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Electronic Supplementary Information (ESI)

Base induced isomerisation of a phosphaethynolato-borane: Mechanistic insights into boryl migration and decarbonylation to afford a triplet phosphinidene

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Contents

1. Experimental section

1.1. General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at <0.1 ppm H_2O and <0.1 ppm O_2). [B]OCP (**1**) and 1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium-2-ide were synthesized according to previously reported synthetic procedures.[1,2] 2,4,6-trimethylphenyl isocyanide (Fluorochem) and *t*-butyl isocyanide (Sigma Aldrich) were used as received. Hexane (hex; Sigma Aldrich HPLC grade), benzene (Rathburn, HPLC grade) and toluene (Sigma Aldrich HPLC grade) were purified using an MBraun SPS-800 solvent system. C_6D_6 (Aldrich, 99.5%) was degassed prior to use. All dry solvents were stored under argon in gas-tight ampoules. Additionally, hexane, benzene and toluene were stored over activated 3 Å molecular sieves. Photolysis experiments were performed using a medium pressure 125 W mercury lamp from Photochemical Reactors Ltd, unless otherwise stated.

Characterization techniques: NMR spectra were acquired on Bruker AVIII 500 MHz (^{1}H 500 MHz, ^{13}C 126 MHz) and Bruker AVIII 400 MHz NMR spectrometers (^{31}P 162 MHz, ^{11}B 128 MHz, ^{19}F 470 MHz). ^{1}H and ^{13}C NMR spectra were referenced to the most downfield solvent resonance (^{1}H NMR C_6D_6: δ = 7.16 ppm; ^{13}C NMR C_6D_6: δ = 188.06 ppm). ^{31}P and ^{11}B spectra were externally referenced to an 85% solution of H_3PO_4 in H_2O and $BF_3{\cdot}Et_2O$ in C_6D_6, respectively. Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U.K.). Samples (approx. 5 mg) were submitted in flame-sealed glass vials.

1.2. Compound syntheses

*1.2.1. Synthesis of [B]C(PCO)NMes (**2a**)*

To a solution of [B]OCP (**1**) (100 mg, 22 mmol) in benzene (1 mL) was added 2,4,6-trimethylphenyl isocyanide (32 mg, 22 mmol). The solution immediately changed from pale yellow to orange. Removal of the solvent yielded an oily orange solid. Recrystallization from hexane yielded analytically pure orange crystals of [B]C(PCO)NMes (**2a**) (93 mg, 71.9% yield).

CHN Anal. Calcd. for $C_{37}H_{47}BN_3OP$: C, 75.12%; H, 8.01%; N, 7.10%. Found: C, 74.96%; H, 8.14%; N, 7.00%.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.23 (dd, $^{3}J_{H–H}$ = 8.5 Hz, 6.8, 2H; *para*-Ar*H* Dipp), 7.14 (m, br, 4H; *meta*-Ar*H* Dipp), 6.57 (s, 2H; *meta*-Ar*H* Mes), 6.22 (s, 2H; {(NC*H*)$_2$}), 3.40 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 4H; {C*H*(CH$_3$)$_2$}), 2.06 (s, 3H; *para*-C*H*$_3$ Mes), 1.53 (s, 6H; *ortho*-C*H*$_3$ Mes), 1.37 (d, $^{3}J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$}), 1.21 (d, $^{3}J_{H–H}$= 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$}).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 205.24 (d, $^{1}J_{C–P}$ = 117.2 Hz; P*C*O) , 154.22 (d, $^{1}J_{C–P}$ = 15.1 Hz; [B]*C*(NMes)(PCO)), 146.69 (Ar*C*), 138.40 (Ar*C*), 135.94 (Ar*C*), 129.14 (Ar*C*), 126.73 (Ar*C*), 123.70 (Ar*C*), 120.40 ({(N*C*H)$_2$}), 28.98 (methyl*C* Mes), 26.03 (methyl*C* Mes), 23.46 (methine*C* Dipp), 20.95 (methyl*C* Dipp), 17.12 (methyl*C* Dipp).

^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 22.79 (s, br).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = –195.16 (s).

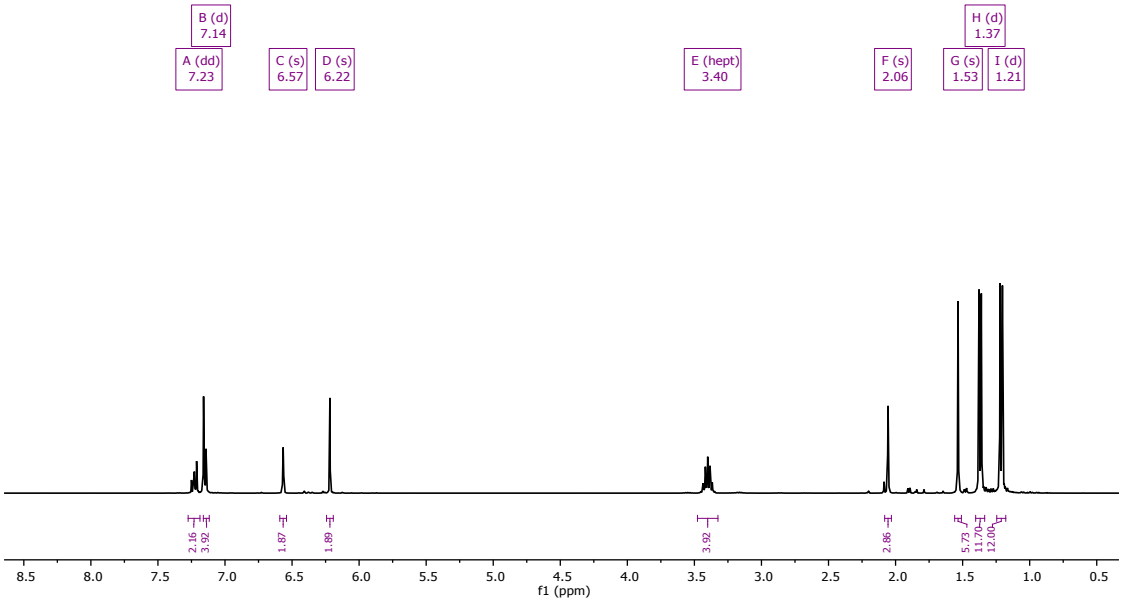

Figure S1. Room temperature ^{1}H NMR (500 MHz) spectrum of **2a** in C_6D_6.

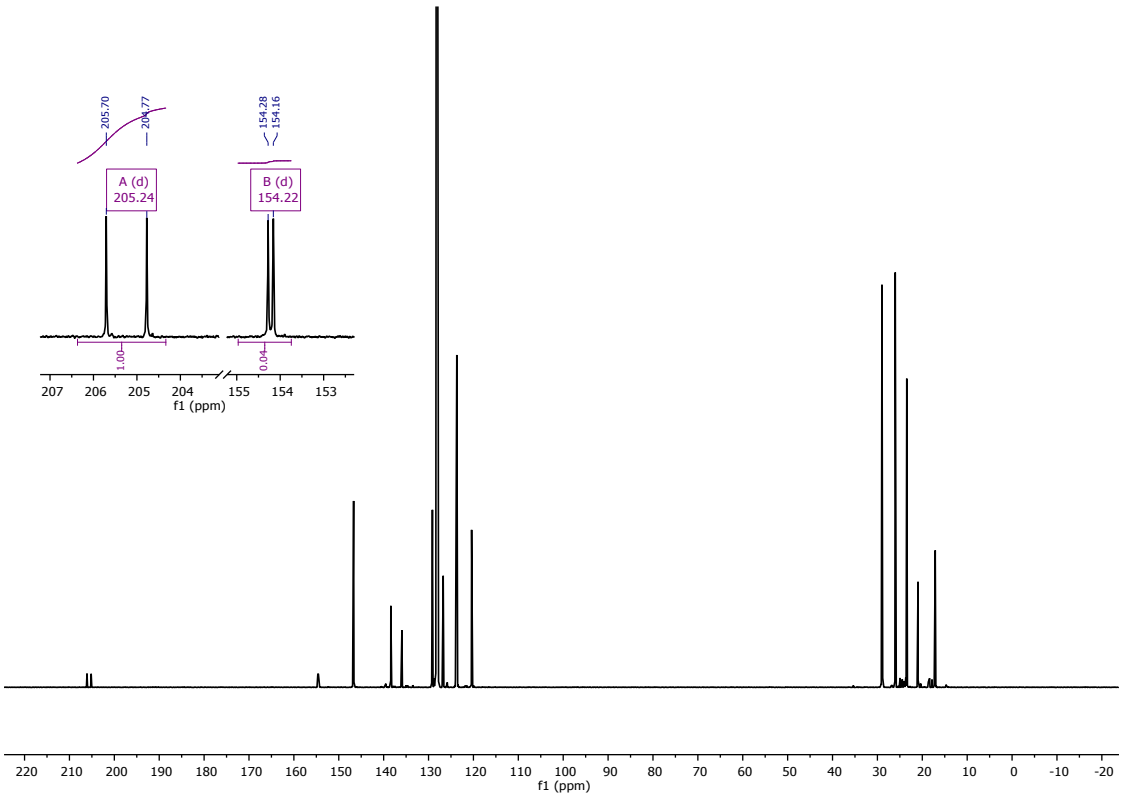

Figure S2. Room temperature $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

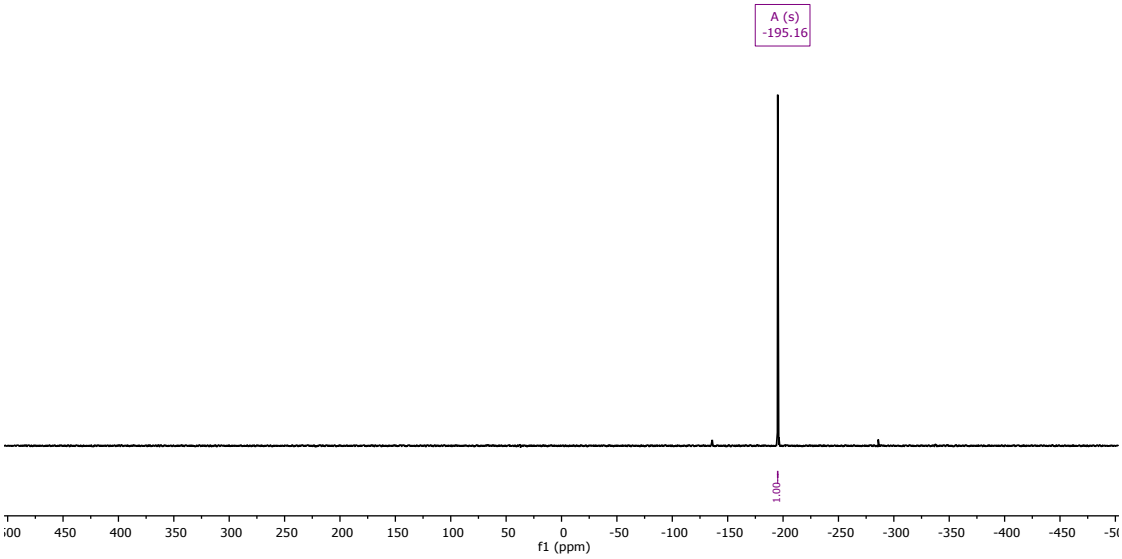

Figure S3. Room temperature $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

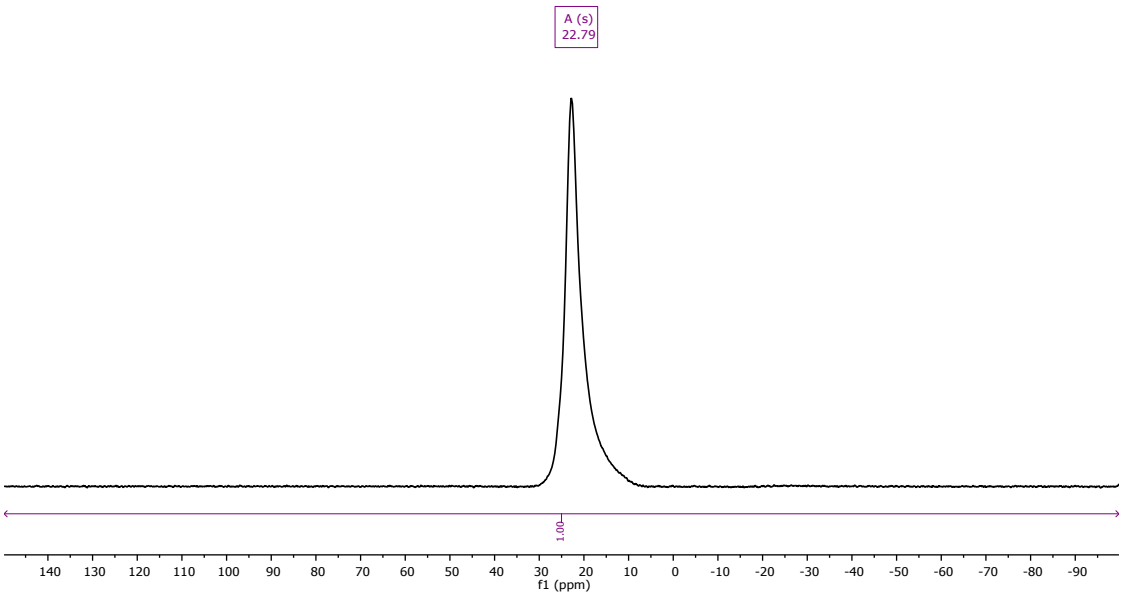

Figure S4. Room temperature $^{11}B\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

*1.2.2. Irradiation of **2a** to yield [B]PCNMes (**3a**) and an unidentified product*

Irradiation of a solution of **2a** (50 mg) in toluene (1 mL) yields two products as determined by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy, independent of the concentration and temperature at which irradiation is conducted. Attempts to separate these products were unsuccessful. Crystallisation from a concentrated hexane solution lead to the identification of a MesNC supported phosphinidene (**3a**), however it was not possible to identify the second product. Redissolving the crystals revealed a mixture of the two products observed during the reaction. A qualitative assignment of the observed peaks was still attempted.

^{1}H NMR (400 MHz, C_6D_6): A characteristic $^{4}J_{P-H}$ (1.4 Hz) coupling was observed at 6.27 ppm, consistent with the phosphaketene later characterised, likely belonging to the phosphinidene complex. The second product has a distinct boryl backbone resonance at 6.29 ppm, with no phosphorus coupling observed.

^{11}B{^{1}H} NMR (128 MHz, C_6D_6): Reveals two broad resonances at 28.23 and 23.42 ppm consistent with the presence of two boryl moieties.

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): The phosphinidene has a resonance at –262.55 ppm (s), in good agreement with the calculated structure. The unknown product is responsible for the phosphorus resonance at +8.55 ppm.

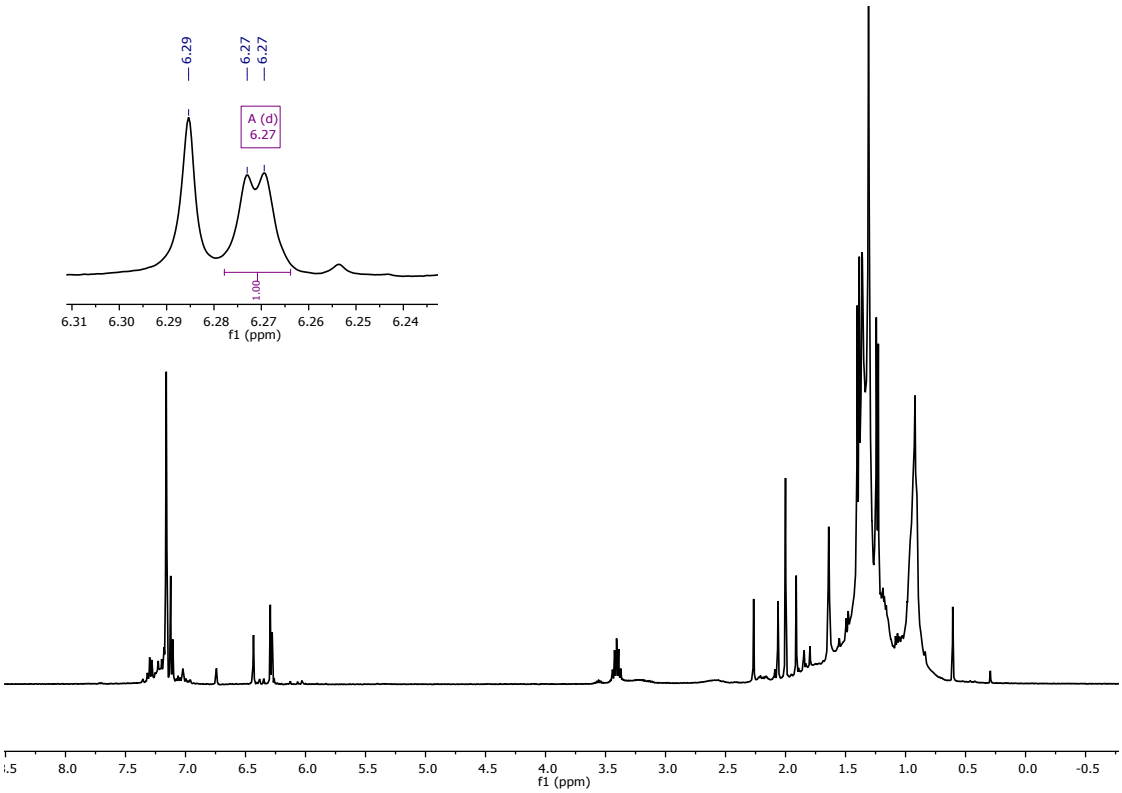

Figure S5. Room temperature ^{1}H NMR (500 MHz) spectrum of a reaction mixture containing **3a** in C_6D_6.

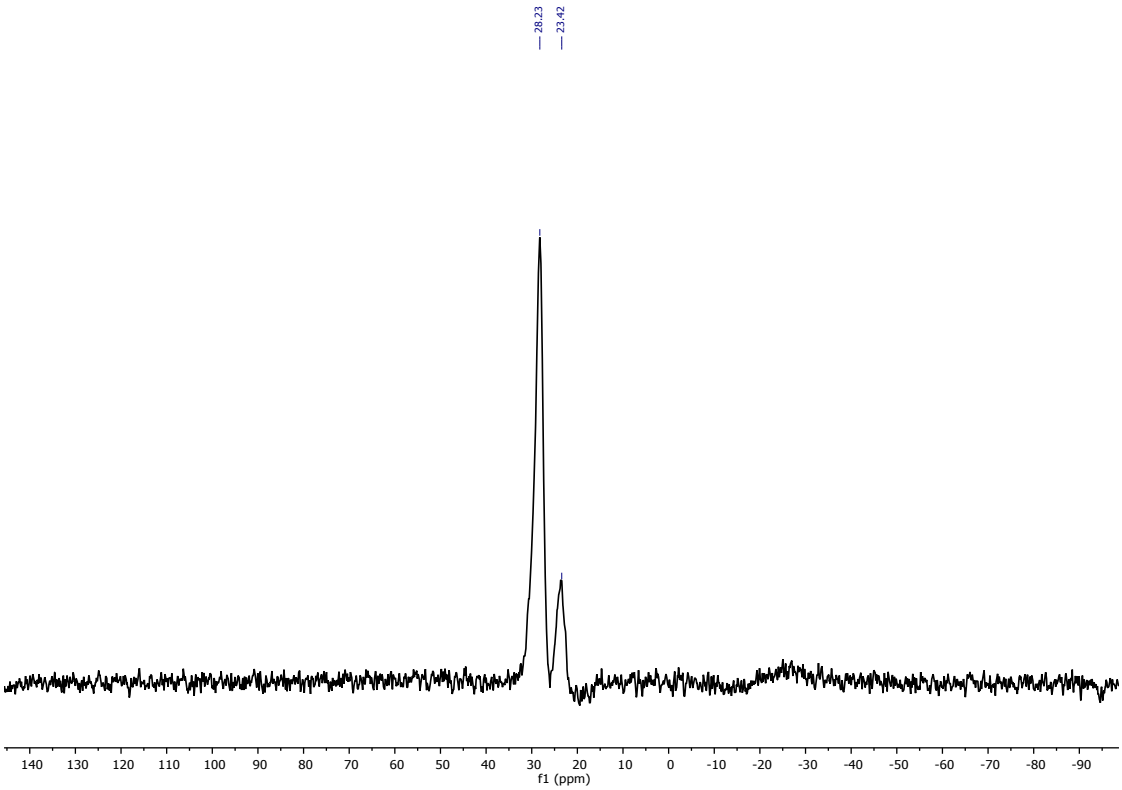

Figure S6. Room temperature $^{11}B\{^{1}H\}$ NMR spectrum of a reaction mixture containing **3a** in C_6D_6.

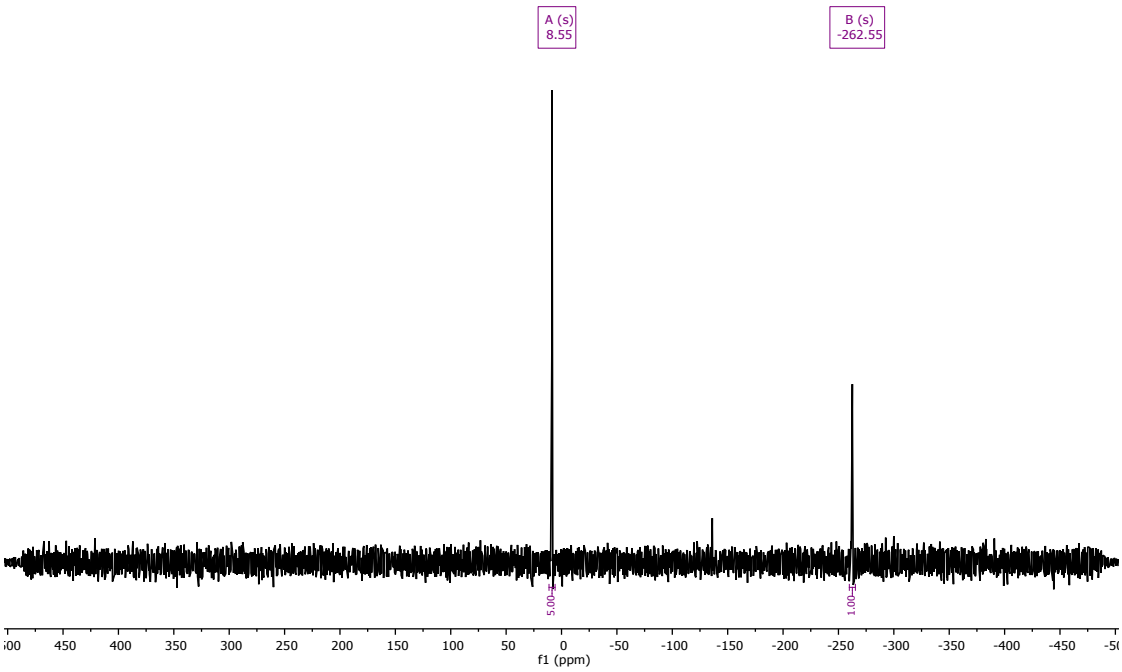

Figure S7. Room temperature $^{31}P\{^{1}H\}$ NMR spectrum of a reaction mixture containing **3a** in C_6D_6.

