Electronic Supplementary Material (ESI) for Dalton Transactions.

Access to a Pair of Ambiphilic Phosphine–Borane Regioisomers by Rhodium-Catalyzed Hydroboration

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Supporting Information

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Fig. S-1. Stackplot of 1D NMR Spectra for Crude Hydroboration Product Mixture.

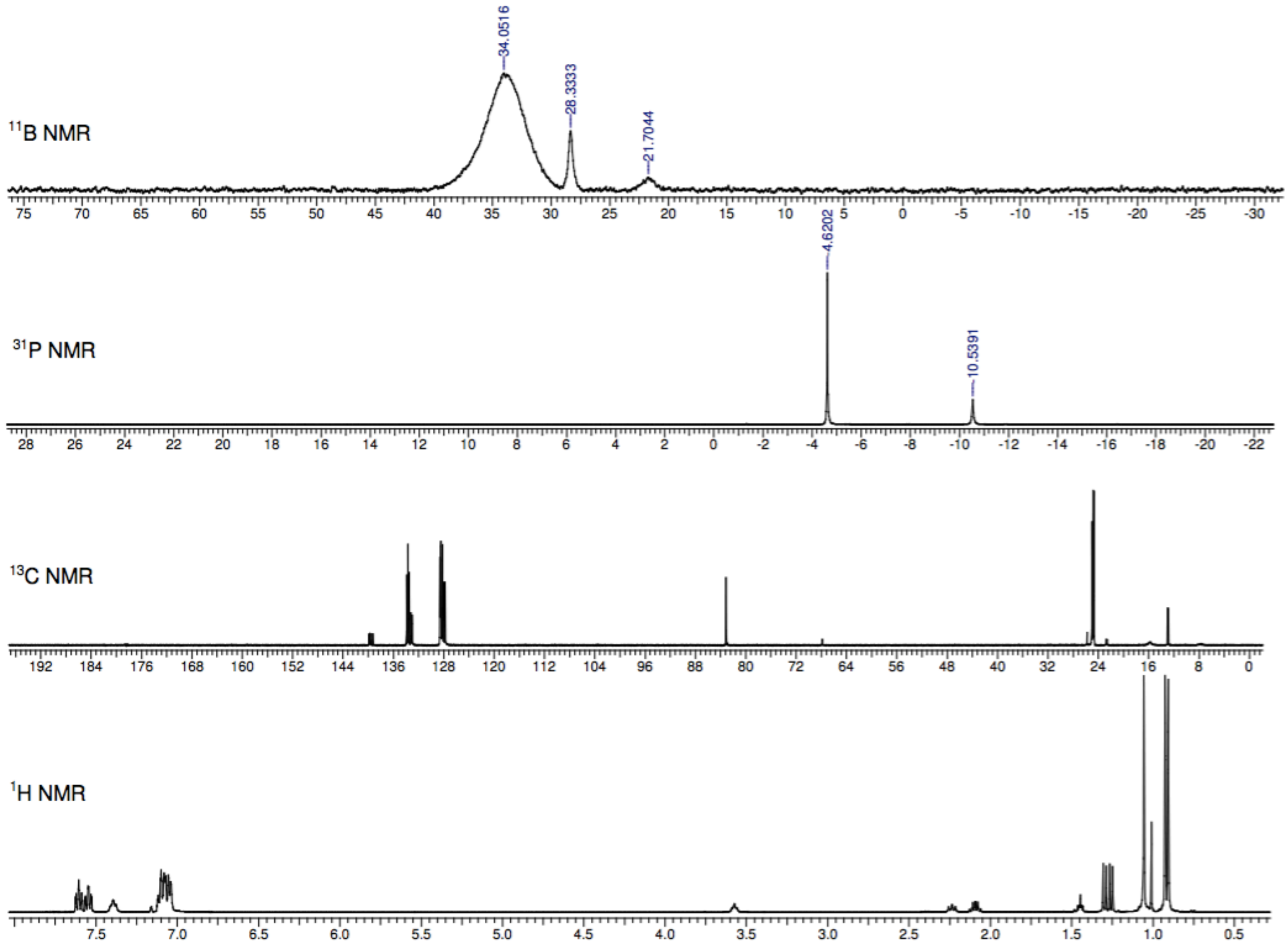


Fig. S-2. Crude hydroboration product characterization: (a) ^{1}H NMR and (b) ^{1}H{^{31}P} NMR spectra.

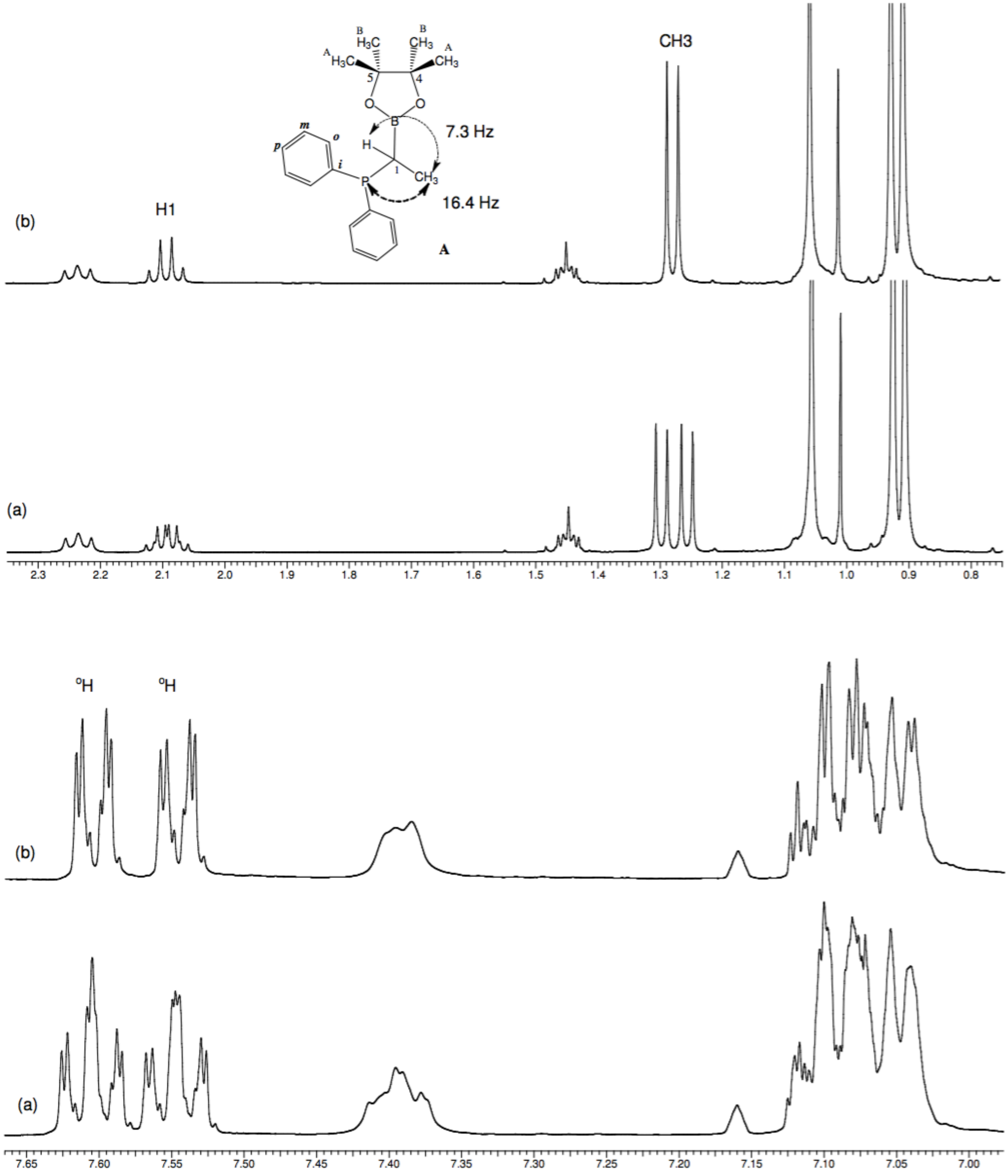


Fig. S-3. Crude hydroboration product characterization: 1D TOCSY NMR spectrum (mix time = 80 ms) with selective excitation of resonance 1-CH_2.

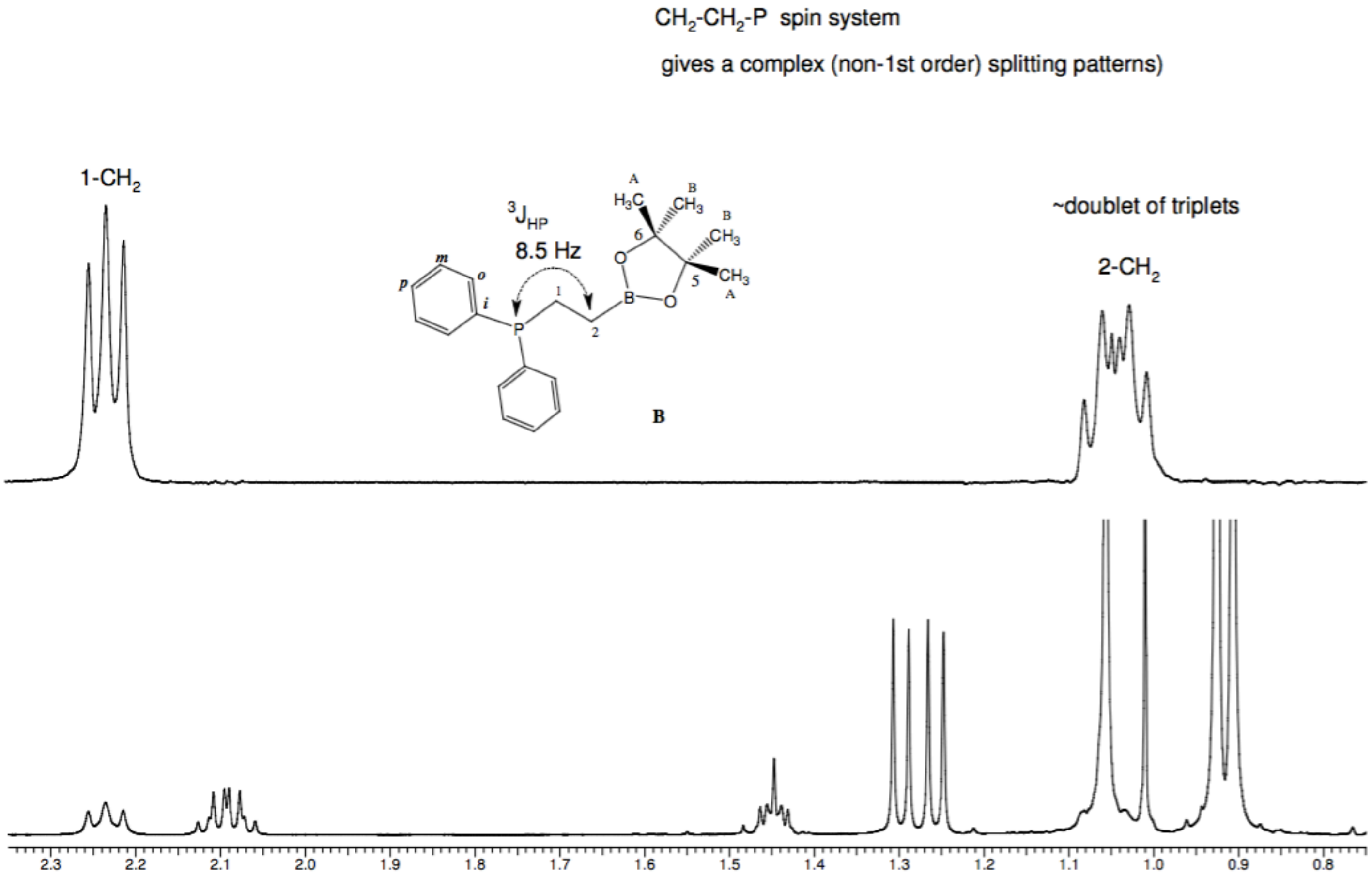


Fig. S-4. Crude hydroboration product characterization: 2D gHSQCAD NMR spectrum with structural assignment.

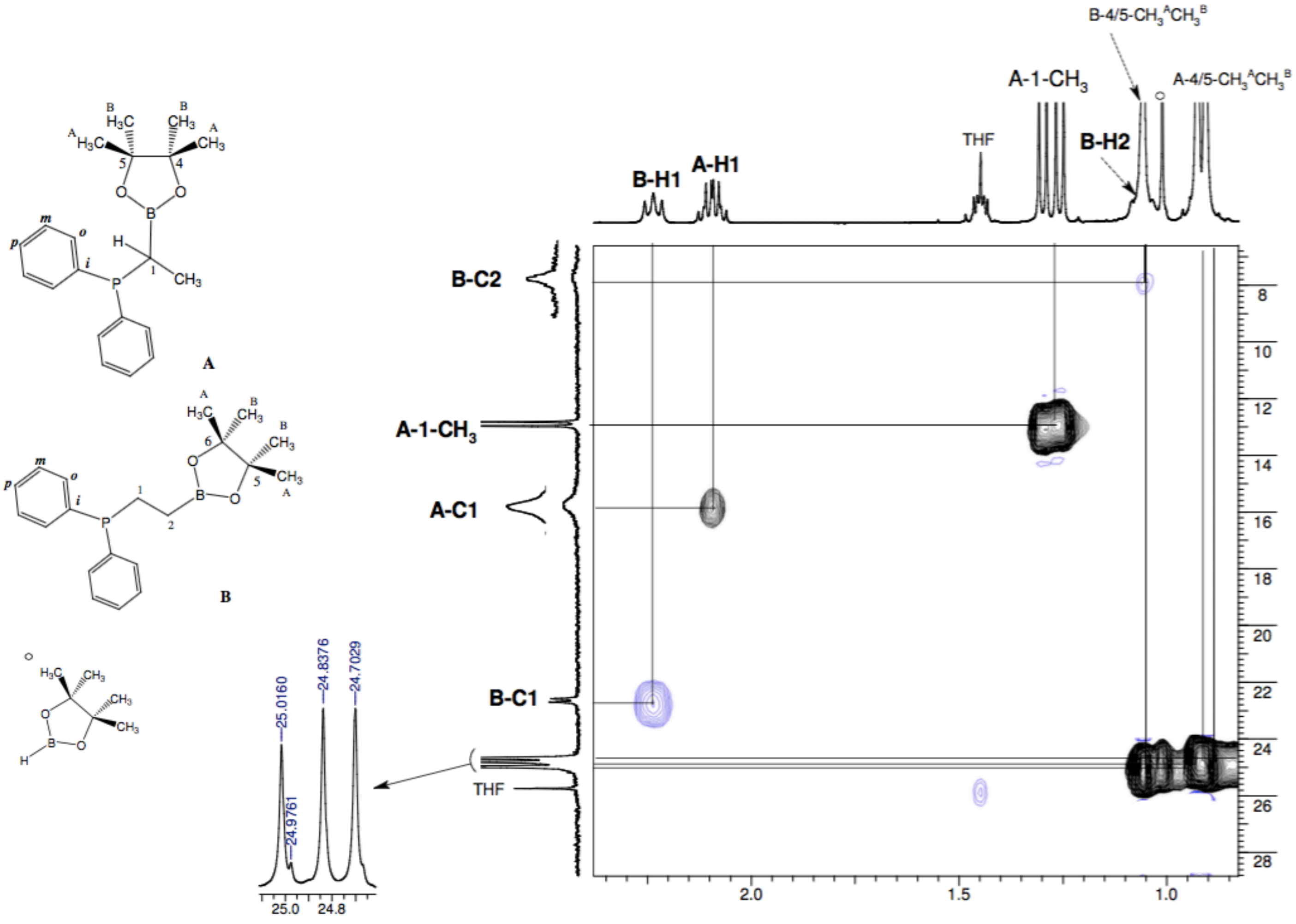


Fig. S-5. Crude hydroboration product characterization: $^{13}C\{^{1}H\}$ NMR spectrum with structural assignment.

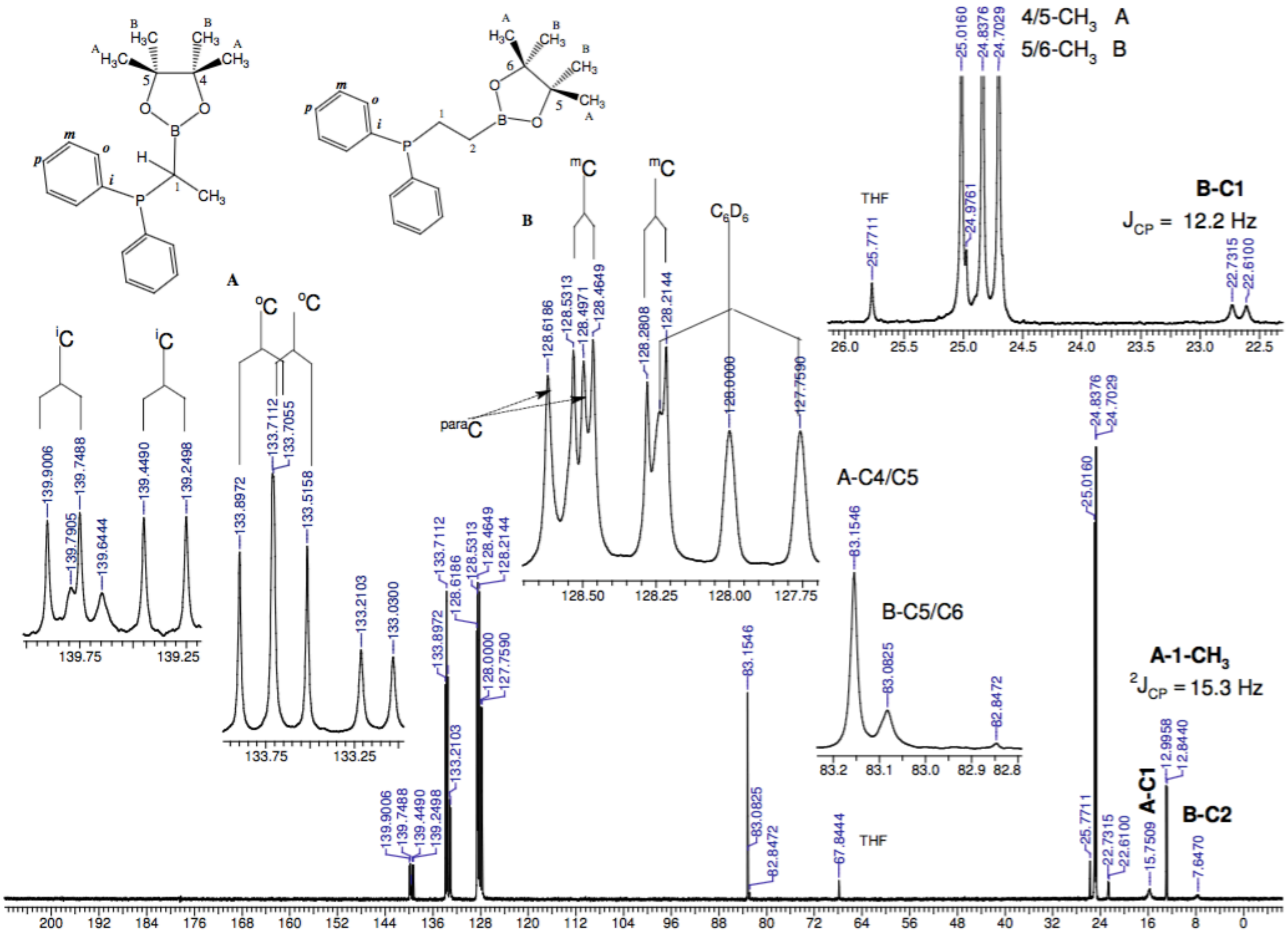
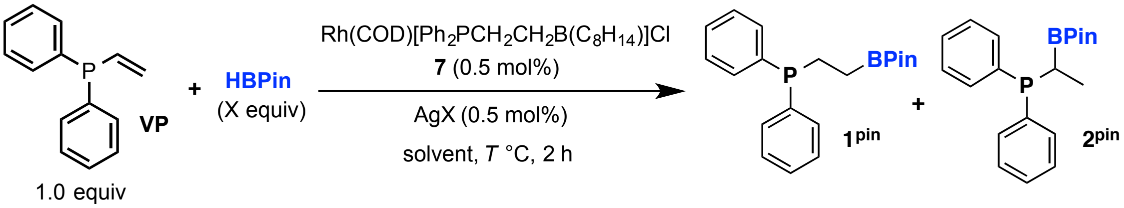


Fig. S-6. Hydroboration reaction parameter screening with pre-catalyst **7**.



