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Synthesis, structures and reactivity of Sc^{3+} and Y^{3+} bis(alkyl) complexes coordinated by [O,N,O] pincer amido ligand

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EXPERIMENTAL SECTION

General consideration. All experiments were performed by using standard Schlenk or glove-box techniques, with rigorous exclusion of traces of moisture and air. After being dried over CaH_2, THF and Et_2O were purified by distillation from sodium/benzophenone ketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. C_6D_6 and were dried with sodium and was condensed *in vacuo* into NMR tubes prior to use. $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y)[S1] and bis(2-diisopropylphosphanyl-4-methylphenyl)amine $(2\text{-}Pr^i{}_2P\text{-}4\text{-}Me\text{-}C_6H_3)_2NH$ [S2,S3] were obtained according previously published procedures.

NMR spectra were recorded using a Bruker NMR spectrometer (400 or 300 MHz). Chemical shifts for ^1H, $^{13}C\{^1H\}$, NMR spectra were referenced internally to the residual solvent resonances and are reported relative to $SiMe_4$. IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. The C, H, and N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry. Lanthanide metal analysis were carried out by complexometric titration.[S4]

Synthesis of $[2\text{-}Pr^i{}_2PO\text{-}4\text{-}MeC_6H_3]_2NH$ (2). To a solution of bis(2-diisopropylphosphanyl-4-methylphenyl)amine 1.500 g (3.50 mmol) in toluene (50 mL) was added dropwise 1.5 mL of 20% solution of H_2O_2 (0.300 g, 8.80 mmol) in H_2O (20%). The reaction mixture was stirred for 12 hours at ambient temperature. The solvents were removed at reduced pressure, and the solid residue was extracted with ethylacetate. Then the solvent was removed under reduced pressure, and the solid residue was washed small amount of hexane. Compound **2** was isolated in 86% yield (1.385 g, 3.01 mmol). Elemental analysis calculated for $C_{26}H_{41}NO_2P_2$ (461.57 g/mol) (%): C, 67.66; H, 8.95; N, 3.03. Found (%): C, 67.53; H, 8.90; N, 2.94.

^1H NMR (400 MHz, $CDCl_3$, 293 K): 1.06 (dd, J_{HH} = 16.1, 7.2 Hz, 12H, C*H*$_3$ iPr), 1.27 (dd, J_{HH} = 15.2, 7.2 Hz, 12H, C*H*$_3$ iPr), 2.30 (s, 6H, C*H*$_3$ Ar), 2.44 (m, 4H, C*H* iPr), 6.93 (m, 2H, C*H* Ar), 7.11 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C*H* Ar), 7.35 (d, $^3J_{HH}$ = 11.3 Hz, 2H, C*H* Ar), 9.19 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): 15.6 (d, $^2J_{CP}$ = 3.1 Hz, *C*H$_3$ iPr), 16.7 (d, $^2J_{CP}$ = 2.3 Hz, *C*H$_3$ iPr), 20.7 (s, *C*H$_3$ Ar), 26.6 (d, $^1J_{CP}$ = 66.3 Hz, *C*H iPr), 121.0 (br s, *C*H Ar), 127.4 (br s, *C* Ar), 130.4 (s, *C* Ar), 133.3 (s, *C*H Ar), 133.4 (br s, *C*H Ar), 146.1 (br s, *C* Ar); determined according to ^1H–^{13}C HMQC and HMBC spectra. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 293 K): 58.0 (br s).

^1H NMR (400 MHz, C_6D_6, 293 K): 1.00 (dd, J_{HH} = 15.8, 7.2 Hz, 12H, C*H*$_3$ iPr), 1.21 (dd, J_{HH} = 14.8, 7.0 Hz, 12H, C*H*$_3$ iPr), 2.05 (s, 6H, C*H*$_3$ Ar), 2.31 (br s, 4H, C*H* iPr), 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 2H, C*H* Ar), 7.10 (dd, *J* = 8.4, 4.5 Hz, 2H, C*H* Ar), 7.54 (br s, 2H, C*H* Ar), 9.81 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 15.5 (s, $^2J_{CP}$ = 3.1 Hz, *C*H$_3$ iPr), 16.6 (s, $^2J_{CP}$ = 2.3 Hz, *C*H$_3$ iPr), 20.3 (s, *C*H$_3$ Ar), 26.5 (d, $^1J_{CP}$ = 66.5 Hz, *C*H iPr), 119.9 (br s, *C*H Ar), 128.9 (br s, *C* Ar), 132.4 (br s, *C* Ar), 132.9 (d, J_{CP} = 2.1 Hz, *C*H Ar), 133.8 (br s, *C*H Ar), 145.9 (br s, *C* Ar);

determined according to $^{1}H–^{13}C$ HMQC and HMBC spectra. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, C_6D_6, 293 K): 54.6 (br s).

IR (KBr, Nujol), cm^{-1}: 3175 (s), 3145 (s), 1615 (m), 1580 (s), 1510 (s), 1280 (m), 1220 (w), 1175 (s), 1145 (s), 1125 (m), 1065 (m), 1030 (s), 1010 (m), 930 (w), 885 (s), 850 (s), 815 (s), 800 (m), 735 (s), 700 (s), 690 (s), 680 (s), 650 (s), 630 (m), 595 (w), 555 (m), 535 (s), 505 (s), 485 (m).

Synthesis of [2-Pr$^{i}_2$PS-4-MeC$_6$H$_3$]$_2$NH (3). To a solution of bis(2-diisopropylphosphanyl-4-methylphenyl)amine (1 g, 2.33 mmol) in toluene (40 mL), sulfur S_8 was added in portions (0.148 g, 0.58 mmol, one S atom per one P atom). The reaction mixture was stirred at ambient temperature for 12 h, then toluene was removed at reduced pressure and pale yellow crystals of **3** formed. The crystals were washed with small amount of toluene and were dried in vacuum for 20 min. Compound **2** was isolated in 93% yield (1.070 g, 2.16 mmol). Elemental analysis calculated for $C_{26}H_{41}NP_2S_2$ (493.69 g/mol): C, 63.26; H, 8.37; N, 2.84. Found: C, 63.08; H, 8.50; N, 2.77.

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 1.05 (m, 12H, C*H*$_3$ iPr), 1.23–1.35 (m, 12H, C*H*$_3$ iPr), 2.32 (s, C*H*$_3$ Ar) 2.79 (br s, 2H, C*H* iPr), 2.87 (br s, 2H, C*H* iPr), 6.84 (br s, 2H, C*H* Ar), 7.12 (d, *J* = 8.0 Hz, 2H, C*H* Ar), 7.67 (br s, 2H, C*H* Ar), 9.36 (s, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 293 K): 16.4 (br s, *C*H$_3$ iPr), 17.1 (br s, *C*H$_3$ iPr), 17.4 (br s, *C*H$_3$ iPr), 17.6 (br s, *C*H$_3$ iPr), 20.8 (s, *C*H$_3$ Ar), 28.0 (d, $^{1}J_{CP}$ = 51.0 Hz, *C*H iPr), 29.5 (d, $^{1}J_{CP}$ = 50.3 Hz, *C*H iPr), 122.5 (br s, *C*H Ar), 133.3 (s, *C*H Ar), 134.3 (br s, *C*H Ar); signals of other C atoms were not observed. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, $CDCl_3$, 293 K): 68.4 (br s), 72.0 (br s).

^{1}H NMR (400 MHz, C_6D_6, 293 K): 0.95–1.03 (m, 12H, C*H*$_3$ iPr), 1.11 (dd, *J* = 17.4, 6.6 Hz, 6H, C*H*$_3$ iPr), 1.30 (br d, *J* = 13.3 Hz, 6H, C*H*$_3$ iPr), 2.03 (s, 6H, C*H*$_3$ Ar) 2.58 (br m, 4H, C*H* iPr), 6.82 (br d, *J* = 7.9 Hz, 2H, C*H* Ar), 7.12 (br s, 2H, C*H* Ar), 7.77 (br s, 2H, C*H* Ar), 9.82 (s, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 293 K): 16.2 (br s, *C*H$_3$ iPr), 17.0 (br s, *C*H$_3$ iPr), 17.2 (br s, *C*H$_3$ iPr), 17.4 (br s, *C*H$_3$ iPr), 20.3 (s, *C*H$_3$ Ar), 27.9 (d, $^{1}J_{CP}$ = 51.0 Hz, *C*H iPr), 29.5 (d, $^{1}J_{CP}$ = 50.4 Hz, *C*H iPr), 133.3 (d, J_{CP} = 2.4 Hz, *C*H Ar); signals of other C atoms were not observed. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, C_6D_6, 293 K): 64.4 (br s), 70.0 (br s).

IR (KBr, Nujol), cm^{-1}: 3215 (s), 1605 (m), 1570 (s), 1505 (s), 1310 (m), 1295 (s), 1285 (m), 1260 (m), 1250 (s), 1210 (w), 1150 (s), 1095 (w), 1060 (s), 1040 (s), 1025 (m), 935 (w), 900 (w), 885 (s), 820 (s), 810 (s), 705 (s), 690 (s), 670 (s), 660 (s), 610 (s), 585 (s), 570 (s), 540 (m), 520 (m), 485 (s).