*1.2.3. Synthesis of [B]PCN^{t}Bu (**3b**)*

3b can by synthesised starting with [B]OCP (i) or [B]PCO, **5**, (ii)**:**

(i) [B]OCP (30 mg, 6.7 mmol) was dissolved in benzene (1 mL) and ^{t}BuNC (25 mg, 30 mmol, 4.5 eq.) was added. After 2 hours complete conversion to **4** was observed. The reaction was monitored for 2 days, after which *ca.* 95% of **4** had been consumed. The solvent and excess ^{t}BuNC was removed under vacuum and the orange oil recrystallized from hexane (1 mL concentrated to 0.3 mL) yielding orange crystals of **3b** (10 mg, 33%). The reduced yield is likely due to the high solubility of the species, as the only observed product of the reaction is **3b**. The NMR spectra of the crystalline material contained small amounts of impurities which were difficult to remove due to their solubility being similar to that of the desired product. Further recrystallizations gave diminishing improvements to purity and significantly lower yields.

(ii) [B]PCO (**5**) (50 mg, 11 mmol) was dissolved in benzene (1 mL) and ^{t}BuNC (23.5 mg, 28 mmol, 2.5 eq.) was added. The reaction was monitored for 4 days, by which time *ca.* 95% of the starting material had been consumed. Further stirring did not lead to substantial changes in the NMR spectrum. The solvent and excess ^{t}BuNC was removed under vacuum and the orange oil recrystallized from hexane (1 mL concentrated to 0.3 mL) yielding orange crystals of **3b** (24 mg, 42 %).

CHN Anal. Calcd. for $C_{31}H_{45}BN_3P$: C, 74.24 %; H, 9.04 %; N, 8.38 %. Found: C, 76.78 %, H, 9.84 %; N 6.25 %. Calcd. with 1 eq. of hexane as $C_{37}H_{59}BN_3P$: C, 75.62 %; H, 10.12 %; N, 7.15 %.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.24–7.09 (m, 6H; Ar*H*), 6.23 (d, $^4J_{P–H}$ =1.4 Hz, 2H; {(NC*H*)$_2$}), 3.39 (sept, $^3J_{H–H}$ =7.1 Hz, 4H; {C*H*(CH$_3$)$_2$}), 1.45 (d, $^3J_{H–H}$ = 6.9 Hz, 12H;

{CH(CH_3)$_2$}), 1.31 (s, 11H; hexane), 1.23 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(CH_3)$_2$}), 0.91 (s, 5H, hexane), 0.70 (s, 9H; ^{t}Bu).

^{13}C NMR (126 MHz, C_6D_6): δ = 173.68 (d, $^1J_{C–P}$ = 70.4 Hz; isocyanide*C*), 147.00 (Ar*C*), 139.66 (Ar*C*), 124.01 (Ar*C*), 121.72 ({(N*C*H)$_2$}), 60.00 (d, $^3J_{C–P}$ = 5.3 Hz; N*C*(CH$_3$)$_3$), 38.81 (hexane), 31.92 (NC(*C*H$_3$)$_3$), 30.00 (methyl*C* Dipp), 29.04 (hexane), 25.06 (methyl*C* Dipp), 24.30 (methine*C* Dipp), 14.60 (hexane).

^{11}B NMR (128 MHz, C_6D_6): δ = +27.68 (s, br), impurity at 14.83 ppm.

^{31}P NMR (162 MHz, C_6D_6): δ = –256.17 (s, br)

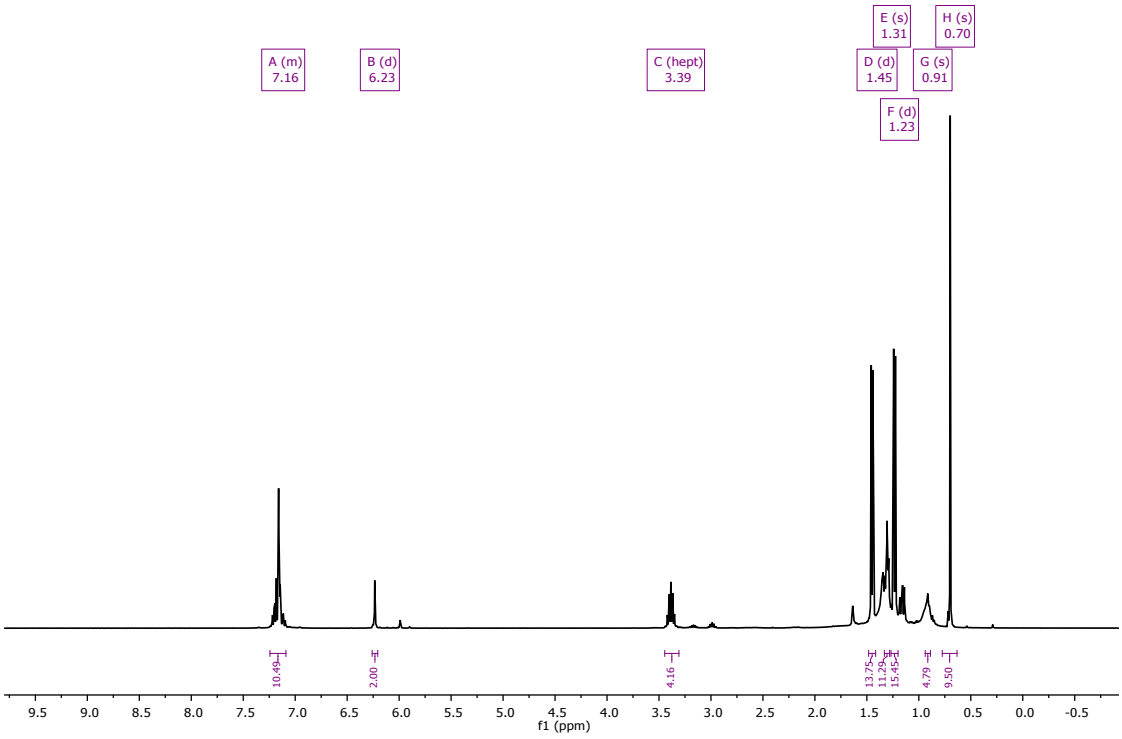

Figure S8. Room temperature ^{1}H NMR (500 MHz) spectrum of **3b** in C_6D_6.

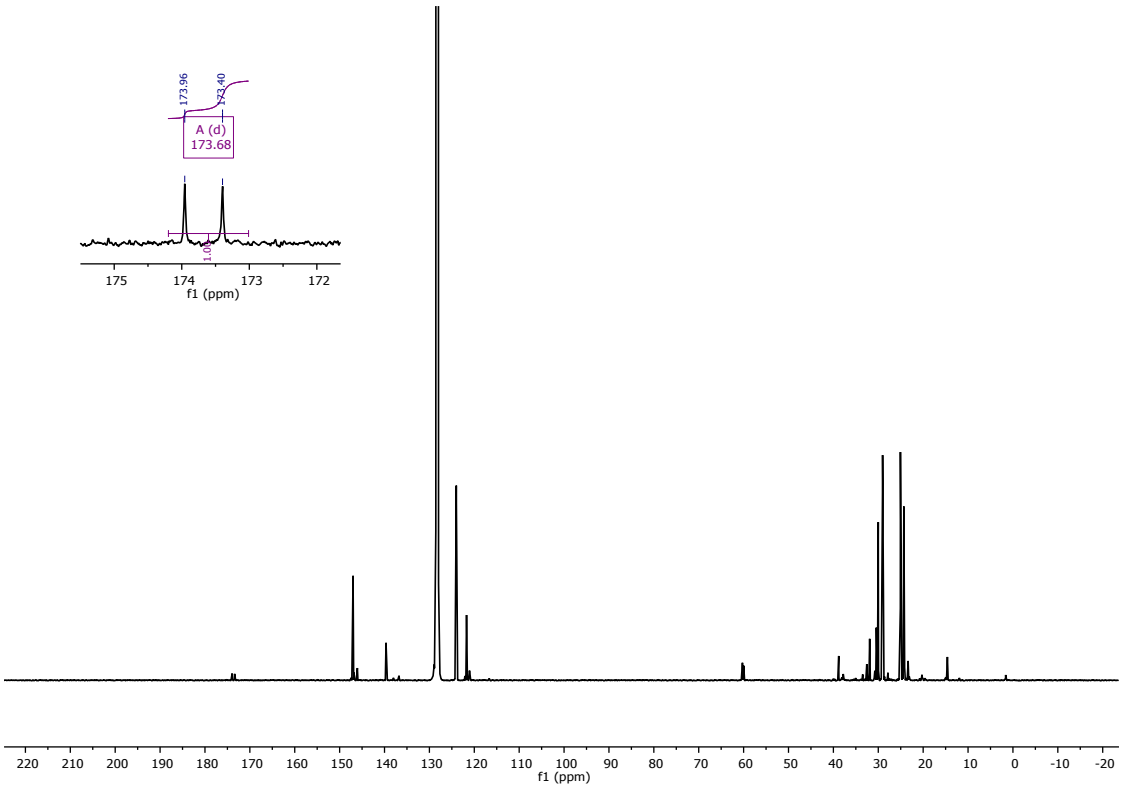

Figure S9. Room temperature $^{13}C\{^{1}H\}$ spectrum of **3b** in C_6D_6.

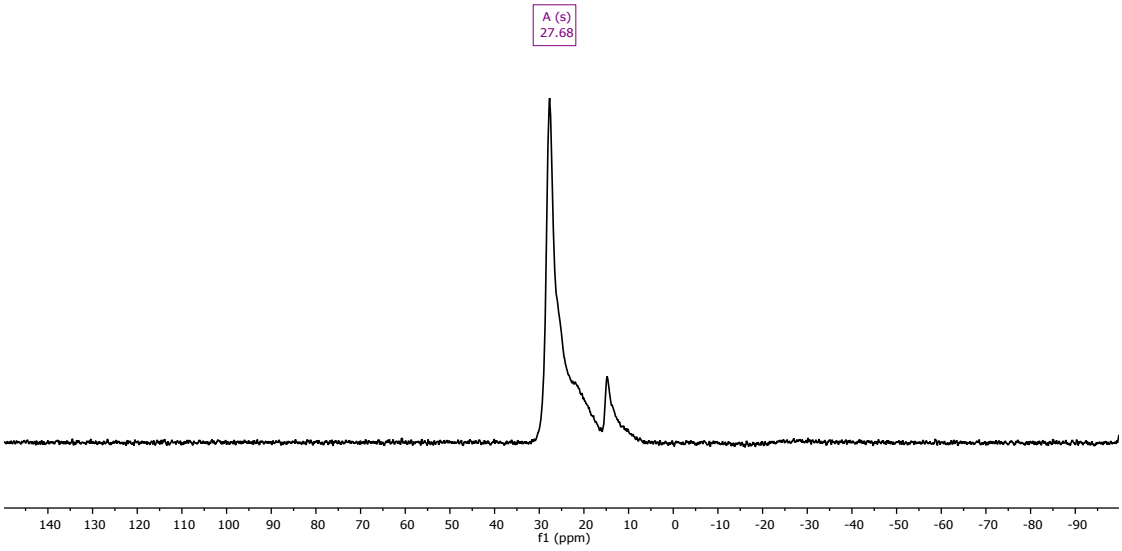

Figure S10. Room temperature $^{11}B\{^{1}H\}$ spectrum of **3b** in C_6D_6.

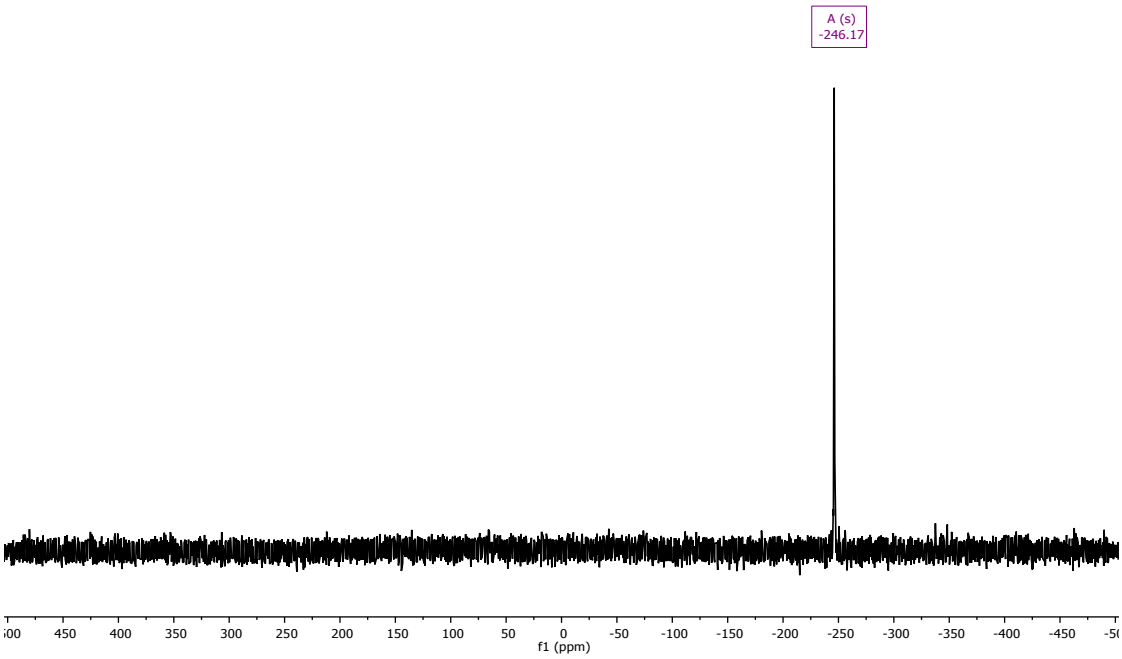

Figure S11. Room temperature $^{31}P\{^{1}H\}$ spectrum of **3b** in C_6D_6.

*1.2.4. Synthesis of [B]C(PCNMes)NMes (**4a**).*

[B]C(PCNMes)NMes (**4a**) can be synthesised either from **2a** (i) or directly from [B]OCP (ii):

(i) **2a** (50 mg, 9 mmol) was dissolved in benzene (1 mL) and 2,4,6-trimethylphenyl isocyanide (15 mg, 10.8 mmol, 1.2 eq) was added. The reaction mixture was monitored by ^{31}P NMR spectroscopy and after 24 hours complete consumption of **2a** was observed. The solvent was removed and the oily orange solid recrystallized from hexane, yielding pale orange crystals of [B]C(PCNMes)NMes (**4a**) (42 mg, 73.5%).

(ii) [B]OCP (50 mg, 11 mmol) was dissolved in benzene (1 mL) and 2,4,6-trimethylphenyl isocyanide (35 mg, 24mmol, 2.2 eq) was added. The reaction was monitored by ^{31}P NMR spectroscopy and showed complete conversion after 24 hours. The solvent was removed and the oily solid recrystallized from hexane, yielding pale orange crystals of [B]C(PCNMes)NMes (**4a**) (46 mg, 60.0%).

CHN Anal. Calcd. For $C_{46}H_{58}BN_4P$: C, 77.95%; H, 8.25%; N, 7.90%. Found: C, 77.56%; H, 8.34 %; N, 7.67%.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.25–7.12 (m, 2H; ArC*H* Dipp), 7.07–7.15 (m, 4H; ArC*H* Dipp), 6.32 (s, 2H; *meta*-Ar*H* Mes), 6.28 (s, 2H; *meta*-Ar*H* Mes), 6.21 (s, 2H; {(NC*H*)$_2$}), 3.49 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H; {C*H*(CH$_3$)$_2$} Dipp), 1.78 (s with shoulder, 9H; *para*-C*H*$_3$ Mes and *ortho*-C*H*$_3$ Mes) 1.73 (s, 6H; *ortho*-C*H*$_3$ Mes), 1.48 (s, 3H, *para*-C*H*$_3$; Mes), 1.42 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$} Dipp), 1.22 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$} Dipp).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 165.34 (d, $^1J_{C–P}$ = 110.1 Hz; P*C*NMes) , 152.29 (d, $^1J_{C–P}$ = 11.3 Hz; [B]*C*(NR)(PCNMes)), 146.87(Ar*C*), 139.52 (Ar*C*), 138.14 (Ar*C*), 134.96 (Ar*C*), 133.54 (Ar*C*), 128.76 (Ar*C*), 125.83 (Ar*C*), 123.56 (Ar*C*), 120.25 ({(N*C*H)$_2$}), 29.07 (methyl*C* Mes), 25.98 (methyl*C* Mes), 23.67 (methine*C* Dipp), 20.90 (methyl*C* Dipp), 20.36 (methyl*C* Dipp), 18.36 (methyl*C* Mes), 17.84 (methyl*C* Mes).

^{11}B{^{1}H} NMR (128 MHz, C_6D_6) δ = 23.04 (s, br).

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ = –136.13 (s) (small amount of impurity observed at +152.90 ppm).

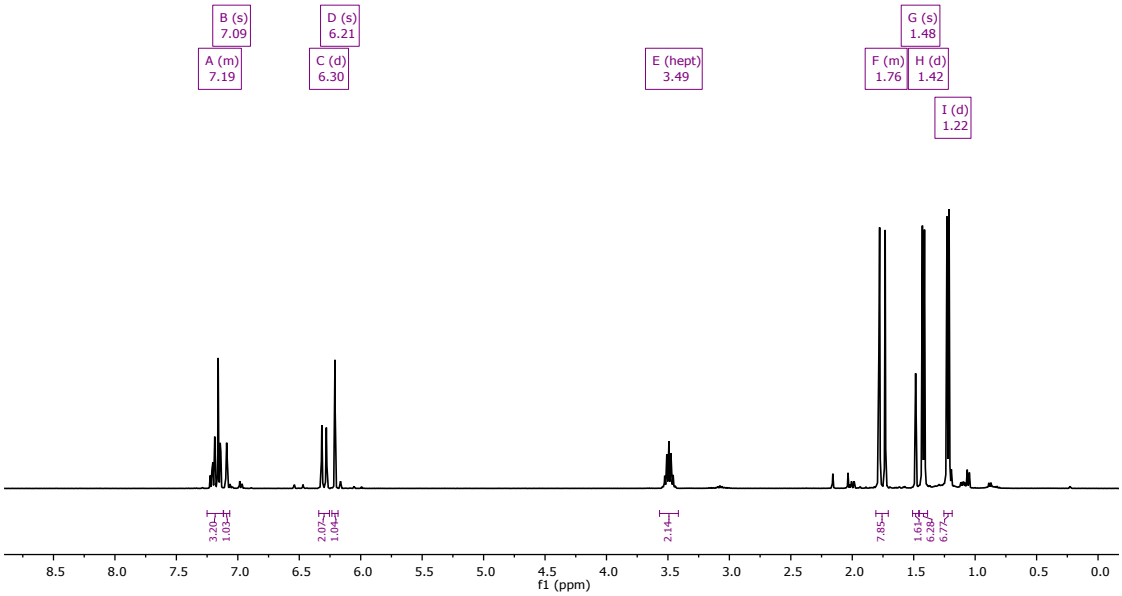

Figure S12. Room temperature ^{1}H NMR (500 MHz) spectrum of **4a** in C_6D_6.

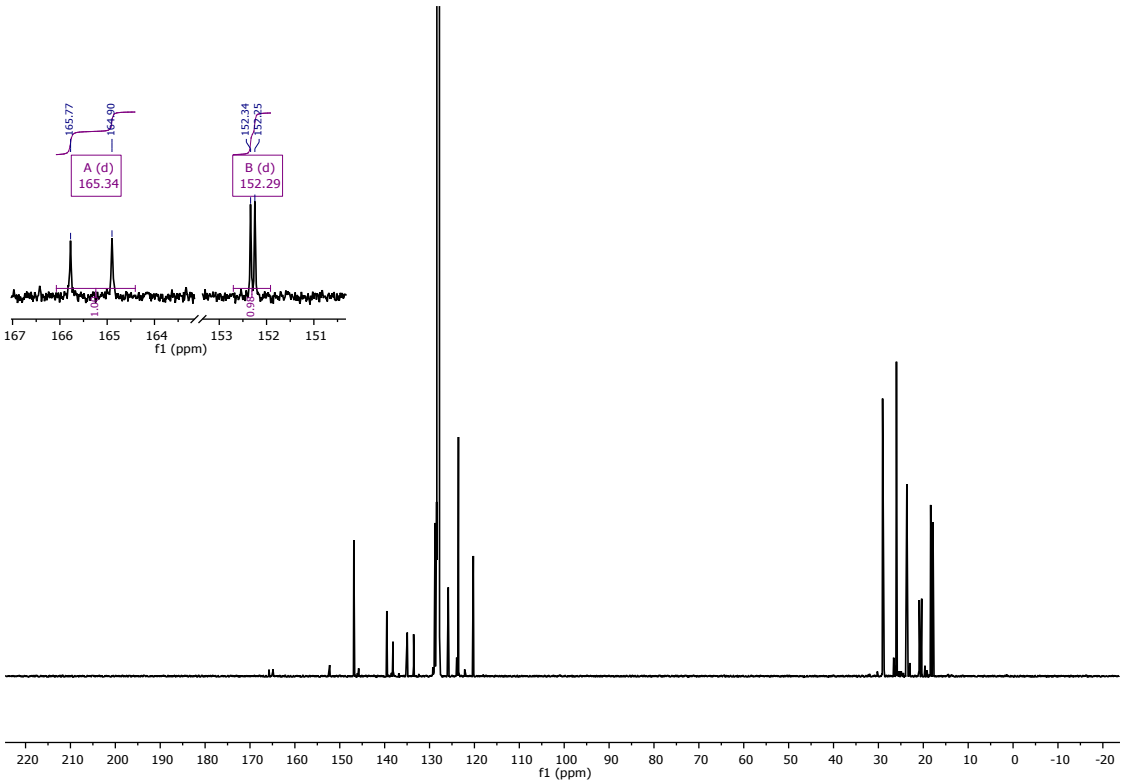

Figure S13. Room temperature $^{13}C\{^{1}H\}$ spectrum of **4a** in C_6D_6.

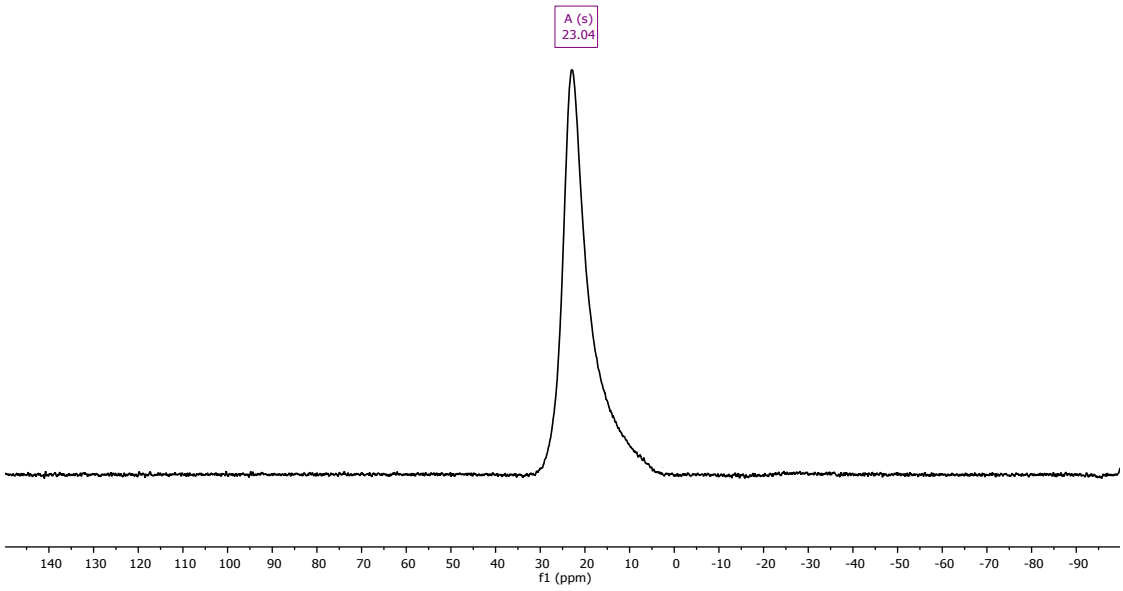

Figure S14. Room temperature $^{11}B\{^{1}H\}$ spectrum of **4a** in C_6D_6.

