Supporting Information For:

A Dual-Metal Strategy for *N*-Heterocycle Coordination Using Nickel and Aluminum

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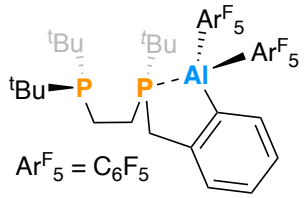
1. Experimental Section:

General Considerations. All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents. Nonhalogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective moisture removal. Fluorobenzene and $CDCl_3$ were dried over molecular sieves and degassed by three freeze-pump-thaw cycles. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Compound **2** was prepared as previously reported.[1]

Physical methods. ^{1}H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent e.g., $^{1}H(C_6D_6)$: $\delta = 7.16$; $^{13}C(C_6D_6)$: $\delta = 128.06$; coupling constants are reported in Hz. ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectra were performed as proton-decoupled experiments (unless explicitly stated otherwise) and are reported in ppm.

2. Preparation of Compounds:

tri-*tert*-butyl-benzyl-2-dipentafluorophenylaluminyl-diphosphinoethane, $^{t}Bu_2PCH_2CH_2P^{t}Bu(Bz)$-*o*-$Al(C_6F_5)_2$ (**3**, $C_{33}H_{37}AlF_{10}P_2$, M_w = 712 g/mol). In a glovebox, **2** (32 mg, 0.074 mmol) was weighed into a 20 mL scintillation vial equipped with a stir bar and dissolved in approximately 2 mL of pentane. A solution of *n*-BuLi (30 µL, 0.074 mmol) was added dropwise, and the reaction mixture was stirred for 30 min. During this time, the solution changed color from colorless to yellow. The solvent was removed *in-vacuo*, and the residue was dissolved in 1 mL of toluene. This solution was then added to a vial containing $AlCl(C_6F_5)_2$ (29 mg, 0.074 mmol) and stirred vigorously for 1 min. Upon addition of $AlCl(C_6F_5)_2$, the clear yellow solution turned cloudy white. The mixture was concentrated to dryness and washed with pentane (3 × 2 mL). Filtration afforded **3** as a clear, colorless oil (43 mg, 81%).



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 8.26 (t, $J_{H,H}$ = 4.07, 1H; C*H* *o*-Al), 7.21 (m, 1H; Aryl C*H*), 7.20 (m, 1H; Aryl C*H*), 7.03 (dd, $J_{H,H}$ = 4.89 Hz, $J_{H,H}$ = 3.89 Hz, 1H; Aryl C*H*), 3.21 (dd, $J_{H,P}$ = 4.75 Hz, $J_{H,H}$ = 16.4 Hz, 1H; PC*H*$_2$ (Bz)), 2.63 (dd, $J_{H,P}$= 4.75 Hz, $J_{H,H}$ = 16.4 Hz, 1H; PC*H*$_2$ (Bz)), 2.11 (m, 2H; PC*H*$_2$CH$_2$P), 1.84 (m, 2H; PCH$_2$C*H*$_2$P), 0.74 (d, $J_{H,P}$ = 10.9 Hz, 18H; P(^{t}Bu)$_2$), 0.70 (d, $J_{H,P}$ = 14.6 Hz, 9H; P(^{t}Bu)(Bz)).

^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ_P = 37.4 (d, $J_{P,P}$ = 39.3 Hz; *P*(^{t}Bu)$_2$), 1.13 (br. d, $J_{P,P}$ = 39.3 Hz; *P*-Al).

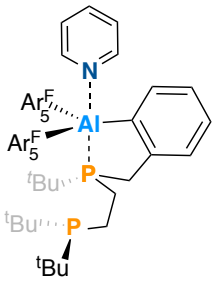
^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298 K): δ_F = -119.2 (m, 2F; *o*-C$_6$*F*$_5$), -119.6 (m, 2F; *o*-C$_6$*F*$_5$), -152.0 (t, $J_{F,F}$ = 19.3 Hz, 1F; *p*-C$_6$*F*$_5$), -152.98 (t, $J_{F,F}$ = 19.9 Hz, 1F; *p*-C$_6$*F*$_5$), -160.4 (m, 2F; *m*-C$_6$*F*$_5$), -161 (m, 2F; *m*-C$_6$*F*$_5$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ_C = 151.1-149.0 (br.; *C*$_6$F$_5$), 144.4 (d, $J_{C,P}$ =2.60 Hz, Bz *ipso*-Aryl *C*), 138.2 (br.; *C*$_6$F$_5$), 138.0 (m; Aryl *C*H *o*-Al), 136.5 (br.; *C*$_6$F$_5$), 129.5 (d, $J_{C,P}$ = 1.2 Hz; Aryl *C*H), 128.0 (Aryl *C*H, buried), 127.0 (d, $J_{C,P}$ = 3.3 Hz; Aryl *C*H), 31.5 (dd, $J_{C,P}$ = 26.1, 21.3 Hz, P(^{t}Bu)$_2$ C-

(CH_3)), 30.4 (d, $J_{C,P}$ = 24.0 Hz; Bz CH_2), 29.3 (dd, $J_{C,P}$ = 9.20 Hz, 4.70 Hz, P(^{t}Bu)(Bz) *C*-(CH_3)), 29.2 (d, $J_{P,C}$ = 13.7 Hz; P(^{t}Bu)$_2$-CH_3), 28.9 (d, $J_{P,C}$ = 13.8 Hz; P(^{t}Bu)$_2$-CH_3), 26.3 (d, $J_{P,C}$ = 3.43 Hz; P(^{t}Bu)(Bz)-CH_3), 22.6 (m; PCH_2CH_2P).

HR-APCI-MS: $C_{33}H_{38}AlF_{10}P_2$ ([M+H]$^+$) (713.210, calculated); (713.211, observed) & $C_{33}H_{38}AlOF_{10}P_2$ ([M+O+H]$^+$) (729.205, calculated); (729.205, observed).

tri-*tert*-butyl-benzyl-2-dipentafluorophenylaluminyl-diphosphinoethane, ^{t}Bu$_2$PCH_2CH_2P^{t}Bu(Bz)-*o*-Al(C_6F_5)$_2$-pyridine (**3-pyr**; $C_{38}H_{42}AlF_{10}NP_2$, M_w = 791 g/mol). In a glovebox, **3** (23 mg, 0.032 mmol) was weighed into a 20 mL scintillation vial equipped with a stir bar and dissolved in approximately 0.5 mL C_6D_6. Pyridine (3.6 µL, 0.045 mmol) was added *via* microsyringe, and the reaction mixture was stirred for 10 min. Transfer a NMR tube and analysis by ^{31}P NMR spectroscopy, showed formation of **3-pyr** in >99% conversion (80% purity, 7% (^{t}Bu)$_2$PCH_2CH_2P(^{t}Bu)(Bz), 13% dimer carried through from synthesis of **3**). This compound was not isolated and used immediately as it was found to undergo Al-C hydrolysis upon standing.

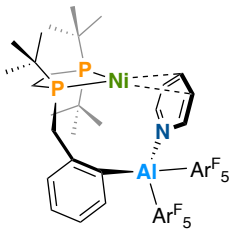


^{1}H NMR (400 MHz, C_6D_6, 298 K, selected signals): δ_H = 7.64 (d, $J_{H,H}$ = 7.16 Hz, 1H; Aryl-C*H* *o*-Al), 7.23 (t, $J_{H,H}$ = 7.18 Hz, 1H; Bz Aryl-C*H*), 7.15 (d, $J_{H,H}$ = 7.79 Hz, 1H; Bz Aryl-C*H*) 7.10 (t, $J_{H,H}$ = 7.31 Hz, 1H; Aryl-C*H*), 3.48 (d, $J_{H,H}$ = 15.4 Hz, 1H; Bz CH_2), 2.90 (dd, $J_{P,H}$ = 7.97 Hz, $J_{H,H}$ = 15.4 Hz, 1H; Bz CH_2), 1.74 (m, 4H; PCH_2CH_2P), 0.88 (d, $J_{P,H}$ = 10.8 Hz, 9H; P(^{t}Bu)$_2$), 0.87 (d, $J_{P,H}$ = 10.8 Hz, 9H; P(^{t}Bu)$_2$), 0.74 (d, $J_{P,H}$ = 12.1 Hz, 9H; P(^{t}Bu)(Bz).

^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ_P = 37.3 (d, $J_{P,P}$ = 31.1 Hz; *P*(^{t}Bu)$_2$), -1.10 (br. m, *P*(^{t}Bu)(Bz)).

^{19}F NMR (376 MHz, C_6D_6, 298 K): δ_P = -118.7 (br. m, 2F, *o*-C_6F_5), -119.7 (m, 2F, *o*-C_6F_5), -154.0 (br. m, 2F, *p*-C_6F_5), -161.0 (br. m, 2F, *m*-C_6F_5), -161.3 (br. m, 2F, o-C_6F_5).

nickel tri-tert-butyl-benzyl-2-dipentafluorophenylaluminyl-diphosphinoethane-η²-C,C-pyridine, Ni(^{t}Bu$_2$PCH$_2$CH$_2$P^{t}Bu(Bz)-*o*-Al(C$_6$F$_5$)$_2$-pyr (4-pyr; $C_{38}H_{42}AlF_{10}NNiP_2$, M_w = 850 g/mol). In a glovebox, **3-pyr** (27 mg, 0.032 mmol) was dissolved in approximately 0.5 mL of C_6D_6. [Ni(COD)$_2$] (8 mg, 0.029 mmol) was then added to this and stirred until complete dissolution was observed. After 30 min of stirring, the solution changed from clear yellow to dark orange, with full conversion confirmed by ^{31}P NMR spectroscopy. The solvent was removed *in vacuo*, and the residue was washed with pentane (3 × 3 mL); removal of solvent in-vacuo afforded **4-pyr** as an orange powder (12 mg, 44%).



^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ_H = 8.43 (br. s, 1H; C*H* *o*-N), 7.38 (d, $J_{H,H}$ = 6.34 Hz, 1H; Aryl C*H* *o*-Al), 7.11 (m, 2H; Bz C*H*, overlapping signals), 6.85 (d, $J_{H,H}$ = 7.75 Hz, 1H; Bz C*H* *m*-Al), 6.40 (m, 1H; pyr C*H*), 5.26 (t, $J_{H,H}$ = 6.24 Hz, 1H; pyr C*H*), 4.21 (br. s, 1H; pyr Ni-C*H*), 3.71 (br. s, 1H; pyr Ni-C*H*), 3.55 (d, $J_{H,H}$ = 13.4 Hz, 1H; Bz C*H*$_2$), 3.23 (t, $J_{H,H}$ = 13.4 Hz, $J_{H,P}$ = 14.5 Hz, 1H; Bz C*H*$_2$), 1.70 (m, 2H; (^{t}Bu)(Bz)PC*H*$_2$CH$_2$P(^{t}Bu)$_2$), 1.26 (m, 2H; (^{t}Bu)(Bz)PCH$_2$C*H*$_2$P(^{t}Bu)$_2$, buried), 0.71 (d, $J_{H,P}$ = 12.3 Hz, 9H; P(^{t}Bu)$_2$), 0.58 (d, $J_{H,P}$ = 12.4 Hz, 9H,; P(^{t}Bu)(Bz), 0.57 (d, $J_{H,P}$ = 12.8 Hz, 9H; P(^{t}Bu)$_2$).

^{31}P{^{1}H} NMR (243 MHz, C$_6$D$_6$, 298 K): δ_P = 79.7 (d, $J_{P,P}$ = 58.5 Hz; *P*(^{t}Bu)$_2$), 56.7 (d, $J_{P,P}$ = 58.5 Hz; *P*(^{t}Bu)(Bz)).

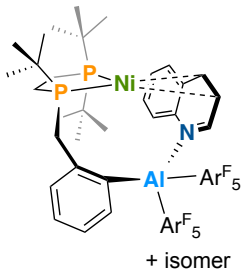
^{19}F{^{1}H} NMR (376 MHz, C$_6$D$_6$, 298 K): δ_F = -119.5 (m, 2F; *o*-C$_6$F$_5$), -120.0 (m, 2F; *o*-C$_6$F$_5$), -153.9 (t, $J_{F,F}$ = 20.1 Hz, 1F; *p*-C$_6$F$_5$), -154. 5 (t, $J_{F,F}$ = 19.2 Hz, 1F; *p*-C$_6$F$_5$), -161.2 (m, 2F; *m*-C$_6$F$_5$), -161.6 (m, 2F; *m*-C$_6$F$_5$).

^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 298 K): δ_C = 151.2 (br. m; *C*$_6$F$_5$), 149.7 (br. m; *C*$_6$F$_5$), 142.9 (br. s; Bz *ipso*-Aryl *C*), 139.2 (s; Aryl *C*H *o*-Al), 138.5 (br. s; pyr *C*H), 138.1 (br. m; *C*$_6$F$_5$), 136.4 (br. m; *C*$_6$F$_5$), 129.1 (d, $J_{C,P}$ = 3.80 Hz; Bz Aryl-*C*H), 128.8 (d, $J_{C,P}$ = 1.7 Hz, pyr *C*H), 127.6 (s; Bz Aryl-*C*H, buried), 125.4, (d, $J_{C,P}$ = 2.65 Hz; Bz Aryl-*C*H), 114.3 (s; pyr *C*H), 62.7 (br. m; Ni-*C*H), 51.1 (br. m; Ni-*C*H), 35.4 (dd, $J_{C,P}$ = 5.28, 4.17 Hz; P(^{t}Bu)$_2$ *C*-(CH$_3$)$_3$, 34.3 (m; Bz *C*H$_2$), 31.6 (dd, $J_{C,P}$ = 7.22, 4.06 Hz;

P(tBu)(Bz) *C*-(CH_3)$_3$), 30.2 (d, $J_{P,C}$ = 6.02 Hz; P(^{t}Bu)$_2$ CH_3), 28.8 (d, $J_{C,P}$ = 4.92 Hz; P(^{t}Bu)$_2$ CH_3), 27.3 (d, $J_{P,C}$ = 5.33 Hz; P(^{t}Bu)$_2$ CH_3), 22.3 (m; PCH_2PCH_2P), 22.2 (m; PCH_2CH_2P).

HR-LIFDI-MS: $C_{38}H_{42}AlF_{10}NNiP_2$ ([M]$^+$) (849.180, calculated); (849.179, observed).

nickel tri-tert-butyl-benzyl-2-dipentafluorophenylaluminyl-diphosphinoethane-η²-C,C-quinoline, Ni(^{t}Bu$_2$PCH_2CH_2P^{t}Bu(Bz)-*o*-Al(C_6F_5)$_2$-quin (**5-quin**; $C_{42}H_{44}AlF_{10}NP_2$, M_w = 900.43 g/mol). In a glovebox, **3** and quinoline were combined to putatively give **3-quin** (27 mg, 0.032 mmol) in approximately 0.5 mL of C_6D_6. [Ni(COD)$_2$] (8 mg, 0.029 mmol) was then added to this and stirred until complete dissolution was observed. After 30 minutes of stirring, the solution changed from a clear yellow to a dark red solution, with full conversion by ^{31}P NMR. Solvent was then removed *in-vacuo*, followed by repeated washing with pentane (3 x 3 mL). The compound was then dried to give **5-quin** as an orange powder as a mixture of primarily two isomers in a 1:0.35 ratio (14 mg, 54%).



^{1}H NMR (400 MHz, C_6D_6, 298 K, major isomer): δ_H = 8.80 (m, 1H; Quin C*H* *o*-N), 8.06 (d, $J_{H,H}$ = 7.00 Hz, 1H; Aryl C*H* *o*-Al), 7.54 (d, $J_{H,H}$ = 8.13 Hz, 1H; Quin-C_6H_4 C*H*), 7.13 (t, $J_{H,H}$ = 7.13 Hz, 1H; Bz Ar-C*H*), 7.08 (t, $J_{H,H}$ = 7.45 Hz, 1H; Bz Ar-C*H*), 6.83 (d, $J_{H,H}$ = 7.60 Hz, 1H; Bz Ar-CH), 6.81 (m, 1H; Quin-C_6H_4 C*H*), 6.78 (d, $J_{H,H}$ = 7.56 Hz, 1H; Quin C_6H_4 CH), 6.67 (t, $J_{H,H}$ = 7.46 Hz, 1H; Quin C_6H_4 C*H*), 4.73 (br. s, 1H; Quin Ni-C*H*), 3.89 (d, $J_{H,H}$ = 13.6 Hz, 1H; Bz CH_2), 3.86 (br. s, 1H; Quin Ni-C*H*), 3.25 (t, 1H, $J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 14.9 Hz; Bz CH_2), 1.66 (m, 4H; PCH_2CH_2P), 0.73 (d, $J_{P,H}$ = 12.4 Hz, 9H; P(^{t}Bu)$_2$), 0.54 (d, $J_{P,H}$ = 12.6 Hz, 9H; P(^{t}Bu)(Bz)), 0.15 (d, $J_{P,H}$ = 13.3 Hz, 9H; P(^{t}Bu)$_2$).

^{1}H NMR (400 MHz, C_6D_6, 298 K, selected signals for minor isomer): δ_H = 8.86 (m, 1H; Quin C*H* *o*-N), 7.28 (d, $J_{H,H}$ = 13.0 Hz, 1H; Quin C*H*), 7.12 (m, 1H; Quin C*H*, buried), 6.81 (m, 1H; Quin C*H*, buried), 6.64 (t, $J_{H,H}$ = 7.49 Hz, 1H; Quin C*H*), 4.90 (br. s, 1H; Quin Ni-C*H*), 3.92 (br. s, 1H; Quin Ni-C*H*, buried).

$^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6, 298 K, major isomer): δ_P = 78.0 (d, $J_{P,P}$= 44.0 Hz; P(^{t}Bu)$_2$), 55.0 (d, $J_{P,P}$= 44.0 Hz; P(^{t}Bu)(Bz)).

$^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6, 298 K, minor isomer): δ_P = 86.3 (d, $J_{P,P}$= 44.0 Hz; P(^{t}Bu)$_2$), 60.9 (d, $J_{P,P}$= 39.0 Hz; P(^{t}Bu)(Bz)).

$^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 298 K, major isomer): δ_F = -119.1 (m, 2F, *o*-C_6F_5), -119.5 (m, 2F, *o*-C_6F_5), -154.2 (t, $J_{F,F}$ = 19.5 Hz, 1F; *p*-C_6F_5), -154. 6 (t, $J_{F,F}$ = 20.0 Hz, 1F; *p*-C_6F_5), -161.4 (m, 2F, *m*-C_6F_5), -161.7 (m, 2F, *m*-C_6F_5).

$^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 298 K, minor isomer): δ_F = -117.1 (m, 2F, *o*-C_6F_5), -119.5 (m, 2F, *o*-C_6F_5, buried), -154.9 (t, $J_{F,F}$ = 20.1 Hz, 1F; *p*-C_6F_5), -155. 7 (t, $J_{F,F}$ = 19.5 Hz, 1F; *p*-C_6F_5), -162.8 (m, 2F, *m*-C_6F_5), -163.3 (m, 2F, *m*-C_6F_5).

$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K, major isomer only): δ_C = 151.3 (br. m; *C*$_6F_5$), 149.7 (br. m; *C*$_6F_5$), 142.3 (br. s; Bz *ipso*-Aryl *C*), 139.7 (s; Aryl-*C*H *o*-Al), 138.3 (br. m; *C*$_6F_5$), 136.4 (br. m; *C*$_6F_5$), 130.3 (s; Quin *C*H *o*-N), 129.3 (s; Bz Ar-*C*H), 127.6 (d, $J_{C,P}$ = 11.6 Hz; Bz Aryl-*C*H*),* 126.4 (s; Quin C_6H_4 *C*H), 125.7 (s; Quin C_6H_4 *C*H), 125.3 (br. s; Bz Aryl-*C*H*),* 124.3 (s; Quin C_6H_4 *C*H*),* 120.1 (s; Quin-C_6H_4 *C*H), 64.2 (m; Quin Ni-*C*H*),* 54.1 (d, $J_{C,P}$ = 23.4 Hz; Quin Ni-*C*H), 35.5 (t, $J_{C,P}$ = 10.3 Hz; Bz *C*H$_2$), 34.3 (dd, $J_{C,P}$ = 7.35, 2.24 Hz; P(^{t}Bu)$_2$ *C*-(CH$_3$)$_3$, 32.2 (dd, $J_{C,P}$ = 8.03, 4.01 Hz; P(tBu)(Bz) *C*-(CH$_3$)$_3$) 29.8 (d, $J_{C,P}$ = 5.16 Hz; P(^{t}Bu)$_2$ *C*H$_3$), 28.4 (d, $J_{C,P}$ = 4.95 Hz; P(^{t}Bu)$_2$ *C*H$_3$), 27.1 (d, $J_{C,P}$ = 4.92 Hz; P(^{t}Bu)(Bz) *C*H$_3$), 22.5 (br, m.; P*C*H$_2$*C*H$_2$P).

HR-LIFDI-MS: $C_{42}H_{44}AlF_{10}NNiP_2$ ([M]$^+$) (899.195, calculated); (899.195, observed).

3. Spectroscopic Data:

Figure S1. 2[1], ^{1}H NMR, C_6D_6, 400 MHz, 298 K.

