Electronic Supporting Information for:

Synthesis and reactivity of iridium complexes of a macrocyclic PNP pincer ligand

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1 Preparation of [Ir(PNP-14)(η^2:η^2-COD)][BAr$^F_4$] (1)

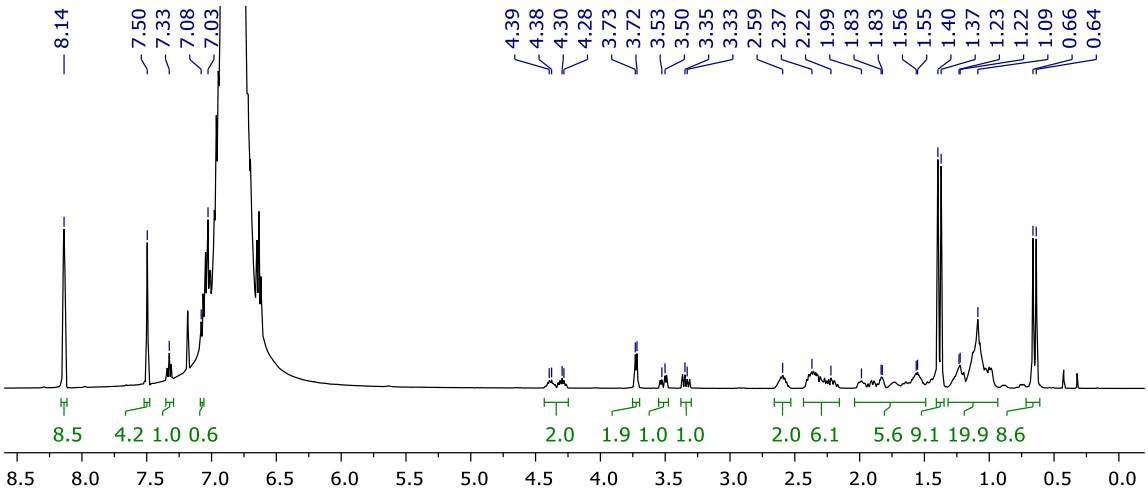

Figure S1. ^{1}H NMR spectrum of **1** (DFB, 500 MHz).

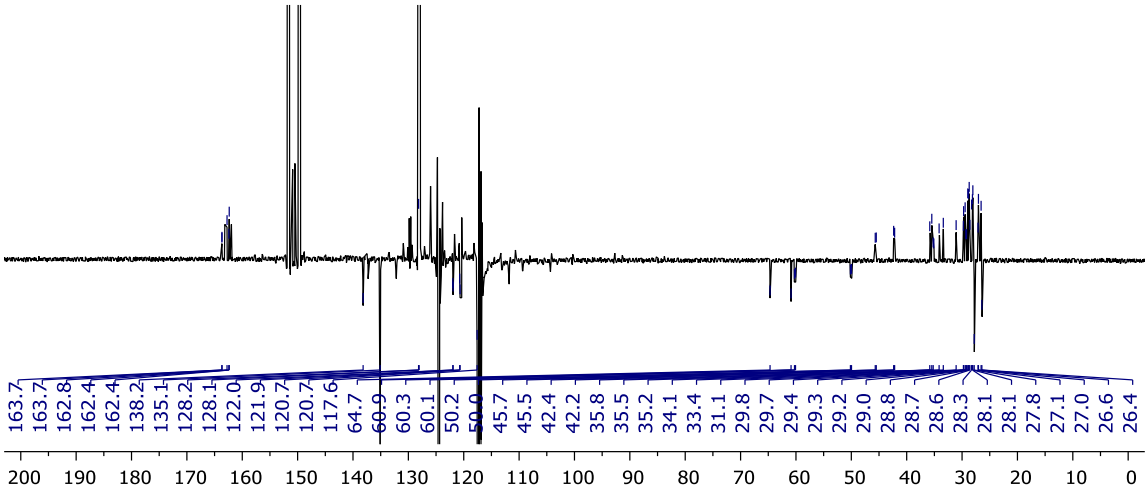

Figure S2. ^{13}C{^{1}H} APT NMR spectrum of **1** (DFB, 126 MHz).

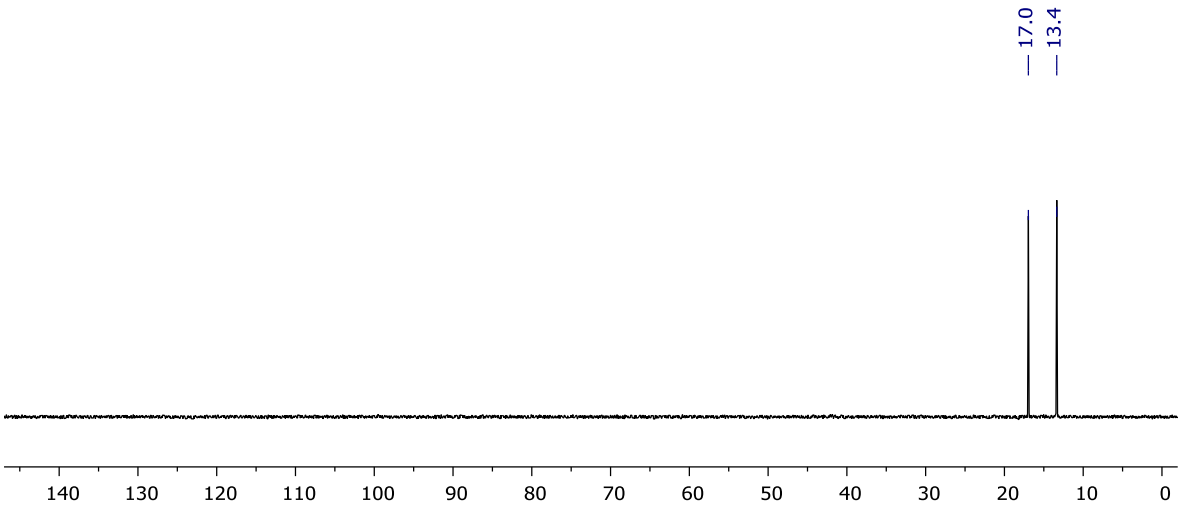

Figure S3. ^{31}P{^{1}H} NMR spectrum of **1** (DFB, 162 MHz).

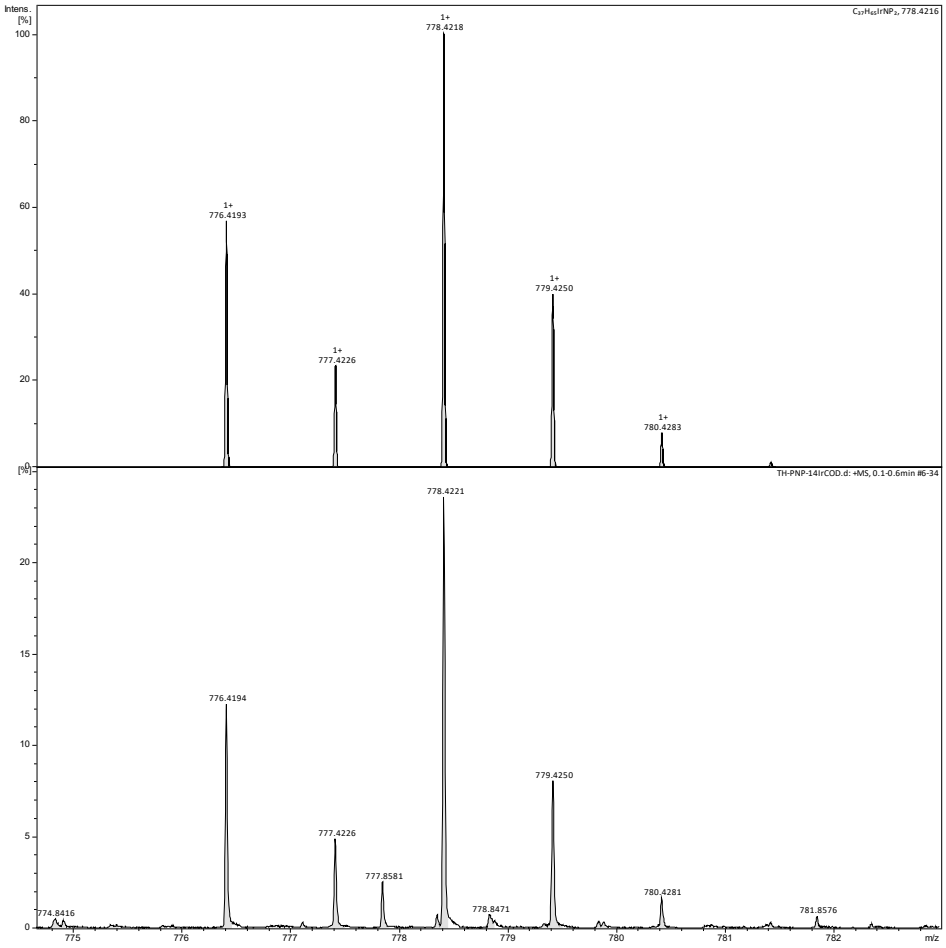

Figure S4. HR ESI-MS of **1**.

2 NMR scale reaction of 1 with dihydrogen

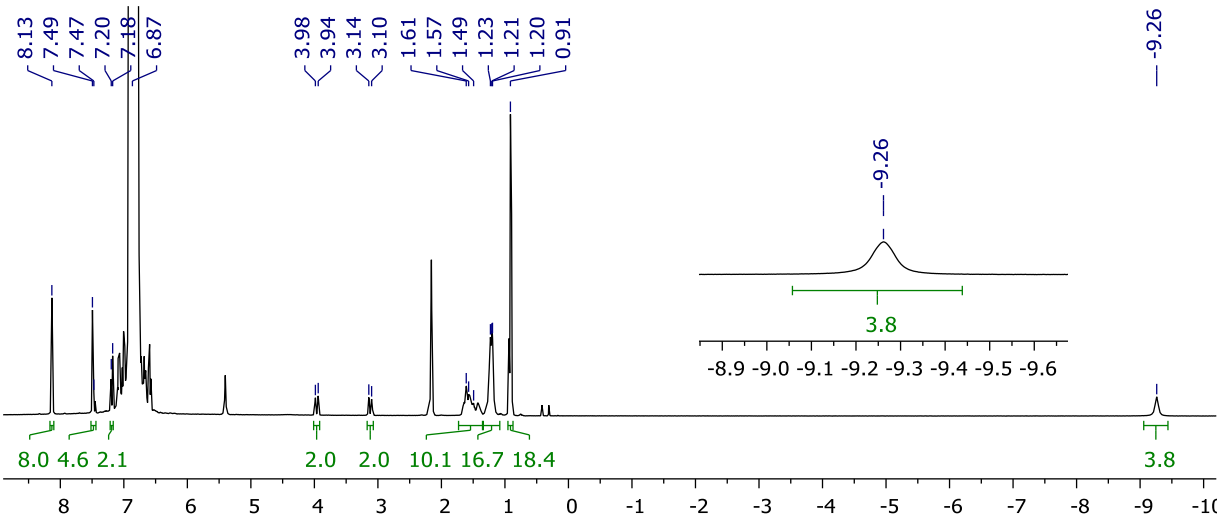

Figure S5. ^{1}H NMR spectrum showing formation of **4** (DFB, 400 MHz).

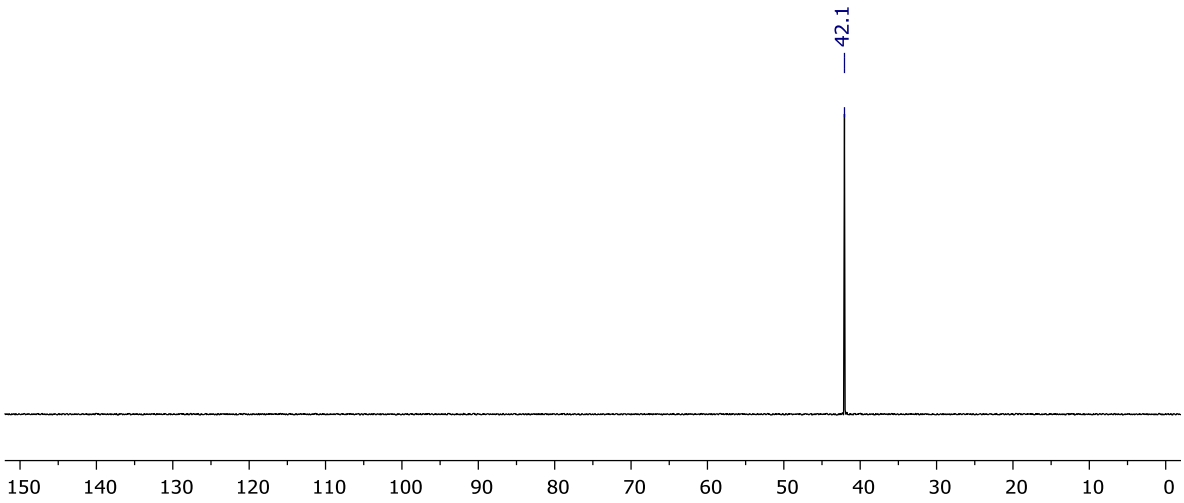

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum showing formation of **4** (DFB, 162 MHz).

3 Preparation of [Ir(PNP-14)(biph)][BAr$^{F}_{4}$] (2)

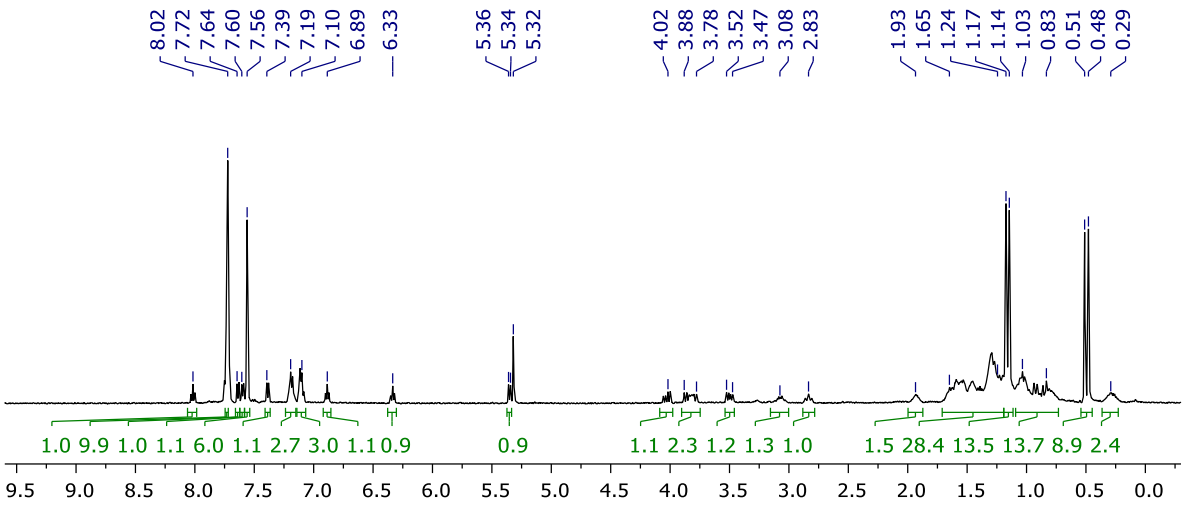

Figure S7. ^{1}H NMR spectrum of **2** (DFB, 500 MHz).

