Electronic Supplementary Material (ESI) for ChemComm.

Allenic Phosphonium Borate Zwitterions via a Phosphonium Allenylidene Intermediate

Electronic Supplementary Information

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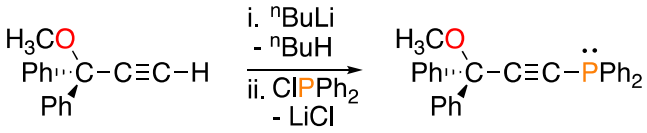
General Considerations

Unless otherwise stated, all reactions and manipulations were performed using oven or flame dried Schlenk glassware, where reactions were conducted under a positive pressure of nitrogen (N_2) either within a MBraun LABstar Glove Box Workstation or by employing standard Schlenk techniques. Disposable hypodermic syringes were utilized to transfer air and moisture sensitive reagents. Commercial reagents were purchased from either Sigma-Aldrich, TCI Chemicals, or Oakwood Chemicals and employed without further purification, with the exception of *P*-chlorodiphenylphosphine ($ClPPh_2$), which was purified by vacuum distillation immediately before use. Trispentafluorophenylborane ($B(C_6F_5)_3$) was purified by sublimation prior to use. 1-methoxy-1-phenylprop-2-yn-1-yl benzene was synthesized according to previous reports. [1] Trimethylsilyl trifluoromethanesulfonate (TMSOTf) was used as purchased from Sigma-Aldrich, handled under extremely stringent conditions, and used immediately upon opening. Solvents were prepared from an MBraun MB-SPS 800 solvent drying system and stored over activated molecular sieves prior to use. Separations were preformed using high-purity grade silica (60 Å pore size, 200425 mesh particle size) and employing HPLC grade solvents. Nuclear magnetic resonance (NMR) experiments utilized deuterated solvents (chloroform-*d*, benzene-d_6 and toluene-d_8) which were dried over activated molecular sieves, then degassed by freeze-pump-thaw prior to use. NMR experiments were conducted with tubes (8" x 5 mm) equipped with J-young screw caps. Proton (^1H), boron (^{11}B), carbon (^{13}C), fluorine (^{19}F), and phosphorus (^{31}P) NMR spectra were recorded on either Bruker Neo 700 MHz, DRX 600 MHz, Bruker ARX 400 MHz, or Bruker ARX 300 MHz spectrometers. Chemical shifts for protons and carbons are reported relative to tetramethylsilane ($SiMe_4$), listed in parts per million (ppm), and referenced to either the residual protium or carbon resonances of the deuterated solvents (chloroform-*d*,: δ 7.26, δ 77.16). Chemical shifts for boron and fluorine nuclei are reported relative to 15% boron trifluoride etherate (BF_3-Et_2O). Chemical shifts for phosphorus nuclei are reported relative to phosphoric acid (H_3PO_4). 2D NMR spectra were analyzed using either TopSpin 4.0.1 or MestreNova 12.0.3-21384 software. Coupling constants are reported in Hertz (Hz) and the conventional abbreviations for denoting multiplicity were used. (br = broad, s = singlet, d = doublet, dt = doublet of triplets, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. Elemental analysis was performed by using Vario EL Cube Elemental Analyzer and the best obtainable data has been presented. Mass spectrometry data was provided from the AIMS Mass Spectrometry Laboratory at the University of Toronto. Samples were run in DART positive ion mode, utilizing an AccuTOF 4G instrument.

Synthetic Procedures and Characterization

P,P-diphenyl-3,3-diphenyl-3-methoxy-propynyl-phosphane (**1**)



^{n}BuLi (0.75 mL, 1.6M in hexanes, 1.2 mmol, 1.05 equiv) was added dropwise to a solution of 1-methoxy-1-phenylprop-2-yn-1-yl benzene 256.3 mg, 1.15 mmol) in THF (5 ml) at -78 ˚C. The mixture was allowed to warm to 25 ˚C and stirred for an hour. *P*-chlorodiphenylphosphine (0.217 mL, 1.2 mmol, 1.05 equiv) was added dropwise, and the mixture was gradually warmed to room temperature, then allowed to stir for 3 hrs under a positive flow of N_2. The reaction mixture was dried *in vacuo*, diluted with diethyl ether and water. The organic phase was removed and extracted three times with diethyl ether, combined, dried over magnesium sulfate, and concentrated. The residue was purified by flash chromatography (eluting with 5% EtOAc, 95% hexanes), then recrystallized from hot ethanol, yielding a white powder. (267 mg, 0.66 mmol, 60% yield).

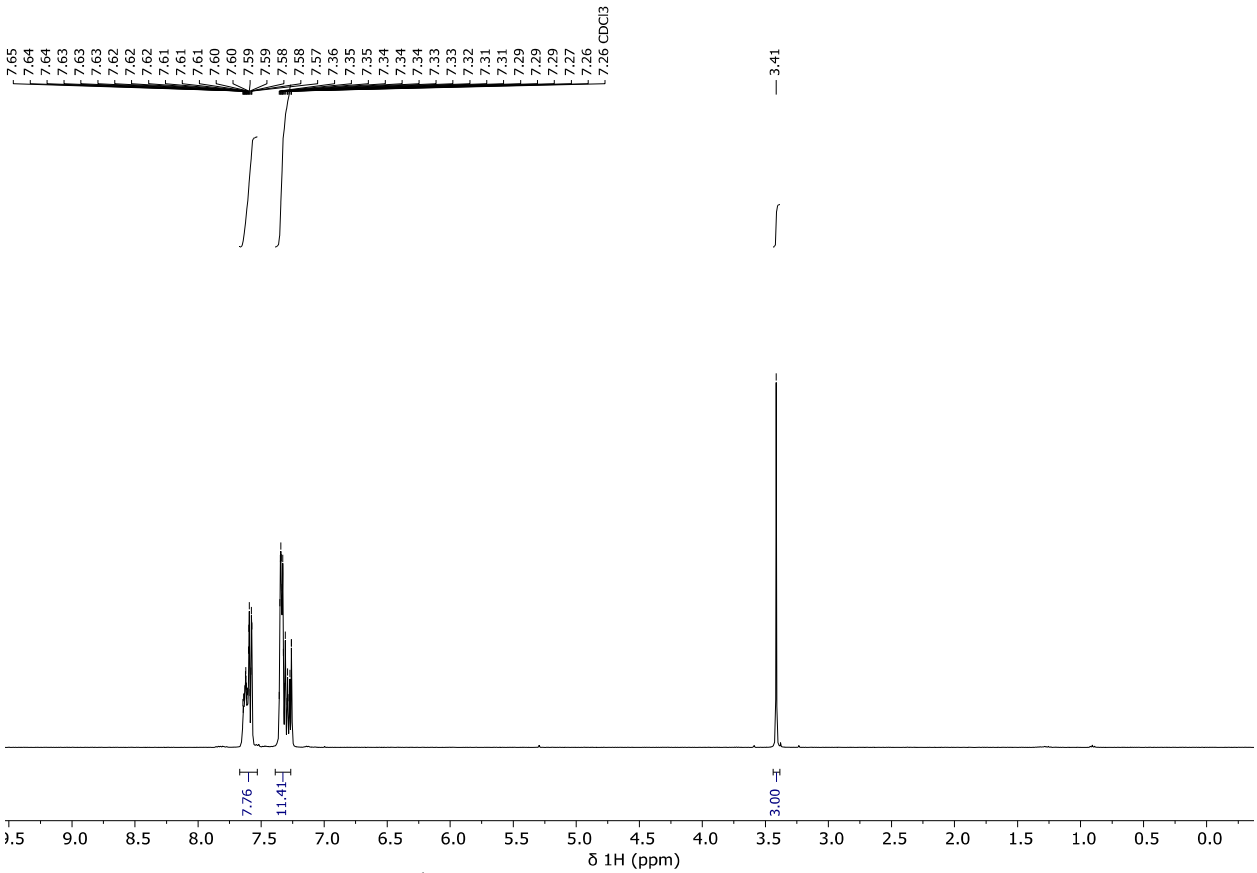
^{1}H NMR (300 MHz, Me_4Si, $CDCl_3$) δ 7.68 – 7.49 (br, 8H, overlapping aromatic resonances), 7.36 – 7.27 (br, 12H, overlapping aromatic resonances), 3.39 (s, 3H), ppm.

^{13}C {^{1}H} NMR (101 MHz, Me_4Si, $CDCl_3$): δ 143.1 ((s, -C(OCH_3)(C_6H_5)$_2$ (ipso-C)), 136.3 (d, $^{1}J_{PC}$ = 6.5 Hz, P(C_6H_5)$_2$ (*ipso*-C), 132.7 (d, $^{2}J_{PC}$ = 21 Hz, P(C_6H_5)$_2$ (*o*-C), 129.2 (s, P(C_6H_5)$_2$ (*p*-C), 128.8 (d, $^{3}J_{PC}$ = 7.6 Hz, P(C_6H_5)$_2$ (*m*-C)), 128.4, 127.9, and 126.9 (s, aryl carbons of -C(OCH_3)(C_6H_5)$_2$), 107.8 (s, P-C≡*C*), 86.9 (d, $^{1}J_{PC}$ = 11.9 Hz, P-*C*≡C), 81.8 (s, ≡C-*C*(OCH_3)(C_6H_5)$_2$), 53.0 (s, P-O*C*H_3) ppm.

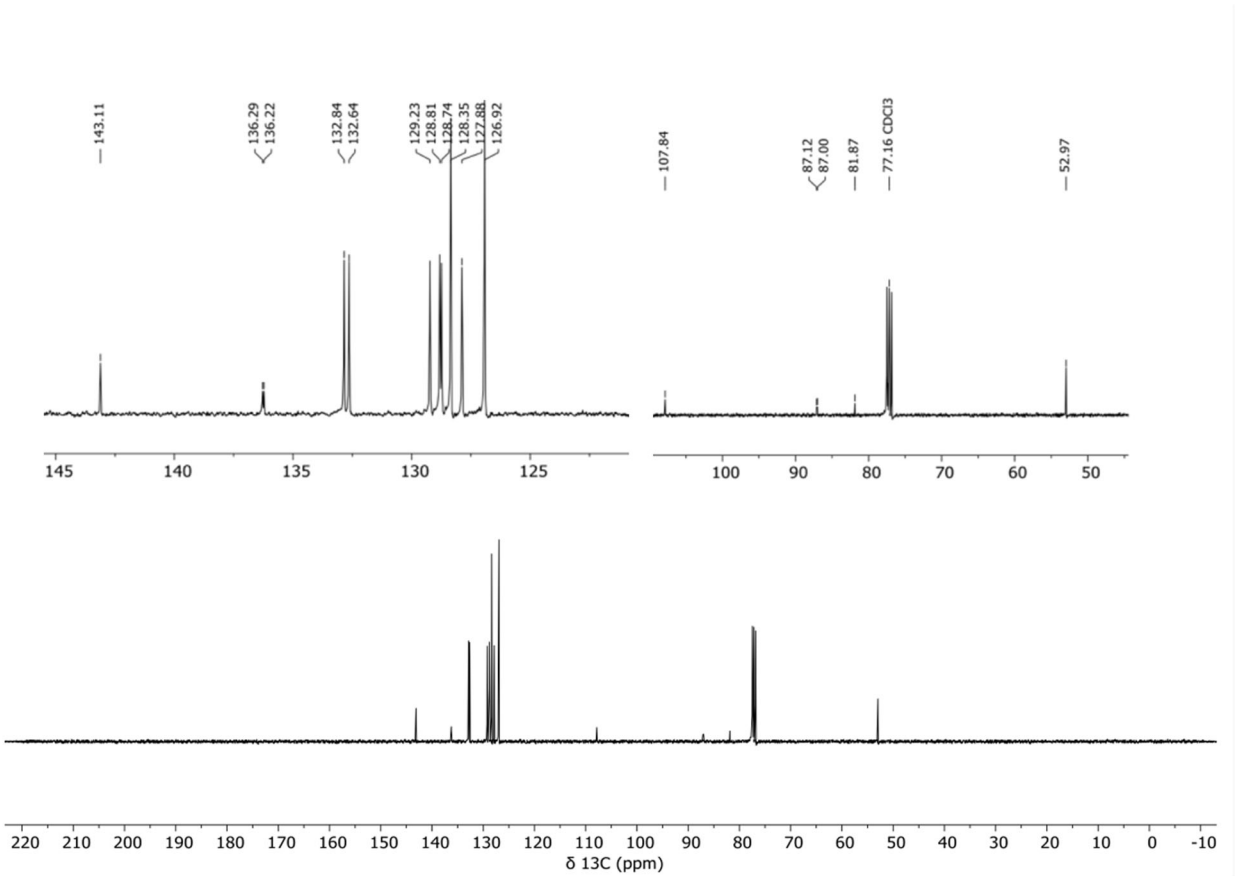
^{31}P NMR (162 MHz, H_3PO_4, $CDCl_3$) δ -34.0 (p, 8.7 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, H_3PO_4, $CDCl_3$) δ -34.0 (s) ppm.

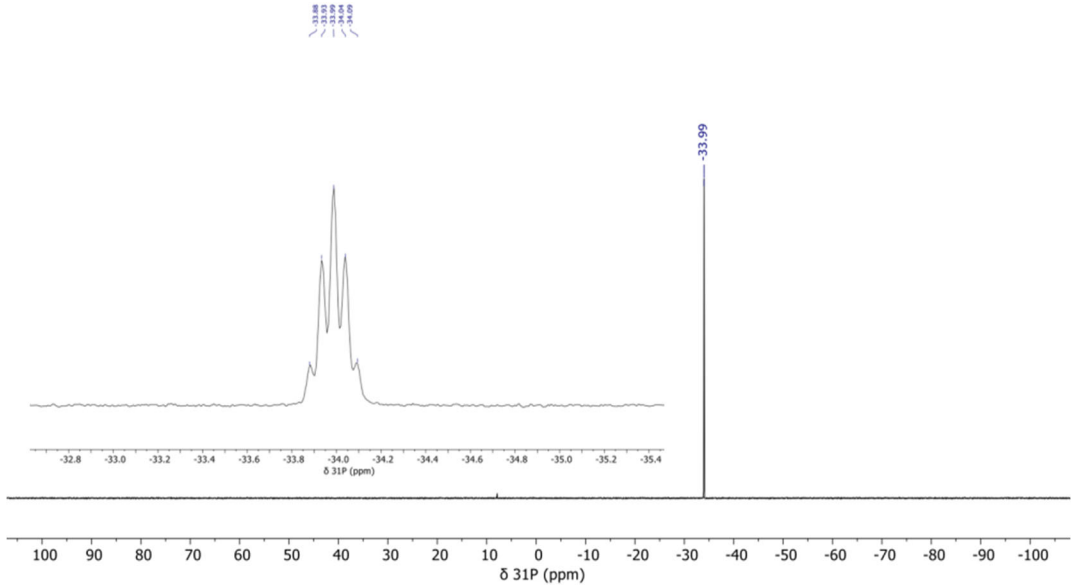
HRMS: (DART^{+}) *m/z* calculated for {M+H]$^{+}$: 407.1559. Found: 407.1568



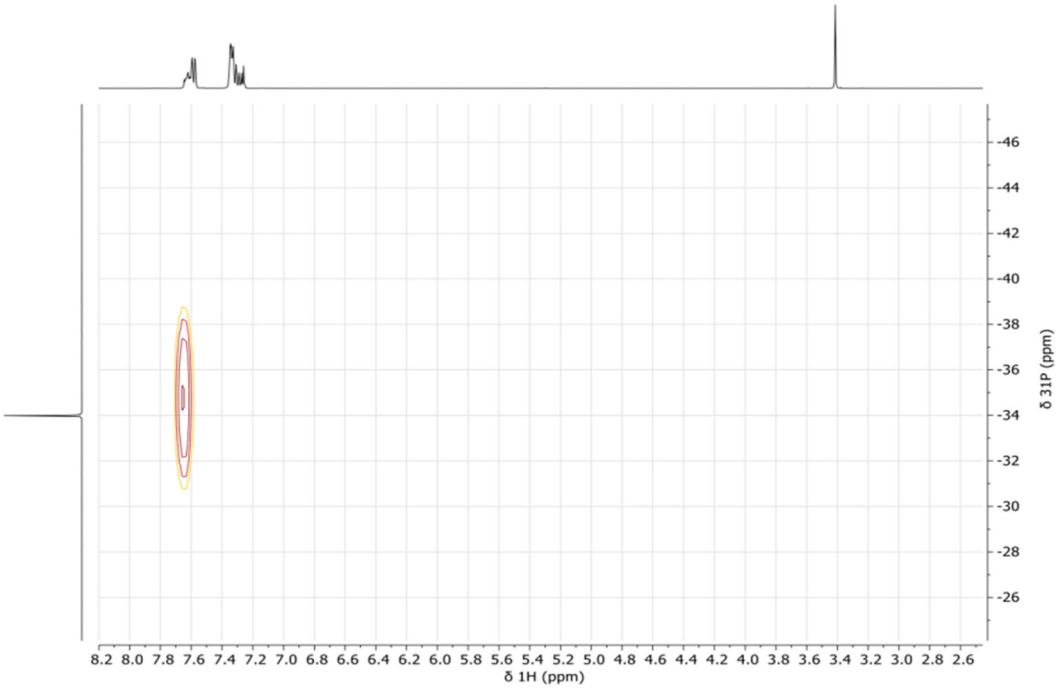
Supplementary Figure 1-A: ^{1}H NMR spectrum (300 MHz, Me_4Si) of **1a** in $CDCl_3$ at 300 K



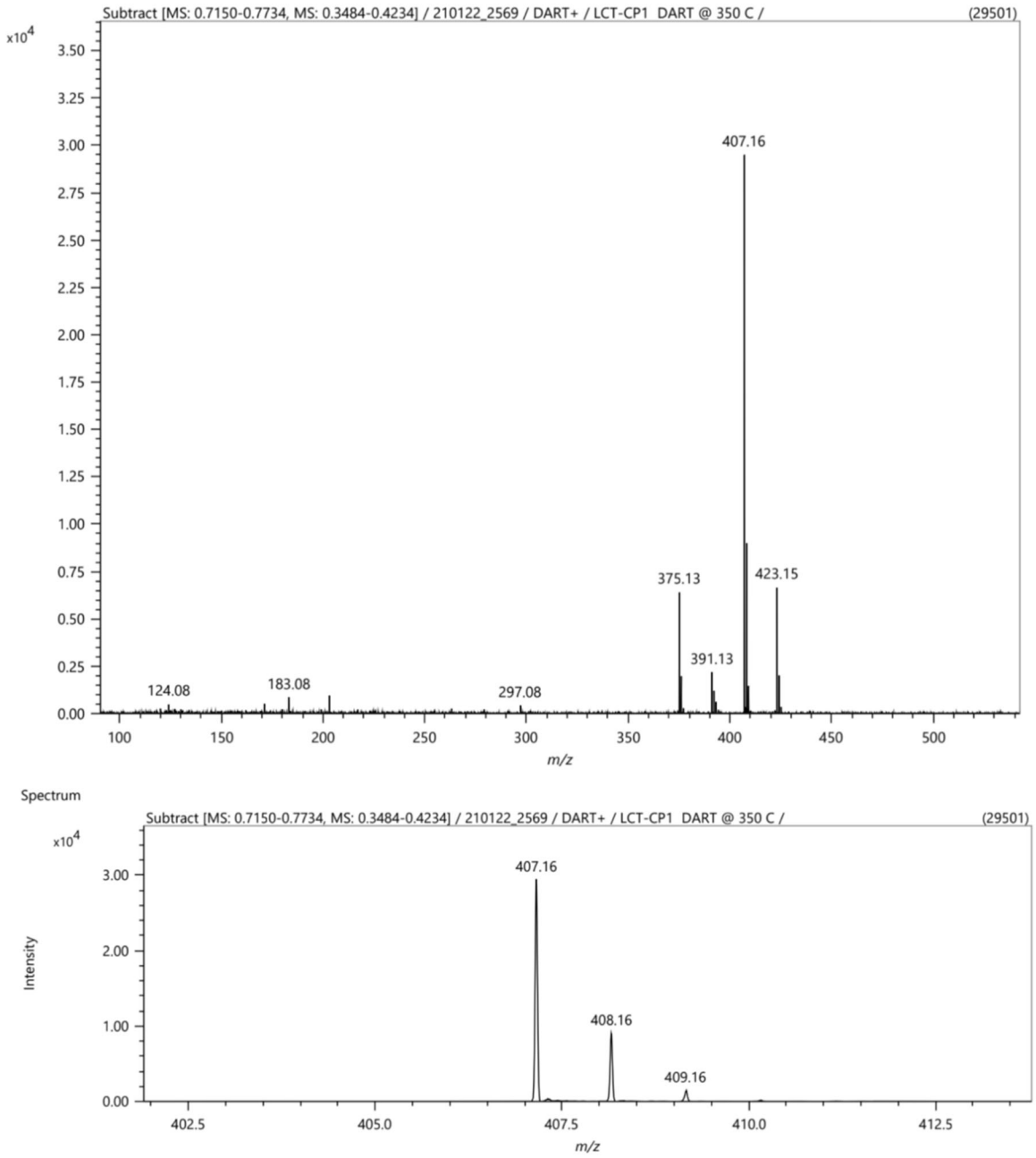
Supplementary Figure 1-B: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Me_4Si) of **1** in $CDCl_3$ at 301K.



Supplementary Figure 1-C: $^{31}P\{^{1}H\}$ NMR and ^{31}P NMR spectrum (121 MHz, H_3PO_4,) of **1** in $CDCl_3$ at 301K.

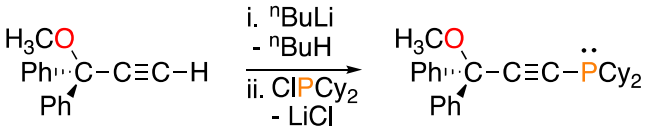


Supplementary Figure 1-D: 2D HMBC (^{1}H x ^{31}P) NMR spectrum (400 MHz, 162 MHz) of **1** in $CDCl_3$ 300 K.



Supplementary Figure 1-E: Mass spectrometry report, $[M+H]^+$ of **1** using DART in positive ion mode.

P,P-dicyclohexyl-3,3-diphenyl-3-methoxy-propynyl-phosphane (**2**)



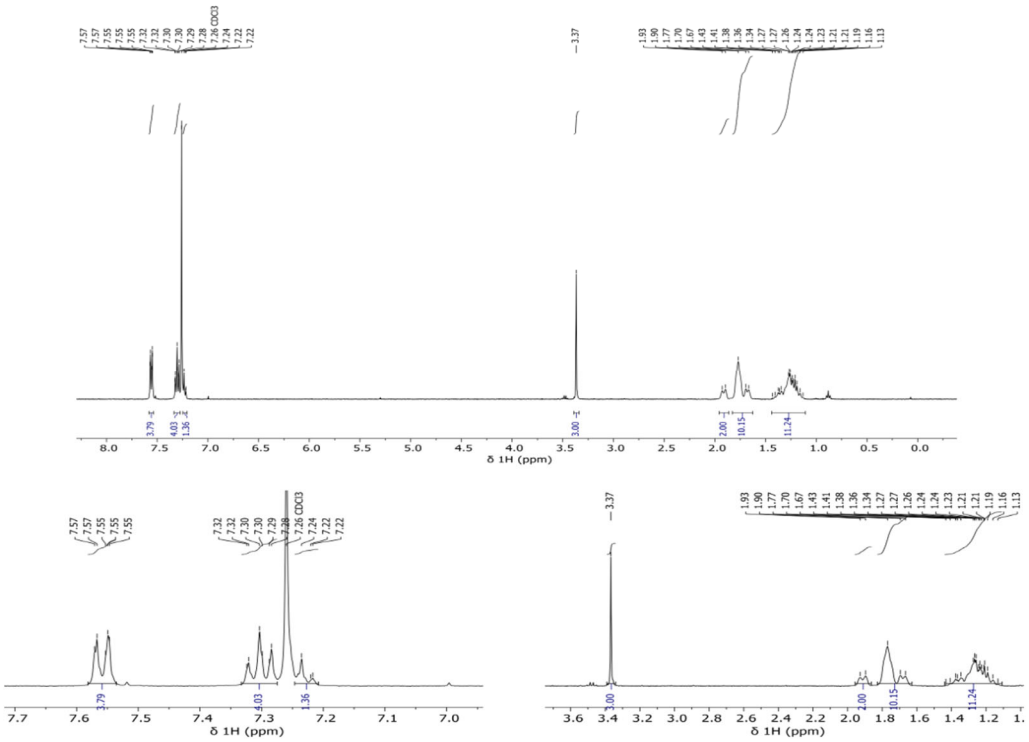
^{n}BuLi (1.3 mL, 1.6M in hexanes, 2.07 mmol, 1.15 equiv) was added dropwise to a solution of 1-methoxy-1-phenylprop-2-yn-1-yl benzene (400 mg, 1.8 mmol) in THF (10 ml) at -78 ˚C. The mixture was allowed to warm to 25 ˚C and stirred for 1 hr. *P*-chlorodicyclohexylphosphine (441 mg, 1.9 mmol, 1.05 equiv) was added dropwise, and the mixture was gradually warmed to room temperature, and allowed to stir for 3 hrs under a positive flow of N_2. The reaction mixture was dried *in vacuo*, then diluted with diethyl ether and water. The organic phase was removed and extracted three times with diethyl ether, combined, dried over magnesium sulfate and concentrated. The residue was purified on silica gel eluting with hexane, yielding an orange oil. (565 mg, 1.35 mmol, 75% yield).