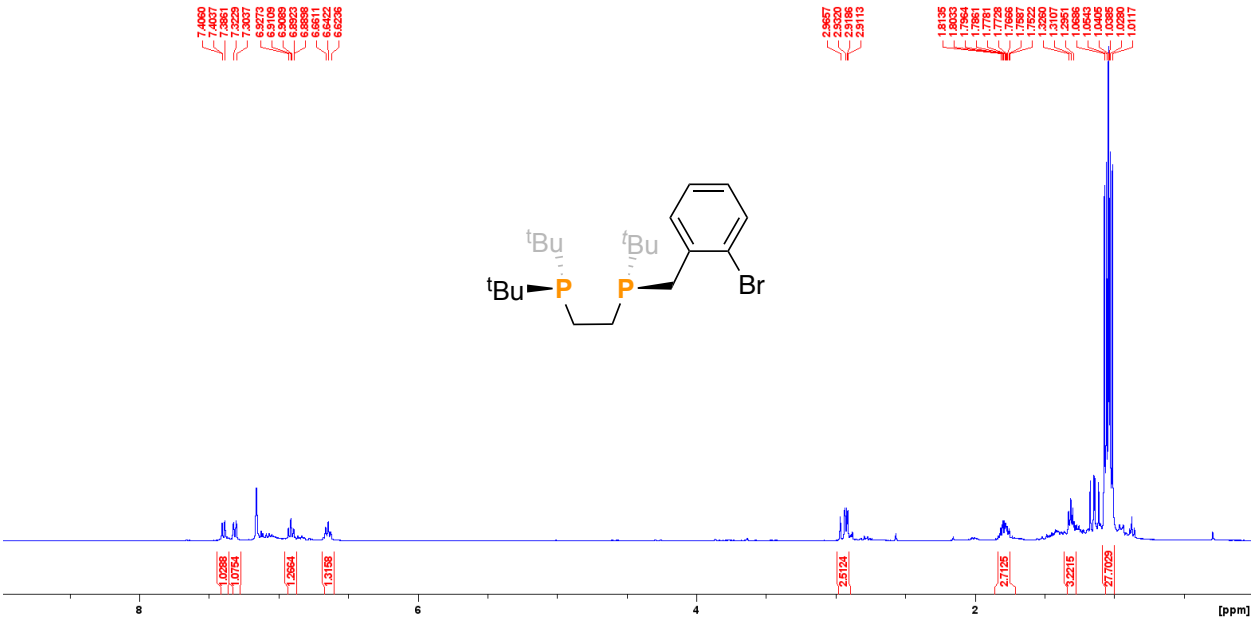


Figure S2. 2[1], ^{31}P{^{1}H} NMR, C_6D_6, 162 MHz, 298 K.

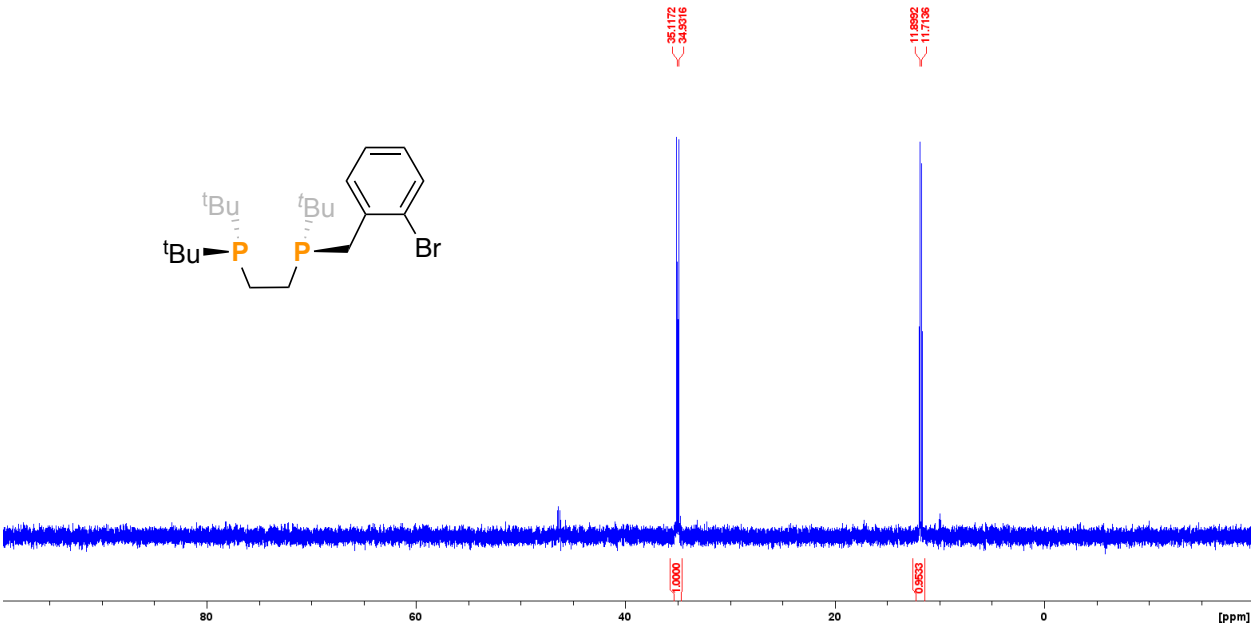


Figure S3. 3, ^{1}H NMR, C_6D_6, 400 MHz, 298 K. *= P(^{t}Bu) peaks arising from minor phosphine impurities

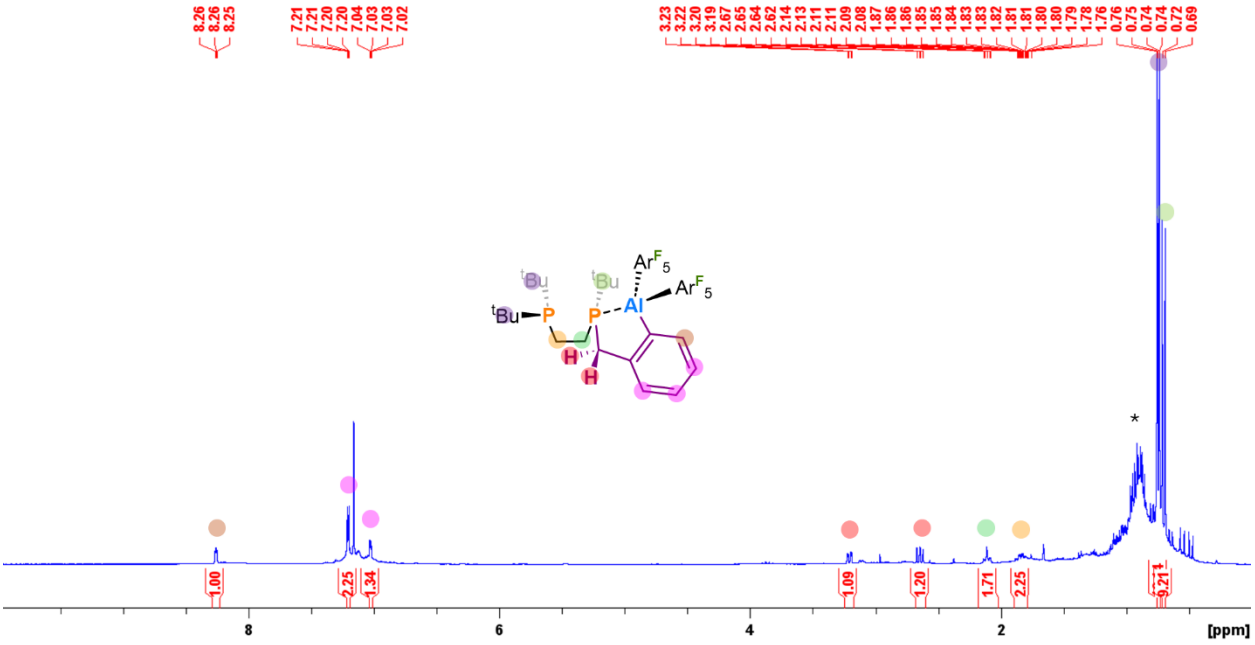


Figure S4. 3, ^{1}H and ^{1}H{^{31}P} NMR (expansion), C_6D_6, 400 MHz, 298 K.

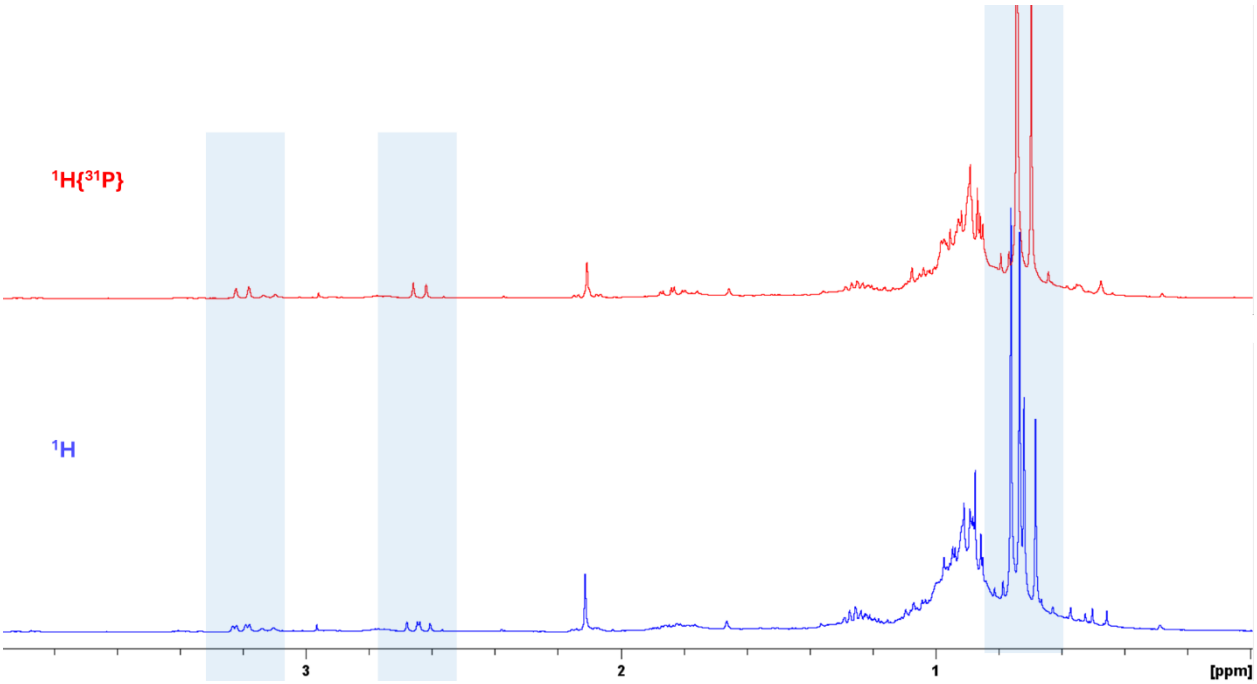


Figure S5. 3, ^{1}H-^{1}H COSY NMR, C_6D_6, 600 MHz, 298 K.

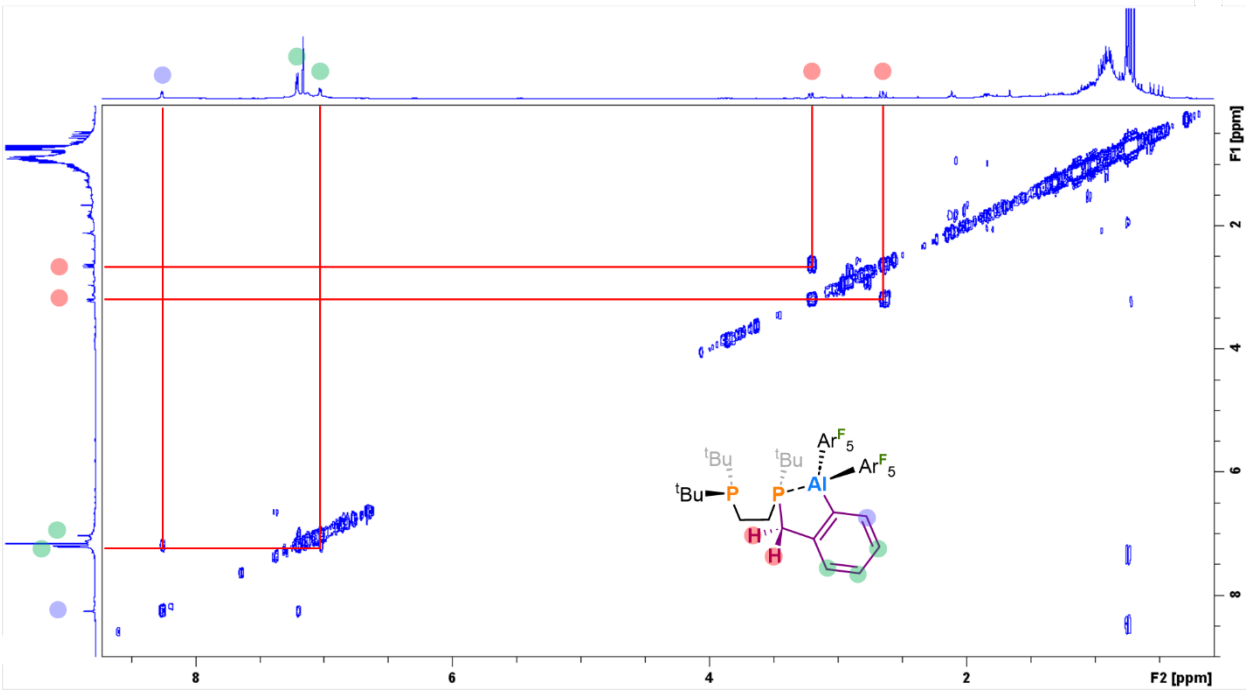


Figure S6. 3, $^{31}P\{^{1}H\}$ NMR, C_6D_6, 162 MHz, 298 K.

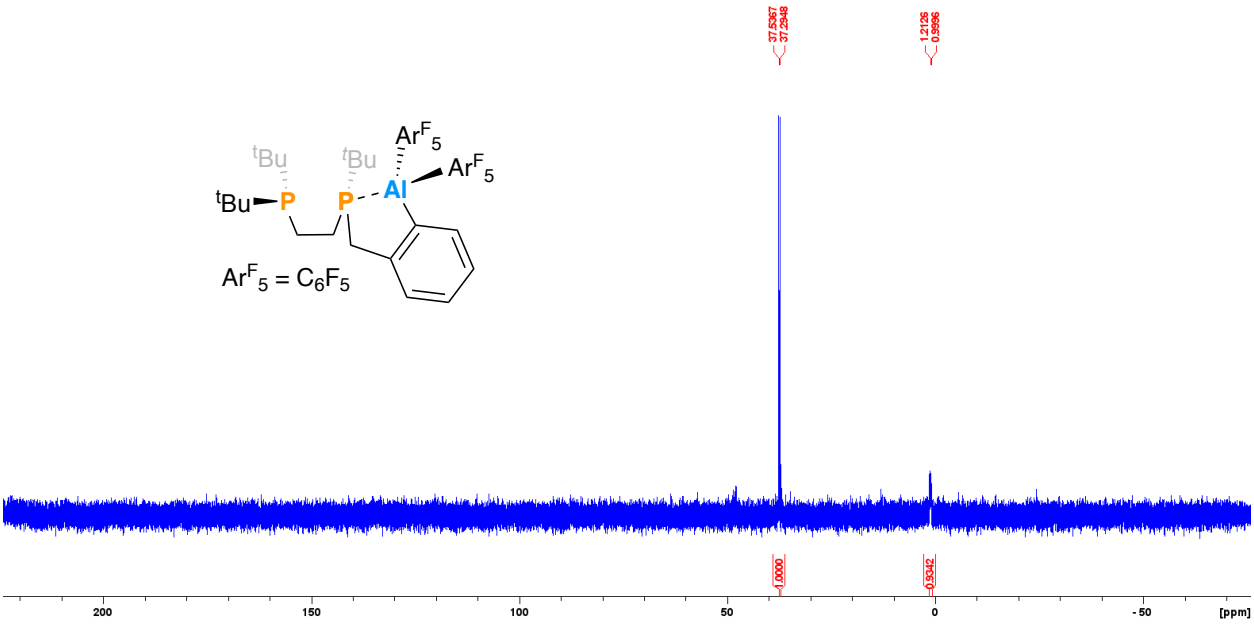


Figure S7. 3, ^{1}H-^{31}P HMBC NMR, C_6D_6, 600 MHz, 298 K.

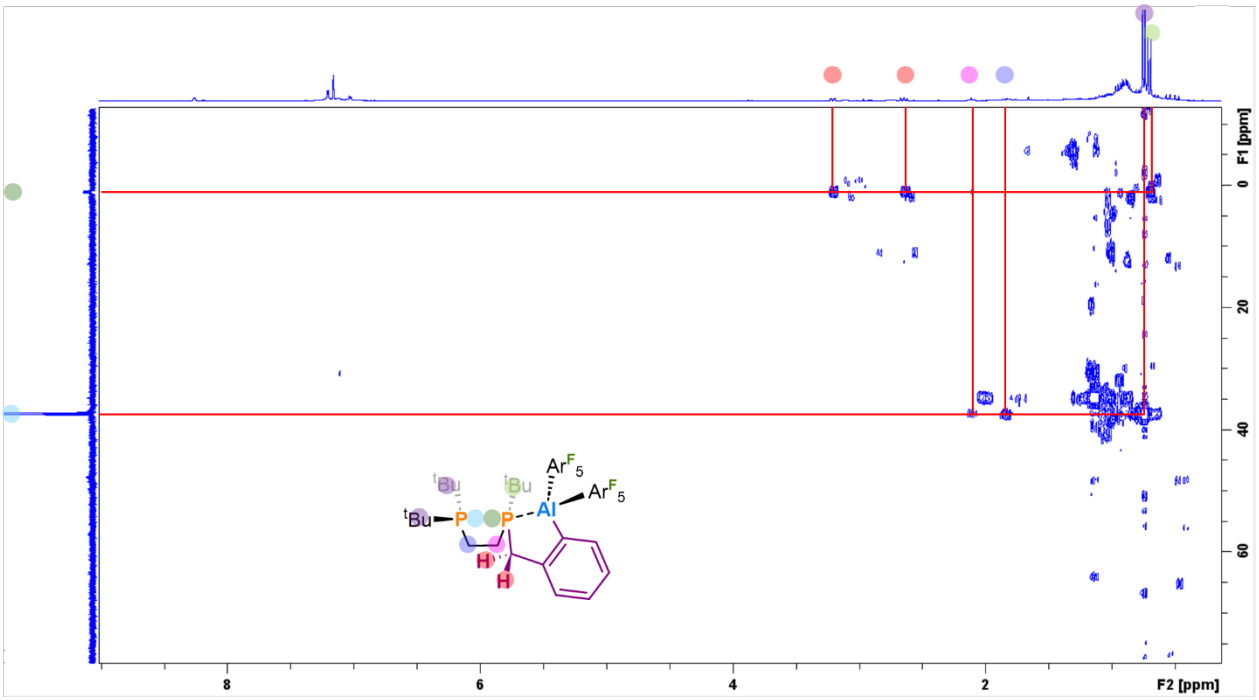


Figure S8. 3, ^{19}F NMR, C_6D_6, 376 MHz, 298 K, *= unknown impurity.

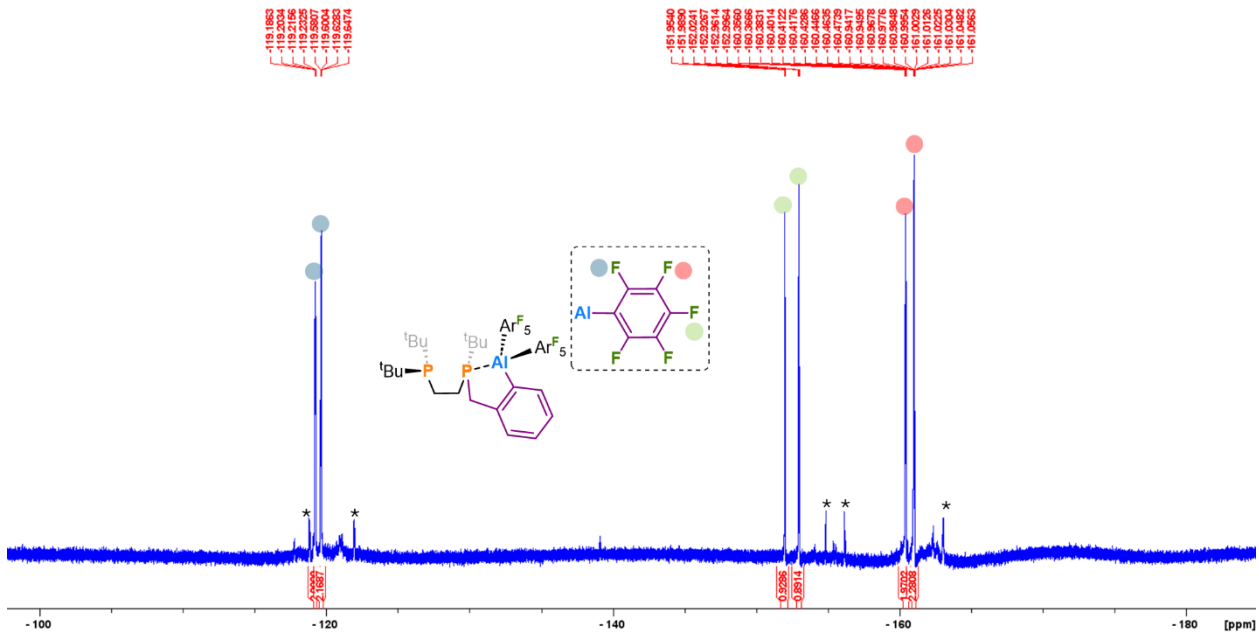


Figure S9. 3, ^{19}F-^{19}F COSY NMR, C_6D_6, 376 MHz, 298 K.