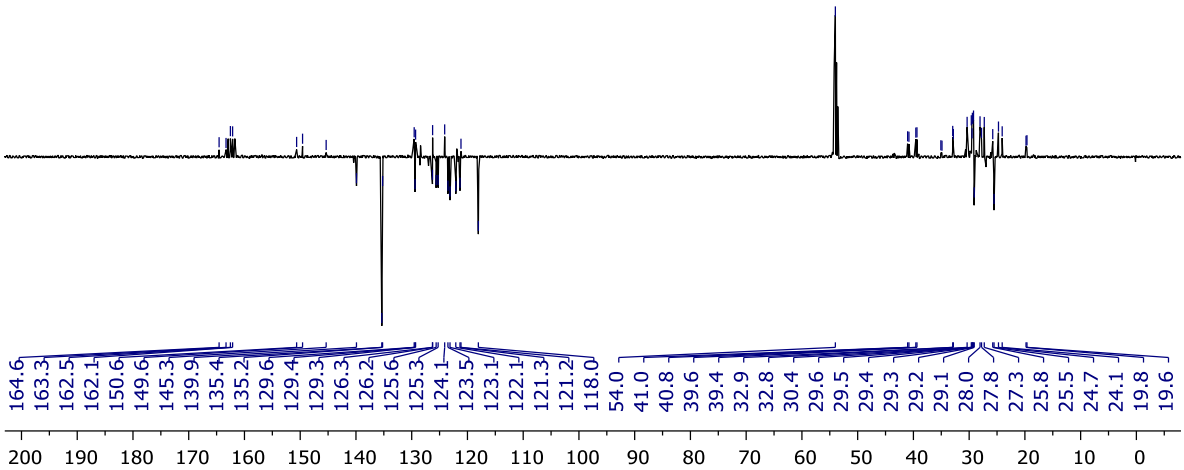

Figure S8. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2** (DFB, 126 MHz).

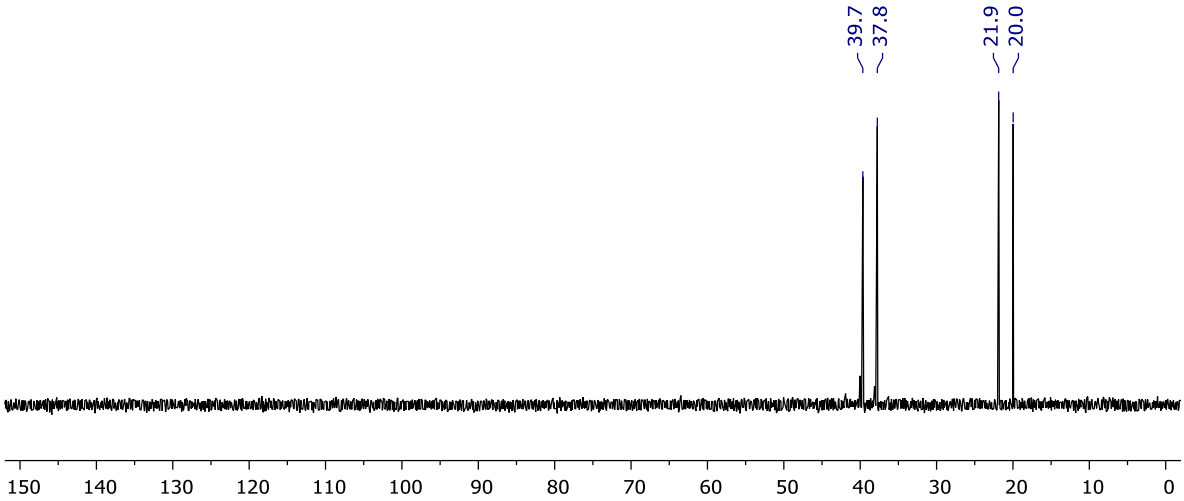

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (DFB, 162 MHz).

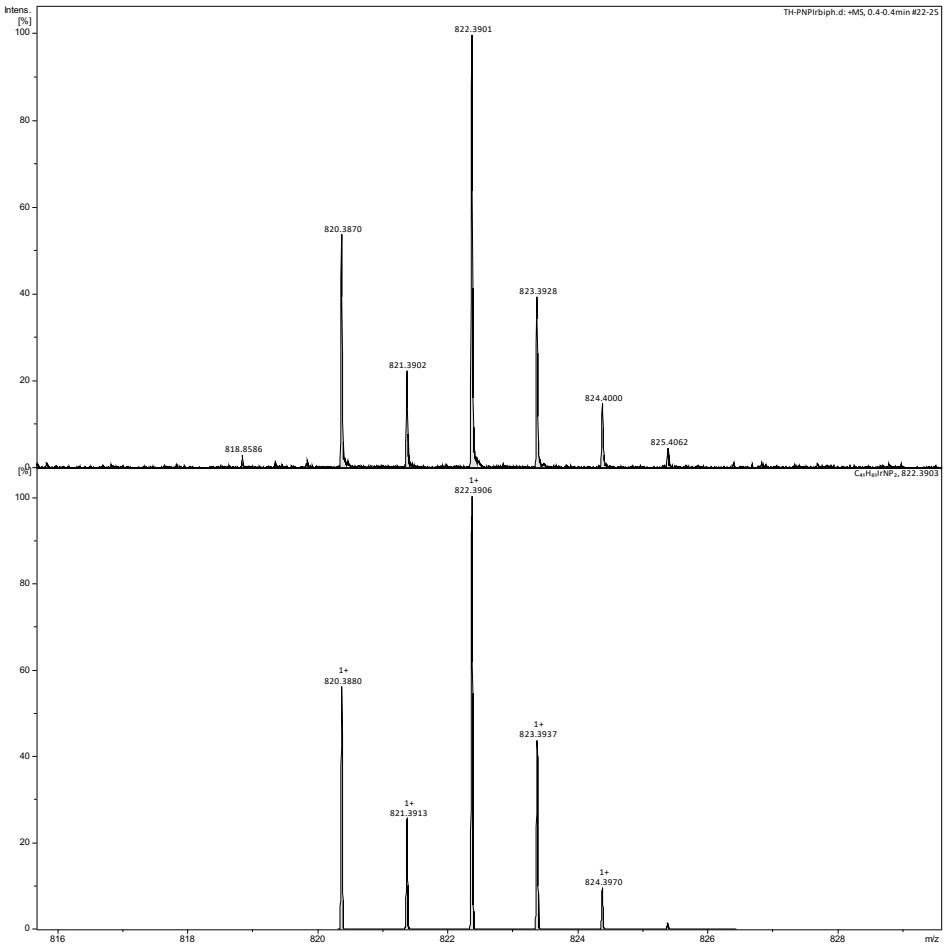

Figure S10. HR ESI-MS of **2**.

4 NMR scale reactions of 2

4.1 Synthesis of [Ir(PNP-14)(2-biphenyl)H][BAr$^{F}_{4}$] (**3**)

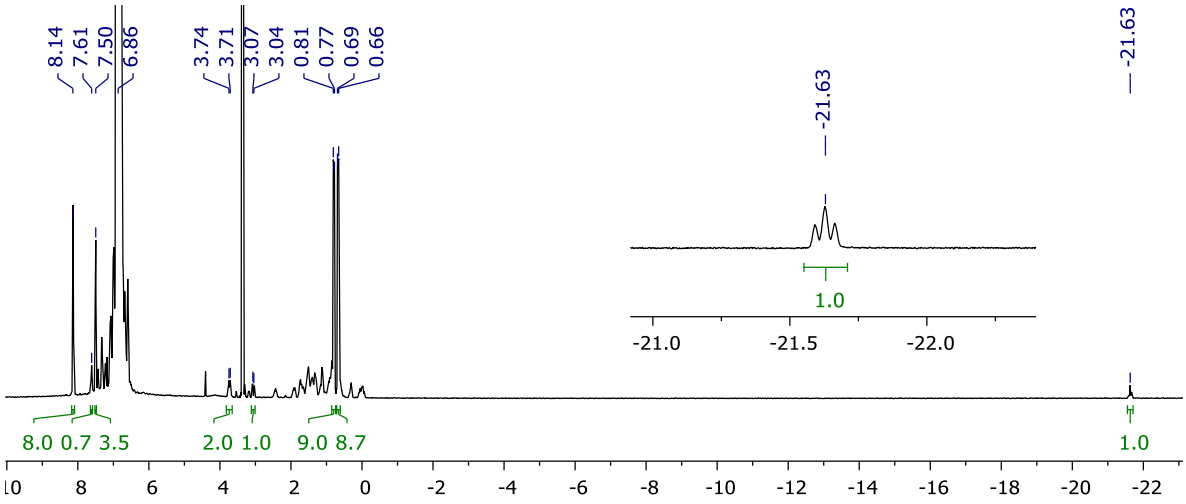

Figure S11. ^{1}H NMR spectrum showing formation of **3** (DFB, 400 MHz).

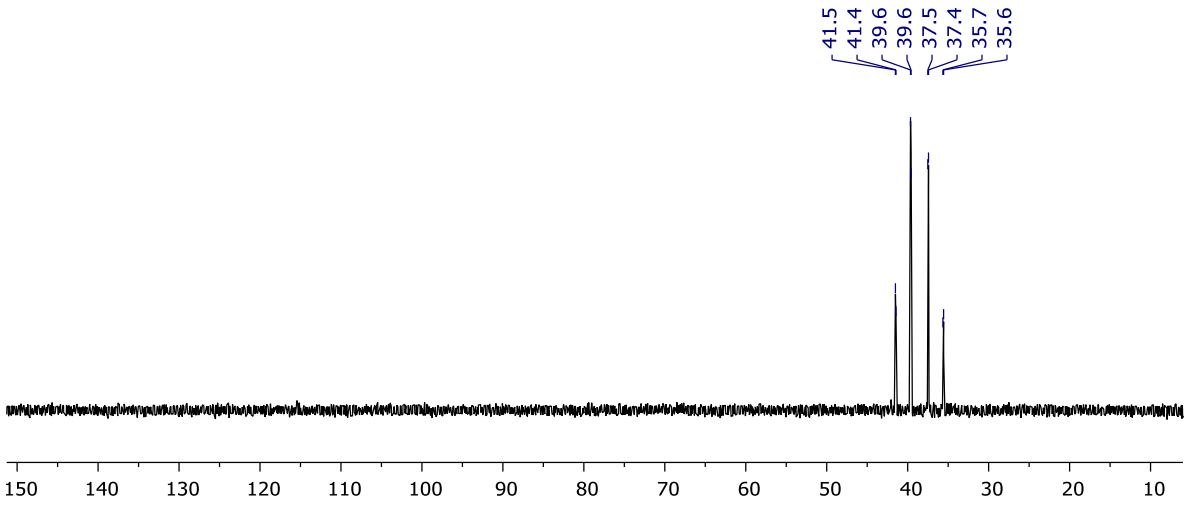

Figure S12. ^{31}P{^{1}H} NMR spectrum showing formation of **3** (DFB, 162 MHz).

4.2 Synthesis of [Ir(PNP-14)$H_2(H_2)$][BAr^F_4] (**4**)

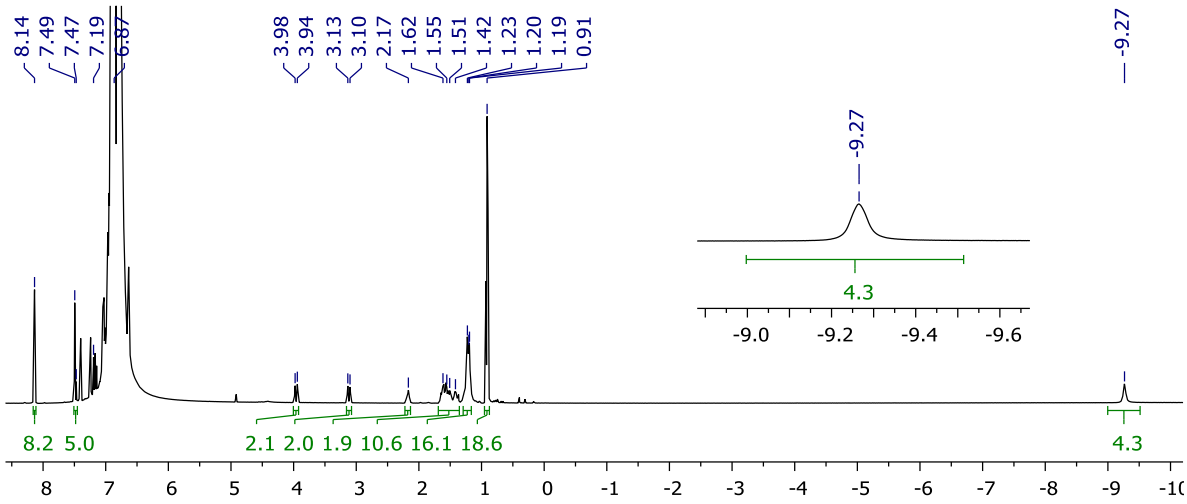

Figure S13. ^{1}H NMR spectrum showing formation of **4** (DFB, 500 MHz).

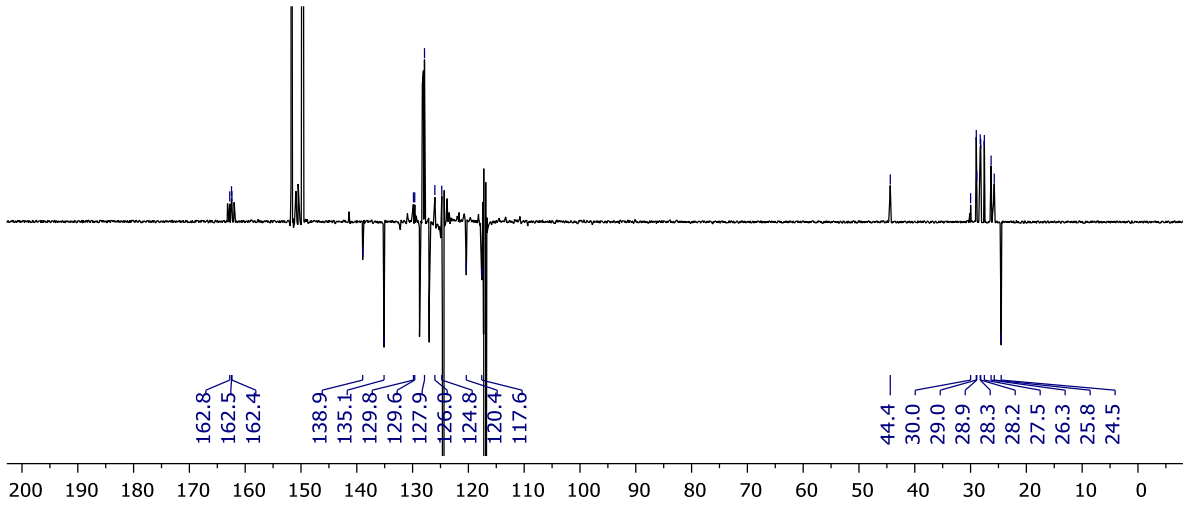

Figure S14. ^{13}C{^{1}H} APT NMR spectrum showing formation of **4** (DFB, 126 MHz).

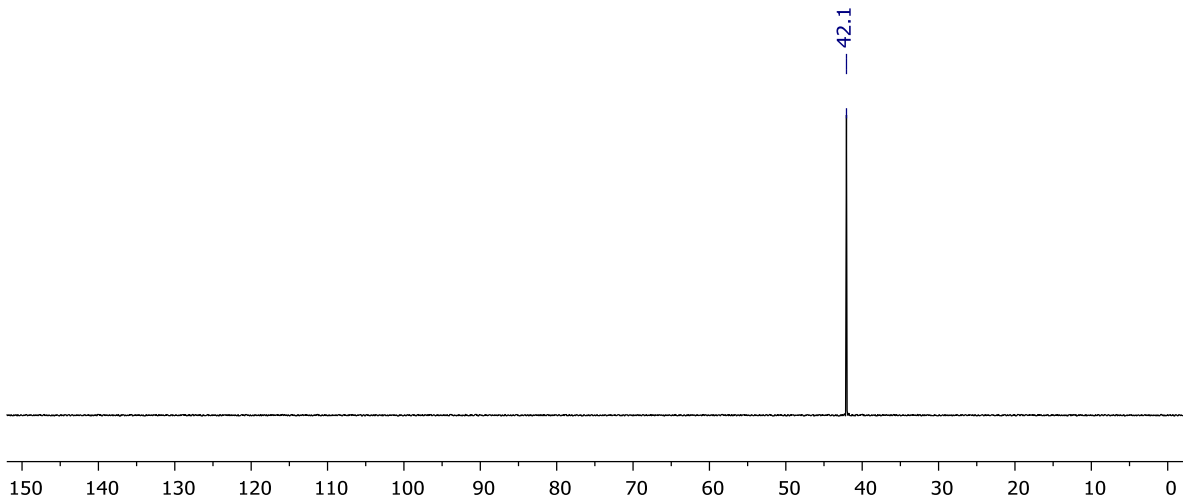

Figure S15. ^{31}P{^{1}H} NMR spectrum showing formation of **4** (DFB, 162 MHz).