^{1}H NMR (400 MHz, Me_4Si, $CDCl_3$) δ 7.58 – 7.54 (m, 4H), 7.34 – 7.28 (m, 4H), 7.24-7.22 (m, 2H), 3.37 (s, 3H), 1.91 (d, $^{3}J_{HH}$ = 12.9 Hz, 2H), 1.77 (br, 8H)*, 1.68 (d, $^{3}J_{HH}$ = 12.9 Hz, 2H)*, 1.44-1.11 (m, 10H).
***partially overlapped**

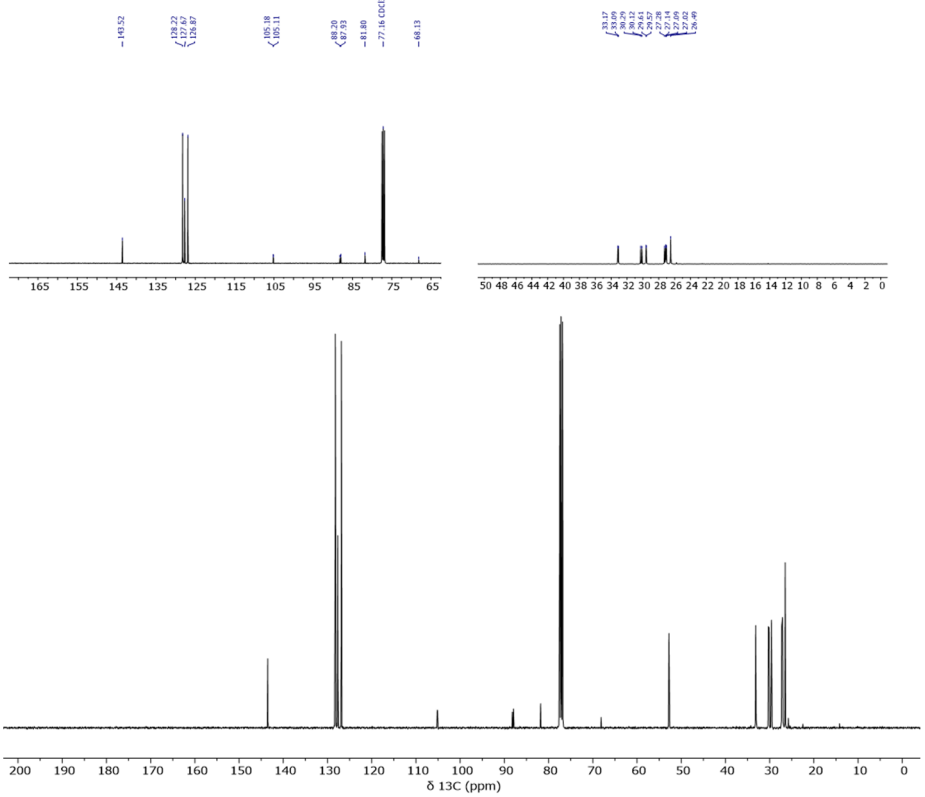
^{13}C{^{1}H} NMR (101 MHz, Me_4Si, $CDCl_3$): 143.5 (s, -C(OCH_3)(C_6H_5)$_2$ (ipso-C)), 128.2, 127.7 and 126.9 (s, aryl carbons of -C(OCH_3)(C_6H_5)$_2$), 105.2 (d, $^{2}J_{PC}$ =6.5, P-C≡*C*), 88.7 (d, $^{1}J_{PC}$ = 27.2 Hz, P-*C*≡C), 81.8 (s, ≡C-*C*(OCH_3)(C_6H_5)$_2$), 52.8 (s, P-O*C*H_3), (P-Cy: 33.1 (d, *J* = 8 Hz) 30.2 (d, J = 17.4 Hz), 29.6 (d, *J* = 4.5 Hz), 27.2 (d, *J* = 13.9 Hz), 27.1 (d, *J* = 6.9 Hz), 26.5 (s)), ppm.

^{31}P{^{1}H} NMR (162 MHz, H_3PO_4, $CDCl_3$) δ -21.9.

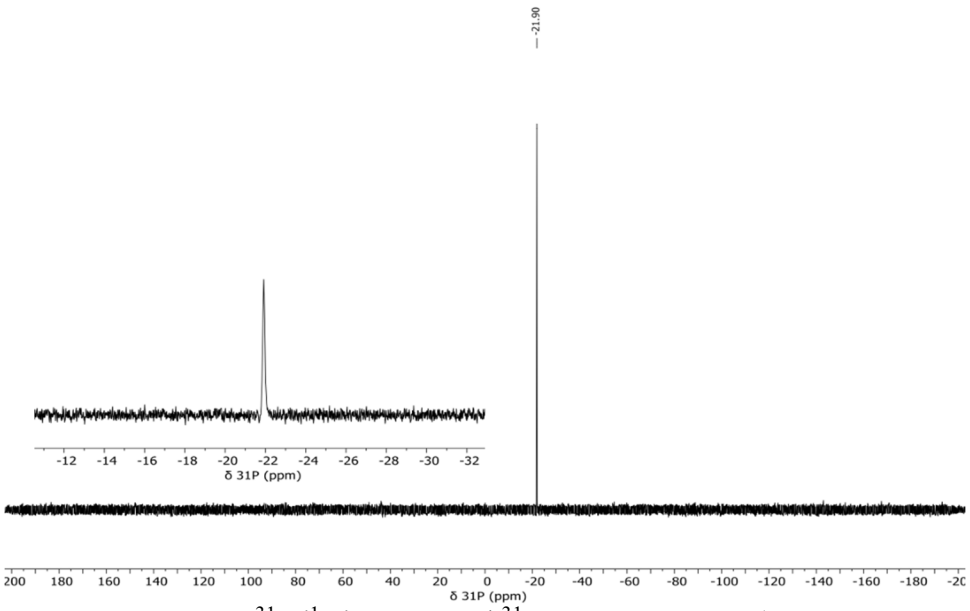
HRMS: (DART^{+}) *m/z* calculated for {M+H}$^{+}$ **:** 419.2498, Found: 419.2505



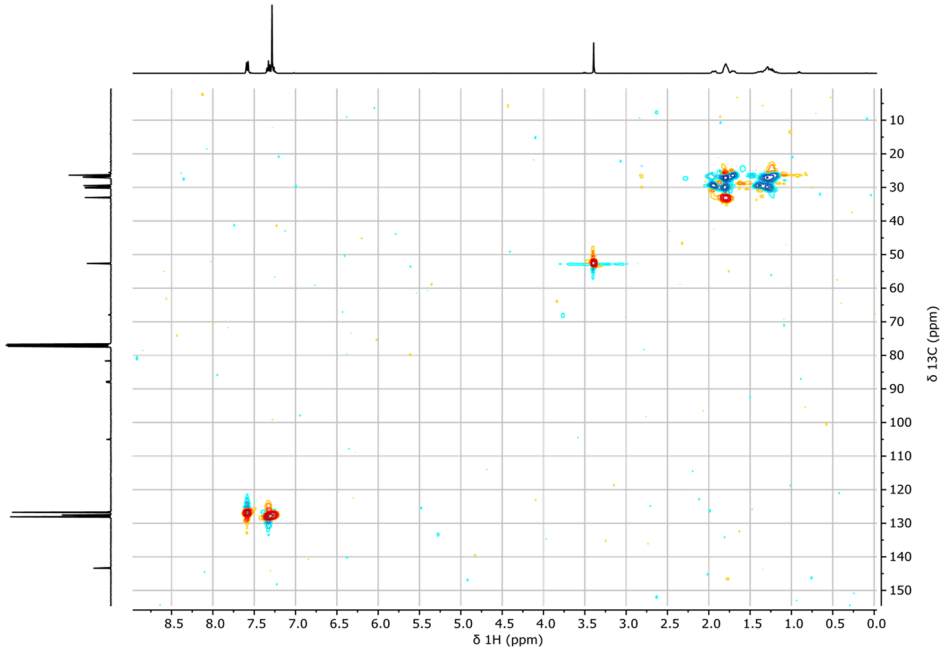
Supplementary Figure 2-A: ^{1}H NMR spectrum (400 MHz, Me_4Si) of **2** in $CDCl_3$ at 299 K. Residual ethyl acetate in sample*



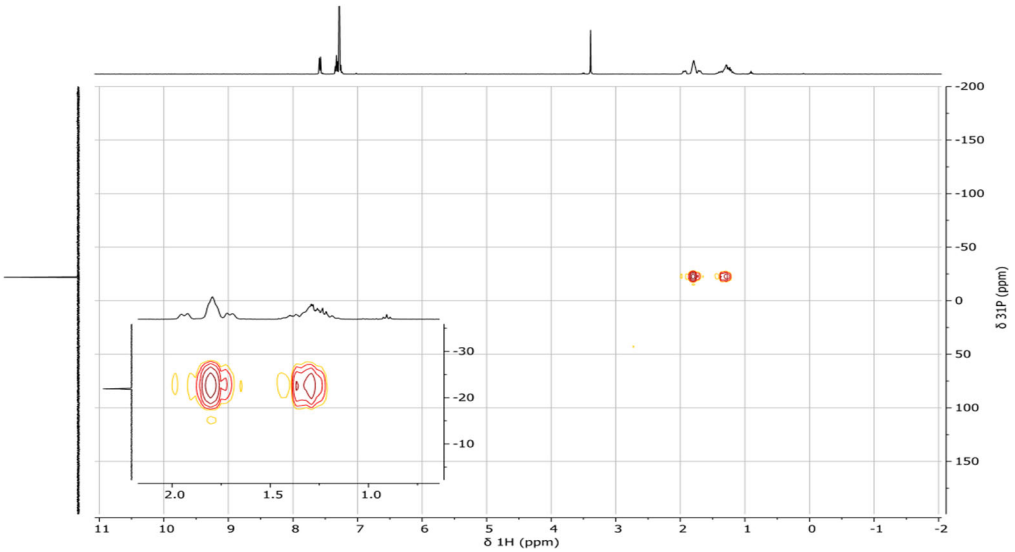
Supplementary Figure 2-B: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Me_4Si) of **2** in $CDCl_3$ at 299 K. Residual THF in NMR solvent at 68.13 and 25.77 ppm.



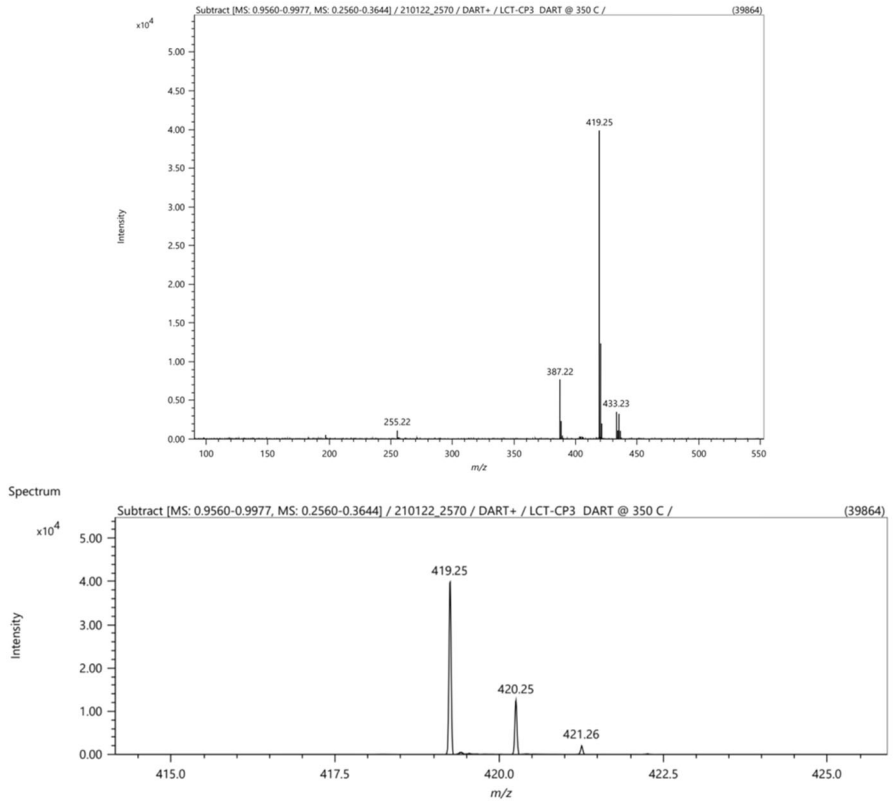
Supplementary Figure 2-C: $^{31}P\{^{1}H\}$ NMR and ^{31}P NMR spectrum (121 MHz, H_3PO_4,) of **2** in $CDCl_3$ at 291 K.



Supplementary Figure 2-D: 2D HSQC DEPT (^{1}H x ^{13}C) NMR spectrum (400 MHz, 101 MHz) of **2** in $CDCl_3$ at 298 K.

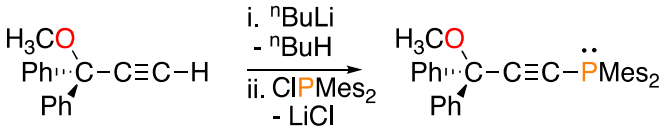


Supplementary Figure 2-E: 2D HMBC (^{1}H x ^{31}P) NMR spectrum (400 MHz, 162 MHz) of **2** in $CDCl_3$ 299 K.



Supplementary Figure 2-F: Mass spectrometry report, **[**M+H]$^{+}$ of **2** using DART in positive ion mode.

P,P-dimesytl-3,3-diphenyl-3-methoxy-propynyl-phosphane (**3**)



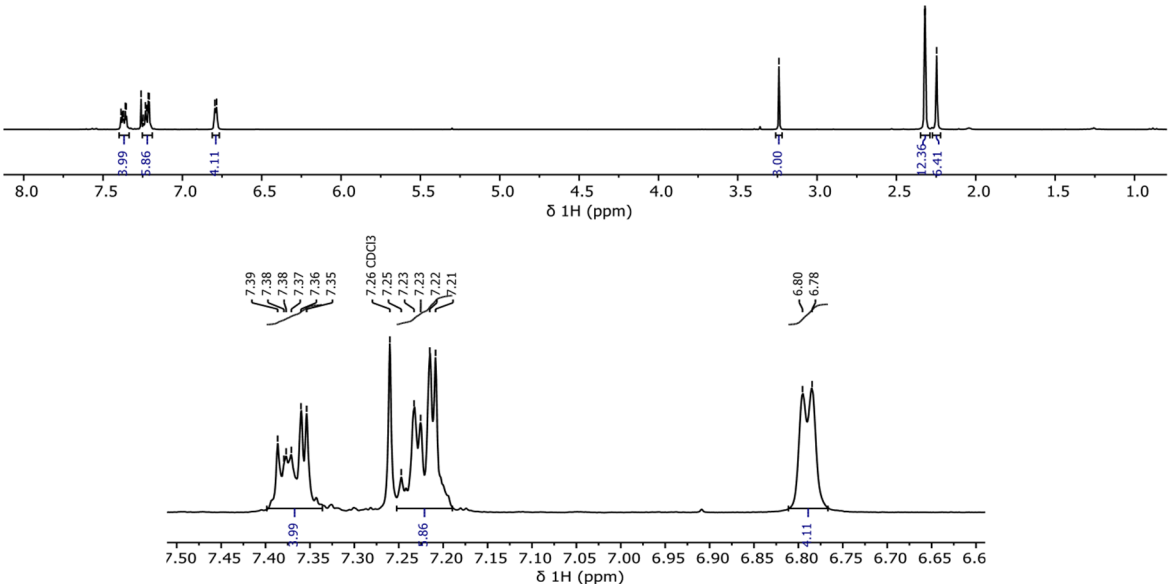
^{n}BuLi (1.65 mL, 1.6M in hexanes, 2.64 mmol, 1.15 equiv) was added dropwise to a solution of 1,1'-(3-methoxyprop-1-yne-3,3-diyl) dibenzene (0.511 mg, 2.3 mmol) in THF (10 ml) at -78 ˚C. The mixture was allowed to warm to 25 ˚C and stirred for 1 hr. Bis(2,4,6-trimethylphenyl) phosphorus chloride (735 mg, 2.41 mmol, 1.05 equiv) was added dropwise, and the mixture was gradually warmed to room temperature, and allowed to stir for 3 hrs under a positive flow of N_2. The reaction mixture was dried *in vacuo*, then diluted with diethyl ether and water. The organic phase was removed and extracted three times with diethyl ether, combined, dried over magnesium sulfate and concentrated. The residue was purified on silica gel eluting with pure hexane, then washed with cold ethanol yielding a white solid. (335 mg, 0.68 mmol, 30% yield).

^{1}H NMR (300 MHz, Me_4Si, $CDCl_3$) δ 7.37 (m, 4H), 7.22 (m, 6H), 6.79 (d, $^{4}J_{PH}$ = 3.3 Hz, 4H), 3.24 (s, 3H), 2.32, (s, 12H), 2.25 (s, 6H).

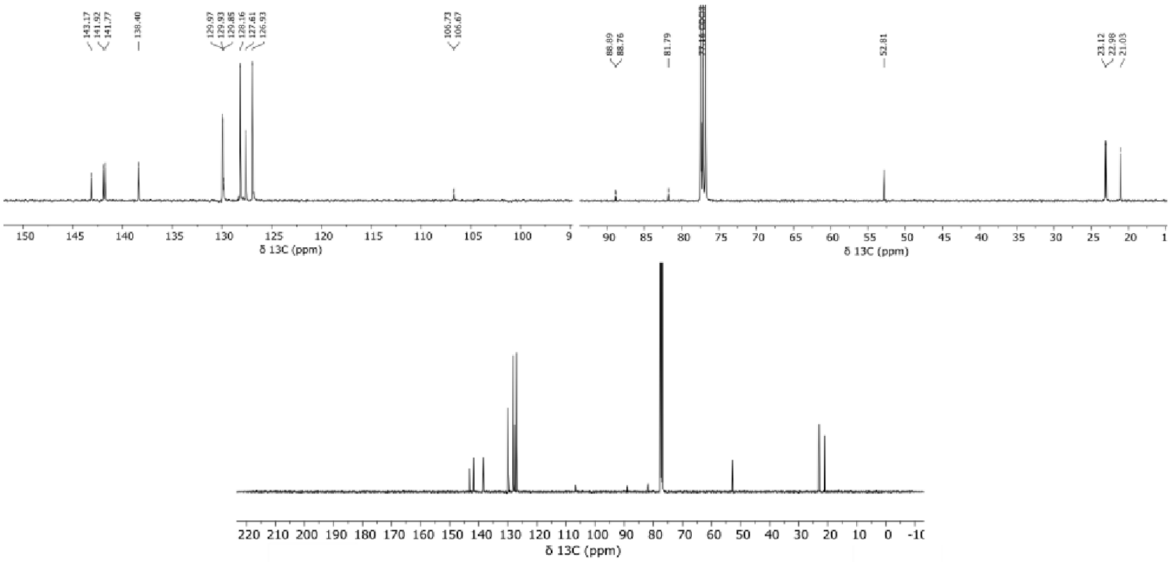
^{13}C{^{1}H} NMR (101 MHz, Me_4Si, $CDCl_3$) δ 143.1 ((s, -C(OCH_3)(C_6H_5)$_2$ (ipso-C)), 141.8 (d, $^{1}J_{PC}$ = 15.6 Hz, P-$C_6H_2(CH_3)_3$, (*ipso*-C)), 138.4 (s, P-$C_6H_2(CH_3)_3$, (*p*-C)), 129.97-93 (br, P-$C_6H_2(CH_3)_3$, (*m*-C)), 129.9 ($C_6H_2(CH_3)_3$, (*o*-C)), 128.2, 127.6, and 126.9 (s, aryl carbons of -C(OCH_3)(C_6H_5)$_2$), 106.7 (d, $^{2}J_{PC}$= 5.7 Hz, P-C≡*C*), 88.8 (d, $^{1}J_{PC}$ = 12.7 Hz, P-*C*≡C)), 81.8 (s, ≡C-*C*(OCH_3)(C_6H_5)$_2$), 52.8 (s, P-O*C*H_3), 23.1 (d, $^{3}J_{PC}$= 5.7 Hz, $C_6H_3(CH_3)_3$, (*o*-CH_3)), 21.0 (s, P-$C_6H_2(CH_3)_3$, (*p*-CH_3)).

^{31}P{^{1}H} NMR (121.49 MHz, H_3PO_4, $CDCl_3$) δ -57.9.

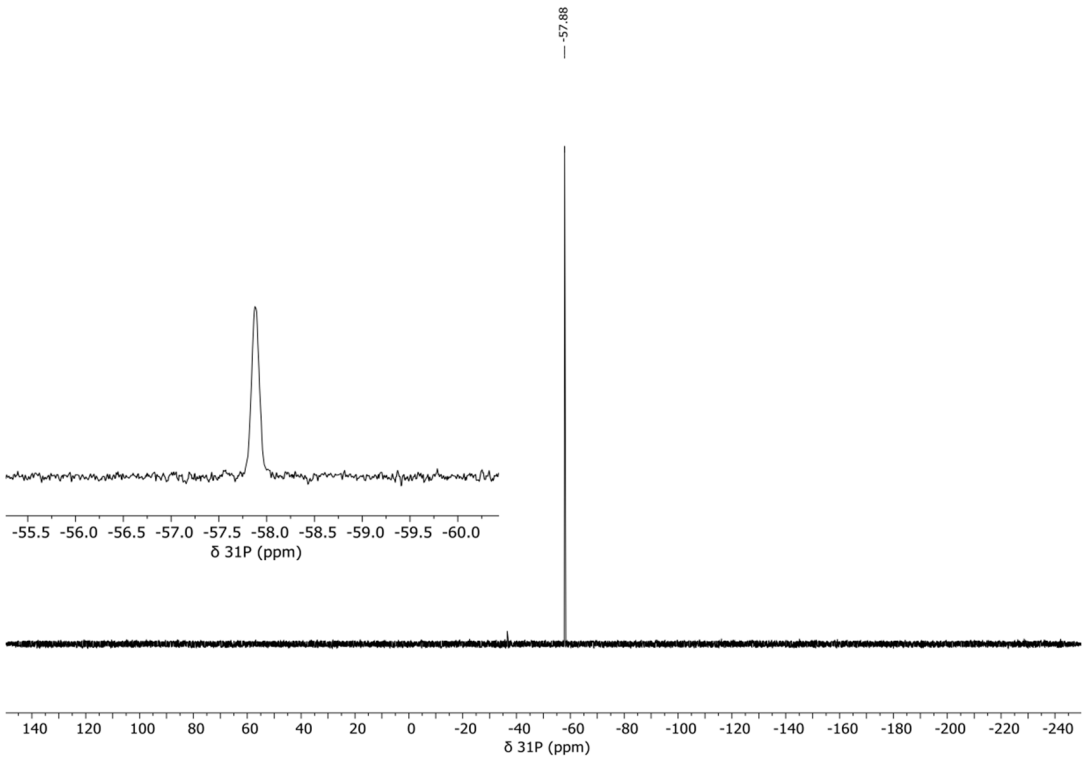
HRMS: (DART^{+}) *m/z* calculated for {M+H]$^{+}$ **:** 491.2498, m/z Found: 491.2504



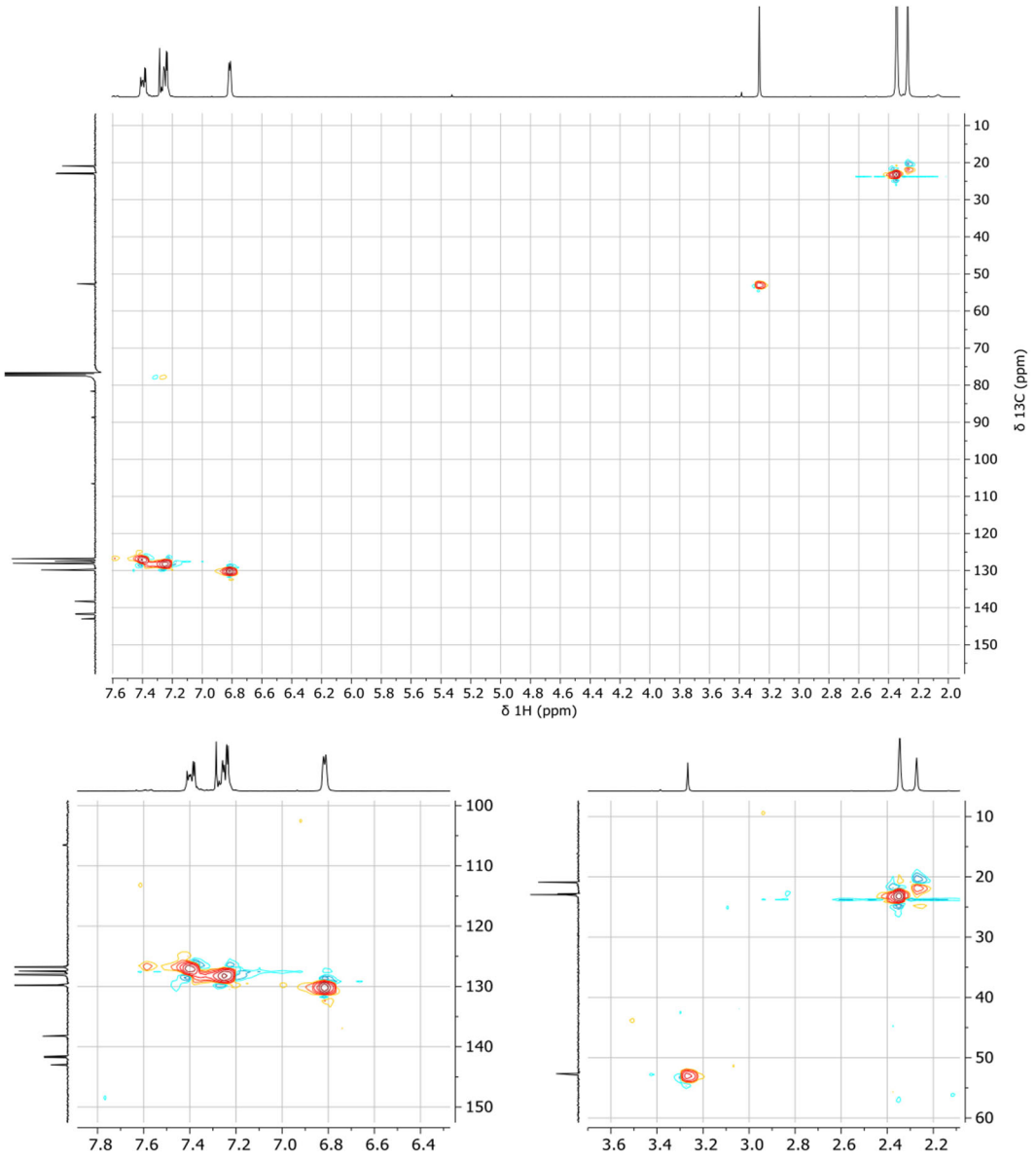
Supplementary Figure 3-A: 1H NMR spectrum (300MHz, Me4Si) of 3 in $CDCl_3$ at 291K



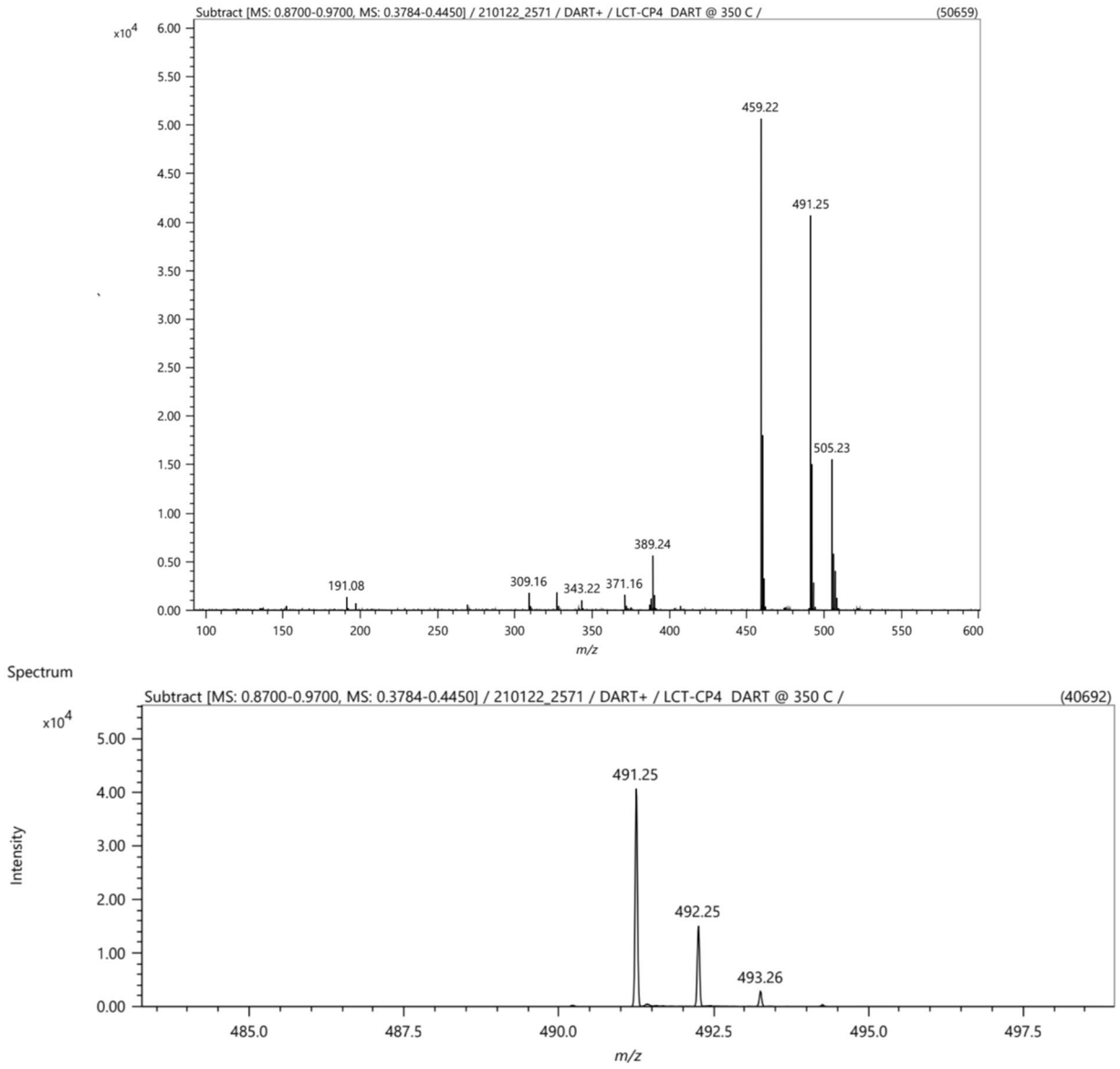
Supplementary Figure 3-B: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Me_4Si) of **3** in $CDCl_3$ at 301 K.



