Supporting Information

(31 pages total)

Contents:

1. General experimental considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in benzene-d_6 (which was dried over potassium) or toluene-d_8 (which was dried over CaH_2), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker NEO 600 MHz spectrometers at ambient temperature and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{31}P resonances are referenced externally to H_3PO_4 (85 %). Assignments were confirmed using two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were measured on Elemental analyses were carried out by London Metropolitan University. IR spectra were measured on a Shimadzu FT-IR Spirit equipped with an attenuated total reflectance (ATR) surface, contained in a dinitrogen glovebox. Mass spectrometry was performed by an Agilent 6120 bench top single quadrupole machine.

(NON)AlCuP^{t}Bu$_3$ was prepared according to literature procedure.[s1] 3-hexyne and 1-phenyl-1-pentyne were dried over 4 Å molecular sieves. All other reagents were used as received.

2. Syntheses of novel compounds

2-Et

To a stirred suspension of **1** (100 mg, 0.103 mmol) in toluene (3 ml) was added 3-hexyne (18 µl, 0.154 mmol). The resulting colourless solution was stirred for 30 minutes and then concentrated to 2 ml. Colourless crystals suitable for X-ray diffraction could be obtained from slow cooling of this solution to 4 °C (78 mg, 72%)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 0.90 (d, $^3J_{HP}$ = 12.8 Hz, 27H, PC(C*H*$_3$)$_3$), 1.07 (d, $^3J_{HH}$ = 7.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.43 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 1.48 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 1.60 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$)1.71 (s, 6H, C(C*H*$_3$)$_2$), 2.86 (qd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 3.0 Hz, 2H, C*H*$_2$CH$_3$), 2.92 (q, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 3.51 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 4.35 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 6.07 (d, $^4J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.72 (d, $^4J_{HH}$ = 1.9 Hz , 2H, XA-*p*-C*H*), 7.01-38 (m, 6H Ar*H*).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C = 15.5, 16.8, (CH$_2$*C*H$_3$), 25.9, 26.4 (*C*H(CH$_3$)$_2$), 27.3 (d, $^3J_{CP}$ = 7.0 Hz , *C*H$_2$CH$_3$), 29.1 (*C*H$_2$CH$_3$), 31.8 (C(*C*H$_3$)$_3$), 28.2, 29.2 (CH(*C*H$_3$)$_2$), 32.1 (d, $^2J_{CP}$ = 6.0 Hz, P{C(*C*H$_3$)$_3$}$_3$), 35.1 (*C*(CH$_3$)$_3$), 36.0 (d, $^1J_{CP}$ = 6.0 Hz, P{*C*(CH$_3$)$_3$}$_3$), 37.9 (*C*(CH$_3$)$_2$), 106.6, 111.8, 123.8, 126.2, 133.6, 141.0, 142.8, 144.7, 146.9, 148.3, 149.3 (Ar*C*), 154.1 (C=*C*-Al), 188.3 (d, $^2J_{CP}$ = 73 Hz, C=*C*-Cu)

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ_P = 55.5

$C_{65}H_{99}AlCuN_2OP$ requires: C, 74.64%; H, 9.54%; N, 2.68%; found: C, 74.55%; H, 9.38%; N, 2.47%

(NON)AlEt

A solution of **2-Et** (60 mg, 0.057 mmol) in benzene (2 ml) was left standing at room temperature for 48 hours, during which time a metallic precipitate formed. The solution was filtered and the volatiles removed *in vacuo*. The residue was taken up in hexane (1 ml), from which colourless crystals suitable for x-ray diffraction were obtained. (35 mg, 84%)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.40 (q, $^3J_{HH}$ = 8.4 Hz, 2H, C*H*$_2$CH$_3$), 0.87 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 1.12 (d, $^3J_{HH}$ = 7.2 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.18 (s, 18H, C(C*H*$_3$)$_3$), 1.30 (d, $^3J_{HH}$ = 7.4 Hz, 12H, ArCH(C*H*$_3$)2), 1.58 (s, 6H, C(C*H*$_3$)$_2$), 3.57 (sept., $^3J_{HH}$ = 6.6 Hz, 4H, ArC*H*(CH$_3$)$_2$), 6.35 (d, $^4J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.75 (d, $^4J_{HH}$ = 1.9 Hz , 2H, XA-*p*-C*H*), 7.20-27 (m, 6H Ar*H*)

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = -1.27 (*C*H$_2$CH$_3$), 8.80 (CH$_2$*C*H$_3$), 23.0, 25.9 (CH(*C*H$_3$)$_2$), 27.1 (XA-C(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 31.7 (C(*C*H$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 37.6 (XA-*C*(CH$_3$)$_2$), 107.8, 111.5, 124.5, 125.3, 126.7, 134.0, 141.0, 142.0, 143.7, 147.0, 149.3 (Ar-*C*)

2-Pr,Ph (*in situ)*

To a suspension of **1** (20 mg, 0.023 mmol) in C_6D_6 was added 1-phenyl-pentyne (3.0 µl, 0.023 mmol). This compound was not isolated due to onward reaction.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 0.82 (d, $^3J_{HP}$ = 12.0 Hz, 27H, PC(C*H*$_3$)$_3$), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (overlap) (t, $^3J_{HH}$ = 7.0 Hz , 3H, CH$_2$CH$_2$C*H*$_3$), 1.29 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.61 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.67 (s, 3H, C(C*H*$_3$)$_2$), 1.74 (s, 3H, C(C*H*$_3$)$_2$), 1.95 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 2.74 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 3.55 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 4.21 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.16 (d, $^4J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.76 (d, $^4J_{HH}$ = 1.9 Hz , 2H, XA-*p*-C*H*), 6.94 (m, 2H ArH), 7.18-7.40 (m, 9H ArH)

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ_P = 60.2

3-Pr,Ph

1-phenyl-1-pentyne (20 µl, 0.123 mmol) was added to a stirred suspension of **1** (100 mg, 0.103 mmol) in benzene (4 ml). The reaction mixture was stirred at 45 °C for 18 hours. The resulting solution was lyophilized twice from benzene to give an off-white solid. Colourless crystals were obtained by cooling a hexane solution to -30 °C (64 mg, 56%)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, $^3J_{HP}$ = 12.2 Hz, 27H, PC(C*H*$_3$)$_3$), 1.23 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (overlap) (t, $^3J_{HH}$ = 7.0 Hz , 3H, CH$_2$CH$_2$C*H*$_3$), 1.29 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.34 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.66 (s, 3H, C(C*H*$_3$)$_2$), 1.68 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.80 (s, 3H, C(C*H*$_3$)$_2$), 2.17 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 3.11 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 3.32 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 3.93 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.18 (d, $^4J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.52-6.70 (m, 2H ArH), 6.73 (d, $^4J_{HH}$ = 1.9 Hz , 2H, XA-*p*-C*H*), 6.85 (d, 8.08 Hz, 2H, *m-H*-Ar), 7.18-7.30 (m, 2H ArH), 7.35 (dd, 8.08 Hz, 2H, *o-H*-Ar)

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 14.4 (CH$_2$*C*H$_2$CH$_3$), 16.23 (CH$_2$*C*H$_2$*C*H$_3$), 22.3 (*C*(CH$_3$)$_2$), 23.2, 24.0 (CH(*C*H$_3$)$_2$), 27.4 (*C*H(CH$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 31.7 (CH(*C*H$_3$)$_2$), 31.8 (C(*C*H$_3$)$_3$), 32.1 (d, $^2J_{CP}$ = 6.0 Hz, P{C(*C*H$_3$)$_3$}$_3$), 32.6 (*C*(CH$_3$)$_2$), 35.4 (*C*(CH$_3$)$_2$), 36.7 (d, $^2J_{CP}$ = 6.0 Hz P{*C*(CH$_3$)$_3$}$_3$), 48.7 (*C*H$_2$CH$_2$CH$_3$) 106.5, 112.1, 122.6, 123.6, 125.1, 125.9, 128.3, 129.8, 133.7, 141.6, 142.5, 144.6, 146.9, 148.1, 148.3, 160.7, 163.9 (C-Ar), 163.9 (C=*C*-Al) 187.0 (d, $^2J_{CP}$ = 63.0 Hz, C=*C*-Cu)

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ_P = 57.0

$C_{70}H_{101}AlCuN_2OP$ requires: C, 75.88%; H, 9.19%; N, 2.53%; found: C, 76.02%; H, 9.31%; N, 2.40%

4-Et

A solution of **2-Et** (100 mg, 0.095 mmol) in benzene (2 ml) in a J. Young's tap ampoule was degassed *via* freeze-pump-thaw. The headspace was backfilled with CO (1 bar) and the solution turned from colourless to yellow. The volatiles were removed *in vacuo* and the residue was dissolved in hexane (~1 ml). Yellow crystals formed upon standing at room temperature (45 mg, 44%)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 0.90 (d, $^3J_{HP}$ = 11.9 Hz, 27H, PC(C*H*$_3$)$_3$), 1.18 (d, $^3J_{HH}$ = 7.3 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.27 (s, 18H, C(C*H*$_3$)$_3$), 1.48 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.56 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.78 (s, 3H, C(C*H*$_3$)$_2$), 1.83 (s, 3H, C(C*H*$_3$)$_2$), 2.72 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.76 (q, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*$_2$CH$_3$), 3.52 (sept, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$), 4.05 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.21 (d, $^4J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.72 (d, $^4J_{HH}$ = 1.9 Hz , 2H, XA-*p*-C*H*), 6.99-28 (m, 6H Ar*H*).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C = 15.2, 16.2 (CH$_2$*C*H$_3$), 22.9, (*C*H(CH$_3$)$_2$), 25.1, 27.4 (*C*H$_2$CH$_3$), 24.8, 25.6, 26.4 (C(*C*H$_3$)$_3$), 27.6, 28.2 (*C*(CH$_3$)$_2$), 28.7, 29.2 (CH(*C*H$_3$)$_2$), 31.8 (d, $^2J_{CP}$ = 6.0 Hz, P{C(*C*H$_3$)$_3$}$_3$), 31.9 (*C*(CH$_3$)$_3$), 35.2 (d, $^1J_{CP}$ = 6.0 Hz, P{*C*(CH$_3$)$_3$}$_3$), 105.2, 110.8, 123.1, 124.0, 124.9, 128.35, 132.6, 140.9, 142.8, 144.0, 145.4, 147.8 (Ar*C*), 157.3 (d, $^3J_{CP}$ = 6.9 Hz, Al-C=*C*), 184.9 (Al-*C*) 288.6 (d, $^2J_{CP}$ = 66.6 Hz, *C*=O)

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ_P = 60.6

IR *ν* (cm^{-1}) 2954, 2863, 1632, 1573, 1538, 1504, 1456, 1403, 1291, 1243, 1200, 1137, 1089, 1009, 891, 774

$C_{66}H_{99}AlCuN_2O_2P$ requires: C, 73.81%; H, 9.29%; N, 2.61%; found: C, 73.57%; H, 9.31%; N, 2.50%

4-Pr,Ph

To a suspension of **1** (50 mg, 0.051 mmol) in benzene (2 ml) was added 1-phenyl-1-pentyne (15 µl, 0.103 mmol). The solution was immediately frozen and the headspace evacuated. The headspace was backfilled with CO (1 atm) and the was solution allowed to thaw, upon which a colour change from colourless to yellow was observed. The solution was lyophilised from benzene twice and the resulting yellow powder was dissolved in hexane. The solution was filtered and concentrated to ~2 ml. Yellow crystals formed upon standing at room temperature (40 mg, 69%)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 0.83 (d, $^{3}J_{HP}$ = 13.3 Hz, 27H, PC(CH_3)$_3$), 0.89 (t, $^{3}J_{HH}$ = 6.3 Hz, 3H, $CH_2CH_2CH_3$), 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.24 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.27 (s, 18H, C(CH_3)$_3$), 1.48 (d, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$, 1.81 (s, 3H, C(CH_3)$_2$), 1.85 (s, 3H, C(CH_3)$_2$), 2.07 (m, 2H, $CH_2CH_2CH_3$), 2.91 (m, 2H, $CH_2CH_2CH_3$), 3.60 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 4.00 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 6.34 (d, $^{4}J_{HH}$ = 1.9 Hz, 2H, XA-*o*-C*H*), 6.77 (d, $^{4}J_{HH}$ = 1.9 Hz, 2H, XA-*p*-C*H*), 7.03-7.30 (m, 11H ArH)