Synthesis of [{2-Pr$^{i}_2$PO-4-MeC$_6$H$_3$}$_2$N]Sc(CH$_2$SiMe$_3$)$_2$ 4. To a stirred solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.325 g, 0.72 mmol) in toluene (15 mL) was added in one portion diphenylamine **2** (0.320 g, 0.69 mmol). The solution turned bright yellow after a few minutes. The reaction mixture was stirred at ambient temperature for 30 min and then the solvent was then removed in vacuum. The oil residue was washed with small amount of hexane and dried in a vacuum for 10 minutes. To the resulted yellow microcristalline powder was added toluene-hexane

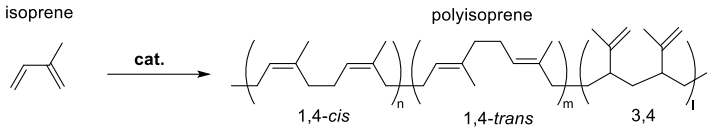
mixture (1:1, approx. 3 mL). The resulting suspension was periodically heated to 40 °C and cooled to room temperature during several days. The bright yellow X-Ray suitable crystals of **4** were obtained. The mother liquid was decanted and the crystal were dried in vacuum for 20 min. Complex **4** was isolated in 68% yield (0.330 g, 0.49 mmol). Elemental analysis calculated for $C_{34}H_{62}NO_2P_2ScSi_2$ (679.95 g/mol): C, 60.06; H, 9.19; N, 2.06; Sc, 6.61. Found: C, 60.20; H, 9.43; N, 1.94; Sc, 6.51.

^{1}H NMR (400 MHz, C_6D_6, 293 K): −0.19 (d, $^2J_{HH}$ = 11.2, Hz, 2H, ScC*H*$_2$), 0.17 (d, $^2J_{HH}$ = 11.2 Hz, 2H, ScC*H*$_2$), 0.45 (s, 18H, Si*Me*$_3$), 0.74 (dd, *J* = 17.1, 7.2 Hz, 6H, C*H*$_3$ iPr), 1.11 (m, 12H, C*H*$_3$ iPr), 1.23 (dd, *J* = 15.6, 7.1 Hz, 6H, C*H*$_3$ iPr), 1.92 (sept d, *J* = 7.0, 1.8 Hz, 2H, C*H* iPr), 2.04 (s, 6H, C*H*$_3$ Ar), 2.12 (m, 2H, C*H* iPr), 6.61 (dd, *J* = 12.4, 1.4 Hz, 2H, C*H* Ar), 6.87 (d, *J* = 8.8 Hz, 2H, C*H* Ar), 6.97 (dd, *J* = 8.5, 5.0 Hz, 2H, C*H* Ar). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 4.4 (s, Si*Me*$_3$), 14.7 (d, $^2J_{CP}$ = 3.0 Hz, *C*H$_3$ iPr), 15.6 (d, $^2J_{CP}$ = 2.7 Hz, *C*H$_3$ iPr), 16.0 (s, *C*H$_3$ iPr), 16.4 (d, $^2J_{CP}$ = 3.9 Hz, *C*H$_3$ iPr), 20.5 (s, *C*H$_3$ Ar), 22.8 (d, $^1J_{CP}$ = 68.9 Hz, *C*H iPr), 26.9 (d, $^1J_{CP}$ = 67.7 Hz, *C*H iPr), 35.1 (br s, Sc*C*H$_2$), 113.1 (d, $^1J_{CP}$ = 89.2 Hz, *C* Ar), 125.2 (d, J_{CP} = 12.2 Hz, *C* Ar,), 126.6 (d, J_{CP} = 8.9 Hz, *C*H Ar), 131.0 (d, J_{CP} = 11.4 Hz, *C*H Ar), 134.7 (d, J_{CP} = 2.2 Hz, *C*H Ar), 162.2 (d, J_{CP} = 2.6 Hz, *C* Ar). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): 63.4 (s).

Synthesis of [2-Pr$^i_2$PO-4-Me-C$_6$H$_3$)$_2$N]Y(CH$_2$SiMe$_3$)$_2$ 5. Complex **5** was synthesized and isolated similarly as it is described for **4**, starting from Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.380 g, 0.77 mmol) and diphenylamine **2** (0.340 g, 0.74 mmol). Complex **5** was isolated in 79% yield (0.425 g, 0.59 mmol). Elemental analysis calculated for $C_{34}H_{62}NO_2P_2Si_2Y$ (723.90 g/mol): C, 56.41; H, 8.63; N, 1.93; Y, 12.28. Found: C, 56.70; H, 8.71; N, 1.99; Y, 12.09.

^{1}H NMR (400 MHz, C_6D_6, 293 K): −0.40 (dd, $^2J_{HH}$ = 11.2, $^2J_{YH}$ = 3.1 Hz, 2H, YC*H*$_2$), −0.28 (dd, $^2J_{HH}$ = 11.2, $^2J_{YH}$ = 3.1, Hz, 2H, YC*H*$_2$), 0.45 (s, 18H, Si*Me*$_3$), 0.75 (dd, *J* = 16.9, 7.2 Hz, 6H, C*H*$_3$ iPr), 1.03 (m, 12H, C*H*$_3$ iPr), 1.18 (dd, *J* = 15.5, 7.1 Hz, 6H, C*H*$_3$ iPr), 1.87 (sept d, *J* = 7.1, 2.3 Hz, 2H, C*H* iPr), 2.04 (s, 6H, C*H*$_3$ Ar), 2.10 (m, 2H, C*H* iPr), 6.61 (br d, *J* = 12.6 Hz, 2H, C*H* Ar), 6.89 (d, *J* = 8.9 Hz, 2H, C*H* Ar), 6.95 (dd, *J* = 8.6, 5.0 Hz, 2H, C*H* Ar). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 4.6 (s, Si*Me*$_3$), 14.8 (d, $^2J_{CP}$ = 3.0 Hz, *C*H$_3$ iPr), 15.5 (d, $^2J_{CP}$ = 2.0 Hz, *C*H$_3$ iPr), 16.0 (s, *C*H$_3$ iPr), 16.3 (d, $^2J_{CP}$ = 3.8 Hz, *C*H$_3$ iPr), 20.5 (s, *C*H$_3$ Ar), 22.9 (d, $^1J_{CP}$ = 68.5 Hz, *C*H iPr), 27.0 (d, $^1J_{CP}$ = 67.5 Hz, *C*H iPr), 30.0 (d, $^1J_{YC}$ = 40.1 Hz, Y*C*H$_2$), 113.5 (d, $^1J_{CP}$ = 89.4 Hz, *C* Ar), 125.4 (d, J_{CP} = 12.5 Hz, *C* Ar,), 127.1 (d, J_{CP} = 9.1 Hz, *C*H Ar), 131.4 (d, J_{CP} = 11.7 Hz, *C*H Ar), 134.9 (s, *C*H Ar), 162.4 (s, *C* Ar). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): 63.2 (d, $^2J_{YP}$ = 3.5 Hz).

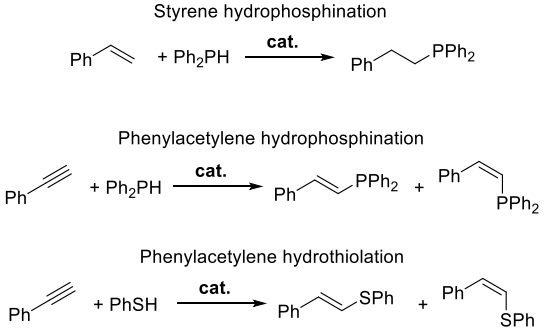
General procedure for isoprene polymerization.



Under a nitrogen atmosphere and room temperature, a toluene solution (2 mL) of $[HNMe_2Ph][B(C_6F_5)_4]$ (8.0 mg, 10 μmol) or $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added to a toluene solution (3 mL) of complexes **5** (10 μmol) in a 25 mL flask. Then 10 equiv. of $AlBu^i_3$ (0.1 mL, 100 μmol, 1.0 M in toluene) were added under stirring after a few minutes. Upon the addition of 1000 equiv of isoprene (1 mL, 0.01 mol), polymerization was initiated and carried out until a viscous solution is formed. The reaction mixture was poured into methanol and then dried under vacuum at ambient temperature to a constant weight. Then, 1,4- and 3,4-regioselectivity was determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. GPC of polyisoprenes was performed in THF at 20 °C. The number average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the polymers were calculated with reference to a universal calibration against polystyrene standards.

Typical procedure of *rac*-LA polymerization. In a glovebox, a Schlenk flask was charged with a solution of initiator **5** (10μmol) in toluene or THF (1 mL). To this solution, *rac*-LA (1 mmol, 100 equiv.) in toluene (1 mL) or THF (1 mL) respectively was added rapidly. The mixture was immediately stirred with a magnetic stir bar at 20 °C. After the reaction was quenched with acidic methanol (ca. 1 mL of 1.2 M HCl solution in MeOH), and the polymer was precipitated with excess methanol (ca. 50 mL). The polymer was then filtered and dried under vacuum to constant weight.

General procedure for hydrophosphination and hydrothiolation reactions.



