Supporting Information

Ring-opening of Enantiomerically Pure Oxa-containing Heterocycles with Phosphorus Nucleophiles

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(A) Single crystal X-ray structure determinations

X-Ray Data: Single crystals of enantiopure compounds **2a**, ***ent*-2b**, **2c**, **2d**, **5**, and **11** suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into EtOAc solutions of each compound at room temperature. Single crystals of enantiopure compound **9** suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into DCM solutions of each compound at room temperature. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determinations of **2c**, **2d**, **5**, **9**, and **11** were carried out using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Crystal structure determinations for **2a**, and ***ent*-2b** was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using $Mo_{K\alpha}$ radiation, Quazar MX multilayer Optics as monochromator and a Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection APEX-2,[1] data reduction Bruker Saint,[2] and absorption correction SADABS.[3]

Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implemented in SHELXTL[4] and visualized using the program XP. Absolute configuration was determined based on the Flack parameter.[5] Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

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[1] Data collection with: *APEX II* versions v1.0-22, v2009.1-0 and v2009.1-02, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.

[2] Data reduction with: *SAINT* versions V.2.10, V/.60A and V7.60A, Bruker AXS Inc., Madison, Wisconsin, USA, 2003/2007.

[3] *SADABS*, V.2.10, V2008 and V2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2003/2001, see: R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

[4] *SHELXTL*, versions V6.12 and 6.14, see: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

[5] a) H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876; b) H. D. Flack and G. J. Bernardelli, *J. Appl. Crystallogr.,* 2000, **33**, 1143.

Crystal data for 2a: $C_{22}H_{26}B_1O_2P_1$, Mr = 364.21; monoclinic; space group $P2_1$, a = 9.3550(7) Å, b = 33.043(3) Å, c = 13.5151(11) Å, β = 107.899(2)°, V = 3975.6(5) Å³, Z = 8, ρcal = 1.217 Mg/m³, μ = 0.151 mm-1, 52980 reflections were collected of which 20660 are unique (Rint = 0.0572), 18650 Fo > 4sig(Fo), 1003 refined parameters, R1 [I>2sigma(I)]= 0.0554, wR2 [I>2sigma(I)] = 0.1304, Flack parameter: 0.06(6), Goodness of fit on F2 = 1.077, maximum residual electron density 0.553 (–0.326) e Å³.

Crystal data for *ent*-2b: $C_{40}H_{38}B_1O_2P_1$, Mr = 592.48; monoclinic; space group $P2_1$, a = 9.3160(15) Å, b = 14.835(3) Å, c = 12.0350(19) Å, β = 102.299(3)°, V = 1625.1(5) Å³, Z = 2, ρcal = 1.211 Mg/m³, μ = 0.119 mm-1, 10052 reflections were collected of which 6869 are unique (Rint = 0.0210), 6204 Fo > 4sig(Fo), 688 refined parameters, R1 [I>2sigma(I)]= 0.0400, wR2 [I>2sigma(I)] = 0.0907, Flack parameter: 0.00(7), Goodness of fit on F2 = 1.037, maximum residual electron density 0.224 (–0.239) e Å³.

Crystal data for 2c: $C_{22}H_{38}B_1O_2P_1$, Mr = 376.30; orthorhombic; space group $P2_12_12_1$, a = 9.8800(6) Å, b = 10.5070(6) Å, c = 20.9290(13) Å, V = 2172.6(2) Å³, Z = 4, ρcal = 1.150 Mg/m³, μ = 0.140 mm-1, 28028 reflections were collected of which 10164 are unique (Rint = 0.0249), 9515 Fo > 4sig(Fo), 238 refined parameters, R1 [I>2sigma(I)]= 0.0327, wR2 [I>2sigma(I)] = 0.0878, Flack parameter: -0.01(4), Goodness of fit on F2 = 1.073, maximum residual electron density 0.427 (–0.207) e Å³.

Crystal data for 2d: $C_{40}H_{50}B_1O_2P_1$, Mr = 604.58; monoclinic; space group $P2_1$, a = 9.6592(6) Å, b = 12.9354(11) Å, c = 14.2059(9) Å, β = 106.664(2)°, V = 604.58 Å³, Z = 2, ρcal = 1.181 Mg/m³, μ = 0.114 mm-1, 23001 reflections were collected of which 12939 are unique (Rint = 0.0249), 12301 Fo > 4sig(Fo), 399 refined parameters, R1 [I>2sigma(I)]= 0.0552, wR2 [I>2sigma(I)] = 0.1408, Flack parameter: -0.04(5), Goodness of fit on F2 = 1.056, maximum residual electron density 0.857 (–0.806) e Å³.

Crystal data for 5: $C_{22}H_{26}B_1O_2P_1$, Mr = 364.21; orthorhombic; space group $P2_12_12_1$, a = 14.456(3) Å, b = 15.0089(18) Å, c = 28.280(4) Å, V = 6135.8(17) Å³, Z = 12, ρcal = 1.183 Mg/m³, μ = 0.147 mm-1, 28811 reflections were collected of which 16496 are unique (Rint = 0.0249), 11016 Fo > 4sig(Fo), 706 refined parameters, R1 [I>2sigma(I)]= 0.0514, wR2 [I>2sigma(I)] = 0.1031, Flack parameter: -0.07(7), Goodness of fit on F2 = 1.007, maximum residual electron density 0.277 (–0.314) e Å³.

Crystal data for 9: $C_{22}H_{32}B_1O_1P_1$, Mr = 354.26; monoclinic; space group $P2_1$, a = 10.2789(7) Å, b = 12.6688(7) Å, c = 16.3394(12) Å, β = 101.241(3), V = 2086.9(2) Å³,

Z = 4, ρcal = 1.128 Mg/m³, μ = 0.138 mm-1, 15818 reflections were collected of which 10592 are unique (Rint = 0.0449), 8724 Fo > 4sig(Fo), 459 refined parameters, R1 [I>2sigma(I)]= 0.0516, wR2 [I>2sigma(I)] = 0.1270, Flack parameter: -0.06(8), Goodness of fit on F2 = 1.015, maximum residual electron density 0.521 (–0.334) e Å³.