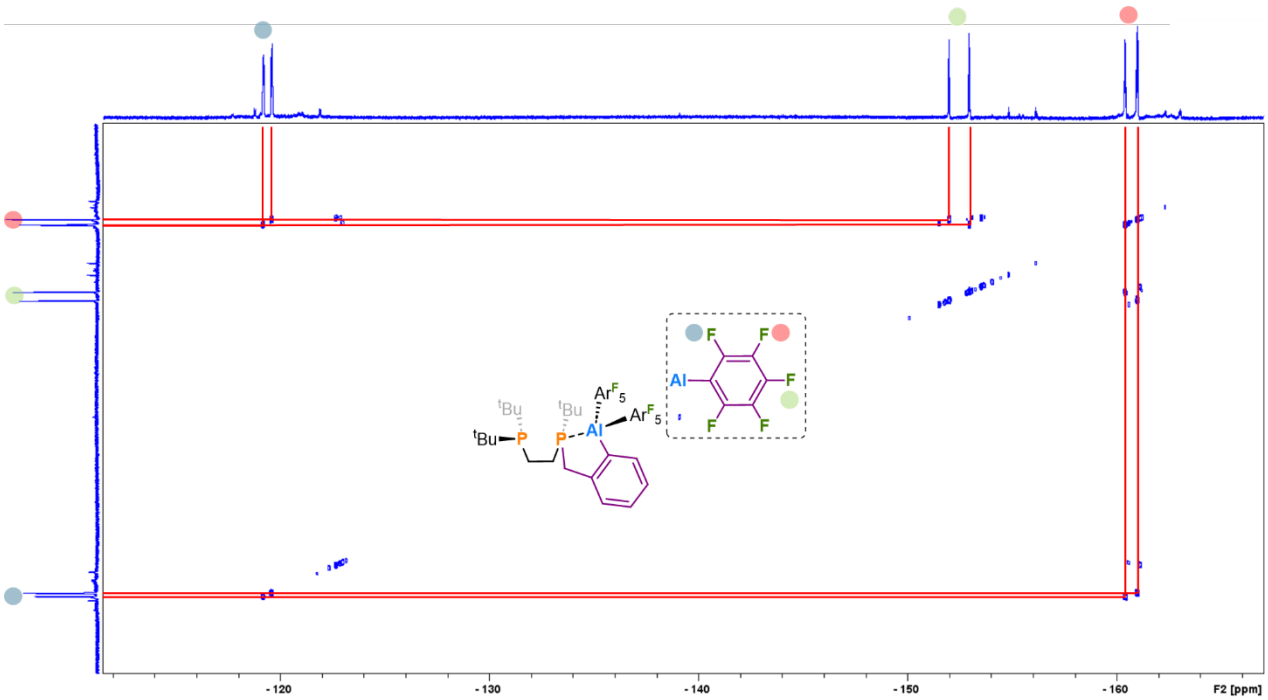


Figure S10. 3, $^{13}C\{^1H\}$ NMR, C_6D_6, 376 MHz, 298 K.

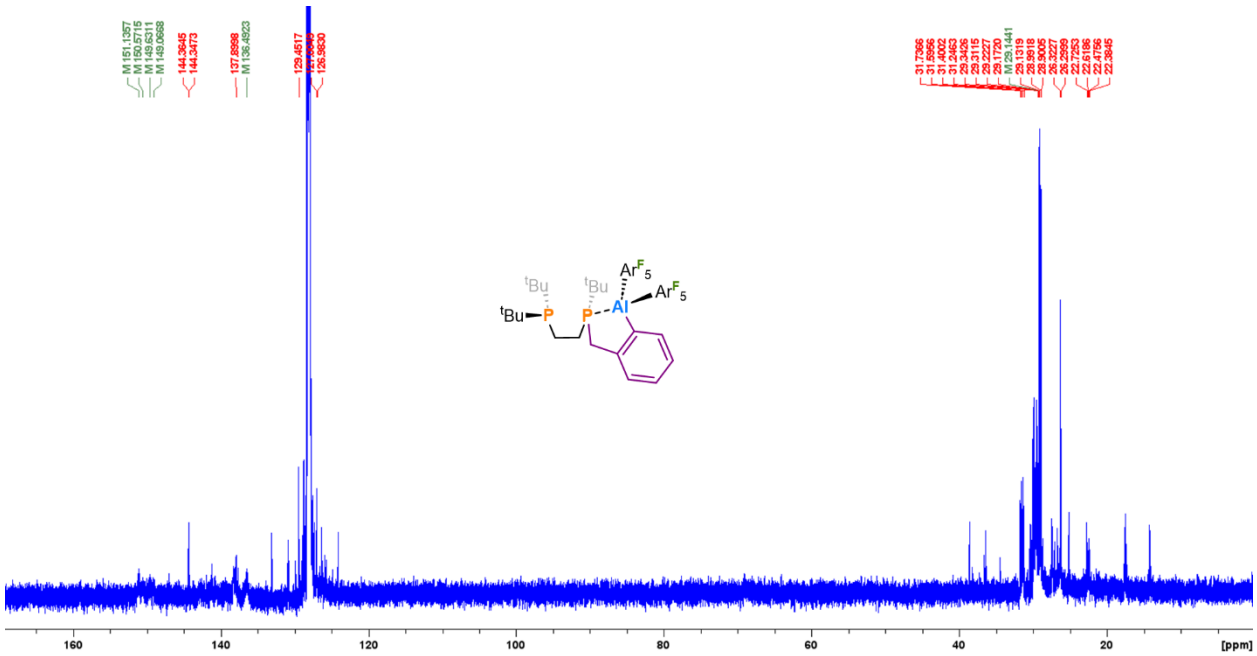


Figure S11. 3, ^{1}H-^{13}C HSQC NMR, C_6D_6, 376 MHz, 298 K.

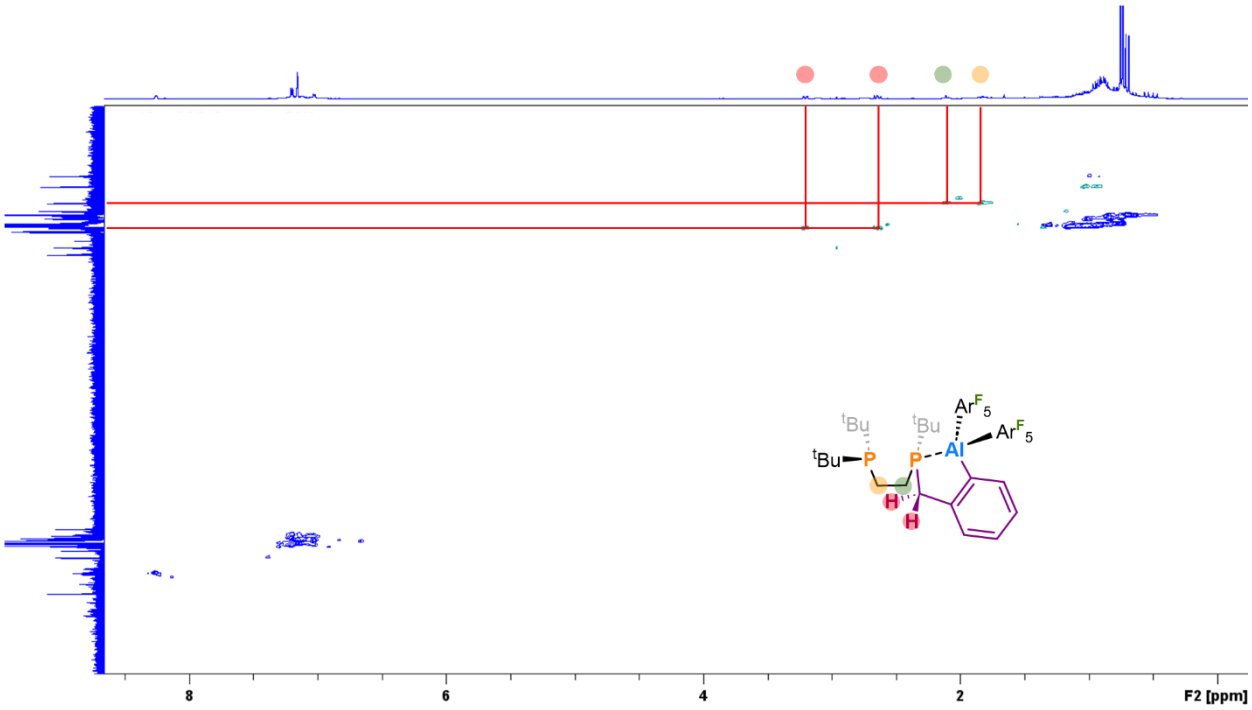


Figure S12. 3, ^{1}H-^{13}C HMBC NMR, Highlighting Aromatic Region, C_6D_6, 376 MHz, 298 K.

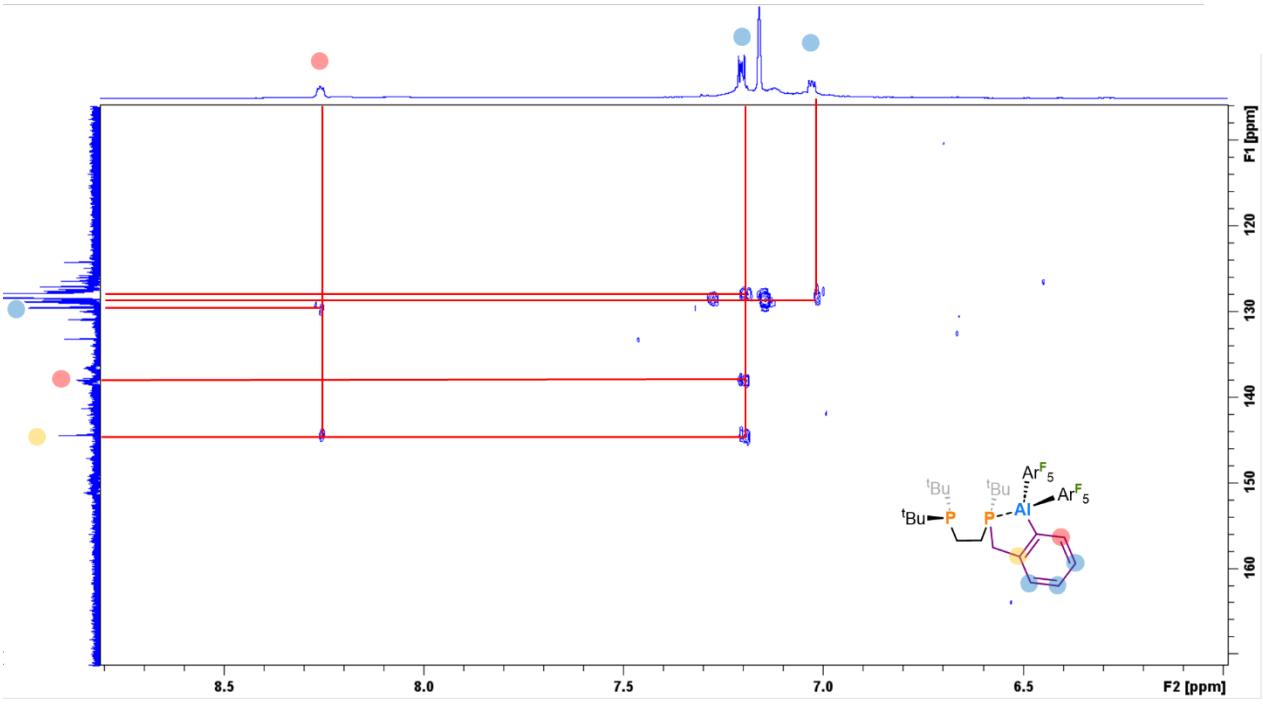


Figure S13. 3, ^{1}H-^{13}C HMBC NMR, Highlighting P(^{t}Bu) Region, C_6D_6, 376 MHz, 298 K.

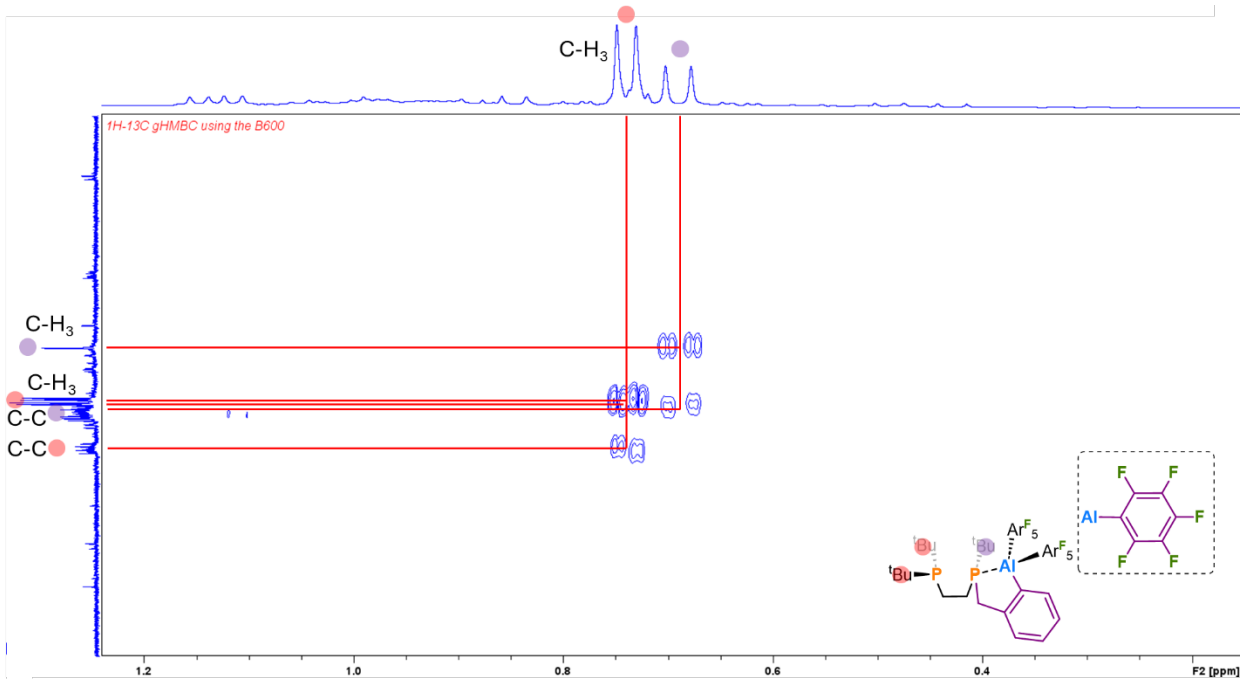


Figure S14. 3-pyr, ^{1}H NMR, C_6D_6, 400 MHz, 298 K. * = (^{t}Bu)$_2$PCH$_2$CH$_2$P(^{t}Bu)(Bz).

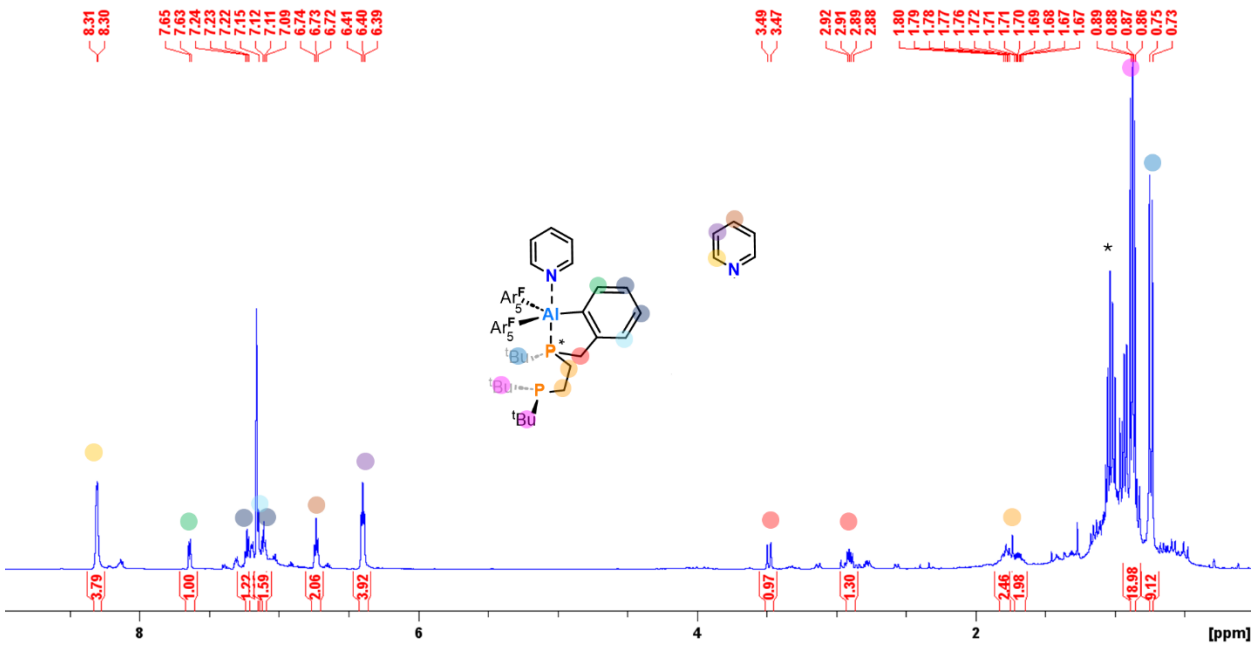


Figure S15. 3-pyr, ^{1}H-^{1}H COSY NMR, C_6D_6, 400 MHz, 298 K.

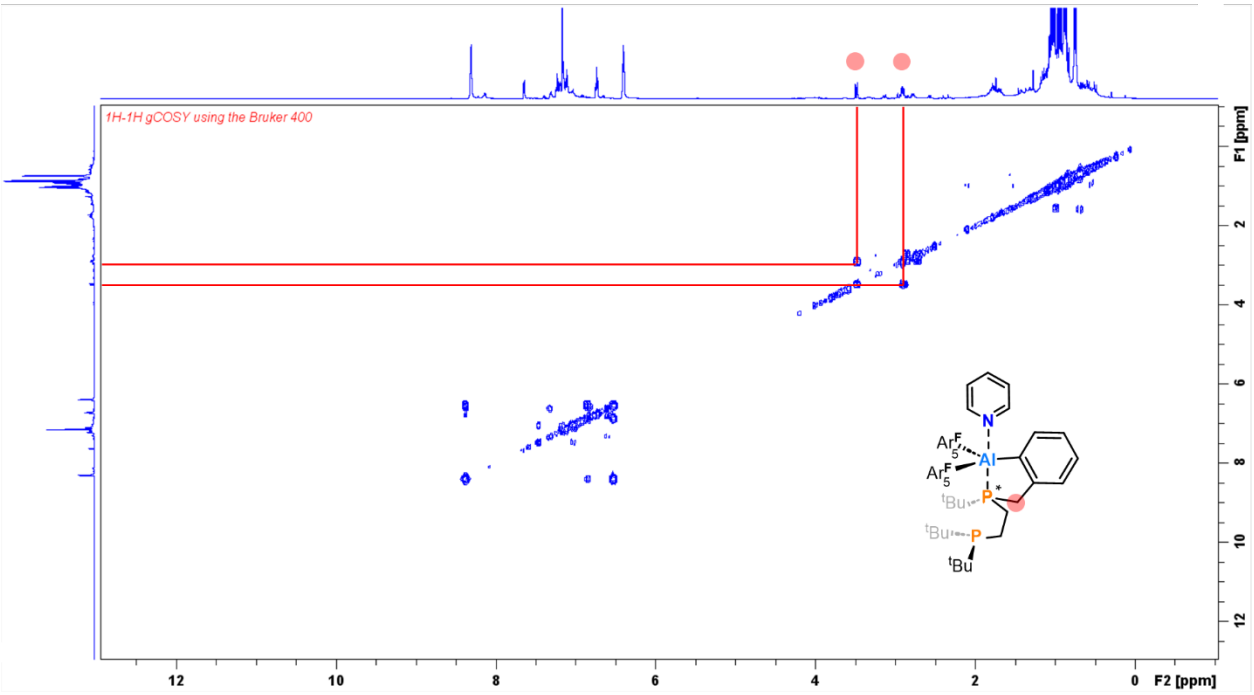


Figure S16. 3-pyr, 1D 1H TOCSY NMR, Irradiation at δ_H = 3.48 ppm, C_6D_6, 600 MHz, 298 K.