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C = 14.3 ($CH_2CH_2CH_3$), 16.0 (*C*H(CH$_3$)$_2$), 23.1 (C(*C*H$_3$)$_2$), 25.0, 26.0, 26.4 (*C*H(CH$_3$)$_2$), 24.7 ($CH_2CH_2CH_3$), 27.9, 28.7, (CH(*C*H$_3$)$_2$), 31.8 (d, $^{2}J_{CP}$ = 6.0 Hz, P{C(*C*H$_3$)$_3$}$_3$), 31.9 (C(*C*H$_3$)$_3$), 32.0 (*C*(CH$_3$)$_3$), 32.8 (C(*C*H$_3$)$_2$), 35.1 (*C*(CH$_3$)$_2$), 36.4 (d, $^{1}J_{CP}$ = 9.0 Hz, P{*C*(CH$_3$)$_3$}$_3$), 38.89 ($CH_2CH_2CH_3$) 105.2, 110.6, 123.2, 123.9, 124.8, 125.8, 130.2, 132.7, 141.0, 143.6, 143.6, 145.2, 147.7, 147.9, 148.0 (Ar*C*), 157.1 (d, $^{3}J_{CP}$ = 7.0 Hz, Al-C=*C*), 186.2 (Al-*C*) 287.4 (d, $^{2}J_{CP}$ = 65.3 Hz, *C*=O)

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ_P = 60.3

IR *ν* (cm^{-1}) 2954, 2863, 1632, 1569, 1537, 1467, 1382, 1307, 1254, 1174, 1105, 1014, 891, 785, 689

$C_{71}H_{101}AlCuN_2O_2P$ requires: C, 75.06%; H, 8.96%; N, 2.47%; found: C, 75.37%; H, 9.53%; N, 2.29%

Formation of (*E*)-2-ethylpent-2-enal

To a solution of **12-Et** in C_6D_6 in a J. Young's NMR tube was added H_2O (excess). The reaction mixture was sonicated for 10 min, after which time a precipitate formed. The volatiles were vacuum transferred to another NMR tube. Conversion was quantitative by ^{1}H NMR.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ_H = 0.68 (t, 1H, $^{3}J_{HH}$ = 6.8 Hz, CH_2CH_3), 1.79 (m, 2H, CH_2CH_3), 2.70 (q, $^{3}J_{HH}$ = 7.9 Hz, 2H, CH_2CH_3), 5.72 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, *H*C=C), 9.20 (s, 1H, O=C*H*)

ESI mass spec: 113.1 (m/z = 112.1)

3. Representative ^{1}H NMR spectra

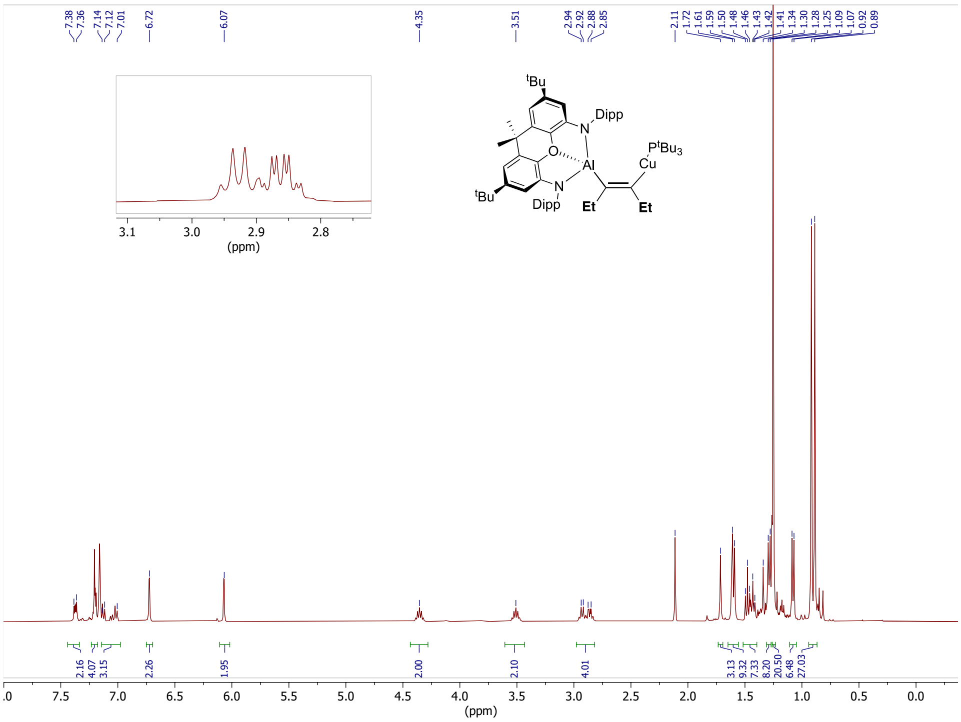

Figure S1 ^{1}H NMR spectrum of **2**-Et measured in C_6D_6

The CH_2CH$_3$ signals are inequivalent, appearing as a quartet and a double quartet in the ^{1}H NMR, arising from additional coupling to ^{31}P. In the HMBC spectrum, the quaternary carbons Cu-C and Al-C couple to both the quartet and double quartet. However, Cu-*C* couples only to the triplet signal for CH_2CH_3 associated with the double quartet, and not the triplet associated with the quartet. Likewise, Al-C couples only to the CH_2CH_3 triplet associated with the quartet. Therefore, it can be concluded that the CH_2CH$_3$ that is on the same carbon as CuP^{t}Bu$_3$ experiences ^{31}P coupling. This is key for later characterisation.

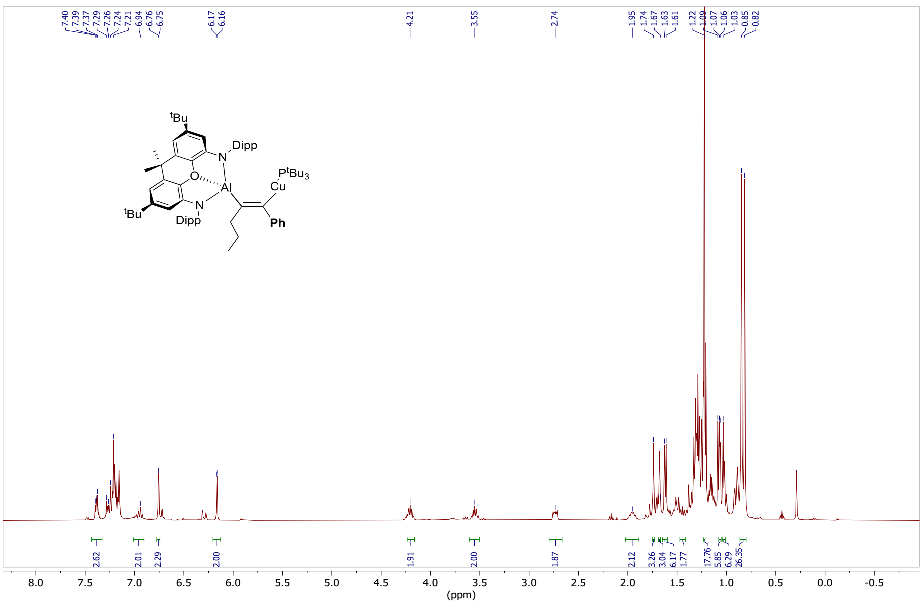

Figure S2. In situ [1]H NMR spectrum of **2**-Pr,Ph measured in C_6D_6

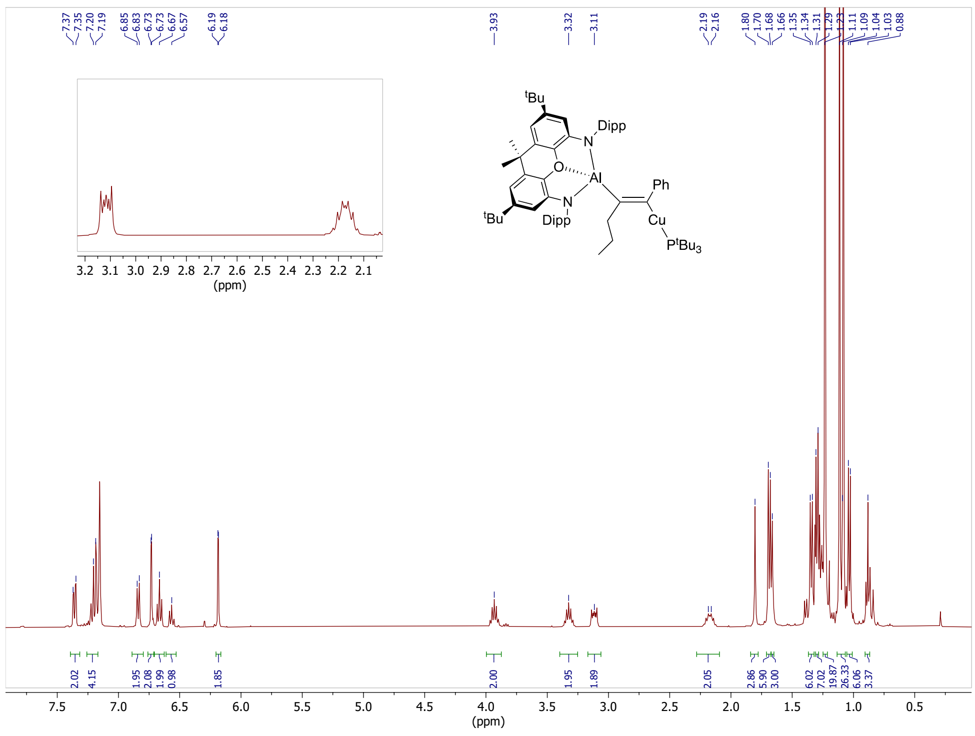

Figure S3. [1]H NMR spectrum of **3**-Pr,Ph measured in C_6D_6. Inset: close up of resonances for C**H**$_2$CH$_2$CH$_3$ and CH$_2$C**H**$_2$CH$_3$

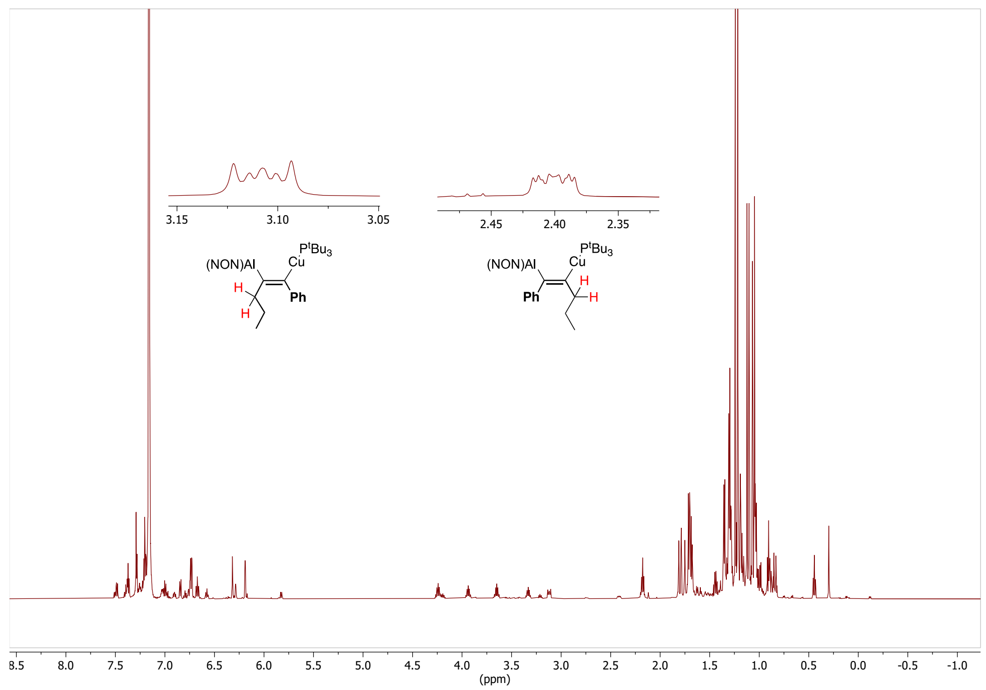

Figure S4. ^{1}H NMR spectrum of a mixture of **2**-Pr,Ph and **2**-Ph,Pr measured in C_6D_6. The inset shows the different multiplets corresponding to the $CH_2CH_2CH_3$ protons. For the systems **2**-Pr,Ph, **3**-Pr,Ph and **4**-Pr,Ph, a triplet with second order coupling is observed. For the alternate regioisomer **2**-Ph,Pr, it is a doublet of triplets with coupling to ^{31}P. For a discussion of second order coupling in n-propyl groups, see ref s2.[s2]

