Electronic Supplementary Material (ESI) for Dalton Transactions.

- Supporting Information -

Synthesis, Characterisation and Reactivity of Group 2 Complexes with a Thiopyridyl Scorpionate Ligand

Matthew P. Stevens,[a] Emily Spray,[a] Iñigo J. Vitorica-Yrezabal,[b] Kuldip Singh,[a] Vanessa M. Timmermann,[a] Lia Sotorrios,[c] Stuart Macgregor,[c]* Fabrizio Ortu[a]*

[a]School of Chemistry, University of Leicester, University Road, LE1 7RH Leicester, UK

[b]Department of Chemistry, The University of Manchester, Oxford Road, M13 9PL Manchester, UK

[c]Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK

*email: s.a.macgregor@hw.ac.uk; fabrizio.ortu@leicester.ac.uk

S1. Experimental details

Synthesis of [{Mg(κ^3*C,N,N*-C{Me}{S-C_5H_4N}$_2$)(μ-OSiMe$_3$)}$_2$] (2): HTptm (0.343 g, 1.00 mmol) and Me_2Mg (0.054 g, 1.00 mmol) were added into a flamed Schlenk flask and dissolved in diethyl ether (40 mL). The reaction mixture was stirred for 1 hour at room temperature, leading to the formation of a precipitate, which was filtered off and dried under vacuum. The filtrate was concentrated *in vacuo* (ca. 10 mL) and stored at room temperature, affording a very small crop of colourless crystals of **2** (<10 mg), sufficient only for XRD characterisation.

Attempted synthesis of [Sr(Tptm)(N″)] (3-Sr): Sr(N″)$_2$ (0.408 g, 1.00 mmol) and HTptm (0.343 g, 1.00 mmol) were added into a flamed Schlenk flask fitted with a stir bar. The flask was cooled to –15 °C and diethyl ether (30 mL) was then added slowly with rapid stirring. The reaction mixture was allowed to stir at −15 °C for 15 minutes, generating an orange suspension. The solvent was then removed *in vacuo* affording an orange powder (0.560 g). This was shown to be a mixture of **3-Sr** (2.1%), Sr(S-C_5H_4N)$_2$ (**4-Sr**, 1.6%), HN″ (82.2%), Sr(N″)$_2$ (0.8%), and HTptm (13.2%). ^{1}H NMR (400 MHz, 298 K, C_7D_8): 0.11 (18H, s, **3-Sr** SiC*H*$_3$), 5.78 (3H, t, $^3J_{HH}$ = 6.2 Hz, **3-Sr** C_5H_4N-C*H*^{b}), 6.45 (2H, t, $^3J_{HH}$ = 6.1 Hz, **4-Sr** C_5H_4N-C*H*^{b}), 6.54 (3H, t, $^3J_{HH}$ = 7.6 Hz, **3-Sr** C_5H_4N-C*H*^{d}), 6.80 (3H, **3-Sr** C_5H_4N-C*H*^{c}), 6.89 (2H, *t*, $^3J_{HH}$ = 8.6 Hz, **4-Sr** C_5H_4N-C*H*^{d}), 7.24 (2H, d, $^3J_{HH}$ = 7.9 Hz, **4-Sr** C_5H_4N-C*H*^{c}), 8.00 (3H, d, $^3J_{HH}$ = 5.4 Hz, **3-Sr** C_5H_4N-C*H*^{a}), 8.23 (2H, d, $^3J_{HH}$ = 5.0 Hz, **4-Sr** C_5H_4N-C*H*^{a}) ppm. Signals belonging to HN″, Sr(N″)$_2$ and HTptm have been omitted from this assignment for clarity.

Attempted synthesis of [Ba(Tptm)(N″)] (3-Ba): Ba(N″)$_2$ (0.457 g, 1.00 mmol) and HTptm (0.343 g, 1.00 mmol) were added into a flamed Schlenk flask fitted with a stir bar. The flask was cooled to –15 °C and diethyl ether (30 mL) was then added slowly with rapid stirring. The reaction mixture was allowed to stir at −15 °C for 15 minutes, generating an orange suspension. The solvent was then removed *in vacuo* affording a brown powder (0.613 g), which was shown to be a mixture of Ba(S-C_5H_4N)$_2$ (**4-Ba**, (31%), Ba(N″)$_2$ (21%), and HN″ (48%) *via* ^{1}H NMR analysis. ^{1}H NMR (400 MHz, 298 K, C_7D_8): 6.47 (4H, dd, $^3J_{HH}$ = 7.6, 4.9 Hz, **4-Ba** C_5H_4N-C*H*), 6.77 (4H, t, $^3J_{HH}$ = 7.8 Hz, **4-Ba** C_5H_4N-C*H*), 6.89 (4H, d, $^3J_{HH}$ = 7.1 Hz, **4-Ba** C_5H_4N-C*H*), 8.48 (4H, br, fwhm = 11.0 Hz, **4-Ba** C_5H_4N-C*H*) ppm. Signals belonging to HN″ and Ba(N″)$_2$ have been omitted from this assignment for clarity.

Attempted synthesis of [Mg(Tptm)(PPh$_2$)] *via* Mg(PPh$_2$)$_2$ and isolation of [Mg(Bptm)$_2$] (5):

$HPPh_2$ (0.692 mL, 4.00 mmol) was added into a flamed Schlenk flask fitted with a stir bar and dissolved in hexane (30 mL). $^nBu_2Mg$ (4.0 mL, 2.00 mmol, 0.5 M in heptane) was then added dropwise with stirring, and the reaction mixture allowed to stir at room temperature for 1 hour, leading to the formation of a suspension. The white precipitate was then filtered off, washed with hexane, and dried under vacuum, affording Mg(PPh$_2$)$_2$ as a white powder (0.426 g, 1.08 mmol, 54%).

$Mg(PPh_2)_2$ (0.394 g, 1.00 mmol) and HTptm (0.343 mg, 1.00 mmol) were then added to a flamed Schlenk fitted with a stir bar. THF (30 mL) was added at room temperature and the reaction mixture was stirred for 16 hours. The deep ruby solution was concentrated to a quarter of its volume, and hexane (40 mL) added, leading to the precipitation of a red solid. The precipitate was filtered off and dried *in vacuo*. Recrystallisation of this precipitate from toluene gave a small crystalline crop of **5**·Ph_2P-PPh_2 (<10 mg), sufficient only for XRD characterisation.

$Mg(PPh_2)_2$: ^{1}H NMR (400 MHz, 298 K, C_4H_8O): 7.11 (2H, t, $^3J_{HH}$ = 7.5 Hz, P-C_6H_5-CH^c), 7.28 (4H, t, $^3J_{HH}$ = 7.5 Hz, P-C_6H_5-CH^b), 7.72 (4H, dd, $^3J_{HH}$ = $^3J_{HP}$ = 6.9 Hz, P-C_6H_5-CH^a) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_4H_8O): 122.5 (s, P-C_6H_5-CH^c), 127.5 (d, $^3J_{CP}$ = 5.7 Hz, P-C_6H_5-CH^b), 132.3 (d, $^2J_{CP}$ = 16.3 Hz, P-C_6H_5-CH^a), 148.2 (d, $^1J_{CP}$ = 33.8 Hz, P-C_6H_5-C) ppm. ^{31}P{^{1}H} NMR (160 MHz, C_4H_8O): −46.8 ppm. FTIR $\tilde{\nu}$ = 2953, 1580, 1479, 1431, 1025, 978, 871, 733, 693, 502, 473 cm^{-1}.

Attempted synthesis of [Mg(Tptm)(PPh_2)] *via* 3-Mg: To an NMR tube fitted with a Young's valve was added **3-Mg** (5.3 mg, 10 µmol), diphenylphosphine (17.3 µL, 100 µmol), d_6-benzene (ca. 1 mL), and six drops of d_8-THF to aid solubility. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at daily intervals for three days (after which time it was determined no change had occurred). The sample was then heated to 50 °C for 12 hours, and another set of spectra recorded. No significant change was observed.

S2. NMR data

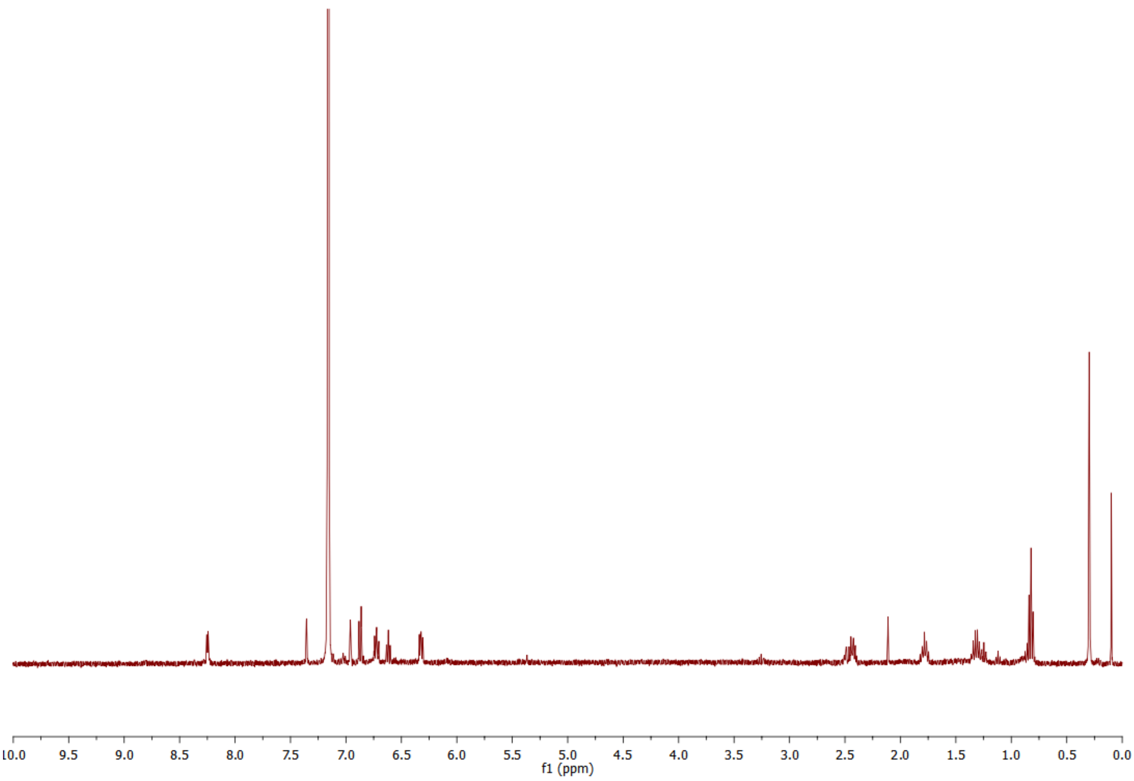


Figure S1: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of **1**.

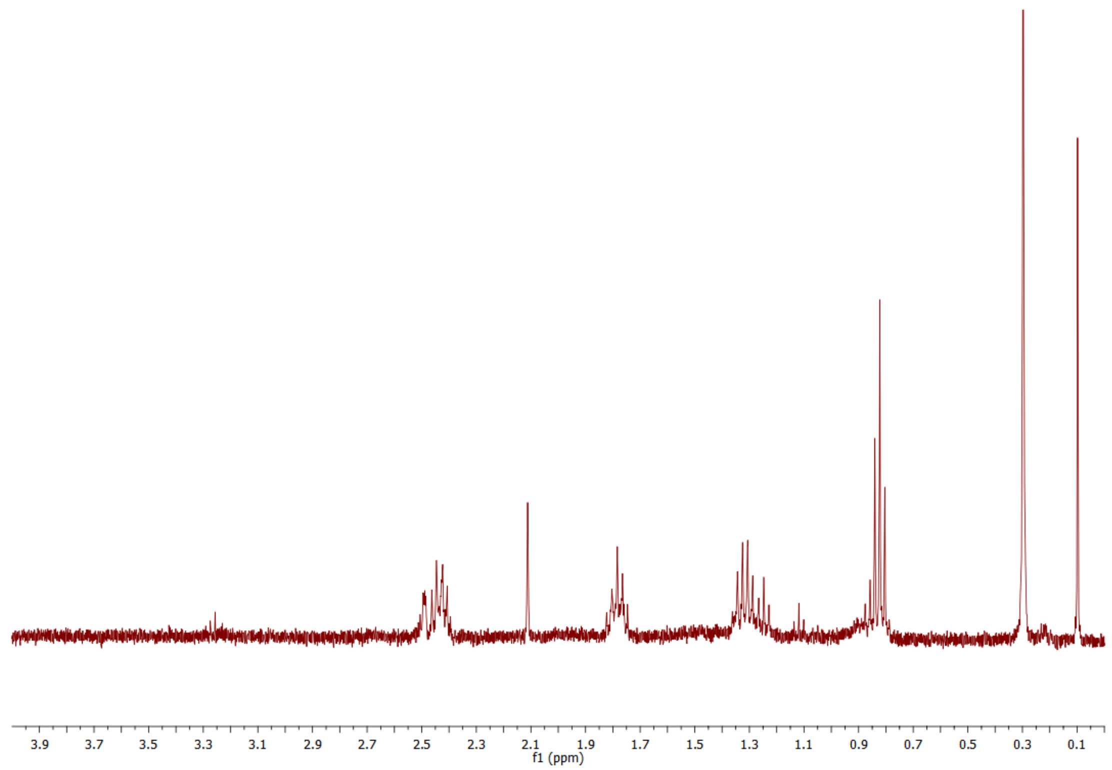


Figure S2: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of **1** in the region 4.0 to 0.0 ppm.

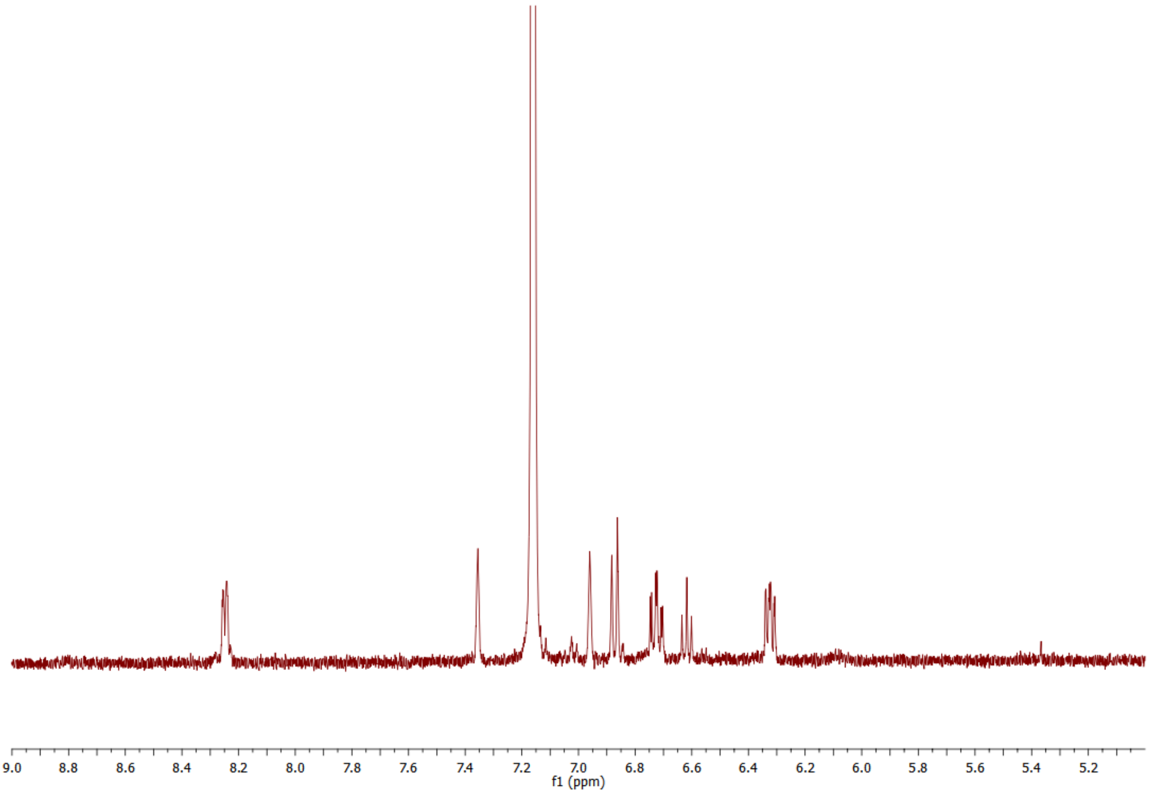


Figure S3: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of **1** in the region 5.0-10.0 ppm.

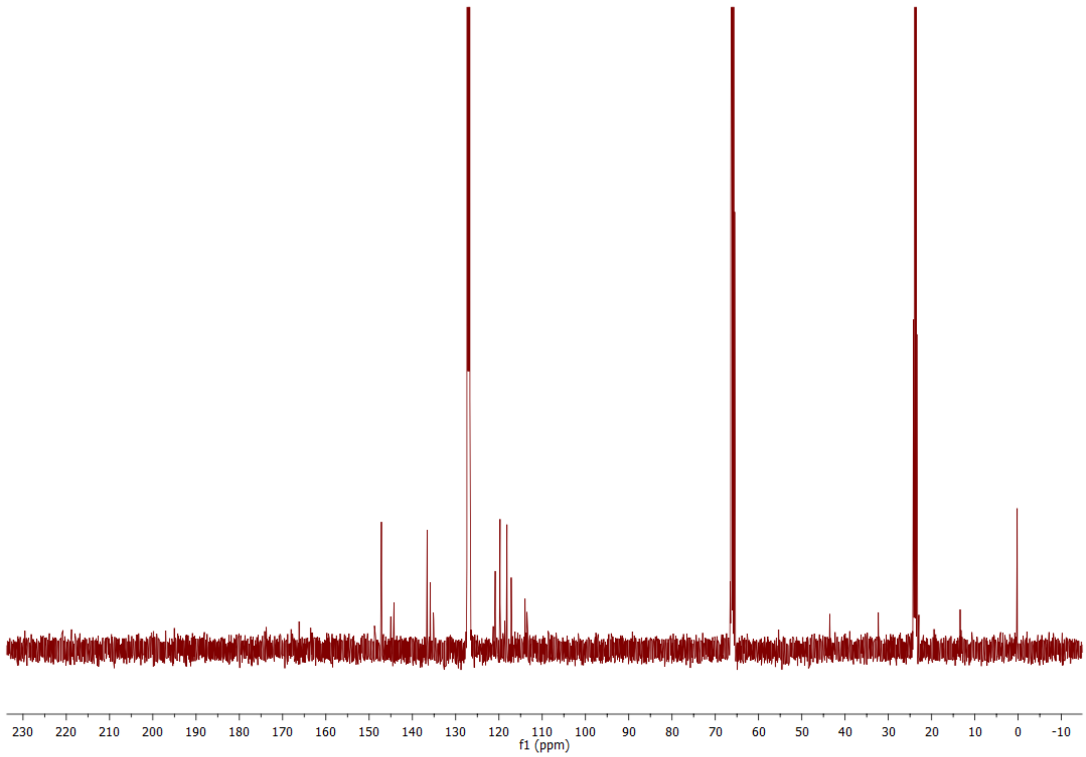


Figure S4: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_6D_6) spectrum of **1**.

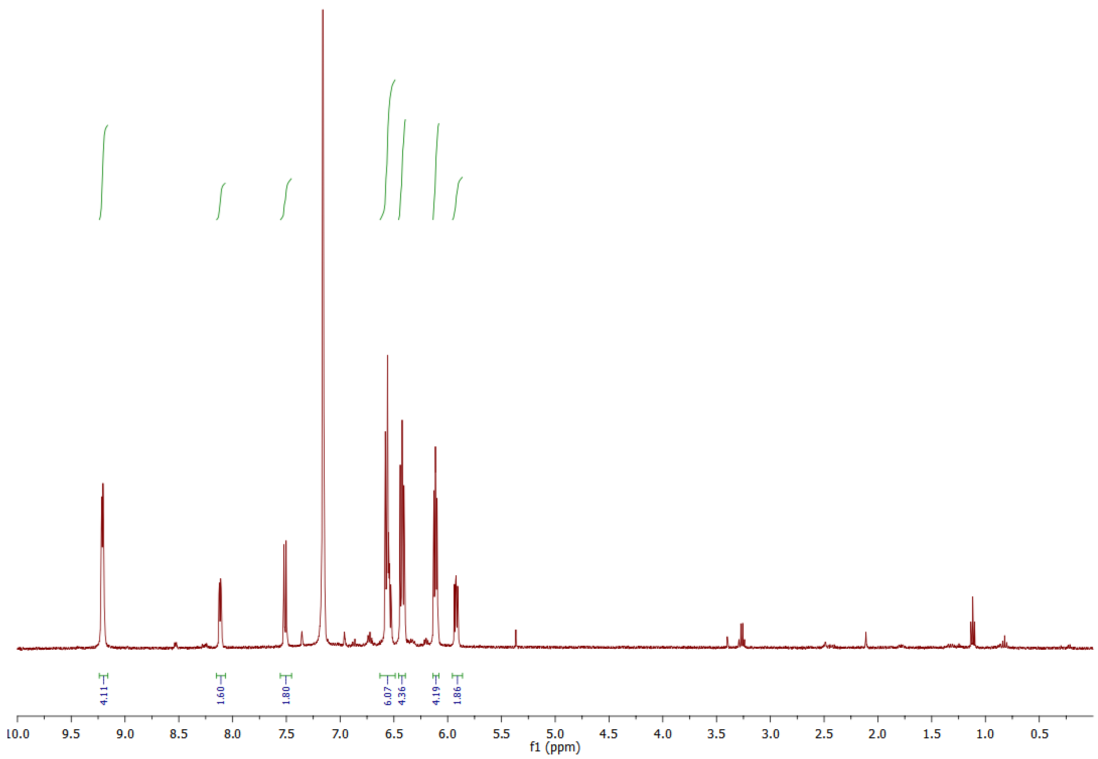


Figure S5: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of the precipitate also formed in the reaction between HTptm and $^{n}Bu_2Mg$.

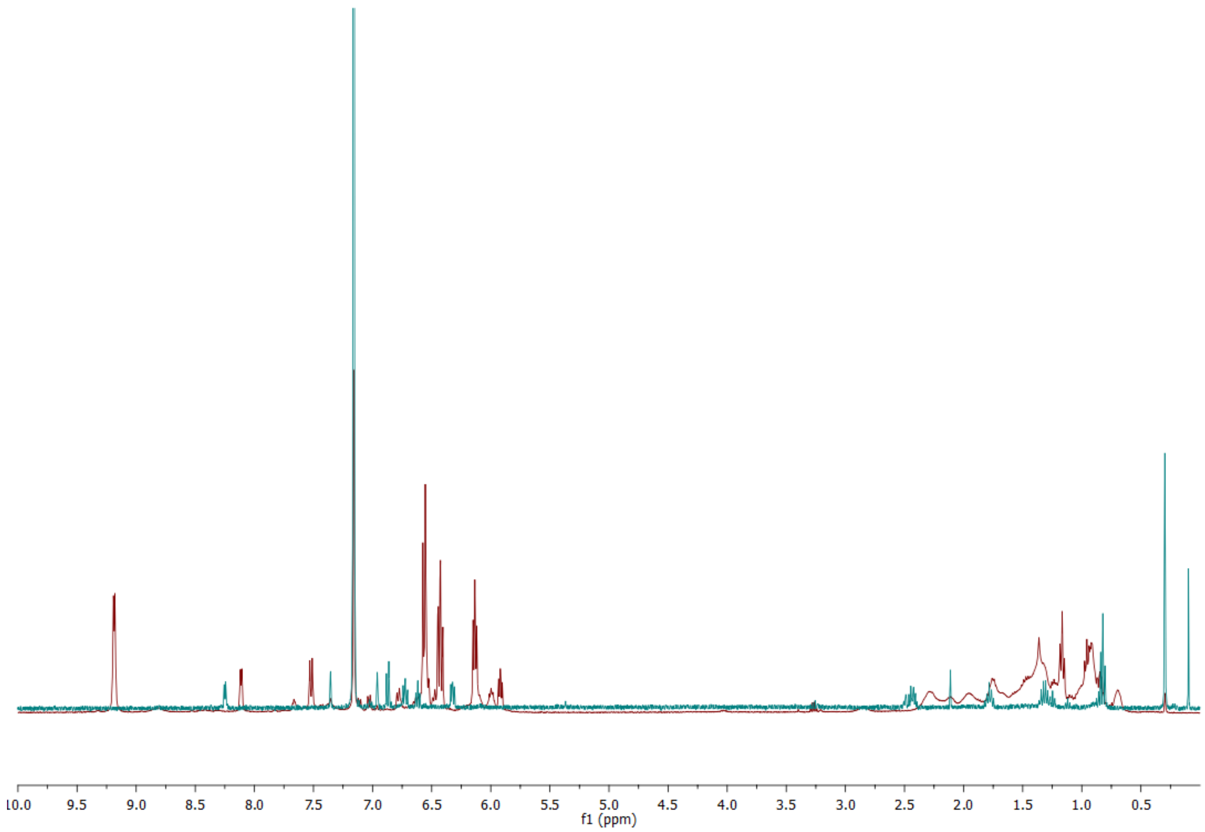


Figure S6: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of the reaction mixture without any further processing (red) overlaid with the crystalline precipitate obtained (**1**, teal).

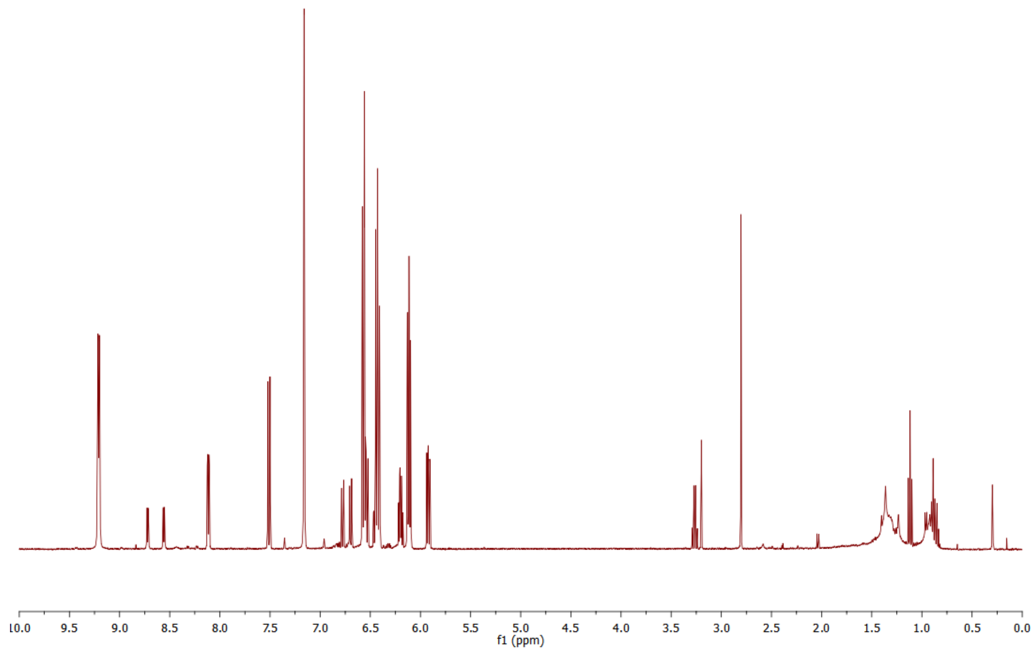


Figure S7: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of the precipitate from the reaction between HTptm and Me_2Mg.

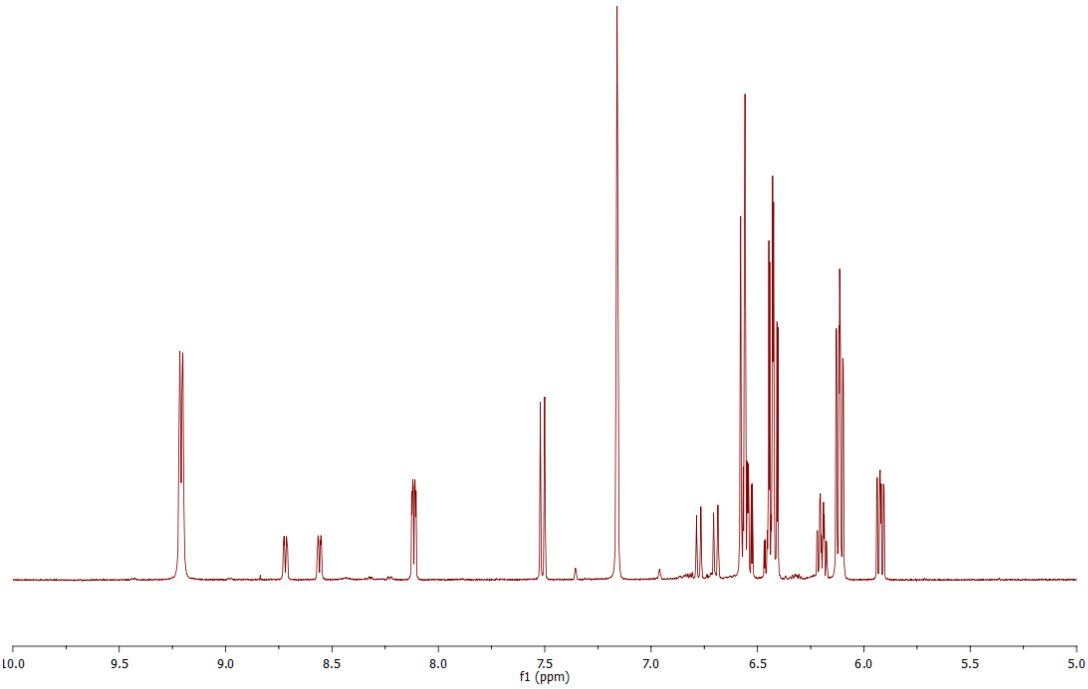


Figure S8: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of the precipitate from the reaction between HTptm and $MgMe_2$ in the region 5.0-10.0 ppm.

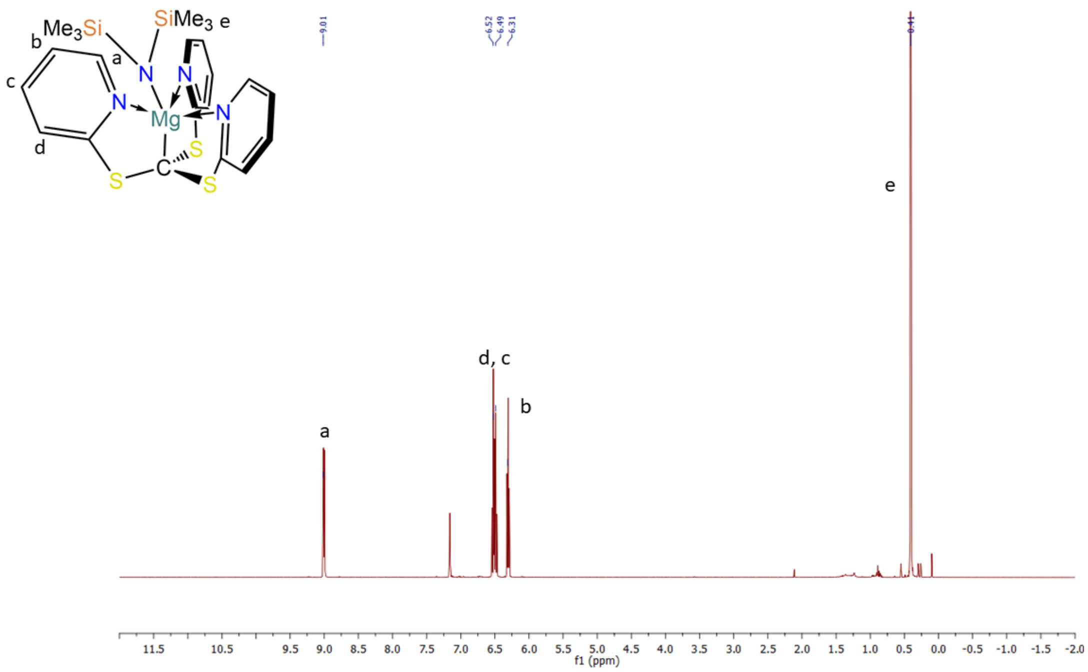


Figure S9: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of **3-Mg**, with assignment.

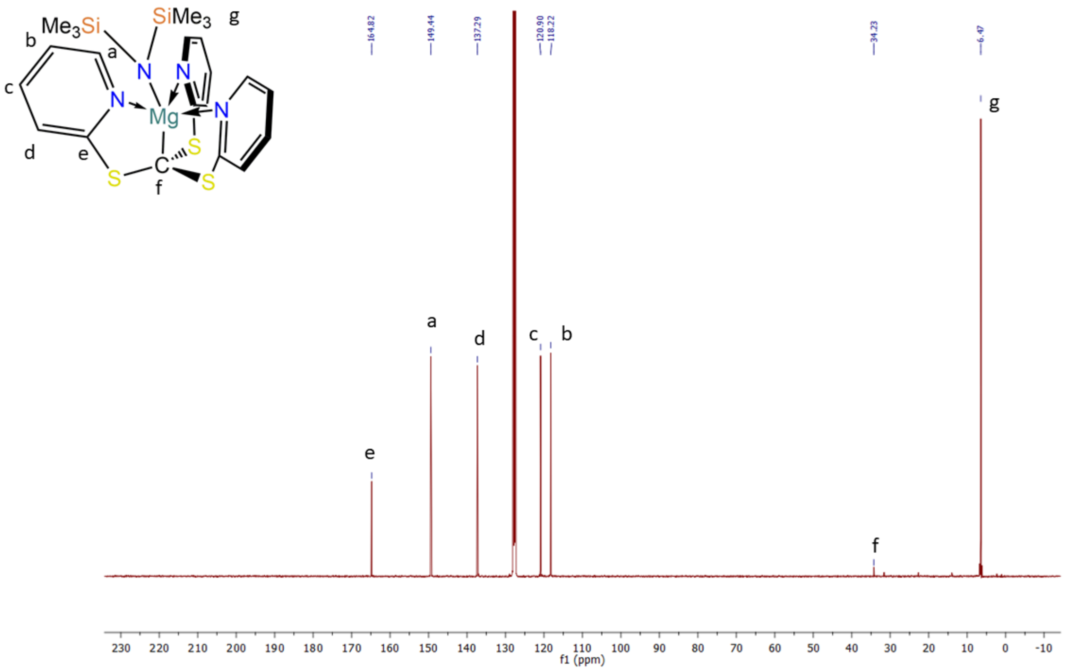


Figure S10: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_6D_6) spectrum of **3-Mg**, with assignment.

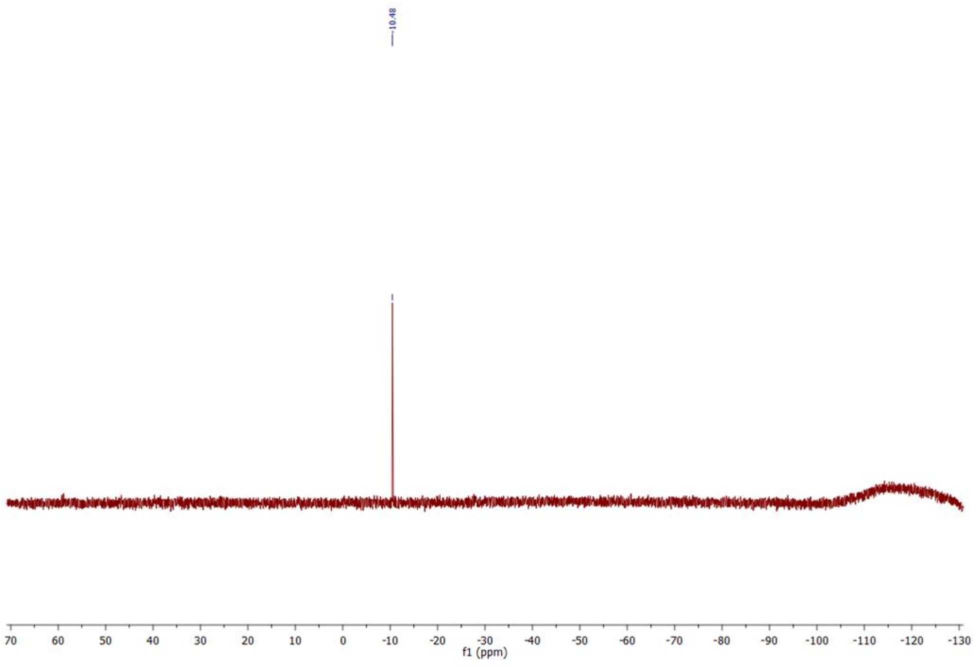


Figure S11: $^{29}Si\{^{1}H\}$ NMR (79 MHz, 298 K, C_6D_6) spectrum of **3-Mg**.

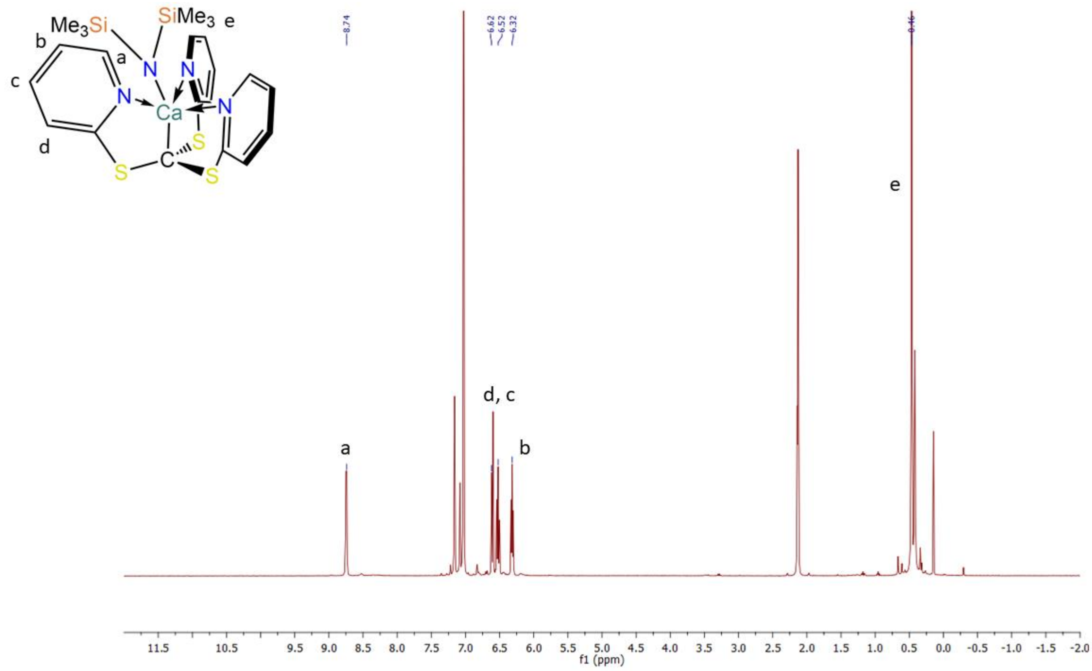


Figure S12: ^{1}H NMR (400 MHz, 263 K, C_7D_8) spectrum of **3-Ca**, with assignment.

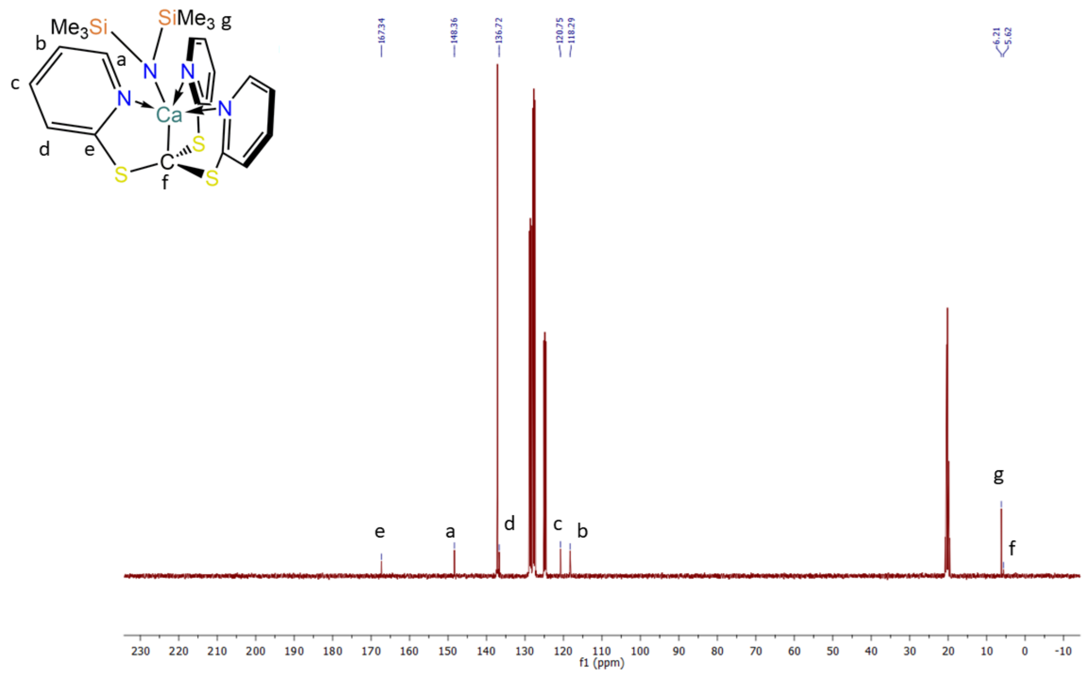


Figure S13: ^{13}C{^{1}H} NMR (100 MHz, 263 K, C_7D_8) spectrum of **3-Ca**, with assignment.

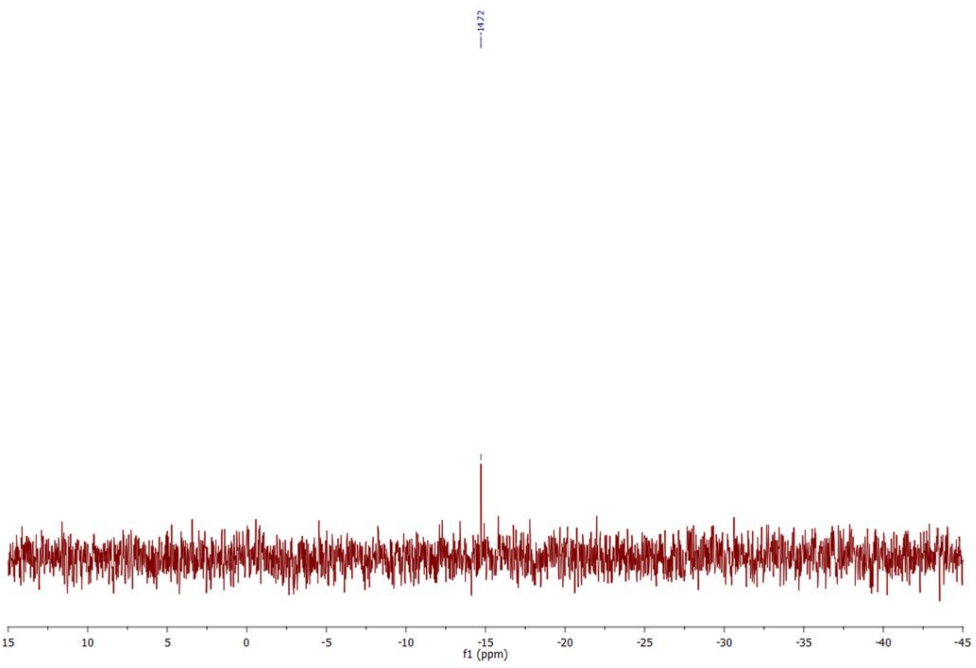


Figure S14: $^{29}Si\{^{1}H\}$ NMR (79 MHz, 263 K, C_7D_8) spectrum of **3-Ca**.

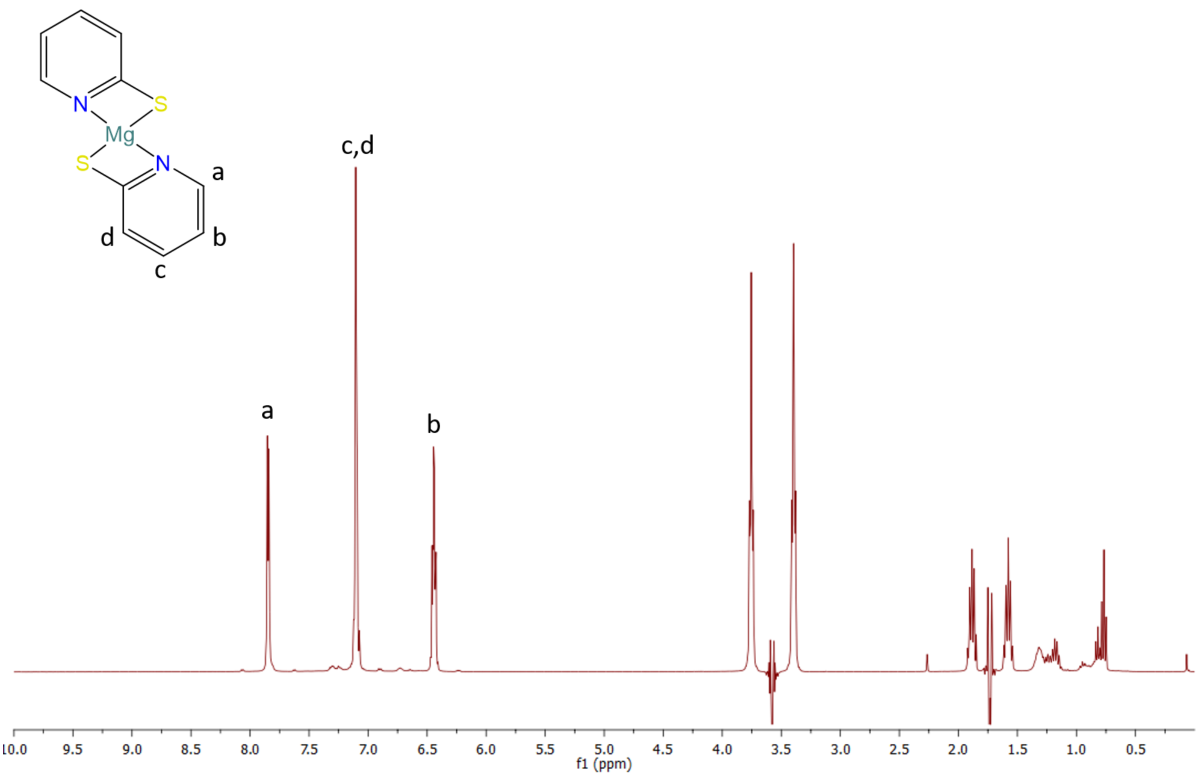


Figure S15: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum of **4-Mg**, with assignment

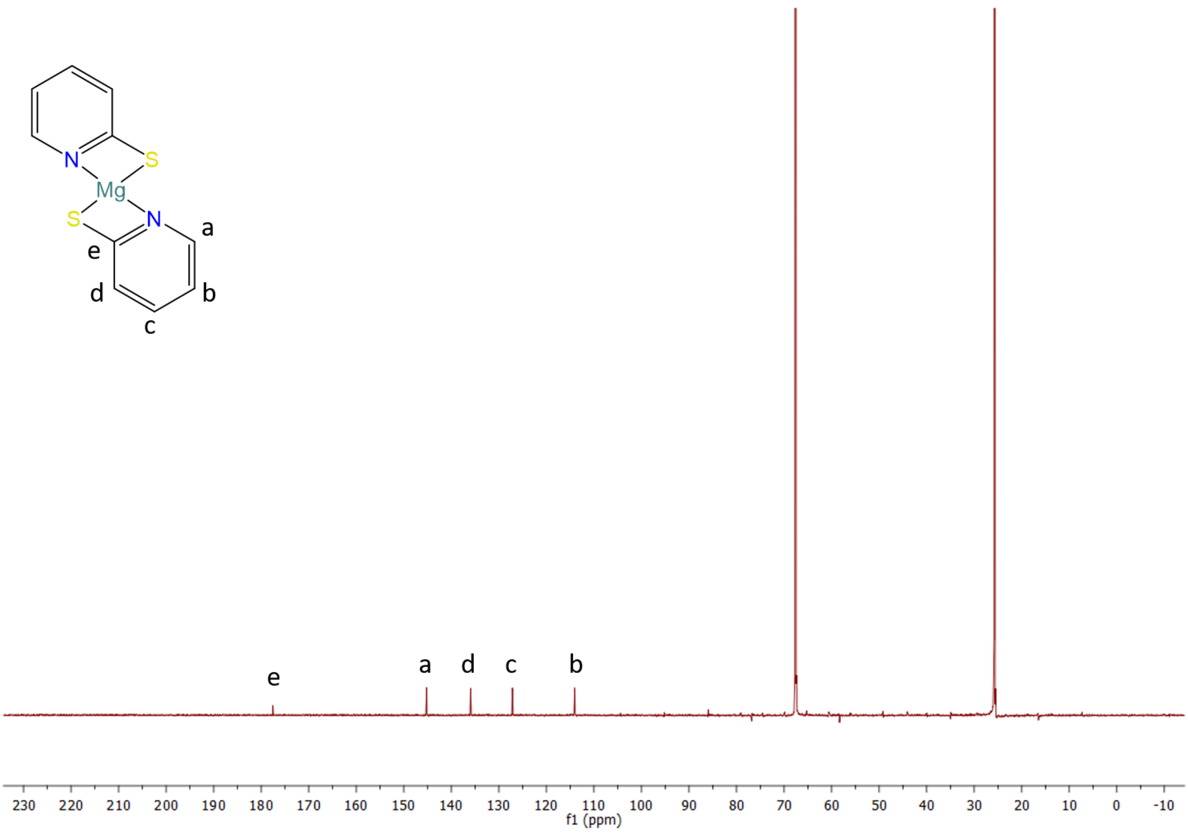


Figure S16: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_4H_8O) spectrum of **4-Mg**, with assignment

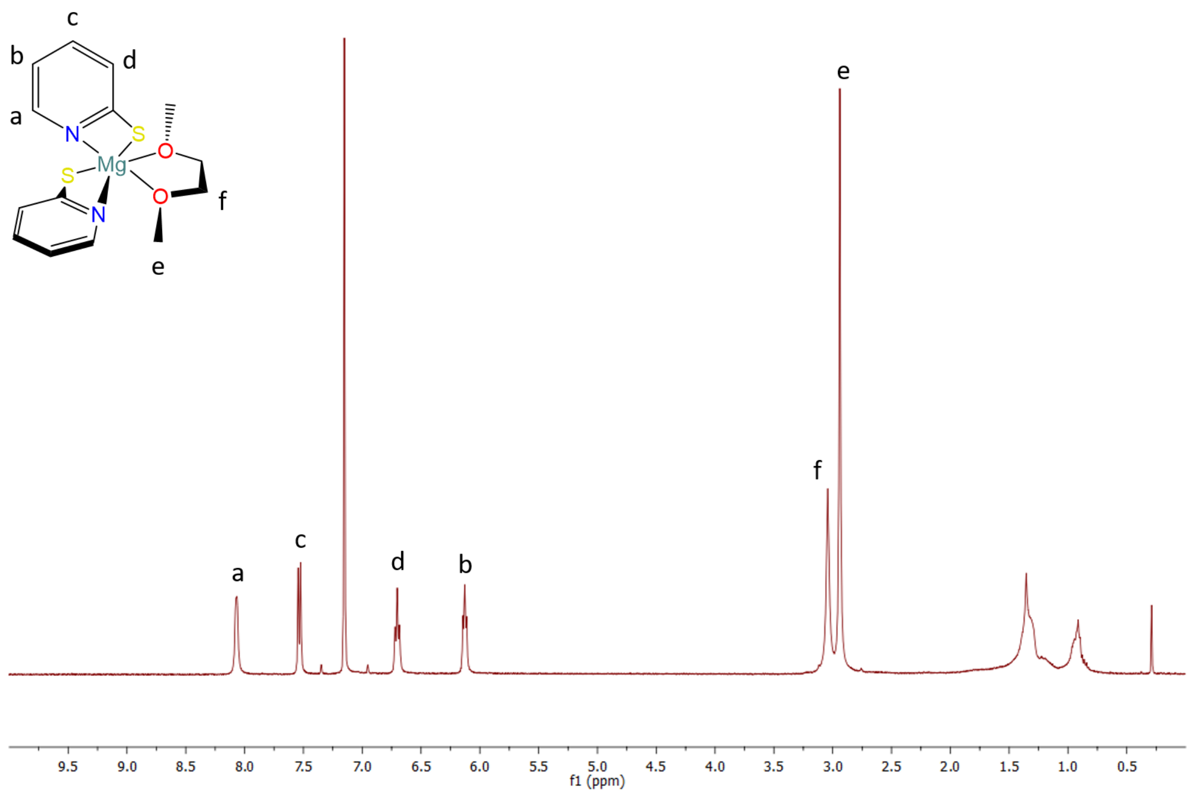


Figure S17: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum of **4-Mg-DME**, with assignment

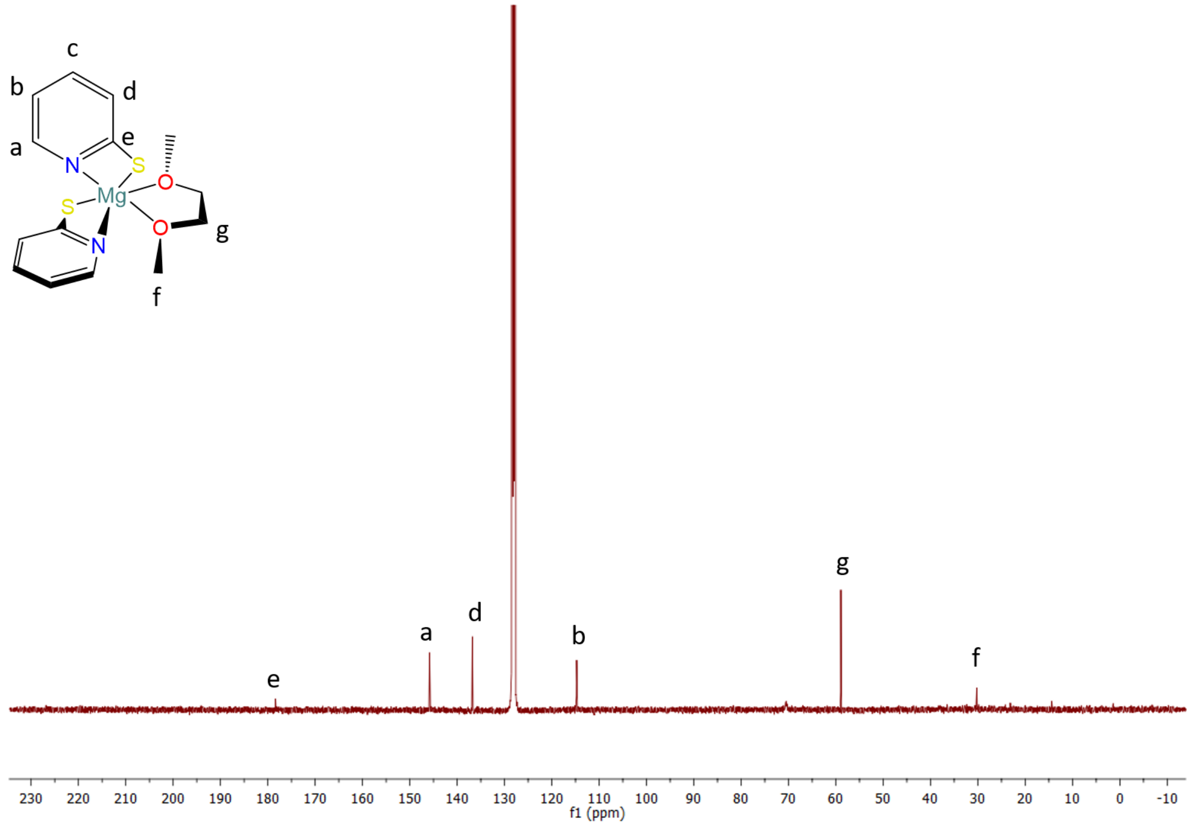


Figure S18: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_4H_8O) spectrum of **4-Mg-DME**, with assignment

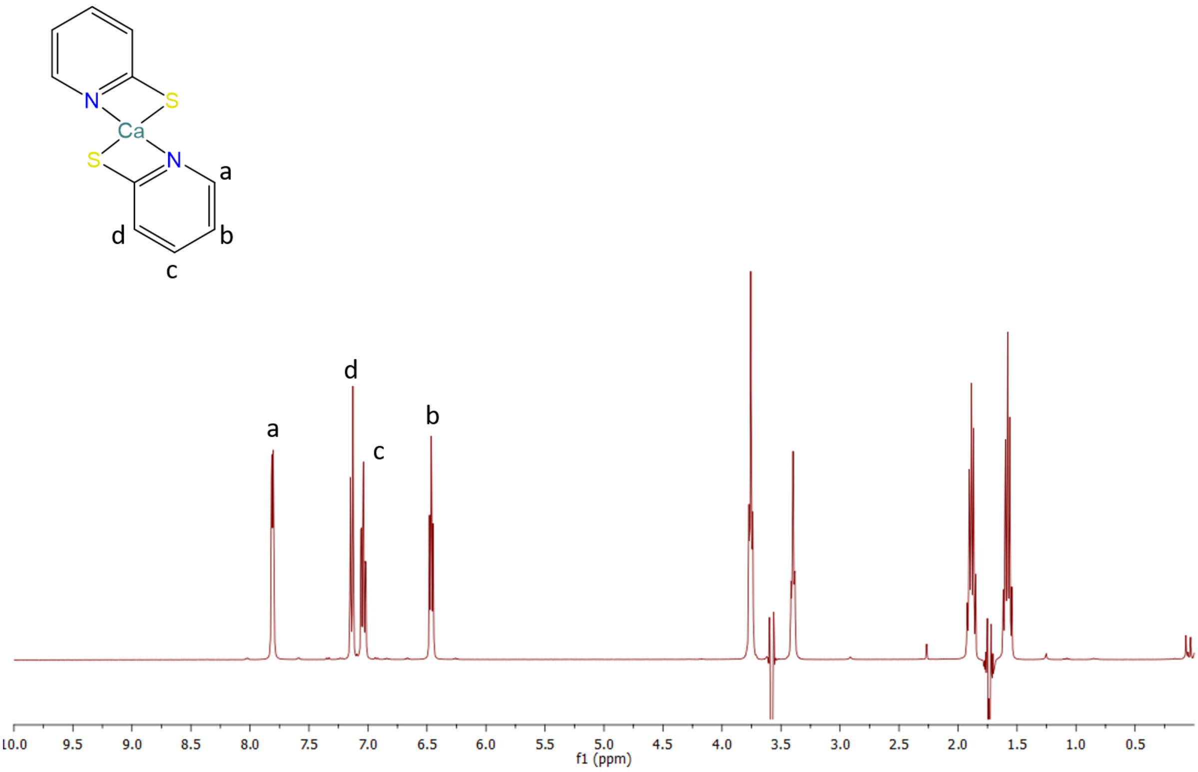


Figure S19: [1]H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum of **4-Ca**, with assignment

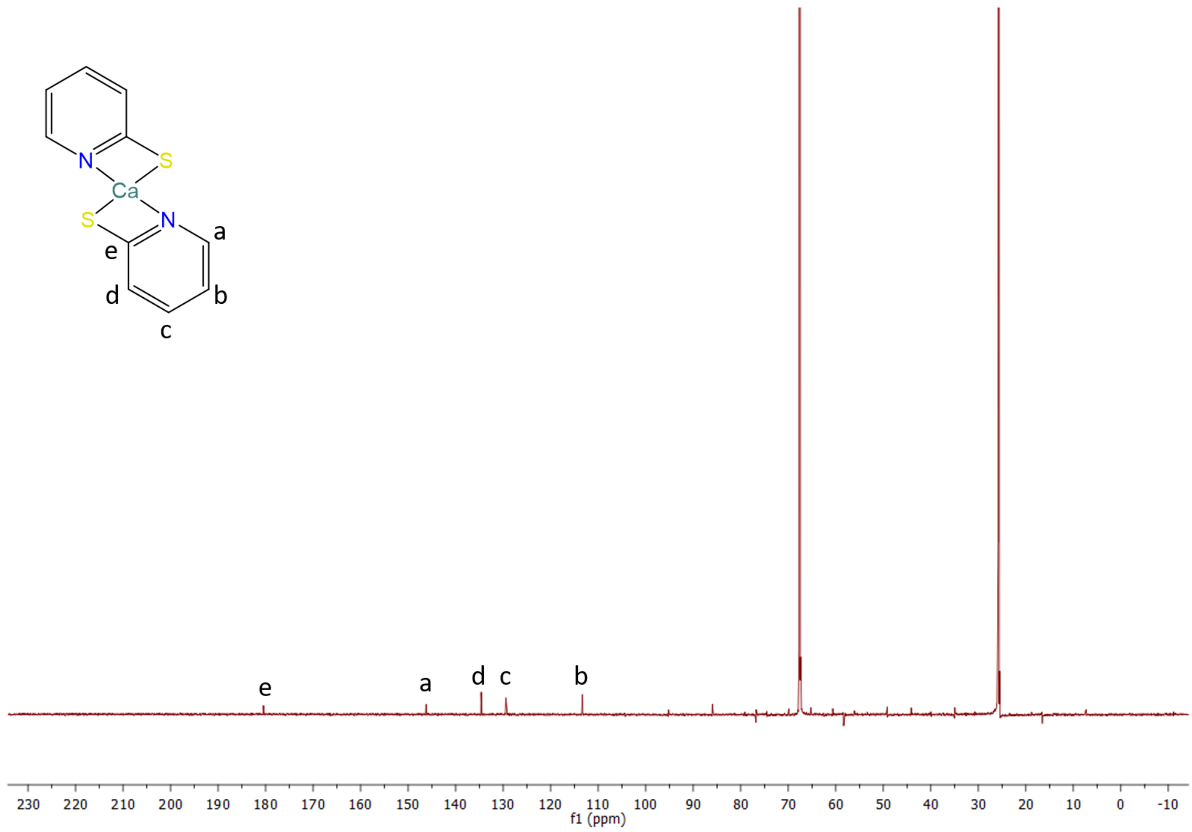


Figure S20: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_4H_8O) spectrum of **4-Ca**, with assignment

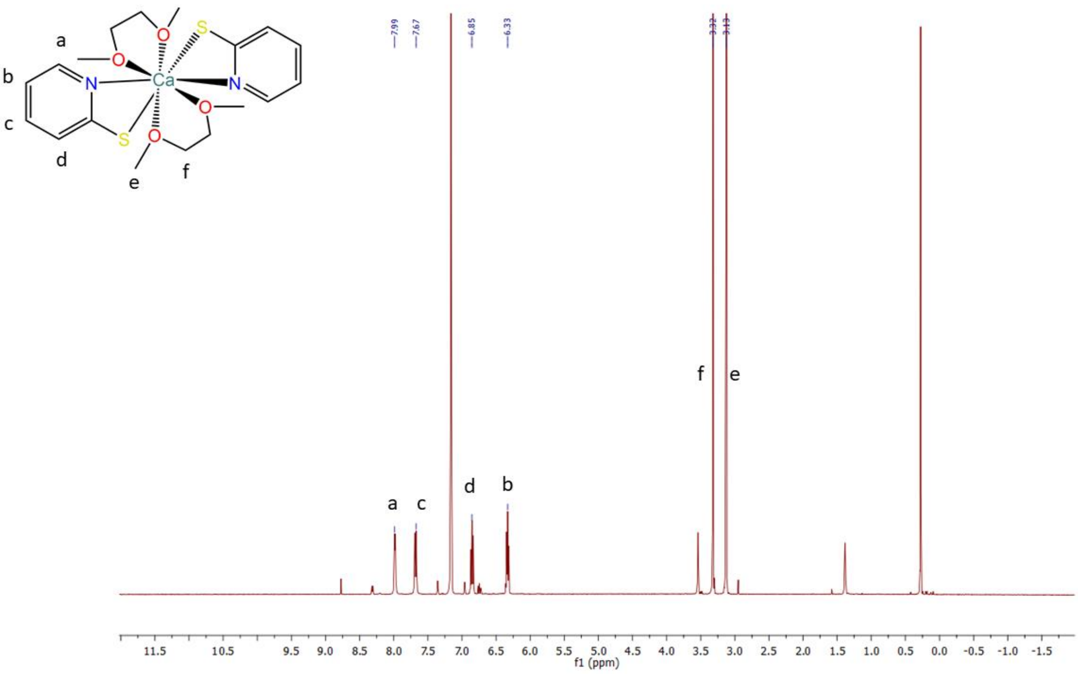


Figure S21: ^{1}H NMR (400 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of **4-Ca-DME**, with assignment.

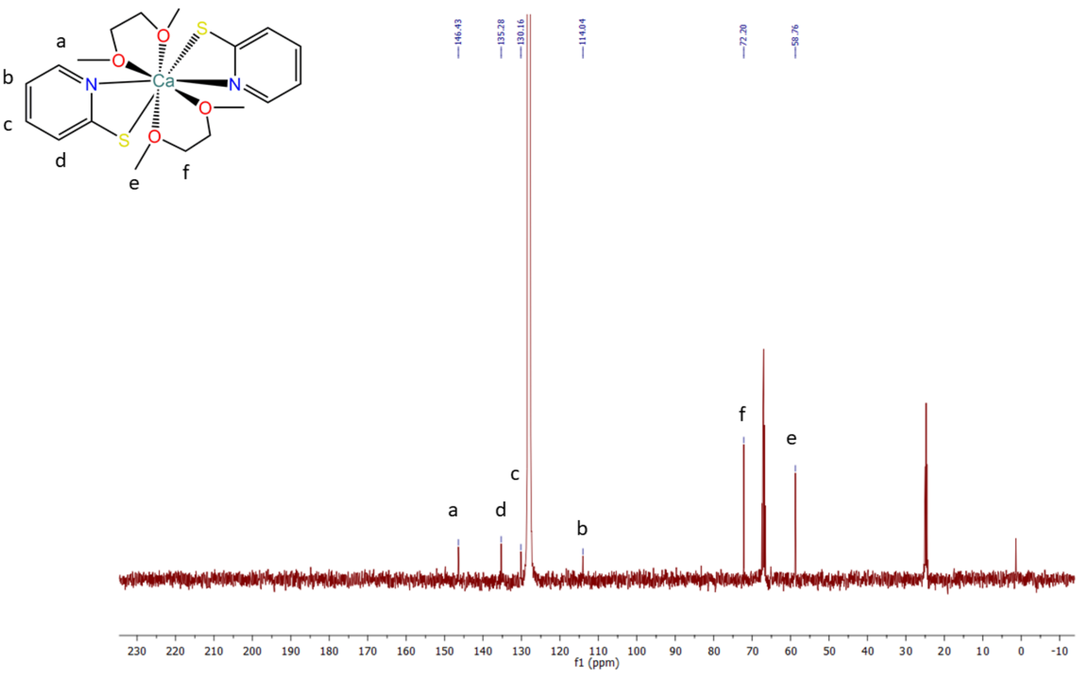


Figure S22: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_6D_6/C_7D_8O) spectrum of **4-Ca-DME**, with assignment.

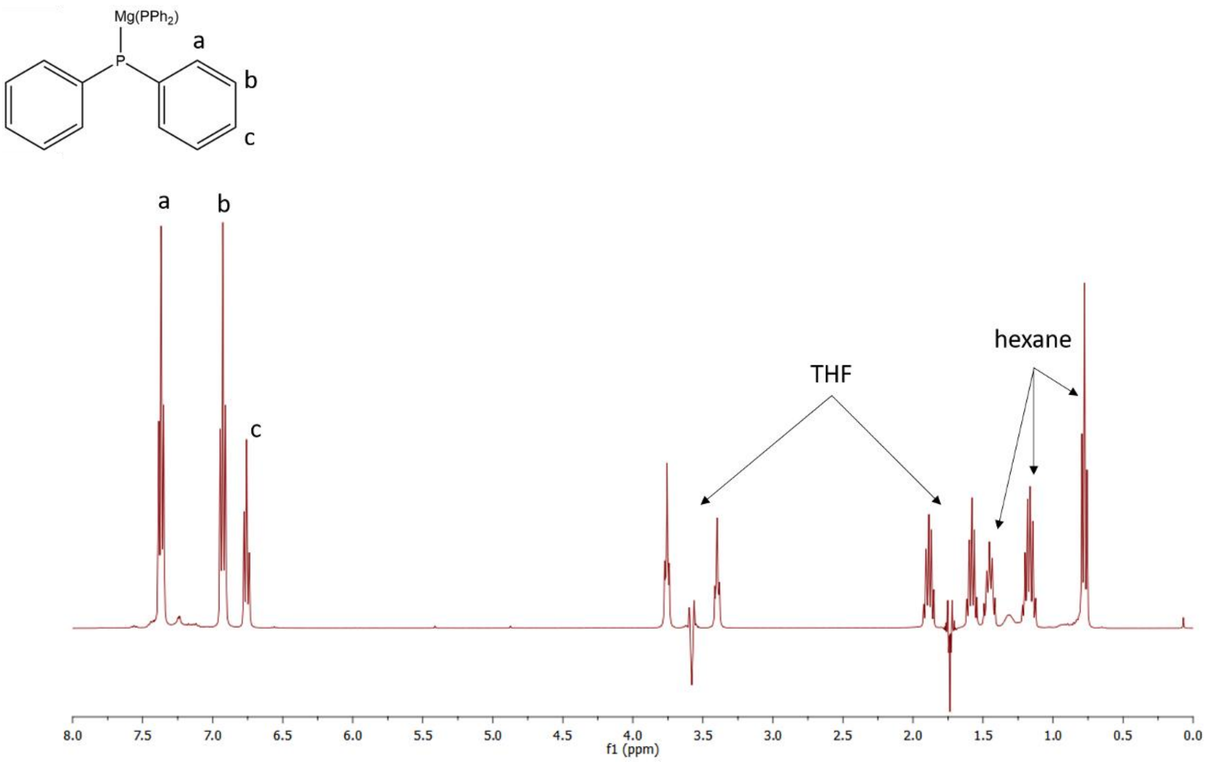


Figure S23: [1]H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum of $Mg(PPh_2)_2$.

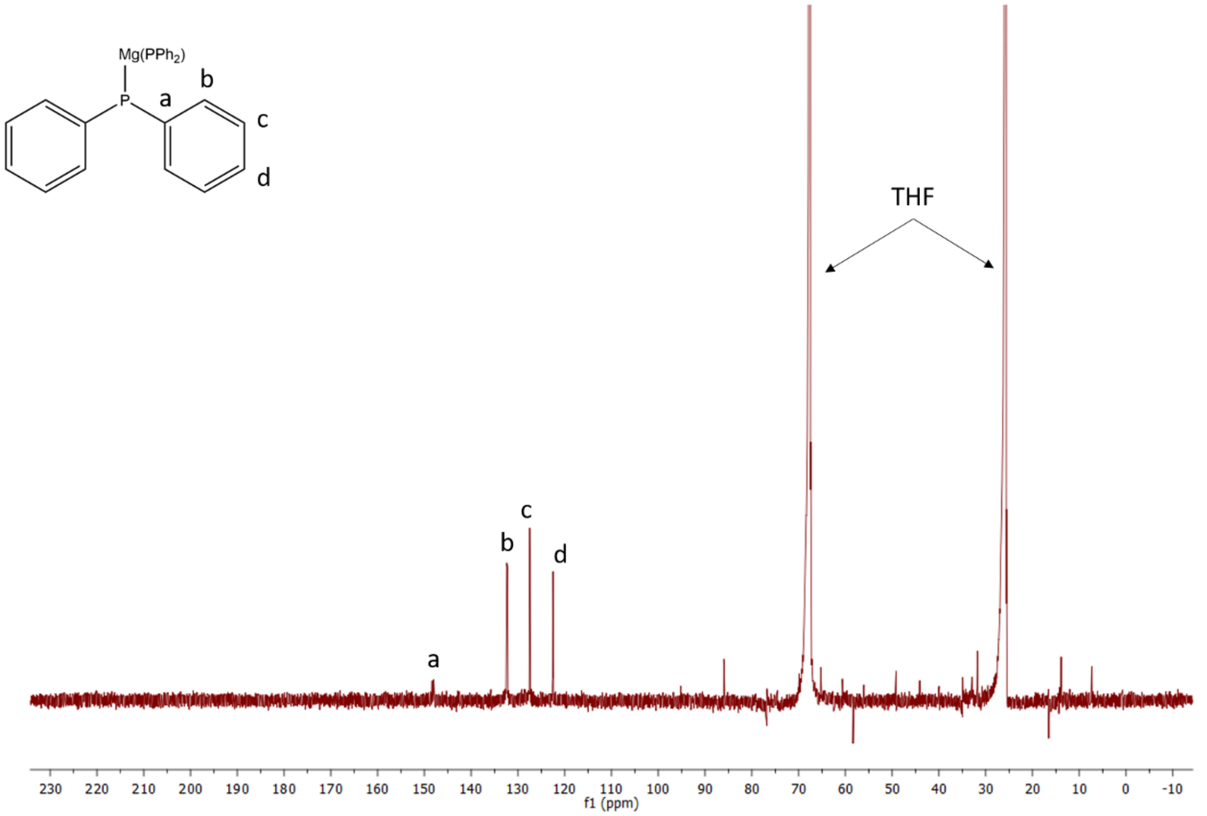


Figure S24: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, C_4H_8O) spectrum of $Mg(PPh_2)_2$, with assignment.

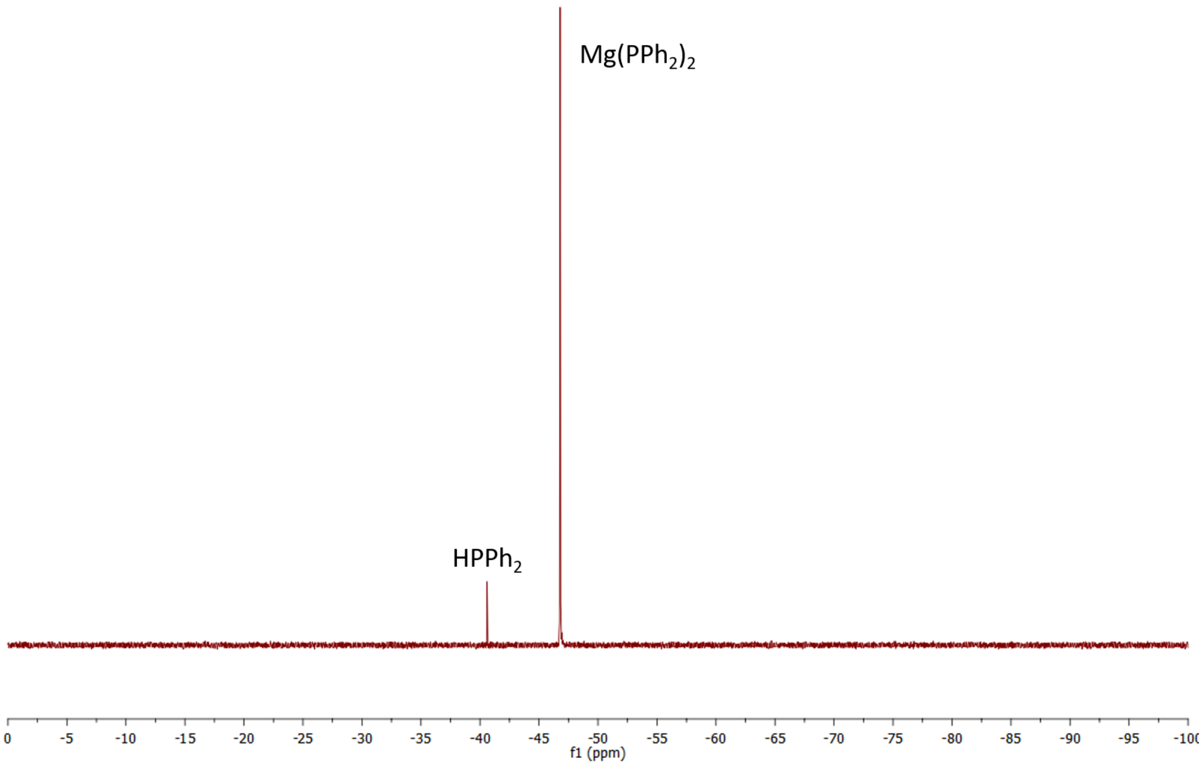


Figure S25: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum of $Mg(PPh_2)_2$.

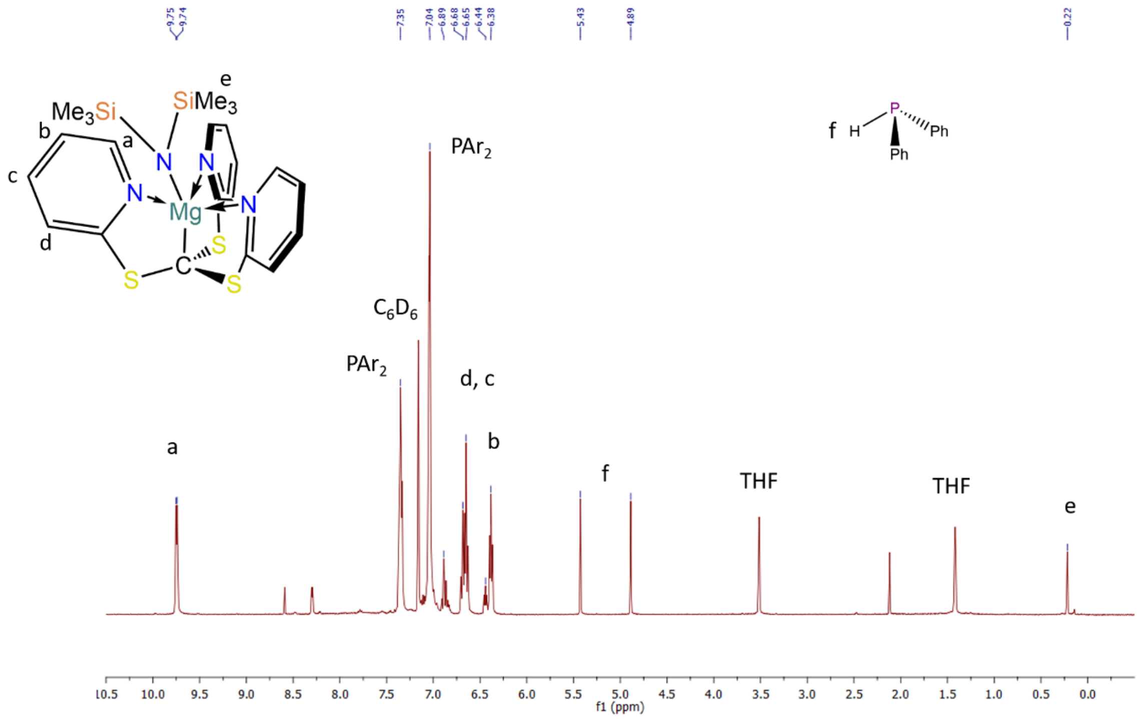


Figure S26: ^{1}H NMR (400 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of the reaction between **3-Mg** and $HPPh_2$, with assignment.

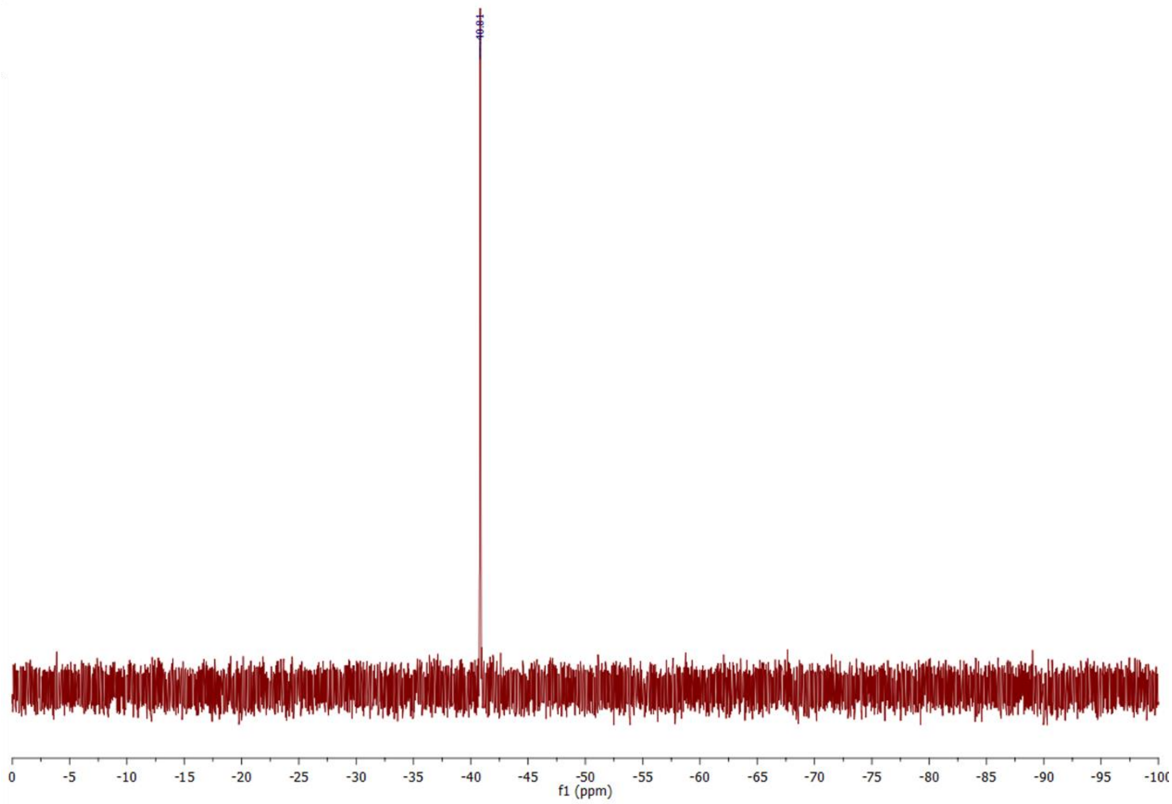


Figure S27: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of the reaction between **3-Mg** and $HPPh_2$.

