Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

An Unusual Mixed Valent Cobalt Dimer as a Catalyst for Anti-Markovnikov Hydrophophination of Alkynes

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Table S1 Table for Crystallographic parameters of **2**.

Complex	**2**
Formula	$C_{55}H_{87}Co_2N_3P_5$
Size [mm]	0.11 x 0.16x 0.28
System	Monoclinic
Space Group	$P2_1/c$
a [Å]	15.1713(4)
b [Å]	13.6450(3)
c [Å]	27.4359(6)
α [°]	90.0
β [°]	98.096(2)
γ [°]	90.0
V [Å^3]	5623.6(2)
Z	4
$\rho_{cal.}$ [g/cm^3]	1.205
2Θ	50.0
Radiation	Mo Kα
λ [Å]	0.71073
T [K]	150
R1 (%)	5.27
wR2 (%)	17.01

Table S2 The selected bond length of complex **2**.

Atom	**Atom**	**Bond Length(Å) (Exptl.)**	**Bond Length(Å)(calcd.)**
Co1	P1	2.235(4)	2.414
Co1	P2	2.234(3)	2.307
Co1	N3	2.000(1)	2.030
Co1	N1	1.850(1)	1.868
Co1	N2	2.000(1)	2.024
Co2	P4	2.194(4)	2.214
Co2	P3	2.166(4)	2.213
Co2	P5	2.184(4)	2.212
Co2	C10	1.910(1)	1.942
Co2	C9	2.110(1)	2.120
Co2	C11	2.130(1)	2.122

Table S3 The Selected bond angle of complex **2**.

Atom	**Atom**	**Atom**	**Bond Angle(Exptl.)/°**	**Bond Angle (calc.)/°**
P1	Co1	P2	99.9(1)	95.7
P1	Co1	N3	104.8(3)	102.4
P1	Co1	N1	86.3(3)	85.9

P1	Co1	N2	105.6(3)	101.6
P2	Co1	N3	99.3(3)	98.4
P2	Co1	N1	173.7(3)	178.1
P2	Co1	N2	98.4(3)	100.2
N3	Co1	N1	79.3(4)	80.3
N3	Co1	N2	141.4(4)	147.8
N1	Co1	N2	79.4(4)	80.3
P4	Co2	P3	101.8(2)	103.5
P4	Co2	P5	102.1(2)	101.8
P4	Co2	C9	86.7(4)	87.8
P4	Co2	C11	147.0(4)	144.4
P3	Co2	P5	102.6(2)	100.6
P3	Co2	C10	136.5(4)	136.4
P3	Co2	C9	109.3(4)	106.6
P3	Co2	C11	105.9(4)	108.5
P5	Co2	C10	103.8(4)	106.5
P5	Co2	C9	144.3(4)	148.1
P5	Co2	C11	88.9(4)	87.2
C10	Co2	C9	41.0(5)	41.6
C10	Co2	C11	41.4(5)	41.5
C9	Co2	C11	67.6(5)	68.7

Table S4 Selected Bond length table for different electronically reduced pincer ligands and calculated average deformation constant.

	$d_{C_{im}=N_{im}}$ *(ave)* Å	$d_{Cim\text{-}CPy}$ *(av)* Å	Δd Å (Av. deformation)
0e Reduction	1.280	1.493	0
1e Reduction	1.330	1.437	0.053
2e Reduction	1.337	1.425	0.063
3e Reduction	1.394	1.381	0.113
Complex **2**	1.367	1.402	0.090

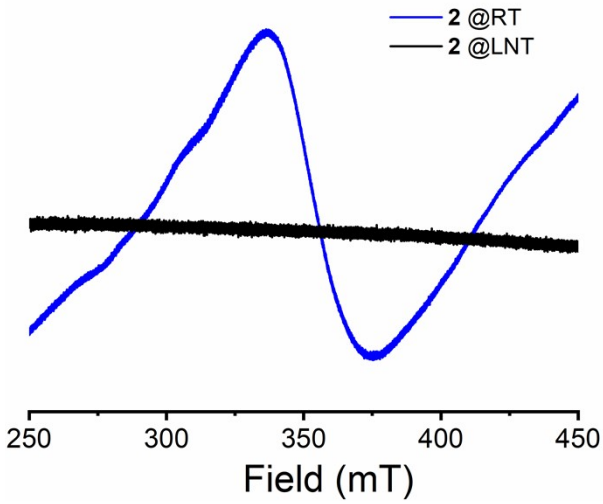


Fig. S1 The X-band EPR spectra of 2 were recorded in toluene at room temperature (blue trace) and 77 K (black trace) (Experimental condition: Microwave frequency: 9.444 GHz, Modulation Frequency = 100.00 kHz ; Power = 5.0 mW)

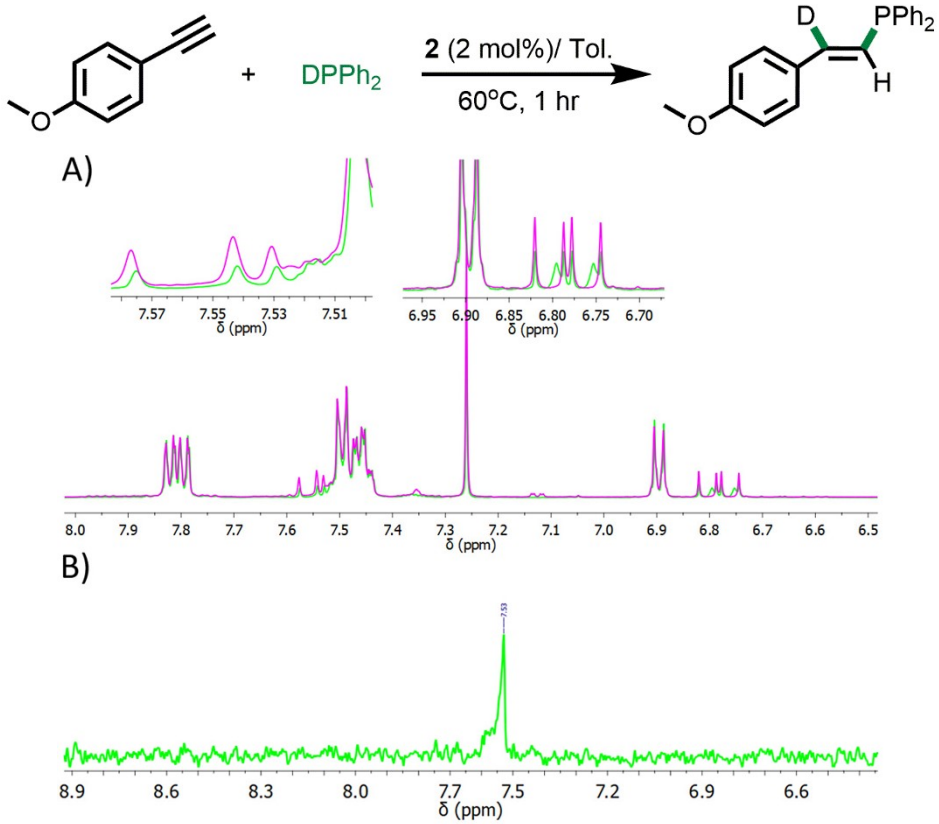
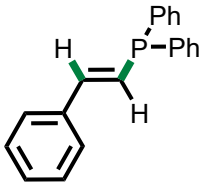


Fig. S2 Deuterated reaction scheme and their corresponding **(A)** ^{1}H-NMR and **(B)** ^{2}H-NMR spectrum. Suppression in the peak of the internal proton of alkyne suggests the exchange of H by D, which was further confirmed by ^{2}H-NMR panel (**B)**.

Spectroscopic data of product formation after sulfidation:



3a

δ_H (400 MHz, $CDCl_3$) 7.86 – 7.77 (3 H, m), 7.66 – 7.55 (1 H, m), 7.55 – 7.42 (7 H, m), 7.42 – 7.34 (3 H, m), 6.96 (1 H, dd, *J* 21.1, 16.7).

δ_C (101 MHz, $CDCl_3$) 147.90, 133.88, 133.02, 131.50, 130.11, 128.74, 127.99, 120.18, 119.32.

δ_P (202 MHz, $CDCl_3$) 37.19

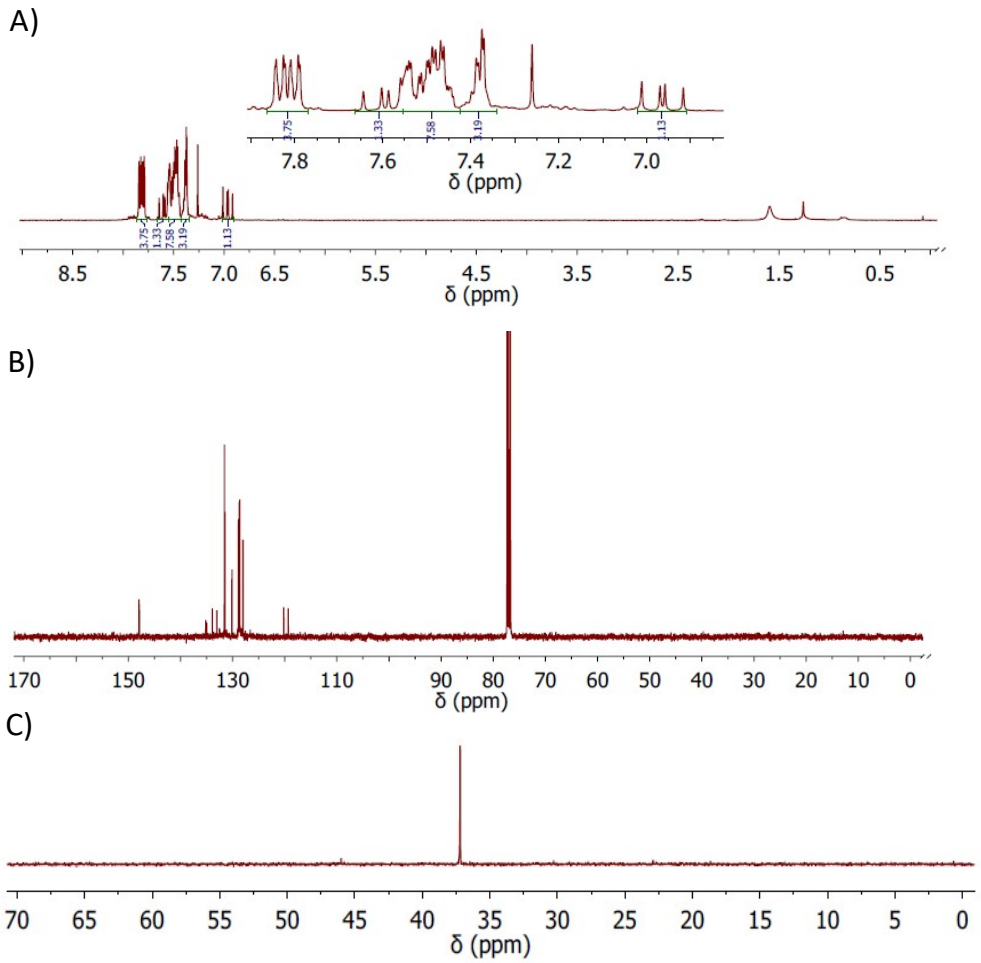
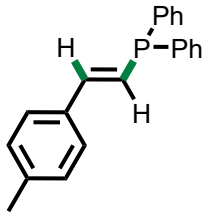


Fig. S3 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3b

δ_H (500 MHz, $CDCl_3$) 7.86 – 7.77 (4H, m), 7.56 (2H, dd, *J* 22.9, 16.6), 7.52 – 7.41 (8H, m), 7.19 (2H, d, *J* 7.9), 6.89 (1H, dd, *J* 21.3, 16.6), 2.37 (3H, s).

δ_C (126 MHz, $CDCl_3$) 147.94, 147.89, 140.49, 133.93, 133.24, 132.42, 131.55, 131.50, 131.47, 129.58, 128.71, 128.61, 127.99, 118.63, 117.93, 21.45.

