

Supporting Information

Catalyst-free and Solvent-free Hydroboration of Ketones

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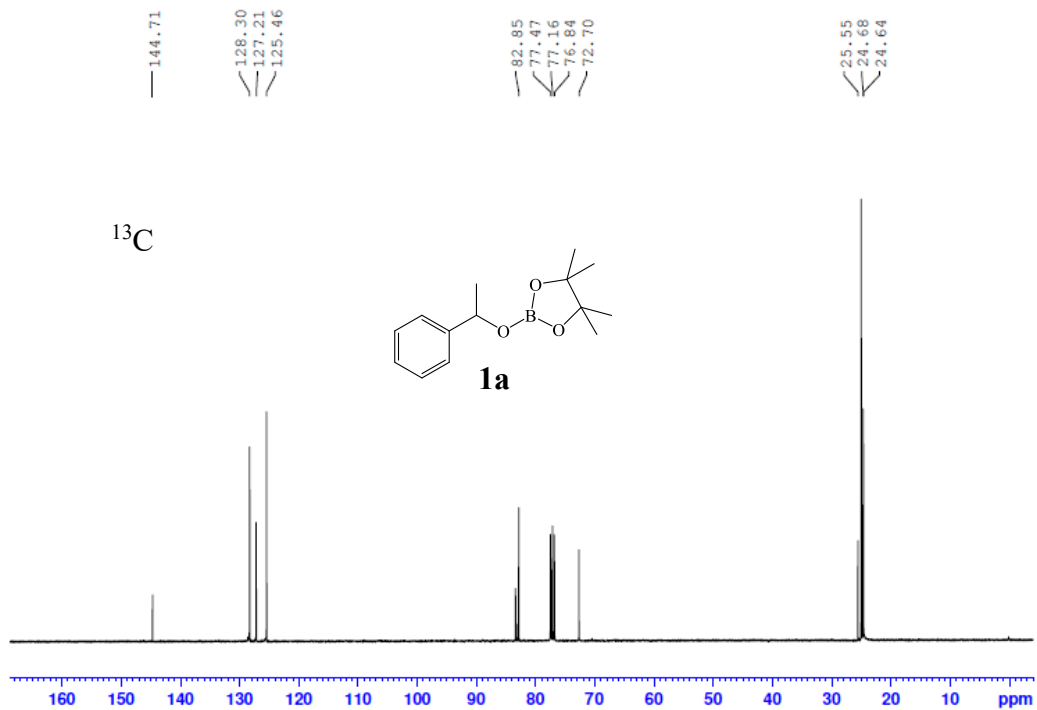
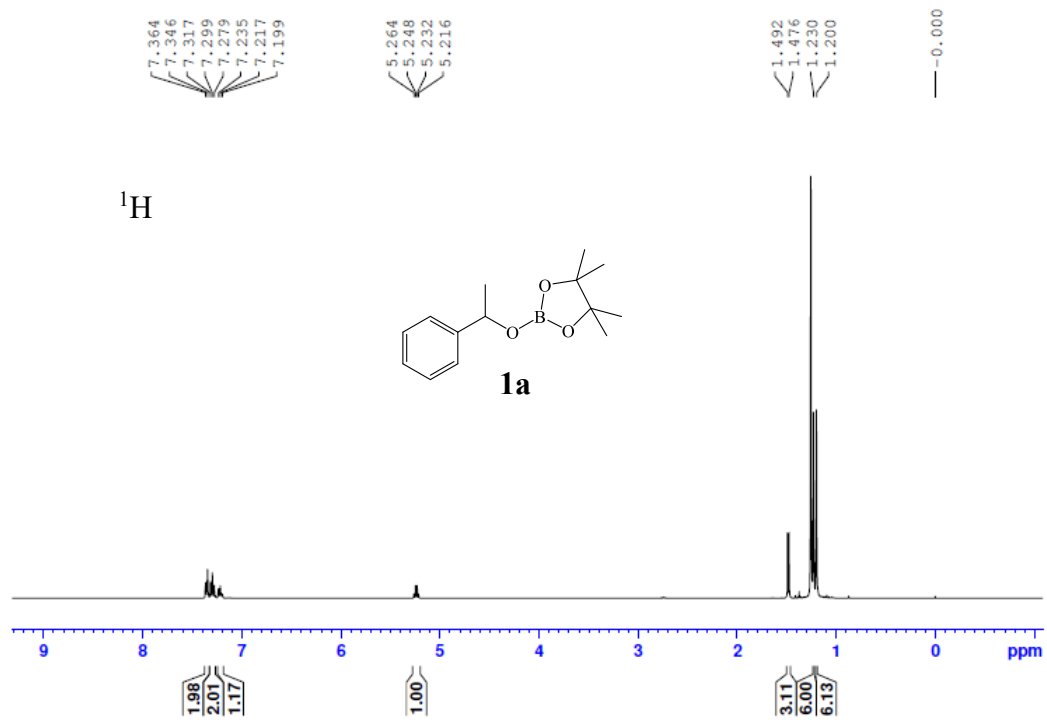
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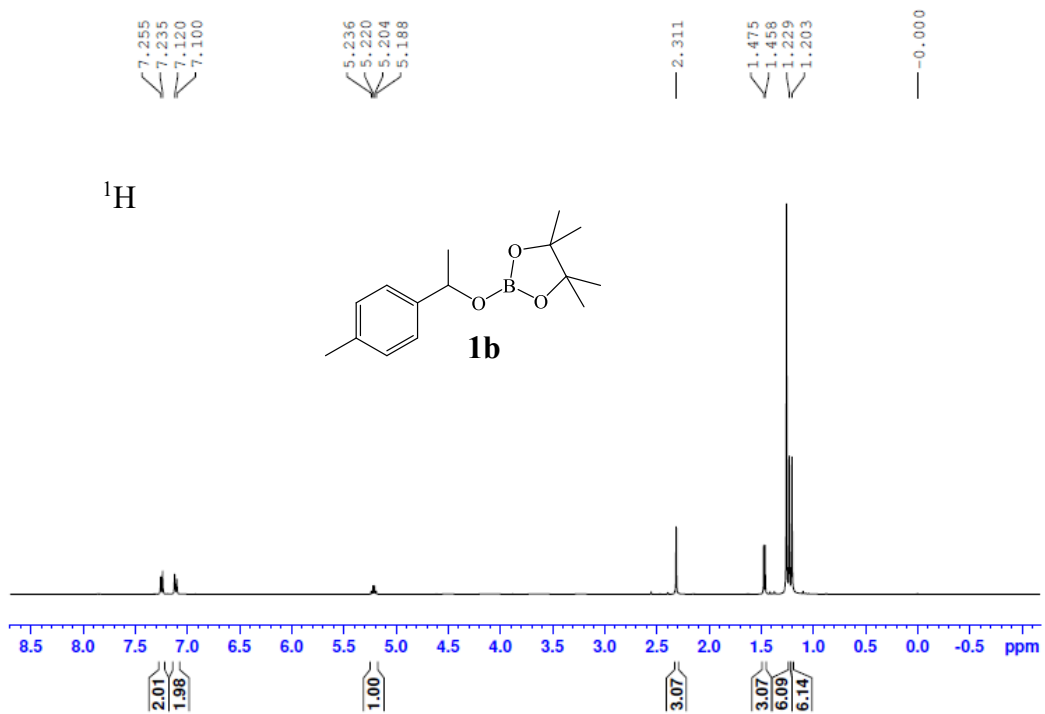
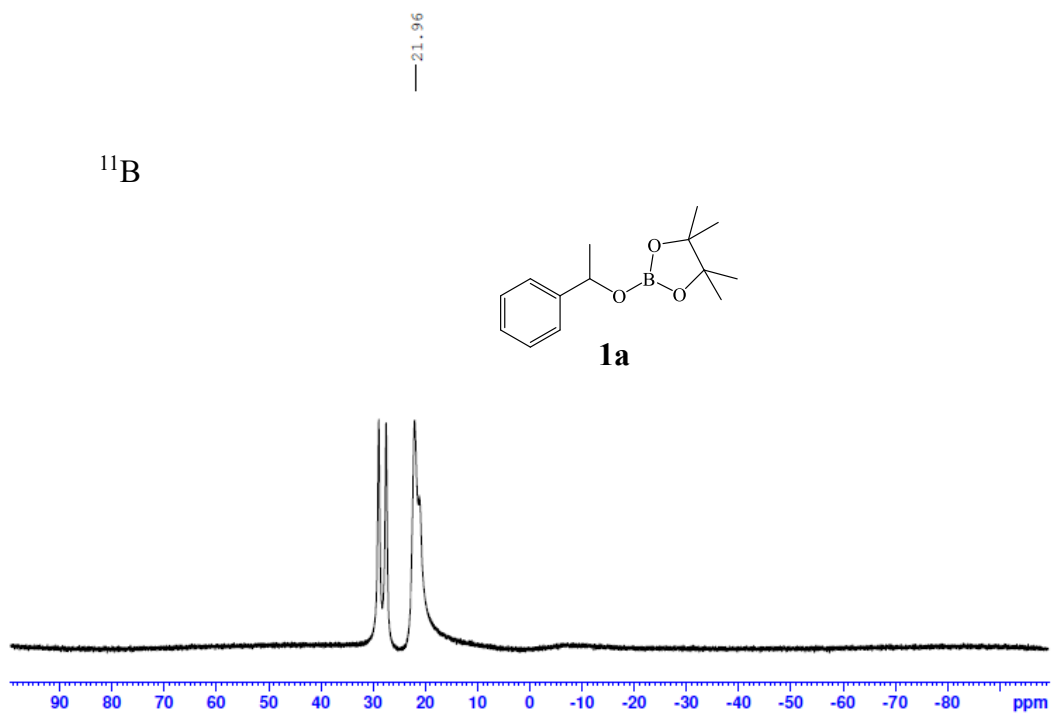
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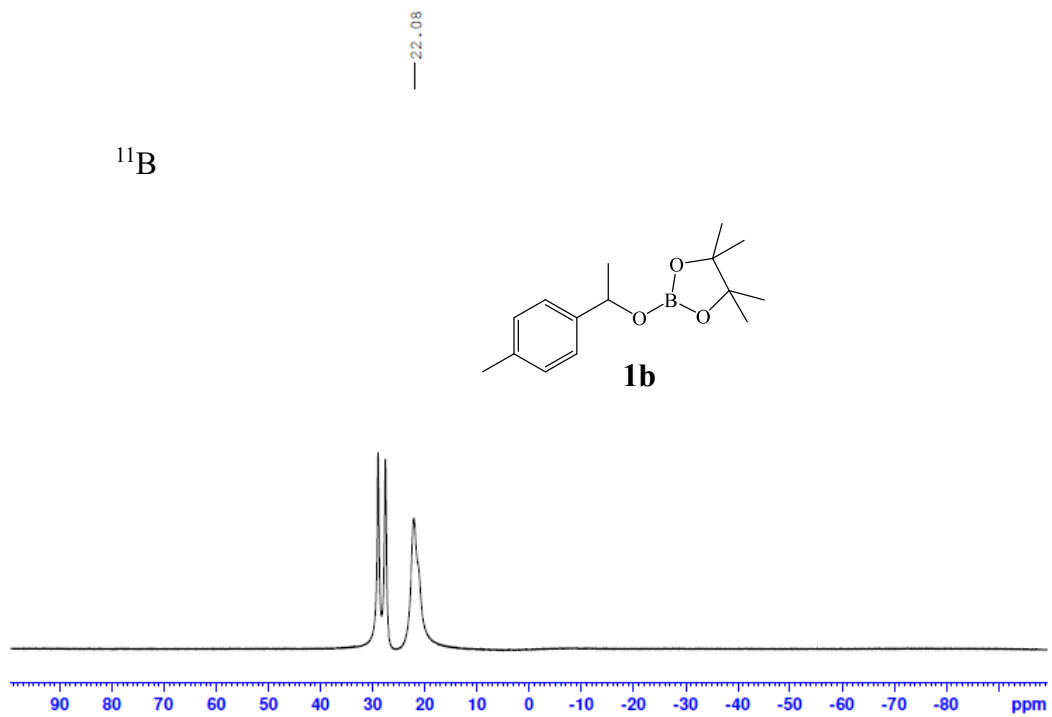
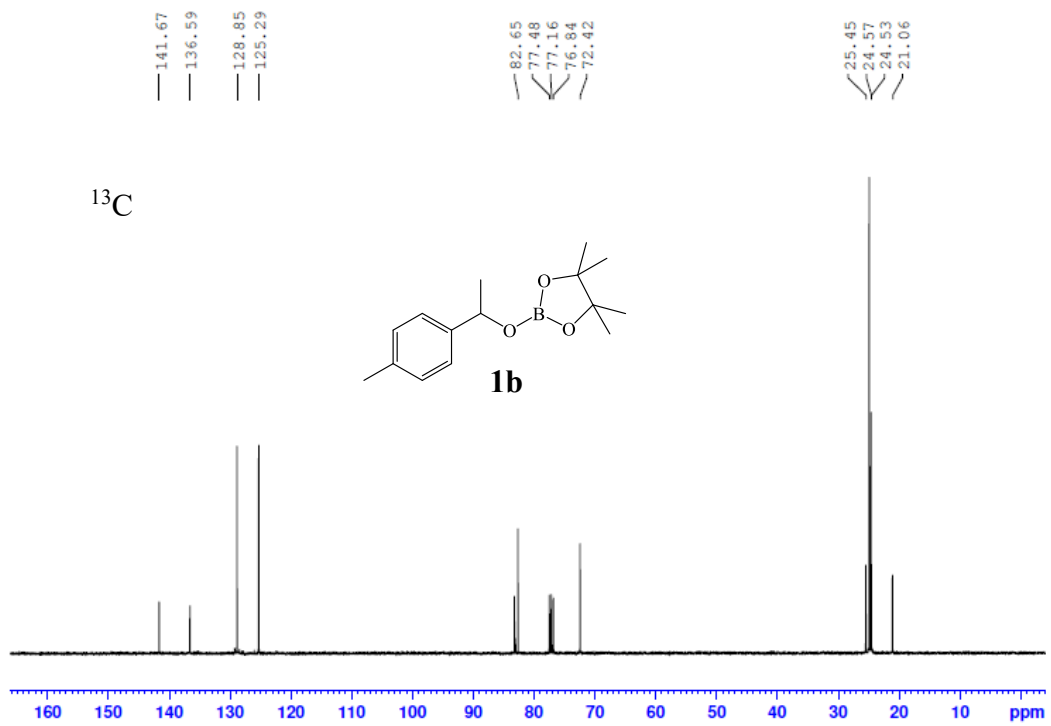
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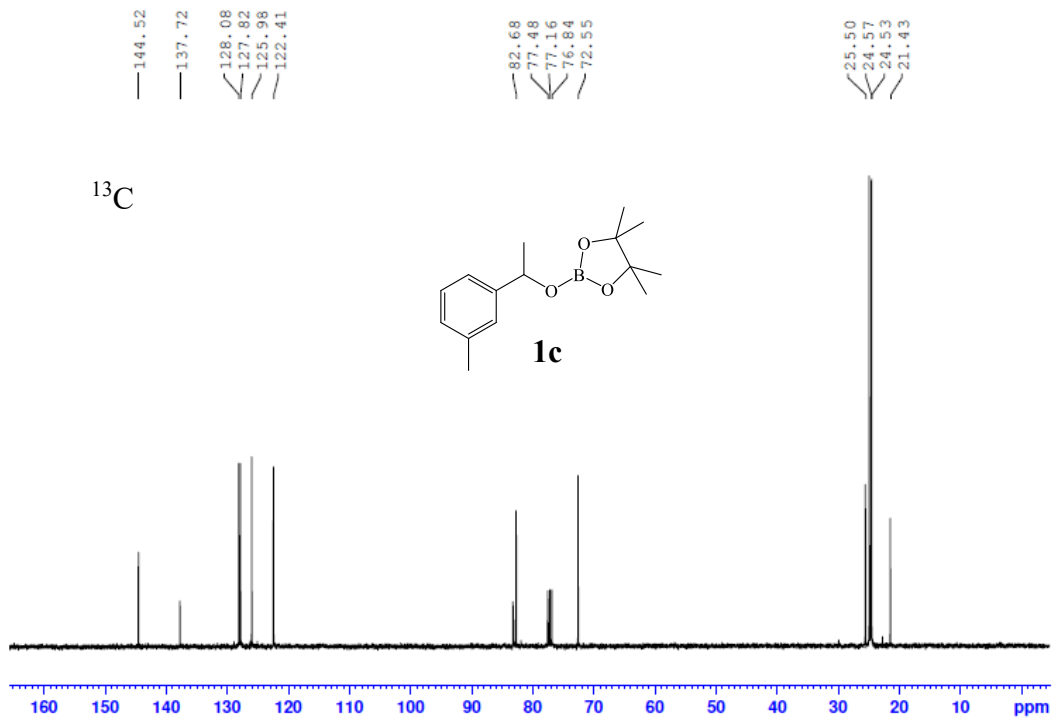
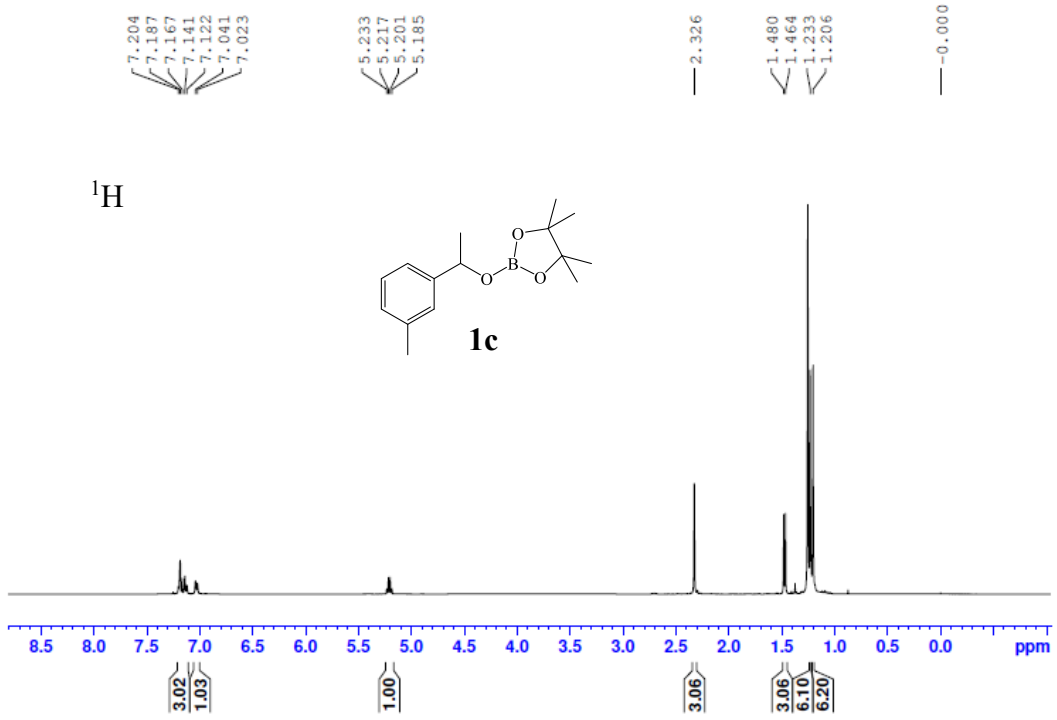
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NMR Spectra of Hydroboration Products

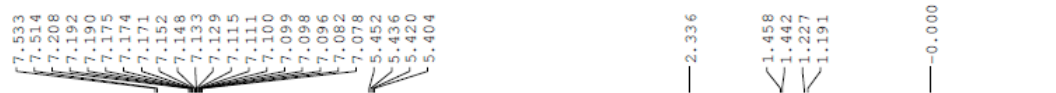
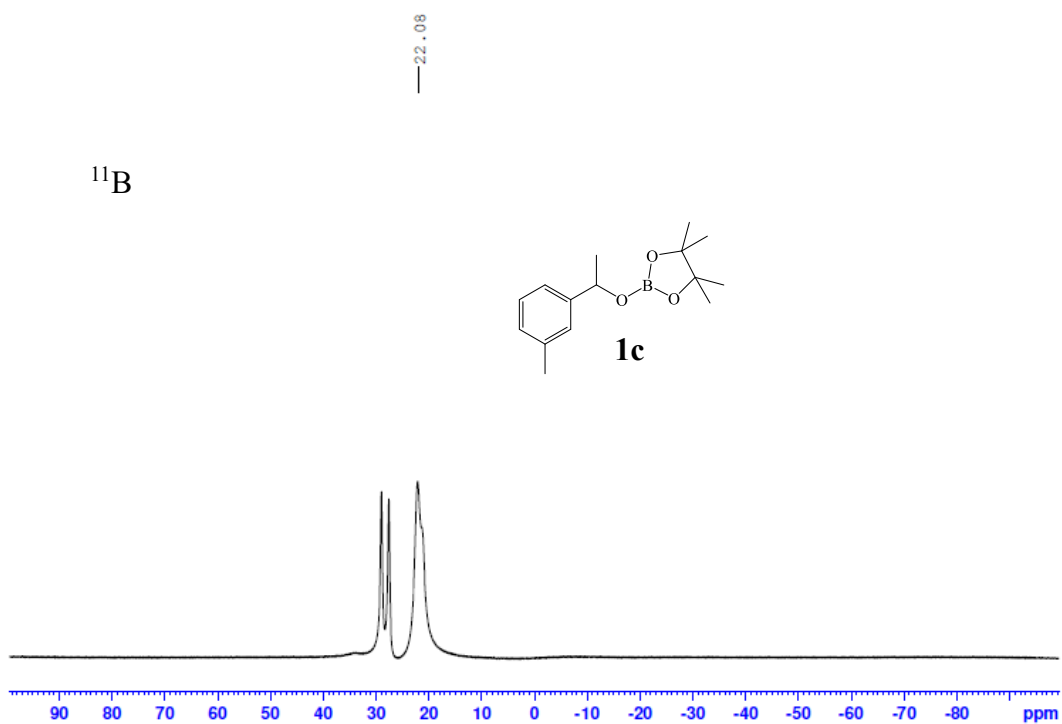
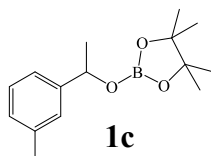




