SUPPLEMENTARY INFORMATION

FOR

New Journal of Chemistry

Synthesis and molecular structures of divalent bridged bis(guanidinate) europium complexes and their application in intermolecular hydrophosphination of alkenes and alkynes

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S1 Table S1 X-ray Crystallography Data for Complexes **1**–**3**

	1·THF	**2**	**3**·2THF
Formula	$C_{35}H_{76}ClN_6O_3Si_2Eu$	$C_{46}H_{104}N_{12}Si_4Eu_2$	$C_{64}H_{104}N_{12}O_4Eu_2$
Mw	872.61	1241.69	1409.51
T (K)	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Crystal size/mm	0.55 × 0.35 × 0.30	0.40 ×0.20 × 0.10	0.80× 0.70 ×0.70
a (Å)	14.6965(5)	13.5784(13)	12.834(4)
b (Å)	13.2218(4)	13.6097(10)	14.323(4)
c (Å)	23.7134(8)	19.0544(10)	19.638(7)
α (Å)	90	71.442(10)	90
β (Å)	92.135	75.023(9)	107.298(6)
γ (°)	90	83.412(12)	90
V ($Å^3$)	4604.6(3)	3222.7(5)	3447(2)
Z ($Å^3$)	4	2	2
Dcalcd (g cm^{-3})	1.259	1.280	1.358
(μ(mm^{-1})	1.508	2.040	1.855
F (000)	1840	1292	1460
θ range (°)	2.77-26.37	3.02-25.50	3.04-25.50
Collcdrflcns	32205	26124	17199
Unique rflcns	9410	11920	6363
Rint	0.0482	0.0635	0.0447
GOF	1.036	1.086	1.122
R [I >2σ(I)]	0.0726	0.0851	0.0499
wR	0.1857	0.1836	0.1298
Largest diff. peak and hole (e $Å^{-3}$)	3.959, -2.437	2.368, -3.183	1.266, -1.287
R_{int}	0.0482	0.0635	0.0447

S2 Experimental

General procedures

All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. The solvents of THF, toluene, and n-hexane were dried and freed of oxygen by distilling from sodium benzophenoneketyl under argon before use.Diphenylphosphine were purchased from Aldrich and used as received. All the liquid alkenes and alkynes were dried over CaH_2, freshly distilled, and degassed prior to use. All the solid alkenes and alkynes were degassed prior to use. The ligand precursor $L^1Li_2(THF)$ (L^1Li_2 = [*i*Pr(Me_3Si)NC(N*i*Pr)N(CH_2)$_3$NC(N*i*Pr)N($SiMe_3$)*i*Pr]$Li_2$was prepared according to the literature procedure.[1]

NMR spectra were recordedon a Bruker AVANCE III HD-400 spectrometer($CDCl_3$ as solvent).Chemical shifts for ^1H, ^{13}C and ^{31}P NMR spectra were referenced internallyusing the residual solvent resonances and reported relative to TMS.Elemental analysis was performed by directusing a Carlo-Erba EA1110 instrument. The IR spectrawere recorded on a Magna-IR 550spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

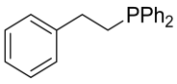
NMR-Scale Catalytic Reactions

The catalyst (1 mol%) was loaded in a 10 mL Sample bottle (with a stirring bar) in the glovebox under dried nitrogen. To the bottle were added the diphenylphosphine (Ph_2PH) (5.747 M, 1.00 mmol) and the alkene/alkyne (1.00 mmol). The responding mixture started at 60 ^oC or room temperature. After the desired reaction time, $CDCl_3$ was added to the selected reaction mixture, and the ^1H NMR and ^{31}P NMR spectrum was recorded shortly after regular time intervals.Conversion was determined by integrating the remaining alkene/alkyne and the newly formed addition product.

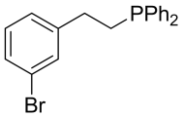
Preparative-scale Catalytic Reactions

The complex **2**(12.5 mg, 0.01 mmol, 1 mol%)was loaded ina10 mL Samplebottle (with a stirring bar) in the glovebox under dried nitrogen. To the bottle were addedthediphenylphosphine (Ph_2PH) (5.747 M, 1.00 mmol)and the alkene (1.00 mmol). The respondingmixture started at 60 ^oC. After the desired reaction time, the resulting mixturewas dissolved in EtOAcfollowed by the addition of silica gel and removal of the excessof solvent in vacuo. The reaction crude absorbed on silicagel was subjected to columnchromatography (silica gel, petroleum ether/EtOAc) to give the pure phosphanes**4**.

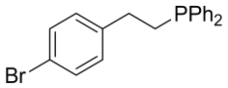
S3 Spectroscopic data for the addition products of alkenes



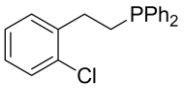
phenethyldiphenylphosphine (4a).[21]H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.15 (m, 14H), 2.74-2.68 (m,2H), 2.38-2.33 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$):δ = -15.9 ppm (s).



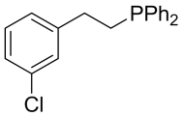
(3-bromophenethyl)diphenylphosphine (4b).[31]H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.42 (m, 4H), 7.38-7.30 (m, 8H),7.15-7.08 (m, 2H), 2.72-2.66 (m,2H), 2.36-2.32 (m, 2H).[31]P NMR (162 MHz,$CDCl_3$):δ = -16.0 ppm (s).



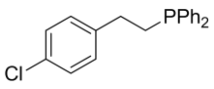
(4-bromophenethyl)diphenylphosphine (4c).[41]H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.34 (m, 12H,), 7.04 (m, 2H),2.71-2.65 (m,2H), 2.36-2.32 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$) δ = -16.2 ppm (s).



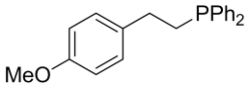
(2-chlorophenethyl)diphenylphosphine (4d).[1]H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.47 (m, 4H), 7.38-7.31 (m, 7H),7.21-7.11 (m, 3H), 2.88-2.82 (m, 2H), 2.39-2.35 (m, 2H).[13]C NMR (101 MHz, $CDCl_3$) δ = 140.3 (d, J_{cp} = 13.8Hz), 138.4 (d, J_{cp} = 12.9Hz), 133.8, 132.9 (d, J_{cp} = 18.3 Hz), 130.4, 129.6, 128.8, 128.5 (d, J_{cp} = 6.7 Hz), 127.7, 127.0, 30.5 (d, J_{cp} = 19.2 Hz), 28.5 (d, J_{cp} = 13.3 Hz).[31]P NMR (162 MHz, $CDCl_3$) δ = -15.5 ppm (s).HRMS (EI):m/z calcd. for $C_{20}H_{18}ClP$ 325.0839, found 325.0826.



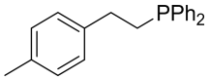
(3-chlorophenethyl)diphenylphosphine (4e).[1]H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.33 (m, 10H), 7.22-7.04(m, 4H), 2.74-2.68 (m,2H), 2.38-2.34 (m, 2H).[13]C NMR (101 MHz, $CDCl_3$) δ = 144.7 (d, J_{cp} = 13.3 Hz), 138.3 (d, J_{cp} = 12.9 Hz), 134.3, 132.8 (d, J_{cp} = 18.6 Hz), 129.8, 128.9, 128.6 (d, J_{cp} = 6.7 Hz), 128.4, 126.4 (d, J_{cp} = 19.4 Hz), 32.0 (d, J_{cp} = 18.3 Hz), 30.0 (d, J_{cp} = 13.2 Hz). [31]P NMR (162 MHz, $CDCl_3$) δ = -16.0 ppm (s).HRMS (EI):m/z calcd. for $C_{20}H_{18}ClP$ 325.0816, found 325.0831.



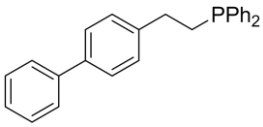
(4-chlorophenethyl)diphenylphosphine (4f).[51]H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.21 (m, 10H), 7.11-7.09 (m, 2H), 6.97-6.95 (m, 2H), 2.60-2.54 (m, 2H), 2.24-2.19 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$) δ = -16.2 ppm(s).



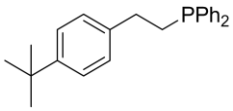
(4-methoxyphenethyl)diphenylphosphine (4g).[21]H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.42 (m, 4H), 7.35-7.33 (m, 6H),7.09 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.70-2.64 (m, 2H),2.36-2.32 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$) δ = -16.2 ppm(s).



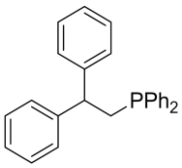
(4-methylphenethyl)diphenylphosphine (4h).[61]H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.32 (m, 10H), 7.09-7.07 (m, 4H), 2.71-2.65 (m,2H), 2.36-2.33 (m, 2H), 2.31 (s, 3H).[31]P NMR (162 MHz, $CDCl_3$) δ = -16.0 ppm(s).



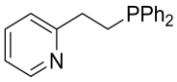
(2-([1,1'-biphenyl]-4-yl)ethyl)diphenylphosphine (4i).[41]H NMR (400 MHz, $CDCl_3$) δ= 7.50-7.16 (m, 19H), 2.72-2.68 (m, 2H), 2.35-2.31 (m, 2H).[31]P NMR (161.9 MHz, $CDCl_3$) δ = -15.7 ppm(s).



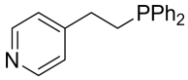
(4-(tert-butyl)phenethyl)diphenylphosphine (4j).[71]H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.30 (m, 12H), 7.13 (d, J = 8.2 Hz, 2H),2.75-2.69 (m,2H), 2.40-2.36 (m, 2H), 1.32 (s, 9H).[31]P NMR (162 MHz,$CDCl_3$) δ = -15.7 ppm(s).



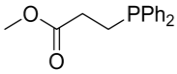
(2,2-diphenylethyl)diphenylphosphine (4k).[81]H NMR (400 MHz, $CDCl_3$) δ=7.42-7.15 (m, 20 H), 3.97–3.91 (m, 1H), 2.85 (d, J = 8.0 Hz, 2H).[31]P NMR (162 MHz, $CDCl_3$) δ = -20.8 ppm(s).



2-(2-(diphenylphosphino)ethyl)pyridine (4l).[21]H NMR (400 MHz, $CDCl_3$) δ= 8.52 (d, J = 4.8 Hz, 1H), 7.58-7.53 (m, 1H), 7.48-7.44 (m, 4H), 7.36-7.31 (m, 6H), 7.11-7.07 (m, 2H), 2.94-2.87 (m, 2H), 2.53-2.49 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$) δ = -15.4 ppm(s).



4-(2-(diphenylphosphino)ethyl)pyridine (4m).[21]H NMR (400 MHz, $CDCl_3$)δ= 8.48-8.46 (m, 2H), 7.46-7.34 (m, 10H), 7.09 (d, *J* = 5.9 Hz, 2H), 2.74-2.67 (m, 2H), 2.38-2.33 (m, 2H).[31]P NMR (162 MHz, $CDCl_3$)δ = -16.0 ppm(s).



Methyl-3-(diphenylphosphanyl)propanoate (4o).[31]H NMR (400 MHz, $CDCl_3$) δ= 7.45-7.40 (m, 4H), 7.36-7.33 (m, 6H), 3.64 (s, 3H), 2.44-2.32 (m, 4H).[31]P NMR (162 MHz, $CDCl_3$) δ = -15.7 ppm(s).

S4 Copies of NMR Spectra for all compounds

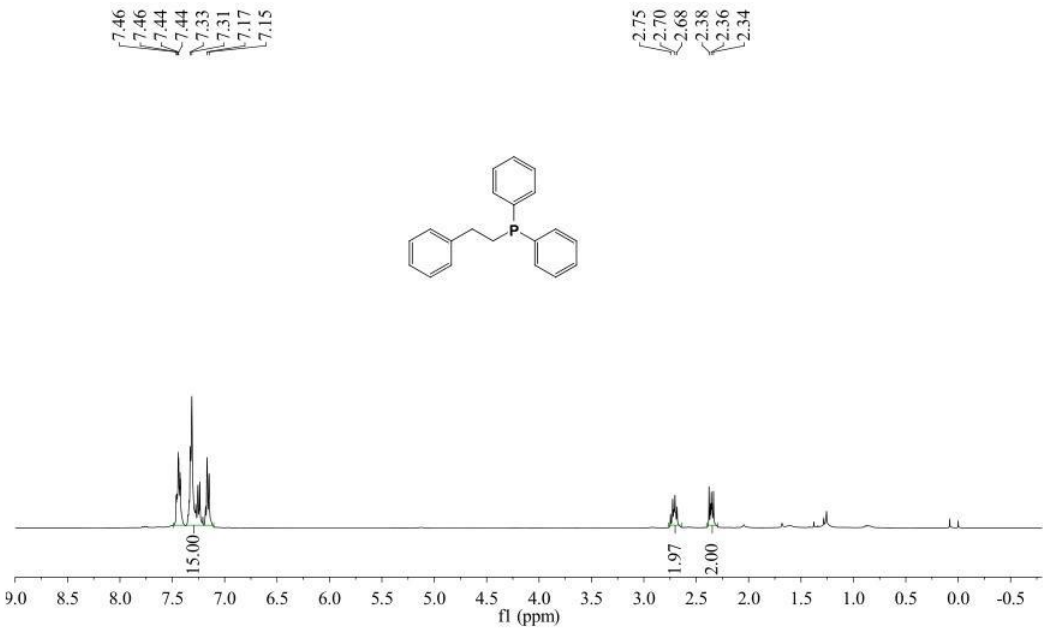


Figure S1. ^{1}H NMR spectrum of **phenethyldiphenylphosphine (4a)**in $CDCl_3$.

