# Supplementary Materials: A PAlP Pincer Ligand Bearing a 2-Diphenylphosphinophenoxy Backbone

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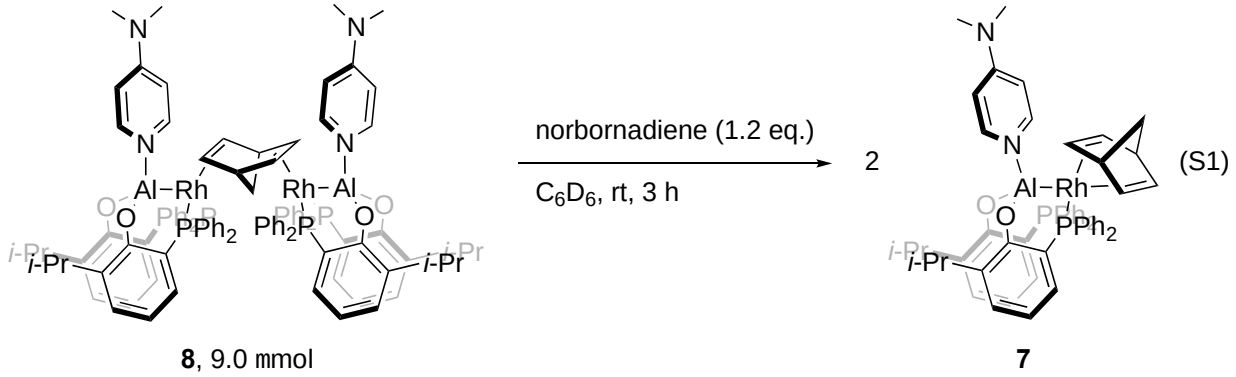
## 1. Reaction of 8 and norbornadiene

In a glove box, **8** (17 mg, 9.0 μmol) and norbornadiene (0.8 mg, 11 μmol) were placed together in a J-young NMR tube and dissolved in $C_6D_6$ (500 μL) for 3 h at room temperature (Scheme S1). The resulting mixture was analyzed by NMR spectroscopies (Figure S1). **7** was formed quantitatively.




**Scheme S1.** Preparation of **7** from **8**.

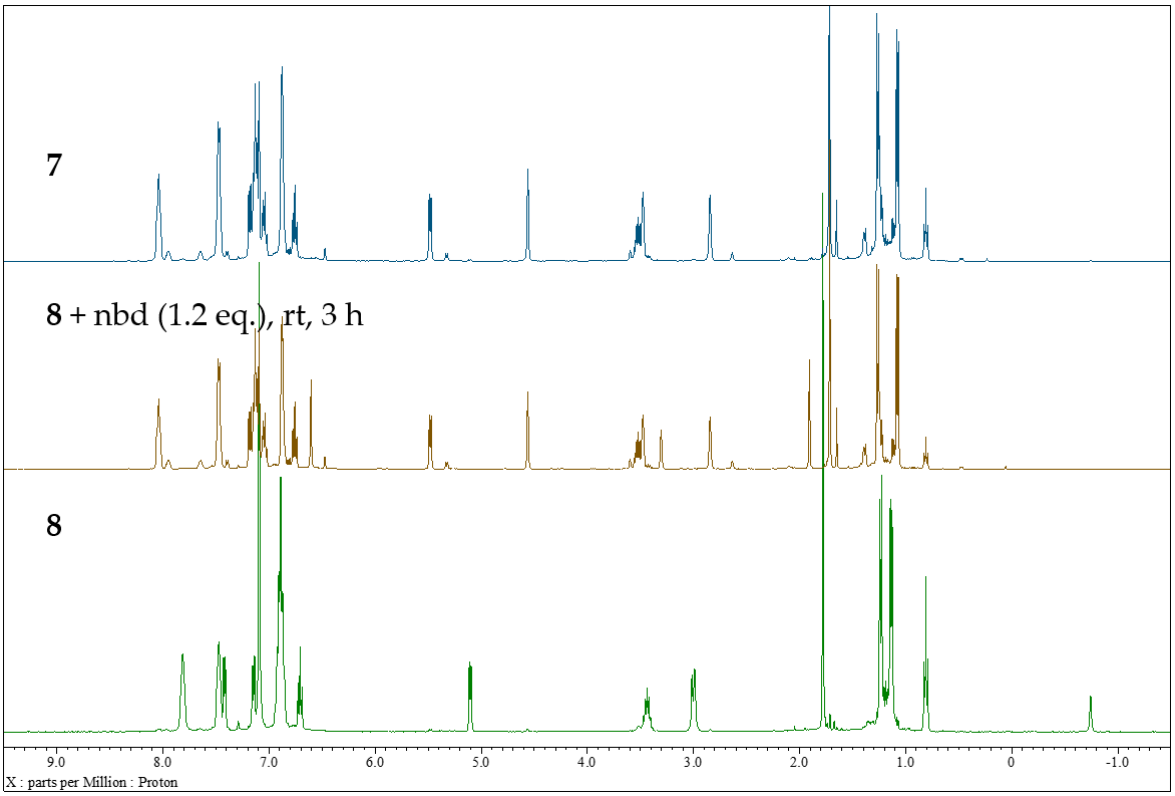



**Figure S1.** $^1$H NMR spectra of Scheme S1.

## 2. X-ray diffraction study and X-ray Crystallographic Analysis

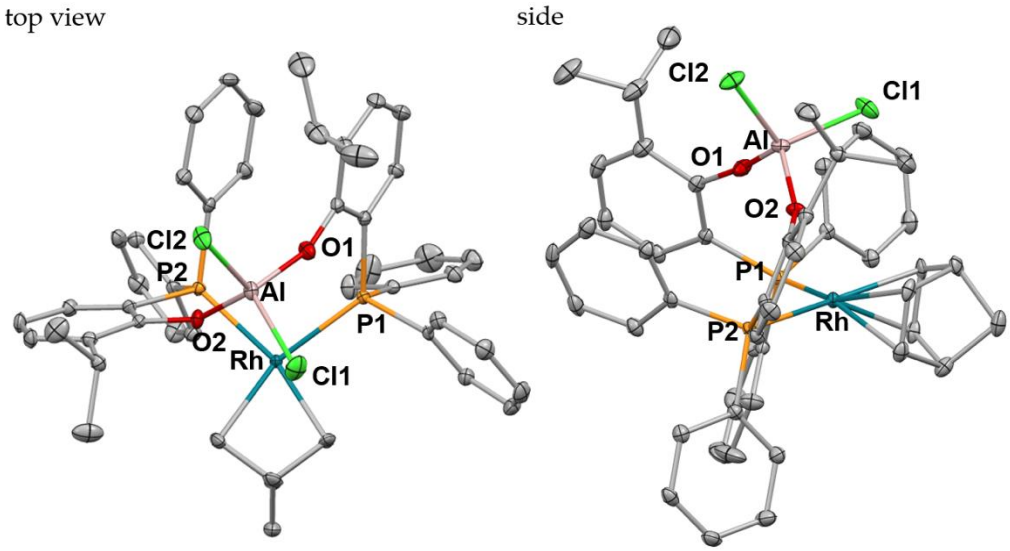



**Figure S2.** Crystal structure of **6** (atomic displacement parameters set at 30% probability; all hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Complex **6**: Rh–P1 2.3441(9), Rh–P2 2.3666(9), Al–Cl1 2.1333(14), Al–Cl2 2.1534(14), Al–O1 1.719(3), Al–O2 1.723(2), P1–Rh–P2 99.72(3).

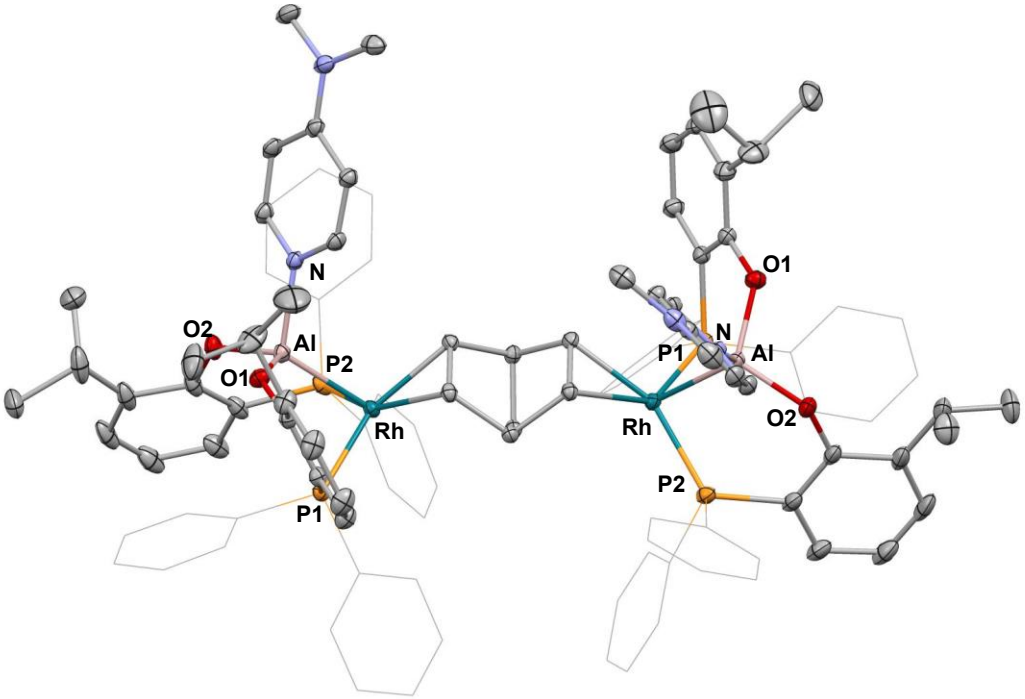



**Figure S3.** Crystal structure of **8** (atomic displacement parameters set at 30% probability; all hydrogen atoms and solvents are omitted for clarity). Selected bond lengths (Å) and angles (°): Complex **8**: Rh–Al 2.3183(8), Rh–P1 2.2821(8), Rh–P2 2.2570(9), Al–O1 1.753(2), Al–O2 1.753(2), Al–N 1.945(2), P1–Rh–P2 111.88(3).