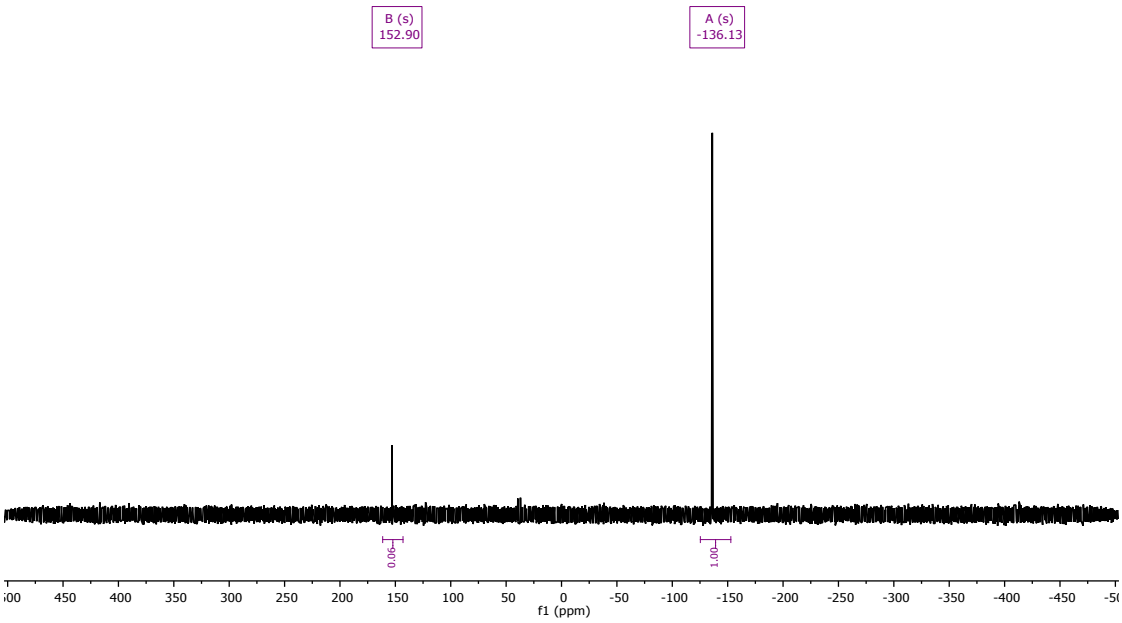

Figure S15. Room temperature $^{31}P\{^{1}H\}$ spectrum of **4a** in C_6D_6.

*1.2.5. Synthesis of [B]PCO (**5**).*

[B]OCP (100 mg, 22 mmol) was dissolved in a benzene (1 mL) solution containing ^{t}BuNC (1.9 mg, 2 mmol, 10 mol%). The reaction was monitored by ^{31}P NMR spectroscopy, after 48 hours the starting material was completely consumed. The solvent and ^{t}BuNC were removed under vacuum, and the resulting oily solid recrystallized from hexane yielding [B]PCO (**5**) as a yellow powder (71 mg, 71%). Crystals suitable for X-ray diffraction were obtained from a cooled hexane solution.

CHN Anal. Calcd. for $C_{27}H_{36}BN_2OP$: C, 72.65%; H, 8.13%; N, 6.28%. Found: C, 71.73%; H, 8.02 %; N, 6.66%.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.26–7.17 (dd, $^3J_{H–H}$ = 8.1, 6.9 Hz, 4H; *para*-Ar*H*), 7.14 (dd, $^3J_{H–H}$ = 7.2, 8.2 Hz, 2H; *ortho*-Ar*H*), 6.27 (d, $^4J_{H–P}$ = 1.6 Hz, 2H; {(NC*H*)$_2$}), 3.19 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H; {C*H*(CH$_3$)$_2$}), 1.36 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$}), 1.19 (d, $^3J_{H–H}$ =6.9 Hz, 12H;{CH(C*H*$_3$)$_2$}).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 191.09 (d, $^1J_{C–P}$ = 89.3 Hz; P*C*O), 146.62 (Ar*C*), 137.84 (Ar*C*), 128.74 (Ar*C*), 124.02, 121.87 ({(N*C*H)$_2$}), 28.82 (methyl*C* Dipp), 24.93 (methyl*C* Dipp), 23.93(methine*C* Dipp).

^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 25.55 (s, br).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = –337.13 (br).

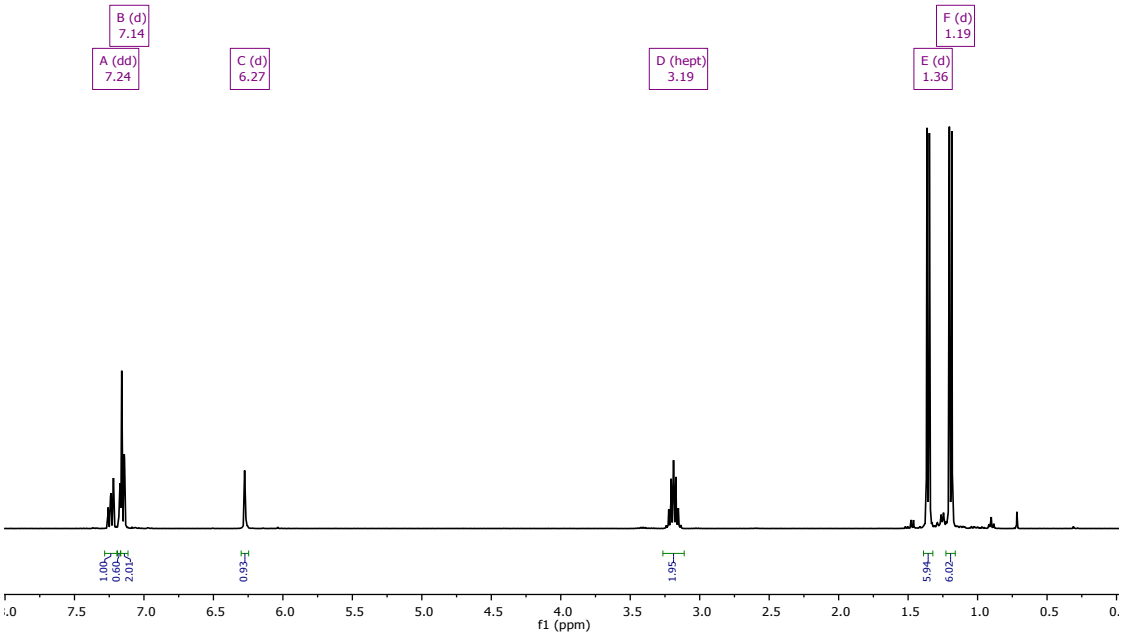

Figure S16. Room temperature ^{1}H NMR (500 MHz) spectrum of **5** in C_6D_6.

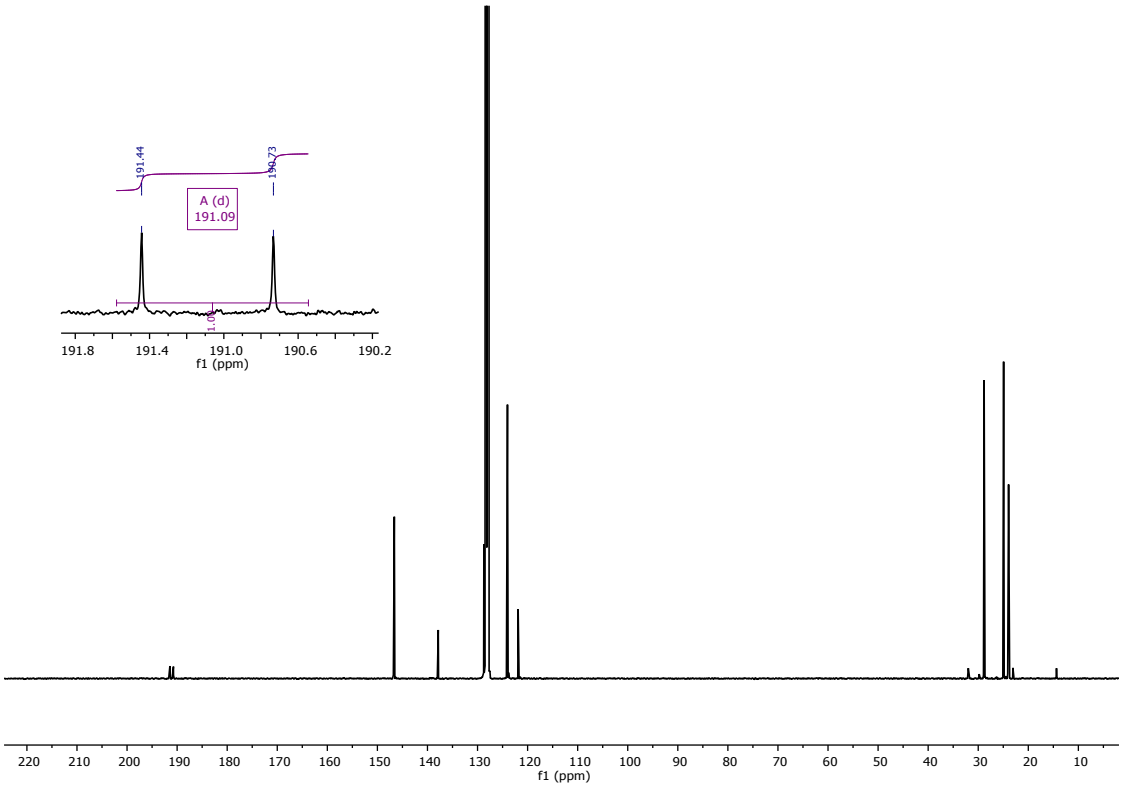

Figure S17. Room temperature $^{13}C\{^{1}H\}$ spectrum of **5** in C_6D_6.

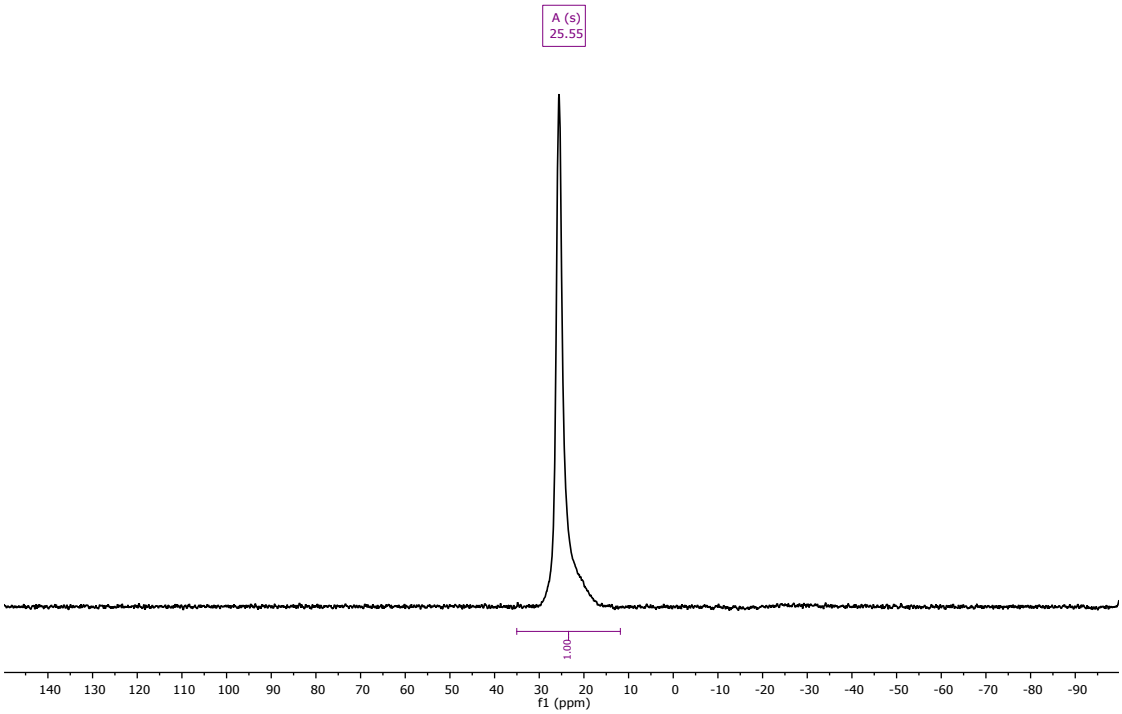

Figure S18. Room temperature $^{11}B\{^{1}H\}$ spectrum of **5** in C_6D_6.

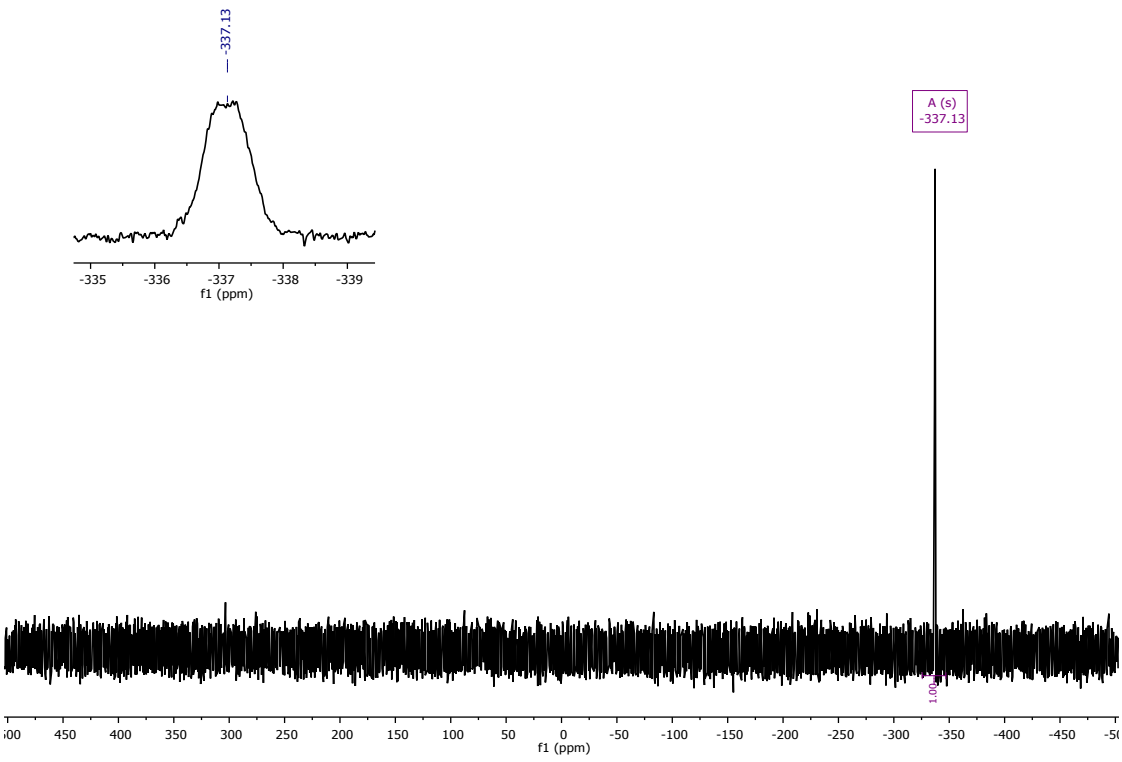

Figure S19. Room temperature $^{31}P\{^{1}H\}$ spectrum of **5** in C_6D_6.

When a stoichiometric amount of ^{t}BuNC was used, the solution turned a deep purple colour and two major intermediates were determined by ^{31}P NMR spectroscopy (Figure S20).

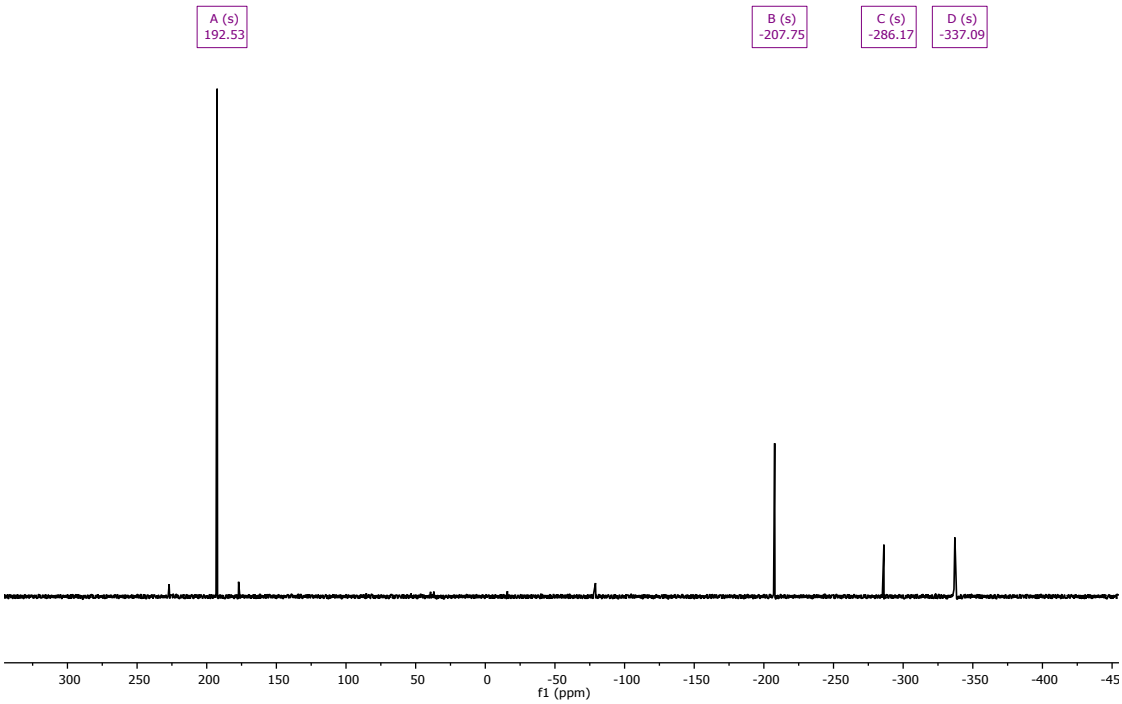

Figure S20. ^{31}P{^{1}H} of reaction mixture containing stoichiometric amounts of [B]OCP and ^{t}BuNC after approximately 1 minute.

*1.2.6. Synthesis of [B]P=P[B] (**6**).*

[B]PCO (**5**; 30 mg, 6.7 mmol) was dissolve in benzene (1 mL) and irradiated for 30 minutes, resulting in complete consumption of the starting material and formation a single product in the ^{31}P NMR spectrum at +596 ppm. The solvent was removed and the resulting orange solid dissolved in hexane. Concentration of the solution and cooling to –35°C for a week resulted in orange crystals of **6** (19 mg, 67.6 %).

CHN Anal. Calcd. for $C_{26}H_{36}BN_2P$: C, 74.64%; H, 8.67%; N, 6.70%. Found: C, 74.03%; H, 8.38%; N, 7.11%.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.23–7.16 (m, 4H; Ar*H*), 7.06–7.03 (m, 2H; Ar*H*), 6.26 (s, 2H; {(NC*H*)$_2$}), 3.14 (sept, $^3J_{H–H}$ = 7.1 Hz, 4H; {C*H*(CH$_3$)$_2$}), 1.17 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$}), 0.98 (d, $^3J_{H–H}$ = 6.9 Hz, 12H; {CH(C*H*$_3$)$_2$}).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 146.18 (Ar*C*), 138.93 (Ar*C*), 123.47 (Ar*C*), 121.12 ({(N*C*H)$_2$}), 28.74 (methyl*C* Dipp), 25.36 (methyl*C* Dipp), 23.81 (methine*C* Dipp).

^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = +30.03 (s, br).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = +595.99 (br).

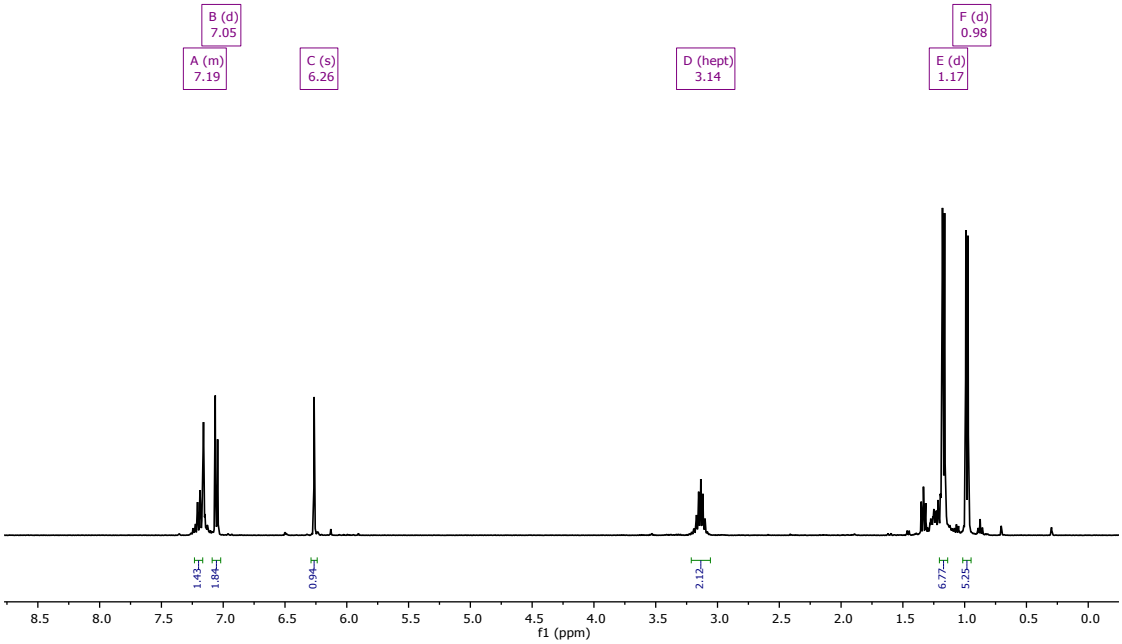

Figure S21. Room temperature ^{1}H NMR (500 MHz) spectrum of **6** in C_6D_6.

