Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

1,1-Phosphinoboration of Diazomethanes

Alina Trofimova,[†[a]] James H. W. LaFortune,[†[a]] Zheng-Wang Qu,[*[b]] Stephen A. Westcott[[c]] and Douglas W. Stephan[*a]

[†] = equal contribution

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Materials and Methods

General Remarks

All manipulations were performed in a MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. All glassware was oven- or flame-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane, diethyl ether, and *n*-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone. $CDCl_3$ (Aldrich) was deoxygenated, distilled over CaH_2, then stored over 3 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals, or Alfa Aesar, and were used without further purification unless indicated otherwise. Phosphinoboranes Ph_2PBcat,[1] Ph_2PBpin,[1] Ph_2PBMes_2,[2, 3] tBu$_2$PBcat,[4] and tBu$_2$PBMes$_2$[4] were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz, or a Varian Mercury-300 MHz spectrometer. ^{1}H, ^{13}C, ^{31}P, ^{19}F, and ^{11}B NMR chemical shifts (δ/ppm) are referenced to Me_4Si, Me_4Si, H_3PO_4, $CFCl_3$, and BF_3•OEt_2, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, ^{1}H-^{1}H–COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. These compounds are hydrolytically sensitive and efforts to obtain EA were problematic. We do however, provide pristine NMR and HRMS data as well as crystal structures of 7 of the 8 compounds.

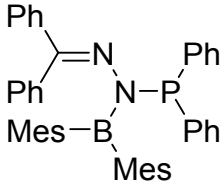
X-ray Diffraction Studies

Single crystals were coated with paratone oil, mounted on a cryoloop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-3 software and processed using SAINT. An empirical absorption correction was applied using SADABS. All structures were solved and refined by direct methods within the

SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Product Synthesis

1-(dimesitylboraneyl)-2-(diphenylmethylene)-1-(diphenylphosphineyl)hydrazine ($Ph_2CNN(PPh_2)(BMes_2)$)



In a 20 mL vial, a solution of Ph_2PBMes_2 (0.1 mmol, 43.4 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.4 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a white solid (51.6 mg, 82.2% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 629.32627 (calc'd for $C_{43}H_{43}B_1N_2P_1$: 629.32569). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 1.17 (s, 3H), 1.99 (s, 3H), 2.18 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), 2.52 (s, 3H), 5.72 (dd, *J* = 8 Hz, *J* = 1 Hz, 2H), 6.46 (s, 1H), 6.67 (dd, *J* = 7 Hz, *J* = 1 Hz, 2H), 6.82 (s, 1H), 7.01 (t, *J* = 8 Hz, 2H), 7.22 (tt, *J* = 7 Hz, *J* = 1 Hz, 1H), 7.25-7.30 (m, 4H), 7.34-7.40 (m, 8H), 7.86 (td, *J* = 7 Hz, *J* = 1 Hz, 2H), 7.93 (td, *J* = 8 Hz, *J* = 1 Hz, 2H) ppm. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 45.8 (s, br) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 57.2 (s) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 21.1, 21.3, 22.6, 22.7, 23.6, 25.0 (d, *J* = 9 Hz), 127.4, 127.5, 127.8 (d, *J* = 6 Hz), 128.0, 128.0, 128.1, 128.2, 128.4, 128.7 (d, *J* = 3 Hz), 128.7, 129.8, 130.5, 132.7 (d, *J* = 22 Hz), 135.1, 136.9, 137.0, 137.0, 137.1, 137.4 (d, *J* = 5 Hz), 137.6, 138.8, 139.4 (d, *J* = 20 Hz), 140.6 (d, *J* = 1 Hz), 141.0, 141.2 (d, *J* = 3 Hz), 143.2, 165.8 (d, *J* = 1 Hz) ppm.

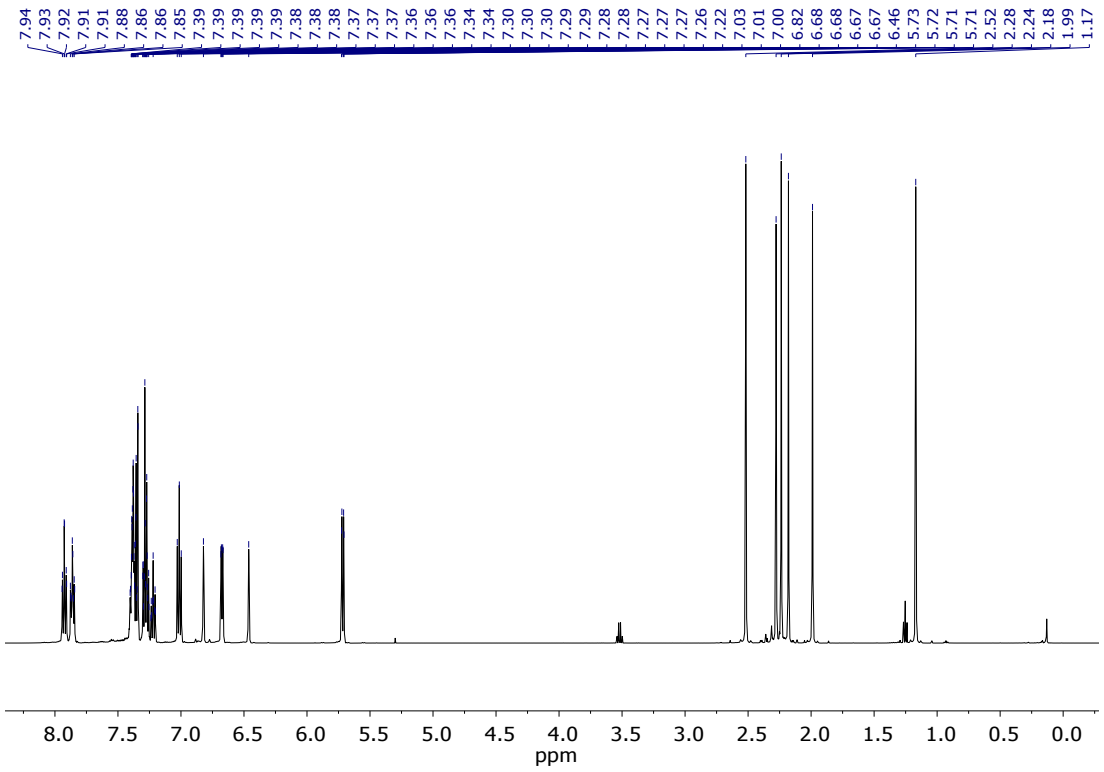


Figure 1. ^{1}H ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(BMes_2)$.

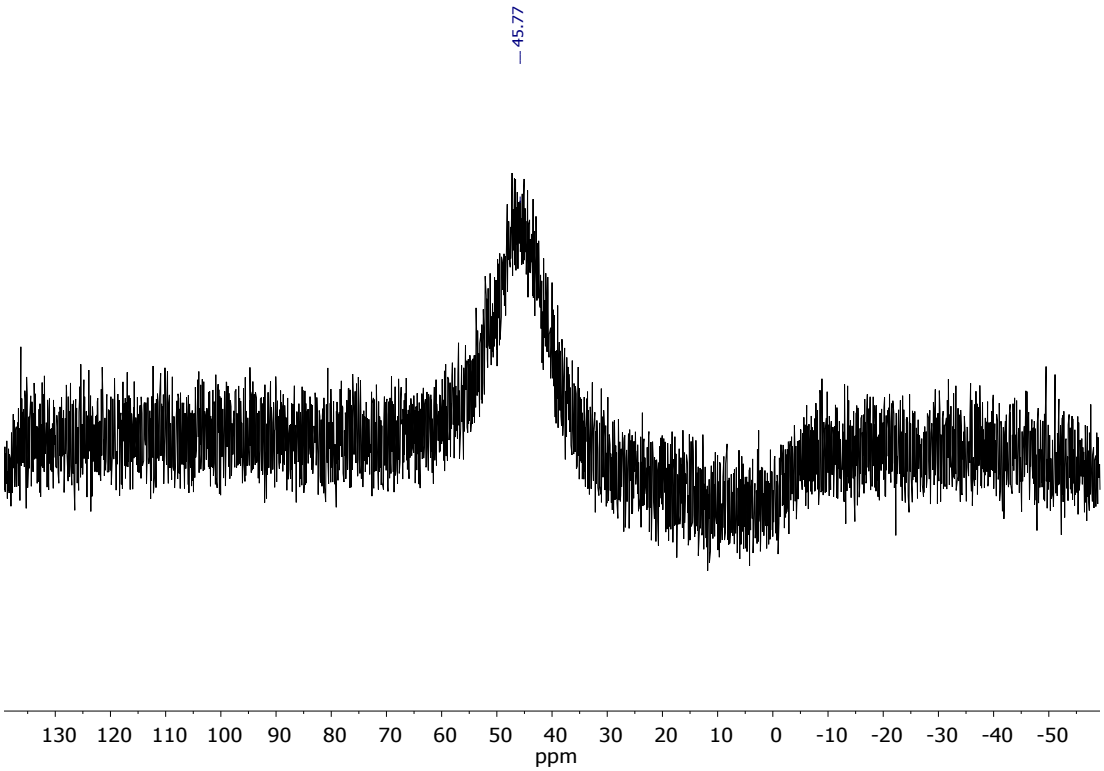


Figure 2. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(BMes_2)$.

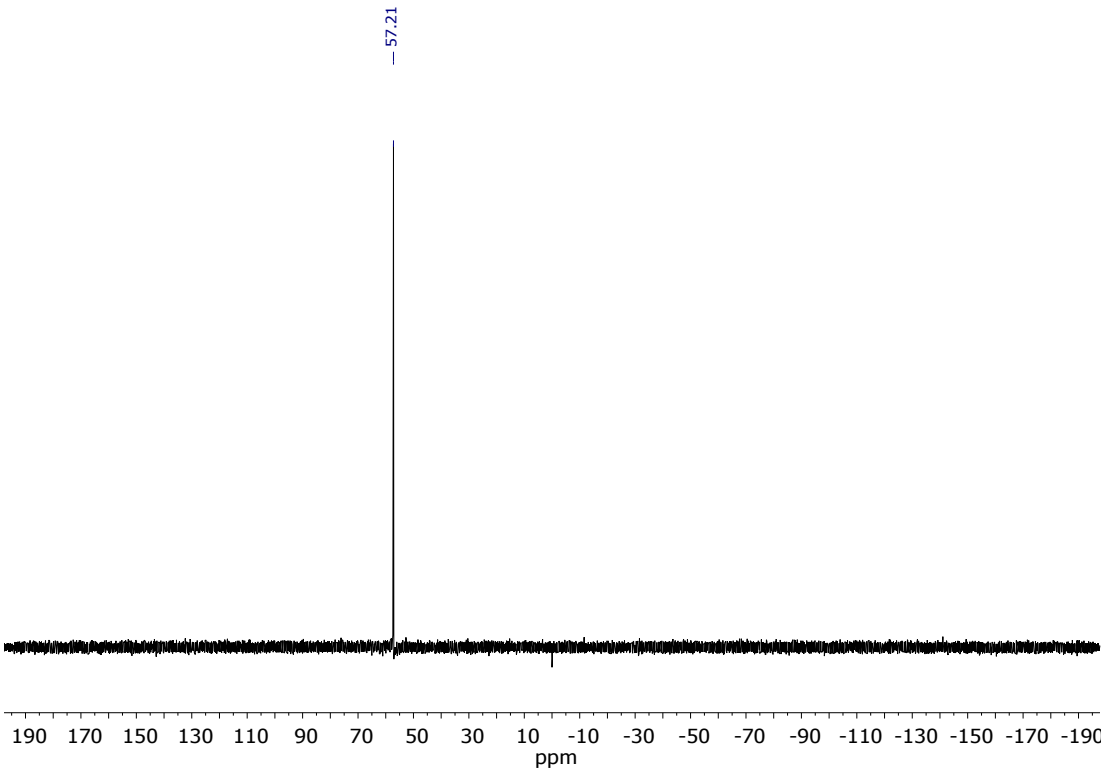


Figure 3. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(BMes_2)$.

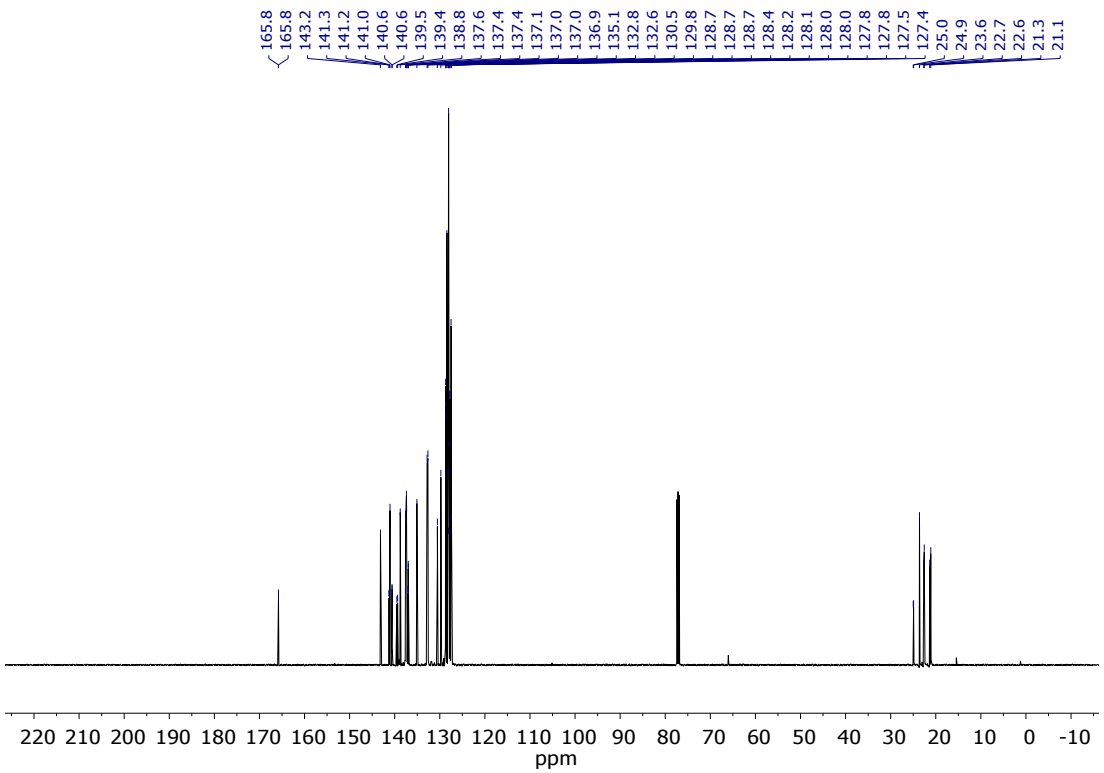


Figure 4. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(BMes_2)$.

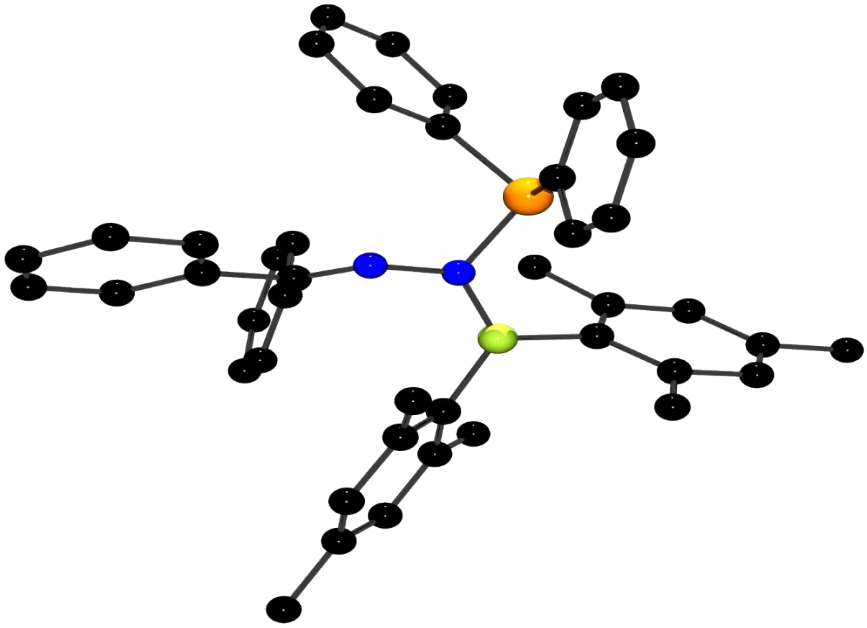
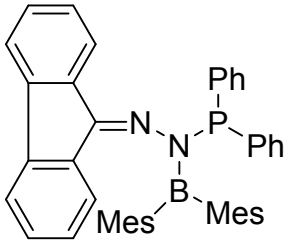


Figure 5. Solid-state structure of $Ph_2CNN(PPh_2)(BMes_2)$.

1-(dimesitylboraneyl)-1-(diphenylphosphineyl)-2-(9*H*-fluoren-9-ylidene)hydrazine ($FluorenylNN(PPh_2)(BMes_2)$)



In a 20 mL vial, a solution of Ph_2PBMes_2 (0.01 mmol, 45.0 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of fluorenyldiazomethane (0.01 mmol, 19.9 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a yellow solid (61.4 mg, 95% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 627.30921 (calc'd for $C_{43}H_{41}B_1N_2P_1$: 627.31004). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 1.66 (s, 3H), 1.86 (s, 3H), 1.88 (s, 3H), 2.00 (s, 3H), 2.34 (s, 3H), 3.00 (s, 3H), 6.19 (d, *J* = 10 Hz, 2H), 6.78 (s, 1H), 6.98 (s, 1H), 7.02-7.05 (m, 3H), 7.19 (td, *J* = 7 Hz, *J* = 1 Hz, 1H), 7.23 (td, *J* = 7 Hz, *J* = 1 Hz, 1H), 7.27-7.33 (m, 4H), 7.28 (ddt, *J* = 7 Hz, *J* = 4 Hz, *J* = 1 Hz, 2H), 7.44-7.47 (m, 2H), 7.49-7.52 (m, 1H), 7.57 (dt, *J* = 7 Hz, *J* = 1 Hz, 1H), 7.82 (td, *J* = 8 Hz, *J* = 1 Hz, 2H), 8.51 (dt, *J* = 7 Hz, *J* = 1 Hz, 1H) ppm. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 52.7 (s, br) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 64.3 (s) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 20.8, 21.4, 22.5, 22.7, 22.9, 25.2 (d, *J* = 11 Hz), 119.3, 119.7, 122.6, 126.7, 127.3, 127.6 (d, *J* = 8 Hz), 127.8 (d, *J* = 2 Hz), 127.8, 127.9 ,127.9, 128.2 (d, *J* = 21 Hz), 128.4, 128.8, 129.2, 130.4 (d, *J* = 5 Hz), 130.7, 131.0 (d, *J* = 18 Hz), 131.1, 136.1 (d, *J* = 26 Hz), 137.0, 137.1, 137.2, 137.6 (d, *J* = 1 Hz), 138.3, 138.7 (d, *J* = 13 Hz), 140.2, 140.6 (d, *J* = 3 Hz), 141.0 (d, *J* = 28 Hz), 141.6 (d, *J* = 1 Hz), 142.5, 159.5 (d, *J* = 1 Hz) ppm.

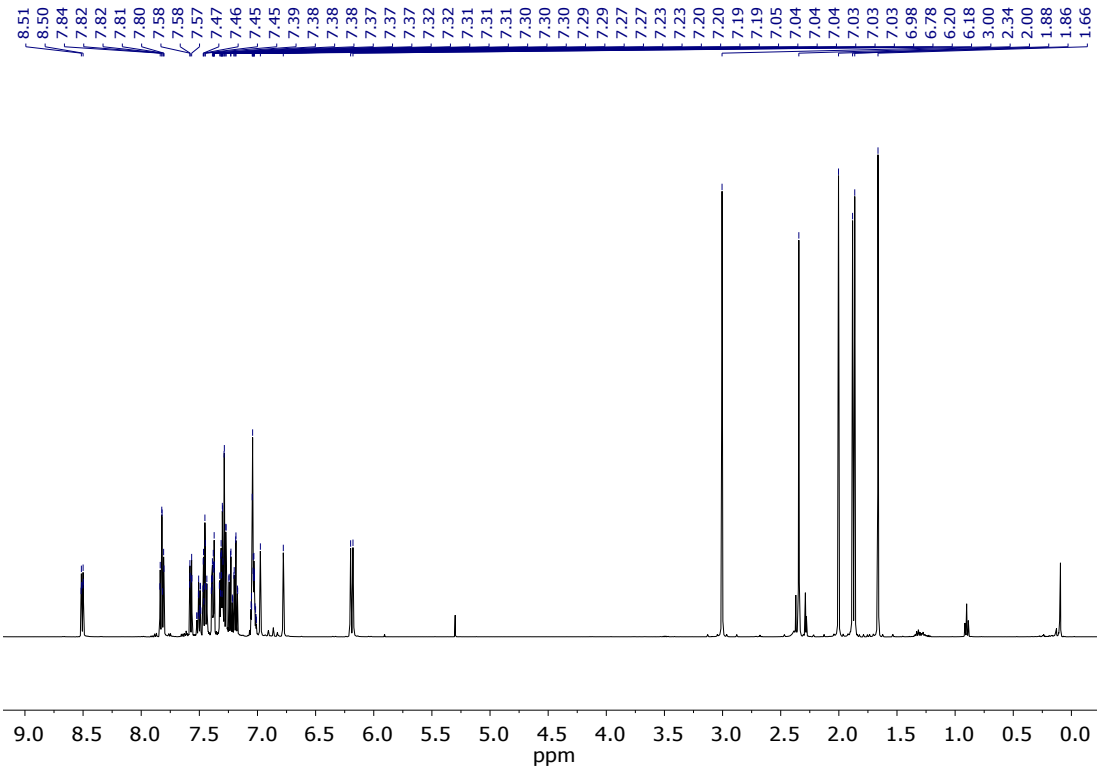


Figure 6. ^1H ($CDCl_3$) NMR of FluorenylNN(PPh_2)($BMes_2$).

