sElectronic Supplementary Information (ESI):

Synthesis of a Sterically Bulky Diphosphine Synthon and Ru(II) Complexes of a Cooperative Tridentate Enamide-Diphosphine Ligand Platform

Vincent T. Annibale, Thomas G. Ostapowicz, Stefan Westhues, Truman C. Wambach, Michael D. Fryzuk*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada, V6T 1Z1
Email: fryzuk@chem.ubc.ca

Contents:

NMR Spectra:

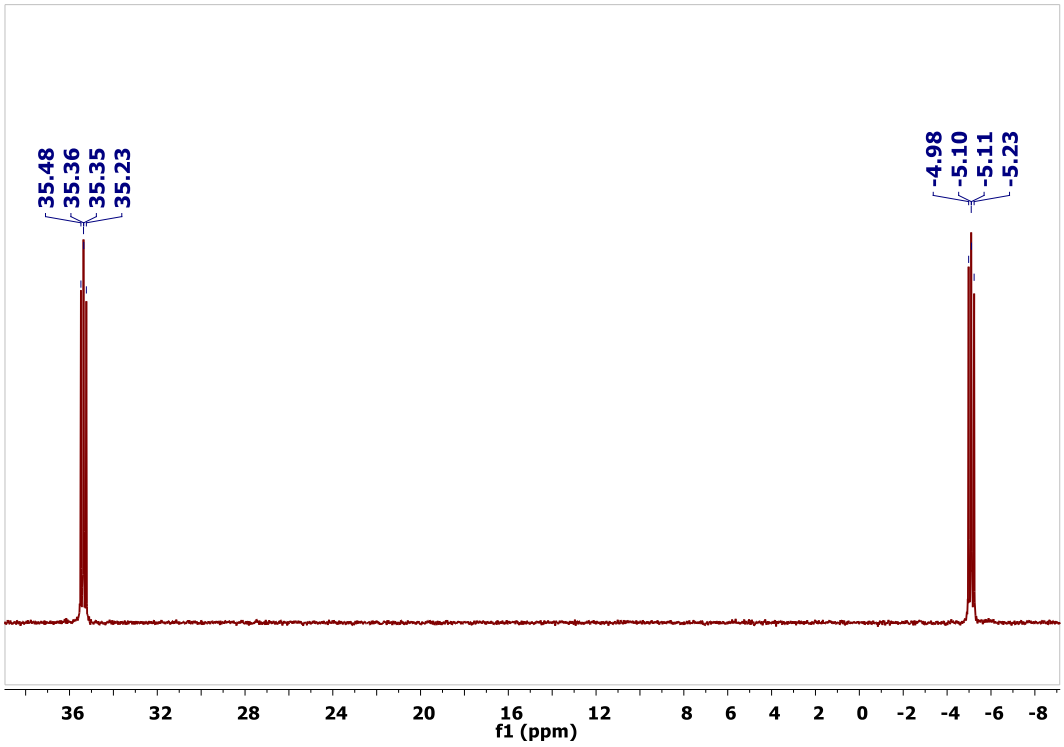


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (121.49 MHz, 25 °C) for compound **2** in C_6D_6.

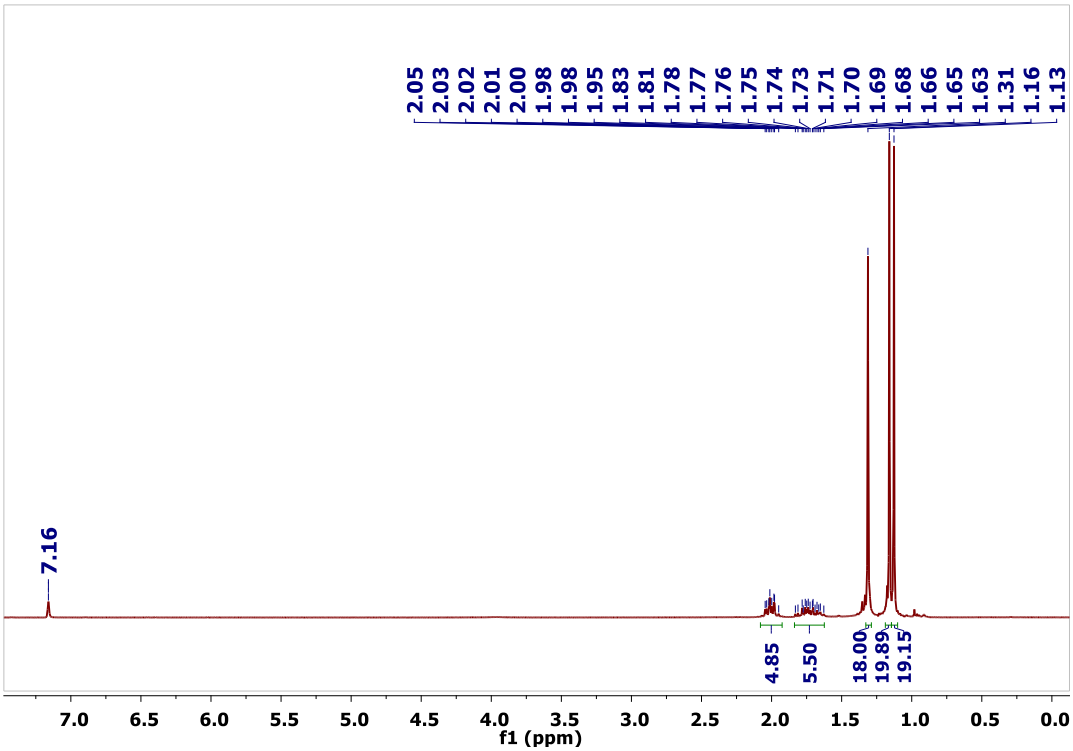


Figure S2. $^{1}H\{^{31}P\}$ NMR spectrum (300 MHz, 25 °C) for compound **2** in C_6D_6.

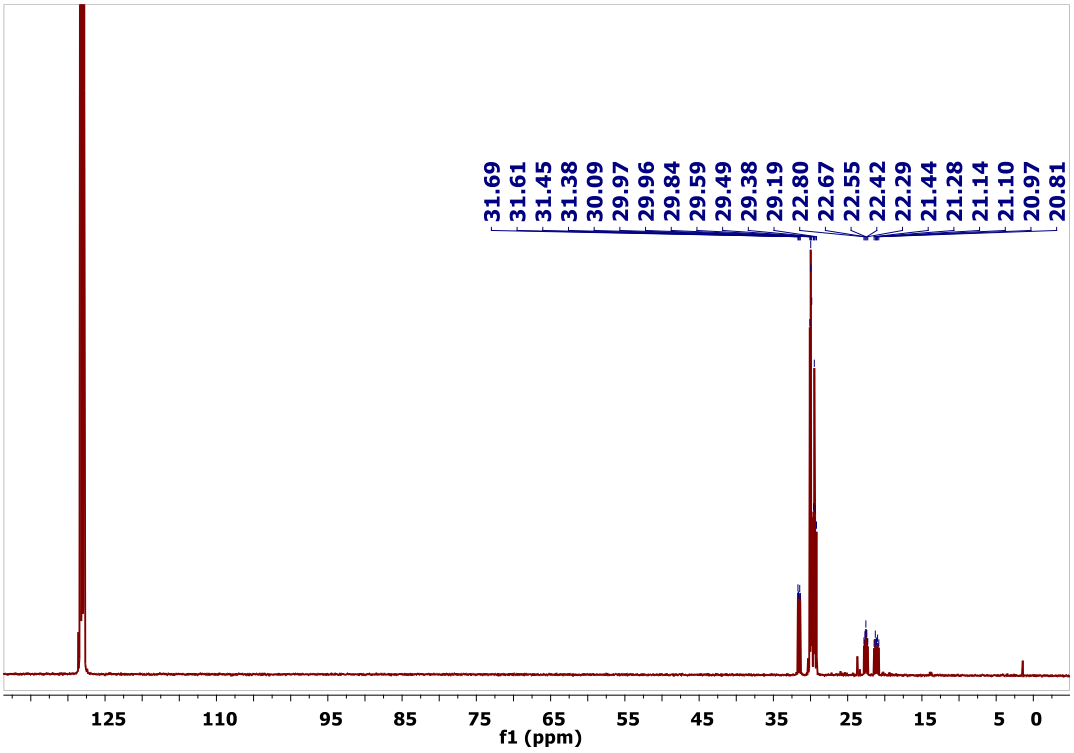


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100.63 MHz, 25 °C) for compound **2** in C_6D_6.

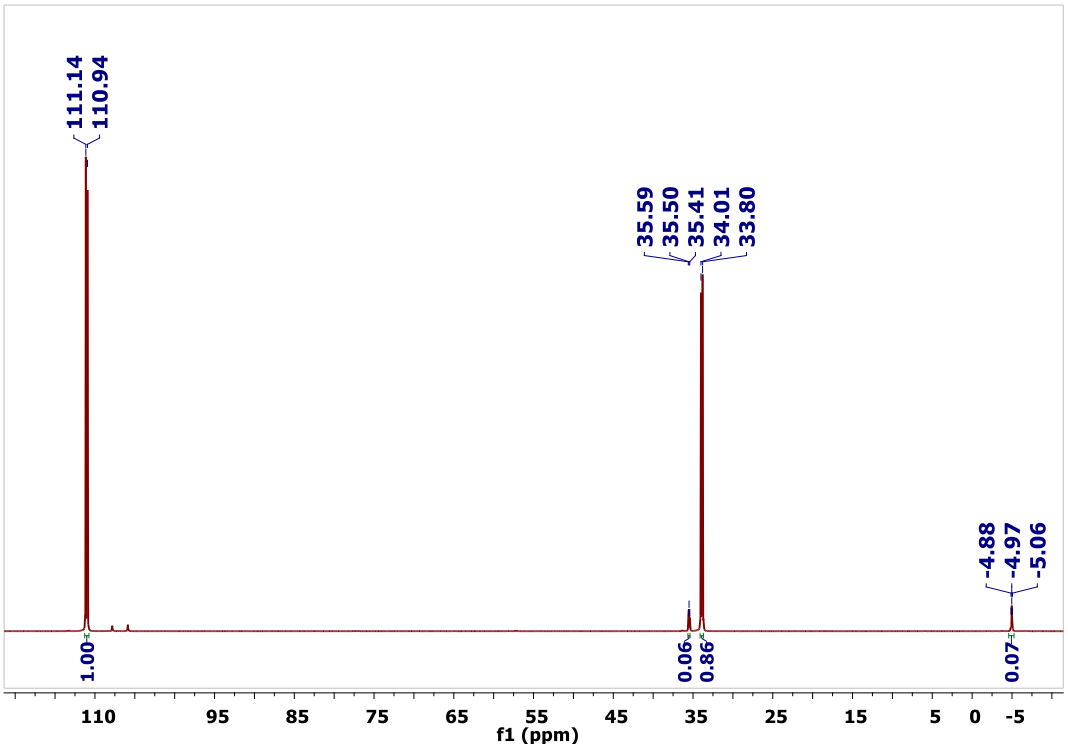


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C) for compound **1** in C_6D_6, note the two virtual triplets at 35.50 and -4.97 ppm belong to the impurity compound **2**.

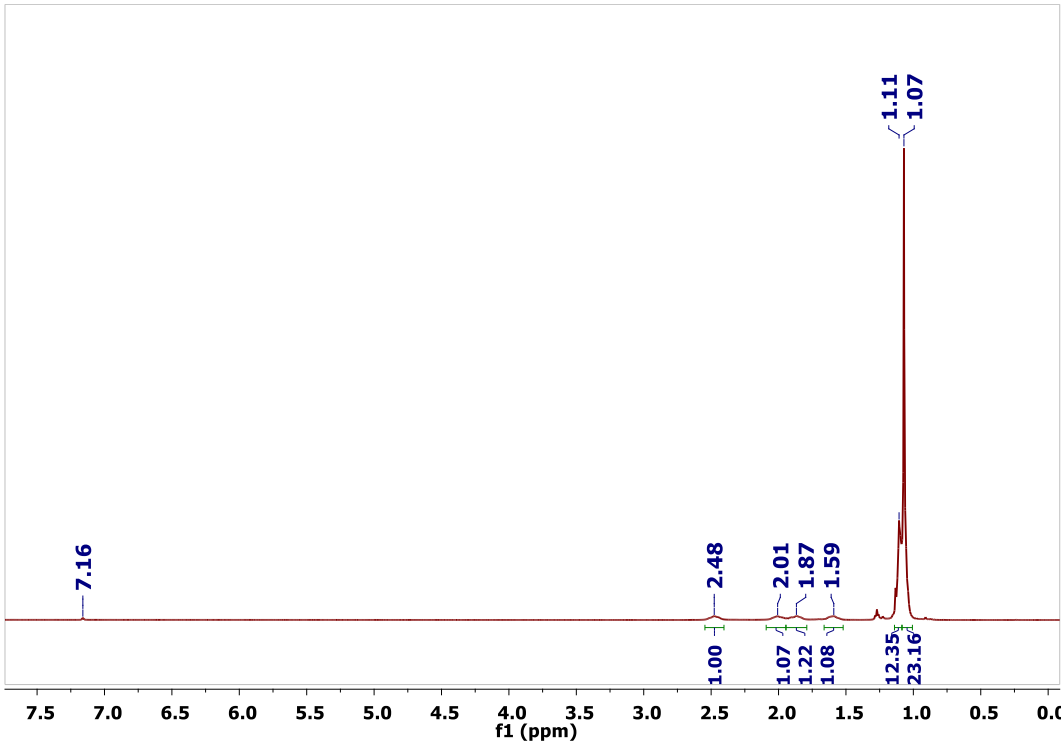


Figure S5. $^{1}H\{^{31}P\}$ NMR spectrum (400 MHz, 25 °C) for compound **1** in C_6D_6.

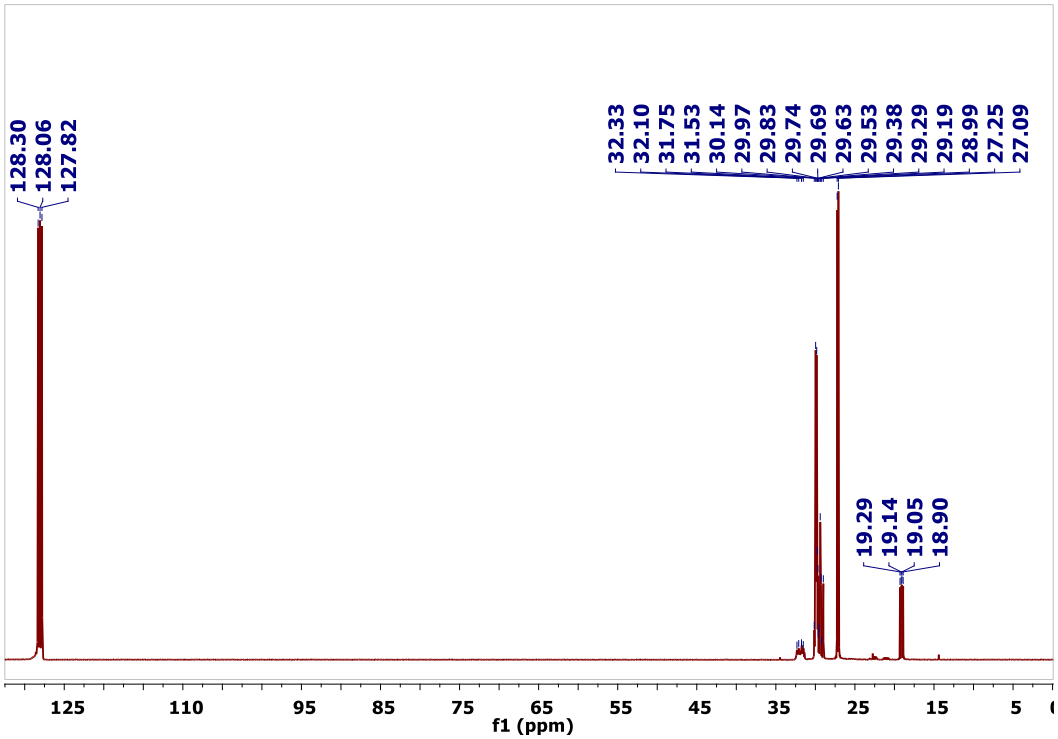


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 25 °C) for compound **1** in C_6D_6.