**Table S1.** Crystallographic data of **6** and **8**.

| **Compound** | **6** | **8** |
|---|---|---|
| Empirical formula | $C_{49}H_{48}AlCl_2O_2P_2Rh$ | $C_{131}H_{127.39}Al_2N_4O_4P_4Rh_2$ |
| Formula weight | 931.66 | 2205.42 |
| Crystal system | triclinic | orthorhombic |
| Space group | $P\,\bar{1}$ (#2) | Pbcn (#60) |
| *a*, Å | 11.5108(13) | 21.467(2) |
| *b*, Å | 11.7477(12) | 23.846(3) |
| *c*, Å | 17.714(2) | 22.560(3) |
| $\alpha$, deg. | 77.954(5) | 90 |
| $\beta$, deg. | 82.044(5) | 90 |
| $\gamma$, deg. | 68.932(4) | 90 |
| *V*, Å$^3$ | 2180.7(4) | 11549(2) |
| *Z* | 2 | 4 |
| *D*calcd, g/cm$^{-3}$ | 1.419 | 1.268 |
| μ (Mo-K$\alpha$), mm$^{-1}$ | 0.646 | 0.411 |
| *T*, K | 143 | 143 |
| Crystal size, mm | 0.180 × 0.140 × 0.100 | 0.190 × 0.070 × 0.060 |
| θ range for data collection (deg.) | 2.24 to 25.03 | 3.11 to 27.49 |
| no. of reflections measured | 14942 | 90312 |
| Unique data | 7551 | 13125 |
| Data / restraints / parameters | 7551 / 0 / 514 | 13125 / 0 / 680 |
| *R*1 ($I > 2.0\sigma(I)$) | 0.0400 | 0.0467 |
| *wR*2 ($I > 2.0\sigma(I)$) | 0.1079 | 0.1120 |
| *R*1 (all data) | 0.0490 | 0.0530 |
| *wR*2 (all data) | 0.1291 | 0.1163 |
| GOF on $F^2$ | 1.166 | 1.104 |

(a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2 - Fc^2)^2\}/\{\Sigma w(Fo^2)^2\}]^{1/2}$