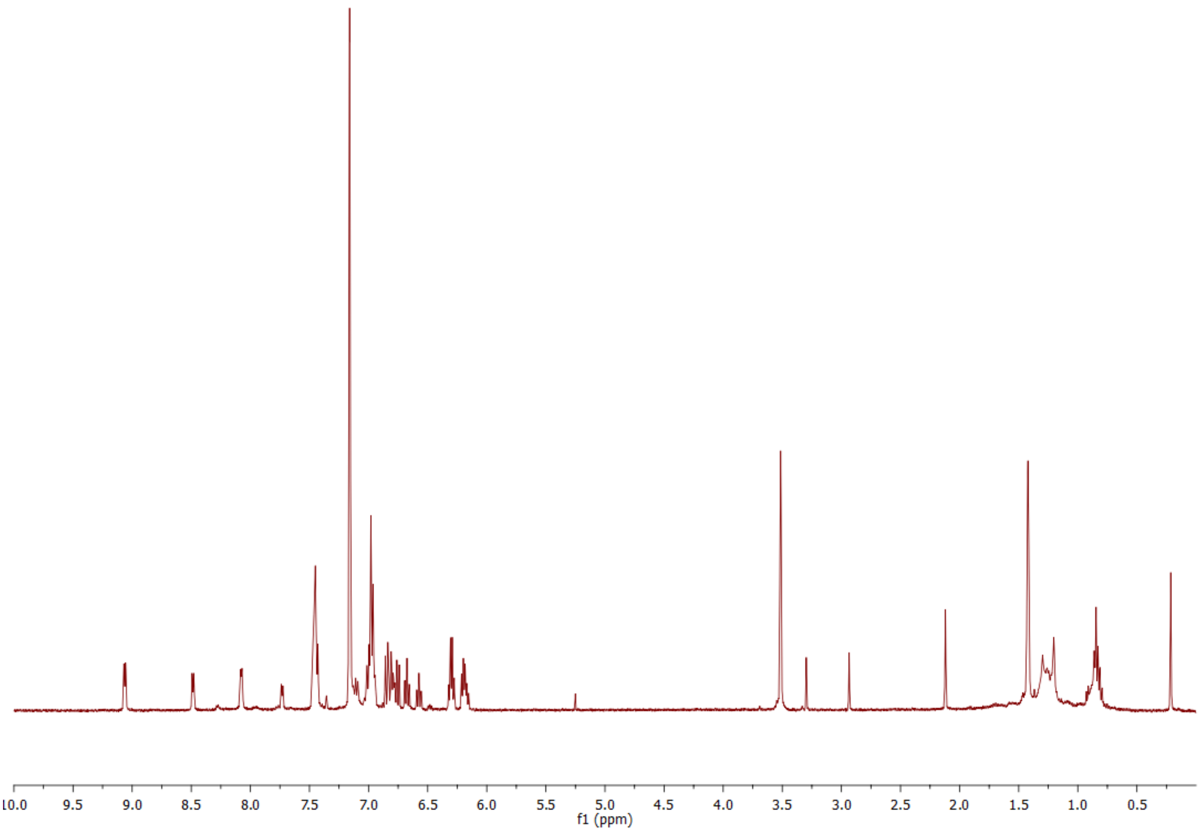


Figure S28: [1]H NMR (400 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of the crude reaction mixture from which **5** was isolated.

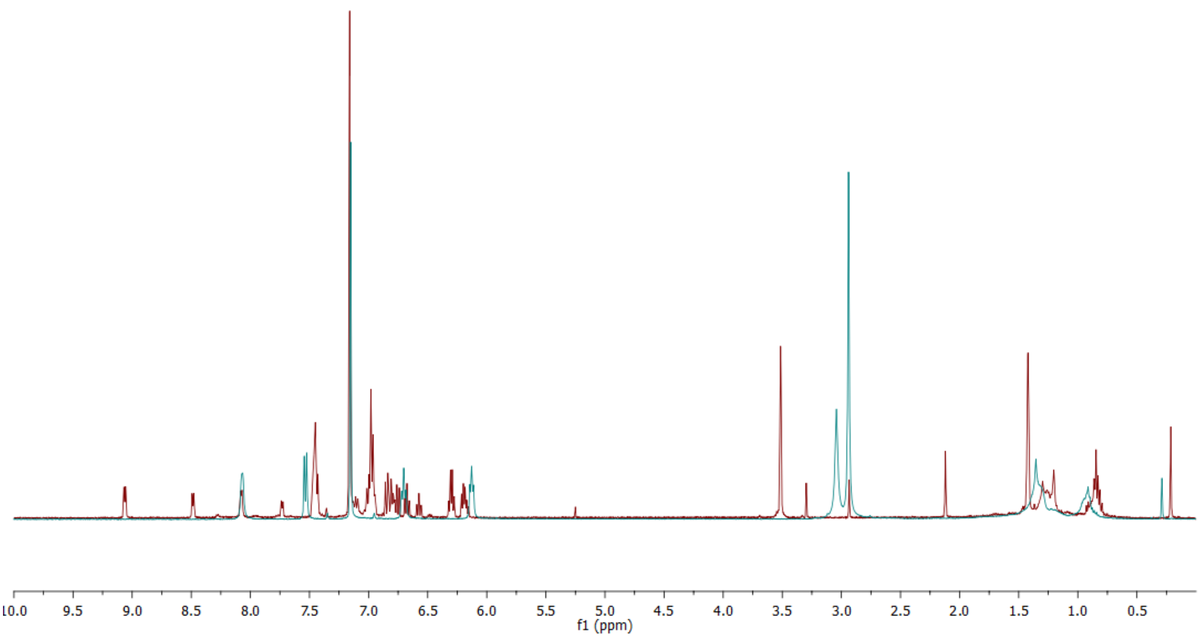


Figure S28A: ^{1}H NMR (400 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of the crude reaction mixture from which **6** was isolated (red) overlaid with the ^{1}H NMR of **4-Mg** (teal).

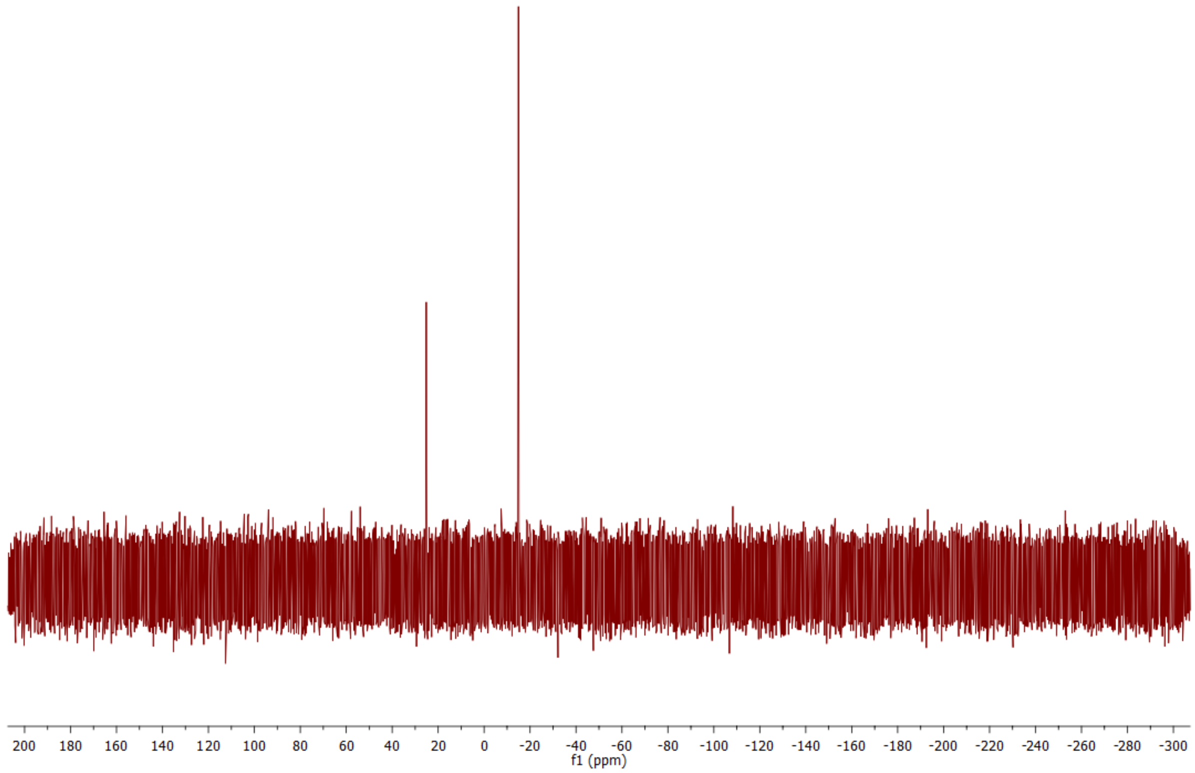


Figure S29: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6/C_4D_8O) spectrum of the crude reaction mixture from which **5** was isolated.

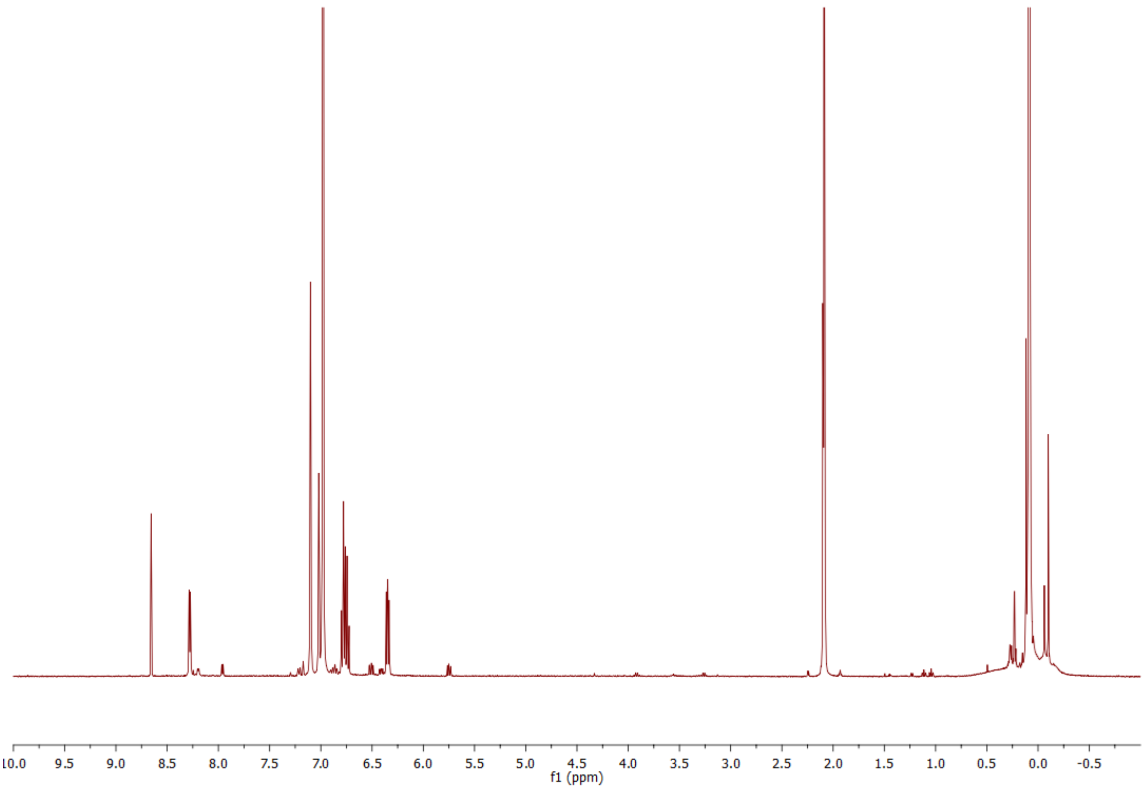


Figure S30: ^{1}H NMR (400 MHz, 298 K, C_7D_8) spectrum of the reaction between HTptm and $[Sr(N'')_2]_2$.

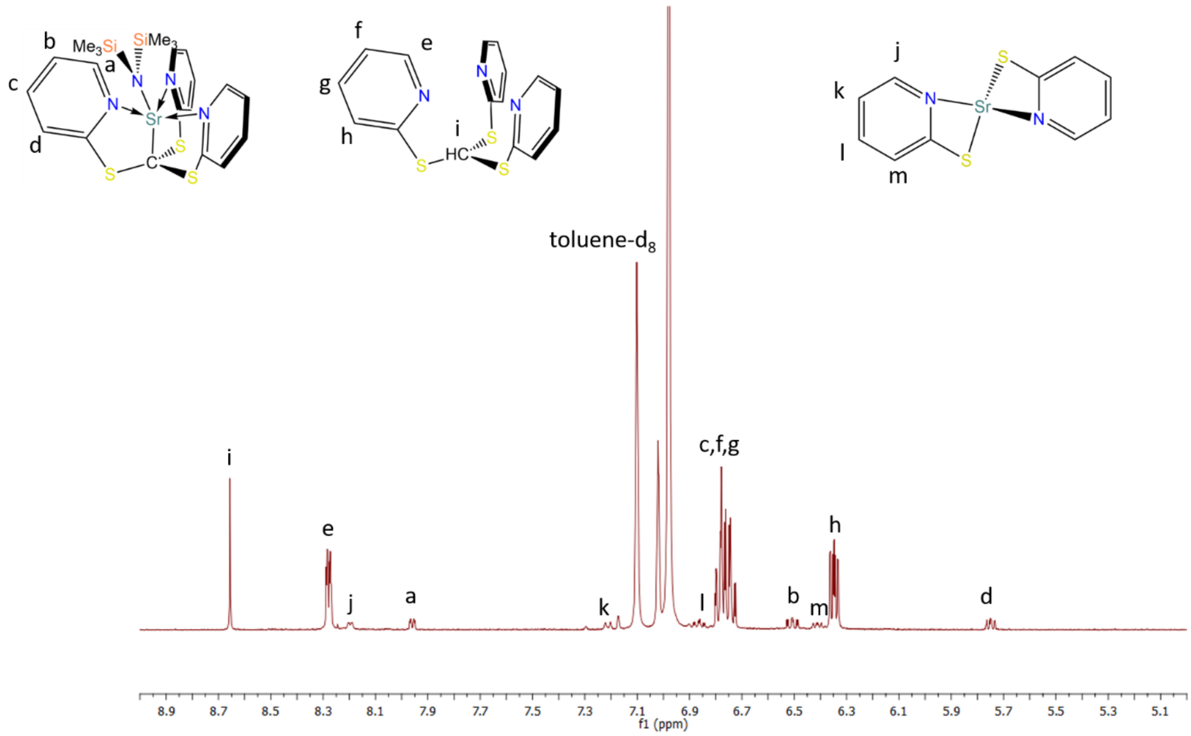


Figure S31: ^{1}H NMR (400 MHz, 298 K, C_7D_8) spectrum of the reaction between HTptm and $[Sr(N'')_2]_2$ in the region 5.0-9.0 ppm with assignment.

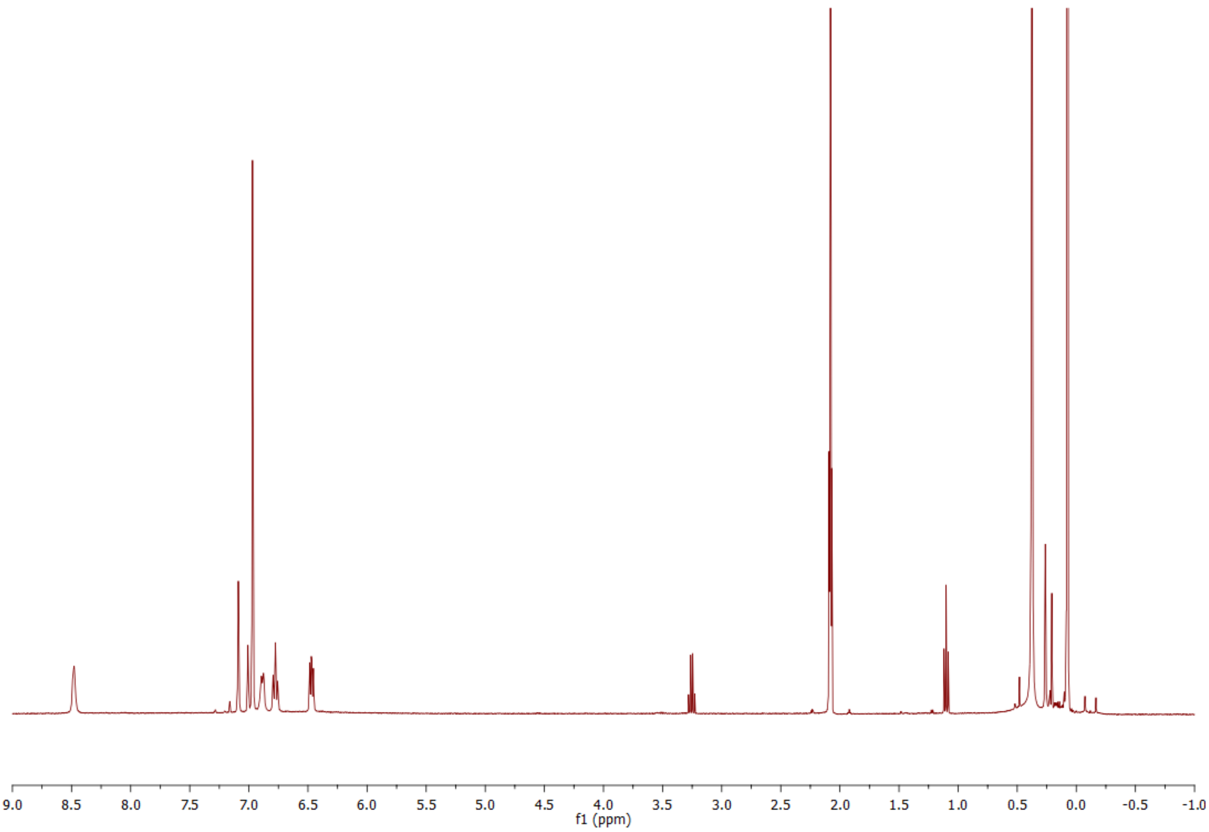


Figure S32: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum of the reaction between HTptm and Ba(N″)$_2$.

S3. IR data

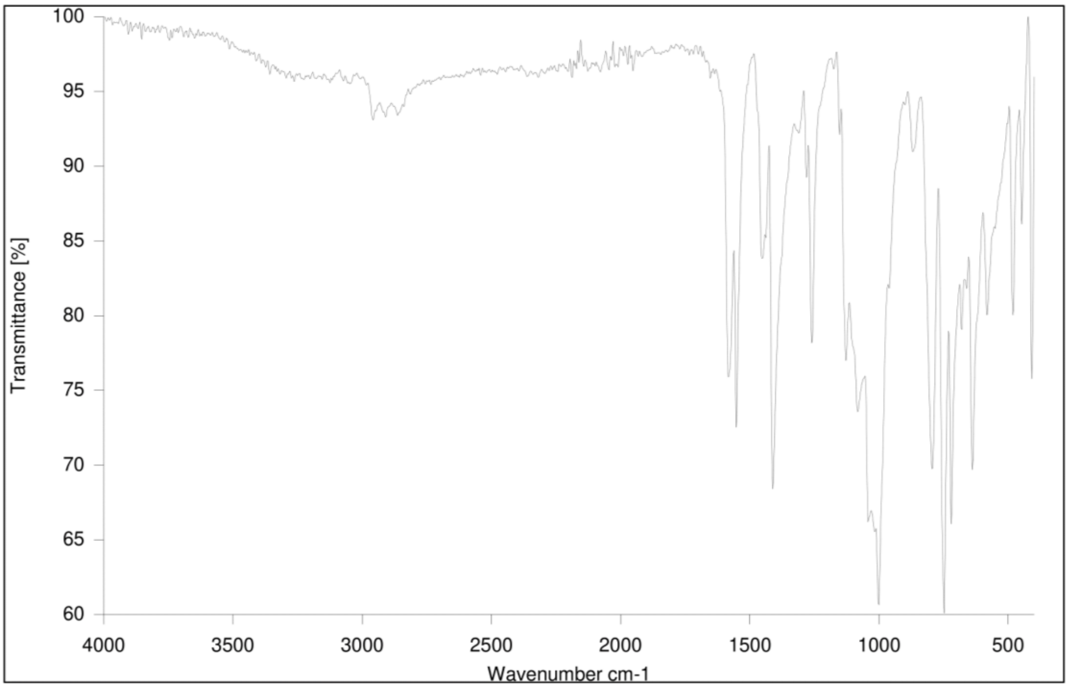


Figure S33: FTIR spectrum of **1**.

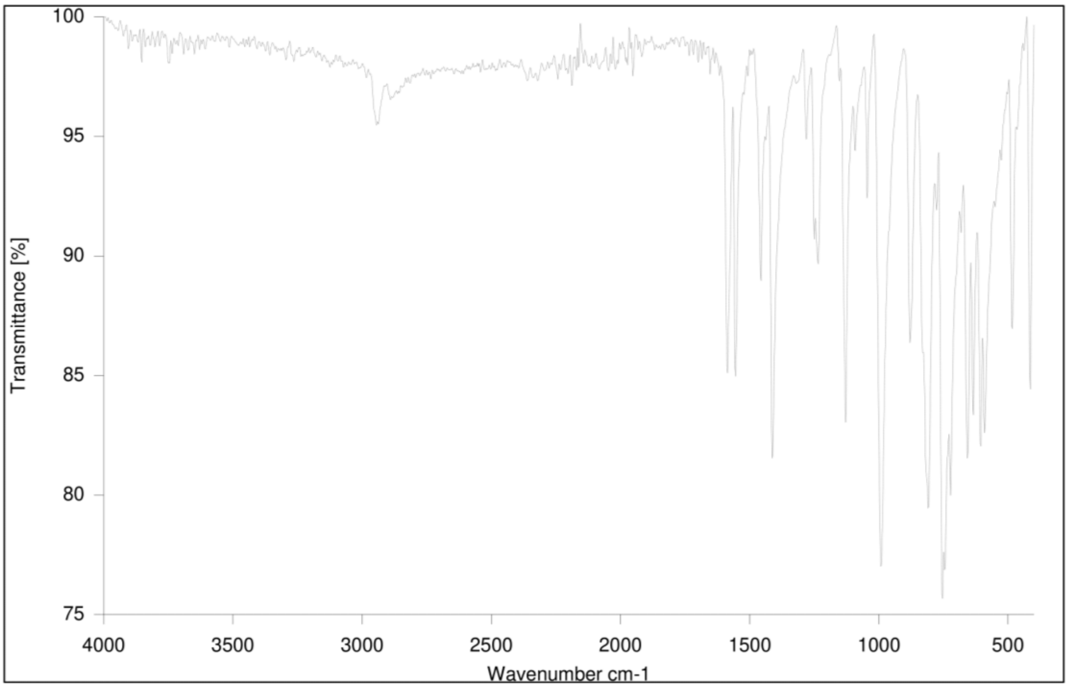


Figure S34: FTIR spectrum of **3-Mg**.

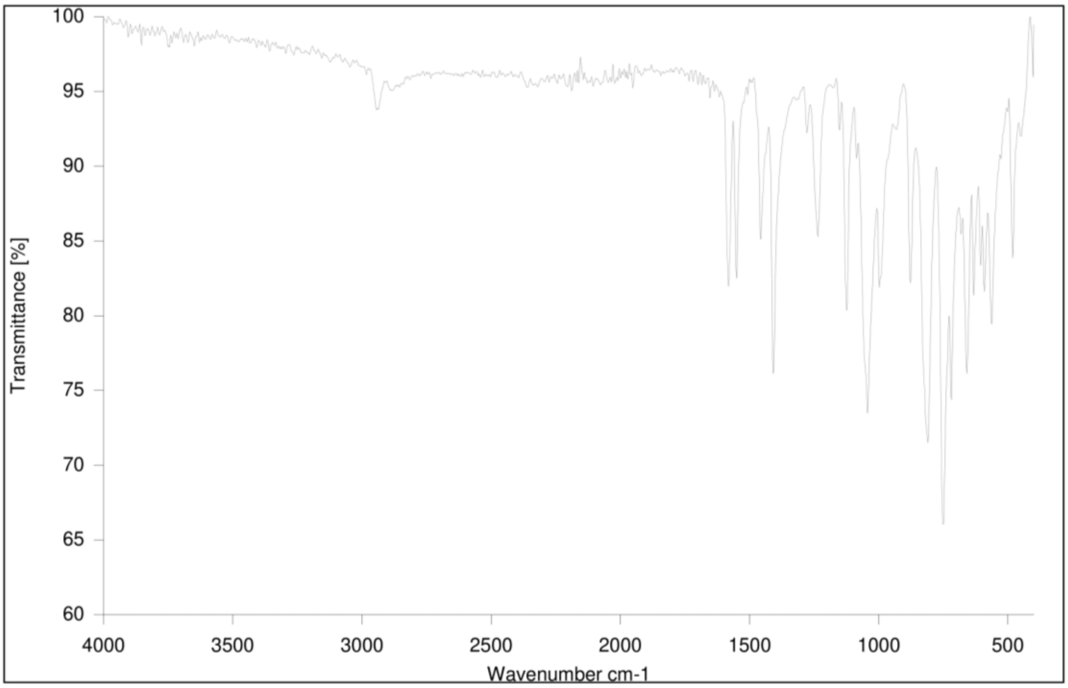


Figure S35: FTIR spectrum of **3-Ca**.

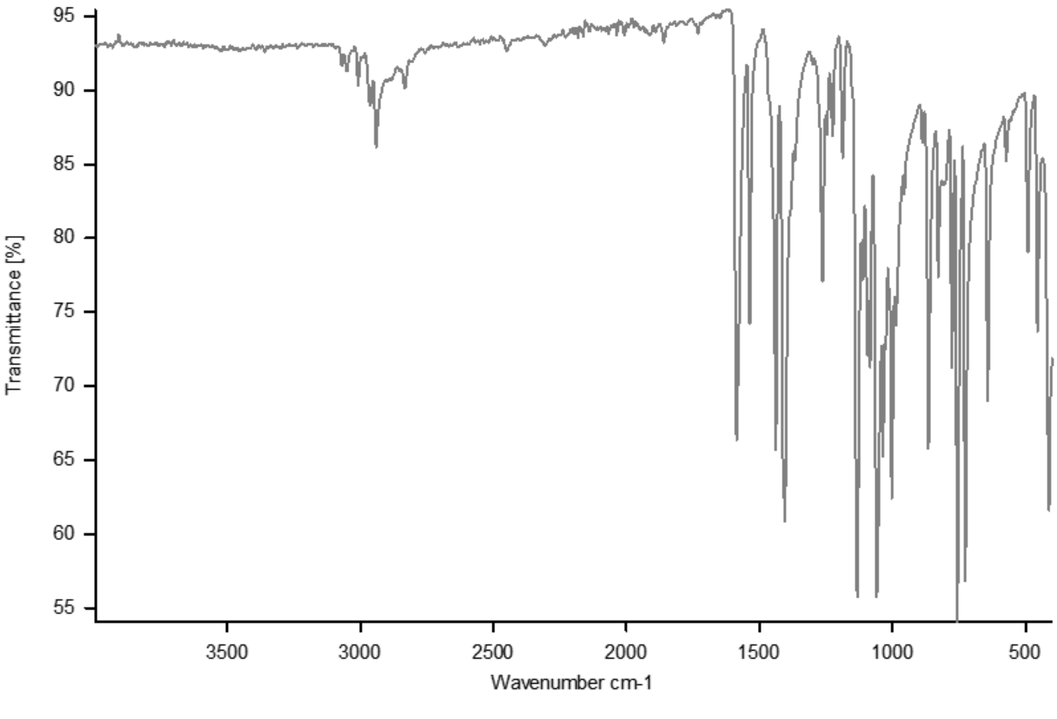


Figure S36: FTIR spectrum of **4-Mg•DME**.

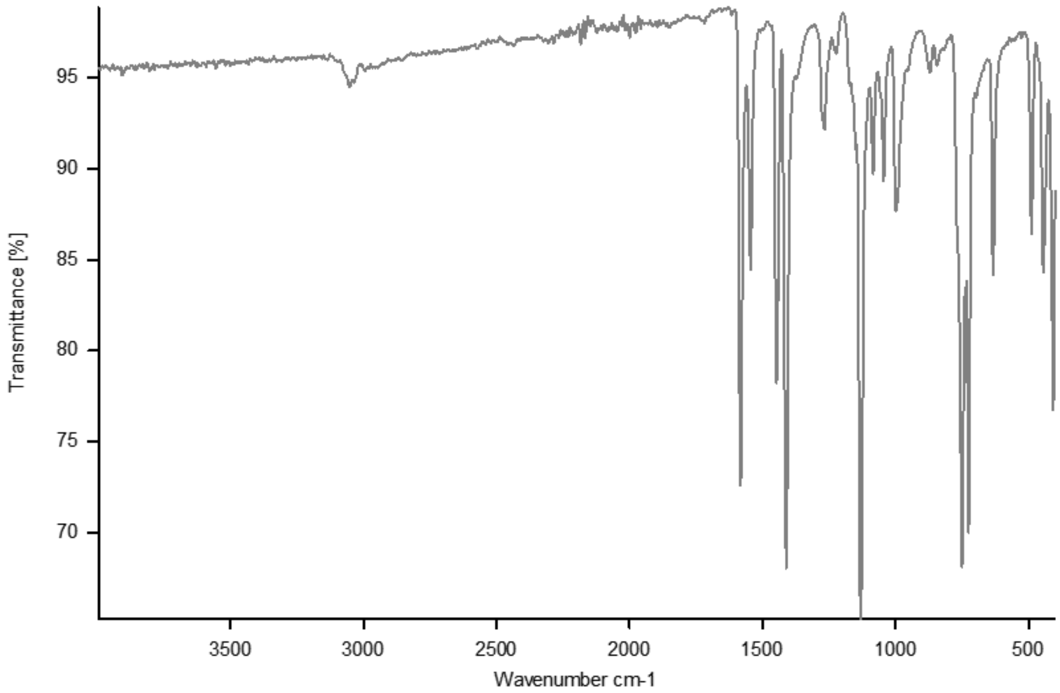


Figure S37: FTIR spectrum of **4-Ca**.

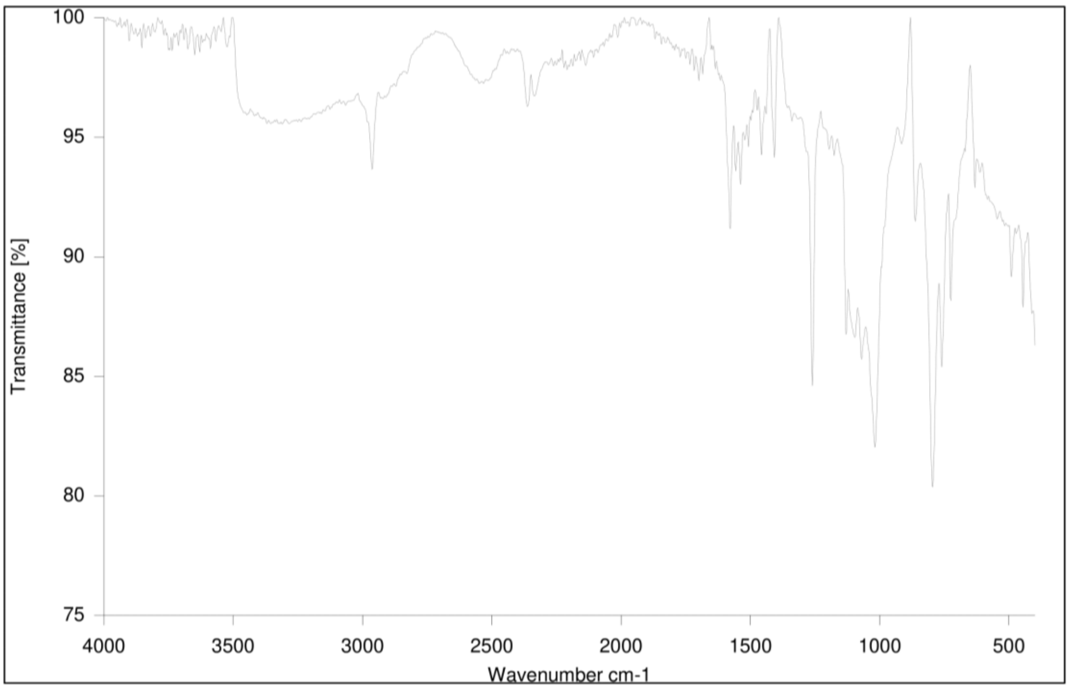


Figure S38: FTIR spectrum of **4-Ca•DME$_2$**.

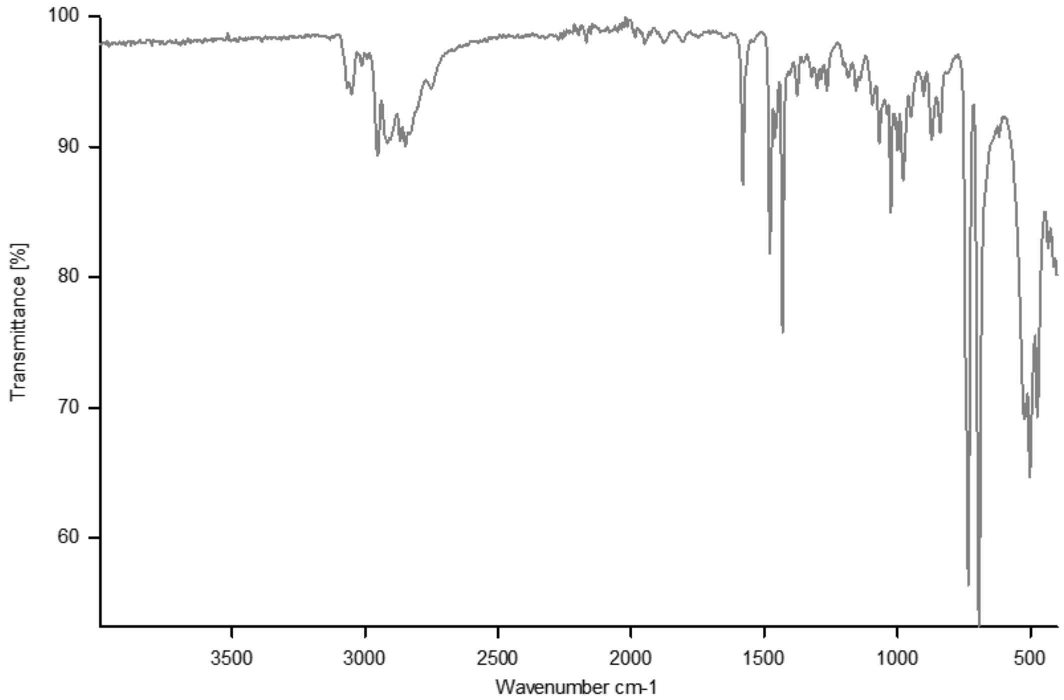


Figure S39: FTIR spectrum of $Mg(PPh_2)_2$

S4. Crystallography

Crystallographic method

The crystal data for all compounds are compiled in Tables S1 and S2. Crystals of **1** were examined using an Oxford Diffraction Supernova diffractometer with a CCD area detector and a microfocus source with Mo-Kα radiation (λ = 0.71073). Crystals of **HTptm**, **3** and **4** were examined using a Bruker Apex 2000 CCD area detector diffractometer and data was collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073). Crystals of **2** and **5** were examined using a dual wavelength [Mo-Kα (λ = 0.71073) or Cu-Kα (λ = 1.54178)] Rigaku FR-X diffractometer with a HyPix 6000HE photon-counting detector. Crystals of **4-Mg** were examined using or a Bruker D8 Quest diffractometer with a Photon III detector and a microfocus source with Cu- Kα radiation (λ = 1.54178). Intensities were integrated from data recorded on 0.3° (**HTptm**, **3-Mg**, **4-Ca**) or 1° (**1**, **2**, **4-Mg**, **5**) frames by ω rotation. A multiscan method (SADABS)[1] or a Gaussian grid faced-indexed absorption correction with a beam profile were applied.[2] The structures were solved using SHELXS;[3] the datasets were refined by full-matrix least-squares on reflections with $F^2 \geq 2\sigma(F^2)$ values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries;[4] U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. SHELX[3,4] was employed through OLEX2 for structure solution and refinement.[5] ORTEP-3[6] and POV-Ray[7] were employed for molecular graphics. The structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2097914-2097920 and 2170882). This information can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystallographic data for **1**, **2** and **3-Mg**

[a]Conventional $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $Rw = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; $S = [\Sigma w(Fo^2 - Fc^2)^2$/no. data – no. params)]$^{1/2}$ for all data.

	1	**2**	**3-Mg**
Formula	$C_{40}H_{44}Mg_2N_6S_6$	$C_{30}H_{40}Mg_2N_4O_2S_4Si_2$	$C_{22}H_{30}MgN_4S_3Si_2$
Formula weight	848.78	721.70	527.17
Crystal size, mm	0.13 × 0.19 × 0.21	0.06 × 0.08 × 0.11	0.26 × 0.29 × 0.49
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/c$
a, Å	12.1983(6)	13.12561(18)	19.1597(6)
b, Å	12.2683(8)	9.98641(13)	15.3351(5)
c, Å	14.8689(10)	13.71565(17)	18.2805(6)
α, °	87.806(5)	90	90
β, °	76.581(5)	94.6324(12)	94.556(3)
γ, °	79.929(5)	90	90
V, Å^3	2131.1(2)	1791.94(4)	5354.1(3)
Z	2	2	8
ρ_{calc}, g cm^3	1.323	1.338	1.308
μ, mm^{-1}	0.387	3.690	0.408
F(*000*)	890	760	2224
No. of reflections (unique)	18614 (9752)	10871 (3609)	43635 (12969)
S[a]	1.04	1.06	1.14
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0753 (0.1429)	0.0309 (0.0825)	0.0838 (0.1588)
R_{int}	0.062	0.017	0.077
Min./max. diff map, Å^{-3}	-0.67, 0.45	-0.34, 0.46	-0.36, 0.62

Table S2: Crystallographic data for **4-Ca·DME₂**, **5** and **6·Ph₂P-PPh₂**.

[a]Conventional $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $Rw = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; $S = [\Sigma w(Fo^2 - Fc^2)^2$/no. data – no. params)]$^{1/2}$ for all data.

	4-Mg·DME	**4-Ca·DME$_2$**	**6·Ph$_2$P-PPh$_2$**
Formula	$C_{14}H_{18}MgN_2O_2S_2$	$C_{18}H_{28}CaN_2O_4S_2$	$C_{46}H_{38}MgN_4P_2S$
Formula weight	334.73	440.62	861.29
Crystal size, mm	0.14 × 0.14 × 0.14	0.14 × 0.15 × 0.24	0.05 × 0.07 × 0.11
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	*Fdd*2	$P2_1/c$
a, Å	9.6270(3)	32.025(2)	9.69497(18)
b, Å	12.5306(5)	14.1100(12)	16.4661(3)
c, Å	14.0589(5)	10.1240(9)	13.4773(2)
α, °	90	90	90
β, °	102.135(2)	90	108.2140(19)
γ, °	90	90	90
V, Å^3	1658.06(10)	4574.8(6)	2043.70(7)
Z	4	8	2
ρ_{calc}, g cm^3	1.341	1.280	1.400
μ, mm^{-1}	3.323	0.480	3.337
F(*000*)	704	1872	896
No. of reflections (unique)	23132 (3267)	9556 (2728)	13292 (4131)
S[a]	1.03	1.07	1.04
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0365 (0.0958)	0.0673 (0.1388)	0.0330 (0.0852)
R_{int}	0.080	0.097	0.020
Min./max. diff map, Å^{-3}	-0.32, 0.36	-0.28, 0.24	-0.37, 0.36

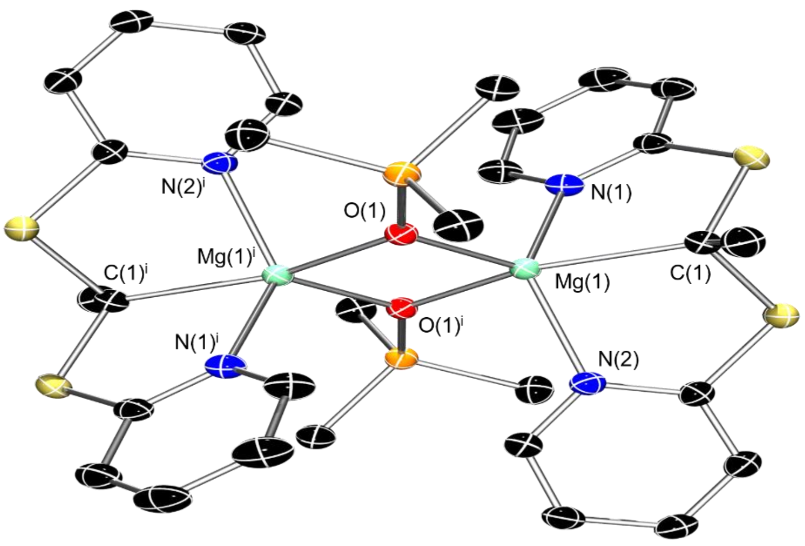


Figure S40: Crystal structure of **2**. Ellipsoids are set at 30% probability level and hydrogens omitted for clarity. The asymmetric unit contains half a molecule; the full molecule has been reproduced here. Symmetry operation used to generate equivalent atoms: i = 1−*x*, −*y*, 1−*z*. C: black; N: blue; O: red; S: yellow; Si: orange; Mg: aquamarine.

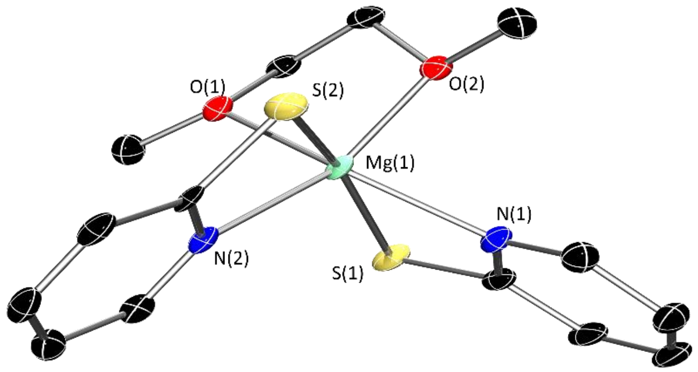


Figure S41: Crystal structure of **4-Mg**·DME. Ellipsoids are set at 30% probability level and hydrogens omitted for clarity. C: black; N: blue; O: red; S: yellow; Mg: aquamarine.

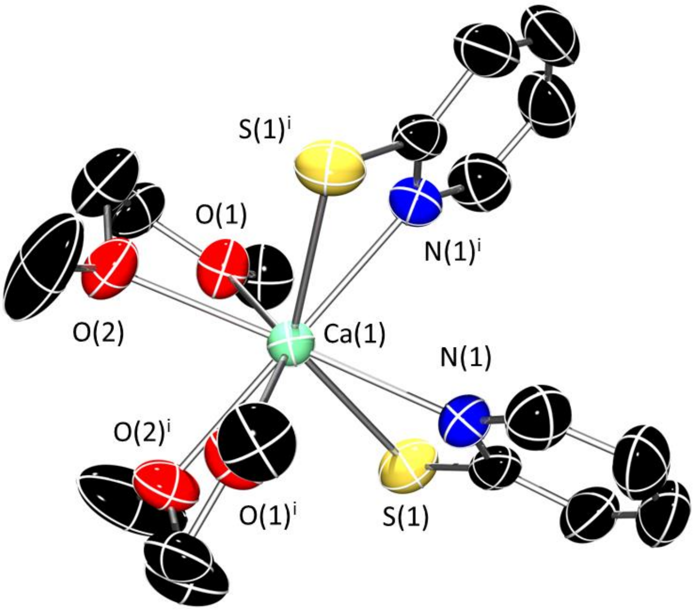


Figure S42: Crystal structure of **4-Ca**·DME_2. Ellipsoids are set at 30% probability level and hydrogens omitted for clarity. The asymmetric unit contains half a molecule; the full molecule has been reproduced here. Symmetry operation used to generate equivalent atoms: i = −*x*, −*y*, +*z*. C: black; N: blue; O: red; S: yellow; Ca: aquamarine.

S5. Catalytic studies

All reactions were performed on NMR scale, in either C_6D_6 or THF. All spectra were recorded at 298 K unless otherwise stated.

Room temperature reactions

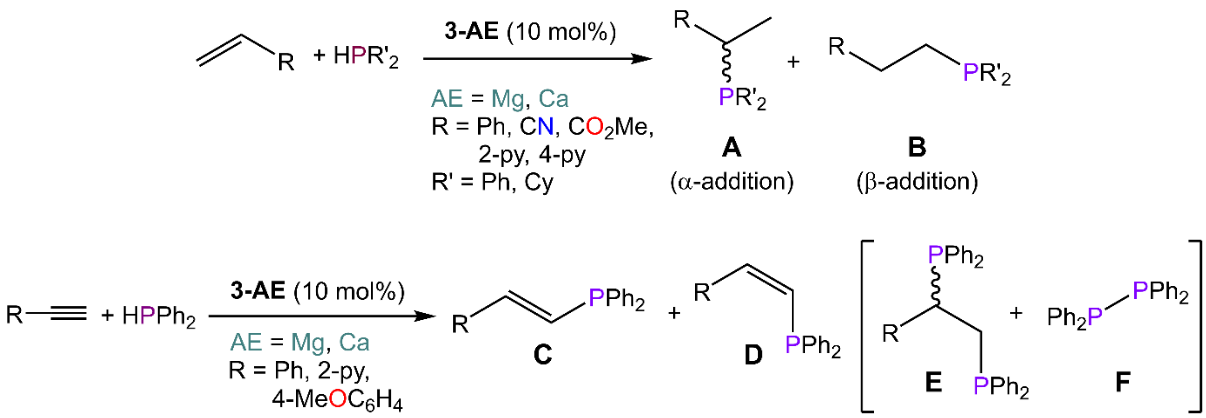
To an NMR tube fitted with a Young's valve was added **3-AE** (10 µmol), phosphine (100 µmol), alkene or alkyne (100 µmol), and hexamethylbenzene (100 µmol) if it was used, along with the relevant solvent (ca. 1 mL). In the case of **3-Mg** in C_6D_6, a few drops of THF were used to help solubilise the catalyst. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at daily intervals (**3-Mg)** or hourly intervals (**3-Ca**) until no further change was seen in the spectra.

Reflux reactions

To an NMR tube fitted with a Young's valve was added **3-AE** (10 µmol), phosphine (100 µmol), alkene or alkyne (100 µmol), and hexamethylbenzene (16.4 mg, 100 µmol) if it was used, along with the relevant solvent (ca. 1 mL). In the case of **3-Mg** in C_6D_6, a few drops of THF were used to help solubilise the catalyst. The NMR tube was then heated to 60 °C (THF) or 80 °C (C_6D_6) in an oil bath. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at daily intervals (**3-Mg**) until no further change was seen in the spectra.

Estimates of conversions and product distribution

Conversions and product distribution were estimated using ^{31}P{^{1}H} NMR analysis. Spectra are usually presented zoomed in the region of interest for clarity, owing the proximity of some of the signals of the hydrophospination products which would not be distinguishable showing the full spectral window. In all cases, no signals have been omitted.

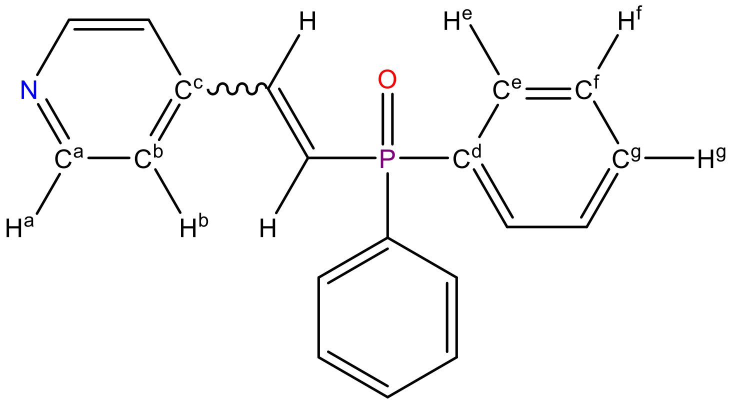


Scheme S1: Hydrophosphination of alkenes and alkynes with HPR_2 (R = Ph, Cy) catalysed by **3-AE** (AE = Mg, Ca).

Isolation of hydrophosphination products

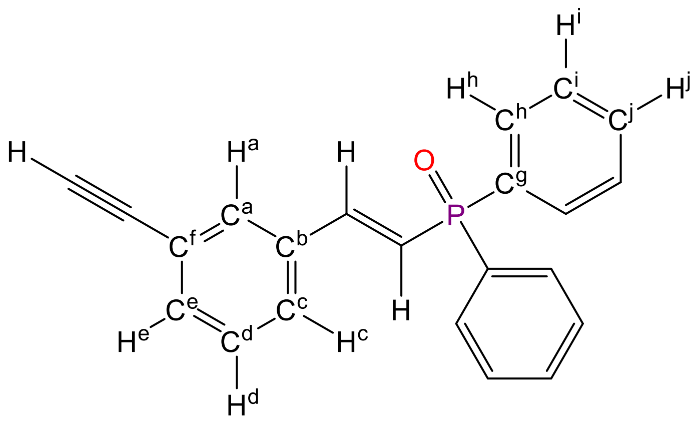
The complete NMR sample was digested with hydrogen peroxide (6%, 10 mL), and extracted four times with dichloromethane (10 mL). The combined organic extracts were dried with anhydrous magnesium sulphate, and the solvent removed *in vacuo*. The residue was separated by flash column chromatography on silica, using a gradient elution mixture from 30:70 ethyl acetate:hexane to 100% ethyl acetate. (Note: all reaction mixtures treated in this way were in THF).

Hydrophosphination of 4-ethynylpyridine: From $HPPh_2$ (17 µl, 100 µmol), 4-ethynylpyridine (10.3 mg, 100 µmol) and **3-Mg** (5.3 mg, 10 µmol). Yield (27 mg, 88 µmol, 88%).



^{1}H NMR (400 MHz, 298 K, $CDCl_3$): 6.59 (1H, dd, $^2J_{HP}$ = 19.0 Hz, $^3J_{HH}$ = 14.1 Hz, *cis* CH=C*H*P(=O)Ph_2), 7.07 (1H, dd, $^2J_{HP}$ = 21.6 Hz, $^3J_{HH}$ = 17.5 Hz, *trans* CH=C*H*P(=O)Ph_2), 7.34-7.58 (8H, m), 7.66-7.77 (4H, m), 8.43 (1H, br), 8.64 (1H, br) ppm. ^{13}C{^{1}H} NMR (100 MHz, 298 K, $CDCl_3$): 125.2 (d, $^1J_{PC}$ = 102 Hz), 127.6 (d, $^1J_{PC}$ = 128 Hz), 128.7 (d, $^2J_{PC}$ = 12.3 Hz), 128.9 (d, $^2J_{PC}$ = 12.3 Hz), 131.0 (d, $^2J_{PC}$ = 10.0 Hz), 131.7 (s), 132.0 (d, $^3J_{PC}$ = 2.6 Hz), 132.3 (d, $^3J_{PC}$ = 2.9 Hz), 132.6 (s), 132.7 (s), 133.7 (s), 142.1 (s), 142.2 (s), 142.3 (s), 144.9 (d, $^3J_{PC}$ = 3.4 Hz), 146.9 (d, $^4J_{PC}$ = 2.0 Hz), 149.7 (s), 150.6 (s) ppm. ^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): 19.4 (s, *trans P*=O), 23.5 (s, *cis P*=O) ppm. MS (ESI): 306 $[M+H]^+$. HRMS (ESI): 306.1048 $[M+H]^+$ m/z calculated for $C_{19}H_{17}NOP$, found 306.1048.

Hydrophosphination of 1,3-diethynylbenzene: From $HPPh_2$ (17 µl, 100 µmol), 1,3-diethynylbenzene (12 µl, 100 µmol) and **3-Mg** (5.3 mg, 10 µmol). Yield (3 mg, 1.2 µmol, 1.2%).



^{1}H NMR (400 MHz, 298 K, $CDCl_3$): 3.03 (1H, s, *H*C≡C), 6.40 (1H, dd, $^3J_{HH}$ = 13.9 Hz, $^2J_{HP}$ = 18.9 Hz, CH=C*H*P(=O)Ph_2), 7.12 (1H, t, $^3J_{HH}$ = 7.9 Hz, CH^b), 7.27 (1H, d, $^3J_{HH}$ = 7.2 Hz, CH^c), 7.39 (7H, m, PPh_2 C$H^{i,j}$ and CH^e), 7.52 (1H, d, $^3J_{HH}$ = 14.0 Hz, C*H*=CHP(=O)Ph_2), 7.65 (1H, s, CH^a), 7.74 (4H, ddd, $^3J_{HP}$ = 12.0 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz, PPh_2 CH^h), 7.81 (1H, d, $^3J_{HH}$ = 7.8 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 298 K, $CDCl_3$): 77.6 (s, H*C*≡C), 83.2 (s, HC≡*C*), 122.0 (s, C^f), 123.7 (d, $^1J_{CP}$ = 48.7 Hz, CH=*C*HP(=O)Ph_2), 128.2 (s, C^d), 128.6 (d, $^2J_{CP}$ = 12.2 Hz, *C*H=CHP(=O)Ph_2), 130.5 (d, $^4J_{CP}$ = 1.6 Hz, C^c), 131.1 (d, $^2J_{CP}$ = 9.6 Hz, C^h), 131.7 (d, $^3J_{CP}$ = 2.7 Hz, C^i), 132.8 (s, C^e), 133.7 (d, $^1J_{CP}$ = 56.8 Hz, C^g), 133.9 (d, $^4J_{CP}$ = 1.5 Hz, C^j), 135.1 (d, $^3J_{CP}$ = 7.4 Hz, C^b), 148.8 (d, $^4J_{CP}$ = 1.8 Hz, C^a) ppm. ^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): 19.5 (s, P=O) ppm. MS (ESI): 329 $[M+H]^+$. HRMS (ESI): $[M+H]^+$ m/z calculated for $C_{22}H_{17}OP$: 329.1095, found 329.1095; $[2M+H]^+$ m/z calculated for $C_{44}H_{35}O_2P_2$: 657.2107, found 657.2170.

Table S3: Hydrophosphination reactions with alkenes and HPR_2 (R = Ph, Cy), including yields and selectivities.

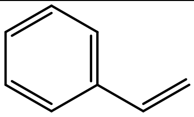
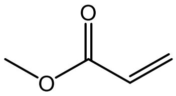
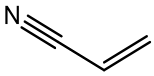
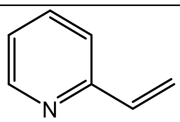
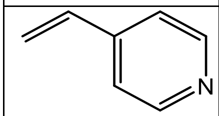
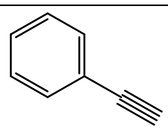
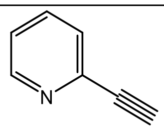
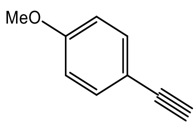
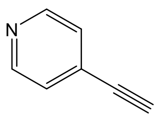
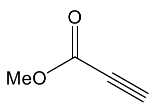
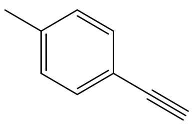
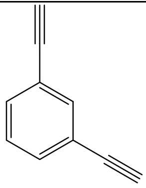
Alkene	Entry	HPR₂	Catalyst	Solvent	Conditions	NMR yield (%)	Selectivity (A:B)	Polymer yield (%)
	**1**	$HPPh_2$	**3-Mg**	C_6D_6	80 °C/29 h	23	0:100	-
	2	$HPPh_2$	**3-Mg**	THF	r.t./100 h	-	-	<1
	3	$HPPh_2$	**3-Mg**	THF	60 °C/120 h	17	9:91	~1
	4	$HPPh_2$	**3-Ca**	C_6D_6	r.t./1 h	-	-	<1
	5	$HPPh_2$	**3-Ca**	THF	r.t./1 h	-	-	<1
	**6**	$HPPh_2$	**3-Mg**	C_6D_6	80 °C/29 h	35	17:83	<1
	7	$HPPh_2$	**3-Mg**	THF	r.t./100 h	14	23:77	~1
	8	$HPPh_2$	**3-Mg**	THF	60 °C/120 h	28	17:83	-
	9	$HPCy_2$	**3-Mg**	THF	r.t./170 h	29	33:67	~1
	10	$HPCy_2$	**3-Mg**	THF	60 °C/70 h	40	27:73	-
	11	$HPPh_2$	**3-Ca**	-	-	-	-	-
	**12**	$HPPh_2$	**3-Mg**	C_6D_6	80 °C/29 h	13	0:100	-
	13	$HPPh_2$	**3-Mg**	THF	r.t./100 h	47	0:100	<1
	14	$HPPh_2$	**3-Mg**	THF	60 °C/120 h	31	0:100	<1
	15	$HPPh_2$	**3-Ca**	C_6D_6	r.t./1 h	5	100:0	<1
	16	$HPPh_2$	**3-Ca**	THF	r.t./1 h	-	-	~4
	**17**	$HPPh_2$	**3-Mg**	C_6D_6	80 °C/29 h	36	9:91	-
	18	$HPPh_2$	**3-Mg**	THF	r.t./100 h	34	91:9	-
	19	$HPPh_2$	**3-Mg**	THF	60 °C/120 h	30	9:91	<1
	20	$HPPh_2$	**3-Ca**	C_6D_6	r.t./1 h	19	83:17	~2
	21	$HPPh_2$	**3-Ca**	THF	r.t./1 h	20	9:91	<1
	**22**	$HPPh_2$	**3-Mg**	C_6D_6	80 °C/29 h	21	9:91	~1
	23	$HPPh_2$	**3-Mg**	THF	r.t./100 h	62	17:83	5
	24	$HPPh_2$	**3-Mg**	THF	60 °C/120 h	15	9:91	~1
	25	$HPPh_2$	**3-Ca**	C_6D_6	r.t./1 h	37	23:77	5
	26	$HPPh_2$	**3-Ca**	THF	r.t./1 h	36	17:83	17

Table S4: Hydrophosphination yields of 4-vinylpyridine with **3-Mg** and **3-Ca** under varying conditions in the presence of an internal standard (C_6Me_6)

Conditions	Catalyst	Entry	Conversion $^{31}P\{^1H\}$ NMR (%)	Conversion ^1H NMR (%)	Selectivity (A:B)	Polymer yield (%)
THF, 60 °C	**3-Mg**	**1**	15	14	10:90	<1
THF, r.t.	**3-Mg**	**2**	6	14	6:94	0
C_6D_6, r.t.	**3-Mg**	**3**	12	22	31:69	~3
THF, r.t.	**3-Ca**	**4**	36	44	30:70	9
C_7D_8, 0 °C	**3-Ca**	**5**	38	34	27:73	8

Table S5: Hydrophosphination reactions with alkynes and $HPPh_2$, including yields and selectivities.

Alkyne	Entry	Catalyst	Solvent	Conditions	NMR yield (%)	Selectivity α:β (C:D)	Ph_2P-PPh_2 yield (%)
	**1**	**3-Mg**	THF	r.t./96 h	-	-	-
	2	**3-Mg**	THF	60 °C /135 h	9	7:93 (7:93)	<1
	3	**3-Ca**	THF	r.t./1 h	6	14:86 (21:79)	2
	**4**	**3-Mg**	THF	r.t./96 h	-	-	-
	5	**3-Mg**	THF	60 °C /135 h	7	0:100 (49:51)	<1
	6	**3-Ca**	THF	r.t./1 h	95	0:100 (46:54)	~1
	**7**	**3-Mg**	THF	r.t./96 h	3	0:100 (0:100)	<1
	8	**3-Mg**	THF	60 °C /135 h	5	0:100 (0:100)	<1
	9	**3-Ca**	THF	r.t./1 h	3	0:100 (0:100)	3
	**10**	**3-Mg**	THF	r.t./72 h	96	0:100 (96:4)	3
	11	**3-Mg**	THF	60 °C /135 h	85	0:100 (78:7)	1
	12	**3-Ca**	THF	r.t./1 h	40	0:100 (34:66)	<1
	**13**	**3-Mg**	THF	r.t./96 h	14	0:100 (75:25)	<1
	14	**3-Mg**	THF	60 °C /135 h	18	11:89 (77:23)	1
	15	**3-Ca**	THF	r.t./1 h	11	0:100 (69:31)	<1
	**16**	**3-Mg**	THF	r.t./96 h	3	4:96 (84:16)	6
	17	**3-Mg**	THF	60 °C /135 h	8	0:100 (76:24)	37
	18	**3-Ca**	THF	r.t./1 h	4	0:100 (74:26)	<1
	19	**3-Mg**	THF	r.t./96 h	4	0:100 (49:51)	5

	**20**	**3-Mg**	THF	60 °C /135 h	3	45:55 (57:43)	8
	21	**3-Ca**	THF	r.t./1 h	8	30:70 (39:61)	<1

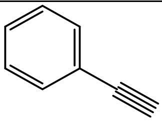
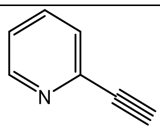
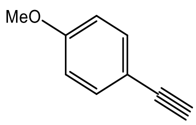
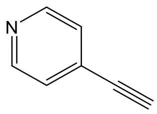
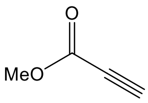
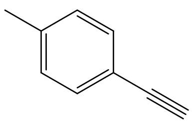
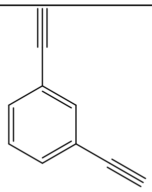
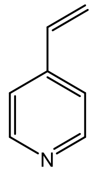
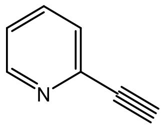
Alkyne	Entry	Catalyst	Solvent	Conditions	NMR yield (%)	Selectivity α:β (C:D)	Ph_2P-PPh_2 yield (%)
	**1**	**3-Mg**	THF	r.t./96 h	-	-	-
	2	**3-Mg**	THF	60 °C /135 h	9	7:93 (7:93)	<1
	3	**3-Ca**	THF	r.t./3 h	6	14:86 (21:79)	2
	**4**	**3-Mg**	THF	r.t./96 h	-	-	-
	5	**3-Mg**	THF	60 °C /135 h	7	0:100 (49:51)	<1
	6	**3-Ca**	THF	r.t./3 h	97	0:100 (46:54)	~1
	**7**	**3-Mg**	THF	r.t./96 h	3	0:100 (0:100)	<1
	8	**3-Mg**	THF	60 °C /135 h	5	0:100 (0:100)	<1
	9	**3-Ca**	THF	r.t./3 h	3	0:100 (0:100)	3
	**10**	**3-Mg**	THF	r.t./72 h	96	0:100 (96:4)	3
	11	**3-Mg**	THF	60 °C /135 h	85	0:100 (78:7)	1
	12	**3-Ca**	THF	r.t./3 h	45	0:100 (34:66)	<1
	**13**	**3-Mg**	THF	r.t./96 h	14	0:100 (75:25)	<1
	14	**3-Mg**	THF	60 °C /135 h	18	11:89 (77:23)	1
	15	**3-Ca**	THF	r.t./3 h	12	0:100 (69:31)	<1
	**16**	**3-Mg**	THF	r.t./96 h	3	4:96 (84:16)	6
	17	**3-Mg**	THF	60 °C /135 h	8	0:100 (76:24)	37
	18	**3-Ca**	THF	r.t./3 h	4	0:100 (74:26)	<1
	**19**	**3-Mg**	THF	r.t./96 h	4	0:100 (49:51)	5
	20	**3-Mg**	THF	60 °C /135 h	3	45:55 (57:43)	8
	21	**3-Ca**	THF	r.t./3 h	8	30:70 (39:61)	<1

Table S6: Hydrophosphination control reactions with 4-vinylpyridine and 2-ethynylpyridine, with $HPPh_2$, including yields and selectivities.

Substrate	Entry	Catalyst	Solvent	Conditions	NMR yield (%)	Selectivity α:β (C:D)	Ph_2P-PPh_2 yield (%)
	**1**	**-**	C_6D_6	r.t. / 135 h	0	-	-
	2	**-**	C_6D_6	80°C / 135 h	8	100:0	<1
	3	**4-Mg**	THF	60 °C / 135 h	71	93:7	<1
	4	**4-Ca**	THF	r.t. / 135 h	36	95:5	<1
	5	**4-Ca**	THF	r.t. / 3 h	4	0:100	<1
	6	**4-Ca**	C_6D_6	r.t. / 3 h	2	0:100	<1
	7	$[Ca(N'')_2]_2$	C_6D_6	r.t. / 3 h	50	37:63	<1
	**8**	**-**	C_6D_6	r.t. / 135 h	0	-	-
	9	**-**	C_6D_6	80°C / 135 h	4	18:82 (54:46)	<1
	10	**4-Mg**	THF	60°C / 135 h	2	0:100 (40:60)	<1
	11	**4-Ca**	THF	r.t. / 135 h	0	-	-

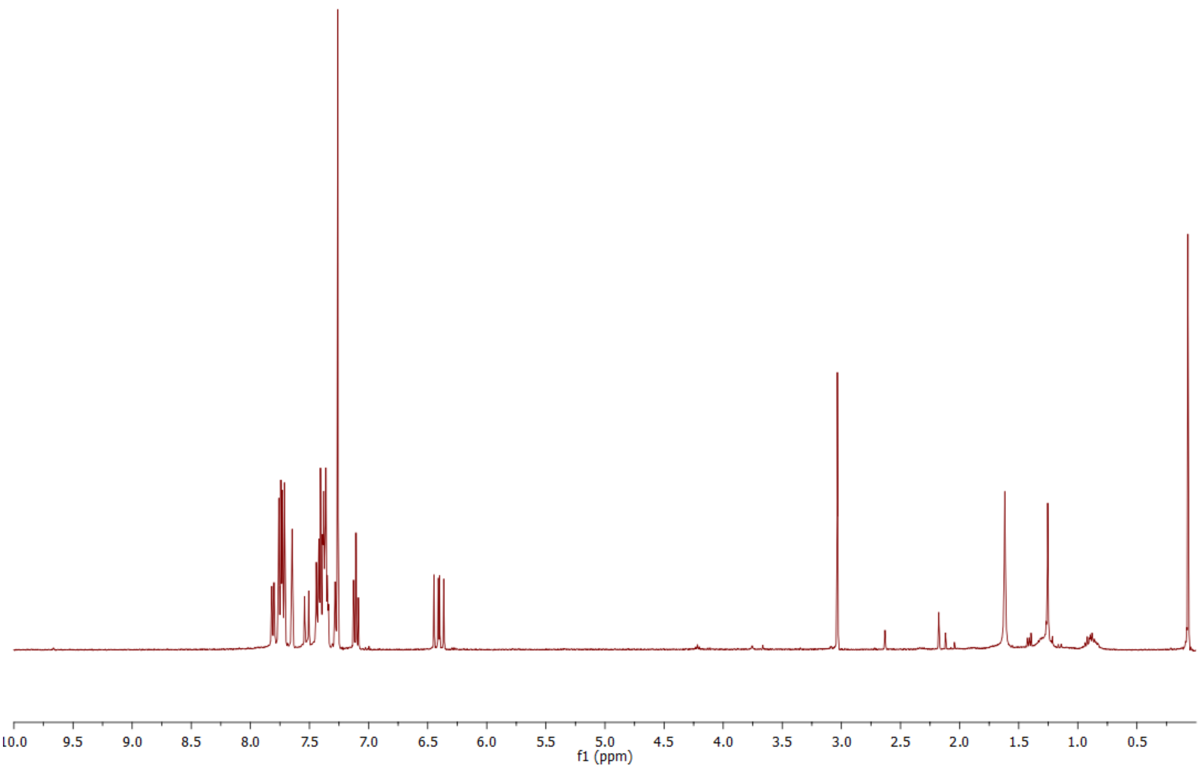


Figure S43: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 1,3-diethynylbenzene.

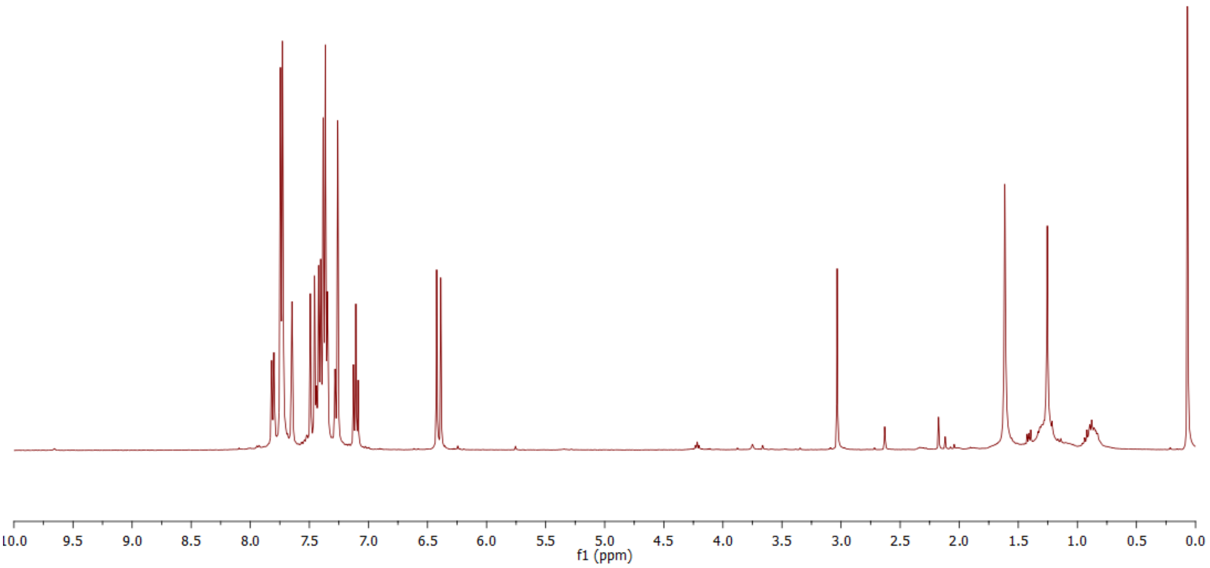


Figure S44: $^{1}H\{^{31}P\}$ NMR (400 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 1,3-diethynylbenzene.

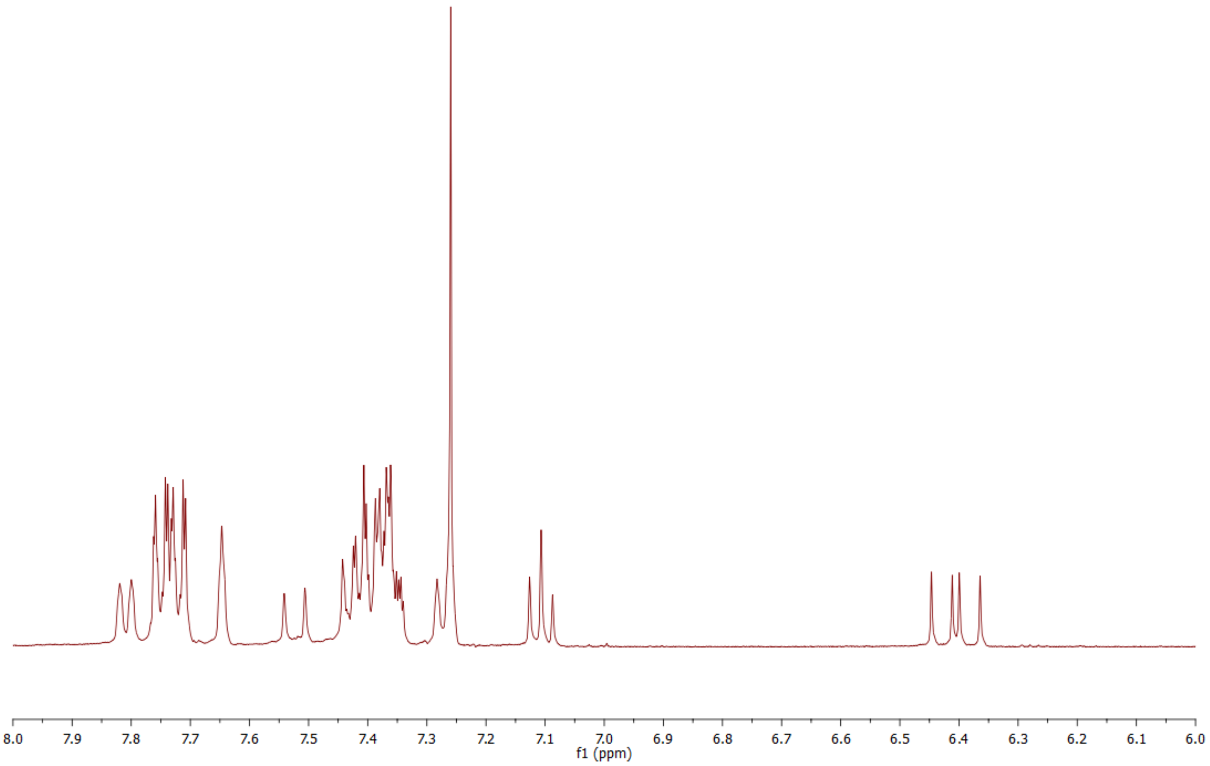


Figure S45: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum in the region 6.0–8.0 ppm of the hydrophosphination product of 1,3-diethynylbenzene.

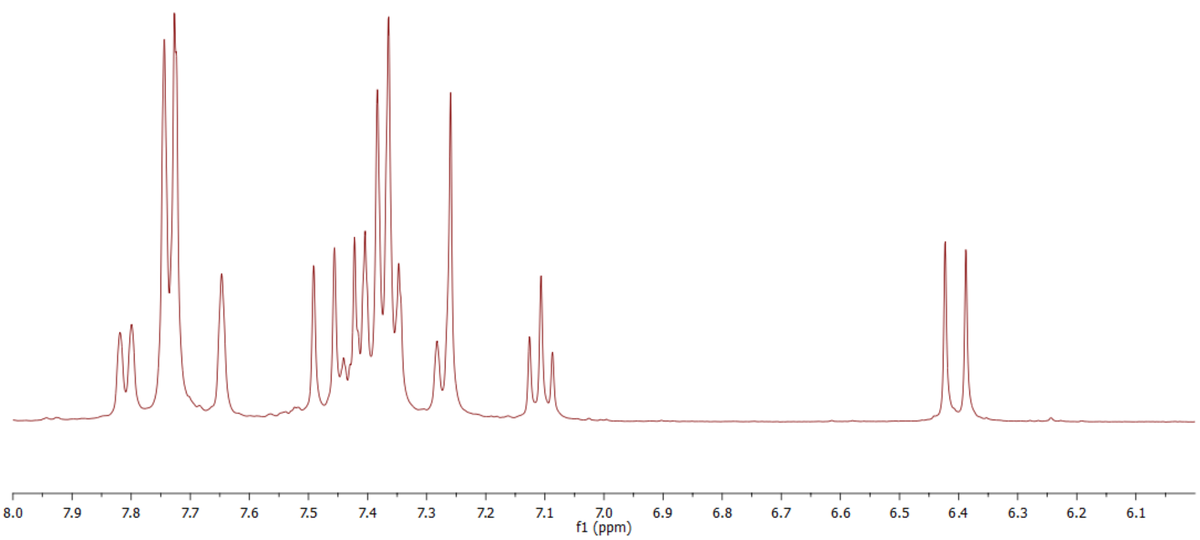


Figure S46: $^{1}H\{^{31}P\}$ NMR (400 MHz, 298 K, $CDCl_3$) spectrum in the region 6.0–8.0 ppm of the hydrophosphination product of 1,3-diethynylbenzene.

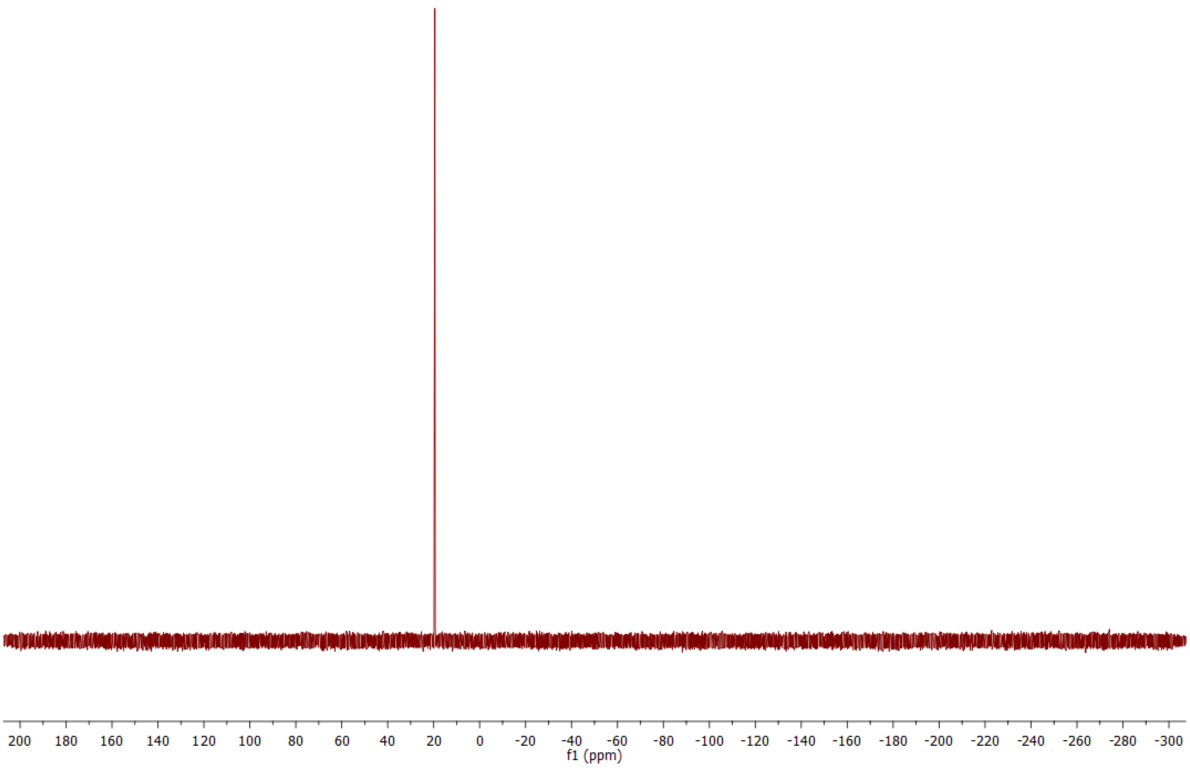


Figure S47: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 1,3-diethynylbenzene.

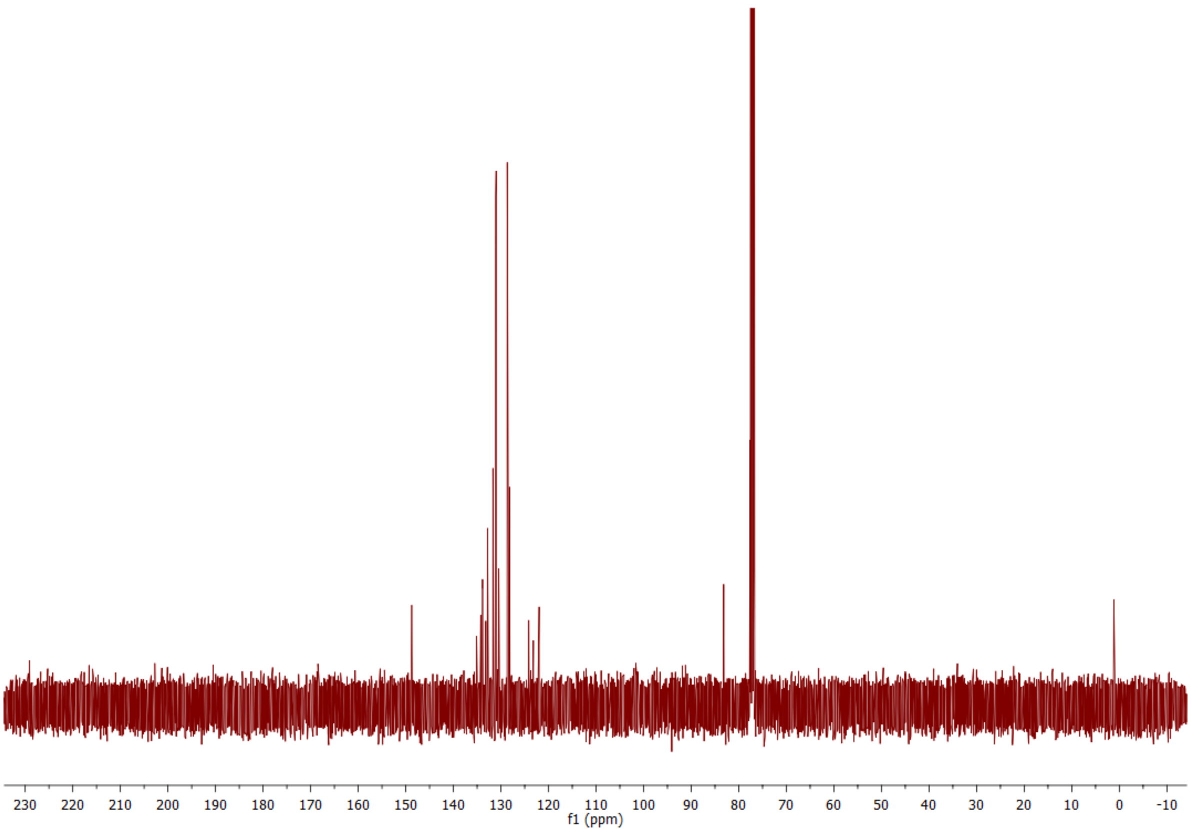


Figure S48: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 1,3-diethynylbenzene.

