Supporting Information

Proton to Hydride Umpolung at a Phosphonium Centre Via Electron Relay: A New Strategy for Main-Group Based Water Reduction

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Supporting Information

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1. Experimental section

Experimental Procedures

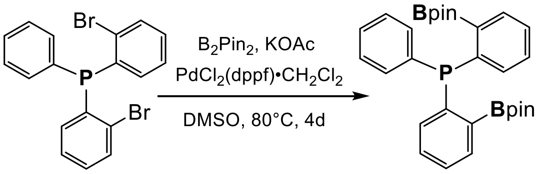
Instrumentation and Chemicals

All manipulations were performed under Ar or N_2 atmosphere by using standard Schlenk or glove box techniques. All the solvents were dried prior to use. Column chromatography was carried out using Merck silica gel 60 and KANTO CHEMICAL silica gel 60N. JNM-ECA 600 NMR spectrometer [^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz), ^{11}B{^{1}H} NMR (193 MHz) and ^{31}P{^{1}H} NMR (243 MHz)]. JNM-ECA 500 NMR spectrometer [^{1}H NMR (500 MHz), ^{2}H NMR (92 MHz), ^{13}C{^{1}H} NMR (126 MHz), ^{11}B{^{1}H} NMR (160 MHz) and ^{31}P{^{1}H} NMR (202 MHz)]. JNM-AL400S NMR spectrometer [^{1}H NMR (400 MHz), ^{11}B{^{1}H} NMR (127 MHz) and ^{31}P{^{1}H} NMR (160 MHz)]. Chemical shift (δ) are given in ppm with reference against external $SiMe_4$ (^{1}H, ^{13}C{^{1}H}), $BF_3\cdot Et_2O$ (^{11}B) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded with a Thermo Fisher Scientific samples. The DFT calculations were performed using the *Gaussian09* program package.[1]

1.1 Synthesis of bis(2-bromophenyl)(phenyl)phosphane

In a nitrogen atmosphere, the *n*BuLi hexane solution (21.4 mL,1.55 M) was added to a solution of 1,2-dibromobenzene (4.00 mL, 33.2 mol) in THF and ether (1:1) (120 mL) at –112 ˚C (liquid nitrogen ethanol bath) through a dropping funnel. After stirring for 20 minutes at –112 ˚C, dichlorophenylphosphine (2.23 mL 16.4 mmol) was added to the reaction mixture at the same temperature. After an additional stirring for 2 hours (30 minutes at –112 ˚C before gradually warming over 1.5 hours), the reaction mixture was quenched by NH_4Cl aq. and evaporated. The residue was dissolved in DCM and washed with brine. After drying with Na_2SO_4 and removing DCM, the crude product was recrystallized with ethanol at –20 ˚C. The product was purified with column chromatography (DCM : hexane=1 : 1) (4.22 g, 10.0 mmol, 61%).

1.2 Synthesis of BPB-pin (1a)

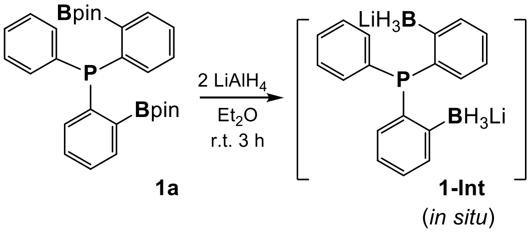


1a

(y. 45%, air stable)

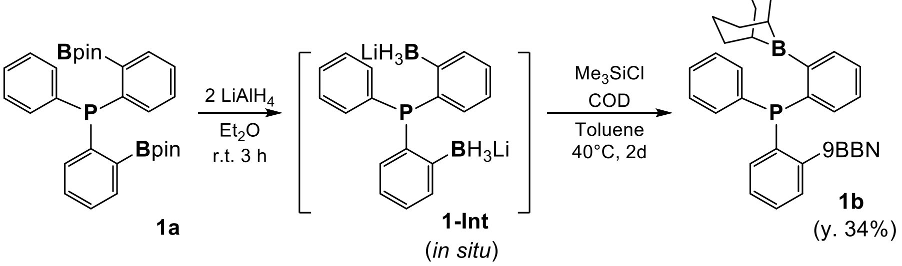
In a nitrogen filled Schlenk flask, bis(2-bromophenyl)(phenyl)phosphane (3.00 g, 7.14 mmol), bis(pinacolato)diboron (3.63 g, 14.3 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (525 mg, 0.642 mmol), potassium acetate (4.24 g, 43.2 mmol) and degassed super dehydrated DMSO (180 mL) were mixed and stirred for 4 days at 80 ˚C. After the reaction, water (540 mL) was added to the mixture, which was extracted with benzene until the solution color became colorless. The combined benzene solution was died over Na_2SO_4 and evaporated. The resulting solid residue was dissolved in a small amount of DCM, to which a large amount hexane was added. Storage at –20 ˚C overnight led to precipitation of an olive-green solid, which was mostly undesired byproducts. The filtrate was evaporated again, and the resulting oily residue was redissolved in hexane. Cooling at –20 ˚C allowed precipitation of a second crop of byproduct, which was then removed by filtration. This resulting filtrate was then evaporated to afford greenish oily residue, to which hexane was added. With scratching, crude product formed as an off-white solid from the solution. This crude product could be further purified by redissolving in hot hexane, evaporation to form an oily residue, followed by an addition of a small amount of hexane and scratching. This procedure was repeated 5 times to afford **1a** as a white solid in 45% (1.66 g, 3.22 mmol). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.69-7.68 (m, 2H), 7.29 (m, 5H), 7.25-7.21 (m, 2H), 6.81-6.80 (m, 2H), 1.12-1.11 (m, 24 H), ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz) δ 145.4 (d, J_{PC} = 21.7Hz), 139.2 (d, J_{PC} = 15.8 Hz), 135.0 (s), 134.9 (d, J_{PC} = 13.0 Hz), 132.6 (s), 130.2 (s), 128.3 (s), 128.2 (d, J_{PC} = 7.09 Hz), 126.9 (s), 83.8 (s), 24.5-24.3 (m), ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 MHz) δ –4.1, ^{11}B{^{1}H} NMR (C_6D_6, 192 MHz) δ 30.0. MS(ESI) m/z $[M+H]^+$ $C_{30}H_{38}O_4B_2P$ Calcd for: 515.26883 Found: 515.26941. Anal. Calcd. for $C_{30}H_{38}O_4B_2P$: C, 70.07; H, 7.25. Found: C, 69.66; H 7.20.

1.3 Crystallization of 1-Int



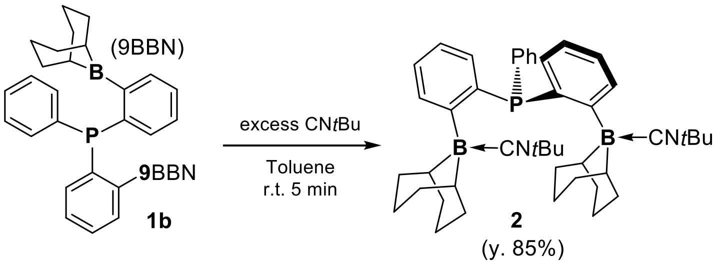
In an argon atmosphere, $LiAlH_4$ (1 M ether solution, 0.39 mL, 0.39 mmol) was added to a solution of BPB-pin (**1a**, 100 mg, 0.194 mmol) in ether (6 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then 2 h at room temperature. After removing salt by filtration in glove box, cyclooctadiene (1 M ether solution, 0.39 mL, 0.3. mmol) and trimethylsilyl chloride (1 M ether solution, 0.39 mL, 0.3. mmol) were added. The resulting reaction mixture was stirred for 15 h at room temperature. After evaporation, **1-Int** crystals suitable for X-ray crystal structure analysis were obtained by crystallization from a toluene/hexane two layer system at r.t.. ^{1}H NMR (C_6D_6, 400 MHz) δ 7.69 (br), 7.39 (br), 7.30 (m, 6.4 Hz), 7.14-6.95 (m, Including toluene peak), 1.76-1.52 (br), ^{31}P{^{1}H} NMR (C_6D_6, 160 MHz) δ –11.6, ^{11}B{^{1}H} NMR (C_6D_6, 127 MHz) δ –26.1.

1.4 Synthesis of BPB-9BBN (1b)



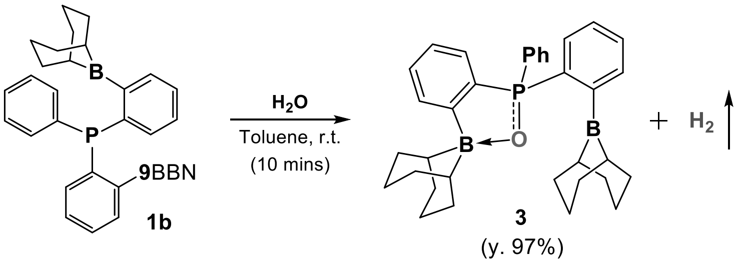
In an argon atmosphere, 1 M $LiAlH_4$ ether solution (3.9 mL, 3.9 mmol) was added to a solution of BPB-pin (**1a**, 1.00 g, 1.94 mmol) in ether (20 mL) at 0 °C. Reaction mixture was stirred for 1 h at 0 °C and then 2 h at room temperature. After stirring, salt is removed by filtration in glove box. Toluene (30 mL), Cyclooctadiene (30 mL) and Trimethylsilyl chloride (3 mL) are added after complete evaporation of ether solvent at room temperature. After stirring for 2 days at 40 °C, all volatile was evaporated and then salt was removed by celite filtration using toluene in the glove box. The toluene filtrate was concentrated and layered with pentane to precipitate product **1b** as a white solid (328 mg, 0.654 mmol, 34%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.54-7.53 (m, 2H), 7.36-7.34 (m, 2H), 7.29-7.26 (m, 5H), 7.24-7.21 (m, 2H), 6.99-6.97 (m, 2H), 1.98-1.82 (m, 20 H), 1.74-1.68 (m, 4H), 1.32-1.27 (m, 4H), ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz) δ 154.3 (d, J_{PC} = 30.4 Hz), 139.0 (d, J_{PC} = 7.2 Hz), 138.3 (s), 133.9 (d, J_{PC} = 17.4 Hz), 132.7 (s), 129.9 (d, J_{PC} = 17.4 Hz), 129.0 (s), 128.6 (d, J_{PC} = 7.10 Hz), 128.5 (s), 128.2 (s), 34.5-34.4 (m), 34.0-33.9 (m), 32.83 (br), 23.36 (br), ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 MHz) δ –7.0, ^{11}B{^{1}H} NMR (C_6D_6, 192 MHz) δ 79.2. MS(ESI) m/z [**1b**+OH]$^-$ $C_{34}H_{42}OB_2P$ Calcd for: 519.31649 Found: 519.31575.

1.5 Synthesis of compound 2



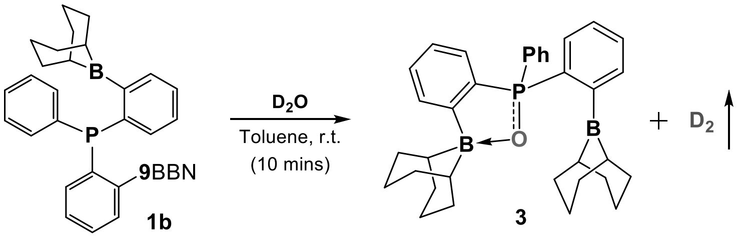
In an argon atmosphere, BPB-9BBN (**1b**, 80 mg, 0.16 mmol) was dissolved in toluene (2 mL), to which *tert*-Butyl isocyanate (53 μL, 0.48 mmol) was then added at room temperature. After stirring for 5 min., all volatile was evaporated and washed with hexane (1 mL × 3) to afford **2** as a white solid in 85% yield (56 mg, 0.084 mmol). Crystals suitable for X-ray crystal structure analysis were grown from a C_6D_6 reaction solution. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.99 (br, 2H), 7.32 (br, 2H), 7.24-7.19 (m, 4H), 7.02-7.00 (m, 2H), 6.96-6.94 (m, 2H), 6.90-6.87 (m, 1H), 2.46-1.73 (m, 28 H), 0.73 (s, 18H), ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ 155.3 (br), 146.6 (s), 143.6 (d, J_{PC} = 13.2 Hz), 136.1 (s), 135.1 (d, J_{PC} = 9.6 Hz), 133.9 (d, J_{PC} = 18.0 Hz), 128.0 (s), 126.6 (s), 125.7 (s), 57.0 (br), 35.0-34.5 (m), 30.4-30.1 (m), 28.7 (br), 24.8 (br), 23.8 (br), $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ –11.7, $^{11}B\{^1H\}$ NMR (C_6D_6, 161 MHz) δ –17.6. MS(ESI) m/z [**1b**+H]$^+$ $C_{34}H_{42}B_2P$ Calcd for: 503.32048 Found: 503.31946. [**1b**+OH]$^+$ $C_{34}H_{42}OB_2P$ Calcd for: 519.31539 Found: 519.31429.

1.6 Synthesis of compound 3



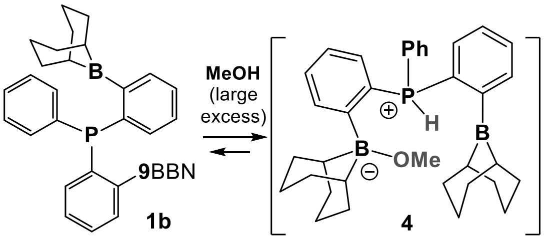
To a toluene (2 mL) solution of BPB-9BBN (**1b**, 30 mg, 0.060 mmol), degassed water (0.1 mL) was added. The reaction mixture was stirred at room temperature for 10 min. Product **3** was obtained by evaporation (30 mg, 0.058 mmol, 97%). Crystals suitable for X-ray crystal structure analysis were grown from a THF/hexane diffusion system at –30 ˚C. H_2 gas was detected from the reaction mixture by GC measurement. ^1H NMR (C_6D_6, 500 MHz) δ 7.84 (dd, 2H, *J* = 7.5 Hz, 2.0 Hz), 7.39 (dd, 2H, *J* = 12.5 Hz, 6.5 Hz), 7.32 (dd, 2H, *J* = 12.0 Hz, 7.5 Hz), 7.16 (t, 2H, *J* = 7.5 Hz), 6.88-6.84 (m, 2H), 6.81 (dt, 1H, *J* = 7.5 Hz, 3.5 Hz), 6.72 (dt, 2H, *J* = 7.5 Hz, 2.0 Hz), 2.26-1.95 (m, 20 H), 1.69 (br, 4H), 1.60-1.56 (m, 4H), $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ 161.2 (br), 132.6 (s), 132.0 (d, J_{PC} = 10.8 Hz), 131.8 (d, J_{PC} = 15.6 Hz), 131.6 (s), 131.3 (d, J_{PC} = 16.9 Hz), 130.7 (d, J_{PC} = 103.3 Hz), 128.9 (d, J_{PC} = 12.0 Hz), 128.8 (d, J_{PC} = 107.0 Hz), 126.9 (d, J_{PC} = 12.0 Hz), 33.9-33.3 (m), 30.9 (br), 24.3 (s), $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 60.4, $^{11}B\{^1H\}$ NMR (C_6D_6, 161 MHz): δ 49.1. MS(ESI) m/z [M+H]$^+$ $C_{34}H_{42}OB_2P$ Calcd for: 519.31539 Found: 519.31501.

1.7 Reaction of compound 1b and D_2O



To a toluene (0.3 mL) solution of BPB-9BBN (**1b**, 6 mg, 0.01 mmol), degassed D_2O (25 μL) was added by vacuum transfer (some amount of D_2O remained). Bubbling was observed at r.t. after addition of D_2O. ^2H NMR (C_6D_6, 92 MHz): δ 4.50 (s).

1.8 Reaction of compound 1b and methanol and detection of 4 by NMR



MeOH (40 μL, 1.0 mmol) was added to a solution of BPB-9BBN (**1b**, 10 mg, 0.020 mmol) in C_6D_6 (0.3 mL) at r.t.. ^1H NMR (C_6D_6, 400 MHz): δ 8.05 (br), 7.28-7.17 (m), 6.96-6.86 (m), 6.80-6.76 (m), 6.88-6.84 (m), 2.49-1.57 (m), $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ –4.6 ($^1J_{PH}$=525 Hz in ^{31}P NMR).

1.9 Control reaction

$$PPh_3 \quad + \quad 2\ BCy_3 \quad \xrightarrow[C_6D_6 \\ 50\ °C,\ 16\ h]{\mathbf{H_2O}} \quad \text{no reaction}$$

To a C_6D_6 (0.3 mL) solution of PPh_3 (5 mg, 0.02 mmol) and BCy_3 (10 mg, 0.04 mmol), degassed H_2O (0.2 mL) was added by vacuum transfer (some amount of H_2O remained). Reaction mixture was stored at room temperature for one hour followed by 16 hours at 50 °C. No H_2 was observed in the ^1H NMR of the reaction mixture. The $^{11}B\{^1H\}$ NMR spectra indicated presence of large amount of starting material BCy_3 and some formation of $BCy_3•H_2O$. The ^{31}P NMR spectra showed no formation of phosphine oxide nor any other reactivity.

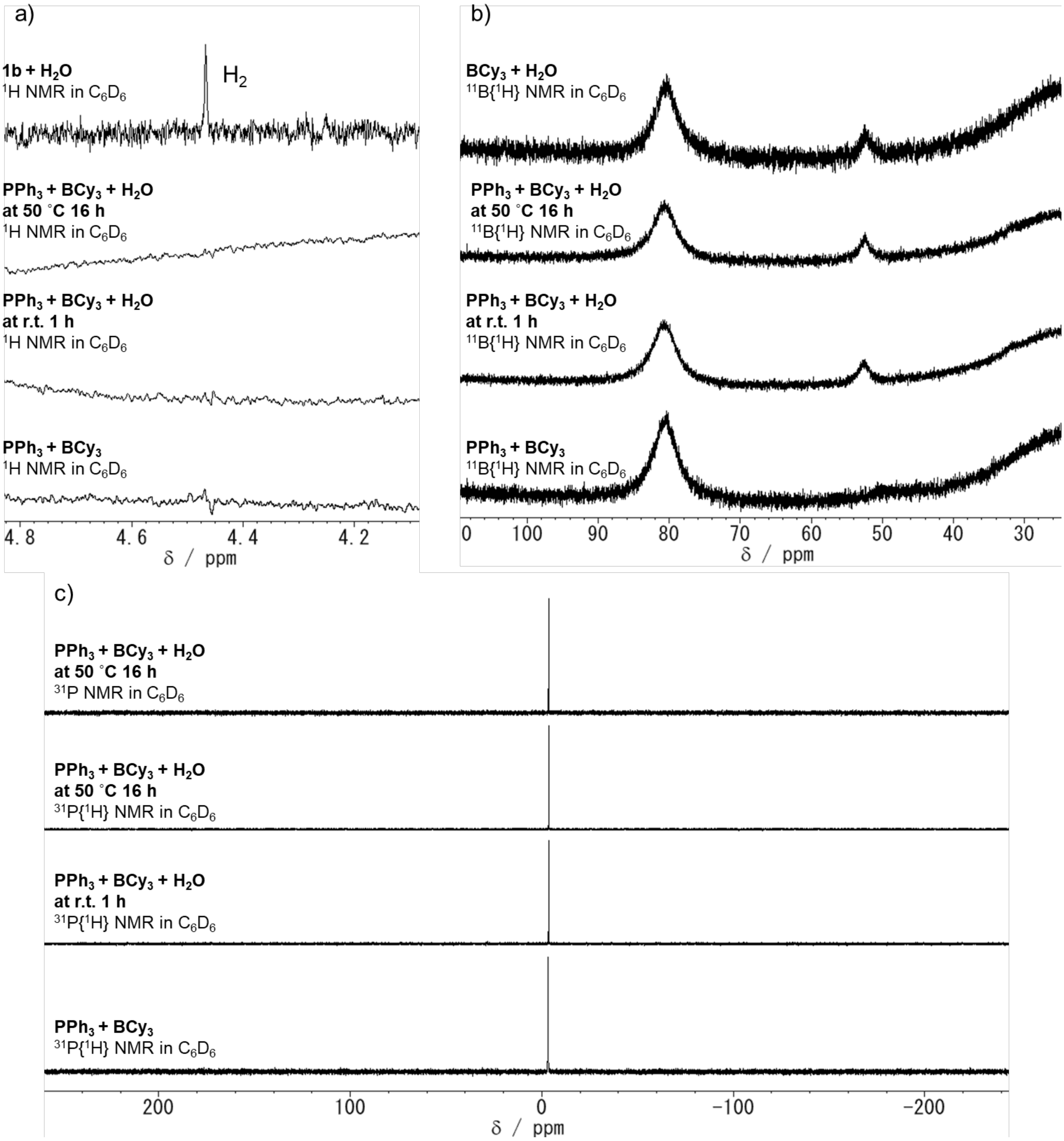


Figure S1 ^1H (a, 400 MHz in C_6D_6), $^{11}B\{^1H\}$ (b,128 MHz in C_6D_6) and $^{31}P\{^1H\}$/^{31}P (c,160 MHz in C_6D_6) NMR spectra of the control reaction.

2. Crystal structure determination

Crystals suitable for X-ray structural determination were mounted on a *Bruker SMART APEXII* CCD diffractometer. Samples were irradiated with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) at 173 K for data collection. The data were processed using the *APEX* program suite. All structures were solved by the *SHELXT* program (ver. 2014/5). Refinement on F^2 was carried out by full-matrix least-squares using the *SHELXL* in the *SHELX* software package (ver. 2014/7)[1] and expanded using Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were assigned to idealized geometric positions and included in the refinement with isotropic thermal parameters. The *SHELXL* was interfaced with *ShelXle* GUI (*ver.* 742) for most of the refinement steps.[2] The pictures of molecules were prepared using *Pov-Ray* 3.7.0.[3] The crystallographic data are summarized in Table S1. These data (CCDC 2096462-465) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S1 X-ray diffraction analysis parameters of complexes **1a**, **1-Int**, **2**, **3** and **3·H$_2$O**.

Compound Name CCDC No.	**1a** 2096462	**1-Int** 2096463	**2** 2096464	**3** 2096465	**3·H$_2$O** 2109052
Formula	$C_{60}H_{74}B_4O_8P_2$	$C_{22}H_{29}B_2Cl_{0.25}Li_{2.25}OP$	$C_{44}H_{59}B_2N_2P$	$C_{38}H_{49}B_2O_2P$	$C_{42}H_{59}B_2O_4P$
Mol wt	1028.37	386.52	668.52	590.36	680.48
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	C2/c	P2$_1$/c	P2$_1$/n	P-1
a, Å	10.9474(18)	28.597(6)	15.557(18)	10.020(8)	10.542(8)
b, Å	14.320(2)	14.635(3)	14.394(16)	15.571(12)	10.722(8)
c, Å	19.292(3)	23.112(4)	17.425(19)	21.243(17)	17.445(14)
α, deg	104.883(2)	90	90	90	96.766(7)
β, deg	91.015(2)	106.257(4)	97.347(8)	102.039(14)	96.231(14)
γ, deg	99.535(2)	90	90	90	104.461(9)
V, Å^3	2876.7(8)	9286(3)	3870(8)	3242(4)	1877(3)
Z	2	16	4	4	2
D$_{calc}$, Mg/m^3	1.187	1.106	1.147	1.210	1.204
Abs coeff, mm^{-1}	0.128	0.155	0.104	0.118	0.114
F(000)	1096	3280	1448	1272	736
Temp, K	173(2)	173(2)	173(2)	173(2)	123(2)
Reflections	34791	54701	36660	39296	22543
Independent	13873	11216	6880	8268	8919
*R*int	0.0381	0.0521	0.0590	0.0312	0.0336
Parameters	769	575	448	434	504
R1 [$I > 2\sigma(I)$]	0.0527	0.0761	0.0410	0.0456	0.0430
wR_2 (all data)	0.1481	0.2533	0.1018	0.1221	0.1103

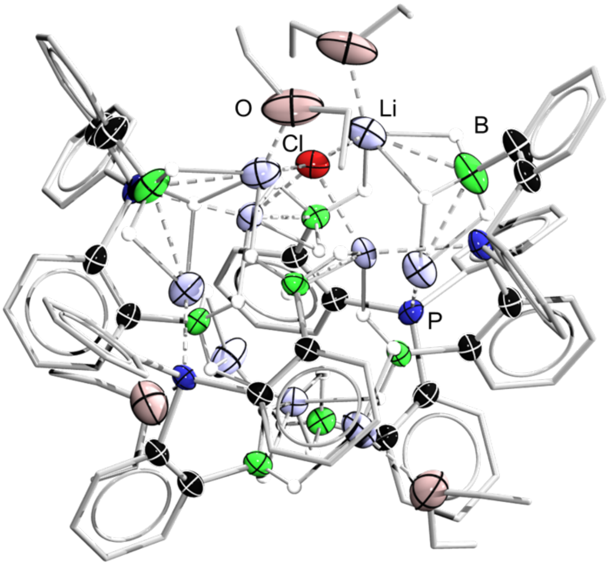


Figure S2 Solid-state structures of **1-Int**. The structure is constructed with 4 molecules of **1-Int**, 1 molecule of LiCl and 4 molecules of Et2O. Thermal ellipsoids are drawn at 30% probability. Periphery ellipsoids are omitted for clarity.