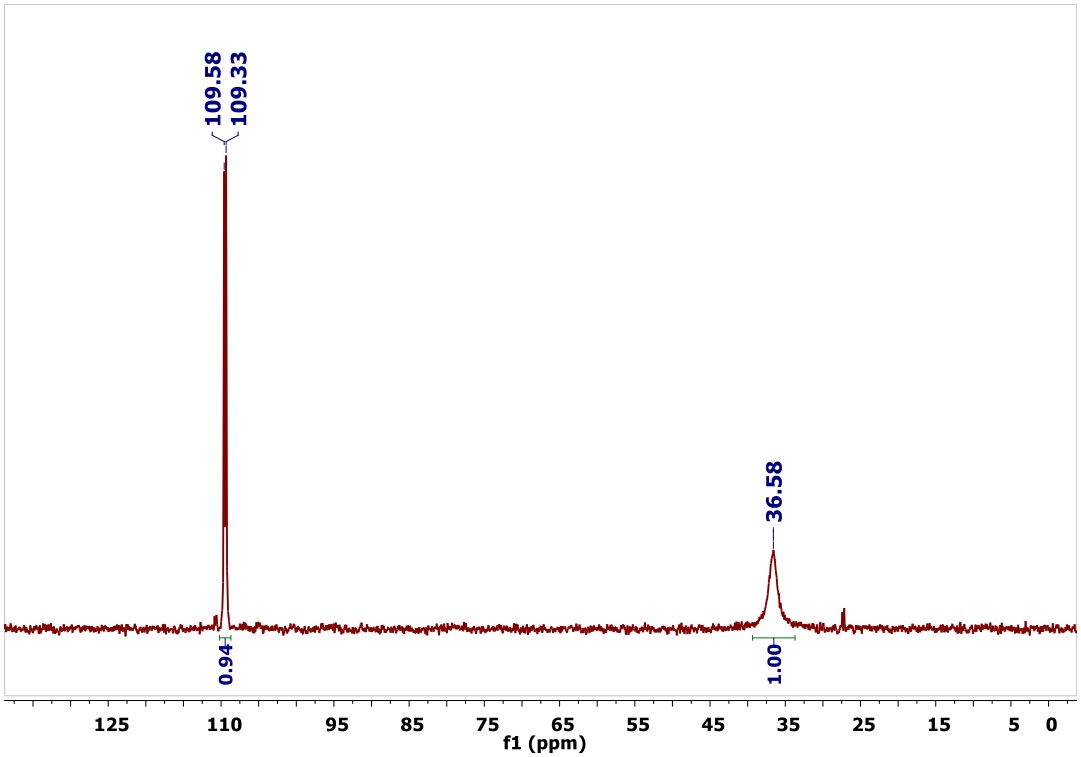


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (121.49 MHz, 25 °C) for by-product [I*t*Bu$_2$P(C$_2$H$_4$)P*t*BuI]I in C_6D_6.

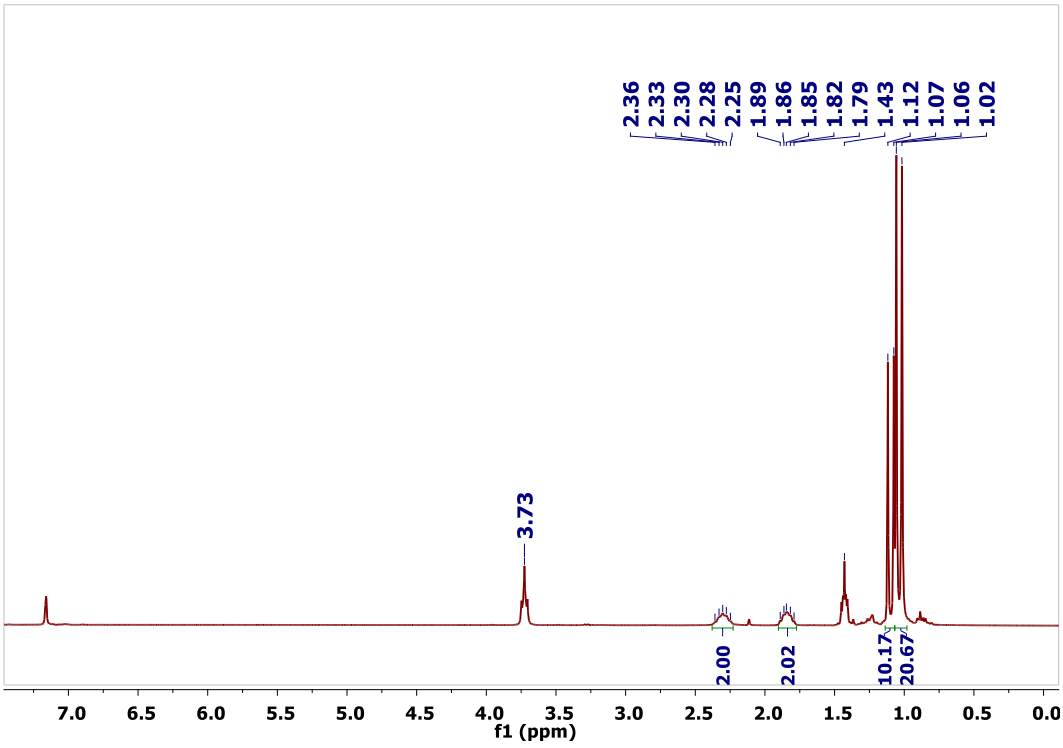


Figure S8. ^{1}H NMR spectrum (300 MHz, 25 °C) for by-product [I*t*Bu$_2$P(C$_2$H$_4$)P*t*BuI]I in C_6D_6, peaks at 3.73 and 1.43 are residual THF.

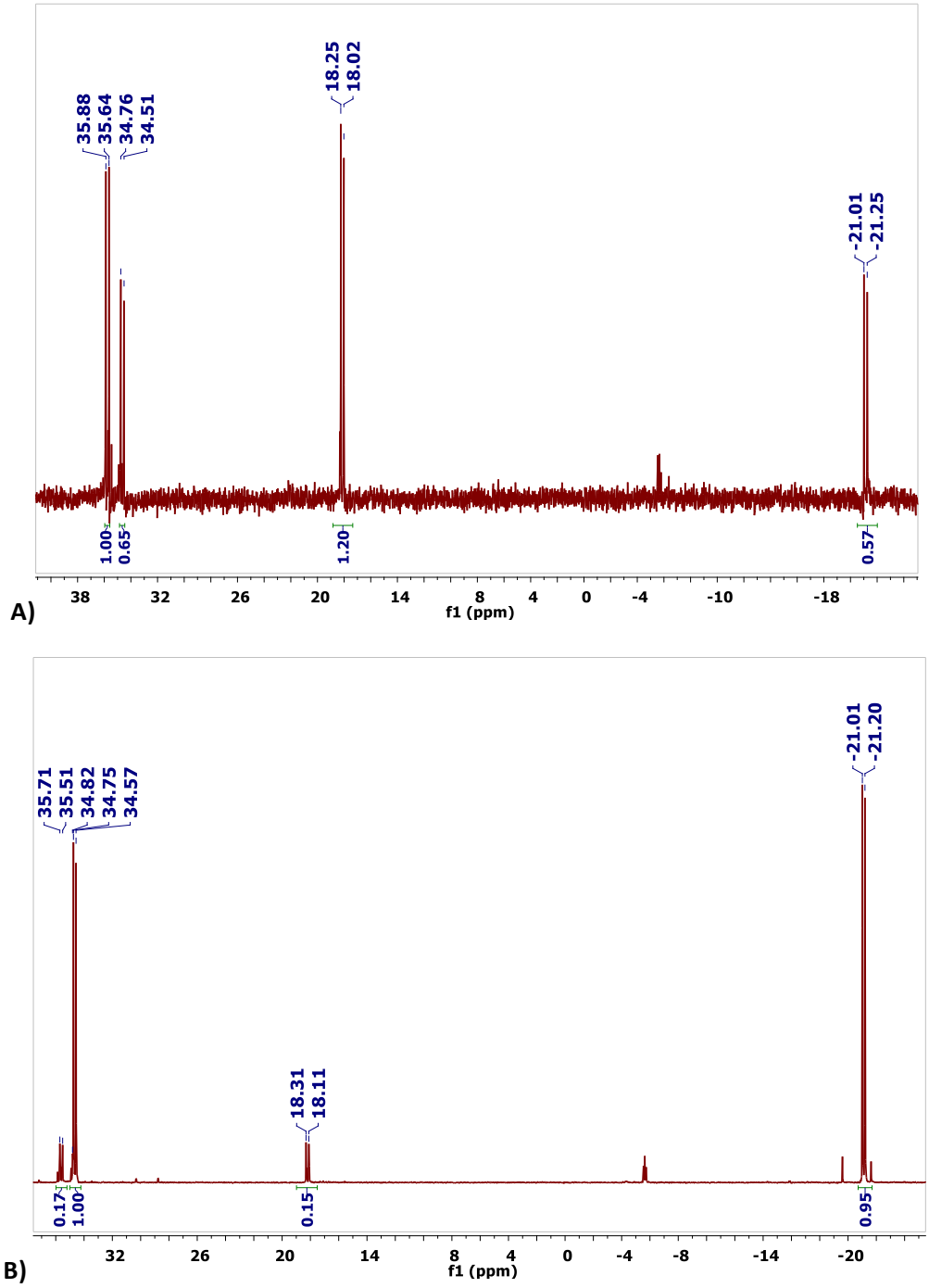


Figure S9. $^{31}P\{^{1}H\}$ NMR spectra from two separate syntheses where in A) the ratio of the two tautomers **3a**:**3b** is ~1:2, and in B) the ratio of **3a**:**3b** is ~7:1.The enamine **3a** gives rise to two doublets at 34.6 (P*t*Bu$_2$) and -21.1 ppm (enamine-P*t*Bu), whereas the minor imine tautomer **3b** shows two doublets at 35.6 (P*t*Bu$_2$) and 18.2 ppm (P*t*Bu), respectively.

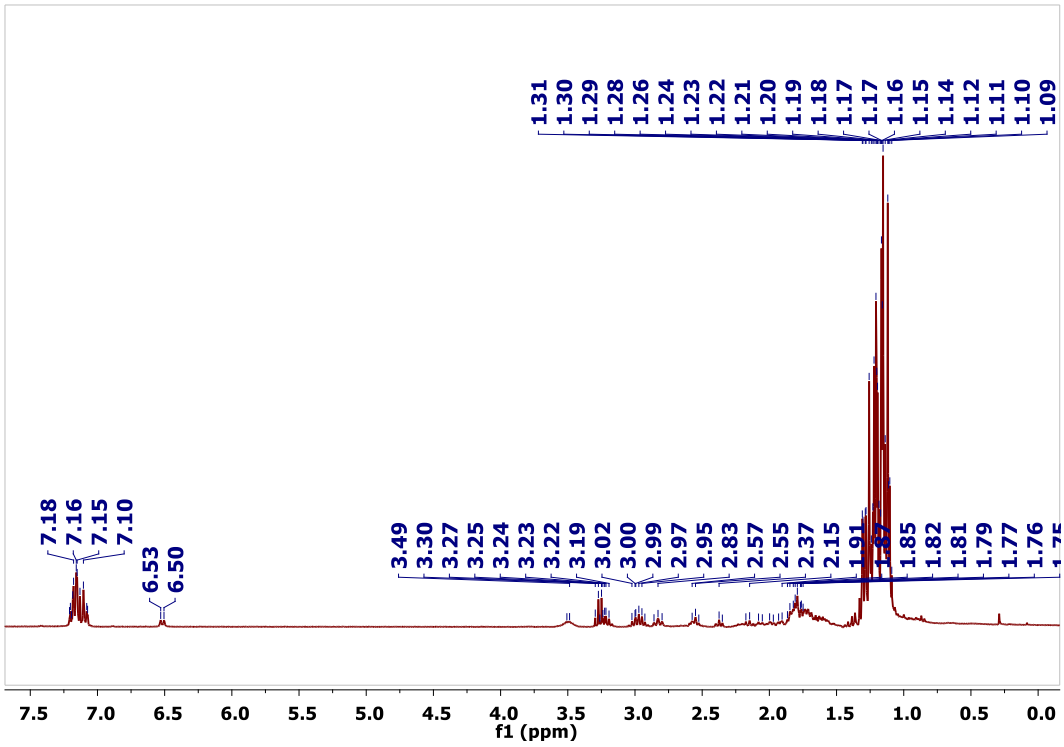


Figure S10. ^{1}H NMR spectrum (300 MHz, 25 °C) for a mixture of tautomers **3a**/**3b** in C_6D_6.

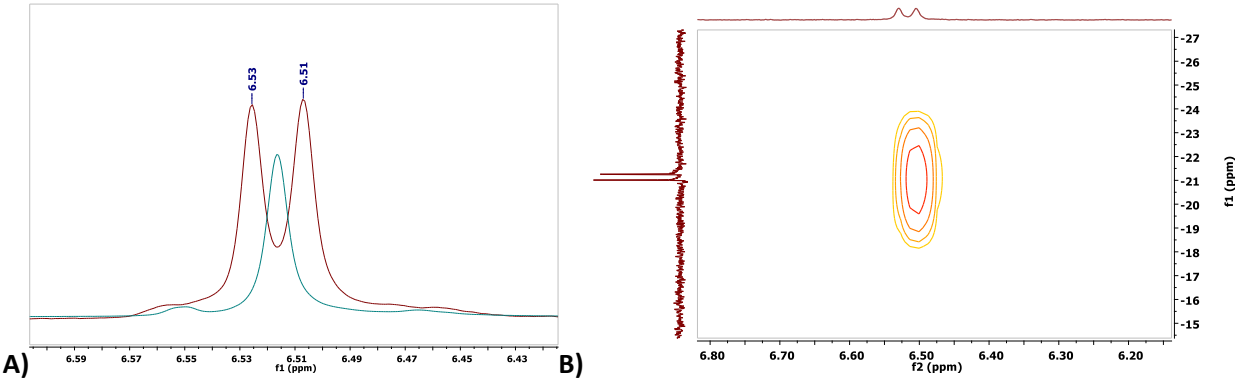


Figure S11. A) A comparison between portions of the ^{1}H (red) and ^{1}H{^{31}P} (teal) NMR spectra highlighting that the enamine N-H resonance couples to phosphorus, and B) a portion of the ^{1}H,31P-HMBC 2DNMR spectrum indicating a strong correlation between the N-H at 6.52 ppm in ^{1}H trace, and the enamine-P*t*Bu at -21.1 ppm in ^{31}P trace.

