Electronic Supplementary Material (ESI) for New Journal of Chemistry.

- Fig. S1-S3. IR spectra of rhodium complexes $HRh(CO)\{P(NC_4H_4)_3\}_3$, $HRh(CO)\{PhP(NC_4H_4)_2\}_3$ and $HRh(CO)\{Ph_2P(NC_4H_4)\}_3$.
- Fig. S4-S6. ^1H NMR, ^{31}P NMR and IR-spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).
- Fig. S7. ^{31}P NMR spectra of post-reaction (**$HRh(CO)\{PhP(NC_4H_4)_2\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).
- Fig. S8. ^{31}P NMR spectra of post-reaction (**$HRh(CO)\{Ph_2P(NC_4H_4)\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).
- Fig. S9-S11. ^1H NMR, ^{31}P NMR and IR-spectra of post-reaction (**$Rh(acac)(CO)_2$ + (R)-BINAP + $P(NC_4H_4)_3$ + CO + H_2 + benzene-d**).
- Fig. S12-S14. ^1H NMR, ^{31}P NMR and IR-spectra of post-reaction (HRh**$(CO)\{P(NC_4H_4)_3\}_3$ + (R)-BINAP + CO + H_2 + benzene-d**).
- Fig. S15-S17. ^1H NMR and ^{31}P NMR spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).
- Fig. S18-S21. ^{31}P NMR spectra at different temperature of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).
- Fig. S22-S23 ^1H NMR and ^{31}P NMR spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + benzene-d)**
- Fig. S24-S27 ^{31}P NMR spectra at different temperature of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + benzene-d)**
- Fig. S28-S29 ^1H NMR and ^{31}P NMR spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE +Benzene-d. 25 ^oC for 40 min**)
- Table S1. The effect of excess $P(NC_4H_4)_3$ ligand on hydroformylation of allyl acetate
- Table S2. The effect of temperature on hydroformylation of vinyl acetate.

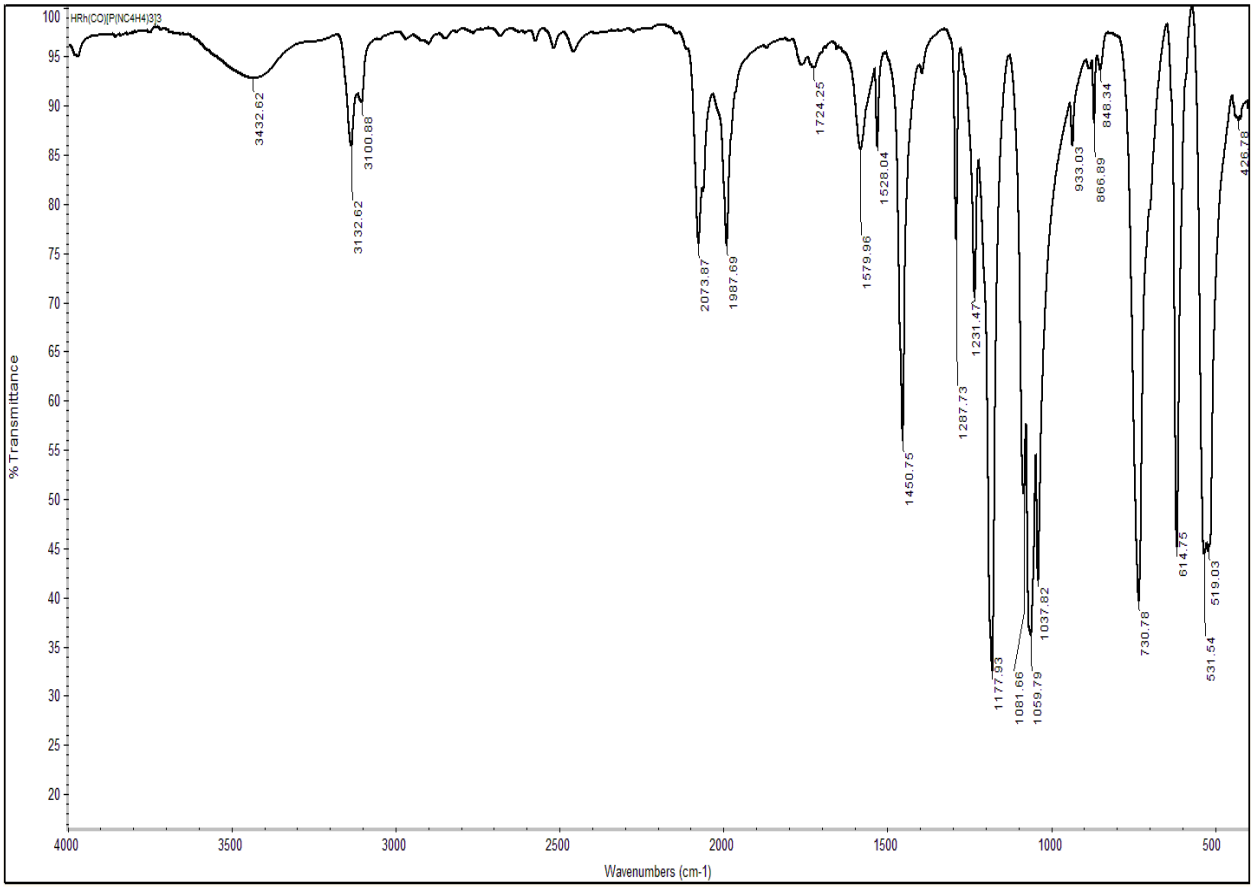

Fig. S1. IR- spectra (KBr) of $HRh(CO)\{P(NC_4H_4)_3\}_3$

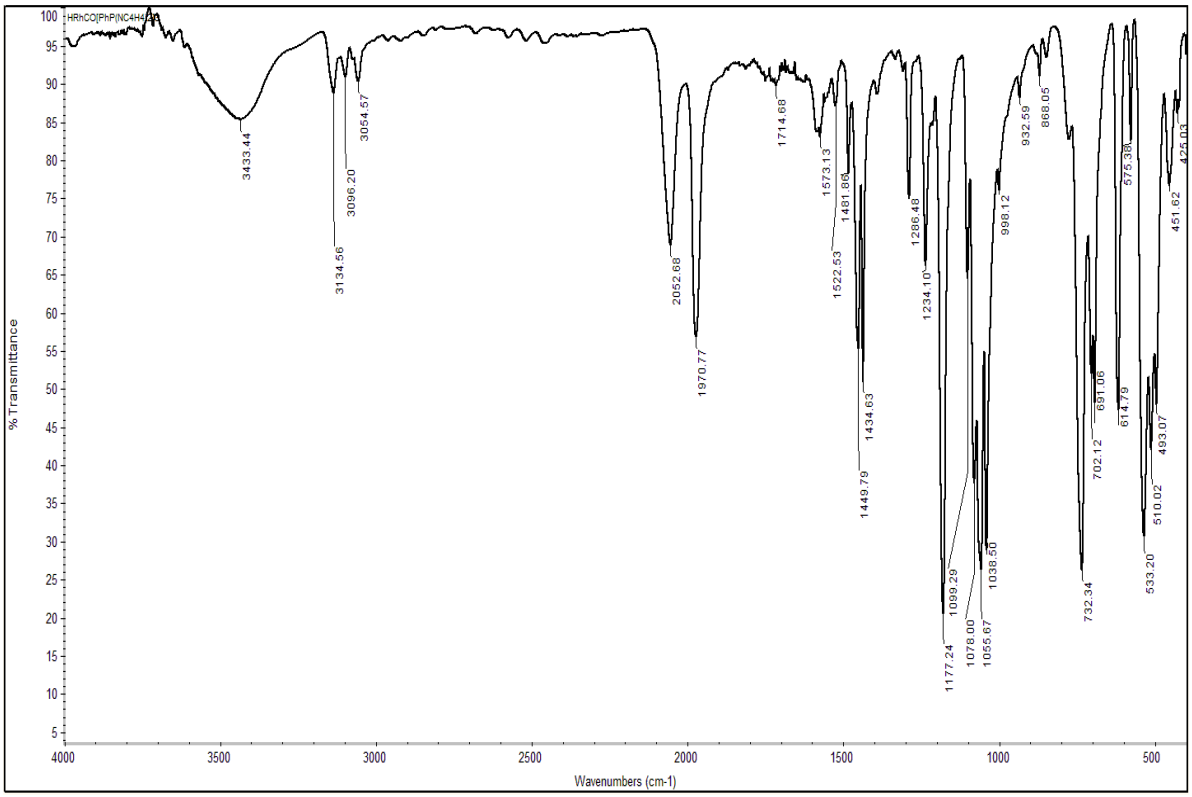

Fig. S2. IR- spectra (KBr) of $HRh(CO)\{PhP(NC_4H_4)_2\}_3$

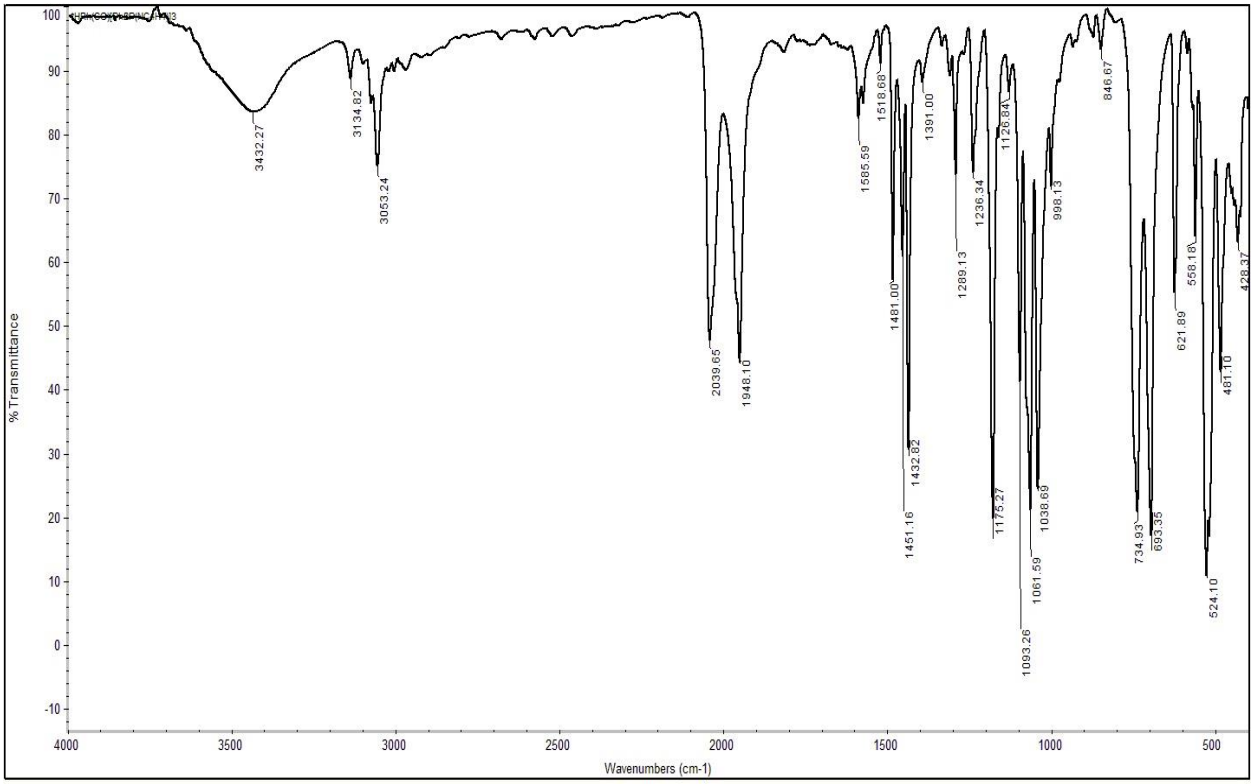

Fig. S3. IR- spectra (KBr) of $HRh(CO)\{Ph_2P(NC_4H_4)\}_3$

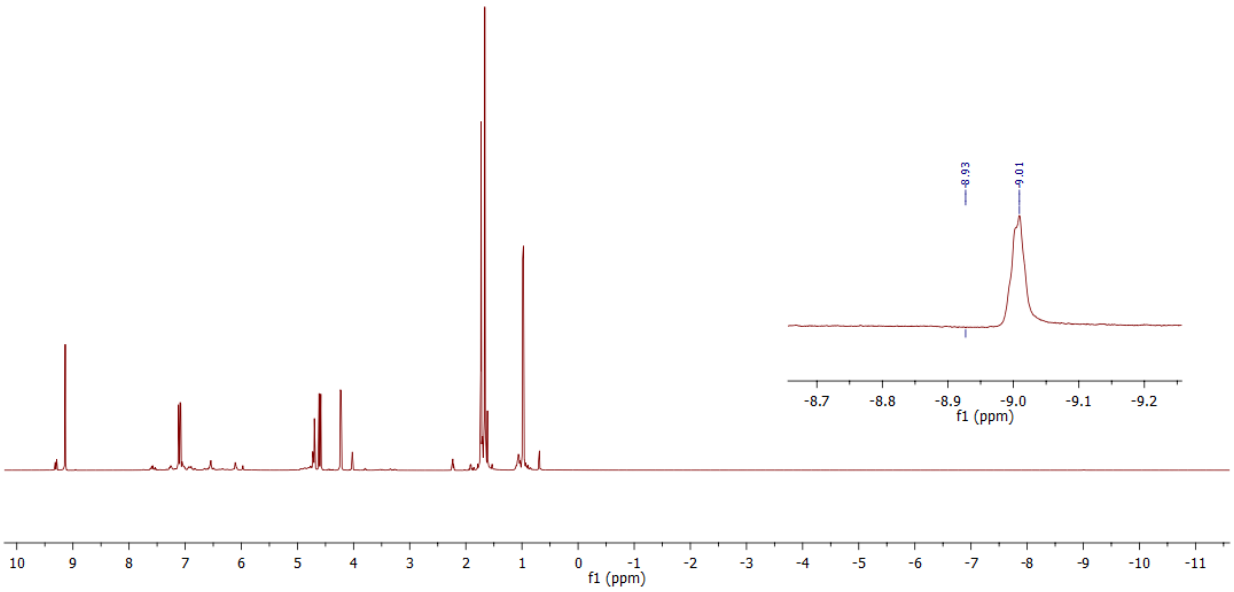

Fig. S4. ^{1}H NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate)**.