In typical hydrophosphination, hydroamination or hydrothiolation experiments, a precatalyst **5** (10 μmol) was loaded in a tube in a glovebox, then alkene or acetylene (0.5 mmol; 50 equiv.) EH substrate (0.5 mmol, 50 equiv.) was added at ambient temperature. The reaction mixture was heated at 70 °C for a definite time in a preheated oil bath. After the desired reaction time, $CDCl_3$ was added to the reaction mixture, and the ^1H and $^{31}P\{^1H\}$ (for hydrophosphination) or $^{13}C\{^1H\}$ (for hydroamination and hydrothiolation) NMR spectra were recorded. Conversion was determined by integrating the remaining substrates and the newly formed addition product in the ^1H spectra. In case of hydrophosphination the conversion was determined also according to $^{31}P\{^1H\}$ NMR spectra.

X-Ray crystallography. Single crystals of **2**, **2·0.5(C$_7$H$_8$)**, **4** and **5** were obtained by recrystallization from CH_2Cl_2, toluene, or toluene-hexane solutions. The intensities of reflections were measured Bruker Apex II CCD diffractometer by standard procedure (graphite monochromated MoKα radiation, ω-scanning) at 120.0(2) K. The structures were solved with a dual-space method with SHELXT[S5] program and refined by the full-matrix least-squares technique against F^2(hkl) in anisotropic approximation for non-hydrogen atoms with SHELXL [S6] and Olex2 [S7] software package. The CH_2SiMe_3 group and the Pr^i_2PO fragments in **5** are equally disordered over two sites and were refined RIGU, EADP and ISOR instructions. The positions of H(C) atoms were calculated and those of H(N) and H(O) atoms were taken from Fourier maps. All H atoms were refined in riding model with $U_{iso}(H) = 1.5U_{eq}(C_i)$ for methyl groups, and $1.2U_{eq}(C_i)$ for other atoms. Contribution of highly disordered toluene molecules to intensities of reflections was taken into account using solvent mask procedure in Olex2.[S7] Detailed crystallographic information is given in Tables S1–S4. Geometry parameters are listed in Tables S5–S16.

References.

S1 H. Schumann and J. Müller, *J. Organomet. Chem.*, 1979, **169**, C1; https://doi.org/10.1016/S0022-328X(00)81463-1.

S2 L. Fan, B. M. Foxman and O. V. Ozerov, *Organometallics*, 2004, **23**, 326; https://doi.org/10.1021/om034151x.

S3 J. J. Davidson, J. C. DeMott, C. Douvris, C. M. Fafard, N. Bhuvanesh, C.-H. Chen, D. E. Herbert, C.-I. Lee, B. J. McCulloch, B. M. Foxman and O. V. Ozerov, *Inorg. Chem.*, 2015, **54**, 2916; https://doi.org/10.1021/ic503062w.

S4 S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177; https://doi.org/10.1016/0039-9140(63)80170-8.

S5 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3; https://doi.org/10.1107/S2053273314026370.

S6 G. M. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem.*, 2015, **71**, 3; https://doi.org/10.1107/S2053229614024218.

S7 O. V Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; https://doi.org/10.1107/S0021889808042726.

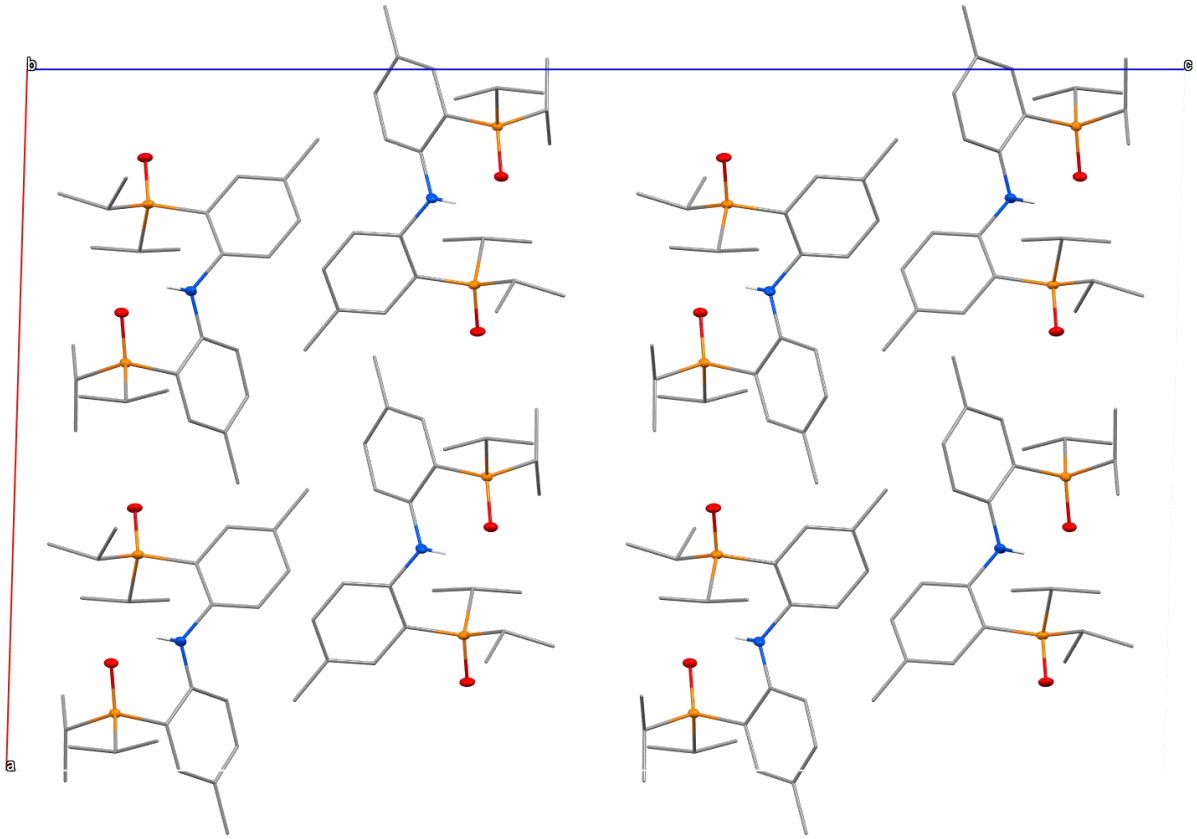


Figure S1. View of the unit cell for **2** along the crystallographic axis *b*. Color code: orange P; blue N; red O; grey C. Hydrogen atoms (except NH) have been omitted for clarity.

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**
Empirical formula	$C_{26}H_{41}NO_2P_2$
Formula weight	461.54
Temperature/K	120
Crystal system	monoclinic
Space group	C2/c
a/Å	20.1753(10)
b/Å	7.8516(4)
c/Å	33.3005(16)
α/°	90
β/°	91.706(2)
γ/°	90
Volume/Å^3	5272.7(5)
Z	8
ρ_{calc}g/cm^3	1.163
μ/mm^{-1}	0.186
F(000)	2000.0
Crystal size/mm^3	0.21 × 0.06 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.04 to 61.02
Index ranges	$-28 \leq h \leq 28$, $-11 \leq k \leq 10$, $-47 \leq l \leq 47$
Reflections collected	32458
Independent reflections	8047 [R_{int} = 0.0462, R_{sigma} = 0.0561]
Data/restraints/parameters	8047/0/293
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1074
Final R indexes [all data]	R_1 = 0.0717, wR_2 = 0.1167
Largest diff. peak/hole / e Å^{-3}	0.33/-0.36

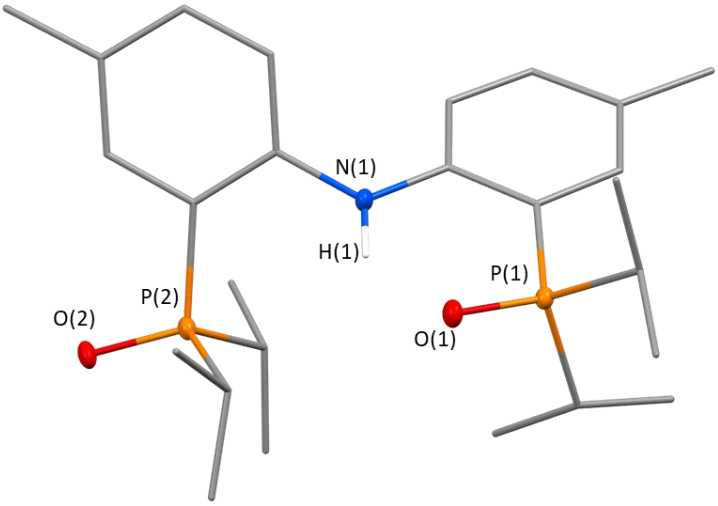


Figure S2. Molecular structure of **2**·0.5(C_7H_8). Thermal ellipsoids are given with 30% probability; H atoms (except NH) are omitted for clarity.