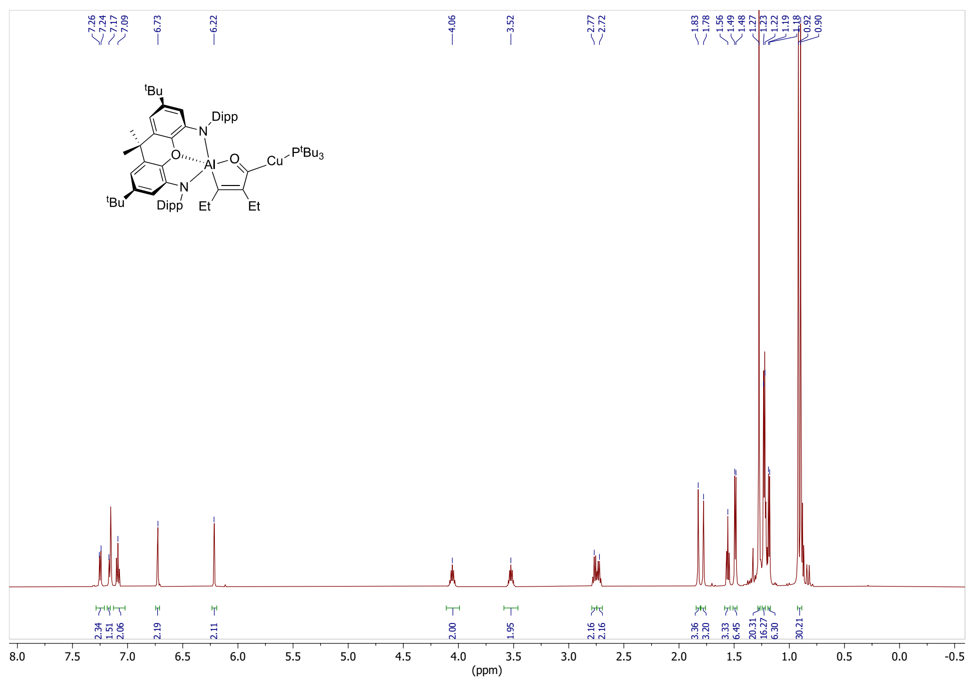

Figure S5. ^{1}H NMR spectrum of **4**-Et measured in C_6D_6

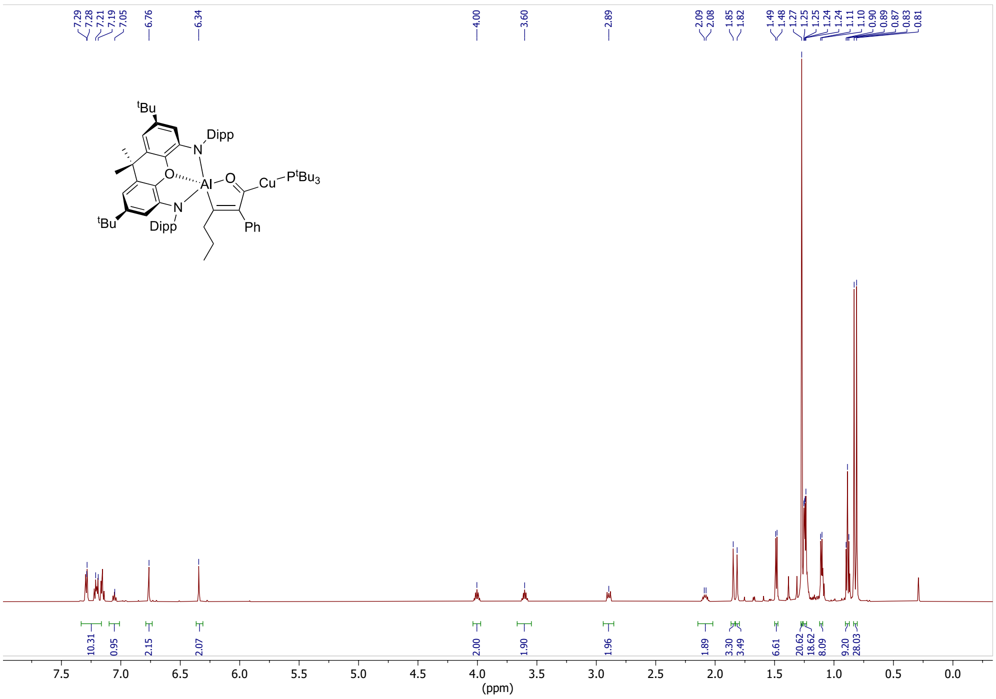

Figure S6. ^{1}H NMR spectrum of **4**-Pr,Ph measured in C_6D_6

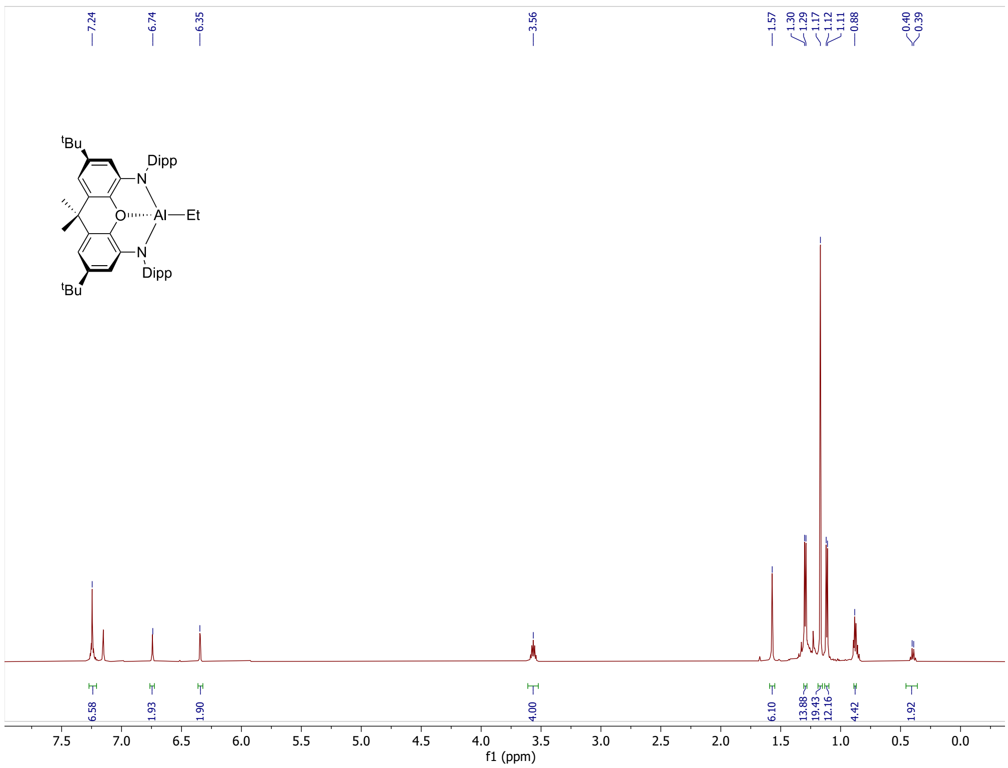

Figure S7. ^{1}H NMR spectrum of (NON)AlEt measured in C_6D_6

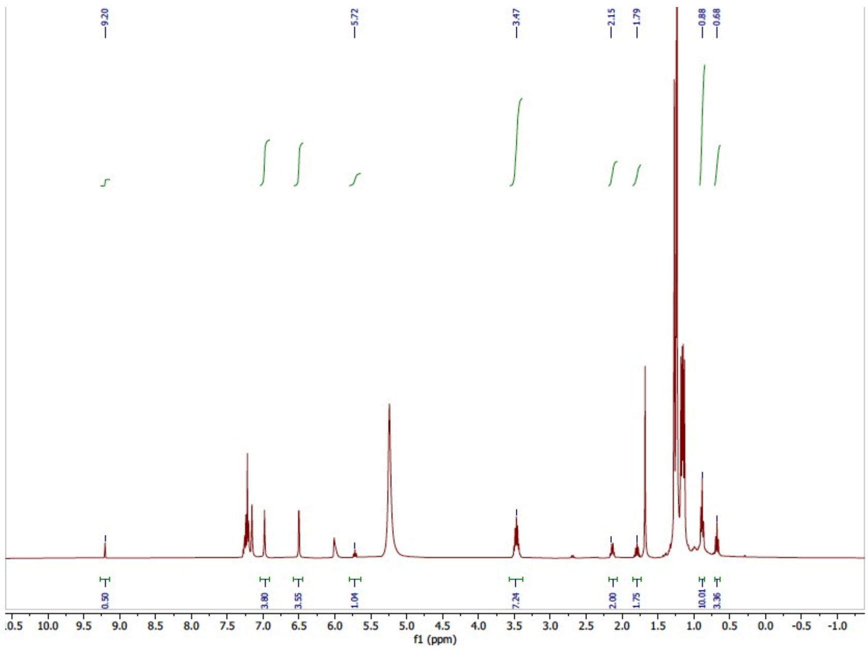

Figure S8. ^{1}H NMR spectrum of the hydrolysis reaction mixture following addition of water to **4**-Et, prior to vacuum transfer to capture the volatiles (measured in C_6D_6)

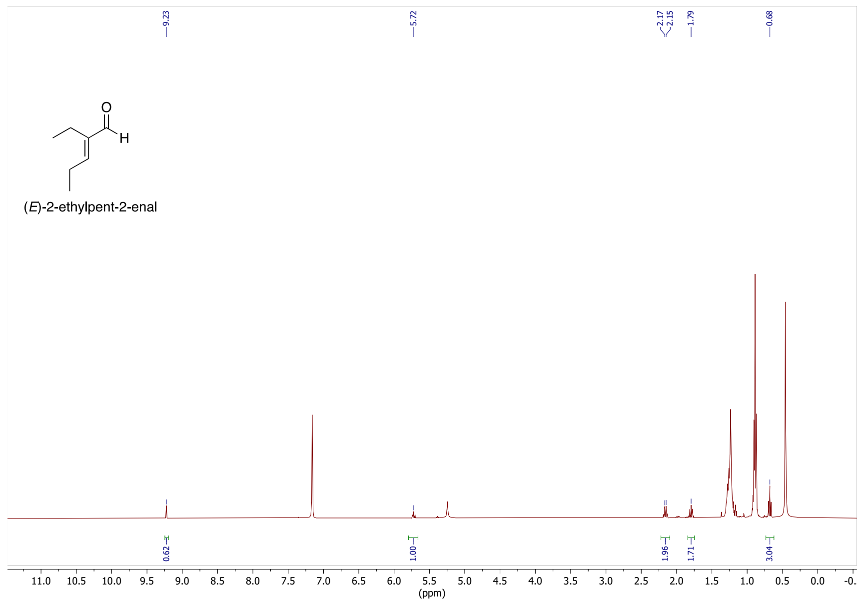

Figure S9. ^{1}H NMR spectrum of the hydrolysis reaction mixture following addition of water to **4**-Et, after vacuum transfer to capture the volatiles (measured in C_6D_6)