Entry[a]	Silver Salt	Yield (%)[b]		Convn (%)[b]
		2	**1**	**VP**
1	None	56	43	45
2	AgOTf	79	21	100
3	$AgBF_4$	71	29	99
4	$AgSbF_6$	63	37	66

[a] **VP** (100 mM) and HBpin (2 equiv) in THF. Reactions conducted with 0.5 mol% **7** and 0.5 mol**%** ***catalytic Ag additive*** at 25 °C. [b] Yield and conversion were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Entry[a]	Solvent	Yield (%)[b]		Convn (%)[b]
		2	**1**	**VP**
1	THF	79	21	100
2	DCM	58	37	20
3	Toluene	74	26	100

[a] **VP** (100 mM) and HBpin (2 equiv) in ***solvent***. Reactions conducted with 0.5 mol% **7** and 0.5 mol% AgOTf at 25 °C. [b] Yield and conversion were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Entry[a]	Temp (°C)	Yield (%)[b]		Convn (%)[b]
		2	**1**	**VP**
1	-78	41	59	68
2	0	47	52	54
3	25	78	22	100
4	60	90	10	100
5	70	93	7	100

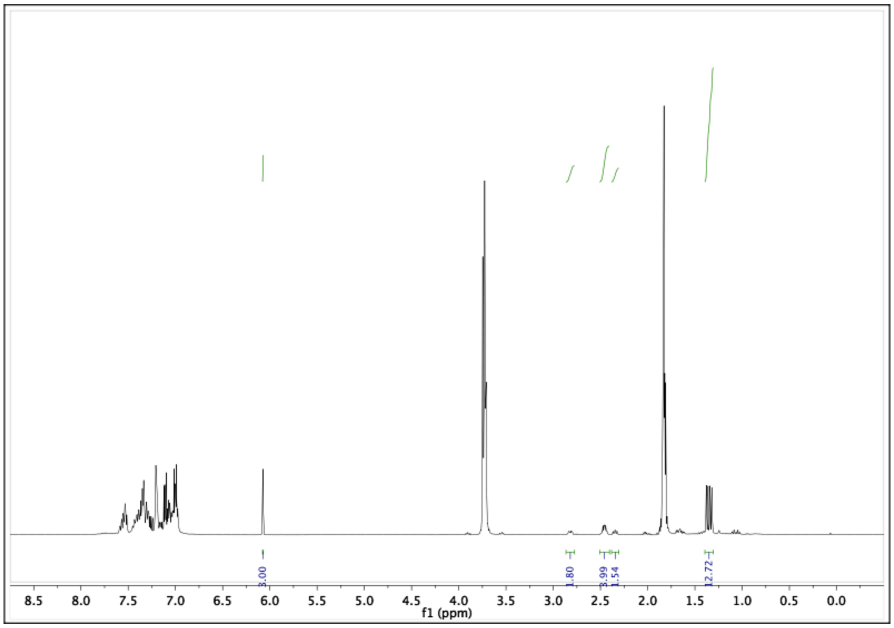
[a] **VP** (100 mM) and HBpin (2 equiv) in THF. Reactions conducted with 0.5 mol% **7** and 0.5 mol% AgOTf at ***X* °C**. [b] Yield and conversion were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Entry[a]	VP:HBPin	Yield (%)[b]		Convn (%)[b]
		2	**1**	**Limiting Reagent**
1	2:1	43	57	98
2	1:1	72	28	84
3	1:2	78	22	100

[a] **VP** (100 mM) and HBpin (***X* equiv**) in THF. Reactions conducted with 0.5 mol% **7** and 0.5 mol% AgOTf at 25 °C. [b] Yield and conversion were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

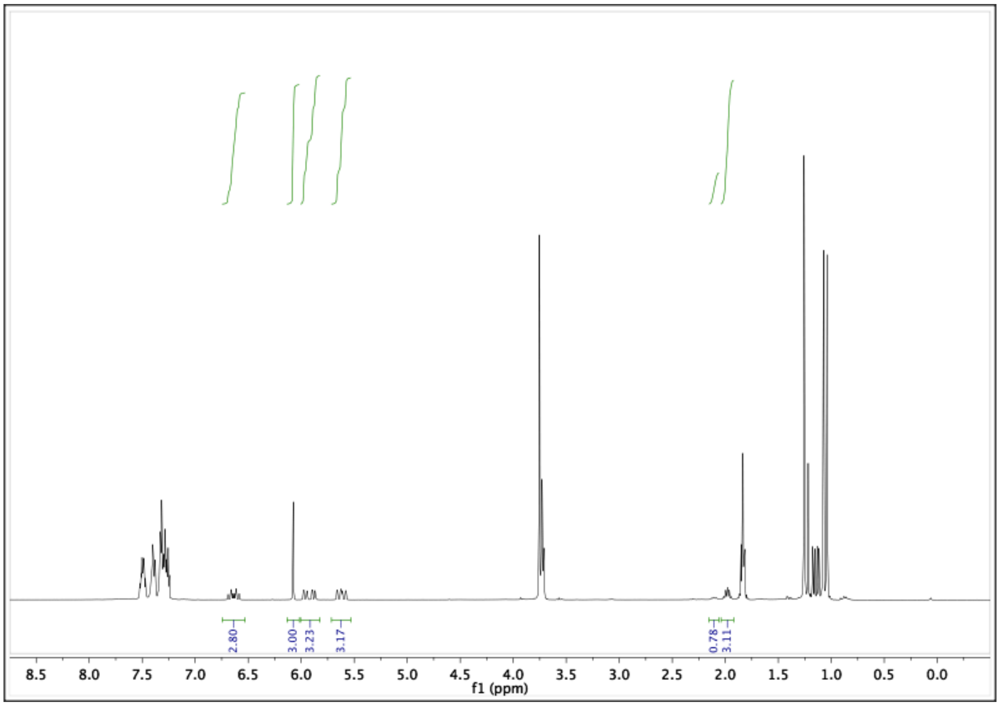
Representative examples of ^{1}H NMR spectra obtained from reactions reported in Table 1 and 2.

Fig. S-7. NMR spectra of manuscript Table 1 (Entry 6): 0.5 mol% Rh(COD)PBCl with 2 equivalents of HBCat



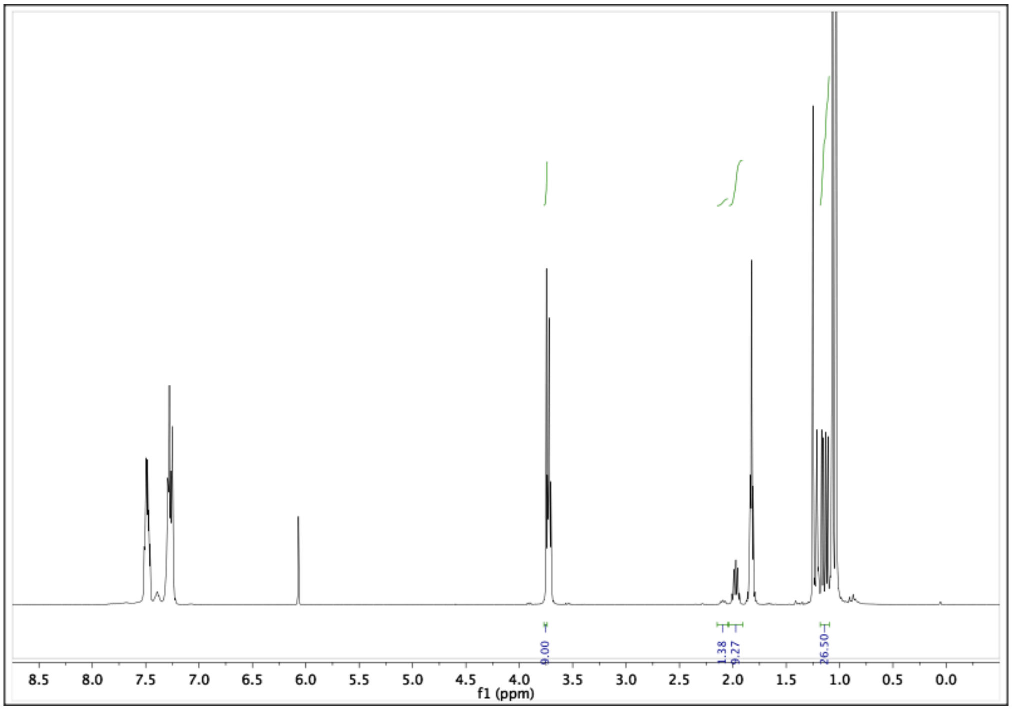
Concentration of 1,3,5-trimethoxybenzene: 0.139 M
Yield of branched product = 59%
Yield of linear product = 11%
Yield of diborane product = 25%

Fig. S-8. NMR spectra of manuscript Table 1 (Entry 7): 0.5 mol% Rh(PB)$_2$COCl



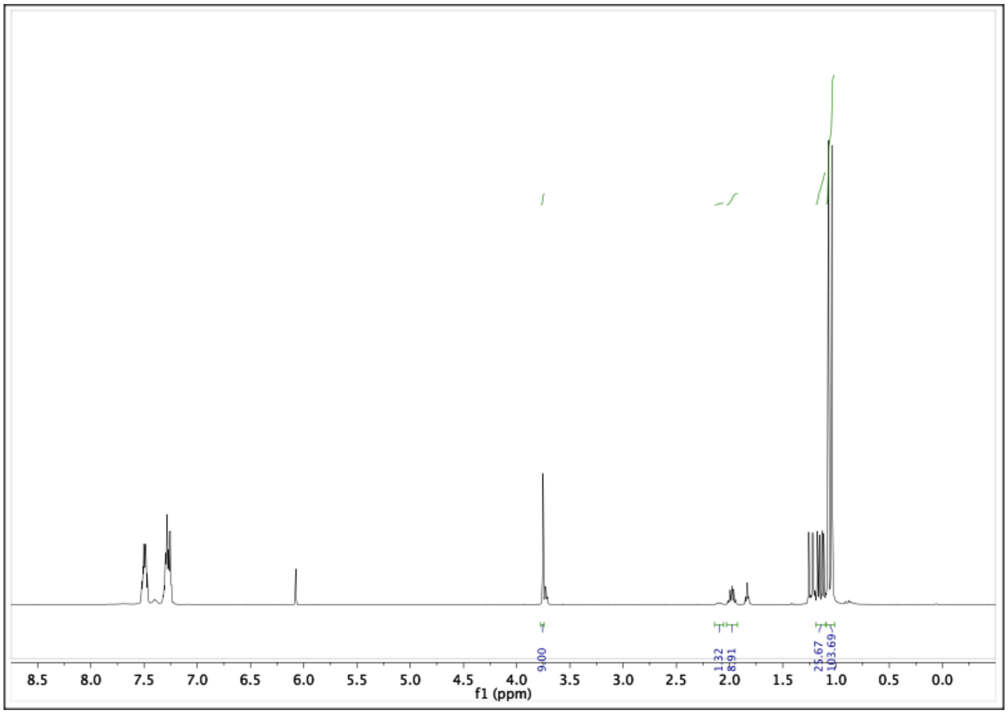
Concentration of 1,3,5-trimethoxybenzene: 0.158 M
Yield of branched product = = 52%
Yield of linear product = 6%
Conversion of Alkene = 58%

Fig. S-9. NMR spectra of manuscript Table 1 (Entry 8): 0.5 mol% Rh(COD)(PPh_3)Cl



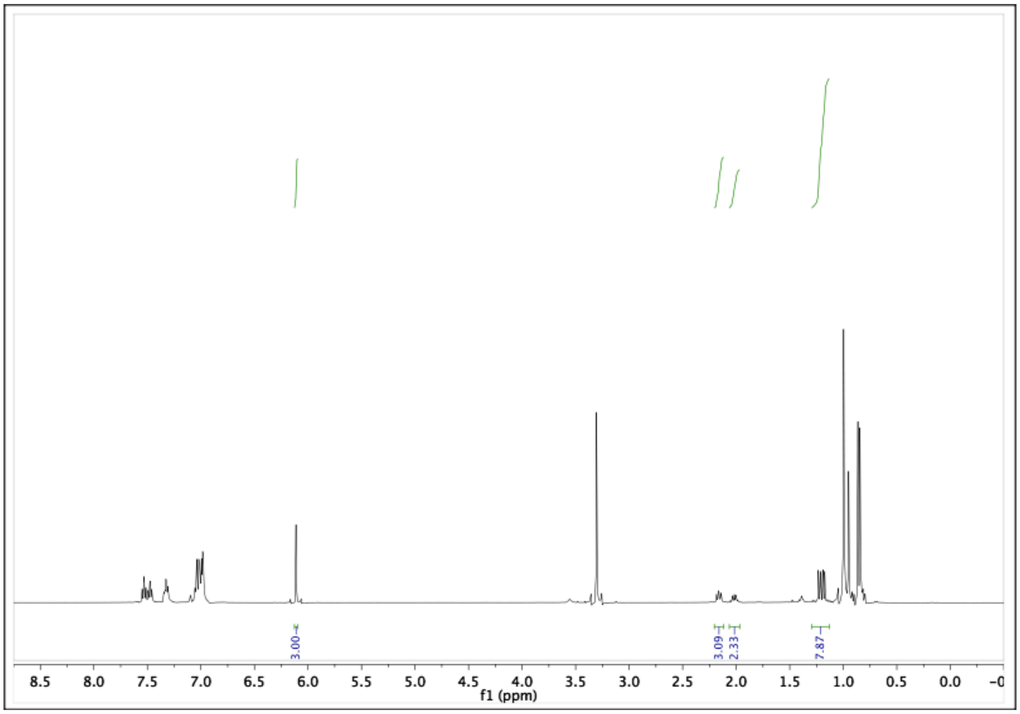
Concentration of 1,3,5-trimethoxybenzene: 0.105 M
Yield of branched product = 92%
Yield of linear product = 7%

Fig. S-10. NMR spectra of manuscript Table 2 (Entry 1): 0.5 mol% $[Rh(COD)Cl]_2$



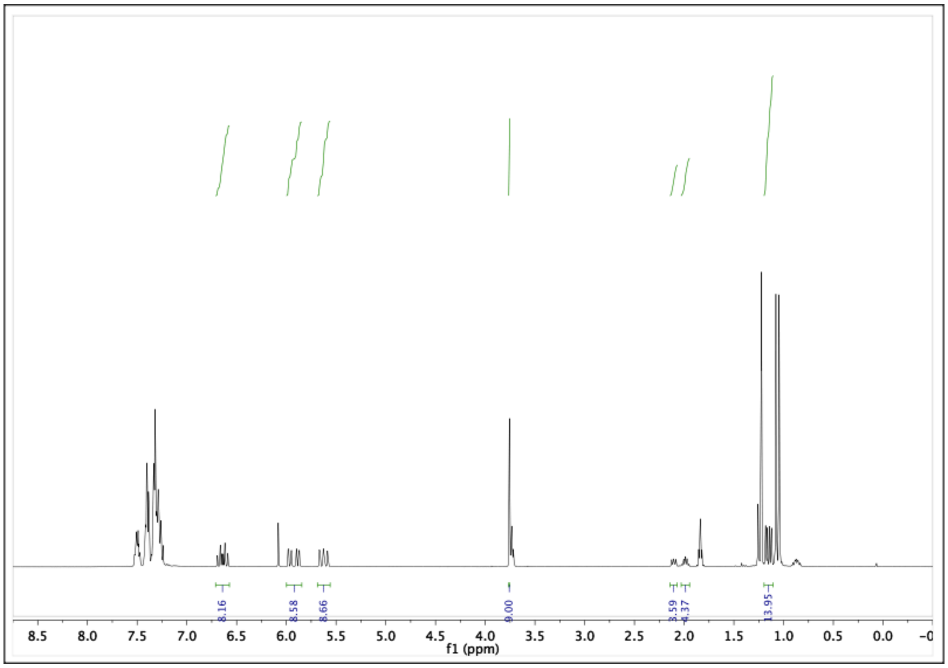
Concentration of 1,3,5-trimethoxybenzene: 0.105 M
Yield of branched product = 93%
Yield of linear product = 7%

Fig. S-11. NMR spectra of manuscript Table 2 (Entry 5): 0.5 mol% $RhCl_3$



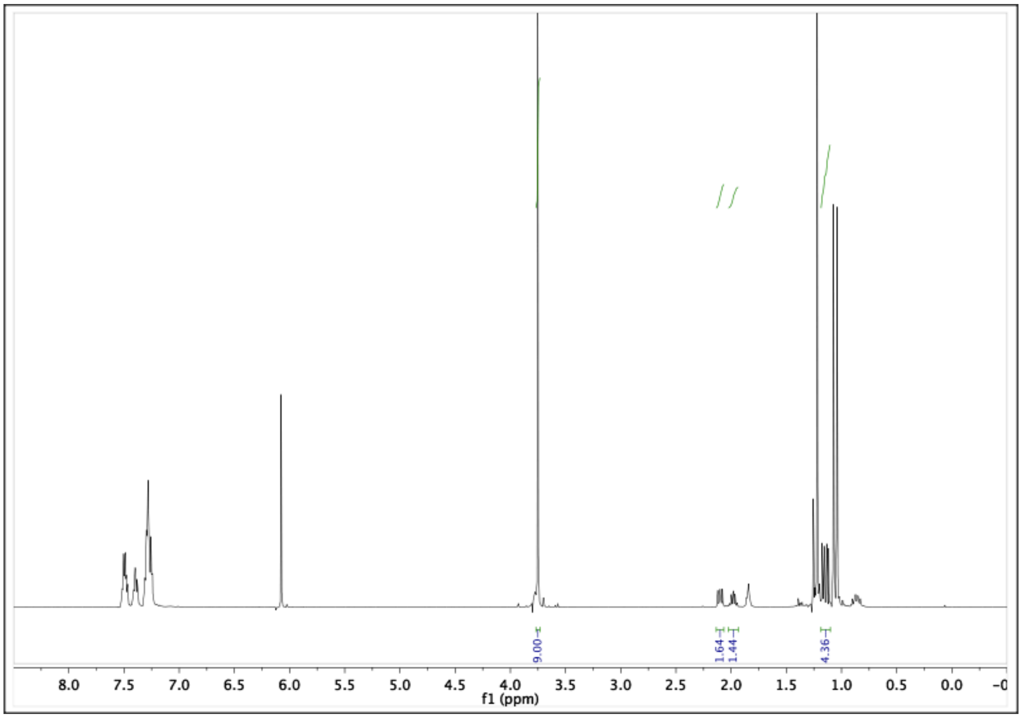
1,3,5-trimethoxybenzene: 43 mg
Ratio of vinylphosphine to 1,3,5-trimethoxybenzene = 0.255
Yield of branched product = 60%
Yield of linear product = 40%