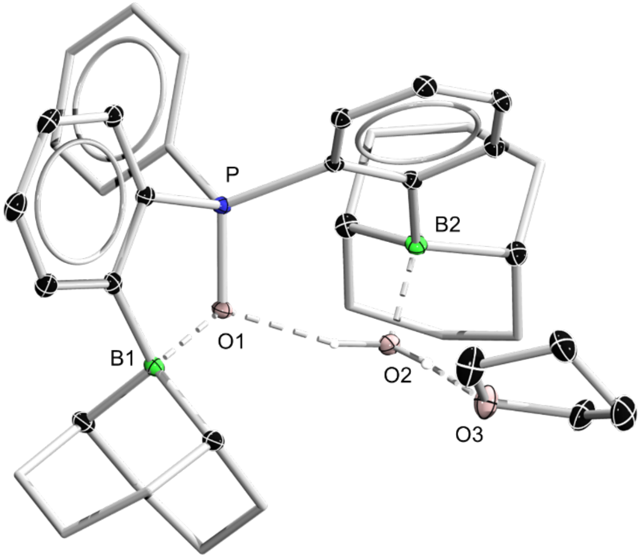


Figure S3 Solid-state structures of **3·H_2O**. Thermal ellipsoids are drawn at 30% probability. Periphery ellipsoids are omitted for clarity.

3. Computational section

Computational details

All the electronic structure calculations were performed using Gaussian09 rev. C.01 package.[4] Geometry optimizations were carried out with the long-range hybrid functional ωB97X–D[5] in conjunction with the Pople's 6-311G(d) triple-ζ quality basis set with one polarization function. Subsequent harmonic frequency calculations were performed to corroborate the character of each optimized species. Depending on the number of negative eigenvalues of the hessian matrix, it is possible to classify each optimized structure as minimum (zero) or transition state (only one). Thermal and entropy corrections to the total energy were taken from the thermochemistry analyses in the output file at 298K and 1 atm.

Finally, the solvation effects added to the electronic Hamiltonian were taken into consideration by performing single-point calculations over the optimized geometries at the ω-B97XD/6-311G(d) level of theory though the PCM[6] model using the SMD[7] parameters according to the Truhlar's model with benzene as solvent (ε = 2.2706). These energies were added to the gas-phase calculations and are reported as the final energy values. Therefore, the final reported energy values are in solvent-phase calculated at the SMD(benzene):ω-B97XD/6-311G(d).

3.1 Reaction of 1b with CN*t*Bu

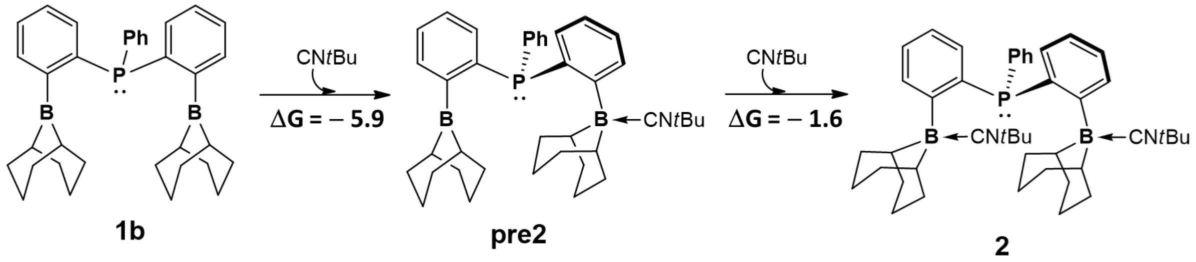


Figure S4 Reaction free energies (kcal/mol) of **1b** with CNtBu.

3.2 Reaction of 1b and H_2O

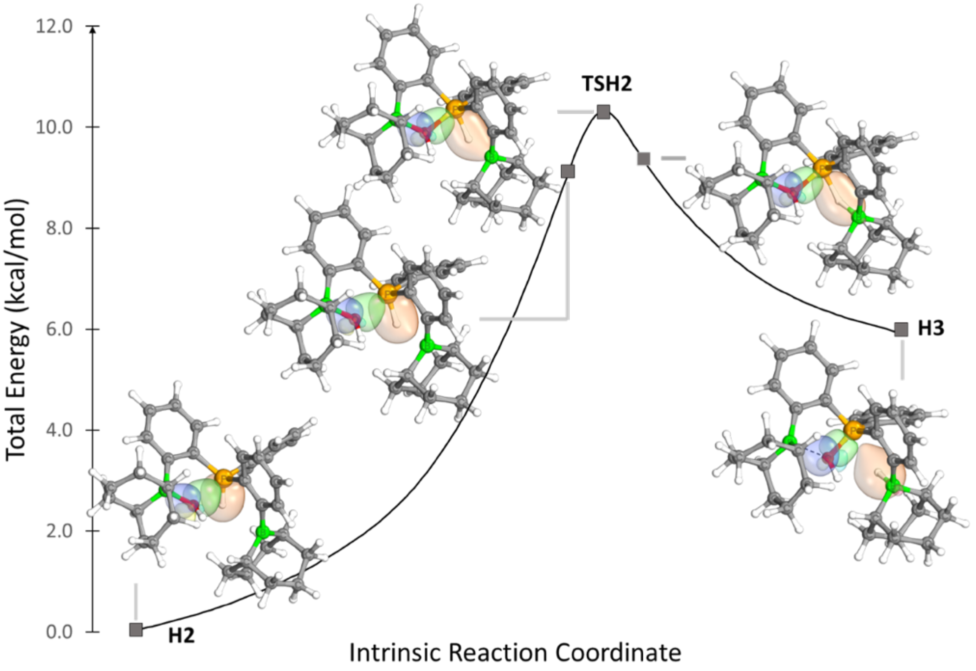


Figure S5 Intrinsic bonding orbitals (IBO) between **H2** and **H3** during the reaction of **1b** and H_2O

3.3 Isomerization of 3 to 3-Iso

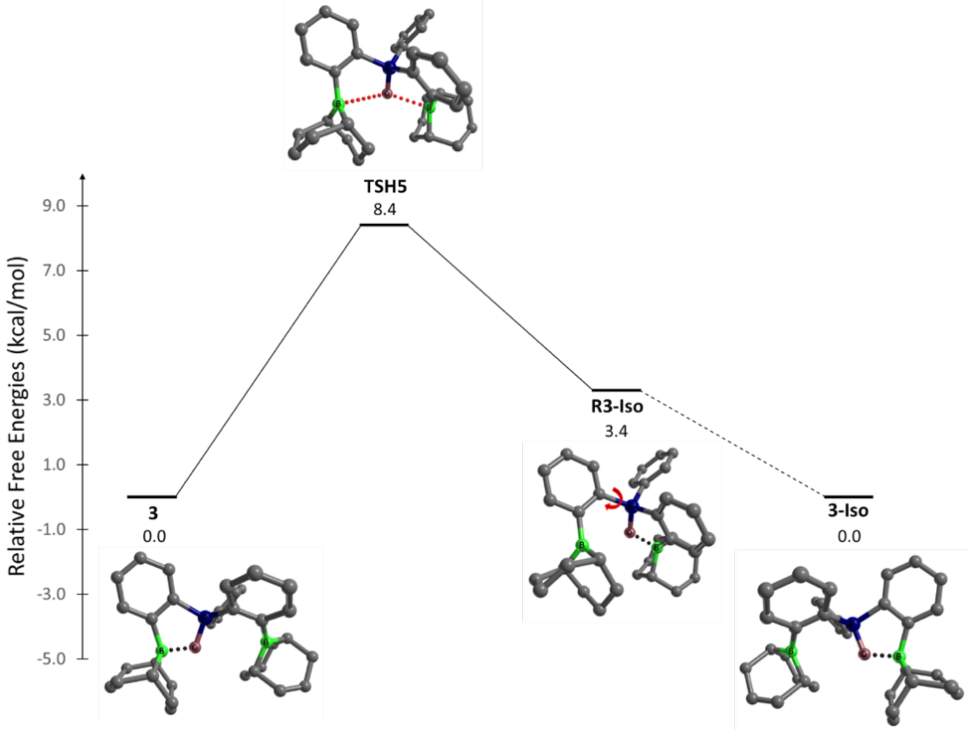


Figure S6 Computed relative free energy profile (kcal/mol) for the proposed isomerization mechanism of **3** into **3-iso**. Optimized geometries shown for clarity.

3.4 Reaction of 1b with MeOH

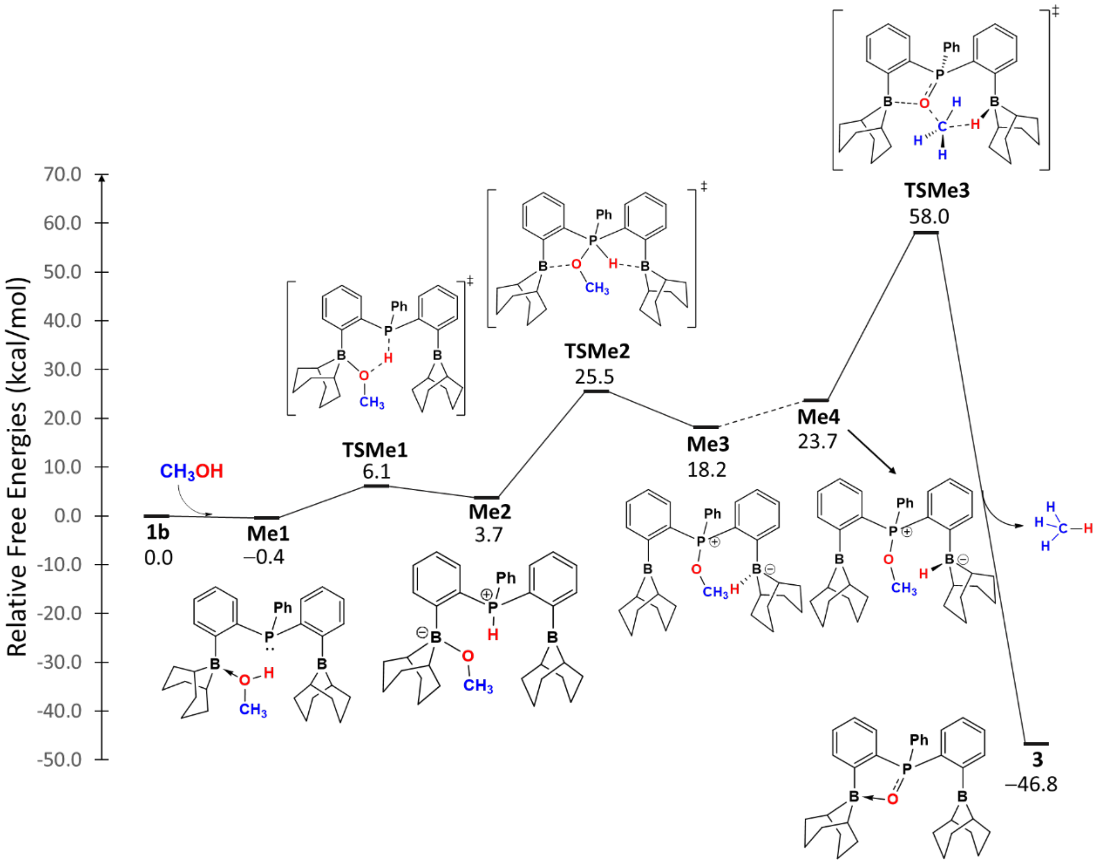


Figure S7 Energy profile of the reaction of **1b** with MeOH.

3.4 Reaction of 1b with H_2O and D_2O

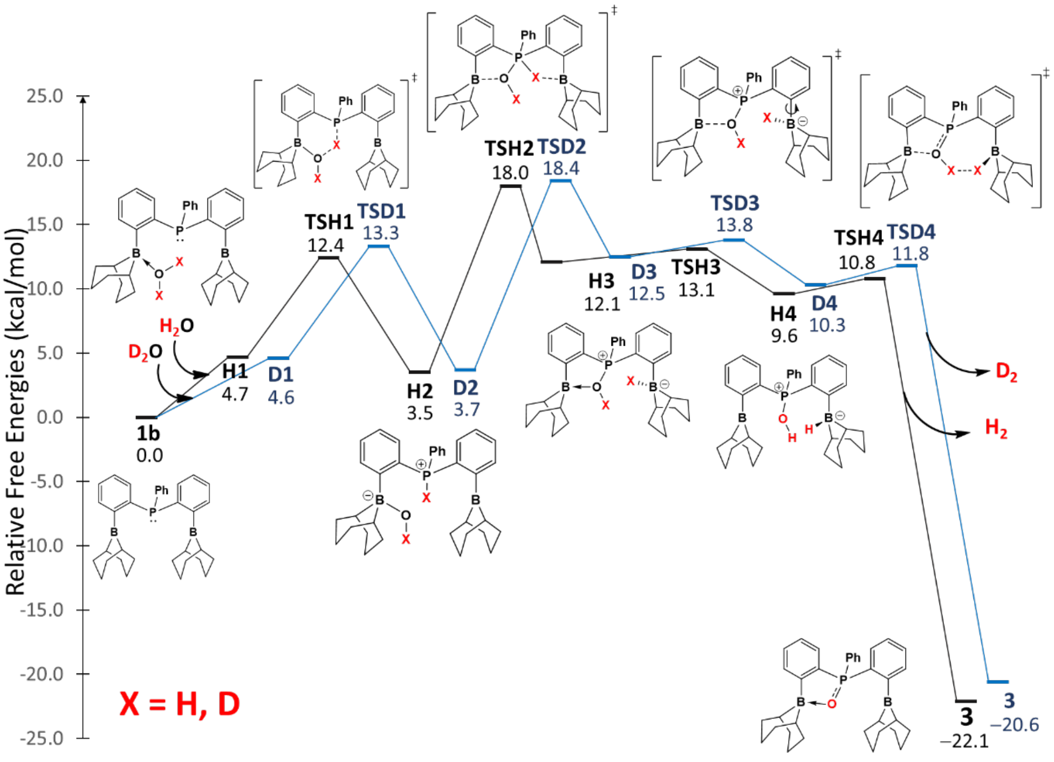


Figure S8. Energy profile of the reaction of **1b** with H_2O (black line) and D_2O (blue line).

3.5 Kinetic Isotope Effect of the reaction of 1b with H_2O/D_2O

To compute the Kinetic Isotope Effect (KIE)[8] of the reaction of **1b** with H_2O/D_2O, we calculated the energetic profile for **1b** with D_2O as shown in **Figure S8**. For this, we used the optimized geometries of the reaction mechanism of **1b** with H_2O (**Figure S8**, X = H), followed by calculation of the Hessian matrix from which harmonic vibrational frequencies for all isotopomers are derived by introducing isotope masses. The computed energetic span is then used to calculate reaction rates in the framework of transition-state theory by using Boltzmann expression:

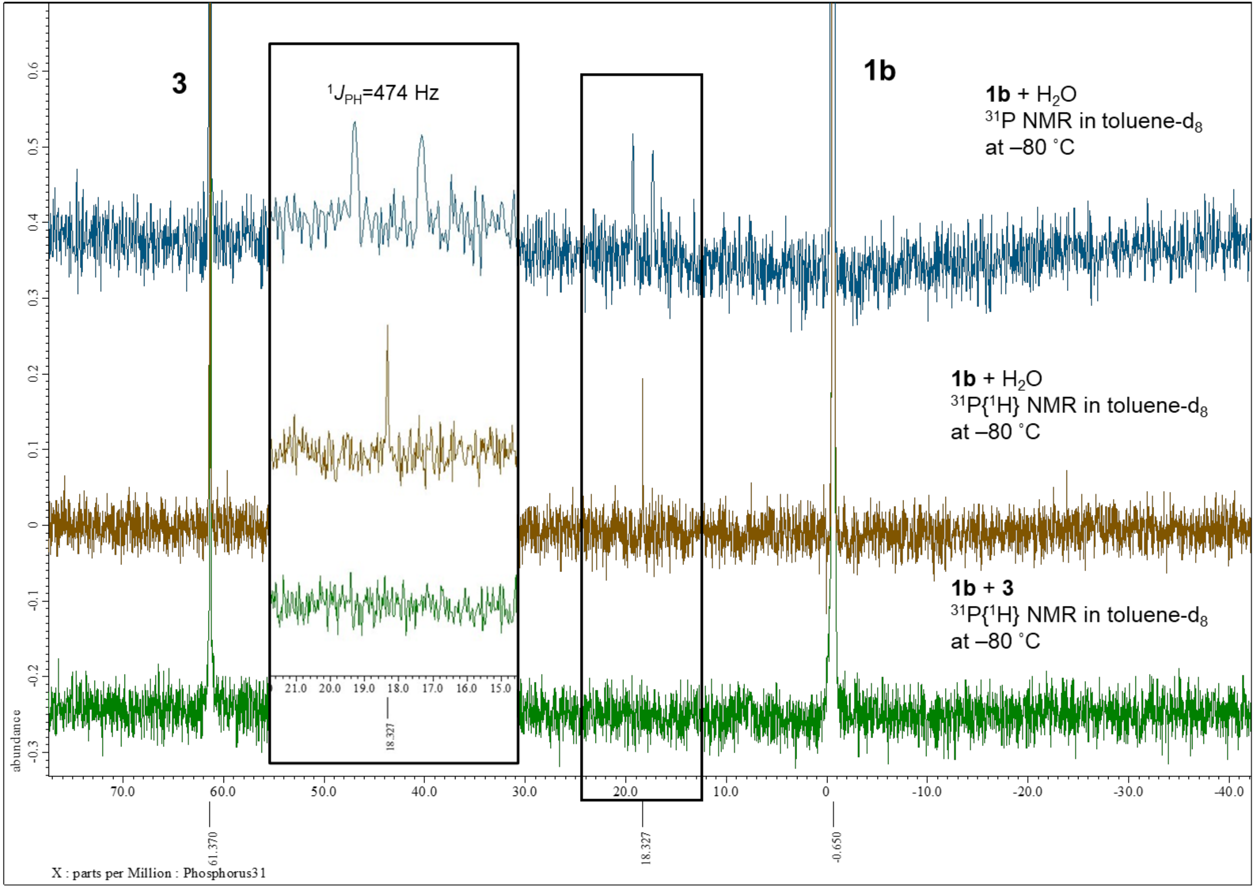
$$KIE = \frac{k_{light}}{k_{heavy}} = \exp\left(\frac{\Delta \mathrm{G}^{\ddagger}_{\mathrm{heavy}} - \Delta \mathrm{G}^{\ddagger}_{\mathrm{light}}}{RT}\right)$$

Where $\Delta \mathrm{G}^{\ddagger}_{\mathrm{heavy}}$ is the highest barrier energy that involves the isotopically labeled species and $\Delta \mathrm{G}^{\ddagger}_{\mathrm{light}}$ for the one that does not involve the isotopes. The calculated $\Delta \mathrm{G}^{\ddagger}_{\mathrm{heavy}}$ and $\Delta \mathrm{G}^{\ddagger}_{\mathrm{light}}$ values for energetic profile shown in **Figure S8** are 14.7 and 14.5 kcal/mol respectively, this gives a value of KIE of 1.402.

4. NMR spectra

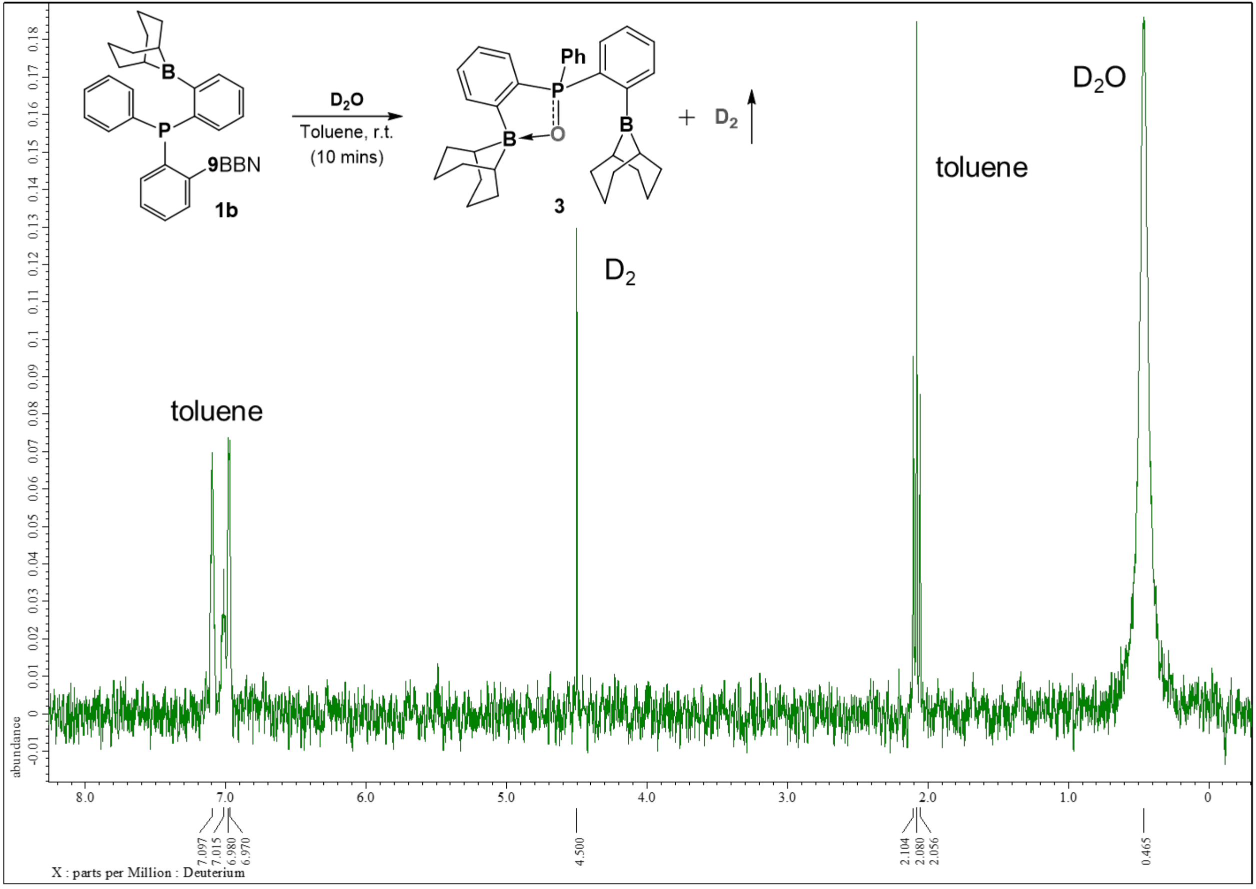
4.1 Reaction of compound 1b + H_2O at –80 °C

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 MHz)