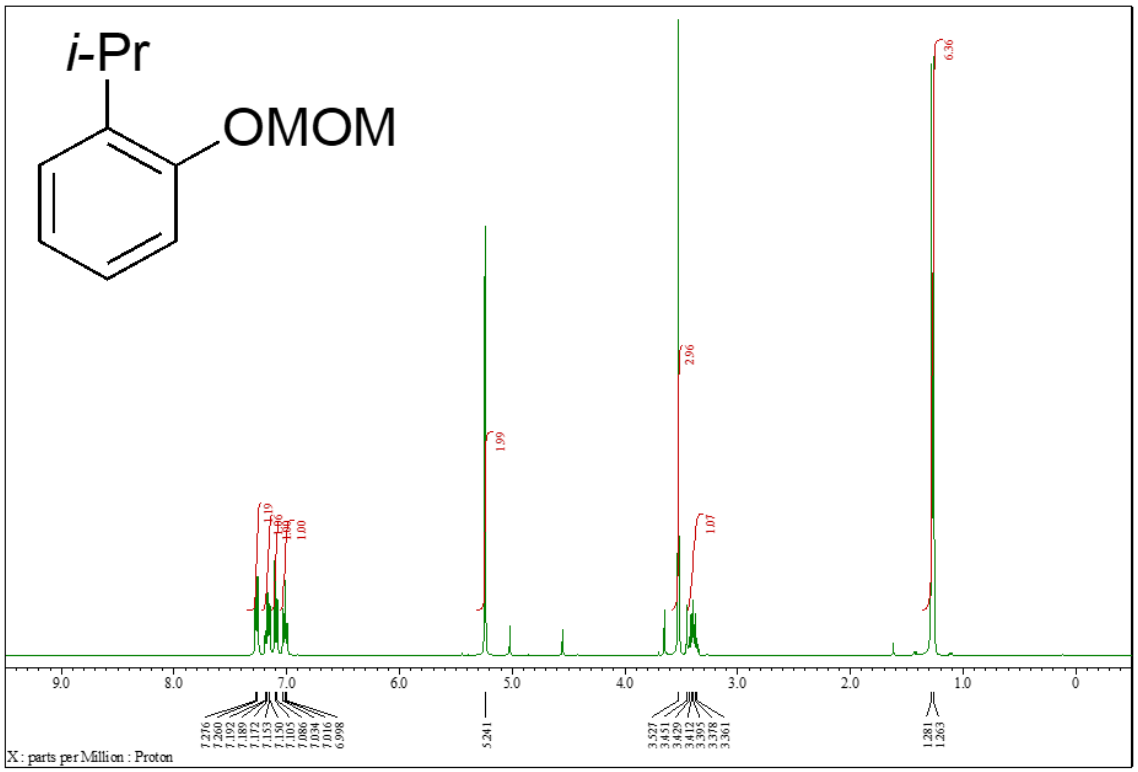



**Figure S4.** A $^{1}$H NMR spectrum of **4**.

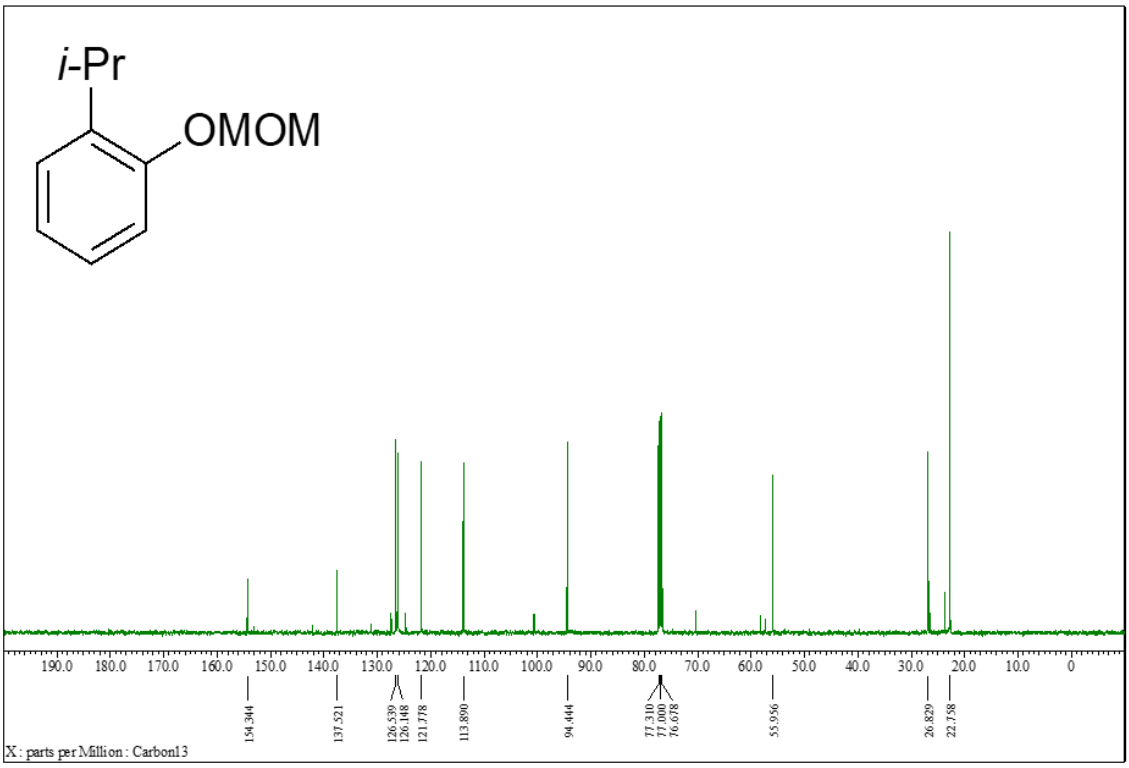



**Figure S5.** A $^{13}$C NMR spectrum of **4**.

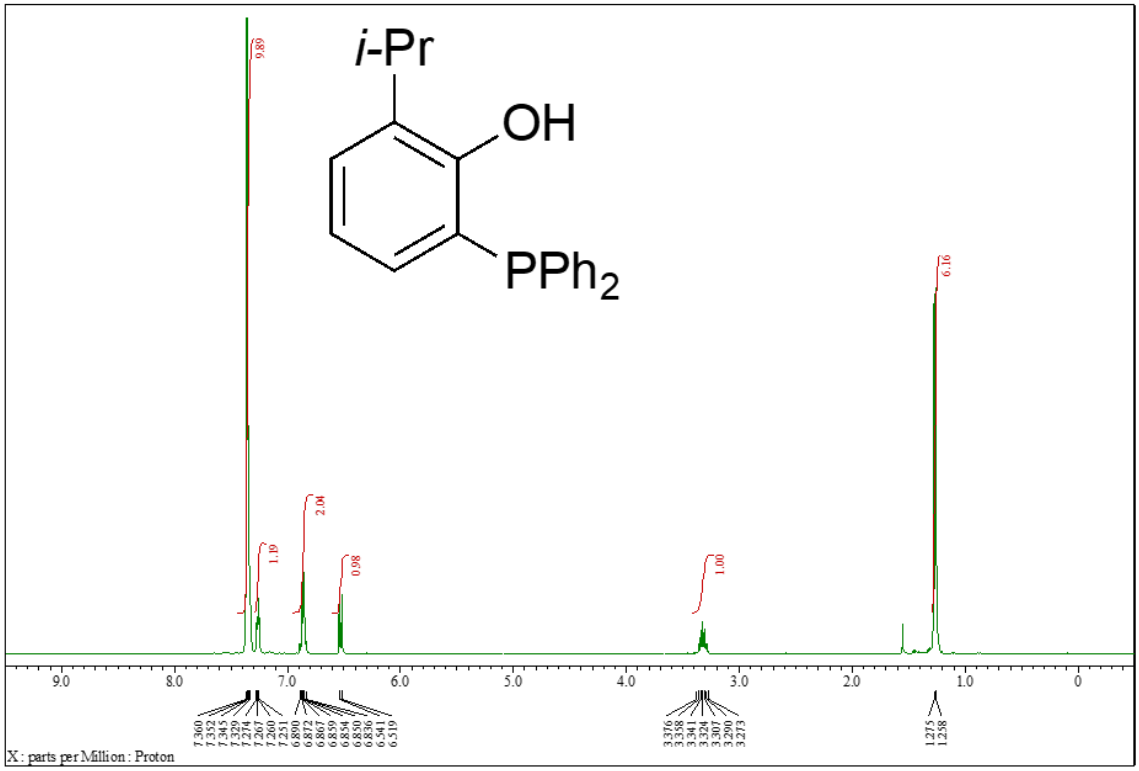



**Figure S6.** A $^{1}$H NMR spectrum of **5**.

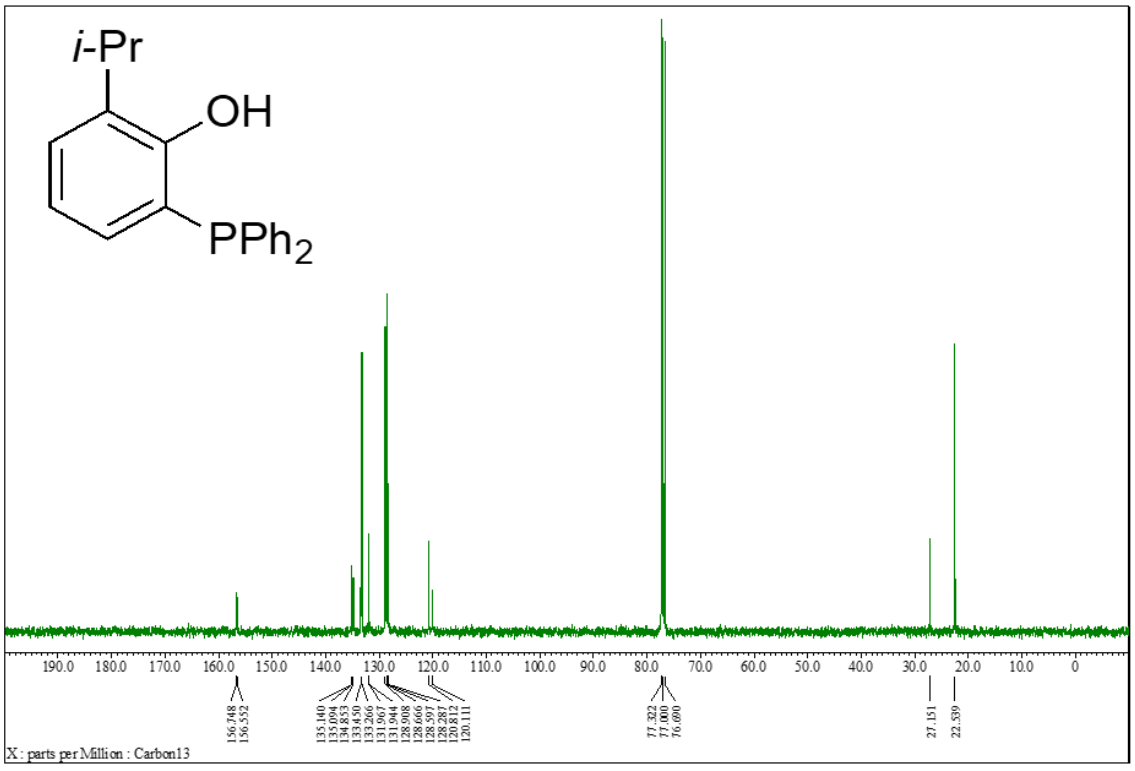



**Figure S7.** A $^{13}$C NMR spectrum of **5**.

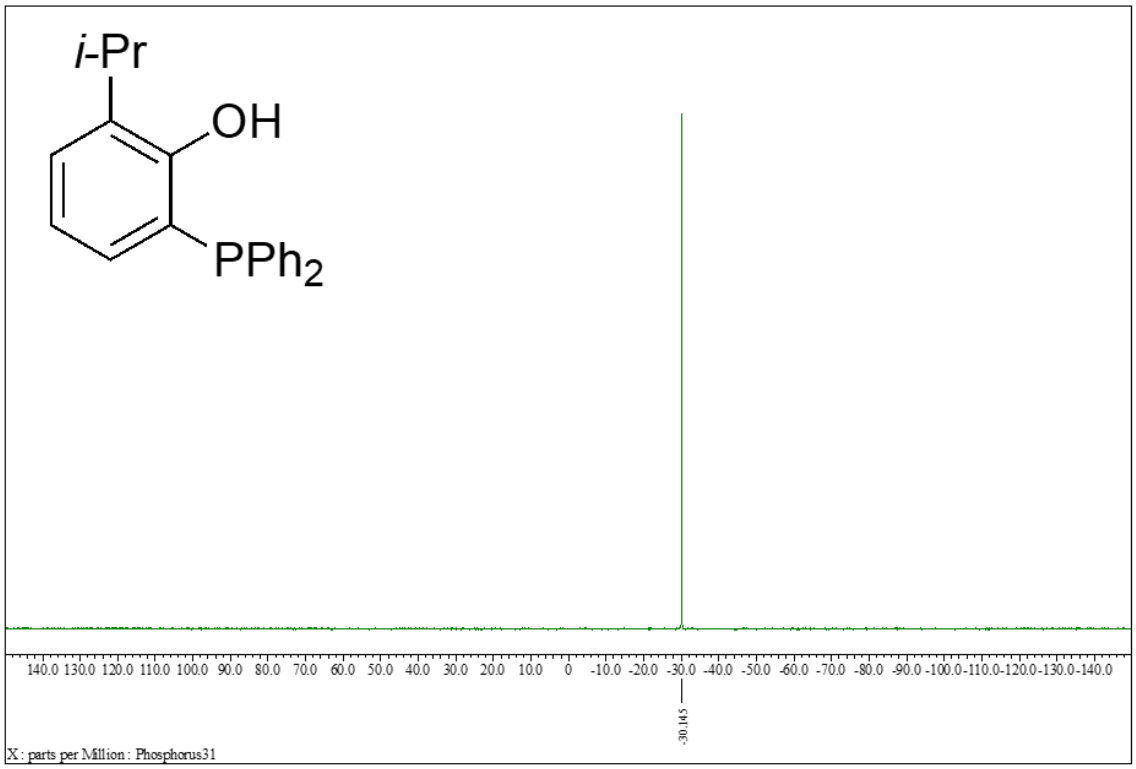