Fig. S-12. NMR spectra of manuscript Table 2 (Entry 6): 0.5 mol% $[Rh(COE)_2Cl]_2$



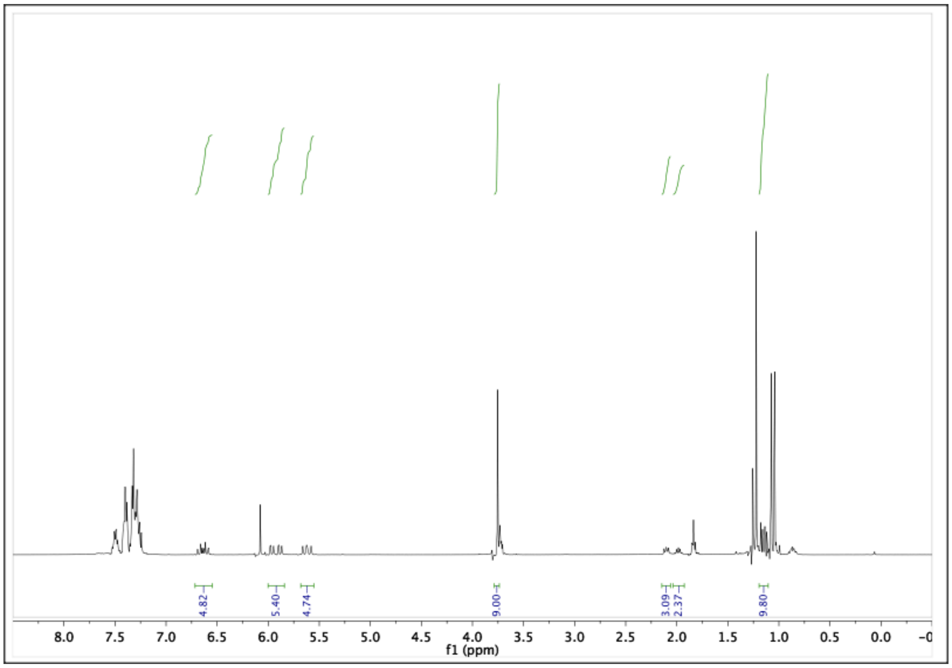
Concentration of 1,3,5-trimethoxybenzene: 0.0705 M
Yield of branched product = 31%
Yield of linear product = 12%
Conversion of Alkene = 58%

Fig. S-13. NMR spectra of manuscript Table 2 (Entry 7): 0.5 mol% $[Rh(PPh_3)_2Cl]_2$



1,3,5-trimethoxybenzene: 43 mg
Ratio of vinylphosphine to 1,3,5-trimethoxybenzene = 0.42
Yield of branched product = 62%
Yield of linear product = 35%

Fig. S-14. NMR spectra of manuscript Table 2 (Entry 8): 0.5 mol% $Rh(PPh_3)_3Cl$



Concentration of 1,3,5-trimethoxybenzene: 0.115 M
Yield of branched product = 27%
Yield of linear product = 17%
Conversion of Alkene = 46%

Fig. S-15. Isolated product characterization: $^{1}H\{^{13}C\}$ NMR spectrum of Rh complex **9**.

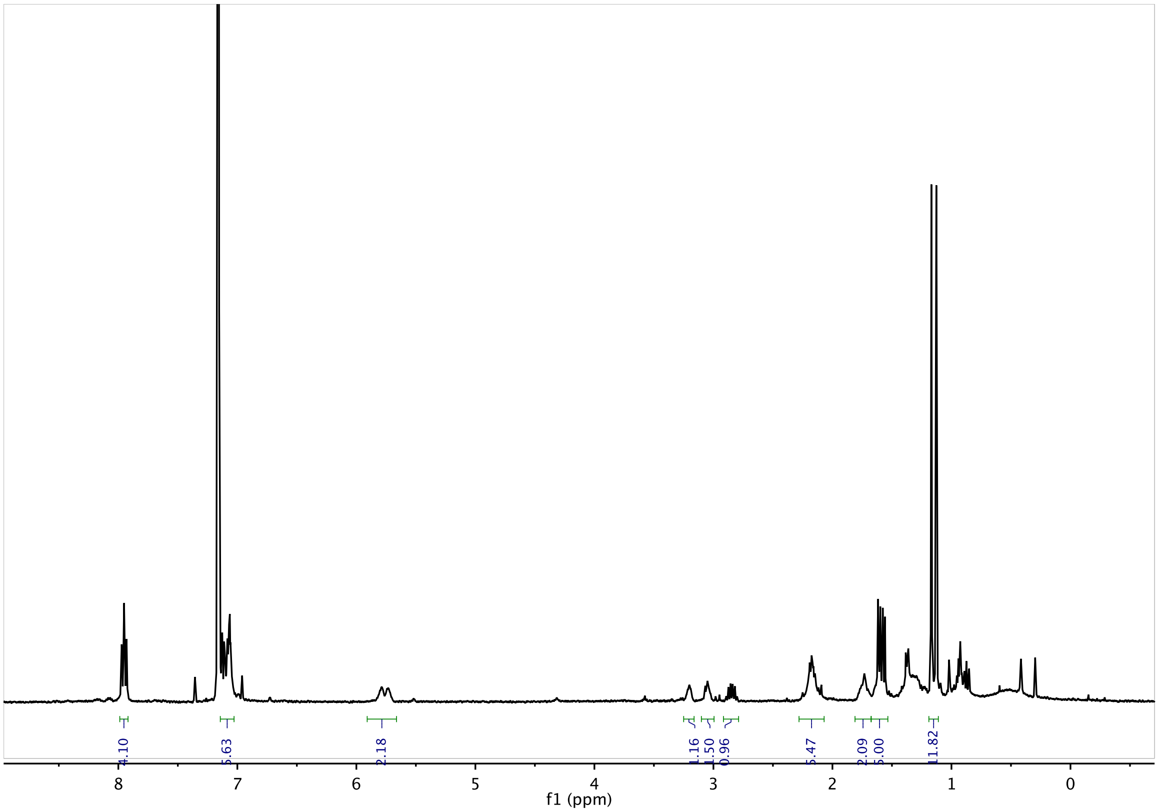


Fig. S-16. Isolated product characterization: $^{31}P\{^{1}H\}$ NMR spectrum of Rh complex **9**.

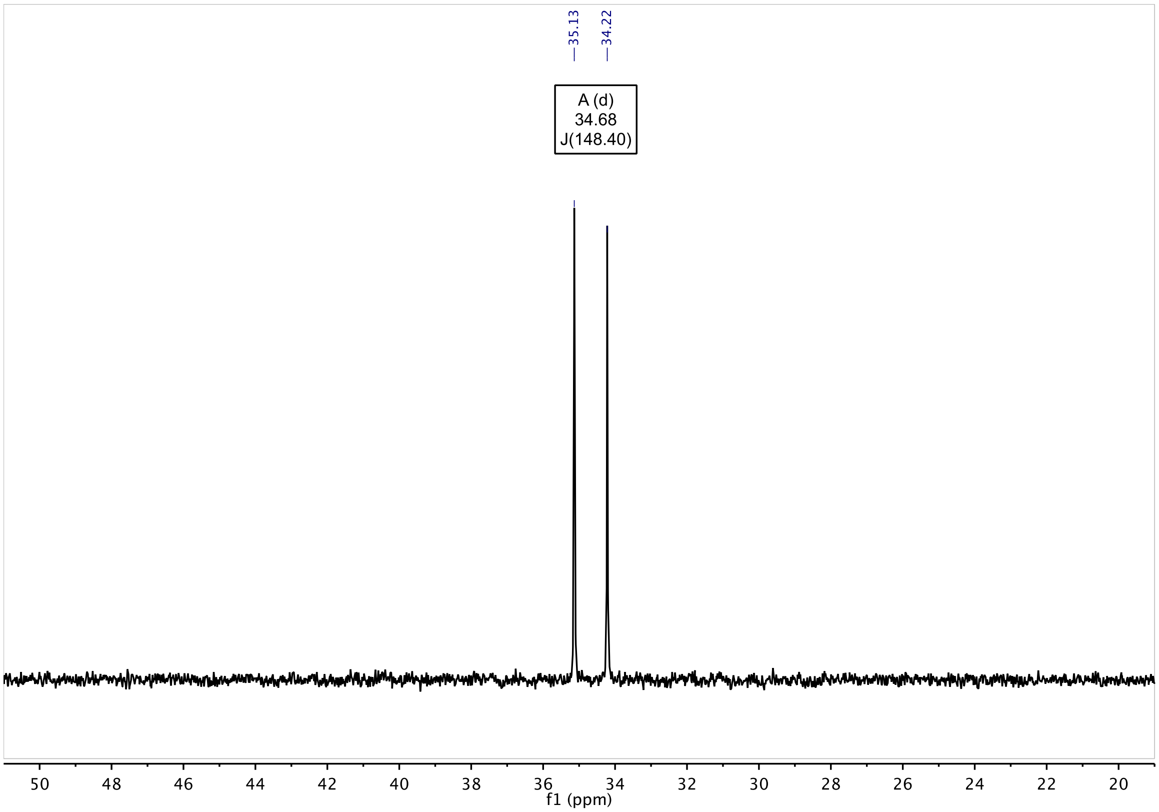


Fig. S-17. Isolated product characterization: $^{11}B\{^{1}H\}$ NMR spectrum of Rh complex **9**.

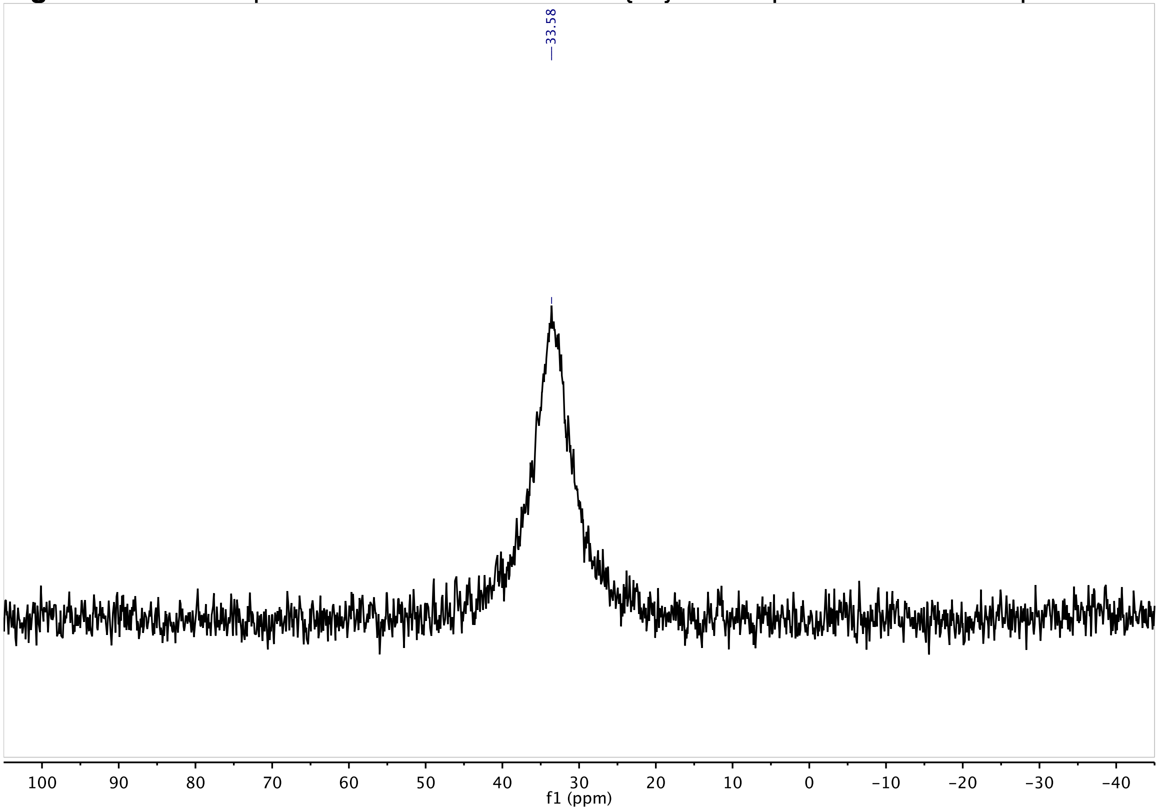


Fig. S-18. Isolated product characterization: $^{13}C\{^{1}H\}$ NMR spectrum of Rh complex **9**.

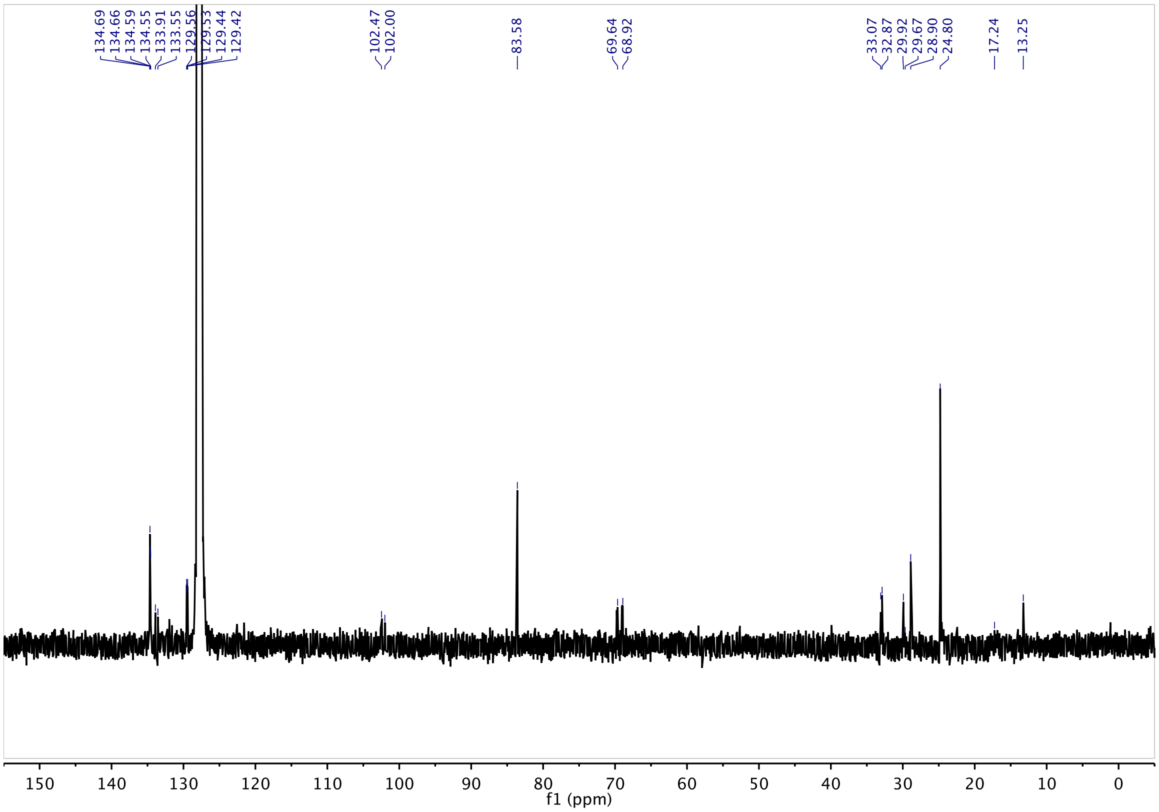


Fig. S-19. Crude product characterization: $^1H\{^{13}C\}$ NMR spectrum of protected phosphines **10** and **11**.

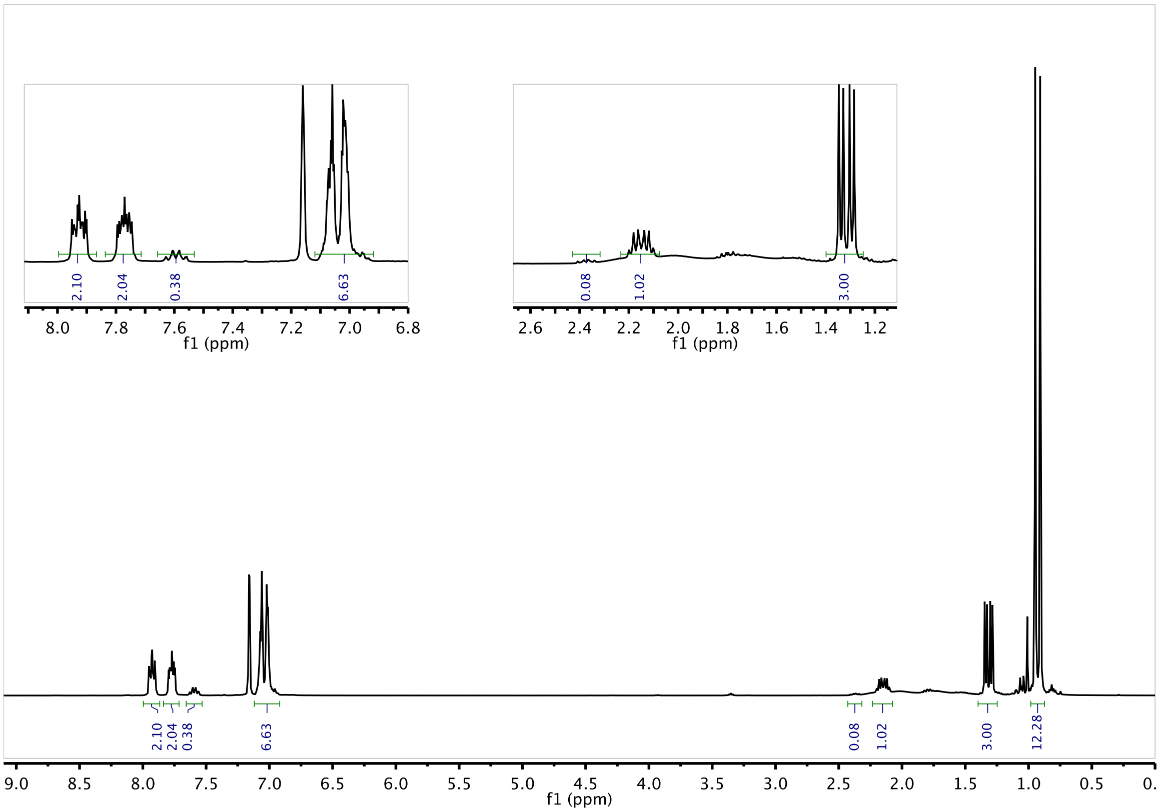


Fig. S-20. Crude product characterization: $^{31}P\{^1H\}$ NMR spectrum of protected phosphines **10** and **11**.