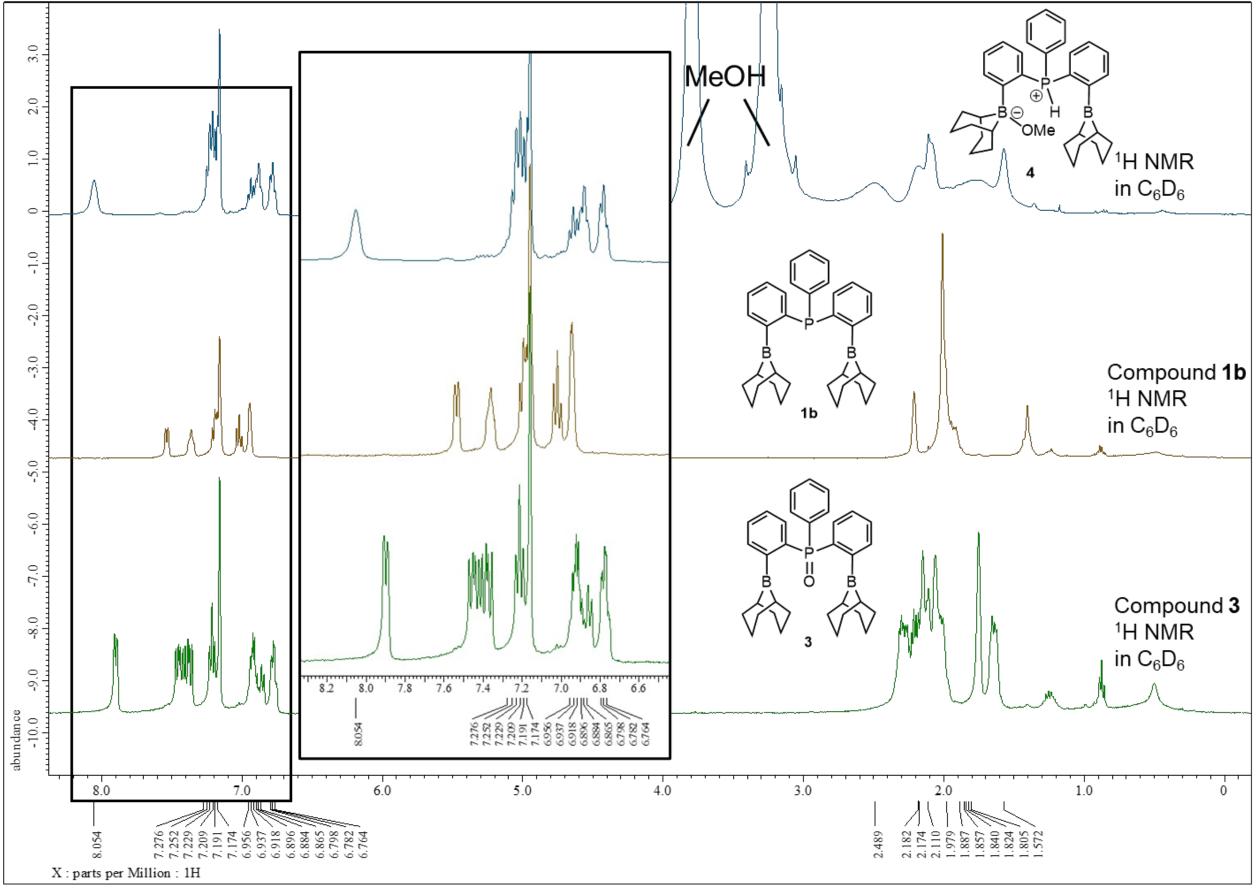
4.2 Reaction of compound 1b + D_2O

^2H NMR (toluene, 92 MHz)

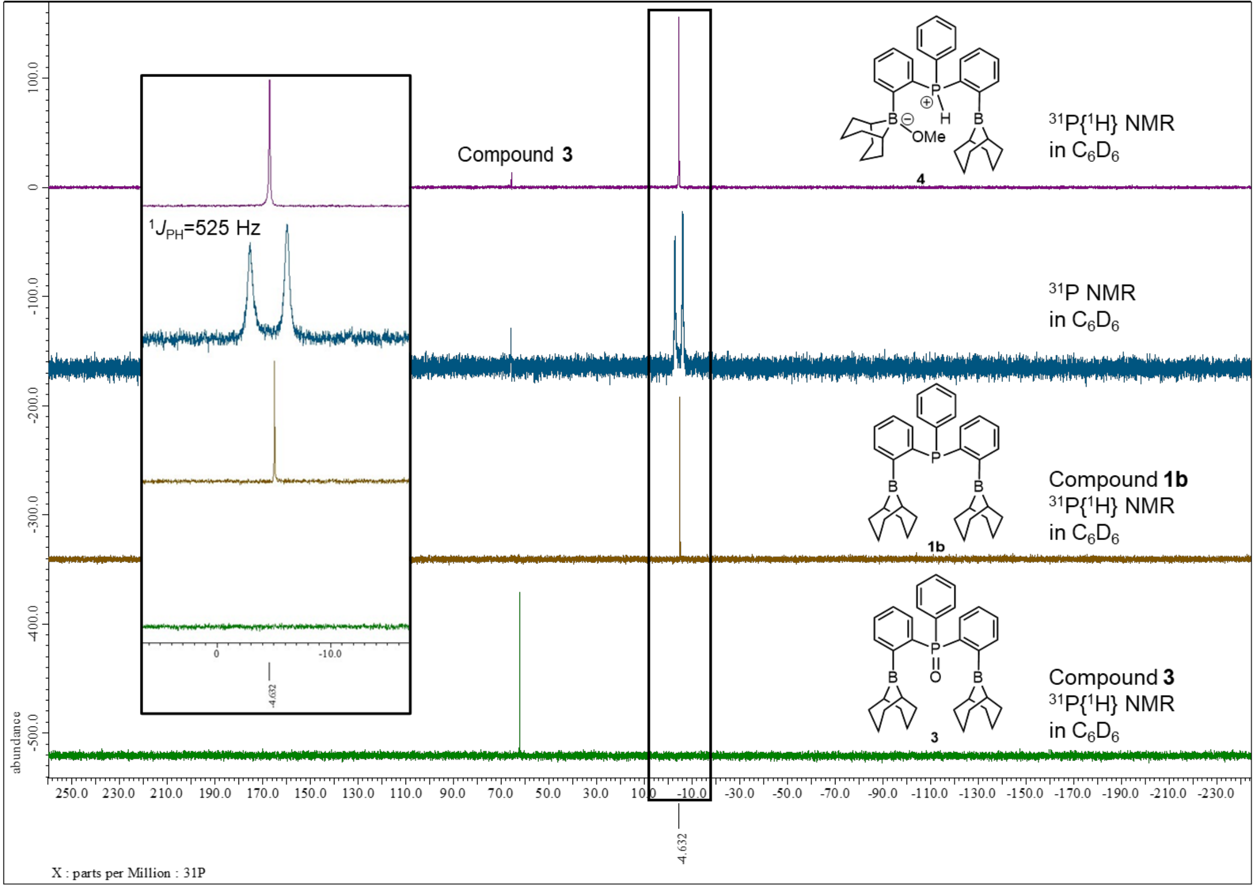


4.3 Formation of 4 from 1b with MeOH (ca. 50 eqv.)

^{1}H NMR (C_6D_6, 400 MHz)

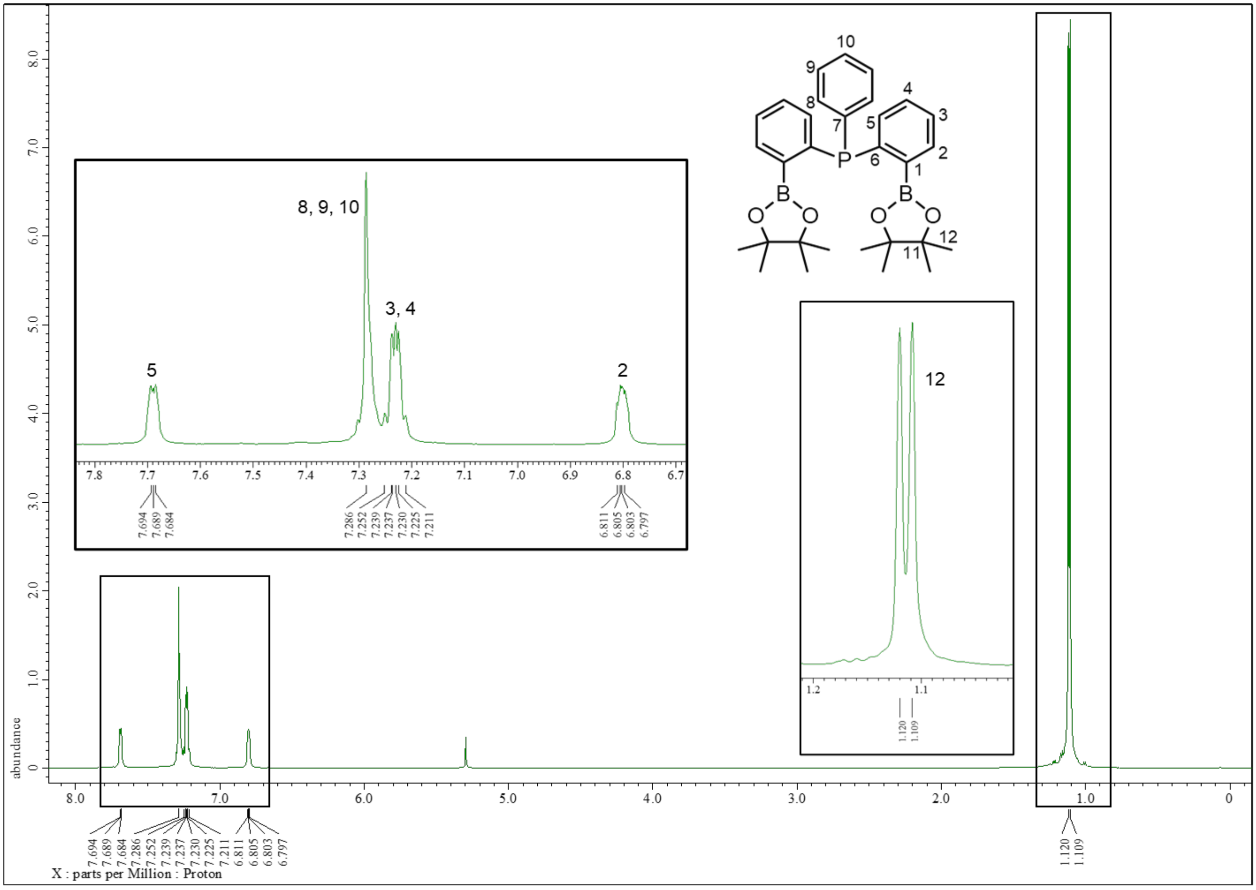


$^{31}P\{^1H\}/^{31}P$ NMR of the reaction of 1b with MeOH (C_6D_6, 160 MHz)

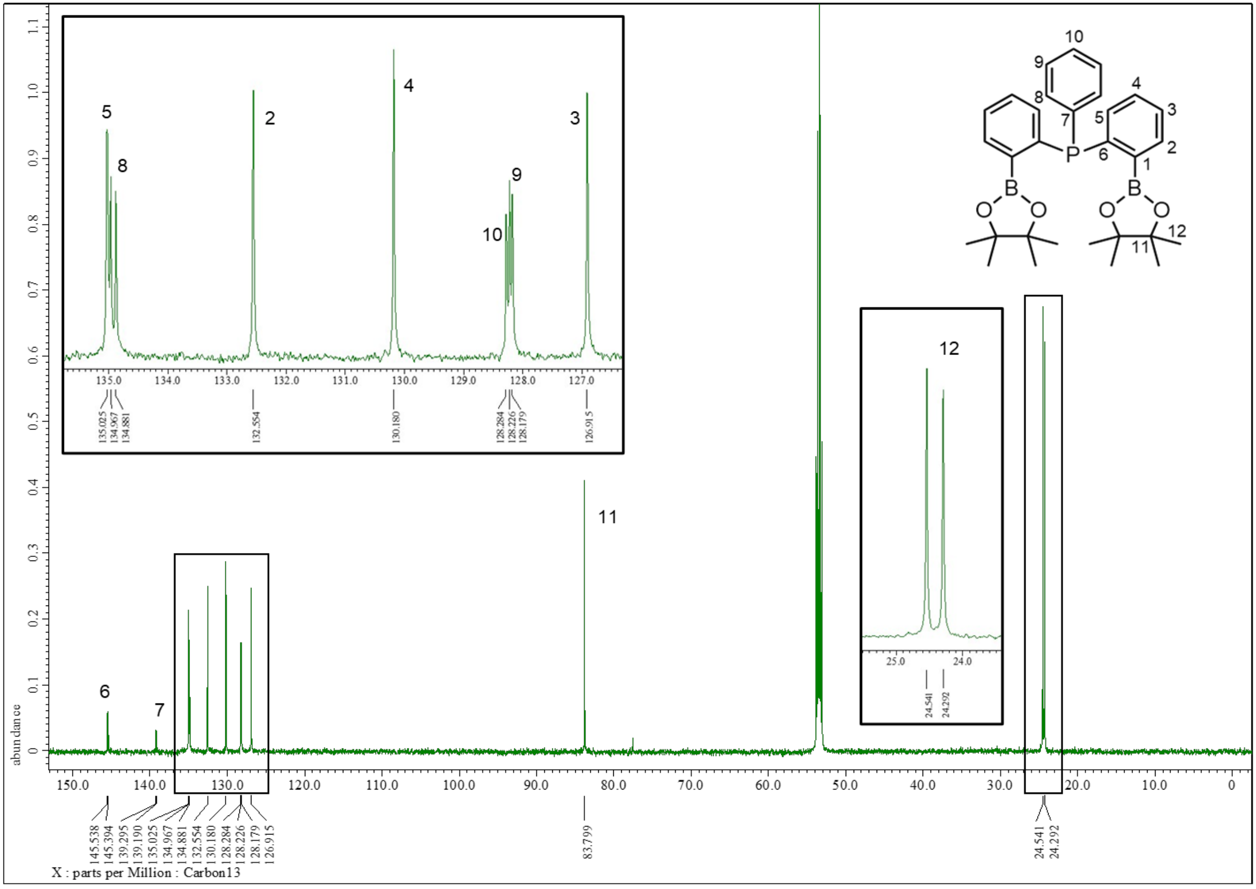


4.4 Compound 1a

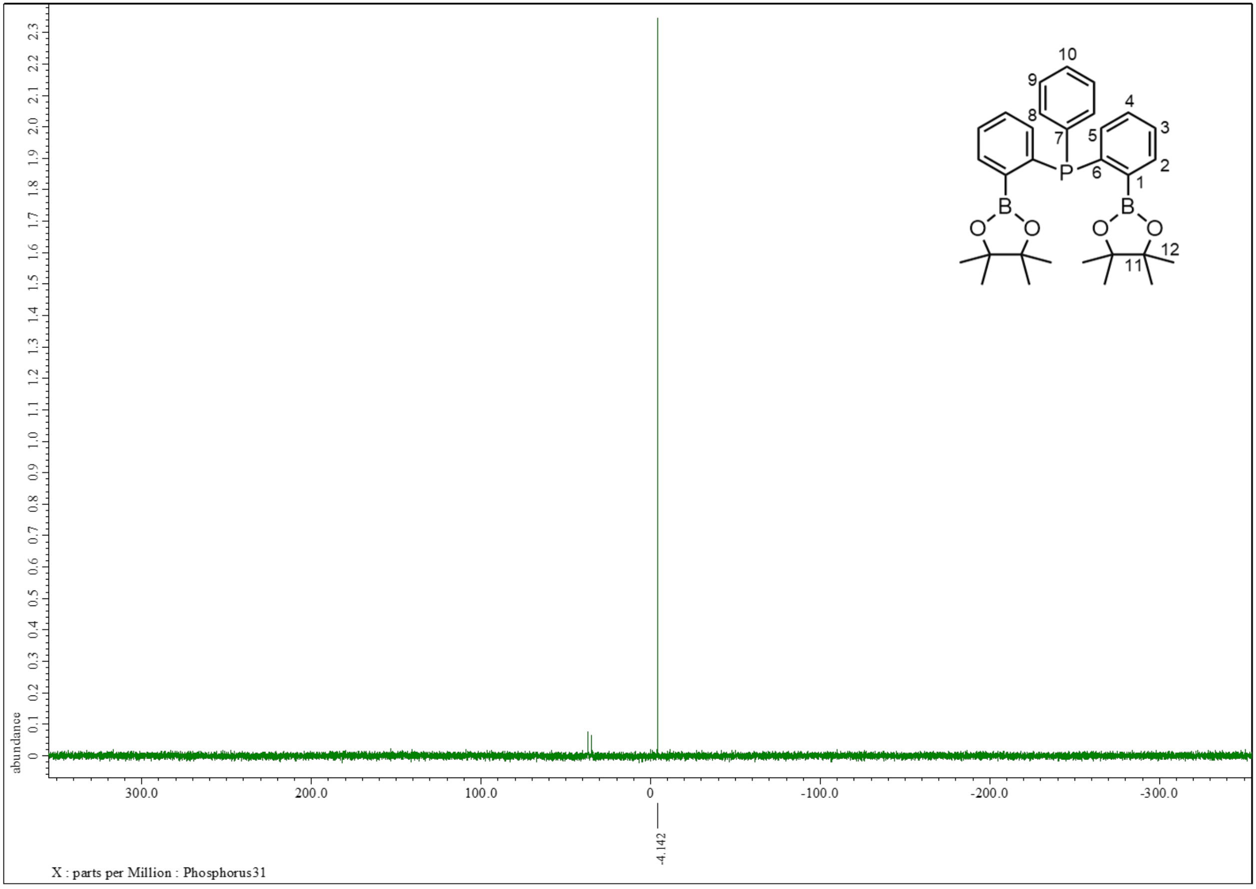
^{1}H NMR (CD_2Cl_2, 600 MHz)



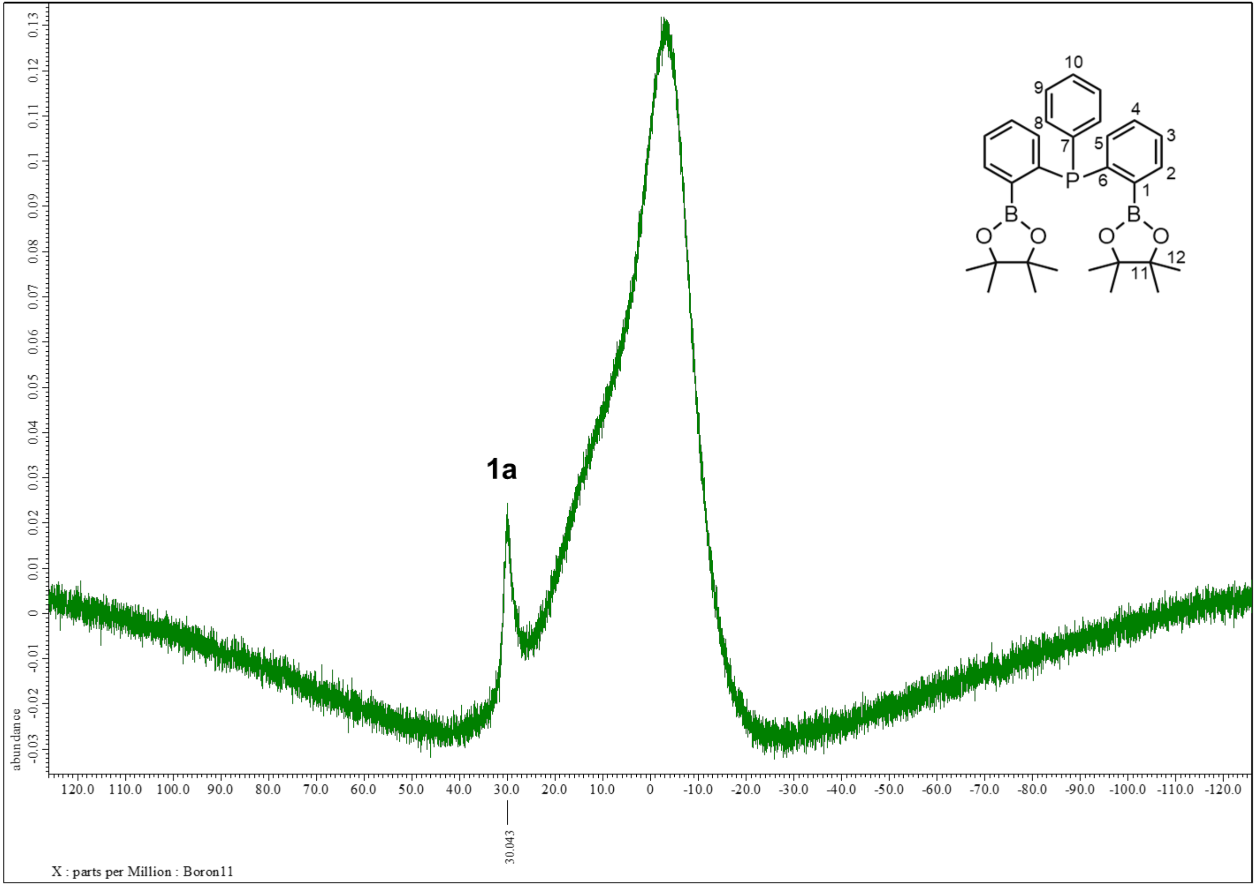
^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz)



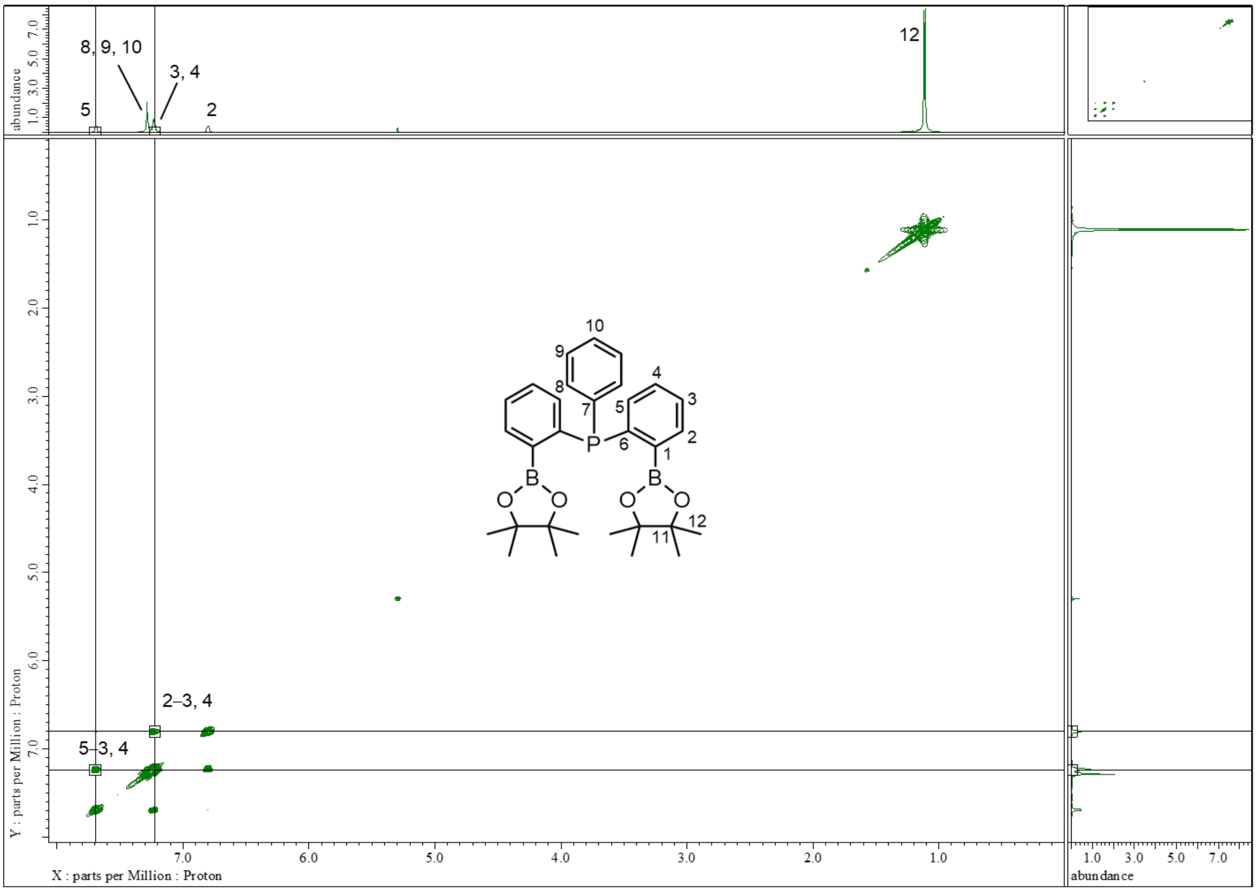
$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 MHz)



$^{11}B\{^1H\}$ NMR (CD_2Cl_2, 192 MHz)



