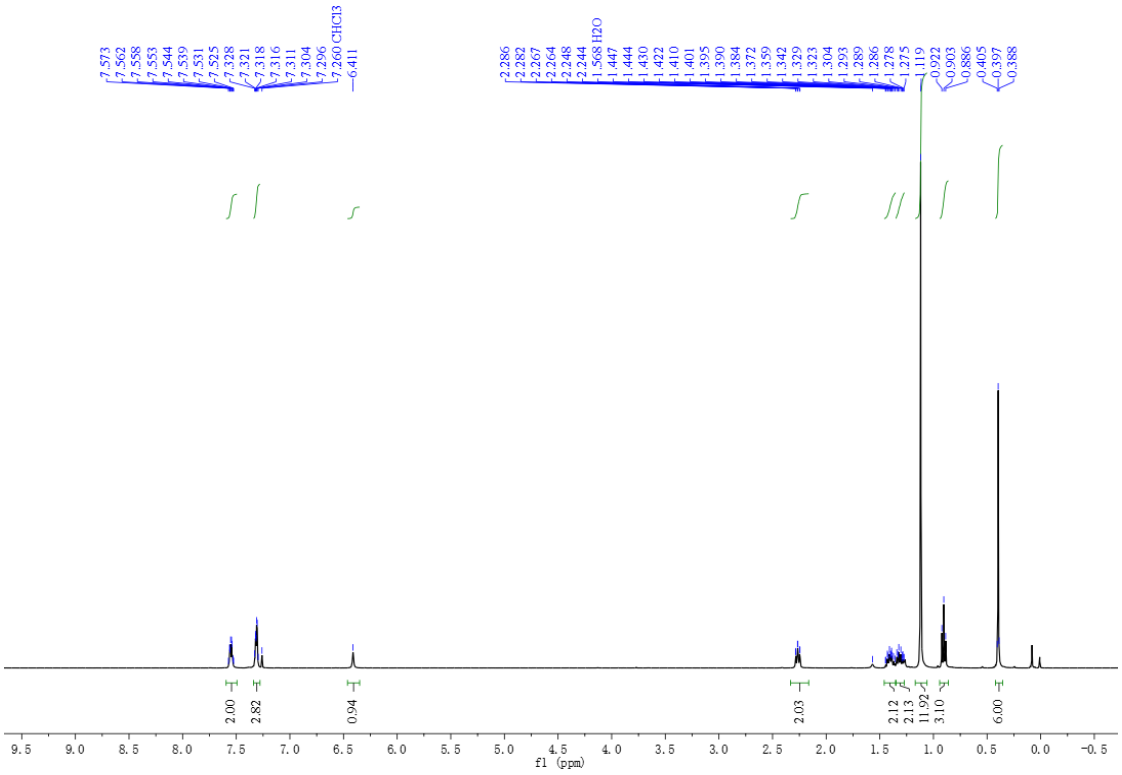
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 90% yield (60.7 mg). R_f = 0.69 (Petroleum ether:EtOAc = 98:2).

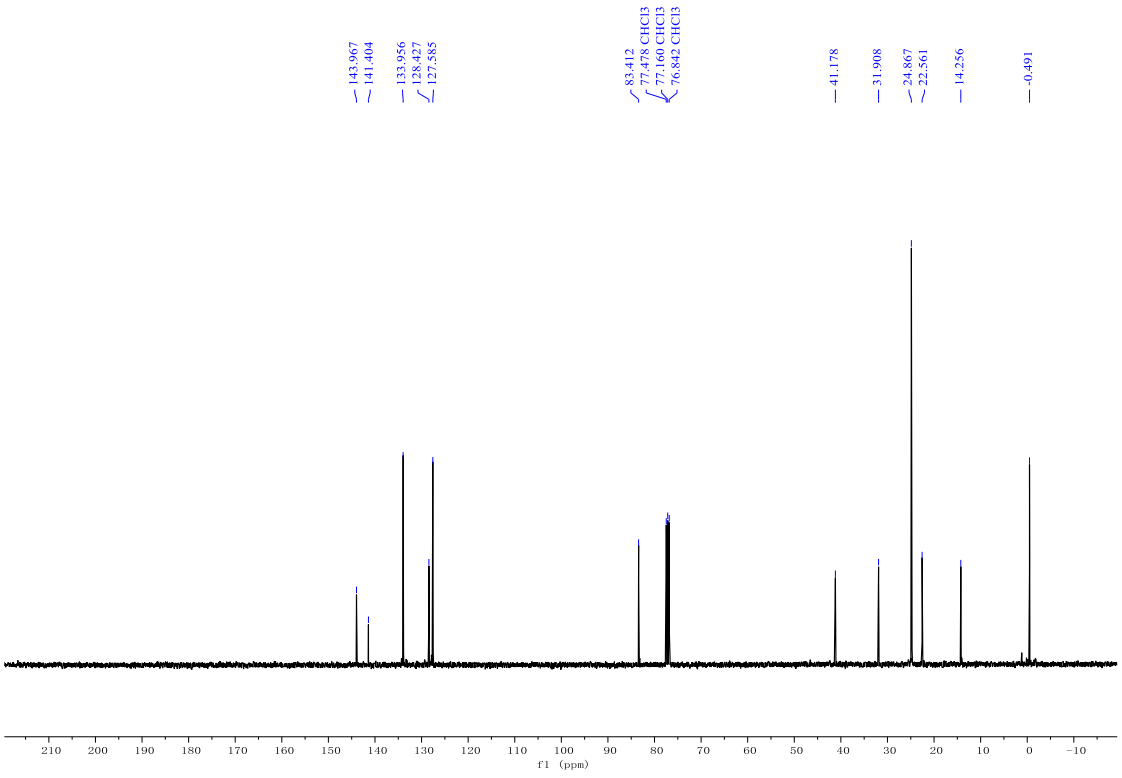
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.35 – 7.27 (m, 3H), 6.41 (s, 1H), 2.32 – 2.19 (m, 2H), 1.47 – 1.33 (m, 2H), 1.37 – 1.27 (m, 2H), 1.12 (s, 12H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.40 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.97, 141.40, 133.96, 128.43, 127.59, 83.41, 41.18, 31.91, 24.87, 22.56, 14.26, -0.49.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.39.

HRMS (ESI) m/z calculated for $C_{20}H_{33}BO_2SiNa$ $[M+Na]^+$: 367.2241, found: 367.2241.




143.967
141.404
133.956
128.427
127.585
83.412
77.478 CHCl3
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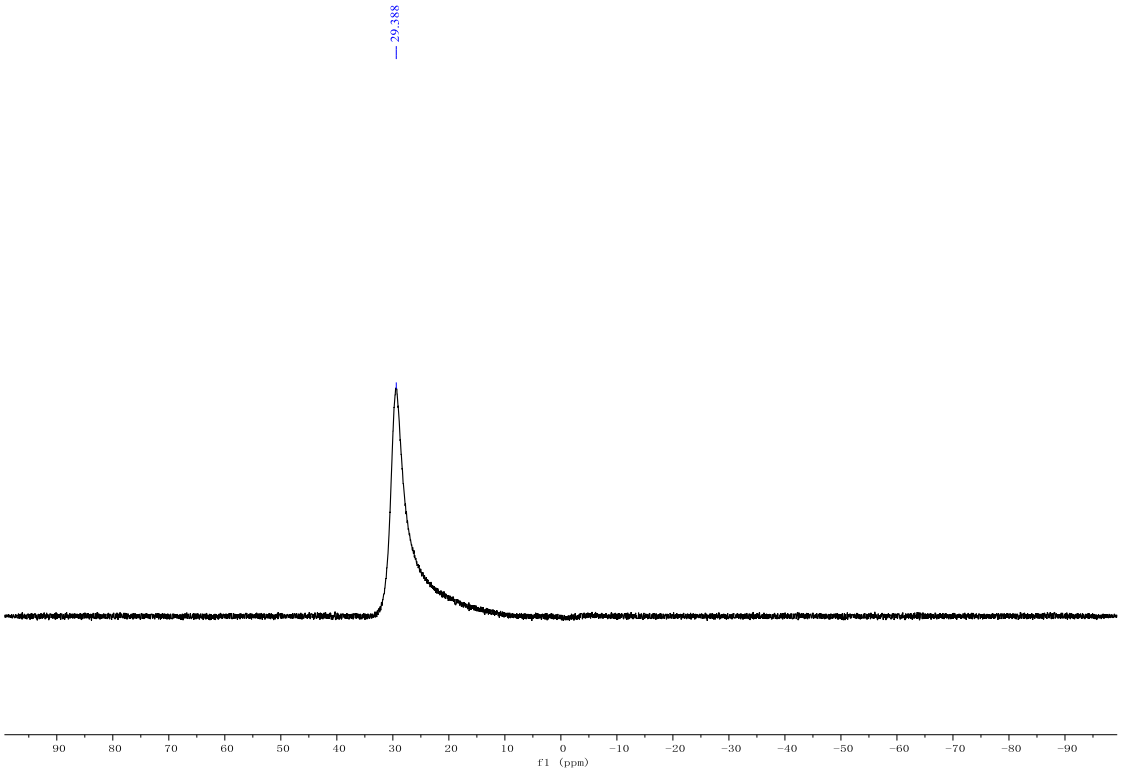
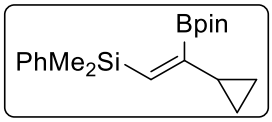
76.842 CHCl3
41.178
31.908
24.867
22.561
14.256
-0.491
f1 (ppm)


29.388
f1 (ppm)

(*E*)-(2-cyclopropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl) silane (3d).



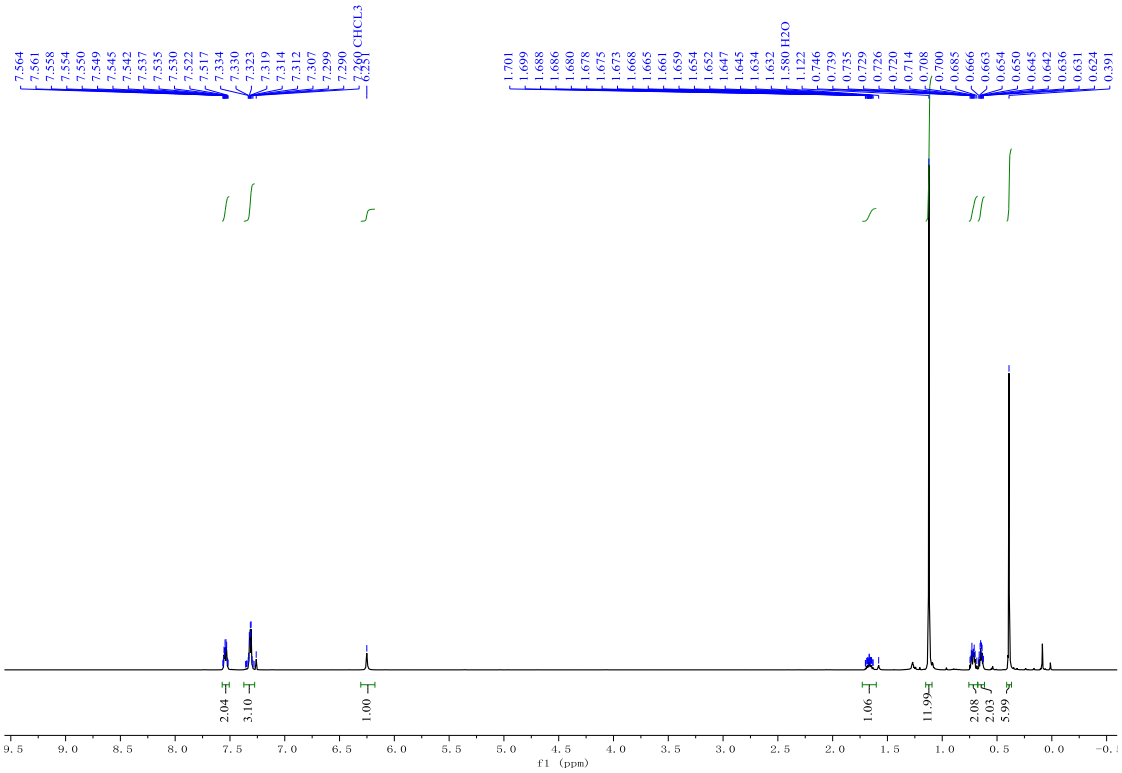
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 64% yield (42.0 mg). R_f = 0.44 (Petroleum ether:EtOAc = 99:1).

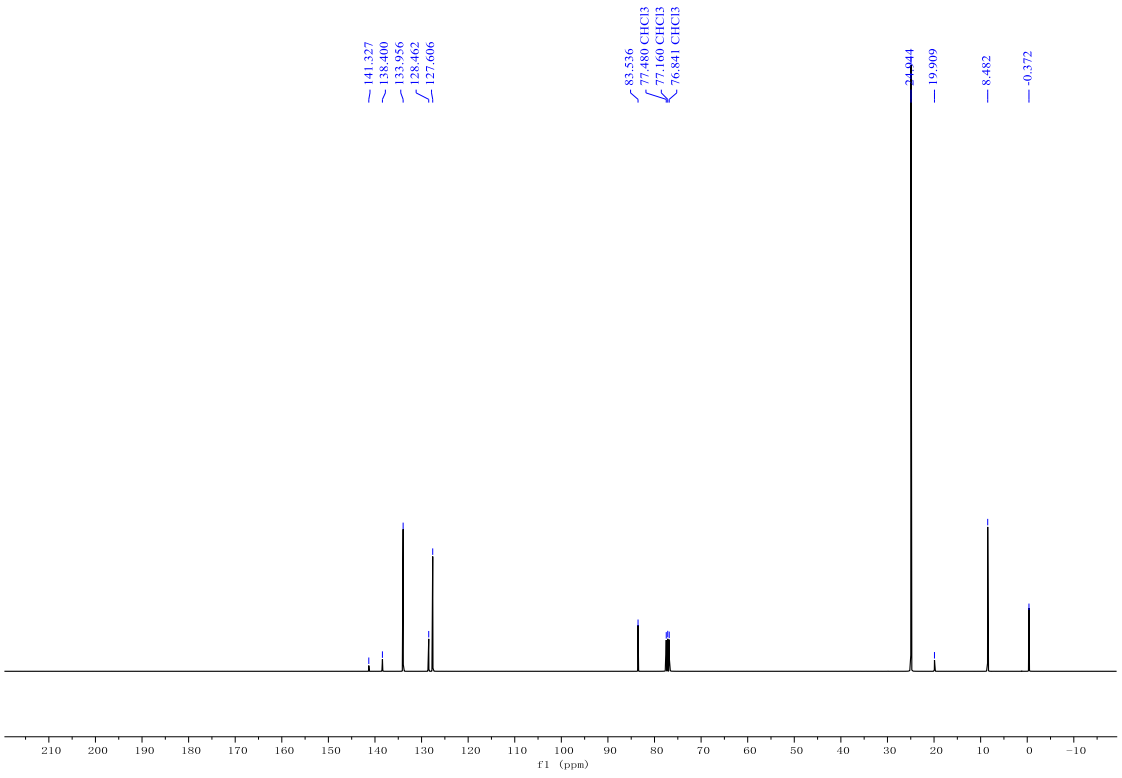
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.46 (m, 2H), 7.36 – 7.28 (m, 3H), 6.25 (s, 1H), 1.67 (ttd, *J* = 8.3, 5.2, 0.8 Hz, 1H), 1.12 (s, 12H), 0.77 – 0.68 (m, 2H), 0.65 (qd, *J* = 4.8, 2.0 Hz, 2H), 0.39 (s, 6H).

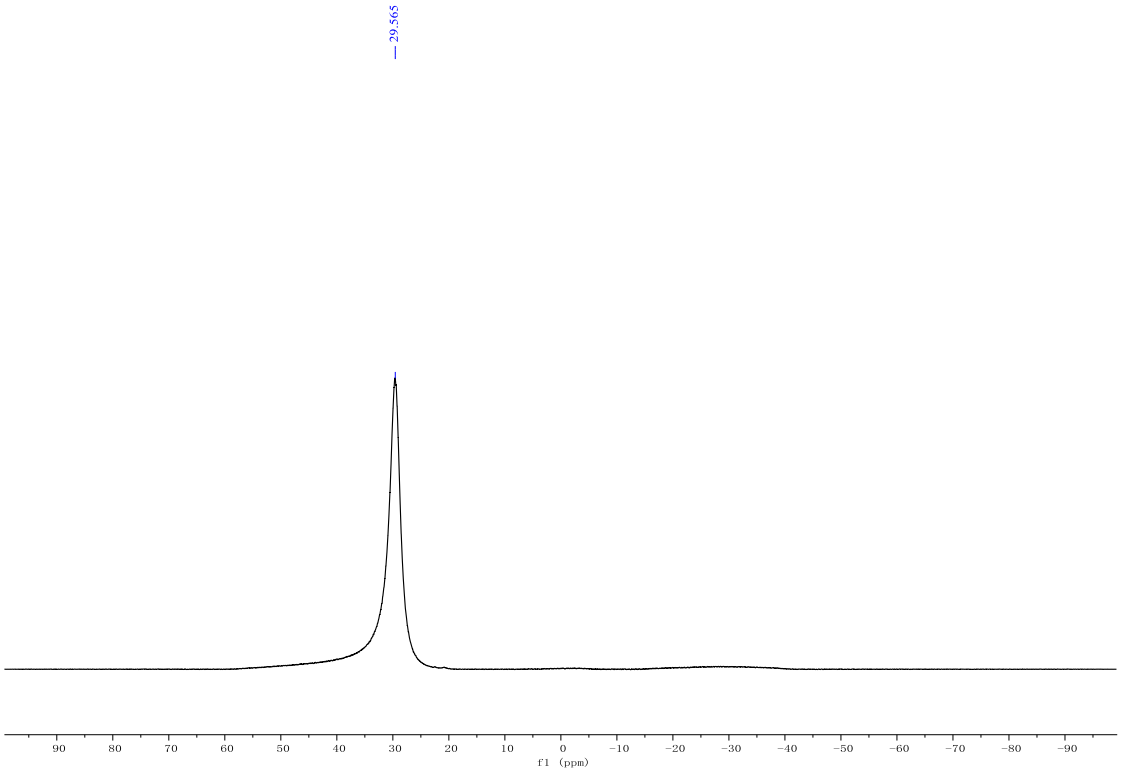
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.33, 138.40, 133.96 , 128.46 , 127.61 , 83.54, 24.94, 19.91, 8.48, -0.37.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.57 .

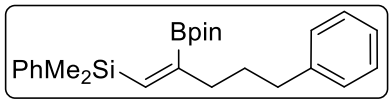
HRMS (ESI) m/z calculated for $C_{19}H_{29}BO_2SiNa$ $[M+Na]^+$: 351.1928, found: 351.1929.




141.327
138.400
133.956
128.462
127.606
83.536
77.480 CHCl3
77.160 CHCl3
76.841 CHCl3
31.044
19.909
8.482
-0.372
f1 (ppm)


29.565
f1 (ppm)

(*E*)-dimethyl(phenyl)(5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl) silane (3e).



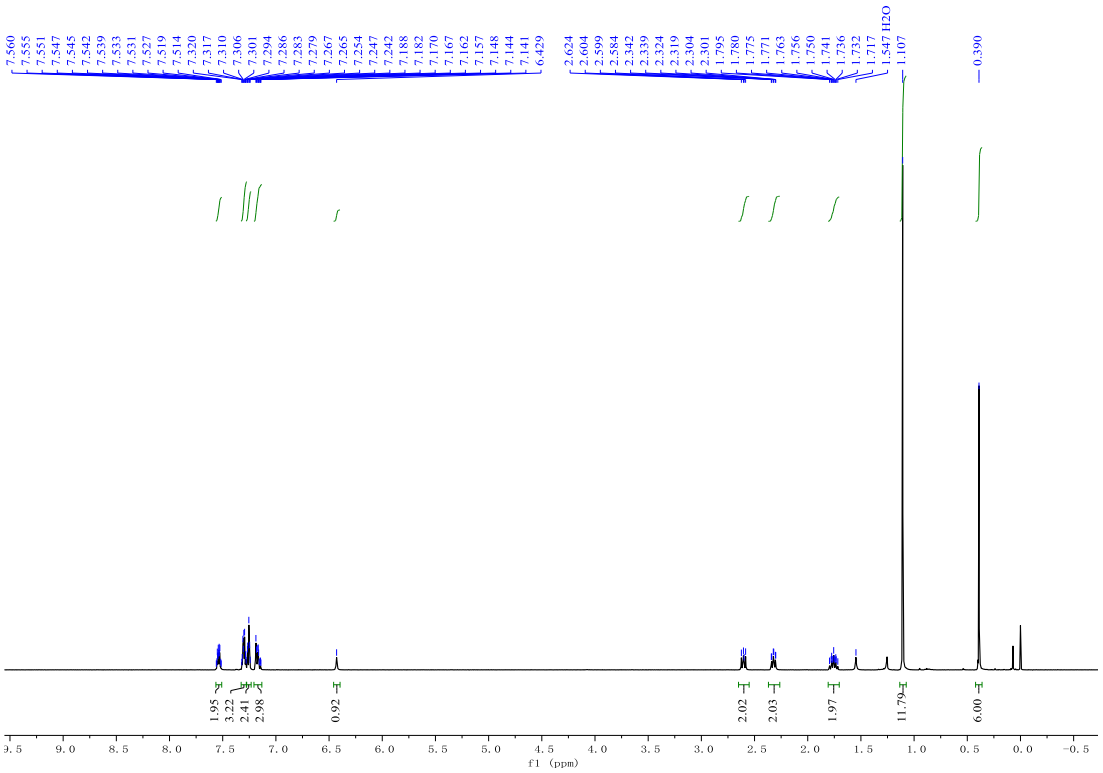
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 80% yield (76.1 mg). R_f = 0.46 (Petroleum ether:EtOAc = 99:1).

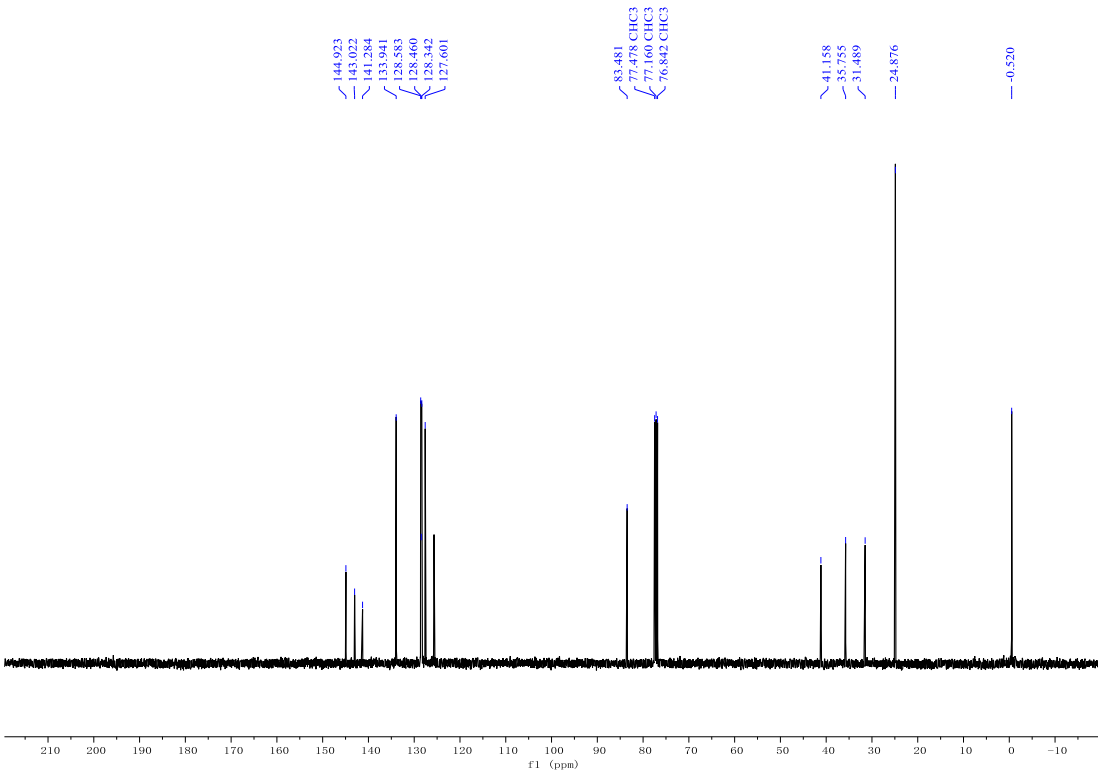
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 2H), 7.35 – 7.25 (m, 3H), 7.29 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 6.43 (s, 1H), 2.64 – 2.56 (m, 2H), 2.32 (td, *J* = 7.5, 1.4 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.11 (s, 12H), 0.39 (s, 6H).

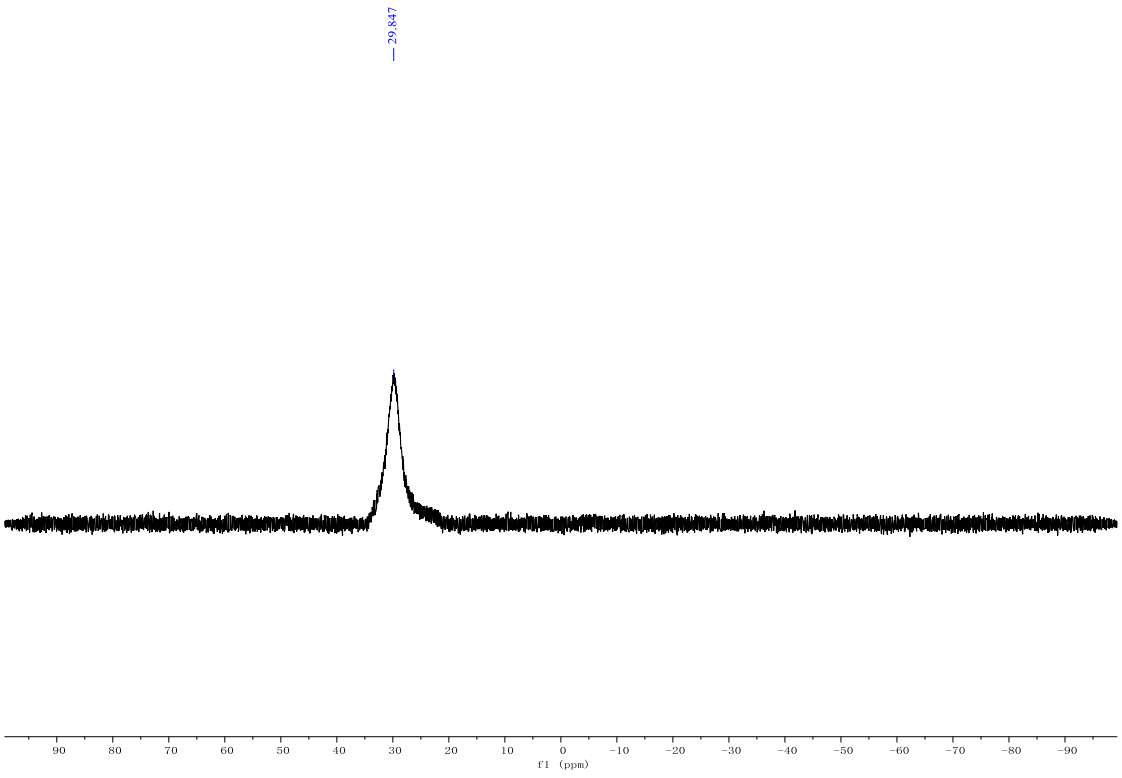
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.92, 143.02, 141.28, 133.94, 128.58, 128.46, 128.34, 127.60, 83.48, 41.16, 35.75, 31.49, 24.88, -0.52.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.85.

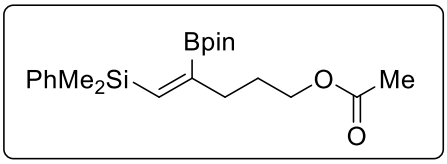
HRMS (ESI) m/z calculated for $C_{25}H_{35}BO_2SiNa$ $[M+Na]^+$: 429.2397, found: 429.2404.




144.923
143.022
141.284
133.941
128.583
128.460
128.342
127.601
83.481
77.478 CHC3
77.160 CHC3
76.842 CHC3
41.158
35.755
31.489
24.876
-0.520
f1 (ppm)


29.847
f1 (ppm)

(*E*)-5-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl acetate (3f).



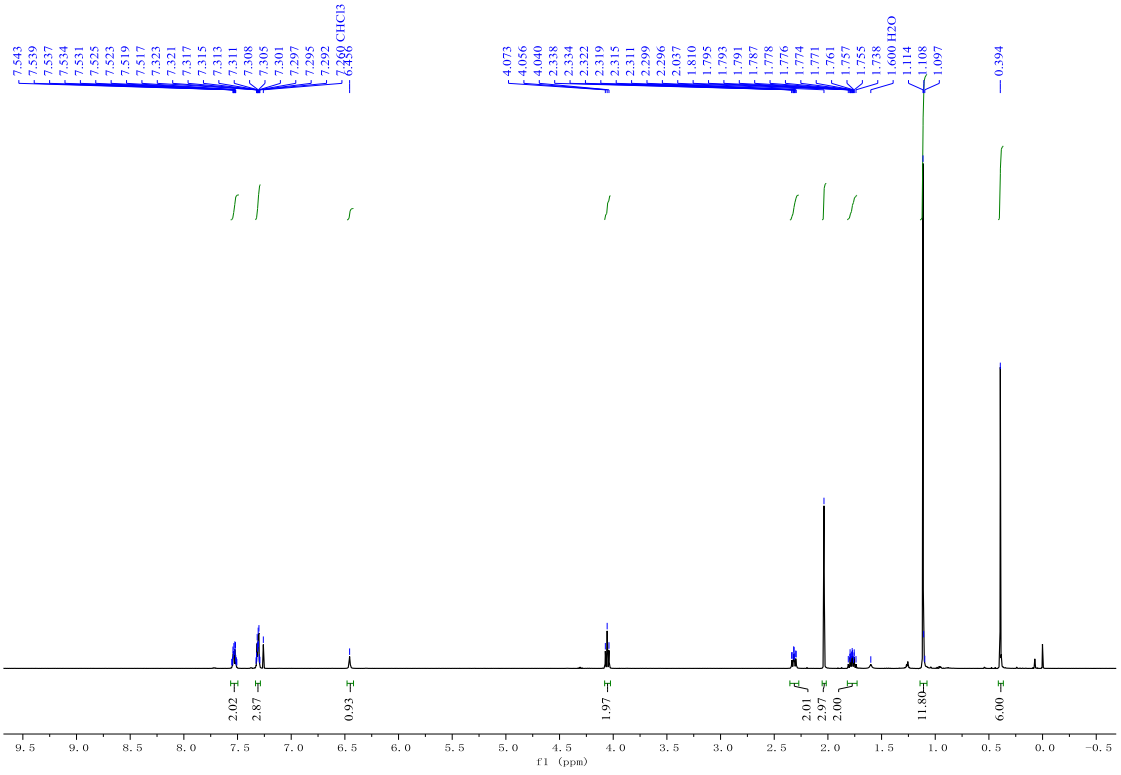
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 60% yield (46.9 mg). R_f = 0.20 (Petroleum ether:EtOAc = 98:2).

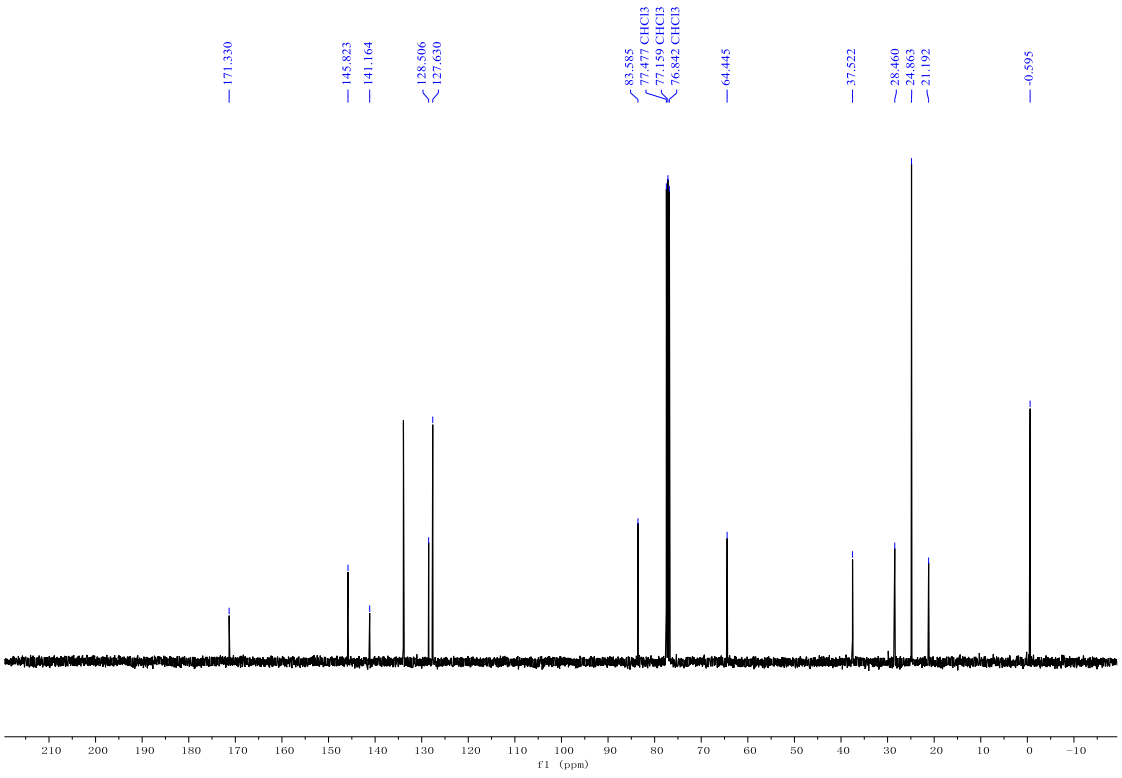
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.48 (m, 2H), 7.33 – 7.29 (m, 3H), 6.46 (s, 1H), 4.06 (t, *J* = 6.7 Hz, 2H), 2.32 (ddd, *J* = 7.6, 6.8, 1.4 Hz, 2H), 2.04 (s, 3H), 1.77 (ddt, *J* = 9.3, 7.5, 6.7 Hz, 2H), 1.11 (s, 12H), 0.39 (s, 6H).

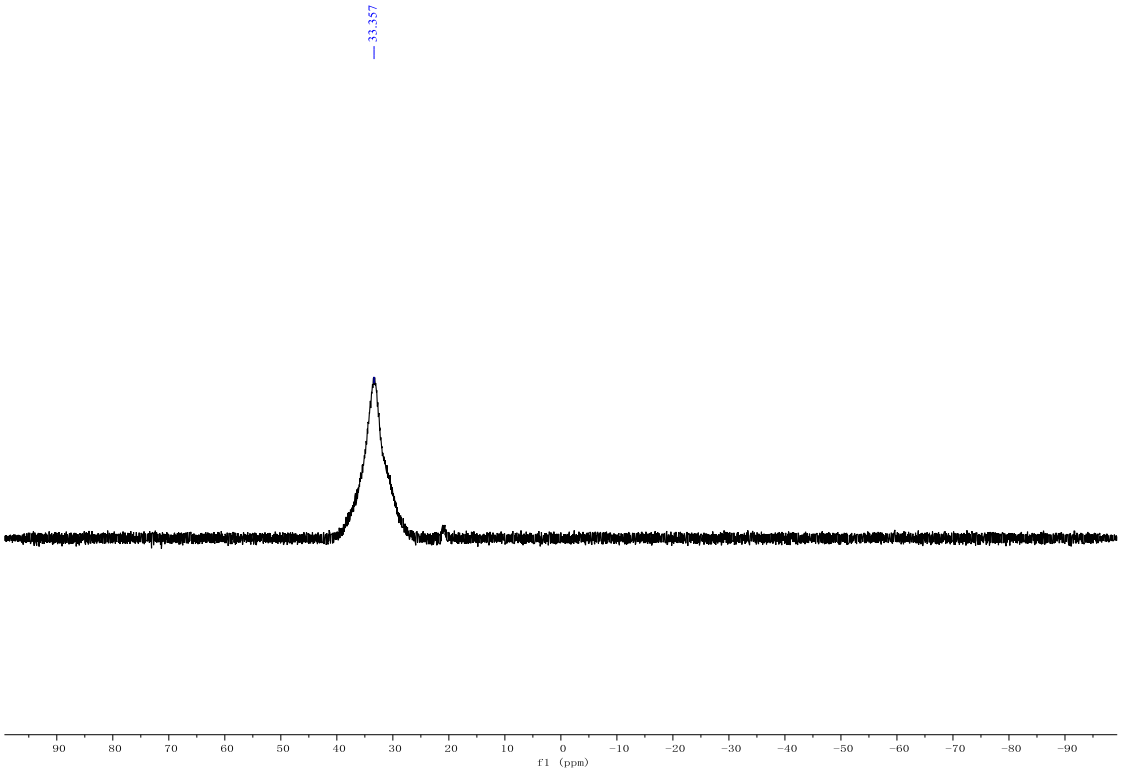
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.33, 145.82, 141.16, 128.51, 127.63, 83.59, 64.45, 37.52, 28.46, 24.86, 21.19, -0.60.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.36.

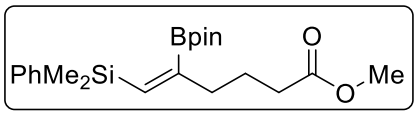
HRMS (ESI) m/z calculated for $C_{21}H_{33}BO_4SiNa$ $[M+Na]^+$: 411.2139, found: 411.2142.




171.330
145.823
141.164
128.506
127.630
83.585
77.477 CHCl3
77.159 CHCl3
76.842 CHCl3
64.445
37.522
28.460
24.863
21.192
-0.595
f1 (ppm)


33.357
f1 (ppm)

methyl (*E*)-6-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (3g).



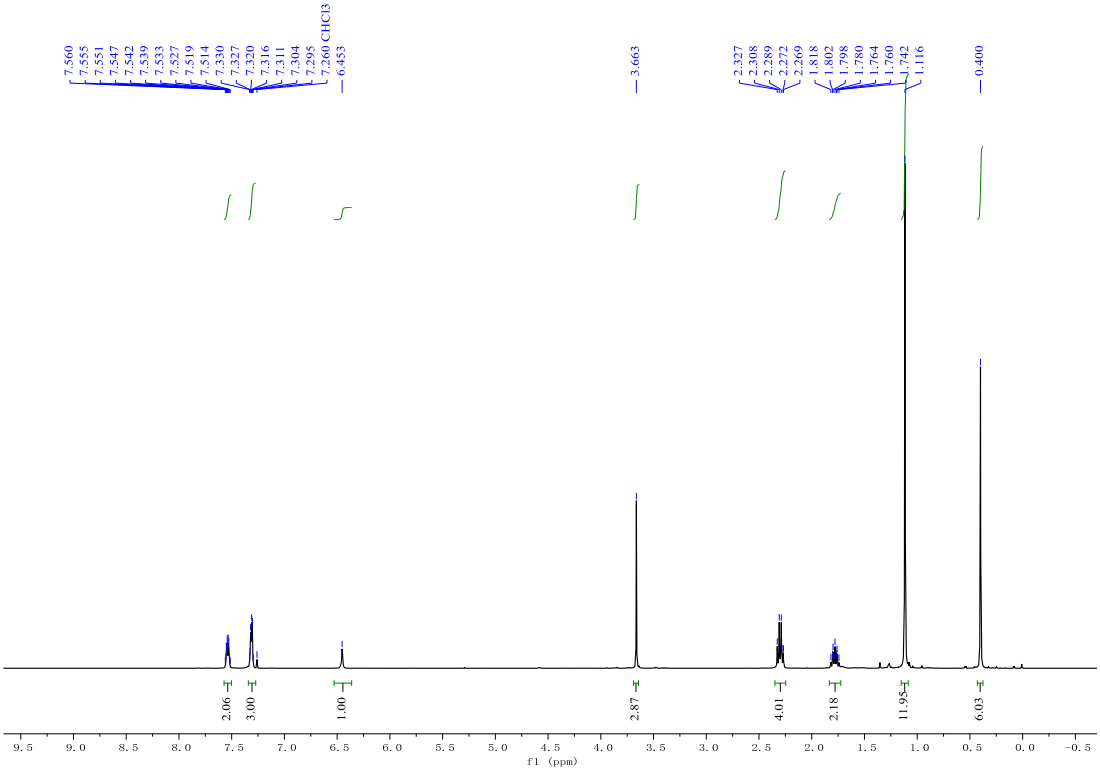
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 63% yield (48.9 mg). R_f = 0.46 (Petroleum ether:EtOAc = 98:2).

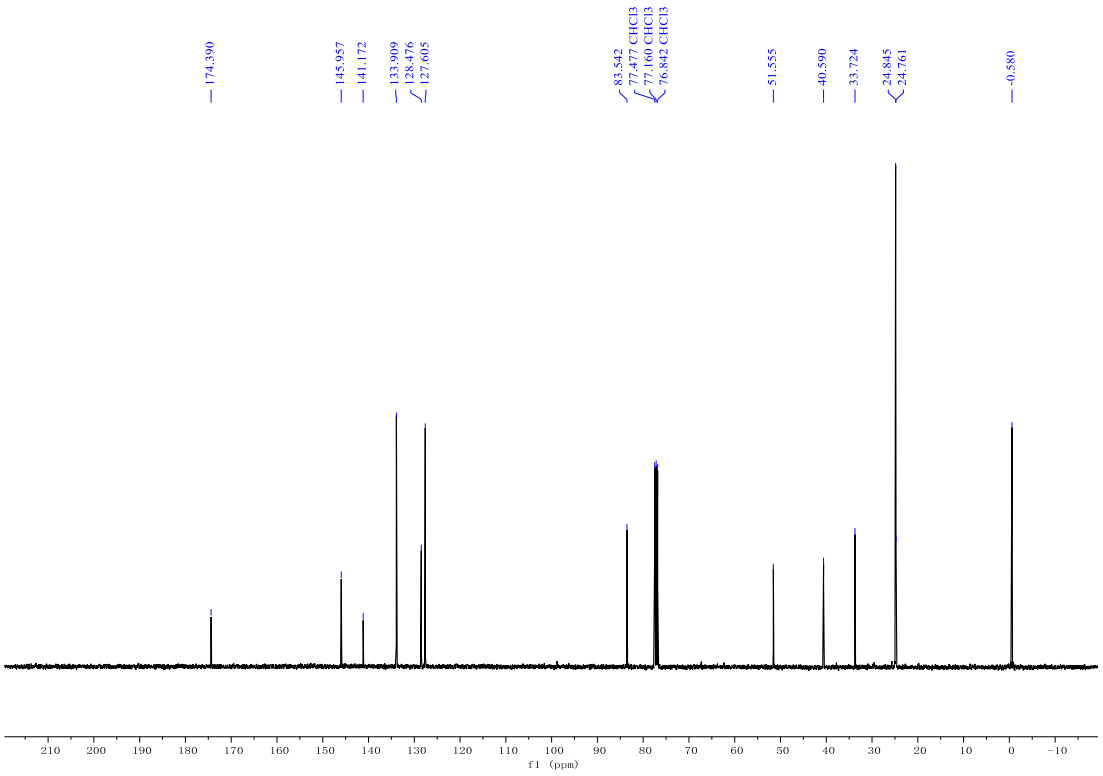
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.34 – 7.29 (m, 3H), 6.45 (s, 1H), 3.66 (s, 3H), 2.36 – 2.24 (m, 4H), 1.78 (p, *J* = 7.6 Hz, 2H), 1.12 (s, 12H), 0.40 (s, 6H).