4.3 Synthesis of $[Ir(PNP\text{-}14)H_2(C_2H_4)][BAr^F{}_4]$ (**5**)

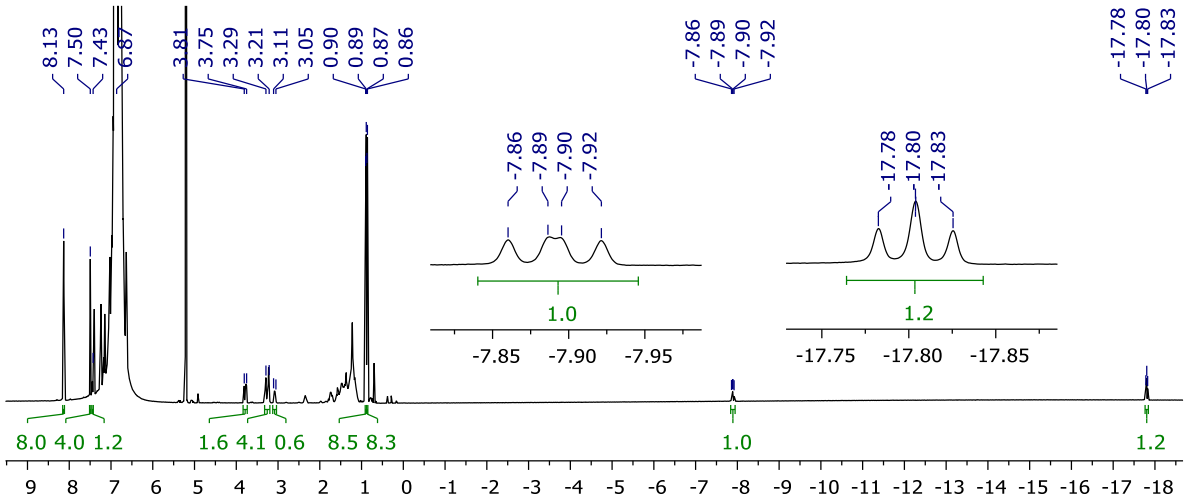

Figure S16. ^{1}H NMR spectrum showing formation of **5** (DFB, 500 MHz).

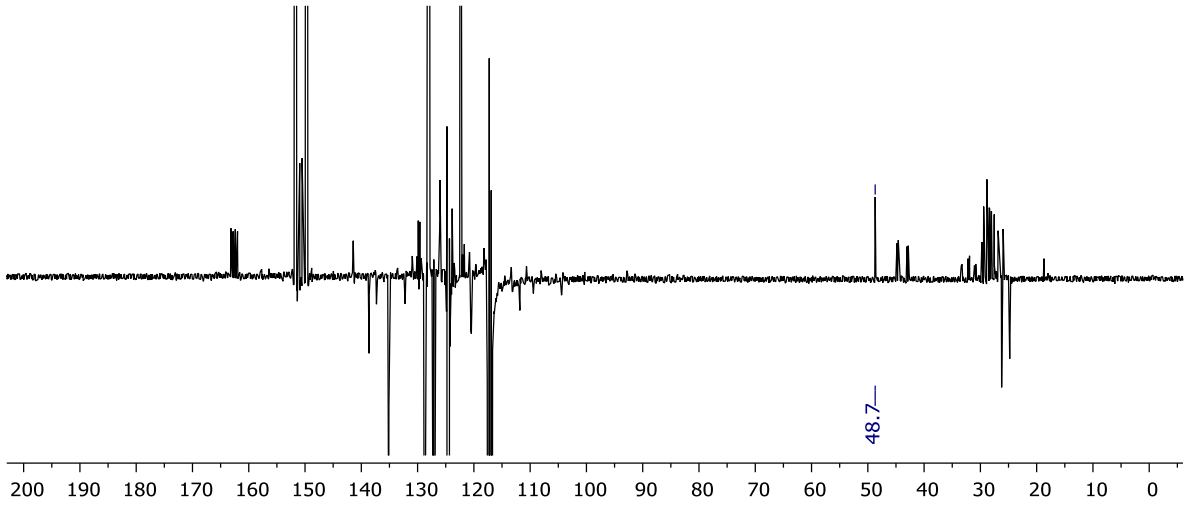

Figure S17. $^{13}C\{^{1}H\}$ APT NMR spectrum showing formation of **5** (DFB, 126 MHz).

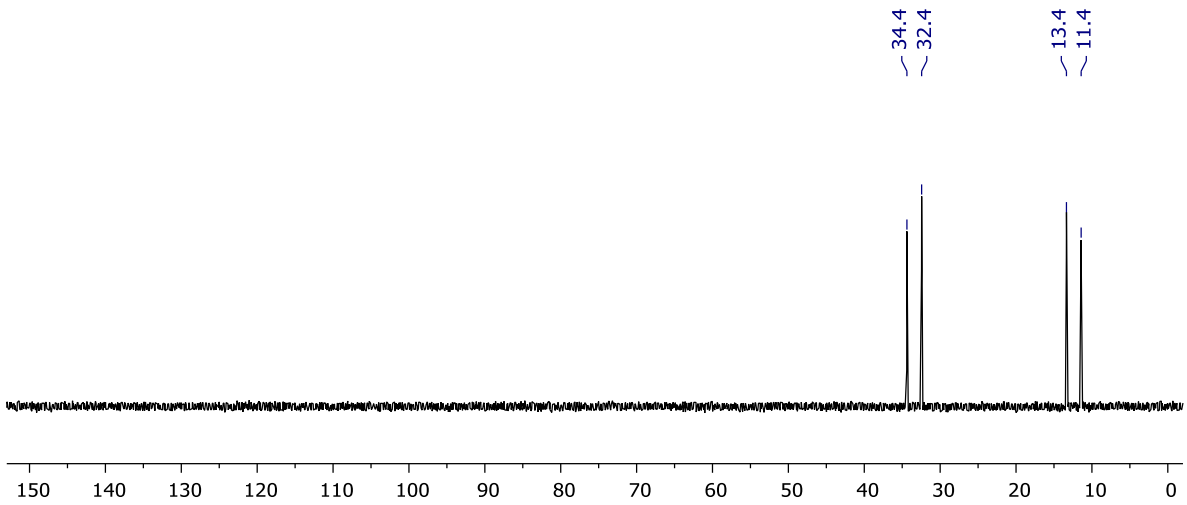

Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum showing formation of **5** (DFB, 162 MHz).

4.4 Synthesis of [Ir(PNP-14)(C_2H_4)$_2$][BAr^F_4] (**6**)

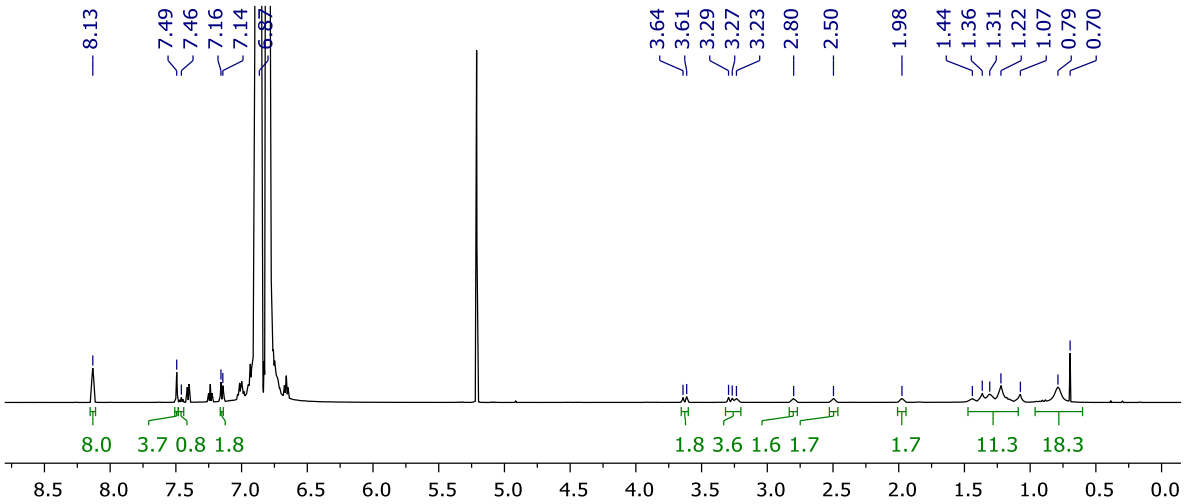

Figure S19. ^{1}H NMR spectrum showing formation of **6** (DFB, 600 MHz).

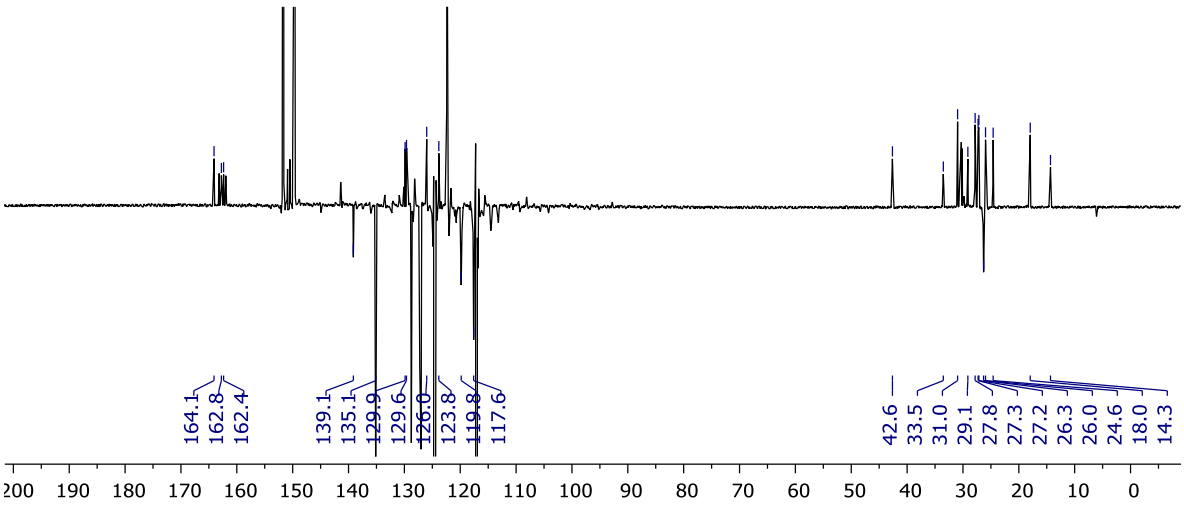

Figure S20. ^{13}C{^{1}H} APT NMR spectrum showing formation of **6** (DFB, 126 MHz).

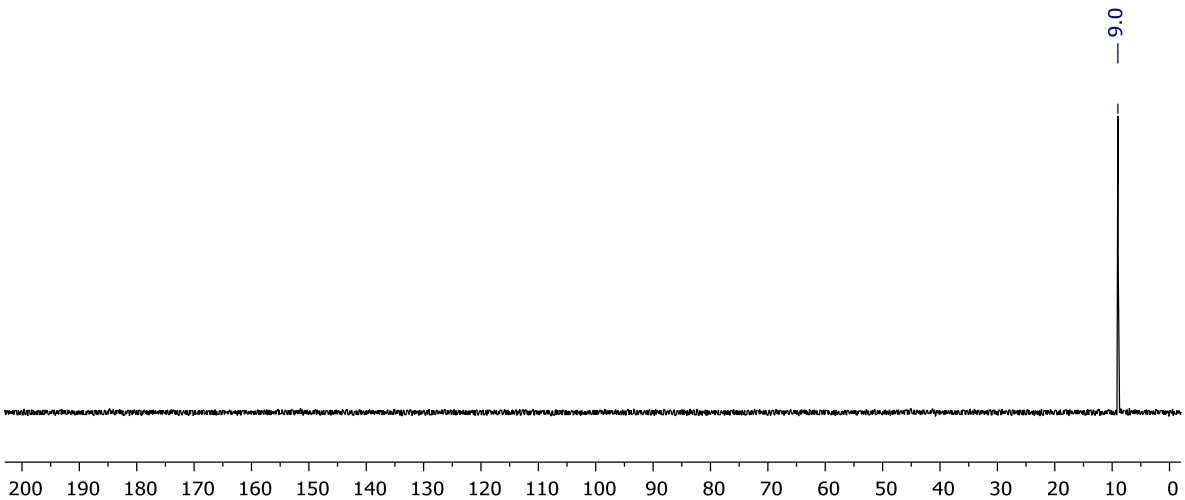

Figure S21. ^{31}P{^{1}H} NMR spectrum showing formation of **6** (DFB, 162 MHz).

4.5 Synthesis and isolation of [Ir(PNP-14)(CO)][BAr^F_4] (**8**)

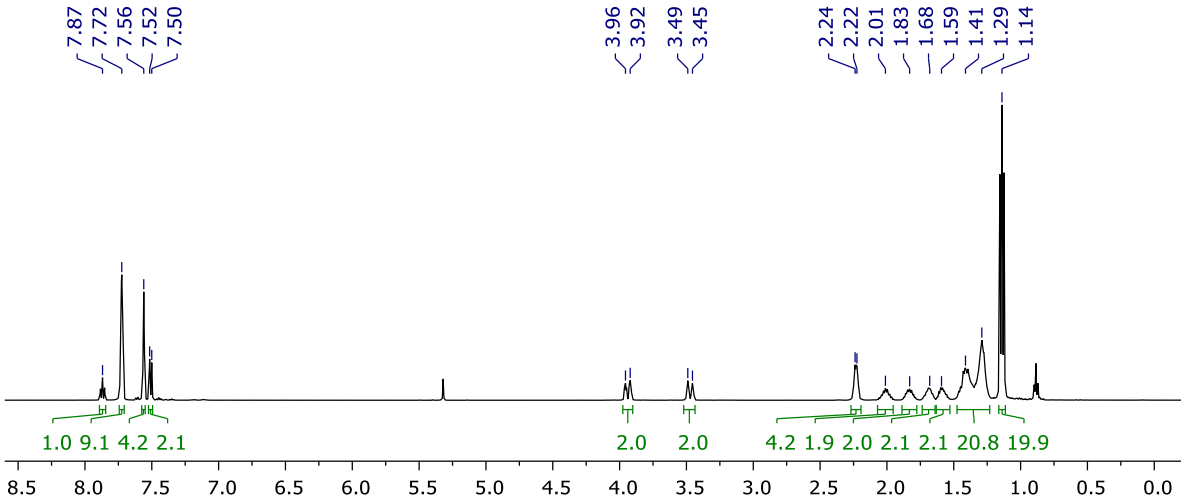

Figure S22. ^{1}H NMR spectrum of isolated **8** (CD_2Cl_2, 500 MHz).