δ_P (202 MHz, $CDCl_3$) 37.31

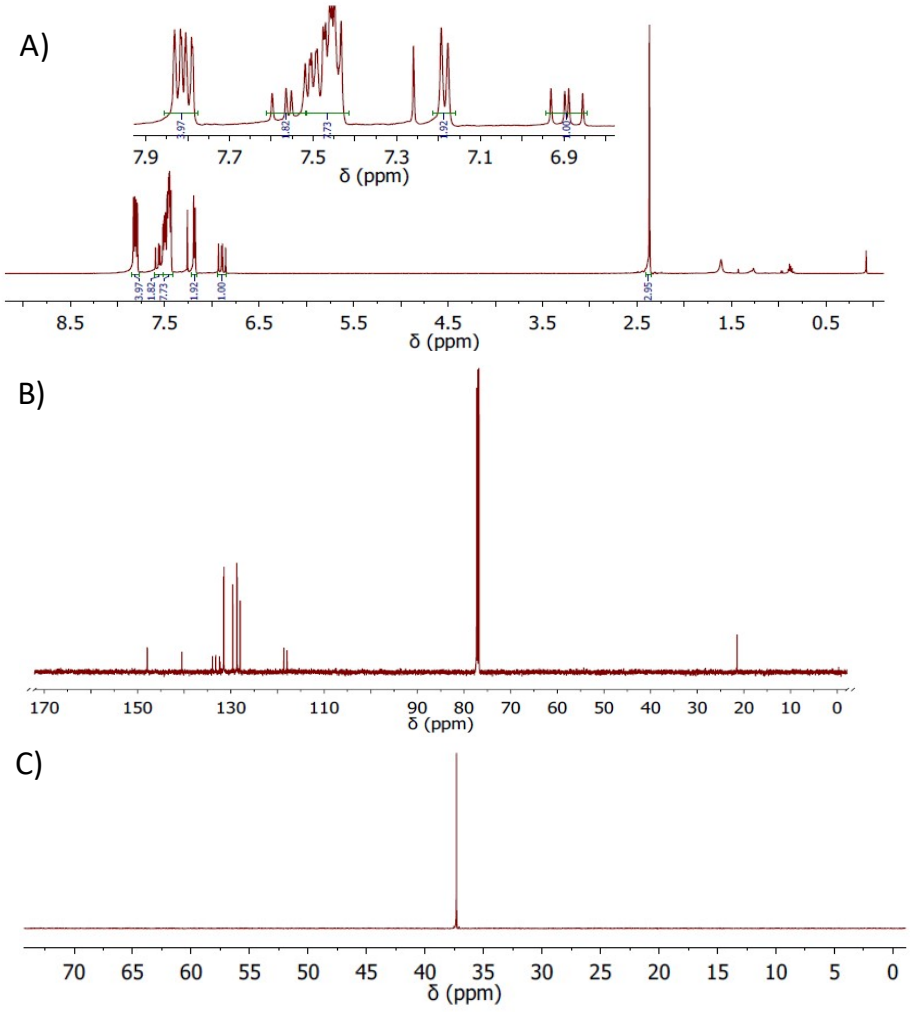
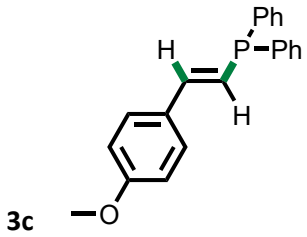


Fig. S4 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3c

δ_H (500 MHz, $CDCl_3$) 7.80 (4H, ddd, *J* 25.5, 13.5, 12.1), 7.60 – 7.53 (1H, m), 7.52 – 7.41 (8H, m), 6.90 (2H, d, *J* 8.7), 6.78 (1H, dd, *J* 21.3, 16.6), 3.83 (3H, s).

δ_C (126 MHz, $CDCl_3$) 161.20, 147.58, 134.10, 133.38, 131.53, 129.62, 128.69, 128.59, 116.87, 116.17, 114.24, 55.41.

δ_P (202 MHz, $CDCl_3$) 37.43

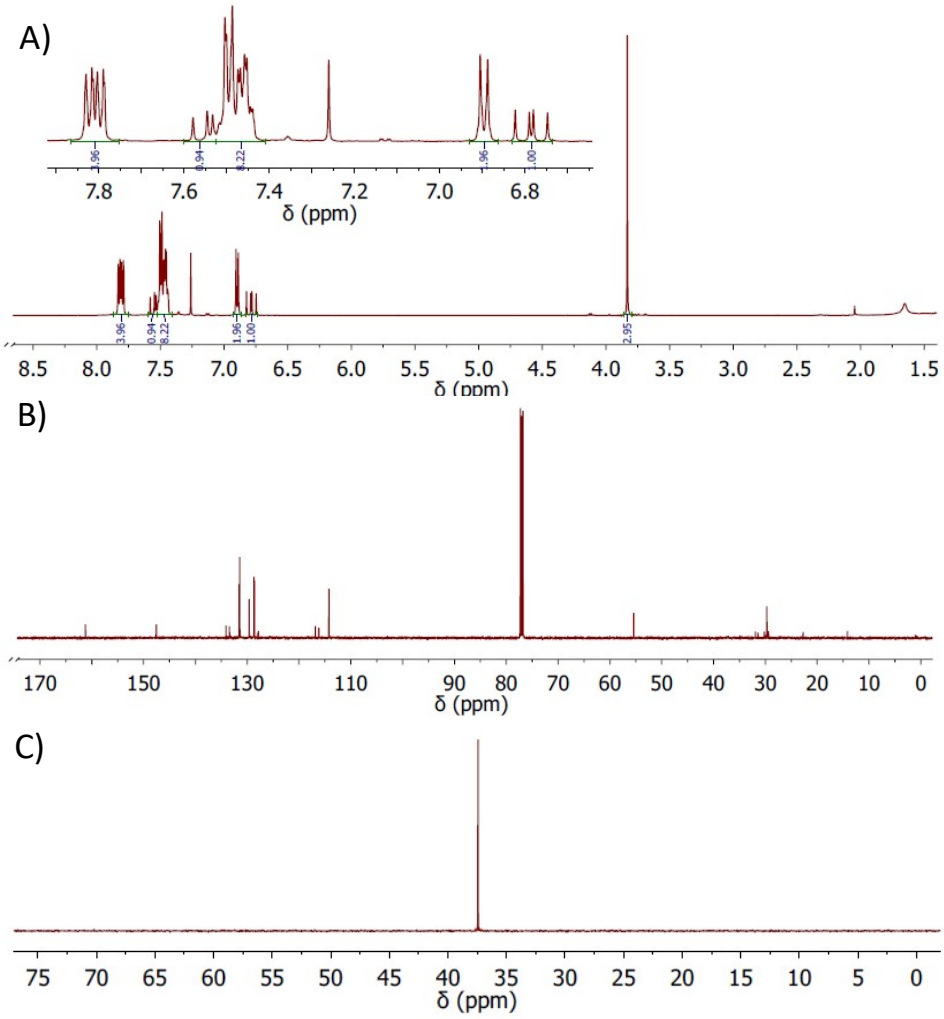
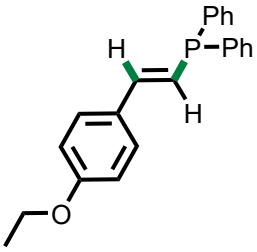


Fig. S5 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3d

δ_H (500 MHz, $CDCl_3$) 7.86 – 7.77 (4H, m), 7.54 (1H, dd, *J* 16.4, 9.9), 7.51 – 7.42 (8H, m), 6.88 (2H, d, *J* 8.7), 6.77 (1H, dd, *J* 21.3, 16.6), 4.06 (2H, q, *J* 7.0), 1.42 (3H, t, *J* 7.0).

δ_C (126 MHz, $CDCl_3$) δ 160.77, 147.73, 134.20, 133.48, 131.53, 129.62, 128.68, 116.68, 115.98, 114.71, 63.77, 14.89.

δ_P (202 MHz, $CDCl_3$) 37.45

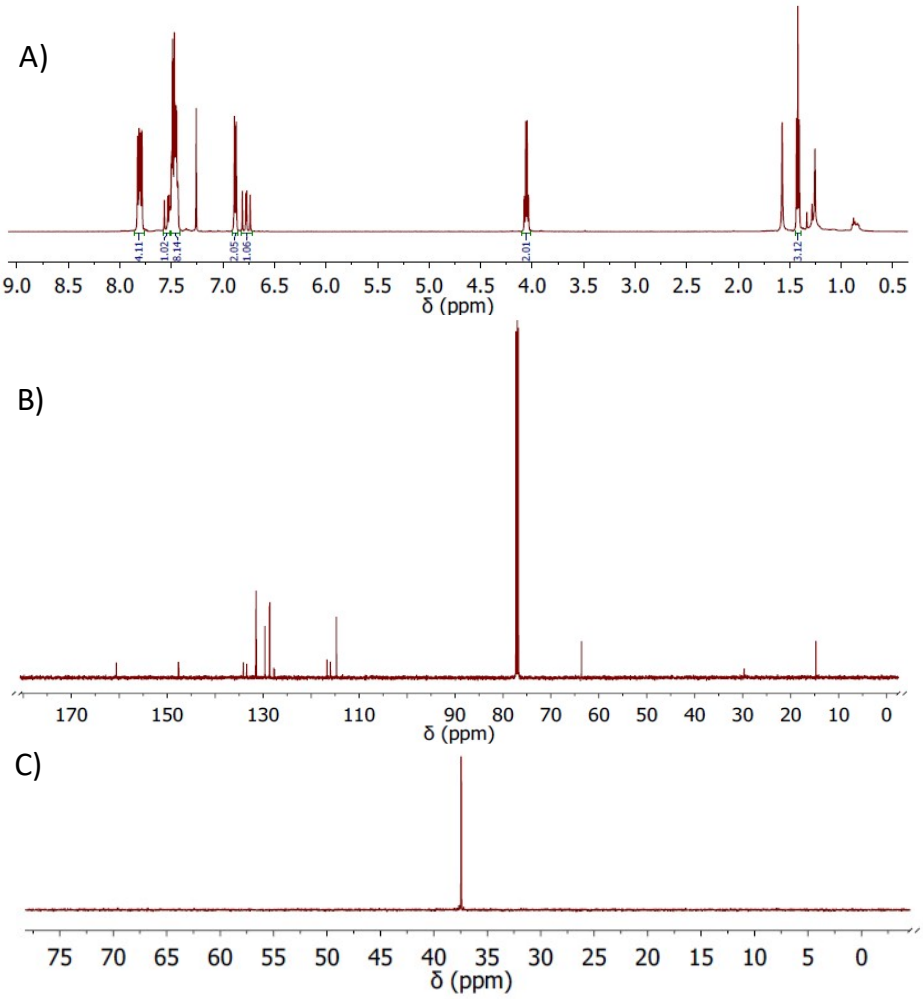
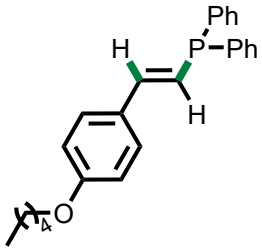


Fig. S6 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3e

δ_H (500 MHz, $CDCl_3$) 7.86 – 7.78 (4H, m), 7.59 – 7.53 (1H, m), 7.52 – 7.41 (8H, m), 6.88 (2H, t, *J* 8.3), 6.84 – 6.74 (1H, m), 3.97 (2H, t, *J* 6.6), 1.82 – 1.75 (2H, m), 1.48 – 1.34 (4H, m), 0.93 (3H, dd, *J* 14.5, 7.3).

δ_C (126 MHz, $CDCl_3$) 160.85, 147.69, 134.16, 133.46, 131.54, 129.63, 128.70, 127.65, 116.61, 115.91, 115.02, 114.76, 68.24, 28.49, 22.64, 14.18.