**Figure S8.** A $^{31}$P NMR spectrum of **5**.

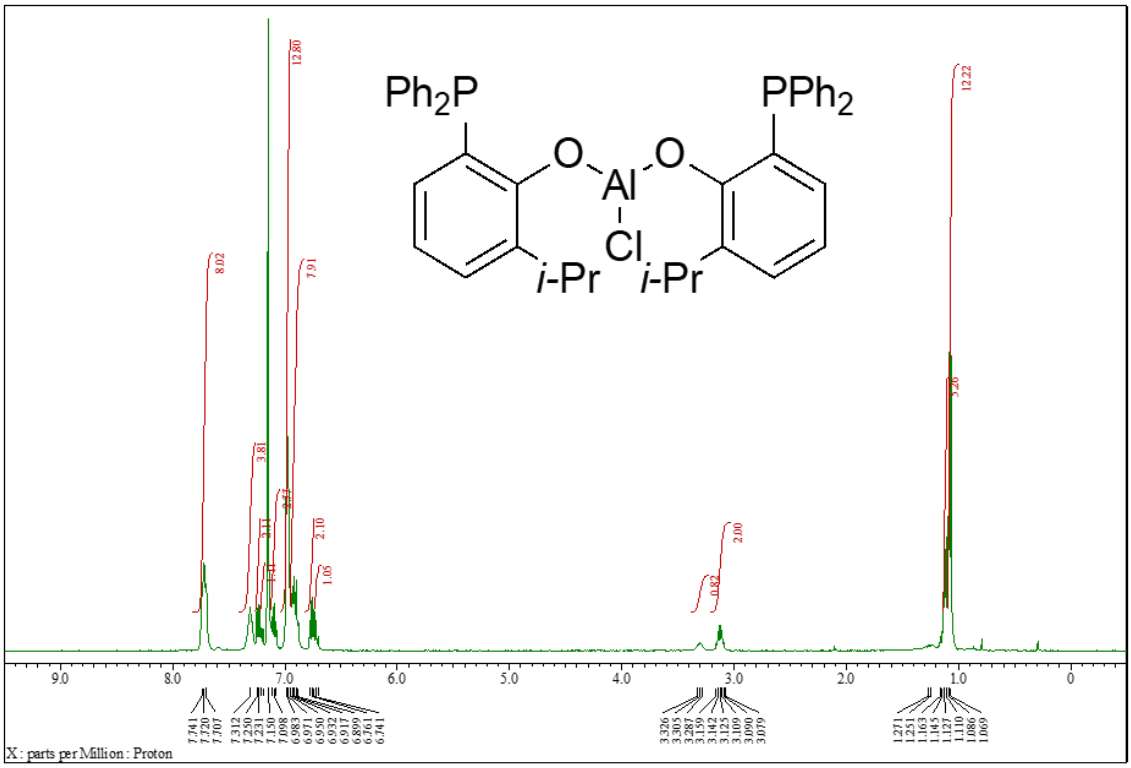



**Figure S9.** A $^{1}$H NMR spectrum of **2**.

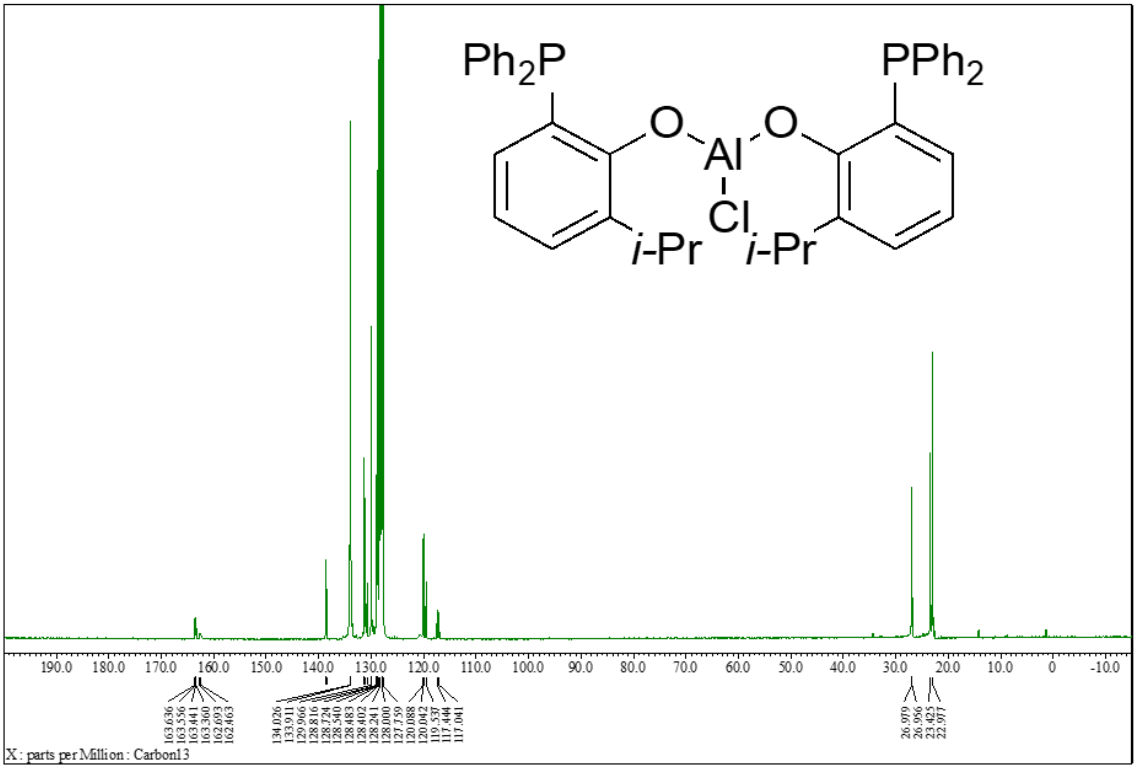



**Figure S10.** A $^{13}C$ NMR spectrum of **2**.

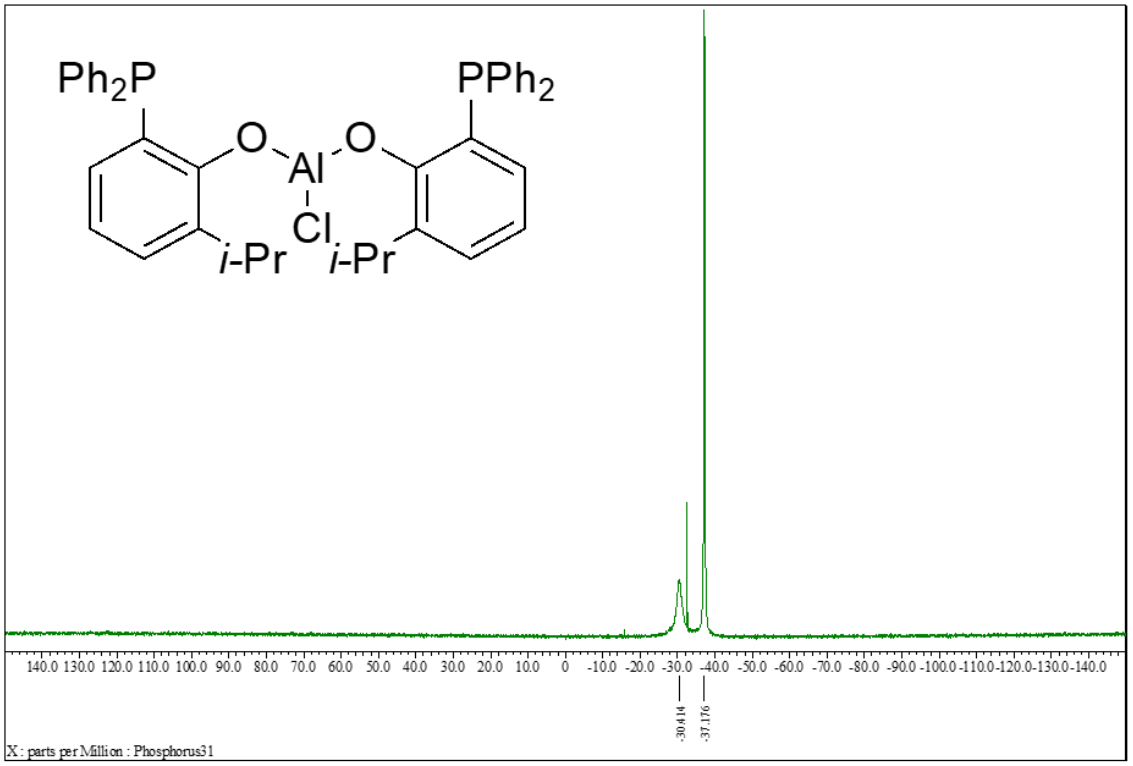



**Figure S11.** A $^{31}P$ NMR spectrum of **2**.

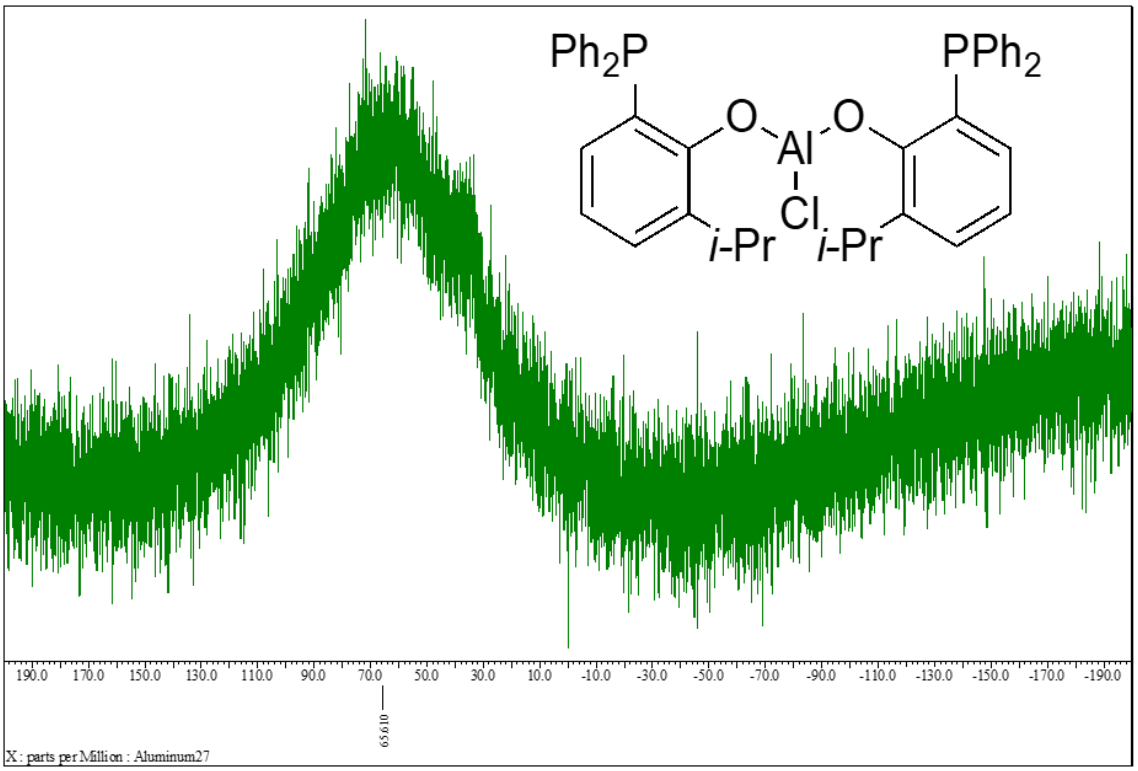