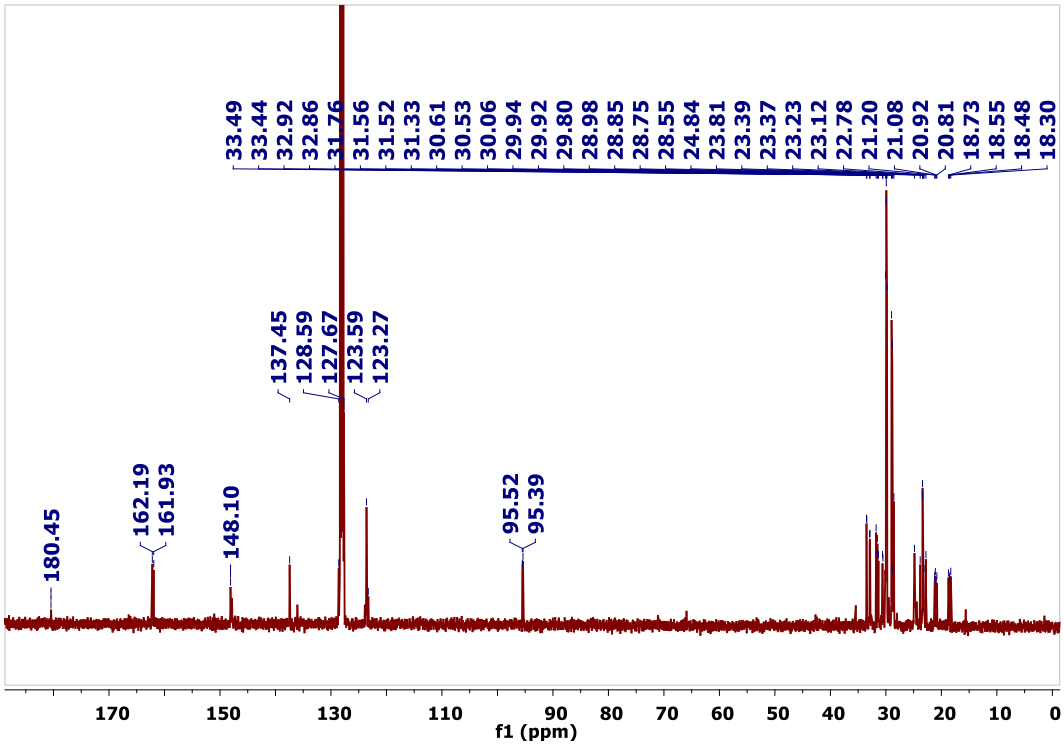


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 25 °C) for a mixture of **3a**:**3b** (where ratio is ~7:1) in C_6D_6.

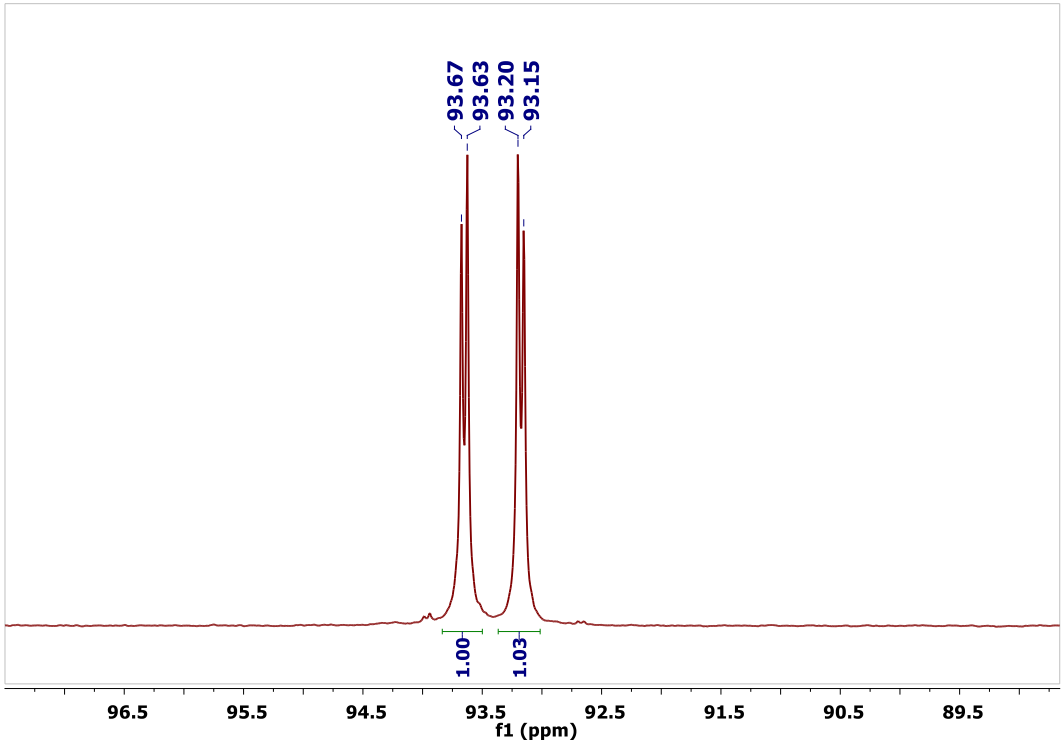


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C) for compound **4** in THF-d_8.

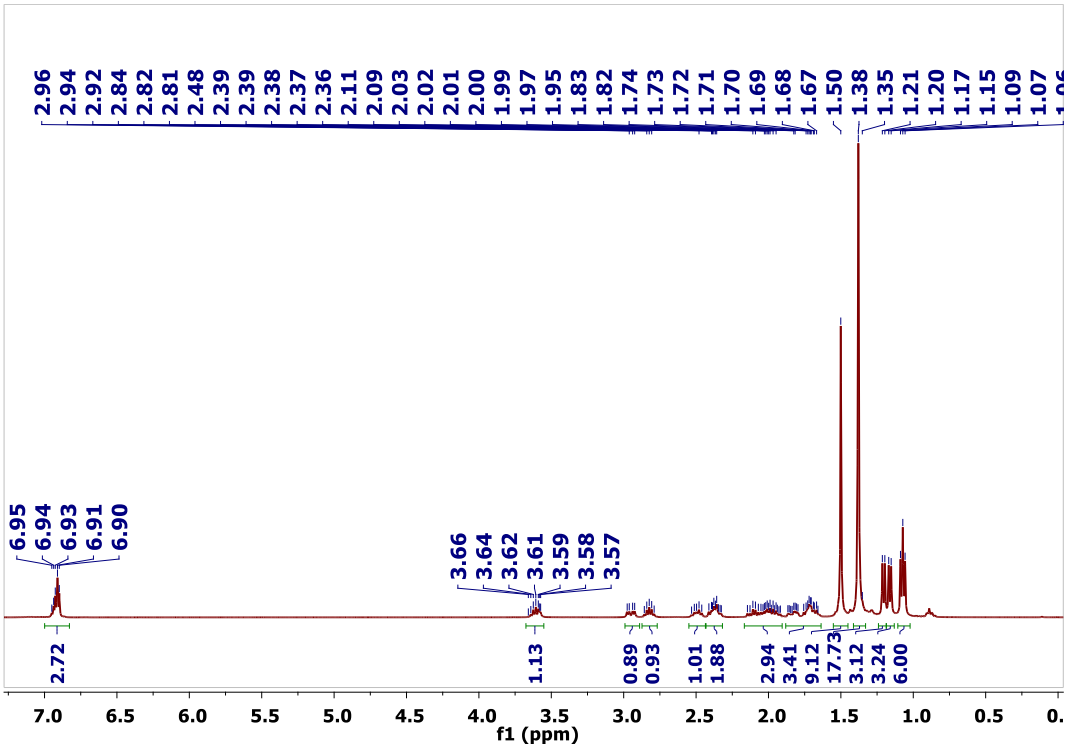


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum (400 MHz, 25 °C) for compound **4** in THF-d_8.

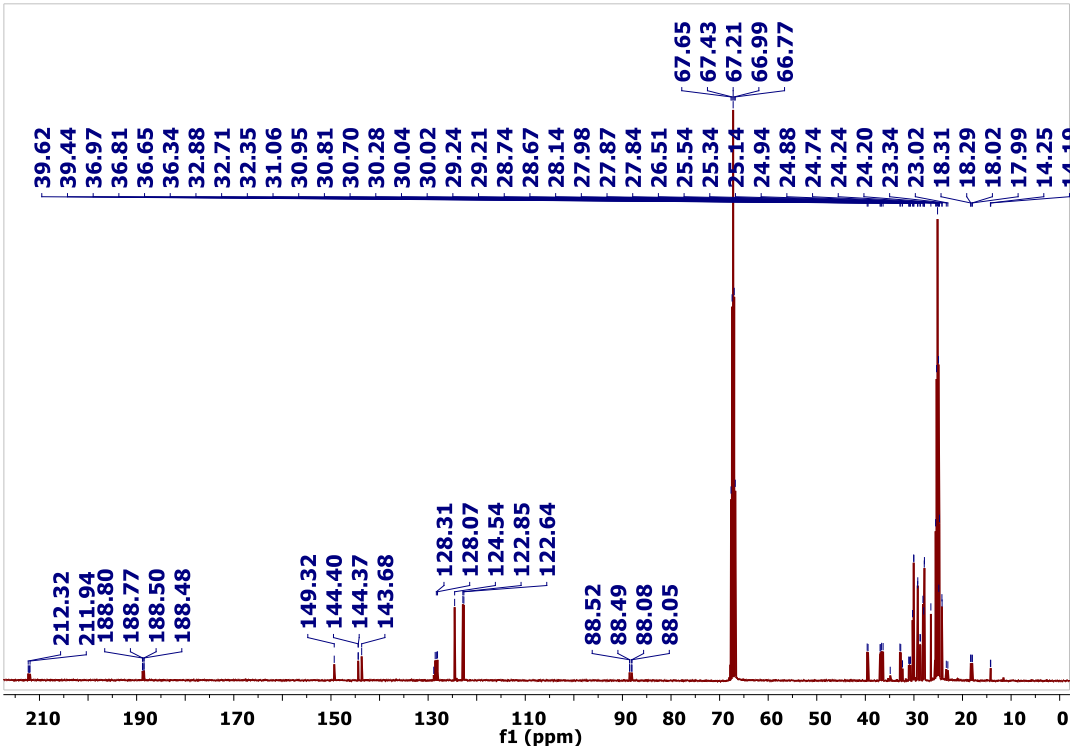


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 25 °C) for compound **4** in THF-d_8.

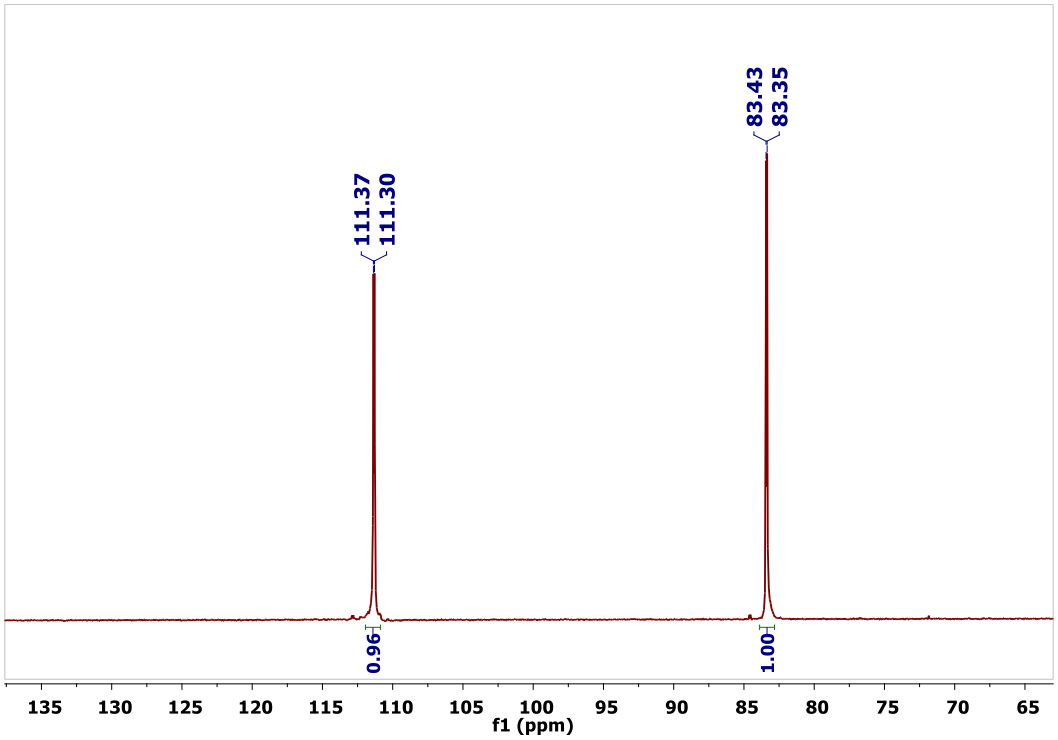


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C) for compound **5** in C_6D_6.

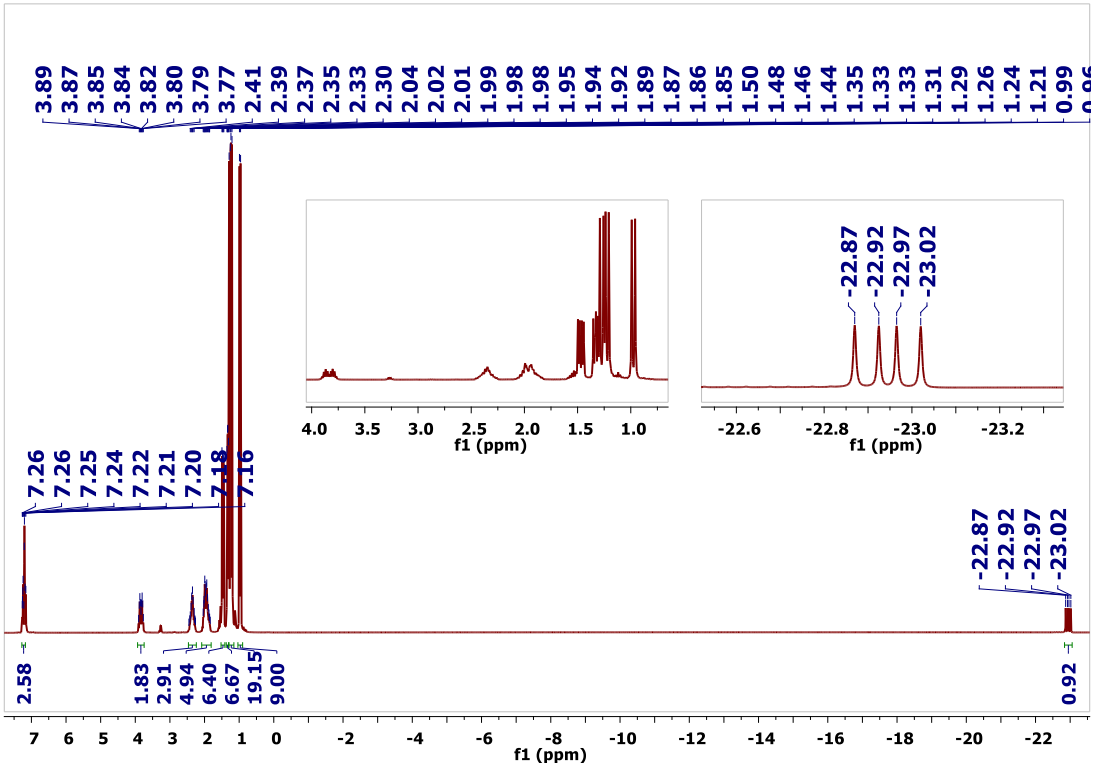


Figure S17. ^{1}H NMR spectrum (400 MHz, 25 °C) for compound **5** in C_6D_6. Insets show expansions of the aliphatic and hydride regions of the ^{1}H NMR spectrum.