δ_P (202 MHz, $CDCl_3$) 37.46

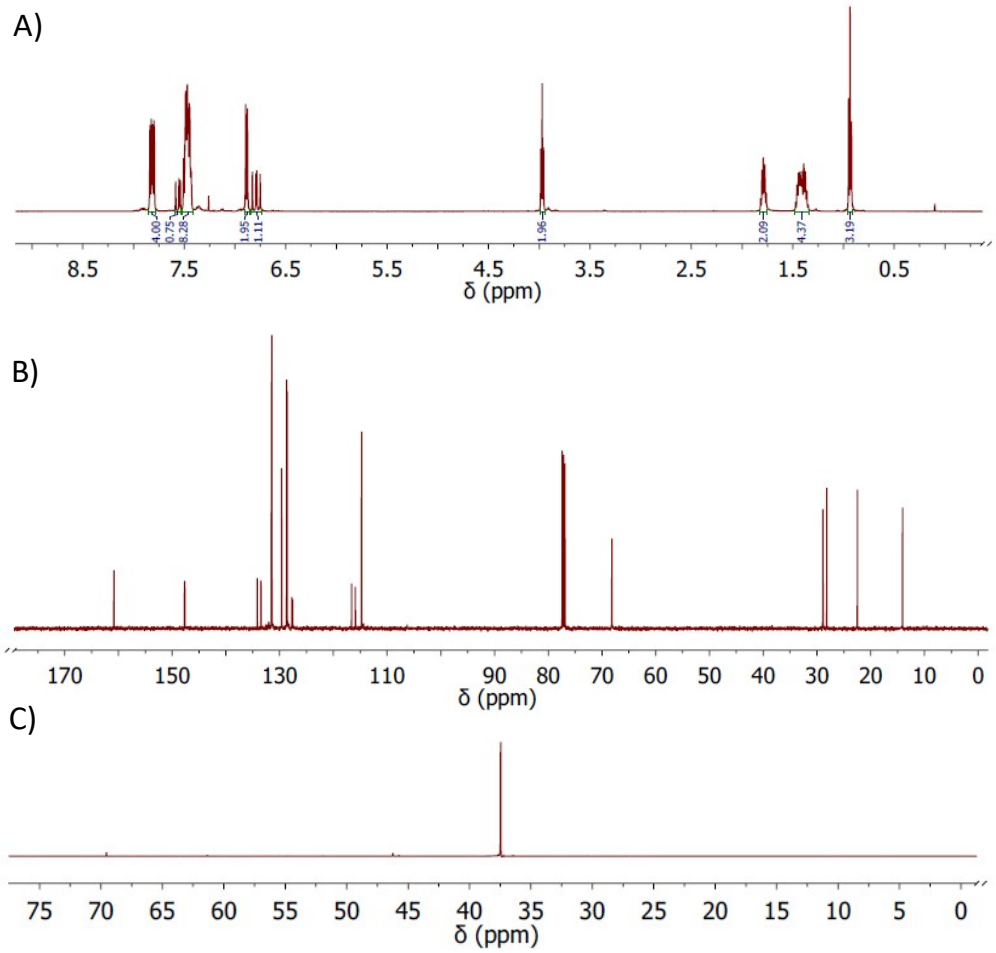
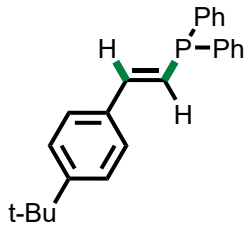


Fig. S7 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3f

δ_H (500 MHz, $CDCl_3$) 7.84 – 7.77 (4H, m), 7.57 (2H, dd, *J* 22.9, 16.6 Hz), 7.47 (8H, dddd, *J* 9.8, 7.0, 4.2, 1.8), 7.40 (2H, d, *J* 8.4), 6.91 (1H, dd, *J* 21.3, 16.6), 1.32 (9H, s).

δ_C (126 MHz, $CDCl_3$) 147.76, 131.55, 131.49, 131.46, 128.70, 128.60, 127.82, 125.83, 118.90, 34.88, 31.19.

δ_P (202 MHz, $CDCl_3$) 37.29

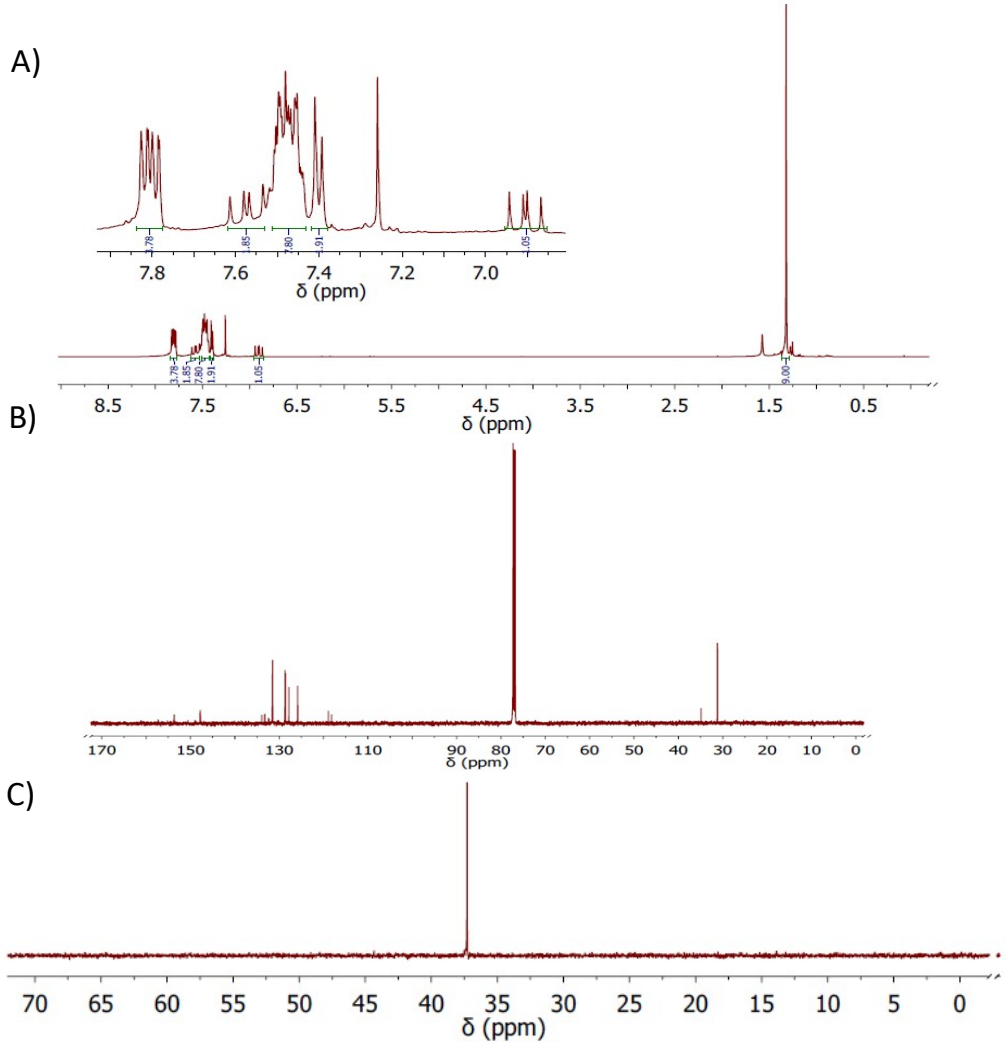
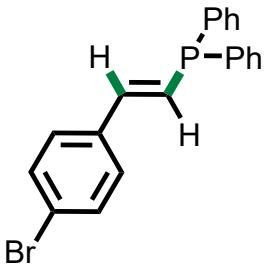


Fig. S8 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3g

δ_H (400 MHz, $CDCl_3$) 7.87 – 7.76 (4 H, m), 7.57 (1 H, dd, *J* 16.2, 9.9), 7.48 (8 H, tdd, *J* 6.7, 5.7, 2.1), 7.07 (2 H, t, *J* 8.6), 6.88 (1 H, dd, *J* 20.8, 16.7).

δ_C (101 MHz, $CDCl_3$) 146.60, 133.83, 132.96, 131.52, 129.86, 128.70, 116.07, 115.85.

δ_P (162 MHz, $CDCl_3$) 37.12

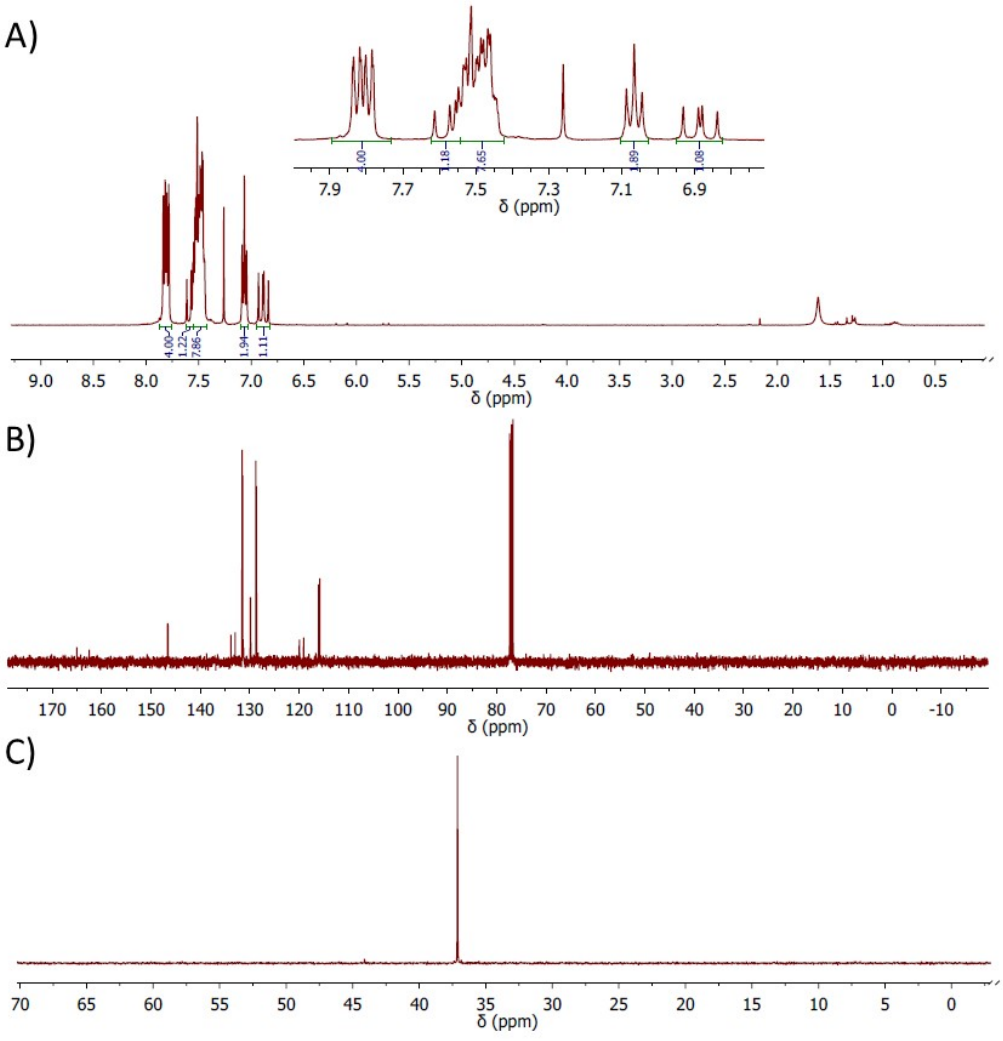
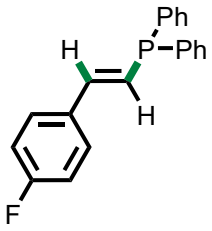


Fig. S9 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3h

δ_H (500 MHz, $CDCl_3$) 7.85 – 7.77 (4 H, m), 7.57 (1 H, dd, *J* 19.1, 12.9), 7.54 – 7.42 (8 H, m), 7.09 – 7.03 (2 H, m), 6.94 – 6.84 (1 H, m).

δ_C (126 MHz, $CDCl_3$) 164.76, 162.77, 146.63, 133.70, 133.00, 131.55, 131.25, 129.89, 128.69, 119.78, 119.09, 116.07, 115.89.