Crystal data for 11: $C_{20}H_{22}B_1O_1P_1$, Mr = 320.16; monoclinic; space group $P2_1$, a = 9.1144(6) Å, b = 10.1755(7) Å, c = 9.5868(9) Å, β = 97.133(4)°, V = 882.23(12) Å³, Z = 2, ρcal = 1.205 Mg/m³, μ = 0.157 mm-1, 14246 reflections were collected of which 6941 are unique (Rint = 0.0258), 6195 Fo > 4sig(Fo), 215 refined parameters, R1 [I>2sigma(I)]= 0.0382, wR2 [I>2sigma(I)] = 0.0937, Flack parameter: 0.14(5), Goodness of fit on F2 = 1.052, maximum residual electron density 0.526 (–0.204) e Å³.

CCDC 931316–931319, CCDC 931321, CCDC 931323 and CCDC 931325 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

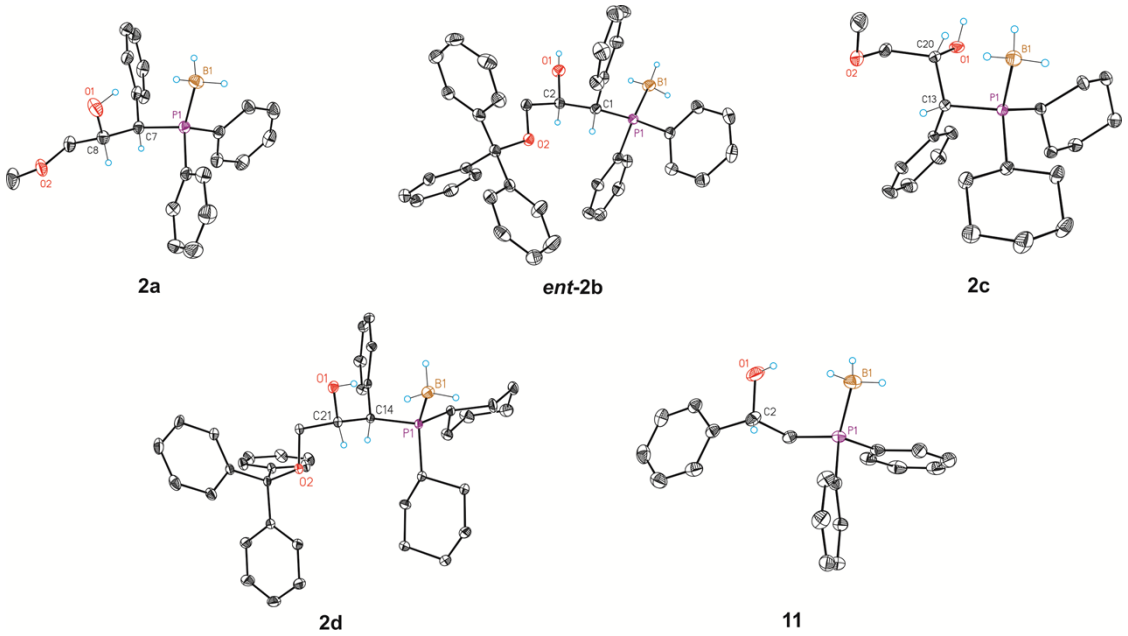
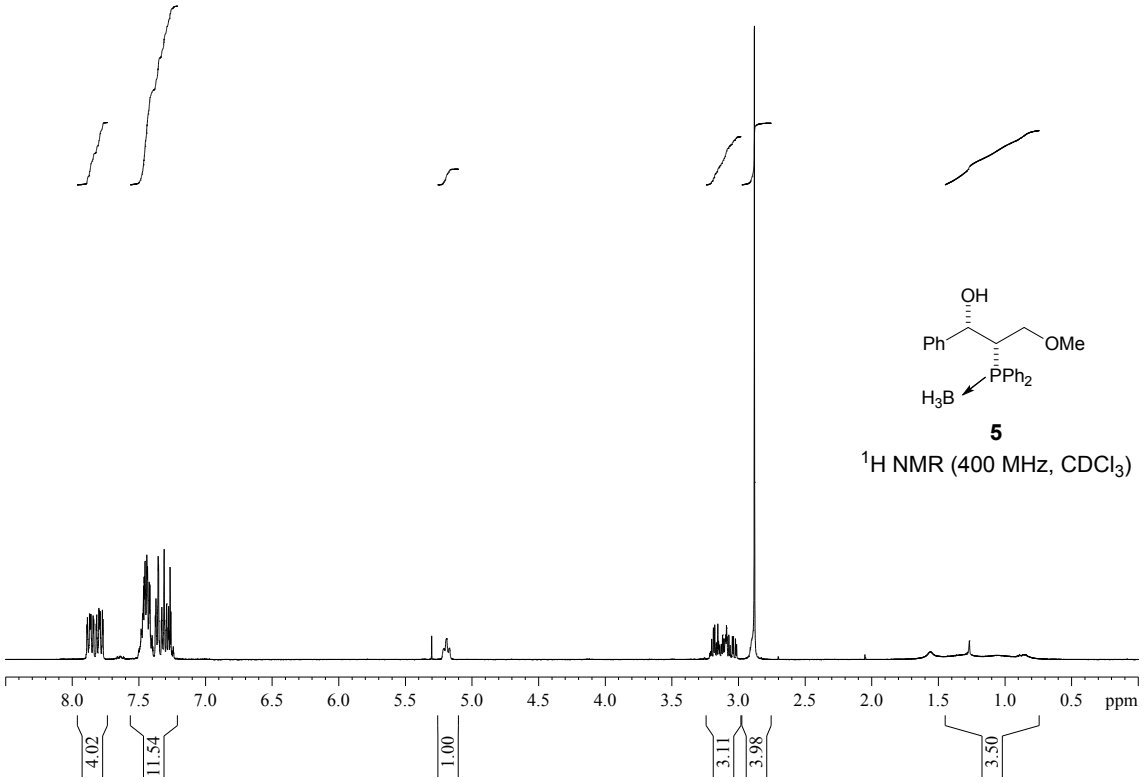