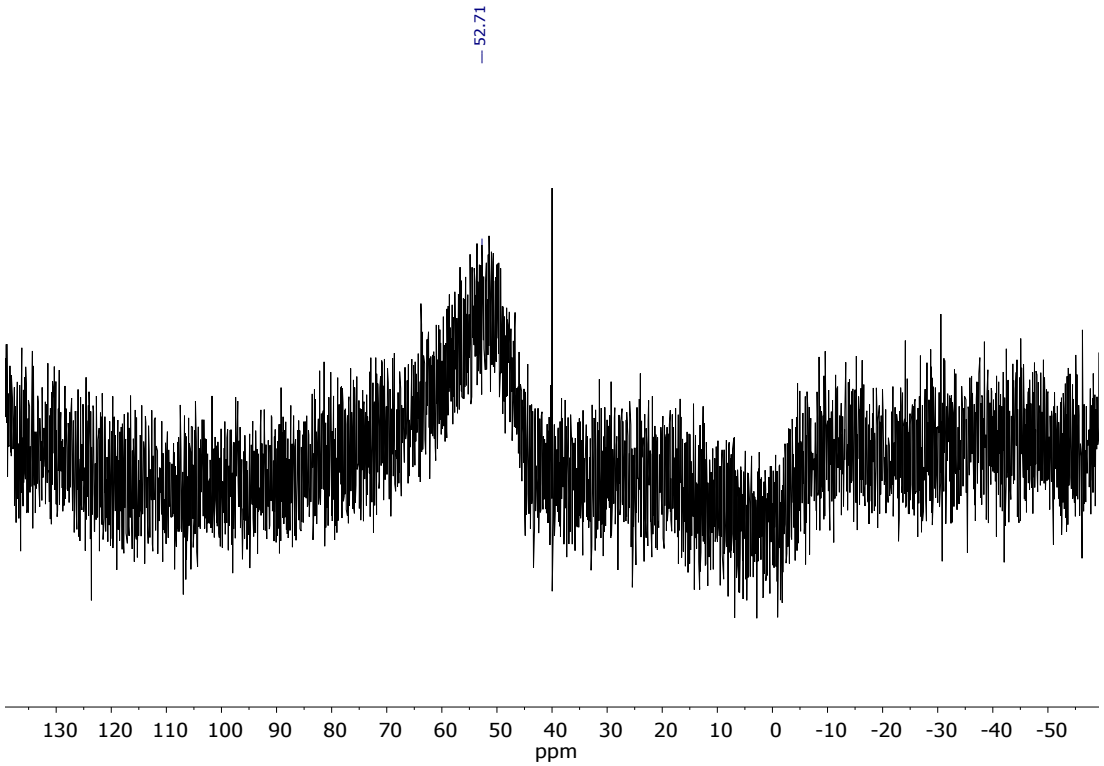


Figure 7. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)($BMes_2$).

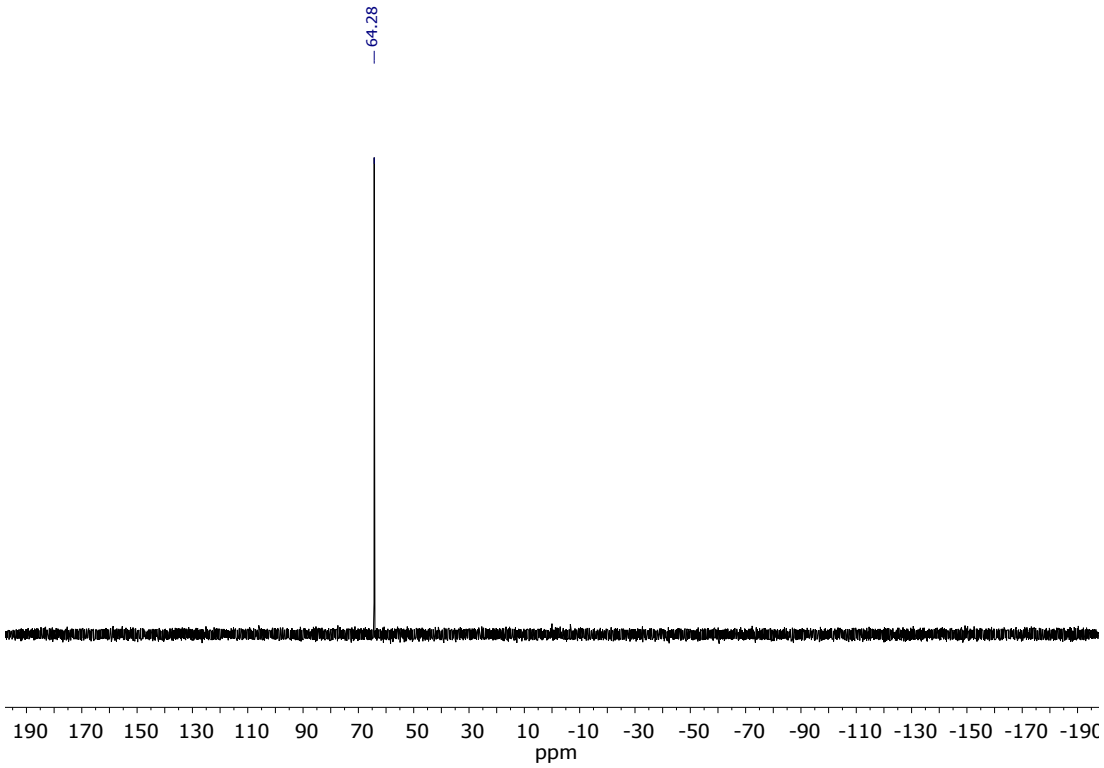


Figure 8. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)($BMes_2$).

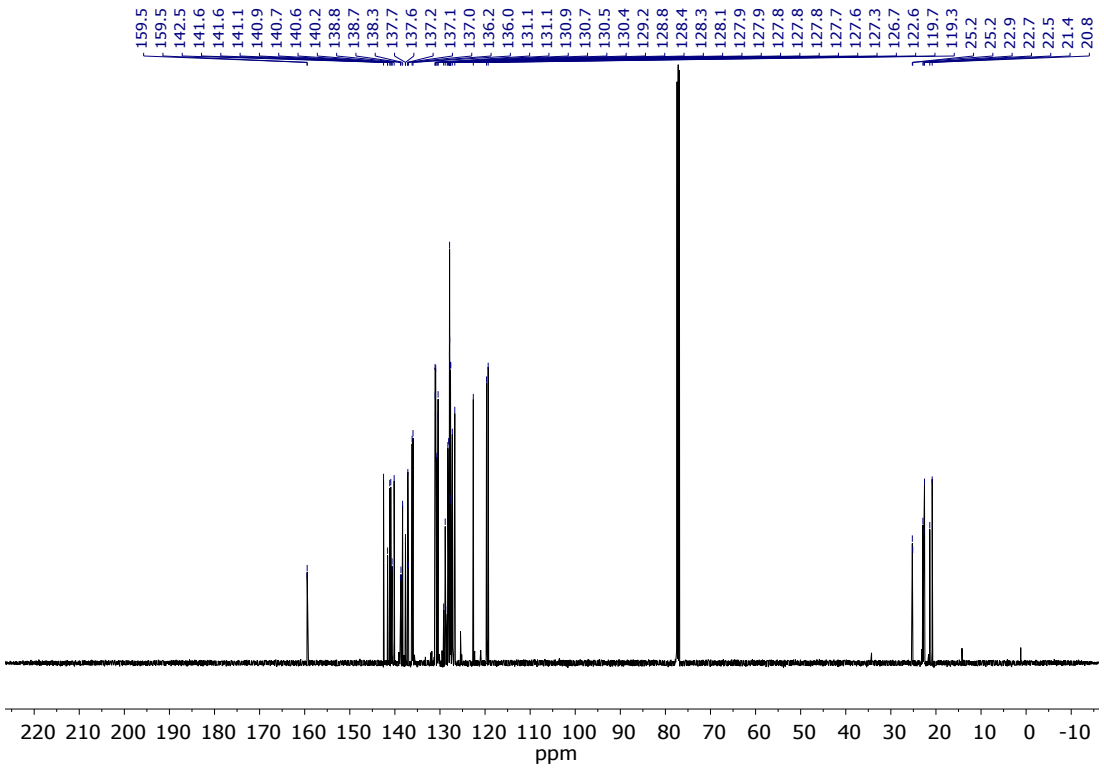


Figure 9. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)($BMes_2$).

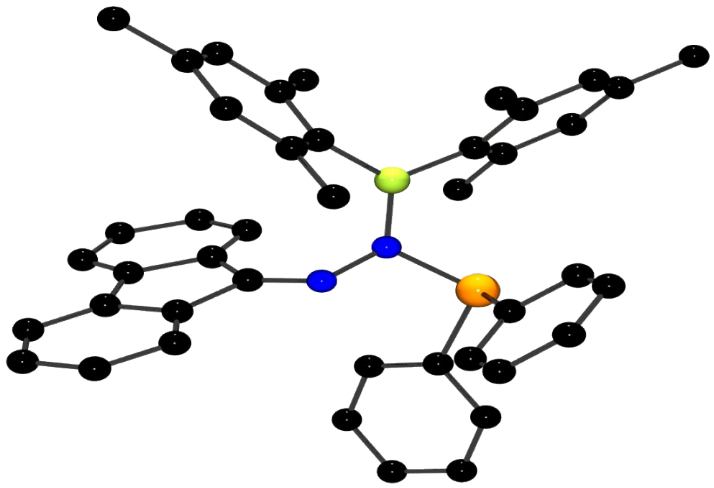
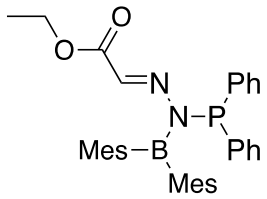


Figure 10. Solid-state structure of FluorenylNN(PPh_2)($BMes_2$).

ethyl (E)-2-(2-(dimesitylboraneyl)-2-(diphenylphosphaneyl)hydrazineylidene)acetate ((EtOOC)CNN(PPh$_2$)(BMes$_2$))



In a 20 mL vial, a solution of Ph_2PBMes_2 (0.1 mmol, 43.4 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of ethyl 2-diazoacetate (0.1 mmol, 11.4 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a yellow solid (48.7 mg, 88.9% isolated yield). **HRMS (DART-ESI+):** m/z [M+H] 549.28368 (calc'd for $C_{34}H_{39}B_1N_2O_2P_1$: 549.28422). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.54 (t, *J* = 8 Hz, 4H), 7.36 – 7.31 (m, 6H), 7.15 (s, 1H), 6.81 (s, 2H), 6.59 (s, 2H), 4.10 (q, $^3J_{HH}$ = 7 Hz, 2H), 2.30 (s, 3H), 2.26 (s, br, 6H), 2.16 (s, 3H), 1.82 (s, br, 6H), 1.17 ppm (t, $^3J_{HH}$ = 7 Hz, 3H). **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 46.4 (s, br) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 57.9 (s) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 162.3 (d, *J* = 1Hz), 148.8, 140.9 (d, *J* = 2 Hz), 140.6 (s, br), 138.2 (d, *J* = 1 Hz), 138.1, 138.1 (s, br), 137.9 (s, br), 135.0 (s, br), 133.8 (d, br, *J* = 21 Hz), 129.4 (s, br), 128.4, 128.2, 128.0 (d, *J* = 7 Hz), 61.2, 23.2 (s, br), 22.0, 21.4, 21.1, 14.1 ppm.

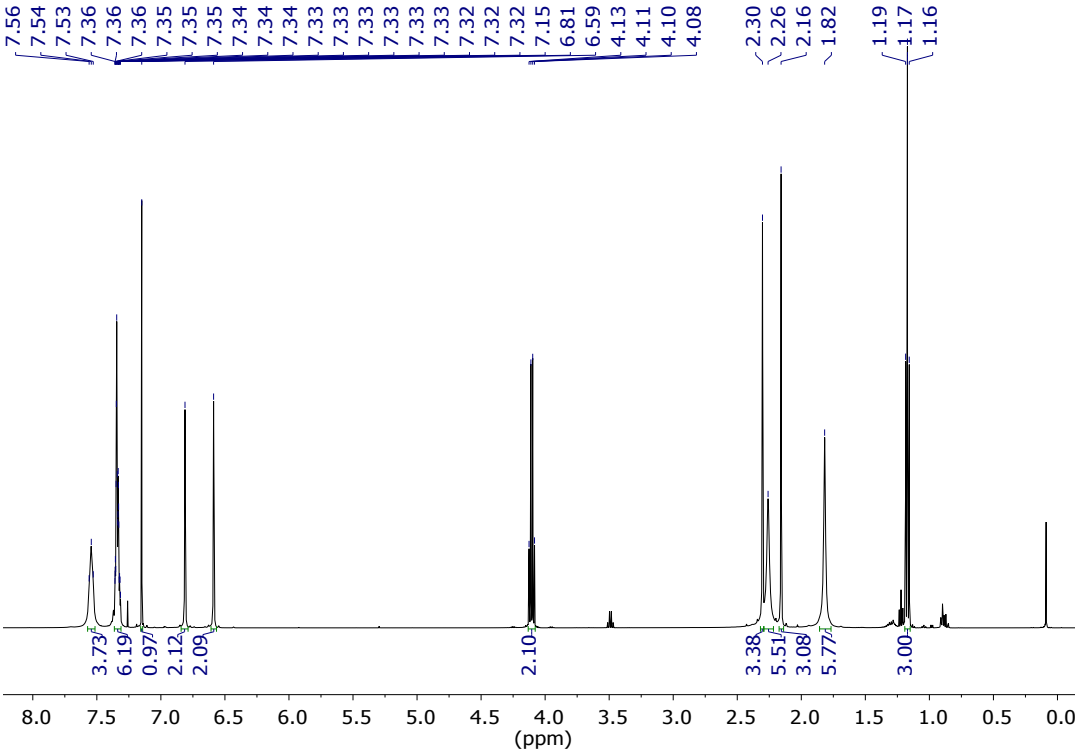


Figure 11. ^{1}H ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)($BMes_2$).

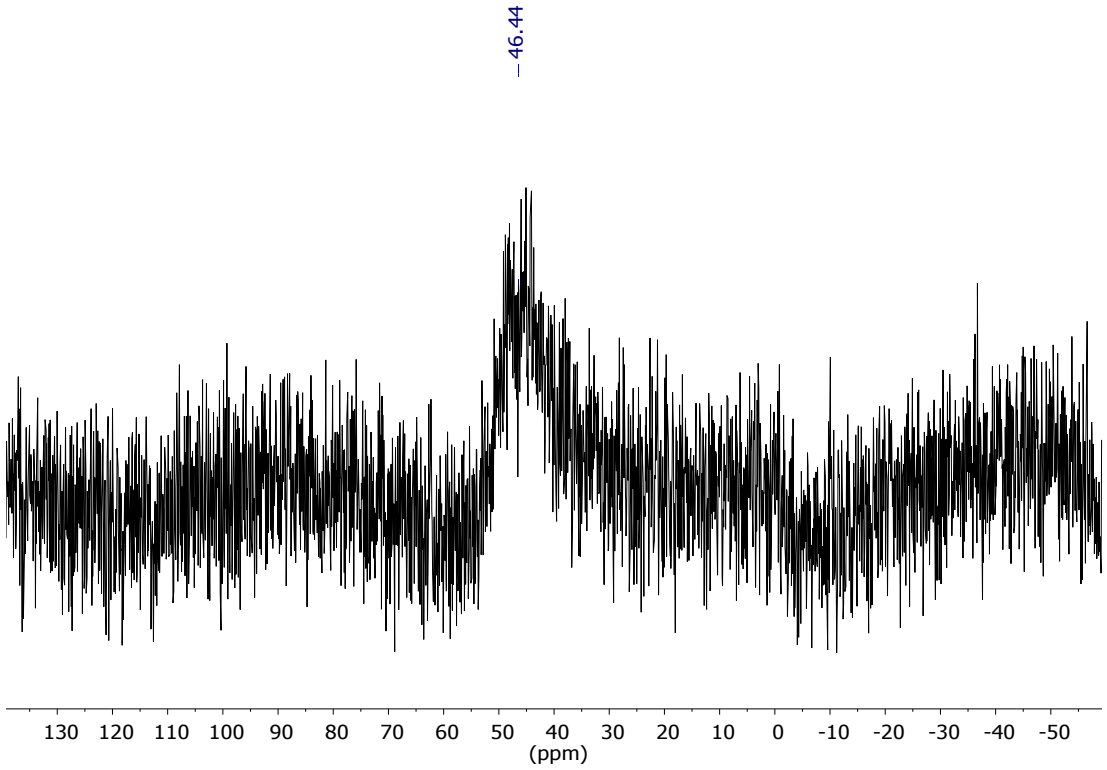


Figure 12. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)($BMes_2$).

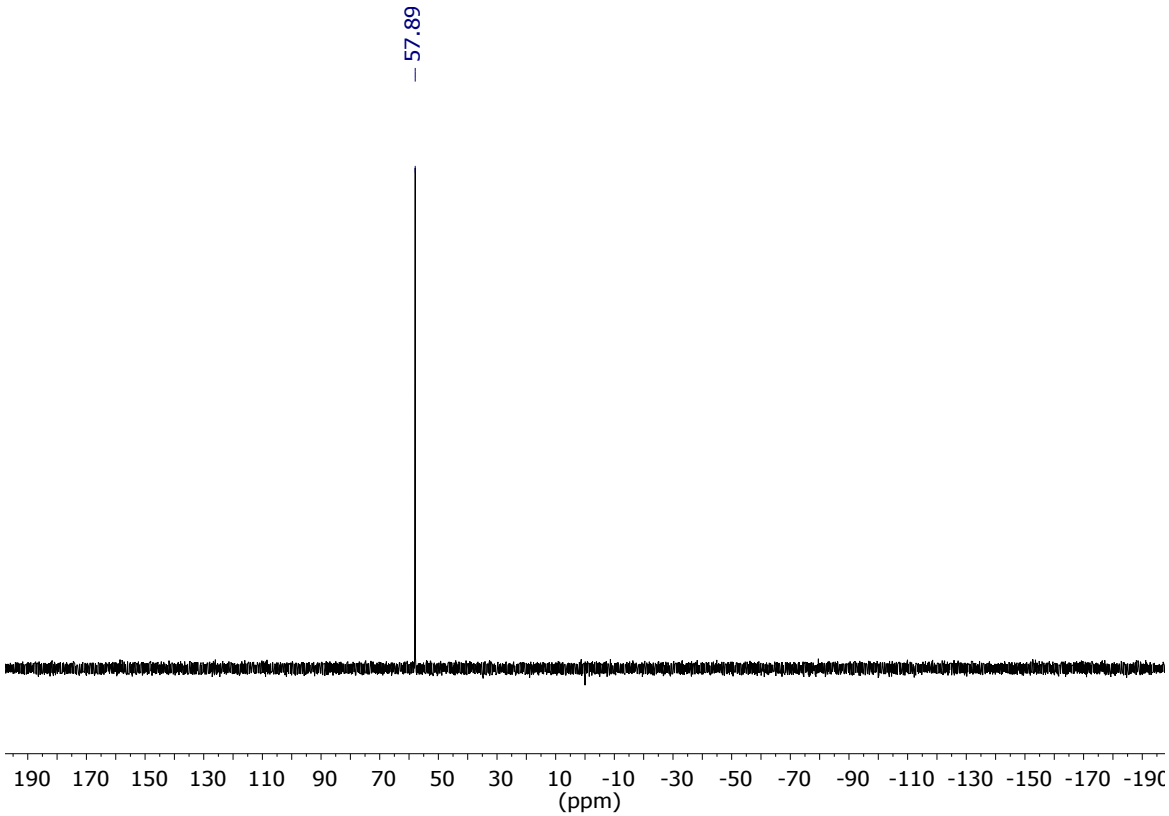


Figure 13. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)($BMes_2$).

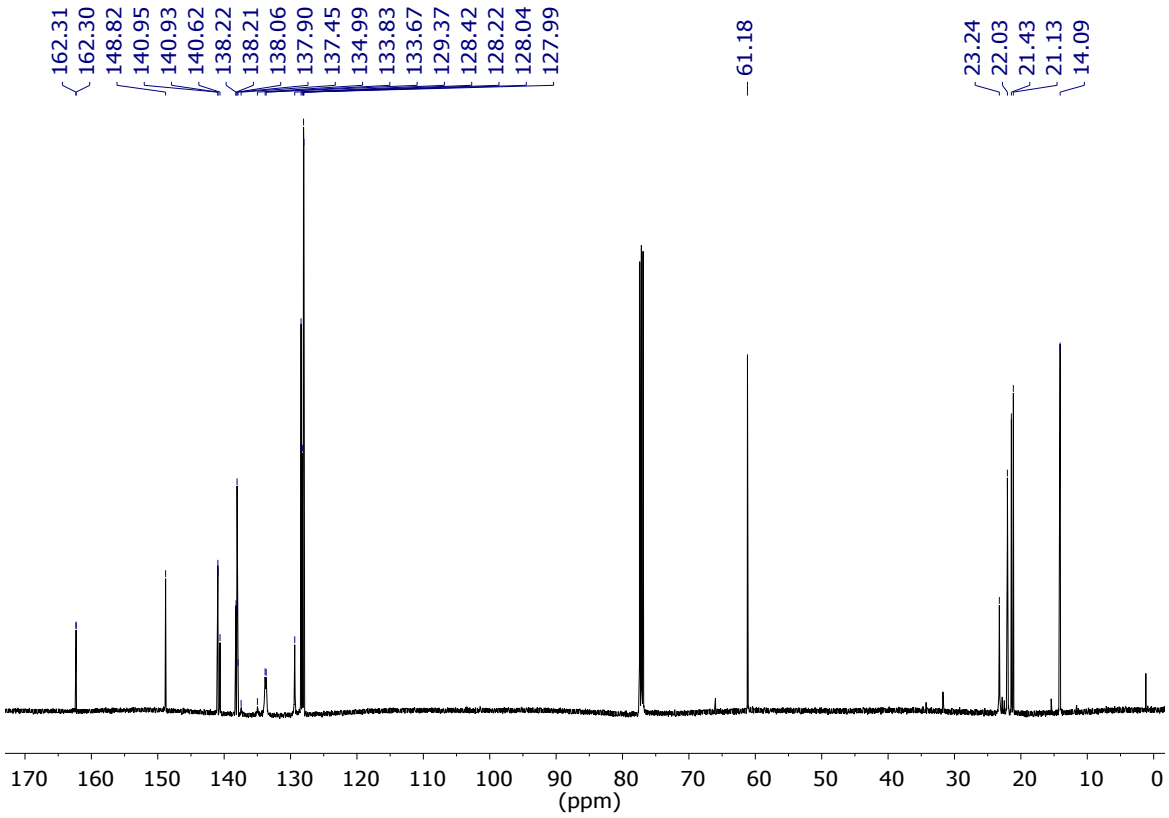


Figure 14. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)($BMes_2$).