Supplementary Figure 3-C: $^{31}P\{^{1}H\}$ NMR and ^{31}P NMR spectrum (121 MHz, H_3PO_4,) of **3** in $CDCl_3$ at 291 K.

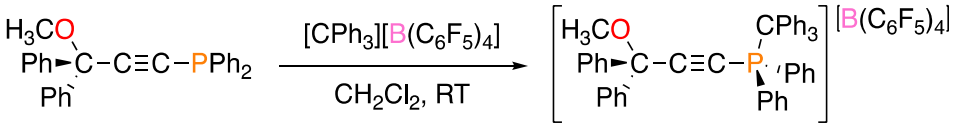


Supplementary Figure 3-D: 2D HSQC DEPT (^{1}H x ^{13}C) NMR spectrum (400 MHz, 101 MHz) of **3** in $CDCl_3$ at 301 K.



Supplementary Figure 3-F: Mass spectrometry report, $[M+H]^+$ of **3** using DART in positive ion mode.

[1 CPh_3][$B(C_6F_5)_4$]



1 (12.19 mg, 0.03 mmol) and [CPh_3][$B(C_6F_5)_4$] (27.67 mg, 0.03 mmol) were dissolved in CH_2Cl_2 and stirred for 16 hrs at room temperature. Solvent was removed *in vacuo*. Crude material was rinsed with pentane, yielding a green solid. (33.7 mg, 0.025 mmol, 84% yield).

^{1}H NMR (400 MHz, Me_4Si, CD_3CN) δ 7.76 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H), (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 3H), (dd, $^3J_{H\text{–}H}$ = 8 Hz, $^4J_{P\text{–}H}$ = 4 Hz, 4H) 7.42-7.34 (m, 12H), 7.34-7.26 (m, 2H), 7.26-7.12 (m, 12H), 3.24 (s, 3H).

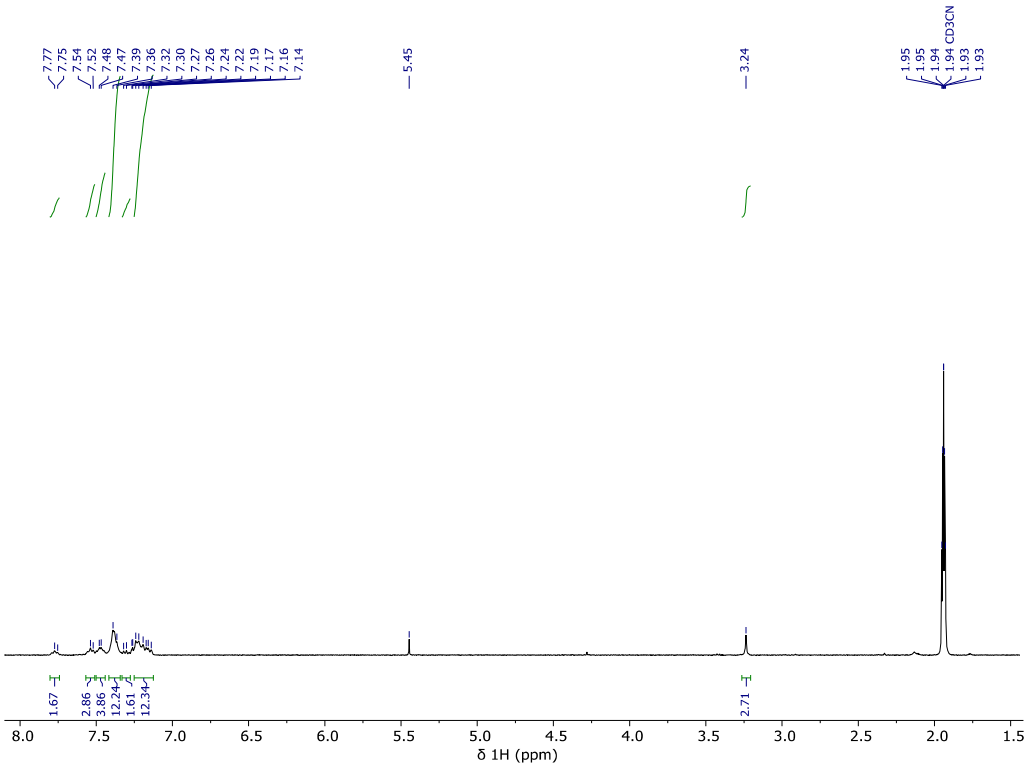
^{11}B{^{1}H} NMR (128 MHz, BF_3-OEt_2, C_6D_6) δ -15.9 (s) ppm.

^{13}C{^{1}H} NMR partial (176 MHz, Me_4Si, $CDCl_3$) 148.3 (dm, $^1J_{CF}$ = 242 Hz, B(C_6F_5)$_4$ (o-C)), 139.5 (s, -C(OCH_3)(C_6H_5)$_2$ (ipso-C)), 138.3 (dm, $^1J_{CF}$ = 244 Hz, B(C_6F_5)$_4$ (p-C)), 136.4 (dm, $^1J_{CF}$ =242 = Hz, B(C_6F_5)$_4$ (m-C)), 135.8 (d, $^3J_{PC}$ = 3.2 (CPh_3, ipso-C), 134.2 (d, $^2J_{PC}$ = 10 Hz, P(C_6H_5)$_2$ (o-C)), 131.4 (d, $^4J_{PC}$ = 6.8 Hz, P(C_6H_5)$_2$ (p-C)), 130.4 (d, $^3J_{PC}$ = 6.8 Hz, P(C_6H_5)$_2$ (m-C)), 129.5 (s, br (*o*, *m*, *p*-C), 129.4, 129.1, and 126.7 (s, C_{aryl} of -C(OCH_3)(C_6H_5)$_2$), 119.8 (d, $^1J_{PC}$ = 85 Hz, P(C_6H_5)$_2$ (ipso-C)), 119.4 (d, $^2J_{PC}$ = 17.8 Hz, P-C≡*C*) 82.5 (d, $^3J_{PC}$ = 2.5 Hz, ≡C-*C*(OCH_3)(C_6H_5)$_2$), 73.3 (d, $^1J_{PC}$ = 162 Hz, P-*C*≡C)) 67.8 (d, $^1J_{PC}$ = 45.1 Hz, CPh_3), 53.7 (s, -O*C*H_3) ppm. B(C_6F_5)$_4$ (*ipso*-C) not observed.

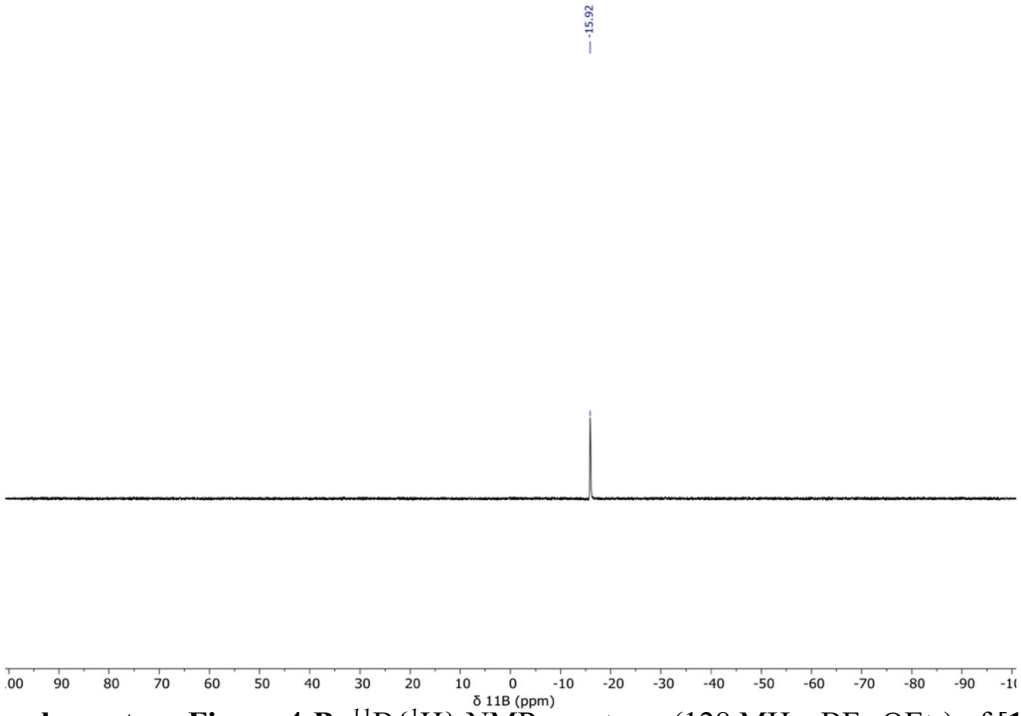
^{19}F{^{1}H} NMR (282 MHz, BF_3-OEt_2, $CDCl_3$) δ -132.56 (br, 8F, (o-F)), -163.18 (t, $^3J_{FF}$ = 21 Hz, 4F (p-F)), -166.88 (t, 20 Hz, 8F (m-F)) ppm.

^{31}P{^{1}H} NMR (162 MHz, H_3PO_4, C_6D_6) δ 10.7 (s) ppm.

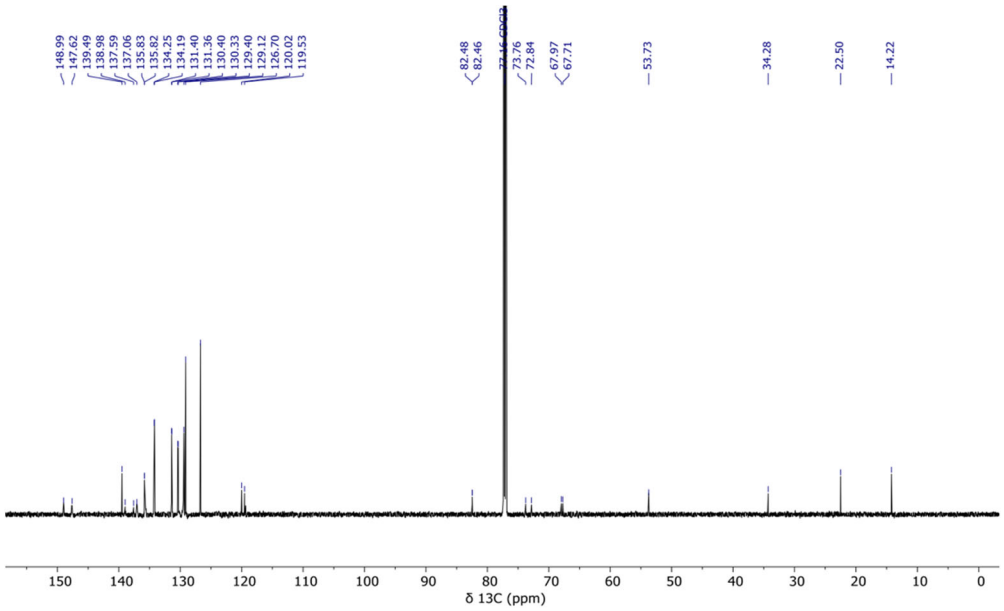
EA: Calculated (%): C, 64.18; H, 2.88. Found (%): C, 65.10; H, 2.51.



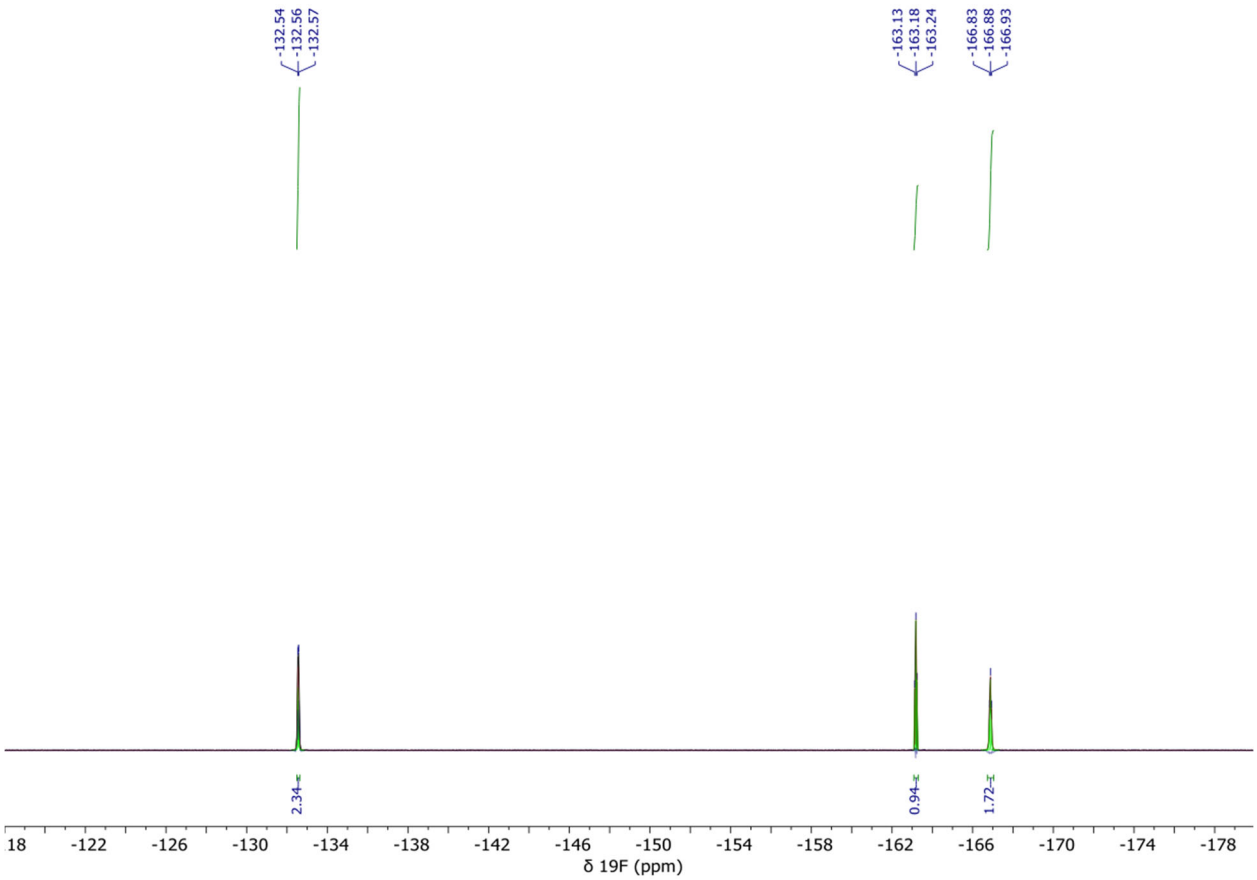
Supplementary Figure 4-A: ^{1}H NMR spectrum (400 MHz, Me_4Si) of [**1** CPh_3][$B(C_6F_5)_4$] in CD_3CN at 297 K. Residual CH_2Cl_2 at δ 5.45 ppm.



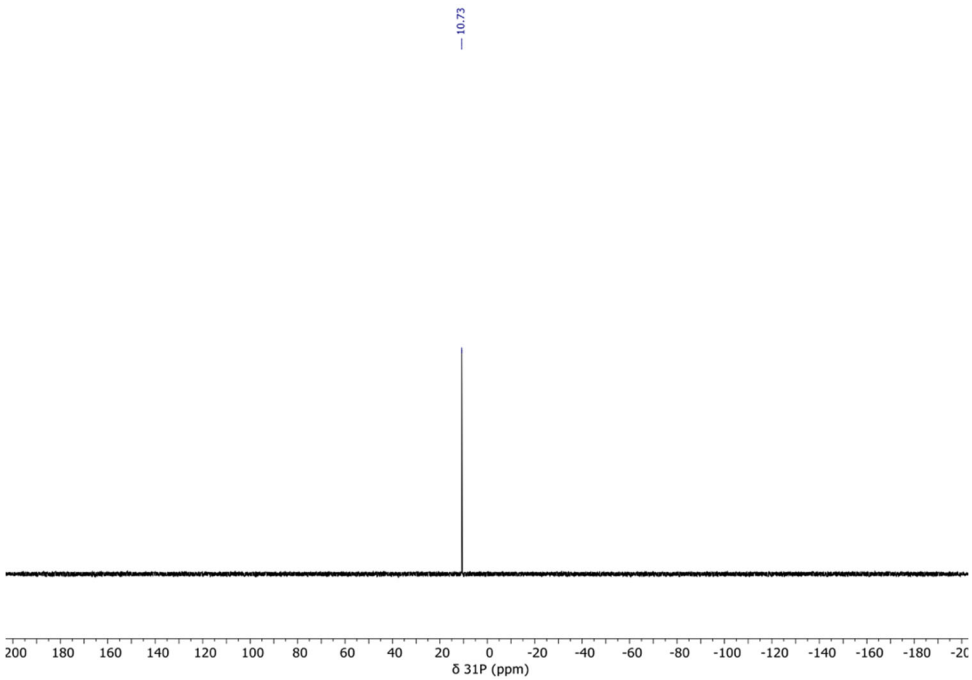
Supplementary Figure 4-B: $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, BF_3-OEt_2) of [**1** CPh_3][$B(C_6F_5)_4$] in C_6D_6 at 297 K.



Supplementary Figure 4-C: $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, Me_4Si, $CDCl_3$) of [**1** CPh_3][$B(C_6F_5)_4$] in $CDCl_3$ at 298 K. Residual pentane at indicated by peaks at δ 34.38, 22.50 and 14.22 ppm.

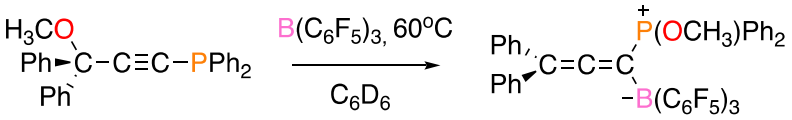


Supplementary Figure 4-D: $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, BF_3-OEt_2) of [**1**CPh_3][$B(C_6F_5)_4$] in $CDCl_3$ at 298 K.



Supplementary Figure 4-E: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, H_3PO_4) of [**1** CPh_3][$B(C_6F_5)_4$] in C_6D_6 at 296.6 K.

Diphenylmethoxy-phosphonium borate zwitterion(**4**)



NMR Scale

An equimolar amount of **1** (8.13 mg, 0.02 mmol) and $B(C_6F_5)_3$ (10.23 mg, 0.02 mmol) were dissolved in deuterated benzene (600 uL) and transferred to an NMR tube equipped with a J-young Teflon tap. The tube was heated at 60 ˚C with constant agitation for 3 hours. ^{1}H and ^{31}P NMR analysis indicated quantitative conversion to **4.**

Preparative Scale

An equimolar amount of **1** (81.35 mg, 0.2 mmol) and $B(C_6F_5)_3$ (100.23 mg, 0.2 mmol) were dissolved in 3 mL of benzene, gradually heated to 60 ˚C and stirred for 8 hrs under a positive flow of N_2. Solvent was removed *in vacuo* and the product was washed with a generous amount of pentane, yielding a bright yellow/green solid (123.4 mg, 0.13 mmol, 68% yield).

^{1}H NMR: (300 MHz, Me_4Si, C_6D_6) δ 7.03 (m, 9H), 6.98 - 6.90 (m, 5H), 6.91– 6.82 (m, 2H), 6.72 (td, $^{3}J_{HH}$ = 7.7, 3.6, 4H), 2.93 (d, $^{3}J_{PH}$ = 11.4 Hz, 3H), ppm.

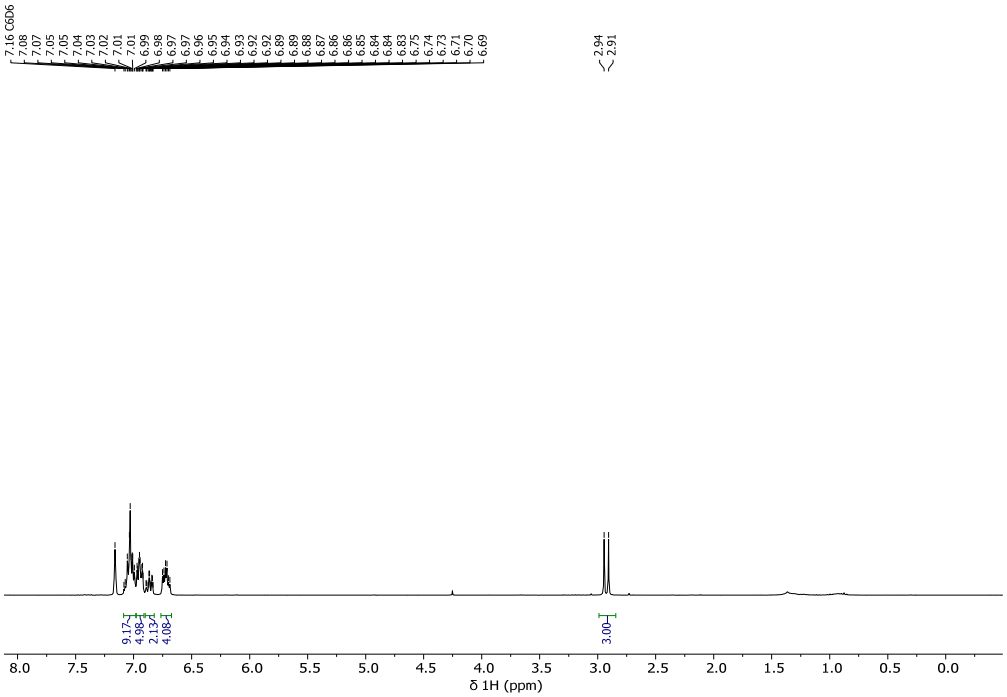
$^{11}B\{^{1}H\}$ NMR (96 MHz, BF_3-OEt_2, C_6D_6) δ -13.6 ppm.

$^{13}C\{^{1}H\}$ NMR partial: (100.68 MHz, Me_4Si, C_6D_6) δ 214.0 (s, C2 allene), 149.1 (dm, $^{1}J_{CF}$ = 240 Hz, -$B(C_6F_5)_3$, (o-F)), 139.6 (dm, $^{1}J_{CF}$ = 244 Hz, -$B(C_6F_5)_3$, (p-F)), 137.2 (dm, $^{1}J_{CF}$ = 238 Hz, -$B(C_6F_5)_3$, (m-F)), 136.4 (d, $^{4}J_{PC}$ = 3.0 Hz, P(C_6H_5)$_2$ (*p*-C)), 134.6 (d, $^{1}J_{PC}$ = 10 Hz, C1 allene), 132.3 (d, $^{2}J_{PC}$ = 10.8 Hz, P(C_6H_5)$_2$ (*o*-C)), 129.1 (d, $^{3}J_{PC}$ = 12.8 Hz, P(C_6H_5)$_2$ (*m*-C)), 128.9 (d, *J* = 5 Hz), 128.9, 122.9 (d, $^{1}J_{PC}$ = 99 Hz, P(C_6H_5)$_2$ (*ipso*-C)), 110.3 (d, $^{3}J_{PC}$ = 24.2 Hz, C3 allene), 57.6 (d, $^{2}J_{PC}$ = 11.1 Hz, P-O*C*H_3)

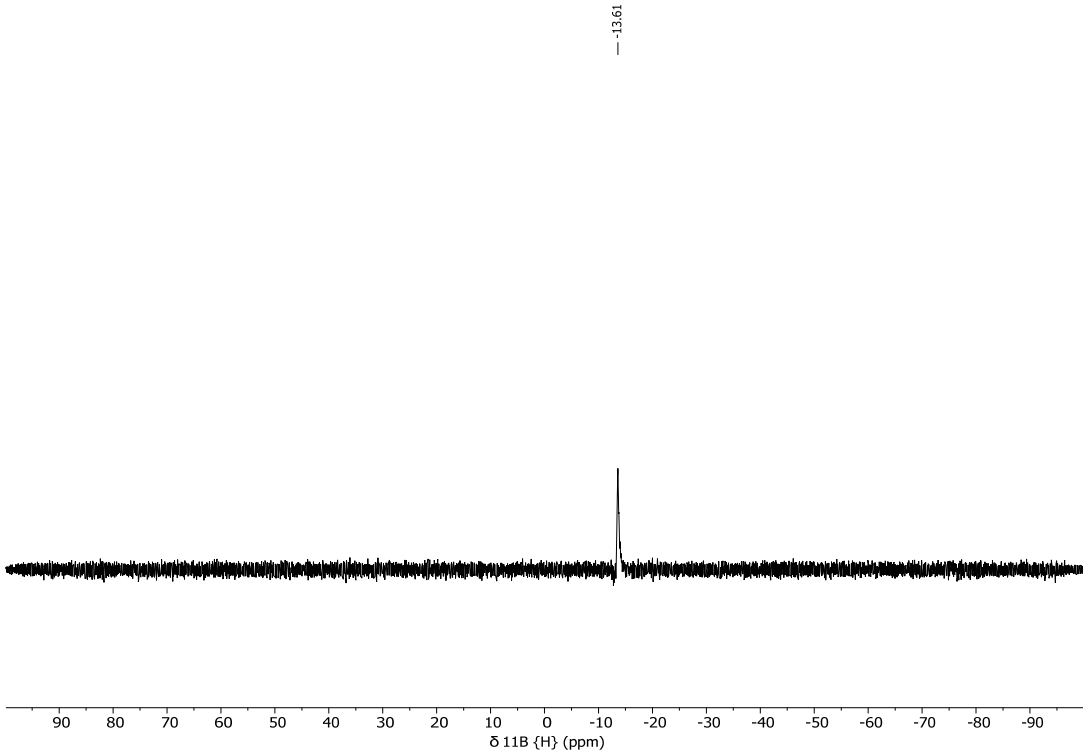
$^{19}F\{^{1}H\}$ NMR: (101 MHz, BF_3-OEt_2, C_6D_6) δ -129.62 (s, br, (*o*-F), 6F), -159.73 (t, *J* = 21 Hz (*p*-F) 3F) -165.10 (dt, br, (*m*-F) 6F) ppm.