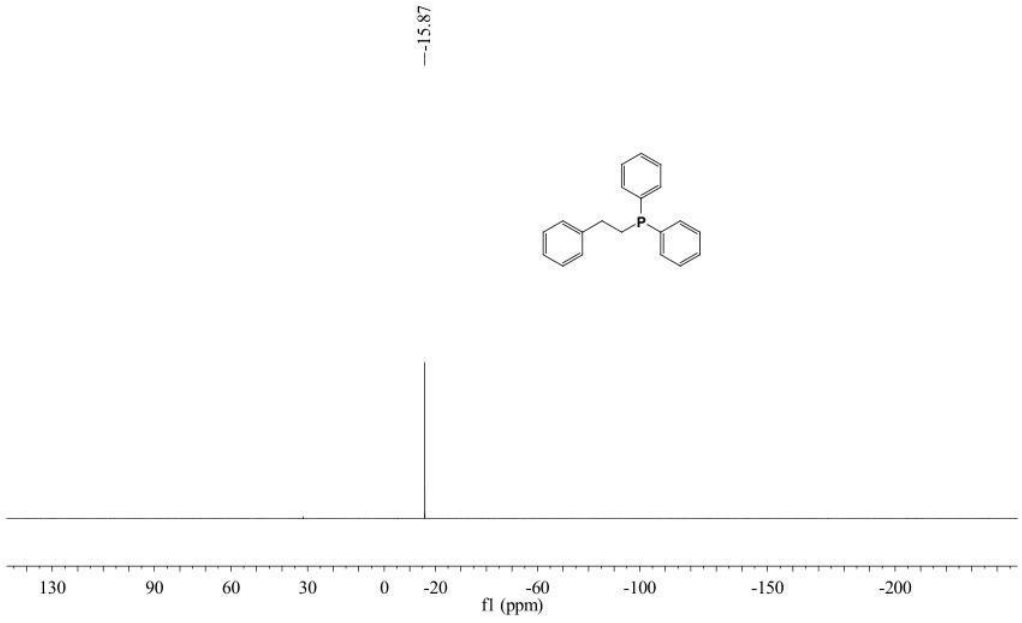


Figure S2. ^{31}P NMR spectrum of **phenethyldiphenylphosphine (4a)**in $CDCl_3$.

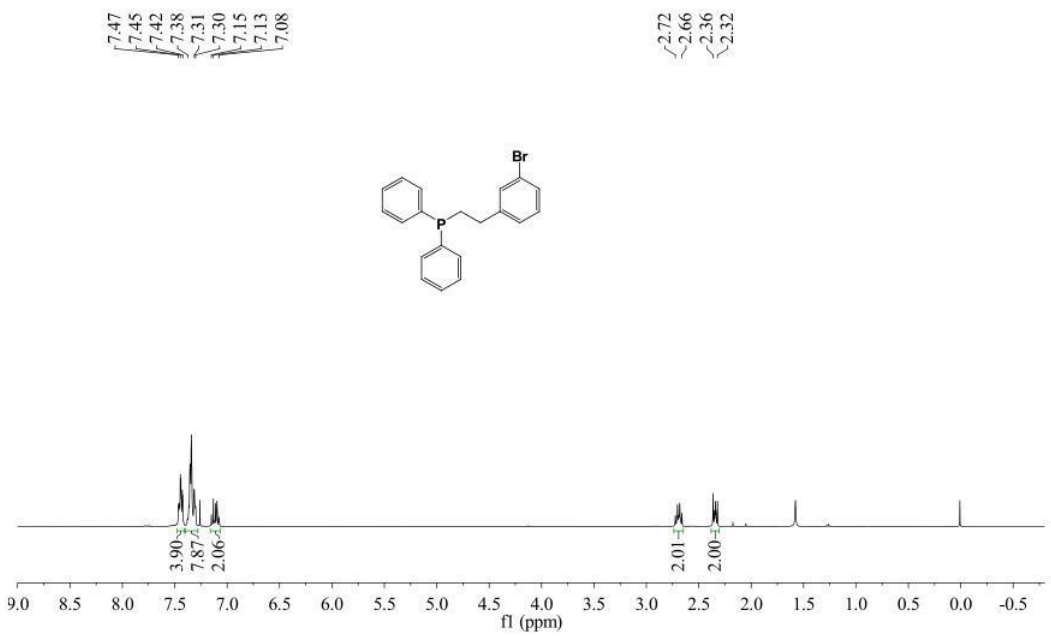


Figure S3. ^{1}H NMR spectrum of **(3-bromophenethyl)diphenylphosphine (4b)**in $CDCl_3$.

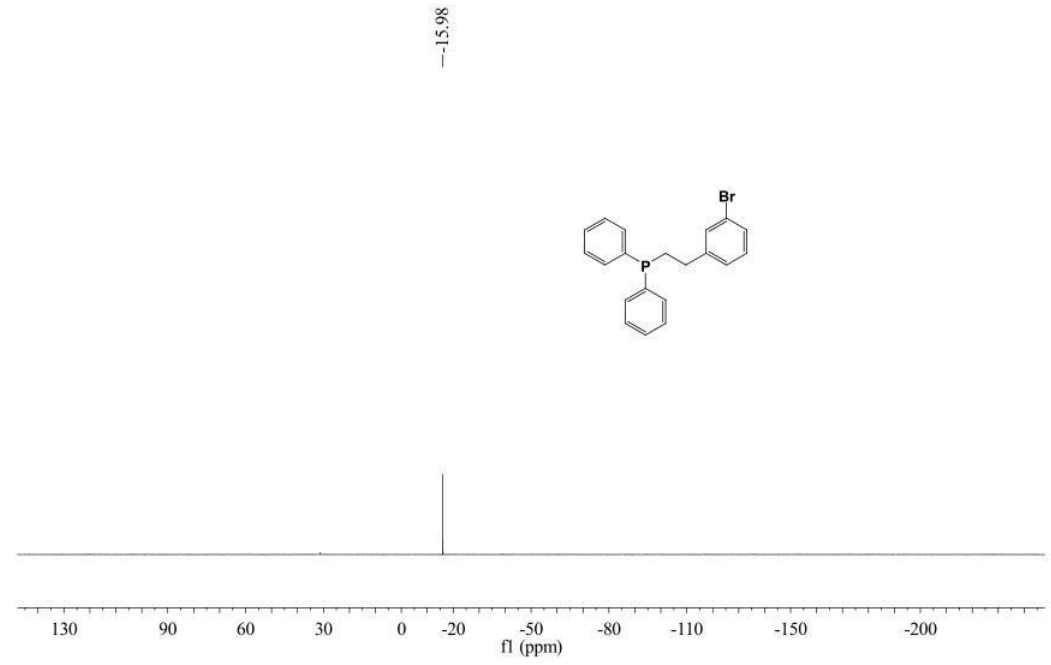


Figure S4. ^{31}P NMR spectrum of **(3-bromophenethyl)diphenylphosphine (4b)**in $CDCl_3$.

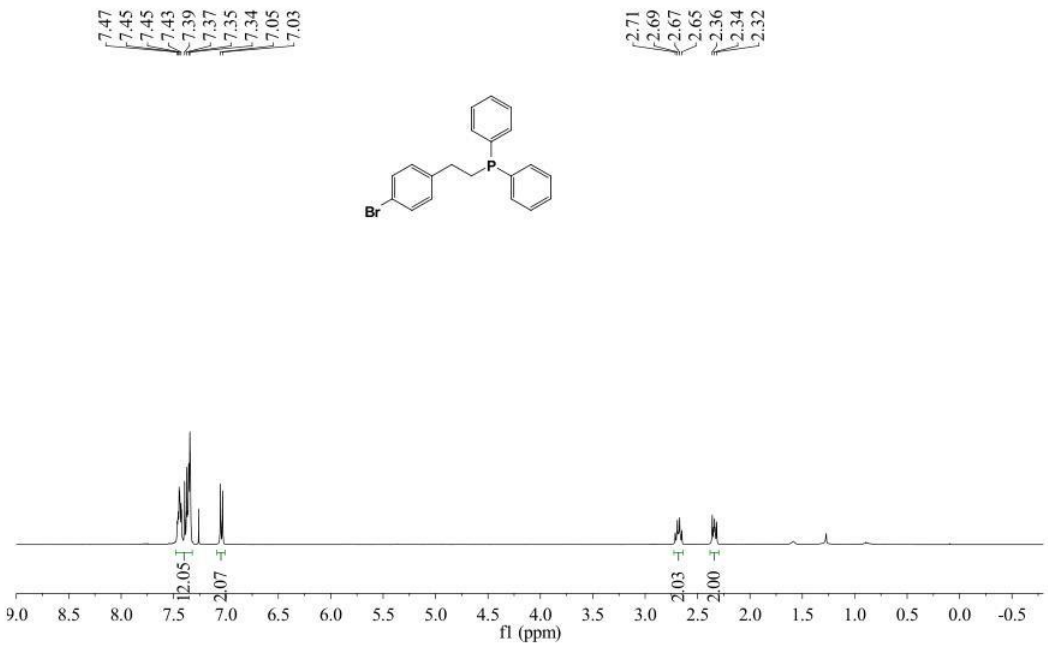


Figure S5. ^{1}H NMR spectrum of **(4-bromophenethyl)diphenylphosphine (4c)**in $CDCl_3$.

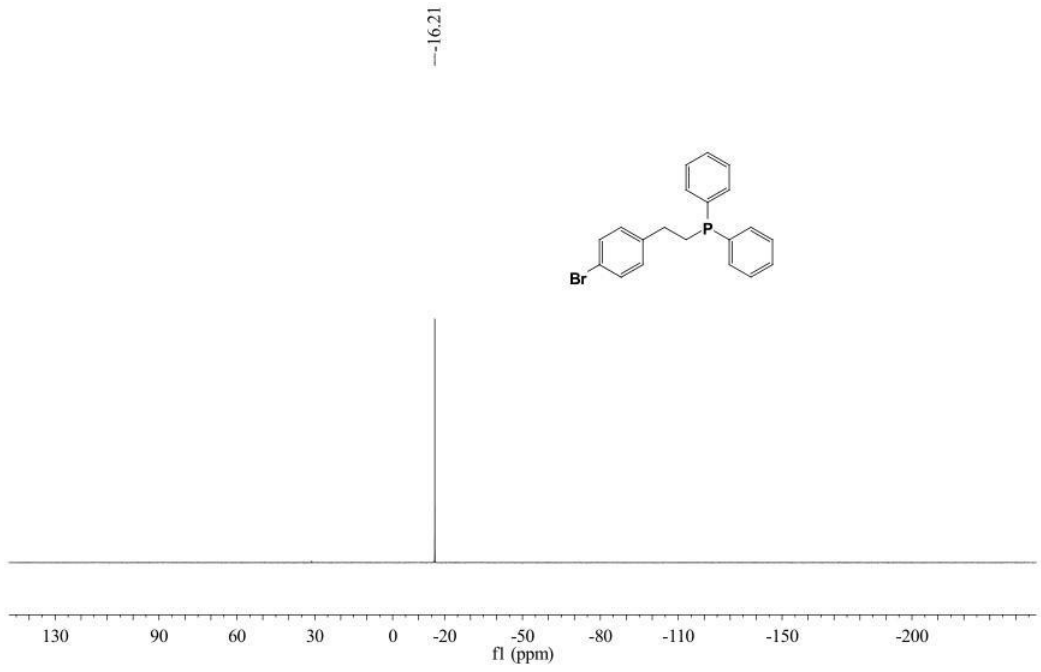


Figure S6. ^{31}P NMR spectrum of **(4-bromophenethyl)diphenylphosphine (4c)**in $CDCl_3$.

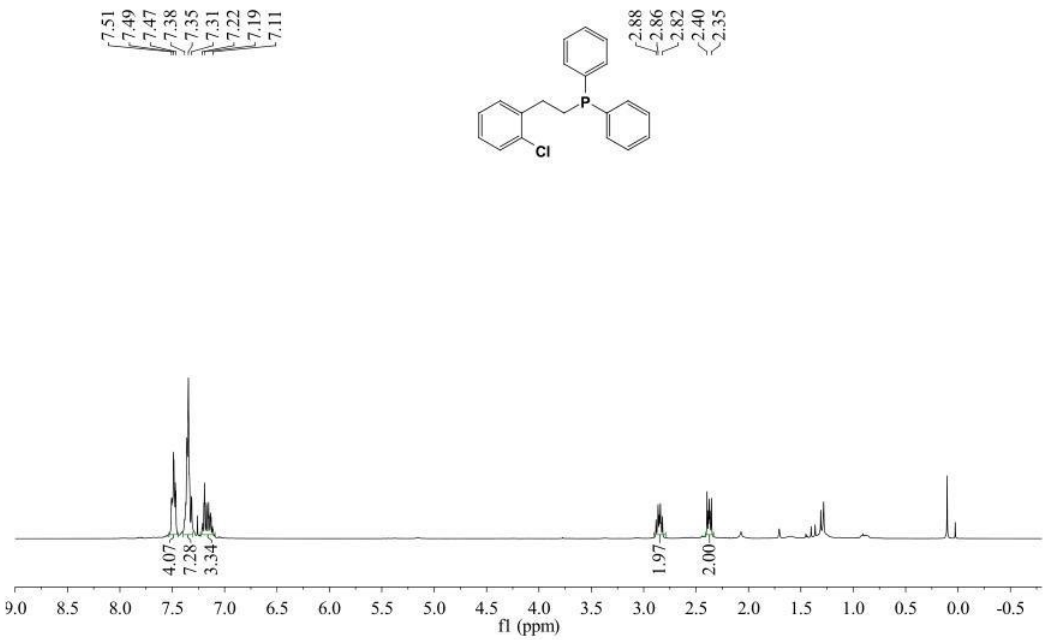


Figure S7. [1]H NMR spectrum of **(2-chlorophenethyl)diphenylphosphine (4d)**in $CDCl_3$.

