Role of Catechol in the Radical Reduction of *B*-Alkylcatecholboranes in Presence of Methanol

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General Informations: Unless otherwise stated, all reagents were obtained from commercial sources and used without further purification. All glassware was oven-dried at 130 °C or flame dried under vacuum, assembled hot and allowed to cool under nitrogen. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker Avance II 400 spectrometer (^{1}H: 400.12 MHz, ^{11}B: 128.38 MHz). The ^{13}C and some ^{1}H NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300.18 MHz, ^{13}C: 75.48 MHz). Chemical shifts are reported in units of δ (ppm) using the internal standart residual (C_6H_6 $\delta = 7.16$ ppm for ^{1}H NMR spectra and C_6D_6 $\delta = 120.06$ ppm for ^{13}C NMR spectra) or Et_2OBF_3 as an external standart ($\delta = 0$ ppm) for ^{11}B NMR spectra. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. GC analyses were carried out on a CE instruments MEGA Series HRGC fitted with an Optima delta-3 (Macherey-Nagel) capillary column (30 m and 10 m). GC/MS analyses were carried out on a Finnigan Trace GC/MS fitted with an Optima delta-3 (30 m).

General Procedure for the preparation of NMR samples

C_6D_6 was purchased from Cambridge Isotopes and degassed by 5 cycles freezing / vacuum / nitrogen then stored on MS 4A in the glove box under Argon (MBRAUN Uni-Lab (1200/780)). Commercially available *B*-*n*-propylcatecholborane (PrBCat) and catecholborane (CatBH) were distilled under reduced pressure prior to use (respectively 73 °C, 1 mbar and 50 °C, 67 mbar). Catechol was recrystallised from benzene then sublimed under reduced pressure. Commercial anhydrous methanol (Aldrich) was used without further purification. All the samples were prepared in the glove box and readily sealed under vacuum.

B-Methoxy-1,2,3-benzodioxaborole (4)

To a solution of CatBH (15 mmol, 1,6 mL) in C_6H_6 (10 mL), MeOH (1 equiv, 15 mmol, 0.6 mL) was added dropwise. The resulting solution was stirred until no more H_2 evolution was visible (c.a. 15 min). After evaporation of the solvent, the residue was distilled under reduced pressure to yield MeOBCat **4** as a colorless oil. ^{1}H-NMR (400 MHz, C_6D_6): 6.88-6.93 (m, 2H), 6.71-6.77 (m, 2H), 3.37 (s, 1H). ^{13}C-NMR (75 MHz, C_6D_6): 148.6, 122.5, 112.2, 53.1. ^{11}B-NMR (128 MHz, C_6D_6): 23.5.

Dimethyl-propylboronicester (7b)

Propylboronic acid (5 mmol, 0.44 g) was dissolved in C_6D_6 (2 mL) with MeOH (5 equiv., 25 mmol, 1 mL). After 5 min stirring, the resulting solution was distilled at atmospheric pressure. 0.550 g of an azeotropic mixture (T = 45 – 55 °C) of $B(OMe)_3$, $PrB(OMe)_2$ and MeOH (1:10:50 determined by integration of ^1H NMR spectra) was obtained as a colorless liquid. This mixture was readily dissolved in C_6D_6 over MS 4 Å to trap the excess of MeOH. The resulting solution was used as obtained for NMR experiments. ^1H-NMR (400 MHz, C_6D_6): 3.36 (s, 6H), 1.53-1.62 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H), 0.69 (t, J = 7.6 Hz, 2H). ^{13}C-NMR (75 MHz, C_6D_6): 51.2, 17.8, 17.4.^{11}B-NMR (128 MHz, C_6D_6): 31.9. NMR data are in good accordance with the literature.[1]

***B*- isopinocampheyl-1,2,3-benzodioxaborole (3a)**

Catecholborane (1.2 mL, 9 mmol) was added dropwise to α-pinene **1a** (5 mmol). The reaction mixture was heated neat at 100 °C for 12 h. Distillation of the crude material furnished pure **3a** (80 °C, 10^{-3} mbar) as a colorless oil. ^1H-NMR (300 MHz, C_6D_6): 7.09-7.03 (m, 2H), 6.85-6.76 (m, 2H), 2.44-2.10 (m, 4H), 1.93-1.87 (m, 1H), 1.65-1.56 (m, 1H), 1.19 (d, J = 7.2 Hz, 1H), 1.16 (s, 3H), 1.03 (s, 3H), 0.92 (d, J = 9.7 Hz, 1H). ^{13}C-NMR (75 MHz, C_6D_6): 149.1, 122.8, 112.6, 48.3, 41.6, 38.9, 38.8, 34.4, 29.0, 28.6, 23.3, 23.0.

***cis*-Pinane (2a)**

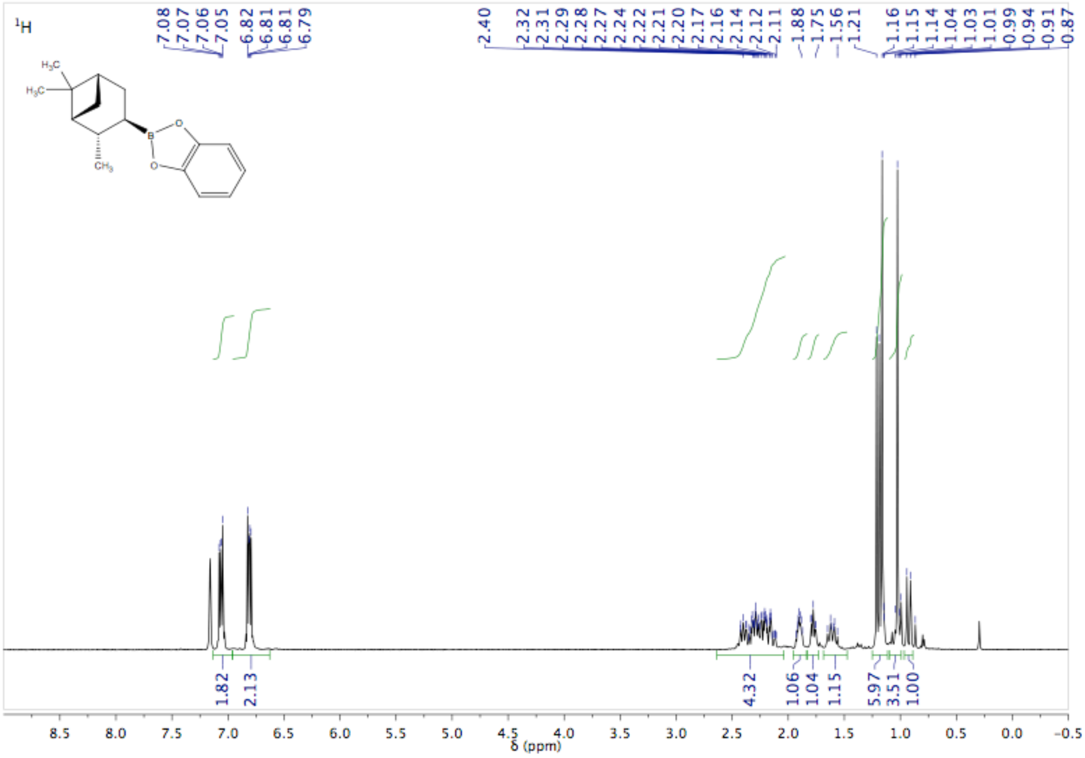
From α-pinene **1a**: Catecholborane (0.4 ml, 3 mmol) was added dropwise at 0 °C to a solution of **1a** (1.5 mmol) and *N*,*N*-dimethylacetamide (14 µl, 0.15 mmol) in CH_2Cl_2 (2.0 ml) under N_2. The reaction mixture was heated under reflux for 5 h. After cooling down to 0 °C, MeOH (0.24 ml, 6 mmol) was added. The solution was heated under reflux and air (60 ml, 0.5 mmol O_2) was introduced over 1.5 h using a syringe pump (needle placed just below the surface of the reaction mixture).

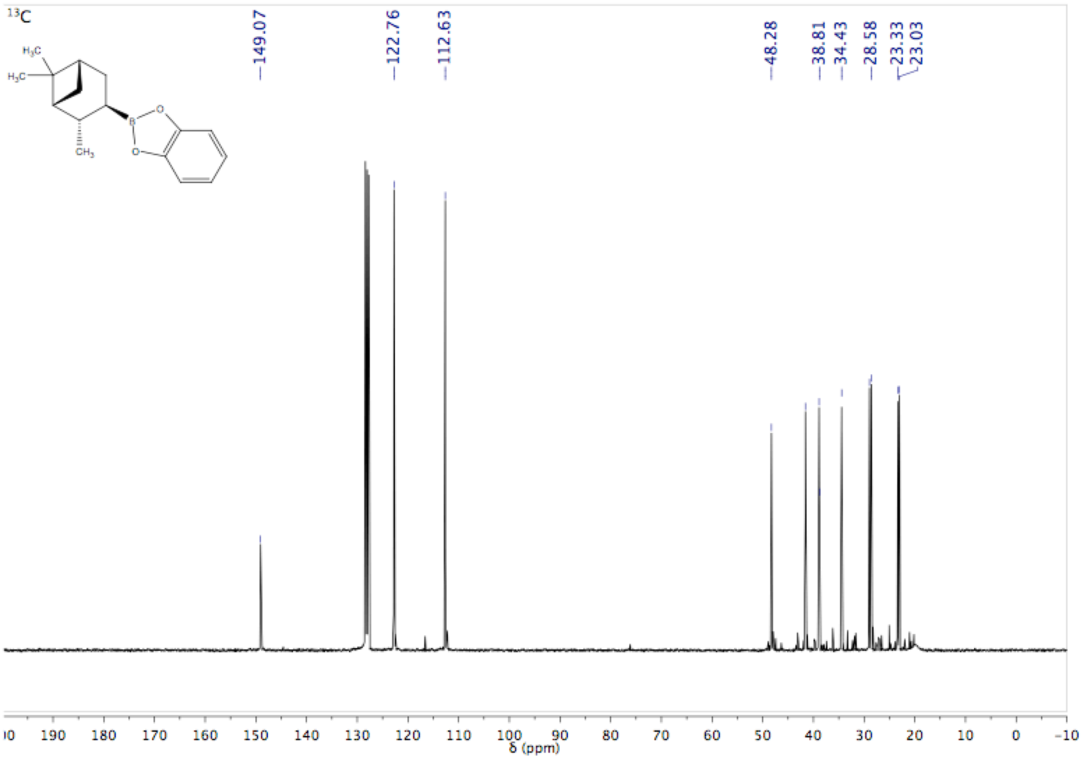
From *B*-isopinocampheylcatecholborane **(3a)**: To a solution of **3a** (1.5 mmol, 384 mg) in CH_2Cl_2 (2.0 ml) under N_2, MeOH (0.24 ml, 6 mmol) or catechol (1.5 mmol, 249 mg) was added. The solution was heated under reflux and air (60 ml, 0.5 mmol O_2) was introduced over 1.5 h with a syringe.

GC yield was determined using phenylcyclohexane as internal standard. The retention time (t_r = 2.57 min, 60°C-280 °C, rate: 6 °C/min, 45 KPa, helium, l = 10 m) and CG/MS analysis of the reduced product were found to be identical with commercially available (1*R*)-(+)- *cis*-pinane.

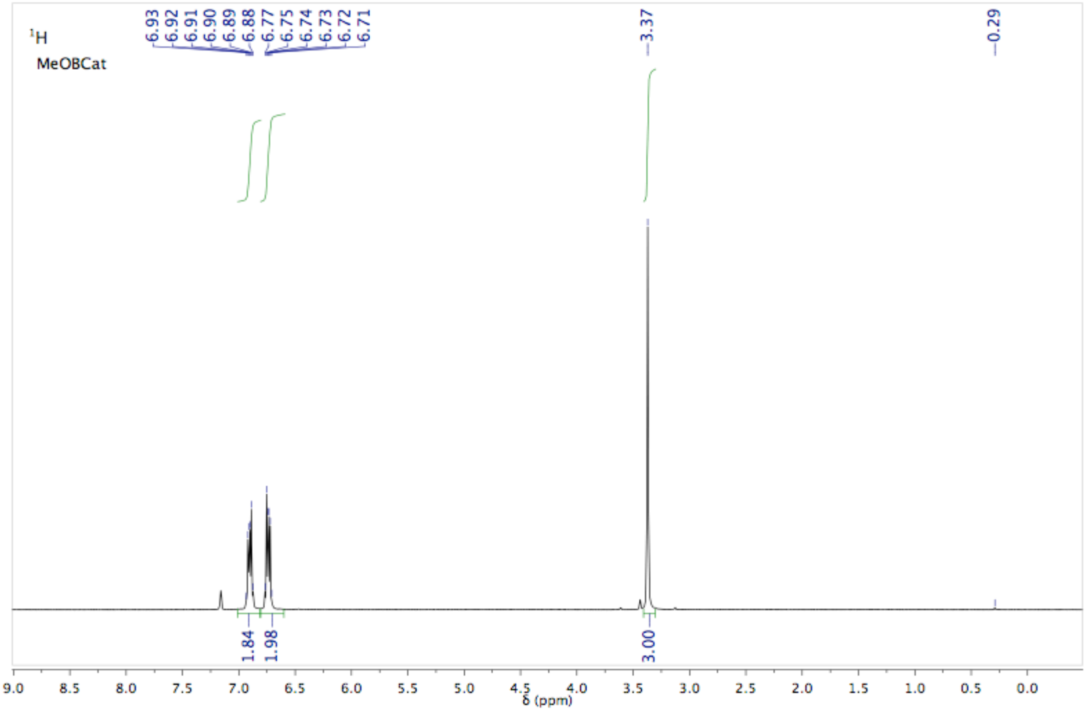
[1] J. P. Costes, G. Cros, J. P. Laurent, *J. Organomet. Chem.* **1979**, *175*, 257-71

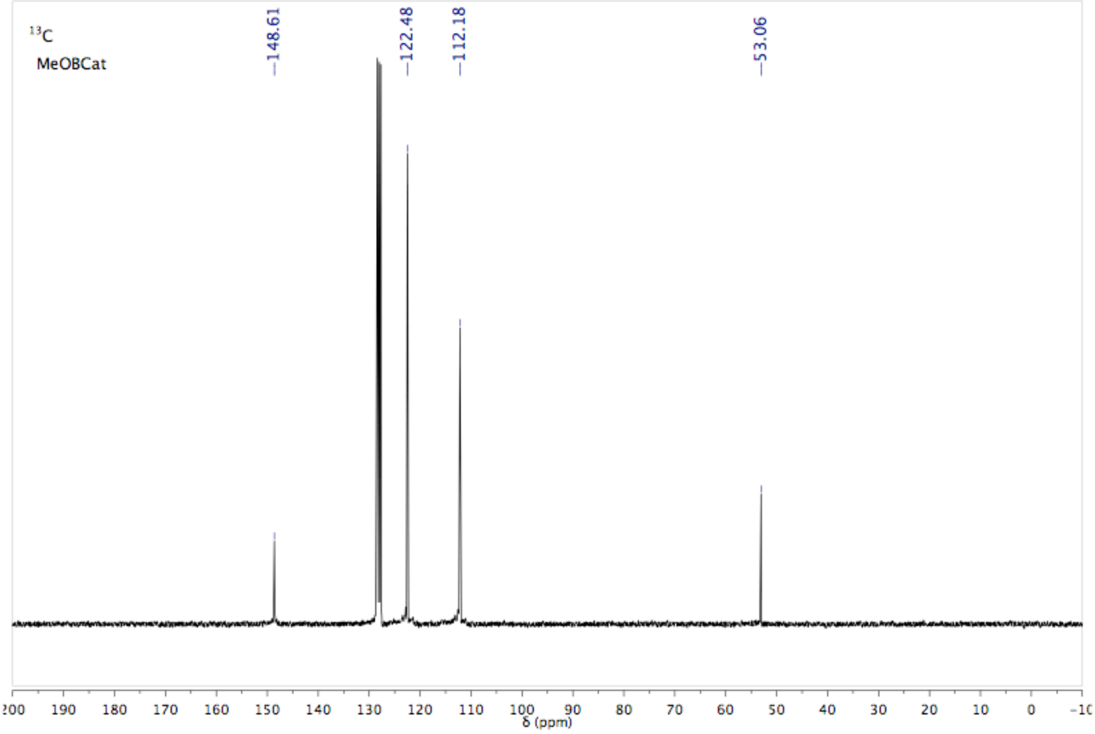
B-*cis*-α-Pinyl-1,2,3-benzodioxaborole (3a)