Reaction condition: $HRh(CO)\{P(NC_4H_4)_3\}_3$ (3.4 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Vinyl acetate (0.7 mL), $P(H_2/CO = 1)$ = 10 bar, 80 ^{o}C and t= 40 min.

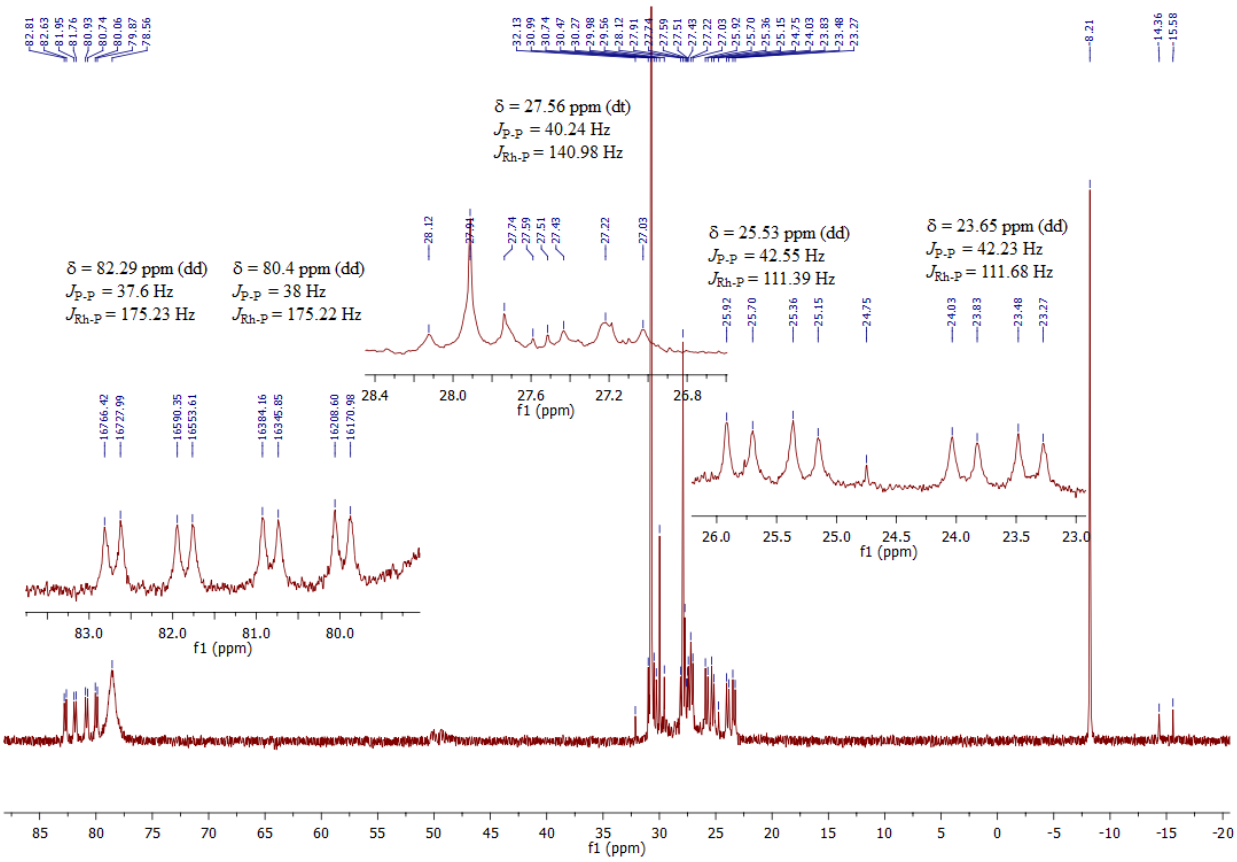

Fig. S5. ^{31}P NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).

Reaction condition: $HRh(CO)\{P(NC_4H_4)_3\}_3$ (3.4 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Vinyl acetate (0.7 mL), P(H_2/CO =1) = 10 bar, 80 ^oC and t= 40 min.

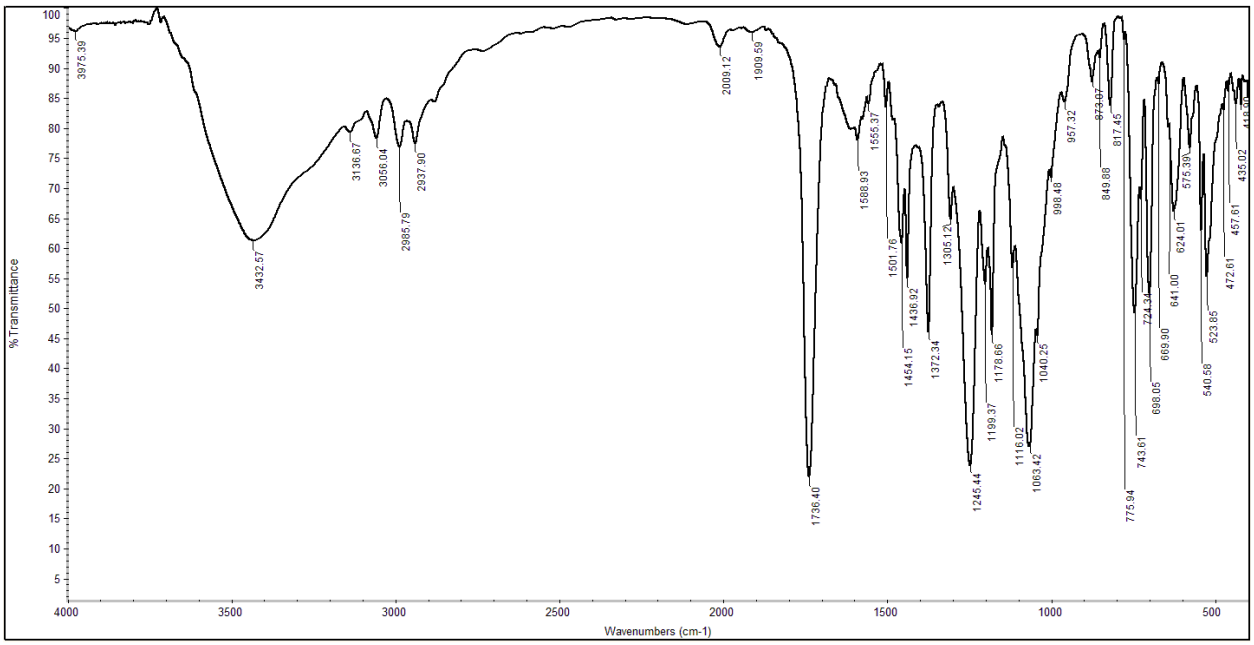

Fig. S6. IR-spectra (KBr) of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).

Reaction condition: $HRh(CO)\{P(NC_4H_4)_3\}_3$ (3.4 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Vinyl acetate (0.7 mL), $P(H_2/CO = 1)$ = 10 bar, 80 ^oC and t= 40 min.

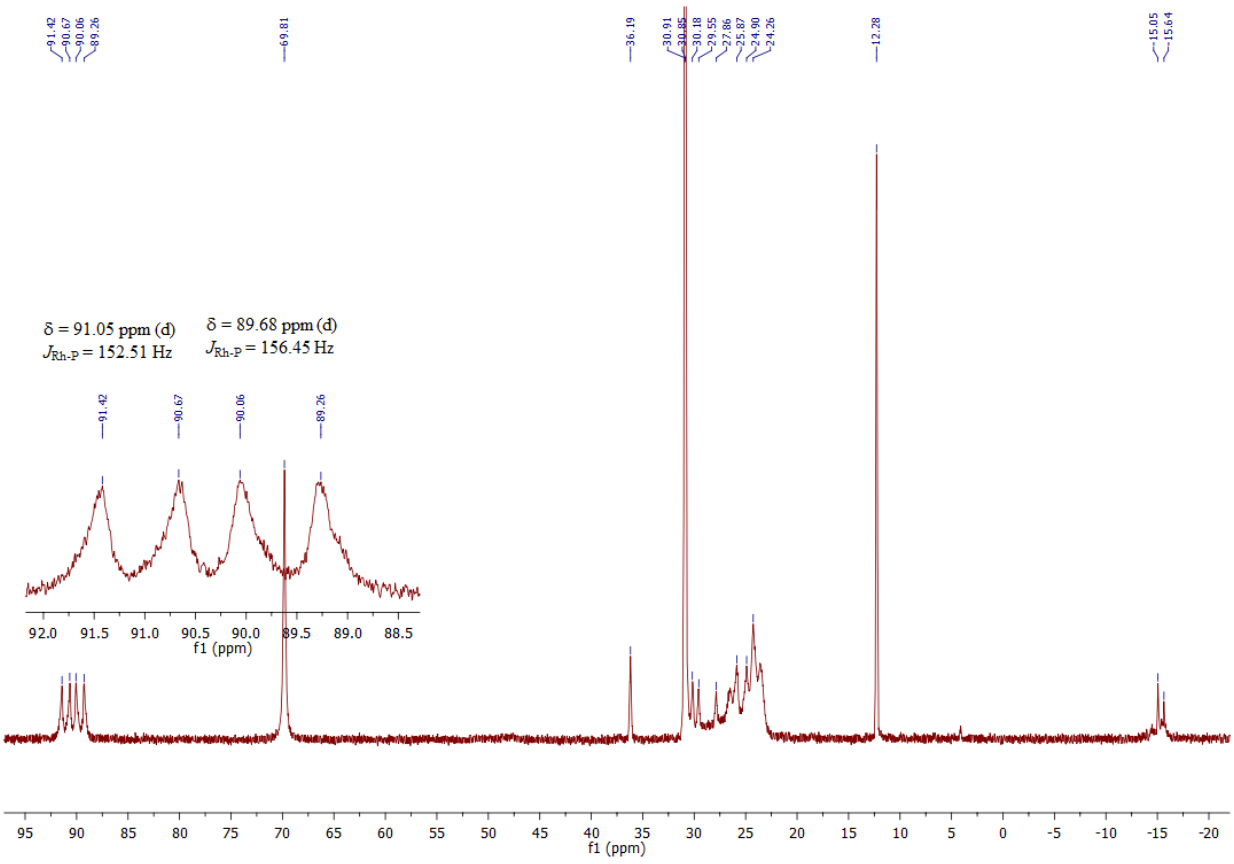

Fig. S7. ^{31}P NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{PhP(NC_4H_4)_2\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).
Reaction condition: $HRh(CO)\{PhP(NC_4H_4)_2\}_3$ (3.4 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Vinyl acetate (0.7 mL), P(H_2/CO =1) = 10 bar, 80 ^oC and t= 40 min.