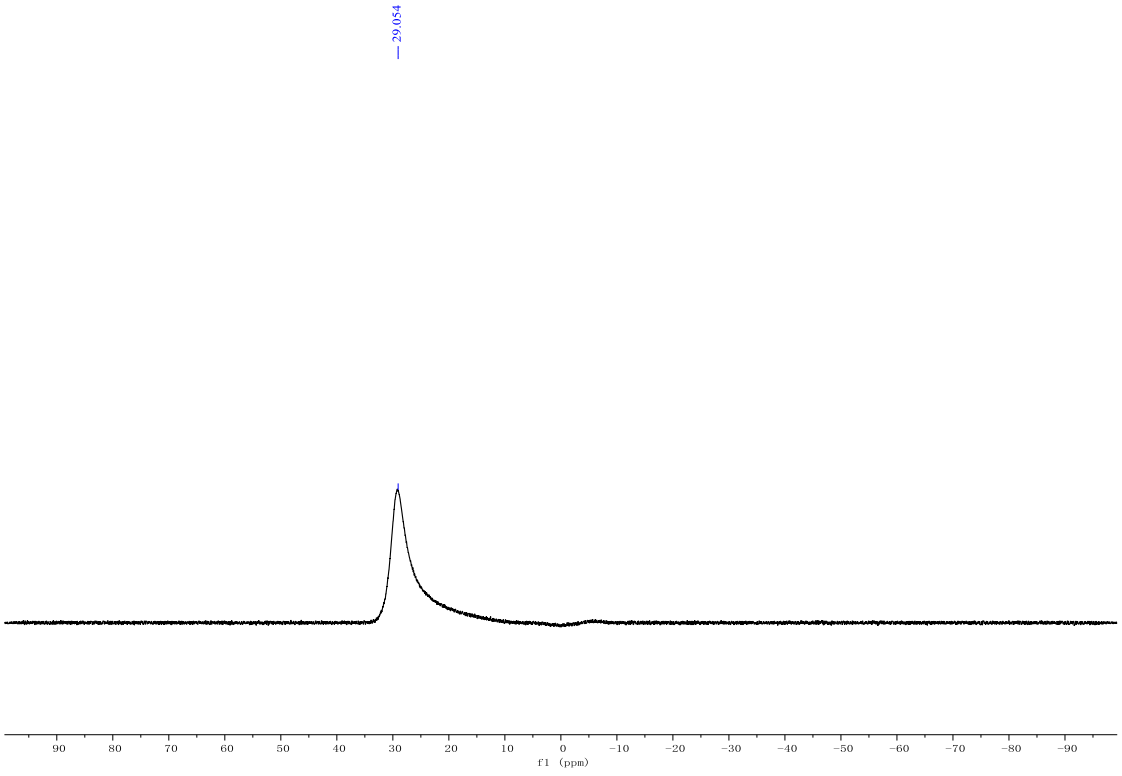
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.39, 145.96, 141.17, 133.91, 128.48, 127.61, 83.54, 51.55, 40.59, 33.72, 24.85, 24.76, -0.58.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.05.

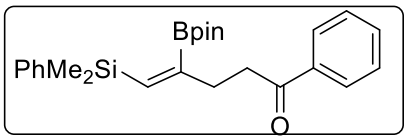
HRMS (ESI) m/z calculated for $C_{21}H_{33}BO_4SiNa$ $[M+Na]^+$: 411.2139, found: 411.2141.




174.390
145.957
141.172
133.909
128.476
127.605
83.542
77.477 CHCl3
77.160 CHCl3
76.842 CHCl3
51.555
40.590
33.724
24.845
24.761
-0.580
f1 (ppm)


29.054
f1 (ppm)

(*E*)-5-(dimethyl(phenyl)silyl)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (3h).



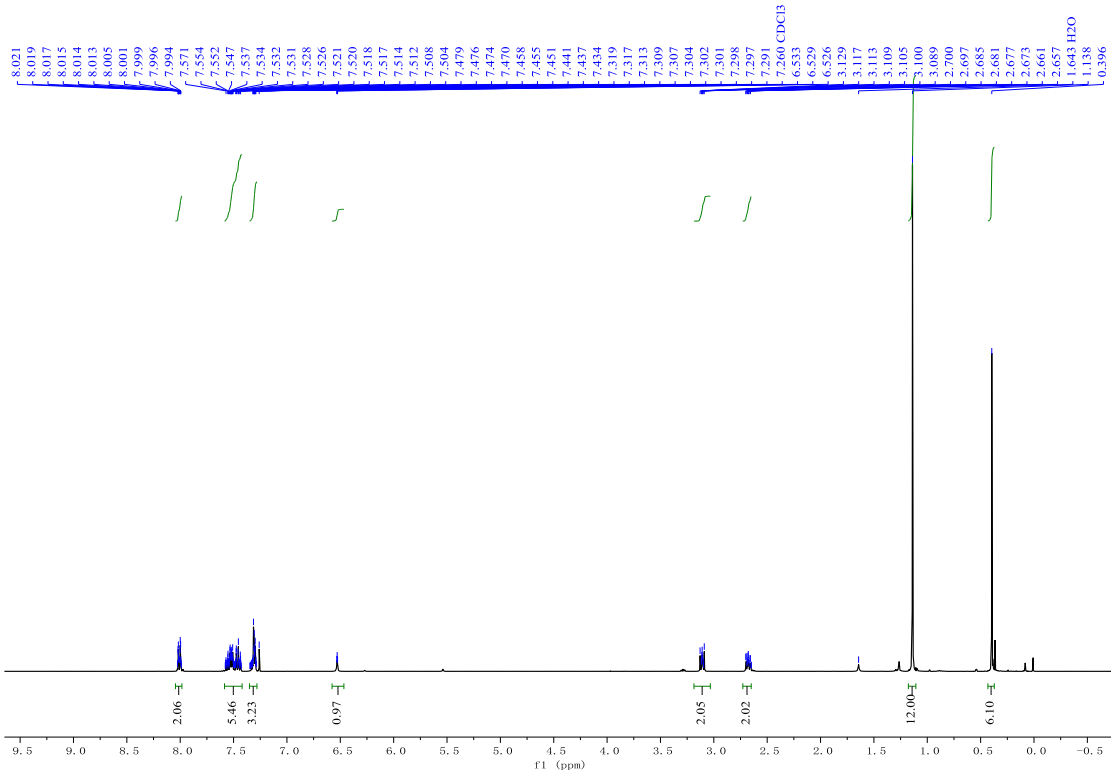
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 55% yield (41.7 mg). R_f = 0.50 (Petroleum ether:EtOAc = 95:5).

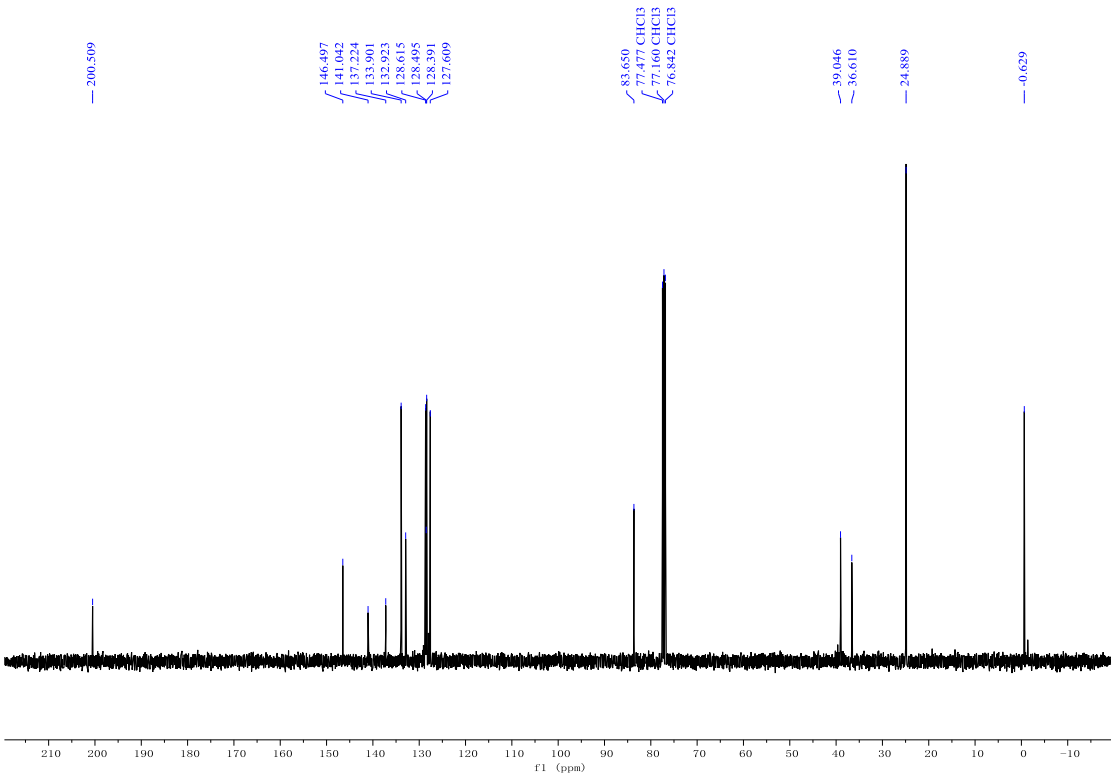
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.98 (m, 2H), 7.58 – 7.42 (m, 5H), 7.35 – 7.28 (m, 3H), 6.53 (t, *J* = 1.5 Hz, 1H), 3.17 – 3.04 (m, 2H), 2.68 (ddd, *J* = 9.4, 6.1, 1.4 Hz, 2H), 1.14 (s, 12H), 0.40 (s, 6H).

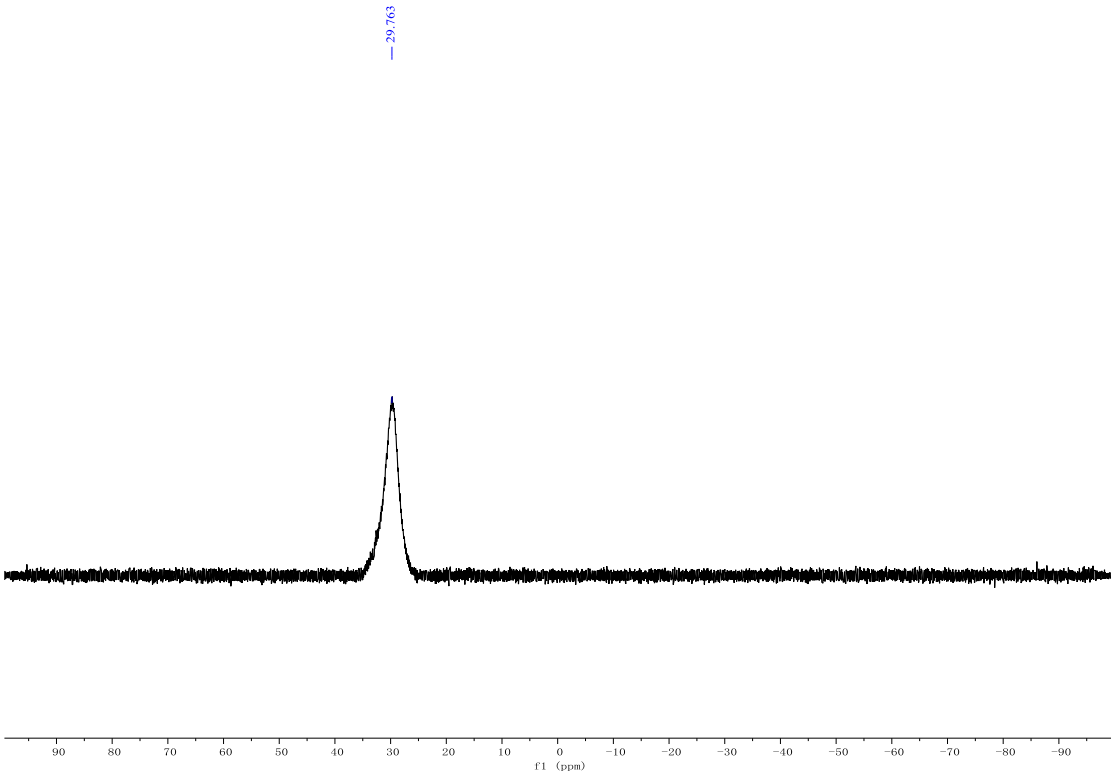
^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.51, 146.50, 141.04, 137.22, 133.90, 132.92, 128.62, 128.49, 128.39, 127.61, 83.65, 39.05, 36.61, 24.89, -0.63.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.76.

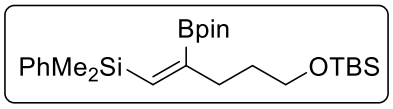
HRMS (ESI) m/z calculated for $C_{25}H_{33}BO_3SiNa$ $[M+Na]^+$: 443.2190, found: 443.2184.




200.509
146.497
141.042
137.224
133.901
132.923
128.615
128.495
128.391
127.609
83.650
77.477 CHCl3
77.160 CHCl3
76.842 CHCl3
39.046
36.610
24.889
0.629
f1 (ppm)


29.763
f1 (ppm)

(*E*)-*tert*-butyl((5-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)dimethylsilane (3i).



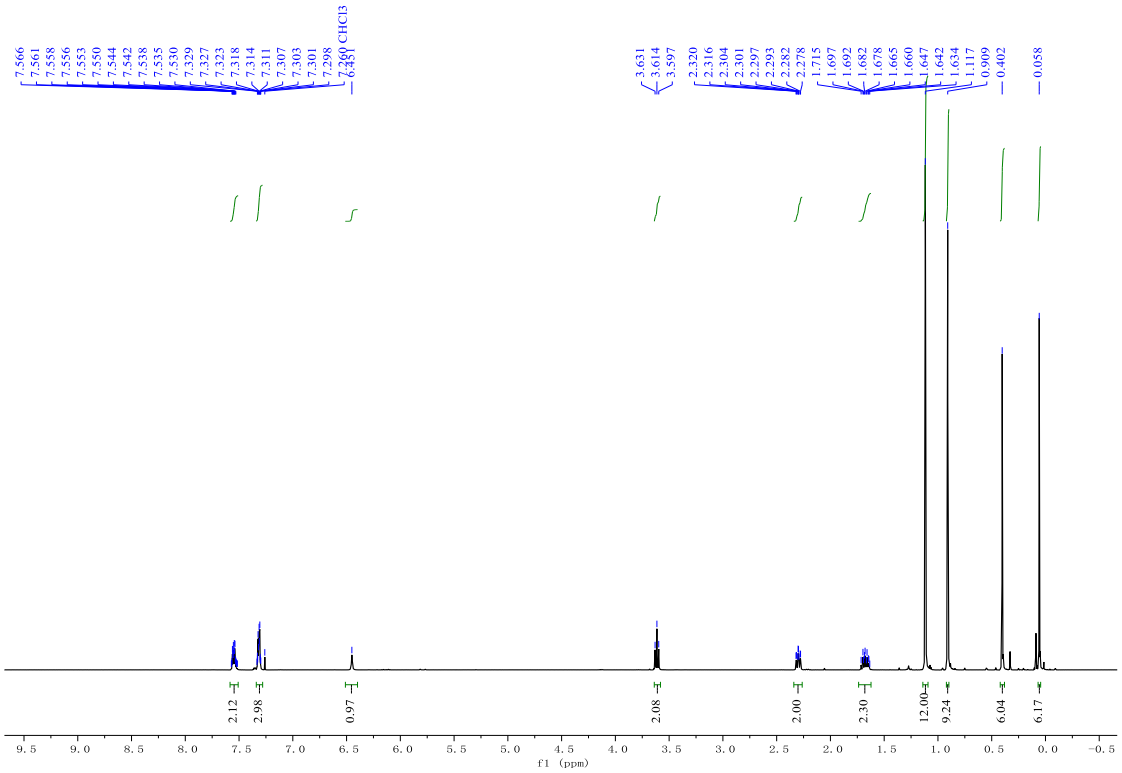
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 64% yield (42.0 mg). R_f = 0.26 (Petroleum ether:EtOAc = 99:1).

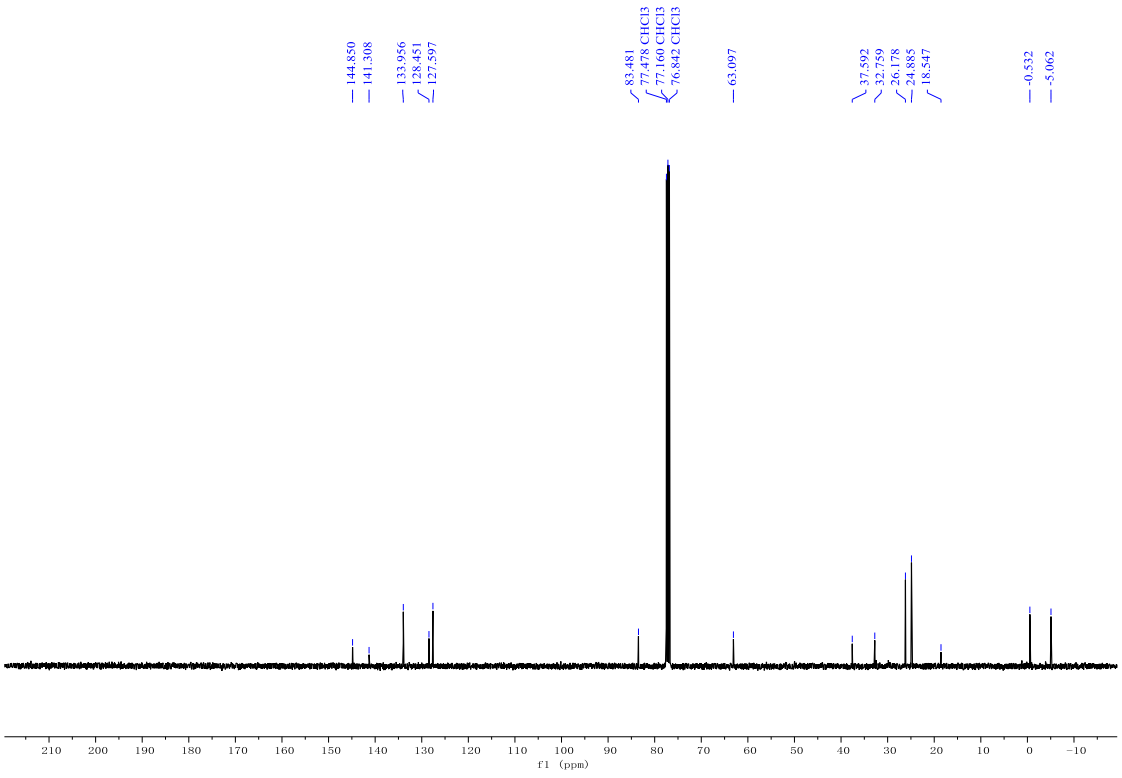
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.49 (m, 2H), 7.36 – 7.27 (m, 3H), 6.45 (s, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.34 – 2.26 (m, 2H), 1.74 – 1.61 (m, 2H), 1.12 (s, 12H), 0.91 (s, 9H), 0.40 (s, 6H), 0.06 (s, 6H).

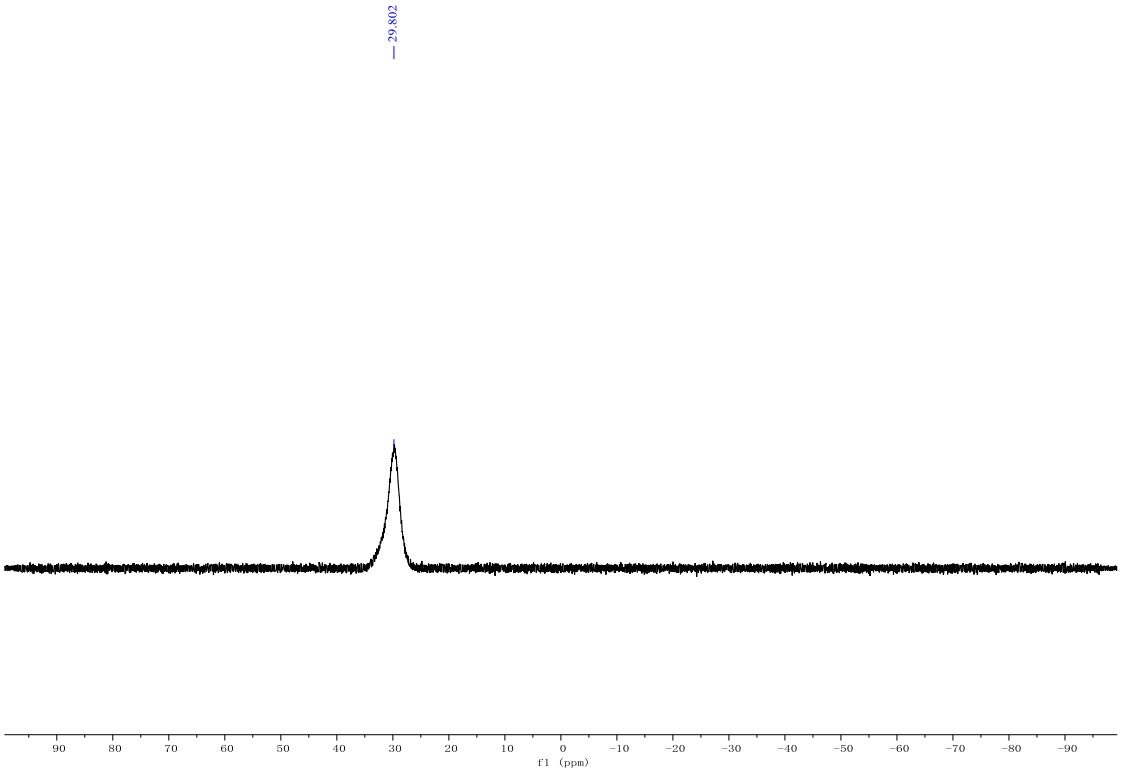
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.85, 133.96, 128.45, 127.60, 83.48, 63.10, 37.59, 32.76, 26.18, 24.89, 18.55, -0.53, -5.06.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.80.

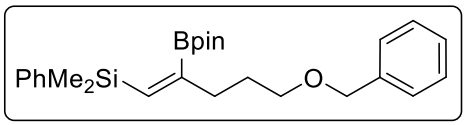
HRMS (ESI) m/z calculated for $C_{25}H_{45}BO_3Si_2Na$ $[M+Na]^+$: 483.2898, found: 483.2903.




144.850
141.308
133.956
128.451
127.597
83.481
77.478 CHCl3
77.160 CHCl3
76.842 CHCl3
63.097
37.592
32.759
26.178
24.885
18.547
0.532
-5.062
f1 (ppm)


29.802
f1 (ppm)

(*E*)-(5-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)dimethyl (phenyl)silane (3j).



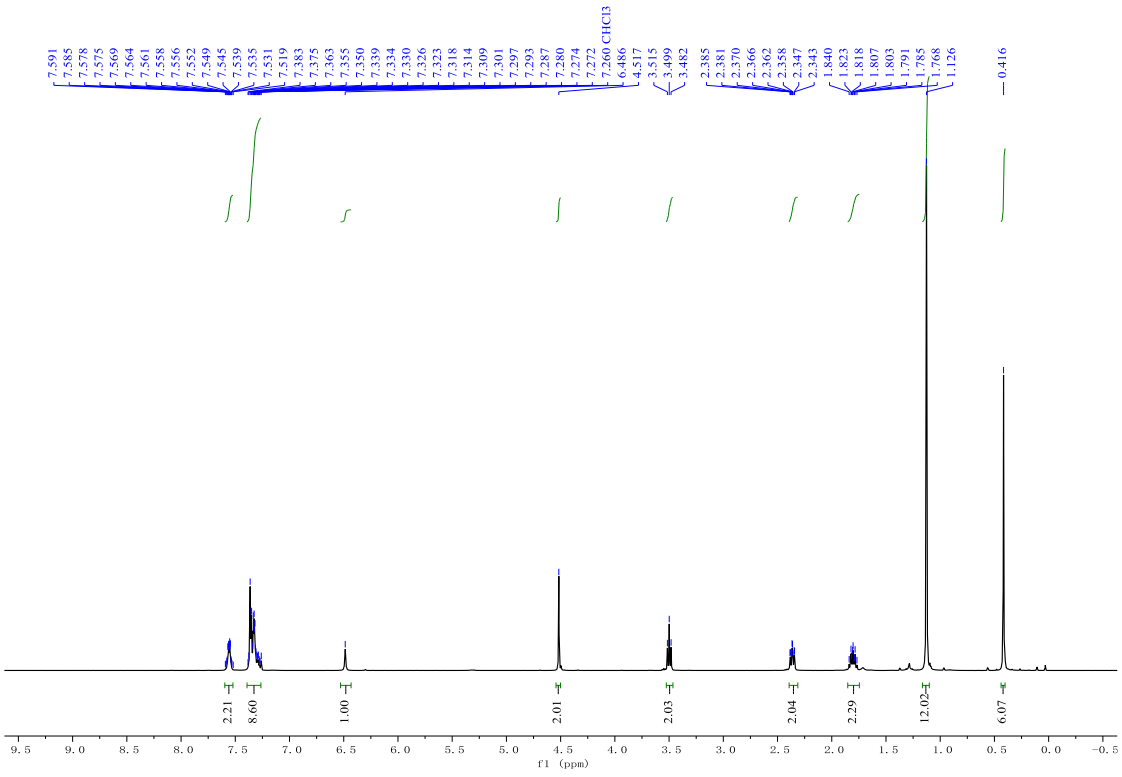
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 83% yield (72.6 mg). R_f = 0.44 (Petroleum ether: EtOAc = 98:2).

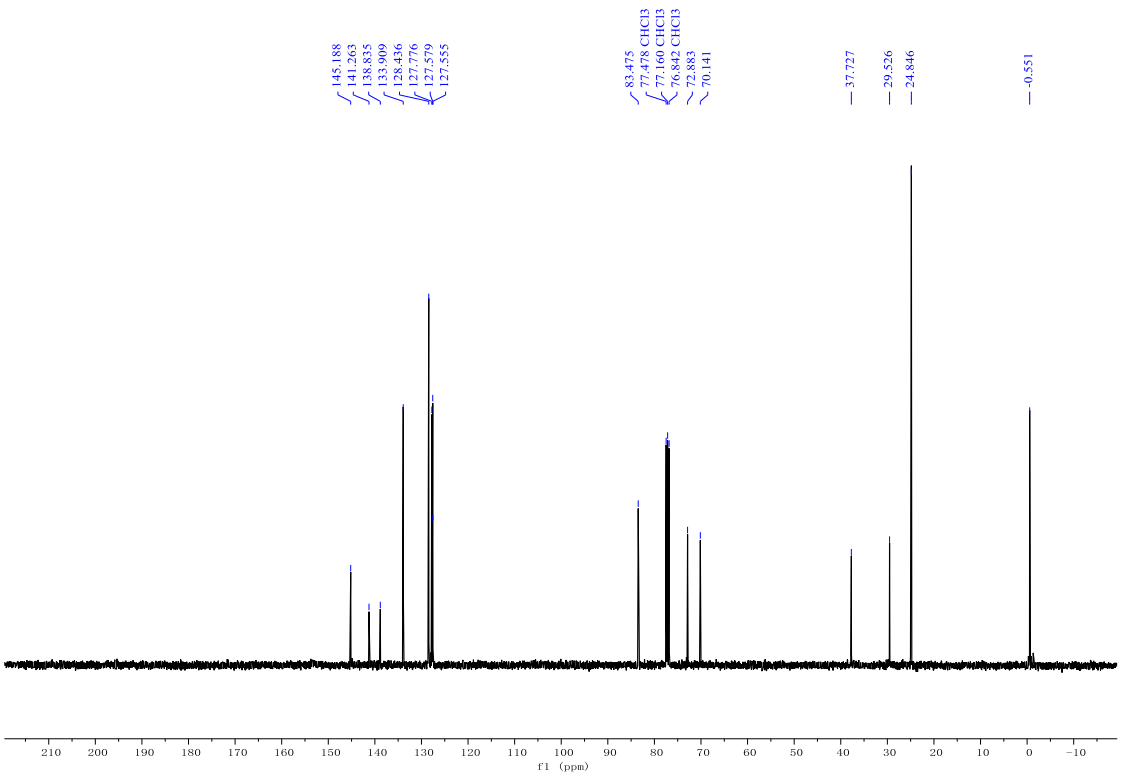
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.51 (m, 2H), 7.42 – 7.27 (m, 8H), 6.49 (s, 1H), 4.52 (s, 2H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.40 – 2.31 (m, 2H), 1.80 (dq, *J* = 9.3, 6.8 Hz, 2H), 1.13 (s, 12H), 0.42 (s, 6H).

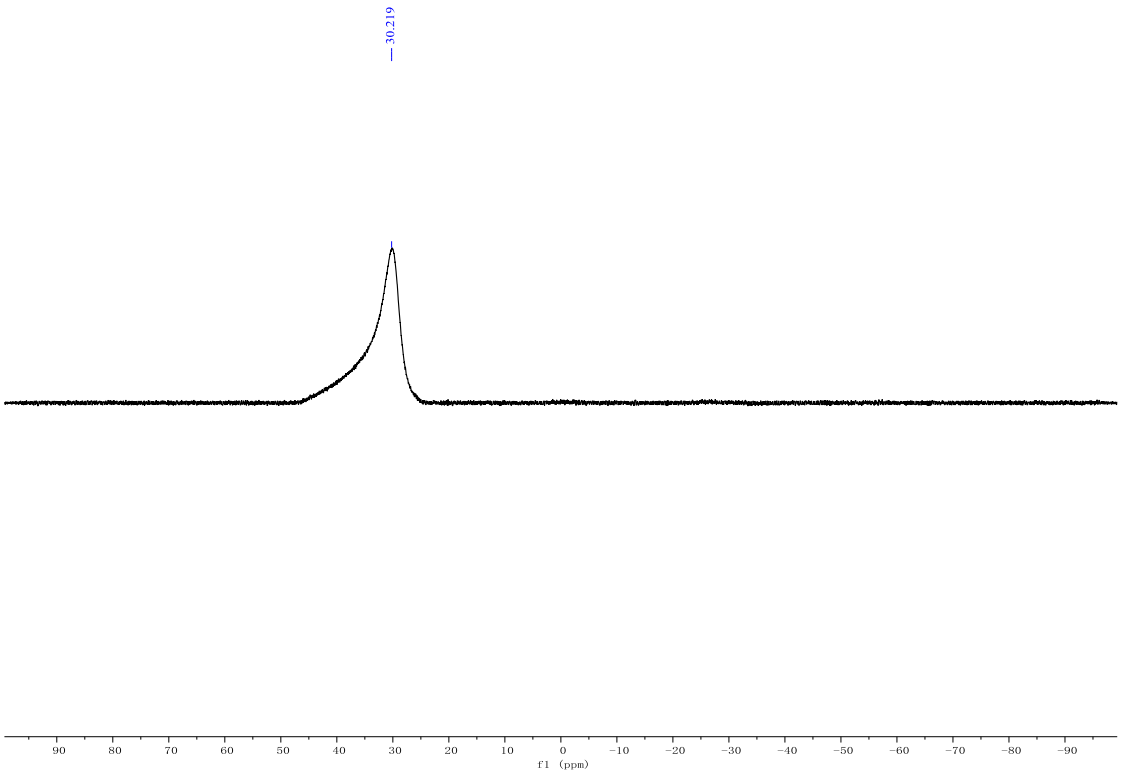
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.19, 141.26, 138.84, 133.91, 128.44, 127.78, 127.58, 127.56, 83.47, 72.88, 70.14, 37.73, 29.53, 24.85, -0.55.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.22.

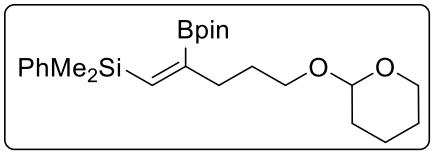
HRMS (ESI) m/z calculated for $C_{26}H_{37}BO_3SiNa$ $[M+Na]^+$: 459.2503, found: 459.2510.




145.188
141.263
138.835
133.909
128.436
127.776
127.579
127.555
83.475
77.478 CHCl3
77.160 CHCl3
76.842 CHCl3
72.883
70.141
37.727
29.526
24.846
-0.551
f1 (ppm)


30.219
f1 (ppm)

(*E*)-dimethyl(phenyl)(5-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)silane (3k).

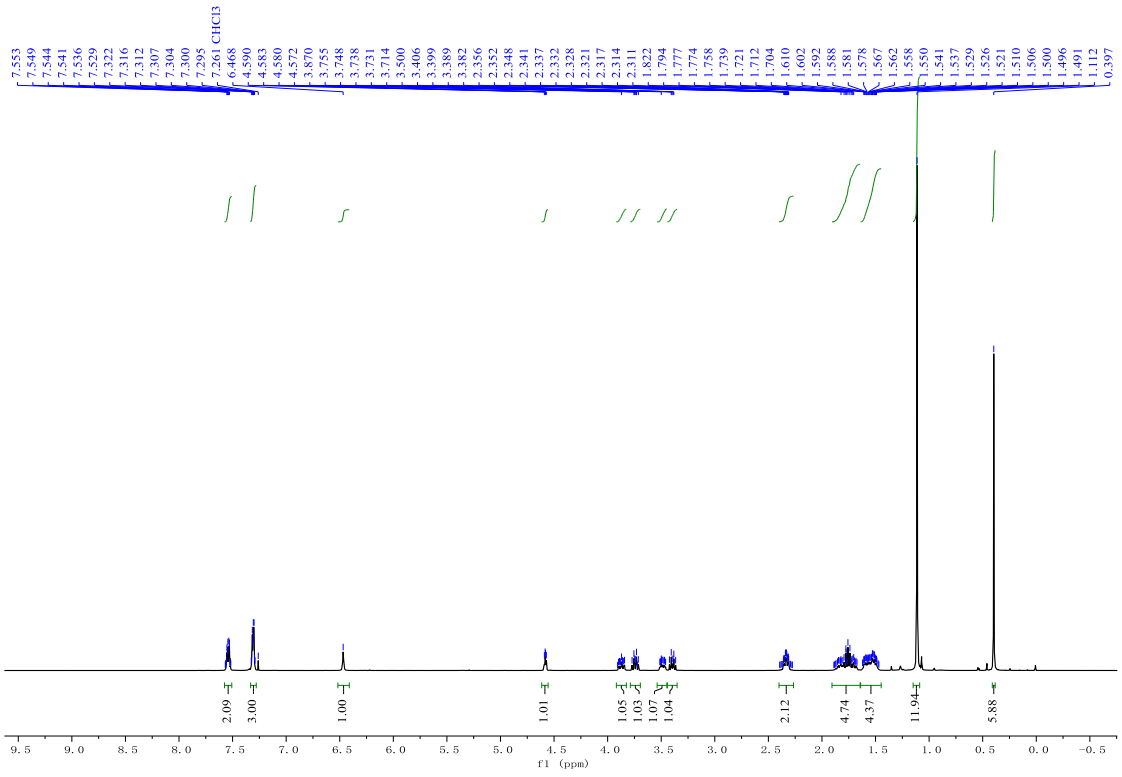


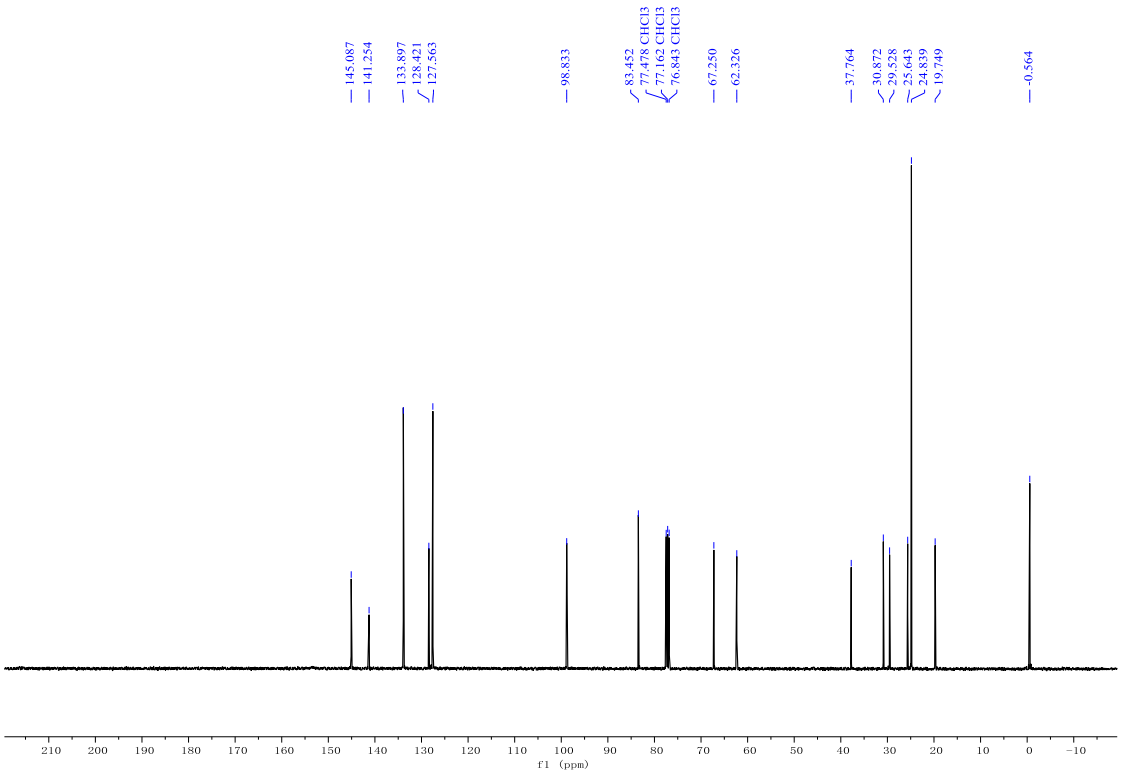
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 75% yield (64.6 mg). R_f = 0.25 (Petroleum ether:EtOAc = 99:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 2H), 7.35 – 7.26 (m, 3H), 6.47 (s, 1H), 4.58 (dd, *J* = 4.4, 2.9 Hz, 1H), 3.87 (ddd, *J* = 11.1, 7.8, 3.1 Hz, 1H), 3.74 (dt, *J* = 9.6, 6.9 Hz, 1H), 3.54 – 3.44 (m, 1H), 3.39 (dt, *J* = 9.7, 6.8 Hz, 1H), 2.33 (tdd, *J* = 7.1, 2.9, 1.5 Hz, 2H), 1.91 – 1.65 (m, 4H), 1.65 – 1.44 (m, 4H), 1.11 (s, 12H), 0.40 (s, 6H).

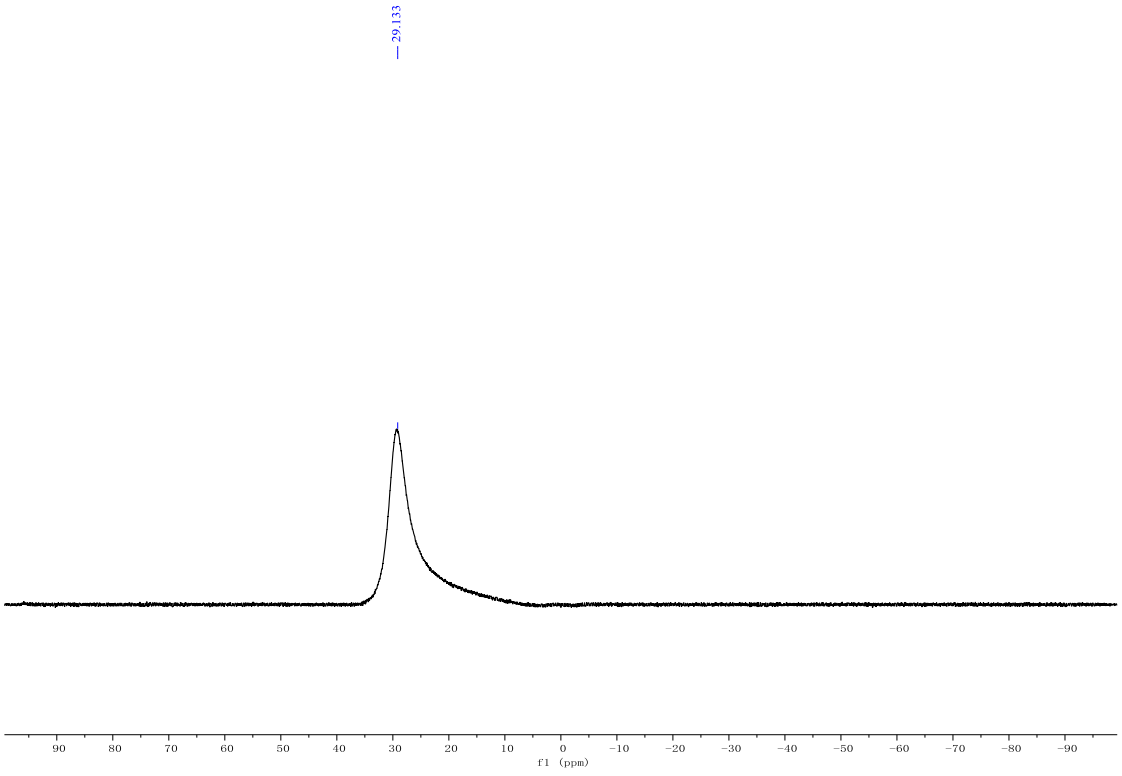
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.09, 141.25, 133.90, 128.42, 127.56, 98.83, 83.45, 67.25, 62.33, 37.76, 30.87, 29.53, 25.64, 24.84, 19.75, -0.56.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.13.

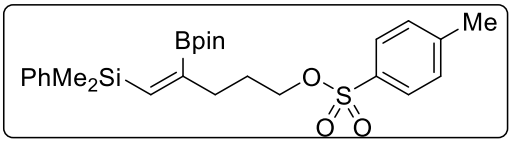
HRMS (ESI) m/z calculated for $C_{24}H_{39}BO_4SiNa$ $[M+Na]^+$: 453.2608, found: 453.2617.




145.087
141.254
133.897
128.421
127.563
98.833
83.452
77.478 CHCl3
77.162 CHCl3
76.843 CHCl3
67.250
62.326
37.764
30.872
29.528
25.643
24.839
19.749
-0.564
f1 (ppm)


29.133
f1 (ppm)

(*E*)-5-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl benzenesulfonate (3l).