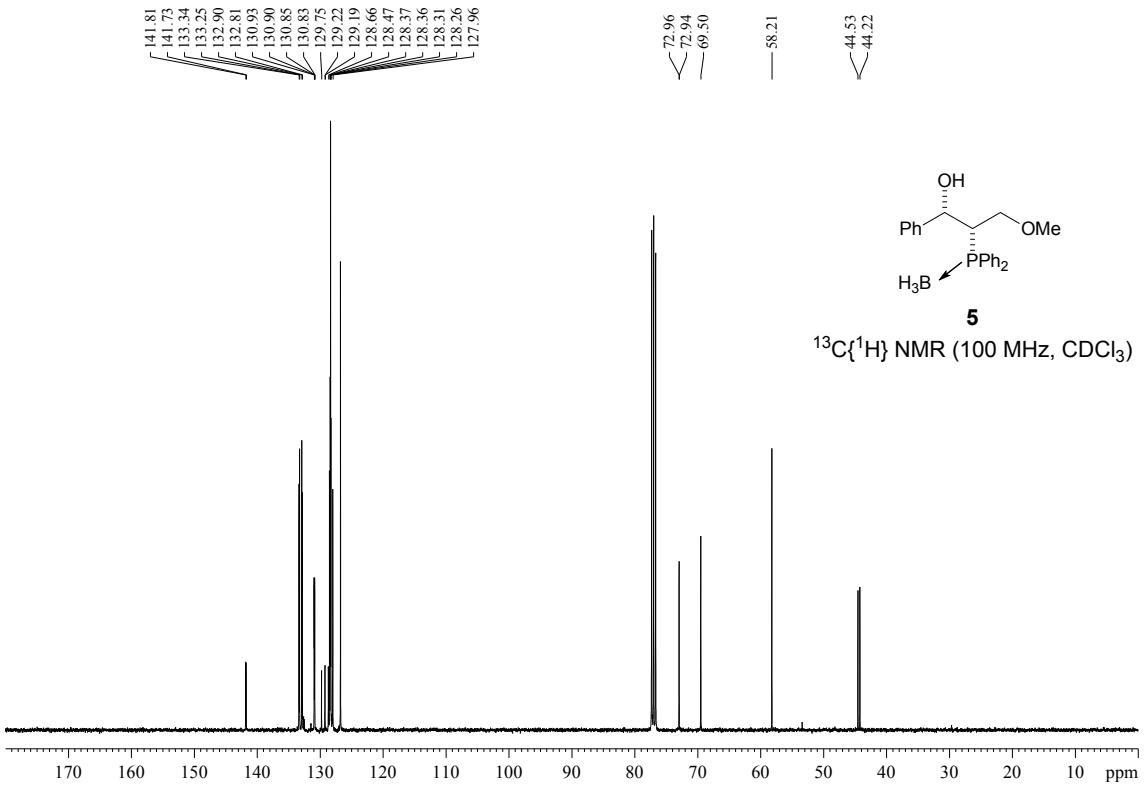
Fig. SI 1. Crystal structures of **2a**, ***ent*-2b**, **2c**, **2d**, and **11** (ORTEP drawing showing thermal ellipsoids at 50% probability). Non-relevant hydrogen atoms have been omitted for clarity.