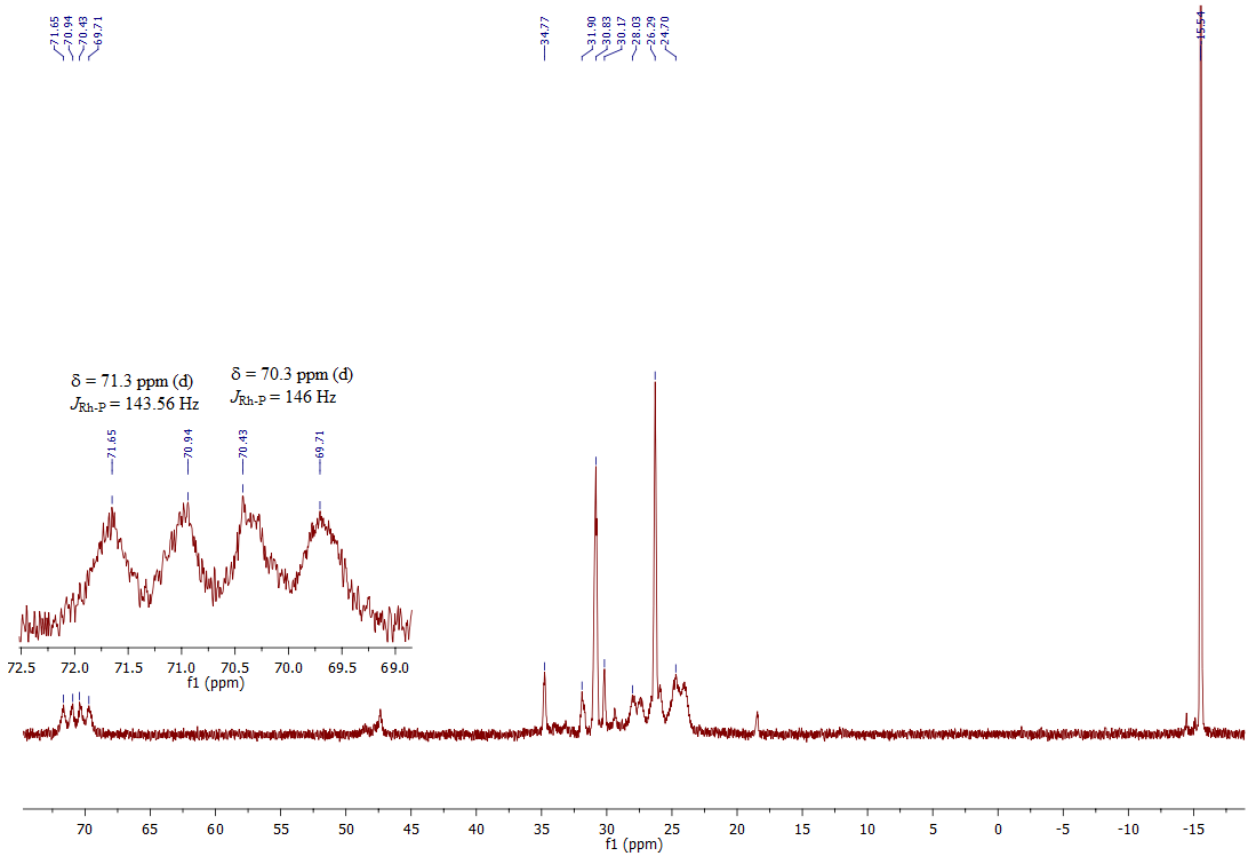

Fig. S8. ^{31}P NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{Ph_2P(NC_4H_4)\}_3$ + (R)-BINAP + CO + H_2 + Vinyl acetate**).

Reaction condition: $HRh(CO)\{Ph_2P(NC_4H_4)\}_3$ (2.15 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Vinyl acetate (0.7 mL), $P(H_2/CO$ =1) = 10 bar, 80 ^oC and t= 40 min.

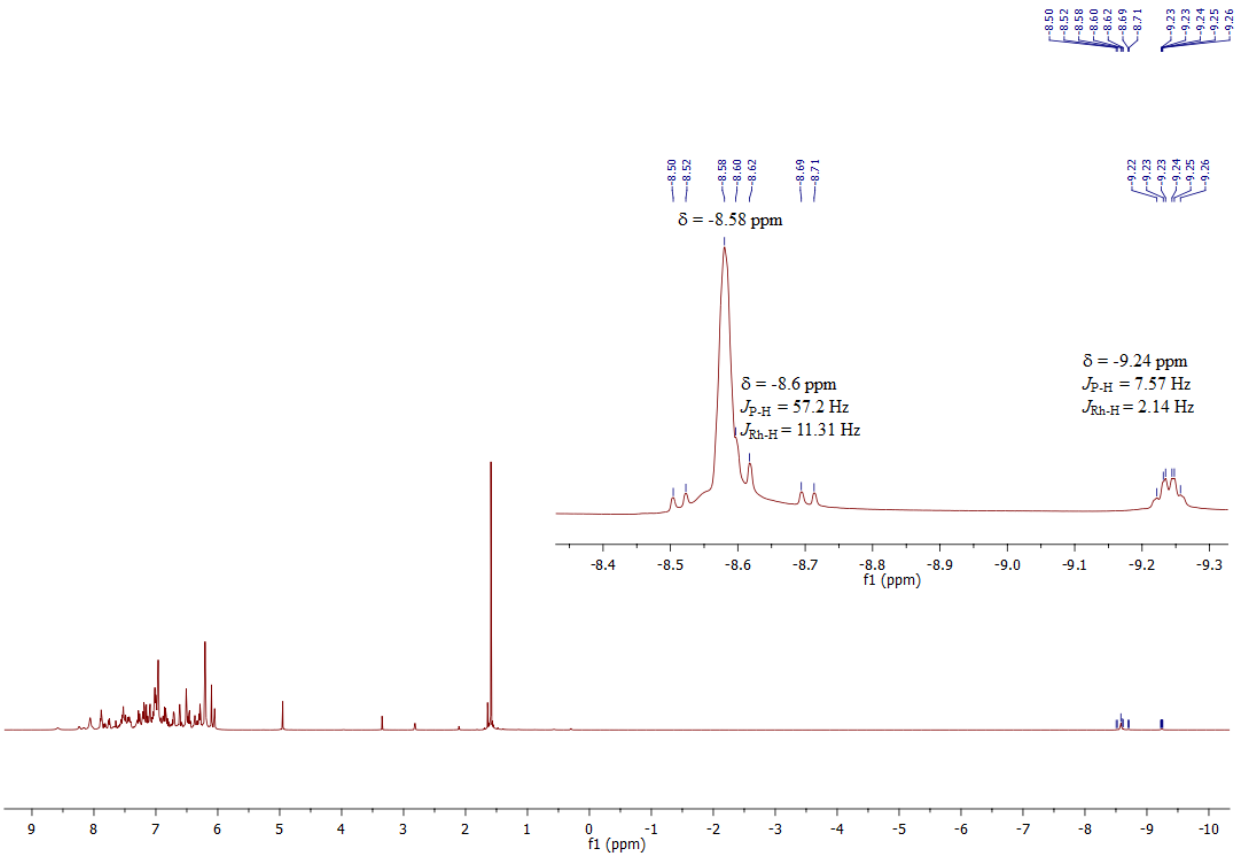

Fig. S9. ^{1}H NMR (C_6D_6) spectra of post-reaction (**$Rh(acac)(CO)_2$ + (R)-BINAP + $P(NC_4H_4)_3$ + CO + H_2 + benzene-d**).

Reaction condition: $Rh(acac)(CO)_2$ (5 X 10^{-5} mol), with 1.5-fold excess of (R)-BINAP, and 1.5-fold excess of $P(NC_4H_4)_3$, Benzene-d (1 mL), $P(H_2/CO$ =1) = 10 bar, 80 ^{o}C and t= 40 min.

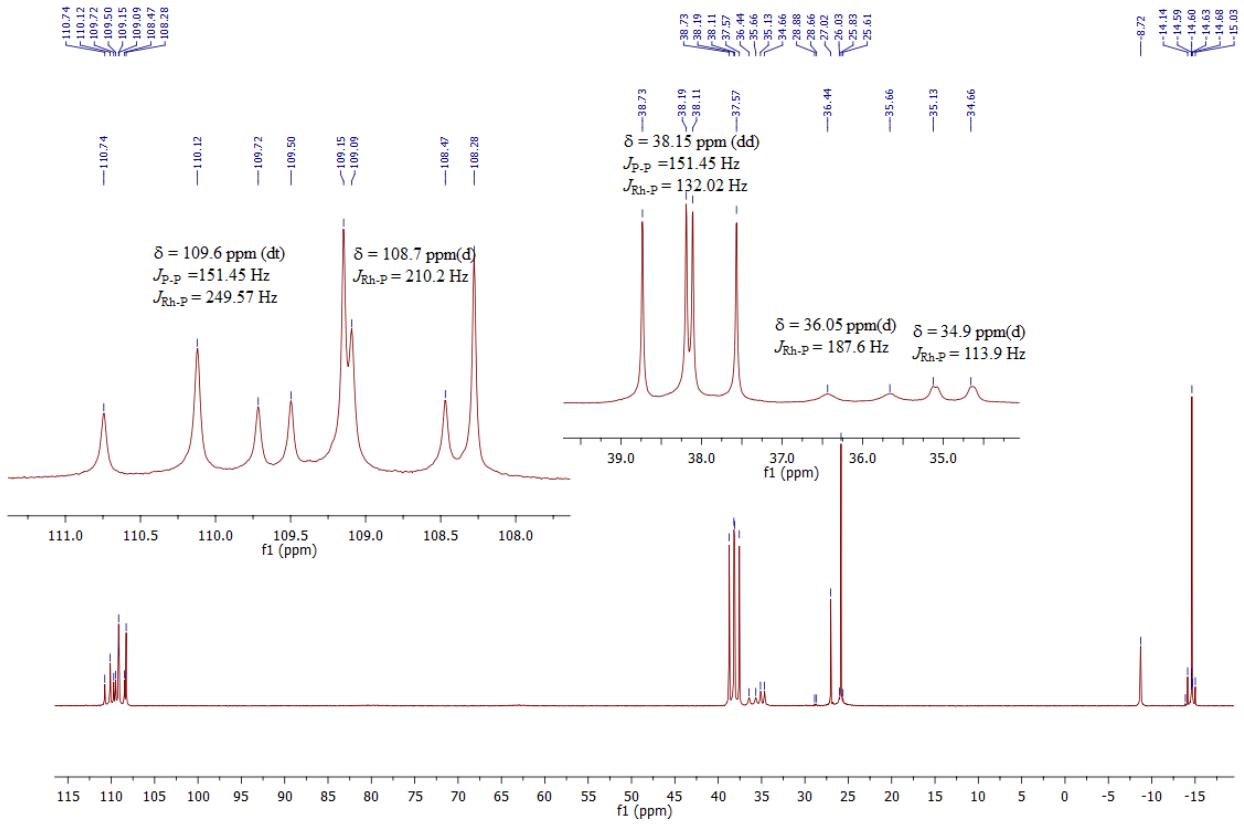

Fig. S10. ^{31}P NMR (C_6D_6) spectra of post-reaction (**$Rh(acac)(CO)_2$ + (R)-BINAP + $P(NC_4H_4)_3$ + CO + H_2 + benzene-d**).

Reaction condition: $Rh(acac)(CO)_2$ (5 X 10^{-5} mol), with 1.5-fold excess of (R)-BINAP, and 1.5-fold excess of $P(NC_4H_4)_3$, Benzene-d (1 mL), $P(H_2/CO$ =1) = 10 bar, 80 ^oC and t= 40 min.

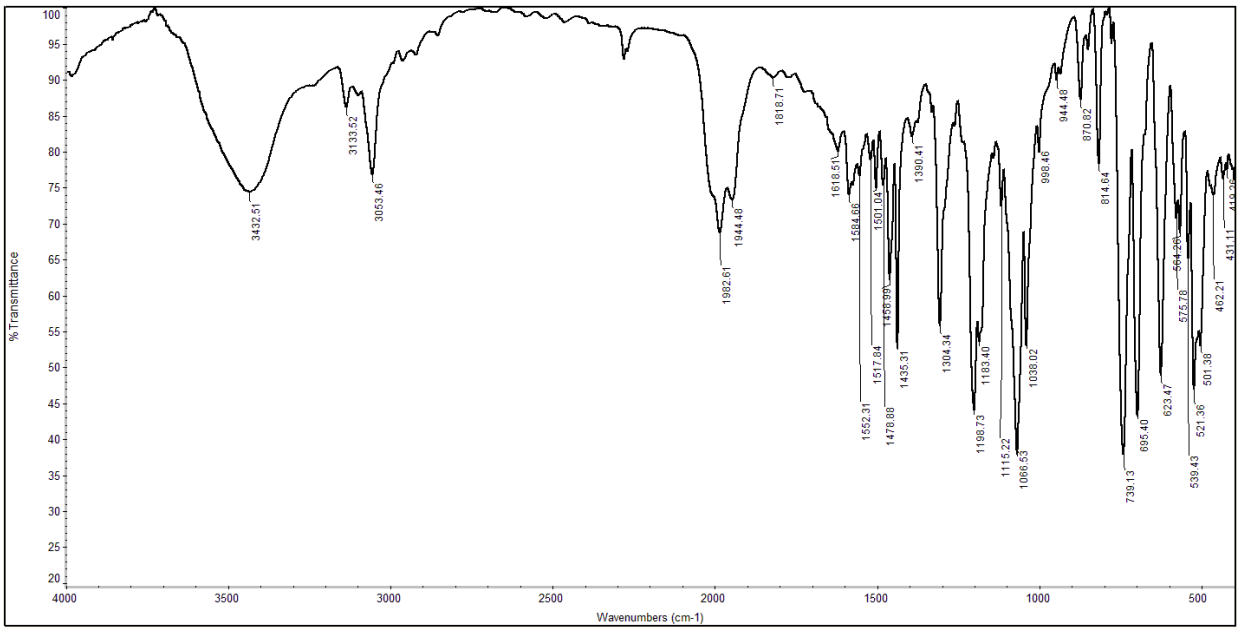

Fig. S11. IR-spectra (KBr) of post-reaction (**$Rh(acac)(CO)_2$ + (R)-BINAP + $P(NC_4H_4)_3$ + CO + H_2 + benzene-d**).