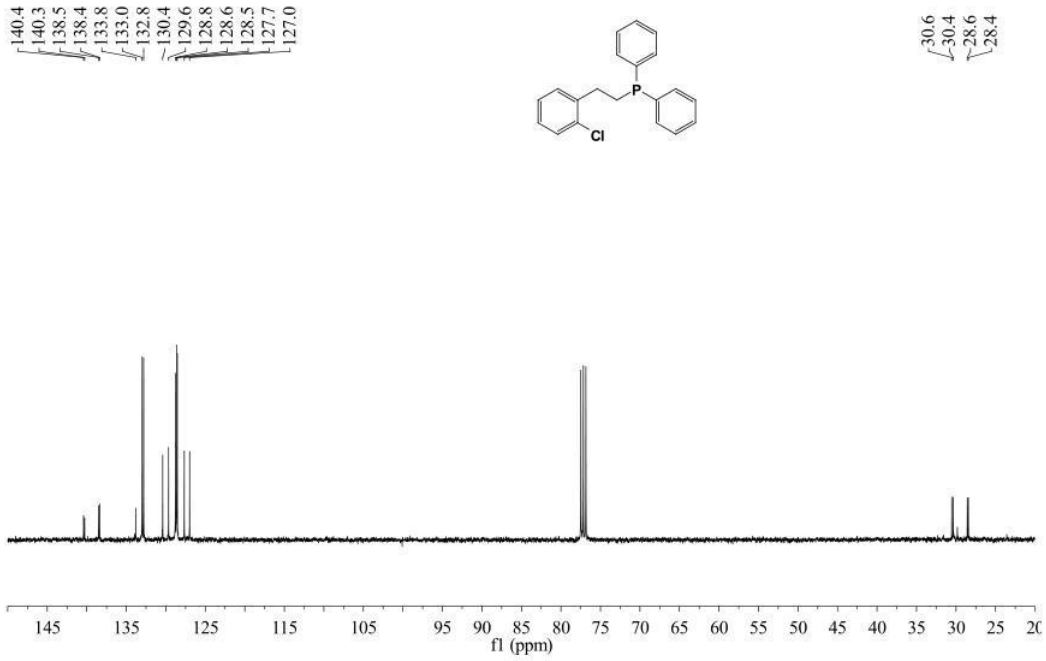


Figure S8. [13]C NMR spectrum of **(2-chlorophenethyl)diphenylphosphine (4d)**in $CDCl_3$.

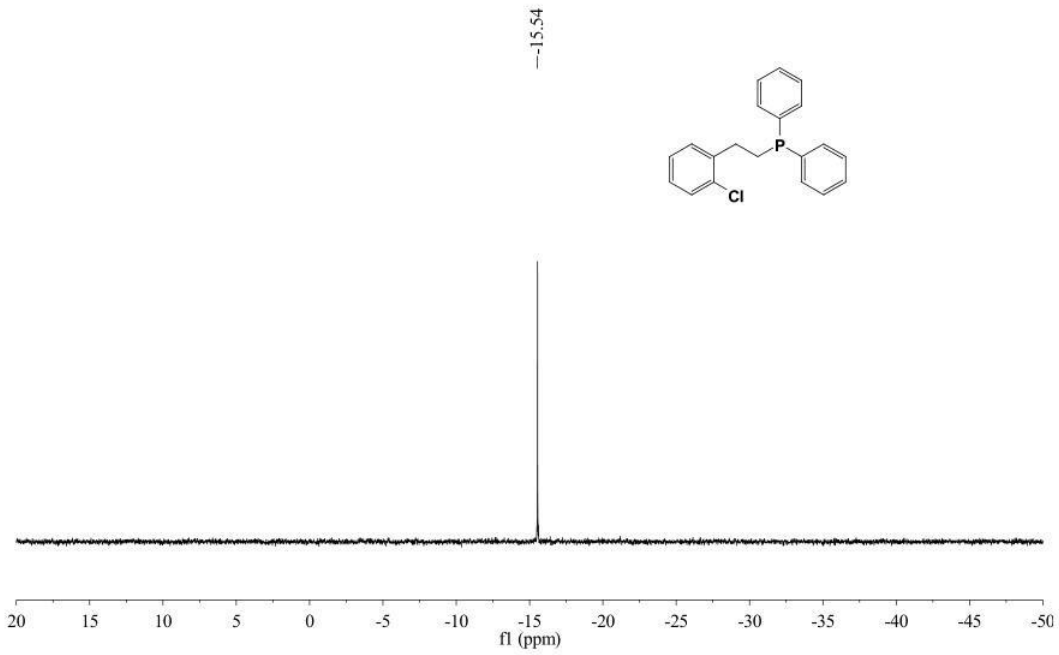


Figure S9. ^{31}P NMR spectrum of **(2-chlorophenethyl)diphenylphosphine (4d)**in $CDCl_3$.

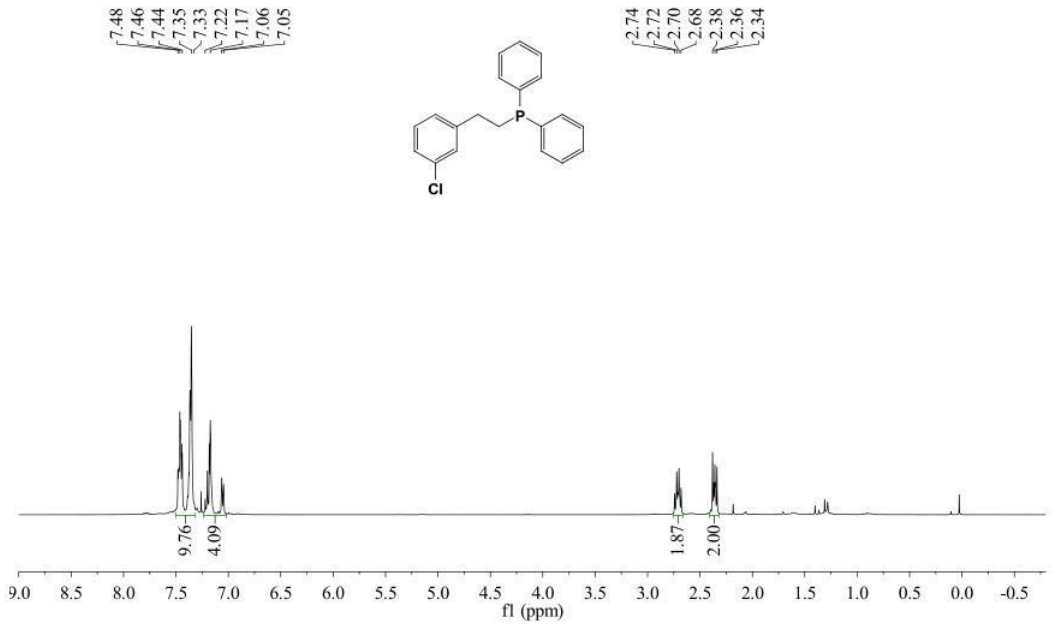


Figure S10. ^{1}H NMR spectrum of **(3-chlorophenethyl)diphenylphosphine (4e)**in $CDCl_3$.

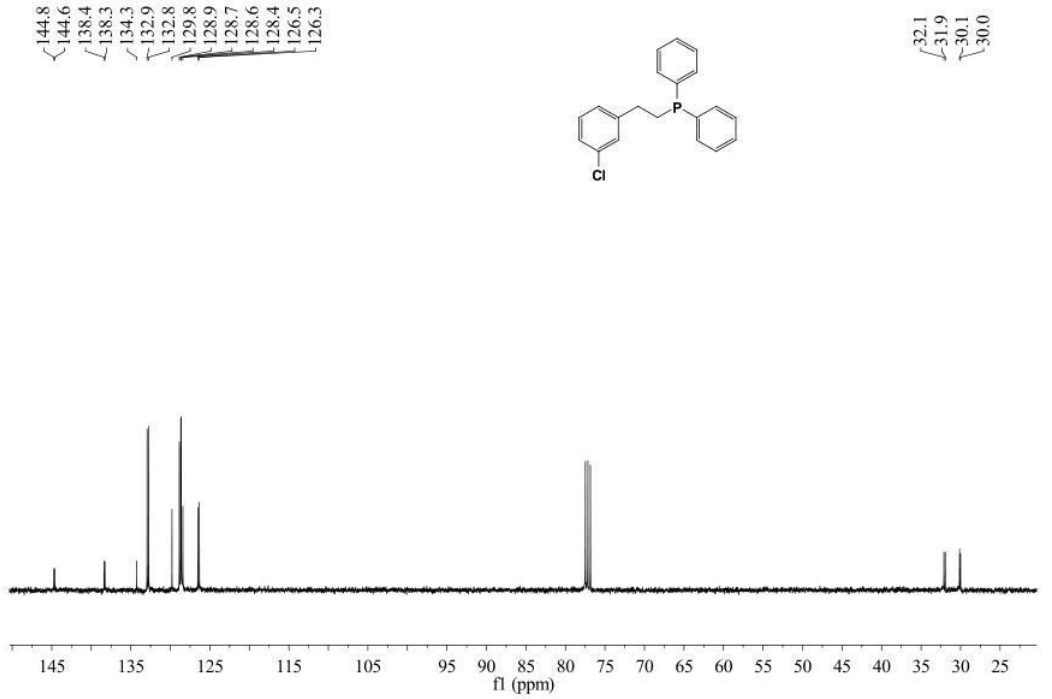


Figure S11. ^{13}C NMR spectrum of **(3-chlorophenethyl)diphenylphosphine (4e)**in $CDCl_3$.

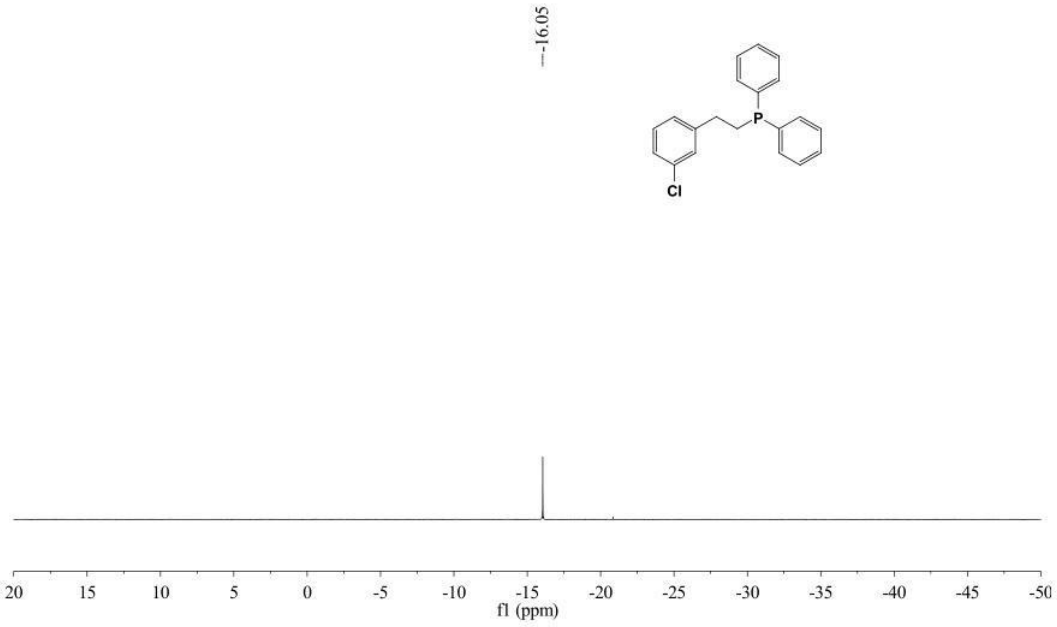


Figure S12. ^{31}P NMR spectrum of **(3-chlorophenethyl)diphenylphosphine (4e)**in $CDCl_3$.

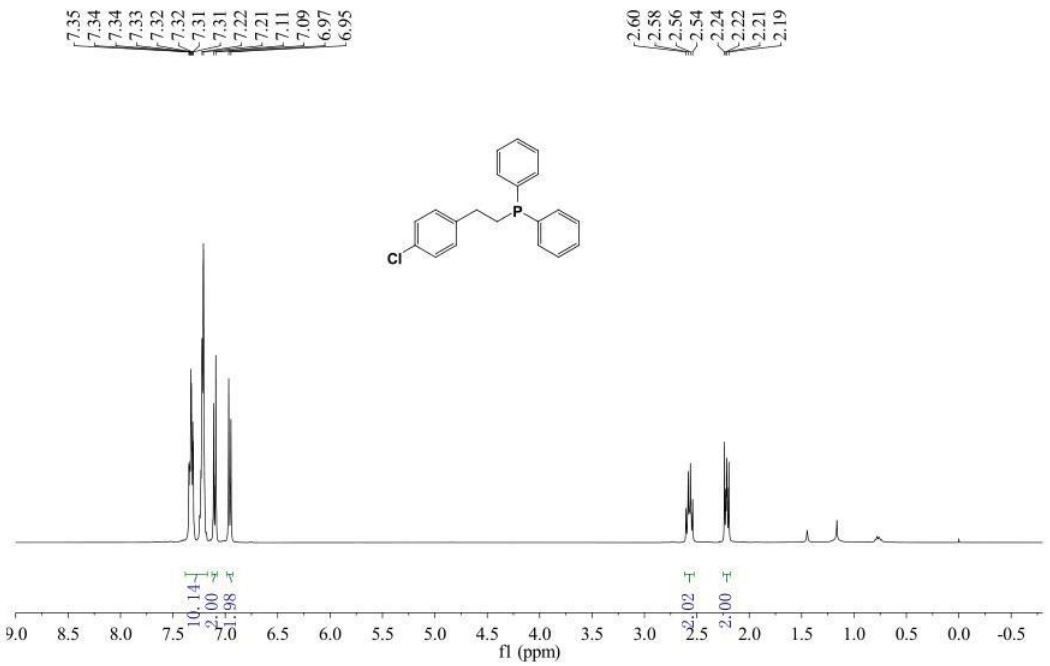


Figure S13. ^{1}H NMR spectrum of **(4-chlorophenethyl)diphenylphosphine (4f)**in $CDCl_3$.