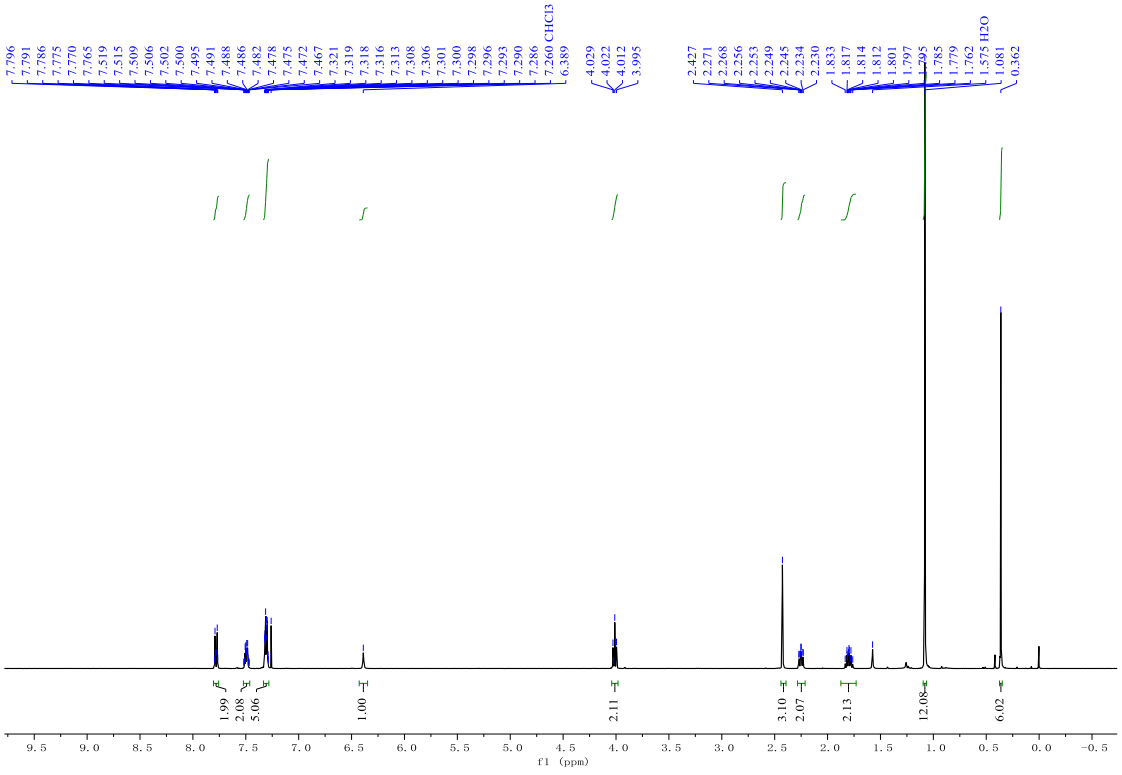
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 78% yield (78.0 mg). R_f = 0.38 (Petroleum ether:EtOAc = 90:10).

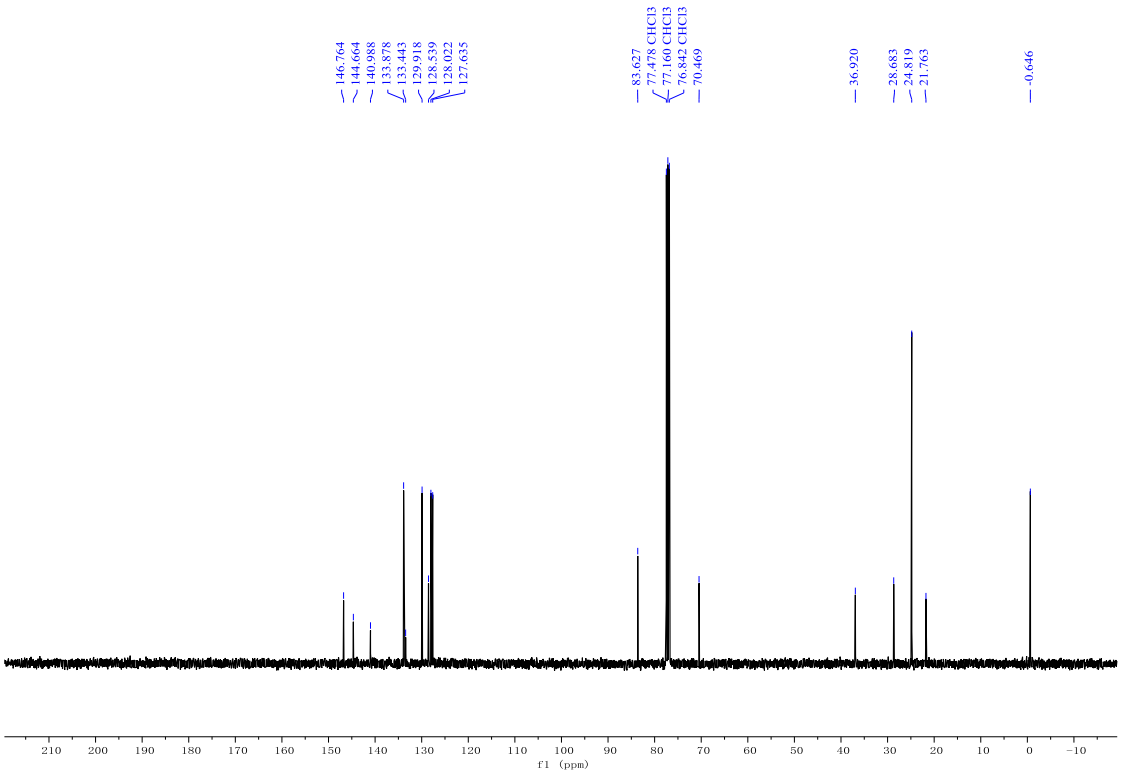
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.52 – 7.46 (m, 2H), 7.33 – 7.28 (m, 5H), 6.39 (s, 1H), 4.01 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 2.30 – 2.20 (m, 2H), 1.86 – 1.72 (m, 2H), 1.08 (s, 12H), 0.36 (s, 6H).

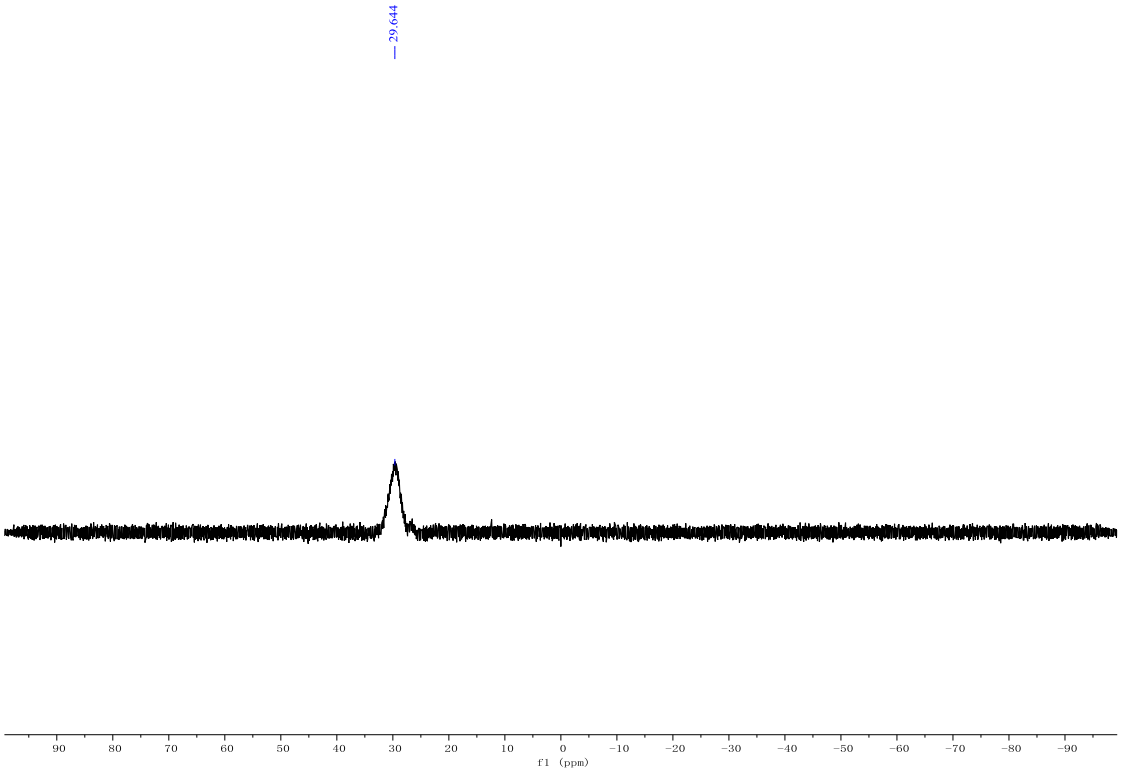
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.76, 144.66, 140.99, 133.88, 133.44, 129.92, 128.54, 128.02, 127.64, 83.63, 70.47, 36.92, 28.68, 24.82, 21.76, -0.65.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.64.

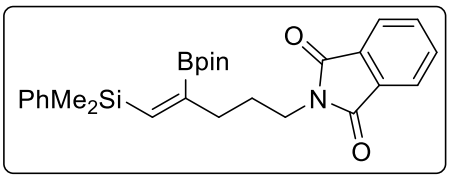
HRMS (ESI) m/z calculated for $C_{26}H_{37}BO_5SSiNa$ $[M+Na]^+$: 523.2122, found: 523.2132.




146.764
144.664
140.988
133.878
133.443
129.918
128.539
128.022
127.635
83.627
77.478 CHCl3
77.160 CHCl3
76.842 CHCl3
70.469
36.920
28.683
24.819
21.763
-0.646
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


29.644
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

(*E*)-2-(5-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)isoindoline-1,3-dione (3m) .



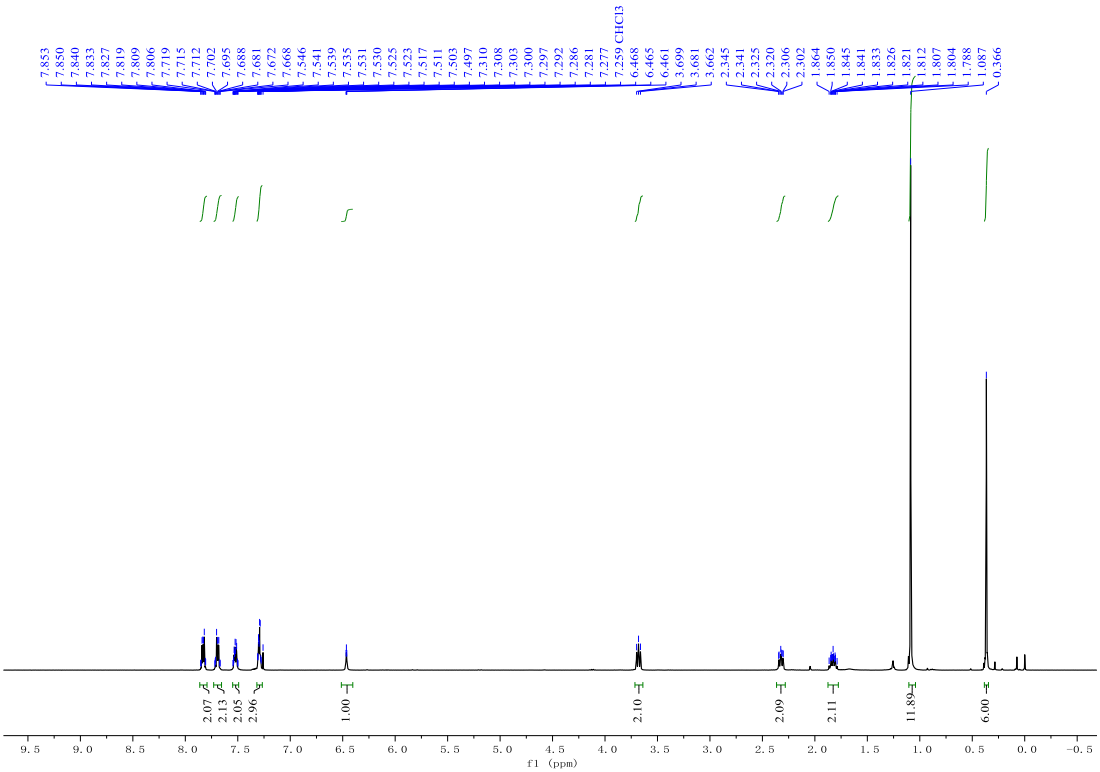
This compound was prepared by the general procedure A described above and was obtained as white solid in 80% yield (76.1 mg). R_f = 0.45 (Petroleum ether:EtOAc = 90:10).

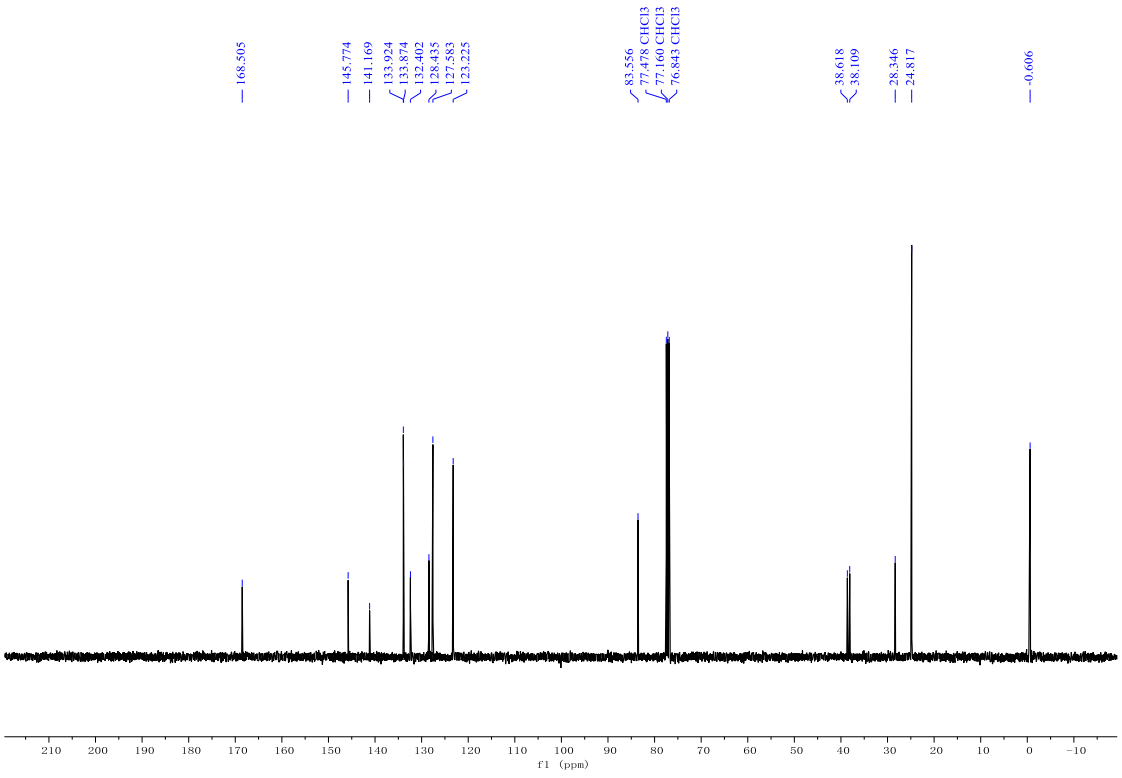
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.79 (m, 2H), 7.75 – 7.65 (m, 2H), 7.59 – 7.47 (m, 2H), 7.31 (dt, *J* = 4.4, 2.8 Hz, 3H), 6.47 (t, *J* = 1.4 Hz, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 2.33 (td, *J* = 7.4, 7.0, 1.4 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.10 (s, 12H), 0.38 (s, 6H).

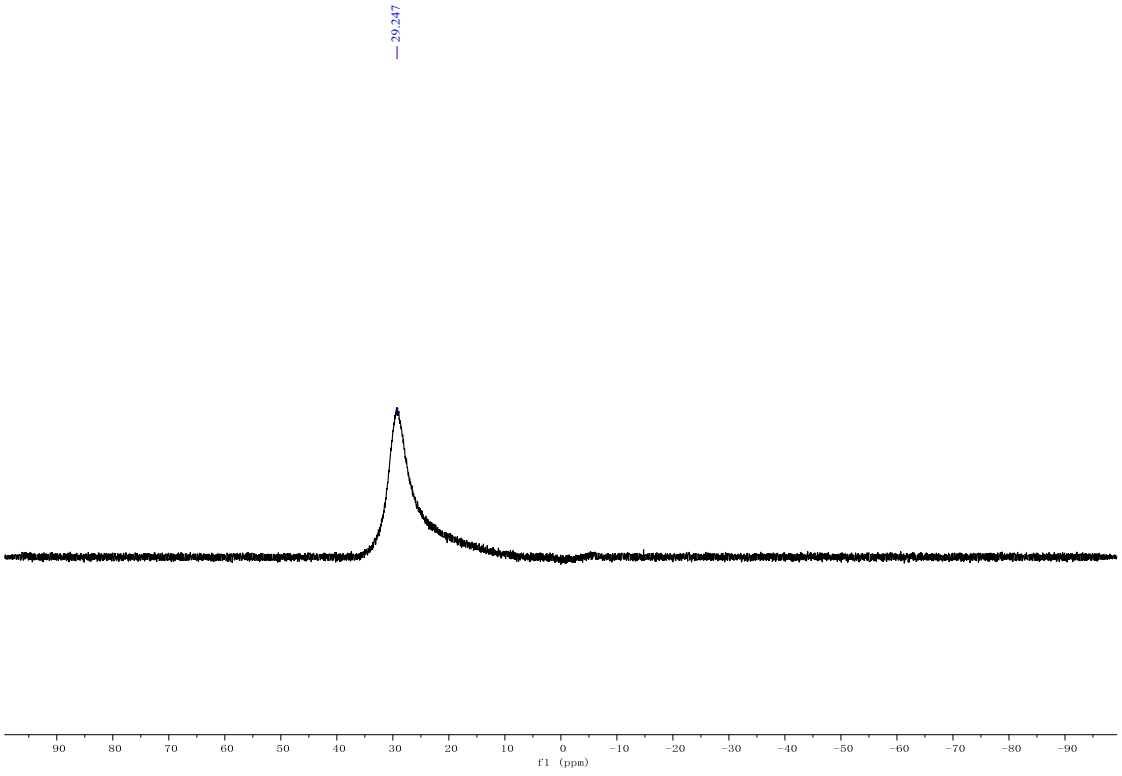
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.50, 145.77, 141.17, 133.92, 133.87, 132.40, 128.44, 127.58, 123.22, 83.56, 38.62, 38.11, 28.35, 24.82, -0.61.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.25.

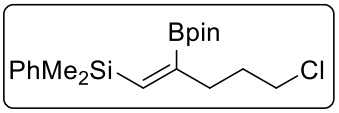
HRMS (ESI) m/z calculated for $C_{27}H_{34}BNO_4SiNa$ $[M+Na]^+$: 498.2248, found: 498.2249.




168.505
145.774
141.169
133.924
133.874
132.402
128.435
127.583
123.225
83.556
77.478 CHCl3
77.160 CHCl3
76.843 CHCl3
38.618
38.109
28.346
24.817
-0.606
f1 (ppm)


29.247
f1 (ppm)

(*E*)-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)dimethyl(phenyl) silane (3n).



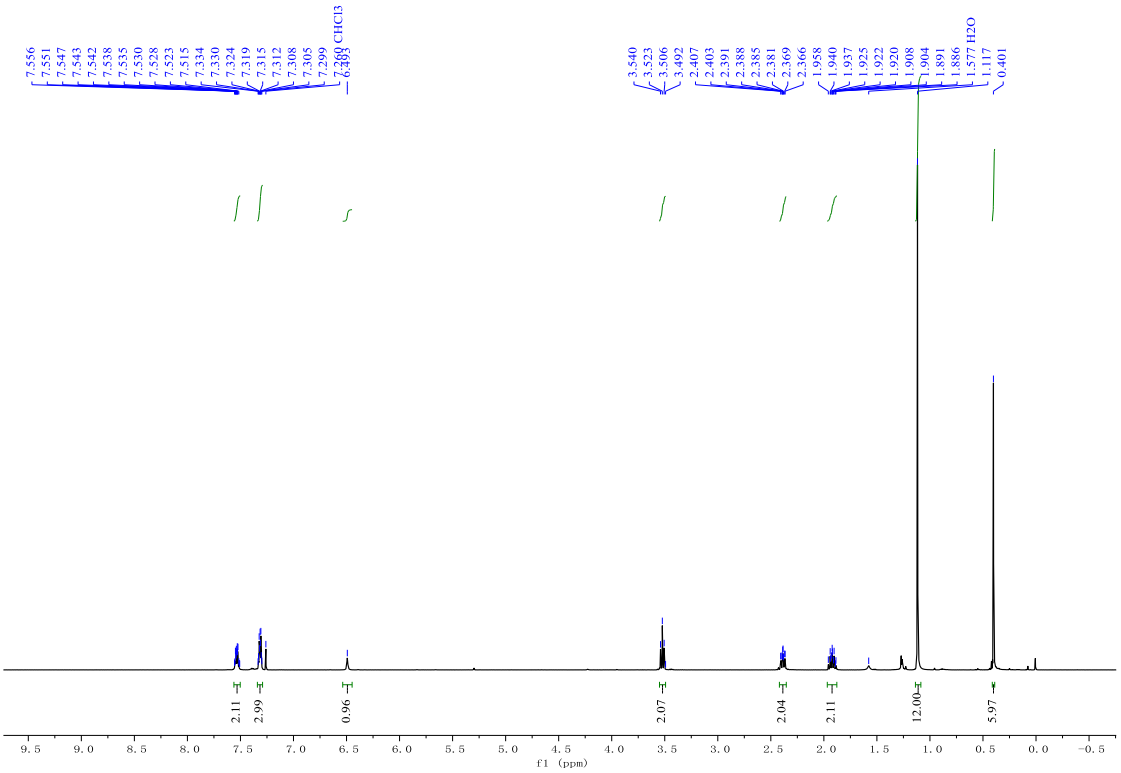
This compound was prepared by the general procedure A described above and was obtained as yellow oil in 51% yield (29.9 mg). R_f = 0.48 (Petroleum ether:EtOAc = 98:2).

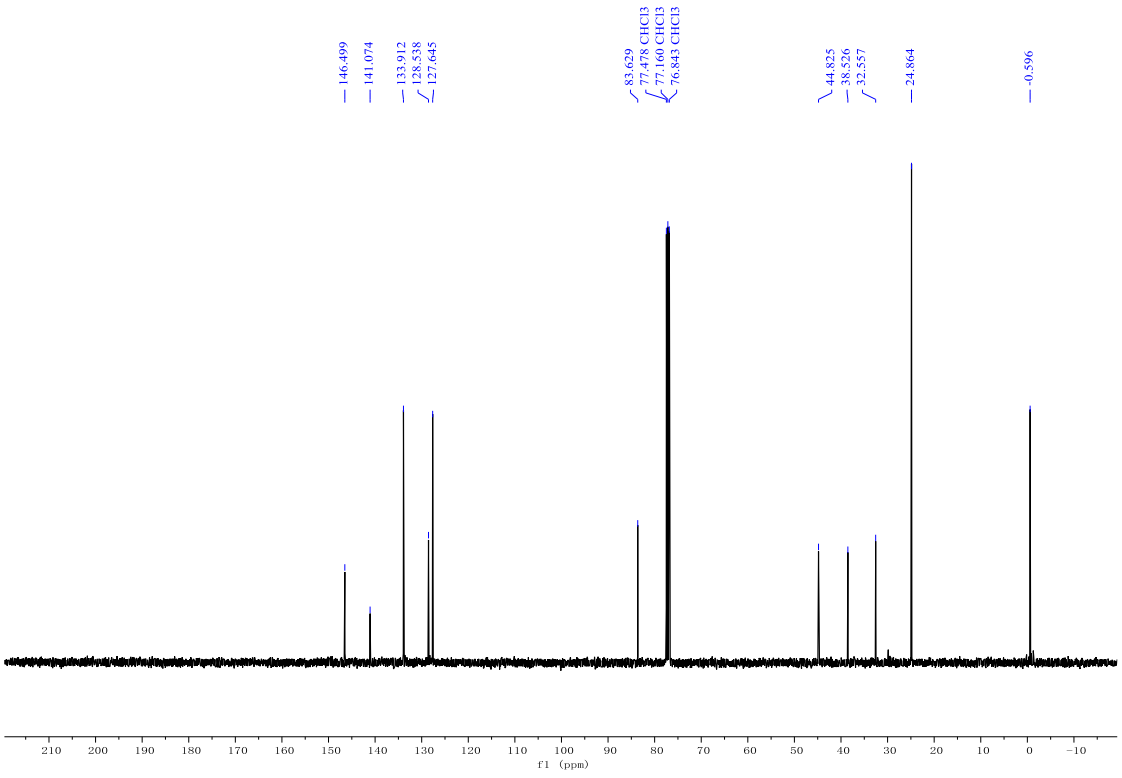
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.48 (m, 2H), 7.36 – 7.27 (m, 3H), 6.49 (s, 1H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.39 (ddd, *J* = 7.6, 6.7, 1.4 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.12 (s, 12H), 0.40 (s, 6H).

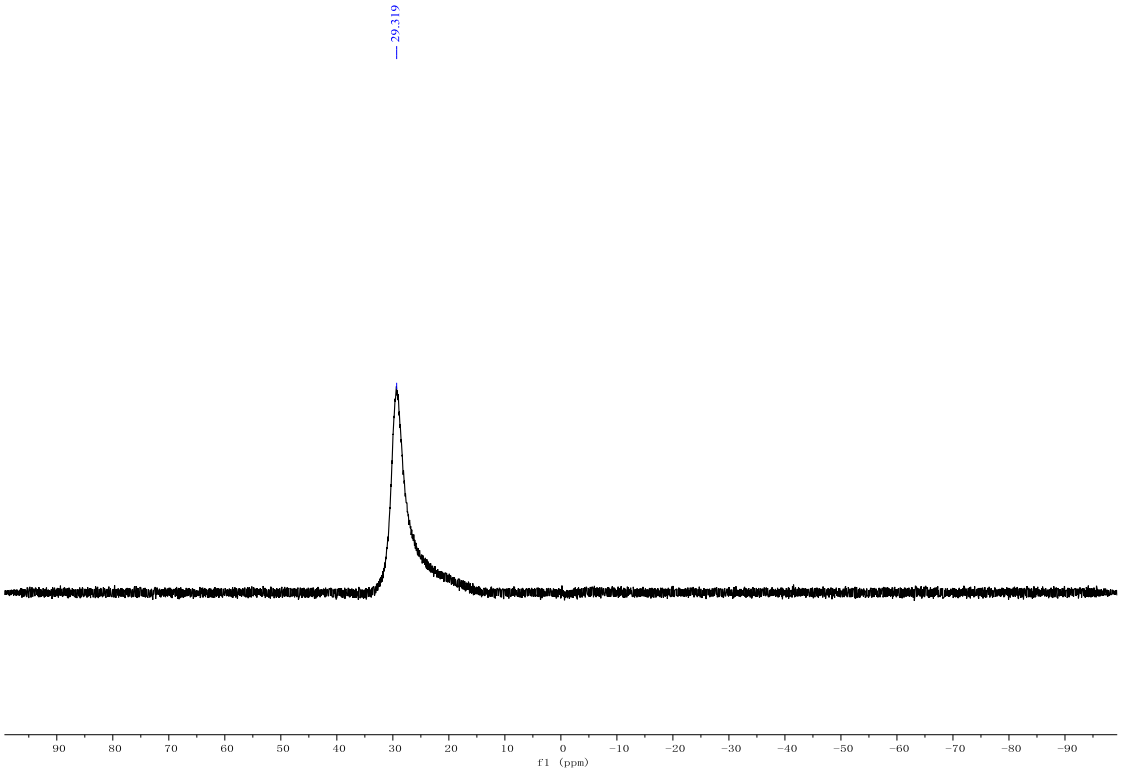
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.50, 141.07, 133.91, 128.54, 127.64, 83.63, 44.82, 38.53, 32.56, 24.86, -0.60.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.32.

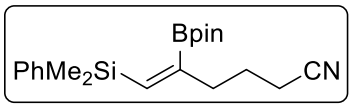
HRMS (ESI) m/z calculated for $C_{19}H_{30}BClOSiNa$ $[M+Na]^+$: 387.1694, found: 387.1701.




146.499
141.074
133.912
128.538
127.645
83.629
77.478 CHCl3
77.160 CHCl3
76.843 CHCl3
44.825
38.526
32.557
24.864
-0.596
f1 (ppm)


29.319
f1 (ppm)

(*E*)-6-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enenitrile (3o).



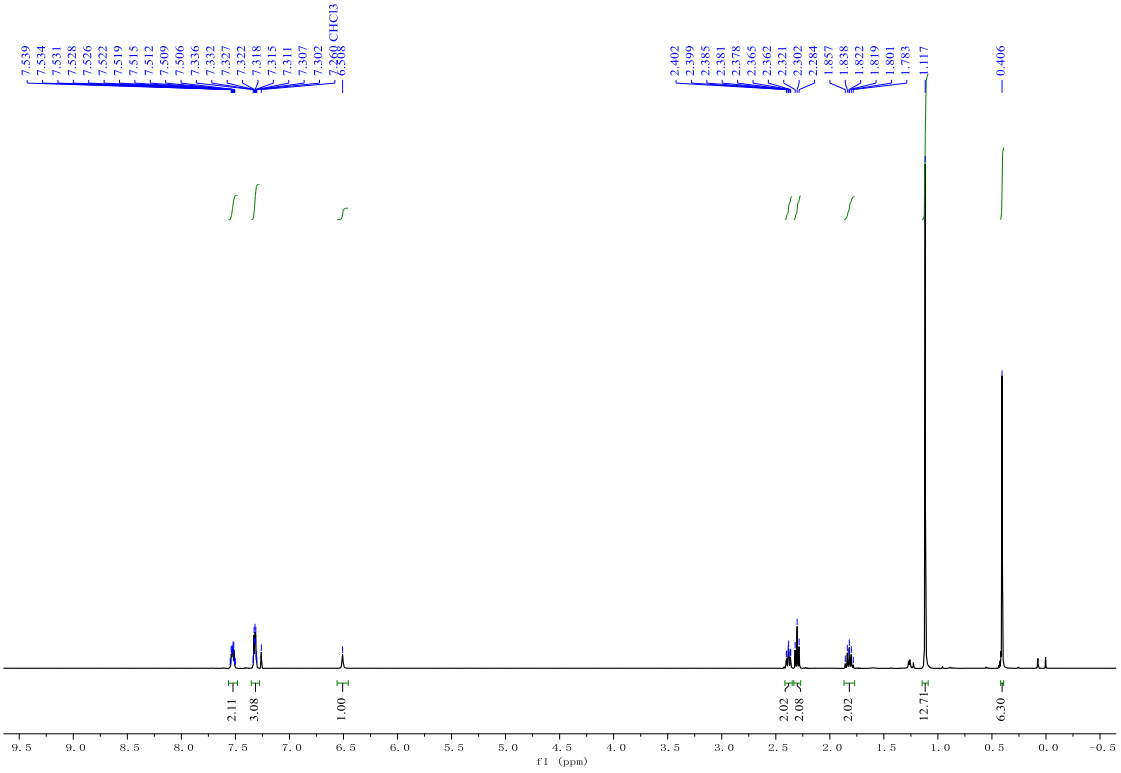
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 47% yield (33.2 mg). R_f = 0.33 (Petroleum ether:EtOAc = 95:5).

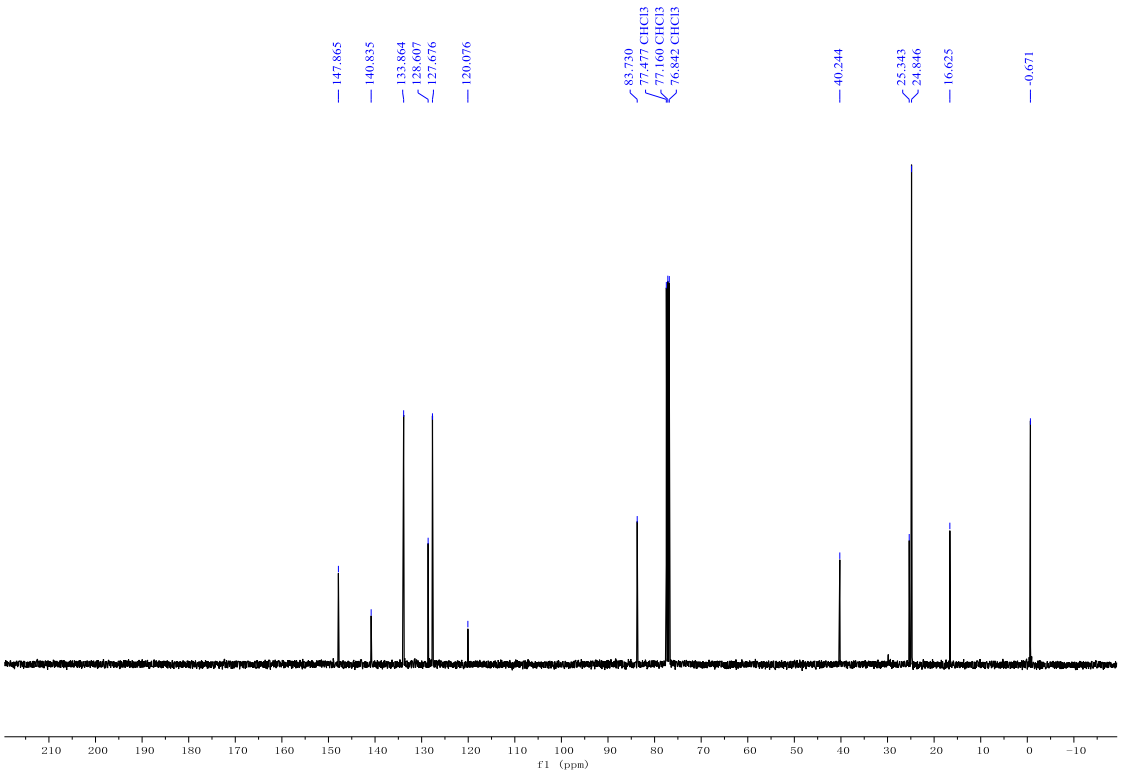
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.48 (m, 2H), 7.36 – 7.28 (m, 3H), 6.51 (s, 1H), 2.41 – 2.35 (m, 2H), 2.30 (t, *J* = 7.3 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.12 (s, 12H), 0.41 (s, 6H).

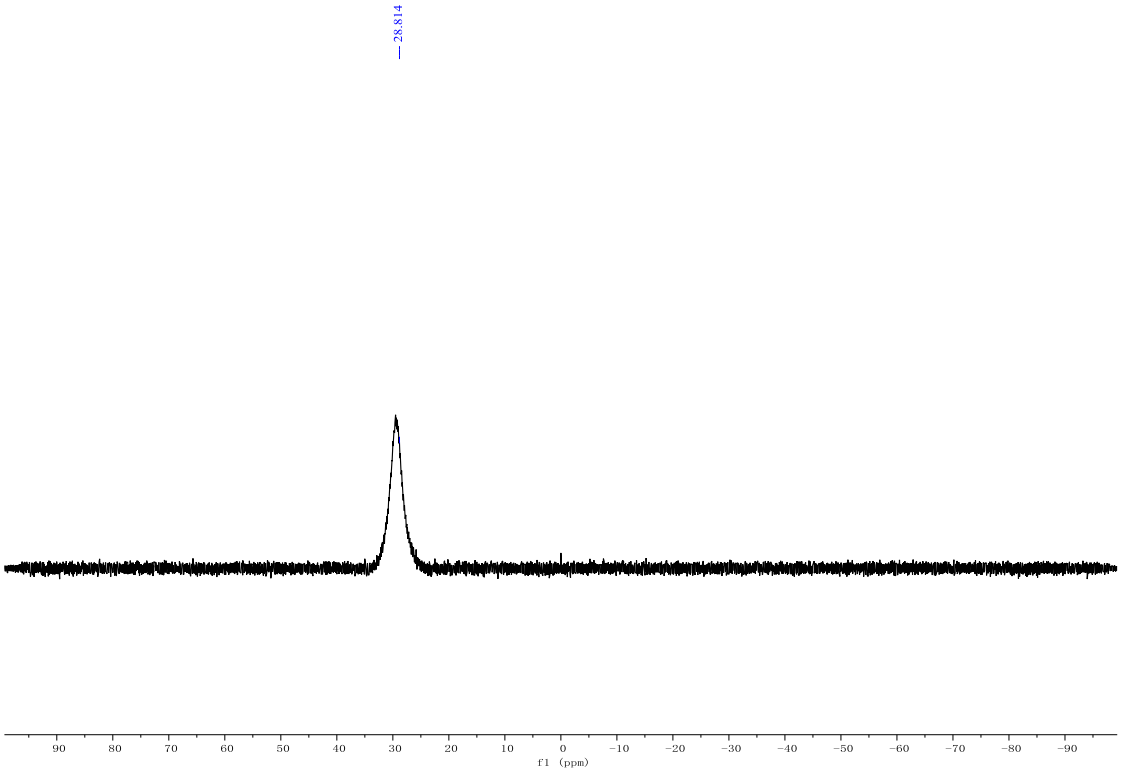
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.87, 140.83, 133.86, 128.61, 127.68, 120.08, 83.73, 40.24, 25.34, 24.85, 16.62, -0.67.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.81.

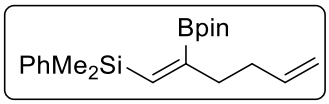
HRMS (ESI) m/z calculated for $C_{20}H_{30}BNO_2SiNa$ $[M+Na]^+$: 378.2037, found: 378.2039.




147.865
140.835
133.864
128.607
127.676
120.076
83.730
77.477 CHCl3
77.160 CHCl3
76.842 CHCl3
40.244
25.343
24.846
16.625
-0.671
f1 (ppm)


28.814
f1 (ppm)

(*E*)-dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dien-1-yl) silane (3p).



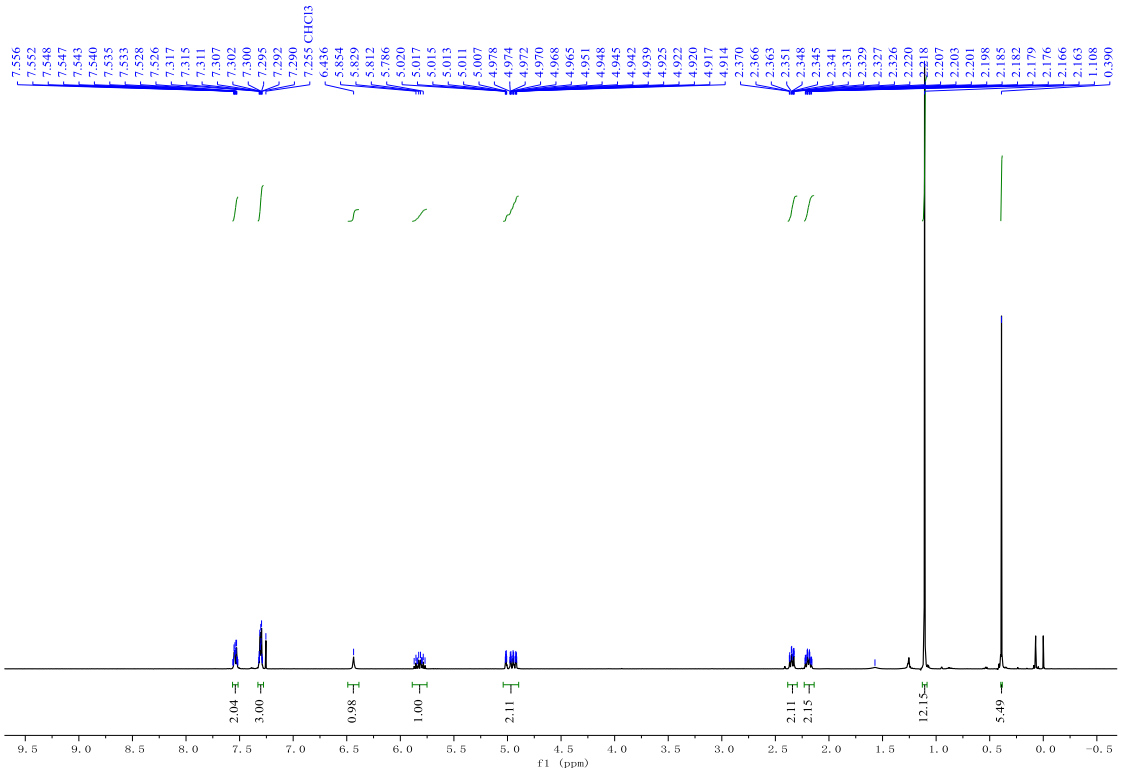
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 63% yield (42.6 mg). R_f = 0.26 (Petroleum ether:EtOAc = 98:2).

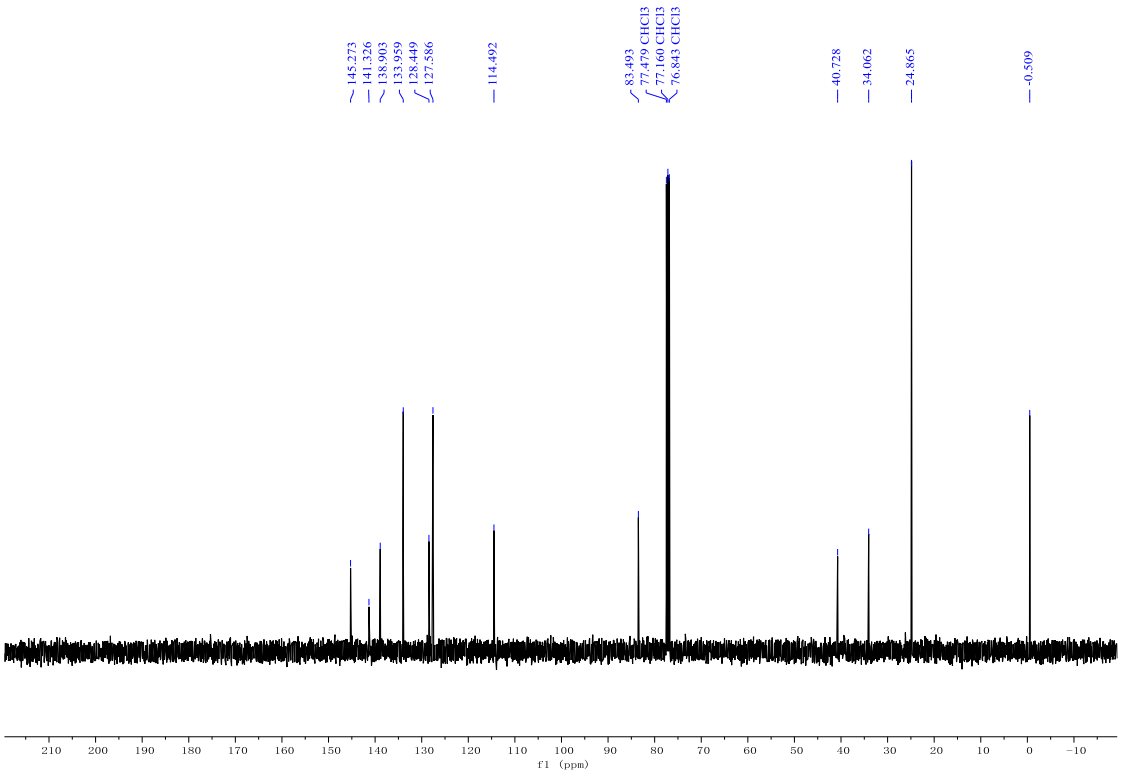
^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.52 (m, 2H), 7.33 – 7.28 (m, 3H), 6.44 (s, 1H), 5.82 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.03 – 4.91 (m, 2H), 2.39 – 2.31 (m, 2H), 2.23 – 2.15 (m, 2H), 1.11 (s, 12H), 0.39 (s, 6H).