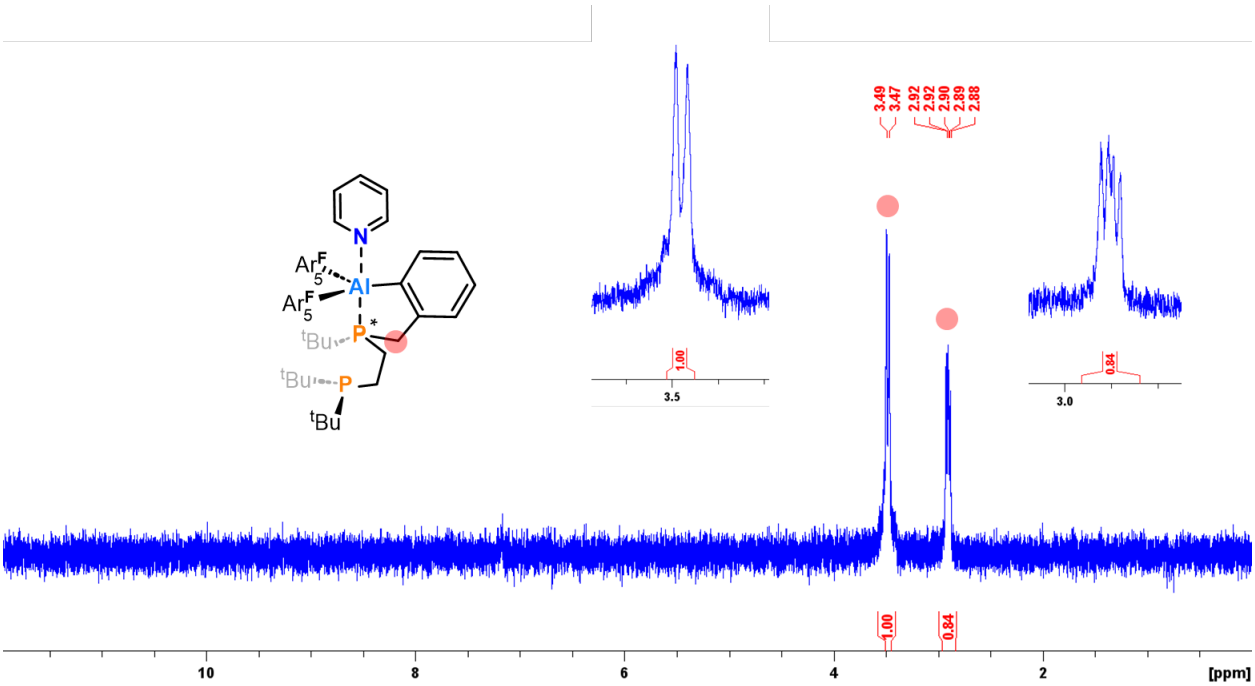


Figure S17. 3-pyr, 1D 1H TOCSY NMR, Irradiation at δ_H = 7.64 ppm, C_6D_6, 600 MHz, 298 K.

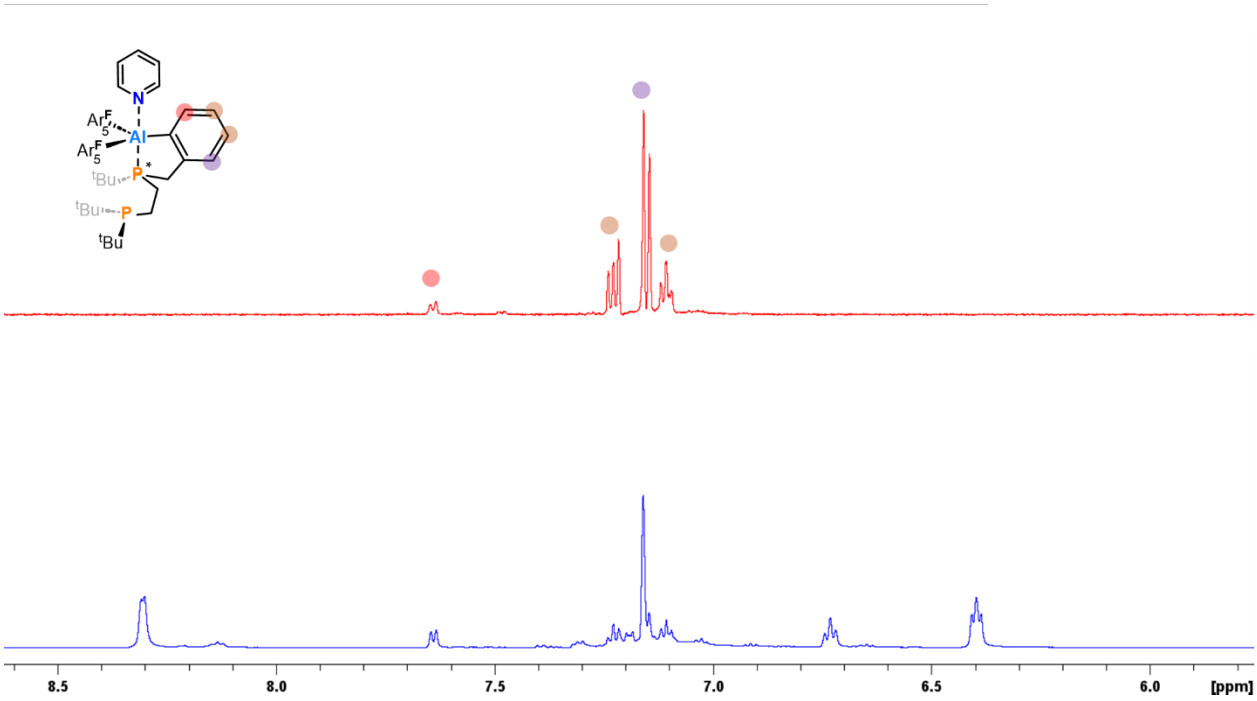


Figure S18. 3-pyr, ^{1}H NMR, **excess pyridine**, **3-pyr** post vacuum, C_6D_6, 600 MHz, 298 K.

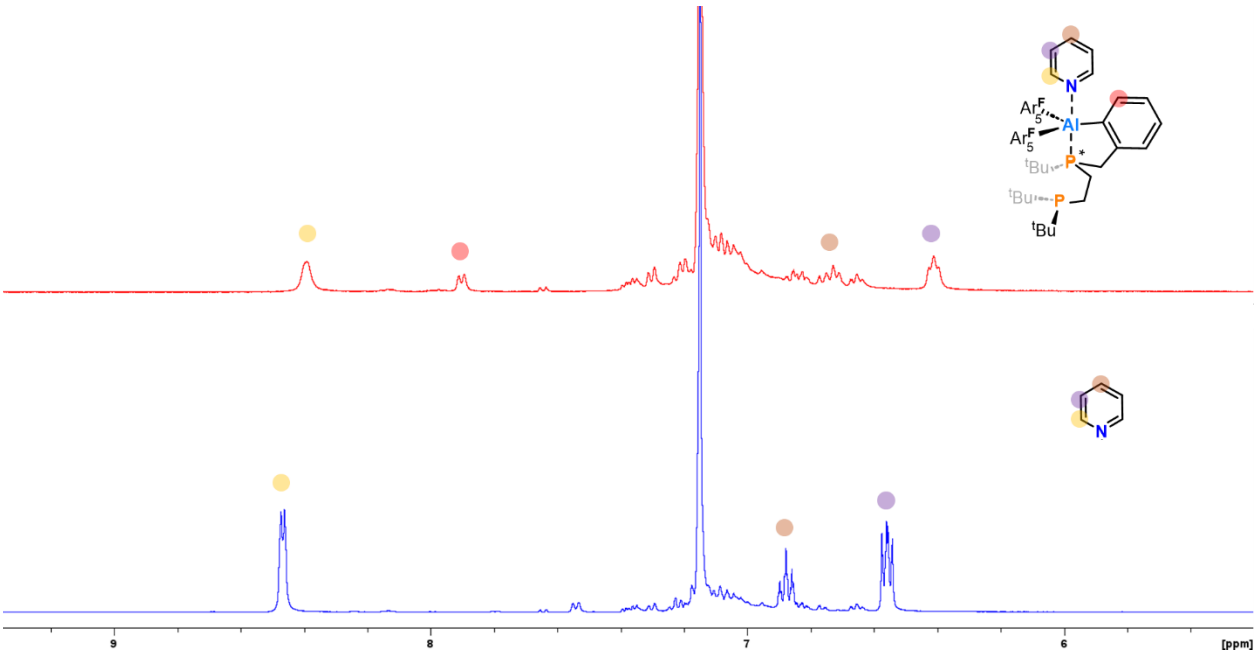


Figure S19. Generation of **3-pyr** (**red**) from **3** (**blue**) and removal of excess pyridine *in-vacuo* (**green**), $^{31}P\{^{1}H\}$ NMR, C_6D_6, 162 MHz, 298 K. *= Phosphine dimer $[(^{t}Bu)_2PCH_2CH_2P(tBu)]_2$[2] carried through from synthesis of **2**, # = $(^{t}Bu)_2PCH_2CH_2P(^{t}Bu)(CH_2C_6H_5)$.

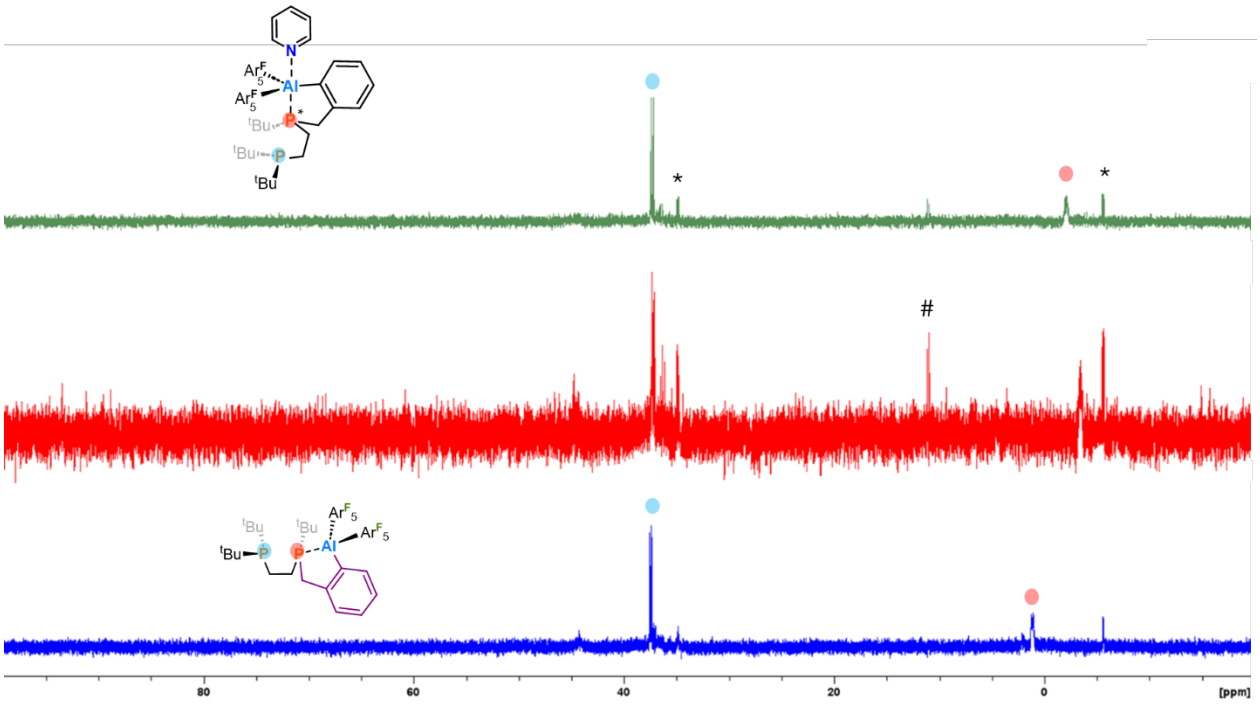


Figure S20. 3-pyr, $^{31}P\{^{1}H\}$ NMR, C_6D_6, 162 MHz, 298 K, *= Phosphine dimer $[(^{t}Bu)_2PCH_2CH_2P(tBu)]_2$[2] carried through from synthesis of **2**, # = $(^{t}Bu)_2PCH_2CH_2P(^{t}Bu)(CH_2C_6H_5)$.

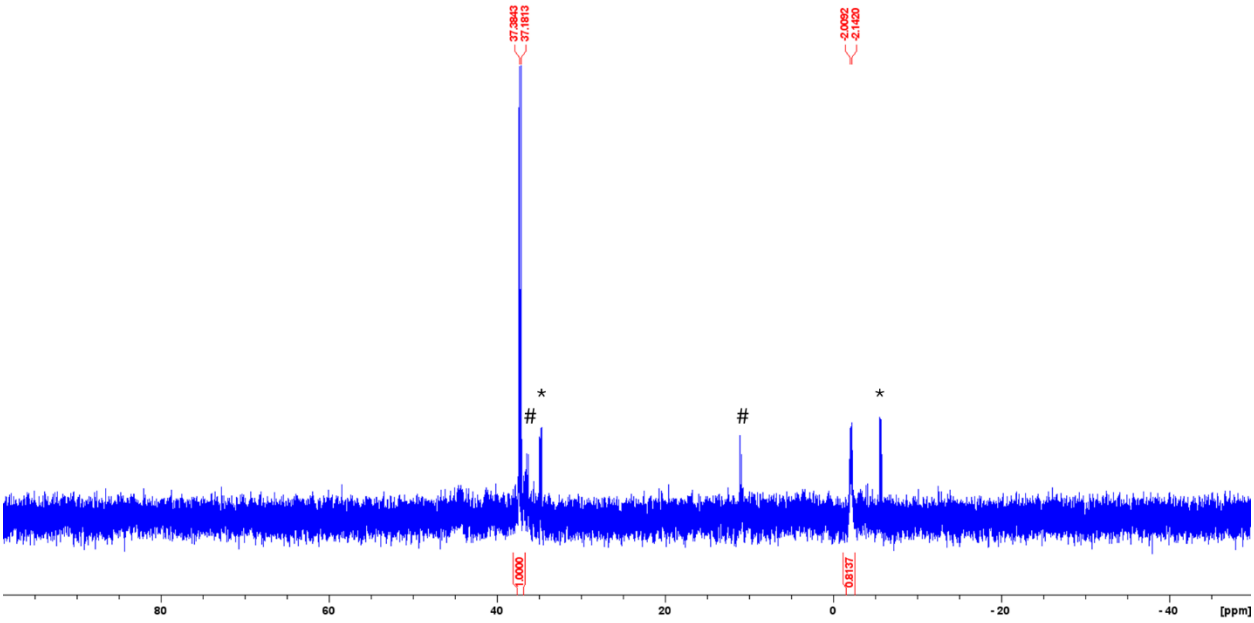


Figure S21. 3-pyr, ^{1}H-^{31}P HMBC NMR, C_6D_6, 400 MHz, 298 K.

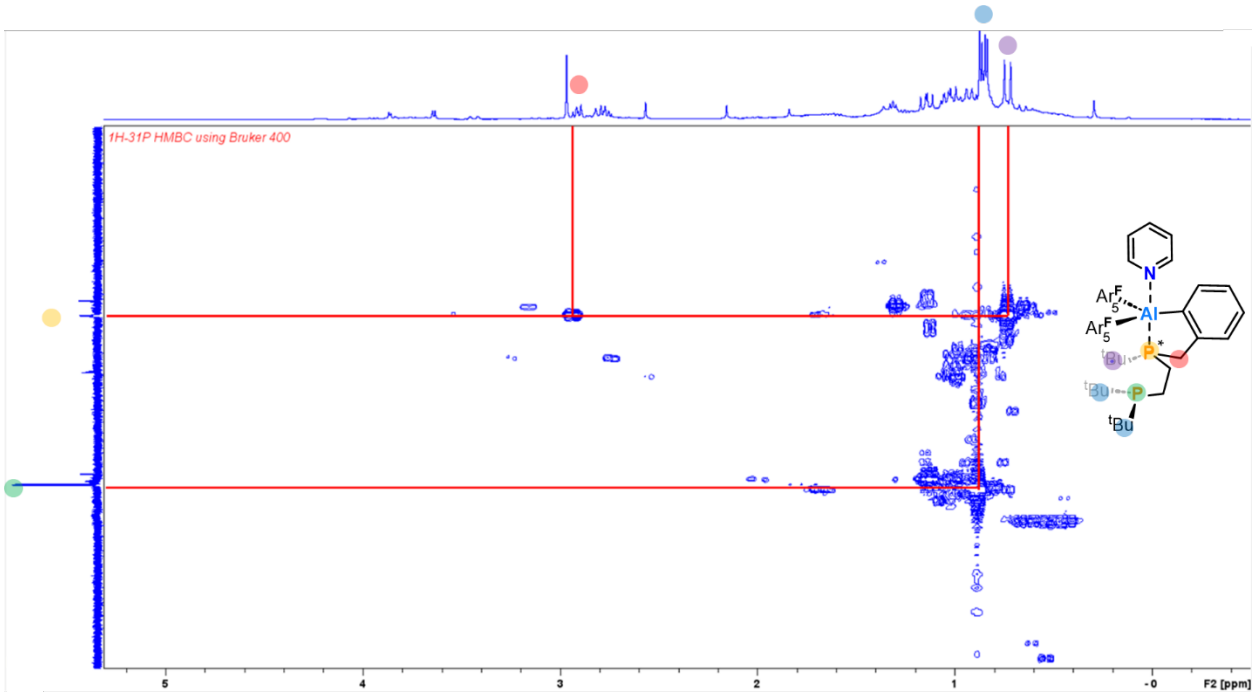


Figure S22. Generation of **3-pyr** (**red**) from **3** (**blue**), ^{19}F NMR, C_6D_6, 376 MHz, 298 K.

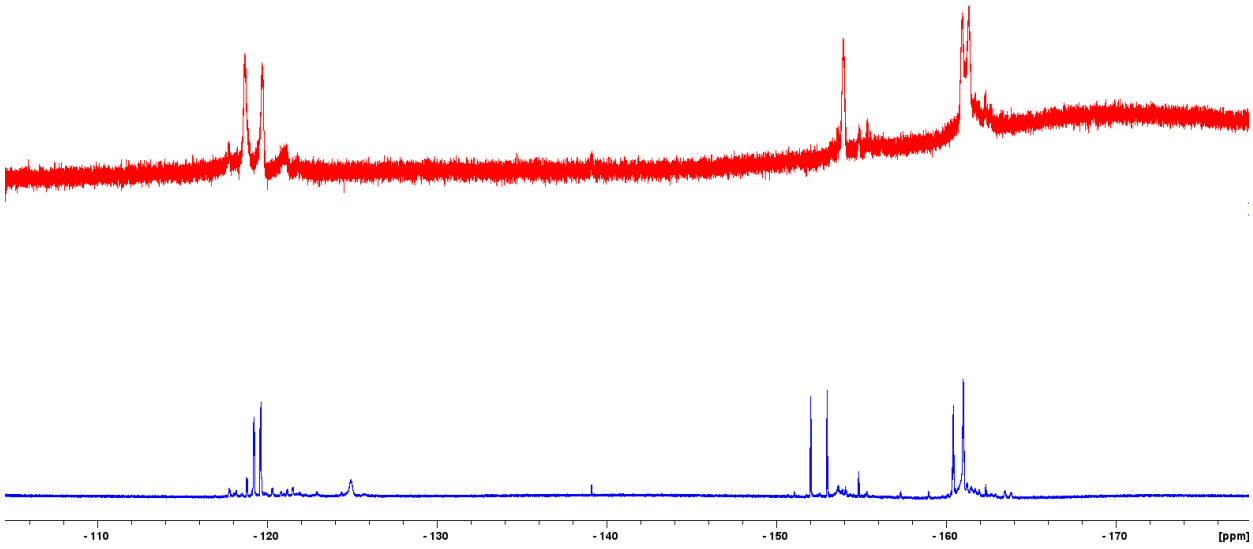


Figure S23. 3-pyr, ^{19}F NMR, C_6D_6, 376 MHz, 298 K.

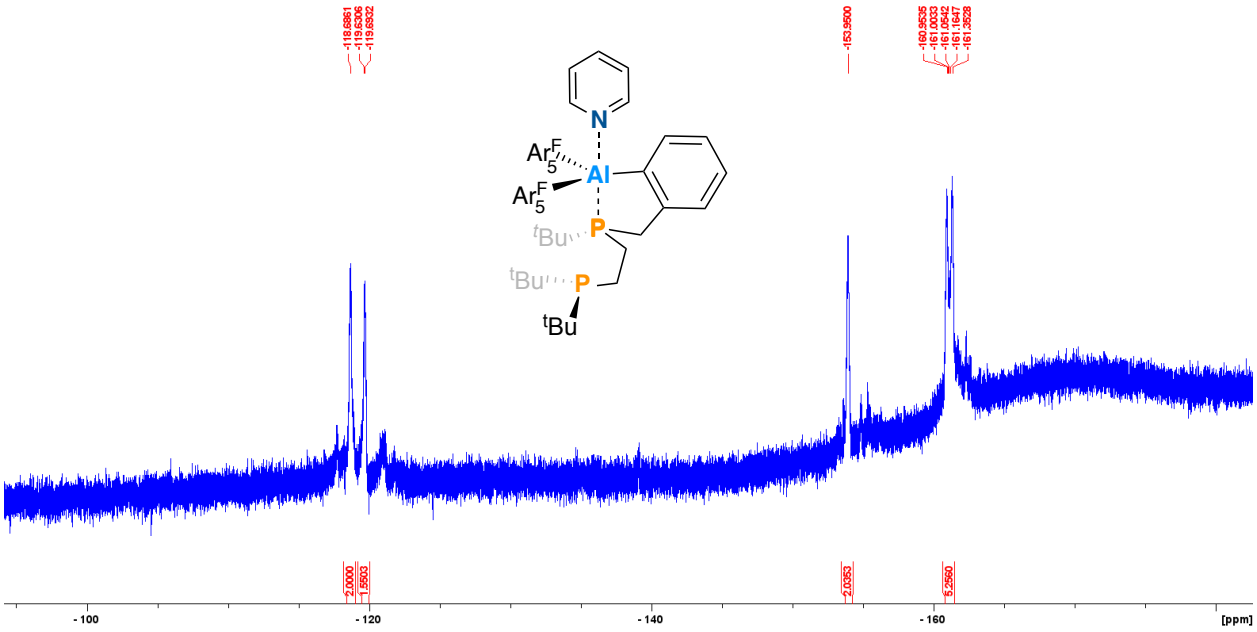


Figure S24. 3-THF, $^{31}P\{^1H\}$ NMR, C_6D_6, 162 MHz, 298 K. Addition of excess THF (**red**) and removal *in-vacuo* (**green**). *= Phosphine dimer $[(^tBu)_2PCH_2CH_2P(tBu)]_2$[2] carried through from synthesis of **2**, # = $(^tBu)_2PCH_2CH_2P(^tBu)(CH_2C_6H_5)$.