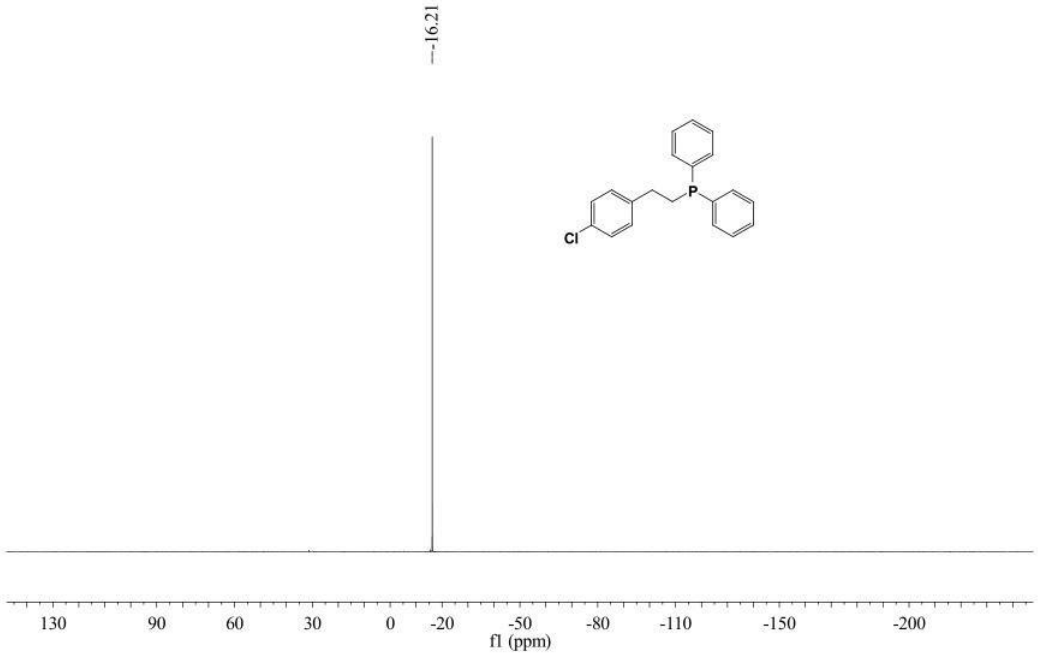


Figure S14. ^{31}P NMR spectrum of **(4-chlorophenethyl)diphenylphosphine (4f)**in $CDCl_3$.

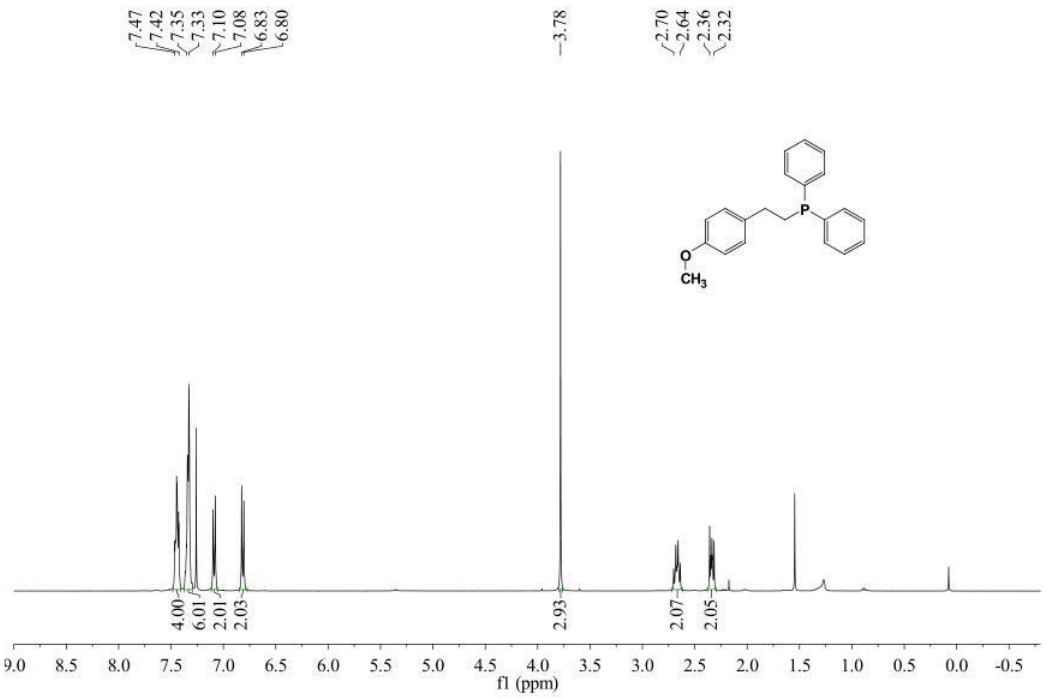


Figure S15. ^{1}H NMR spectrum of **(4-methoxyphenethyl)diphenylphosphine (4h)**in $CDCl_3$.

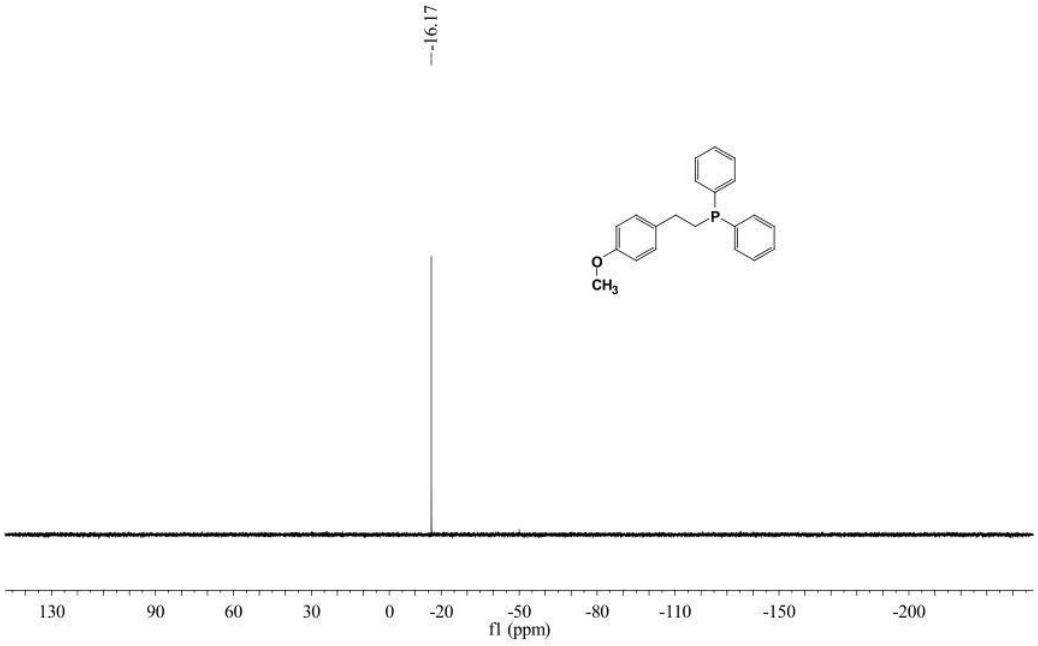


Figure S16. ^{31}P NMR spectrum of **(4-methoxyphenethyl)diphenylphosphine (4h)**in $CDCl_3$.

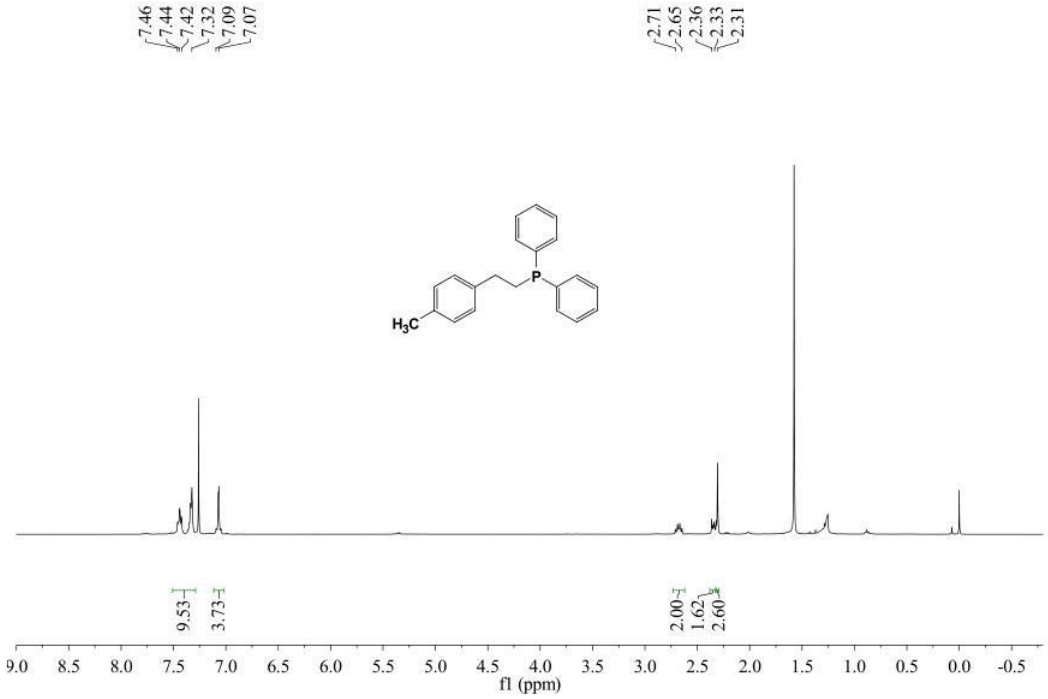


Figure S17. ^{1}H NMR spectrum of **(4-methylphenethyl)diphenylphosphine (4i)**in $CDCl_3$.

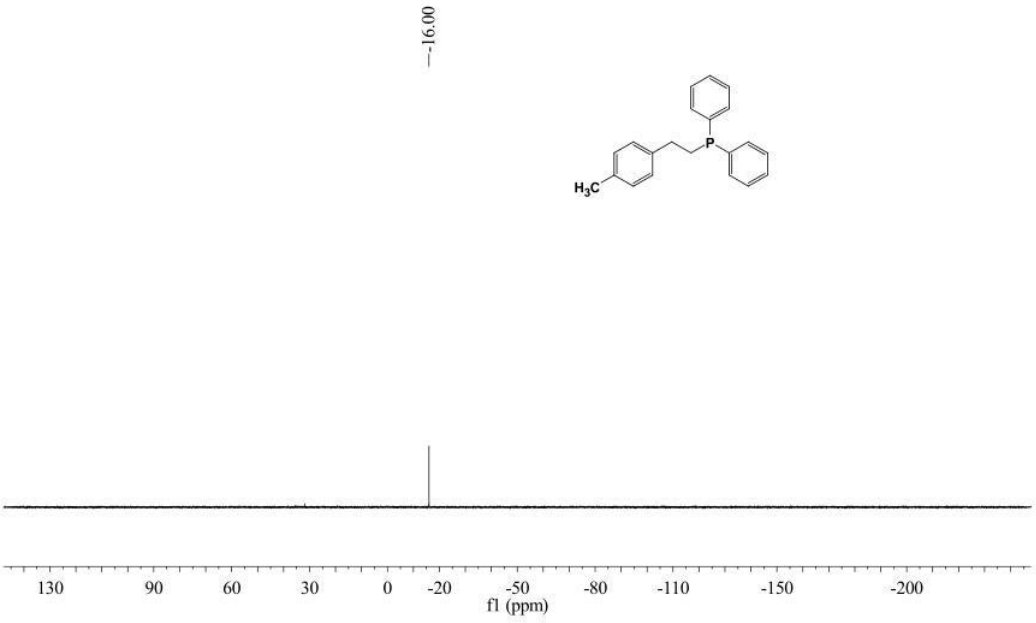


Figure S18. ^{31}P NMR spectrum of **(4-methylphenethyl)diphenylphosphine (4i)**in $CDCl_3$.

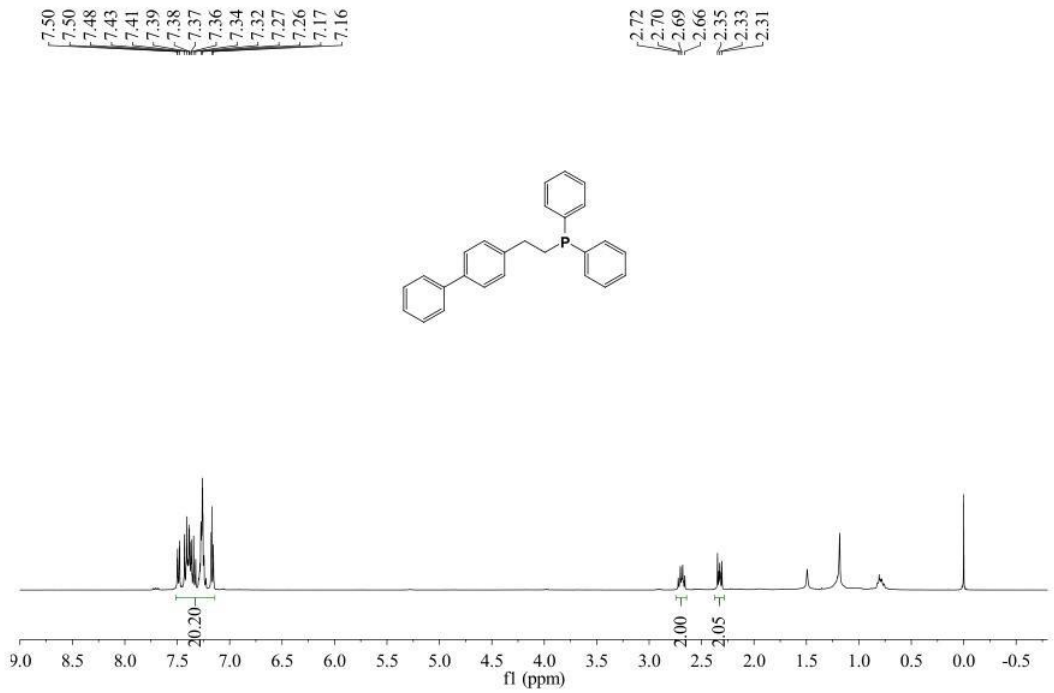


Figure S19. [1]H NMR spectrum of **(2-([1,1'-biphenyl]-4-yl)ethyl)diphenylphosphine (4j)**in $CDCl_3$.