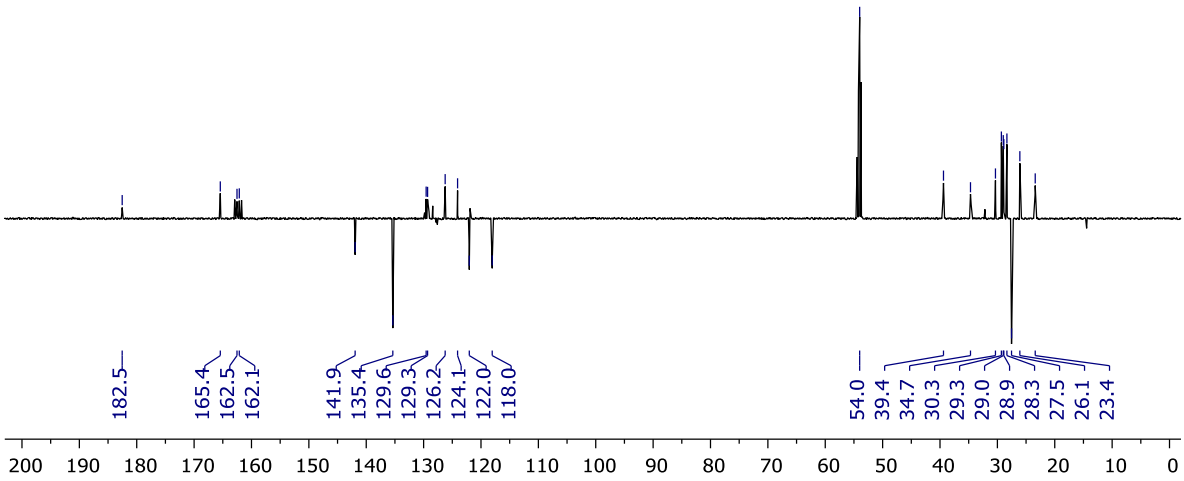

Figure S23. $^{13}C\{^1H\}$ APT NMR spectrum of isolated **8** (CD_2Cl_2, 126 MHz).

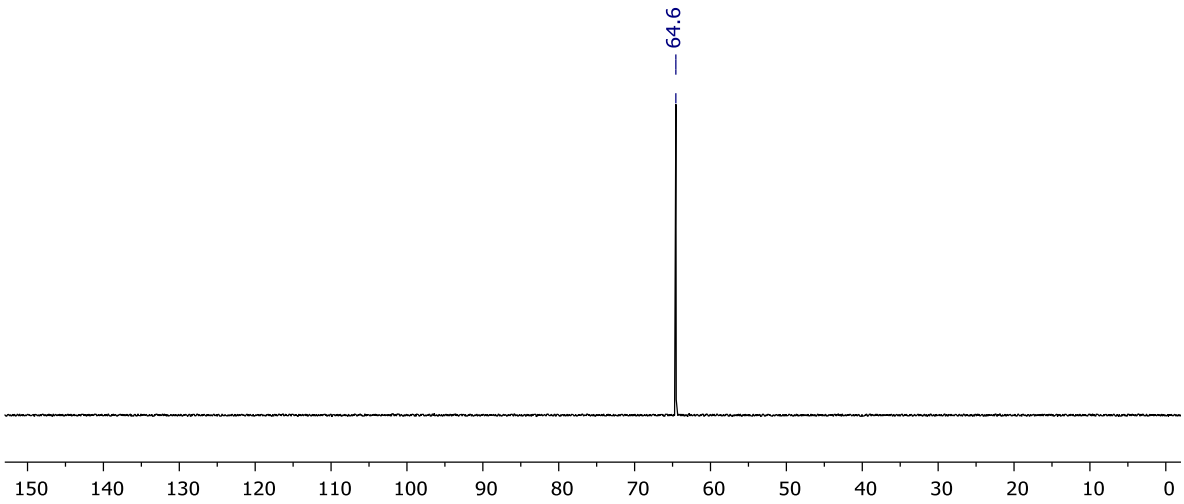

Figure S24. $^{31}P\{^1H\}$ NMR spectrum of isolated **8** (CD_2Cl_2, 162 MHz).

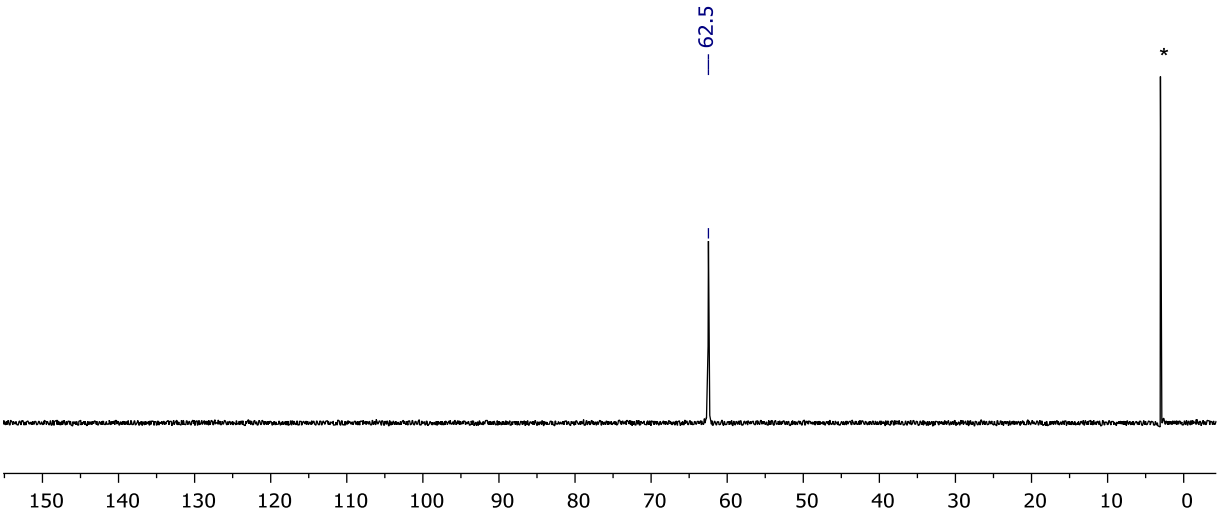

Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of isolated **8** (DFB, 162 MHz). * = internal reference.

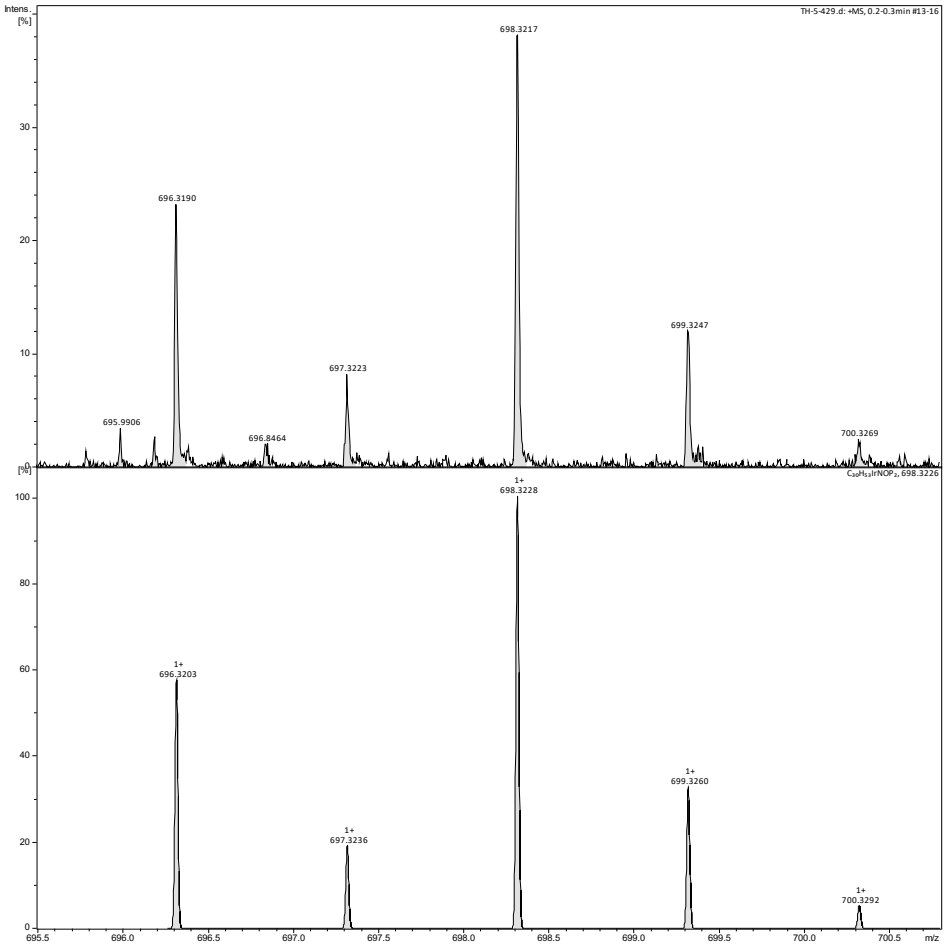

Figure S26. HR ESI-MS of isolated **8**.

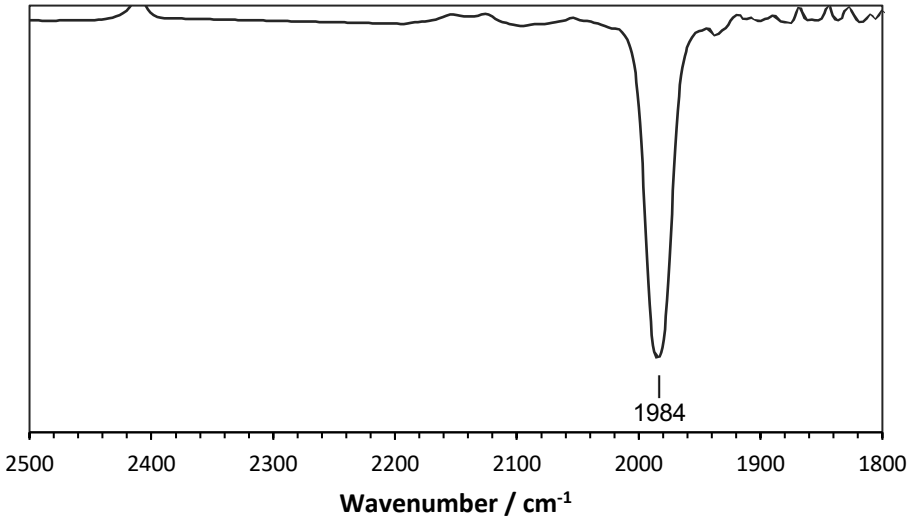

Figure S27. IR spectrum of isolated **8** recorded in CH_2Cl_2.

5 NMR scale reaction of [Ir(PNP-*t*Bu)(biph)][BAr$^F_4$] (II) with dihydrogen

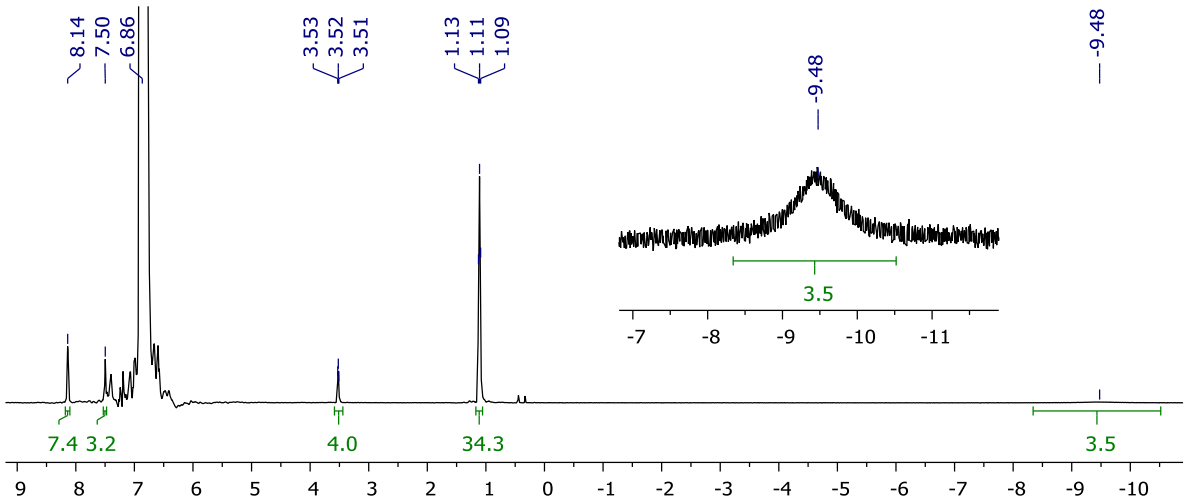

Figure S28. ^{1}H NMR spectrum showing formation of [Ir(PNP-*t*Bu)$H_2(H_2)$][BAr$^F_4$] (DFB, 400 MHz).

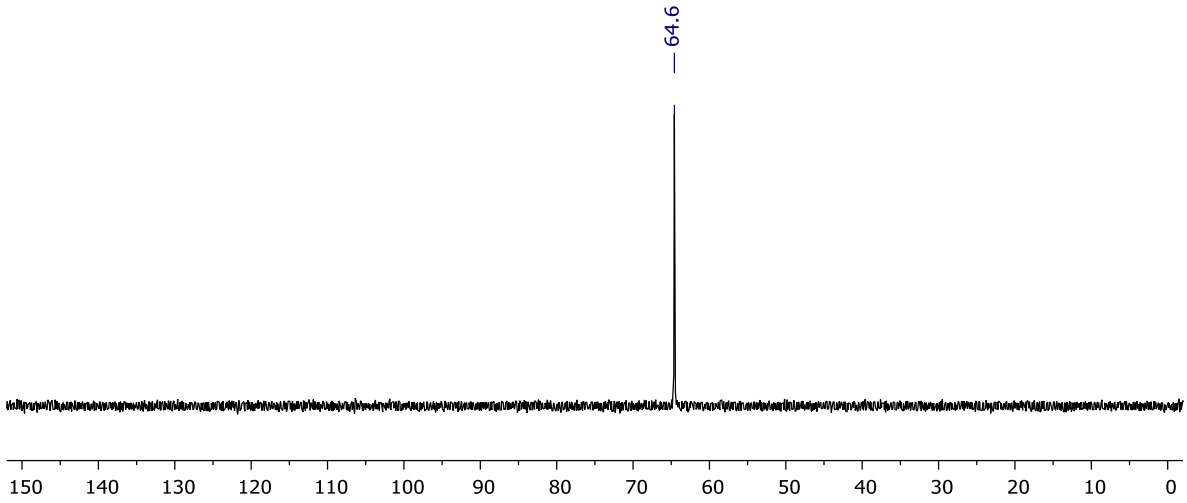

Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum showing formation of [Ir(PNP-*t*Bu)$H_2(H_2)$][$BAr^F{}_4$] (DFB, 162 MHz).

6 Preparation of [Ir(PNP-14*)H][$BAr^F{}_4$] (7)

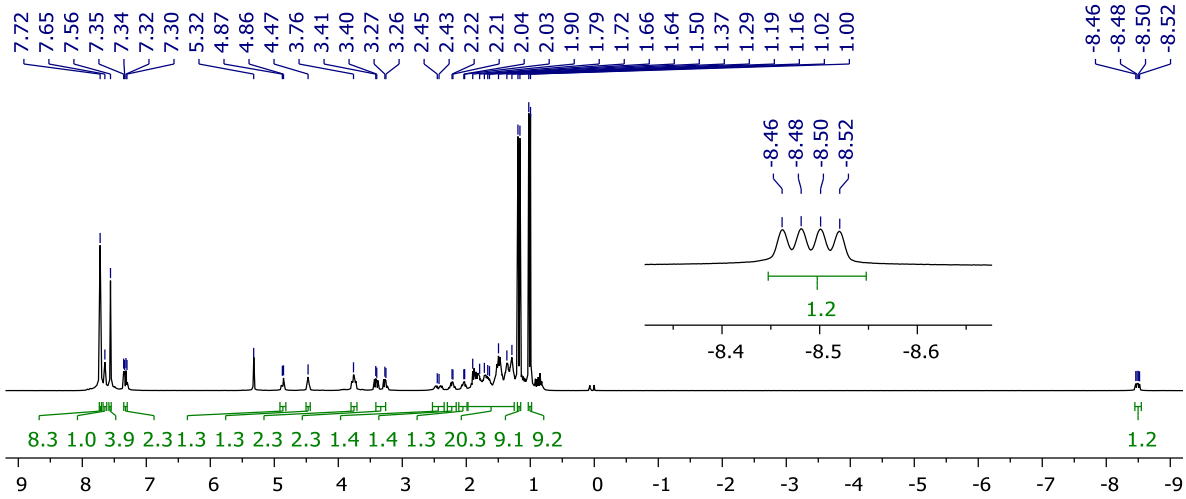

Figure S30. ^{1}H NMR spectrum of **7** (CD_2Cl_2, 500 MHz).