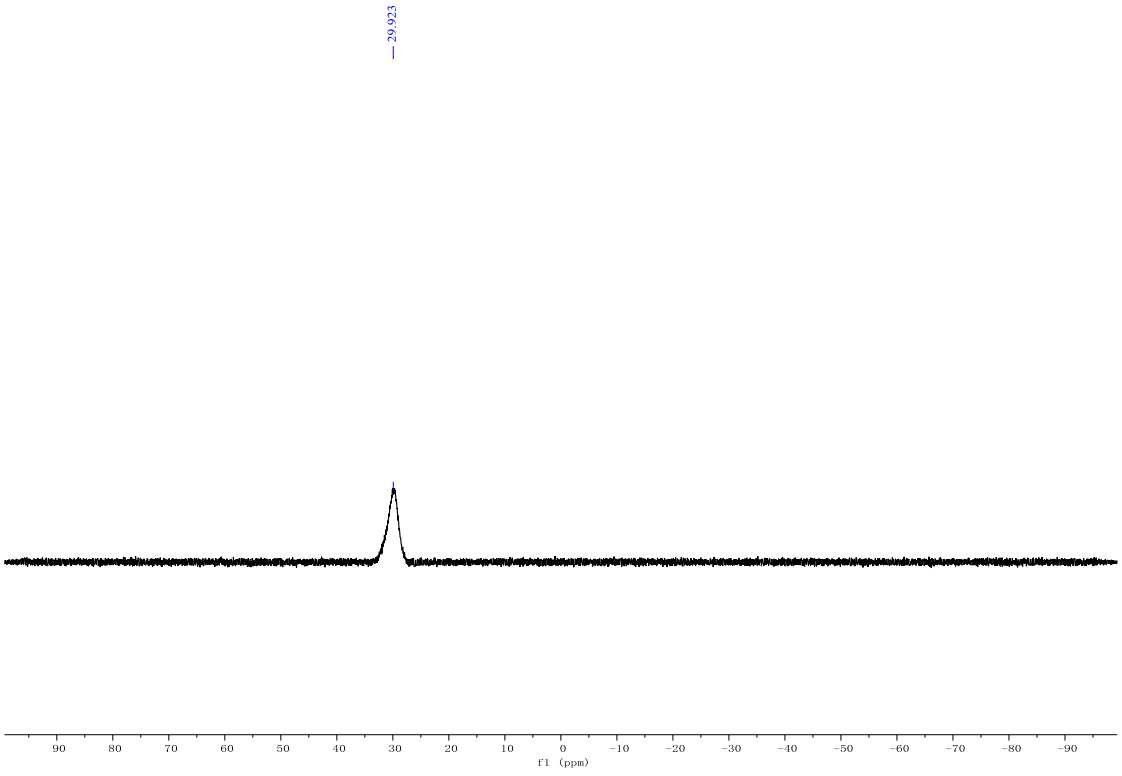
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.27, 141.33, 138.91, 133.96, 128.45, 127.59, 114.49, 83.49, 40.73, 34.07, 24.87, -0.51.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.92.

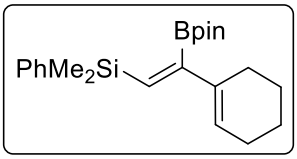
HRMS (ESI) m/z calculated for $C_{20}H_{31}BO_2SiNa$ $[M+Na]^+$: 365.2084, found: 365.2080.




145.273
141.326
138.903
133.959
128.449
127.586
114.492
83.493
77.479 CHCl3
77.160 CHCl3
76.843 CHCl3
40.728
34.062
24.865
-0.509
f1 (ppm)


29.923
f1 (ppm)

(*E*)-(2-(cyclohex-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl (phenyl)silane (3r).



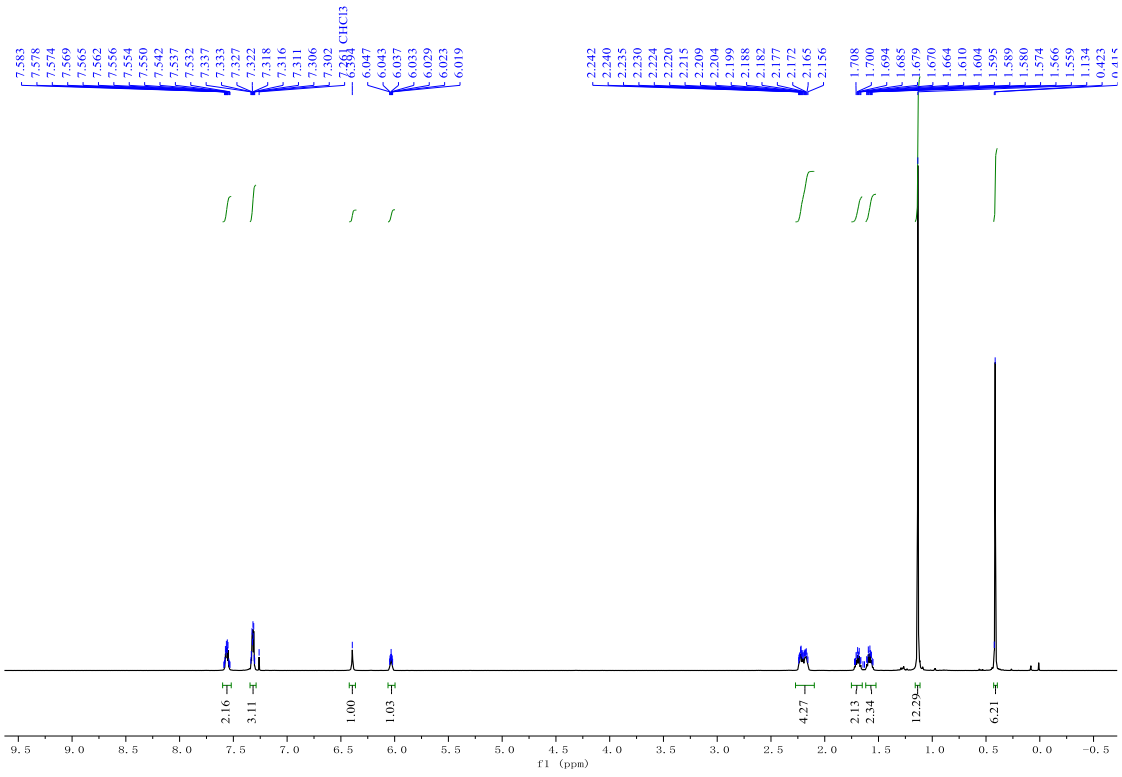
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 56% yield (41.1 mg). R_f = 0.15 (Petroleum ether:EtOAc = 99:1).

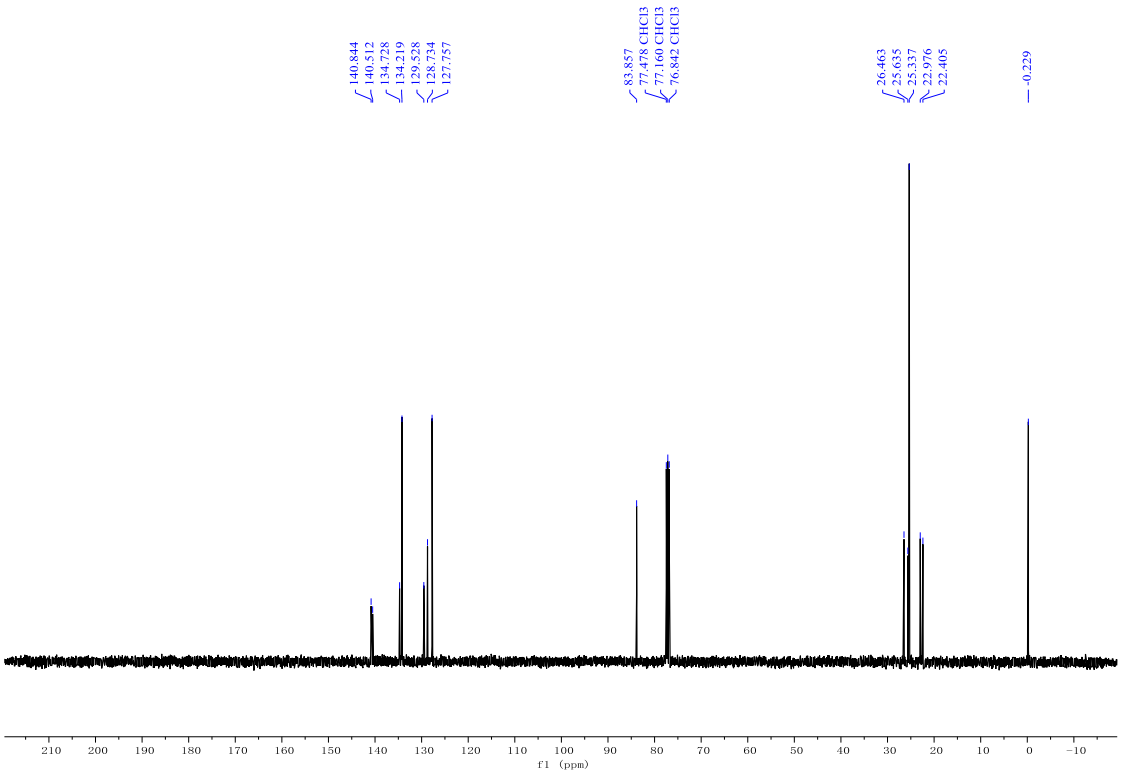
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.36 – 7.28 (m, 3H), 6.39 (s, 1H), 6.04 (td, *J* = 3.9, 1.9 Hz, 1H), 2.20 (dddt, *J* = 15.5, 6.8, 4.9, 2.3 Hz, 4H), 1.75 – 1.62 (m, 2H), 1.64 – 1.53 (m, 2H), 1.13 (s, 12H), 0.41 (s, 6H).

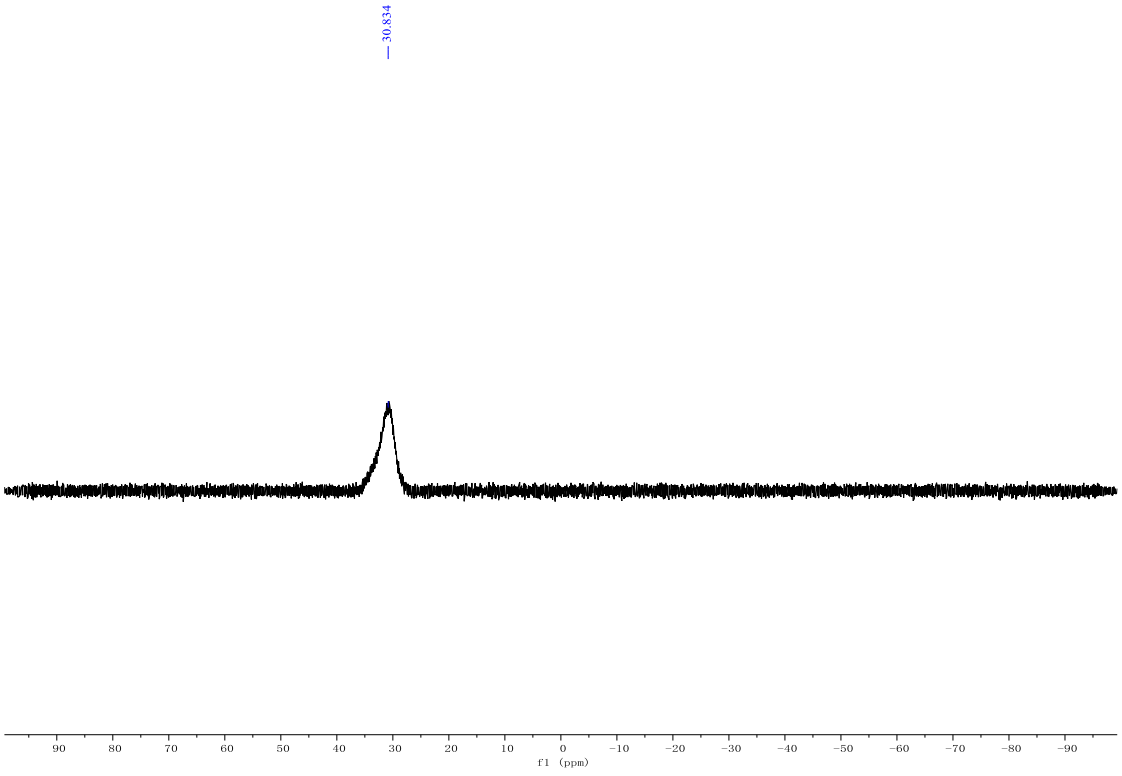
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.84, 140.51, 134.73, 134.22, 129.53, 128.73, 127.76, 83.86, 26.46, 25.64, 25.34, 22.98, 22.40, -0.23.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.83.

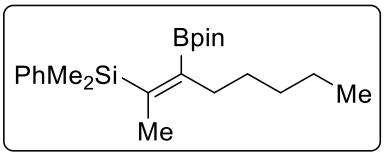
HRMS (ESI) m/z calculated for $C_{22}H_{33}BO_2SiNa$ $[M+Na]^+$: 391.2241, found: 391.2247.




140.844
140.512
134.728
134.219
129.528
128.734
127.757
83.857
77.478 CHCl3
77.160 CHCl3
76.842 CHCl3
26.463
25.635
25.337
22.976
22.405
-0.229
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


30.834
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

(*E*)-dimethyl(phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-2-yl)silane (3s).



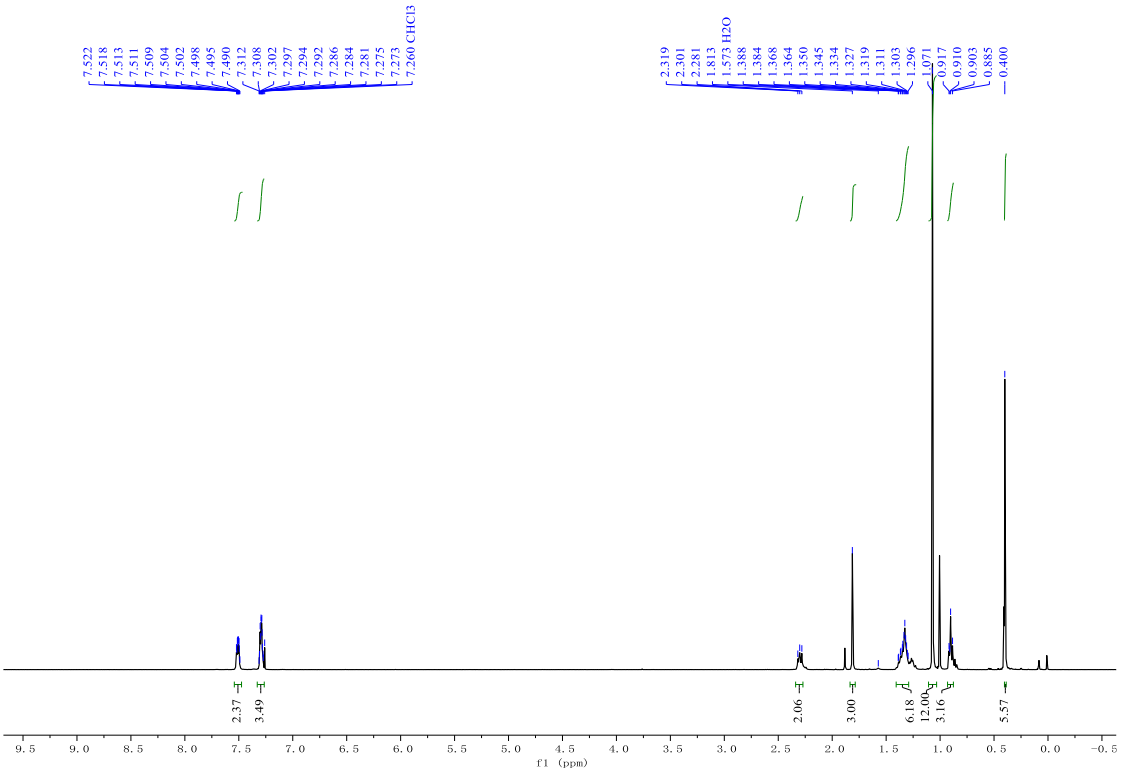
This compound was prepared by the general procedure A described above and was obtained as colorless oil of inseparable mixture (2/3 = 85:15) in 59% yield (44.8 mg). R_f = 0.48 (Petroleum ether:EtOAc = 98:2).

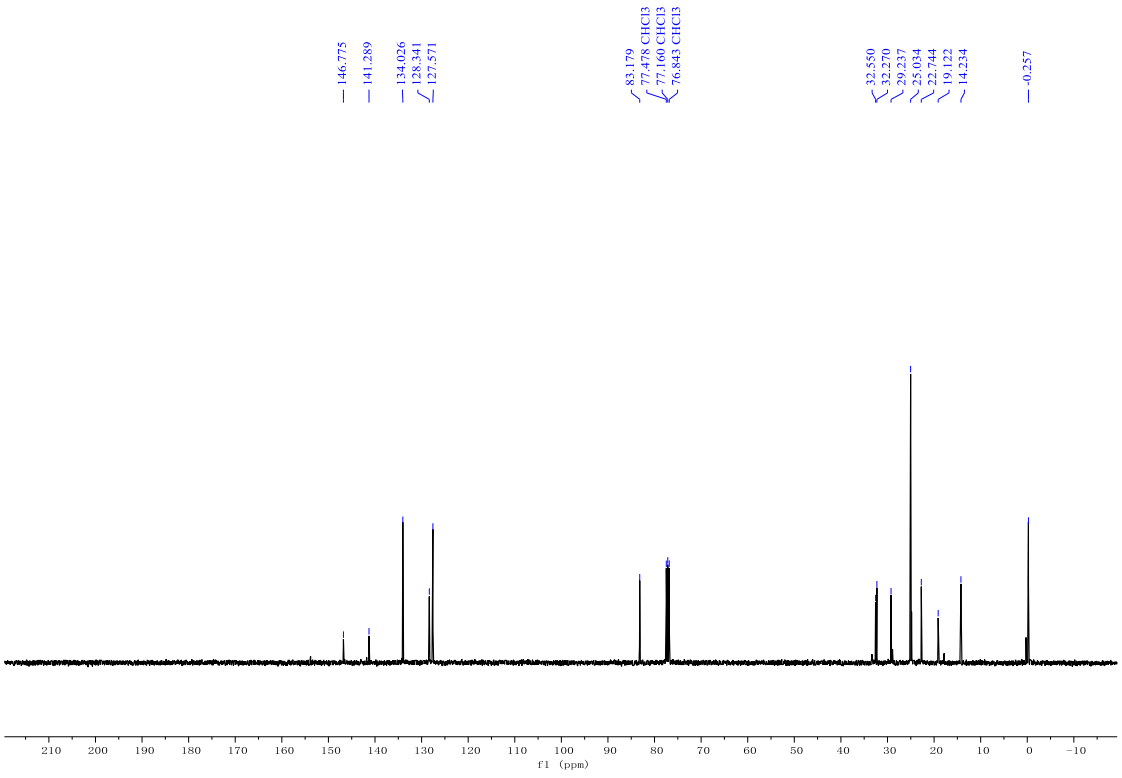
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 7.32 – 7.26 (m, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.81 (s, 3H), 1.34 (tdd, *J* = 12.2, 6.9, 2.1 Hz, 6H), 1.07 (s, 12H), 0.94 – 0.88 (m, 3H), 0.40 (s, 6H).

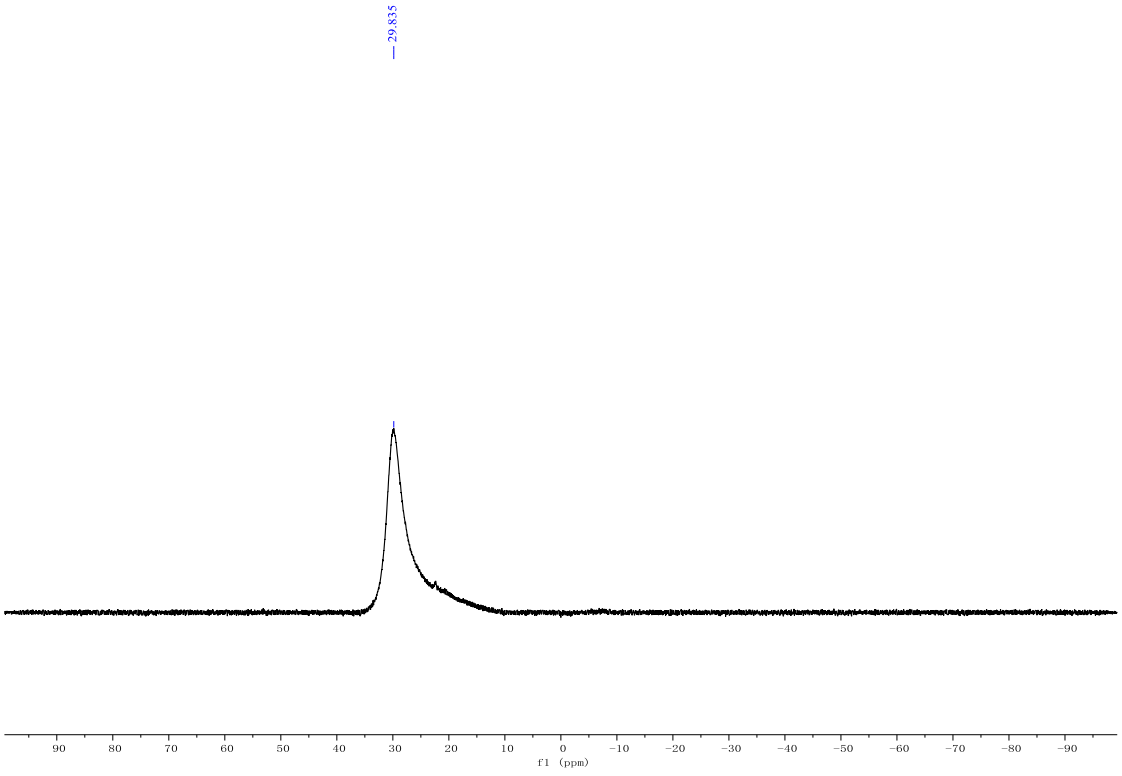
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.78, 141.29, 134.03, 128.34, 127.57, 83.18, 32.55, 32.27, 29.24, 25.03, 22.74, 19.12, 14.23, -0.26.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.84.

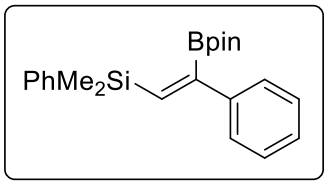
HRMS (ESI) m/z calculated for $C_{22}H_{37}BO_2Si$ Na $[M+Na]^+$: 395.2554, found: 395.2565.




146.775
141.289
134.026
128.341
127.571
83.179
77.478 CHCl3
77.160 CHCl3
76.843 CHCl3
32.550
32.270
29.237
25.034
22.744
19.122
14.234
-0.257
f1 (ppm)


29.835
f1 (ppm)

(*E*)-dimethyl(phenyl)(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3t).



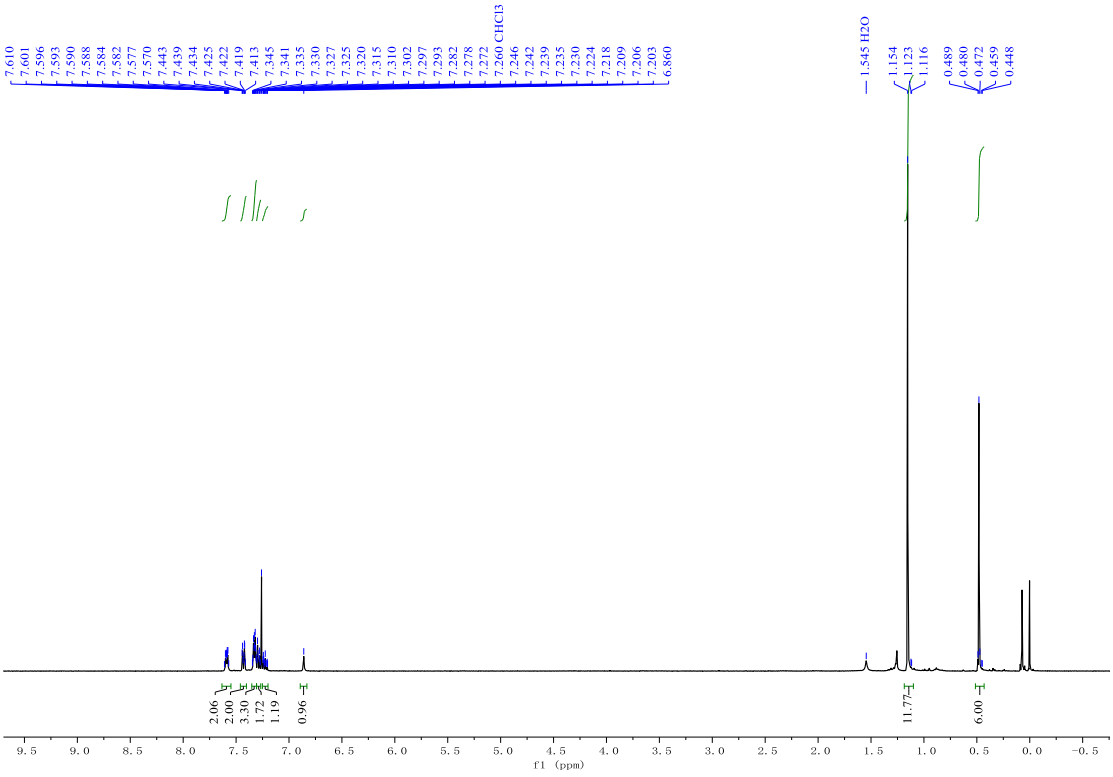
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 10% yield (7.3 mg). R_f = 0.28 (Petroleum ether:EtOAc = 98:2).

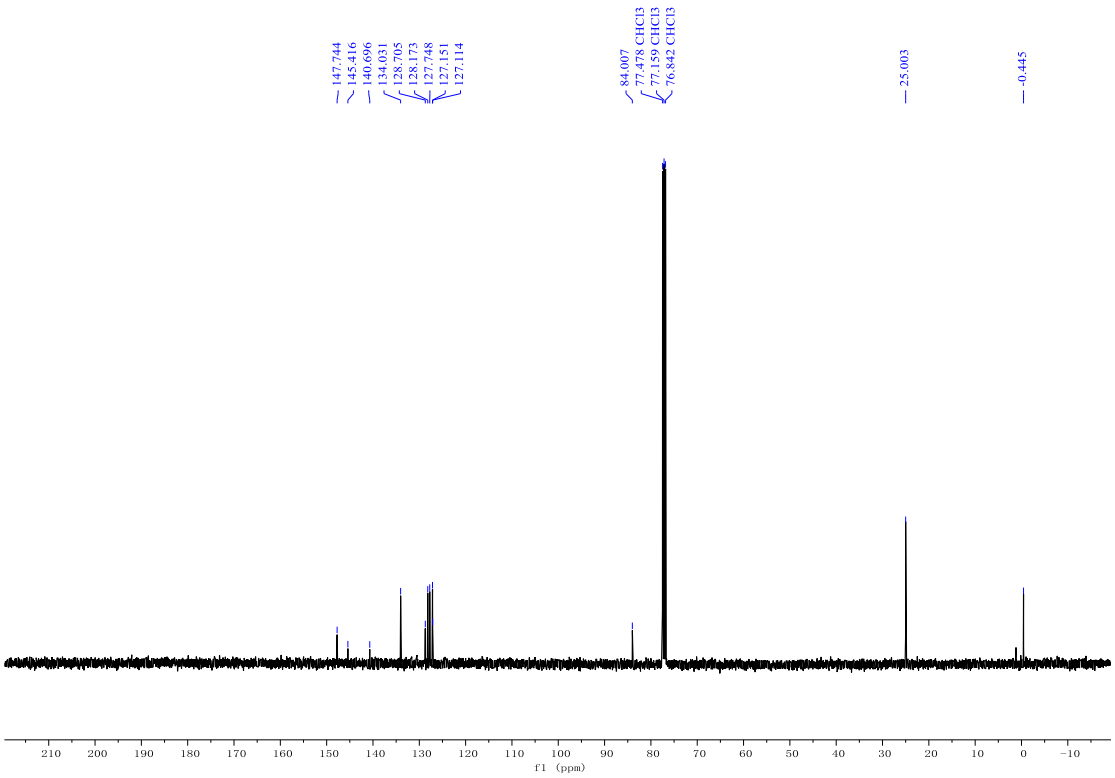
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.46 – 7.40 (m, 2H), 7.35 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 6.86 (s, 1H), 1.15 (s, 12H), 0.48 (s, 6H).

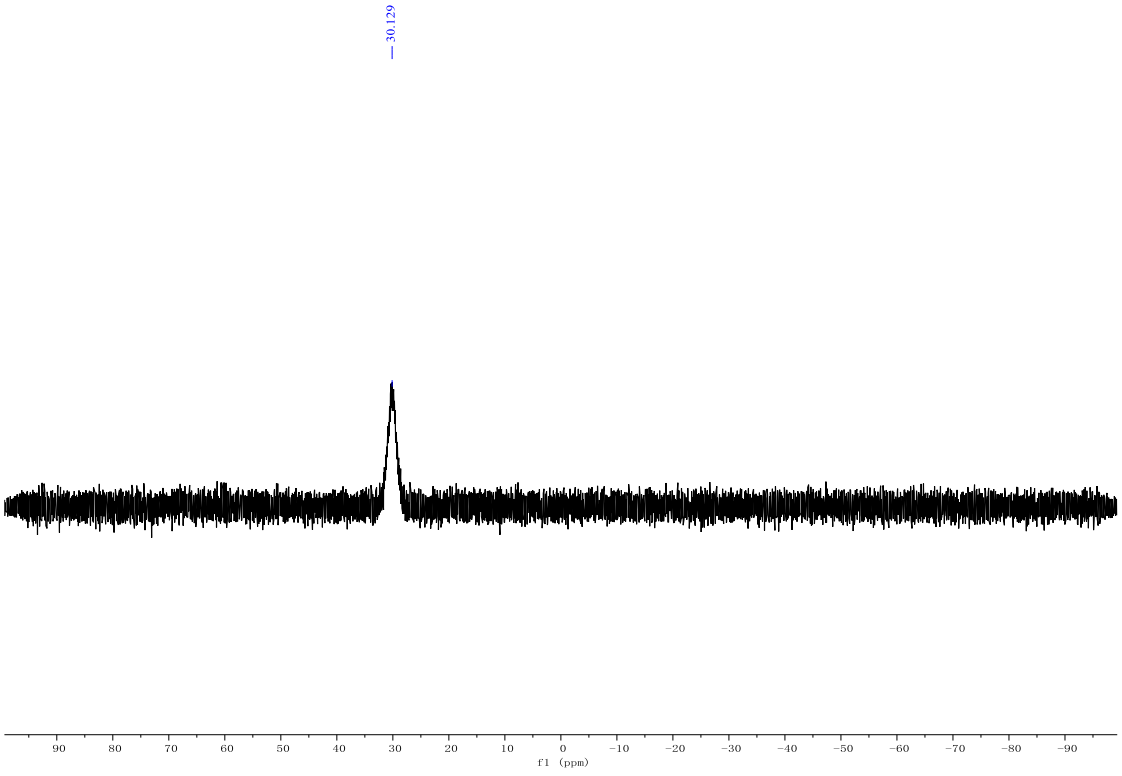
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.74, 145.42, 140.70, 134.03, 128.71, 128.17, 127.75, 127.15, 127.11, 84.01, 25.00, -0.44.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.13.

HRMS (ESI) m/z calculated for $C_{22}H_{29}BO_2SiNa$ $[M+Na]^+$: 387.1928, found: 387.1933.

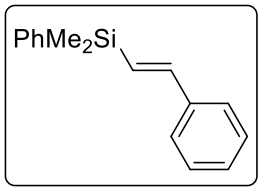



147.744
145.416
140.696
134.031
128.705
128.173
127.748
127.151
127.114
84.007
77.478 CHCl3
77.159 CHCl3
76.842 CHCl3
25.003
-0.445
f1 (ppm)


30.129
f1 (ppm)

B. Characterization data and spectrum of products 5

(E)-dimethyl(phenyl)(styryl)silane (5t).

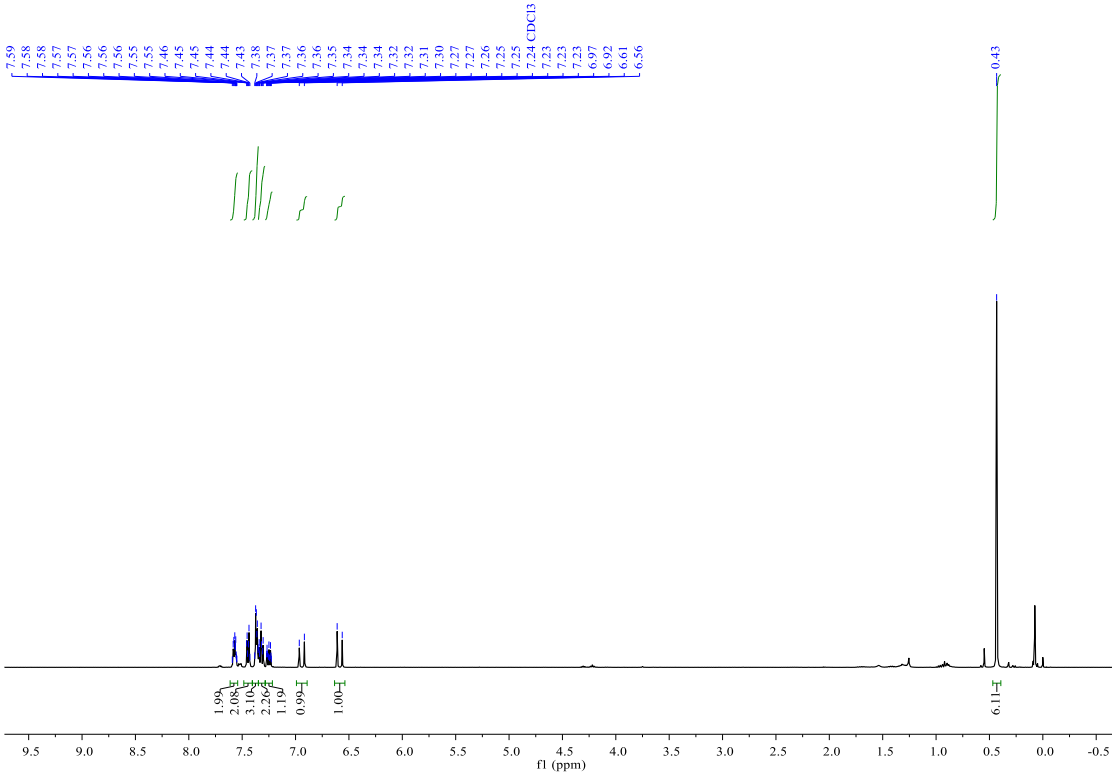


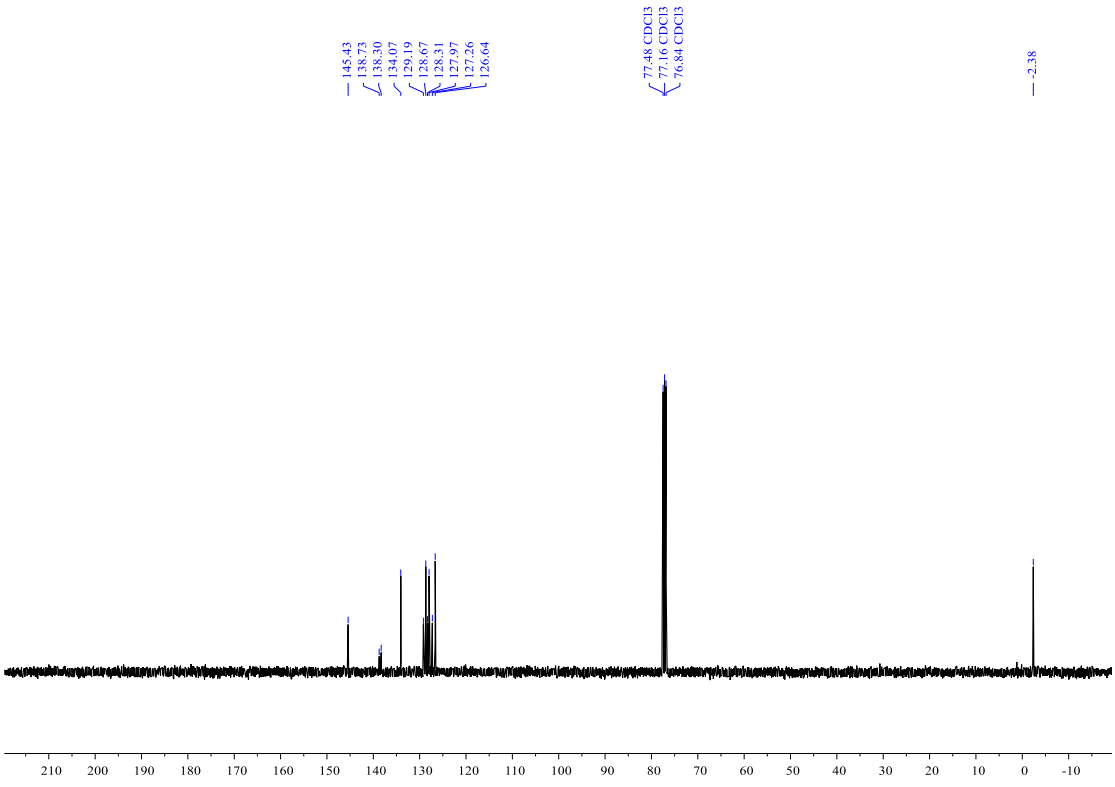
This compound was prepared by the general procedure A described above and was obtained as white solid in 53% yield (25.2 mg). R_f = 0.70 (Petroleum ether:EtOAc = 98:2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 2H), 7.45 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 6.94 (d, *J* = 19.1 Hz, 1H), 6.59 (d, *J* = 19.1 Hz, 1H), 0.43 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.43, 138.73, 138.30, 134.07, 129.19, 128.67, 128.31, 127.97, 127.26, 126.64, -2.38.

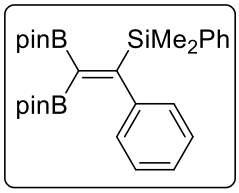
HRMS (ESI) m/z calculated for $C_{16}H_{18}SiNa$ $[M+Na]^+$: 261.1070, found: 261.1062.




145.43
138.73
138.30
134.07
129.19
128.67
128.31
127.97
127.26
126.64
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
-2.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

C. Characterization data and spectrum of products 7

dimethyl(phenyl)(1-phenyl-2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (7t).



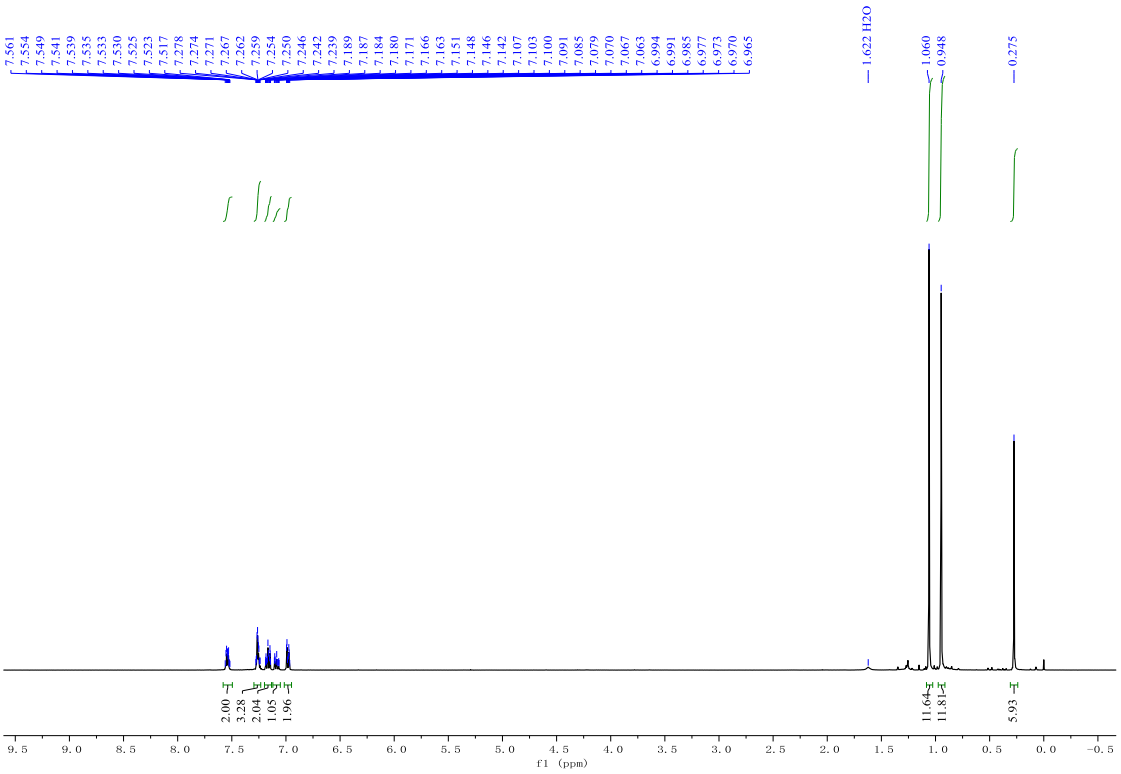
This compound was prepared by the general procedure A described above and was obtained as white solid in 32% yield (31.4 mg). R_f = 0.10 (Petroleum ether:EtOAc = 95:5).

