Supporting Information for

Allylic Borylation of Tertiary Allylic Alcohols: A Divergent and Straightforward Access to Allylic Boronates

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Table of Contents

1. General

1-1. Instrumentation

NMR spectra were obtained on a Bruker Ascend 400 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet, and brs = broad singlet. IR spectra were obtained on a JASCO FT/IR-4700. ESI mass spectra were measured on a Bruker micrOTOF-II spectrometer. FI mass spectra were measured on a JEOL JMS-T100GCV. EI mass spectra were measured on a JEOL JMS- 700V spectrometer.

1-2. Materials

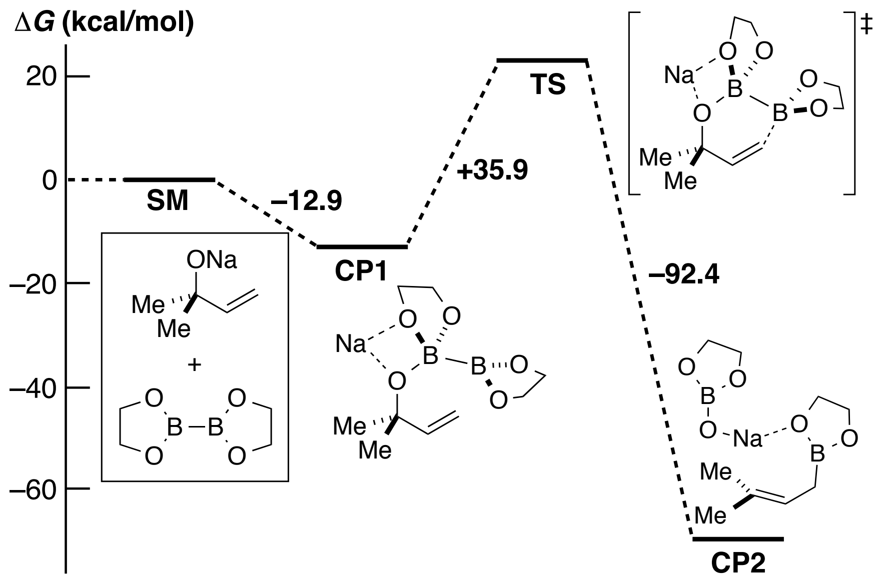
Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., and other commercial suppliers. n-Butyllithium in hexane, were obtained from Kanto Chemical Co., Inc. Anhydrous THF was purchased from Kanto Chemical Co., Inc. All other chemicals were of reagent grade and used as received. Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques under argon atmosphere. Normal-phase column chromatography to purify allylic boronates was performed with silica gel 60N for flash chromatography (spherical, neutral, 40–100 μm) from Kanto Chemical Co., Inc. For purification of the compound **2p** and **2q** was used CHROMATOREX®-DIOL from Fuji Silysia Chemical Ltd. Thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

2. Computational Details

2-1. Methods

All calculations were carried with the Gaussian 09 program package.[1] The molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-Yang-Parr nonlocal correlation functional (B3LYP).[2] We used 6–31+G* basis set for all atoms. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[3]

2-2. DFT Calculations on Our Initially Proposed Mechanism (Scheme 4)



2-2-1. Cartesian Coordinates

Sodium 2-methylbut-3-en-2-olate

Energy (RB3LYP) = –433.4744272 A.U.

Gibbs Free Energy = –433.380122 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.939894	-1.174232	-1.261847
1	-2.020688	-1.369820	-1.307357
1	-0.648919	-0.622616	-2.163665
1	-0.414246	-2.137886	-1.260415
6	-0.524223	-0.365069	-0.000083
6	-1.342148	0.928536	0.001238
1	-2.427791	0.799540	0.003112
6	-0.836720	2.165166	0.000185
1	0.240265	2.316498	-0.001783
1	-1.472264	3.048309	0.001132
8	0.832127	-0.144231	-0.001995
11	2.784854	0.088462	-0.000140
6	-0.936369	-1.174635	1.262567
1	-2.017019	-1.370300	1.311008
1	-0.410666	-2.138251	1.259334
1	-0.642957	-0.623300	2.163783

Bis(ethyleneglycolato)diboron

Energy (RB3LYP) = –508.0269175 A.U.

Gibbs Free Energy = –507.923903 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.003761	0.539325	-0.554179
6	-3.003740	-0.539297	0.554243
1	-3.554506	1.442485	-0.275633
1	-3.392877	0.166328	-1.507870
1	-3.554561	-1.442427	0.275749
1	-3.392749	-0.166278	1.507970
6	3.003706	0.539624	0.554010
6	3.003821	-0.539537	-0.553894

1	3.392989	0.167155	1.507843
1	3.554227	1.442766	0.274971
1	3.393206	-0.167040	-1.507674
1	3.554371	-1.442638	-0.274783
5	-0.851659	-0.000043	-0.000062
5	0.851651	-0.000052	-0.000071
8	1.613148	-0.880522	-0.732937
8	1.612986	0.880501	0.732875
8	-1.613089	0.880409	-0.733018
8	-1.613073	-0.880459	0.732957

CP1

Energy (RB3LYP) = –941.548663 A.U.

Gibbs Free Energy = –941.324637 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-2.426283	-1.748504	1.535867
1	-3.066639	-2.607638	1.305316
1	-1.627253	-2.094113	2.206271
1	-3.024547	-0.997059	2.065585
6	-1.834324	-1.132020	0.252104
6	-0.917031	-2.165953	-0.385266
1	-0.106677	-2.493319	0.270565
6	-1.007379	-2.696649	-1.607518
1	-1.780607	-2.406424	-2.313454
1	-0.287369	-3.433876	-1.955241
8	-1.066300	-0.000701	0.684443
6	3.301921	-0.993937	0.639465
6	3.522115	-0.748340	-0.869181
5	1.422494	0.028440	-0.308042
8	2.265431	-0.250010	-1.355342
8	2.038754	-0.353608	0.919144
6	-0.736932	3.072837	0.137343
6	-0.858408	2.734874	-1.355404
5	-0.122373	0.826744	-0.216901
8	-0.748054	1.323974	-1.423540
8	0.134346	2.061614	0.640426
11	0.392435	0.572059	2.273778
1	-0.300826	4.061786	0.325319
1	-1.719245	3.016349	0.633211
1	-0.045213	3.207533	-1.931060
1	-1.816469	3.060390	-1.782976
1	4.080622	-0.546868	1.265623
1	3.216981	-2.059272	0.884588
1	3.779811	-1.661507	-1.414576
1	4.295137	0.005084	-1.060305
6	-2.978444	-0.685273	-0.671192
1	-3.624728	-1.531342	-0.935713
1	-3.586720	0.061511	-0.148629
1	-2.588477	-0.222149	-1.579722

TS

Energy (RB3LYP) = –941.4941578 A.U.

Gibbs Free Energy = –941.267406 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.421688	-0.964103	0.848628
1	-4.219700	-1.524308	0.349365
1	-2.950054	-1.639795	1.575774
1	-3.867965	-0.122768	1.390623
6	-2.409881	-0.479138	-0.187657
6	-1.665446	-1.584614	-0.835381
1	-1.607225	-2.514063	-0.262838
6	-0.494623	-1.199639	-1.565698
1	-0.622021	-0.409365	-2.310261
1	0.017401	-2.052996	-2.035990
8	-1.392582	0.311553	0.649952
6	2.655015	-1.902990	0.387891
6	3.223623	-0.893803	-0.623578
5	0.912008	-0.719367	-0.631327
8	2.079230	-0.426607	-1.342632
8	1.267651	-1.540629	0.500990
6	1.251602	2.574621	0.849720
6	0.903234	2.747400	-0.643047
5	-0.262410	0.948334	0.135702
8	-0.291657	1.991864	-0.818908
8	0.695077	1.303113	1.199202
11	-0.000803	-0.649685	2.144530
1	2.331318	2.576162	1.040749
1	0.780601	3.352699	1.467306
1	1.697532	2.344625	-1.285824
1	0.714751	3.791502	-0.914952
1	3.137054	-1.845560	1.370408
1	2.720014	-2.937019	0.023844
1	3.938046	-1.343712	-1.321095
1	3.706945	-0.043115	-0.124136
6	-3.068231	0.524895	-1.139636
1	-3.898014	0.033762	-1.660626
1	-3.455497	1.387193	-0.582689
1	-2.365725	0.898327	-1.887649

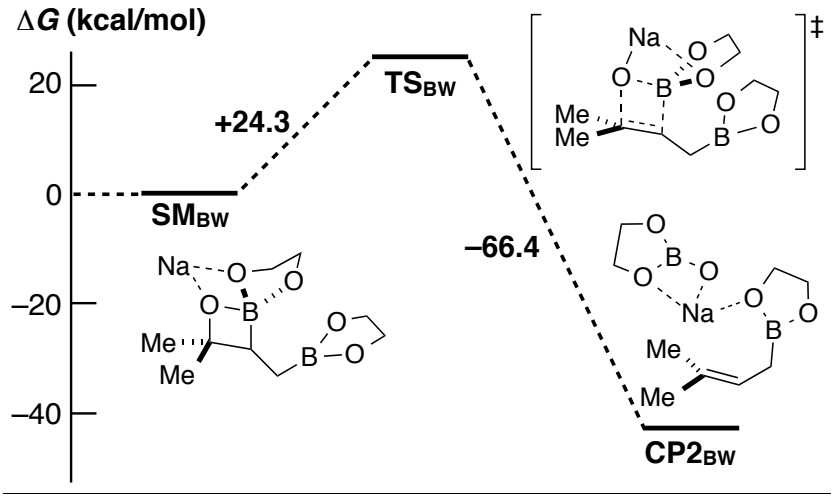
CP2

Energy (RB3LYP) = –941.6345955 A.U.

Gibbs Free Energy = –941.414693 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.073811	3.312325	1.076635
1	-0.180013	4.399271	0.953348
1	-0.219578	3.078420	2.137804
1	0.953546	3.054098	0.787689
6	-1.060284	2.584325	0.190940
6	-1.986341	1.754913	0.717062
1	-1.999372	1.651524	1.805191
6	-3.065405	0.971746	0.000343
1	-3.168993	1.302940	-1.042749
1	-4.043617	1.181367	0.458639
8	1.972279	1.123589	-0.661516
6	-1.839408	-2.645509	0.109510
6	-3.306047	-2.811038	-0.349220
5	-2.872195	-0.589629	-0.024133
8	-3.878003	-1.493612	-0.232888
8	-1.636064	-1.209730	0.133354
6	3.543321	-1.764445	0.722071
6	4.648948	-1.220394	-0.209047
5	2.826424	0.196248	-0.359475
8	4.214486	0.081685	-0.575479
8	2.387228	-1.017924	0.352889
11	0.317082	0.041268	0.257820
1	3.362819	-2.838202	0.589282
1	3.778838	-1.577876	1.780560
1	4.751873	-1.841608	-1.111748
1	5.626597	-1.163584	0.283686
1	-1.116050	-3.092856	-0.576469
1	-1.664489	-3.030726	1.119093
1	-3.874516	-3.501474	0.279221
1	-3.385207	-3.131865	-1.393230
6	-0.880404	2.866036	-1.281641
1	-0.957959	3.945696	-1.470635
1	0.127493	2.556262	-1.589946
1	-1.613241	2.361749	-1.918510

2-3. DFT Calculations on DFT Calculations on Boron Wittig Reaction (Scheme 5)



2-3-1. Cartesian Coordinates

SM_{BW}

Energy (RB3LYP) = –941.5753322 A.U.
Gibbs Free Energy = –941.347838 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.430099	-1.578338	-0.034544
6	-2.690939	-2.272051	0.488968
1	-3.278394	-1.592500	1.123782
1	-3.325389	-2.619176	-0.339191
1	-2.431374	-3.144383	1.102188
6	-0.638366	-2.518735	-0.939963
1	-1.267823	-2.842499	-1.779402
1	0.250543	-2.027837	-1.341473
1	-0.316251	-3.413532	-0.391536
6	-0.630905	-0.784253	1.046108
1	-1.244822	-0.740689	1.956825
6	0.806540	-1.207644	1.452628
1	0.884915	-2.306122	1.499815
1	0.978965	-0.858156	2.479842
8	-1.811385	-0.375407	-0.792338
6	3.405838	-0.293008	-1.169744
6	3.887744	0.519727	0.052424
6	-0.863116	2.815853	0.559901
6	0.144730	2.519538	-0.560466
5	-0.903681	0.501156	0.072059
5	1.992896	-0.642455	0.580250
8	-1.735407	1.689566	0.528021
8	0.252540	1.110495	-0.574086
8	2.853166	0.344780	1.031336
8	2.387471	-1.153784	-0.642726
1	-1.431595	3.742204	0.405462
1	-0.226953	2.890793	-1.532681
1	1.127021	2.973312	-0.374655
1	-0.361727	2.870278	1.537535
1	4.006533	1.586521	-0.163868
1	4.830422	0.137130	0.464720
1	4.195467	-0.901585	-1.622413
1	2.956264	0.345823	-1.939051
11	-3.482865	0.952289	-0.556452

TS_{BW}

Energy (RB3LYP) = –941.5344619 A.U.
Gibbs Free Energy = –941.308096 A.U.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	1.360900	1.679348	0.353274
6	2.822923	1.913790	0.638906
1	3.284554	1.039399	1.109093
1	3.374835	2.184610	-0.266275
1	2.903497	2.750080	1.351229
6	0.687367	2.734567	-0.477329
1	1.326215	3.050604	-1.306302
1	-0.268968	2.393166	-0.873921
1	0.498693	3.607113	0.170334
6	0.632720	0.821817	1.214143
1	1.216556	0.460620	2.063445
6	-0.858370	1.019589	1.542193
1	-1.066041	2.080701	1.764922
1	-1.056657	0.486760	2.481128
8	1.602508	0.315137	-1.164811
6	-3.188596	0.352328	-1.388523
6	-3.832645	-0.496315	-0.270098
6	0.991114	-2.467017	1.016765
6	-0.301008	-2.401086	0.175439
5	0.973896	-0.437337	-0.181107
5	-1.937362	0.519266	0.499945
8	1.856546	-1.523417	0.397330
8	-0.296931	-1.111053	-0.419907
8	-2.892925	-0.436056	0.814104
8	-2.202974	1.140190	-0.707923
1	1.452997	-3.462049	1.020297
1	-0.298192	-3.164259	-0.619609
1	-1.205293	-2.537367	0.781315
1	0.803755	-2.169976	2.059715
1	-3.984704	-1.540773	-0.561827
1	-4.789880	-0.082402	0.072450
1	-3.899273	1.016817	-1.890521
1	-2.681313	-0.268782	-2.135746
11	3.162758	-1.115859	-1.362989

$CP2_{BW}$

Energy (RB3LYP) = –941.6347497 A.U.

Gibbs Free Energy = –941.414944 A.U.