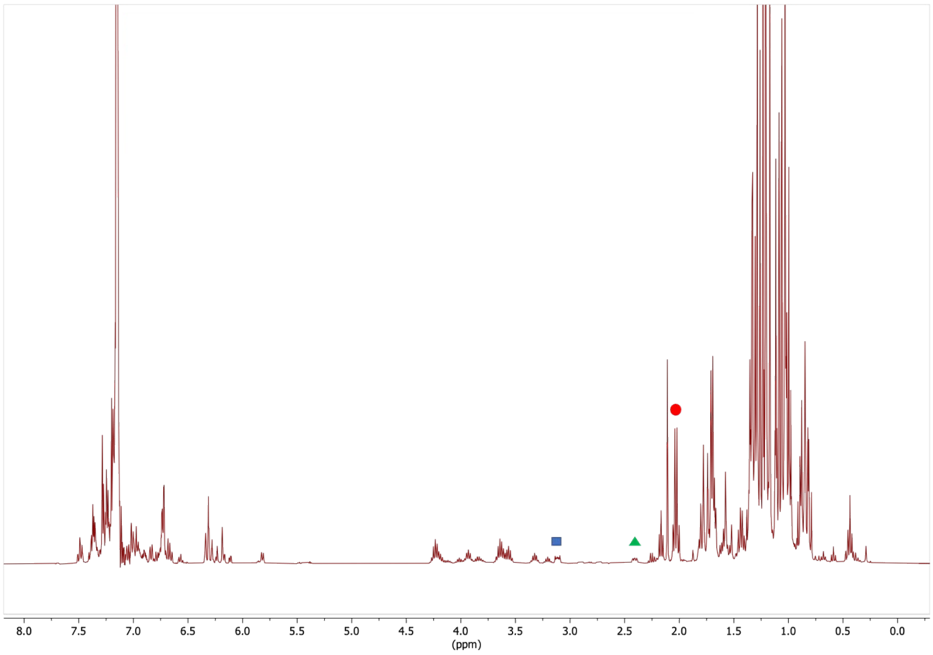

*Figure S10. ^{1}H NMR of the reaction of **2**-Et with PhCC^{n}Pr showing the formation of **2**-Pr,Ph (blue), **2-**Ph,Pr (green) and 3-hexyne (red). Measured in C_6D_6*

4. Representative ^{31}P NMR spectra

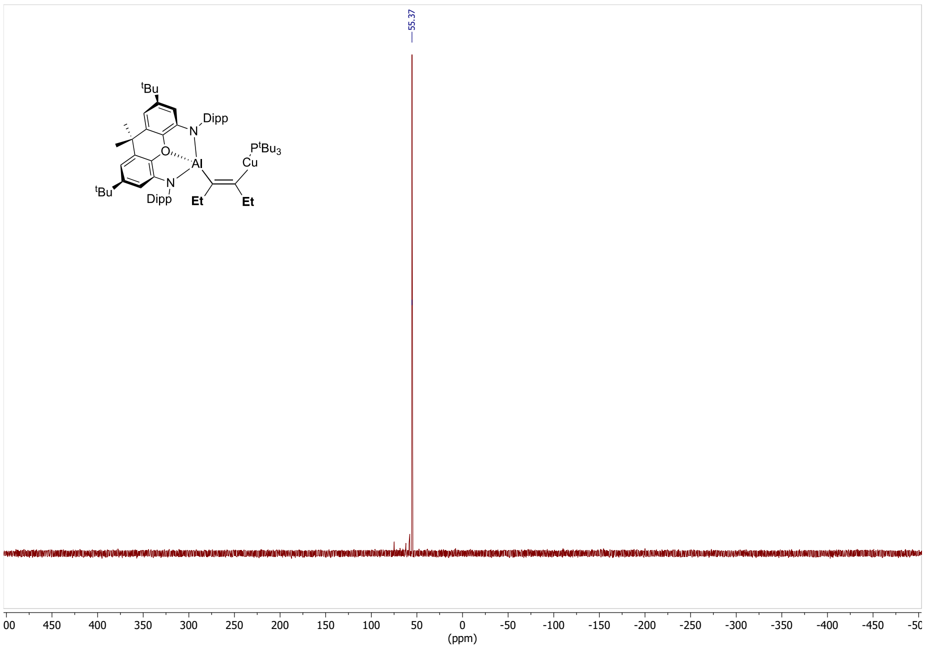

Figure S11. ^{31}P NMR spectrum of **2**-Et measured in C_6D_6

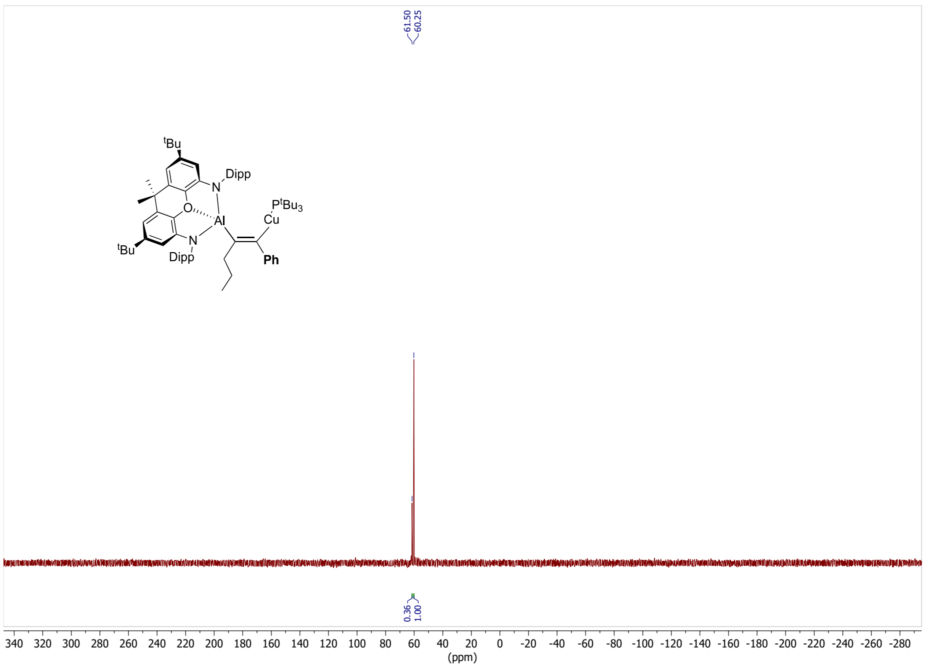

Figure S12. ^{31}P NMR spectrum of the reaction mixture of **1** and PhCCnPr at 5 min at room temperature, showing **2**-Pr,Ph and **2**-Ph,Pr in a 1:0.3 ratio, measured in C_6D_6