$^{31}P\{^{1}H\}$ NMR (121 MHz, H_3PO_4, C_6D_6) δ 67.0 ppm.

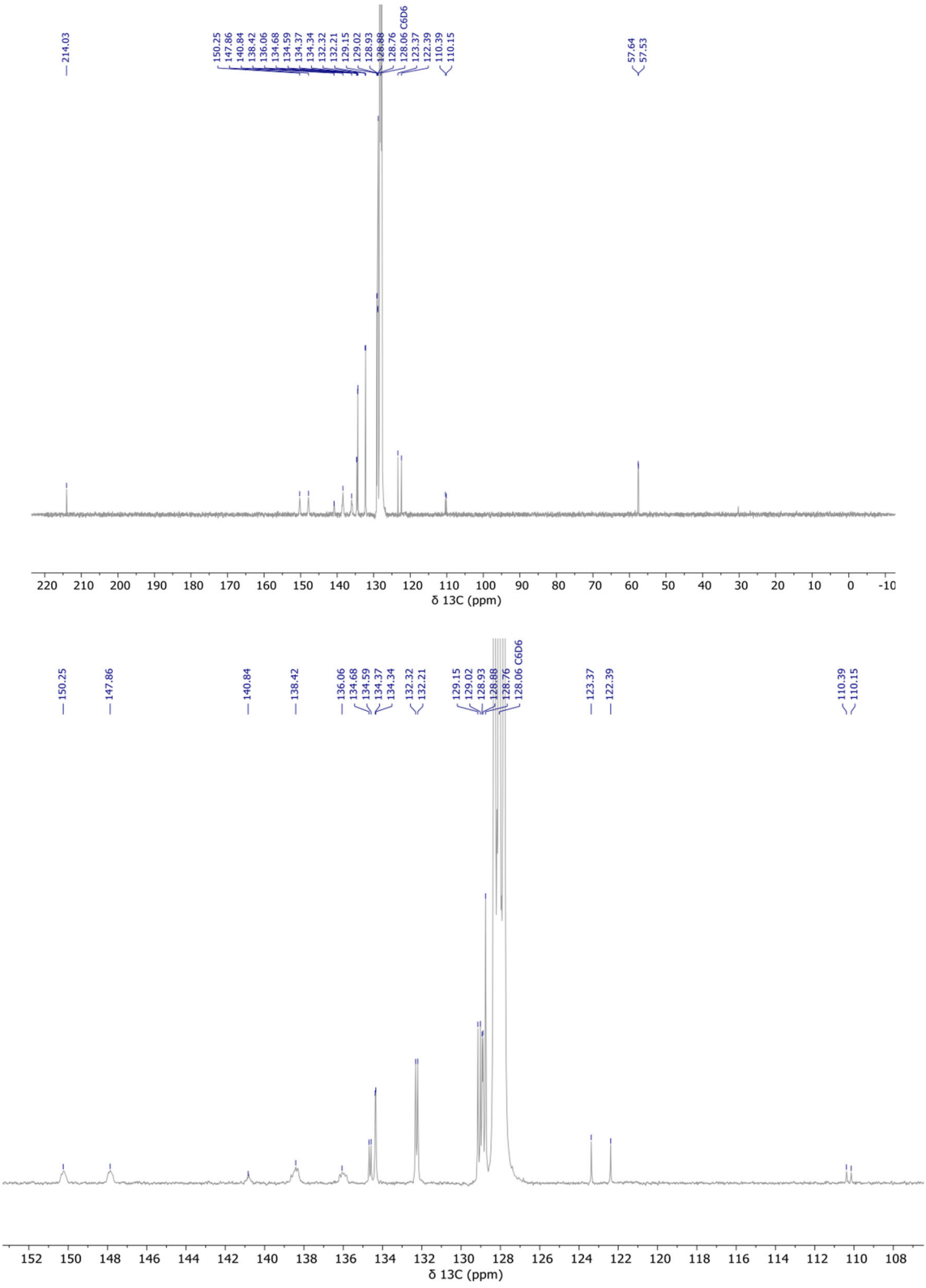
EA: Calculated (%): C, 60.16; H, 2.52. Found (%): C, 59.58; H, 3.19 (averaged over four samples).



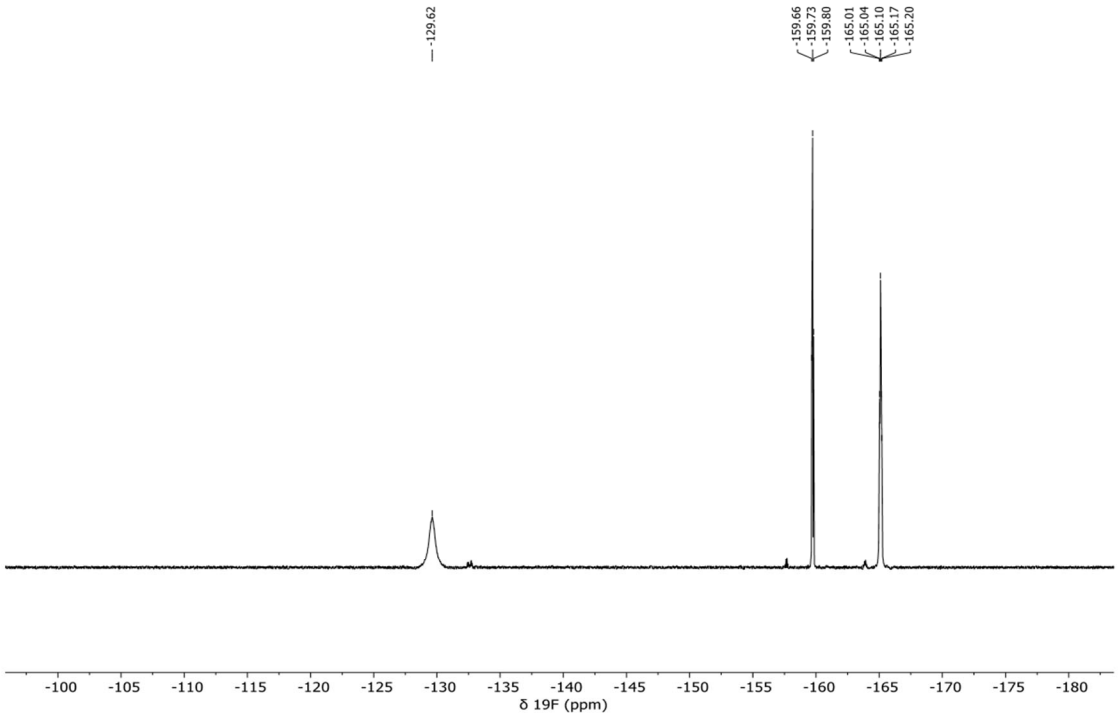
Supplementary Figure 5-A: ^{1}H NMR spectrum (300 MHz, Me_4Si) of **4** in C_6D_6 at 290 K.



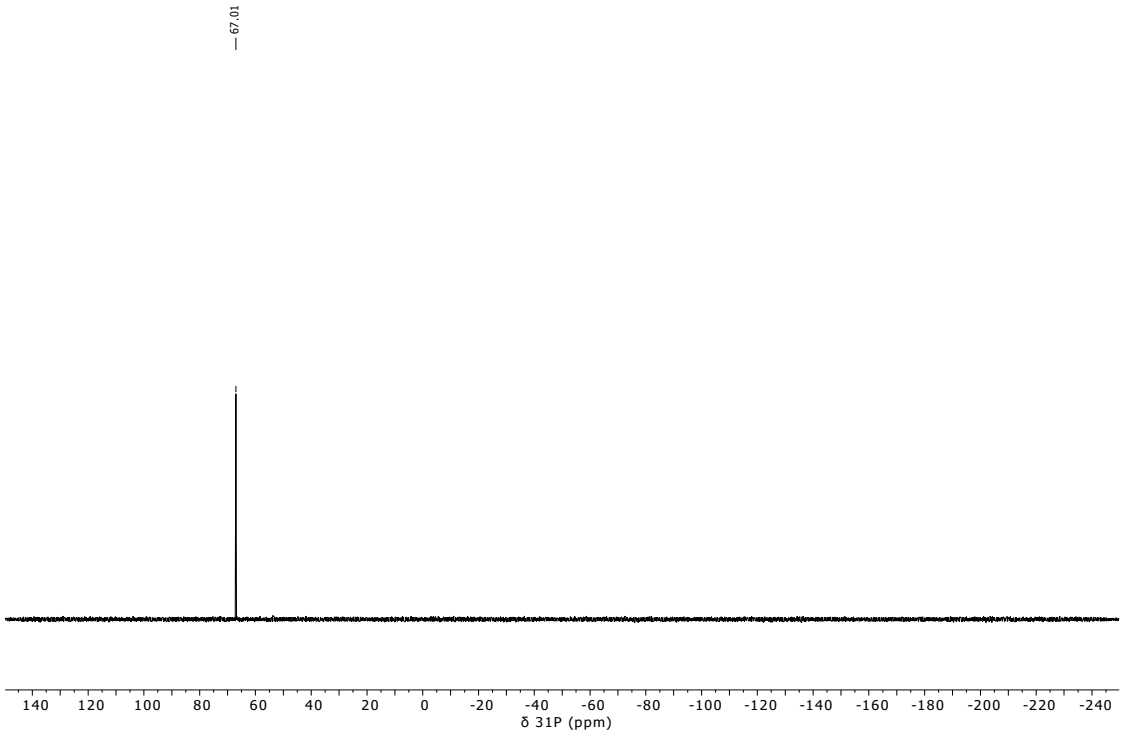
Supplementary Figure 5-B: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, Me_4Si) of **4** in C_6D_6 at 291 K.



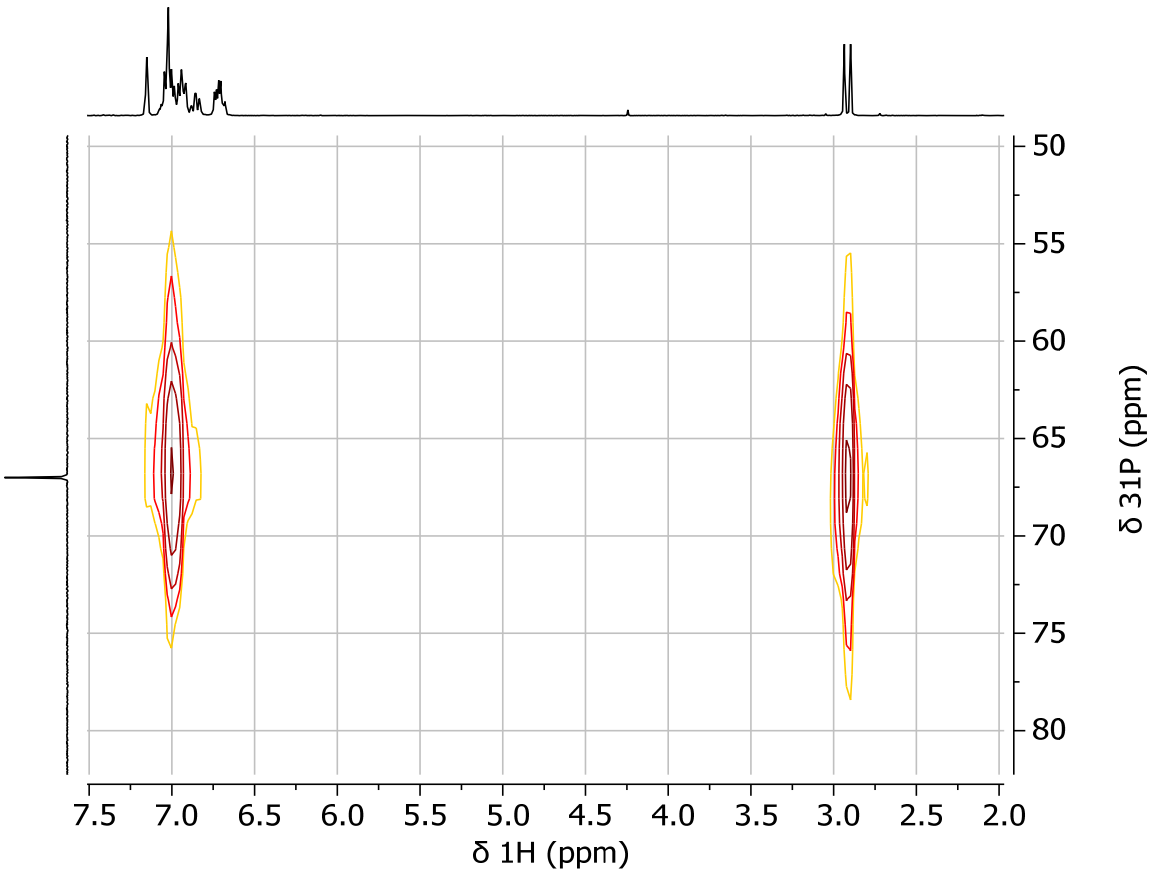
Supplementary Figure 5-C: $^{13}C\{^{1}H\}$ NMR spectrum (100.68 MHz, Me_4Si) of **4** in C_6D_6 at 300 K.



Supplementary Figure 4-D: $^{19}F\{^{1}H\}$ NMR spectrum (101 MHz, Me_4Si) of **4** in C_6D_6 at 291 K.

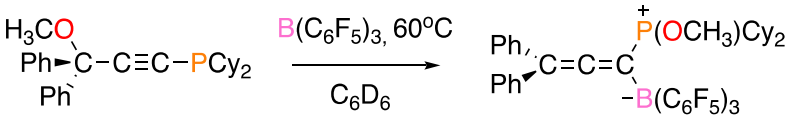


Supplementary Figure 5-E: $^{31}P\{^{1}H\}$NMR (121 MHz, H_3PO_4,) of **4** in C_6D_6 at 291 K.



Supplementary Figure 5-F: 2D HMBC (^{1}H x ^{31}P) NMR spectrum (400 MHz, 162 MHz) of **4** in C_6D_6 300 K.

Dicyclohexylmethoxy-phosphonium borate zwitterion (**5**)



NMR Scale

An equimolar amount of **2** (8.37 mg, 0.02 mmol) and $B(C_6F_5)_3$ (10.23 mg, 0.02 mmol) were dissolved in 600 uL of deuterated benzene and transferred to an NMR tube equipped with a J-Young Teflon tap. The tube was constantly agitated for 3 hr. ^{1}H and ^{31}P NMR analysis indicated quantitative conversion to **5.**

Preparative Scale

An equimolar amount of **2** (41.85 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51.15 mg, 0.1 mmol) were dissolved in 3 mL of benzene, gradually heated to 60 ˚C and stirred for 3 hrs under a positive flow of N_2. Solvent was removed *in vacuo* and the product was washed with pentanes, yielding a yellow/orange solid (59.0 mg, 0.063 mmol, 63% yield).

In situ analysis **^{1}H NMR** (300 MHz, Me_4Si, C_6D_6) 2.71 (d, $^{3}J_{PH}$= 10.2 Hz, 3H)*
*for comparison of -OC*H*$_3$ resonance

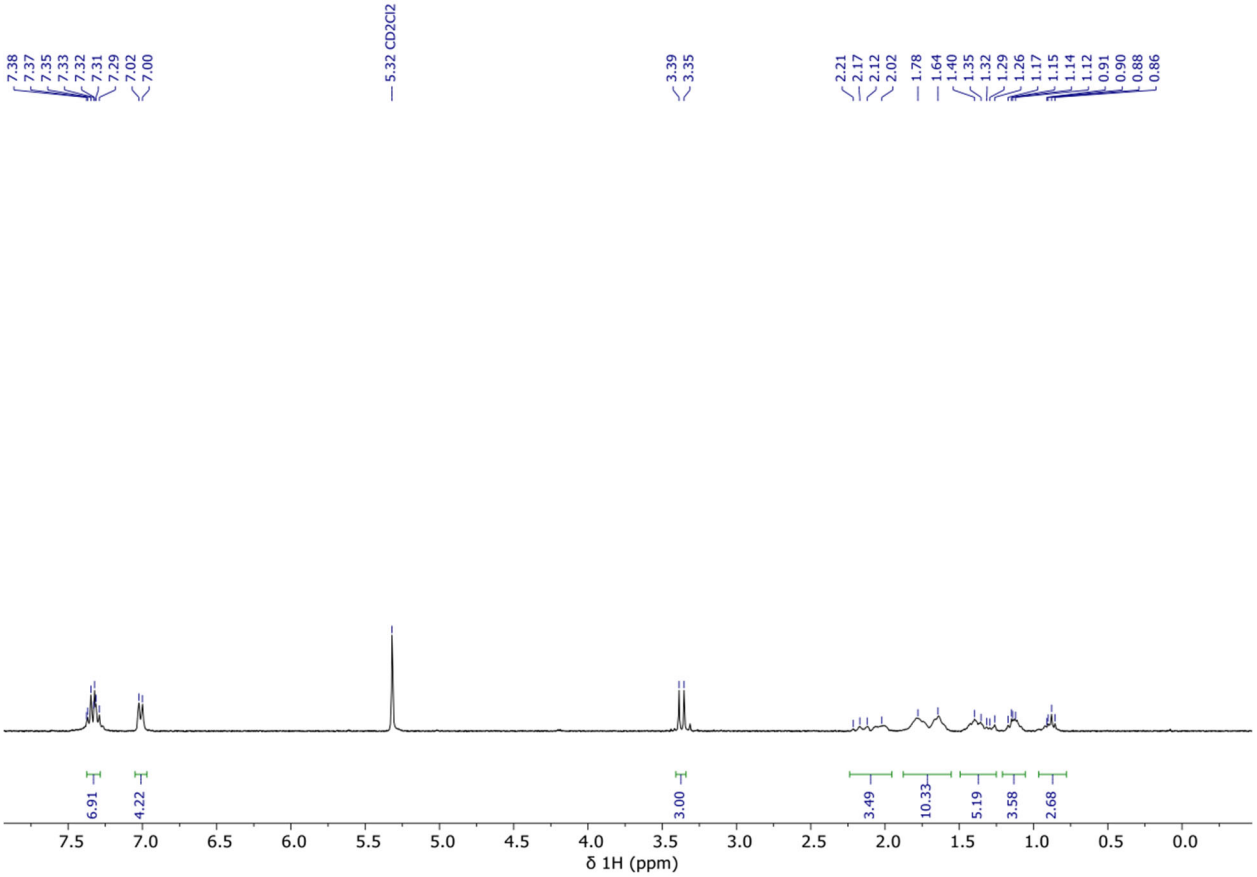
^{1}H NMR (300 MHz, Me_4Si, CD_2Cl_2) 7.49-7.16 (m, 6H), 7.01 (d, *J*= 7.3 Hz, 4H), 3.37 (d, $^{3}J_{PH}$= 10.2 Hz, 3H), 2.23-1.93 (br, 3H) 1.52-1.89 (br, 10H) 1.47-1.23 (br, 5H), 1.19-1.03 (br, 4H), 0.99-0.79 (m, 3H)* ppm
*aliphatic protons corresponding to the -Cy substituents integrate higher than expected due to a pentane contaminant that could not be removed from the sample even with extended time under vacuum.

$^{11}B\{^{1}H\}$ NMR (128 MHz, BF_3-OEt_2, C_6D_6) δ -13.4 (s) ppm.

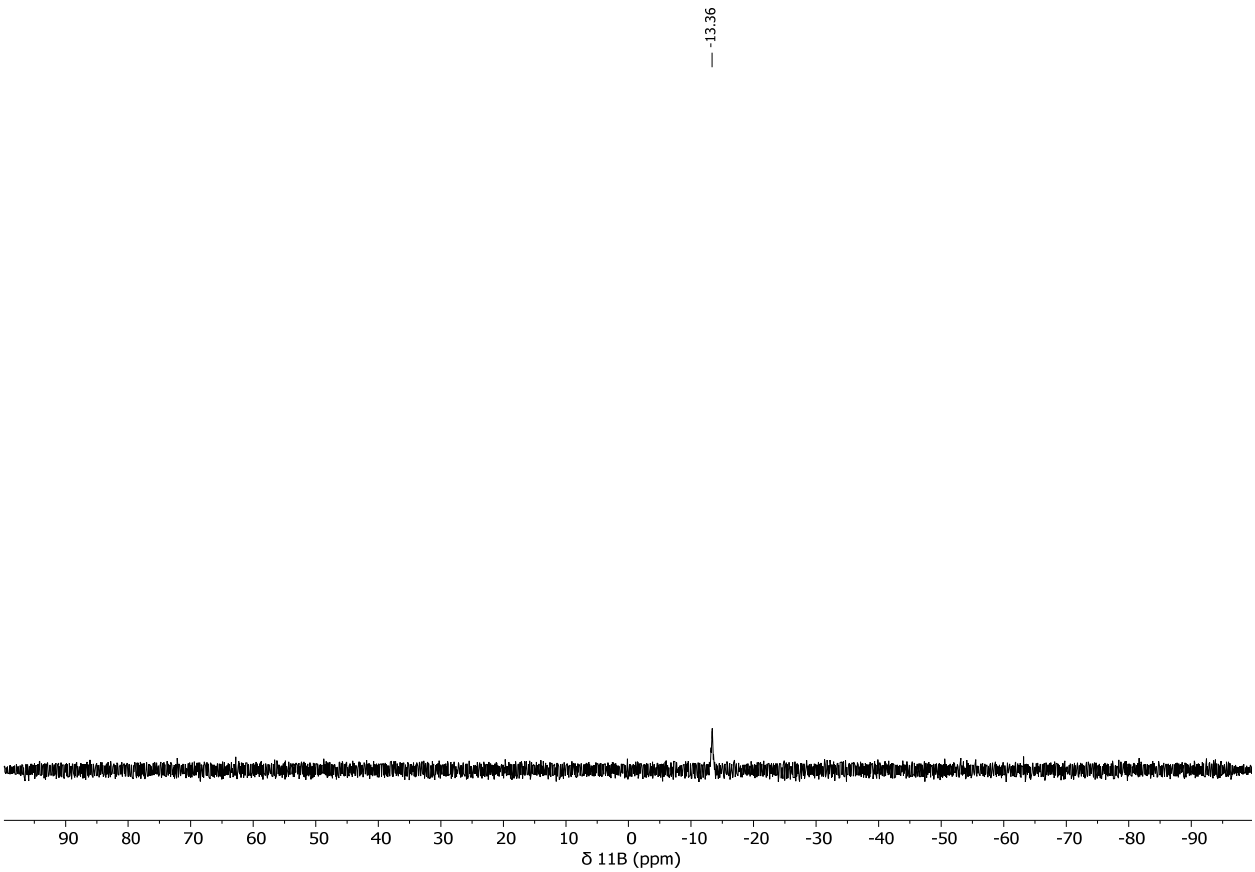
$^{13}C\{^{1}H\}$ NMR partial (101 MHz, Me_4Si, C_6D_6) δ 212.9 (s, C2 allene) 149.1 (dm, $^{1}J_{CF}$ = 241 Hz, -$B(C_6F_5)_3$, (o-F)), 139.8 (dm, $^{1}J_{CF}$ = 236 Hz, -$B(C_6F_5)_3$, (p-F)), 137.4 (dm, $^{1}J_{CF}$ = 236 Hz, -$B(C_6F_5)_3$, (m-F)), 134.8 (d, $^{1}J_{PC}$ = 8.1 Hz, C1 allene), 128.9 (d, *J* = 5 Hz), 128.8 (s), 108.9 (d, $^{3}J_{PC}$ = 20 Hz, C3 allene), 55.3 (d, $^{2}J_{PC}$ = 10.1 Hz, P-O*C*H_3), P-*Cy* carbons: 38.4 (d, *J* = 50.5 Hz) 27.15– 26.74 (overlapped), 25.6 (s) ppm.

$^{19}F\{^{1}H\}$ NMR (282 MHz, BF_3-OEt_2, C_6D_6) δ -128.7 (s, br, (*o*-F), 6F), -158.94 (t, $^{3}J_{FF}$ = 21 Hz (*p*-F) 3F) -164.90 (s, br, (*m*-F) 6F) ppm.