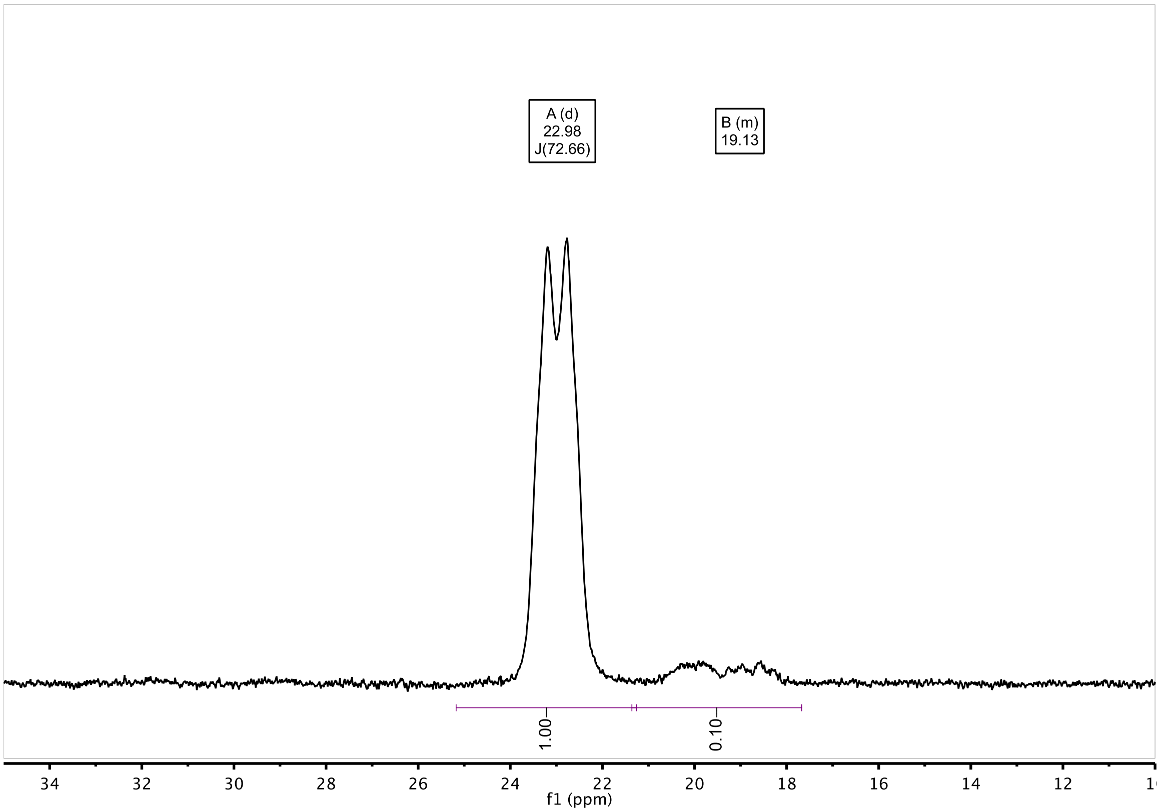


Fig. S-21. Crude product characterization: $^{11}B\{^1H\}$ NMR spectrum of protected phosphines **10** and **11**.

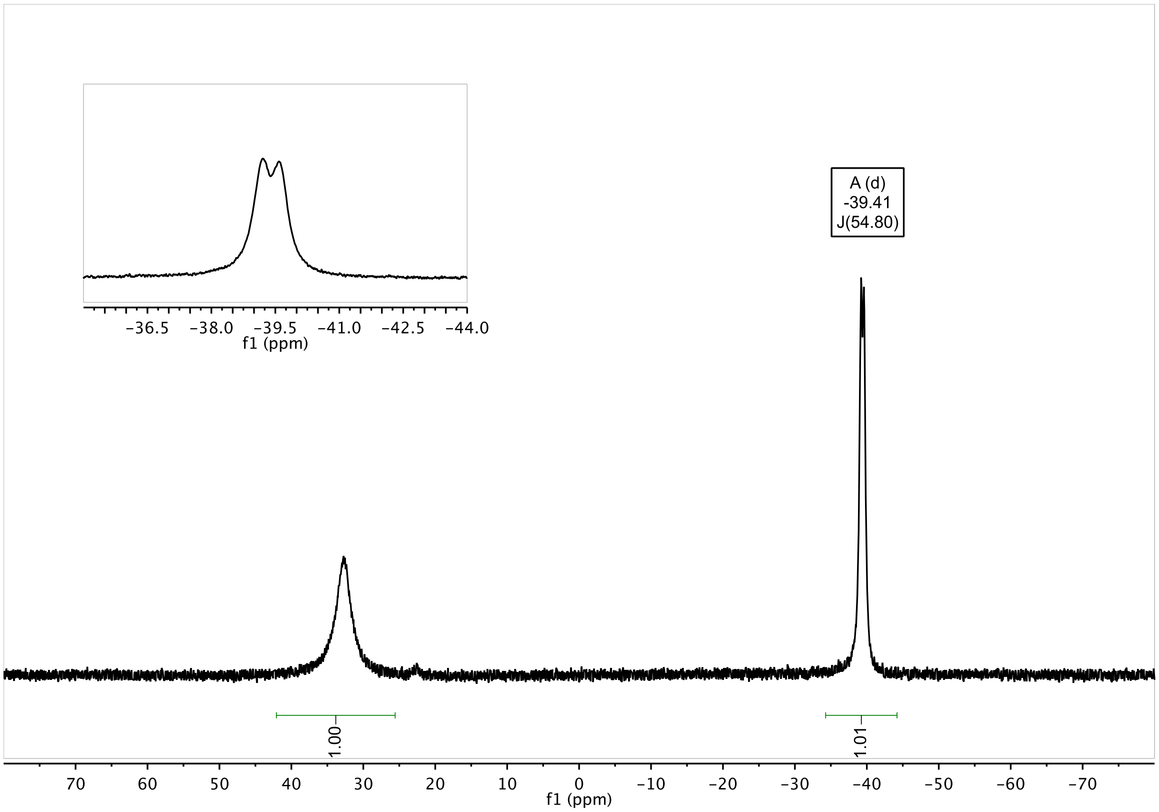


Fig. S-22. Crude product characterization: ^{11}B NMR spectrum of protected phosphines **10** and **11**.

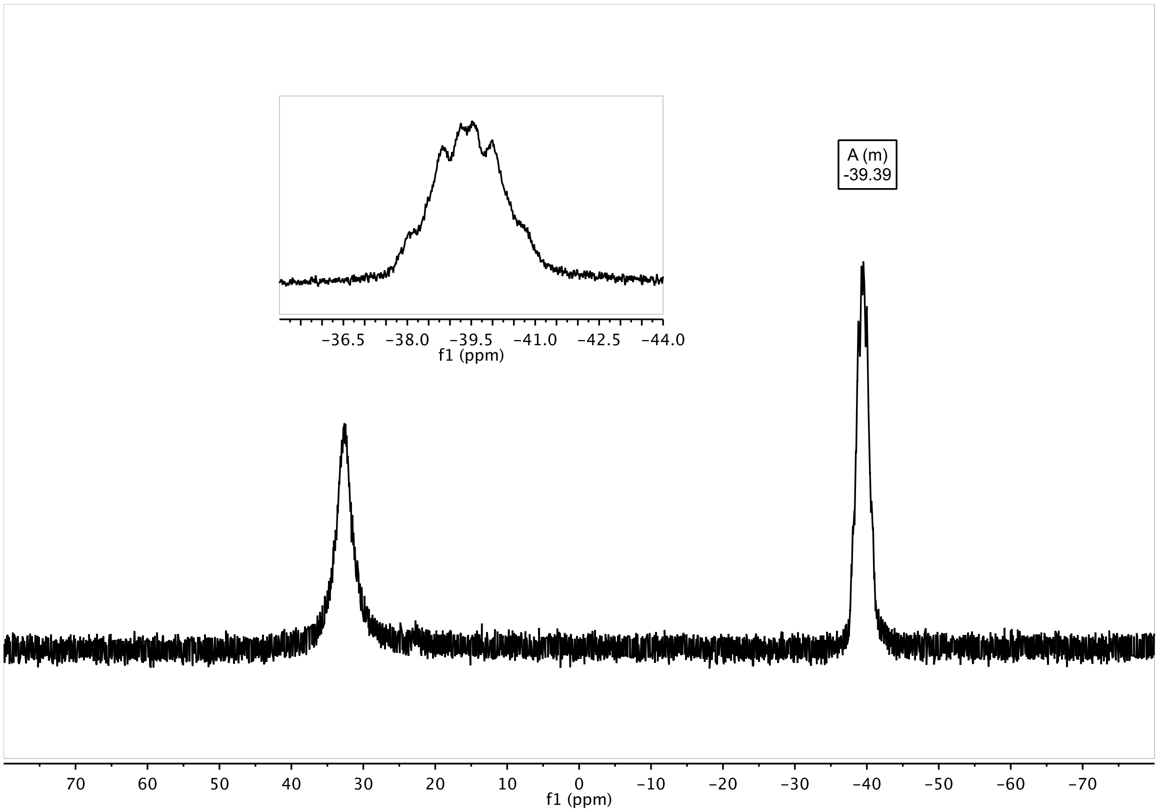


Fig. S-23. Crude product characterization: $^{13}C\{^{1}H\}$ NMR spectrum of protected phosphines **10** and **11**.

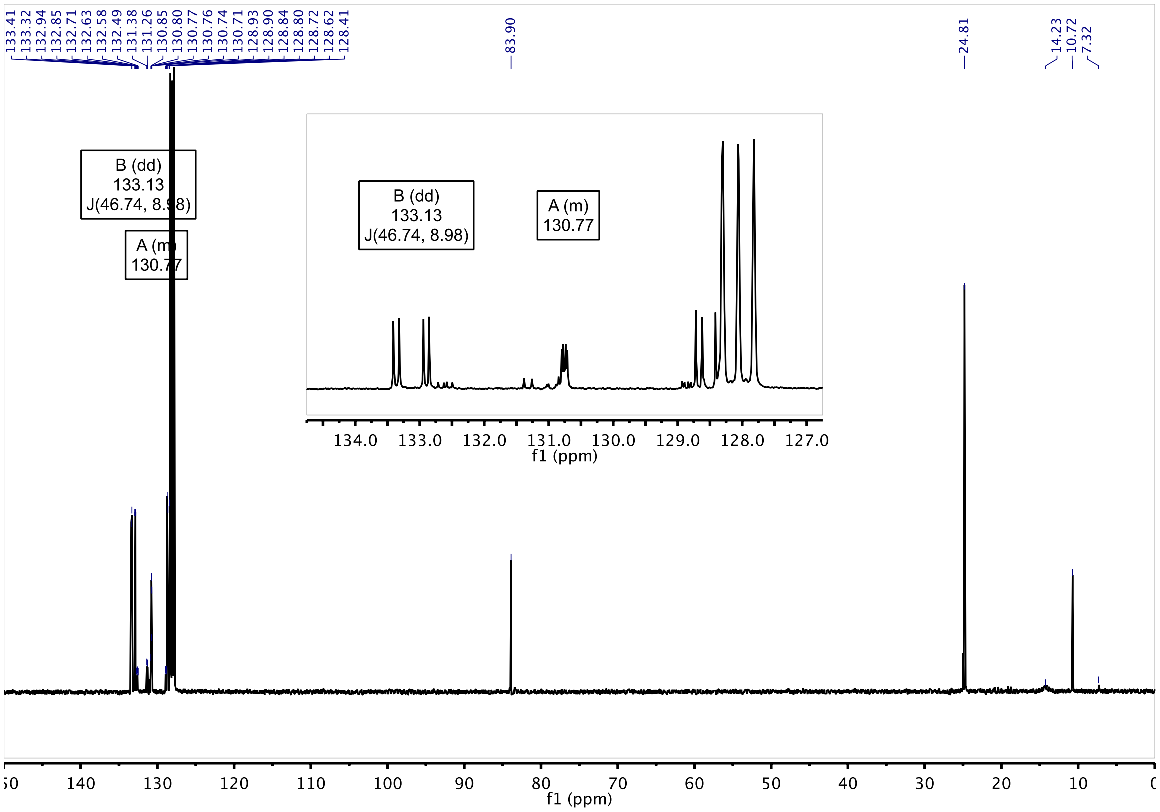


Fig. S-24. Isolated product characterization: $^{1}H\{^{13}C\}$ NMR spectrum of protected potassium trifluoroborate salt **12**.

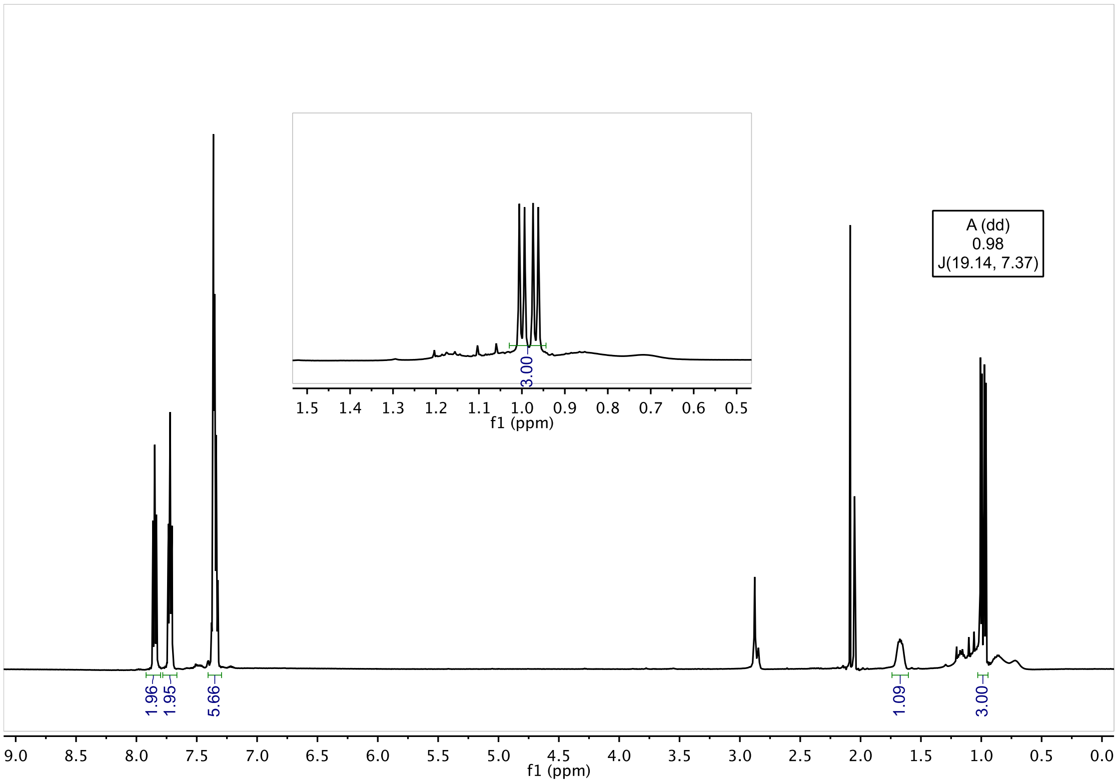


Fig. S-25. Isolated product characterization: $^{31}P\{^{1}H\}$ NMR spectrum of protected potassium trifluoroborate salt **12**.

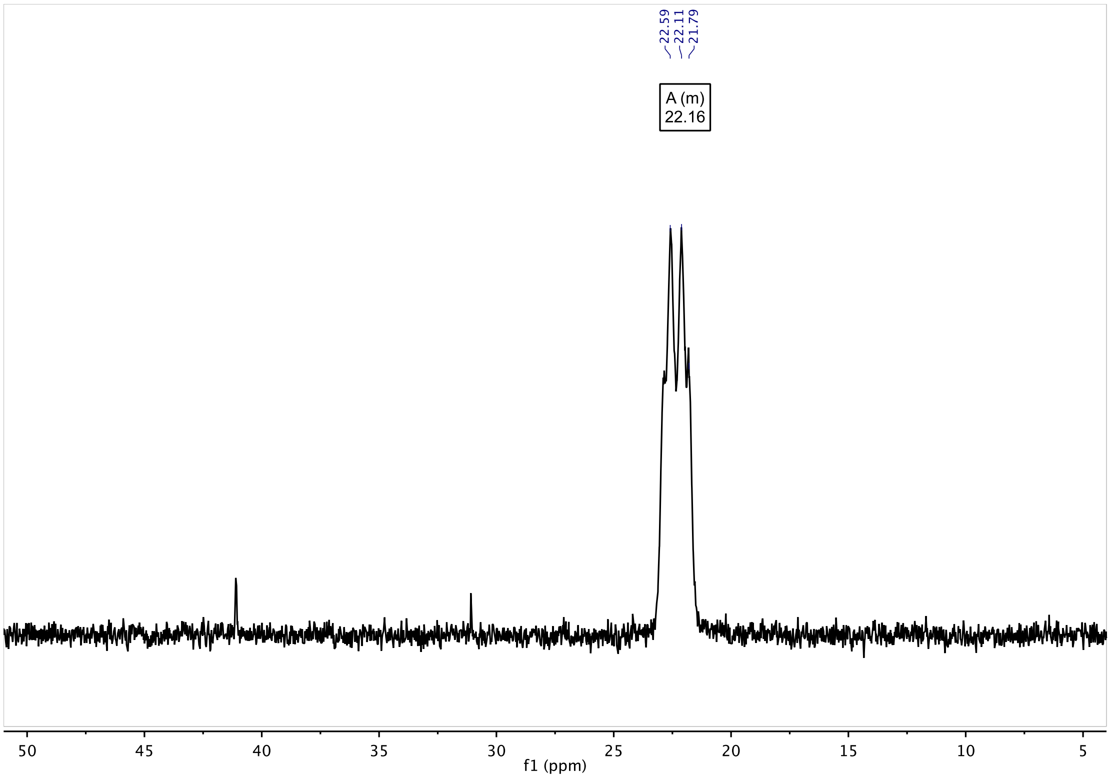


Fig. S-26. Isolated product characterization: ^{31}P NMR spectrum of protected potassium trifluoroborate salt **12**.

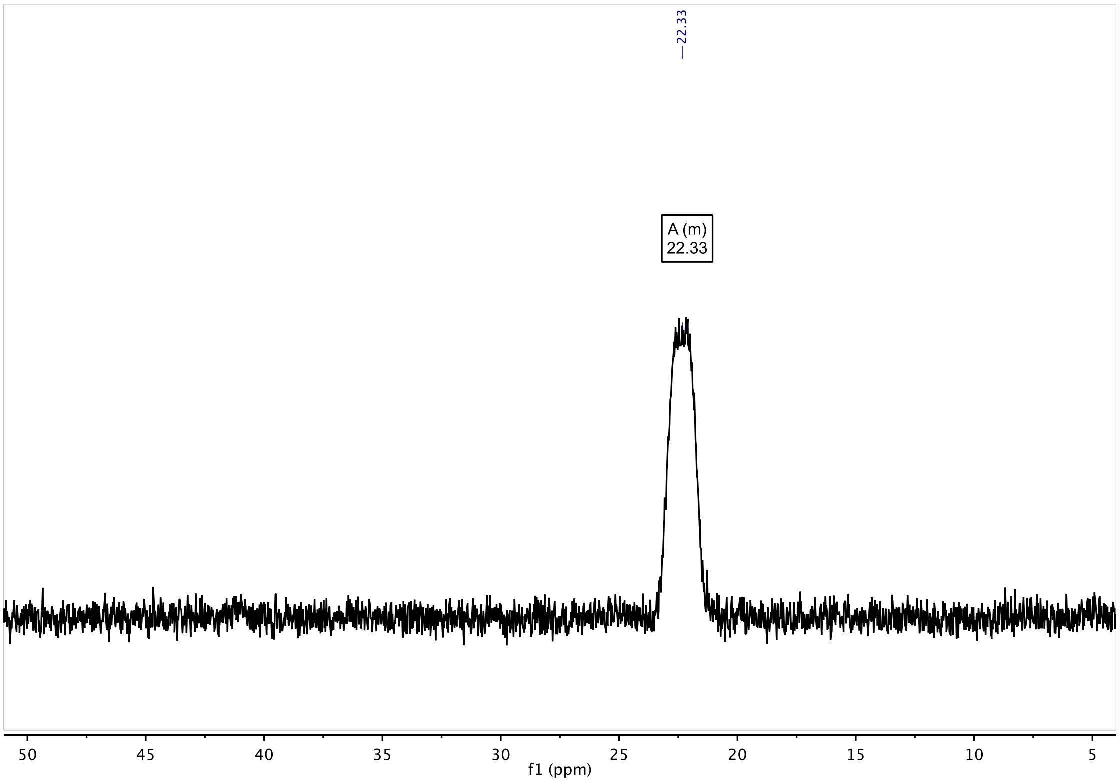


Fig. S-27. Isolated product characterization: $^{11}B\{^1H\}$ NMR spectrum of protected potassium trifluoroborate salt **12**.

