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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Experimental Procedures

Instrumentation and Chemicals

All manipulations were performed under Ar or N₂ 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-AL 400S 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 SiMe₄ \(^{(1)}\)H\), \(^{13}C\)\(^{(1)}\)H\), BF₃·Et₂O (\(^{11}B\)) and 85% H₃PO₄ (\(^{31}P\)). 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 nBuLi hexane solution (21.4 mL, 1.55 M) was added to a solution of 1,2-dibromobenzene (4.00 mL, 33.2 mmol), \([1,1′\text{-bis(diphenylphosphino)ferrocene}]\text{dichloropalladium(II)}\) (525 mg, 0.642 mmol) and potassium acetate (4.24 g, 43.2 mmol) in THF and ether (1:1) (120 mL) at 92 °C. 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 NH₄Cl aq. and evaporated. The residue was dissolved in DCM and washed with brine. After drying with Na₂SO₄ 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)

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\]

DMSO, 80°C, 4 d

(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 Na₂SO₄ 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 (CD₂Cl₂, 600 MHz) \(\delta\) 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 (CD₂Cl₂, 151 MHz) \(\delta\) 145.4 (d, \(J_{PC} = 21.7\) Hz), 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 (CD₂Cl₂, 243 MHz) \(\delta\) −4.1, \(^{11}B\)\(^{(1)}\)H\) NMR (CD₂D₆, 192 MHz) \(\delta\) 30.0. MS(ESI) m/z [M+H]⁺ C₃₀H₃₂O₂B₂P Calcd for: 515.26883 Found: 515.26941. Anal. Calcd. for C₃₀H₃₂O₂B₂P: C, 70.07; H, 7.25. Found: C, 69.66; H 7.20.
1.3 Crystallization of 1-Int

In an argon atmosphere, LiAlH₄ (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..

1H NMR (C₆D₆, 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), 31P{¹H} NMR (C₆D₆, 160 MHz) δ –11.6, ¹¹B{¹H} NMR (C₆D₆, 127 MHz) δ –26.1.

1.4 Synthesis of BPB-9BBN (1b)

In an argon atmosphere, 1 M LiAlH₄ 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%). 1H NMR (CD₂Cl₂, 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), ¹³C{¹H} NMR (CD₂Cl₂, 151 MHz) δ 154.3 (d, JPC = 30.4 Hz), 139.0 (d, JPC = 7.2 Hz), 138.3 (s), 133.9 (d, JPC = 17.4 Hz), 132.7 (s), 129.9 (d, JPC = 17.4 Hz), 129.0 (s), 128.6 (d, JPC = 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), ³¹P{¹H} NMR (CD₂Cl₂, 243 MHz) δ –7.0, ¹¹B{¹H} NMR (C₆D₆, 192 MHz) δ 79.2. MS(ESI) m/z [1b+OH] C₃₄H₄₂OB₂P 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 C₆D₆ reaction solution. ¹H NMR (C₆D₆, 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), ¹³C{¹H} NMR (C₆D₆, 126 MHz) δ 155.3 (br), 146.6 (s), 143.6 (d, JPC = 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($^1$H) NMR (C$_6$D$_6$, 202 MHz) $\delta$ –17.6. MS(ESI) m/z [1b+H]$^+$ C$_{34}$H$_{42}$B$_2$P Calcd for: 503.32048 Found: 503.31946. [1b+OH]$^+$ C$_{34}$H$_{42}$OB$_2$P Calcd for: 519.31501. 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. $^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 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($^1$H) NMR (C$_6$D$_6$, 126 MHz) $\delta$ 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($^1$H) NMR (C$_6$D$_6$, 202 MHz) $\delta$ 60.4, $^{11}$B($^1$H) NMR (C$_6$D$_6$, 161 MHz): $\delta$ 49.1. MS(ESI) m/z [M+H]$^+$ C$_{34}$H$_{42}$OB$_2$P Calcd for: 519.31501. Found: 519.31501.

1.7 Reaction of compound 1b and D$_2$O

To a toluene (0.3 mL) solution of BPB-9BBN (1b, 6 mg, 0.01 mmol), degassed D$_2$O (25 μL) was added by vacuum transfer (some amount of D$_2$O remained). Bubbling was observed at r.t. after addition of D$_2$O. $^2$H NMR (C$_6$D$_6$, 92 MHz): $\delta$ 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$_6$D$_6$ (0.3 mL) at r.t. $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 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($^1$H) NMR (C$_6$D$_6$, 160 MHz): $\delta$ –4.6 ($^{1}J_{PH}$=525 Hz in $^{31}$P NMR).
1.9 Control reaction

\[
\text{PPh}_3 + 2 \text{BCy}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_{6}\text{D}_6 \quad \text{no reaction}
\]

To a C\text{D}_6 (0.3 mL) solution of PPh\text{3} (5 mg, 0.02 mmol) and BCy\text{3} (10 mg, 0.04 mmol), degassed H\text{2}O (0.2 mL) was added by vacuum transfer (some amount of H\text{2}O remained). Reaction mixture was stored at room temperature for one hour followed by 16 hours at 50 °C. No H\text{2} was observed in the \textsuperscript{1}H NMR of the reaction mixture. The \textsuperscript{11}B\{\textsuperscript{1}H\} NMR spectra indicated presence of large amount of starting material BCy\text{3} and some formation of BCy\text{3}\cdot\text{H}_2\text{O}. The \textsuperscript{31}P NMR spectra showed no formation of phosphine oxide nor any other reactivity.