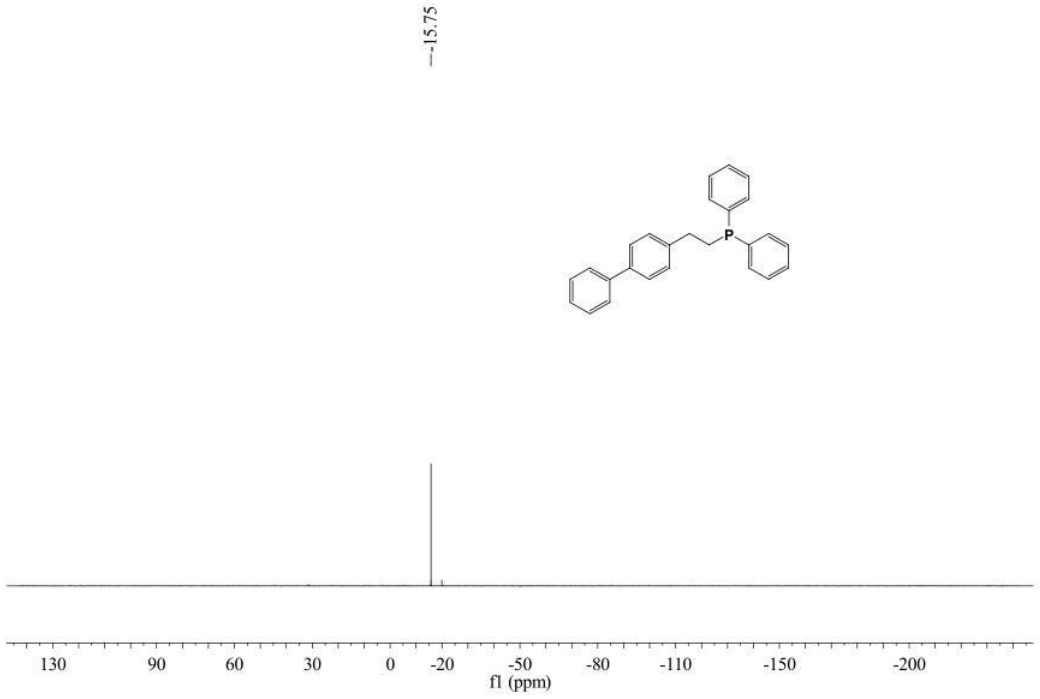


Figure S20. [31]PNMR spectrum of **(2-([1,1'-biphenyl]-4-yl)ethyl)diphenylphosphine (4j)**in $CDCl_3$.

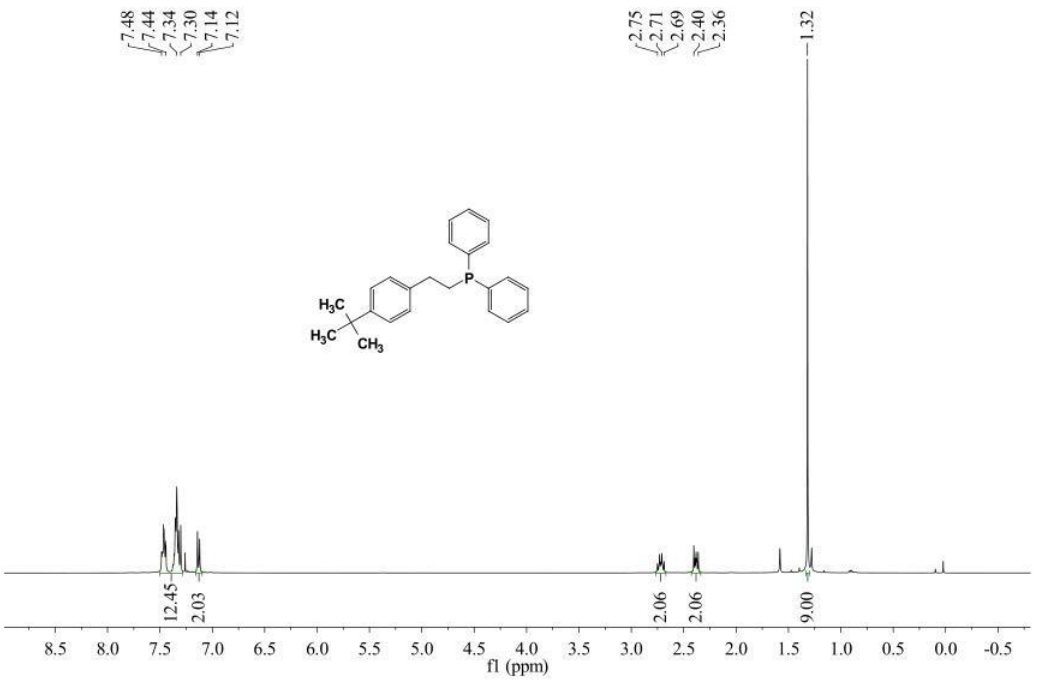


Figure S21. [1]H NMR spectrum of **(4-(tert-butyl)phenethyl)diphenylphosphine (4k)**in $CDCl_3$.

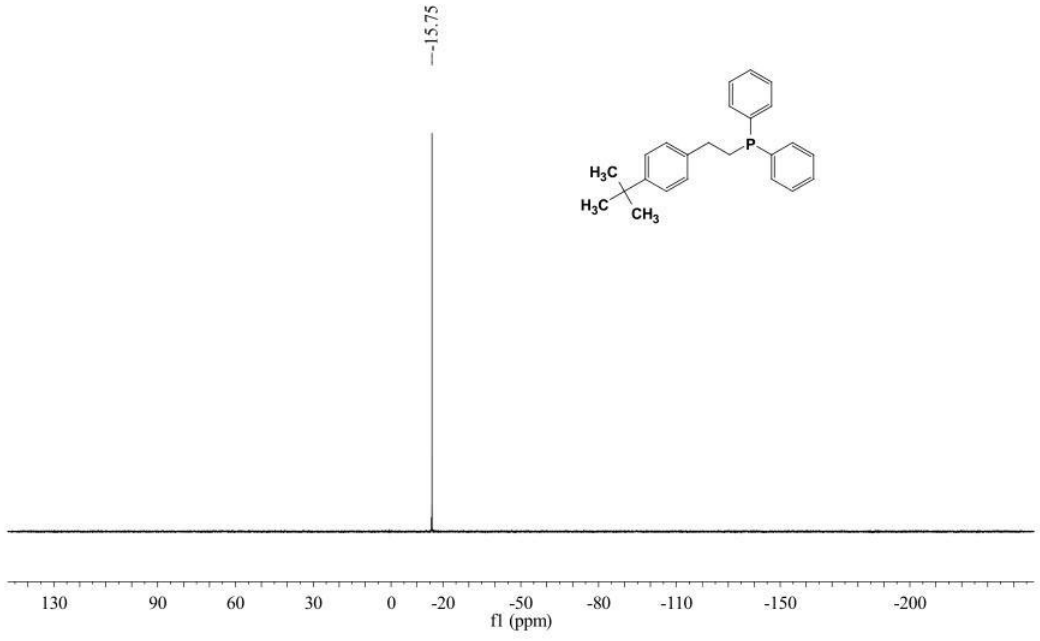


Figure S22. [31]PNMR spectrum of **(4-(tert-butyl)phenethyl)diphenylphosphine (4k)**in $CDCl_3$.

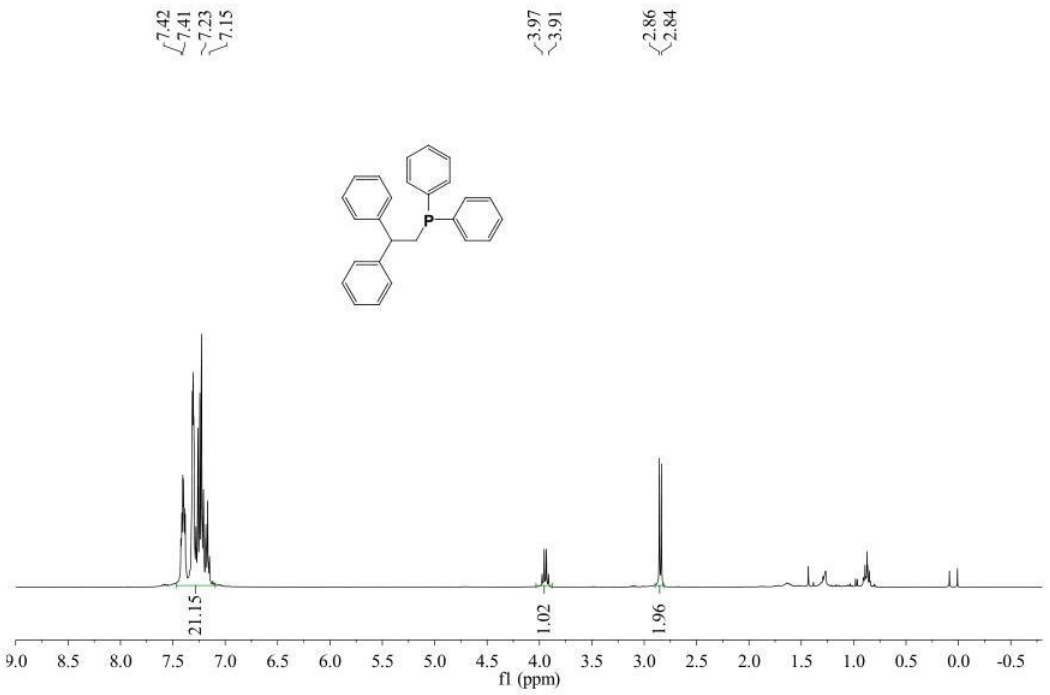


Figure S23. ^{1}H NMR spectrum of **(2,2-diphenylethyl)diphenylphosphine (4l)**in $CDCl_3$.

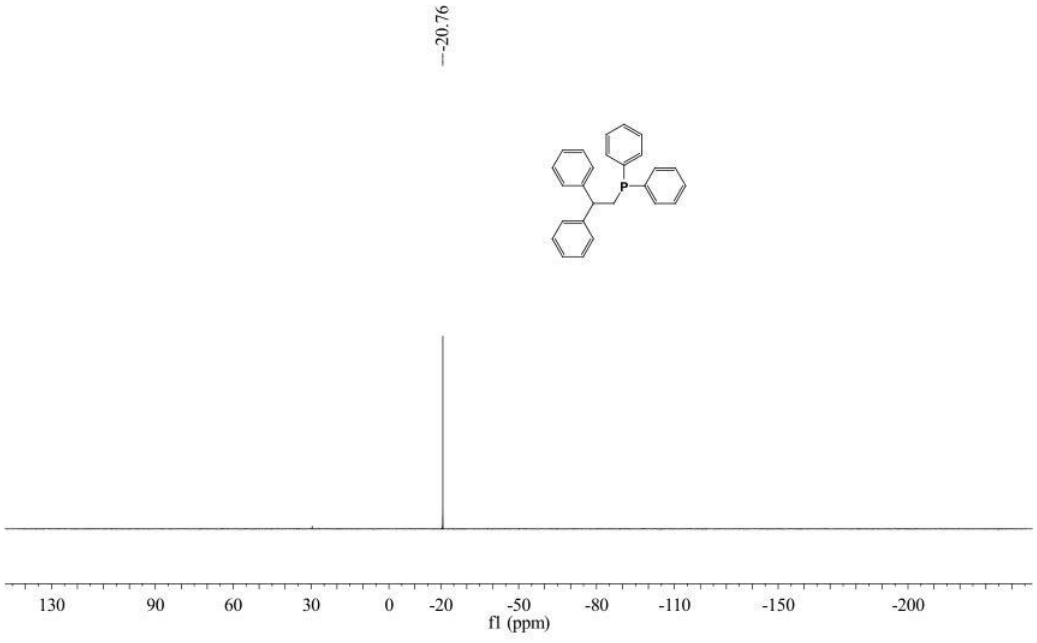


Figure S24. ^{31}PNMR spectrum of **(2,2-diphenylethyl)diphenylphosphine (4l)**in $CDCl_3$.