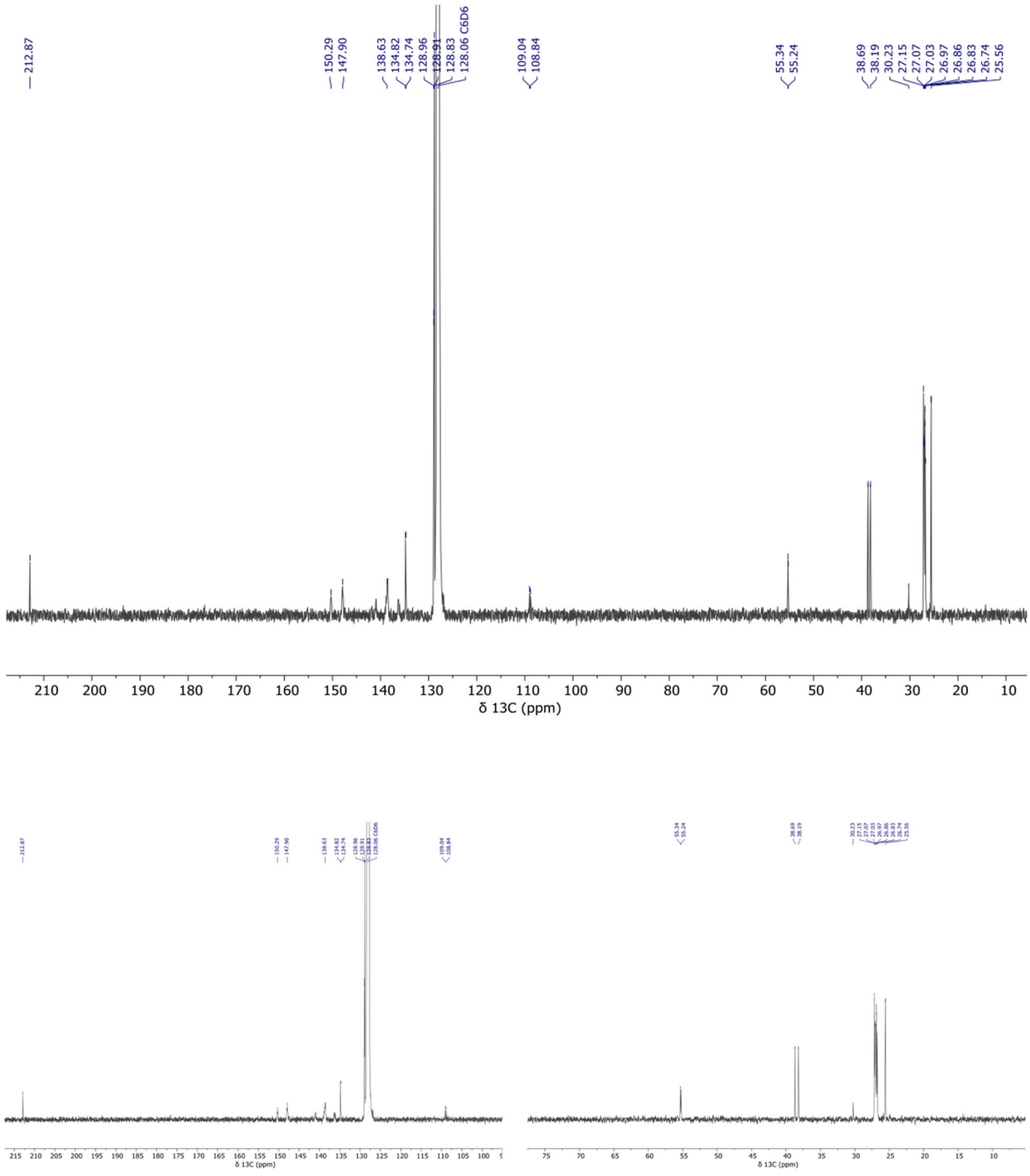
$^{31}P\{^{1}H\}$ NMR (162 MHz, H_3PO_4, C_6D_6) δ 82.8 ppm.
Elemental Analysis: Calculated (%): C, 59.37; H, 3.79. Found (%): C, 58.58; H, 3.27



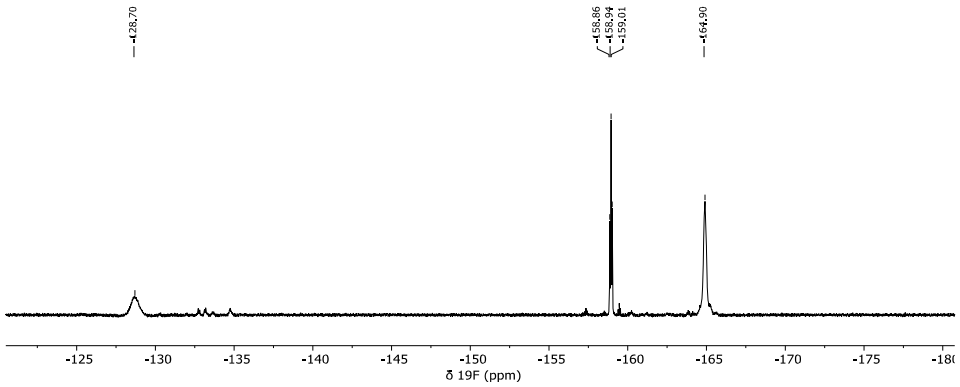
Supplementary Figure 5-A: ^{1}H NMR spectrum (300 MHz, Me_4Si) of **5** in CD_2Cl_2 at 298 K.



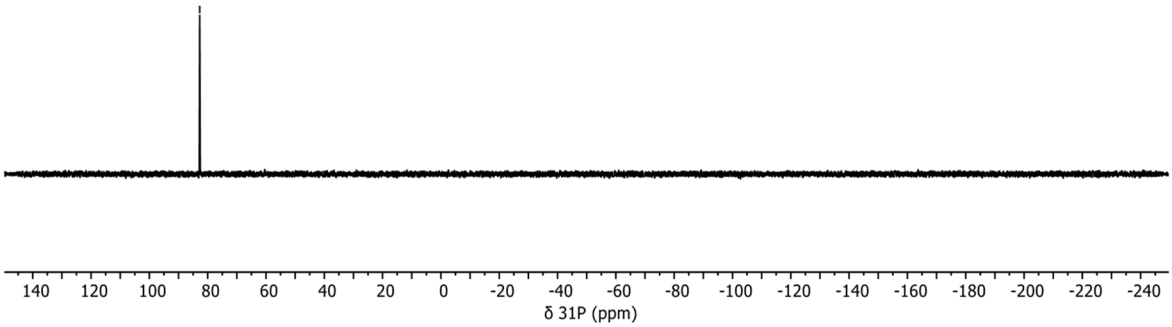
Supplementary Figure 5-B: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, Me_4Si) of **5** in C_6D_6 at 293 K.



Supplementary Figure 5-C: $^{13}C\{^{1}H\}$ NMR spectrum (100.68 MHz, Me_4Si) of **5** in C_6D_6 at 301K.

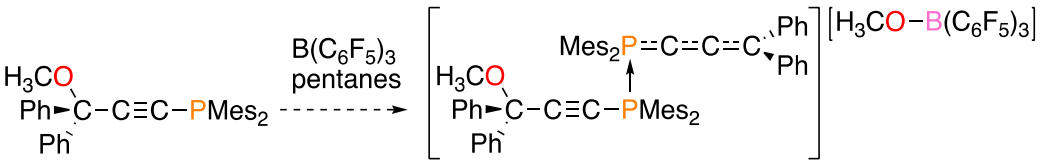


Supplementary Figure 5-D: $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, Me_4Si) of **5** in C_6D_6 at 293K.



Supplementary Figure 5-E: $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz, H_3PO_4,) of **5** in C_6D_6 at 293 K.

Phosphane phosphonium Dimer (**6**)



3 (9.8 mg, 0.02 mmol) was dissolved in a minimal amount of pentane, added to $B(C_6F_5)_3$, and subsequently allowed to stir for 30 minutes. A white solid proceeded to crash out of solution, was washed with pentane repeatedly, dried briefly *in vacuo*, and reconstituted in deuterated benzene for NMR analysis.

^{1}H NMR (400 MHz, Me_4Si, C_6D_6) δ 7.12–7.02 (m, 12 H, Ph-H), 6.95 (t, J = 7.7 Hz, 4H, Ph-H), 6.63 (d, $^4J_{PH}$ = 5.6 Hz, 4H, Mes-H) 6.60 (d, $^4J_{PH}$ = 3.5 Hz, 4H, Mes-H), 6.16 (d, $^2J_{HH}$ = 7.8 Hz, 4H, Ph-H), 3.55 (s, 3H, CH_3O-B$(C_6F_5)_3$) 2.76 (s, 3H, CH_3O-C), 2.24 (s, 12H), 2.09 (s, 12H), 2.02 (s, 6H), 2.01 (s, 6H), ppm.

^{11}B{^{1}H} NMR {^{1}H} (128 MHz, BF_3-OEt_2, C_6D_6) δ -1.7 (s)

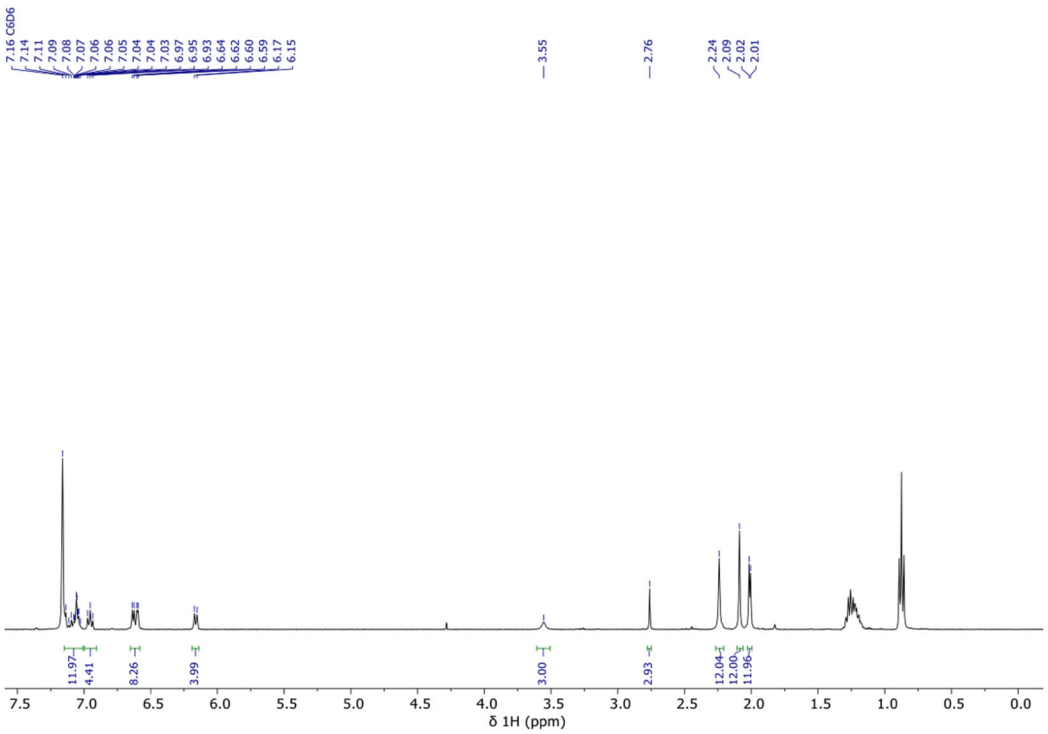
^{13}C{^{1}H} NMR Partial {^{1}H} (176 MHz, Me_4Si, C_6D_6) δ 149.1 (dm, J_{CF} = 241 Hz, CH_3O-B(C_6F_5)$_3$, (o-F)), 137.5 (dm, J_{CF} = 250 Hz, CH_3O-B(C_6F_5)$_3$, (p-F)), [146.3 (d, J_{PC} = 3.2 Hz) 143.4 (d, J_{PC} = 18 Hz) 142.5 (d, J_{PC} = 11.1 Hz), 140.6 (s), 133.3 (d, J_{PC} = 12.7 Hz), 131.2 (s) P-*Mes*$_2$ aryl carbons], 140.0 (s, quaternary Ph), [131.7 (d, J = 6.8 Hz), 130.1 (s), 129.14 (s), 129.08 (s), 129.0 (s), 128.4 (s), 128.3 (s), and 127.2 (s) Ph aryl carbons],121.1 (d, J = 20.4 Hz), 118.5 (d, $^1J_{PC}$ = 87.6 Hz, Mes_2P=*C*), 117.1 (d, J = 17.2 Hz), 93.9 (dd, $^1J_{PC}$ = Hz 87.2, $^2J_{PC}$ = Hz 64.7, Mes_2P-*C*≡C), 82.7 (d, $^3J_{PC}$ = 2.8 Hz, CH_3O-*C*RPh_2), 74.8 (d, J_{PC} = 167 Hz) *53.1 (s, *C*H_3O-B$(C_6F_5)_3$), *53.1 (s, *C*H_3O-C) *signals partially overlapped, 23.9 (s) 23.6 (d, $^3J_{PC}$ = 15.1 Hz) and 20.7 (s) P-*Mes*$_2$ methyl carbons.

Note: meta-carbon and ipso carbon of the CH_3O-B(C_6F_5)$_3$ counteranion are not observed.

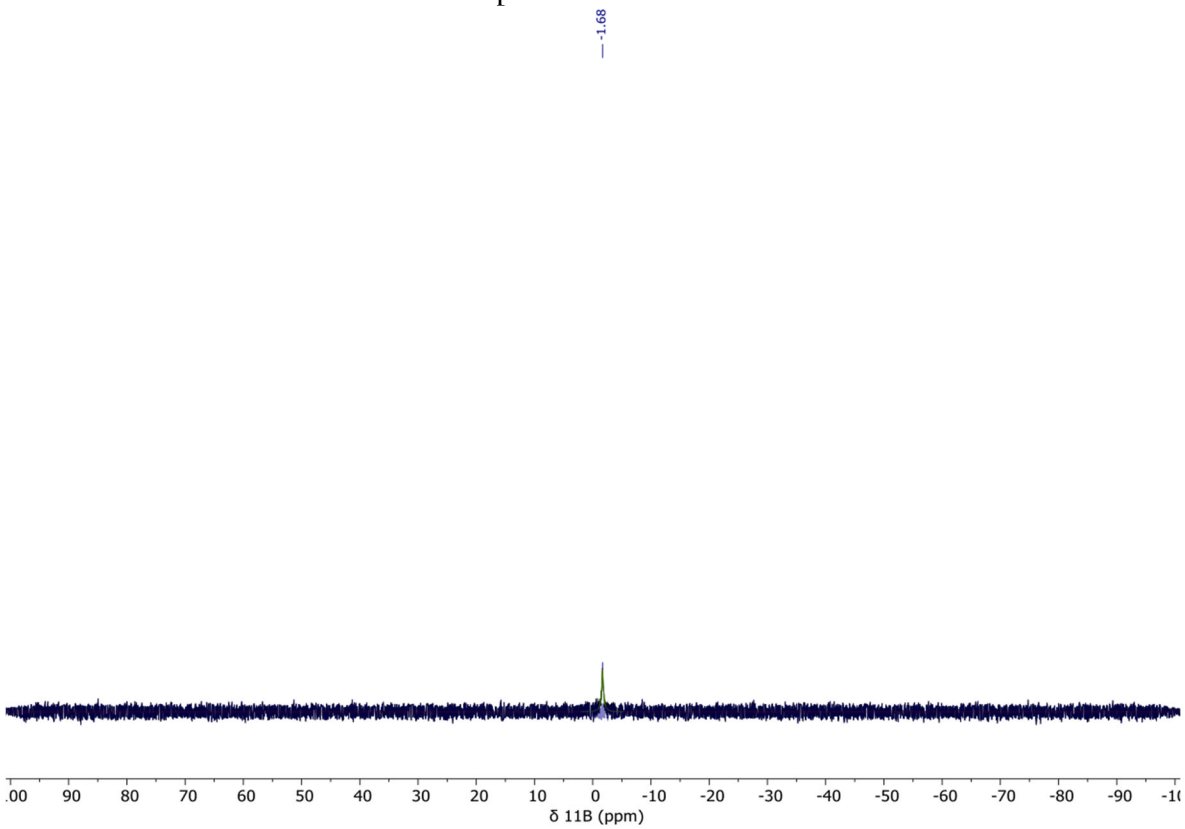
^{19}F{^{1}H} NMR (282 MHz, BF_3-OEt_2, C_6D_6) δ -133.66 (d, $^3J_{FF}$ = 23.9 Hz, (*o*-F), 6F), -162.97 (s, br, 6F (*p*-F) 3F) -166.46 (s, br, (*m*-F) 6F).
*spectrum displays significant broadening of the *p*-F resonance

^{31}P{^{1}H} NMR (162 MHz, H_3PO_4, C_6D_6) δ -5.3 ($^1J_{PP}$ = 211 Hz) -18.7 ($^1J_{PP}$ = 211 Hz) ppm.

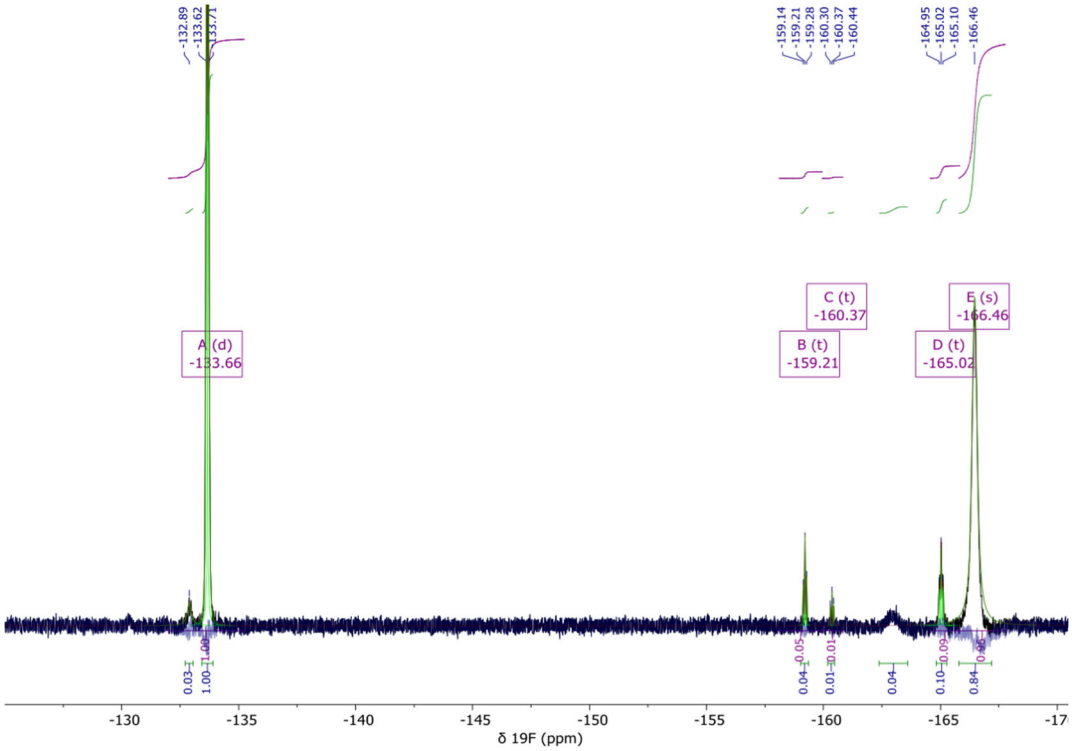
HRMS (ESI$^+$): *m/z* calculated for $(M+2H)^{2+}$, $[C67H68OP2]^{2+}$:475.2367, m/z Found: 475.2400



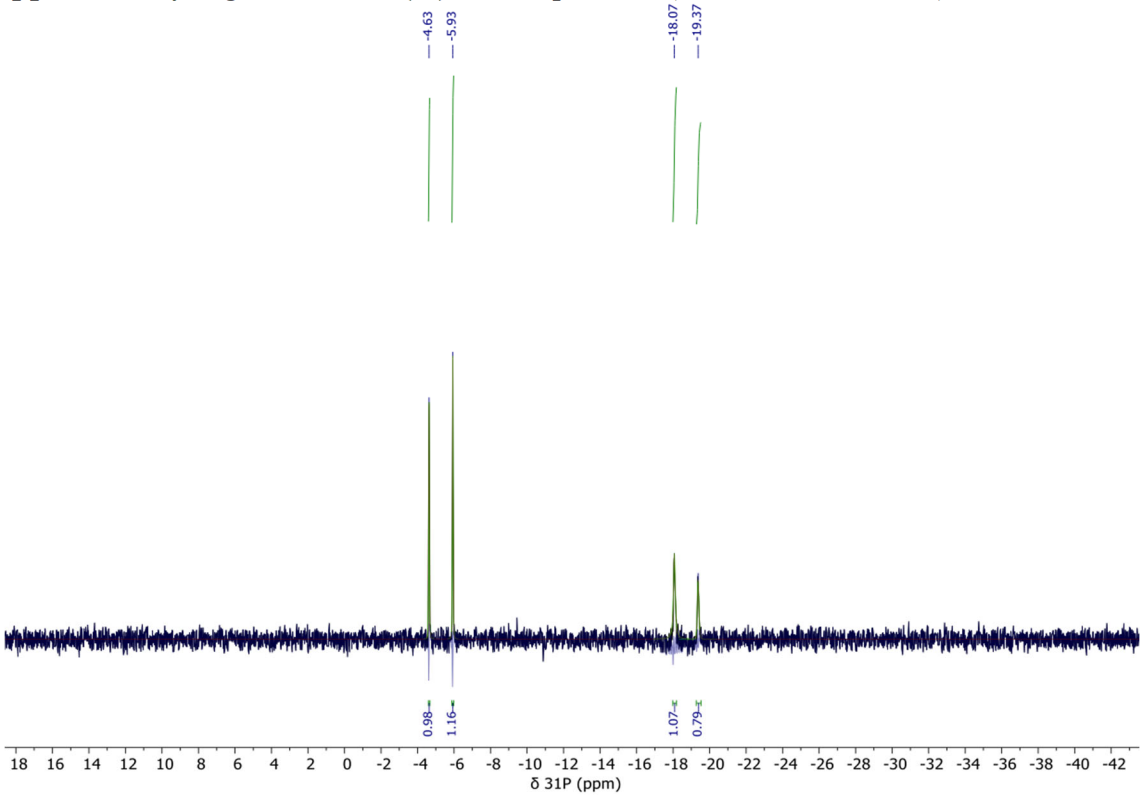
Supplementary Figure 6-A: ^{1}H NMR spectrum (400 MHz, Me_4Si) of **6** in C_6D_6 at 303K. Residual pentane at 0.87 and 1.23



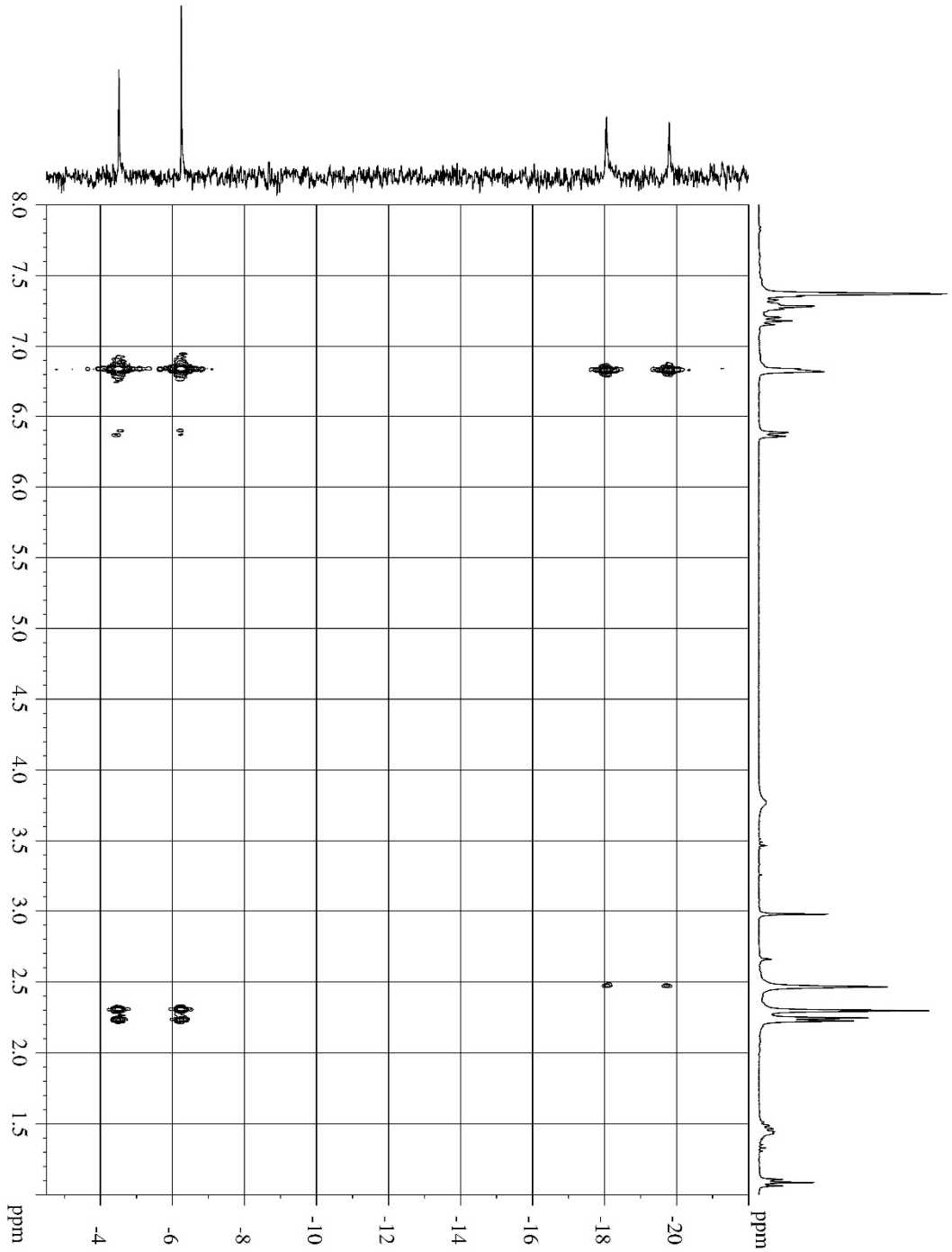
Supplementary Figure 6-B $^{11}B\{H\}$ NMR spectrum (128 MHz, BF_3-OEt_2) of **6** in C_6D_6 at 303K



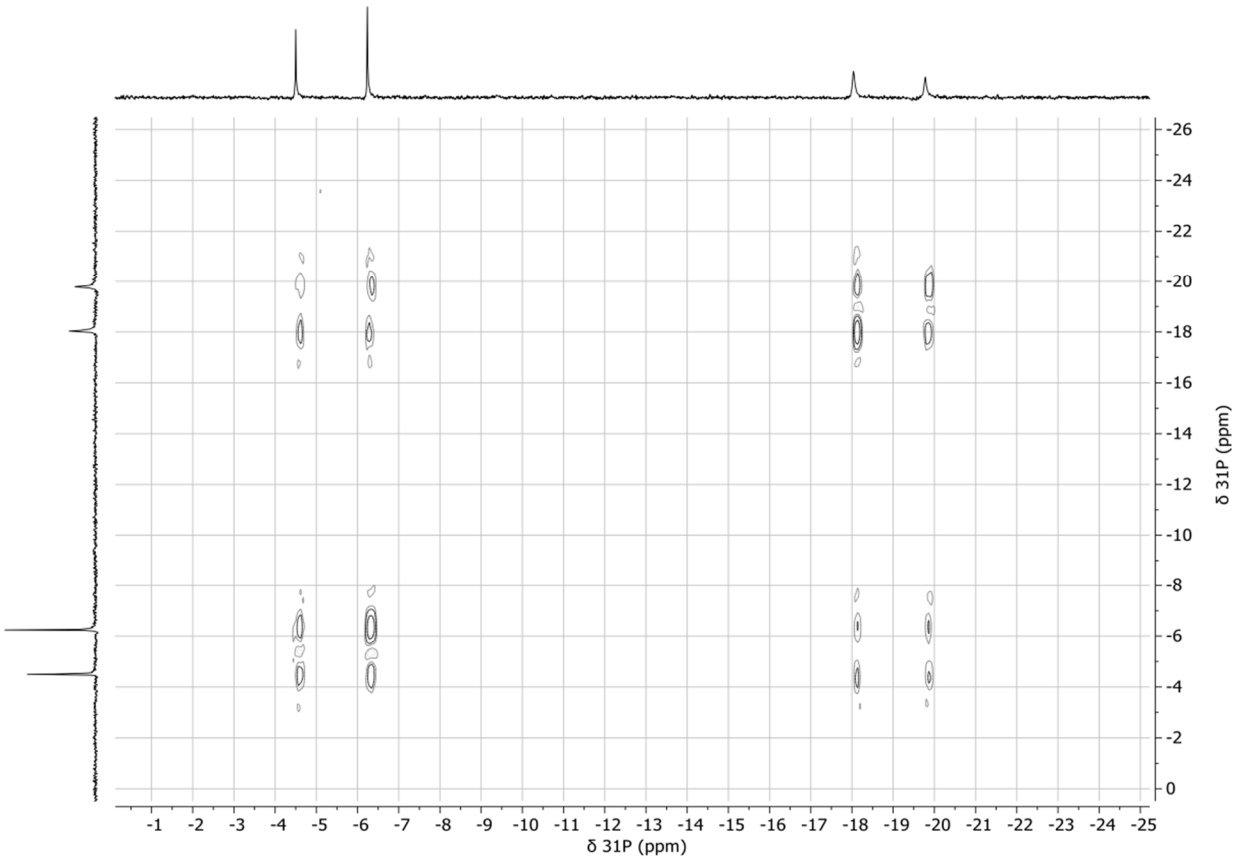
Supplementary Figure 6-C ^{19}F {H} NMR spectrum (282 MHz, BF_3-OEt_2) $CDCl_3$ at 296 K.