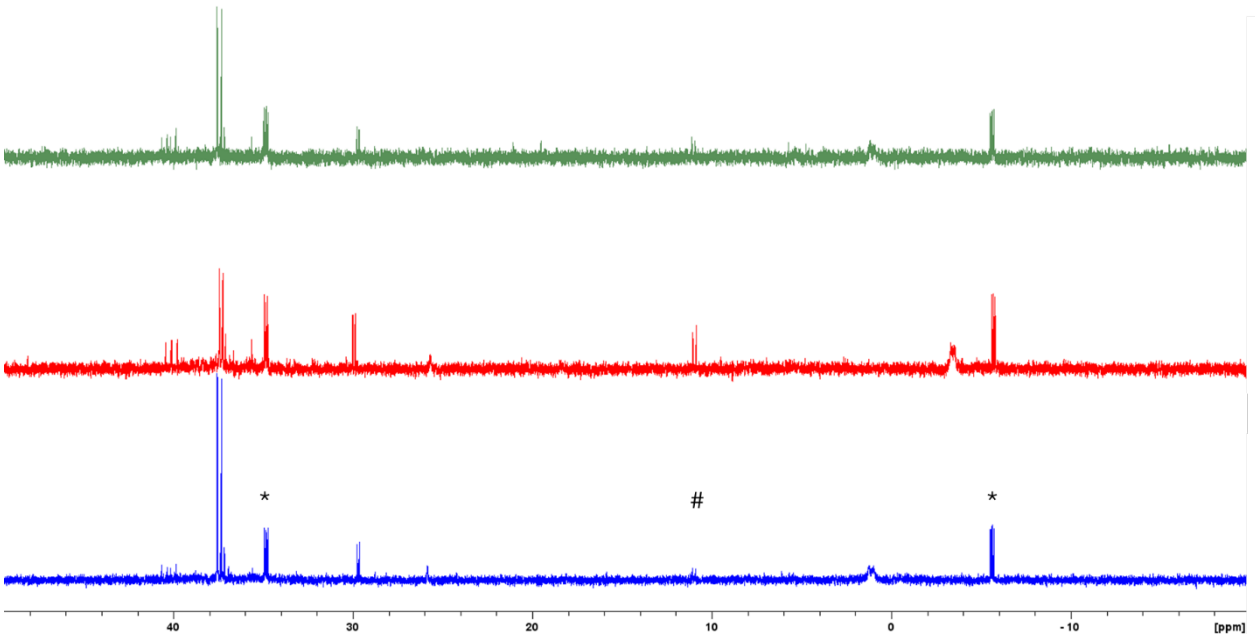


Figure S25. 3-THF, ^{19}F NMR, C_6D_6, 376 MHz, 298 K. Complex **3** (**blue**), addition of excess THF to **3** (**red**) to give **3-THF**, and removal of THF *in-vacuo* and re-dissolution in C_6D_6 (**green**), which shows return of **3**.

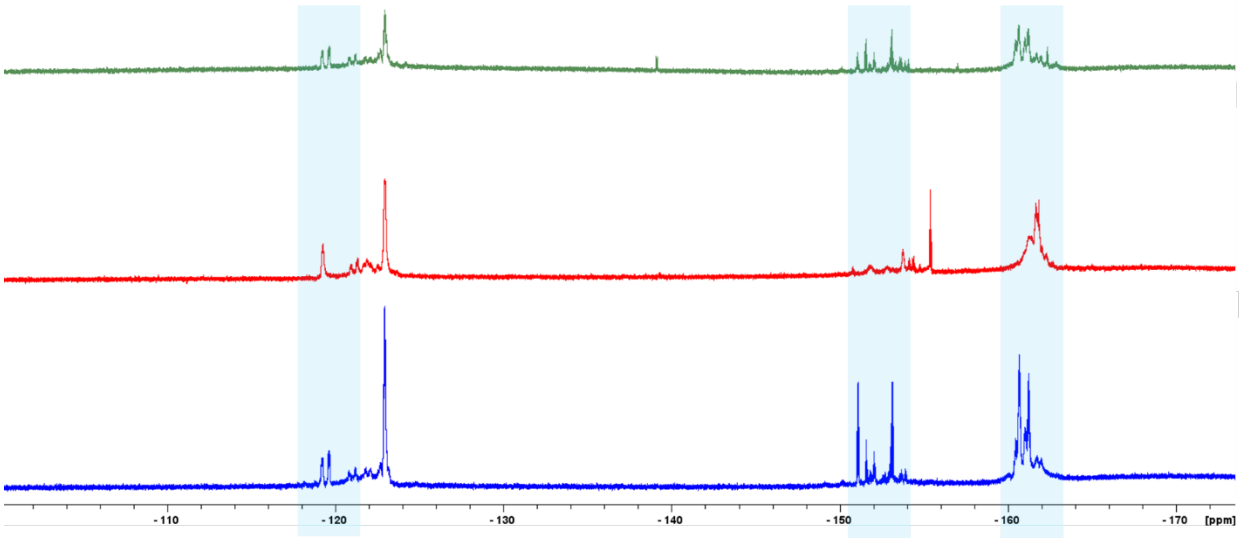


Figure S26. 4-pyr, ^{1}H NMR, C_6D_6, 400 MHz, 298 K.

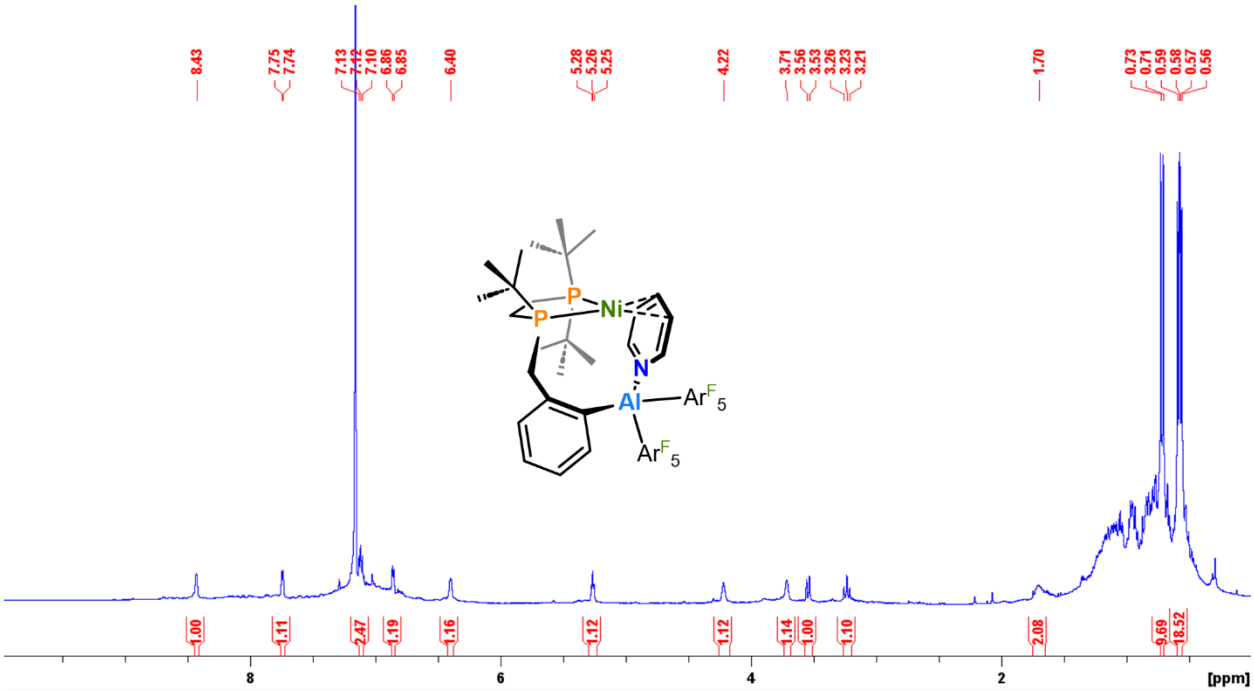


Figure S27. 4-pyr, ^{1}H-^{1}H COSY NMR, C_6D_6, 400 MHz, 298 K.

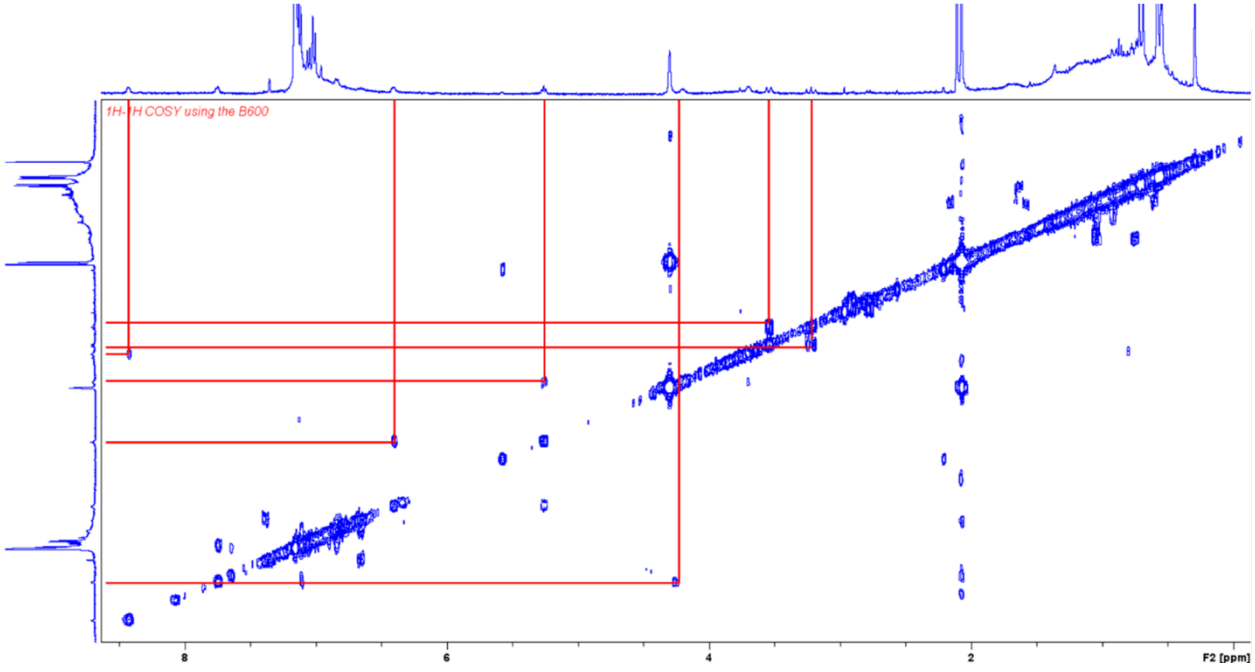


Figure S28. 4-pyr, 1D 1H TOCSY NMR, Irradiation at δ_H = 8.43 ppm, C_6D_6, 600 MHz, 298 K.

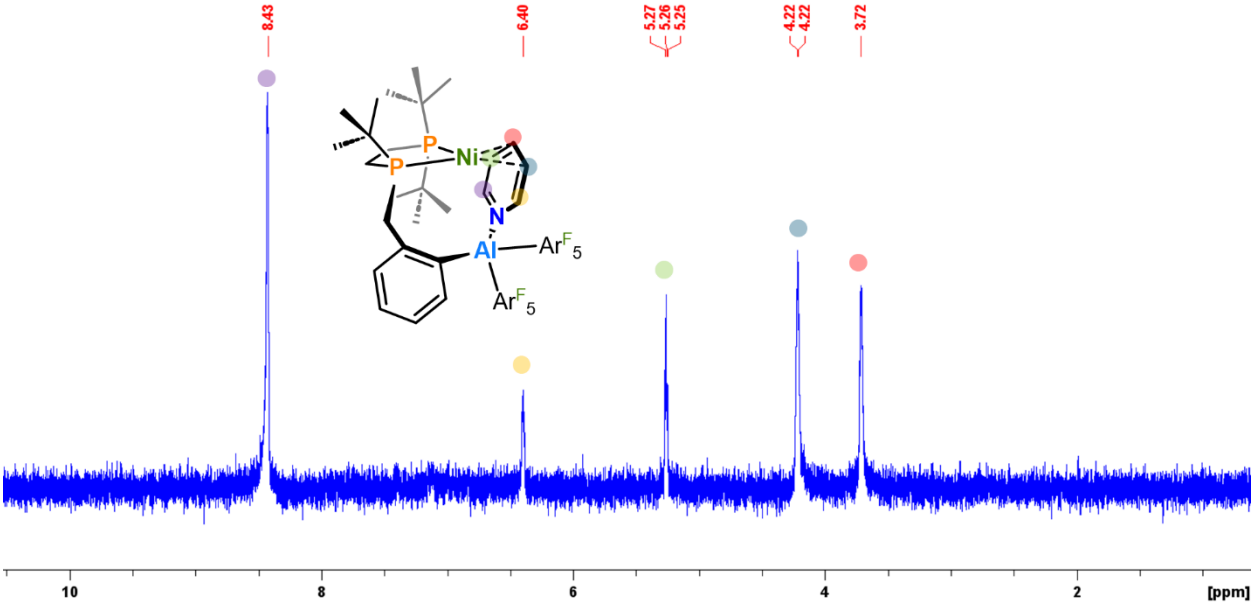


Figure S29. 4-pyr, VT-^{1}H NMR, tol-d_8, 400 MHz.

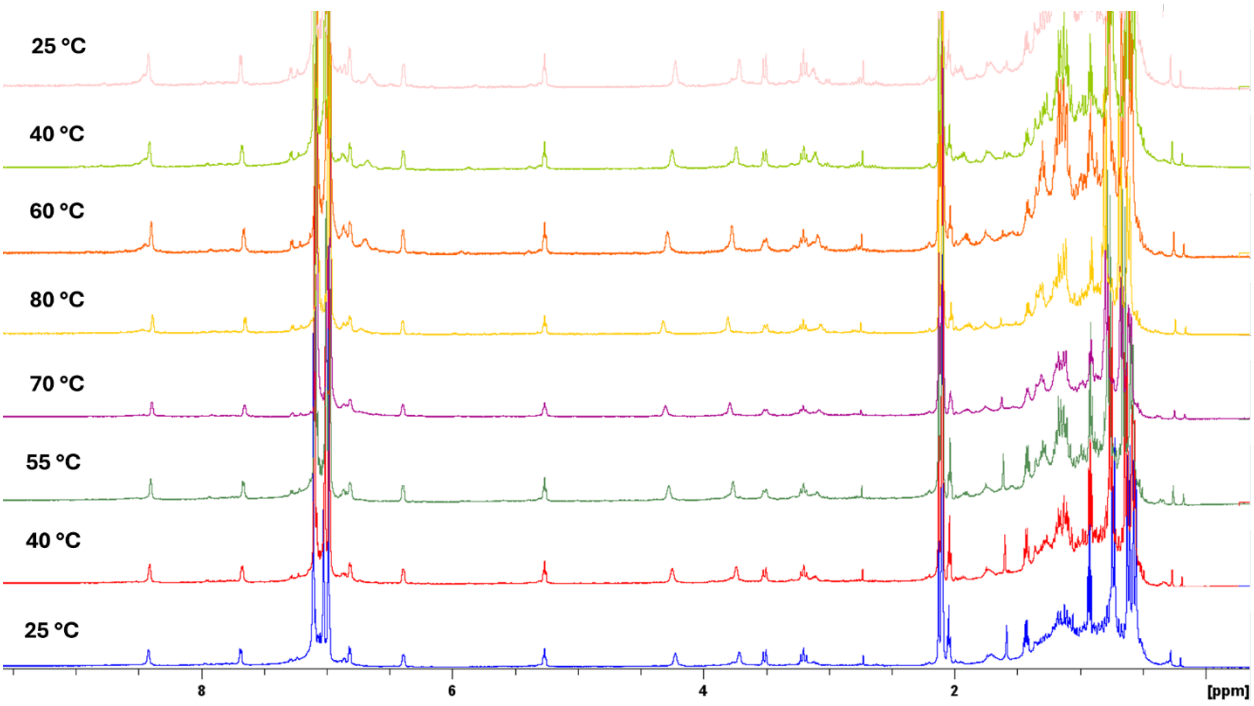


Figure S30. 4-pyr, ^{31}P{^{1}H} NMR, C_6D_6, 162 MHz, 298 K.

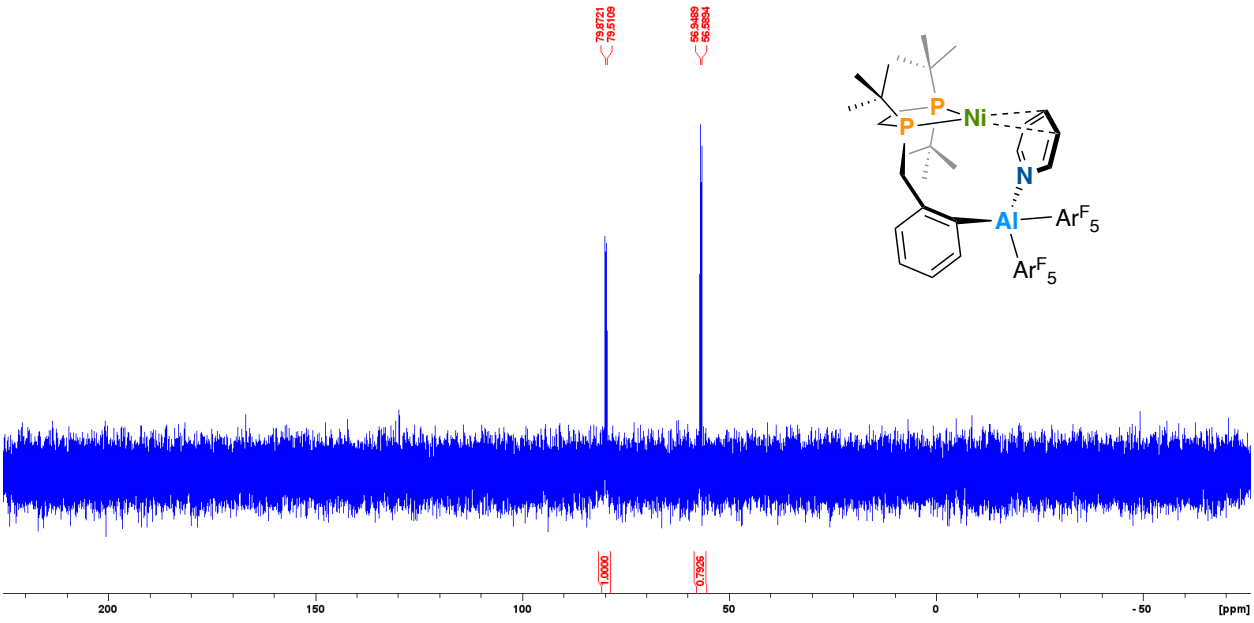


Figure S31. 4-pyr, ^{31}P NMR, tol-d_8, 162 MHz, Variable Temperature.

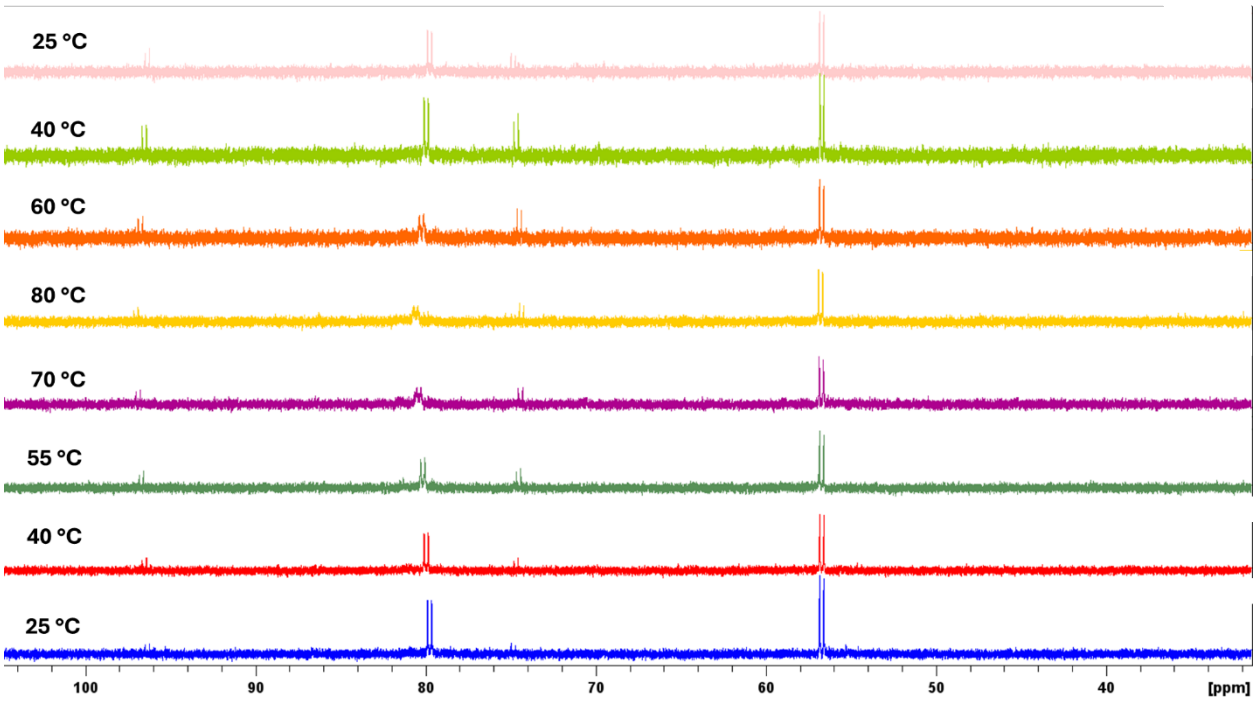


Figure S32. 4-pyr, ^{1}H-^{31}P HMBC NMR, C_6D_6, 400 MHz, 298 K.