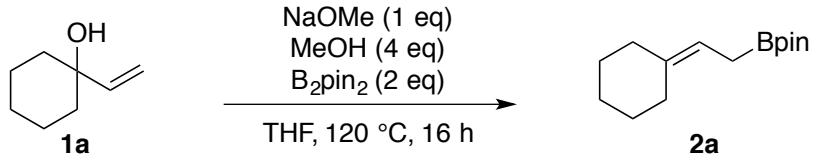
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.517085	2.553859	0.118602
6	-0.477094	3.417973	0.801514
1	-0.295018	3.104229	1.834834
1	0.482704	3.403892	0.265496
1	-0.802736	4.467614	0.820783
6	-1.815720	2.943277	-1.311676
1	-0.899504	2.951345	-1.919018
1	-2.534454	2.281535	-1.800841
1	-2.215949	3.966297	-1.351227
6	-2.144648	1.565784	0.790206
1	-1.849547	1.413569	1.831400
6	-3.239863	0.636387	0.312542
1	-3.698932	1.010432	-0.611770
1	-4.039551	0.603361	1.063602
8	1.495376	-1.598921	0.262050
6	-1.346860	-2.503624	-0.753375
6	-2.384349	-3.082394	0.233979
6	3.925304	0.997134	-0.037029
6	4.807694	-0.269508	-0.091160
5	2.609859	-0.943043	0.164075
5	-2.708369	-0.831504	0.059348
8	2.597481	0.494620	-0.164439
8	3.954842	-1.332096	0.313615
8	-3.263265	-1.974676	0.556284
8	-1.566708	-1.060490	-0.682786
1	4.143772	1.705098	-0.845386
1	5.171283	-0.459213	-1.112233
1	5.673635	-0.210098	0.578216
1	4.028172	1.520743	0.924930
1	-1.924759	-3.429663	1.164263
1	-2.984043	-3.889711	-0.194328
1	-1.530479	-2.812442	-1.787411
1	-0.307395	-2.691695	-0.471840
11	0.317206	0.196056	-0.196909

3. Experimental Details

Allylic alcohols (**1a**-**1m**, **1p**) were prepared according to the procedure by Mihovilovic *et al*.[4] Substrates **1n** and **1o** were prepared according to the literature.[5]

3-1. General Procedure for Synthesis of Allylic Boronates

2-(2-cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[6]

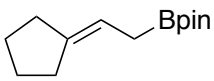


In a glovebox, NaOMe (54.0 mg, 1 mmol) was added to a greaseless Schlenk tube and the tube was taken out from the box. To the tube were added anhydrous THF (6 mL), MeOH (128.2 mg, 162 μL, 4 mmol), allylic alcohol **1a** (126.2 mg, 1 mmol), and B_2pin_2 (507.8 mg, 2 mmol) were added. Then, the reaction vessel was sealed and stirred at 120 ˚C. After 16 h, the reaction was cooled to rt and quenched with aqueous NH_4Cl, followed by extraction with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and purified by column chromatography (eluent: hexane/EtOAc = 30 : 1). The product was obtained as a colorless oil in 68% yield (160.6 mg) (89% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.17 (t, *J* = 7.6 Hz, 1H), 2.13-2.05 (m, 4H), 1.60 (d, *J* = 7.6 Hz, 2H), 1.51 (m, 6H), 1.24 (s, 12H). ^{1}H NMR spectrum was in agreement with the literature.[6]

Larger Scale (10 mmol):
Following the **General Procedure**, NaOMe (540 mg, 10 mmol), anhydrous THF (60 mL), MeOH (1.6 mL, 40 mmol), allylic alcohol **1a** (1.33 mL 10 mmol), and B_2pin_2 (5.1 g, 20 mmol) were employed and the product was obtained as a colorless oil in 46% yield (1.09 g) (87% ^{1}H NMR yield).

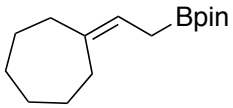
The reactions were carried out on 1 mmol scale unless otherwise noted.

2-(2-cyclopentylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



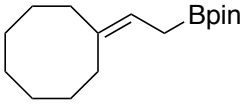
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 84% yield (185.7 mg, 97% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.37-5.30 (m, 1H), 2.2 (t, *J* = 6.4 Hz, 2H), 2.15 (t, *J* = 6.4 Hz, 2H), 1.67-1.55 (m, 6H), 1.24 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.49, 113.98, 83.06, 33.56, 28.72, 26.67, 26.29, 24.78. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2978, 2950, 2869, 1370, 1338, 1319, 1144, 968, 845, 883 cm^{-1}. **HRMS (FI):** *m*/*z* calculated for $C_{13}H_{23}BO_2$ $[M]^+$ = 222.1791, found: 222.1821.

2-(2-cycloheptylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



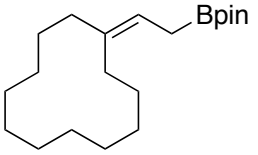
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 66% yield (165.2 mg, 84% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.26 (t, *J* = 7.6 Hz, 1H), 2.17-2.22 (m, 4H), 1.59-1.48 (m, 10H), 1.24 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 141.28, 118.75, 83.03, 37.77, 30.10 (2C: overlapped), 29.62, 29.22, 26.85, 24.76. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2920, 2851, 1447, 1373, 1322, 1143, 967, 885, 847, 673 cm^{-1}. **HRMS (ESI):** *m*/*z* calculated for $C_{15}H_{27}BO_2$ [M+Na]$^+$ = 273.1996, found: 273.1968.

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



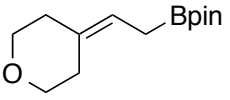
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 72% yield (190.2 mg, 86% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.284 (t, *J* = 7.6 Hz, 1H), 2.19-2.12 (m, 4H), 1.63-1.60 (m, 6H), 1.51-1.45 (m, 6H), 1.24 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 104.65, 119.21, 83.05, 37.81, 28.96, 27.32, 26.68, 26.26 (2C: overlapped), 26.08, 24.79. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2920, 2858, 1466, 1447, 1373, 1323, 1214, 1144, 1108, 967, 886, 847 cm^{-1}. **HRMS (ESI):** *m*/*z* calculated for $C_{16}H_{29}BO_2$ [M+Na]$^+$ = 287.2153, found: 287.2170.

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



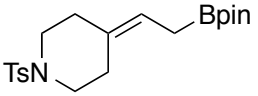
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 68% yield (217.7 mg, quant. ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.32 (t, *J* = 8.0 Hz, 1H), 2.04 (t, *J* = 6.4 Hz, 2H), 2.03 (t, *J* = 5.6 Hz, 2H), 1.66 (d, *J* = 7.6 Hz, 2H), 1.54-1.48 (m, 2H), 1.48-1.40 (m, 2H), 1.34-1.25 (m, 14H), 1.235 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 137.01, 119.31, 83.00, 31.88, 28.50, 25.18, 24.96, 24.80, 24.37, 24.13 (2C: overlapped), 23.81, 23.32, 23.30, 22.36. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2975, 2862, 2927, 1377, 1469, 1321, 1143, 967, 817 cm^{-1}. **HRMS (ESI):** *m*/*z* calculated for $C_{20}H_{37}BO_2$ [M+Na]$^+$ = 343.2779 found: 343.2784.

4,4,5,5-tetramethyl-2-(2-(tetrahydro-4*H*-pyran-4-ylidene)ethyl)-1,3,2-dioxaborolane (2f)



Following the **General Procedure** (eluent for column chromatography: $CHCl_3$/MeOH = 100 : 1), 3 eq. of B_2pin_2 were used), the titled compound was obtained as a colorless oil in 64% yield (152.7mg, 67% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.23 (t, *J* = 7.6 Hz, 1H), 3.67-3.62 (m, 4H), 2.247 (t, *J* = 4.8 Hz, 2H), 2.21 (t, *J* = 4.8 Hz, 2H), 1.62 (d, *J* = 7.6 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 134.16, 117.26, 83.20, 69.75, 68.73, 36.86, 29.55, 24.76. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2976, 2843, 1370, 1321, 1229, 1144, 1099, 967, 885, 845, 659 cm^{-1}. **HRMS (ESI):** *m*/*z* calculated for $C_{13}H_{23}BO_3$ [M+Na]$^+$ = 261.1632, found: 261.1605.

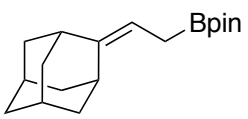
4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-1-tosylpiperidine (2g)



Following the **General Procedure** (purification by column chromatography two times, eluent for column chromatography: hexane/EtOAc = 10 : 1, 0.5 mmol scale), the titled compound was obtained as a colorless oil in 61% yield (119.7 mg, 80% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.26 (t, *J* = 7.6 Hz, 1H), 2.99

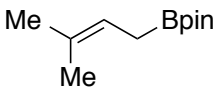
(apparent t, J = 5.2 Hz, 2H), 2.98 (apparent t, J = 5.2 Hz, 2H), 2.29 (apparent t, J = 5.2 Hz, 2H), 2.24 (apparent t, J = 5.2 Hz, 2H), 1.54 (d, J = 7.6 Hz, 2H), 1.18 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.30, 133.36, 133.17, 129.52, 127.69, 118.89, 83.23, 48.17, 47.21, 35.14, 27.44, 24.69, 21.48. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2932, 1370, 1313, 1136, 1128, 987, 897, 852, 799, 671 cm^{-1}. **HRMS (ESI):** m/z calculated for $C_{20}H_{30}BNO_4$ $[M+Na]^+$ = 414.1881, found: 414.1872.

2-(2-((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



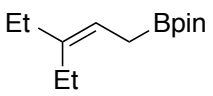
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), 3 eq. of B_2pin_2 were used), the titled compound was obtained as a colorless oil in 83% yield (243.5 mg, 92% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.13 (t, J = 8.0 Hz, 1H), 2.78 (brs, 1H), 2.35 (brs, 1H), 1.93 (brs, 2H), 1.85 (brs, 2H), 1.81 (brs, 4H), 1.75-1.69 (m, 4H), 1.58 (d, J = 8.0 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 147.59, 109.60, 82.98, 40.28, 39.86, 38.62, 37.35, 31.87, 28.67, 24.74. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2902, 2847, 1373, 1319, 1143, 967, 885, 840, 756 cm^{-1}. **HRMS (ESI):** m/z calculated for $C_{18}H_{29}BNO_2$ $[M+Na]^+$ = 311.2153, found 311.2155.

4,4,5,5-tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (2i)



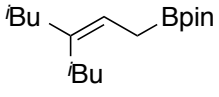
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 52% yield (100.1 mg, 68% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.23 (t, 1H, J = 7.2 Hz), 1.69 (s, 3H), 1.60 (d, 2H, J = 7.2 Hz), 1.59 (s, 3H), 1.25 (s, 12H). ^{1}H NMR spectrum was in agreement with the literature.[7]

2-(3-ethylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)



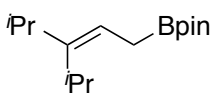
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 55% yield (123.9 mg, 65% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.19 (t, J = 7.6 Hz, 1H), 2.04 (q, J = 7.2 Hz, 2H), 2.00 (q, J = 7.2 Hz, 2H), 1.62 (d, J = 7.6 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 142.78, 116.57, 83.01, 29.30, 24.72, 22.87, 13.03, 12.79. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2964, 2932, 2875, 1462, 1370, 1345, 1320, 1145, 967, 885, 847, 674 cm^{-1}. **HRMS (FI):** m/z calculated for $C_{13}H_{25}BO_2$ $[M]^+$ = 224.1948, found: 224. 1978.

2-(3-isobutyl-5-methylhex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



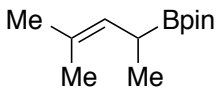
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 52% yield (145.6 mg, 67% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** 5.27 (t, J = 8.0 Hz, 3H), 1.85 (d, J = 7.2 Hz, 2H), 1.82 (d, J = 7.2 Hz, 2H), 1.76-1.66 (m, 2H), 1.64 (d, J = 8.0 Hz, 2H), 1.23 (s, 12H), 0.86 (d, J = 6.4 Hz, 6H), 0.83 (d, J = 6.4 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 137.05, 120.97, 82.99, 46.84, 38.43, 26.78, 26.26, 24.77, 22.63, 22.50. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2952, 2928, 2868, 1464, 1370, 1320, 1146, 968, 885, 845 cm^{-1}. **HRMS (ESI):** m/z calculated for $C_{17}H_{33}BO_2$ $[M+Na]^+$ = 303.2466, found: 303.2471.

2-(3-isopropyl-4-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)



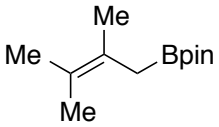
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1, 0.5 mmol scale, 3 eq. of B_2pin_2 were used at 140 °C), the titled compound was obtained as a colorless oil in 36% yield (45.2 mg, 70% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.23 (t, *J* = 8.0 Hz, 1H), 2.80 (sep, *J* = 6.8 Hz, 1H), 2.27 (sep, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 8.4 Hz, 2H), 1.23 (s, 12H), 0.99 (d, *J* = 6.8 Hz, 6H), 0.99 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 151.08, 114.93, 82.94, 29.71, 28.96, 28.62, 24.70, 24.63, 20.93 (2C: overlapped). The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2958, 2928, 2869, 1460, 1322, 1145, 967, 843, 674 cm^{-1}. **HRMS (ESI):** *m/z* calculated for $C_{15}H_{29}BO_2$ $[M+Na]^+$ = 275.2152, found 275.2133.

4,4,5,5-tetramethyl-2-(4-methylpent-3-en-2-yl)-1,3,2-dioxaborolane (2n)



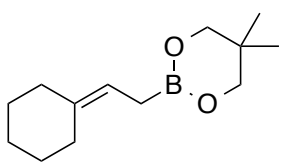
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1, 0.5 mmol scale, B_2pin_2 (3eq.) was used reaction at 140 °C), the titled compound was obtained as a colorless oil in 31% yield (34.7 mg, 35% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.09 (d, 1H, *J* = 9.2 Hz), 1.98 (dq, 1H, J^1 = 9.2 Hz, J^2 = 7.2 Hz), 1.69 (s, 3H), 1.60 (s, 3H), 1.23 (s, 12H), 1.03 (d, 3H, *J* = 7.2 Hz). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 130.20, 126.90, 82.89, 25.80, 24.68, 17.94, 16.22. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2978, 2928, 2872, 1457, 1373, 1338, 1314, 1214, 1144, 967, 865, 835, 686 cm^{-1}. **HRMS (ESI):** *m/z* calculated for $C_{12}H_{23}BO_2$ $[M+Na]^+$ = 233.1683, found: 233.1606.

2-(2,3-dimethylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)[8]



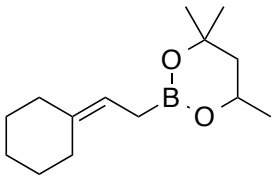
Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1, 0.5 mmol scale), the titled compound was obtained as a colorless oil in 31% yield (34.7 mg, 35% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.69-1.66 (m, 5H), 1.66 (s, 3H), 1.63 (s, 3H), 1.23 (s, 12H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 123.85, 123.53, 82.95, 24.71, 20.72, 20.54 (2C: overlapped). The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2922, 2862, 1273, 1141, 968, 846, 751, 678 cm^{-1}. **HRMS (FI):** *m/z* calculated for $C_{12}H_{23}BO_2$ $[M]^+$ = 210.1791, found: 210.1812.

2-(2-cyclohexylideneethyl)-5,5-dimethyl-1,3,2-dioxaborinane (2p)



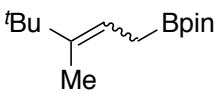
Following the **General Procedure** (eluent for column chromatography: Hexane/EtOAc = 10 : 1, 1.0 mmol scale, Bis(neopentyl glycolato) diboron (3 eq.) was used) and following Kugelrohr distillation, the titled compound was obtained as a colorless oil in 60% yield (133.5 mg, 66% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.18 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 4H), 2.13-2.06 (m, 4H), 1.57-1.45 (m, 8H), 0.95 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 138.95, 116.13, 72.14, 37.16, 31.68, 28.71, 28.51, 27.63, 27.04, 21.82. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2972, 2925, 2852, 1390, 1289, 1272, 1207, 1168, 1034, 896, 794, 767, 514 cm^{-1}. **HRMS (EI):** *m/z* calculated for $C_{12}H_{23}BO_2$ $[M]^+$ = 222.1791, found: 222.1797.

2-(2-cyclohexylideneethyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2q)



Following the **General Procedure** (eluent for column chromatography: Hexane, 1.0 mmol scale, Bis(hexylene glycolato) diboron (3 eq.) was used), the titled compound was obtained as a colorless oil in 66% yield (155.9 mg, 68% ^{1}H NMR yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.18 (t, *J* = 7.6 Hz, 1H), 4.19-4.12 (m, 1H), 2.12-2.05 (m, 4H), 1.75 (dd, *J* = 14.0 Hz, 2.8 Hz, 1H), 1.57-1.42 (m, 9H), 1.27 (s, 6H), 1.24 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 138.61, 116.66, 70.54, 64.66, 45.91, 37.15, 31.26, 28.79, 28.59, 28.08, 27.69, 27.08, 23.21. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2960, 2924, 2852, 1476, 1415, 1375, 1291, 1254, 1173, 1076, 1007, 851, 814, 739, 665 cm^{-1}. **HRMS (EI):** *m*/*z* calculated for $C_{12}H_{23}BO_2$ [M]$^+$ = 236.1948, found: 236.1958.