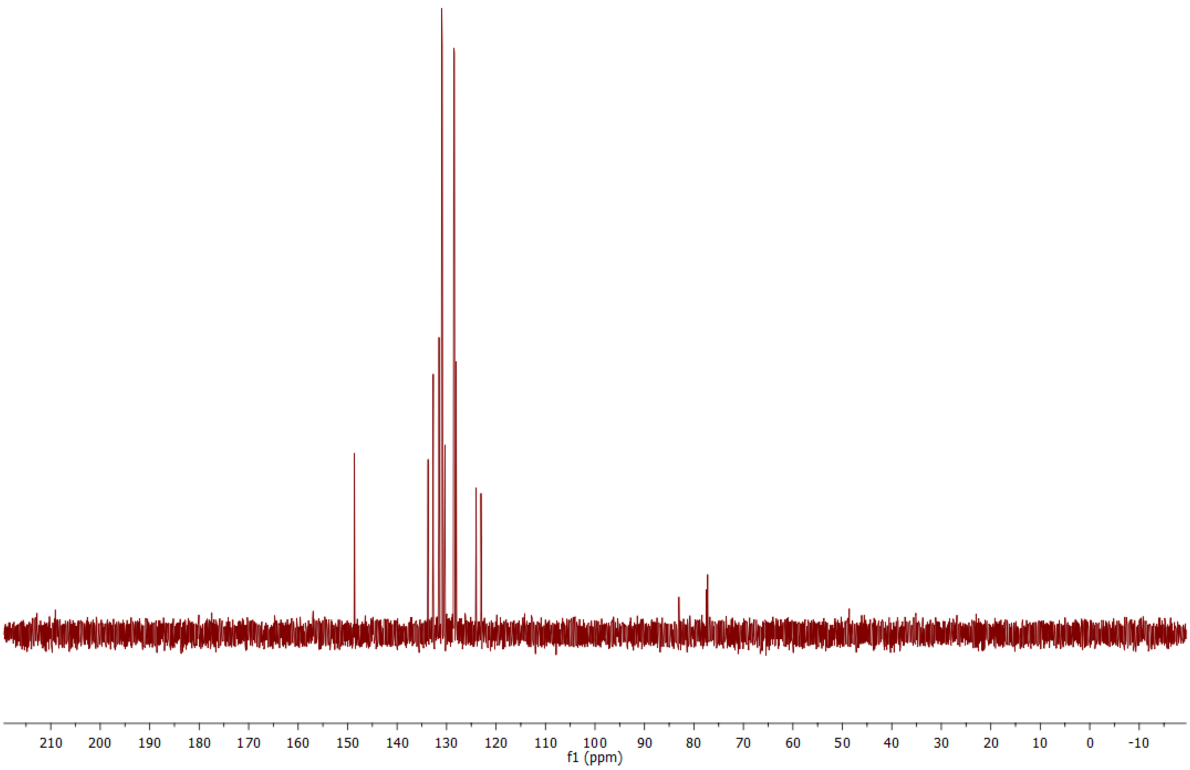


Figure S49: $^{13}C\{^{1}H\}$ DEPT90 NMR (100 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 1,3-diethynylbenzene.

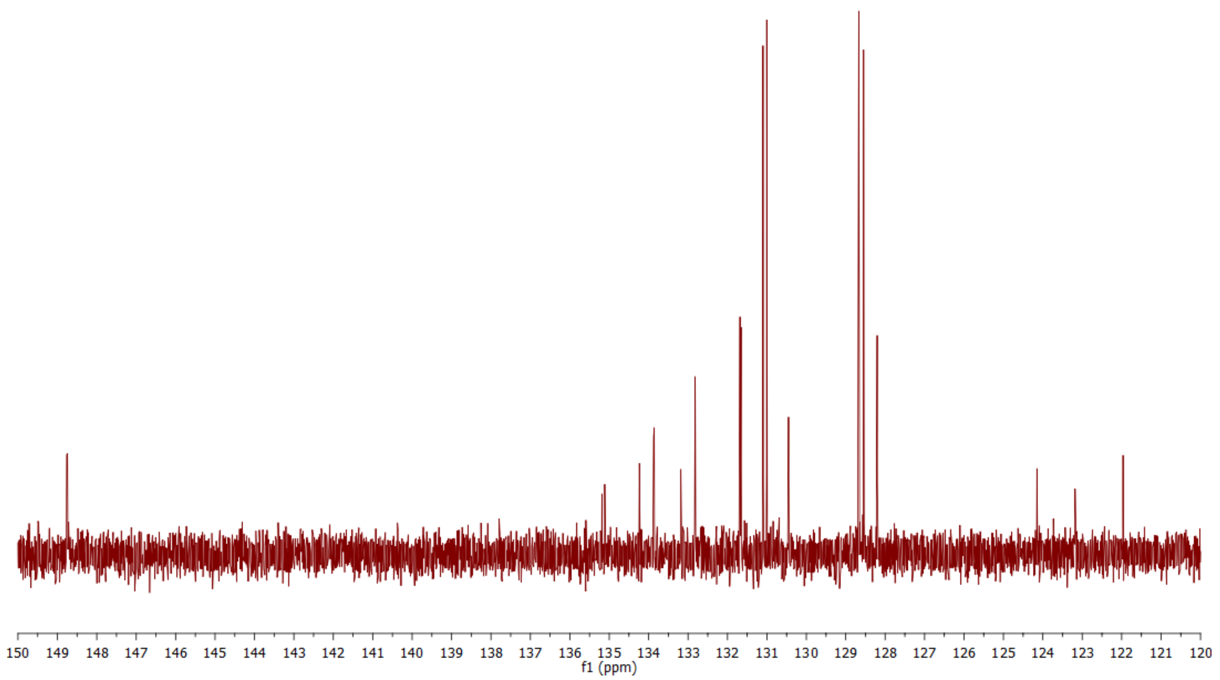


Figure S50: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, $CDCl_3$) spectrum in the region 120−150 ppm of the hydrophosphination product of 1,3-diethynylbenzene.

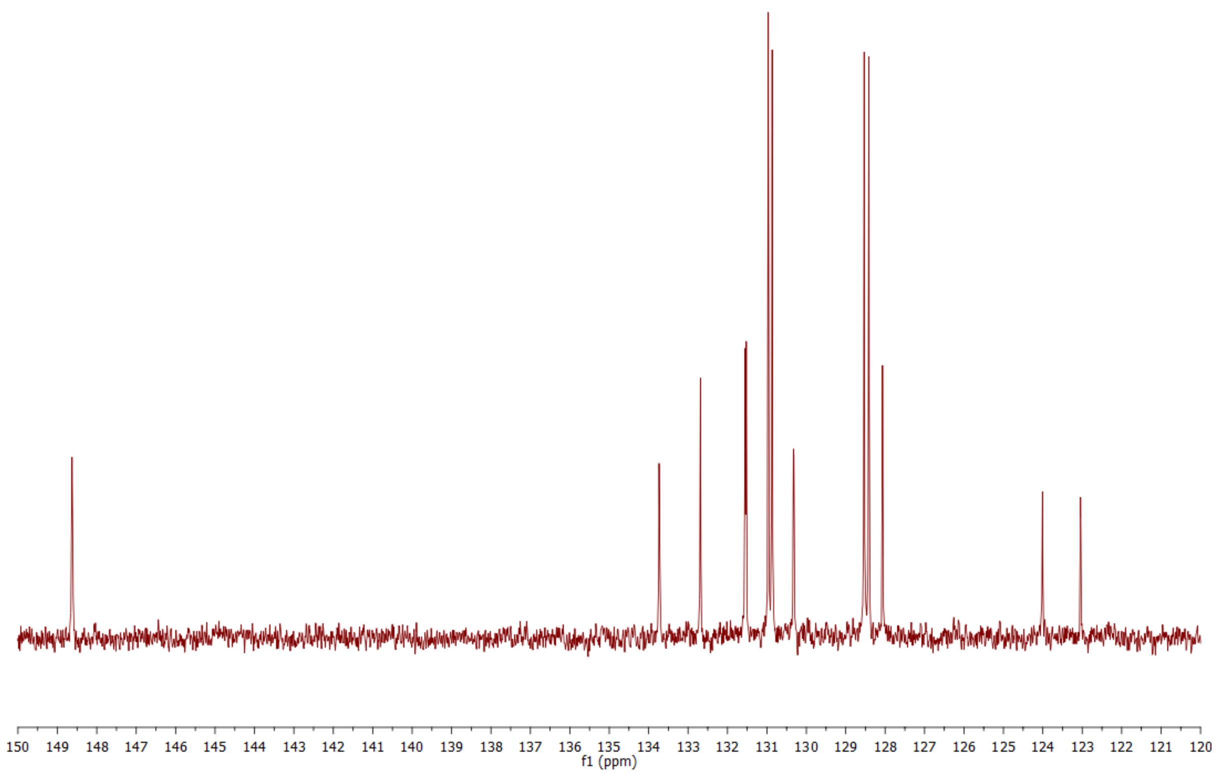


Figure S51: $^{13}C\{^{1}H\}$ DEPT90 NMR (100 MHz, 298 K, $CDCl_3$) spectrum in the region 120−150 ppm of the hydrophosphination product of 1,3-diethynylbenzene.

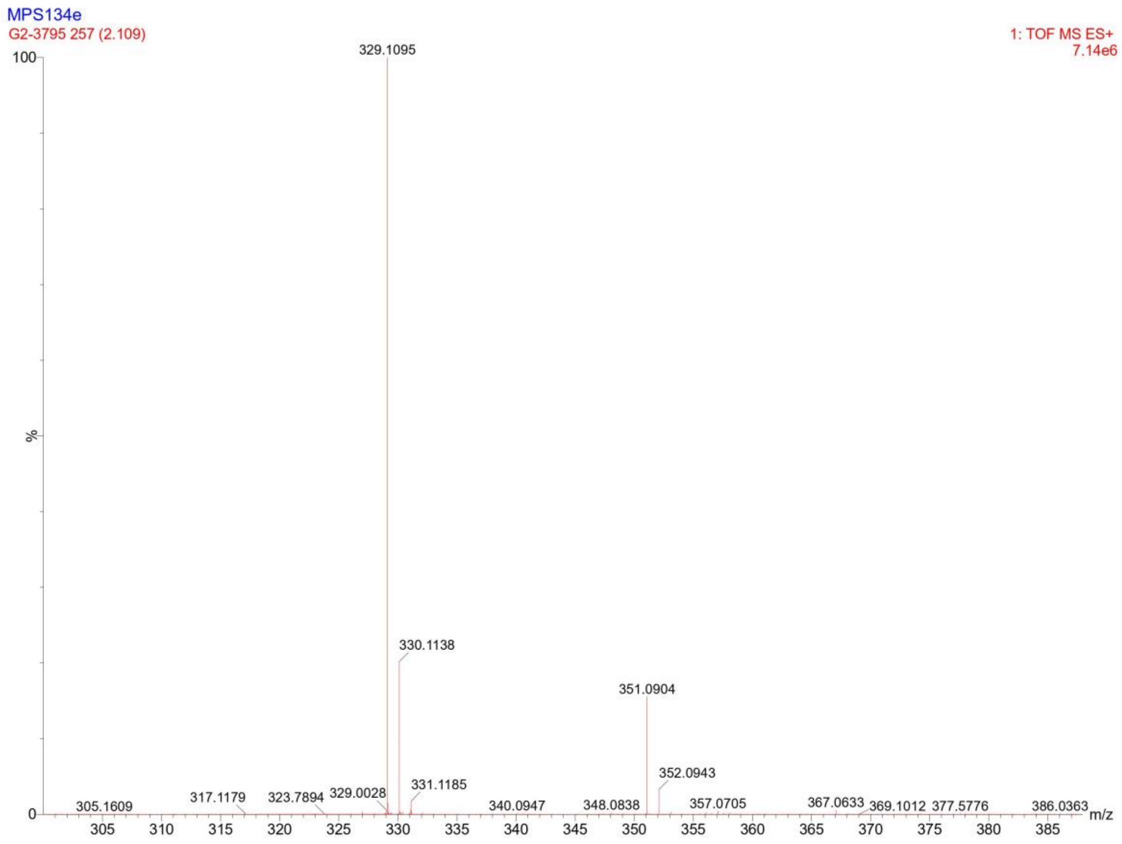


Figure S52: HRMS of the hydrophosphination product of 1,3-diethynylbenzene.

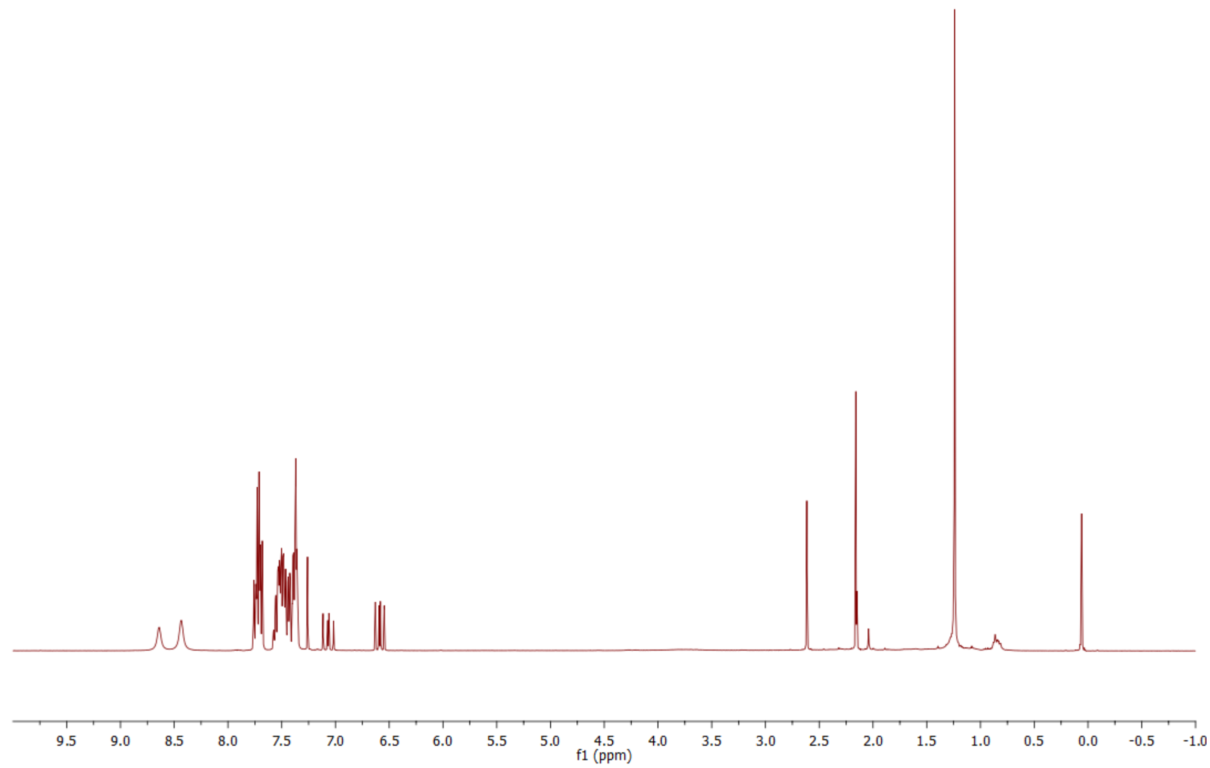


Figure S53: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 4-ethynylpyridine.

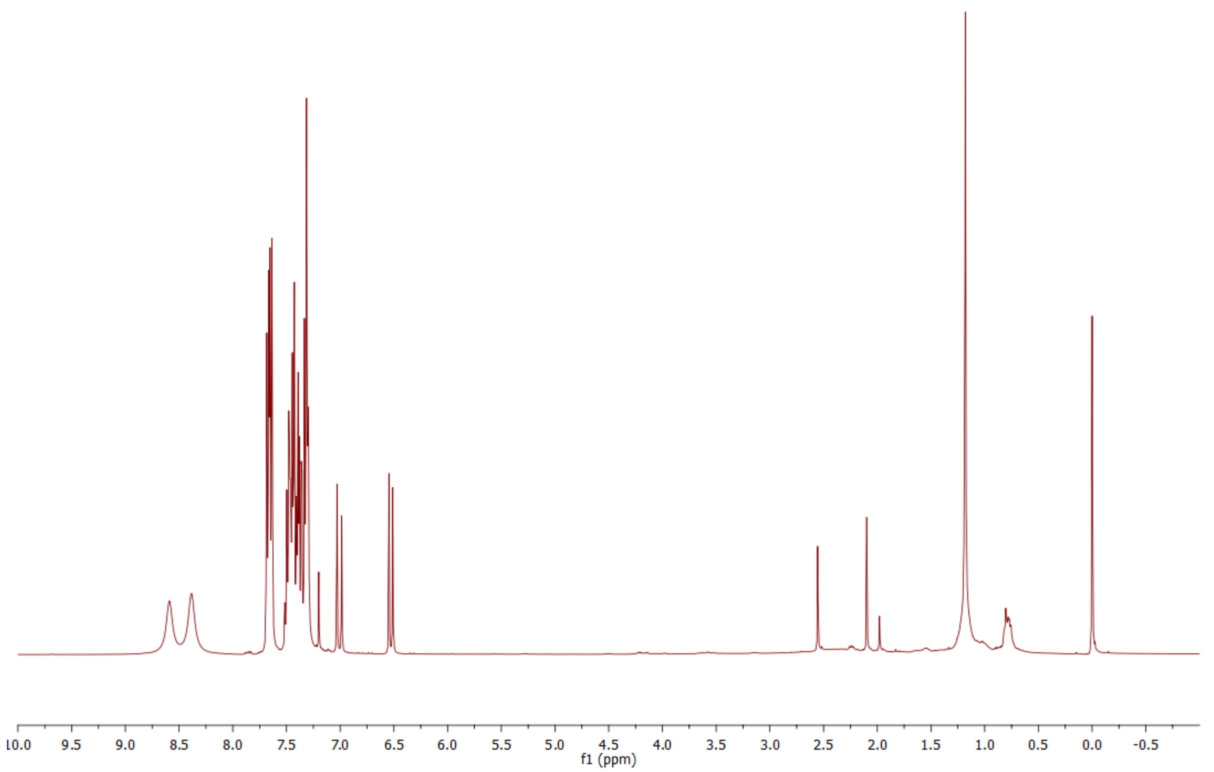


Figure S54: $^{1}H\{^{31}P\}$ NMR (400 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 4-ethynylpyridine.

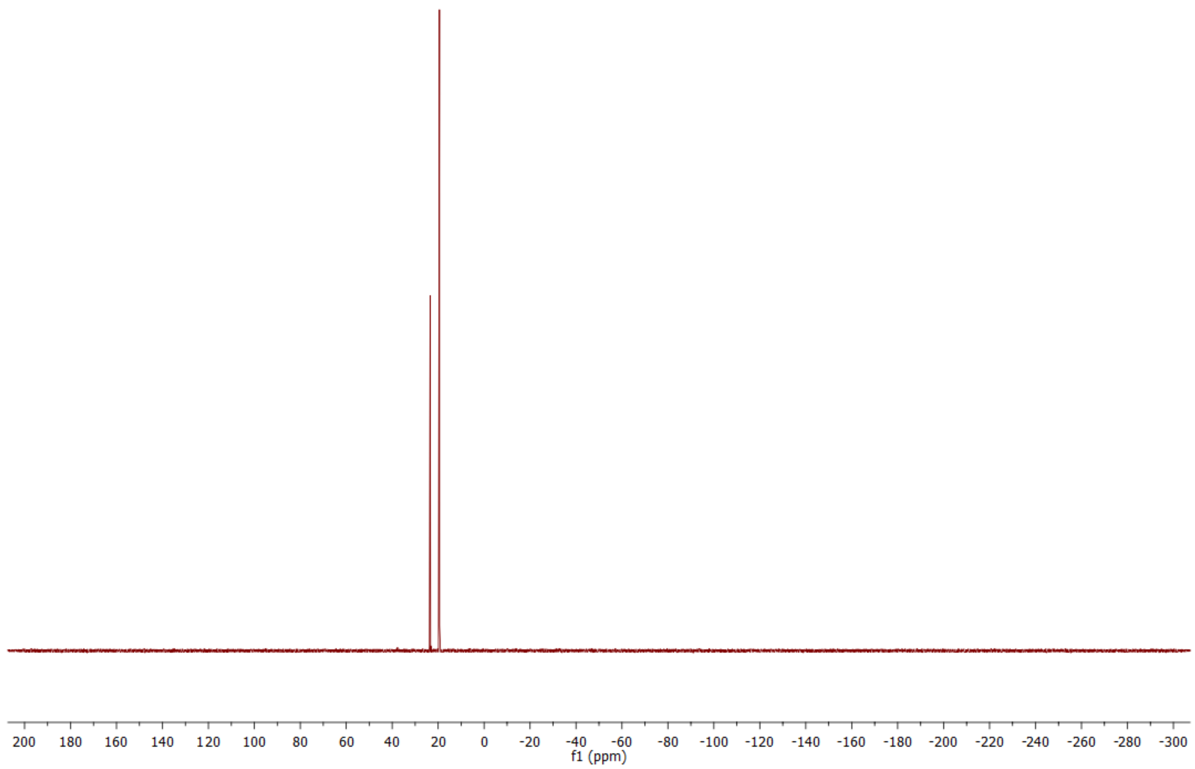


Figure S55: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 4-ethynylpyridine.

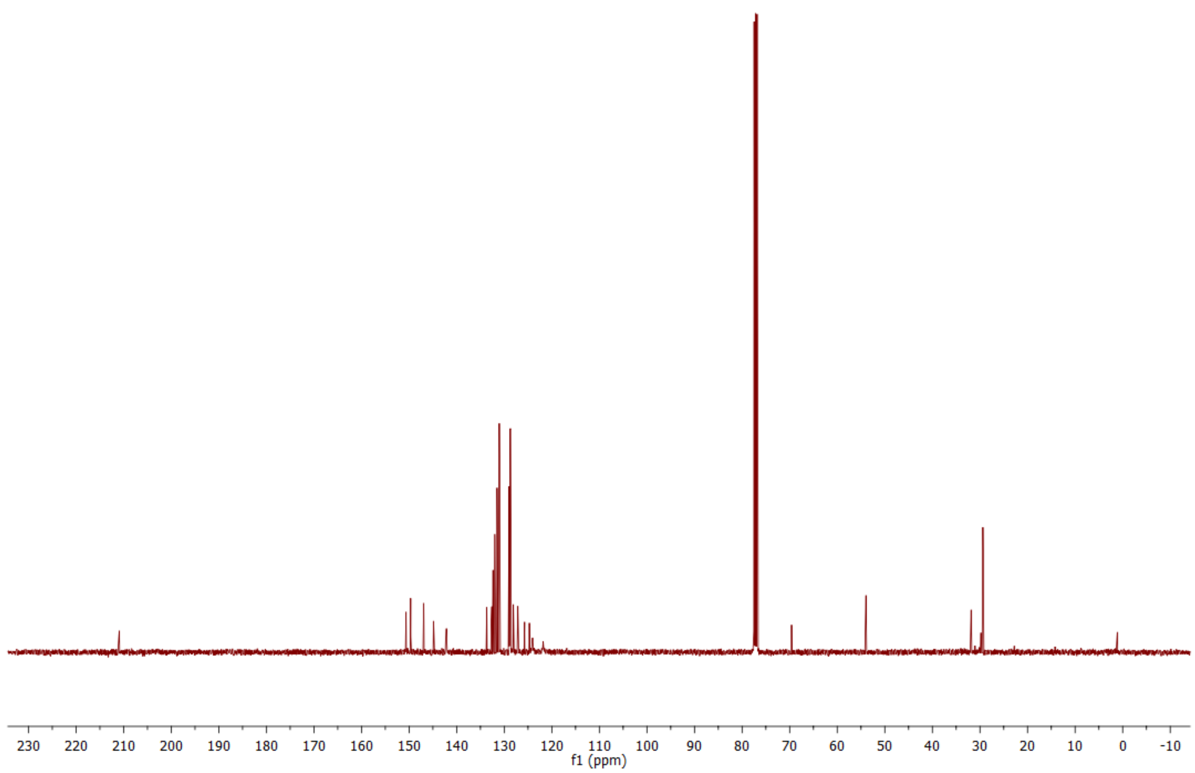


Figure S56: $^{13}C\{^{1}H\}$ NMR (100 MHz, 298 K, $CDCl_3$) spectrum of the hydrophosphination product of 4-ethynylpyridine.

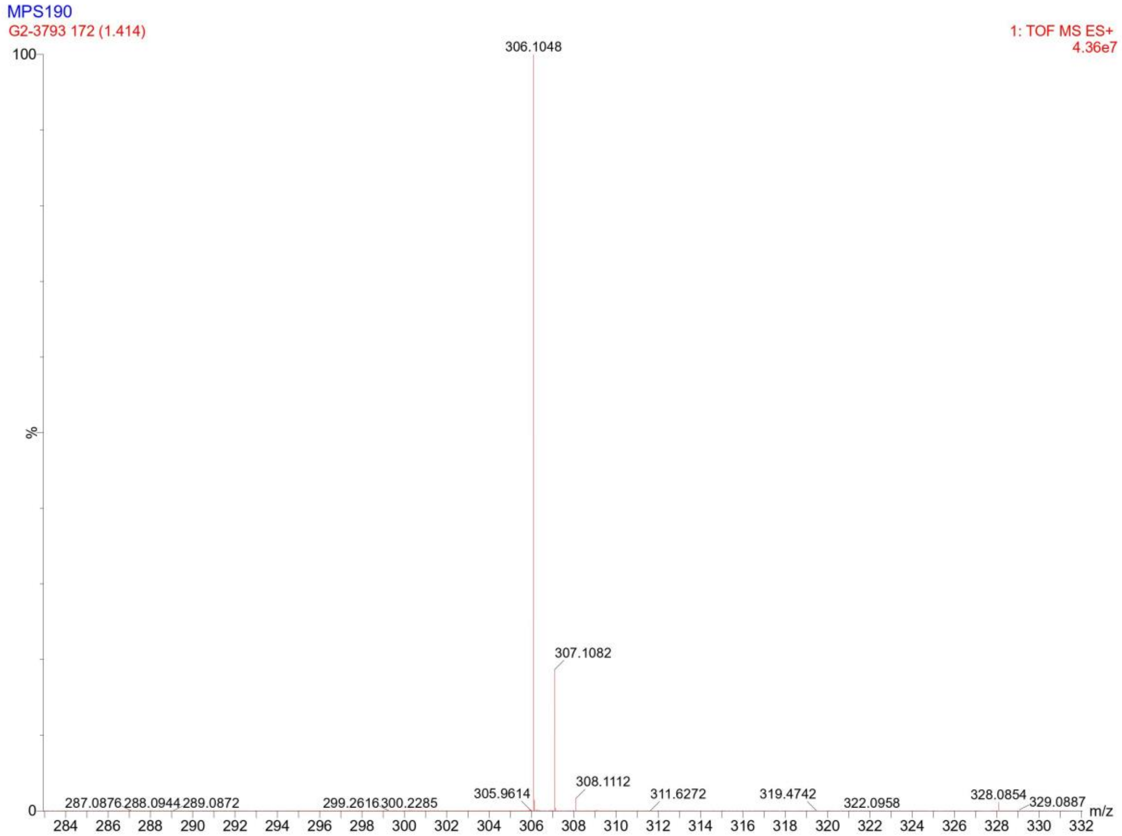


Figure S57: HRMS of the hydrophosphination product of 4-ethynylpyridine.

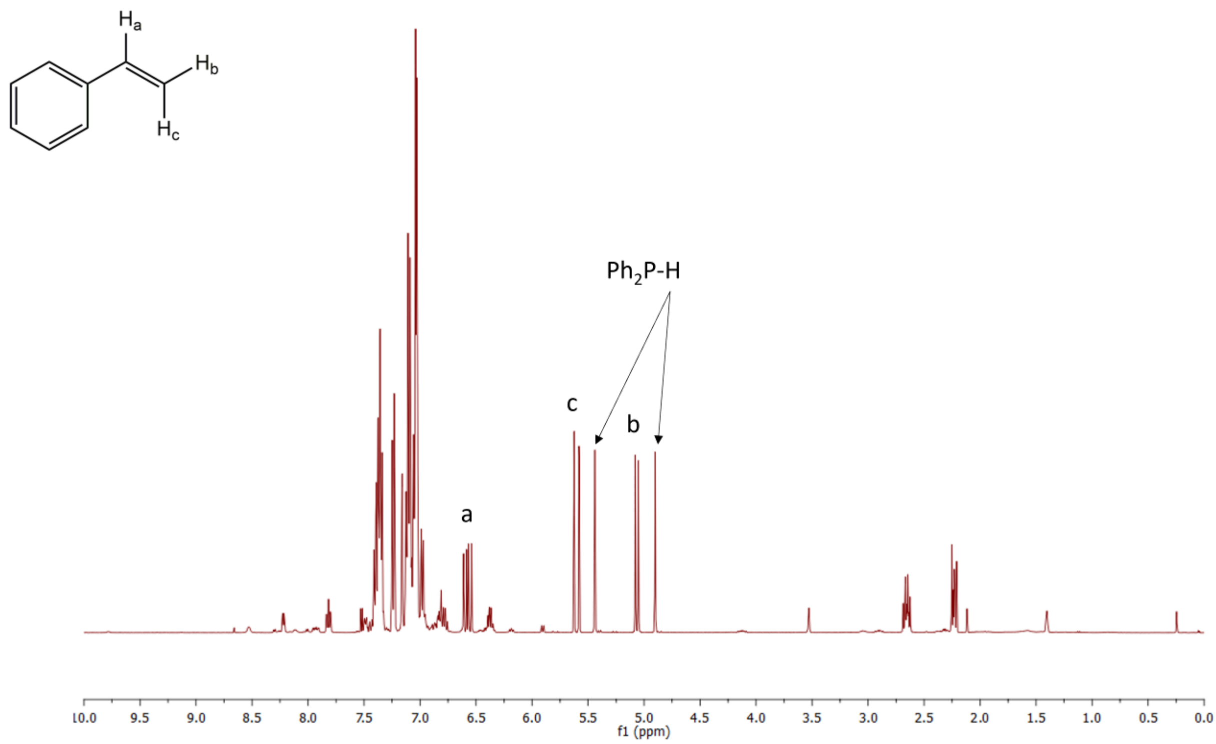


Figure S58: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 1 of Table S3.

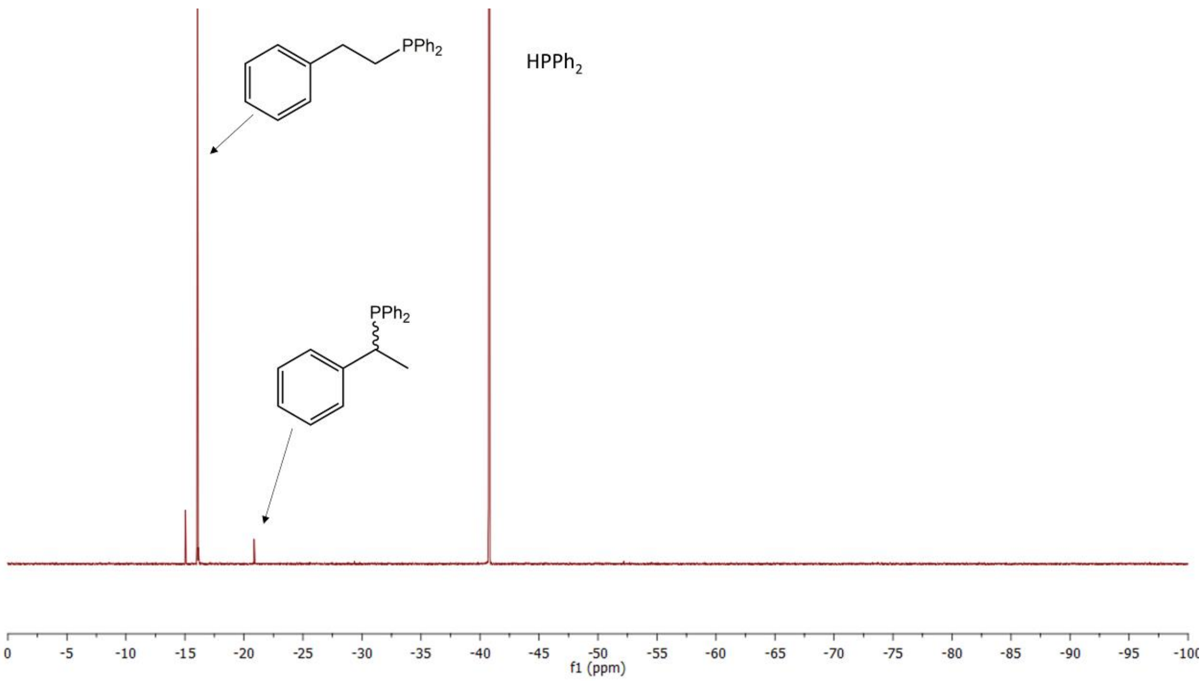


Figure S59: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 1 of Table S3.

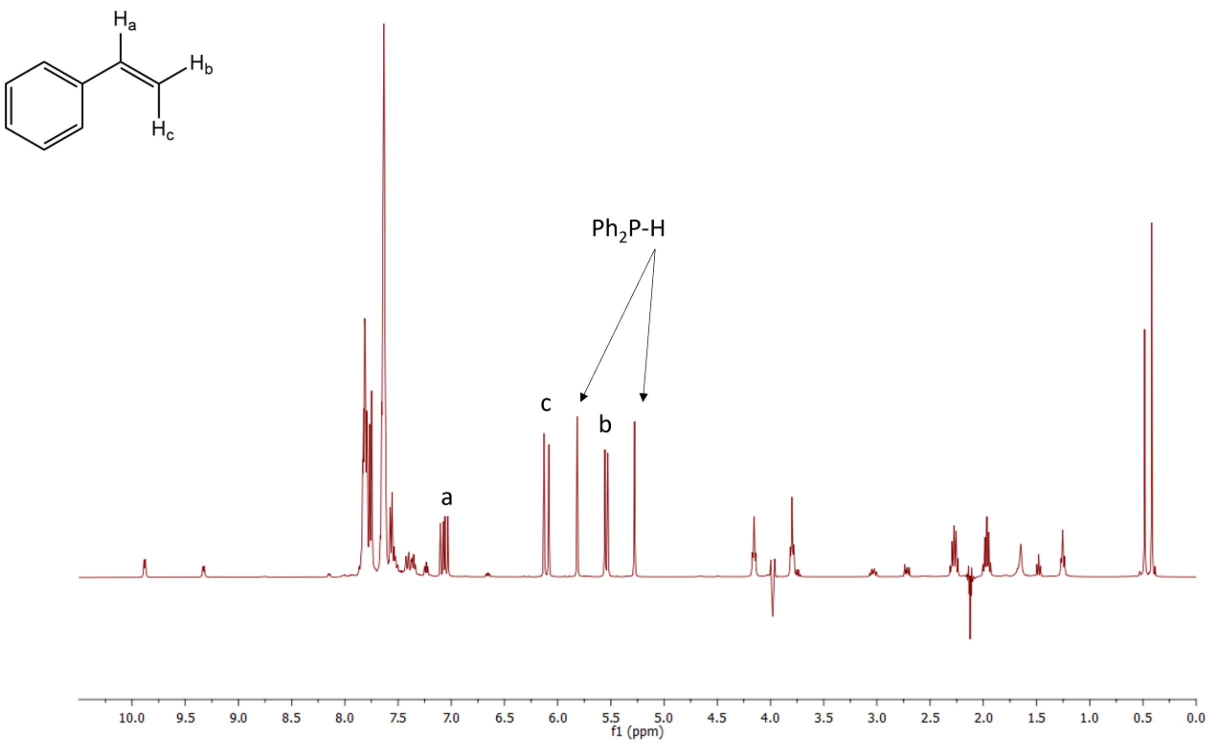


Figure S60: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 2 of Table S3.

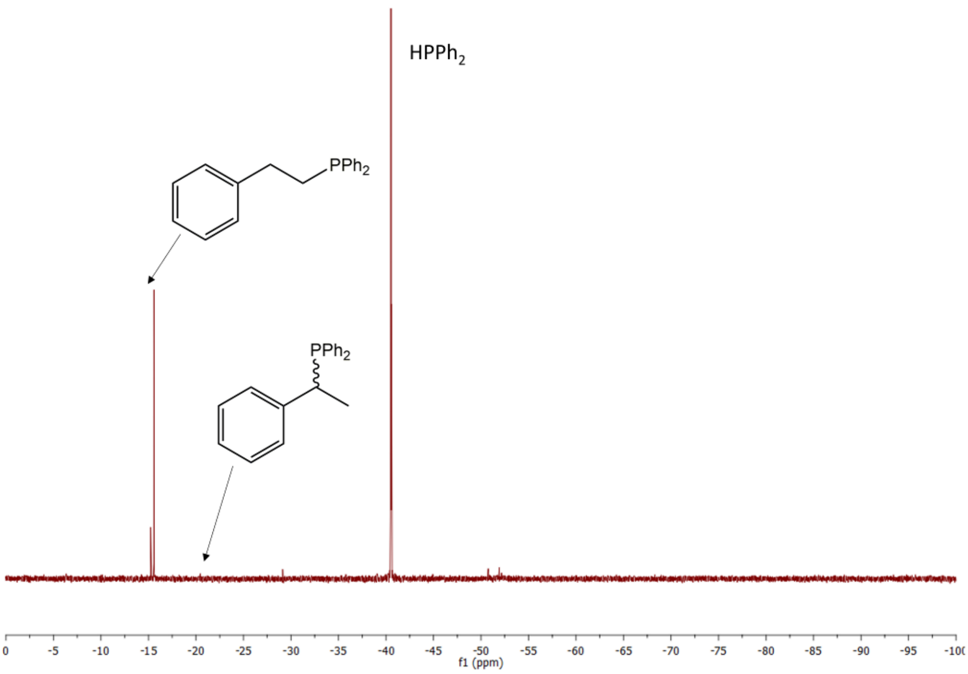


Figure S61: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 2 of Table S3.

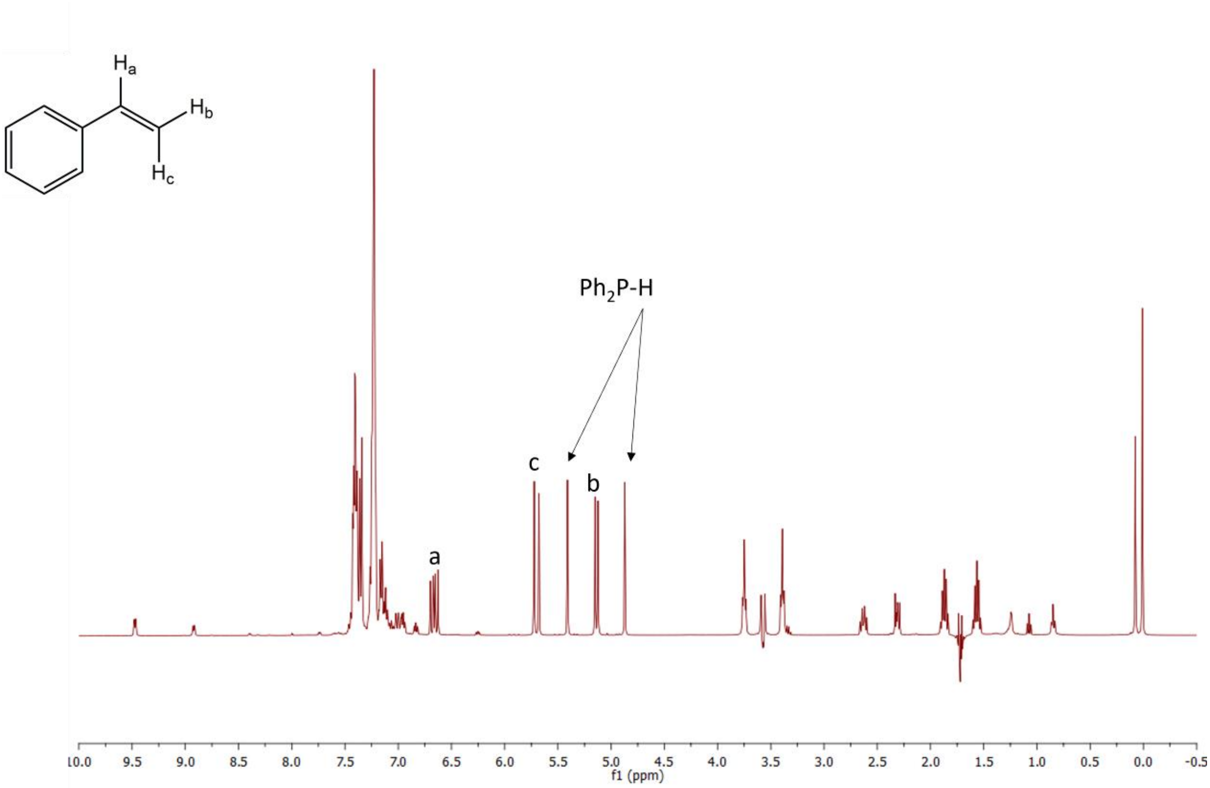


Figure S62: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 3 of Table S3.

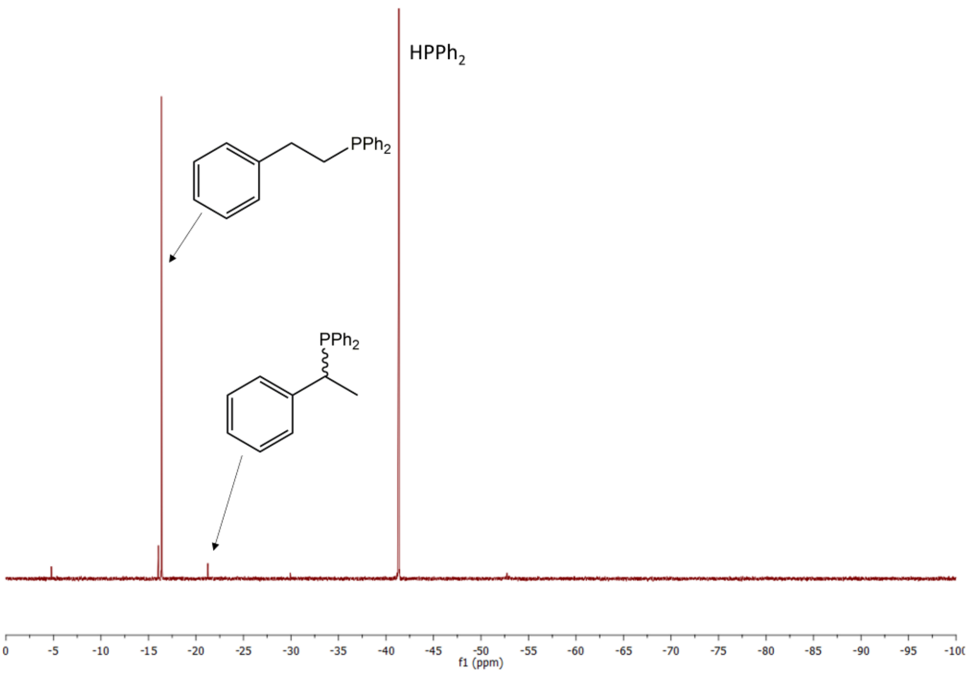


Figure S63: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 3 of Table S3.

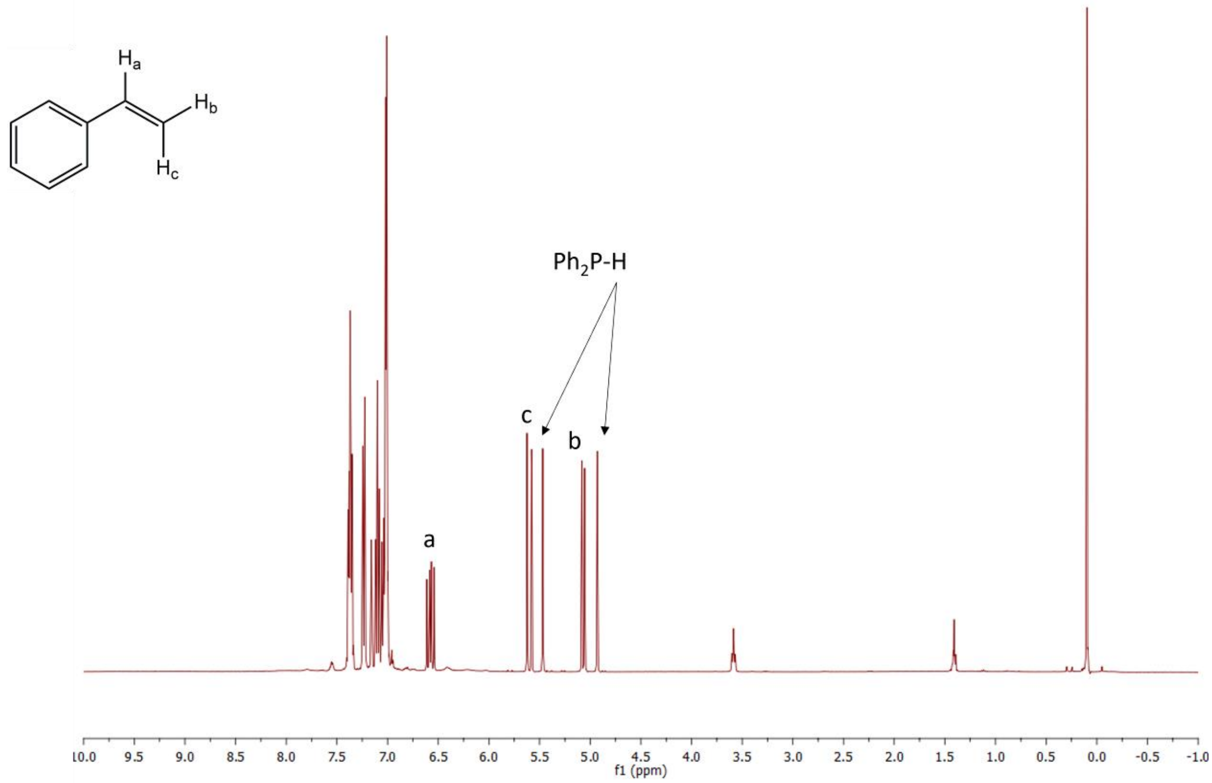


Figure S64: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −1 to 10 ppm for entry 4 of Table S3.

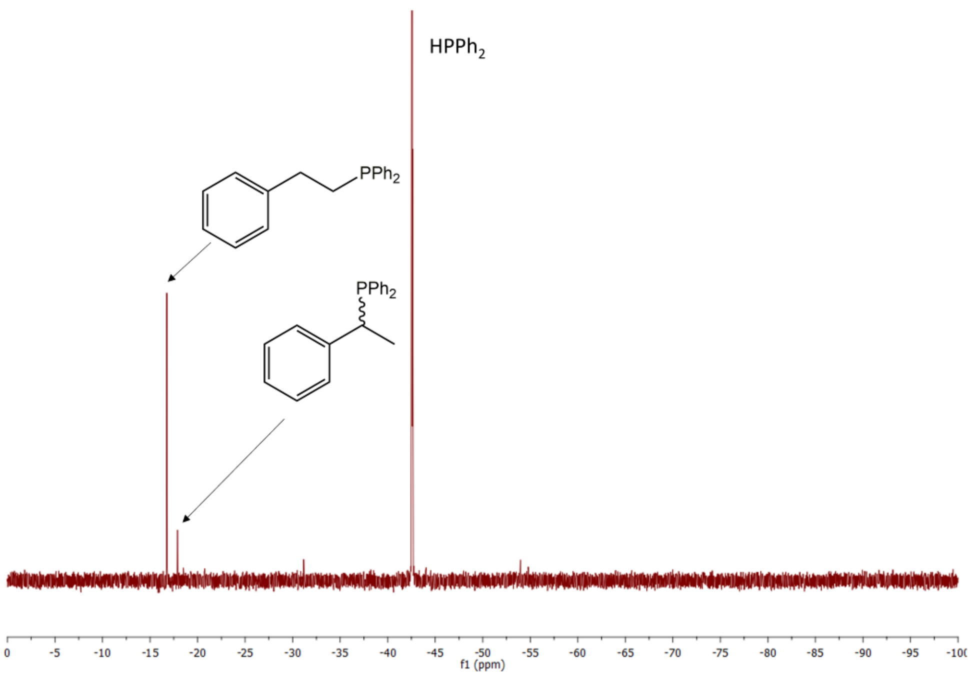


Figure S65: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 4 of Table S3.

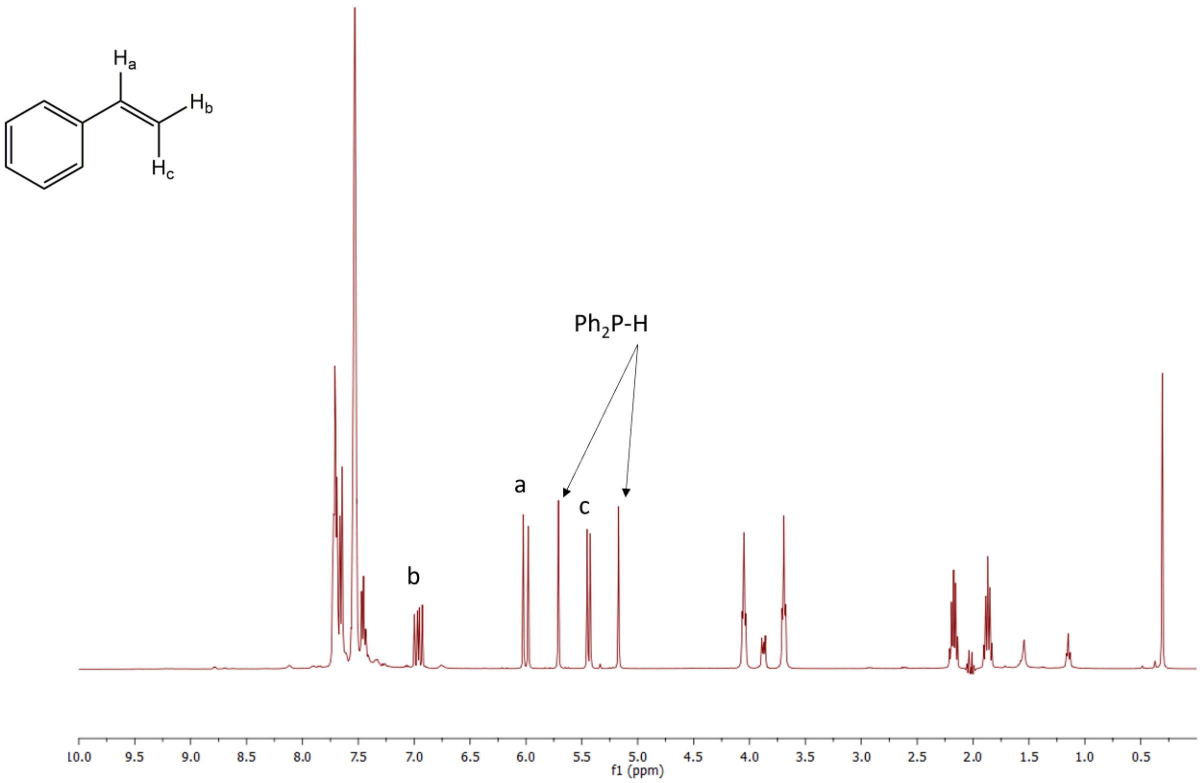


Figure S66: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 5 of Table S3.

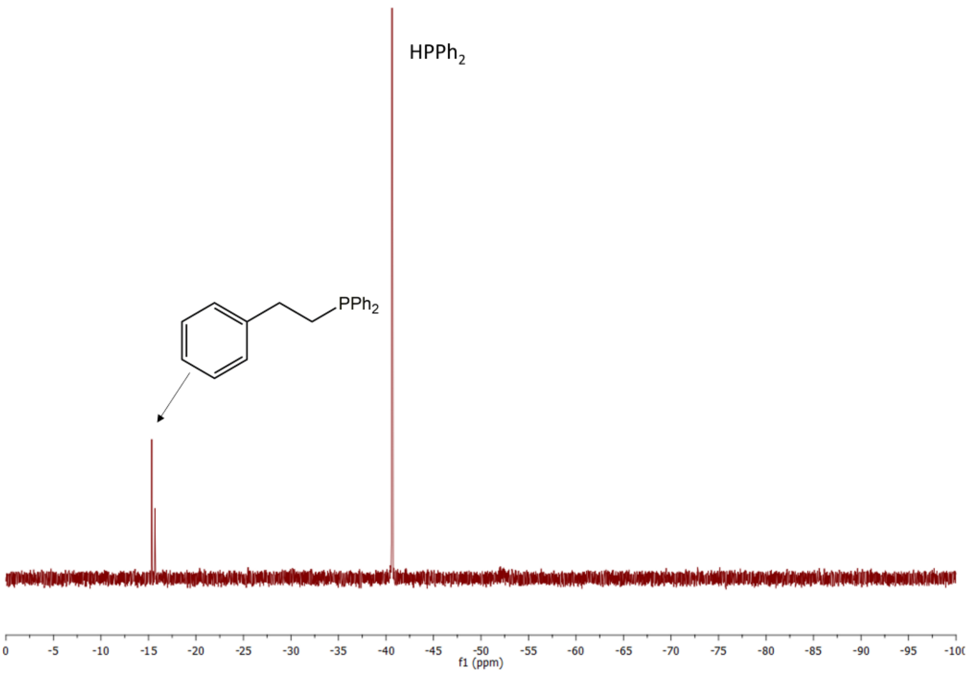


Figure S67: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 5 of Table S3.

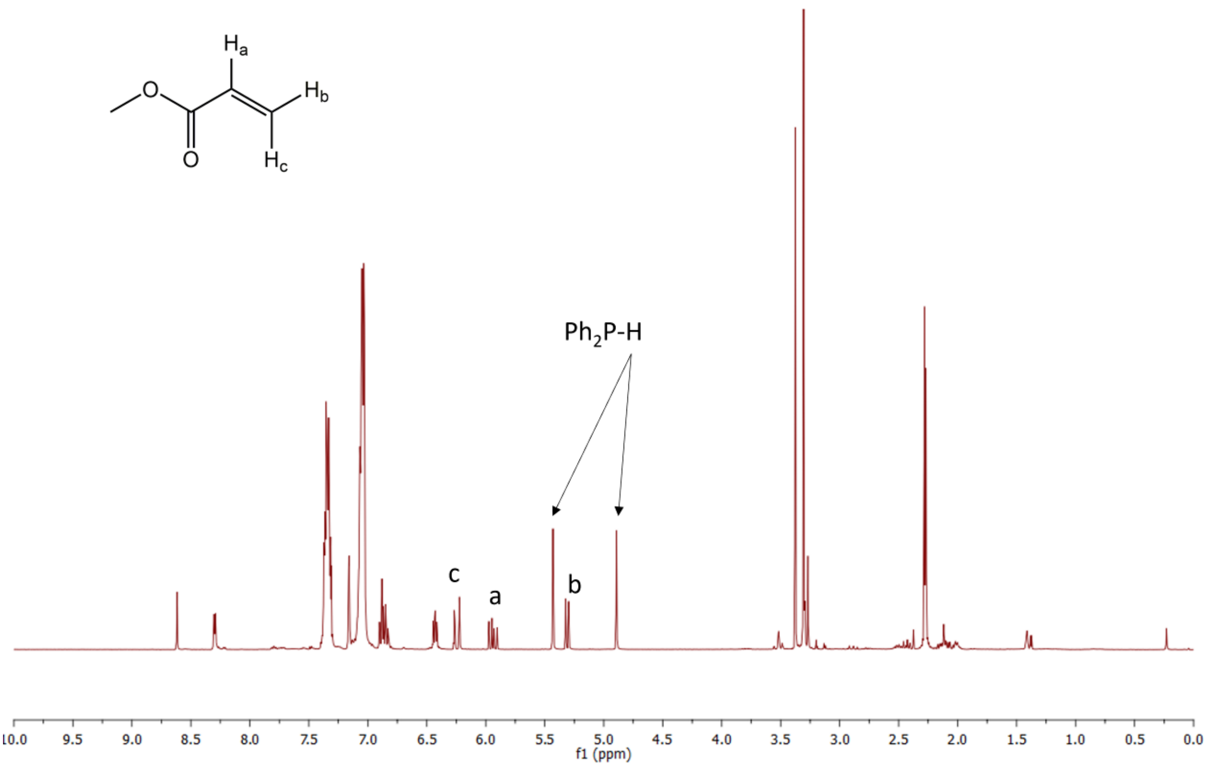


Figure S68: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 6 of Table S3.

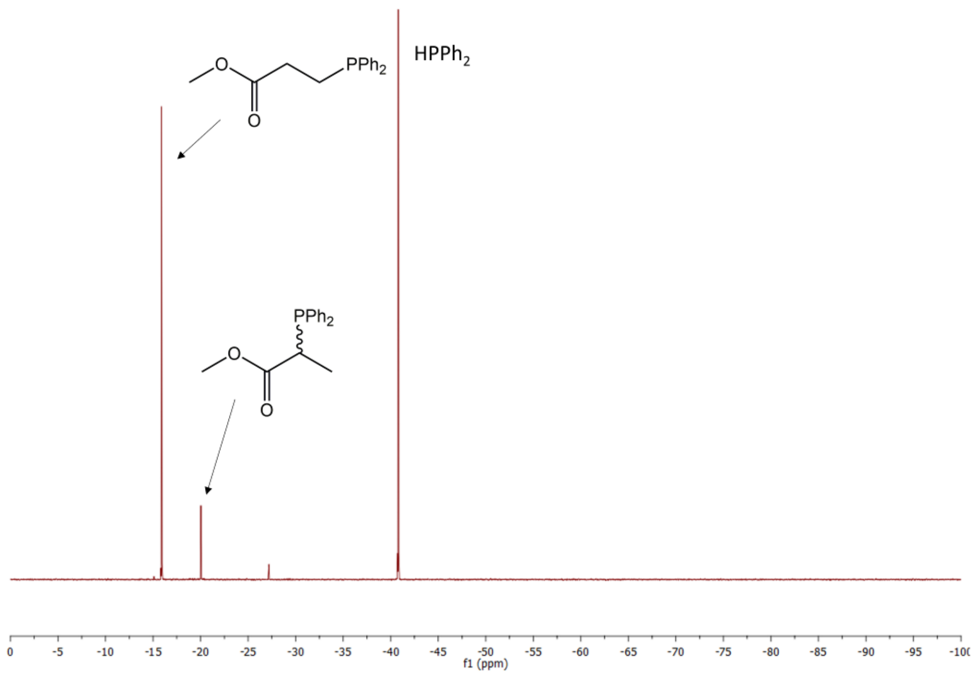


Figure S69: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 6 of Table S3.

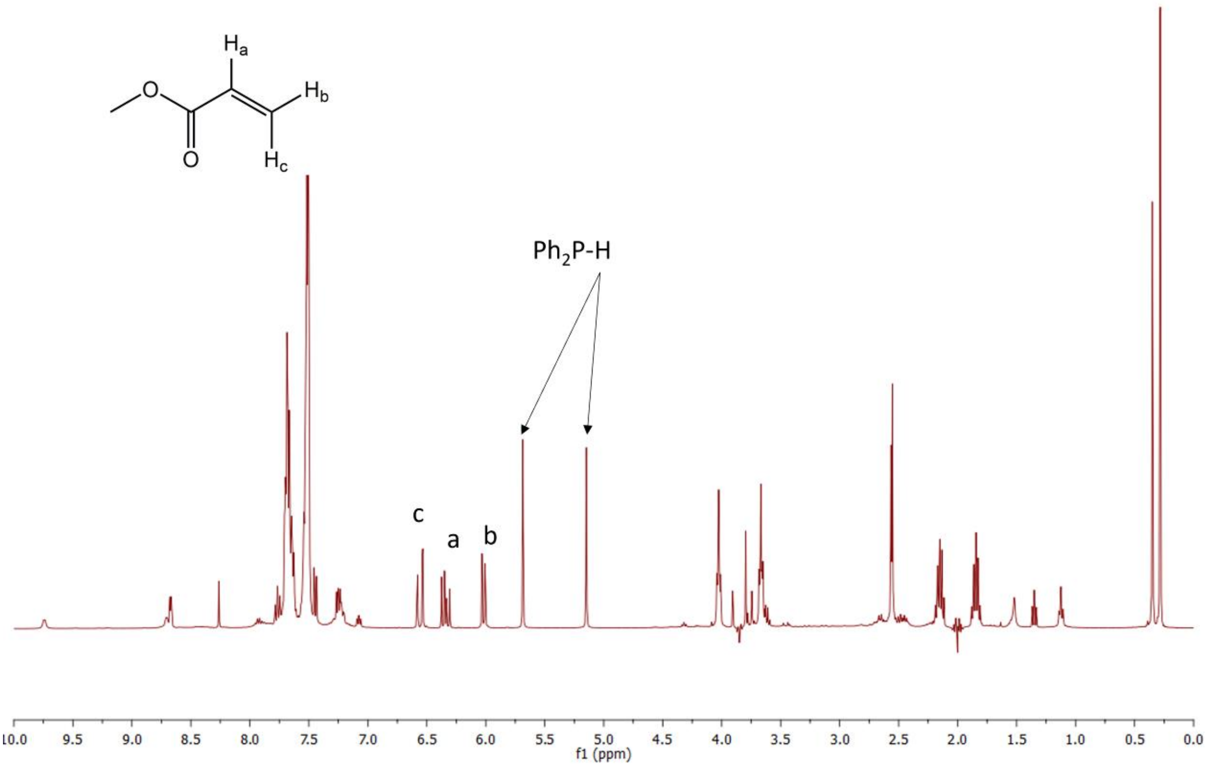


Figure S70: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 7 of Table S3.

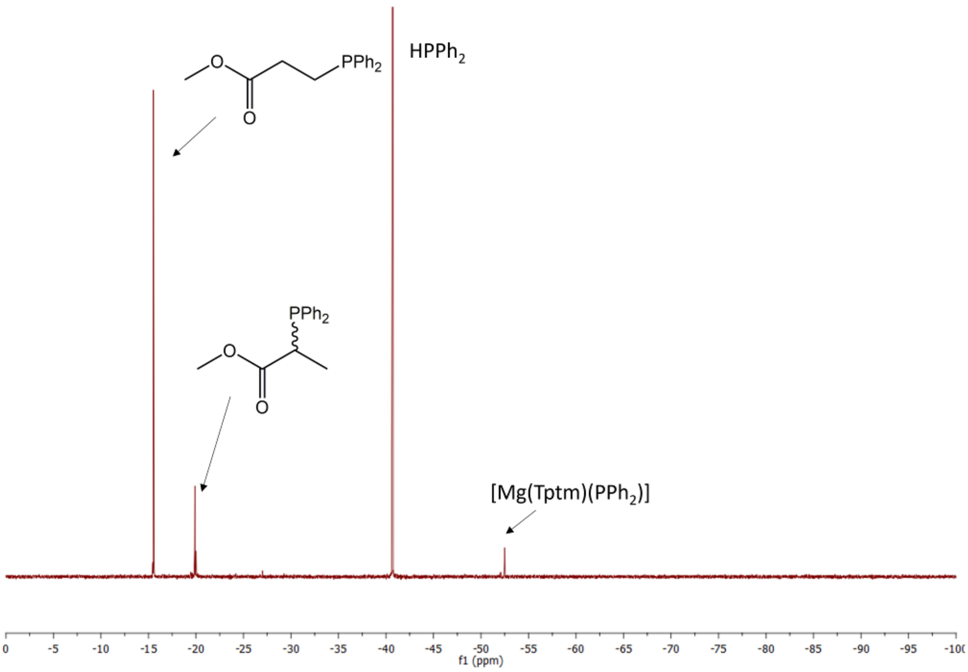


Figure S71: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 7 of Table S3.

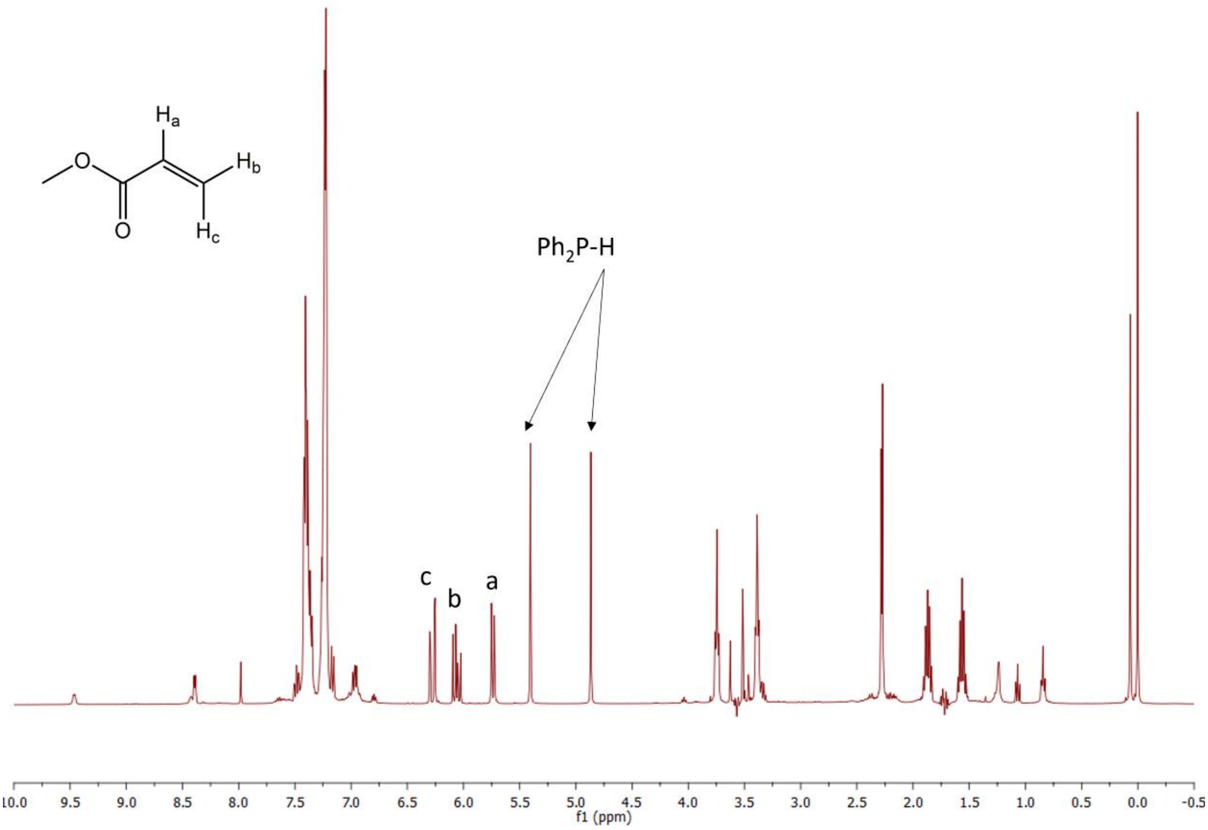


Figure S72: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 8 of Table S3.

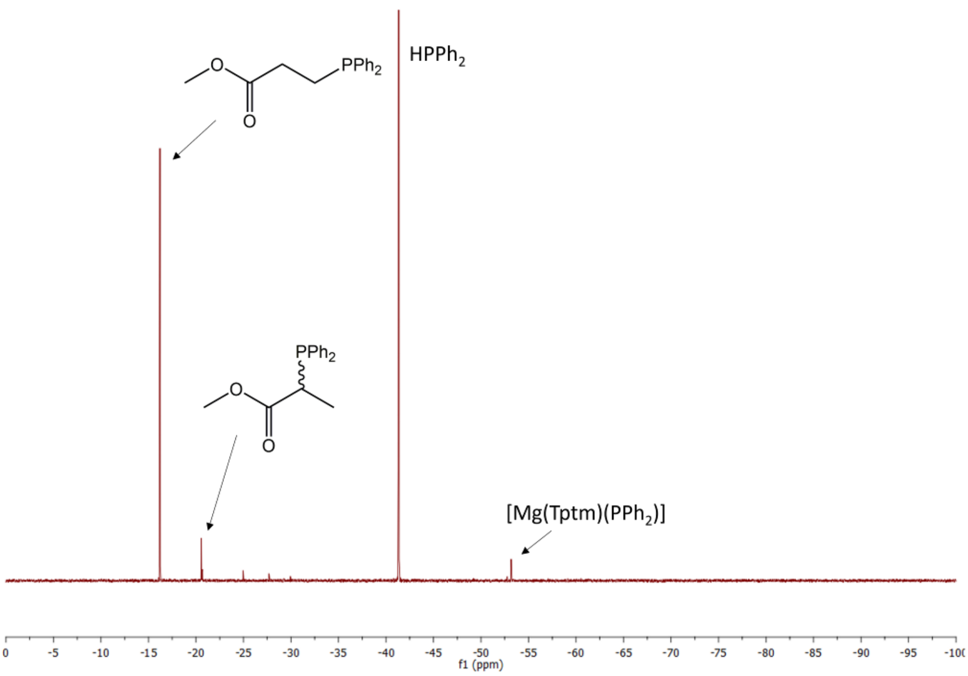


Figure S73: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 8 of Table S3.

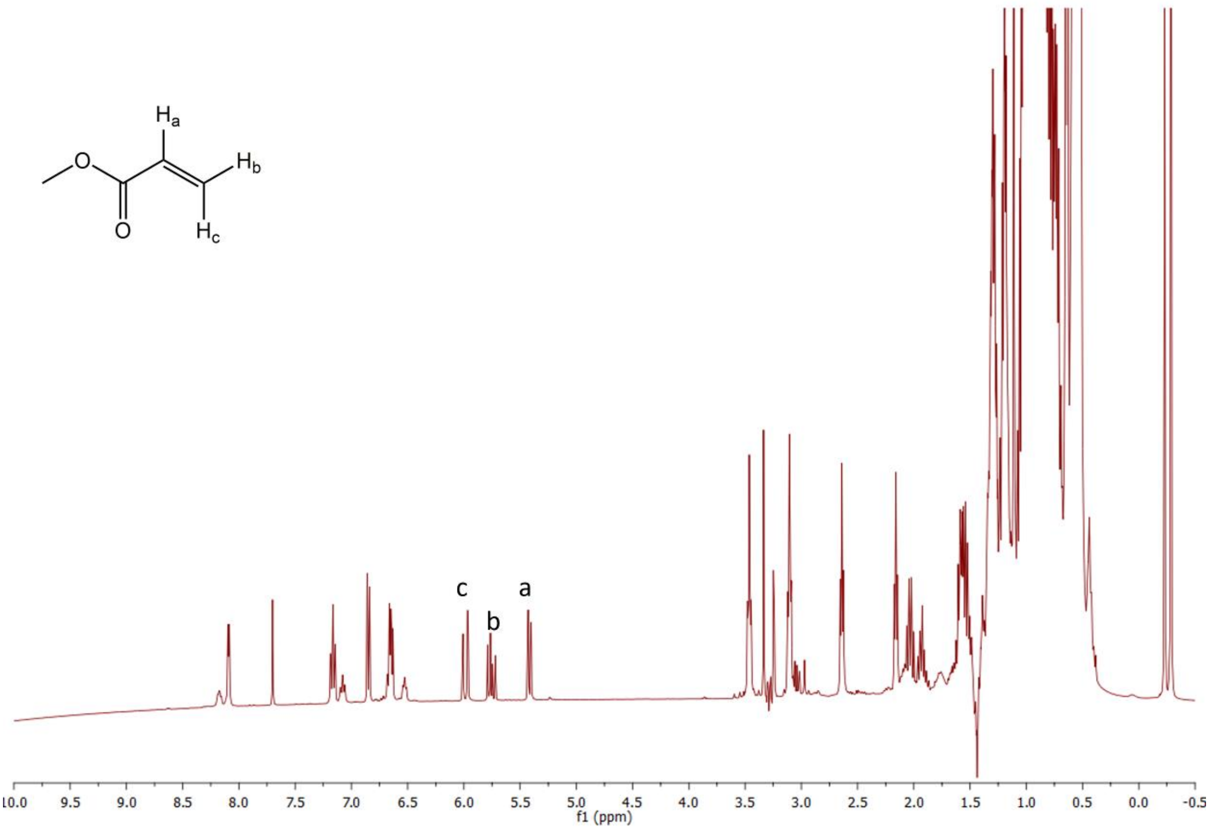


Figure S74: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 9 of Table S3.

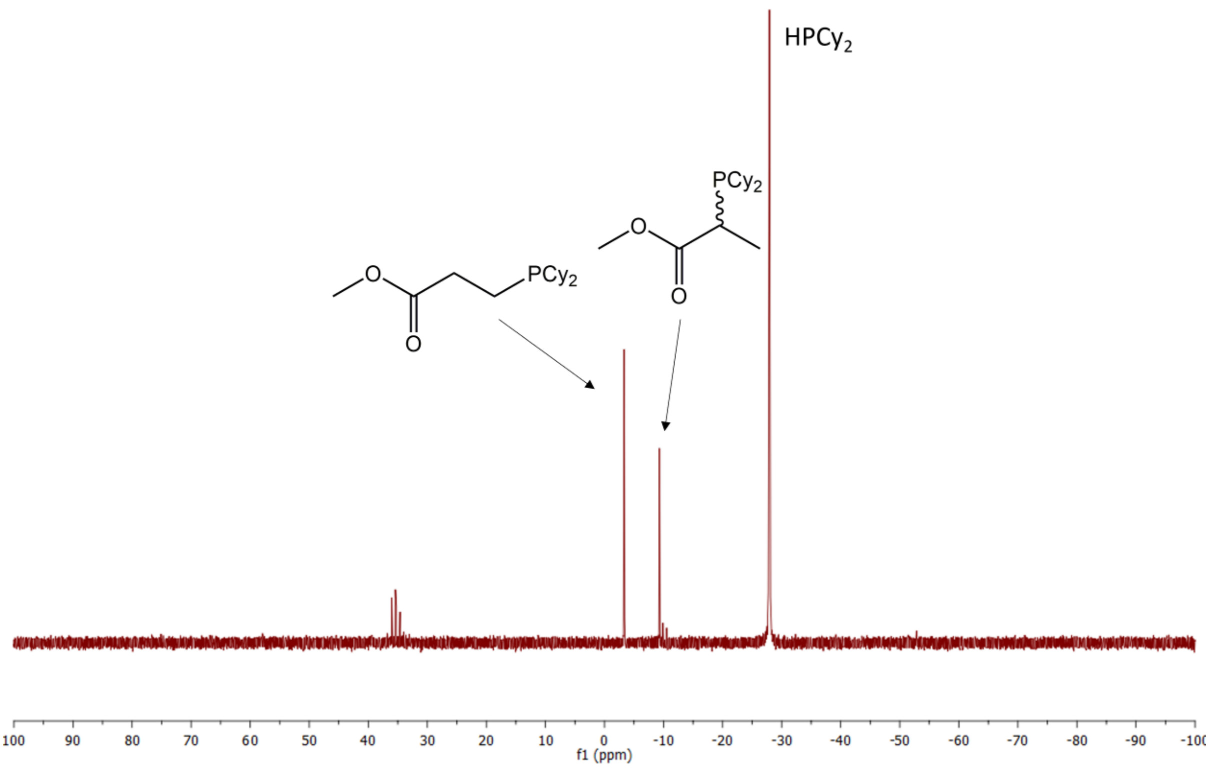


Figure S75: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for entry 9 of Table S3.

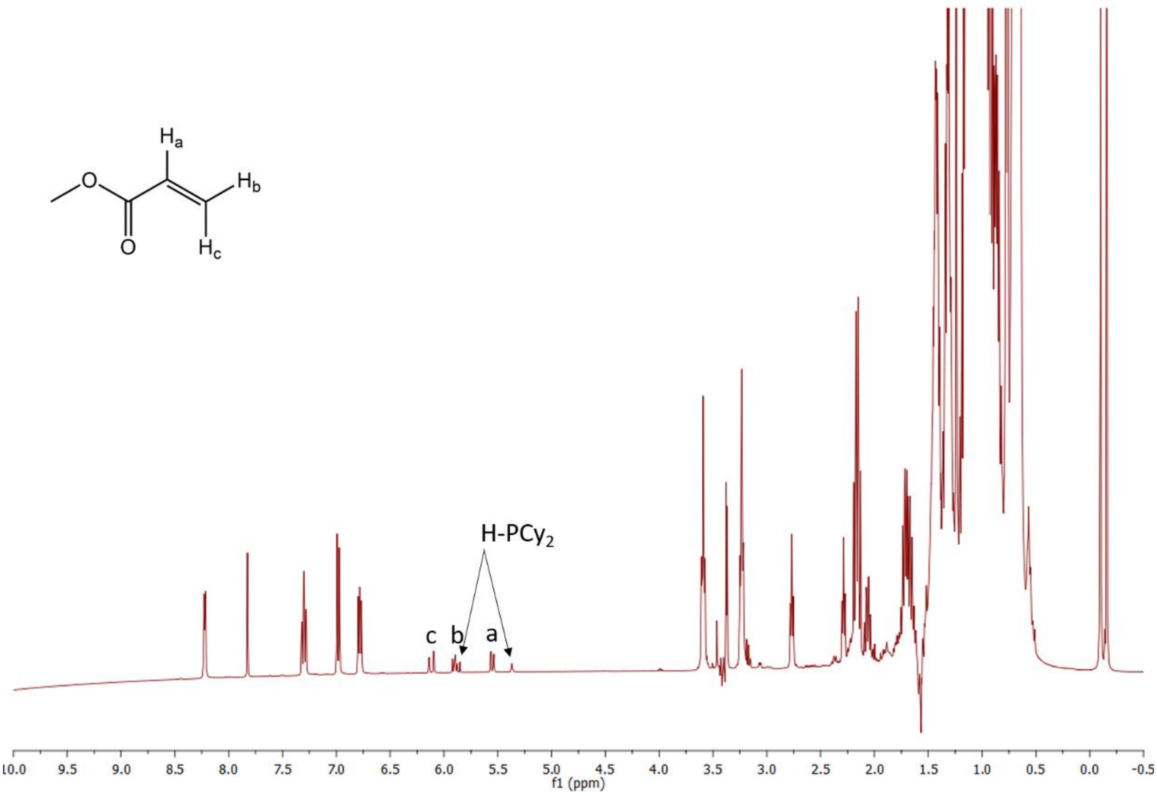


Figure S76: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 10 of Table S3.

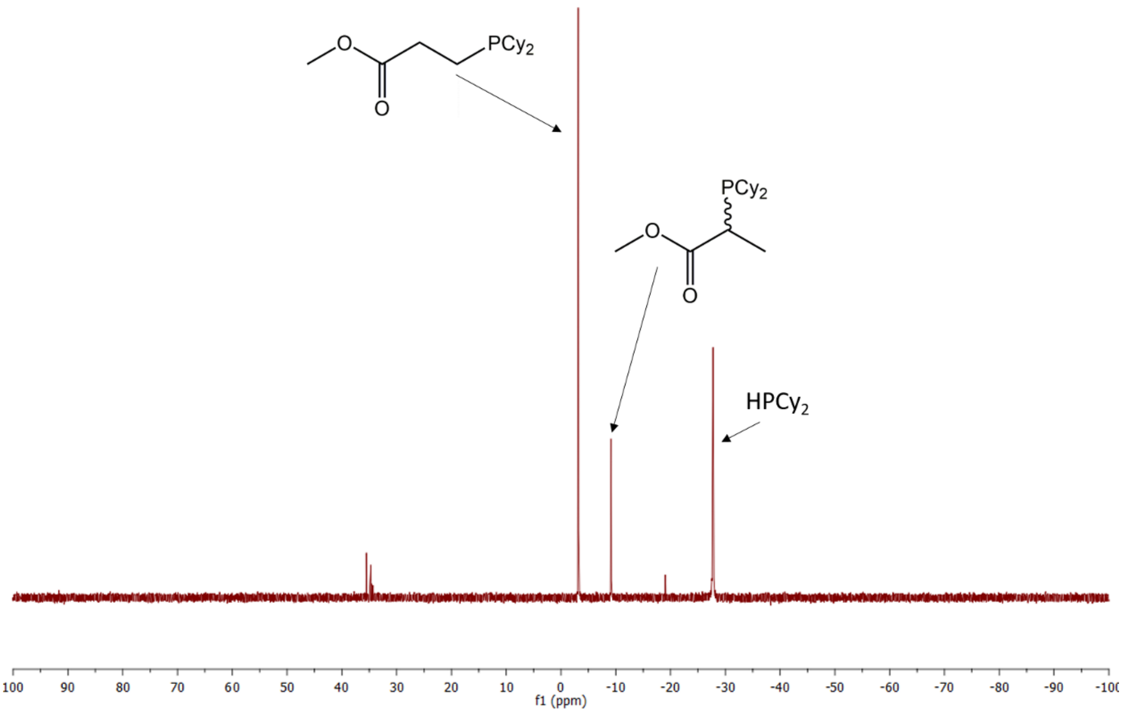


Figure S77: $^{31}P\{^1H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for entry 10 of Table S3.

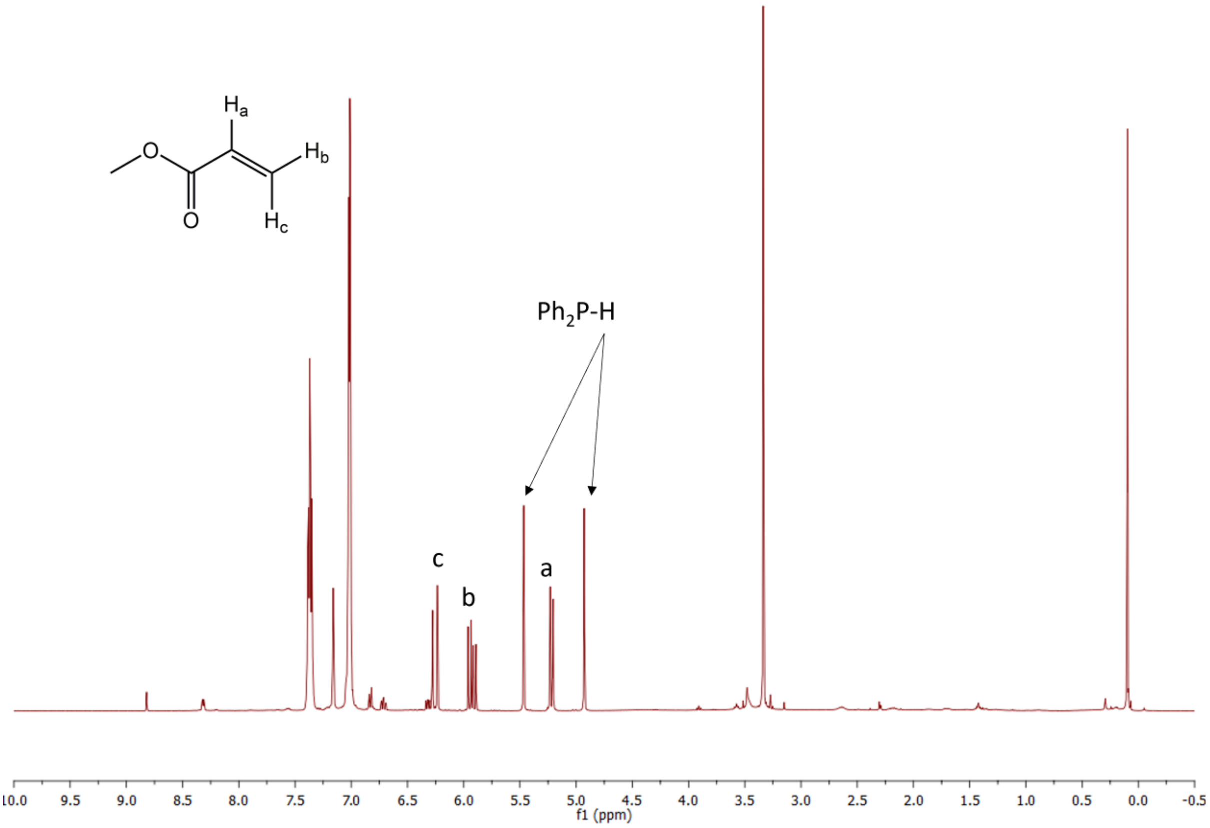


Figure S78: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 11 of Table S3.