HH COSY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5–3, 4
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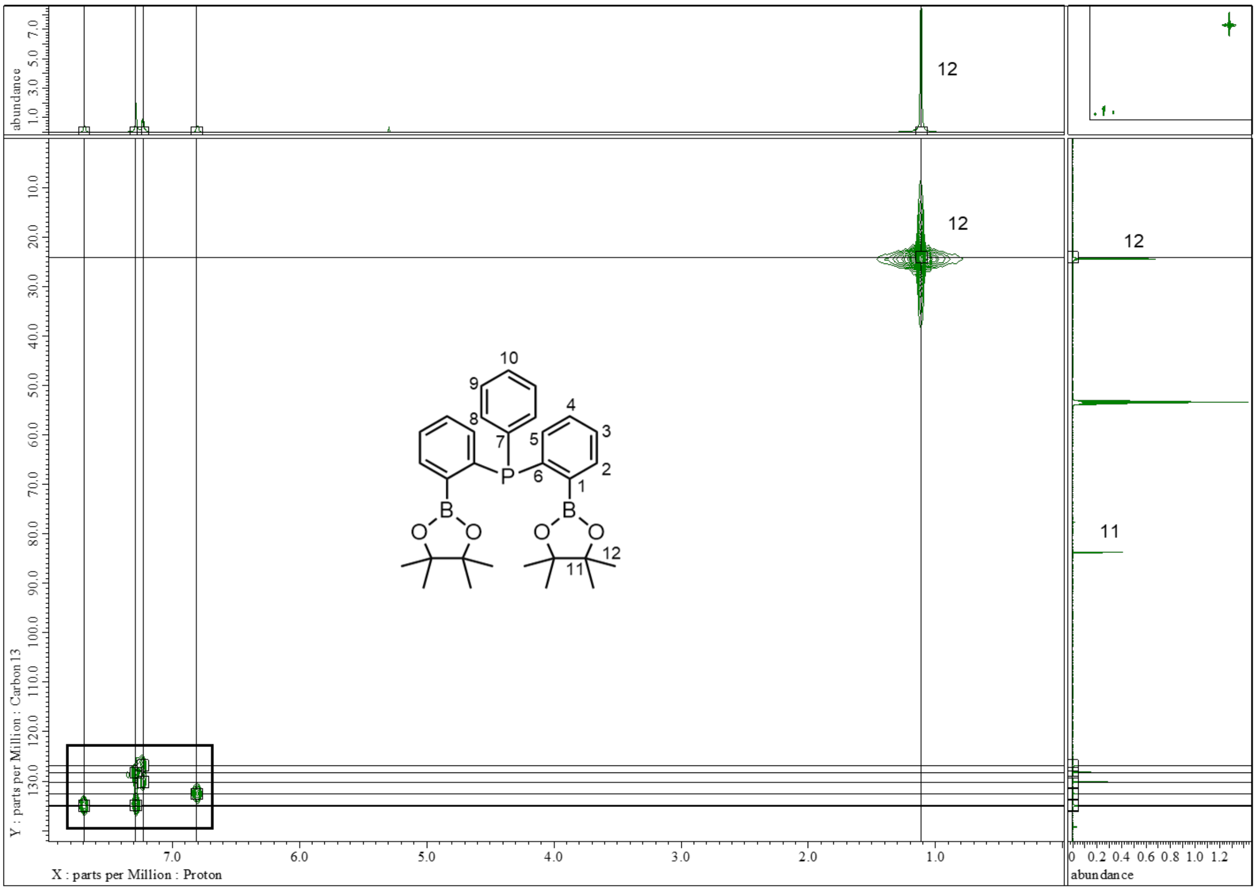
2
1
P
B
O
11
12
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
7.0
6.0
5.0
4.0
3.0
2.0
1.0
abundance

HMQC


12
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6
2
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B
O
11
12
abundance
Y : parts per Million : Carbon 13
X : parts per Million : Proton
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40.0
50.0
60.0
70.0
80.0
90.0
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130.0
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5.0
4.0
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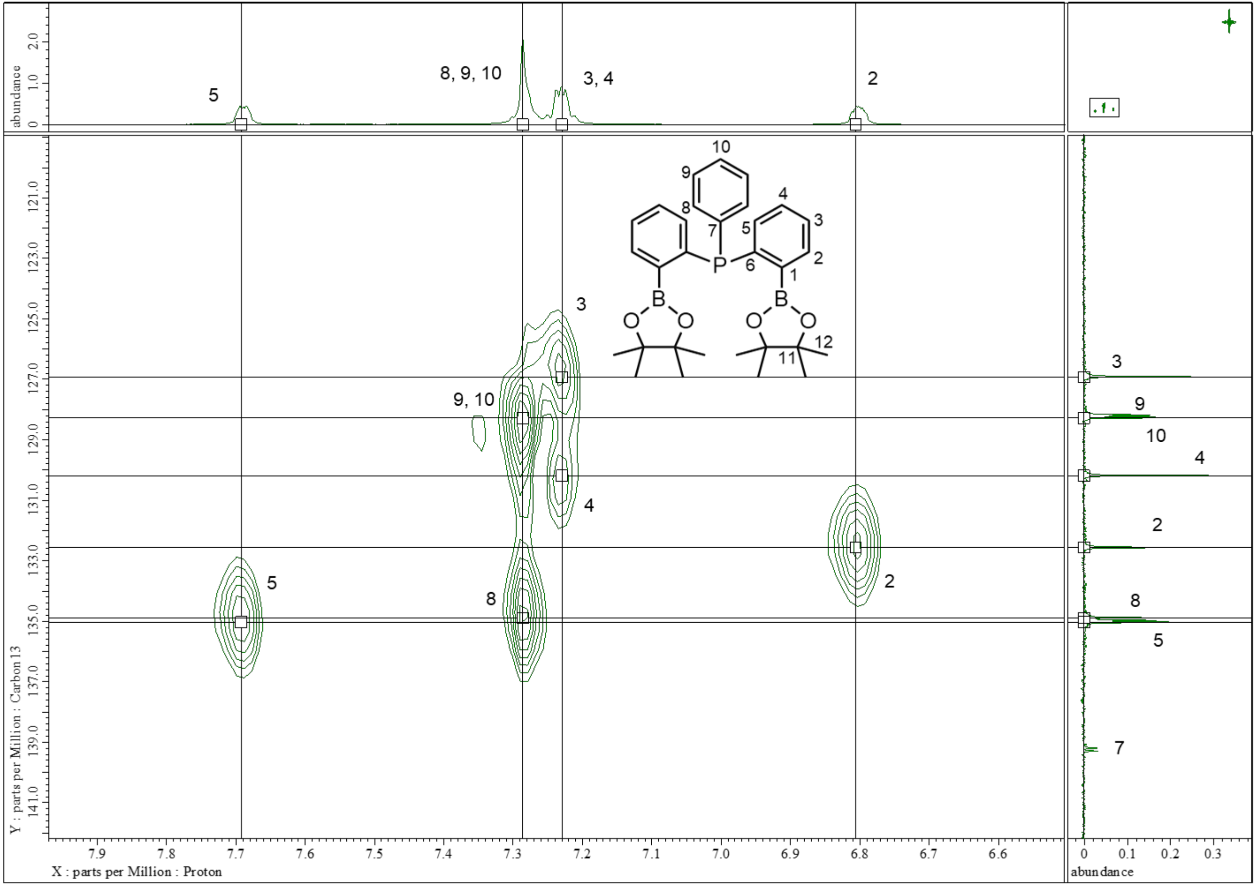
1.0
1.2
abundance

HMQC (Phenyl region)



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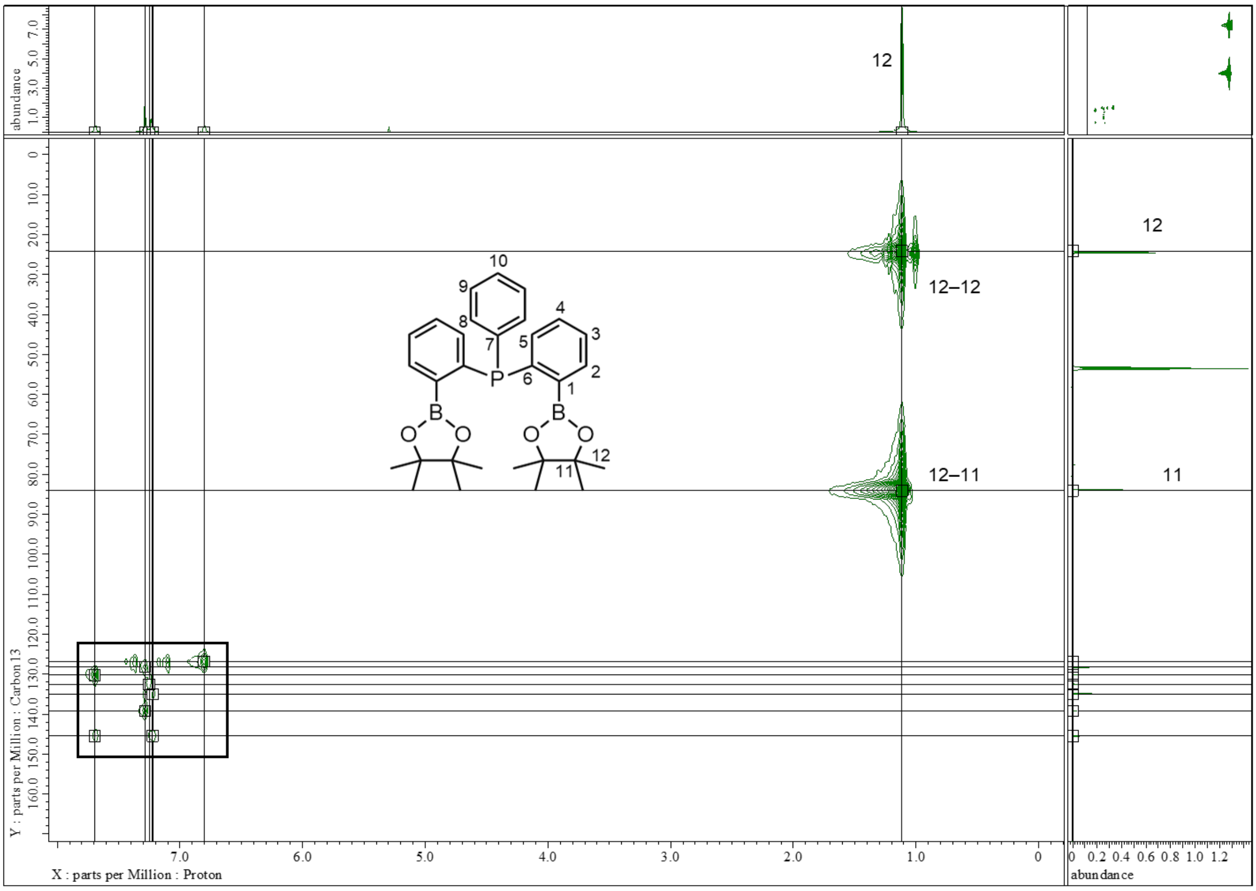
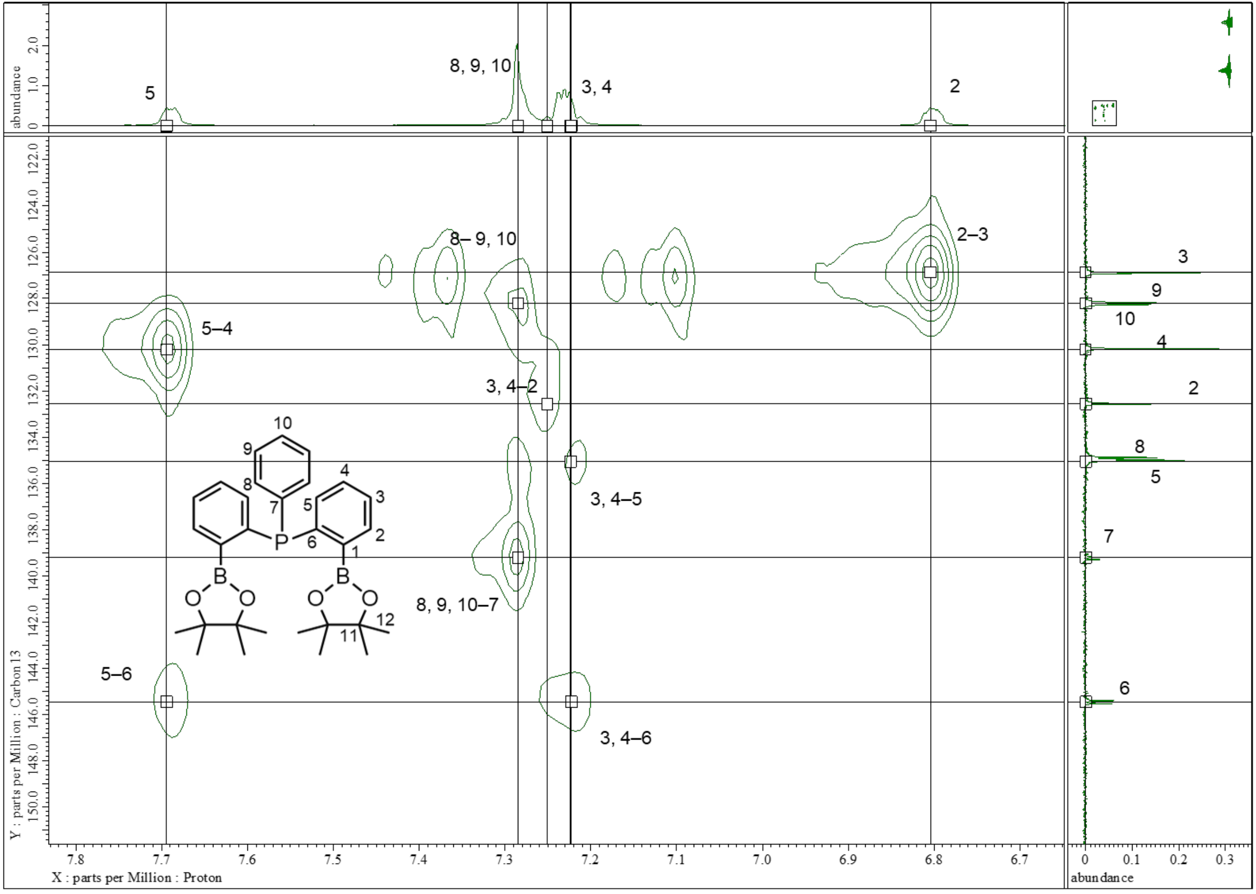
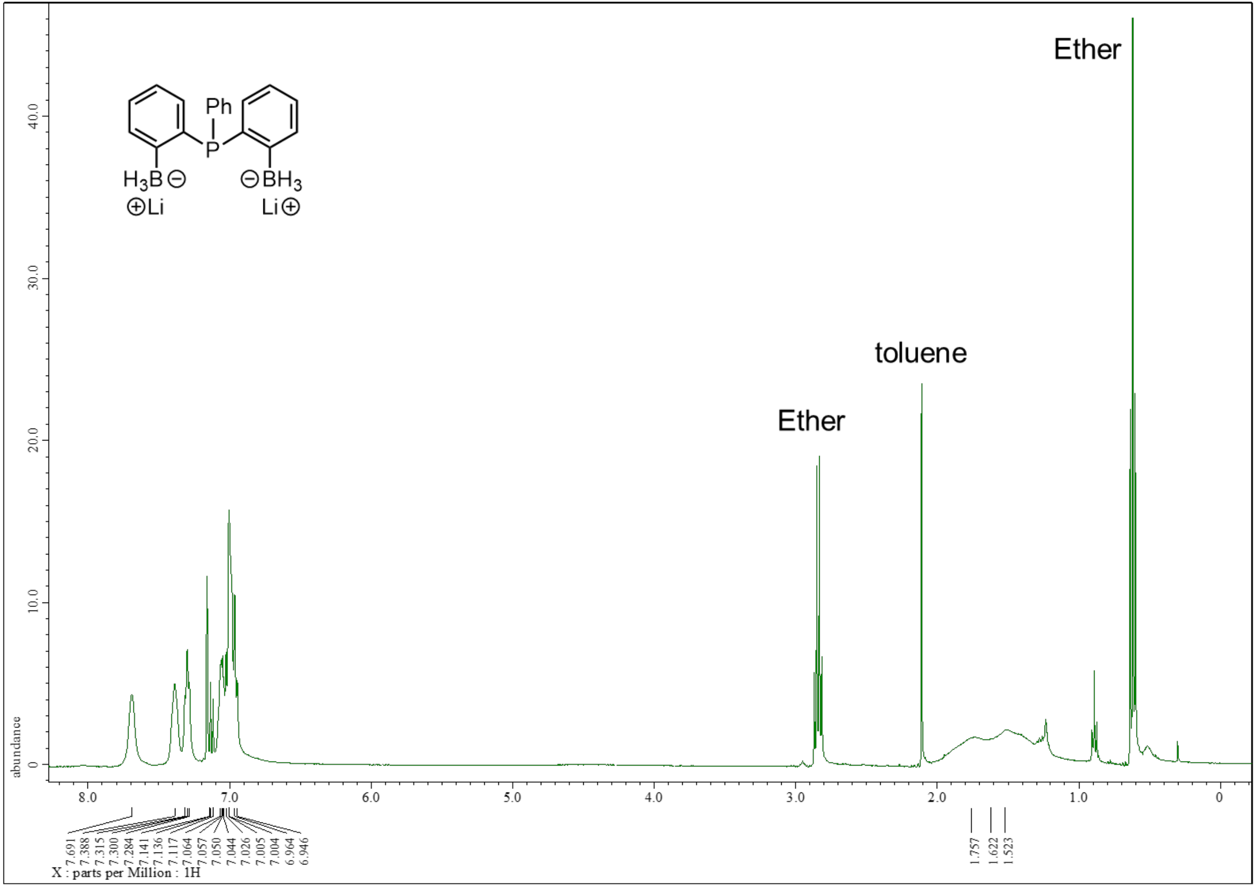


HMBC (Phenyl region)

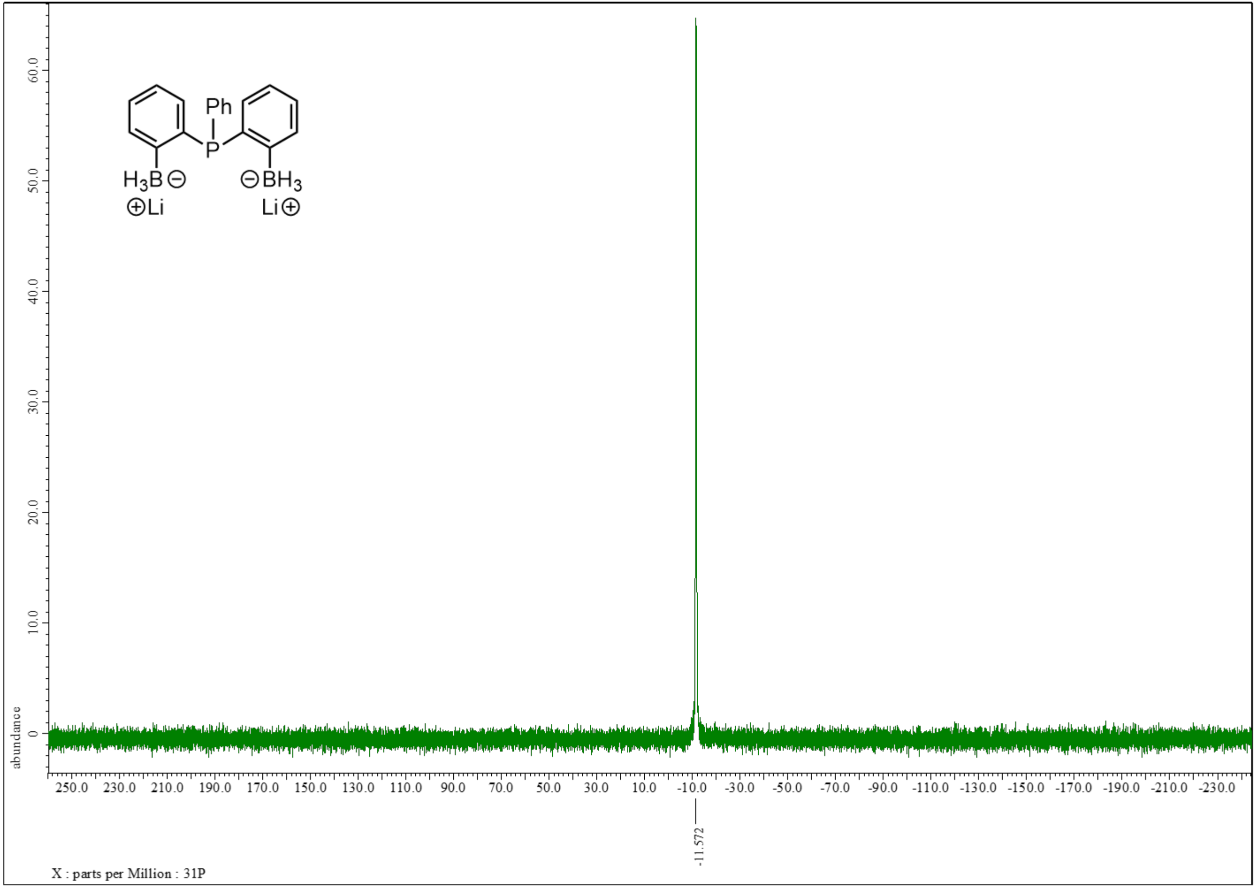


4.5 Intermediate 1-Int

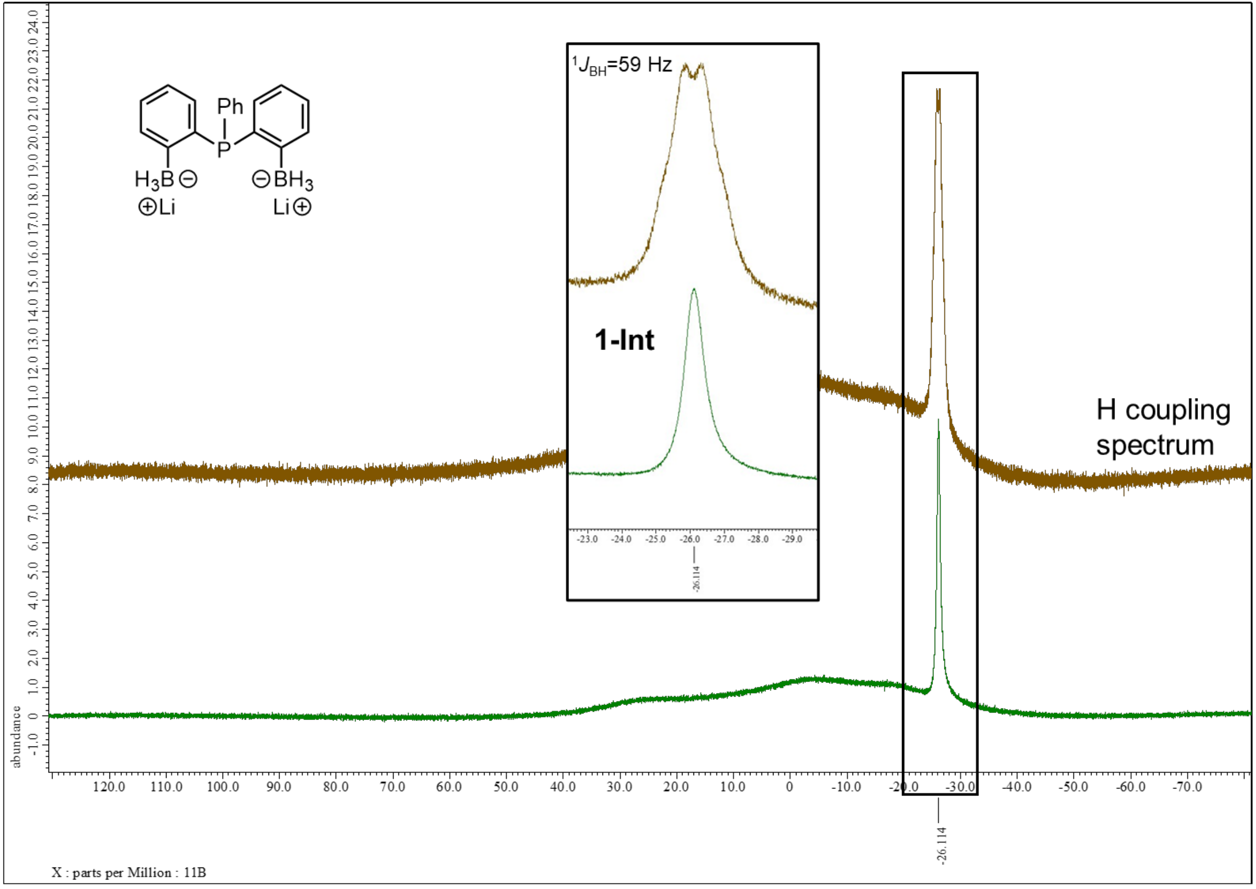
^{1}H NMR (C_6D_6, 400 MHz)



^{31}P{^{1}H} NMR (C_6D_6, 160 MHz)