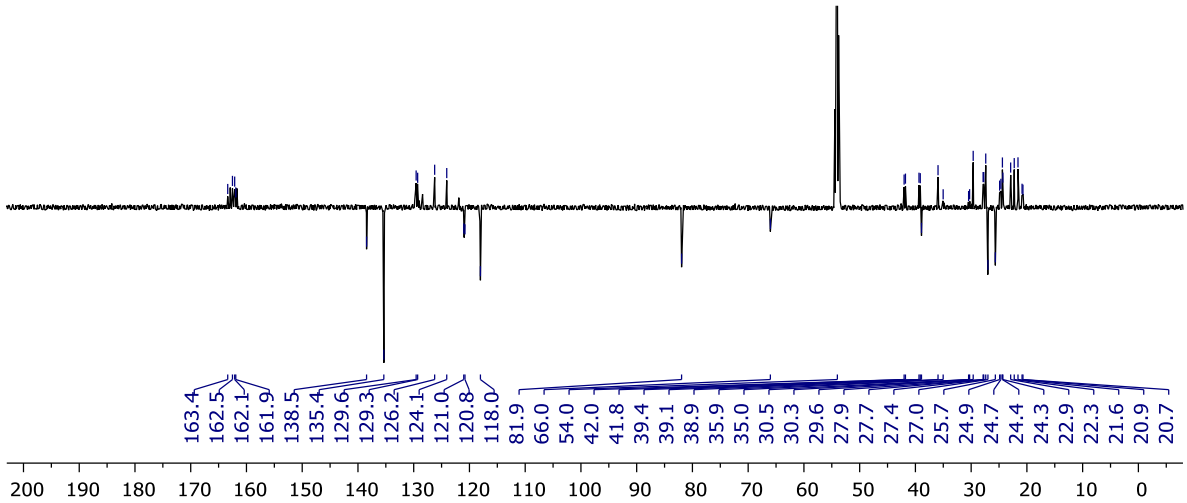

Figure S31. $^{13}C\{^{1}H\}$ APT NMR spectrum of **7** (CD_2Cl_2, 126 MHz).

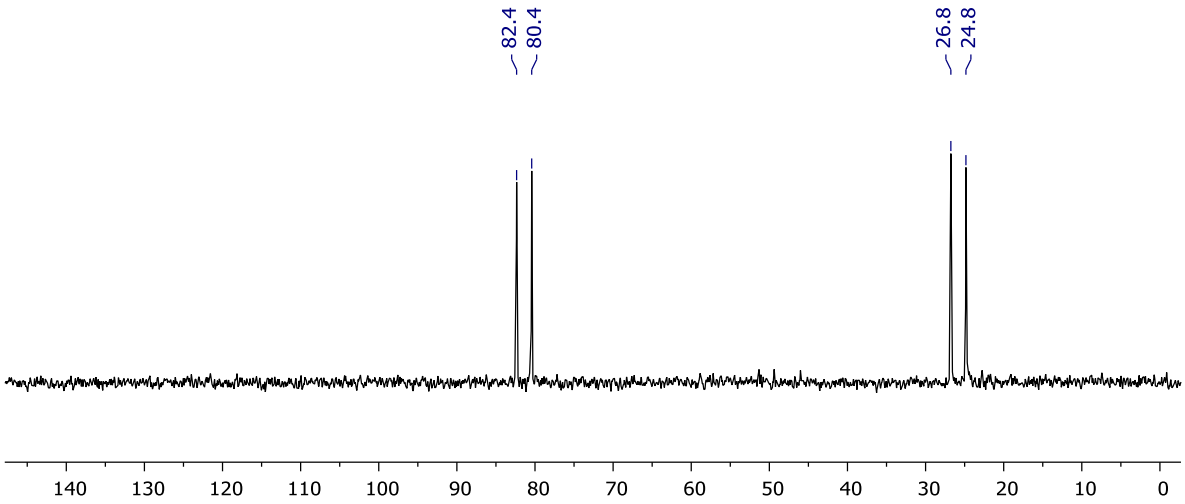

Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of **7** (CD_2Cl_2, 162 MHz).

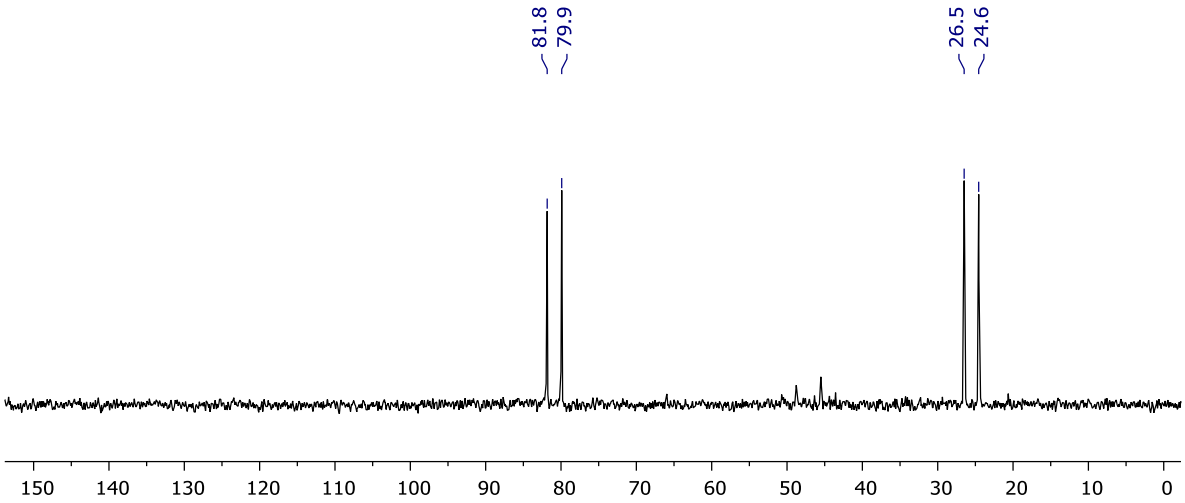

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **7** (DFB, 162 MHz).

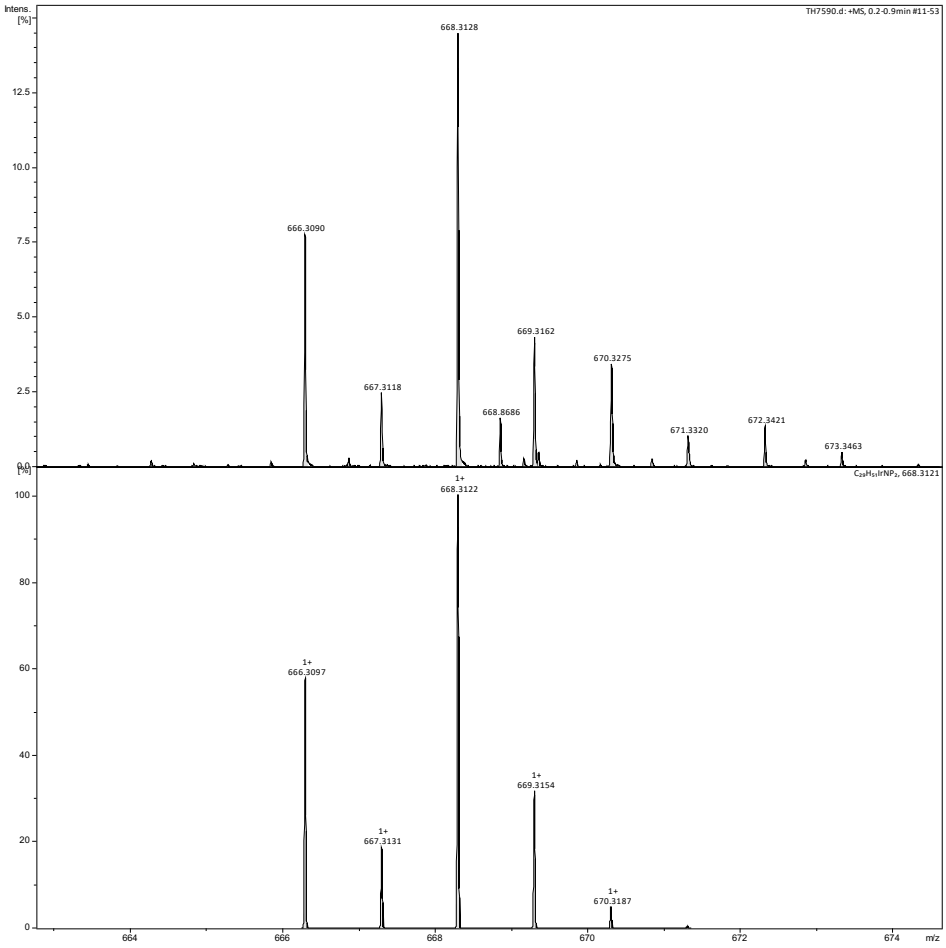

Figure S34. HR ESI-MS of **7**.

7 NMR scale reaction of 7 with dihydrogen

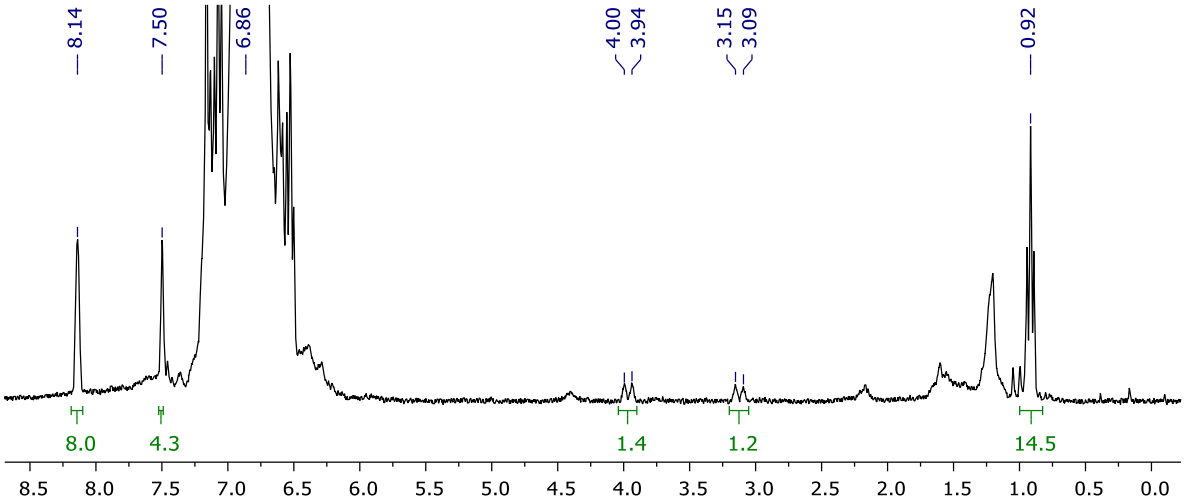

Figure S35. ^{1}H NMR spectrum showing formation of **4** (DFB, 300 MHz).

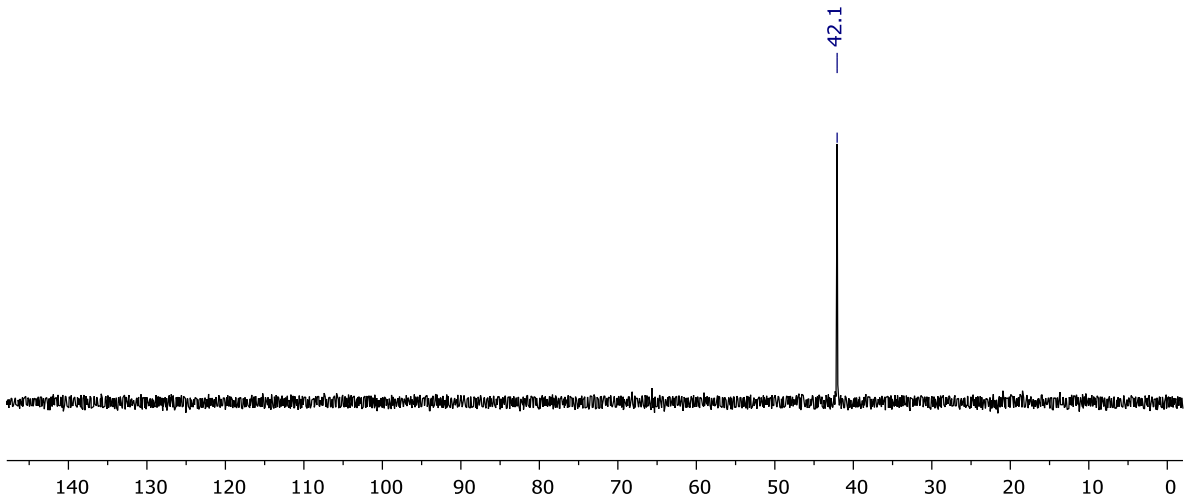

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum showing formation of **4** (DFB, 121 MHz).

8 Catalytic homocoupling of 3,3-dimethylbutyne promoted by 1

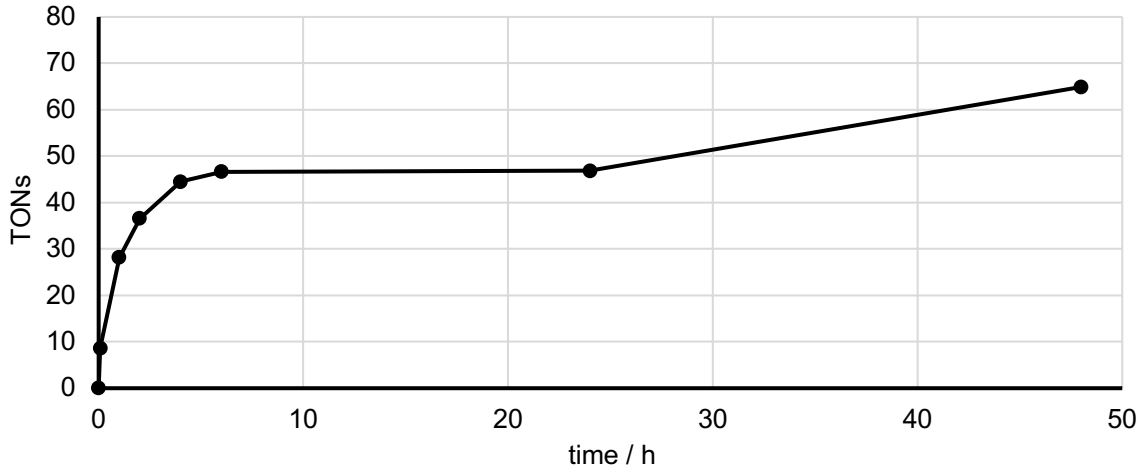

Figure S37. Catalytic homocoupling of 3,3-dimethylbutyne promoted by **1** (1 mol%, initially) and producing *Z*-*t*BuC≡CCHCH*t*Bu. Full experimental details provided in the manuscript. An additional 50 equivalents of substrate were added to the reaction mixture after 24 h.