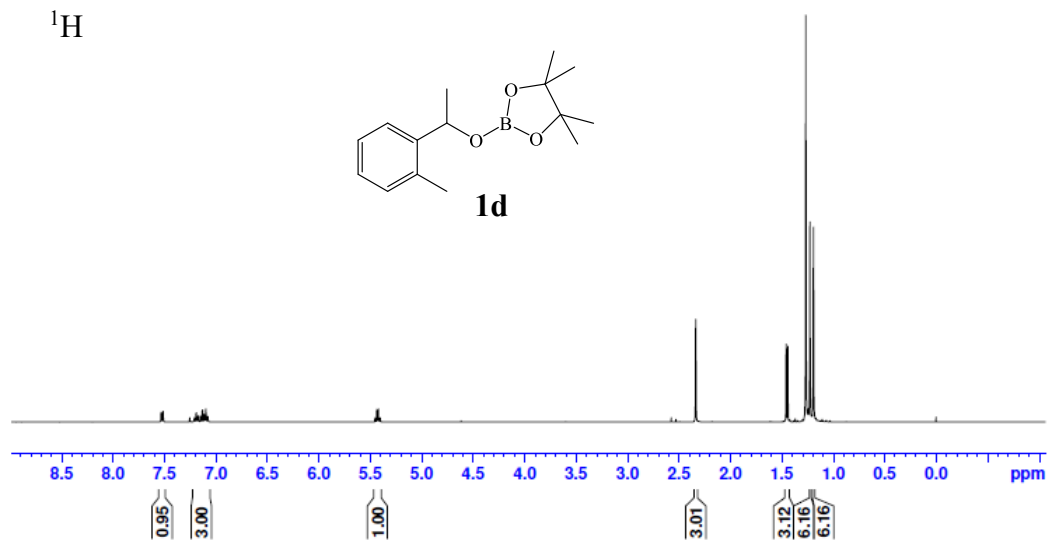
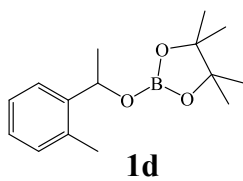


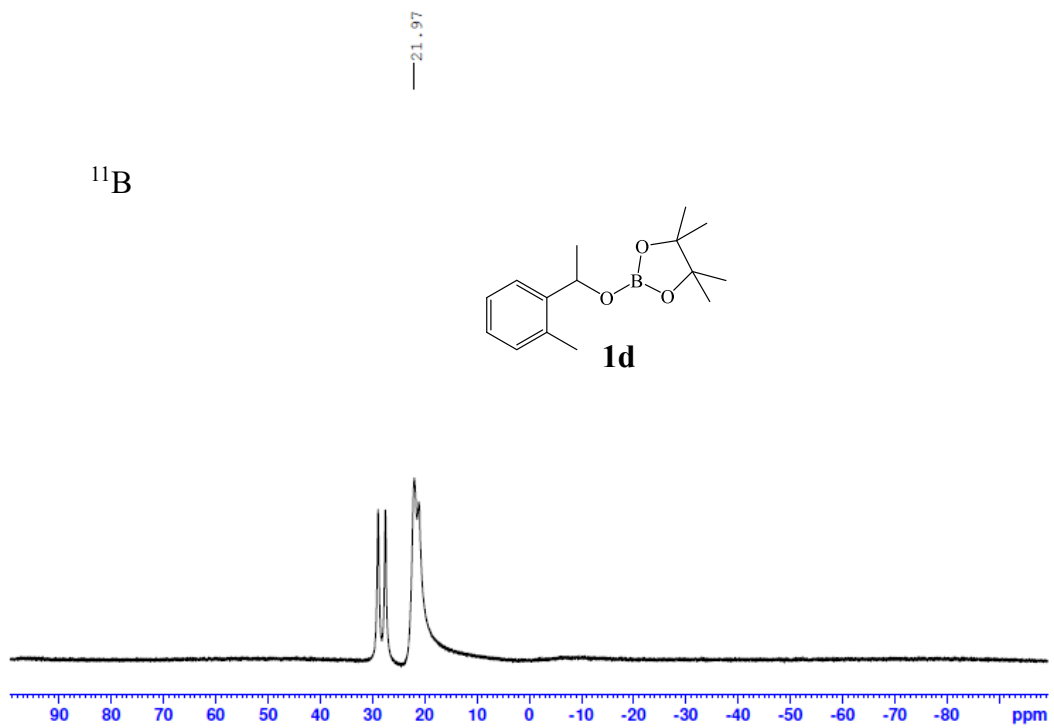
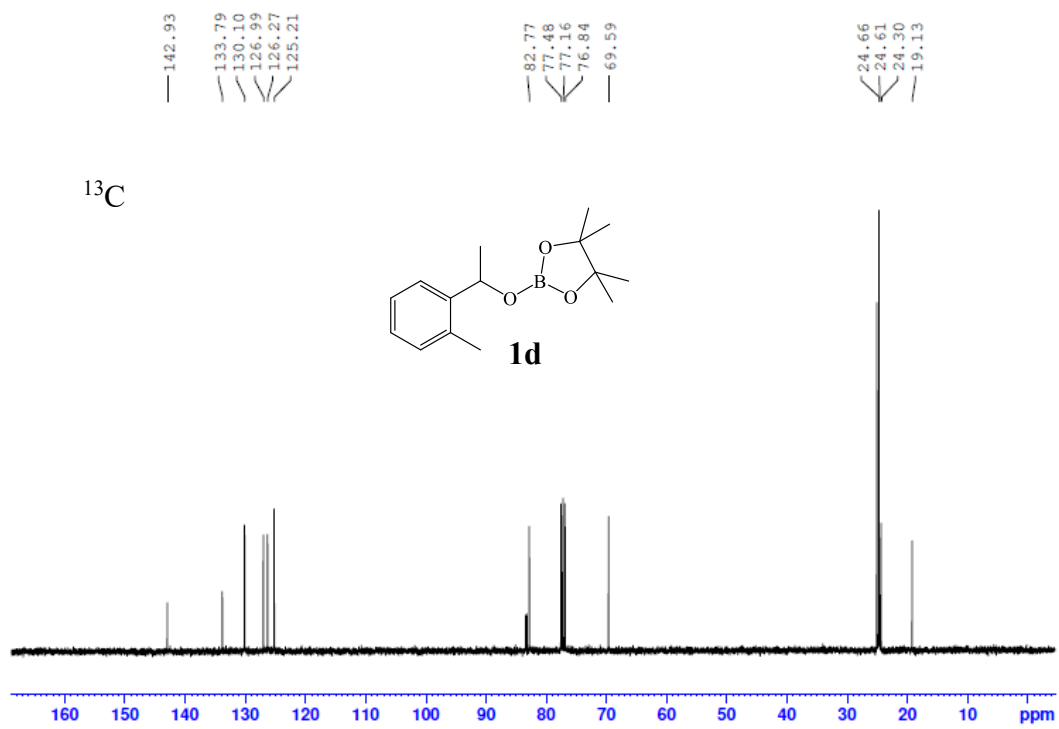


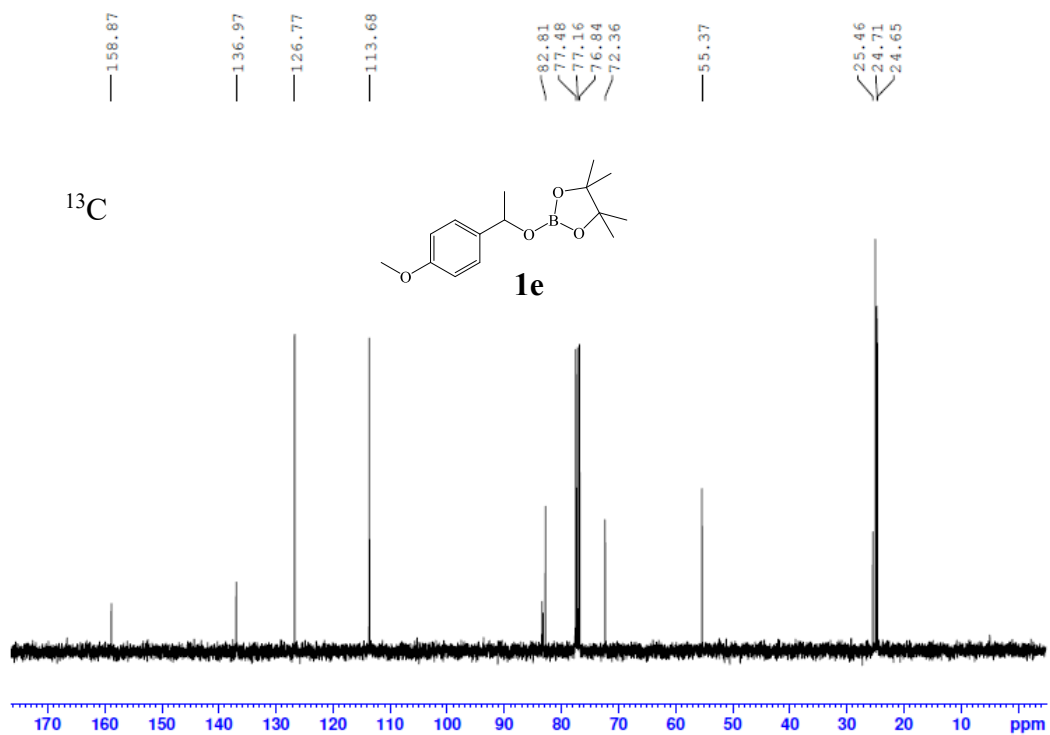
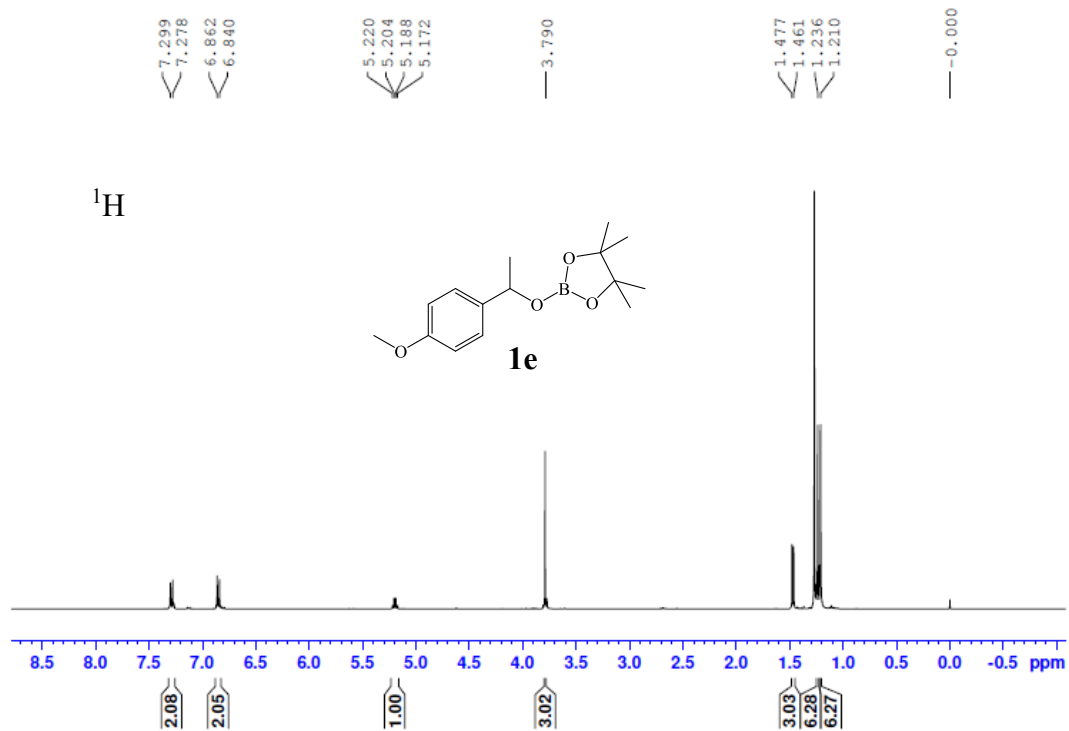
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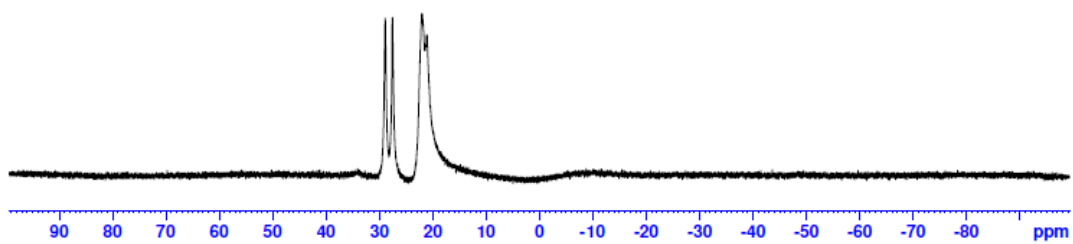
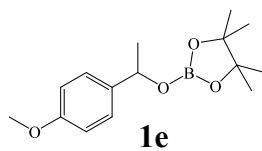




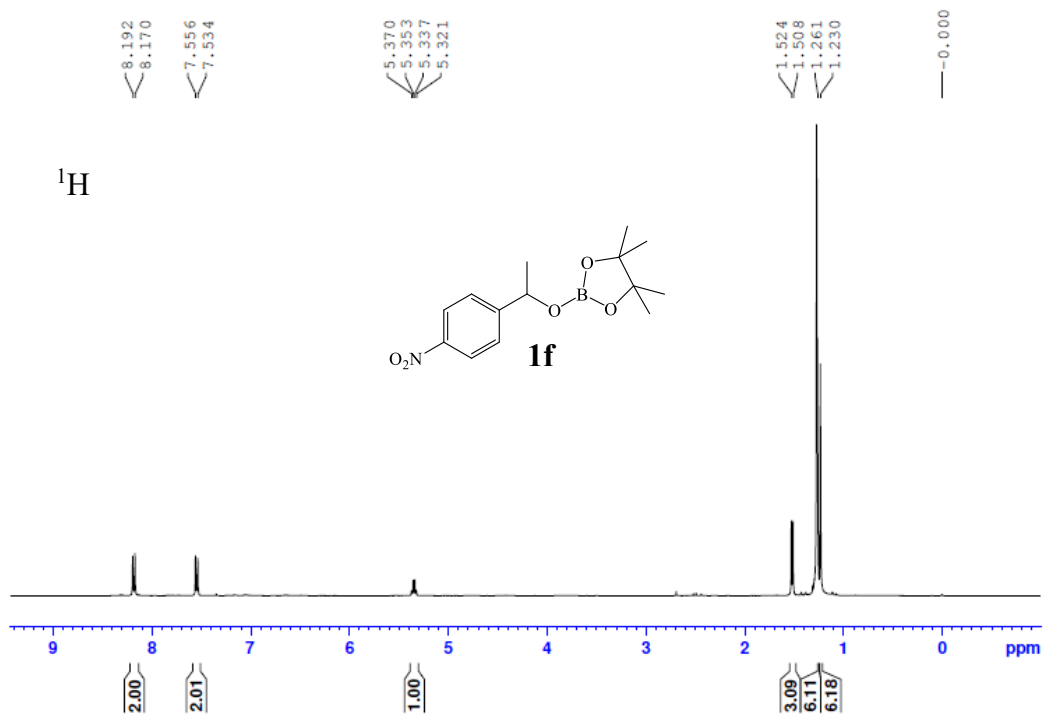
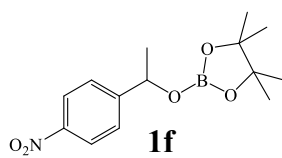