(B) NMR spectra of new compounds



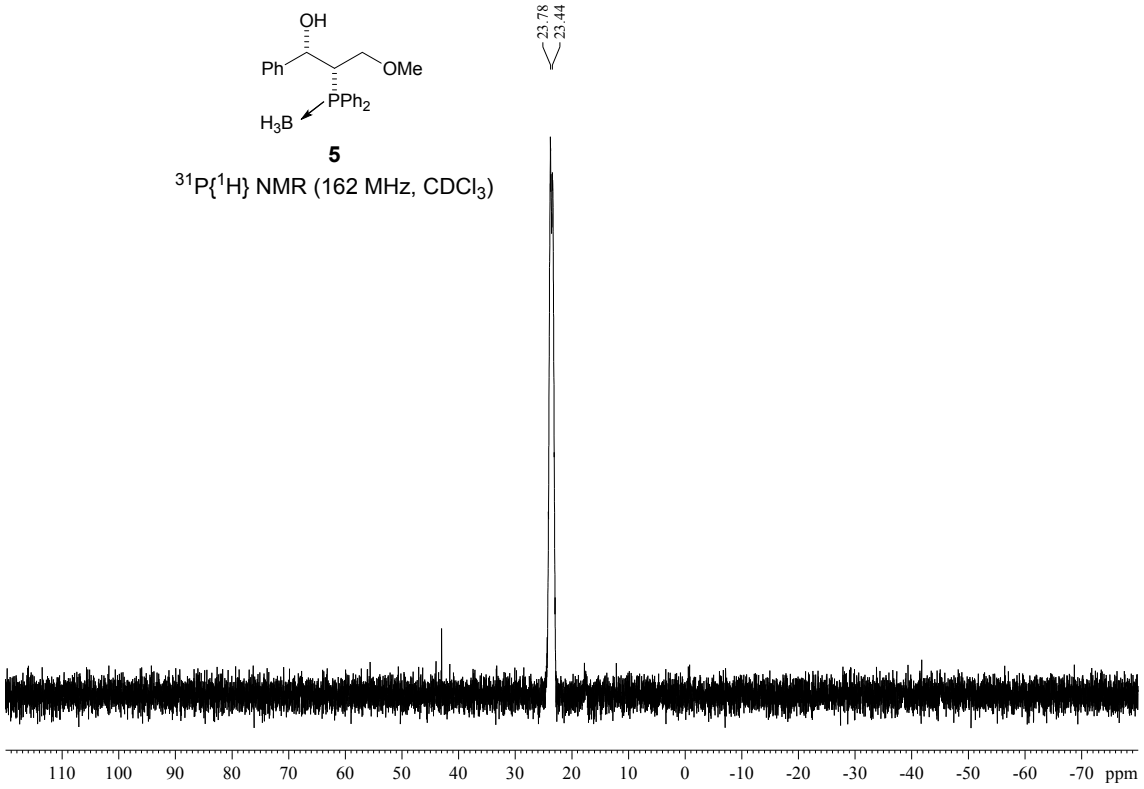
5

^{1}H NMR (400 MHz, $CDCl_3$)