δ_P (202 MHz, $CDCl_3$) 37.17

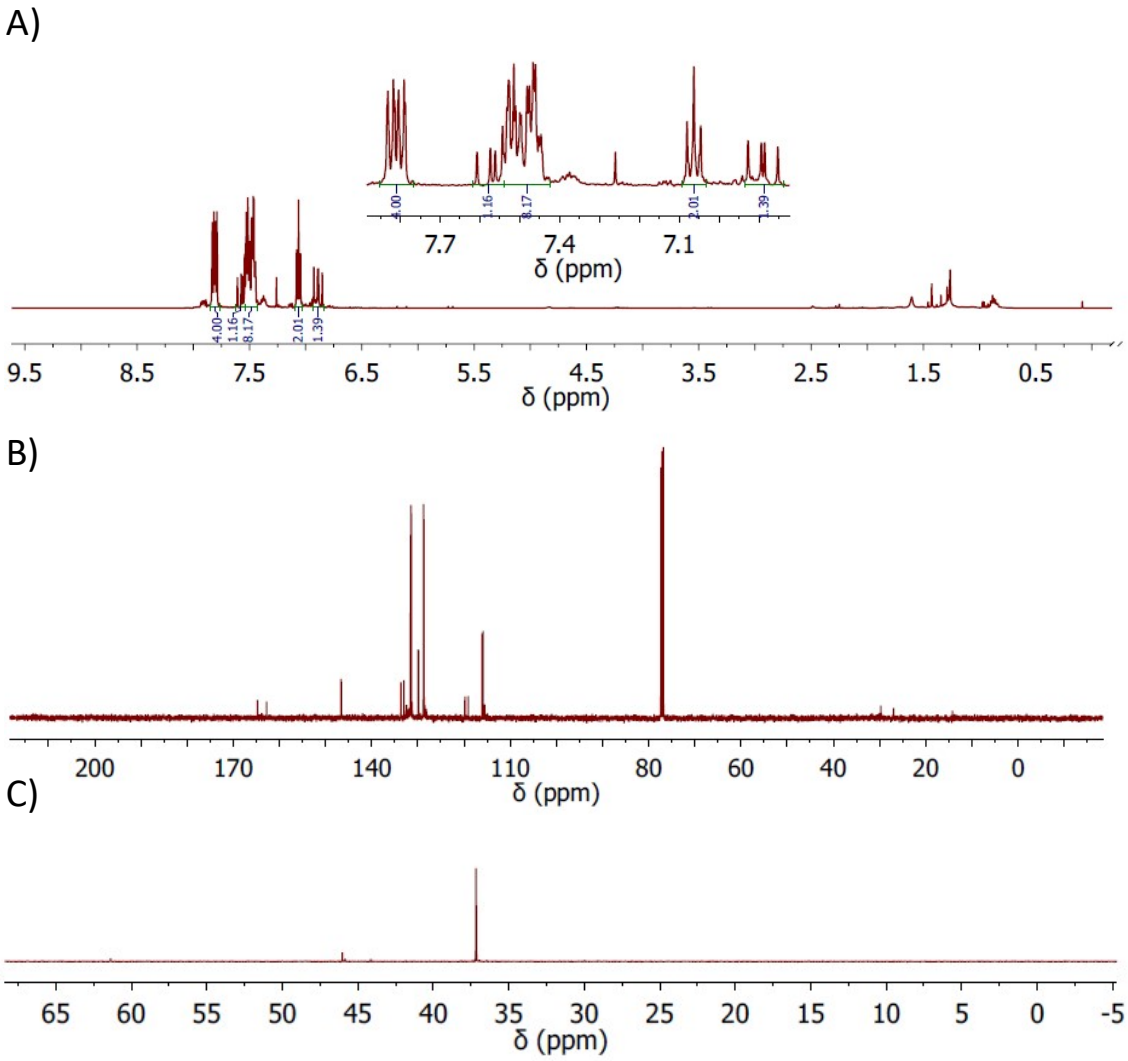
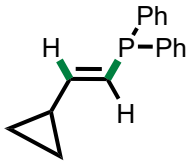


Fig. S10 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.

3i



δ_H (500 MHz, $CDCl_3$) 7.75 (4H, dd, *J* 13.3, 7.1), 7.49 – 7.39 (6H, m), 6.49 – 6.23 (2H, m), 1.77 – 1.69 (1H, m), 0.96 – 0.90 (2H, m), 0.70 – 0.62 (2H, m).

δ_C (126 MHz, $CDCl_3$) 157.25, 157.21, 134.35, 133.66, 132.34, 132.26, 131.38, 131.32, 131.29, 128.61, 128.51, 118.12, 117.42, 29.71, 16.45, 16.27, 8.68.

δ_P (202 MHz, $CDCl_3$) 35.5

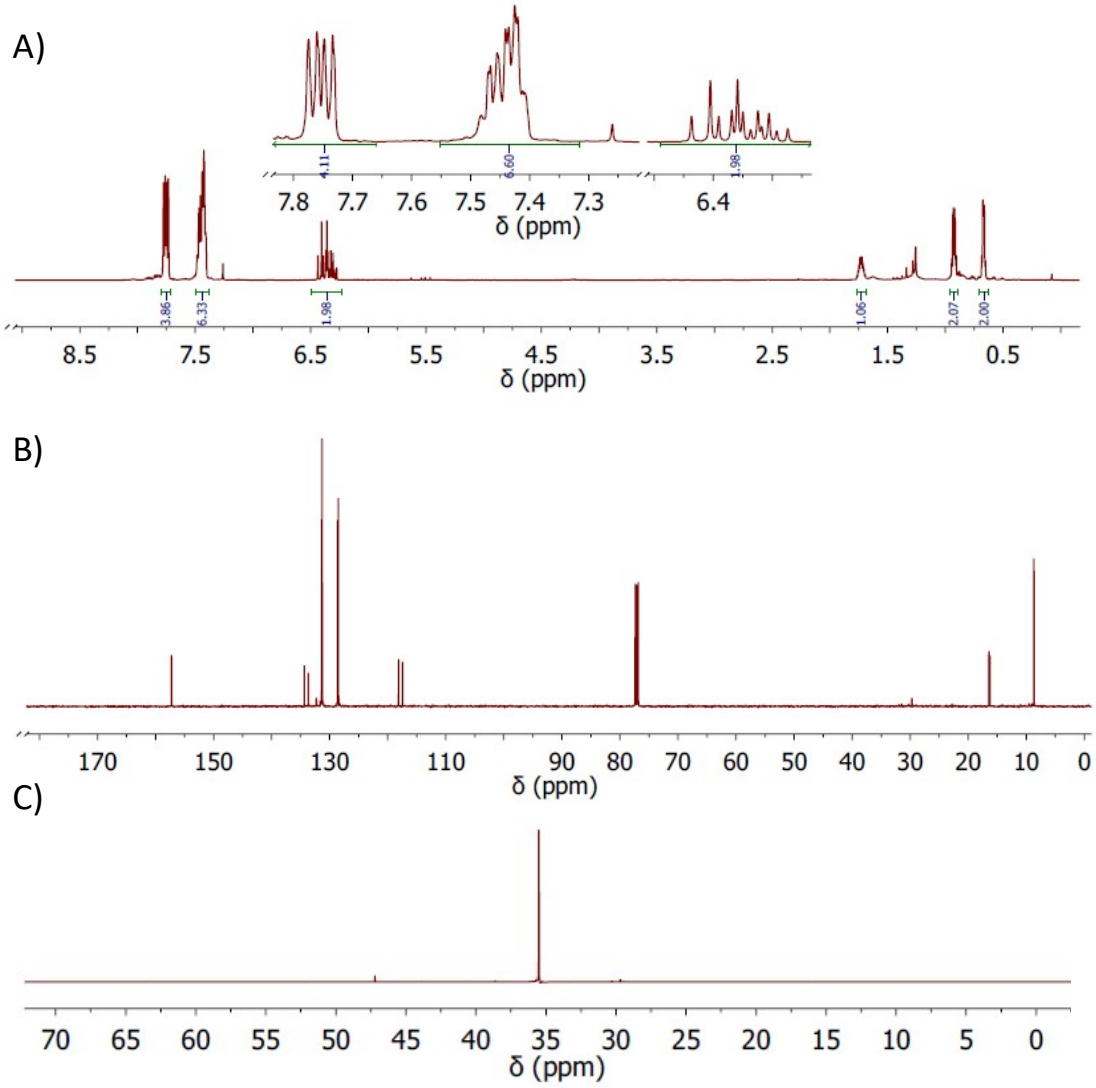
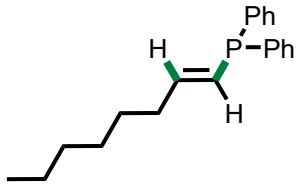


Fig. S11 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3j

δ_H (400 MHz, $CDCl_3$) 7.49 – 7.40 (6 H, m), 6.85 (1 H, ddt, *J* 22.8, 16.2, 6.6), 6.41 – 6.27 (1 H, m), 2.33 (2 H, td, *J* 7.0, 1.8), 1.54 – 1.44 (2 H, m), 1.28 (6 H, dd, *J* 9.9, 7.4), 0.88 (3 H, t, *J* 6.8).

δ_C (101 MHz, $CDCl_3$) 152.99, 134.13, 133.28, 131.35, 128.54, 122.19, 121.35, 34.16, 31.54, 28.86, 27.96, 22.55, 14.03.

δ_P (162 MHz, $CDCl_3$) 35.79

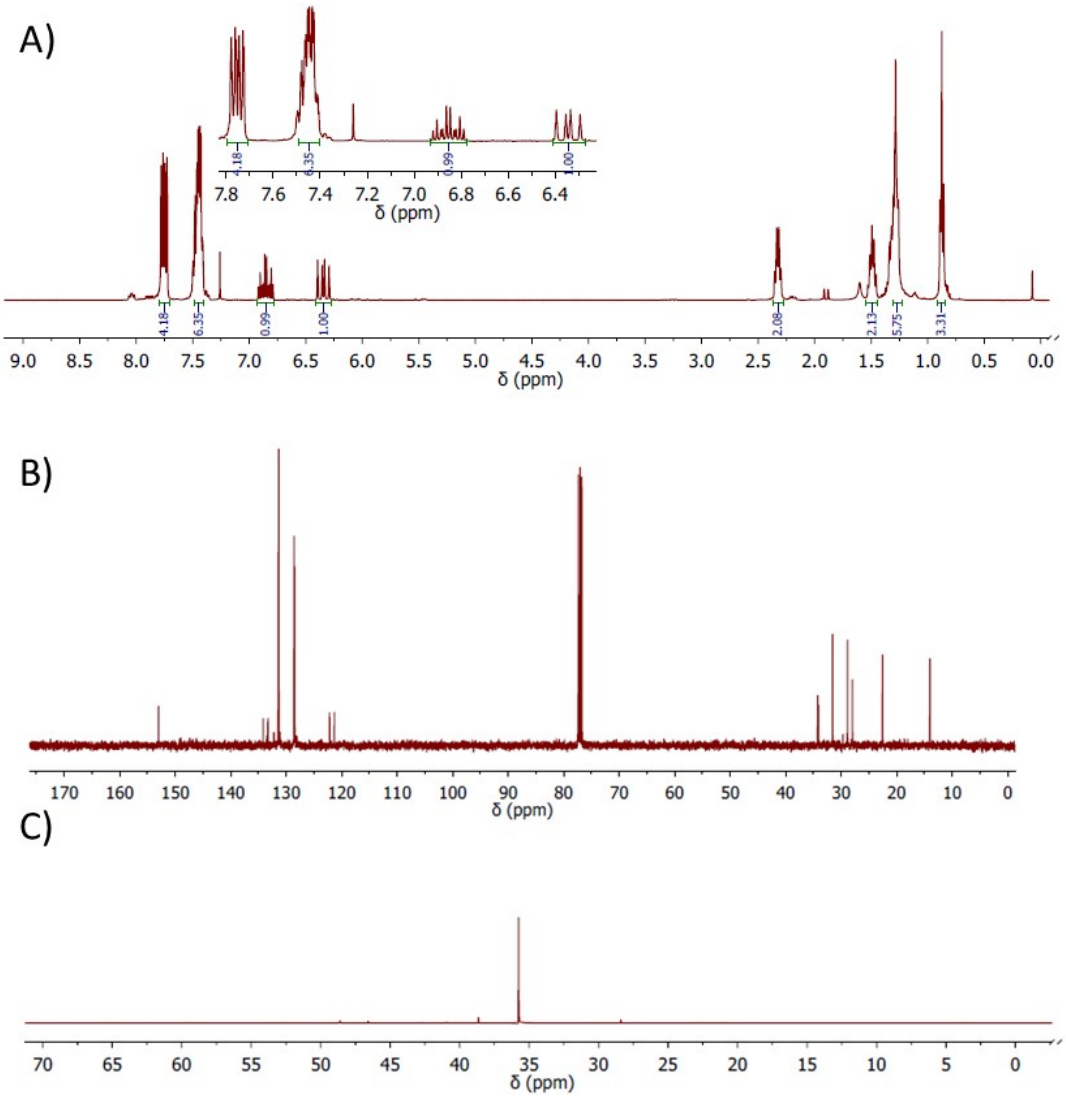
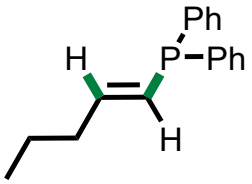


Fig. S12 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3k

δ_H (400 MHz, $CDCl_3$) 7.79 – 7.72 (4 H, m), 7.50 – 7.40 (7 H, m), 6.85 (1 H, ddt, *J* 22.8, 16.2, 6.6), 6.35 (1 H, dd, *J* 24.2, 16.2), 2.31 (2 H, td, *J* 7.1, 1.8), 1.52 (2 H, dt, *J* 13.9, 7.0), 0.94 (3 H, t, *J* 7.4).