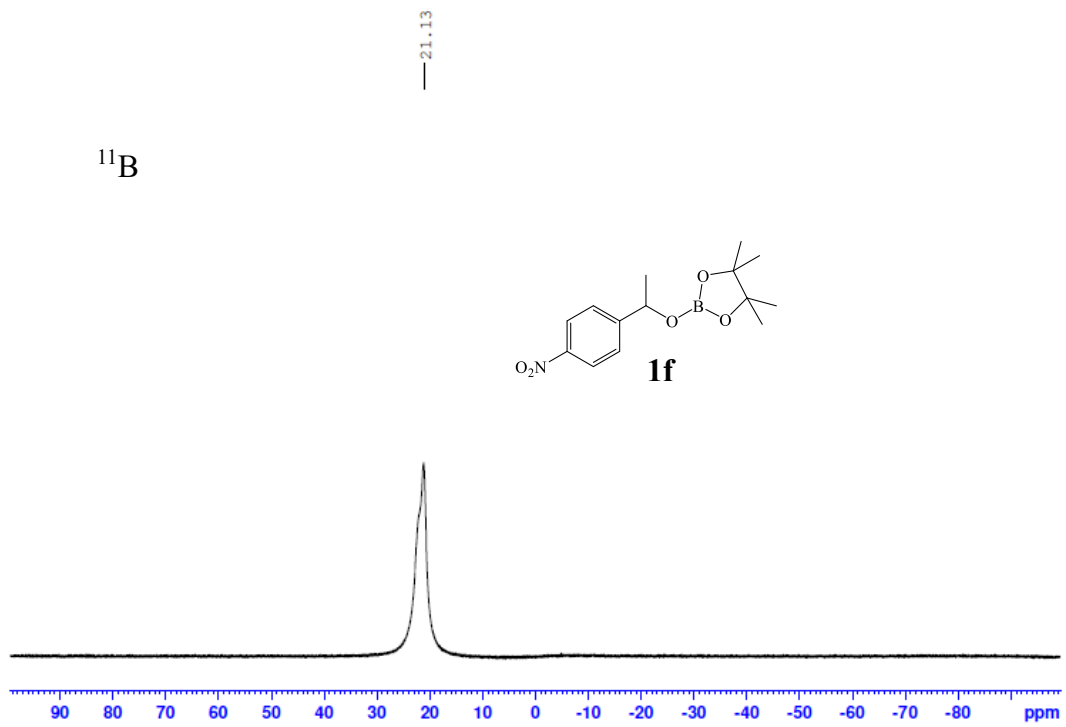
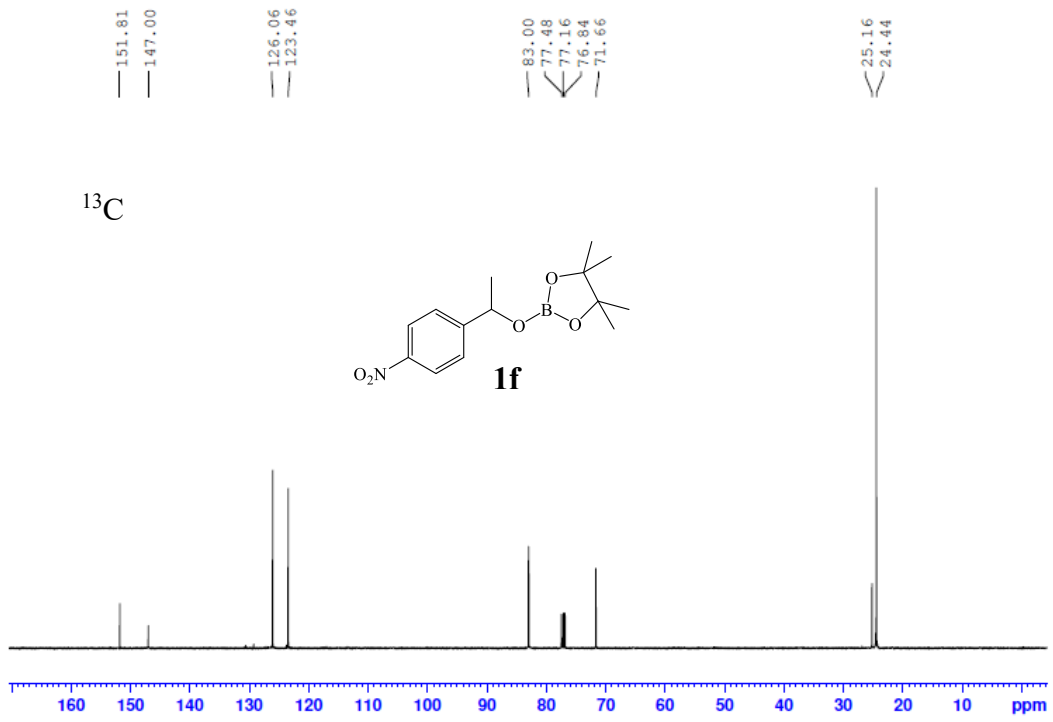
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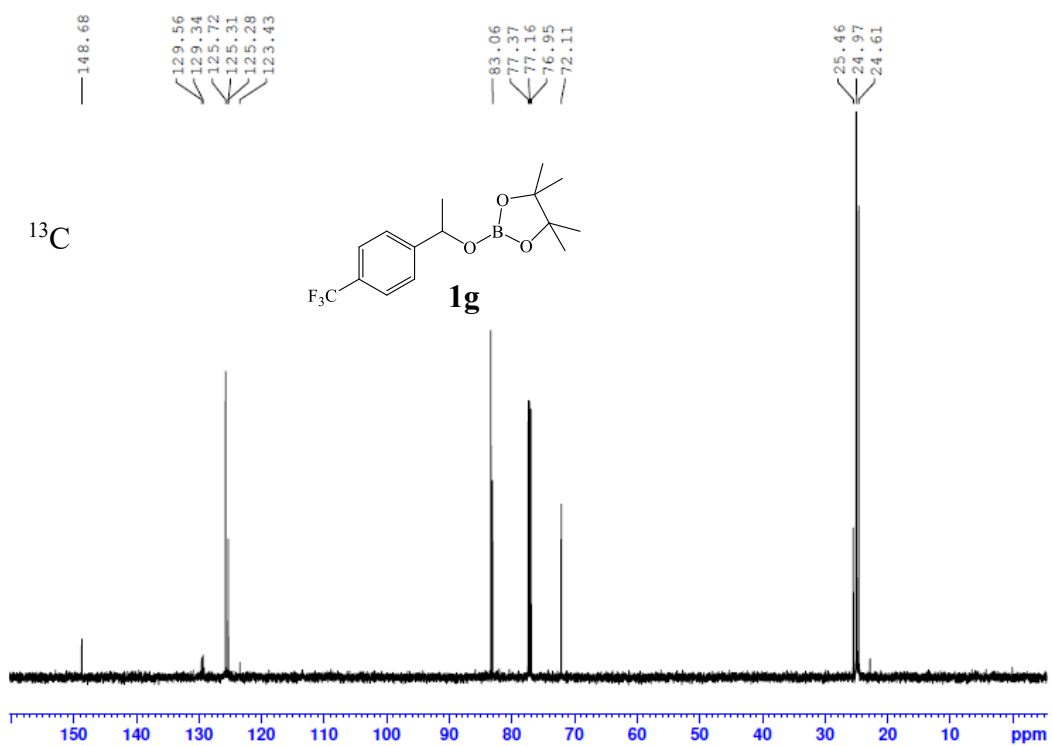
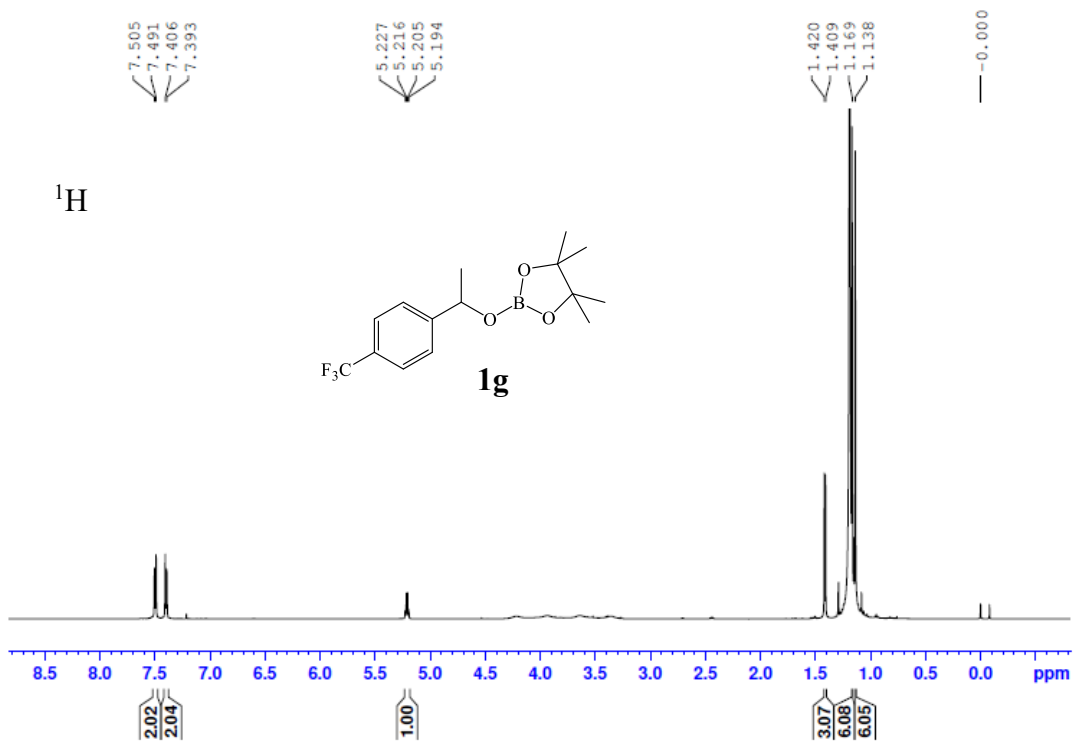
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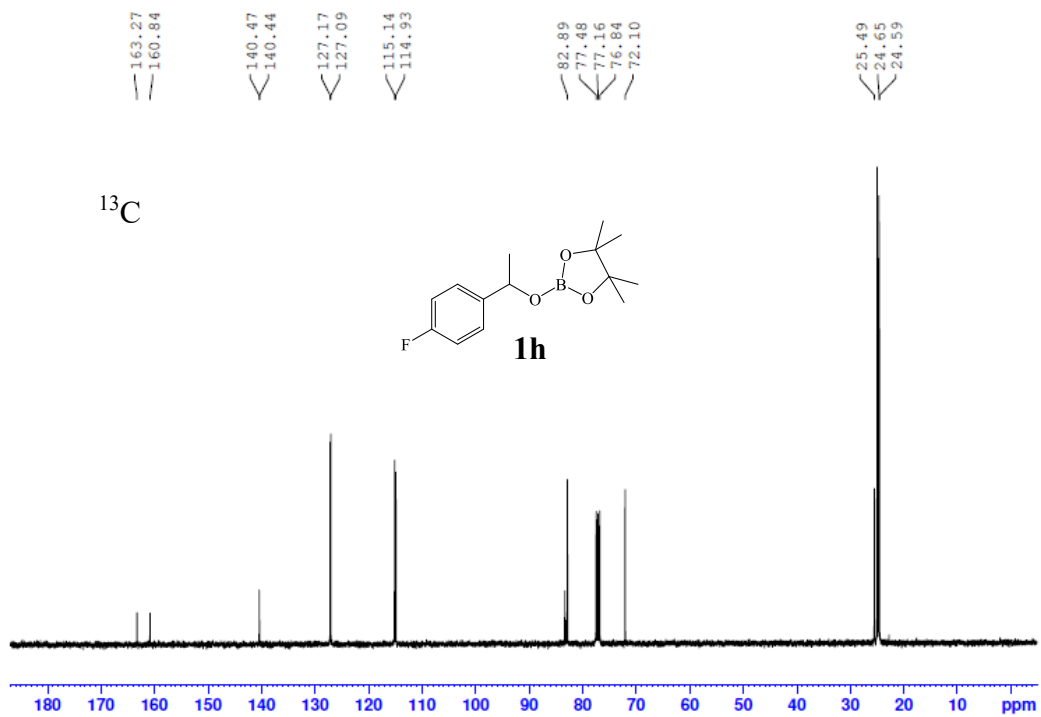
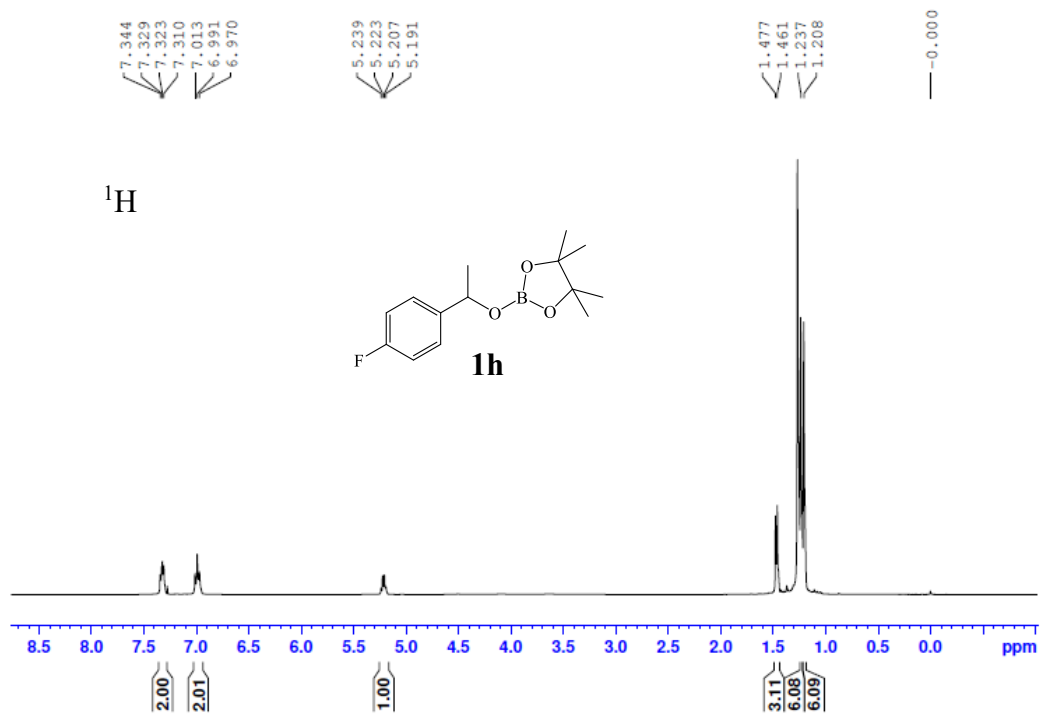


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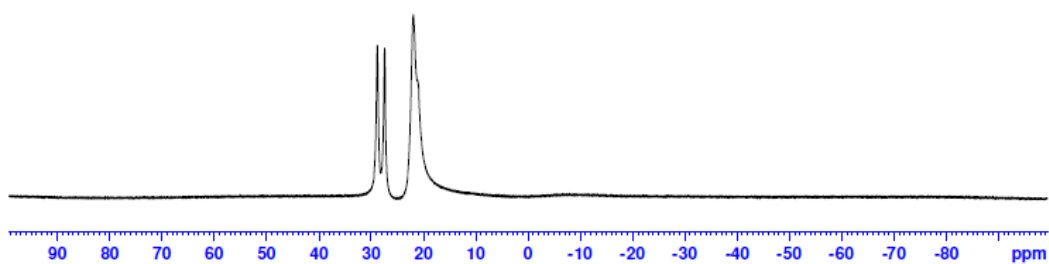
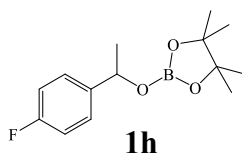






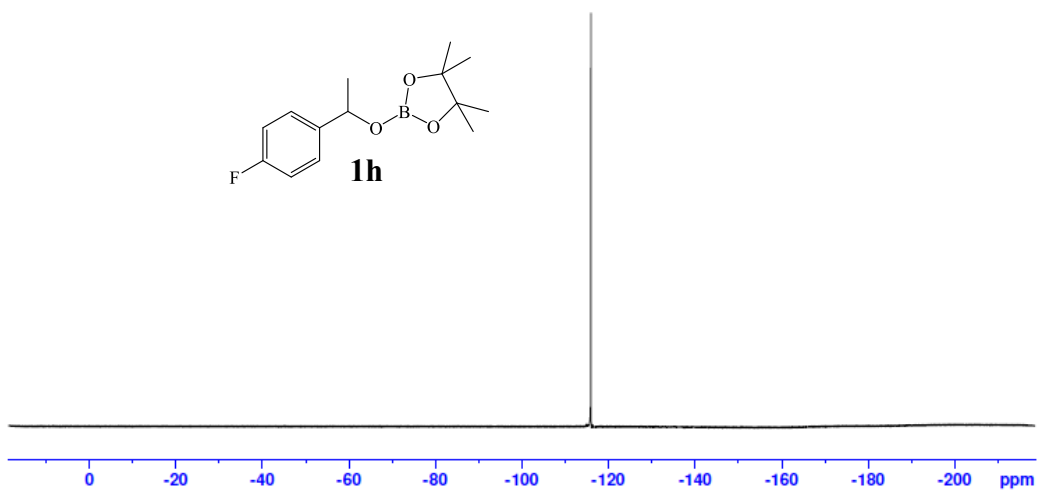
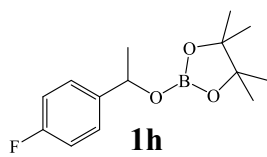
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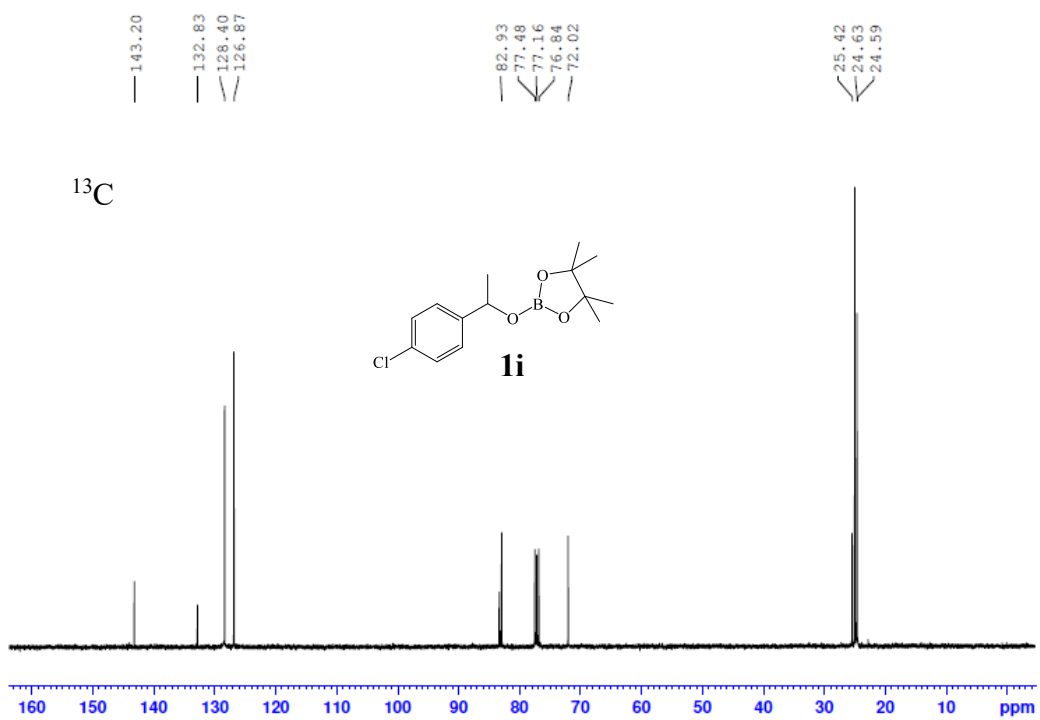
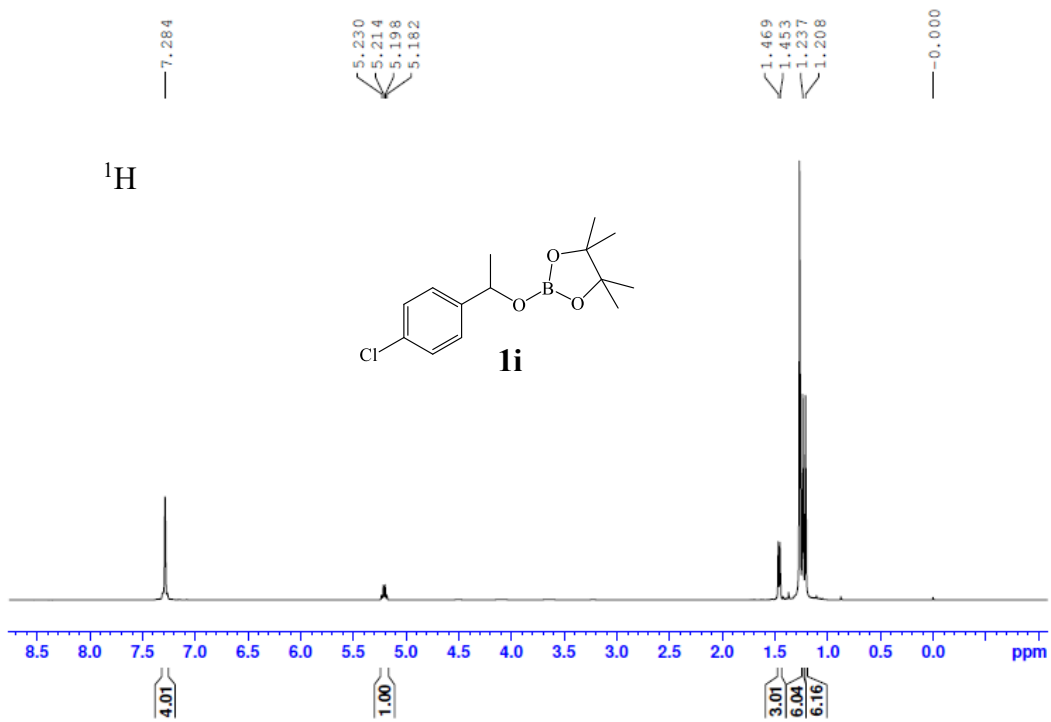
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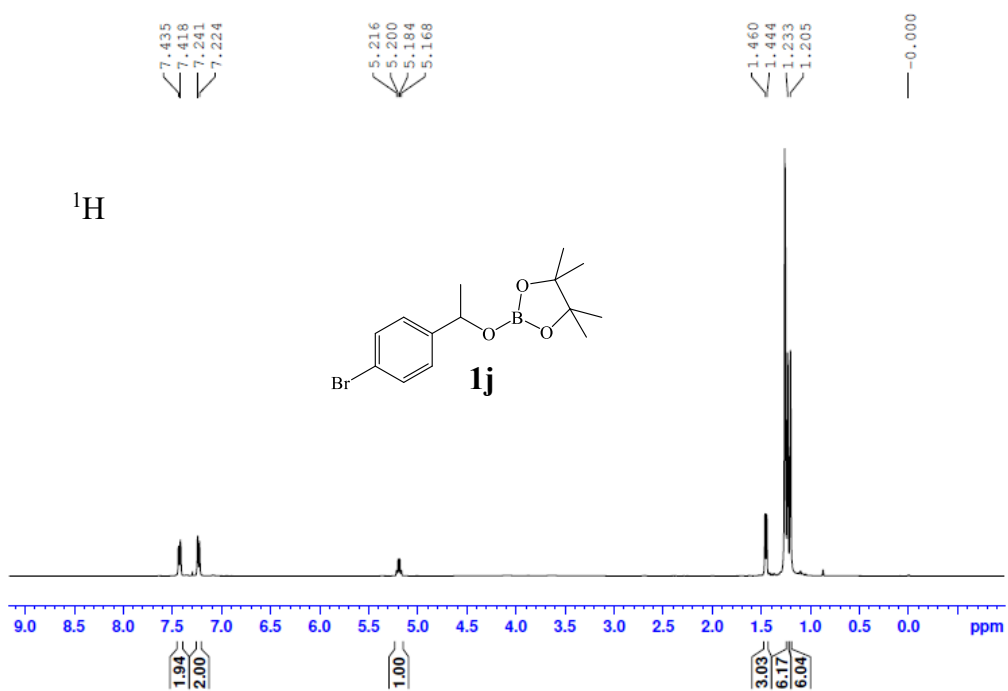
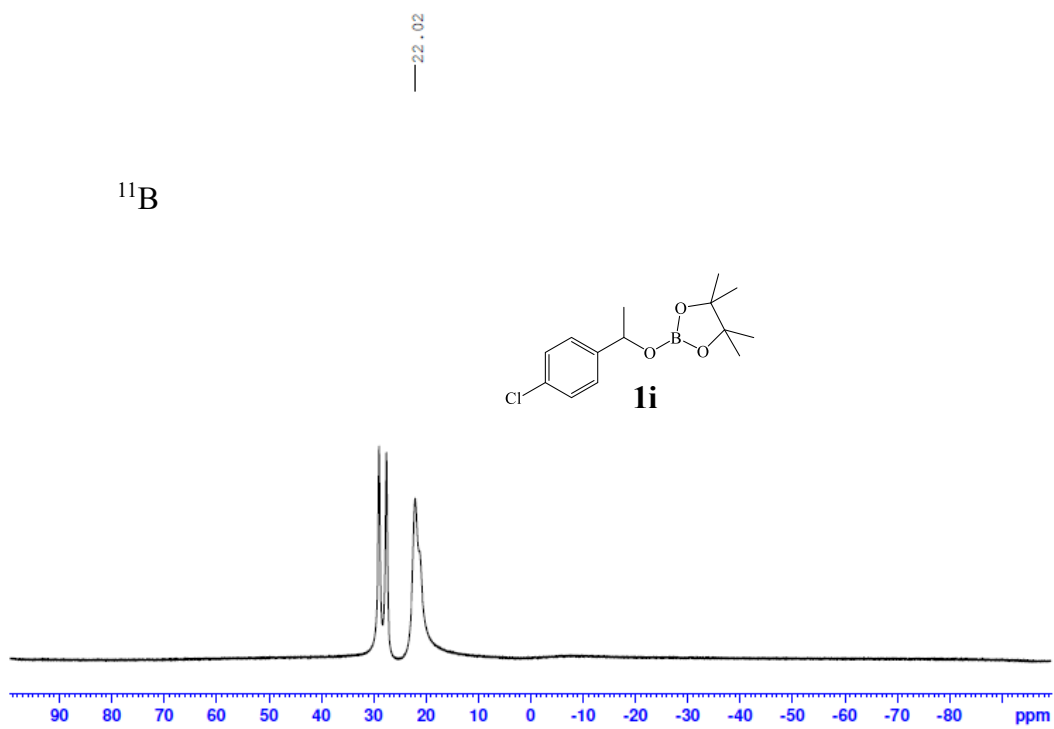