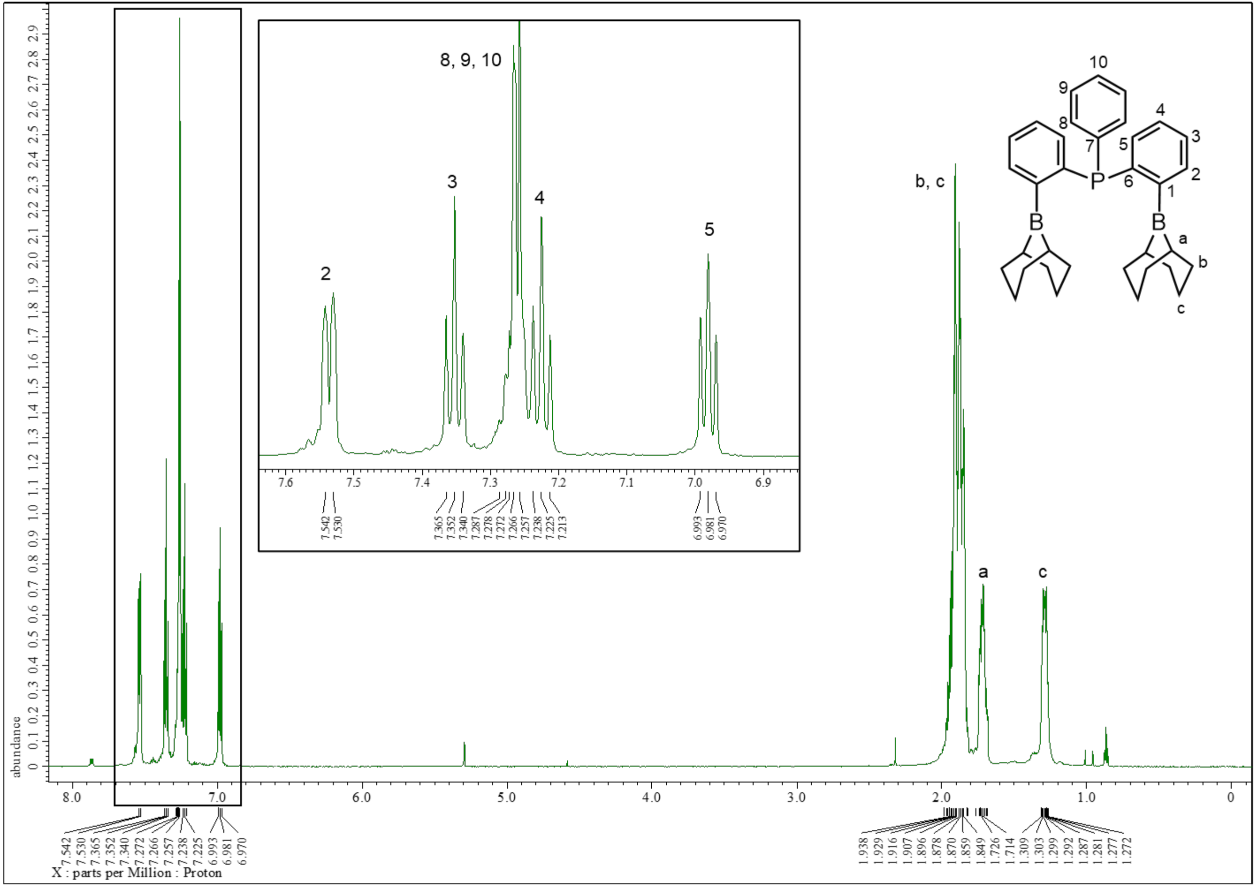


$^{11}B\{^{1}H\}$ NMR (C_6D_6, 127 MHz)

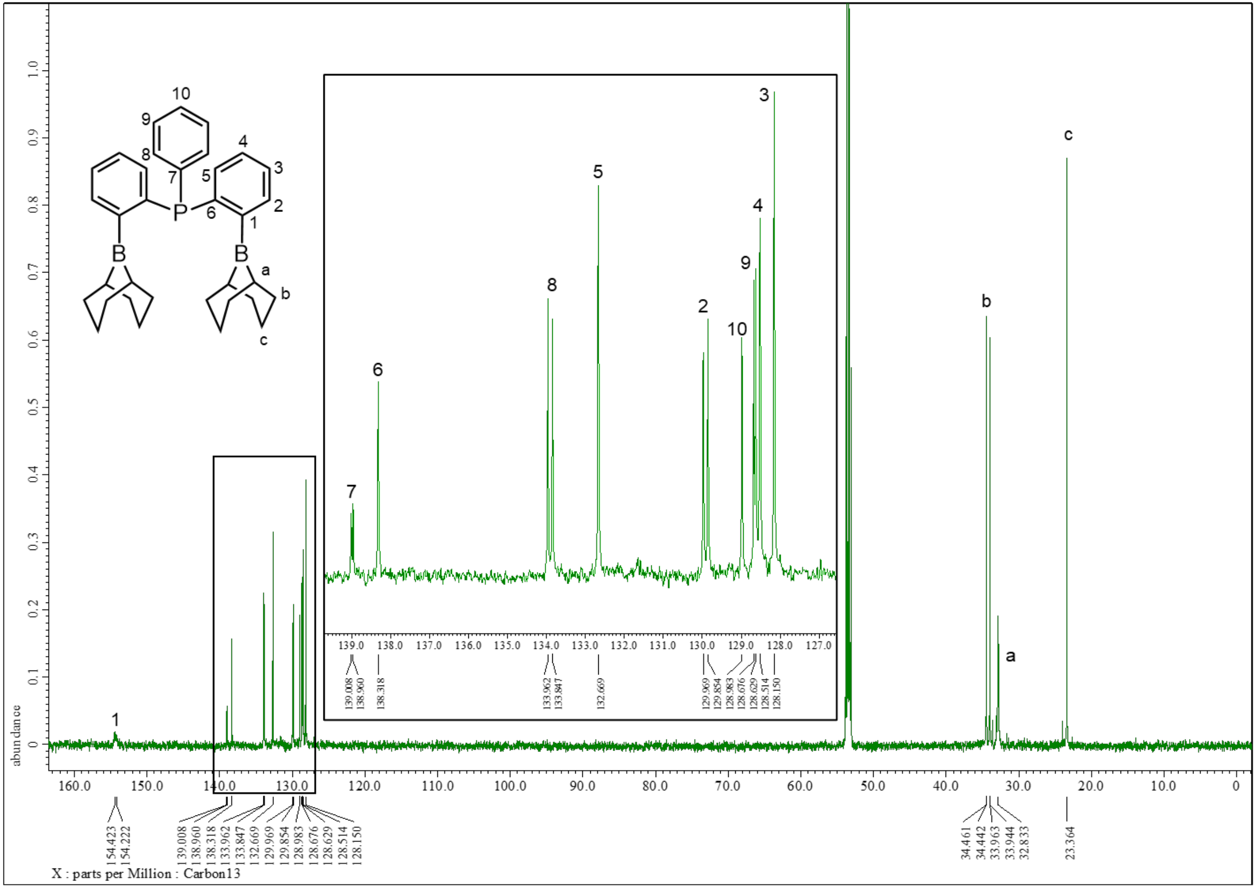


4.6 Compound 1b

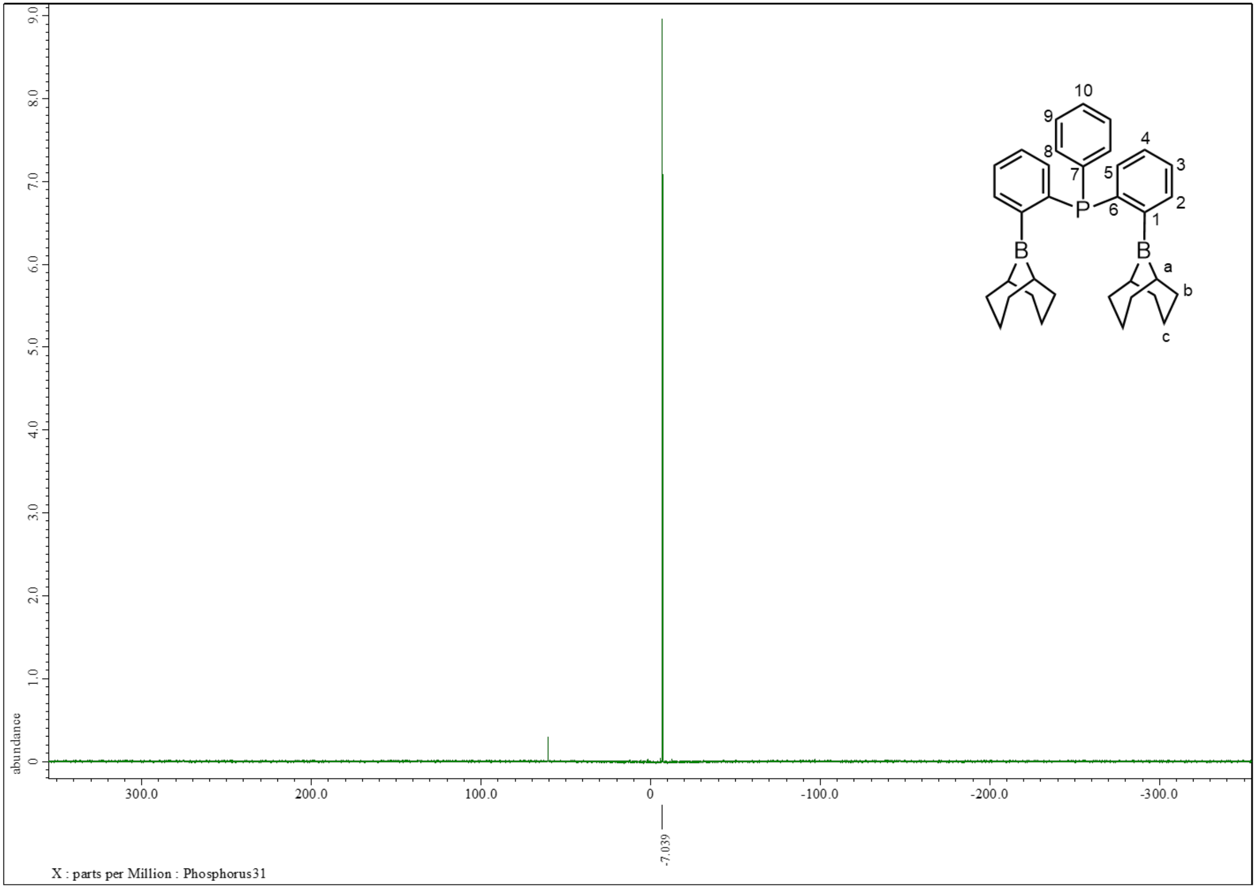
^{1}H NMR (CD$_2$Cl$_2$, 600 MHz)



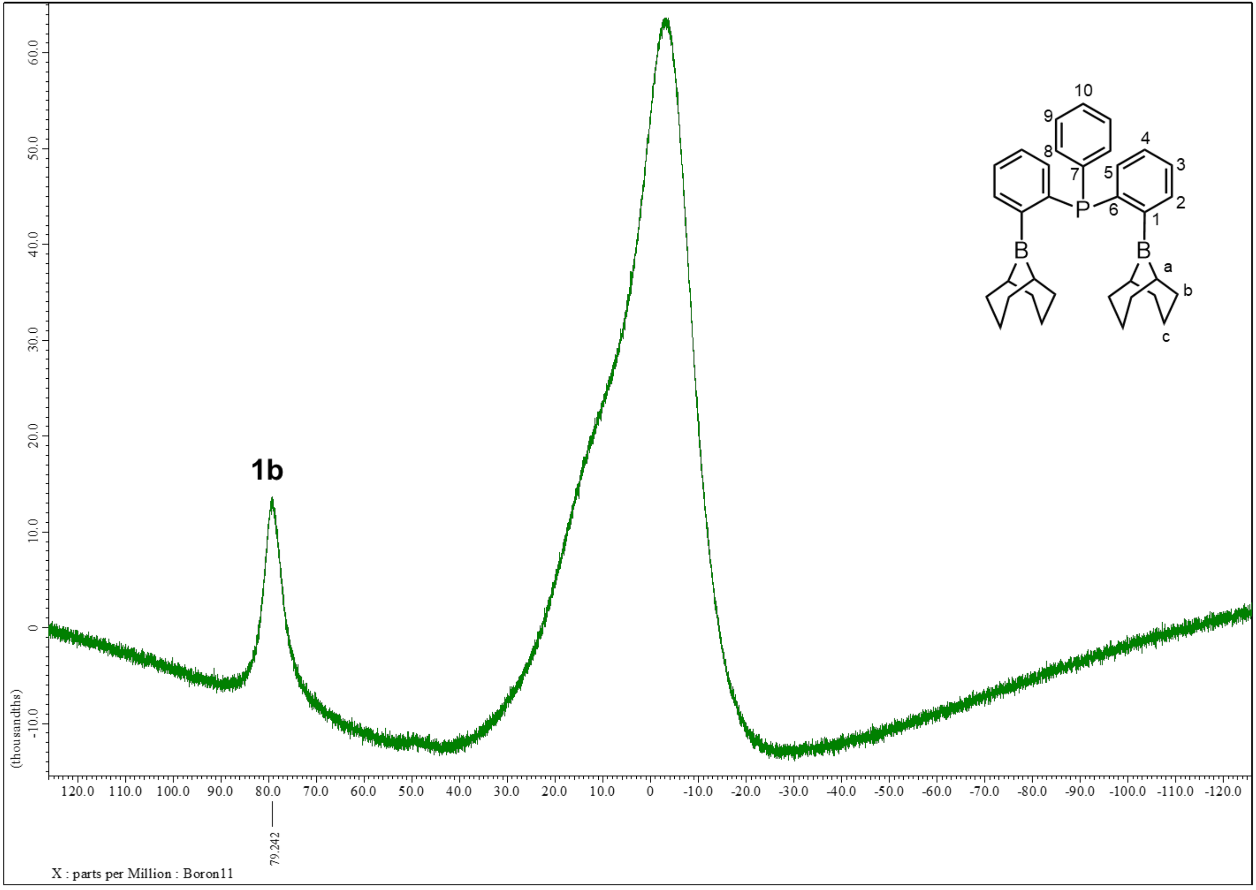
^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 151 MHz)



$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 MHz)



$^{11}B\{^1H\}$ NMR (CD_2Cl_2, 192 MHz)



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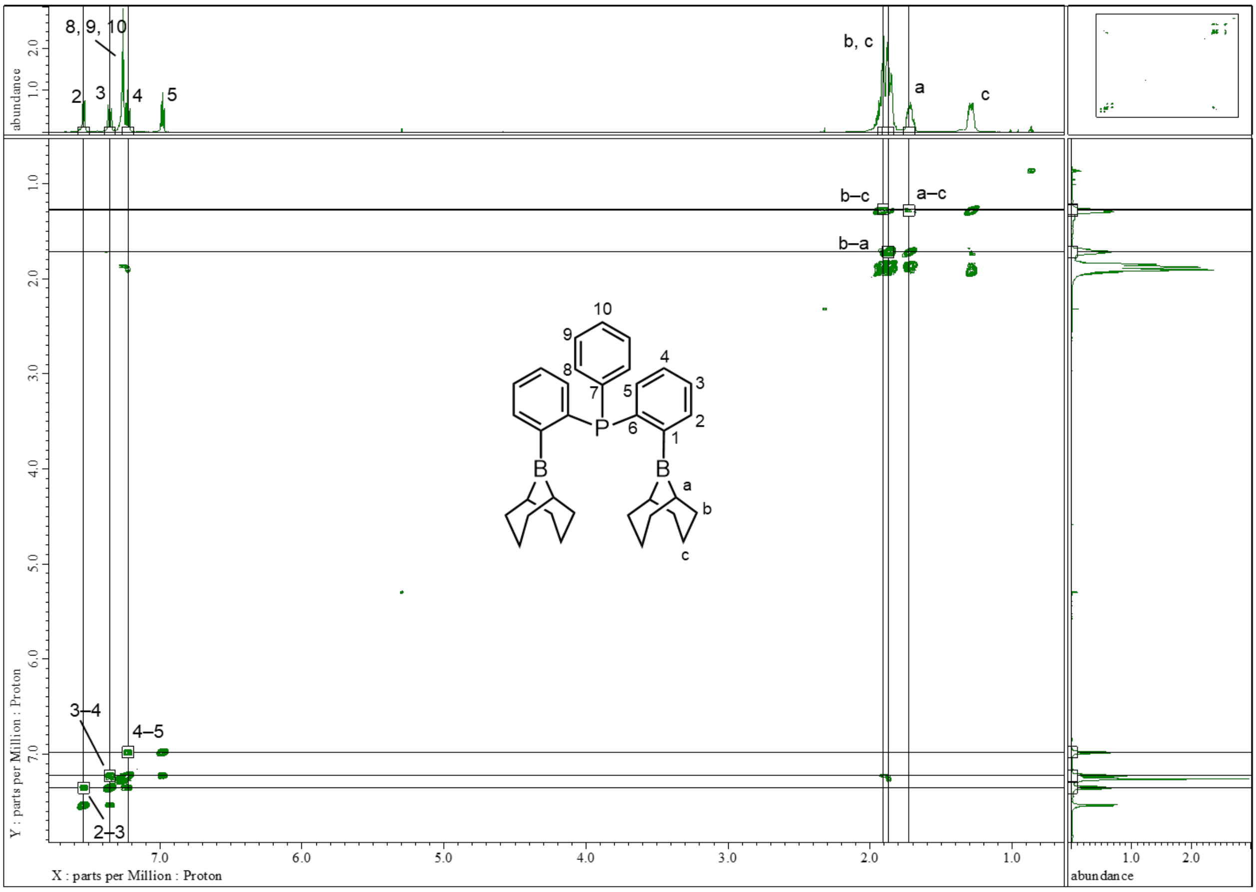

abundance
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1.0
8, 9, 10
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b, c
a
c
b–c
a–c
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3–4
4–5
2–3
10
9
8
7
4
5
3
6
2
1
P
B
B
a
b
c
Y : parts per Million : Proton
1.0
2.0
3.0
4.0
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6.0
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X : parts per Million : Proton
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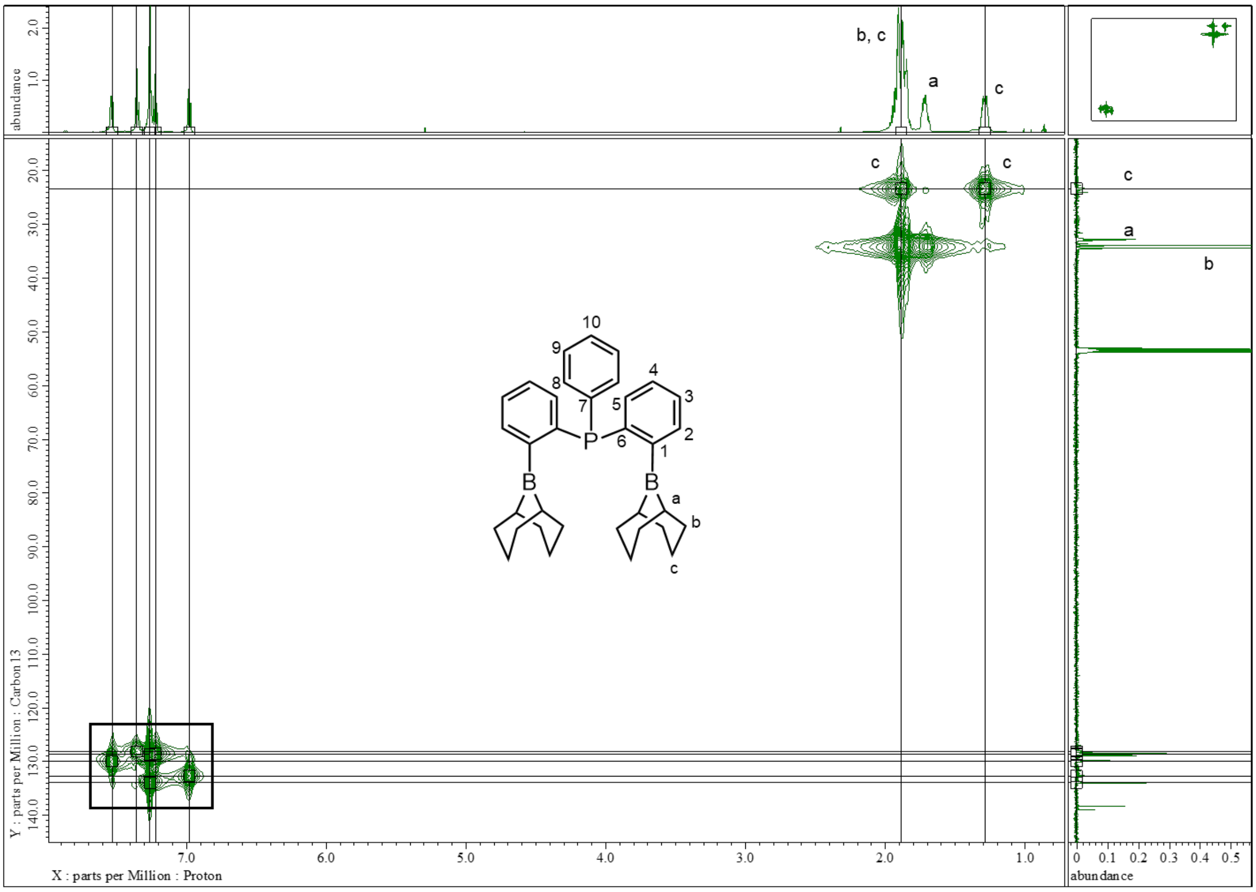
abundance
1.0
2.0

HMQC



abundance
2.0
1.0
b, c
a
c
c
c
c
a
b
10
9
8
7
4
5
3
6
2
1
P
B
B
a
b
c
Y : parts per Million : Carbon13
20.0
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40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
X : parts per Million : Proton
7.0
6.0
5.0
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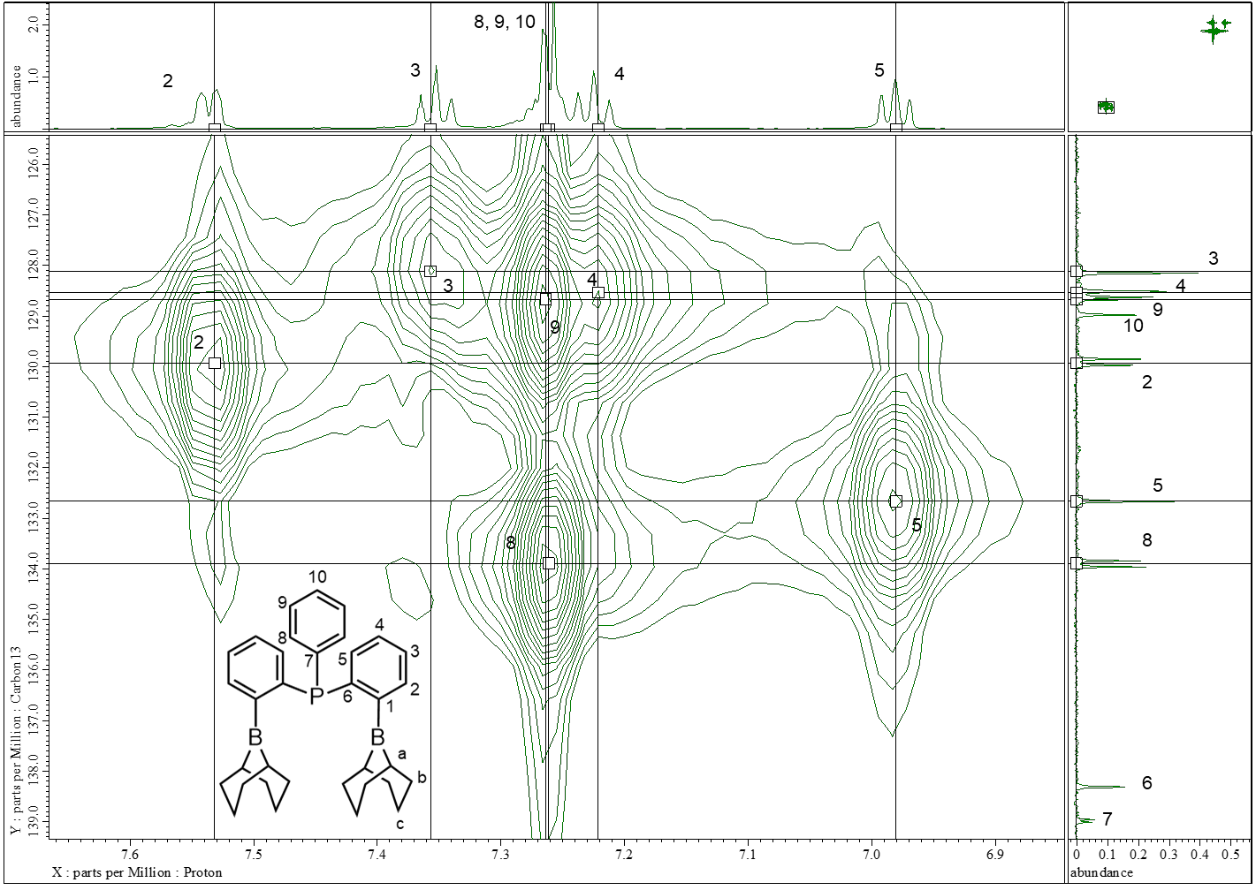
0
0.1
0.2
0.3
0.4
0.5
abundance

HMQC (Phenyl region)