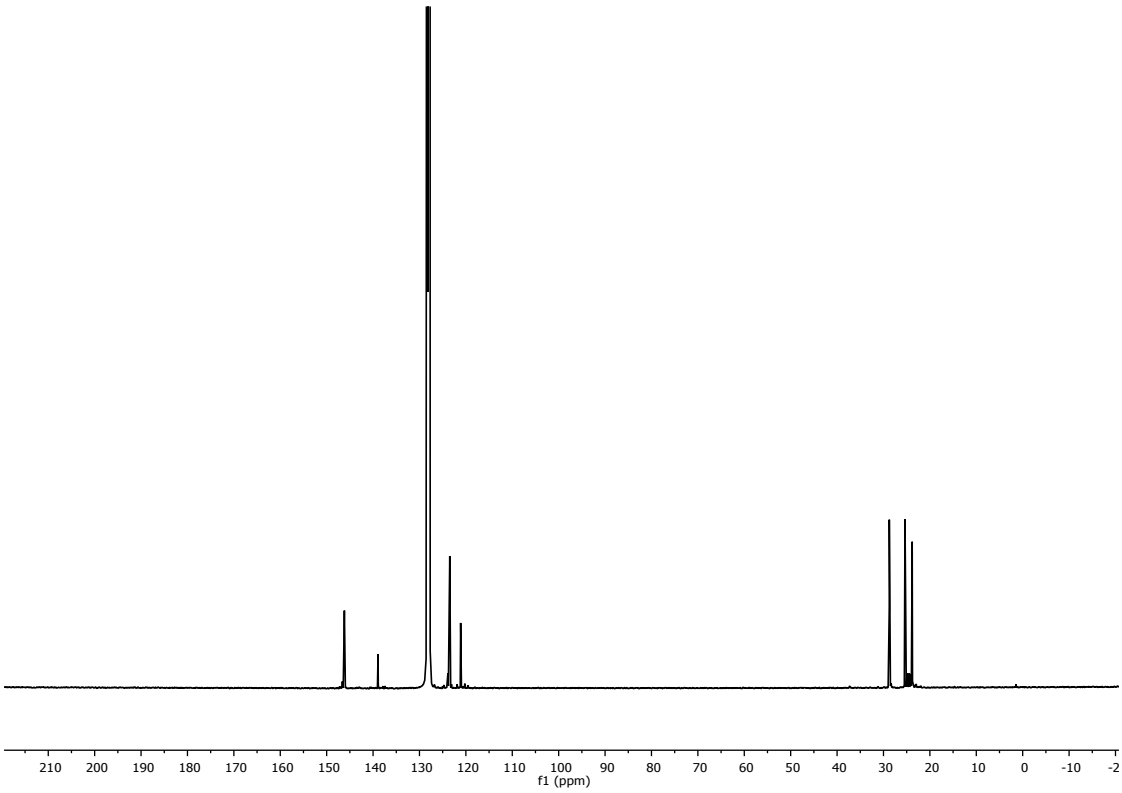

Figure S22. Room temperature $^{13}C\{^{1}H\}$ spectrum of **6** in C_6D_6.

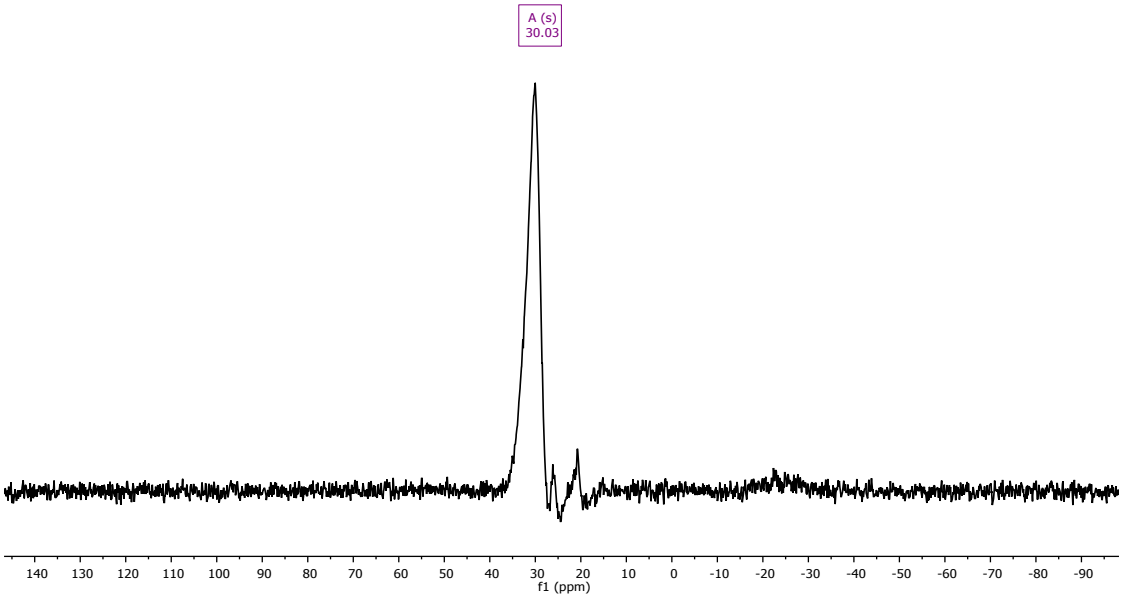

Figure S23. Room temperature $^{13}C\{^{1}H\}$ spectrum of **6** in C_6D_6.

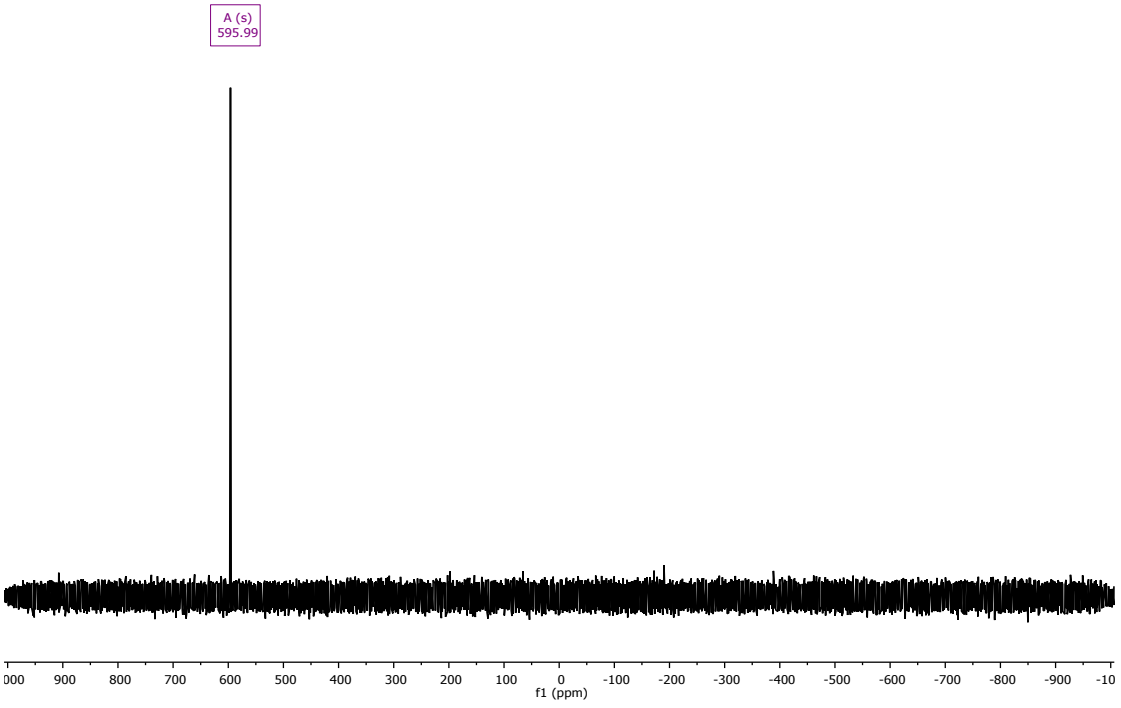

Figure S24. Room temperature $^{31}P\{^{1}H\}$ spectrum of **6** in C_6D_6.

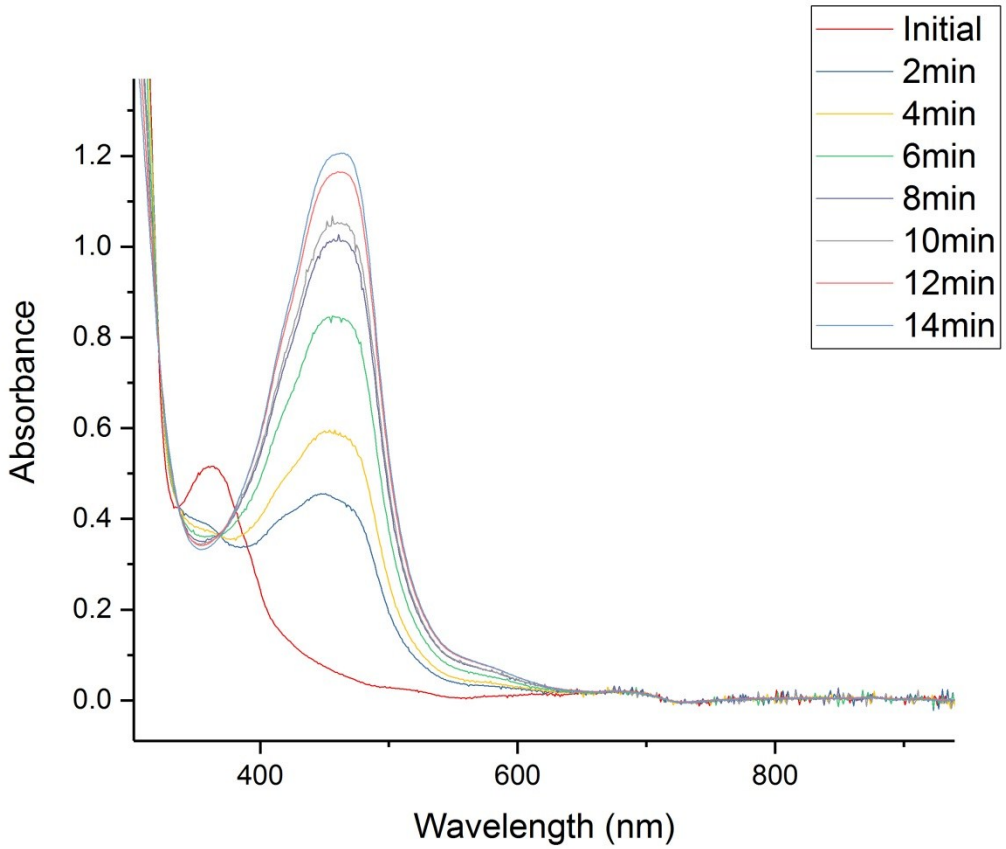

Figure S25. UV/vis spectra of irradiation of **5** (red) to yield **6** (light blue) over time.

*1.2.7. Synthesis of cyclo-[B]PP(O[B])C(^{Me2}IPr)C(O) (**7**)*

Addition of one equivalent of 1,3-diisopropyl-4,5-dimethyl-1,3-dihydro-2λ^2-imidazole (19 mg, 11 mmol) to a toluene solution of [B]PCO (100 mg, 22 mmol) resulted in complete consumption of the [B]PCO. The solvent was removed and product extracted with hexane and filtered to remove the excess carbene. Concentration of the hexane solution followed by cooling to –35 °C resulted in light orange crystals of **7** (57 mg, 47.9%).

CHN Anal. Calcd. for $C_{65}H_{92}B_2N_6O_2P_2$: C, 72.76 %; H, 8.64 %; N, 7.83 %. Found: C, 73.86%; H, 8.89 %; N, 7.46 %.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.28–7.17 (m, 4H; Ar*H*), 7.12 (dd, *J* = 7.3, 1.7, 2H; Ar*H*), 7.09–7.02 (m, 6H; Ar*H*), 6.24 (d, $^4J_{H–P}$ = 1.1 Hz, 2H; {(NC*H*)$_2$}), 5.85 (s, 2H; {(NC*H*)$_2$}), 5.04 (s, very broad, 1H, NHC iPr protons), 3.86 (s, very broad, NHC iPr protons), 3.65 (sept, $^3J_{H–H}$ = 6.9 Hz, 2H; {C*H*(CH$_3$)$_2$}), 3.34 (sept, $^3J_{H–H}$ = 6.9 Hz, 2H; {C*H*(CH$_3$)$_2$}), 3.23 (d sept, *J* =13.8 Hz $^3J_{H–H}$ = 6.9 Hz, 4H; {C*H*(CH$_3$)$_2$}), 1.64 (s, 2H; hex), 1.52 (s, 4H; Ali*H*), 1.51 (s, 6H, NHC methyl*H*)), 1.33 (d, $^3J_{H–H}$ = 6.9 Hz, 10H, Dipp*H*), 1.29–1.21 (m, 29H; Dipp*H* and iPr *H*), 1.20 (d, $^3J_{H–H}$ = 6.9 Hz, 6H; Dipp*H)*, 1.01 (d, $^3J_{H-H}$ = 6.9, 6H; Dipp*H*), 0.91 (br, 16H, NHC Dipp*H*).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 178.37 (dd, $^1J_{C–P}$ = 29.75 Hz, $^2J_{C–P}$ = 10.3 Hz, 1,2-diphosphetan-3-one carbon), 146.76 (Ar*C*), 146.15 (Ar*C*), 146.08 (Ar*C*), 145.70 (Ar*C*), 143.20 (t, $^2J_{C–P}$ = 11.2 Hz, carbene*C*), 139.82 (Ar*C*), 139.02 (Ar*C*), 126.74 (d, $^3J_{C–P}$ = 6.4 Hz; ({(N*C*H)$_2$}), 123.36 (NHC), 123.07 (NHC), 122.93 (NHC), 122.69 (NHC), 121.41 ({(N*C*H)$_2$}, 117.26 (NHC), 96.65 (dd, $^1J_{C–P}$ = 52.2 Hz, $^2J_{C–P}$ = 16.0 Hz; 1,2-diphosphetan-3-one carbon), 59.68 (NHC iPr), 38.24 (NHC iPr), 31.34 (hex), 29.86 (aliphatic C), 28.65 (aliphatic C), 28.20 (aliphatic C), 28.00 (aliphatic C), 25.77 (aliphatic C), 25.55 (aliphatic C), 25.00 (aliphatic C), 24.46 (aliphatic C), 24.41 (aliphatic C), 23.85 (aliphatic C), 23.67 (hex), 23.14 (aliphatic C), 14.02 (hex), 9.66 (aliphatic C).

$^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = 26.51 (br s), 19.24 (br s).

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 90.58 (d, $^1J_{P-P}$ = 191.3 Hz), -22.54 (d, $^1J_{P-P}$ = 191.0 Hz).

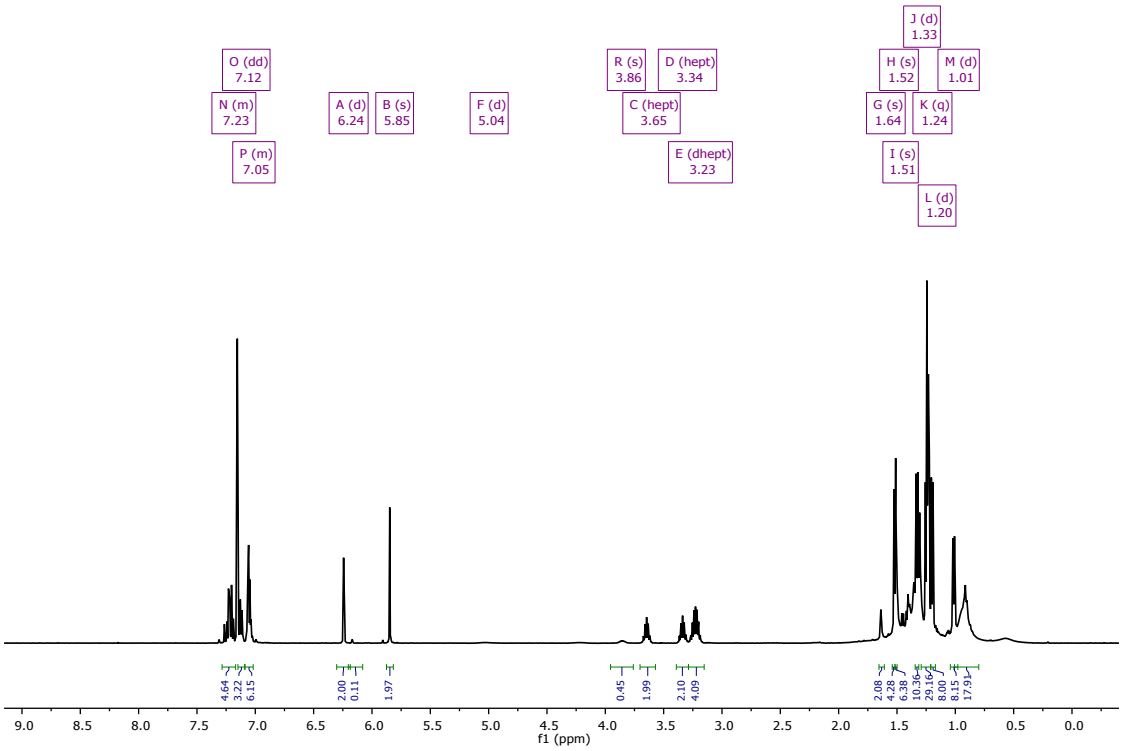

Figure S26. Room temperature ^1H NMR (500 MHz) spectrum of **7** in C_6D_6.

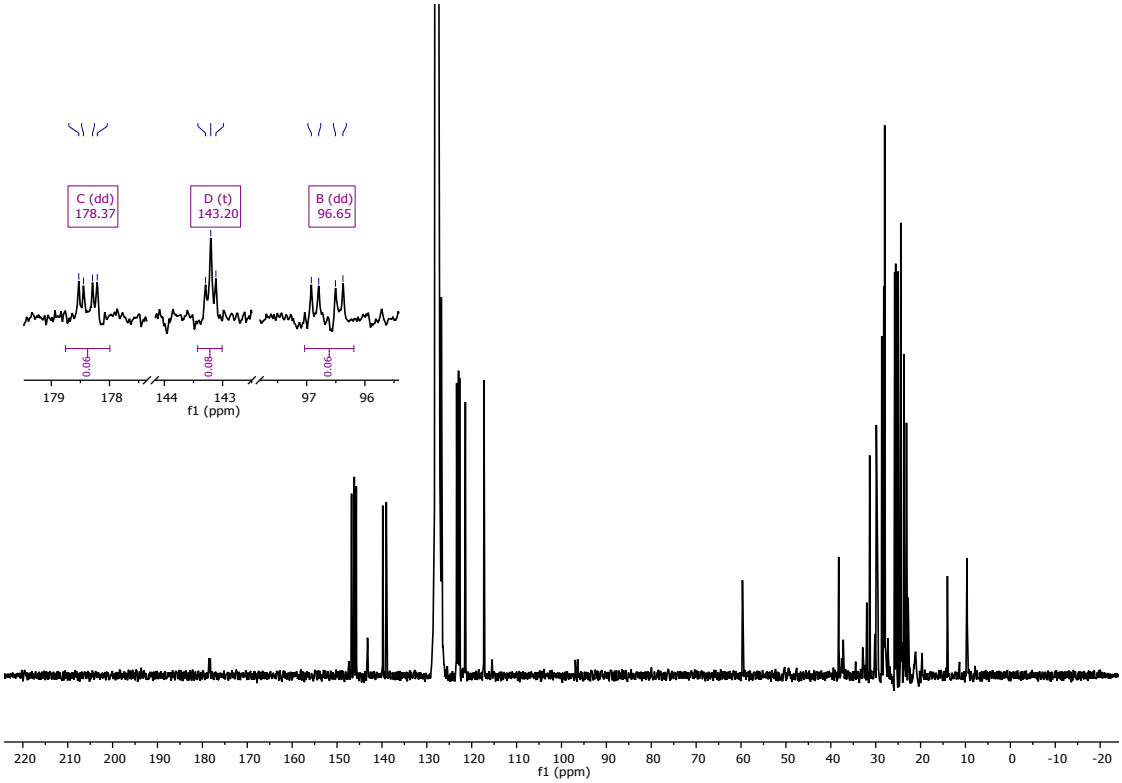

Figure S27. Room temperature $^{13}C\{^{1}H\}$ spectrum of **7** in C_6D_6.

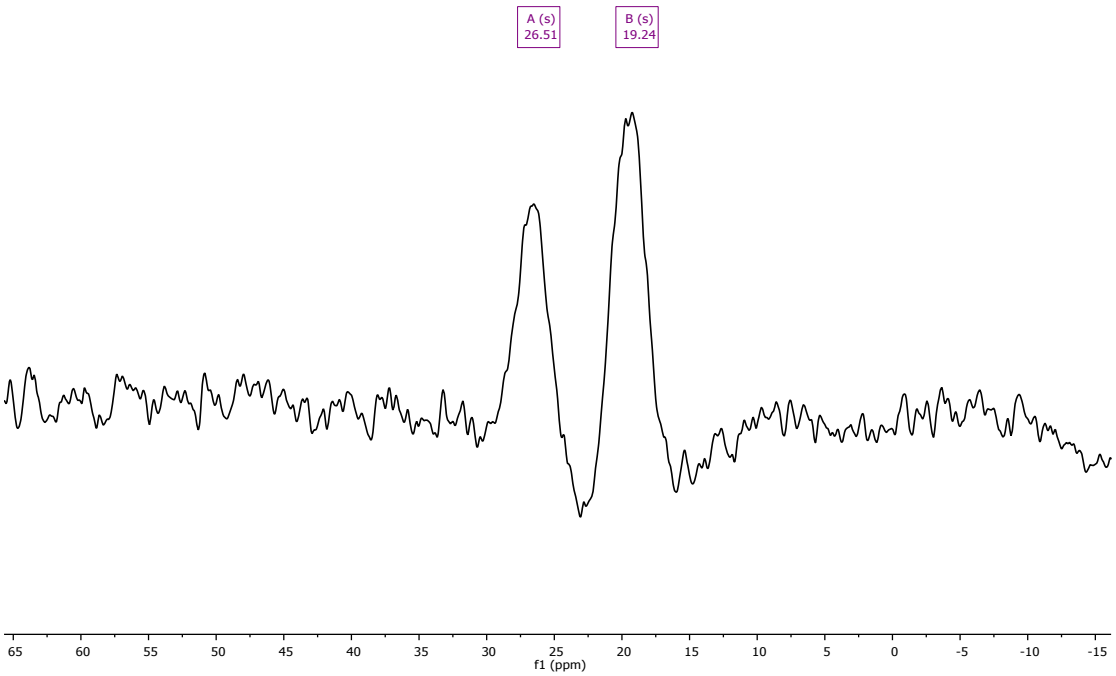

Figure S28. Room temperature $^{11}B\{^{1}H\}$ spectrum of **7** in C_6D_6.

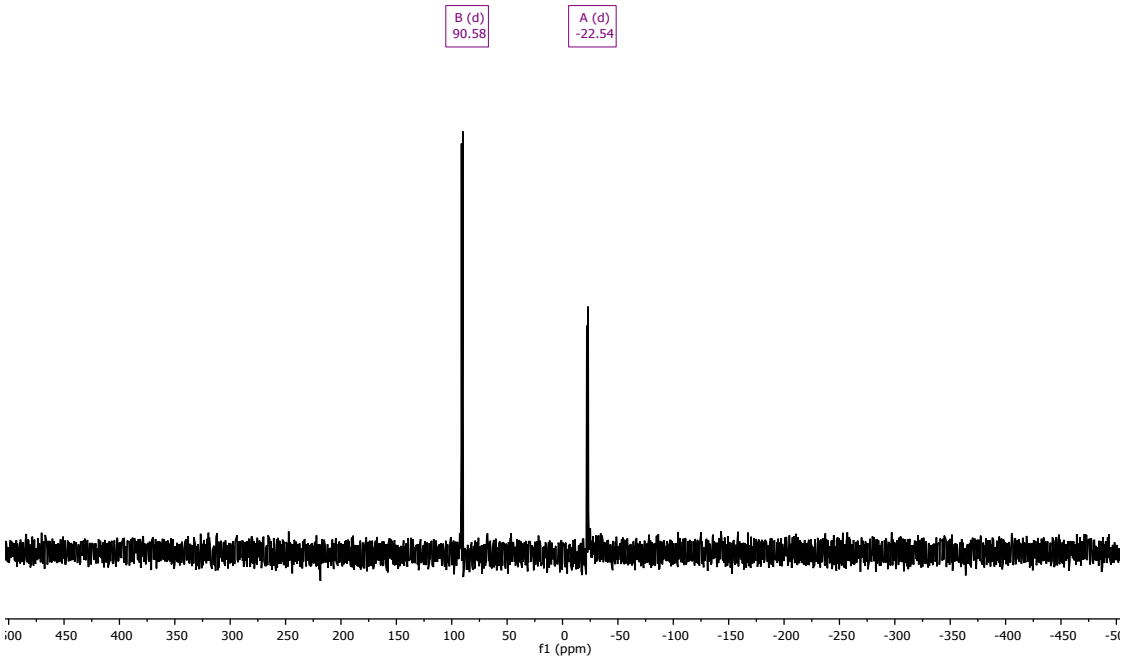

Figure S29. Room temperature $^{31}P\{^{1}H\}$ spectrum of **7** in C_6D_6.