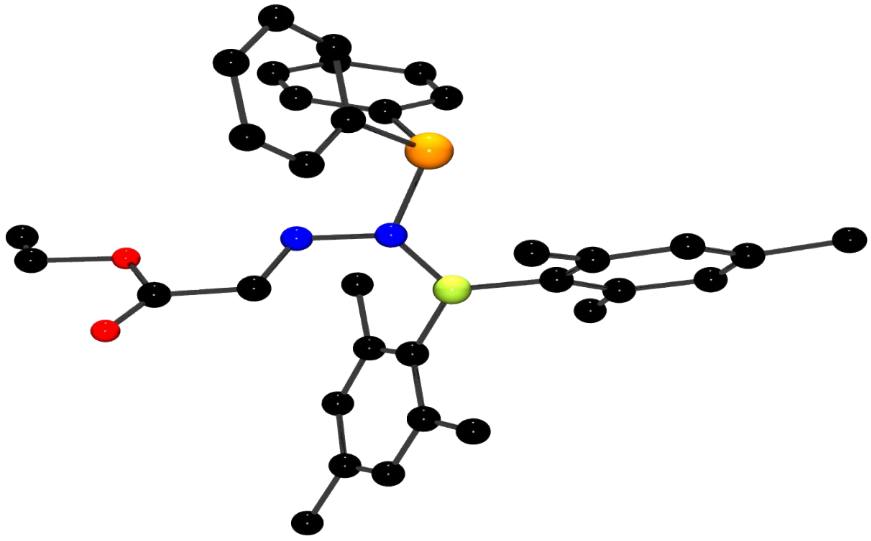
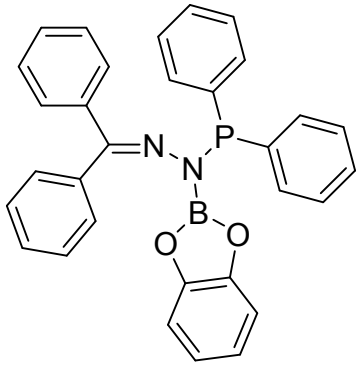


Figure 15. Solid-state structure of (EtOOC)CNN(PPh_2)($BMes_2$).

1-(benzo[d][1,3,2]dioxaborol-2-yl)-2-(diphenylmethylene)-1-(diphenylphosphinyl)hydrazine ($Ph_2CNN(PPh_2)(Bcat)$)



In a 20 mL vial, a solution of Ph_2PBcat (0.1 mmol, 30.4 mg, 1 eq.) was prepared in DCM (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from Et_2O to afford a colourless crystalline solid (45.4 mg, 91% isolated yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 6.40 – 6.43 (m, 2H), 6.94 (dd, *J* = 6, 3 Hz, 2H), 7.01 – 7.06 (m, 4H), 7.11 (tt, *J* = 8, 2 Hz, 1H), 7.26 – 7.30 (m, 2H), 7.32 – 7.40 (m, 8H), 7.48 – 7.51 (m, 2H), 7.63 – 7.67 (m, 4H) ppm. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 25.6 (s, br) ppm. **^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$):** δ = 49.8 (s) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 112.0, 122.15, 127.6, 128.1, 128.2, 128.3, 128.5, 128.9, 129.4, 130.5, 133.8, 134.0, 134.7, 137.3, 137.4, 137.7, 148.3, 148.3, 172.0 ppm.

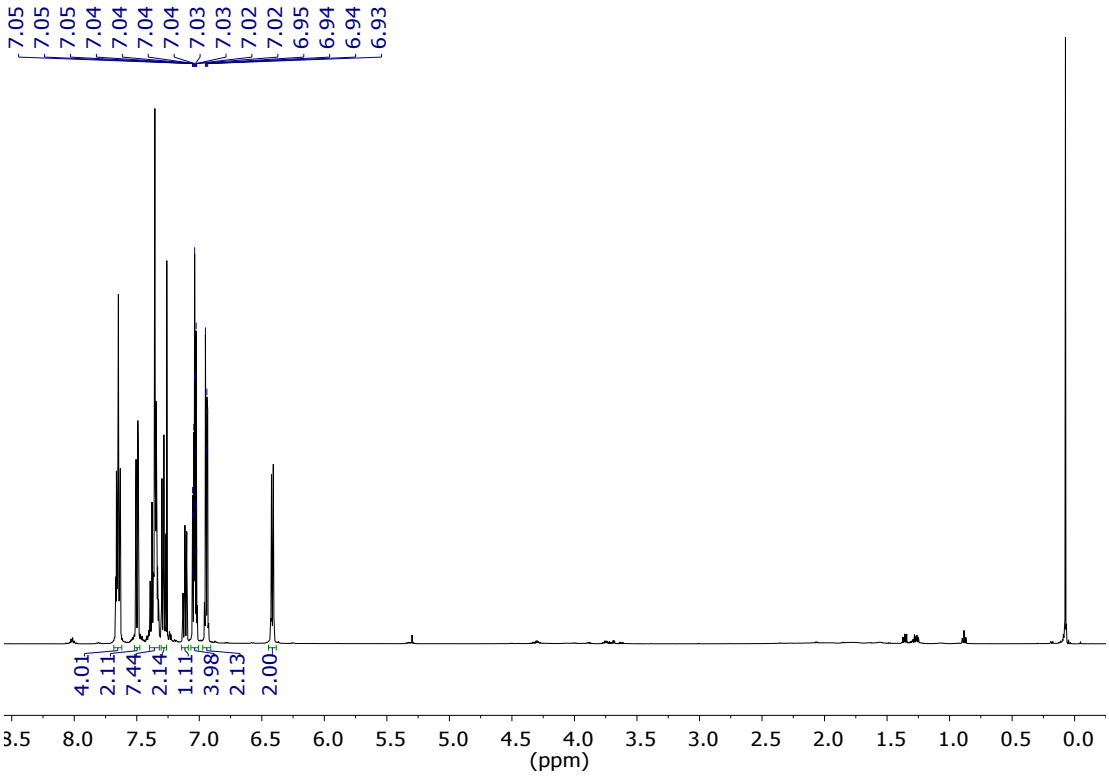


Figure 16. ^{1}H ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(Bcat)$.

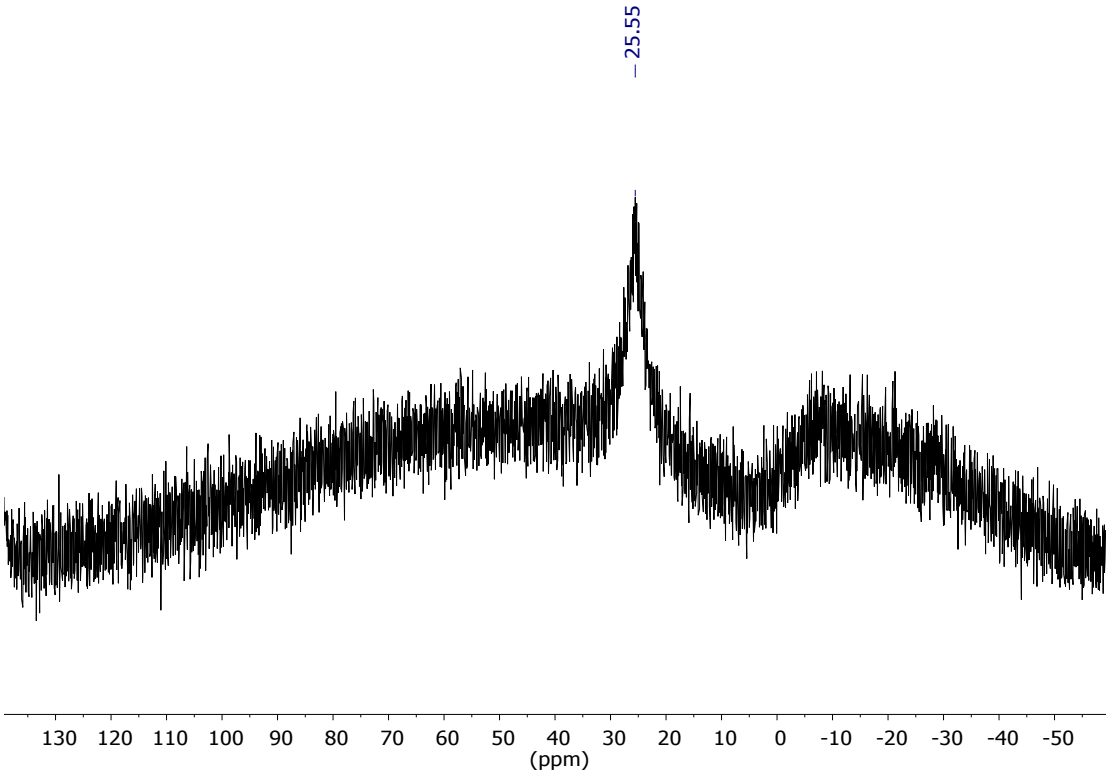


Figure 17. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(Bcat)$.

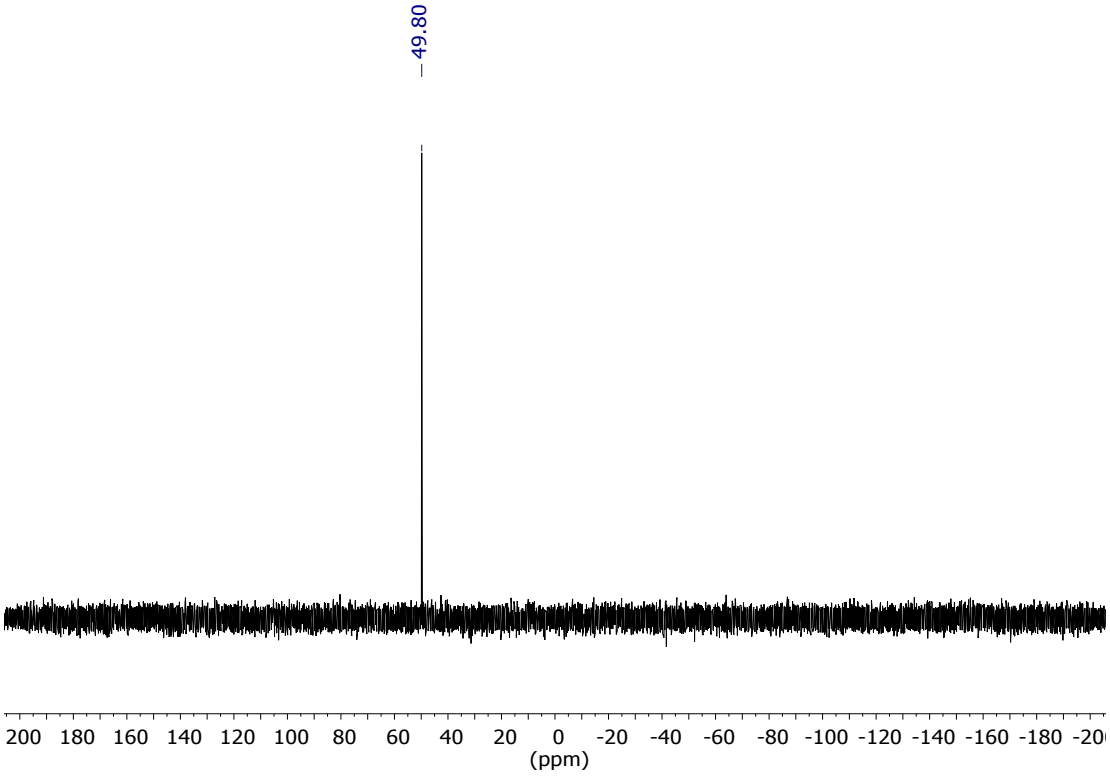


Figure 18. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(Bcat)$.

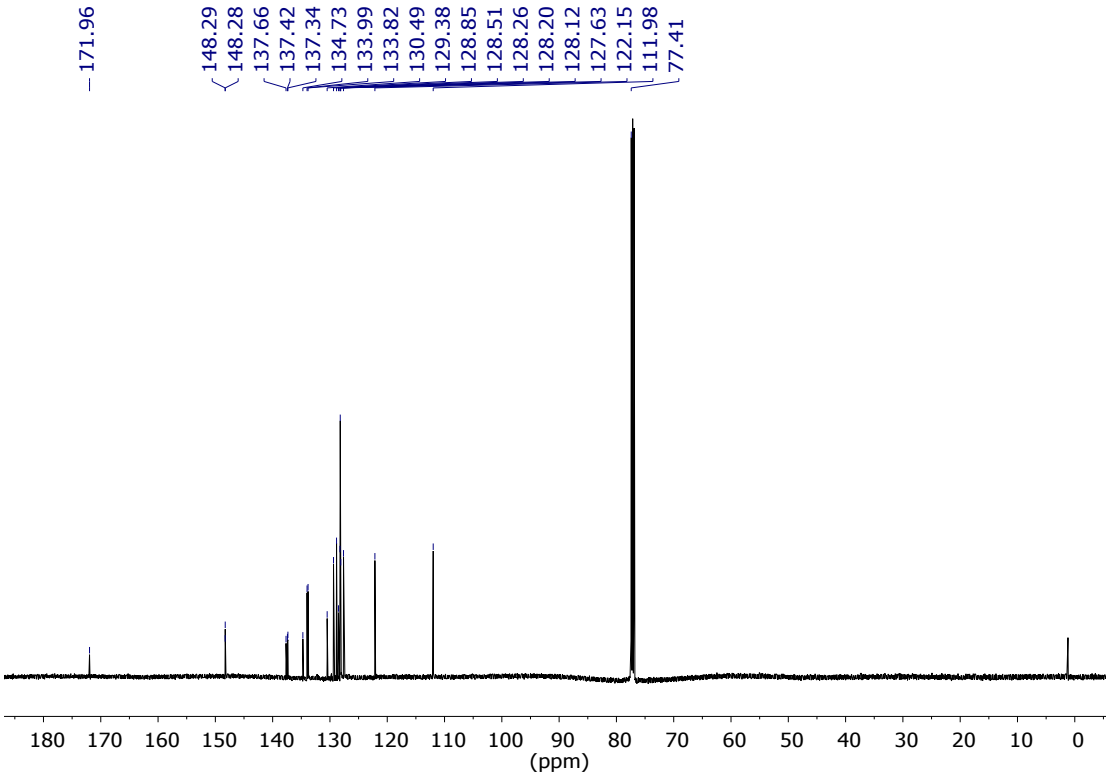


Figure 19. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2CNN(PPh_2)(Bcat)$.

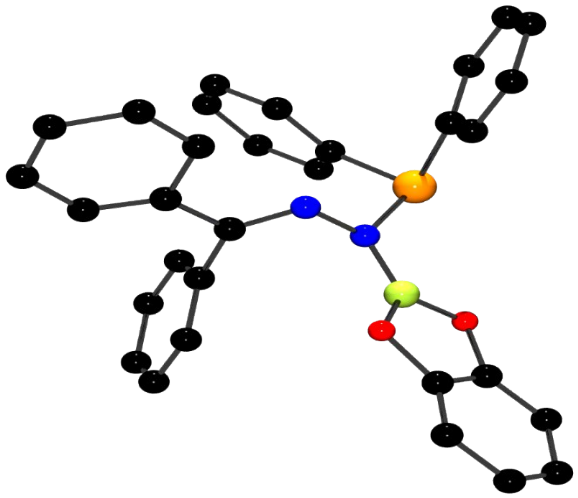
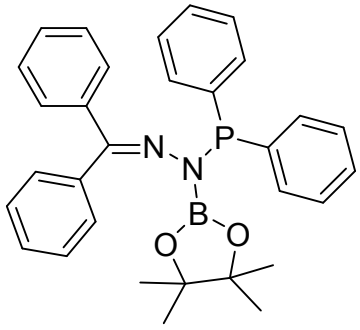


Figure 20. Solid-state structure of $Ph_2CNN(PPh_2)(Bcat)$.

2-(diphenylmethylene)-1-(diphenylphosphaneyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (Ph_2C=NN(PPh_2)(Bpin))



In a 20 mL vial, a solution of Ph_2PBpin (0.1 mmol, 31.2 mg, 1 eq.) was prepared in DCM (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* to afford a colourless solid (48.1 mg, 95% isolated yield). **HRMS (ESI+):** m/z [M+H] 506.2403 (calc'd for $C_{31}H_{33}B_1N_2O_2P_1$: 506.2404). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 1.11 (s, 12H), 6.59 – 6.62 (m, 2H), 7.18 – 7.22 (m, 2H), 7.23 – 7.29 (m, 4H), 7.33 – 7.36 (m, 6H), 7.46 – 7.49 (m, 2H), 7.63 – 7.67 (m, 4H) ppm. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 24.3 (s, br) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 48.5 (s) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 24.5, 83.5, 127.4, 127.9, 127.9, 128.1, 128.7, 128.8 (br), 129.0, 129.7, 133.8 (d, br, *J* = 21 Hz), 135.3, 138.3, 138.8 (d, *J* = 12 Hz), 169.2 ppm.

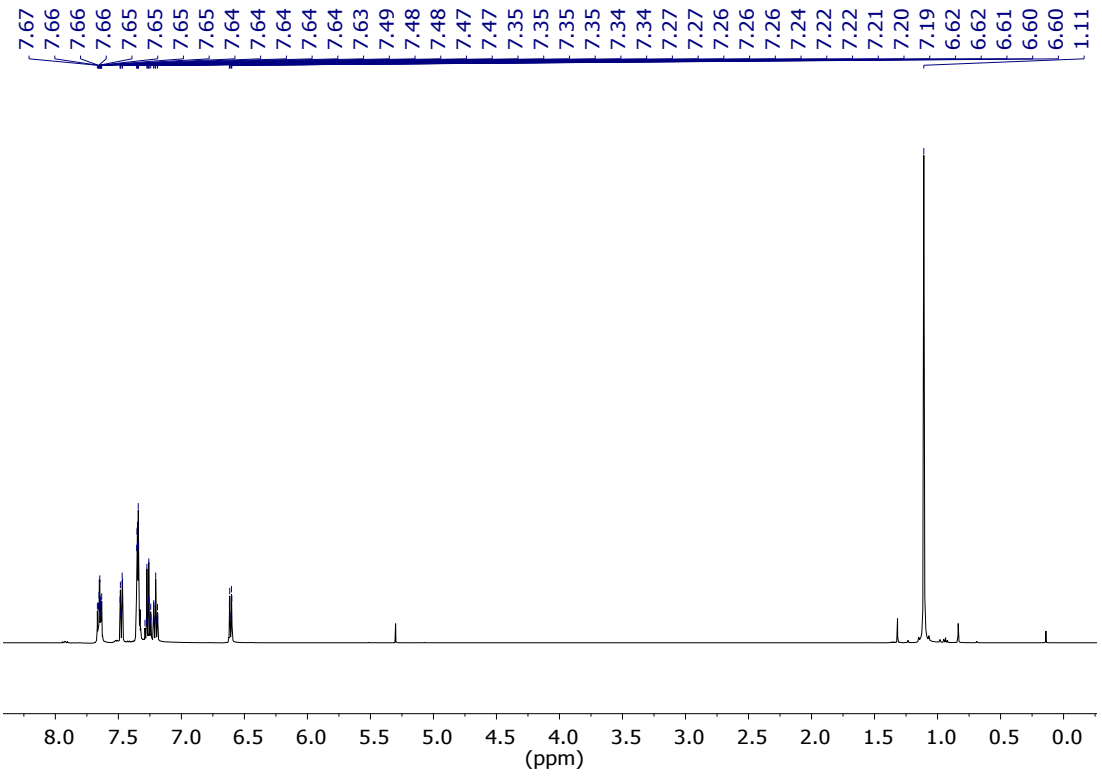


Figure 21. ^{1}H ($CDCl_3$) NMR of Ph_2C=NN(PPh_2)(Bpin).

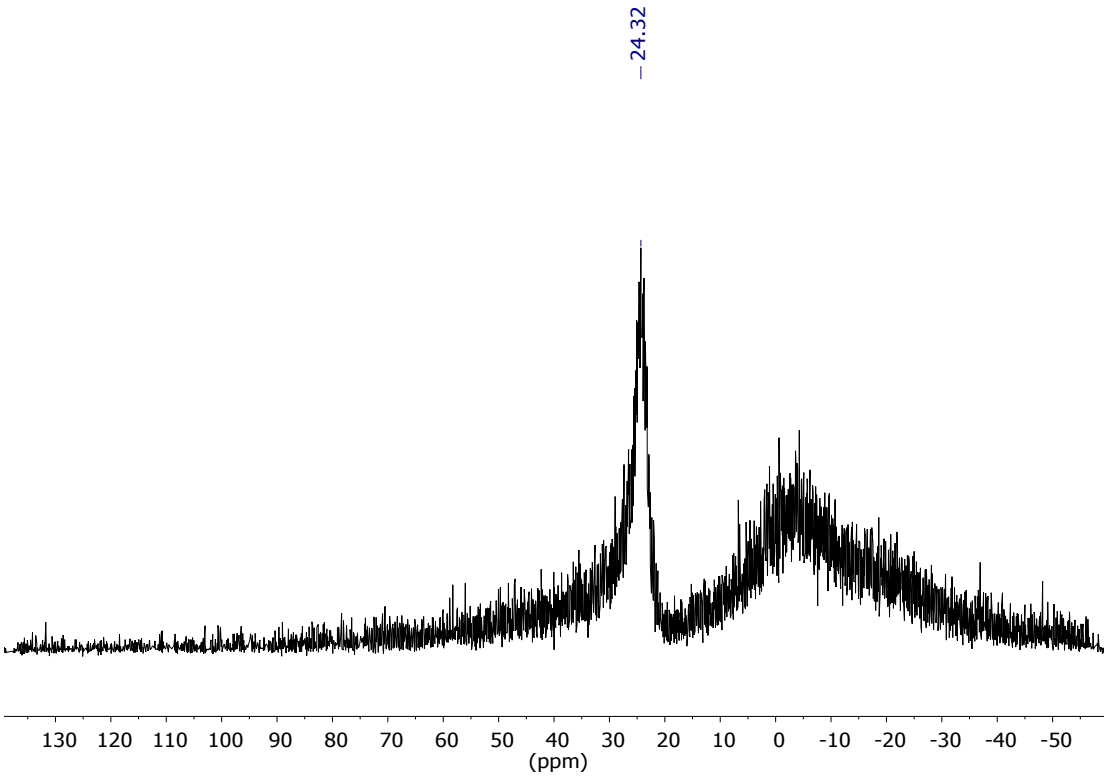


Figure 22. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2C{=}NN(PPh_2)(Bpin)$.