\textbf{Figure S1} \textsuperscript{1}H (a, 400 MHz in C\text{D}_6), \textsuperscript{11}B\{\textsuperscript{1}H\} (b, 128 MHz in C\text{D}_6) and \textsuperscript{31}P\{\textsuperscript{1}H\}/\textsuperscript{31}P \text{(c, 160 MHz in C\text{D}_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) 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. The pictures of molecules were prepared using Pov-Ray 3.7.0. 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·H2O.

| Compound Name | 1a | 1-Int | 2 | 3 | 3·H2O |
|---------------|----|-------|---|---|-------|
| CCDC No.      | 2096462 | 2096463 | 2096464 | 2096465 | 2109052 |
| Formula       | $\text{C_{60}H_{74}B_{4}O_{8}P_{2}}$ | $\text{C_{22}H_{28}B_{2}O_{2}L_{2}Cl}_{25}$ | $\text{C_{64}H_{56}B_{2}N_{2}P}$ | $\text{C_{30}H_{28}B_{2}O_{2}P}$ | $\text{C_{42}H_{22}B_{2}O_{2}P}$ |
| 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 | P21/c | P21/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) |
| $\alpha$, deg | 104.883(2) | 90 | 90 | 90 | 96.766(7) |
| $\beta$, deg  | 91.015(2) | 106.257(4) | 97.347(8) | 102.039(14) | 96.231(14) |
| $\gamma$, deg | 99.535(2) | 90 | 90 | 90 | 104.461(9) |
| V, Å³         | 2876.7(8) | 9286(3) | 3870(8) | 3242(4) | 1877(3) |
| Z             | 2 | 16 | 4 | 4 | 2 |
| $D_{\text{calc}}$, Mg/m³ | 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 |
| $R_{1}$ [I > 2σ(I)] | 0.0381 | 0.0521 | 0.0590 | 0.0312 | 0.0336 |
| Parameters    | 769 | 575 | 448 | 434 | 504 |
| $wR_{2}$ (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·H₂O. 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\(_{tBu}\)

![Figure S4](image1.png)

**Figure S4** Reaction free energies (kcal/mol) of 1b with CN\(_{tBu}\).

3.2 Reaction of 1b and H\(_2\)O

![Figure S5](image2.png)

**Figure S5** Intrinsic bonding orbitals (IBO) between H2 and H3 during the reaction of 1b and H\(_2\)O.
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 H₂O and D₂O

Figure S8. Energy profile of the reaction of 1b with H₂O (black line) and D₂O (blue line).

3.5 Kinetic Isotope Effect of the reaction of 1b with H₂O/D₂O

To compute the Kinetic Isotope Effect (KIE) of the reaction of 1b with H₂O/D₂O, we calculated the energetic profile for 1b with D₂O as shown in Figure S8. For this, we used the optimized geometries of the reaction mechanism of 1b with H₂O (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:

\[ KIE = \frac{k_{\text{light}}}{k_{\text{heavy}}} = \exp \left( \frac{\Delta G^\ddagger_{\text{heavy}} - \Delta G^\ddagger_{\text{light}}}{RT} \right) \]

Where \( \Delta G^\ddagger_{\text{heavy}} \) is the highest barrier energy that involves the isotopically labeled species and \( \Delta G^\ddagger_{\text{light}} \) for the one that does not involve the isotopes. The calculated \( \Delta G^\ddagger_{\text{heavy}} \) and \( \Delta G^\ddagger_{\text{light}} \) 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 + H₂O at –80 °C

³¹P{¹H} NMR (CD₂Cl₂, 243 MHz)

4.2 Reaction of compound 1b + D₂O

²H NMR (toluene, 92 MHz)
4.3 Formation of 4 from 1b with MeOH (ca. 50 eqv.)

$^1$H NMR ($\text{C}_6\text{D}_6$, 400 MHz)

$^{31}$P{$^1$H}/$^{31}$P NMR of the reaction of 1b with MeOH ($\text{C}_6\text{D}_6$, 160 MHz)
4.4 Compound 1a

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

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 151 MHz)
$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 243 MHz)

$^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 192 MHz)
HMBC (Phenyl region)
4.5 Intermediate 1-Int

$^1$H NMR (C$_6$D$_6$, 400 MHz)

$^{31}$P($^1$H) NMR (C$_6$D$_6$, 160 MHz)
$^1\text{H}$ NMR (CD$_6$, 127 MHz)

![Chemical Structure](image)

$J_{\text{int}} = 59$ Hz

1-Int

H coupling spectrum

X: parts per Million: 11B
4.6 Compound 1b

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

$^{13}\text{C}^{'(\text{H})}$ NMR (CD$_2$Cl$_2$, 151 MHz)
$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 243 MHz)

$^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 192 MHz)
4.7 Compound 2

\(^1\)H NMR (C\(_6\)D\(_6\), 500 MHz)

\(^{13}\)C\({}^1\)H NMR (C\(_6\)D\(_6\), 126 MHz)
$^{31}\text{P}({}^1\text{H})$ NMR (CD$_6$D$_6$, 202 MHz)

$^{11}\text{B}({}^1\text{H})$ NMR (CD$_6$D$_6$, 161 MHz)
4.8 Compound 3

$^1$H NMR (C$_6$D$_6$, 500 MHz)

$^{13}$C($^1$H) NMR (C$_6$D$_6$, 126 MHz)
$^{31}\text{P}^\text{(H)}$ NMR (C$_6$D$_6$, 202 MHz)

$^{11}\text{B}^\text{(H)}$ NMR (C$_6$D$_6$, 161 MHz)
HMQC (Aliphatic region)

HMQC (Phenyl region)
HMBC (Phenyl region)

VT $^1$H NMR (CD$_2$Cl$_2$, 600 MHz)
VT $^{11}$B($^1$H) NMR (CD$_2$Cl$_2$, 192 MHz)
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