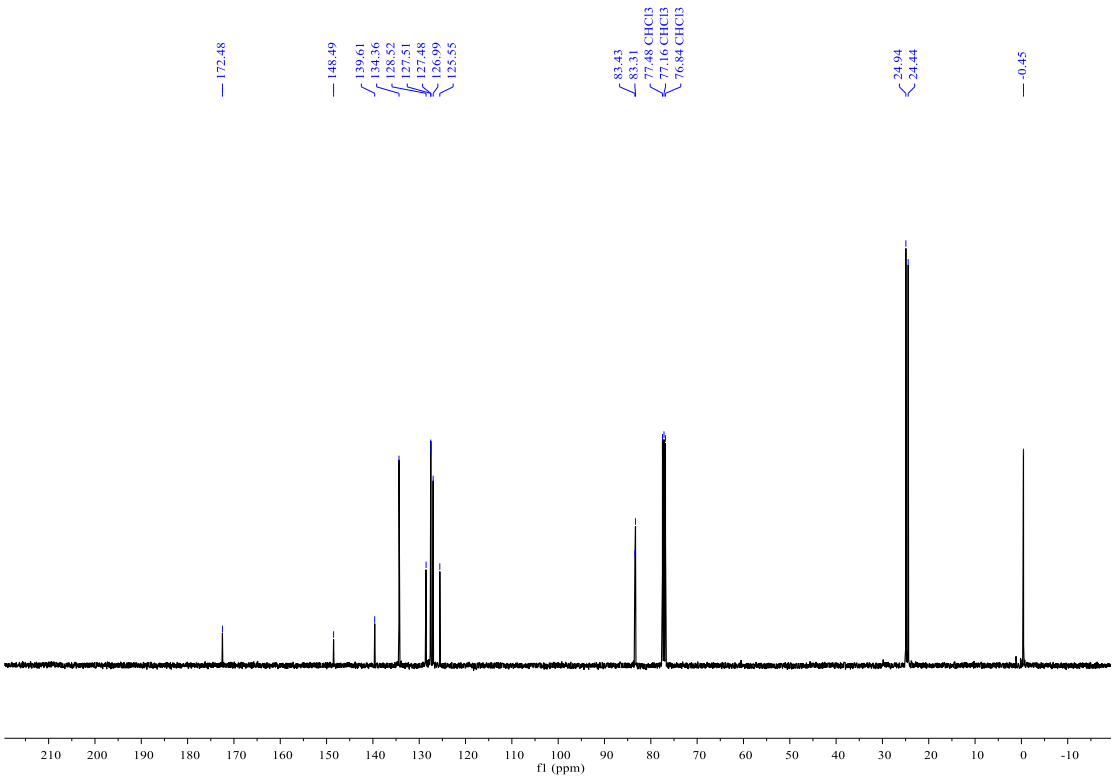
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 2H), 7.30 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 7.03 – 6.94 (m, 2H), 1.06 (s, 12H), 0.95 (s, 12H), 0.28 (s, 6H).

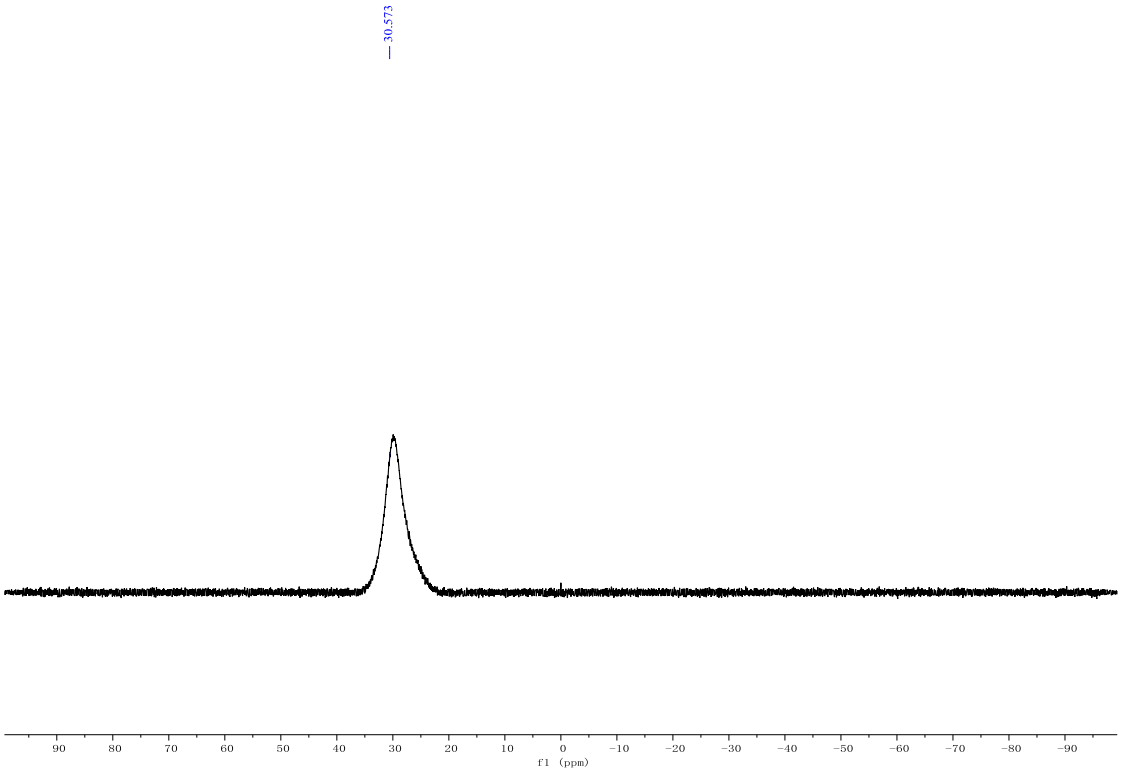
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.48, 148.49, 139.61, 134.36, 128.52, 127.51, 127.48, 126.99, 125.55, 83.43, 83.31, 24.94, 24.44, -0.45.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.57.

HRMS (ESI) m/z calculated for $C_{28}H_{40}B_2O_4SiNa$ $[M+Na]^+$: 513.2780, found: 513.2791.

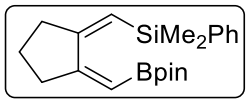



172.48
148.49
139.61
134.36
128.52
127.51
127.48
126.99
125.55
83.43
83.31
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
24.94
24.44
-0.45
f1 (ppm)


30.573
f1 (ppm)

C. Characterization data and spectrum of products 8

dimethyl(phenyl)((*Z*)-((*Z*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentylidene)methyl)silane (8v)



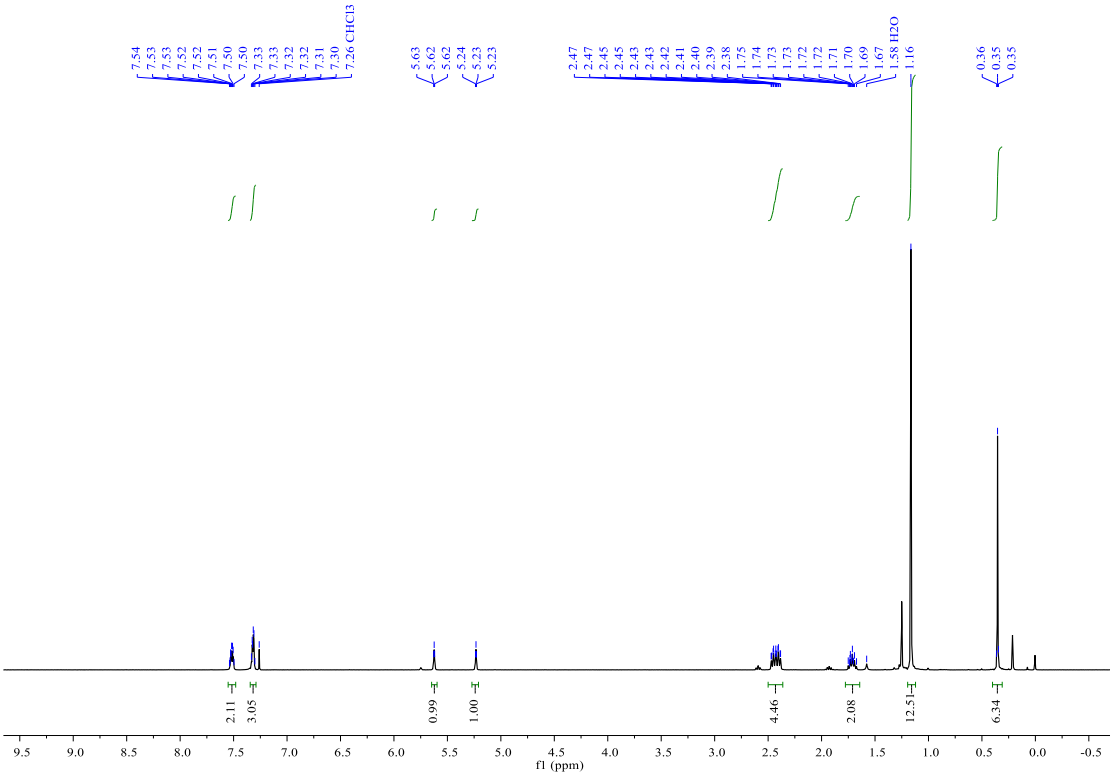
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 43% yield by preparative HPLC (30.3 mg). R_f = 0.49 (Petroleum ether:EtOAc= 95:5).

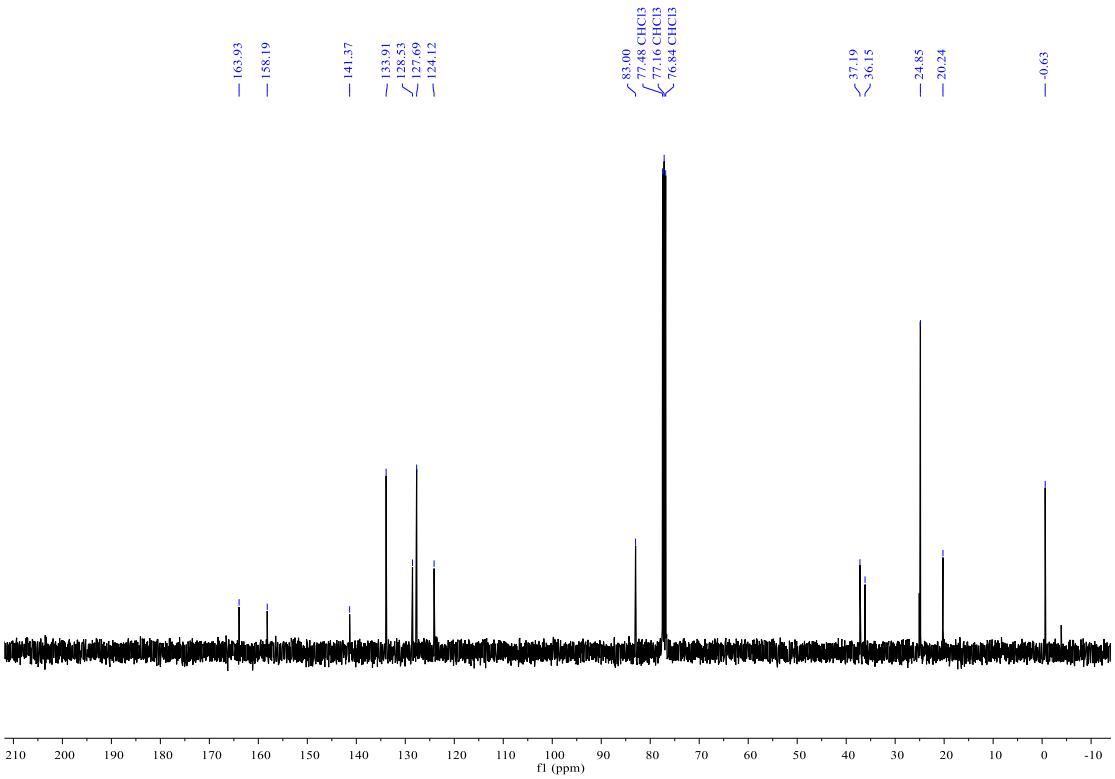
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.34 – 7.30 (m, 3H), 5.62 (t, *J* = 1.7 Hz, 1H), 5.23 (t, 1H), 2.43 (dtd, *J* = 17.7, 7.6, 1.7 Hz, 4H), 1.71 (p, *J* = 7.8 Hz, 2H), 1.16 (s, 12H), 0.35 (s, 6H).

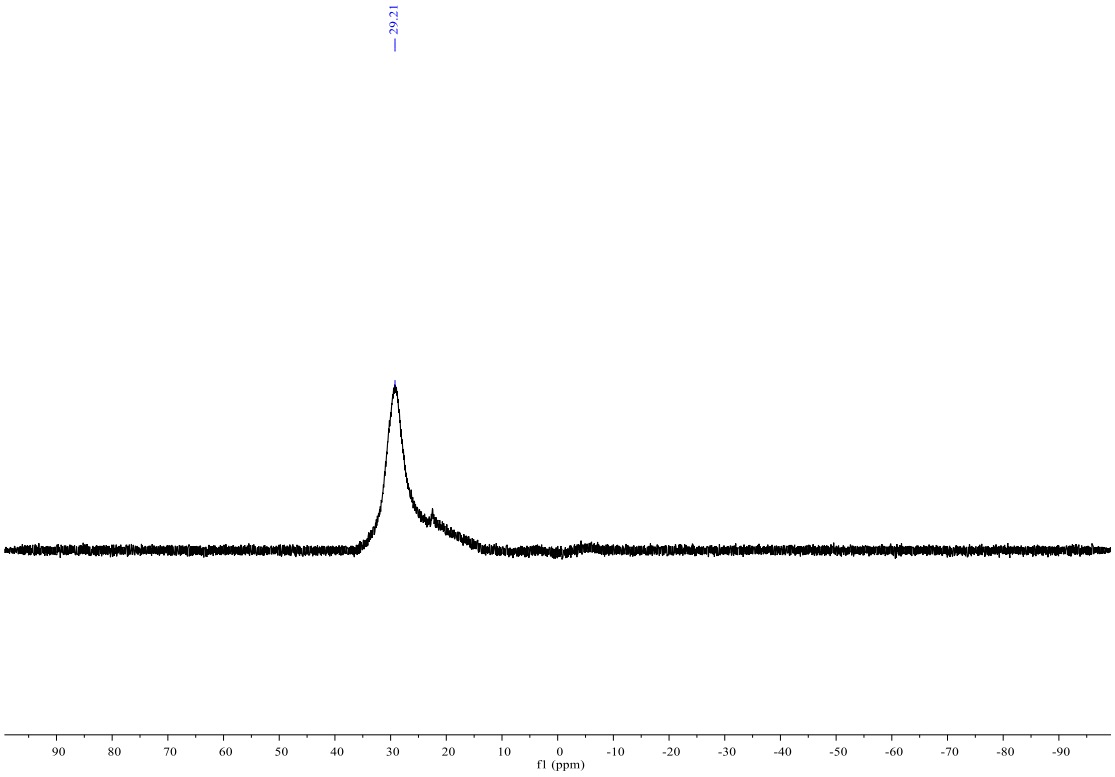
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.93, 158.19, 141.37, 133.91, 128.53, 127.69, 124.12, 83.00, 37.19, 36.15, 24.85, 20.24, -0.63.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.21.

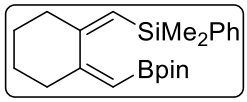
HRMS (ESI) m/z calculated for $C_{21}H_{31}BO_2SiNa$ $[M+Na]^+$: 377.2084, found: 377.2084.




163.93
158.19
141.37
133.91
128.53
127.69
124.12
83.00
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
37.19
36.15
24.85
20.24
-0.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


29.21
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

dimethyl(phenyl)((Z)-((Z)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexylidene)methyl)silane (8w)



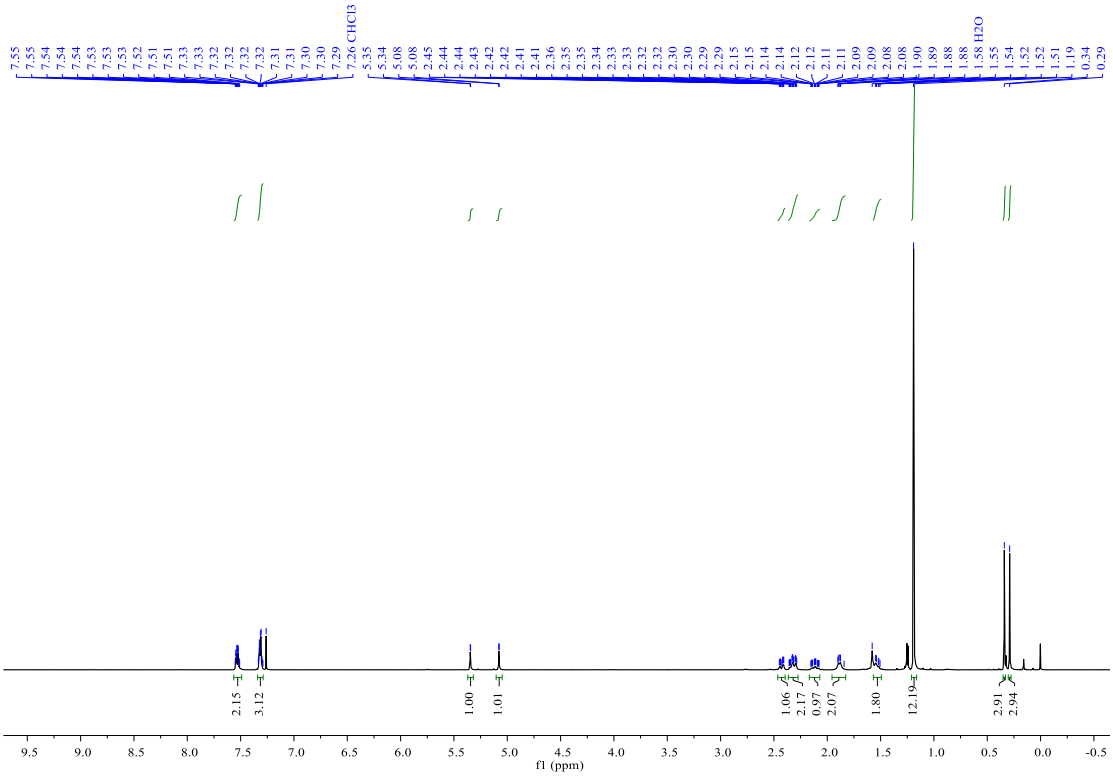
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 70% yield by preparative HPLC (52.2 mg). R_f = 0.50 (Petroleum ether:EtOAc = 95:5).

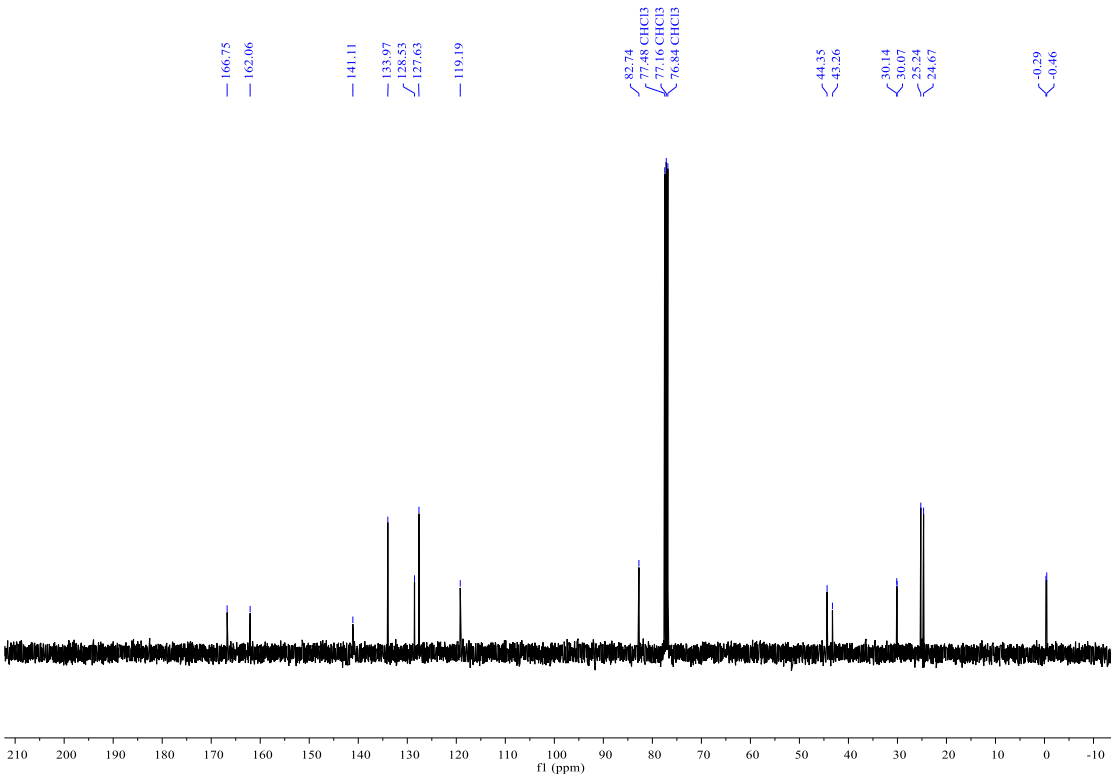
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H), 7.35 – 7.28 (m, 3H), 5.35 (d, *J* = 1.3 Hz, 1H), 5.08 (d, *J* = 1.3 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.32 (tdd, *J* = 11.8, 4.1, 1.7 Hz, 2H), 2.11 (tdd, *J* = 11.9, 4.4, 1.6 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.53 (d, *J* = 12.1 Hz, 2H), 1.19 (s, 12H), 0.34 (s, 3H), 0.29 (s, 3H).

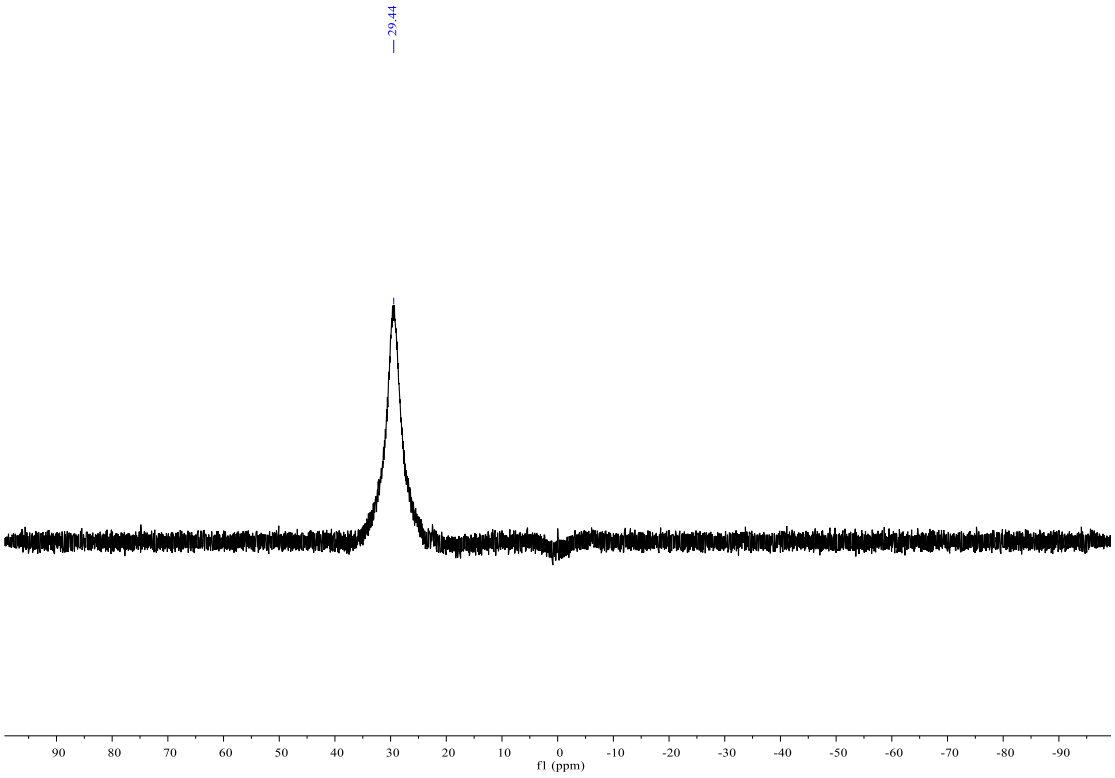
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.75, 162.06, 141.11, 133.97, 128.53, 127.63, 119.19, 82.74, 44.35, 43.26, 30.14, 30.07, 25.24, 24.67, -0.29, -0.46.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.44.

HRMS (ESI) m/z calculated for $C_{22}H_{33}BO_2SiNa$ $[M+Na]^+$: 391.2241, found: 391.2243.

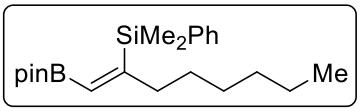



166.75
162.06
141.11
133.97
128.53
127.63
119.19
82.74
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
44.35
43.26
30.14
30.07
25.24
24.67
0.29
-0.46
f1 (ppm)


29.44
f1 (ppm)

E. Characterization data and spectrum of products 4

(*Z*)-dimethyl(phenyl)(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-2-yl)silane (4a).



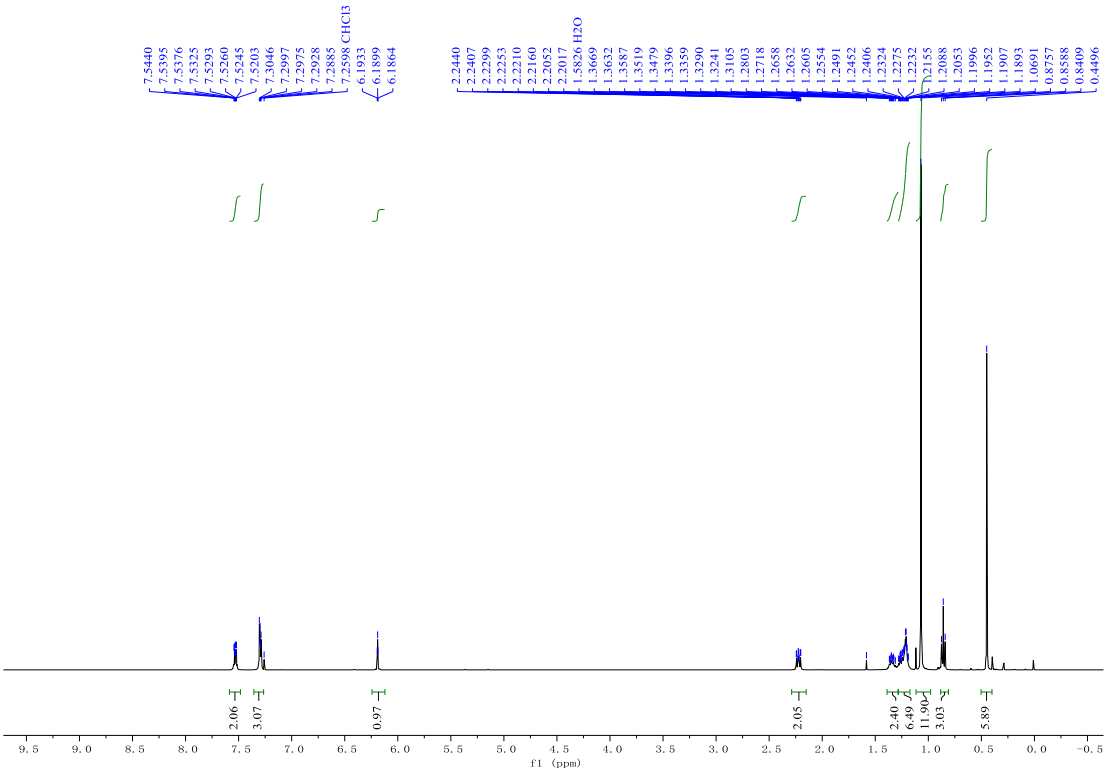
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 71% yield (52.9 mg). R_f = 0.58 (Petroleum ether:Et_2O= 96:4).

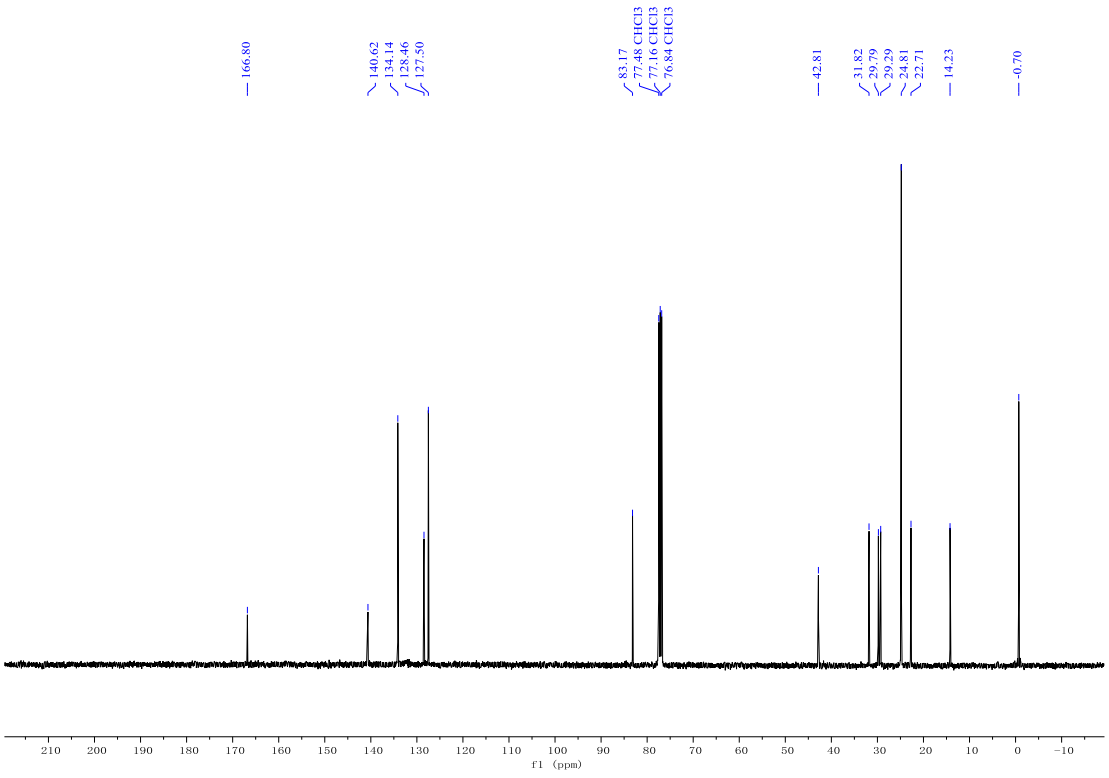
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.31 – 7.28 (m, 3H), 6.19 (t, *J* = 1.4 Hz, 1H), 2.22 (ddd, *J* = 9.4, 5.7, 1.4 Hz, 2H), 1.38 – 1.31 (m, 2H), 1.29 – 1.18 (m, 6H), 1.07 (s, 12H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.45 (s, 6H).

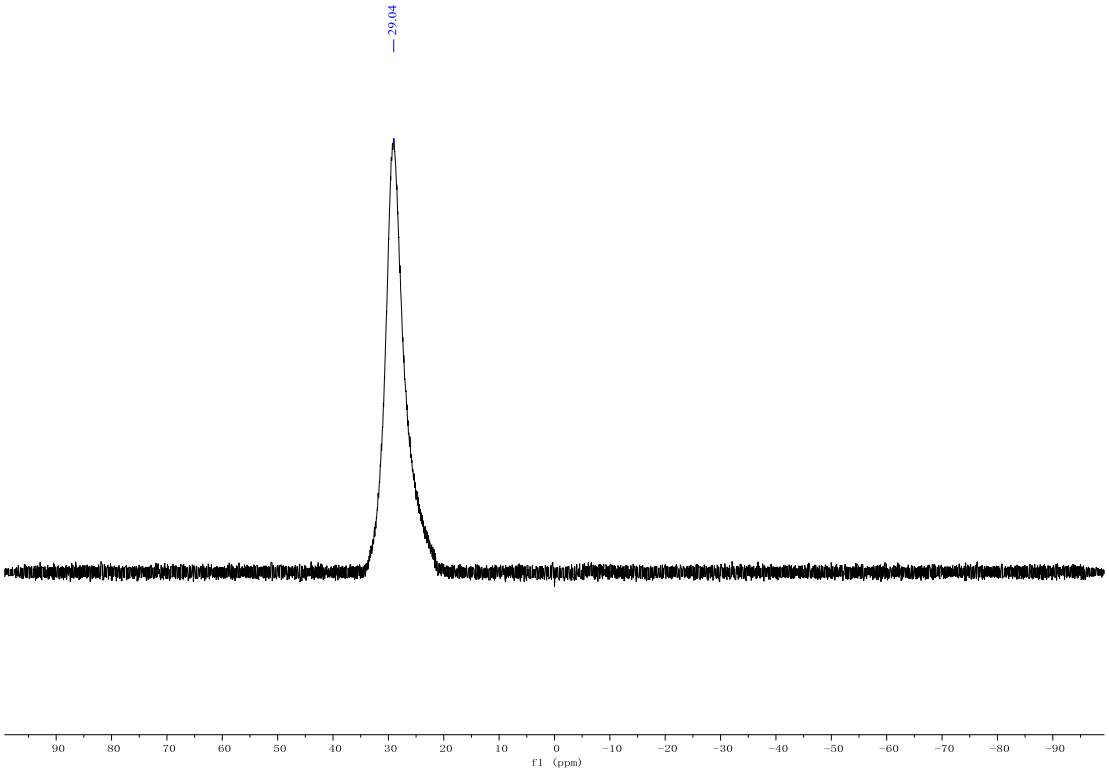
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.80, 140.62, 134.14, 128.46, 127.50, 83.17, 42.81, 31.82, 29.79, 29.29, 24.81, 22.71, 14.23, -0.70.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.04.

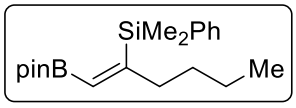
HRMS (ESI) m/z calculated for $C_{22}H_{37}BO_2SiNa$ $[M+Na]^+$: 395.2554, found: 395.2570.




166.80
140.62
134.14
128.46
127.50
83.17
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
42.81
31.82
29.79
29.29
24.81
22.71
14.23
-0.70
f1 (ppm)


29.04
f1 (ppm)

(*Z*)-dimethyl(phenyl)(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-2-yl)silane (4b).



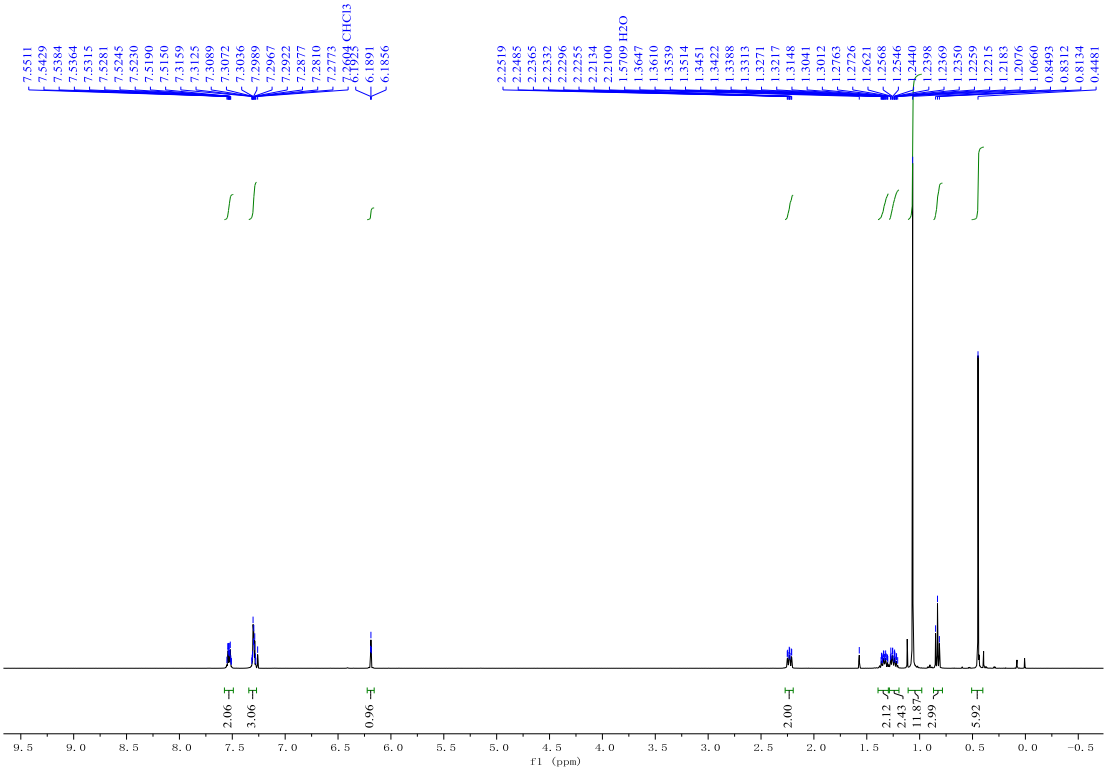
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 65% yield (44.8 mg). R_f = 0.54 (Petroleum ether:EtOAc= 98:2).

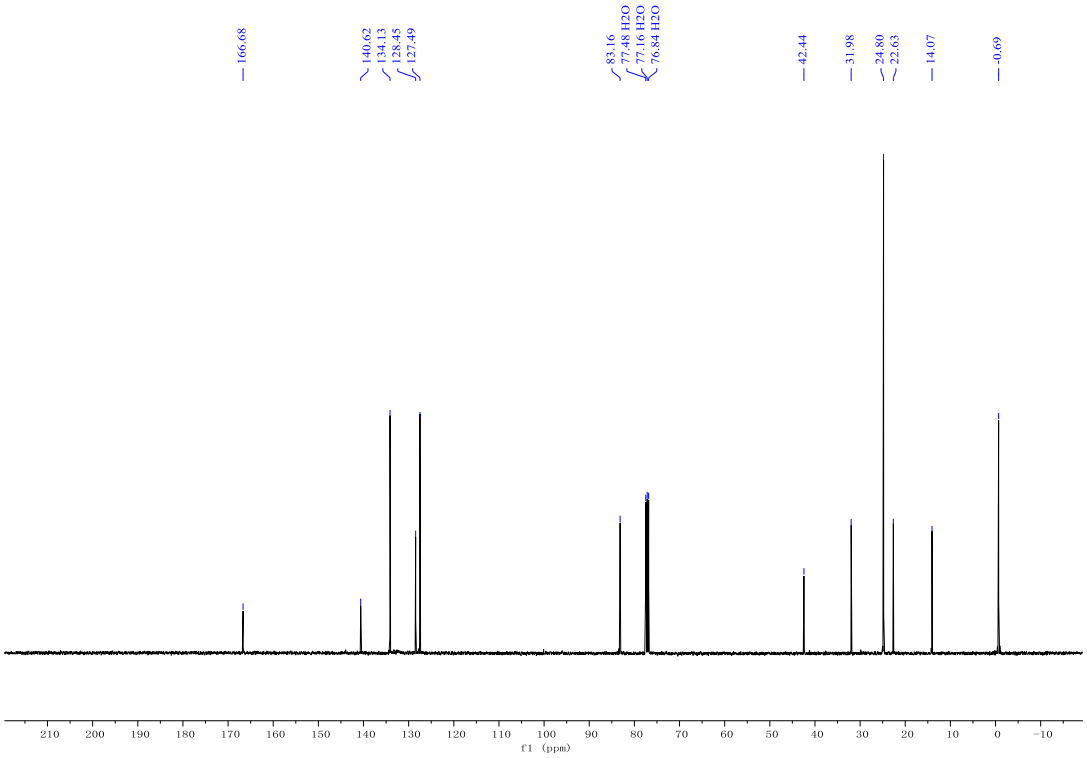
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.33 – 7.27 (m, 3H), 6.19 (t, *J* = 1.4 Hz, 1H), 2.23 (ddd, *J* = 9.3, 6.2, 1.4 Hz, 2H), 1.39 – 1.30 (m, 2H), 1.28 – 1.19 (m, 2H), 1.07 (s, 12H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.45 (s, 6H).

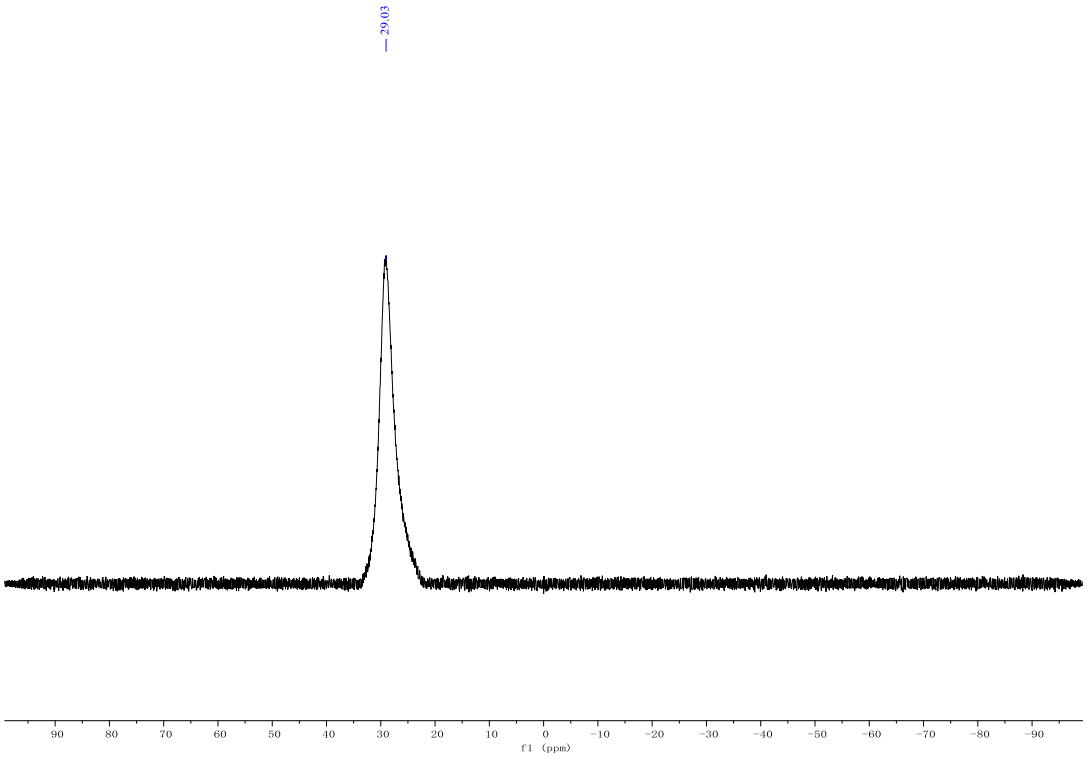
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.68, 140.62, 134.13, 128.45, 127.49, 83.16, 42.44, 31.98, 24.80, 22.63, 14.07, -0.69.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.03.

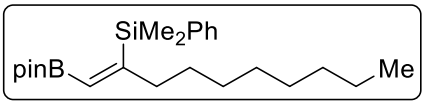
HRMS (ESI) m/z calculated for $C_{20}H_{33}BO_2SiNa$ $[M+Na]^+$: 367.2241, found: 367.2242.




166.68
140.62
134.13
128.45
127.49
83.16
77.48 H2O
77.16 H2O
76.84 H2O
42.44
31.98
24.80
22.63
14.07
-0.69
f1 (ppm)


29.03
f1 (ppm)

(*Z*)-dimethyl(phenyl)(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-1-en-2-yl)silane (4c).