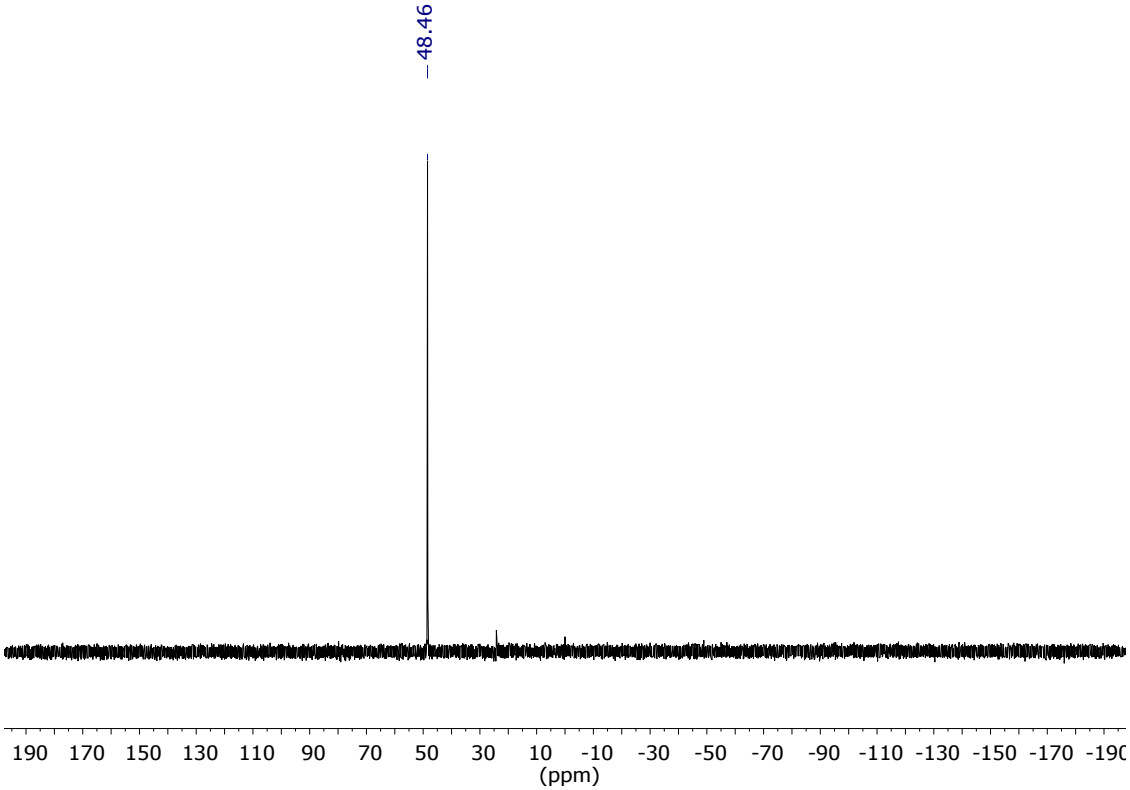


Figure 23. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2C{=}NN(PPh_2)(Bpin)$.

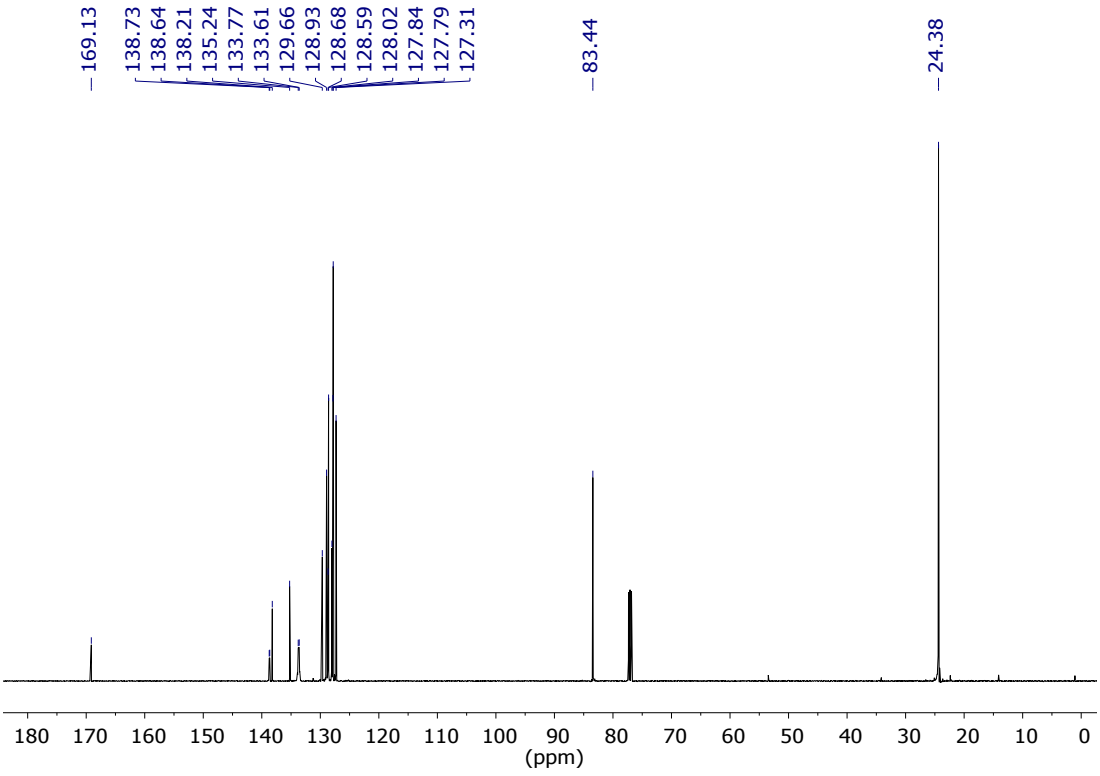


Figure 24. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of $Ph_2C{=}NN(PPh_2)(Bpin)$.

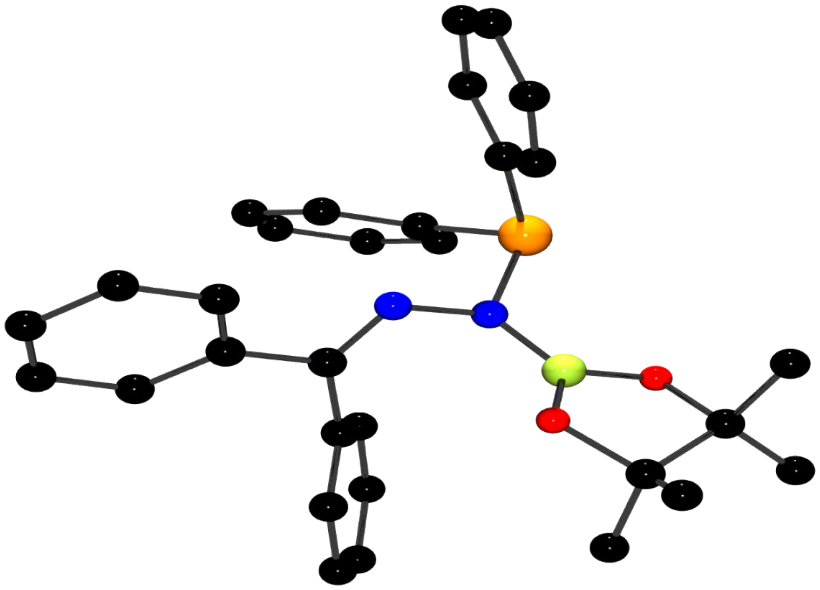
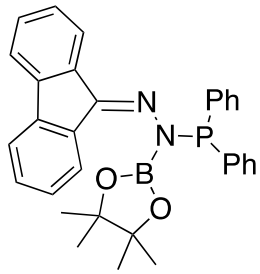


Figure 25. Solid-state structure of $Ph_2C{=}NN(PPh_2)(Bpin)$.

1-(diphenylphosphaneyl)-2-(9H-fluoren-9-ylidene)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (FluorenylNN(PPh_2)(Bpin))



In a 20 mL vial, a solution of Ph_2PBpin (0.1 mmol, 31.2 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.2 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a yellow solid (48.5 mg, 96.3% isolated yield). **HRMS (ESI+):** m/z [M+H] 504.2255 (calc'd for $C_{31}H_{30}B_1N_2O_2P_1$: 504.2266). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.11 (dt, *J* = 8, 1 Hz, 1H), 7.71 (dt, *J* = 8, 1 Hz, 1H), 7.57 (s, br, 4H), 7.47 (dt, *J* = 8, 1 Hz, 2H), 7.31 (dtd, *J* = 18, 8, 1 Hz, 3H), 7.21 (s, br, 4H), 7.16 (dtd, *J* = 29, 8, 1 Hz, 3H), 1.18 (s, br, 12H). **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 24.5 (s, br) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 57.5 (s) ppm. **^{3}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 165.2, 142.3, 140.7, 137.1, 131.2, 131.1, 130.6, 128.6 (br), 127.8, 127.7, 127.6 (br), 127.5, 122.9, 119.5, 119.2, 83.8, 24.6 (br) ppm.

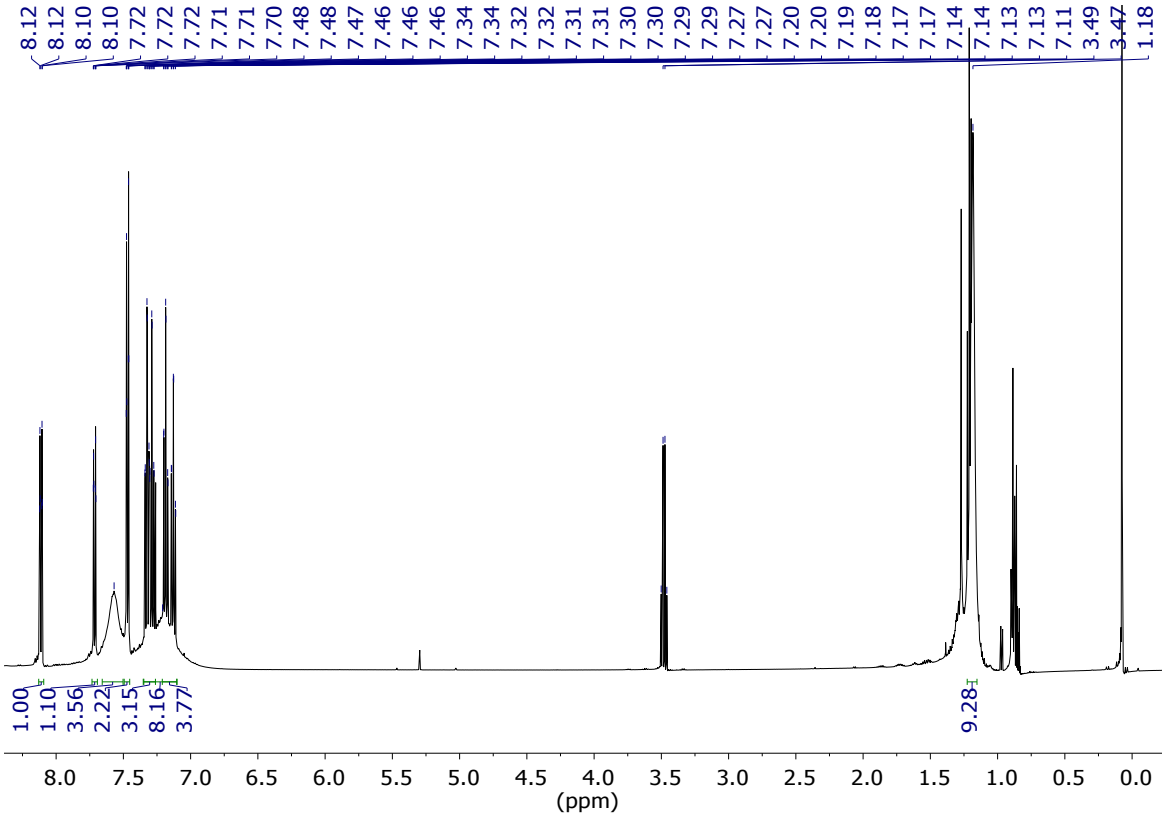


Figure 26. ^{1}H ($CDCl_3$) NMR of FluorenylNN(PPh_2)(Bpin) (residual diethylether present).

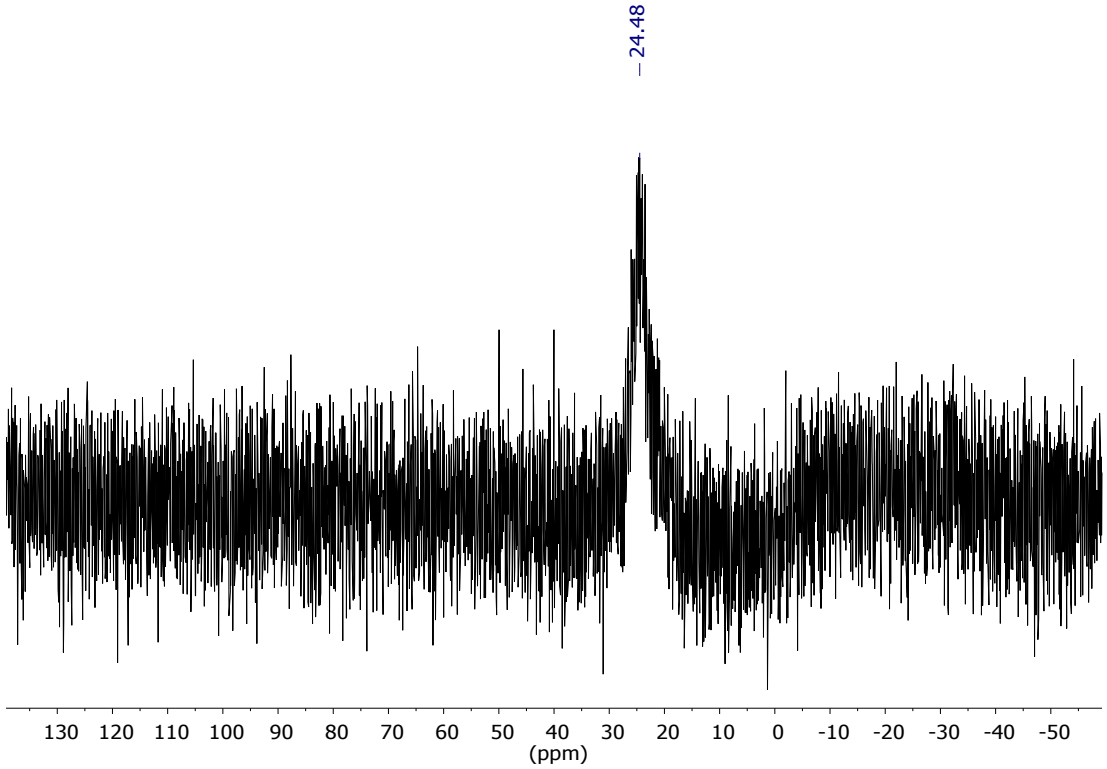


Figure 27. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)(Bpin).

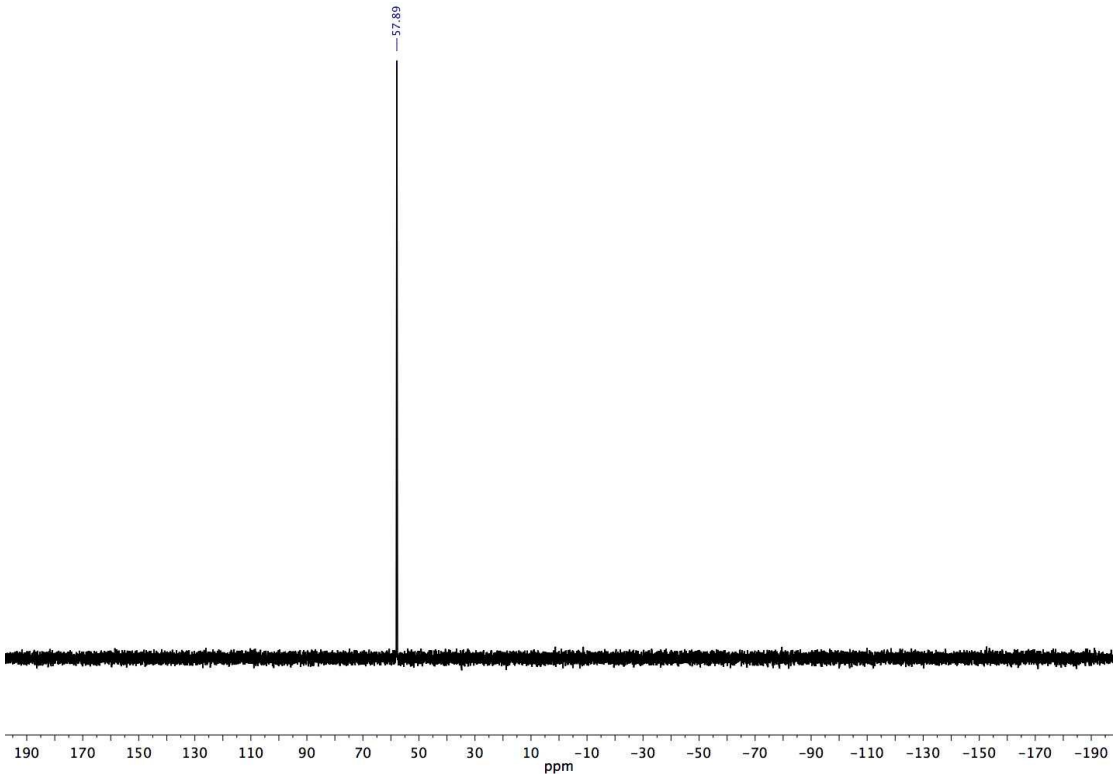


Figure 28. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)(Bpin).

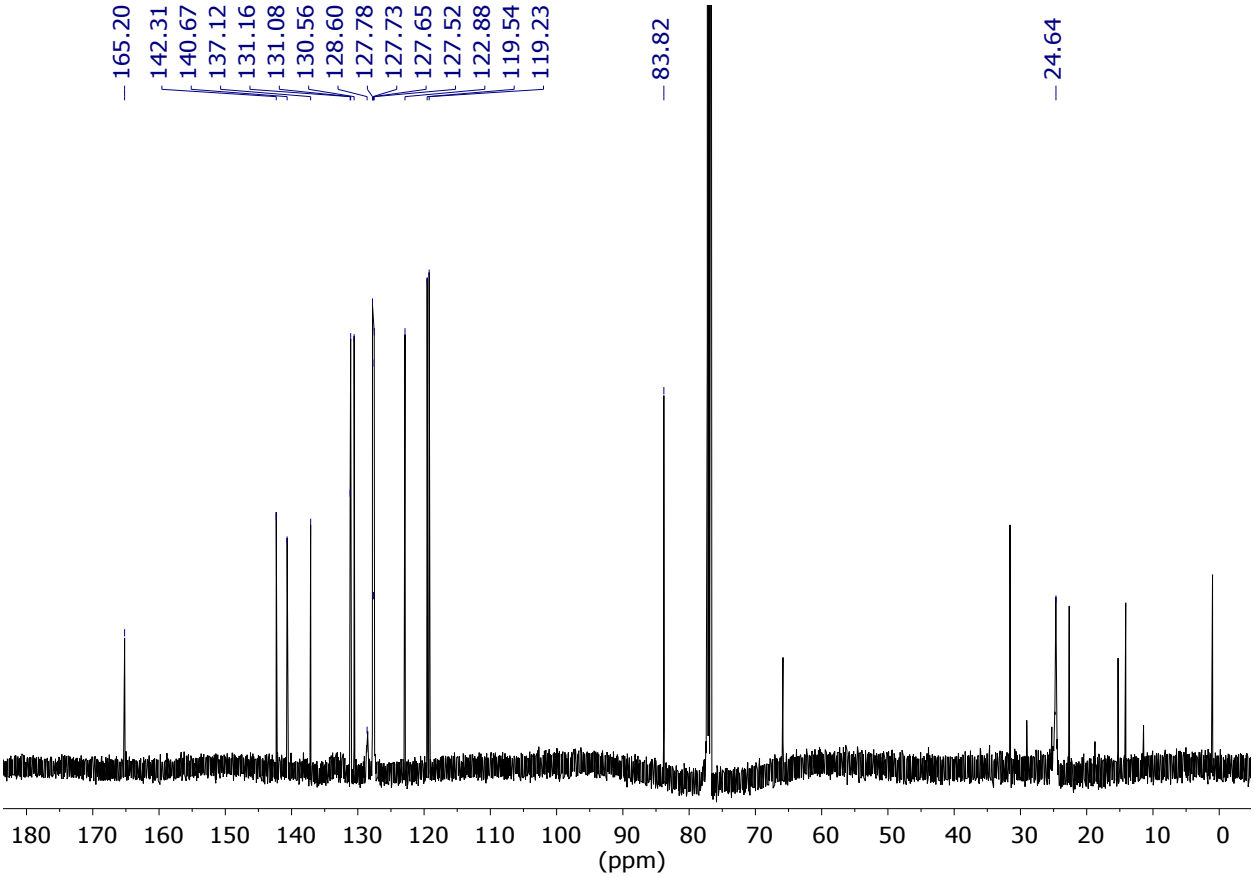
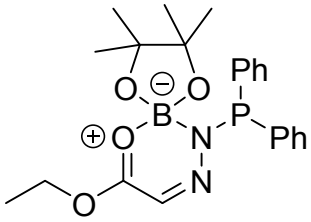


Figure 29. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of FluorenylNN(PPh_2)(Bpin). Peak at 1 ppm corresponds to residual silicone grease, peaks at 15.3 and 65.8 ppm correspond to residual diethyl ether, and peaks at 14.1, 22.6, and 31.6 correspond to residual *n*-pentane.

6-(diphenylphosphaneyl)-9-ethoxy-2,2,3,3-tetramethyl-1,4,10λ³-trioxa-6,7-diaza-5λ⁴-boraspiro[4.5]deca-7,9-diene ((EtOOC)CNN(PPh_2)(Bpin))



In a 20 mL vial, a solution of Ph_2PBpin (0.1 mmol, 31.2 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of ethyl 2-diazoacetate (0.1 mmol, 11.4 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a yellow solid (36.7 mg, 86.2% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 427.19622 (calc'd for $C_{22}H_{29}B_1N_2O_4P_1$: 427.19580). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.48 – 7.44 (m, 4H), 7.33 – 7.30 (m, 6H), 7.16 (d, *J* = 1 Hz, 1H), 4.42 (q, $^{3}J_{HH}$ = 7 Hz, 2H), 1.39 (t, $^{3}J_{HH}$ = 7 Hz, 3H), 1.34 ppm (s, 12H).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 11.9 (s) ppm. **$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$):** δ = 52.9 (s) ppm. **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$):** δ = 164.0, 138.8 (d, *J* = 16 Hz), 133.1 (d, *J* = 22 Hz), 129.0, 128.1 (d, *J* = 6 Hz), 120.7, 81.7, 64.8, 26.3 (d, *J* = 4 Hz), 24.7, 14.1 ppm.