**Figure S12.** A $^{27}$Al NMR spectrum of **2**.

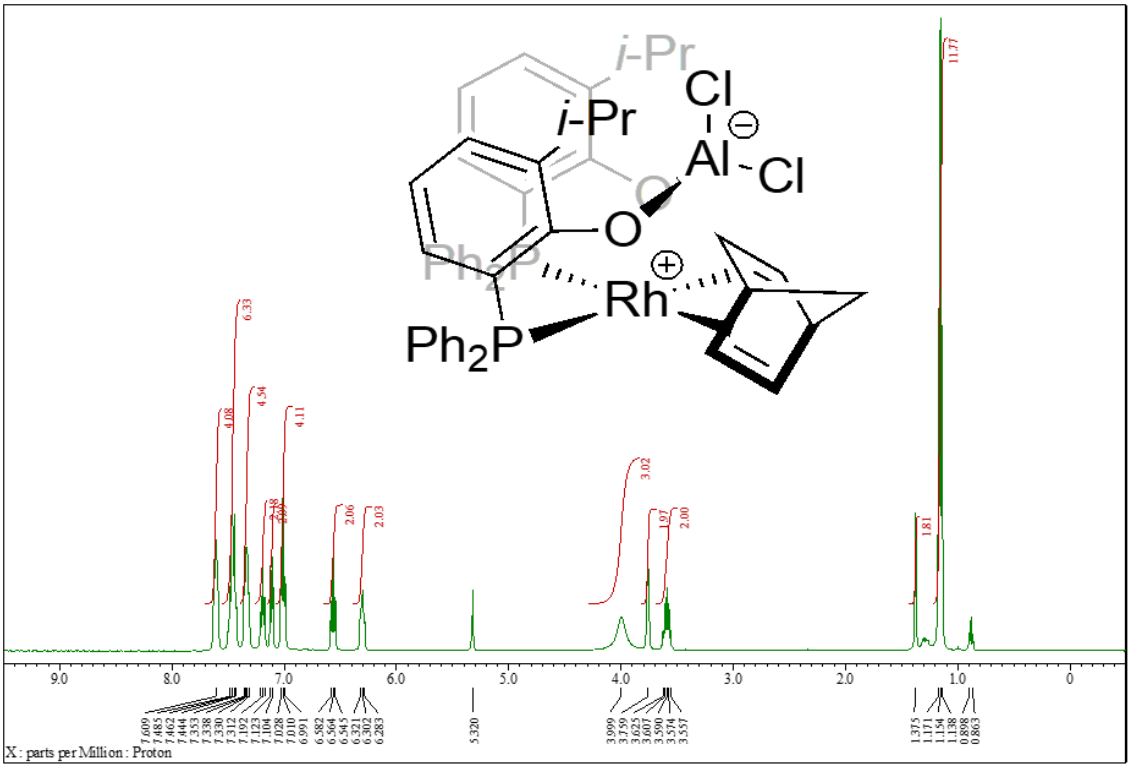



**Figure S13.** A $^{1}$H NMR spectrum of **6**.

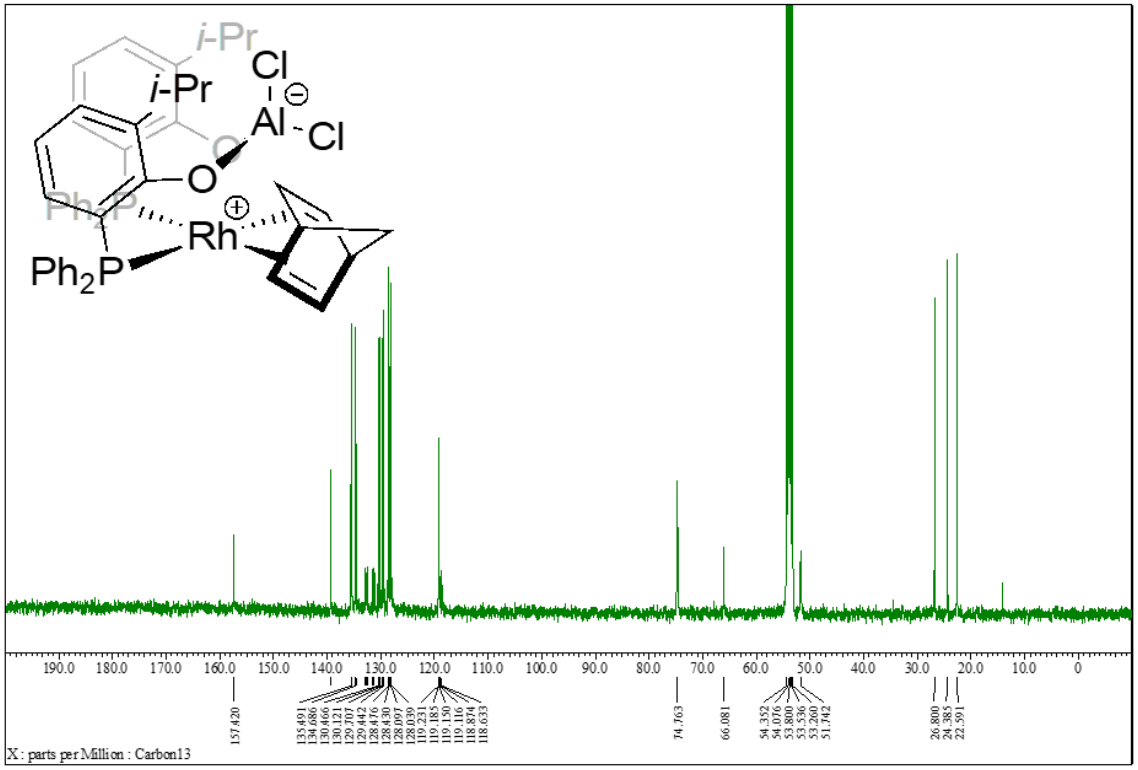



**Figure S14.** A $^{13}C$ NMR spectrum of **6**.

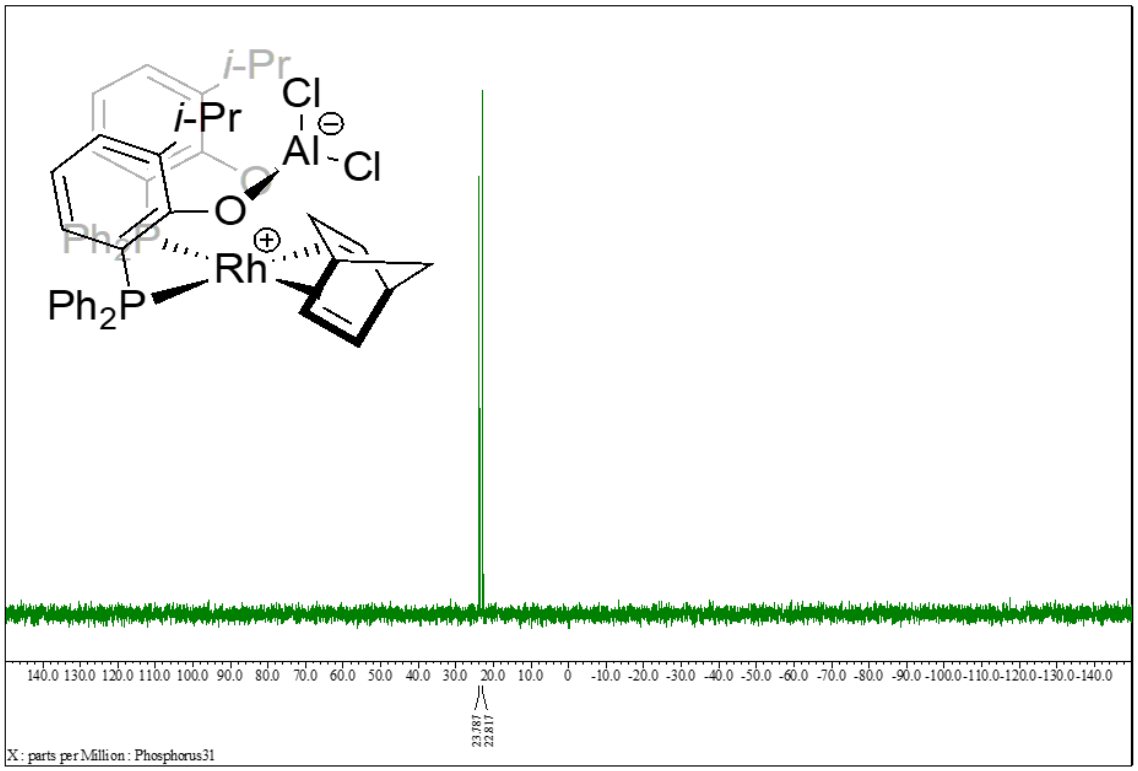



**Figure S15.** A $^{31}P$ NMR spectrum of **6**.

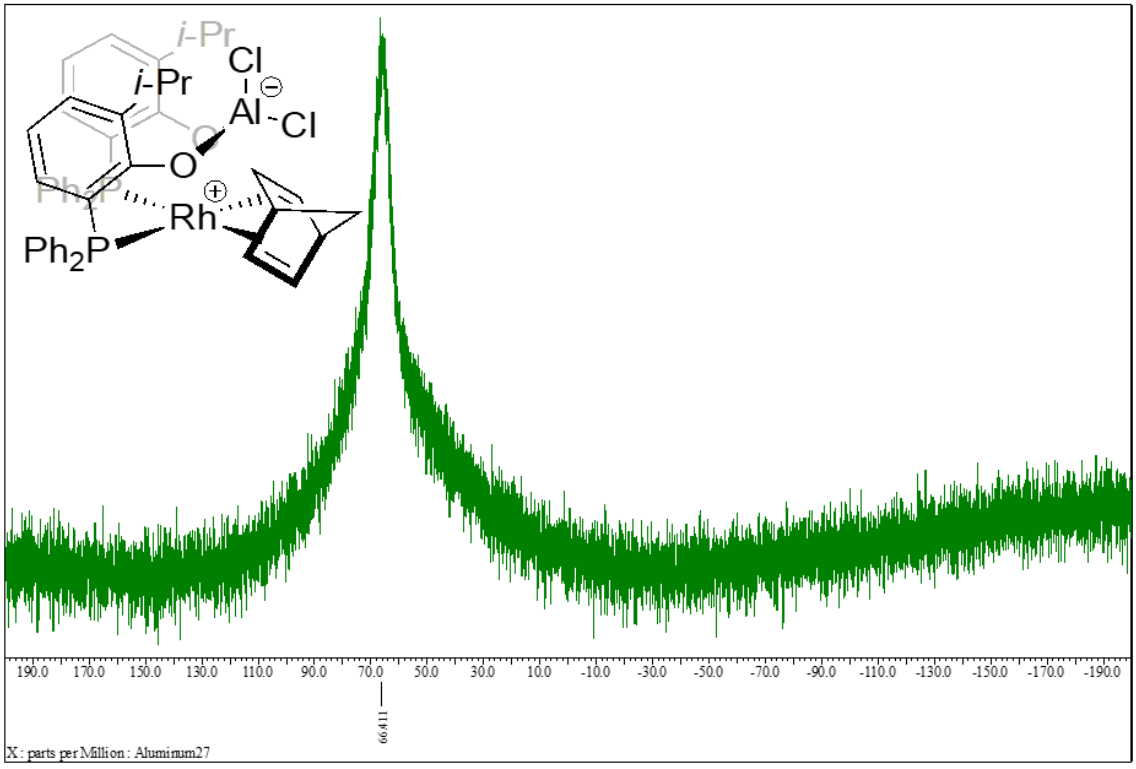