δ_C (101 MHz, $CDCl_3$) 152.75, 134.13, 133.36, 131.37, 128.55, 122.43, 121.58, 36.15, 21.30, 13.72.

δ_P (162 MHz, $CDCl_3$) 35.74

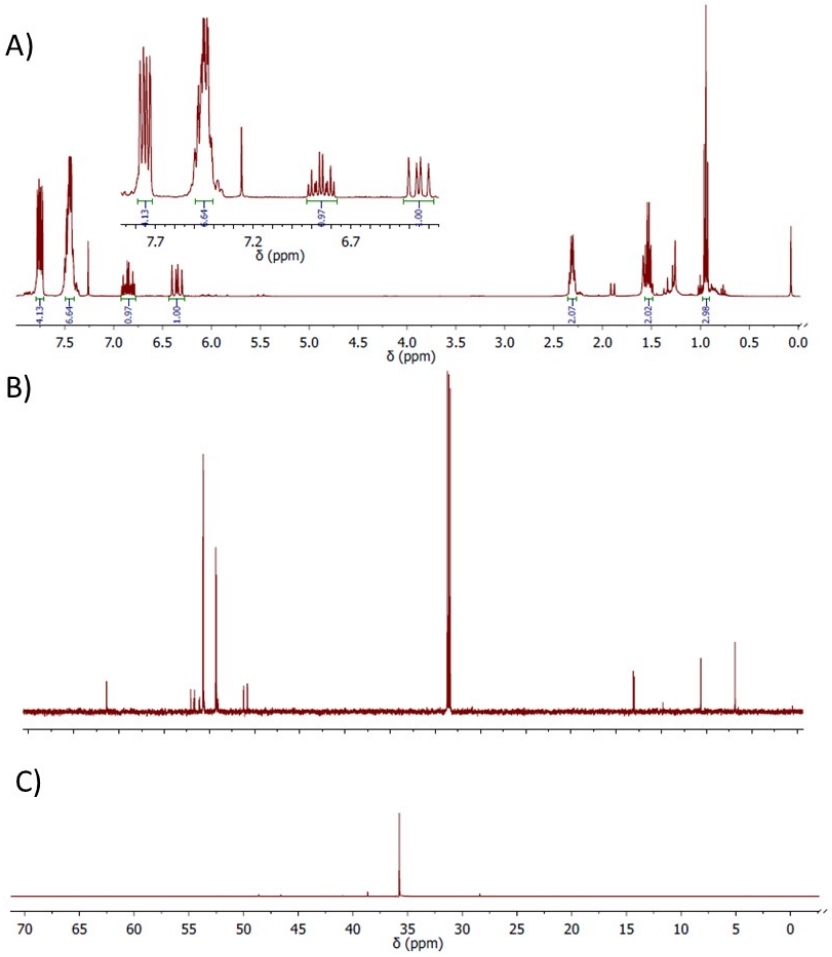
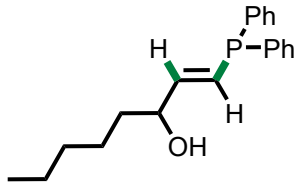


Fig. S13 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3l

δ_H (400 MHz, $CDCl_3$) 7.74 (4 H, dd, *J* 11.7, 6.0), 7.54 – 7.36 (6 H, m), 7.01 – 6.83 (1 H, m), 6.67 (1 H, dd, *J* 23.5, 16.3), 4.39 (1 H, s), 1.85 (2 H, s), 1.49 – 1.35 (3 H, m), 1.25 (3 H, s), 0.87 (5 H, d, *J* 5.9).

δ_C (126 MHz, $CDCl_3$) 154.08, 131.45, 128.64, 121.07, 120.40, 72.27, 36.64, 31.61, 72, 25.01, 22.56, 14.01.

δ_P (202 MHz, $CDCl_3$) 36.03

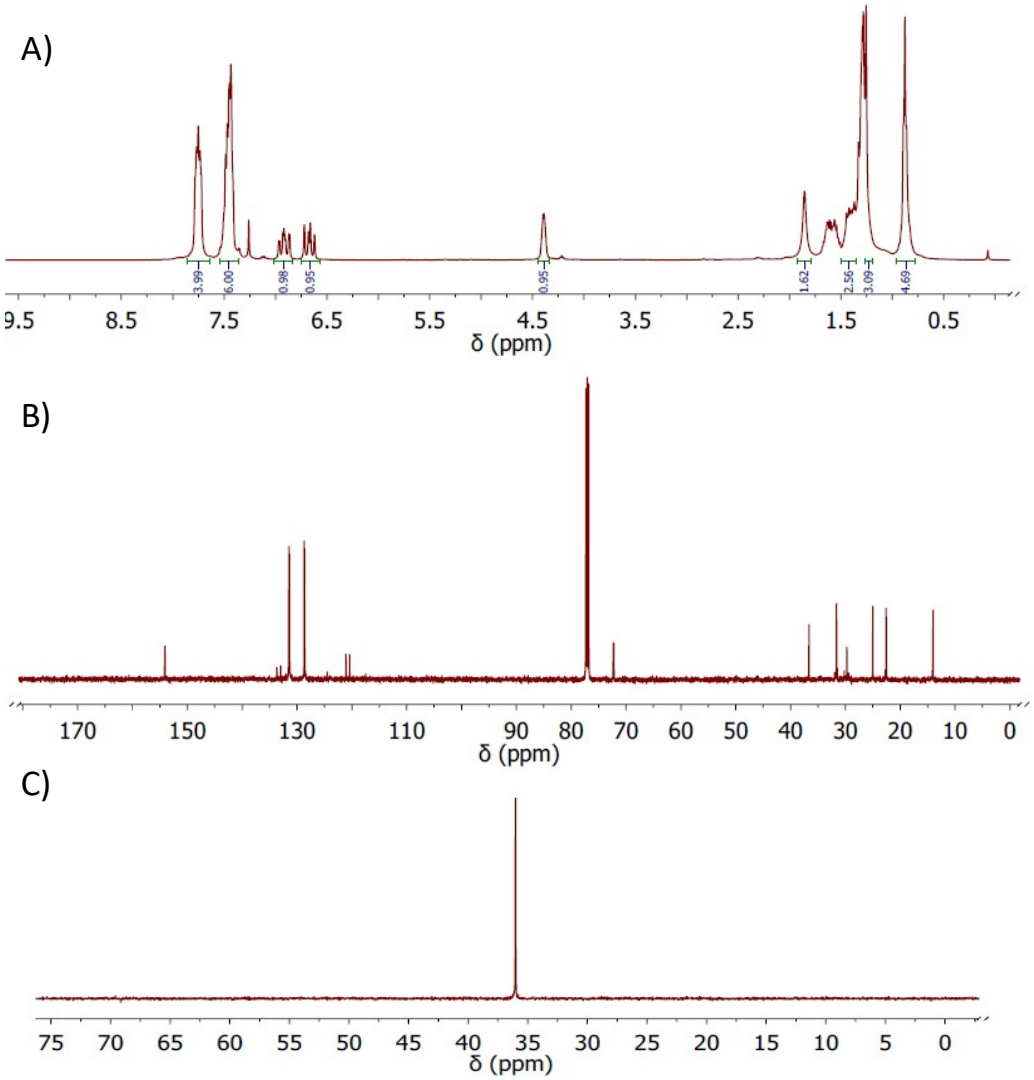
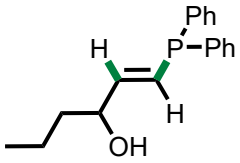


Fig. S14 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.

3m



δ_H (500 MHz, $CDCl_3$) 7.82 – 7.70 (4 H, m), 7.51 – 7.39 (6 H, m), 6.91 (1 H, ddd, *J* 22.8, 16.2, 3.9), 6.74 – 6.60 (1 H, m), 4.40 (1 H, d, *J* 2.8), 1.89 (1 H, s), 1.64 – 1.52 (2 H, m), 1.48 – 1.37 (2 H, m), 0.93 (3 H, t, *J* 7.3).

δ_C (126 MHz, $CDCl_3$) 154.12, 133.65, 132.96, 131.44, 128.65, 120.55, 72.05, 71.91, 38.76, 18.59, 13.93.

δ_P (202 MHz, $CDCl_3$) 36.04

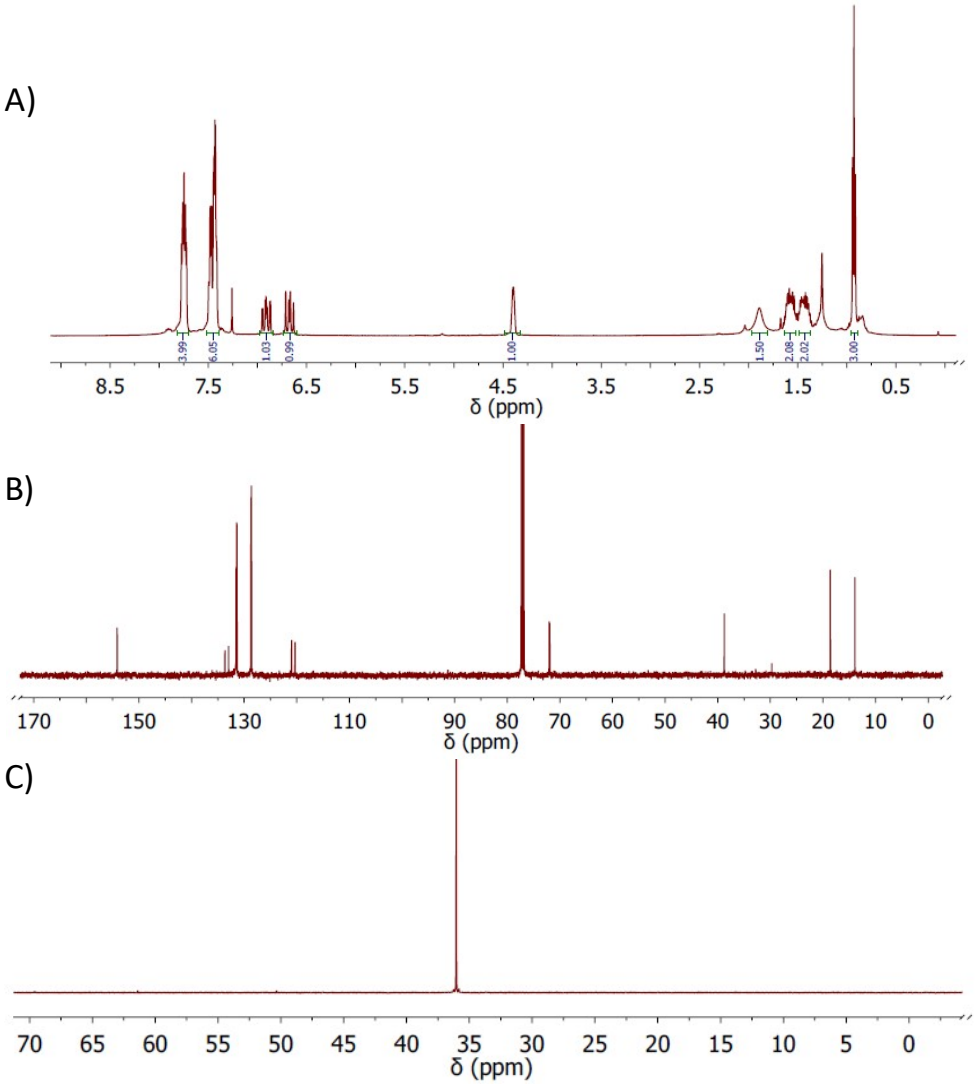
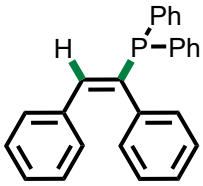


Fig. S15 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.