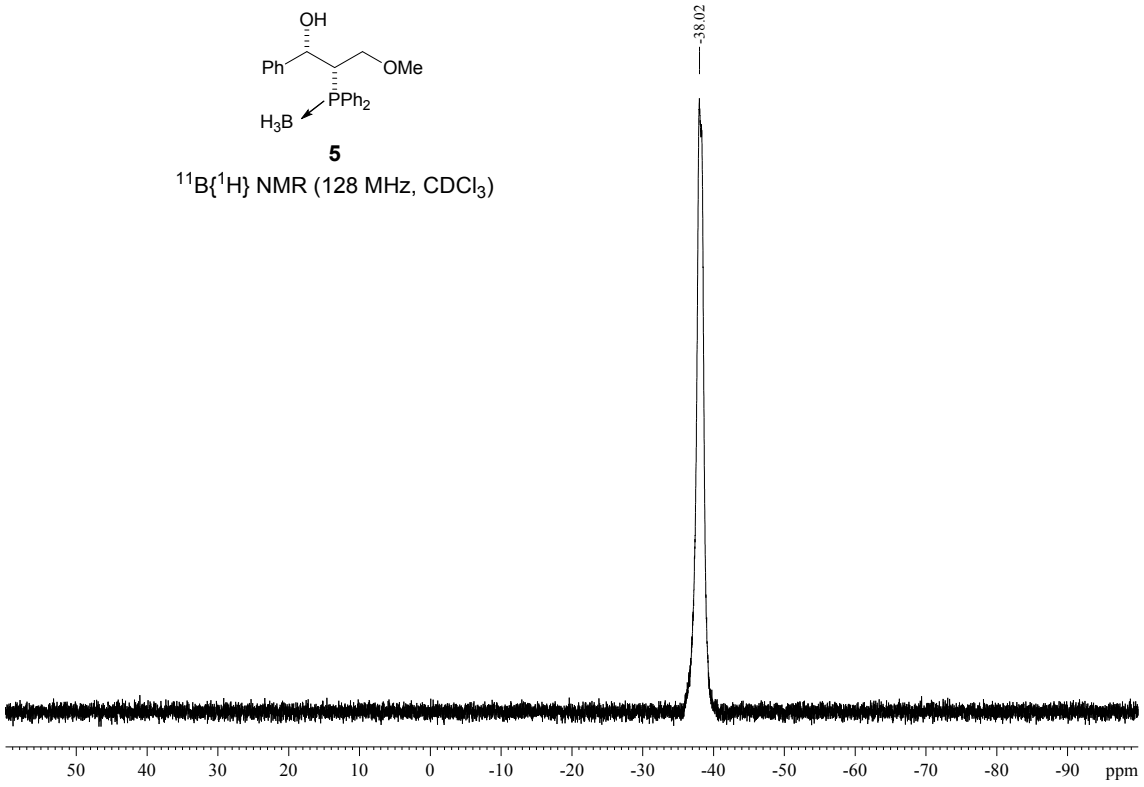
5

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



5

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



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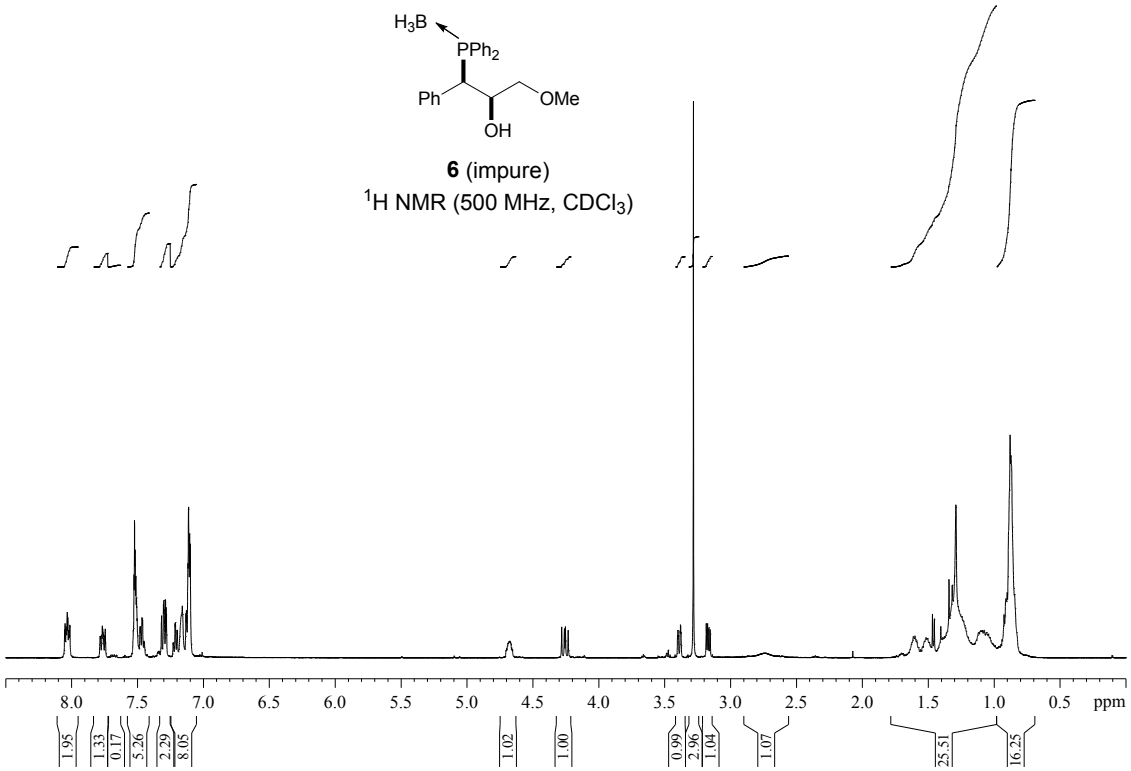
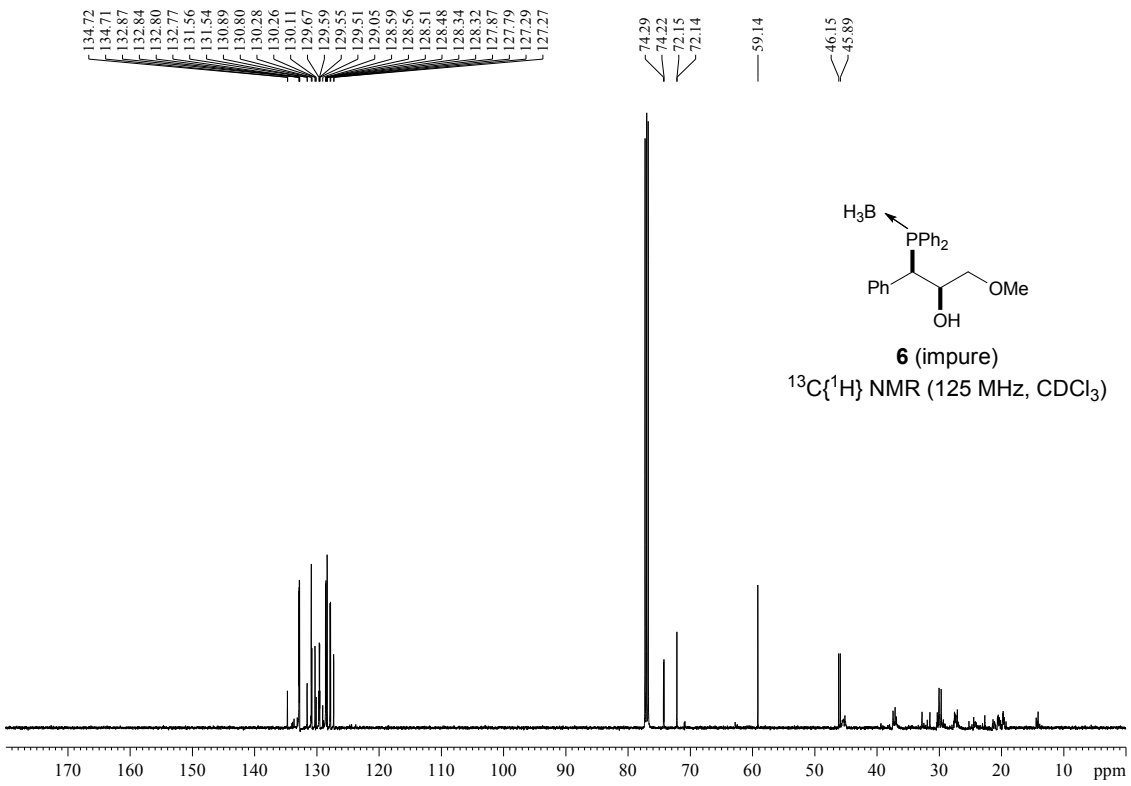
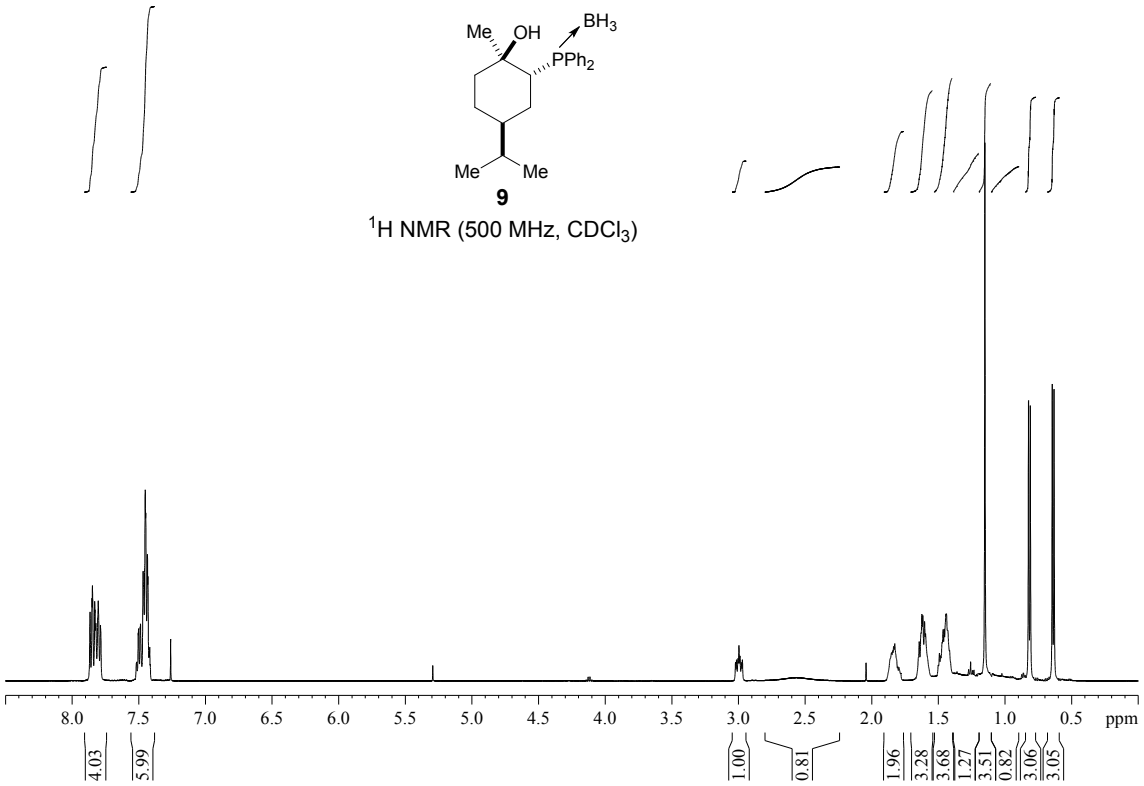
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