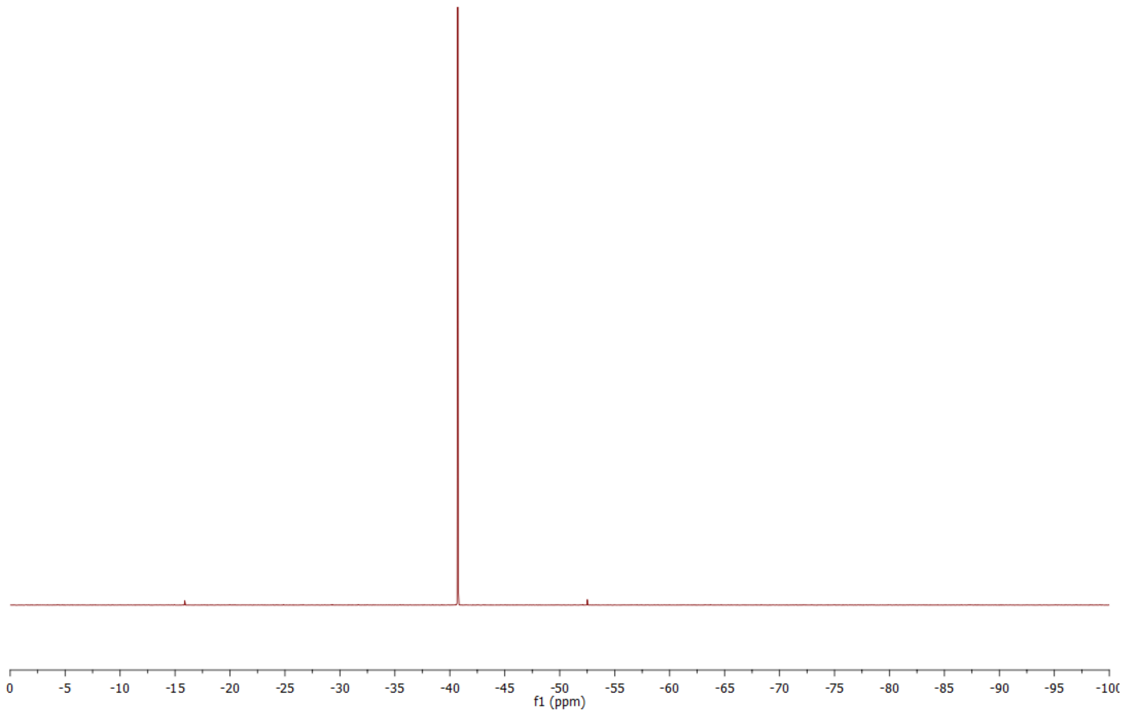


Figure S79: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 11 of Table S3.

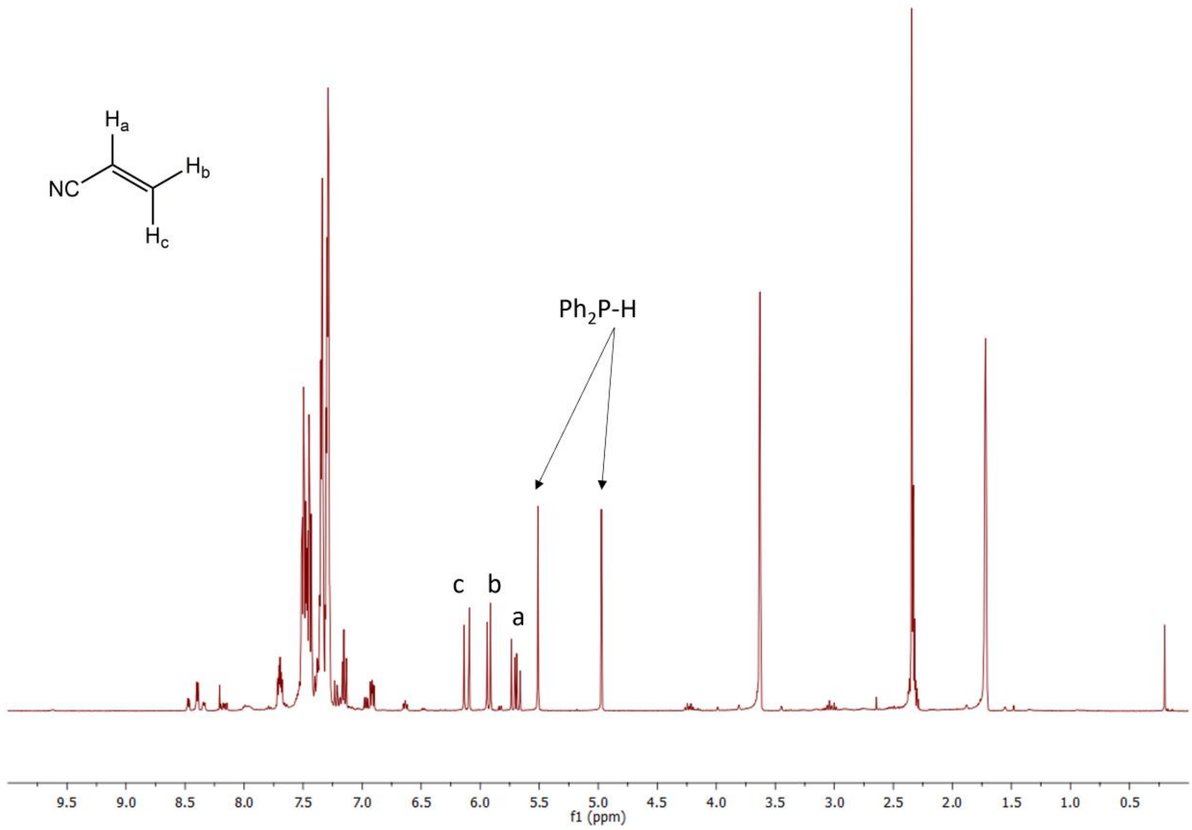


Figure S80: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum for entry 12 of Table S3.

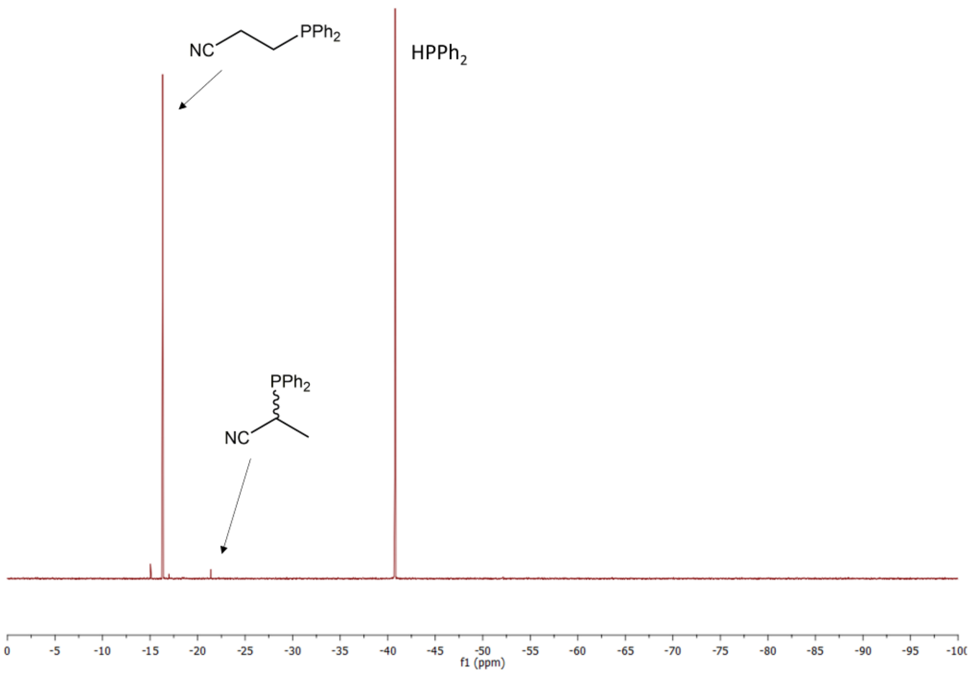


Figure S81: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 12 of Table S3.

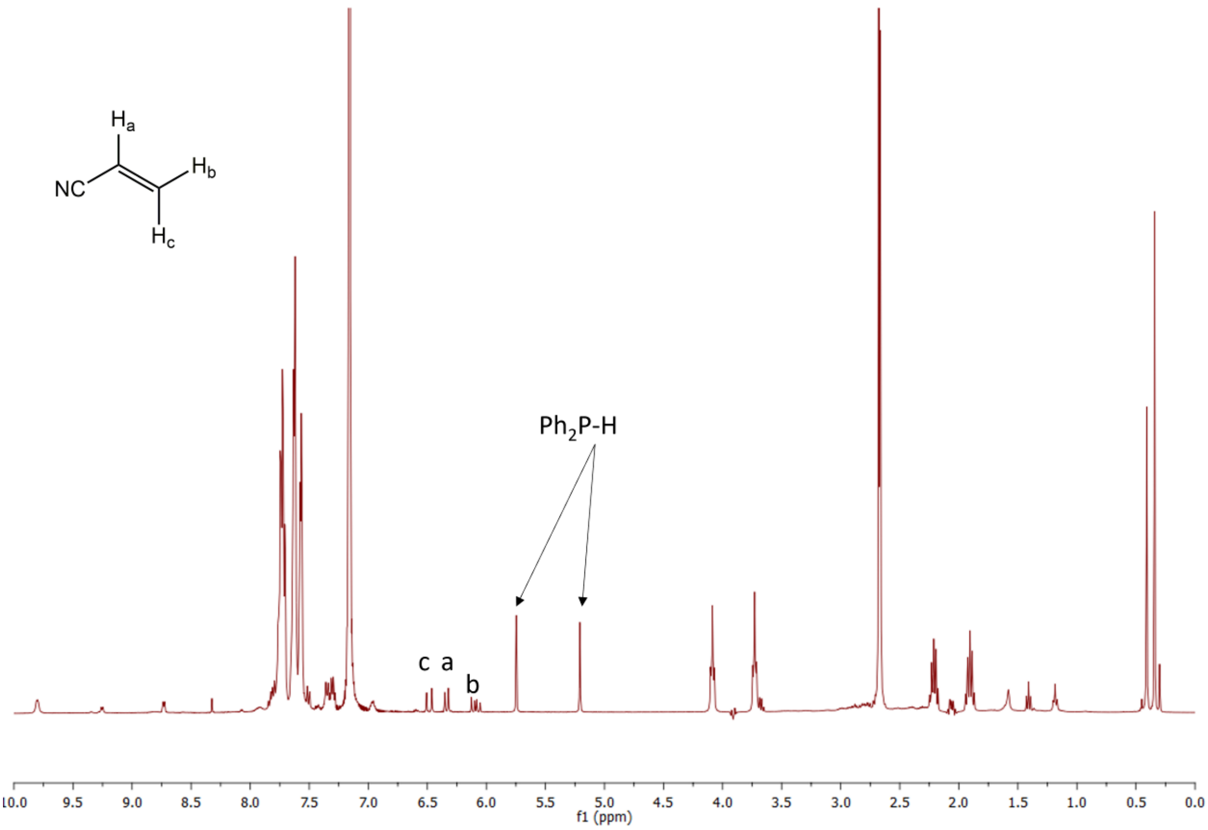


Figure S82: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 13 of Table S3.

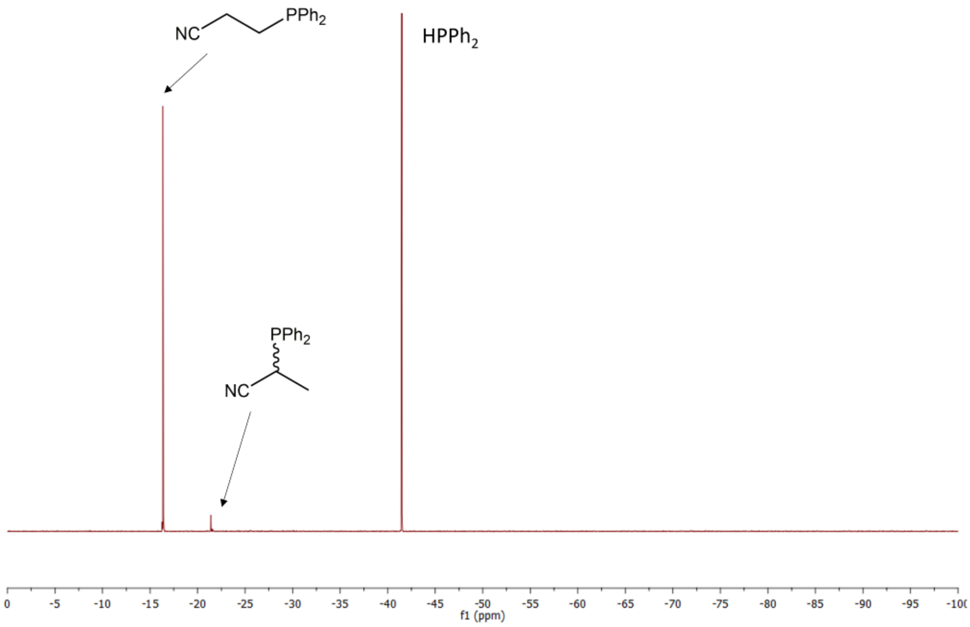


Figure S83: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 13 of Table S3.

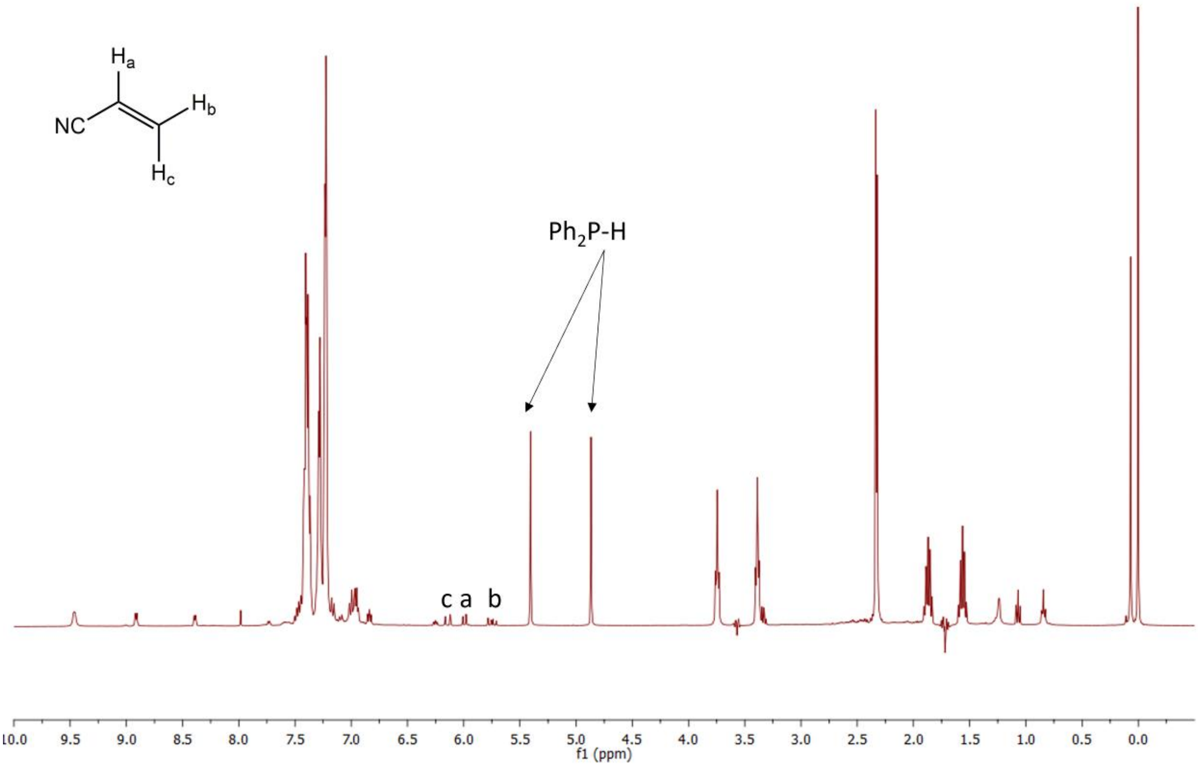


Figure S84: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 14 of Table S3.

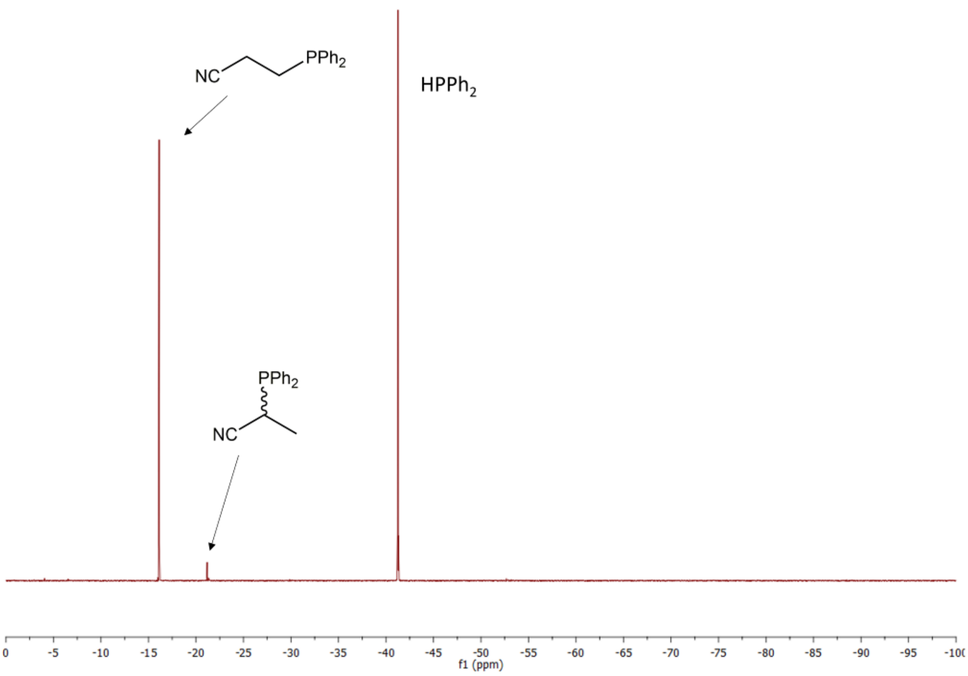


Figure S85: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 14 of Table S3.

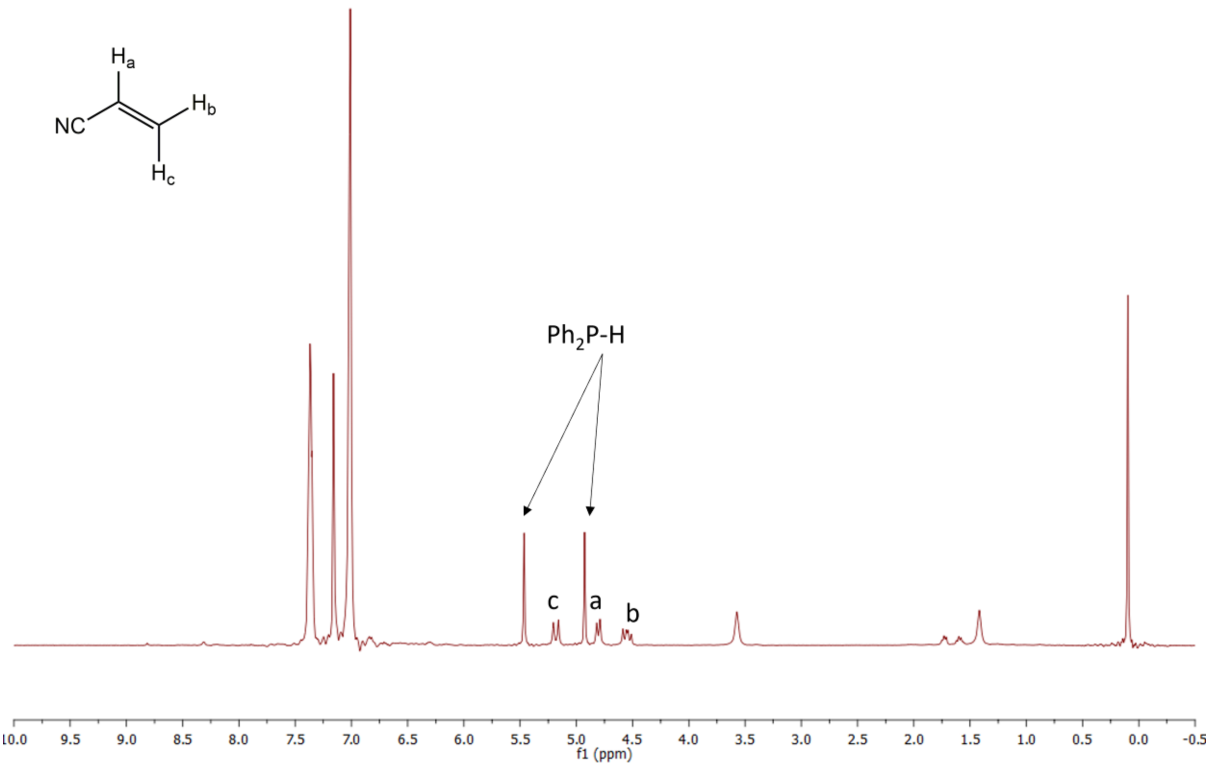


Figure S86: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 15 of Table S3.

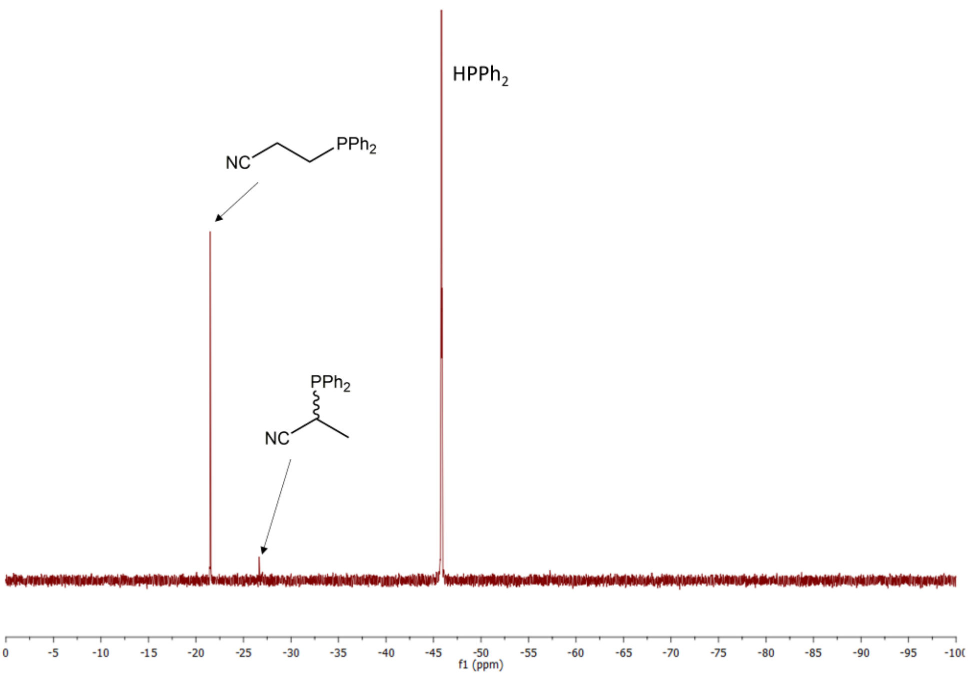


Figure S87: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 15 of Table S3.

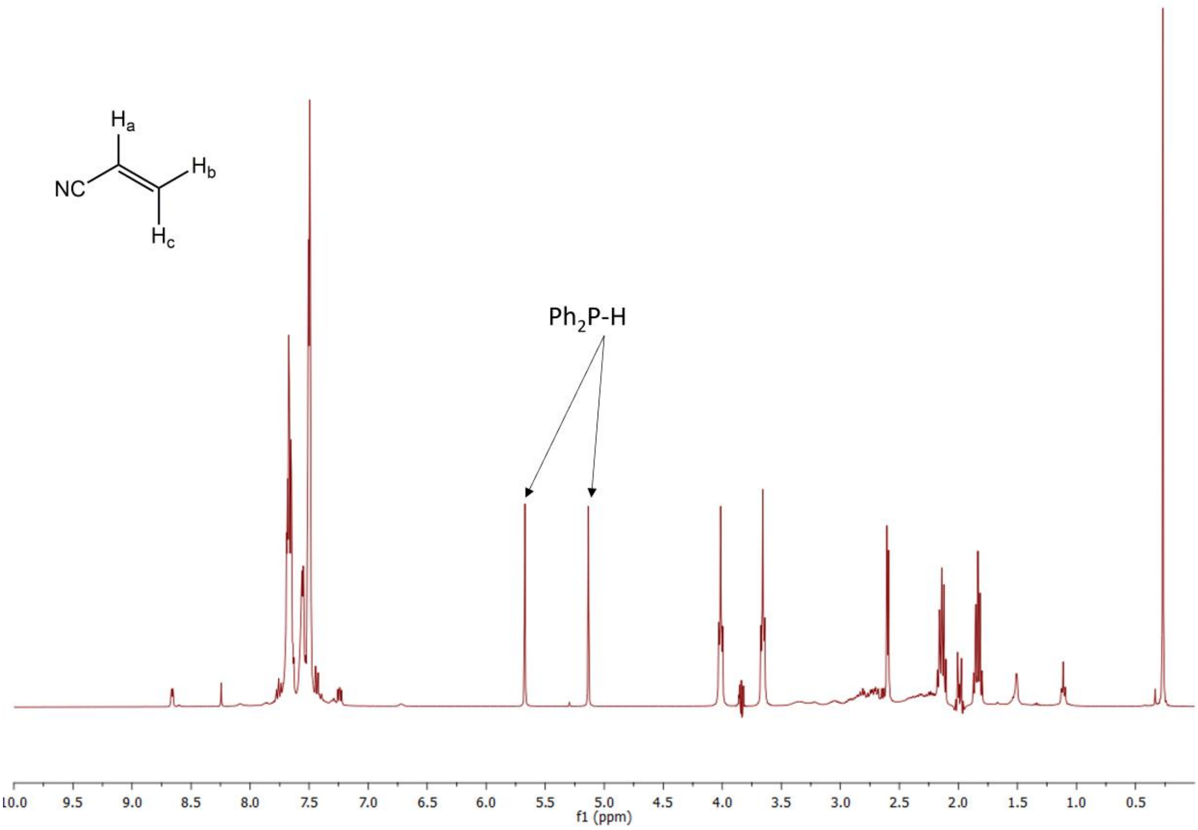


Figure S88: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 16 of Table S3.

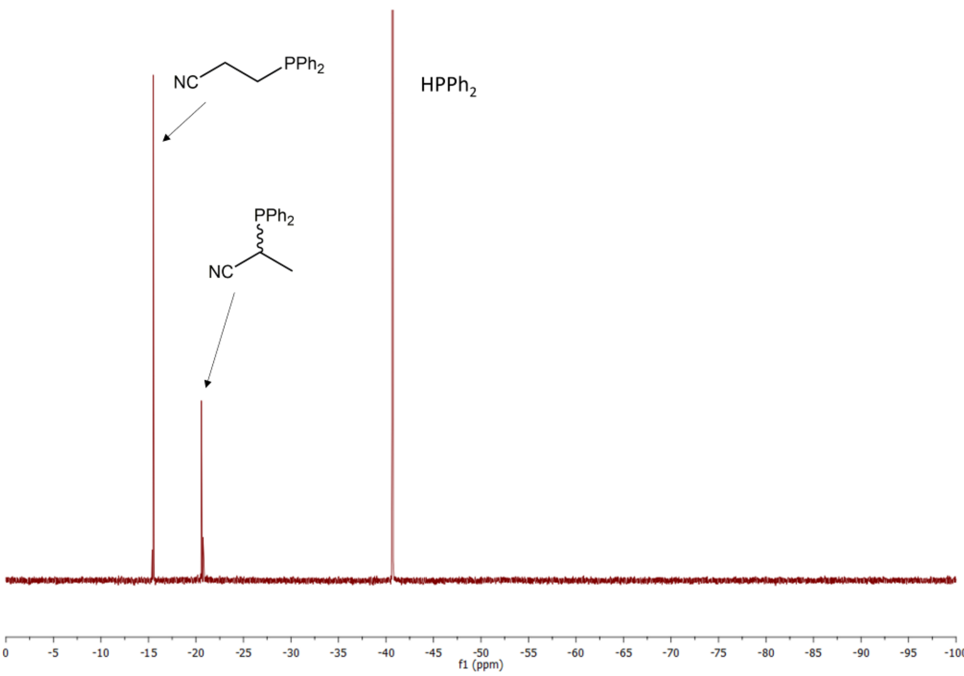


Figure S89: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 16 of Table S3.

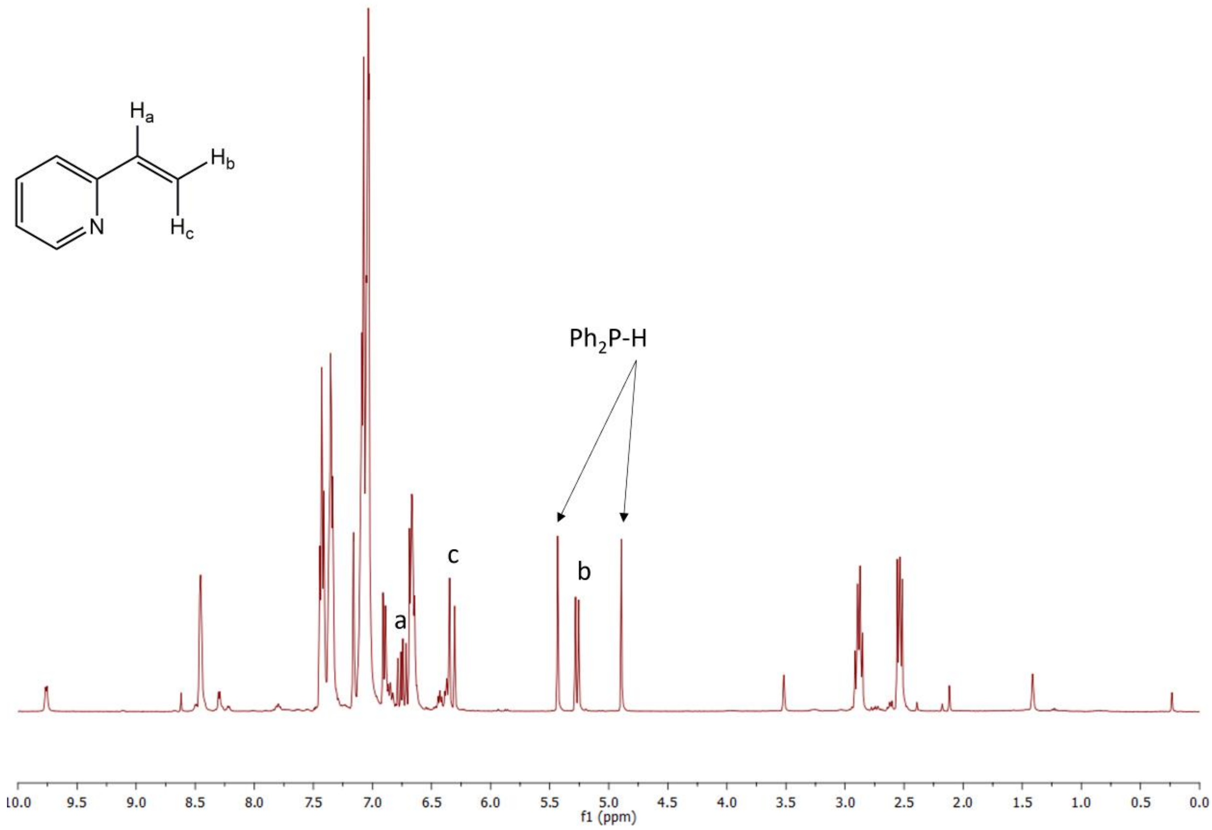


Figure S90: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 17 of Table S3.

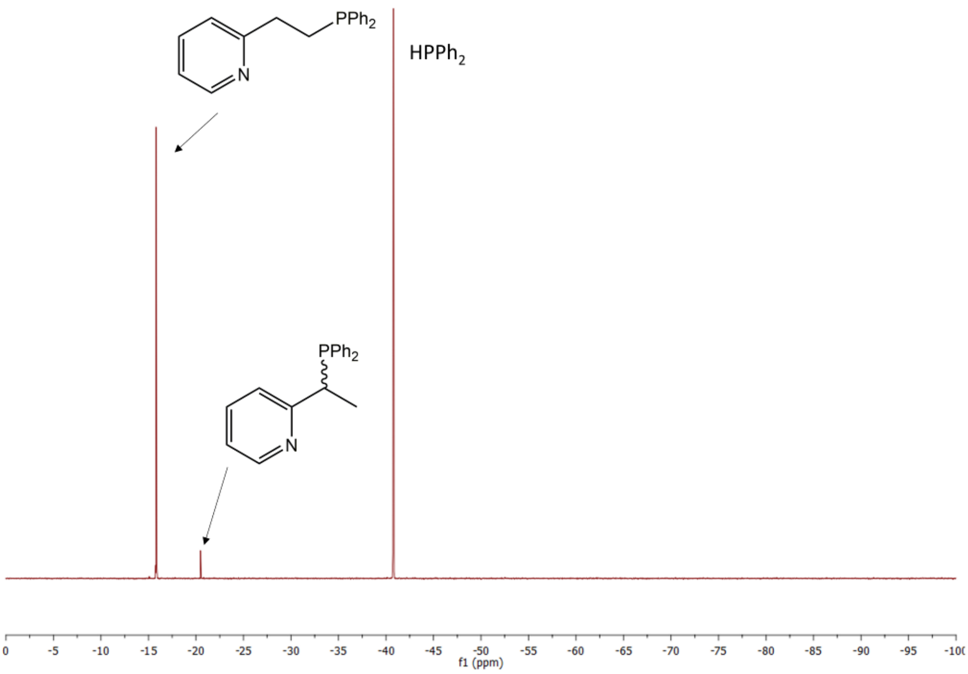


Figure S91: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 17 of Table S3.

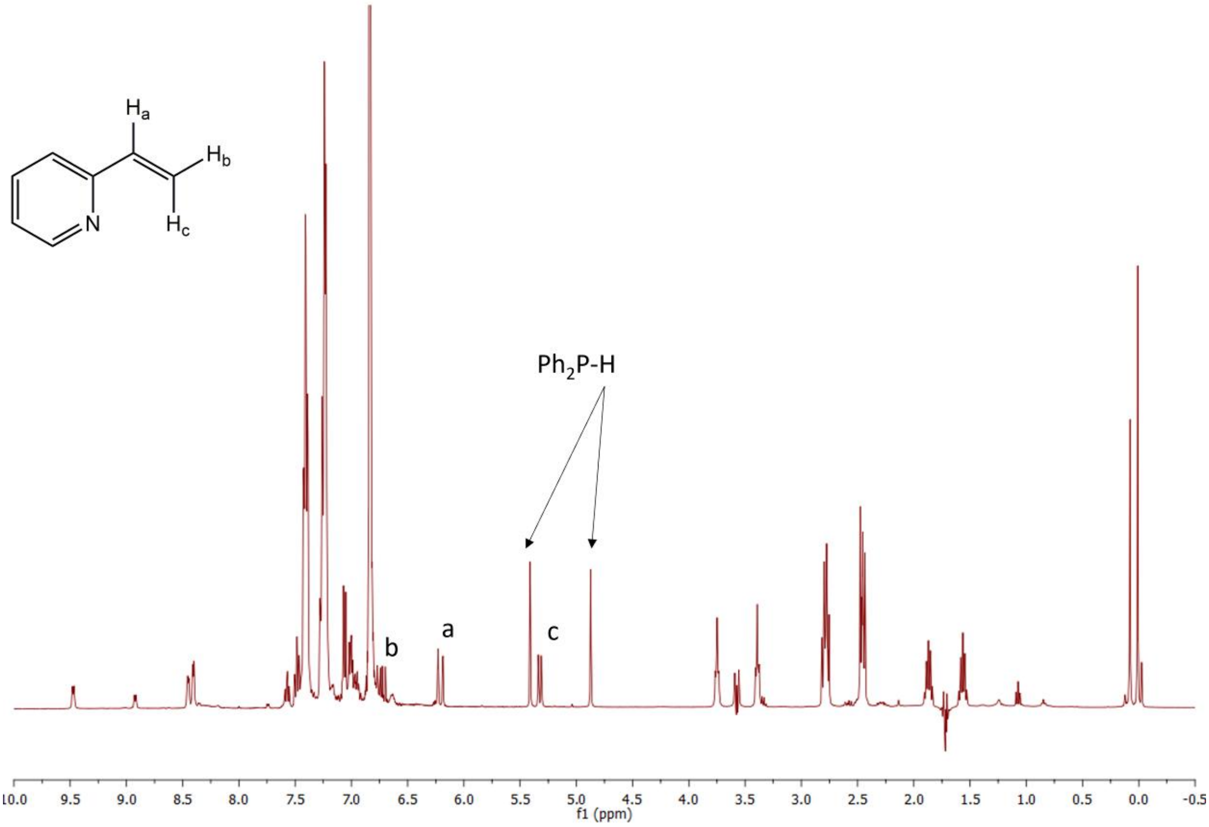


Figure S92: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 18 of Table S3.

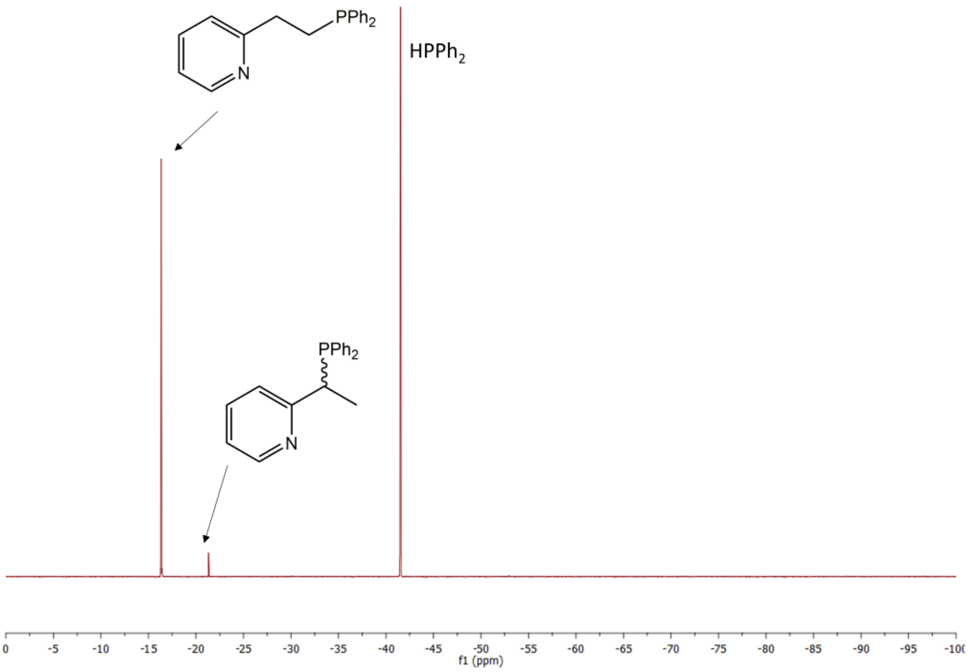


Figure S93: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 18 of Table S3.

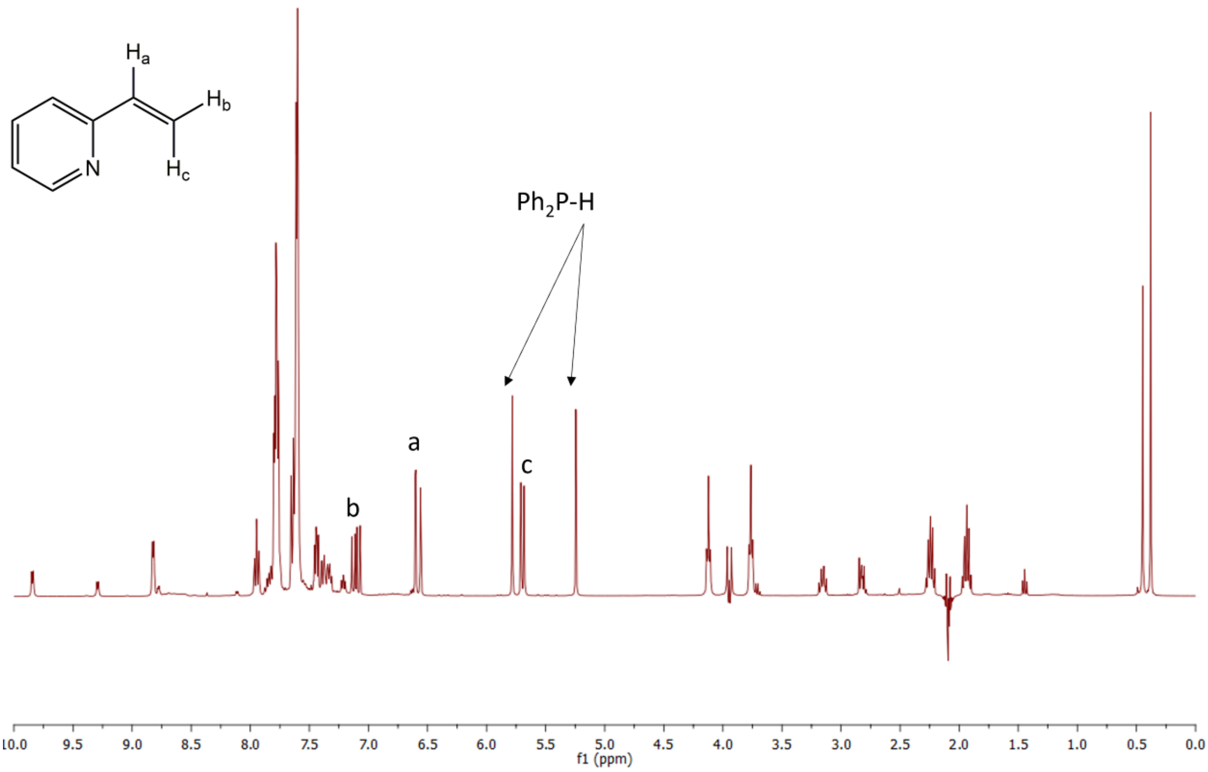


Figure S94: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 19 of Table S3.

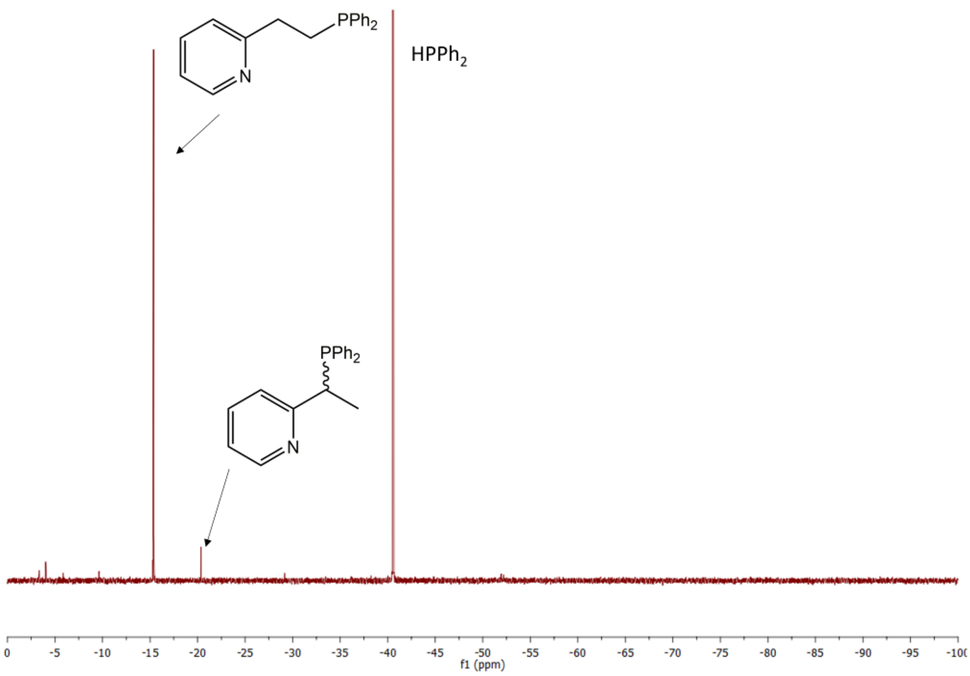


Figure S95: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 19 of Table S3.

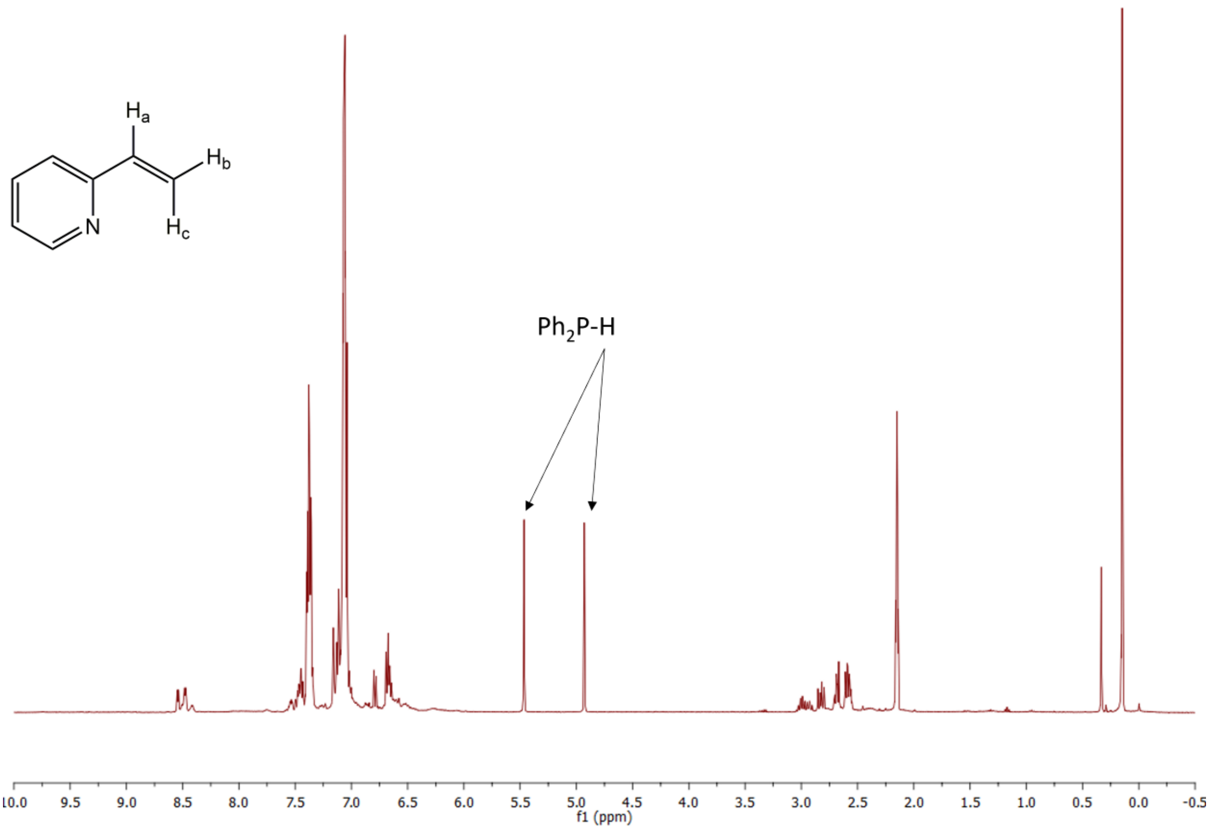


Figure S96: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 20 of Table S3.

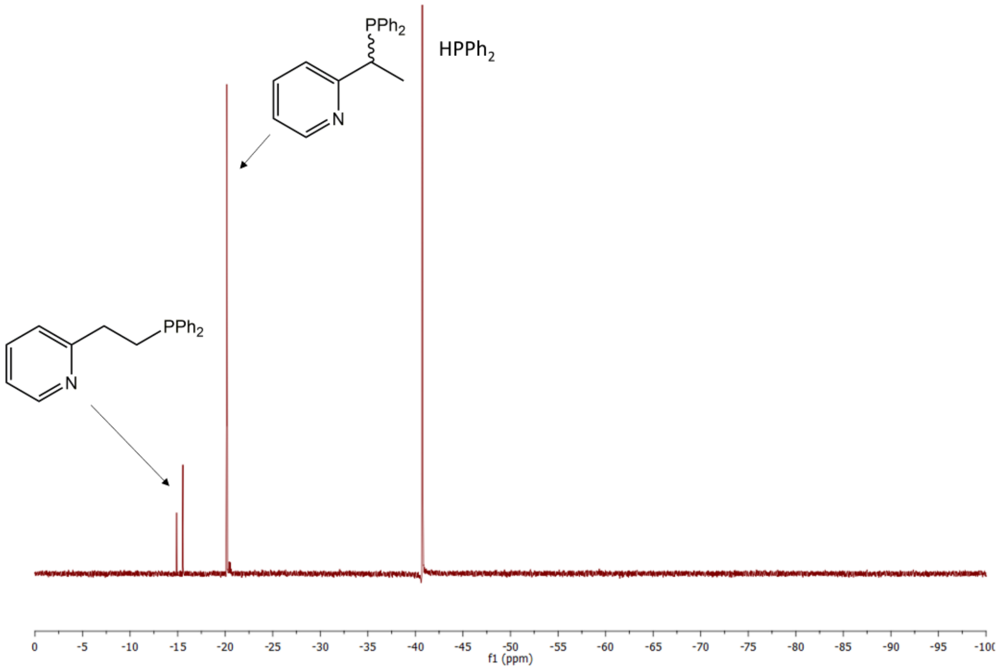


Figure S97: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 20 of Table S3.

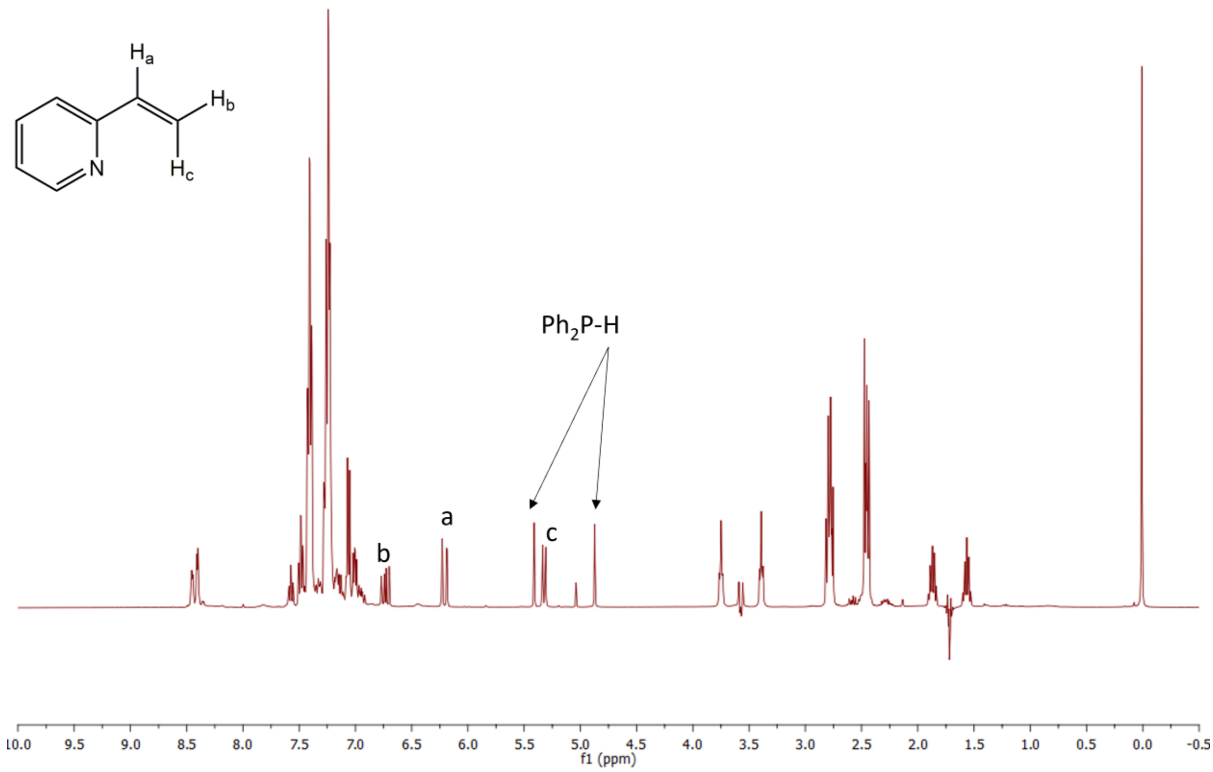


Figure S98: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 21 of Table S3.

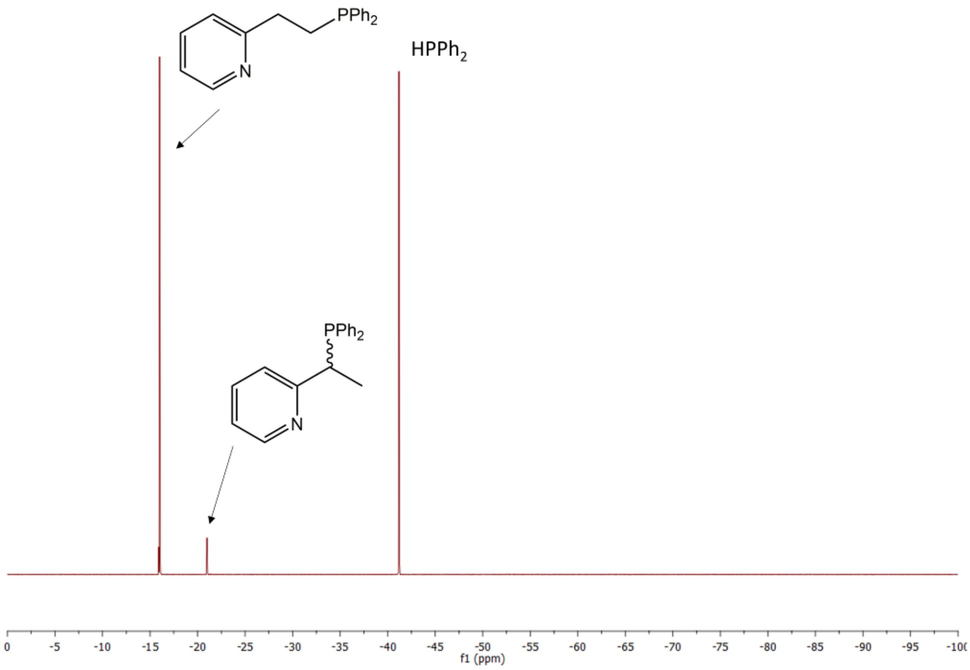


Figure S99: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 21 of Table S4.

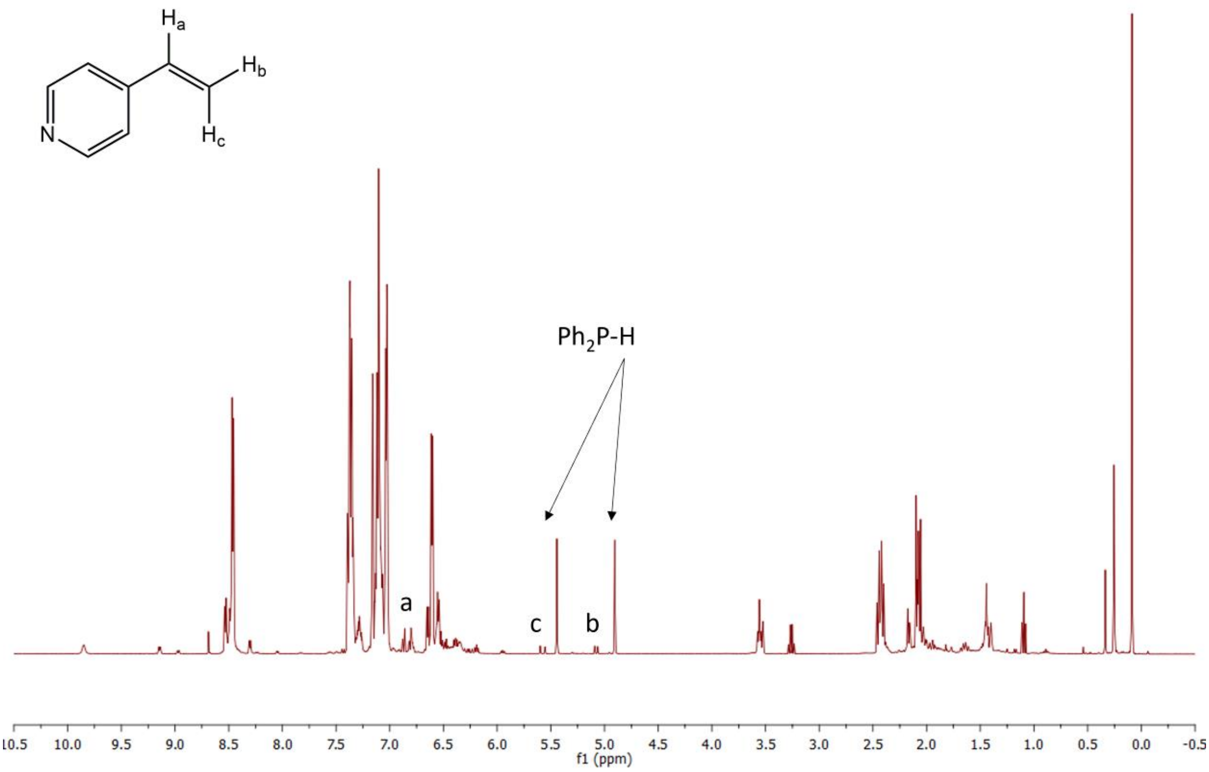


Figure S100: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 22 of Table S3.

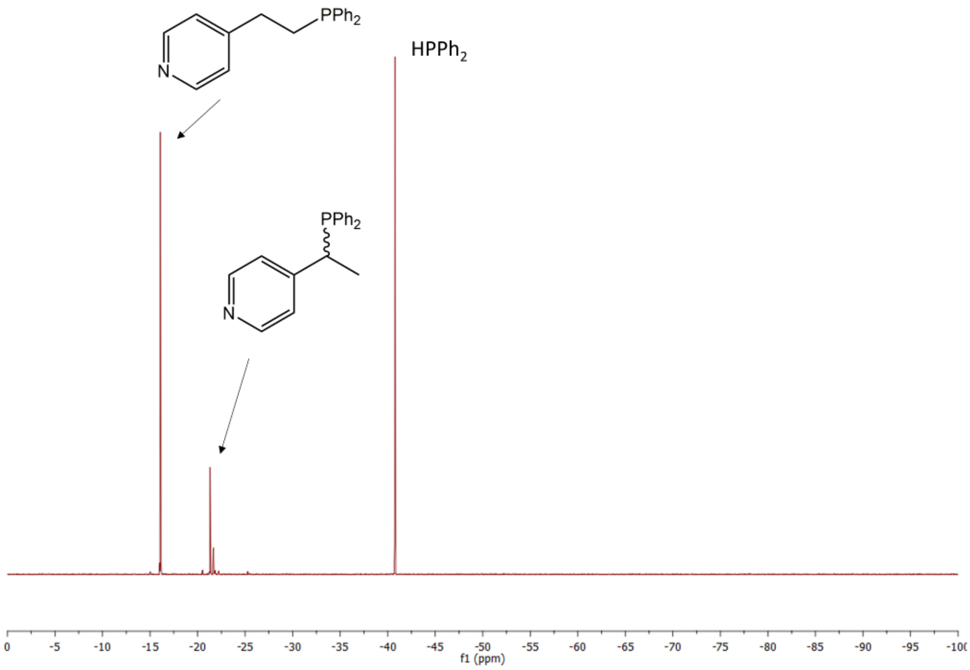


Figure S101: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 22 of Table S3.

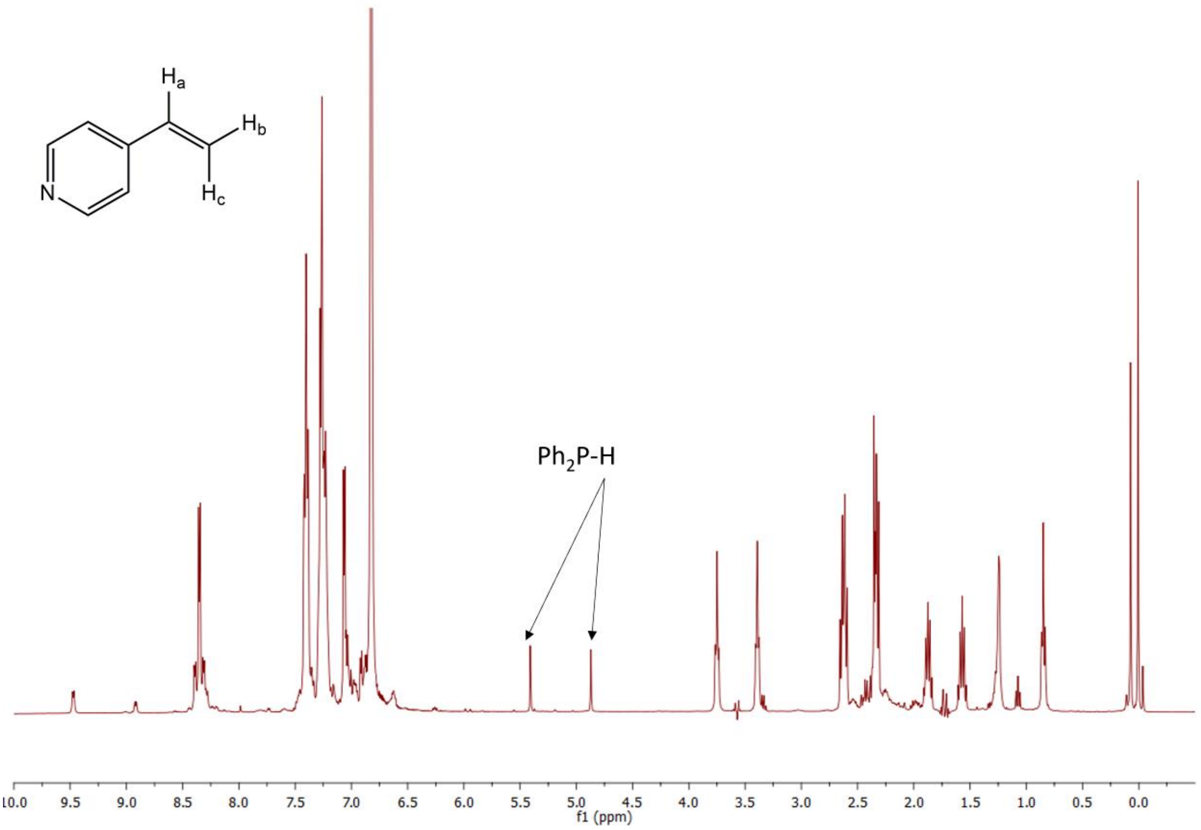


Figure S102: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 23 of Table S3.

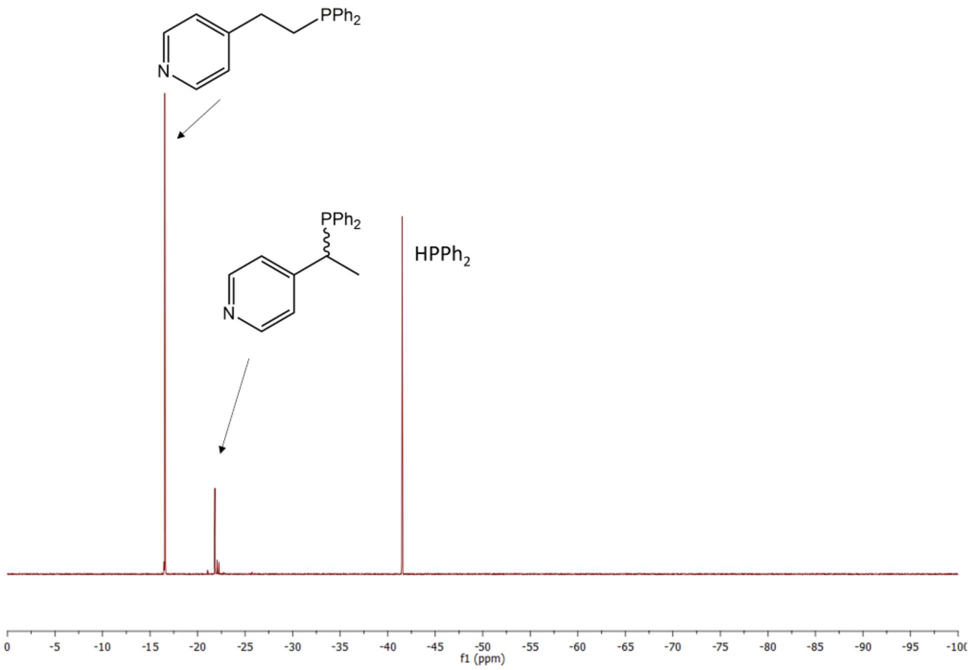


Figure S103: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 23 of Table S3.

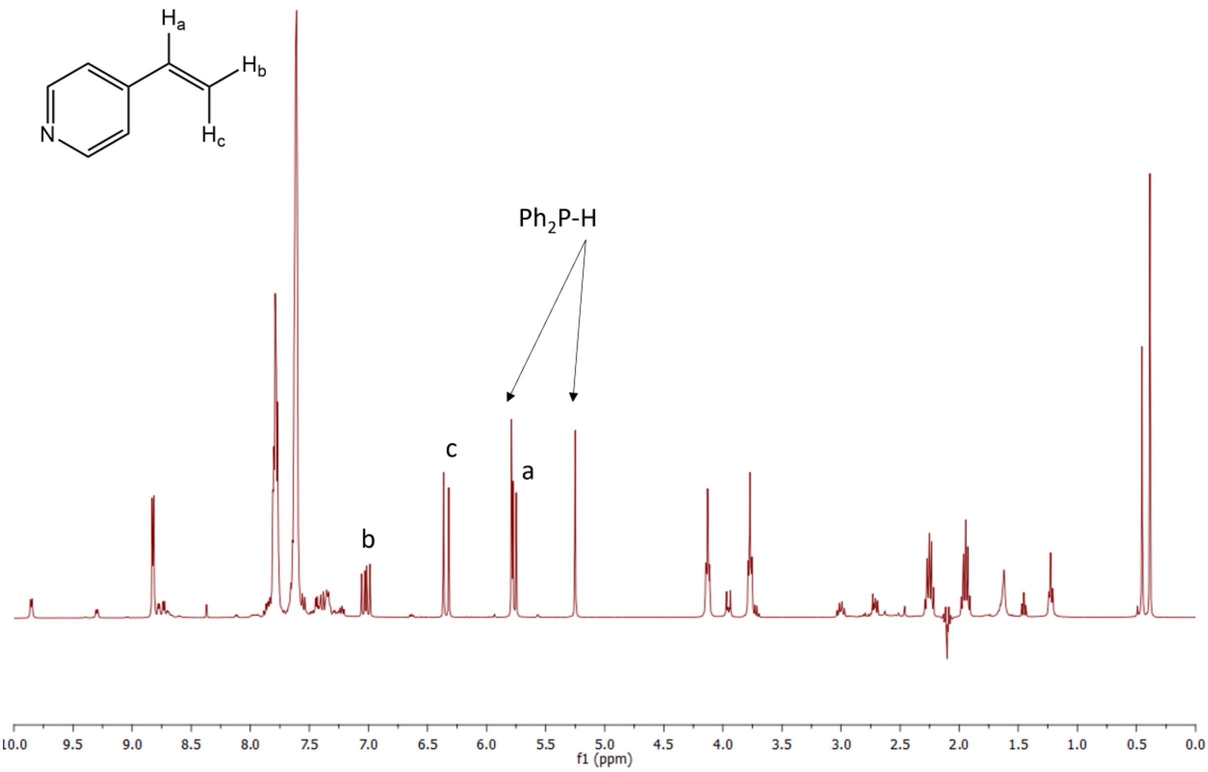


Figure S104: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 24 of Table S3.

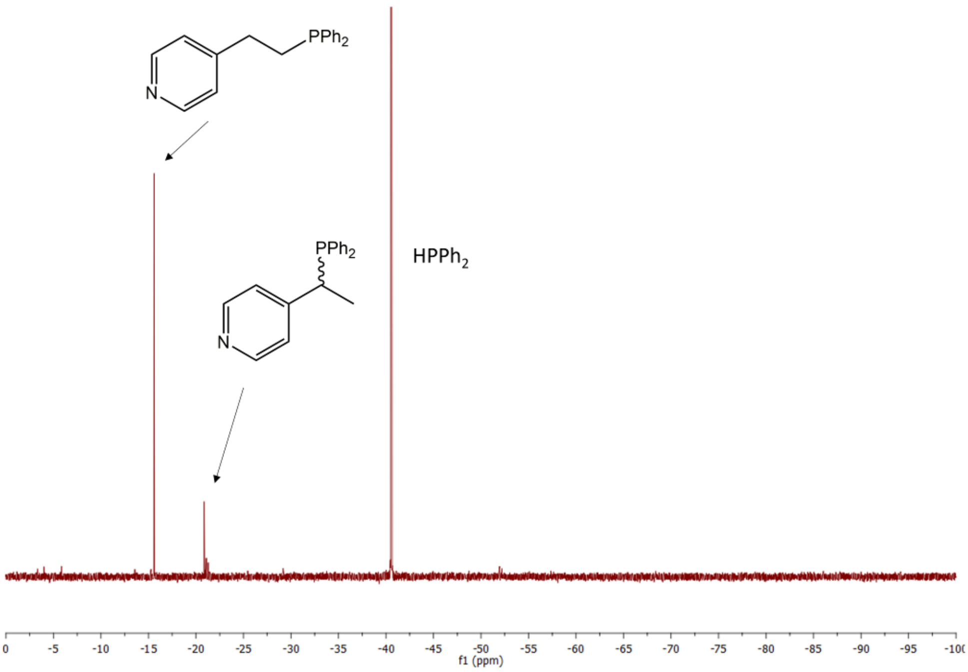


Figure S105: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 24 of Table S3.

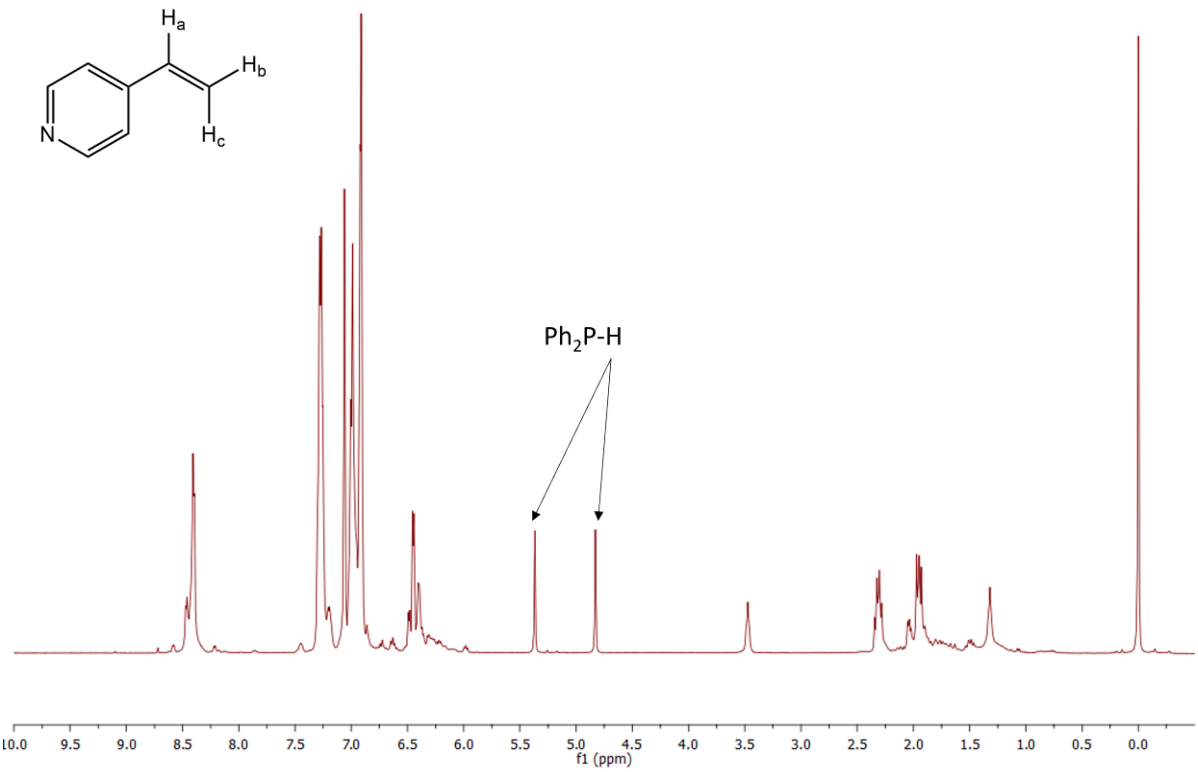


Figure S106: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 25 of Table S3.

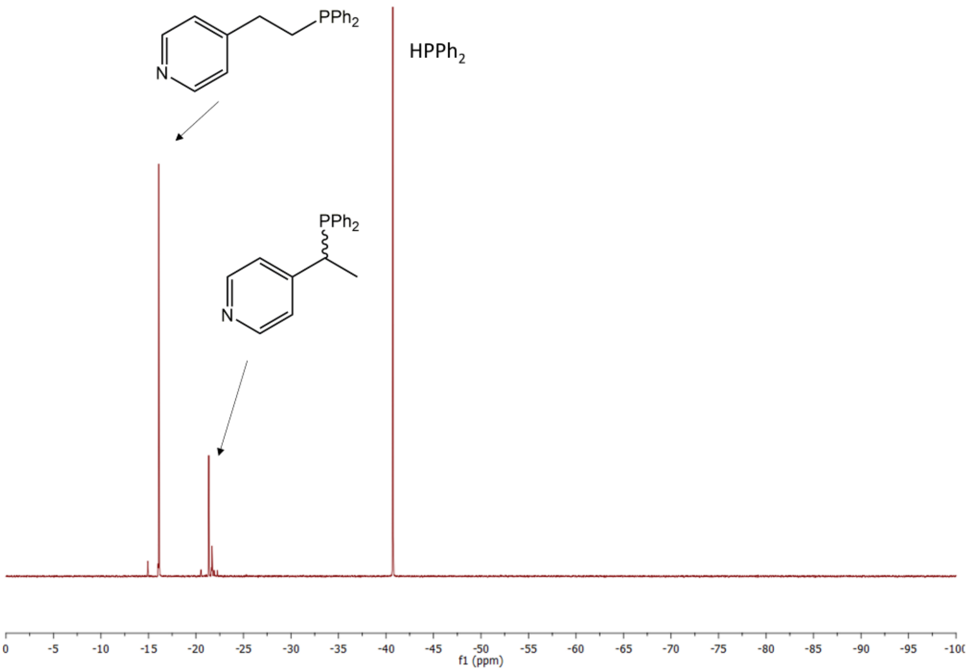


Figure S107: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for entry 25 of Table S3.

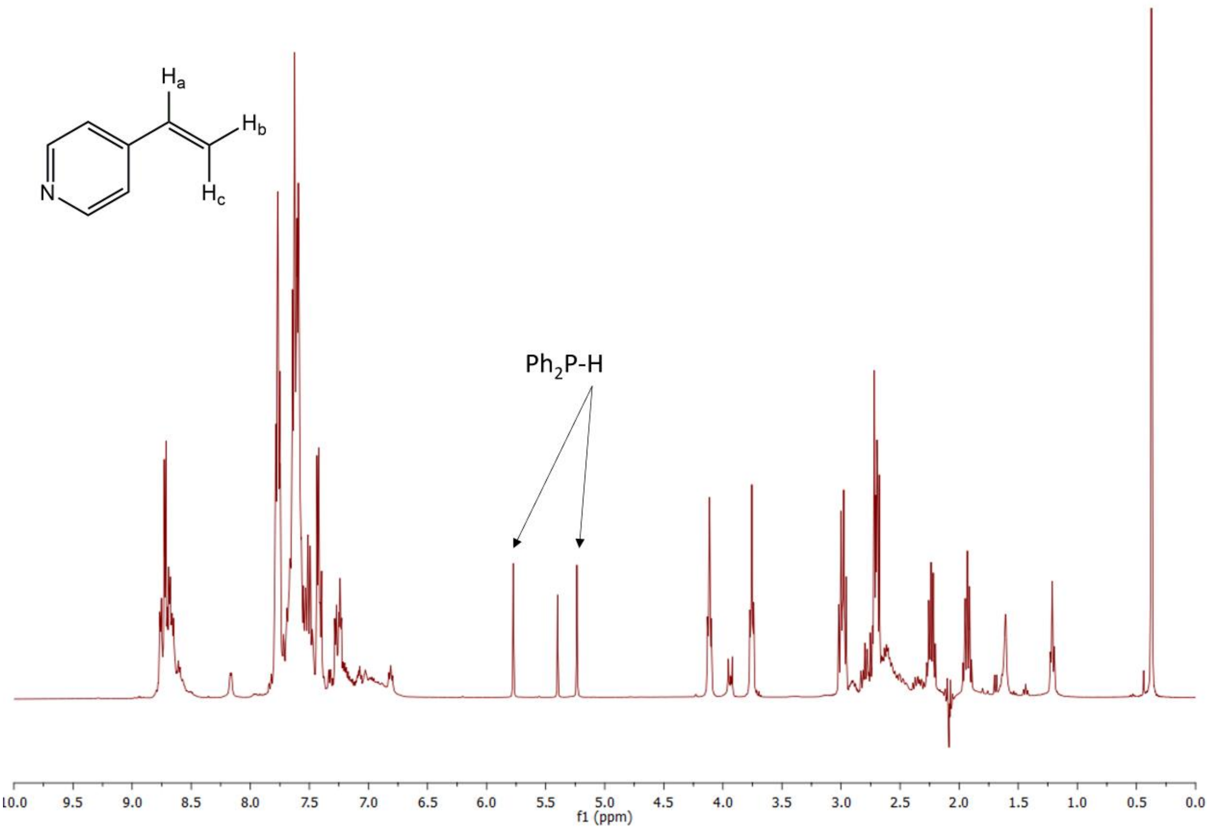


Figure S108: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 26 of Table S3.

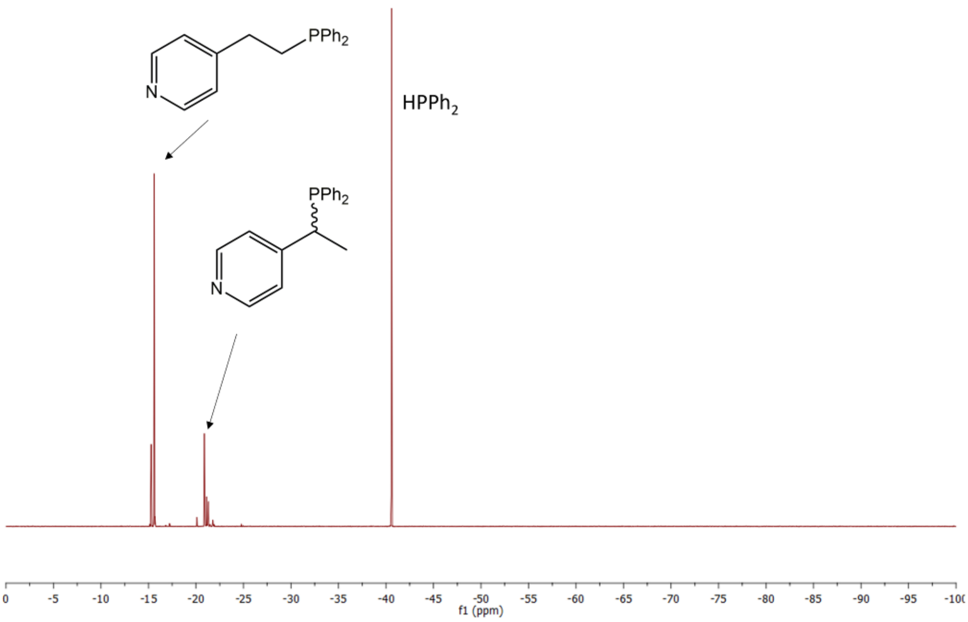


Figure S109: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 26 of Table S3.