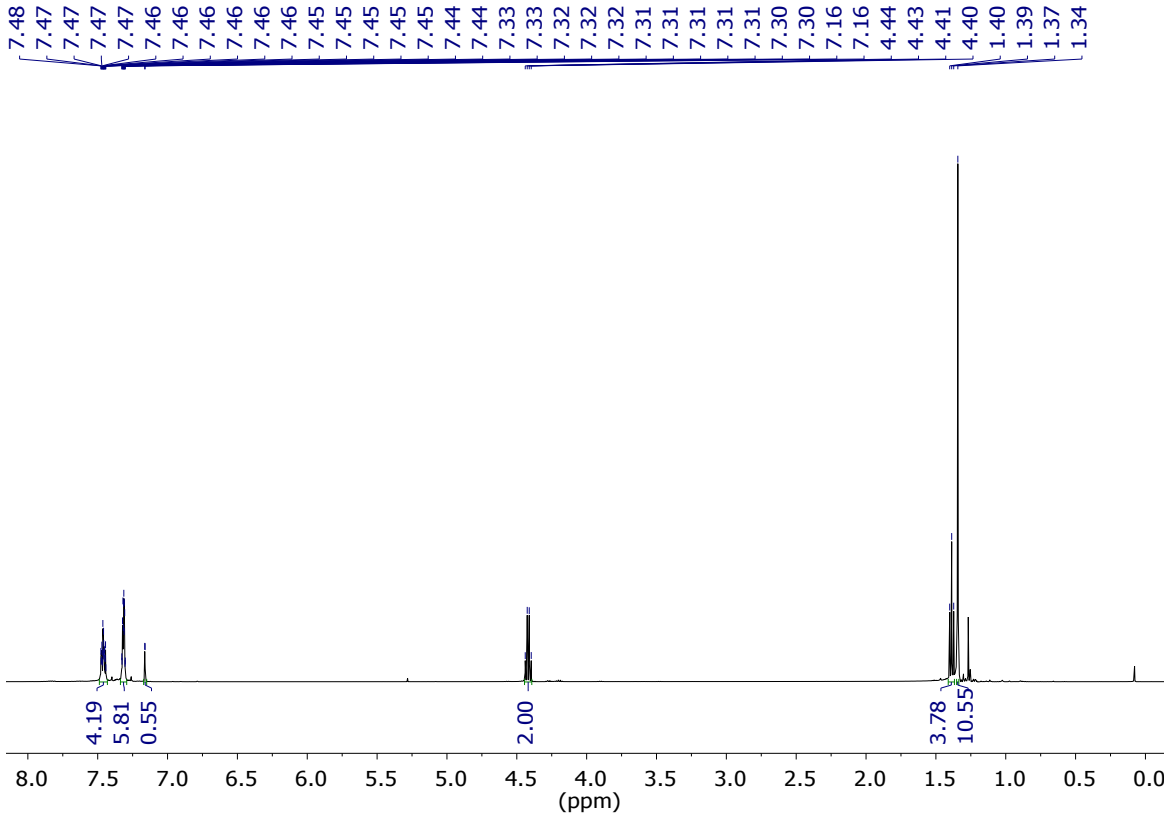


Figure 30. ^1H ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)(Bpin).

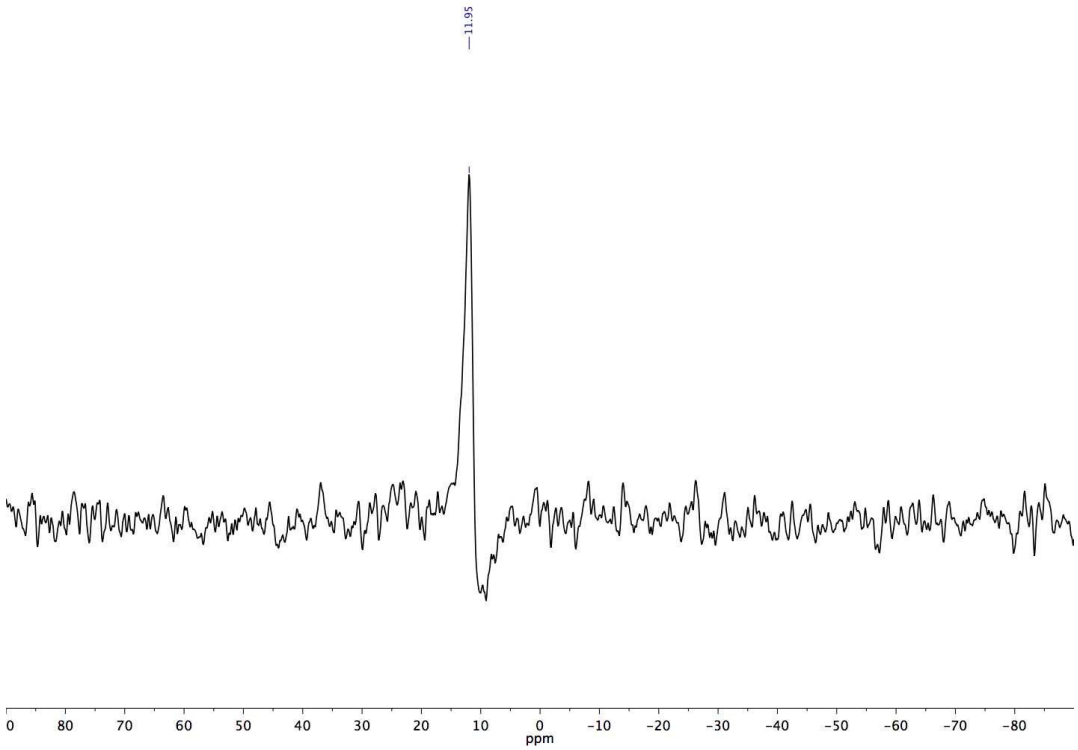


Figure 31. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)(Bpin).

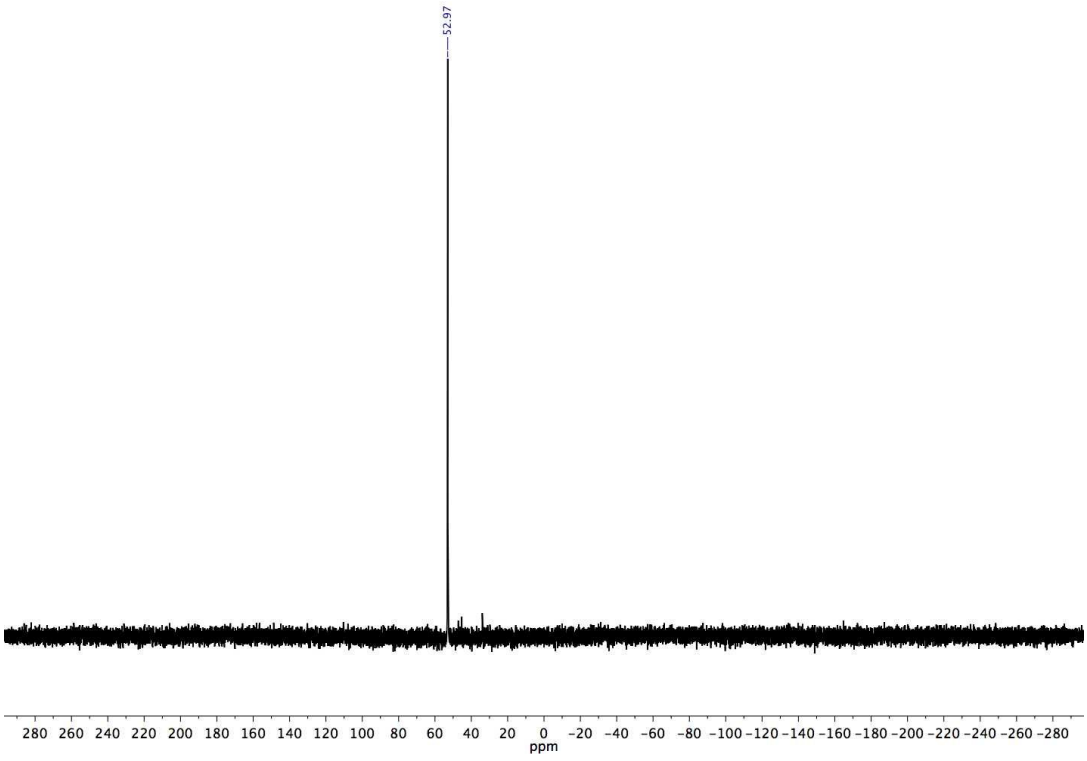


Figure 32. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)(Bpin).

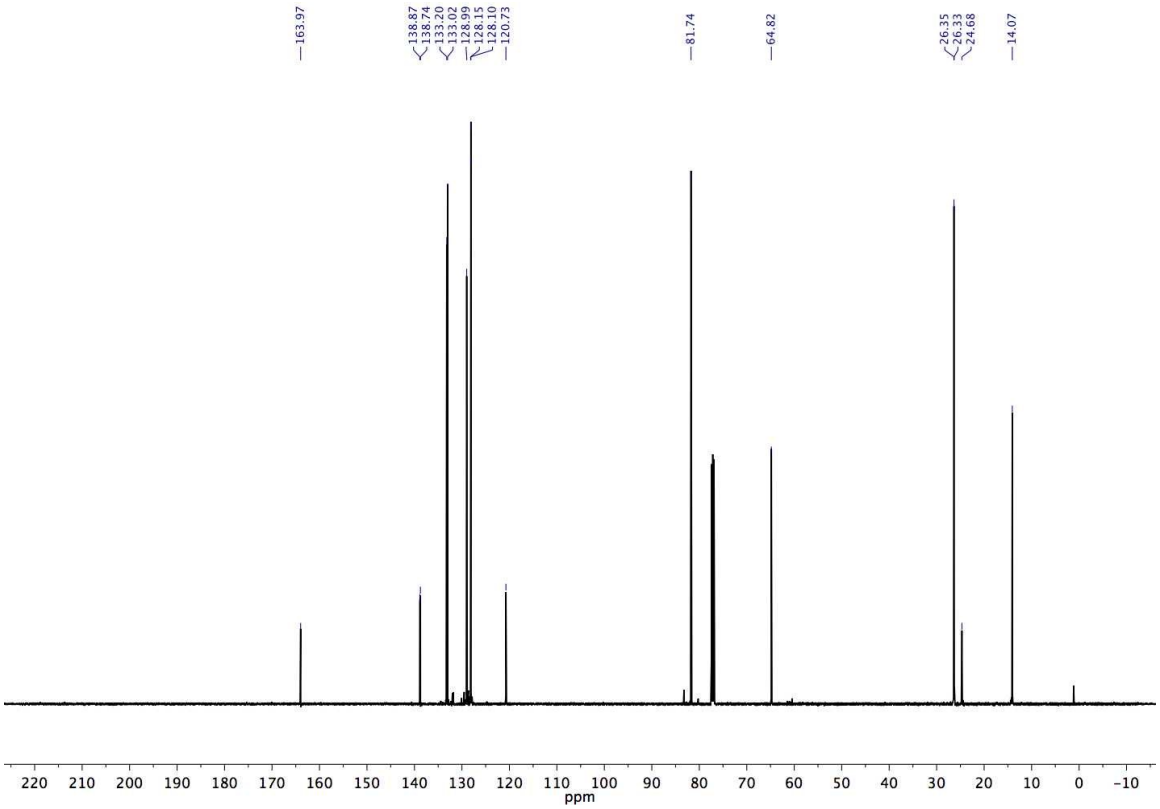


Figure 33. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(PPh_2)(Bpin).

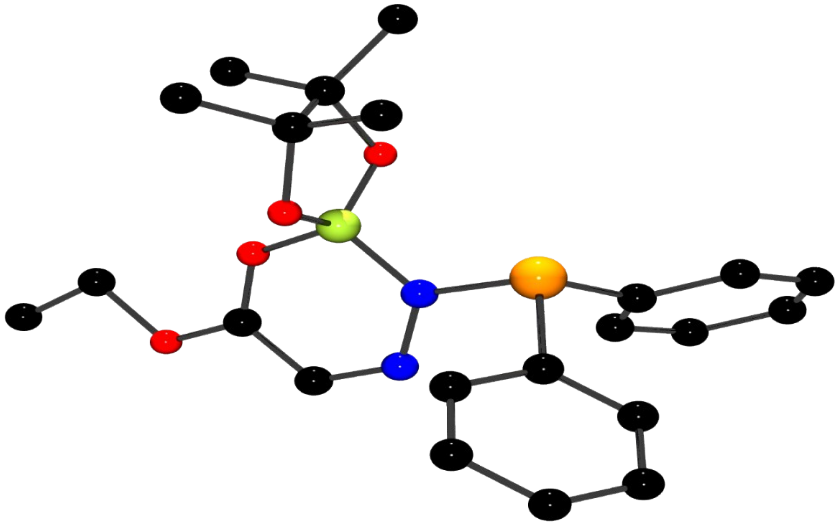
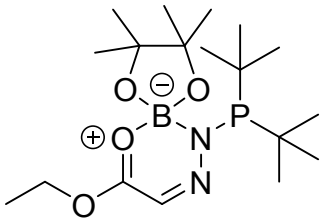


Figure 34. Solid-state structure of (EtOOC)CNN(PPh_2)(Bpin).

6-(di-tert-butylphosphaneyl)-9-ethoxy-2,2,3,3-tetramethyl-1,4,10λ^3-trioxa-6,7-diaza-5λ^4-boraspiro[4.5]deca-7,9-diene ((EtOOC)CNN(P*t*Bu$_2$)(Bpin))



In a 20 mL vial, a solution of *t*Bu$_2$PBpin (0.1 mmol, 27.2 mg, 1 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of 2-diazoacetate (0.1 mmol, 11.4 mg, 1 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et_2O to afford a yellow solid (34.8 mg, 90.1% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 387.25824 (calc'd for $C_{18}H_{37}B_1N_2O_4P_1$: 387.25804). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.17 (d, *J* = 1 Hz, 1H), 4.38 (q, $^3J_{HH}$ = 7 Hz, 2H), 1.38 (t, $^3J_{HH}$ = 7 Hz, 3H), 1.30 (s, 12H), 1.19 ppm (d, $^3J_{PH}$ = 12 Hz). **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$):** δ = 8.8 (s) ppm. **^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):** δ = 89.0 (s) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ = 163.2, 119.1, 81.6, 63.87 (d, *J* = 1 Hz), 35.7 (d, *J* = 29 Hz), 31.7, 29.6 (d, *J* = 16 Hz), 26.6 (d, *J* = 4 Hz), 24.7 (d, *J* = 2 Hz), 22.8, 14.2 (d, *J* = 14 Hz) ppm.

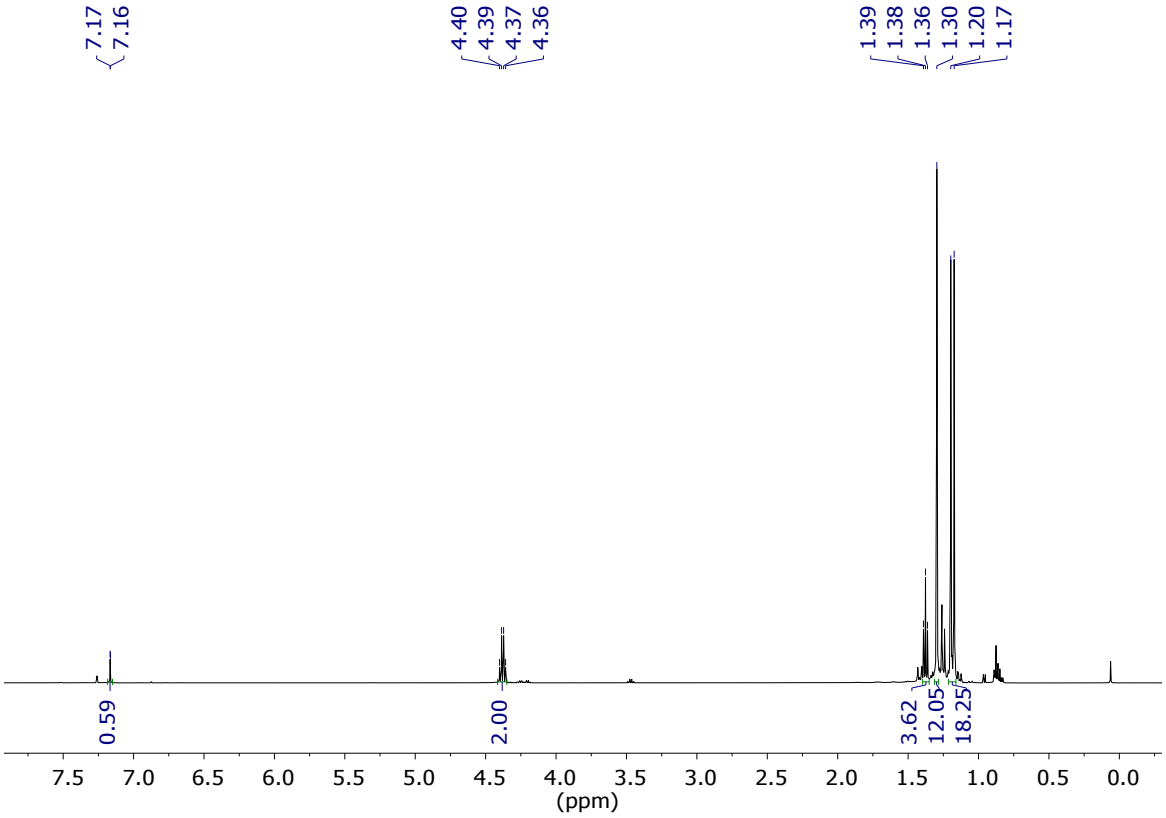


Figure 35. ^{1}H ($CDCl_3$) NMR of (EtOOC)CNN(P*t*Bu_2)(Bpin).

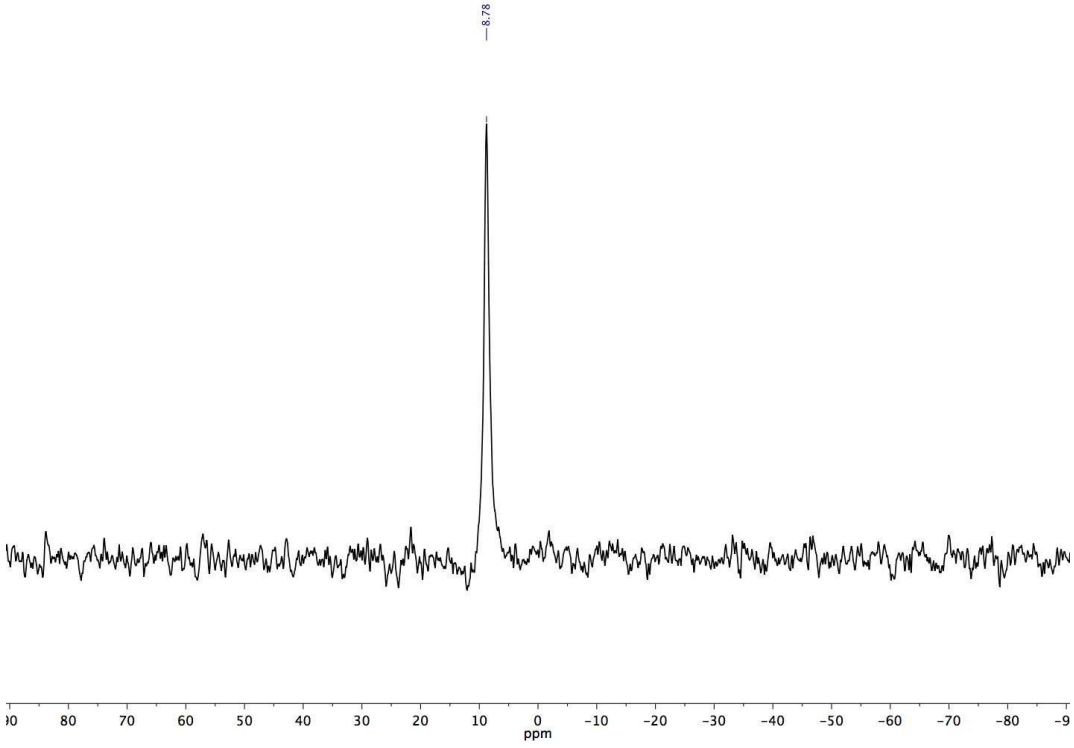


Figure 36. $^{11}B\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(P*t*Bu_2)(Bpin).

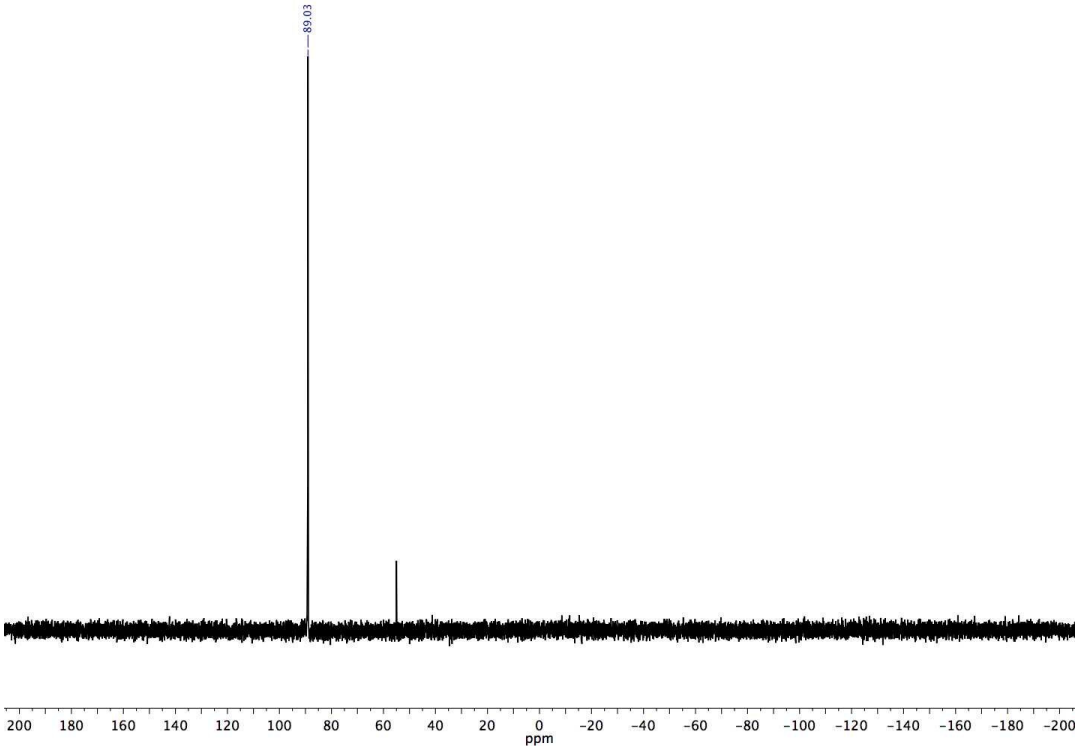


Figure 37. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(P*t*Bu_2)(Bpin).

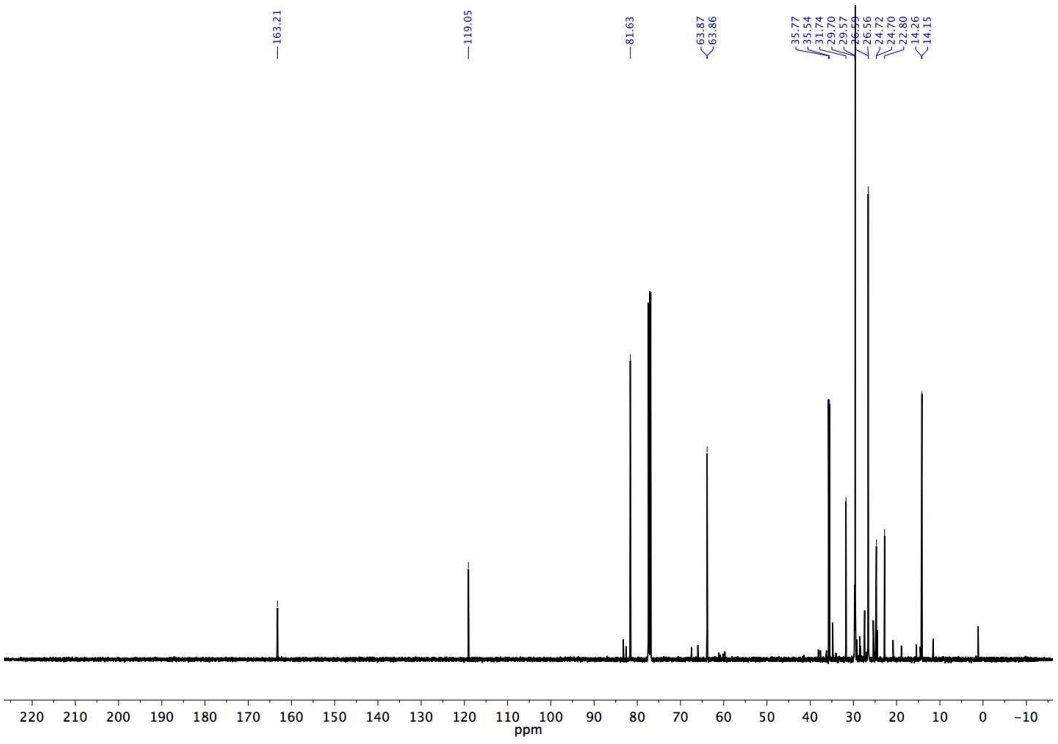


Figure 38. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR of (EtOOC)CNN(P*t*Bu_2)(Bpin).