2. Single crystal X-ray diffraction data

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected at 150 K using mirror monochromated Cu K_α radiation (λ = 1.5418 Å; Oxford Diffraction Supernova) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[3] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using direct methods and refined on F^2 using the SHELXL package.[4]

Table S1. Selected X-ray data collection and refinement parameters for **2a**, **3a**, **3b** and **4**.

	2a	**3a**	**3b**	**4**
Formula	$C_{37}H_{47}BN_3OP$	$C_{36}H_{47}BN_3P$	$C_{31}H_{45}BN_3P$	$C_{46}H_{58}BN_4P$
CCDC	1963000	1963001	1963002	1963003
Fw [g mol^{-1}]	591.55	563.54	501.48	708.74
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	10.6925(3)	18.9679(3)	17.2385(2)	10.6744(3)
b (Å)	19.6374(5)	7.4054(1)	10.9928(1)	13.4621(4)
c (Å)	17.0321(5)	25.1568(3)	33.0859(4)	14.8146(4)
α (°)	90	90	90	82.534(2)
β (°)	101.118(3)	107.290(1)	96.506(1)	88.654(2)
γ (°)	90	90	90	84.679(2)
V (Å^3)	3509.16(17)	3373.97(8)	6229.38(12)	2101.57(10)
Z	4	4	8	2
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184	Cu Kα, 1.54184	Cu Kα, 1.54184
Temp (K)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.120	1.109	1.069	1.120
μ (mm^{-1})	0.923	0.914	0.932	0.836
Reflections collected	80990	29145	25322	37991
Independent reflections	7355	7067	10979	8780
Parameters	399	381	671	483
R(int)	0.0675	0.0300	0.0229	0.0336
R1/wR2,[a] $I \geq 2\sigma I$ (%)	5.67/15.64	4.71/12.27	6.41/18.42	3.63/9.14
R1/wR2,[a] all data (%)	6.66/16.75	5.37/12.83	7.56/19.46	4.40/9.69
GOF	1.071	1.048	1.110	1.041

$R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0826 and 1.65 for **2a**, 0.0592 and 1.49 for **3a**, 0.0995 and 3.40 for **3b**, and 0.0444 and 0.54 for **4**.

Table S2. Selected X-ray data collection and refinement parameters for **5**, **6**, and **7**·1.5hex.

	5	**6**	**7**·1.5hex
Formula	$C_{27}H_{36}BN_2OP$	$C_{52}H_{72}B_2N_4P_2$	$C_{74}H_{113}B_2N_6O_2P_2$
CCDC	1963004	1963005	1963006
Fw [g mol^{-1}]	446.36	836.69	1202.26
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.3904(1)	13.0269(2)	14.0563(4)
b (Å)	14.2038(1)	14.1779(1)	14.7947(4)
c (Å)	20.3914(2)	14.8915(2)	20.1864(5)
α (°)	90	90	73.781(2)
β (°)	99.177(1)	112.746(1)	76.257(2)
γ (°)	90	90	67.558(2)
V (Å^3)	2684.98(4)	2536.47(6)	3684.82(18)
Z	4	2	2
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184	Cu Kα, 1.54184
Temp (K)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.104	1.096	1.084
μ (mm^{-1})	1.046	1.045	0.880
Reflections collected	20355	41427	59780
Independent reflections	5608	5310	15378
Parameters	327	279	797
R(int)	0.0212	0.0281	0.0366
R1/wR2,[a] $I \geq 2\sigma I$ (%)	4.00/10.51	3.70/9.67	5.23/13.99
R1/wR2,[a] all data (%)	4.59/11.06	4.33/10.16	6.40/15.08
GOF	1.017	1.037	1.043

R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0556 and 0.78 for **5**, 0.0460 and 0.87 for **6**, and 0.0756 and 1.76 for **7**·1.5hex.

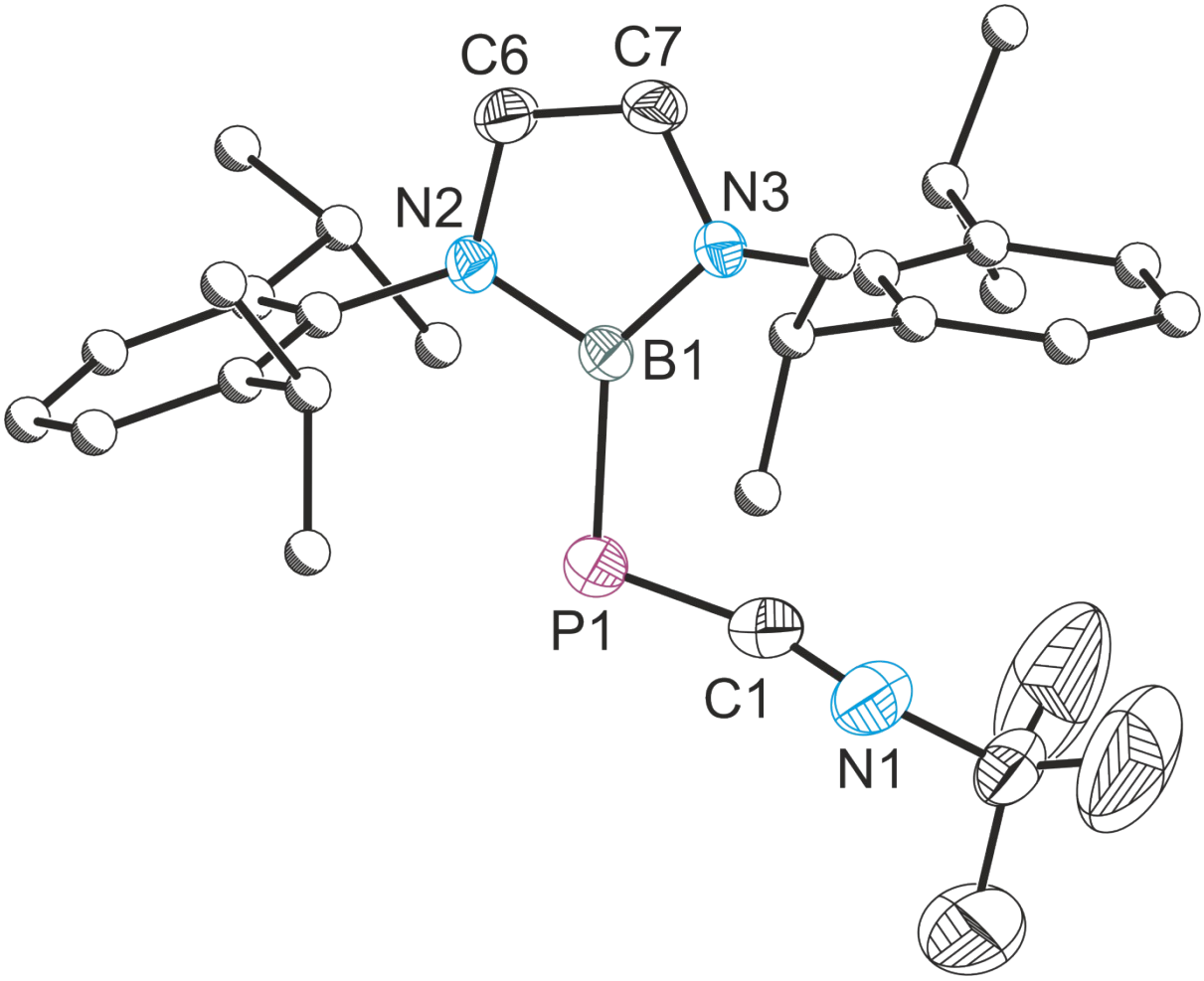

Figure S30. Molecular structure of **3b**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. Atoms of the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: P1–C1 1.661(3), C1–N1 1.201(3), P1–B1 1.916(2); P1-C1-N1 166.0(2), C1-P1-B1 103.32(11).

3. EPR

3.1. EPR Supplemental Text

The measurement of an EPR signal from **5** depends on photolytic conditions. In two measurement regimes, under frozen conditions at 5 K and at room temperature in liquid, open shell molecules are produced by photolysis. At low temperature, photolysis of CO from the PCO moiety generates an EPR signal consistent with a phosphinidene triplet state. At the DFT level of theory (PBE/DZ basis) the ground state is found to be a triplet, and the calculated spin density distribution (Figure S31) and Mulliken spin densities ($\rho_{\alpha-\beta}$(P) = 1.79 electrons, $\rho_{\alpha-\beta}$(B) = –0.12 electrons) are fully consistent with a phosphorus-centred diradical. Using coupled-perturbed spin orbit coupling (CP-SOC) calculations with PBE functional and DZ basis set, the zero-field splitting of the triplet state was computed to be D = 3.85 cm^{-1} E/D = 0.024, while with Peterson-Khanna spin-orbit coupling the corresponding values were D = 1.95 cm^{-1}, E/D = 0.0038. Expanding the basis set to TZVPP (CP-SOC) gives D = 3.38 cm^{-1}, E/D = 0.024. The closer match in D value to experiment (4 cm^{-1}) with the PBE functional and DZ basis set are in close agreement extensive calculations within Akimov, *et al*. (ref. 14 of the main text). Photolytic conditions may be at 5 K and also up to 40 K, shown as 30 K with a 355 nm LASER pulse in the main text and as described in section 3.3. While 30 K will suppress spectral contributions of O_2, further elevation of temperatures allows thermal motion and reactive variations in the EPR signal that are possible in thermal annealing steps (not shown).

The triplet ground state arises from a configuration with two singly occupied, orthogonal orbitals. As a result, the corresponding singlet state is intrinsically multi-determinantal, so we have turned to the CAS-NEVPT2 methodology implemented in ORCA to estimate the singlet–triplet splitting. Using the DFT-optimised geometry of the triplet state (shown

below), modified by the replacement of the Dipp groups with hydrogens (C–H = 1.1 Å), a CAS(2,2) calculation (TZVP basis) including the two phosphorus 3p orbitals that lie orthogonal to the B–P axis also yields a triplet ground state, well-separated from singlets at +7348 cm^{-1}, +7533 cm^{-1} and +16520 cm^{-1}. These correspond to the $^1\Delta$ and $^1\Sigma$ states of linear P–H, the former being split by 185 cm^{-1} as a result of the absence of rigorous axial symmetry. At the DFT level, a singlet configuration that represents an average of the aforementioned states is found at +7310 cm^{-1}, consistent with a wider study of phosphinidene systems which reported an average singlet–triplet gap of 7360 cm^{-1}.

Under the photolytic EPR measurements (section 3.3) at room temperature variation of in radical lifetime with total molecular concentration is consistent with intermolecular reactions shown in Figure S35. Variation in several g ≈ 2 EPR signals are observed in photolysis at room temperature in time as shown in Figure S32. Using scaled difference spectra from two time points at 616 and 1278 seconds, it is possible to extract spectral changes and obtain candidate spectral components. In Figure S33 the variation of spectra at 25 mM concentration leads to at least three components described by three large values of isotropic $A(^{31}P)$ and a g-value of 2.010 ±0.001, indicating ^{31}P-centred radicals in all three cases. Remarkably a sample measured at one fifth the concentration (5 mM) gave only a single component, shown in Figure S34, where use of similar short and long times of 661 and 1322 seconds clearly fit with the values of the most prevalent component in Figure S33. These component EPR simulations are summarized in Table S3. While not unequivocally assigned, the most prominent component fits with a Grützmacher-type radical by scaling hyperfine values by a single factor of two, shown in a reaction scheme of Figure S35, which is generated in analogy to the precedent of Li, *et al*.[5] The radical **S35_5** in the scheme features six ^{31}P atoms, but strongly unequal distribution of spin density in the approximate form of an allyl radical shown in Figure S36 and therefore unequal hyperfine values, means that only three nuclei are

required for accurate EPR simulation. The match of the isotropic g-value of the Grützmacher radical in DFT calculation and experiment is excellent.

3.2. EPR Supplemental Figures

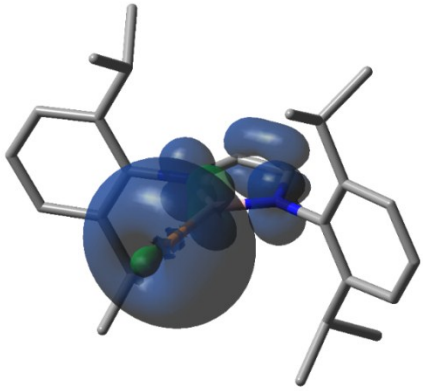

Figure S31. Spin density plot of the phosphinidene ground state triplet radical, H atoms omitted, with a contour of level of 0.0018 e/au^3. The geometry optimization in the triplet state and final properties calculation used a B3LYP functional and EPRIII basis set with TZVPP basis set for P, B, N, and carbons of the central ring. Positive densities are blue and negative are green.

Mulliken Spin Populations

P	s:	0.103250	s:	0.103250
	p_z:	0.019393	p	1.690659
	p_x:	0.910622		
	p_y:	0.760644		
B	s:	–0.053647	s:	–0.053647
	p_z:	–0.071915	p:	–0.072265
	p_x:	0.052769		
	py:	–0.053120		

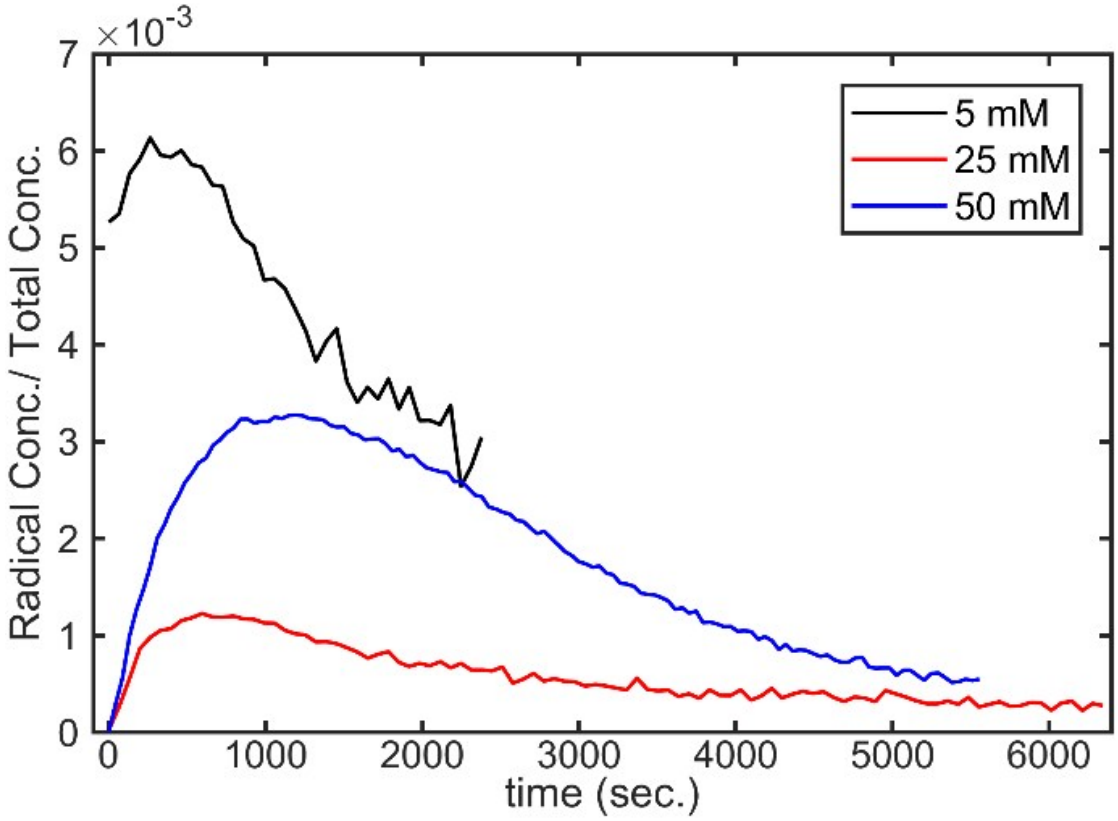

Figure S32. Spin concentration of radical intermediates produced in a room temperature photolysis experiments, by in situ irradiation in an X-band EPR resonator.

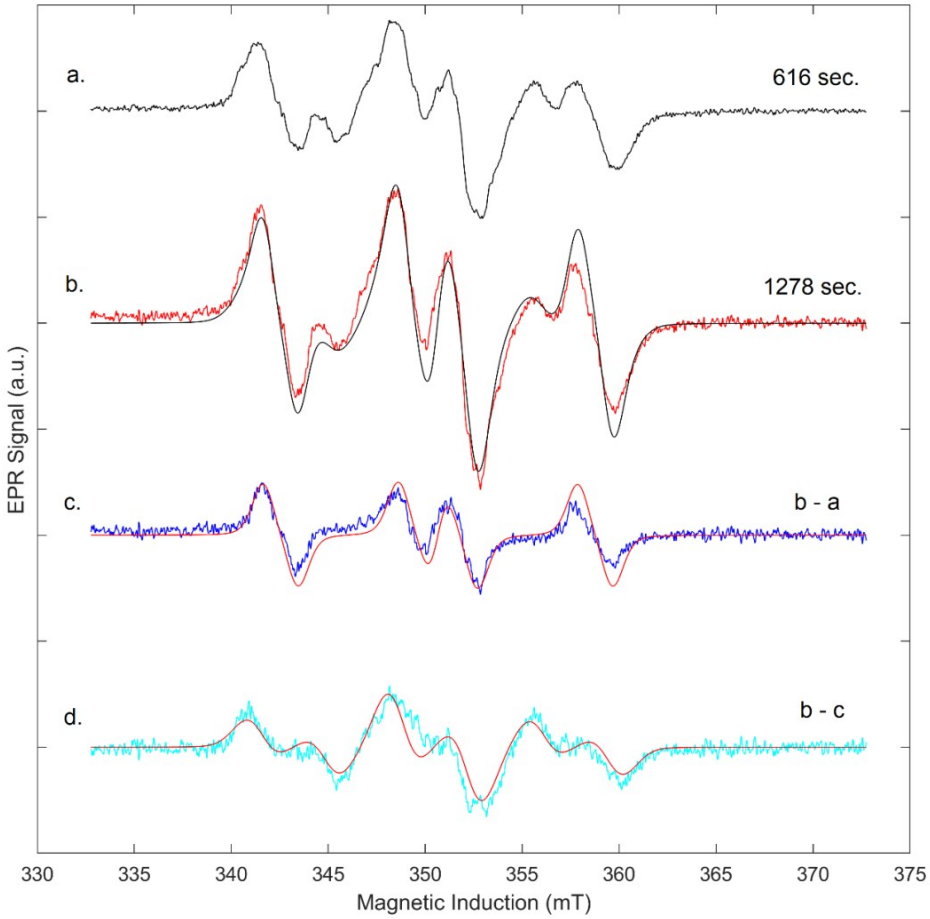

Figure S33. EPR simulations of radical difference spectra derived from room temperature photolytic time course at 25 mM. EPR simulation of trace c. component 1 of Table S3. EPR simulation in trace d. is the composite of components 2 & 3 in Table S3. The microwave frequency was 9.8676 GHz, microwave power 5 mW, and modulation amplitude 0.1 mT.

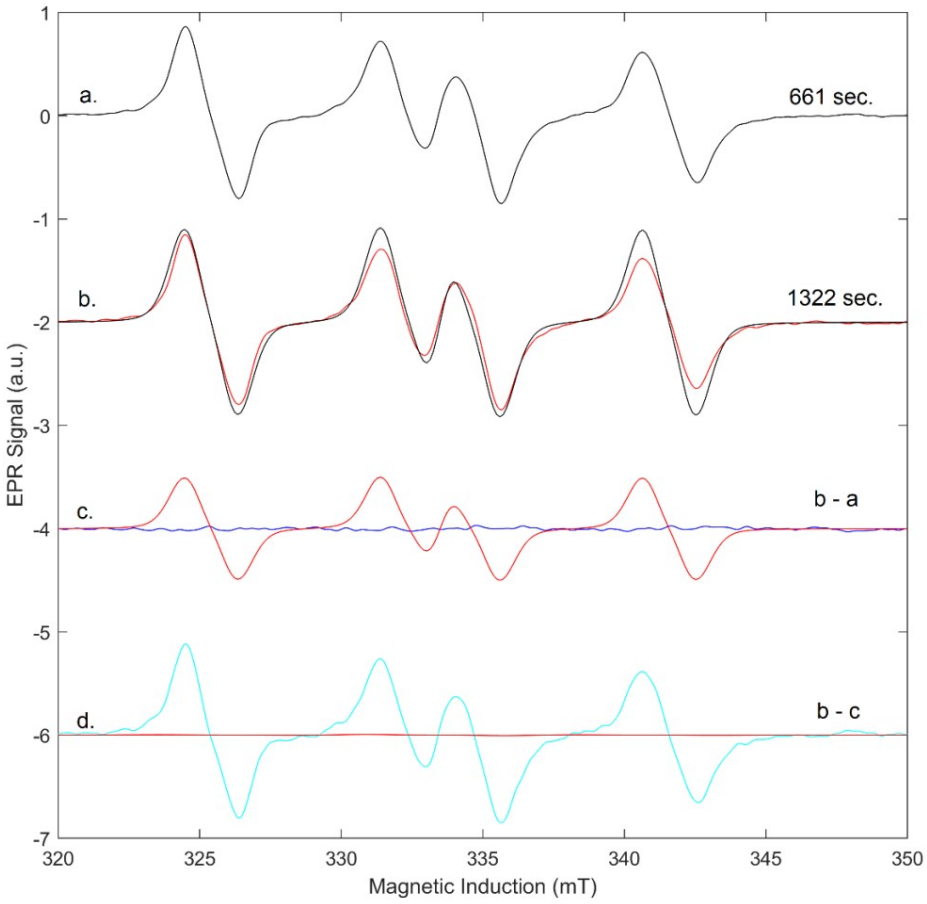

Figure S34. EPR simulations of radical difference spectra derived from room temperature photolytic time course at 5 mM. EPR simulation in trace c. is component 1 in table S3. The components 2 & 3 of are given a null coefficient in traces d. and b. The microwave frequency was 9.3851 GHz, microwave power 5 mW, and modulation amplitude 0.2 mT.

Table S3. EPR simulation values of room temperature radicals.

Component	*Coeff.* (Fig. S33)	$A(^{31}P)_{iso}(1)$	$A(^{31}P)_{iso}(2)$	$A(^{31}P)_{iso}(3)$	g_{iso}
1	3.72	261	195	25	2.01
2	0.75	205	205	90	2.011
3	0.25	205	205	10	2.011
DFT[a]	n/a	110	97	12	2.0109

[a] Remaining three isotropic $A(^{31}P)$ hyperfine values are less than 3 MHz, product **S35_5** Figure S35.