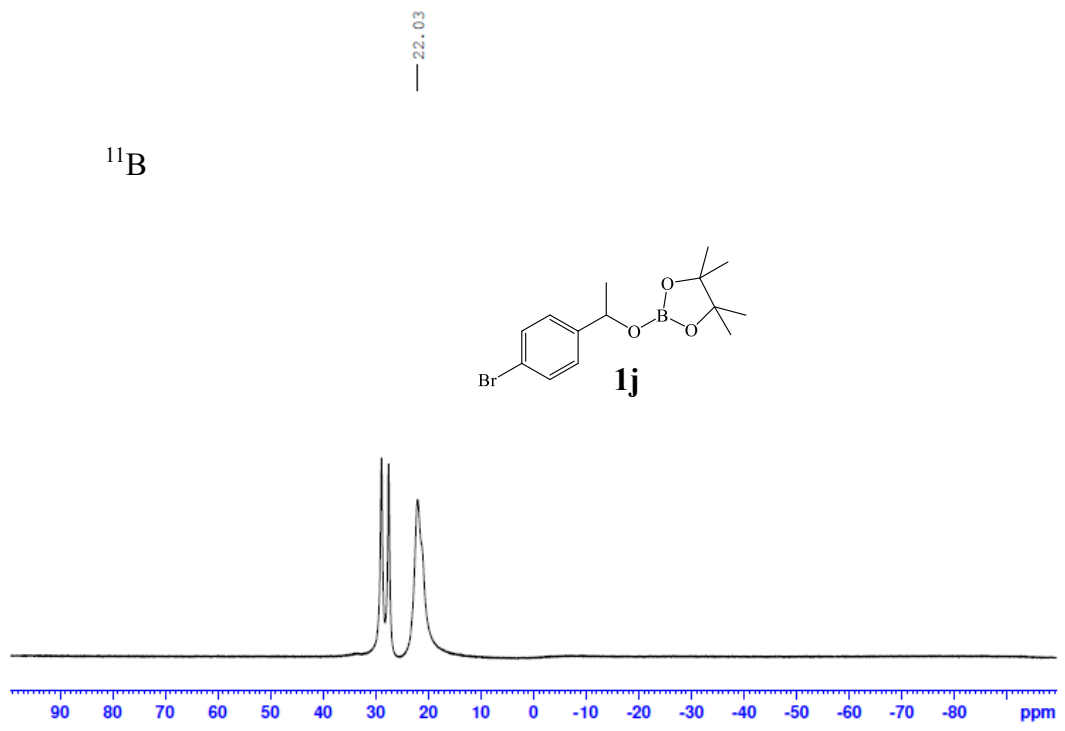
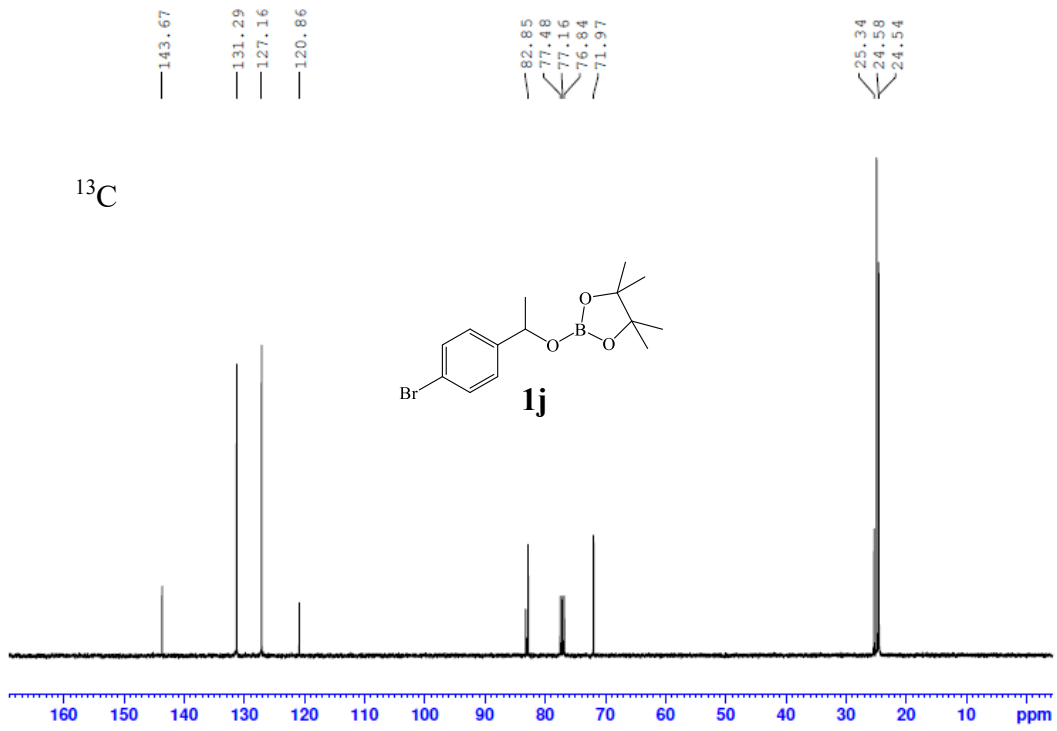
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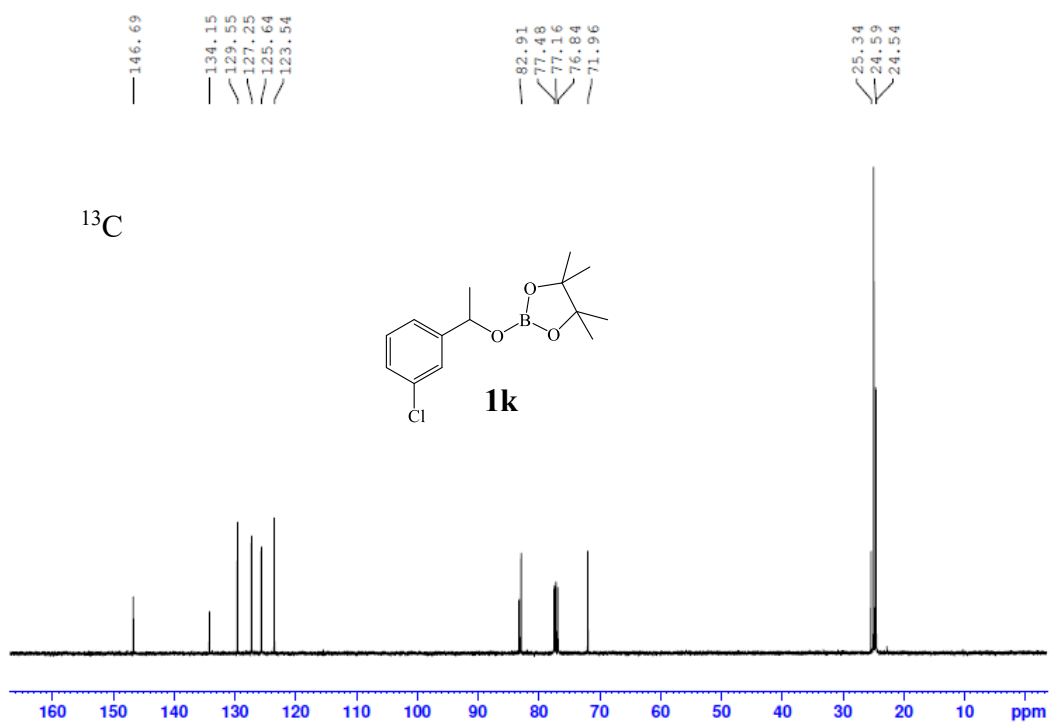
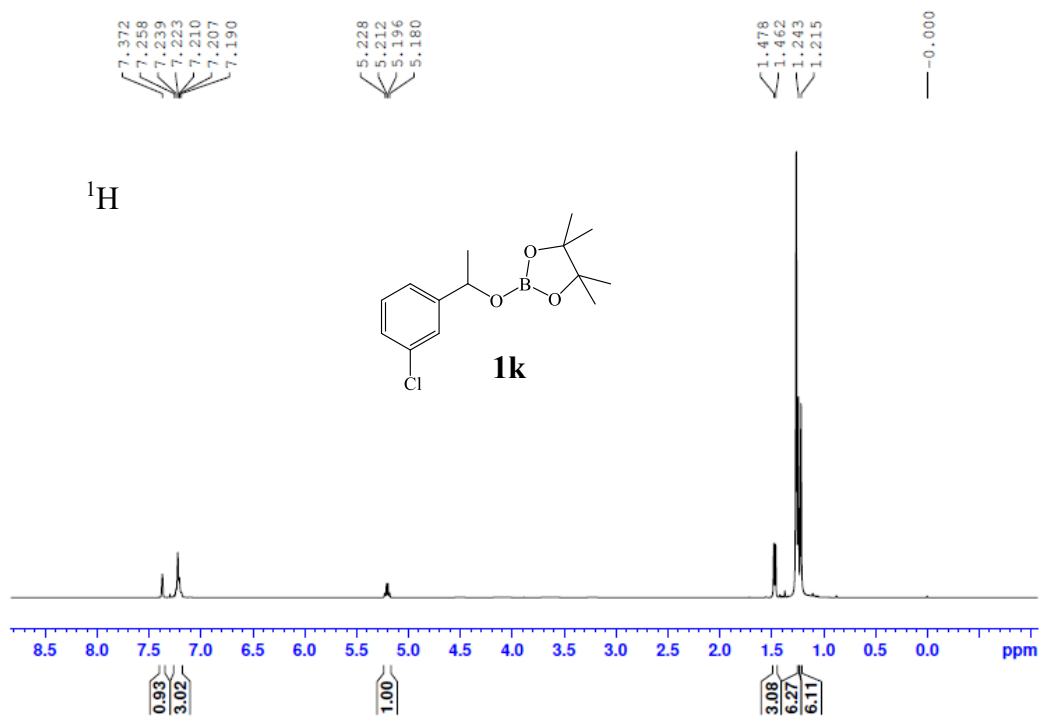
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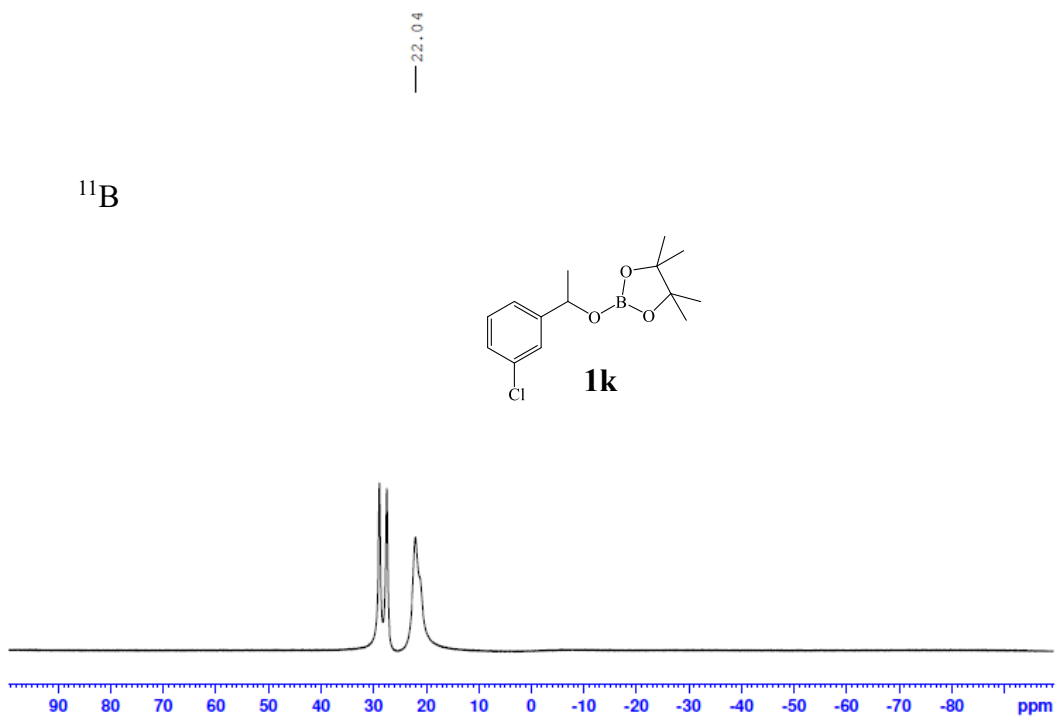
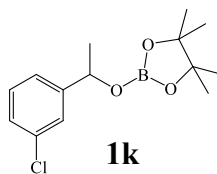




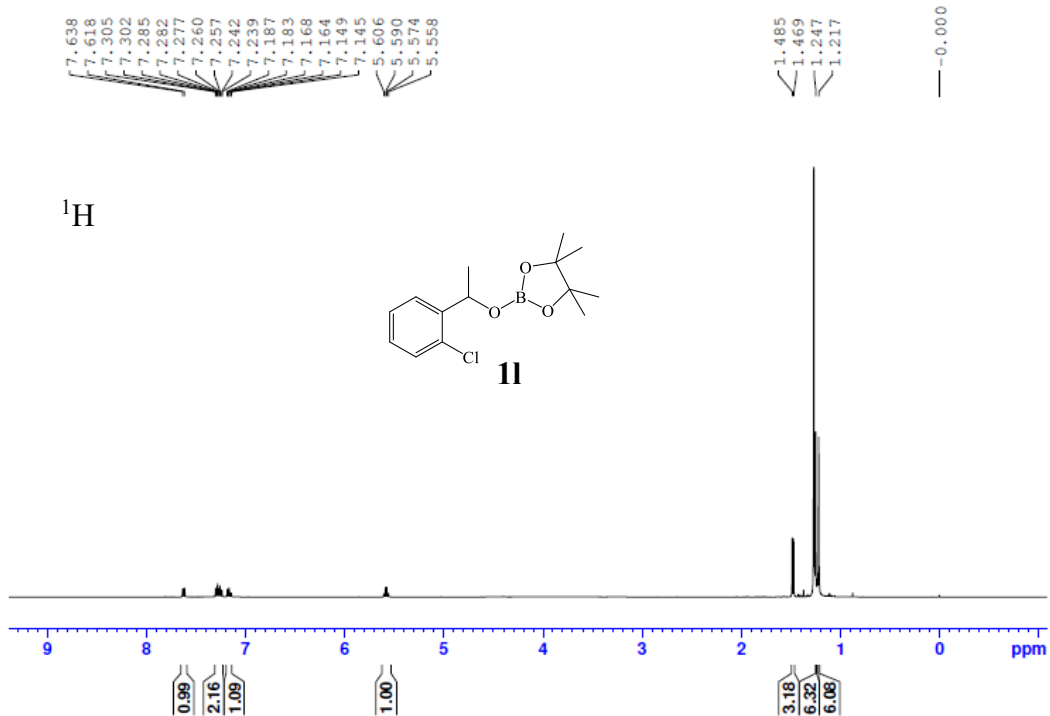
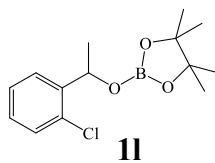


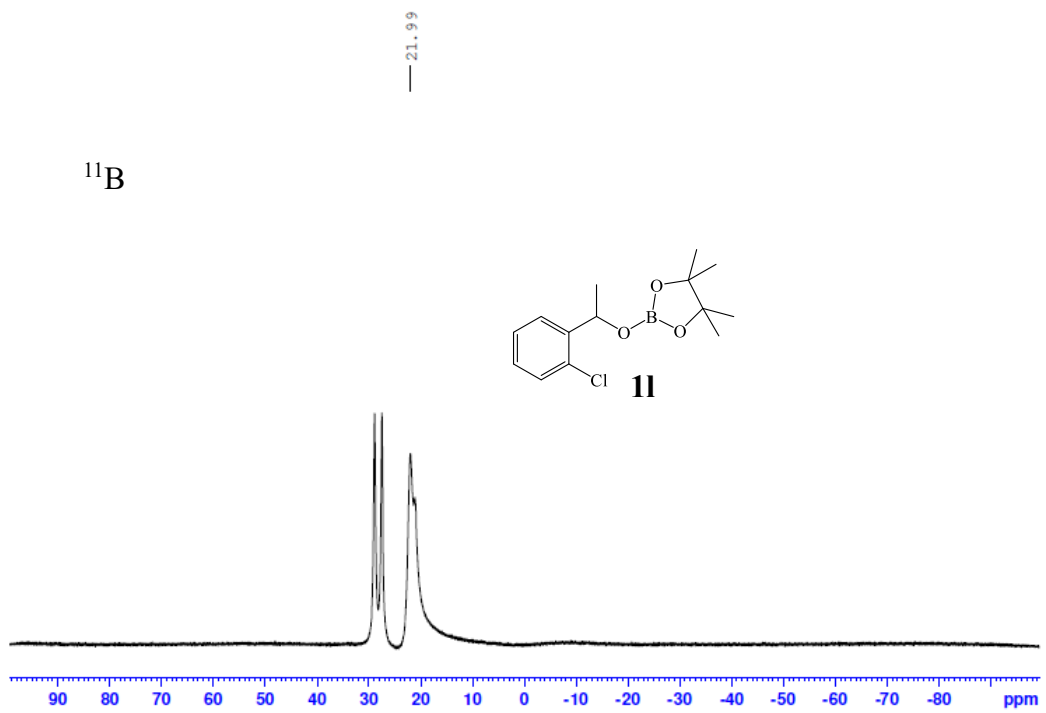
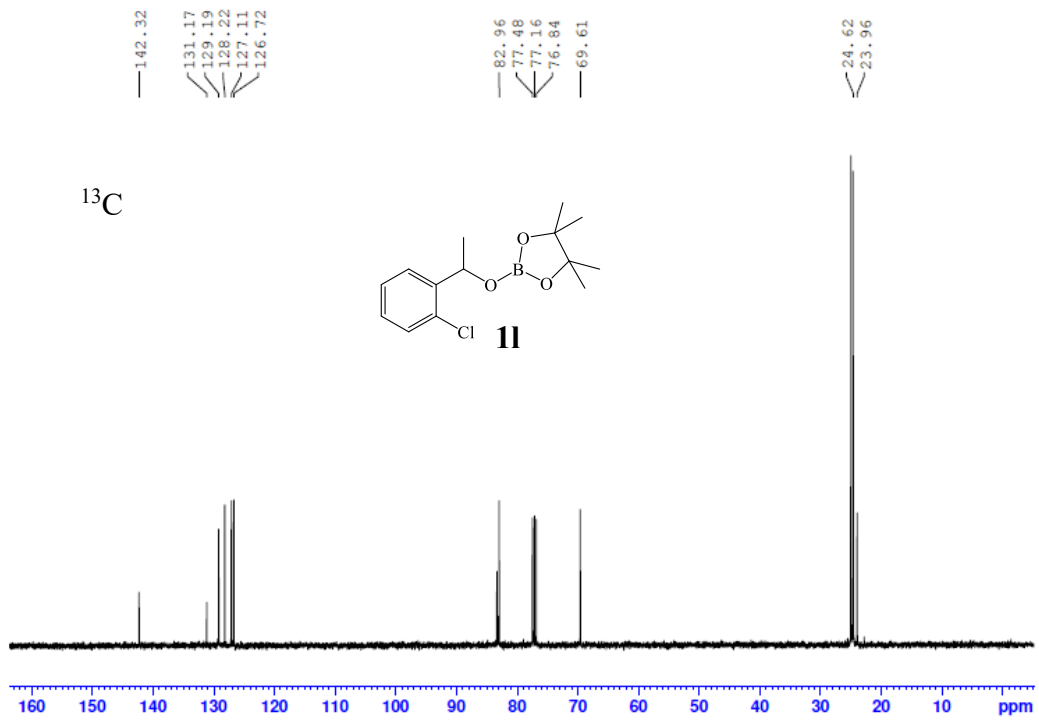