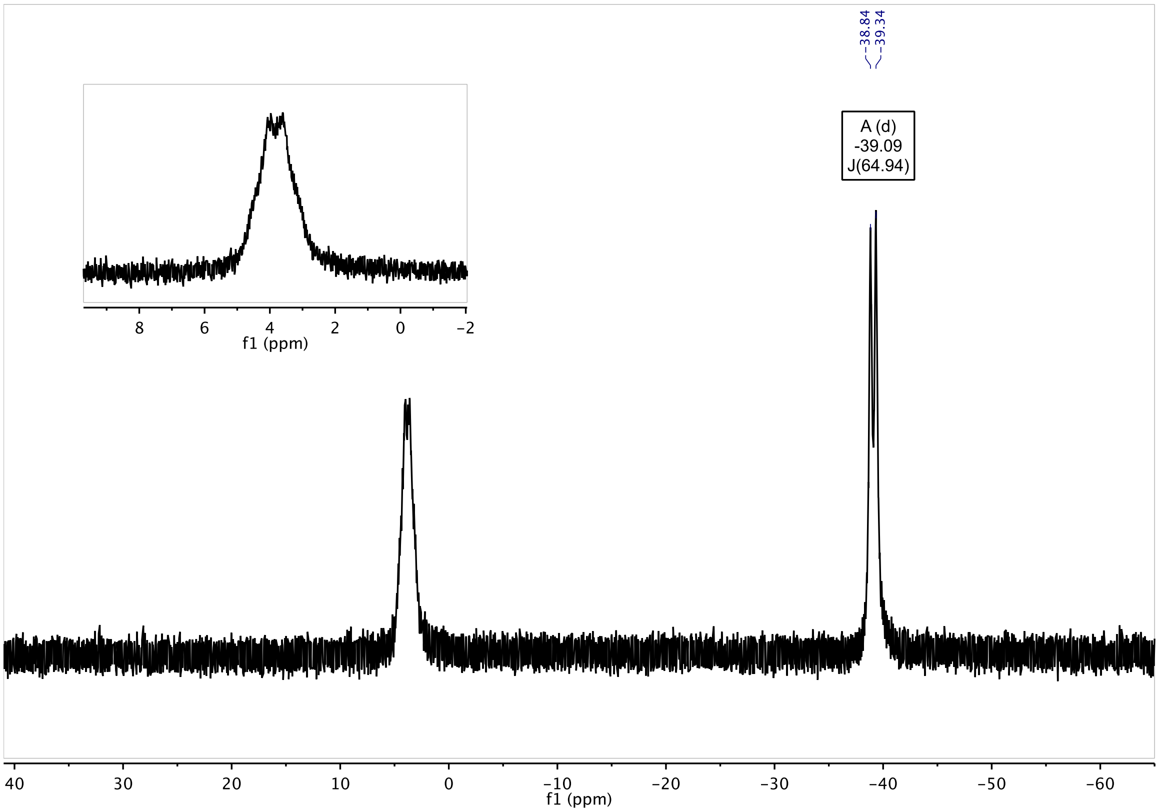


Fig. S-28. Isolated product characterization: ^{11}B NMR spectrum of protected potassium trifluoroborate salt **12**.

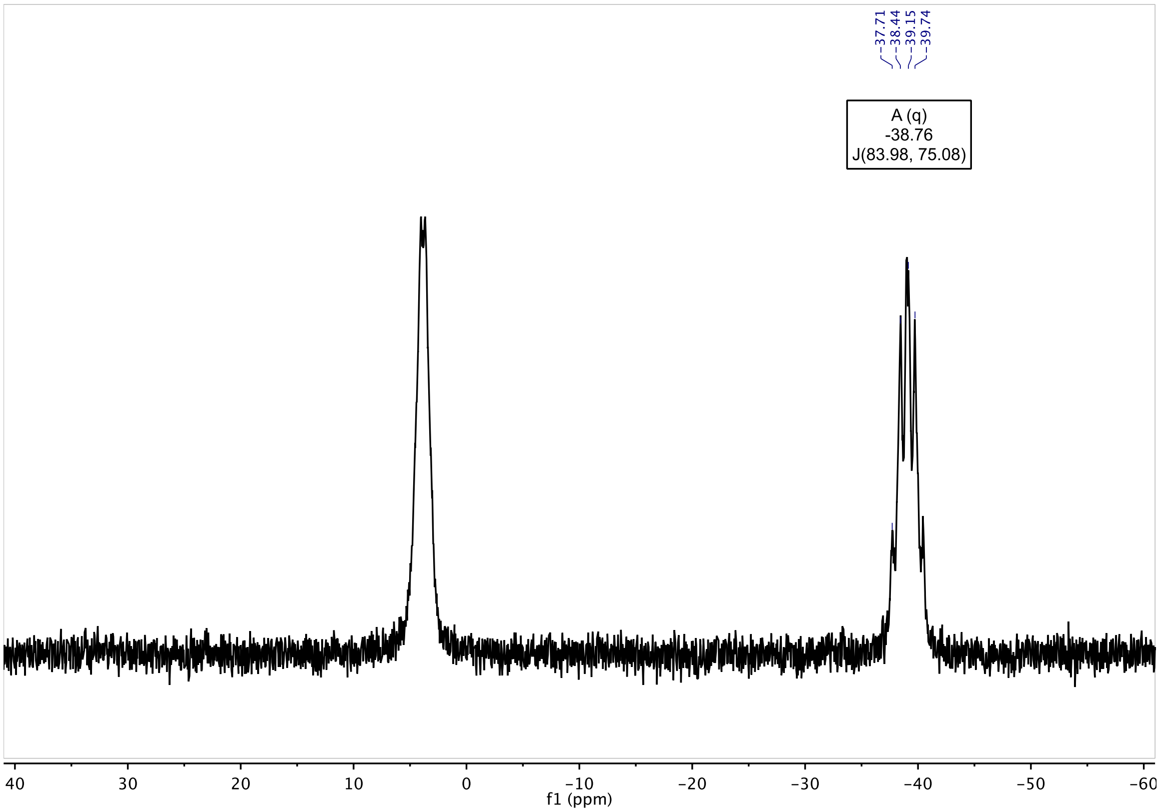


Fig. S-29. Isolated product characterization: $^{19}F\{^{13}C\}$ NMR spectrum of protected potassium trifluoroborate salt **12**.

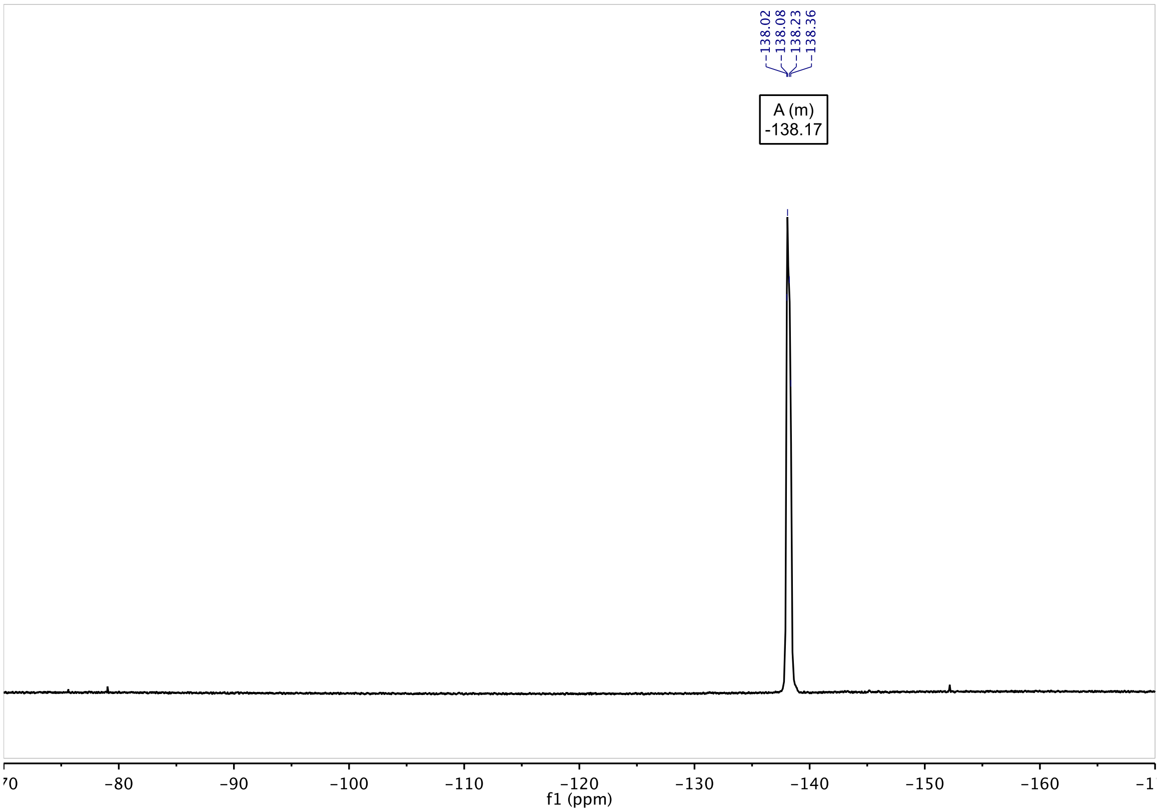
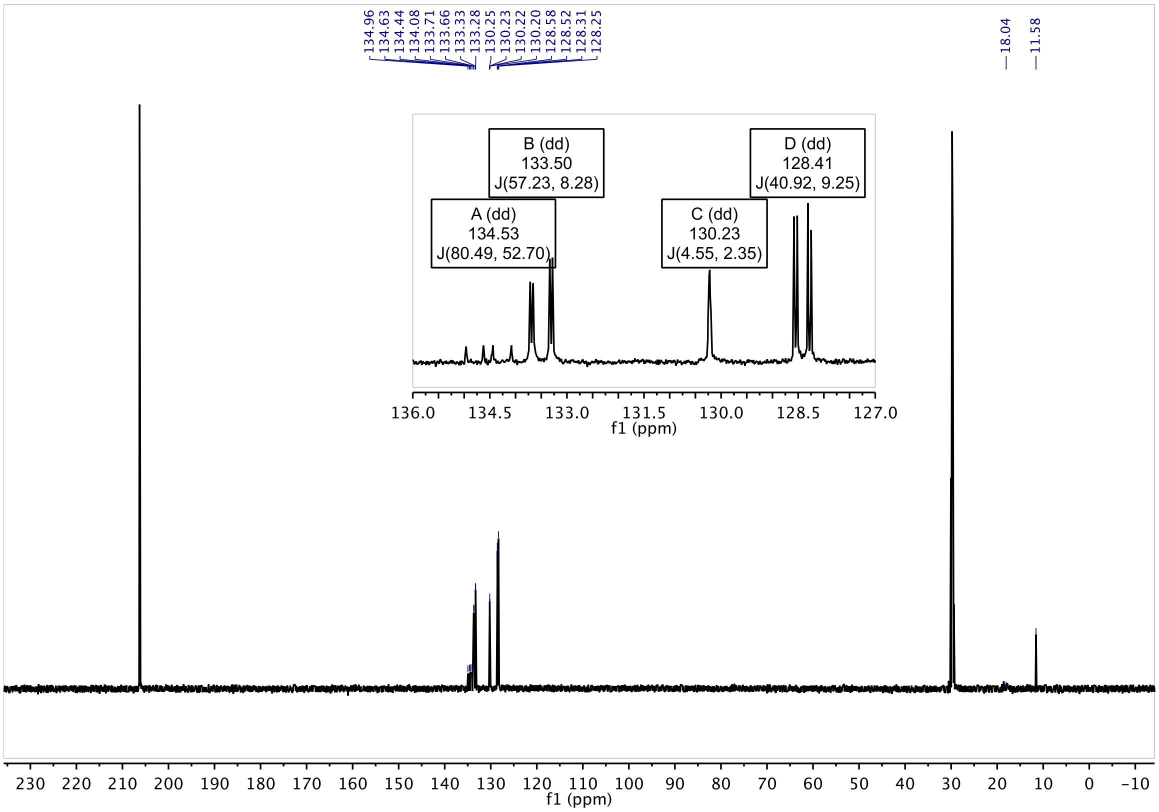


Fig. S-30. Isolated product characterization: $^{13}C\{^{1}H\}$ NMR spectrum of protected potassium trifluoroborate salt **12**.



ORTEP Representation and X-ray Crystallographic Structure Data for Compound 7

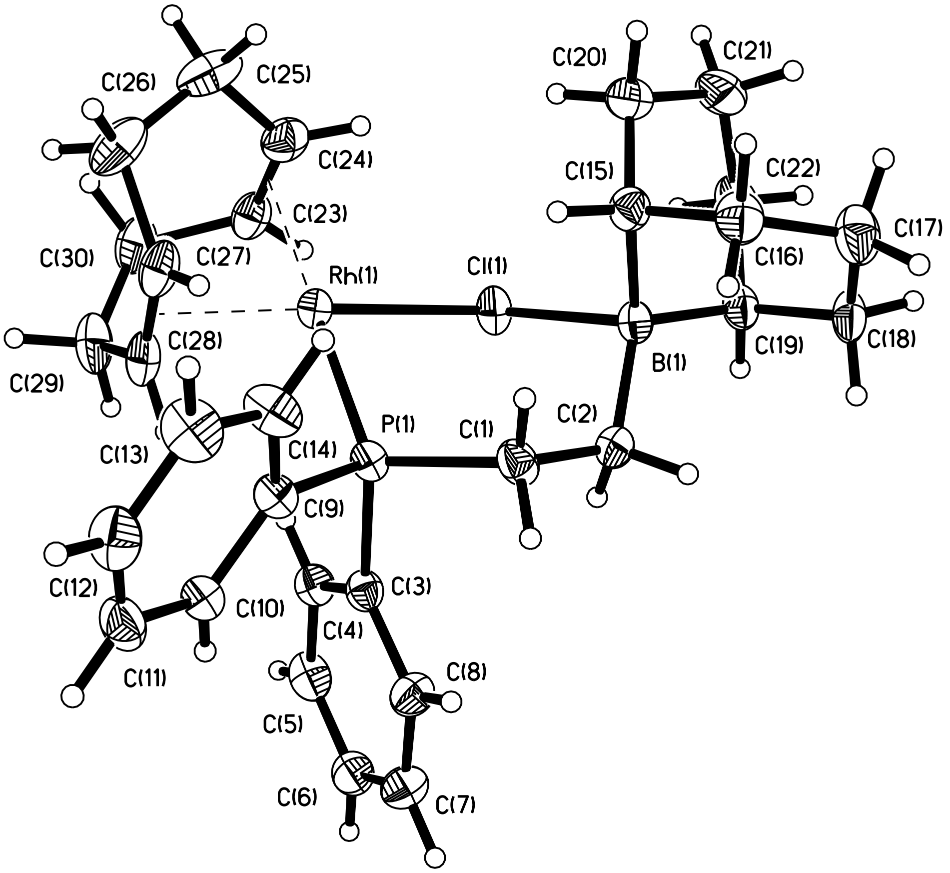


Figure S-31. Perspective view of the molecular structure of $RhCl(COD)[PPh_2CH_2CH_2B(C_8H_{14})]$ with the atom labeling scheme for the independent non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.

Description of the X-ray Structural Analysis of $\mathrm{RhCl(COD)[PPh_2CH_2CH_2B(C_8H_{14})]}$

A yellow crystal of $\mathrm{RhCl(COD)[PPh_2CH_2CH_2B(C_8H_{14})]}$ was washed with the perfluoropolyether PFO-XR75 (Lancaster) and sealed under a nitrogen atmosphere in a glass capillary. The sample was optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromator, a monocap collimator, a Mo Kα radiation source (λ = 0.71073 Å), and a SMART CCD detector held at 5.050 cm from the crystal. Four sets of 20 frames each were collected using the ω scan method and with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the triclinic crystal lattice.

Data collection consisted of the measurement of a total of 1650 frames in five different runs covering a hemisphere of data. Frame scan parameters are summarized below:

Table S-1. Data collection details for $\mathrm{RhCl(COD)[PPh_2CH_2CH_2B(C_8H_{14})]}$.

Run	2□	□	□	□	Scan axis	Scan width (°)	Frames (#)	Exposure time (sec.)
1	28	43.00	0.00	280.00	2	-0.3	100	40
2	28	43.00	90.00	280.00	2	-0.3	100	40
3	28	43.00	180.00	280.00	2	-0.3	100	40
4	28	43.00	270.00	280.00	2	-0.3	100	40
5	28	28.00	0.00	30.00	3	0.3	1250	40

The program SMART (version 5.6)[1] was used for diffractometer control, frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. All 1650 crystallographic raw data frames were read by the program SAINT (version 5/6.0)[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce a total of 9378 reflections and their intensities and estimated standard deviations. An absorption correction was applied using the SADABS routine available in SAINT.[1] The data were corrected for Lorentz and polarization effects. No evidence of crystal decomposition was observed. Data preparation was carried out by using the program XPREP,[1] which gave 5969 unique reflections (R_{int} = 3.84 %) with indices $-14 \le h \le 14$, $-13 \le k \le 15$, $-16 \le l \le 16$. The triclinic space group was determined to be $P\bar{1}$ (No. 2).

The structure was solved by a combination of direct methods and difference Fourier analysis with the use of SHELXTL 6.1.[2] Idealized positions for the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 times that of the adjacent carbon atom. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i |F_o^2 - F_c^2|^2$, with weighting $w_i^{-1} = [\sigma^2(F_o^2) + (0.0395 P)^2 + 4.503 P]$, where $P = (\mathrm{Max}(F_o^2, 0) + 2 F_c^2)/3$, converged to give final discrepancy indices[3] of R1 = 0.0547, wR2 = 0.1591 for 5318 diffraction data with $I > 2\sigma(I)$. The goodness of fit (GOF) value was 1.098.

A correction for secondary extinction was not applied. The maximum and minimum residual electron density peaks in the final difference Fourier map were 1.328 and -0.682 e/Å^3, respectively. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray Crystallography.[4]

References

1. SMART, SAINT and XPREP programs are part of Bruker crystallographic software package for single crystal data collection, reduction and preparation.
2. Sheldrick, G. M., SHELXTL6.1 (2000), Crystallographic software package, Bruker AXS, Inc. Madison, Wisconsin, USA.
3. $R_1 = \Box(||F_o| - |F_c||) / \Box|F_o|$, $wR_2 = [\Box\Box w(F_o^2 - F_c^2)^2] / \Box\Box w\Box F_o^2\Box^2]]^{1/2}$, $R_{int.} = \Box\Box F_o^2 - F_o^2(mean)|^2 / \Box\Box F_o^2]$, and GOF = $[\Box\Box w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.

4. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).

Table S-2. Crystal data and structure refinement for RhCl(COD)[$PPh_2CH_2CH_2B(C_8H_{14})$].