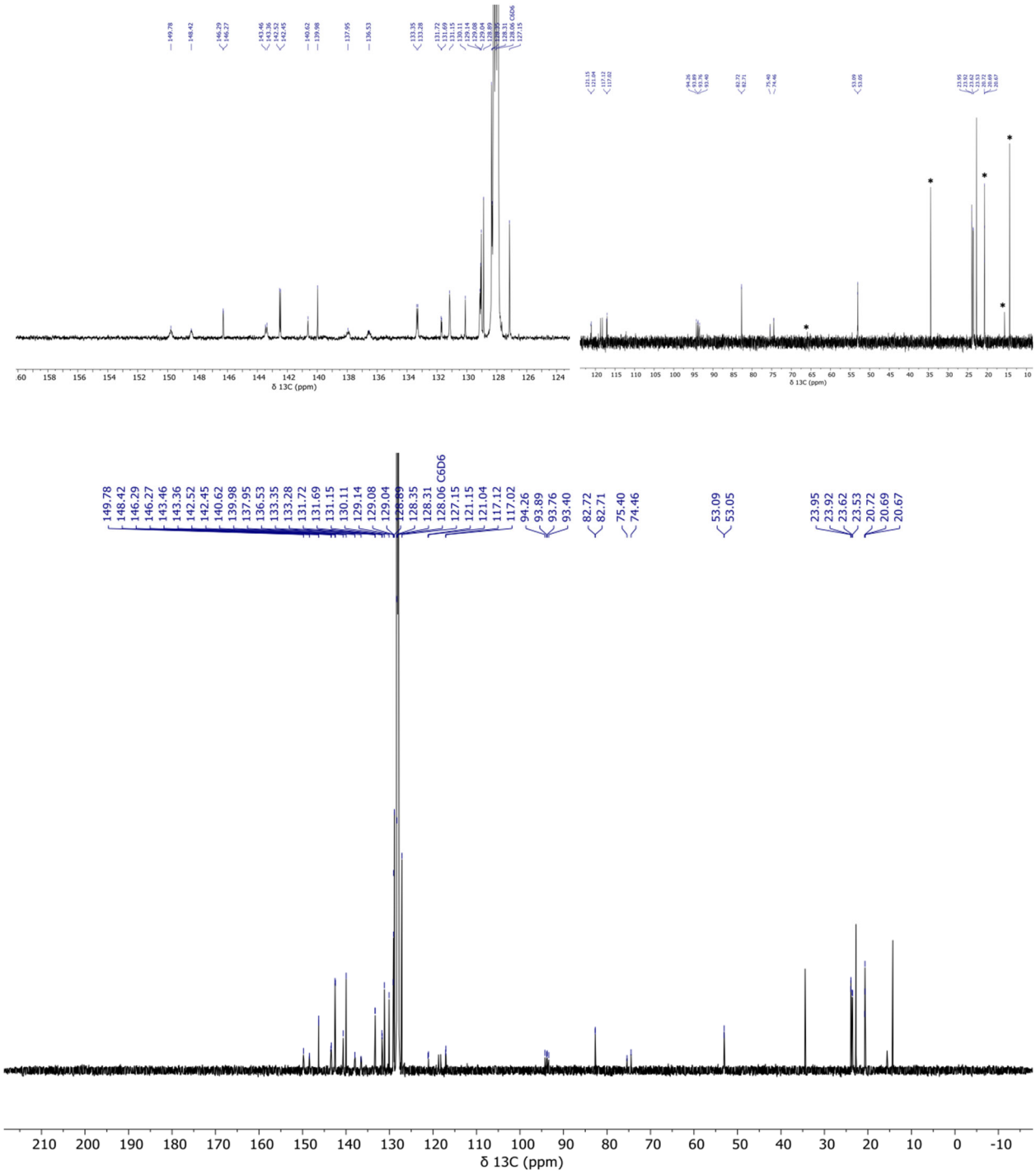
Supplementary Figure 6-D: ^{31}P {H} NMR spectrum (162 MHz, H_3PO_4) of **6** in C_6D_6 at 303 K



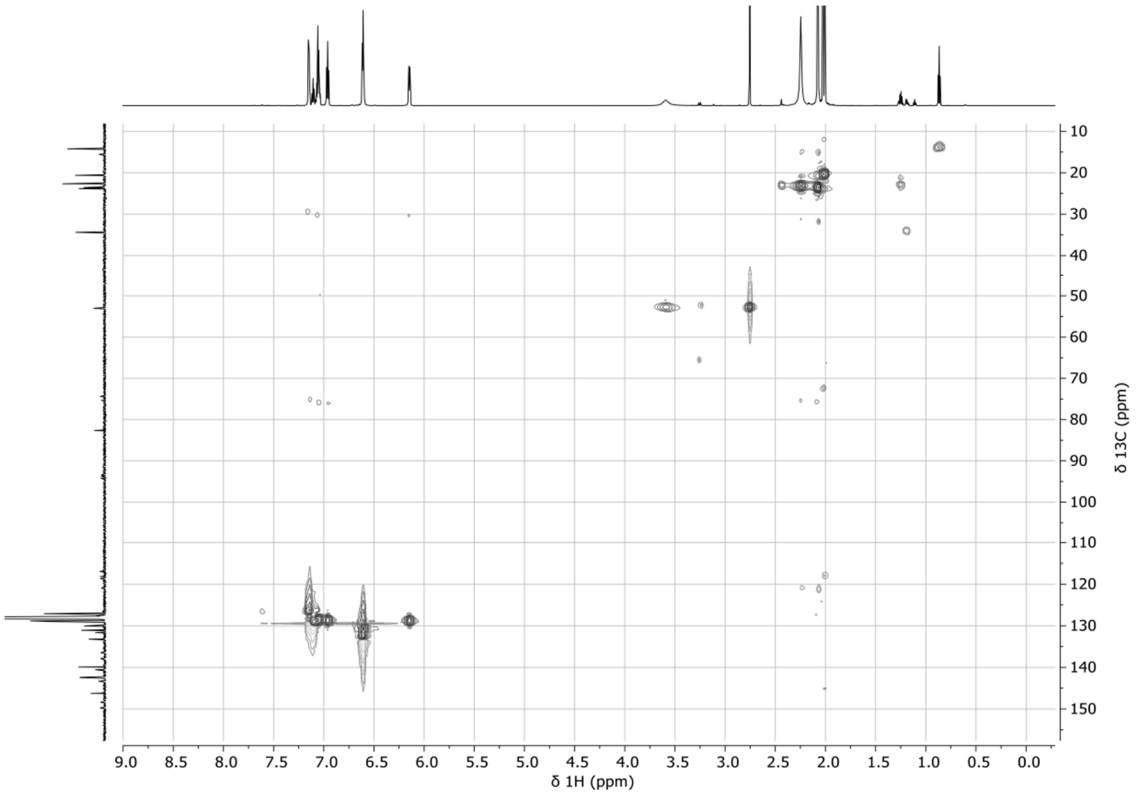
Supplementary Figure 6-E: 2D HMBC (^{1}H x ^{31}P) NMR spectrum (300.13 MH, 162 MHz) of **6** in C_6D_6 at 298 K.



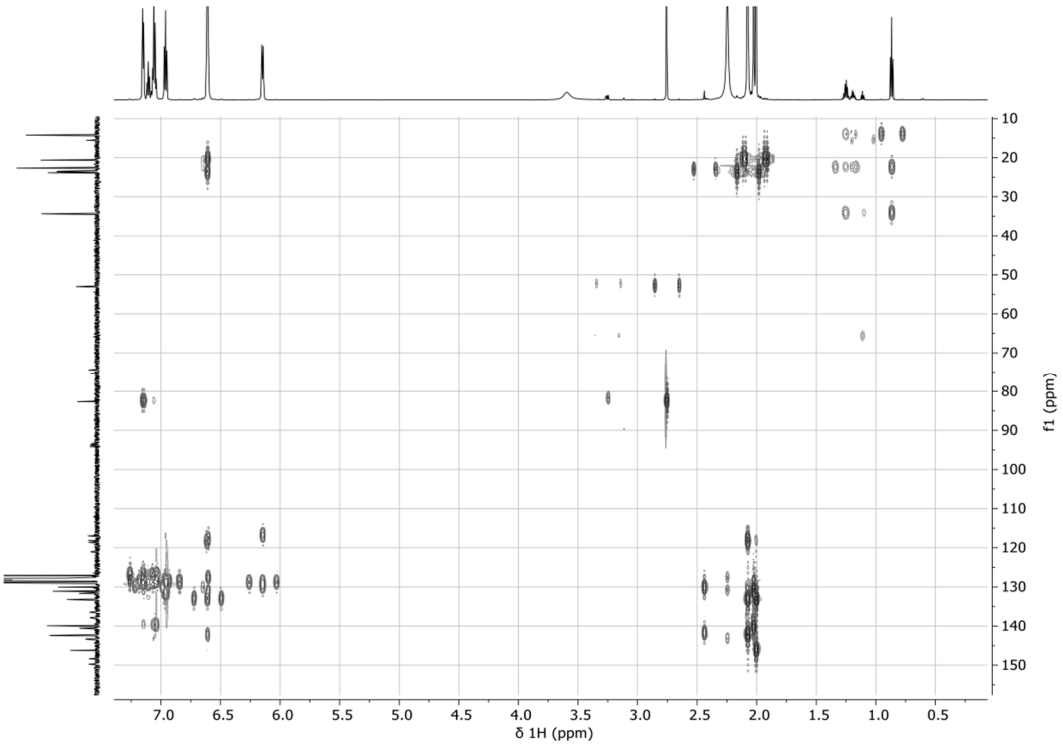
Supplementary Figure 6-F: COSY (^{31}P x ^{31}P) spectrum (162 MHz, H_3PO_4) of **6** in C_6D_6 at 298 K.



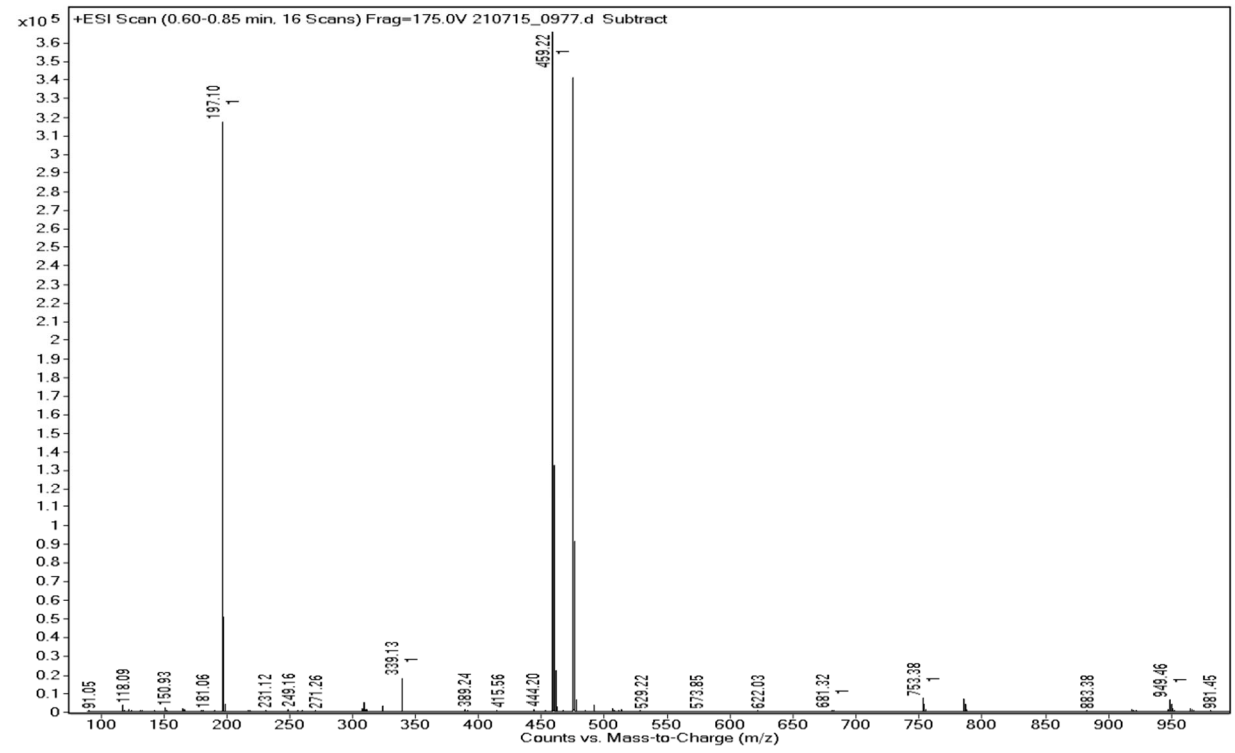
Supplementary Figure 6-G: ^{13}C {H} NMR spectrum (176 MHz, Me_4Si) of **6** in C_6D_6 at 295K. (top: zoomed view, Bottom: full spectra) *Pentanes and ether solvent impurities.

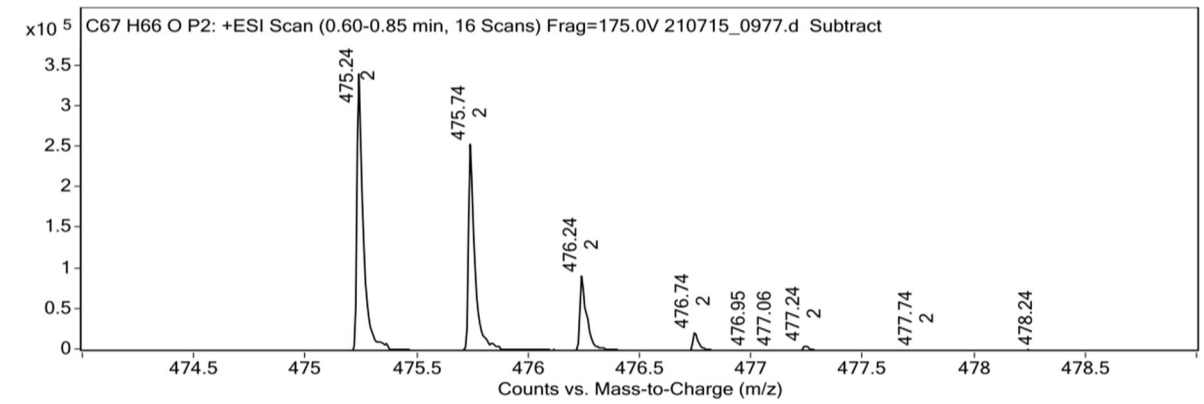


Supplementary Figure 6-H: 2D HSQC (^{1}H x ^{13}C) NMR spectrum (700 MHz, 176 MHz) of **6** in C_6D_6 at 295 K.



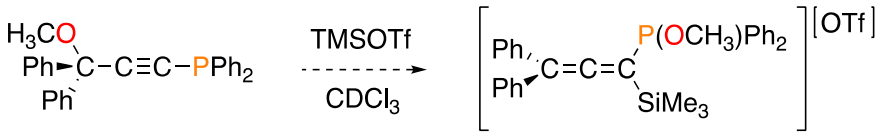
Supplementary Figure 6-H: 2D HMBC (^{1}H x ^{13}C) NMR spectrum (700 MHz, 176 MHz) of **6** in C_6D_6 at 295 K.

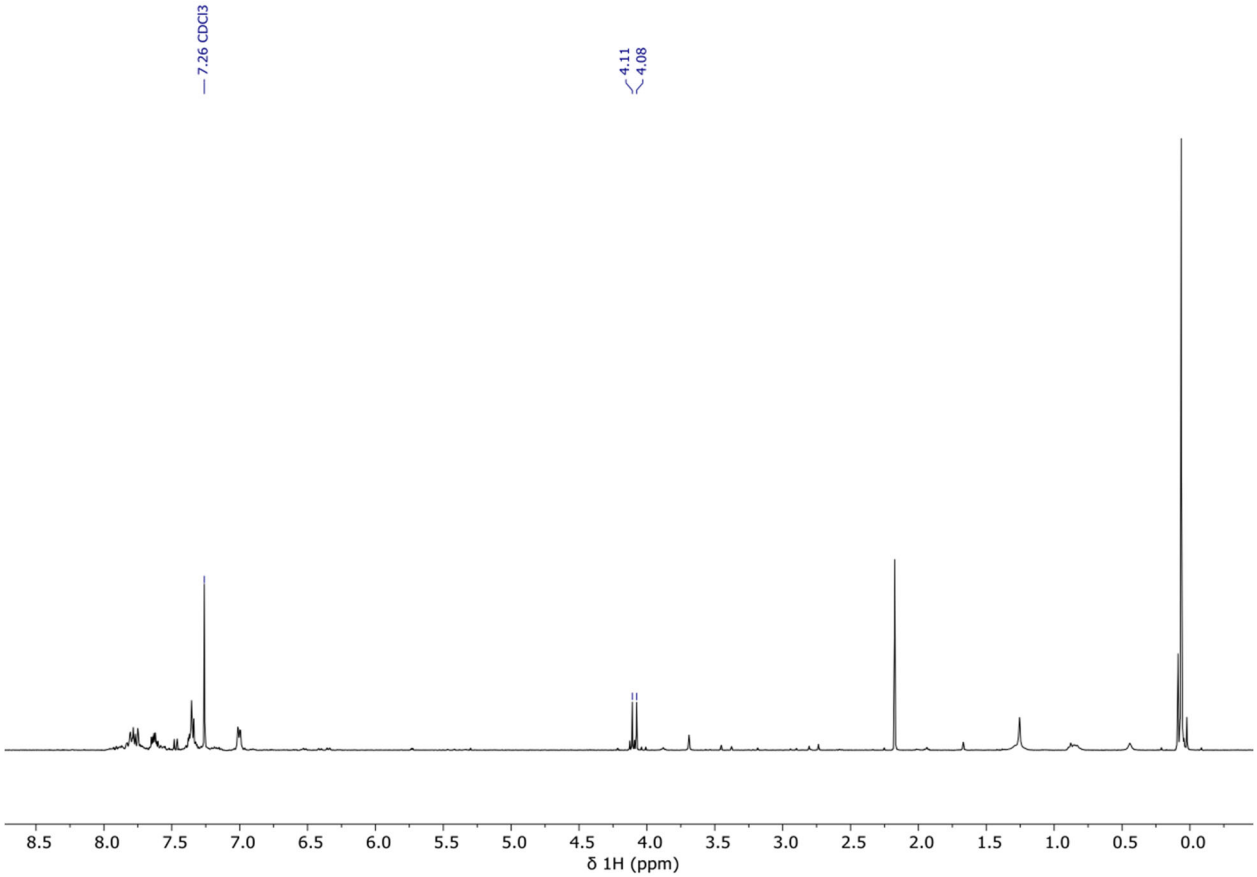




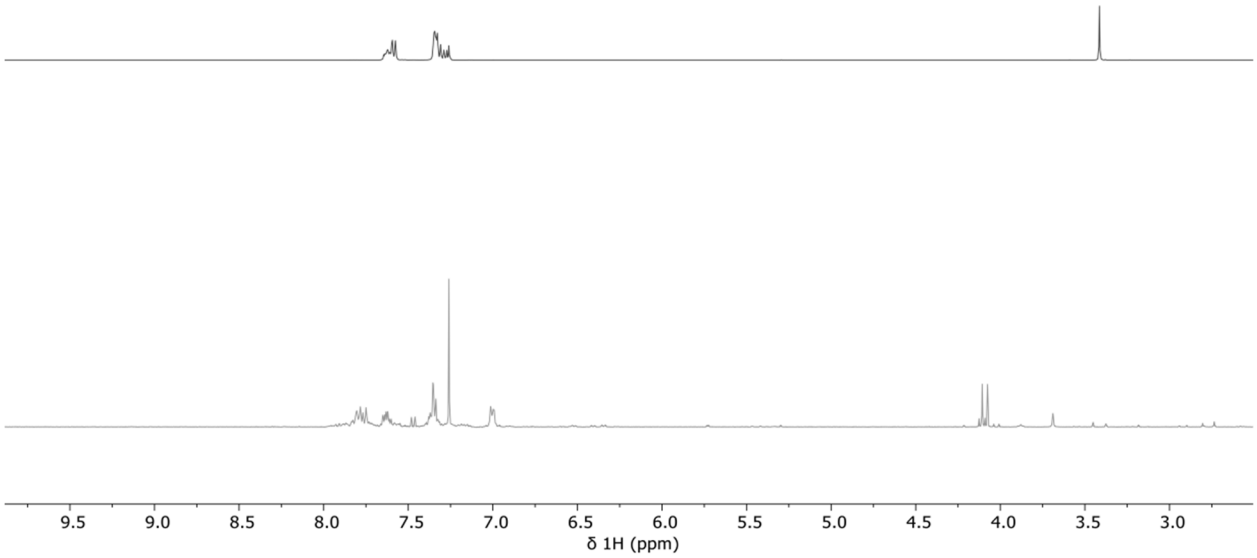
Supplementary Figure 6-I: Mass spectrometry report, $[M+2H]^{2+}$ of **6** using ESI^{+} in positive ion mode.

Reaction with TMSOTf: a chloroform-*d* solution of **1** (0.02 mmol, 8.126 mg) was added via syringe to a chloroform-*d* solution of TMSOTf (0.03 mmol, 1.5 equiv) at -94°C, in the absence of light. The reaction mixture was allowed to warm to room temperature and stir, resulting in a gradual colour change to bright yellow-green. An aliquot was taken for NMR analysis after 2 hours. 1H and 31P NMR are consistent with the formation of a methoxy phosphonium salt. The cationic species drawn remains elusive in our experimentation.

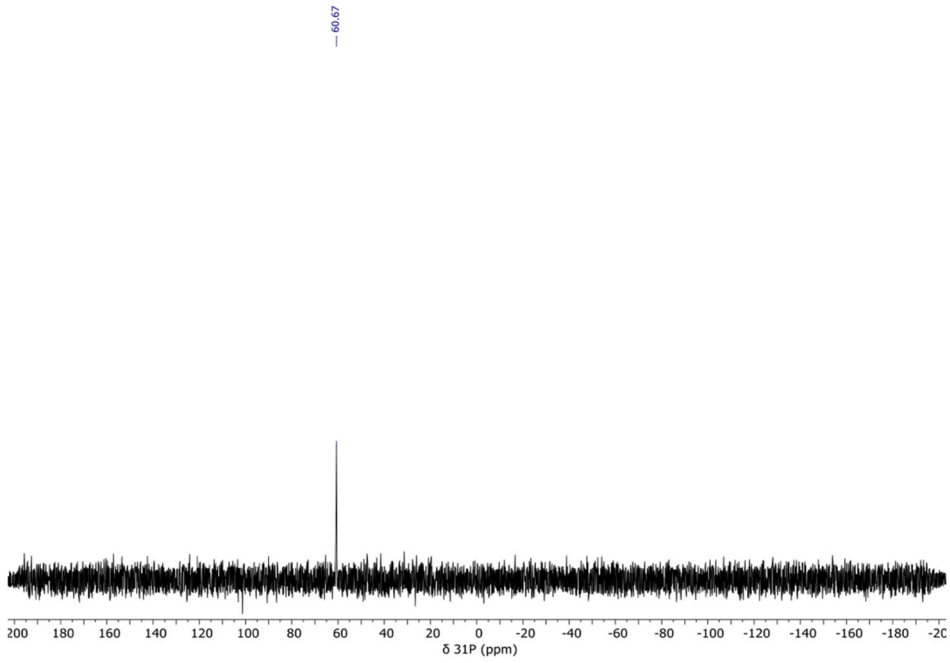




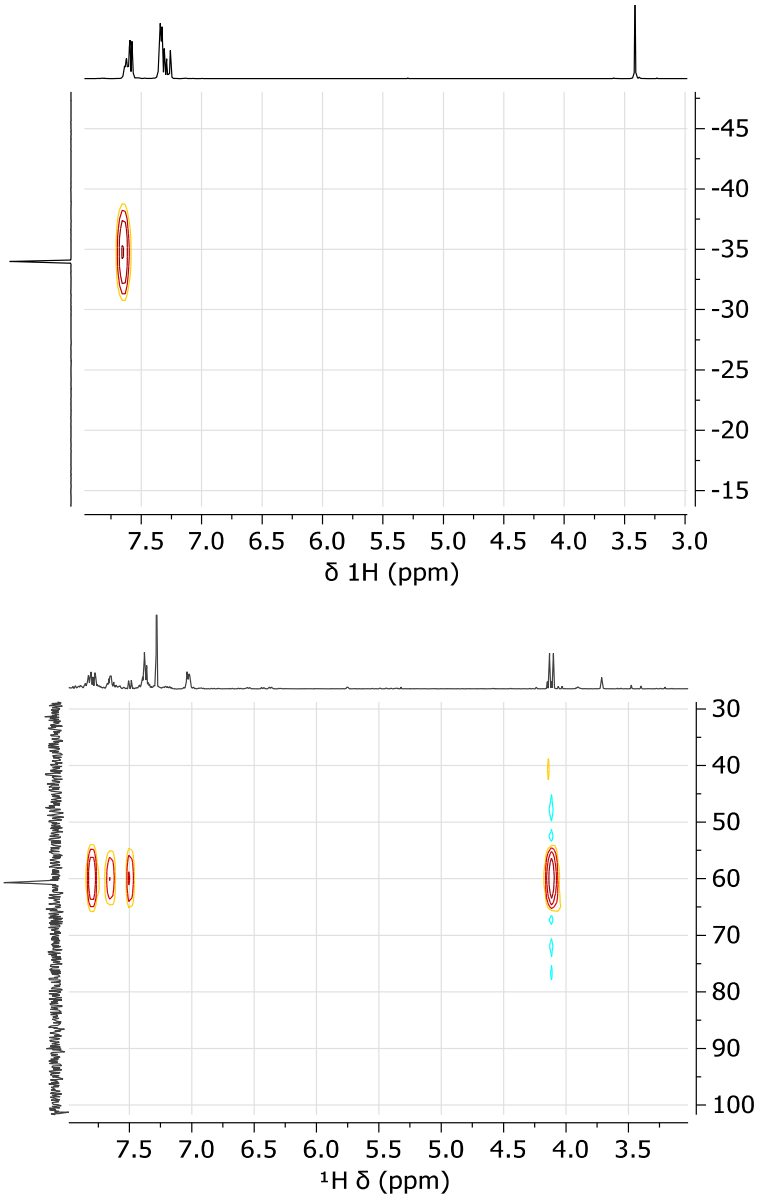
Supplementary Figure 7-A: ^{1}H NMR spectrum (400 MHz, Me_4Si) of **4** in C_6D_6 at 299 K.