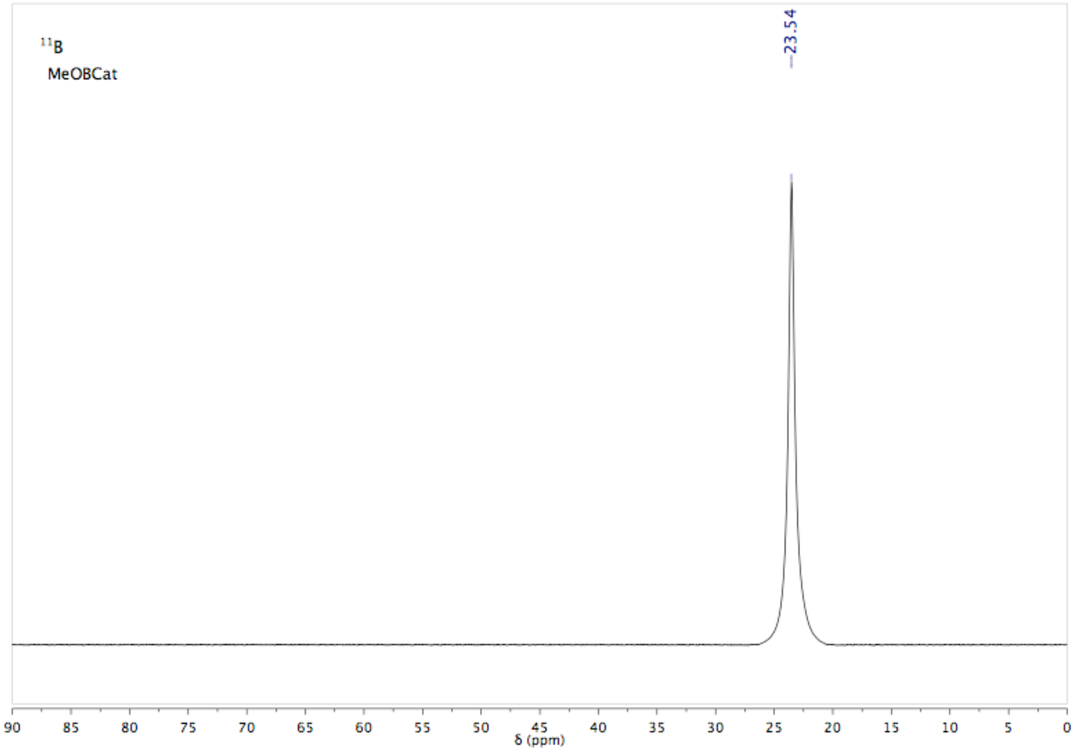


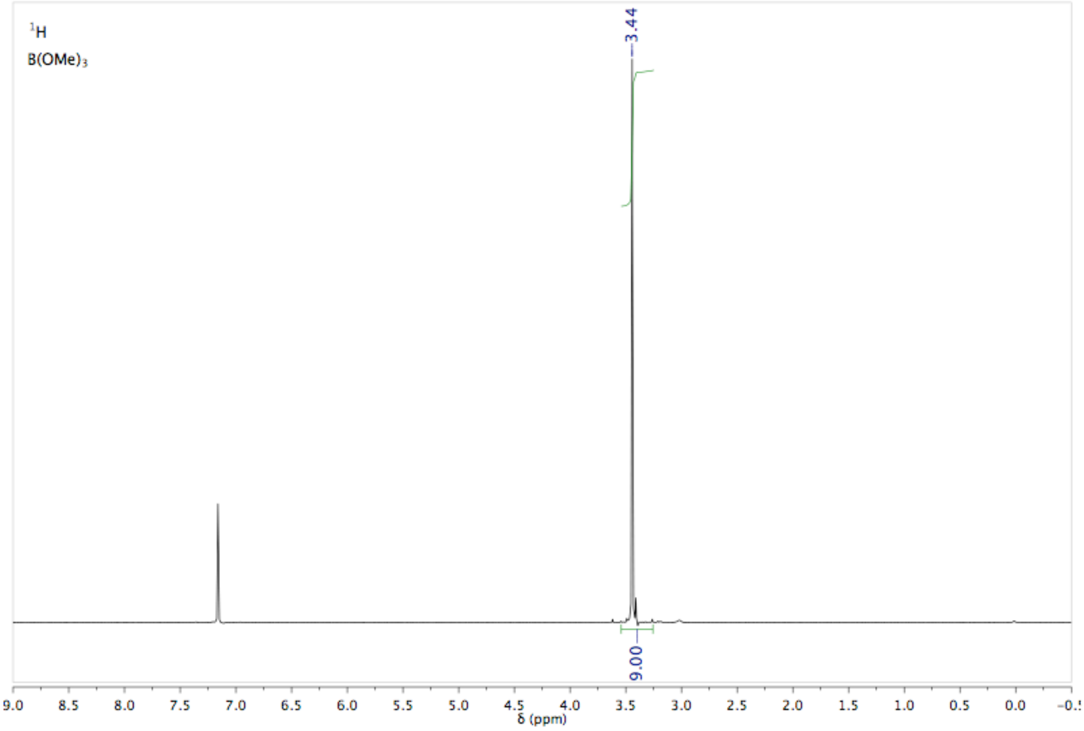


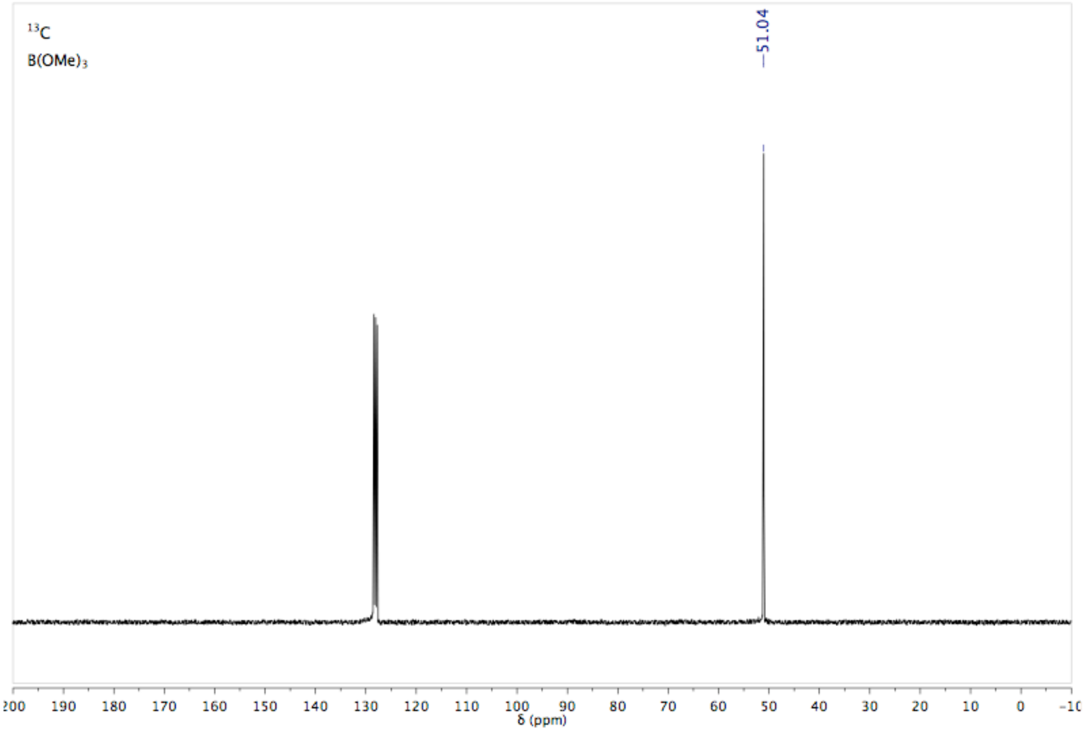
MeOBCat/MeOH NMR study

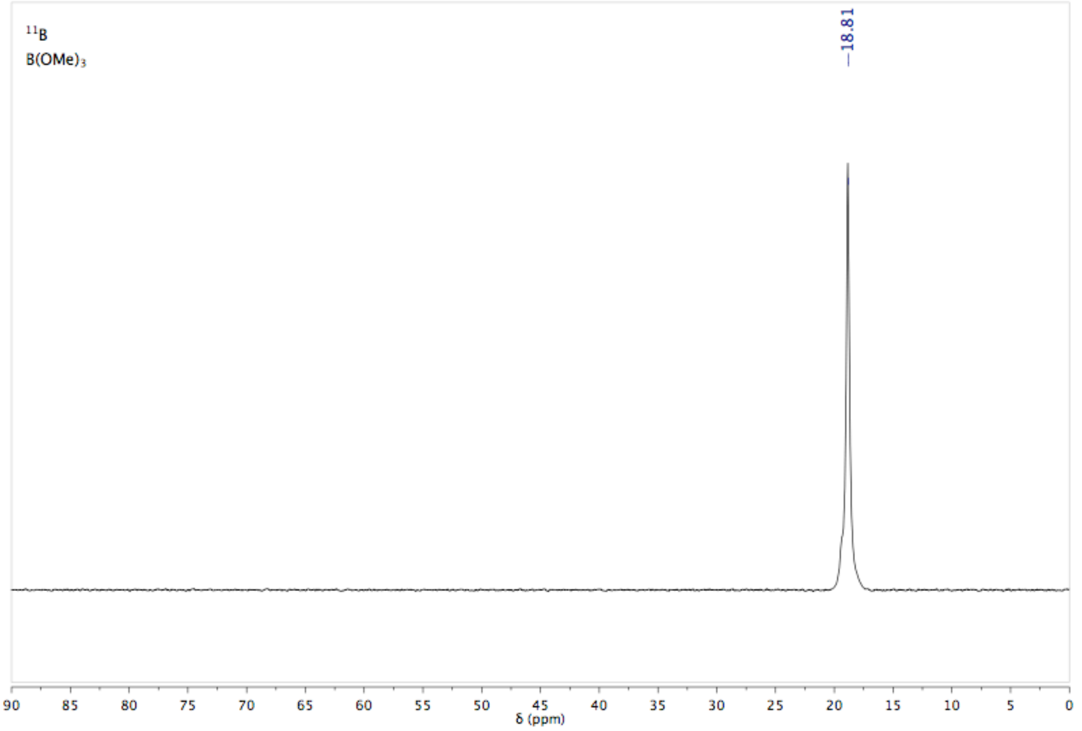


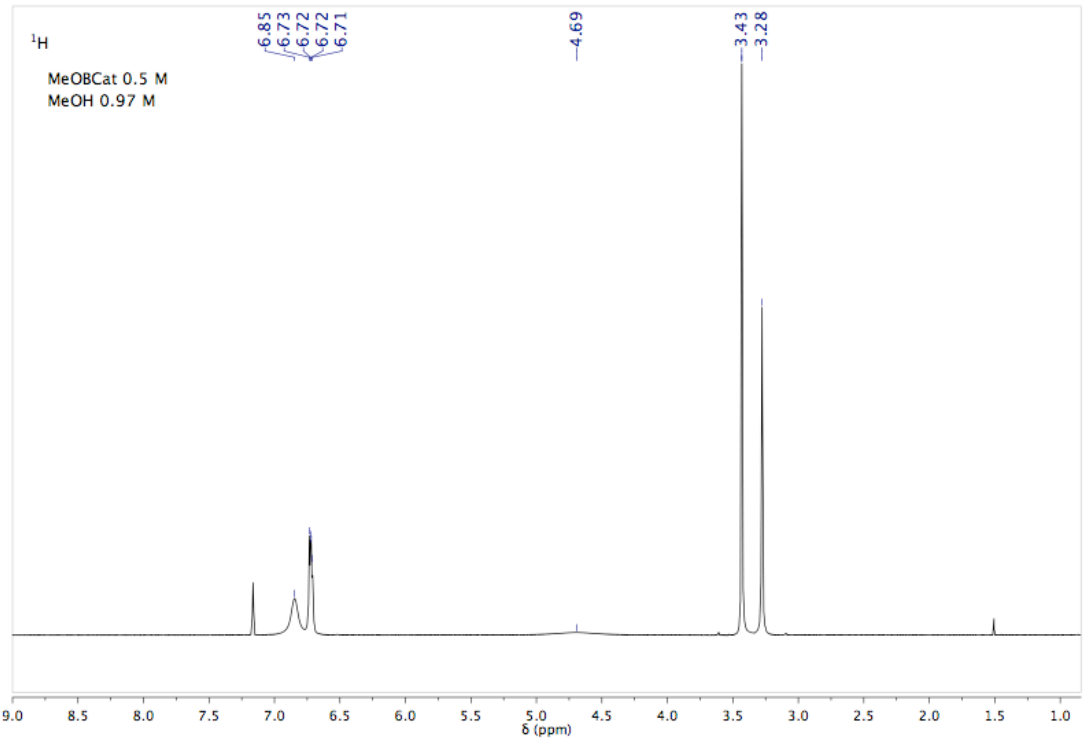


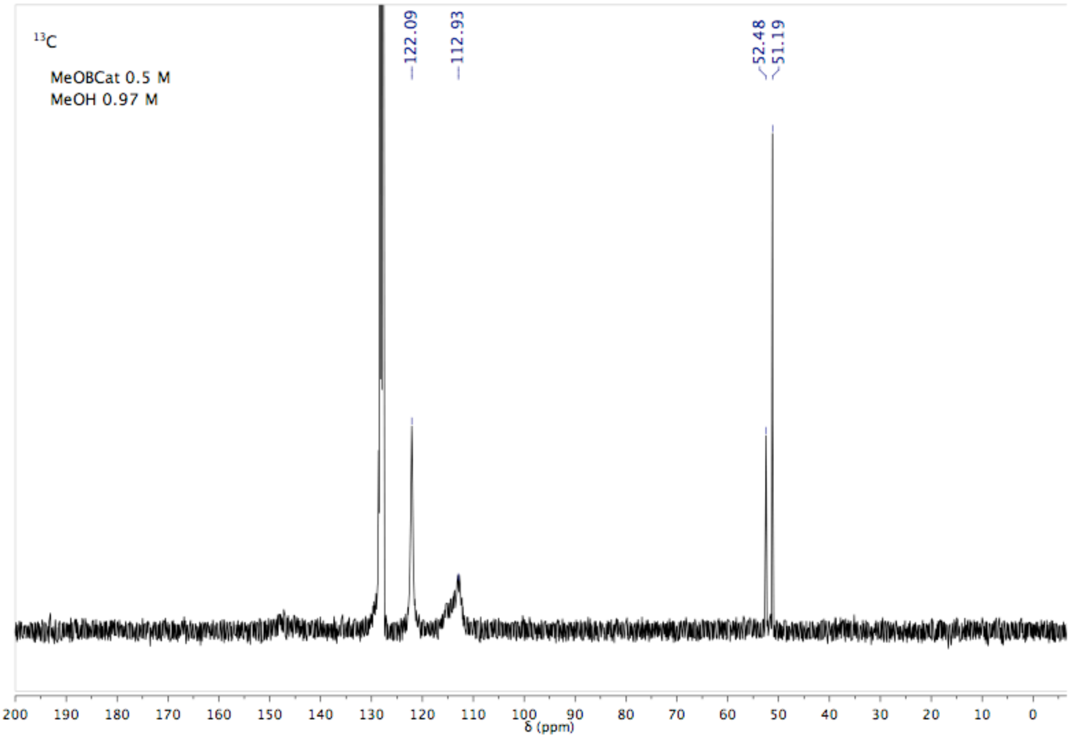

11B
MeOBCat
23.54
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)


1H
B(OMe)3
3.44
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
δ (ppm)

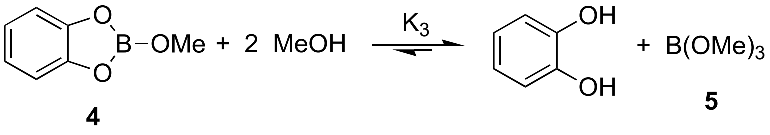

^{13}C
$B(OMe)_3$
51.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)


^{11}B
$B(OMe)_3$
18.81
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)


1H
MeOBCat 0.5 M
MeOH 0.97 M
6.85
6.73
6.72
6.72
6.71
4.69
3.43
3.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
δ (ppm)

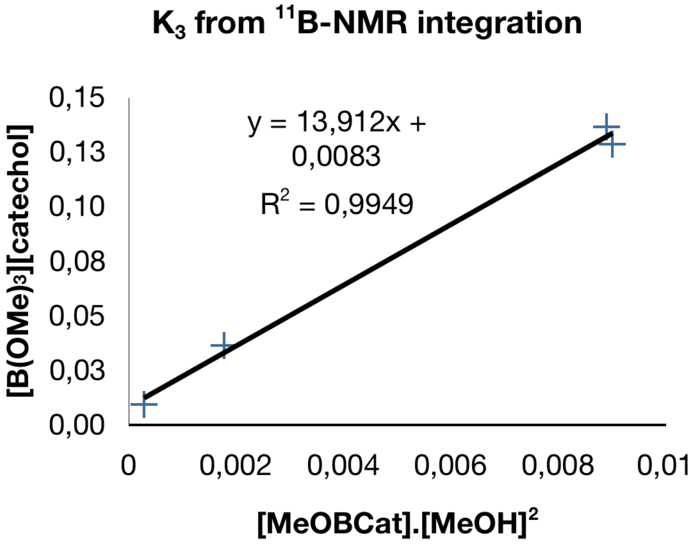

13C
MeOBCat 0.5 M
MeOH 0.97 M
122.09
112.93
52.48
51.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

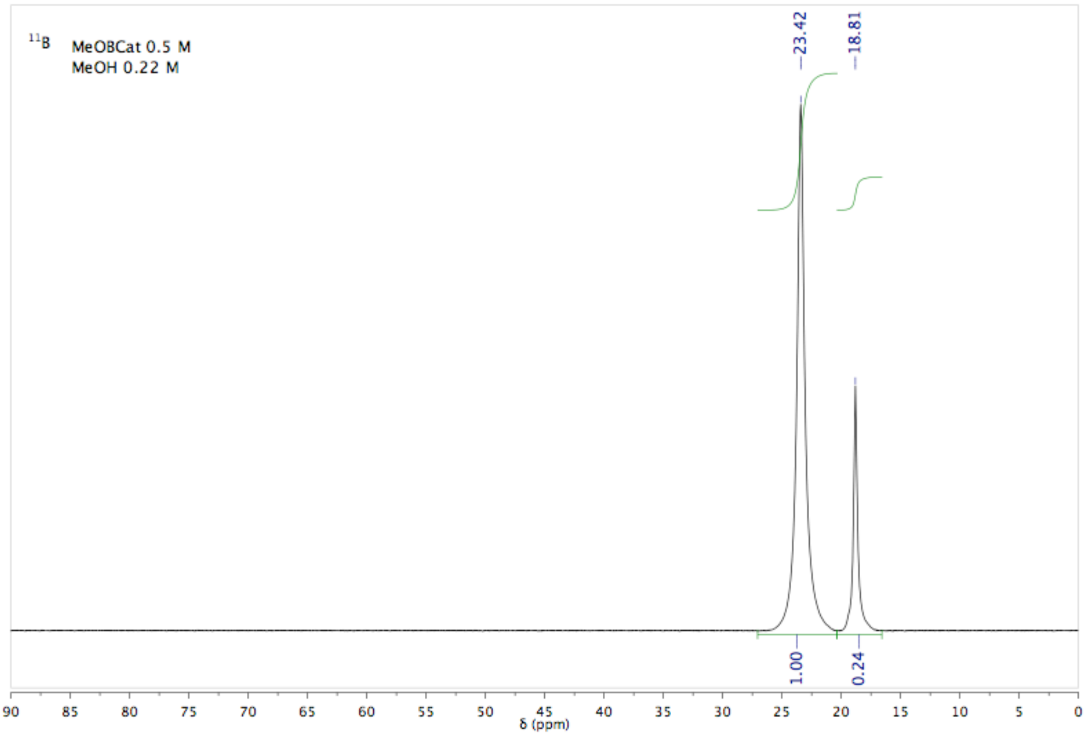
Determination of the equilibrium constant: K_3