**Figure S16.** A $^{27}$Al NMR spectrum of **6**.

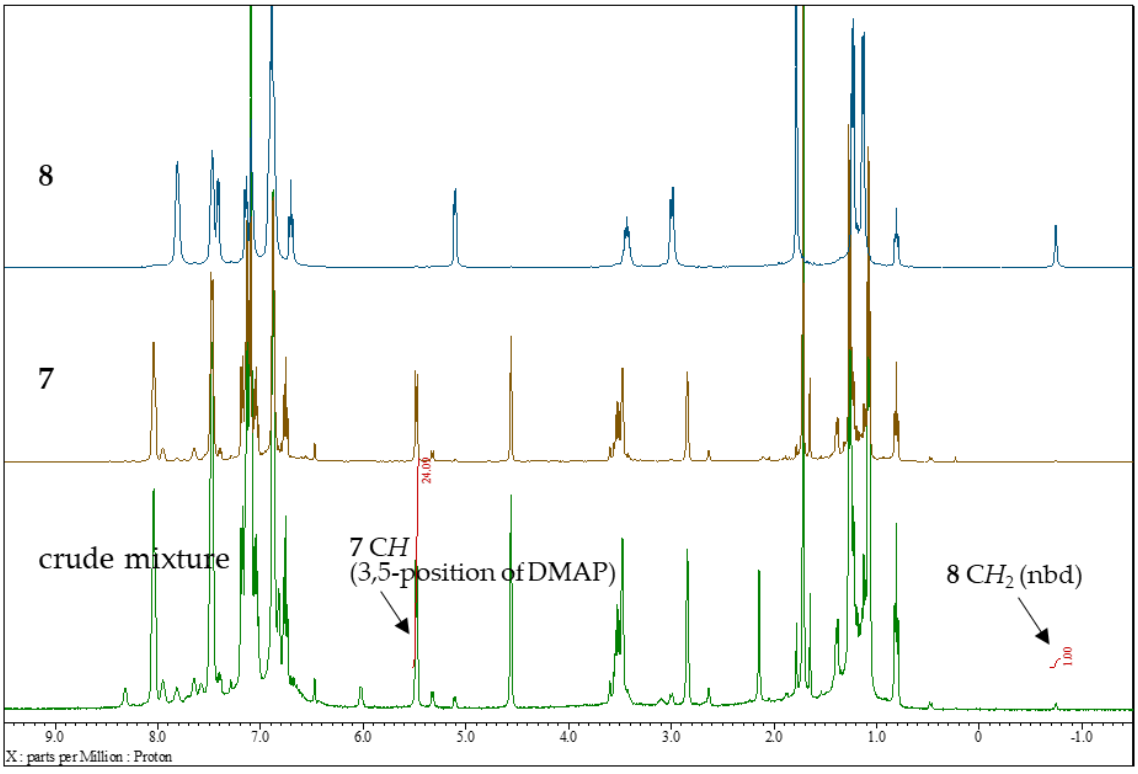



**Figure S17.** $^{1}$H NMR spectra of Scheme 4.

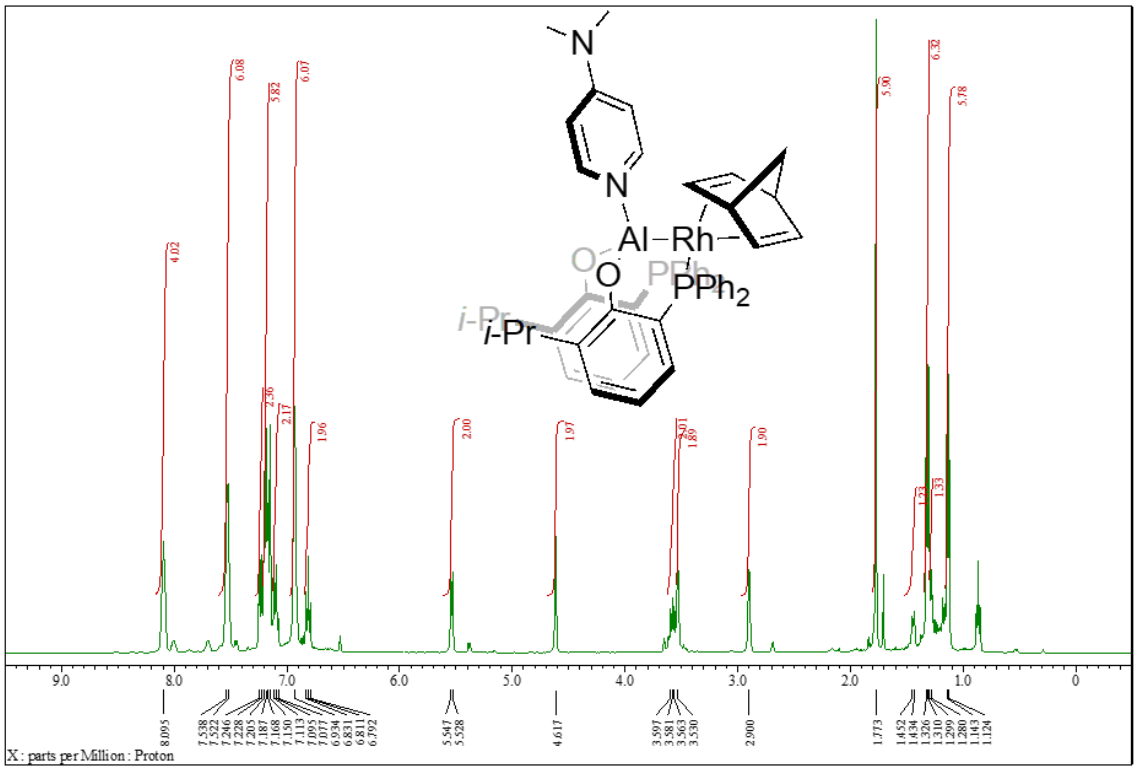



**Figure S18.** A $^{1}$H NMR spectrum of **7**.

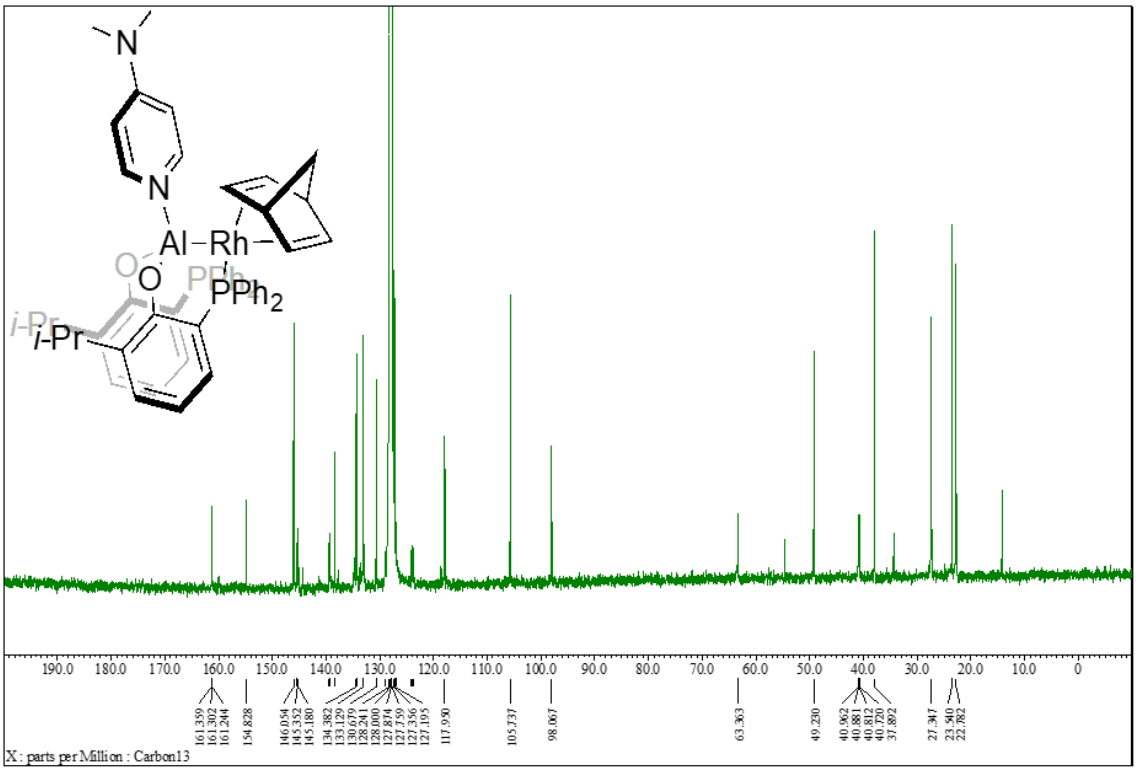



**Figure S19.** A $^{13}$C NMR spectrum of **7**.

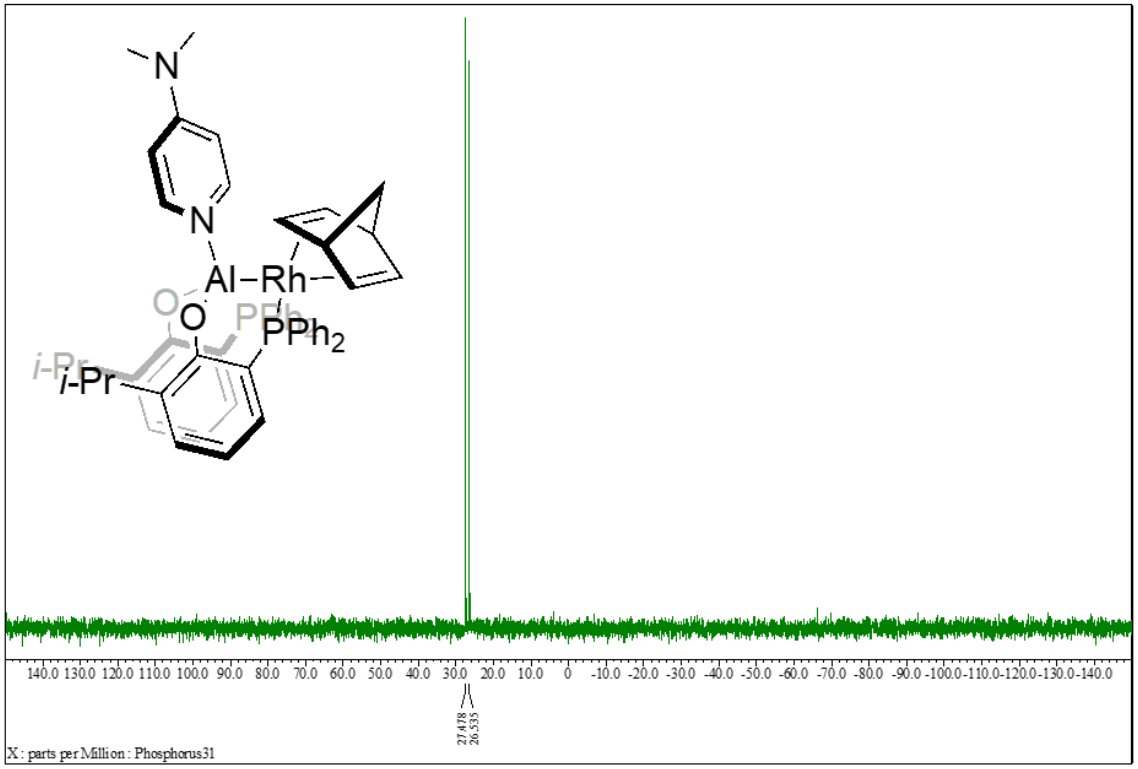