Identification code	bp1ccd	
Empirical formula	$C_{30}H_{40}BClPRh$	
Formula weight	580.76	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.074(1) Å	□= 65.811(2)°
	b = 11.690(1) Å	□= 75.634(1)°
	c = 13.074(1) Å	□ = 62.642(1)°
Volume	1367.4(2) $Å^3$	
Z	2	
Density (calculated)	1.410 g/cm^3	
Absorption coefficient	7.98 cm^{-1}	
F(000)	604	
Crystal size	0.06 x 0.24 x 0.58 mm	
θ range for data collection	1.71 to 27.59°	
Index ranges	$-14 \le h \le 14$, $-13 \le k \le 15$, $-16 \le l \le 16$	
Reflections collected	9378	
Independent reflections	5969 [R(int) = 0.0384]	
Completeness to θ = 27.59°	94.1 %	
Max. and min. transmission	0.954 and 0.655	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5969 / 0 / 307	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2σ(I)]	R1 = 0.0547, wR2 = 0.1591	
R indices (all data)	R1 = 0.0604, wR2 = 0.1632	
Largest diff. peak and hole	1.324 and -0.682 $e/Å^3$	

Table S-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for RhCl(COD)[PPh$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)]. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

	x	y	z	U(eq)
Rh(1)	6564(1)	2178(1)	6379(1)	34(1)
Cl(1)	4493(1)	3877(1)	6865(1)	44(1)
P(1)	7701(1)	2478(1)	7432(1)	35(1)
C(1)	6914(5)	2654(6)	8799(4)	45(1)
C(2)	5492(6)	3807(6)	8792(4)	44(1)
C(3)	8023(5)	4023(5)	6663(4)	37(1)
C(4)	7798(5)	4694(5)	5528(4)	42(1)
C(5)	8056(6)	5866(6)	4920(5)	51(1)
C(6)	8523(6)	6369(6)	5437(6)	54(1)
C(7)	8755(7)	5716(6)	6577(6)	57(1)
C(8)	8490(6)	4558(6)	7185(5)	47(1)
C(9)	9397(5)	1109(5)	7832(4)	39(1)
C(10)	10597(5)	1285(6)	7411(5)	44(1)
C(11)	11850(6)	204(7)	7715(5)	57(2)
C(12)	11901(6)	-1073(7)	8443(5)	57(2)
C(13)	10721(7)	-1263(7)	8867(5)	61(2)
C(14)	9463(6)	-178(6)	8571(5)	54(1)
C(15)	4193(6)	2087(5)	9307(4)	43(1)
C(16)	4015(7)	1903(6)	10569(5)	54(1)
C(17)	2781(8)	3053(6)	10913(5)	63(2)
C(18)	2514(6)	4512(6)	10092(5)	52(1)
C(19)	2721(6)	4694(5)	8824(4)	44(1)
C(20)	3082(6)	1934(6)	8947(6)	56(1)
C(21)	1653(6)	3079(7)	8954(7)	64(2)
C(22)	1627(6)	4543(7)	8449(5)	57(2)
C(23)	5625(6)	2442(6)	4915(4)	47(1)
C(24)	5379(7)	1443(6)	5838(5)	53(1)
C(25)	6168(9)	-82(7)	6100(6)	73(2)
C(26)	7707(9)	-518(6)	5926(6)	70(2)
C(27)	8173(6)	360(6)	6177(5)	53(1)

C(28)	8378(6)	1508(6)	5362(5)	53(1)
C(29)	8059(7)	2095(7)	4140(5)	65(2)
C(30)	6701(7)	2180(7)	3976(5)	60(2)
B(1)	4226(6)	3577(6)	8659(4)	38(1)

Table S-4. Interatomic distances [Å] and bond angles [°] for RhCl(COD)[$PPh_2CH_2CH_2B(C_8H_{14})$].

Rh(1)-C(28)	2.120(6)
Rh(1)-C(27)	2.123(5)
Rh(1)-C(24)	2.226(6)
Rh(1)-C(23)	2.246(5)
Rh(1)-P(1)	2.295(1)
Rh(1)-Cl(1)	2.394(1)
Cl(1)-B(1)	2.188(5)
P(1)-C(3)	1.824(5)
P(1)-C(1)	1.833(5)
P(1)-C(9)	1.844(5)
C(1)-C(2)	1.530(8)
C(2)-B(1)	1.605(8)
C(3)-C(4)	1.389(7)
C(3)-C(8)	1.394(7)
C(4)-C(5)	1.395(8)
C(5)-C(6)	1.360(9)
C(6)-C(7)	1.396(9)
C(7)-C(8)	1.385(8)
C(9)-C(10)	1.380(7)
C(9)-C(14)	1.395(7)
C(10)-C(11)	1.389(8)
C(11)-C(12)	1.387(9)
C(12)-C(13)	1.368(9)
C(13)-C(14)	1.393(8)
C(15)-C(20)	1.524(8)
C(15)-C(16)	1.548(8)
C(15)-B(1)	1.608(7)
C(16)-C(17)	1.542(9)
C(17)-C(18)	1.531(8)
C(18)-C(19)	1.552(7)
C(19)-C(22)	1.517(8)
C(19)-B(1)	1.607(8)
C(20)-C(21)	1.534(9)
C(21)-C(22)	1.551(10)

C(23)-C(24)	1.367(8)
C(23)-C(30)	1.506(8)
C(24)-C(25)	1.508(9)
C(25)-C(26)	1.524(12)
C(26)-C(27)	1.508(9)
C(27)-C(28)	1.406(9)
C(28)-C(29)	1.519(8)
C(29)-C(30)	1.524(11)
P(1)-Rh(1)-Cl(1)	89.07(5)
B(1)-Cl(1)-Rh(1)	112.55(16)
C(3)-P(1)-C(1)	104.1(3)
C(3)-P(1)-C(9)	104.2(2)
C(1)-P(1)-C(9)	100.6(2)
C(3)-P(1)-Rh(1)	110.74(16)
C(1)-P(1)-Rh(1)	119.14(18)
C(9)-P(1)-Rh(1)	116.37(18)
C(2)-C(1)-P(1)	116.1(4)
C(1)-C(2)-B(1)	117.9(4)
C(4)-C(3)-C(8)	118.7(5)
C(4)-C(3)-P(1)	119.6(4)
C(8)-C(3)-P(1)	121.7(4)
C(3)-C(4)-C(5)	120.5(5)
C(6)-C(5)-C(4)	120.2(5)
C(5)-C(6)-C(7)	120.4(5)
C(8)-C(7)-C(6)	119.5(6)
C(7)-C(8)-C(3)	120.6(5)
C(10)-C(9)-C(14)	118.8(5)
C(10)-C(9)-P(1)	123.4(4)
C(14)-C(9)-P(1)	117.8(4)
C(9)-C(10)-C(11)	120.9(5)
C(12)-C(11)-C(10)	119.7(6)
C(13)-C(12)-C(11)	120.0(6)
C(12)-C(13)-C(14)	120.4(6)
C(13)-C(14)-C(9)	120.2(6)
C(20)-C(15)-C(16)	112.9(5)

C(20)-C(15)-B(1)	113.2(4)
C(16)-C(15)-B(1)	104.7(4)
C(17)-C(16)-C(15)	115.4(5)
C(18)-C(17)-C(16)	115.5(5)
C(17)-C(18)-C(19)	115.8(5)
C(22)-C(19)-C(18)	112.6(5)
C(22)-C(19)-B(1)	112.9(5)
C(18)-C(19)-B(1)	105.3(4)
C(15)-C(20)-C(21)	115.3(5)
C(20)-C(21)-C(22)	114.1(5)
C(19)-C(22)-C(21)	114.9(5)
C(24)-C(23)-C(30)	124.8(6)
C(23)-C(24)-C(25)	125.8(6)
C(24)-C(25)-C(26)	113.3(6)
C(27)-C(26)-C(25)	113.3(6)
C(28)-C(27)-C(26)	124.0(6)
C(27)-C(28)-C(29)	124.9(6)
C(28)-C(29)-C(30)	114.0(5)
C(23)-C(30)-C(29)	113.7(5)
C(2)-B(1)-C(19)	117.5(5)
C(2)-B(1)-C(15)	118.6(5)
C(19)-B(1)-C(15)	107.4(4)
C(2)-B(1)-Cl(1)	101.1(3)
C(19)-B(1)-Cl(1)	104.4(3)
C(15)-B(1)-Cl(1)	106.0(3)

Table S-5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for RhCl(COD)[$PPh_2CH_2CH_2B(C_8H_{14})$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U_{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	33(1)	34(1)	32(1)	-13(1)	-3(1)	-10(1)
Cl(1)	36(1)	52(1)	37(1)	-20(1)	-3(1)	-8(1)
P(1)	31(1)	38(1)	32(1)	-11(1)	-2(1)	-13(1)
C(1)	38(3)	65(3)	34(2)	-18(2)	0(2)	-23(2)
C(2)	46(3)	53(3)	42(3)	-25(2)	3(2)	-23(2)
C(3)	34(2)	34(2)	39(2)	-12(2)	-2(2)	-10(2)
C(4)	39(3)	42(3)	41(2)	-12(2)	-4(2)	-14(2)
C(5)	47(3)	41(3)	47(3)	-7(2)	-1(2)	-11(2)
C(6)	53(3)	35(3)	70(4)	-21(2)	9(3)	-19(2)
C(7)	62(4)	49(3)	69(4)	-26(3)	0(3)	-27(3)
C(8)	54(3)	47(3)	44(3)	-18(2)	-4(2)	-22(3)
C(9)	38(2)	45(3)	34(2)	-10(2)	-5(2)	-16(2)
C(10)	39(3)	47(3)	49(3)	-20(2)	1(2)	-19(2)
C(11)	34(3)	80(4)	62(4)	-37(3)	0(3)	-18(3)
C(12)	46(3)	59(4)	53(3)	-19(3)	-17(3)	-3(3)
C(13)	58(4)	49(3)	52(3)	2(3)	-18(3)	-12(3)
C(14)	43(3)	51(3)	52(3)	0(2)	-11(2)	-19(3)
C(15)	41(3)	38(2)	47(3)	-16(2)	-1(2)	-12(2)
C(16)	60(4)	44(3)	47(3)	-11(2)	-1(3)	-18(3)
C(17)	70(4)	52(3)	47(3)	-14(3)	6(3)	-17(3)
C(18)	50(3)	53(3)	46(3)	-28(2)	12(2)	-14(3)
C(19)	41(3)	41(3)	43(3)	-17(2)	5(2)	-12(2)
C(20)	53(3)	54(3)	66(4)	-23(3)	3(3)	-28(3)
C(21)	41(3)	77(4)	83(5)	-32(4)	1(3)	-29(3)
C(22)	34(3)	65(4)	59(3)	-21(3)	-1(2)	-10(3)
C(23)	50(3)	48(3)	41(3)	-20(2)	-11(2)	-11(2)
C(24)	64(4)	60(3)	46(3)	-21(3)	-10(3)	-29(3)
C(25)	111(7)	54(4)	72(4)	-16(3)	-30(4)	-42(4)
C(26)	98(6)	35(3)	69(4)	-16(3)	-28(4)	-12(3)

C(27)	50(3)	42(3)	55(3)	-24(2)	-11(3)	2(2)
C(28)	43(3)	52(3)	52(3)	-30(3)	1(2)	-3(2)
C(29)	63(4)	69(4)	44(3)	-26(3)	12(3)	-15(3)
C(30)	71(4)	55(3)	41(3)	-19(2)	-8(3)	-10(3)
B(1)	40(3)	43(3)	32(2)	-16(2)	3(2)	-17(2)

Table S-6. Hydrogen atom coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for RhCl(COD)[PPh$_2$CH$_2$CH$_2$B(C$_8$H$_{14}$)].

	x	y	z	U(eq)
H(1A)	6858	1793	9297	54
H(1B)	7513	2801	9116	54
H(2A)	5512	4629	8184	53
H(2B)	5317	3985	9489	53
H(4)	7472	4358	5171	50
H(5)	7907	6304	4159	62
H(6)	8689	7153	5028	65
H(7)	9086	6055	6926	68
H(8)	8624	4133	7948	56
H(10)	10566	2138	6916	53
H(11)	12651	337	7432	69
H(12)	12739	-1801	8644	69
H(13)	10759	-2120	9355	74
H(14)	8664	-313	8866	64
H(15)	5078	1394	9157	52
H(16A)	3930	1040	11003	65
H(16B)	4836	1838	10771	65
H(17A)	1973	2887	11001	75
H(17B)	2916	2995	11640	75
H(18A)	3111	4820	10238	62
H(18B)	1583	5108	10248	62
H(19)	2702	5611	8384	53
H(20A)	3039	1067	9442	67
H(20B)	3343	1894	8193	67
H(21A)	1257	2925	9724	77
H(21B)	1084	3025	8533	77
H(22A)	1726	4813	7636	69
H(22B)	743	5174	8653	69
H(23)	5089	3350	4864	56
H(24)	4662	1728	6350	64
H(25A)	5894	-364	5625	87

H(25B)	5934	-553	6875	87
H(26A)	8146	-1463	6408	84
H(26B)	7999	-477	5153	84
H(27)	8334	128	6916	64
H(28)	8735	1942	5589	63
H(29A)	8782	1529	3740	78
H(29B)	8053	3007	3808	78
H(30A)	6369	2910	3276	73
H(30B)	6848	1327	3912	73

ORTEP Representation and X-ray Crystallographic Structure Data for Compound 8

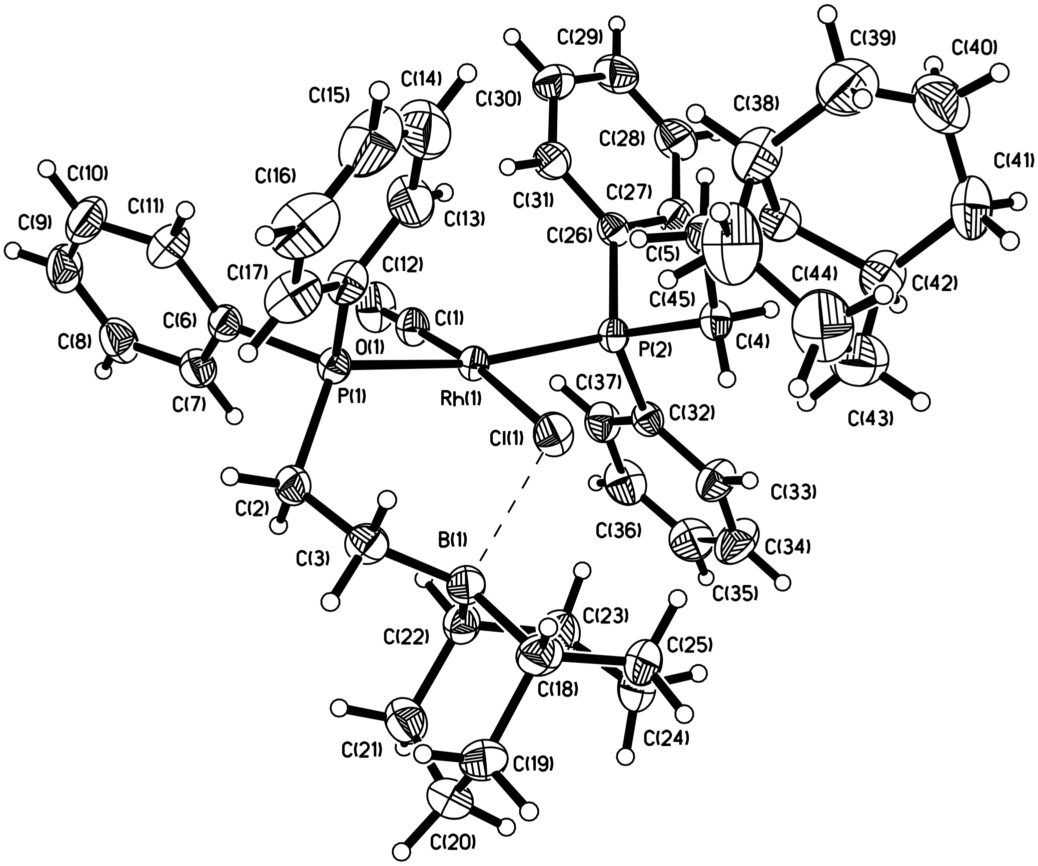


Figure S-32. Perspective view of the molecular structure of Rh(CO)Cl($PPh_2CH_2CH_2$-9-BBN$)_2$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Description of the X-ray Structural Analysis of $Rh(CO)Cl(PPh_2CH_2CH_2\text{-9-BBN})_2 \cdot C_4H_{10}O$

An orange crystal of $Rh(CO)Cl(PPh_2CH_2CH_2\text{-9-BBN})_2 \cdot C_4H_{10}O$ was washed with the perfluoropolyether PFO-XR75 (Lancaster) and sealed in a glass capillary under nitrogen. The sample was optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromator, a Mo Kα radiation source (λ = 0.71073 Å), and a SMART CCD detector held at 5.050 cm from the crystal. Four sets of 20 frames each were collected using the ω scan method and with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the monoclinic crystal lattice.

Data collection consisted of the measurement of a total of 1650 frames in five different runs covering a hemisphere of data. Frame scan parameters are summarized below:

Table S-7. Data collection details for $Rh(CO)Cl(PPh_2CH_2CH_2\text{-9-BBN})_2 \cdot C_4H_{10}O$

					Scan	Scan	Frames	Exposure
Run	2□	□	□	□	axis	width (°)	(#)	time (sec.)
1	28	43.00	0.00	280.00	2	-0.3	100	40
2	28	43.00	90.00	280.00	2	-0.3	100	40
3	28	43.00	180.00	280.00	2	-0.3	100	40
4	28	43.00	270.00	280.00	2	-0.3	100	40
5	28	28.00	0.00	30.00	3	0.3	1250	40

The program SMART (version 5.6)[1] was used for diffractometer control, frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. All 1650 crystallographic raw data frames were read by program SAINT (version 5/6.0)[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce a total of 35144 reflections and their intensities and estimated standard deviations. An absorption correction was applied using the SADABS routine available in SAINT.[1] The data were corrected for Lorentz and polarization effects. Data preparation was carried out by using the program XPREP,[1] which gave 11231 unique reflections (R_{int} = 5.08 %) with indices $-14 \leq h \leq 14$, $-30 \leq k \leq 30$, $-24 \leq l \leq 24$. The monoclinic space group was determined to be $P2_1/n$, a nonstandard setting of $P2_1/c$ (No. 14).

The structure was solved by a combination of direct methods and difference Fourier analysis with the use of SHELXTL 6.1.[2] The crystallographic asymmetric unit contains independent molecules of $Rh(CO)Cl(PPh_2CH_2CH_2\text{-}9\text{-}BBN)_2 \cdot C_4H_{10}O$ and highly disordered molecules of ether. Idealized positions for the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 (aromatic and B-H protons) or 1.5 (methyl protons) times that of the adjacent non-hydrogen atom. The positions of the methyl hydrogen atoms were optimized by a rigid rotating group refinement with idealized tetrahedral angles. The diethyl ether was treated as a diffuse electron density contribution with the aid of the SQUEEZE routine in the program PLATON.[3] Although specific positions for the independent carbon, hydrogen, and oxygen atoms of the diethyl ether were not determined, the calculated density, absorption coefficient and empirical formula weight reflect their presence within the crystal lattice. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i |F_o^2 - F_c^2|^2$, with weighting $w_i^{-1} = [\sigma^2(F_o^2) + (0.0898 P)^2 + 0.7165 P]$, where $P = (\text{Max}(F_o^2, 0) + 2 F_c^2)/3$, converged to give final discrepancy indices[4] of R1 = 0.0367, wR2 = 0.1461 for 6739 data with $I > 2\sigma(I)$. The goodness of fit (GOF) value was 1.031.