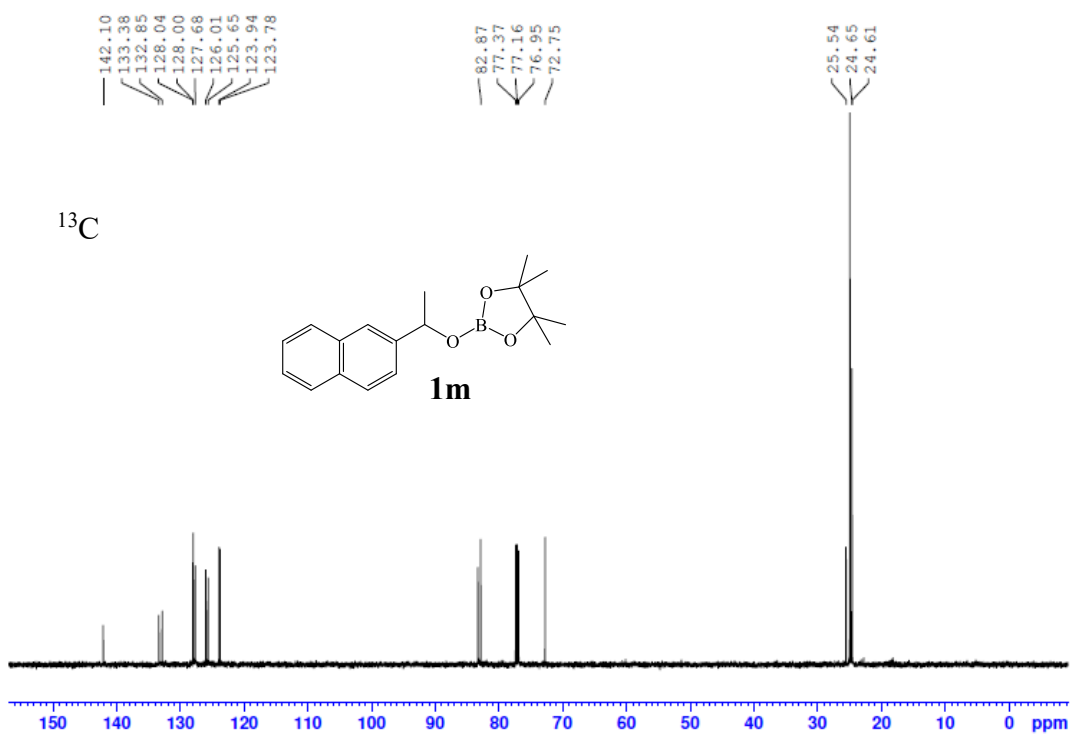
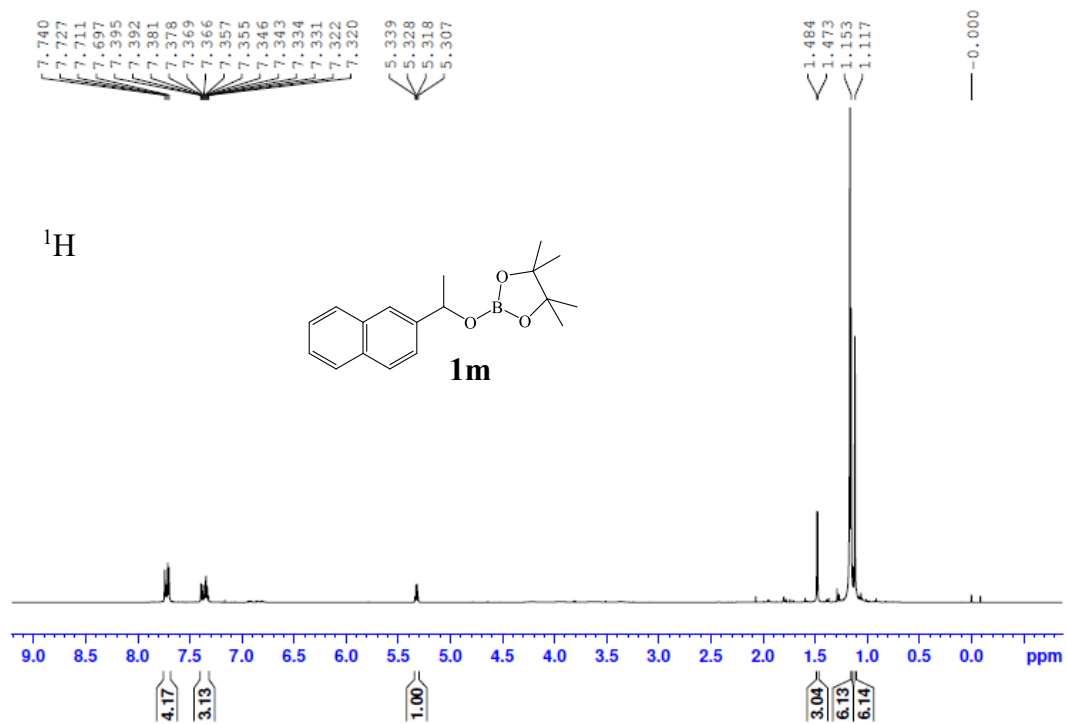
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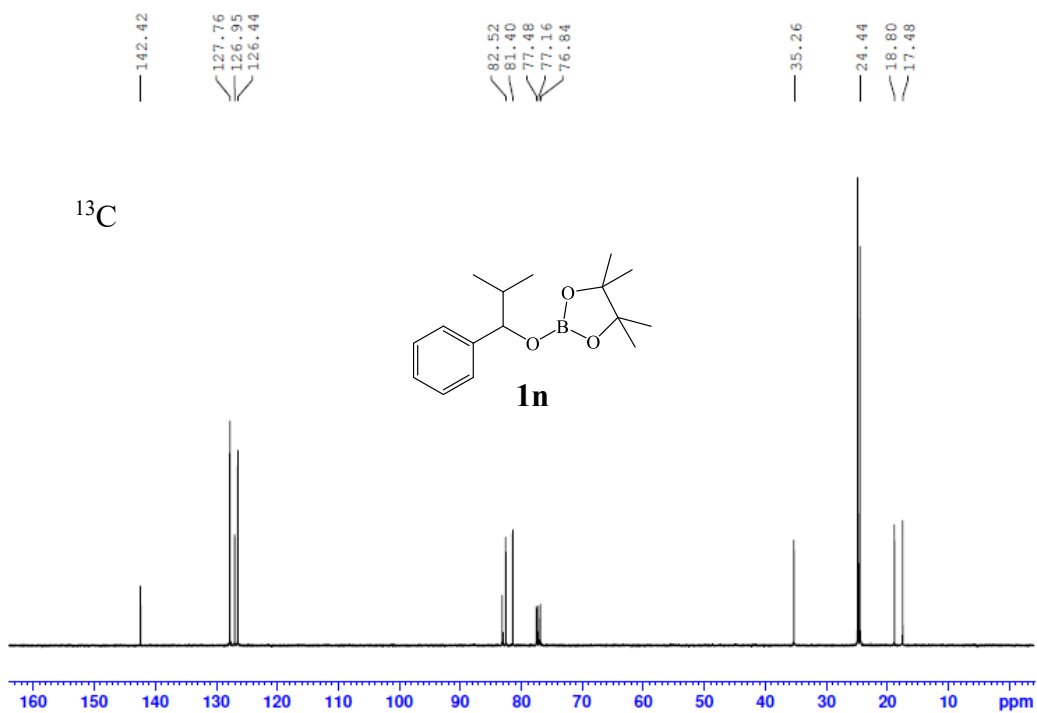
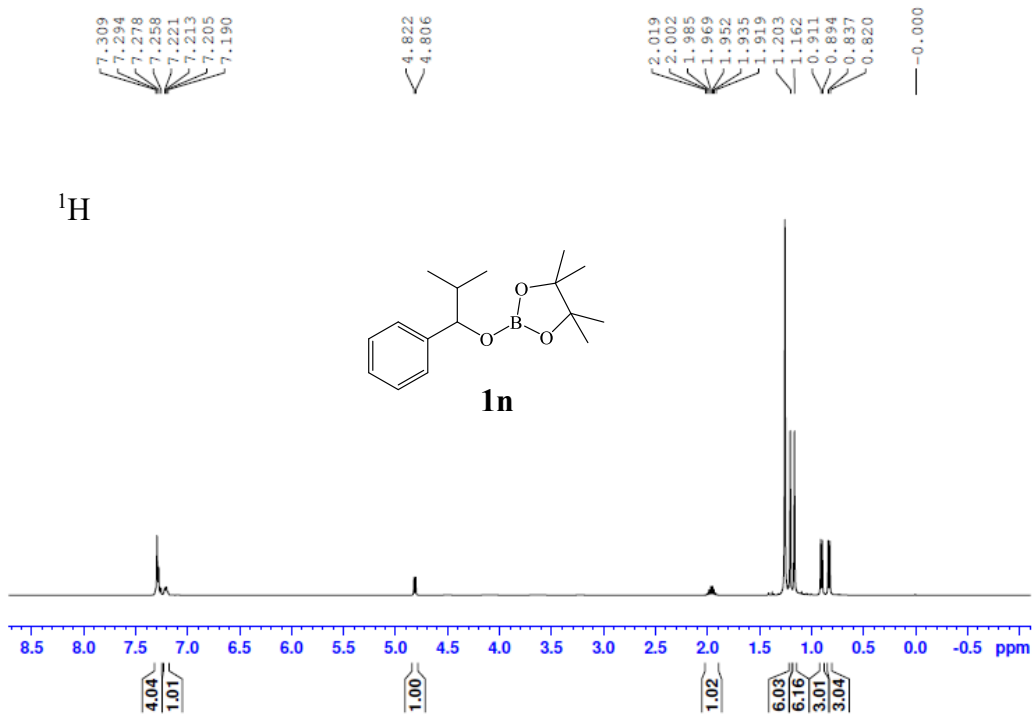


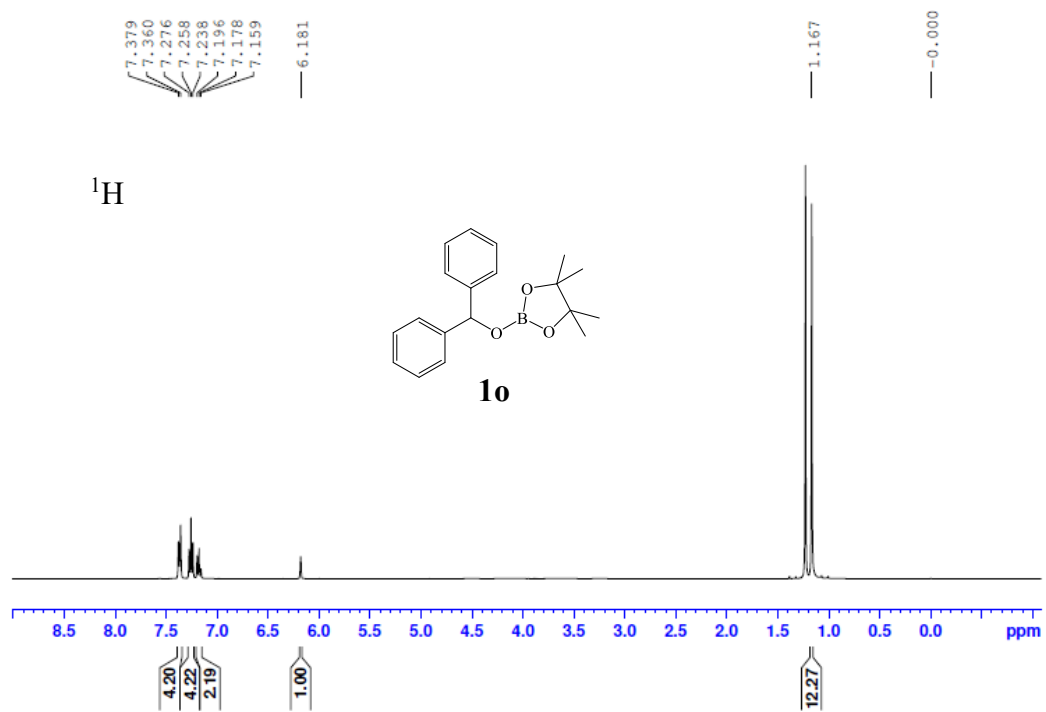
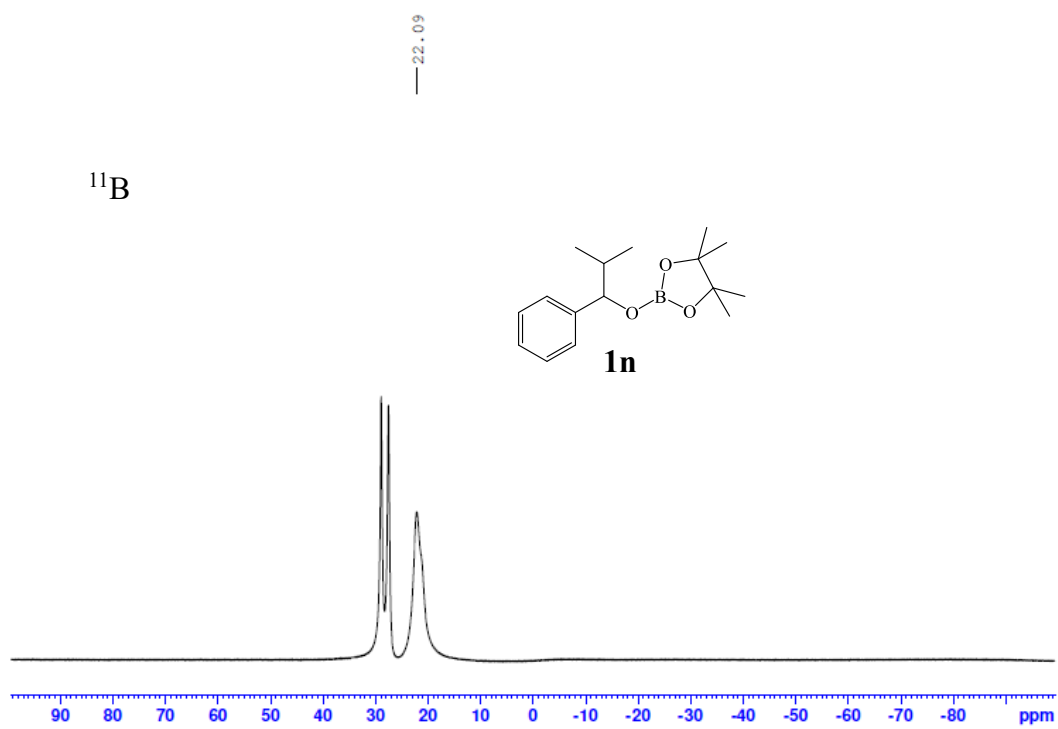
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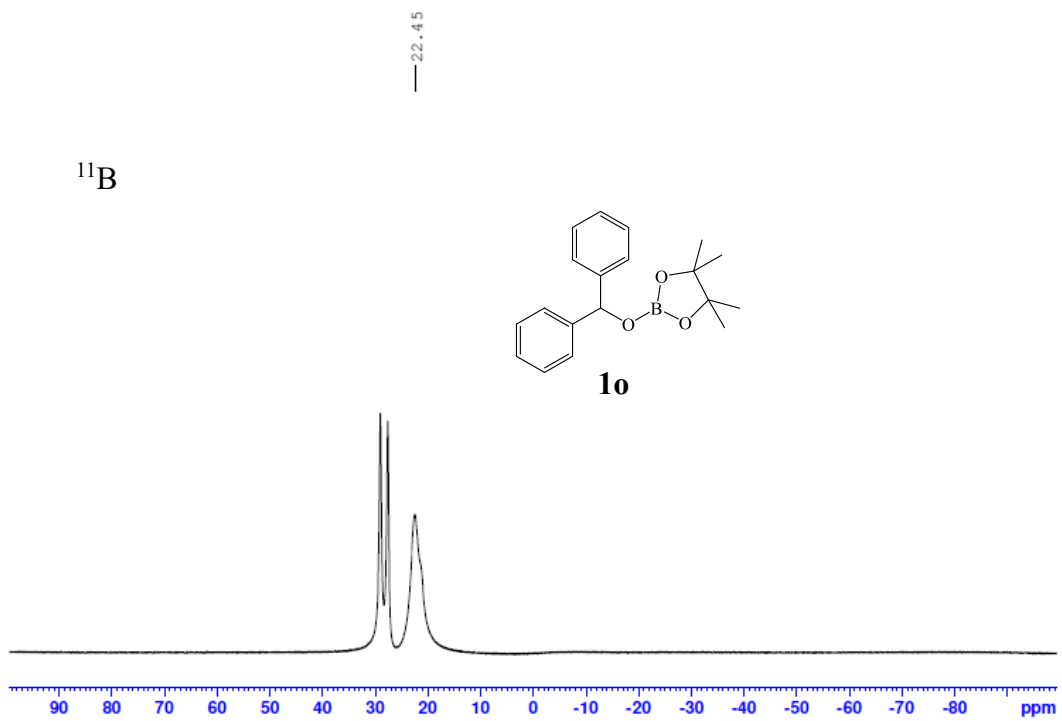
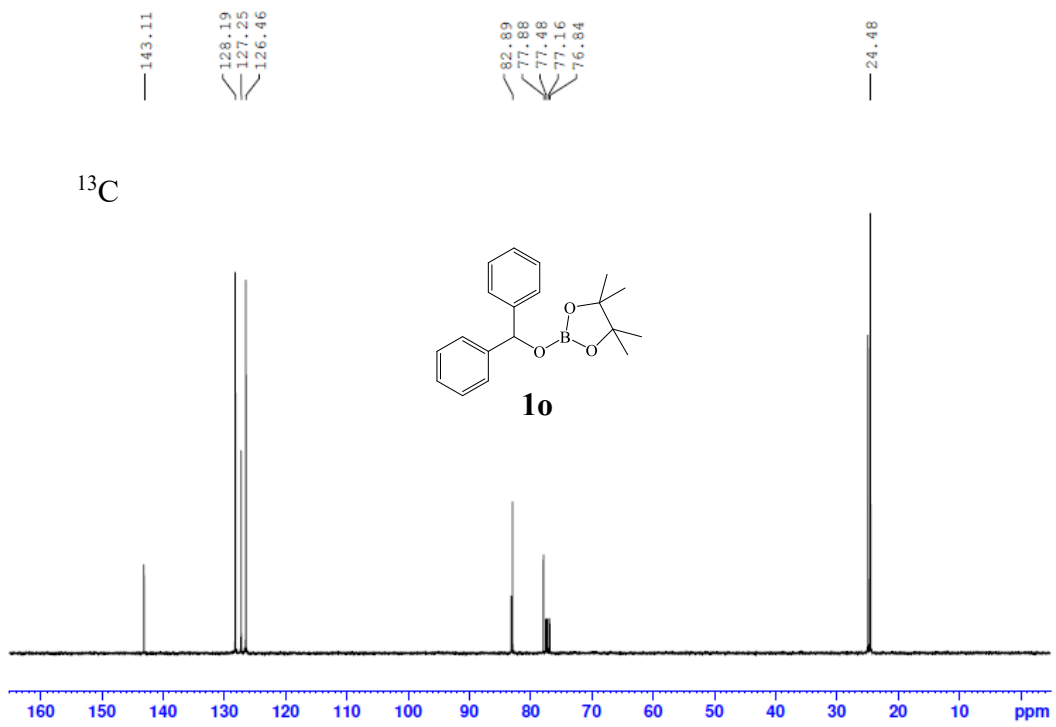