Reaction condition: $Rh(acac)(CO)_2$ (5 X 10^{-5} mol), with 1.5-fold excess of (R)-BINAP, and 1.5-fold excess of $P(NC_4H_4)_3$, Benzene-d (1 mL), $P(H_2/CO$ =1) = 10 bar, 80 ^oC and t= 40 min.

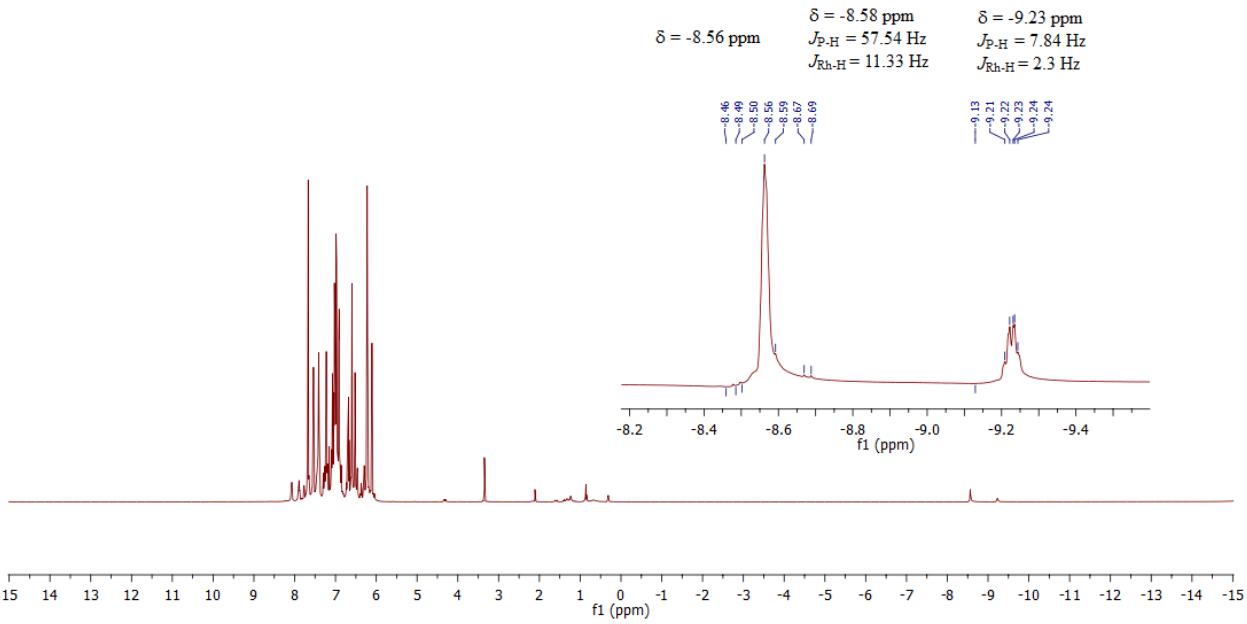

Fig. S12. ^{1}H NMR (C_6D_6) spectra of post-reaction (HRh**(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R)-BINAP + CO + H$_2$ + benzene-d**).

Reaction condition: $HRh(CO)\{P(NC_4H_4)_3\}_3$ (5 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Benzene-d (1 mL), $P(H_2/CO = 1)$ = 10 bar, 80 ^{o}C and t= 40 min.

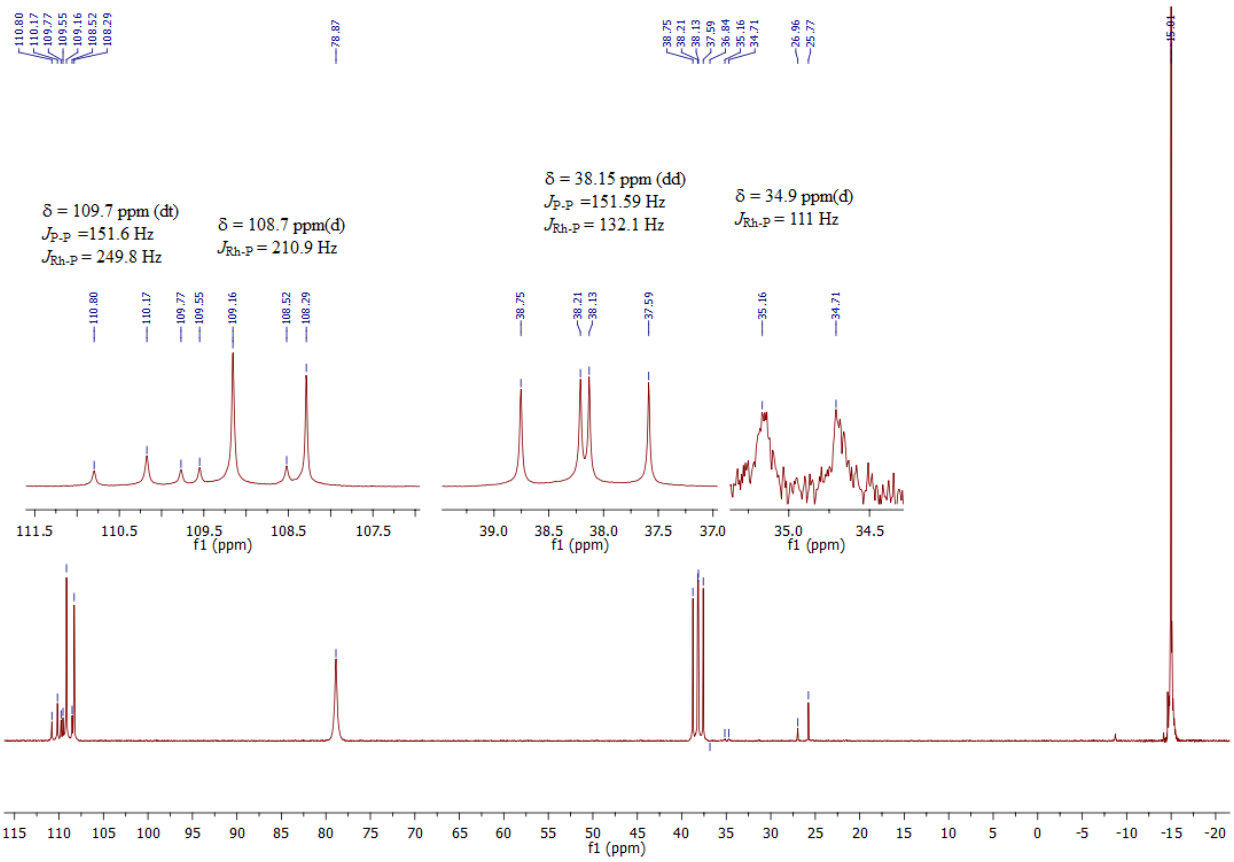

Fig. S13. ^{31}P NMR (C_6D_6) spectra of post-reaction (HRh**(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R)-BINAP + CO + H$_2$ + benzene-d**).

Reaction condition: HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ (5 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Benzene-d (1 mL), P(H$_2$/CO =1) = 10 bar, 80 ^{o}C and t= 40 min.

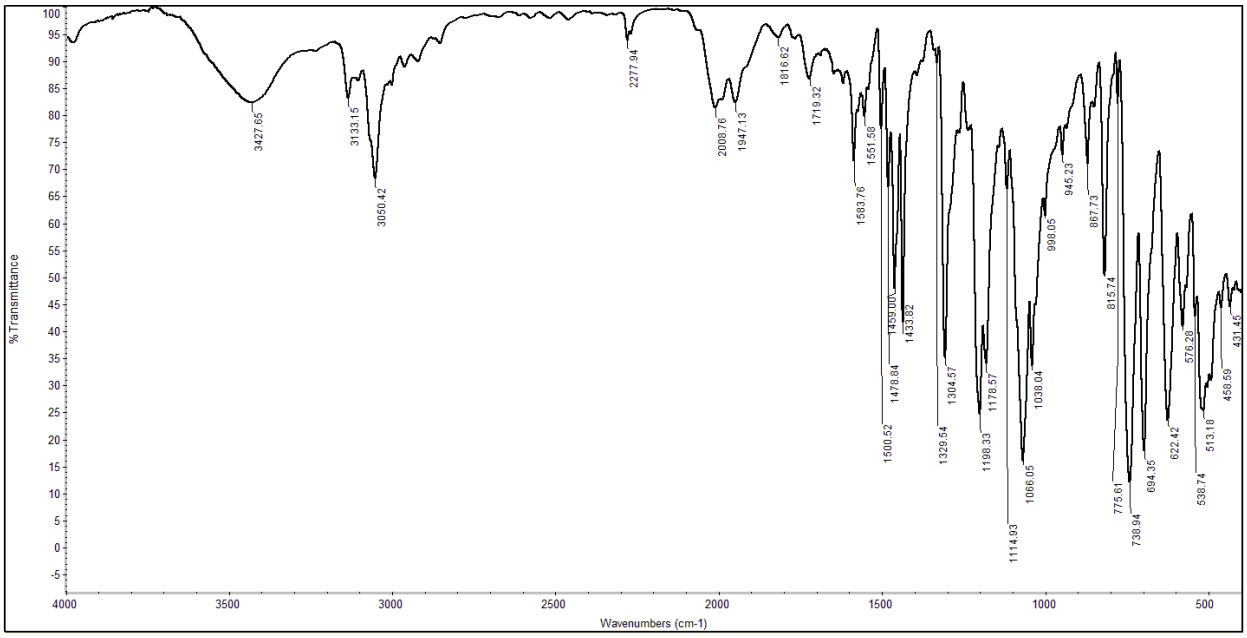

Fig. S14. IR-spectra (KBr) of post-reaction (HRh**(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R)-BINAP + CO + H$_2$ + benzene-d**).

Reaction condition: HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ (5 X 10^{-5} mol), with 3-fold excess of (R)-BINAP, Benzene-d (1 mL), P(H$_2$/CO =1) = 10 bar, 80 ^{o}C and t= 40 min.

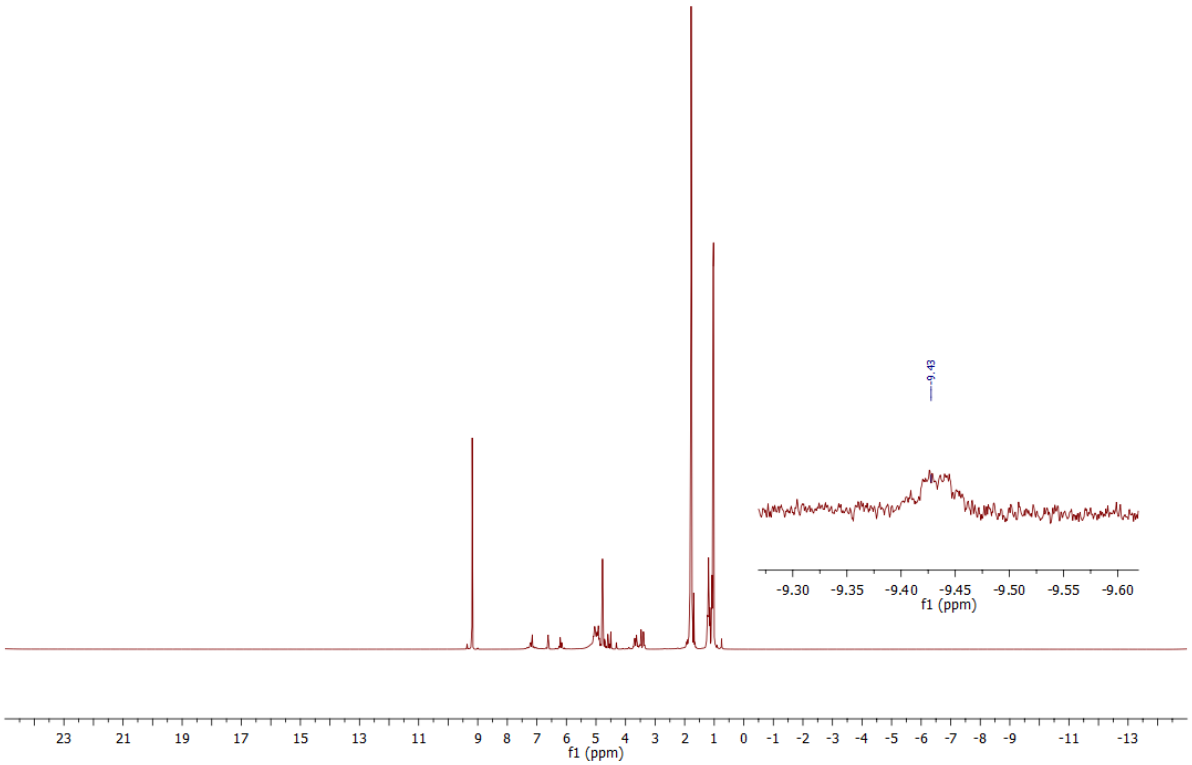

Fig. S15 ^{1}H NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).