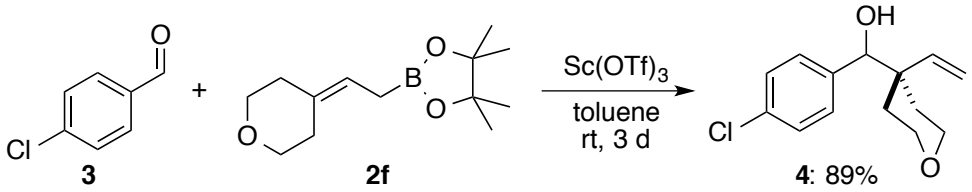
4,4,5,5-tetramethyl-2-(3,4,4-trimethylpent-2-en-1-yl)-1,3,2-dioxaborolane (2r)



Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 62% yield (146.5 mg, 72% ^{1}H NMR yield, *E* : *Z* = 1:1.5 determined by NOESY). *Z* isomer **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.26 (t, *J* = 8.4 Hz, 1H), 1.79 (d, *J* = 8.4 Hz, 2H), 1.70 (s, 3H), 1.25 (s, 12H), 1.13 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 141.94, 119.52, 83.08, 35.25, 30.21, 24.76, 12.81. The carbon directly attached to the boron atom was not detected. *E* isomer **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.32 (t, *J* = 7.2 Hz, 1H), 1.60 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 2H), 1.23 (s, 12H), 1.02 (s, 9H). **HRMS (ESI):** *m*/*z* calculated for $C_{15}H_{29}BO_2$ [M+Na]$^+$ = 261.1996, found: 261.2047.

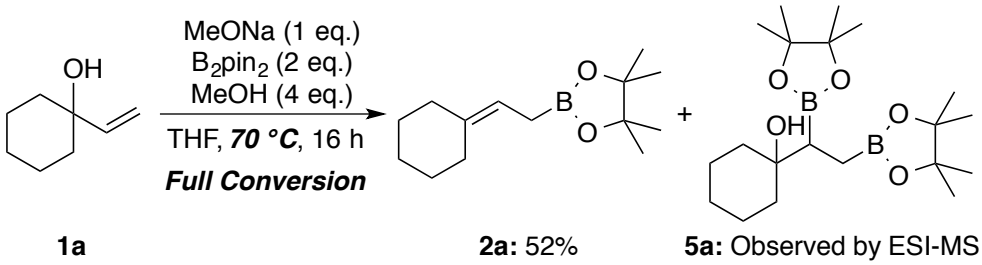
3-2. Allylboration Reaction (Table 3)

(4-chlorophenyl)(4-vinyltetrahydro-2*H*-pyran-4-yl)methanol (4)



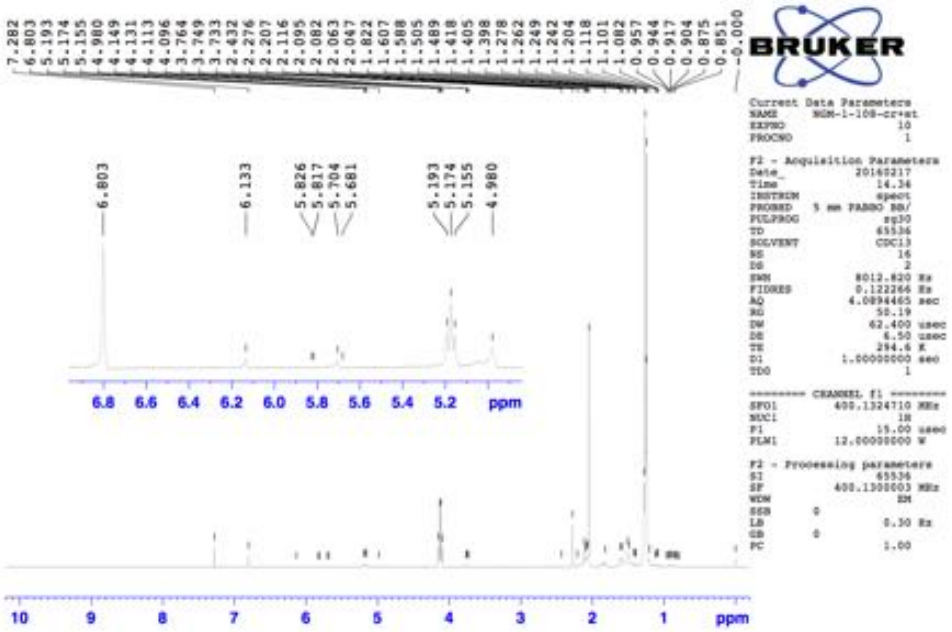
To a heatgun-dried schlenk tube were added compound **2f** (42.5 mg, 0.178 mmol), toluene (2 mL), aldehyde **3** (37.7 mg, 0.268 mmol), and $Sc(OTf)_3$. The resultant mixture was stirred at room temperature for 3 days, then quenched with NH_4Cl, extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and purified by column chromatography (eluent: hexane/EtOAc = 5 : 3). The product was obtained as a pale yellow liquid 89% yield (40.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.57-5.47 (m, 2H), 5.06 (d, *J* = 16.8 Hz, 1H), 4.35 (d, *J* = 4.0 Hz, 1H), 3.82-3.72 (m, 2H), 3.50 (t, *J* = 11.6 Hz, 1H), 3.46 (t, *J* = 11.6 Hz, 1H), 2.20-2.16 (m, 1H), 1.86-1.66 (m, 3H), 1.30 (d, *J* = 13.6 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 139.61, 138.48, 133.44, 129.23, 127.73, 119.16, 80.62, 64.25, 63.90, 43.68, 32.97, 31.71. **IR (ATR-IR):** 3399, 2953, 2862, 1490, 1409, 1262, 1239, 1089, 1044, 1013, 921, 833, 760, 738, 541 cm^{-1}. **HRMS (ESI):** *m/z* calculated for $C_{14}H_{17}ClO_2$ $[M+Na]^+$ = 275.0809, found: 275.0799.

3-3. Reaction at 70 °C (Scheme 6)

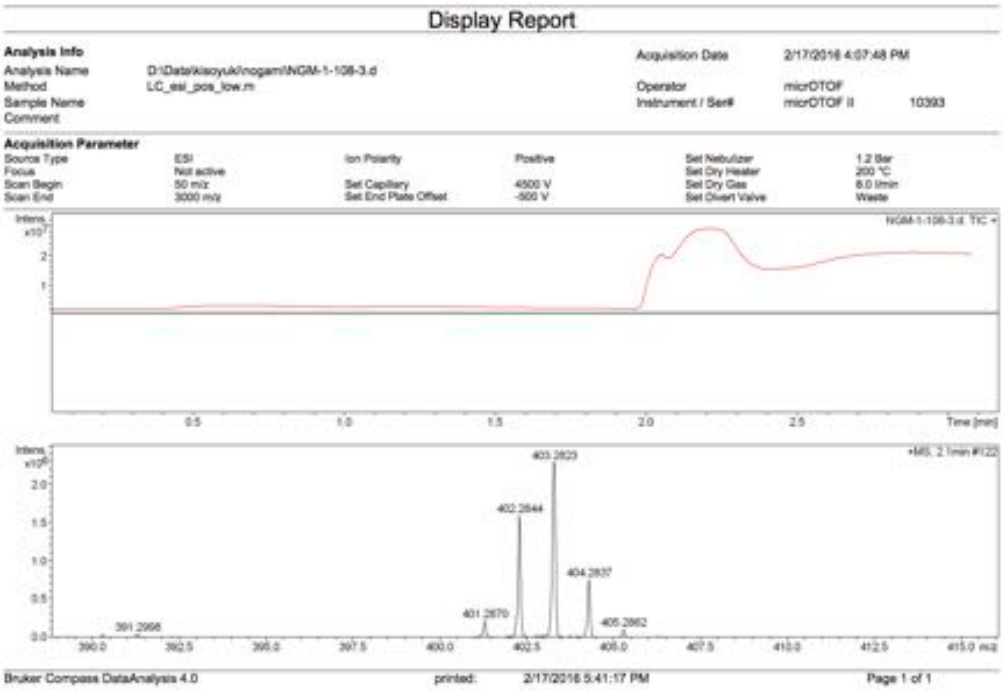


Following the **General Procedure**, the reaction was performed at 70 °C. After workup, extraction, drying the combined organic layer over Na_2SO_4, and filtration, the volatiles were carefully removed on a rotary evaporator under 120 hPa at 40 °C not to lose potentially remaining **1a**. Resultant residue was analyzed by ^{1}H NMR using mesitylene (24.7 mg) as an internal standard to give the desired product **2a** in 52% ^{1}H NMR yield. Allylic alcohol **1a** was observed neither in ^{1}H NMR nor GC-MS analyses of the crude mixture (Full conversion of **1a**). The formation of **5a** was confirmed by ESI-MS (+) analysis (*m/z* calculated for $C_{20}H_{38}B_2NaO_5$ $[M+Na]^+$ 403.2798).

^{1}H NMR Spectrum of the Crude Mixture:

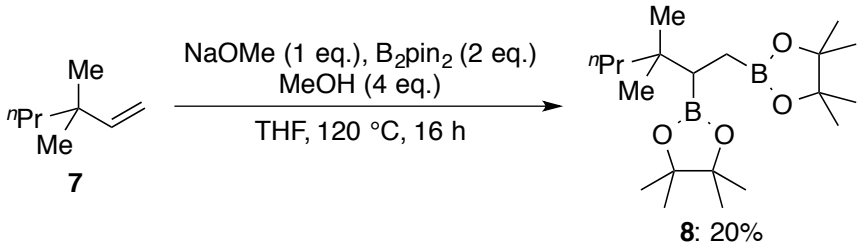


ESI-MS (+) Spectrum:



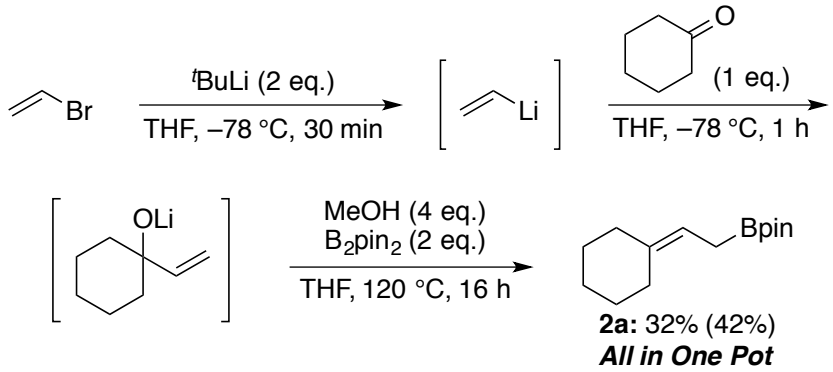
3-4. Diborylation Reaction (Scheme 7)

2,2'-(3,3-dimethylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8)



Following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 30 : 1), the titled compound was obtained as a colorless oil in 20% yield (38.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.25 (s, 12H), 1.225 (s, 6H), 1.217 (s, 6H), 1.19-1.12 (m, 4H), 1.05 (t, *J* = 8.0 Hz, 1H), 0.89 (s, 3H), 0.88-0.83 (m, 6H), 0.80 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 82.81, 82.65, 44.36, 34.68, 25.99, 25.18, 25.11, 24.89, 24.59, 17.14, 15.05. The carbon directly attached to the boron atom was not detected. **IR (ATR-IR):** 2979, 2958, 2932, 2872, 1469, 1368, 1309, 1401, 969, 848 cm^{-1}. **HRMS (ESI):** *m/z* calculated for $C_{20}H_{40}B_2O_4$ $[M+Na]^+$ =389.3005, found: 389.3023.

3-5. One Pot Reaction (Scheme 8)



A solution of vinyl bromide (1 M in THF, 1 mL, 1 mmol) were added THF (2 mL) and ^{t}BuLi (1.55 M in pentane, 1.42 mL, 2.2 mmol) at –78 °C. After the resultant mixture was stirred at the same temperature for 30 min, cyclohexanone (103.7 μL, 1 mmol) was added to the mixture. The reaction was allowed to warm to rt, while stirred for 1 h. Then, the solution was diluted by THF (3 mL), and MeOH (164 μL, 4 mmol) and B_2pin_2 (507.9 mg, 2 mmol) were added. The resultant mixture was immersed in a pre-heated oil bath at 120 °C and stirred for 16 h. After workup and purification following the **General Procedure** (eluent for column chromatography: hexane/EtOAc = 40 : 1), the titled compound was obtained as a colorless oil in 32% yield (76.3 mg).

4. References

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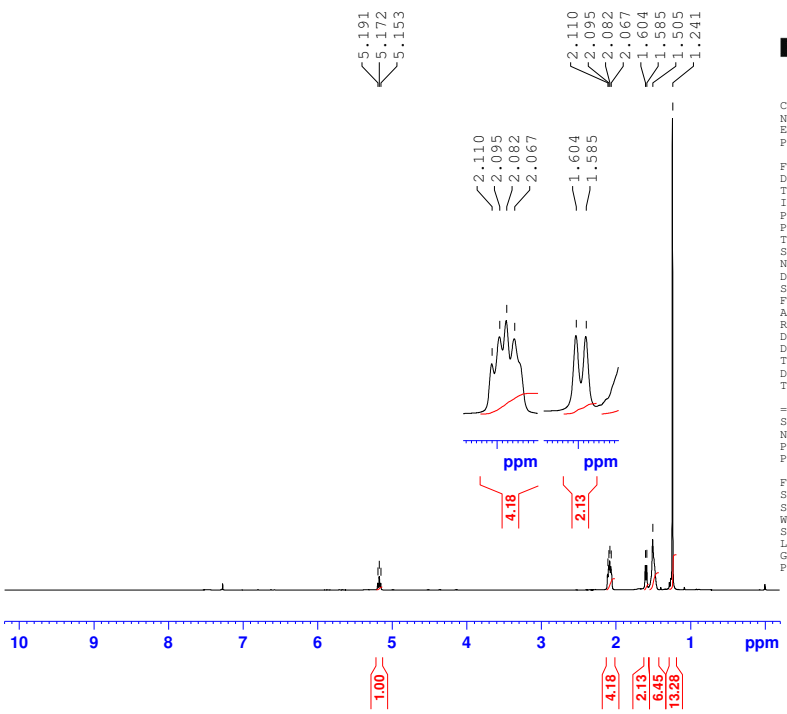
5. Copies of NMR Spectra

2-(2-cyclohexylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)

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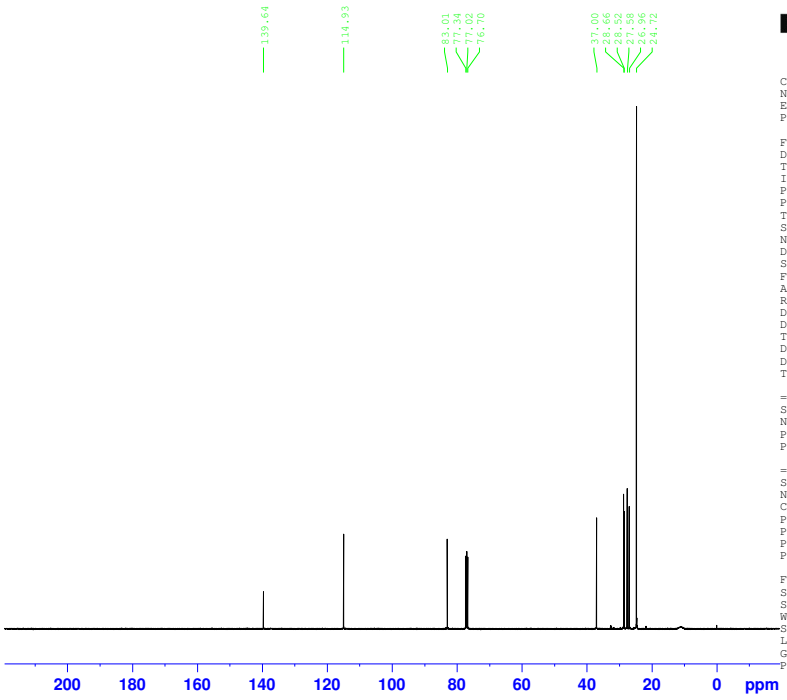