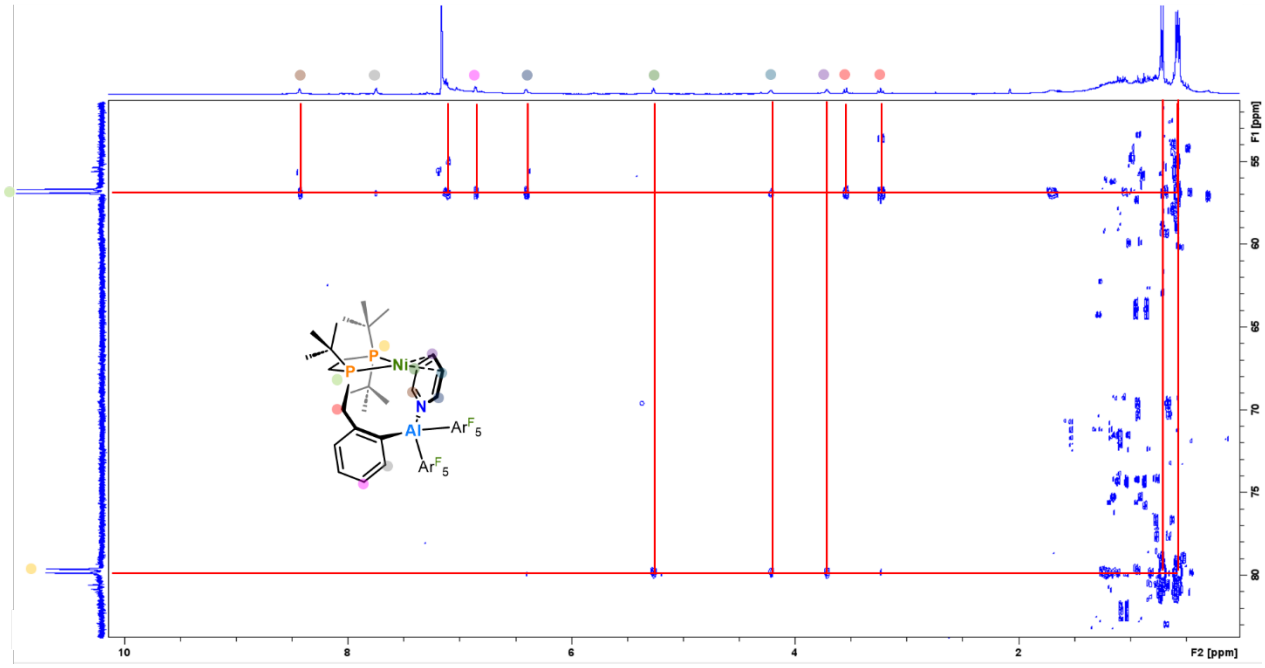


Figure S33. 4-pyr, ^{19}F NMR, C_6D_6, 150 MHz, 298 K.

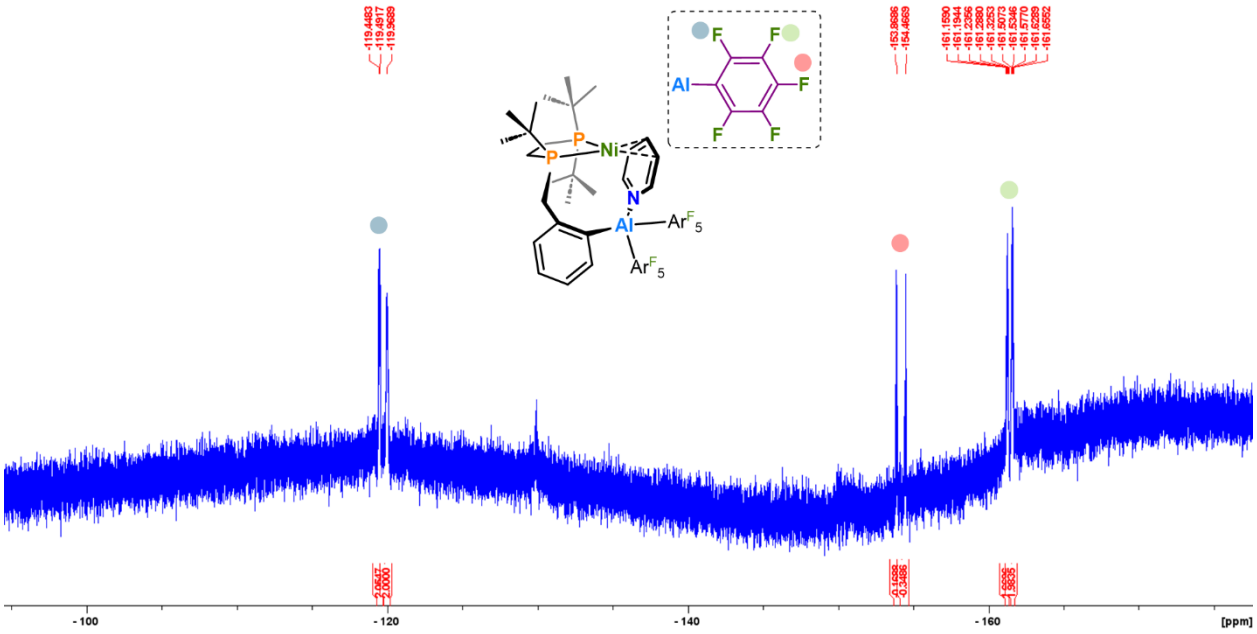


Figure S34. 4-pyr, $^{13}C\{^1H\}$ NMR, C_6D_6, 150 MHz, 298 K.

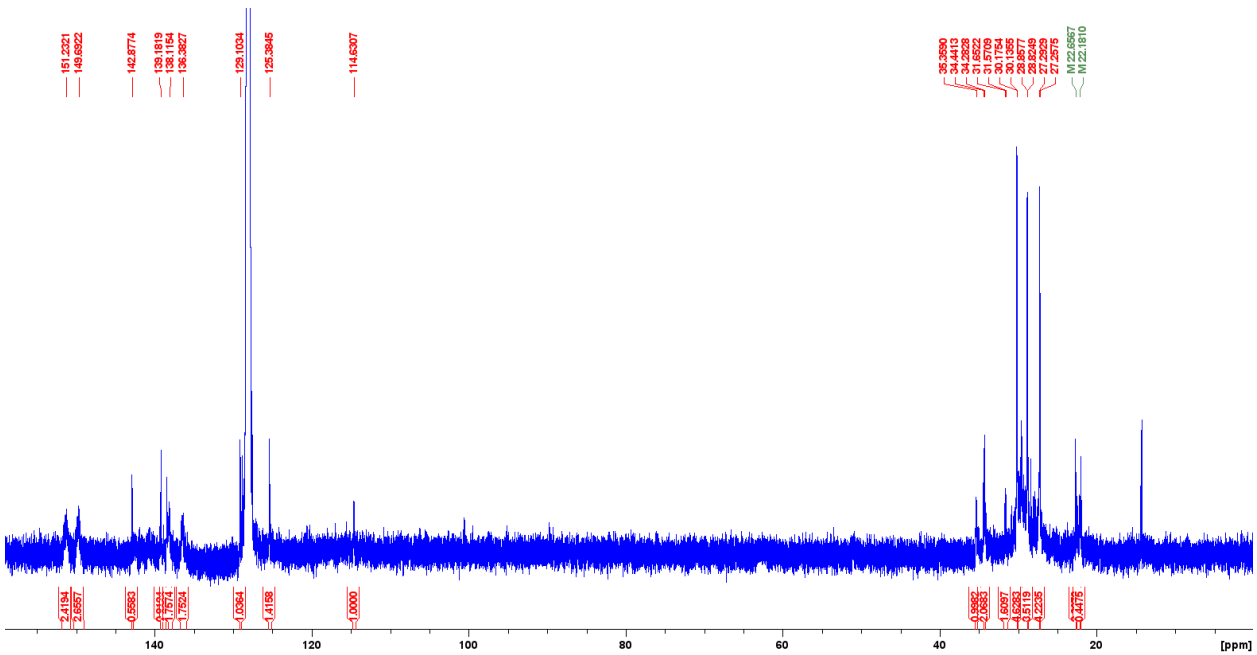


Figure S35. 4-pyr, ^{1}H-^{13}C HSQC, C_6D_6, 600 MHz, 298 K.

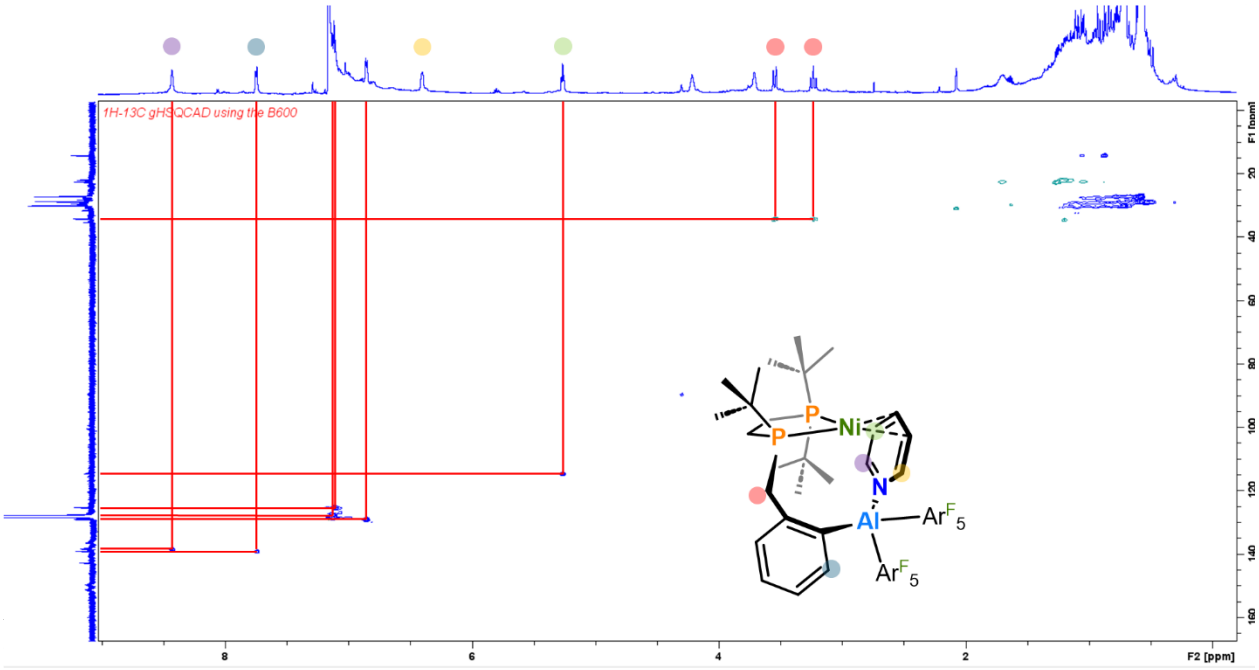


Figure S36. 4-pyr-d$_5$, ^{1}H NMR, C_6D_6, 400 MHz, 298 K.

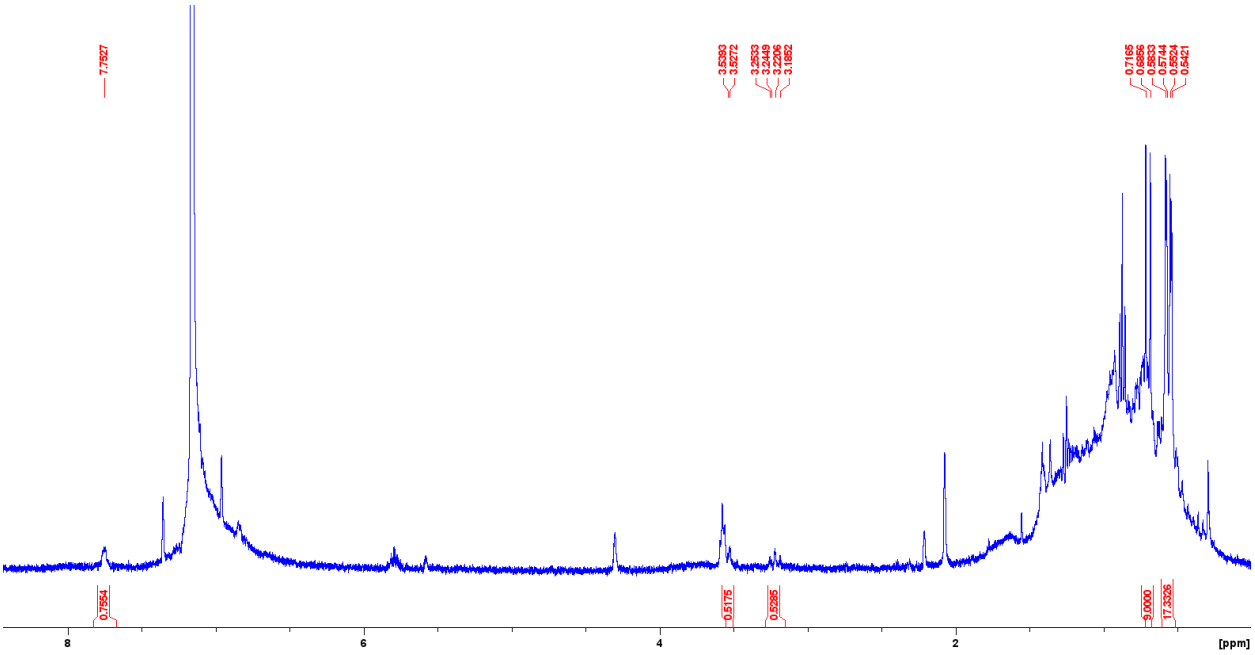


Figure S37. 4-pyr-d$_5$, ^{1}H NMR, C_6D_6, 400 MHz, 298 K, showing pyr signals are missing due to deuteration.

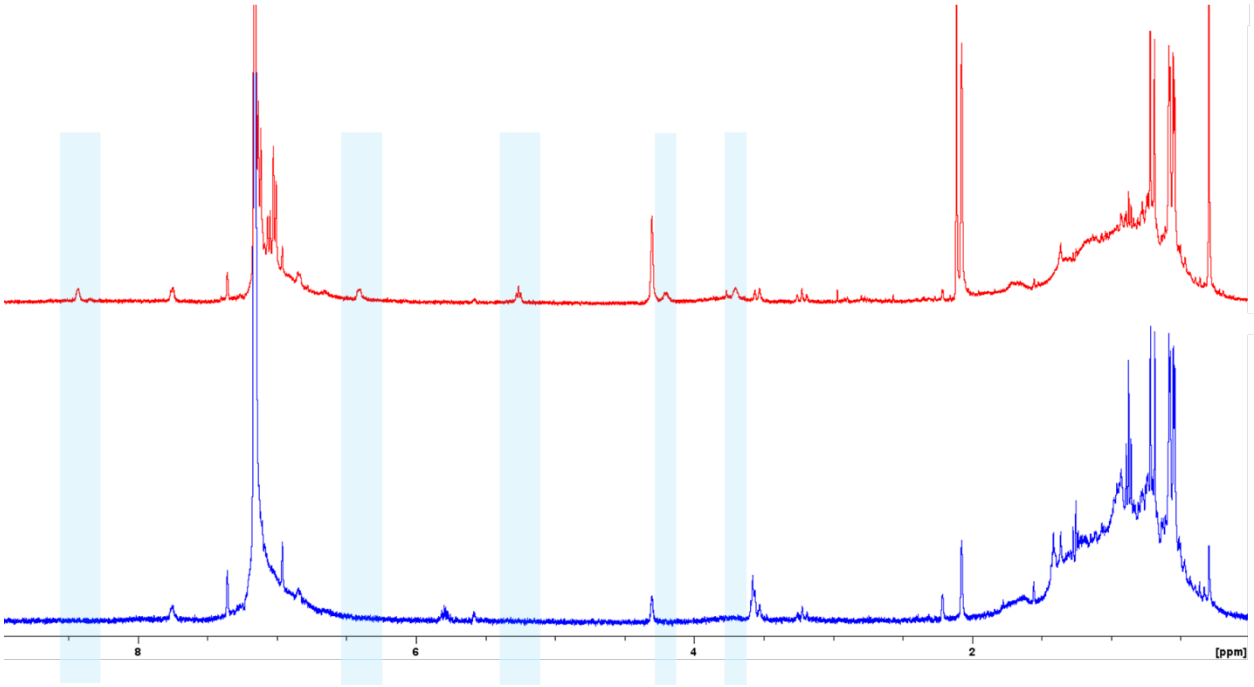


Figure S38. 4-pyr-d$_5$, ^{31}P{^{1}H} NMR, C_6D_6, 162 MHz, 298 K.

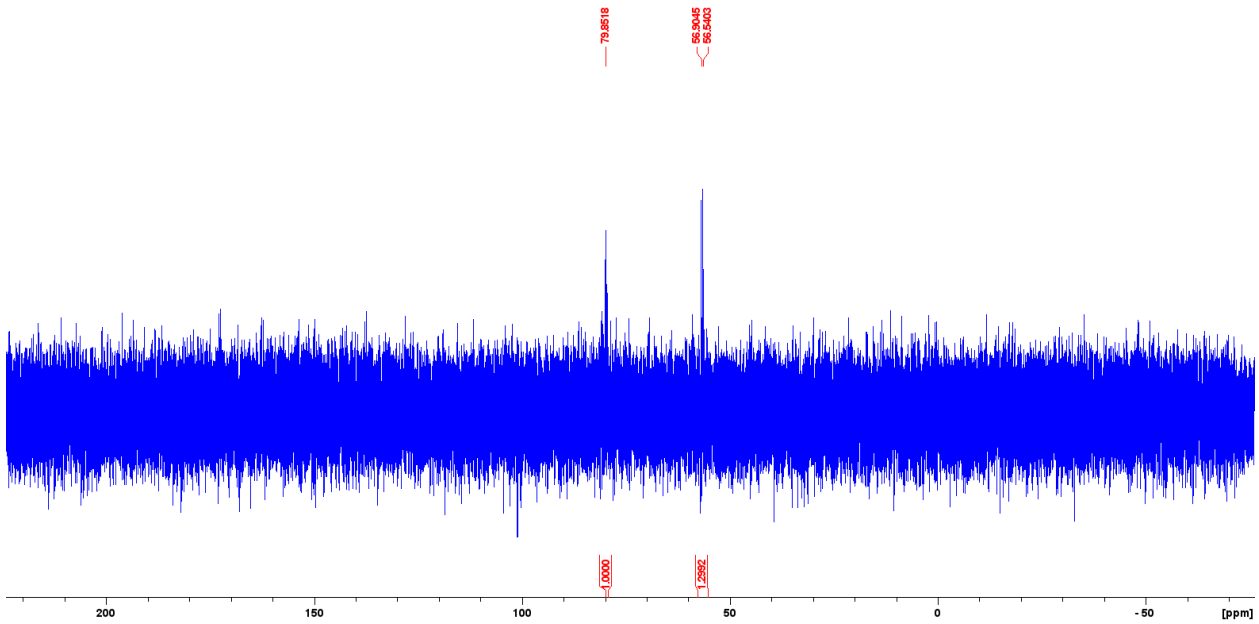


Figure S39. 5-quin, $^{1}H\{^{31}P\}$ NMR, C_6D_6, 400 MHz, 298 K.

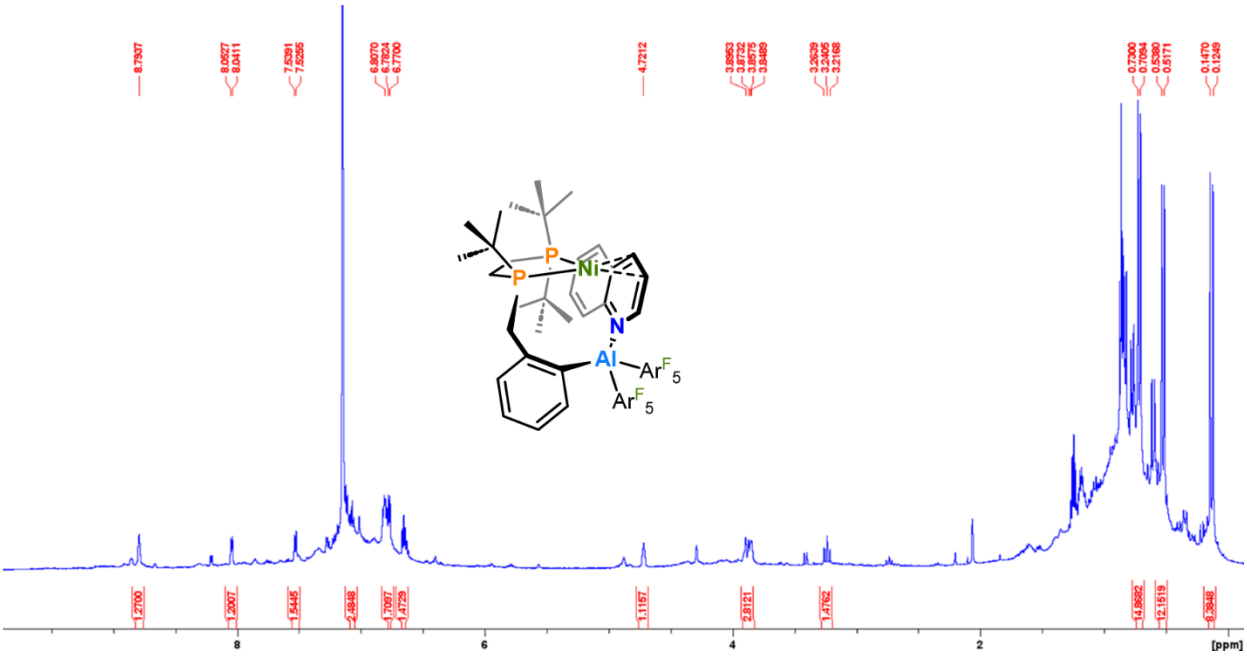


Figure S40. 5-quin, ^{1}H-^{1}H COSY NMR, C_6D_6, 400 MHz, 298 K.