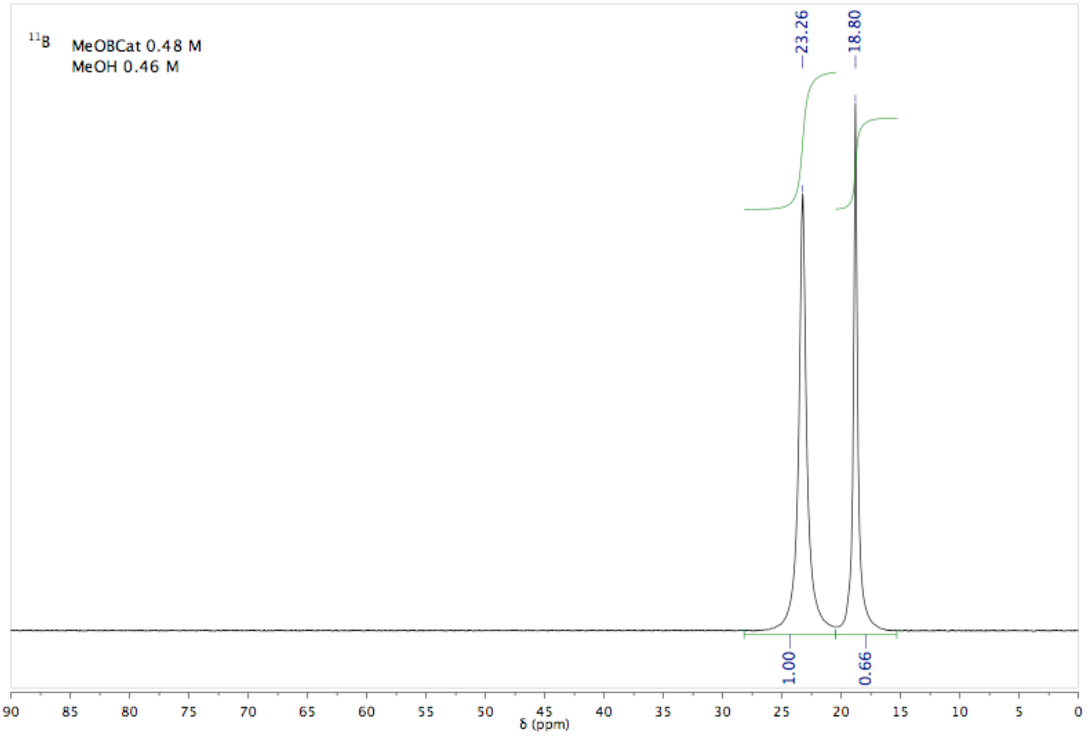


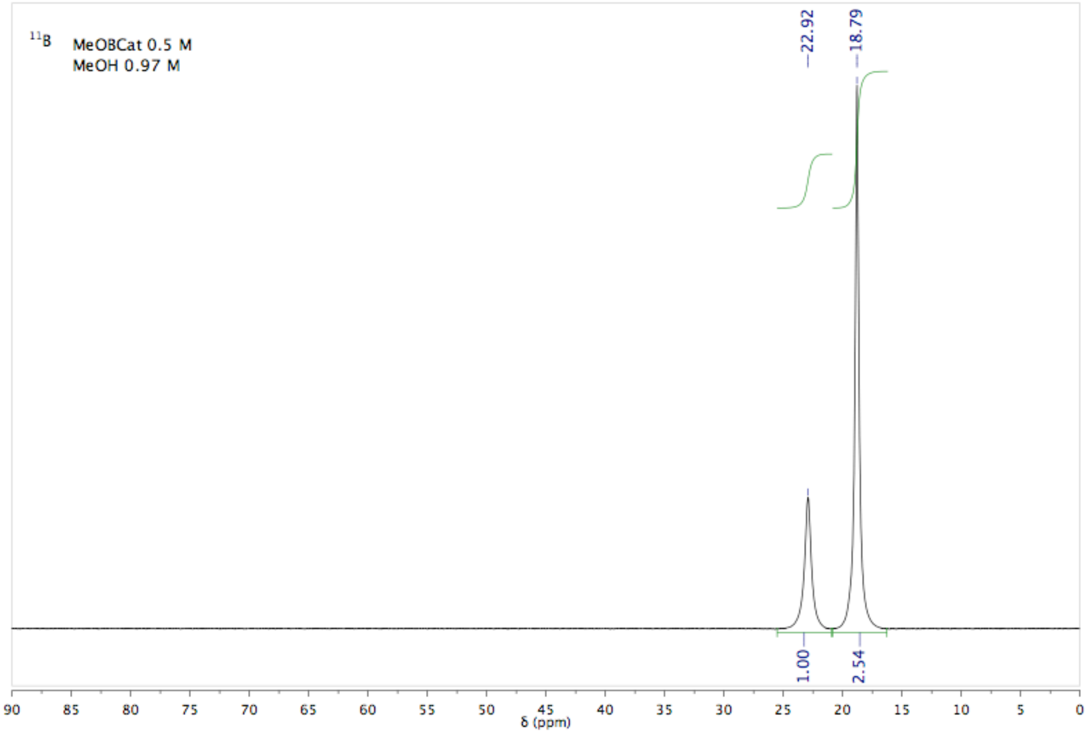
$$K_3 = \frac{[B(OMe)_3][catechol]}{[MeOBCat][MeOH]^2}$$

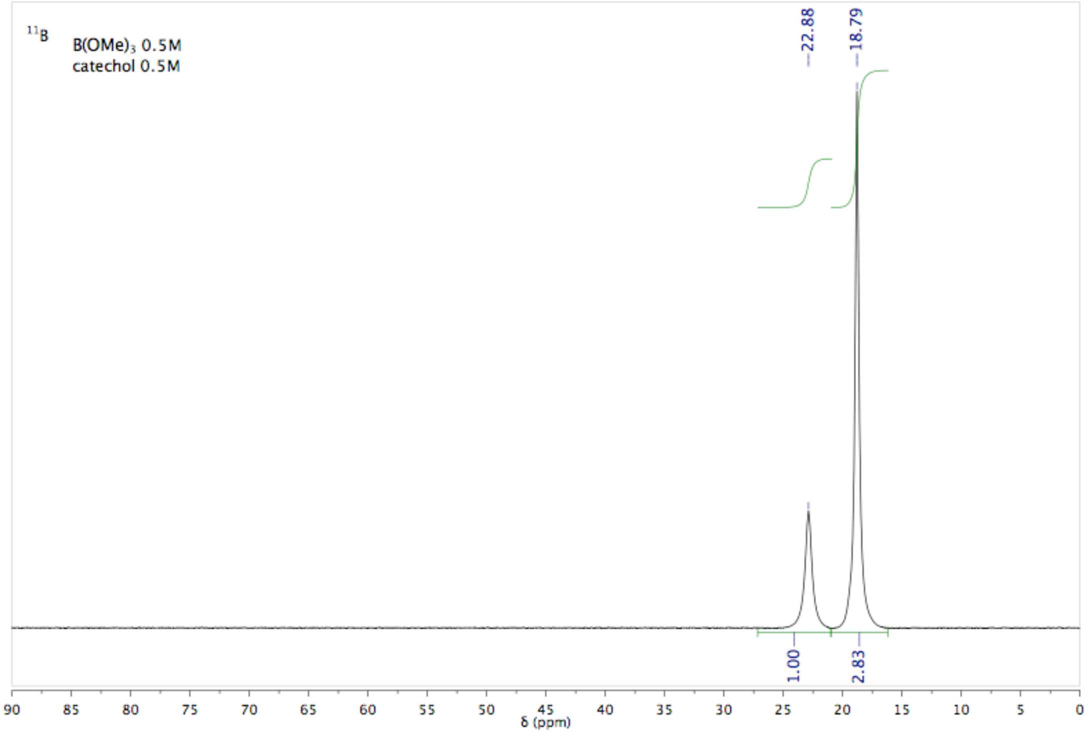
equilibrium constant MeOBCat + MeOH								
$[MeOBCat]_0$	$[MeOH]_0$	$[B(OMe)_3]/[MeOBCat]$	[MeOBCat]	[MeOH]	$[B(OMe)_3]$	$[B(OMe)_3]$	$[MeOBCat][MeOH]^2$	$[B(OMe)_3][Catechol]$
0,5	0,22	0,24	0,403	0,026	0,097	0,097	0,0003	0,009
0,48	0,46	0,66	0,289	0,078	0,191	0,191	0,0018	0,036
0,5	0,97	2,54	0,141	0,252	0,359	0,359	0,0090	0,129
$[B(OMe)_3]_0$	$[Catechol]_0$	$[B(OMe)_3]/[MeOBCat]$	[MeOBCat]	[MeOH]	$[B(OMe)_3]$	[Catechol]	$[MeOBCat][MeOH]^2$	$[B(OMe)_3][Catechol]$
0,5	0,5	2,83	0,131	0,261	0,369	0,369	0,0089	0,136



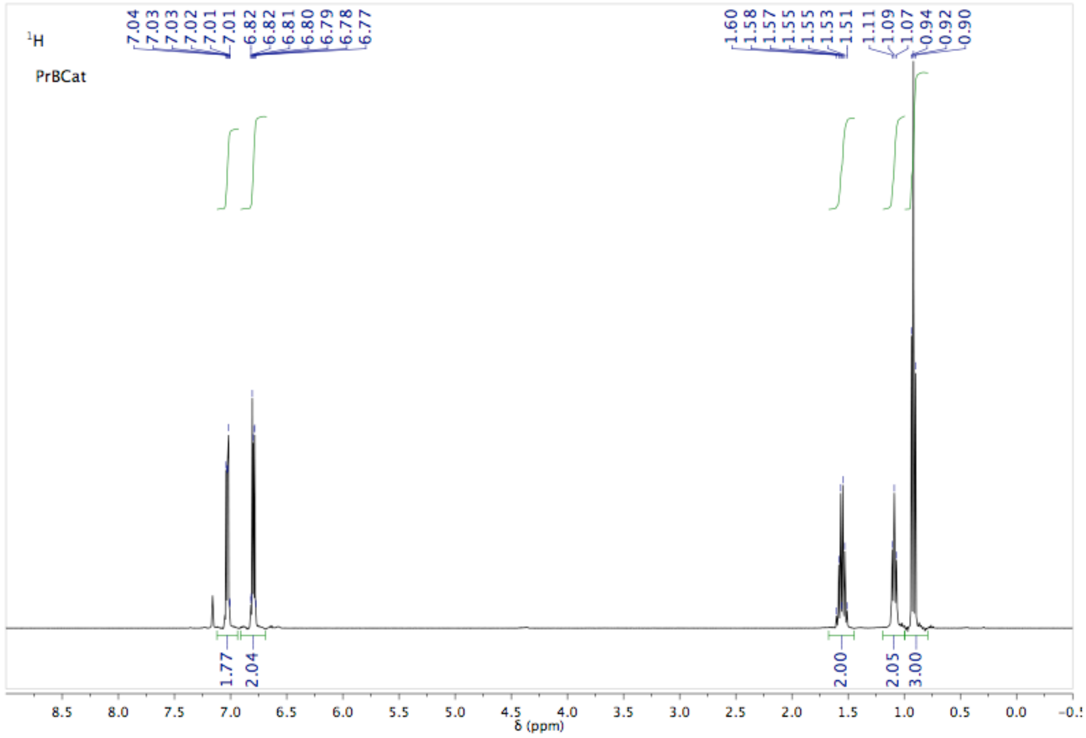

11B
MeOBCat 0.5 M
MeOH 0.22 M
23.42
18.81
1.00
0.24
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)

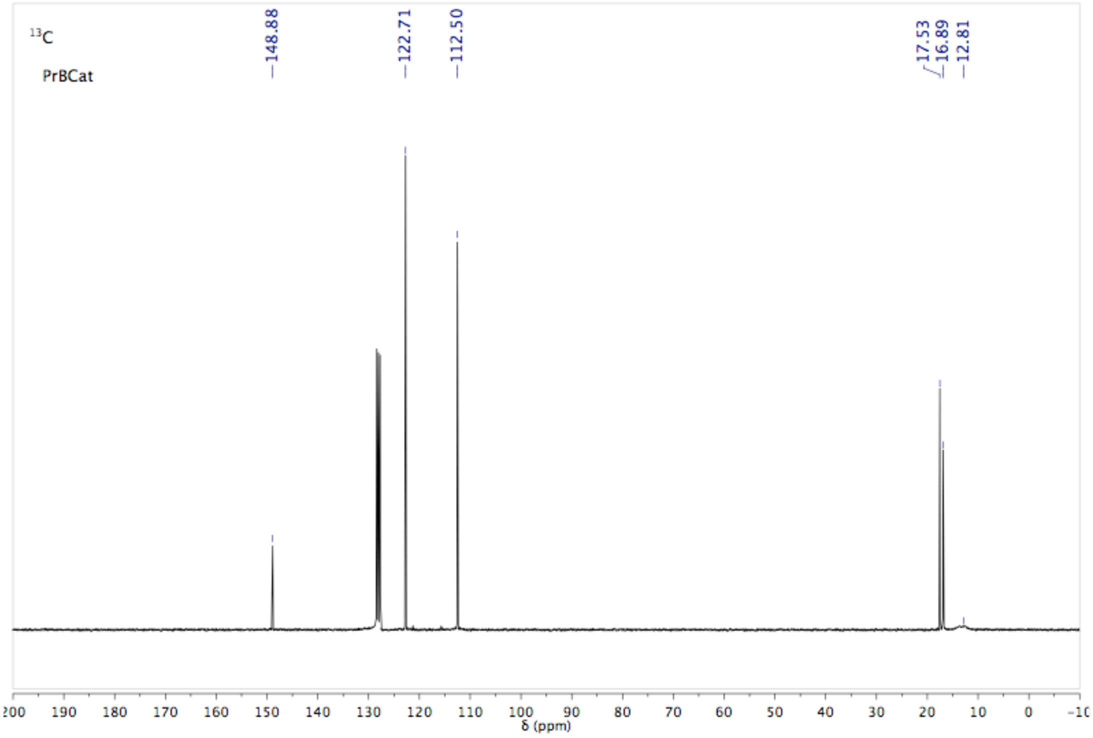

11B
MeOBCat 0.48 M
MeOH 0.46 M
23.26
18.80
1.00
0.66
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)

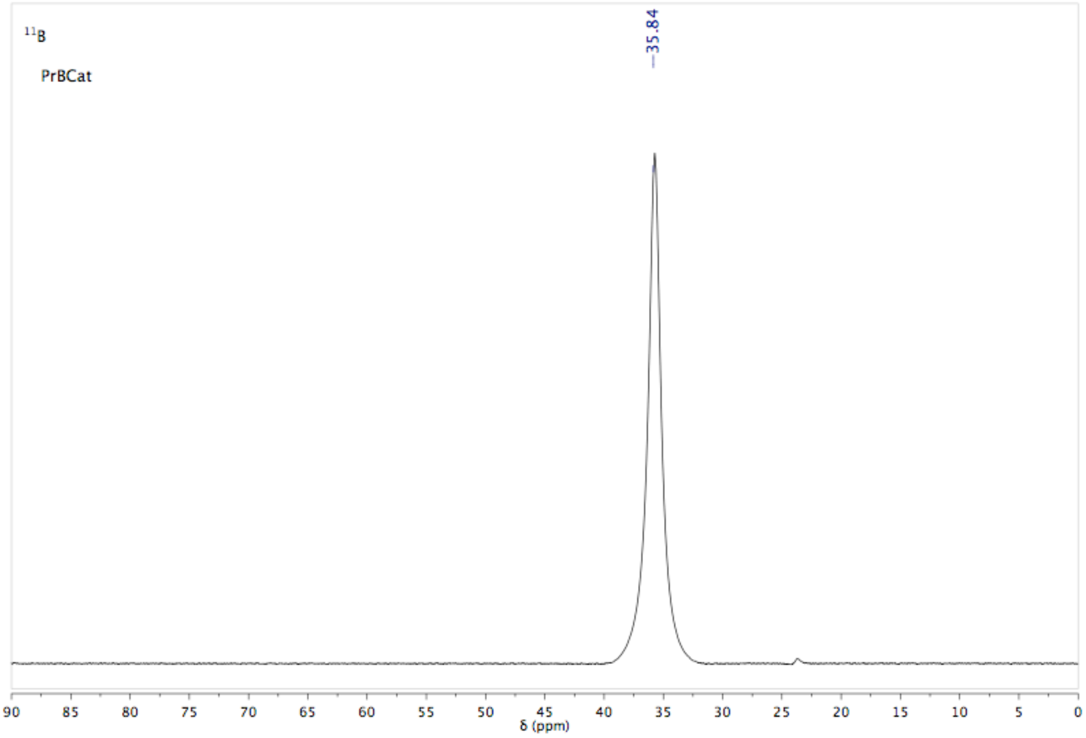

^{11}B
MeOBCat 0.5 M
MeOH 0.97 M
22.92
18.79
1.00
2.54
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)


^{11}B
$B(OMe)_3$ 0.5M
catechol 0.5M
22.88
18.79
1.00
2.83
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)