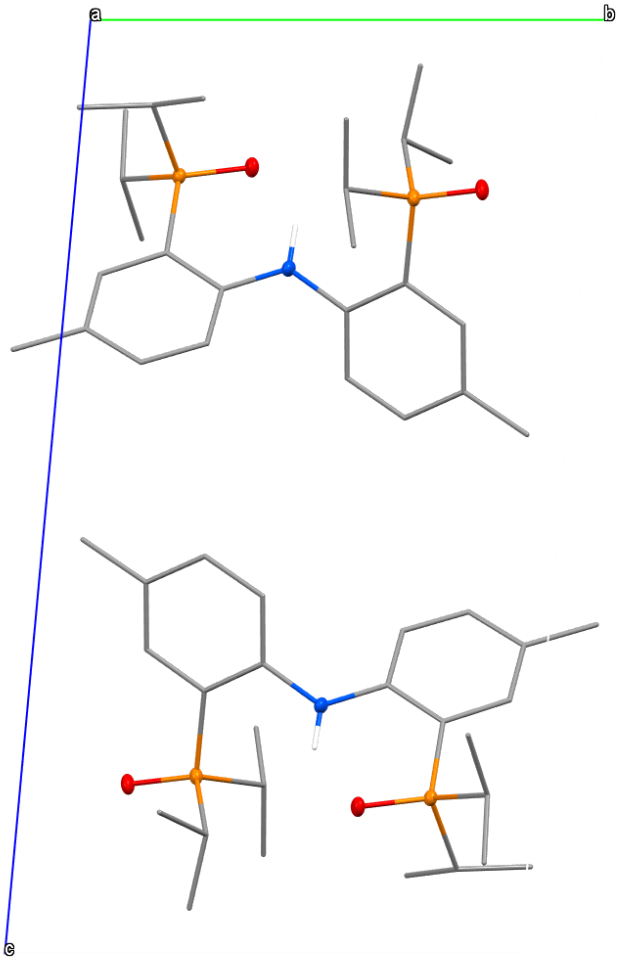


Figure S3. View of the unit cell for **2**·0.5(C_7H_8) along the crystallographic axis *a*. Color code: orange P; blue N; red O; grey C. Hydrogen atoms (except NH) and solvated toluene molecule have been omitted for clarity.

Table S2. Crystal data and structure refinement for **2**·0.5**(C_7H_8)**.

Identification code	**2**·0.5**(C_7H_8)**
Empirical formula	$C_{26}H_{41}NO_2P_2$
Formula weight	461.54
Temperature/K	140
Crystal system	triclinic
Space group	P-1
a/Å	7.7730(2)
b/Å	10.7426(3)
c/Å	18.6197(6)
α/°	92.287(1)
β/°	97.739(1)
γ/°	109.671(1)
Volume/Å^3	1444.65(7)
Z	2
ρ_{calc}g/cm^3	1.061
μ/mm^{-1}	0.170
F(000)	500.0
Crystal size/mm^3	0.26 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.044 to 61.162
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	19548
Independent reflections	8724 [R_{int} = 0.0361, R_{sigma} = 0.0694]
Data/restraints/parameters	8724/0/290
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1250
Final R indexes [all data]	R_1 = 0.0745, wR_2 = 0.1327
Largest diff. peak/hole / e Å^{-3}	0.37/-0.46

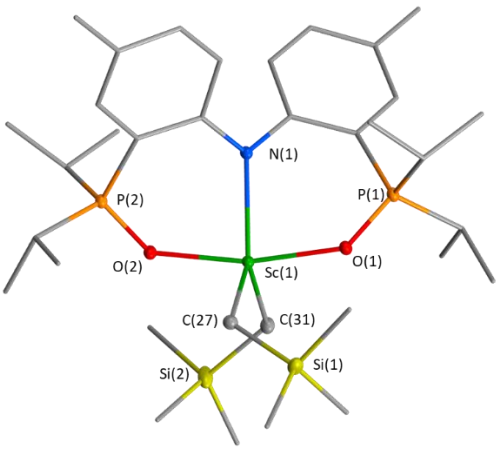


Figure S4. Molecular structure of **4**. Thermal ellipsoids are given with 30% probability; H atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **4**.

Identification code	**4**
Empirical formula	$C_{34}H_{62}NO_2P_2ScSi_2$
Formula weight	679.92
Temperature/K	140.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9491(3)
b/Å	20.6401(6)
c/Å	18.3947(5)
α/°	90
β/°	105.717(1)
γ/°	90
Volume/Å^3	4001.60(19)
Z	4
ρ_{calc}g/cm^3	1.129
μ/mm^{-1}	0.351
F(000)	1472.0
Crystal size/mm^3	0.31 × 0.24 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.03 to 61.192
Index ranges	$-15 \le h \le 15$, $-23 \le k \le 29$, $-26 \le l \le 26$
Reflections collected	43466
Independent reflections	12227 [R_{int} = 0.0461, R_{sigma} = 0.0696]
Data/restraints/parameters	12227/18/395
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0899
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.0969
Largest diff. peak/hole / e Å^{-3}	0.35/-0.38

Table S4. Crystal data and structure refinement for **5**.

Identification code	**5**
Empirical formula	$C_{34}H_{62}NO_2P_2Si_2Y$
Formula weight	723.87
Temperature/K	120
Crystal system	monoclinic
Space group	C2/c
a/Å	10.9803(4)
b/Å	21.0395(8)
c/Å	18.3303(7)
α/°	90
β/°	105.496(2)
γ/°	90
Volume/Å^3	4080.7(3)
Z	4
ρ_{calc}g/cm^3	1.178
μ/mm^{-1}	1.593
F(000)	1544.0
Crystal size/mm^3	0.21 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.872 to 61.192
Index ranges	$-15 \leq h \leq 15$, $-30 \leq k \leq 30$, $-26 \leq l \leq 26$
Reflections collected	27417
Independent reflections	6249 [R_{int} = 0.0807, R_{sigma} = 0.0989]
Data/restraints/parameters	6249/48/317
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0516, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.1163, wR_2 = 0.1190
Largest diff. peak/hole / e Å^{-3}	0.53/-1.29

Table S5. Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.5021(10)	C5	C7	1.513(2)
P1	C1	1.8072(14)	C8	C9	1.4068(19)
P1	C16	1.8223(15)	C8	C13	1.400(2)
P1	C19	1.8153(15)	C9	C10	1.391(2)
P2	O2	1.4966(11)	C10	C11	1.389(2)
P2	C8	1.8190(15)	C11	C12	1.384(2)
P2	C22	1.8263(15)	C12	C13	1.392(2)
P2	C25	1.8284(17)	C12	C14	1.512(2)
N1	C2	1.3965(18)	C15	C16	1.536(2)
N1	C9	1.4218(19)	C16	C17	1.535(2)
C1	C2	1.4180(19)	C18	C19	1.536(2)
C1	C6	1.4068(18)	C19	C20	1.525(2)
C2	C3	1.400(2)	C21	C22	1.533(2)
C3	C4	1.384(2)	C22	C23	1.524(2)
C4	C5	1.397(2)	C24	C25	1.531(3)
C5	C6	1.385(2)	C25	C26	1.529(2)

Table S6. Bond Angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	C1	111.92(6)	C9	C8	P2	124.87(11)
O1	P1	C16	109.99(6)	C13	C8	P2	116.12(11)
O1	P1	C19	112.51(7)	C13	C8	C9	118.94(14)
C1	P1	C16	106.30(7)	C8	C9	N1	119.67(13)
C1	P1	C19	108.39(7)	C10	C9	N1	121.59(13)
C19	P1	C16	107.45(7)	C10	C9	C8	118.74(14)
O2	P2	C8	109.98(7)	C11	C10	C9	121.09(15)
O2	P2	C22	111.28(7)	C12	C11	C10	121.18(15)
O2	P2	C25	111.06(7)	C11	C12	C13	117.82(14)
C8	P2	C22	105.51(7)	C11	C12	C14	121.33(16)
C8	P2	C25	107.01(7)	C13	C12	C14	120.85(16)
C22	P2	C25	111.75(7)	C12	C13	C8	122.22(14)
C2	N1	C9	123.22(13)	C15	C16	P1	108.55(10)
C2	C1	P1	121.96(10)	C17	C16	P1	115.38(10)
C6	C1	P1	118.49(10)	C17	C16	C15	111.42(13)
C6	C1	C2	119.33(13)	C18	C19	P1	109.41(10)
N1	C2	C1	121.22(13)	C20	C19	P1	110.43(11)
N1	C2	C3	120.87(13)	C20	C19	C18	110.86(14)
C3	C2	C1	117.78(13)	C21	C22	P2	111.90(10)
C4	C3	C2	121.18(14)	C23	C22	P2	108.28(10)
C3	C4	C5	121.91(14)	C23	C22	C21	110.79(13)
C4	C5	C7	121.35(14)	C24	C25	P2	108.96(12)
C6	C5	C4	117.14(13)	C26	C25	P2	111.41(13)
C6	C5	C7	121.49(14)	C26	C25	C24	109.78(15)
C5	C6	C1	122.49(13)				