Supplementary Figure 7-B: Stacked ^{1}H NMR spectra (400 MHz, Me_4Si) of **1** and the reaction of **1** with TMSOTf.

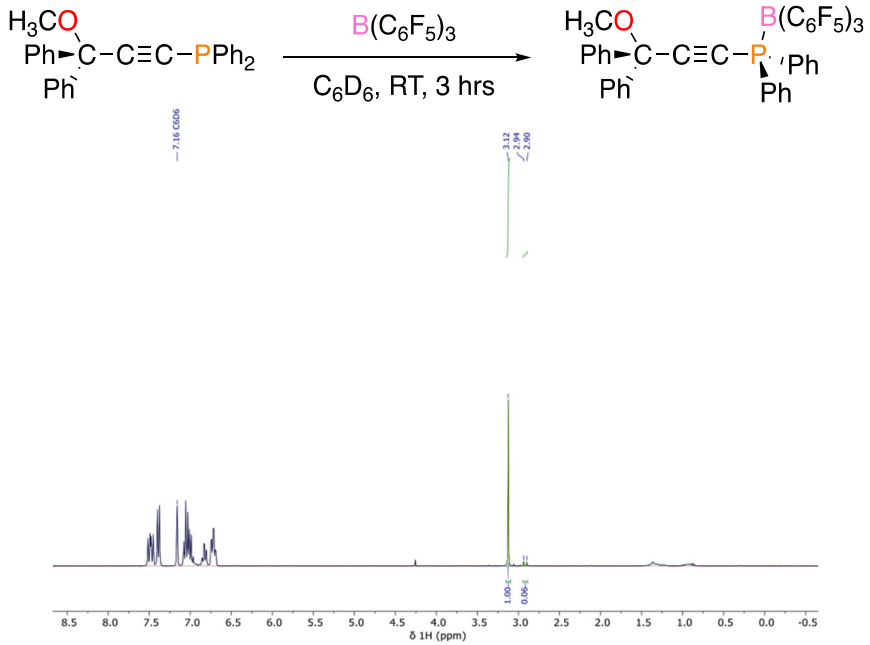


Supplementary Figure 7-C: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, H_3PO_4) of **1** and the reaction of **1** with TMSOTf at 299 K.

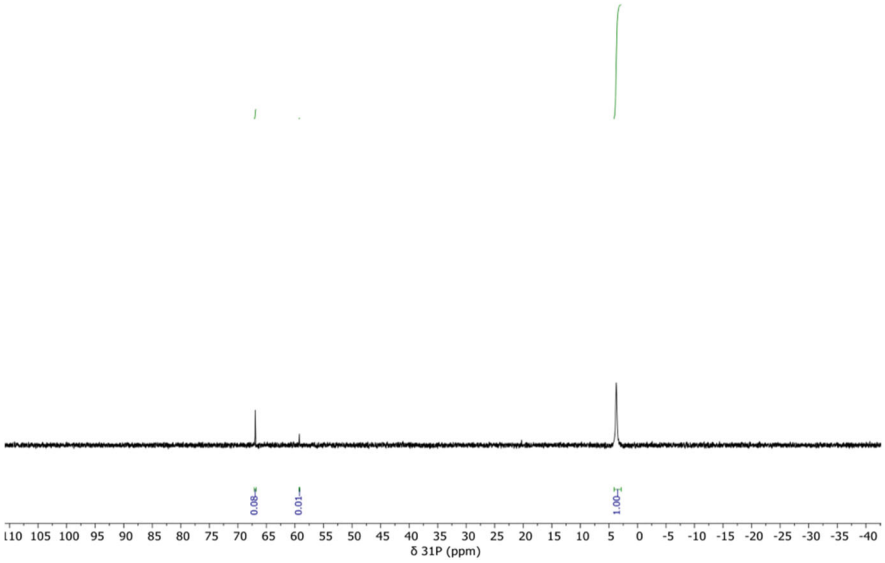


Supplementary Figure 7-D: Stacked ^{1}H x ^{31}P HMQC spectra (400, Me_4Si; 162 MHz, H_3PO_4) of **1** and the reaction of **1** with TMSOTf at 299 K.

Room temperature reaction of **1** and $B(C_6F_5)_3$. Following the outlined conditions for the synthesis of **4,** except allowing the reaction to stir at room temperature, gives primarily the P-B adduct in the scheme below. After 3 hours, the reaction only gives ~6 percent of the methoxyphosphonium salt **4.**



Supplementary Figure 8-A: ^{1}H spectrum showing the P-B adduct of **1** and $B(C_6F_5)_3$ as the predominant species in solution at room temperature (300MHz, Me_4Si, C_6D_6)



Supplementary Figure 8-B: ^{31}P spectrum showing the diagnostic resonance (δ_P = 3.71 ppm) of the P-B adduct of **1** and $B(C_6F_5)_3$ as the predominant species in solution at room temperature (121 MHz, $H3PO_4$, C_6D_6).

Single Crystal X-ray Diffraction

General: Diffraction data was collected on a Bruker APEX-II CCD diffractometer with a MoK_α (λ = 0.71073) radiation source. Crystals were chosen under paratone oil and mounted to the diffractometer under a stream of N_2 and kept at 173.0 K during data collection. Olex2,[2] the structure was solved with the XS structure solution program using Direct Methods and refined with the SHELXL[3] refinement package using Least Squares minimization.

P,P-diphenyl-3,3-diphenyl-3-methoxy-propynyl-phosphane (**1**)

Colourless single crystals were obtained by layering a saturated solution CH_2Cl_2 with isopropanol at 298 K. X-ray structure analysis of **1** demonstrates that crystallization occurs in the triclinic space group. The unit cell contains 2 molecules.

Diphenylmethoxy-phosphonium borate inner salt (**4)**

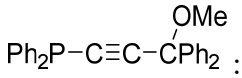
Transparent green/yellow single crystals obtained by layering a saturated solution CH_2Cl_2 with n-pentane at 298 K. X-ray structure analysis of **4** demonstrates that crystallization occurs in the orthorhombic space group. The unit cell contains eight molecules.

Supplementary Table 1. Crystal data and structure refinement for **1 and 4**

Molecule	1a	2a
Formula	C28H23OP	C46H23OBF15P
CCDC ID	2055307	2055304
Formula wt (g mol^{-1})	406.46	918.42
Temperature (K)	173.0	173.0
Crystal System	Triclinic	Orthorhombic
Space Group	P-1	Pbca
a/Å	6.1570(9)	17.915(3)
b/Å	10.7695(15)	20.056(4)
c/Å	17.131(2)	22.245(4)
α/°	79.693(5)	90
β/°	81.084(5)	90
γ/°	88.594(5)	90
Volume/$Å^3$	1104.1(3)	7993(3)
Z	2	8
ρcalc g/cm3	1.223	1.527
μ/mm^{-1}	0.141	0.177
F(000)	428.0	3696.0
Crystal Size/mm^3	0.3 x 0.2 x 0.2	0.5 x 0.4 x 0.8
Radiation	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2Θ range for data collection/°	4.908 to 55.284	4.456 to 55.014
Index ranges	$-8 \le h \le 7$, $-14 \le k \le 14$, $-22 \le l \le 22$	$-23 \le h \le 23$, $-26 \le k \le 26$, $-28 \le l \le 28$
Reflections Collected	33207	272402
Independent Reflections	5069 [R_{int} = 0.0776, R_{sigma} = 0.0444	9180 [R_{int} = 0.0716, R_{sigma} = 0.0193]
Data/restraints/parameters	5069/0/272	9180/0/578
Goodness-of-fit on F^2	1.087	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0710, wR_2 = 0.1760	R_1= 0.0416, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0782, wR_2 = 0.1814	R_1= 0.0585, wR_2 = 0.1229
Largest diff. peak/hole/ e $Å^{-3}$	0.45/-0.27	0.38/-0.36

Computational Details

DFT calculations were performed using Gaussian 09.2.[4] Geometry optimization of all the molecules, intermediates, and the transition state were carried out using the BP86(D3)/def2-SVP basis sets implemented in the Gaussian 09 software.[5,6] Thermal energy corrections were extracted from the results of frequency analysis performed at the same level of theory. Frequency analysis of all the molecules and intermediates contained no imaginary frequency showing that these are energy minima. The transition states geometries gave one imaginary frequency at expected reaction coordinates confirming that it is a first-order saddle point.



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C	1.95029	-2.64808	-1.67311
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$B(C_6F_5)_3$:

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C	1.23923	-4.24876	-0.00060
C	-1.52721	0.37448	-0.00036
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C	-2.02608	1.49147	0.70978
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C	0.91042	2.34330	-0.71290
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F	-1.19448	2.26263	1.43106
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F	3.98699	4.15656	0.00220
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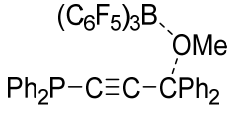

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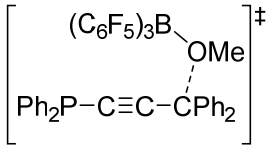

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C	4.73226	3.51977	-1.50302
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C	1.38532	1.32699	4.27305
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F	0.64694	2.85609	-3.38871
F	0.36711	0.45525	-2.26130
F	-2.58086	-2.53312	1.51656
F	-5.07698	-3.51694	1.52461
F	-7.06875	-2.27035	0.08709
F	-4.02484	1.00058	-1.38122
F	-6.48393	-0.00472	-1.35235
F	0.26102	-2.48655	1.25930
F	-1.99111	-0.89083	-2.64423
F	-0.96605	-2.94214	-4.05191
F	0.69395	-4.77294	-2.83134
F	1.26775	-4.49425	-0.14800

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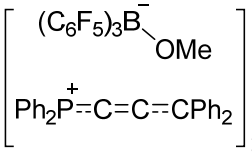
Sum of electronic and thermal Enthalpies= -3702.560519
Sum of electronic and thermal Free Energies= -3702.709789



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C	4.77644	-2.40978	-0.35933
C	4.81469	-2.35183	2.45145
H	3.50856	-0.61687	2.29323
C	5.51821	-3.36462	0.35161
H	4.72714	-2.46180	-1.45895
C	5.53666	-3.33868	1.75745
H	4.82141	-2.33473	3.55272
H	6.06513	-4.14746	-0.19640
H	6.10675	-4.09840	2.31478
C	4.10720	0.96363	-1.47049

C	5.50422	0.94907	-1.27540
C	3.51680	1.92627	-2.31952
C	6.30518	1.90772	-1.92119
H	5.96638	0.19829	-0.61563
C	4.32681	2.88764	-2.94533
H	2.43084	1.93025	-2.49215
C	5.72035	2.87979	-2.75132
H	7.39564	1.89570	-1.76513
H	3.85939	3.64104	-3.59883
H	6.35234	3.63007	-3.25208
C	2.09597	0.62661	0.46964
C	1.27949	1.21642	1.20575
C	0.43123	1.90648	2.05979
C	-0.18073	3.15240	1.58025
C	-1.45043	3.57632	2.06266
C	0.49124	3.95663	0.62134
C	-1.99633	4.79331	1.64118
H	-2.02732	2.91036	2.71990
C	-0.05604	5.17888	0.21542
H	1.45861	3.61985	0.21791
C	-1.29480	5.60539	0.72986
H	-2.99337	5.09462	1.99470
H	0.47375	5.79378	-0.52733
H	-1.73341	6.55549	0.38908
C	0.30476	1.45392	3.44785
C	0.59493	0.10130	3.77908
C	-0.05721	2.35035	4.49262
C	0.48143	-0.34576	5.09720
H	0.84471	-0.59828	2.97264
C	-0.16083	1.89506	5.81349
H	-0.21602	3.41555	4.27163
C	0.09647	0.54576	6.11938
H	0.68032	-1.40331	5.32967
H	-0.43378	2.60113	6.61298
H	0.00551	0.18958	7.15776
C	-2.32030	-0.26015	2.46140
H	-3.35048	-0.13709	2.06263
H	-2.25528	-1.24323	2.98144
H	-2.15255	0.52693	3.23381
C	-1.46853	0.92463	-0.78101
C	-0.51327	1.40221	-1.69125
C	-2.47974	1.85764	-0.48063
C	-0.56293	2.67530	-2.29226
C	-2.59291	3.12540	-1.06900
C	-1.60591	3.55118	-1.97085
C	-2.92296	-1.37636	-0.25954

C	-3.16529	-2.56741	0.45435
C	-3.87673	-1.08984	-1.25452
C	-4.28383	-3.39521	0.25691
C	-5.01098	-1.88988	-1.49754
C	-5.21770	-3.05128	-0.73560
C	-0.33532	-1.60767	-0.42095
C	-0.19644	-1.94808	-1.77918
C	0.50293	-2.32743	0.45028
C	0.79017	-2.81863	-2.27378
C	1.47600	-3.24845	0.01233
C	1.64036	-3.47375	-1.36180
B	-1.51776	-0.53468	0.03904
O	-1.32798	-0.14740	1.47363
F	-3.45230	1.53939	0.40565
F	-3.59011	3.96181	-0.72916
F	-1.63801	4.79384	-2.47842
F	0.42130	3.08463	-3.12202
F	0.55302	0.65021	-2.07255
F	-2.28453	-2.98380	1.39642
F	-4.45866	-4.51038	0.98559
F	-6.29163	-3.82363	-0.95291
F	-3.75367	-0.01443	-2.06168
F	-5.89052	-1.55889	-2.45697
F	0.42707	-2.19325	1.79532
F	-1.02284	-1.39423	-2.69222
F	0.92180	-3.04743	-3.58891
F	2.60464	-4.29805	-1.80287
F	2.26173	-3.88970	0.89388

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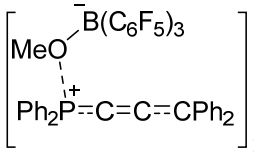
Sum of electronic and thermal Free Energies= -3702.723013



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C	-1.62143	1.71540	-3.81540
H	-2.84457	0.53562	-2.46365
C	0.73387	1.11004	-3.96320

H	1.37098	-0.53090	-2.70736
C	-0.33572	1.93478	-4.34799
H	-2.46056	2.36374	-4.10898
H	1.74758	1.27670	-4.35641
H	-0.16816	2.76122	-5.05590
C	-0.11589	-2.86459	-1.25246
C	0.59395	-3.24497	-2.41235
C	-0.19057	-3.74005	-0.14275
C	1.22715	-4.49843	-2.45390
H	0.64414	-2.57945	-3.28573
C	0.42778	-4.99478	-0.20759
H	-0.72175	-3.43351	0.77018
C	1.14203	-5.37456	-1.35943
H	1.79986	-4.78525	-3.34889
H	0.37855	-5.66963	0.65990
H	1.65475	-6.34760	-1.39273
C	-2.58489	-1.43578	-0.71736
C	-3.70261	-1.10668	-0.20614
C	-4.89774	-0.67223	0.27187
C	-5.72816	-1.53464	1.13860
C	-6.61333	-0.97270	2.09488
C	-5.61951	-2.94839	1.06729
C	-7.36596	-1.79857	2.94292
H	-6.68818	0.12141	2.18671
C	-6.37312	-3.76824	1.91710
H	-4.94405	-3.39722	0.32149
C	-7.25216	-3.19807	2.85793
H	-8.04182	-1.34367	3.68423
H	-6.28134	-4.86328	1.84084
H	-7.84615	-3.84396	3.52344
C	-5.29653	0.70349	-0.13051
C	-4.30631	1.70008	-0.32836
C	-6.65059	1.03245	-0.39417
C	-4.65201	2.97891	-0.78553
H	-3.25524	1.47181	-0.10747
C	-6.99355	2.31756	-0.84220
H	-7.43093	0.26585	-0.27096
C	-5.99941	3.29400	-1.04289
H	-3.85608	3.72522	-0.93312
H	-8.04904	2.55551	-1.04932
H	-6.27615	4.29938	-1.39754
C	-0.63130	-0.56037	1.78226
H	0.00144	-0.86838	2.63910
H	-1.13463	0.40196	2.00148
H	-1.41006	-1.33679	1.63127
C	2.49998	-0.85961	-0.14281

C	3.23485	-0.82476	-1.33993
C	2.53258	-2.10912	0.51371
C	3.90747	-1.94061	-1.88183
C	3.21772	-3.23497	0.04020
C	3.88734	-3.15945	-1.19204
C	2.04268	0.76874	2.04617
C	1.31592	1.73364	2.77692
C	3.26199	0.39018	2.64633
C	1.71232	2.25128	4.02208
C	3.70615	0.88461	3.88920
C	2.92568	1.82118	4.58487
C	1.32889	1.68614	-0.30941
C	2.44878	2.45984	-0.66401
C	0.09035	2.26533	-0.62787
C	2.36863	3.64348	-1.41854
C	-0.04846	3.45122	-1.36736
C	1.10234	4.13825	-1.78349
B	1.52490	0.29308	0.54474
O	0.16803	-0.47679	0.60505
F	1.88547	-2.27149	1.69069
F	3.20535	-4.39273	0.72140
F	4.47551	-4.24799	-1.70763
F	4.52111	-1.85220	-3.07352
F	3.30923	0.29134	-2.10694
F	0.15291	2.22950	2.28961
F	0.95725	3.15555	4.66470
F	3.33208	2.29997	5.76714
F	4.10947	-0.47164	2.04867
F	4.87460	0.47678	4.40653
F	-1.07571	1.69880	-0.22123
F	3.67855	2.06585	-0.27306
F	3.47390	4.31767	-1.77065
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F	-1.26929	3.93220	-1.67724

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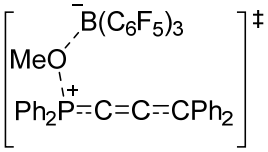

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C	-0.82860	-0.28963	-2.91231
C	1.16488	-2.04712	-3.81278
H	2.56338	-0.81952	-2.68691
C	-1.17153	-1.36292	-3.74904
H	-1.60924	0.39095	-2.55818
C	-0.17593	-2.24847	-4.19409
H	1.94721	-2.74301	-4.15135
H	-2.22529	-1.51019	-4.02960
H	-0.44400	-3.10435	-4.83310
C	0.04908	2.74832	-1.67248
C	-0.57284	3.00394	-2.91322
C	0.05681	3.74505	-0.66991
C	-1.20286	4.24008	-3.13591
H	-0.56009	2.24481	-3.70920
C	-0.54054	4.98996	-0.91554
H	0.52074	3.54404	0.30796
C	-1.18407	5.23385	-2.14222
H	-1.70728	4.42798	-4.09630
H	-0.53150	5.76214	-0.13230
H	-1.67942	6.20041	-2.32112
C	2.60670	1.42868	-1.34220
C	3.69100	1.07407	-0.75957
C	4.82723	0.59839	-0.18756
C	5.72076	1.48617	0.58742
C	6.54776	0.98307	1.62612
C	5.73937	2.88571	0.34356
C	7.36131	1.84285	2.37989
H	6.53361	-0.09360	1.85471
C	6.54825	3.74132	1.10352
H	5.11348	3.29379	-0.46660
C	7.36901	3.22638	2.12526
H	7.99087	1.42653	3.18291
H	6.54768	4.82237	0.88916
H	8.01038	3.89850	2.71689
C	5.06991	-0.86128	-0.36396
C	3.97268	-1.75880	-0.42681
C	6.37328	-1.39590	-0.52690
C	4.15882	-3.12806	-0.66227
H	2.95555	-1.37101	-0.28012
C	6.56047	-2.77016	-0.74698
H	7.24220	-0.72023	-0.50052
C	5.45859	-3.64360	-0.82105
H	3.27725	-3.78633	-0.71376
H	7.58214	-3.16260	-0.87661

H	5.61393	-4.71943	-0.99946
C	1.07600	0.71316	1.34493
H	0.42734	0.97740	2.20080
H	1.51803	-0.29056	1.49774
H	1.88786	1.46297	1.25587
C	-2.60796	0.76471	0.06986
C	-3.37350	0.76503	-1.11890
C	-2.43835	2.04342	0.65577
C	-3.92021	1.92810	-1.69213
C	-3.00458	3.21770	0.14519
C	-3.72784	3.16572	-1.05907
C	-1.85528	-0.64016	2.30224
C	-0.90254	-1.44520	2.97257
C	-2.84860	-0.07260	3.14034
C	-0.88089	-1.62764	4.36541
C	-2.87371	-0.24445	4.53449
C	-1.87967	-1.02557	5.15189
C	-1.67782	-1.85922	-0.09555
C	-2.84043	-2.60618	-0.36722
C	-0.46878	-2.45077	-0.50396
C	-2.84079	-3.80761	-1.09343
C	-0.41999	-3.66044	-1.21928
C	-1.61125	-4.33384	-1.53185
B	-1.91528	-0.50426	0.72348
O	0.22895	0.71040	0.16958
F	-1.68691	2.19240	1.76377
F	-2.82696	4.39085	0.76559
F	-4.22346	4.28350	-1.59421
F	-4.59138	1.86330	-2.84901
F	-3.62321	-0.37343	-1.79677
F	0.07268	-2.06490	2.28633
F	0.06505	-2.37556	4.94386
F	-1.88620	-1.19620	6.47437
F	-3.85873	0.64755	2.62276
F	-3.83914	0.31083	5.27531
F	0.72267	-1.88824	-0.23283
F	-4.02755	-2.15405	0.09367
F	-3.98121	-4.46089	-1.35022
F	-1.57680	-5.47392	-2.23013
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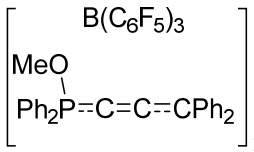
Sum of electronic and thermal Free Energies= -3702.710719



P	1.04649	1.64538	-1.04985
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C	1.37531	-0.10334	-3.23073
C	-0.88960	0.72651	-2.83884
C	0.89200	-0.88835	-4.28803
H	2.44382	-0.11883	-2.96699
C	-1.36825	-0.06594	-3.89322
H	-1.57672	1.37682	-2.28275
C	-0.47761	-0.87797	-4.61636
H	1.59022	-1.52658	-4.85005
H	-2.44152	-0.05123	-4.13419
H	-0.85085	-1.51082	-5.43677
C	0.21860	3.26676	-1.07880
C	-0.03397	3.91241	-2.30918
C	-0.11861	3.90157	0.13451
C	-0.63678	5.18027	-2.32053
H	0.23360	3.41739	-3.25568
C	-0.69952	5.18096	0.11566
H	0.05174	3.38636	1.09214
C	-0.96820	5.81479	-1.10941
H	-0.84694	5.67624	-3.28092
H	-0.97353	5.66679	1.06340
H	-1.44418	6.80765	-1.12068
C	2.72903	1.75940	-1.10103
C	3.74780	1.17982	-0.57867
C	4.81281	0.49943	-0.08216
C	5.68253	1.11618	0.94532
C	6.37088	0.32806	1.90527
C	5.80871	2.52841	1.03517
C	7.15584	0.92774	2.90208
H	6.26960	-0.76769	1.87767
C	6.58801	3.12339	2.03697
H	5.28988	3.15743	0.29380
C	7.27195	2.32780	2.97591
H	7.67625	0.29189	3.63664
H	6.67215	4.22149	2.07947
H	7.89066	2.79559	3.75795
C	4.99616	-0.89114	-0.58125
C	3.87025	-1.67034	-0.95515
C	6.28145	-1.47019	-0.73921
C	4.01506	-2.96565	-1.47131
H	2.86180	-1.25262	-0.82922

C	6.42518	-2.77174	-1.24606
H	7.17486	-0.88226	-0.47769
C	5.29699	-3.52780	-1.61664
H	3.11358	-3.53362	-1.74997
H	7.43505	-3.19717	-1.36396
H	5.41736	-4.54766	-2.01503
C	1.15593	0.46877	1.38976
H	0.50716	0.44433	2.28544
H	1.54320	-0.54837	1.18317
H	2.00583	1.15948	1.56739
C	-2.64249	0.68326	0.41517
C	-3.35709	1.08299	-0.73905
C	-2.42224	1.71729	1.35981
C	-3.80625	2.39853	-0.95743
C	-2.88540	3.02738	1.19816
C	-3.56116	3.38055	0.01599
C	-1.90640	-1.33490	2.10503
C	-0.89875	-2.25140	2.48937
C	-2.87811	-1.05327	3.09872
C	-0.81956	-2.81716	3.77327
C	-2.84698	-1.61373	4.38539
C	-1.80634	-2.49951	4.72475
C	-1.79805	-1.76525	-0.56645
C	-2.94305	-2.41059	-1.06894
C	-0.57545	-2.14510	-1.14557
C	-2.91000	-3.32761	-2.13136
C	-0.49183	-3.08304	-2.18925
C	-1.66571	-3.65997	-2.69994
B	-2.04424	-0.75470	0.64415
O	0.31687	0.93017	0.30452
F	-1.69795	1.48955	2.47119
F	-2.62785	3.96244	2.12276
F	-3.95022	4.64047	-0.17910
F	-4.43617	2.71972	-2.09346
F	-3.64740	0.20610	-1.71708
F	0.06933	-2.60142	1.62777
F	0.17078	-3.65599	4.09326
F	-1.75726	-3.03591	5.94386
F	-3.91360	-0.23933	2.83015
F	-3.79447	-1.32513	5.28366
F	0.58936	-1.62379	-0.72014
F	-4.14062	-2.14227	-0.50357
F	-4.03197	-3.89425	-2.59232
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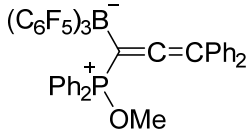