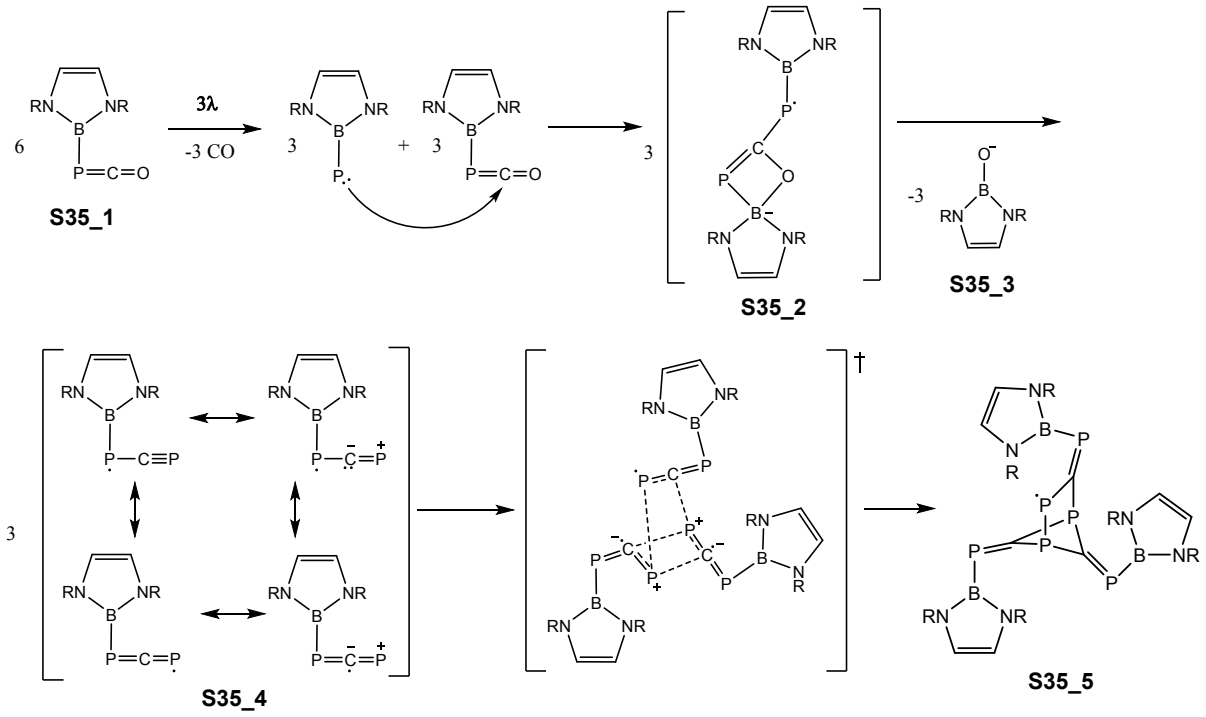

Figure S35. Representative formation of an intermediate radical analogous to Grützmacher and coworkers.[5]

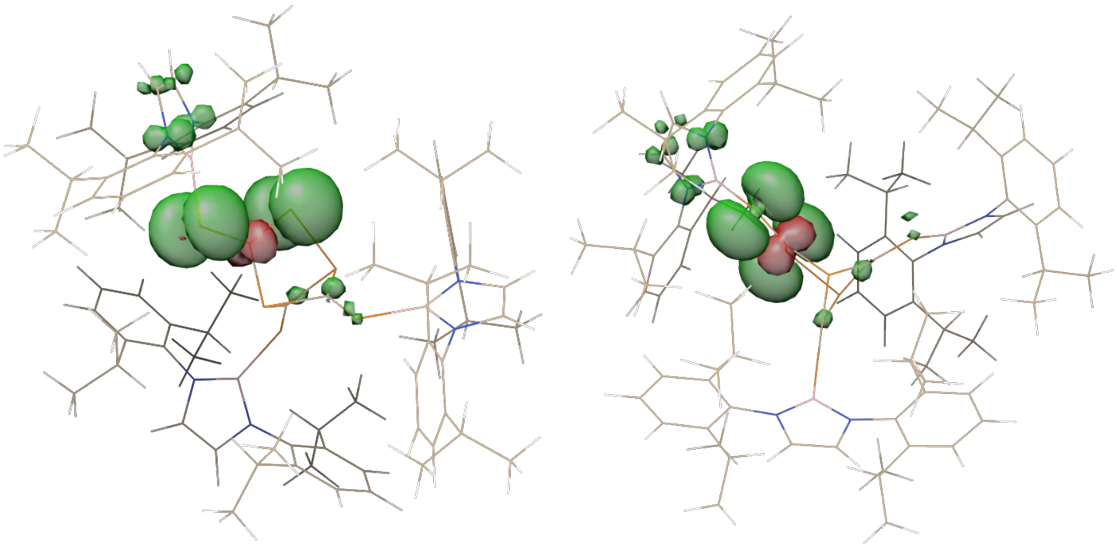

Figure S36. Spin density plots of product **S35_5** in Fig. S35 in two perspectives, corresponding to Figure S35, at a contour of level of 0.002 e/au^3. Positive densities are green and negative are red. For both geometry optimization and final properties calculations, the functional was BP86 with a TZVPP basis for P & B atoms, DZ for N, and def2-SVP basis set for other atoms.

3.3. EPR Instrumentation and Methodology

Measurements of continuous wave electron paramagnetic resonance (CW-EPR) were performed in the Centre for Advanced ESR (CAESR) in the Department of Chemistry in the University of Oxford. X-band CW-EPR was acquired on a Bruker BioSpin EleXSys I E680 spectrometer with an XPB bridge, 1.5 T electromagnet, a Bruker BioSpin ER4122-SHQE-W resonator coupled to an Oxford Instruments ESR900 cryostat, and subsequently, a Bruker BioSpin ER4118X-MD-5-W resonator in an Oxford Instruments CF935W cryostat, both controlled with an Oxford Instruments ITC-503S temperature controller. Liquid helium was used as a cryogen. Samples were held in a J. Young adapted 4 mm O.D. clear fused quartz tube in the ER4122 resonator and other samples were collapsed and cut via a hydrogen/oxygen torch by JMG for a flame seal under vacuum to rigorously avoid O_2

inclusion in measurements within the ER4118X resonator. Illumination of the sample was achieved in two ways: one with a Newport/Oriel 1000W Xenon Arc lamp with a 10 cm water filter and liquid light guide with no other filter, having a total illumination power of 700 mW/cm^2 as determined by a model 3W Ophir LASER power meter sensor. Alternative measurements were performed using the 355 nm pump wavelength of an OpoTek Opolette HE355 20 Hz pulsed OPO LASER with 1.5 mJ pulse energy and pulse length of 9 ns. Photolytic EPR signals were stable below 40 K, but may be complex with concentration and sample dependent species.

Room temperature CW-EPR was collected on a Bruker BioSpin EMXmicro Premium spectrometer with an ER4122-SHQE-W resonator coupled to an Oxford Instruments ESR900 cryostat. Illumination was achieved with the aforementioned arc lamp. EPR simulations involved use of the EasySpin routines in the MatLAB software environment (Mathworks, Natick, NJ).[6] DFT calculations supporting EPR simulations were performed with the Orca 3.0.3 software package. The Ahlrichs basis sets was obtained from the TurboMole basis set library under ftp.chemie.uni-karlsruhe.de/pub/basen[7–9]

3.4. Coordinates for DFT EPR Properties Calculations

Coordinates of Triplet phosphinidene in DFT calculations (fig. S31).
Final single point energy = -1486.091849024627 a.u.

P	-0.010019	0.012397	2.125076
B	0.084183	0.035040	0.233456
N	-1.010318	0.073544	-0.717836
N	1.268829	0.019928	-0.603957
C	-0.483463	0.081273	-1.998465
H	-1.112180	0.109784	-2.872218
C	0.873554	0.049052	-1.930480
H	1.586788	0.043704	-2.737212
C	-2.425331	0.103794	-0.479398
C	-3.129551	-1.108891	-0.363703
C	-4.504876	-1.049505	-0.137093
H	-5.068041	-1.968847	-0.041717
C	-5.164368	0.164733	-0.030827
H	-6.232233	0.188289	0.145555
C	-4.453738	1.348625	-0.149678
H	-4.977052	2.292226	-0.064517
C	-3.076995	1.346410	-0.375088
C	-2.447608	-2.464912	-0.476090
H	-1.387968	-2.290160	-0.656166
C	-2.560475	-3.266797	0.830164
H	-2.143158	-2.711741	1.671008
H	-2.017780	-4.210502	0.743983
H	-3.600001	-3.502743	1.066511
C	-2.984864	-3.274856	-1.667016
H	-4.043634	-3.511805	-1.545699
H	-2.442809	-4.218100	-1.759045
H	-2.872113	-2.727202	-2.603851
C	2.652362	-0.035773	-0.225943
C	3.274899	-1.290328	-0.089274
C	4.621834	-1.318993	0.272447
H	5.122223	-2.271950	0.386064
C	5.331363	-0.148917	0.492192
H	6.375796	-0.192448	0.773782
C	4.700937	1.077299	0.352243
H	5.263831	1.984751	0.528278
C	3.355998	1.163132	-0.008700
C	2.533011	-2.599024	-0.321845
H	1.500824	-2.355525	-0.568394
C	2.505425	-3.469445	0.944170
H	1.914664	-4.371292	0.771017
H	2.064021	-2.930658	1.783280
H	3.509430	-3.782803	1.237040
C	3.116286	-3.377175	-1.512266
H	3.102258	-2.778585	-2.424283
H	2.536694	-4.284462	-1.694382

H	4.149792	-3.675906	-1.326260
C	2.705186	2.531175	-0.154984
H	1.660994	2.375760	-0.422030
C	2.725243	3.314548	1.166994
H	2.242536	2.751745	1.966627
H	2.197557	4.263719	1.052935
H	3.745824	3.539320	1.483235
C	3.349423	3.347961	-1.286769
H	4.397353	3.568214	-1.074086
H	2.829549	4.300044	-1.411040
H	3.307950	2.813663	-2.237107
C	-2.335636	2.670111	-0.497958
H	-1.282251	2.446807	-0.659535
C	-2.431830	3.496743	0.793933
H	-3.463442	3.778676	1.013664
H	-2.047678	2.938564	1.648443
H	-1.849862	4.415915	0.699686
C	-2.821389	3.481960	-1.709408
H	-2.240735	4.401295	-1.807574
H	-2.716314	2.915102	-2.635694
H	-3.871736	3.761949	-1.608536

Coordinates of Radical intermediate S35_5 (fig. S35).
Final single point energy = -5600.726954058293 au

P	-0.098544	1.159692	1.419317
B	1.107290	-0.225716	0.808038
N	0.975770	-0.626811	-0.591719
N	2.168135	-1.081347	1.315628
C	1.900952	-1.639711	-0.864007
H	1.981804	-2.087272	-1.862420
C	2.612606	-1.911876	0.277093
H	3.415246	-2.641390	0.441557
C	0.099407	-0.140450	-1.631732
C	-1.186548	-0.725783	-1.786738
C	-2.011643	-0.244629	-2.823988
H	-3.016070	-0.679035	-2.961866
C	-1.578148	0.772122	-3.685356
H	-2.240818	1.135799	-4.488774
C	-0.298166	1.320982	-3.528380
H	0.037476	2.114234	-4.217750
C	0.567420	0.876594	-2.507867
C	-1.677951	-1.861746	-0.891079
H	-0.902339	-2.032790	-0.113719
C	-2.983812	-1.493706	-0.157882
H	-2.859584	-0.562237	0.437433
H	-3.281083	-2.310239	0.537488
H	-3.828174	-1.334882	-0.866809
C	-1.828350	-3.177682	-1.686154

H	-2.601382	-3.087925	-2.483010
H	-2.134586	-4.009539	-1.011734
H	-0.872426	-3.468628	-2.175688
C	2.748024	-1.231446	2.628273
C	2.153821	-2.150742	3.535913
C	2.766222	-2.319945	4.795135
H	2.327493	-3.023106	5.522659
C	3.936973	-1.624722	5.130848
H	4.401554	-1.774141	6.120047
C	4.519178	-0.744047	4.209290
H	5.442743	-0.207694	4.484003
C	3.940022	-0.524695	2.942999
C	0.933978	-2.989112	3.151237
H	0.541389	-2.585046	2.193243
C	-0.207835	-2.901866	4.181341
H	-1.115140	-3.420075	3.796385
H	-0.481129	-1.845097	4.399412
H	0.064234	-3.384977	5.145956
C	1.337373	-4.460093	2.898247
H	2.113416	-4.540998	2.105431
H	0.455664	-5.059337	2.575403
H	1.747543	-4.928942	3.821742
C	4.604577	0.425008	1.945663
H	3.896993	0.562440	1.099732
C	4.875836	1.818198	2.548098
H	3.954575	2.249345	2.997814
H	5.233870	2.518761	1.761019
H	5.655599	1.782221	3.341943
C	5.899329	-0.190867	1.368617
H	6.653116	-0.368808	2.169533
H	6.357405	0.492665	0.617834
H	5.703376	-1.165094	0.868065
C	1.970138	1.470887	-2.387521
H	2.452111	1.016346	-1.495694
C	1.931664	2.993811	-2.153320
H	1.492823	3.534751	-3.022540
H	1.328601	3.245191	-1.254032
H	2.960390	3.388399	-1.995230
C	2.839542	1.112613	-3.612955
H	3.874666	1.503759	-3.486942
H	2.905195	0.011417	-3.757619
H	2.425133	1.550796	-4.549388
C	0.172126	1.663895	3.020455
P	1.365803	1.514084	4.452601
P	-0.803886	3.095850	3.784133
C	0.872913	3.318618	4.607835
C	-1.482814	2.007593	5.170852
P	-0.330435	0.842148	5.814052
P	1.970233	4.523036	5.069096
B	1.349255	6.329368	4.646848

N	0.807191	7.360669	5.512142
N	1.812580	7.049593	3.473763
C	0.941898	8.605679	4.862188
C	0.199989	7.329927	6.818462
C	1.542234	8.420184	3.649436
C	2.504903	6.603970	2.290454
H	0.589126	9.529368	5.336796
C	1.023173	7.221394	7.973769
C	-1.206821	7.524152	6.918979
H	1.810560	9.154307	2.879839
C	1.766120	6.411818	1.089734
C	3.919196	6.449864	2.331346
C	0.403153	7.308294	9.237961
C	2.543652	7.087735	7.884286
C	-2.105896	7.641268	5.685761
C	-1.770991	7.617381	8.207279
C	0.252715	6.624557	1.022840
C	2.479358	6.061635	-0.074932
C	4.579527	6.083582	1.140113
C	4.735264	6.734689	3.593286
C	-0.977690	7.514190	9.358426
H	1.020776	7.235073	10.149007
C	3.238850	8.403429	8.301057
H	2.799830	6.908651	6.817906
C	3.081506	5.887474	8.689606
C	-2.846759	8.995698	5.638743
H	-1.454698	7.591195	4.787548
C	-3.099173	6.464283	5.593126
H	-2.857926	7.774251	8.311181
C	-0.086109	7.958044	0.317240
H	-0.119559	6.695766	2.067459
C	-0.487996	5.449767	0.353036
H	1.931518	5.919237	-1.020852
C	3.871032	5.895519	-0.054286
H	5.675458	5.960579	1.145170
C	5.493541	8.075293	3.463420
H	4.019540	6.842121	4.436737
C	5.693999	5.583454	3.957960
H	-1.439391	7.596740	10.356952
H	2.894858	9.257282	7.676467
H	4.343362	8.316852	8.185963
H	3.027683	8.655720	9.365346
H	4.177516	5.775291	8.529975
H	2.915957	6.012032	9.784018
H	2.593615	4.939174	8.373712
H	-2.138567	9.853308	5.673042
H	-3.440775	9.080733	4.700721
H	-3.553541	9.108836	6.492167
H	-3.708974	6.541348	4.665065
H	-3.799736	6.448415	6.458307

H	-2.571921	5.485437	5.565817
H	0.388490	8.824755	0.827512
H	-1.186742	8.127736	0.308519
H	0.265601	7.953521	-0.739832
H	-1.588296	5.604869	0.414407
H	-0.227486	5.350682	-0.725076
H	-0.259220	4.481818	0.850598
H	4.408601	5.623449	-0.978530
H	4.795716	8.918203	3.263467
H	6.049005	8.305380	4.401044
H	6.231834	8.041657	2.629784
H	6.197335	5.794065	4.928599
H	6.494154	5.445537	3.195363
H	5.144652	4.621783	4.060130
P	-3.185518	2.168220	5.521583
B	-3.762289	0.922100	6.891168
N	-5.140358	0.453822	6.776959
N	-3.333195	0.429750	8.199540
C	-5.479456	-0.261214	7.929086
C	-6.094987	0.646884	5.711169
C	-4.405314	-0.262907	8.783227
C	-2.165107	0.728473	8.997369
H	-6.466344	-0.726459	8.045895
C	-6.169771	-0.313489	4.666451
C	-6.959387	1.776055	5.753732
H	-4.323643	-0.685742	9.791555
C	-2.095332	1.995260	9.639665
C	-1.155275	-0.258505	9.184944
C	-7.122151	-0.108845	3.646925
C	-5.260332	-1.540525	4.627450
C	-6.908925	2.795243	6.891822
C	-7.895345	1.930471	4.710921
C	-3.247754	2.997631	9.590803
C	-0.947632	2.292000	10.403577
C	-0.036543	0.087479	9.970410
C	-7.977293	1.001389	3.664453
H	-7.196733	-0.835340	2.820069
C	-6.069553	-2.855317	4.662871
H	-4.626773	-1.517312	5.539611
C	-4.312785	-1.495836	3.411867
C	-8.161971	2.694030	7.789954
H	-6.029205	2.541510	7.521811
C	-6.699640	4.234916	6.378412
H	-8.574674	2.799490	4.716994
C	-3.912517	3.135499	10.979731
H	-4.017758	2.593693	8.899062
C	-2.814360	4.367525	9.041259
H	-0.865357	3.275777	10.895226
C	0.080041	1.353867	10.560002
H	0.767027	-0.651114	10.121827

H	-8.714646	1.143278	2.856328
H	-6.735301	-2.900008	5.553356
H	-5.385213	-3.733042	4.701920
H	-6.708690	-2.970112	3.757838
H	-3.624263	-2.371015	3.418808
H	-4.878332	-1.516994	2.453272
H	-3.691277	-0.573153	3.417398
H	-8.280959	1.669915	8.208228
H	-8.091078	3.405935	8.643562
H	-9.089679	2.936759	7.223158
H	-6.577449	4.935292	7.235441
H	-7.566341	4.593832	5.778267
H	-5.788558	4.305010	5.744386
H	-4.264238	2.151737	11.362495
H	-4.792827	3.815822	10.925345
H	-3.205543	3.557378	11.730102
H	-3.689764	5.051991	8.974209
H	-2.057076	4.858431	9.691615
H	-2.373724	4.278781	8.024300
H	0.972512	1.604404	11.157936
C	-1.287782	-1.677753	8.629418
C	-1.850822	-2.637477	9.705220
C	0.032181	-2.246342	8.072814
H	-2.017799	-1.637214	7.791511
H	-2.832079	-2.298301	10.100164
H	-1.989100	-3.659583	9.284672
H	-1.151230	-2.715061	10.568541
H	0.487864	-1.559487	7.327460
H	0.778724	-2.435746	8.8772
H	-0.157930	-3.222641	7.573407

4. Optimised energies and geometries of stationary points.

4.1. Optimised Cartesian coordinates (Å) and total energies of **1**, **5 and TS1**

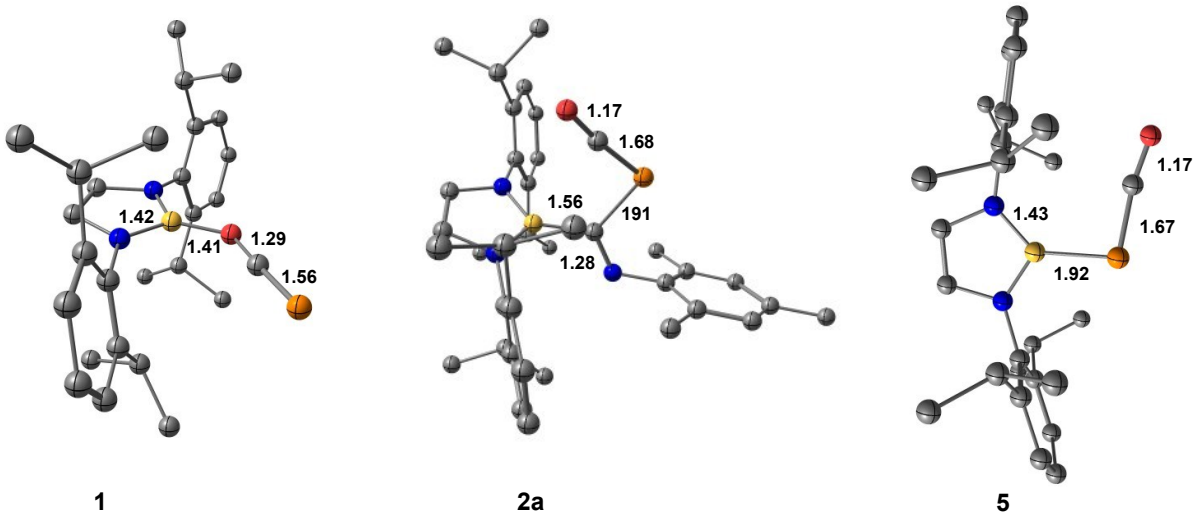

Figure S37. Optimised geometries of the isolated species **1**, **2a** and **5**.