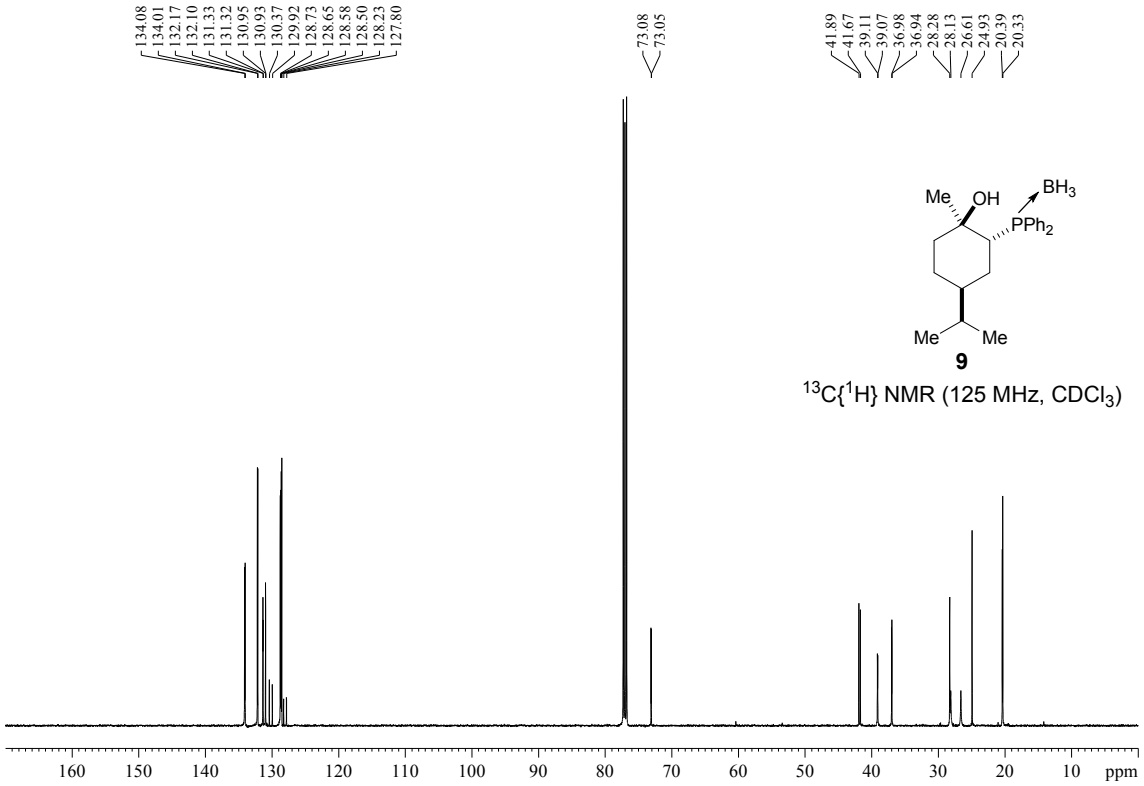


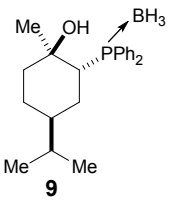
6 (impure)
^{1}H NMR (500 MHz, $CDCl_3$)



6 (impure)
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

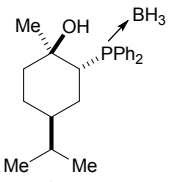

Me
OH
BH3
PPh2
Me
Me
9
1H NMR (500 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.03
5.99
1.00
0.81
1.96
3.28
3.68
1.27
3.51
0.82
3.06
3.05


134.08
134.01
132.17
132.10
131.33
131.32
130.95
130.93
130.37
129.92
128.73
128.65
128.58
128.50
128.23
127.80
73.08
73.05
41.89
41.67
39.11
39.07
36.98
36.94
28.28
28.13
26.61
24.93
20.39
20.33
Me
OH
BH3
PPh2
Me
Me
9
13C{1H} NMR (125 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