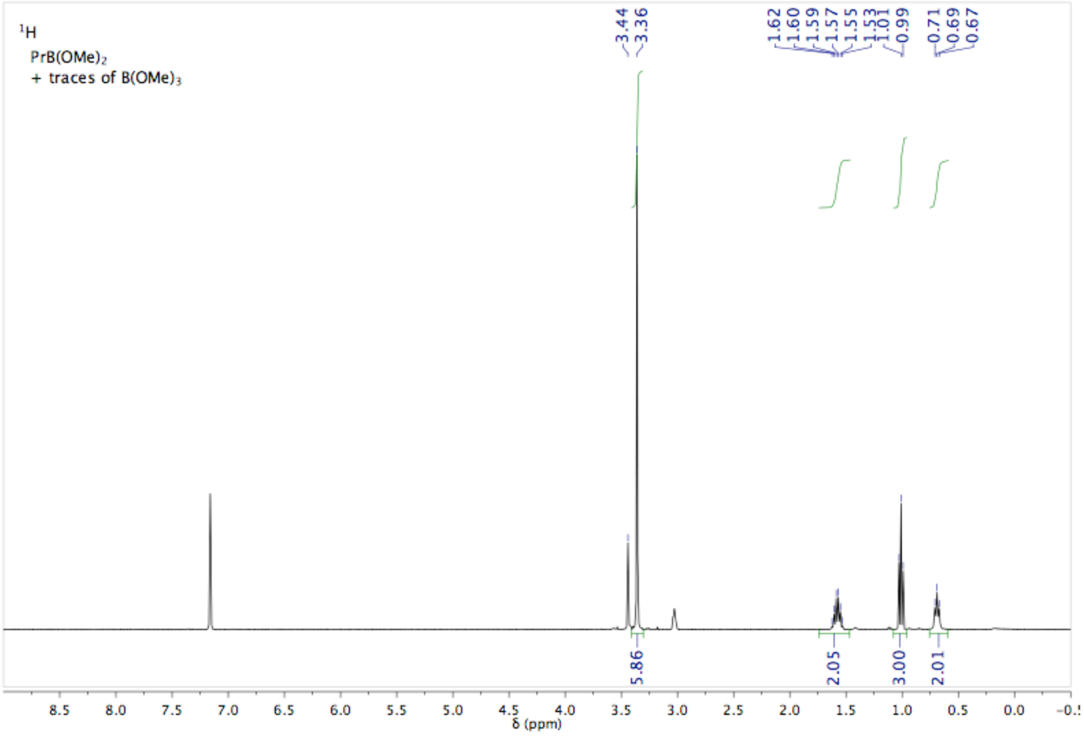
PrBCat/MeOH NMR study



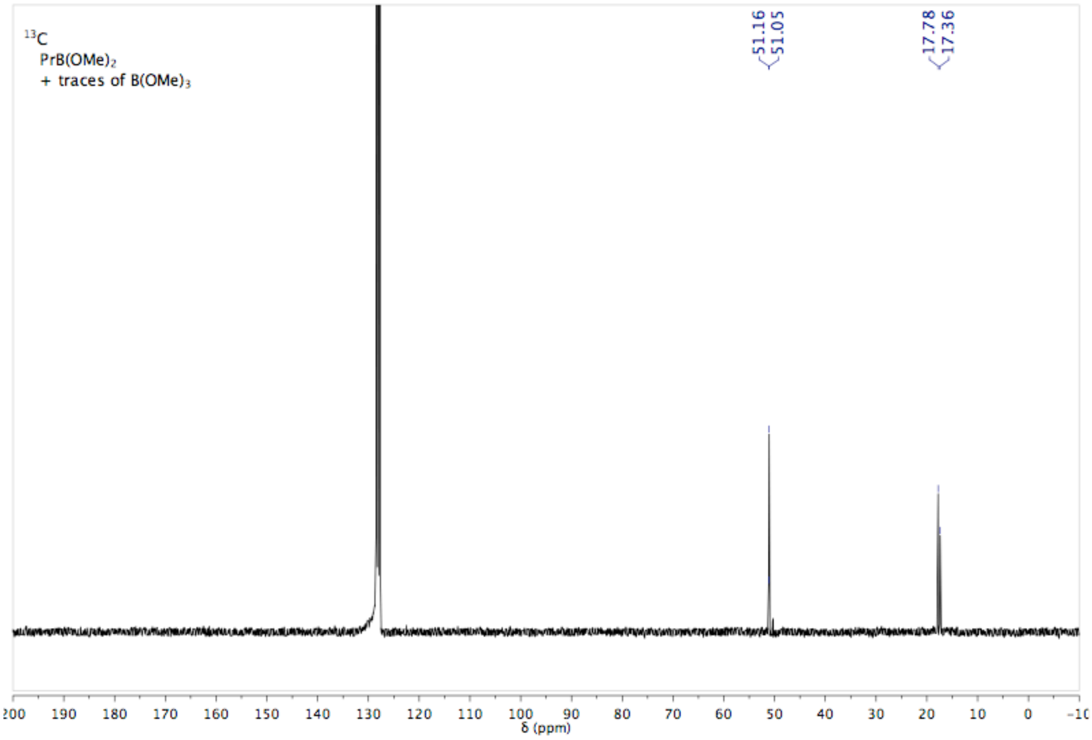


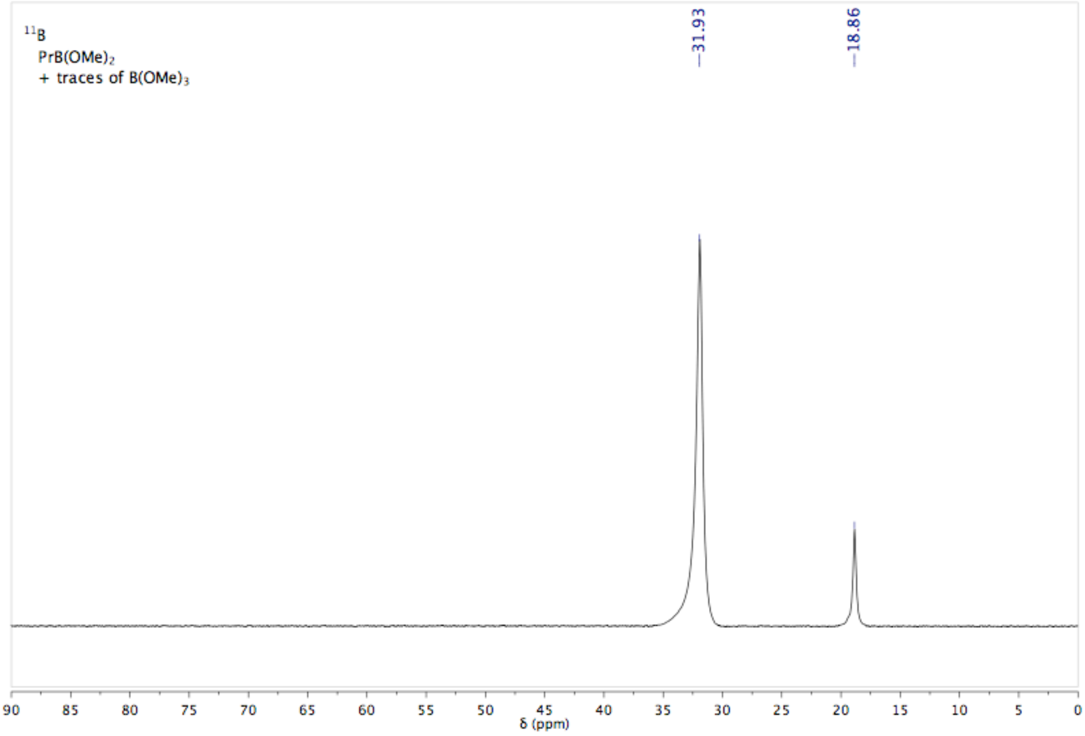


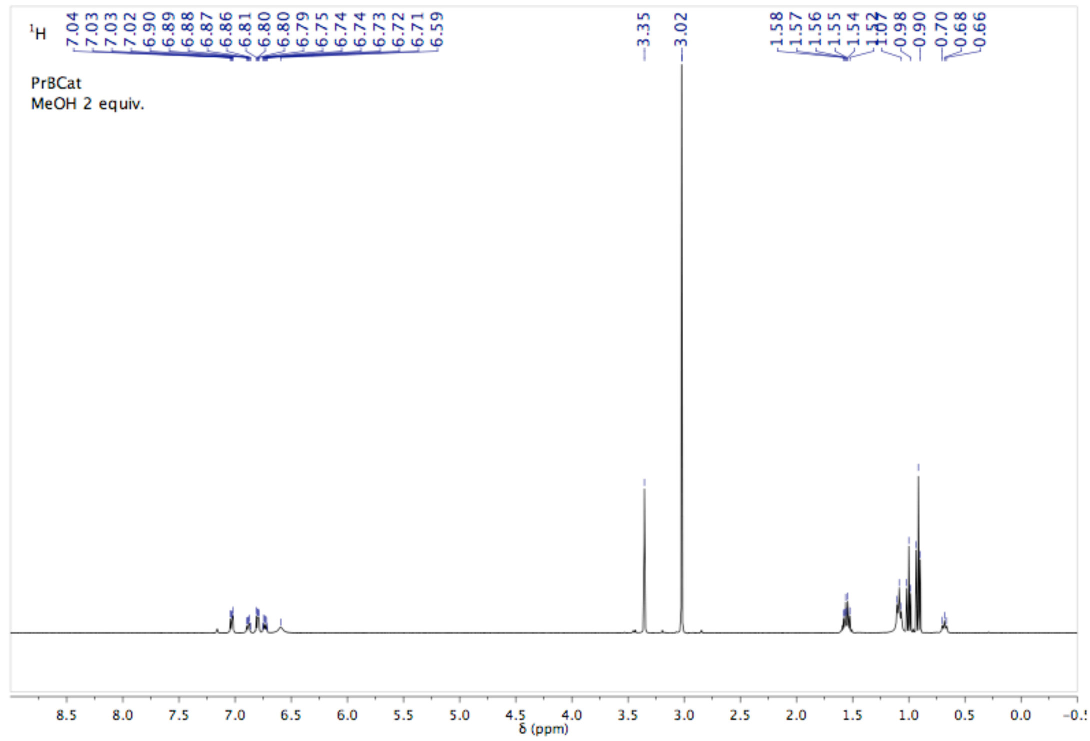
11B
PrBCat
35.84
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)

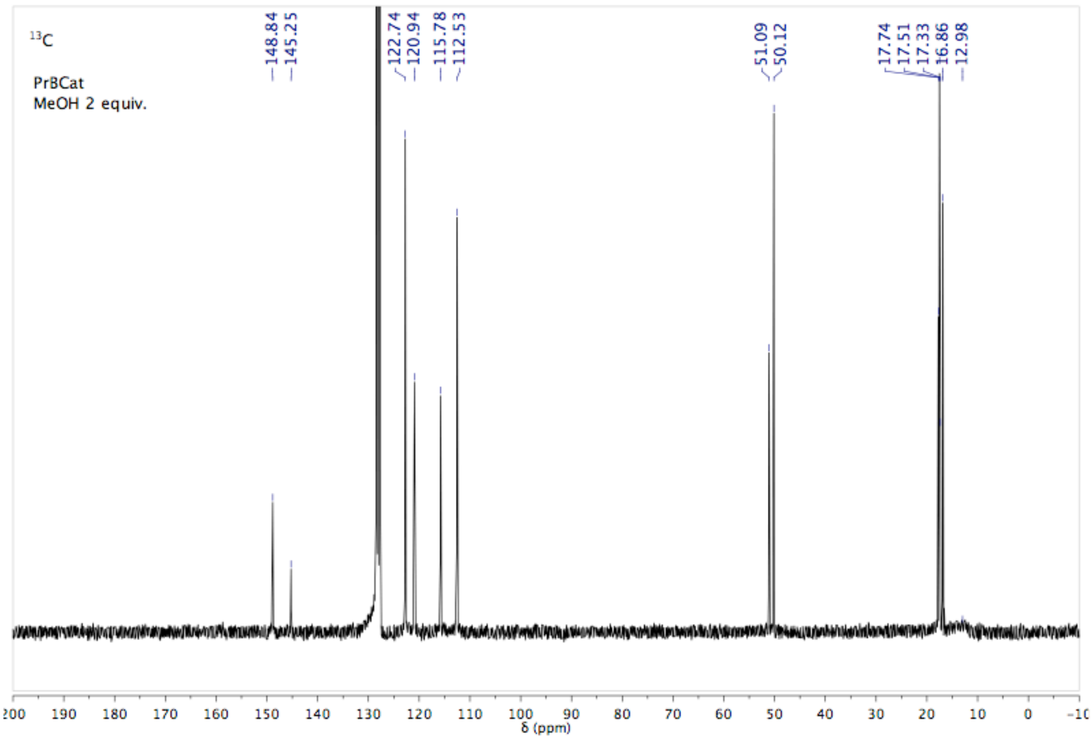


1H
PrB(OMe)2
+ traces of B(OMe)3
3.44
3.36
1.62
1.60
1.59
1.57
1.55
1.53
1.01
0.99
0.71
0.69
0.67
5.86
2.05
3.00
2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

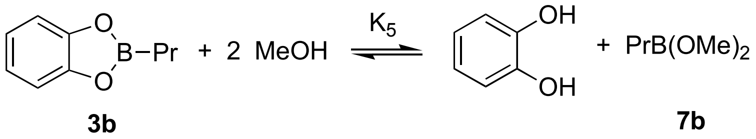

13C
PrB(OMe)2
+ traces of B(OMe)3
51.16
51.05
17.78
17.36
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


11B
PrB(OMe)2
+ traces of B(OMe)3
31.93
18.86
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)


1H
PrBCat
MeOH 2 equiv.
7.04
7.03
7.03
7.02
6.90
6.89
6.88
6.87
6.86
6.81
6.80
6.80
6.79
6.75
6.74
6.74
6.73
6.72
6.71
6.59
3.35
3.02
1.58
1.57
1.56
1.55
1.54
1.52
1.07
0.98
0.90
0.70
0.68
0.66
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

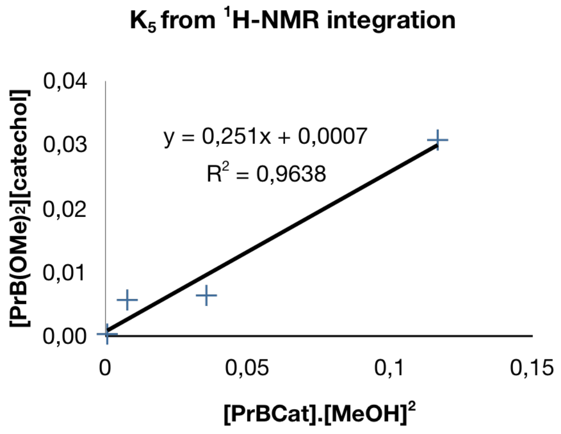

13C
PrBCat
MeOH 2 equiv.
148.84
145.25
122.74
120.94
115.78
112.53
51.09
50.12
17.74
17.51
17.33
16.86
12.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)

Determination of the equilibrium constant: K_5



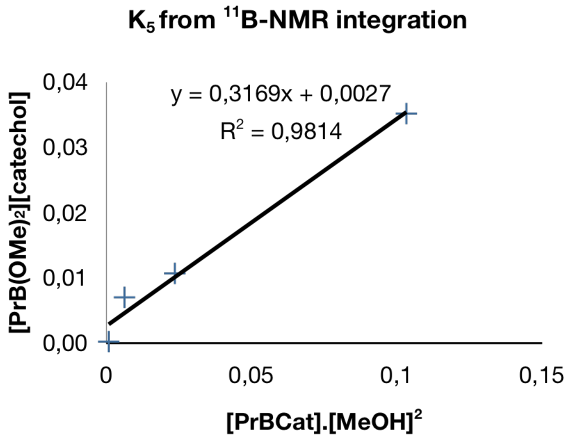
$$K_5 = \frac{[\mathrm{Pr}B(OMe)_2][catechol]}{[\mathrm{Pr}BCat][MeOH]^2}$$

^{1}H-NMR									
$[\mathrm{PrBCat}]_0$	$[\mathrm{MeOH}]_0$	$[\mathrm{PrB(OMe)_2}]/[\mathrm{PrBCat}]$	$[\mathrm{PrB(OMe)_2}]/[\mathrm{MeOH}]$	[PrBCat]	[MeOH]	$[\mathrm{PrB(OMe)_2}]$	[Catechol]	$[\mathrm{PrBCat}][\mathrm{MeOH}]^2$	$[\mathrm{PrB(OMe)_2}][\mathrm{Catechol}]$
0,2	0,1	0,1	0,550	0,182	0,064	0,018	0,018	0,0007	0,0003
0,2	0,4	0,6	2,290	0,125	0,250	0,075	0,075	0,0078	0,0056
0,5	0,45	0,19		0,420	0,290	0,080	0,080	0,0354	0,0064
0,5	0,95	0,54		0,325	0,599	0,175	0,175	0,1166	0,0307

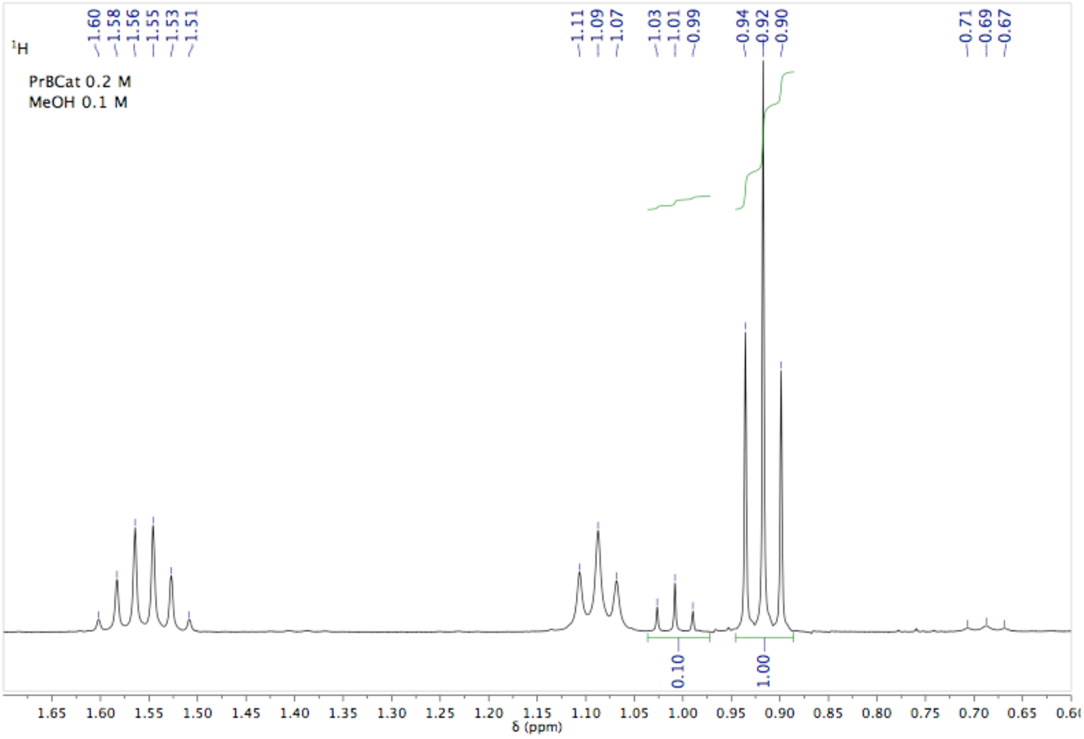


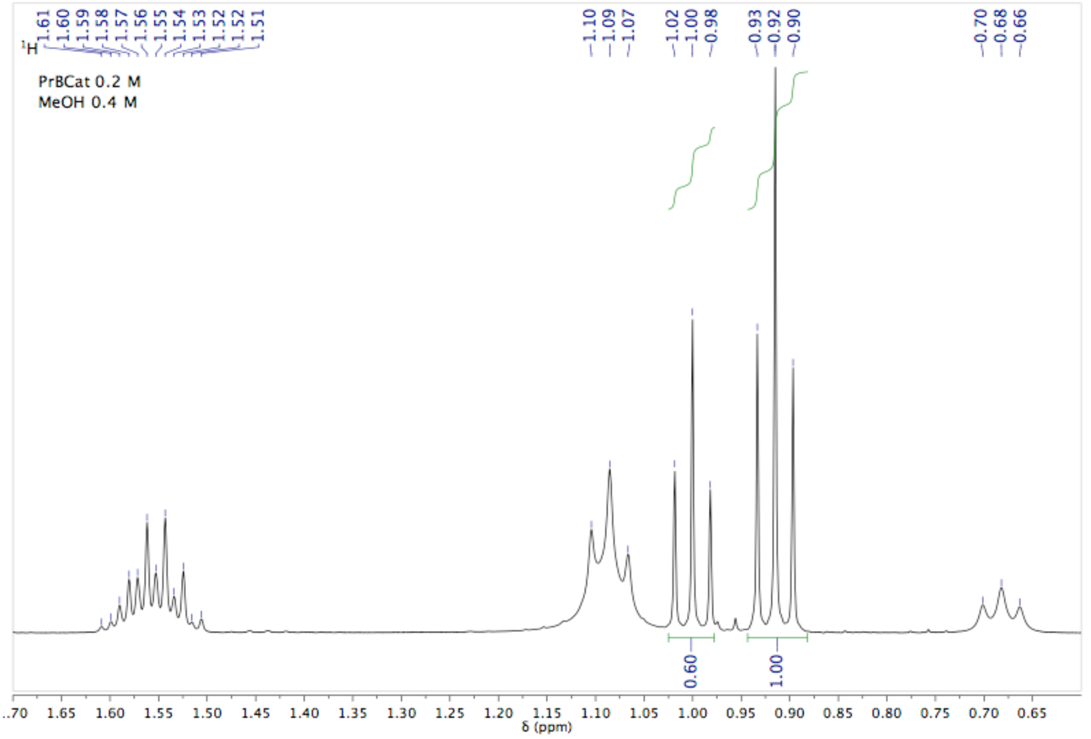
K_5 from ^{1}H-NMR integration

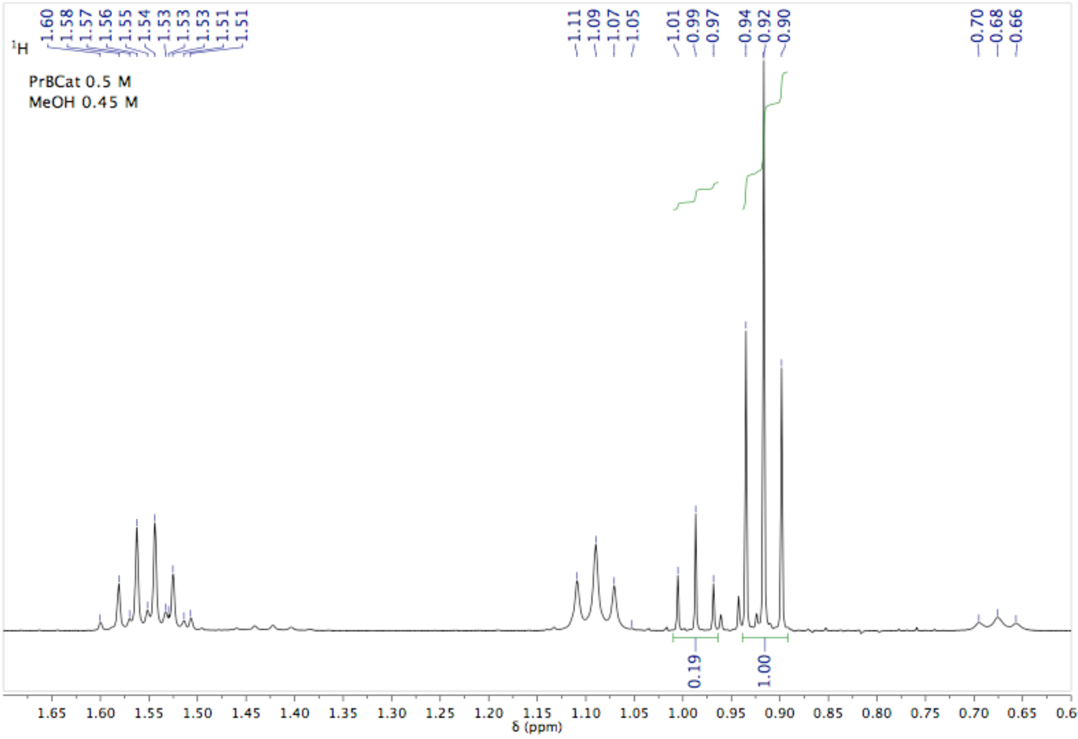
^{11}B-NMR									
$[\mathrm{PrBCat}]_0$	$[\mathrm{MeOH}]_0$	$[\mathrm{PrB(OMe)_2}]/[\mathrm{PrBCat}]$	$[\mathrm{PrB(OMe)_2}]/[\mathrm{MeOH}]$	[PrBCat]	[MeOH]	$[\mathrm{PrB(OMe)_2}]$	[Catechol]	$[\mathrm{PrBCat}][\mathrm{MeOH}]^2$	$[\mathrm{PrB(OMe)_2}][\mathrm{Catechol}]$
0,2	0,1	0,09	0,550	0,183	0,067	0,017	0,016513761	0,0008	0,0003
0,2	0,4	0,72	2,290	0,116	0,233	0,084	0,08372093	0,0063	0,0070
0,5	0,45	0,26		0,397	0,244	0,103	0,103174603	0,0236	0,0106
0,5	0,95	0,6		0,313	0,575	0,188	0,1875	0,1033	0,0352