3n



δ_H (500 MHz, $CDCl_3$) 7.80 (4H, ddd, *J* 18.2, 9.7, 8.5), 7.68 (1H, d, *J* 24.0), 7.49 (2H, dd, *J* 7.5, 5.7), 7.41 (4H, tt, *J* 12.1, 6.0), 7.26 – 7.20 (1H, m), 7.19 – 7.10 (5H, m), 7.02 (2H, d, *J* 7.6), 6.96 – 6.90 (2H, m).

δ_C (126 MHz, $CDCl_3$) 144.04, 143.93, 135.62, 135.38, 135.00, 134.79, 132.69, 131.54, 130.94, 130.28, 129.06, 128.62, 128.39, 128.29, 127.93.

δ_P (202 MHz, $CDCl_3$) 48.09

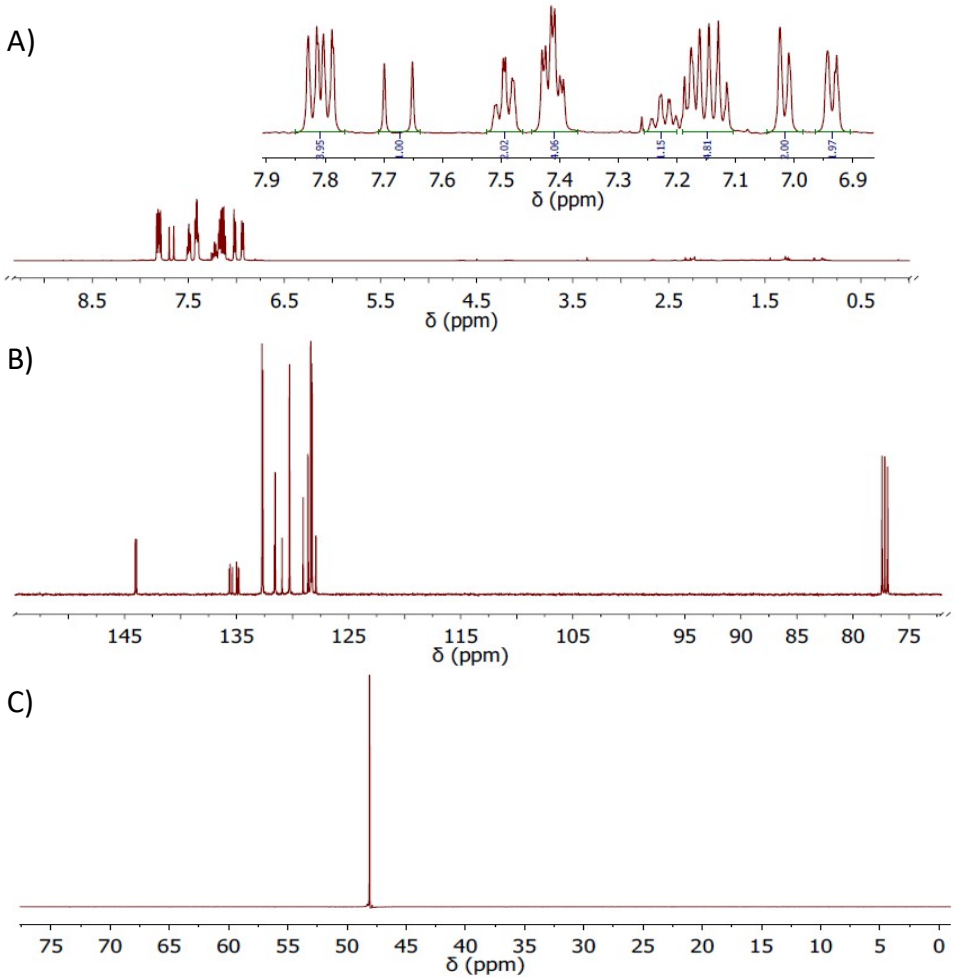
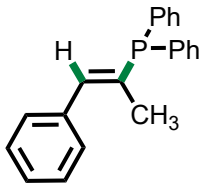


Fig. S16 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.

3o



δ_H (500 MHz, $CDCl_3$) 7.91–7.85 (4 H, m), 7.56 (2 H, dd, *J* 7.2, 1.7), 7.54 – 7.49 (4 H, m), 7.37 (5 H, dt, *J* 26.2, 7.6), 7.04 (1 H, d, *J* 24.1), 2.20 (3 H, dd, *J* 15.0, 1.2).

δ_C (126 MHz, $CDCl_3$) 142.29, 142.20, 132.40, 132.31, 131.65, 129.36, 128.69, 128.59, 128.40, 128.34., 15.37.

δ_P (202 MHz, $CDCl_3$) 50.55

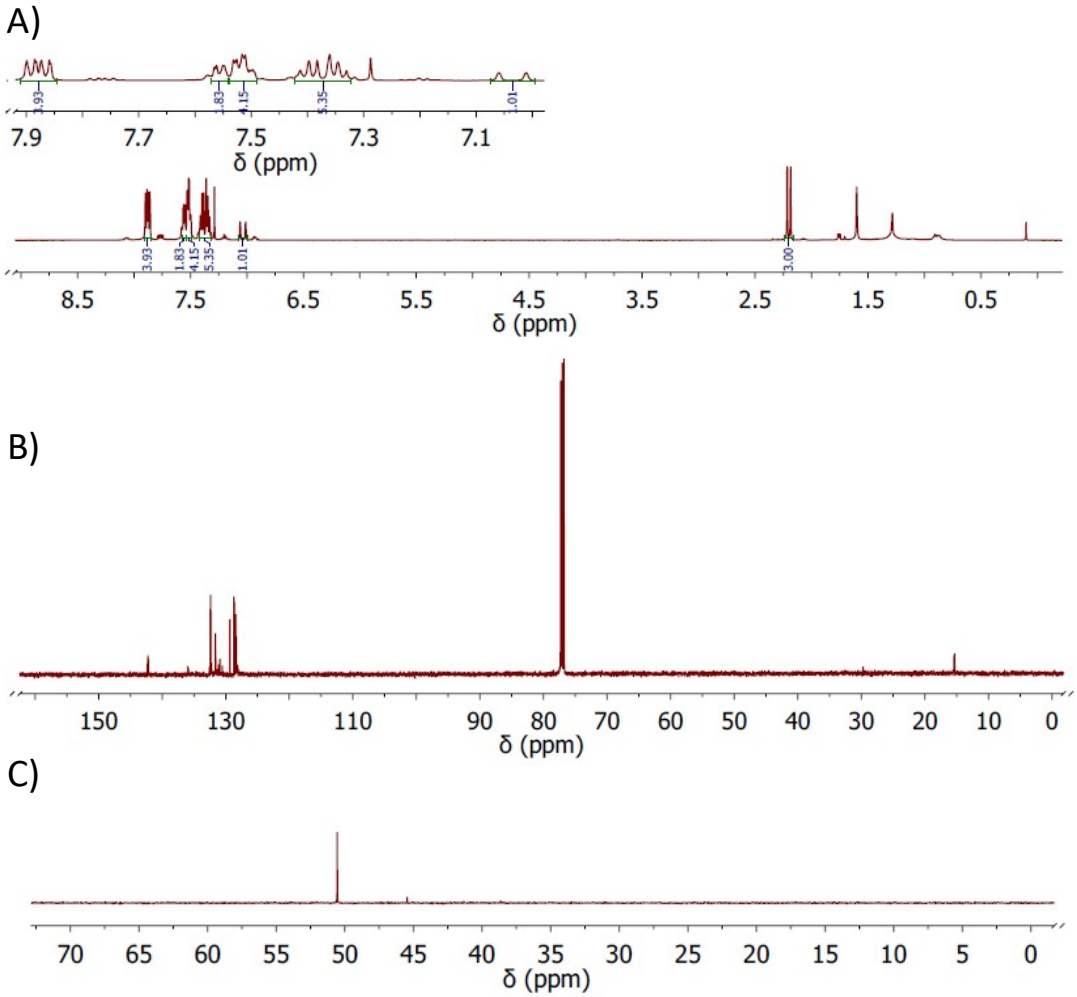
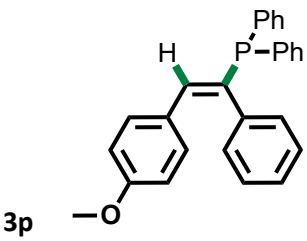


Fig. S17 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3p

δ_H (500 MHz, $CDCl_3$), δ_C (126 MHz, $CDCl_3$), and δ_P (202 MHz, $CDCl_3$) 48.11 and 69.57 ppm

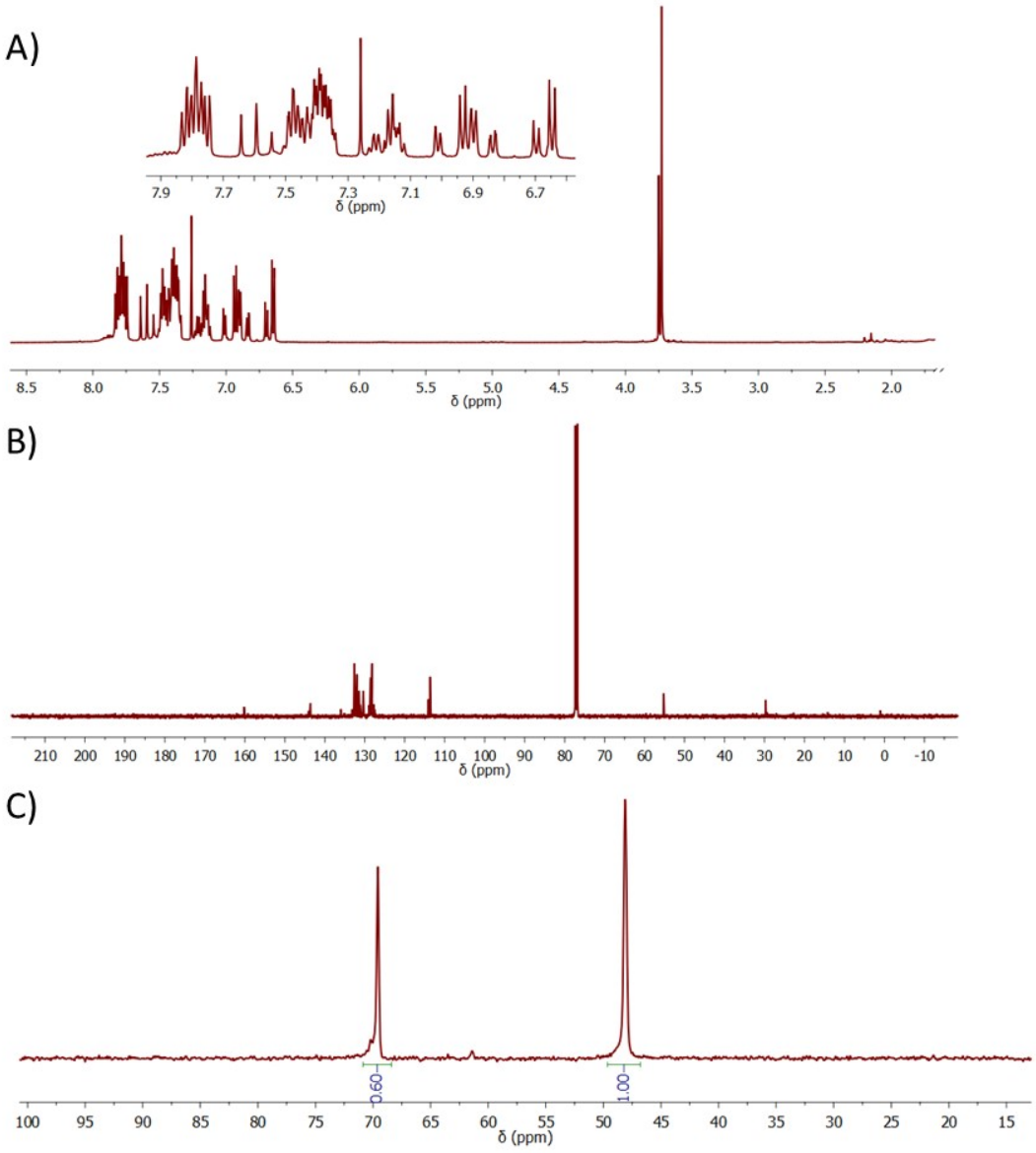
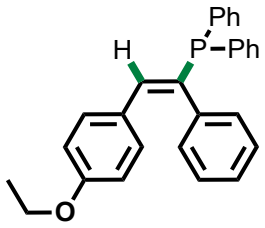


Fig. S18 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.