**Figure S20.** A $^{31}$P NMR spectrum of **7**.

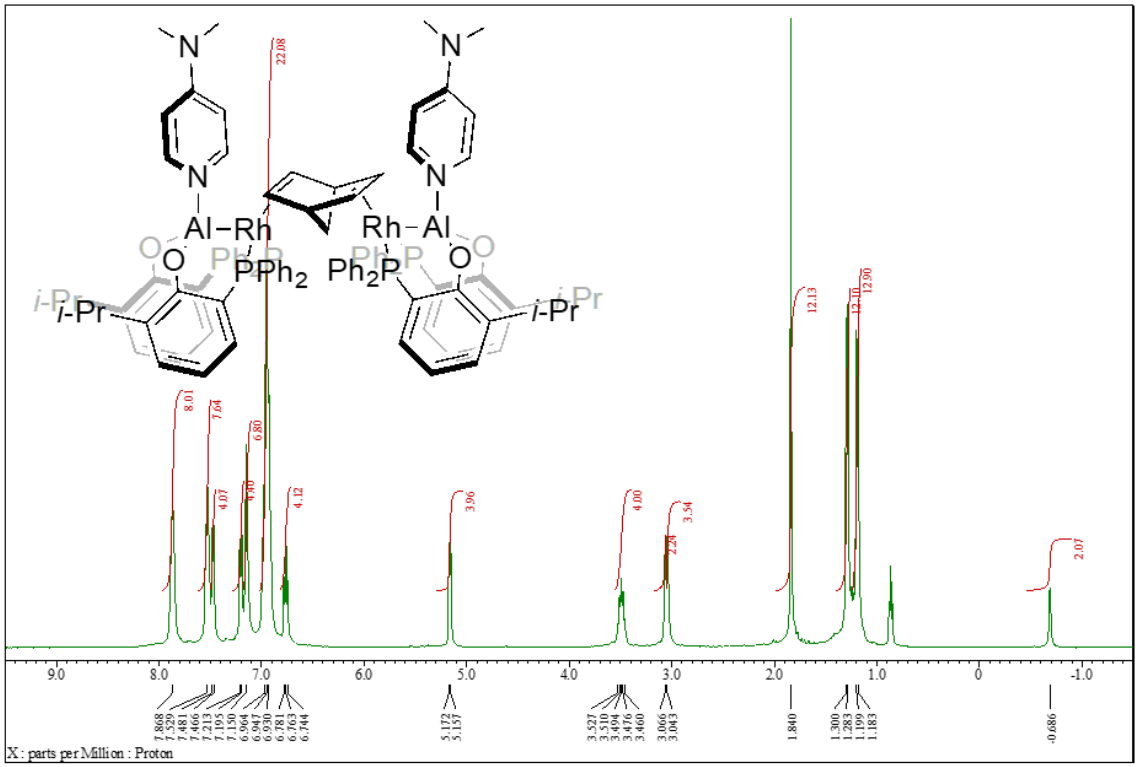



**Figure S21.** A $^{1}$H NMR spectrum of **8**.

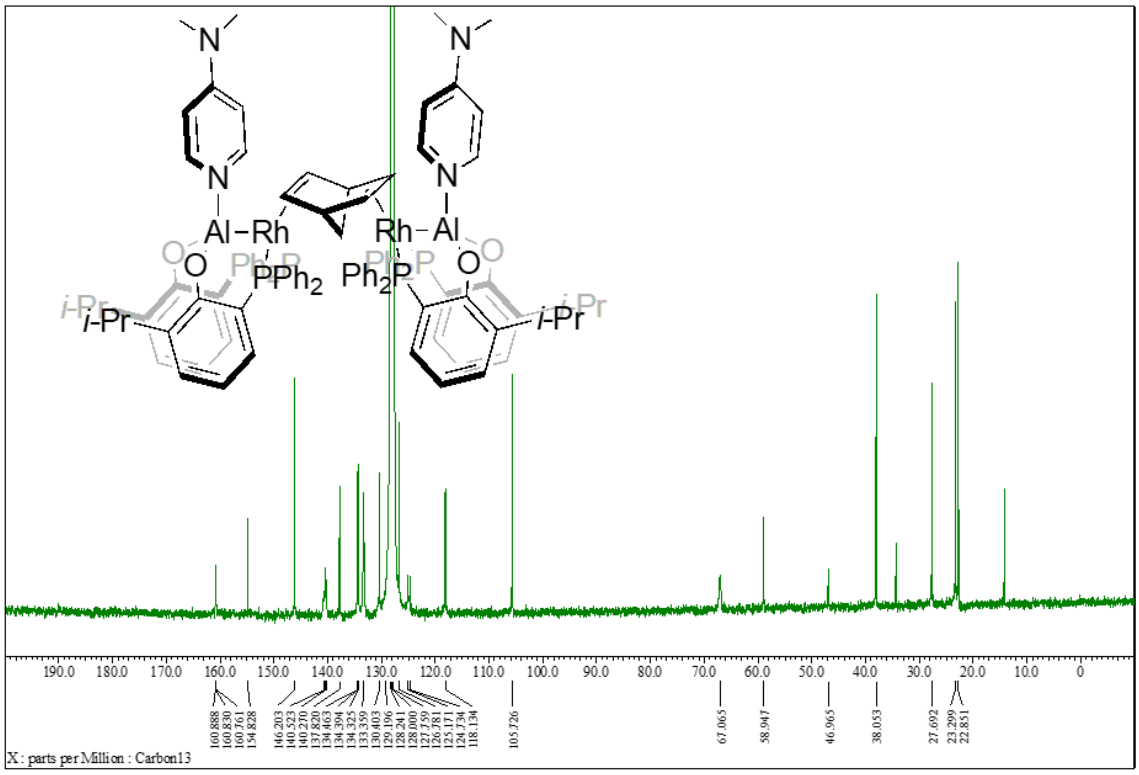



**Figure S22.** A $^{13}C$ NMR spectrum of **8**.

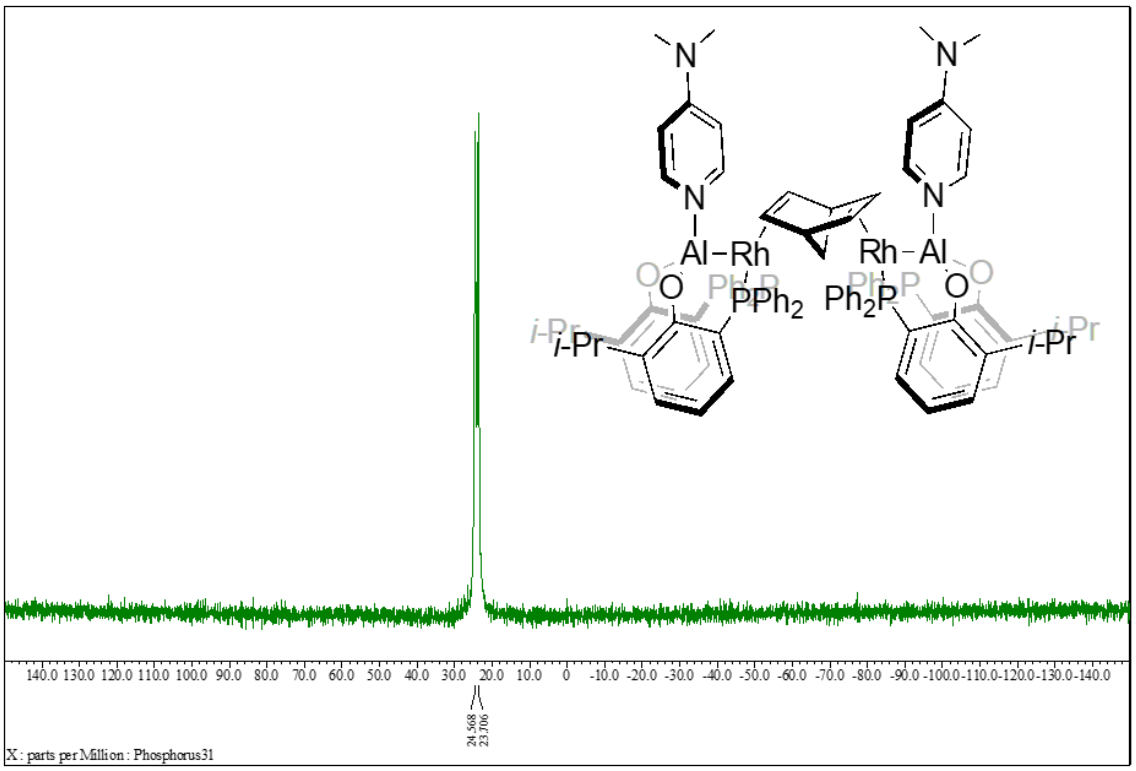



**Figure S23.** A $^{31}P$ NMR spectrum of **8**.

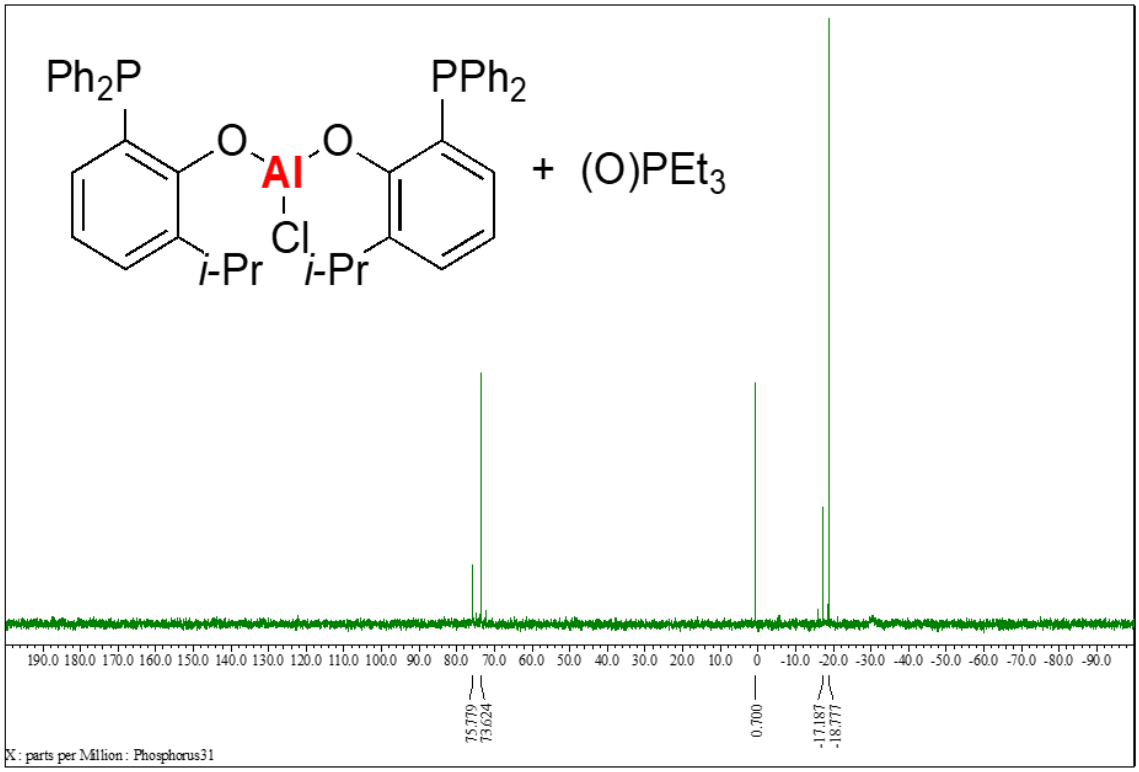