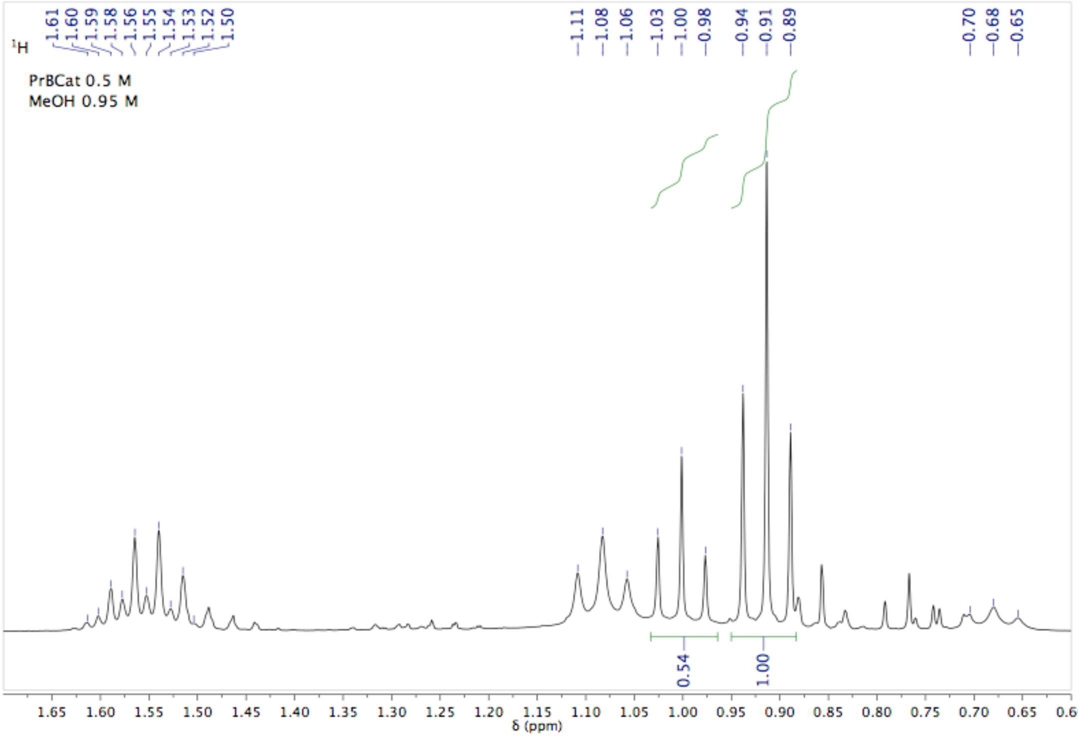


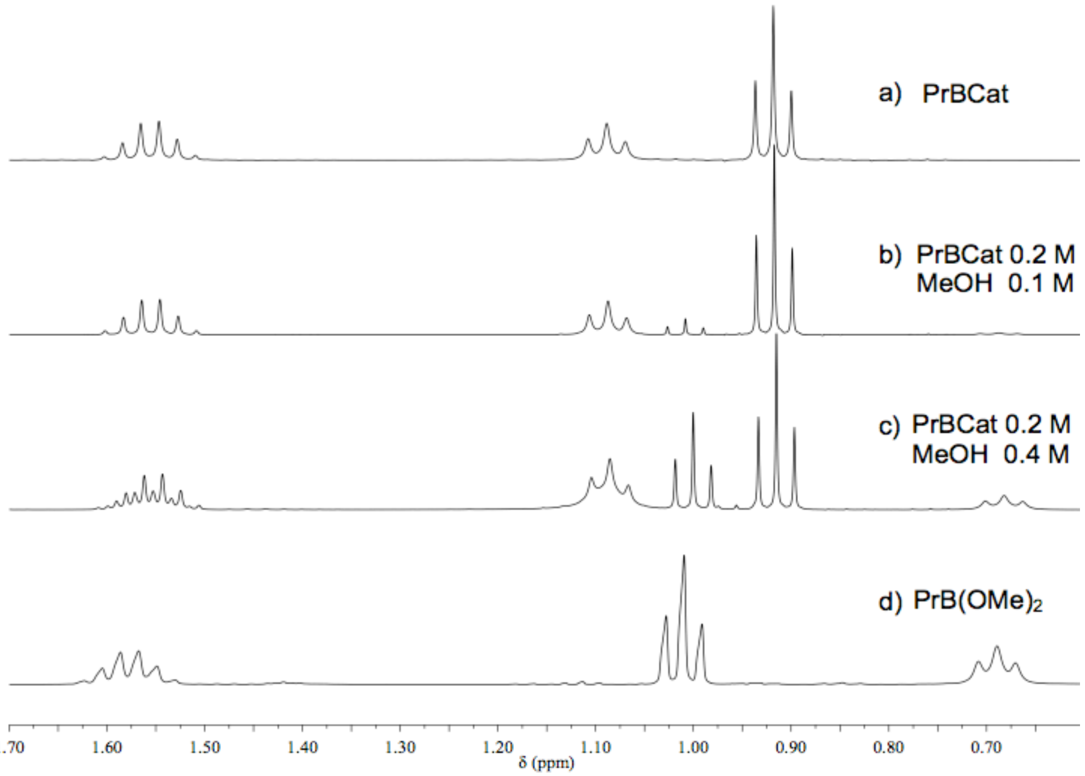
K_5 from ^{11}B-NMR integration

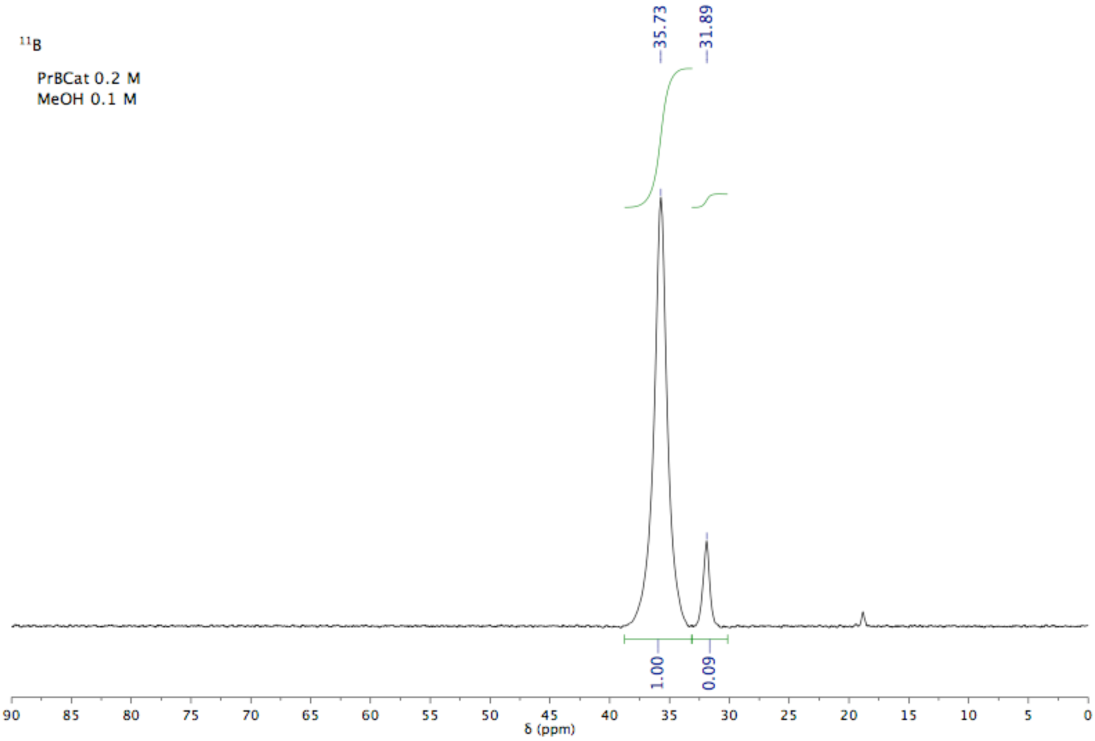

1H
PrBCat 0.2 M
MeOH 0.1 M
1.60
1.58
1.56
1.55
1.53
1.51
1.11
1.09
1.07
1.03
1.01
0.99
0.94
0.92
0.90
0.71
0.69
0.67
0.10
1.00
1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60
δ (ppm)

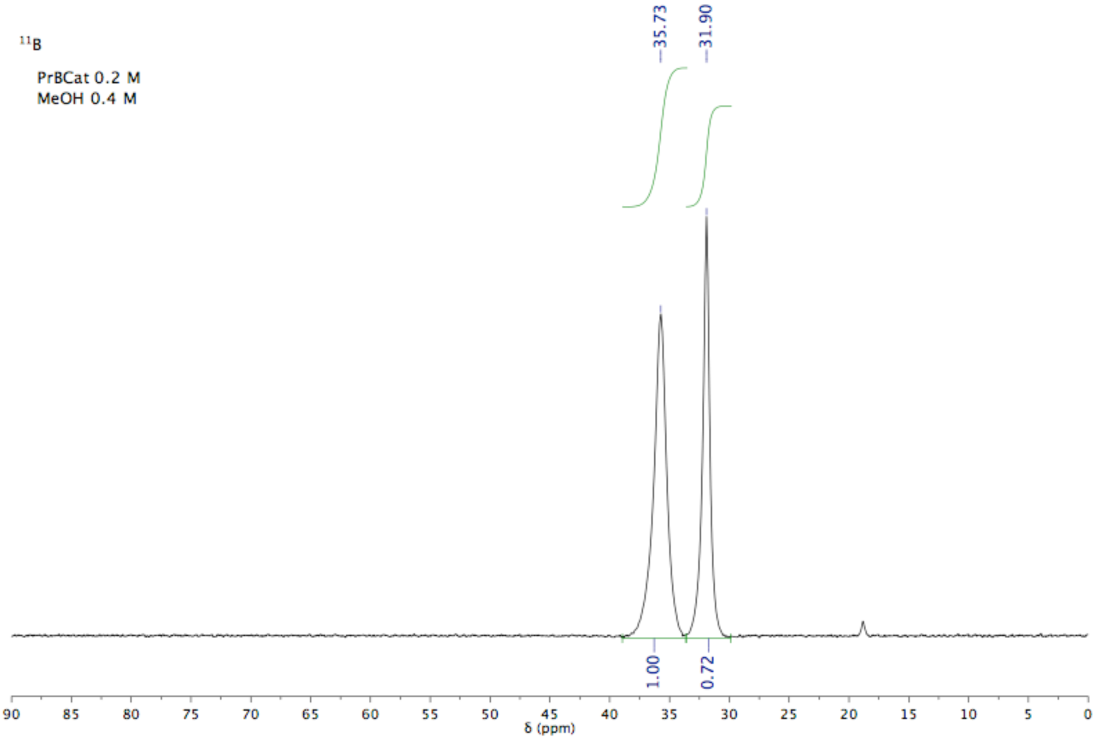

1H
PrBCat 0.2 M
MeOH 0.4 M
1.61
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.51
1.10
1.09
1.07
1.02
1.00
0.98
0.93
0.92
0.90
0.70
0.68
0.66
0.60
1.00
.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65
δ (ppm)

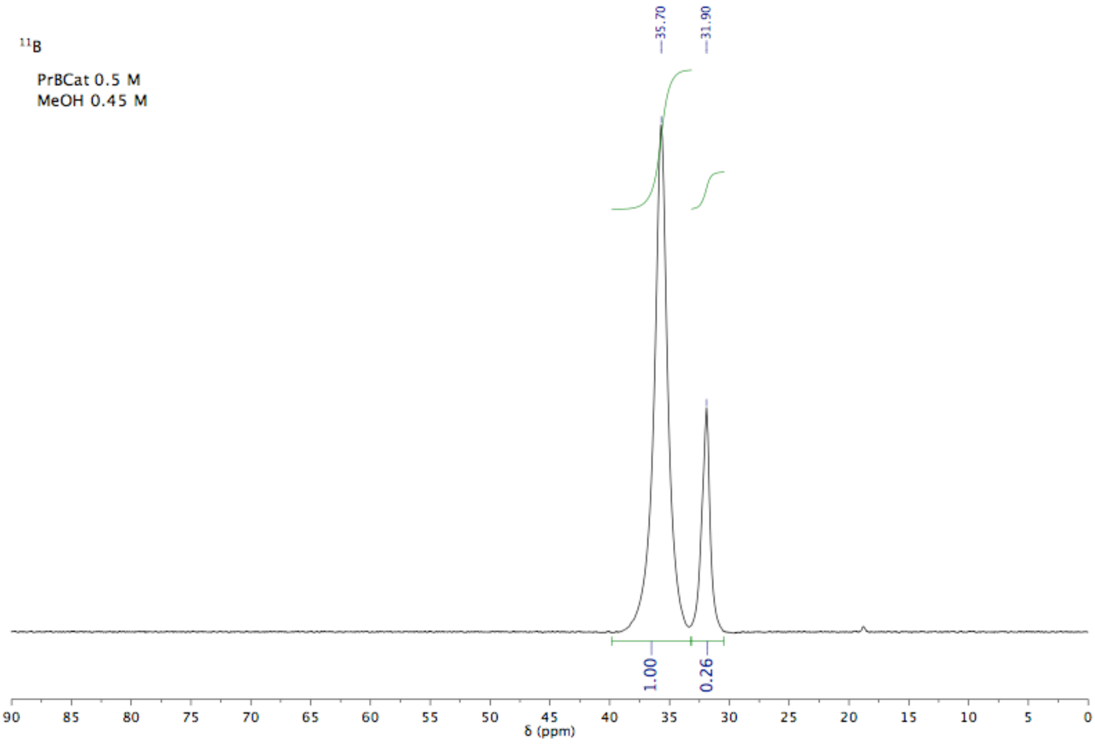

1.60 1.58 1.57 1.56 1.55 1.54 1.53 1.53 1.53 1.51 1.51
1.11 1.09 1.07 1.05
1.01 0.99 0.97
0.94 0.92 0.90
0.70 0.68 0.66
¹H
PrBCat 0.5 M
MeOH 0.45 M
0.19
1.00
1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.6
δ (ppm)


1.61 1.60 1.59 1.58 1.56 1.55 1.54 1.53 1.52 1.50
1.11 1.08 1.06 1.03 1.00 0.98
0.94 0.91 0.89
0.70 0.68 0.65
¹H
PrBCat 0.5 M
MeOH 0.95 M
0.54
1.00
1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.6
δ (ppm)

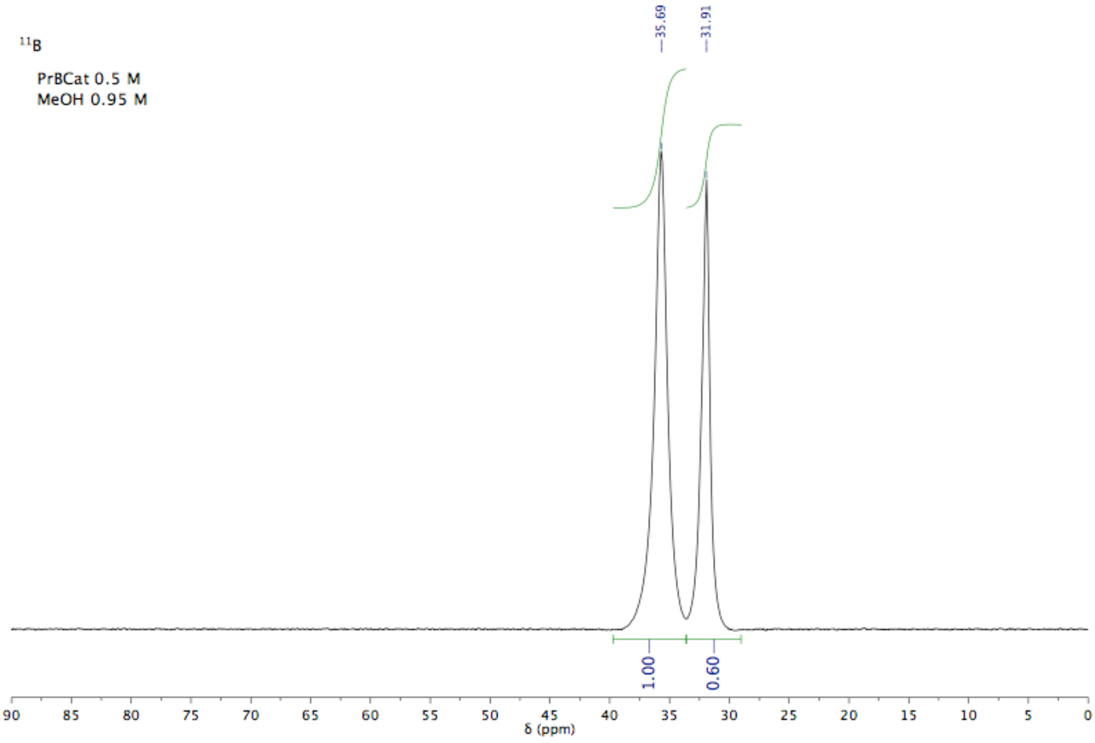

a) PrBCat
b) PrBCat 0.2 M
MeOH 0.1 M
c) PrBCat 0.2 M
MeOH 0.4 M
d) PrB(OMe)$_2$
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
δ (ppm)