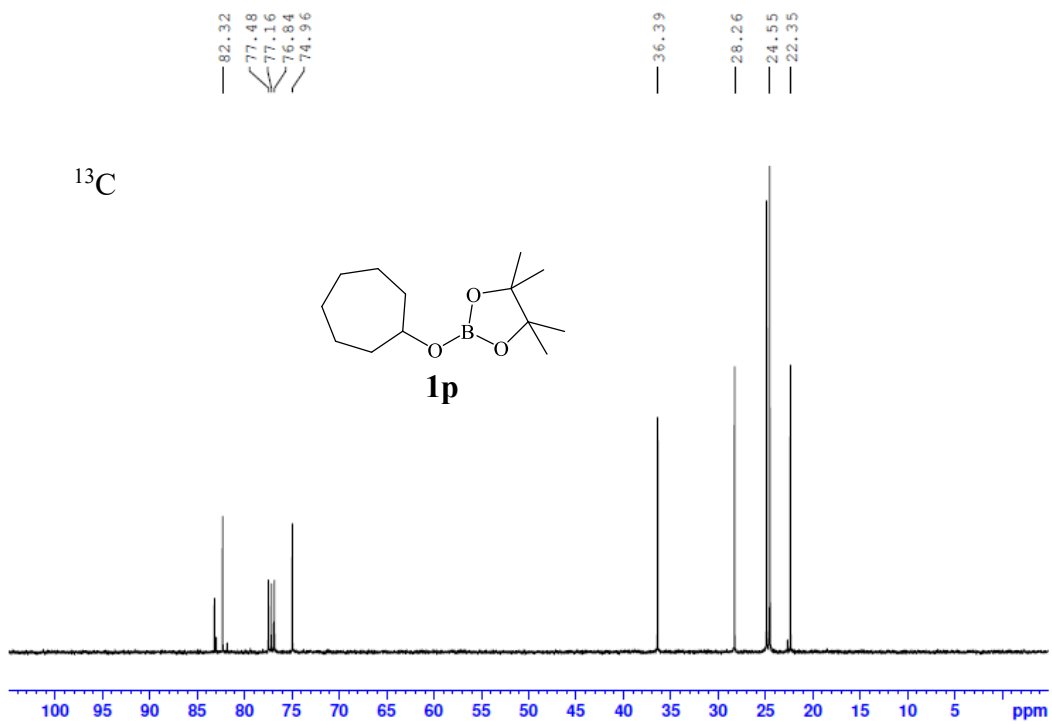
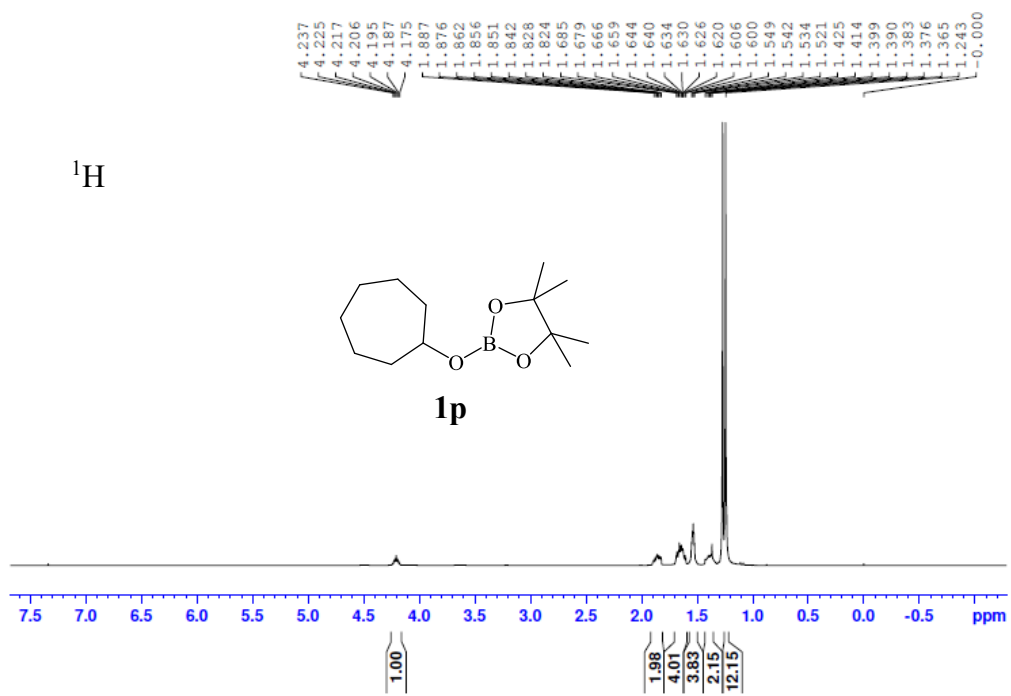






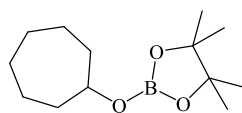




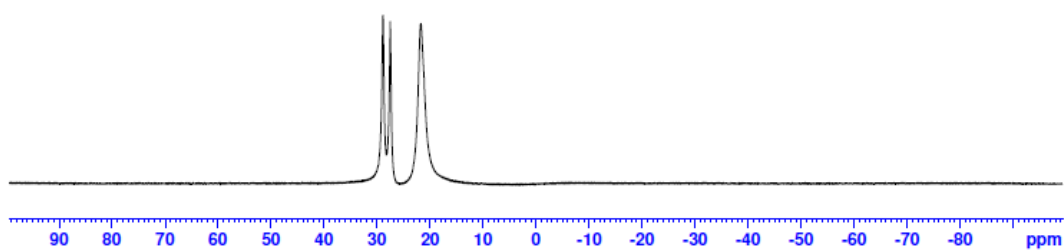


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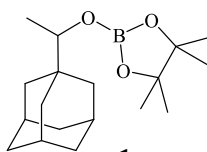
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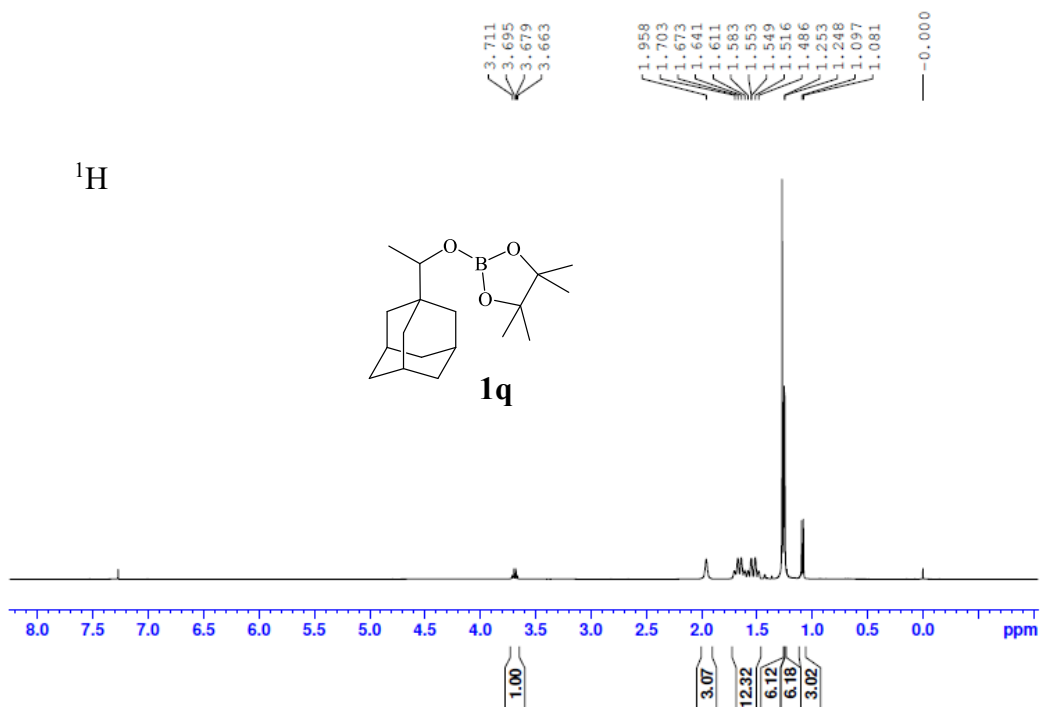
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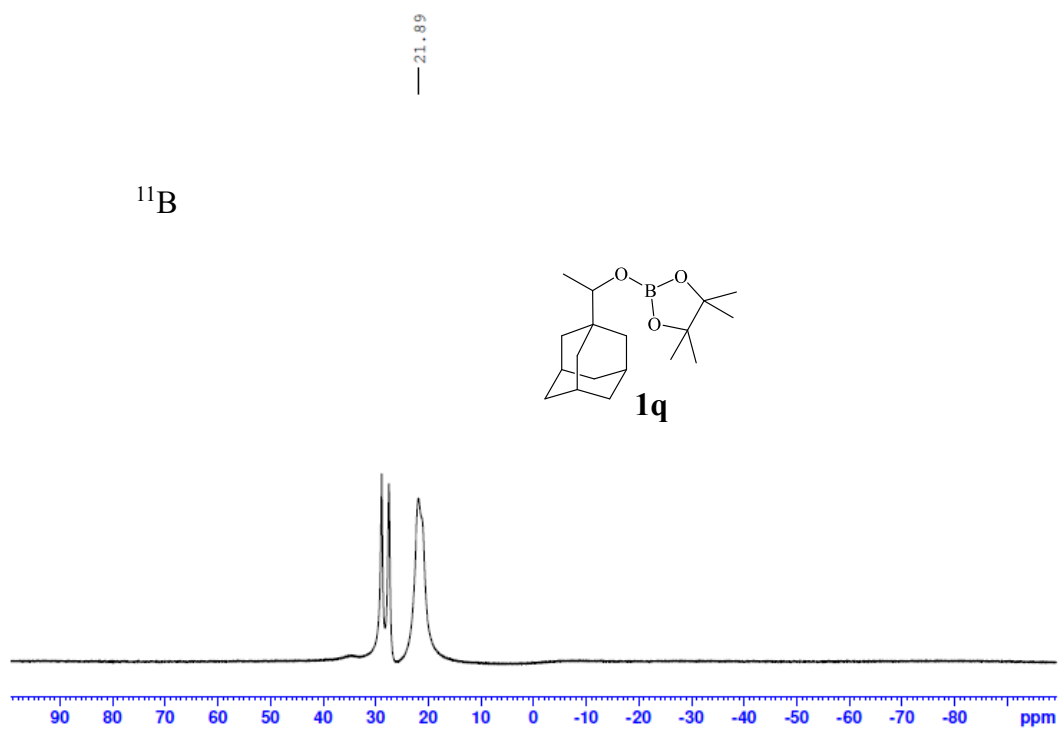
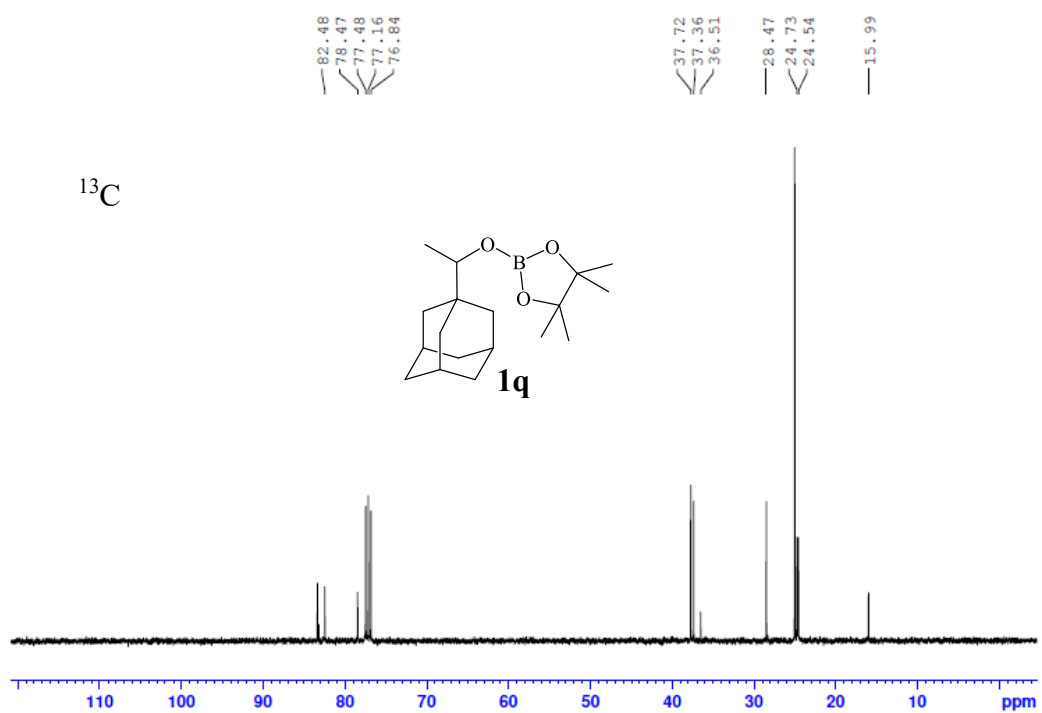


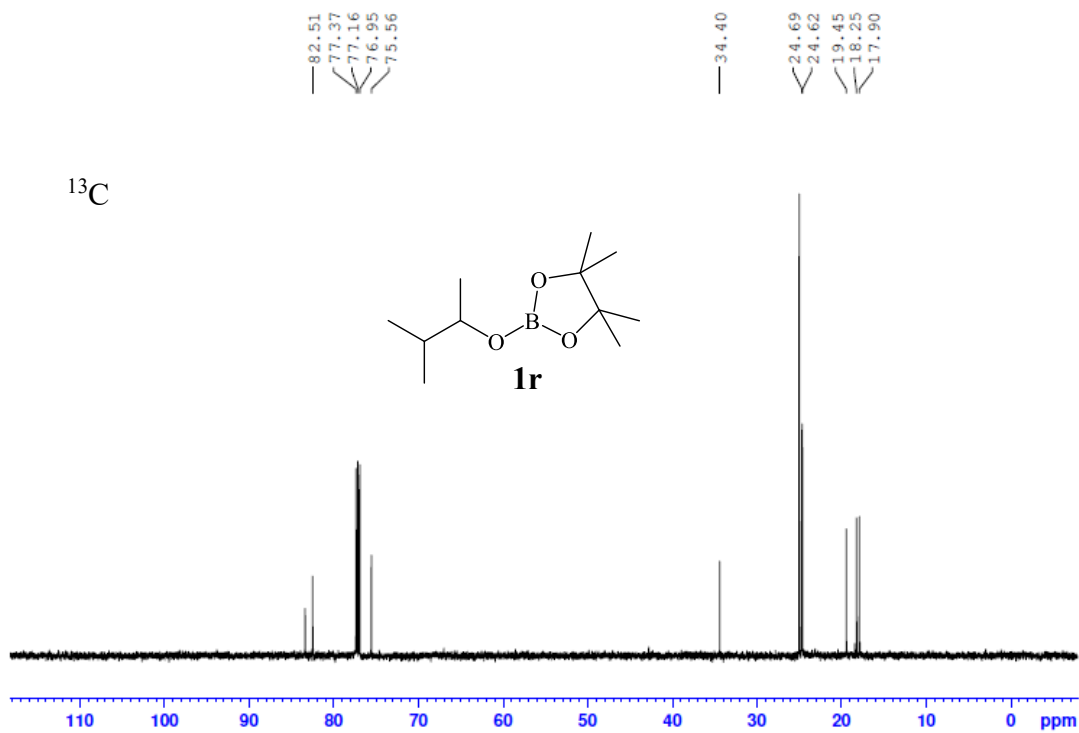
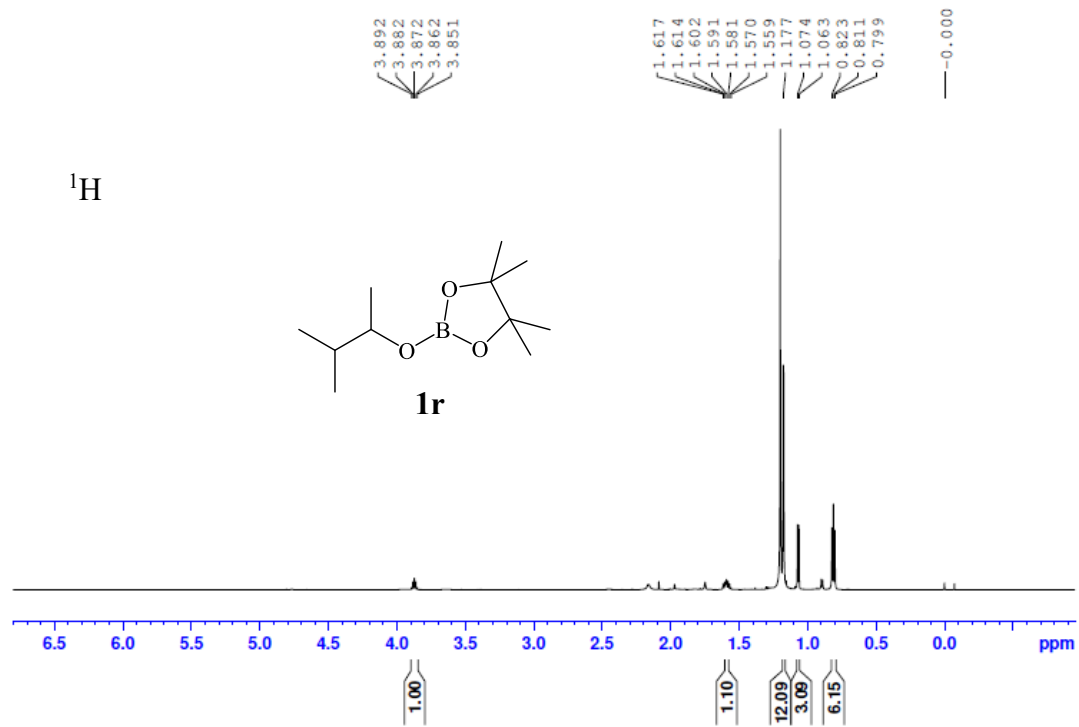
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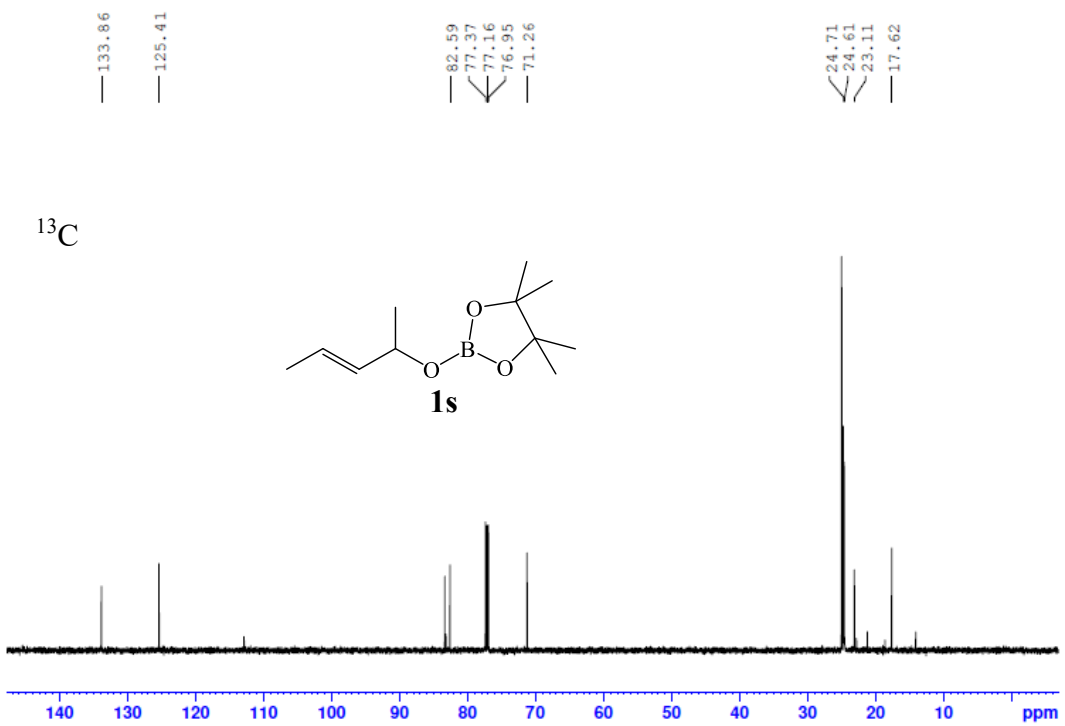
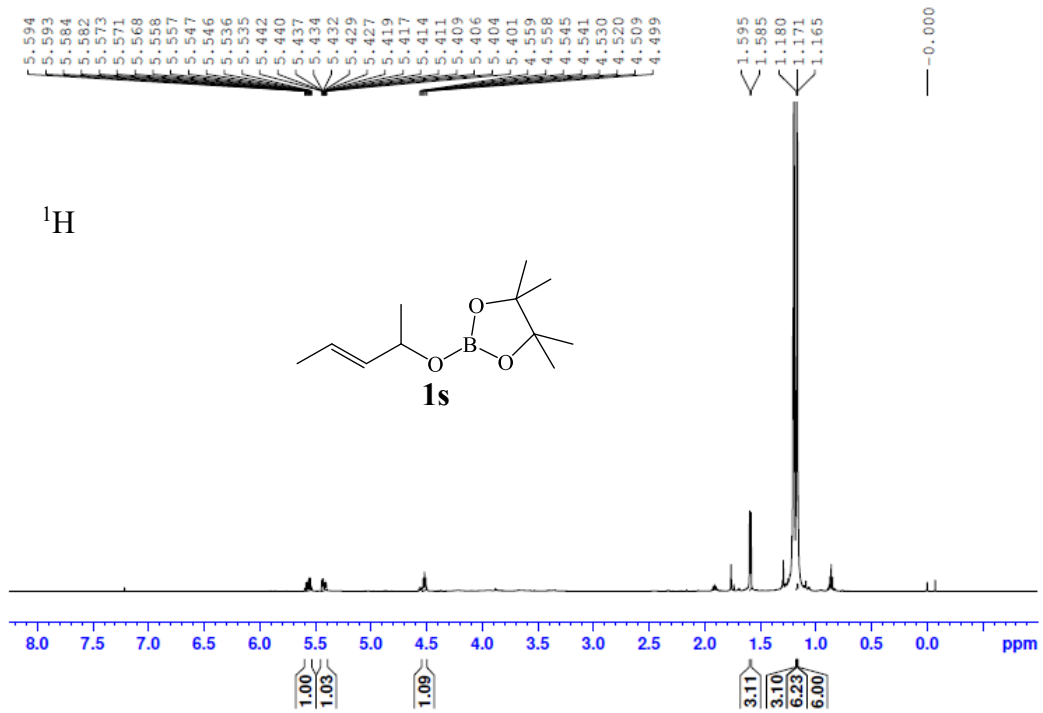