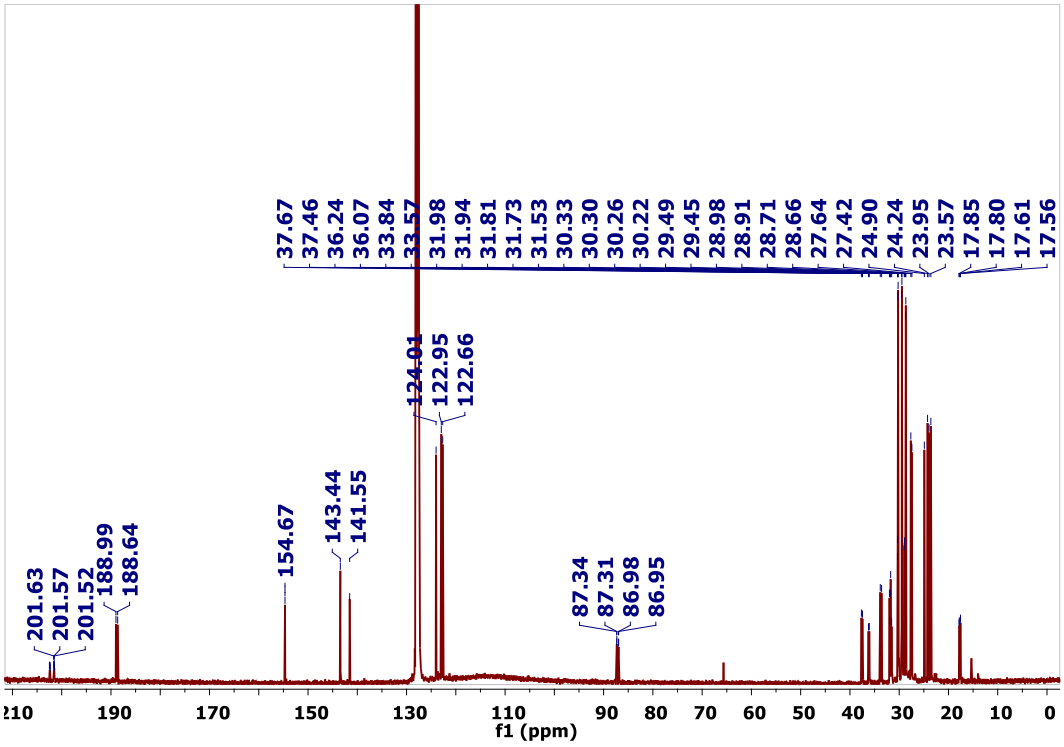


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 25 °C) for compound **5** in C_6D_6.

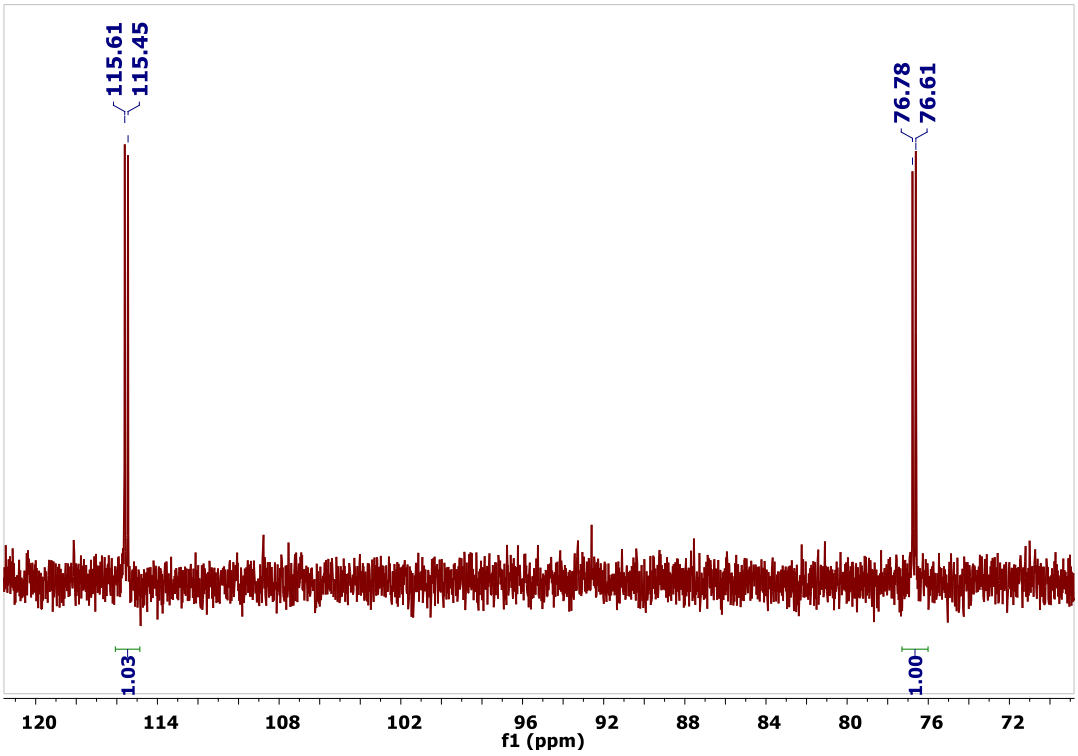


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (121.49 MHz, 25 °C) for compound **6** in C_6D_6.

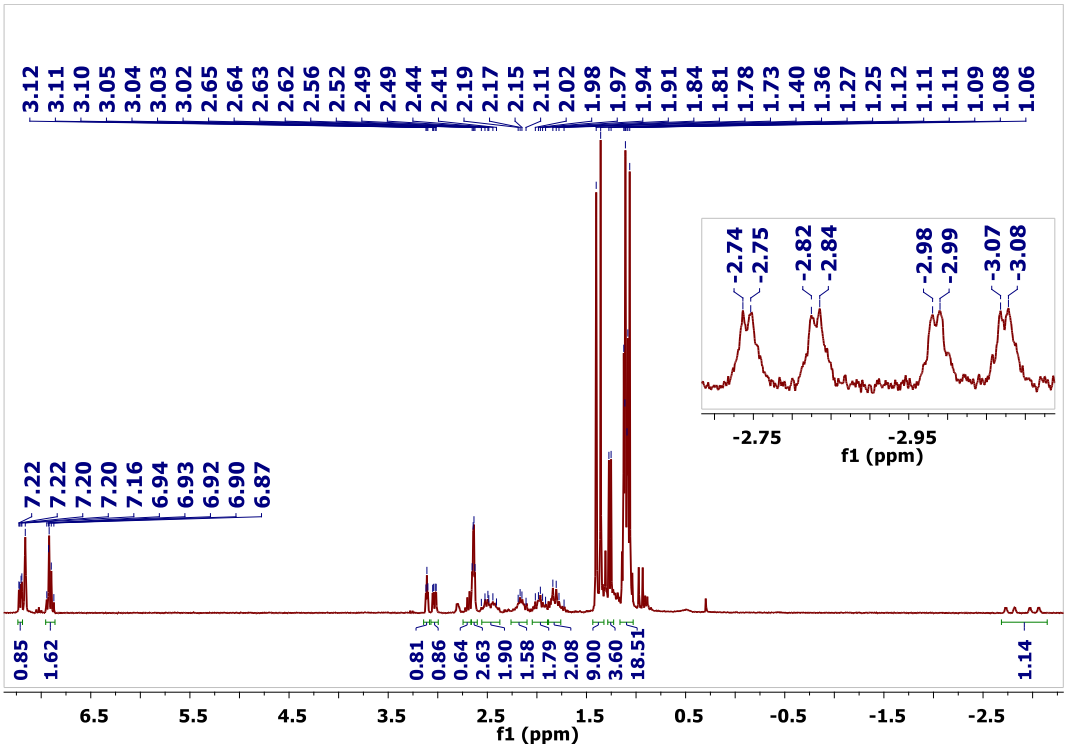


Figure S20. ^{1}H NMR spectrum (300 MHz, 25 °C) for compound **6** in C_6D_6, inset shows expansion of the hydride region of the ^{1}H NMR spectrum.

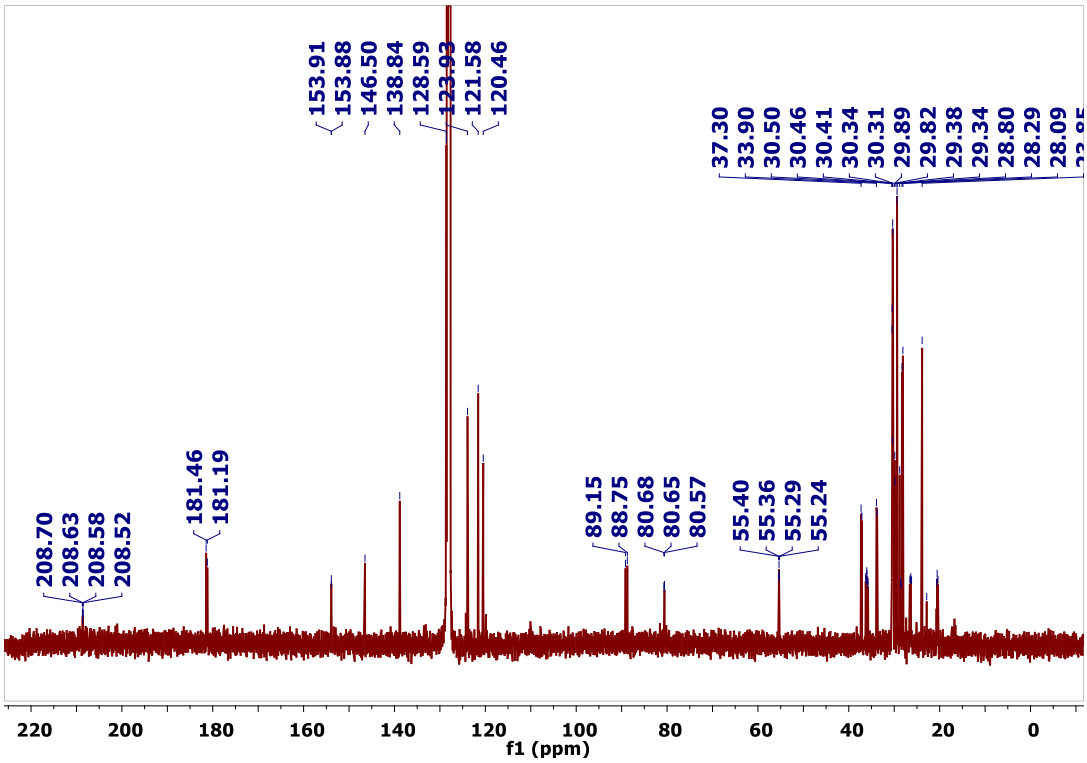


Figure S21. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, 25 °C) for compound **6** in C_6D_6.

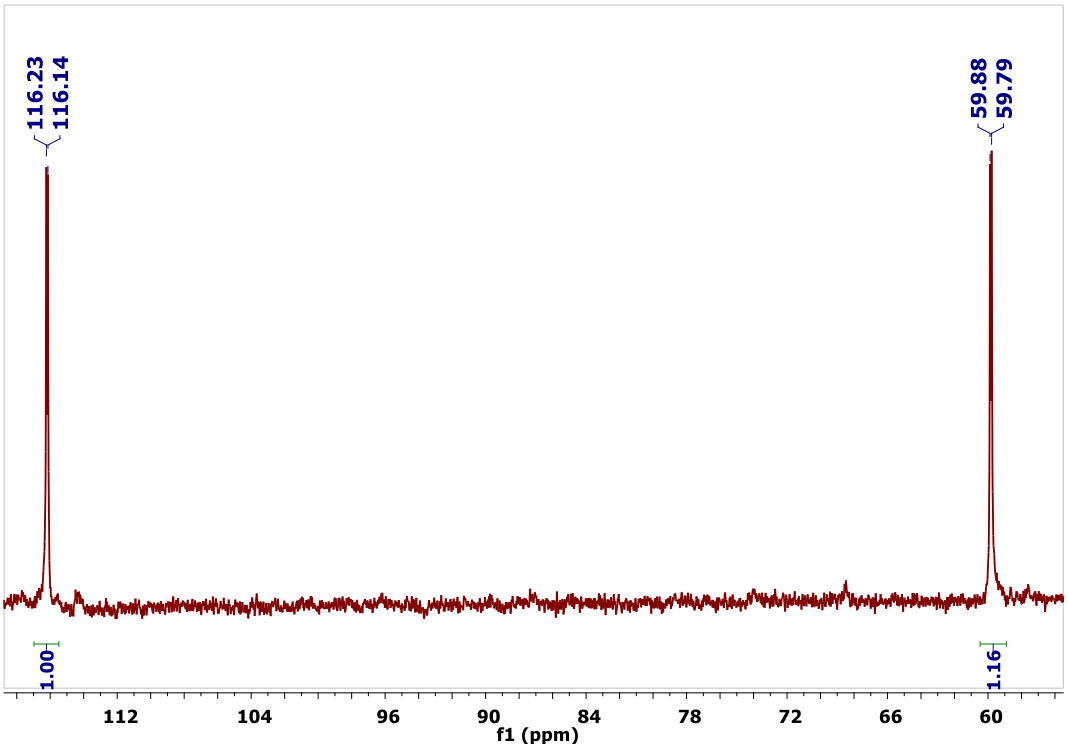


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C) for compound **7** in toluene-d_8.