^{11}B
PrBCat 0.2 M
MeOH 0.1 M
35.73
31.89
1.00
0.09
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)


^{11}B
PrBCat 0.2 M
MeOH 0.4 M
35.73
31.90
1.00
0.72
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)

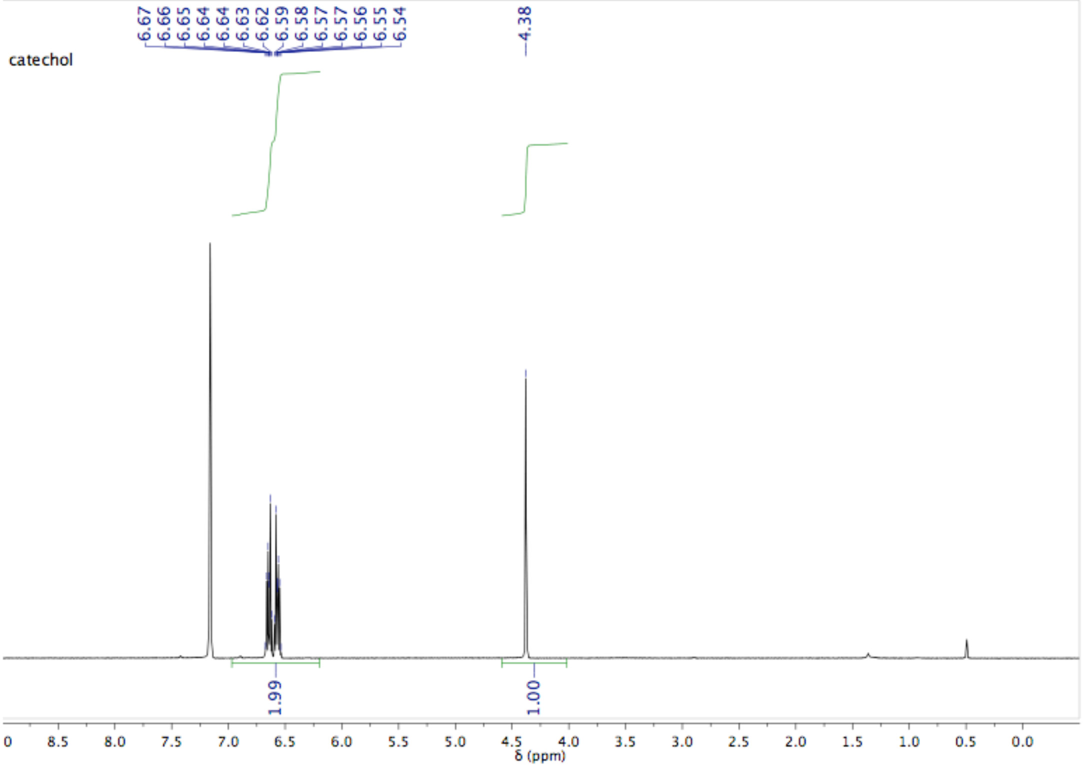


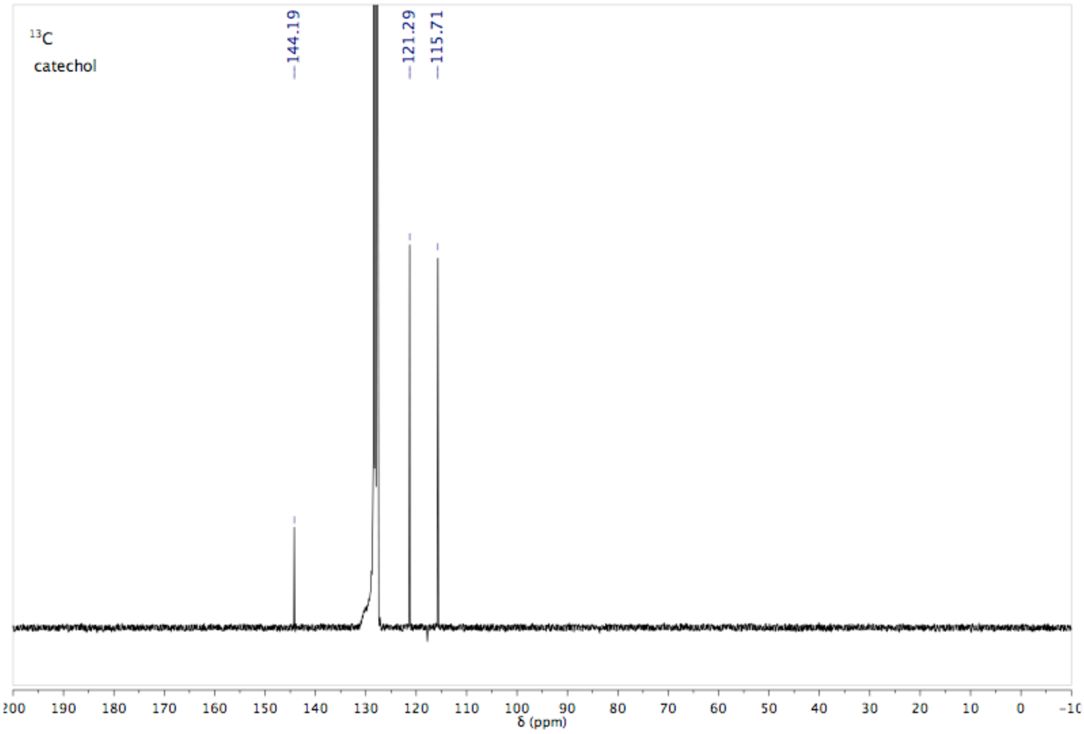
^{11}B
PrBCat 0.5 M
MeOH 0.45 M
35.70
31.90
1.00
0.26
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)

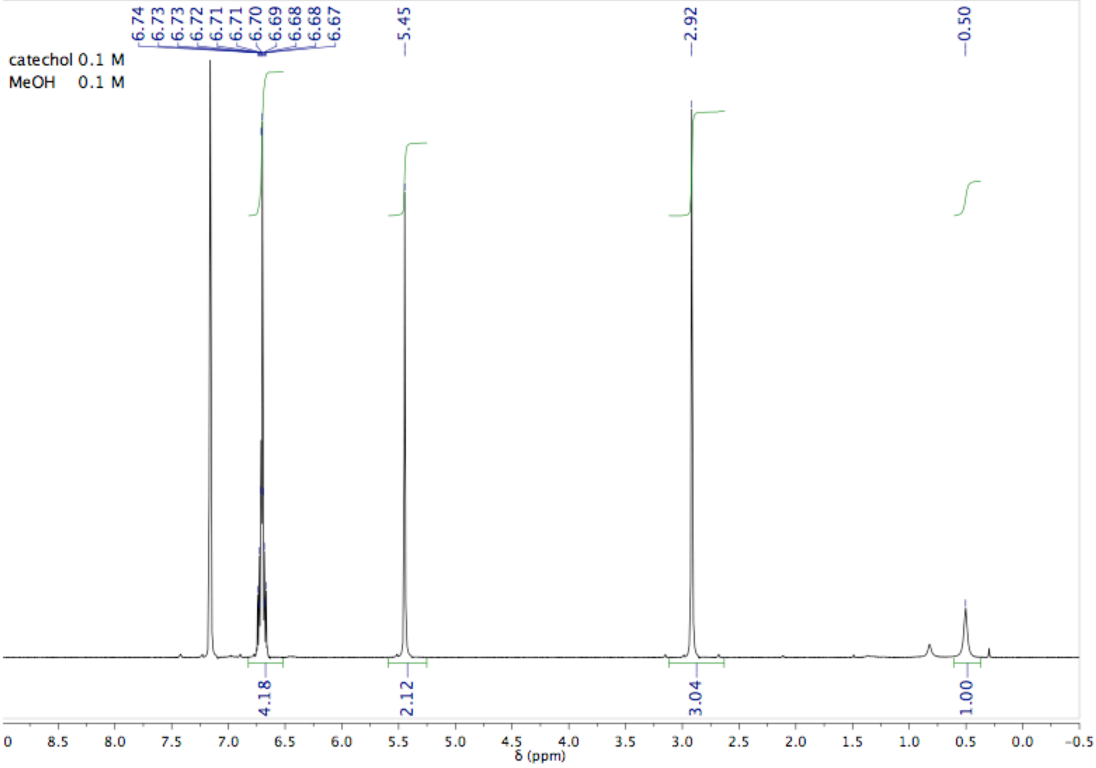


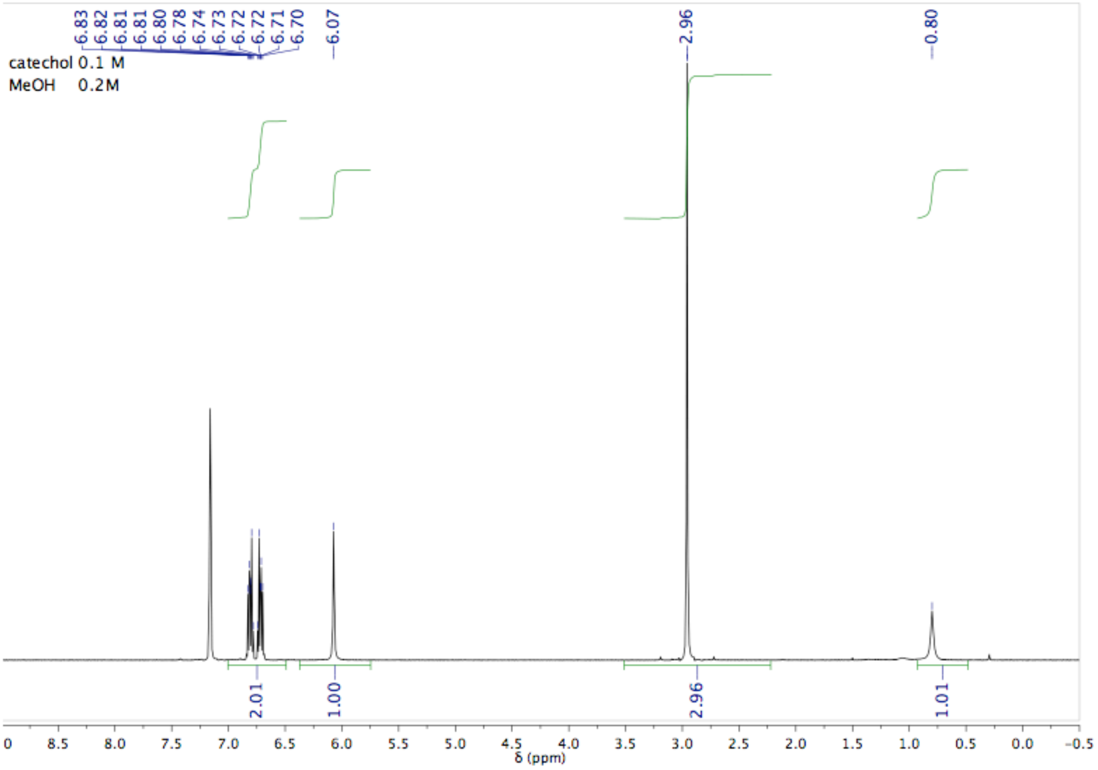
^{11}B
PrBCat 0.5 M
MeOH 0.95 M
35.69
31.91
1.00
0.60
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ (ppm)

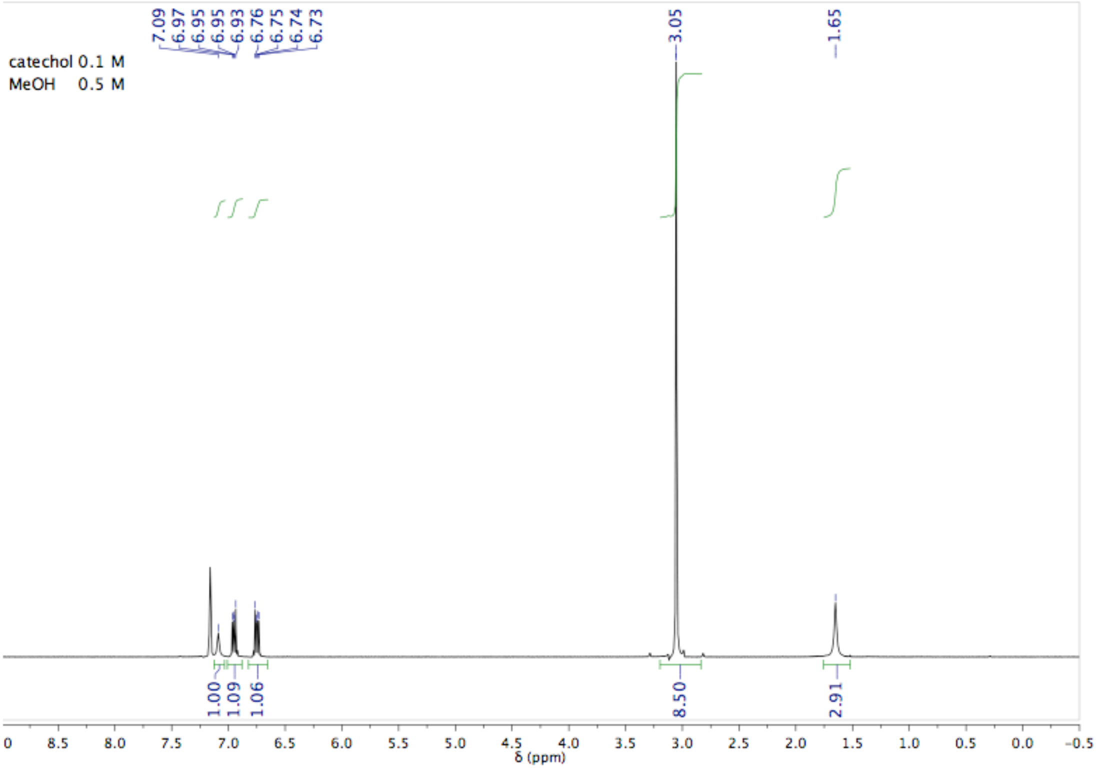
Catechol / MeOH ^{1}H-NMR study: Evidence for strong H-bonding in benzene solution

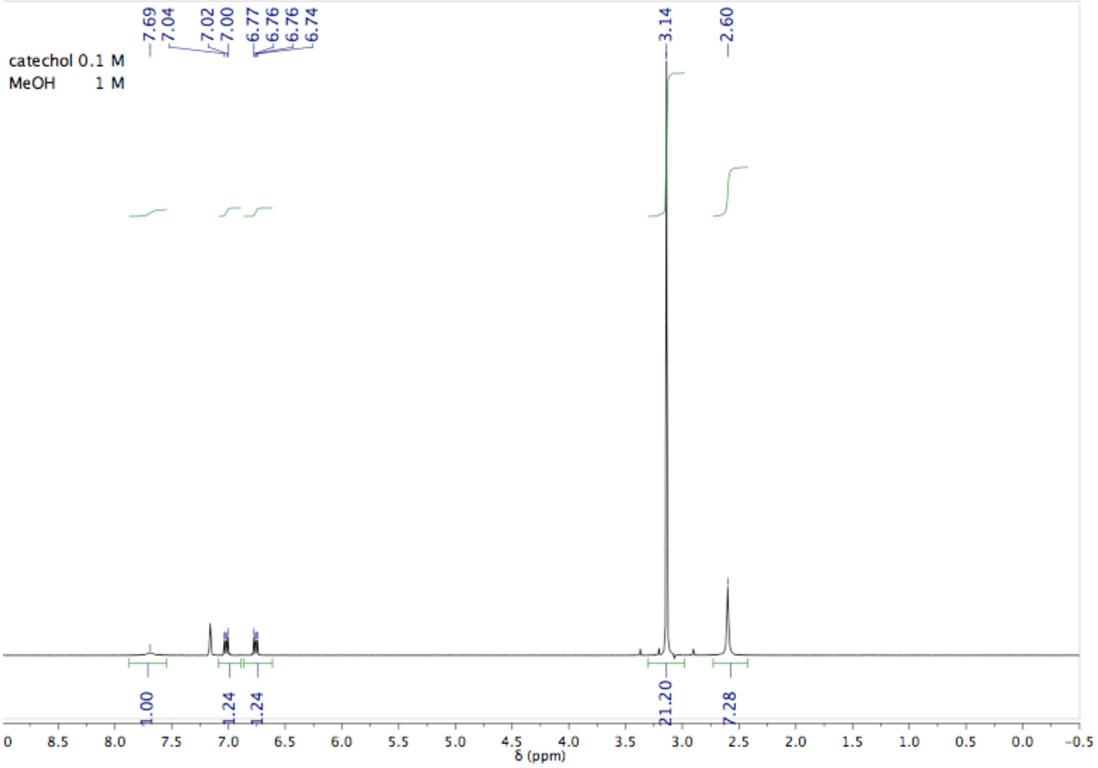


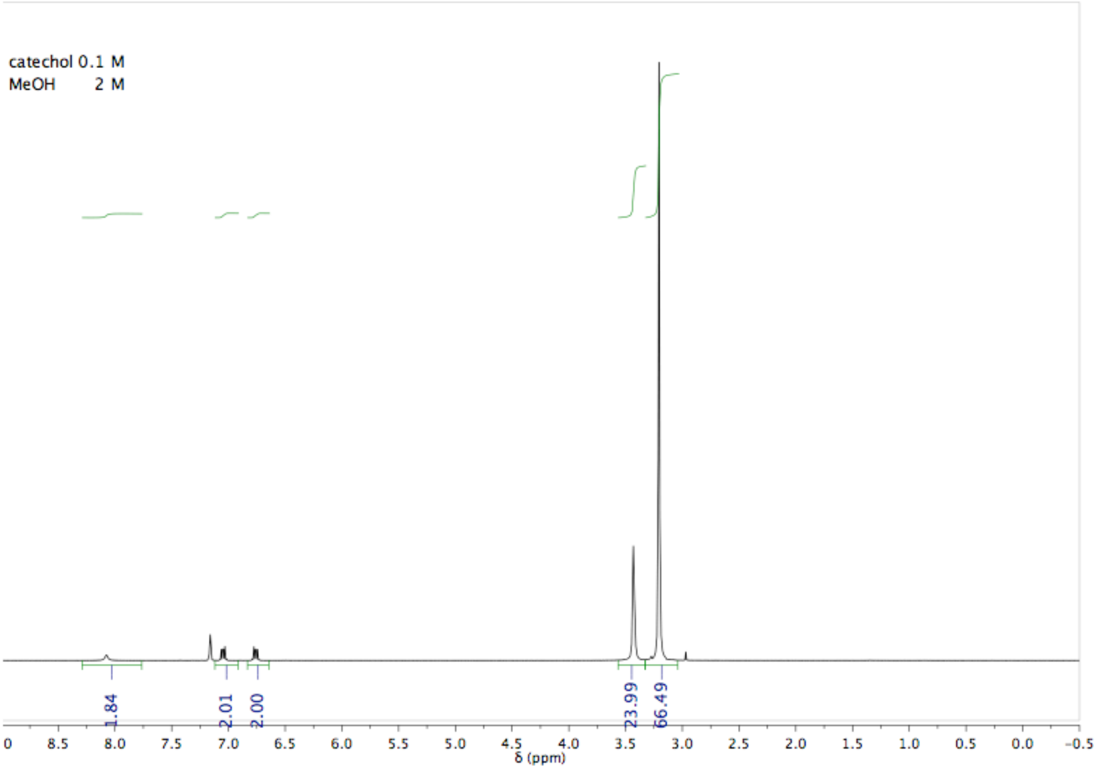

13C
catechol
144.19
121.29
115.71
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