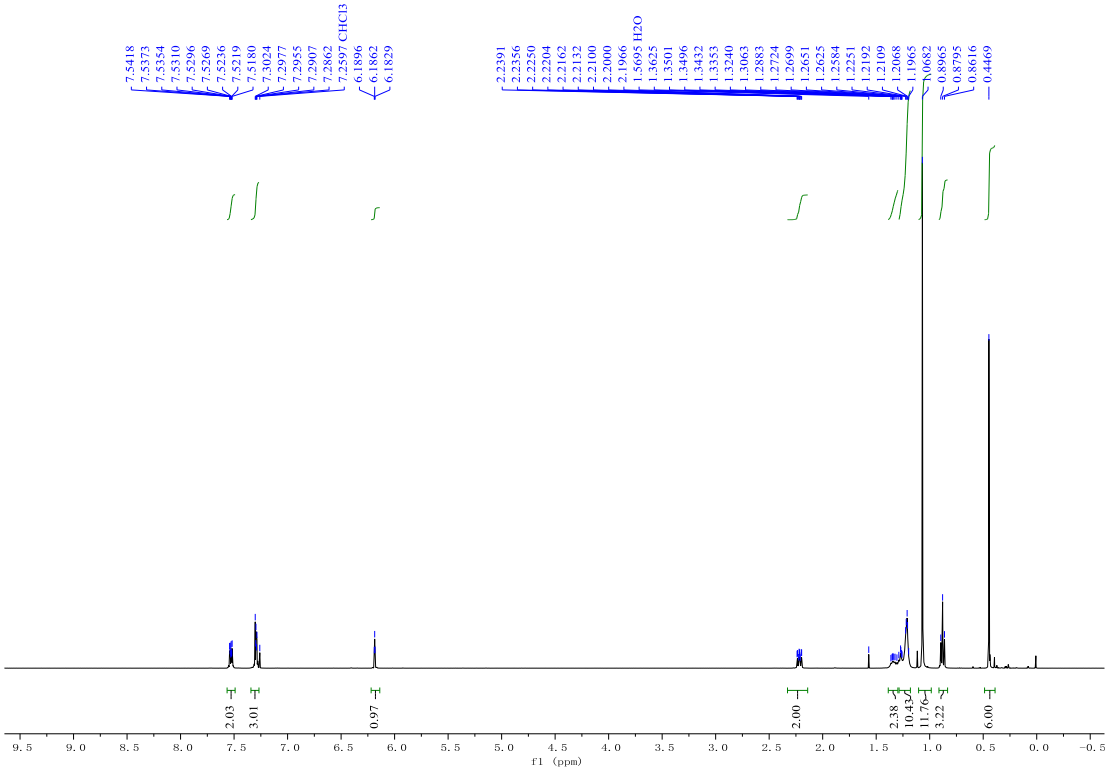
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 68% yield (54.5 mg). R_f = 0.54 (Petroleum ether:EtOAc= 98:2).

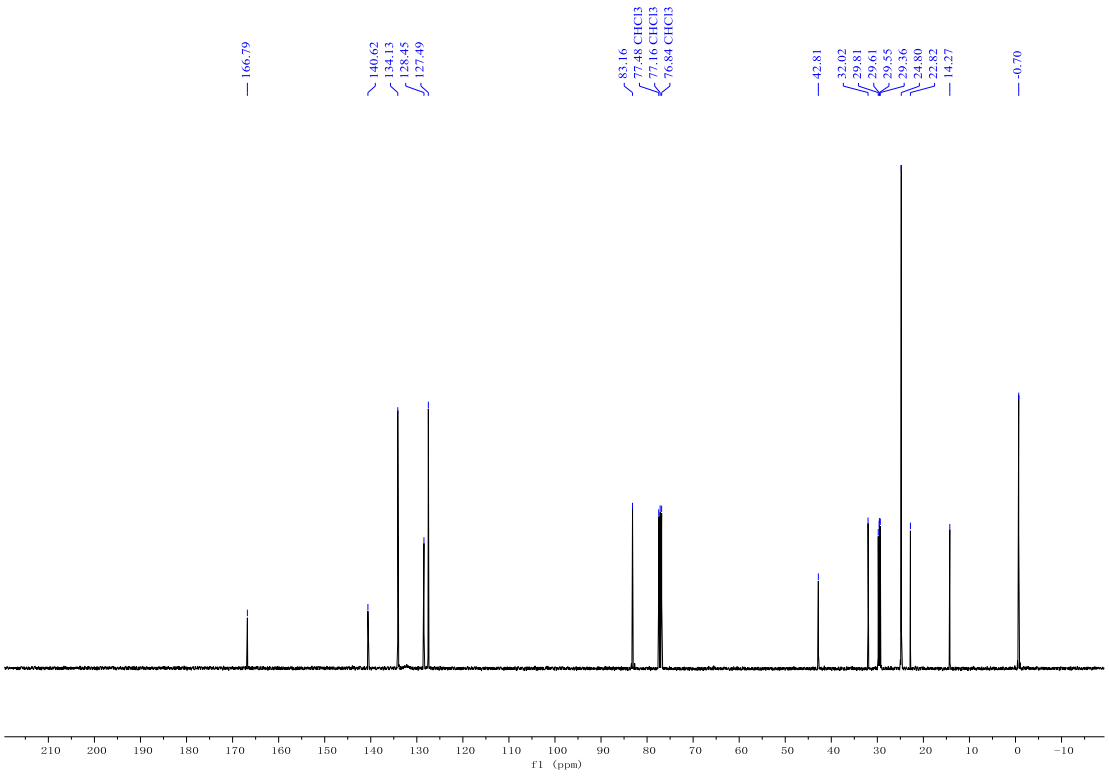
^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.49 (m, 2H), 7.32 – 7.27 (m, 3H), 6.19 (t, J = 1.4 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.40 – 1.29 (m, 2H), 1.30 – 1.17 (m, 10H), 1.07 (s, 12H), 0.88 (t, J = 7.0 Hz, 3H), 0.45 (s, 6H).

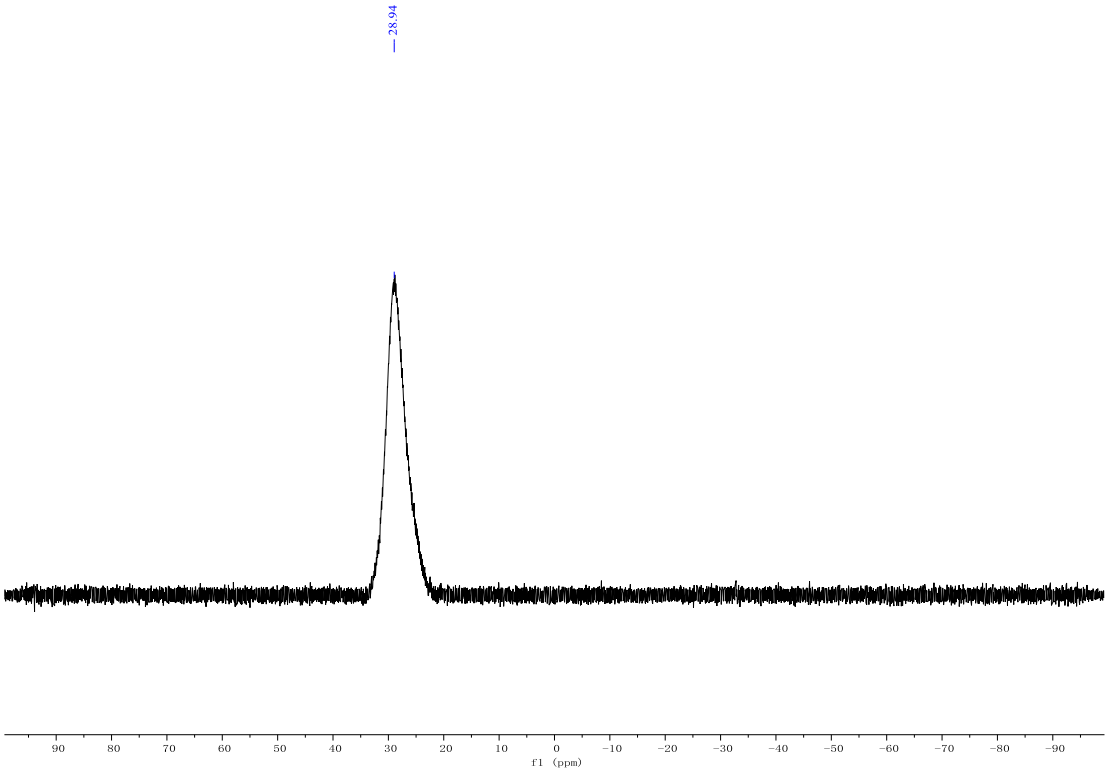
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.79, 140.62, 134.13, 128.45, 127.49, 83.16, 42.81, 32.02, 29.81, 29.61, 29.55, 29.36, 24.80, 22.82, 14.27, -0.70.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.94.

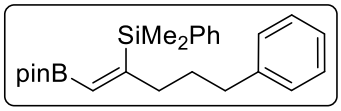
HRMS (ESI) m/z calculated for $C_{24}H_{41}BO_2SiNa$ $[M+Na]^+$: 423.2867, found: 423.2882.




166.79
140.62
134.13
128.45
127.49
83.16
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
42.81
32.02
29.81
29.61
29.55
29.36
24.80
22.82
14.27
-0.70
f1 (ppm)


28.94
f1 (ppm)

(*Z*)-dimethyl(phenyl)(5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl) silane (4e).



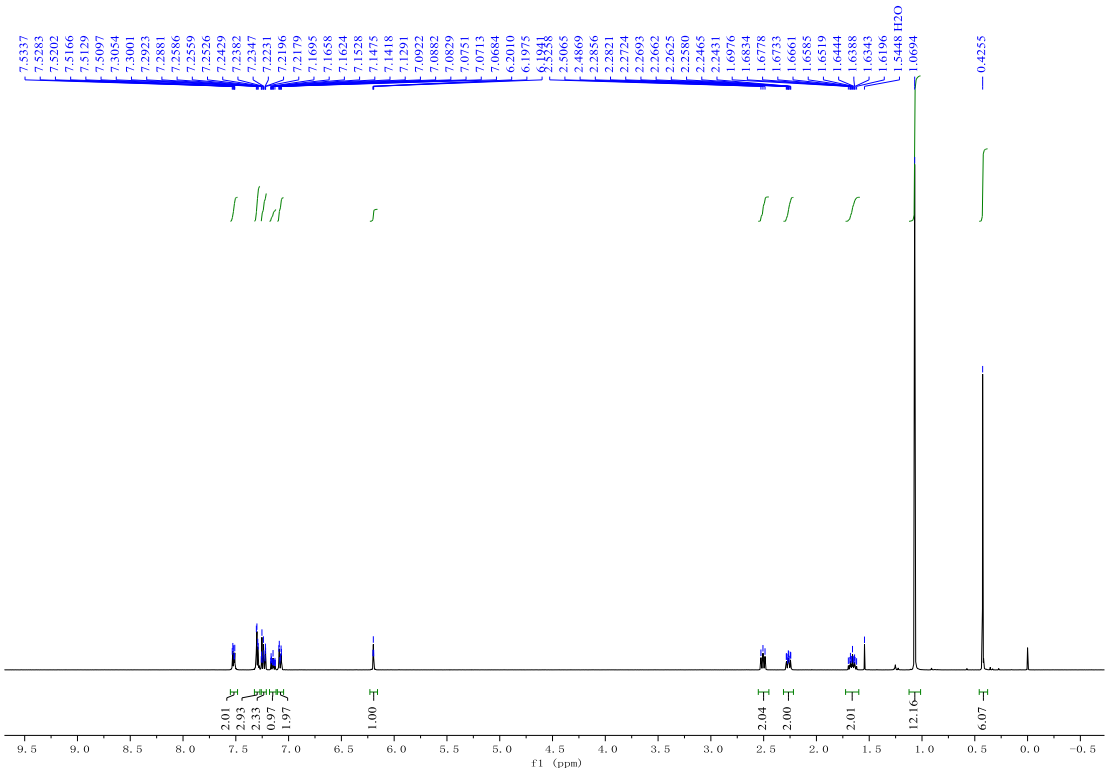
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 75% yield (61.0 mg). R_f = 0.42 (Petroleum ether:EtOAc= 98:2).

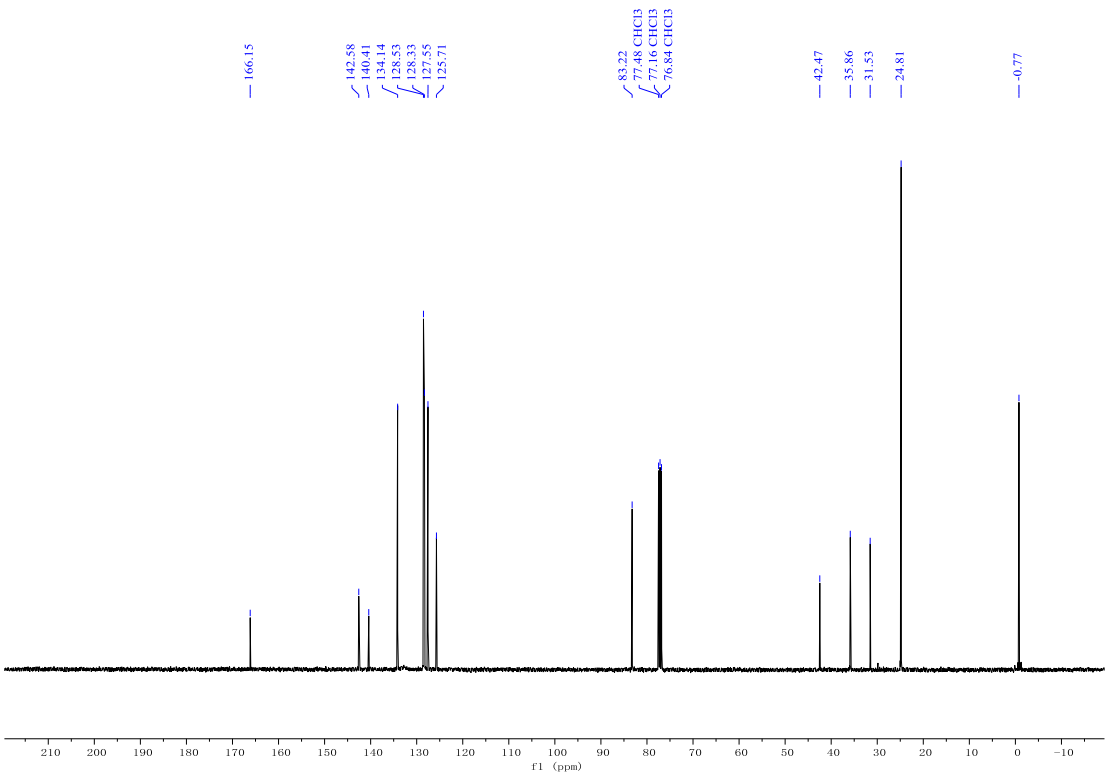
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.32 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 7.18 – 7.12 (m, 1H), 7.10 – 7.06 (m, 2H), 6.20 (t, *J* = 1.4 Hz, 1H), 2.53 – 2.47 (m, 2H), 2.26 (ddd, *J* = 9.3, 6.2, 1.4 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.07 (s, 12H), 0.43 (s, 6H).

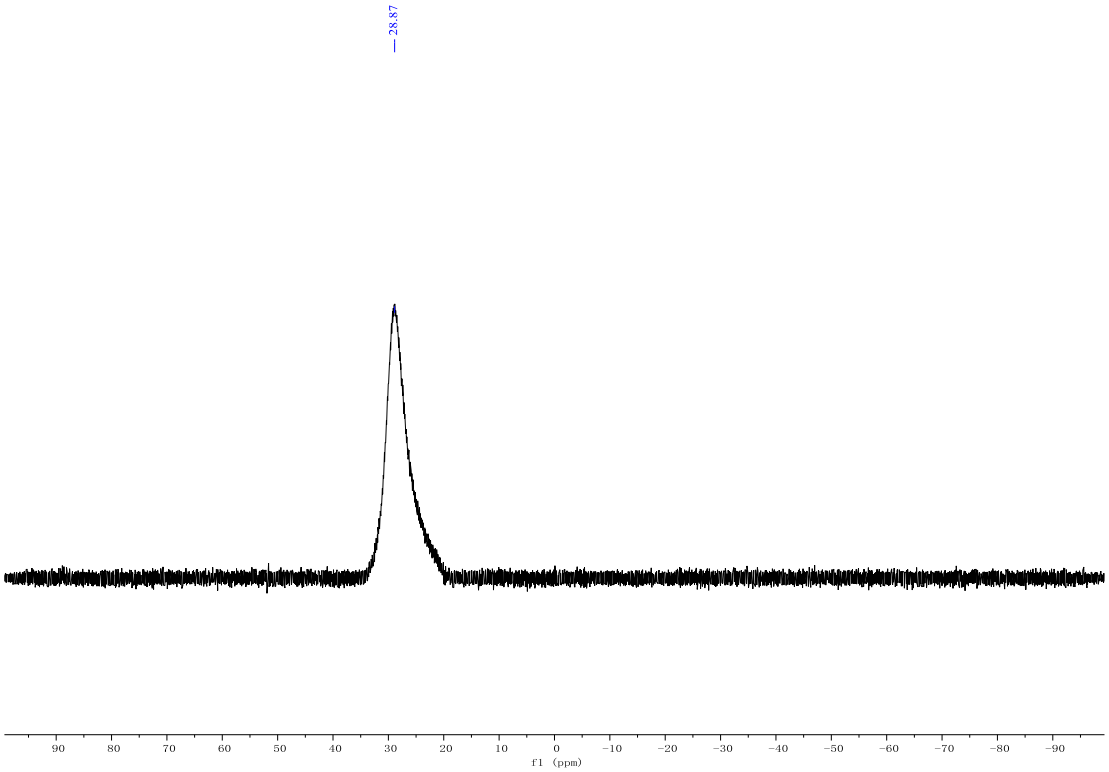
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.15, 142.58, 140.41, 134.14, 128.53, 128.33, 127.55, 125.71, 83.22, 42.47, 35.86, 31.53, 24.81, -0.77.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.87.

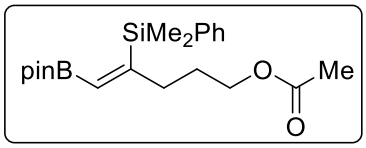
HRMS (ESI) m/z calculated for $C_{25}H_{35}BO_2SiNa$ $[M+Na]^+$: 429.2397, found: 429.2396.




166.15
142.58
140.41
134.14
128.53
128.33
127.55
125.71
83.22
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
42.47
35.86
31.53
24.81
-0.77
f1 (ppm)


28.87
f1 (ppm)

(*Z*)-4-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl acetate (4f).



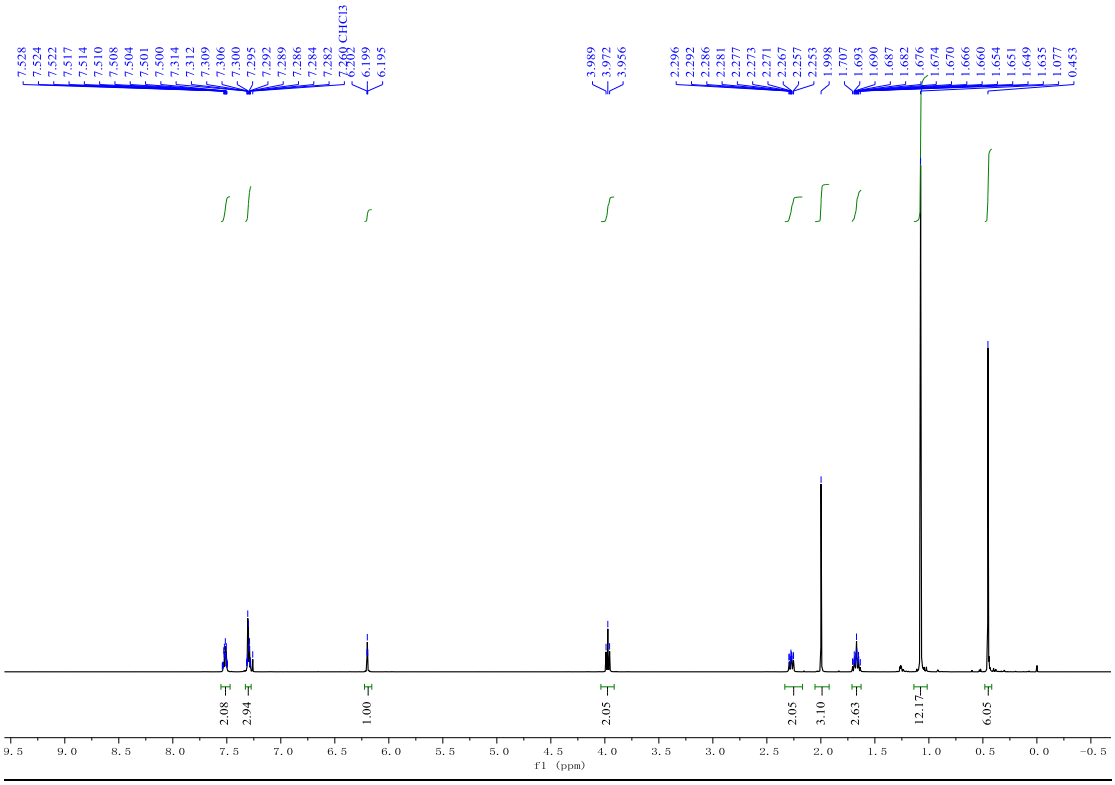
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 54% yield (42.2 mg). R_f = 0.13 (Petroleum ether:EtOAc= 98:2).

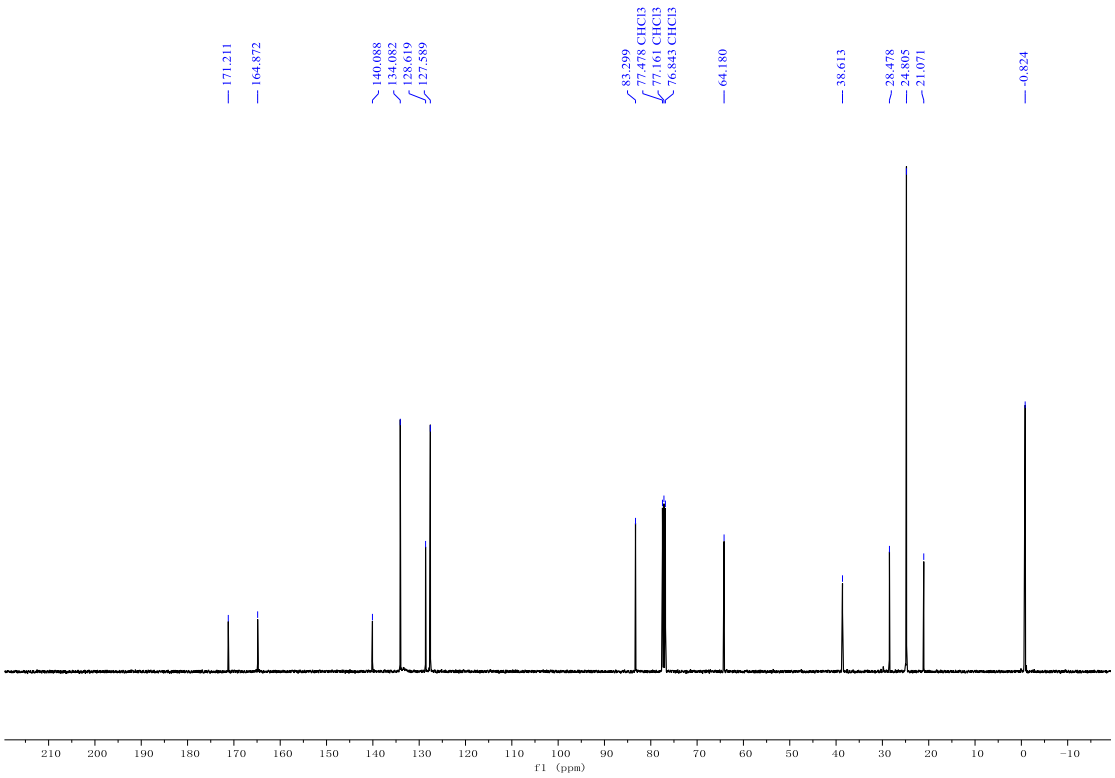
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.46 (m, 2H), 7.34 – 7.25 (m, 3H), 6.20 (t, *J* = 1.4 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 2.33 – 2.20 (m, 2H), 2.00 (s, 3H), 1.74 – 1.59 (m, 2H), 1.08 (s, 12H), 0.45 (s, 6H).

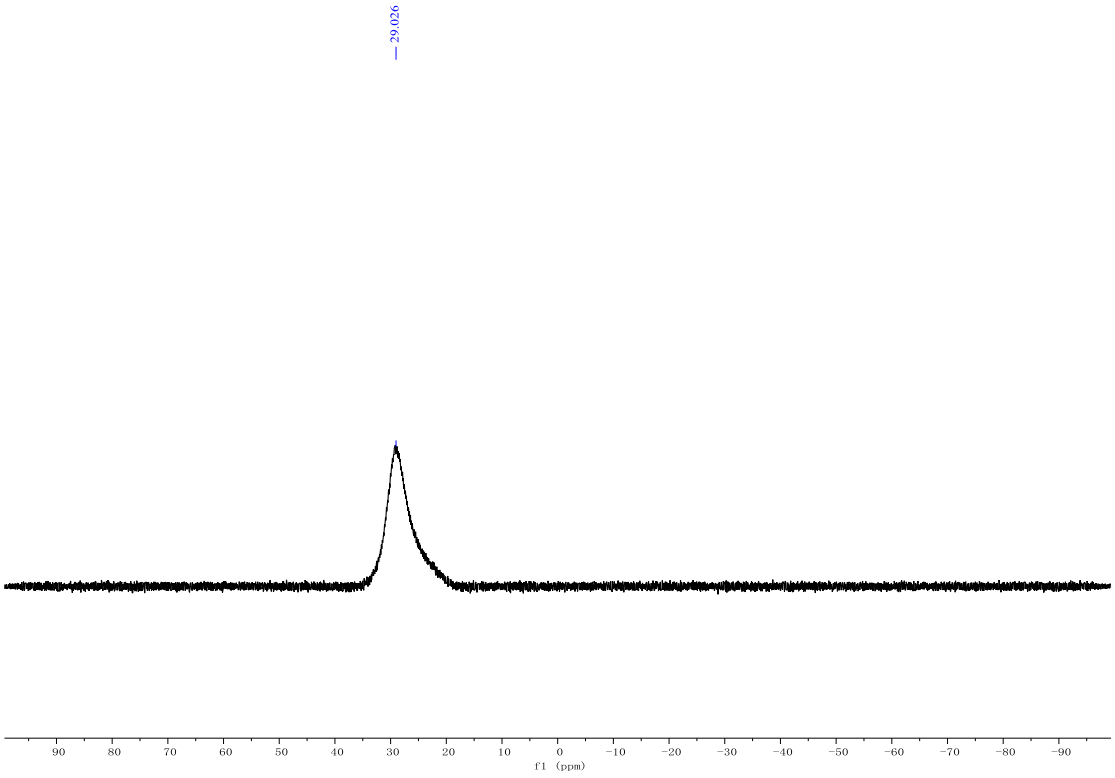
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.21, 164.87, 140.09, 134.08, 128.62, 127.59, 83.30, 64.18, 38.61, 28.48, 24.81, 21.07, -0.82.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.03.

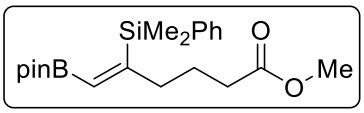
HRMS (ESI) m/z calculated for $C_{21}H_{33}BO_4SiNa$ $[M+Na]^+$: 411.2139, found: 411.2138.




171.211
164.872
140.088
134.082
128.619
127.589
83.299
77.478 CHCl3
77.161 CHCl3
76.843 CHCl3
64.180
38.613
28.478
24.805
21.071
0.824
f1 (ppm)


29.026
f1 (ppm)

methyl (*Z*)-5-(dimethyl(phenyl)silyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (4g).



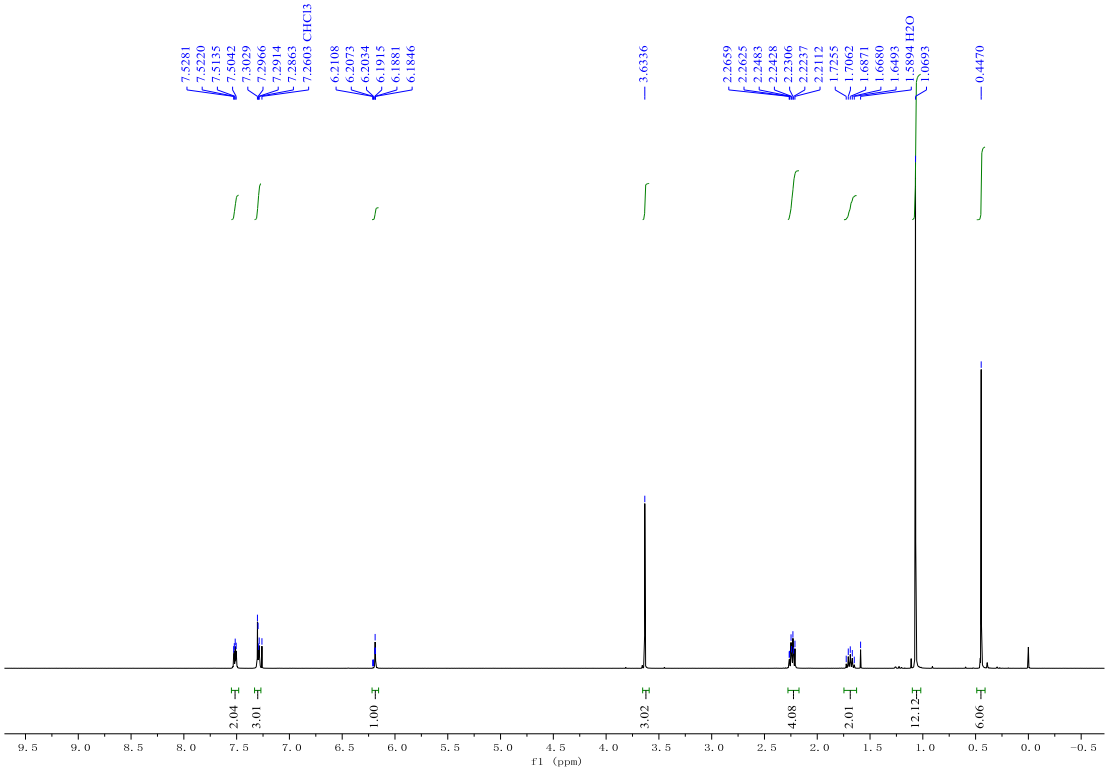
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 62% yield (48.1 mg). R_f = 0.32 (Petroleum ether:EtOAc = 95:5).

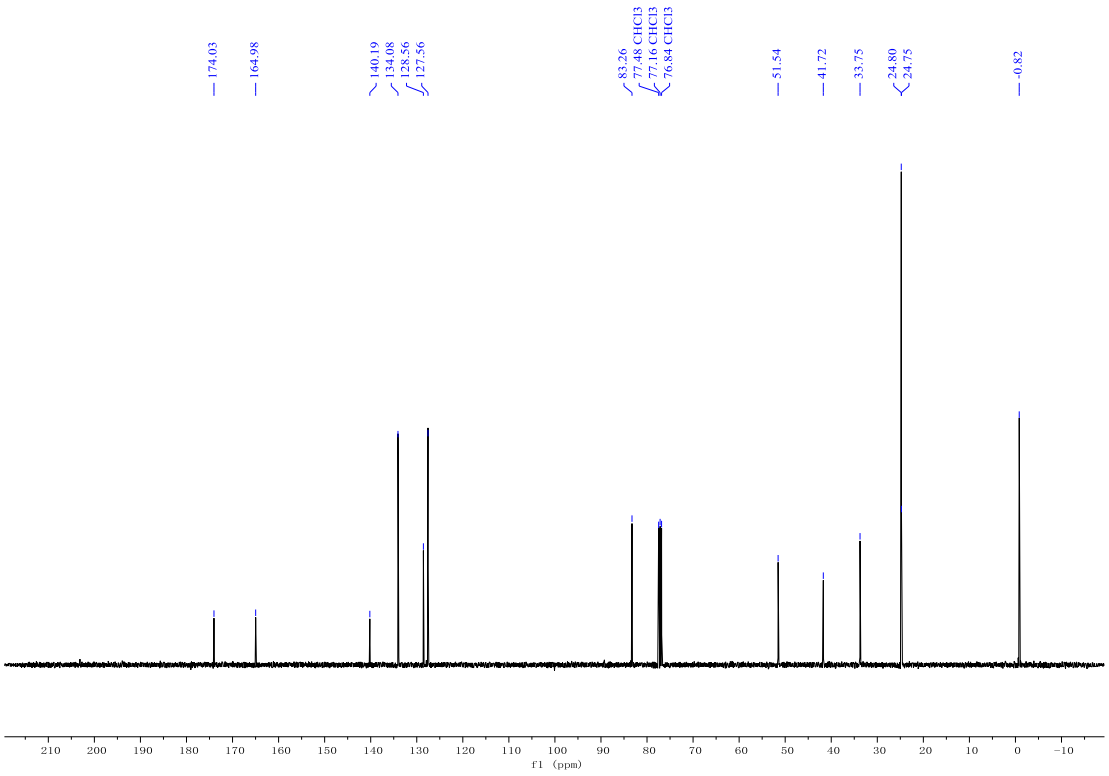
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 2H), 7.33 – 7.26 (m, 3H), 6.19 (t, *J* = 1.4 Hz, 1H), 3.63 (s, 3H), 2.29 – 2.18 (m, 4H), 1.75 – 1.62 (m, 2H), 1.07 (s, 12H), 0.45 (s, 6H).

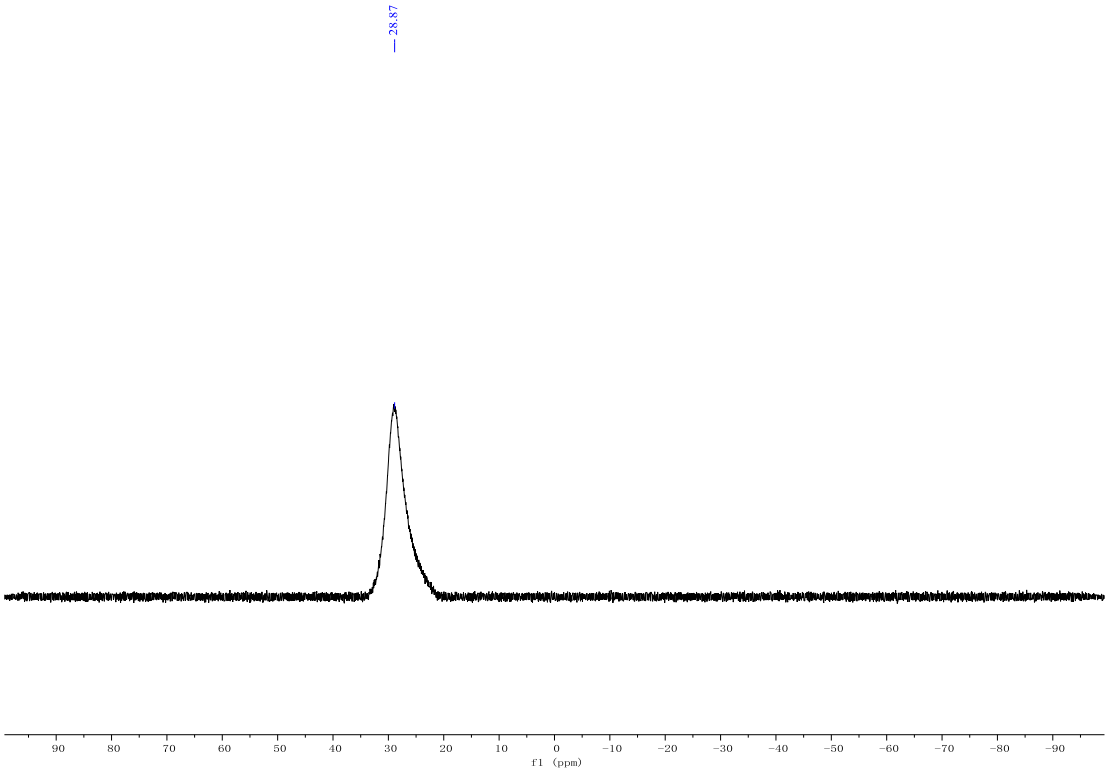
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.03, 164.98, 140.19, 134.08, 128.56, 127.56, 83.26, 51.54, 41.72, 33.75, 24.80, 24.75, -0.82.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.87.

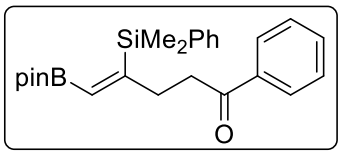
HRMS (ESI) m/z calculated for $C_{21}H_{33}BO_4SiNa$ $[M+Na]^+$: 411.2139, found: 411.2131.




174.03
164.98
140.19
134.08
128.56
127.56
83.26
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
51.54
41.72
33.75
24.80
24.75
-0.82
f1 (ppm)


28.87
f1 (ppm)

(*Z*)-4-(dimethyl(phenyl)silyl)-1-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-one (4h).



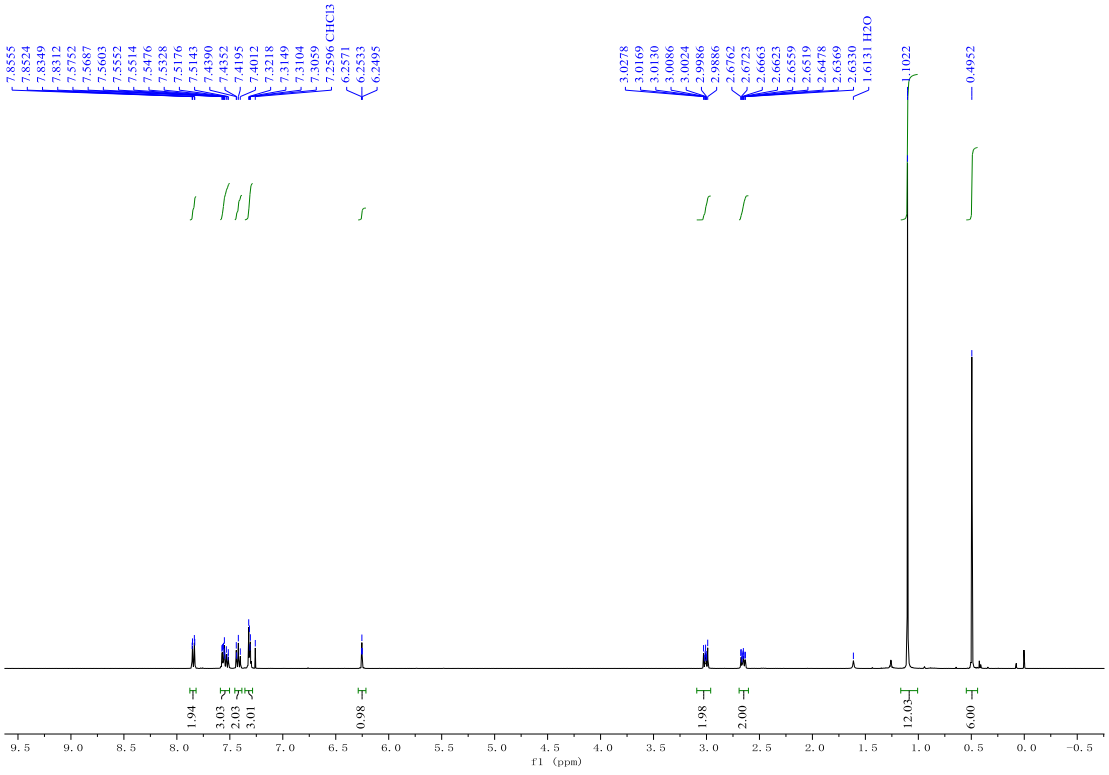
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 55% yield (46.2 mg). R_f = 0.24 (Petroleum ether:EtOAc = 98:2).

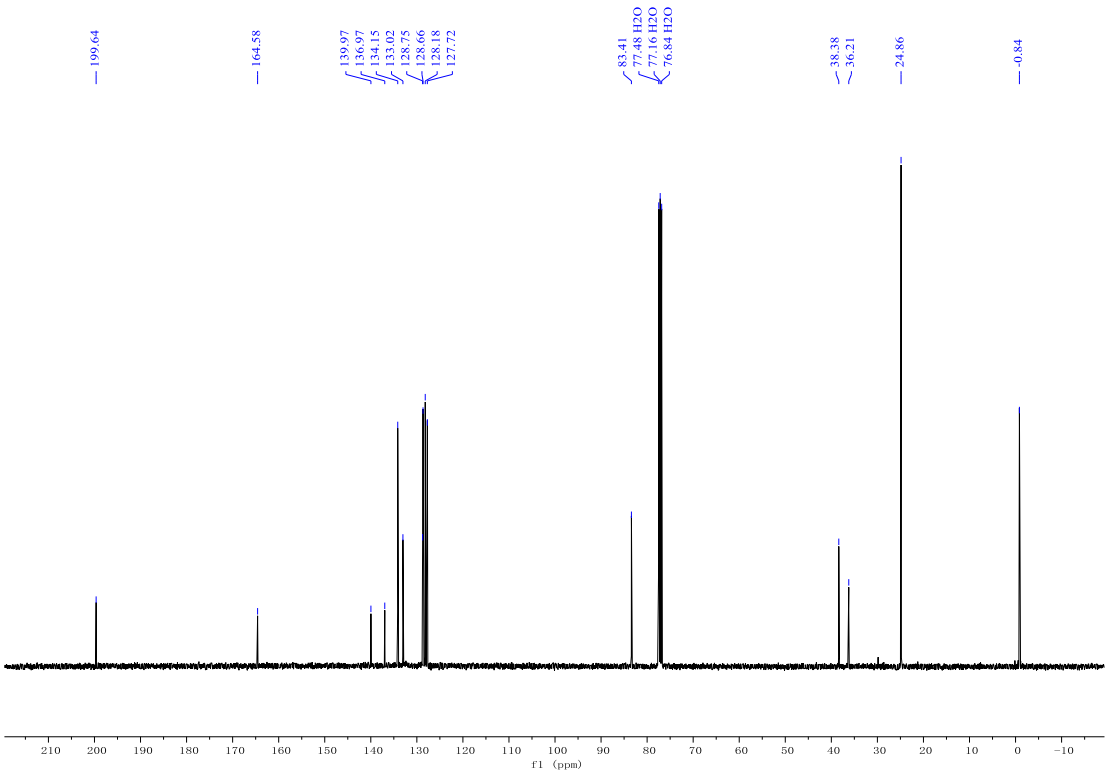
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 2H), 7.59 – 7.50 (m, 3H), 7.46 – 7.38 (m, 2H), 7.35 – 7.29 (m, 3H), 6.25 (t, *J* = 1.5 Hz, 1H), 3.07 – 2.94 (m, 2H), 2.69 – 2.62 (m, 2H)., 1.10 (s, 12H), 0.50 (s, 6H).