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FIDRES         0.366798 Hz
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DE                6.50 usec
TE               299.9 K
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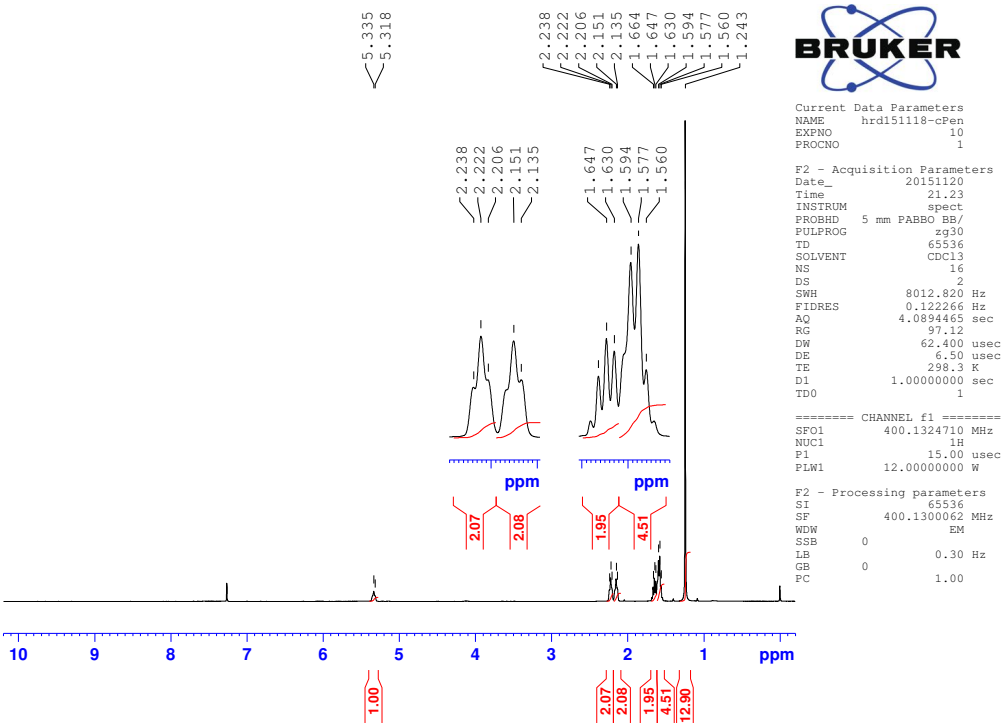
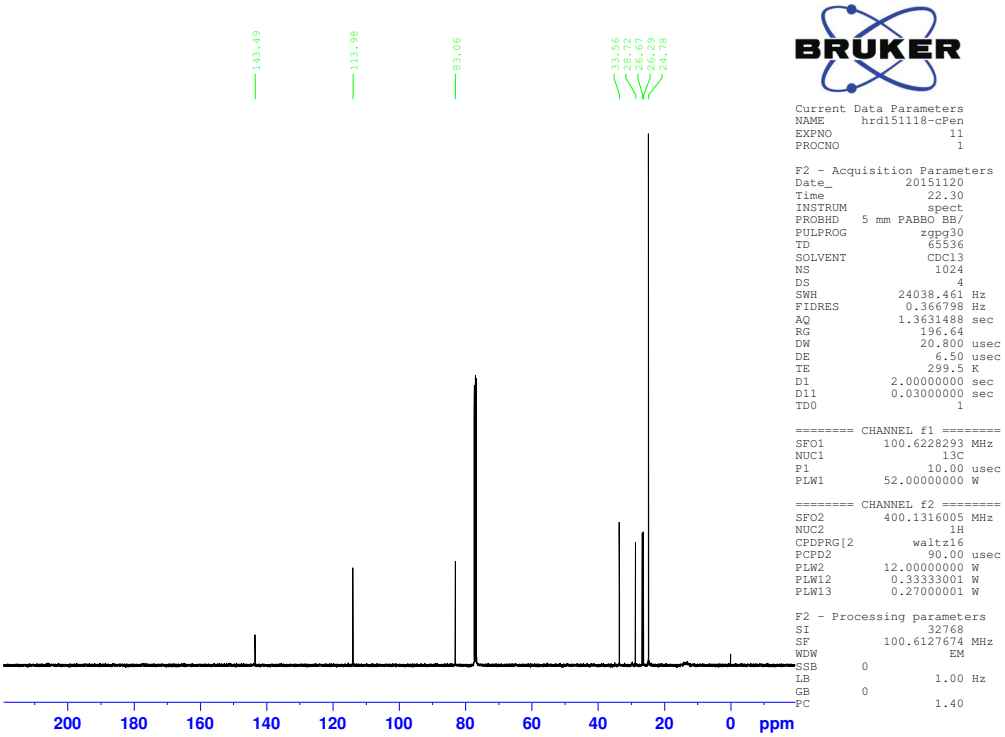
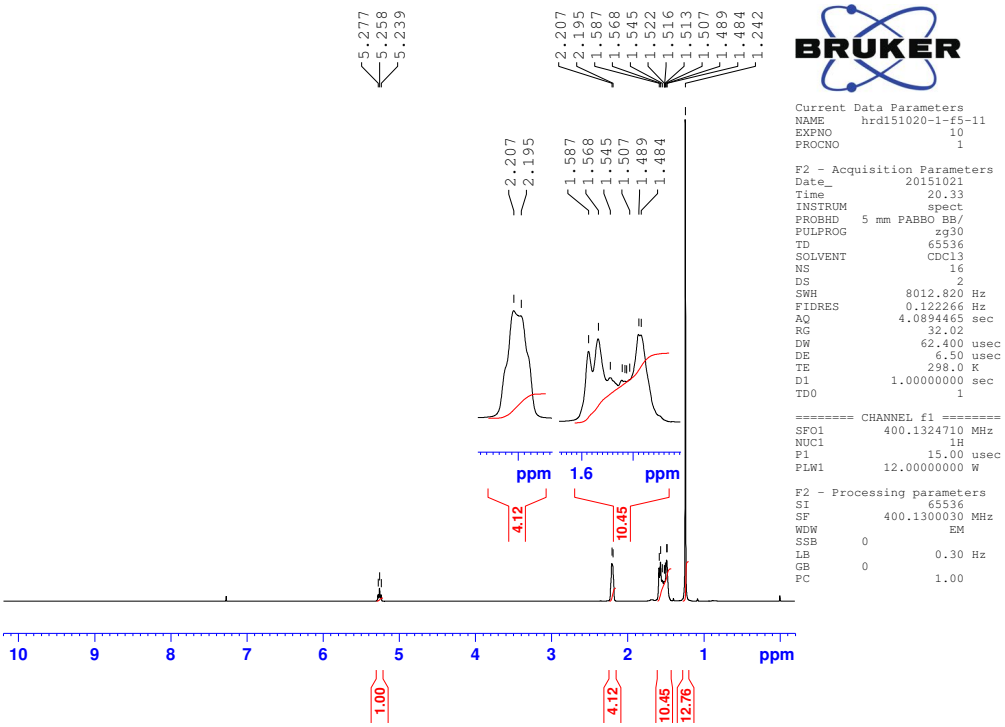
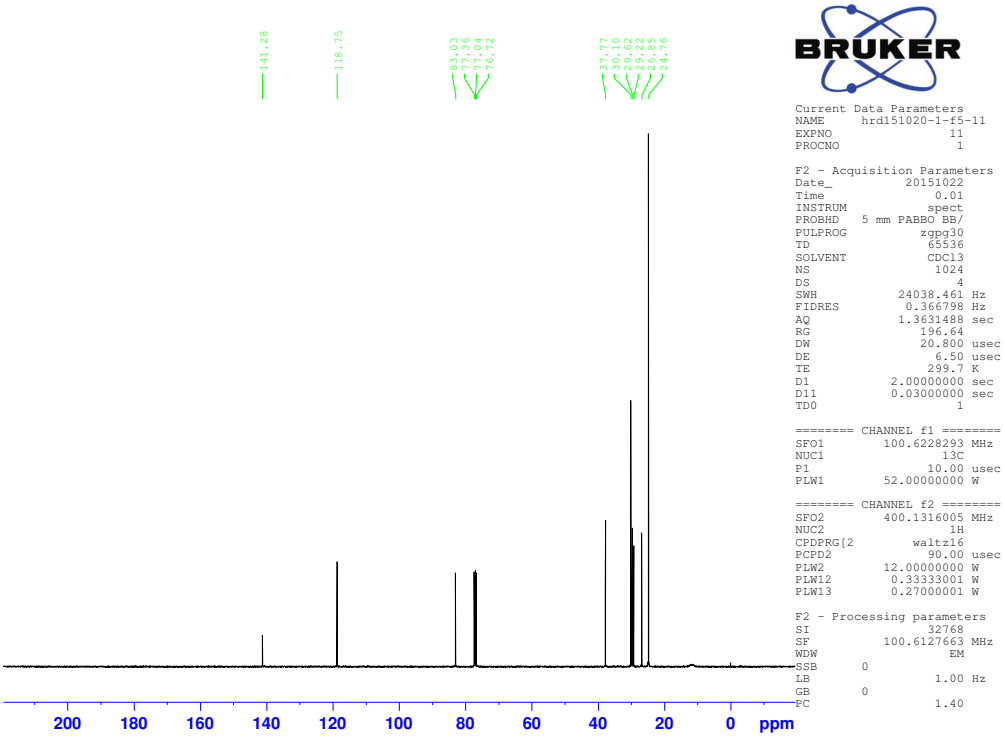
2-(2-cyclopentylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)





2-(2-cycloheptylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)





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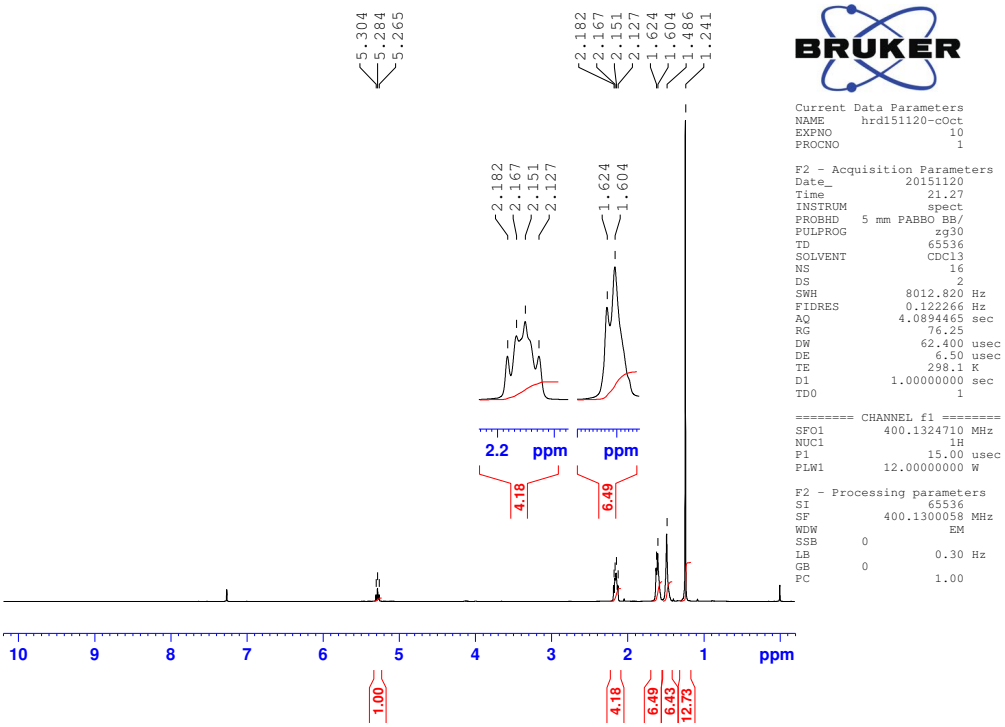


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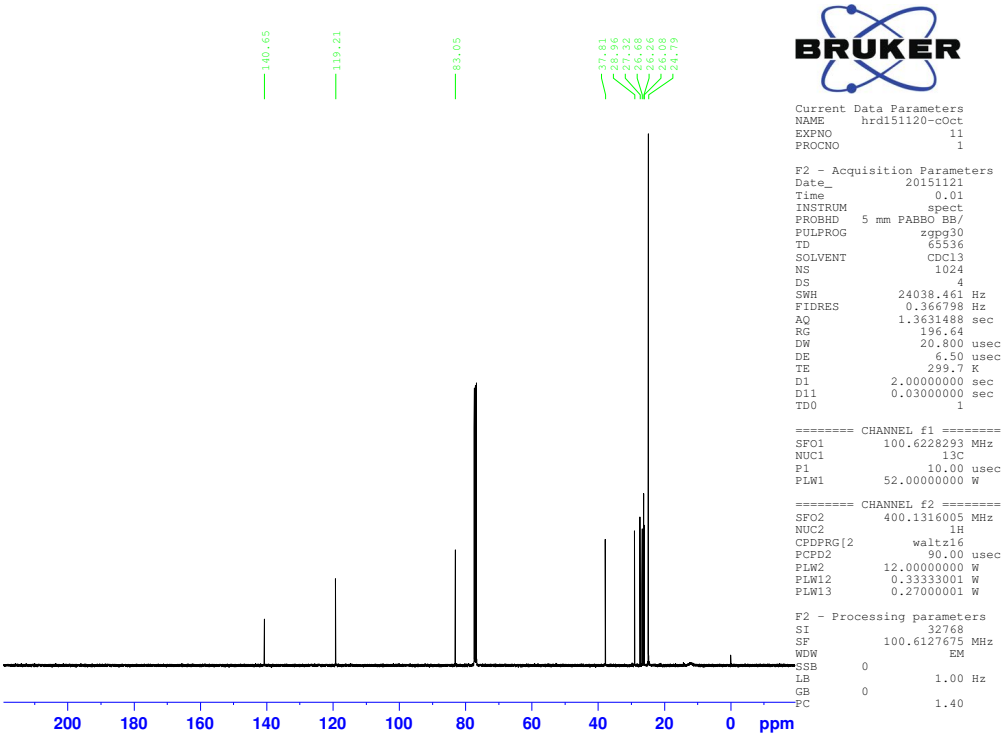