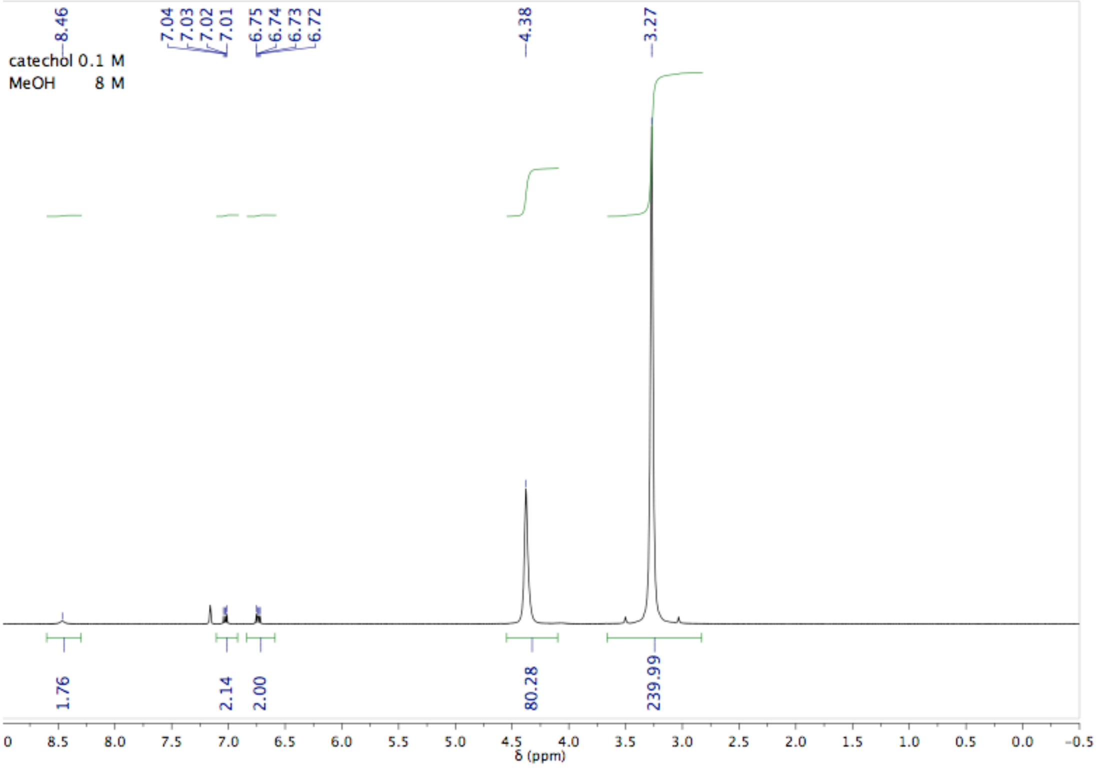

catechol 0.1 M
MeOH 0.1 M
6.74
6.73
6.73
6.72
6.71
6.71
6.70
6.69
6.68
6.68
6.67
5.45
2.92
0.50
4.18
2.12
3.04
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

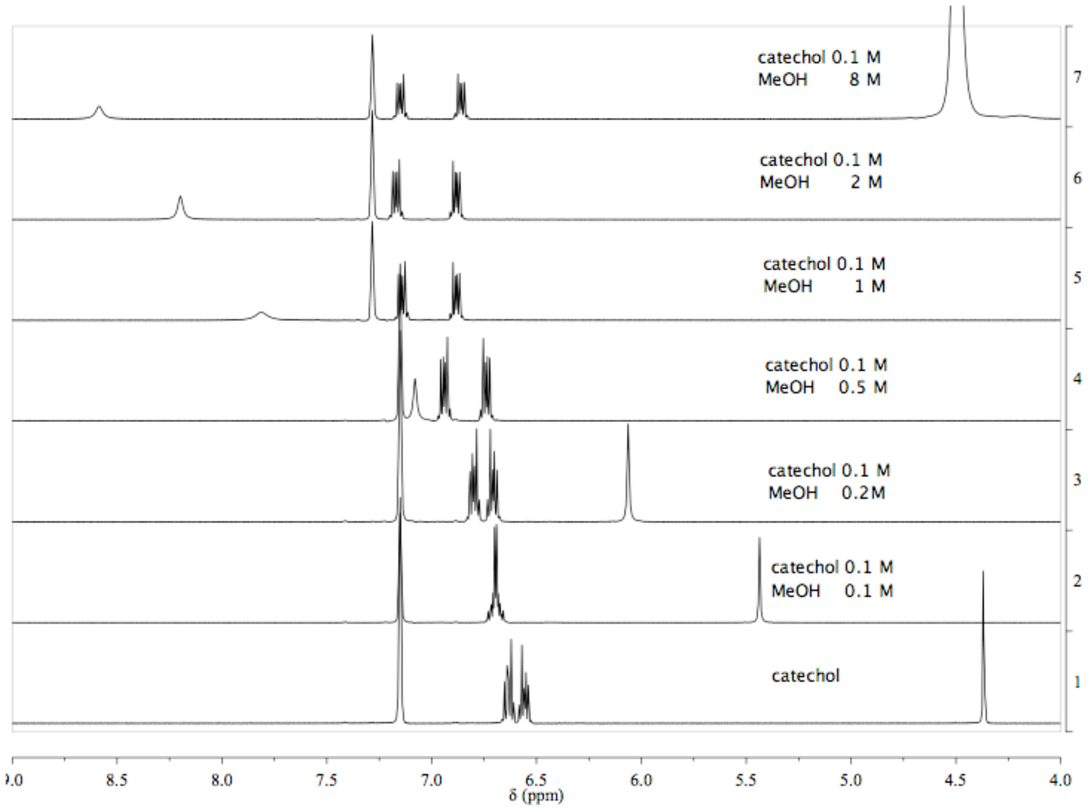

catechol 0.1 M
MeOH 0.2M
6.83
6.82
6.81
6.81
6.80
6.78
6.74
6.73
6.72
6.72
6.71
6.70
6.07
2.96
0.80
2.01
1.00
2.96
1.01
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

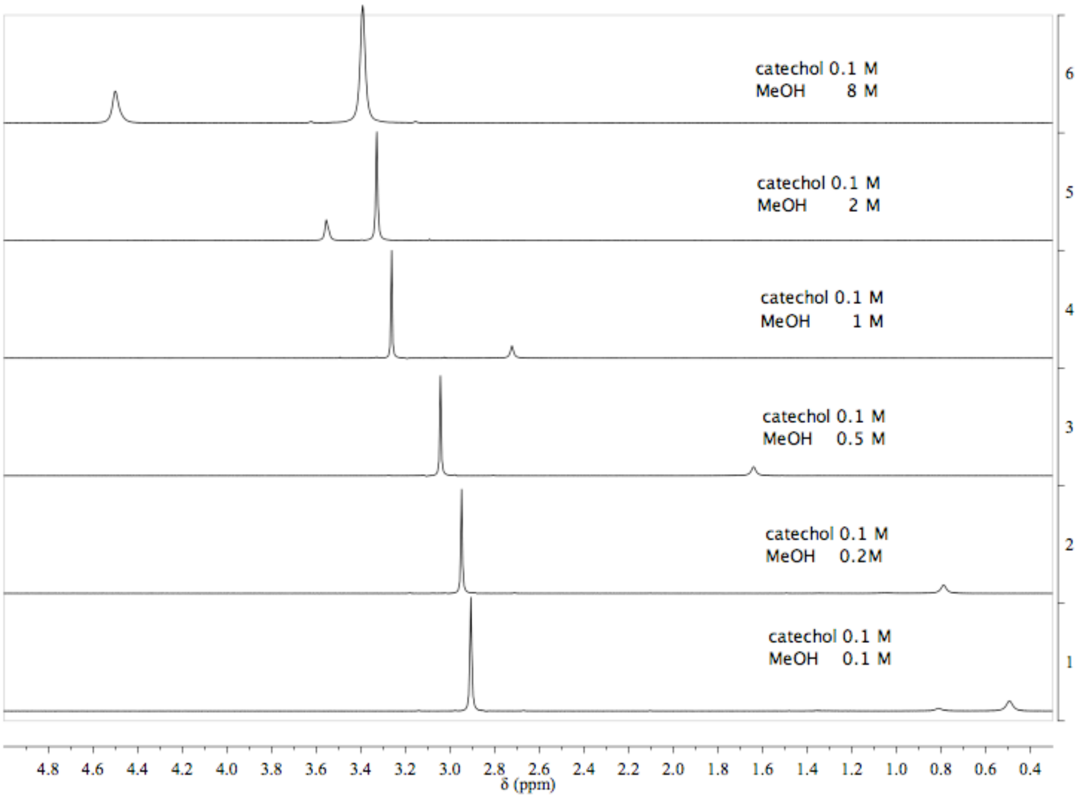

catechol 0.1 M
MeOH 0.5 M
7.09
6.97
6.95
6.95
6.93
6.76
6.75
6.74
6.73
3.05
1.65
1.00
1.09
1.06
8.50
2.91
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)


catechol 0.1 M
MeOH 1 M
7.69
7.04
7.02
7.00
6.77
6.76
6.76
6.74
3.14
2.60
1.00
1.24
1.24
21.20
7.28
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

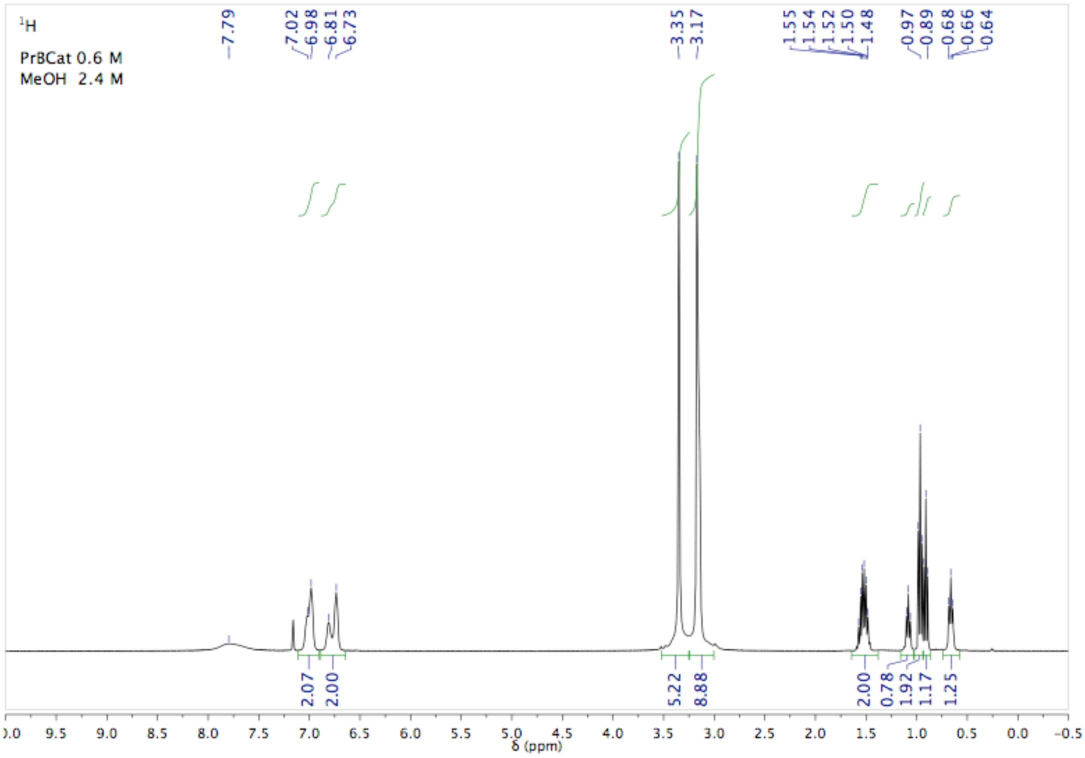

catechol 0.1 M
MeOH 2 M
1.84
2.01
2.00
23.99
66.49
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)


8.46
7.04
7.03
7.02
7.01
6.75
6.74
6.73
6.72
4.38
3.27
catechol 0.1 M
MeOH 8 M
1.76
2.14
2.00
80.28
239.99
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

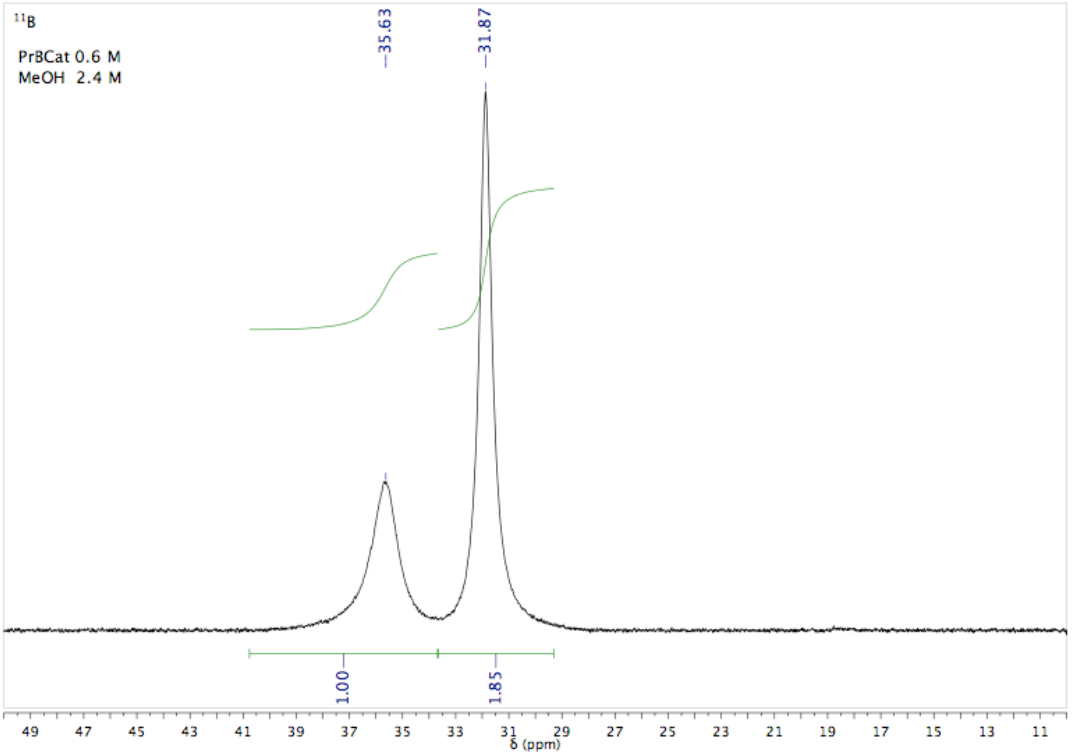

catechol 0.1 M
MeOH 8 M
7
catechol 0.1 M
MeOH 2 M
6
catechol 0.1 M
MeOH 1 M
5
catechol 0.1 M
MeOH 0.5 M
4
catechol 0.1 M
MeOH 0.2 M
3
catechol 0.1 M
MeOH 0.1 M
2
catechol
1
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
δ (ppm)



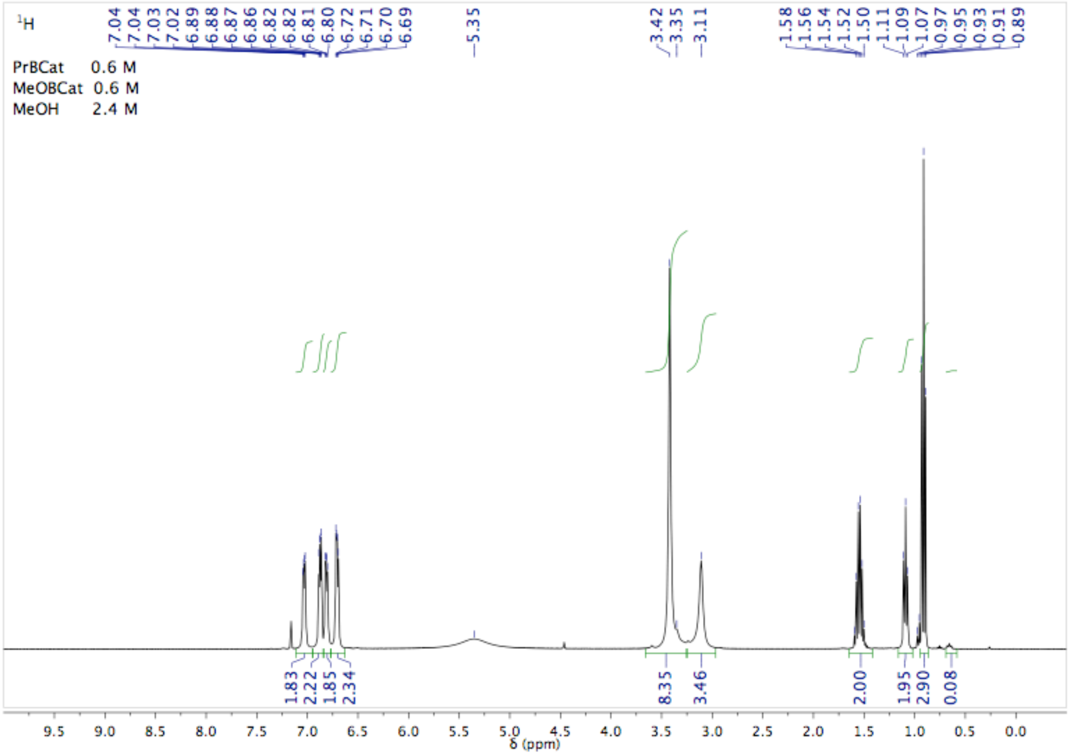
Effective concentrations of borane species in the reaction conditions:

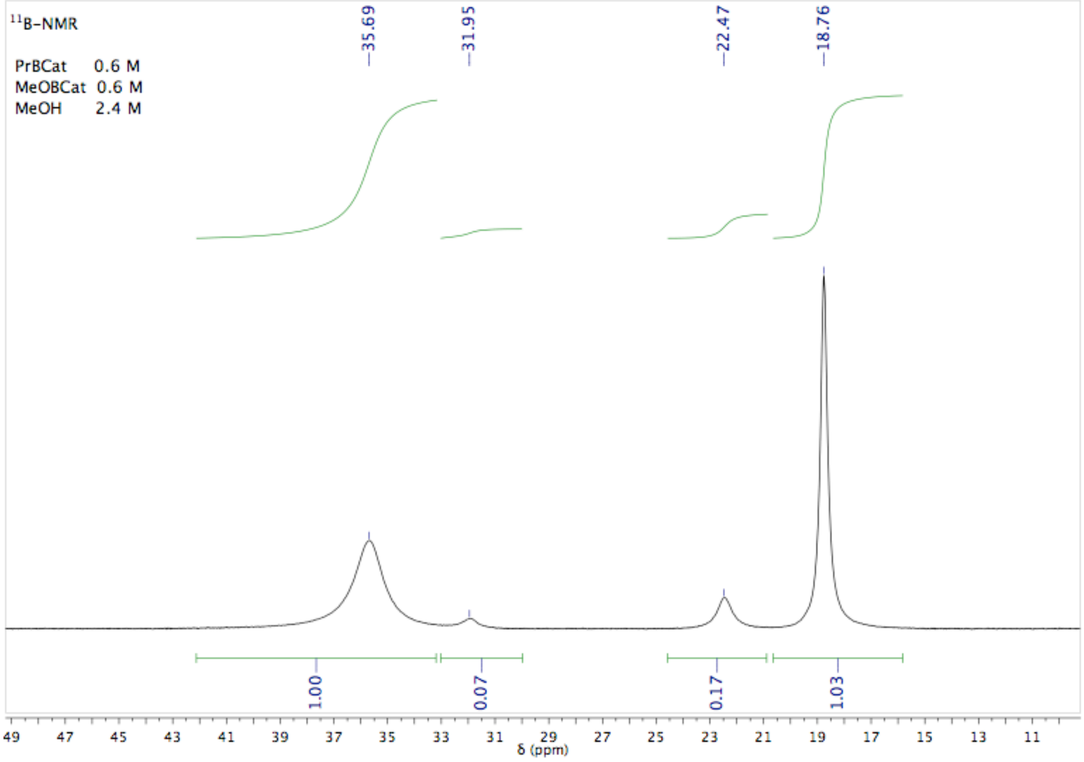


^{1}H
PrBCat 0.6 M
MeOH 2.4 M
7.79
7.02
6.98
6.81
6.73
3.35
3.17
1.55
1.54
1.52
1.50
1.48
0.97
0.89
0.68
0.66
0.64
2.07
2.00
5.22
8.88
2.00
0.78
1.92
1.17
1.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
δ (ppm)

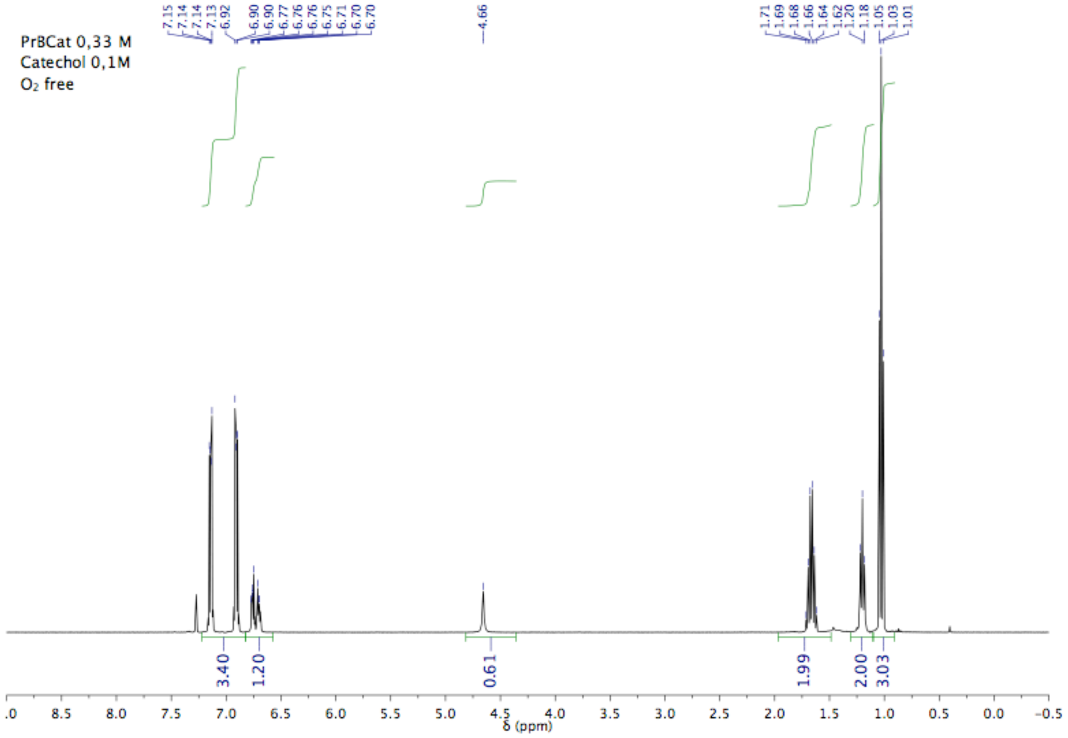


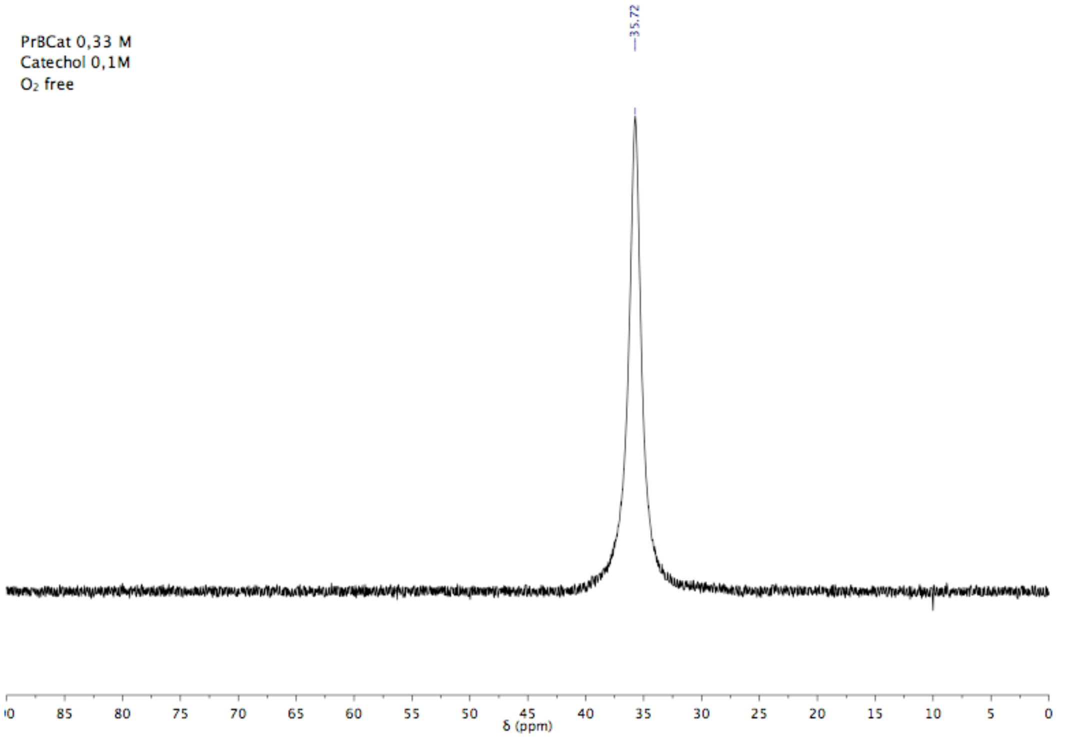
^{11}B
PrBCat 0.6 M
MeOH 2.4 M
35.63
31.87
1.00
1.85
49
47
45
43
41
39
37
35
33
31
29
27
25
23
21
19
17
15
13
11
δ (ppm)


1H
PrBCat 0.6 M
MeOBCat 0.6 M
MeOH 2.4 M
7.04 7.04 7.03 7.02 6.89 6.88 6.87 6.86 6.82 6.82 6.81 6.80 6.72 6.71 6.70 6.69
5.35
3.42 3.35 3.11
1.58 1.56 1.54 1.52 1.50 1.11 1.09 1.07 0.97 0.95 0.93 0.91 0.89
1.83 2.22 1.85 2.34
8.35 3.46
2.00 1.95 2.90 0.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

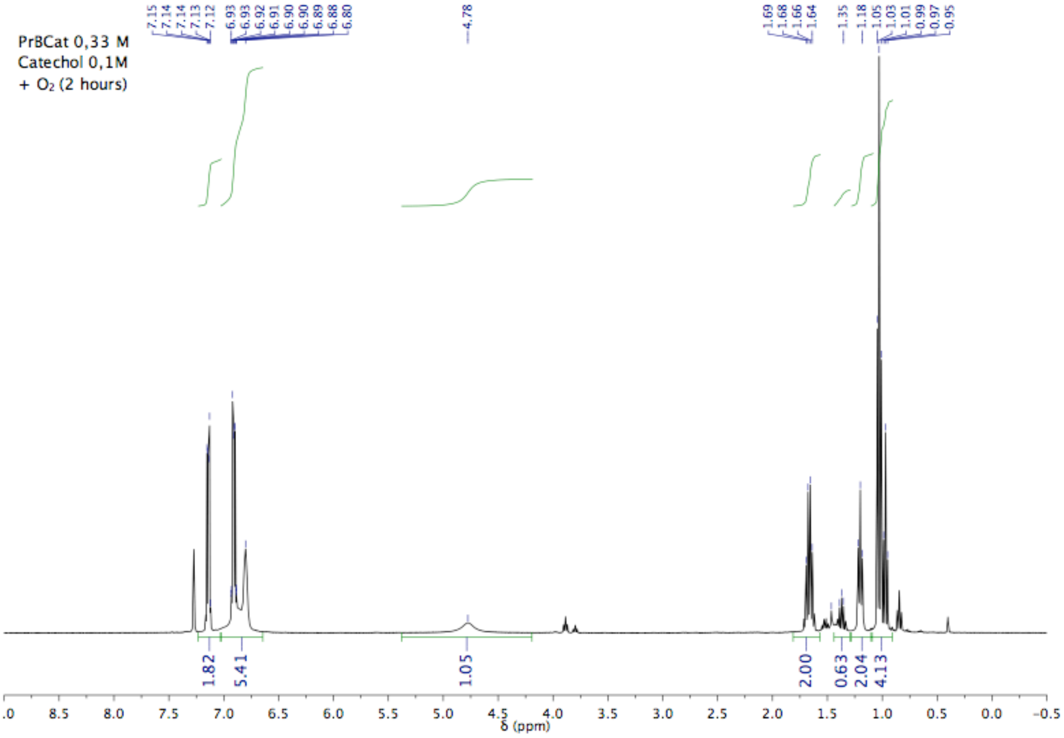

11B-NMR
PrBCat 0.6 M
MeOBCat 0.6 M
MeOH 2.4 M
35.69
31.95
22.47
18.76
1.00
0.07
0.17
1.03
49 47 45 43 41 39 37 35 33 31 29 27 25 23 21 19 17 15 13 11
δ (ppm)

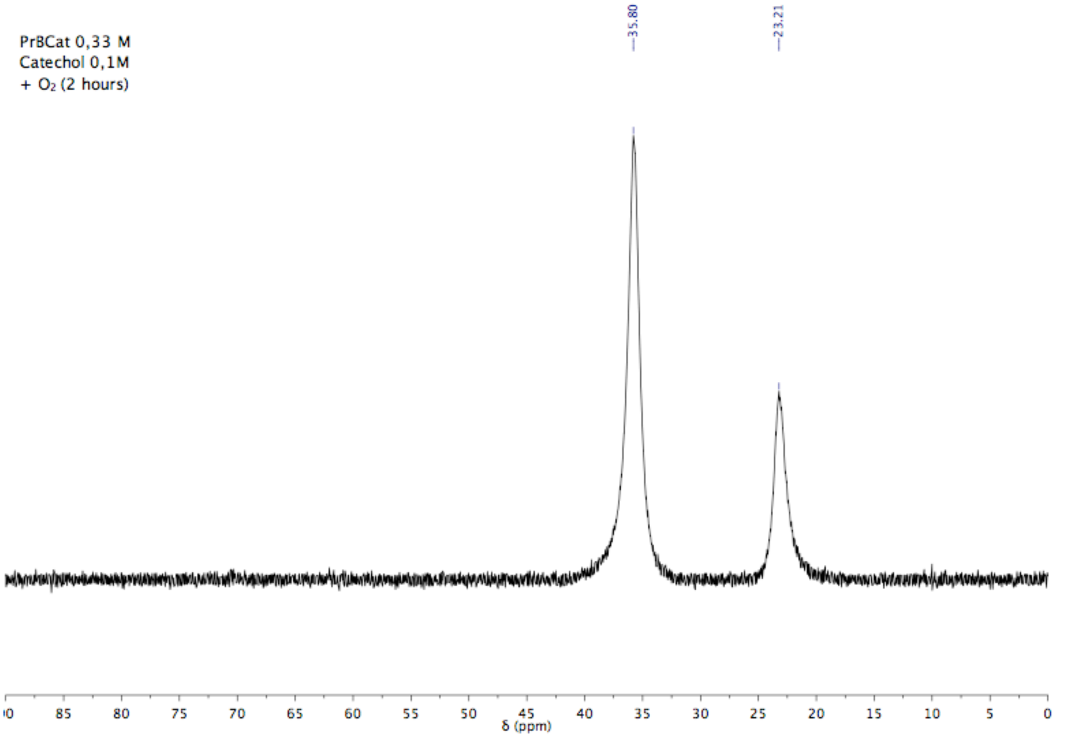
PrBCat + catechol: O_2 free



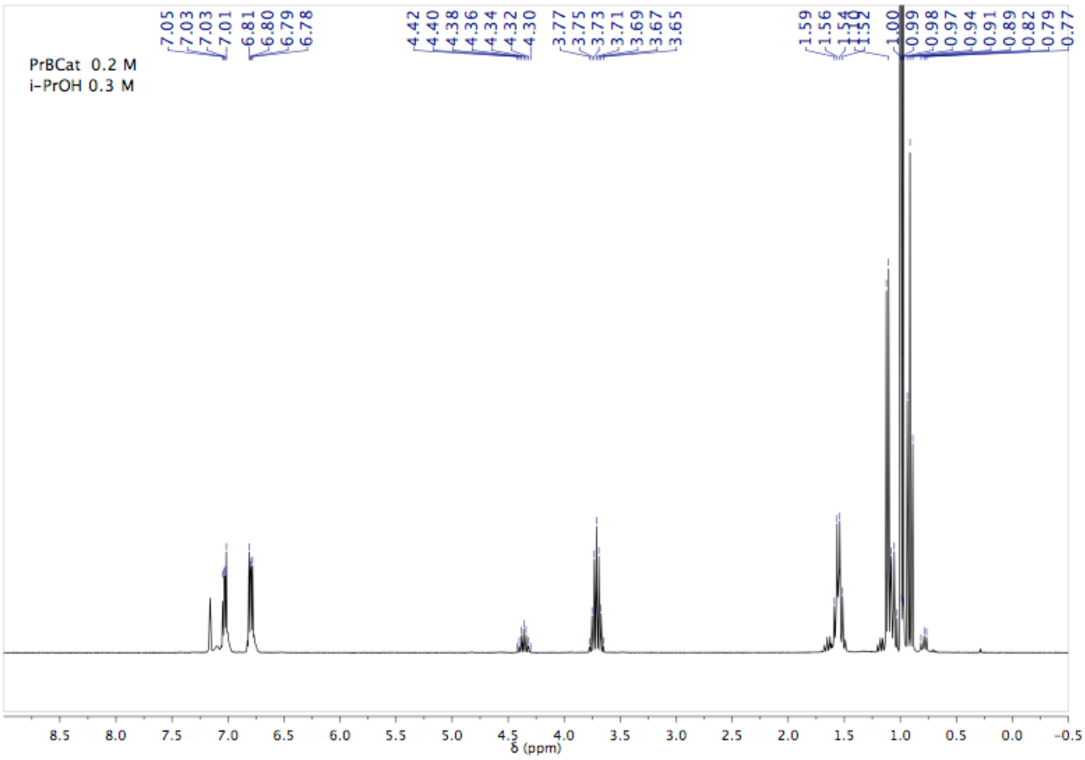


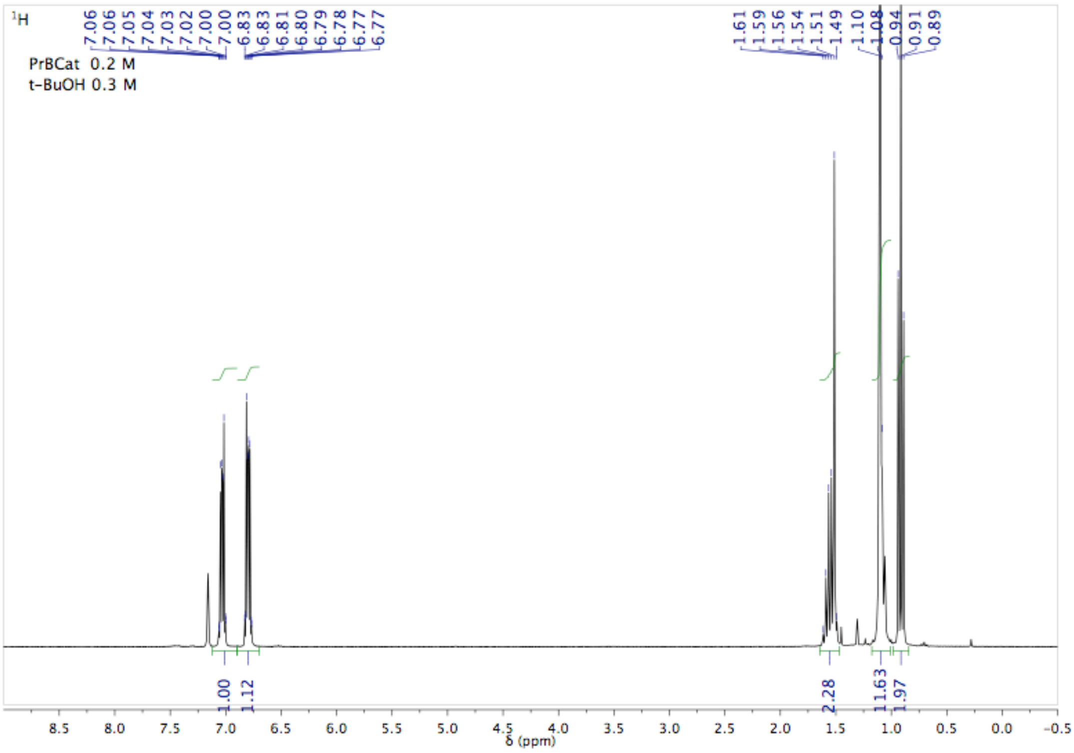
PrBCat + catechol: O_2 (2 hours)





PrBCat / ROH


PrBCat 0.2 M
i-PrOH 0.3 M
7.05
7.03
7.03
7.01
6.81
6.80
6.79
6.78
4.42
4.40
4.38
4.36
4.34
4.32
4.30
3.77
3.75
3.73
3.71
3.69
3.67
3.65
1.59
1.56
1.54
1.50
1.52
1.00
0.99
0.98
0.97
0.94
0.91
0.89
0.82
0.79
0.77
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
δ (ppm)


1H
PrBCat 0.2 M
t-BuOH 0.3 M
7.06
7.06
7.05
7.04
7.03
7.02
7.00
7.00
6.83
6.83
6.81
6.80
6.79
6.78
6.77
6.77
1.61
1.59
1.56
1.54
1.51
1.49
1.10
1.08
0.94
0.91
0.89
1.00
1.12
2.28
11.63
1.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
δ (ppm)