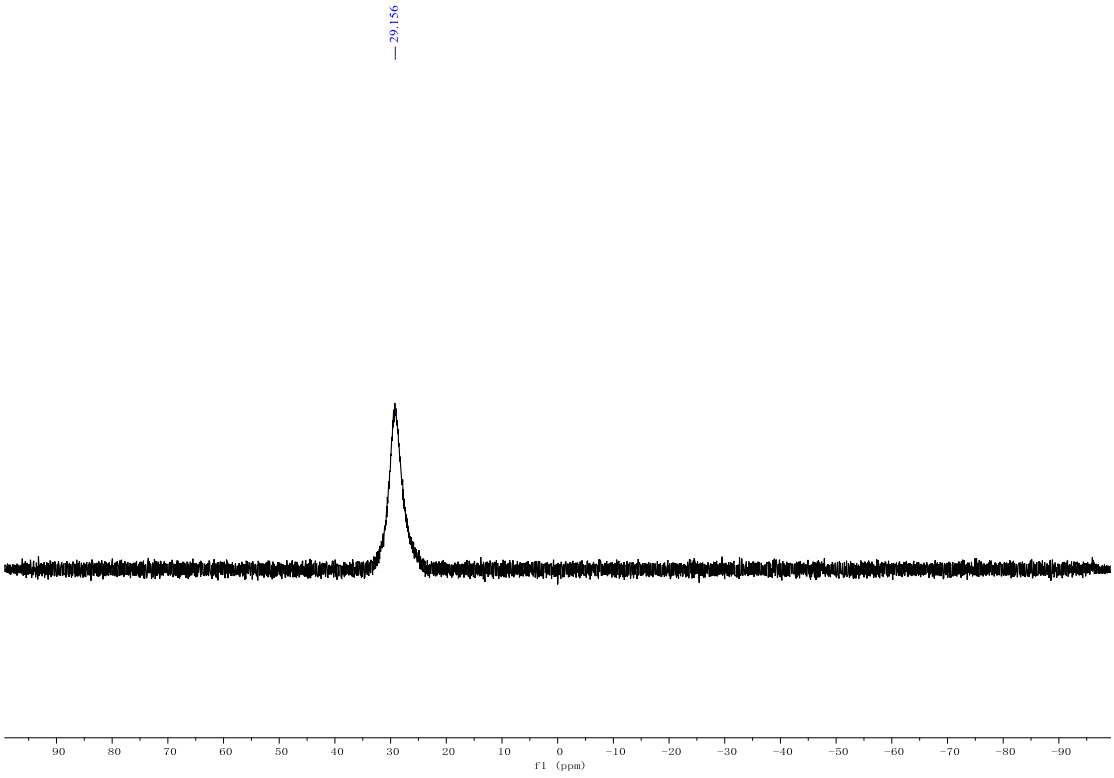
^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.64, 164.58, 139.97, 136.97, 134.15, 133.02, 128.75, 128.66, 128.18, 127.72, 83.41, 38.38, 36.21, 24.86, -0.84.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.81.

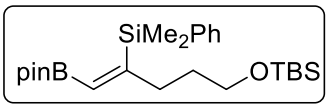
HRMS (ESI) m/z calculated for $C_{25}H_{33}BO_3SiNa$ $[M+Na]^+$: 443.2190, found: 443.2178.




199.64
164.58
139.97
136.97
134.15
133.02
128.75
128.66
128.18
127.72
83.41
77.48 H2O
77.16 H2O
76.84 H2O
38.38
36.21
24.86
0.84
f1 (ppm)


29.156
f1 (ppm)

(*Z*)-*tert*-butyl((4-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)dimethylsilane (4i).



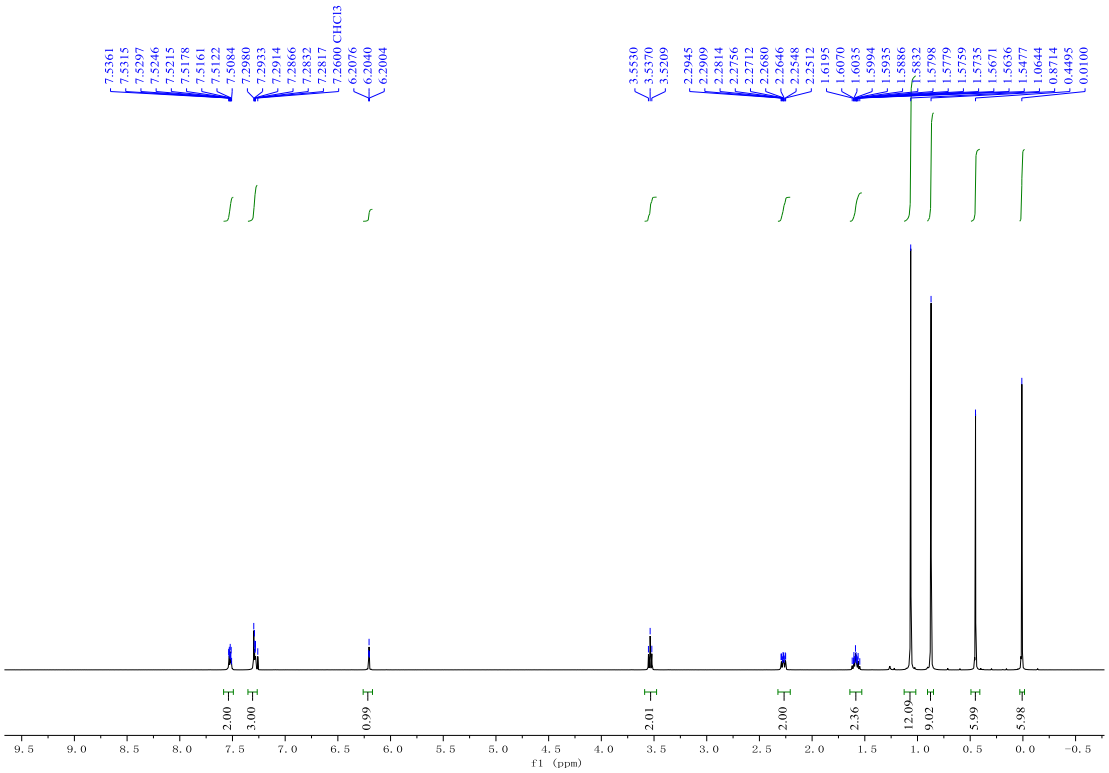
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 70% yield (64.5 mg). R_f = 0.40 (Petroleum ether:Et_2O= 98:2).

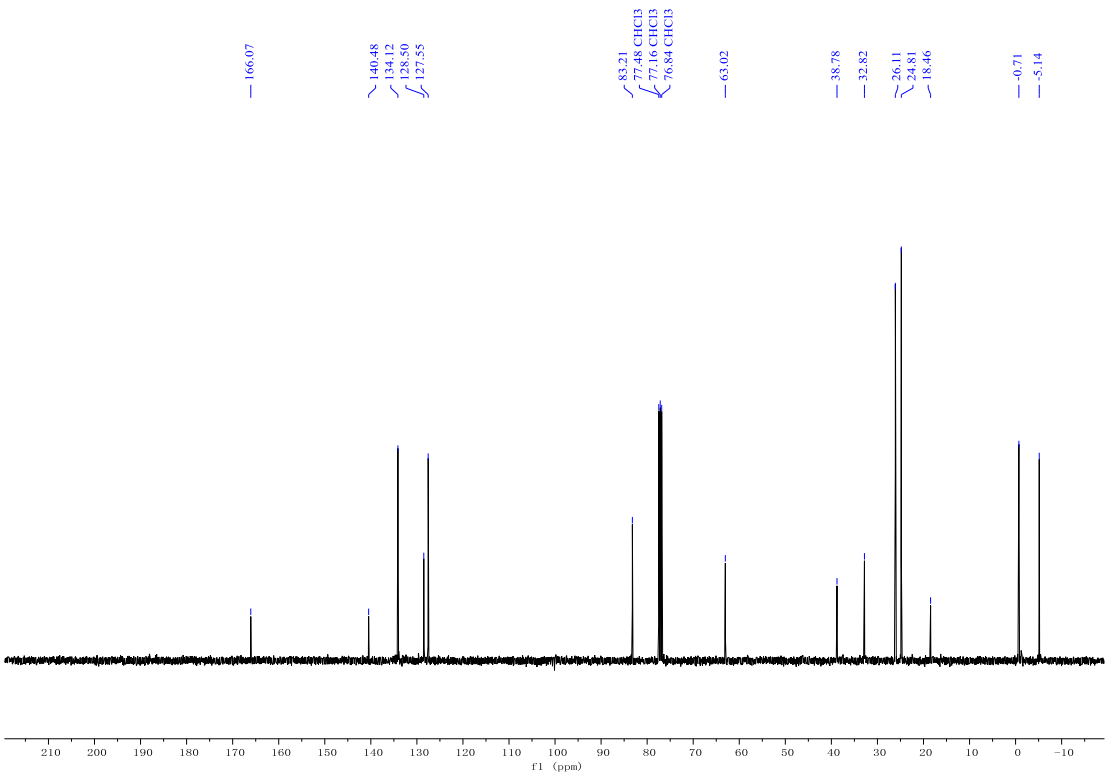
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H), 7.33 – 7.27 (m, 3H), 6.20 (t, *J* = 1.4 Hz, 1H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.32 – 2.21 (m, 2H), 1.65 – 1.52 (m, 2H), 1.06 (s, 12H), 0.87 (s, 9H), 0.45 (s, 6H), 0.01 (s, 6H).

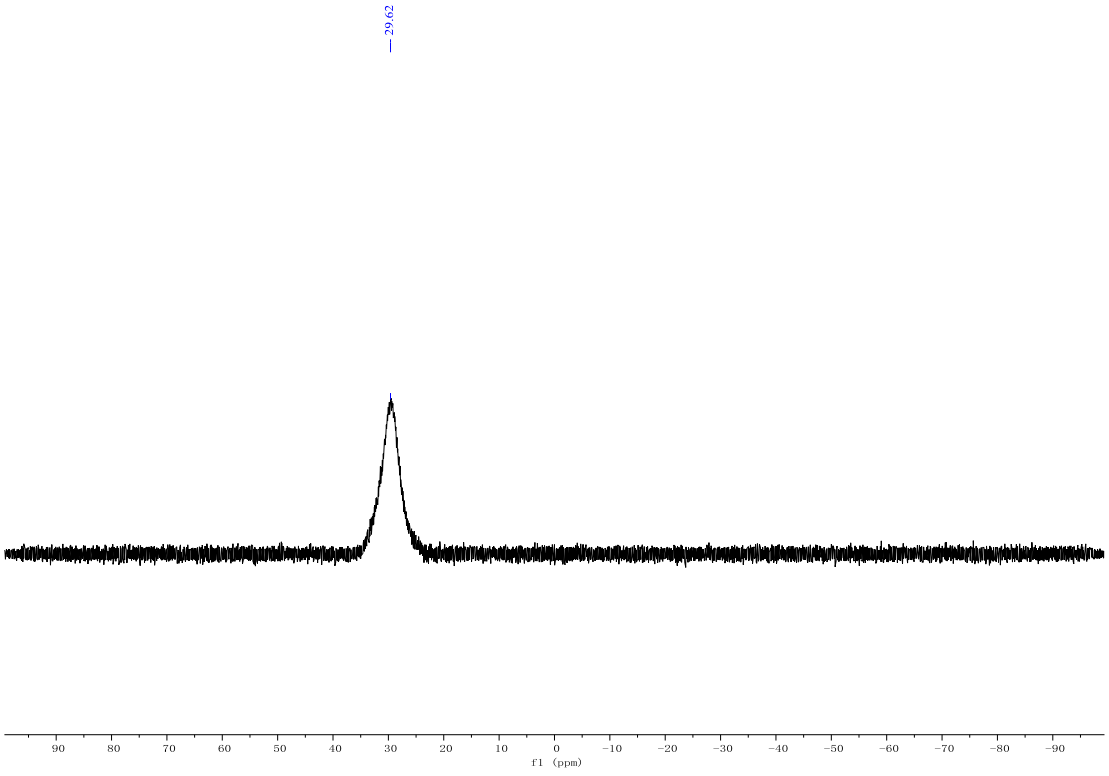
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.07, 140.48, 134.12, 128.50, 127.55, 83.21, 63.02, 38.78, 32.82, 26.11, 24.81, 18.46, -0.71, -5.14.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.62.

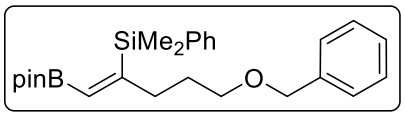
HRMS (ESI) m/z calculated for $C_{25}H_{45}BO_3Si_2Na$ $[M+Na]^+$: 483.2898, found: 483.2902.




166.07
140.48
134.12
128.50
127.55
83.21
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
63.02
38.78
32.82
26.11
24.81
18.46
-0.71
-5.14
f1 (ppm)


29.62
f1 (ppm)

(*Z*)-(5-(benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)dimethyl (phenyl)silane (4j).



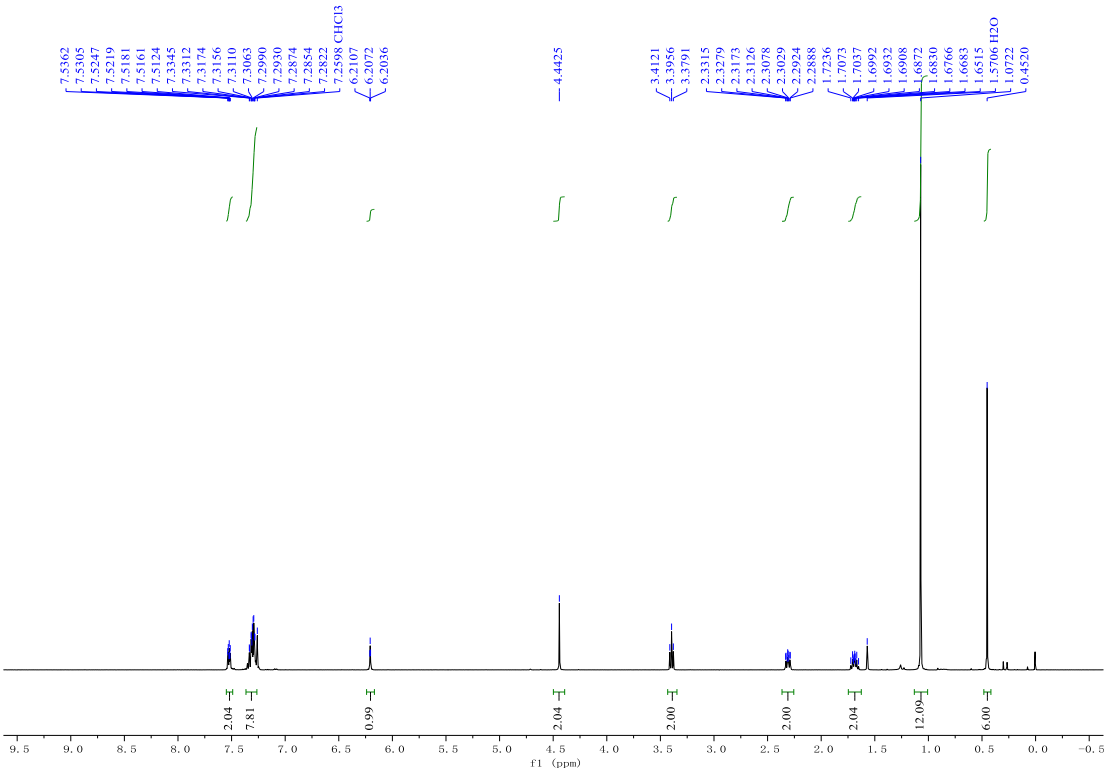
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 54% yield (47.1 mg). R_f = 0.38 (Petroleum ether:EtOAc = 95:5).

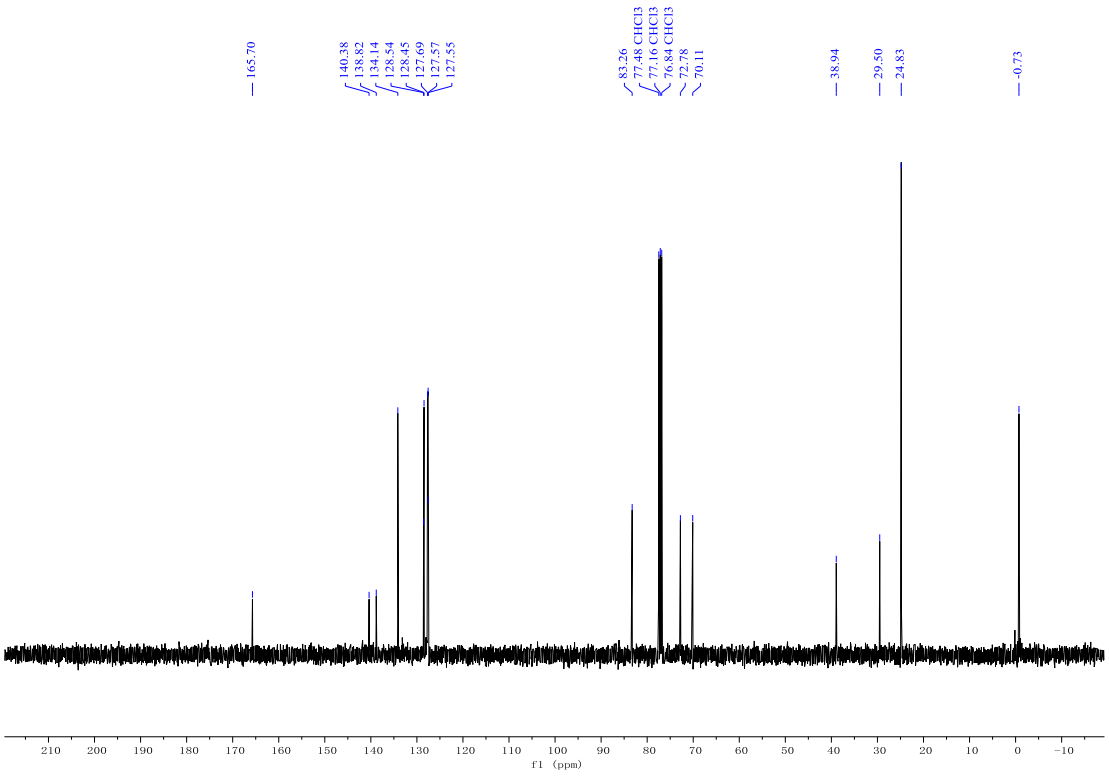
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.50 (m, 2H), 7.36 – 7.26 (m, 8H), 6.21 (t, J = 1.4 Hz, 1H), 4.44 (s, 2H), 3.40 (t, J = 6.6 Hz, 2H), 2.31 (ddd, J = 9.5, 5.7, 1.4 Hz, 2H), 1.81 – 1.62 (m, 2H), 1.07 (s, 12H), 0.45 (s, 6H).

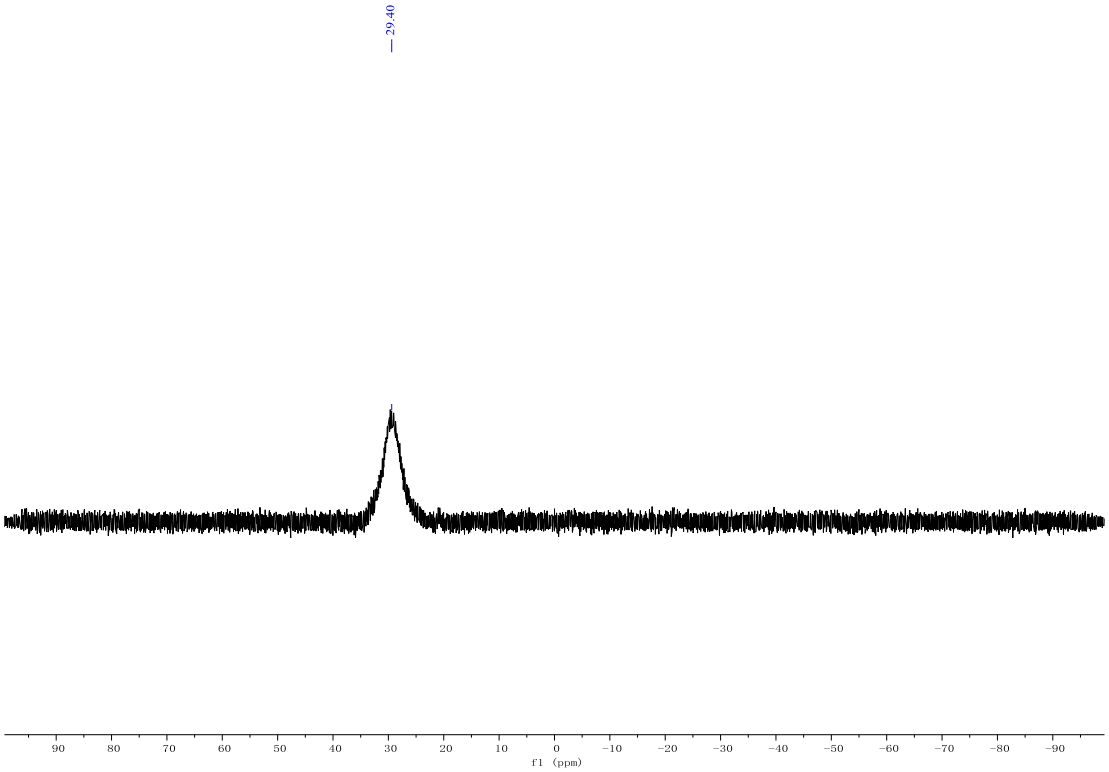
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.70, 140.38, 138.82, 134.14, 128.54, 128.45, 127.69, 127.57, 127.55, 83.26, 72.78, 70.11, 38.94, 29.50, 24.83, -0.73.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.40.

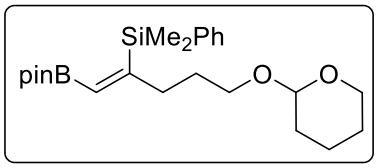
HRMS (ESI) m/z calculated for $C_{26}H_{37}BO_3SiNa$ $[M+Na]^+$: 459.2503, found: 459.2503.




165.70
140.38
138.82
134.14
128.54
128.45
127.69
127.57
127.55
83.26
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
72.78
70.11
38.94
29.50
24.83
-0.73
f1 (ppm)


29.40
f1 (ppm)

(*Z*)-dimethyl(phenyl)(5-((tetrahydro-*2H*-pyran-2-yl)oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)silane (4k).



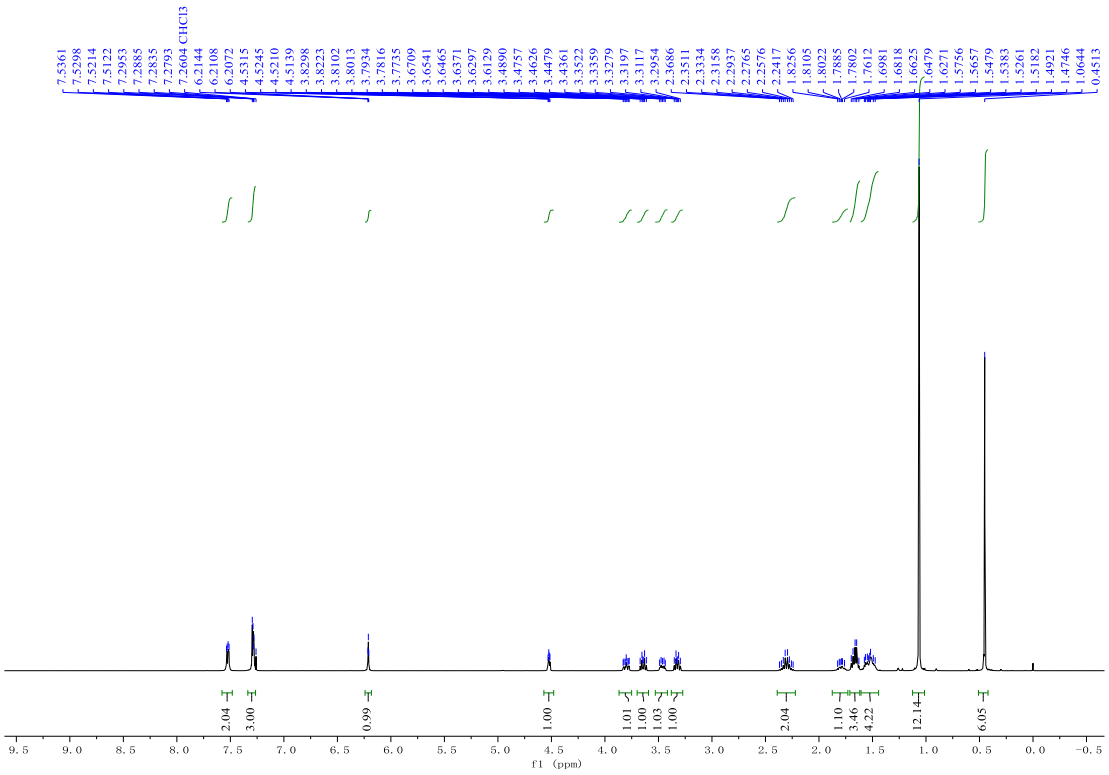
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 72% yield (62.0 mg). R_f = 0.32 (Petroleum ether:EtOAc = 95:5).

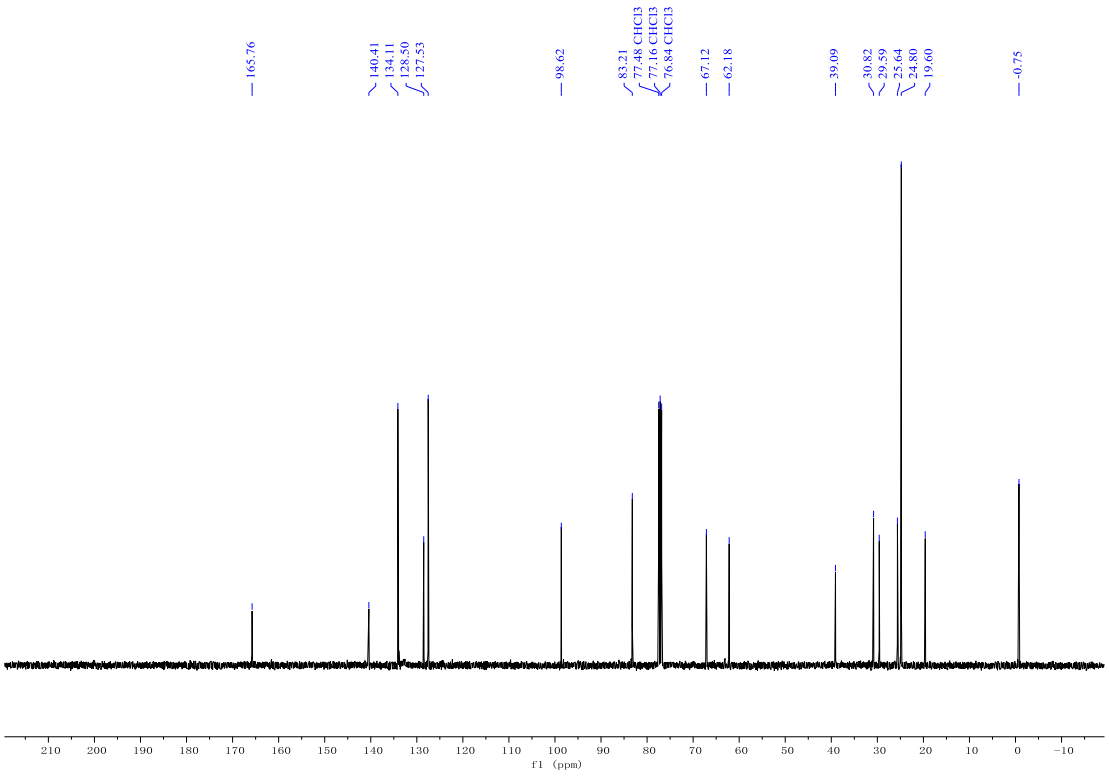
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 2H), 7.32 – 7.25 (m, 3H), 6.21 (t, *J* = 1.4 Hz, 1H), 4.52 (dd, *J* = 4.2, 2.8 Hz, 1H), 3.80 (ddd, *J* = 11.1, 7.9, 3.1 Hz, 1H), 3.64 (dt, *J* = 9.7, 6.7 Hz, 1H), 3.46 (dt, *J* = 10.6, 5.0 Hz, 1H), 3.32 (dt, *J* = 9.7, 6.5 Hz, 1H), 2.39 – 2.21 (m, 2H), 1.86 – 1.73 (m, 1H), 1.72 – 1.60 (m, 3H), 1.60 – 1.44 (m, 4H), 1.06 (s, 12H), 0.45 (s, 6H).

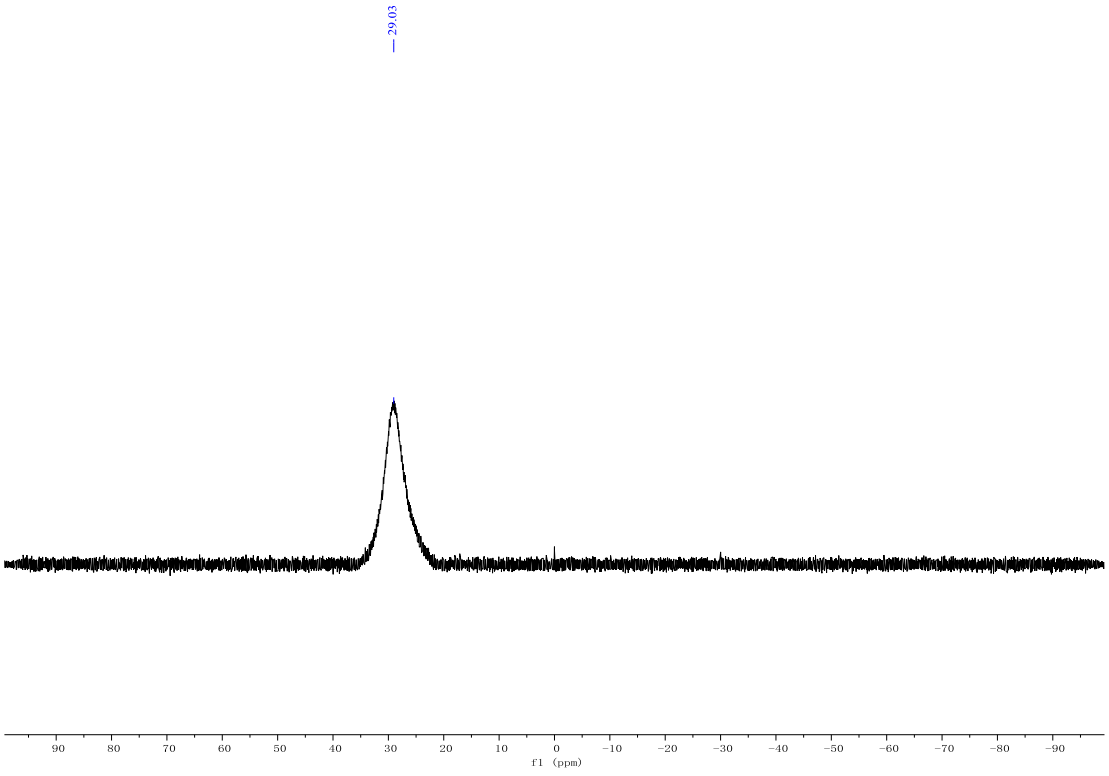
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.76, 140.41, 134.11, 128.50, 127.53, 98.62, 83.21, 67.12, 62.18, 39.09, 30.82, 29.59, 25.64, 24.80, 19.60, -0.75.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.03.

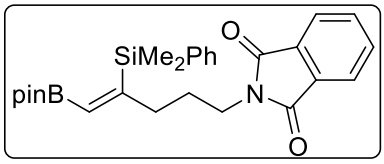
HRMS (ESI) m/z calculated for $C_{24}H_{39}BO_4SiNa$ $[M+Na]^+$: 453.2608, found: 453.2603.




165.76
140.41
134.11
128.50
127.53
98.62
83.21
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
67.12
62.18
39.09
30.82
29.59
25.64
24.80
19.60
-0.75
f1 (ppm)


29.03
f1 (ppm)

(Z)-2-(4-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)isoindoline-1,3-dione (4m).



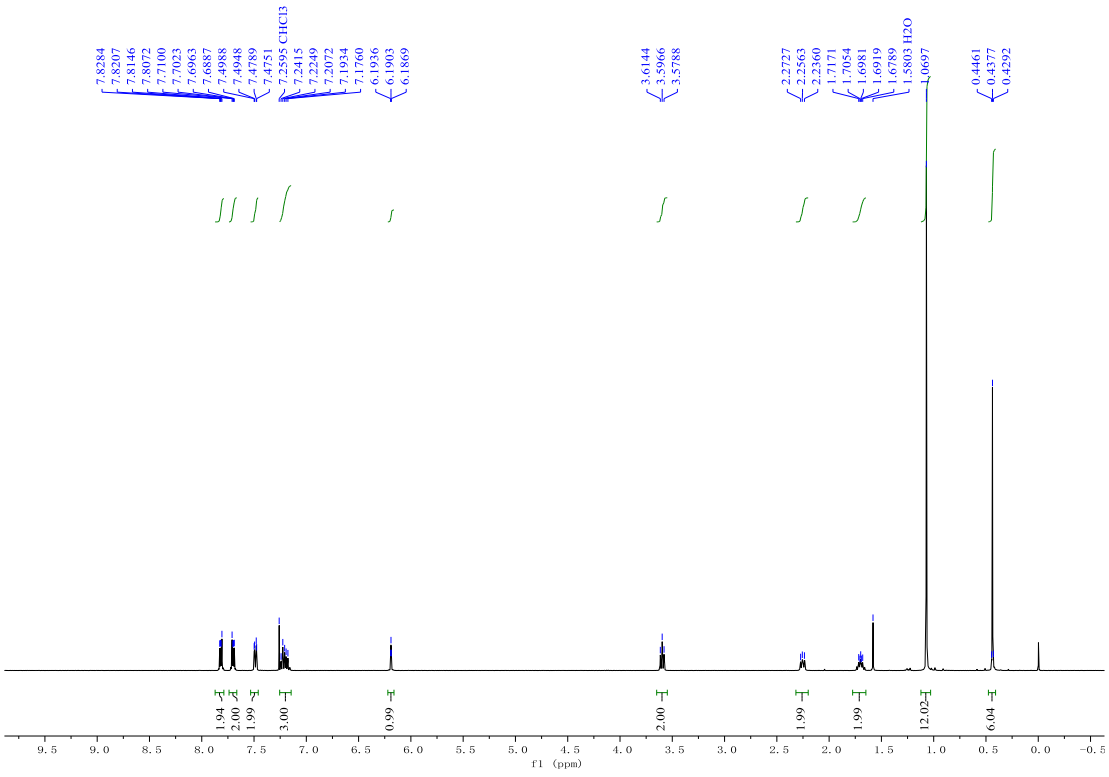
This compound was prepared by the general procedure B described above and was obtained as white solid in 50% yield (47.5 mg). R_f = 0.21 (Petroleum ether:Et_2O = 75:25).

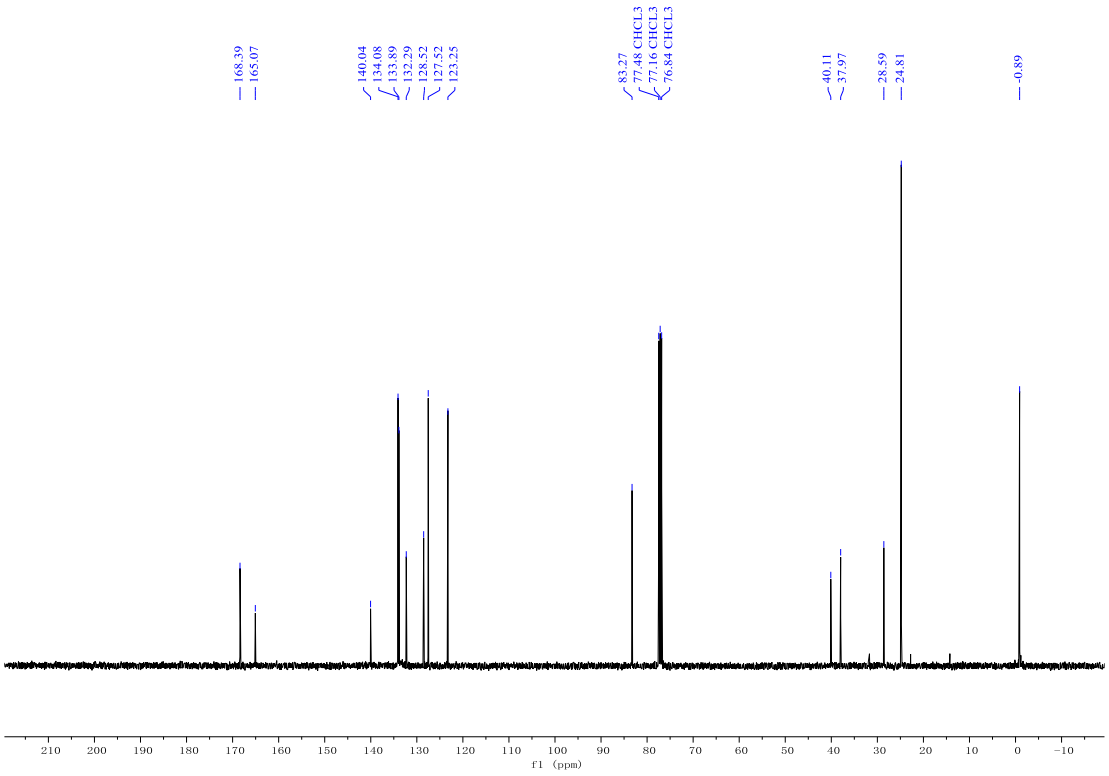
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (dd, J = 5.4, 3.0 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.27 – 7.14 (m, 3H), 6.19 (s, 1H), 3.60 (t, J = 7.1 Hz, 2H), 2.32 – 2.19 (m, 2H), 1.75 – 1.65 (m, 2H), 1.07 (s, 12H), 0.44 (s, 6H).

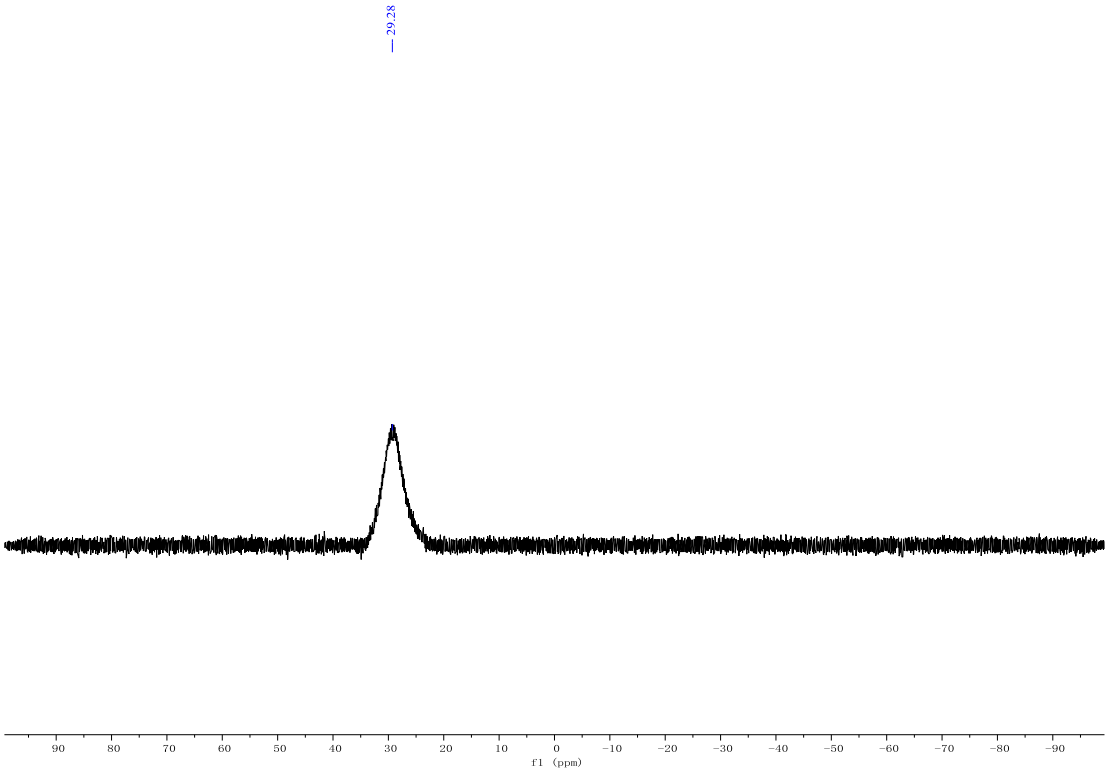
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39, 165.07, 140.04, 134.08, 133.89, 132.29, 128.52, 127.52, 123.25, 83.27, 40.11, 37.97, 28.59, 24.81, -0.89.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.28.

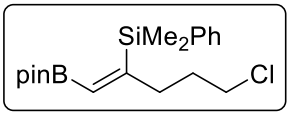
HRMS (ESI) m/z calculated for $C_{27}H_{34}BNO_4SiNa$ $[M+Na]^+$: 498.2248, found: 498.2245.




168.39
165.07
140.04
134.08
133.89
132.29
128.52
127.52
123.25
83.27
77.48 CHCL3
77.16 CHCL3
76.84 CHCL3
40.11
37.97
28.59
24.81
-0.89
f1 (ppm)


29.28
f1 (ppm)

(*Z*)-(5-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)dimethyl(phenyl) silane (4n).



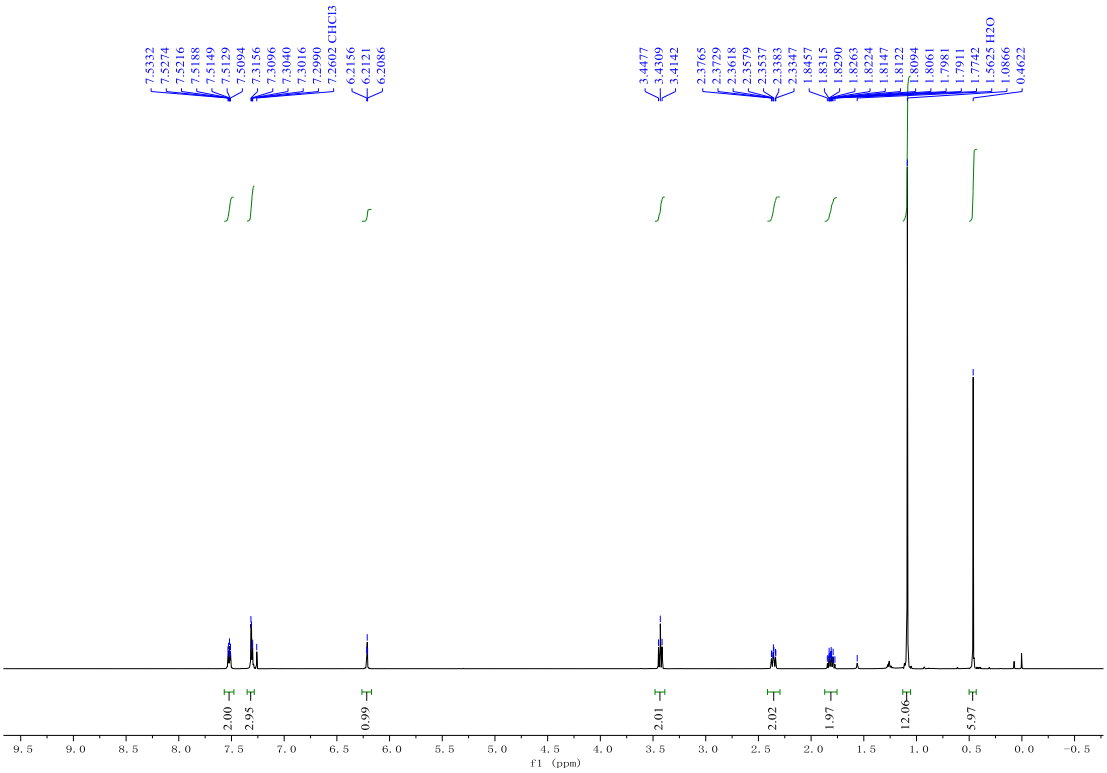
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 55% yield (40.1 mg). R_f = 0.33 (Petroleum ether:EtOAc = 98:2).