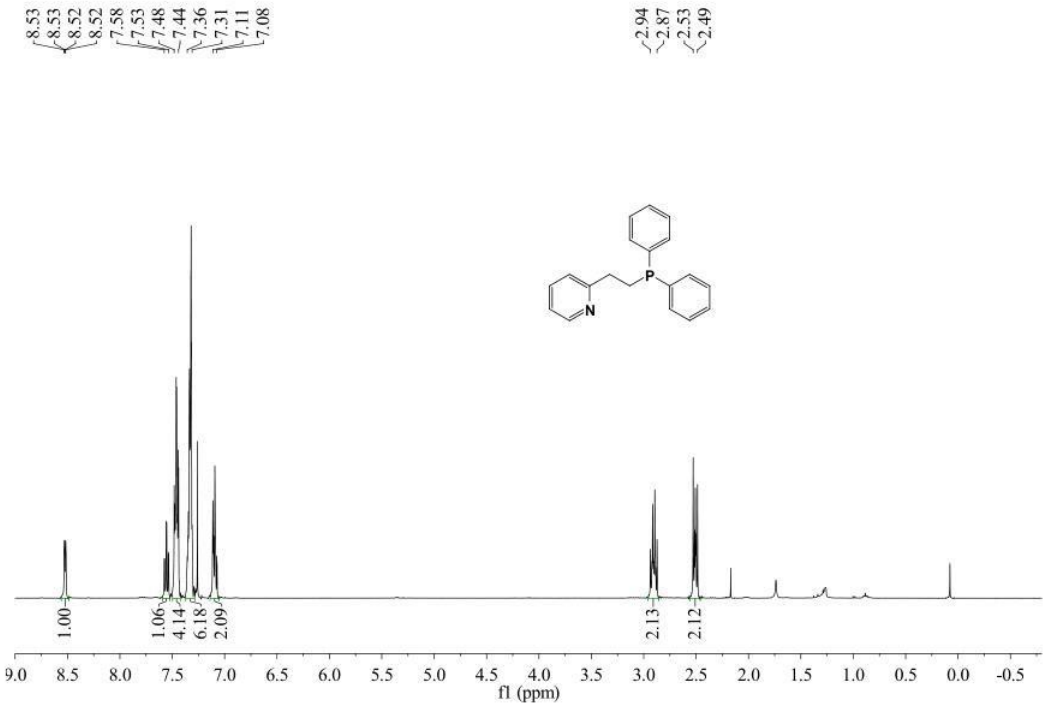


Figure S25. ^{1}H NMR spectrum of **2-(2-(diphenylphosphino)ethyl)pyridine (4m)**in $CDCl_3$.

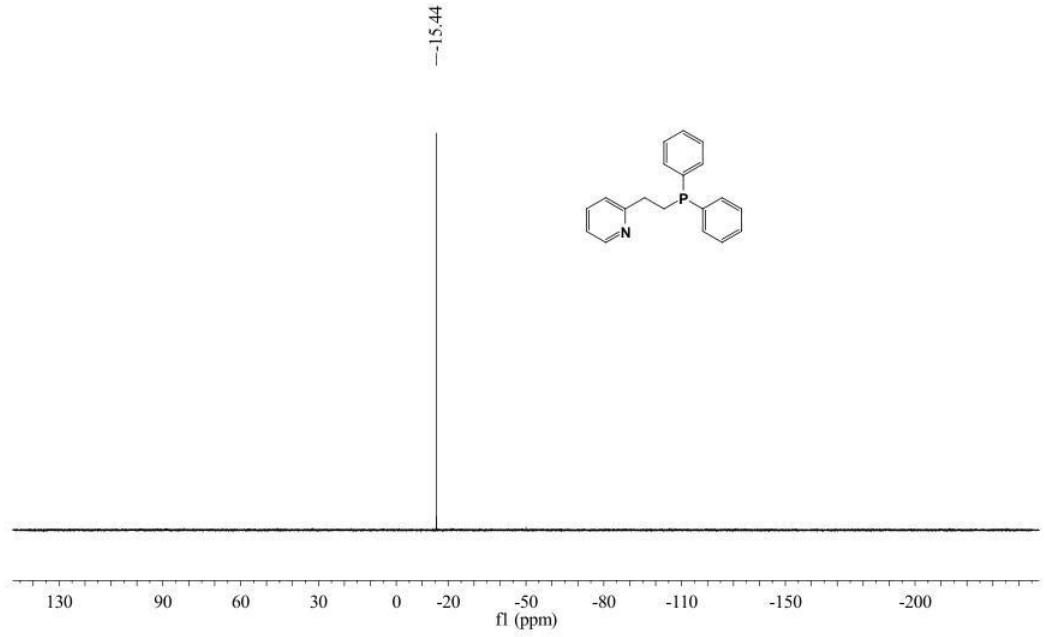


Figure S26. ^{31}P NMR spectrum of **2-(2-(diphenylphosphino)ethyl)pyridine (4m)**in $CDCl_3$.

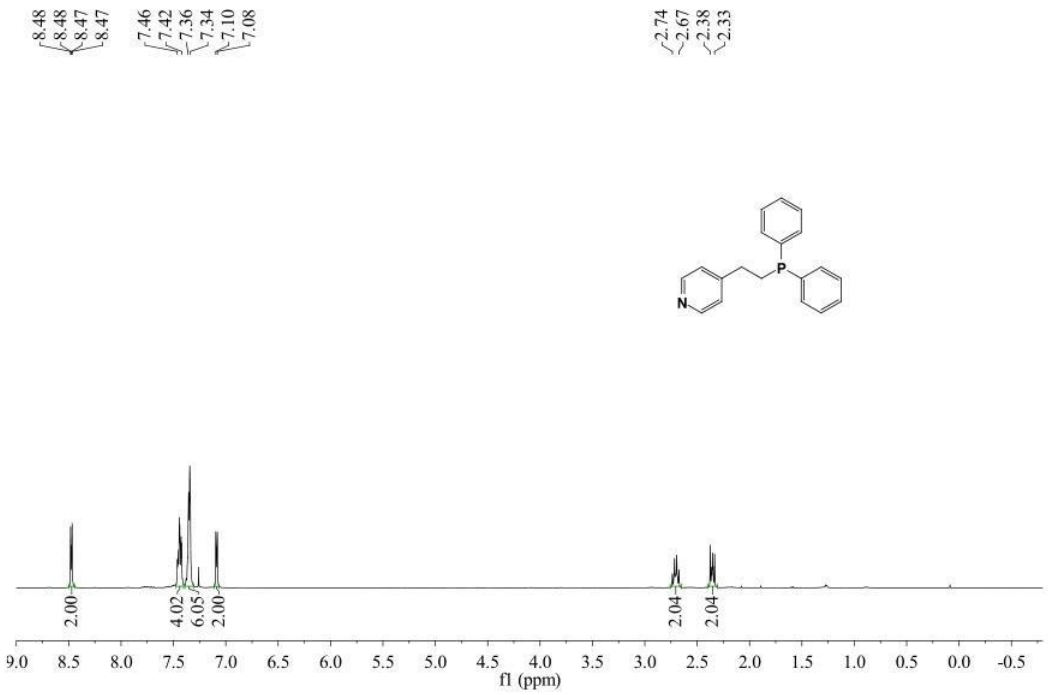


Figure S27. ^{1}H NMR spectrum of **4-(2-(diphenylphosphino)ethyl)pyridine (4n)**in $CDCl_3$.

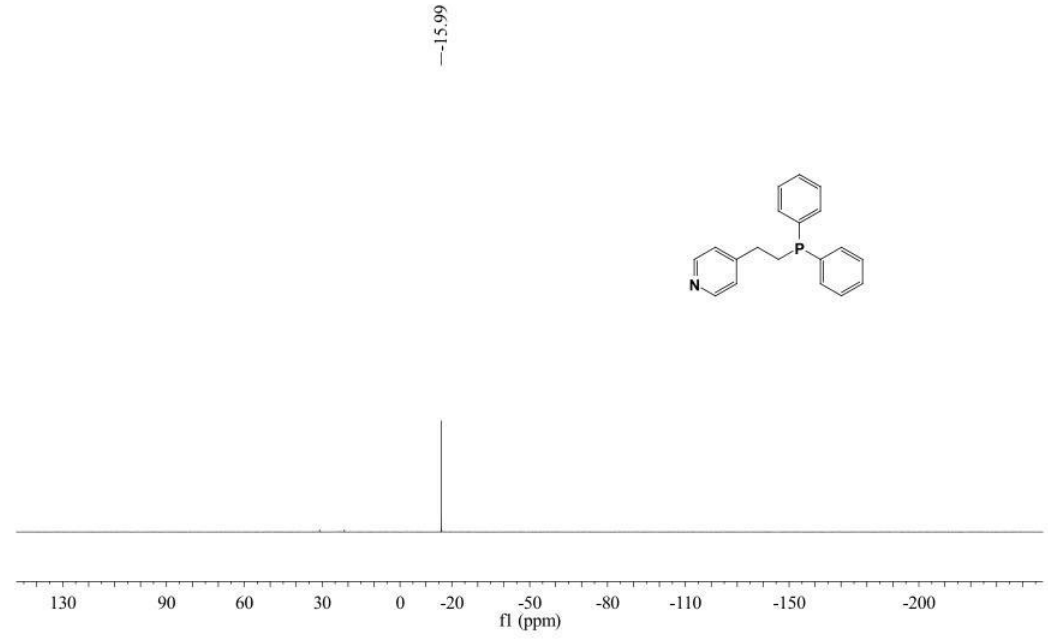


Figure S28. ^{31}P NMR spectrum of **4-(2-(diphenylphosphino)ethyl)pyridine (4n)**in $CDCl_3$.

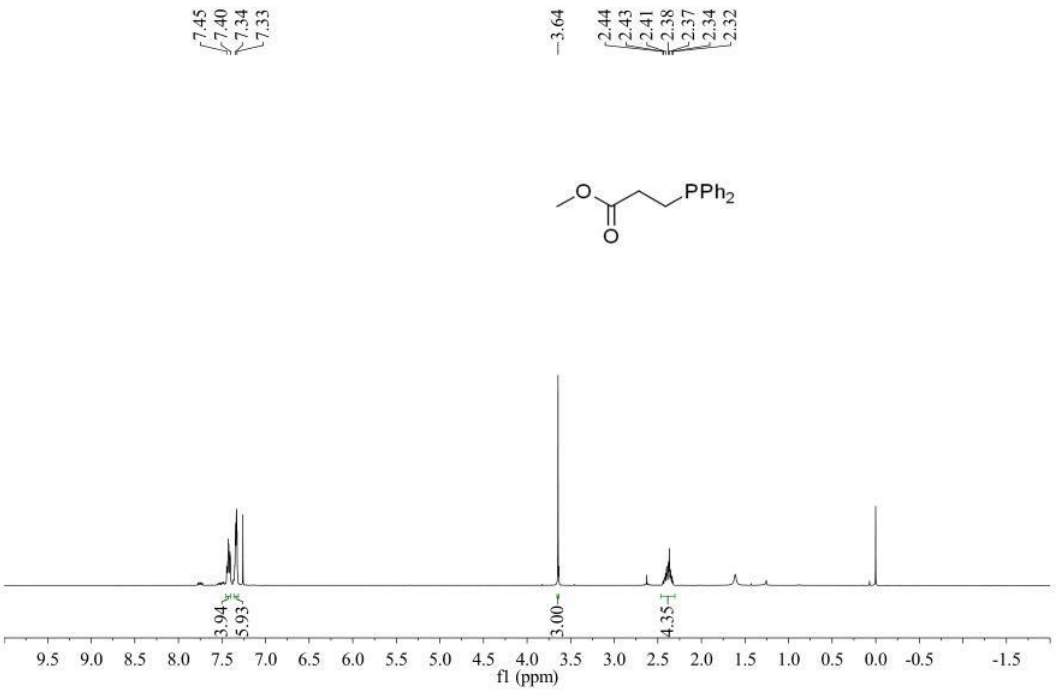


Figure S29. ^{1}H NMR spectrum of **methyl-3-(diphenylphosphanyl)propanoate (4p)**in $CDCl_3$.