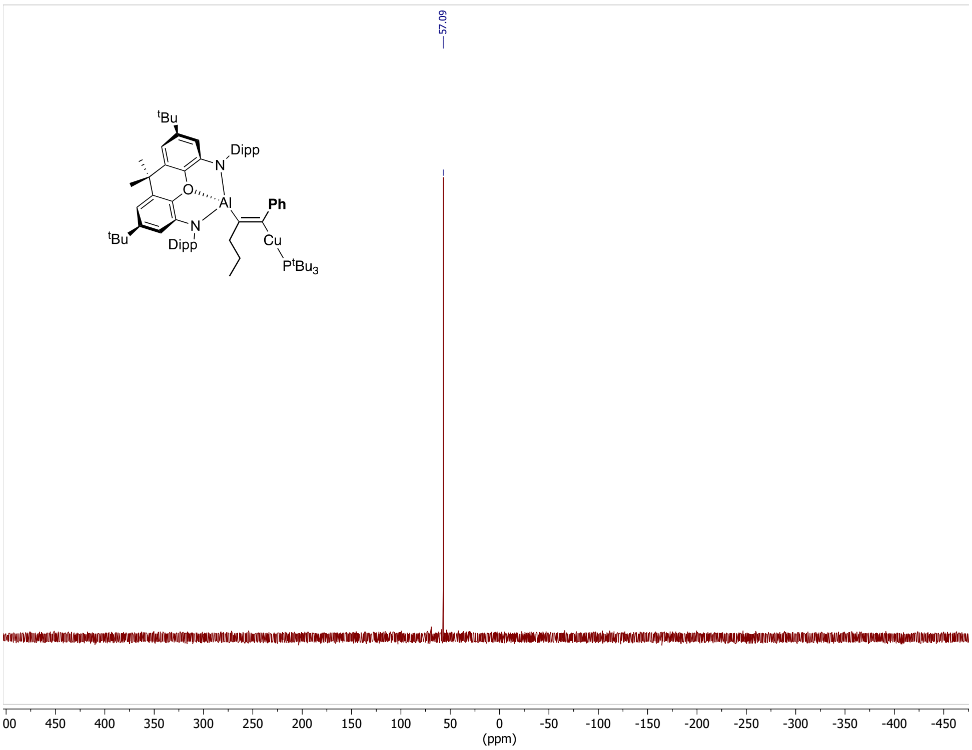

Figure S13. [31]P NMR spectrum of **3**-Pr,Ph measured in C_6D_6

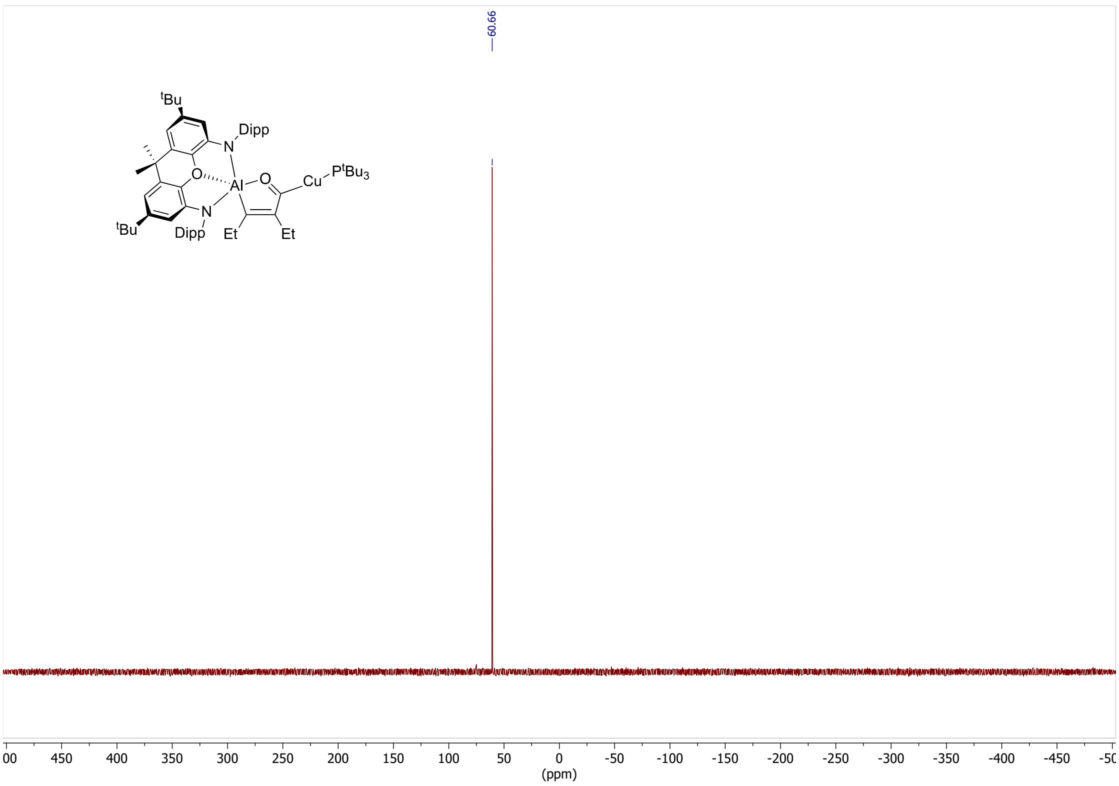

Figure S14. [31]P NMR spectrum of **4**-Et measured in C_6D_6

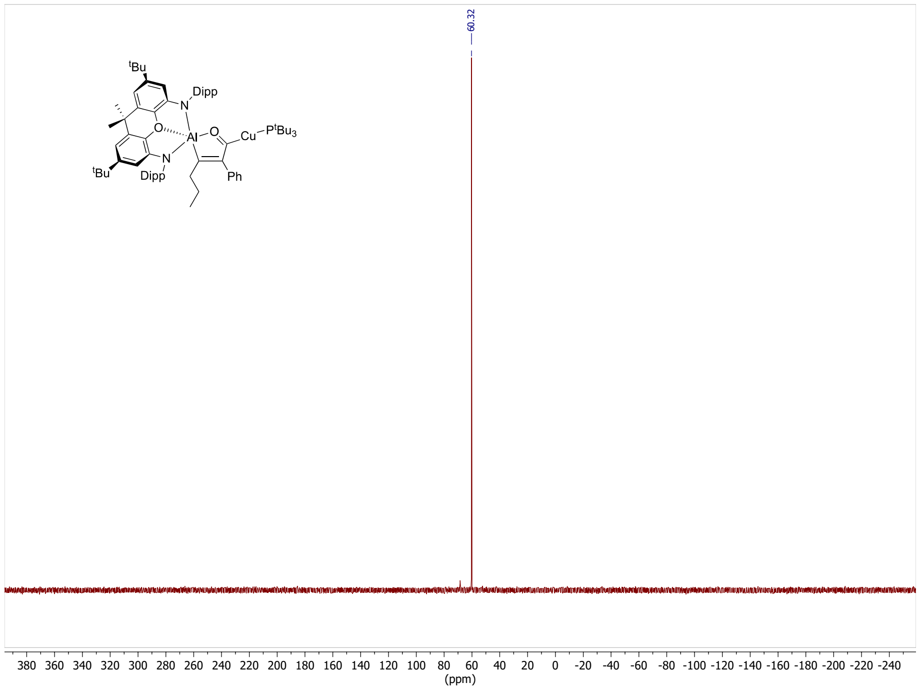

Figure S15. ^{31}P NMR spectrum of **3**-Pr,Ph measured in C_6D_6

5. Representative ^{13}C and 2D-NMR spectra

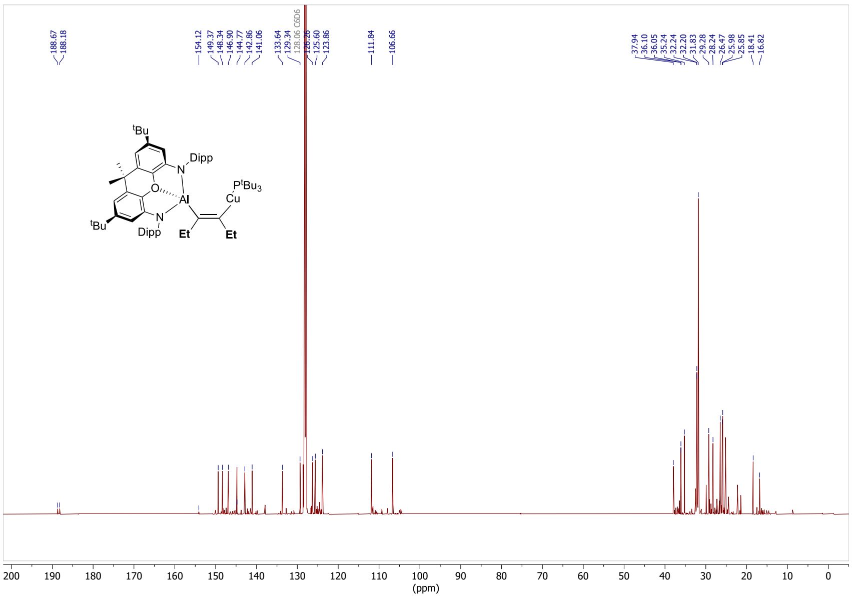

Figure S16. ^{13}C NMR spectrum of **2**-Et measured in C_6D_6

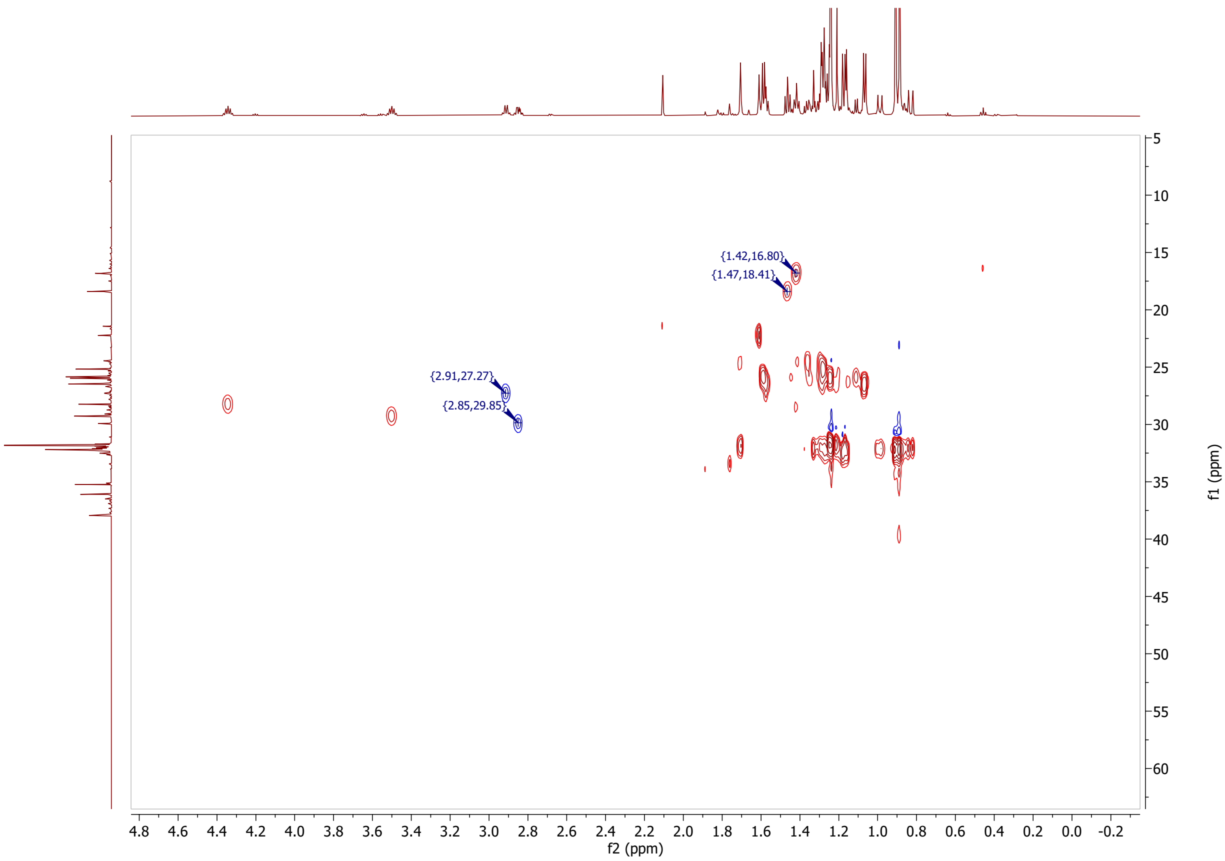

*Figure S17. HSQC NMR spectrum of **2**-Et*

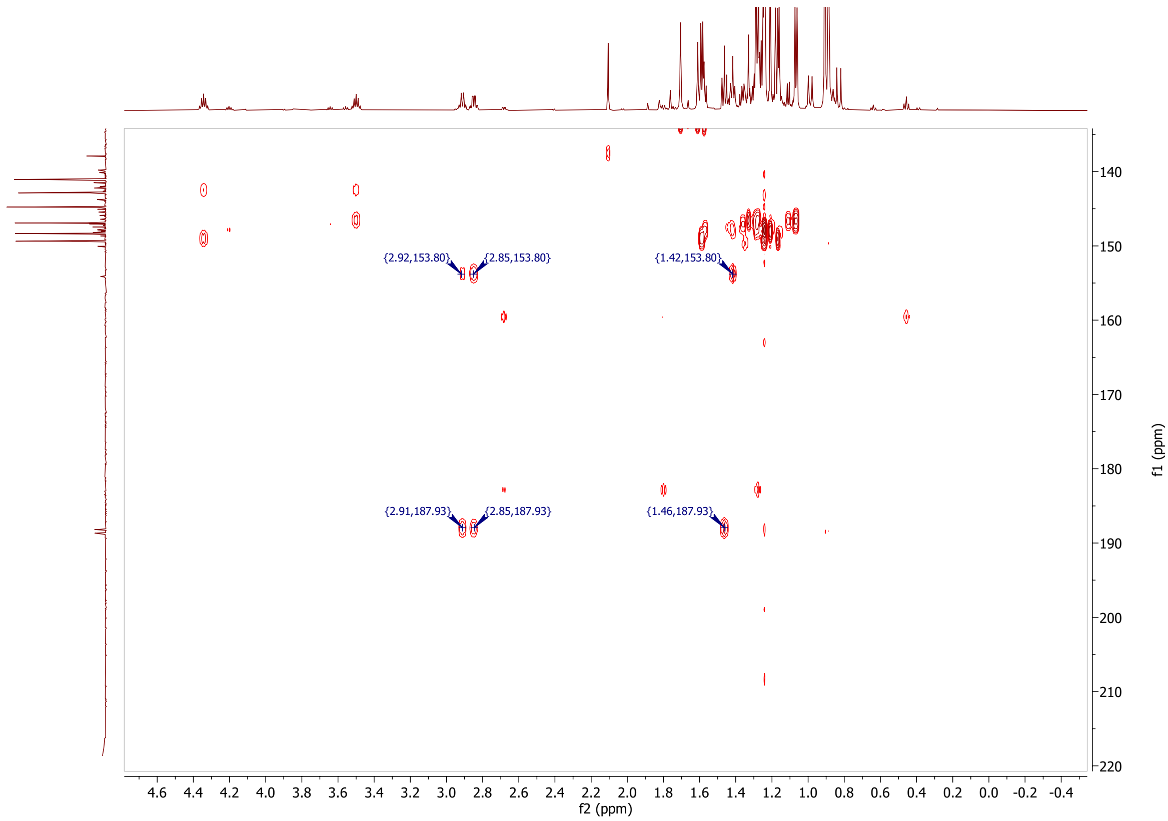

*Figure S18. HMBC NMR spectrum of **2**-Et, in which it can be seen that the ethyl group adjacent to the CuP^{t}Bu$_3$ unit experiences ^{31}P coupling, resulting in a double quartet*