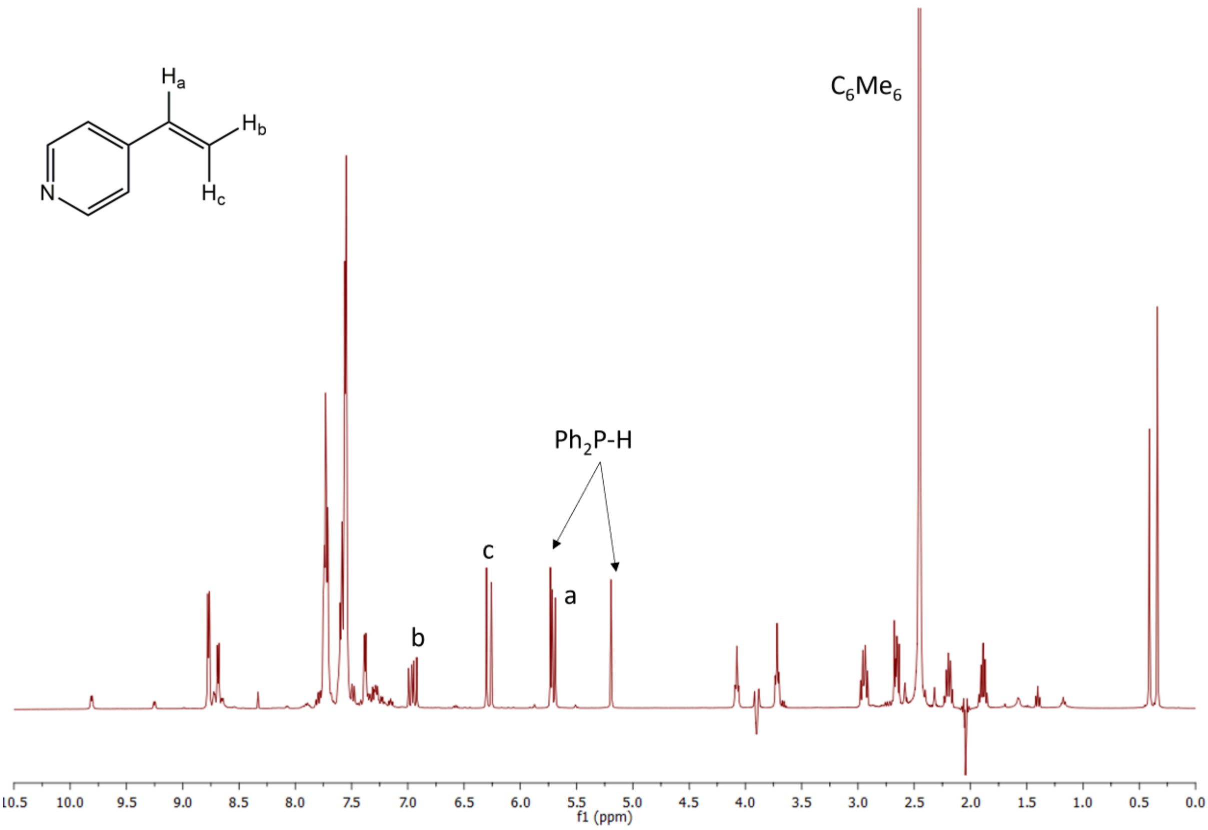


Figure S110: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 1 of Table S4.

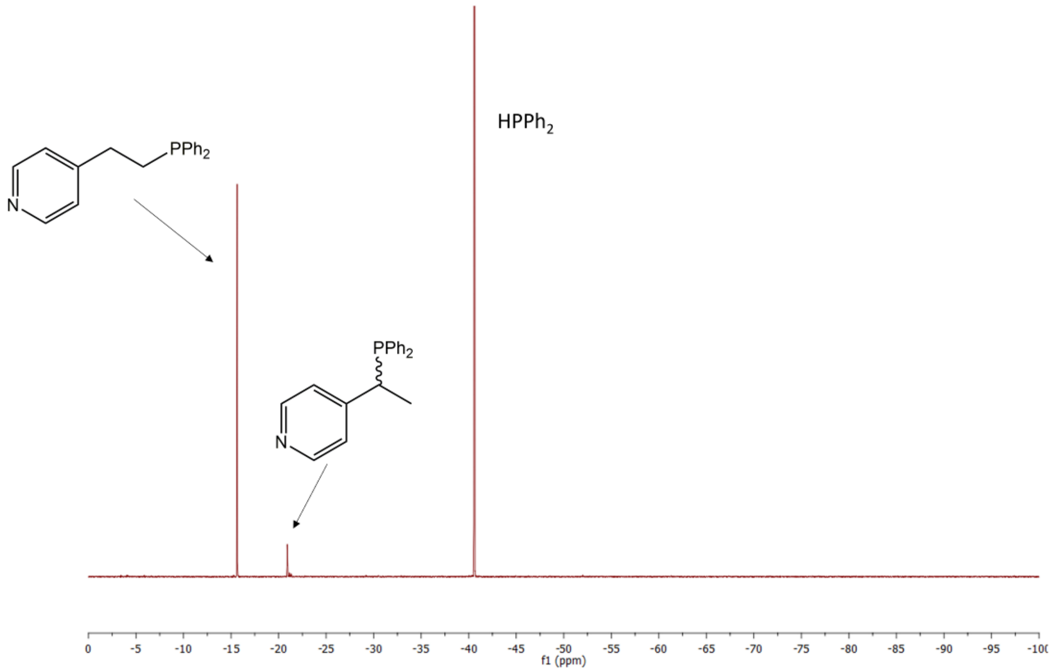


Figure S111: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 1 of Table S4.

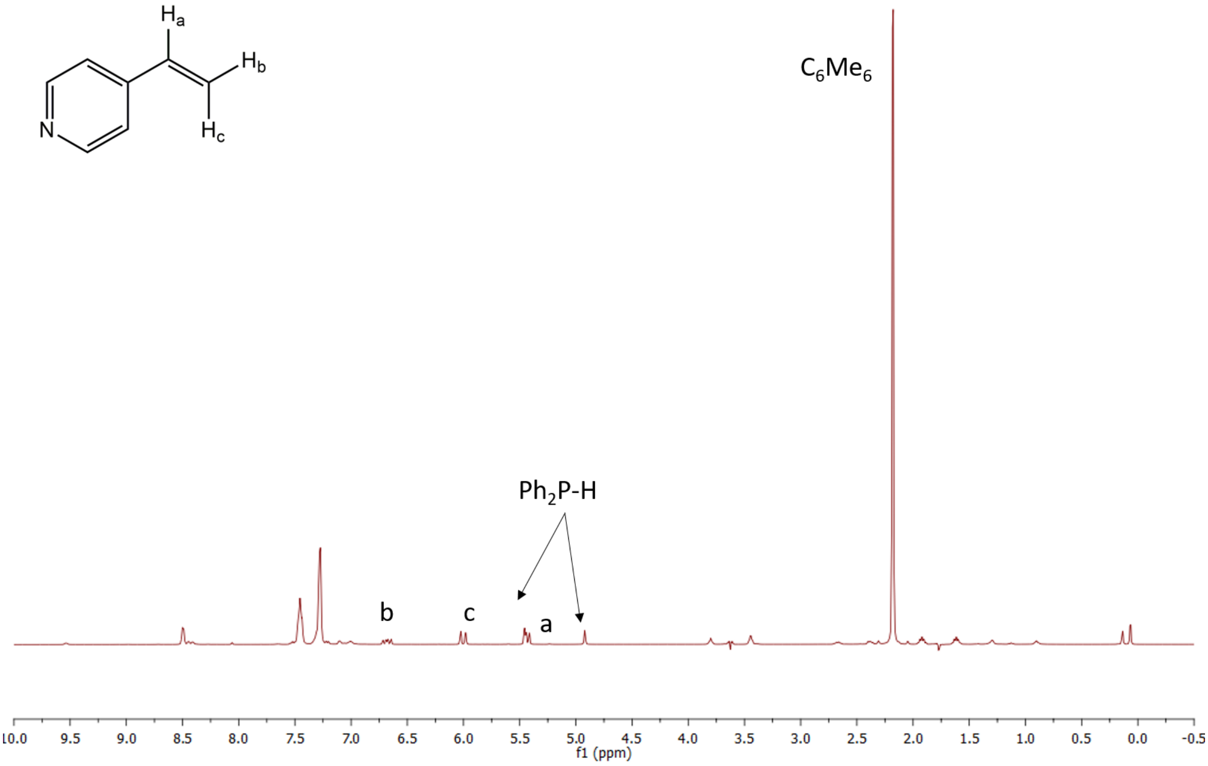


Figure S112: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from −0.5 to 10 ppm for entry 2 of Table S4.

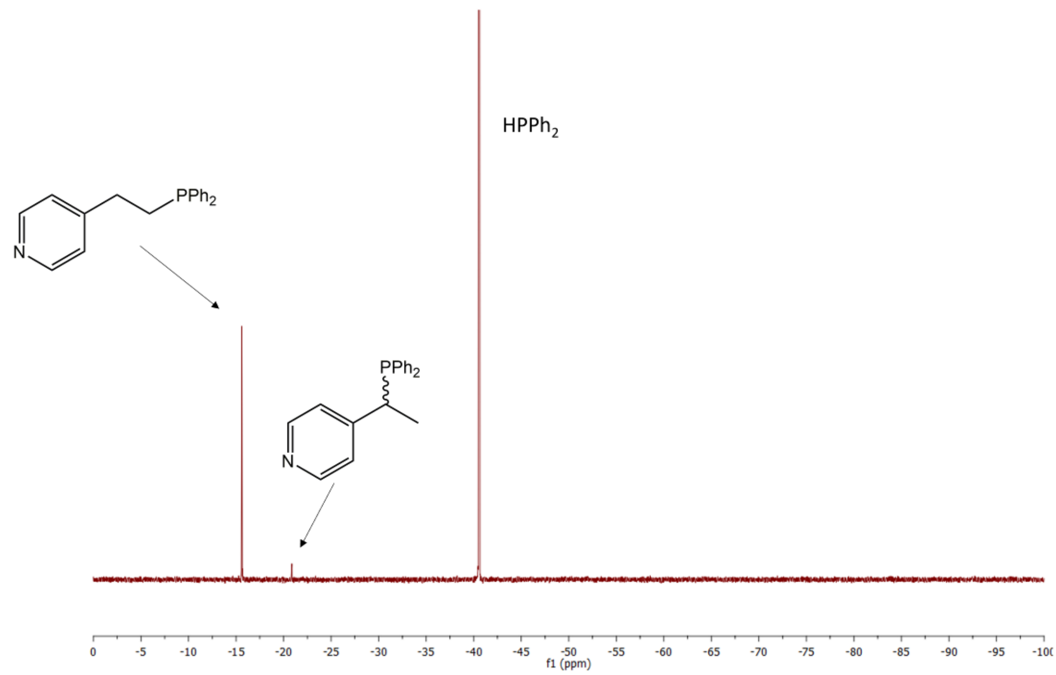


Figure S113: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm entry 2 of Table S4.

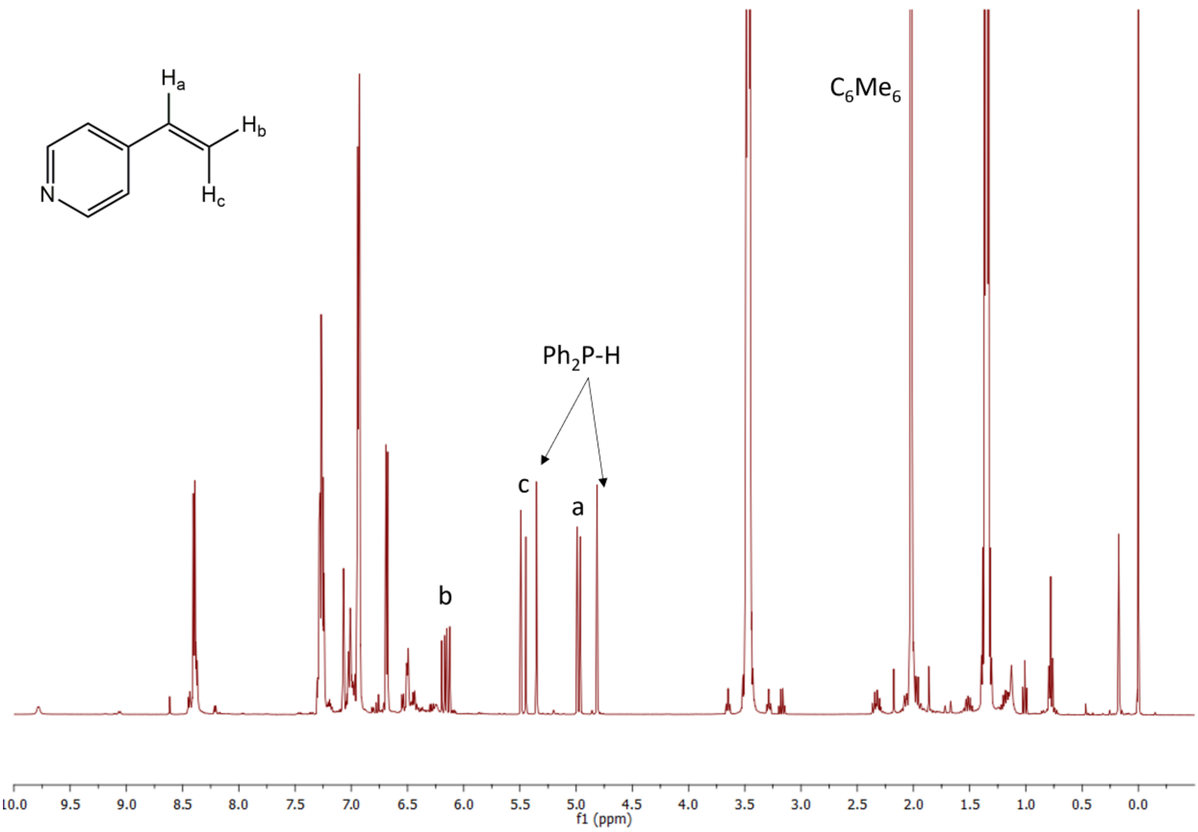


Figure S114: ^{1}H NMR (400 MHz, 298 K, C_4H_8O) spectrum from 0 to 10 ppm for entry 3 of Table S4.

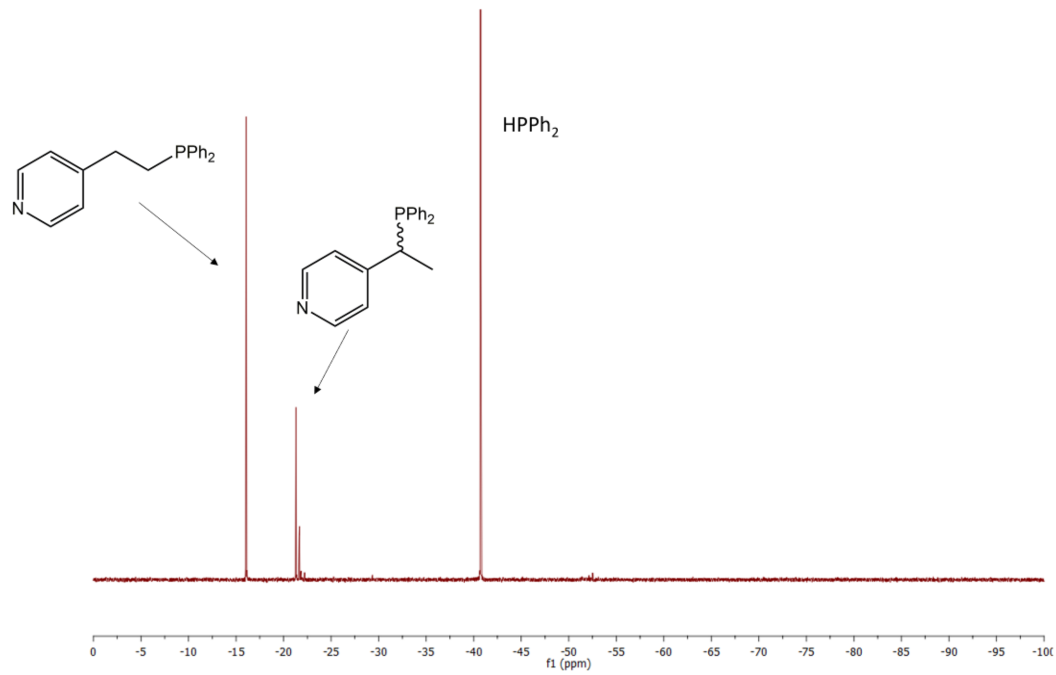


Figure S115: $^{31}P\{^{1}H\}$ NMR(160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 3 of Table S4.

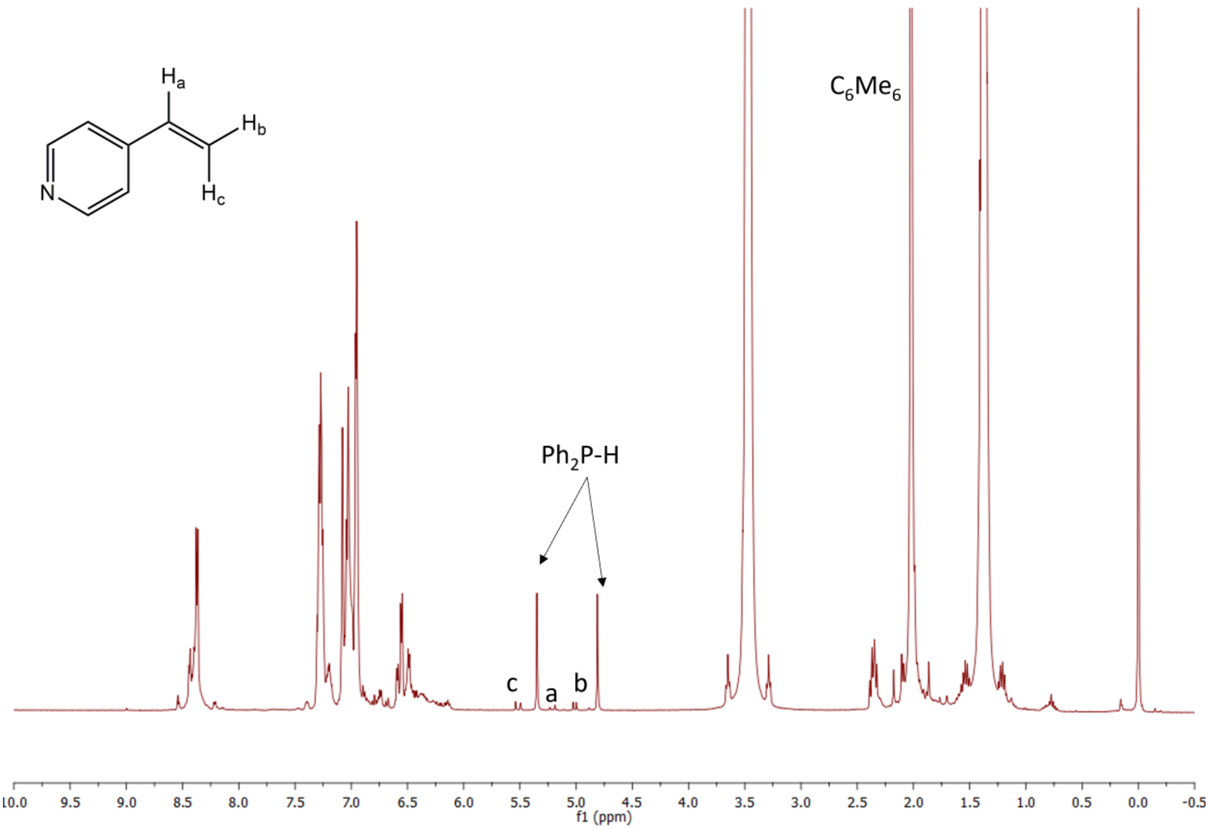


Figure S116: ^{1}H NMR (400 MHz, 298 K, C_4H_8O) spectrum from 0 to 10 ppm for entry 4 of Table S4.

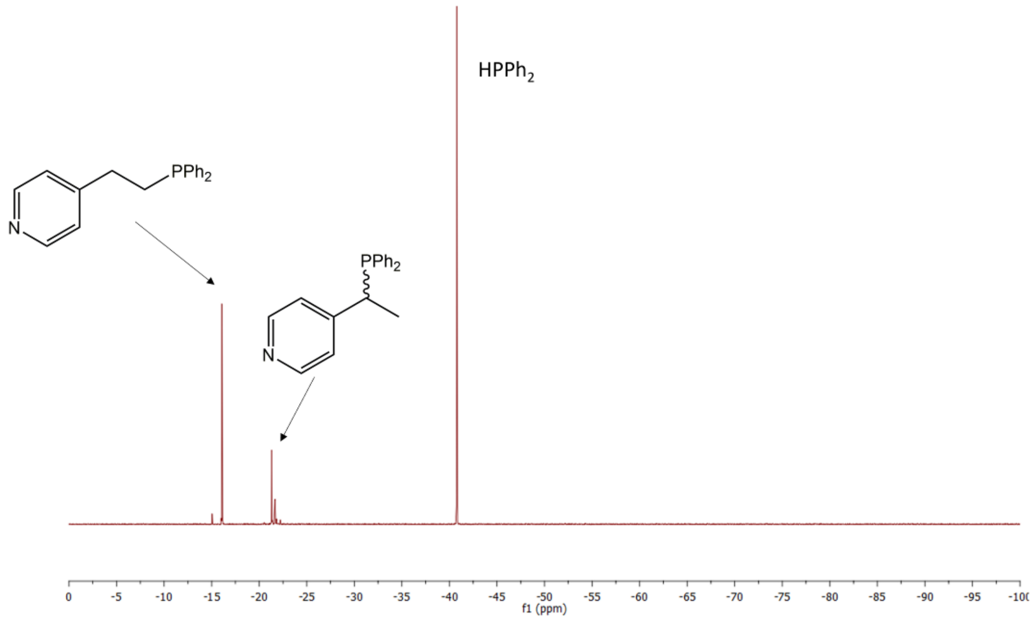


Figure S117: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm entry 4 of Table S4.

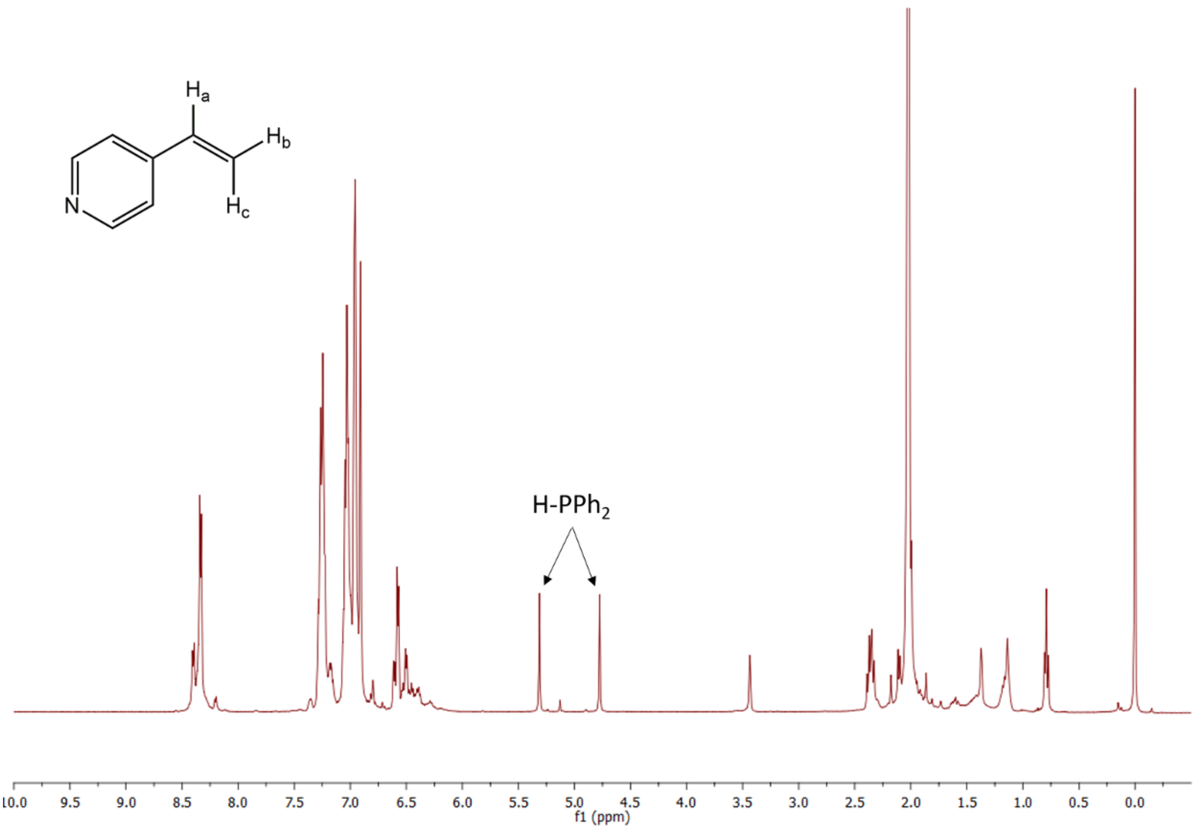


Figure S118: ^{1}H NMR (400 MHz, 298 K, C_7D_8) spectrum from 0 to 10 ppm for entry 5 of Table S4.

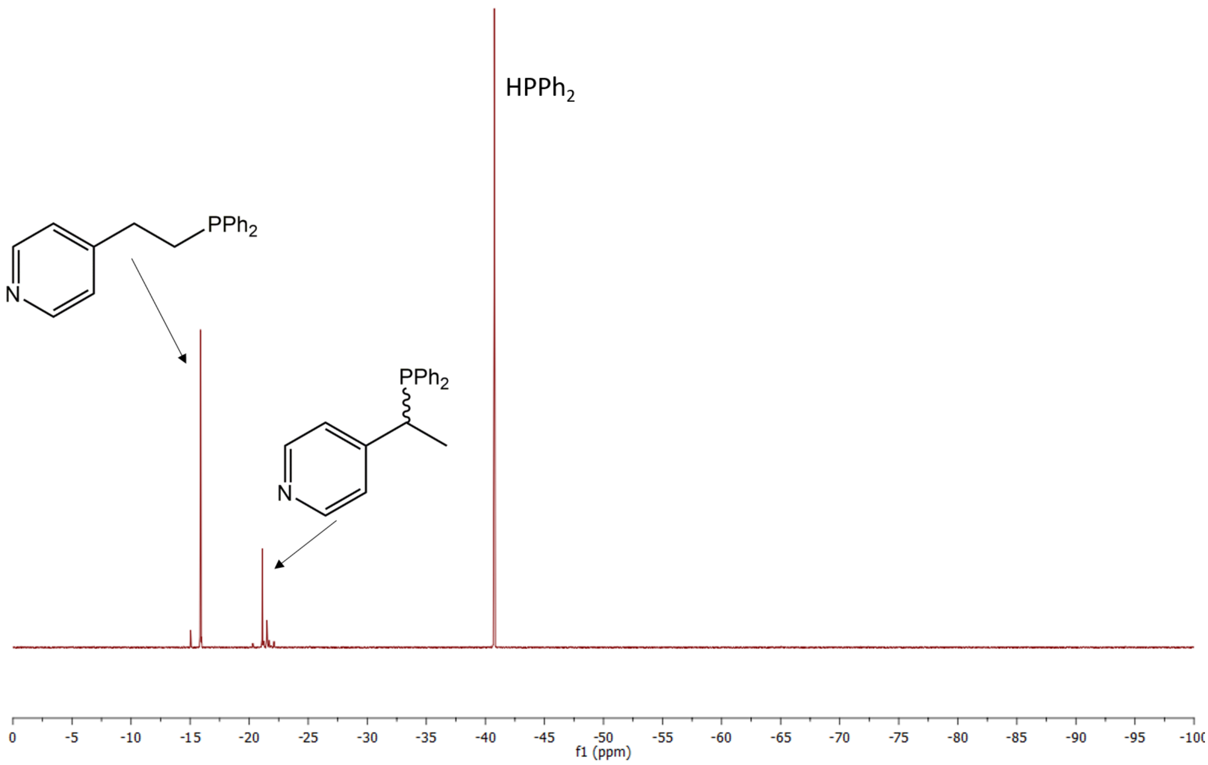


Figure S119: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_7D_8) spectrum from −100 to 0 ppm for entry 5 of Table S4.

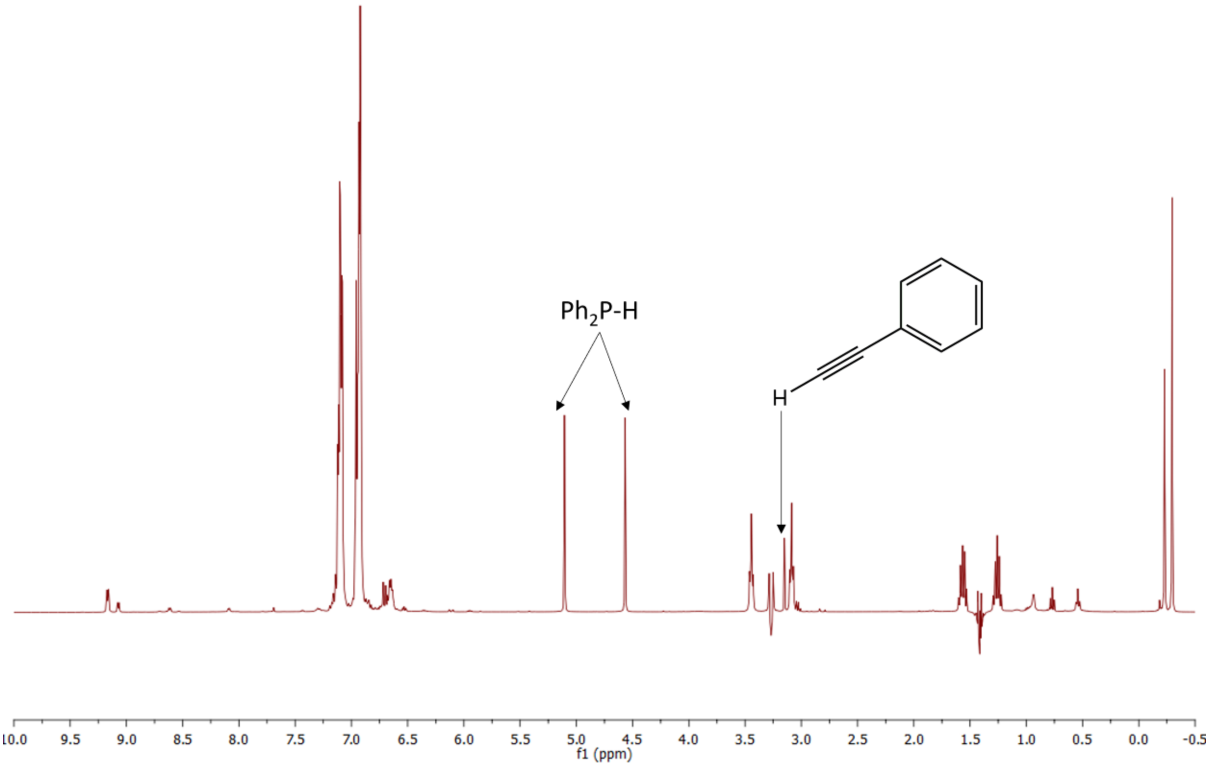


Figure S120: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 1 of Table S5.

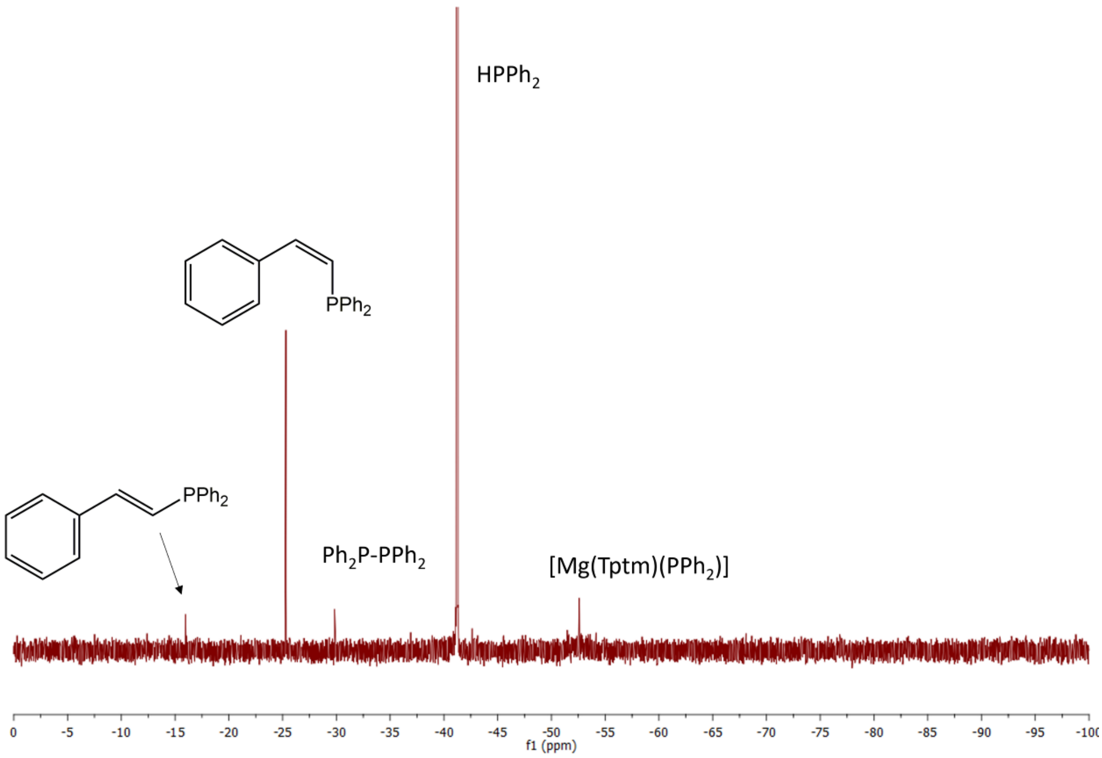


Figure S121: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm Table S5.

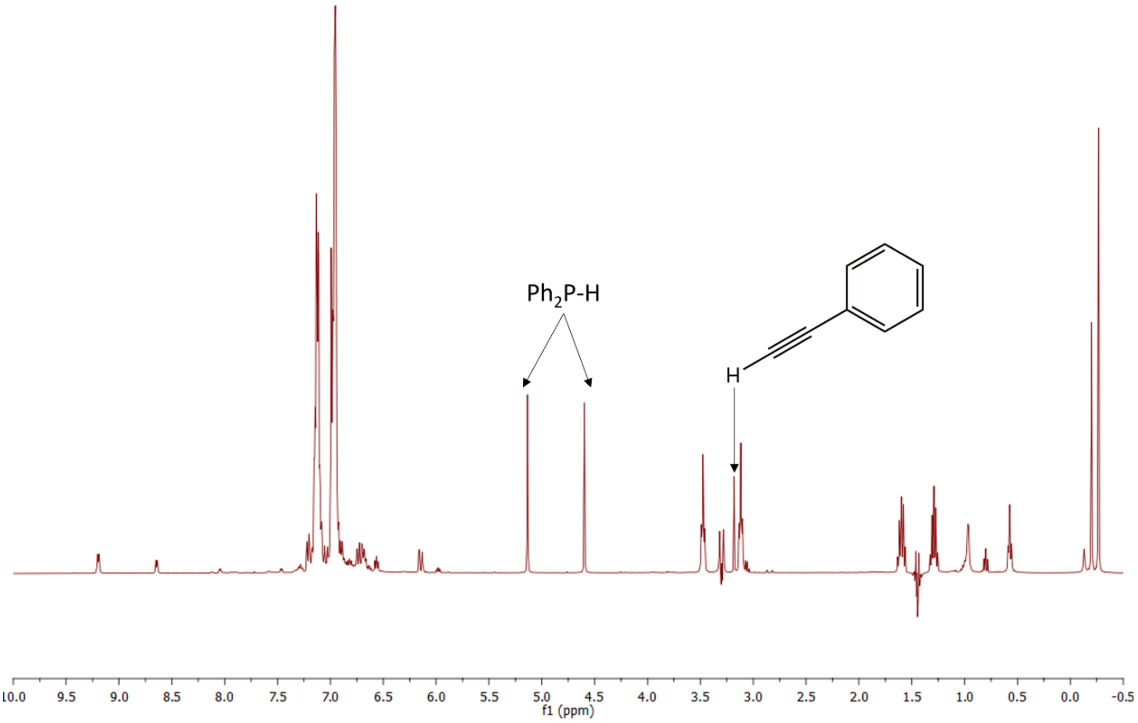


Figure S122: ${}^{1}H$ NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 2 of Table S5.

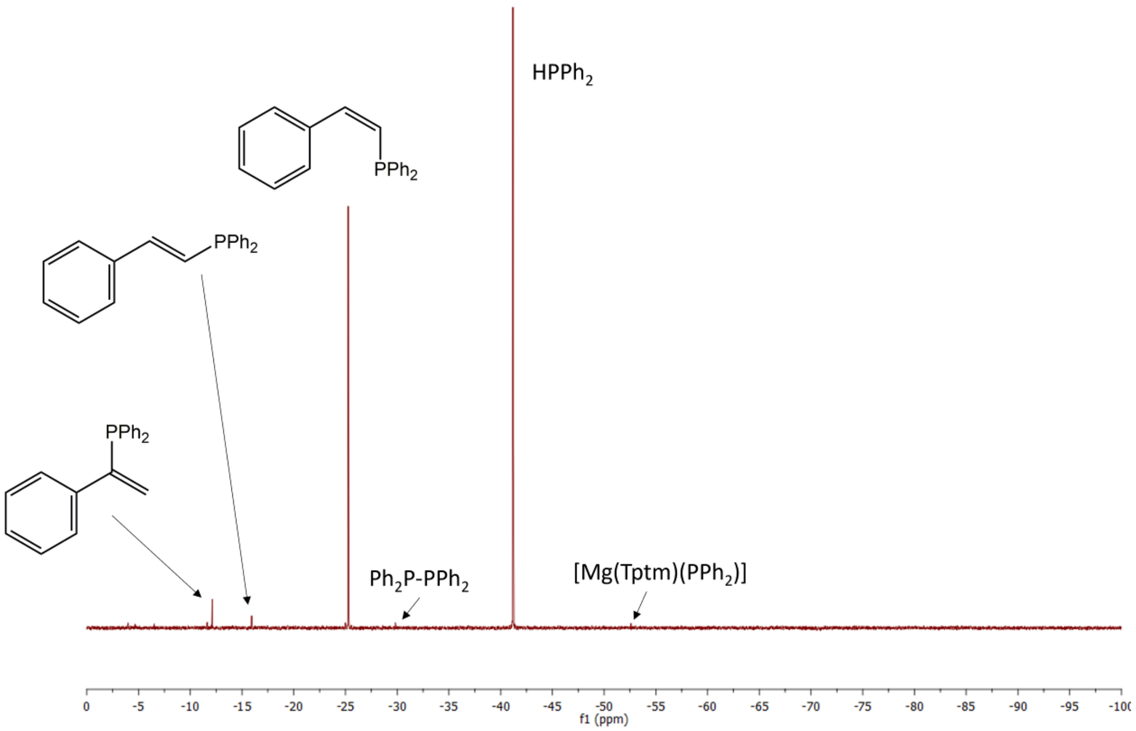


Figure S123: ${}^{31}P\{{}^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 2 of Table S5.

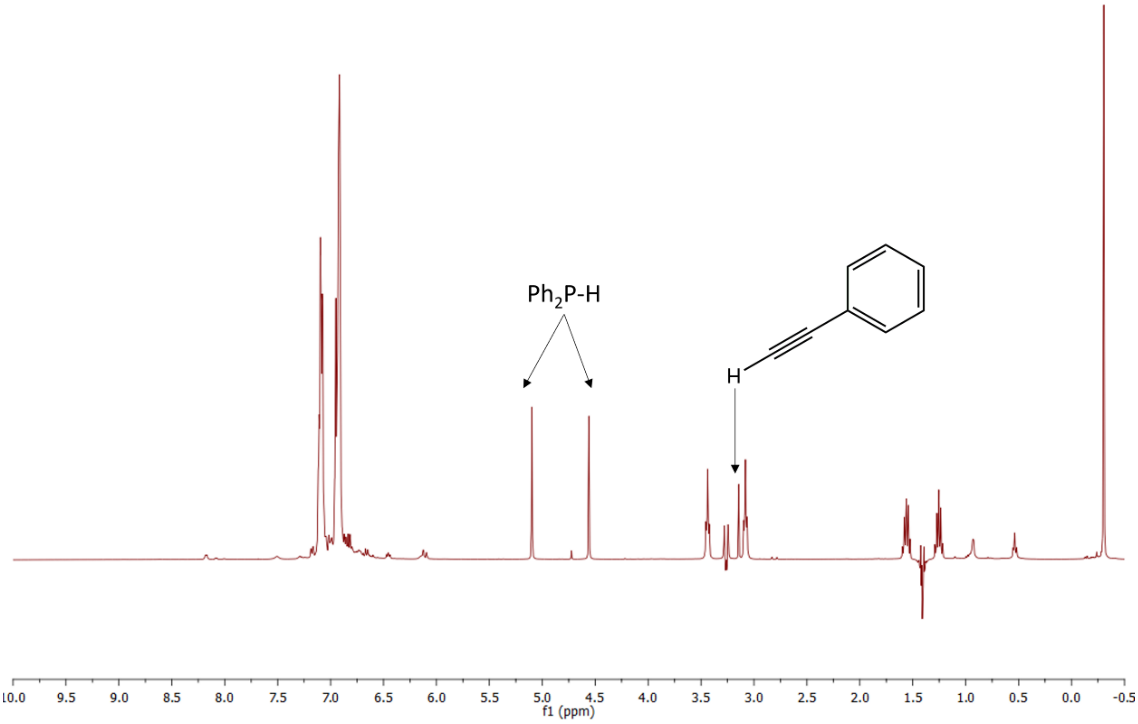


Figure S124: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 3 of Table S5.

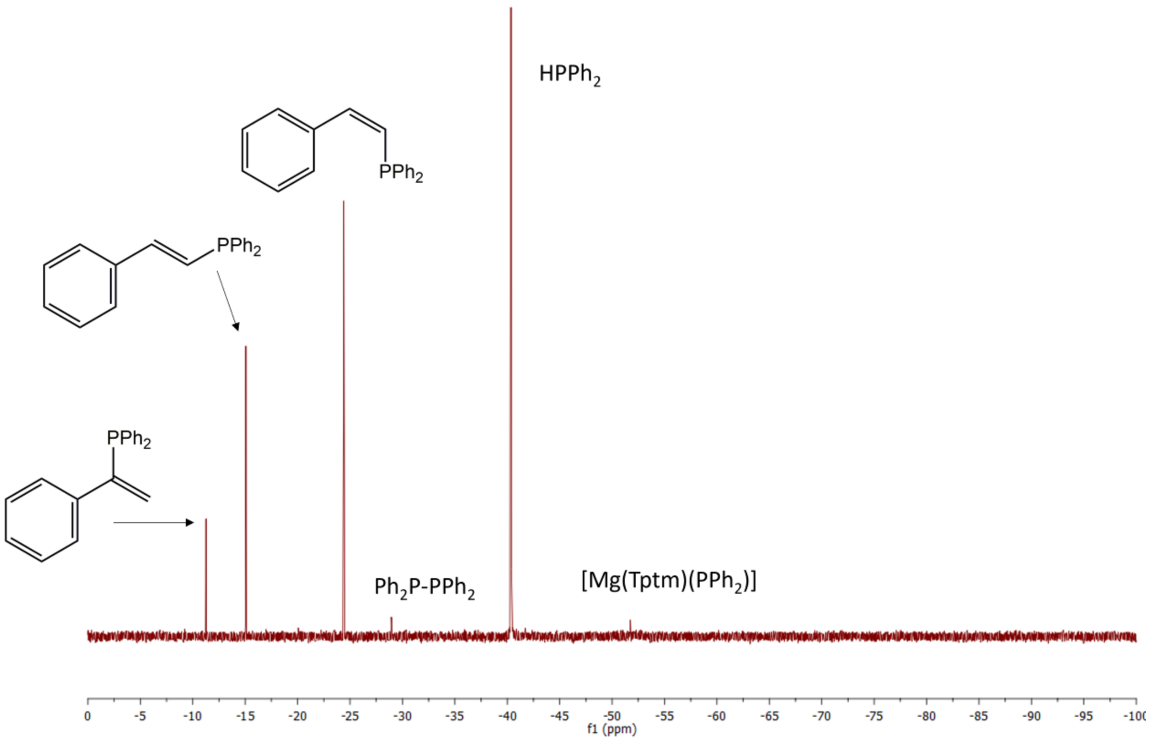


Figure S125: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 3 of Table S5.

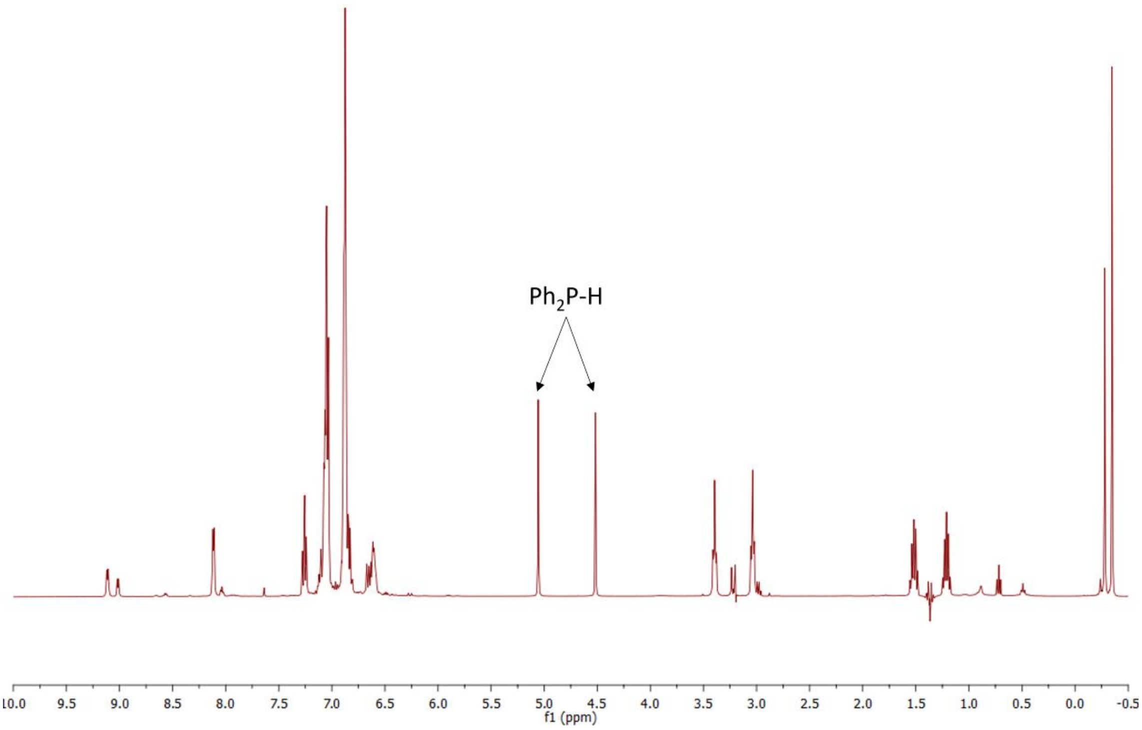


Figure S126: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 4 of Table S5.

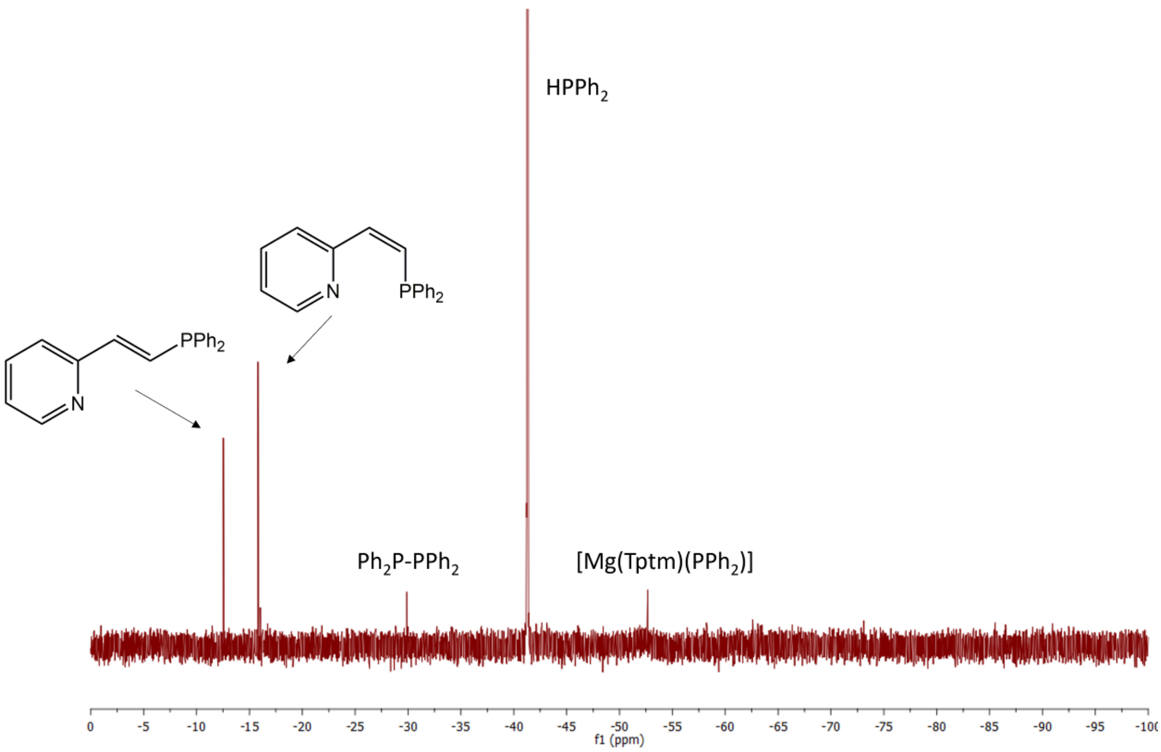


Figure S127: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from 100 to 0 ppm for entry 4 of Table S5.

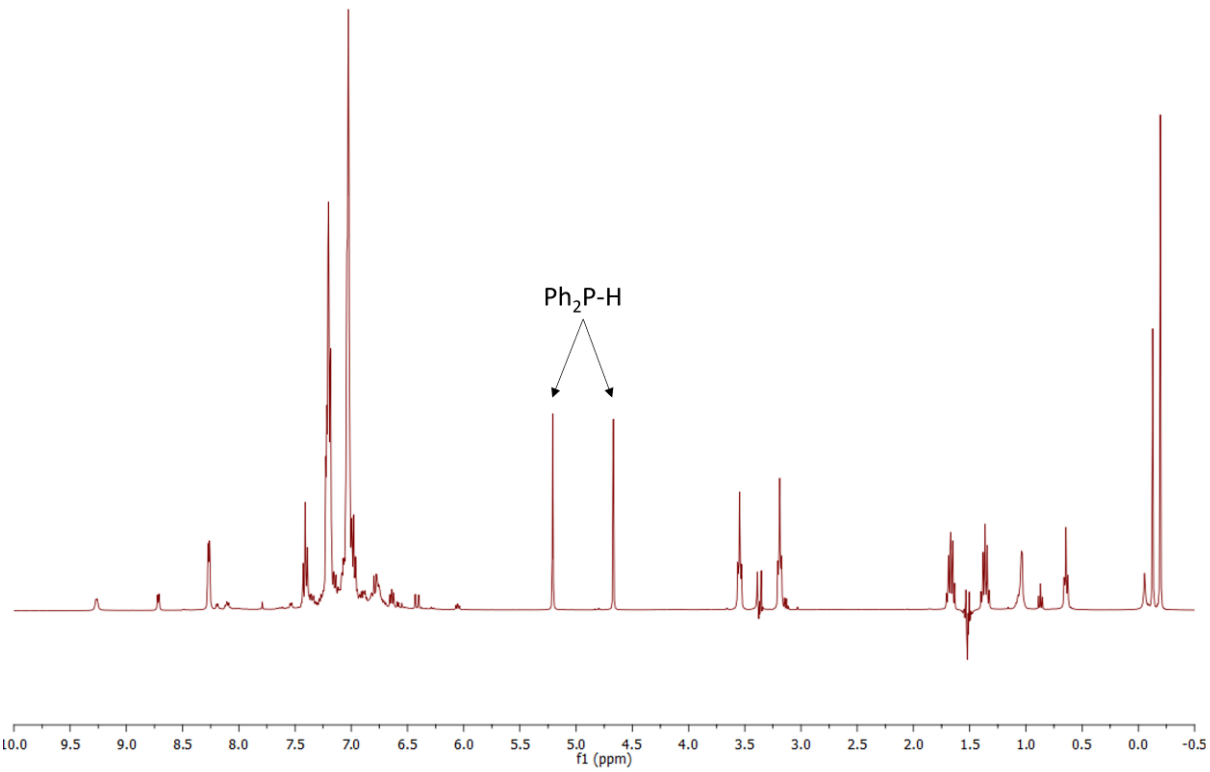


Figure S128: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 5 of Table S5.

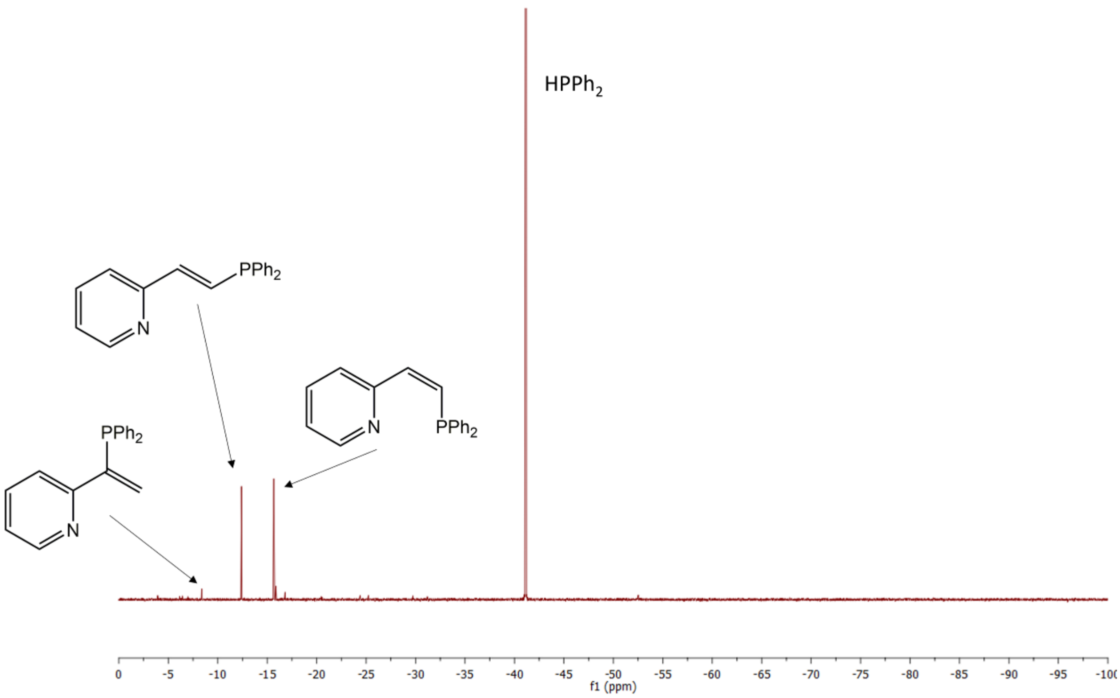


Figure S129: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 5 of Table S5.

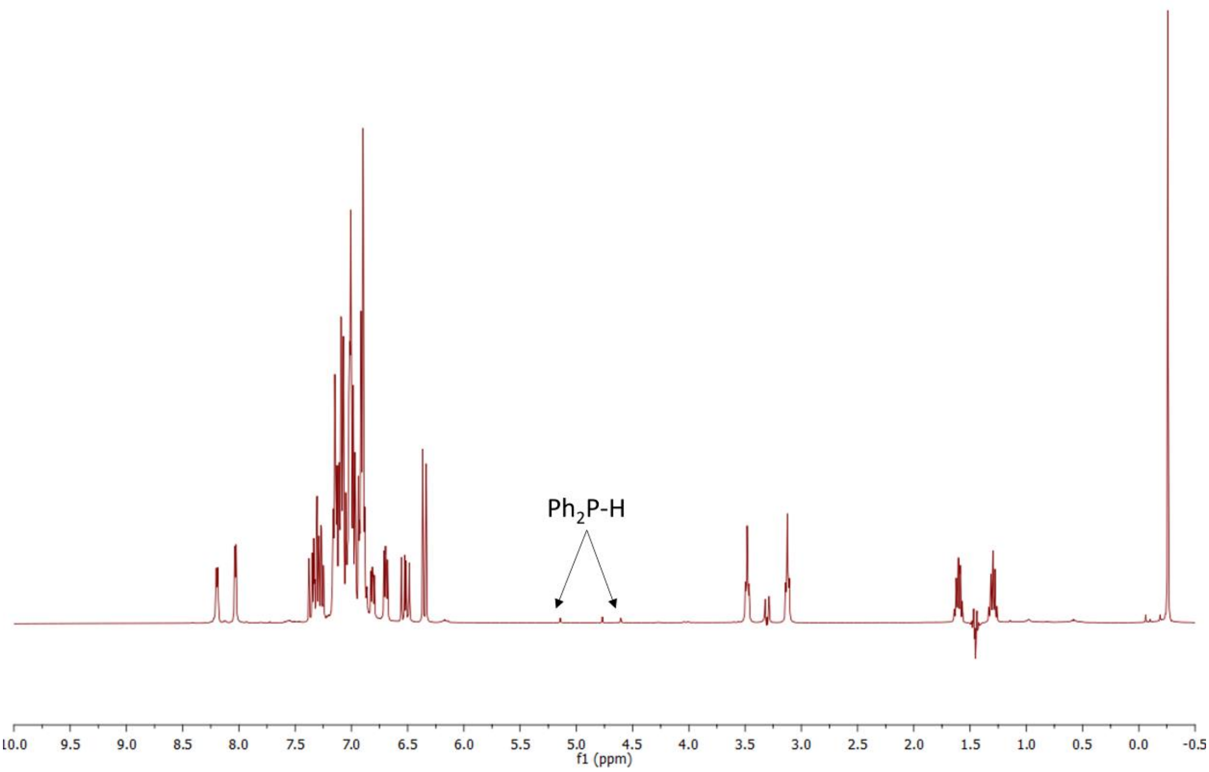


Figure S130: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 6 of Table S5.

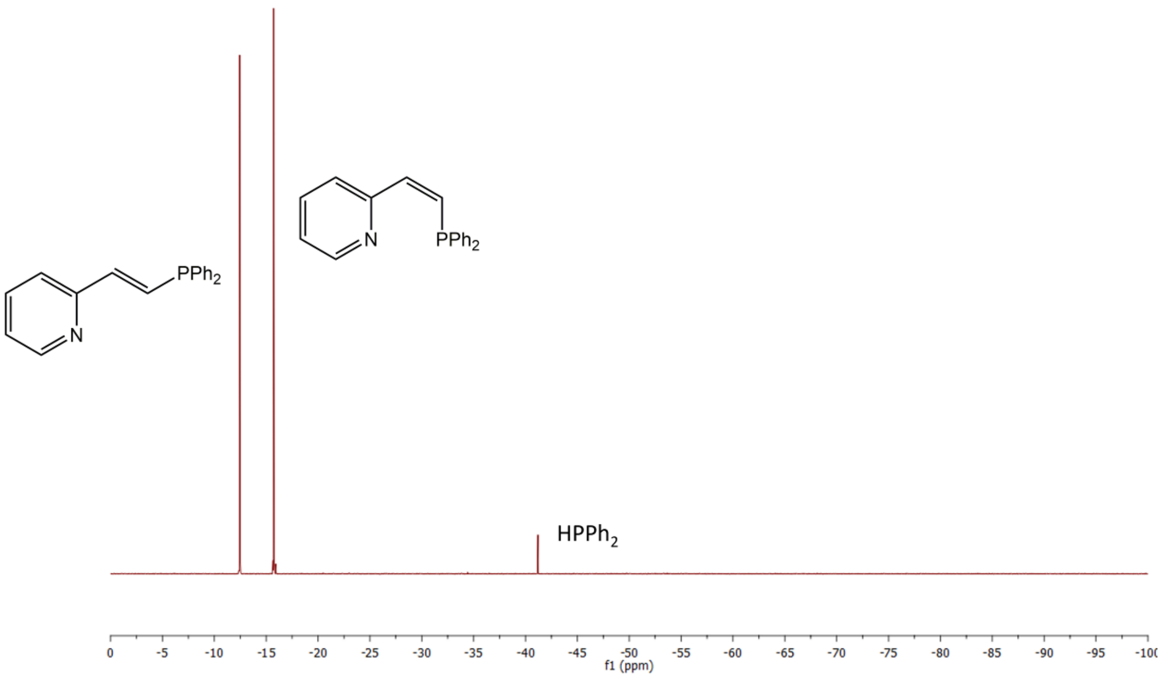


Figure S131: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 6 of Table S5.

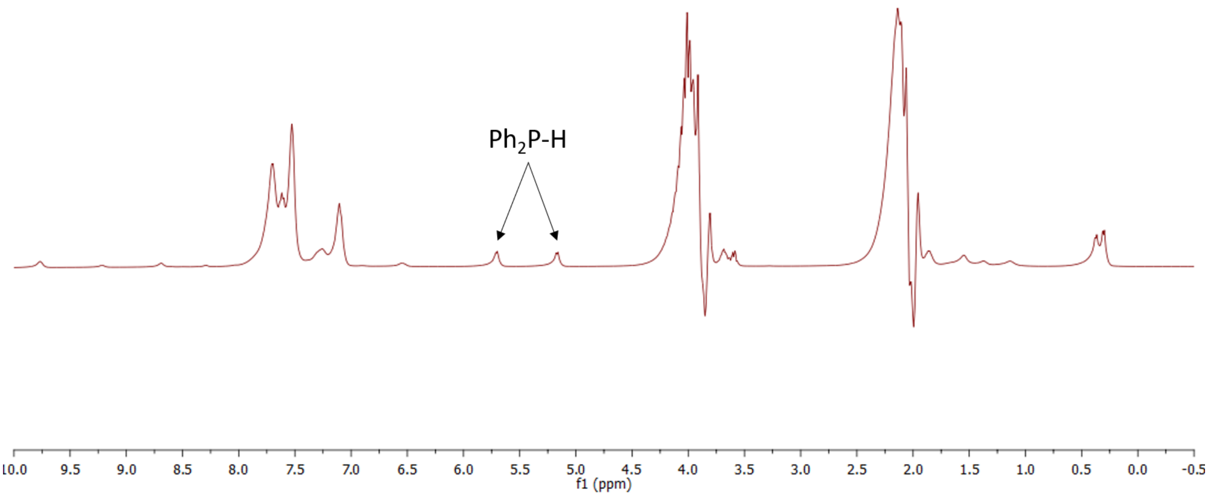


Figure S132: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 7 of Table S5.

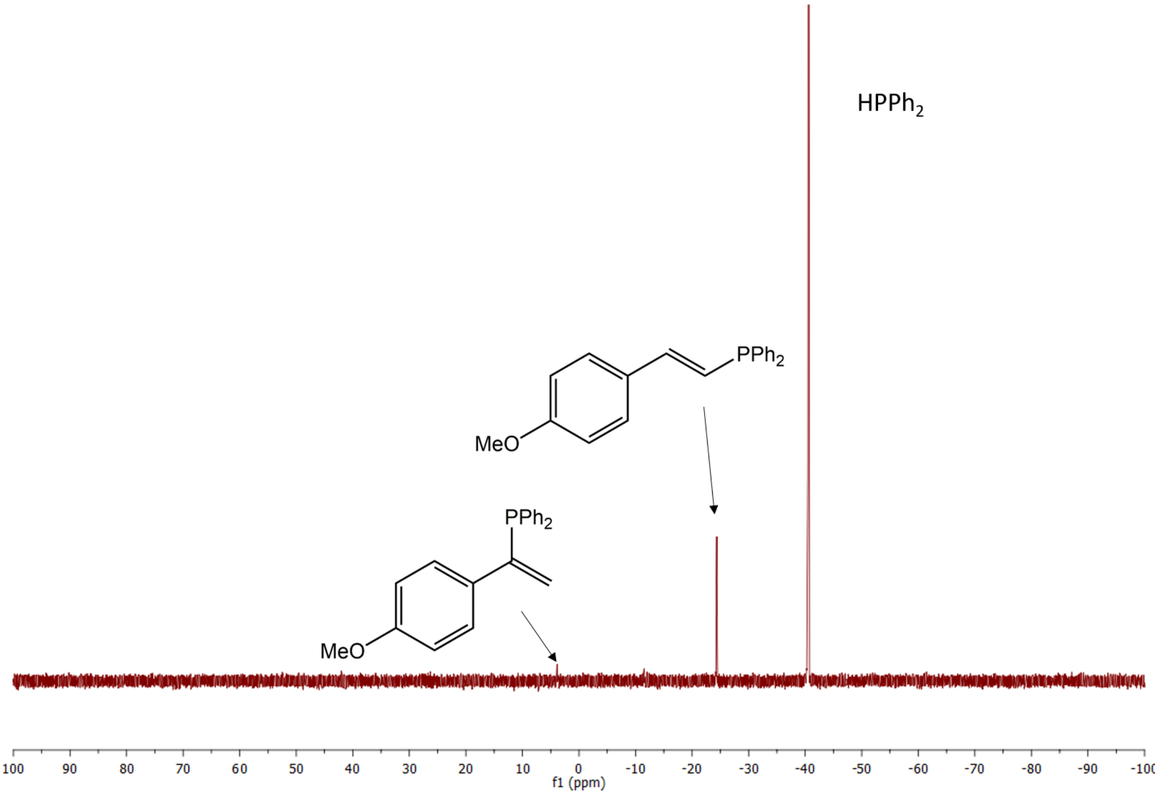


Figure S133: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for entry 7 of Table S5.

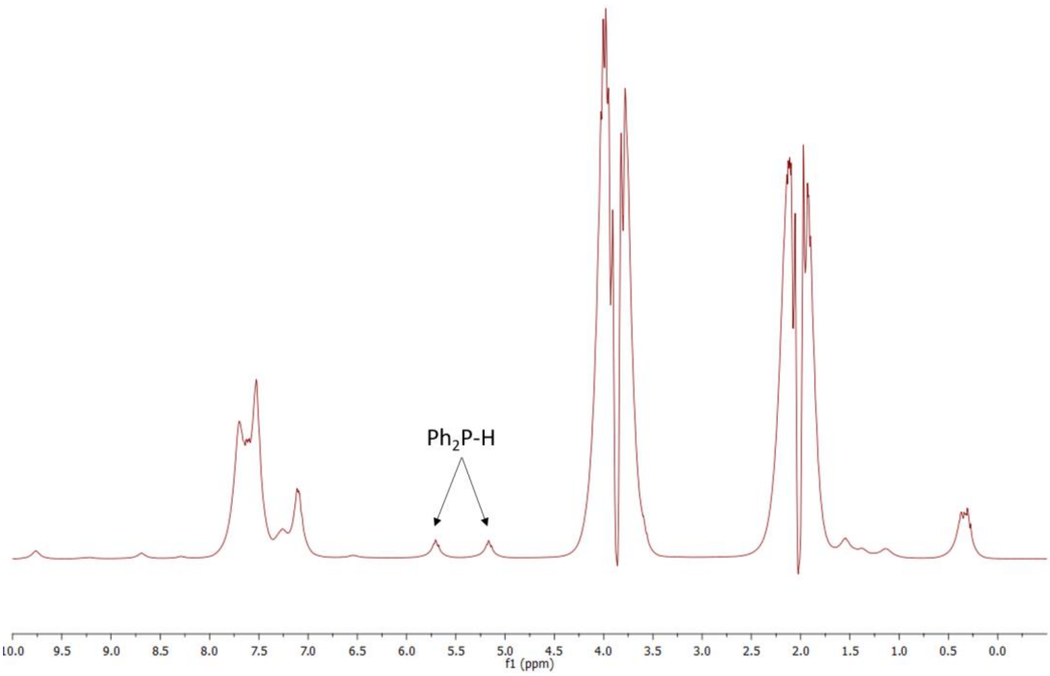


Figure S134: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 8 of Table S5.

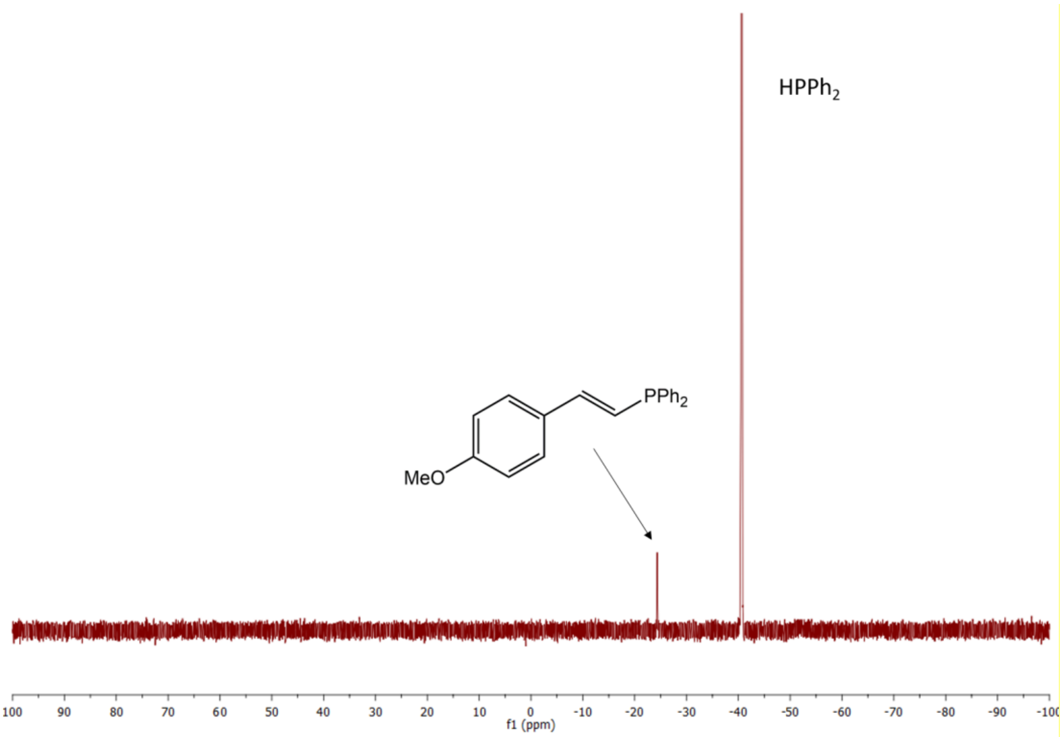


Figure S135: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for entry 8 of Table S5.

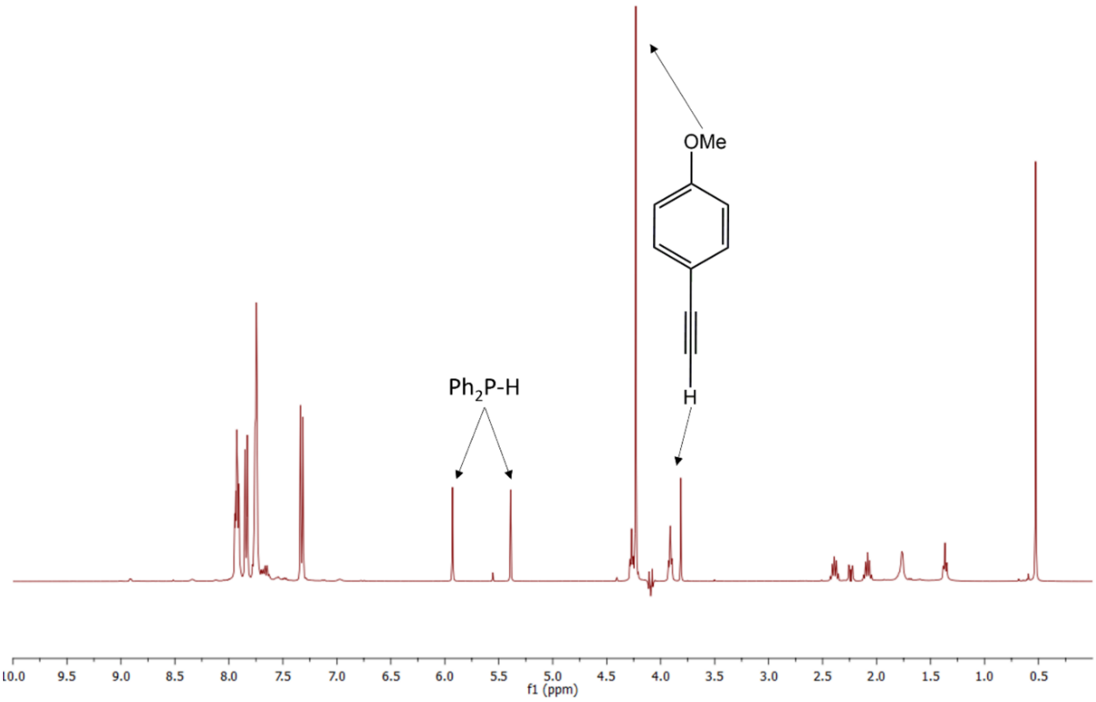


Figure S136: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −0.5 to 10 ppm for entry 9 of Table S5.

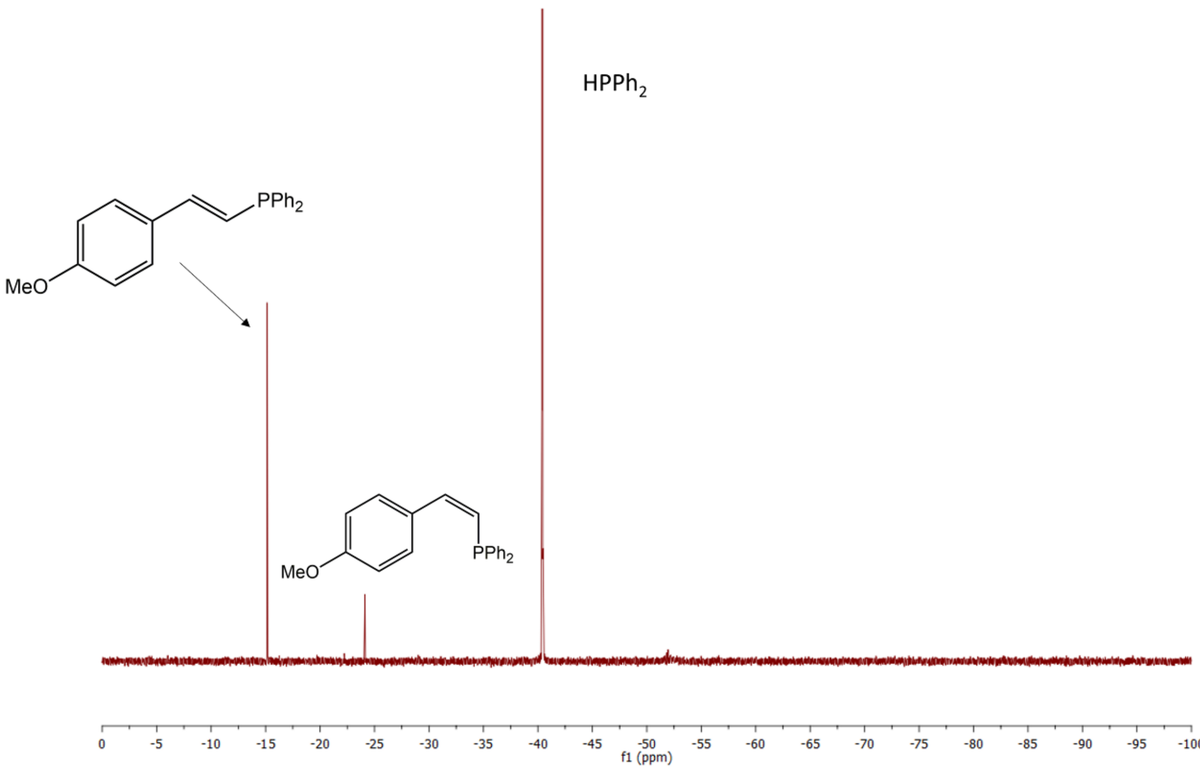


Figure S137: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for entry 9 of Table S5.

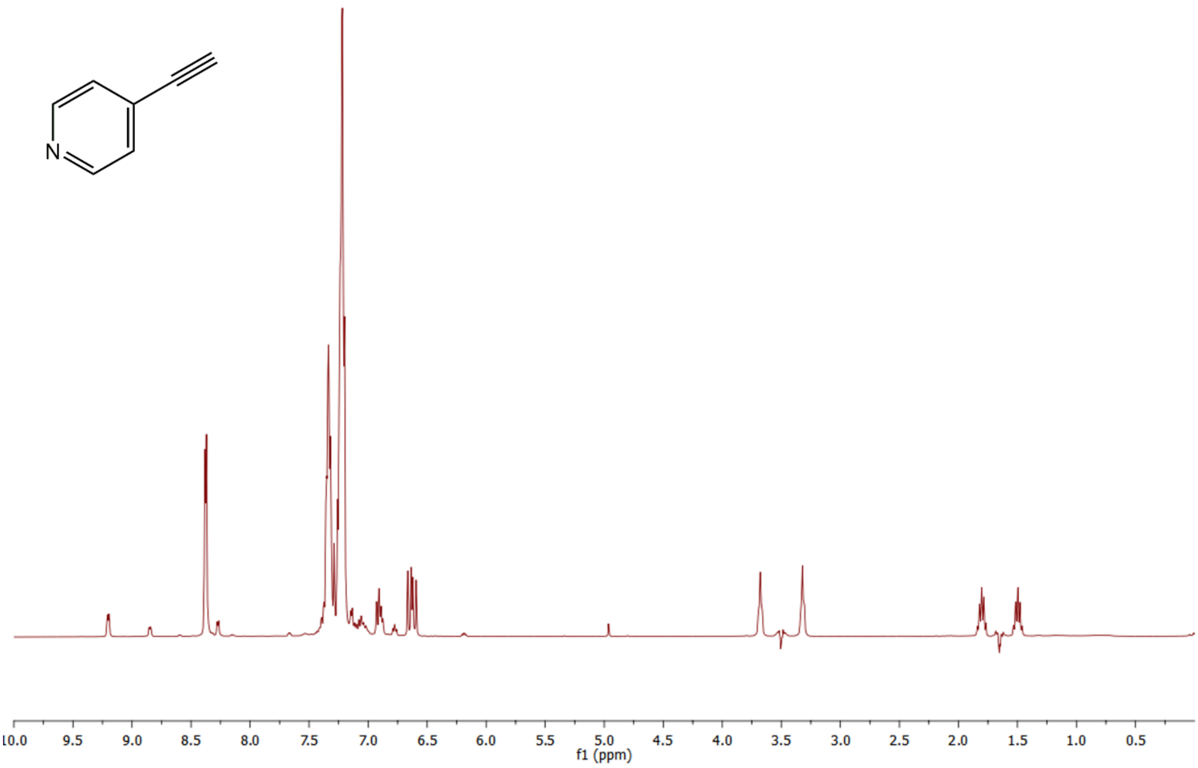


Figure S138: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 10 of Table S5.

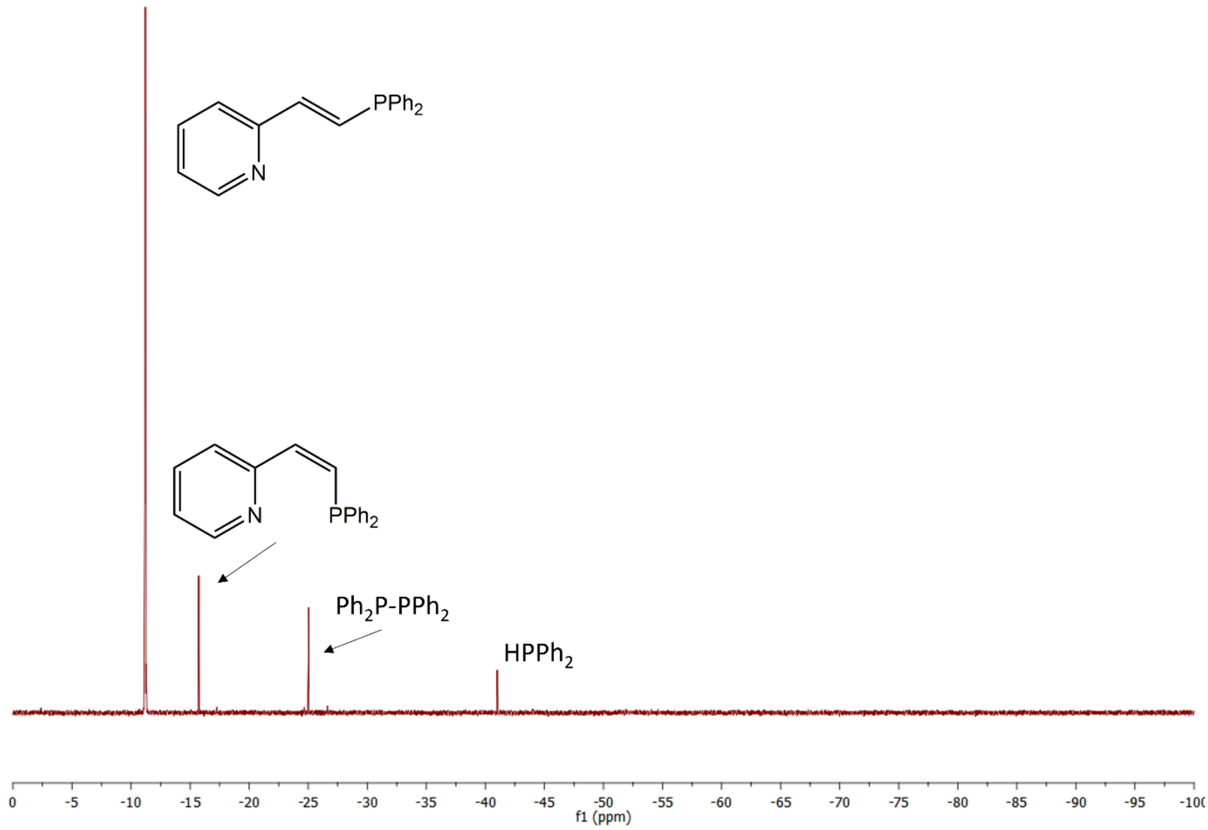


Figure S139: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 10 of Table S5.