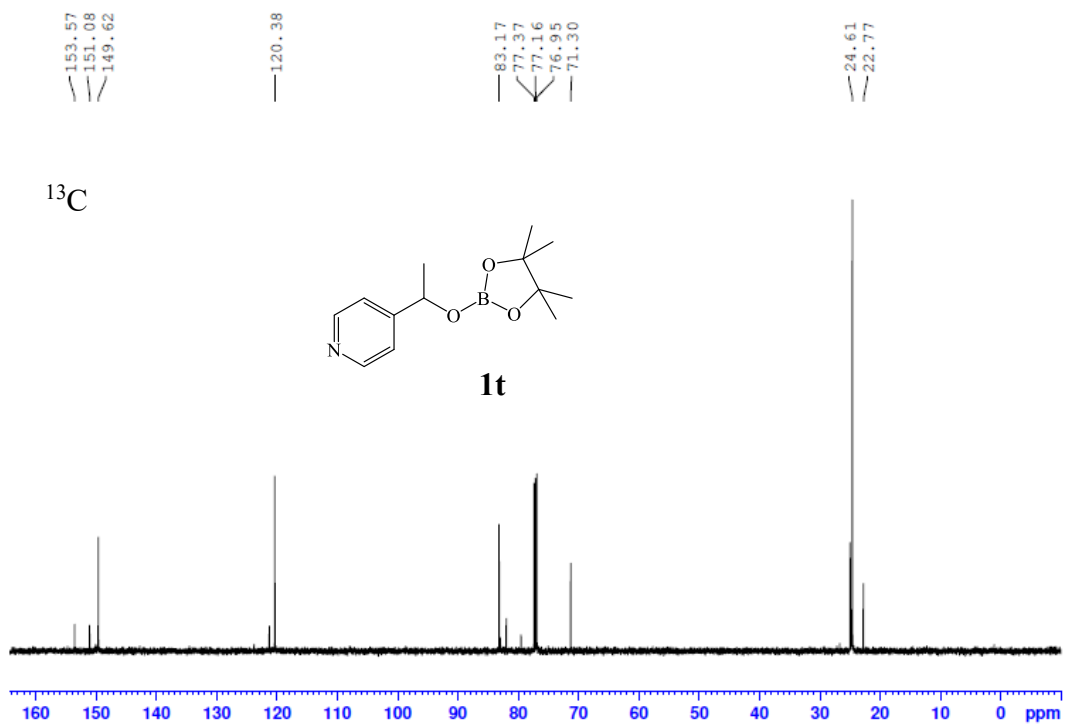
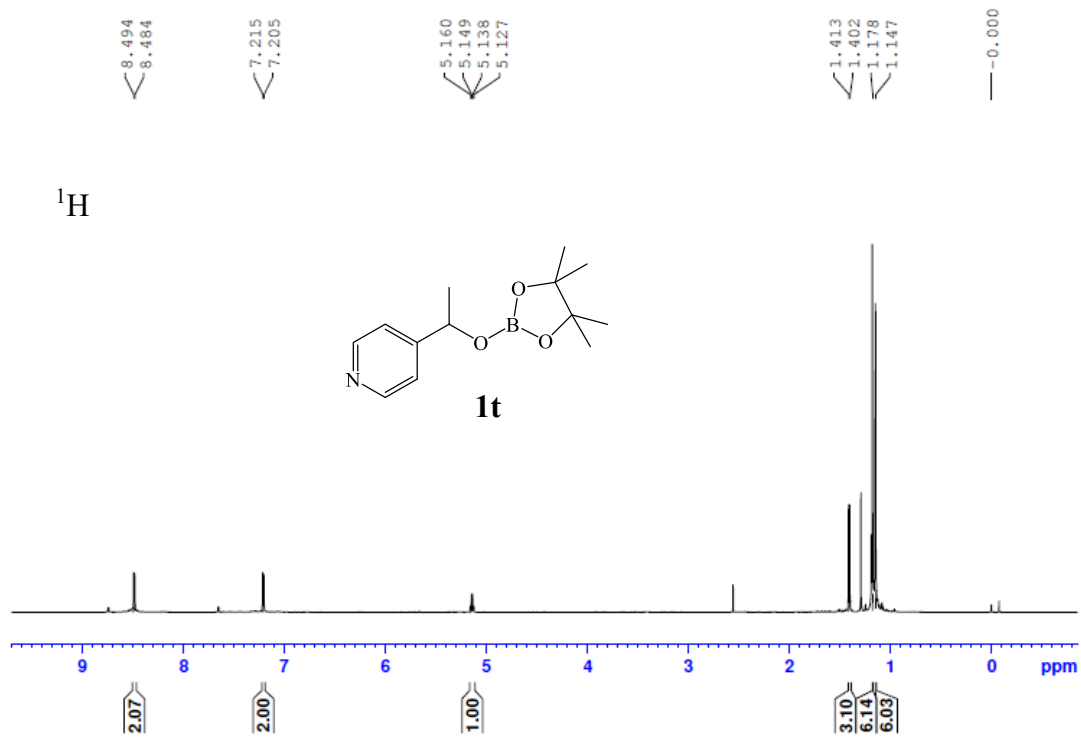
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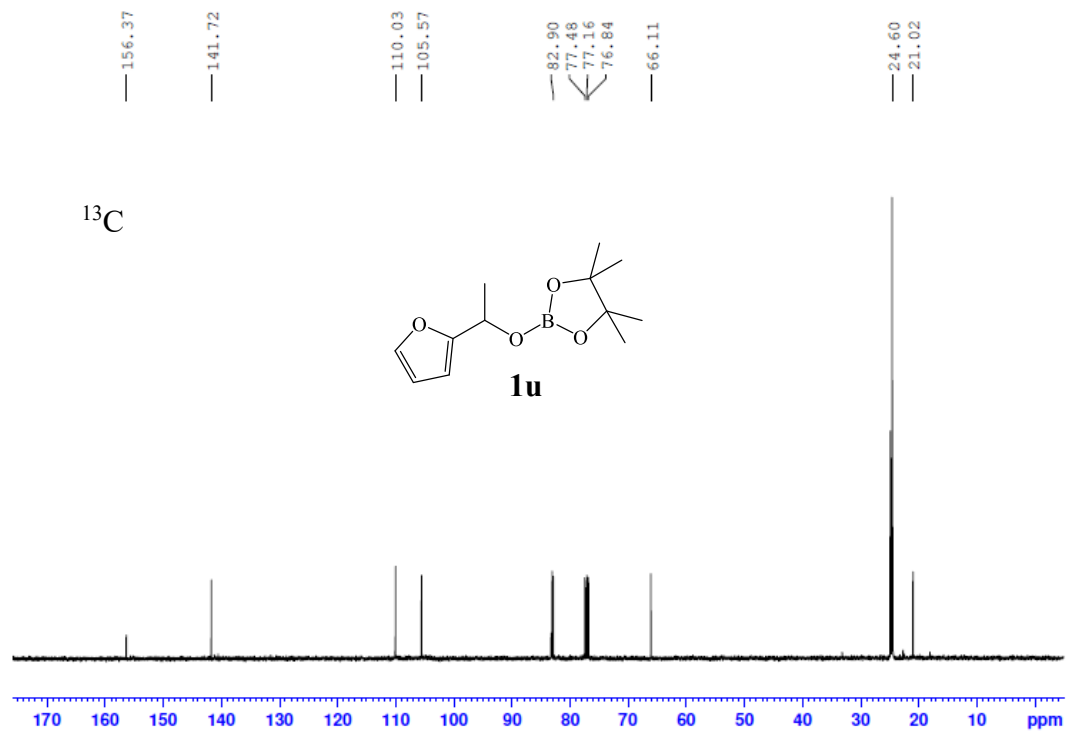
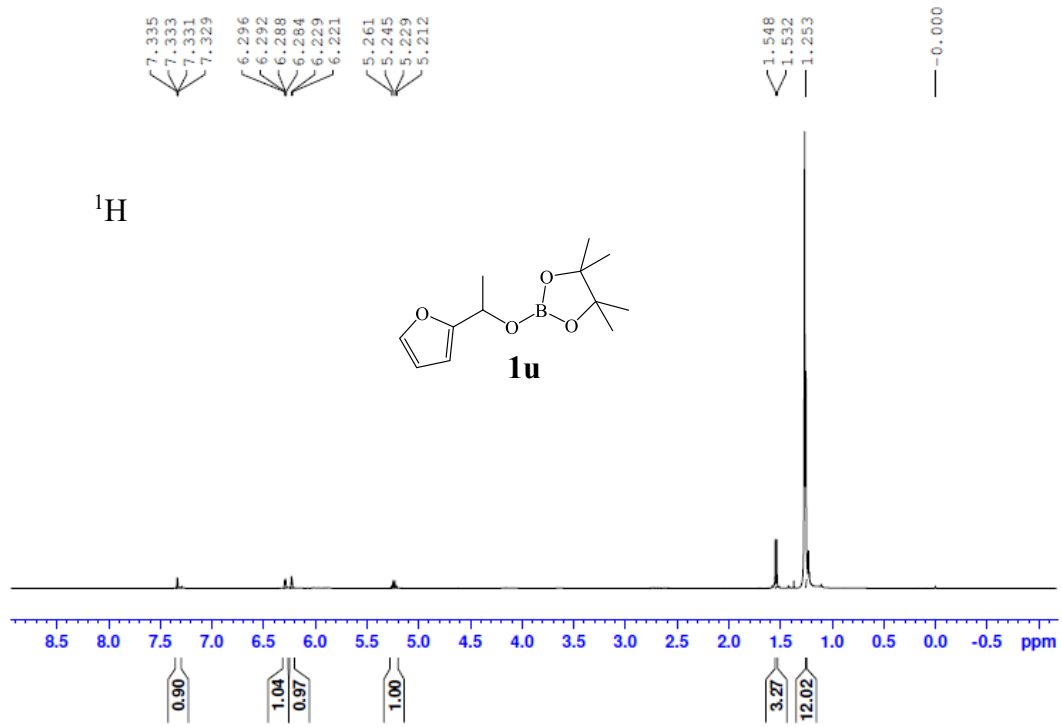






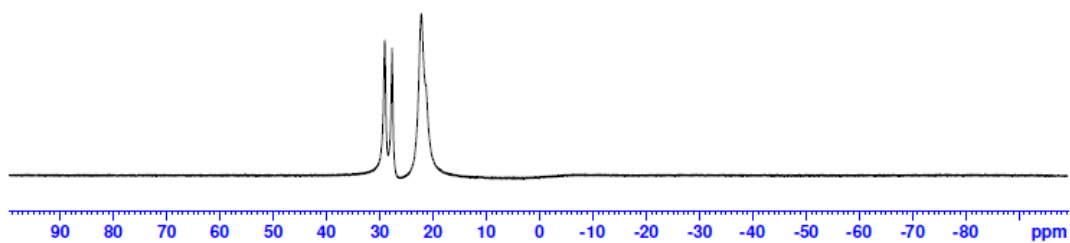
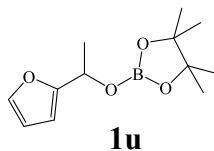




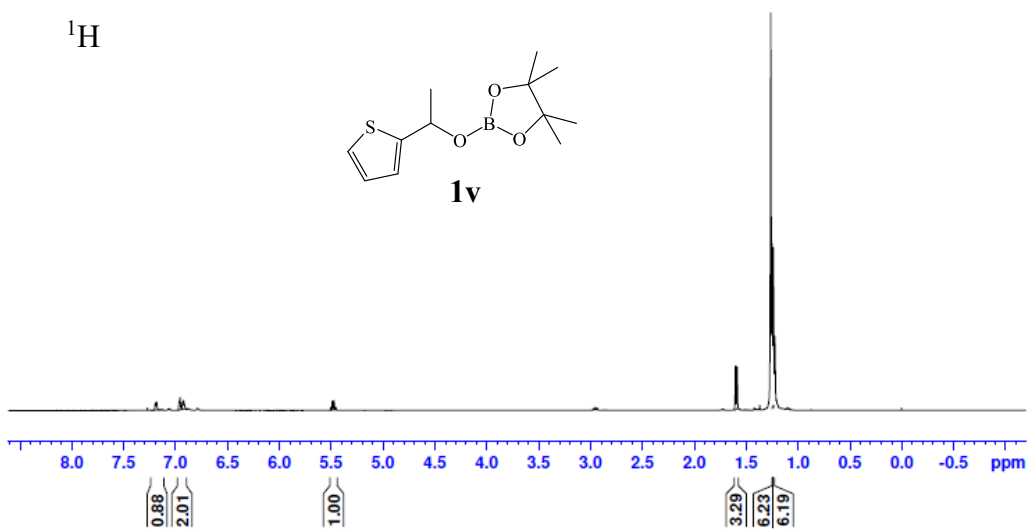
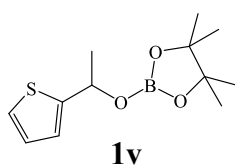