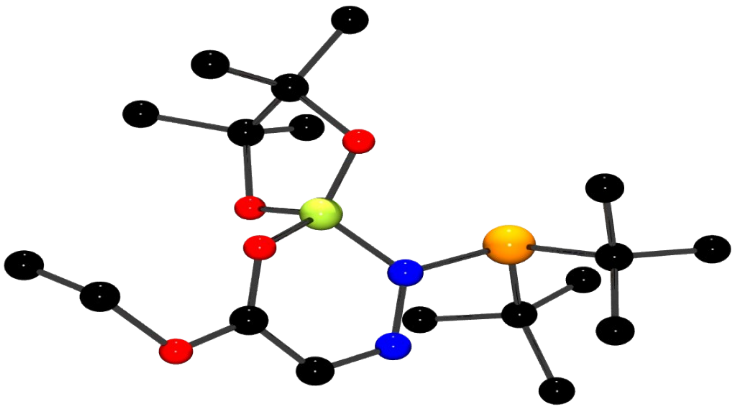


Figure 39. Solid-state structure of (EtOOC)CNN(P*t*Bu$_2$)(Bpin).

Computational Details

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.3 suite of programs[5] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(CH2Cl2) level of theory, which combines the TPSS meta-GGA density functional[6] with the BJ-damped DFT-D3 dispersion correction[7, 8] and the def2-TZVP basis set,[9, 10] using the Conductor-like Screening Model (COSMO) continuum solvation model[11] for CH_2Cl_2 solvent (dielectric constant $\varepsilon = 8.93$ and solvent diameter $R_{solv} = 2.94$ Å). The density-fitting RI-J approach[9, 12, 13] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[14] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model.[15] This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in CH2Cl2 are computed with the COSMO-RS solvation model12 (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package[13 on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol−1 to account for higher reference solute concentration of 1 mol·L−1 usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the

meta-GGA TPSS-D32 and hybrid-meta-GGA PW6B95-D314 levels are performed using a larger def2-QZVP basis set.6, 15 The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. The computed reaction free energies from both DFT functionals are in good mutual agreement of -0.1 ± 2.7 kcal/mol but the barriers at PW6B95-D3 level are usually 5.0 ± 3.5 kcal/mol higher (average and standard deviations, see Table S1 below), with the final results being somewhat sensitive to the choice of DFT functional. In our discussion, the higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L standard state concentration) will be used in our discussion unless specified otherwise. Meta-GGA functionals like TPSS tend to underestimate reaction barriers that can be evidently improved by hybrid meta-GGA functionals like PW6B95.

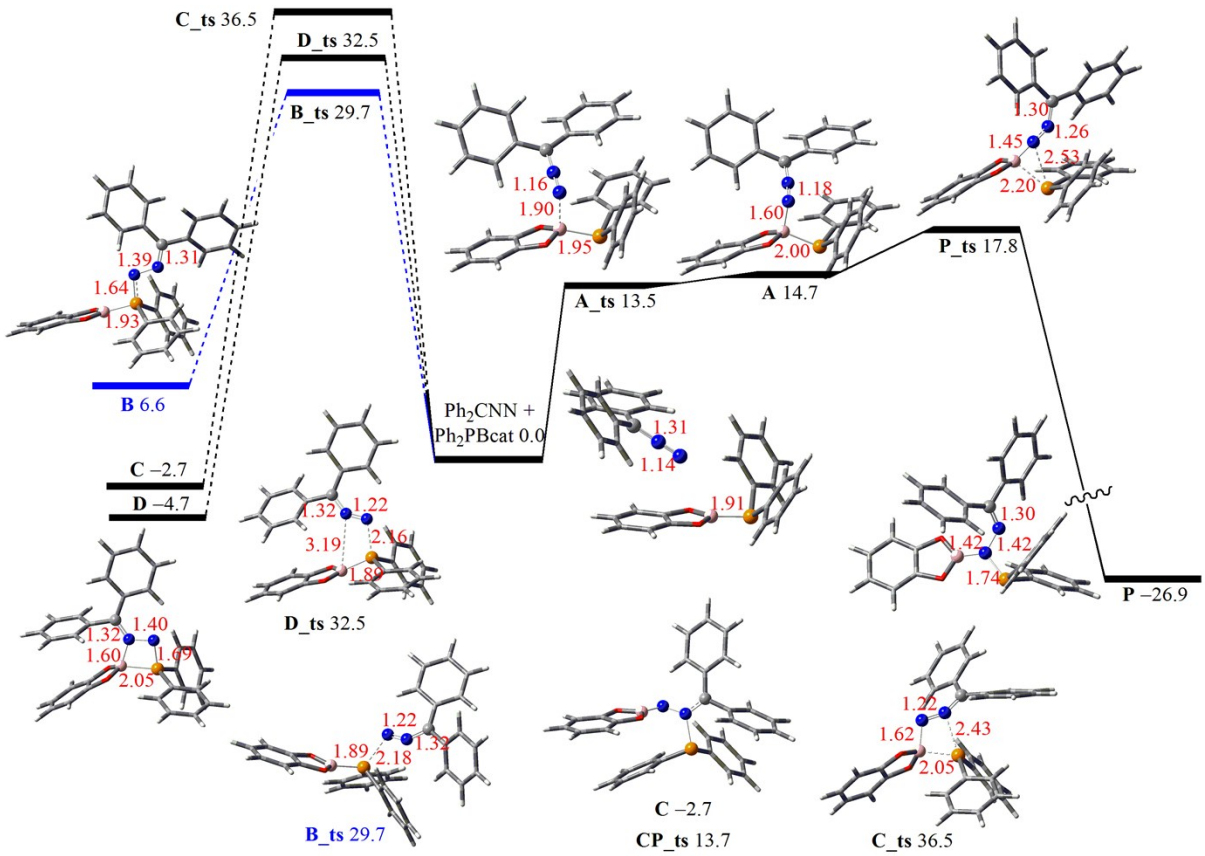


Figure S1. The The detailed reaction free energy paths in CH2Cl2 solution (in kcal/mol, at 298 K and 1 mol/L reference concentration) for the addition reaction of Ph2CNN and Ph2PBcat, computed at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-TZVP + COSMO level of theory. More detailed energies and brief description of potential reactions are given in ESI Tables S1. It is clearly seen that the lowest-free energy path is related to the endergonic terminal N-to-B addition (via transition structure A_ts) followed by the highly exergonic 1,2-phosphoryl shift along the new B-N bond (via P_ts), with an overall barrier of only 17.8 kcal/mol. Similar reaction from the P lone pair side may encounter a 4.7 kcal/mol higher free energy barrier via Pa_ts (not shown, see Table S1,); other possible reactions are also examined but even higher barriers of 29.7, 36.5 and 32.5 kcal/mol are found for the terminal N-to-P addition (B_ts), the N=N over P–B addition (C_ts) and the N=N over B–P addition (D_ts) between Ph2CNN and Ph2PBcat, respectively.

Table S1. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in CH_2Cl_2 solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔET and ΔEP) and Gibbs free-energies (ΔGT and ΔGP) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold. Transition structures (with only one imaginary frequency) are indicated by the "**_ts**" appendix. See also Figure S1 for labellings.

Reactions	ImF	ZPE	Hc	Gc	Hsol	Gsol	TPSS-D3	PW6B95-D3	ΔET	ΔEP	ΔGP	ΔGT
	cm^{-1}	kcal/mol	kca/mol	kcal/mol	kcal/mol	kcal/mol	E_h	E_h	kcal/mol	kcal/mol	kcal/mol	kcal/mol
terminal N to B addition from side opposite to P lone pair												
$Ph_2CNN + Ph_2PBcat$	0	291.76	311.73	240.78	-39.47	-28.78	-1822.98776	-1824.86419	0.0	0.0	0.0	0.0
$Ph_2CNN.Ph_2PBcat$	0	292.23	312.99	255.53	-33.02	-25.40	-1823.00684	-1824.88457	-12.0	-12.8	3.5	4.3
A_ts (or **TSA in text**)	-194	292.04	312.05	256.37	-35.93	-27.42	-1822.99572	-1824.86668	-5.0	-1.6	13.5	10.1
A	0	293.07	313.05	257.68	-37.21	-28.38	-1822.99576	-1824.86523	-5.0	-0.7	14.8	10.4
P_ts (or **TSP in text**)	-32	292.15	311.95	256.32	-36.01	-27.20	-1822.99454	-1824.86002	-4.3	2.6	17.8	11.0
P	0	293.66	313.58	257.91	-34.84	-26.20	-1823.05384	-1824.93546	-41.5	-44.7	-26.9	-23.7
terminal N to B addition from P lone pair side												
$Ph_2CNN + Ph_2PBcat$	0	291.76	311.73	240.78	-39.47	-28.78	-1822.98776	-1824.86419	0.0	0.0	0.0	0.0
Aa_ts	-136	291.95	312.03	256.00	-36.08	-27.55	-1822.99442	-1824.86664	-4.2	-1.5	13.0	10.4

Pa_ts	-192	292.15	311.95	256.92	-35.24	-26.89	-1822.98811	-1824.85410	-0.2	6.3	22.5	15.9
Pa	0	293.75	313.60	258.14	-36.10	-27.14	-1823.05003	-1824.93105	-39.1	-42.0	-24.9	-22.0
PaP_ts (P-inversion)	-319	292.63	312.40	256.45	-37.04	-28.07	-1822.99896	-1824.87602	-7.0	-7.4	7.1	7.5
P (or product **3**)	0	293.66	313.58	257.91	-34.84	-26.20	-1823.05384	-1824.93546	-41.5	-44.7	-26.9	-23.7
terminal N to P addition												
$Ph_2CNN + Ph_2PBcat$	0	291.76	311.73	240.78	-39.47	-28.78	-1822.98776	-1824.86419	0.0	0.0	0.0	0.0
B_ts	-150	291.53	311.64	255.08	-37.70	-28.80	-1822.97085	-1824.83664	10.6	17.3	29.7	23.0
B	0	292.76	312.95	256.32	-39.17	-29.56	-1822.99870	-1824.87418	-6.9	-6.3	6.6	6.0
Ph_2CN=N over P–B and B–P additions												
$Ph_2CNN + Ph_2PBcat$	0	291.76	311.73	240.78	-39.47	-28.78	-1822.98776	-1824.86419	0.0	0.0	0.0	0.0
C_ts	-49	291.93	311.67	256.56	-36.49	-27.57	-1822.97111	-1824.83014	10.5	21.4	36.5	25.5
C	0	294.02	313.71	258.70	-36.17	-27.42	-1823.02342	-1824.89618	-22.4	-20.1	-2.7	-5.0
CP_ts	-181	292.66	312.33	257.27	-35.32	-26.88	-1822.99456	-1824.86871	-4.3	-2.8	13.7	12.2
P	0	293.66	313.58	257.91	-34.84	-26.20	-1823.05384	-1824.93546	-41.5	-44.7	-26.9	-23.7
D_ts	-207	291.49	311.64	255.26	-36.73	-28.14	-1822.96801	-1824.83352	12.4	19.2	32.5	25.6
D	0	293.76	313.38	258.57	-36.69	-27.62	-1823.02561	-1824.89891	-23.8	-21.8	-4.7	-6.7

Table S2. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in CH2Cl2 solution. Each structure is labeled by the specific name (See also **Figure S1** and **Table S1**), followed by the number of atoms, the total energy, and the detailed atomic coordinates.

A_ts (or **TSA** in text)
61
Energy = -1822.916861620

B	-1.8472871	0.0140717	-0.5542308
P	-1.8509638	-1.8717762	-1.0651284
O	-3.0349856	0.5141734	0.0799859
O	-1.3543247	1.0073006	-1.4710043
C	-3.1154762	1.8364844	-0.2949624
C	-2.1155455	2.1343897	-1.2271224
C	-1.9707021	3.3989879	-1.7717725
C	-2.8788673	4.3804937	-1.3403784
C	-3.8780476	4.0853094	-0.4085047
C	-4.0156552	2.7971100	0.1356396
H	-1.1874439	3.6196661	-2.4899148
H	-2.7988375	5.3871456	-1.7399424
H	-4.5635822	4.8669322	-0.0941129
H	-4.7873642	2.5630165	0.8620937
C	-0.1364720	-2.2723607	-1.5666362
C	0.2985264	-3.6102828	-1.5301524
C	0.7101753	-1.3110098	-2.1438918
C	1.5486831	-3.9676313	-2.0298994
H	-0.3473912	-4.3768247	-1.1098937
C	1.9553778	-1.6760119	-2.6561532
H	0.3956819	-0.2736293	-2.1978754
C	2.3830848	-3.0012884	-2.5968163
H	1.8691425	-5.0050479	-1.9810706
H	2.5992081	-0.9149100	-3.0872564
H	3.3591282	-3.2794414	-2.9833752
C	-2.0733123	-2.6644253	0.5799432
C	-1.0245354	-3.1473895	1.3753646
C	-3.3864366	-2.7553561	1.0681502
C	-1.2811723	-3.7054039	2.6273755
H	-0.0034558	-3.0898644	1.0111949
C	-3.6416003	-3.2998082	2.3267610
H	-4.2104931	-2.3901208	0.4602368
C	-2.5898985	-3.7808095	3.1097479
H	-0.4562296	-4.0765555	3.2303269
H	-4.6638331	-3.3565581	2.6914262
H	-2.7885690	-4.2146843	4.0858631
N	-0.6357038	0.0612430	0.9078121
N	0.4512287	0.4591658	0.7885566
C	1.6563219	0.9249949	0.6846176
C	1.8414282	2.3710458	0.9160719
C	2.7316331	-0.0408033	0.3900792
C	0.7962778	3.2799049	0.6816551
C	3.0684256	2.8512616	1.4047417
C	2.6448827	-1.3650840	0.8479403
C	3.8417716	0.3506552	-0.3741034
C	0.9770836	4.6385238	0.9214605
H	-0.1550674	2.9293393	0.2943916
C	3.2437179	4.2138975	1.6366880
H	3.8764834	2.1577427	1.6132779
C	3.6474944	-2.2800336	0.5460737
H	1.7949324	-1.6687992	1.4521587
C	4.8481387	-0.5681612	-0.6629336
H	3.9066988	1.3655187	-0.7532021
C	2.2024426	5.1133645	1.3961723
H	0.1602772	5.3277000	0.7265043
H	4.1969922	4.5714484	2.0155164
C	4.7552958	-1.8842291	-0.2066080
H	3.5660261	-3.3031143	0.9006330

H 5.7010415 -0.2561081 -1.2589074
H 2.3443794 6.1746565 1.5779448
H 5.5385752 -2.5990752 -0.4409470

A
61
Energy = -1822.918423120
B -1.7074122 0.0693773 -0.3167078
P -1.6670120 -1.8261319 -0.9490601
O -3.0005505 0.4250023 0.2694513
O -1.3925218 1.0700503 -1.3419855
C -3.3308182 1.6368310 -0.2833241
C -2.3791125 2.0227292 -1.2377628
C -2.4813060 3.2175753 -1.9295099
C -3.5928382 4.0313128 -1.6427473
C -4.5450111 3.6457652 -0.6975320
C -4.4272599 2.4326538 0.0055546
H -1.7351046 3.5096953 -2.6618476
H -3.7081188 4.9744620 -2.1688697
H -5.3940682 4.2926050 -0.4961836
H -5.1609744 2.1313802 0.7467852
C 0.0565039 -2.1582450 -1.4445094
C 0.6062180 -3.4511614 -1.3584392
C 0.8088922 -1.1528762 -2.0799882
C 1.8713994 -3.7216572 -1.8738792
H 0.0371207 -4.2496848 -0.8910604
C 2.0742145 -1.4301430 -2.5967657
H 0.3982269 -0.1521458 -2.1779917
C 2.6119037 -2.7124914 -2.4945966
H 2.2807962 -4.7248317 -1.7905026
H 2.6440245 -0.6368499 -3.0717950
H 3.6013002 -2.9238440 -2.8886520
C -1.9284082 -2.7834601 0.5920766
C -0.9044398 -3.1633740 1.4735824
C -3.2532637 -3.1133855 0.9192781
C -1.1958257 -3.8541417 2.6477123
H 0.1259272 -2.9186546 1.2352888
C -3.5477600 -3.7929983 2.1022135
H -4.0563992 -2.8303577 0.2436572
C -2.5197471 -4.1692866 2.9679443
H -0.3905773 -4.1410461 3.3188869
H -4.5794078 -4.0361957 2.3412333
H -2.7459088 -4.7068121 3.8844781
N -0.6227545 0.1121944 0.8623586
N 0.4993446 0.4645837 0.7246799
C 1.6794447 0.9723877 0.7090244
C 1.7857834 2.4199864 1.0089047
C 2.8354892 0.1014145 0.4252766
C 0.7529588 3.3003169 0.6504918
C 2.9202353 2.9138224 1.6717629
C 2.8303822 -1.2381527 0.8400033
C 3.9453585 0.6092139 -0.2655360
C 0.8542589 4.6551157 0.9527850
H -0.1146927 2.9273305 0.1147900
C 3.0151802 4.2721542 1.9673670
H 3.7148138 2.2349024 1.9634526
C 3.9181725 -2.0592929 0.5654508
H 1.9775724 -1.6250278 1.3889134
C 5.0327352 -0.2181053 -0.5361341
H 3.9471654 1.6412750 -0.6010770
C 1.9851124 5.1455522 1.6108858
H 0.0540445 5.3305761 0.6650495
H 3.8938179 4.6465924 2.4841808
C 5.0228422 -1.5513773 -0.1219697
H 3.9051307 -3.0958486 0.8873497
H 5.8857340 0.1784256 -1.0787285
H 2.0642357 6.2035531 1.8422668

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H     5.8712817   -2.1939582   -0.3374411
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B_ts

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Energy = -1822.892806151
B    -2.8002144    0.2347434    0.4022142
P    -1.0511759   -0.3852156    0.7581586
O    -3.8879147   -0.5917545    0.1107571
O    -3.1080551    1.5823181    0.2116168
C    -4.9080705    0.2797125   -0.2572684
C    -4.4356400    1.5899362   -0.1985823
C    -5.2334748    2.6767687   -0.5112268
C    -6.5512765    2.3855381   -0.8926471
C    -7.0257212    1.0689199   -0.9504428
C    -6.2058154   -0.0229653   -0.6299784
H    -4.8595878    3.6937681   -0.4632937
H    -7.2181236    3.2028931   -1.1488486
H    -8.0526943    0.8861057   -1.2509013
H    -6.5654681   -1.0452977   -0.6732501
C    -1.0776495   -1.8920406    1.7378979
C    -2.2552681   -2.4316873    2.2791318
C     0.1429396   -2.5671732    1.9206900
C    -2.2077909   -3.6247602    2.9987479
H    -3.2023437   -1.9208319    2.1412504
C     0.1842464   -3.7492084    2.6561968
H     1.0525693   -2.1663762    1.4838716
C    -0.9906215   -4.2814850    3.1932380
H    -3.1224075   -4.0372011    3.4145712
H     1.1316150   -4.2598118    2.8016451
H    -0.9576361   -5.2074625    3.7598123
C    -0.1557174    0.9124542    1.6092611
C     0.0481387    2.1189204    0.9160040
C     0.4155868    0.7336529    2.8787761
C     0.7707925    3.1492401    1.5123322
H    -0.3665169    2.2509349   -0.0785770
C     1.1465259    1.7666816    3.4615939
H     0.2753544   -0.2021566    3.4108131
C     1.3169419    2.9772743    2.7847181
H     0.9228924    4.0799481    0.9745494
H     1.5783221    1.6277756    4.4484526
H     1.8861054    3.7798957    3.2441703
N     0.2659692   -0.9238835   -0.8950769
N     1.2811401   -0.2554500   -0.8549246
C     2.4617735   -0.1544753   -1.4409099
C     2.8437210   -1.1300562   -2.4712345
C     3.3488508    0.9306757   -0.9802670
C     1.8809135   -1.9555143   -3.0874234
C     4.1935294   -1.3106262   -2.8462138
C     3.4019300    1.2881577    0.3782048
C     4.1493870    1.6546978   -1.8838798
C     2.2449790   -2.8922322   -4.0522178
H     0.8367109   -1.8597464   -2.8026306
C     4.5531744   -2.2527066   -3.8056988
H     4.9652425   -0.7162409   -2.3684051
C     4.2232413    2.3237463    0.8168616
H     2.7871609    0.7448328    1.0901145
C     4.9730880    2.6893482   -1.4440692
H     4.1089322    1.4153644   -2.9426062
C     3.5827438   -3.0473389   -4.4232864
H     1.4771571   -3.5076907   -4.5141435
H     5.6016017   -2.3720960   -4.0673703
C     5.0188166    3.0289537   -0.0893712
H     4.2458403    2.5775115    1.8730260
H     5.5747654    3.2381394   -2.1641653
H     3.8660203   -3.7812853   -5.1723971
H     5.6637726    3.8330374    0.2541476
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B
61
Energy = -1822.919623865