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F2 - Processing parameters
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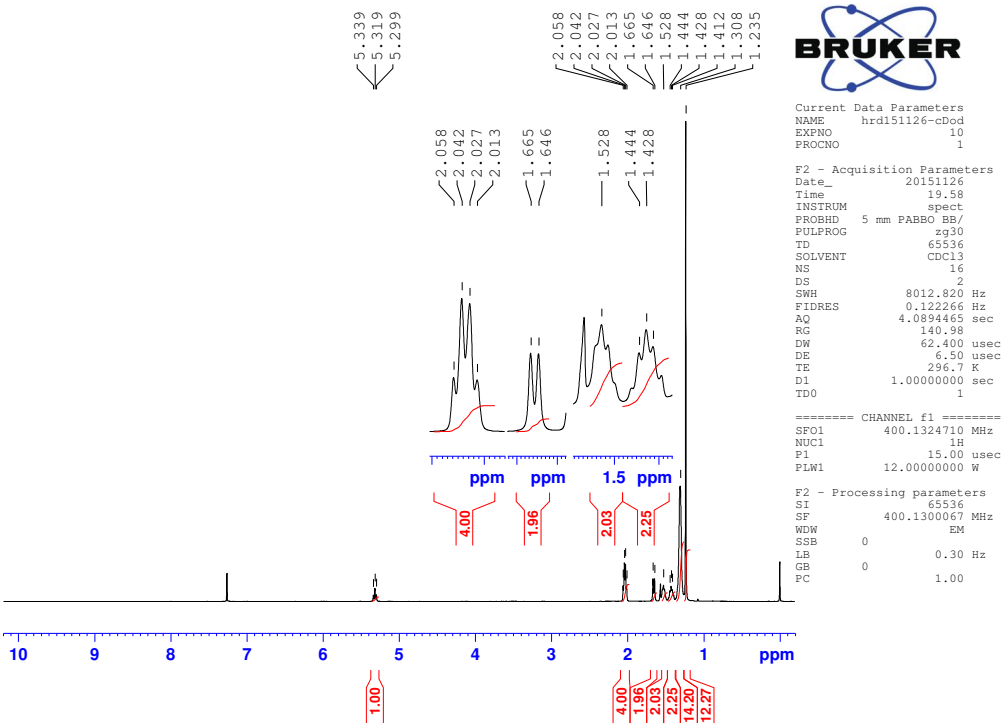
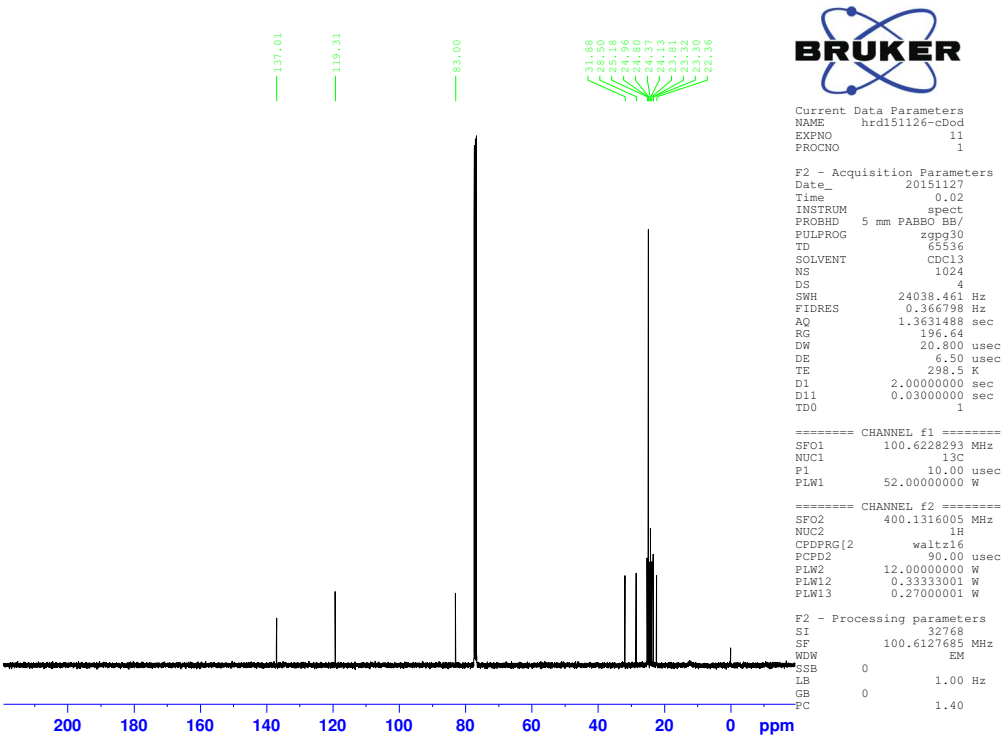
2-(2-cyclododecylideneethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)





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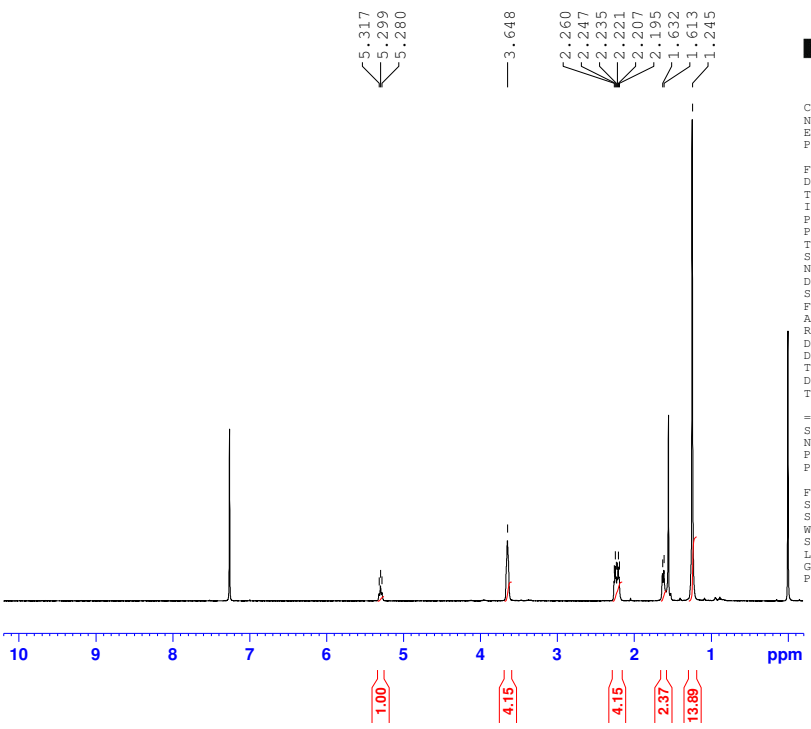


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TE                  296.6 K
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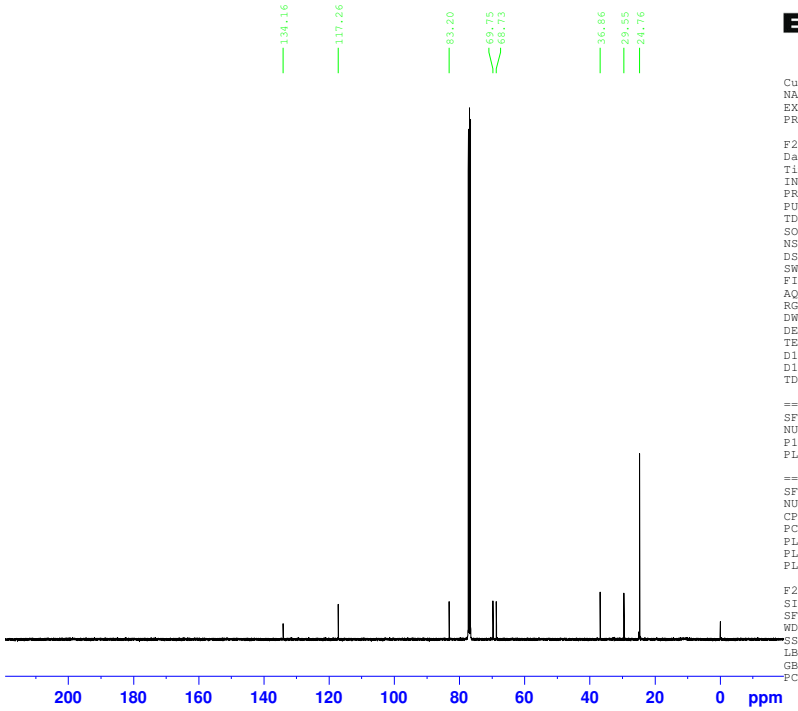


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PLW13         0.27000001 W

F2 - Processing parameters
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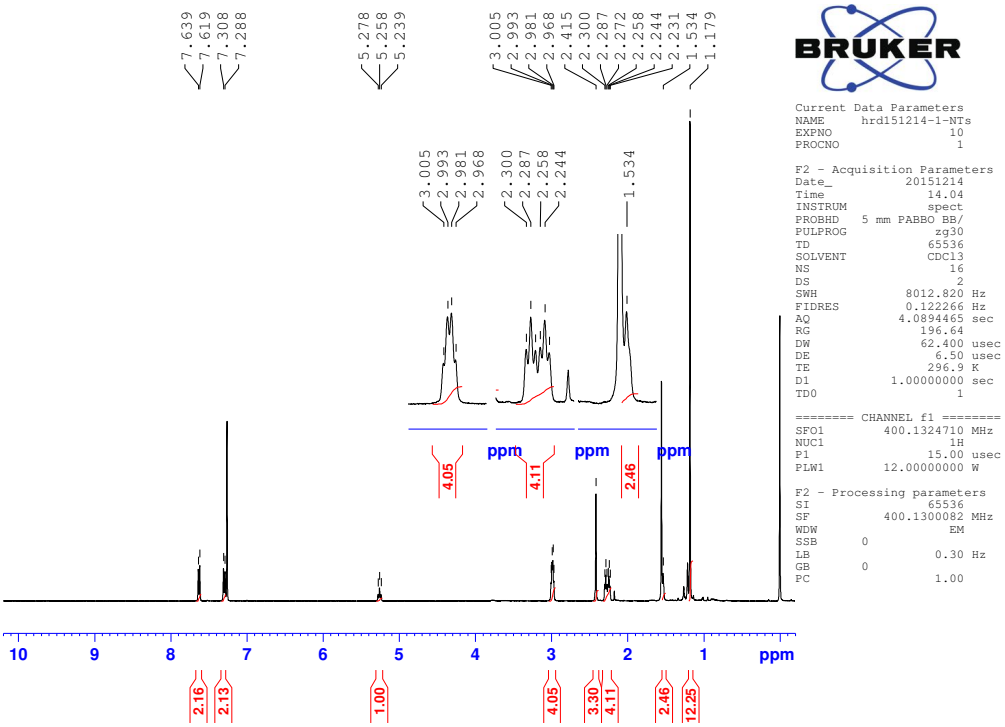
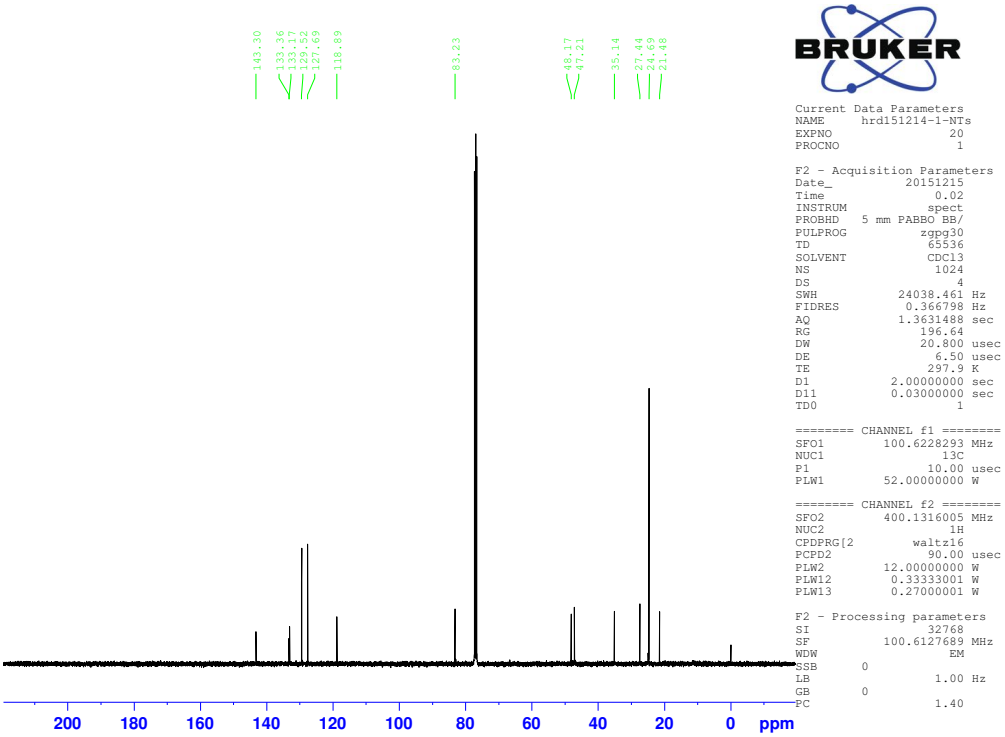
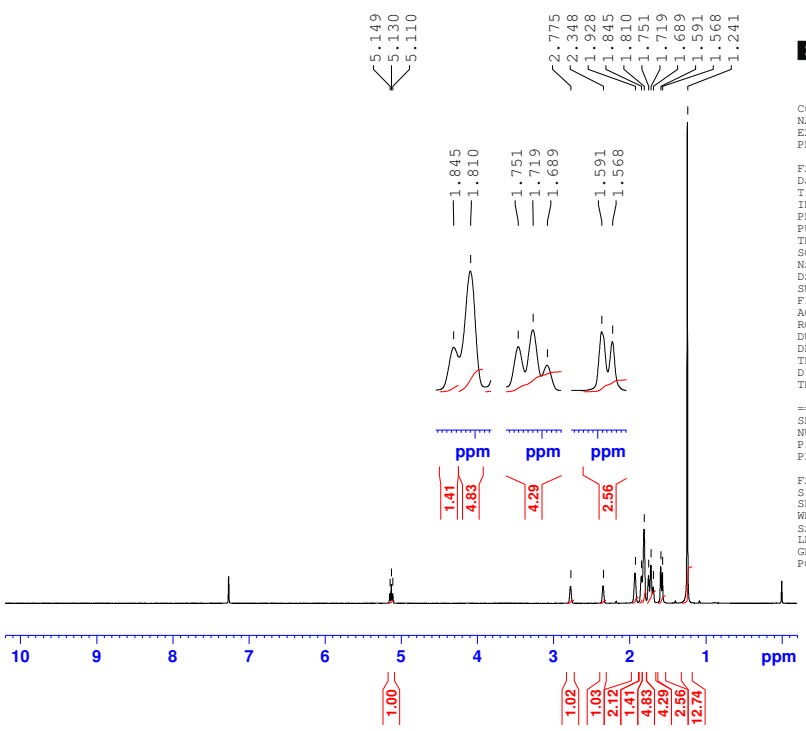
4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-1-tosylpiperidine (2g)





2-(2-((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)

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FIDRES            0.122266 Hz
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RG                    110.61
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TE                    294.1 K
D1                1.00000000 sec
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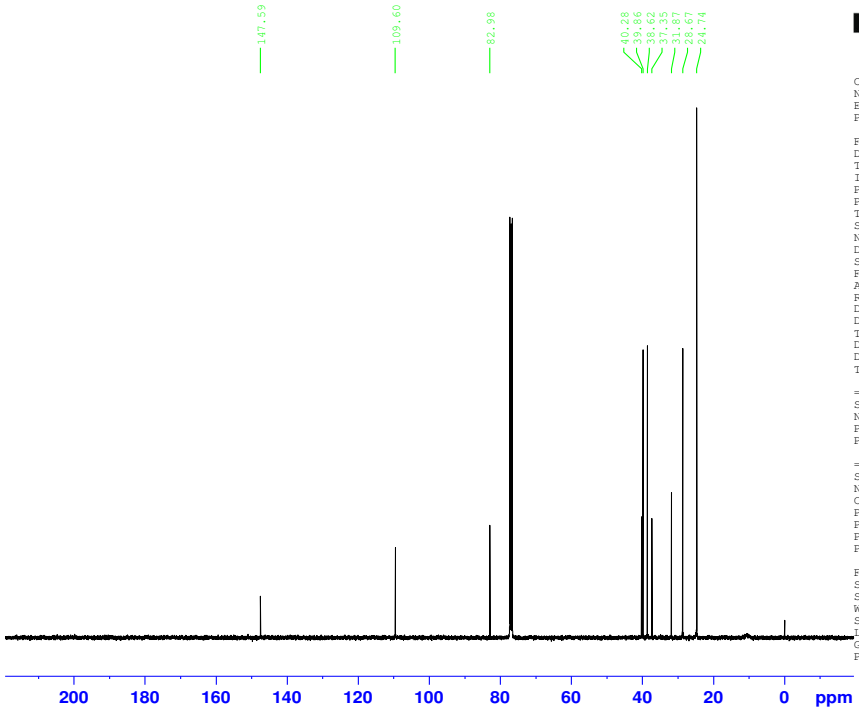