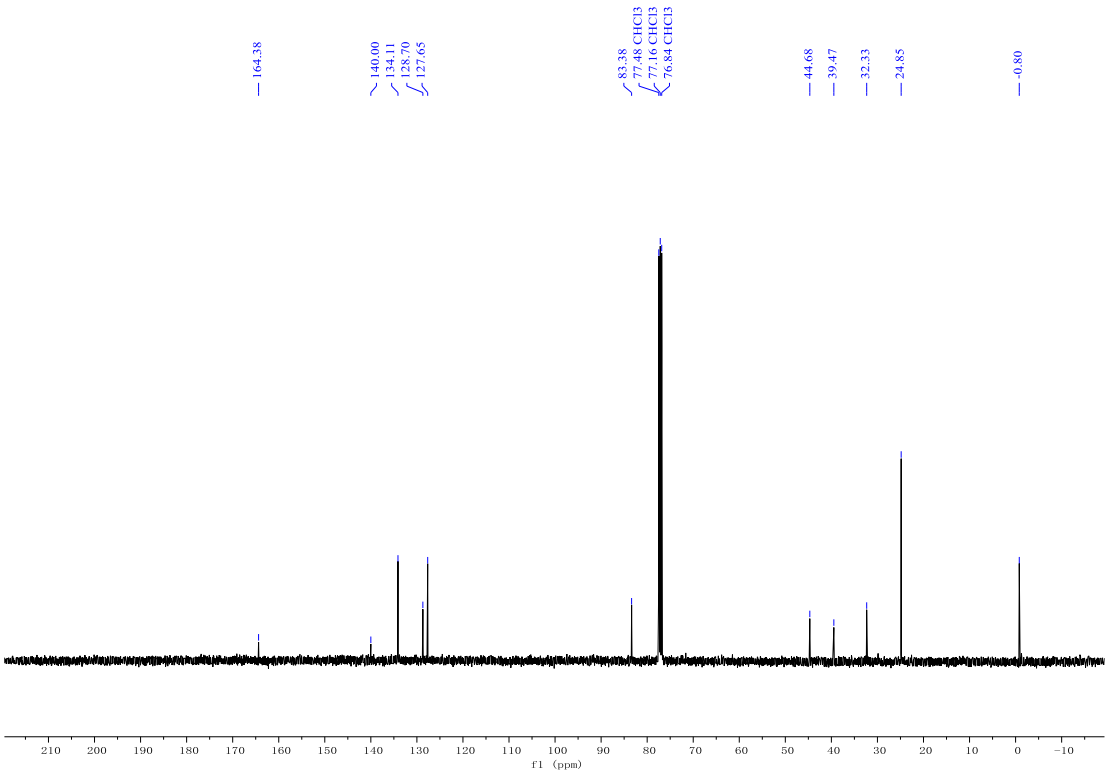
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.34 – 7.28 (m, 3H), 6.21 (t, *J* = 1.4 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.36 (td, *J* = 7.5, 1.4 Hz, 2H), 1.88 – 1.75 (m, 2H), 1.09 (s, 12H), 0.46 (s, 6H).

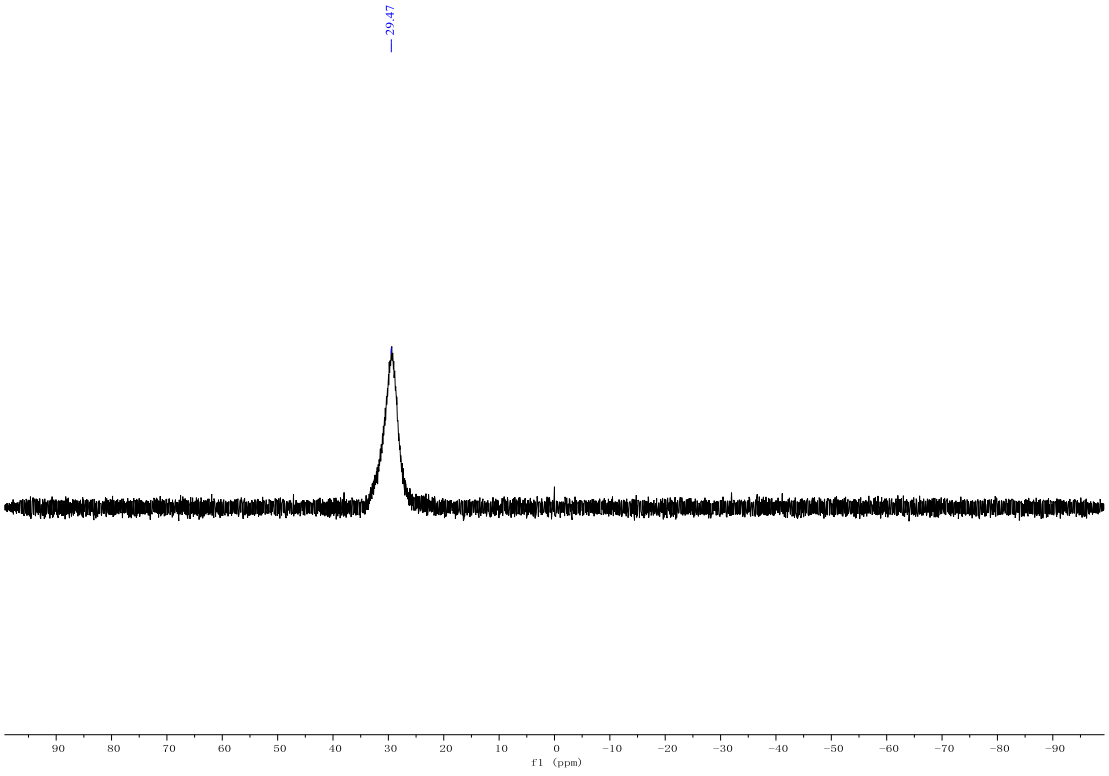
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.38, 140.00, 134.11, 128.70, 127.65, 83.38, 44.68, 39.47, 32.33, 24.85, -0.80.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.47.

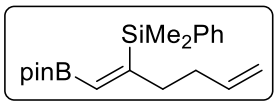
HRMS (ESI) m/z calculated for $C_{19}H_{30}BClOSiNa$ $[M+Na]^+$: 387.1694, found: 387.1681.




164.38
140.00
134.11
128.70
127.65
83.38
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
44.68
39.47
32.33
24.85
-0.80
f1 (ppm)


29.47
f1 (ppm)

(*Z*)-dimethyl(phenyl)(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dien-2-yl) Silane (4p).



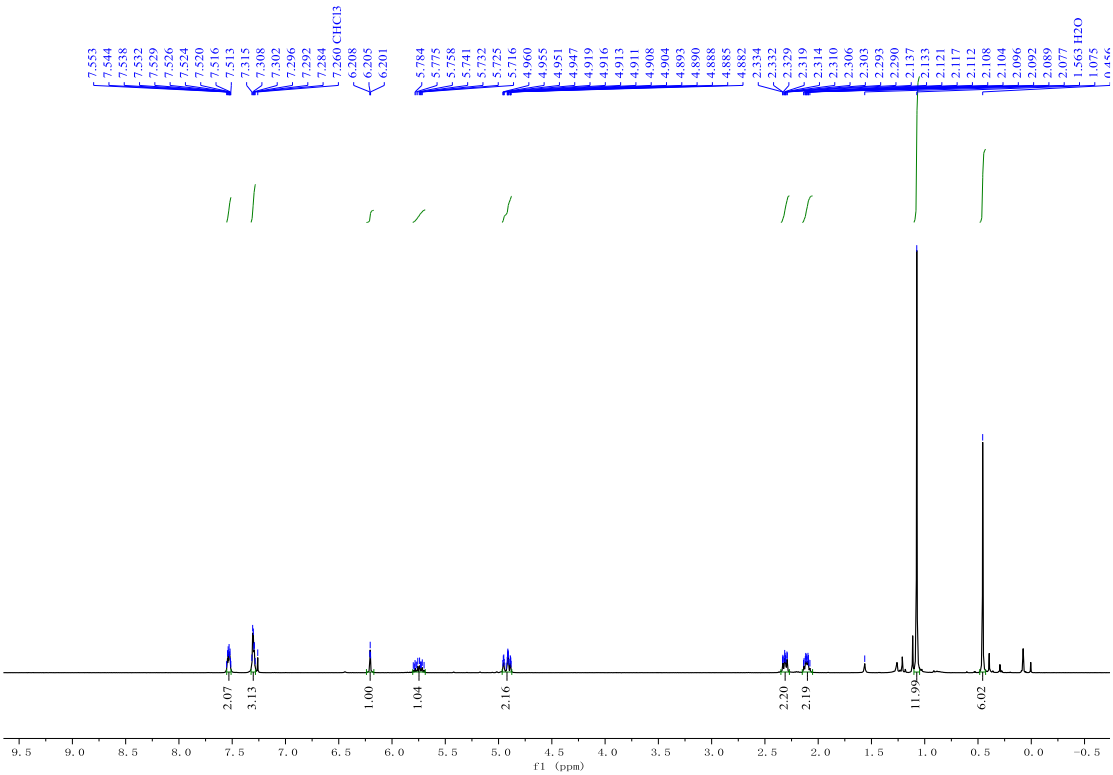
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 63% yield (42.6 mg). R_f = 0.48 (Petroleum ether:EtOAc = 98:2).

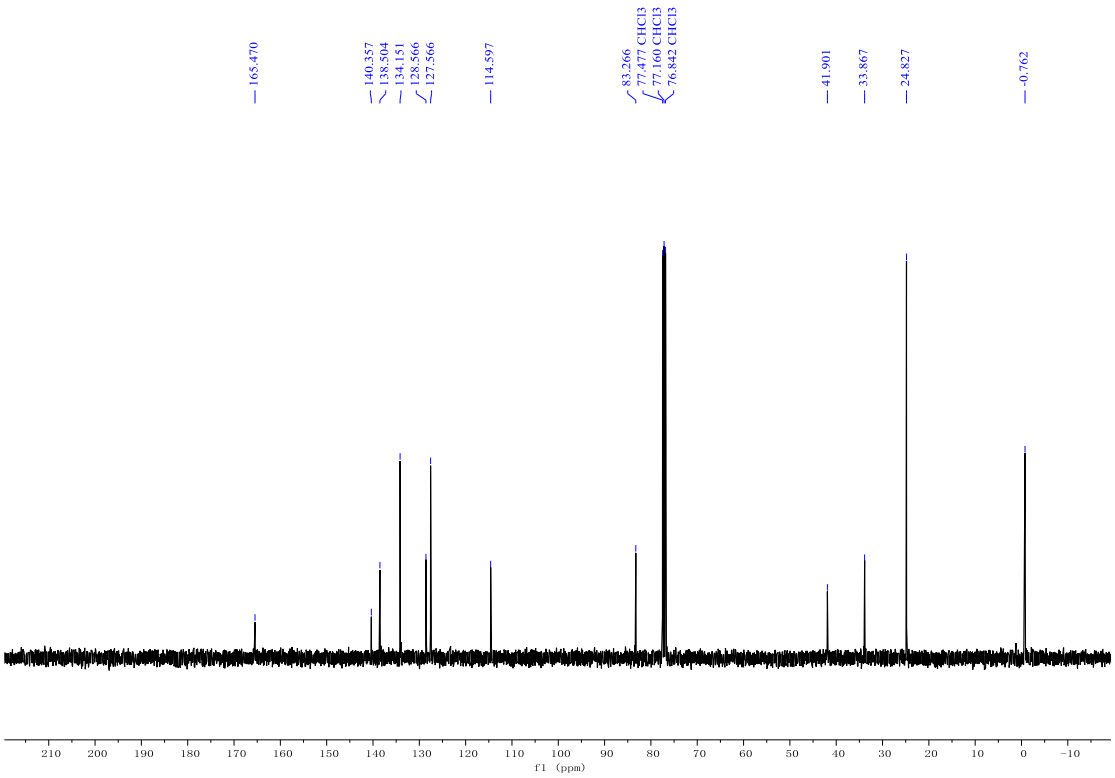
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.34 – 7.26 (m, 3H), 6.20 (t, *J* = 1.4 Hz, 1H), 5.75 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 4.97 – 4.87 (m, 2H), 2.34 – 2.28 (m, 2H), 2.15 – 2.06 (m, 2H), 1.07 (s, 12H), 0.46 (s, 6H).

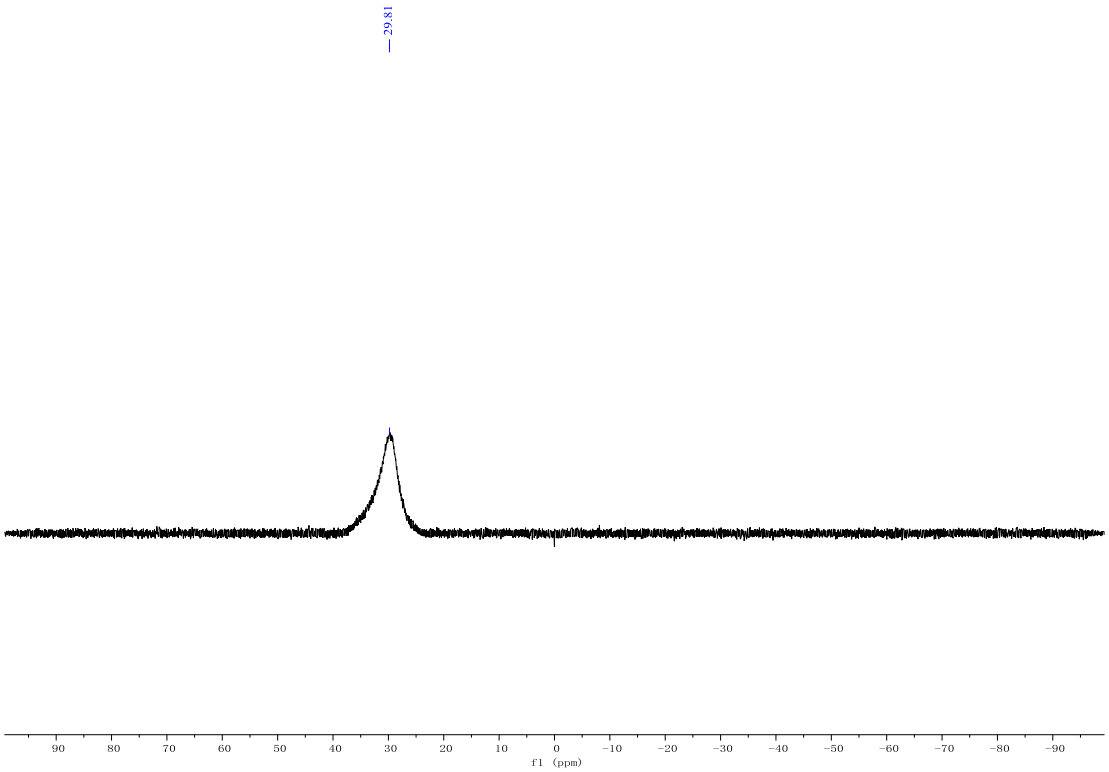
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.47, 140.36, 138.50, 134.15, 128.57, 127.57, 114.60, 83.27, 41.90, 33.87, 24.83, -0.76.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.81.

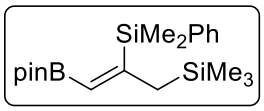
HRMS (ESI) m/z calculated for $C_{20}H_{31}BO_2SiNa$ $[M+Na]^+$: 365.2084, found: 365.2086.




165.470
140.357
138.504
134.151
128.566
127.566
114.597
83.266
77.477 CHCl3
77.160 CHCl3
76.842 CHCl3
41.901
33.867
24.827
0.762
f1 (ppm)


29.81
f1 (ppm)

(*Z*)-(2-(dimethyl(phenyl)silyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)trimethyl Silane (4q).



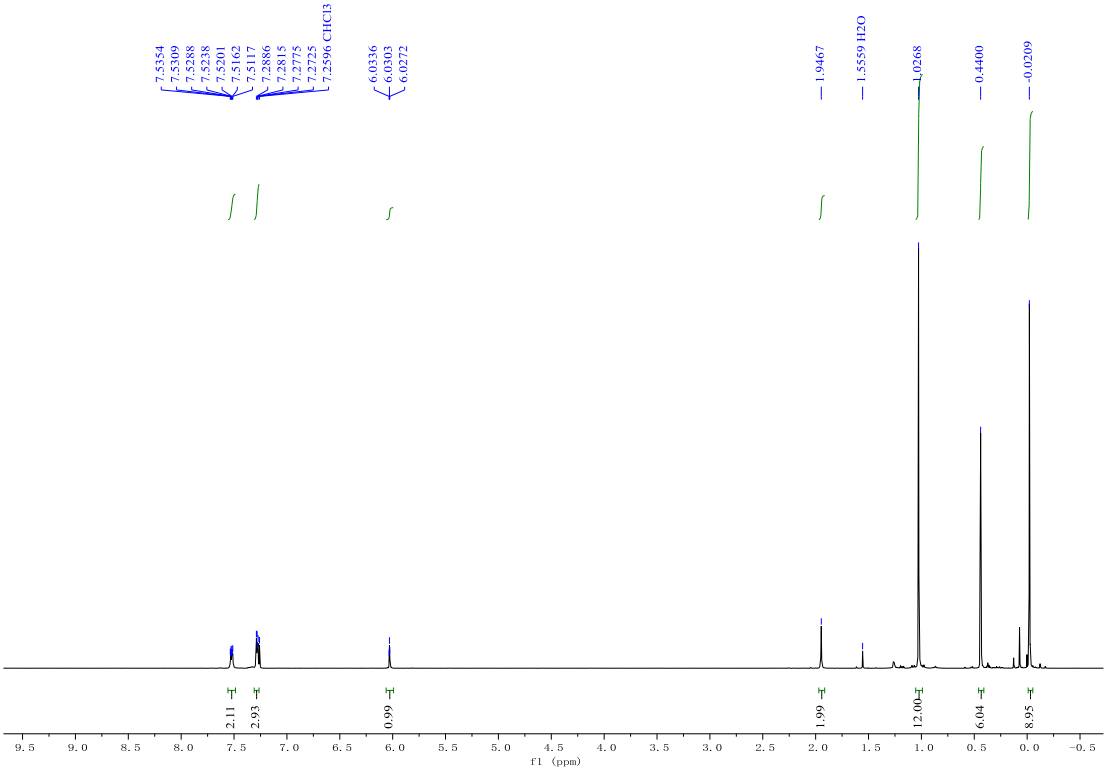
This compound was prepared by the general procedure B described above and was obtained as colorless oil in 62% yield (46.4 mg). R_f = 0.44 (Petroleum ether:Et_2O = 98:2).

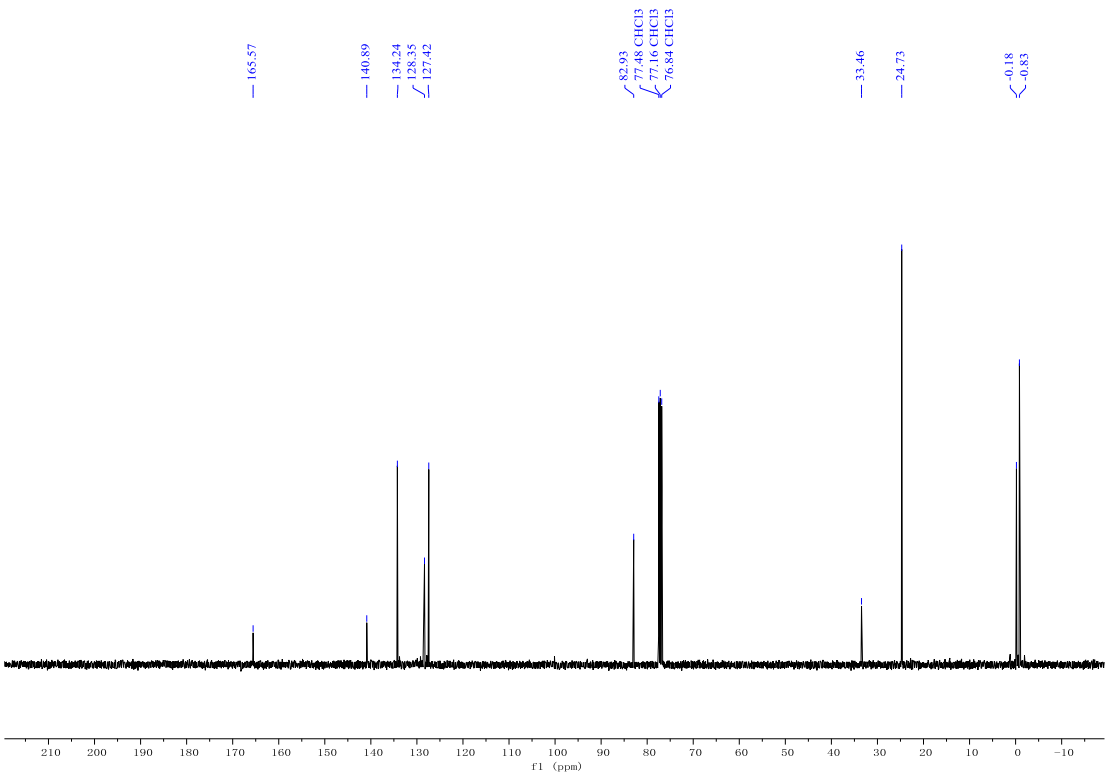
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.31 – 7.26 (m, 3H), 6.03 (t, *J* = 1.2 Hz, 1H), 1.95 (s, 2H), 1.03 (s, 12H), 0.44 (s, 6H), -0.02 (s, 9H).

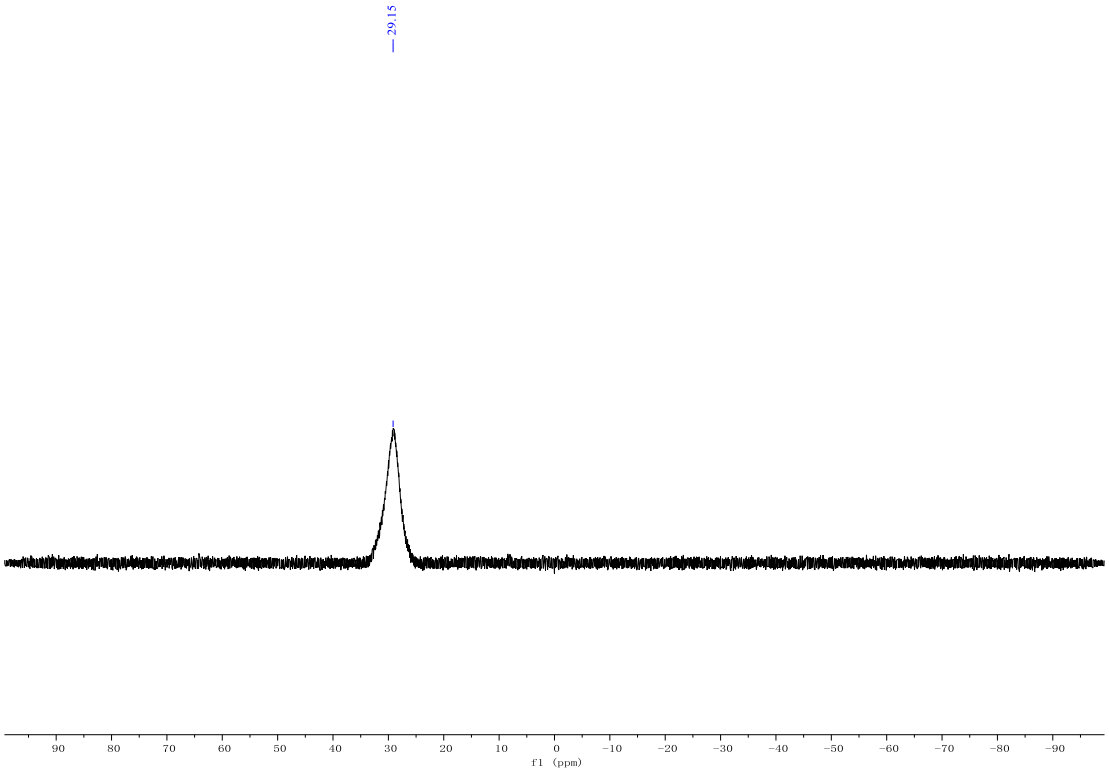
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.57, 140.89, 134.24, 128.35, 127.42, 82.93, 33.46, 24.73, -0.18, -0.83.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.15.

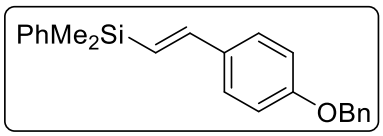
HRMS (ESI) m/z calculated for $C_{20}H_{35}BO_2SiNa$ $[M+Na]^+$: 397.2166, found: 397.2178.




165.57
140.89
134.24
128.35
127.42
82.93
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
33.46
24.73
-0.18
-0.83
f1 (ppm)


29.15
f1 (ppm)

(*E*)-(4-(benzyloxy)styryl)dimethyl(phenyl)silane (5u).

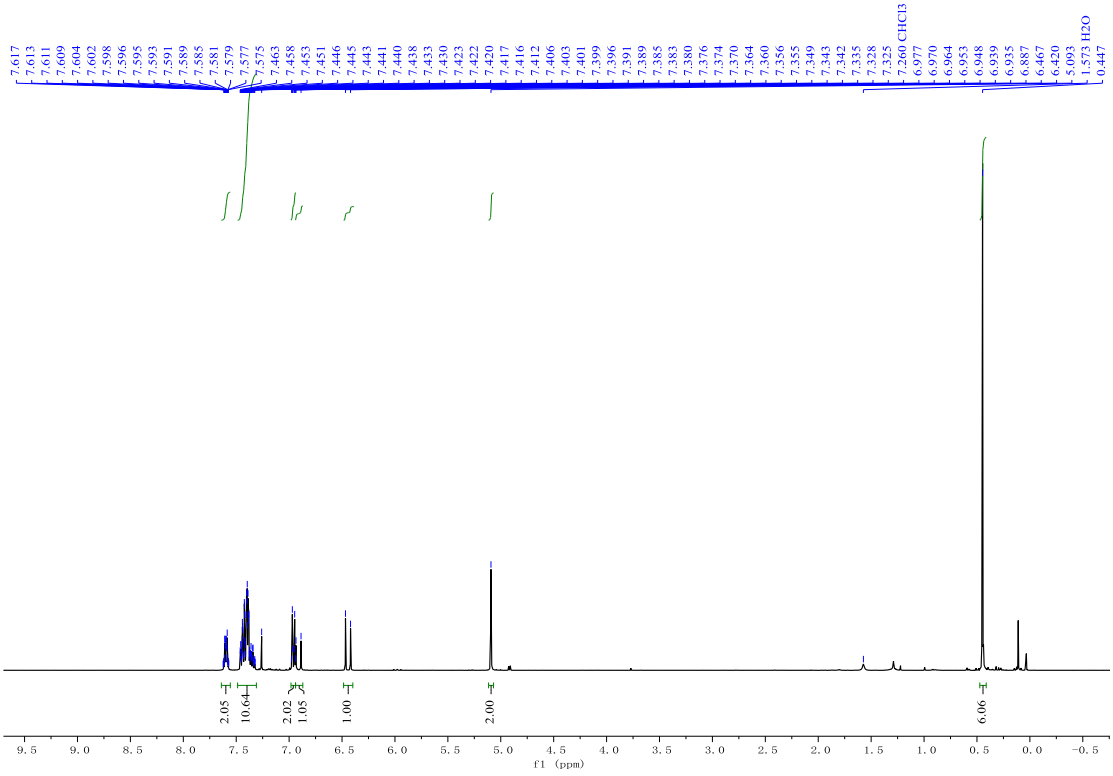


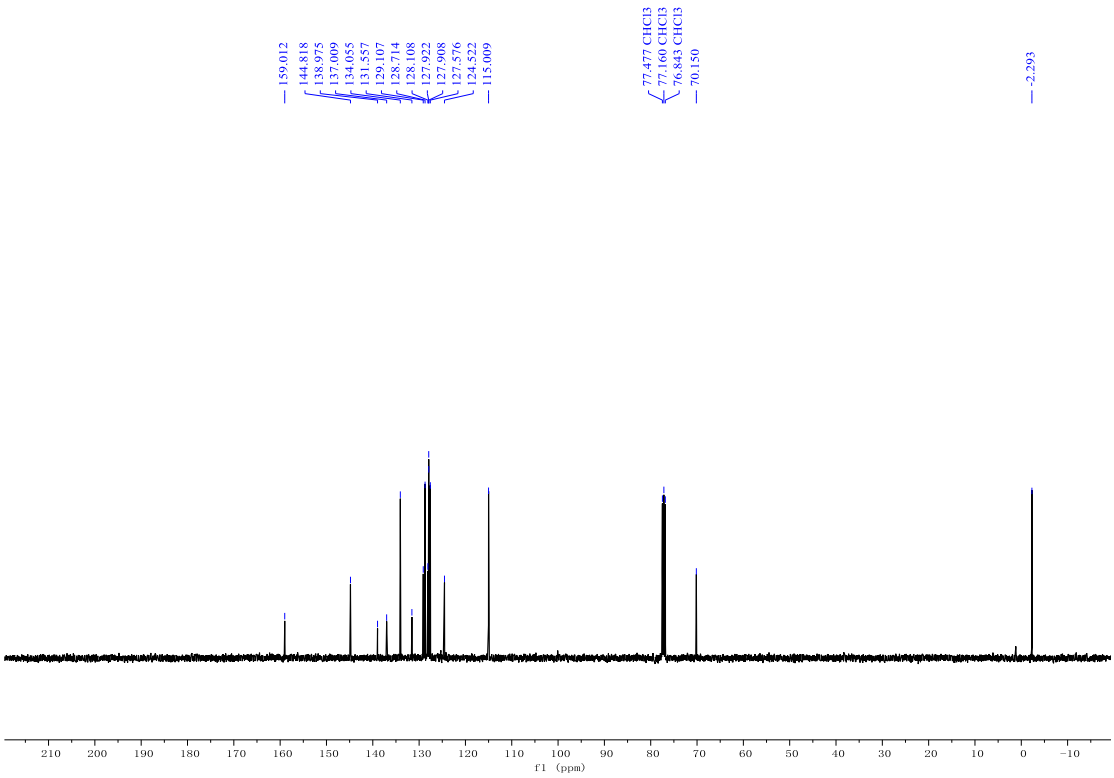
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 43% yield (29.7 mg). R_f = 0.40 (Petroleum ether:EtOAc = 98:2).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.56 (m, 2H), 7.48 – 7.32 (m, 10H), 6.98 – 6.94 (m, 2H), 6.91 (d, *J* = 19.1 Hz, 1H), 6.44 (d, *J* = 19.1 Hz, 1H), 5.09 (s, 2H), 0.45 (s, 6H).

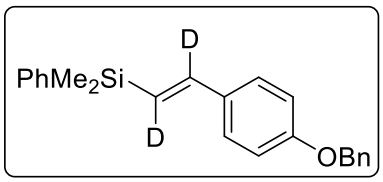
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.01, 144.82, 138.98, 137.01, 134.05, 131.56, 129.11, 128.71, 128.11, 127.92, 127.91, 127.58, 124.52, 115.01, 70.15, -2.29.

HRMS (ESI) m/z calculated for $C_{23}H_{25}OSi$ $[M+H]^+$: 345.1675, found: 345.1665.





(*E*)-(4-(benzyloxy)styryl)dimethyl(phenyl)silane (5u').

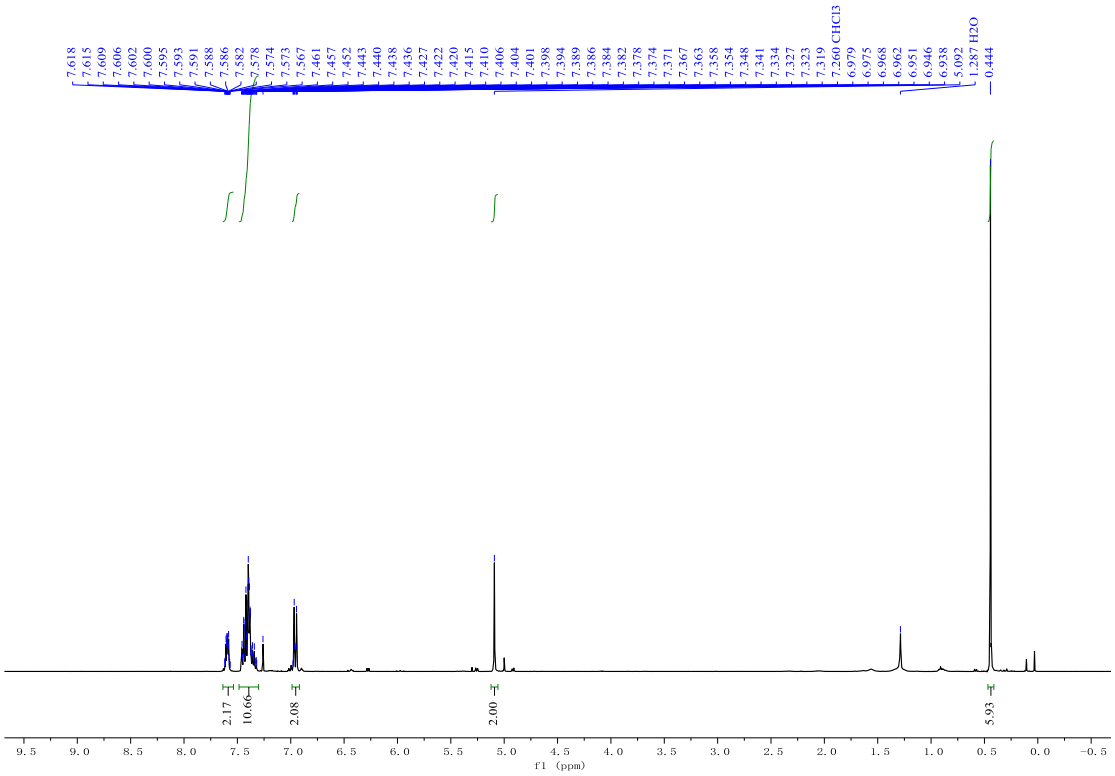


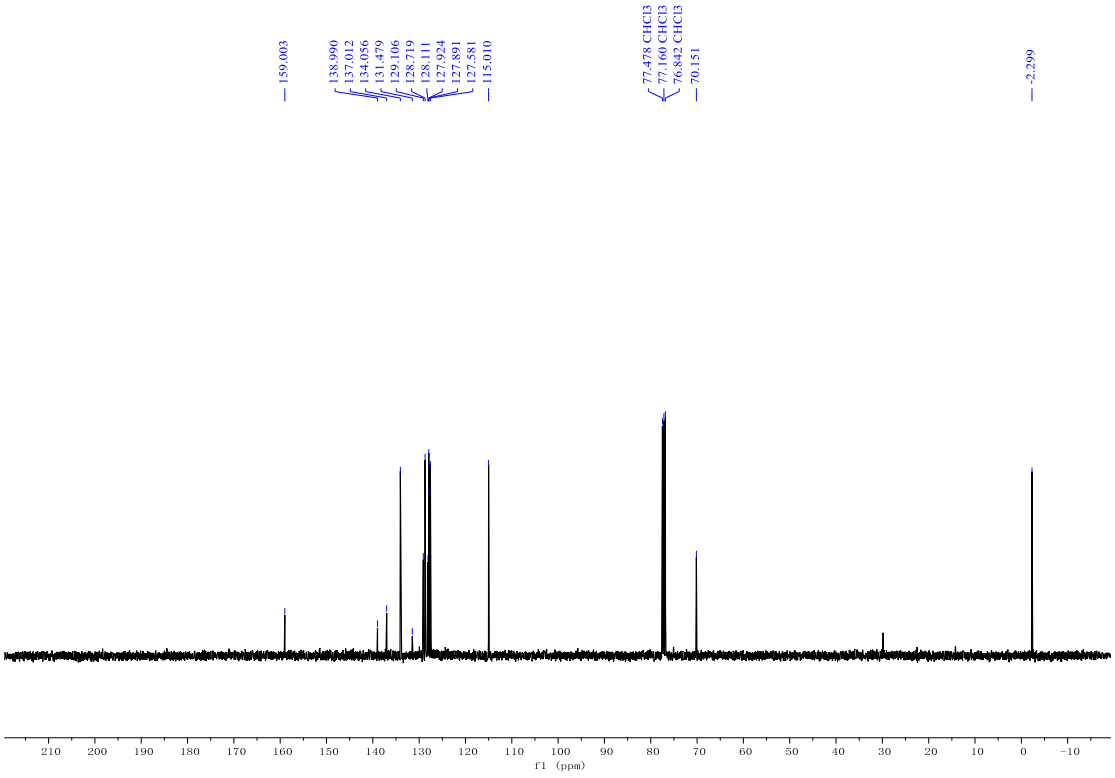
This compound was prepared by the general procedure A described above and was obtained as colorless oil in 46% yield (31.8 mg). R_f = 0.40 (Petroleum ether:EtOAc = 98:2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 2H), 7.48 – 7.31 (m, 10H), 6.98 – 6.92 (m, 2H), 5.09 (s, 2H), 0.44 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.00, 138.99, 137.02, 134.06, 131.48, 129.11, 128.72, 128.12, 127.93, 127.89, 127.58, 115.01, 70.16, -2.30.

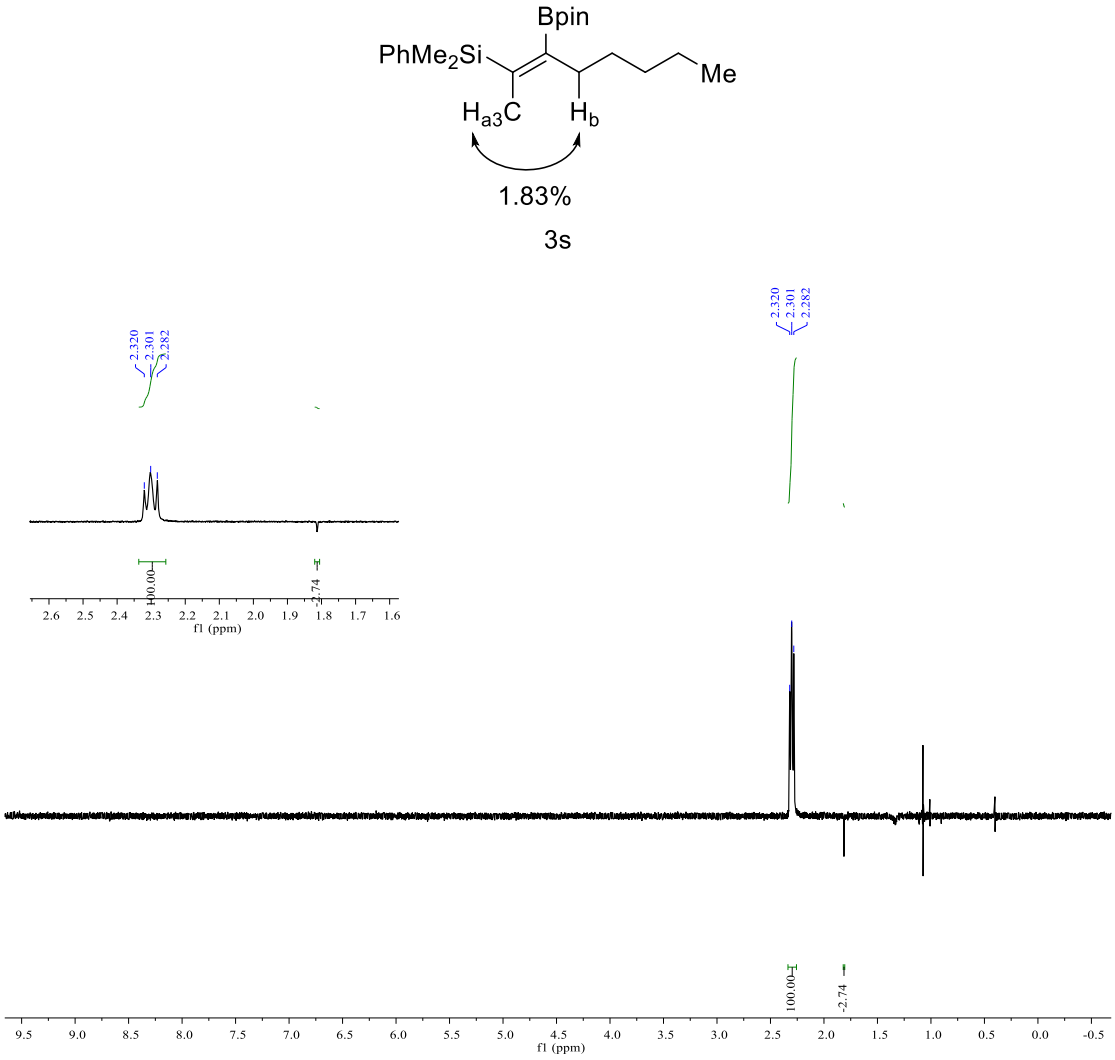
HRMS (ESI) m/z calculated for $C_{23}H_{23}D_2OSiN$ $[M+H]^+$: 347.1800, found: 347.1793.


7.618
7.615
7.609
7.606
7.602
7.600
7.595
7.593
7.591
7.588
7.586
7.582
7.578
7.574
7.573
7.567
7.461
7.457
7.452
7.443
7.440
7.438
7.436
7.427
7.422
7.420
7.415
7.410
7.406
7.404
7.401
7.398
7.394
7.389
7.386
7.384
7.382
7.378
7.374
7.371
7.367
7.363
7.358
7.354
7.348
7.341
7.334
7.327
7.323
7.319
7.260 CHCl3
6.979
6.975
6.968
6.962
6.951
6.946
6.938
5.092
1.287 H2O
0.444
2.17
10.66
2.08
2.00
5.93
f1 (ppm)


159.003
138.990
137.012
134.056
131.479
129.106
128.719
128.111
127.924
127.891
127.581
115.010
77.478 CHCl3
77.160 CHCl3
76.842 CHCl3
70.151
-2.299
f1 (ppm)

IV. Stereochemistry Analysis of Products

Figure S1. 1D-NOE spectroscopy of 3s



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