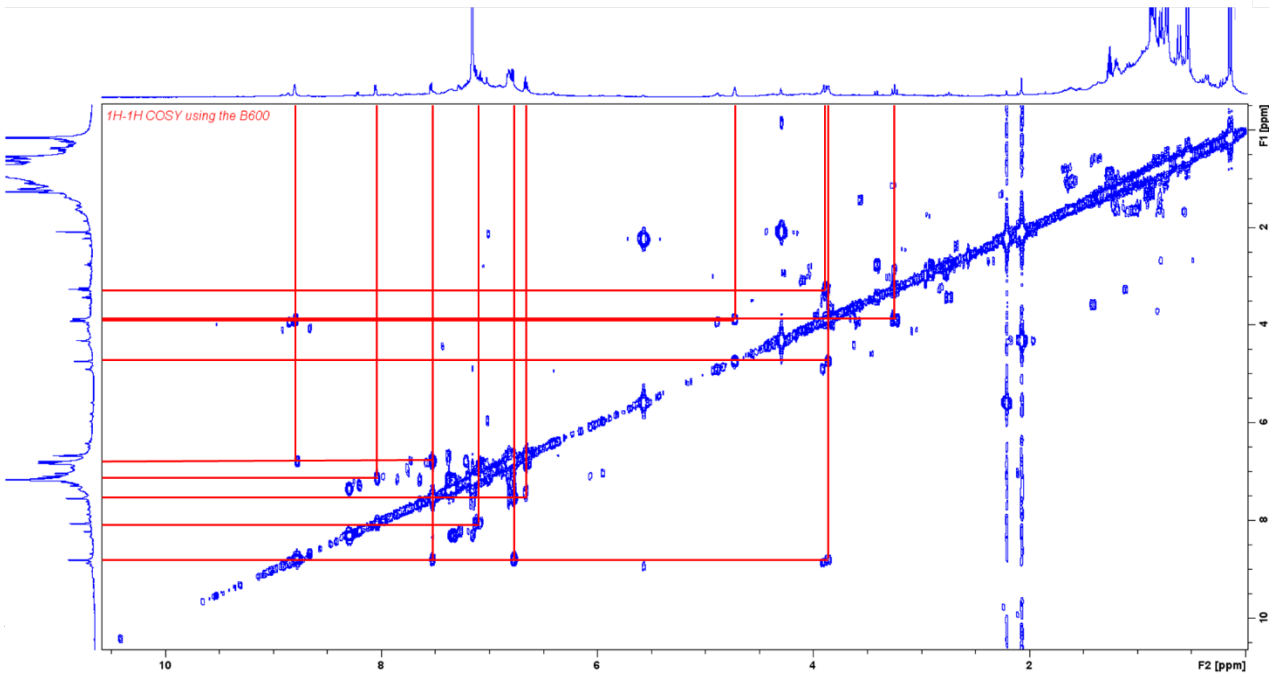


Figure S41. 5-Quin, 1D 1H TOCSY NMR, Irradiation at δ_H = 4.73 ppm (Red), 7.53 ppm (Green), C_6D_6, 600 MHz, 298 K.

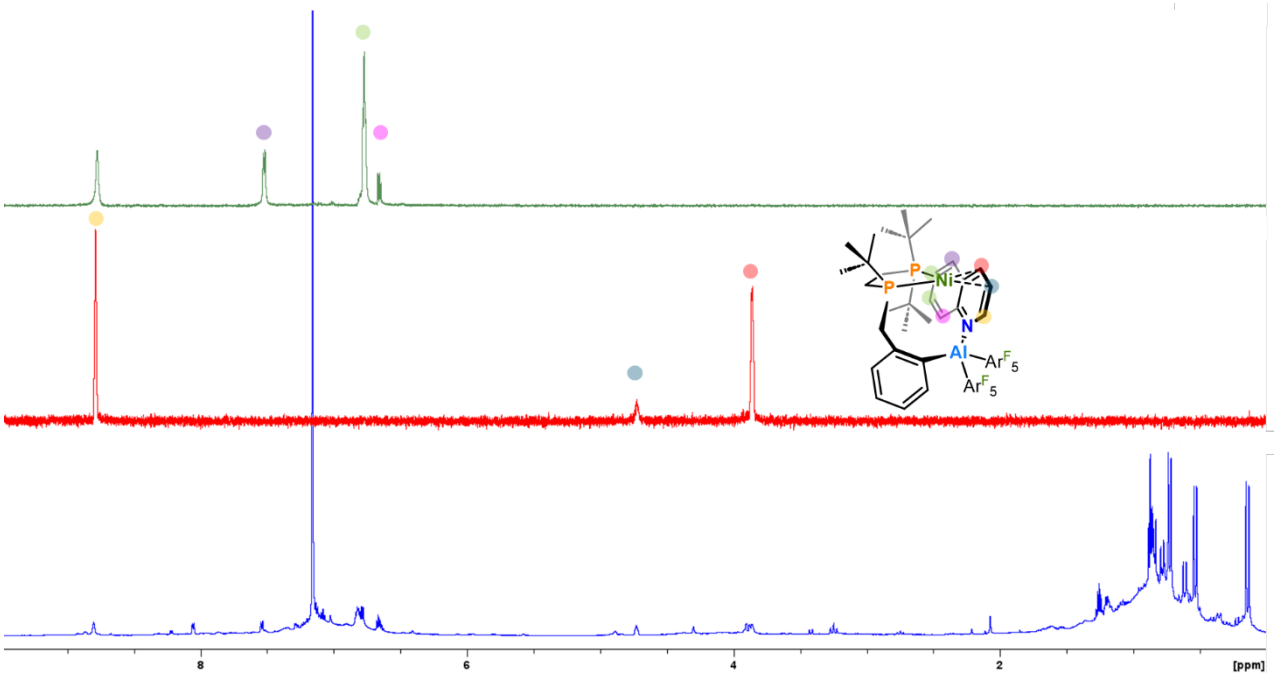


Figure S42. 5-Quin, 1D 1H TOCSY NMR, Irradiation at δ_H = 8.04 ppm, C_6D_6, 600 MHz, 298 K.

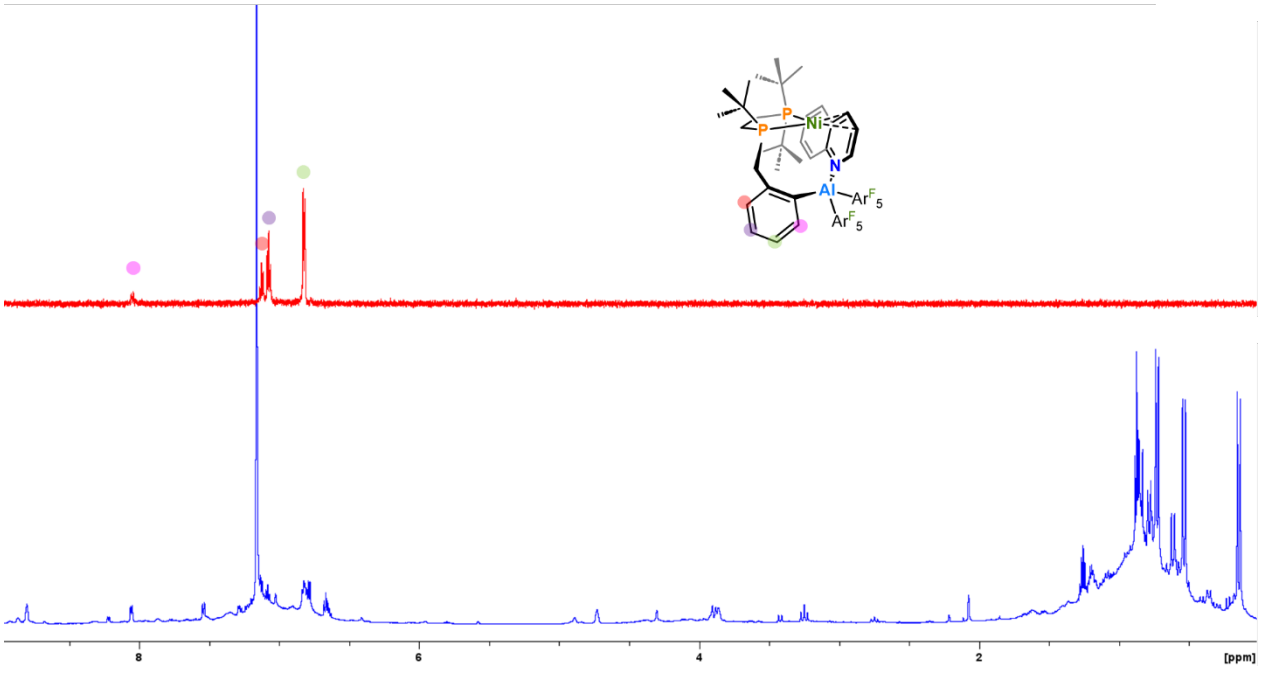


Figure S43. 5-quin, ^{31}P NMR, C_6D_6, 162 MHz, 298 K (* = Minor Isomer).

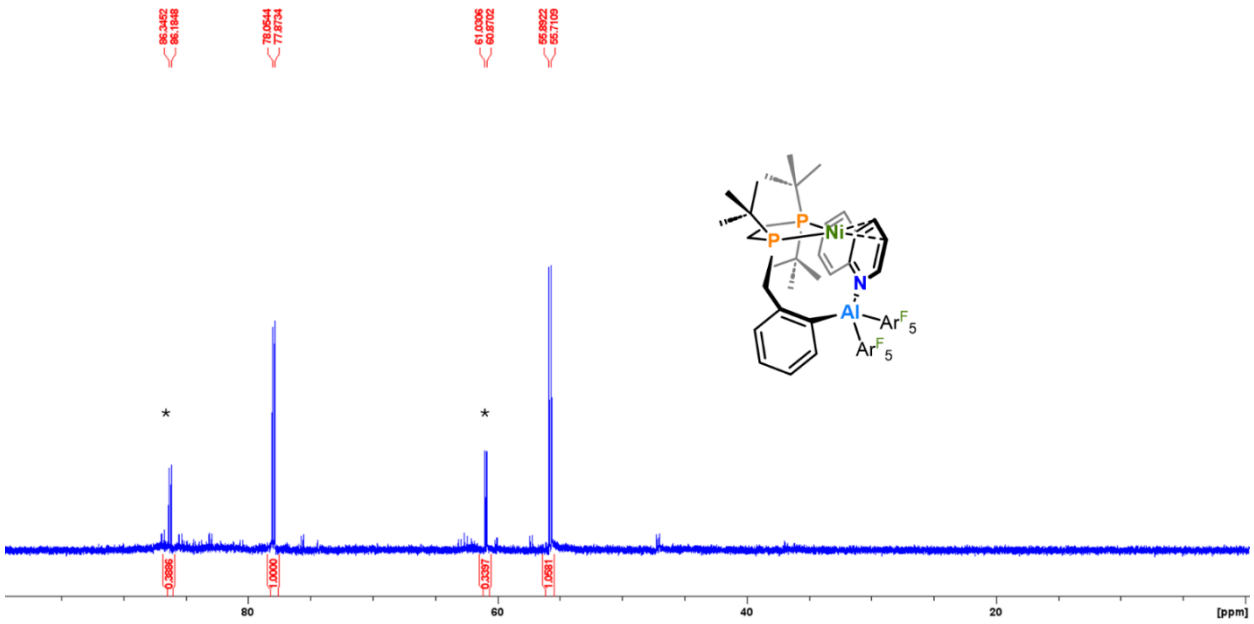


Figure S44. 5-quin, Major Isomer, ^{1}H-^{31}P HMBC NMR, C_6D_6, 400 MHz, 298 K.

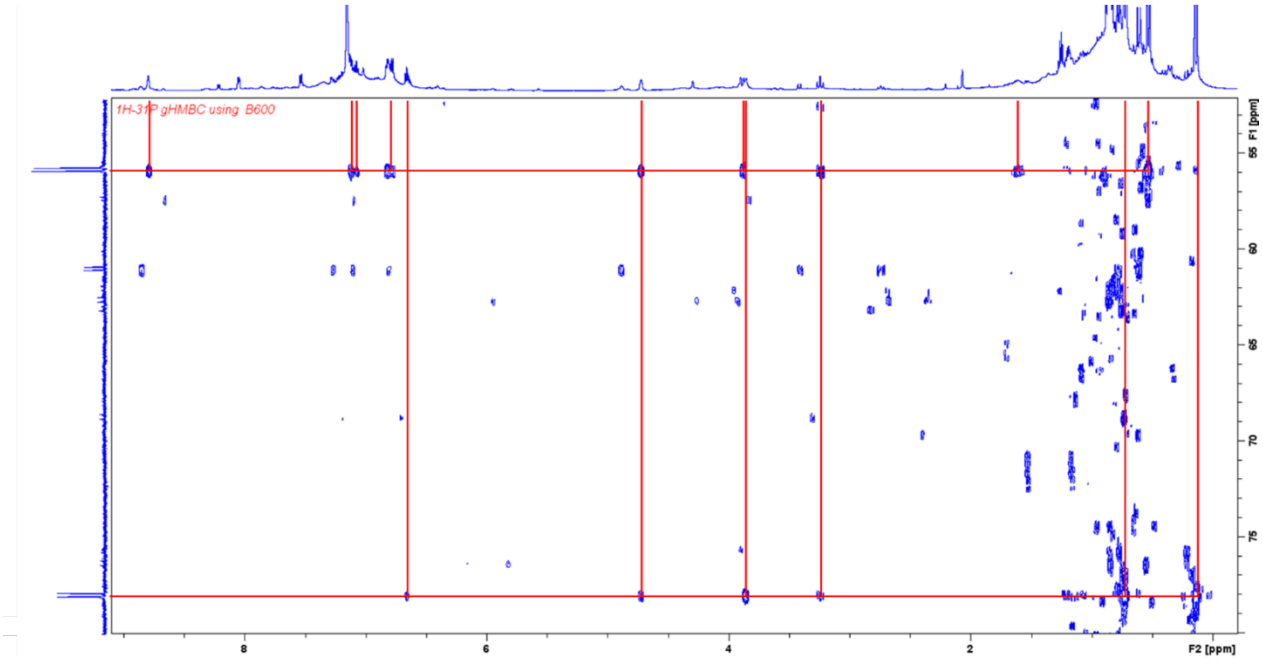


Figure S45. 5-quin, Minor Isomer, ^{1}H-^{31}P HMBC NMR, C_6D_6, 400 MHz, 298 K.

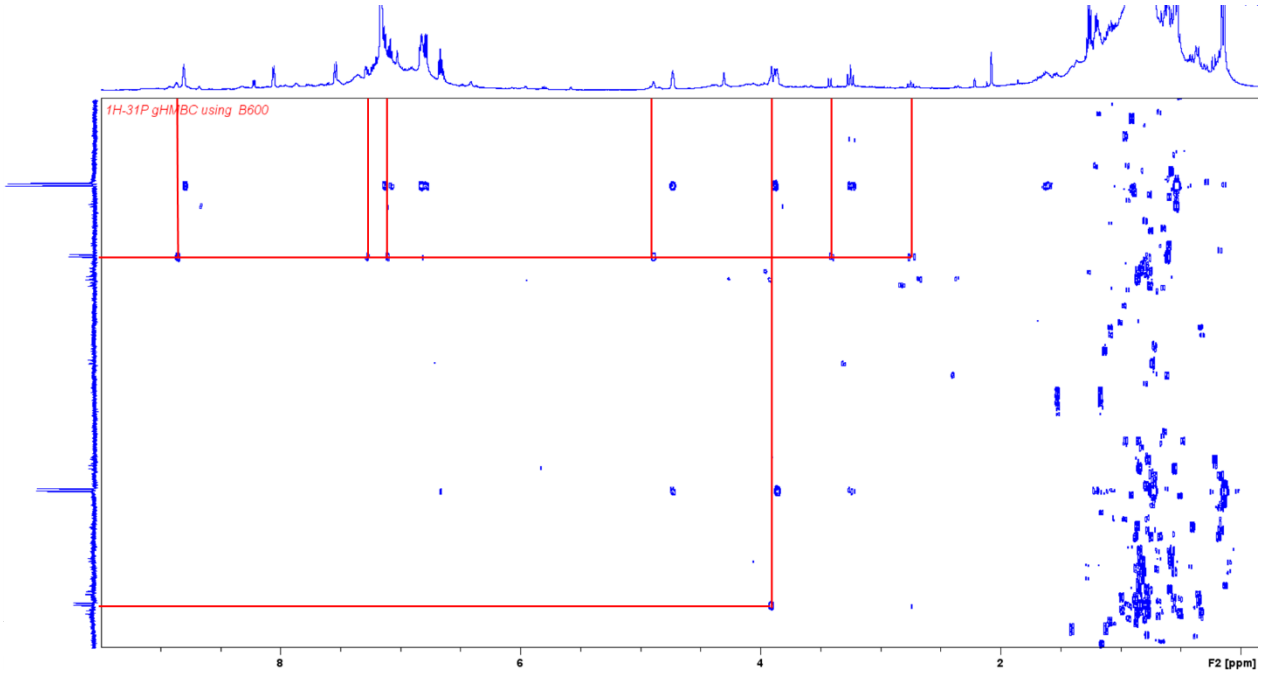


Figure S46. 5-quin, ^{19}F NMR, C_6D_6, 376 MHz, 298 K (* = minor isomer, # = unknown impurity.).

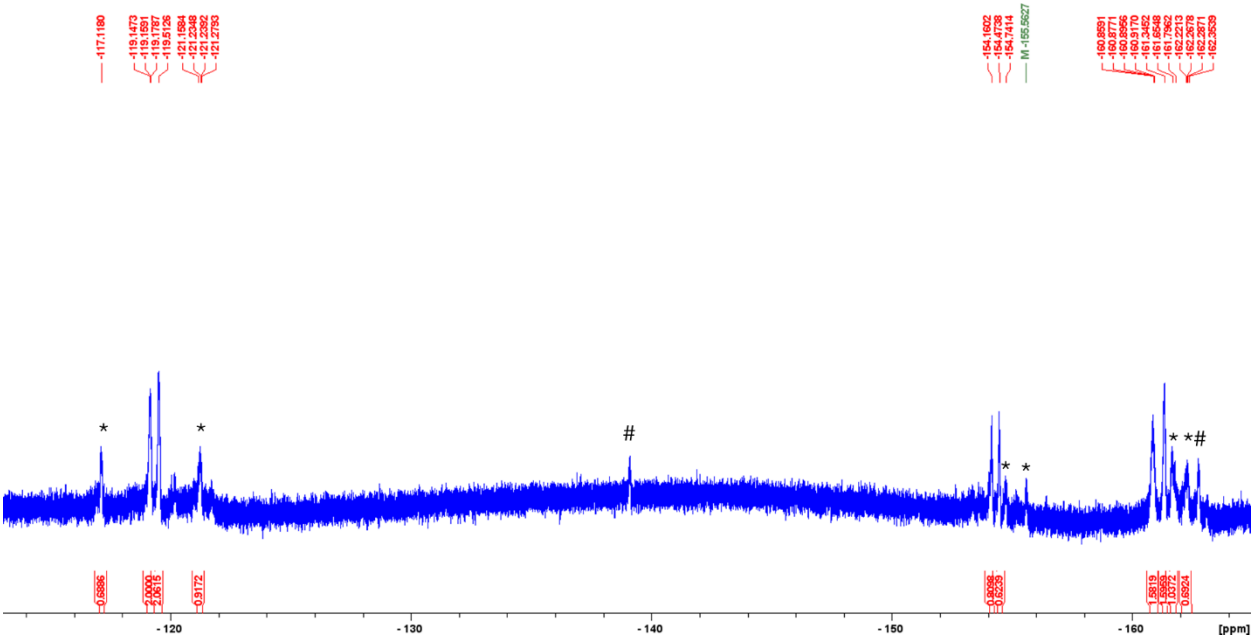


Figure S47. 5-quin, ^{19}F NMR Stacked Plot, C_6D_6, 376 MHz, 298, **4-pyr** (**red**), **5-quin** (**blue**).