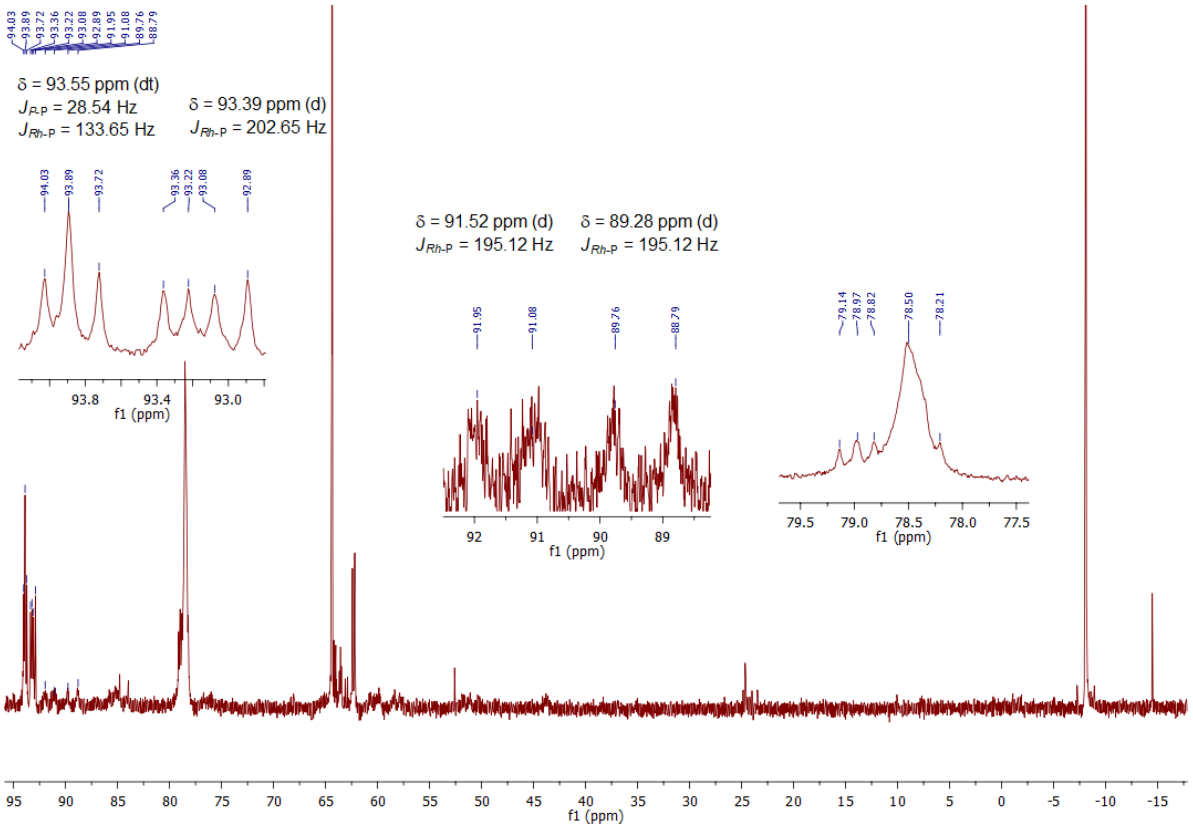

Fig. S16 ^{31}P NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).

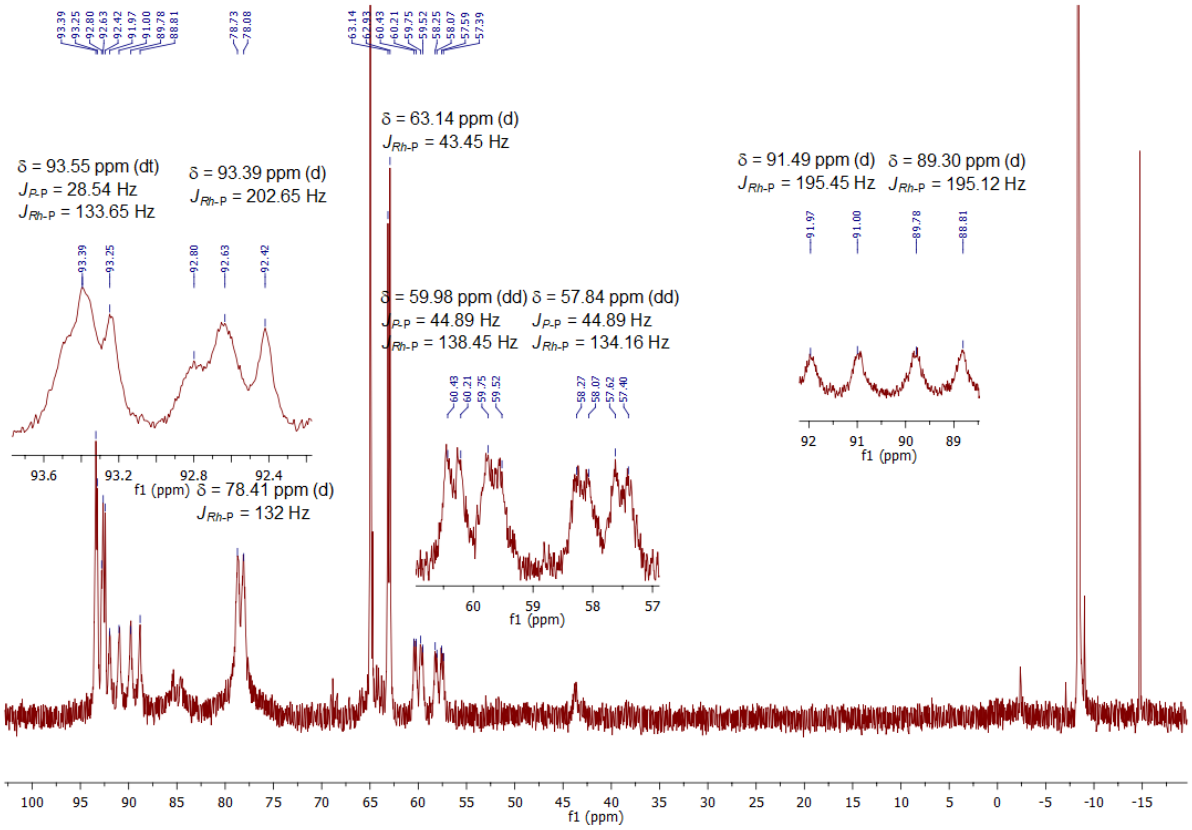

Fig. S17 ^{31}P NMR (C_6D_6) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + Vinyl acetate**).

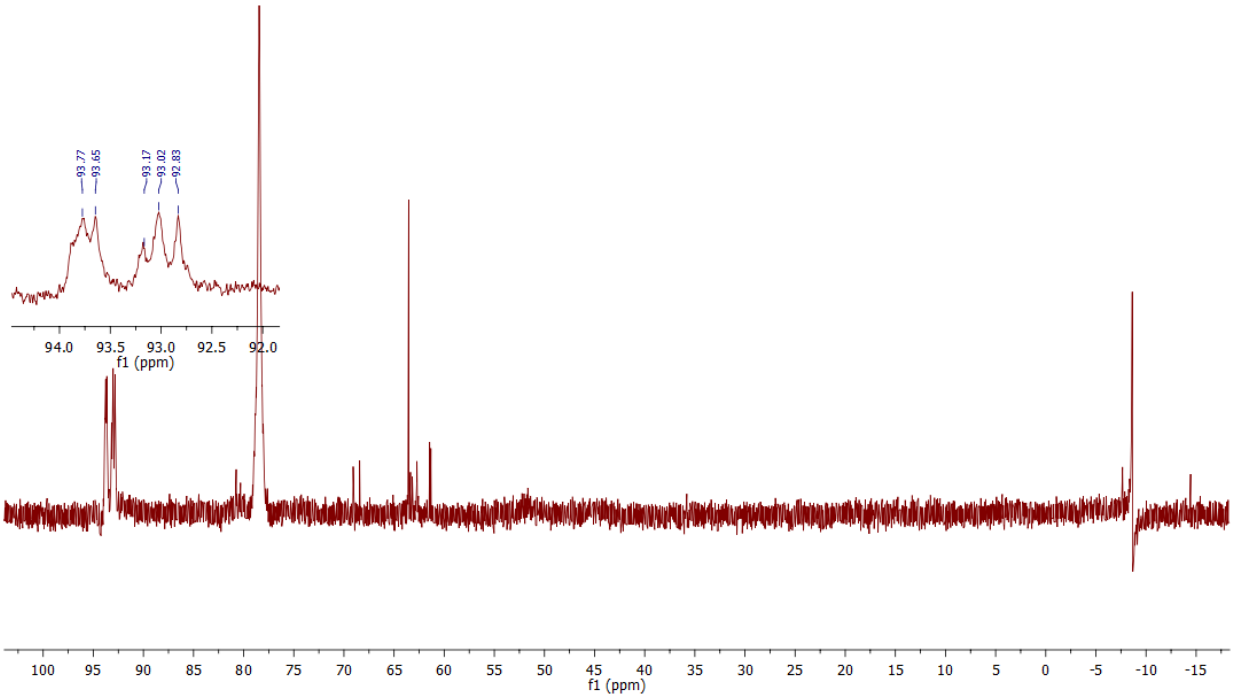

Fig. S18 ^{31}P NMR (toluene-d8) (26 ^{o}C) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).

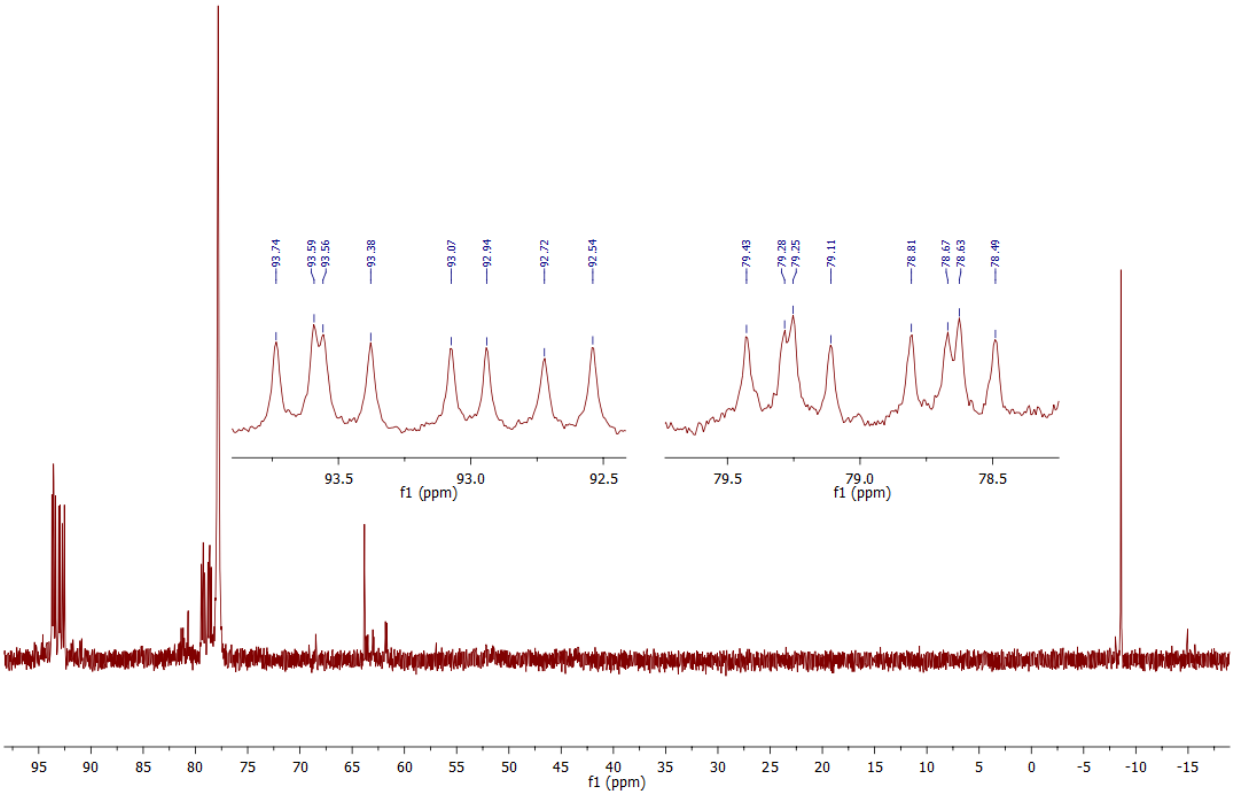

Fig. S19 ^{31}P NMR (toluene-d8) (0 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + Vinyl acetate**).