B	-2.4206915	0.0069614	-0.0827314
P	-0.7116873	0.1427830	0.7891001
O	-3.2060896	-1.1342540	-0.0259607
O	-2.9891301	0.9983224	-0.8702851
C	-4.3052314	-0.8497218	-0.8309478
C	-4.1754819	0.4403768	-1.3411255
C	-5.1225413	1.0050720	-2.1773106
C	-6.2278510	0.1995436	-2.4851092
C	-6.3582191	-1.0984041	-1.9729301
C	-5.3903092	-1.6564352	-1.1263006
H	-5.0145247	2.0100927	-2.5702922
H	-7.0006505	0.5933216	-3.1378062
H	-7.2300983	-1.6886168	-2.2370332
H	-5.4836245	-2.6602992	-0.7266243
C	-0.4845902	-1.3065936	1.8623022
C	-0.8845902	-1.3117488	3.2045255
C	0.1005667	-2.4500271	1.3012144
C	-0.7050958	-2.4575650	3.9791388
H	-1.3264609	-0.4223747	3.6445031
C	0.2844947	-3.5900582	2.0812444
H	0.4197739	-2.4297910	0.2636319
C	-0.1193598	-3.5948487	3.4187628
H	-1.0150196	-2.4601069	5.0202594
H	0.7460302	-4.4730903	1.6485310
H	0.0267170	-4.4838362	4.0259227
C	-0.6993504	1.5566523	1.9237857
C	-1.8102188	2.3968702	2.0762023
C	0.4923507	1.8409704	2.6131966
C	-1.7377273	3.5047284	2.9218688
H	-2.7323343	2.1902386	1.5394455
C	0.5611568	2.9539358	3.4471625
H	1.3551716	1.1955584	2.4763997
C	-0.5535321	3.7834367	3.6060092
H	-2.6035611	4.1491355	3.0431942
H	1.4832028	3.1760082	3.9769128
H	-0.4970777	4.6471922	4.2622271
N	0.3097526	0.2013441	-0.4821771
N	1.6137661	0.1426579	-0.0196621
C	2.5769546	0.1199066	-0.9013601
C	2.3822647	0.1616757	-2.3721043
C	3.9423833	0.0112012	-0.3439171
C	1.4772150	1.0540564	-2.9703567
C	3.0980261	-0.7193168	-3.2004534
C	4.1491161	-0.5433970	0.9342364
C	5.0637997	0.4767873	-1.0532273
C	1.3052482	1.0700988	-4.3534045
H	0.9087983	1.7287159	-2.3419028
C	2.9166608	-0.7123566	-4.5828578
H	3.7995333	-1.4174765	-2.7517445
C	5.4258949	-0.6202589	1.4818002
H	3.2862480	-0.9127008	1.4796374
C	6.3436516	0.3976265	-0.5037702
H	4.9277783	0.9153246	-2.0374929
C	2.0205366	0.1865669	-5.1660775
H	0.6065206	1.7729801	-4.8000822
H	3.4760678	-1.4067583	-5.2044626
C	6.5334407	-0.1507467	0.7662607
H	5.5638333	-1.0578181	2.4675843
H	7.1944686	0.7695532	-1.0690035
H	1.8807203	0.1983755	-6.2437793
H	7.5308204	-0.2166565	1.1924670

CP_ts (1,2-P-shift from **C** into **P**)
61

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Energy = -1822.914639033
B    -2.0251648   -0.3071013    0.7449981
P     1.0184425   -1.4131857    1.2128140
O    -3.0001912   -1.3276985    0.6871633
O    -2.6237712    0.9550086    0.9499334
C    -4.2094453   -0.6688139    0.8242001
C    -3.9831893    0.7020572    0.9757873
C    -5.0211007    1.6051781    1.1199983
C    -6.3212322    1.0737792    1.1116665
C    -6.5477085   -0.2983721    0.9638567
C    -5.4849368   -1.2050302    0.8156947
H    -4.8370889    2.6685402    1.2322651
H    -7.1669921    1.7458482    1.2219127
H    -7.5662801   -0.6747080    0.9618280
H    -5.6535765   -2.2705906    0.6989310
C     0.8337592   -2.8254519    0.0359853
C     1.9087933   -3.7304106   -0.0698022
C    -0.3566378   -3.1330518   -0.6382951
C     1.7892987   -4.9018081   -0.8144510
H     2.8468671   -3.5161887    0.4336253
C    -0.4705276   -4.2991150   -1.3983348
H    -1.1981981   -2.4532568   -0.5785984
C     0.5991557   -5.1899538   -1.4880751
H     2.6314945   -5.5857536   -0.8773838
H    -1.3994858   -4.5083873   -1.9224439
H     0.5104729   -6.0966076   -2.0800540
C     2.7790624   -1.0063018    0.7195860
C     3.7179441   -0.8983550    1.7519320
C     3.1786220   -0.7266427   -0.5948645
C     5.0374210   -0.5282047    1.4777745
H     3.4114600   -1.0999395    2.7766492
C     4.4851579   -0.3308906   -0.8683678
H     2.4593941   -0.8099682   -1.4062076
C     5.4181726   -0.2335602    0.1690566
H     5.7603473   -0.4544239    2.2860307
H     4.7793240   -0.0955289   -1.8877089
H     6.4375438    0.0755835   -0.0448919
N    -0.6510226   -0.5786457    0.6554480
N     0.3931695    0.3247332    0.5848816
C     0.4873444    1.3894135   -0.1700112
C     1.7219832    2.1746991   -0.0814546
C    -0.5958684    1.7797264   -1.0965393
C     2.1681587    2.9153046   -1.1900950
C     2.4914827    2.1728730    1.0948454
C    -1.1379314    0.8388467   -1.9865651
C    -1.0845171    3.0928953   -1.1002301
C     3.3712549    3.6126427   -1.1305935
H     1.5801010    2.9192632   -2.1026087
C     3.6943836    2.8668851    1.1475154
H     2.1316738    1.6283904    1.9610215
C    -2.1626497    1.2071563   -2.8541225
H    -0.7472400   -0.1737892   -2.0022285
C    -2.1190118    3.4543543   -1.9605960
H    -0.6616100    3.8220427   -0.4156217
C     4.1397895    3.5866064    0.0355430
H     3.7136757    4.1711645   -1.9969572
H     4.2850227    2.8513853    2.0584479
C    -2.6631621    2.5118058   -2.8348796
H    -2.5714864    0.4771846   -3.5466773
H    -2.5006050    4.4710920   -1.9480777
H     5.0788700    4.1307743    0.0803447
H    -3.4709438    2.7932195   -3.5042403
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C_ts

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61
Energy = -1822.892567347
B    -1.4920852   -0.4130929   -0.6697506
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P    -0.1955495    1.0649268   -0.1026516
O    -2.2503297   -1.0020498    0.4184164
O    -2.4285300   -0.0674585   -1.7291995
C    -3.5306763   -1.1300899   -0.0475578
C    -3.6383305   -0.5891279   -1.3373564
C    -4.8361329   -0.5908383   -2.0336314
C    -5.9475942   -1.1567060   -1.3859556
C    -5.8428423   -1.6900421   -0.0975050
C    -4.6237958   -1.6823173    0.6013167
H    -4.9098170   -0.1700846   -3.0315887
H    -6.9052806   -1.1763630   -1.8978087
H    -6.7196262   -2.1235010    0.3749855
H    -4.5355185   -2.0957671    1.6010156
C     0.1610859    0.7976183    1.6546441
C     0.0950361    1.8215295    2.6162544
C     0.5833355   -0.4844887    2.0606326
C     0.4517292    1.5713168    3.9394834
H    -0.2406563    2.8127212    2.3287504
C     0.9321303   -0.7312424    3.3837139
H     0.6162715   -1.2912942    1.3378658
C     0.8773804    0.2983168    4.3269802
H     0.3943955    2.3726692    4.6709866
H     1.2493052   -1.7273134    3.6796116
H     1.1566557    0.1073591    5.3591734
C    -0.8271986    2.7628605   -0.2034816
C    -2.1802771    3.0156781   -0.4862166
C     0.0598209    3.8458122   -0.0657024
C    -2.6380250    4.3284086   -0.6013968
H    -2.8720579    2.1889182   -0.6071720
C    -0.4044453    5.1545744   -0.1780357
H     1.1130782    3.6585296    0.1269773
C    -1.7548064    5.3984448   -0.4445765
H    -3.6881013    4.5145381   -0.8090270
H     0.2872085    5.9844737   -0.0638840
H    -2.1153219    6.4190633   -0.5354178
N    -0.3297602   -1.3656167   -1.2840148
N     0.7961182   -0.9452779   -1.0514682
C     2.0688715   -1.2426551   -0.9177203
C     2.4302267   -2.6353426   -0.5982445
C     3.0168264   -0.1205183   -0.9576864
C     1.4690275   -3.5653637   -0.1605506
C     3.7594049   -3.0734668   -0.7642437
C     2.8053797    0.9555251   -1.8382961
C     4.0900593   -0.0530335   -0.0516453
C     1.8277383   -4.8806789    0.1202454
H     0.4326776   -3.2615598   -0.0436271
C     4.1096847   -4.3923045   -0.4871024
H     4.5098873   -2.3841292   -1.1352070
C     3.6599313    2.0569279   -1.8290710
H     1.9819585    0.9130354   -2.5438918
C     4.9330618    1.0541815   -0.0377906
H     4.2385235   -0.8543613    0.6648184
C     3.1502416   -5.3019732   -0.0370439
H     1.0698810   -5.5796721    0.4624054
H     5.1380153   -4.7109764   -0.6333509
C     4.7263028    2.1103115   -0.9304843
H     3.4896113    2.8742104   -2.5240957
H     5.7474779    1.0987083    0.6797743
H     3.4273446   -6.3294429    0.1795465
H     5.3901729    2.9700961   -0.9208686
```

C

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61
Energy = -1822.944773996
B    -1.7864772    0.4150837   -1.0821603
P     0.3232034   -1.1078337    0.9438978
O    -2.7479100    0.1171331   -2.0835753
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O    -2.4450603    0.8107554    0.1226129
C    -3.9714033    0.2603923   -1.4662829
C    -3.7902264    0.6708693   -0.1404942
C    -4.8589743    0.8642822    0.7175250
C    -6.1417952    0.6329563    0.1928455
C    -6.3225186    0.2259058   -1.1324362
C    -5.2299018    0.0304287   -1.9938946
H    -4.7101210    1.1754165    1.7466578
H    -7.0081594    0.7723860    0.8327807
H    -7.3275058    0.0534484   -1.5064260
H    -5.3634106   -0.2936019   -3.0210830
C    -1.0019394   -2.0590994    0.1243090
C    -0.8738817   -2.7660855   -1.0824790
C    -2.2250067   -2.1072170    0.8152595
C    -1.9528658   -3.4795784   -1.5959068
H     0.0667261   -2.7522269   -1.6215400
C    -3.3080960   -2.8156770    0.2959845
H    -2.3281632   -1.5648450    1.7509370
C    -3.1722593   -3.4998150   -0.9118794
H    -1.8473924   -4.0162715   -2.5344723
H    -4.2540760   -2.8255805    0.8287870
H    -4.0144523   -4.0499156   -1.3219287
C     1.8381243   -1.9353856    0.3314956
C     2.5493895   -2.7045296    1.2622829
C     2.3302047   -1.8137299   -0.9773742
C     3.7275400   -3.3529263    0.8902845
H     2.1882854   -2.7797549    2.2848946
C     3.5104544   -2.4560778   -1.3447853
H     1.8008308   -1.2019712   -1.7029594
C     4.2109085   -3.2271922   -0.4124602
H     4.2742885   -3.9415125    1.6214710
H     3.8876418   -2.3521422   -2.3583862
H     5.1344935   -3.7212182   -0.7006312
N    -0.4123772    0.4018568   -1.3078115
N     0.4139470    0.3754311   -0.2567270
C     1.4242692    1.2211622   -0.0840187
C     2.3023412    1.0198625    1.1008063
C     1.7369588    2.3312625   -0.9903786
C     3.6547977    0.6921700    0.9212185
C     1.8067079    1.1915467    2.4011579
C     1.2988801    2.4135589   -2.3307359
C     2.5604781    3.3697889   -0.4974945
C     4.4853732    0.5006359    2.0211867
H     4.0428872    0.5672209   -0.0847280
C     2.6422089    1.0067213    3.5024933
H     0.7677213    1.4717177    2.5437335
C     1.6871002    3.4821367   -3.1356771
H     0.6569709    1.6355846   -2.7195929
C     2.9227716    4.4442027   -1.3015371
H     2.9085426    3.3320196    0.5290447
C     3.9793185    0.6529836    3.3147695
H     5.5254727    0.2273414    1.8702681
H     2.2481153    1.1422300    4.5054431
C     2.4916918    4.5047105   -2.6294790
H     1.3489754    3.5187026   -4.1676653
H     3.5446770    5.2348068   -0.8915458
H     4.6277817    0.5037929    4.1734172
H     2.7780007    5.3412363   -3.2606849
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D_ts

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61
Energy = -1822.889458862
B    -1.6713908    0.0420856    0.6987634
P    -0.1690135    0.3028422    1.8227939
O    -1.8209832   -1.1410376   -0.0170109
O    -2.5846652    1.0148413    0.2955377
C    -2.8711143   -0.8976476   -0.8934475
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C    -3.3374046    0.4014832   -0.7031076
C    -4.3815082    0.9298192   -1.4409319
C    -4.9454994    0.0798945   -2.4028089
C    -4.4730794   -1.2241621   -2.5984787
C    -3.4167997   -1.7457056   -1.8400154
H    -4.7362451    1.9433612   -1.2886742
H    -5.7645016    0.4463254   -3.0138614
H    -4.9322208   -1.8467468   -3.3598881
H    -3.0396976   -2.7509580   -1.9914646
C     0.1418210   -1.2298485    2.7344627
C    -0.5221841   -1.5041897    3.9417823
C     1.0445097   -2.1651388    2.2089945
C    -0.2790994   -2.6993010    4.6136356
H    -1.2243007   -0.7840348    4.3509791
C     1.2785875   -3.3631922    2.8850768
H     1.5599494   -1.9458583    1.2801079
C     0.6207716   -3.6305132    4.0860578
H    -0.7960683   -2.9072882    5.5459279
H     1.9778956   -4.0852626    2.4736609
H     0.8066721   -4.5625892    4.6118918
C    -0.4179102    1.6268596    3.0100907
C    -1.2727960    2.7092599    2.7262913
C     0.3745255    1.6634097    4.1734084
C    -1.3491522    3.7865335    3.6051583
H    -1.8827694    2.7011966    1.8290904
C     0.2902529    2.7465931    5.0448169
H     1.0490180    0.8423442    4.3971644
C    -0.5717148    3.8100230    4.7664232
H    -2.0218942    4.6100841    3.3835084
H     0.9013450    2.7596924    5.9426856
H    -0.6363741    4.6523953    5.4486725
N     1.5421796    0.3985755    0.5071555
N     1.2054475    0.3073306   -0.6633237
C     1.6979881    0.1823440   -1.8790010
C     3.1489039    0.1511999   -2.0909472
C     0.6914753    0.0800262   -2.9570300
C     4.0357337    0.0148702   -1.0019133
C     3.7132168    0.3001297   -3.3773844
C    -0.4897758    0.8408427   -2.8871588
C     0.8355444   -0.8137405   -4.0327994
C     5.4156109    0.0028351   -1.1924152
H     3.6321295   -0.0804314    0.0028044
C     5.0932256    0.2920011   -3.5614781
H     3.0628470    0.4416618   -4.2341224
C    -1.4910210    0.7085203   -3.8450435
H    -0.6137322    1.5394068   -2.0633415
C    -0.1646499   -0.9411734   -4.9966724
H     1.7236709   -1.4355010   -4.0979307
C     5.9572549    0.1368108   -2.4734077
H     6.0720632   -0.1092905   -0.3332649
H     5.4969671    0.4150793   -4.5633105
C    -1.3337724   -0.1825088   -4.9091522
H    -2.3984988    1.2987658   -3.7590956
H    -0.0350562   -1.6493940   -5.8112078
H     7.0334709    0.1294502   -2.6206624
H    -2.1155132   -0.2890726   -5.6559094
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D

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61
Energy = -1822.945961974
B    -0.7604851    0.0557287   -0.0862223
P     0.0870664    0.1379995    1.7785419
O    -1.3393978   -1.1767130   -0.5531938
O    -1.6467777    1.1503383   -0.4348070
C    -2.5144533   -0.8209620   -1.1719207
C    -2.7027674    0.5642452   -1.0962085
C    -3.8050664    1.1828800   -1.6583177
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C    -4.7328857    0.3565506   -2.3170351
C    -4.5425208   -1.0244890   -2.3983667
C    -3.4182879   -1.6419204   -1.8221986
H    -3.9363592    2.2592284   -1.6068970
H    -5.6106384    0.8054013   -2.7731162
H    -5.2736876   -1.6368378   -2.9183442
H    -3.2557245   -2.7125383   -1.8937745
C     0.3611462   -1.3566826    2.7554185
C    -0.5108509   -1.7082155    3.7981077
C     1.4101851   -2.2170045    2.4045746
C    -0.3246898   -2.9049836    4.4866528
H    -1.3283949   -1.0473690    4.0727814
C     1.5954188   -3.4106544    3.1016725
H     2.0757656   -1.9357277    1.5934303
C     0.7293603   -3.7557328    4.1412587
H    -1.0002849   -3.1735793    5.2935844
H     2.4151316   -4.0710150    2.8334353
H     0.8739847   -4.6864433    4.6823238
C    -0.2441608    1.4652351    2.9556018
C    -1.0363344    2.5453128    2.5305532
C     0.3088917    1.4716516    4.2456128
C    -1.2729244    3.6155662    3.3910783
H    -1.4635679    2.5354551    1.5319414
C     0.0732682    2.5485970    5.0985245
H     0.9216275    0.6394754    4.5787420
C    -0.7180608    3.6186763    4.6734990
H    -1.8927854    4.4452837    3.0639492
H     0.5063331    2.5525406    6.0945485
H    -0.9031868    4.4544260    5.3421824
N     1.4303393    0.4422664    0.7989575
N     0.7895962    0.2647842   -0.4276258
C     1.3652147    0.2232440   -1.6113410
C     2.8025114    0.3176127   -1.8636612
C     0.4317256    0.0318423   -2.7616086
C     3.7838154    0.3038413   -0.8459405
C     3.2407204    0.4126934   -3.2046238
C    -0.3770025    1.0800882   -3.2133038
C     0.3616421   -1.2128054   -3.4033383
C     5.1374612    0.3645512   -1.1691472
H     3.4639587    0.2509422    0.1860819
C     4.5937621    0.4845506   -3.5157959
H     2.5069889    0.4337579   -4.0032715
C    -1.2580762    0.8827072   -4.2777149
H    -0.3254631    2.0443102   -2.7181118
C    -0.5202504   -1.4093018   -4.4627579
H     0.9873975   -2.0291178   -3.0540743
C     5.5525918    0.4572882   -2.4991607
H     5.8749521    0.3446218   -0.3712276
H     4.9012752    0.5626437   -4.5548095
C    -1.3341816   -0.3613922   -4.9010996
H    -1.8920499    1.6996461   -4.6089822
H    -0.5800759   -2.3829946   -4.9408076
H     6.6100791    0.5128102   -2.7416682
H    -2.0281490   -0.5180041   -5.7219017
```

PaP_ts (inversion from **Pa** into **P**)

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61
Energy = -1822.919666217
B     0.4126410   -0.9686953   -0.2091548
P    -2.0906337   -0.1472032    0.3392239
O     0.4980471   -2.0460020    0.6795165
O     1.2522081   -1.1435047   -1.3154833
C     1.4569703   -2.8848780    0.1277963
C     1.9191365   -2.3356350   -1.0695945
C     2.8992252   -2.9455432   -1.8300039
C     3.4079864   -4.1562158   -1.3333209
C     2.9437175   -4.7079555   -0.1343025
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C	1.9475703	-4.0768508	0.6278722
H	3.2558940	-2.5098885	-2.7572152
H	4.1805634	-4.6731683	-1.8943306
H	3.3628437	-5.6452334	0.2188050
H	1.5858032	-4.4967671	1.5604376
C	-3.1124931	-0.7513120	-0.9738009
C	-2.6633680	-0.6157211	-2.3052173
C	-4.3506093	-1.3815692	-0.7293176
C	-3.4330706	-1.1082421	-3.3544378
H	-1.7157843	-0.1259988	-2.5077818
C	-5.1167980	-1.8480231	-1.7942666
H	-4.7031844	-1.5213746	0.2874940
C	-4.6671614	-1.7196765	-3.1116267
H	-3.0693059	-1.0008633	-4.3728425
H	-6.0688516	-2.3296876	-1.5878694
H	-5.2678451	-2.0918117	-3.9359226
C	-2.6236375	0.1137585	2.0064549
C	-3.9740065	0.3841877	2.3133104
C	-1.6815069	0.0631845	3.0552062
C	-4.3615989	0.5837180	3.6358043
H	-4.7107320	0.4591661	1.5200045
C	-2.0796829	0.3008081	4.3669565
H	-0.6482111	-0.1830346	2.8338227
C	-3.4214126	0.5530236	4.6699745
H	-5.4063733	0.7862321	3.8552510
H	-1.3392005	0.2654961	5.1615260
H	-3.7296165	0.7224214	5.6970908
N	-0.4864966	0.1483454	-0.0389275
N	-0.1855524	1.4709645	-0.5152381
C	1.0323037	1.8934772	-0.3586221
C	1.3308782	3.2207776	-0.9439272
C	2.1189166	1.1774454	0.3663658
C	2.4125844	3.9825280	-0.4729141
C	0.5244626	3.7460263	-1.9688863
C	1.9491146	0.8063525	1.7079177
C	3.3330402	0.8875473	-0.2739557
C	2.6731395	5.2450927	-1.0042042
H	3.0421301	3.5898115	0.3193628
C	0.7880376	5.0052689	-2.4979374
H	-0.3014556	3.1491432	-2.3411631
C	2.9652103	0.1381563	2.3891551
H	1.0231784	1.0564017	2.2151370
C	4.3420623	0.2093307	0.4046669
H	3.4717928	1.1767076	-1.3112291
C	1.8631819	5.7604779	-2.0174088
H	3.5086428	5.8263285	-0.6247081
H	0.1611314	5.3975120	-3.2938144
C	4.1595621	-0.1702856	1.7365685
H	2.8233718	-0.1410174	3.4290812
H	5.2708305	-0.0259528	-0.1065226
H	2.0706838	6.7411727	-2.4360284
H	4.9469190	-0.6999838	2.2646000

Pa_ts

61

Energy = -1822.909668696

B	-1.1400166	-0.8255879	-0.8643734
P	-0.9034470	-0.8817660	1.3675720
O	-2.2534488	-1.7136738	-1.1480291
O	-1.4597209	0.4951769	-1.3588087
C	-3.2409209	-0.8965250	-1.6456696
C	-2.7724462	0.4176346	-1.7685396
C	-3.5783600	1.4391253	-2.2381498
C	-4.8942957	1.0995920	-2.5961647
C	-5.3621126	-0.2109721	-2.4760343
C	-4.5363018	-1.2396688	-1.9921231
H	-3.2092889	2.4565526	-2.3188828