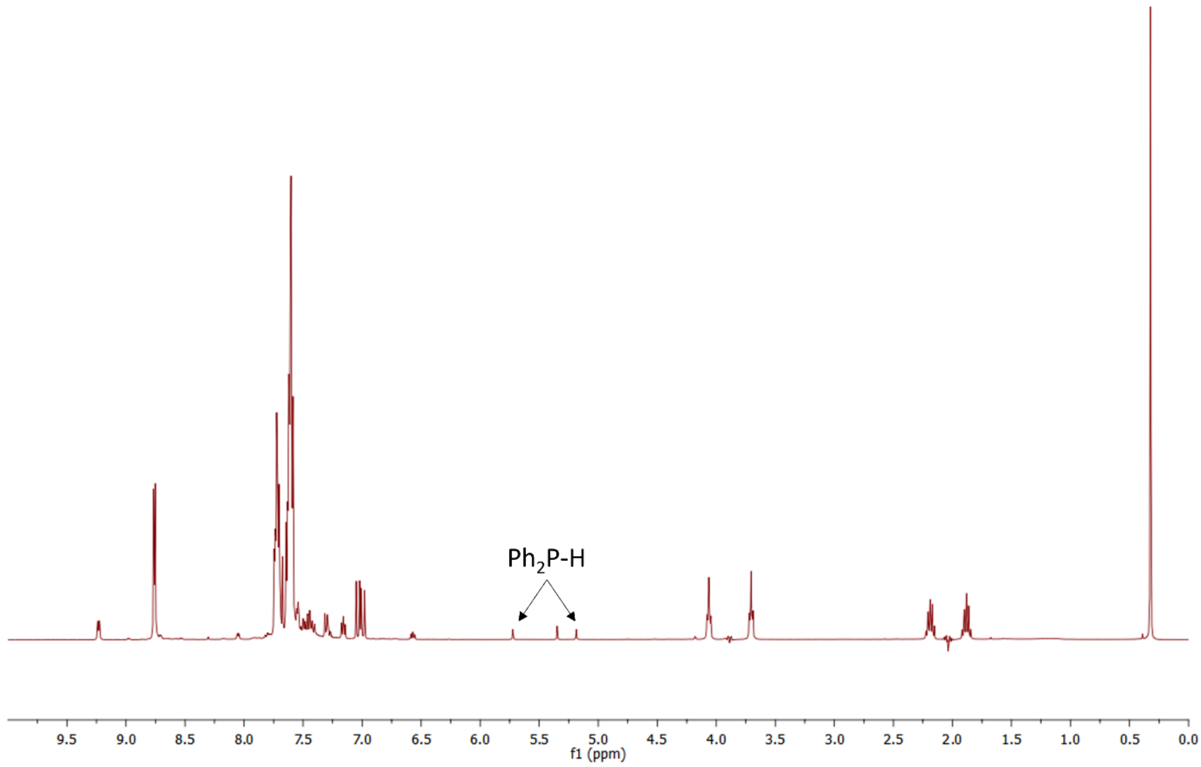


Figure S140: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 11 of Table S5.

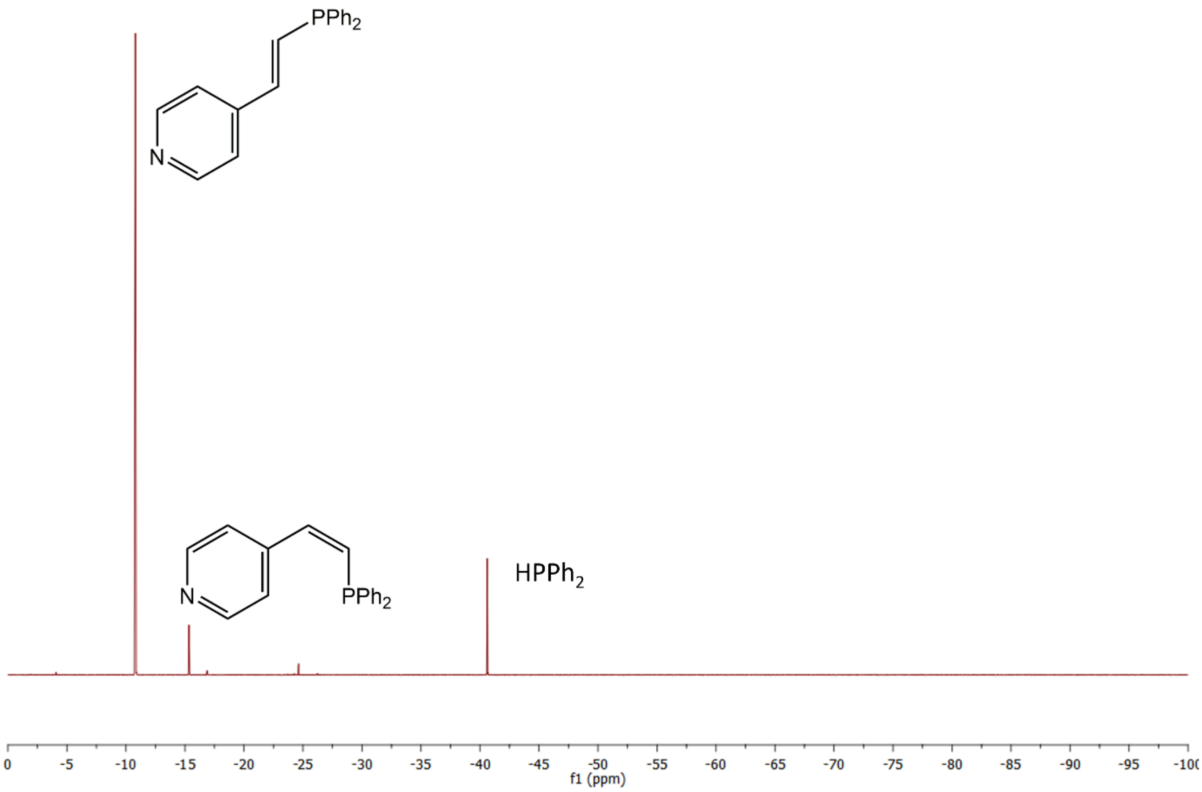


Figure S141: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 11 of Table S5.

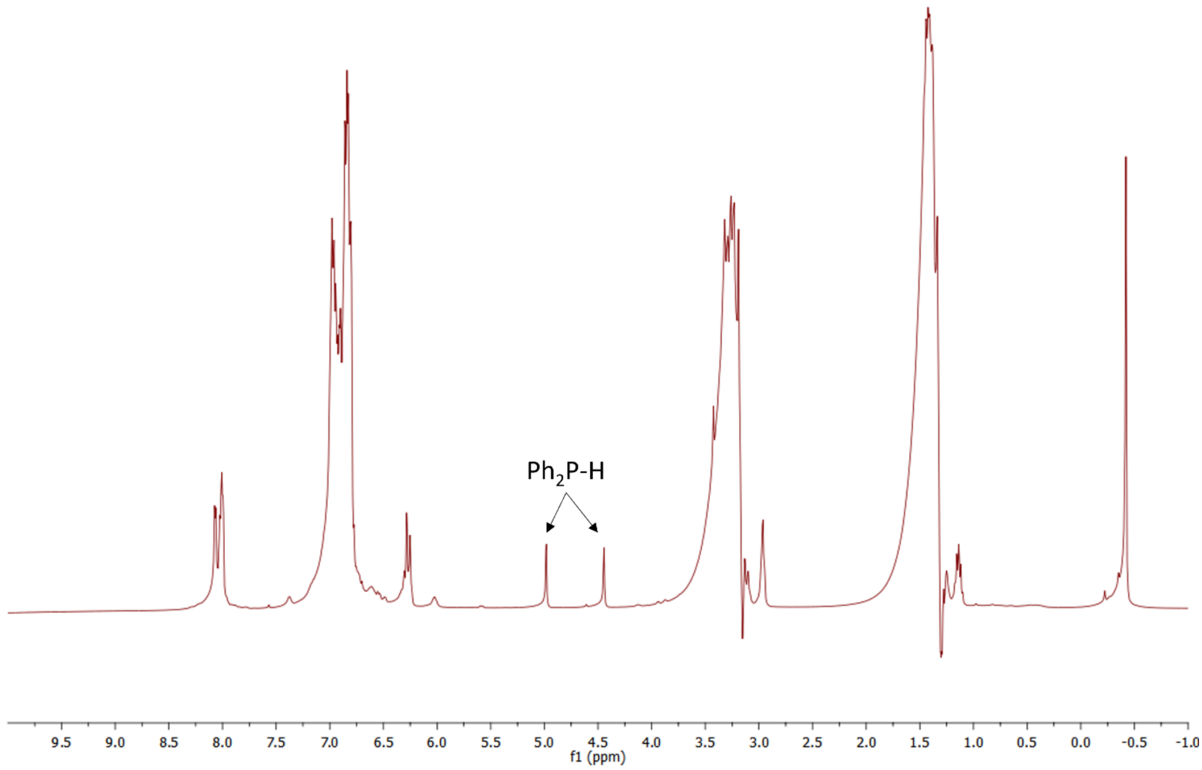


Figure S142: [1]H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −1.0 to 10 ppm for entry 12 of Table S5.

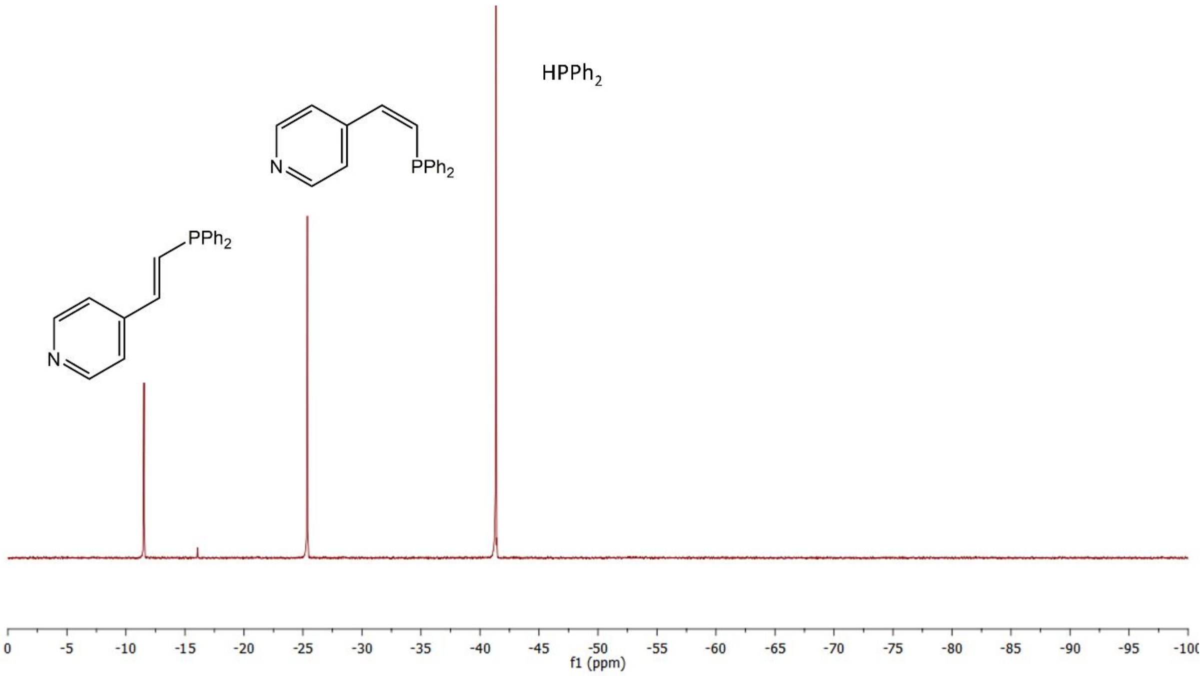


Figure S143: [31]P{[1]H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 12 of Table S5.

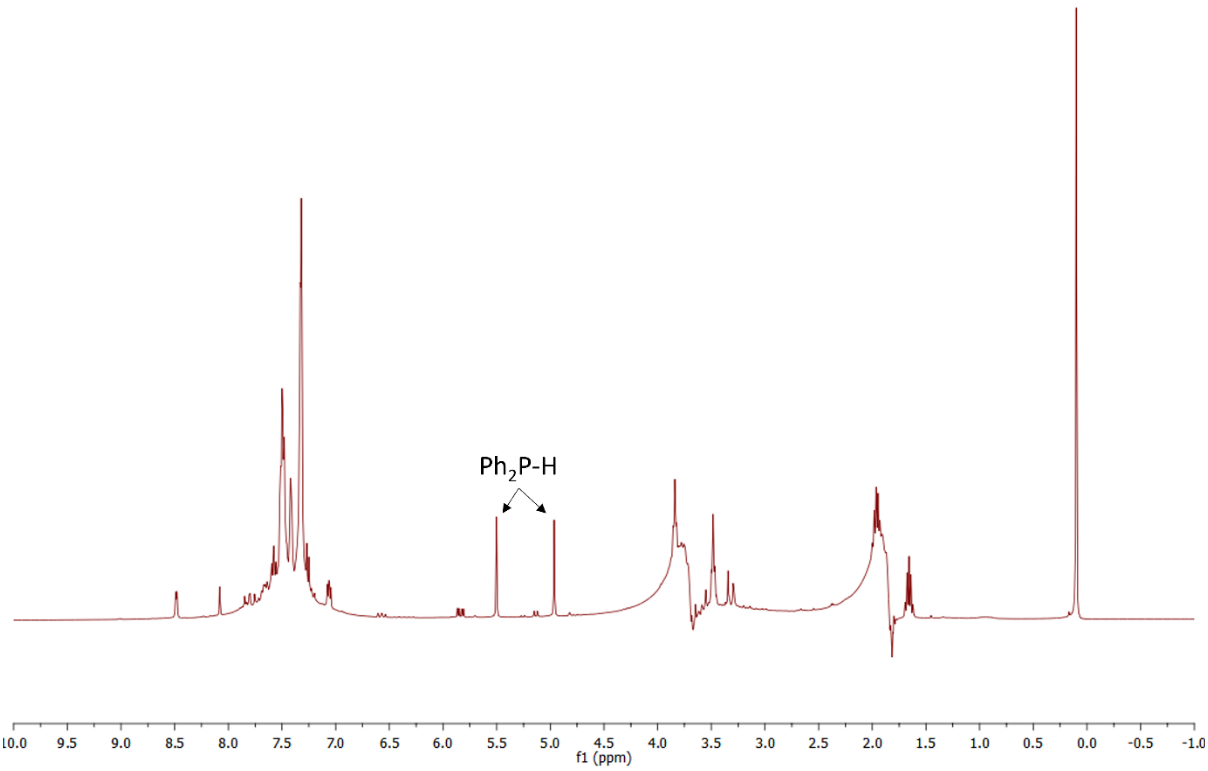


Figure S144: [1]H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −1.0 to 10 ppm for entry 13 of Table S5.

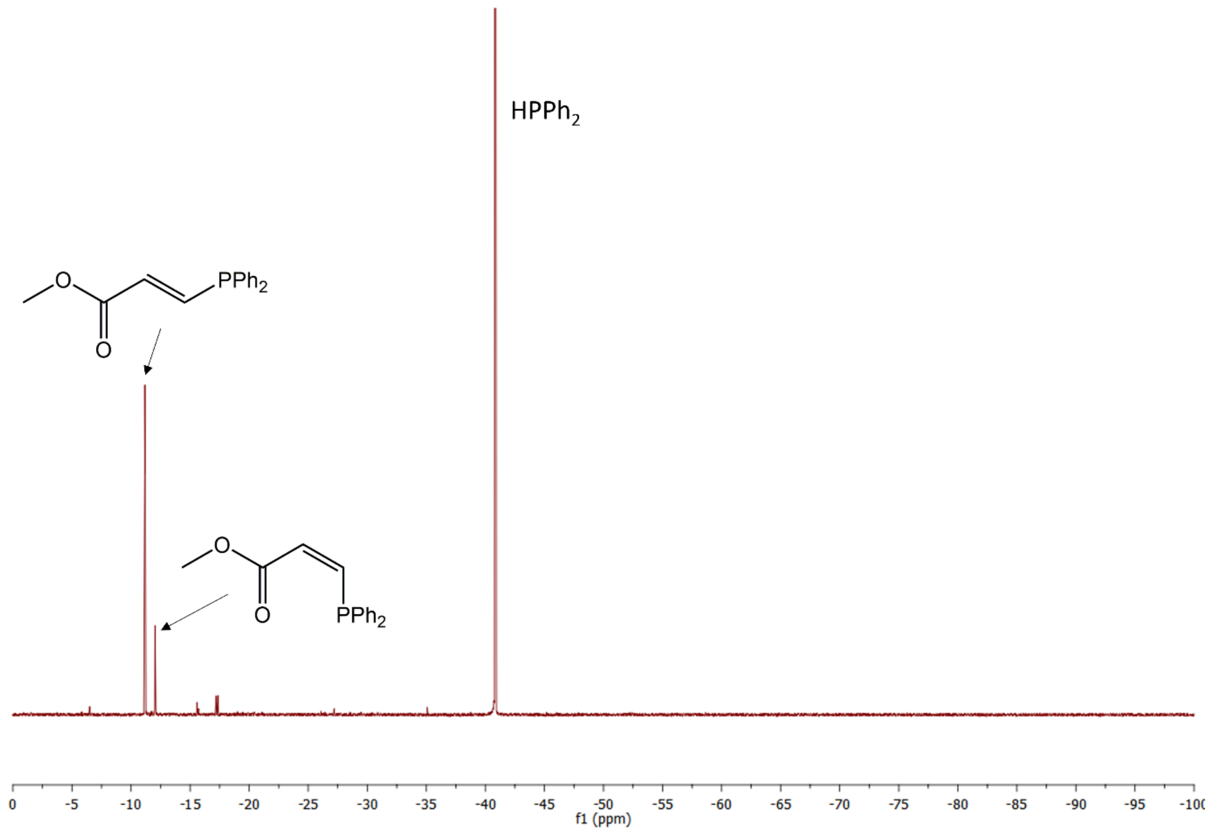


Figure S145: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 13 of Table S5.

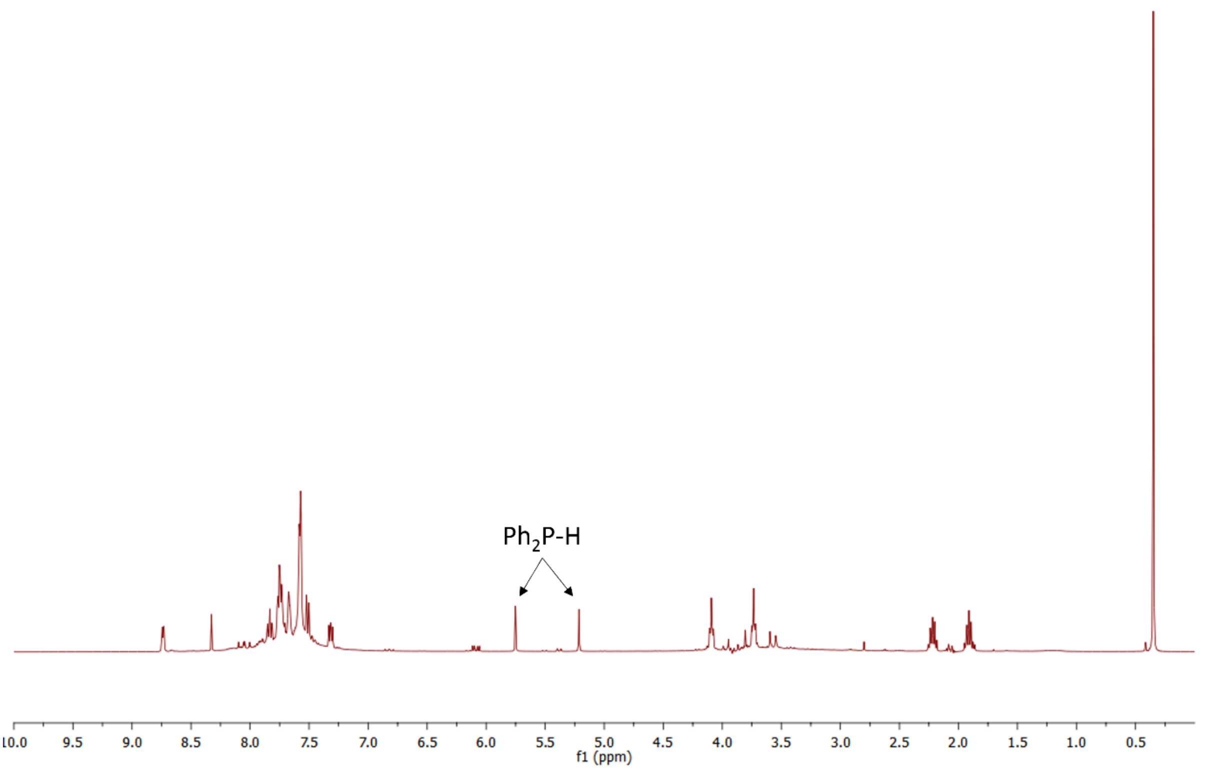


Figure S146: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 14 of Table S5.

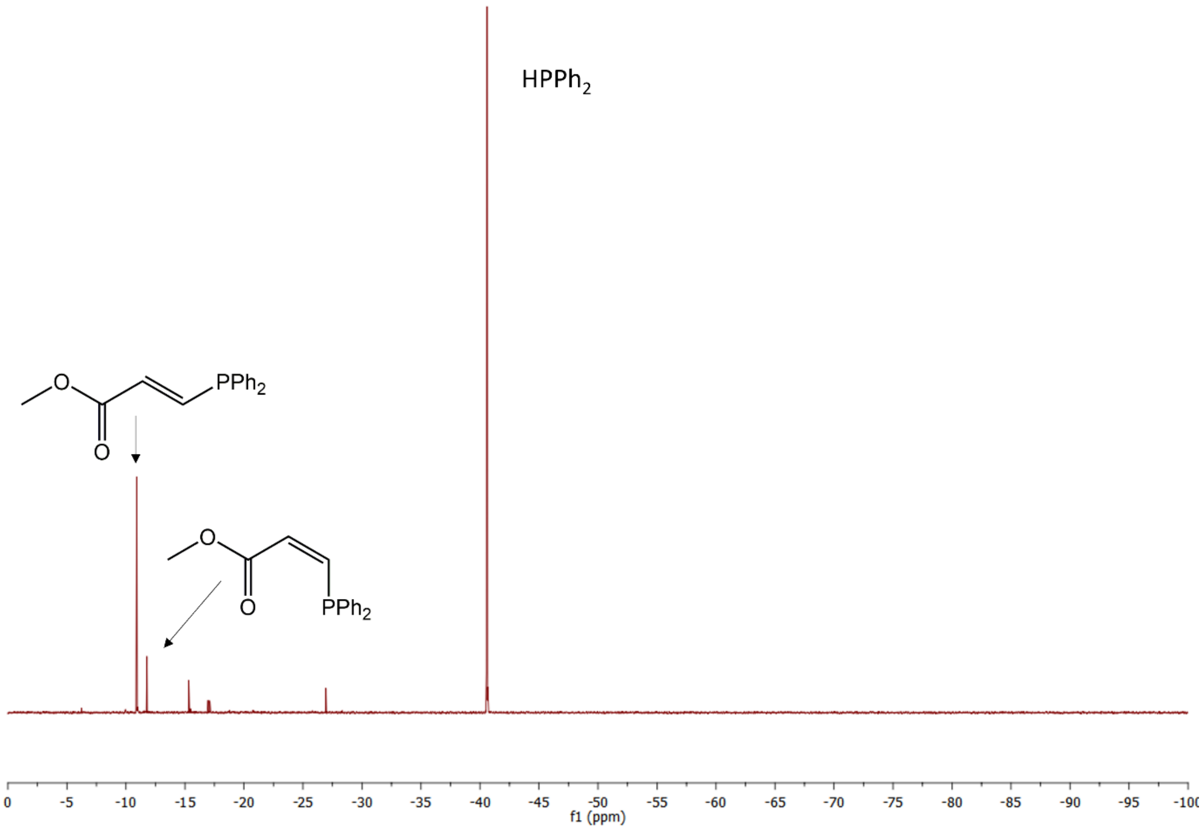


Figure S147: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 14 of Table S5.

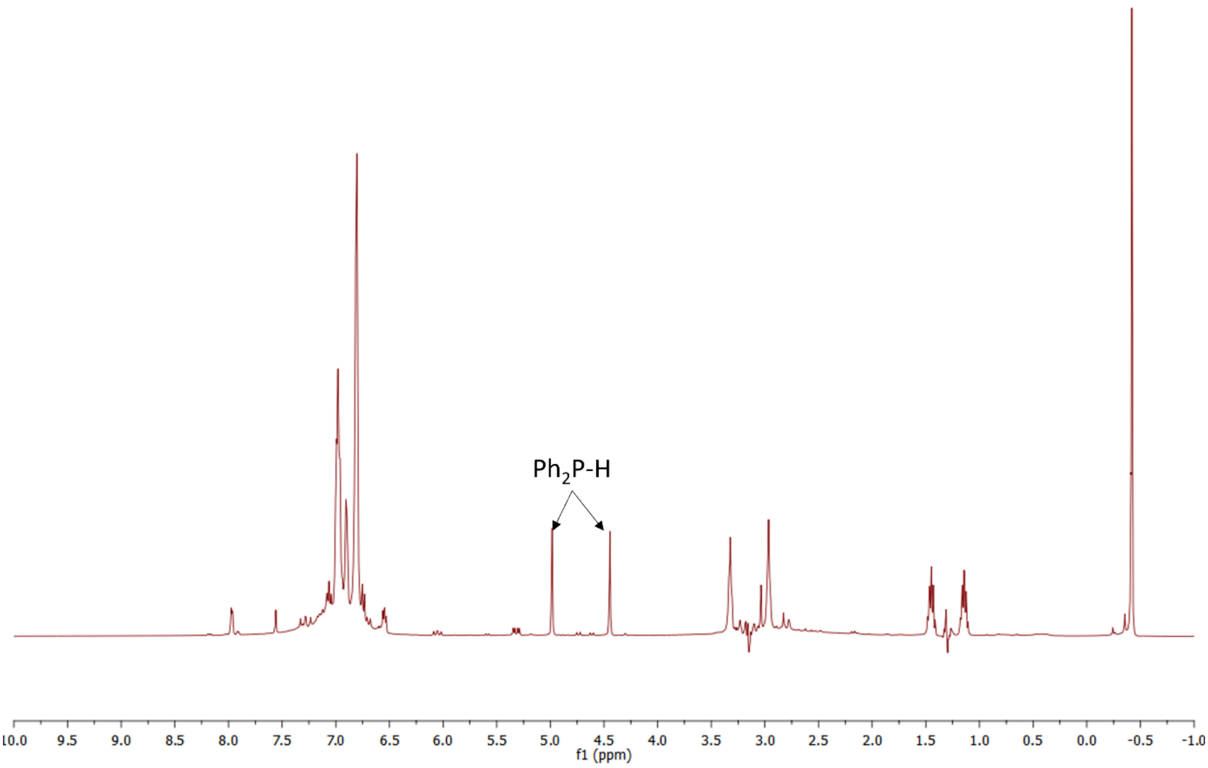


Figure S148: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from −1.0 to 10 ppm for entry 15 of Table S5.

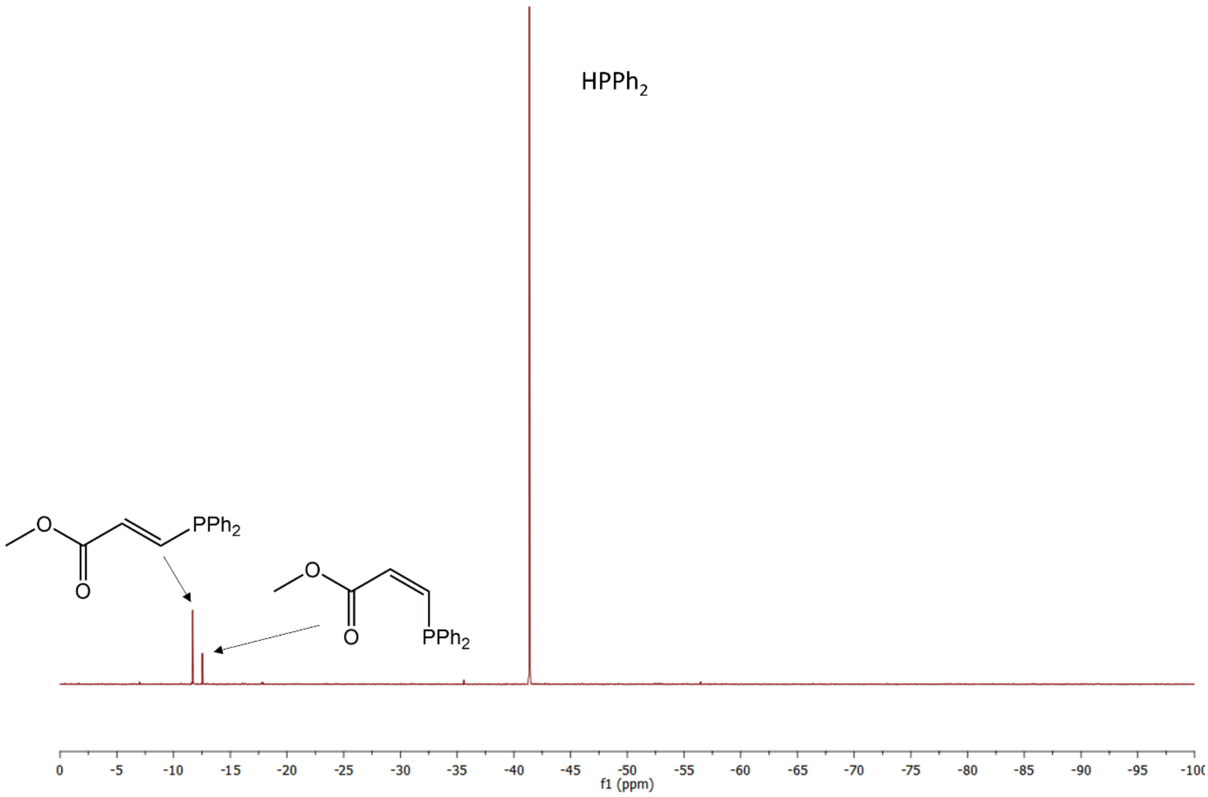


Figure S149: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 15 of Table S5.

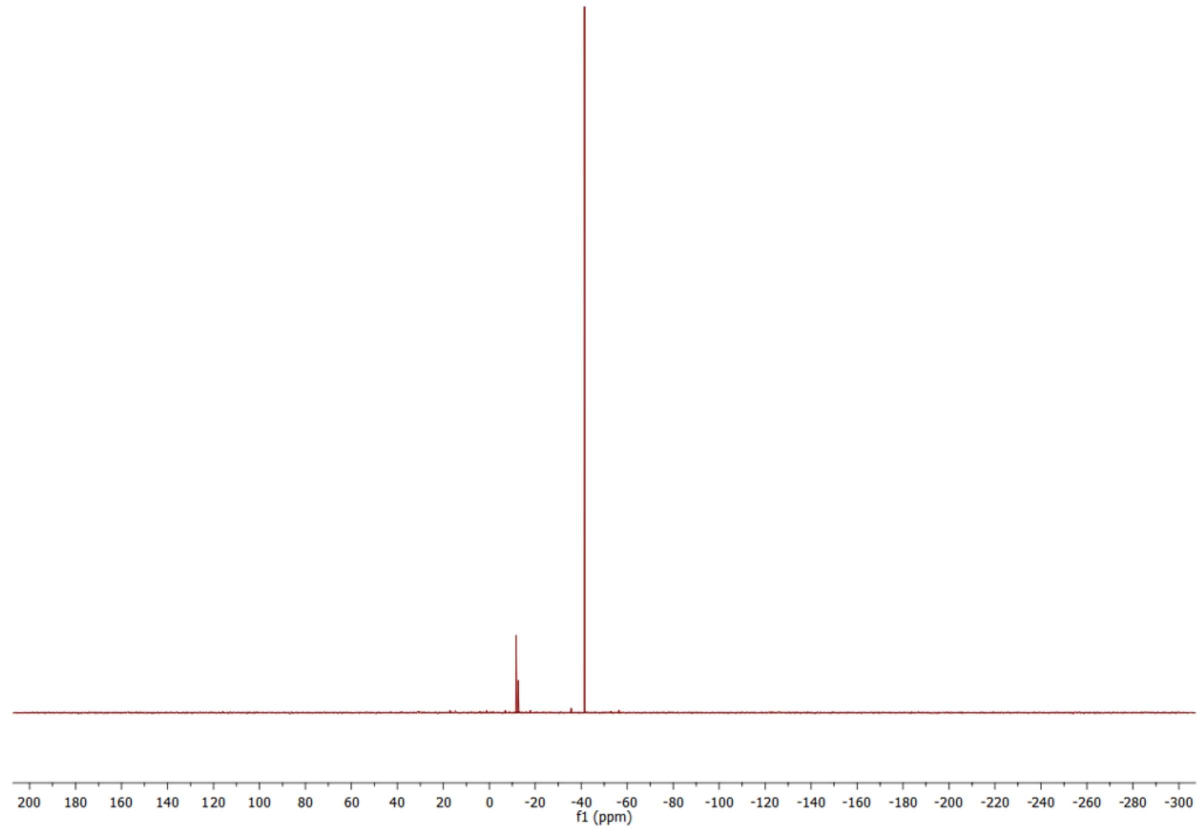


Figure S150: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) full spectrum for entry 15 of Table S5.

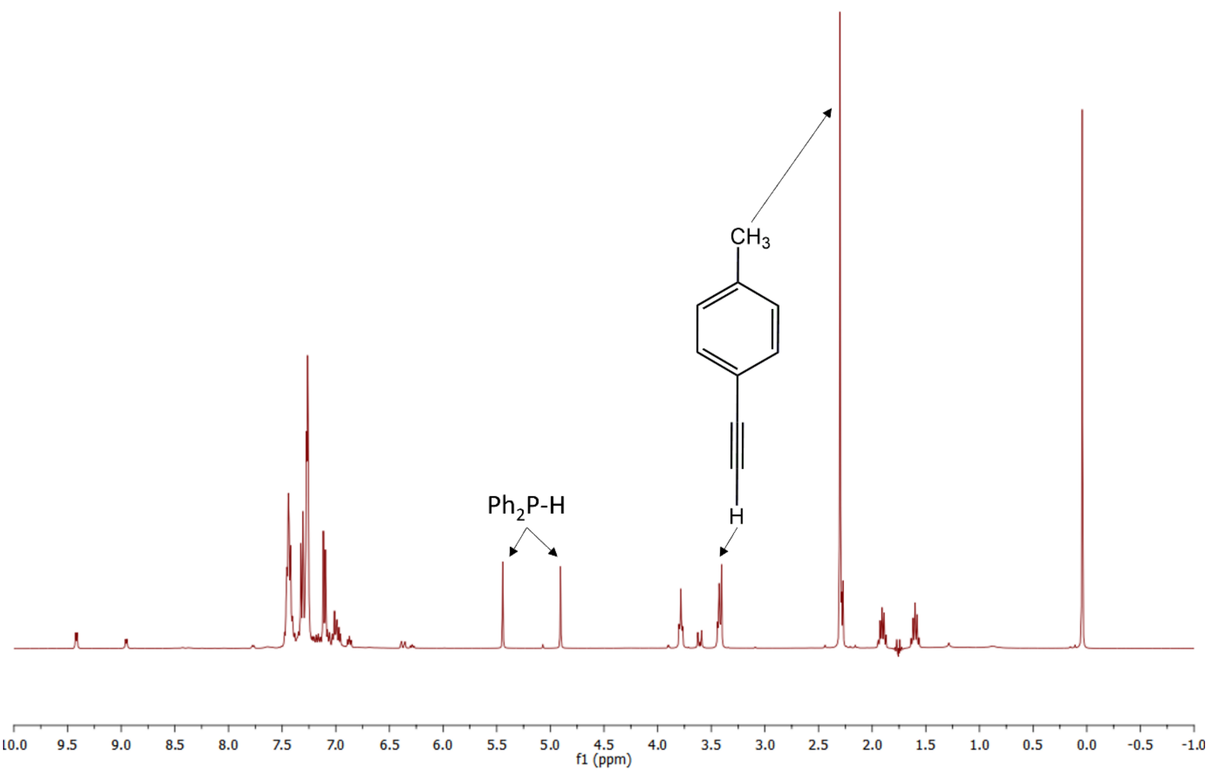


Figure S151: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from -1.0 to 10 ppm for entry 16 of Table S5.

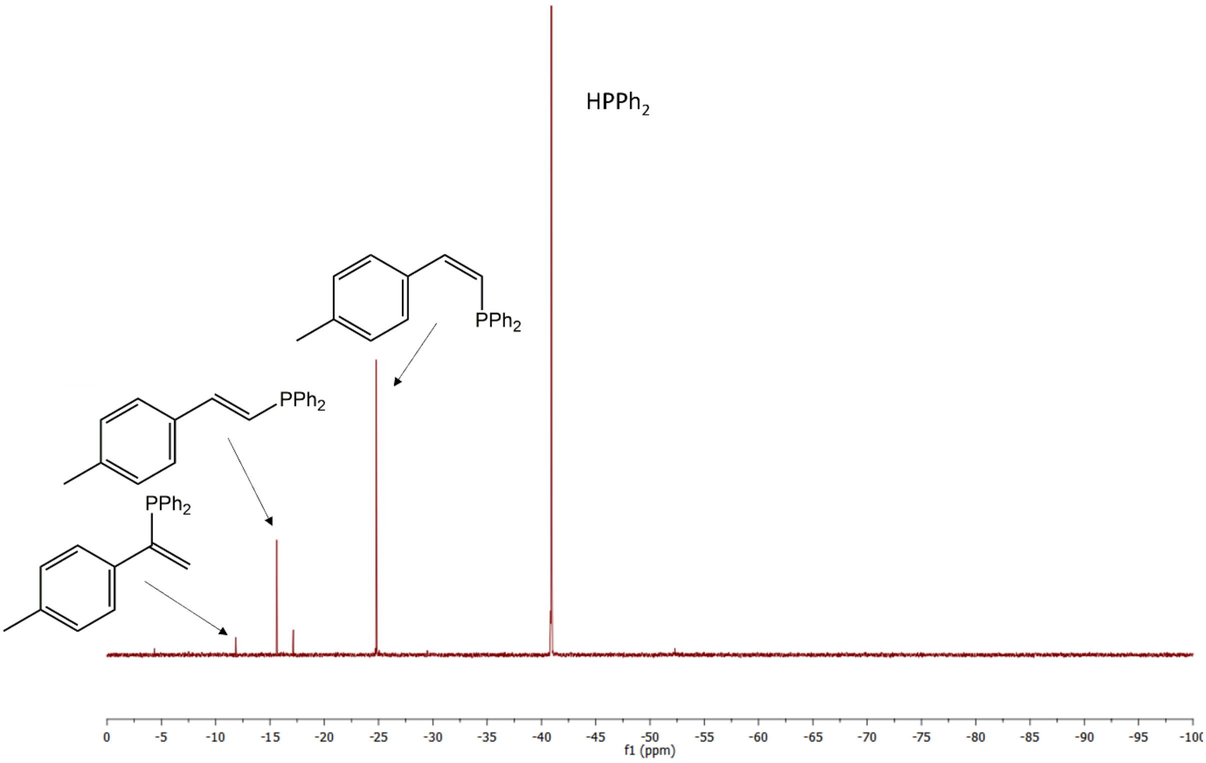


Figure S152: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 16 of Table S5.

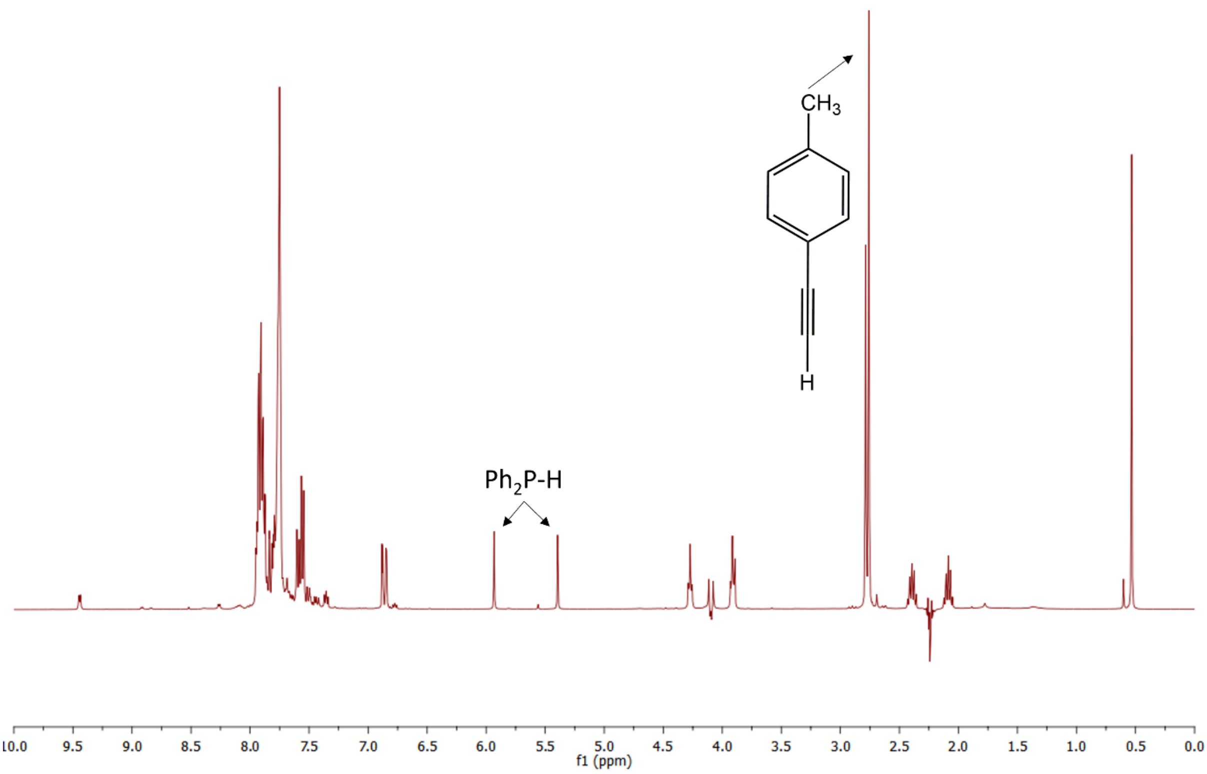


Figure S153: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 17 of Table S5.

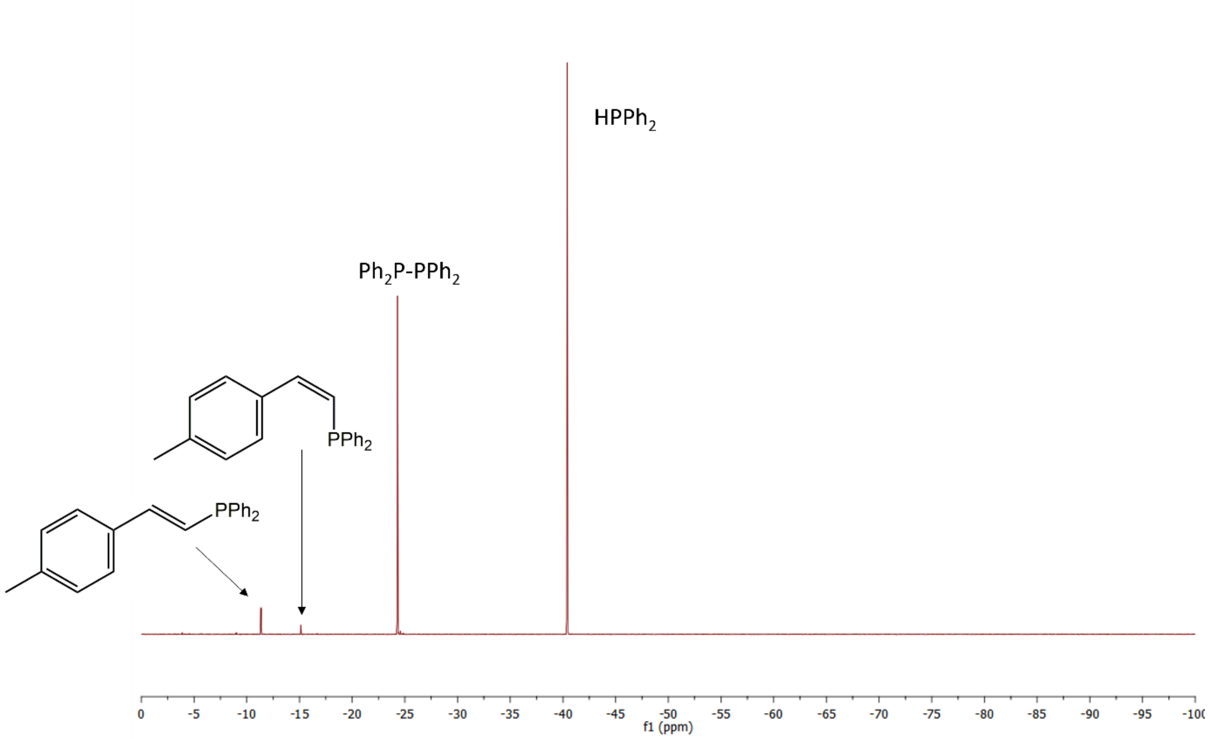


Figure S154: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 17 of Table S5.

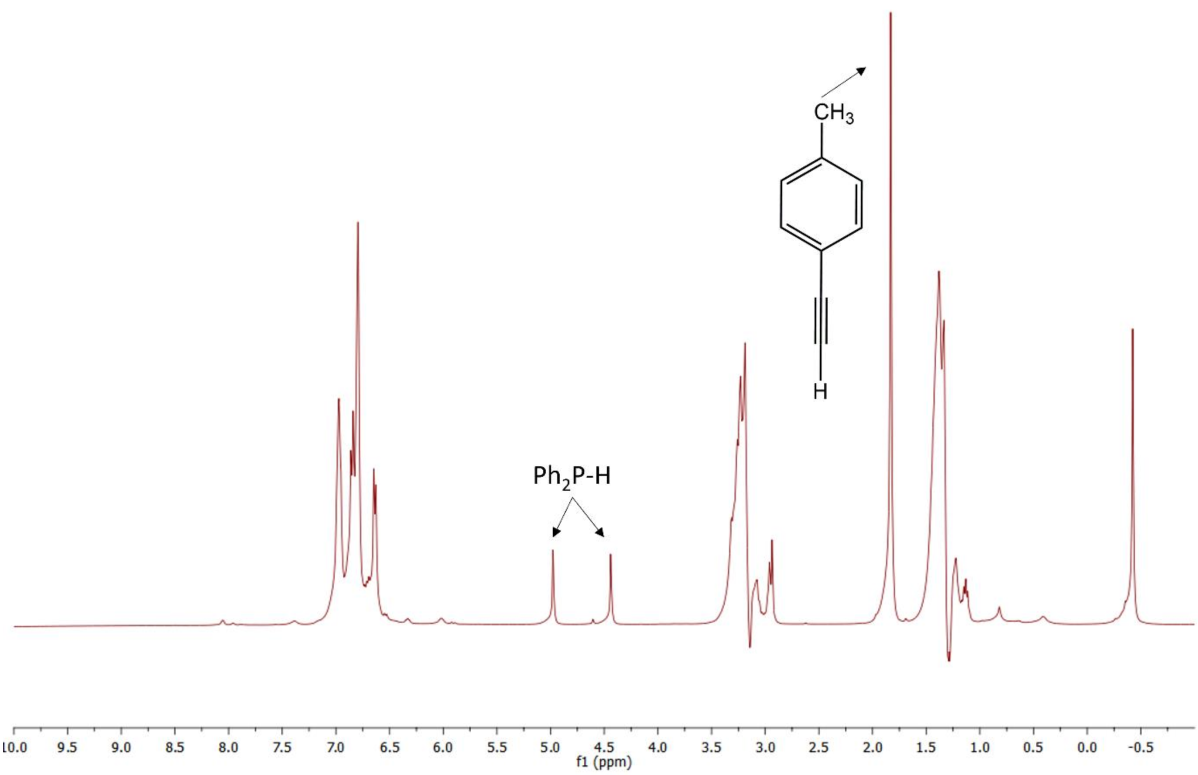


Figure S155: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 18 of Table S5.

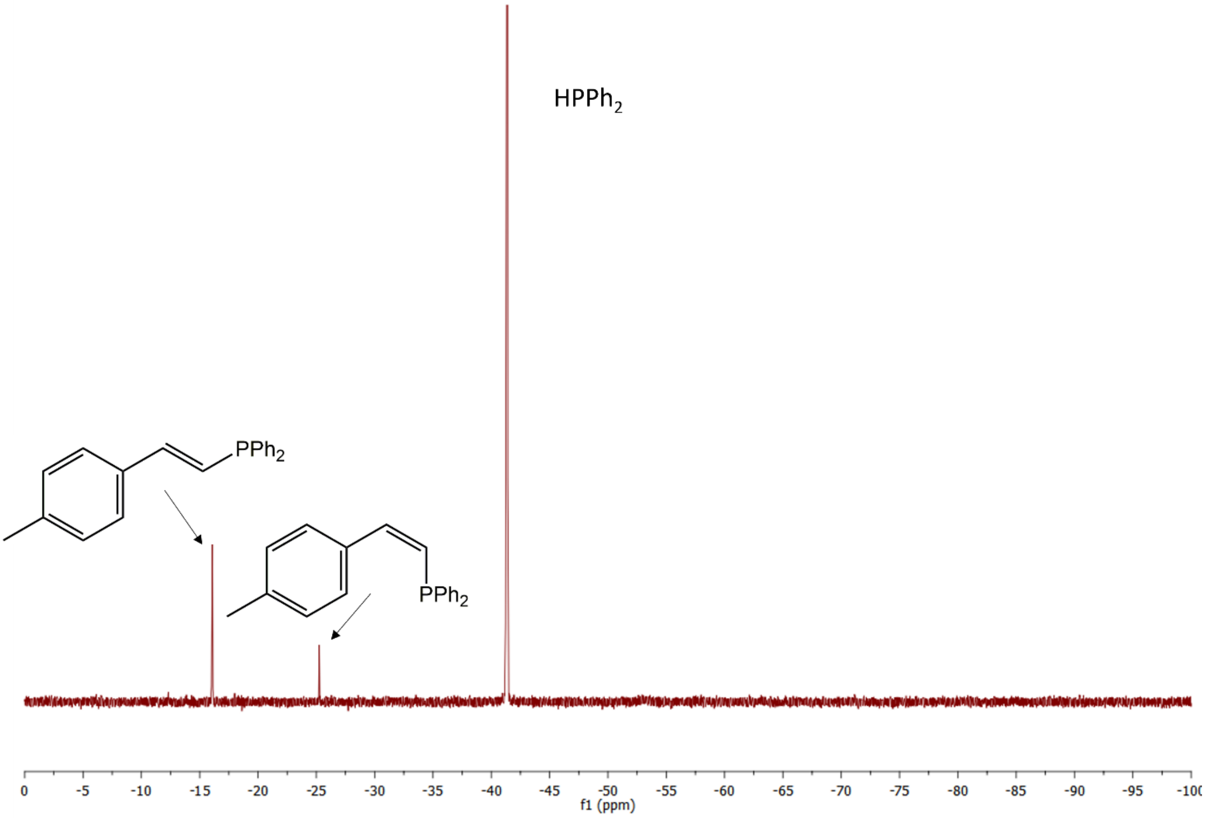


Figure S156: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 18 of Table S5.

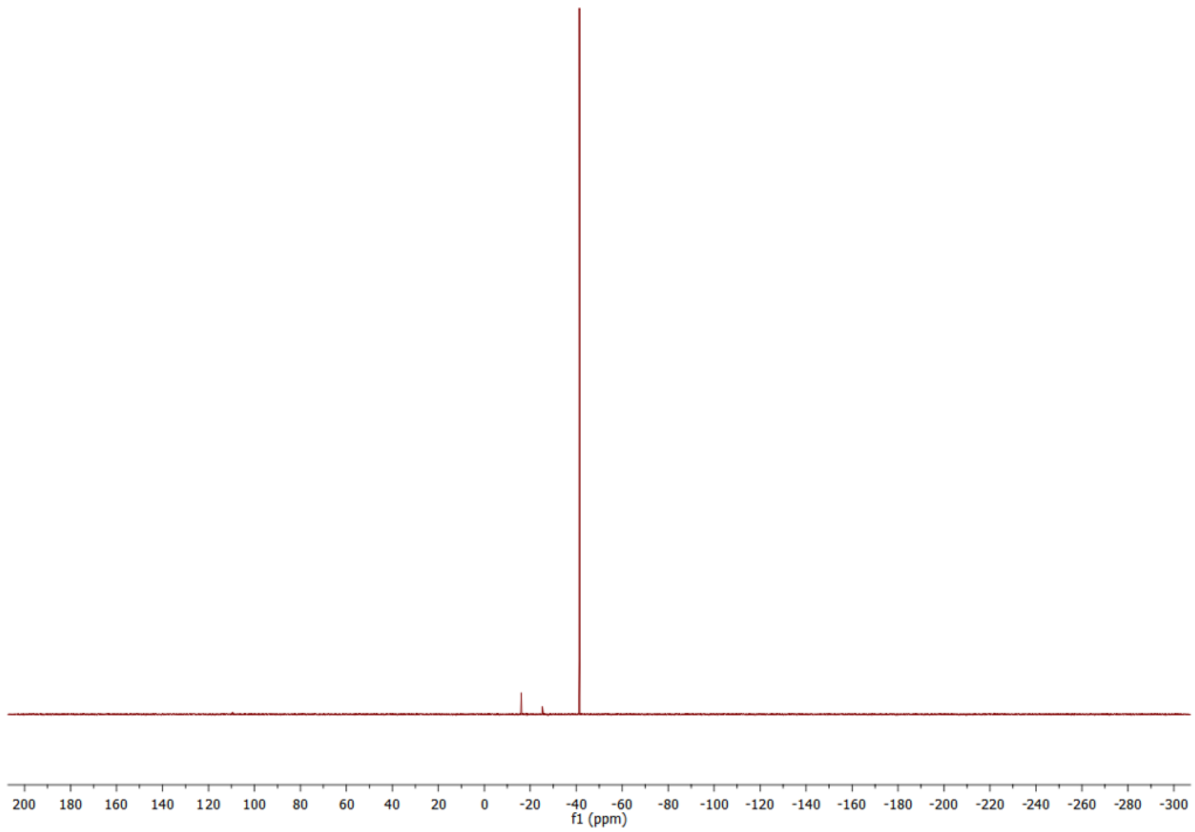


Figure S157: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) full spectrum for entry 18 of Table S5.

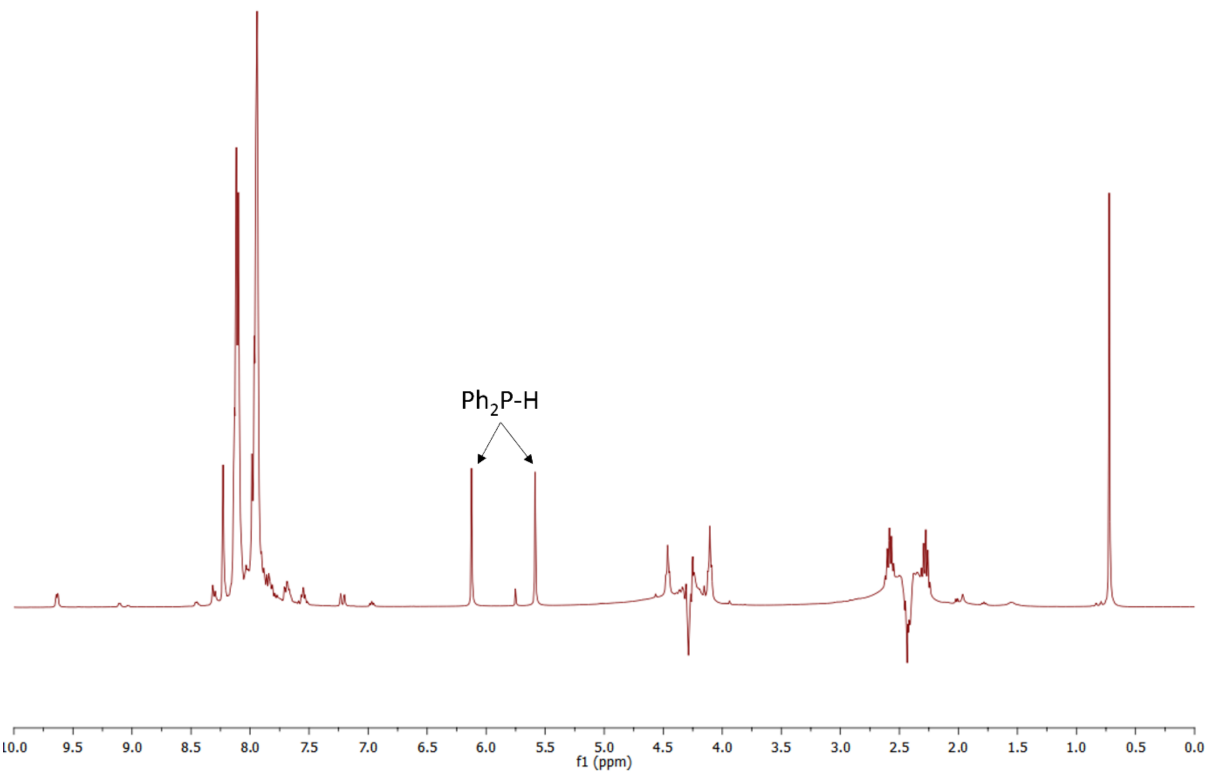


Figure S158: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 19 of Table S5.

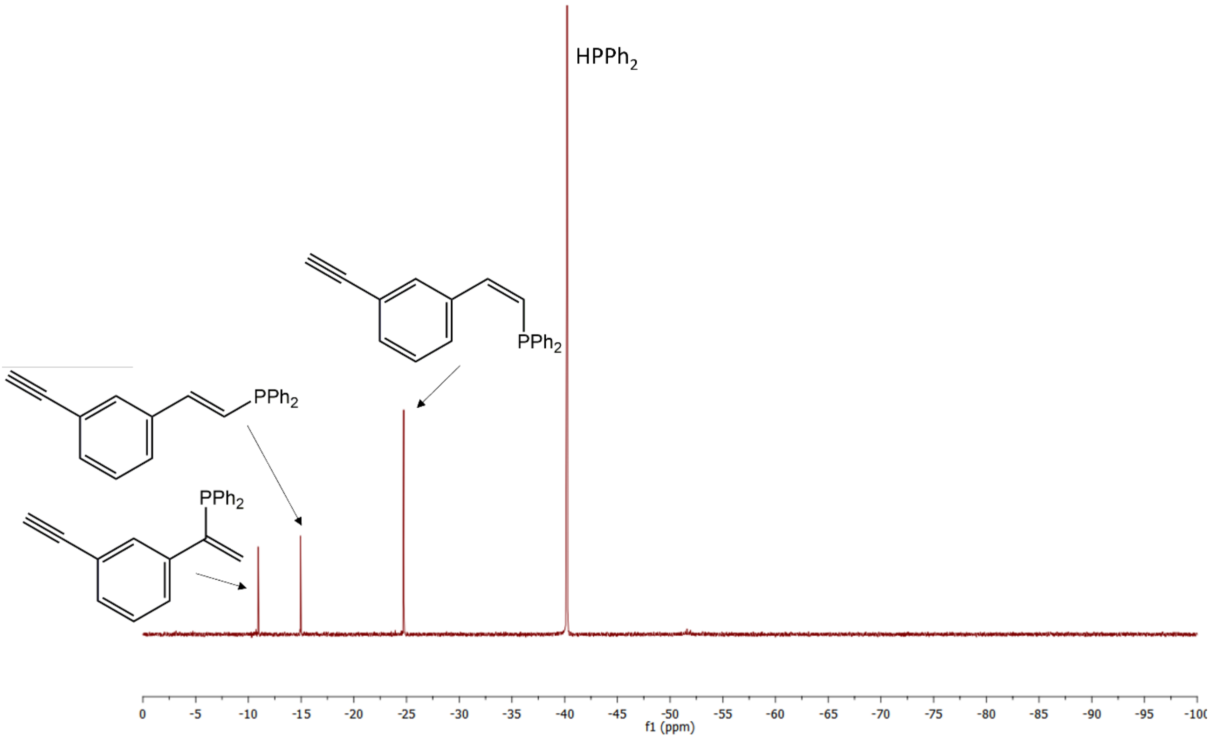


Figure S159: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 19 of Table S5.

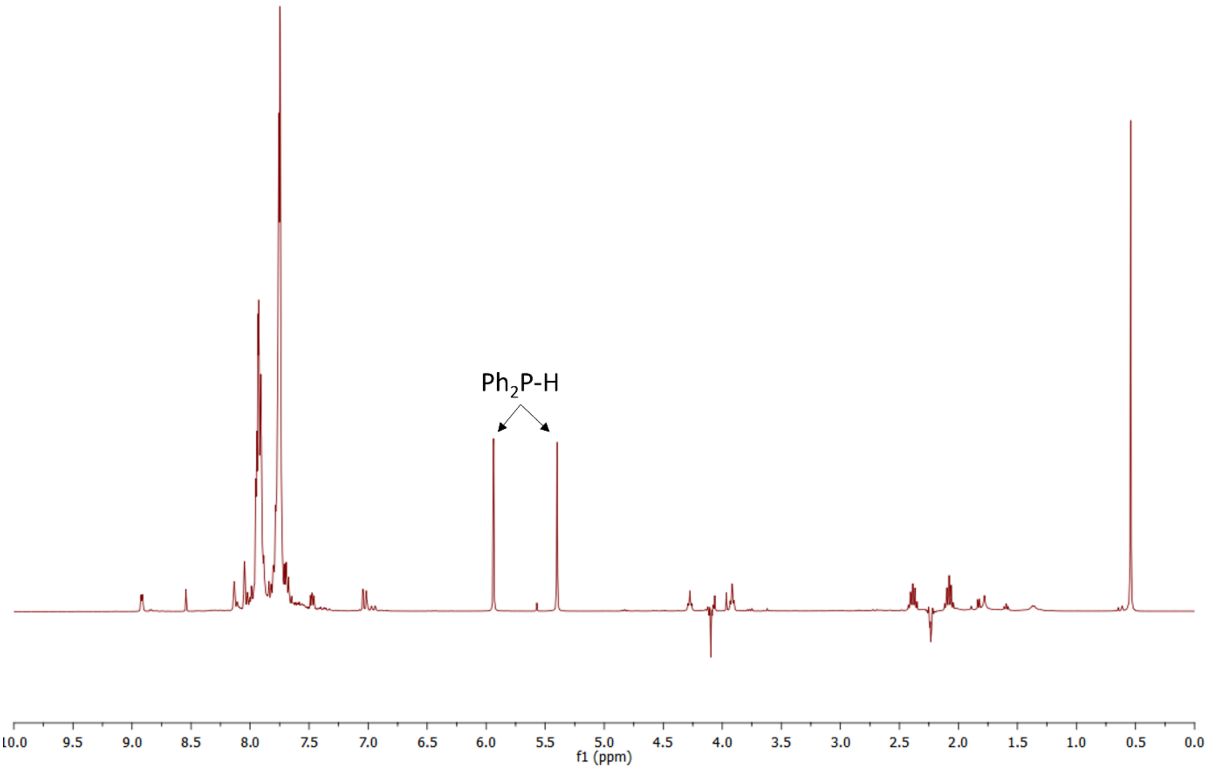


Figure S160: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 20 of Table S5.

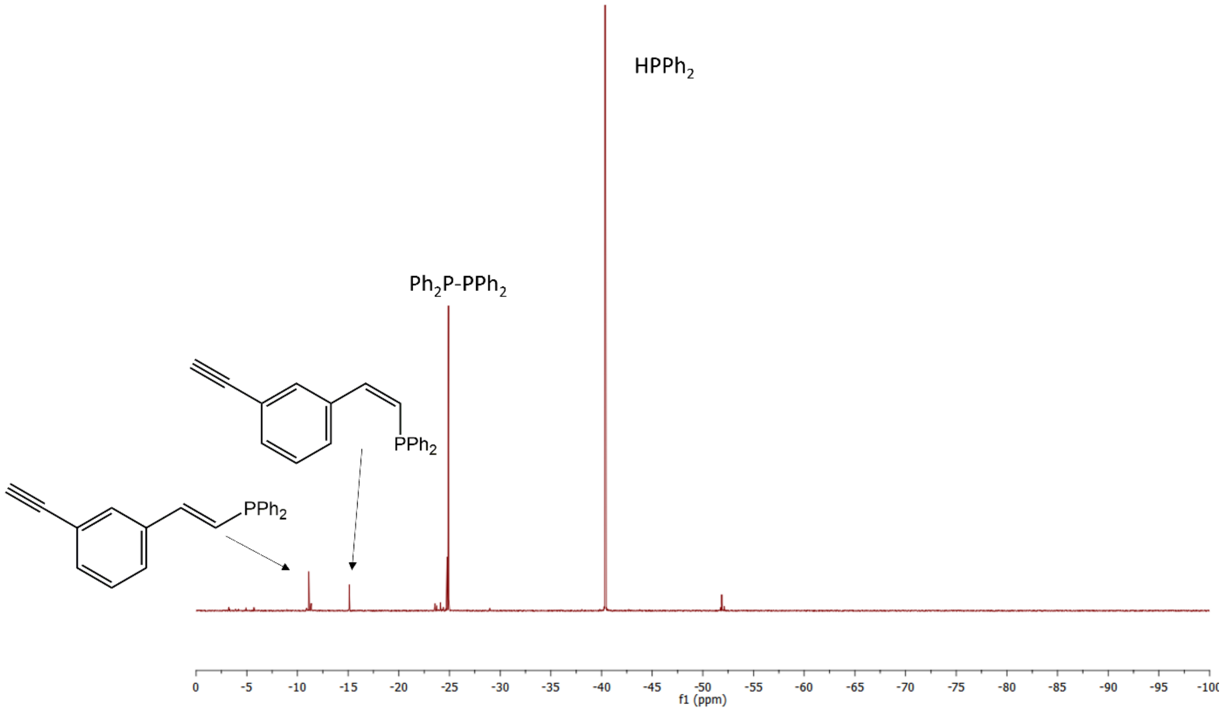


Figure S161: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 20 of Table S5.

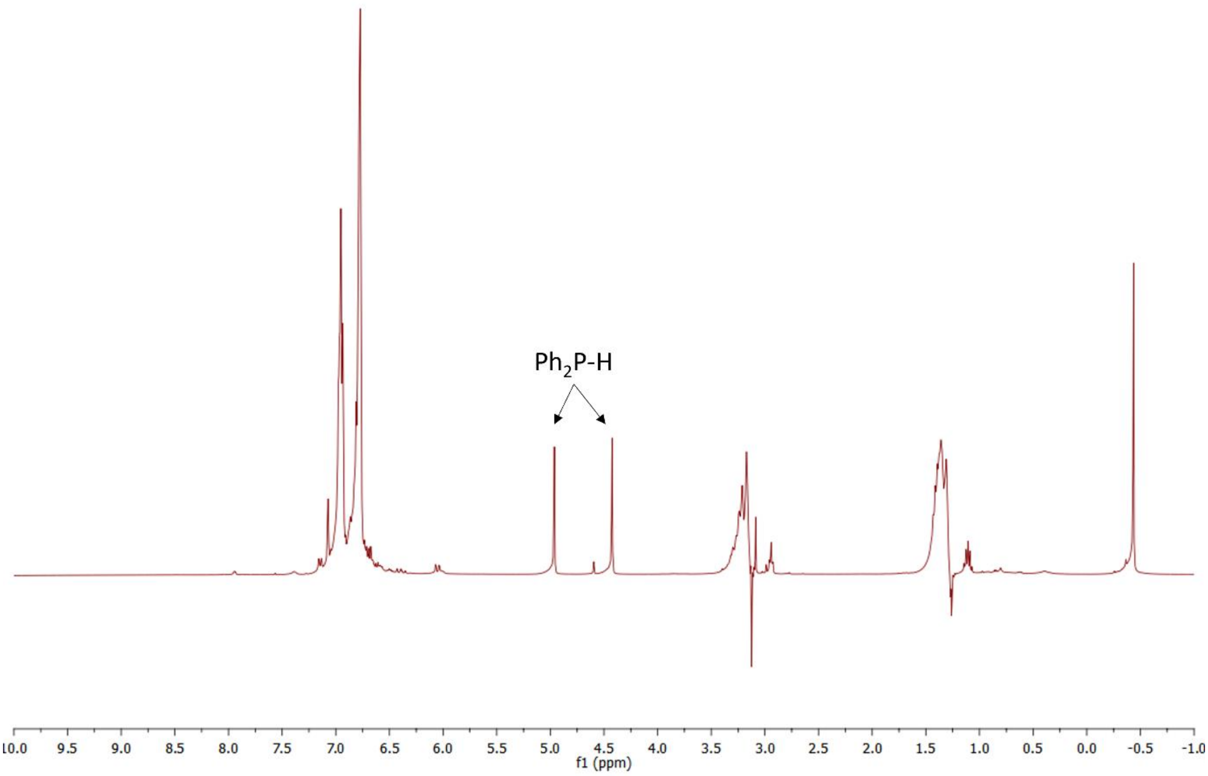


Figure S162: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 21 of Table S5.

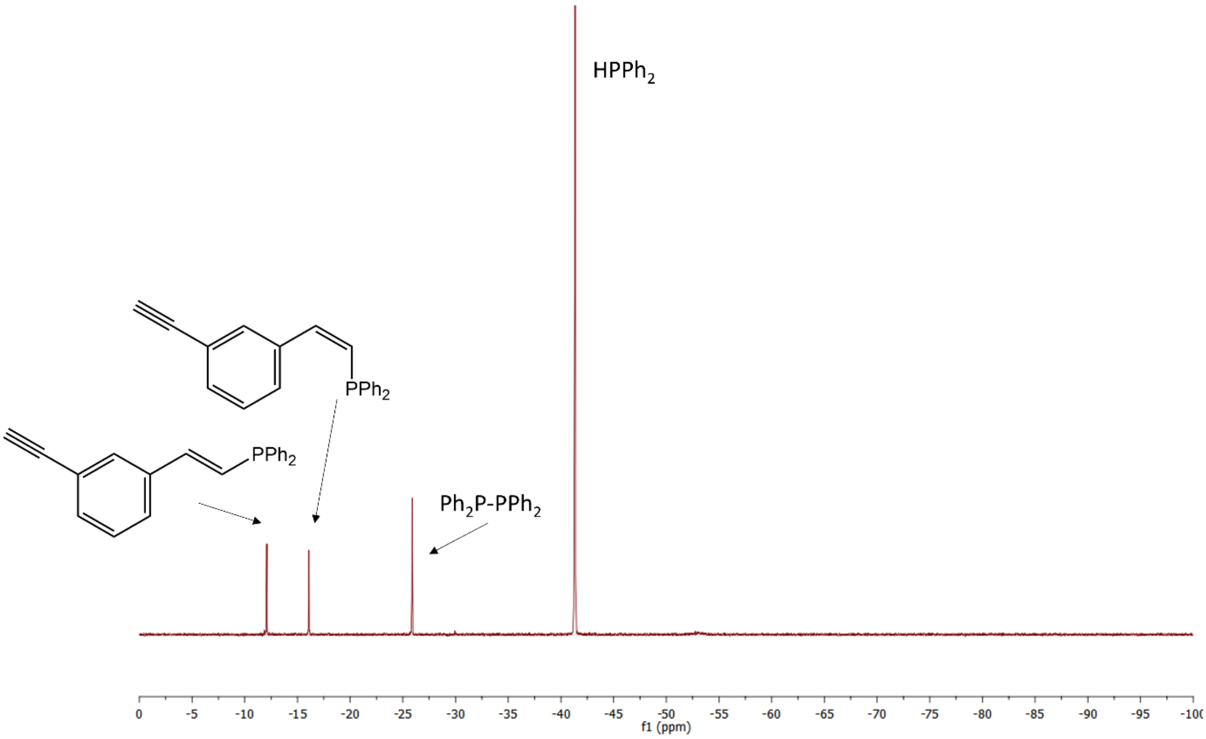


Figure S163: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 21 of Table S5.

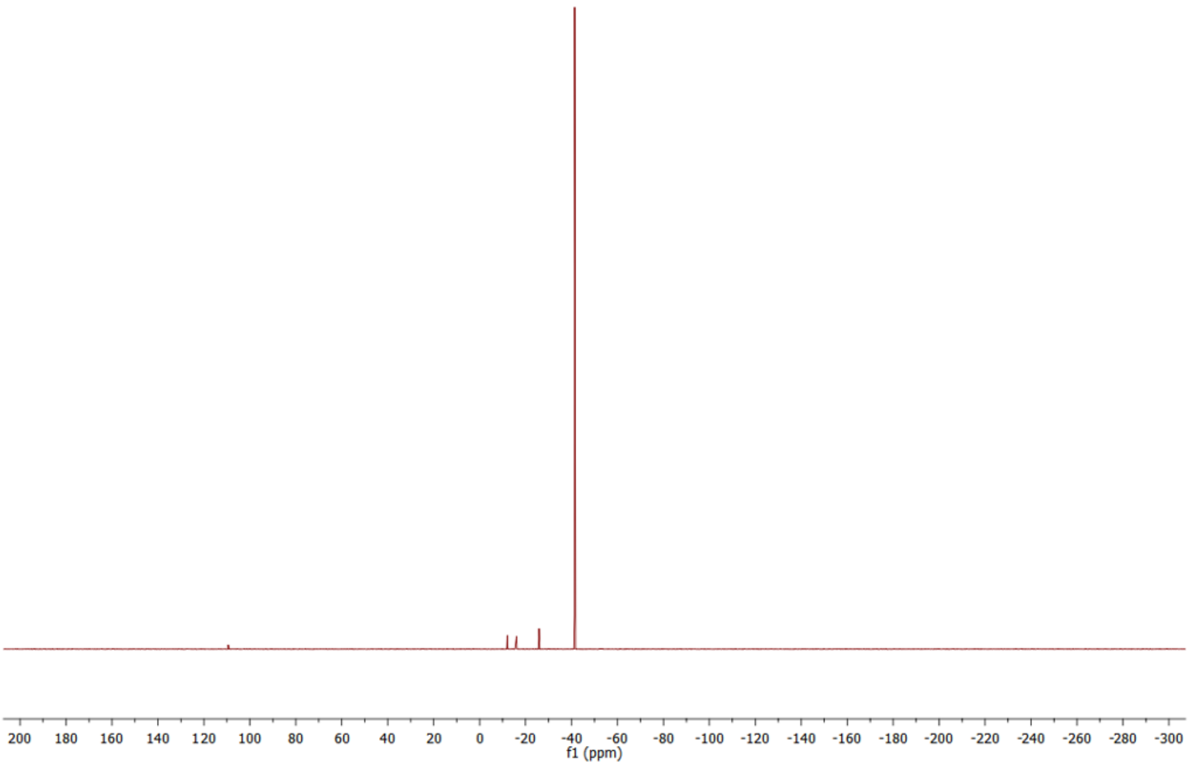


Figure S164: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) full spectrum for entry 21 of Table S5.

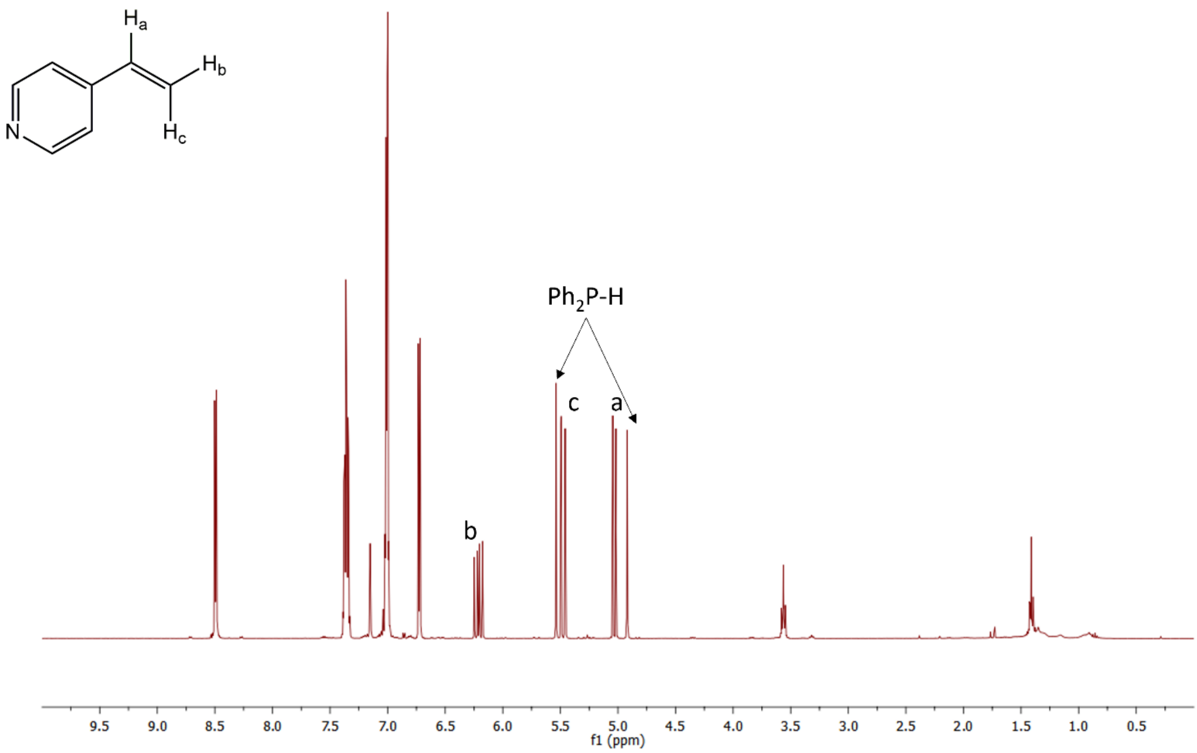


Figure S165: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 1 of Table S6.

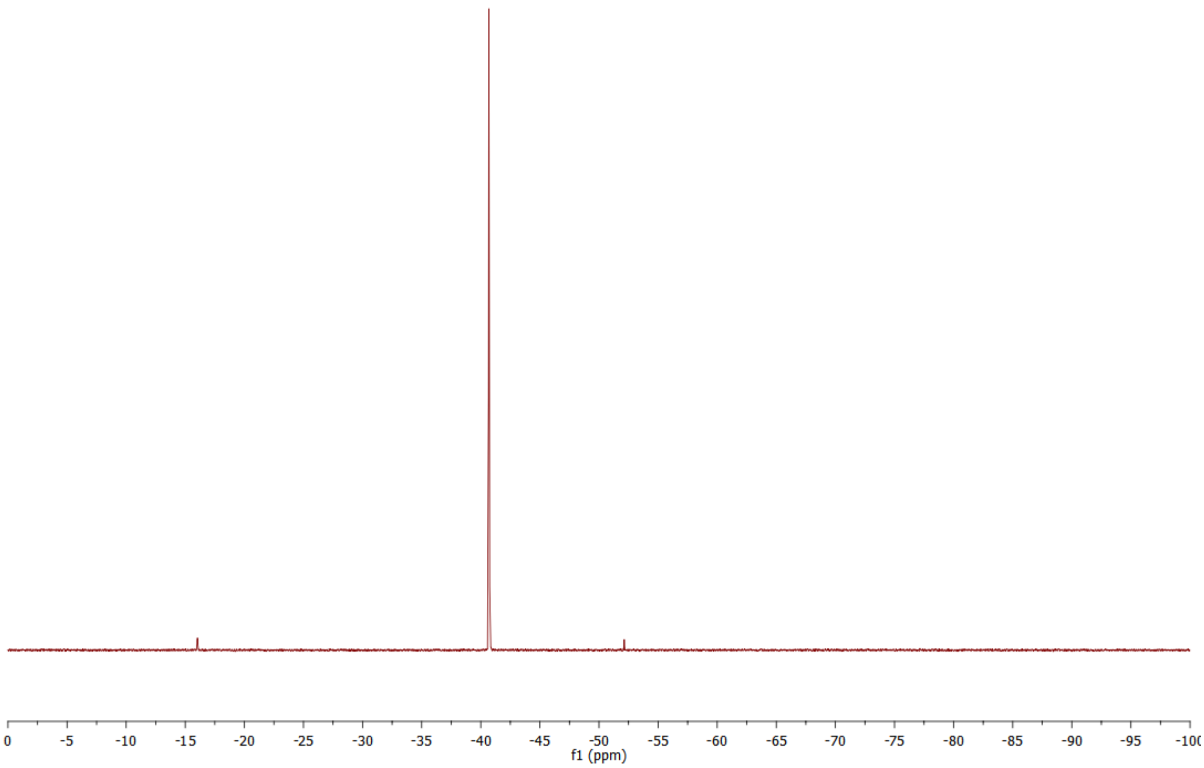


Figure S166: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 1 of Table S6.

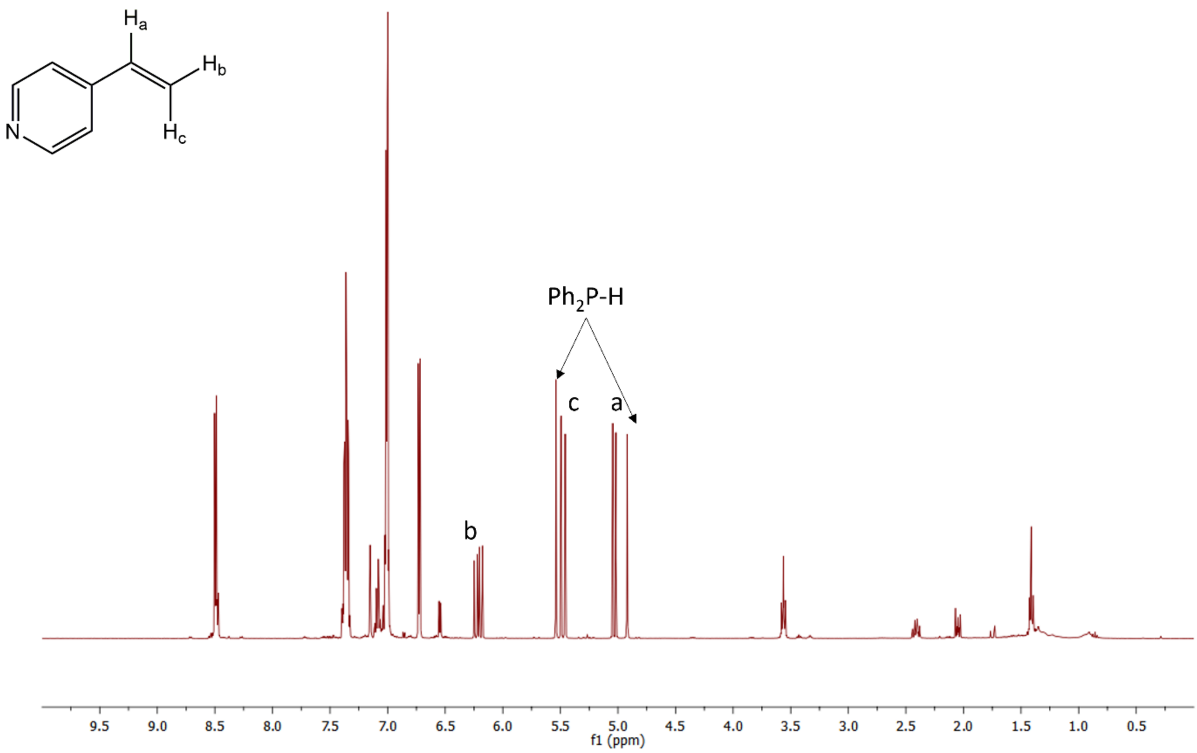


Figure S167: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 2 of Table S6.