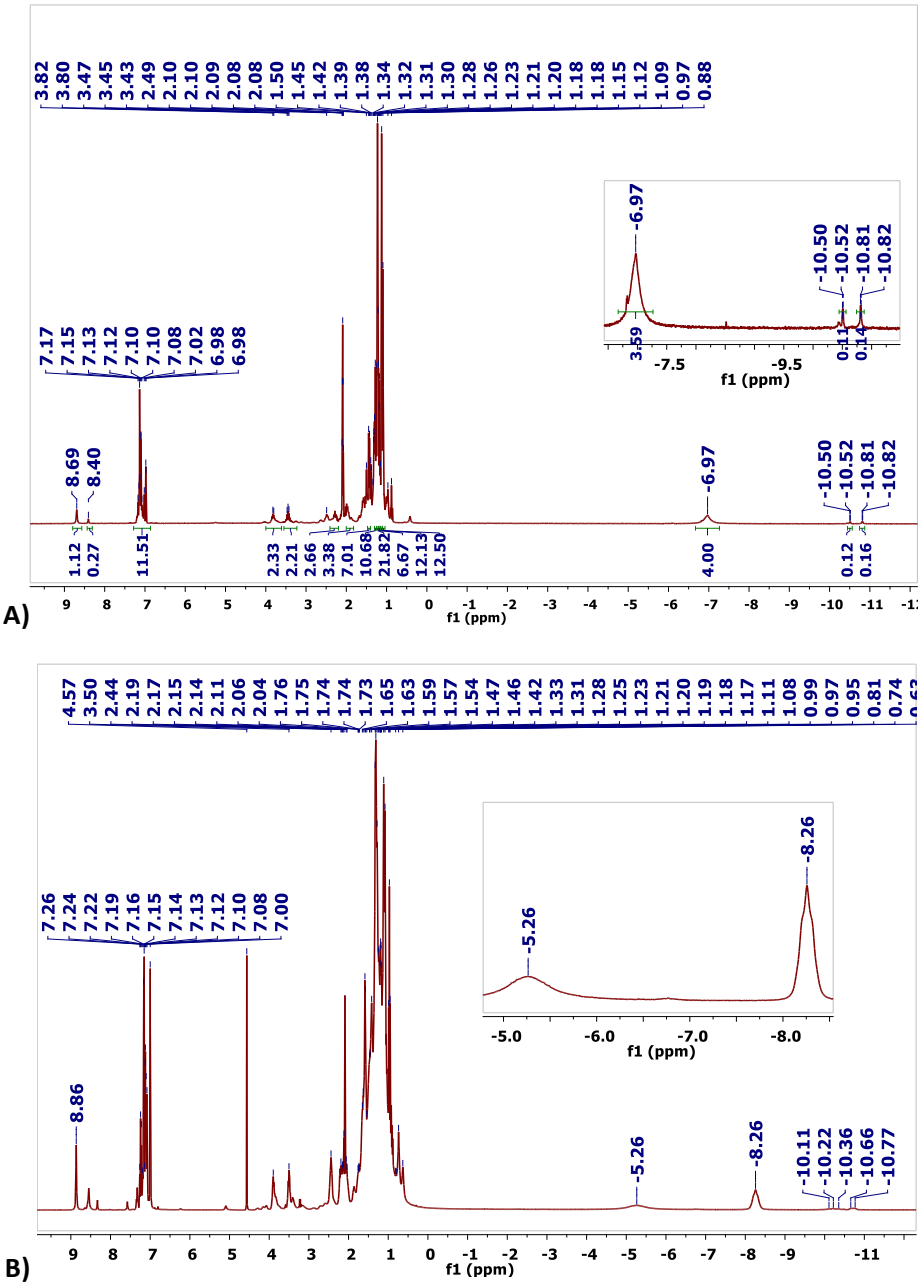


Figure S23. A) ^{1}H NMR spectrum (400 MHz, 25 °C, toluene-d_8) for compound **7**. Inset shows hydride region of ^{1}H NMR spectrum, where the coalesced broad resonance at -6.97 ppm is due to dynamic dihydrogen and dihydride ligands with a minor amount of **8** given by multiplets at -10.51 and -10.81 ppm. B) ^{1}H NMR spectrum (400 MHz) for compound **7** in toluene-d_8 at -80 °C. Inset shows the hydride region of the ^{1}H NMR spectrum, where the peak originally at -6.97 ppm at 25 °C has been partially resolved into two broad signals at -5.25 (T_1 ~26 ms) and -8.26 (T_1 ~75 ms) ppm at -80 °C. The exchange between hydride and dihydrogen chemical sites is extremely rapid even at -80 °C, given by the broadness of the signals, and the estimated T_1 values.

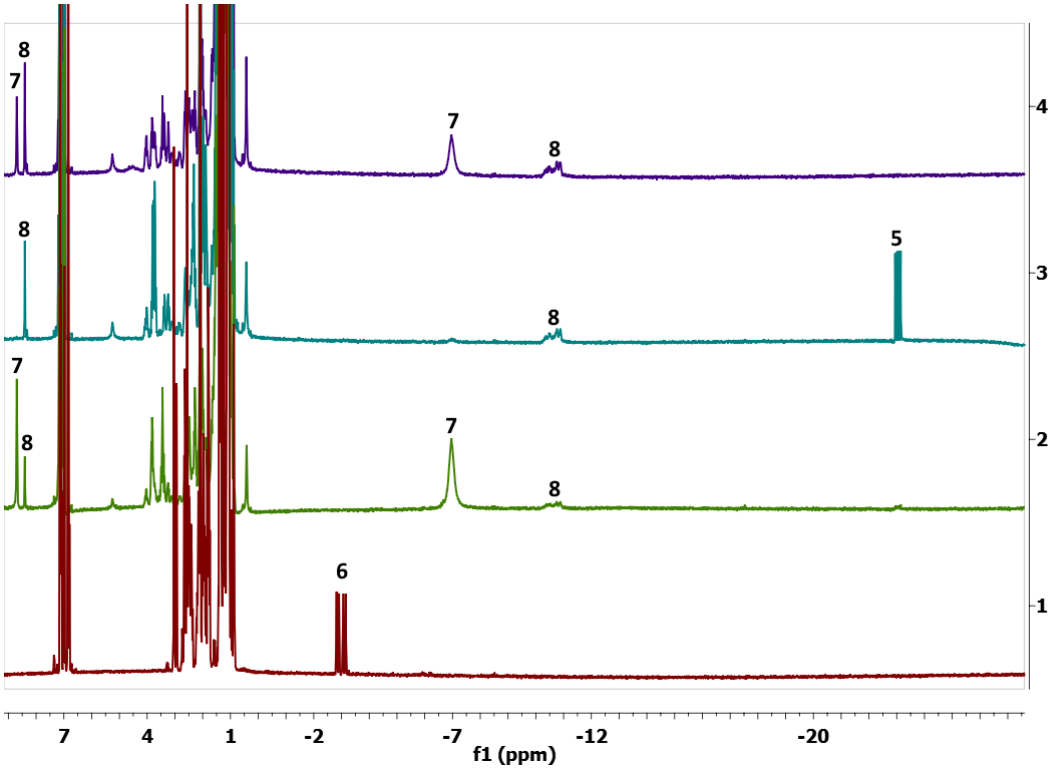


Figure S24. Stacked ^{1}H NMR spectra (300 MHz, 25 °C, toluene-d_8) demonstrating reversibility of reactions where diagnostic resonances of reactants/products are highlighted/labelled.

1) Initial ^{1}H NMR spectrum of complex **6**, diagnostic hydride resonance at -2.98 ppm.

2) ^{1}H NMR spectrum after addition of 1atm of H_2 to solution complex **6**, shows the formation of complex **7** with diagnostic resonances at 8.69 ppm belonging to the NH moiety, and the broad resonance at -6.98 ppm belonging to coalesced rapidly exchanging dihydrogen and hydride ligands.

3) ^{1}H NMR spectrum after pumping the headspace of the J. Young NMR tube to remove H_2 from sample shown in spectrum 2, shows the formation of complex **5** with diagnostic hydride resonance at -23.04 ppm.

4) ^{1}H NMR spectrum after re-introducing 1atm of H_2 to the sample shown in spectrum 3, shows the reformation of complex **7**. Over the course of these reversibility experiments the peaks belonging to complex **8** are gradually increasing, diagnostic resonances are at 8.44 and -10.66 ppm.

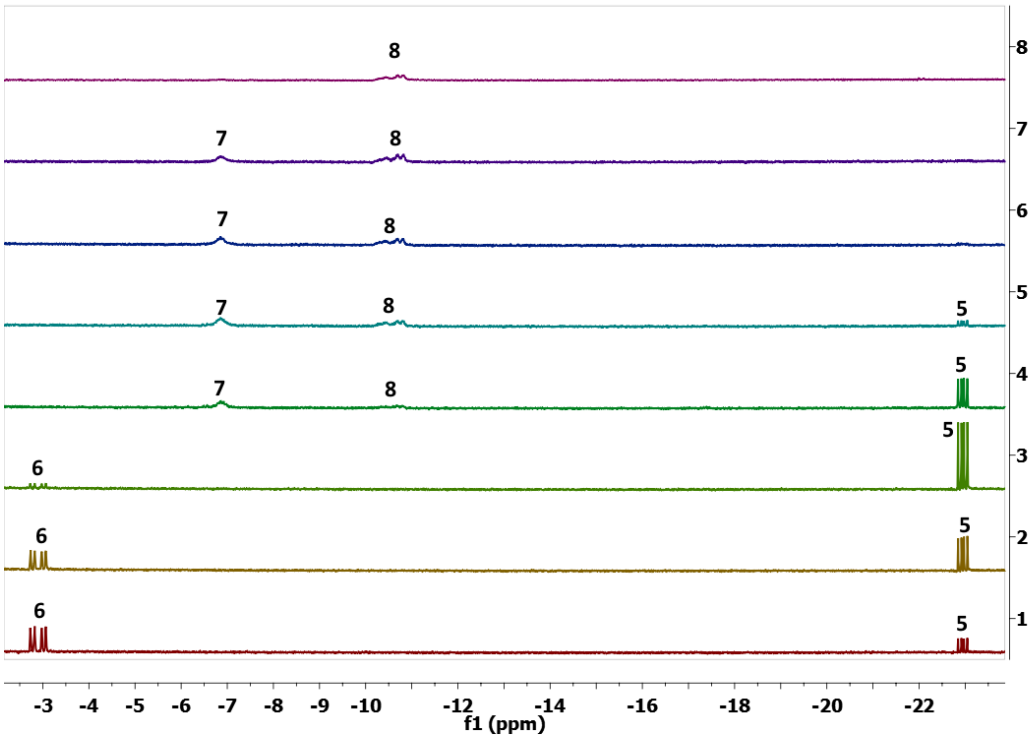


Figure S25. Stacked ^{1}H NMR spectra (hydride region, 300 MHz, 25 °C, C_6D_6) showing a series of stepwise stoichiometric reactions with H_2 showing conversion of **6** to **5** (spectra 1, 2, 3), then conversion of species **5** to **7** with concomitant conversion to species **8** (spectra 4, 5), followed by conversion of species **7** to **8** (spectra 6, 7, 8). 1) NMR spectrum collected 10 min after a total of 0.5 equiv of H_2 was injected into the NMR sample. 2) NMR spectrum collected 20 min after a total of 0.5 equiv of H_2 was injected into the NMR sample. 3) NMR spectrum collected 10 min after another 0.5 equiv of H_2 (total of 1 equiv) was injected. 4) NMR spectrum collected 20 min after another 0.5 equiv of H_2 (total of 1.5 equiv) was injected. 5) NMR spectrum collected 40 min after another 0.5 equiv of H_2 (total of 2 equiv) was injected. 6) NMR spectrum collected 60 min after another 0.5 equiv of H_2 (total of 2.5 equiv) was injected. 7) NMR spectrum collected 40 min after another 0.5 equiv of H_2 (total of 3 equiv) was injected. 8) NMR spectrum collected 16 h after previous spectrum (with a total of 3 equiv of H_2 added).

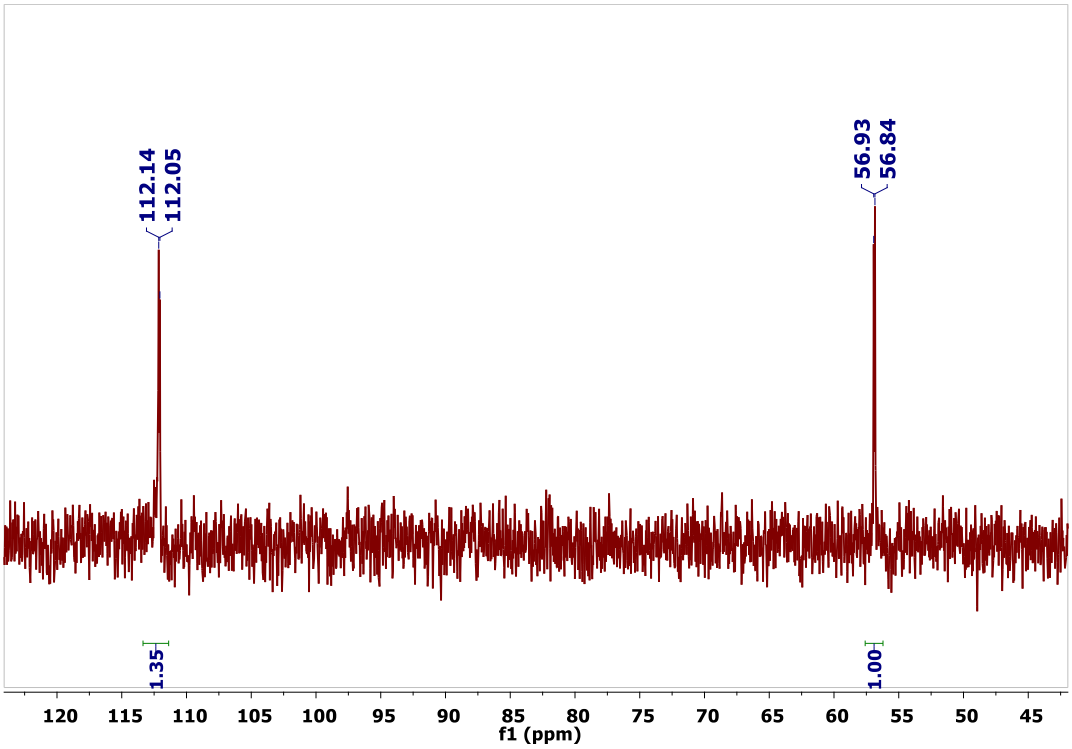


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (121.49 MHz, 25 °C) for compound **9** in C_6D_6.

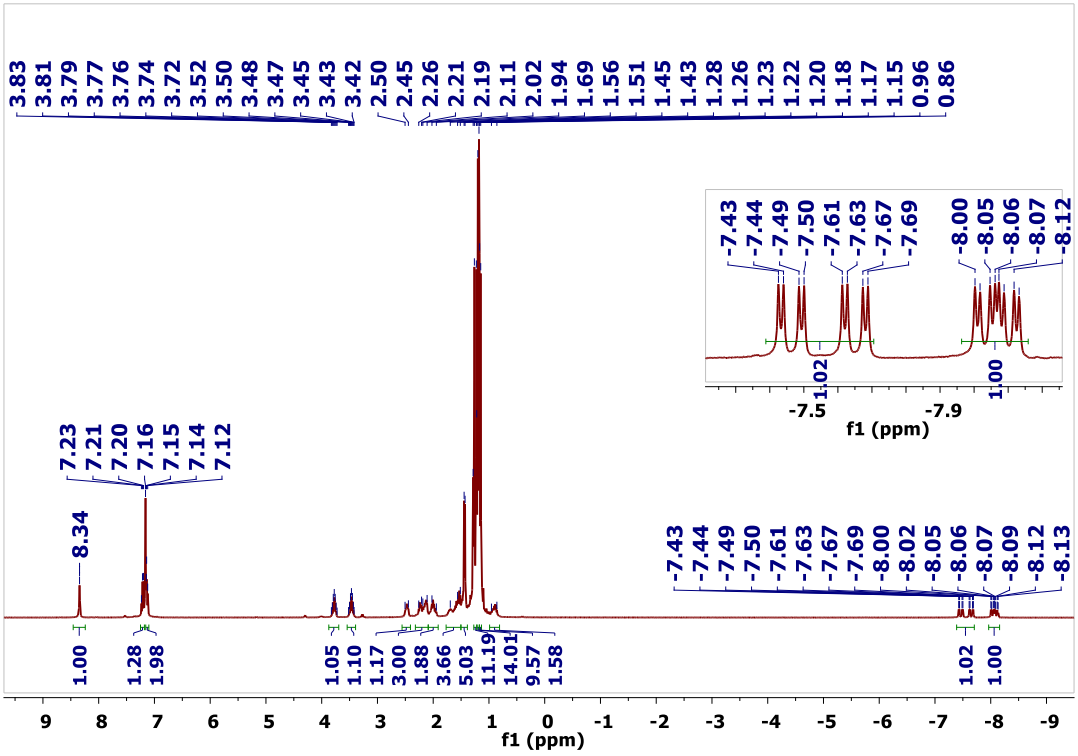


Figure S27. ^{1}H NMR spectrum (400 MHz, 25 °C) for compound **9** in C_6D_6, inset shows expansion of the hydride region of ^{1}H NMR spectrum.