1 Energy = -1601.17127652 au
ZPE = -1600.580262 au
Free Energy = -1600.643067 au

C	-0.871542	-0.267362	2.271223
N	-0.961527	0.265161	-0.765115
C	-2.375189	0.114247	-0.567538
C	-2.901517	-1.177781	-0.351943
C	-4.286000	-1.295567	-0.174025
H	-4.721279	-2.273505	0.001694
C	-5.112029	-0.172399	-0.203303
H	-6.182661	-0.286137	-0.063476
C	-4.568421	1.096244	-0.399275
H	-5.220172	1.963706	-0.404628
C	-3.189795	1.265589	-0.580823
C	-1.990791	-2.396406	-0.304983
H	-1.084768	-2.112040	0.251247
C	-2.610134	-3.583507	0.435793
H	-2.971889	-3.293854	1.427846
H	-1.863750	-4.374402	0.563452
H	-3.448767	-4.014122	-0.124294
C	-1.551092	-2.821965	-1.717131
H	-2.423693	-3.105041	-2.317959
H	-0.881707	-3.689077	-1.663852
H	-1.022338	-2.017256	-2.239233
C	-2.567688	2.647297	-0.703660
H	-1.733143	2.582096	-1.415321
C	-1.978723	3.080573	0.651739
H	-2.769783	3.153321	1.407626

H	-1.491378	4.058574	0.566885
H	-1.239029	2.360902	1.018226
C	-3.540213	3.709924	-1.220116
H	-4.019346	3.402204	-2.155615
H	-3.008488	4.649508	-1.401736
H	-4.329179	3.920713	-0.488862
C	-0.416892	0.528785	-2.041226
N	1.326493	0.326142	-0.623703
C	2.684764	0.067616	-0.247412
C	3.114413	-1.270752	-0.139394
C	4.444034	-1.505338	0.238800
H	4.797135	-2.529903	0.327274
C	5.313224	-0.447317	0.493749
H	6.340324	-0.647436	0.783112
C	4.868515	0.870914	0.377606
H	5.555119	1.687223	0.579186
C	3.548204	1.154168	0.008542
C	2.193419	-2.440706	-0.440605
H	1.201318	-2.041932	-0.689105
C	2.030849	-3.363739	0.775246
H	1.654083	-2.815120	1.644745
H	1.325951	-4.172508	0.548846
H	2.986379	-3.823522	1.055167
C	2.689238	-3.227038	-1.663189
H	3.682074	-3.654956	-1.478611
H	2.005843	-4.051766	-1.894200
H	2.759736	-2.583338	-2.546780
C	3.024391	2.578517	-0.056682
H	2.242454	2.610185	-0.827641
C	2.365141	2.957678	1.281926
H	3.109767	2.954686	2.087086
H	1.925176	3.959842	1.227274
H	1.575381	2.250367	1.555620
C	4.097206	3.604383	-0.430506
H	4.627755	3.321920	-1.345940
H	3.639986	4.586261	-0.589831
H	4.839117	3.720628	0.368206
C	0.939863	0.552025	-1.959719
H	1.675957	0.706911	-2.733606
H	-1.060499	0.670923	-2.896207
B	0.136194	0.135223	0.131929
O	0.160299	-0.146118	1.512414
P	-2.073948	-0.417923	3.255174

5 Energy = -1601.18517026 au
ZPE = -1600.595717 au
Free Energy = -1600.659709 au

C	-1.383684	0.046053	2.448288
N	-1.019021	0.183536	-0.721274

C	-2.420736	0.030618	-0.468340
C	-2.924471	-1.256009	-0.171984
C	-4.298351	-1.377184	0.076265
H	-4.714308	-2.351656	0.310937
C	-5.136652	-0.264423	0.034219
H	-6.198218	-0.380265	0.230387
C	-4.617362	0.997946	-0.250421
H	-5.279824	1.857161	-0.271241
C	-3.251033	1.172107	-0.503629
C	-2.008256	-2.470361	-0.142856
H	-1.045708	-2.150515	0.281105
C	-2.534337	-3.600603	0.744770
H	-2.785769	-3.240193	1.748547
H	-1.773120	-4.381442	0.845284
H	-3.428405	-4.071757	0.318955
C	-1.732567	-2.984780	-1.566330
H	-2.666904	-3.288816	-2.053851
H	-1.067568	-3.856444	-1.536311
H	-1.257029	-2.214781	-2.184121
C	-2.654971	2.550395	-0.743519
H	-1.856024	2.446357	-1.490570
C	-2.005190	3.082906	0.547199
H	-2.760097	3.201248	1.334007
H	-1.538548	4.058693	0.369679
H	-1.231911	2.401586	0.919840
C	-3.667390	3.565271	-1.279421
H	-4.192775	3.188247	-2.163345
H	-3.158054	4.494187	-1.555436
H	-4.417902	3.820224	-0.522133
C	-0.512620	0.349116	-2.022630
N	1.255293	0.284435	-0.631509
C	2.623013	0.070451	-0.264357
C	3.084334	-1.256552	-0.129771
C	4.414292	-1.451917	0.268576
H	4.791920	-2.465573	0.378870
C	5.253418	-0.367711	0.517897
H	6.280073	-0.537574	0.827853
C	4.781141	0.936586	0.364197
H	5.446587	1.773140	0.555012
C	3.460442	1.182075	-0.031795
C	2.199186	-2.450941	-0.445387
H	1.190215	-2.081394	-0.667813
C	2.085934	-3.418888	0.739824
H	1.700981	-2.914212	1.633016
H	1.402612	-4.240356	0.493499
H	3.058887	-3.858199	0.991420
C	2.707868	-3.180675	-1.698595
H	3.718581	-3.575745	-1.538430
H	2.052989	-4.023078	-1.947959
H	2.742500	-2.507240	-2.561727

C	2.923130	2.596291	-0.169292
H	2.091687	2.564905	-0.886315
C	2.351708	3.087017	1.172298
H	3.141678	3.133546	1.931805
H	1.920750	4.089090	1.065387
H	1.568955	2.415818	1.543546
C	3.967128	3.584060	-0.698831
H	4.426584	3.228374	-1.626975
H	3.500787	4.554570	-0.897717
H	4.767739	3.754420	0.030386
C	0.846322	0.396680	-1.971581
H	1.565649	0.500863	-2.770027
H	-1.174308	0.415869	-2.873528
B	0.087594	0.138284	0.188558
O	-2.463798	0.181827	2.876068
P	0.232935	-0.172403	2.075157

TS1 Energy = -1601.11507560 au
ZPE = -1600.527067 au
Free Energy = -1600.590442 au

C	0.009748	-0.382878	-1.959085
N	1.159098	-0.166515	0.598521
C	2.529080	0.044779	0.236335
C	3.370078	-1.066890	0.023344
C	4.703939	-0.827090	-0.333560
H	5.371278	-1.669293	-0.495411
C	5.186427	0.473207	-0.474749
H	6.223511	0.640072	-0.749780
C	4.339500	1.559750	-0.261080
H	4.720504	2.572069	-0.372102
C	2.997313	1.369653	0.092886
C	2.874914	-2.485885	0.235853
H	1.778550	-2.452091	0.280308
C	3.274309	-3.423880	-0.908403
H	2.939103	-3.034287	-1.875377
H	2.825346	-4.412670	-0.763803
H	4.361019	-3.561298	-0.956184
C	3.378692	-3.028065	1.583752
H	4.474959	-3.064549	1.600112
H	3.002979	-4.042436	1.758148
H	3.051126	-2.394210	2.414787
C	2.098854	2.569348	0.341132
H	1.079039	2.201640	0.505239
C	2.062696	3.519970	-0.861933
H	3.052762	3.947133	-1.062124
H	1.376773	4.352387	-0.665465
H	1.724194	3.003242	-1.764853
C	2.532006	3.318941	1.610872
H	2.524079	2.660193	2.485937

H	1.857388	4.159389	1.809649
H	3.547177	3.719785	1.500594
C	0.683435	0.015416	1.917168
N	-1.142829	-0.080493	0.582097
C	-2.521281	0.054802	0.221106
C	-3.339824	-1.093993	0.181670
C	-4.687847	-0.932459	-0.164436
H	-5.337959	-1.802534	-0.194723
C	-5.204572	0.326467	-0.468276
H	-6.252229	0.432431	-0.733557
C	-4.377823	1.448129	-0.433899
H	-4.784790	2.427211	-0.674000
C	-3.022840	1.336272	-0.093918
C	-2.797298	-2.463220	0.550032
H	-1.700753	-2.402273	0.532960
C	-3.228049	-3.548524	-0.443271
H	-2.970442	-3.271555	-1.470863
H	-2.732315	-4.496966	-0.208456
H	-4.309435	-3.725360	-0.401220
C	-3.220076	-2.844170	1.978732
H	-4.312820	-2.903726	2.053885
H	-2.807295	-3.820399	2.256419
H	-2.872637	-2.106467	2.709662
C	-2.148255	2.576596	-0.042297
H	-1.112941	2.252754	0.115524
C	-2.193656	3.364010	-1.358007
H	-3.201490	3.746747	-1.559901
H	-1.517054	4.224375	-1.309332
H	-1.889393	2.739217	-2.203000
C	-2.543906	3.473114	1.141196
H	-2.484519	2.930839	2.090992
H	-1.879620	4.343070	1.202218
H	-3.571413	3.840412	1.026961
C	-0.675222	0.060021	1.908620
H	-1.368042	0.154806	2.730970
H	1.369983	0.076371	2.747978
B	0.008998	-0.222622	-0.244648
O	0.090571	0.843195	-1.743819
P	-0.102673	-1.976530	-2.051428

4.2 Reaction pathway with HNC as model isonitrile.

HNC Energy = -93.3879469133 au
ZPE = -93.372310 au
Free Energy = -93.391796 au

H	0.000000	0.000000	1.437907
N	0.000000	0.000000	0.433762
C	0.000000	0.000000	-0.745706

2 Energy = -1694.60941001 au
ZPE = -1693.998351 au
Free Energy = -1694.065153 au

C	0.068312	-0.048946	1.738148
C	-0.789912	-2.528610	1.460829
H	1.425376	-0.160399	-2.848394
B	0.066771	-0.033844	0.176376
C	0.741100	-0.089989	-2.015725
C	-0.616741	0.032667	-2.015039
N	1.199552	-0.128508	-0.690820
N	-1.074360	0.060488	-0.688731
H	-1.299806	0.107751	-2.848009
O	-0.642538	-3.409027	0.703490
P	-1.020352	-1.348284	2.623524
N	0.730032	0.808683	2.417371
H	0.682465	0.675665	3.432388
C	2.594999	-0.022366	-0.373537
C	3.357190	-1.186431	-0.158916
C	3.160221	1.267784	-0.277570
C	4.718507	-1.037089	0.141881
C	4.525127	1.366780	0.019342
C	5.300300	0.226240	0.227227
H	5.324697	-1.923964	0.310208
H	4.981294	2.350564	0.095025
H	6.356761	0.322887	0.458748
C	-2.428160	0.394080	-0.345796
C	-2.697506	1.681731	0.179470
C	-3.448522	-0.562368	-0.521747
C	-4.021672	1.985252	0.521498
C	-4.759298	-0.204614	-0.176408
C	-5.045494	1.054250	0.343932
H	-4.254318	2.964698	0.927587
H	-5.558705	-0.928349	-0.309842
H	-6.065038	1.312852	0.612720
C	2.337467	2.525711	-0.498273
C	2.737058	3.217743	-1.810747
C	2.444360	3.491899	0.688751
H	1.284061	2.232080	-0.586269
H	2.610386	2.548848	-2.669407
H	2.121780	4.108927	-1.979210
H	3.787369	3.533090	-1.782346
H	2.118035	3.004691	1.613129
H	3.473101	3.846773	0.825869
H	1.812746	4.372200	0.518336
C	2.746070	-2.572529	-0.243542
C	2.851782	-3.304704	1.101916
C	3.392230	-3.397215	-1.365649
H	1.682374	-2.459444	-0.484210

H	2.382470	-2.727682	1.906830
H	2.360917	-4.282587	1.048916
H	3.900533	-3.468984	1.377902
H	3.285188	-2.899651	-2.335707
H	4.463321	-3.543750	-1.180593
H	2.925197	-4.385653	-1.434306
C	-1.606342	2.736050	0.300041
C	-1.860196	3.753444	1.414647
C	-1.405497	3.446850	-1.050646
H	-0.663150	2.233242	0.544837
H	-2.066263	3.257953	2.369807
H	-0.976479	4.387065	1.545693
H	-2.704992	4.412810	1.182638
H	-1.125775	2.735217	-1.836155
H	-2.327129	3.955045	-1.359768
H	-0.610839	4.198692	-0.975413
C	-3.164289	-1.943420	-1.082569
C	-3.648739	-2.052974	-2.537704
C	-3.799526	-3.052524	-0.232837
H	-2.077581	-2.091512	-1.074936
H	-3.179898	-1.298896	-3.178748
H	-3.417195	-3.041752	-2.948550
H	-4.734708	-1.908258	-2.593832
H	-3.539292	-2.946360	0.825677
H	-4.893058	-3.037869	-0.310801
H	-3.455649	-4.035096	-0.573064

TS2 Energy = -1694.54823819 au
ZPE = -1693.941759 au
Free Energy = -1694.008753 au

C	0.219909	0.132476	1.533352
C	-0.583858	-2.282690	1.509194
H	1.445381	0.546886	-2.847512
B	0.043649	-0.416135	0.043049
C	0.758273	0.327789	-2.044299
C	-0.596761	0.486995	-2.003189
N	1.217900	-0.173902	-0.821663
N	-1.078044	0.116336	-0.750415
H	-1.264543	0.840619	-2.775477
O	-0.213005	-2.083800	0.336623
P	-1.026347	-2.335562	3.031846
N	0.607261	0.998625	2.269686
H	0.643829	1.013498	3.283599
C	2.589780	0.008254	-0.438886
C	3.412606	-1.119579	-0.233969
C	3.084406	1.325400	-0.258120
C	4.747002	-0.909224	0.141355
C	4.430838	1.481428	0.095686
C	5.258118	0.376830	0.295425

H	5.389832	-1.770170	0.305616
H	4.831275	2.483045	0.228736
H	6.297279	0.520367	0.575644
C	-2.446308	0.320677	-0.370181
C	-2.806742	1.544505	0.241797
C	-3.396692	-0.691980	-0.614796
C	-4.142537	1.724788	0.621976
C	-4.721329	-0.463898	-0.216106
C	-5.092578	0.727890	0.401578
H	-4.440924	2.657548	1.092886
H	-5.466147	-1.234920	-0.394523
H	-6.122875	0.884044	0.706557
C	2.205463	2.555989	-0.430805
C	2.511737	3.280568	-1.751879
C	2.337289	3.538776	0.740383
H	1.160470	2.221949	-0.465800
H	2.388256	2.618589	-2.614682
H	1.842435	4.138902	-1.882685
H	3.544295	3.650875	-1.757588
H	2.132011	3.049889	1.697559
H	3.341511	3.975935	0.789253
H	1.627451	4.365447	0.617145
C	2.891715	-2.534073	-0.396816
C	2.797211	-3.229969	0.969980
C	3.757555	-3.354637	-1.362103
H	1.881155	-2.474538	-0.813216
H	2.196469	-2.646975	1.676598
H	2.331145	-4.216472	0.870737
H	3.794881	-3.365373	1.406760
H	3.830150	-2.873919	-2.343247
H	4.775420	-3.485176	-0.975347
H	3.327890	-4.352420	-1.500937
C	-1.795689	2.663276	0.432122
C	-1.928213	3.357506	1.791637
C	-1.892374	3.683939	-0.714247
H	-0.793813	2.223087	0.381230
H	-1.915961	2.630929	2.611545
H	-1.100096	4.059205	1.942011
H	-2.860029	3.930226	1.866080
H	-1.733750	3.202427	-1.685573
H	-2.879931	4.160987	-0.729477
H	-1.134766	4.468314	-0.596811
C	-3.033964	-1.977741	-1.334439
C	-3.644578	-1.988623	-2.745800
C	-3.472090	-3.219409	-0.548046
H	-1.944183	-2.014018	-1.434347
H	-3.311369	-1.126741	-3.334734
H	-3.357989	-2.900018	-3.282021
H	-4.740085	-1.956309	-2.696369
H	-3.050705	-3.219518	0.462245

H	-4.564076	-3.271560	-0.459322
H	-3.137855	-4.129130	-1.058526

TS3 Energy = -1694.54981146 au
ZPE = -1693.945727 au
Free Energy = -1694.014094 au

C	-1.098728	0.074854	2.601146
C	0.030419	-2.012778	0.874673
N	1.269898	-0.361943	-0.687642
C	0.810354	-0.160731	-2.015861
N	-1.047134	-0.119818	-0.715914
C	-0.539756	-0.026921	-2.023492
H	-1.204073	0.124056	-2.863273
H	1.508667	-0.118452	-2.838888
B	0.070605	-0.437058	0.196414
O	-2.140900	-0.224728	3.056064
P	0.397744	0.500909	2.020848
N	0.408835	-3.043009	1.303235
H	0.868728	-3.703365	1.905445
C	-2.440468	-0.010415	-0.416850
C	-2.971760	1.243612	-0.026759
C	-3.259948	-1.158802	-0.480566
C	-4.334015	1.319351	0.288487
C	-4.618727	-1.034171	-0.159743
C	-5.153219	0.192086	0.225766
H	-4.757974	2.271483	0.593060
H	-5.258989	-1.911639	-0.209952
H	-6.206302	0.271816	0.478124
C	2.572555	0.106832	-0.314748
C	3.599355	-0.815425	-0.022199
C	2.807517	1.504126	-0.236668
C	4.855193	-0.328109	0.365583
C	4.079850	1.944310	0.151170
C	5.096179	1.040297	0.457374
H	5.652027	-1.033944	0.588887
H	4.275189	3.011732	0.213519
H	6.073539	1.402937	0.760949
C	3.389538	-2.311667	-0.155211
C	3.696033	-3.041741	1.160412
C	4.241112	-2.881386	-1.299543
H	2.336817	-2.474696	-0.411885
H	3.136630	-2.606770	1.997832
H	3.452332	-4.109051	1.079367
H	4.760716	-2.971516	1.413385
H	3.996521	-2.394752	-2.249647
H	5.309532	-2.724771	-1.107338
H	4.073312	-3.958451	-1.412987
C	1.739622	2.521455	-0.606957
C	2.025951	3.109828	-1.999066

C	1.604954	3.646510	0.426069
H	0.775904	1.999103	-0.657525
H	2.078451	2.323602	-2.758961
H	1.237329	3.813370	-2.289475
H	2.981501	3.649417	-2.001226
H	1.382815	3.249764	1.422680
H	2.518701	4.248792	0.492781
H	0.790198	4.321678	0.138578
C	-2.713332	-2.509822	-0.904069
C	-3.272174	-2.926376	-2.273402
C	-3.004211	-3.588403	0.148601
H	-1.625129	-2.415096	-1.009174
H	-3.030112	-2.185718	-3.042862
H	-2.858028	-3.891899	-2.584867
H	-4.363976	-3.023984	-2.233078
H	-2.660307	-3.278443	1.141572
H	-4.079617	-3.790153	0.220136
H	-2.506920	-4.529405	-0.114535
C	-2.097580	2.484922	0.008449
C	-2.500477	3.474593	1.105117
C	-2.076293	3.172103	-1.367513
H	-1.073995	2.156990	0.223438
H	-2.575102	2.980542	2.080263
H	-1.753684	4.272202	1.185394
H	-3.464519	3.952429	0.892474
H	-1.682366	2.499277	-2.137997
H	-3.086523	3.480305	-1.664434
H	-1.442161	4.066667	-1.342022

4.3. Modification to the **2**→**TS3**→**5** section of the free energy surface for (a) MesNC and (b) ^{t}BuNC.

a) MesNC

2a Energy = -2043.5049 au
+ZPE = -2042.7272 au
Free Energy = -2042.8039 au

6	-0.718883000	0.444625000	-2.693014000
6	0.315066000	-0.493105000	-0.449127000
7	-2.077524000	0.500747000	0.362053000
6	-2.493361000	1.752123000	0.853001000
7	-0.259746000	1.862663000	0.599626000
6	-1.408829000	2.564693000	0.994555000
1	-1.355337000	3.587569000	1.337329000
1	-3.530800000	1.947094000	1.079500000
5	-0.655601000	0.553297000	0.181526000
8	-1.293932000	1.384123000	-3.093708000
15	0.172988000	-0.918260000	-2.301424000

7	1.245124000	-1.049513000	0.227138000
6	-2.975911000	-0.619977000	0.310071000
6	-2.813418000	-1.675492000	1.245459000
6	-4.011809000	-0.636598000	-0.647378000
6	-3.714703000	-2.745872000	1.183096000
6	-4.894920000	-1.726617000	-0.655415000
6	-4.748316000	-2.774052000	0.246541000
1	-3.615308000	-3.566144000	1.884811000
1	-5.699390000	-1.748017000	-1.386096000
1	-5.436330000	-3.613615000	0.225157000
6	1.067251000	2.381574000	0.765229000
6	1.599329000	3.260323000	-0.198933000
6	1.818162000	1.971413000	1.891304000
6	2.903539000	3.740096000	-0.009660000
6	3.114494000	2.481610000	2.039882000
6	3.655135000	3.359660000	1.099792000
1	3.329511000	4.418651000	-0.744596000
1	3.705798000	2.183609000	2.901150000
1	4.662511000	3.742779000	1.231566000
6	-4.205054000	0.484162000	-1.652964000
6	-5.475490000	1.290042000	-1.338343000
6	-4.261370000	-0.049850000	-3.091384000
1	-3.346831000	1.161349000	-1.580161000
1	-5.447444000	1.713701000	-0.328413000
1	-5.595837000	2.113848000	-2.050362000
1	-6.365490000	0.652195000	-1.406039000
1	-3.393423000	-0.676353000	-3.320361000
1	-5.162548000	-0.652333000	-3.256643000
1	-4.280218000	0.781283000	-3.804495000
6	-1.737426000	-1.637951000	2.325998000
6	-1.534773000	-2.982351000	3.032215000
6	-2.047001000	-0.563742000	3.386010000
1	-0.778915000	-1.375754000	1.852295000
1	-1.386582000	-3.806009000	2.326692000
1	-0.652111000	-2.927181000	3.678817000
1	-2.391898000	-3.231028000	3.669738000
1	-2.086112000	0.442964000	2.959673000
1	-3.011712000	-0.772177000	3.864871000
1	-1.274114000	-0.571586000	4.164033000
6	1.233247000	1.048261000	2.945628000
6	0.729145000	1.869381000	4.144790000
6	2.211456000	-0.039925000	3.400109000
1	0.369935000	0.537619000	2.501524000
1	-0.027786000	2.599632000	3.837312000
1	0.282769000	1.216011000	4.903106000
1	1.556669000	2.416268000	4.613341000
1	2.605343000	-0.595580000	2.543086000
1	3.054273000	0.376149000	3.965481000
1	1.696250000	-0.750864000	4.057994000
6	0.811009000	3.688745000	-1.423379000

6	1.501764000	3.224330000	-2.713662000
6	0.597568000	5.209416000	-1.440268000
1	-0.174979000	3.211080000	-1.381671000
1	1.606354000	2.132924000	-2.736019000
1	0.920403000	3.525885000	-3.591512000
1	2.504968000	3.658811000	-2.803536000
1	0.080256000	5.550170000	-0.536851000
1	1.555153000	5.740974000	-1.496796000
1	-0.000578000	5.503612000	-2.309215000
6	2.206809000	-1.909856000	-0.347917000
6	2.031285000	-3.305061000	-0.234843000
6	3.363899000	-1.362047000	-0.941759000
6	3.009881000	-4.144309000	-0.773512000
6	4.318467000	-2.244564000	-1.459364000
6	4.157626000	-3.634731000	-1.396811000
1	2.875456000	-5.221624000	-0.696792000
1	5.214273000	-1.831980000	-1.919610000
6	0.823163000	-3.846203000	0.469740000
1	-0.114016000	-3.530960000	-0.008295000
1	0.836317000	-4.939229000	0.498063000
1	0.780939000	-3.474559000	1.501629000
6	5.184097000	-4.559416000	-1.988475000
1	4.871928000	-4.924210000	-2.975083000
1	6.147957000	-4.058337000	-2.118082000
1	5.343522000	-5.440845000	-1.358580000
6	3.556491000	0.124697000	-0.996221000
1	2.824012000	0.606014000	-1.658661000
1	3.423019000	0.585344000	-0.008962000
1	4.554106000	0.379401000	-1.364618000

TS3a Energy = -2043.4471 au
+ZPE = -2042.6724 au
Free Energy = -2042.7475 au

6	-1.693098000	2.293805000	-2.015736000
6	0.266871000	-0.924873000	-0.349703000
7	-2.255806000	0.041238000	0.448828000
6	-2.464729000	0.648912000	1.698200000
7	-0.421266000	1.336387000	1.005499000
6	-1.386074000	1.399544000	2.035523000
1	-1.230718000	2.033148000	2.896566000
1	-3.400560000	0.524107000	2.224322000
5	-0.927015000	0.435641000	-0.058345000
8	-2.367221000	3.257146000	-2.052588000
15	-0.716785000	0.956365000	-2.077251000
7	1.382111000	-1.137384000	-0.682412000
6	-3.065499000	-1.067129000	0.038636000
6	-2.822431000	-2.339456000	0.611961000
6	-4.104721000	-0.885249000	-0.899300000
6	-3.609066000	-3.423711000	0.202461000