Table S7. Torsion Angles for **2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	C1	C2	N1	5.9(2)	C6	C1	C2	C3	4.5(2)
P1	C1	C2	C3	-170.04(11)	C7	C5	C6	C1	-179.71(15)
P1	C1	C6	C5	171.90(12)	C8	P2	C22	C21	-177.82(11)
P2	C8	C9	N1	-4.2(2)	C8	P2	C22	C23	-55.43(12)
P2	C8	C9	C10	176.72(13)	C8	P2	C25	C24	48.86(13)
P2	C8	C13	C12	-175.73(13)	C8	P2	C25	C26	170.13(13)
O1	P1	C1	C2	-16.32(14)	C8	C9	C10	C11	-0.9(3)
O1	P1	C1	C6	169.12(11)	C9	N1	C2	C1	159.26(14)
O1	P1	C16	C15	54.29(11)	C9	N1	C2	C3	-24.9(2)
O1	P1	C16	C17	-179.87(11)	C9	C8	C13	C12	1.5(2)
O1	P1	C19	C18	61.90(12)	C9	C10	C11	C12	0.8(3)
O1	P1	C19	C20	-60.38(13)	C10	C11	C12	C13	0.4(3)
O2	P2	C8	C9	-176.82(13)	C10	C11	C12	C14	179.81(18)
O2	P2	C8	C13	0.17(14)	C11	C12	C13	C8	-1.6(2)
O2	P2	C22	C21	-58.56(13)	C13	C8	C9	N1	178.84(14)
O2	P2	C22	C23	63.83(12)	C13	C8	C9	C10	-0.2(2)
O2	P2	C25	C24	-71.19(13)	C14	C12	C13	C8	179.06(16)
O2	P2	C25	C26	50.08(15)	C16	P1	C1	C2	103.78(12)
N1	C2	C3	C4	-178.60(14)	C16	P1	C1	C6	-70.78(12)
N1	C9	C10	C11	-179.91(16)	C16	P1	C19	C18	-59.30(12)
C1	P1	C16	C15	-67.06(11)	C16	P1	C19	C20	178.42(11)
C1	P1	C16	C17	58.78(13)	C19	P1	C1	C2	-140.98(12)
C1	P1	C19	C18	-173.79(10)	C19	P1	C1	C6	44.47(13)
C1	P1	C19	C20	63.93(13)	C19	P1	C16	C15	177.06(10)
C1	C2	C3	C4	-2.6(2)	C19	P1	C16	C17	-57.10(13)
C2	N1	C9	C8	137.63(15)	C22	P2	C8	C9	-56.71(15)
C2	N1	C9	C10	-43.4(2)	C22	P2	C8	C13	120.28(12)
C2	C1	C6	C5	-2.8(2)	C22	P2	C25	C24	163.90(12)
C2	C3	C4	C5	-1.1(3)	C22	P2	C25	C26	-74.84(14)
C3	C4	C5	C6	2.8(2)	C25	P2	C8	C9	62.44(15)
C3	C4	C5	C7	-178.33(16)	C25	P2	C8	C13	-120.56(12)
C4	C5	C6	C1	-0.9(2)	C25	P2	C22	C21	66.23(13)
C6	C1	C2	N1	-179.59(13)	C25	P2	C22	C23	-171.38(11)

Table S8. Bond Lengths for **2·0.5(C_7H_8)**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	O2	1.4970(12)	C1	C2	1.399(2)
P2	C15	1.8071(16)	C1	C6	1.394(2)
P2	C22	1.8269(16)	C2	C3	1.402(2)
P2	C25	1.8117(16)	C22	C21	1.527(2)
P1	O1	1.4949(12)	C22	C23	1.528(2)
P1	C2	1.8147(16)	C3	C4	1.382(2)
P1	C12	1.8181(16)	C19	C18	1.376(2)
P1	C9	1.8245(17)	C12	C13	1.525(2)
N1	C14	1.391(2)	C12	C11	1.528(2)
N1	C1	1.4213(19)	C4	C5	1.388(3)
C15	C14	1.419(2)	C4	C7	1.509(2)
C15	C16	1.400(2)	C25	C26	1.529(2)
C14	C19	1.397(2)	C25	C24	1.534(2)
C16	C17	1.384(2)	C9	C10	1.539(3)
C17	C18	1.400(2)	C9	C8	1.516(3)
C17	C20	1.511(2)	C5	C6	1.387(2)

Table S9. Bond Angles for **2·0.5(C_7H_8)**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	P2	C15	111.96(7)	C6	C1	C2	119.16(15)
O2	P2	C22	109.88(7)	C1	C2	P1	125.67(12)
O2	P2	C25	112.16(7)	C1	C2	C3	118.71(15)
C15	P2	C22	106.80(7)	C3	C2	P1	115.61(12)
C15	P2	C25	108.05(7)	C21	C22	P2	108.52(10)
C25	P2	C22	107.75(7)	C21	C22	C23	111.99(14)
O1	P1	C2	109.65(7)	C23	C22	P2	115.29(11)
O1	P1	C12	111.33(7)	C4	C3	C2	122.36(16)
O1	P1	C9	110.86(8)	C18	C19	C14	121.55(15)
C2	P1	C12	105.84(8)	C13	C12	P1	112.67(12)
C2	P1	C9	106.69(8)	C13	C12	C11	110.34(14)
C12	P1	C9	112.22(8)	C11	C12	P1	108.13(11)
C14	N1	C1	124.56(13)	C19	C18	C17	121.67(15)
C14	C15	P2	121.90(12)	C3	C4	C5	118.01(15)
C16	C15	P2	118.78(11)	C3	C4	C7	120.48(17)
C16	C15	C14	119.22(14)	C5	C4	C7	121.51(16)
N1	C14	C15	120.72(14)	C26	C25	P2	109.89(11)
N1	C14	C19	121.44(14)	C26	C25	C24	111.25(14)
C19	C14	C15	117.72(14)	C24	C25	P2	109.17(12)
C17	C16	C15	122.67(14)	C10	C9	P1	111.05(13)
C16	C17	C18	117.09(15)	C8	C9	P1	108.88(13)
C16	C17	C20	121.27(15)	C8	C9	C10	109.94(16)
C18	C17	C20	121.61(15)	C6	C5	C4	121.02(16)
C2	C1	N1	119.63(14)	C5	C6	C1	120.74(17)
C6	C1	N1	121.19(15)				

Table S10. Torsion Angles for **2·0.5(C_7H_8)**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P2	C15	C14	N1	2.6(2)	C16	C17	C18	C19	1.7(2)
P2	C15	C14	C19	-173.32(12)	C1	N1	C14	C15	161.71(15)
P2	C15	C16	C17	174.44(12)	C1	N1	C14	C19	-22.5(2)
P1	C2	C3	C4	-177.20(13)	C1	C2	C3	C4	1.6(3)
O2	P2	C15	C14	-14.24(15)	C2	P1	C12	C13	-178.94(12)
O2	P2	C15	C16	169.40(12)	C2	P1	C12	C11	-56.72(13)
O2	P2	C22	C21	53.88(12)	C2	P1	C9	C10	171.44(13)
O2	P2	C22	C23	-179.60(11)	C2	P1	C9	C8	50.25(15)
O2	P2	C25	C26	-59.50(14)	C2	C1	C6	C5	0.4(3)
O2	P2	C25	C24	62.77(13)	C2	C3	C4	C5	-0.8(3)
O1	P1	C2	C1	-175.54(14)	C2	C3	C4	C7	179.31(17)
O1	P1	C2	C3	3.11(15)	C22	P2	C15	C14	106.08(13)
O1	P1	C12	C13	-59.86(14)	C22	P2	C15	C16	-70.29(14)
O1	P1	C12	C11	62.36(14)	C22	P2	C25	C26	179.44(12)
O1	P1	C9	C10	52.11(15)	C22	P2	C25	C24	-58.30(13)
O1	P1	C9	C8	-69.08(15)	C3	C4	C5	C6	-0.2(3)
N1	C14	C19	C18	-177.69(15)	C12	P1	C2	C1	-55.35(16)
N1	C1	C2	P1	-4.4(2)	C12	P1	C2	C3	123.30(13)
N1	C1	C2	C3	177.03(15)	C12	P1	C9	C10	-73.07(15)
N1	C1	C6	C5	-177.96(16)	C12	P1	C9	C8	165.74(13)
C15	P2	C22	C21	-67.76(12)	C4	C5	C6	C1	0.4(3)
C15	P2	C22	C23	58.75(14)	C25	P2	C15	C14	-138.24(13)
C15	P2	C25	C26	64.38(14)	C25	P2	C15	C16	45.39(14)
C15	P2	C25	C24	-173.35(11)	C25	P2	C22	C21	176.36(11)
C15	C14	C19	C18	-1.8(2)	C25	P2	C22	C23	-57.12(14)
C15	C16	C17	C18	-0.4(2)	C9	P1	C2	C1	64.34(16)
C15	C16	C17	C20	-178.61(16)	C9	P1	C2	C3	-117.00(13)
C14	N1	C1	C2	138.75(17)	C9	P1	C12	C13	65.06(14)
C14	N1	C1	C6	-42.9(2)	C9	P1	C12	C11	-172.72(12)
C14	C15	C16	C17	-2.0(2)	C20	C17	C18	C19	179.96(17)
C14	C19	C18	C17	-0.6(3)	C6	C1	C2	P1	177.30(13)
C16	C15	C14	N1	178.99(14)	C6	C1	C2	C3	-1.3(2)
C16	C15	C14	C19	3.0(2)	C7	C4	C5	C6	179.68(18)

Table S11. Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sc1	O1	2.0845(10)	Si2	C33	1.865(2)
Sc1	N1	2.2552(13)	Si2	C34	1.8812(18)
Sc1	O2	2.0757(10)	C2	C3	1.4113(19)
Sc1	C27	2.2431(14)	C3	C4	1.375(2)
Sc1	C31	2.2502(15)	C4	C5	1.400(2)
P1	O1	1.5142(10)	C4	C7	1.5062(19)
P1	C2	1.7853(15)	C5	C6	1.376(2)
P1	C8	1.8230(15)	C8	C9	1.521(2)
P1	C11	1.8159(15)	C8	C10	1.532(2)
Si1	C27	1.8305(14)	C11	C12	1.533(2)
Si1	C28	1.8703(19)	C11	C13	1.535(2)
Si1	C29	1.8811(19)	C14	C15	1.4216(18)
Si1	C30	1.874(2)	C14	C19	1.414(2)
N1	C1	1.4032(17)	C15	C16	1.4139(19)
N1	C14	1.4006(17)	C16	C17	1.373(2)
C1	C2	1.4219(19)	C17	C18	1.395(2)
C1	C6	1.416(2)	C17	C20	1.510(2)
P2	O2	1.5148(10)	C18	C19	1.381(2)
P2	C15	1.7826(15)	C21	C22	1.533(2)
P2	C21	1.8156(14)	C21	C23	1.526(2)
P2	C24	1.8188(14)	C24	C25	1.533(2)
Si2	C31	1.8324(15)	C24	C26	1.533(2)
Si2	C32	1.874(2)			