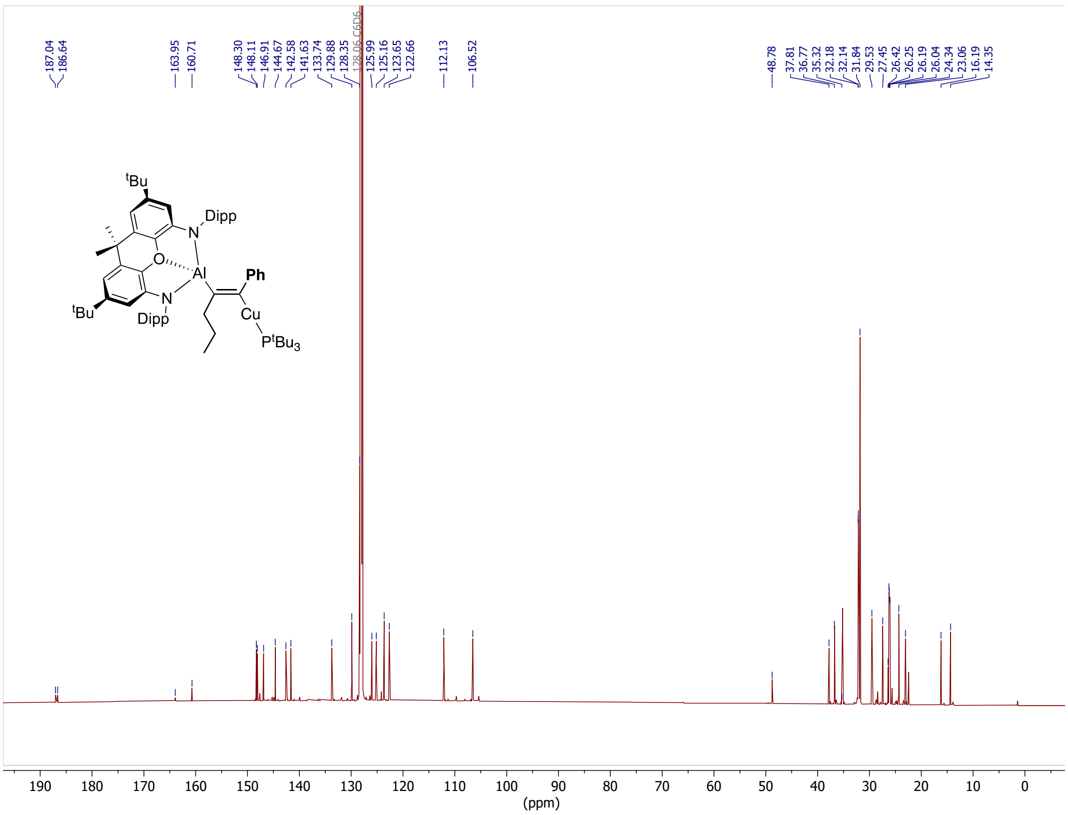

Figure S19. ^{13}C NMR spectrum of **3**-Pr,Ph measured in C_6D_6

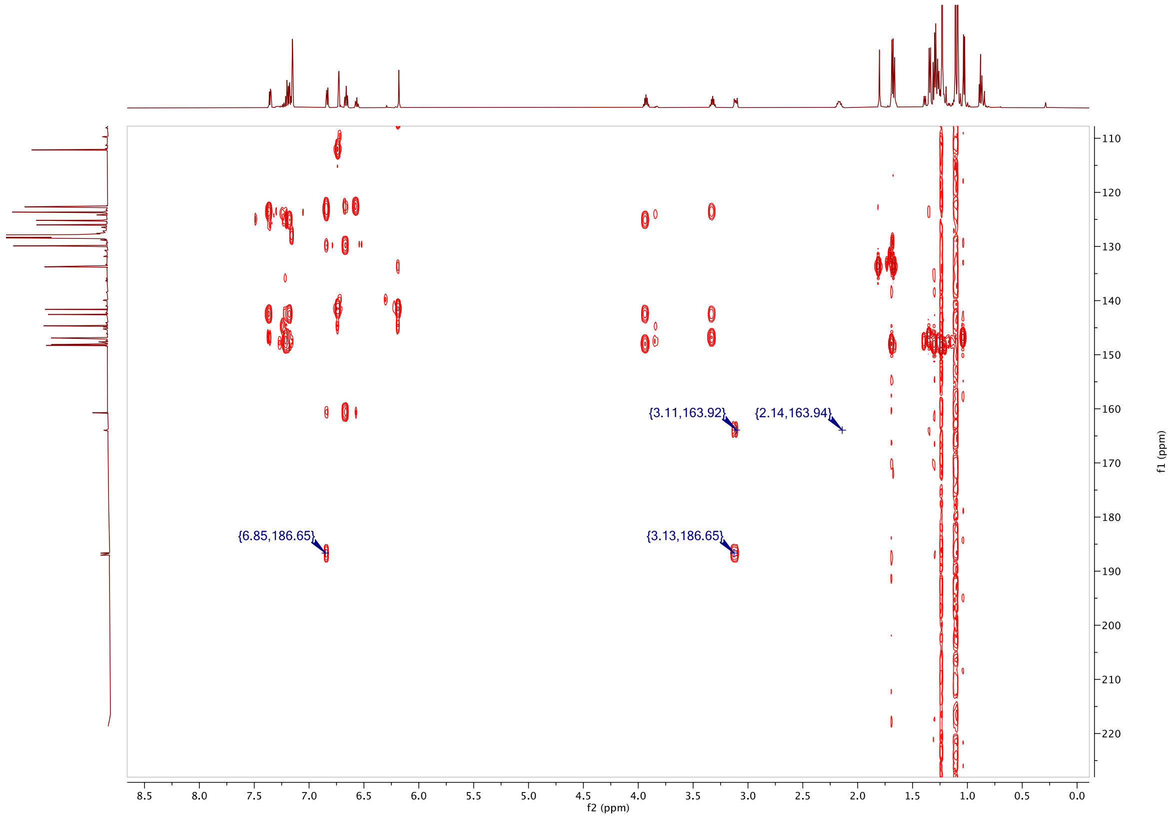

*Figure S20. HMBC NMR spectrum of **3**-Pr,Ph, in which it can be seen that the doublet of C-Cu (186.5 ppm) couples to aryl protons and to the CH_2 of the alkyl chain, whereas C-Al (163.9 ppm) does not couple to any aryl protons, instead coupling to both $C\mathbf{H}_2CH_2CH_3$ and $CH_2C\mathbf{H}_2CH_3$. This supports the regiochemical assignment of the alkyl group geminal to aluminium.*