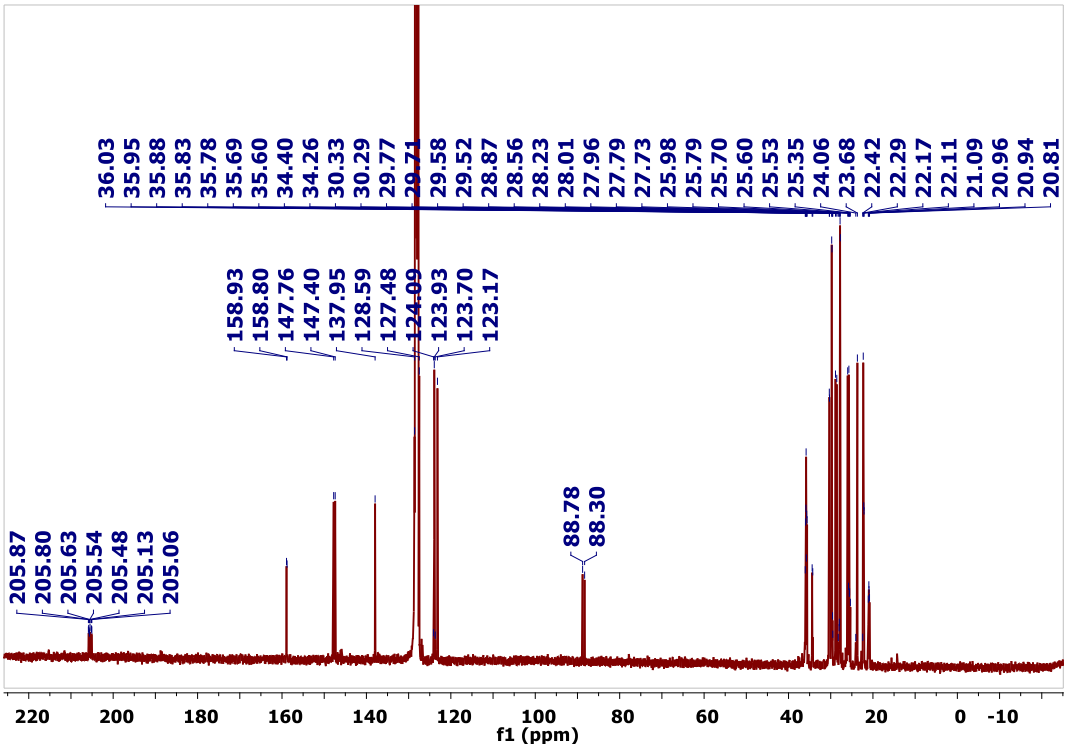


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 25 °C) for compound **9** in C_6D_6.

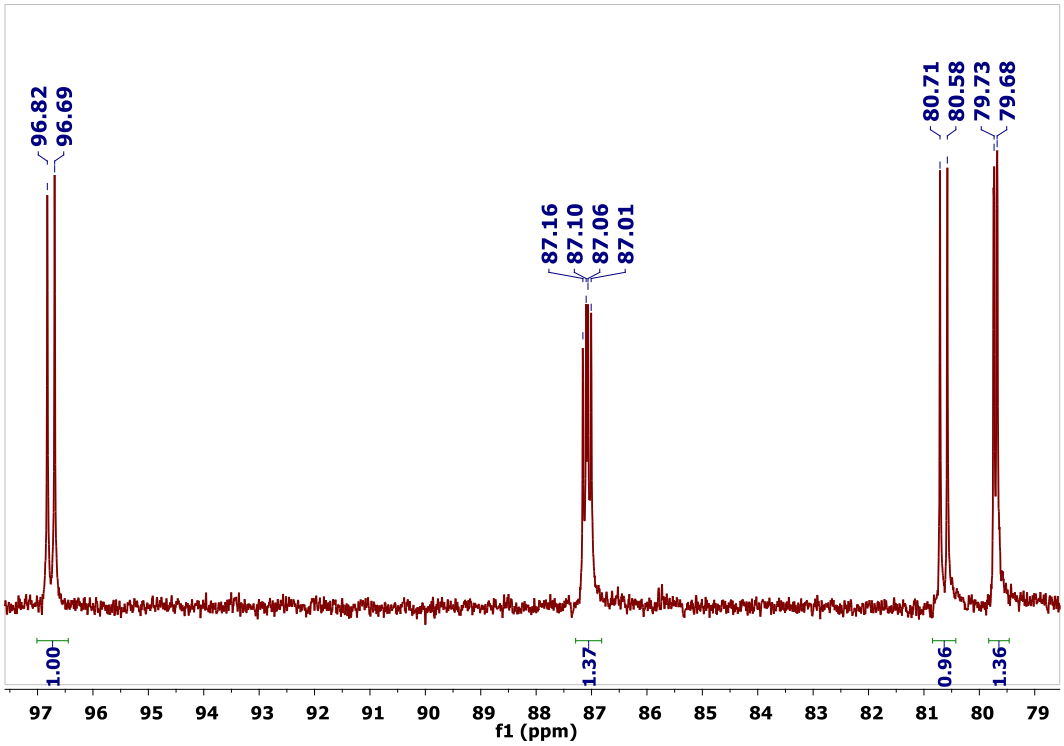


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C) for a mixture of isomers **10a** (peaks at 96.76 and 80.64 ppm) and **10b** (peaks at 87.08 and 79.71 ppm) and in C_6D_6.

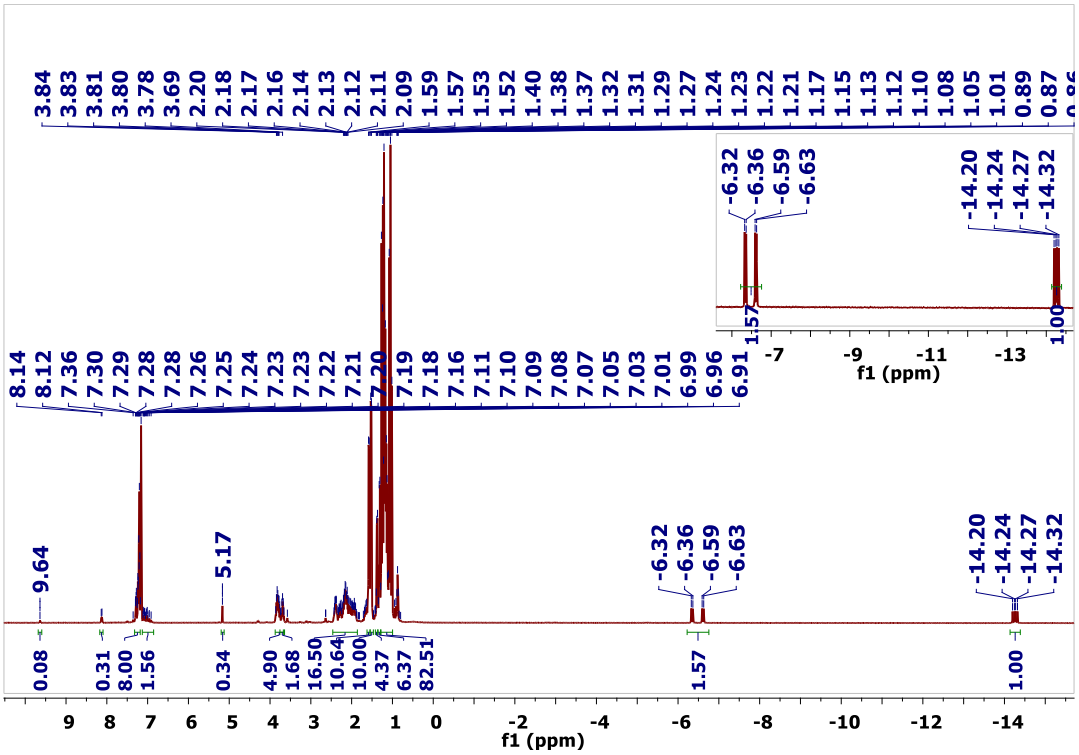


Figure S30. ^{1}H NMR spectrum (400 MHz, 25 °C) for mixture of **10a** and **10b** in C_6D_6, along with some benzaldehyde (diagnostic aldehyde CH peak at 9.64 ppm) and benzyl benzoate (diagnostic CH_2 group at 5.17 ppm), inset shows expansion of the hydride region of ^{1}H NMR spectrum where dd peak at -6.48 ppm belongs to **10b**, and dd peak at -14.26 ppm belongs to **10a**.

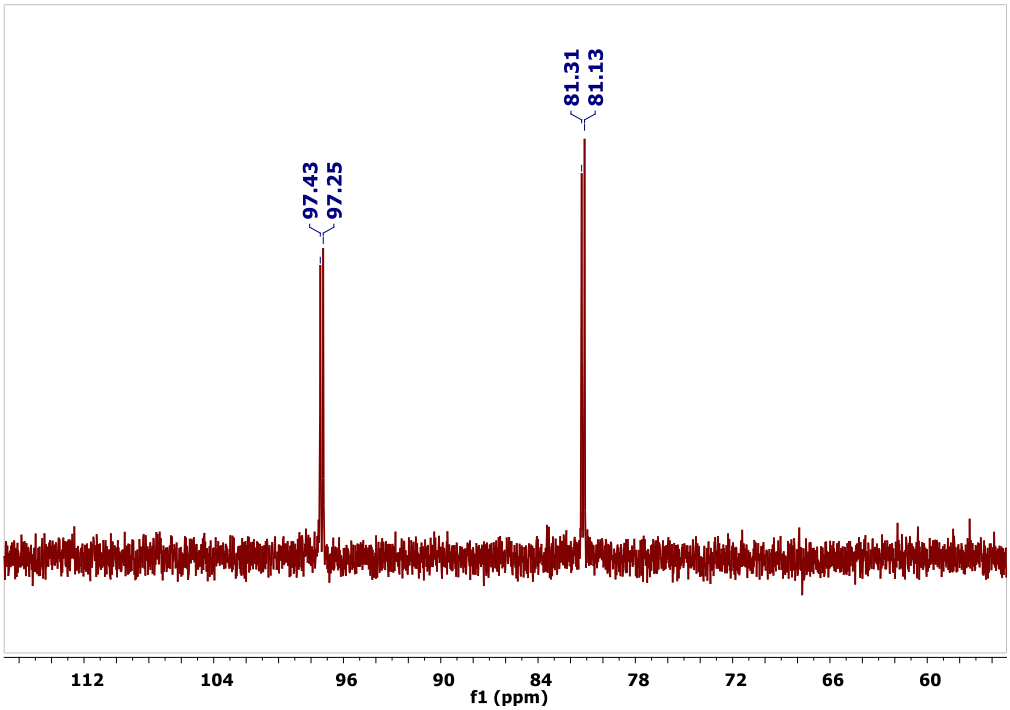


Figure S31. ^{31}P{^{1}H} NMR spectrum (121.49 MHz, 25 °C) for compound **10a** in C_6D_6.

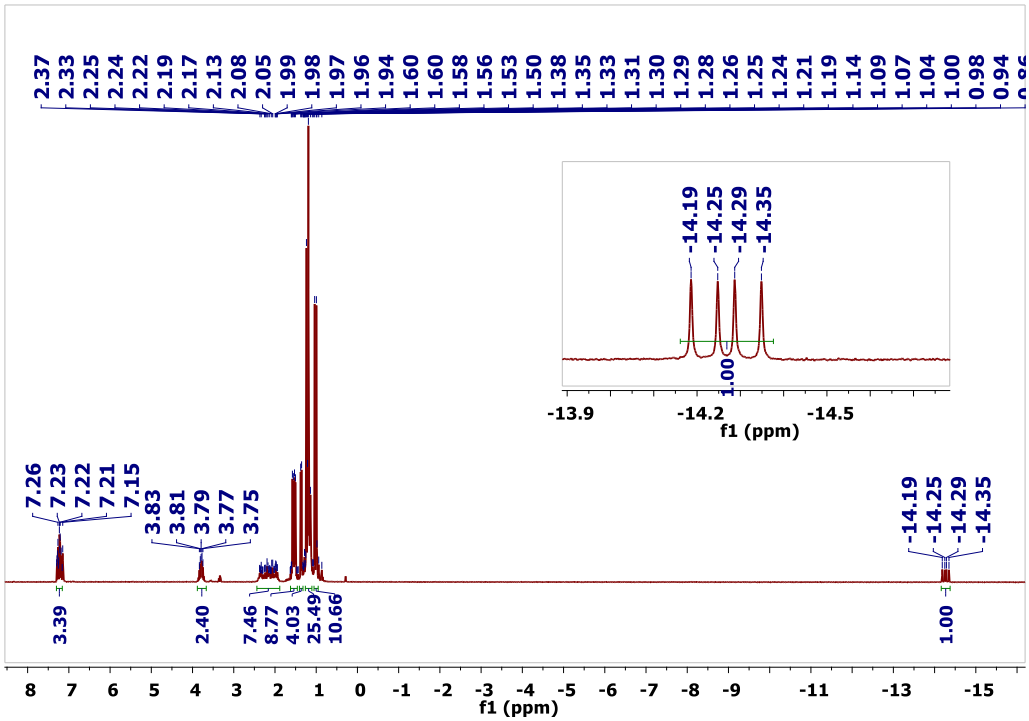


Figure S32. ^{1}H NMR spectrum (300 MHz, 25 °C) for compound **10a** in C_6D_6, inset shows expansion of the hydride region of the ^{1}H NMR spectrum.

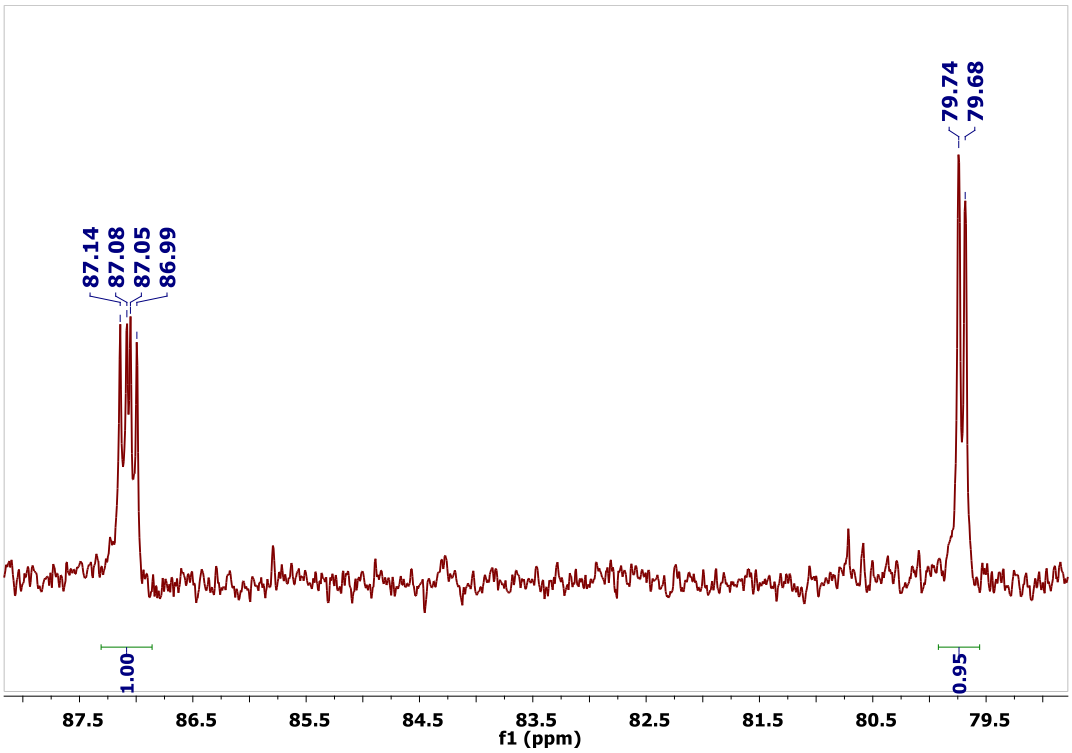


Figure S33. ^{31}P{^{1}H} NMR spectrum (162 MHz, 25 °C) for compound **10b** in C_6D_6.