Table S12. Bond Angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Sc1	N1	83.13(4)	C33	Si2	C32	109.10(12)
O1	Sc1	C27	94.41(5)	C33	Si2	C34	105.12(10)
O1	Sc1	C31	93.48(5)	P2	O2	Sc1	132.28(6)
O2	Sc1	O1	166.83(4)	C1	C2	P1	121.50(10)
O2	Sc1	N1	83.72(4)	C3	C2	P1	118.16(10)
O2	Sc1	C27	92.35(5)	C3	C2	C1	120.15(13)
O2	Sc1	C31	94.80(5)	C4	C3	C2	123.23(13)
C27	Sc1	N1	124.40(5)	C3	C4	C5	116.46(13)
C27	Sc1	C31	110.01(6)	C3	C4	C7	122.00(14)
C31	Sc1	N1	125.59(5)	C5	C4	C7	121.55(14)
O1	P1	C2	111.53(6)	C6	C5	C4	121.96(14)
O1	P1	C8	109.99(6)	C5	C6	C1	122.60(14)
O1	P1	C11	109.58(7)	C9	C8	P1	110.71(10)
C2	P1	C8	108.73(7)	C9	C8	C10	110.99(14)
C2	P1	C11	109.98(7)	C10	C8	P1	112.87(10)
C11	P1	C8	106.92(7)	C12	C11	P1	110.34(10)
C27	Si1	C28	111.10(8)	C12	C11	C13	111.08(14)
C27	Si1	C29	111.47(8)	C13	C11	P1	109.24(11)
C27	Si1	C30	114.19(8)	N1	C14	C15	123.31(13)
C28	Si1	C29	108.04(8)	N1	C14	C19	120.84(12)
C28	Si1	C30	105.31(11)	C19	C14	C15	115.75(13)
C30	Si1	C29	106.33(11)	C14	C15	P2	122.04(11)
P1	O1	Sc1	133.41(6)	C16	C15	P2	117.87(10)
C1	N1	Sc1	122.11(9)	C16	C15	C14	119.86(13)
C14	N1	Sc1	121.85(9)	C17	C16	C15	123.07(13)
C14	N1	C1	116.03(12)	C16	C17	C18	116.96(13)
N1	C1	C2	123.70(13)	C16	C17	C20	121.81(14)
N1	C1	C6	120.75(12)	C18	C17	C20	121.23(14)
C6	C1	C2	115.49(12)	C19	C18	C17	121.63(14)
O2	P2	C15	111.64(6)	C18	C19	C14	122.46(13)
O2	P2	C21	109.32(6)	C22	C21	P2	112.81(10)
O2	P2	C24	109.97(6)	C23	C21	P2	110.62(10)
C15	P2	C21	109.00(7)	C23	C21	C22	111.33(14)
C15	P2	C24	110.23(7)	C25	C24	P2	108.50(10)
C21	P2	C24	106.54(7)	C25	C24	C26	111.60(13)
C31	Si2	C32	109.95(10)	C26	C24	P2	111.49(10)
C31	Si2	C33	111.29(9)	Si1	C27	Sc1	122.11(7)
C31	Si2	C34	114.88(8)	Si2	C31	Sc1	122.71(7)
C32	Si2	C34	106.20(10)				

Table S13. Torsion Angles for **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Sc1	N1	C1	C2	-38.32(17)	C8	P1	C2	C1	-88.08(13)
Sc1	N1	C1	C6	138.67(11)	C8	P1	C2	C3	86.96(12)
Sc1	N1	C14	C15	-35.65(17)	C8	P1	C11	C12	-175.72(11)
Sc1	N1	C14	C19	140.54(11)	C8	P1	C11	C13	61.89(13)
P1	C2	C3	C4	-173.79(12)	C11	P1	O1	Sc1	-124.82(9)
O1	P1	C2	C1	33.38(14)	C11	P1	C2	C1	155.16(12)
O1	P1	C2	C3	-151.59(11)	C11	P1	C2	C3	-29.80(13)
O1	P1	C8	C9	-67.00(12)	C11	P1	C8	C9	174.09(11)
O1	P1	C8	C10	167.90(11)	C11	P1	C8	C10	48.99(14)
O1	P1	C11	C12	65.11(13)	C14	N1	C1	C2	140.68(14)
O1	P1	C11	C13	-57.28(12)	C14	N1	C1	C6	-42.34(18)
N1	C1	C2	P1	-11.36(19)	C14	C15	C16	C17	1.2(2)
N1	C1	C2	C3	173.70(13)	C15	P2	O2	Sc1	0.12(10)
N1	C1	C6	C5	-173.99(13)	C15	P2	C21	C22	-68.26(13)
N1	C14	C15	P2	-14.30(19)	C15	P2	C21	C23	57.19(13)
N1	C14	C15	C16	171.39(13)	C15	P2	C24	C25	179.58(10)
N1	C14	C19	C18	-171.50(13)	C15	P2	C24	C26	-57.12(13)
C1	N1	C14	C15	145.35(13)	C15	C14	C19	C18	5.0(2)
C1	N1	C14	C19	-38.46(18)	C15	C16	C17	C18	2.8(2)
C1	C2	C3	C4	1.3(2)	C15	C16	C17	C20	-177.39(14)
P2	C15	C16	C17	-173.32(12)	C16	C17	C18	C19	-2.9(2)
O2	P2	C15	C14	33.90(14)	C17	C18	C19	C14	-1.0(2)
O2	P2	C15	C16	-151.68(11)	C19	C14	C15	P2	169.33(10)
O2	P2	C21	C22	169.47(11)	C19	C14	C15	C16	-5.0(2)
O2	P2	C21	C23	-65.08(13)	C20	C17	C18	C19	177.28(15)
O2	P2	C24	C25	-56.91(11)	C21	P2	O2	Sc1	120.79(8)
O2	P2	C24	C26	66.39(12)	C21	P2	C15	C14	-86.96(13)
C2	P1	O1	Sc1	-2.81(11)	C21	P2	C15	C16	87.46(12)
C2	P1	C8	C9	55.39(13)	C21	P2	C24	C25	61.46(12)
C2	P1	C8	C10	-69.71(13)	C21	P2	C24	C26	-175.24(11)
C2	P1	C11	C12	-57.83(13)	C24	P2	O2	Sc1	-122.57(8)
C2	P1	C11	C13	179.78(11)	C24	P2	C15	C14	156.43(11)
C2	C1	C6	C5	3.2(2)	C24	P2	C15	C16	-29.15(13)
C2	C3	C4	C5	1.2(2)	C24	P2	C21	C22	50.67(13)
C2	C3	C4	C7	-179.25(13)	C24	P2	C21	C23	176.12(12)
C3	C4	C5	C6	-1.5(2)	C28	Si1	C27	Sc1	72.95(10)
C4	C5	C6	C1	-0.8(2)	C29	Si1	C27	Sc1	-47.60(12)
C6	C1	C2	P1	171.51(10)	C30	Si1	C27	Sc1	-168.13(12)
C6	C1	C2	C3	-3.4(2)	C32	Si2	C31	Sc1	77.41(12)
C7	C4	C5	C6	178.96(14)	C33	Si2	C31	Sc1	-43.59(13)
C8	P1	O1	Sc1	117.92(9)	C34	Si2	C31	Sc1	-162.89(10)

Table S14. Bond Lengths for **5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Y1	N1	2.395(2)	Si1B	C15B	1.874(7)
Y1	C14B[1]	2.516(6)	Si1B	C17B	1.882(7)
Y1	C14B	2.516(6)	Si1B	C16B	1.882(7)
Y1	C14A[1]	2.330(6)	Si1B	C14B	1.825(6)
Y1	C14A	2.330(6)	Si1A	C15A	1.883(6)
Y1	P1A[1]	3.267(3)	Si1A	C16A	1.875(7)
Y1	P1A	3.267(3)	Si1A	C17A	1.903(8)
Y1	O1A[1]	2.031(8)	Si1A	C14A	1.833(6)
Y1	O1A	2.031(8)	C8B	C9B	1.542(9)
Y1	O1B	2.382(8)	C8B	C10B	1.524(8)
Y1	O1B[1]	2.381(8)	C8B	P1B	1.826(7)
N1	C1	1.403(2)	C12A	C11A	1.544(8)
N1	C1[1]	1.403(2)	C11A	C13A	1.536(9)
C1	C2	1.420(3)	C11A	P1A	1.800(7)
C1	C6	1.403(3)	C9A	C8A	1.548(8)
C2	C3	1.416(3)	C11B	C12B	1.546(8)
C2	P1A	1.864(4)	C11B	C13B	1.523(10)
C2	P1B	1.732(4)	C11B	P1B	1.811(6)
C3	C4	1.366(3)	C8A	C10A	1.524(8)
C4	C5	1.388(3)	C8A	P1A	1.823(7)
C4	C7	1.508(3)	P1A	O1A	1.530(7)
C6	C5	1.378(3)	P1B	O1B	1.509(7)