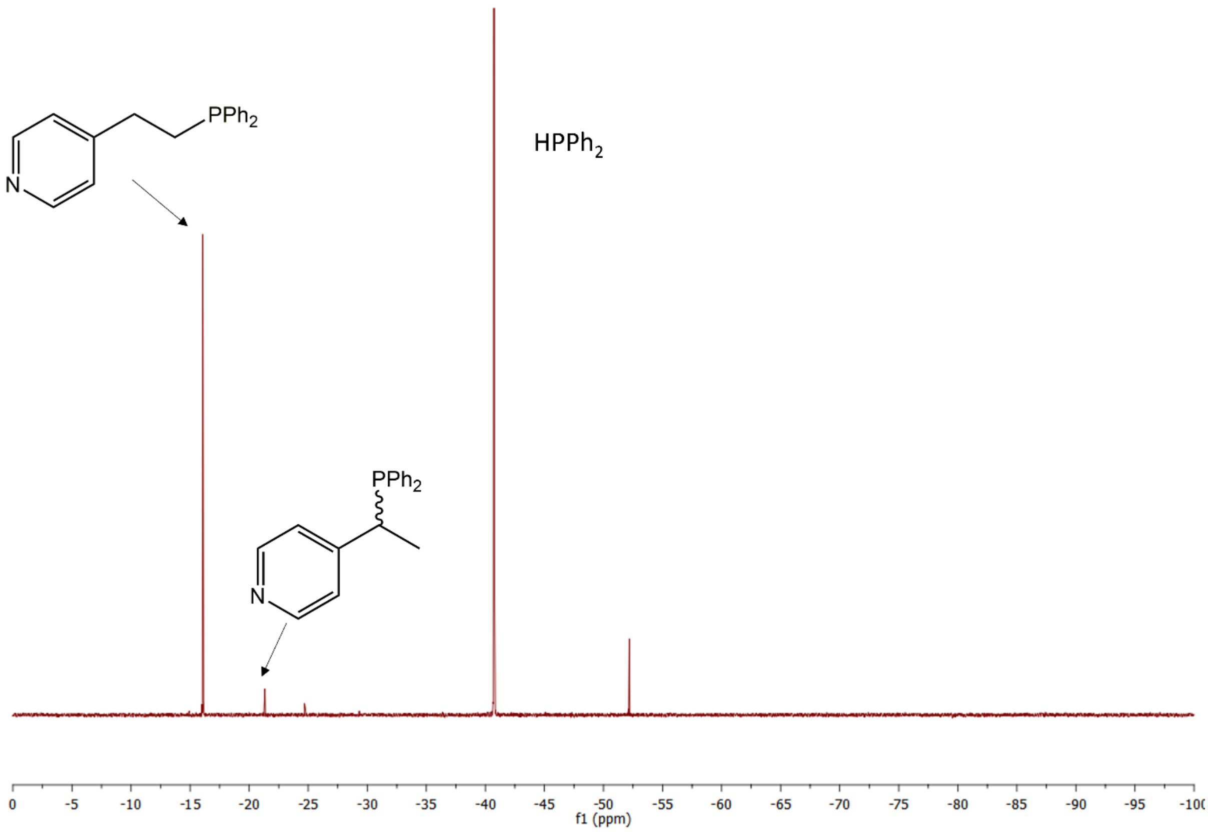


Figure S168: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 2 of Table S6.

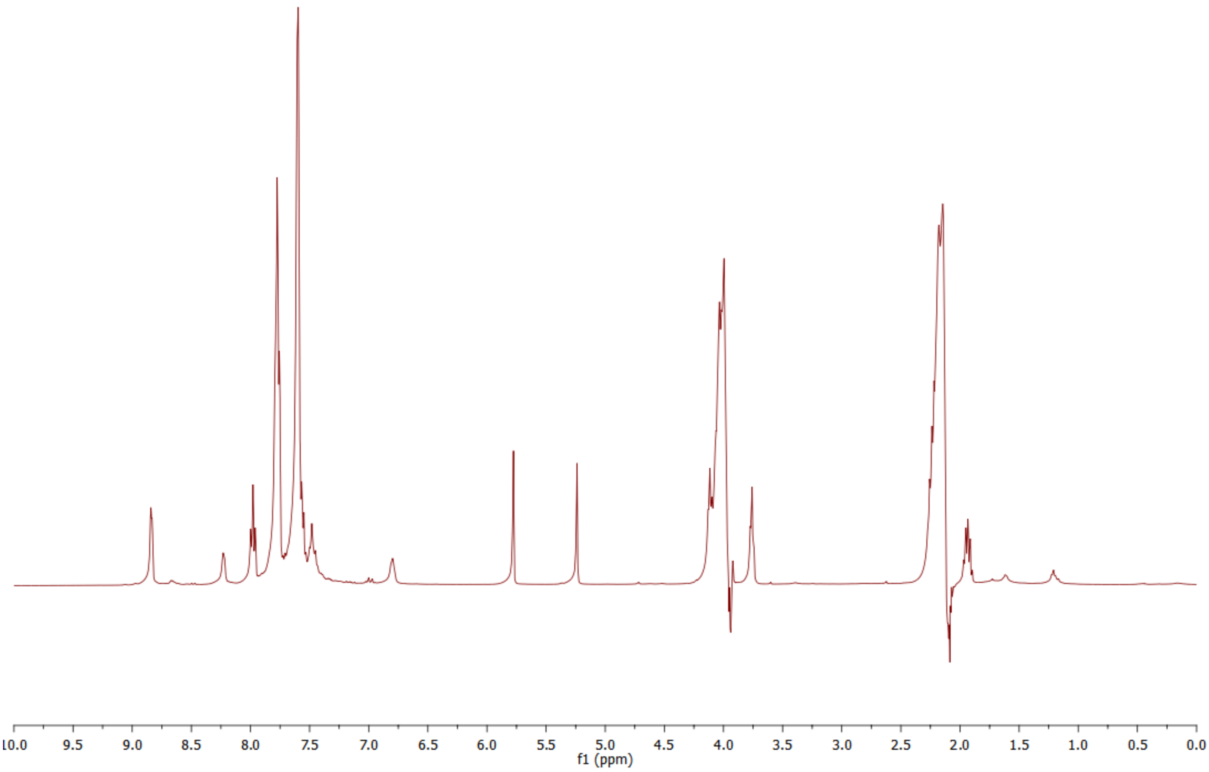


Figure S169: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 3 of Table S6.

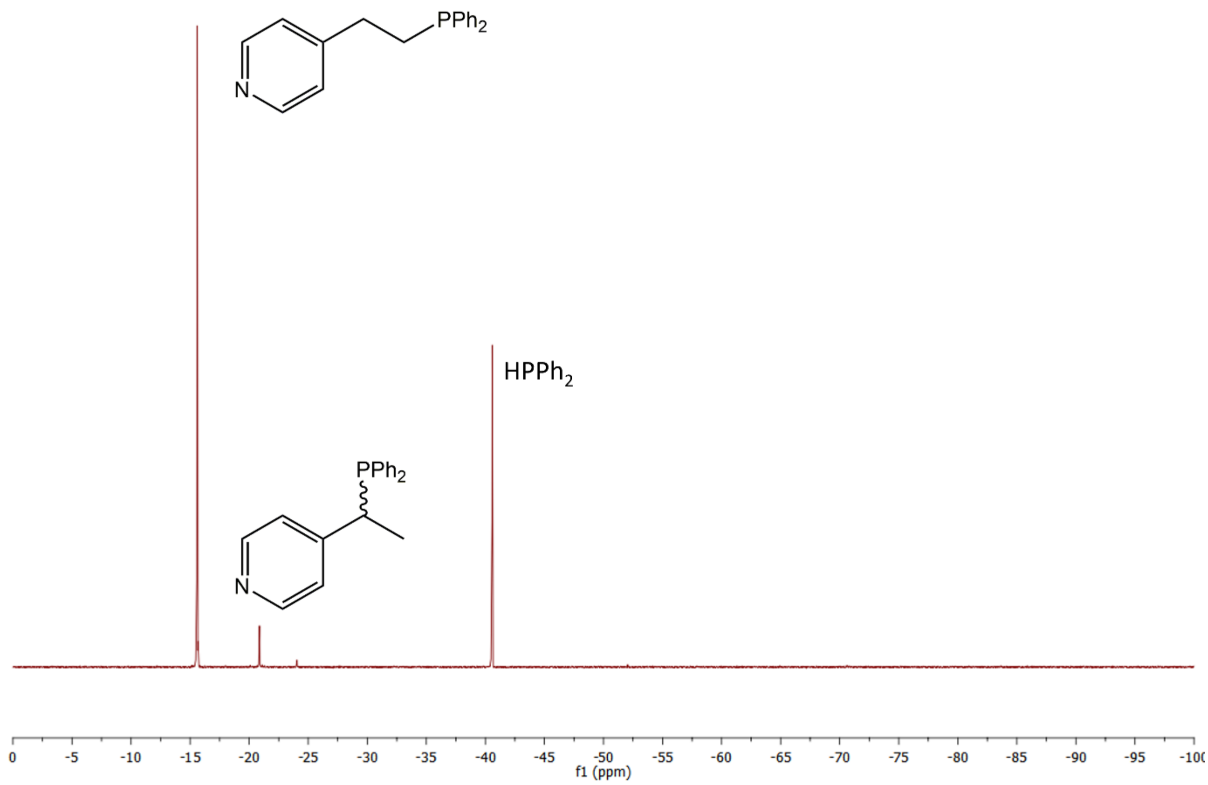


Figure S170: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 3 of Table S6.

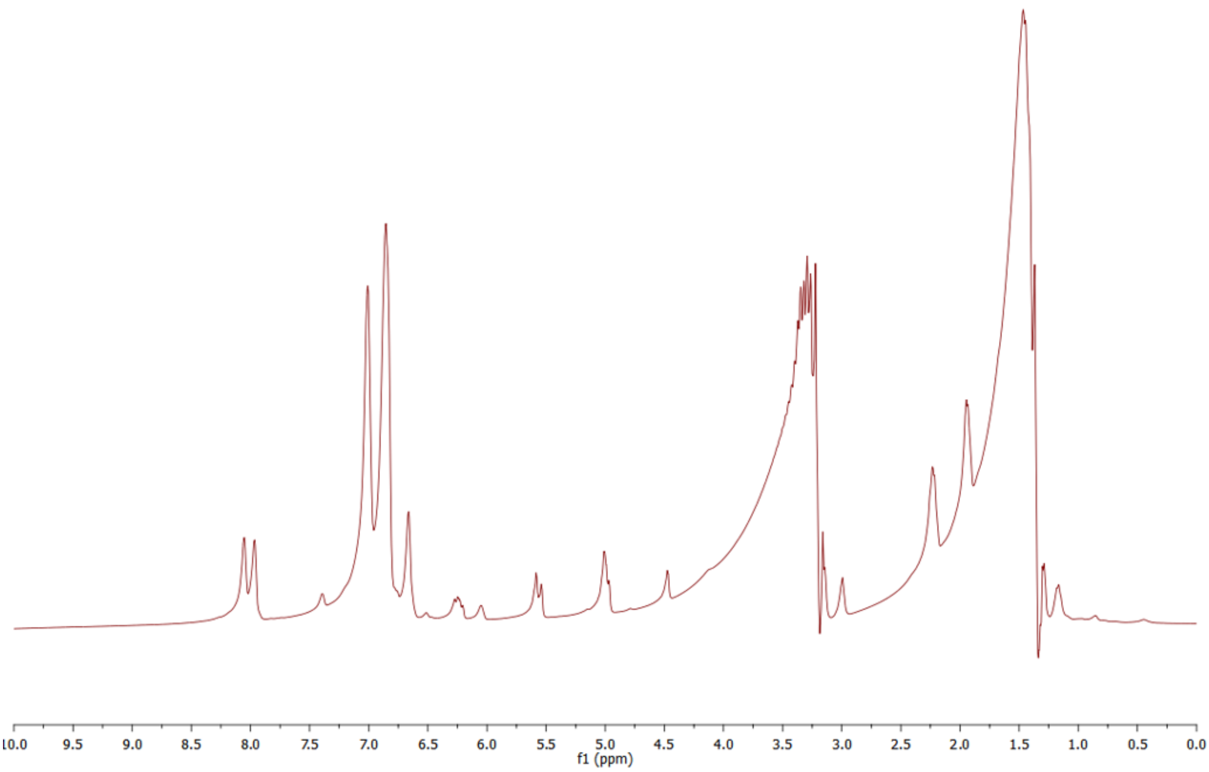


Figure S171: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 4 of Table S6.

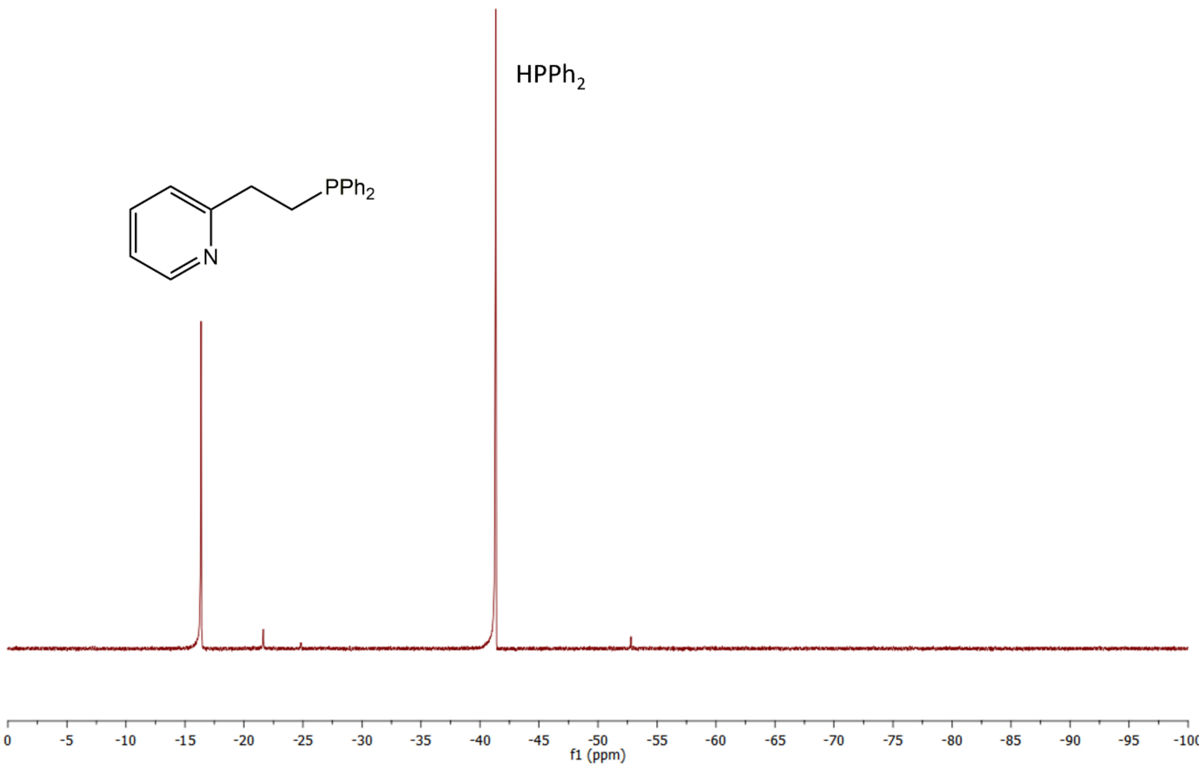


Figure S172: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 4 of Table S6.

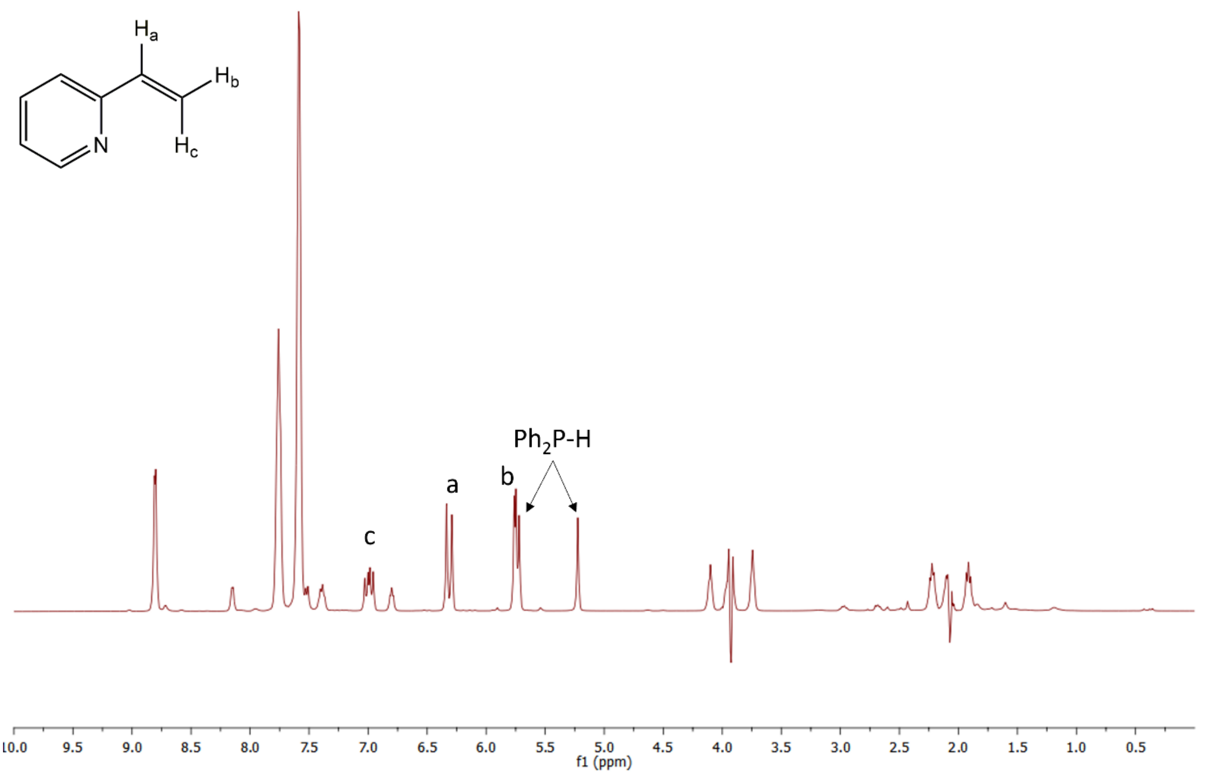


Figure S173: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 5 of Table S6.

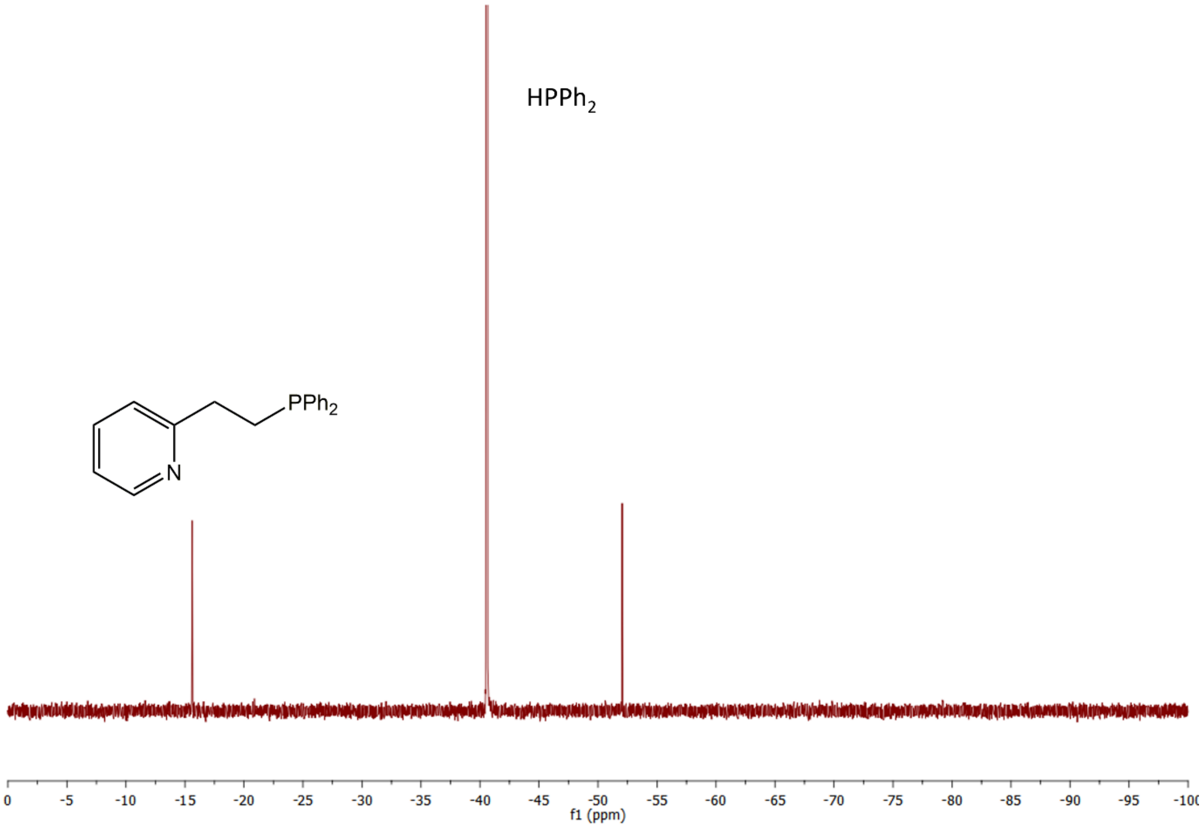


Figure S174: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 5 of Table S6.

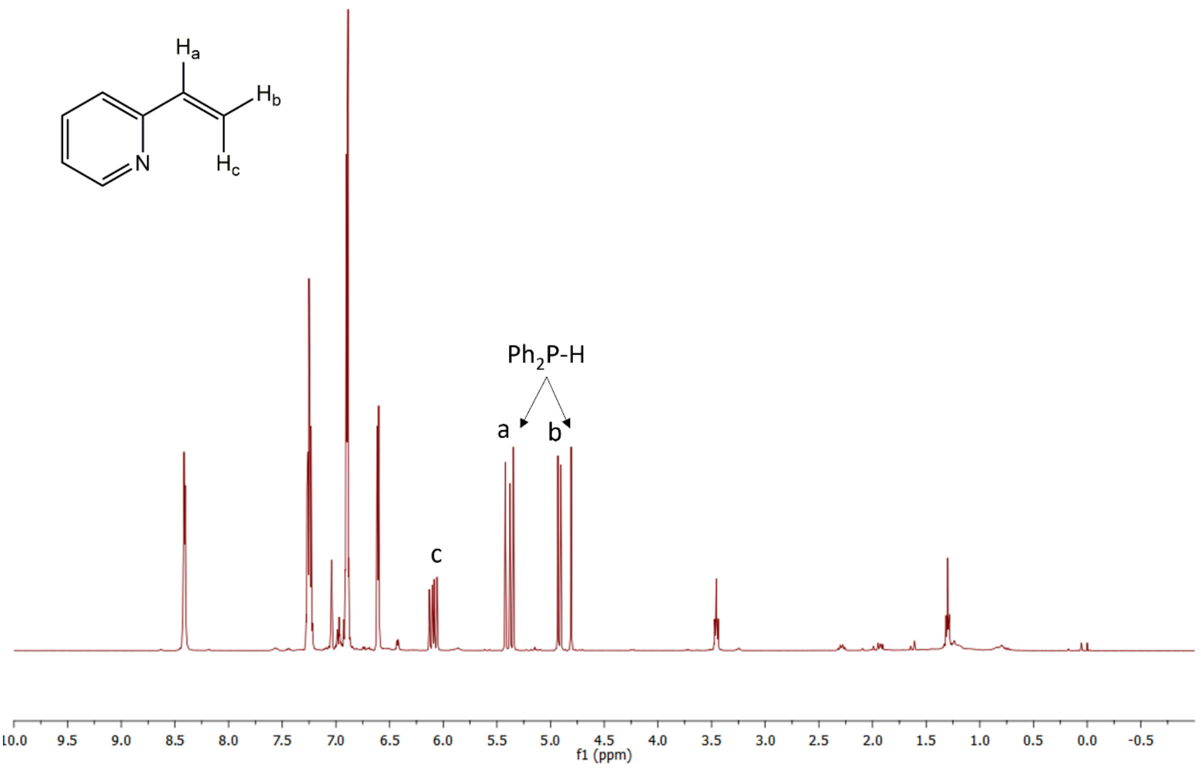


Figure S175: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 6 of Table S6.

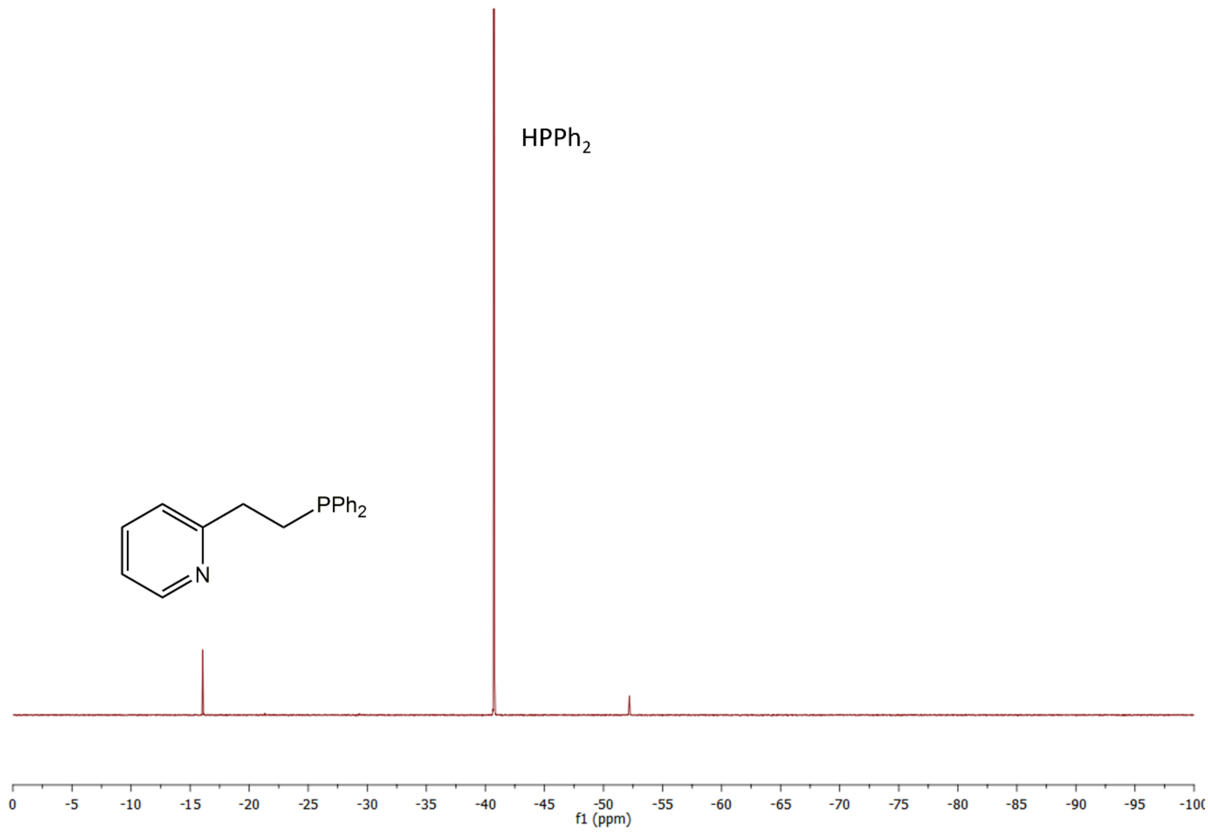


Figure S176: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 6 of Table S6.

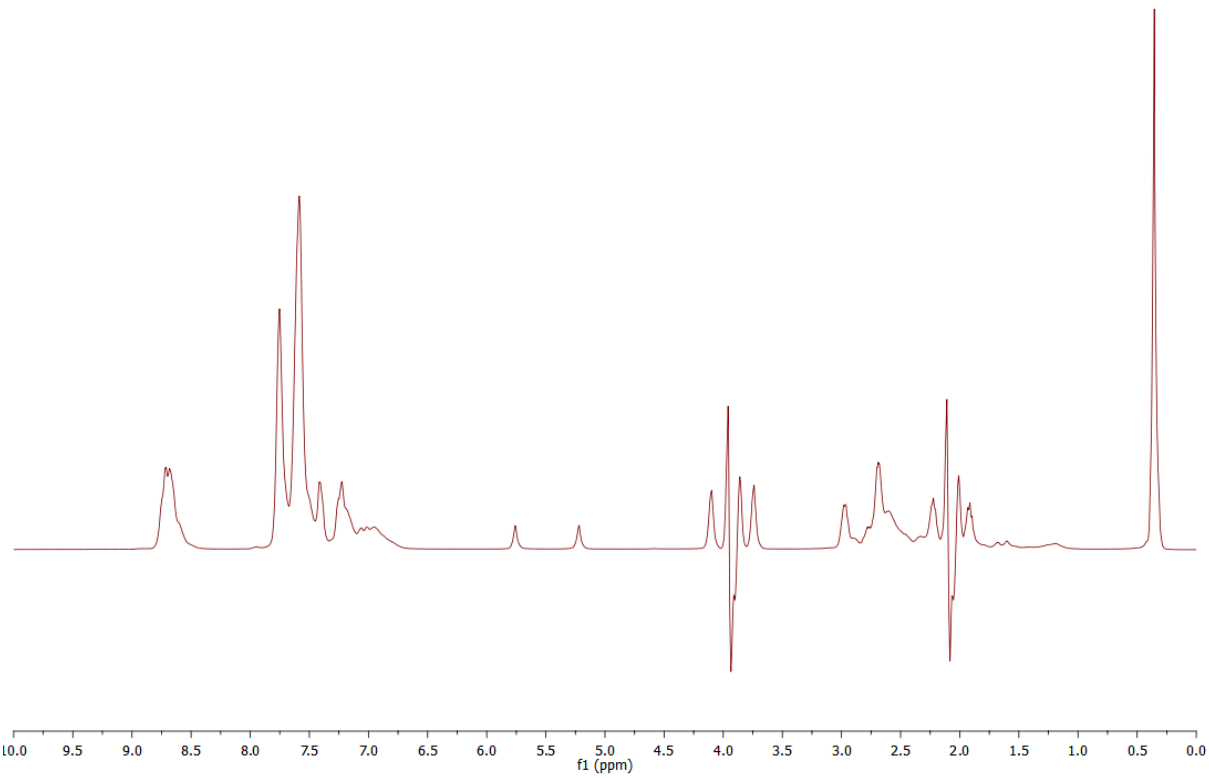


Figure S177: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 7 of Table S6.

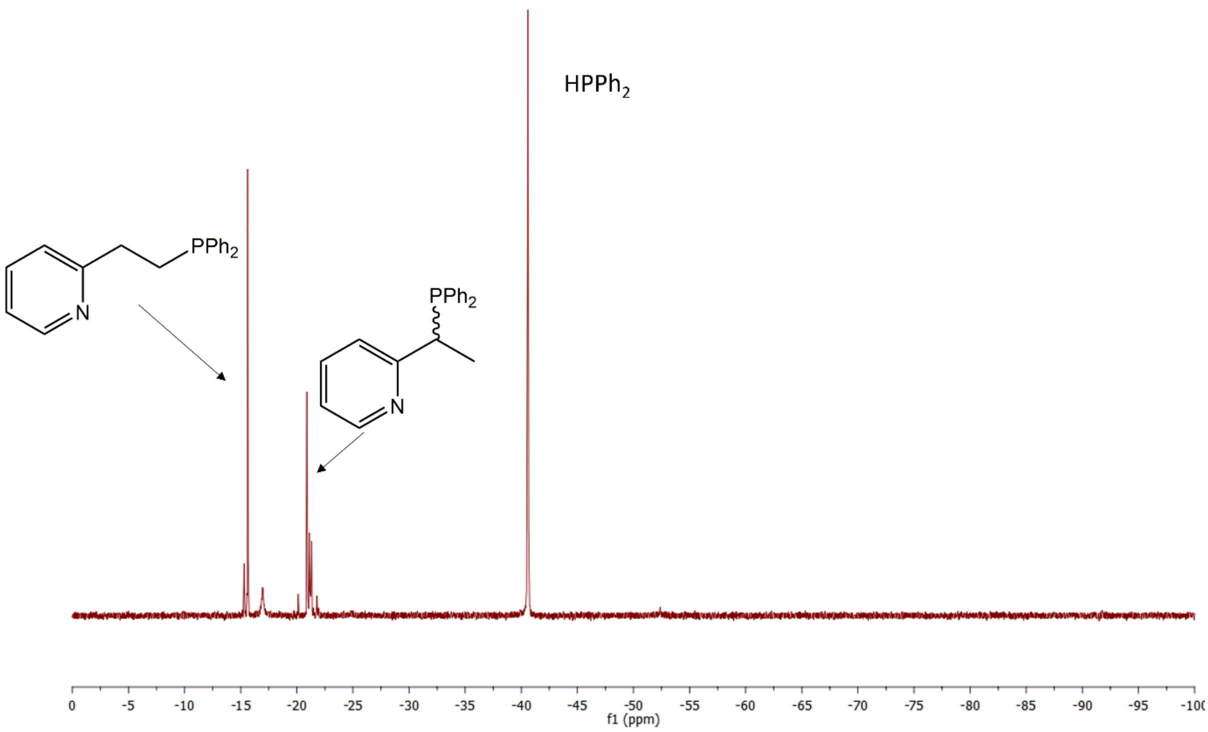


Figure S178: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 7 of Table S6.

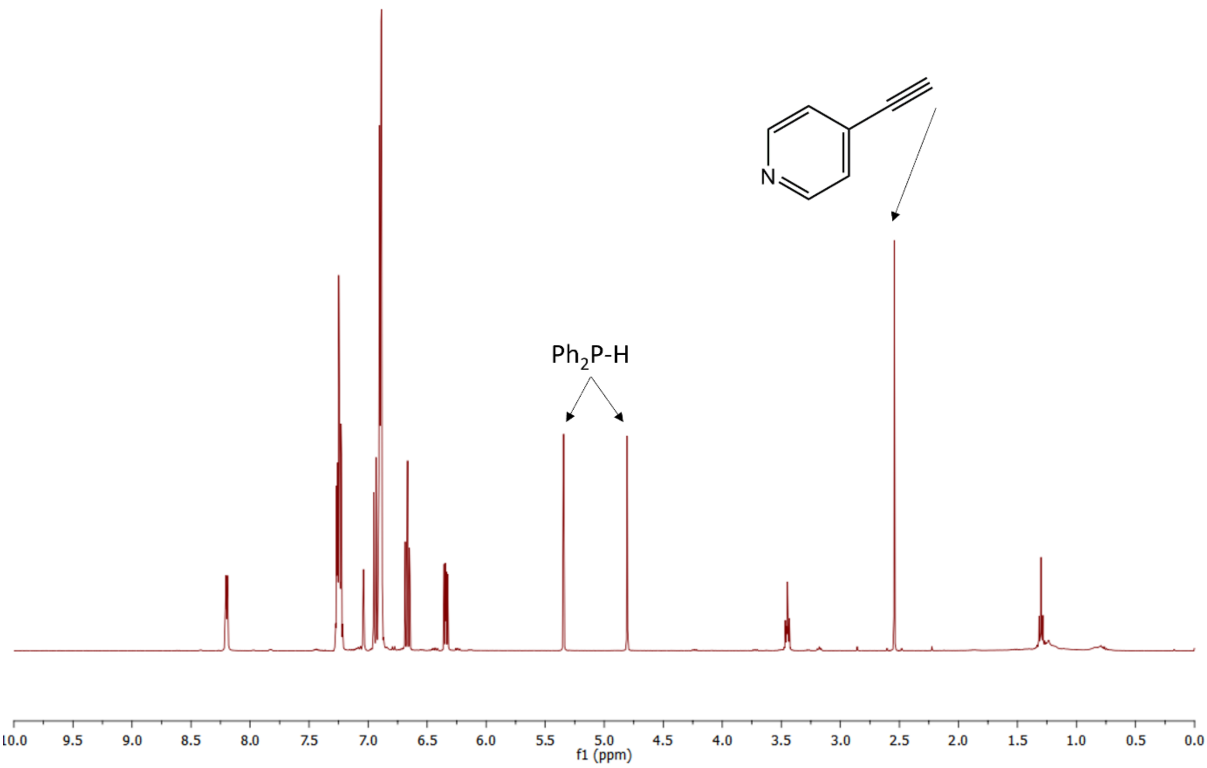


Figure S179: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 8 of Table S6.

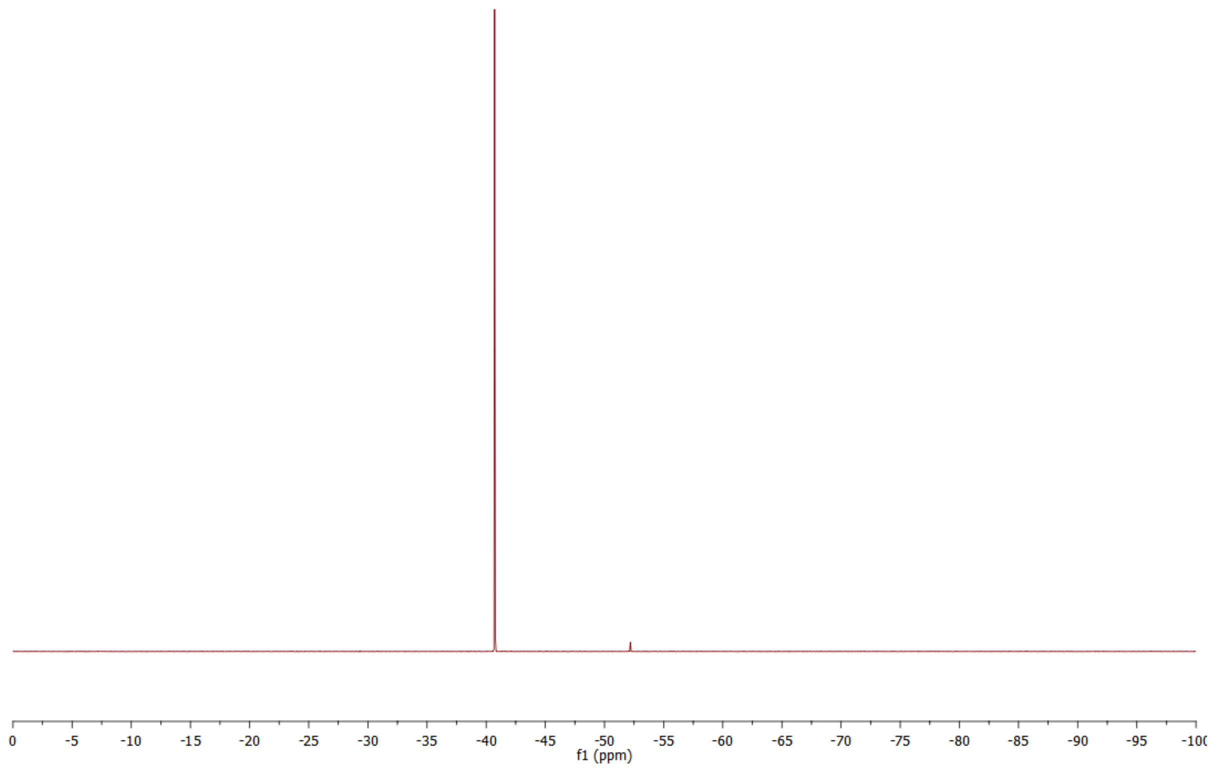


Figure S180: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 8 of Table S6.

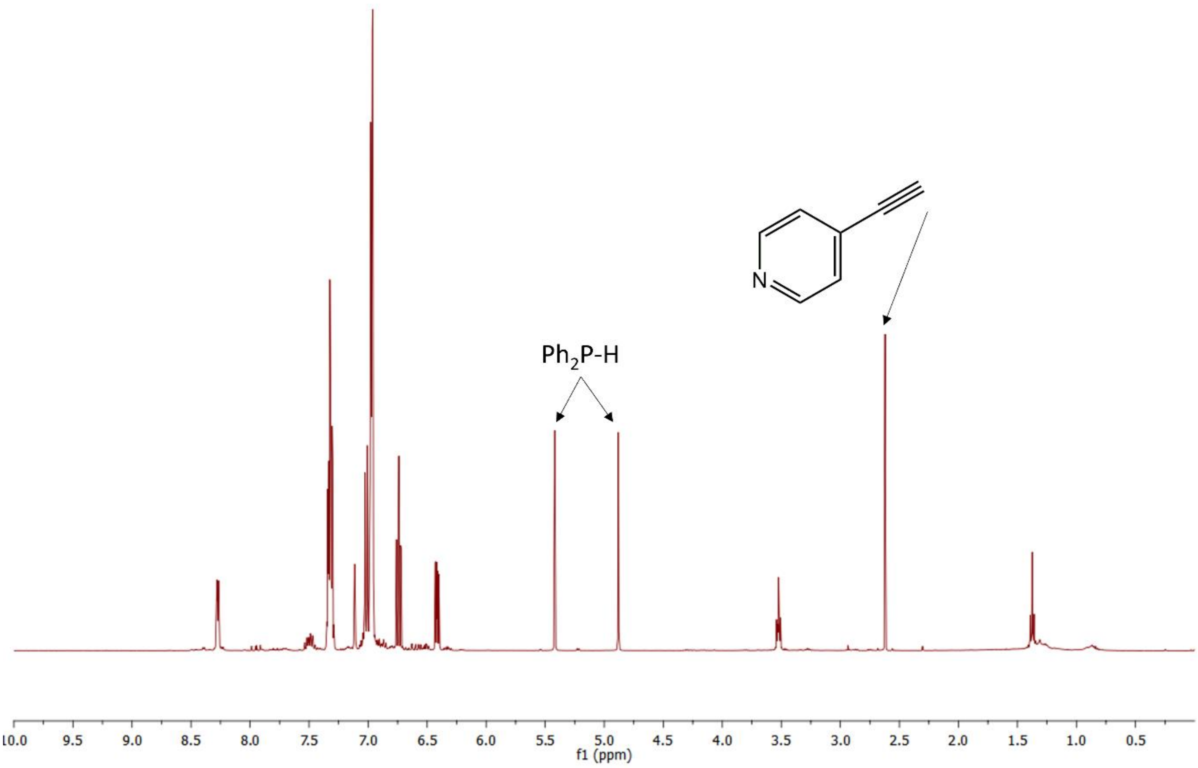


Figure S181: ^{1}H NMR (400 MHz, 298 K, C_6D_6) spectrum from 0 to 10 ppm for entry 9 of Table S6.

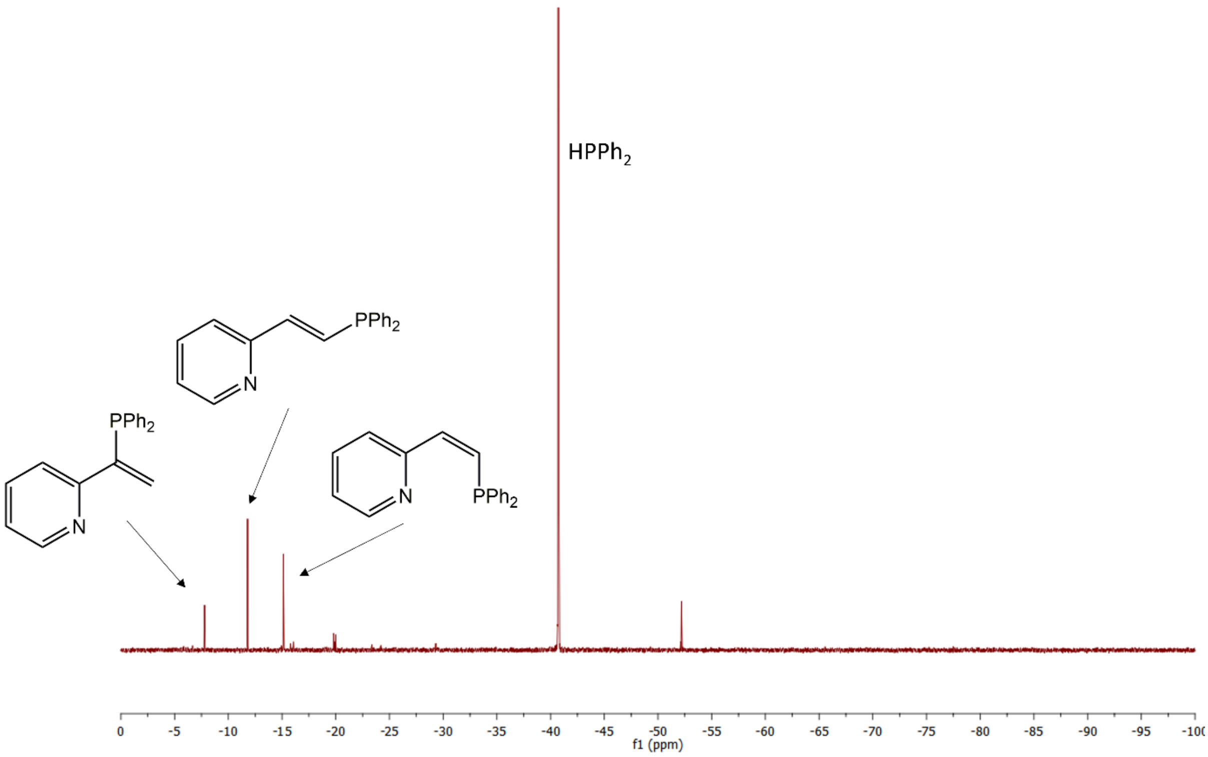


Figure S182: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) spectrum from 0 to -100 ppm for entry 9 of Table S6.

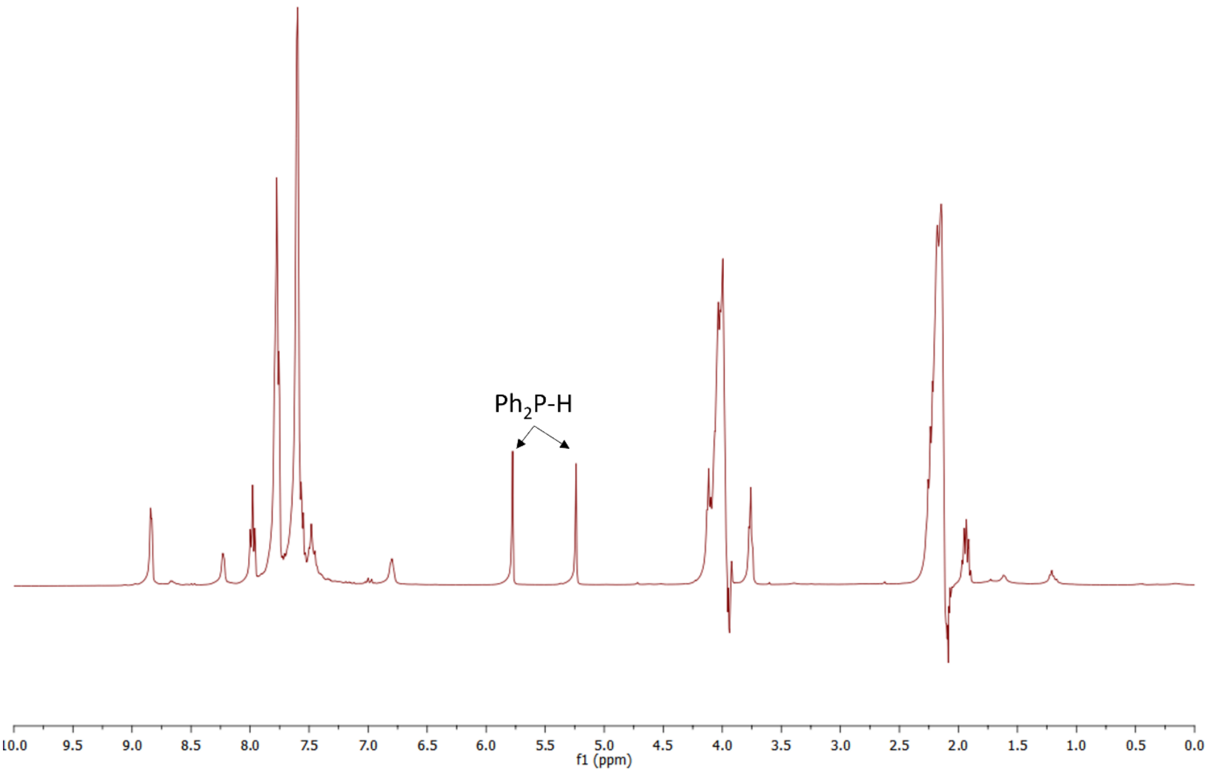


Figure S183: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 10 of Table S6.

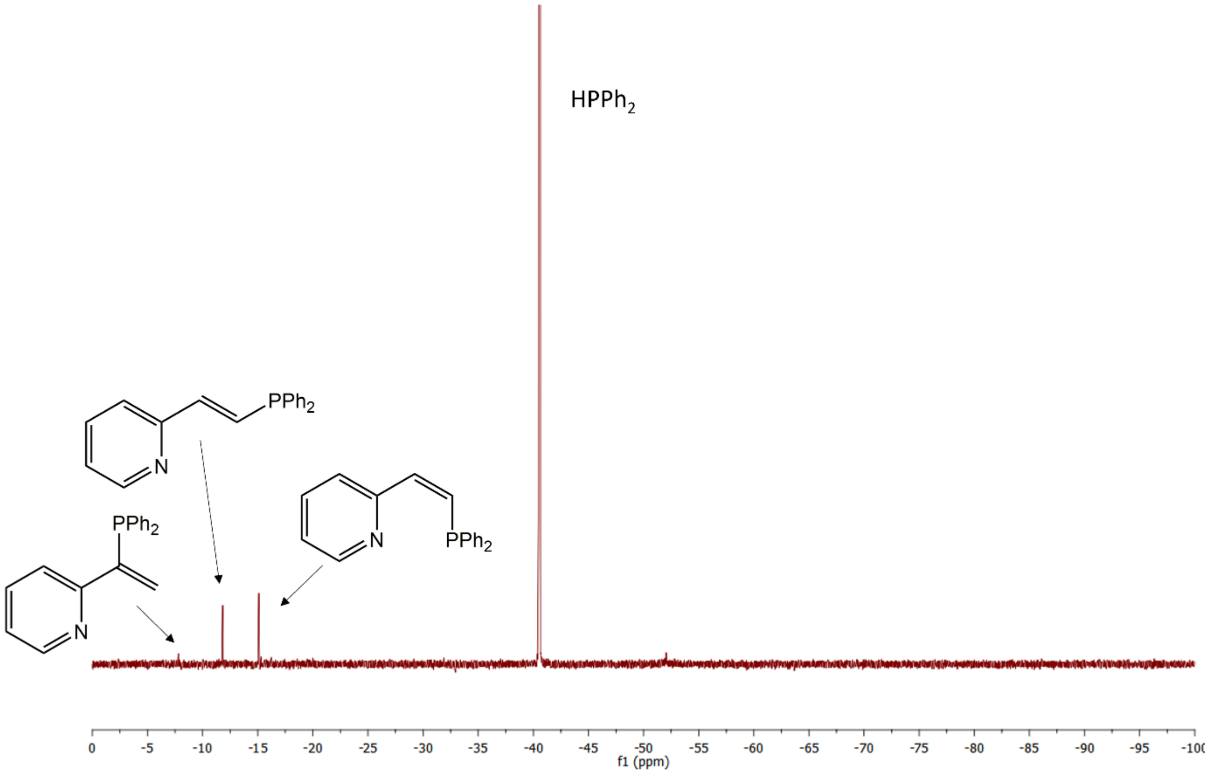


Figure S184: ^{31}P{^{1}H} NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 10 of Table S6.

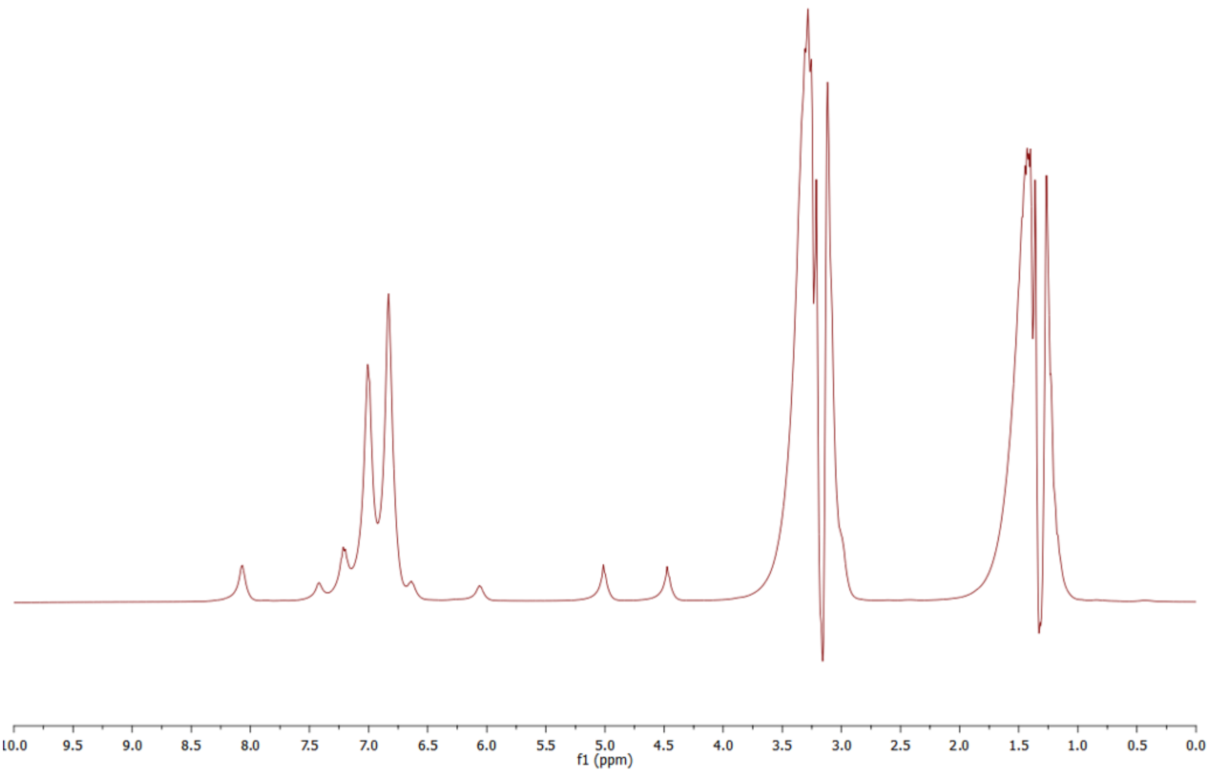


Figure S185: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for entry 11 of Table S6.

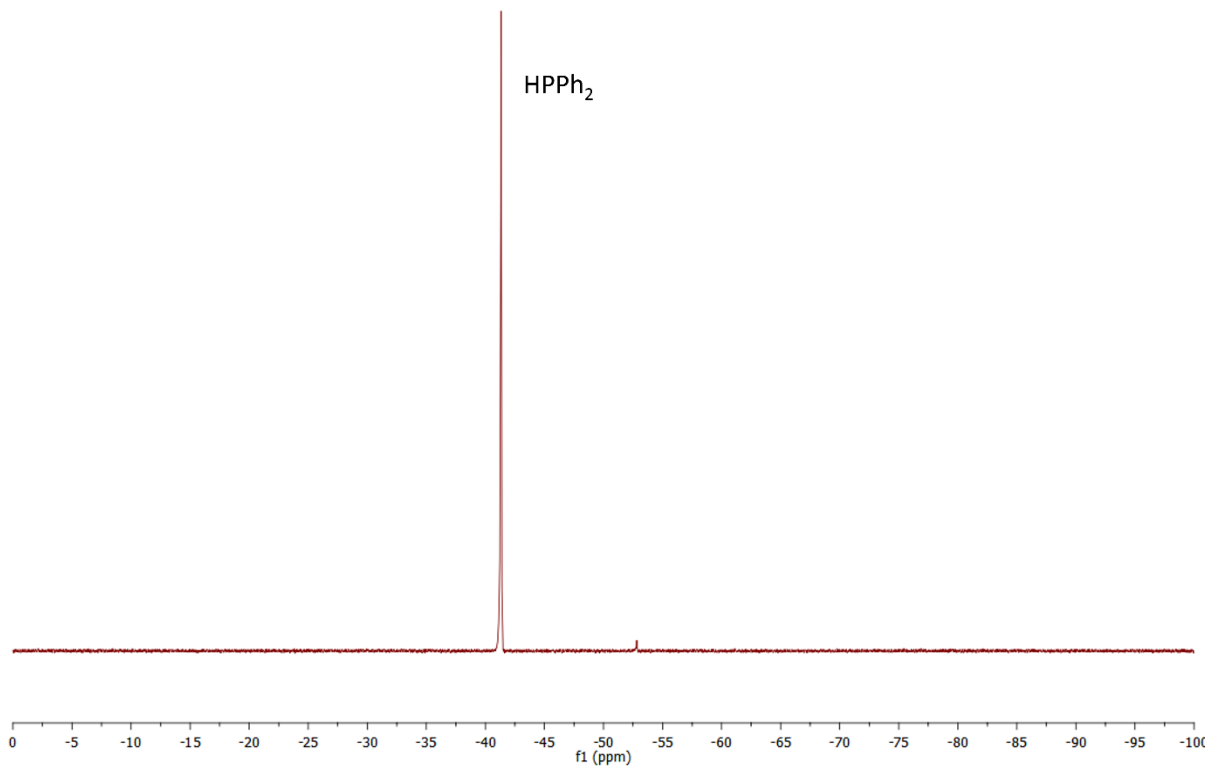


Figure S186: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from 0 to -100 ppm for entry 11 of Table S6.

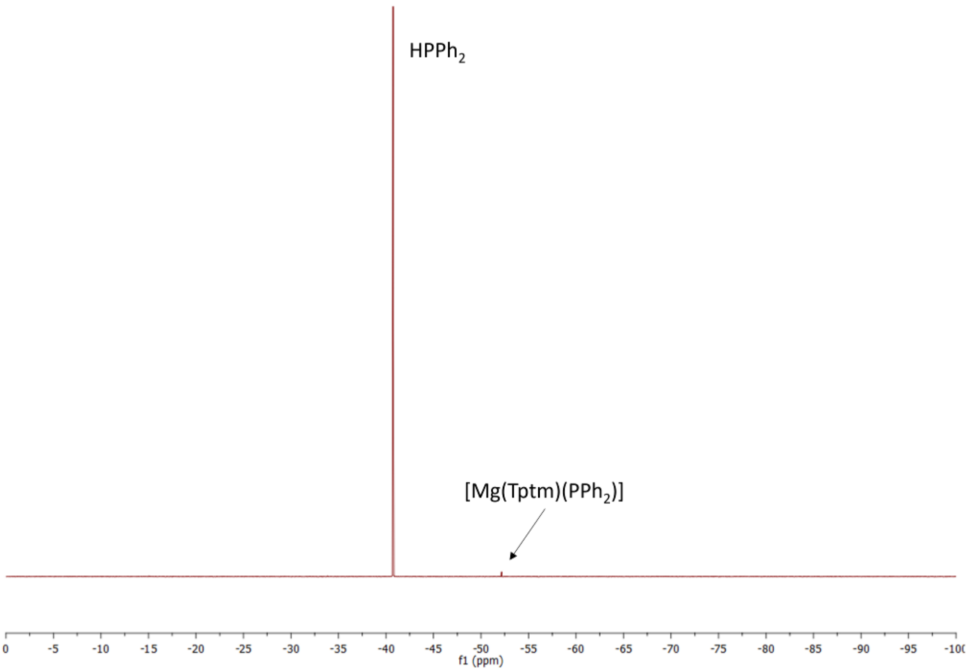


Figure S187: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) from −100 to 0 ppm for the attempted hydrophosphination of maleonitrile, NCC(H)=C(H)CN, with **3-Mg**.

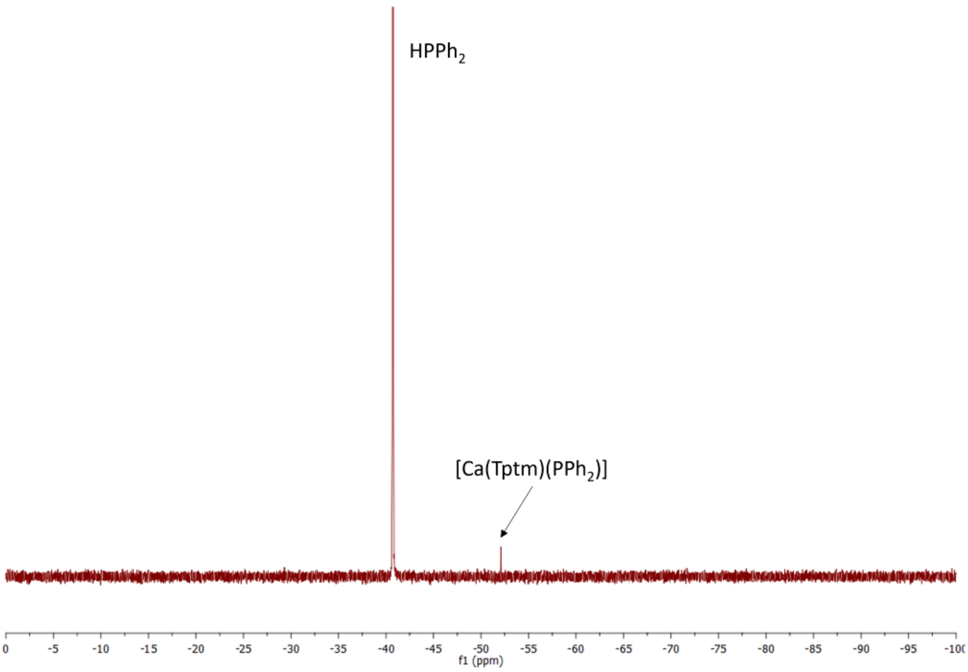


Figure S188: $^{31}P\{^{1}H\}$ NMR(160 MHz, 298 K, C_6D_6) spectrum from −100 to 0 ppm for the attempted hydrophosphination of maleonitrile, NCC(H)=C(H)CN, with **3-Ca**.

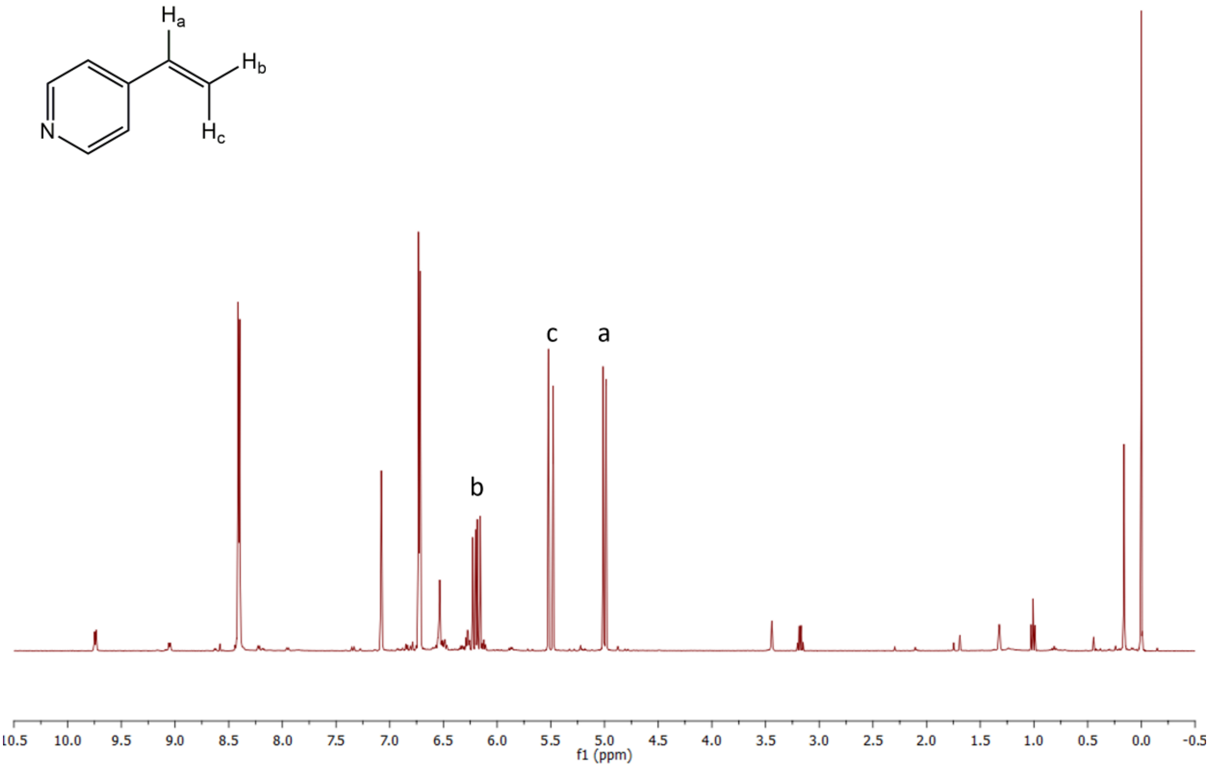


Figure S189: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum of polymerisation test of 4-vinylpyridine by **3-Mg** after 1 week.

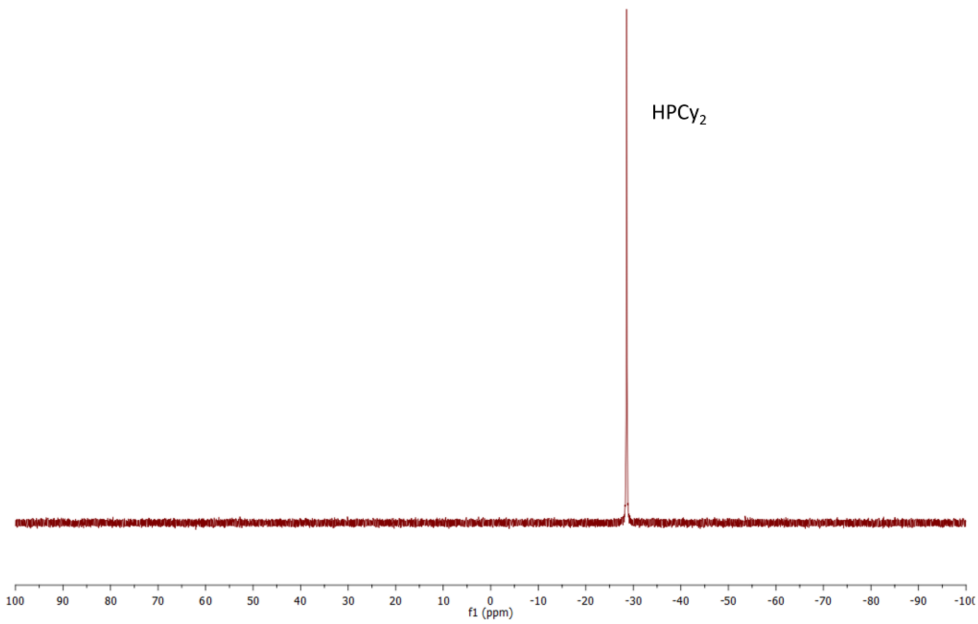


Figure S190: $^{31}P\{^1H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of styrene with $HPCy_2$ by **3-Mg** in THF at room temperature after 1 week.

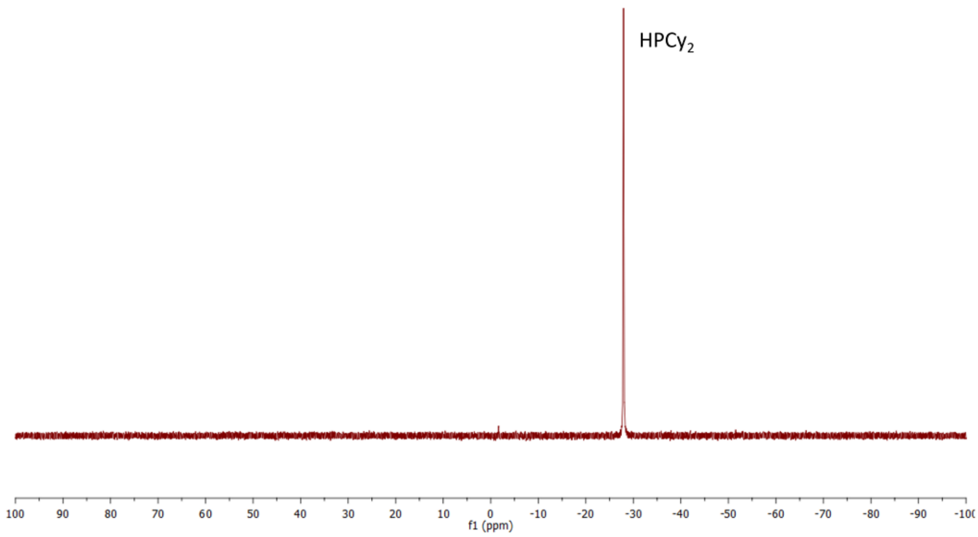


Figure S191: $^{31}P\{^1H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of acrylonitrile with $HPCy_2$ by **3-Mg** in THF at room temperature after 1 week.

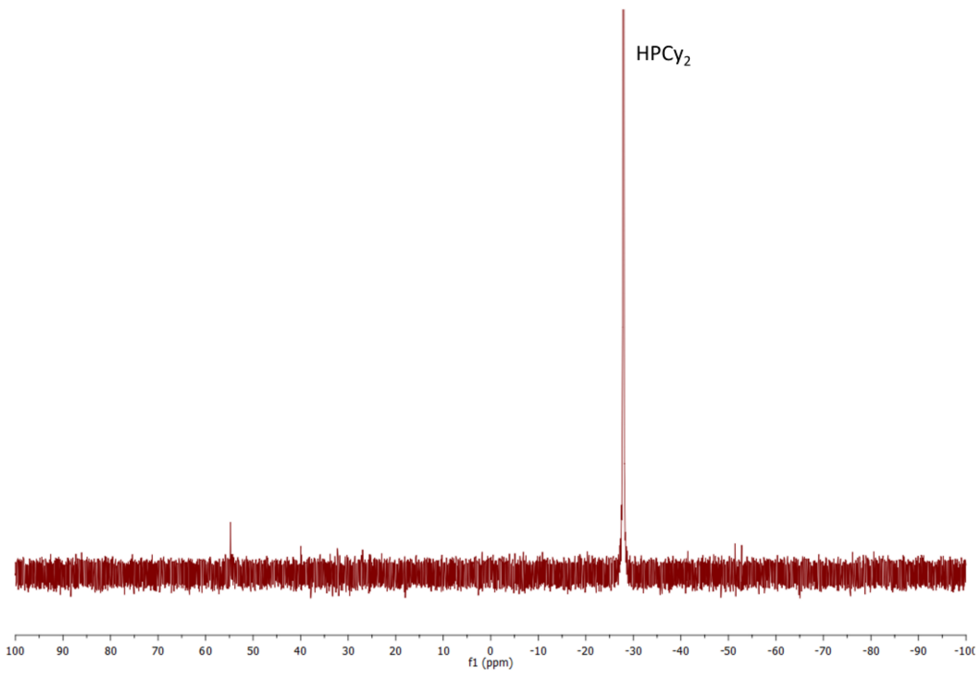


Figure S192: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of 2-vinylpyridine with $HPCy_2$ by **3-Mg** in THF at room temperature after 1 week.

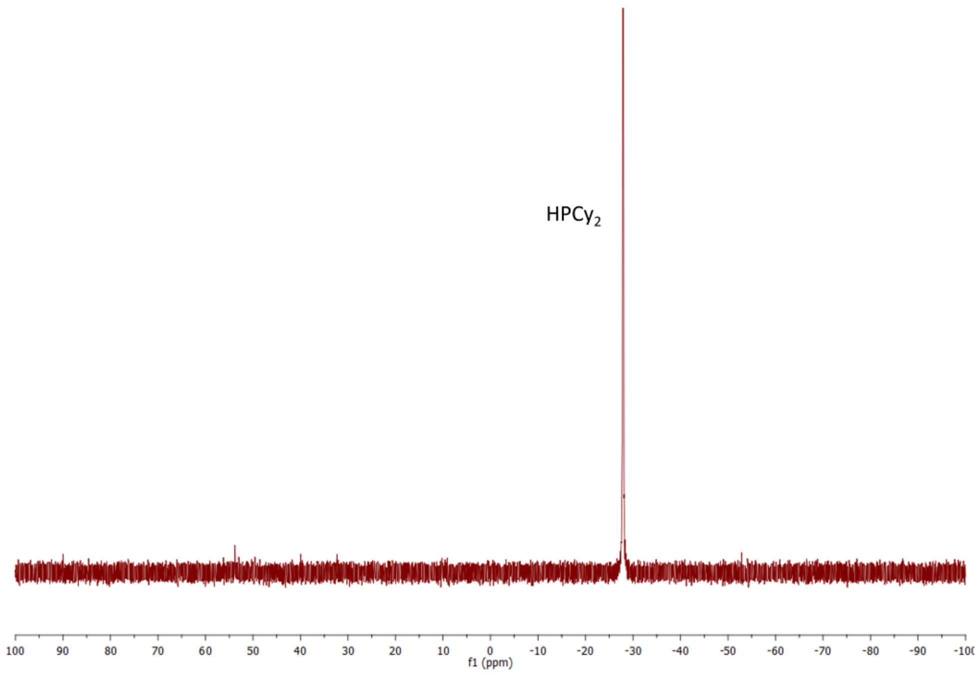


Figure S193: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of 4-vinylpyridine with $HPCy_2$ by **3-Mg** in THF at room temperature after 1 week.

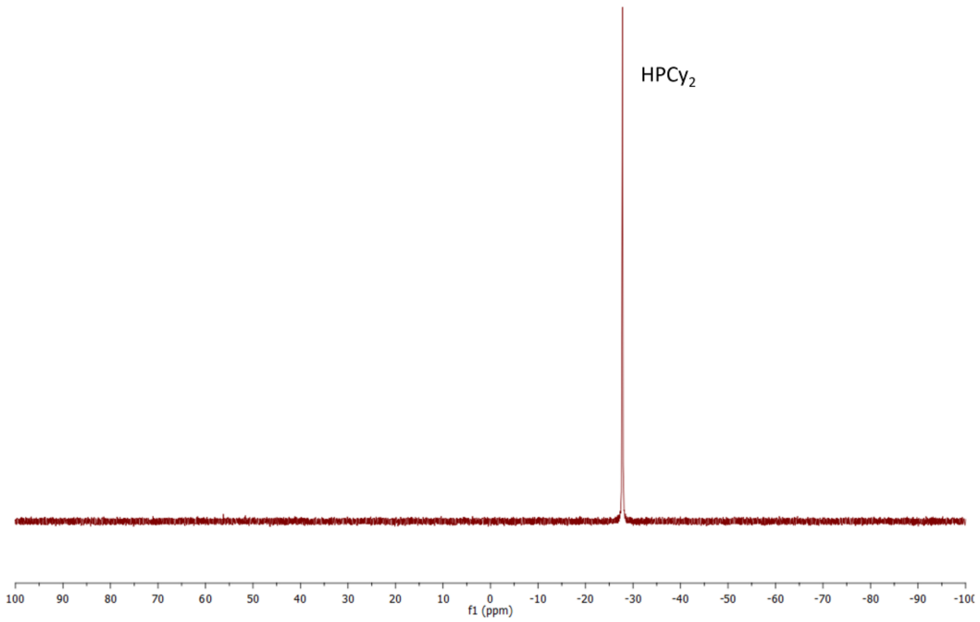


Figure S194: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of styrene with $HPCy_2$ by **3-Ca** in THF at room temperature after 3 hours.

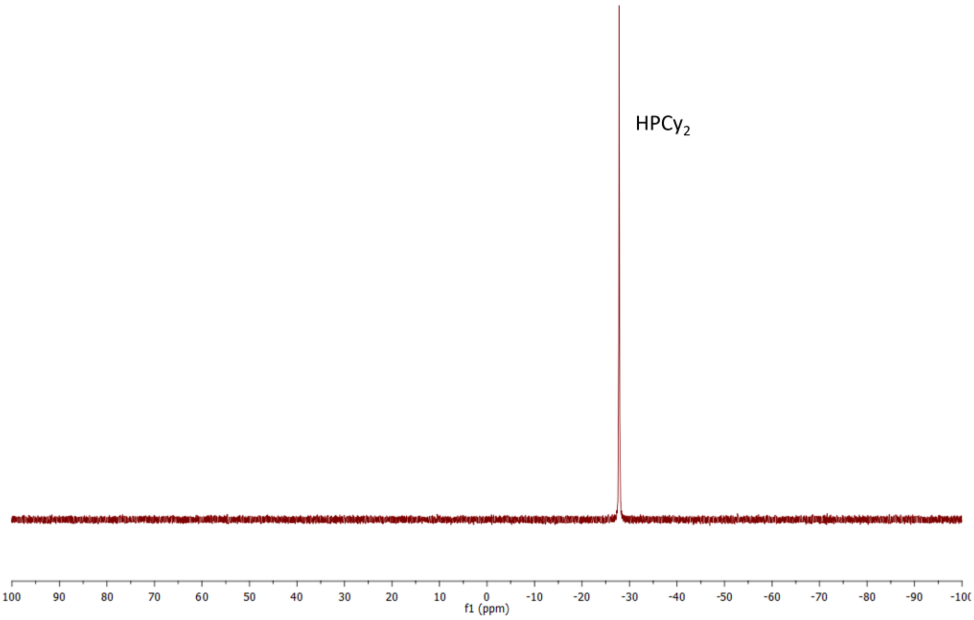


Figure S195: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of acrylonitrile with dicyclohexylphosphine by **3-Ca** in THF at room temperature after 3 hours.

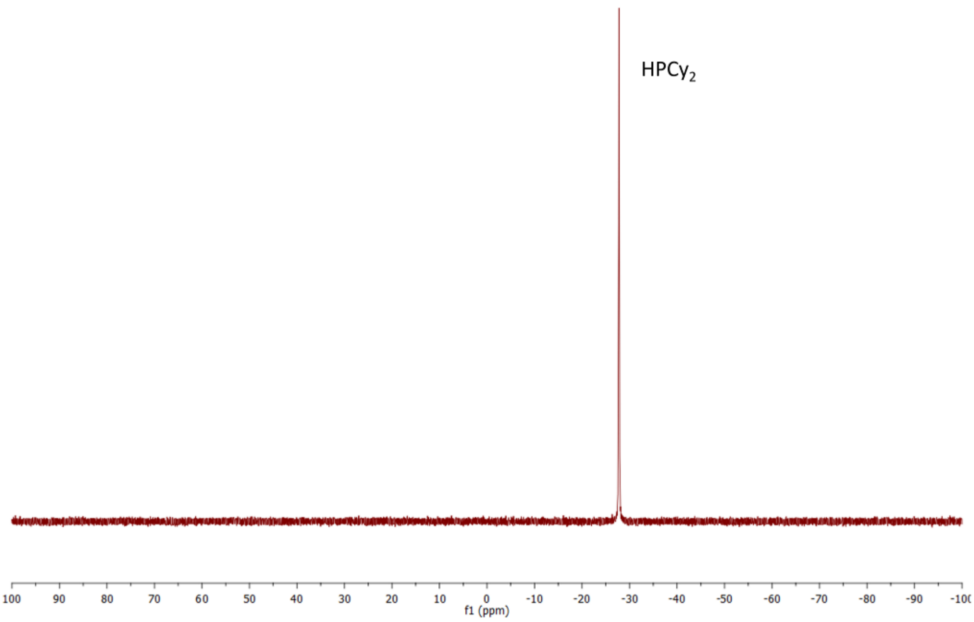


Figure S196: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of 2-vinylpyridine with $HPCy_2$ by **3-Ca** in THF at room temperature after 3 hours.

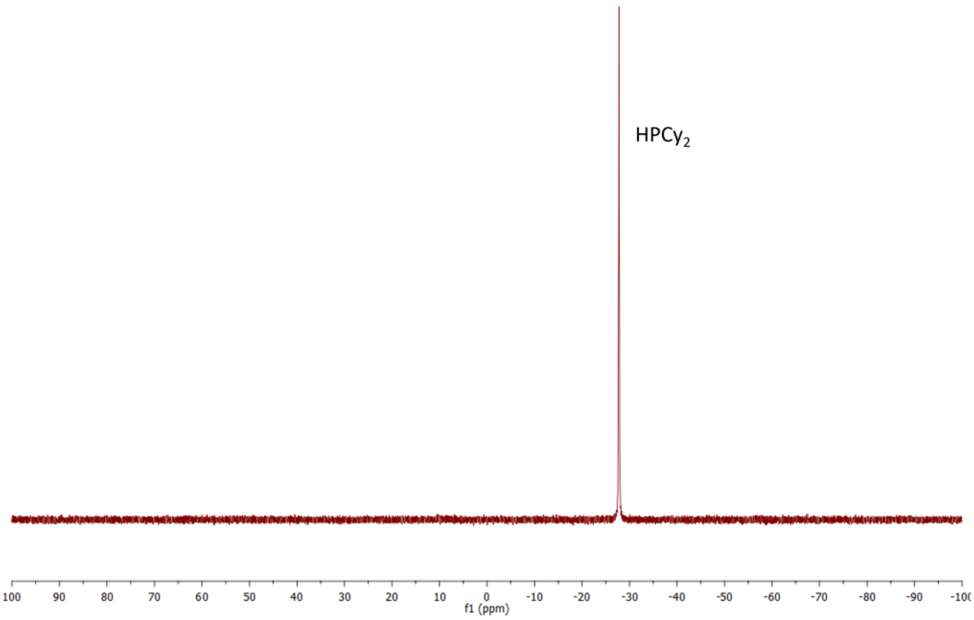


Figure S197: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 100 ppm for the attempted hydrophosphination of 4-vinylpyridine with $HPCy_2$ by **3-Ca** in THF at room temperature after 3 hours.