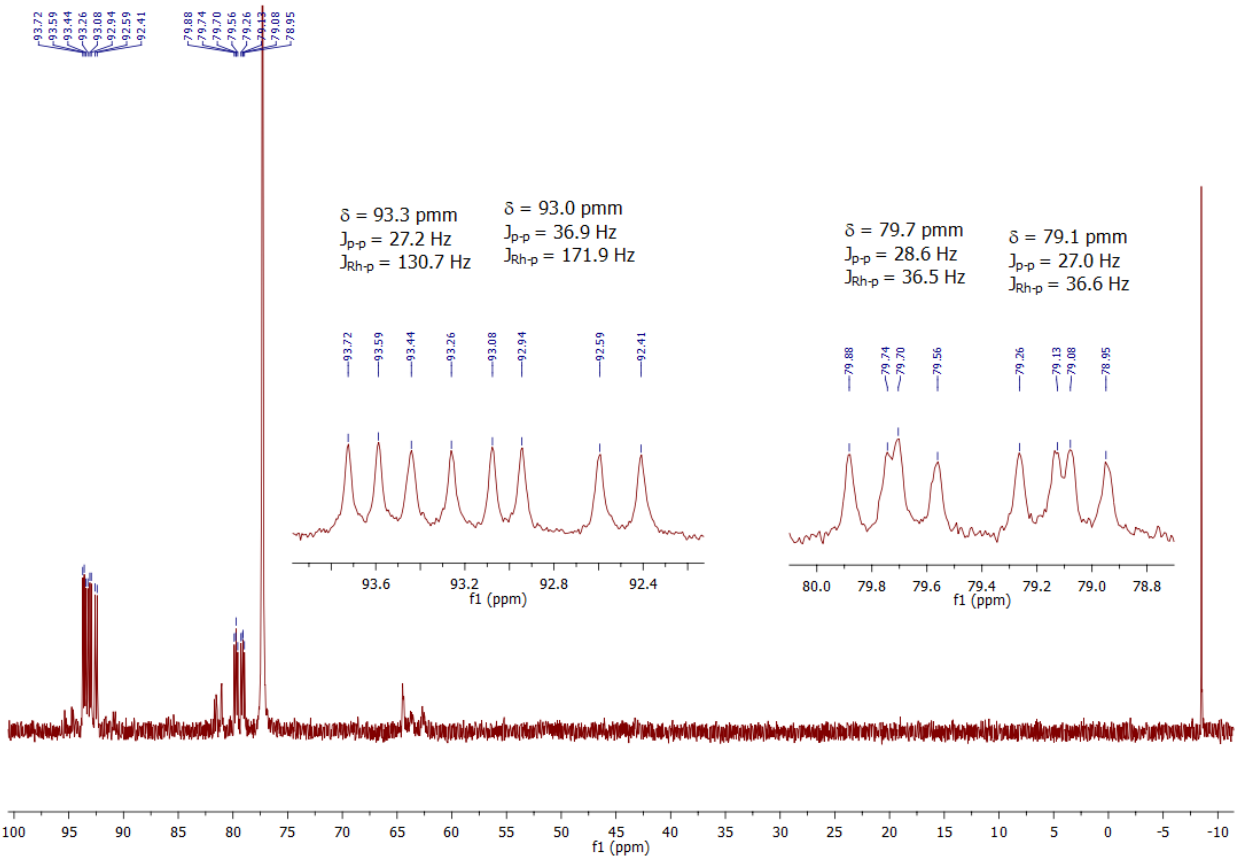

Fig. S20 ^{31}P NMR (toluene-d8) (-20 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + Vinyl acetate**).

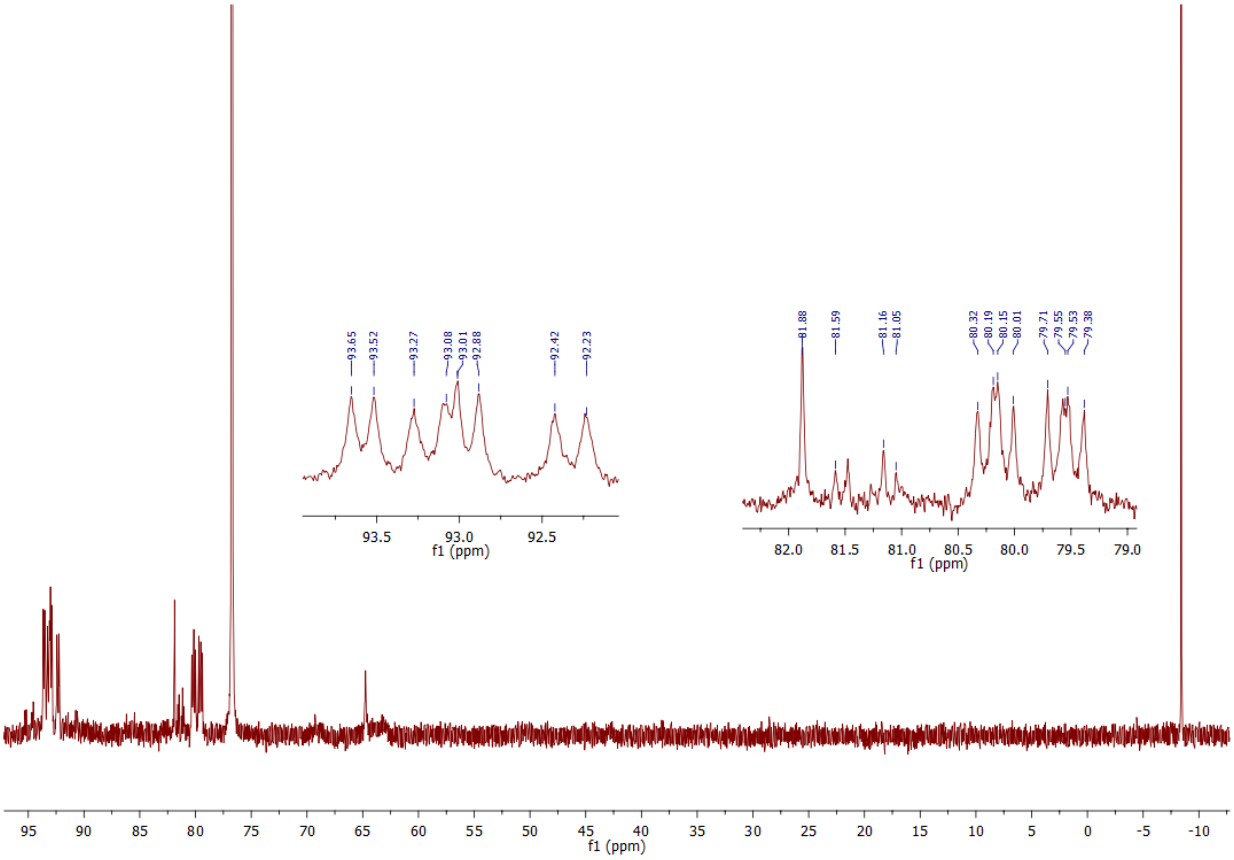

Fig. S21 ^{31}P NMR (toluene-d8) (-40 ^{o}C) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + Vinyl acetate**).

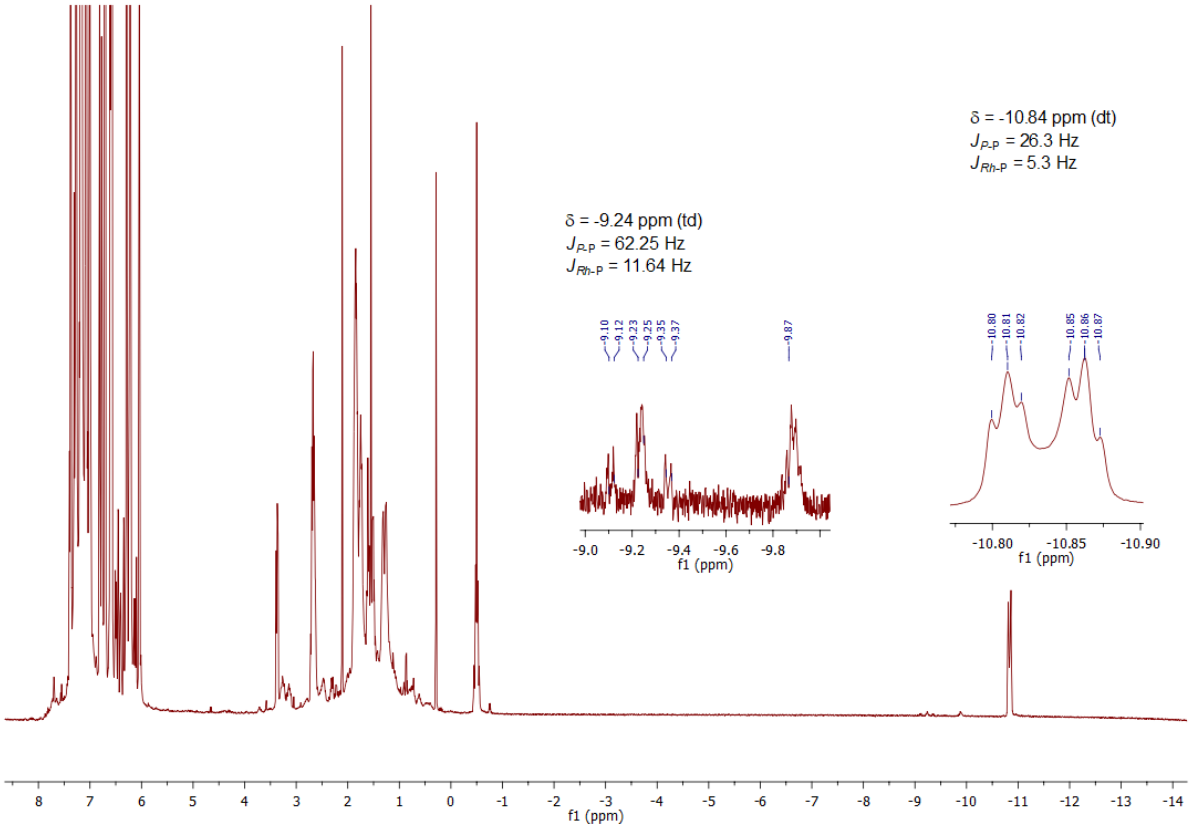

Fig. S22 ^{1}H NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE + CO + H_2 + benzene-d)**

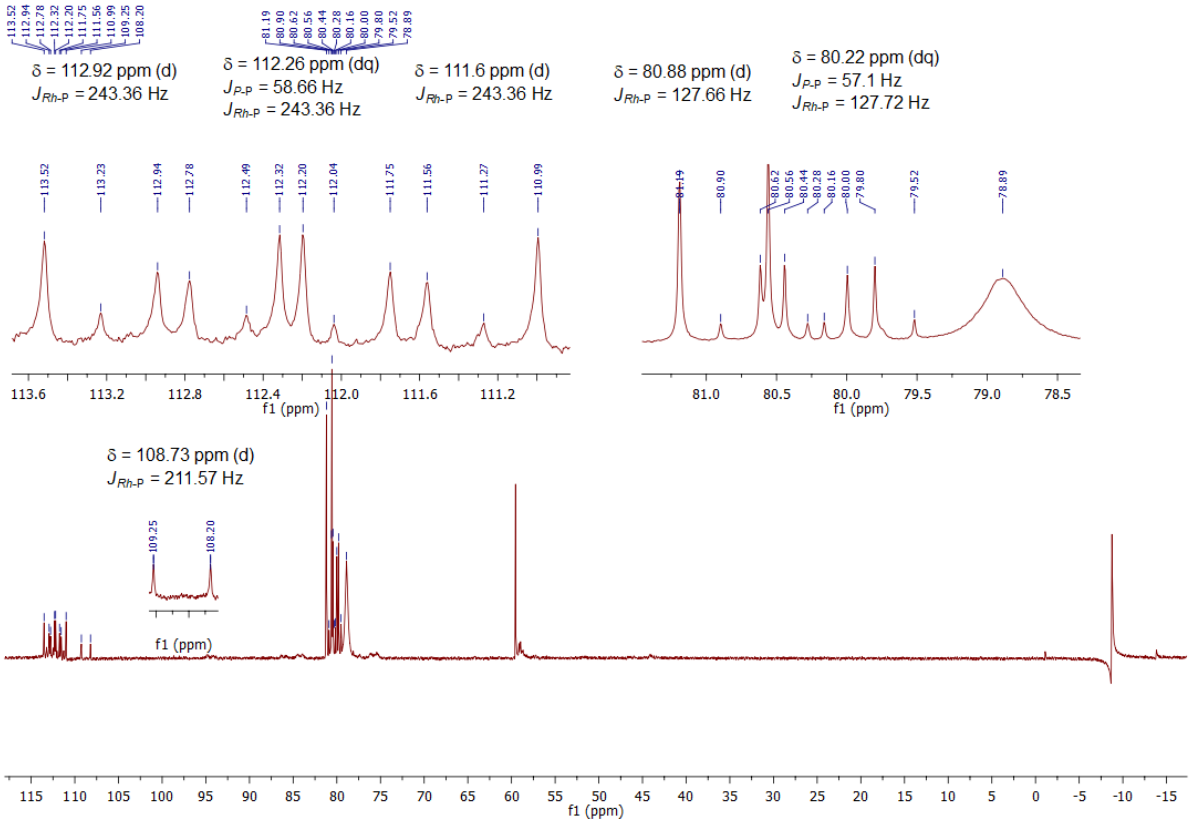

Fig. S23 ^{31}P NMR (C_6D_6) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + benzene-d).**