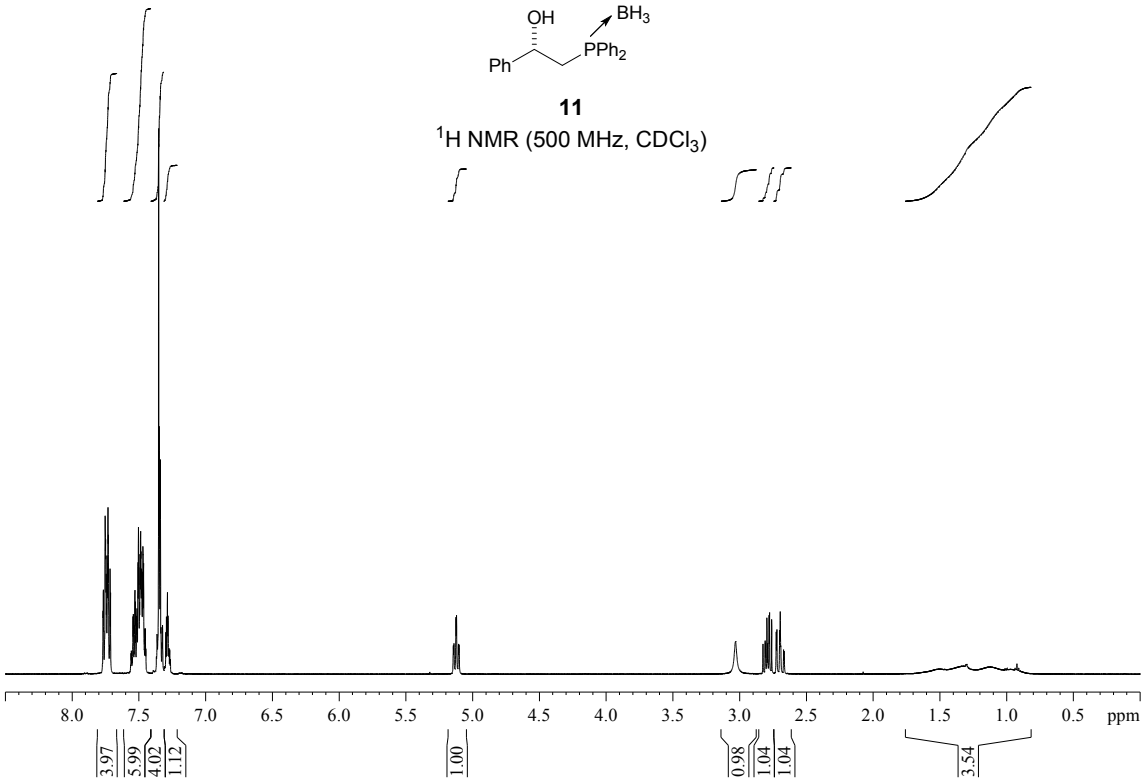
9

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



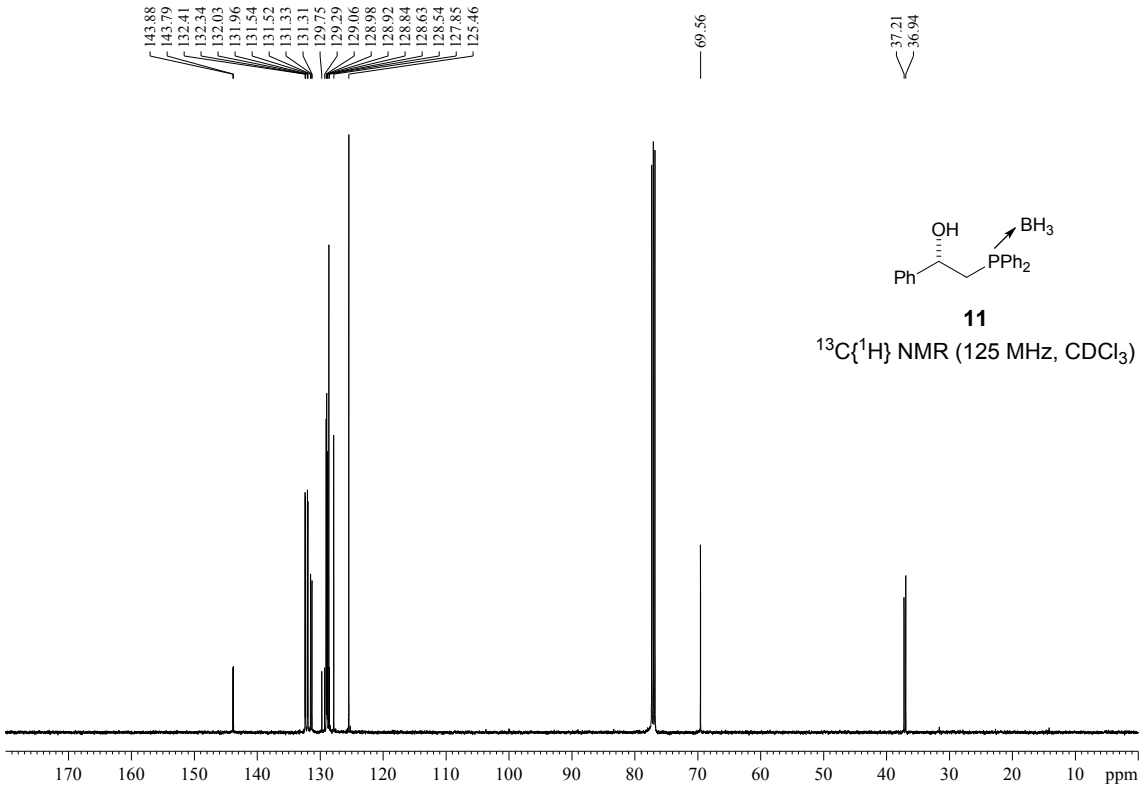
9

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



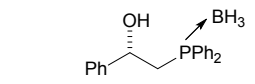
11

^{1}H NMR (500 MHz, $CDCl_3$)