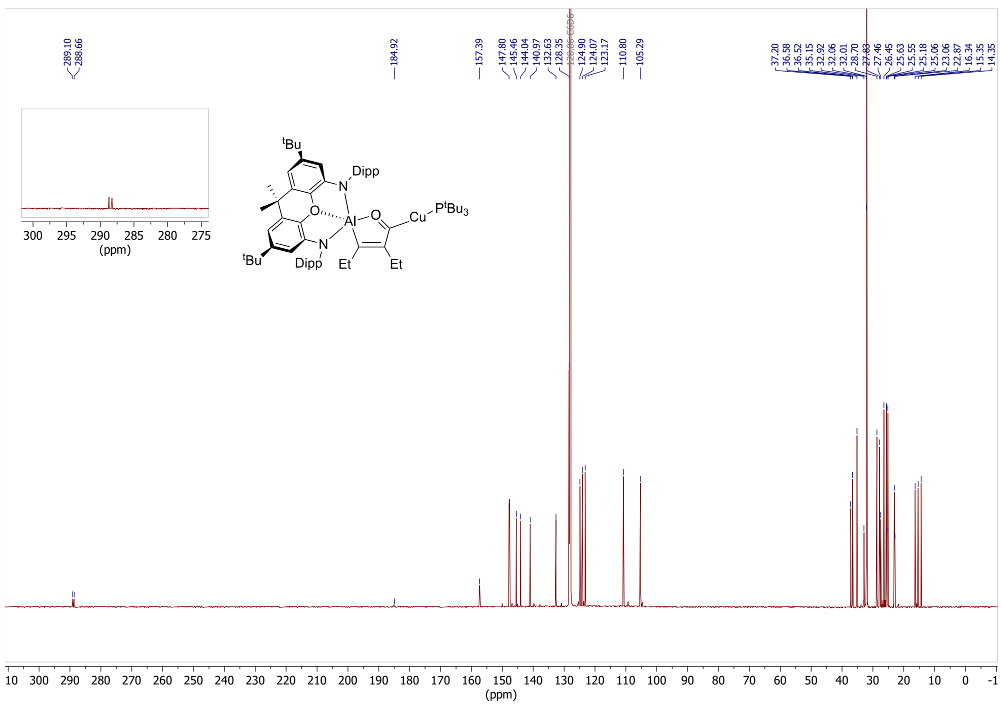

Figure S21. ^{13}C NMR spectrum of **4**-Et measured in C_6D_6

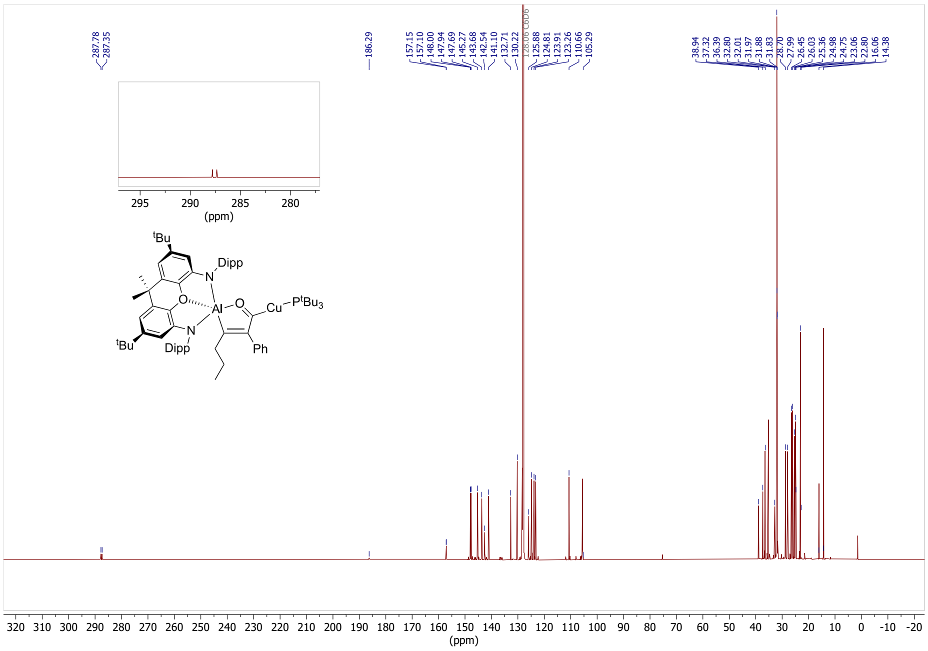

Figure S22. ^{13}C NMR spectrum of **4**-Pr,Ph measured in C_6D_6

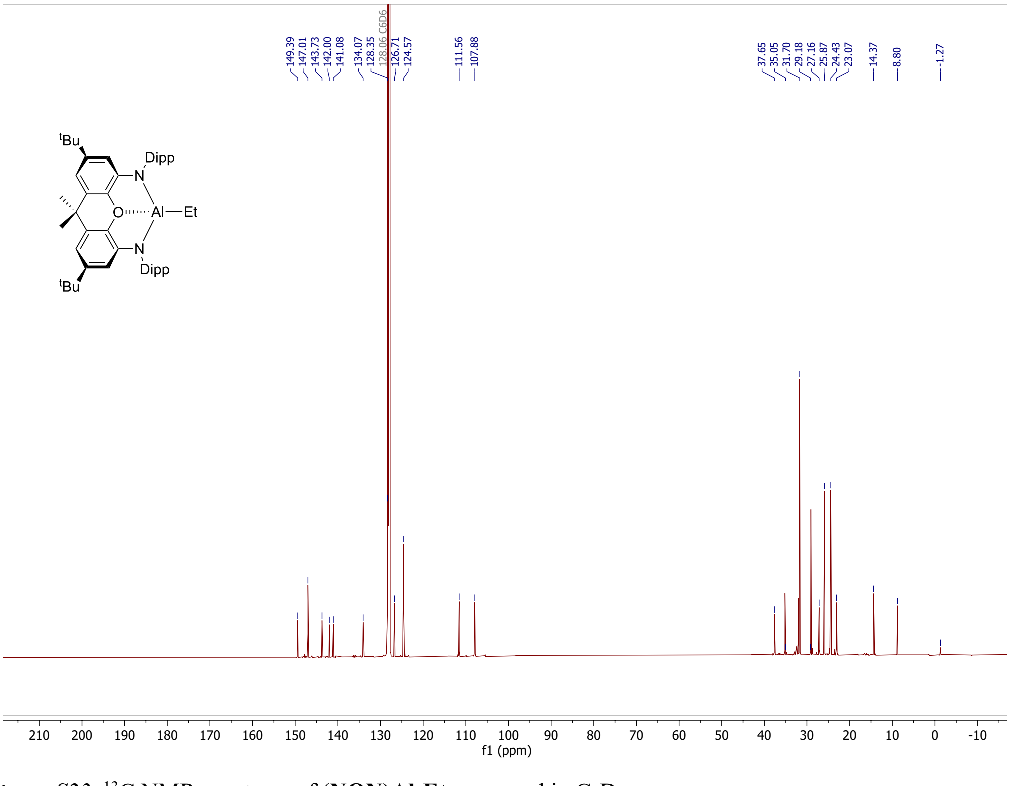

Figure S23. ^{13}C NMR spectrum of **(NON)Al-Et** measured in C_6D_6

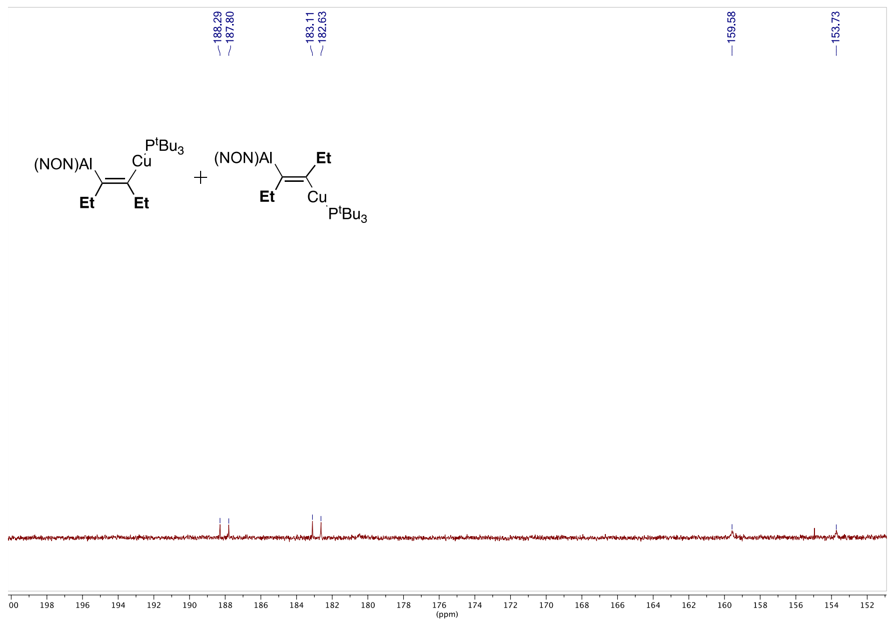

Figure S24. Excerpt from the ^{13}C NMR spectrum of a mixture of **2**-Et and **3**-Et measured in C_6D_6, in which the C-Cu doublet and C-Al resonance for each species can be seen

6. IR, mass spectra and reaction profiles

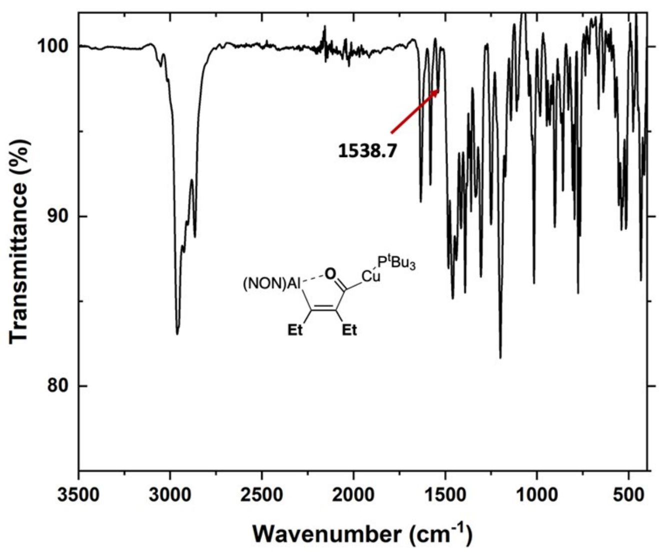

*Figure S25. FT-IR spectrum of **4**-Et. CO stretch labelled.*

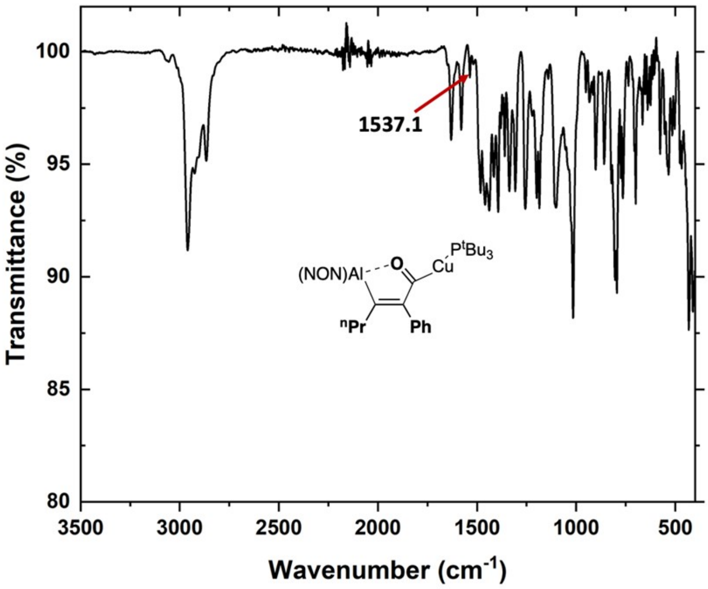

*Figure S26. FT-IR spectrum of **4-**Pr,Ph (CO stretch labelled).*

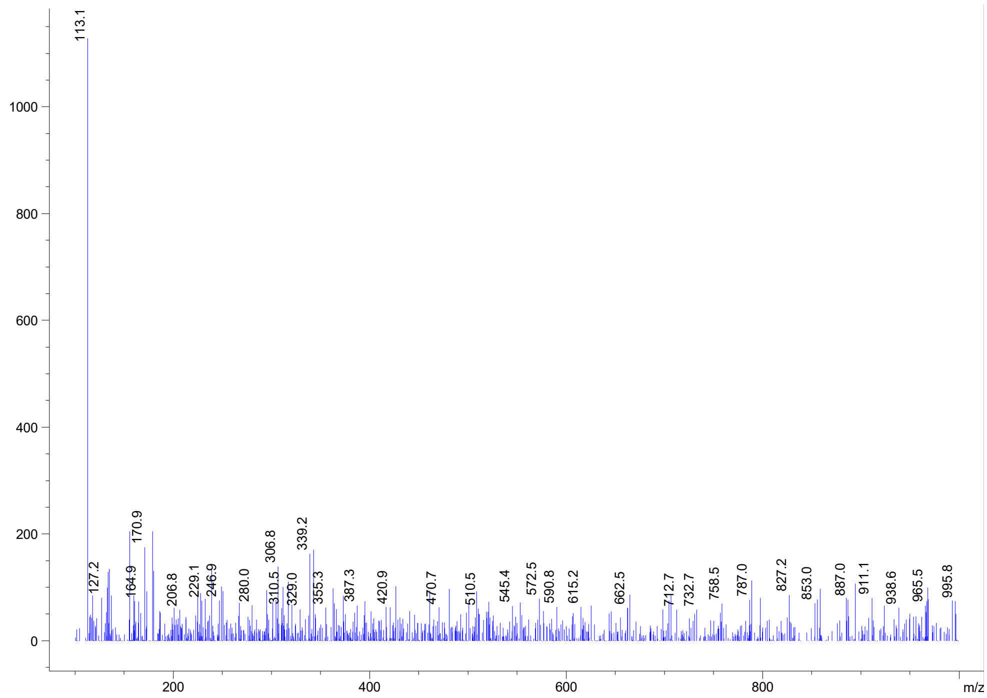

*Figure S27. Mass spectrum obtained from hydrolysis of **4**-Et, showing the presence of 2-ethylpent-2-enal (m/z = 112.1)*

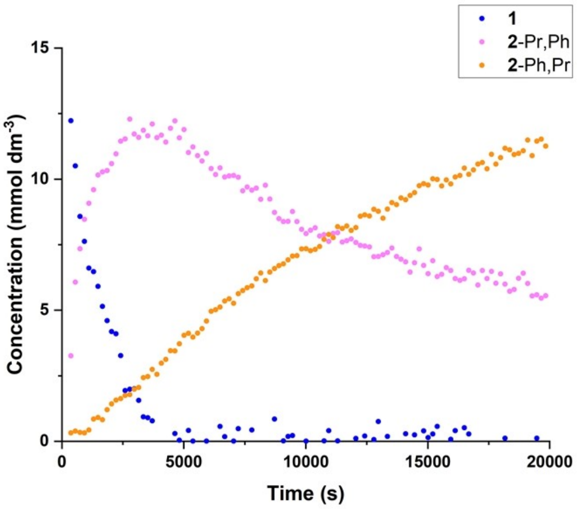

*Figure S28. Temporal profile of the reaction of **1** with 1-phenyl-1-pentyne to give **2**-Pr,Ph and **2**-Ph,Pr. Plot produced by integrating ^{31}P NMR resonances of the relevant species. Measured in C_6D_6 at 283 K. The first 2 spectra have been omitted owing to the partial solubility of **1** at 283 K, making integration unreliable.*

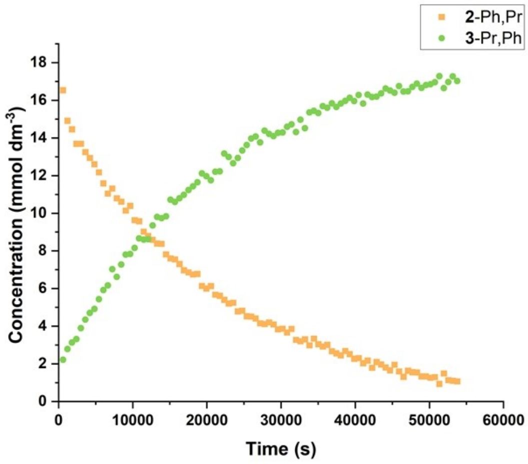

*Figure S29. Temporal profile showing the isomerisation of **2**-Ph,Pr to **3**-Pr,Ph. Plot produced by integrating* ^{31}P *NMR resonances of the relevant species. Measured in* C_6D_6 *at 318 K.*

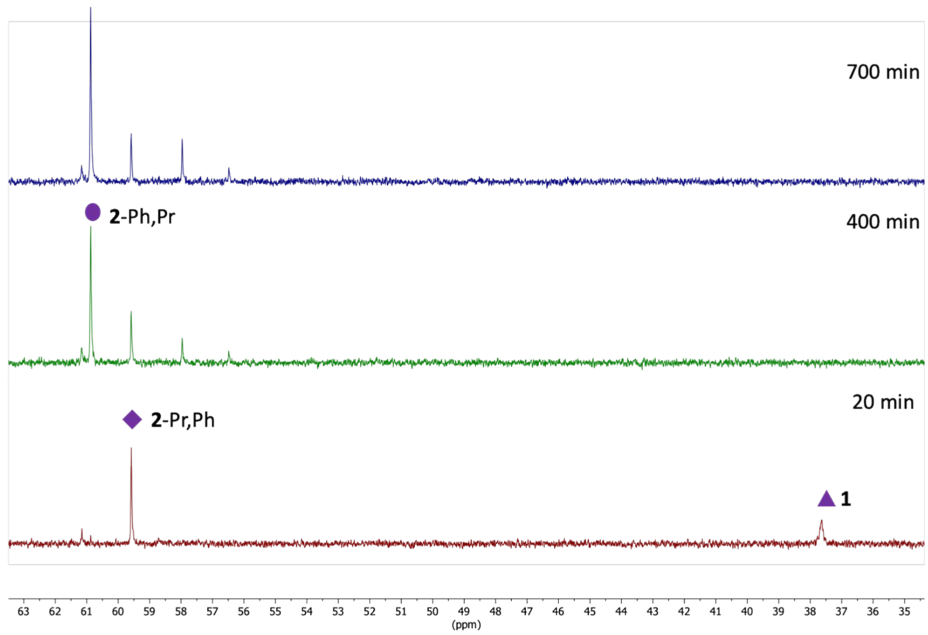

Figure S30. Representative ^{31}P *NMR spectra measured in* C_6D_6 *at 283 K, used to plot the temporal profile in Figure S26. It can be seen that the initial product **2**-Pr,Ph converts to the alternate regioisomer **2**-Ph,Pr*