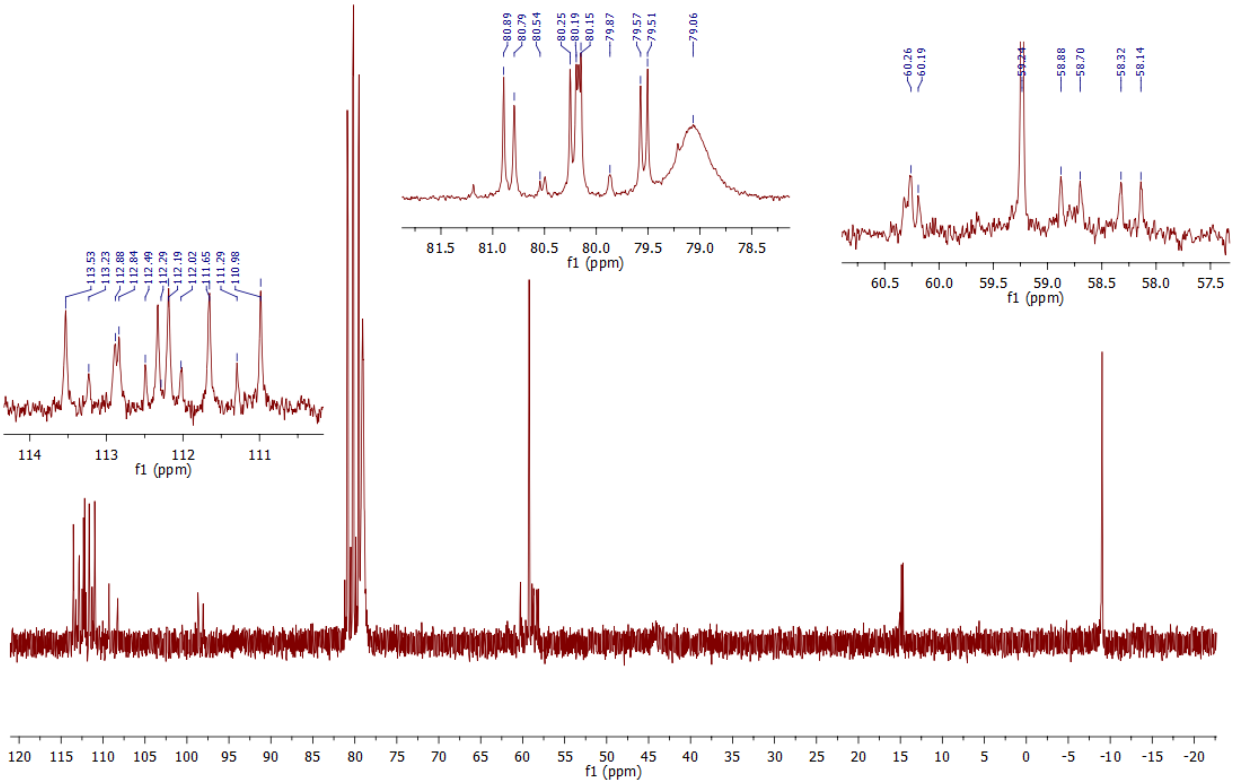

Fig. S24 ^{31}P NMR (toluene-d8) (26 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + benzene-d).**

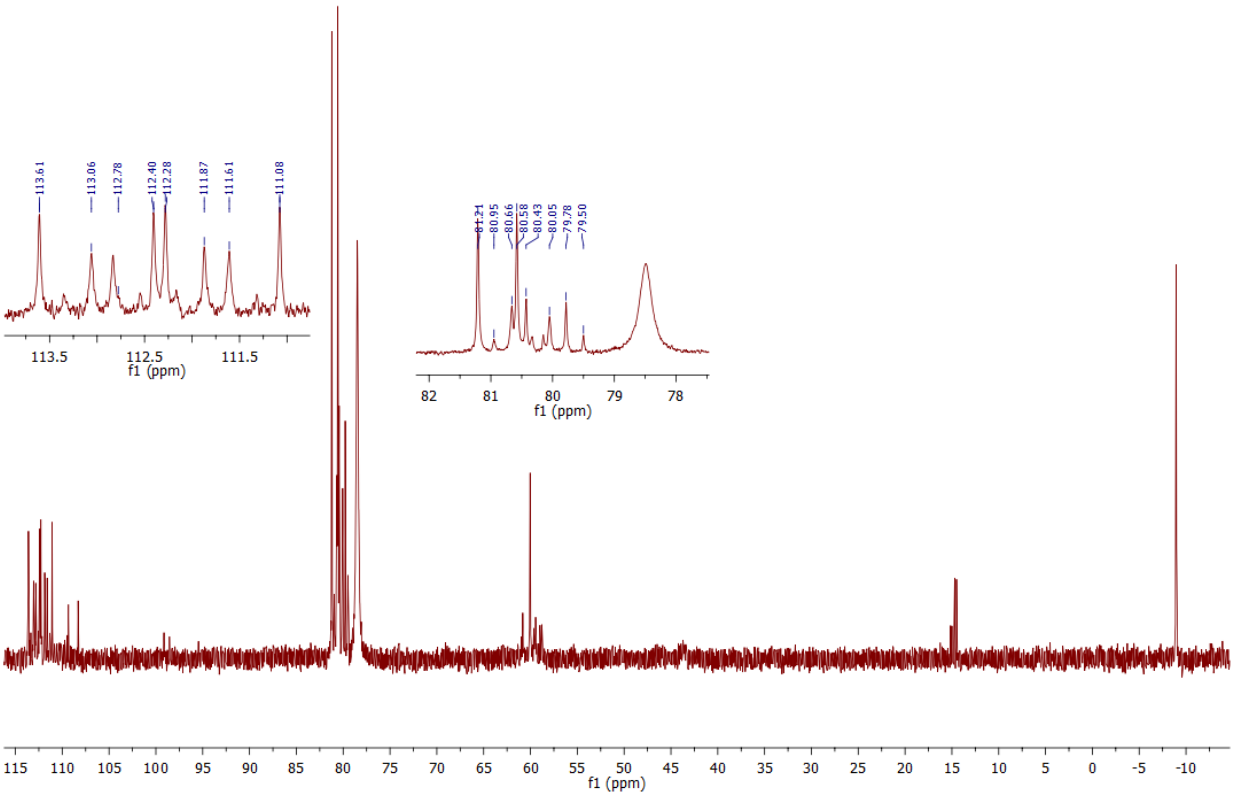

Fig. S25 ^{31}P NMR (toluene-d8) (0 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + benzene-d).**

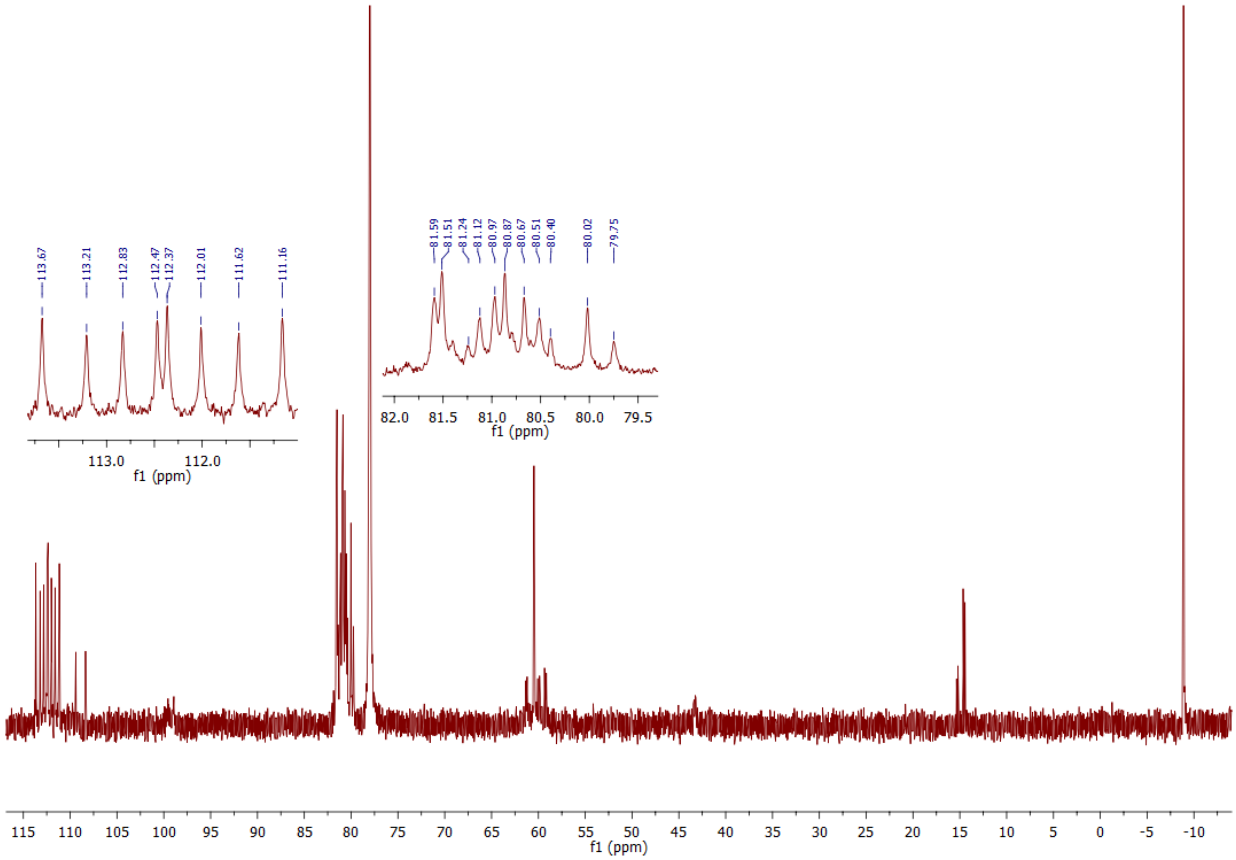

Fig. S26 ^{31}P NMR (toluene-d8) (-20 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + benzene-d).**

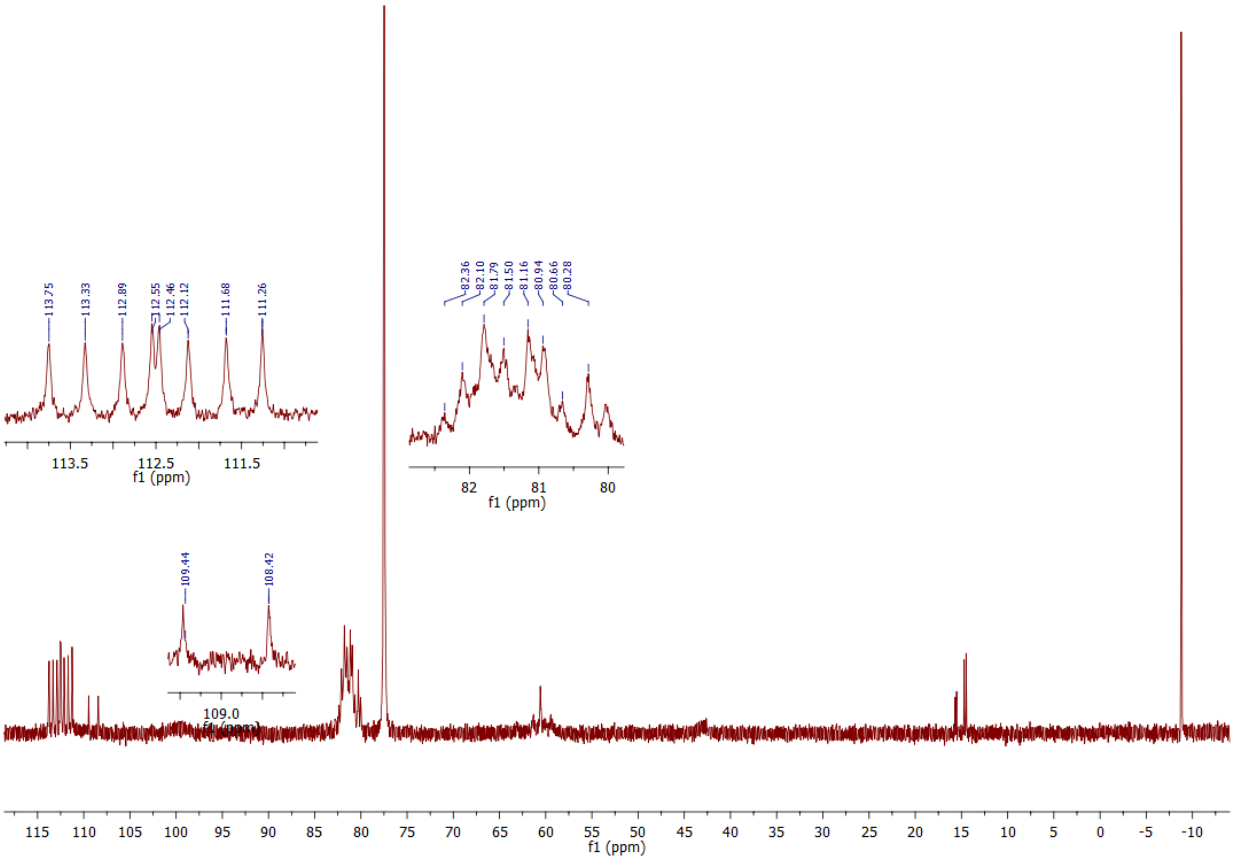

Fig. S27 ^{31}P NMR (toluene-d8) (-40 ^{o}C) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE + CO + H$_2$ + benzene-d).**