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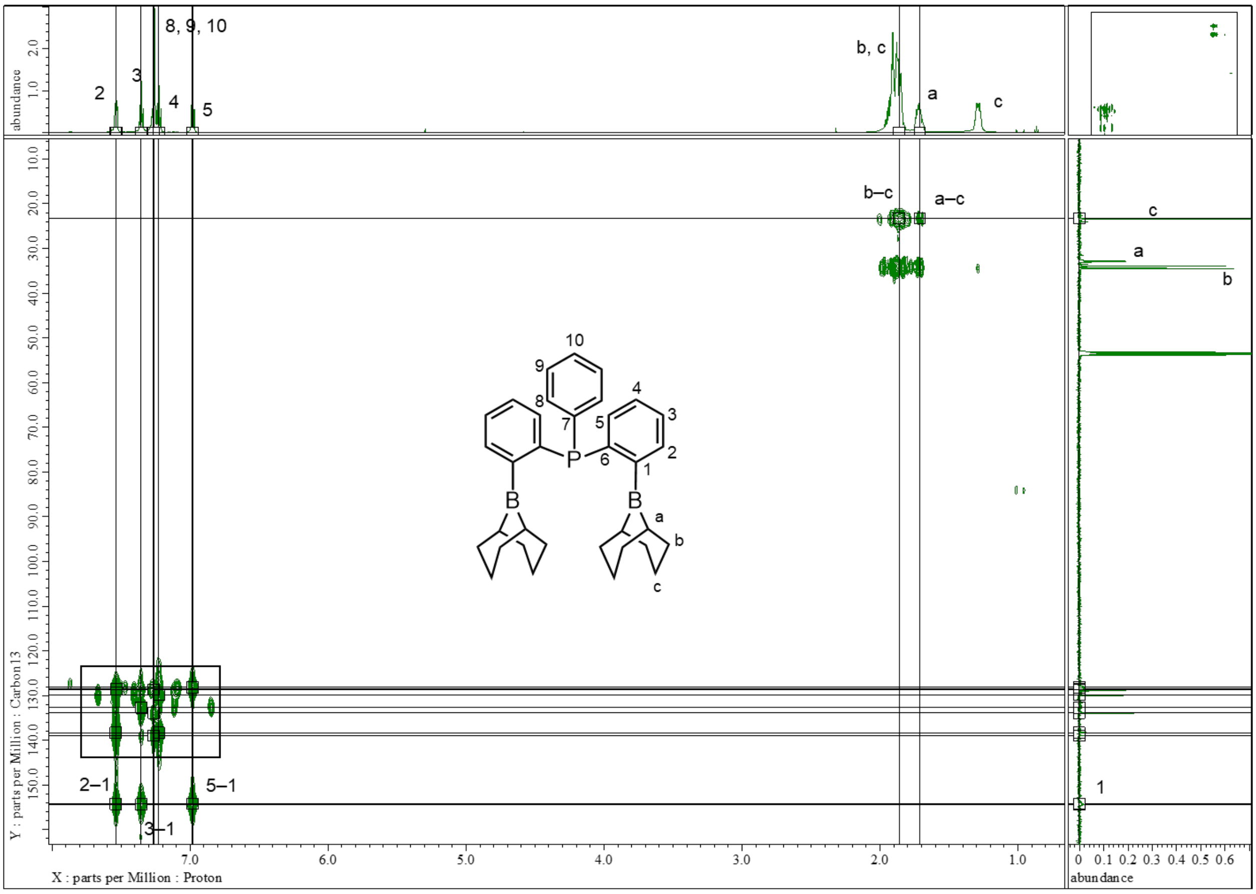
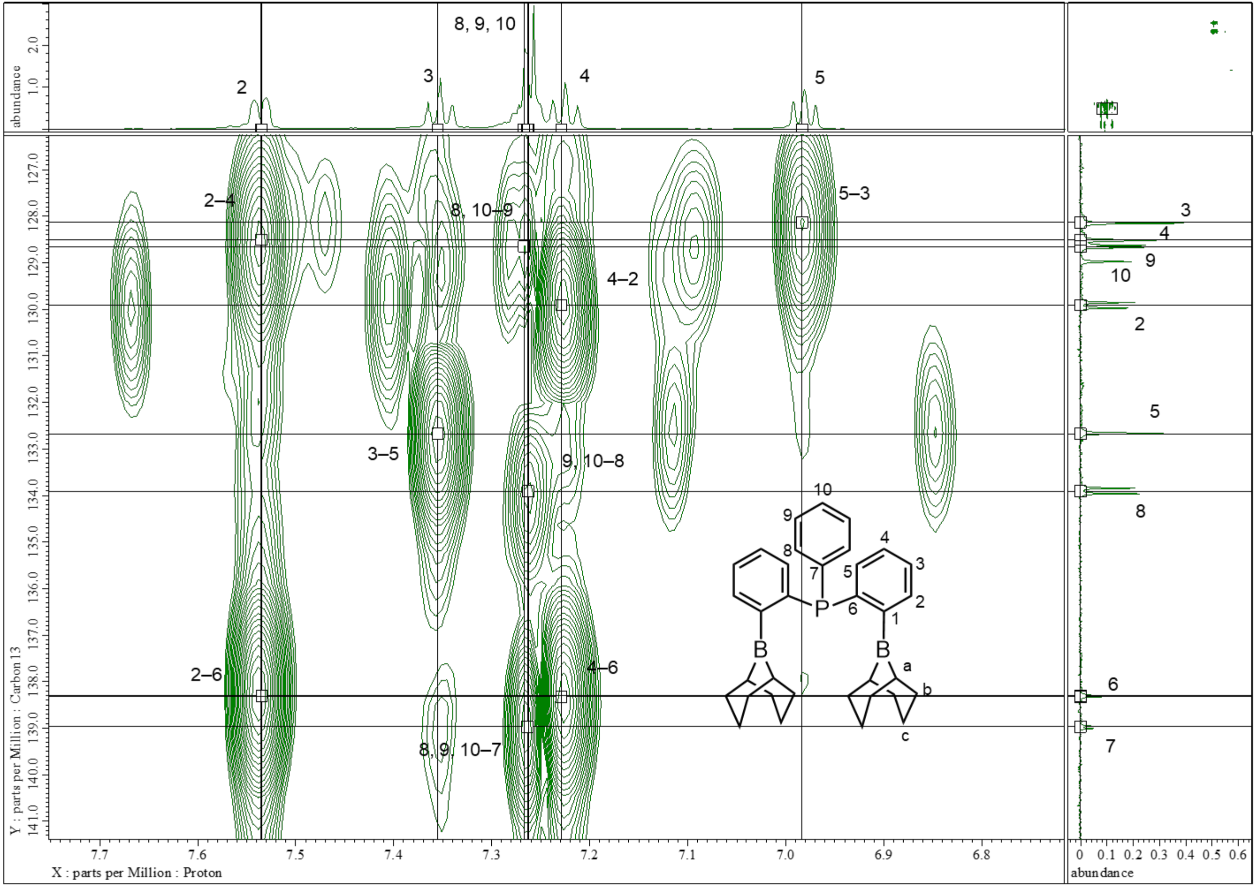
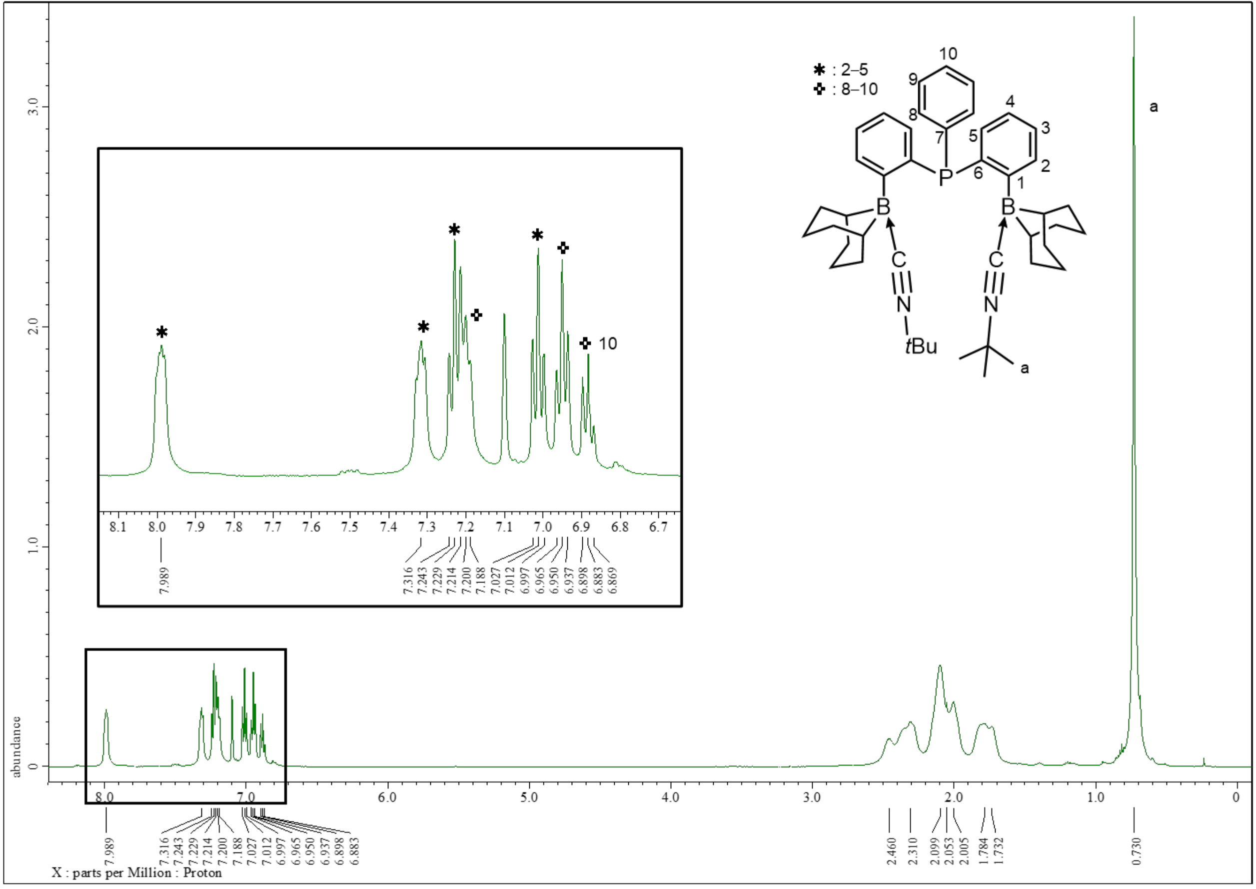


HMBC (Phenyl region)

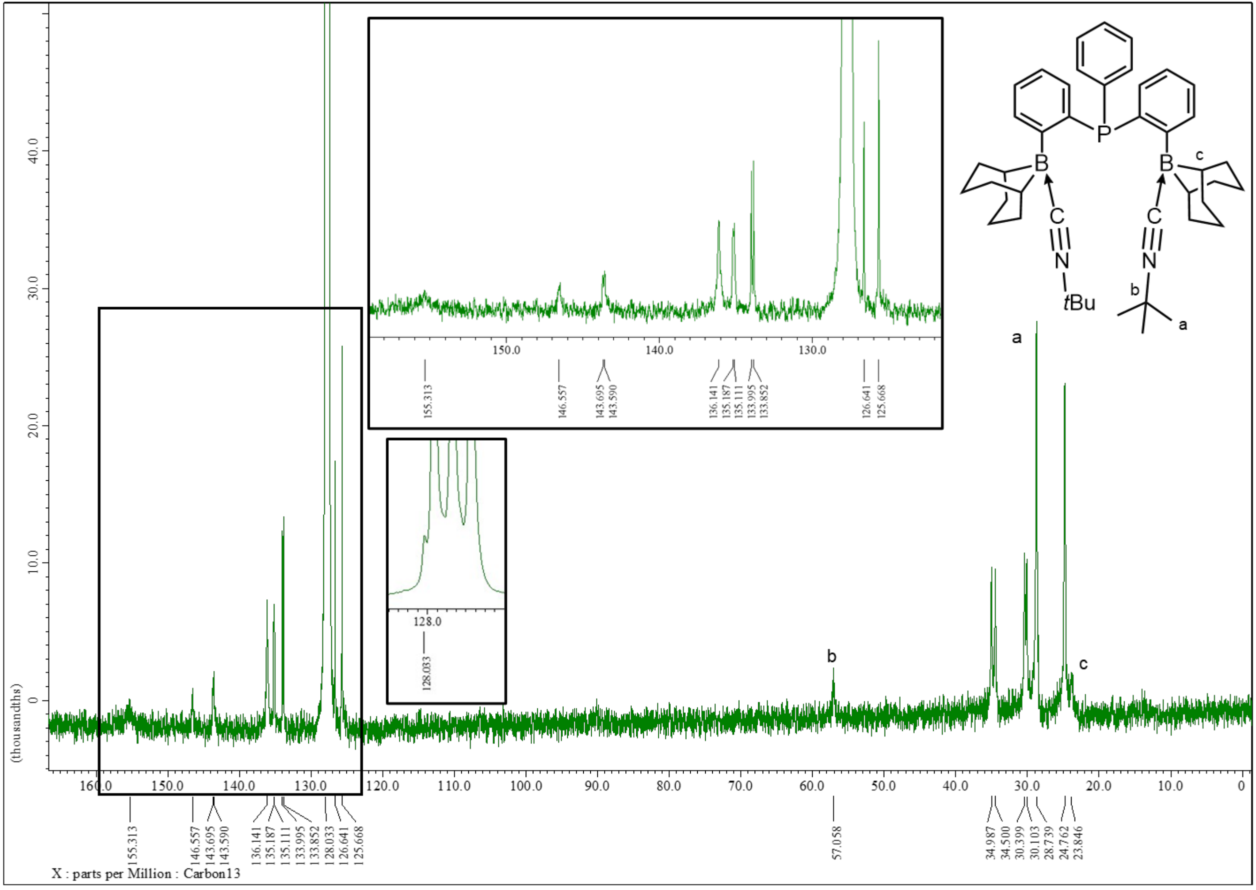


4.7 Compound 2

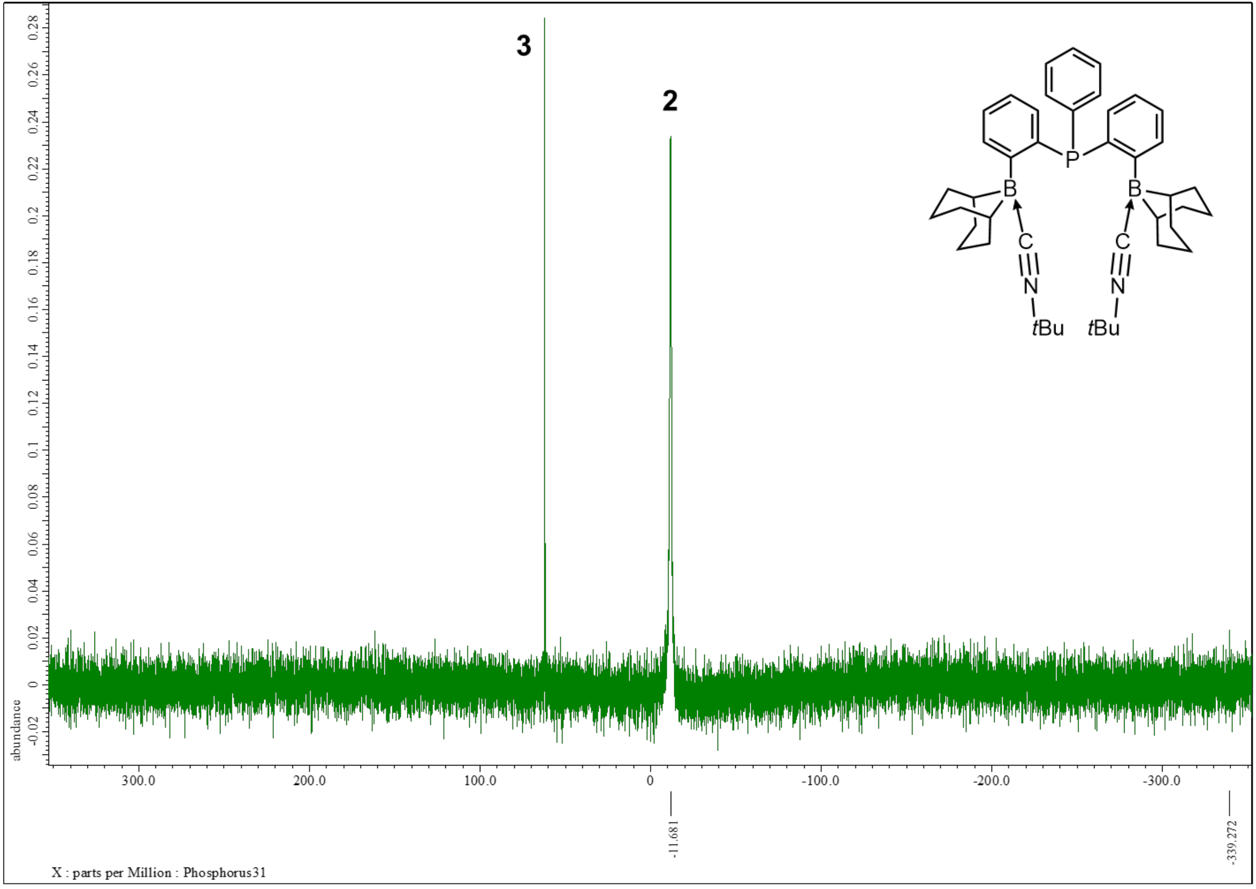
^{1}H NMR (C_6D_6, 500 MHz)



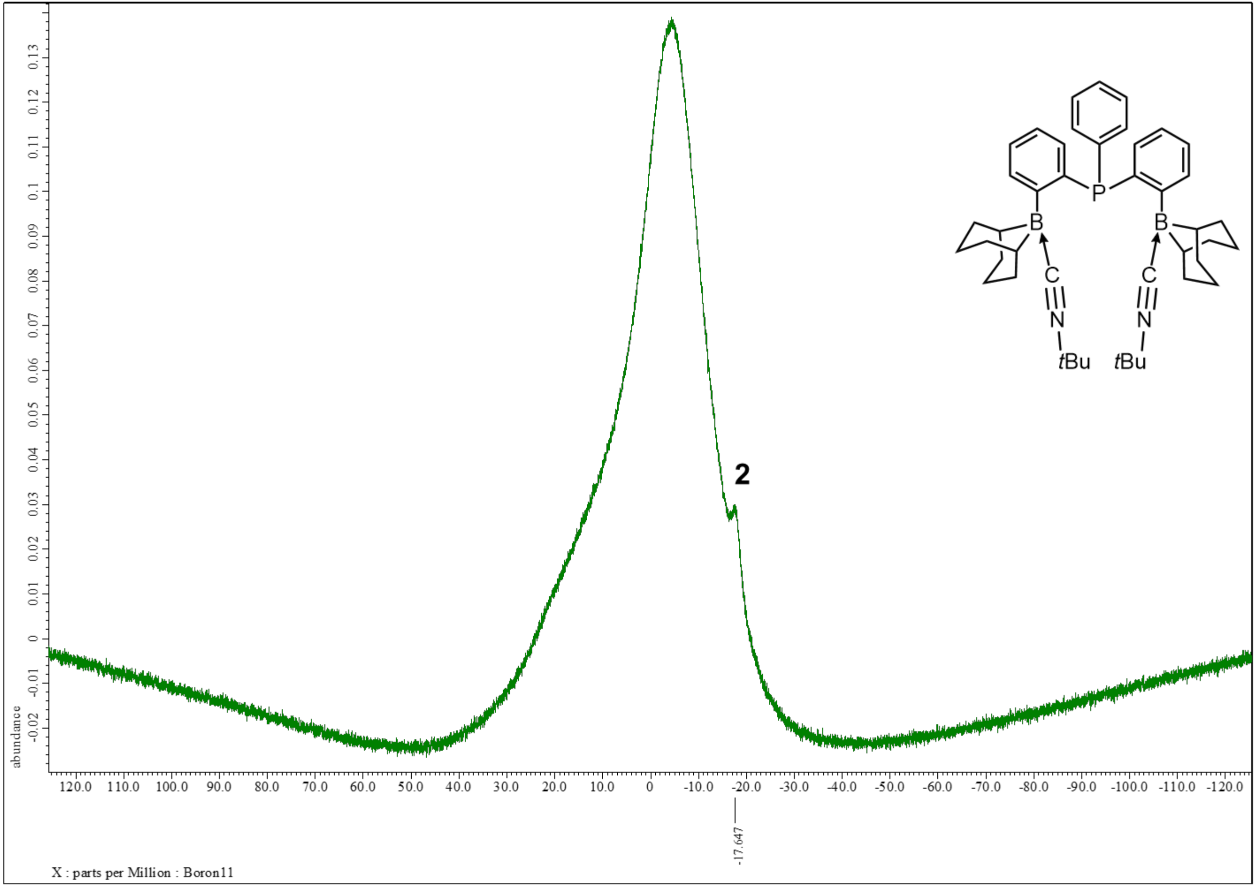
^{13}C{^{1}H} NMR (C_6D_6, 126 MHz)



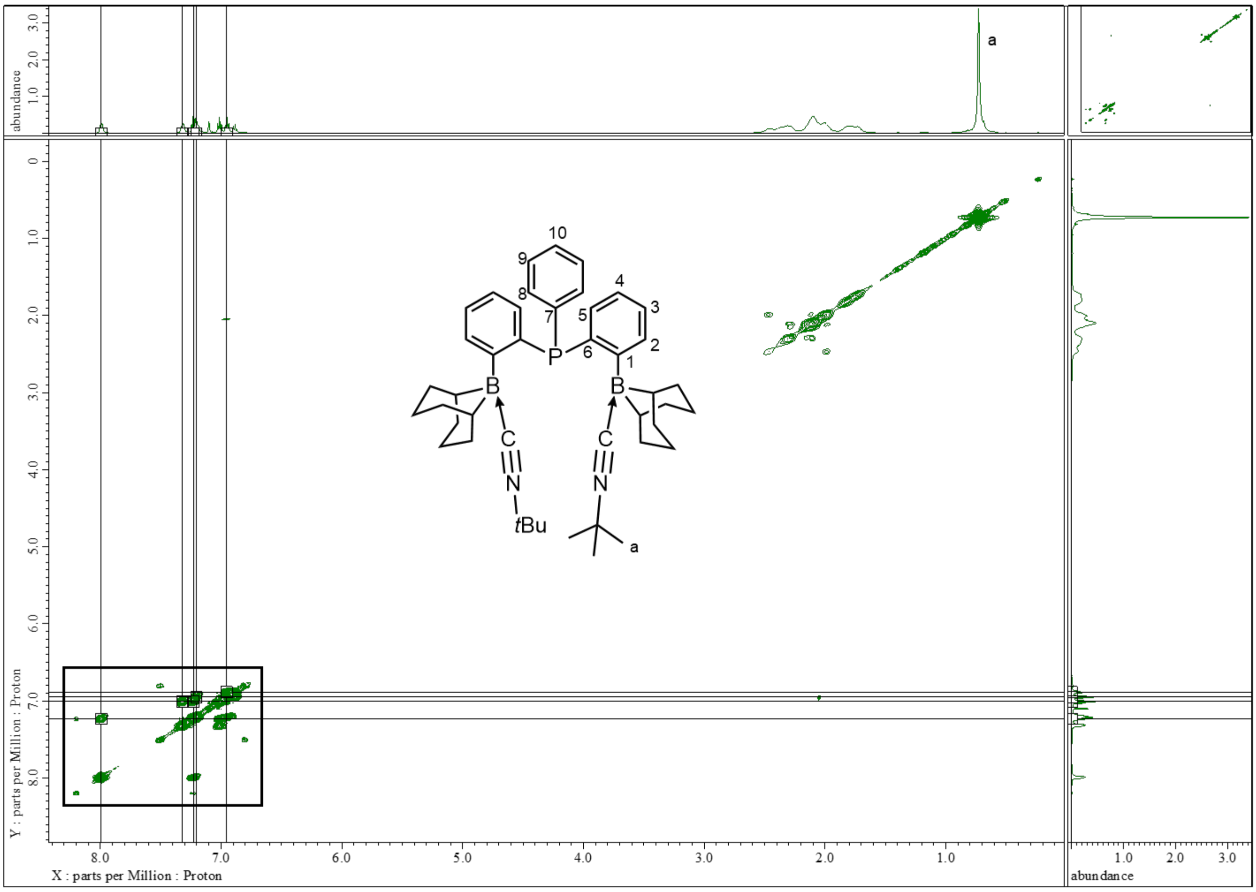
$^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz)