A correction for secondary extinction was not applied. The maximum and minimum residual electron density peaks in the final difference Fourier map were 0.348 and -0.274 e/Å^3, respectively. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray Crystallography.[5]

References

1. SMART, SAINT and XPREP programs are part of Bruker crystallographic software package for single crystal data collection, reduction and preparation.
2. Sheldrick, G. M., SHELXTL6.1 (2000), Crystallographic software package, Bruker AXS, Inc. Madison, Wisconsin, USA.
3. PLATON, written by Professor Anthony L. Spek, Bijvoet Centre for Biomolecular Research, Utrecht University. Current versions of PLATON for Windows are available from Professor Louis J. Farrugia, Department of Chemistry, University of Glasgow at www.chem.gla.ac.uk/~louis/software/.
4. $R_1 = \square(||F_o| - |F_c||) / \square|F_o|$, $wR_2 = [\square\square w(F_o^2 - F_c^2)^2] / \square\square w\square F_o^2\square^2]]^{1/2}$, $R_{int.} = \square\square F_o^2 - F_o^2(mean)|^2 / \square\square F_o^2]$, and $GOF = [\square\square w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.
5. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).

Table S-8. Crystal data and structure refinement for Rh(CO)Cl($PPh_2CH_2CH_2$-9-BBN)$_2 \cdot C_4H_{10}O$.

Identification code	bp5plt	
Empirical formula	$C_{49}H_{66}B_2ClO_2P_2Rh$	
Formula weight	908.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.851(1) Å	α= 90°
	b = 18.685(2) Å	β= 97.510(2)°
	c = 23.362(2) Å	γ = 90°
Volume	4696.1(8) $Å^3$	
Z	4	
Density (calculated)	1.286 g/cm^3	
Absorption coefficient	5.26 cm^{-1}	
F(000)	1912	
Crystal size	0.18 x 0.30 x 0.38 mm	
θ range for data collection	2.07 to 27.56°	
Index ranges	$-13 \le h \le 14$, $-23 \le k \le 24$, $-27 \le l \le 30$	
Reflections collected	33424	
Independent reflections	10790 [R(int) = 0.0384]	
Completeness to θ = 27.56°	99.4 %	
Max. and min. transmission	0.9113 and 0.8253	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10790 / 0 / 469	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2σ(I)]	R1 = 0.0367, wR2 = 0.1025	
R indices (all data)	R1 = 0.0527, wR2 = 0.1085	
Largest diff. peak and hole	0.431 and -0.318 $e/Å^3$	

Table S-9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for Rh(CO)Cl(PPh$_2$CH$_2$CH$_2$-9-BBN)$_2$·C$_4$H$_{10}$O. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

	x	y	z	U(eq)
Rh(1)	7704(1)	5238(1)	1893(1)	35(1)
Cl(1)	9395(1)	4772(1)	2535(1)	55(1)
P(1)	9070(1)	6133(1)	1713(1)	38(1)
P(2)	6525(1)	4205(1)	1948(1)	37(1)
O(1)	5562(2)	5941(1)	1220(1)	67(1)
C(1)	6406(2)	5664(1)	1474(1)	45(1)
C(2)	9791(2)	6652(1)	2332(1)	49(1)
C(3)	10534(2)	6225(2)	2820(1)	51(1)
C(4)	7482(2)	3413(1)	2124(1)	45(1)
C(5)	8369(2)	3278(1)	1671(1)	49(1)
C(6)	8490(2)	6843(1)	1220(1)	43(1)
C(7)	7487(3)	7253(1)	1344(1)	54(1)
C(8)	7042(3)	7808(2)	987(2)	67(1)
C(9)	7560(3)	7958(2)	502(2)	72(1)
C(10)	8537(3)	7562(2)	367(1)	75(1)
C(11)	8999(3)	7000(2)	720(1)	61(1)
C(12)	10342(2)	5746(2)	1383(1)	51(1)
C(13)	10125(4)	5144(2)	1053(2)	80(1)
C(14)	11096(5)	4838(2)	788(2)	113(2)
C(15)	12234(4)	5146(3)	861(2)	113(2)
C(16)	12448(3)	5742(3)	1183(2)	98(1)
C(17)	11514(2)	6046(2)	1443(2)	73(1)
C(18)	10600(3)	5330(2)	3736(1)	61(1)
C(19)	10876(3)	5931(2)	4193(1)	73(1)
C(20)	9754(3)	6342(2)	4337(1)	74(1)
C(21)	8810(3)	6540(2)	3815(1)	68(1)
C(22)	8512(2)	5927(1)	3374(1)	51(1)
C(23)	7812(3)	5306(2)	3606(2)	69(1)
C(24)	8583(4)	4854(2)	4071(2)	82(1)
C(25)	9903(4)	4691(2)	3959(2)	76(1)

C(26)	5610(2)	3952(1)	1268(1)	40(1)
C(27)	4642(3)	3466(2)	1258(1)	56(1)
C(28)	3973(3)	3265(2)	736(2)	70(1)
C(29)	4255(3)	3540(2)	227(2)	73(1)
C(30)	5225(3)	4017(2)	235(1)	70(1)
C(31)	5900(3)	4219(2)	752(1)	56(1)
C(32)	5396(2)	4205(1)	2458(1)	41(1)
C(33)	5608(3)	3851(2)	2976(1)	61(1)
C(34)	4747(3)	3876(2)	3364(2)	82(1)
C(35)	3673(3)	4245(2)	3232(2)	76(1)
C(36)	3441(3)	4609(2)	2720(2)	70(1)
C(37)	4304(3)	4588(2)	2333(1)	56(1)
C(38)	10606(3)	2735(2)	1507(2)	77(1)
C(39)	11050(4)	2001(3)	1356(2)	108(2)
C(40)	10389(5)	1417(3)	1568(2)	120(2)
C(41)	9996(4)	1440(2)	2144(2)	86(1)
C(42)	9538(3)	2169(2)	2312(2)	69(1)
C(43)	10426(4)	2534(3)	2755(2)	94(1)
C(44)	11637(4)	2703(3)	2566(2)	117(2)
C(45)	11557(4)	3097(3)	1981(3)	120(2)
B(1)	9811(3)	5710(2)	3204(1)	48(1)
B(2)	9424(3)	2724(2)	1810(1)	51(1)

Table S-10. Interatomic distances [Å] and bond angles [°] for Rh(CO)Cl(PPh$_2$CH$_2$CH$_2$-9-BBN)$_2$·C$_4$H$_{10}$O.

Rh(1)-C(1)	1.793(3)
Rh(1)-P(1)	2.3091(6)
Rh(1)-P(2)	2.3293(6)
Rh(1)-Cl(1)	2.3781(7)
P(1)-C(6)	1.816(2)
P(1)-C(12)	1.816(3)
P(1)-C(2)	1.829(3)
P(2)-C(32)	1.818(2)
P(2)-C(26)	1.821(2)
P(2)-C(4)	1.823(2)
O(1)-C(1)	1.147(3)
C(2)-C(3)	1.532(4)
C(3)-B(1)	1.591(4)
C(4)-C(5)	1.541(3)
C(5)-B(2)	1.546(4)
C(6)-C(11)	1.385(4)
C(6)-C(7)	1.392(4)
C(7)-C(8)	1.379(4)
C(8)-C(9)	1.359(5)
C(9)-C(10)	1.363(5)
C(10)-C(11)	1.387(4)
C(12)-C(13)	1.366(5)
C(12)-C(17)	1.380(4)
C(13)-C(14)	1.411(5)
C(14)-C(15)	1.353(7)
C(15)-C(16)	1.348(7)
C(16)-C(17)	1.370(5)
C(18)-C(25)	1.540(5)
C(18)-C(19)	1.552(4)
C(18)-B(1)	1.582(4)
C(19)-C(20)	1.514(5)
C(20)-C(21)	1.530(4)
C(21)-C(22)	1.547(4)

C(22)-C(23)	1.525(4)
C(22)-B(1)	1.567(4)
C(23)-C(24)	1.535(5)
C(24)-C(25)	1.519(5)
C(26)-C(31)	1.379(4)
C(26)-C(27)	1.387(3)
C(27)-C(28)	1.388(4)
C(28)-C(29)	1.366(5)
C(29)-C(30)	1.377(5)
C(30)-C(31)	1.380(4)
C(32)-C(33)	1.371(4)
C(32)-C(37)	1.383(4)
C(33)-C(34)	1.385(4)
C(34)-C(35)	1.355(5)
C(35)-C(36)	1.371(5)
C(36)-C(37)	1.384(4)
C(38)-C(39)	1.509(5)
C(38)-B(2)	1.545(4)
C(38)-C(45)	1.565(6)
C(39)-C(40)	1.429(6)
C(40)-C(41)	1.464(6)
C(41)-C(42)	1.520(5)
C(42)-C(43)	1.484(5)
C(42)-B(2)	1.557(4)
C(43)-C(44)	1.474(6)
C(44)-C(45)	1.546(7)
C(1)-Rh(1)-P(1)	93.28(8)
C(1)-Rh(1)-P(2)	89.97(8)
P(1)-Rh(1)-P(2)	168.67(2)
C(1)-Rh(1)-Cl(1)	173.32(8)
P(1)-Rh(1)-Cl(1)	85.40(2)
P(2)-Rh(1)-Cl(1)	92.59(2)
C(6)-P(1)-C(12)	103.9(1)
C(6)-P(1)-C(2)	101.0(1)
C(12)-P(1)-C(2)	106.1(1)

C(6)-P(1)-Rh(1)	117.85(8)
C(12)-P(1)-Rh(1)	109.3(1)
C(2)-P(1)-Rh(1)	117.28(9)
C(32)-P(2)-C(26)	103.5(1)
C(32)-P(2)-C(4)	105.3(1)
C(26)-P(2)-C(4)	102.5(1)
C(32)-P(2)-Rh(1)	117.26(8)
C(26)-P(2)-Rh(1)	114.10(8)
C(4)-P(2)-Rh(1)	112.62(8)
O(1)-C(1)-Rh(1)	178.1(2)
C(3)-C(2)-P(1)	116.2(2)
C(2)-C(3)-B(1)	119.0(2)
C(5)-C(4)-P(2)	111.4(2)
C(4)-C(5)-B(2)	118.4(2)
C(11)-C(6)-C(7)	117.9(3)
C(11)-C(6)-P(1)	123.1(2)
C(7)-C(6)-P(1)	119.0(2)
C(8)-C(7)-C(6)	120.5(3)
C(9)-C(8)-C(7)	120.7(3)
C(8)-C(9)-C(10)	119.9(3)
C(9)-C(10)-C(11)	120.4(3)
C(6)-C(11)-C(10)	120.5(3)
C(13)-C(12)-C(17)	118.7(3)
C(13)-C(12)-P(1)	118.9(2)
C(17)-C(12)-P(1)	122.5(3)
C(12)-C(13)-C(14)	119.9(4)
C(15)-C(14)-C(13)	119.6(4)
C(16)-C(15)-C(14)	120.7(4)
C(15)-C(16)-C(17)	120.4(4)
C(16)-C(17)-C(12)	120.8(4)
C(25)-C(18)-C(19)	112.8(3)
C(25)-C(18)-B(1)	112.0(3)
C(19)-C(18)-B(1)	104.5(2)
C(20)-C(19)-C(18)	115.6(3)
C(19)-C(20)-C(21)	114.9(3)
C(20)-C(21)-C(22)	114.3(3)

C(23)-C(22)-C(21)	113.4(2)
C(23)-C(22)-B(1)	113.5(2)
C(21)-C(22)-B(1)	104.1(2)
C(22)-C(23)-C(24)	114.8(3)
C(25)-C(24)-C(23)	115.3(3)
C(24)-C(25)-C(18)	114.8(3)
C(31)-C(26)-C(27)	118.8(2)
C(31)-C(26)-P(2)	120.5(2)
C(27)-C(26)-P(2)	120.7(2)
C(26)-C(27)-C(28)	120.0(3)
C(29)-C(28)-C(27)	120.8(3)
C(28)-C(29)-C(30)	119.4(3)
C(29)-C(30)-C(31)	120.4(3)
C(26)-C(31)-C(30)	120.7(3)
C(33)-C(32)-C(37)	118.4(2)
C(33)-C(32)-P(2)	121.9(2)
C(37)-C(32)-P(2)	119.6(2)
C(32)-C(33)-C(34)	120.8(3)
C(35)-C(34)-C(33)	120.2(3)
C(34)-C(35)-C(36)	120.3(3)
C(35)-C(36)-C(37)	119.5(3)
C(32)-C(37)-C(36)	120.8(3)
C(39)-C(38)-B(2)	113.8(3)
C(39)-C(38)-C(45)	110.9(3)
B(2)-C(38)-C(45)	101.0(3)
C(40)-C(39)-C(38)	115.0(3)
C(39)-C(40)-C(41)	121.0(4)
C(40)-C(41)-C(42)	114.1(3)
C(43)-C(42)-C(41)	112.8(3)
C(43)-C(42)-B(2)	101.5(3)
C(41)-C(42)-B(2)	113.5(3)
C(44)-C(43)-C(42)	114.4(4)
C(43)-C(44)-C(45)	114.6(4)
C(44)-C(45)-C(38)	112.1(3)
C(22)-B(1)-C(18)	109.3(2)
C(22)-B(1)-C(3)	120.8(2)

C(18)-B(1)-C(3)	117.3(2)
C(38)-B(2)-C(5)	122.0(3)
C(38)-B(2)-C(42)	111.4(3)
C(5)-B(2)-C(42)	126.0(2)

Table S-11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Rh(CO)Cl(PPh_2CH_2CH_2\text{-}9\text{-}BBN)_2 \cdot C_4H_{10}O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	31(1)	35(1)	39(1)	3(1)	1(1)	-2(1)
Cl(1)	50(1)	51(1)	58(1)	4(1)	-12(1)	4(1)
P(1)	33(1)	40(1)	41(1)	3(1)	3(1)	-4(1)
P(2)	33(1)	35(1)	43(1)	3(1)	4(1)	-1(1)
O(1)	46(1)	63(1)	86(2)	16(1)	-14(1)	6(1)
C(1)	38(1)	43(1)	53(1)	2(1)	3(1)	-7(1)
C(2)	53(1)	45(2)	49(1)	2(1)	1(1)	-12(1)
C(3)	42(1)	61(2)	49(2)	-2(1)	-6(1)	-11(1)
C(4)	41(1)	39(1)	54(2)	7(1)	9(1)	2(1)
C(5)	47(1)	46(1)	54(2)	3(1)	10(1)	7(1)
C(6)	42(1)	42(1)	42(1)	3(1)	-1(1)	-8(1)
C(7)	62(2)	44(2)	54(2)	-1(1)	3(1)	2(1)
C(8)	77(2)	44(2)	76(2)	-2(2)	-7(2)	6(2)
C(9)	91(2)	49(2)	69(2)	17(2)	-19(2)	-5(2)
C(10)	91(2)	78(2)	57(2)	24(2)	7(2)	-10(2)
C(11)	60(2)	72(2)	52(2)	15(1)	9(1)	-2(2)
C(12)	43(1)	57(2)	56(2)	11(1)	13(1)	7(1)
C(13)	85(2)	63(2)	104(3)	-7(2)	53(2)	-5(2)
C(14)	145(4)	76(3)	134(4)	-5(3)	80(4)	20(3)
C(15)	91(3)	131(4)	131(4)	46(3)	70(3)	54(3)
C(16)	46(2)	148(4)	104(3)	21(3)	23(2)	21(2)
C(17)	41(1)	106(3)	73(2)	9(2)	9(1)	-1(2)
C(18)	63(2)	65(2)	50(2)	1(1)	-7(1)	12(1)
C(19)	89(2)	73(2)	49(2)	1(2)	-19(2)	-10(2)
C(20)	98(2)	60(2)	61(2)	-13(2)	6(2)	-7(2)
C(21)	74(2)	55(2)	76(2)	-5(2)	14(2)	2(2)
C(22)	51(1)	48(2)	53(2)	6(1)	2(1)	1(1)
C(23)	69(2)	66(2)	74(2)	4(2)	20(2)	-11(2)
C(24)	119(3)	55(2)	76(2)	10(2)	25(2)	-17(2)
C(25)	117(3)	49(2)	59(2)	13(1)	-7(2)	8(2)

C(26)	37(1)	37(1)	45(1)	-3(1)	2(1)	1(1)
C(27)	57(2)	51(2)	58(2)	-4(1)	2(1)	-10(1)
C(28)	67(2)	64(2)	75(2)	-15(2)	-3(2)	-22(2)
C(29)	83(2)	69(2)	61(2)	-15(2)	-10(2)	-11(2)
C(30)	89(2)	73(2)	45(2)	-2(1)	3(2)	-11(2)
C(31)	60(2)	54(2)	53(2)	-3(1)	4(1)	-12(1)
C(32)	38(1)	38(1)	48(1)	-2(1)	8(1)	-3(1)
C(33)	57(2)	70(2)	59(2)	16(2)	14(1)	13(1)
C(34)	91(2)	96(3)	67(2)	23(2)	36(2)	12(2)
C(35)	76(2)	80(2)	83(2)	-6(2)	45(2)	0(2)
C(36)	51(2)	67(2)	96(3)	-5(2)	26(2)	13(1)
C(37)	53(2)	51(2)	66(2)	4(1)	13(1)	7(1)
C(38)	63(2)	86(3)	87(2)	25(2)	30(2)	24(2)
C(39)	114(3)	123(4)	96(3)	13(3)	40(3)	56(3)
C(40)	155(4)	80(3)	138(4)	-13(3)	65(4)	11(3)
C(41)	85(2)	61(2)	113(3)	24(2)	11(2)	13(2)
C(42)	60(2)	74(2)	75(2)	14(2)	23(2)	21(2)
C(43)	95(3)	101(3)	85(3)	-5(2)	10(2)	12(2)
C(44)	98(3)	105(4)	132(4)	3(3)	-51(3)	-19(3)
C(45)	68(2)	109(4)	183(5)	21(4)	14(3)	-27(2)
B(1)	49(2)	47(2)	46(2)	2(1)	-4(1)	-3(1)
B(2)	43(1)	55(2)	56(2)	3(1)	10(1)	6(1)

Table S-12. Hydrogen atom coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3)
for Rh(CO)Cl(PPh$_2$CH$_2$CH$_2$-9-BBN)$_2$·C$_4$H$_{10}$O.

	x	y	z	U(eq)
H(2A)	10341	7003	2193	59
H(2B)	9141	6913	2491	59
H(3A)	11000	6565	3077	62
H(3B)	11135	5937	2650	62
H(4A)	7965	3476	2500	53
H(4B)	6949	2999	2143	53
H(5A)	8748	3731	1593	58
H(5B)	7869	3129	1316	58
H(7)	7114	7151	1671	64
H(8)	6381	8083	1079	81
H(9)	7248	8330	261	86
H(10)	8896	7668	37	90
H(11)	9655	6727	621	73
H(13)	9340	4936	1004	96
H(14)	10954	4428	564	135
H(15)	12875	4944	688	135
H(16)	13234	5949	1230	118
H(17)	11672	6459	1662	88
H(18)	11386	5161	3619	73
H(19A)	11290	5719	4546	88
H(19B)	11451	6267	4055	88
H(20A)	10039	6779	4536	88
H(20B)	9337	6058	4600	88
H(21A)	9127	6945	3620	81
H(21B)	8044	6689	3953	81
H(22)	8004	6121	3031	61
H(23A)	7504	4996	3286	83
H(23B)	7098	5496	3765	83
H(24A)	8621	5103	4437	99