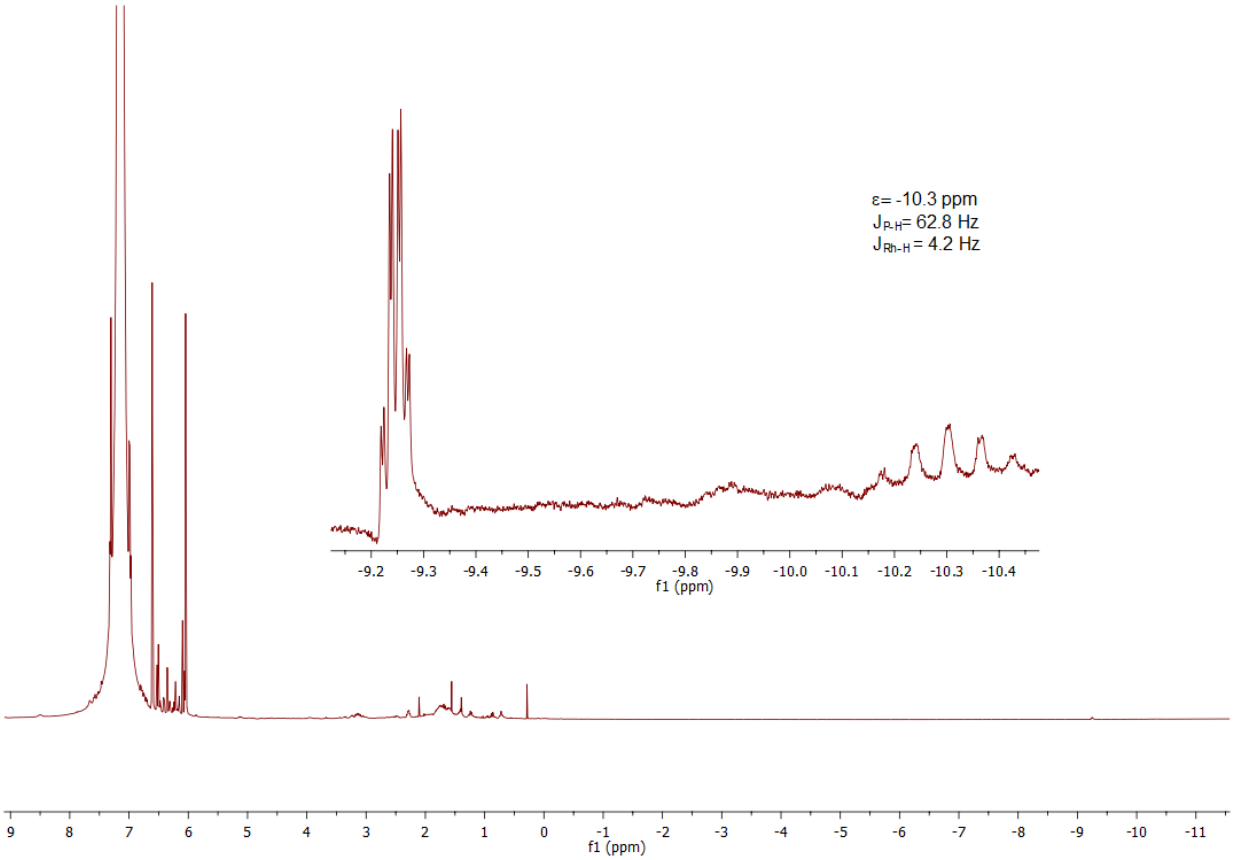

Fig. S28. ^{1}H NMR (C_6D_6) spectra of post-reaction (**HRh(CO){P(NC$_4$H$_4$)$_3$}$_3$ + (R,R)Ph-PBE +Benzene-d. 25 ºC for 40 min**).

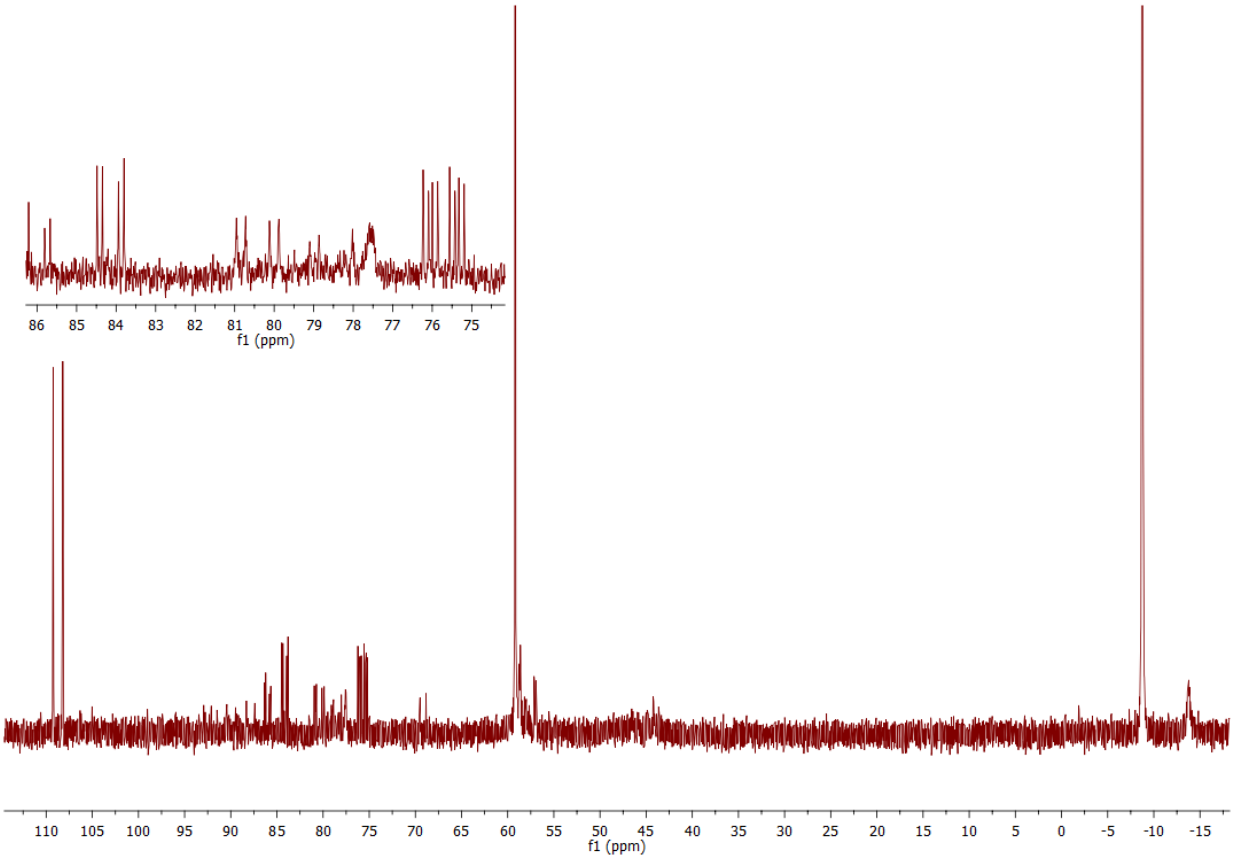

Fig. S29. ^{31}P NMR (C_6D_6) spectra of post-reaction (**$HRh(CO)\{P(NC_4H_4)_3\}_3$ + (R,R)Ph-PBE +Benzene-d. 25 ºC for 40 min**).

Table S1. The effect of the [L]/[Rh] ratio on the hydroformylation of allyl acetate using catalyst **I** with the $P(NC_4H_4)_3$ ligand under solventless conditions[a]

Entry	[L]/[Rh]	t, min.	Conv. %	**1%**	**2%**	**3%**	**1/2** ratio	TOF[b], mol mol^{-1} h^{-1}
1	2	20	100	65.5	32.8	1.7	2	2383
2	4		100	67.2	29.3	3.5	2.3	2339.4
3	6	30	100	68.7	28.1	3.2	2.5	1548.8
4	8		100	68.5	27	4.5	2.5	1528
5	10		100	67.9	26.3	5.8	2.6	1507.2

[a] Reaction condition: allyl acetate (1 mL), [substrate]/[Rh]=800, P = 20 bar (H_2/CO =1), T= 80 ^oC, L= $P(NC_4H_4)_3$, [b] TOF= (mole of products **(1+2)**)/(mole of catalyst x reaction time).

Table S2. The effect of temperature on Hydroformylation of vinyl acetate using catalyst **I** under solventless conditions[a]

Entry	Catalyst	T, ^oC	t.	Conv. %	**1%**	**2%**	**3%**	TOF[c], mol mol^{-1} h^{-1}
3	I	60	40 min	100	84.5	1.7	2.7	1024
4		50		100	89	1.5	1.5	1079
5		30	4 h	100	89.5	1	1	179

[a] Reaction condition: vinyl acetate (1 ml), [substrate]/[Rh]=800, P = 20 bar (H_2/CO =1). and [c] TOF= (mole of product **1**)/(mole of catalyst x reaction time).

Products of allyl acetate hydroformylation:

4-acetoxybutanal (1): MS: 130 (M+); 102(1), 87(29.8), 86(3.2), 70(12.8), 69(6.4), 61(36.2), 58(2.1), 57(4.3), 43(100), 42(25.5), 39(8.5), 31(6.4), 29(14.9).

3-acetoxy-2-methyl propanal (2): MS: 130 (M+); 87(8.5), 70(2.1), 69(1), 61(50), 58(4.3), 57(2.1), 43(100), 42(37.2), 39(6.4), 31(2.1), 29(7.5).

Propyl acetate (3): MS: 130 (M+); 85(2.1), 72(4.3), 61(10.9), 58(50), 57(34.8), 43(100), 42(19.6), 41(54.3), 40(10.9), 39(47.8), 31(3.3), 29(18.5).

Products of butyl acrylate hydroformylation:

2-Methyl-3-oxopropionic acid butyl ester (1)

MS: 158 (M+); 158(4.8), 130(3.5), 102(14.3), 85(63.5), 84(25.4), 74(99.2), 57(54), 56(100), 43(11.1), 41(55.6), 31(14.3), 29(67.5).

4-Oxo-butyric acid butyl ester (2)

MS: 158 (M+); 130(1.6), 103(4), 86(6.4). 85(100), 75/9, 74(30.2), 57(26.2), 56(36.5), 41(20.6), 29(35.7).

Propanoic acid butyl ester (3)

MS: 130(M+); 101(1.8), 87(10.7), 75(50), 57(100), 56(57.1), 41(27.9), 31(3.6), 29(46.4).

Products of methyl acrylate hydroformylation:

2-Methyl-3-oxopropionic acid methyl ester (1)

MS: 116 (M+); 116(3.6), 88(75.5), 85(43.2), 59(36), 57(63), 56(71.9), 55(41.4), 45(18), 29(100).

4-Oxo-butyric acid methyl ester (2)

MS: 116 (M+); 88(77), 87(11.1), 85(69.4), 59(36.1) 57(88.9), 56(27.8), 55(33.3), 45(19.4), 29(100).

Products of 2,3-dihydrofuran hydroformylation:

2-formyltetrahydrofuran (1); ^{1}H NMR (500 Hz, $CDCl_3$): δ(CHO) 9.42 ppm (d, 1.2 Hz); ^{13}C NMR (500 Hz, $CDCl_3$): 201.8, 82.4, 68.8, 26.9, 25.2

MS (EI) (m/z (relat. int. %)): 72 (6.4), 71(100), 69 (2.6), 55 (1.7), 53 (1.7), 44(6), 43 (93.6), 42 (16), 41(72.3), 39 (23.4), 31 (2.6), 29 (33), 27 (40.4).

3-formyltetrahydrofuran (2); ^{1}H NMR (500 Hz, $CDCl_3$): δ(CHO) 9.19 ppm (d, 1.5 Hz); ^{13}C NMR (500 Hz, $CDCl_3$): 200, 67.4, 66.9, 51, 26.1

MS (EI) (m/z (relat. int. %)):100 (4.3), 99 (10.6), 82 (13.2), 72 (38.3), 71 (35.1), 70 (25.5), 69 (46.8), 57 (45.7), 55 (8.5), 54 (12.8), 53 (6.4), 44 (23), 43 (27.7), 42 (78.7), 41 (100), 39 (46.8), 31 (19.2), 29 (44.7), 27 (31.5).