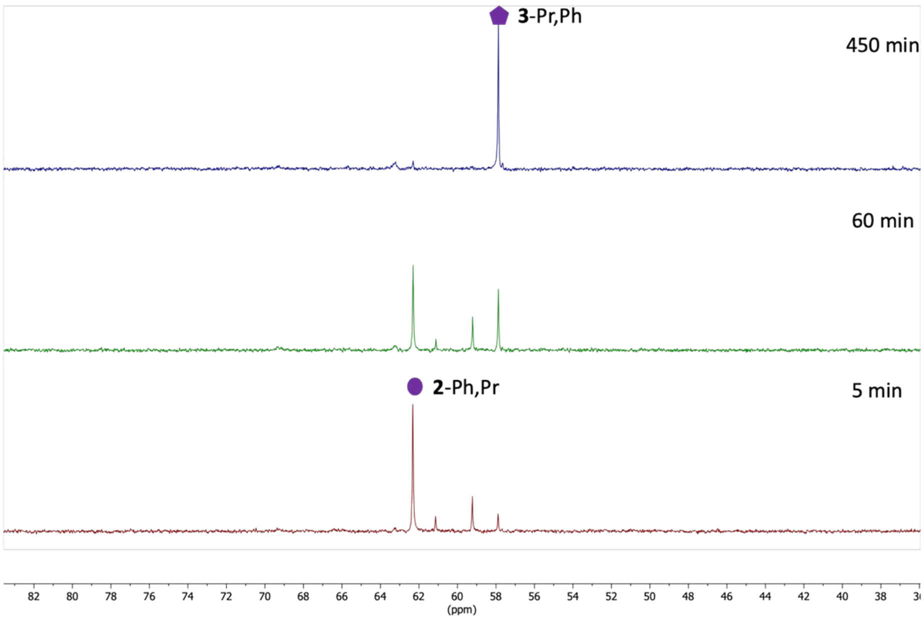

Figure S31. Representative ^{31}P NMR spectra measured in C_6D_6 at 318 K, used to plot the temporal profile in Figure S27, showing the cis-trans isomerism process.

7. X-ray crystallographic studies

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[s3] Data were collected at 150 K using mirror monochromated Cu (λ = 1.5418 Å) or Mo (λ = 0.71073 Å) K_α radiation. All crystallographic data were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[s4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using ShelXT 2018 and refined on F^2 using the ShelXL 2018 package and XSeed.[s5,s6]

Table 1. X-ray crystallographic data

	2-Et	3-Pr,Ph	4-Et	4-Pr,Ph	(NON)Al-Et
Formula	$C_{79}H_{115}AlCuN_2OP$	$C_{76}H_{115}AlCuN_2OP$	$C_{69}H_{106}AlCuN_2O_2P$	$C_{71}H_{101}AlCuN_2O_2P$	$C_{52}H_{74}AlN_2O$
M_r	1230.21	1194.18	1117.04	1864.66	770.11
Cell setting	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	$P2_1$/n	*P-1*	*P-1*
a/Å	12.6157(4)	13.2005(7)	13.8505(2)	12.1884(2)	13.0581(5)
b/Å	15.1843(5)	13.5410(10)	23.4691(4)	17.4389(4)	13.3038(7)
c/Å	20.1243(7)	22.7180(11)	20.3996(3)	19.4541(5)	14.3490(5)
α/°	75.776(3)	97.054(5)	90	71.108(2)	99.705(4)
β/°	78.631(3)	94.267(4)	92.351(2)	79.692(2)	104.191(3)
γ/°	84.115(3)	115.698(6)	90	80.746(2)	98.075(4)
V/Å^3	3657.6(2)	3594.3(4)	6625.49(18)	3825.54(16)	2338.58(18)
Z	2	2	4	2	2
Indep. reflections	15110	14807	13709	15832	9701
R_{int}	0.0477	0.0477	0.0314	0.0262	0.0303
Parameters	795	822	773	791	554
R_1 (all data/$I > 2\sigma(I)$)	0.0800/0.0630	0.1628/0.1253	0.0539/0.0426	0.0475/0.0409	0.0558/0.0430
wR_2 (all data/$I > 2\sigma(I)$)	0.1889/0.1713	0.3547/0.3156	0.1211/0.1115	0.1148/0.1084	0.1187/0.1091
GooF	1.046	1.217	1.031	1.043	1.028
Residual max/min	1.81/–0.64	3.17/–0.78	0.65/–0.54	0.52/-0.46	0.38/–0.32
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
CCDC Deposition No.	2157971	2157972	2157973	2157974	2157976

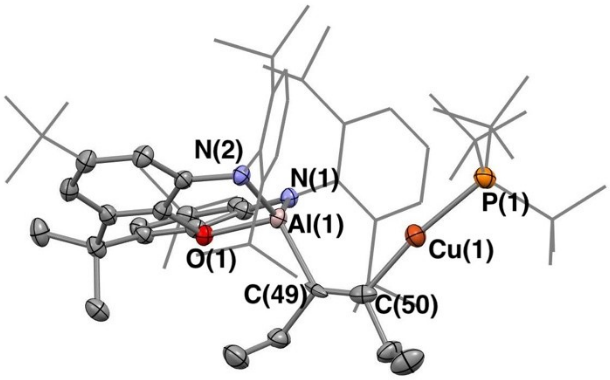

*Figure S32. Molecular structure of **2-Et** in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level. Hydrogen atoms omitted and Dipp/^{t}Bu groups shown in wireframe for clarity. Toluene solvate omitted.*

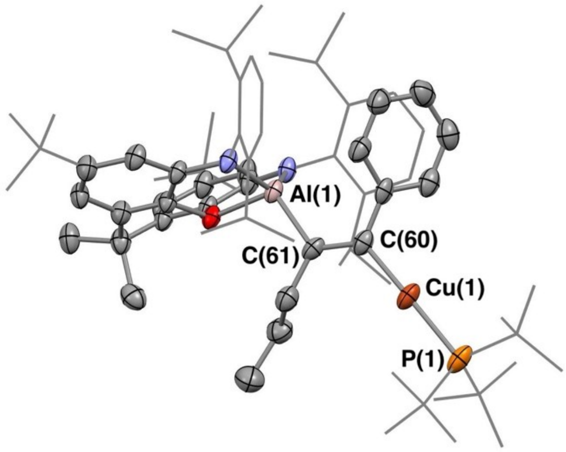

*Figure S33. Molecular structure of **3-Pr,Ph** in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level. Hydrogen atoms omitted and Dipp/^{t}Bu groups shown in wireframe for clarity. Notes on refinement: Crystals were of low quality and therefore an R1 value of 12.5 was obtained. There is a large q speak sitting close to the Ph ring of the alkyne, however this cannot be explained chemically and does not fit any reasonable atom. Hexane solvent molecule (omitted) modelled as disordered across two positions.*

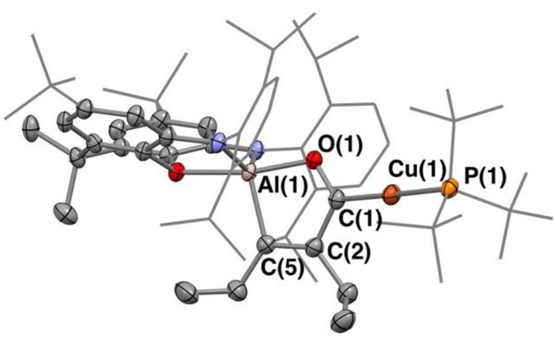

*Figure S34. Molecular structure of **4-Et** in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level. Hydrogen atoms omitted and Dipp/^{t}Bu groups shown in wireframe for clarity. Hexane solvate molecule(omitted) modelled as disordered across two positions.*

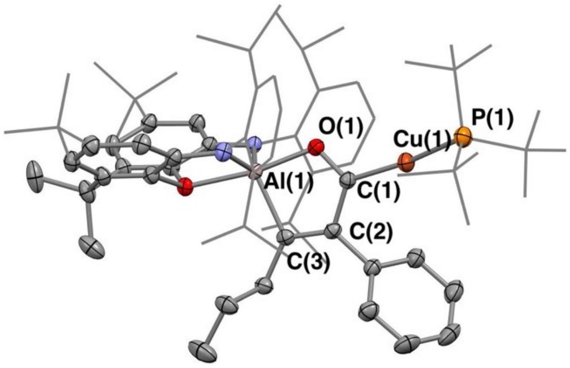

Figure S35. Molecular structure of ***4-Pr,Ph*** *in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level. Hydrogen atoms omitted and Dipp/ᵗBu groups shown in wireframe for clarity. The hexane solvate takes the form of a channel through the lattice which cannot be satisfactorily modelled and therefore a solvent mask was applied. ᵗBu₃ groups were modelled as disordered rotationally.*

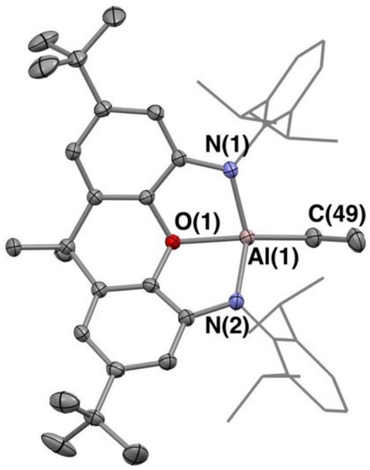

Figure S36. Molecular structure of ***(NON)Al-Et*** *in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level. Hydrogen atoms omitted and Dipp/ᵗBu groups shown in wireframe for clarity.*

8. Computational studies

All computational work reported here was carried out using density functional theory (DFT) performed with Orca (Revision 5.0.2)[s7]. In order to reduce computational cost calculations were performed for model systems with the tBu groups on the xanthene backbone replaced by methyl substituents. Geometry optimisations for model compounds **4'-Et** and **4'-Pr,Ph** were performed using the B3LYP hybrid functional[s8] using the def2-SVP basis sets,[s9] with Grimme's D4 dispersion correction.[s10] Frequency calculations where performed using the optimised geometries using the def2-TZVP basis sets.[s9]

```
4'-Et
  Cu  4.59529981422010      8.43885443203813     14.77643323739226
  P   6.76069143844873      8.87940335173784     15.17982322207638
  Al  1.22668878295247      7.22575161612119     12.08859061457908
  O   -0.40845347448469      7.02152430620701     10.89147250133540
  O   2.89126373038474      7.29601168663627     12.98829147352413
  N   1.86050726855665      8.10661601836687     10.50376977082697
  N   0.77276109739306      5.39264023679272     12.46132151861479
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  C   -2.44832444175264      6.53645994263895      9.05316574963265
  C   3.12300687434133      8.74222724796283     10.34105232615579
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  C   0.33840397617671      4.65203826996479     14.76591146287378
  C   2.45166708700444      4.04781314439343     13.66811461591531
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  H   -2.48377265468446      5.35408190852568      7.21073173264599
  H   -3.53369570553158      6.79675499203741      7.18255104745257
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  C   4.08941410940733      6.53024212895511      9.50053987878129
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C	7.10424439052515	10.75818166129809	14.98860176432155
C	5.56741532093122	10.03974405792883	9.86855687147253
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H	0.64673690043058	12.40952215918819	10.60696224002907
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C	7.72432430418267	7.89014324433763	13.84573098593792
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