H(24B)	8154	4404	4108	99
H(25A)	9875	4306	3678	92
H(25B)	10372	4521	4314	92
H(27)	4440	3275	1602	67
H(28)	3325	2938	732	84
H(29)	3797	3407	-121	87
H(30)	5426	4204	-110	84
H(31)	6556	4539	752	67
H(33)	6339	3592	3068	73
H(34)	4906	3638	3715	99
H(35)	3090	4252	3491	92
H(36)	2709	4869	2633	84
H(37)	4147	4834	1985	67
H(38)	10475	3036	1161	92
H(39A)	10985	1963	939	130
H(39B)	11922	1957	1508	130
H(40A)	10902	994	1553	144
H(40B)	9648	1341	1294	144
H(41A)	10691	1298	2425	104
H(41B)	9337	1093	2160	104
H(42)	8732	2117	2455	82
H(43A)	10051	2975	2866	113
H(43B)	10565	2231	3094	113
H(44A)	12094	2260	2539	141
H(44B)	12109	2997	2859	141
H(45A)	12372	3101	1853	144
H(45B)	11309	3589	2031	144

ORTEP Representation and X-ray Crystallographic Structure Data for Compound 12

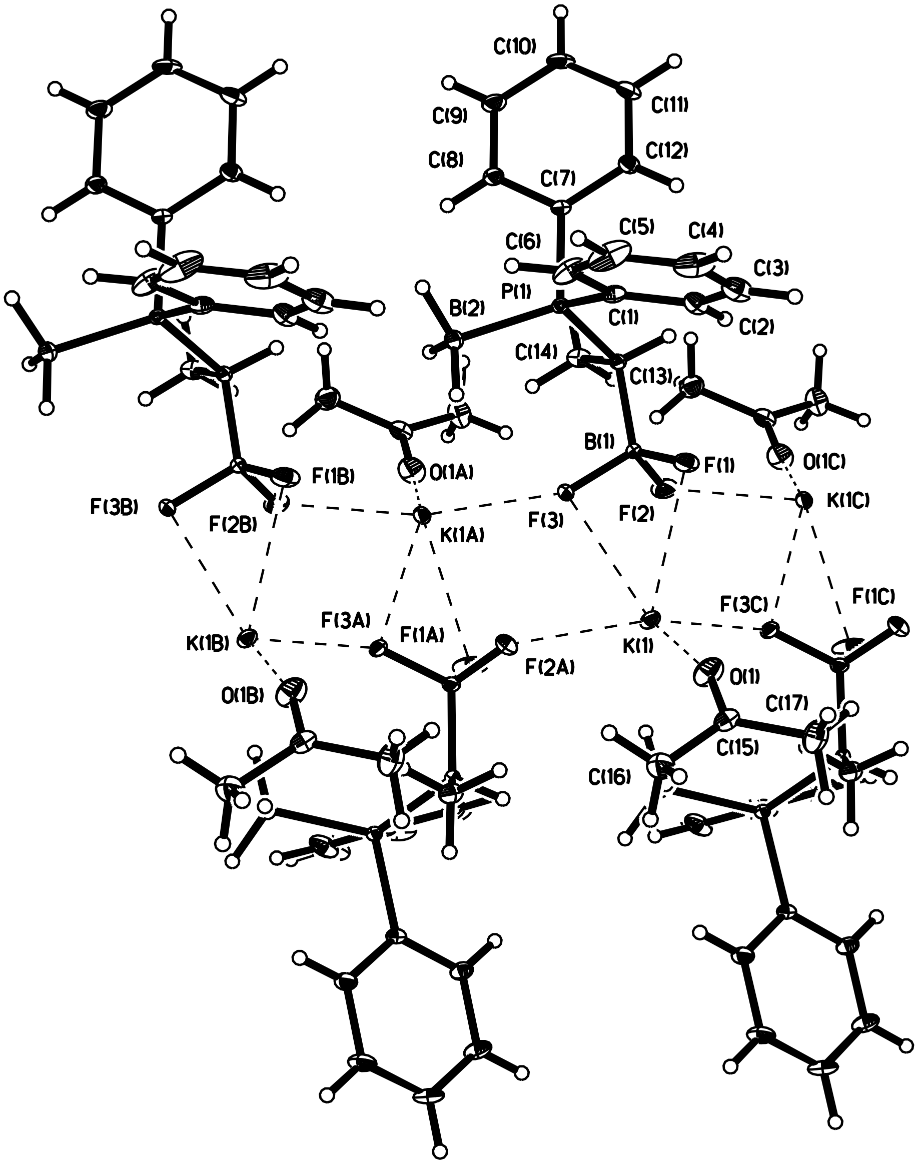


Figure S-33. ORTEP perspective view of the molecular arrangement of four $K[PPh_2(BH_3)(CHMeBF_3)]\cdot OCMe_2$ units in the lattice with an atom labeling scheme for selected non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability. The dashed lines indicate close contacts between K+ cations and the fluorine atoms of the neighboring anions and the O of the closest acetone molecule of solvation.

Description of the X-ray Structural Analysis of K[$PPh_2(BH_3)(CHMeBF_3)$]·$OCMe_2$

A colorless crystal of K[$PPh_2(BH_3)(CHMeBF_3)$]·$OCMe_2$ was covered in a polybutene oil (Sigma-Aldrich) and placed on the end of a MiTeGen loop. The sample was cooled to 100 K with an Oxford Cryostream 700 system and optically aligned on a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo Kα radiation source (λ = 0.71073 Å), and a PHOTON 100 CMOS detector. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the monoclinic crystal lattice that was used for the structural analysis.

Data collection consisted of the measurement of a total of 740 frames in four runs using omega scans with the detector held at 5.00 cm from the crystal. Frame scan parameters are summarized in Table 1 below:

Table S-13. Data collection details for K[$PPh_2(BH_3)(CHMeBF_3)$]·$OCMe_2$.

Run	2θ	ω	φ	χ	Scan Width (°)	Frames	Exposure Time (sec)
1	21.90	-160.79	102.00	54.74	1.00	185	15.00
2	21.90	-160.79	0.00	54.74	1.00	185	15.00
3	21.90	-160.79	153.00	54.74	1.00	185	15.00
4	21.90	-160.79	51.00	54.74	1.00	185	15.00

The APEX3 software program (version 2016.9-0)[1] was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 41036 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 5892 were independent (average redundancy 6.965, completeness = 99.8%, R_{int} = 3.12%, R_{sig} = 1.97%) and 5176 (87.85%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.5781(6) Å, b = 6.9492(3) Å, c = 17.6391(7) Å, β = 96.3164(10)°, volume = 2019.77(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 9966 reflections above 20 σ(I) with 6.363° < 2θ < 65.42°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.892. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.834 and 0.934.

The structure was solved by direct methods and difference Fourier analysis using the programs provided by SHELXL-2014/7.[2] The crystallographic asymmetric unit contains a potassium cation, a $[PPh_2(BH_3)(CHMeBF_3)]^-$ monoanion, and a molecule of acetone. Idealized positions for the hydrogen atoms bound to carbon atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 (methine and aromatic hydrogens) or 1.5 (methyl hydrogens) times that of the adjacent carbon atom. The fractional coordinates and isotropic thermal parameters of the three hydrogens of the BH_3 group bound to the phosphorus atom were refined. The positions of the methyl hydrogen atoms were optimized by a rigid rotating group refinement with idealized angles. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i |F_o^2 - F_c^2|^2$, with weighting $w_i^{-1} = [\sigma^2(F_o^2) + (0.0352\ P)^2 + 1.4010\ P]$, where $P = (\text{Max}\ (F_o^2, 0) + 2\ F_c^2)/3$.[2] The final anisotropic full-matrix least-squares refinement on F^2 with 241 variables converged at R1 = 3.60%, for the 5176 observed data with I>2σ(I) and wR2 = 9.06% for all data. The goodness-of-fit was 1.073.[3]

A correction for secondary extinction was not applied. The largest peak in the final difference electron density synthesis was 0.529 $e^-/Å^3$ and the largest hole was -0.442 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray Crystallography.[4]

References

1. APEX3 is a Bruker AXS crystallographic software package for single crystal data collection, reduction and preparation.
2. Sheldrick, G. M., SHELXL-2014, Crystallographic software package, Bruker AXS, Inc., Madison, Wisconsin, USA.
3. $R_1 = \square(||F_o| - |F_c||) / \square|F_o|$, $wR_2 = [\square\square w(F_o^2 - F_c^2)^2] / \square\square w\square F_o^2\square^2]]^{1/2}$, $R_{int.} = \square\square F_o^2 - F_o^2(mean)|^2/ \square\square F_o^2]$, and $GOF = [\square\square w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.
4. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).

Table S-14. Crystal data for K[$PPh_2(BH_3)(CHMeBF_3)$]·$OCMe_2$.

Ident. code	bp46cms	
Chemical form.	$C_{17}H_{23}B_2F_3KOP$	
Formula weight	392.04 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.188 x 0.489 x 0.509 mm	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell	a = 16.5781(6) Å	α = 90°
	b = 6.9492(3) Å	β = 96.3164(10)°
	c = 17.6391(7) Å	γ = 90°
Volume, $Å^3$	2019.77(14)	
Z	4	
Density (calc)	1.289 g/cm^3	
Abs. coefficient	0.370 mm^{-1}	
F(000)	816	

Table S-15. Data collection and structure refinement for K[$PPh_2(BH_3)(CHMeBF_3)$]·$OCMe_2$.

Theta range	3.15 to 30.00°	
Index ranges	$-23 \le h \le 22$, $-9 \le k \le 9$, $-19 \le l \le 24$	
Reflections	41036	
Independent refls	5892 [R(int) = 0.0312]	
Coverage	99.8%	
Absorption correction	multi-scan	
Max. and min. trans.	0.934 and 0.834	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	5892 / 0 / 241	
Goodness-of-fit on F^2	1.073	
Final R indices	5176 data; $I>2\sigma(I)$	R1 = 0.0360, wR2 = 0.0862
	all data	R1 = 0.0431, wR2 = 0.0906
Largest diff. peak and hole	0.529 and -0.442 $e^-/Å^3$	

Table S-16. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for K[PPh$_2$(BH$_3$)(CHMeBF$_3$)]·OCMe$_2$. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

	x/a	y/b	z/c	U(eq)
K1	0.54210(2)	0.81994(4)	0.18186(2)	0.01921(7)
P1	0.23045(2)	0.99184(4)	0.25973(2)	0.01324(7)
F1	0.38554(6)	0.71123(17)	0.20280(7)	0.0442(3)
F2	0.44094(6)	0.68579(14)	0.32480(7)	0.0414(3)
F3	0.42767(5)	0.97753(11)	0.26915(5)	0.02178(17)
O1	0.55611(8)	0.77334(19)	0.03559(6)	0.0355(3)
C1	0.20214(8)	0.9173(2)	0.16172(7)	0.0192(2)
C2	0.20928(9)	0.7283(2)	0.13661(8)	0.0244(3)
C3	0.18271(10)	0.6802(3)	0.06143(9)	0.0338(4)
C4	0.14868(10)	0.8184(4)	0.01151(9)	0.0436(5)
C5	0.14188(12)	0.0055(4)	0.03594(10)	0.0474(5)
C6	0.16897(10)	0.0569(3)	0.11078(9)	0.0332(4)
C7	0.13644(7)	0.96137(18)	0.30323(7)	0.0150(2)
C8	0.10910(8)	0.1084(2)	0.34776(8)	0.0213(3)
C9	0.03675(9)	0.0863(2)	0.38064(9)	0.0278(3)
C10	0.99210(8)	0.9187(3)	0.36903(9)	0.0280(3)
C11	0.01869(8)	0.7718(2)	0.32477(8)	0.0257(3)
C12	0.09099(8)	0.7926(2)	0.29206(7)	0.0200(3)
C13	0.30023(7)	0.81635(17)	0.30671(7)	0.0149(2)
C14	0.31218(8)	0.8643(2)	0.39262(8)	0.0229(3)
C15	0.58675(9)	0.7716(2)	0.97621(8)	0.0232(3)
C16	0.61850(10)	0.9530(3)	0.94415(10)	0.0338(3)
C17	0.59368(12)	0.5904(2)	0.93177(9)	0.0341(4)
B1	0.38779(9)	0.7985(2)	0.27421(9)	0.0194(3)
B2	0.26397(10)	0.2583(2)	0.26557(10)	0.0230(3)

Table S-17. Interatomic distances (Å) for $K[PPh_2(BH_3)(CHMeBF_3)]\cdot OCMe_2$.[a]

K1···F2'	2.562(1)	K1···F3*	2.562(1)
K1···O1	2.636(1)	K1···F1	2.767(1)
K1···F3	2.795(1)	K1···F2	3.312(12)
P1-C1	1.816(1)	P1-C13	1.817(1)
P1-B2	1.933(2)	P1-C7	1.824(1)
F2-B1	1.419(2)	F1-B1	1.395(2)
F3-B1	1.416(2)	O1-C15	1.213(2)
C1-C2	1.395(2)	C1-C6	1.394(2)
C3-C4	1.381(3)	C2-C3	1.391(2)
C5-C6	1.394(2)	C4-C5	1.378(3)
C7-C12	1.396(2)	C7-C8	1.394(2)
C9-C10	1.384(2)	C8-C9	1.397(2)
C11-C12	1.394(2)	C10-C11	1.386(2)
C13-B1	1.623(2)	C13-C14	1.543(2)
C15-C16	1.500(2)	C15-C17	1.494(2)

[a] The fractional coordinates of the symmetry related primed (') atom was determined from the relationship: 1-x, 1/2+y, 1/2-z, whereas the fractional coordinates of the symmetry related starred atom (*) was determined from the relationship: 1-x, -1/2+y, 1/2-z.

Table S-18. Bond angles (°) for $K[PPh_2(BH_3)(CHMeBF_3)]\cdot OCMe_2$.

C1-P1-C7	102.95(6)	C1-P1-C13	109.11(6)
C1-P1-B2	111.52(7)	C13-P1-C7	105.12(6)
C7-P1-B2	110.05(6)	C13-P1-B2	116.99(6)
C15-O1···K1	159.47(12)	C6-C1-C2	119.47(14)
C6-C1-P1	117.21(12)	C2-C1-P1	123.28(10)
C3-C2-C1	119.96(15)	C4-C3-C2	120.36(17)
C5-C4-C3	119.89(15)	C4-C5-C6	120.62(17)
C5-C6-C1	119.69(17)	C8-C7-C12	119.40(11)
C8-C7-P1	119.86(10)	C12-C7-P1	120.74(9)
C7-C8-C9	120.05(13)	C10-C9-C8	120.04(13)
C9-C10-C11	120.36(13)	C10-C11-C12	119.86(13)
C11-C12-C7	120.28(12)	C14-C13-B1	109.89(11)
C14-C13-P1	108.04(9)	B1-C13-P1	116.07(9)
O1-C15-C17	121.65(15)	O1-C15-C16	120.98(14)
C17-C15-C16	117.37(13)	F1-B1-F3	106.94(12)
F1-B1-F2	106.32(12)	F3-B1-F2	105.23(11)
F1-B1-C13	114.59(11)	F3-B1-C13	113.39(10)
F2-B1-C13	109.73(12)		

Table S-19. Anisotropic atomic displacement parameters (Å^2) for $K[PPh_2(BH_3)(CHMeBF_3)]\cdot OCMe_2$. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K1	0.01978(13)	0.01712(13)	0.02267(14)	0.00581(10)	0.01107(10)	0.00534(10)
P1	0.01215(14)	0.01366(14)	0.01461(14)	0.00195(11)	0.00455(10)	0.00081(10)
F1	0.0240(5)	0.0548(7)	0.0575(7)	-0.0413(5)	0.0208(4)	-0.0140(4)
F2	0.0186(4)	0.0273(5)	0.0787(8)	0.0166(5)	0.0067(5)	0.0089(4)
F3	0.0175(4)	0.0134(3)	0.0365(5)	-0.0040(3)	0.0124(3)	-0.0040(3)
O1	0.0435(7)	0.0417(7)	0.0236(5)	0.0011(5)	0.0147(5)	0.0085(5)
C1	0.0153(5)	0.0292(7)	0.0140(5)	0.0022(5)	0.0063(4)	0.0011(5)
C2	0.0256(7)	0.0313(7)	0.0175(6)	-0.0022(5)	0.0076(5)	-0.0075(6)
C3	0.0292(8)	0.0520(10)	0.0218(7)	-0.0106(7)	0.0096(6)	-0.0124(7)
C4	0.0260(8)	0.0889(16)	0.0159(7)	-0.0085(8)	0.0022(6)	0.0040(9)
C5	0.0399(10)	0.0825(16)	0.0193(7)	0.0103(8)	0.0013(7)	0.0285(10)
C6	0.0320(8)	0.0481(10)	0.0201(7)	0.0070(6)	0.0057(6)	0.0193(7)
C7	0.0108(5)	0.0206(6)	0.0137(5)	-0.0003(4)	0.0017(4)	0.0007(4)
C8	0.0166(6)	0.0239(6)	0.0241(6)	-0.0054(5)	0.0059(5)	-0.0002(5)
C9	0.0185(6)	0.0367(8)	0.0297(7)	-0.0102(6)	0.0098(5)	0.0011(6)
C10	0.0122(6)	0.0463(9)	0.0267(7)	-0.0065(6)	0.0073(5)	-0.0033(6)
C11	0.0174(6)	0.0366(8)	0.0238(7)	-0.0068(6)	0.0046(5)	-0.0106(6)
C12	0.0180(6)	0.0255(6)	0.0174(6)	-0.0045(5)	0.0052(5)	-0.0040(5)
C13	0.0124(5)	0.0120(5)	0.0206(6)	0.0027(4)	0.0035(4)	0.0000(4)
C14	0.0185(6)	0.0315(7)	0.0184(6)	0.0062(5)	0.0012(5)	-0.0002(5)
C15	0.0211(6)	0.0298(7)	0.0187(6)	-0.0005(5)	0.0019(5)	0.0062(5)
C16	0.0317(8)	0.0351(8)	0.0356(8)	-0.0016(7)	0.0089(7)	-0.0027(7)
C17	0.0488(10)	0.0310(8)	0.0225(7)	-0.0026(6)	0.0046(7)	0.0067(7)
B1	0.0131(6)	0.0127(6)	0.0338(8)	-0.0056(5)	0.0084(5)	-0.0012(5)
B2	0.0198(7)	0.0152(6)	0.0348(8)	0.0047(6)	0.0065(6)	-0.0002(5)

Table S-20. Hydrogen atom coordinates and isotropic atomic displacement parameters (Å^2) for K[PPh$_2$(BH$_3$)(CHMeBF$_3$)]·OCMe$_2$.

	x/a	y/b	z/c	U(eq)
H2	0.2323	0.6324	0.1708	0.029
H3	0.1880	0.5517	0.0444	0.041
H4	0.1300	0.7846	-0.0396	0.052
H5	0.1185	1.1002	0.0014	0.057
H6	0.1649	1.1865	0.1270	0.04
H8	0.1397	1.2236	0.3558	0.026
H9	0.0182	1.1866	0.4110	0.033
H10	-0.0570	0.9041	0.3915	0.034
H11	-0.0123	0.6571	0.3167	0.031
H12	0.1094	0.6915	0.2620	0.024
H13	0.2734	0.6875	0.3009	0.018
H14A	0.3421	0.7597	0.4203	0.034
H14B	0.2591	0.8791	0.4115	0.034
H14C	0.3429	0.9844	0.4006	0.034
H16A	0.5886	1.0637	-0.0388	0.051
H16B	0.6113	0.9469	-0.1117	0.051
H16C	0.6763	0.9669	-0.0380	0.051
H17A	0.5773	0.4807	-0.0386	0.051
H17B	0.6500	0.5732	-0.0789	0.051
H17C	0.5583	0.5985	-0.1164	0.051
H1B2	0.2880(11)	1.289(3)	0.3271(11)	0.030(5)
H2B2	0.3124(12)	1.274(3)	0.2274(11)	0.034(5)
H3B2	0.2058(13)	1.344(3)	0.2480(12)	0.045(6)