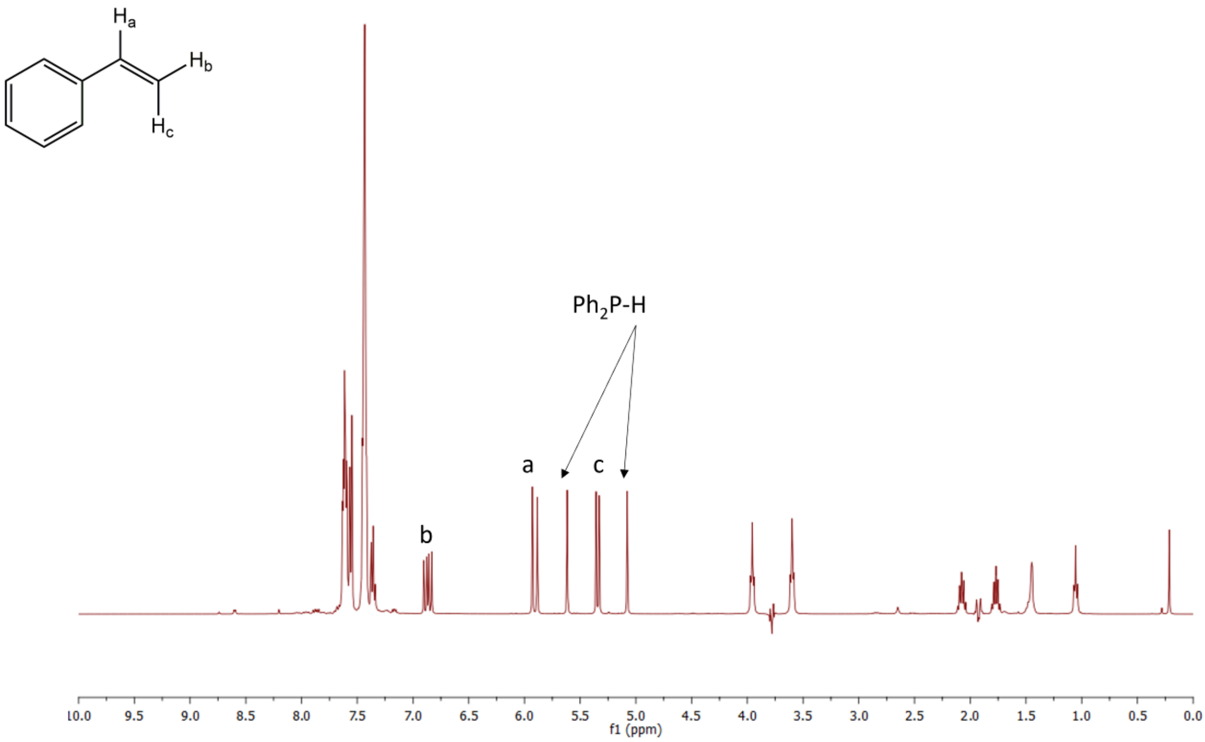


Figure S198: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for the hydrophosphination of styrene with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

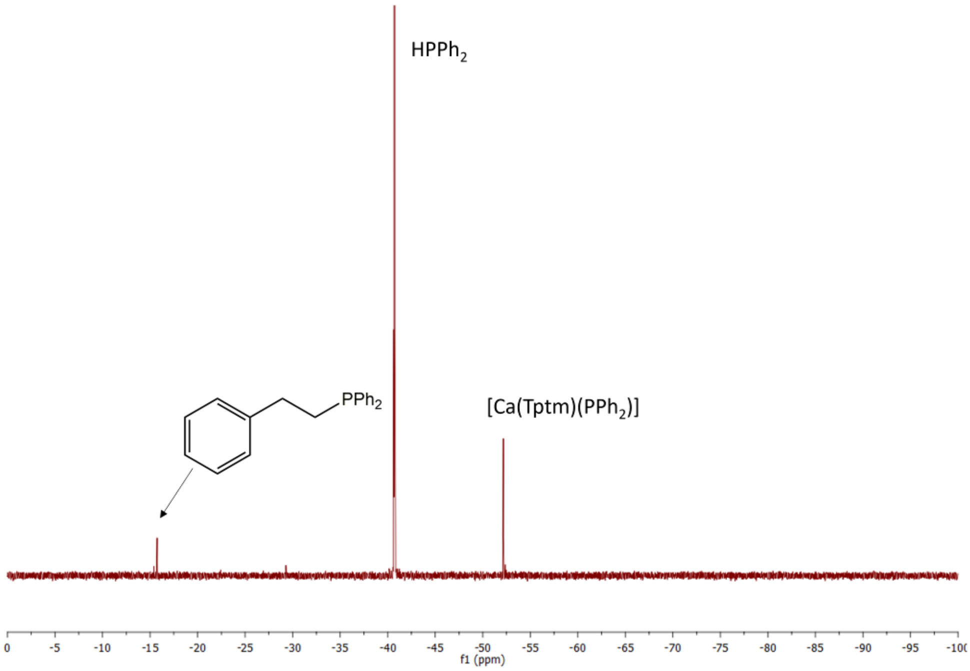


Figure S199: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for the hydrophosphination of styrene with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

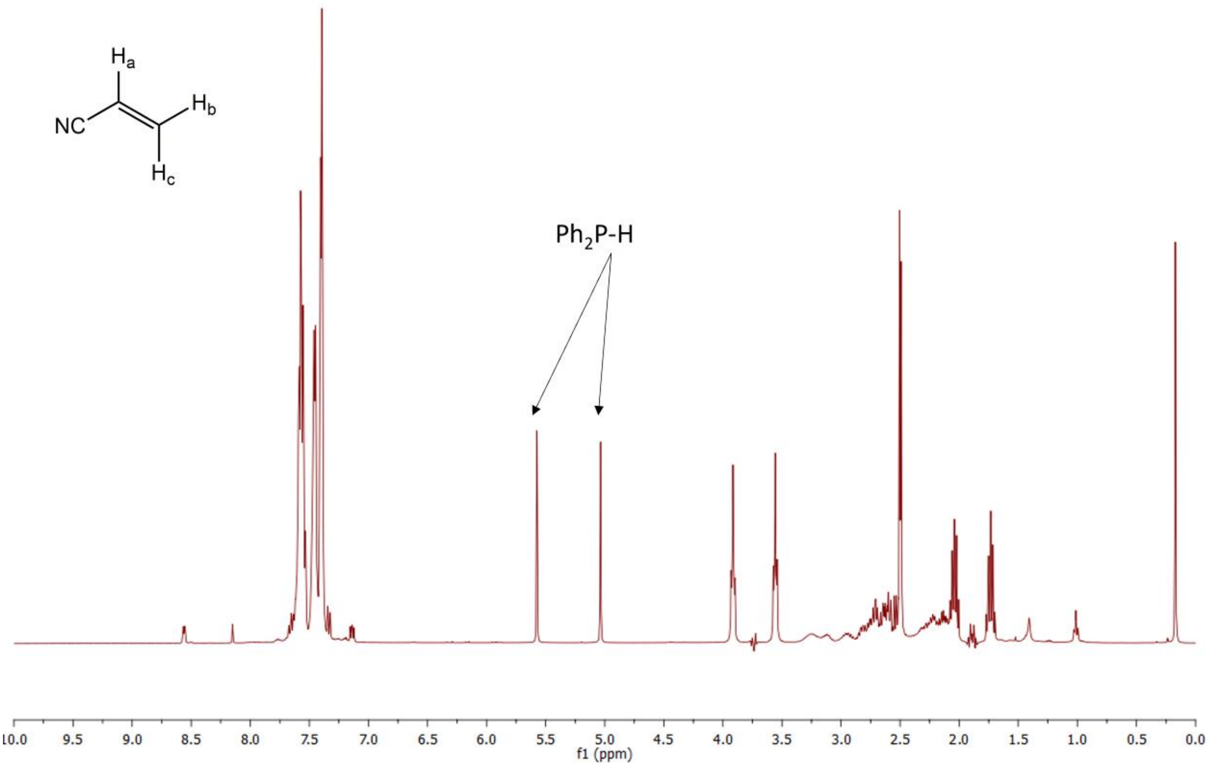


Figure S200: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for the hydrophosphination of acrylonitrile with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

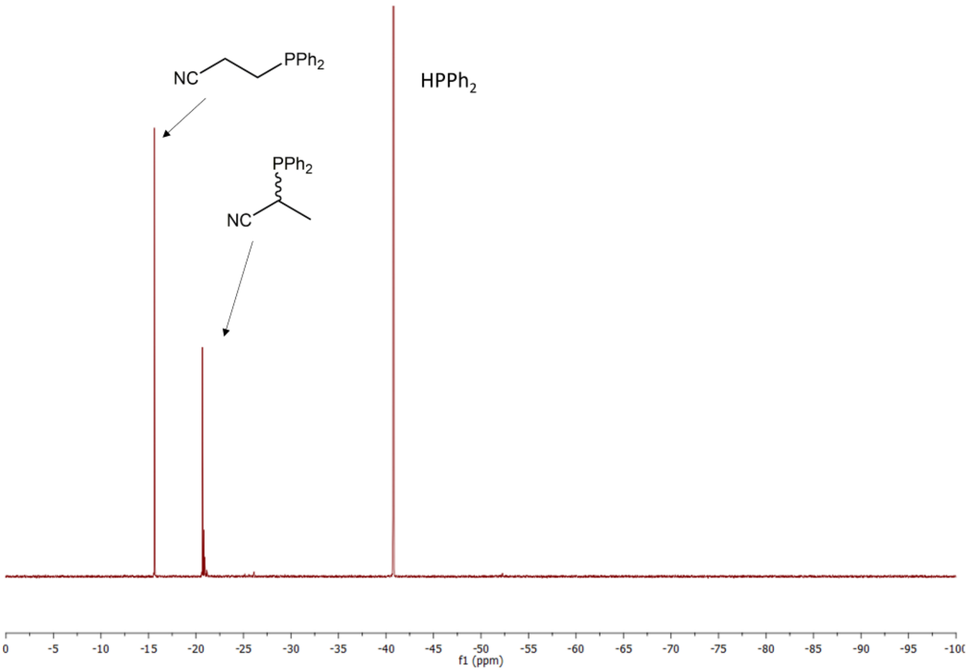


Figure S201: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for the hydrophosphination of acrylonitrile with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

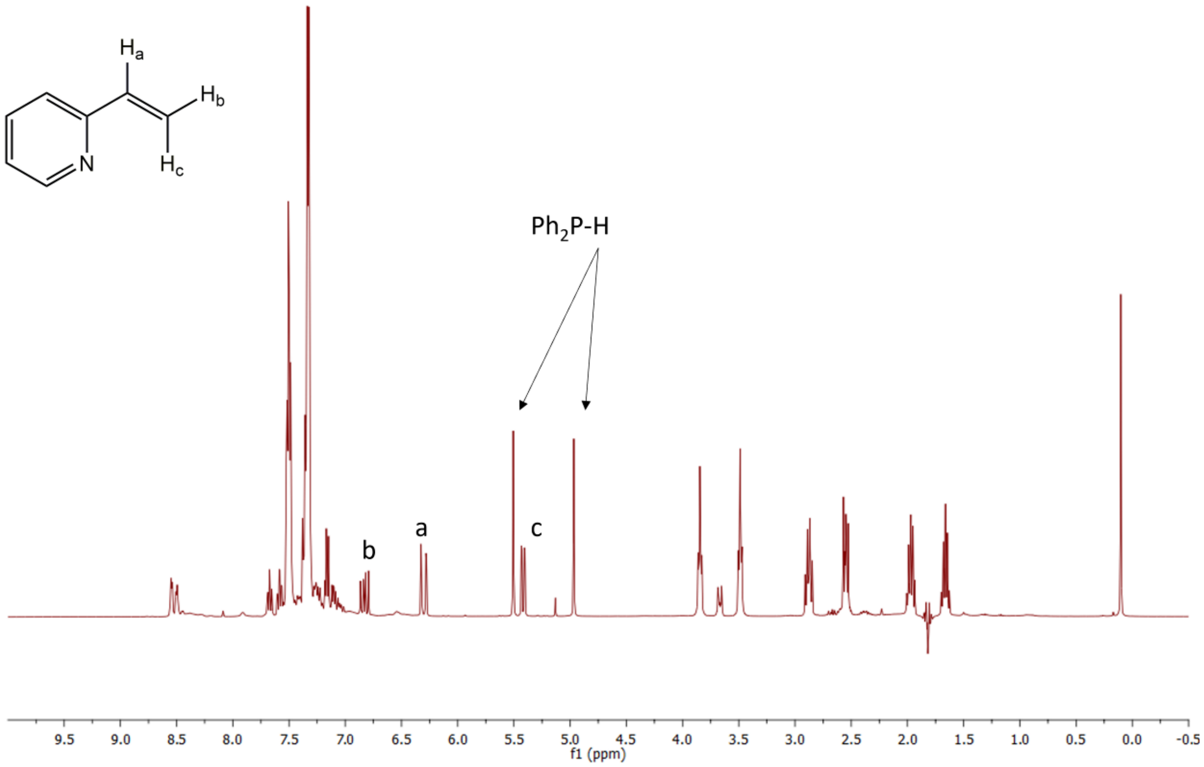


Figure S202: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 0 to 10 ppm for the hydrophosphination of 2-vinylpyridine with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

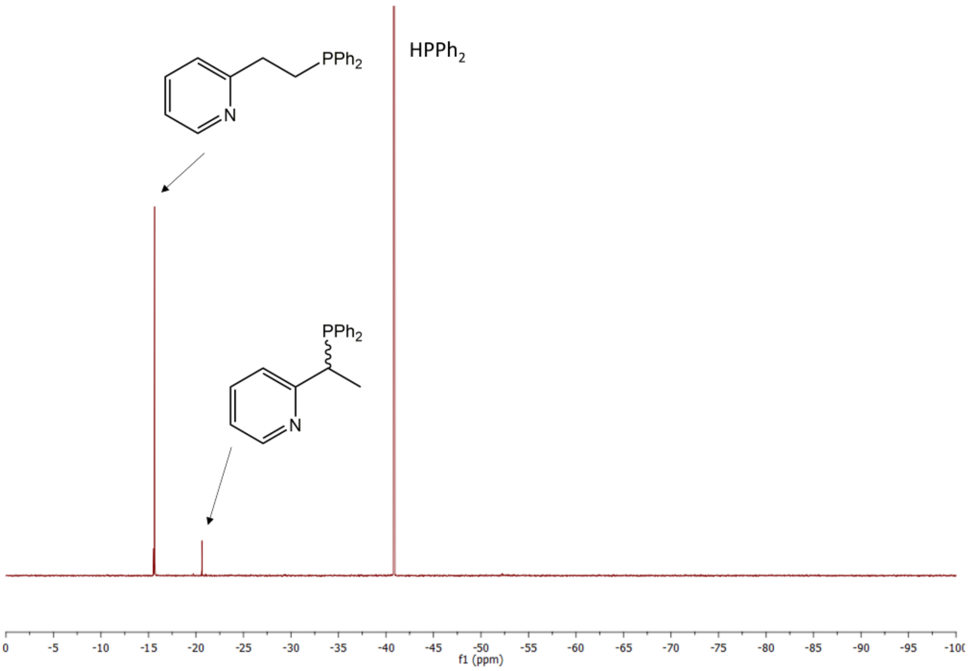


Figure S203: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for the hydrophosphination of 2-vinylpyridine with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

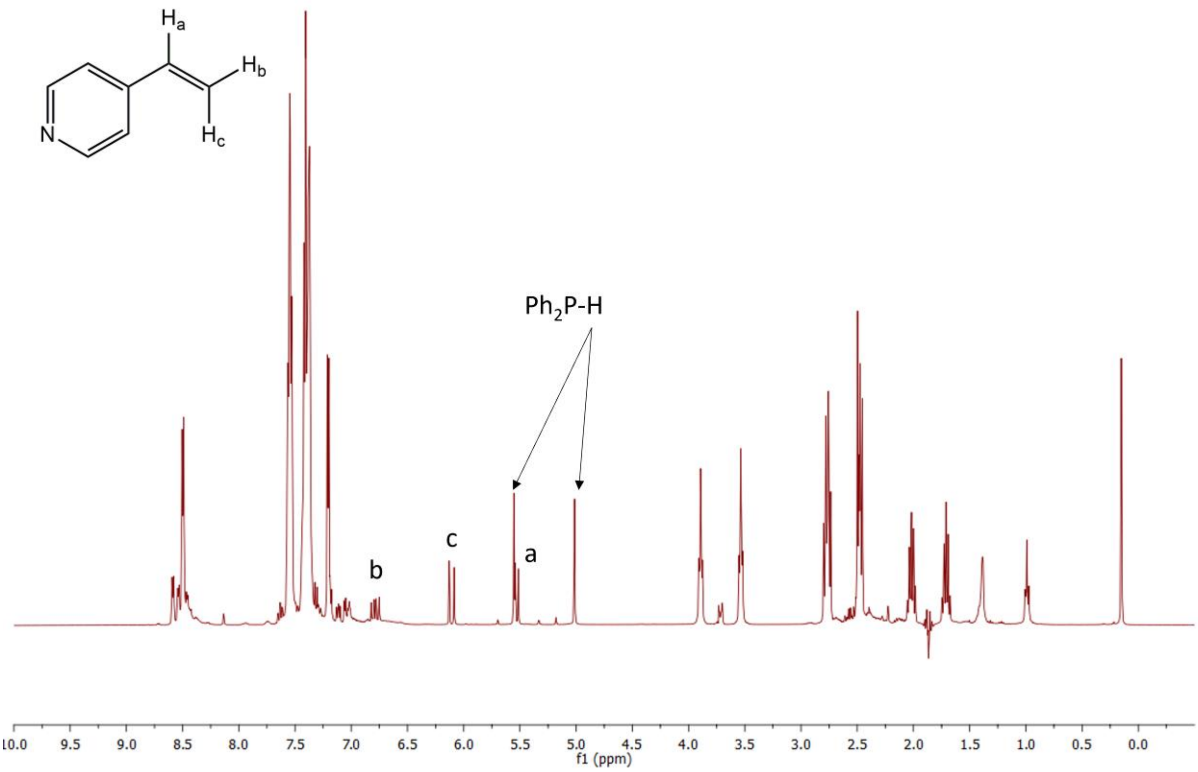


Figure S204: ^{1}H NMR (400 MHz, 298 K, C_4H_8O with automated solvent suppression) spectrum from 10 to 0 ppm for the hydrophosphination of 4-vinylpyridine with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

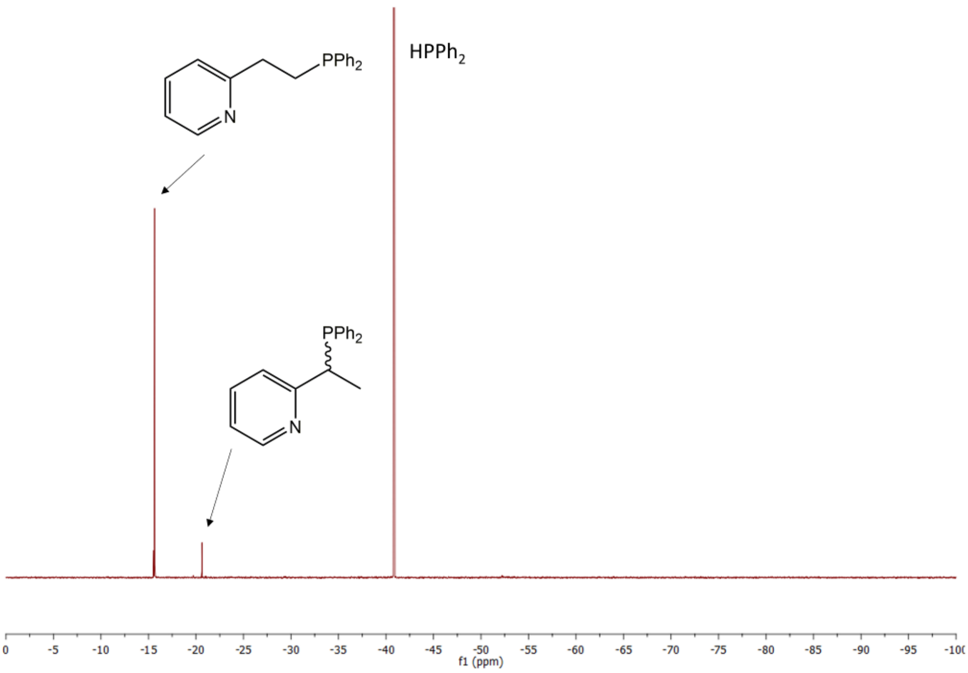


Figure S205: $^{31}P\{^{1}H\}$ NMR (160 MHz, 298 K, C_4H_8O) spectrum from −100 to 0 ppm for the hydrophosphination of 4-vinylpyridine with $HPPh_2$ by **3-Ca** in THF at 2.5 mol% catalyst loading.

S6. Stability studies

Experimental methodology

In an argon-filled glovebox**, 3-AE** (5.4 mg, 10 μmol), cyclohexane (1 μL, 9 μmol), and deuterated solvent (ca. 1 mL, C_6D_6, C_7D_8, or C_4D_8O) were added to an NMR tube fitted with a Young's valve. ^{1}H NMR spectra were then recorded at frequent intervals for the duration of the experiment (*vida infra* for details). Integration of the resulting spectra relative to cyclohexane and subsequent treatment of the data (*vide infra*) enabled calculation of the half-life of decomposition of **3-Mg** in C_7D_8.

Half-life calculations

3-Mg

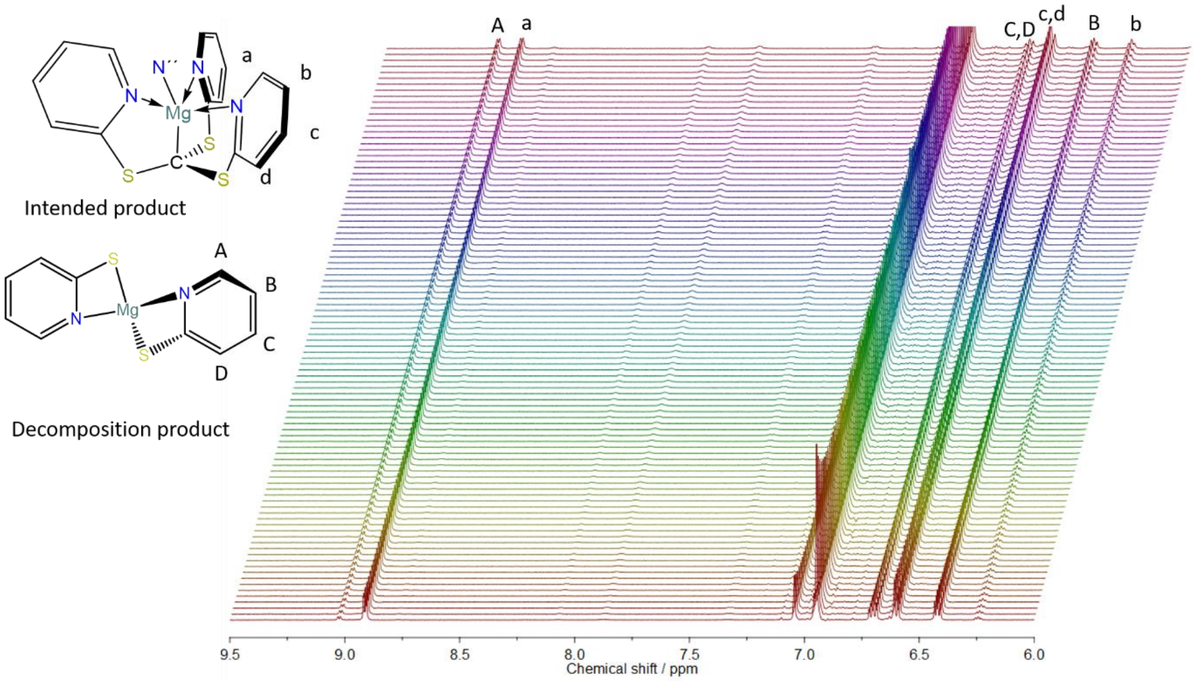


Figure S206: NMR time course of the decomposition of **3-Mg** at 100°C in d_8-toluene. Spectra were acquired at 77 second intervals for 2 h 7 mins.

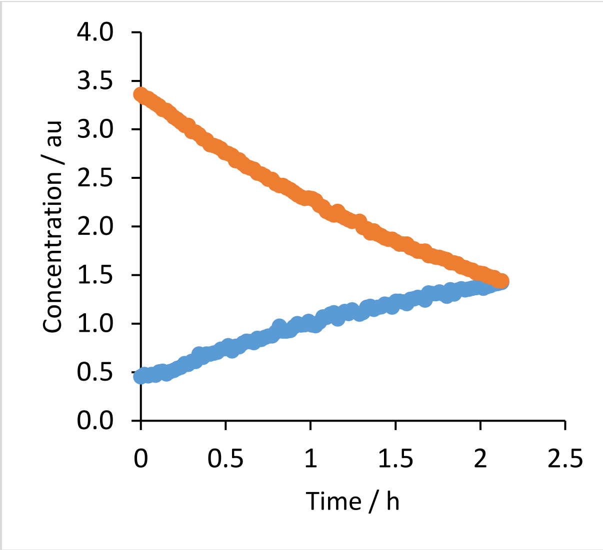


Figure S207: Decomposition of **3-Mg** at 100°C. Blue: **3-Mg**; Orange: **4-Mg**.

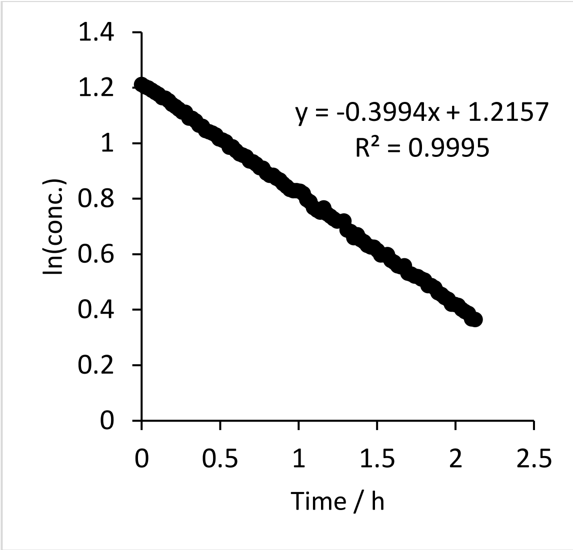


Figure S208: Logarithmic decay in concentration of **3-Mg**.

The plotting of the natural logarithm of the concentration of **3-Mg** against time revealed a linear plot (Figure S208), indicating an apparent first order reaction was taking place. The concentration-time equation for a first order reaction is:

$$\text{Equation (1): } \ln[A] = \ln\,[A]_0 - kt$$

Where $[A]$ is the concentration of the species under study at time t, $[A]_0$ is the initial concentration of said species, and k is the rate constant. Hence, it can be deduced by performing a regression analysis on the data in Figure S208 that for the reaction under study here, $k = 0.3994 \pm 0.00094\ \text{h}^{-1}$.

By setting $[A] = \frac{[A]_0}{2}$ in Equation (1), this can be rearranged as:

$$\text{Equation (2): } t_{1/2} = \frac{\ln 2}{k}$$

where $t_{1/2}$ is the half-life *i.e.* time elapsed when the concentration is halved. Hence, the half-life of decomposition of **3-Mg** was calculated to be 104.13 ± 0.25 minutes. Then, the Eyring equation, Equation (3), was used to extrapolate half-life values at different temperatures:

$$\text{Equation (3): } k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

Where k is the rate constant, T is the absolute temperature, $\Delta G^{\ddagger}$ is the Gibbs energy of activation, and k_B, h, and R are Boltzmann's constant, Planck's constant, and the Ideal Gas constant respectively. The half-life equation (*vide infra*) can be rearranged and set equal to the Eyring equation thus:

$$\text{Equation (4): } \frac{\ln 2}{t_{1/2}} = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

This can be rearranged to yield the following equation:

$$\text{Equation (5): } \Delta G^{\ddagger} = RT \ln \frac{t_{½} k_B T}{h \ln 2}$$

Taking the half-life calculated earlier, $\Delta G^{\ddagger}$ was calculated to be 120.264 ± 0.010 kJ mol^{-1} for the decomposition of **3-Mg**. Assuming the enthalpy of reaction does not vary with temperature, this value can be used to calculate the half-life of decomposition at different temperatures. The relevant equation is given below.

$$\text{Equation (6): } t_{½} = \frac{h \ln(2) e^{\frac{\Delta G^{\ddagger}}{RT}}}{k_B T}$$

In this case, the $\Delta G^{\ddagger}$ was found to be 120.2642 ± 0.0096 kJ mol^{-1}, with a corresponding half-life at room temperature of 115 days, or 1.21 hours at 100 °C.

Unfortunately, the same treatment could not be used for the data obtained for the thermal decomposition of **3-Mg** in d_8-THF as the resulting plot was clearly non-linear. Additionally, the rate of decomposition was extremely slow at the temperature used (55 °C), and 6.44% decomposition was achieved after 11 hours. The stability of **3-Mg** in THF was also assessed at room temperature over an extended period of time, and we found that approximately 10% had decomposed after 4 days.

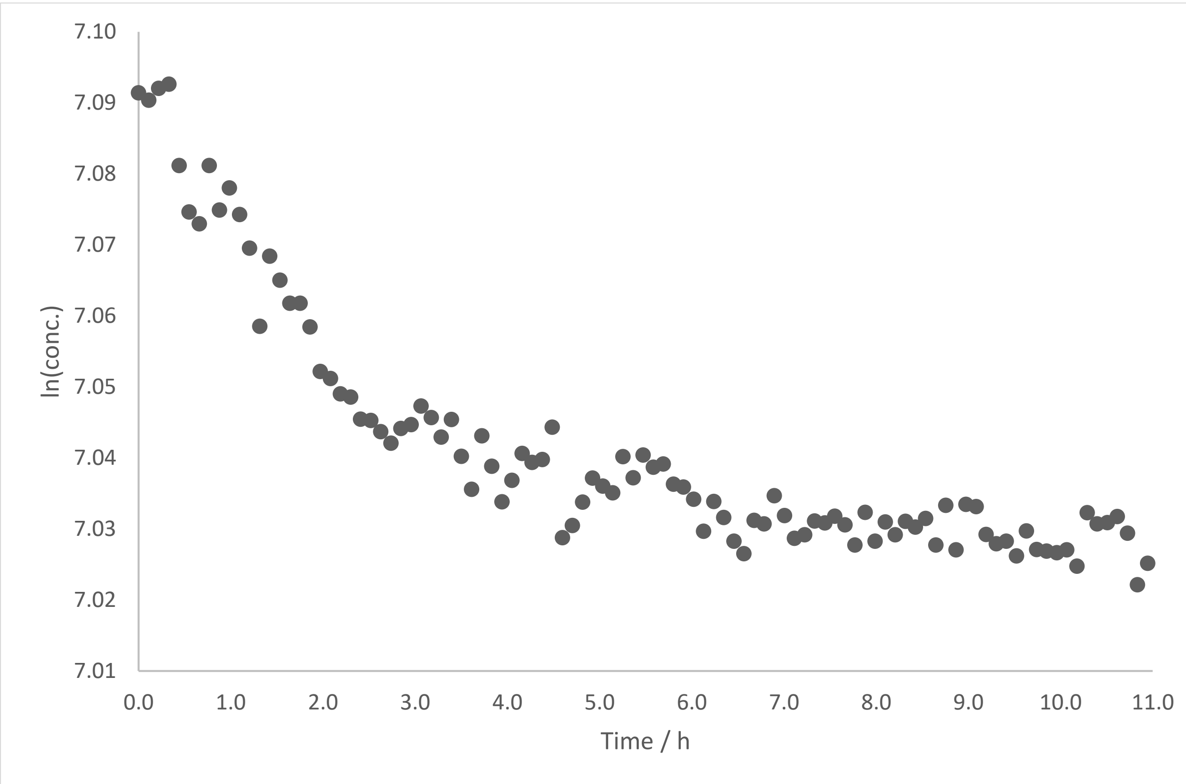


Figure S209: Natural logarithm plot for the decay of **3-Mg** in C_4D_8O at 55°C

3-Ca

Integration of all the peaks assigned to **3-Ca** and **4** in the region 6.0-9.0 ppm and subsequent plotting of this data against time (Figures S129) revealed a steady but non-linear decrease in concentration of **3-Ca**, which was not matched by the increase in concentration of **4-Ca**. This was attributed to this latter falling out of solution as a precipitate, and thus not being detected. This was corroborated by the observation of a significant amount of precipitate in the NMR tube when it was retrieved from the spectrometer.

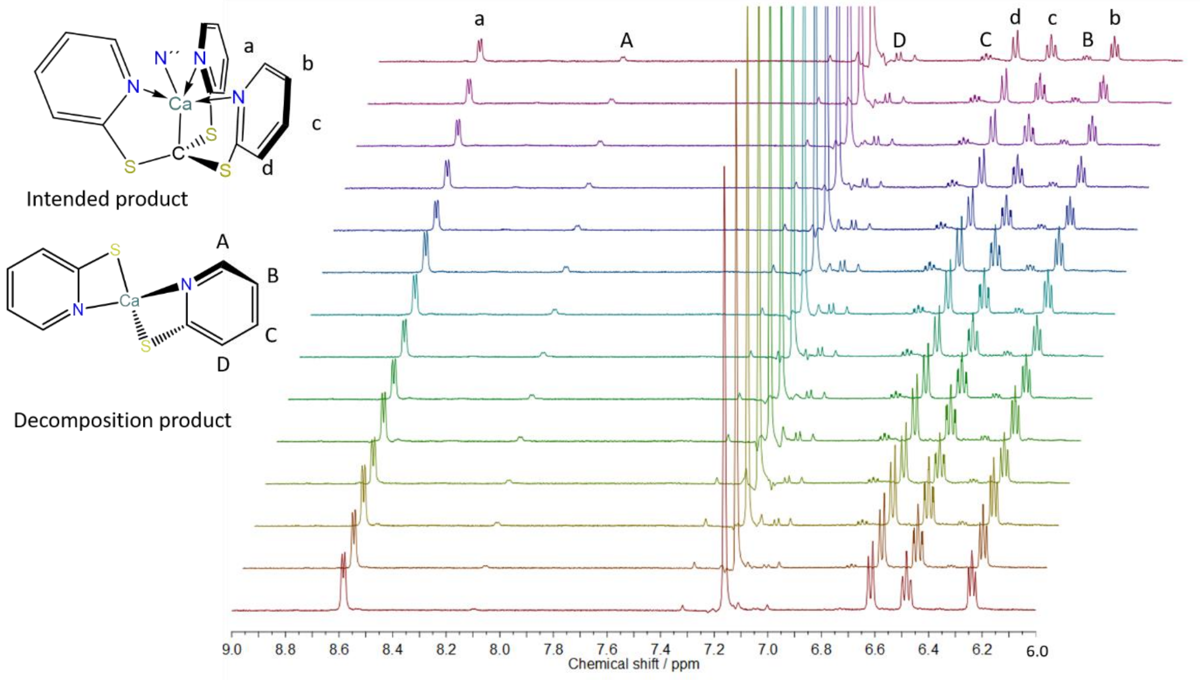


Figure S210: Example NMR time course of the decomposition of **3-Ca** at 25°C in d_6-benzene. Spectra were acquired every 10 minutes for 140 minutes.

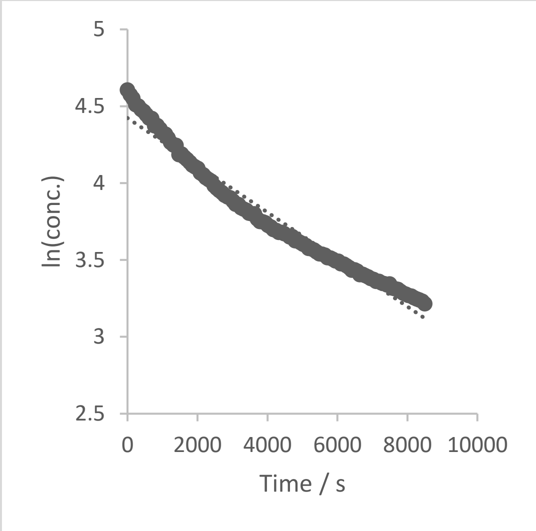


Figure S211: Natural log chart of decay of **3-Ca** in C_6D_6 at 25°C

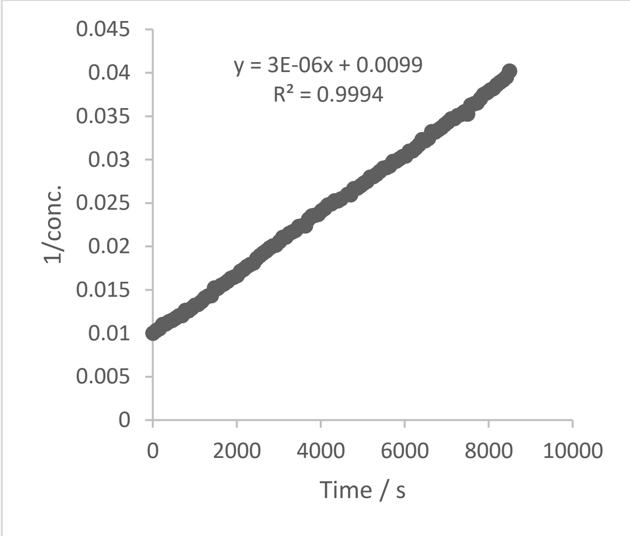


Figure S212: Reciprocal chart for the decay of **3-Ca** in C_6D_6 at 25°C

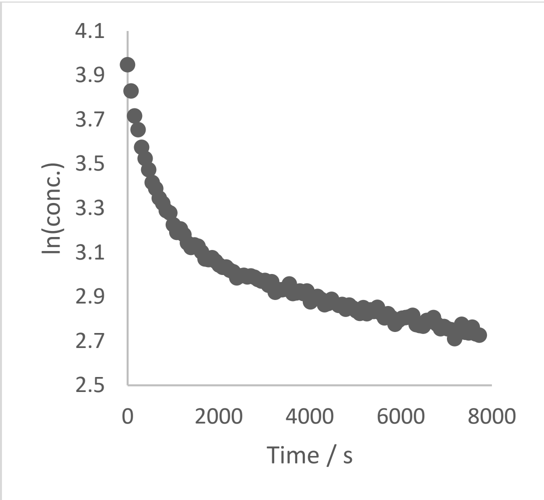


Figure S213: Natural log chart for the decay of **3-Ca** in C_4D_8O at 25°C

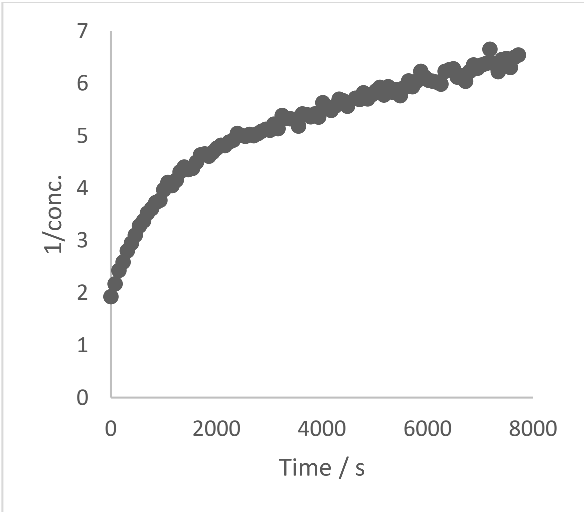


Figure S214: Reciprocal chart for the decay of **3-Ca** in C_4D_8O at 25°C

Because decompositions of **3-Ca** in benzene and THF have non-unit orders of reaction, it is not possible to accurately calculate a half-life for these reactions. However, a crude manual measurement indicates that 50% decomposition has occurred at room temperature after approximately 48 minutes in benzene, and 16 minutes in THF. Moreover, we found that approximately 64% of **3-Ca** had decomposed after 1 hour in THF at room temperature, which dropped to 71% after 2 hours. We used this information to inform the strategy employed in our catalytic studies (all run under 1 hour) and also determined that the half-life of **3-Ca** at 60 °C (THF reflux temperature) would be far too short to make hydrophosphination tests at high temperatures reliable.

Table S7: Half-life NMR experiments for **3-Mg**.

Compound	**Solvent**	**T (K)**	**$[A]_{init}$ (mmol mL^{-1})**	**$t_{½}$ (min)**	**k (s^{-1})**
3-Mg	D_8-toluene	373	0.01	104.13 ± 0.25	0.3994 ± 0.00094

Table S8: Extrapolated half-life values for **3-Mg** across different temperatures used in the catalytic studies.

Compound	**$t_{½}$ at 25 °C**	**$t_{½}$ at 60 °C**	**$t_{½}$ at 80 °C**
3-Mg	115 days	8.46 days	16.35 h

S7. Computational data

Computed Structures (A) and Energies (a. u.)

1m'

```
BP86 energy = -970.608906315
Enthalpy 0K = -970.250794
Enthalpy 298K = -970.222182
Free energy 298K = -970.312016
Low freq. = 6.6448 cm-1
Second freq. = 18.5290 cm-1

C  -1.644973 -0.034948 -1.088535
Mg  0.296627 -0.015544  0.285844
S  -1.655586  1.399766 -2.224884
S  -3.149053  0.035532 -0.033579
S  -1.719589 -1.537926 -2.125554
C  -2.539398 -0.028181  1.640661
N  -1.212408 -0.068079  1.900407
C   2.163082  0.017301  1.453782
H   2.131027  0.866155  2.180477
C   3.526489  0.095072  0.726345
H   2.201853 -0.872515  2.129334
H   3.562957  0.993862  0.072876
H   3.637587 -0.758069  0.021794
C   4.774226  0.121283  1.636864
H   4.690965  0.981849  2.330539
C   6.106023  0.199165  0.872153
H   4.765125 -0.781385  2.280123
H   6.154777  1.109537  0.247285
H   6.229466 -0.666731  0.196420
H   6.975451  0.216196  1.552836
C  -0.803420 -0.112632  3.196185
C  -3.504156 -0.031504  2.678806
C  -3.068603 -0.076886  4.001874
C  -1.686409 -0.119723  4.275719
H   0.282779 -0.140315  3.334632
H  -4.569300 -0.000378  2.429979
H  -3.798582 -0.080463  4.818231
H  -1.305609 -0.157312  5.299339
H   0.871288  5.598013 -2.143852
C   0.744290  4.606193 -1.697246
H   2.335790  4.840540 -0.211495
C   1.560709  4.191238 -0.626195
C   1.358502  2.914765 -0.101113
C  -0.237311  3.743356 -2.182025
H   1.963512  2.523831  0.722800
H  -0.898839  4.035004 -3.003551
N   0.411854  2.057942 -0.567308
C  -0.378480  2.467307 -1.584328
H   1.037348 -5.586115 -2.202039
C   0.891973 -4.595970 -1.757304
H   2.612437 -4.717672 -0.408006
C   1.769584 -4.119457 -0.763054
C   1.538626 -2.848813 -0.235855
C  -0.171453 -3.795094 -2.170255
H   2.182730 -2.414131  0.534608
H  -0.877835 -4.133475 -2.934573
N   0.510462 -2.052393 -0.631884
C  -0.334474 -2.519356 -1.577253
```

TS(1m'-1m)

```
BP86 energy = -970.580877915
Enthalpy 0K = -970.224672
Enthalpy 298K = -970.195793
Free energy 298K = -970.286949
Low freq. = -28.4769 cm-1
Second freq. = 8.5209 cm-1

C   0.00159 -1.04931 -1.60055
Mg -0.00016  0.04506  0.31749
S   1.45268 -1.52094 -2.37764
S  -0.00467  2.20975 -1.64851
S  -1.44796 -1.52651 -2.37713
C  -0.00593  2.93552 -0.06652
N  -0.00412  2.09171  1.02676
C   0.00281 -1.21214  2.13925
H   0.89039 -0.89089  2.72906
C   0.00655 -2.74030  1.99768
H  -0.88627 -0.89524  2.72914
H   0.88941 -3.06713  1.40886
H  -0.87480 -3.07146  1.40904
C   0.00861 -3.52099  3.33359
H   0.89150 -3.21086  3.92692
C   0.01235 -5.04873  3.15790
H  -0.87567 -3.21520  3.92710
H   0.90274 -5.38317  2.59499
H  -0.87648 -5.38755  2.59516
H   0.01374 -5.57709  4.12767
C  -0.00501  2.60813  2.28197
C  -0.00873  4.34823  0.14684
C  -0.00961  4.85726  1.44109
C  -0.00772  3.97611  2.54770
H  -0.00343  1.86629  3.09029
H  -0.01015  5.00791 -0.72470
H  -0.01175  5.94169  1.60033
H  -0.00834  4.34405  3.57684
H   6.04705 -0.55123 -0.90582
C   4.97981 -0.41809 -0.70318
H   5.25659  0.81070  1.08223
```

```
C   4.54511  0.33565  0.40173
C   3.17086  0.46985  0.61988
C   4.02579 -0.99757 -1.54600
H   2.77952  1.04461  1.46575
H   4.31722 -1.58926 -2.41931
N   2.23332 -0.08314 -0.18858
C   2.66665 -0.79408 -1.24484
H  -6.04549 -0.57447 -0.90364
C  -4.97870 -0.43723 -0.70139
H  -5.25955  0.79047  1.08414
C  -4.54650  0.31817  0.40337
C  -3.17269  0.45764  0.62103
C  -4.02276 -1.01303 -1.54456
H  -2.78326  1.03389  1.46676
H  -4.31223 -1.60583 -2.41777
N  -2.23333 -0.09174 -0.18777
C  -2.66430 -0.80432 -1.24389
```

1m

BP86 energy = -970.682329758
Enthalpy 0K = -970.320930
Enthalpy 298K = -970.292609
Free energy 298K = -970.381459
Low freq. = 15.5827 cm-1
Second freq. = 20.9795 cm-1

```
S   1.98743  1.20942 -1.49077
S   1.98831  1.20969  1.48924
S  -3.39802 -0.31609  0.00106
Mg -0.78043  0.07663  0.00026
N  -0.73069  1.18880 -1.88318
N  -0.72938  1.18697  1.88472
N  -1.36021 -2.03413 -0.00049
C   1.46235  0.24917 -0.00056
C   2.18945 -1.11847 -0.00069
H   1.83522 -1.67932  0.88823
H   1.83479 -1.67940 -0.88939
C   3.73327 -1.13345 -0.00109
H   4.10280 -0.58335 -0.88910
H   4.10326 -0.58321  0.88664
C   4.32554 -2.55364 -0.00112
H   3.94959 -3.10477 -0.88569
H   3.94998 -3.10463  0.88370
C   5.86208 -2.57029 -0.00147
H   6.26610 -2.05659 -0.89179
H   6.25781 -3.60041 -0.00146
H   6.26651 -2.05642  0.88858
C   0.47538  1.60642 -2.34400
C   0.59108  2.36980 -3.53266
H   1.58050  2.69459 -3.86852
C  -0.56003  2.68723 -4.24943
H  -0.48700  3.27489 -5.17072
C  -1.81248  2.24435 -3.77758
H  -2.73915  2.46805 -4.31181
C  -1.84685  1.50474 -2.59719
H  -2.78261  1.12038 -2.17330
C   0.47694  1.60517  2.34437
C   0.59349  2.36801  3.53329
H   1.58308  2.69331  3.86818
C  -0.55701  2.68427  4.25156
H  -0.48331  3.27151  5.17307
C  -1.80970  2.24074  3.78095
H  -2.73590  2.46351  4.31637
C  -1.84492  1.50175  2.60020
H  -2.78091  1.11703  2.17712
C  -0.77674 -3.25861 -0.00133
H   0.31817 -3.25983 -0.00173
C  -1.50215 -4.44948 -0.00166
H  -0.98462 -5.41191 -0.00234
C  -2.91108 -4.36444 -0.00108
H  -3.51888 -5.27611 -0.00129
C  -3.52979 -3.11675 -0.00022
H  -4.61806 -3.01680  0.00025
C  -2.73448 -1.93816  0.00005
```

1

BP86 energy = -1941.37378825
Enthalpy 0K = -1940.651200
Enthalpy 298K = -1940.593221
Free energy 298K = -1940.749402
Low freq. = 11.6715 cm-1
Second freq. = 16.0843 cm-1

```
S  -4.20469  2.48466 -0.01460
S  -3.62582  2.51486  2.94406
S  -0.03570 -1.54229  0.99436
Mg -1.65977  0.63675  1.03304
N  -3.21339 -0.05331 -0.36306
N  -2.91437 -0.12397  2.74521
N   0.00579  0.66165  2.49518
C  -2.85233  2.50508  1.25775
C  -2.04192  3.81146  1.09245
H  -1.21534  3.78423  1.83229
H  -1.55873  3.76640  0.09734
C  -2.77746  5.16243  1.23540
H  -3.60473  5.20893  0.49896
H  -3.25045  5.22702  2.23613
C  -1.85330  6.37594  1.03367
H  -1.38259  6.31011  0.03306
H  -1.02168  6.32465  1.76419
C  -2.57774  7.72377  1.17449
H  -3.39202  7.81789  0.43411
H  -1.89015  8.57406  1.02473
H  -3.02944  7.83123  2.17684
```

```
C  -4.20744  0.82253 -0.65470
C  -5.29335  0.45509 -1.48999
H  -6.08394  1.18384 -1.69338
C  -5.33869 -0.83234 -2.01995
H  -6.17413 -1.13181 -2.66192
C  -4.30903 -1.74391 -1.71059
H  -4.30919 -2.76544 -2.09877
C  -3.27648 -1.30634 -0.88138
H  -2.44667 -1.96620 -0.60389
C  -3.60851  0.80413  3.44721
C  -4.34329  0.46312  4.61042
H  -4.89869  1.24080  5.14353
C  -4.35101 -0.86171  5.04262
H  -4.91486 -1.14333  5.93841
C  -3.63778 -1.83025  4.30888
H  -3.62446 -2.88185  4.60686
C  -2.94019 -1.41203  3.17455
H  -2.34982 -2.11302  2.57202
C   0.39384  1.45257  3.52363
H  -0.12225  2.41657  3.59920
C   1.37323  1.07339  4.44426
H   1.65138  1.74314  5.26226
C   1.97580 -0.19085  4.28744
H   2.74638 -0.52763  4.98944
C   1.58313 -1.01911  3.23396
H   2.02719 -2.00610  3.08194
C   0.58002 -0.56945  2.33975
S   4.20469 -2.48466  0.01460
S   3.62582 -2.51486 -2.94406
S   0.03570  1.54229 -0.99436
Mg  1.65977 -0.63675 -1.03304
N   3.21339  0.05331  0.36306
N   2.91437  0.12397 -2.74521
N  -0.00579 -0.66165 -2.49518
C   2.85233 -2.50508 -1.25775
C   2.04192 -3.81146 -1.09245
H   1.21534 -3.78423 -1.83229
H   1.55873 -3.76640 -0.09734
C   2.77746 -5.16243 -1.23540
H   3.60473 -5.20893 -0.49896
H   3.25045 -5.22702 -2.23613
C   1.85330 -6.37594 -1.03367
H   1.38259 -6.31011 -0.03306
H   1.02168 -6.32465 -1.76419
C   2.57774 -7.72377 -1.17449
H   3.39202 -7.81789 -0.43411
H   1.89015 -8.57406 -1.02473
H   3.02944 -7.83123 -2.17684
C   4.20744 -0.82253  0.65470
C   5.29335 -0.45509  1.48999
H   6.08394 -1.18384  1.69338
C   5.33869  0.83234  2.01995
H   6.17413  1.13181  2.66192
C   4.30903  1.74391  1.71059
H   4.30919  2.76544  2.09877
C   3.27648  1.30634  0.88138
H   2.44667  1.96620  0.60389
C   3.60851 -0.80413 -3.44721
C   4.34329 -0.46312 -4.61042
H   4.89869 -1.24080 -5.14353
C   4.35101  0.86171 -5.04262
H   4.91486  1.14333 -5.93841
C   3.63778  1.83025 -4.30888
H   3.62446  2.88185 -4.60686
C   2.94019  1.41203 -3.17455
H   2.34982  2.11302 -2.57202
C  -0.39384 -1.45257 -3.52363
H   0.12225 -2.41657 -3.59920
C  -1.37323 -1.07339 -4.44426
H  -1.65138 -1.74314 -5.26226
C  -1.97580  0.19085 -4.28744
H  -2.74638  0.52763 -4.98944
C  -1.58313  1.01911 -3.23396
H  -2.02719  2.00610 -3.08194
C  -0.58002  0.56945 -2.33975
```

3-Ca

```
BP86 energy = -1150.96129518
Enthalpy 0K = -1150.500051
Enthalpy 298K = -1150.459016
Free energy 298K = -1150.576242
Low freq. = 9.3682 cm-1
Second freq. = 15.2248 cm-1
```

```
C   2.42081  0.44324 -0.70319
Ca -0.03326  0.01900  0.01325
S   3.00492 -0.78808 -1.92170
S   3.54428  0.46387  0.75413
S   2.54890  2.07490 -1.53079
C   2.64377 -0.27941  2.10331
N   1.32109 -0.57586  2.03352
C   0.74104 -1.15612  3.11866
C   3.40616 -0.53891  3.27230
C   2.78551 -1.11686  4.37682
C   1.41703 -1.44494  4.30354
H  -0.32438 -1.39107  3.01592
H   4.47163 -0.28969  3.28516
H   3.36159 -1.32220  5.28513
H   0.89003 -1.91107  5.13959
H   1.55298 -5.29709 -3.13499
C   1.29815 -4.38485 -2.58537
H  -0.62816 -5.11910 -1.84400
C   0.08721 -4.29335 -1.87008
C  -0.18264 -3.10489 -1.19099
C   2.17764 -3.30337 -2.58397
```

H	-1.11621	-2.96291	-0.63298
H	3.13079	-3.34399	-3.12011
N	0.66121	-2.03805	-1.18228
C	1.82611	-2.13372	-1.86432
H	0.27595	6.33848	-0.74386
C	0.25500	5.25732	-0.57119
H	-1.61030	5.26617	0.57681
C	-0.79331	4.66900	0.16422
C	-0.76571	3.28669	0.35317
C	1.27709	4.45147	-1.07092
H	-1.56489	2.76656	0.89405
H	2.11604	4.87624	-1.63042
N	0.21863	2.48406	-0.13228
C	1.22570	3.05536	-0.83495
H	-1.62004	0.53663	3.21015
H	-0.96641	1.36205	-2.37418
H	-1.98041	-2.66723	2.20981
C	-2.71217	0.55539	3.04441
C	-1.52674	0.44556	-2.64055
C	-3.04433	-2.38414	2.10936
H	-3.66860	2.50655	-1.22874
H	-0.81173	-0.39316	-2.73580
N	-2.32691	-0.18451	0.15408
H	-3.19353	0.25194	3.99154
H	-2.99612	1.60587	2.85295
H	-3.53999	-2.60243	3.07239
Si	-3.27006	-0.55148	1.57536
H	-1.92622	0.62018	-3.65520
H	-3.48430	-3.05370	1.34891
Si	-2.99236	0.07804	-1.43842
C	-4.16024	1.58843	-1.59489
H	-4.44857	1.75829	-2.64792
H	-5.08677	1.44900	-1.01316
C	-5.16327	-0.28538	1.43737
C	-3.91127	-1.42925	-2.18510
H	-3.25034	-2.31213	-2.23548
H	-5.65897	-0.58300	2.37896
H	-5.41262	0.77313	1.25147
H	-5.61062	-0.88463	0.62579
H	-4.26714	-1.21743	-3.20938
H	-4.79049	-1.70619	-1.57810

TS(3-4-Ca)1

BP86 energy = -1150.93711157
Enthalpy 0K = -1150.476540
Enthalpy 298K = -1150.435766
Free energy 298K = -1150.551522
Low freq. = -17.7068 cm-1
Second freq. = 15.9698 cm-1

C	-0.33658	-2.56141	-0.27249
Ca	0.18249	0.02392	-0.36257
S	0.70953	-3.73416	0.39916
S	1.25205	0.16141	-3.00262
S	-1.82502	-3.24066	-0.76082
C	2.24642	1.39394	-2.24818
N	2.00767	1.67811	-0.92361
C	2.71992	2.65869	-0.31631
C	3.25846	2.10757	-2.95537
C	3.98387	3.10496	-2.30926
C	3.71406	3.40207	-0.95510
H	2.45936	2.84580	0.73345
H	3.43869	1.85759	-4.00446
H	4.75747	3.65916	-2.85301
H	4.25342	4.18706	-0.41850
H	5.32281	-3.33288	2.00040
C	4.45381	-2.79814	1.60453
H	5.38956	-0.82615	1.61549
C	4.49376	-1.41194	1.39355
C	3.35298	-0.77720	0.88467
C	3.27893	-3.49377	1.29450
H	3.34094	0.29946	0.69102
H	3.20065	-4.57628	1.43533
N	2.20490	-1.43282	0.58504
C	2.19203	-2.75897	0.78901
H	-5.43720	-1.30175	-3.45418
C	-4.46495	-1.12876	-2.98241
H	-4.19730	0.88801	-3.77458
C	-3.78448	0.08641	-3.15665
C	-2.54904	0.26136	-2.51929
C	-3.86886	-2.13184	-2.20795
H	-1.97702	1.18692	-2.63576
H	-4.34588	-3.10672	-2.06687
N	-1.97326	-0.68521	-1.73987
C	-2.61942	-1.85335	-1.62616
H	-0.40531	-1.54015	4.20363
H	-0.09112	-1.83580	2.48061
C	-0.12494	-1.04995	3.25391
H	0.89261	-0.63891	3.37352
H	-3.34457	-1.06286	3.67380
C	-3.10339	-0.52264	2.74051
H	-3.13112	-1.25097	1.91026
H	-1.67512	0.85376	5.28199
Si	-1.38801	0.33191	2.83089
C	-1.41405	1.45200	4.39019
H	-3.90217	0.21680	2.55948
H	-2.15157	2.26888	4.31419
H	-3.96778	2.45679	0.87365
H	-3.54147	3.01235	2.51111
Si	-1.46309	2.78241	1.04648
C	-3.30863	3.13806	1.43987
C	-1.26080	3.25074	-0.80773
H	-0.34020	2.85031	-1.27005
H	-0.51382	3.91539	3.11341
C	-0.43288	4.07196	2.02512

```
H  -3.57645  4.17370  1.16207
H   0.63633  4.01067  1.75697
H  -1.21033  4.34968 -0.90936
H  -0.77380  5.09972  1.80403
H  -0.42557  1.90812  4.57203
H  -2.13088  2.91599 -1.39824
N  -0.95787  1.12751  1.33007
```

I(3-4-Ca)1

```
BP86 energy = -1150.93789197
Enthalpy 0K = -1150.477190
Enthalpy 298K = -1150.435578
Free energy 298K = -1150.554002
Low freq. = 11.6948 cm-1
Second freq. = 19.8841 cm-1
```

```
C  -0.95498 -2.28513 -0.54690
Ca  0.18755  0.08889 -0.48330
S  -0.18194 -3.68820  0.04097
S   1.24441  0.99800 -2.99313
S  -2.63509 -2.46859 -0.77204
C   2.33265  1.84234 -1.90389
N   2.19752  1.58657 -0.55942
C   2.99543  2.23093  0.32662
C   3.32226  2.76399 -2.35403
C   4.13984  3.40752 -1.42792
C   3.98138  3.14518 -0.04925
H   2.81219  1.99041  1.38100
H   3.41495  2.95157 -3.42725
H   4.89986  4.11904 -1.77061
H   4.59841  3.63988  0.70547
H   4.63272 -4.67053  0.12919
C   3.86817 -3.89640  0.01008
H   5.27188 -2.26582 -0.35768
C   4.22565 -2.56648 -0.25863
C   3.20831 -1.61275 -0.39836
C   2.51065 -4.22604  0.11446
H   3.42997 -0.55996 -0.60040
H   2.18330 -5.25207  0.30878
N   1.89150 -1.91374 -0.28918
C   1.57119 -3.19432 -0.05182
H  -5.66984  0.36993 -3.39252
C  -4.66189  0.25751 -2.98087
H  -3.84372  2.04533 -3.92918
C  -3.65528  1.19014 -3.27486
C  -2.38614  1.01191 -2.70641
C  -4.35256 -0.84053 -2.16688
H  -1.55834  1.70260 -2.90732
H  -5.09508 -1.61090 -1.93644
N  -2.08040 -0.02831 -1.89207
C  -3.04115 -0.93605 -1.67063
H   0.86136 -1.96992  4.09696
H   0.87426 -2.12538  2.32501
C   0.87577 -1.39722  3.15211
H   1.82680 -0.83773  3.11227
H  -2.19718 -1.91195  4.12280
C  -2.20341 -1.29098  3.20888
H  -2.29746 -1.96611  2.34033
H  -0.57412  0.07343  5.57599
Si -0.62650 -0.20678  3.07682
C  -0.53167  0.77611  4.72391
H  -3.10785 -0.65861  3.23513
H  -1.36373  1.49026  4.84544
H  -3.69208  1.93575  1.67784
H  -3.09581  2.27238  3.32142
Si -1.20634  2.39804  1.62108
C  -3.00585  2.57258  2.26329
C  -1.23795  3.10059 -0.16722
H  -0.30415  2.92701 -0.73530
H  -0.07337  3.37446  3.68514
C  -0.12190  3.62900  2.61426
H  -3.36021  3.61607  2.18218
H   0.90947  3.64210  2.22137
H  -1.36748  4.19676 -0.12066
H  -0.52600  4.65408  2.52825
H   0.41251  1.34112  4.80631
H  -2.08597  2.70143 -0.74830
N  -0.59657  0.75251  1.60806
```

TS(3-4-Ca)2

```
BP86 energy = -1150.92929666
Enthalpy 0K = -1150.467971
Enthalpy 298K = -1150.427663
Free energy 298K = -1150.542392
Low freq. = -107.8776 cm-1
Second freq. = 9.7737 cm-1
```

```
C   1.52966  0.76228 -0.94911
Ca -0.40987 -0.59522 -0.32157
S   1.36980  2.27155 -1.78773
S  -2.14509 -2.63009 -1.32021
S   3.16856  0.20198 -0.80537
C  -3.02742 -2.17228  0.13545
N  -2.51795 -1.14359  0.88934
C  -3.17102 -0.75294  2.00958
C  -4.22955 -2.82040  0.53692
C  -4.88683 -2.40273  1.69244
C  -4.35524 -1.34203  2.45631
H  -2.70413  0.07305  2.56002
H  -4.61452 -3.63978 -0.07614
H  -5.81286 -2.89876  2.00479
H  -4.84337 -0.98771  3.36797
H  -2.19827  3.55243 -4.92469
C  -1.87231  2.82988 -4.16936
```

```
H  -3.62988  1.54191 -4.33929
C  -2.66900  1.71752 -3.84871
C  -2.20474  0.82452 -2.87623
C  -0.64547  3.00167 -3.51871
H  -2.77252 -0.07092 -2.59082
H   0.00994  3.84783 -3.74769
N  -1.02092  0.98220 -2.23150
C  -0.25899  2.04332 -2.56130
H   4.71580 -4.41401 -1.53275
C   3.84899 -3.76234 -1.38140
H   2.35773 -5.35013 -1.55879
C   2.54495 -4.28527 -1.39761
C   1.47334 -3.40763 -1.19539
C   4.03078 -2.38983 -1.17787
H   0.43181 -3.75587 -1.18559
H   5.02874 -1.94021 -1.16924
N   1.63292 -2.07531 -0.99404
C   2.88842 -1.58558 -0.99844
H  -1.98012  3.97124  0.88134
H  -1.26893  3.22643 -0.56561
C  -1.51903  3.04686  0.49006
H  -2.28756  2.25463  0.53175
H   0.92431  4.93384  1.59675
C   1.34275  3.93676  1.36907
H   1.75736  3.97061  0.34994
H  -1.12551  3.92858  3.37298
Si -0.01543  2.60450  1.58779
C  -0.67234  2.92035  3.36460
H   2.17566  3.75653  2.06974
H   0.12735  2.91458  4.12302
H   3.72117  1.07485  2.21664
H   2.89793  1.95262  3.53311
Si  1.42133  0.11006  2.61433
C   3.06726  0.95350  3.09665
C   1.83305 -1.71730  2.20662
H   0.96517 -2.29911  1.84550
H   0.22163  0.84312  4.76985
C   0.36722 -0.08905  4.20603
H   3.61037  0.35024  3.84581
H  -0.62682 -0.50843  3.97419
H   2.14307 -2.18755  3.15718
H   0.88277 -0.80700  4.86944
H  -1.44859  2.20308  3.67730
H   2.65871 -1.84821  1.49324
N   0.53725  0.93128  1.29722
```

I(3-4-Ca)2

```
BP86 energy = -1150.97319987
Enthalpy 0K = -1150.511130
Enthalpy 298K = -1150.470076
Free energy 298K = -1150.587444
Low freq. = 7.6031 cm-1
Second freq. = 14.8214 cm-1

C   1.17340  0.43776  0.37566
Ca -1.28997 -0.10917  0.44845
S   1.22019 -0.70378  2.00541
S  -3.64298 -0.59765  1.83867
S   1.39741  2.14606  1.26394
C  -4.23290 -0.70133  0.18727
N  -3.34381 -0.48356 -0.84476
C  -3.78015 -0.55451 -2.12671
C  -5.59604 -0.99887 -0.11093
C  -6.02111 -1.06544 -1.43396
C  -5.09854 -0.83901 -2.48003
H  -3.01680 -0.37092 -2.89338
H  -6.28521 -1.16950  0.72045
H  -7.06873 -1.29332 -1.66123
H  -5.39602 -0.88245 -3.53092
H   1.45368 -5.64018  1.74881
C   0.97780 -4.72594  1.37879
H  -0.42142 -5.74953  0.04664
C  -0.05821 -4.79312  0.43163
C  -0.63080 -3.59378 -0.00598
C   1.40670 -3.47587  1.83863
H  -1.45458 -3.59036 -0.72906
H   2.21740 -3.38089  2.56616
N  -0.23758 -2.37893  0.44117
C   0.77050 -2.31350  1.34963
H  -1.29981  6.22169  0.98854
C  -1.29137  5.13262  0.87339
H  -3.41056  4.96197  0.34079
C  -2.46440  4.44121  0.50781
C  -2.38892  3.05539  0.37262
C  -0.11296  4.41871  1.08353
H  -3.27319  2.46204  0.11140
H   0.81688  4.92333  1.36192
N  -1.24916  2.34151  0.57222
C  -0.11931  3.00857  0.92517
H   5.58464 -1.91816  0.30763
H   3.90458 -2.37194  0.71407
C   4.52897 -1.80668  0.00275
H   4.41191 -2.26893 -0.99121
H   5.46788  0.61251  1.90162
C   4.39818  0.79318  1.68854
H   3.80968  0.34448  2.50308
H   6.19197  0.84487 -0.93298
Si  4.02716  0.02985 -0.01295
C   5.14003  0.96790 -1.24816
H   4.23355  1.88271  1.69332
H   4.91298  2.04708 -1.23262
H   1.54976  2.73109 -2.35934
H   3.14768  2.24831 -2.98265
Si  1.79552  0.24205 -2.23676
C   2.08019  1.97674 -2.96504
```

C	-0.05410	-0.16148	-2.45571
H	-0.32251	-1.09721	-1.93493
H	3.84260	-0.94581	-3.20871
C	2.74866	-1.06723	-3.24384
H	1.69706	2.03581	-3.99926
H	2.50757	-2.08233	-2.88528
H	-0.26494	-0.31168	-3.53001
H	2.44443	-1.00317	-4.30380
H	5.06834	0.61613	-2.28934
H	-0.69676	0.66969	-2.11544
N	2.27087	0.16747	-0.49662

TS(3-4-Ca)3

BP86 energy = -1150.97290417
Enthalpy 0K = -1150.510974
Enthalpy 298K = -1150.470653
Free energy 298K = -1150.585402
Low freq. = -67.5852 cm-1
Second freq. = 10.0448 cm-1

C	-1.12552	0.64102	-0.08512
Ca	1.28905	-0.12665	-0.37495
S	-1.10200	-0.22951	-2.07221
S	3.71759	-0.61781	-1.66350
S	-1.35642	2.45202	-0.62682
C	4.21706	-0.82204	0.00851
N	3.28027	-0.63052	1.00228
C	3.65118	-0.77480	2.29871
C	5.55470	-1.17290	0.35806
C	5.91123	-1.31384	1.69542
C	4.94255	-1.11074	2.70312
H	2.85660	-0.61157	3.03732
H	6.27979	-1.32368	-0.44615
H	6.93969	-1.58177	1.96293
H	5.18401	-1.21167	3.76437
H	-1.79967	-5.08255	-2.76734
C	-1.25459	-4.30135	-2.22688
H	0.00973	-5.68201	-1.09494
C	-0.25453	-4.64093	-1.29781
C	0.41091	-3.60295	-0.63836
C	-1.55301	-2.95428	-2.45249
H	1.20829	-3.81171	0.08446
H	-2.32542	-2.65072	-3.16431
N	0.14328	-2.29411	-0.85497
C	-0.82610	-1.96171	-1.75297
H	1.76824	6.19106	-0.97499
C	1.66616	5.10425	-0.88665
H	3.81630	4.68464	-0.93369
C	2.80568	4.27539	-0.85912
C	2.61184	2.89932	-0.74395
C	0.40010	4.52782	-0.80370
H	3.45669	2.19921	-0.75011
H	-0.50646	5.13994	-0.82595
N	1.38417	2.31795	-0.65274
C	0.28900	3.11862	-0.68605
H	-5.61958	-1.49593	-0.72596
H	-3.93440	-1.93577	-1.12739
C	-4.58215	-1.50348	-0.34721
H	-4.54597	-2.16793	0.53083
H	-5.34715	1.20312	-1.77838
C	-4.29967	1.36048	-1.46079
H	-3.64327	1.09247	-2.30235
H	-6.16681	1.00353	1.09263
Si	-4.02047	0.26654	0.06655
C	-5.12110	0.98506	1.44897
H	-4.17105	2.43187	-1.23998
H	-4.82834	2.02398	1.67594
H	-1.44522	2.09466	3.08820
H	-3.10269	1.60402	3.52015
Si	-1.86614	-0.25109	2.32451
C	-2.05811	1.25815	3.46498
C	-0.06708	-0.85193	2.46420
H	0.15732	-1.62683	1.71133
H	-4.04244	-1.45988	2.91609
C	-2.96477	-1.68560	2.92987
H	-1.72343	1.02068	4.49031
H	-2.79622	-2.59167	2.32398
H	0.08499	-1.30556	3.46020
H	-2.69252	-1.92398	3.97361
H	-5.10550	0.41012	2.38831
H	0.64846	-0.01646	2.37582
N	-2.27227	0.20391	0.61616

I(3-4-Ca)3

BP86 energy = -1150.98761732
Enthalpy 0K = -1150.524748
Enthalpy 298K = -1150.483550
Free energy 298K = -1150.601646
Low freq. = 11.9412 cm-1
Second freq. = 18.6158 cm-1

C	-1.24444	0.61168	-0.09639
Ca	1.20515	-0.35526	-0.04615
S	-1.47666	1.78802	-1.44817
S	-0.33144	-2.13153	-1.73334
H	1.50074	4.39843	-4.29120
C	1.44080	3.58130	-3.56499
H	3.57818	3.12318	-3.58049
C	2.59291	2.87873	-3.17542
C	2.45646	1.84672	-2.24209
C	0.20821	3.23145	-3.00600
H	3.32102	1.27999	-1.87363
H	-0.70995	3.76247	-3.27420
N	1.26285	1.48542	-1.70328

```
C   0.16588  2.17097 -2.07520
H   2.15426 -6.42102 -1.47721
C   2.05160 -5.38917 -1.12175
H   3.76303 -5.48127  0.24681
C   2.95005 -4.87546 -0.16193
C   2.77406 -3.55291  0.25023
C   1.03498 -4.57922 -1.62516
H   3.44501 -3.08039  0.97844
H   0.33053 -4.94491 -2.37736
N   1.78422 -2.75670 -0.21895
C   0.90800 -3.24040 -1.15845
H  -2.64921  0.64277  3.62855
H  -3.76998  3.04322  0.40542
H   0.17011 -0.45326  2.42906
C  -3.05607 -0.35351  3.38526
C  -4.37181  2.50061 -0.34190
C  -0.42021 -1.36993  2.25484
H  -5.54259  0.65718  1.90200
H  -4.11044  2.88909 -1.33764
N  -2.41230  0.22169  0.45816
H  -2.81484 -1.02358  4.22927
H  -4.15070 -0.27548  3.32470
H  -0.41376 -1.93190  3.20652
Si -2.23379 -1.04662  1.81800
H  -5.43555  2.72572 -0.14729
H   0.06960 -2.03027  1.51560
Si -4.13505  0.61547 -0.19839
C  -5.49136  0.02985  0.99789
H  -6.44665  0.16031  0.45663
H  -5.43076 -1.02581  1.29974
C  -2.97595 -2.67278  1.19505
C  -4.30504 -0.30755 -1.84202
H  -3.52396 -0.01781 -2.56141
H  -2.79943 -3.46366  1.94529
H  -4.05699 -2.63868  0.99103
H  -2.44568 -2.95206  0.26661
H  -5.29049 -0.08995 -2.29040
H  -4.22926 -1.39542 -1.68186
S   3.92912  0.08391  0.64330
H   5.03145  2.19019  2.37668
C   3.94026  2.25067  2.41117
C   3.18121  1.31683  1.64732
C   3.28790  3.21185  3.17898
H   3.87001  3.92952  3.76842
N   1.80772  1.36686  1.67682
C   1.87678  3.25931  3.19084
C   1.19368  2.31606  2.42147
H   1.32984  4.00254  3.77709
H   0.09640  2.30406  2.38480
```

4-Ca

```
BP86 energy = -552.846228327
Enthalpy 0K = -552.690283
Enthalpy 298K = -552.674782
Free energy 298K = -552.735960
Low freq. = 15.8081 cm-1
Second freq. = 25.4112 cm-1

Ca -0.00000 -0.77303  0.00005
S   2.12138 -1.44109  1.54230
S  -2.12141 -1.44138 -1.54202
H   5.79487  1.36376 -0.22857
C   4.74059  1.07654 -0.30700
H   4.29885  2.40586 -1.99524
C   3.91610  1.66186 -1.29242
C   2.58351  1.25851 -1.34644
C   4.21263  0.13014  0.56743
H   1.89444  1.67562 -2.09062
H   4.82601 -0.34120  1.33954
N   2.05091  0.33872 -0.50276
C   2.84366 -0.24161  0.46243
H  -5.79489  1.36374  0.22843
C  -4.74059  1.07658  0.30687
H  -4.29880  2.40627  1.99480
C  -3.91607  1.66213  1.29212
C  -2.58346  1.25884  1.34614
C  -4.21266  0.13001 -0.56739
H  -1.89437  1.67614  2.09019
H  -4.82606 -0.34153 -1.33936
N  -2.05088  0.33890  0.50263
C  -2.84366 -0.24168 -0.46238
```

6

```
BP86 energy = -1196.29335408
Enthalpy 0K = -1195.677874
Enthalpy 298K = -1195.628370
Free energy 298K = -1195.759479
Low freq. = 12.6322 cm-1
Second freq. = 23.6888 cm-1

C   0.70276  0.15695  0.26263
S   1.50991 -1.09849  1.33563
H   6.18372 -2.57339  1.46788
C   5.34542 -2.27155  0.83085
H   6.39135 -2.59775 -1.06184
C   5.46679 -2.28227 -0.56994
C   4.36320 -1.86636 -1.32653
C   4.14325 -1.84864  1.40550
H   4.41500 -1.84330 -2.42271
H   4.01725 -1.79788  2.49135
N   3.18189 -1.48385 -0.79403
C   3.07891 -1.47685  0.54848
H   3.64900  3.34716  1.61863
H   4.31521  2.81446 -0.52451
```

```
H   2.35988  1.20443  3.28379
C   2.68027  3.84046  1.43443
C   4.00553  2.07946 -1.28270
C   1.41219  1.75748  3.19012
H   1.59992  4.45707 -1.27471
H   4.43500  1.10129 -1.01214
N   1.35624  1.40079  0.09925
H   2.51094  4.55320  2.26202
H   2.75948  4.42876  0.50828
H   1.40379  2.56316  3.94722
Si  1.24663  2.58339  1.48760
H   4.44568  2.38761 -2.24834
H   0.58549  1.07136  3.42199
Si  2.11356  1.94577 -1.46820
C   1.40549  3.64013 -1.98676
H   1.85562  3.92918 -2.95373
H   0.31492  3.56053 -2.12931
C  -0.41106  3.50520  1.40213
C   1.76521  0.74448 -2.88781
H   2.01015 -0.28499 -2.58908
H  -0.53427  4.16251  2.28134
H  -0.47145  4.12733  0.49388
H  -1.25268  2.79218  1.37942
H   2.41220  1.03184 -3.73630
H   0.71968  0.79017 -3.23085
H  -4.02191 -2.06160 -1.64502
H  -4.30911 -1.30195  1.13405
H  -3.33806 -2.74426 -3.14610
C  -3.15790 -2.02312 -2.32858
H  -3.10829 -1.01303 -2.76475
H  -5.97705  2.44019 -1.91660
H  -3.69566  1.74907 -2.72424
C  -3.79000 -2.21800  1.45788
C  -5.20872  2.12309 -1.20344
C  -3.94189  1.74569 -1.65788
H  -2.50230 -4.51745 -0.25503
H  -4.01738 -3.01784  0.73395
H  -4.21192 -2.52749  2.43102
C  -5.48399  2.07224  0.17470
C  -2.97286  1.35225 -0.70342
S  -1.32159  1.01981 -1.32626
H  -6.46355  2.35168  0.57297
H  -1.85408  0.44279  2.51269
C  -4.46112  1.64755  1.03228
C  -0.56512 -0.19366 -0.17135
N  -3.22126  1.30457  0.61808
Si -1.53297 -2.46154 -1.43799
C  -1.64910 -4.28897 -0.91291
N  -1.23446 -1.41533  0.03121
H  -4.62978  1.58480  2.11497
Si -1.91851 -1.90876  1.65069
H  -1.78019 -4.88303 -1.83557
C  -1.64088 -0.54933  2.93778
H  -2.32949 -0.72808  3.78301
H  -0.72470 -4.63221 -0.42183
H  -0.61387 -0.57865  3.33483
C  -0.06827 -2.31863 -2.62765
H  -0.08045 -3.17940 -3.31940
H  -0.11017 -1.39870 -3.22976
C  -1.12777 -3.50119  2.33967
H  -1.46515 -4.41851  1.83473
H  -1.40498 -3.58419  3.40654
H   0.88708 -2.32507 -2.07615
H  -0.02898 -3.44872  2.27757
```

6carbene

```
BP86 energy = -598.093022513
Enthalpy 0K = -597.788308
Enthalpy 298K = -597.762826
Free energy 298K = -597.844220
Low freq. = 9.4528 cm-1
Second freq. = 28.0870 cm-1

C   0.18064  0.29512 -0.15080
S   1.21104 -1.18766 -0.09919
H   5.98784 -0.76115 -1.25288
C   5.15012 -0.35920 -0.67300
H   6.29832  1.23808  0.27644
C   5.32392  0.75214  0.16778
C   4.20941  1.22580  0.87637
C   3.87886 -0.93800 -0.77248
H   4.30422  2.08901  1.54827
H   3.68738 -1.79027 -1.43193
N   2.98044  0.67237  0.80875
C   2.83169 -0.37981 -0.01081
H  -3.09258  1.30252 -2.38435
H  -1.77893 -2.25264 -2.25480
H  -0.31628  2.84054 -1.69562
C  -3.40605  1.73560 -1.41936
C  -1.59671 -2.72457 -1.27483
C  -0.73596  3.07377 -0.70406
H  -4.31248 -1.05480 -0.88561
H  -0.54661 -3.05235 -1.24198
N  -1.15720  0.08233 -0.12154
H  -3.70549  2.78142 -1.61026
H  -4.29612  1.19337 -1.06700
H  -1.25685  4.04775 -0.76189
Si -1.97127  1.74902 -0.16722
H  -2.24066 -3.61929 -1.20451
H   0.10391  3.14436  0.00116
Si -2.04283 -1.53393  0.13634
C  -3.92882 -1.29296  0.11877
H  -4.38845 -2.24765  0.43216
H  -4.27545 -0.51789  0.82099
C  -2.61367  2.11339  1.58356
```

C	-1.54638	-2.20179	1.84169
H	-0.45663	-2.32217	1.93821
H	-3.10002	3.10421	1.61079
H	-3.35085	1.36963	1.92899
H	-1.77723	2.12597	2.30218
H	-2.02001	-3.18581	2.00554
H	-1.89133	-1.52140	2.63807

S8. References

1. G.M. Sheldrick, *Program for Area Detector Absorption Correction, Institute for Inorganic Chemistry*, University of Göttingen: Göttingen, Germany, 1996.
2. CrysAlisPRO, version 40.53; Oxford Diffraction / Agilent Technologies UK Ltd / Rigaku: Yarnton, U.K., 2017.
3. G.M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
4. G.M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.
5. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339-341.
6. L. J. Farrugia, *J. Appl. Crystallogr*., 2012, **45**, 849-854.
7. *POV-Ray*, Persistence of Vision Raytracer Pty. Ltd.: Williamstown, Australia, 2013.