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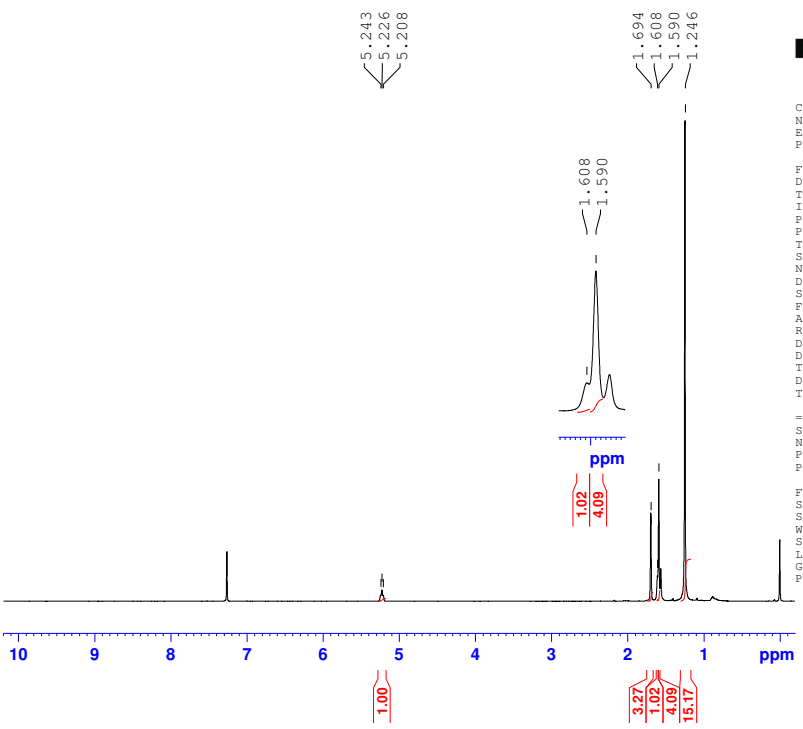
DW                    20.800 usec
DE                     6.50 usec
TE                    295.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                      13C
P1                      10.00 usec
PLW1            52.00000000 W

======== CHANNEL f2 ========
SFO2             400.1316005 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2            12.00000000 W
PLW12            0.33333001 W
PLW13            0.27000001 W

F2 - Processing parameters
SI                        32768
SF              100.6127695 MHz
WDW                          EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

4,4,5,5-tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (2i)

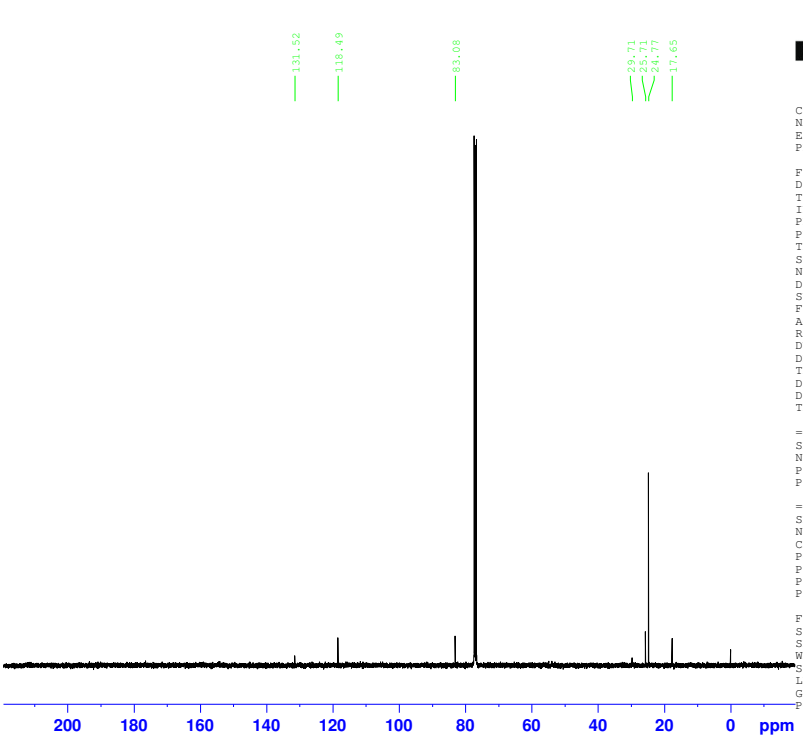



```
Current Data Parameters
NAME      hrd160114-MeMef7-10
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160114
Time              20.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG              196.64
DW              62.400 usec
DE               6.50 usec
TE              294.9 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1               1H
P1              15.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI               65536
SF          400.1300073 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```




```
Current Data Parameters
NAME      hrd160114-MeMef7-10
EXPNO                   21
PROCNO                   1

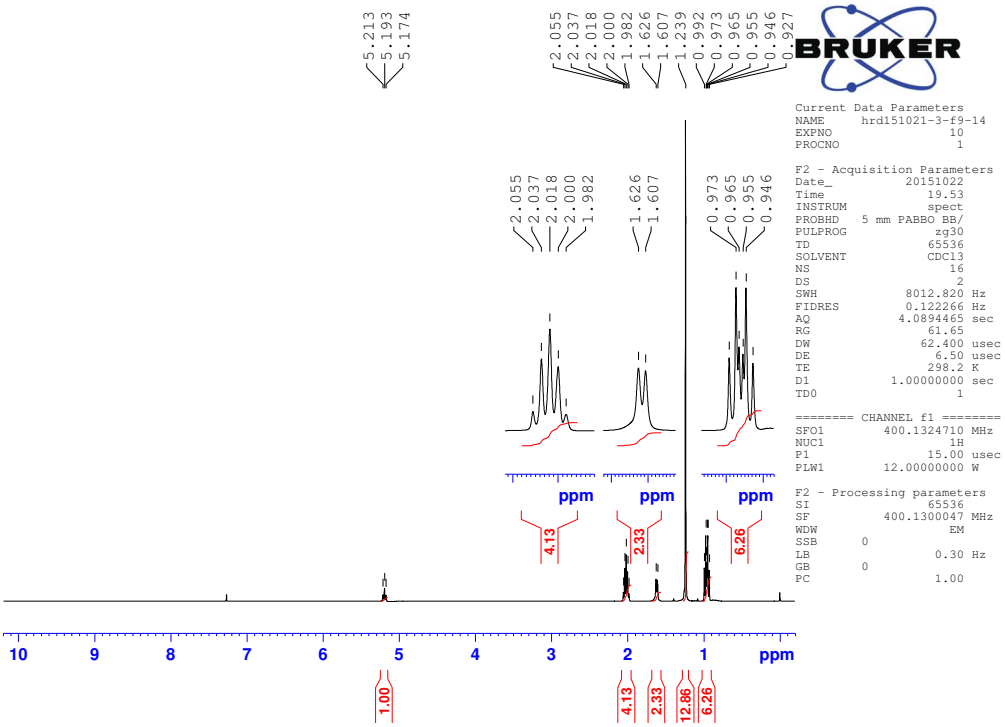
F2 - Acquisition Parameters
Date_           20160115
Time              2.03
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD               65536
SOLVENT           CDCl3
NS                1024
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG              196.64
DW              20.800 usec
DE               6.50 usec
TE              296.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

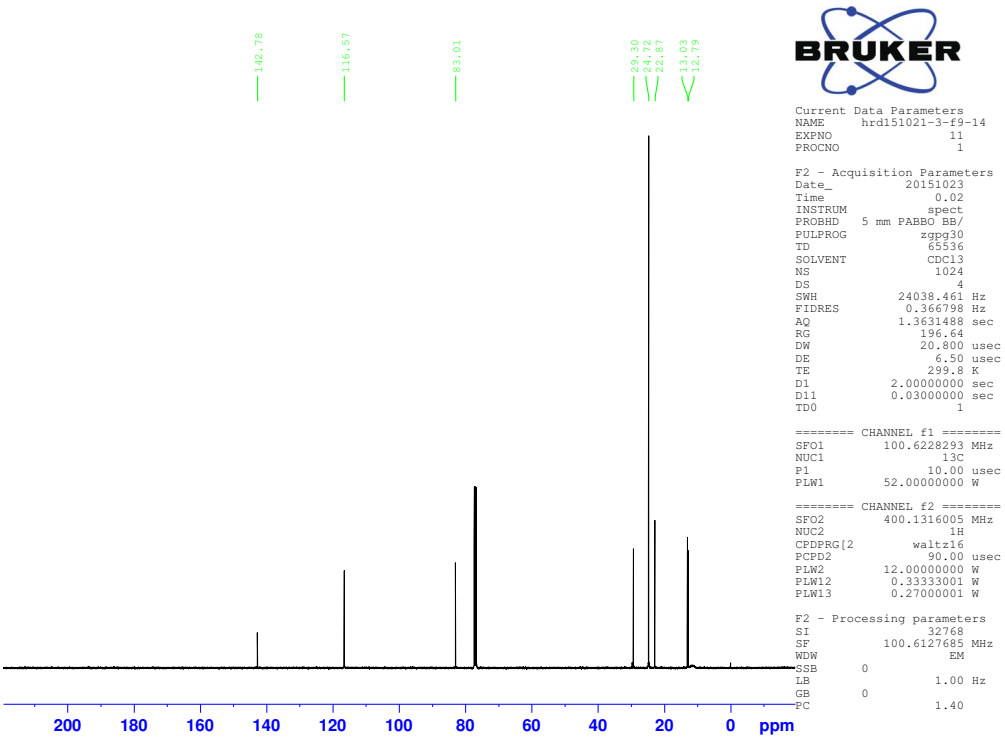
======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1               13C
P1              10.00 usec
PLW1        52.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2           90.00 usec
PLW2        12.00000000 W
PLW12        0.33333001 W
PLW13        0.27000001 W

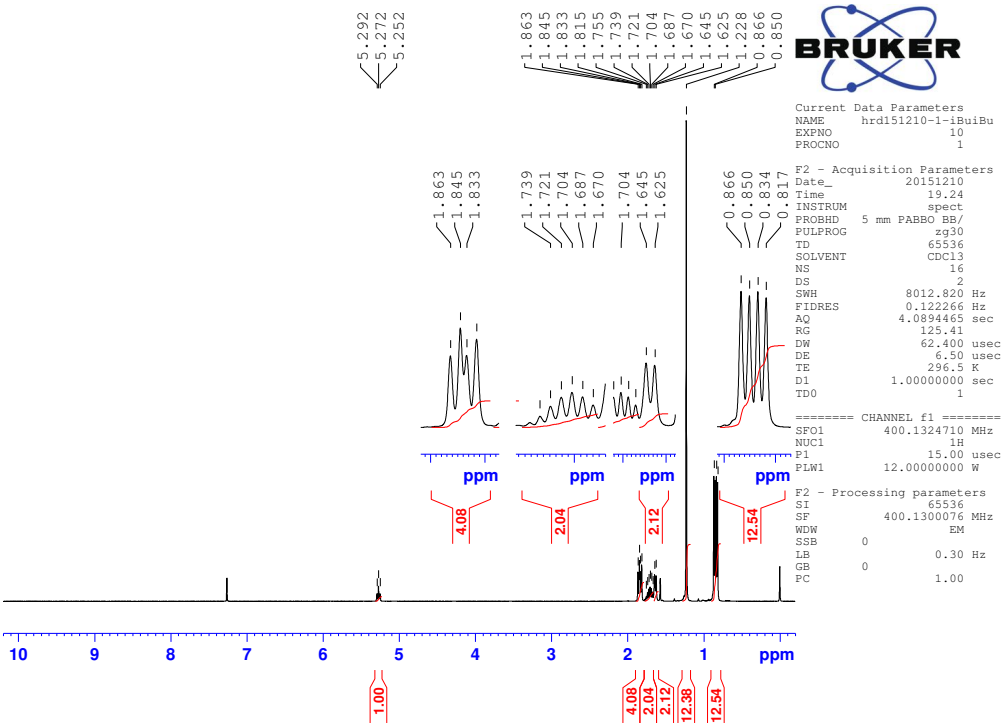
F2 - Processing parameters
SI               32768
SF          100.6127685 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

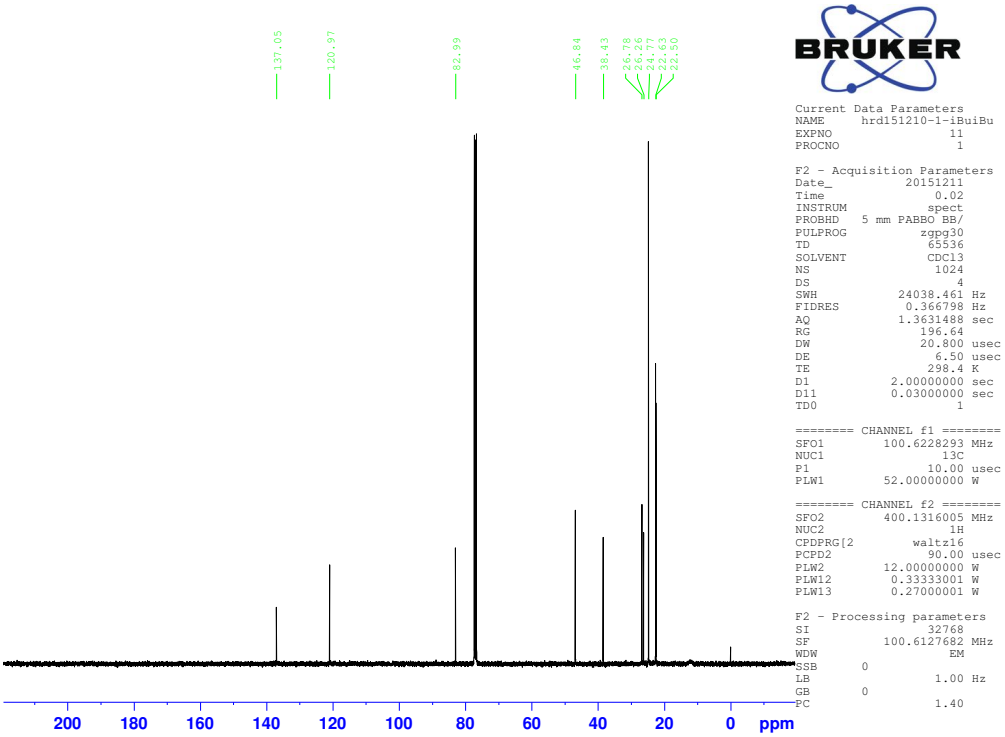
2-(3-ethylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)