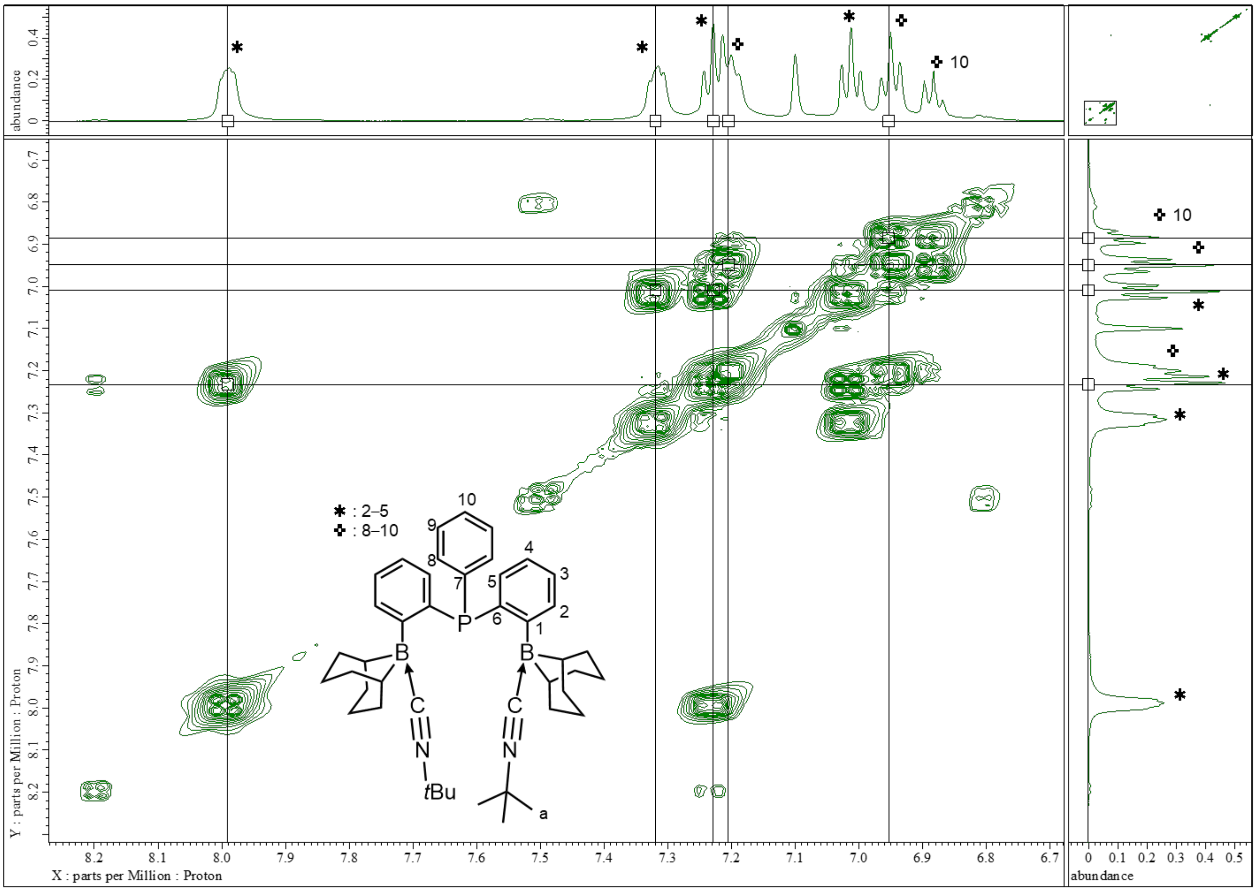
$^{11}B\{^1H\}$ NMR (C_6D_6, 161 MHz)



HH COSY

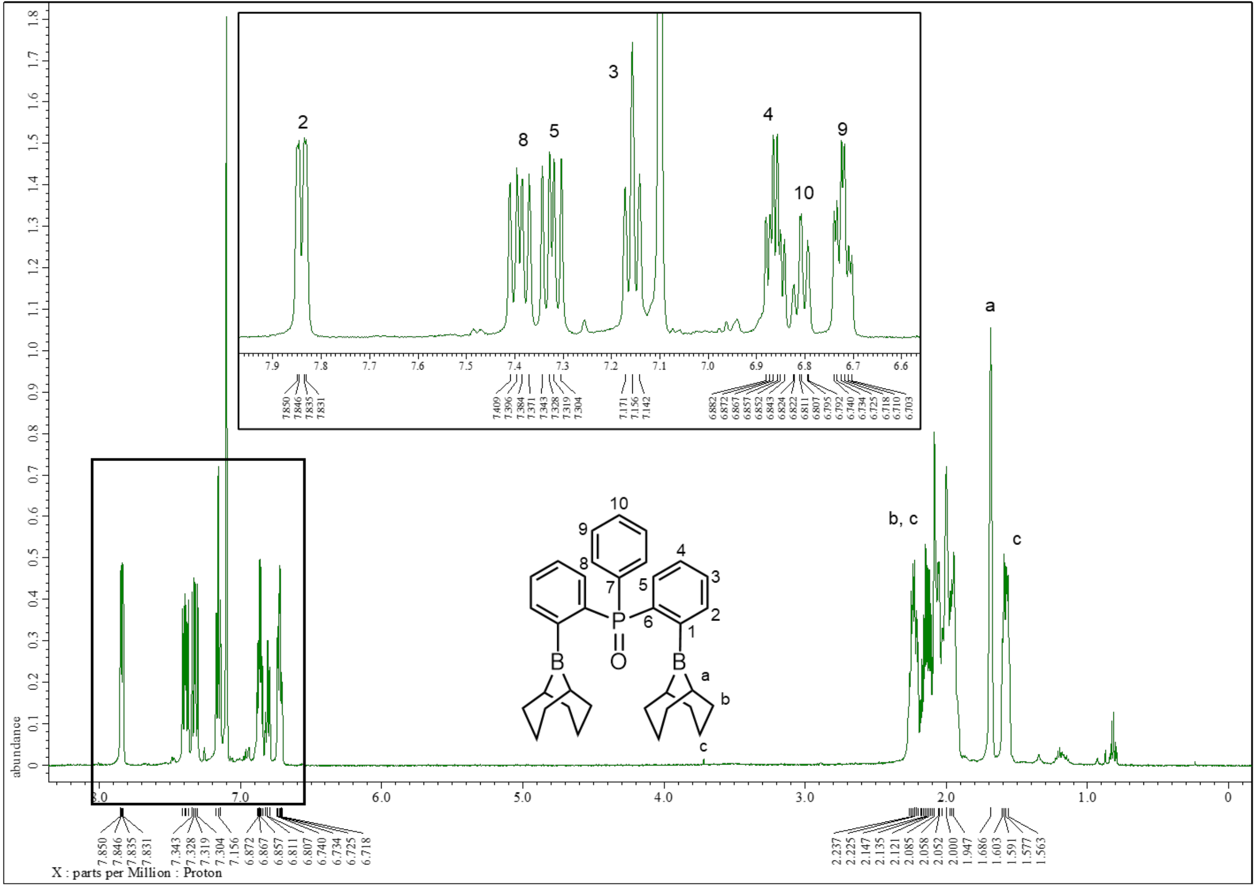


HH COSY (Phenyl region)

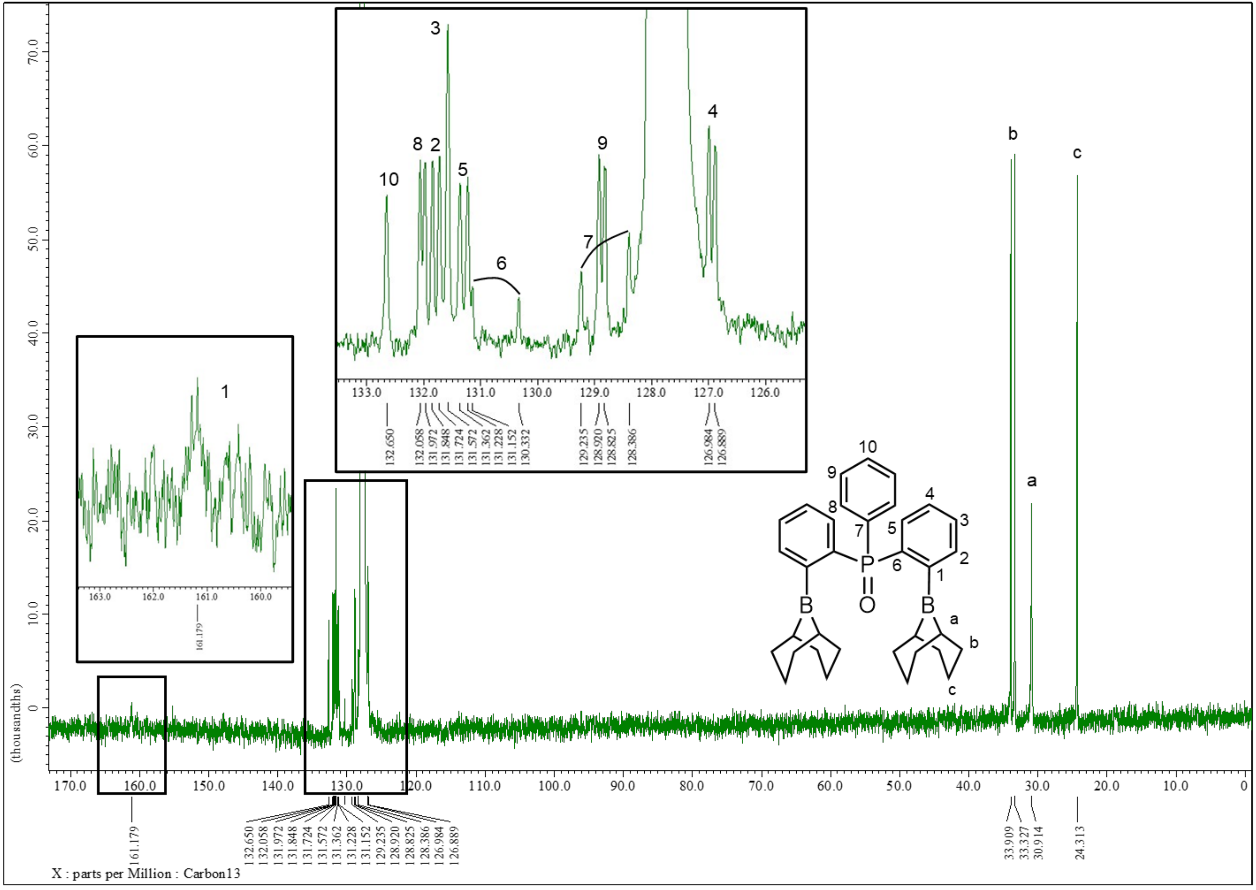


4.8 Compound 3

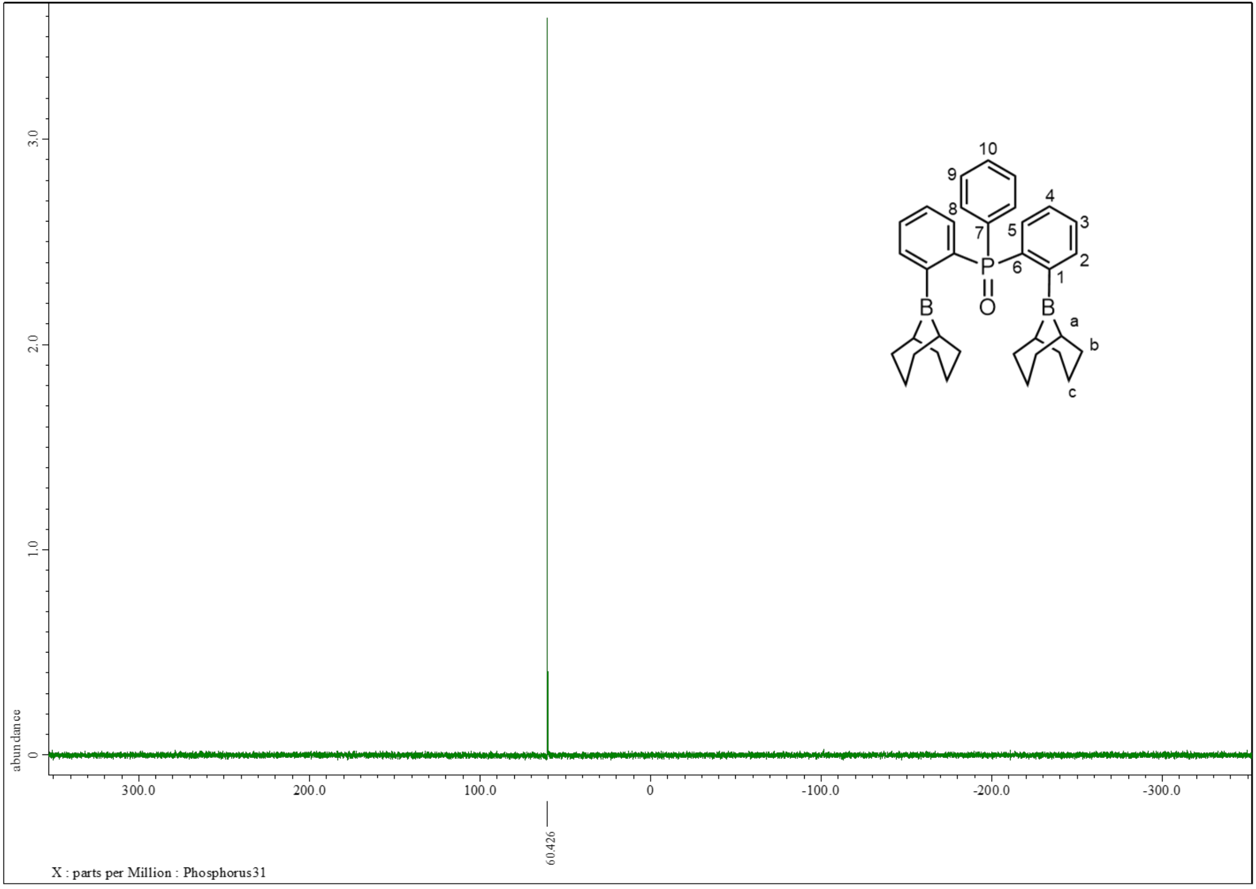
^{1}H NMR (C_6D_6, 500 MHz)



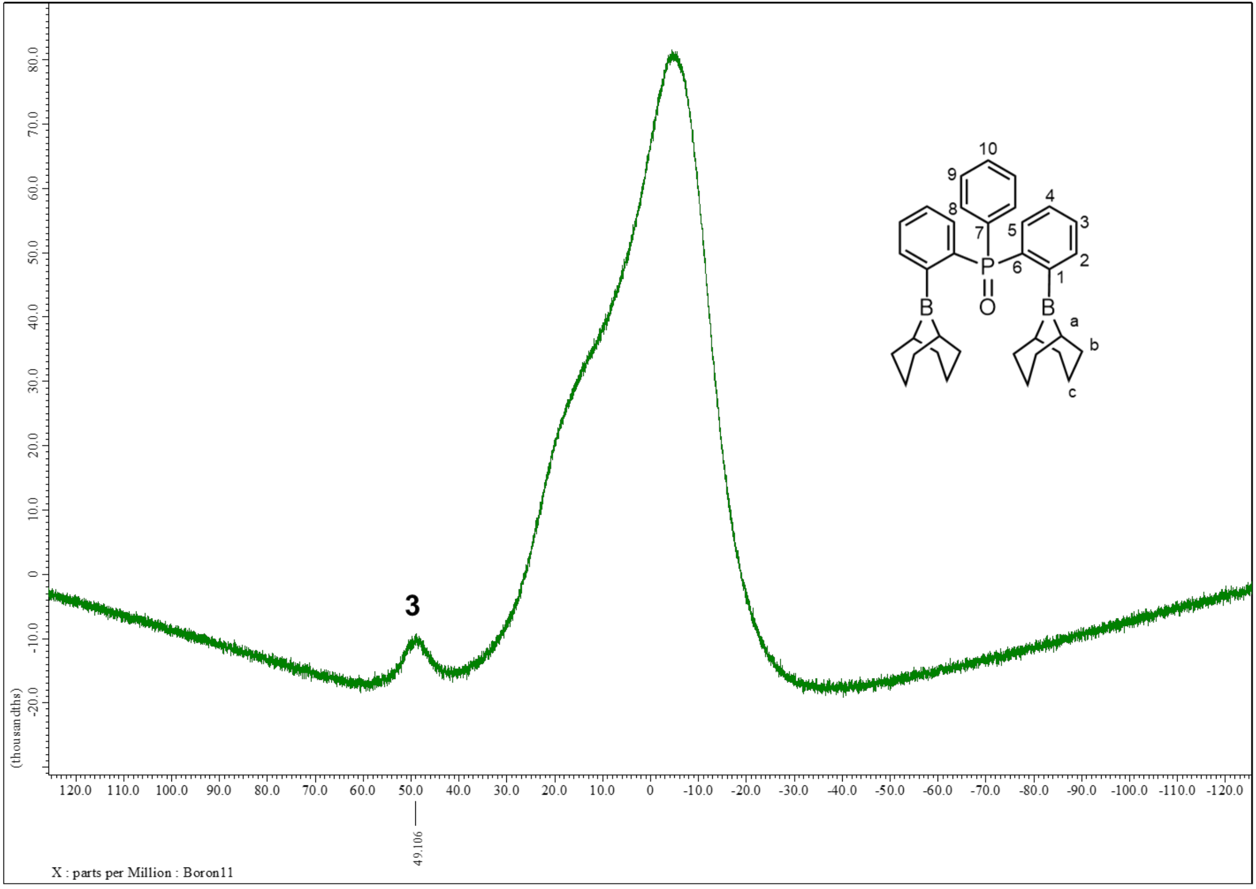
^{13}C{^{1}H} NMR (C_6D_6, 126 MHz)



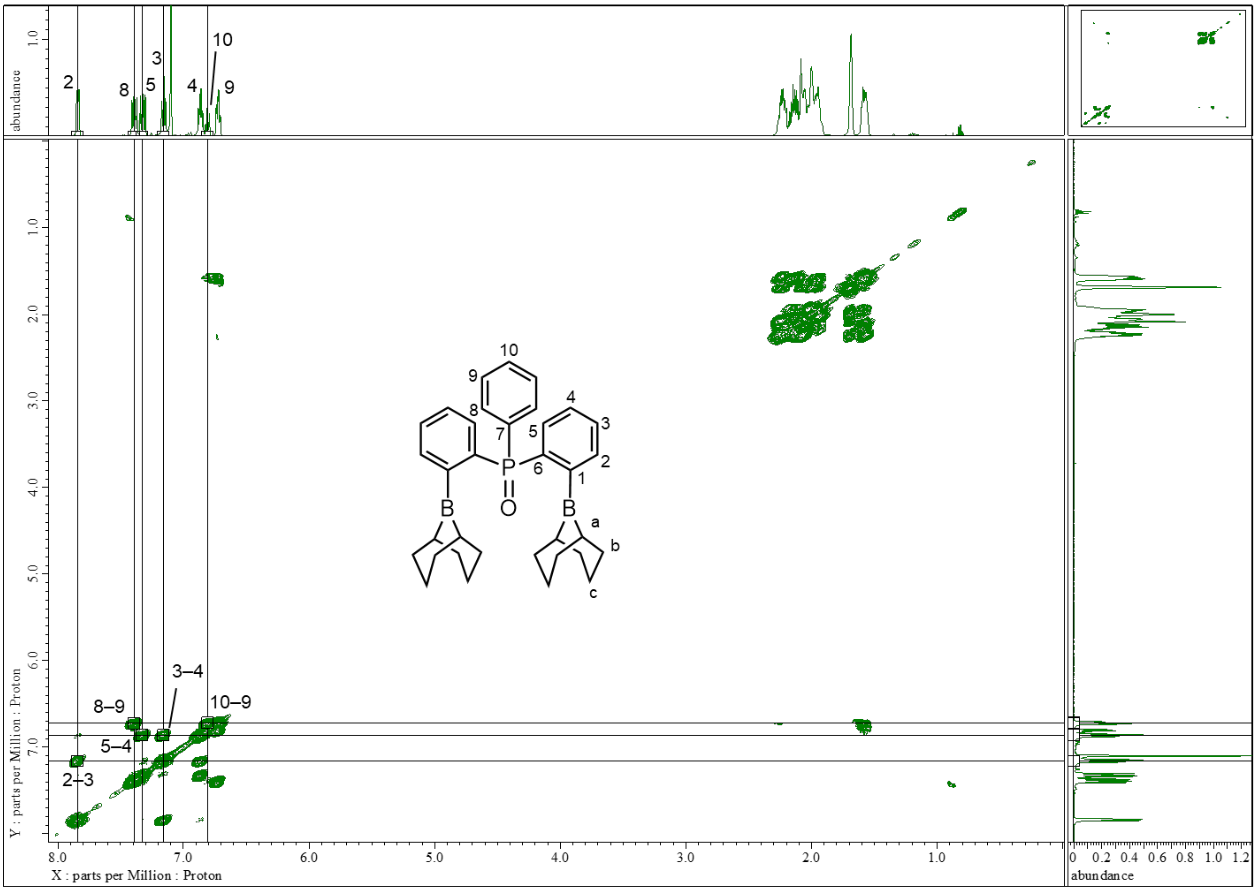
$^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz)



$^{11}B\{^1H\}$ NMR (C_6D_6, 161 MHz)



HH COSY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8
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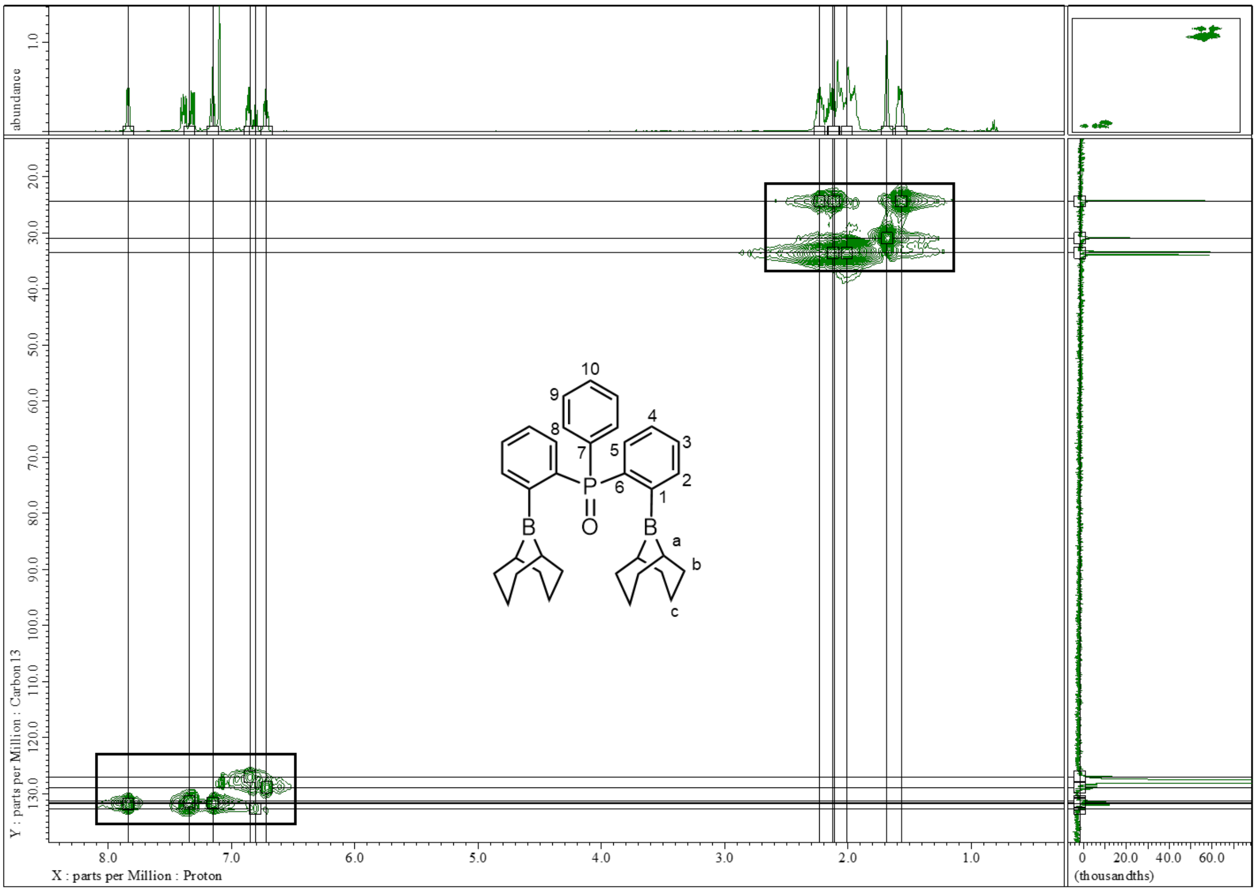
10
9
abundance
8–9
3–4
10–9
5–4
2–3
Y : parts per Million : Proton
X : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 0.2 0.4 0.6 0.8 1.0 1.2
abundance
P
O
B
a
b
c