**Figure S24.** A $^{31}$P NMR spectrum of Scheme 2.

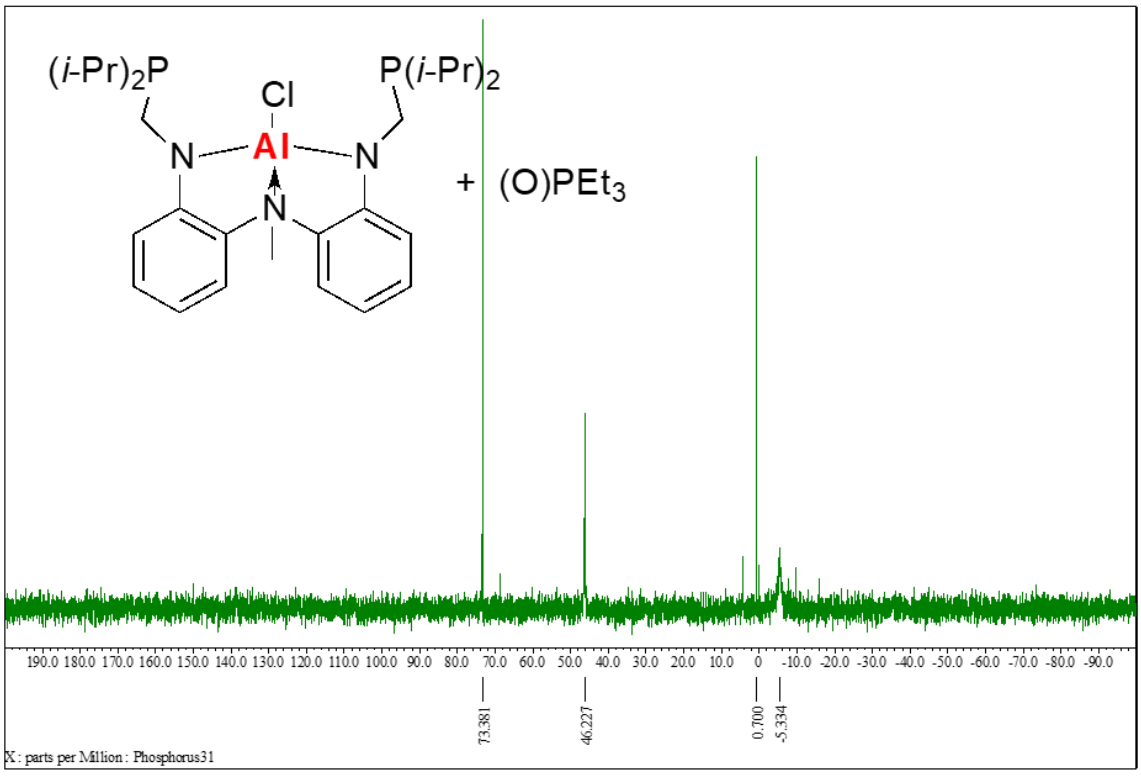



**Figure S25.** A $^{31}$P NMR spectrum of Scheme 2.

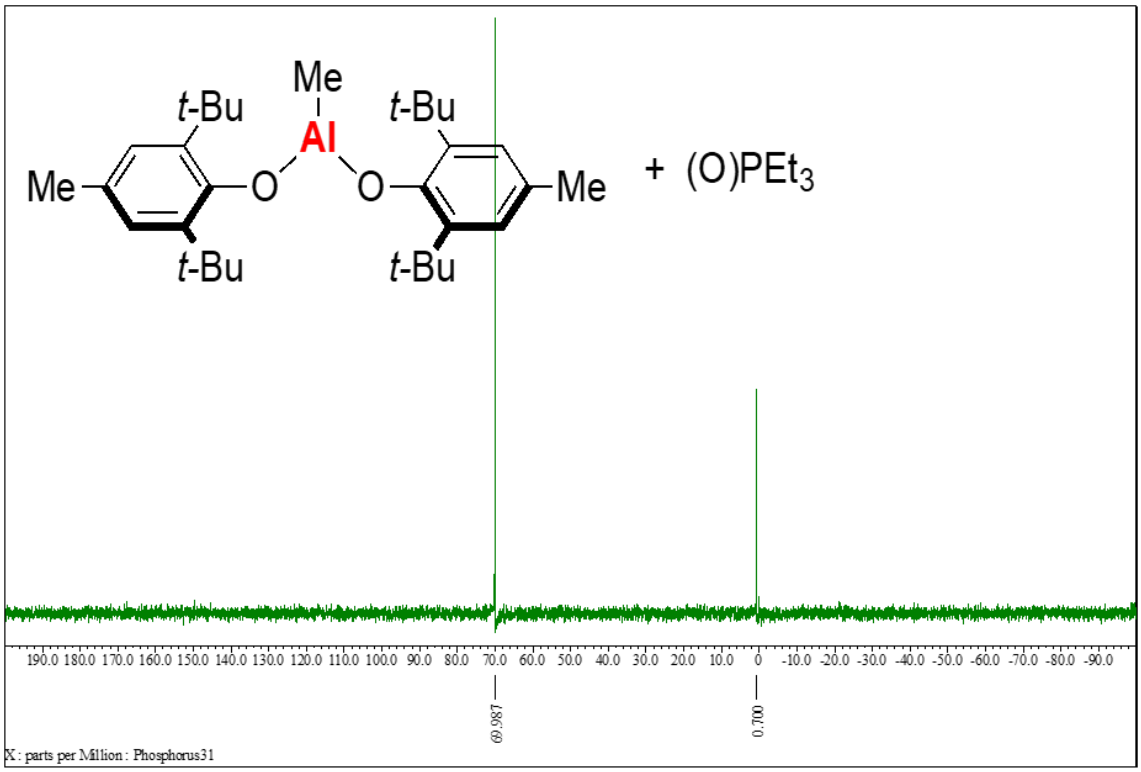



**Figure S26.** A $^{31}$P NMR spectrum of Scheme 2.

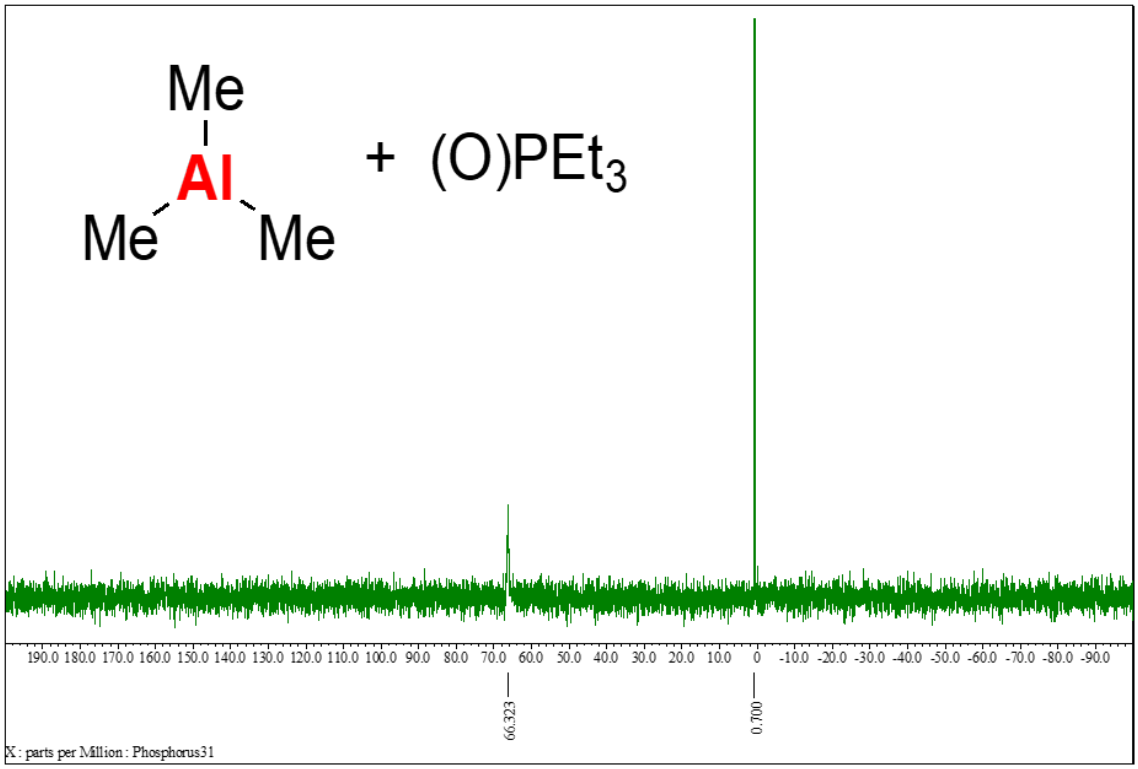



**Figure S27.** A $^{31}$P NMR spectrum of Scheme 2.