[1]1-X,+Y,3/2-Z

Table S15. Bond Angles for **5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Y1	C14B	120.69(14)	C3	C4	C7	122.2(2)
N1	Y1	C14B^1	120.69(14)	C5	C4	C7	121.8(2)
N1	Y1	P1A	67.10(5)	C5	C6	C1	122.6(2)
N1	Y1	P1A^1	67.10(5)	C6	C5	C4	122.3(2)
C14A^1	Y1	N1	128.96(16)	C15B	Si1B	C17B	104.4(4)
C14A	Y1	N1	128.96(16)	C15B	Si1B	C16B	108.6(4)
C14A	Y1	C14B^1	108.65(18)	C16B	Si1B	C17B	107.4(3)
C14A^1	Y1	C14B^1	15.93(15)	C14B	Si1B	C15B	114.4(3)
C14A	Y1	C14A^1	102.1(3)	C14B	Si1B	C17B	111.2(3)
C14A^1	Y1	P1A^1	120.88(15)	C14B	Si1B	C16B	110.4(3)
C14A^1	Y1	P1A	88.63(15)	C15A	Si1A	C17A	107.3(3)
C14A	Y1	P1A	120.88(15)	C16A	Si1A	C15A	105.1(3)
C14A	Y1	P1A^1	88.63(15)	C16A	Si1A	C17A	109.2(4)
C14A	Y1	O1B^1	92.3(2)	C14A	Si1A	C15A	115.4(3)
C14A^1	Y1	O1B^1	104.1(3)	C14A	Si1A	C16A	111.0(3)
P1A	Y1	P1A^1	134.20(10)	C14A	Si1A	C17A	108.7(3)
O1A^1	Y1	N1	84.8(2)	Si1B	C14B	Y1	124.0(3)
O1A	Y1	N1	84.8(2)	Si1A	C14A	Y1	117.4(3)
O1A^1	Y1	C14B^1	88.7(3)	C9B	C8B	P1B	109.1(5)
O1A	Y1	C14B^1	96.6(3)	C10B	C8B	C9B	111.3(6)
O1A	Y1	C14A	102.6(3)	C10B	C8B	P1B	110.1(5)
O1A^1	Y1	C14A^1	102.6(3)	C12A	C11A	P1A	113.5(4)
O1A	Y1	C14A^1	84.0(3)	C13A	C11A	C12A	111.0(5)
O1A^1	Y1	C14A	84.0(3)	C13A	C11A	P1A	110.2(5)
O1A	Y1	P1A	20.2(2)	C12B	C11B	P1B	113.5(4)
O1A^1	Y1	P1A^1	20.1(2)	C13B	C11B	C12B	109.1(5)
O1A^1	Y1	P1A	150.2(2)	C13B	C11B	P1B	111.1(5)
O1A	Y1	P1A^1	150.2(2)	C9A	C8A	P1A	107.2(4)
O1A	Y1	O1A^1	169.6(4)	C10A	C8A	C9A	110.4(6)
O1A^1	Y1	O1B^1	8.9(4)	C10A	C8A	P1A	111.1(6)
O1A	Y1	O1B^1	161.26(18)	C2	P1A	Y1	87.34(14)
O1B^1	Y1	N1	76.98(18)	C11A	P1A	Y1	120.6(2)
O1B	Y1	N1	76.97(18)	C11A	P1A	C2	106.7(2)
O1B^1	Y1	C14B	104.2(3)	C11A	P1A	C8A	107.1(3)
O1B	Y1	C14B	89.1(3)	C8A	P1A	Y1	121.3(2)
O1B^1	Y1	O1B	154.0(4)	C8A	P1A	C2	110.7(3)
C1	N1	Y1	121.70(12)	O1A	P1A	Y1	27.2(4)
C1^1	N1	Y1	121.70(12)	O1A	P1A	C2	114.6(4)
C1	N1	C1^1	116.6(2)	O1A	P1A	C11A	108.9(4)
N1	C1	C2	123.80(19)	O1A	P1A	C8A	108.6(4)

Table S15. Bond Angles for **5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C6	120.40(19)	C2	P1B	C8B	109.4(3)
C6	C1	C2	115.68(19)	C2	P1B	C11B	111.9(2)
C1	C2	P1A	121.75(19)	C11B	P1B	C8B	107.6(3)
C1	C2	P1B	124.1(2)	O1B	P1B	C2	109.6(4)
C3	C2	C1	119.4(2)	O1B	P1B	C8B	108.5(4)
C3	C2	P1A	118.8(2)	O1B	P1B	C11B	109.8(4)
C3	C2	P1B	114.9(2)	P1A	O1A	Y1	132.6(6)
C4	C3	C2	123.9(2)	P1B	O1B	Y1	132.0(6)
C3	C4	C5	116.0(2)				

[1]1-X,+Y,3/2-Z

Table S16 Torsion Angles for **5**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Y1	N1	C1	C2	-36.4(2)	C16B	Si1B	C14B	Y1	-49.7(4)
Y1	N1	C1	C6	139.51(17)	C16A	Si1A	C14A	Y1	-45.5(4)
N1	C1	C2	C3	171.74(19)	C17A	Si1A	C14A	Y1	74.6(4)
N1	C1	C2	P1A	-6.6(3)	C8B	P1B	O1B	Y1	-120.5(6)
N1	C1	C2	P1B	-23.7(3)	C12A	C11A	P1A	Y1	-166.1(3)
N1	C1	C6	C5	-172.0(2)	C12A	C11A	P1A	C2	-69.1(5)
C1[1]	N1	C1	C2	143.6(2)	C12A	C11A	P1A	C8A	49.5(5)
C1[1]	N1	C1	C6	-40.48(17)	C12A	C11A	P1A	O1A	166.7(5)
C1	C2	C3	C4	1.6(4)	C9B	C8B	P1B	C2	-178.3(4)
C1	C2	P1A	Y1	28.5(2)	C9B	C8B	P1B	C11B	60.0(5)
C1	C2	P1A	C11A	-92.7(3)	C9B	C8B	P1B	O1B	-58.7(6)
C1	C2	P1A	C8A	151.1(3)	C11A	P1A	O1A	Y1	120.7(6)
C1	C2	P1A	O1A	27.9(5)	C9A	C8A	P1A	Y1	-81.8(5)
C1	C2	P1B	C8B	161.6(3)	C9A	C8A	P1A	C2	178.3(4)
C1	C2	P1B	C11B	-79.3(3)	C9A	C8A	P1A	C11A	62.4(5)
C1	C2	P1B	O1B	42.8(4)	C9A	C8A	P1A	O1A	-55.1(6)
C1	C6	C5	C4	-1.1(4)	C11B	P1B	O1B	Y1	122.2(6)
C2	C1	C6	C5	4.2(4)	C12B	C11B	P1B	C2	-69.7(5)
C2	C3	C4	C5	1.6(4)	C12B	C11B	P1B	C8B	50.5(5)
C2	C3	C4	C7	-178.7(2)	C12B	C11B	P1B	O1B	168.3(5)
C2	P1A	O1A	Y1	1.4(8)	C8A	P1A	O1A	Y1	-123.0(6)
C2	P1B	O1B	Y1	-1.1(7)	C10A	C8A	P1A	Y1	38.9(6)
C3	C2	P1A	Y1	-149.81(18)	C10A	C8A	P1A	C2	-61.0(6)
C3	C2	P1A	C11A	89.0(3)	C10A	C8A	P1A	C11A	-176.9(5)
C3	C2	P1A	C8A	-27.2(3)	C10A	C8A	P1A	O1A	65.6(7)
C3	C2	P1A	O1A	-150.4(4)	C13B	C11B	P1B	C2	53.8(5)
C3	C2	P1B	C8B	-33.2(3)	C13B	C11B	P1B	C8B	174.0(5)
C3	C2	P1B	C11B	85.9(3)	C13B	C11B	P1B	O1B	-68.2(6)
C3	C2	P1B	O1B	-152.0(4)	C10B	C8B	P1B	C2	-55.8(5)
C3	C4	C5	C6	-1.9(4)	C10B	C8B	P1B	C11B	-177.6(5)
C6	C1	C2	C3	-4.3(3)	C10B	C8B	P1B	O1B	63.7(7)
C6	C1	C2	P1A	177.35(19)	C13A	C11A	P1A	Y1	-40.9(5)
C6	C1	C2	P1B	160.2(2)	C13A	C11A	P1A	C2	56.0(5)
C7	C4	C5	C6	178.5(3)	C13A	C11A	P1A	C8A	174.6(5)
C15A	Si1A	C14A	Y1	-164.9(3)	C13A	C11A	P1A	O1A	-68.1(6)
C15B	Si1B	C14B	Y1	-172.5(4)	P1A	C2	C3	C4	179.9(2)
C17B	Si1B	C14B	Y1	69.5(4)	P1B	C2	C3	C4	-164.4(2)