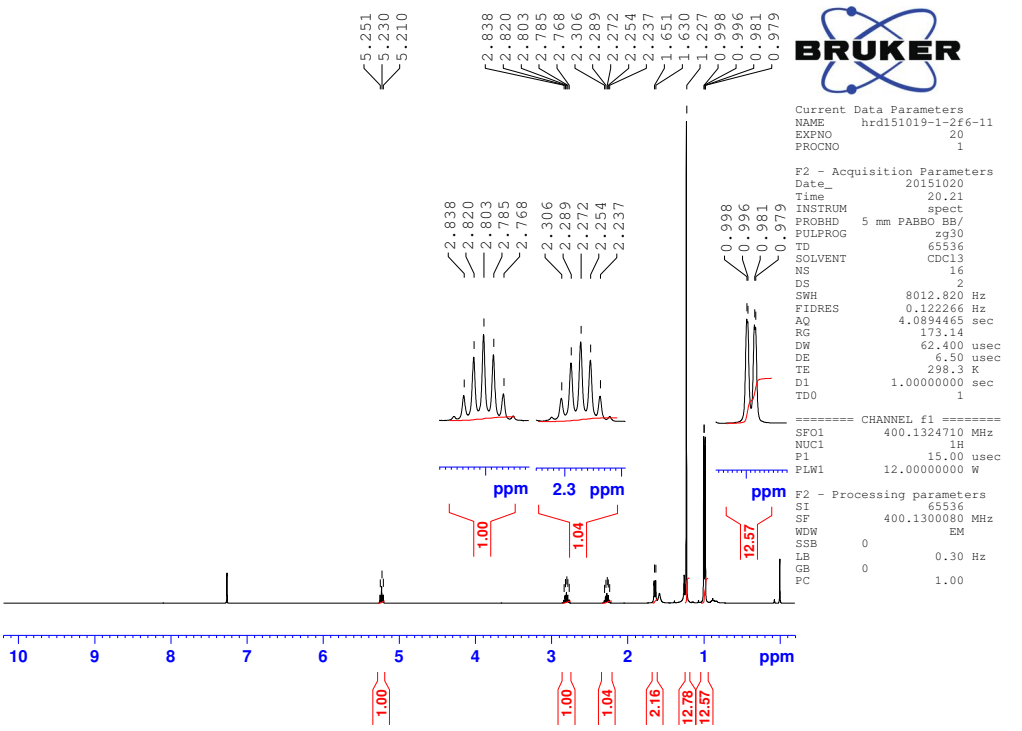


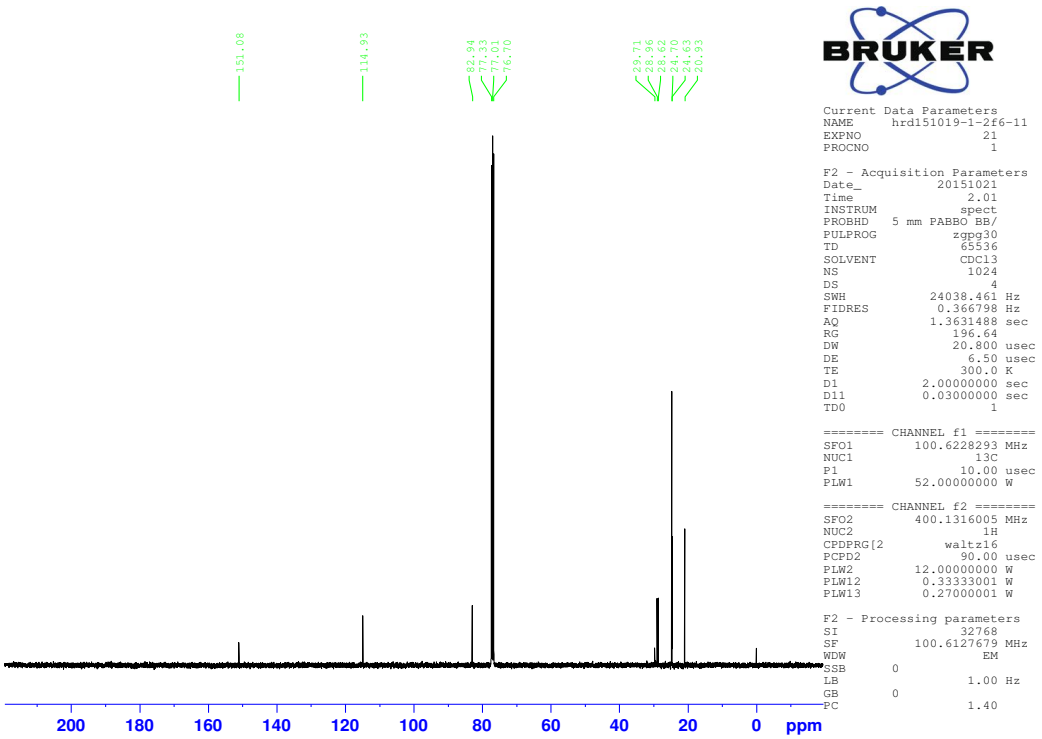
2-(3-isobutyl-5-methylhex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



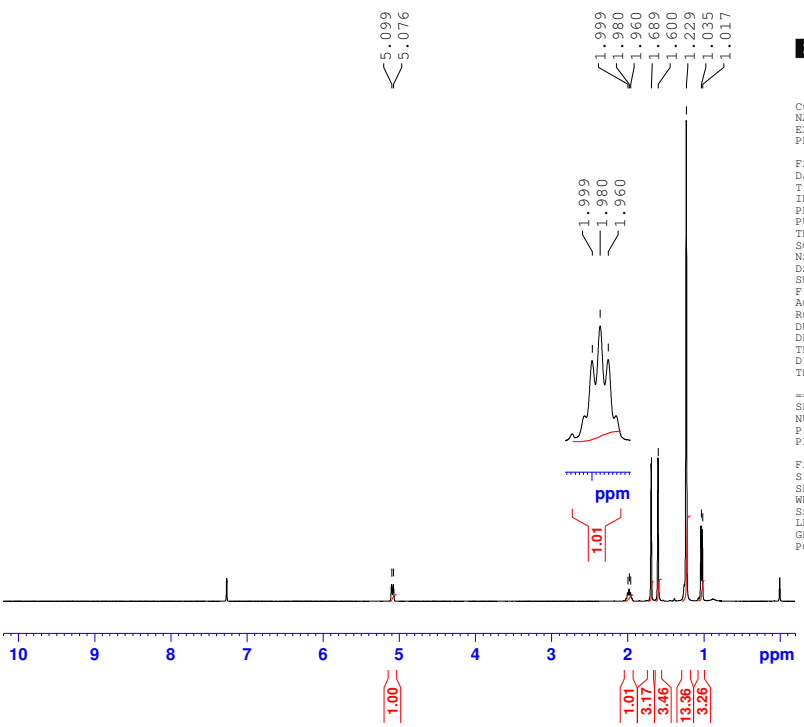


2-(3-isopropyl-4-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)





4,4,5,5-tetramethyl-2-(4-methylpent-3-en-2-yl)-1,3,2-dioxaborolane (2n)

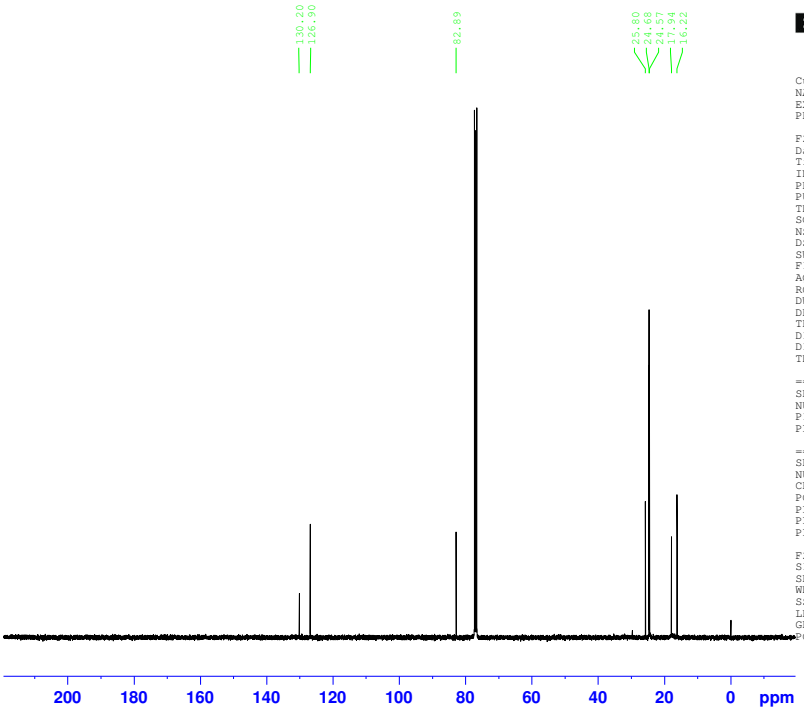



```
Current Data Parameters
NAME      hrd160114-MeMe3Mef5-8
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160114
Time              20.26
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD                65536
SOLVENT           CDC13
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894465 sec
RG                125.41
DW              62.400 usec
DE               6.50 usec
TE               294.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1               1H
P1               15.00 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                65536
SF           400.1300064 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```




```
Current Data Parameters
NAME      hrd160114-MeMe3Mef5-8
EXPNO                    21
PROCNO                    1

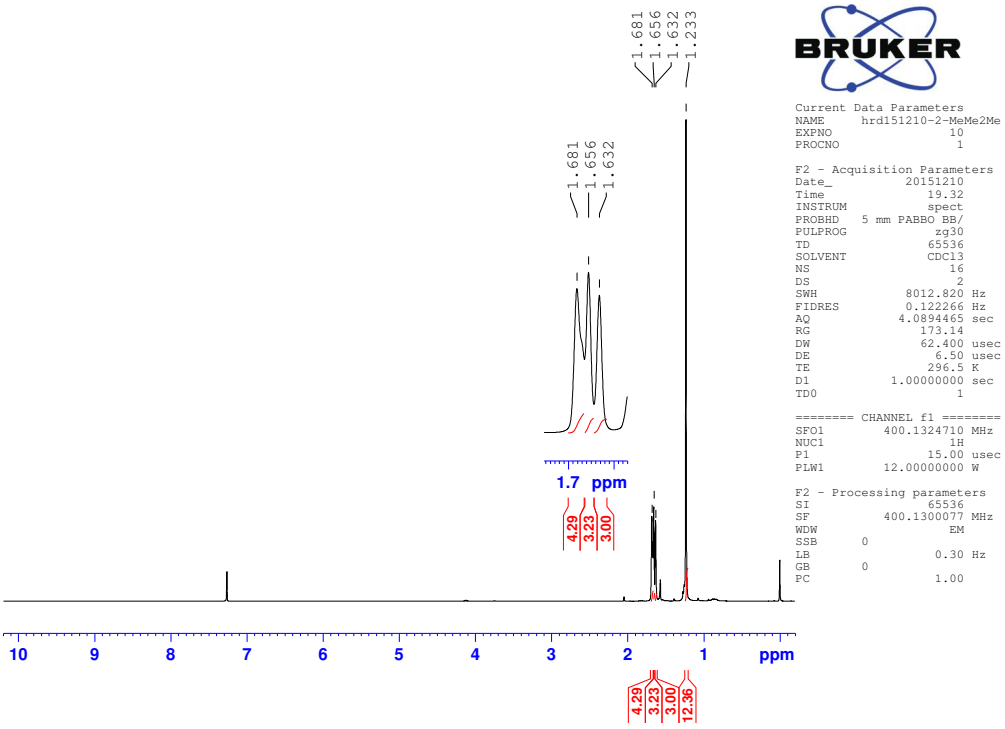
F2 - Acquisition Parameters
Date_           20160115
Time              1.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                65536
SOLVENT           CDC13
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                196.64
DW              20.800 usec
DE               6.50 usec
TE               296.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1              13C
P1               10.00 usec
PLW1         52.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         12.00000000 W
PLW12         0.33333001 W
PLW13         0.27000001 W

F2 - Processing parameters
SI                32768
SF           100.6127688 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

2-(2,3-dimethylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)

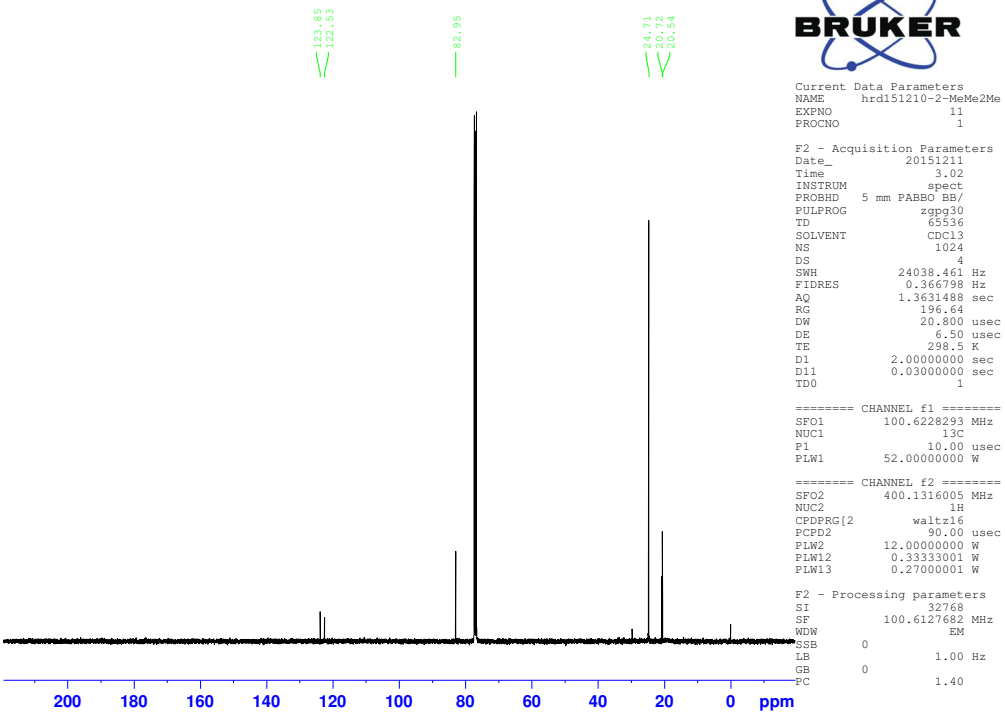



```
Current Data Parameters
NAME      hrd151210-2-MeMe2Me
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151210
Time                19.32
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894465 sec
RG                  173.14
DW                  62.400 usec
DE                   6.50 usec
TE                 296.5 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1300077 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```




```
Current Data Parameters
NAME      hrd151210-2-MeMe2Me
EXPNO                  11
PROCNO                  1

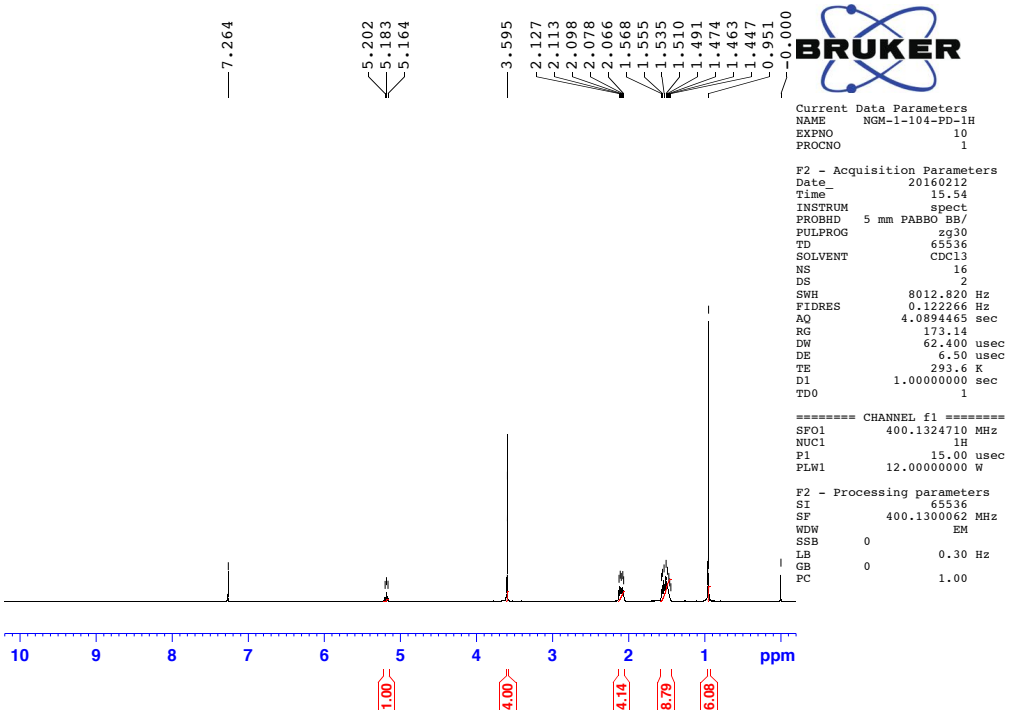
F2 - Acquisition Parameters
Date_            20151211
Time                 3.02
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                  196.64
DW                  20.800 usec
DE                   6.50 usec
TE                 298.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