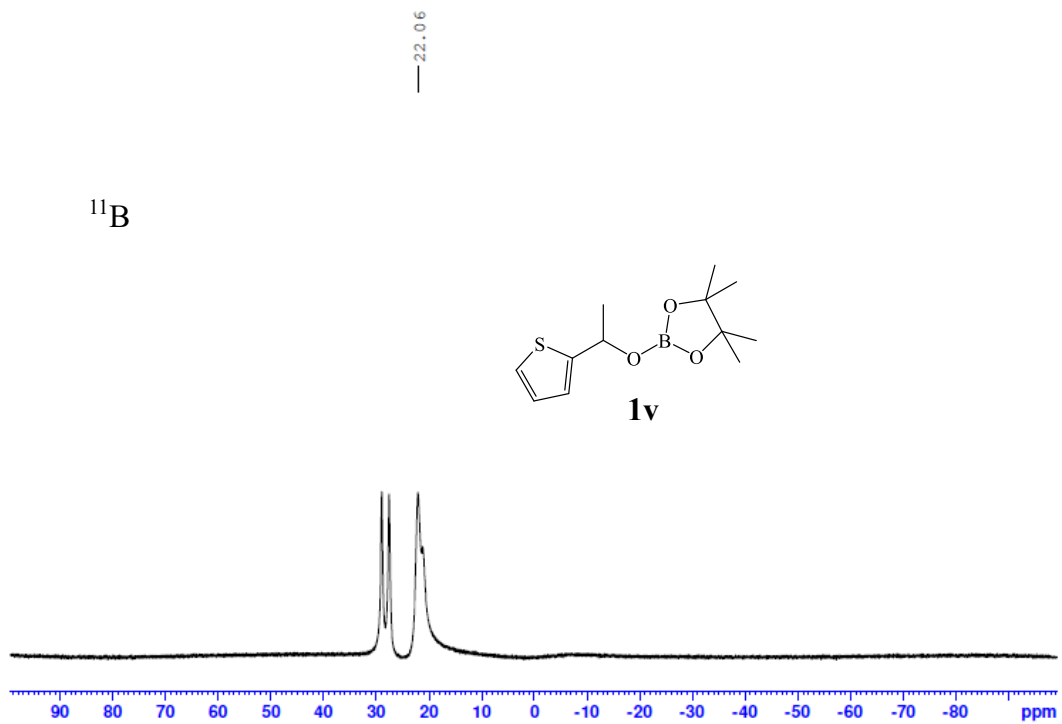
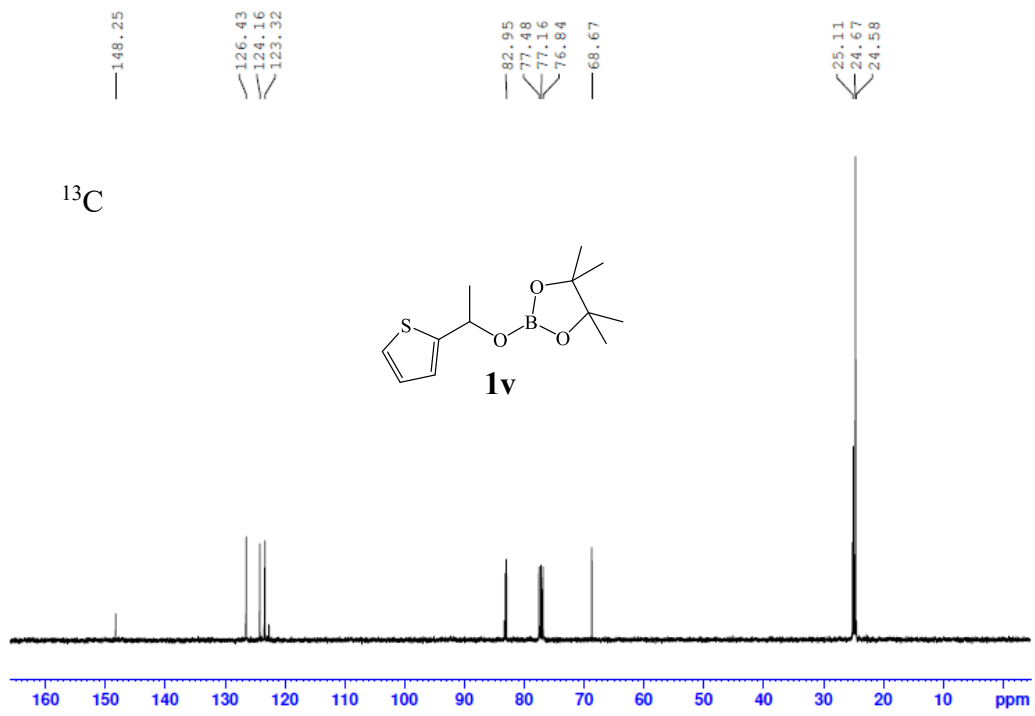
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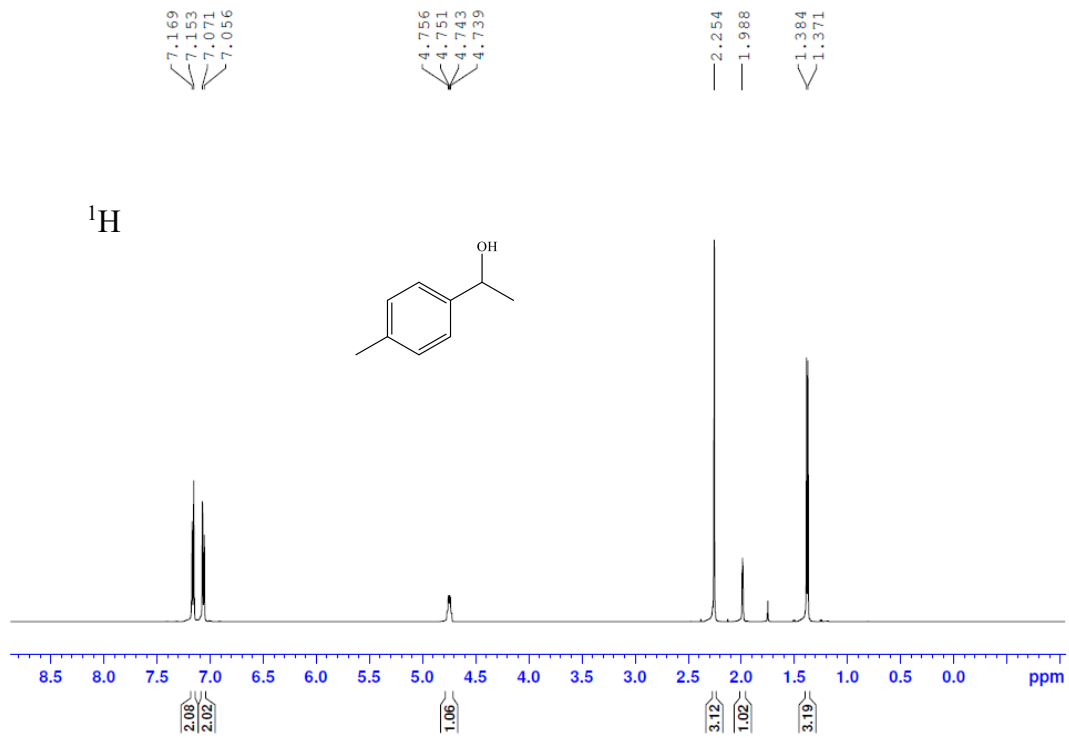
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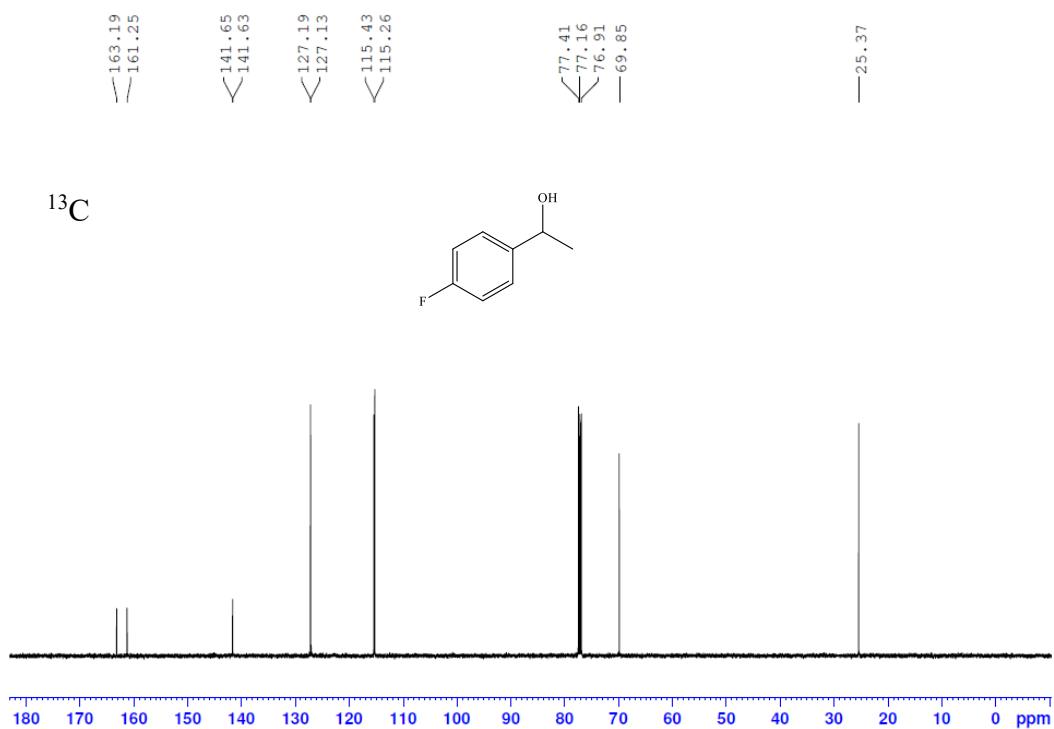
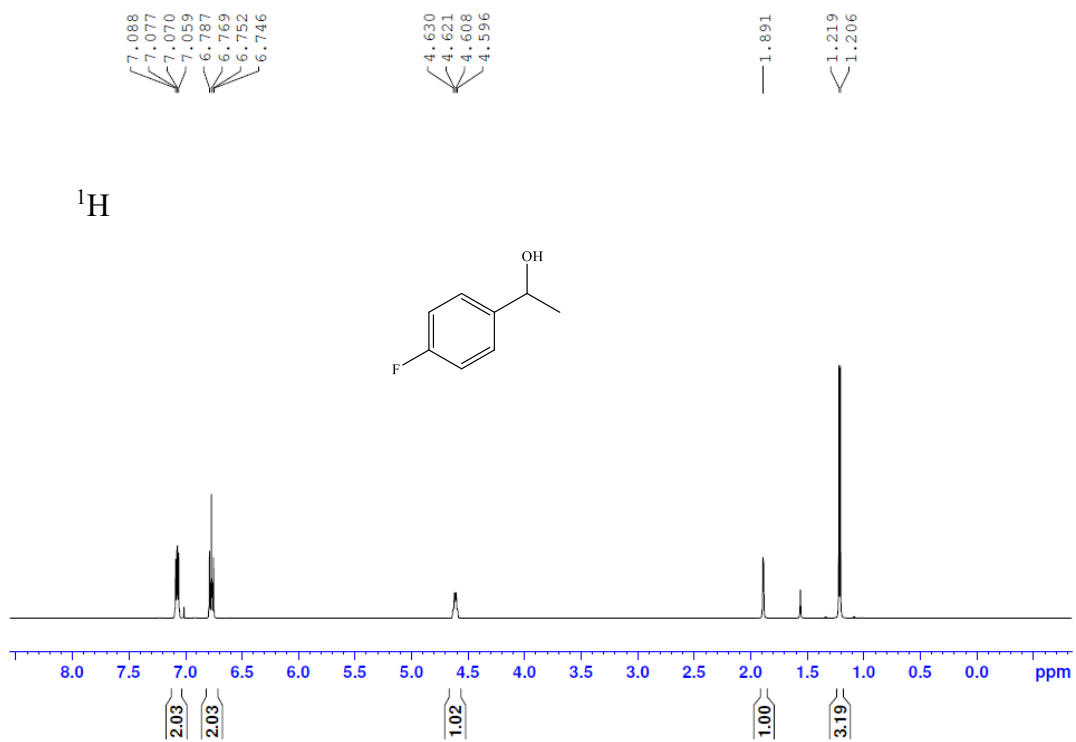


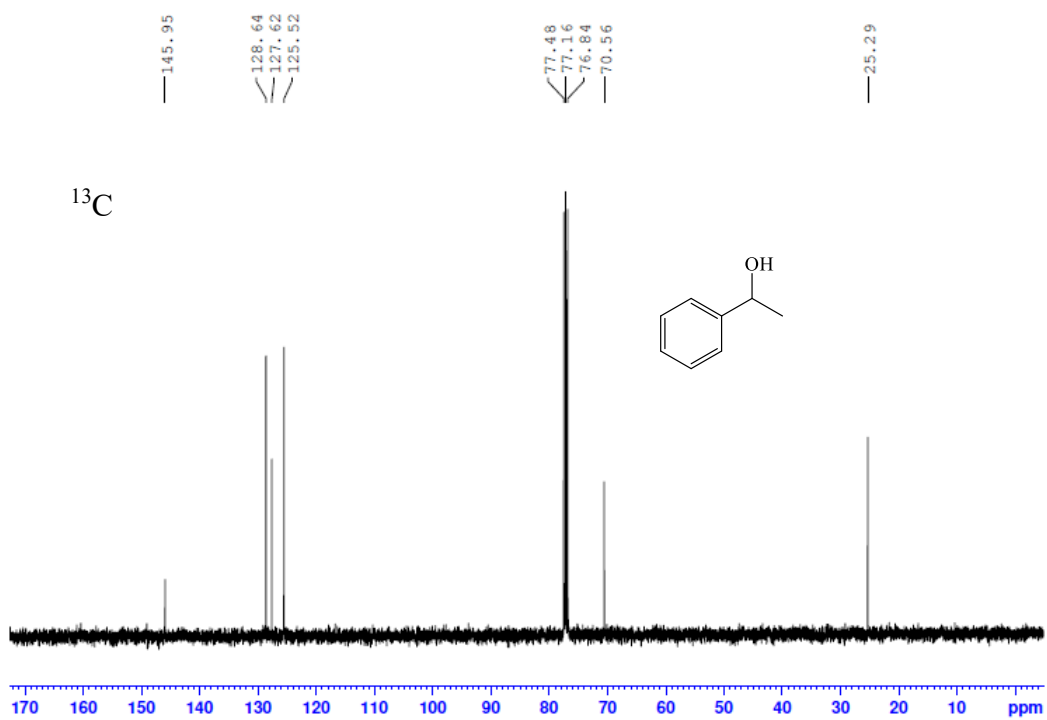
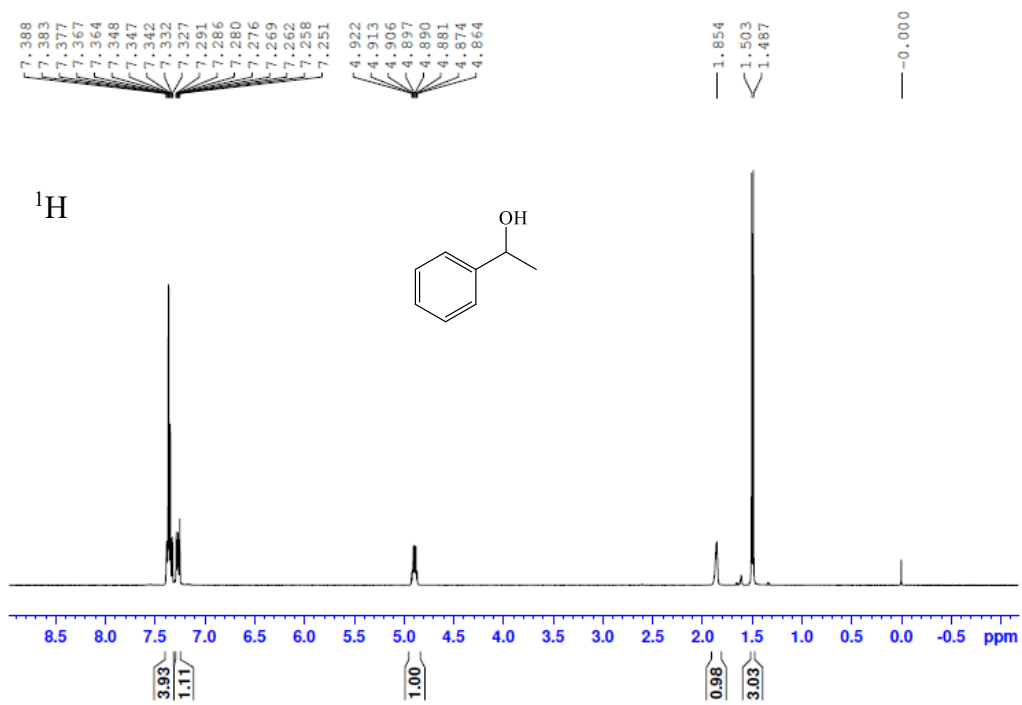
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Computational Studies

The computational studies were completed by using Gaussian 09.D01^[S1] program package. The geometries of the stationary points in ketone catalytic reaction were optimized in gas at the B3LYP^[S2]/6-31G*^[S3] level. Single point energies of the stationary points in gas have further been calculated at B3LYP/def2-TZVP^[S4] level. All reactants, products and intermediates have been identified as minimum (no imaginary frequency) or transition state (only one imaginary frequency) by performing analytical vibrational frequencies. Thermal corrections to Enthalpy and Gibbs free energy were calculated at 298.15K and 1atm. The difference between the Gibbs free energy in solvent and the Gibbs free energy in gas is the Gibbs free energy of dissolution^[S5].

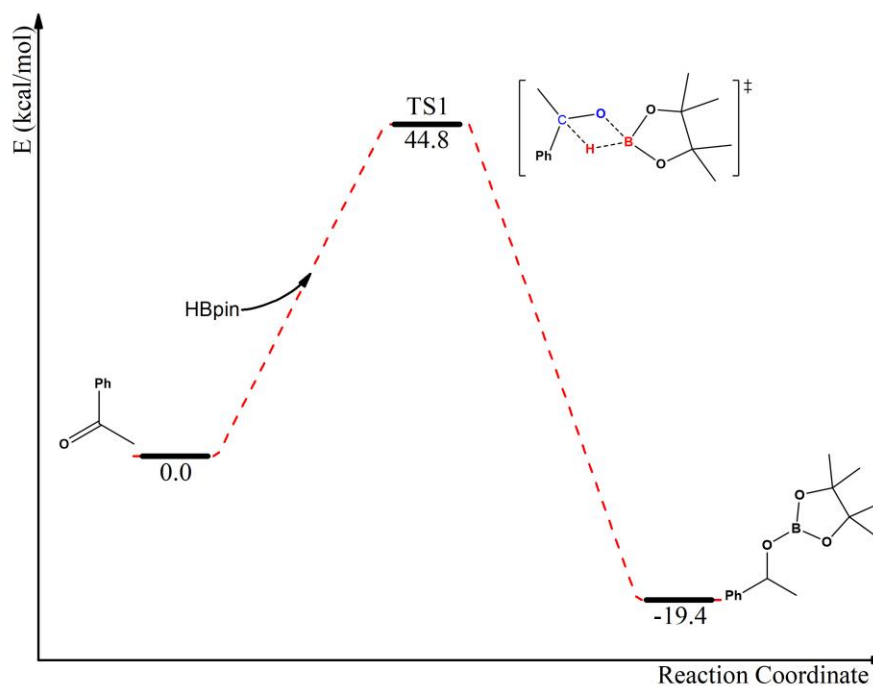


Fig. S1 Free energy profile for the hydroboration of acetophenone via a four-membered ring transition state pathway.

Table S1: E_{el} represents the single point energies at def2-TZVP. Thermal corrections to enthalpy (H_{corr}) and Gibbs free energy (G_{corr}) were calculated at 298.15K and 1atm. ΔG_{sol} are calculated by employing the SMD model at M05-2X/6-31G* level. The

optimized cartesian coordinates are also given.

Hypnone (B3LYP)

Eel = -385.04035

Hcorr = 0.14722

Gcorr = 0.105869

ΔG_{sol} = -384.9464297

C	1.32596200	-1.33139100	-0.00000500
C	2.21650900	-0.25101800	0.00005100
C	1.73577700	1.06049100	0.00000800
C	0.36120600	1.29222200	-0.00000600
C	-0.53398900	0.21472100	-0.00002400
C	-0.04538500	-1.10100900	-0.00005600
H	1.70718000	-2.34890700	-0.00001300
H	3.28796400	-0.43350800	0.00005500
H	2.43018000	1.89607800	0.00000600
H	-0.02480100	2.30978600	-0.00002300
H	-0.75940000	-1.91926400	-0.00008600
C	-1.99206400	0.46907100	-0.00006000
O	-2.84700900	-0.39615200	0.00007900
C	-2.38080267	1.95919926	0.00000639
H	-1.98439612	2.43117653	0.87464877
H	-1.98113982	2.43210387	-0.87265096
H	-3.44696966	2.04966580	-0.00193253

HBpin (B3LYP)

Eel = -412.032

Hcorr = 0.201984

Gcorr = 0.158359

$\Delta G_{sol} = -411.8802041$

B	-0.00007100	1.94494200	-0.00035500
H	-0.00025300	3.13486700	-0.00032600
O	-1.08610200	1.20090400	-0.36752200
O	1.08622900	1.20116200	0.36656500
C	-0.78923700	-0.19149000	-0.04498300
C	0.78924100	-0.19149200	0.04502600
C	-1.37972600	-1.07413000	-1.14309000
H	-1.14054600	-2.12925900	-0.96739700
H	-2.46942100	-0.97057500	-1.14828500
H	-1.01063100	-0.79279000	-2.13191900
C	-1.48003700	-0.48320900	1.29355200
H	-2.54921100	-0.27221500	1.19415500
H	-1.36098600	-1.53070600	1.58961600
H	-1.08481000	0.15102900	2.09318000
C	1.48004300	-0.48415600	-1.29329100
H	2.54929600	-0.27361400	-1.19385600
H	1.36053400	-1.53174500	-1.58884600
H	1.08522900	0.14988100	-2.09328300
C	1.37967700	-1.07329600	1.14380000
H	1.14084900	-2.12860900	0.96870900
H	2.46934500	-0.96942400	1.14926300
H	1.01017500	-0.79143500	2.13233400

TS1(B3LYP)

Eel = -797.02189

Hcorr = 0.34832

Gcorr = 0.284152

$\Delta G_{sol} = -796.7551723$

C	3.54617600	-1.84335300	-0.15784900
C	4.71228100	-1.27422600	0.36276800
C	4.76361400	0.09402600	0.64189700
C	3.64990100	0.89445700	0.40289300
C	2.47700600	0.33130600	-0.12930700
C	2.43348900	-1.04729900	-0.40697500
H	3.50648800	-2.90845300	-0.36669100
H	5.58135100	-1.89786100	0.55469500
H	5.66992600	0.53496200	1.04671200
H	3.70073800	1.95577000	0.62189200
H	1.51214500	-1.46939600	-0.79239200
C	1.28200100	1.14541300	-0.44167900
O	0.36393800	0.63302200	-1.20857800
C	1.30166500	2.64558200	-0.27534700
H	1.75672000	2.96747100	0.66359600
H	1.88561300	3.05929600	-1.10962500
H	0.28104900	3.02375100	-0.34681100
B	-0.60042000	0.44560400	0.04902700
H	0.21652100	0.83789100	0.96812700
O	-0.95165200	-0.91641900	0.25162200
O	-1.75802900	1.25734700	-0.08149300
C	-2.36153300	-1.01597800	-0.04589600
C	-2.87880900	0.43501500	0.30092800
C	-2.95046300	-2.13705200	0.81055100
C	-2.51611200	-1.35897600	-1.53695100
C	-3.12918000	0.63206000	1.80528900

C	-4.10101100	0.89539000	-0.49472800
H	-4.03751100	-2.20366000	0.68181900
H	-2.51609500	-3.09694300	0.51055100
H	-2.73148200	-1.98674300	1.87036800
H	-1.94545600	-2.26913700	-1.74961600
H	-3.56235000	-1.53890300	-1.80968100
H	-2.12285800	-0.55724900	-2.16878000
H	-3.26539500	1.70050200	2.00254500
H	-4.02605700	0.10277500	2.14674200
H	-2.27520000	0.28343700	2.39440300
H	-4.96768500	0.25355400	-0.29580000
H	-4.36503000	1.91817000	-0.20432800
H	-3.90153500	0.89295700	-1.56882600

Product (B3LYP)

Eel = -797.13035

Hcorr = 0.35444

Gcorr = 0.288755

$\Delta G_{sol} = -796.8575883$

H	-0.99477800	1.29369600	0.64120600
C	-1.35918800	0.80577300	-0.27088100
C	-1.38798000	1.83650300	-1.40512500
H	-1.70622400	1.36012200	-2.33826700
H	-2.08817100	2.64627100	-1.17387100
H	-0.39141300	2.26832900	-1.54744300
C	-2.73302800	0.21720000	-0.00195000
C	-3.15076300	-0.96971600	-0.61394700
C	-3.62414600	0.89669200	0.83732900
C	-4.43750700	-1.46331200	-0.39262000

H	-2.45657400	-1.50888100	-1.24988700
C	-4.91181600	0.40647000	1.05644900
H	-3.30638600	1.81501800	1.32779100
C	-5.32296100	-0.77689000	0.44013900
H	-4.74747200	-2.38921500	-0.87059800
H	-5.58995300	0.94399200	1.71433700
H	-6.32378700	-1.16391500	0.61284000
O	-0.45750000	-0.25376200	-0.62574400
B	0.85905000	-0.18296000	-0.30864900
O	1.75094900	-1.15327400	-0.70220200
O	1.43651100	0.83655800	0.42264000
C	2.99069200	-0.89676100	0.00944900
C	2.87667900	0.64457800	0.34520500
C	4.15672000	-1.27769500	-0.90083400
C	2.98175200	-1.78853100	1.25862800
C	3.38379100	1.55033800	-0.78485500
C	3.49331100	1.06813100	1.67671700
H	5.11705200	-1.04470000	-0.42652800
H	4.12933100	-2.35400000	-1.09881300
H	4.10514200	-0.75850300	-1.86047600
H	2.85508700	-2.83025800	0.94850600
H	3.91683700	-1.70656900	1.82257800
H	2.15098800	-1.53151600	1.92362500
H	3.08489000	2.58198400	-0.57395400
H	4.47495800	1.51950200	-0.87106000
H	2.95213300	1.26206300	-1.74868900
H	4.57296600	0.87955200	1.68460400
H	3.33672100	2.14088400	1.82995400
H	3.04037900	0.53808900	2.51761200

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