H	-5.5581985	1.8746130	-2.9680040
H	-6.3855878	-0.4425929	-2.7561928
H	-4.8971485	-2.2576867	-1.8853214
C	-2.5777067	-0.1508378	1.4793962
C	-3.6521567	-1.0571450	1.5662412
C	-2.8531580	1.2270797	1.4729309
C	-4.9639203	-0.5973705	1.6373654
H	-3.4498484	-2.1250969	1.5649803
C	-4.1663384	1.6831415	1.5545049
H	-2.0371224	1.9381321	1.3967119
C	-5.2249921	0.7747131	1.6287857
H	-5.7830582	-1.3087169	1.6931738
H	-4.3663013	2.7510836	1.5451968
H	-6.2487134	1.1346567	1.6781546
C	0.1577746	0.5805764	1.7136393
C	0.4626663	1.6107775	0.8087144
C	0.7005320	0.6421611	3.0083978
C	1.2858987	2.6693546	1.1929151
H	0.0471927	1.5928605	-0.1918703
C	1.5061262	1.7116426	3.3962767
H	0.4928000	-0.1592153	3.7126949
C	1.8052236	2.7270795	2.4870563
H	1.5189847	3.4539434	0.4777979
H	1.9140527	1.7415396	4.4026874
H	2.4457974	3.5533784	2.7825519
N	0.1911506	-1.4122585	-1.0121183
N	1.2693439	-0.8557228	-1.2363112
C	2.4695261	-0.6257346	-0.8141125
C	2.8451033	-0.8576759	0.5981112
C	3.4361642	-0.1436159	-1.8173425
C	2.3300575	-1.9727282	1.2764770
C	3.7579718	-0.0128528	1.2449117
C	2.9865265	0.5795142	-2.9357619
C	4.8065479	-0.4228186	-1.6882410
C	2.7444341	-2.2518039	2.5747798
H	1.6138103	-2.6230192	0.7837438
C	4.1589698	-0.2899888	2.5491877
H	4.1395231	0.8625658	0.7303841
C	3.8867165	1.0038612	-3.9080820
H	1.9303833	0.8187266	-3.0201726
C	5.7040621	0.0065099	-2.6634231
H	5.1625373	-0.9933629	-0.8365390
C	3.6586317	-1.4106244	3.2142301
H	2.3485389	-3.1215539	3.0904083
H	4.8542852	0.3764888	3.0504849
C	5.2489280	0.7201407	-3.7746983
H	3.5285172	1.5681652	-4.7641334
H	6.7605026	-0.2223496	-2.5580842
H	3.9712336	-1.6225448	4.2325908
H	5.9522601	1.0583920	-4.5300228

Pa (higher conformer of **P**)
61
Energy = -1822.970455341

B	2.2263070	-0.5569448	-0.8978599
P	1.8801811	1.6139790	-2.7168625
O	1.1361609	-0.3282934	-0.0475818
O	2.7084945	-1.8714264	-0.7649622
C	0.9583340	-1.5188662	0.6371479
C	1.9155356	-2.4434995	0.2151989
C	1.9906412	-3.7174701	0.7480514
C	1.0443706	-4.0381202	1.7350600
C	0.0821703	-3.1128954	2.1535979
C	0.0197317	-1.8211415	1.6060503
H	2.7408039	-4.4293338	0.4198828
H	1.0617865	-5.0282844	2.1805614
H	-0.6325933	-3.3960668	2.9204525

H	-0.7214049	-1.0970139	1.9276637
C	0.1897979	0.9125643	-2.6753985
C	0.0026241	-0.4249806	-3.0646808
C	-0.9365458	1.6975861	-2.3935330
C	-1.2756470	-0.9745499	-3.1245851
H	0.8634504	-1.0422960	-3.3119414
C	-2.2181447	1.1489198	-2.4677887
H	-0.8144057	2.7367093	-2.1031737
C	-2.3917911	-0.1890607	-2.8236597
H	-1.4013643	-2.0153560	-3.4099634
H	-3.0808222	1.7676663	-2.2358600
H	-3.3889794	-0.6175484	-2.8694306
C	1.7923628	2.9918680	-1.5049762
C	2.4632231	4.1741648	-1.8503744
C	1.1846493	2.8951539	-0.2417290
C	2.5333259	5.2412698	-0.9515775
H	2.9385961	4.2524783	-2.8253612
C	1.2571471	3.9587452	0.6544633
H	0.6723603	1.9813132	0.0393379
C	1.9327893	5.1320670	0.3028316
H	3.0567834	6.1516240	-1.2299979
H	0.7905667	3.8741003	1.6323439
H	1.9912678	5.9568786	1.0077032
N	2.7477216	0.3807242	-1.8420473
N	4.0816240	0.2563075	-2.3180018
C	4.9989345	0.0864921	-1.4113143
C	4.7733656	0.1562743	0.0615162
C	6.3694629	-0.1621016	-1.9064296
C	5.1272398	-0.9156372	0.8930278
C	4.2217152	1.3124332	0.6340673
C	6.5791214	-0.6561522	-3.2060315
C	7.4841742	0.1068717	-1.0947780
C	4.9086179	-0.8441099	2.2672769
H	5.5518973	-1.8135727	0.4545278
C	4.0146226	1.3860563	2.0097351
H	3.9496003	2.1480802	-0.0017028
C	7.8698651	-0.8592545	-3.6842855
H	5.7155901	-0.8801940	-3.8230528
C	8.7763309	-0.0964578	-1.5771170
H	7.3363070	0.4867772	-0.0886811
C	4.3507773	0.3063339	2.8289305
H	5.1707420	-1.6878319	2.8990812
H	3.5853478	2.2864913	2.4393052
C	8.9740884	-0.5797340	-2.8720558
H	8.0182382	-1.2469603	-4.6883634
H	9.6288887	0.1230843	-0.9406475
H	4.1808238	0.3618202	3.9004114
H	9.9810269	-0.7455155	-3.2446995

$Ph_2CNNBcat^-$
38
Energy = -1018.069448170

B	-0.3148245	1.8391796	0.5217427
O	-1.6460013	1.7556117	1.0644441
O	-0.2024819	3.0778865	-0.2026040
C	-2.2893115	2.9011593	0.6740261
C	-1.4213887	3.6957775	-0.0881880
C	-1.8222297	4.9152918	-0.6105061
C	-3.1417476	5.3226131	-0.3428686
C	-4.0064112	4.5297904	0.4167774
C	-3.5908232	3.2935329	0.9432931
H	-1.1457470	5.5271835	-1.1994470
H	-3.4922364	6.2728002	-0.7359371
H	-5.0200133	4.8717229	0.6062151
H	-4.2575266	2.6731588	1.5345761
N	0.6177237	0.8253100	0.7231594
N	1.8291551	1.0908892	0.1681673

```
C     2.7890541    0.1938522    0.2757428
C     2.6422282   -1.1182668    0.9538456
C     4.0863068    0.5683715   -0.3167278
C     3.6163980   -1.5692929    1.8618211
C     1.5227525   -1.9390137    0.7266195
C     4.3892187    1.9204991   -0.5912463
C     5.0578005   -0.3950732   -0.6578646
C     3.4868200   -2.7961401    2.5134800
H     4.4852384   -0.9461017    2.0578830
C     1.3961234   -3.1699199    1.3692040
H     0.7545474   -1.5980019    0.0435510
C     5.5977707    2.2853693   -1.1753542
H     3.6446576    2.6689917   -0.3389752
C     6.2706929   -0.0268129   -1.2403466
H     4.8517957   -1.4456270   -0.4747897
C     2.3754204   -3.6059451    2.2669619
H     4.2535209   -3.1193646    3.2135450
H     0.5266664   -3.7924438    1.1710881
C     6.5537802    1.3154859   -1.5030980
H     5.8037744    3.3358706   -1.3686406
H     6.9962708   -0.7957147   -1.4958051
H     2.2724986   -4.5646967    2.7687587
H     7.5007958    1.6028474   -1.9521819
```

$Ph_2CNN.Ph_2PBcat$ (loose complex)

```
61
Energy = -1822.925684847
B     0.2144117    0.5877120   -0.6006592
P    -1.3712631    1.2216541    0.2509976
O     0.8181562   -0.6609114   -0.4064385
O     1.0320860    1.4257287   -1.3644450
C     2.0542545   -0.5697307   -1.0330254
C     2.1858884    0.6958717   -1.6018591
C     3.3309616    1.0848110   -2.2729978
C     4.3567783    0.1324675   -2.3533979
C     4.2212735   -1.1409027   -1.7879491
C     3.0535993   -1.5230147   -1.1115856
H     3.4320278    2.0763340   -2.7002990
H     5.2798149    0.3930090   -2.8621884
H     5.0397741   -1.8496885   -1.8686614
H     2.9455220   -2.5039143   -0.6619727
C    -2.5532757   -0.1742663    0.2377469
C    -3.7468778    0.0088687    0.9557287
C    -2.3223668   -1.4085996   -0.3848596
C    -4.6914941   -1.0114652    1.0392526
H    -3.9272393    0.9541768    1.4613067
C    -3.2587234   -2.4389458   -0.2807760
H    -1.4059179   -1.5734264   -0.9415152
C    -4.4453741   -2.2433972    0.4275080
H    -5.6110257   -0.8519858    1.5956106
H    -3.0619672   -3.3937188   -0.7610090
H    -5.1735679   -3.0459139    0.5046799
C    -2.0028380    2.3628946   -1.0490732
C    -1.3809348    3.6146384   -1.1815901
C    -3.0919531    2.0559923   -1.8759328
C    -1.8241402    4.5291335   -2.1357536
H    -0.5419349    3.8701480   -0.5391213
C    -3.5449358    2.9799461   -2.8195408
H    -3.5854192    1.0930324   -1.7830105
C    -2.9112550    4.2166319   -2.9561441
H    -1.3271677    5.4907721   -2.2319317
H    -4.3910909    2.7281706   -3.4534686
H    -3.2633809    4.9331256   -3.6929155
N     3.1001759   -2.4914046    2.3286336
N     2.6087112   -1.4595284    2.4070651
C     2.0523524   -0.2779960    2.5109853
C     0.6902695   -0.2538867    3.0819724
```

```
C     2.7889983    0.8637139    1.9563922
C    -0.2278085   -1.2745931    2.7848154
C     0.2921704    0.7895035    3.9345818
C     2.1207912    2.0732565    1.6905837
C     4.1556642    0.7678091    1.6277828
C    -1.5127102   -1.2490734    3.3198458
H     0.0578880   -2.0728619    2.1062637
C    -1.0001525    0.8181852    4.4530328
H     0.9970504    1.5741691    4.1904327
C     2.8006085    3.1459666    1.1185980
H     1.0609892    2.1600167    1.9057062
C     4.8239406    1.8417787    1.0518831
H     4.6951411   -0.1564096    1.8143863
C    -1.9082658   -0.1985462    4.1487186
H    -2.2162775   -2.0342192    3.0593739
H    -1.2965016    1.6369344    5.1029246
C     4.1533693    3.0409421    0.7951750
H     2.2606225    4.0656832    0.9106785
H     5.8748823    1.7396863    0.7968402
H    -2.9176331   -0.1677928    4.5481708
H     4.6769194    3.8766372    0.3405732
```

Ph_2CNN (reactant)

```
25
Energy = -611.2395455107
N     0.1294649   -0.1212320   -1.5569932
N     1.2695260   -0.0895588   -1.4574385
C     2.5757966   -0.0532147   -1.3433332
C     3.2118626    1.2688186   -1.4663555
C     3.2528779   -1.3386460   -1.1051381
C     2.6122805    2.2988016   -2.2142686
C     4.4261397    1.5353444   -0.8076940
C     2.5917801   -2.4018838   -0.4631988
C     4.5744986   -1.5360435   -1.5451323
C     3.2103271    3.5533099   -2.3015999
H     1.6787579    2.1137159   -2.7389035
C     5.0249484    2.7889773   -0.9097524
H     4.8924107    0.7629404   -0.2048959
C     3.2339856   -3.6215847   -0.2660179
H     1.5736808   -2.2697596   -0.1067740
C     5.2149476   -2.7548566   -1.3332782
H     5.0937714   -0.7376374   -2.0650143
C     4.4230773    3.8054316   -1.6553415
H     2.7313796    4.3333578   -2.8866709
H     5.9627464    2.9739216   -0.3933413
C     4.5512938   -3.8046914   -0.6939747
H     2.7057026   -4.4282165    0.2344046
H     6.2358973   -2.8865022   -1.6806853
H     4.8921115    4.7818959   -1.7305474
H     5.0534866   -4.7538819   -0.5328037
```

Ph_2PBcat (reactant)

```
36
Energy = -1211.671535344
B     0.4985299   -0.4363120    0.0191534
P     0.8953765    1.4307653    0.1301559
O     0.4392938   -1.1723461   -1.1677580
O     0.3677811   -1.2693930    1.1352179
C     0.2616937   -2.4915978   -0.7719895
C     0.2166924   -2.5503817    0.6198452
C     0.0395347   -3.7407245    1.3032905
C    -0.0910523   -4.8935968    0.5145350
C    -0.0446006   -4.8348640   -0.8838128
C     0.1333964   -3.6201246   -1.5627913
H     0.0057261   -3.7781289    2.3868708
H    -0.2316065   -5.8530772    1.0025884
H    -0.1485609   -5.7498800   -1.4587053
```

```
H     0.1688228   -3.5663893   -2.6456183
C     0.0576568    2.0791528   -1.3762595
C     0.5250765    1.6730846   -2.6370848
C    -0.9668246    3.0332791   -1.3076409
C    -0.0376785    2.1938923   -3.8009304
H     1.3253640    0.9419323   -2.7096433
C    -1.5208114    3.5603272   -2.4762561
H    -1.3371067    3.3630038   -0.3416838
C    -1.0626365    3.1409661   -3.7258171
H     0.3292169    1.8627142   -4.7686388
H    -2.3155284    4.2980843   -2.4059536
H    -1.4966645    3.5500614   -4.6336384
C    -0.1873002    1.9659119    1.5109919
C     0.2977841    2.9499845    2.3846275
C    -1.4772029    1.4499492    1.7165325
C    -0.4895804    3.4109819    3.4418047
H     1.2953206    3.3543108    2.2344710
C    -2.2622821    1.9085710    2.7723804
H    -1.8690452    0.6904088    1.0457471
C    -1.7691432    2.8900144    3.6370619
H    -0.1017425    4.1727203    4.1121636
H    -3.2585627    1.5016652    2.9210305
H    -2.3817691    3.2454233    4.4607646
```

Ph_2P^+

```
23
Energy = -804.7610901052
P     0.9669716    2.2368317    0.1075330
C     0.0269204    2.4433312   -1.3645708
C     0.6328989    1.8853196   -2.5270796
C    -1.1907690    3.1661700   -1.4950086
C    -0.0023764    1.9741654   -3.7548681
H     1.5845248    1.3685601   -2.4364196
C    -1.7956806    3.2767514   -2.7340584
H    -1.6140992    3.6741136   -0.6362868
C    -1.2142944    2.6681335   -3.8575795
H     0.4449818    1.5245691   -4.6348384
H    -2.7128417    3.8462430   -2.8416610
H    -1.6980160    2.7614954   -4.8250545
C    -0.1409632    2.4020734    1.4631948
C     0.4888918    2.7264662    2.6991932
C    -1.5422375    2.1592038    1.4406147
C    -0.2701036    2.8876987    3.8467456
H     1.5658741    2.8683311    2.7279691
C    -2.2819473    2.2891317    2.6022016
H    -2.0185304    1.8195943    0.5282888
C    -1.6527515    2.6711383    3.7975257
H     0.2059813    3.1618080    4.7820552
H    -3.3467118    2.0811244    2.5939952
H    -2.2438055    2.7749508    4.7022935
```

P_ts (or **TSP** in text)

```
61
Energy = -1822.915334728
B    -1.7192694   -0.0741192    0.0813927
P    -0.8453695   -2.0305593    0.5662464
O    -2.7673692    0.1106045    1.0572948
O    -2.2948765   -0.0832008   -1.2403988
C    -3.9341127   -0.0108801    0.3413939
C    -3.6581584   -0.1207830   -1.0280882
C    -4.6646265   -0.2329846   -1.9709716
C    -5.9872884   -0.2361647   -1.4927220
C    -6.2642341   -0.1285993   -0.1277001
C    -5.2331562   -0.0131075    0.8213716
H    -4.4410656   -0.3143819   -3.0300325
H    -6.8054906   -0.3260952   -2.2011068
H    -7.2959102   -0.1350198    0.2116699
```

```
H    -5.4424912    0.0737800    1.8828277
C     0.4176269   -2.3693933   -0.6685712
C     1.6564916   -2.9748093   -0.3822158
C     0.0662545   -2.1538374   -2.0192104
C     2.5176042   -3.3426908   -1.4124079
H     1.9347393   -3.1797395    0.6459455
C     0.9319254   -2.5245059   -3.0441303
H    -0.8900376   -1.6972825   -2.2554566
C     2.1594354   -3.1204386   -2.7439879
H     3.4687781   -3.8103873   -1.1756761
H     0.6492497   -2.3493583   -4.0782038
H     2.8321844   -3.4142101   -3.5444082
C     0.0010650   -1.9235931    2.1673177
C     1.2862763   -1.3809769    2.3502094
C    -0.7251680   -2.3509909    3.2919119
C     1.8311733   -1.2829133    3.6265073
H     1.8449782   -1.0161563    1.4944455
C    -0.1767439   -2.2488940    4.5705695
H    -1.7228073   -2.7619943    3.1597297
C     1.1032868   -1.7190620    4.7390888
H     2.8229703   -0.8594167    3.7588292
H    -0.7476961   -2.5834440    5.4319196
H     1.5335540   -1.6411350    5.7334857
N    -0.4080756    0.4558558    0.4204096
N     0.6187901    0.6163095   -0.2931608
C     1.4015211    1.6374064   -0.4993968
C     0.9990131    3.0171295   -0.1503161
C     2.7087939    1.3448864   -1.1290684
C     0.0061069    3.2707447    0.8123397
C     1.5884648    4.1129717   -0.8094982
C     2.8225428    0.3430221   -2.1033047
C     3.8690305    2.0190940   -0.7126970
C    -0.3570414    4.5765083    1.1324359
H    -0.4766055    2.4392152    1.3174311
C     1.2107586    5.4167209   -0.4988697
H     2.3352260    3.9390732   -1.5769374
C     4.0615595    0.0268209   -2.6538968
H     1.9293429   -0.1833966   -2.4204938
C     5.1090425    1.6976771   -1.2618965
H     3.8019586    2.7812187    0.0577718
C     0.2422942    5.6557797    0.4785965
H    -1.1170638    4.7514933    1.8885656
H     1.6706322    6.2476516   -1.0262951
C     5.2103855    0.7040454   -2.2382555
H     4.1300210   -0.7483186   -3.4117069
H     5.9981605    2.2213892   -0.9219181
H    -0.0522728    6.6730123    0.7199547
H     6.1767094    0.4589875   -2.6699782
```

P (final product **3**)

```
61
Energy = -1822.973616756
B     2.7542566    1.0556958    0.9006992
P     1.0668897    1.9411676   -1.1106787
O     1.8069743    1.3132601    1.9056939
O     4.0134488    0.7528421    1.4433887
C     2.4976939    1.1245384    3.0943701
C     3.8215202    0.7786935    2.8152523
C     4.7390656    0.5146386    3.8153220
C     4.2711032    0.6176406    5.1356506
C     2.9461502    0.9670888    5.4156325
C     2.0236282    1.2300755    4.3892343
H     5.7647476    0.2427083    3.5895413
H     4.9557531    0.4201852    5.9549458
H     2.6191229    1.0363087    6.4487227
H     0.9935549    1.4986536    4.5990760
C     1.8133844    3.1510989   -2.2672942
```

C	1.0780851	3.5883129	-3.3791950
C	3.0490694	3.7524484	-1.9916077
C	1.5749829	4.5965318	-4.2057705
H	0.1183953	3.1317086	-3.6081638
C	3.5466949	4.7565576	-2.8209319
H	3.6319192	3.4175408	-1.1391860
C	2.8120705	5.1825001	-3.9303702
H	0.9971177	4.9196945	-5.0674708
H	4.5128713	5.2039398	-2.6033429
H	3.2025541	5.9633787	-4.5769421
C	0.4324742	0.6707264	-2.2716119
C	1.1220213	0.2720549	-3.4280151
C	-0.7522957	0.0081720	-1.9181278
C	0.6438325	-0.7844654	-4.2000930
H	2.0377073	0.7840106	-3.7058782
C	-1.2345837	-1.0458501	-2.6964555
H	-1.2902733	0.3151658	-1.0243133
C	-0.5326846	-1.4458932	-3.8344839
H	1.1892640	-1.0968835	-5.0864623
H	-2.1524015	-1.5537074	-2.4139416
H	-0.9015063	-2.2702762	-4.4384632
N	2.4874943	1.1434267	-0.4924931
N	3.4219729	0.7086427	-1.4685198
C	3.8588096	-0.5105203	-1.3857916
C	3.4276840	-1.5237003	-0.3836022
C	4.8462235	-0.9007751	-2.4179697
C	2.0728006	-1.8554723	-0.2472957
C	4.3744029	-2.1576656	0.4330010
C	5.0789727	-2.2537337	-2.7113662
C	5.5344394	0.0825104	-3.1513560
C	1.6726005	-2.7966629	0.6999708
H	1.3384104	-1.3808713	-0.8888942
C	3.9707181	-3.0883838	1.3875612
H	5.4246550	-1.9013793	0.3315833
C	5.9727556	-2.6160926	-3.7187155
H	4.5488966	-3.0219712	-2.1575533
C	6.4266024	-0.2822190	-4.1536788
H	5.3549626	1.1266457	-2.9170725
C	2.6182695	-3.4090315	1.5246912
H	0.6205644	-3.0504129	0.7946157
H	4.7111381	-3.5628696	2.0250748
C	6.6497175	-1.6333134	-4.4419669
H	6.1378042	-3.6669502	-3.9389975
H	6.9571956	0.4856076	-4.7100189
H	2.3034812	-4.1354658	2.2684359
H	7.3508478	-1.9155873	-5.2223291

References

1. E. N. Daley, C. M. Vogels, S. J. Geier, A. Decken, S. Doherty and S. A. Westcott, *Angew. Chem. Int. Ed.*, 2015, **54**, 2121-2125.
2. X. Feng, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1986, **25**, 4615-4616.
3. D. C. Pestana and P. P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 8426-8437.
4. J. H. W. LaFortune, Z.-W. Qu, K. Bamford, A. Trofimova, S. Westcott and D. W. Stephan, *Chem. - Eur, J.*, 2019, **10.1002/chem.201903407**.
5. D. Gudat, A. Haghverdi, H. Hupfer and M. Nieger, *Chem. Eur. J.*, 2000, **6**, 3414-3425.
6. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
7. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104-154119.
8. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
9. F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143-152.
10. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
11. A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799-805.
12. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119-124.
13. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
14. P. Deglmann, K. May, F. Furche and R. Ahlrichs, *Chemical Physics Letters*, 2004, **384**, 103-107.
15. S. Grimme, *Chemistry - A European Journal*, 2012, **18**, 9955-9964.
16. F. Eckert and A. Klamt, *AIChE Journal*, 2002, **48**, 369-385.
17. F. Eckert and A. Klamt, *Journal*, 2015.
18. Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656-5667.
19. F. Weigend, F. Furche and R. Ahlrichs, *The Journal of Chemical Physics*, 2003, **119**, 12753-12762.