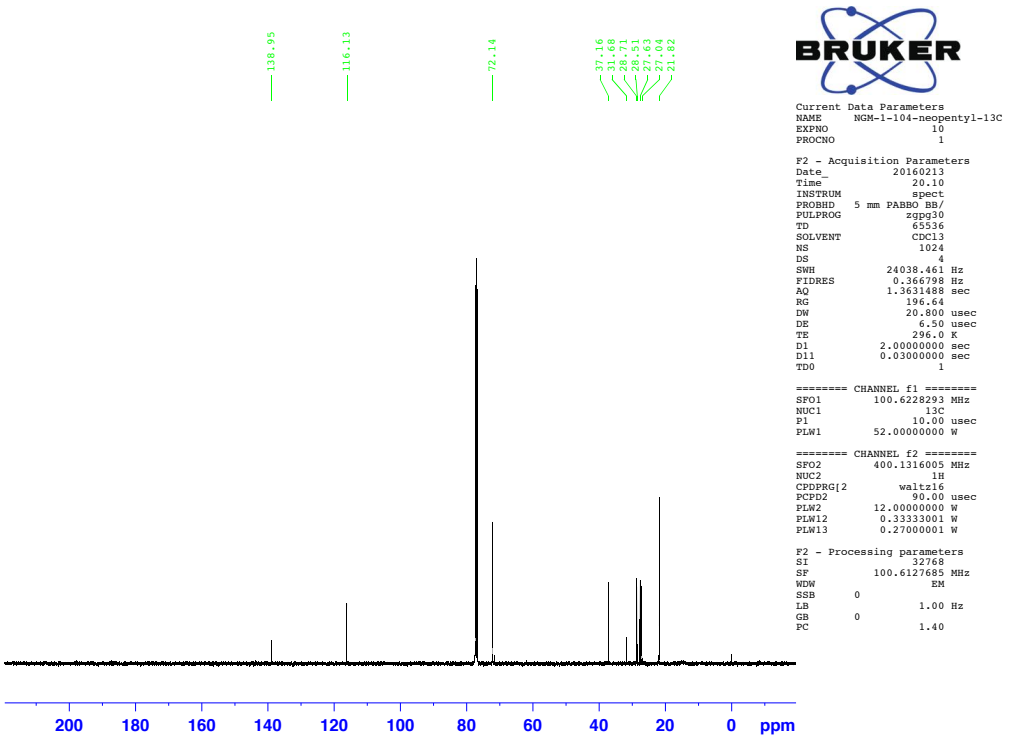
======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                   13C
P1                  10.00 usec
PLW1          52.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          12.00000000 W
PLW12          0.33333001 W
PLW13          0.27000001 W

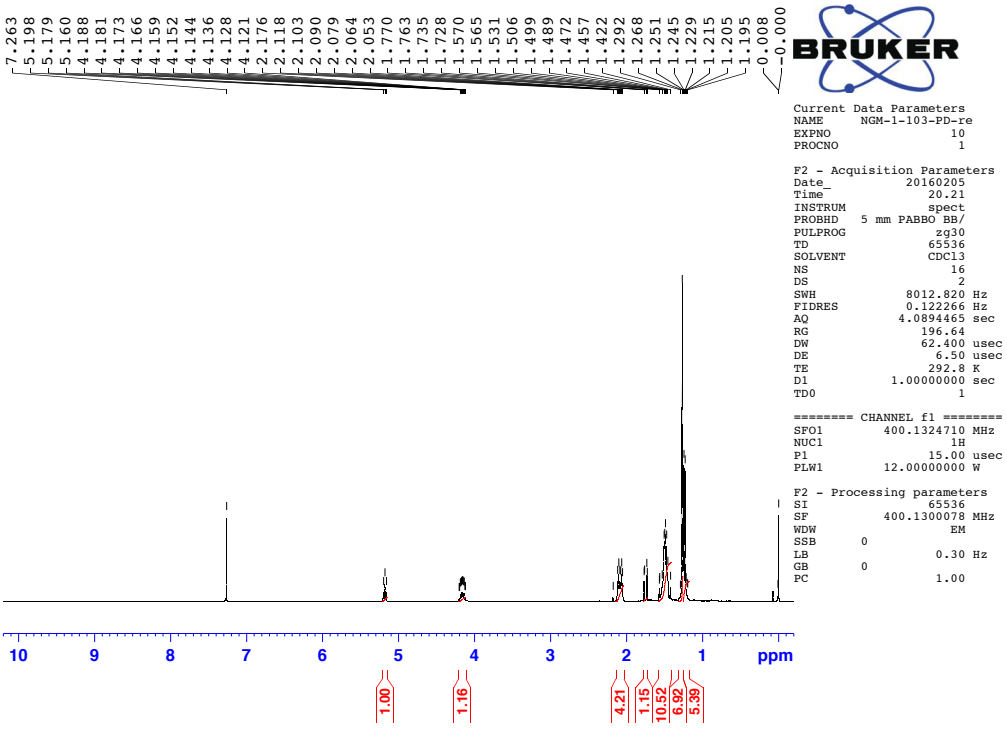
F2 - Processing parameters
SI                 32768
SF            100.6127682 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

2-(2-cyclohexylideneethyl)-5,5-dimethyl-1,3,2-dioxaborinane (2p)





2-(2-cyclohexylideneethyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2q)

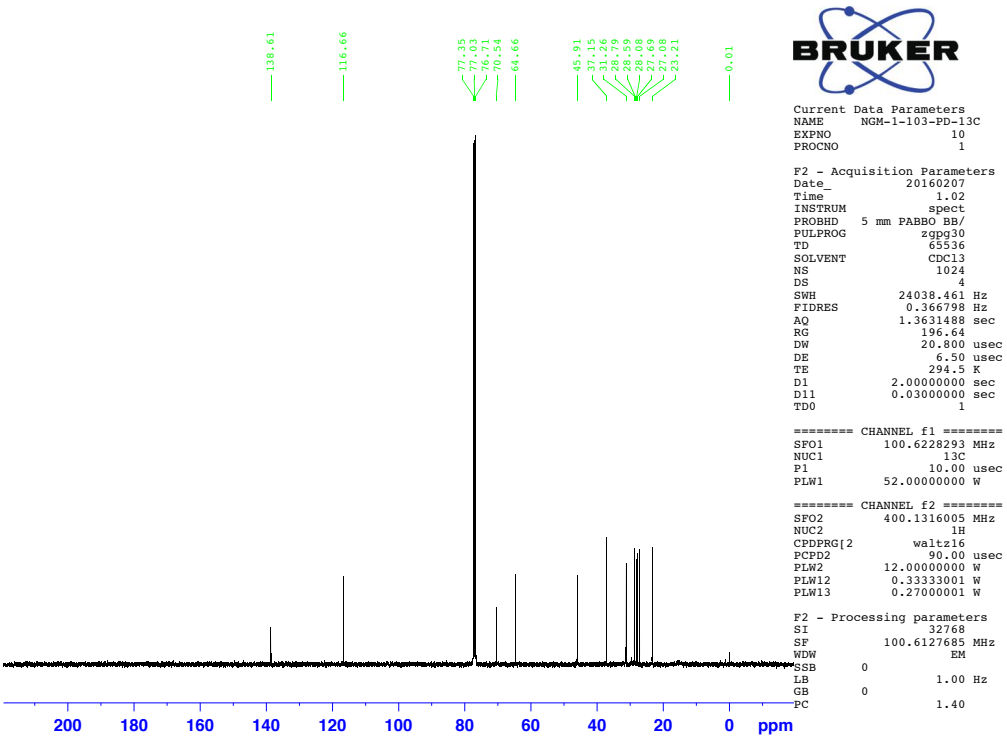



```
Current Data Parameters
NAME      NGM-1-103-PD-re
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160205
Time              20.21
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894465 sec
RG                196.64
DW                62.400 usec
DE                 6.50 usec
TE                292.8 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI               65536
SF           400.1300078 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```




```
Current Data Parameters
NAME      NGM-1-103-PD-13C
EXPNO                 10
PROCNO                 1

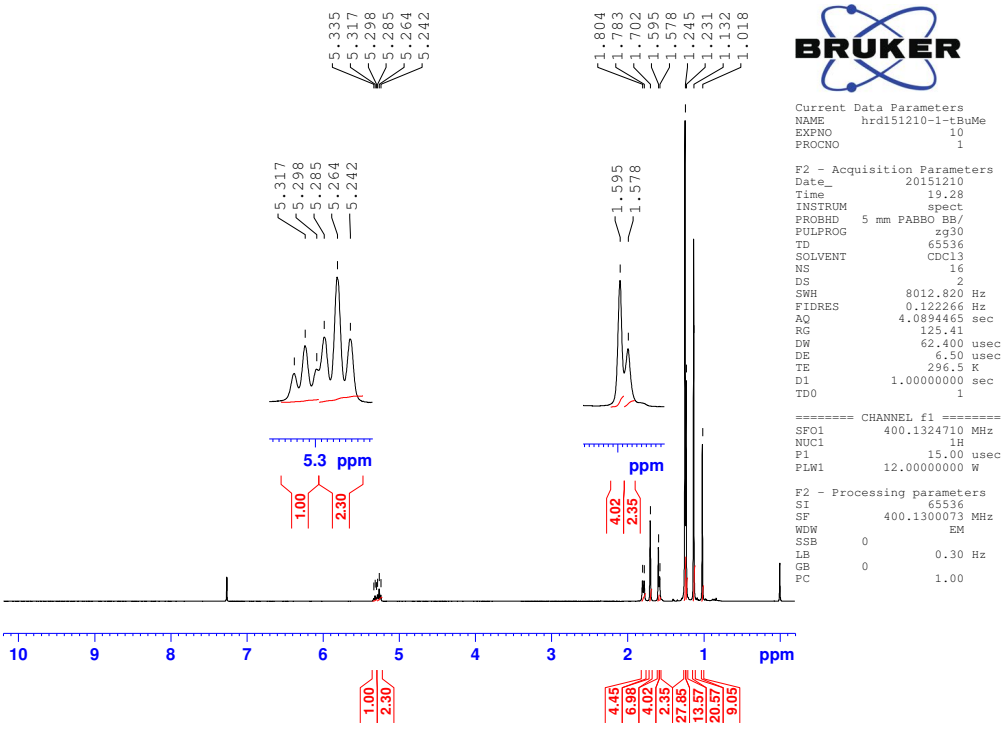
F2 - Acquisition Parameters
Date_           20160207
Time              1.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD               65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                196.64
DW                20.800 usec
DE                 6.50 usec
TE                294.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1

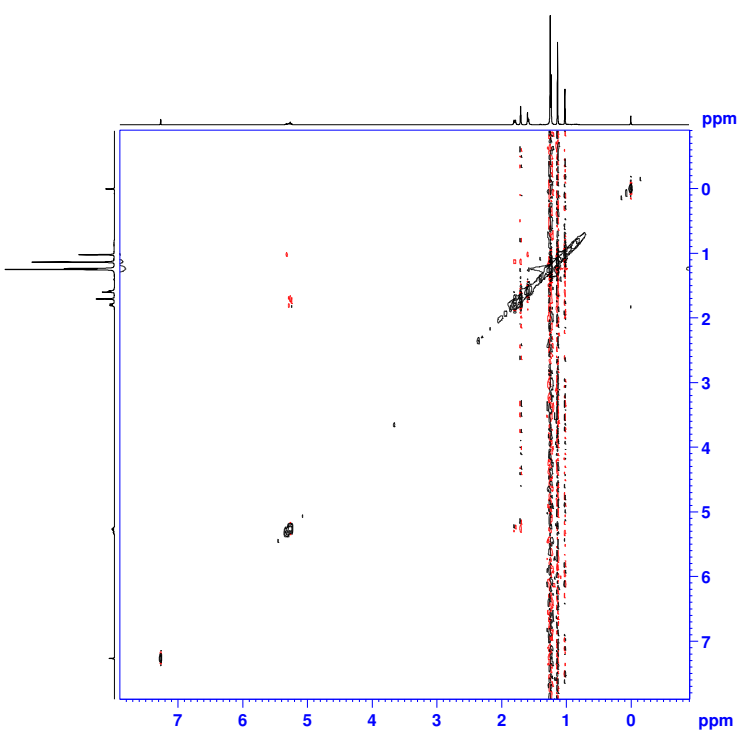
======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                10.00 usec
PLW1         52.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         12.00000000 W
PLW12         0.33333001 W
PLW13         0.27000001 W

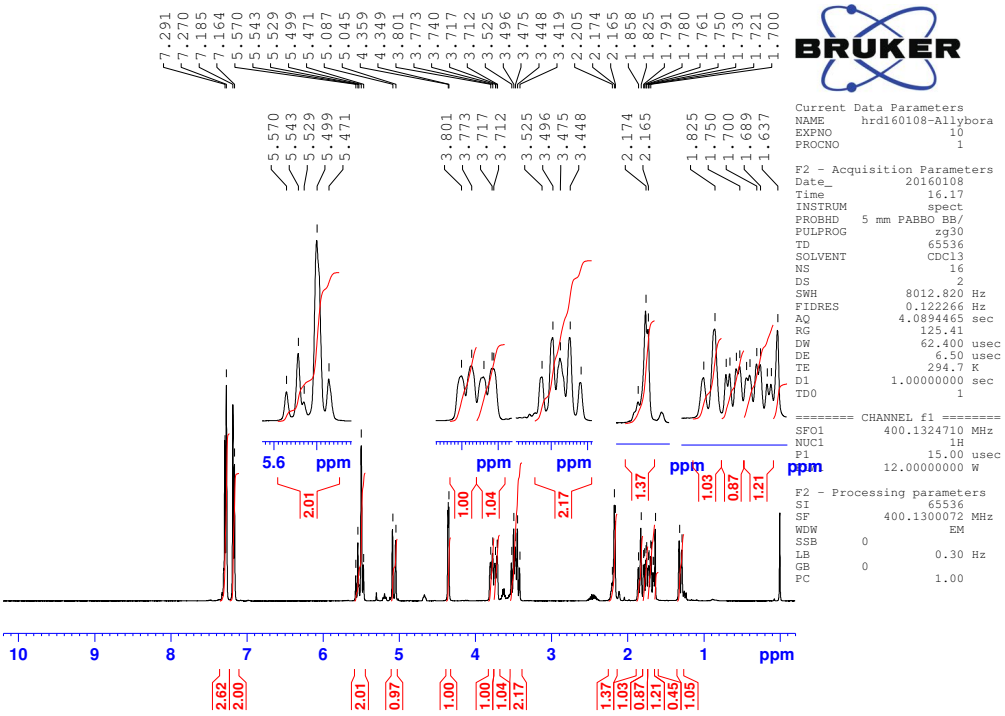
F2 - Processing parameters
SI               32768
SF           100.6127685 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

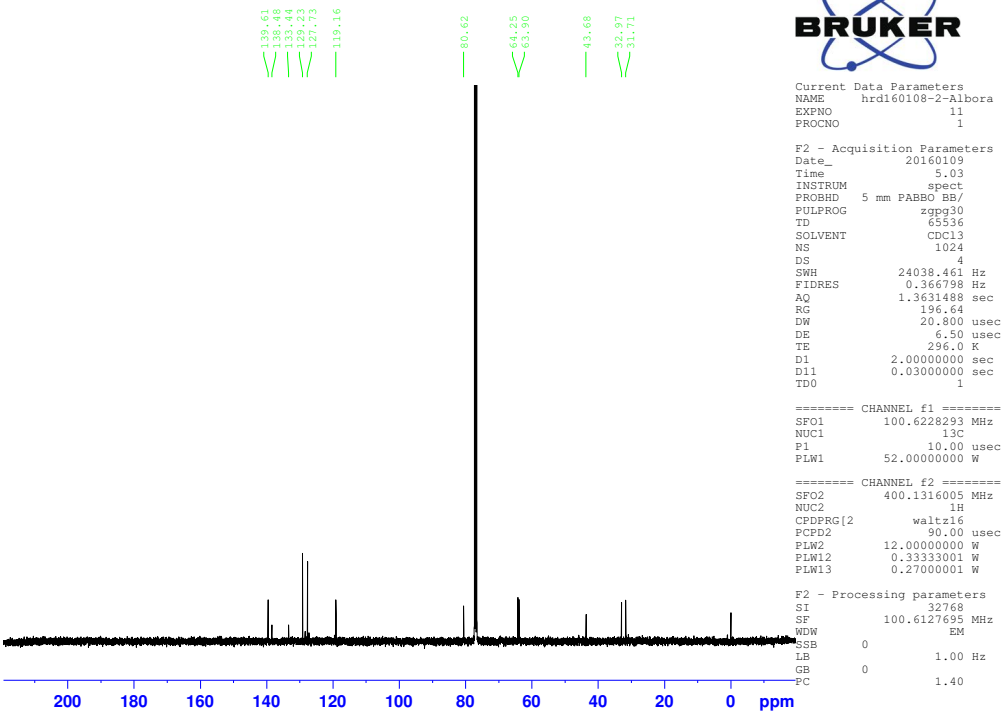
4,4,5,5-tetramethyl-2-(3,4,4-trimethylpent-2-en-1-yl)-1,3,2-dioxaborolane (2r)





(4-chlorophenyl)(4-vinyltetrahydro-2*H*-pyran-4-yl)methanol (4)





2,2'-(3,3-dimethylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8)