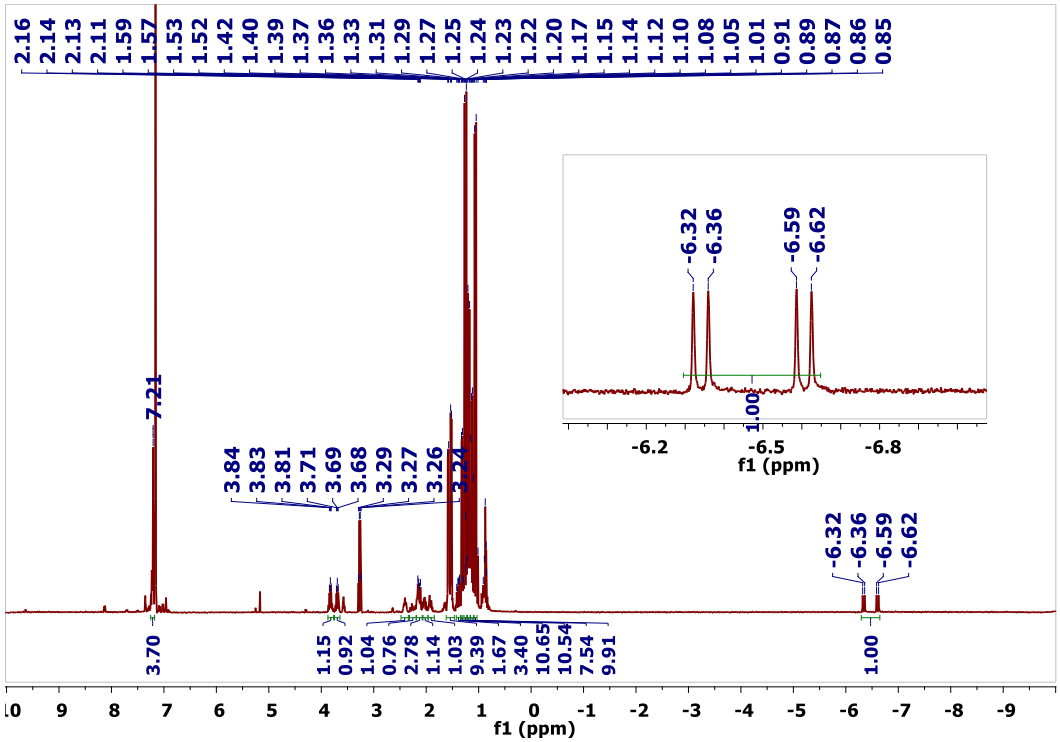


Figure S34. ^{1}H NMR spectrum (400 MHz, 25 °C) for compound **10b** in C_6D_6, inset shows expansion of the hydride region of the ^{1}H NMR spectrum.

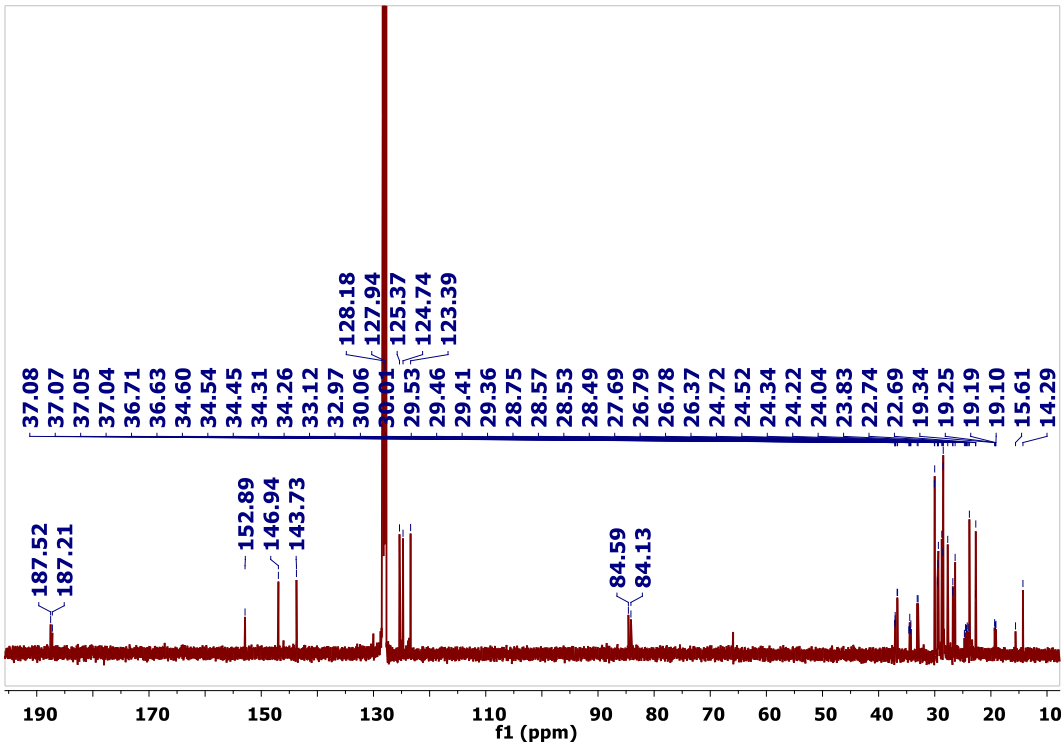


Figure S35. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, 25 °C) for compound **10b** in C_6D_6.

IR Spectra:

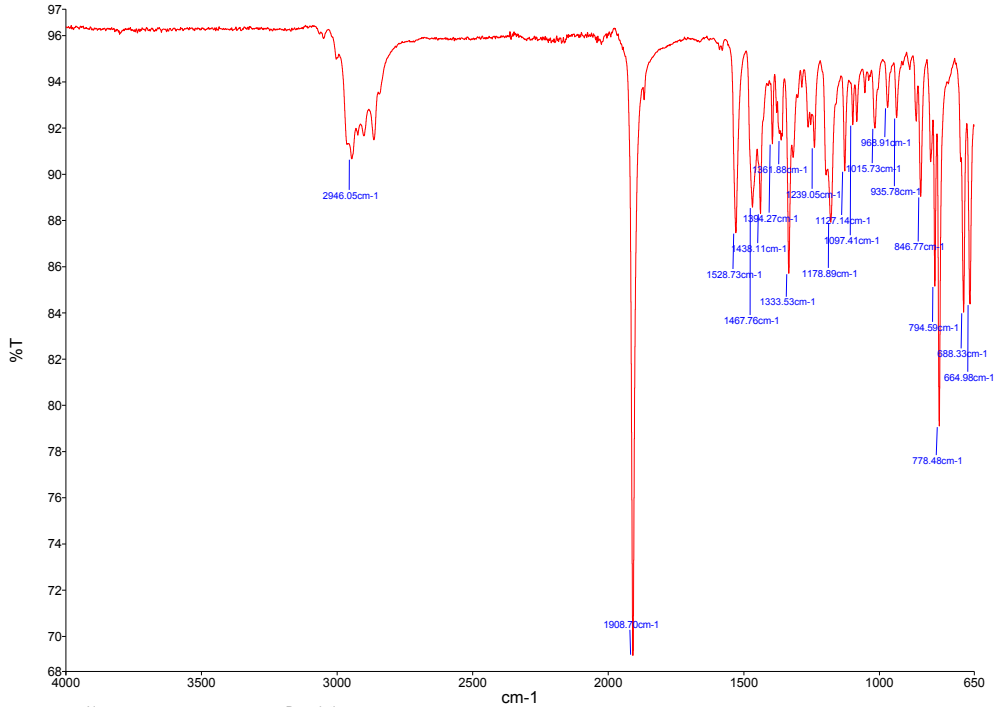


Figure S36. ATR-FTIR spectrum of **4**.

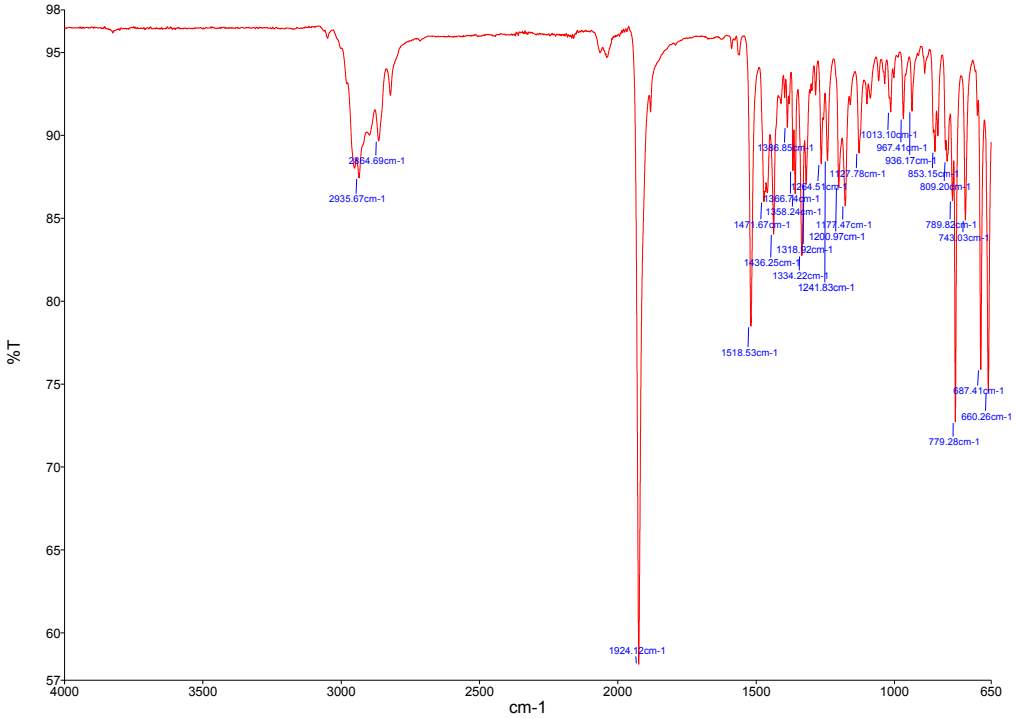


Figure S37. ATR-FTIR spectrum of **5**.

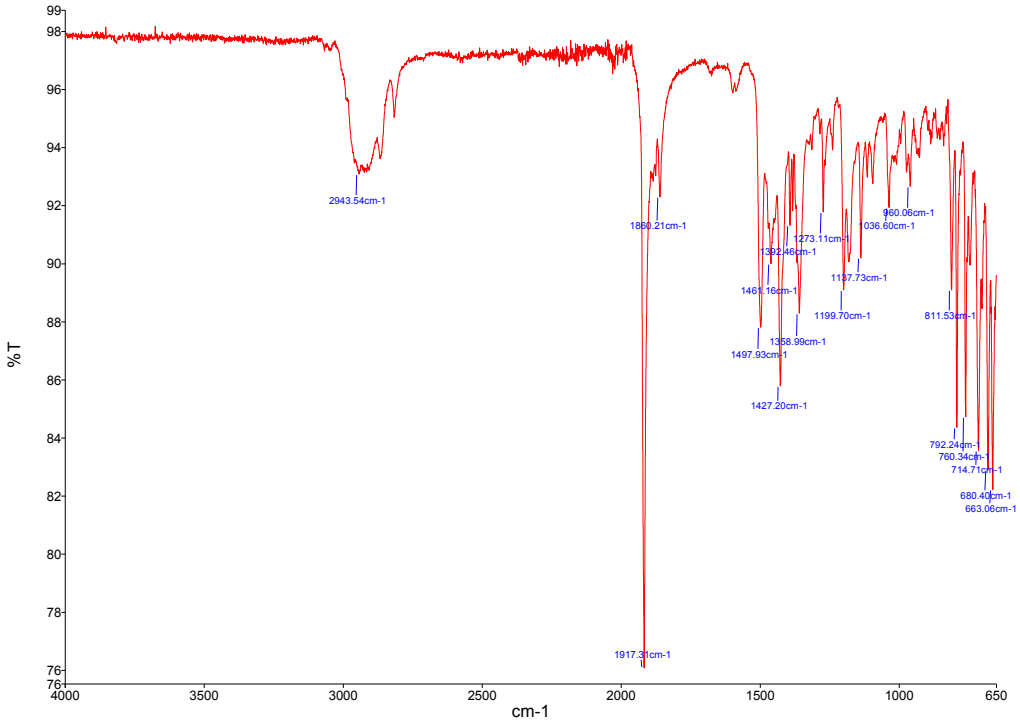


Figure S38. ATR-FTIR spectrum of **6**.

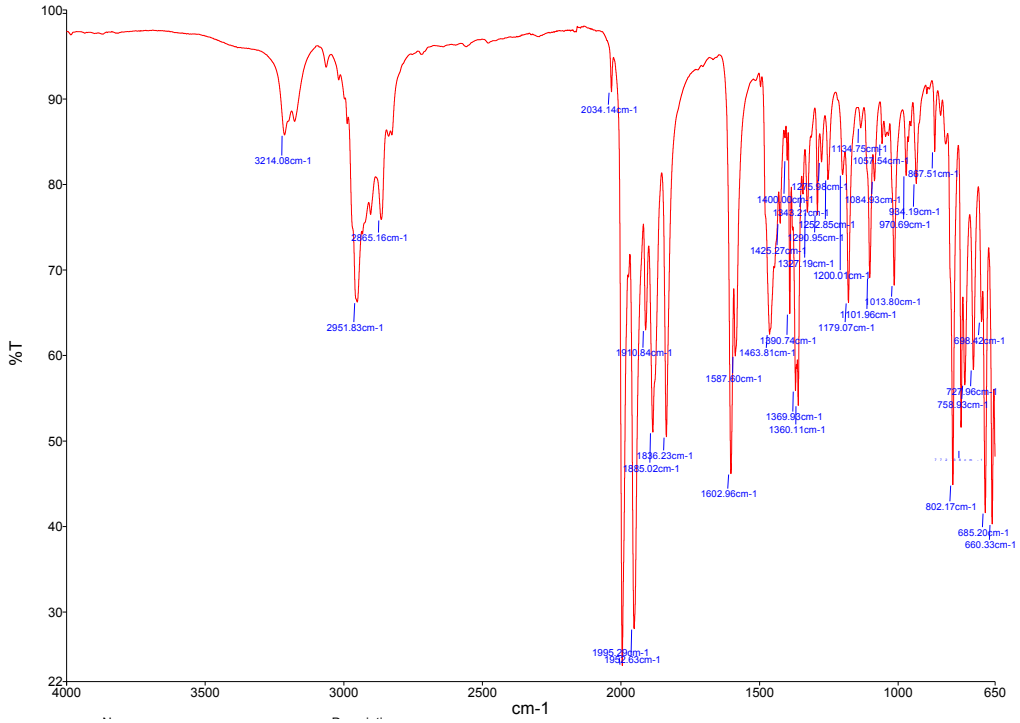


Figure S39. ATR-FTIR spectrum of **9**.