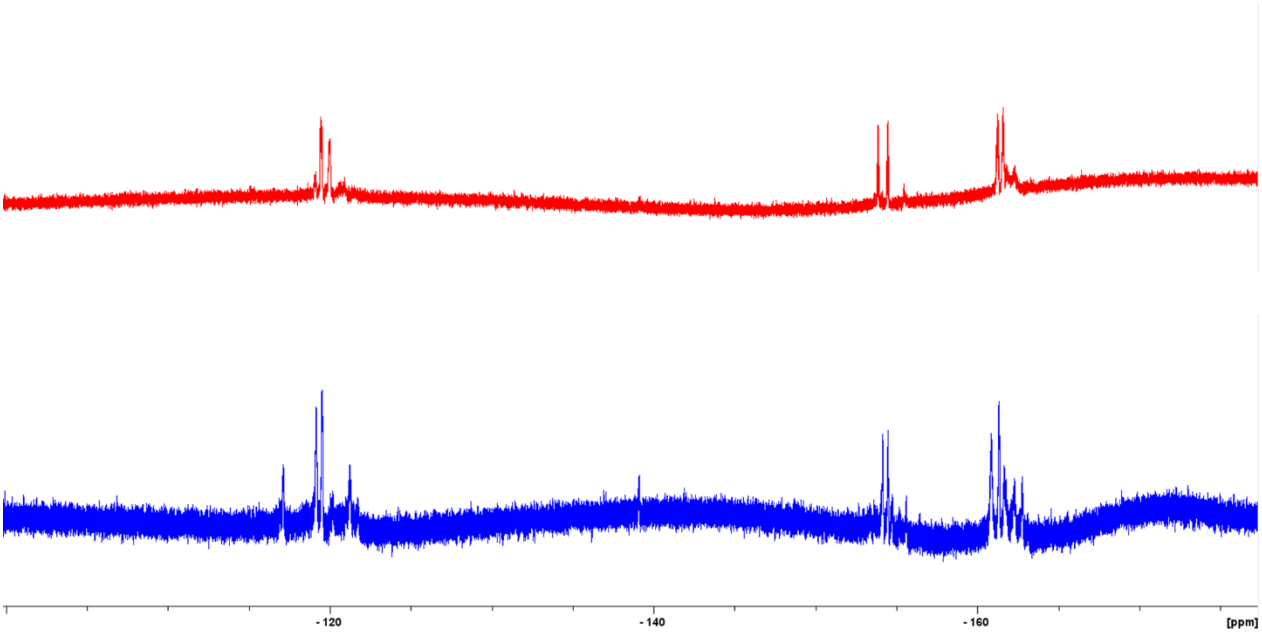


Figure S48. 5-quin, ^{1}H-^{13}C HSQC, C_6D_6, 600 MHz, 298 K showing upfield ^{13}C chemical shifts of Ni-bound carbons.

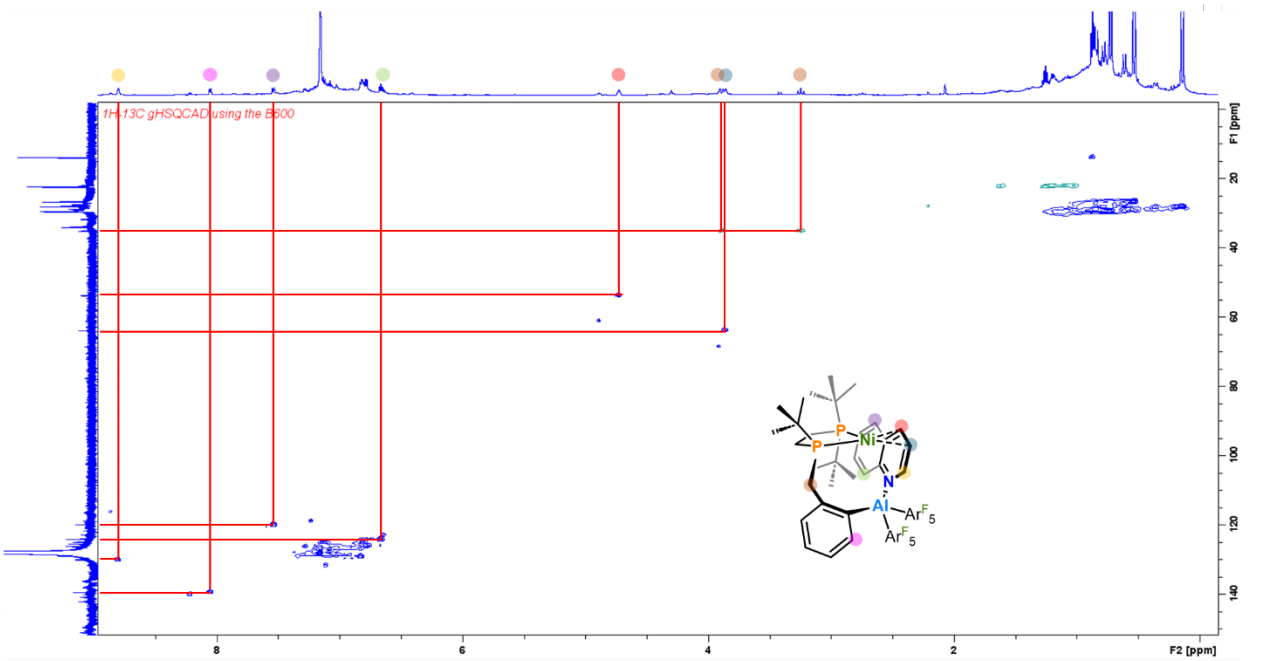


Figure S49. 5-quin, ^{1}H-^{13}C HSQC, C_6D_6, 600 MHz, 298 K_showing diphosphine ethyl backbone.

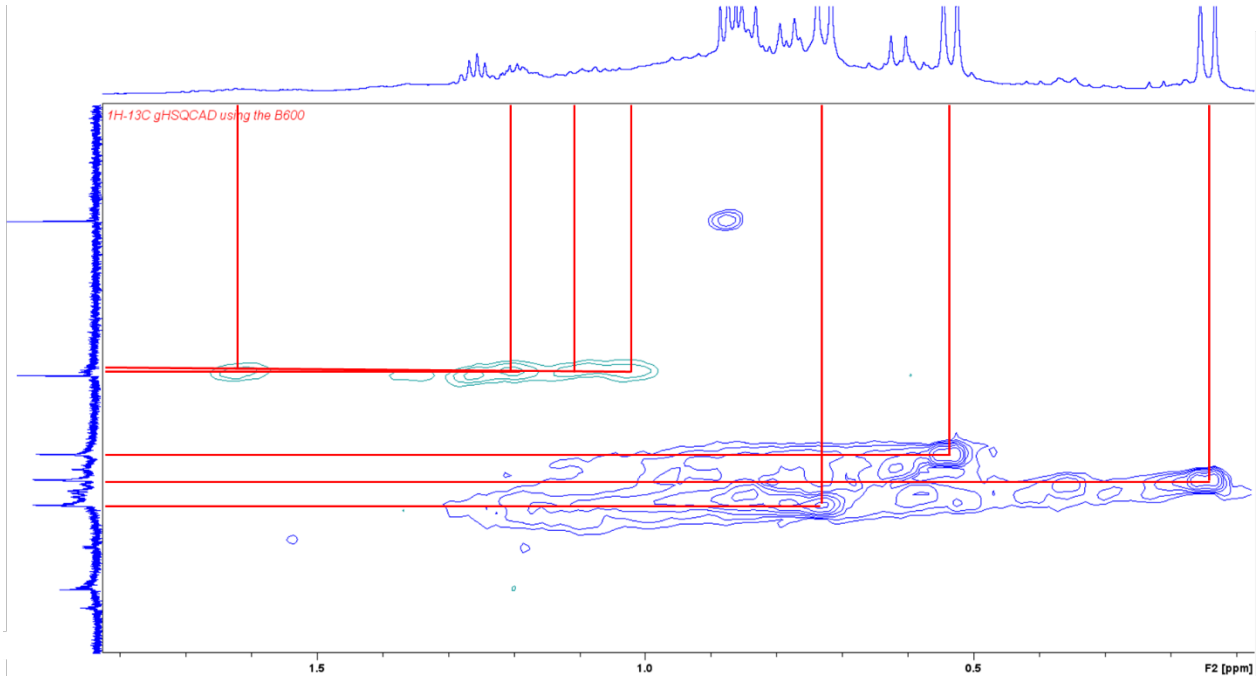


Figure S50. 5-quin, ^{1}H-^{13}C HSQC, C_6D_6, 600 MHz, 298 K showing aromatic region.

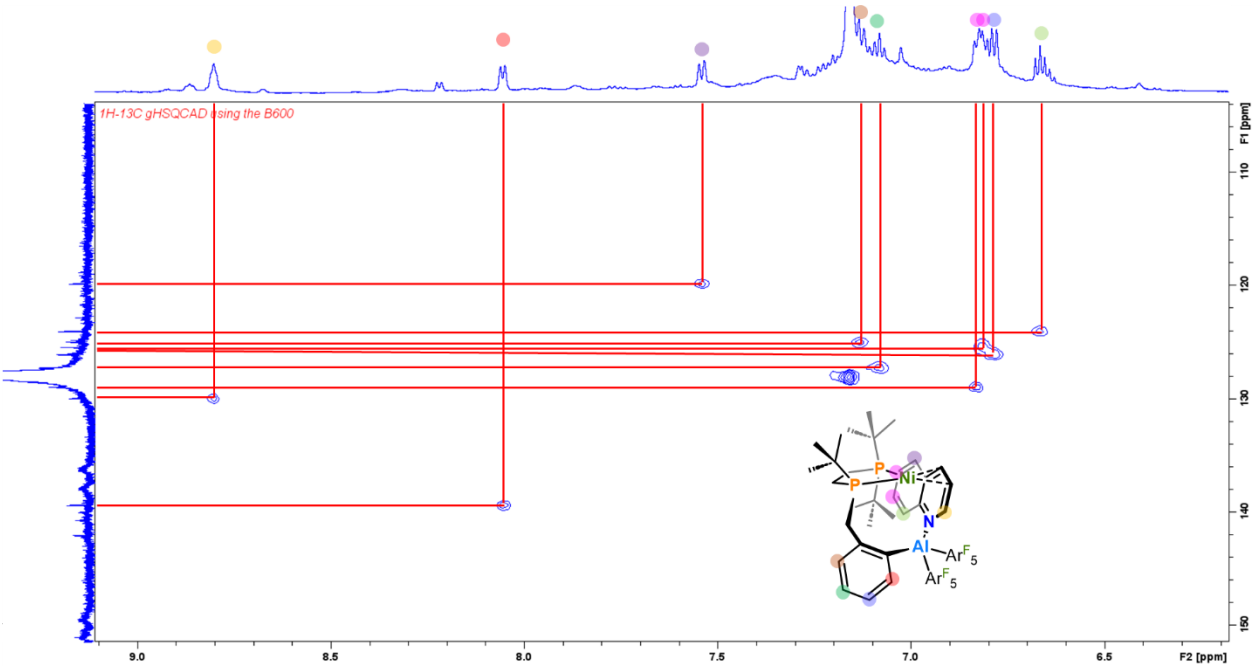
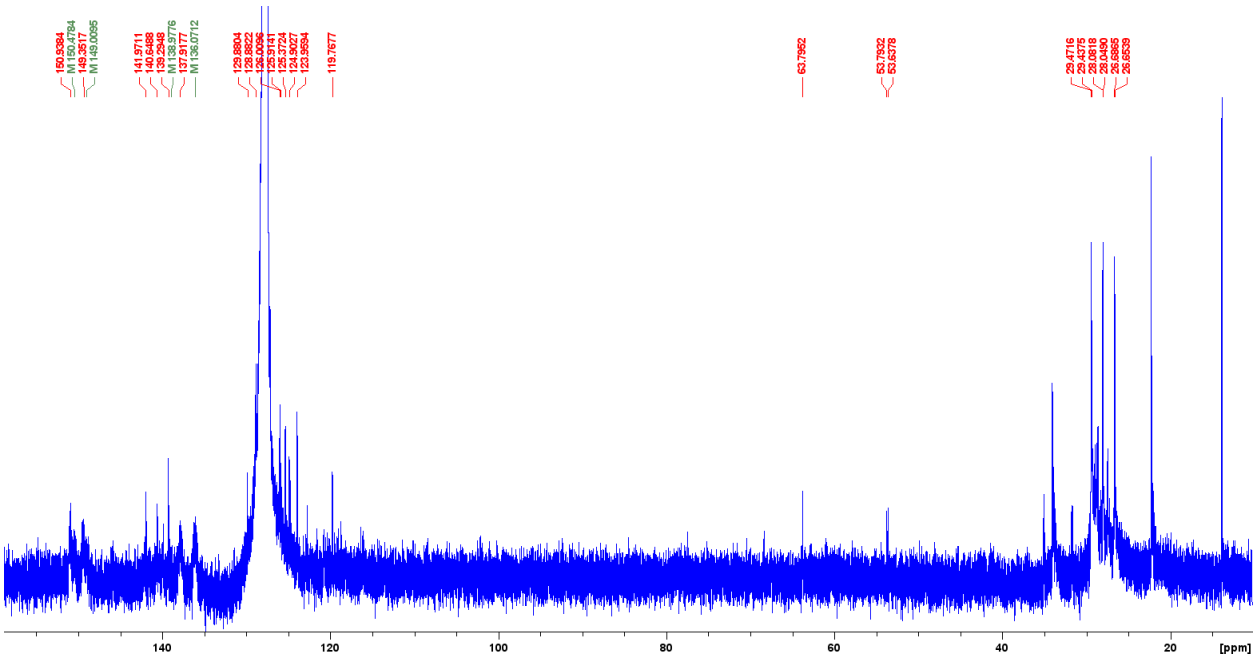


Figure S51: 5-quin, $^{13}C\{^{1}H\}$ NMR, C_6D_6, 150 MHz, 298 K.



3. Mass Spectrometry (APCI-MS):

Figure S52. 3, APCI(+)-MS (calcd. *m*/*z* = 713.2050 for $C_{33}H_{38}AlF_{10}P_2$, calcd. *m*/*z* = 729.2048 for $C_{33}H_{38}AlF_{10}OP_2$).

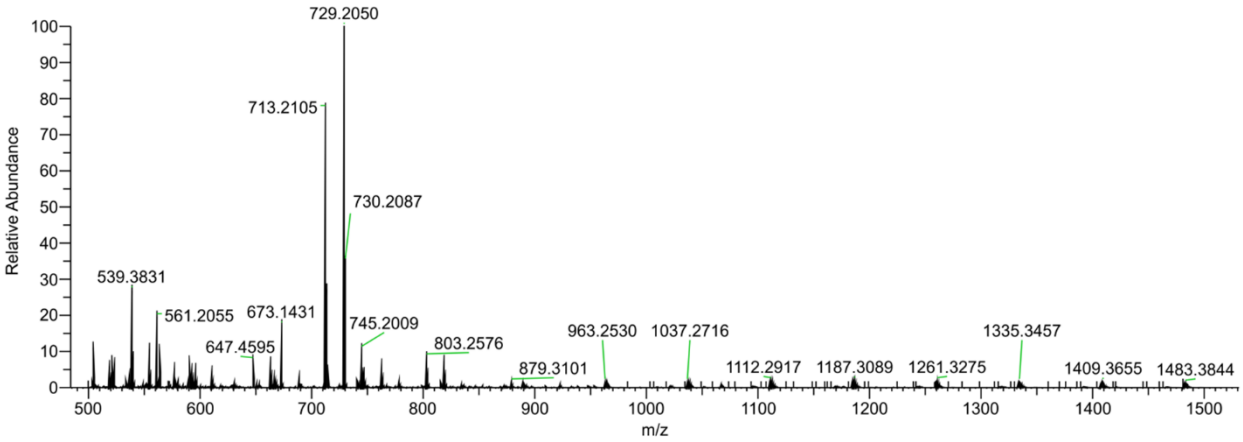


Figure S53. 4-pyr, LIFDI(+)-MS (calcd. *m*/*z* = 849.1802 for $C_{38}H_{42}AlF_{10}NNiP_2$).

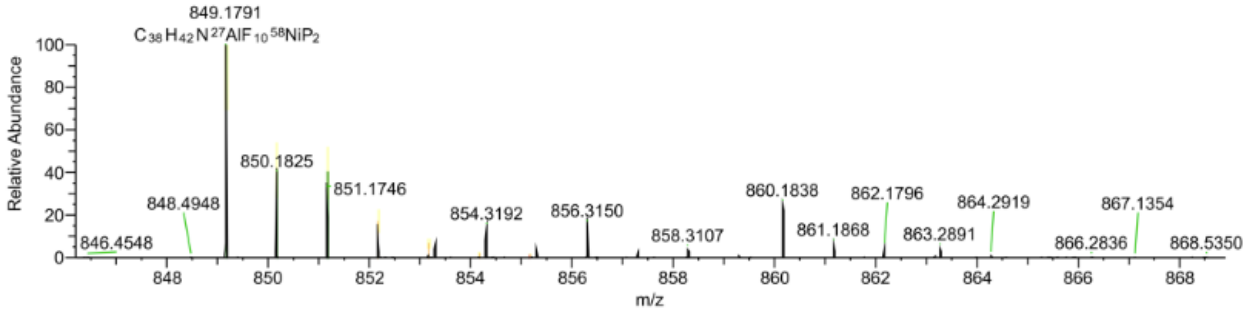
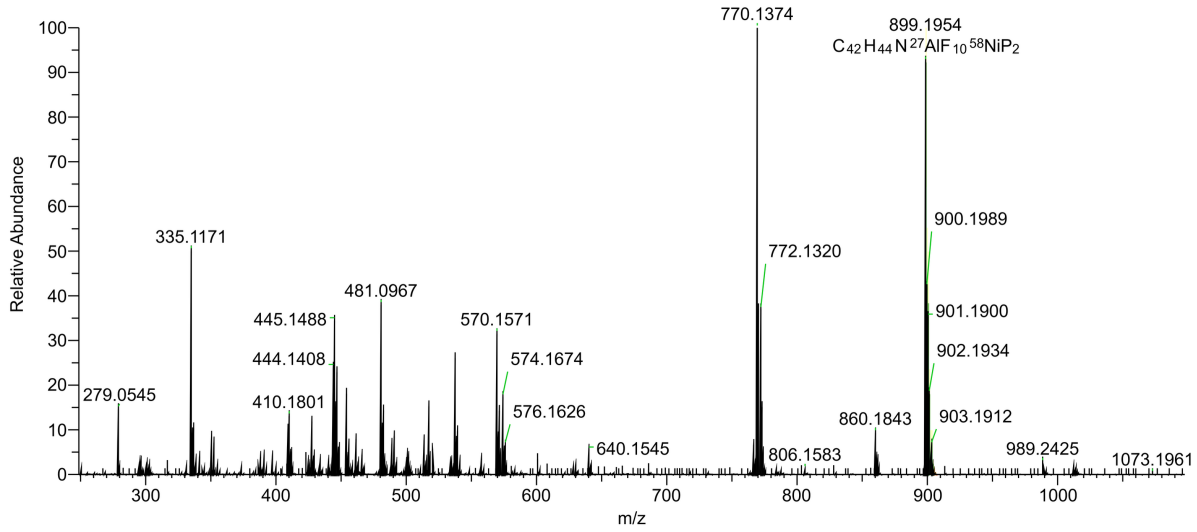


Figure S54. 5-quin, LIFDI(+)-MS (calcd. *m*/*z* = 899.1958 for $C_{42}H_{44}AlF_{10}NNiP_2$).



4.Computational Details:

Calculations were performed using version 6.0.1 of the ORCA computational package.[2] All geometry optimizations and frequency calculations were performed at the r^{2}SCAN-3c level of theory.[3] Frequency calculations (*Freq*) were performed to confirm that each optimized geometry was a true minimum indicated by the absence of imaginary frequencies.

Accurate electronic energies were determined using CCSD(T) at the DLPNO-CCSD(T)/def2-TZVP level of theory.[4] The RIJCOSX approximation was used to enhance computational efficiency, along with *def2/J* and *def2-TZVP/C* auxiliary basis sets. *NormalPNO* and *TIGHTSCF* were used by default.

To obtain thermochemical information, the final Gibbs free energies for each chemical species were calculated using the following equation.

$$\Delta G_{solv} = E_{el}(DLPNO\text{-}CCSD(T)) + \Delta G_{correction}(DFT) + \Delta G^{\circ}_{solv}(DFT)$$

$E_{el}(DLPNO\text{-}CCSD(T))$ is the final electronic energy from a DLPNO-CCSD(T)/def2-TZVP calculation, $\Delta G_{correction}(DFT)$ is the $G\text{-}E_{el}$ (Gibbs free energy minus the electronic energy) from a BP86-D3(BJ)/def2-TZVP calculation, and $\Delta G^{\circ}_{solv}(DFT)$ is the sum of $\Delta G_{ENP}(CPCM\ Dielectric)$ and $\Delta G_{CDS}(Free\text{-}energy(cav+disp))$ from an *SMD=benzene* single point calculation.

5. References:

[1] Zimmerman, A. C.; Fryzuk, M. D. *Organometallics* **2018**, *37*, 2305–2318.
[2] Neese, F. Software Update: The ORCA Program – Version 5.0. *WIREs Comput. Mol. Sci.*, 2022, *12*(1), e1606.
[3] Grimme, S.; Hansen, A.; Ehlert, S.; Mewes, J. *J. Chem. Phys.* **2021**, *154*, 064103.
[4] a) C. Riplinger, P. Pinski, U. Becker, E.F. Valeeve, F. Neese, *J. Chem. Phys.* **2016**, *144*, 024109; b) C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys*. **2013**, *139*, 134101; c) C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106.