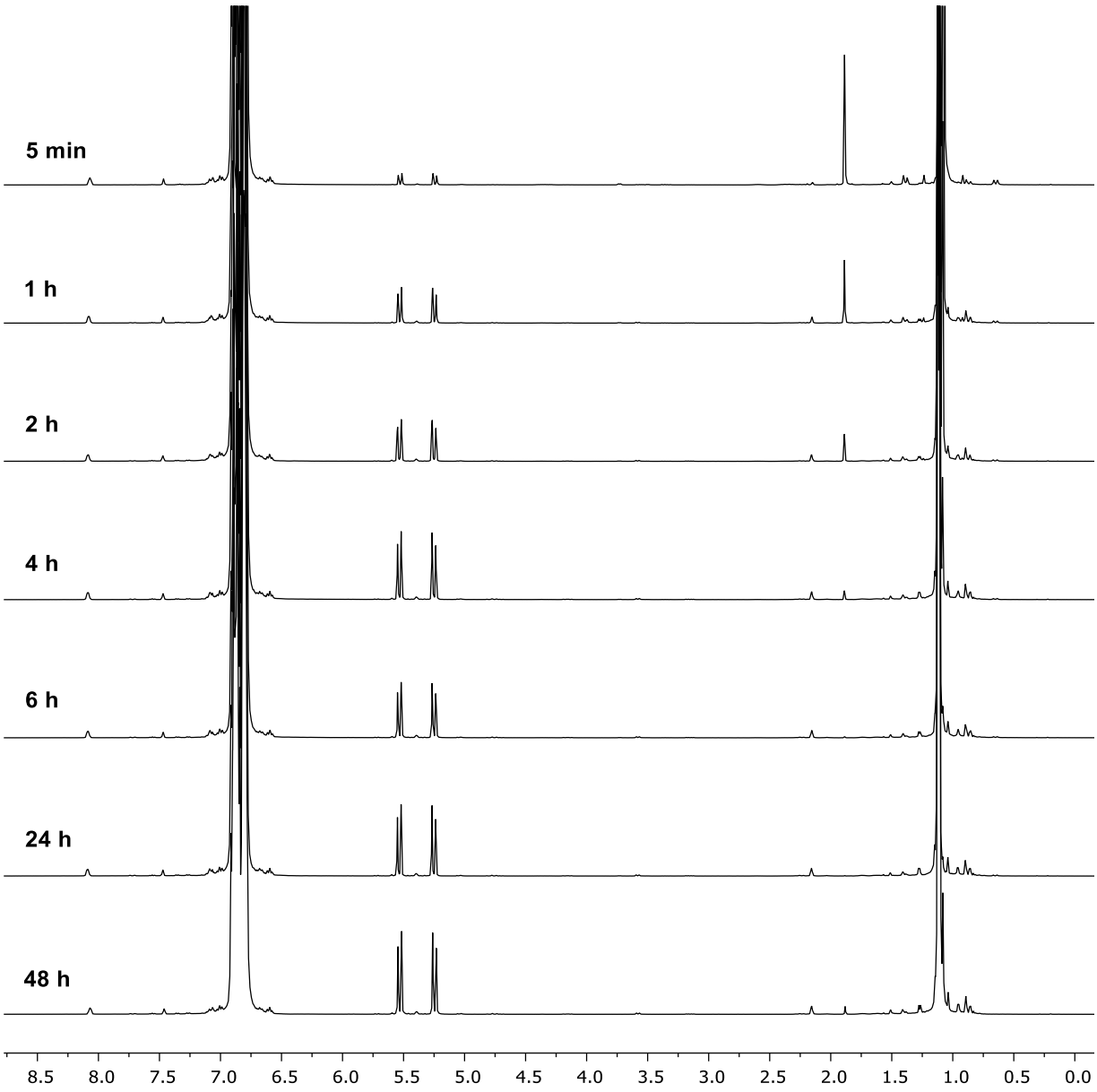

Figure S38. ^{1}H NMR spectra (DFB, 400 MHz) collected during the homocoupling of 3,3-dimethylbutyne promoted by **1** (1 mol%, initially) and producing *Z*-*t*BuC≡CCHCH*t*Bu. Full experimental details provided in the manuscript. An additional 50 equivalents of substrate were added to the reaction mixture after 24 h.

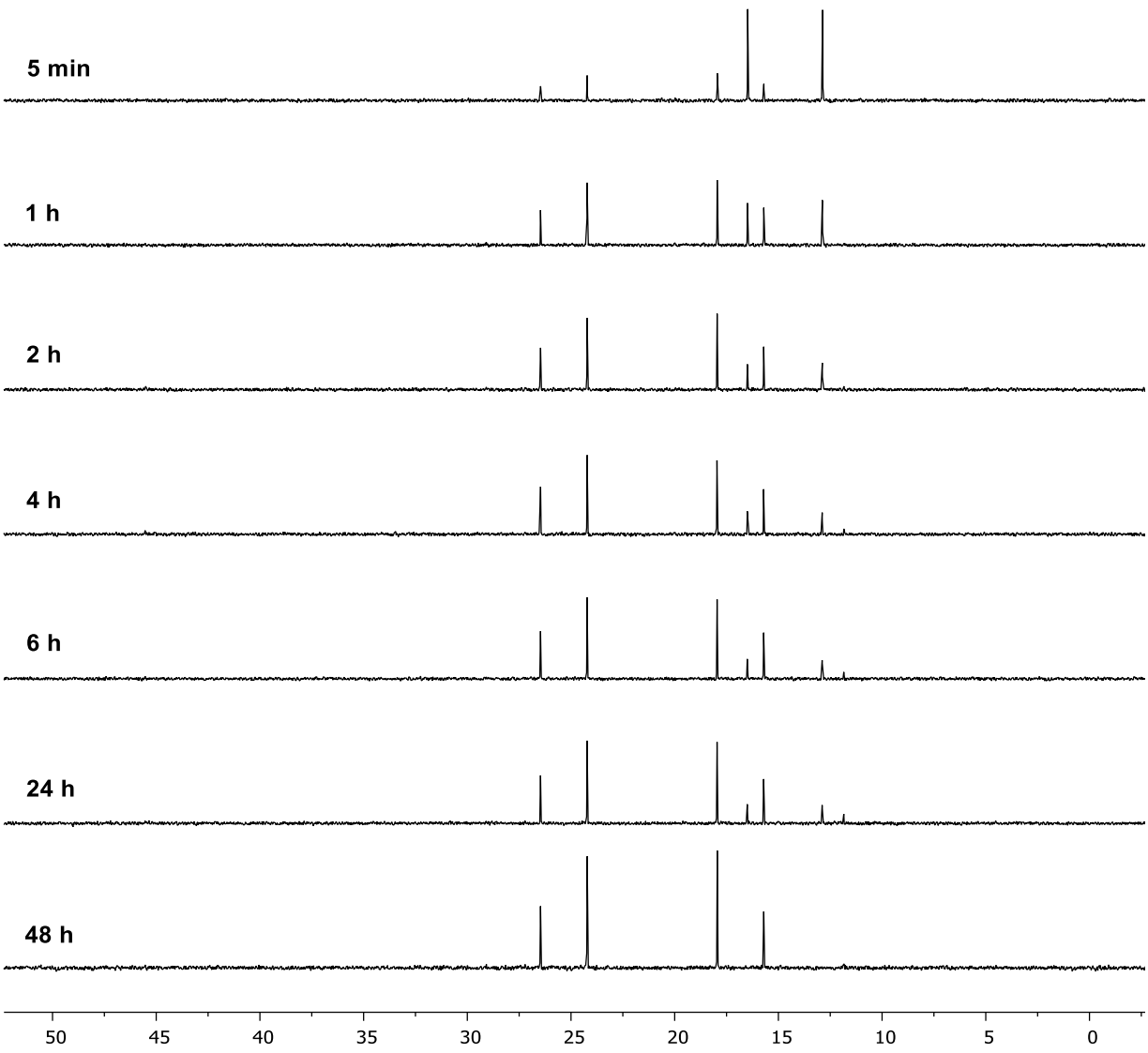

Figure S39. $^{31}P\{^{1}H\}$ NMR spectra (DFB, 162 MHz) collected during the homocoupling of 3,3-dimethylbutyne promoted by **1** (1 mol%, initially) and producing *Z*-*t*BuC≡CCHCH*t*Bu. Full experimental details provided in the manuscript. An additional 50 equivalents of substrate were added to the reaction mixture after 24 h.

9 Catalytic homocoupling of 3,3-dimethylbutyne promoted by 6

A solution of **6** (6.4 μmol, generated in situ) in DFB (512 μL) within a J. Young NMR tube was treated with a solution of 3,3-dimethylbutyne (79 μL, 642 μmol) and the resulting homocoupling reaction producing only *Z*-*t*BuC≡CCHCH*t*Bu followed at RT *in situ* using NMR spectroscopy. The solution was mixed constantly when not in the spectrometer. After 6 h the homocoupling was complete and **10** was observed as the major organometallic species (*ca.* 70%).

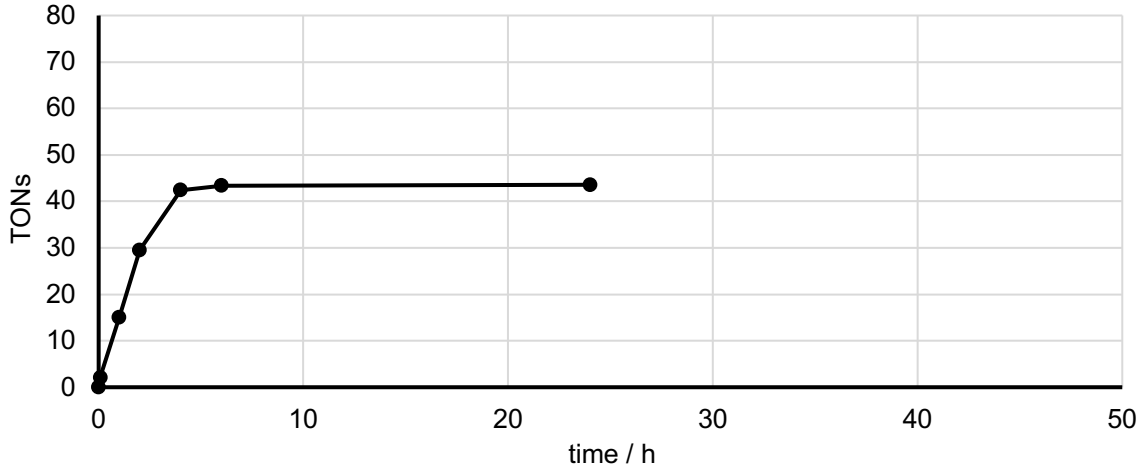

Figure S40. Catalytic homocoupling of 3,3-dimethylbutyne promoted by **6** (1 mol%) and producing *Z*-*t*BuC≡CCHCH*t*Bu.

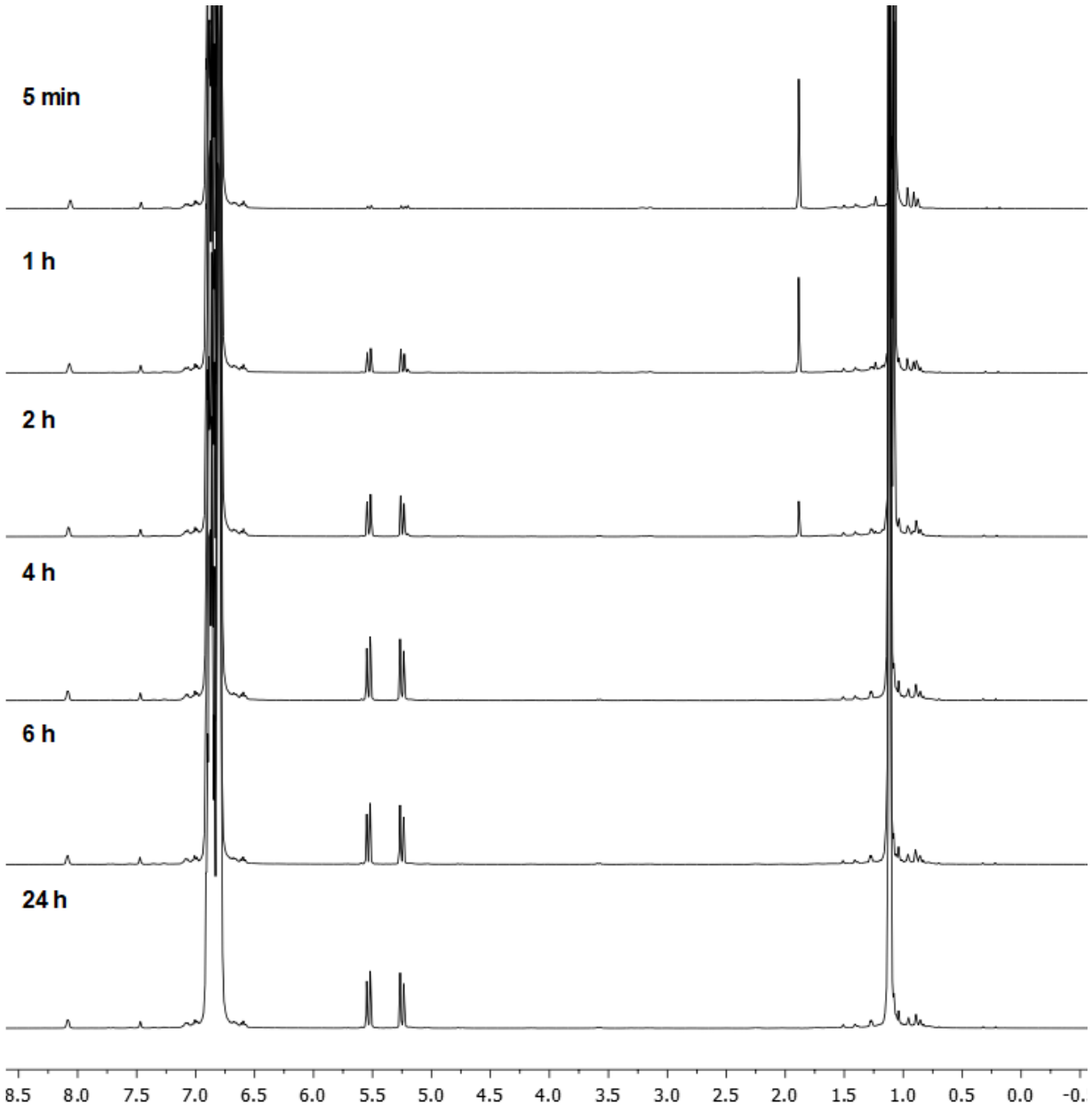

Figure S41. ^{1}H NMR spectra (DFB, 400 MHz) collected during the homocoupling of 3,3-dimethylbutyne promoted by **6** (1 mol%) and producing *Z*-*t*BuC≡CCHCH*t*Bu.

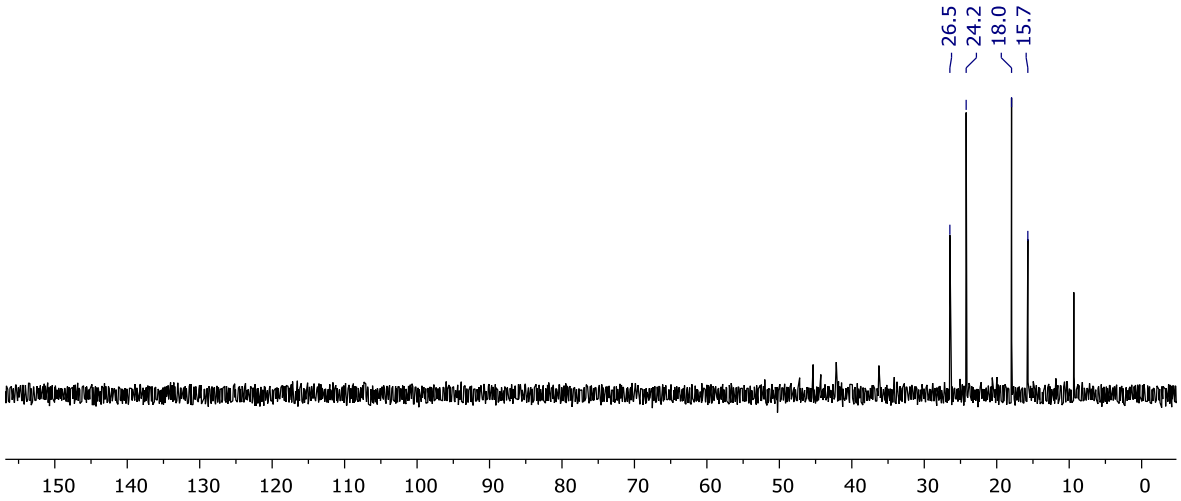

Figure S42. $^{31}P\{^{1}H\}$ NMR spectrum (DFB, 162 MHz) collected during the homocoupling of 3,3-dimethylbutyne promoted by **6** (1 mol%) and producing *Z*-*t*BuC≡CCHCH*t*Bu (6 h).