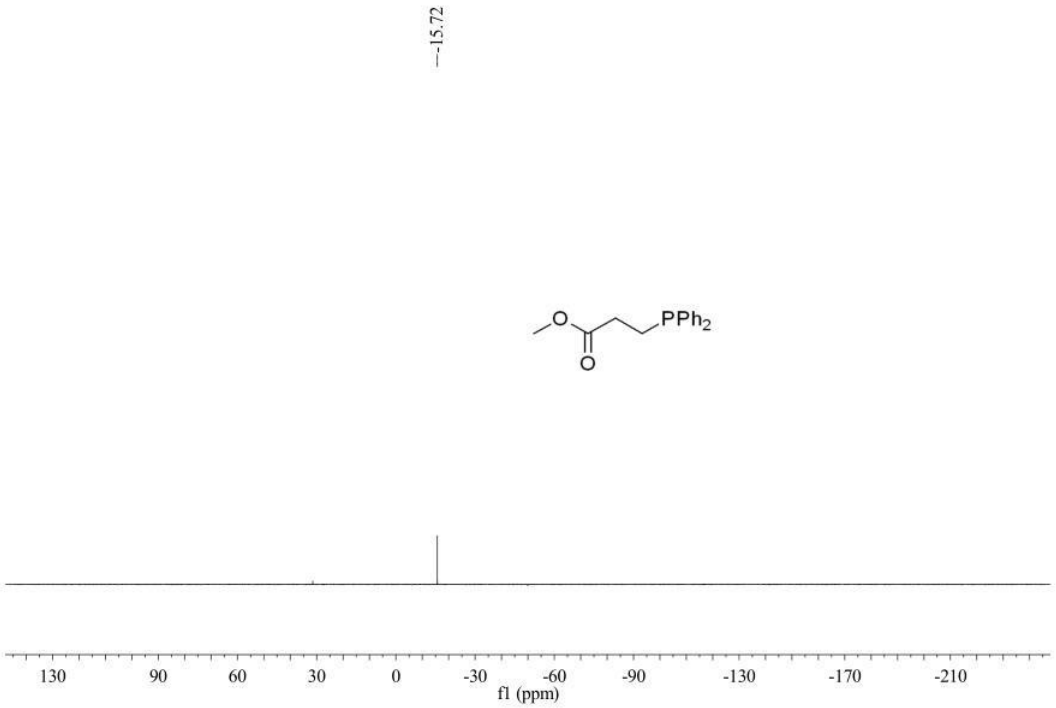
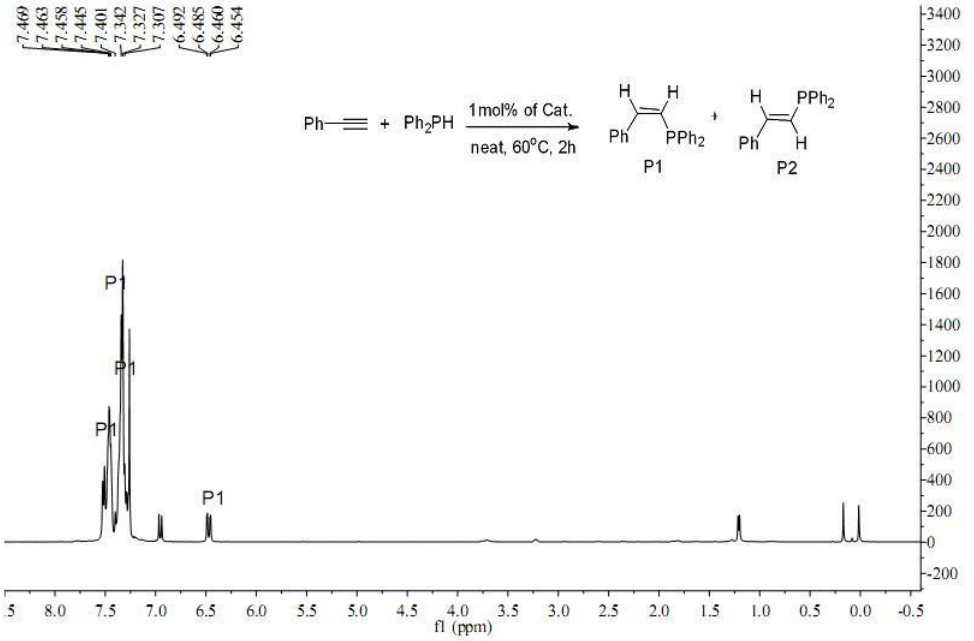
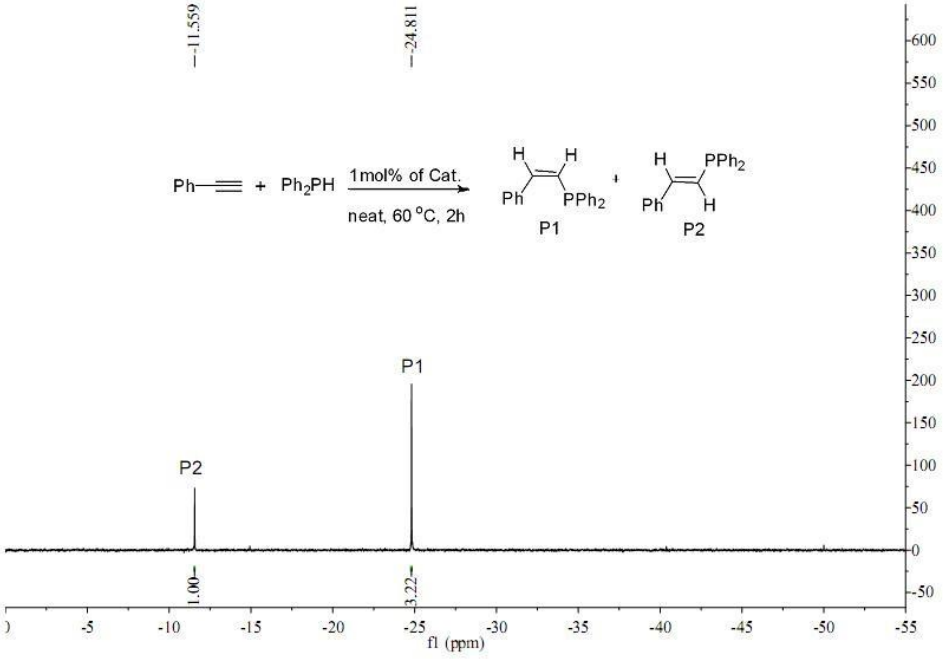


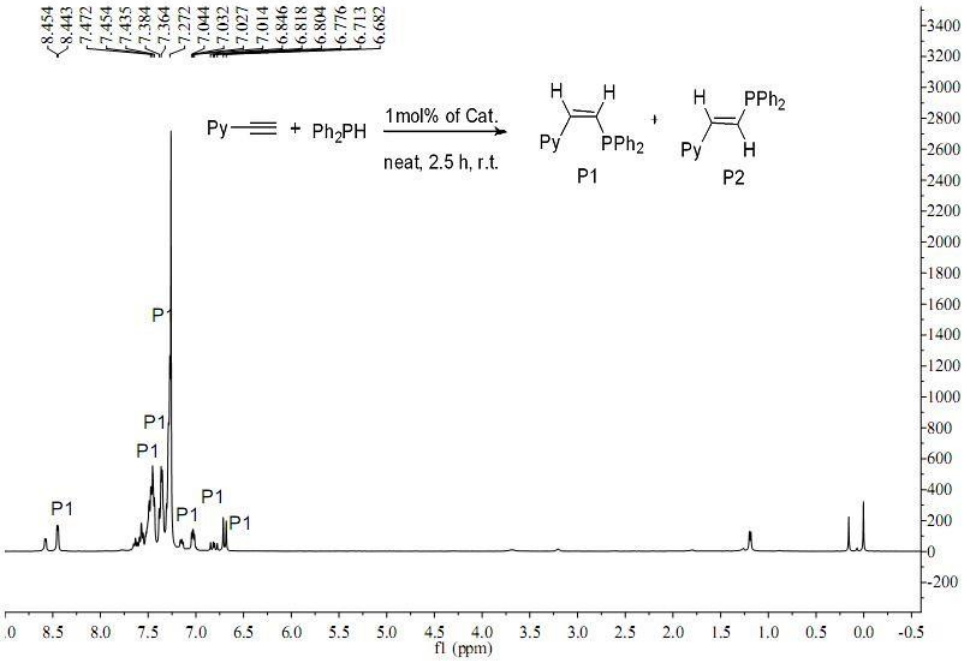
Figure S30. ^{31}P NMR spectrum of **methyl-3-(diphenylphosphanyl)propanoate (4p)**in $CDCl_3$.

S5 Spectral data for NMR-scalereaction of alkynes

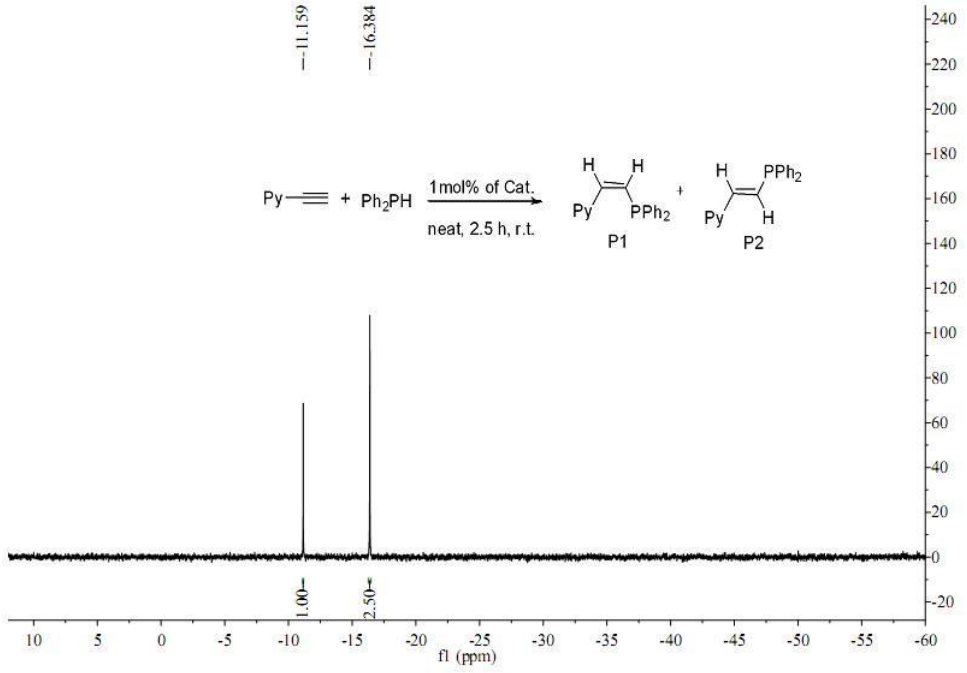


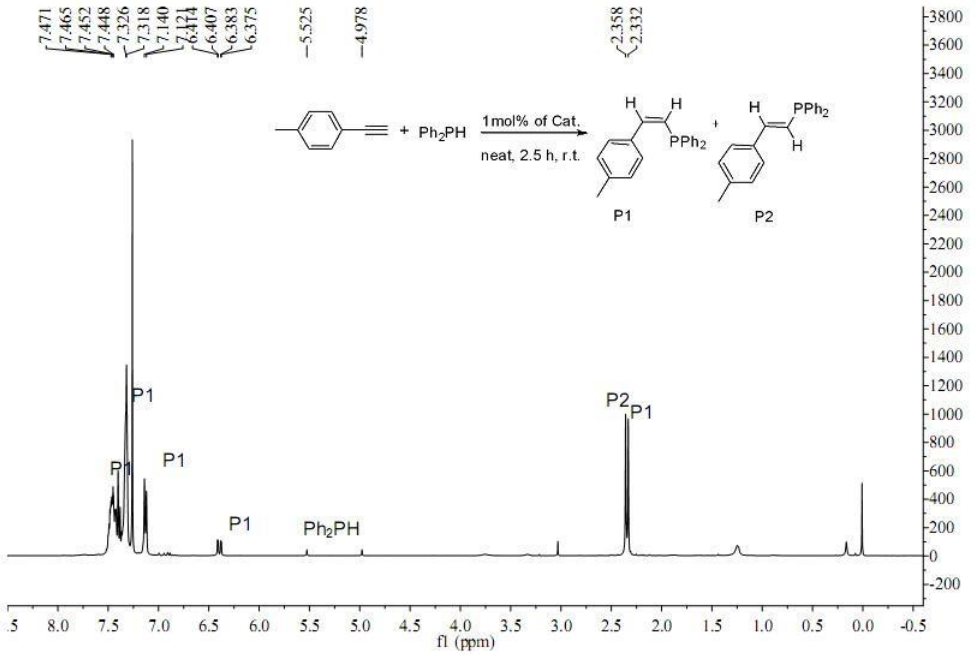
[1] H NMR for P1 (400 MHz, $CDCl_3$)[9]δ = 6.47 (dd, *J* = 12.6, 2.6 Hz, 1 H),7.31-7.34 (m, 9H), 7.40-7.33 (m, 1H), 7.47-7.44 (m, 4H), 7.52 (d, *J* = 7.3 Hz, 2H).



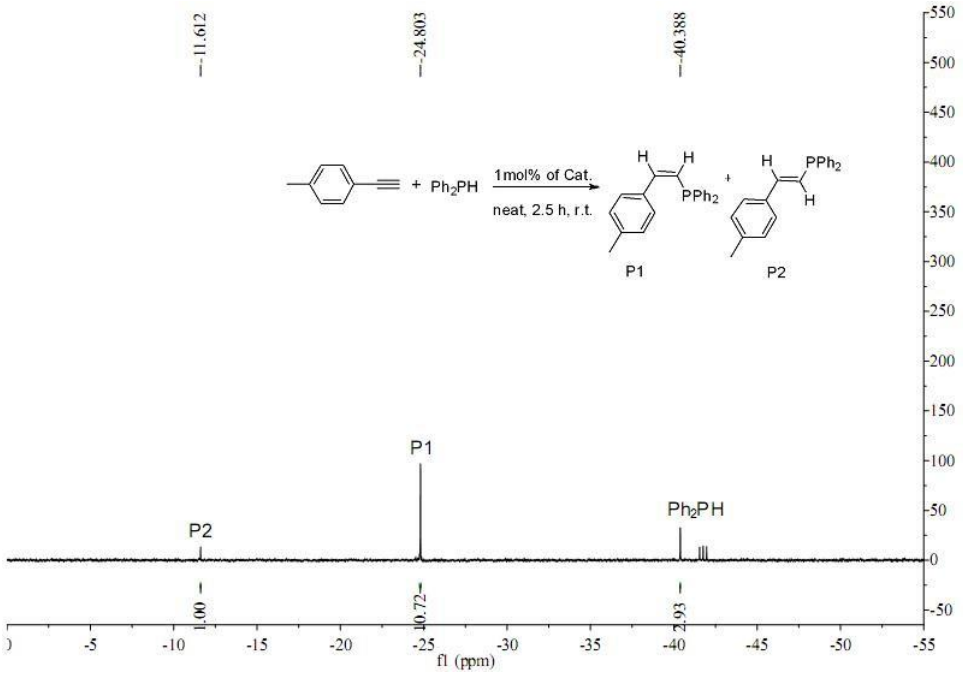


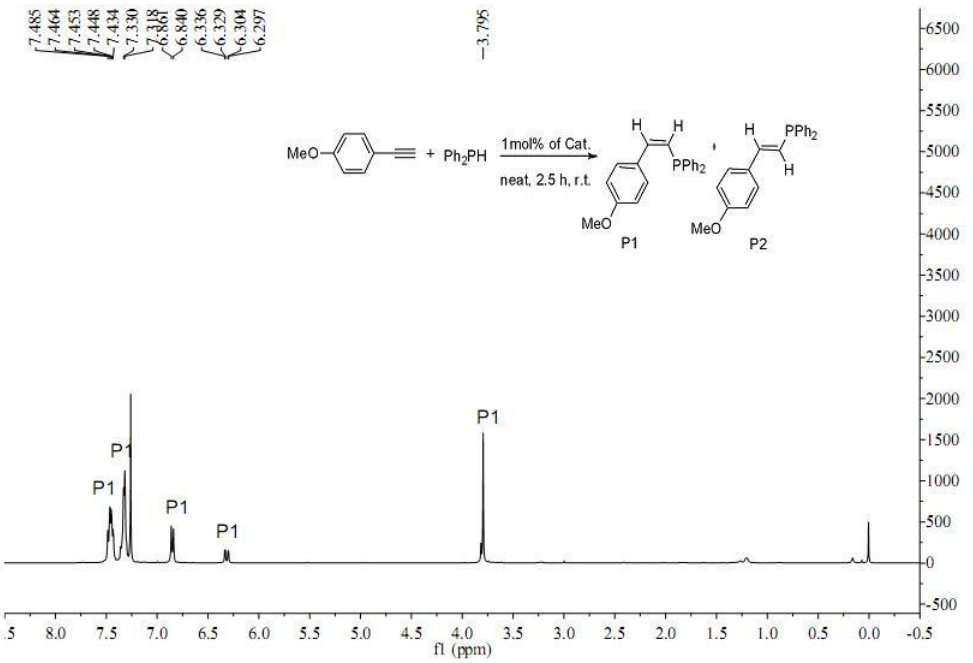
[1] H NMR for P1 (400 Hz,$CDCl_3$)[6] δ = 8.44 (d, *J* = 4.4 Hz, 1H), 7.47-7.43 (m, 5H), 7.38-7.36 (m, 4H), 7.29-7.27 (m, 3H), 7.04-7.01 (m, 1H), 6.84-6.78 (m, 1H), 6.71-6.68 (m, 1H).