HMQC


abundance
Y : parts per Million : Carbon13
X : parts per Million : Proton
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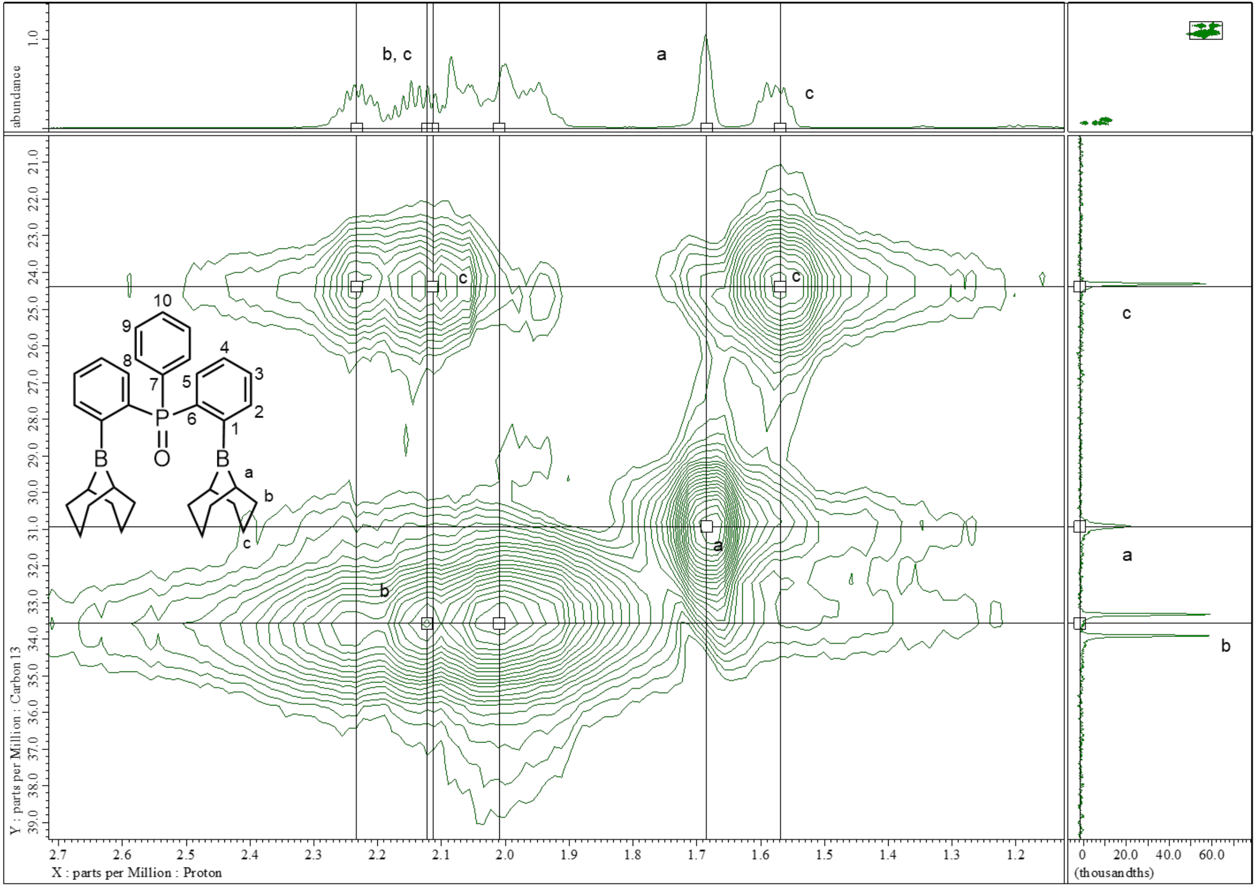
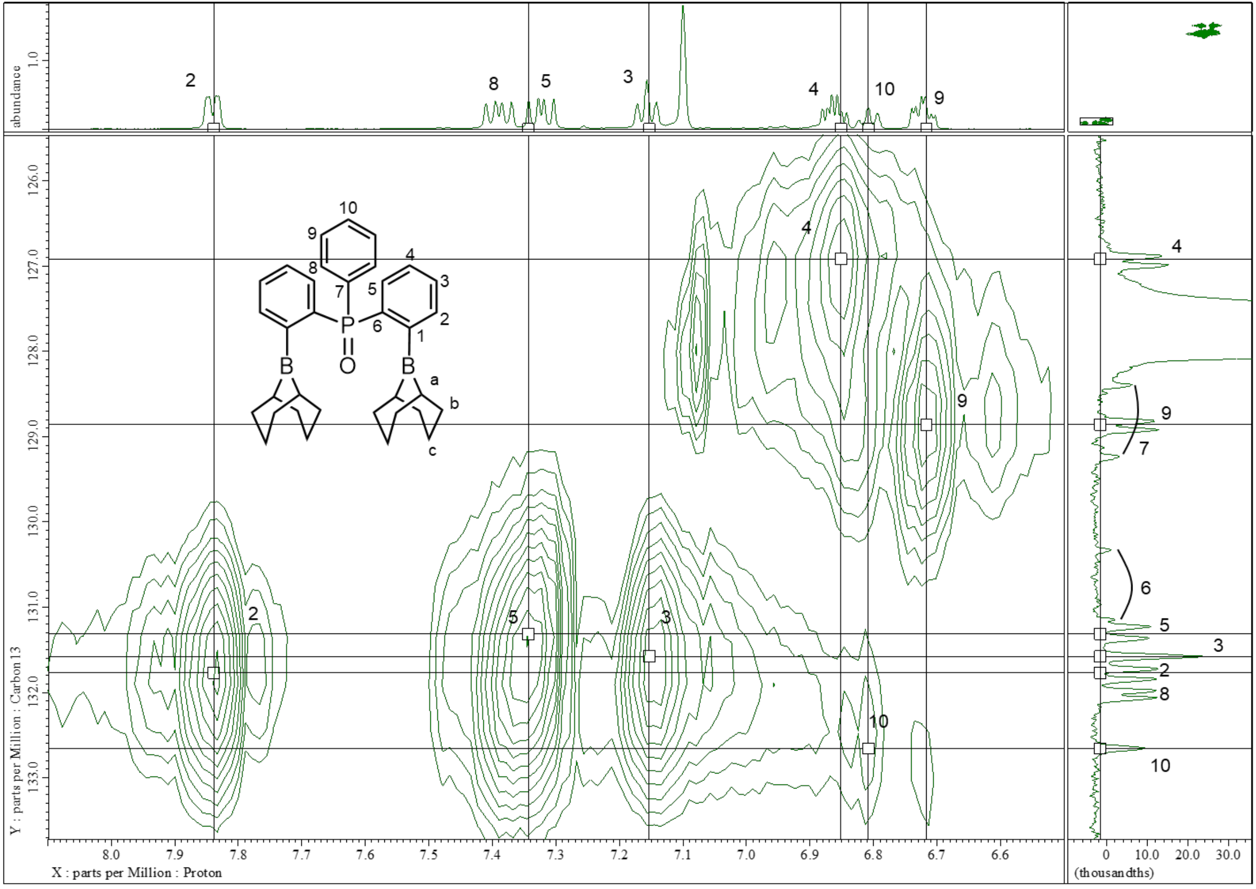
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 20.0 40.0 60.0
(thousandths)
P
O
B
a
b
c

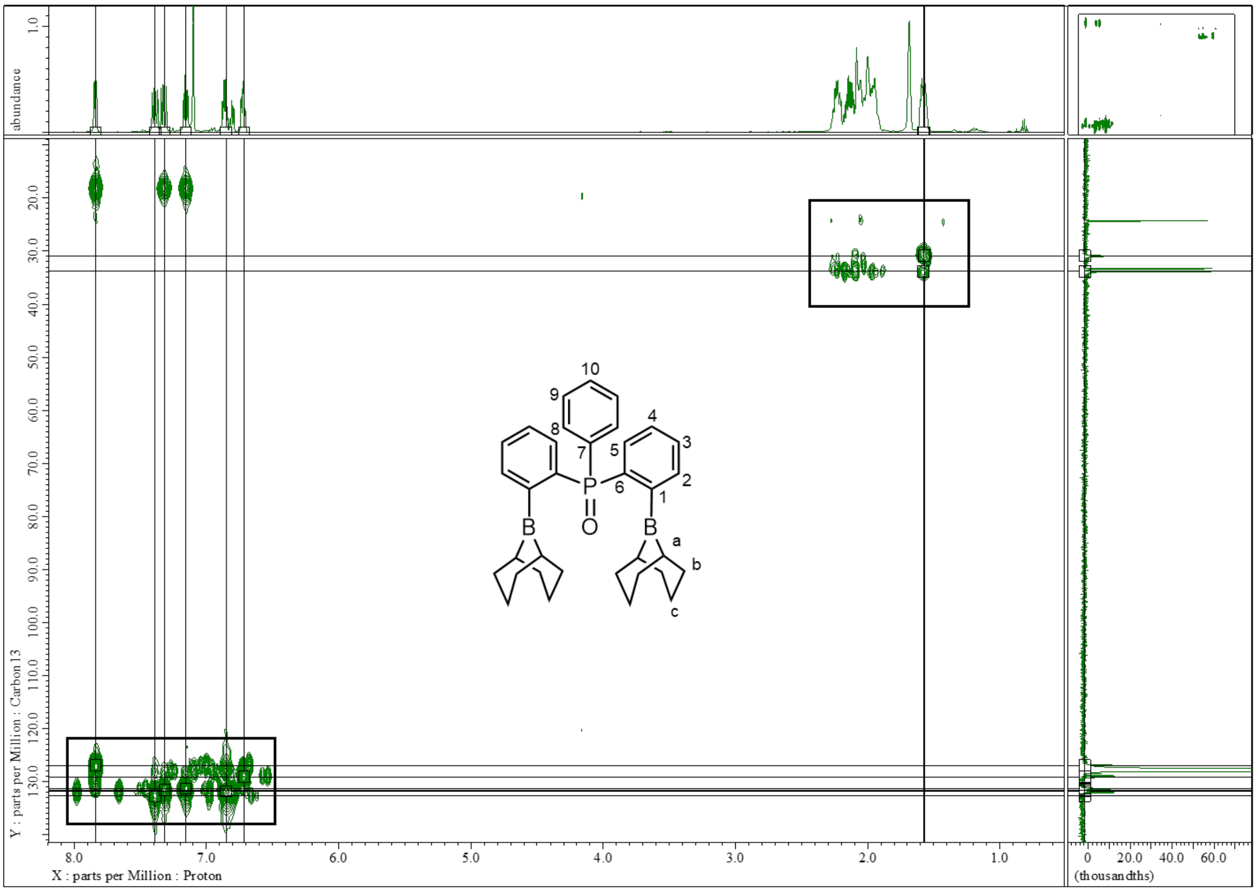
HMQC (Aliphatic region)



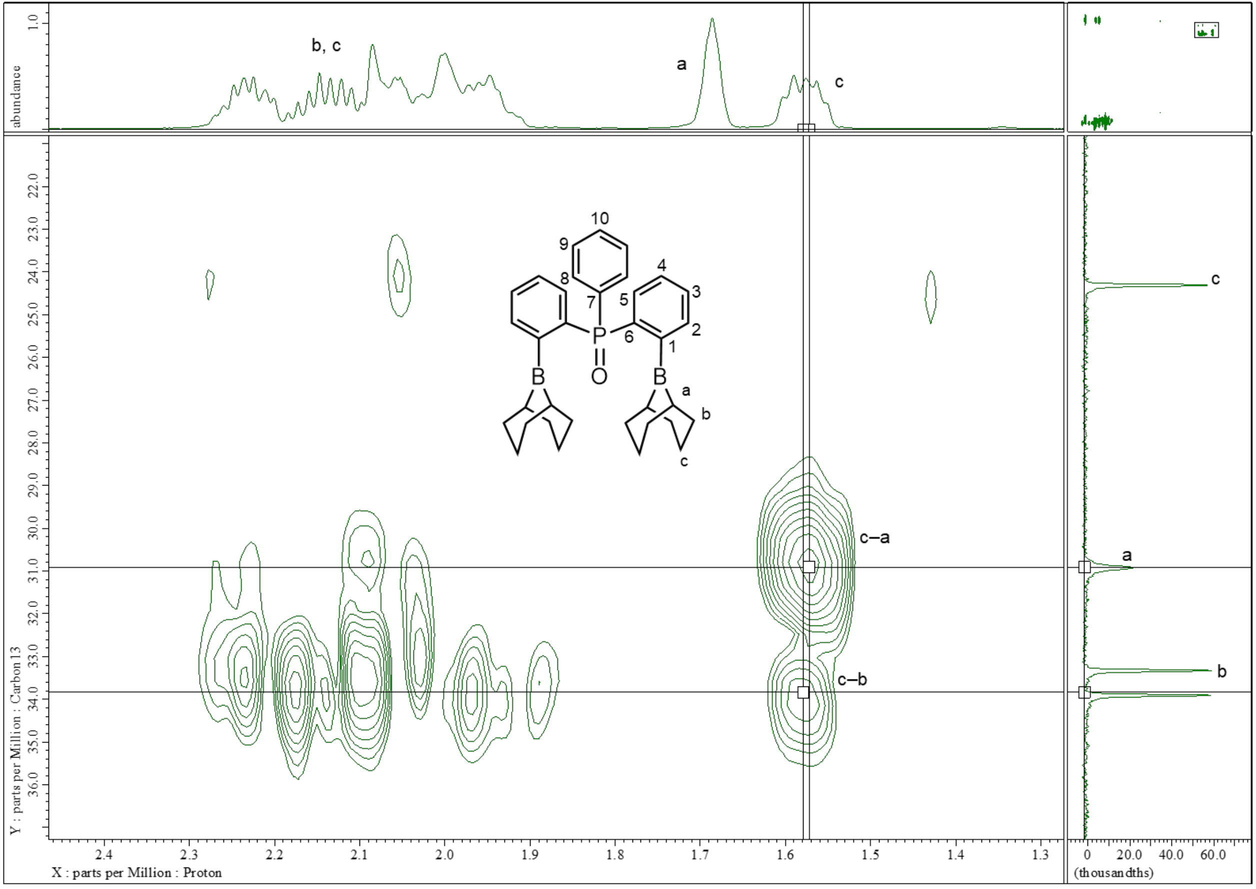
HMQC (Phenyl region)



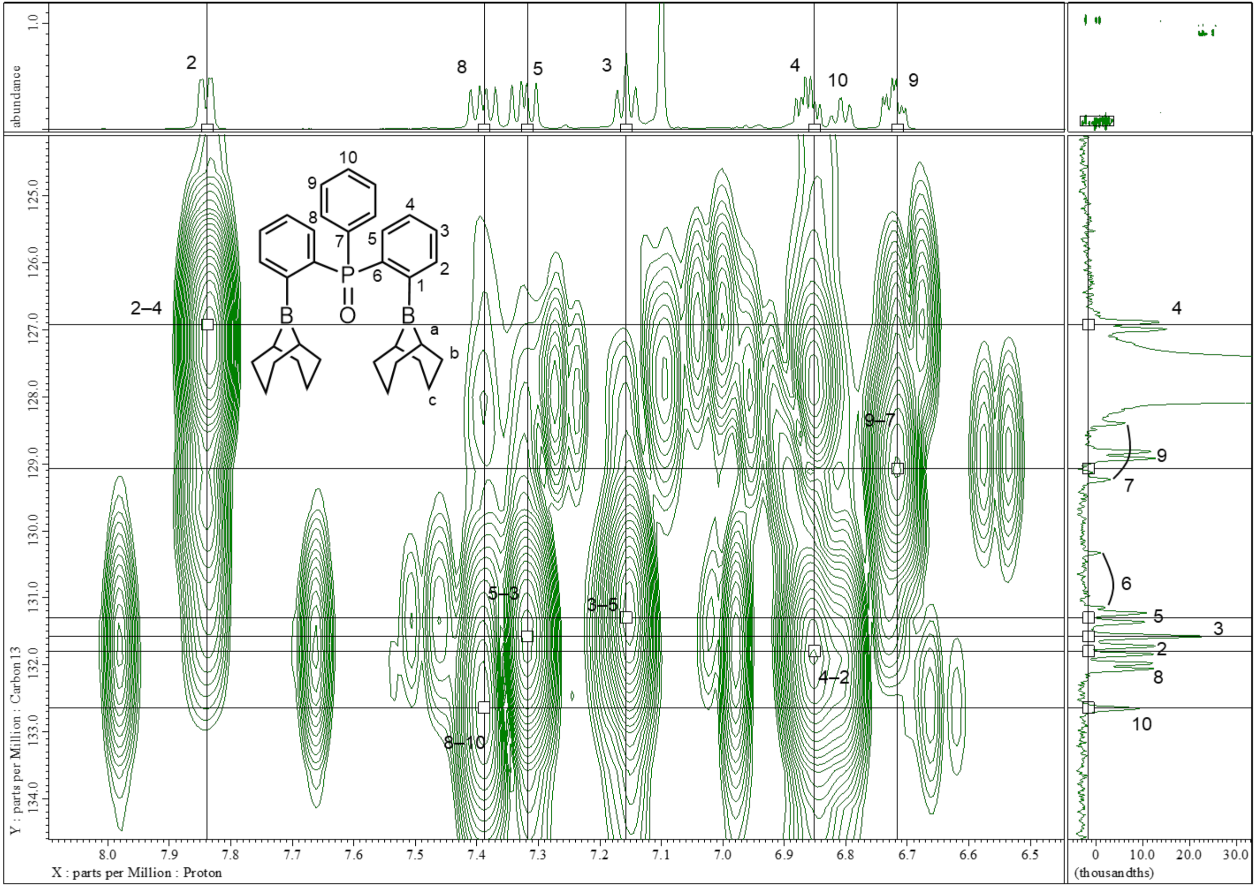
HMBC



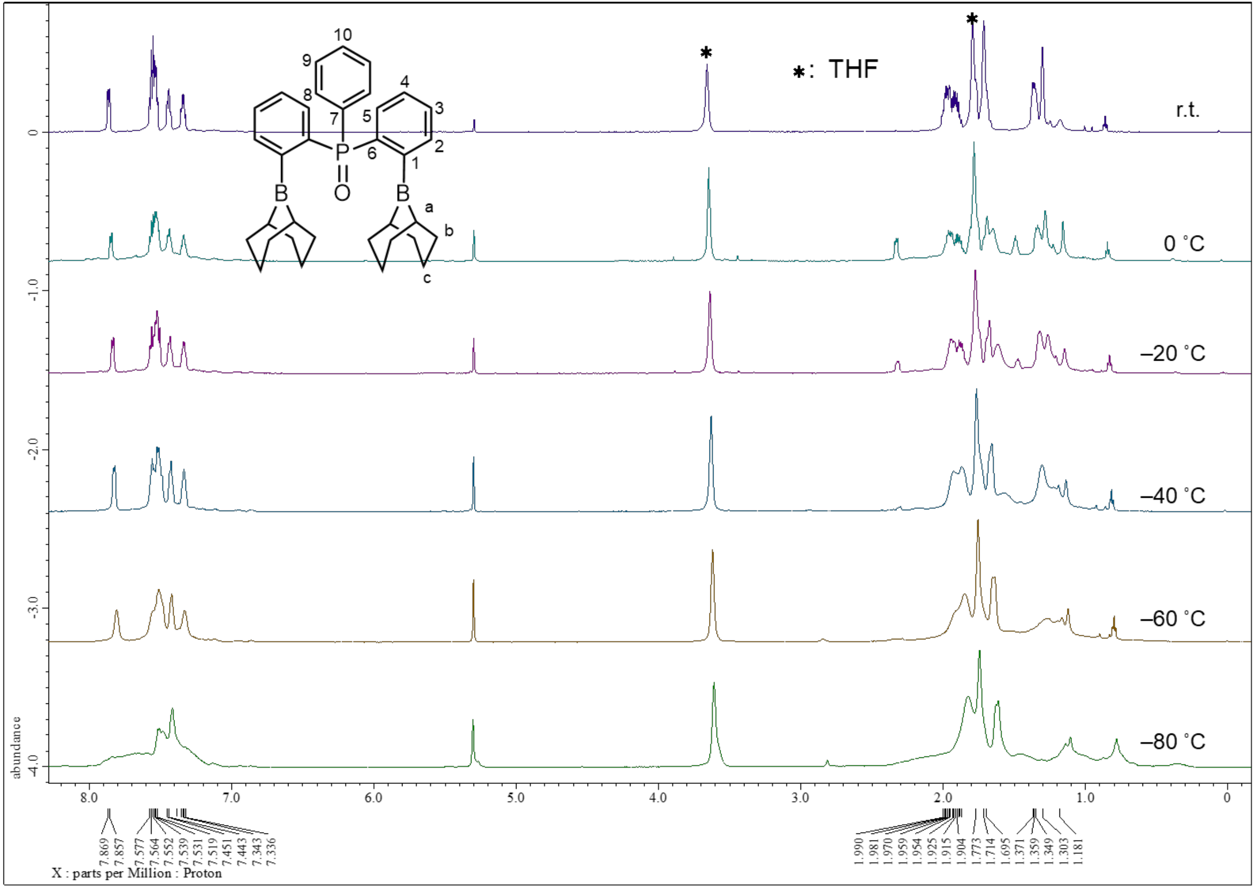
HMBC (Aliphatic region)



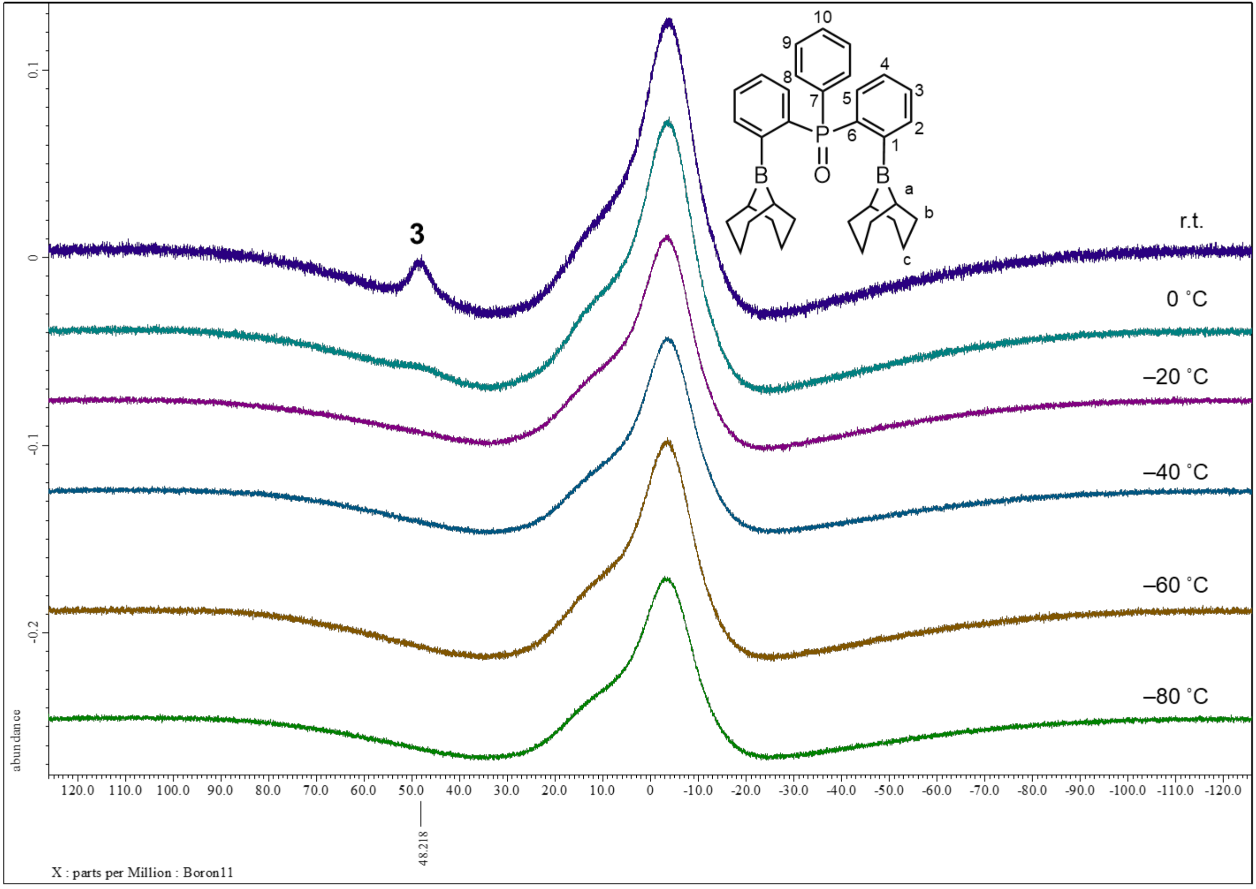
HMBC (Phenyl region)



VT ^{1}H NMR (CD_2Cl_2, 600 MHz)



VT $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 192 MHz)



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[1] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.

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[3] Persistence of Vision Raytracer (*ver.* 3.7.0); Persistence of Vision Pty. Ltd., 2016; Retrieved from http://www.povray.org/download/

[4] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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