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P	0.22732	1.26105	-1.79371
F	-3.67903	-1.68926	0.74327
F	-1.15516	-4.20209	-3.40798
F	0.05665	-2.14908	-2.21107
F	-3.64028	-5.05562	-2.57844
F	-4.89119	-3.77208	-0.49230
F	-2.31489	-0.18310	3.02418
F	1.71737	-3.87745	2.78024
F	0.84299	-2.74540	0.50914
F	0.59358	-3.18295	5.20072
F	-1.43521	-1.33141	5.26805
F	-3.94922	4.51438	0.58936
F	-1.85022	3.94569	2.26988
F	-0.53243	1.61733	2.04109
F	-4.76559	2.64294	-1.25124
F	-3.53098	0.27914	-1.43487
O	-1.06265	1.16731	-2.78328
C	5.70707	-3.13499	-0.79422
H	6.45374	-3.88076	-1.10953
C	6.05175	-2.13357	0.12931
H	7.07095	-2.09295	0.54539
C	5.09967	-1.18504	0.53784
H	5.37820	-0.41791	1.27567
C	3.78320	-1.21372	0.01862
C	2.77917	-0.20442	0.43017
C	1.54655	-0.13667	-0.07716
C	0.30512	0.00560	-0.50256
C	1.75327	1.23890	-2.78012
C	2.33834	0.00550	-3.14673
H	1.89115	-0.93818	-2.80941
C	3.51157	-0.00898	-3.91540
H	3.97711	-0.97262	-4.17237
C	4.09511	1.20047	-4.33292
H	5.02021	1.18681	-4.93053
C	-0.27416	5.47098	0.02135
H	-0.40596	6.46214	0.48202
C	-1.10565	5.07747	-1.04121

H	-1.89057	5.75505	-1.41010
C	-0.96599	3.80292	-1.61640
H	-1.63209	3.47757	-2.42792
C	0.01396	2.92315	-1.11015
C	2.33453	2.45455	-3.20732
H	1.88429	3.41630	-2.91600
C	3.50435	2.42889	-3.98314
H	3.96371	3.37573	-4.30729
C	-1.32819	0.09455	-3.71217
H	-1.69463	0.56305	-4.64579
H	-2.11339	-0.55265	-3.27796
H	-0.42312	-0.50734	-3.92459
C	-1.77487	-1.78792	-0.68061
C	-3.03445	-2.27941	-0.28393
C	-3.68359	-3.35989	-0.90384
C	-3.04487	-4.02105	-1.97001
C	-1.77839	-3.58378	-2.39027
C	-1.17584	-2.49459	-1.73321
C	-0.69461	-1.30580	1.64762
C	-1.28400	-1.04291	2.89990
C	-0.85187	-1.64248	4.09975
C	0.17950	-2.59631	4.06959
C	0.75771	-2.94179	2.83606
C	0.28880	-2.31508	1.66872
C	-2.01069	0.77843	0.35924
C	-3.09064	1.12288	-0.47273
C	-3.76475	2.35716	-0.40203
C	-3.35405	3.31407	0.53920
C	-2.28145	3.02117	1.39612
C	-1.62657	1.78891	1.26407
C	4.39203	-3.19019	-1.29615
H	4.10116	-3.98800	-1.99799
C	3.44026	-2.24563	-0.89333
H	2.40425	-2.32226	-1.25345
C	3.06899	0.87129	1.43832
C	2.28019	0.95512	2.60657
H	1.52287	0.17932	2.79530
C	2.42961	2.03956	3.48552
H	1.79261	2.10416	4.38112
C	3.37501	3.04442	3.21331
H	3.48921	3.89682	3.90168
C	4.17518	2.96005	2.05792
H	4.91319	3.74791	1.83813
C	4.02244	1.88138	1.17088
H	4.61815	1.83013	0.24588
C	0.85817	3.31826	-0.04799

H	1.60869	2.62757	0.36182
C	0.70905	4.59270	0.51370
H	1.35295	4.88284	1.35765
B	-1.08894	-0.58629	0.21178

Sum of electronic and zero-point Energies= -3702.682350
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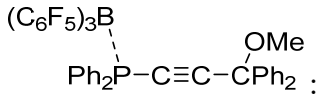
Sum of electronic and thermal Enthalpies= -3702.624243
Sum of electronic and thermal Free Energies= -3702.775428



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C	-0.45577	-2.24263	-2.79088
C	-1.96060	-0.52249	-3.65315
C	-0.81794	-3.08382	-3.85544
H	0.28166	-2.58382	-2.05153
C	-2.31853	-1.37246	-4.71155
H	-2.40187	0.48222	-3.59346
C	-1.75344	-2.65567	-4.81309
H	-0.36077	-4.08266	-3.93384
H	-3.04320	-1.02423	-5.46404
H	-2.03799	-3.32027	-5.64399
C	-0.68844	1.87338	-1.86242
C	0.48742	2.60004	-2.15010
C	-1.93793	2.53548	-1.89857
C	0.41655	3.96989	-2.44915
H	1.46762	2.10309	-2.11191
C	-2.00022	3.90416	-2.20543
H	-2.86219	2.00375	-1.64392
C	-0.82488	4.62770	-2.47112
H	1.34575	4.52454	-2.65358
H	-2.97756	4.41119	-2.21225
H	-0.87672	5.70613	-2.68779
C	1.15050	-0.12139	-1.05920
C	2.30146	-0.15331	-0.63081
C	3.68283	-0.14721	-0.11731
C	4.35650	1.18434	-0.51970
C	5.69536	1.25890	-0.94727
C	3.62919	2.37870	-0.31639
C	6.28780	2.50867	-1.20553
H	6.28292	0.33772	-1.07616
C	4.22112	3.62379	-0.57634

H	2.59879	2.33214	0.06579
C	5.55182	3.69267	-1.02995
H	7.33534	2.55392	-1.54318
H	3.63838	4.54469	-0.41558
H	6.01746	4.66930	-1.23653
C	4.35348	-1.42416	-0.67566
C	4.55339	-2.53912	0.15941
C	4.66157	-1.52405	-2.04959
C	5.08740	-3.72852	-0.36689
H	4.26648	-2.48564	1.21830
C	5.19382	-2.71267	-2.57257
H	4.47348	-0.66576	-2.71376
C	5.41415	-3.81820	-1.72995
H	5.23553	-4.59454	0.29706
H	5.43245	-2.77820	-3.64597
H	5.83002	-4.75204	-2.14018
C	4.68880	0.11496	2.09150
H	4.93788	1.19838	2.04146
H	4.42109	-0.15306	3.13156
H	5.58429	-0.47078	1.78187
C	-1.82577	1.43440	1.09140
C	-3.12843	1.94310	1.26435
C	-0.81271	2.41618	1.07875
C	-3.40998	3.32141	1.35905
C	-1.03808	3.79462	1.16501
C	-2.35995	4.25328	1.30070
C	-0.25203	-0.77769	1.62193
C	0.30174	-2.00550	1.21366
C	0.33410	-0.22581	2.77739
C	1.38739	-2.63468	1.83249
C	1.43900	-0.80862	3.42543
C	1.97211	-2.01188	2.94443
C	-2.72896	-1.14041	0.57497
C	-2.99893	-2.21031	1.45329
C	-3.63393	-1.02566	-0.49234
C	-4.04314	-3.13294	1.24541
C	-4.68477	-1.91583	-0.75229
C	-4.88987	-2.98854	0.13347
B	-1.47474	-0.12208	0.77426
O	3.53456	-0.20476	1.31543
F	0.47485	2.03237	0.90460
F	-0.02265	4.66705	1.08335
F	-2.61607	5.56474	1.37054
F	-4.67212	3.75093	1.50347
F	-4.19548	1.12307	1.33320
F	-0.22356	-2.63356	0.13137

F	1.89831	-3.77913	1.35046
F	3.07751	-2.53277	3.50294
F	-0.14315	0.90618	3.33215
F	2.01882	-0.20288	4.47543
F	-3.52160	0.02834	-1.34497
F	-2.26209	-2.40396	2.56466
F	-4.24547	-4.13820	2.10824
F	-5.88752	-3.85532	-0.07464
F	-5.49512	-1.74296	-1.80591

Sum of electronic and zero-point Energies= -3702.638032
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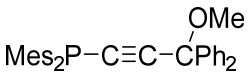
Sum of electronic and thermal Enthalpies= -3702.579783
Sum of electronic and thermal Free Energies= -3702.731927



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C	2.77513	0.68919	0.65453
C	2.56645	2.05777	0.30476
C	4.00042	0.05034	0.29887
C	3.55485	2.71218	-0.45714
C	4.95130	0.75558	-0.46645
C	4.74405	2.08377	-0.87292
H	3.38589	3.76721	-0.73340
H	5.88907	0.24510	-0.74470
C	1.22246	-1.83588	0.56030
C	0.92829	-1.72257	-0.83205
C	1.10816	-3.09602	1.21106
C	0.55478	-2.88339	-1.53649
C	0.71742	-4.22394	0.45814
C	0.44153	-4.14260	-0.91743
H	0.31636	-2.79261	-2.60975
H	0.62426	-5.19671	0.97002
C	0.00141	0.32654	1.50021
C	-1.20640	0.53077	1.36895
C	-2.55976	0.80636	0.86619
C	-3.02272	-0.34834	-0.05227
C	-4.05191	-0.14444	-0.99796
C	-2.46492	-1.63711	0.07394
C	-4.51252	-1.20487	-1.79607
H	-4.48403	0.86025	-1.12404
C	-2.92020	-2.69660	-0.72781
H	-1.64499	-1.81156	0.78640
C	-3.94646	-2.48576	-1.66436
H	-5.31505	-1.02656	-2.52955

H	-2.45303	-3.68786	-0.62102
H	-4.30199	-3.31550	-2.29603
C	-2.39562	2.15672	0.11738
C	-2.54109	3.35979	0.83607
C	-1.94580	2.20390	-1.21883
C	-2.26490	4.59275	0.22161
H	-2.85563	3.31023	1.88950
C	-1.66252	3.43697	-1.82975
H	-1.80329	1.26695	-1.77784
C	-1.82456	4.63623	-1.11309
H	-2.38499	5.52645	0.79404
H	-1.30716	3.45904	-2.87223
H	-1.60194	5.60259	-1.59258
C	-4.79955	1.13423	1.77447
H	-5.28940	0.22739	1.35118
H	-5.25877	1.36079	2.75728
H	-4.99341	1.99177	1.08665
O	-3.41517	0.93726	2.02374
C	1.33987	2.85588	0.69304
H	1.50567	3.93564	0.50740
H	0.44578	2.55749	0.10676
H	1.06905	2.73135	1.75993
C	4.31441	-1.37491	0.70297
H	3.98053	-1.58894	1.74177
H	3.80112	-2.11249	0.04963
H	5.40392	-1.57132	0.65024
C	5.75569	2.82441	-1.71799
H	5.37102	2.98947	-2.74833
H	5.98183	3.82646	-1.29606
H	6.70960	2.26622	-1.80362
C	1.37051	-3.26677	2.69446
H	0.68208	-2.64899	3.30853
H	1.24092	-4.32432	3.00015
H	2.39988	-2.95536	2.97087
C	0.96948	-0.41213	-1.58485
H	0.43608	0.38798	-1.03453
H	2.00945	-0.05469	-1.73341
H	0.49571	-0.51858	-2.58088
C	0.01737	-5.35389	-1.71629
H	-0.94829	-5.17225	-2.23557
H	0.76227	-5.59606	-2.50473
H	-0.10194	-6.25107	-1.07656

Sum of electronic and zero-point Energies= -1731.634279
Sum of electronic and thermal Energies= -1731.597594
Sum of electronic and thermal Enthalpies= -1731.596650

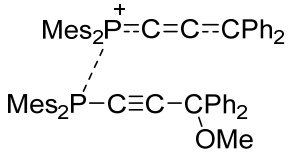
Sum of electronic and thermal Free Energies= -1731.703615

$Mes_2\overset{+}{P}{=}C{=}C{=}CPh_2$:

P	-1.34653	-0.25788	0.80345
C	-2.84609	-1.16221	0.37158
C	-2.87319	-2.33931	-0.44043
C	-4.04779	-0.60761	0.91179
C	-4.12821	-2.90601	-0.72196
C	-5.26902	-1.22263	0.58698
C	-5.33638	-2.37138	-0.22629
H	-4.16483	-3.80639	-1.35687
H	-6.20021	-0.79400	0.99196
C	-1.27746	1.48372	0.24242
C	-1.85306	1.90287	-0.99384
C	-0.55111	2.38713	1.07082
C	-1.69902	3.25460	-1.35633
C	-0.43022	3.72453	0.64730
C	-1.00156	4.18297	-0.55489
H	-2.13416	3.59309	-2.31110
H	0.13487	4.42864	1.27947
C	0.14993	-0.91044	0.34206
C	1.40472	-0.94481	0.23982
C	2.75918	-0.81024	0.04426
C	3.25401	0.57594	-0.07330
C	4.55449	0.92641	0.38548
C	2.40019	1.60581	-0.56213
C	4.98515	2.25873	0.34093
H	5.20728	0.15441	0.81933
C	2.83979	2.93253	-0.60434
H	1.39050	1.35638	-0.92229
C	4.13377	3.26405	-0.15612
H	5.98885	2.51856	0.71095
H	2.16436	3.71195	-0.98884
H	4.47834	4.30941	-0.18883
C	3.62710	-1.99086	-0.01251
C	3.24290	-3.19092	0.64940
C	4.83197	-1.97936	-0.77010
C	4.05099	-4.32940	0.57946
H	2.31535	-3.20505	1.24338
C	5.62941	-3.12794	-0.84489
H	5.11498	-1.07754	-1.33317
C	5.24745	-4.30094	-0.16609
H	3.75449	-5.24623	1.11161
H	6.55179	-3.11373	-1.44550
H	5.88108	-5.19973	-0.22288
C	0.14169	1.94404	2.33865

H	1.09867	1.42788	2.10309
H	0.38037	2.80718	2.98965
H	-0.47223	1.22727	2.92434
C	-2.58869	0.96913	-1.92781
H	-2.04172	0.01558	-2.07495
H	-3.59328	0.69944	-1.53872
H	-2.72870	1.43818	-2.92064
C	-0.89242	5.62971	-0.97092
H	-0.77172	5.73257	-2.06847
H	-1.81697	6.18263	-0.69508
H	-0.04418	6.14104	-0.47407
C	-4.04734	0.63282	1.77774
H	-3.19717	0.64349	2.49409
H	-3.96242	1.55702	1.16561
H	-4.98131	0.70637	2.36795
C	-1.63328	-2.97604	-1.01880
H	-1.04219	-2.25279	-1.62186
H	-0.95466	-3.35615	-0.22721
H	-1.89677	-3.82745	-1.67508
C	-6.65387	-3.04023	-0.52662
H	-6.68247	-3.43920	-1.56083
H	-6.81286	-3.90296	0.15723
H	-7.50943	-2.34968	-0.39185

Sum of electronic and zero-point Energies= -1616.420900
Sum of electronic and thermal Energies= -1616.386537
Sum of electronic and thermal Enthalpies= -1616.385593
Sum of electronic and thermal Free Energies= -1616.489960



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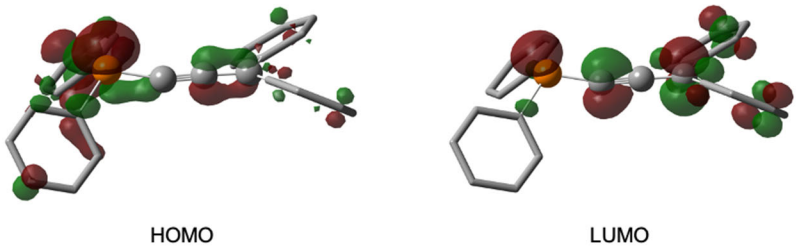
C	-0.61647	3.89235	-0.07804
C	-3.32344	4.07943	0.61298
C	-1.12275	5.04474	0.54915
C	-2.47597	5.16453	0.90486
H	-4.39132	4.15530	0.87792
H	-0.42830	5.87062	0.77478
C	-0.07186	1.72534	-2.79261
C	-0.98113	2.21492	-3.77913
C	1.30208	1.53384	-3.11776
C	-0.48125	2.52866	-5.05696
C	1.74409	1.86452	-4.41507
C	0.87614	2.37111	-5.39836

H	-1.18447	2.90681	-5.81779
H	2.80762	1.71453	-4.66408
C	-1.73831	-0.01262	-1.20255
C	-2.32462	-1.09384	-1.11160
C	-3.11947	-2.31375	-0.89040
C	-4.13531	-2.53628	-2.02516
C	-5.31772	-3.27396	-1.80505
C	-3.83170	-2.10395	-3.33274
C	-6.18645	-3.56114	-2.87141
H	-5.56405	-3.62491	-0.79126
C	-4.69989	-2.39054	-4.39863
H	-2.90409	-1.53805	-3.51402
C	-5.88156	-3.11808	-4.17023
H	-7.10696	-4.13630	-2.68522
H	-4.45268	-2.04237	-5.41380
H	-6.56489	-3.34031	-5.00473
C	-3.76005	-2.08875	0.50577
C	-3.07673	-2.53529	1.65382
C	-4.94688	-1.34223	0.65848
C	-3.58589	-2.26933	2.93482
H	-2.12820	-3.07474	1.53385
C	-5.44882	-1.06503	1.94215
H	-5.48019	-0.97478	-0.23140
C	-4.77347	-1.53132	3.08447
H	-3.03683	-2.63167	3.81871
H	-6.37793	-0.48330	2.04860
H	-5.17323	-1.31862	4.08837
C	-2.68065	-4.71399	-0.76082
H	-3.20706	-5.02537	-1.69016
H	-1.80848	-5.37825	-0.60167
H	-3.37852	-4.82914	0.10028
O	-2.15197	-3.39405	-0.85539
C	-3.91675	1.83250	-0.28402
H	-4.92642	2.20216	-0.01964
H	-3.93721	1.51897	-1.34473
H	-3.73580	0.91356	0.30439
C	0.85074	3.85315	-0.43259
H	1.29971	2.87082	-0.17453
H	1.01815	4.00417	-1.52081
H	1.41535	4.62965	0.11844
C	-3.02167	6.41681	1.54665
H	-3.64906	6.98512	0.82604
H	-3.66921	6.18066	2.41628
H	-2.21431	7.09300	1.88989
C	2.31272	0.98619	-2.13557
H	2.00746	0.00709	-1.71776

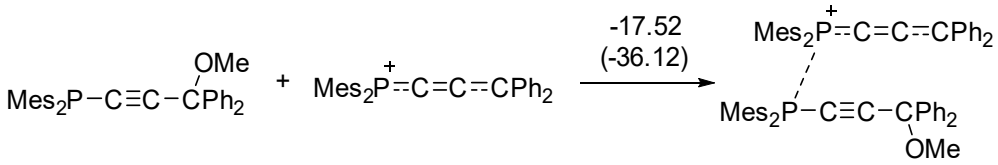
H	3.30064	0.84420	-2.61531
H	2.46099	1.66450	-1.26963
C	-2.45651	2.38768	-3.51448
H	-2.91317	1.43401	-3.17514
H	-2.64283	3.14023	-2.72087
H	-2.99126	2.71334	-4.42726
C	1.37159	2.74401	-6.77515
H	0.72041	2.31908	-7.56710
H	1.36231	3.84733	-6.91058
H	2.40680	2.39209	-6.95321
P	-0.62790	1.33092	-1.06526
P	1.08909	0.32334	1.39106
C	0.49799	1.72709	2.37143
C	0.64363	-1.35032	2.00379
C	2.75907	0.20233	1.15462
C	1.34639	2.81793	2.74587
C	-0.90410	1.76665	2.64908
C	0.50736	-1.62957	3.39771
C	0.55890	-2.38592	1.03154
C	3.78702	-0.31162	0.63008
C	0.75602	3.91626	3.39405
C	2.83685	2.85158	2.50152
C	-1.42600	2.89571	3.30467
C	-1.84057	0.62818	2.32825
C	0.18194	-2.94813	3.76916
C	0.75879	-0.60589	4.48285
C	0.26119	-3.69058	1.47385
C	0.83306	-2.18140	-0.43578
C	4.84729	-1.00465	0.11362
C	-0.62258	3.98575	3.67749
H	1.40334	4.76006	3.68465
H	3.34834	1.97826	2.95786
H	3.09186	2.83197	1.42175
H	3.28008	3.77020	2.93213
H	-2.50858	2.92930	3.50530
H	-1.64674	0.15197	1.34695
H	-1.76497	-0.19008	3.07366
H	-2.89362	0.96528	2.32953
C	0.03749	-3.98993	2.82841
H	0.06594	-3.17630	4.84170
H	1.67382	-0.01355	4.27699
H	-0.06977	0.12533	4.58536
H	0.88747	-1.10372	5.46336
H	0.19267	-4.49113	0.72064
H	1.86190	-2.52411	-0.68093
H	0.10584	-2.75150	-1.04473

H	0.75278	-1.11870	-0.73089
C	4.67830	-2.47723	0.07964
C	6.02999	-0.30240	-0.40679
C	-1.20220	5.19668	4.36347
C	-0.37597	-5.37624	3.25867
C	5.18609	-3.25000	-0.99862
C	3.90894	-3.13075	1.08085
C	5.93323	1.05914	-0.80626
C	7.29790	-0.94014	-0.47553
H	-0.84336	5.26703	5.41297
H	-0.88954	6.13149	3.85386
H	-2.30869	5.16987	4.38328
H	-0.07652	-5.59427	4.30321
H	-1.48258	-5.47940	3.20530
H	0.05440	-6.15732	2.59990
C	4.93482	-4.62788	-1.06476
H	5.74681	-2.75526	-1.80594
C	3.66283	-4.50707	1.00830
H	3.50252	-2.54660	1.92058
C	7.05562	1.74743	-1.27890
H	4.95548	1.56322	-0.75530
C	8.41995	-0.24349	-0.94548
H	7.40568	-1.97778	-0.12604
C	4.17561	-5.26237	-0.06313
H	5.32544	-5.21102	-1.91323
H	3.06241	-4.98958	1.79482
C	8.30410	1.09797	-1.35429
H	6.96057	2.79778	-1.59554
H	9.39744	-0.74883	-0.98341
H	3.98267	-6.34499	-0.12047
H	9.18728	1.64043	-1.72595

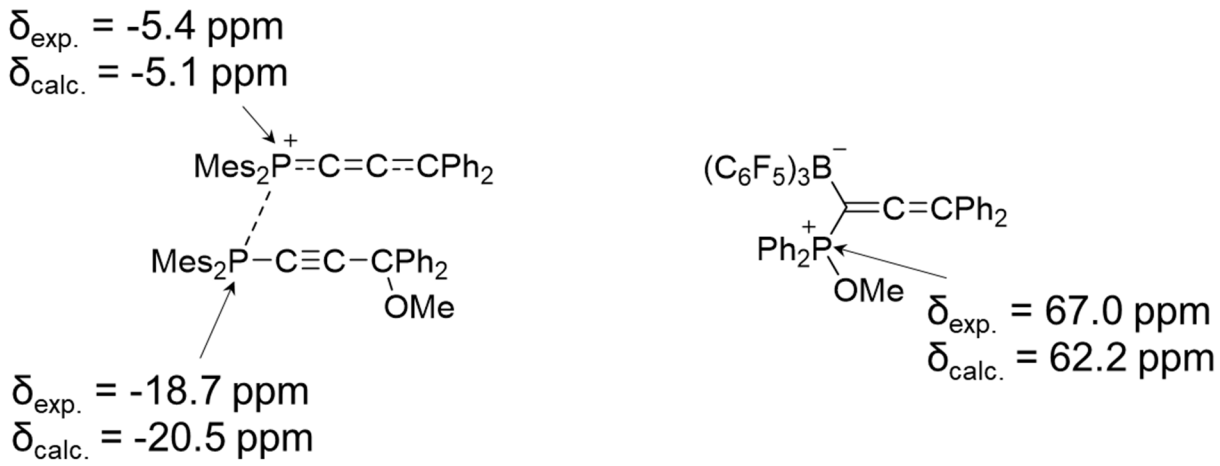
Sum of electronic and zero-point Energies= -3348.112283
Sum of electronic and thermal Energies= -3348.040750
Sum of electronic and thermal Enthalpies= -3348.039805
Sum of electronic and thermal Free Energies= -3348.221495



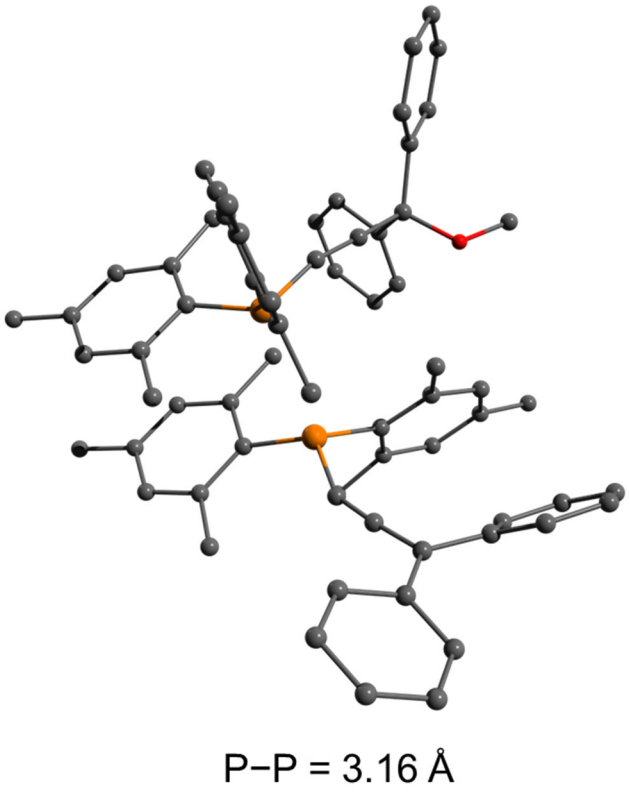
Supplementary Figure 9: Selected frontier molecular orbitals of int2 computed using the BP86(D3)/def2-SVP basis sets.



Supplementary Figure 10: Computational energetic analysis for formation of **6.** Energies are reported relative to the starting materials. Gibbs free energies and enthalpies (in parenthesis) given in kcal mol^{-1}.



Supplementary Figure 11: NMR calculation at PBE1PBE/6-31G(d) level of theory[7] in gas phase. The ^{31}P chemical shifts referenced to calculated H_3PO_4 at the same level of theory.



Supplementary Figure 12: Computed minimized structure of **6**.

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