10 Preparation of [Ir(PNP-14)(η^3-*E*-C(C≡C*t*Bu)CH*t*Bu)(η^1-*E*-CHCH*t*Bu)][BAr^F_4] (10)

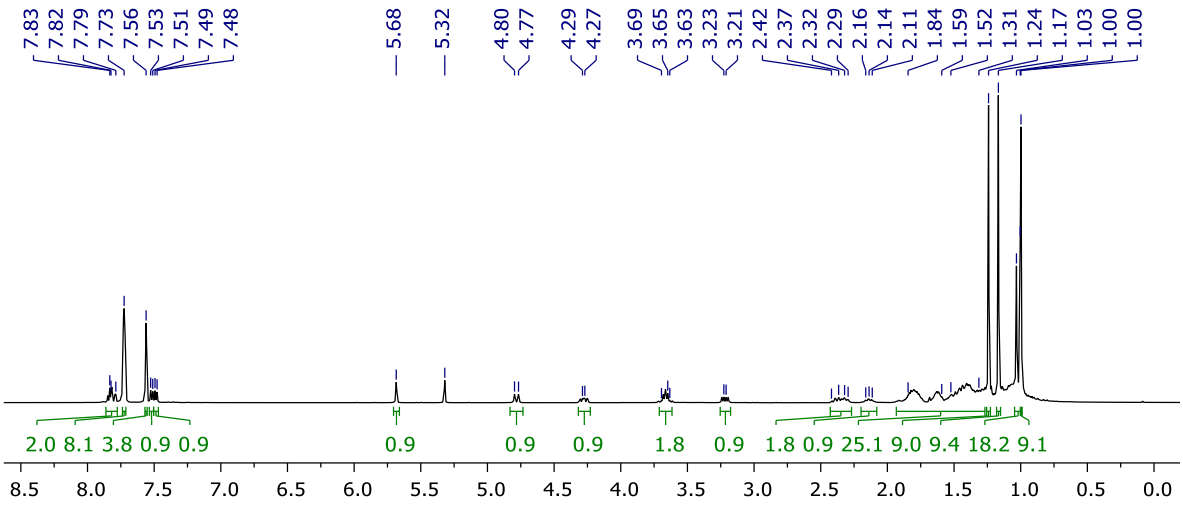

Figure S43. ^{1}H NMR spectrum of **10** (CD_2Cl_2, 500 MHz).

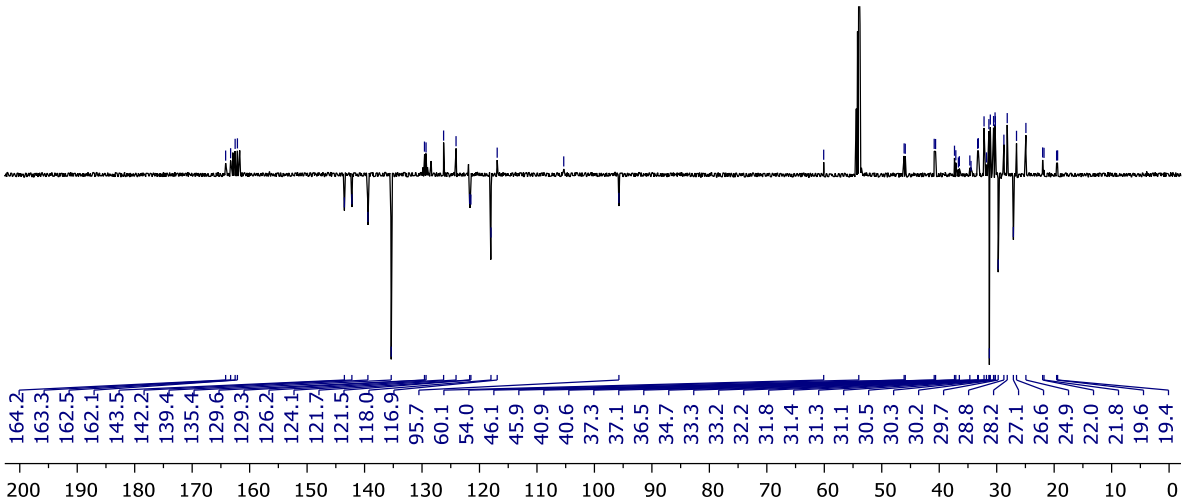

Figure S44. $^{13}C\{^{1}H\}$ APT NMR spectrum of **10** (CD_2Cl_2, 126 MHz).

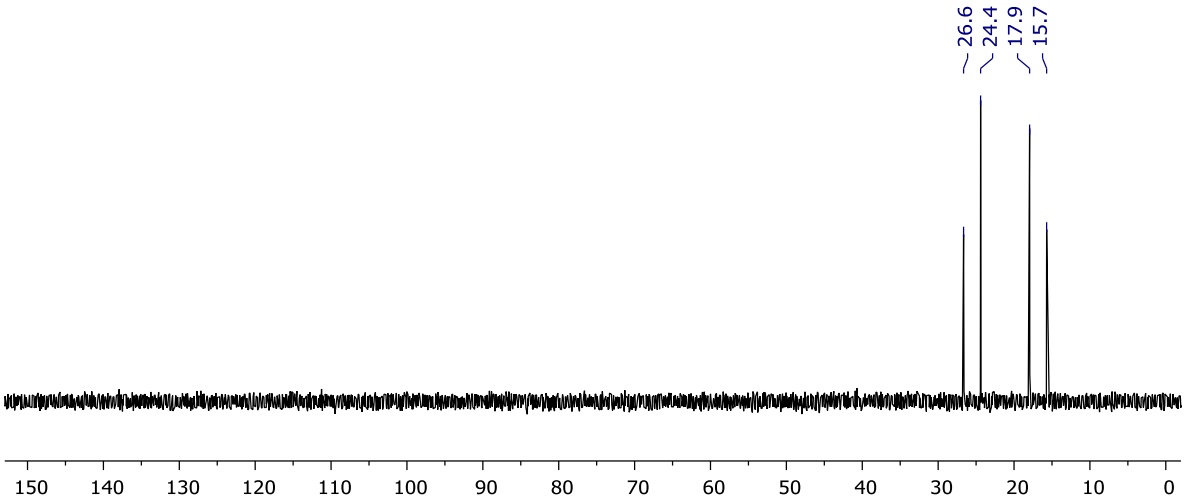

Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum of **10** (CD_2Cl_2, 162 MHz).

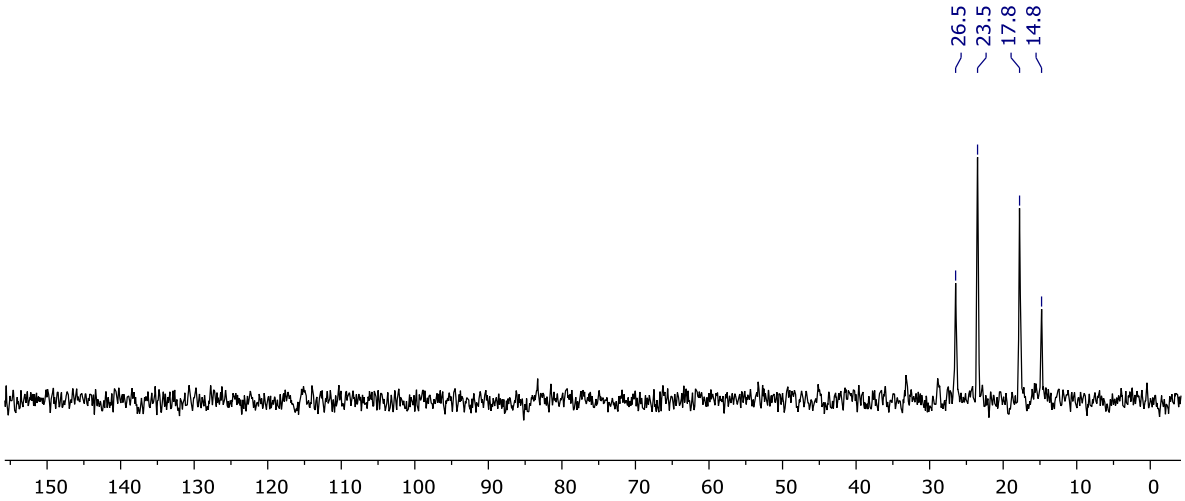

Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **10** (DFB, 121 MHz).

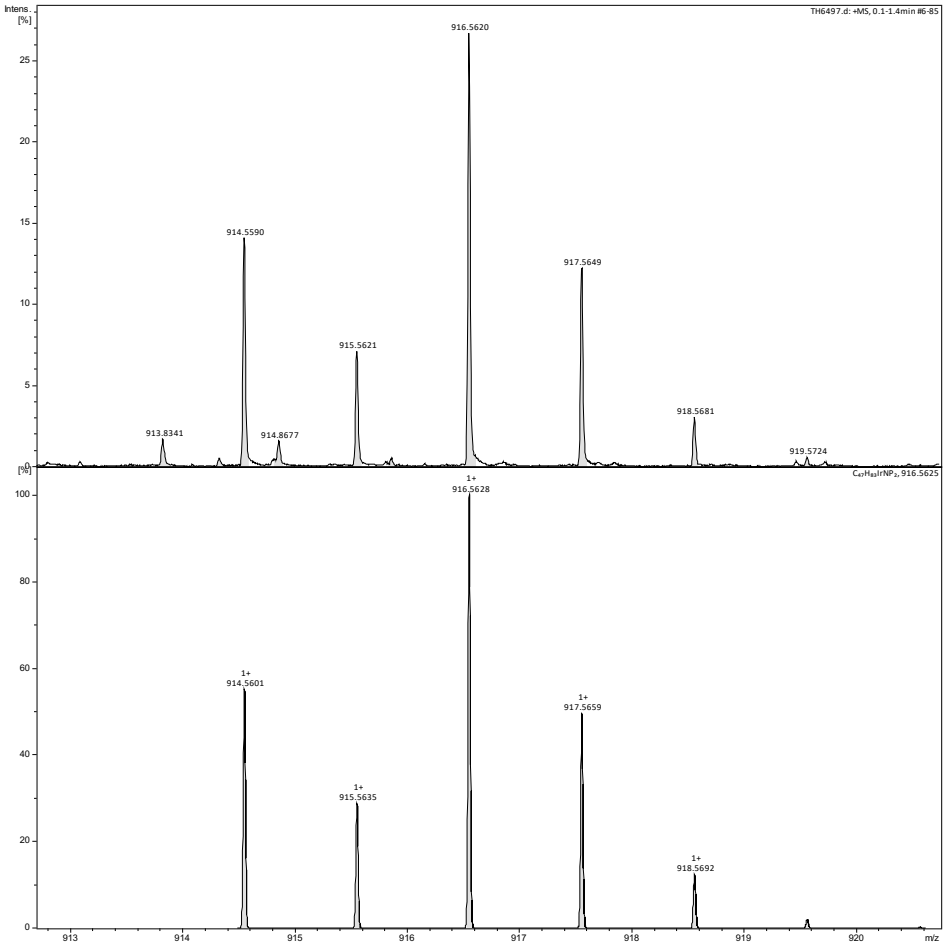

Figure S47. HR ESI-MS of **10**.

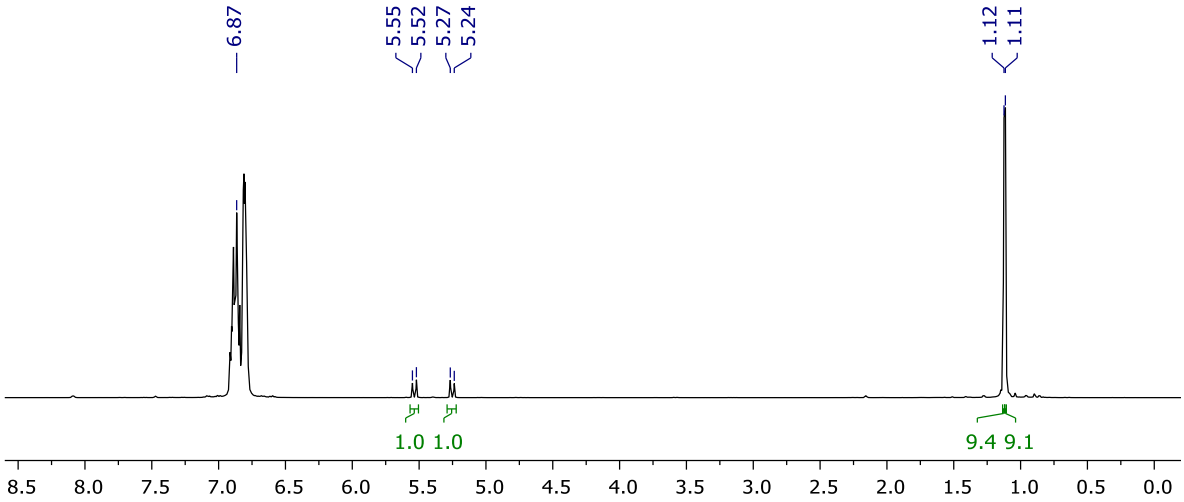

Figure S48. ^{1}H NMR spectrum of *Z*-*t*BuC≡CCHCH*t*Bu isolated during the preparation of **10** (DFB, 400 MHz).

11 NMR scale reaction of 1 with *Z*-*t*BuC≡CCHCH*t*Bu

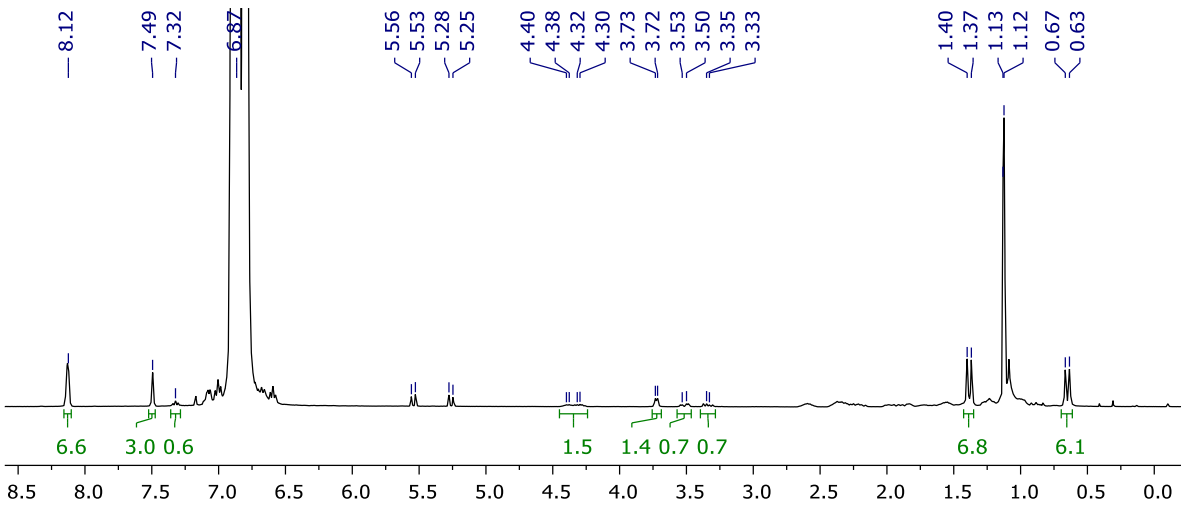

Figure S49. ^{1}H NMR spectrum of the reaction of **1** with *Z*-*t*BuC≡CCHCH*t*Bu (DFB, 400 MHz).