3q

δ_H (500 MHz, $CDCl_3$), δ_C (126 MHz, $CDCl_3$), and δ_P (202 MHz, $CDCl_3$) 48.09 and 61.37 ppm

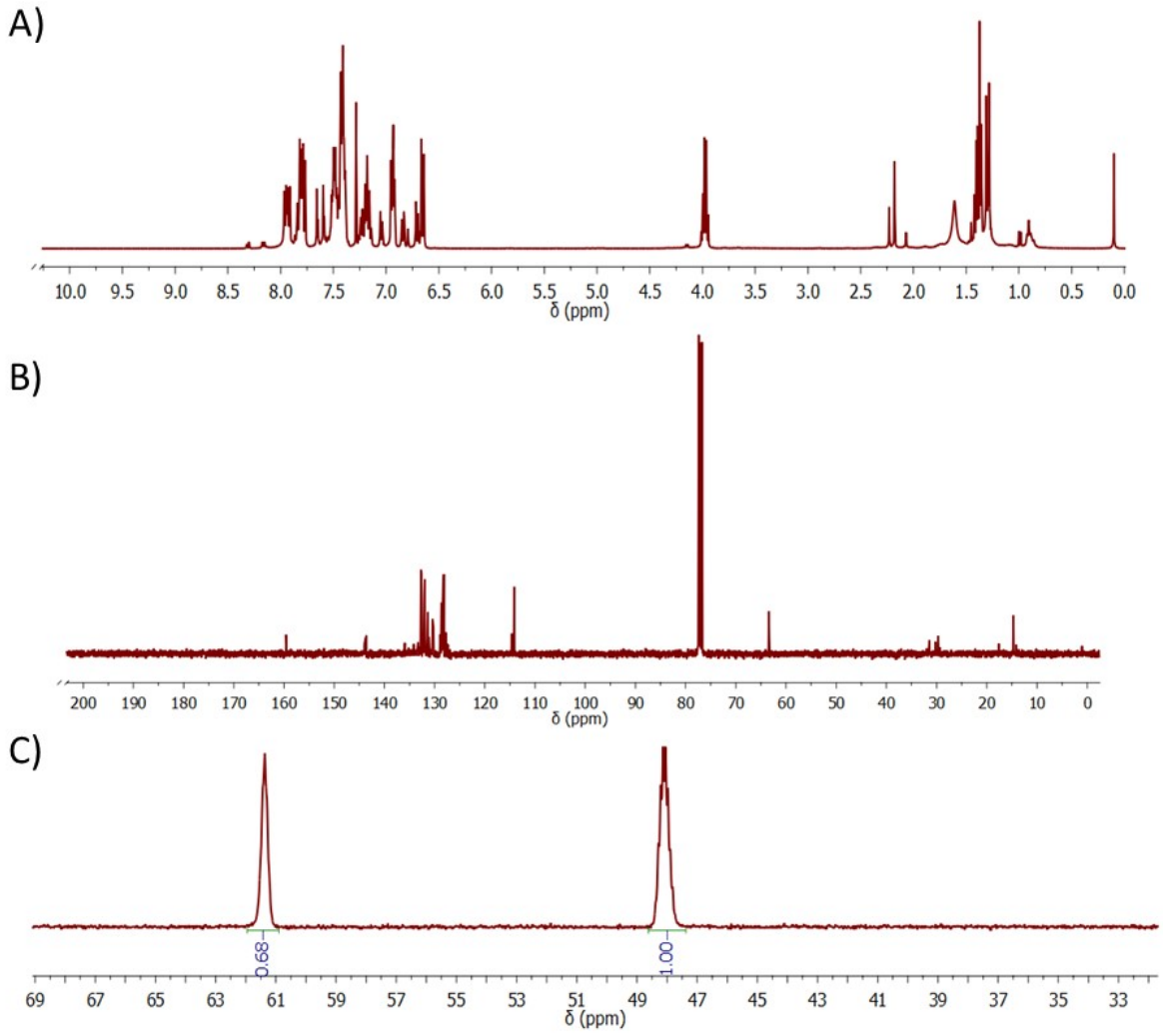


Fig. S19 Panel **(A)** corresponding to ^{1}H-NMR, **(B)** corresponding to ^{13}C-NMR and **(C)** corresponding to ^{31}P-NMR.

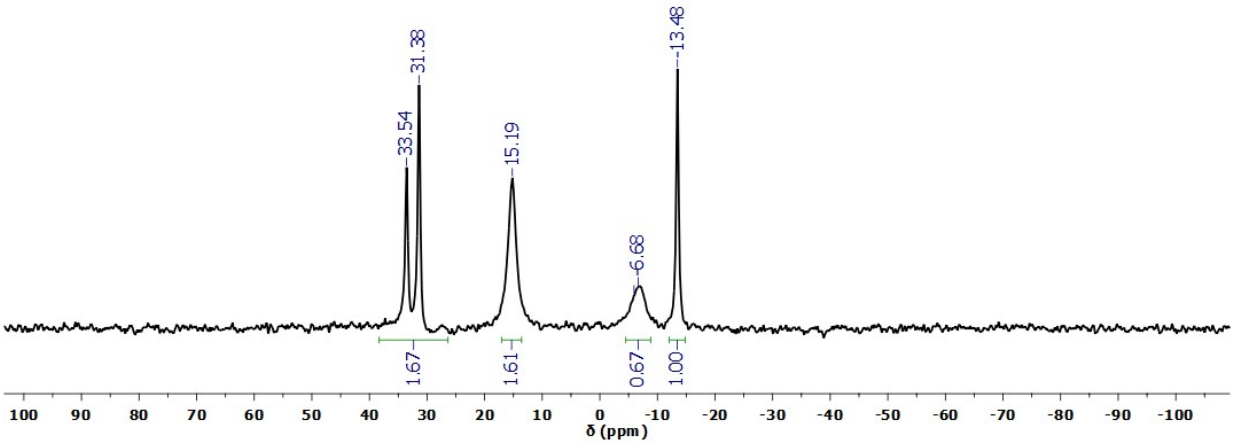


Fig. S20 ^{31}P-NMR spectrum of **2** measured at -40 ^{o}C in d^{8}-THF solvent with the integration value.

Table S5 Selected bond distances and spin densities on the important atoms of the DFT optimized structures of the ground state ^{1}R (S = 0) and 1st and 2nd excited S = 1, S = 2 states respectively. The Wiberg-bond indices and the natural charges of selected bonds and atoms are tabulated for the S = 0 spin state.

bonds	***^{1}R (S = 0, GS)***	***^{3}R (S = 1, 1st-ES)***	***^{5}R (S = 2, 2nd-ES)***	***^{1}R (S = 0, GS)***	**Atom number**	***^{1}R (S = 0, GS)***	***^{1}R (S = 0, GS)***	***^{3}R (S = 1, ES)***	***^{5}R (S = 2, 2nd-ES)***
	Bond Length(Å)	**Bond Length(Å)**	**Bond Length(Å)**	**WB-indices**		**Spin density**	**NPA charges**	**Spin density**	**Spin density**
Co1-N1	1.868	1.870	1.997	0.42	**Co1**	0.841	0.849	1.044	2.573
Co1-N2	2.024	2.009	2.072	0.30	**Co2**	0.142	0.198	-0.187	-0.035
Co1-N3	2.030	2.016	2.062	0.29	**N1**	-0.168	-0.499	0.162	0.264
Co2-C9	2.120	2.127	2.118	0.36	**N2**	-0.181	-0.665	0.169	0.263
Co2-C10	1.942	1.994	1.945	--	**N3**	-0.177	-0.674	0.186	0.272
Co2-C11	2.122	2.129	2.127	0.35	**C7**	-0.198	0.081	0.221	0.201
N1-C8	1.371	1.368	1.363	1.20	**C8**	0.046	0.077	-0.045	-0.014
N1-C12	1.368	1.368	1.360	1.21	**C12**	0.019	0.087	-0.045	0.008
N3-C7	1.395	1.397	1.402	1.25	**C13**	-0.170	0.083	0.210	0.180
N2-C13	1.391	1.395	1.397	1.25	**C9**	-0.067	-0.409	-0.045	0.033
C7-C8	1.408	1.412	1.415	1.32	**C10**	0.006	-0.371	0.162	0.006
C8-C9	1.463	1.461	1.467	1.12	**C11**	-0.065	-0.409	-0.045	0.031
C9-C10	1.453	1.451	1.453	1.22	--	--		--	
C10-C11	1.451	1.450	1.451	1.22	--	--			--
C11-C12	1.460	1.458	1.463	1.12	--	--			--
C12-C13	1.406	1.395	1.413	1.31	--	--			--

Table S6 Turn Over Number (TON) calculated for the hydrophosphination product formed after catalytic reaction with **2**, and the literature comparison of E-selective product.

Substrate	Catalyst	Cat. Loading (mole%)	Time(hr)/Temp.(°C)/Additive	Selectivity (di/E/Z)	TON E-selective/Overall
Phenyl Acetylene	[1]Rh(I)	5	2/110/Ag(OTf)-MeOH	0/96/4	17.1/17.8
Phenyl Acetylene	[2]Rh(I)-NHC	5	24/120/-	66/4/6	0.71/18.0
Phenyl Acetylene	[3]Eu_2-Complex	1	2/60/-	0/22/78	22/100
Phenyl Acetylene	[4]$CuCl_2$[d]	1.25	8/110/I^{t}Bu	95/0/0	0/76.8
Phenyl Acetylene	[5]CpFe(CO)[e]	5.56	2/110/-	96/0/0	0/19.2
Phenyl Acetylene	Complex **2**	2	1/60/-	0/100/0	44.5/50

Table S7 Table for Crystallographic parameters of the catalytic hydrophosphination product formed.

Substrate	**PhAc (3a)**	**4-Me-PhAc (3b)**	**4-OMe-PhAc (3c)**	**4-OEt-PhAc (3d)**	**4-Br-PhAc (3g)**	**4-F-PhAc (3h)**	**CyclopropylAc (3i)**
Formula	$C_{20}H_{17}P_1S_1$	$C_{21}H_{19}P_1S_1$	$C_{21}H_{19}O_1P_1S_1$	$C_{22}H_{21}O_1P_1S_1$	$C_{20}H_{16}Br_1P_1S_1$	$C_{20}H_{16}F_1P_1S_1$	$C_{17}H_{17}$ P_1S_1
System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	10.647(4)	10.5583(2)	10.9751(11)	9.5625(6)	10.9046(5)	13.6620(7)	9.4336(2)
b [Å]	9.422(3)	9.7547(2)	9.3003(9)	11.2770(6)	9.5387(6)	9.0092(3)	9.2923(2)
c [Å]	17.618(8)	17.5966(3)	17.8484(16)	19.3935(11)	17.5064(10)	14.2277(6)	16.9938(4)
α [°]	90.0	90.0	90.0	102.271(5)	90.0	90.0	90.0
β [°]	107.46(4)	97.406(2)	96.874(8)	100.184(5)	97.019(5)	97.679(4)	94.068(2)
γ [°]	90.0	90.0	90.0	98.545(5)	90.0	90.0	90.0
V [Å^3]	1685.9(12)	1797.21(6)	1808.7(3)	1973.3(2)	1807.29(18)	1735.49(13)	1485.92(6)
Z	4	4	4	2	4	4	4
$\rho_{cal.}$ [g/cm^3]	1.262	1.236	1.287	1.227	1.467	1.295	1.271
2Θ	49.998	129.998	49.998	49.998	129.998	129.998	48.998

Radiation	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Mo Kα
λ [Å]	0.71073	1.54184	0.71073	0.71073	1.54184	1.54184	0.71073
T [K]	150	150	150	150	150	150	150
R1 (%)	8.9	4.61	6.48	8.13	7.3	7.73	2.95
wR2 (%)	27.25	12.99	14.10	22.38	22.35	24.57	7.35