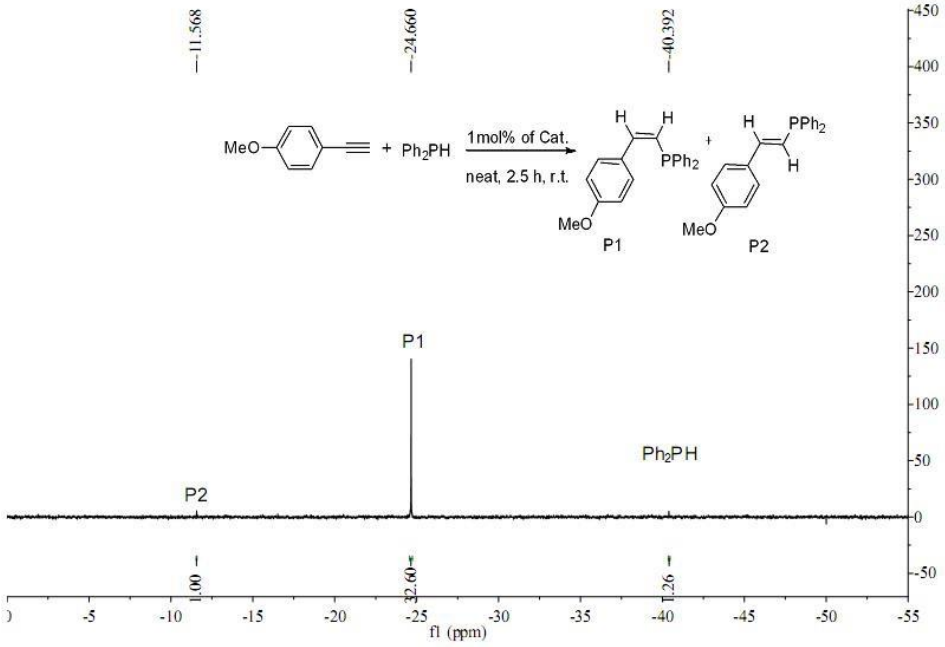


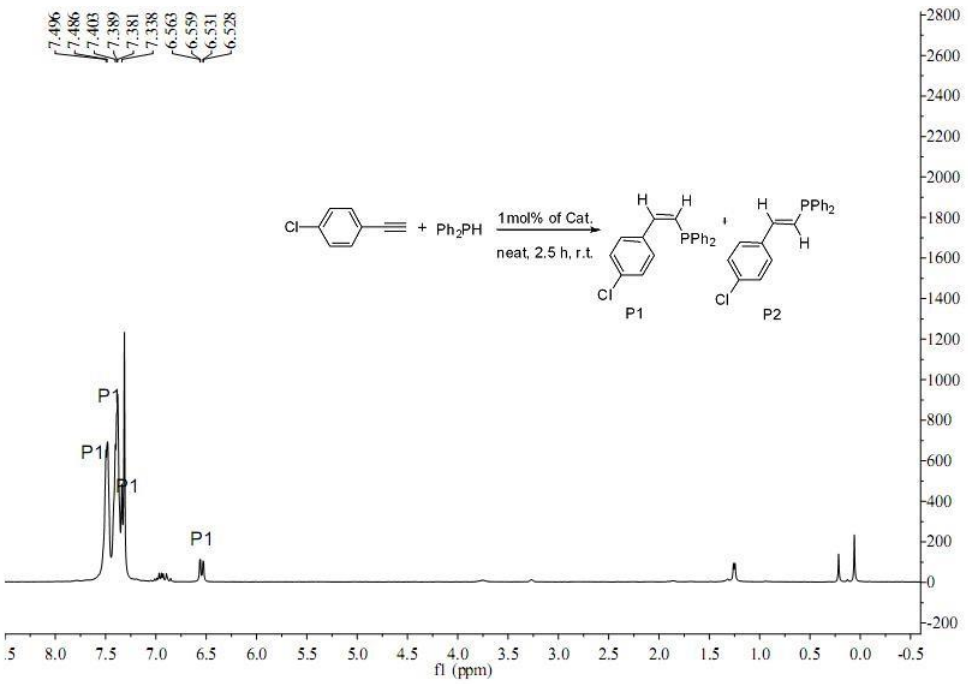
[1] H NMR for P1 (400 Hz, $CDCl_3$)[9]δ = 7.50-7.45 (m, 6H), 7.37-7.32 (m, 7H), 7.12-7.10 (m, 2H), 6.39 (dd, *J* = 12.6, 2.9 Hz, 1H).



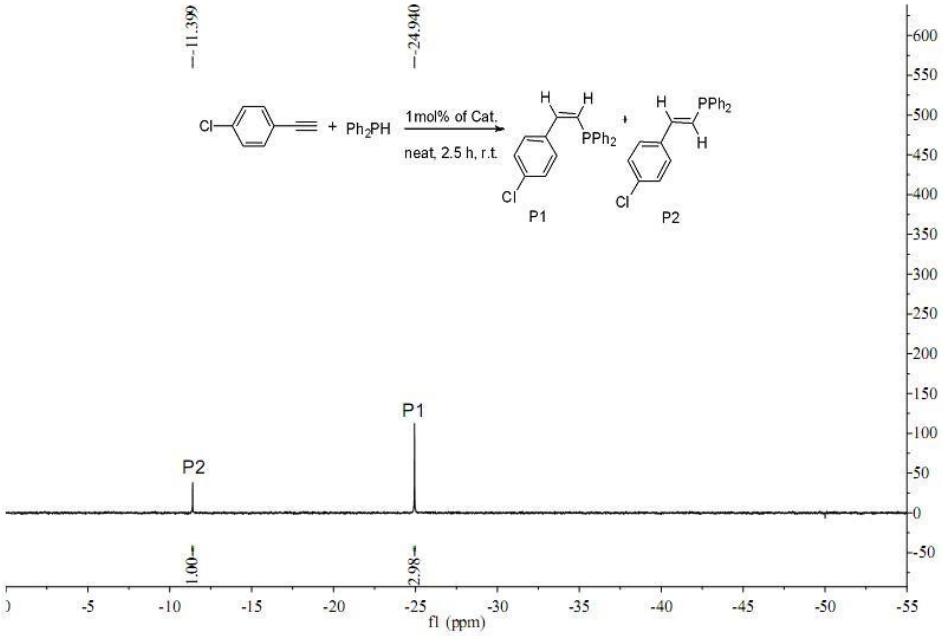


[1] H NMR for P1 (400 Hz, $CDCl_3$)[9]δ = 7.49-7.43 (m, 6H), 7.36-7.32 (m, 7H), 6.85 (d, *J* = 9.0, 2H), 6.31 (dd, *J* = 12.6, 2.8 Hz, 1H), 3.79 (s, 3H).

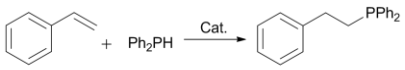




[1] H NMR for P1 (400 Hz, $CDCl_3$)δ = 7.50-7.49 (m, 4H), 7.40-7.38 (m, 9H), 7.34-7.33 (m, 2H), 6.54 (dd, *J* = 12.7, 1.8 Hz, 1H).



S6 Table S2 Hydrophosphination of diphenylphosphane to styrene by complexes **1** and **2**[a]

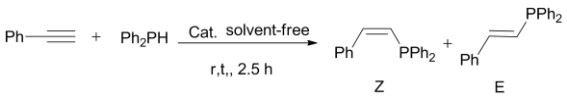


4a

Entry	Cat. (mol)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	**1**(1%)	-	60	6	trace
12	**2**(1%)	-	60	6	98

[a] Conditions: neat substrates in a 1:1 ratio, 60 °C.[b] Yield determined by ^{1}H NMR and ^{31}P NMR spectroscopy in $CDCl_3$.

S7 Table S2 Hydrophosphination of alkynes by complexes **1** and **2**[a]



Entry	Cat. (mol)	Conv. (%)[b]	Selectivity[b]
1	**1**(1%)	-	-
2	**2**(1%)	100	Z:E = 75:25

[a] Conditions: alkyne (1.0 mmol), Ph_2PH (1.00 mmol, 1 eq), **1** (8.7 mg, 1 mol%), **2** (12.5 mg, 1 mol%). [b] Based on ^{1}H and ^{31}P NMR spectroscopy in $CDCl_3$.

Firstly, the intermolecular hydrophosphination of styrene with Ph_2PH was examined by Eu^{III} complex **1**. We found that complex **1** could hardly catalyze the reaction (**Table S2**, Entry 1). Then we explored the model reaction between phenylacetylene and Ph_2PH, only to find that it did not happen under the similar conditions (**Table S3**, Entry 1). From above results, we could conclude that the activity of Eu^{III} complex is obviously less active than that of the Eu^{II} complex. Eu^{II} has larger ion radius compared to Eu^{III}, therefore, the size of metal ions may play an important role in this intermolecular hydrophosphination.

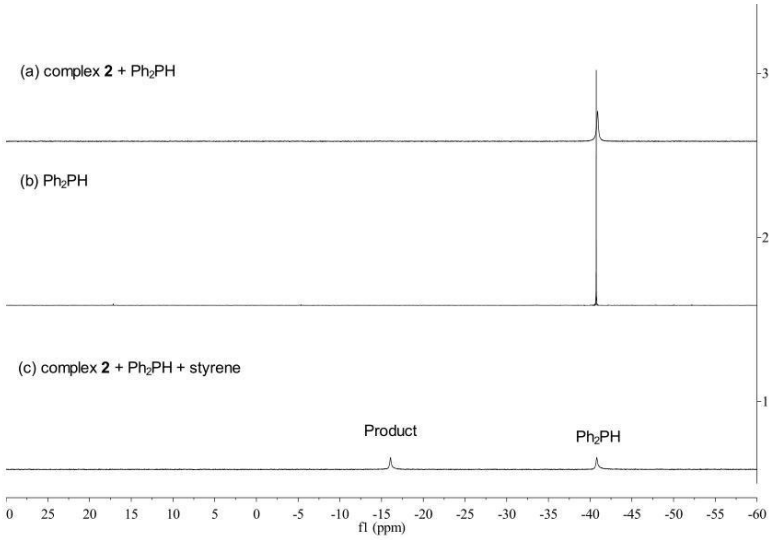


Figure S31. The in situ ^{31}P NMR spectrum of the hydrophosphination of styrene

(a) Complex **2** (124.2 mg) + Ph_2PH (17.40μL) in C_6D_6;(b) Ph_2PH in C_6D_6; (c) Complex **2** + Ph_2PH + styrene (11.46 μL) in C_6D_6

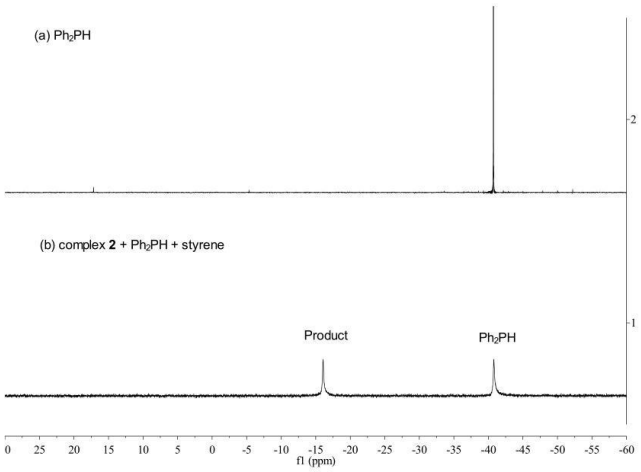


Figure S32. The in situ ^{31}P NMR spectrum of the hydrophosphination of styrene

(a) Ph_2PH in C_6D_6; (b) Complex **2** (122.4 mg) + Ph_2PH (17.15 μL)+ styrene (11.29 μL) in C_6D_6

Ph_2PH was firstly added to complex **2**, then stirred at 60 °C. From **Figure S31**, we can conclude there is no new P emerging, which indicated that the dinuclear species might not dissociate in the presence of $HPPh_2$. Afterwards, styrene was added and new P product appeared. Another way was tried, namely, Ph_2PH and styrene were added to complex **2,** then stired at 60 °C. From **Figure S32**, we can see the P product emerge, which told us that when three components were combined the hydrophosphination reaction occurred. The active species is still under research in our laboratory.

S8 REFERENCES

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S9Crystal Data

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