6	-4.860896000	-2.000754000	-1.287090000
6	-4.613790000	-3.262146000	-0.750902000
1	-3.435416000	-4.402815000	0.642029000
1	-5.663367000	-1.867777000	-2.008798000
1	-5.211912000	-4.113705000	-1.060993000
6	0.905414000	1.817932000	1.253041000
6	1.292053000	3.093412000	0.783695000
6	1.811558000	1.014077000	1.994878000
6	2.605494000	3.527040000	1.017613000
6	3.116007000	1.485394000	2.193780000
6	3.517030000	2.727756000	1.701582000
1	2.907684000	4.507544000	0.657762000
1	3.822087000	0.877819000	2.753337000
1	4.531983000	3.076388000	1.867881000
6	-4.480706000	0.488211000	-1.416924000
6	-5.829318000	0.928537000	-0.823883000
6	-4.522250000	0.545109000	-2.947805000
1	-3.720231000	1.190206000	-1.062165000
1	-5.802942000	0.924398000	0.271426000
1	-6.081632000	1.941484000	-1.156709000
1	-6.635061000	0.255333000	-1.142961000
1	-3.559053000	0.252667000	-3.378960000
1	-5.293104000	-0.124229000	-3.349552000
1	-4.755520000	1.560790000	-3.286076000
6	-1.782390000	-2.530536000	1.701137000
6	-0.898885000	-3.758200000	1.459432000
6	-2.444237000	-2.611718000	3.085832000
1	-1.137773000	-1.644811000	1.701168000
1	-0.466366000	-3.739226000	0.453795000
1	-0.080439000	-3.789712000	2.189840000
1	-1.465260000	-4.691497000	1.563907000
1	-3.021395000	-1.707197000	3.302612000
1	-3.124592000	-3.470677000	3.139983000
1	-1.685741000	-2.727462000	3.869247000
6	1.374372000	-0.290769000	2.640018000
6	0.970817000	-0.063846000	4.107721000
6	2.438261000	-1.391554000	2.563654000
1	0.479253000	-0.640402000	2.113077000
1	0.158130000	0.663807000	4.188686000
1	0.630260000	-1.003818000	4.558375000
1	1.824583000	0.306081000	4.688740000
1	2.823865000	-1.519989000	1.546681000
1	3.291938000	-1.170047000	3.215238000
1	2.016779000	-2.346507000	2.899216000
6	0.317232000	4.015297000	0.080796000
6	0.842863000	4.467328000	-1.287091000
6	-0.010588000	5.230934000	0.962199000
1	-0.610340000	3.455225000	-0.069702000
1	1.085671000	3.606310000	-1.919982000
1	0.088859000	5.069130000	-1.805584000

1	1.746784000	5.080321000	-1.181255000
1	-0.419638000	4.923101000	1.930577000
1	0.887491000	5.832299000	1.151527000
1	-0.748745000	5.871746000	0.467592000
6	2.670453000	-1.420250000	-1.108916000
6	3.129844000	-2.755685000	-1.028401000
6	3.480761000	-0.374335000	-1.604143000
6	4.427679000	-3.023877000	-1.460786000
6	4.774380000	-0.705237000	-2.017346000
6	5.265142000	-2.015057000	-1.960161000
1	4.794728000	-4.045740000	-1.404547000
1	5.414499000	0.087861000	-2.395509000
6	2.242618000	-3.835087000	-0.492283000
1	1.326125000	-3.933589000	-1.085985000
1	2.753813000	-4.800399000	-0.495675000
1	1.926495000	-3.620332000	0.535743000
6	6.650375000	-2.340571000	-2.437210000
1	7.258403000	-1.439193000	-2.550613000
1	7.166384000	-3.013993000	-1.745278000
1	6.624418000	-2.843336000	-3.411696000
6	2.971430000	1.028173000	-1.693404000
1	2.241783000	1.138680000	-2.505405000
1	2.456930000	1.335429000	-0.776630000
1	3.788335000	1.731531000	-1.873918000

b) **^{t}BuNC**

2b Energy = -1851.8054 au
+ZPE = -1851.0804 au
Free Energy = -1851.1520 au

6	-0.080155000	-2.108169000	-1.881531000
6	0.073622000	0.514412000	-1.220099000
7	1.063308000	-0.724548000	0.932432000
6	0.536969000	-1.378212000	2.059827000
7	-1.217277000	-0.568891000	0.889470000
6	-0.821485000	-1.293931000	2.029896000
1	-1.549589000	-1.684414000	2.724897000
1	1.179714000	-1.850267000	2.788087000
5	-0.033356000	-0.201483000	0.169840000
8	-0.176436000	-3.182733000	-1.422900000
15	0.059472000	-0.678412000	-2.738769000
7	0.190149000	1.774550000	-1.307573000
6	0.331285000	2.609237000	-2.532168000
6	1.677464000	2.301909000	-3.203694000
6	-0.852195000	2.400175000	-3.489140000
6	0.319074000	4.064365000	-2.047649000
1	2.495630000	2.422944000	-2.485144000
1	1.720412000	1.281257000	-3.596647000
1	1.842134000	2.991938000	-4.038254000

1	-1.800012000	2.519805000	-2.952510000
1	-0.810796000	3.149982000	-4.286584000
1	-0.851270000	1.415004000	-3.963115000
1	0.432409000	4.749658000	-2.894605000
1	-0.623673000	4.291295000	-1.539323000
1	1.135320000	4.245258000	-1.342199000
6	2.459613000	-0.424321000	0.783871000
6	2.903644000	0.877507000	1.118331000
6	3.348755000	-1.402217000	0.295358000
6	4.255018000	1.185952000	0.919292000
6	4.695401000	-1.048756000	0.123205000
6	5.145107000	0.234622000	0.420194000
1	4.614843000	2.180809000	1.165767000
1	5.392720000	-1.792611000	-0.253959000
1	6.189104000	0.493671000	0.271622000
6	-2.588713000	-0.214817000	0.650521000
6	-3.517711000	-1.215648000	0.297531000
6	-2.978057000	1.142211000	0.785821000
6	-4.852328000	-0.839421000	0.082272000
6	-4.319745000	1.465850000	0.546634000
6	-5.251608000	0.487117000	0.199171000
1	-5.578245000	-1.602422000	-0.187969000
1	-4.643186000	2.497103000	0.640334000
1	-6.286824000	0.762929000	0.022580000
6	2.897195000	-2.814865000	-0.022538000
6	3.533388000	-3.821289000	0.949388000
6	3.215366000	-3.202315000	-1.473184000
1	1.811056000	-2.858747000	0.111078000
1	3.290282000	-3.584661000	1.990759000
1	3.180089000	-4.836307000	0.737346000
1	4.626154000	-3.817945000	0.853604000
1	2.781897000	-2.488796000	-2.182469000
1	4.298091000	-3.231079000	-1.645787000
1	2.813709000	-4.196336000	-1.698426000
6	1.972204000	1.891051000	1.760869000
6	2.262726000	3.331212000	1.333551000
6	2.034398000	1.756790000	3.292991000
1	0.946154000	1.659798000	1.448687000
1	2.341310000	3.408645000	0.244381000
1	1.453594000	3.993484000	1.663241000
1	3.193770000	3.709029000	1.773352000
1	1.744576000	0.750707000	3.615799000
1	3.052469000	1.950860000	3.652900000
1	1.359917000	2.474889000	3.772758000
6	-1.993916000	2.209911000	1.241415000
6	-1.723111000	2.094002000	2.751855000
6	-2.435096000	3.633408000	0.893861000
1	-1.043781000	2.046046000	0.718736000
1	-1.290822000	1.121360000	3.011110000
1	-1.018303000	2.871623000	3.070479000

1	-2.651698000	2.222603000	3.321677000
1	-2.697698000	3.726957000	-0.166166000
1	-3.300632000	3.951380000	1.487886000
1	-1.619416000	4.334160000	1.103313000
6	-3.129356000	-2.675802000	0.152064000
6	-3.499003000	-3.217085000	-1.236011000
6	-3.785476000	-3.529708000	1.248407000
1	-2.043375000	-2.757556000	0.265614000
1	-3.066293000	-2.601571000	-2.031154000
1	-3.129714000	-4.241110000	-1.357446000
1	-4.586287000	-3.232491000	-1.377690000
1	-3.509678000	-3.183062000	2.250415000
1	-4.878994000	-3.487203000	1.172447000
1	-3.481771000	-4.577984000	1.153945000

TS3b Energy = -1851.7595 au
+ZPE = -1851.0379 au
Free Energy = -1851.1095 au

6	-0.610382000	2.862051000	1.098665000
6	0.356661000	-1.122203000	1.001121000
7	0.645108000	0.654969000	-1.040720000
6	2.065963000	0.457600000	-1.024932000
6	2.925189000	1.537554000	-0.730745000
6	4.309178000	1.306573000	-0.695251000
1	4.976355000	2.136712000	-0.475094000
6	4.834992000	0.042398000	-0.950244000
1	5.908505000	-0.119056000	-0.919189000
6	3.978425000	-1.012446000	-1.272159000
1	4.394666000	-1.989693000	-1.506499000
6	2.589874000	-0.829440000	-1.323186000
6	2.396538000	2.942510000	-0.525201000
1	1.304510000	2.886467000	-0.559209000
6	2.814768000	3.523055000	0.830776000
1	2.461575000	2.892713000	1.654652000
1	2.391146000	4.524333000	0.965313000
1	3.906203000	3.607257000	0.907365000
6	2.849940000	3.859479000	-1.672110000
1	3.942943000	3.953266000	-1.694837000
1	2.427179000	4.862371000	-1.548651000
1	2.525942000	3.468641000	-2.642811000
6	1.690890000	-1.966875000	-1.789945000
1	0.655475000	-1.700423000	-1.546720000
6	1.993562000	-3.316723000	-1.130343000
1	3.017279000	-3.652012000	-1.337581000
1	1.314937000	-4.082309000	-1.524797000
1	1.860813000	-3.277885000	-0.045137000
6	1.778461000	-2.109244000	-3.320499000

1	1.549320000	-1.164705000	-3.822758000
1	1.068107000	-2.865199000	-3.674878000
1	2.787418000	-2.417775000	-3.621368000
6	-0.039835000	0.604108000	-2.277354000
7	-1.578352000	0.125457000	-0.693745000
6	-2.848123000	-0.322725000	-0.207652000
6	-3.864662000	0.611655000	0.087510000
6	-5.093610000	0.133211000	0.563490000
1	-5.884781000	0.843967000	0.789502000
6	-5.316118000	-1.230108000	0.742267000
1	-6.274013000	-1.581671000	1.113626000
6	-4.311110000	-2.144201000	0.428863000
1	-4.496539000	-3.208724000	0.547555000
6	-3.068345000	-1.712633000	-0.053064000
6	-3.682759000	2.097981000	-0.152587000
1	-2.632946000	2.268035000	-0.416143000
6	-4.004954000	2.928714000	1.095785000
1	-3.400470000	2.605823000	1.950074000
1	-3.799756000	3.988611000	0.910914000
1	-5.062103000	2.835477000	1.373326000
6	-4.543850000	2.559505000	-1.339944000
1	-5.609769000	2.407633000	-1.128494000
1	-4.386373000	3.625439000	-1.537783000
1	-4.301368000	2.002551000	-2.251492000
6	-2.019681000	-2.729230000	-0.472650000
1	-1.066227000	-2.199157000	-0.569510000
6	-1.829988000	-3.844818000	0.560766000
1	-2.723782000	-4.473844000	0.648020000
1	-0.998329000	-4.497180000	0.269643000
1	-1.610704000	-3.432055000	1.551777000
6	-2.350992000	-3.311365000	-1.856182000
1	-2.412498000	-2.519552000	-2.611008000
1	-1.576669000	-4.022150000	-2.170381000
1	-3.312491000	-3.839193000	-1.838997000
6	-1.347561000	0.310865000	-2.067641000
1	-2.158921000	0.253102000	-2.779124000
1	0.476840000	0.818599000	-3.201146000
5	-0.322641000	0.332750000	0.036699000
8	-0.770701000	3.939887000	0.658757000
15	-0.379001000	1.387999000	1.822416000
7	1.248356000	-1.413288000	1.714605000
6	2.357764000	-1.480853000	2.663268000
6	3.113493000	-0.148853000	2.571242000
6	1.745330000	-1.681641000	4.054984000
6	3.263017000	-2.652584000	2.274013000
1	3.528203000	-0.006036000	1.568552000
1	2.449376000	0.691383000	2.797326000
1	3.935050000	-0.155863000	3.295226000
1	1.174904000	-2.613639000	4.102631000
1	2.548842000	-1.726920000	4.796043000

1	1.082809000	-0.849923000	4.311072000
1	4.083337000	-2.723037000	2.994583000
1	2.712772000	-3.598408000	2.281508000
1	3.688855000	-2.496708000	1.277764000

4.4. Direct attack at P pathway (with HNC only)

I1 Energy = -1694.60940969 au
ZPE = -1693.998368 au
Free Energy = -1694.065215 au

C	0.789279	2.529363	1.460474
C	-0.068077	0.049322	1.738117
N	1.074306	-0.060427	-0.688781
C	0.616673	-0.033286	-2.015107
N	-1.199594	0.128448	-0.690932
C	-0.741161	0.089300	-2.015825
H	-1.425450	0.159352	-2.848518
H	1.299739	-0.108593	-2.848055
B	-0.066804	0.034219	0.176312
O	0.642974	3.409658	0.702785
P	1.020234	1.349122	2.623163
N	-0.729217	-0.808670	2.417448
H	-0.681535	-0.675631	3.432457
C	2.428052	-0.394174	-0.345725
C	2.697173	-1.681821	0.179656
C	3.448578	0.562102	-0.521673
C	4.021269	-1.985527	0.521793
C	4.759262	0.204205	-0.176133
C	5.045234	-1.054670	0.344310
H	4.253722	-2.965011	0.927910
H	5.558776	0.927831	-0.309524
H	6.064716	-1.313394	0.613218
C	-2.595046	0.022361	-0.373618
C	-3.357195	1.186469	-0.159057
C	-3.160296	-1.267763	-0.277552
C	-4.718498	1.037173	0.141835
C	-4.525198	-1.366712	0.019410
C	-5.300323	-0.226137	0.227272
H	-5.324657	1.924064	0.310171
H	-4.981391	-2.350475	0.095199
H	-6.356775	-0.322737	0.458857
C	-2.746031	2.572543	-0.243771
C	-2.850969	3.304467	1.101890
C	-3.392741	3.397556	-1.365315
H	-1.682471	2.459427	-0.485041
H	-2.381250	2.727293	1.906463
H	-2.360140	4.282365	1.048797
H	-3.899576	3.468694	1.378466

H	-3.286353	2.900209	-2.335551
H	-4.463698	3.544231	-1.179599
H	-2.925603	4.385941	-1.434002
C	-2.337546	-2.525702	-0.498182
C	-2.737049	-3.217771	-1.810657
C	-2.444362	-3.491773	0.688949
H	-1.284168	-2.232013	-0.586163
H	-2.610258	-2.548874	-2.669308
H	-2.121763	-4.108966	-1.979050
H	-3.787364	-3.533100	-1.782373
H	-2.117713	-3.004502	1.613193
H	-3.473132	-3.846454	0.826368
H	-1.812923	-4.372190	0.518469
C	3.164634	1.943085	-1.082796
C	3.649503	2.052338	-2.537817
C	3.799764	3.052264	-0.233088
H	2.077948	2.091293	-1.075444
H	3.180621	1.298319	-3.178900
H	3.418350	3.041134	-2.948834
H	4.735451	1.907328	-2.593646
H	3.539451	2.946153	0.825407
H	4.893303	3.037636	-0.310972
H	3.455870	4.034801	-0.573410
C	1.605912	-2.736033	0.300143
C	1.859272	-3.753057	1.415205
C	1.405657	-3.447261	-1.050406
H	0.662639	-2.233099	0.544348
H	2.064881	-3.257239	2.370290
H	0.975512	-4.386655	1.546055
H	2.704209	-4.412461	1.183816
H	1.126277	-2.735861	-1.836249
H	2.327431	-3.955545	-1.358966
H	0.610960	-4.199072	-0.975295

TS4 Energy = -1694.53118082 au
ZPE = -1693.925515 au
Free Energy = -1693.995749 au

C	-0.012849	-0.788316	1.625071
C	-0.002923	0.025375	3.955203
N	-1.144939	-0.071667	-0.962526
C	-0.681334	-0.267047	-2.271858
N	1.145284	-0.081668	-0.958519
C	0.683860	-0.272285	-2.269706
H	1.370351	-0.388081	-3.094952
H	-1.365970	-0.377045	-3.099371
B	-0.001036	0.010949	-0.101325
O	-0.003217	0.475013	1.273145
P	-0.018624	-1.540138	3.193712
N	0.010635	1.236996	3.826618

H	0.017479	1.951543	4.545644
C	-2.528556	0.045379	-0.622230
C	-3.069680	1.330869	-0.405938
C	-3.308859	-1.121544	-0.478513
C	-4.422046	1.427430	-0.052315
C	-4.659489	-0.973965	-0.135258
C	-5.213952	0.287456	0.077138
H	-4.855693	2.409242	0.120963
H	-5.277830	-1.861559	-0.024739
H	-6.261286	0.381336	0.348043
C	2.529681	0.030679	-0.618322
C	3.082402	1.315321	-0.429342
C	3.299828	-1.139838	-0.451109
C	4.436831	1.407553	-0.082521
C	4.652279	-0.997131	-0.112829
C	5.218686	0.263598	0.070130
H	4.879585	2.388869	0.069148
H	5.262743	-1.887715	0.016021
H	6.267558	0.353929	0.336289
C	-2.232296	2.591220	-0.539910
C	-2.051416	3.283069	0.820275
C	-2.838678	3.558532	-1.566212
H	-1.238386	2.300903	-0.904616
H	-1.554013	2.622895	1.538963
H	-1.445587	4.189999	0.710042
H	-3.022116	3.576624	1.239001
H	-2.956153	3.079659	-2.543985
H	-3.825731	3.911272	-1.243832
H	-2.196304	4.437470	-1.689341
C	-2.724694	-2.507222	-0.688657
C	-3.309578	-3.159963	-1.950736
C	-2.949374	-3.405076	0.535539
H	-1.642188	-2.399973	-0.829146
H	-3.118626	-2.552770	-2.842110
H	-2.871834	-4.151232	-2.111793
H	-4.395695	-3.282567	-1.857185
H	-2.529704	-2.954351	1.440627
H	-4.017993	-3.580911	0.708967
H	-2.472892	-4.380088	0.385717
C	2.255288	2.579877	-0.583607
C	2.841993	3.504849	-1.659181
C	2.120820	3.318286	0.756804
H	1.248443	2.289135	-0.909886
H	2.916646	2.994750	-2.625427
H	2.211003	4.391332	-1.786887
H	3.846067	3.848050	-1.381818
H	1.653886	2.681423	1.515414
H	3.104015	3.629416	1.131181
H	1.507480	4.218948	0.638118
C	2.703620	-2.523711	-0.636997

C	2.927084	-3.405483	0.598939
C	3.277158	-3.198800	-1.892573
H	1.621299	-2.409700	-0.773804
H	2.516276	-2.937255	1.499314
H	2.440438	-4.378010	0.466384
H	3.994861	-3.589216	0.769336
H	3.087709	-2.601870	-2.791232
H	4.362599	-3.329297	-1.801527
H	2.830134	-4.188235	-2.038454

TS5 Energy = -1694.55979801 au
ZPE = -1693.951363 au
Free Energy = -1694.017181 au

C	0.107601	0.640692	1.810768
C	-0.062654	-1.588275	1.260364
N	1.154842	-0.193626	-0.627834
C	0.681145	-0.423033	-1.865889
N	-1.154240	-0.108418	-0.603328
C	-0.719804	-0.378523	-1.849995
H	-1.392792	-0.500583	-2.688390
H	1.325861	-0.574868	-2.721779
B	0.015761	-0.134318	0.356256
O	0.246514	1.839075	2.051515
P	-0.032061	-0.787169	2.889555
N	-0.107549	-2.733619	0.739907
H	-0.090781	-3.536088	1.374354
C	2.549605	0.036792	-0.347305
C	3.437390	-1.040557	-0.180763
C	2.961129	1.385330	-0.231787
C	4.771720	-0.740104	0.129869
C	4.302094	1.629112	0.083859
C	5.199548	0.577170	0.270789
H	5.475482	-1.556381	0.269152
H	4.645709	2.654400	0.180468
H	6.234383	0.787736	0.521569
C	-2.546631	0.086577	-0.297076
C	-2.960293	1.400239	0.031397
C	-3.446548	-0.997980	-0.331887
C	-4.309090	1.597944	0.347728
C	-4.787578	-0.739941	-0.013264
C	-5.215915	0.538807	0.330937
H	-4.649969	2.595848	0.604412
H	-5.496320	-1.563649	-0.025189
H	-6.257202	0.713382	0.583122
C	-2.006551	2.577712	-0.067103
C	-2.291130	3.677724	0.956942
C	-2.013241	3.145236	-1.497703
H	-0.993962	2.219589	0.139706
H	-2.341736	3.268899	1.970080

H	-1.481634	4.414630	0.938933
H	-3.227091	4.208046	0.743210
H	-1.732628	2.384288	-2.236679
H	-3.009038	3.520882	-1.763114
H	-1.302818	3.976381	-1.579616
C	-3.025073	-2.413725	-0.681202
C	-3.691542	-2.880678	-1.984294
C	-3.348799	-3.382115	0.465386
H	-1.938424	-2.436195	-0.816580
H	-3.447934	-2.222107	-2.825924
H	-3.364488	-3.894616	-2.238987
H	-4.783718	-2.896436	-1.884188
H	-2.900227	-3.041075	1.403612
H	-4.431089	-3.472994	0.617423
H	-2.955911	-4.379622	0.239481
C	2.011311	2.527088	-0.552110
C	2.134243	2.896777	-2.042083
C	2.217054	3.760670	0.328552
H	0.986087	2.177891	-0.375449
H	1.913450	2.042295	-2.692799
H	1.442084	3.706702	-2.297477
H	3.152407	3.234898	-2.269851
H	2.174850	3.497002	1.388007
H	3.172987	4.256802	0.120958
H	1.421769	4.488919	0.132652
C	3.003148	-2.486088	-0.332380
C	3.233732	-3.274172	0.964641
C	3.728595	-3.154139	-1.510104
H	1.926412	-2.508012	-0.534793
H	2.717851	-2.804695	1.808558
H	2.858276	-4.298143	0.857292
H	4.300911	-3.332532	1.210567
H	3.549581	-2.619188	-2.449909
H	4.812454	-3.179692	-1.344031
H	3.385019	-4.186795	-1.634468

4.5. Calculation of ^{31}P NMR chemical shifts

The isotropic shielding constants, σ, for the ^{31}P nuclei of **1**, **2a**, **2b**, **5** and $\mathbf{I_1}$ were computed using the same protocol adopted for the geometry optimisations (M06L/6-31+G(d,p),6-31G). In converting these isotropic shielding values to chemical shifts, we have taken the starting material, compound 1 (δ –285.9 ppm) as an internal reference, thereby avoiding the problem of calculating the isotropic shielding for 85% aqueous H_3PO_4. The calculated chemical shift is then obtained from the following equation:

$$\delta_{calc} = -285.9 + (629.0 - \sigma_{calc}) \text{ ppm}$$

Table S4. Summary of measured chemical shifts, calculated shielding constants and calculated chemical shifts for **1**, **2a**, **2b**, **5** and **I1** (all in ppm). **1** is used as an internal reference, so the measured and calculated chemical shift are identical by construction.

	δ_{expt} /ppm	σ_{calc} /ppm	δ_{calc} /ppm
1	–285.9	629.0	–285.9
2a	–195.2	530.6	–187.5
2b	–207.8	532.0	–188.9
5	–337.1	682.2	–339.1
I1		434.0	–90.9

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