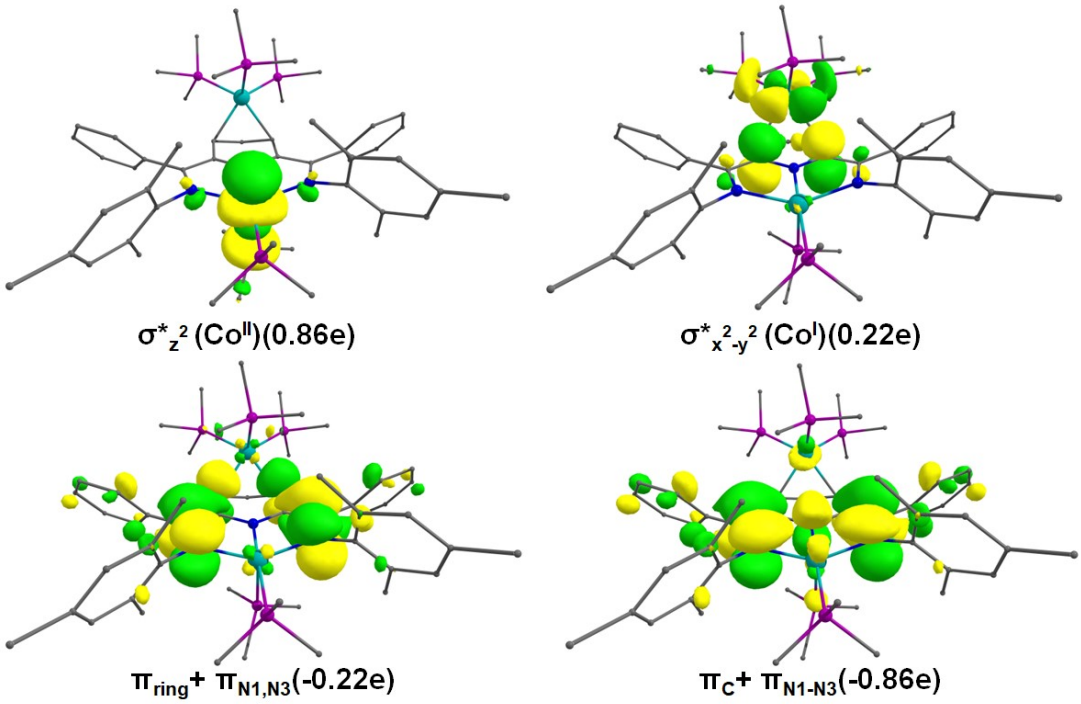


Fig. S21 Spin natural orbital analysis of the singlet ground state.

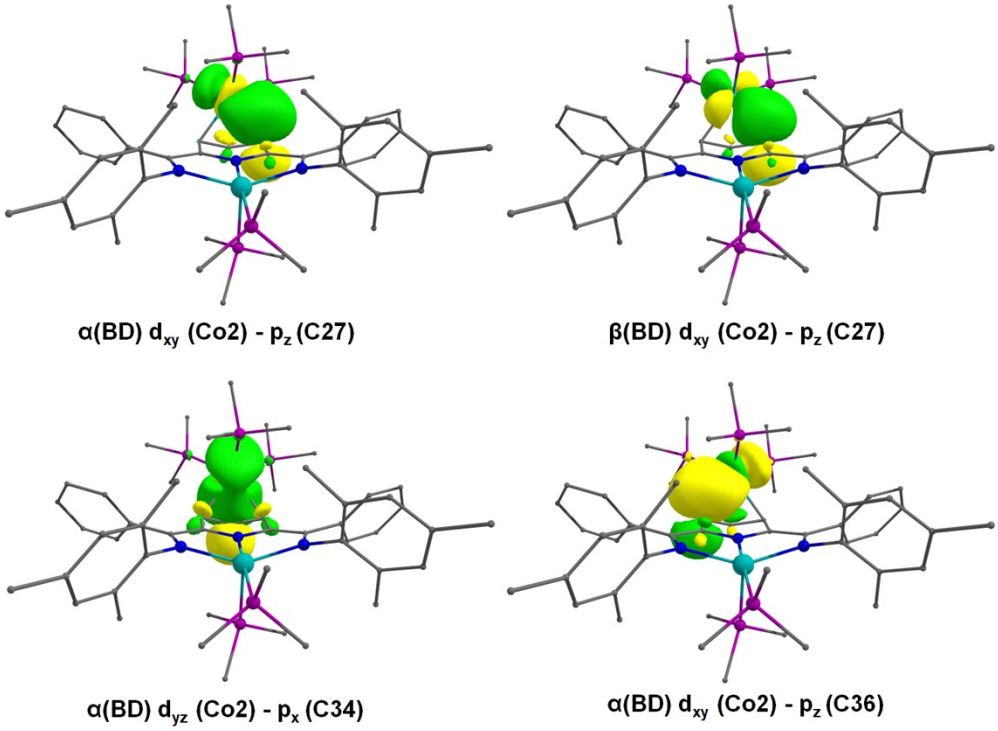


Fig. S22 Orbitals involved in the *η3*-bonding between Co^{I} and p-allylic moiety.

Reaction coordinates.

^{5}R			
Co	-1.864652000	0.167236000	0.401459000
Co	3.394053000	-0.295933000	-0.005356000
P	-1.843313000	0.079430000	3.047079000
P	-4.294468000	0.425444000	0.053978000
P	2.542512000	-0.043523000	-2.048832000
P	5.005596000	1.230631000	0.071398000
P	4.574872000	-2.154751000	-0.293414000
N	-1.538730000	-1.868053000	0.030659000
N	0.121167000	-0.039528000	0.712416000
N	-1.153261000	2.095820000	0.117948000
C	-0.287397000	-2.296145000	0.407394000
C	-0.047522000	-4.404253000	-0.938985000
H	-0.532560000	-3.902868000	-1.768816000
C	0.141600000	-3.705730000	0.269653000
C	0.861716000	1.085407000	0.868213000
C	-2.562928000	-2.751056000	-0.369286000
C	-4.771720000	-4.344857000	-1.201638000
C	0.154280000	2.268242000	0.532167000
C	0.638735000	-1.285964000	0.780428000
C	0.766084000	-4.389975000	1.331870000
H	0.885125000	-3.884074000	2.285645000
C	0.397189000	-5.716397000	-1.087271000
H	0.248820000	-6.227965000	-2.034971000
C	-4.258674000	-4.432347000	0.095636000
H	-4.727993000	-5.112867000	0.804628000
C	-1.901802000	3.122860000	-0.498606000

^{3}R			
Co	-1.731127698	-0.242066312	-0.264707160
Co	3.340201192	0.487192326	0.012622994
P	-1.906975943	-0.159296640	-3.076841846
P	-3.999442801	-0.655769676	-0.104836363
P	2.513604633	0.171789456	2.044766291
P	5.017318943	-0.955000889	-0.095799074
P	4.403308760	2.406782797	0.298908415
N	-1.675573083	1.745629271	0.022954122
N	0.066495355	0.055469947	-0.685561297
N	-1.059498579	-2.134596245	-0.092187439
C	-0.450375348	2.283487673	-0.370610345
C	-0.382381363	4.396592972	0.982956794
H	-0.840736175	3.858945712	1.812266975
C	-0.131253950	3.714947057	-0.226095742
C	0.877235647	-1.027293381	-0.891373675
C	-2.763981144	2.570907121	0.380971106
C	-5.056873355	4.079572936	1.144209802
C	0.253233539	-2.248194725	-0.554968290
C	0.522166709	1.343450858	-0.758227917
C	0.459874609	4.443411400	-1.280581425
H	0.625584877	3.947438436	-2.238689644
C	-0.032503125	5.738302307	1.137777653
H	-0.229823796	6.239587682	2.089164791

C	2.262286000	0.944658000	1.274776000
H	2.744633000	1.842213000	1.640611000
C	-3.075825000	-2.649691000	-1.686428000
C	-3.183786000	-3.652242000	0.531112000
C	-3.035997000	3.986878000	-2.474231000
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C	-2.203756000	3.030101000	-1.878114000
C	2.698334000	-0.325096000	1.801803000
H	3.397878000	-0.428485000	2.628229000
C	2.039970000	-1.438460000	1.168655000
H	2.354424000	-2.436736000	1.443346000
C	1.215525000	-5.701655000	1.181577000
H	1.696647000	-6.204015000	2.017226000
C	0.835780000	3.585496000	0.539110000
C	-4.166686000	-3.433921000	-2.072279000
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C	1.037045000	-6.371987000	-0.031240000
H	1.385431000	-7.394366000	-0.150132000
C	1.502482000	4.040582000	1.695969000
H	1.470201000	3.432985000	2.595489000
C	-3.573693000	5.055231000	-1.757059000
C	-5.921202000	-5.216422000	-1.650683000
H	-5.564818000	-6.176238000	-2.049727000
H	-6.506076000	-4.734415000	-2.442381000
H	-6.600609000	-5.444831000	-0.821400000
C	2.185223000	5.256103000	1.711127000
H	2.691619000	5.576551000	2.618346000
C	0.852593000	4.424740000	-0.592646000
H	0.341277000	4.113672000	-1.495768000
C	-2.430512000	-1.719463000	-2.680941000
H	-2.311816000	-0.713137000	-2.272351000
H	-3.020140000	-1.650430000	-3.601908000
H	-1.423190000	-2.056664000	-2.949862000
C	1.530055000	5.642862000	-0.575593000
H	1.533469000	6.263519000	-1.468138000
C	-1.618683000	1.938752000	-2.743384000
H	-0.871878000	2.346264000	-3.436516000
H	-2.389234000	1.451000000	-3.351863000
H	-1.118627000	1.178683000	-2.141950000
C	-2.758647000	-3.714362000	1.974015000
H	-1.765460000	-4.158867000	2.095651000
H	-3.466512000	-4.300205000	2.569712000
H	-2.708498000	-2.703782000	2.390075000
C	-2.455308000	4.196596000	0.245407000
C	2.206555000	6.064594000	0.571965000
H	2.736219000	7.013390000	0.580694000
C	-5.006666000	0.633997000	-1.632015000
H	-4.557069000	1.510650000	-2.107880000
H	-6.093730000	0.770849000	-1.583747000
H	-4.787631000	-0.253145000	-2.232853000
C	-5.344479000	-0.929165000	0.729519000
H	-5.204187000	-1.838784000	0.141072000
H	-6.404311000	-0.646858000	0.712460000
H	-5.051616000	-1.147685000	1.761131000
C	6.638165000	1.090763000	-0.800971000
H	7.246881000	0.304507000	-0.346483000

C	-4.519557360	4.173870205	-0.144349499
H	-5.007049730	4.825298512	-0.877147803
C	-1.725313627	-3.211971490	0.540910167
C	2.261532109	-0.796163576	-1.296161991
H	2.783696172	-1.660935511	-1.674851285
C	-3.287892550	2.476405060	1.696453888
C	-3.399279599	3.435486435	-0.545975452
C	-2.750406160	-4.150848349	2.548397508
H	-2.975105404	-4.056228282	3.616340169
C	-2.026498034	-3.123909517	1.924491710
C	2.641763425	0.510241170	-1.801616224
H	3.285645135	0.664437600	-2.659794611
C	1.911568144	1.570894943	-1.135957283
H	2.158361596	2.588985403	-1.390838151
C	0.816240560	5.783809963	-1.122125648
H	1.275851110	6.323161703	-1.954919931
C	0.997739361	-3.522664683	-0.590855503
C	-4.423537619	3.214940175	2.047027465
H	-4.817690001	3.123659216	3.064564405
C	-2.855952150	-5.374109824	0.498960699
H	-3.183526097	-6.249775931	-0.071345264
C	0.574670088	6.439629382	0.089989766
H	0.850977872	7.489611767	0.214797279
C	1.664875235	-3.924653122	-1.768599797
H	1.579500424	-3.304393355	-2.662732074
C	-3.176005959	-5.289719811	1.860141640
C	-6.253887638	4.901250793	1.557009862
H	-5.943297636	5.870279113	1.987110842
H	-6.856257509	4.386022656	2.321815452
H	-6.909344571	5.122871812	0.700098855
C	2.408015780	-5.104837452	-1.815232484
H	2.914674949	-5.388655319	-2.741709661
C	1.085969084	-4.371460228	0.532149108
H	0.580545014	-4.096237257	1.456762524
C	-2.599134493	1.615173321	2.720585964
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