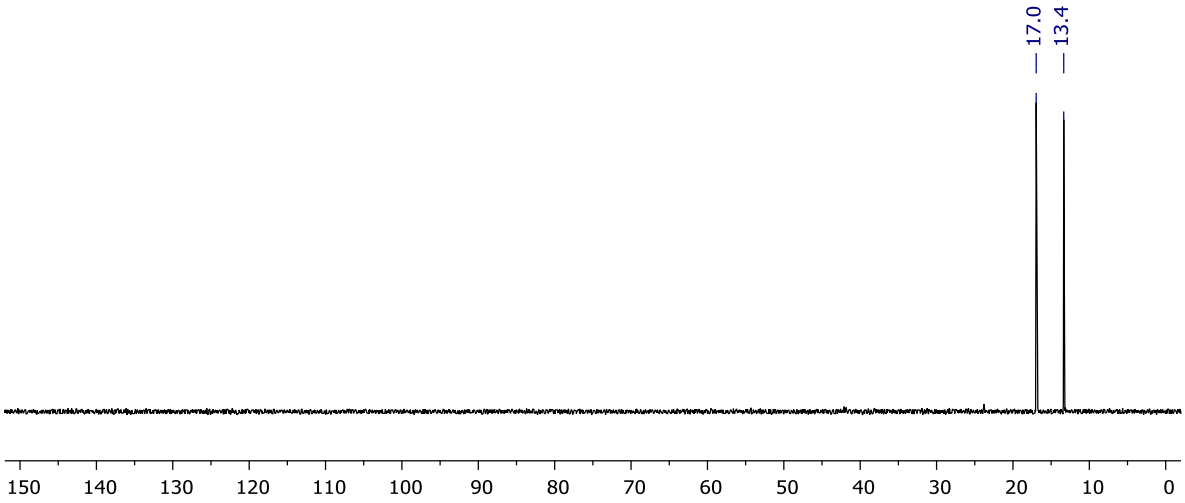

Figure S50. ^{31}P{^{1}H} NMR spectrum of the reaction of **1** with *Z*-*t*BuC≡CCHCH*t*Bu (DFB, 162 MHz).

12 Synthesis and characterisation of [Rh(PNP-14)(η^2-norbornene)][BAr$^F_4$]

A solution of [Rh(PNP-14)(H$_2$)][BAr$^F_4$] (18.6 µmol, generated *in situ* as described in *Dalton Trans.*, 2020, **49**, 2077 – 2086) in DFB (314 µL) was treated with a solution of norbornene in DFB (186 µL, 0.50 M, 93.0 µmol) and stirred at RT for 16 h. The volatiles were removed *in vacuo* and the resulting yellow oil washed with SiMe$_4$ (2 × 0.5 mL) and then dried under vacuum. Recrystallisation by slow diffusion of SiMe$_4$ into an Et$_2$O solution at 4 °C afforded the product as a yellow crystalline solid. Yield: 19.8 mg (12.9 µmol, 69%).

^{1}H NMR (500 MHz, DFB): δ 8.11 – 8.16 (m, 8H, Ar^F), 7.50 (br, 4H, Ar^F), 7.45 (t, $^{3}J_{HH}$ = 7.7, 1H, py), 7.13 (obscured, 1H, py), 7.05 (obscured, 1H, py), 3.67 (app t, J = 7, 1H, Rh(CH=CH)), 3.03 – 3.30 (m, 5H, 4×pyC<u>H</u>$_2$ + 1×Rh(CH=CH) [δ 3.15]), 2.84 (br d, $^{3}J_{HH}$ = 3.3, 1H, CH{NBE}), 2.81 (br d, $^{3}J_{HH}$ = 3.4, 1H, CH{NBE}), 0.90 – 2.39 (m, 32H, CH$_2$ + 4×CH$_2$CH$_2${NBE} [δ 1.51, 1.26; 1.39, 1.26]), 1.10 (d,

$^{3}J_{PH}$ = 13.9, 9H, *t*Bu), 0.86 (br d, $^{2}J_{HH}$ = 9.1, 1H, CHC$\underline{H}_2$CH{NBE}), 0.81 (d, $^{3}J_{PH}$ = 13.5, 9H, *t*Bu), 0.57 (br d, $^{2}J_{HH}$ = 9.0, 1H, CHC$\underline{H}_2$CH{NBE}).

^{13}C{^{1}H} NMR (126 MHz, DFB): *δ* 163.1 (d, $^{2}J_{PC}$ = 8, py), 162.6 (q, $^{1}J_{CB}$ = 50, Ar^{F}), 161.2 (d, $^{2}J_{PC}$ = 7, py), 138.1 (s, py), 135.1 (s, Ar^{F}), 129.7 (qq, $^{2}J_{FC}$ = 32, $^{3}J_{CB}$ = 3, Ar^{F}), 124.9 (q, $^{1}J_{FC}$ = 272, Ar^{F}), 121.0 (d, $^{3}J_{PC}$ = 9, py), 119.8 (d, $^{3}J_{PC}$ = 11, py), 117.6 (sept, $^{3}J_{FC}$ = 4, Ar^{F}), 66.7 (app t, *J* = 10, Rh(CH=CH)), 62.9 (dd, *J* = 10, 8, Rh(CH=CH)), 47.1 (s, CH{NBE}), 44.4 (d, *J* = 2, CH{NBE}), 41.0 (d, *J* = 2, CH$\underline{C}$H$_2$CH{NBE}), 39.0 (dd, $^{1}J_{PC}$ = 19, py$\underline{C}$H$_2$), 38.3 (d, $^{1}J_{PC}$ = 18, py$\underline{C}$H$_2$), 34.4 (d, $^{1}J_{PC}$ = 18, *t*Bu{C}), 33.6 (dd, $^{1}J_{PC}$ = 15, $^{3}J_{PC}$ = 6, *t*Bu{C}), 31.6 (d, $^{2}J_{PC}$ = 11, CH$_2$), 30.2 (d, $^{2}J_{PC}$ = 10, CH$_2$), 30.1 (s, CH$_2$), 29.8 (s, CH$_2$), 29.5 (s, CH$_2$), 29.3 (s, 2×CH$_2$), 28.6 (s, CH$_2$), 27.9 (s, CH$_2$), 27.7 (s, CH$_2$), 27.5 (s, CH$_2$), 27.4 (d, $^{2}J_{PC}$ = 4, *t*Bu{CH$_3$}), 27.2 (d, $^{2}J_{PC}$ = 5, *t*Bu{CH$_3$}), 26.9 (s, CH$_2$), 26.6 (s, CH$_2$), 25.1 (br d, $^{1}J_{PC}$ = 16, PCH$_2$), 23.9 (d, $^{3}J_{PC}$ = 2, CH$_2$), 20.7 (br d, $^{1}J_{PC}$ = 23, PCH$_2$).

^{31}P{^{1}H} NMR (162 MHz, DFB): *δ* 71.2 (dd, $^{2}J_{PP}$ = 244, $^{1}J_{RhP}$ = 131, 1P), 55.9 (dd, $^{2}J_{PP}$ = 244, $^{1}J_{RhP}$ = 125, 1P).

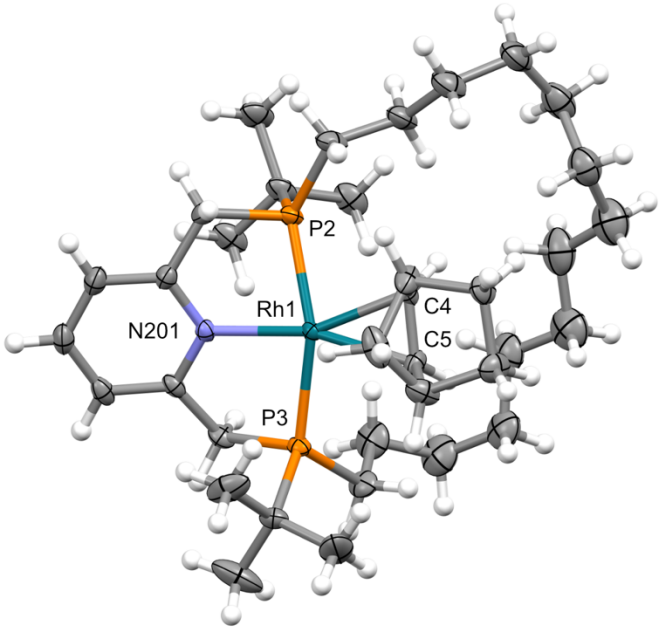

Figure S51. Solid-state structure of [Rh(PNP-14)(η^2-norbornene)][BAr$^{F}_4$]; thermal ellipsoids at 30% probability; anion omitted. Selected bond lengths (Å) and angles (°): Rh1-P2, 2.2916(8); Rh1-P3, 2.3118(7); P2-Rh1-P3, 153.11(3); Rh1-N201, 2.088(2); Rh1-Cnt(C4,C5), 2.085(3); N201-Rh1-Cnt(C4,C5), 169.19(11); Cnt = centroid.

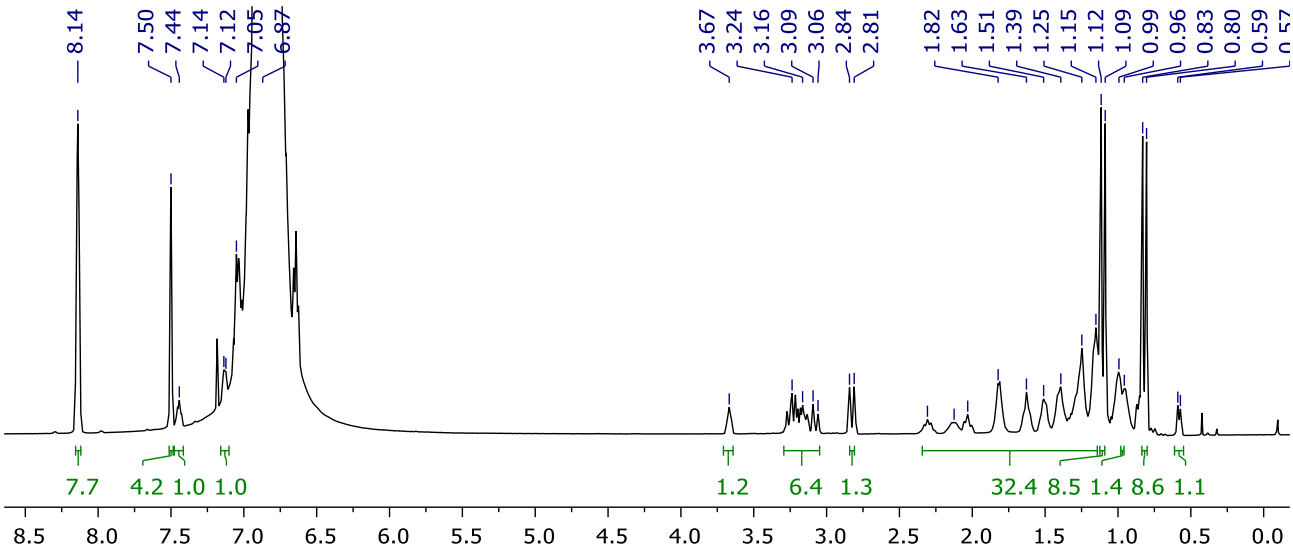

Figure S52. ^{1}H NMR spectrum of [Rh(PNP-14)(η^2-norbornene)][BAr$^{F}_{4}$] (DFB, 500 MHz).

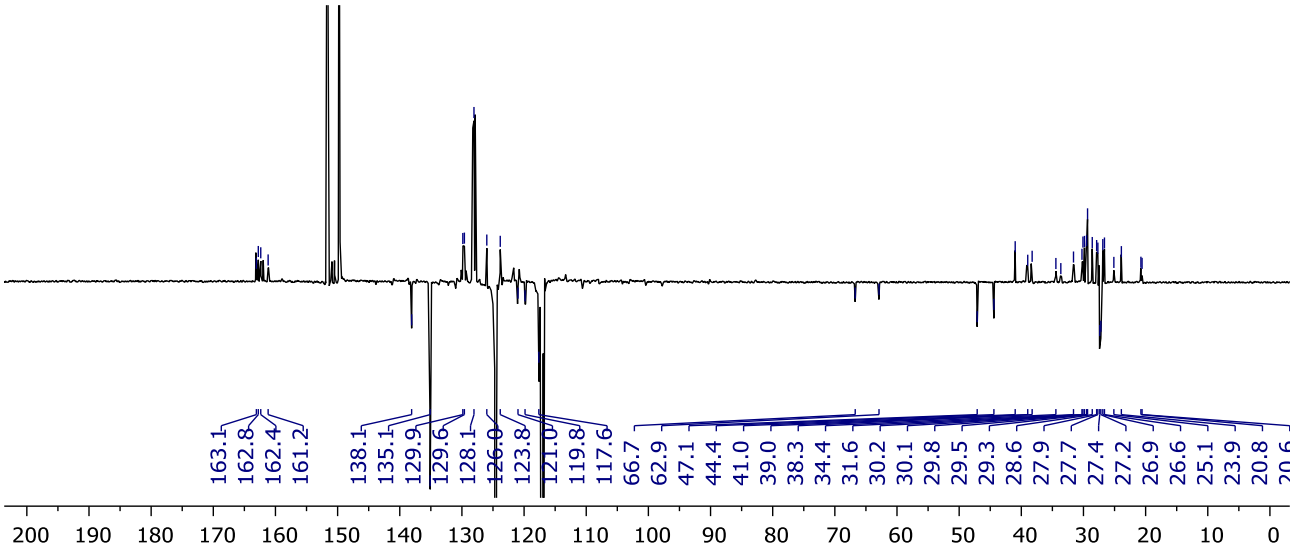

Figure S53. ^{13}C{^{1}H} APT NMR spectrum of [Rh(PNP-14)(η^2-norbornene)][BAr$^{F}_{4}$] (DFB, 126 MHz).

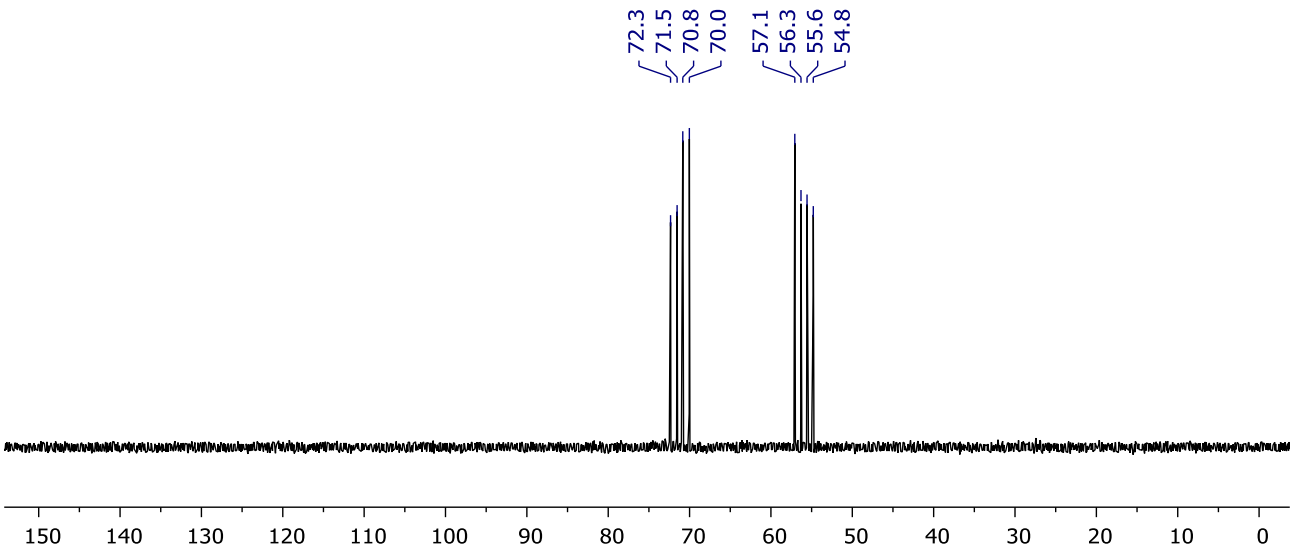

Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum of [Rh(PNP-14)(η^2-norbornene)][BAr^F_4] (DFB, 162 MHz).