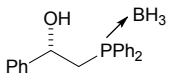
11

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



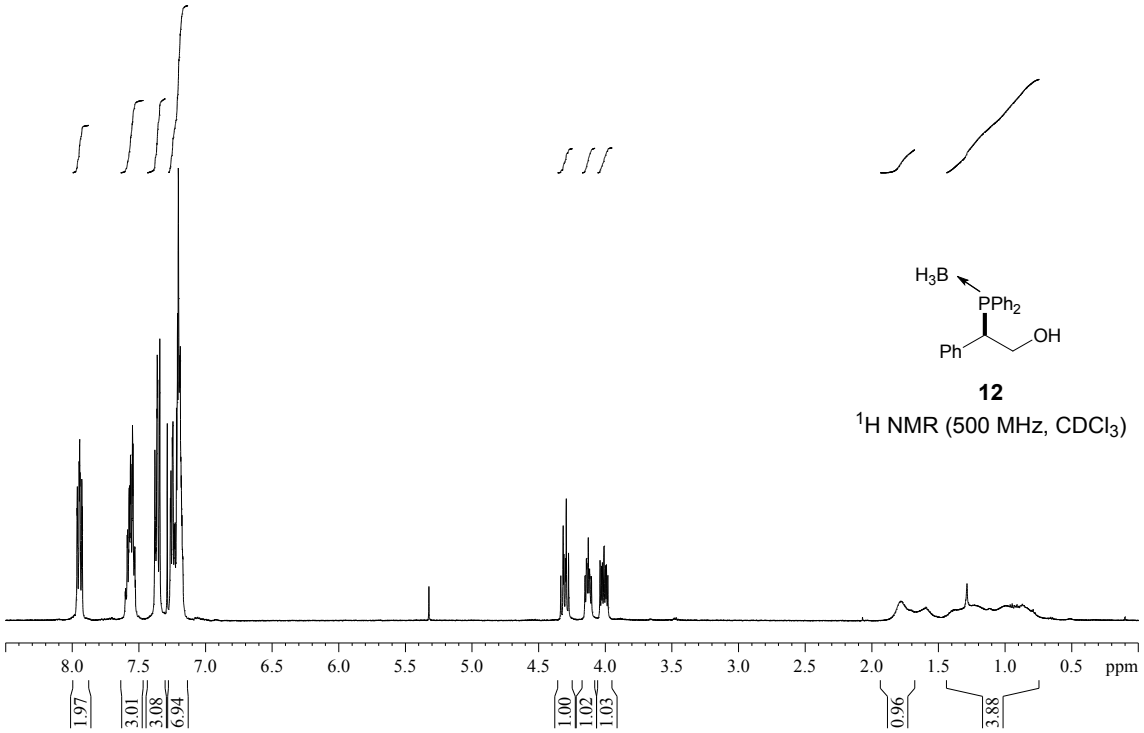
11

$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



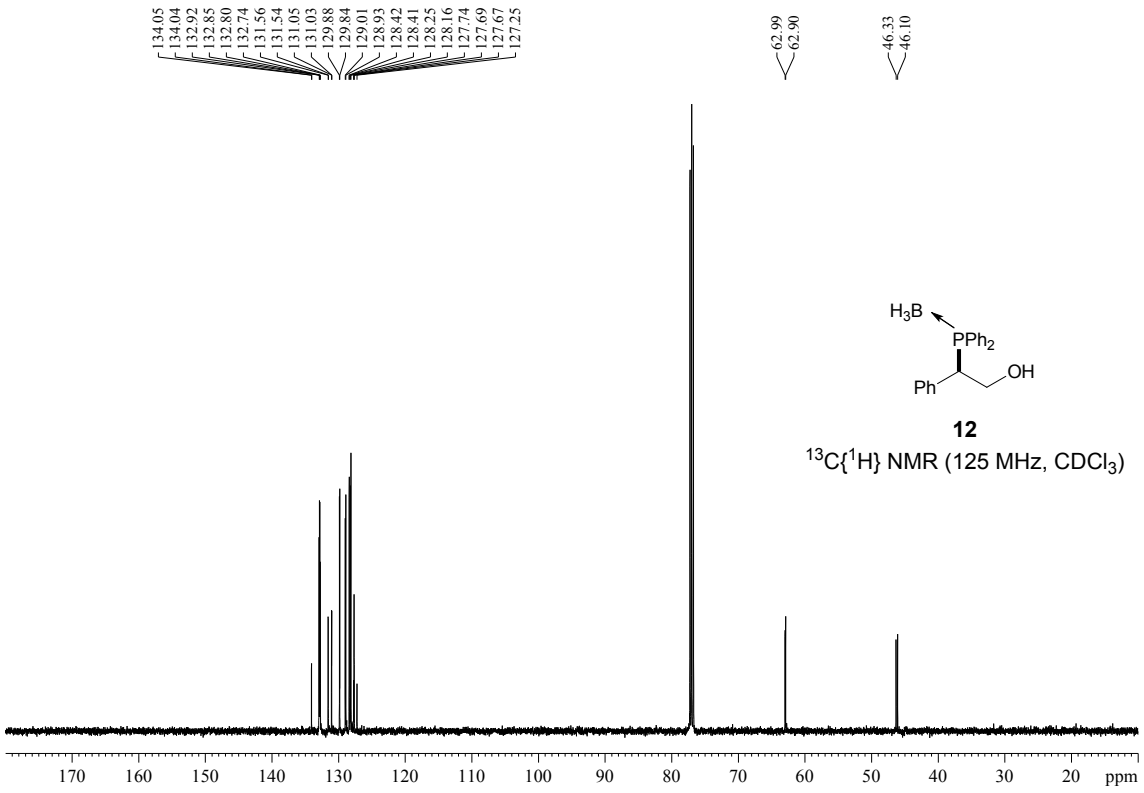
11

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



12

^{1}H NMR (500 MHz, $CDCl_3$)



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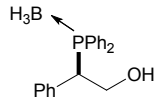
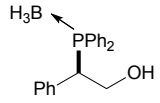
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



12

$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



12

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)