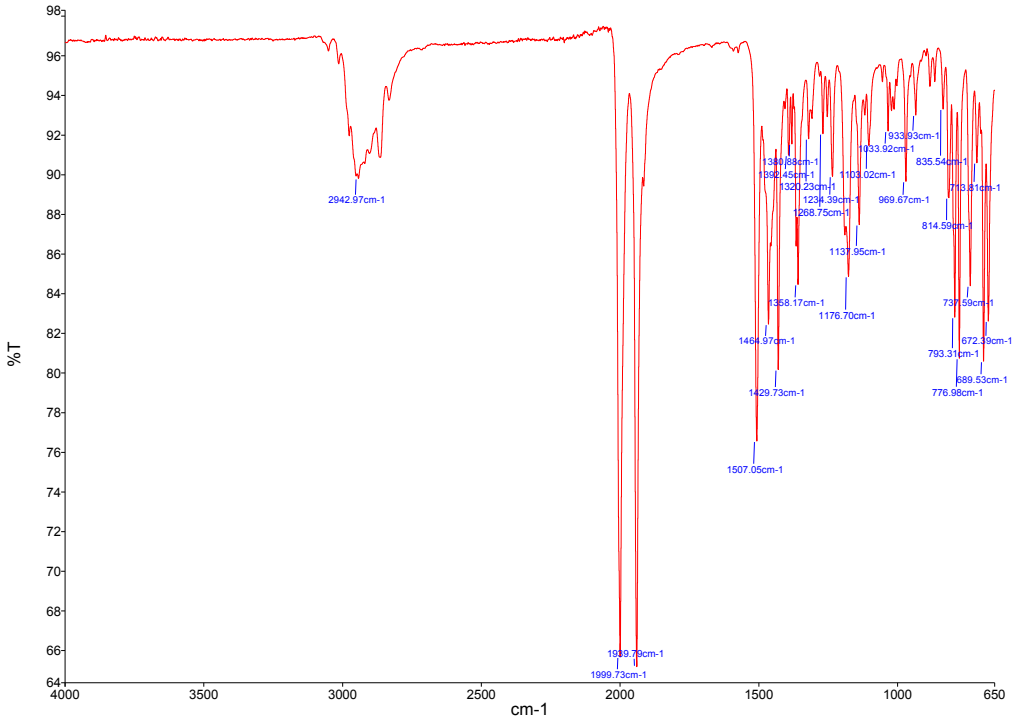
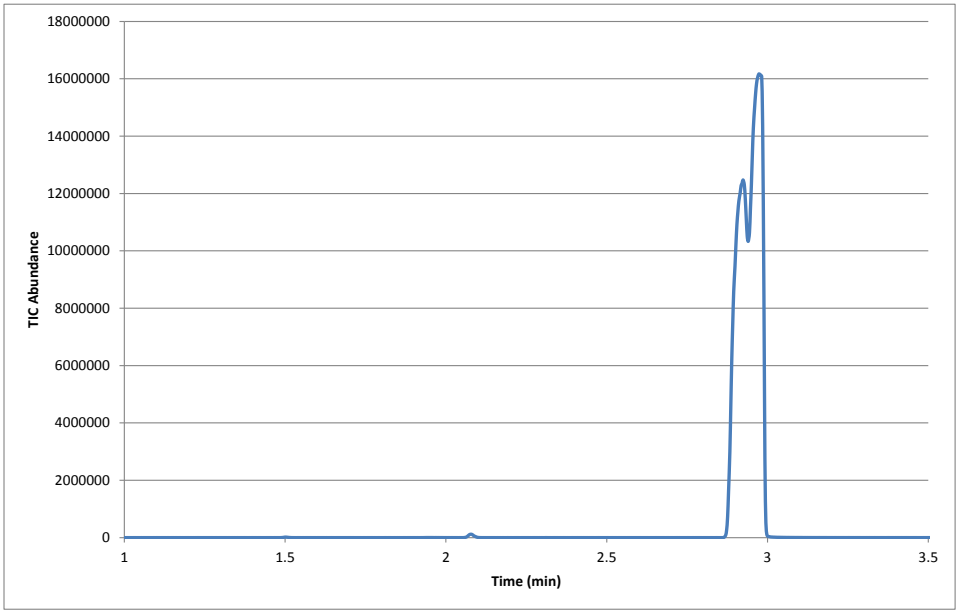


Figure S40. ATR-FTIR spectrum of **10a**.

GC-MS Data:

A)



B)

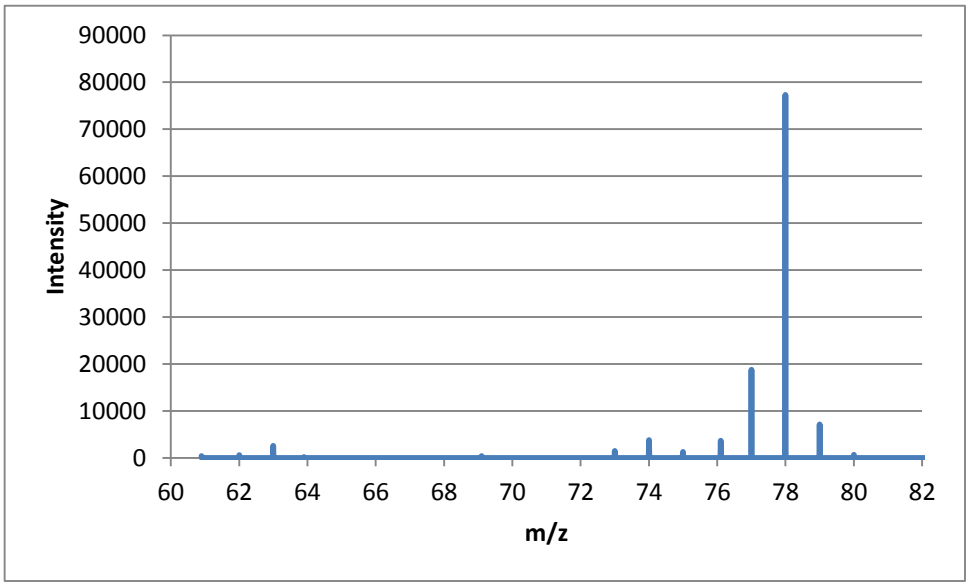
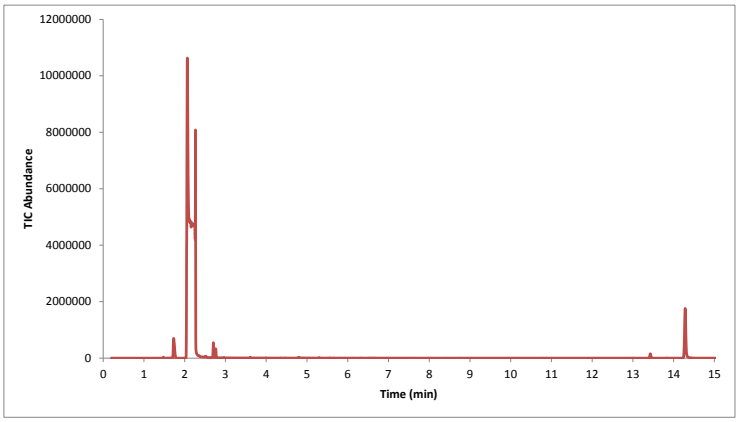
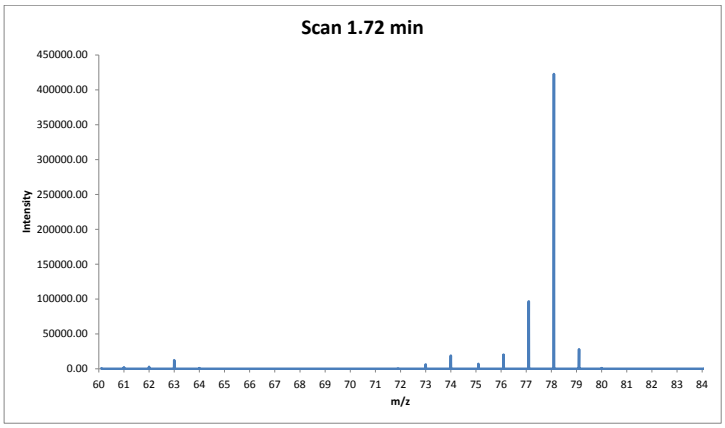


Figure S41. A) GC chromatogram after reaction of **5** with 1 equiv benzyl alcohol in toluene-d_8, shows presence benzene at 2.07 min. Large peaks between 2.8-3 min are from a mixture of toluene-d_8 and protio-toluene used to dilute the sample. B) MS (EI) spectrum from scan at 2.07 min, shows presence of benzene, M^+=78.1.

A)



B)



C)

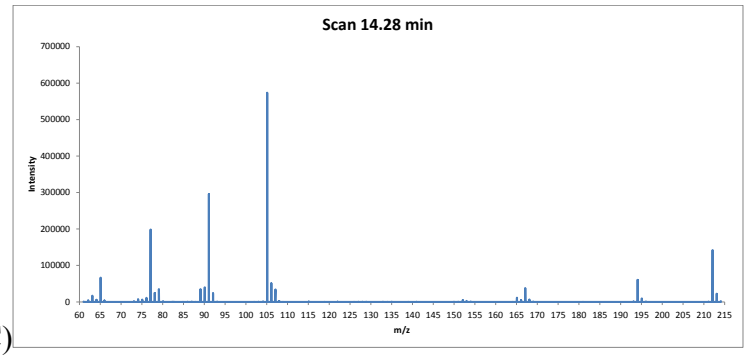


Figure S42. A) GC chromatogram after reaction of **5** with benzaldehyde in toluene-d_8, shows presence benzene at 1.72 min and benzyl benzoate at 14.28 min. Large peaks between 2-2.5 min are from a mixture of toluene-d_8 and protio-toluene used to dilute the sample, small peaks at 2.7 min are xylene derivatives present in the toluene-d_8 and protio-toluene solvent mixture, and a small peak at 3.6 min is unreacted benzaldehyde. B) MS (EI) spectrum from scan at 1.72 min, shows presence of benzene, M^+=78.1. C) MS (EI) spectrum from scan at 14.28 min, shows presence of benzyl benzoate, M^+=212.2.

X-ray Crystallographic Data:

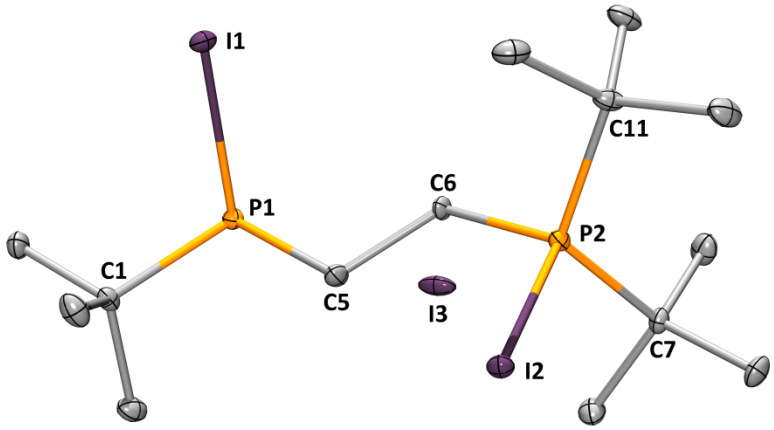


Figure S43. X-ray crystal structure of [I*t*BuP(C_2H_4)P*t*Bu_2I]I, yellow crystals were obtained from a saturated C_6D_6 solution. Non-hydrogen atoms are shown as 30% probability ellipsoids, and H atoms are omitted for clarity. Selected bond lengths (A□), angles (°): P1-I1 2.4733(8); P1-C1 1.876(3); P1-C5 1.856(3); P2-C6 1.831(3); P2-C7 1.864(3); P2-C11 1.868(3); P2-I2 2.4647(8); C1-P1-C5 101.86(13); C1-P1-I1 103.45(10); C5-P1-I1 97.07(10); C6-P2-C7 107.16(13); C6-P2-C11 105.66(13); C7-P2-C11 117.96(14); C6-P2-I2 111.57(10); C7-P2-I2 107.22(9); C11-P2-I2 107.32(10).

Table S1. Selected crystallographic information.

Compound	**2**	**4●**0.5(benzene)	**5**	**6**	**9**	**10a**	**10b**	[I*t*BuP(C_2H_4)P*t*Bu_2I]I
ID code	mf1027	mf1096	mf1002	mf1088	mf1215a	mf1229a	mf1284	mf1090
Formula	$C_{28}H_{62}P_4$	$C_{35}H_{57}ClNOP_2Ru$	$C_{32}H_{55}NOP_2Ru$	$C_{32}H_{53}NOP_2Ru$	$C_{33}H_{57}NO_2P_2Ru$	$C_{33}H_{55}NO_2P_2Ru$	$C_{33}H_{55}NO_2P_2Ru$	$C_{14}H_{31}I_3P_2$
F.W.	522.65	706.27	632.78	630.76	662.80	660.79	660.79	642.03
T (K)	90(2)	90(2)	90(2)	90(2)	100(2)	90(2)	90(2)	90(2)
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	11.854(5)	10.9852(13)	17.069(5	11.4375(9)	22.485(5)	10.6471(9)	19.6571(16)	10.2810(11)
b (Å)	11.785(5)	18.066(2)	10.588(5)	18.7399(19)	9.699(2)	34.438(3)	18.0556(14)	16.7172(19)
c (Å)	24.340(5)	20.127(3)	18.527(5)	14.7262(14)	16.385(4)	9.4579(8)	18.7046(15)	12.7510(14)
α (°)	90	69.079(3)	90	90	90	90	90	90
β (°)	92.241(5)	79.600(3)	105.277(5)	98.732(2)	108.632(15)	105.572(2)	97.292(2)	95.568(2)
γ (°)	90	75.222(3)	90	90	90	90	90	90
V ($Å^3$)	3398(2)	3589.9(8)	3230(2)	3119.8(5)	3385.9(15)	3340.6(5)	6585.0(9)	2181.2(4)
Z	4	4	4	4	4	4	8	4
D_c ($g \cdot cm^{-3}$)	1.022	1.307	1.301	1.343	1.300	1.314	1.333	1.955
μ (mm^{-1})	0.236	0.627	0.609	0.630	0.586	0.594	0.602	4.436
no. reflections collected	29832	62179	30106	28480	37794	31280	56557	20238
no. independent reflections	7803	16624	7927	14243	10274	7638	7610	5037
GOF on F^2	1.015	1.005	1.050	0.979	0.978	1.149	1.055	1.040
R [$I > 2\sigma(I)$]	$R_1 = 0.0394$, $wR_2 = 0.0986$	$R_1 = 0.0334$, $wR_2 = 0.0633$	$R_1 = 0.0490$, $wR_2 = 0.0864$	$R_1 = 0.0493$, $wR_2 = 0.0910$	$R_1 = 0.0561$, $wR_2 = 0.1123$	$R_1 = 0.0370$, $wR_2 = 0.0657$	$R_1 = 0.0358$, $wR_2 = 0.0787$	$R_1 = 0.0218$, $wR_2 = 0.0473$
R (all data)	$R_1 = 0.0556$, $wR_2 = 0.1082$	$R_1 = 0.0550$, $wR_2 = 0.0689$	$R_1 = 0.0756$, $wR_2 = 0.1011$	$R_1 = 0.0701$, $wR_2 = 0.0980$	$R_1 = 0.1017$, $wR_2 = 0.1424$	$R_1 = 0.0486$, $wR_2 = 0.0687$	$R_1 = 0.0504$, $wR_2 = 0.0846$	$R_1 = 0.0282$, $wR_2 = 0.0495$