[1]1-X,+Y,3/2-Z

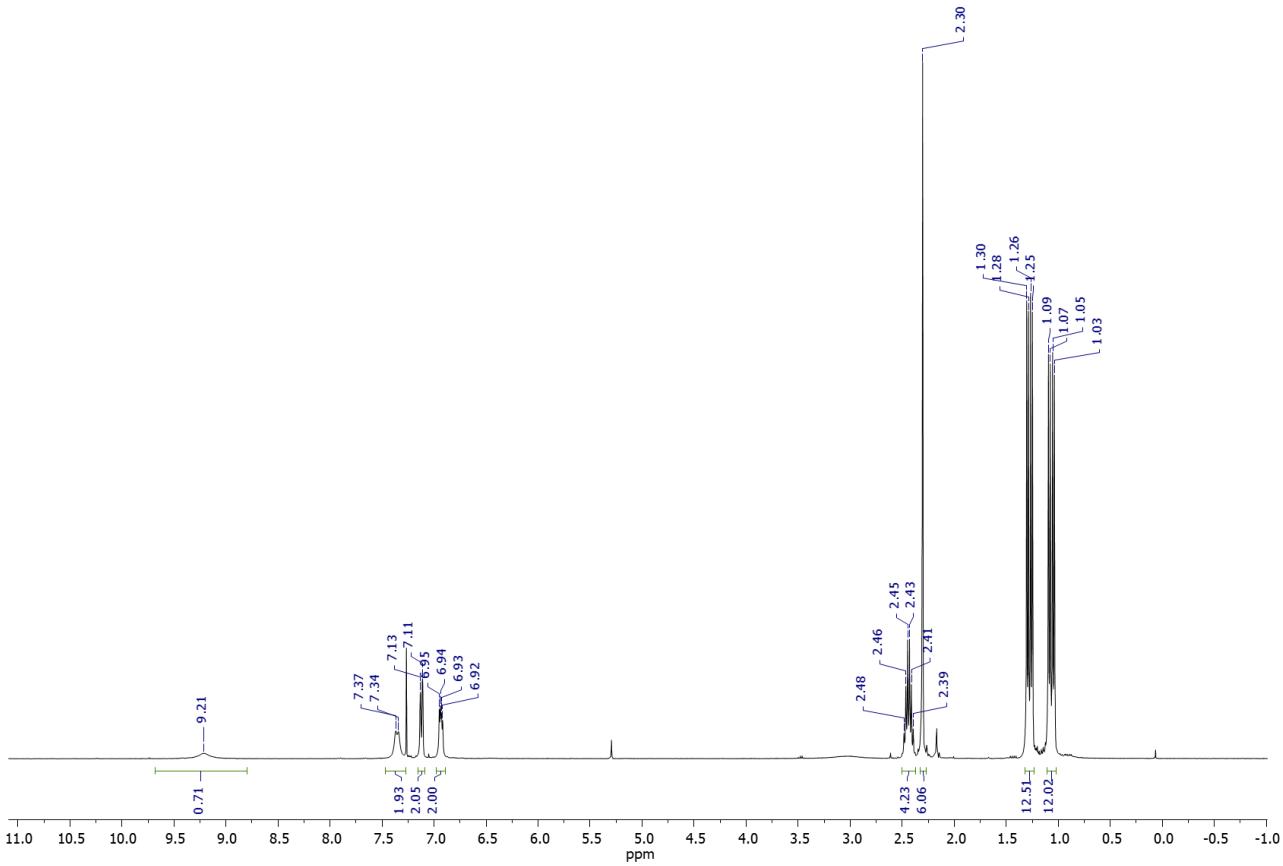


Figure S5. ^{1}H NMR spectrum of [2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$]$_2$NH (**2**) (400 MHz, CDCl$_3$, 293 K).

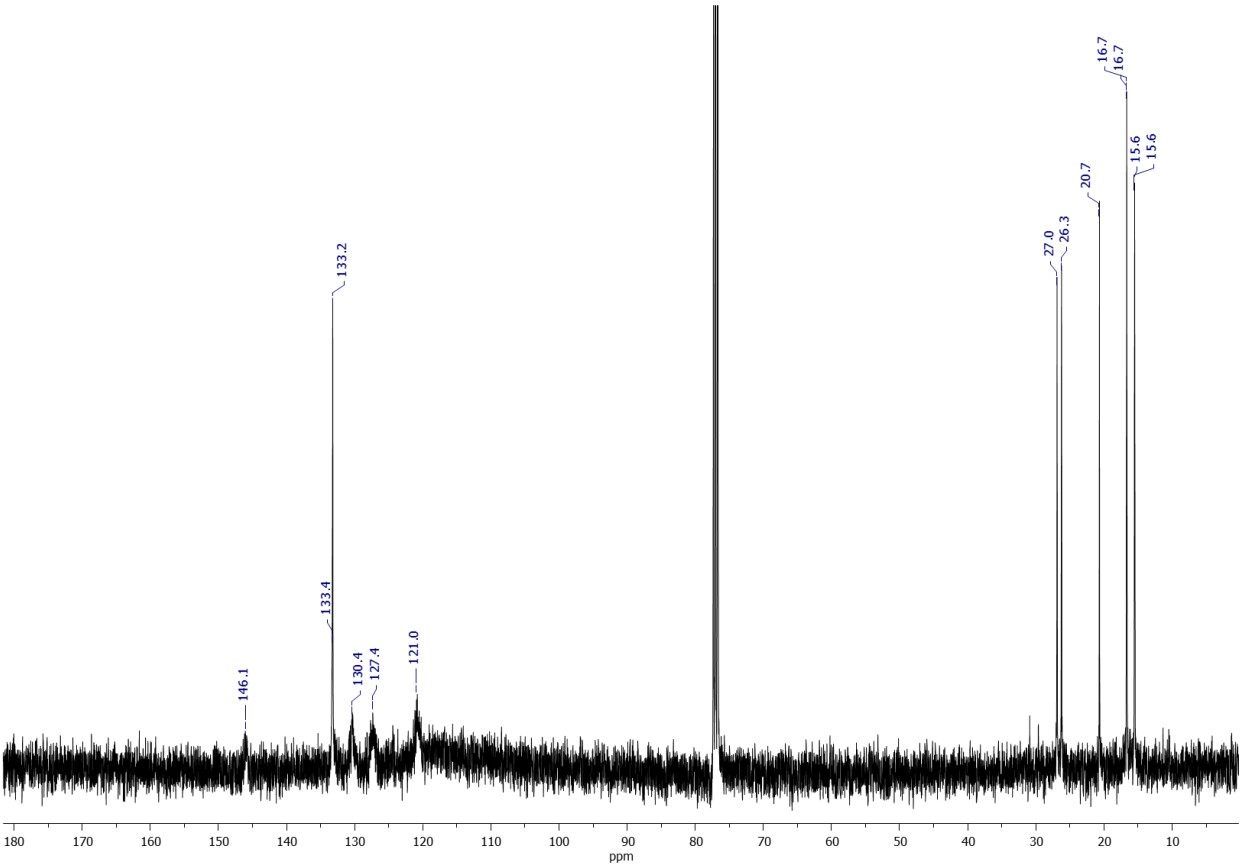


Figure S6. ^{13}C{^{1}H} NMR spectrum of [2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$]$_2$NH (**2**) (100 MHz, CDCl$_3$, 293 K).

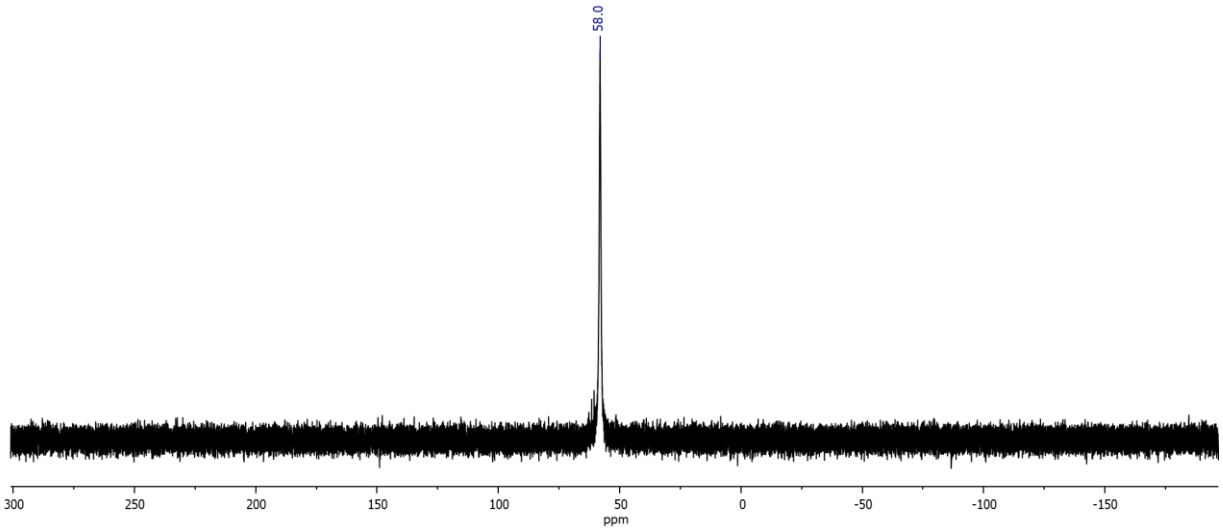


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of [2-Pr^{i}_{2}PO-4-Me-C_6H_3]$_2$NH (**2**) (161.9 MHz, $CDCl_3$, 293 K).

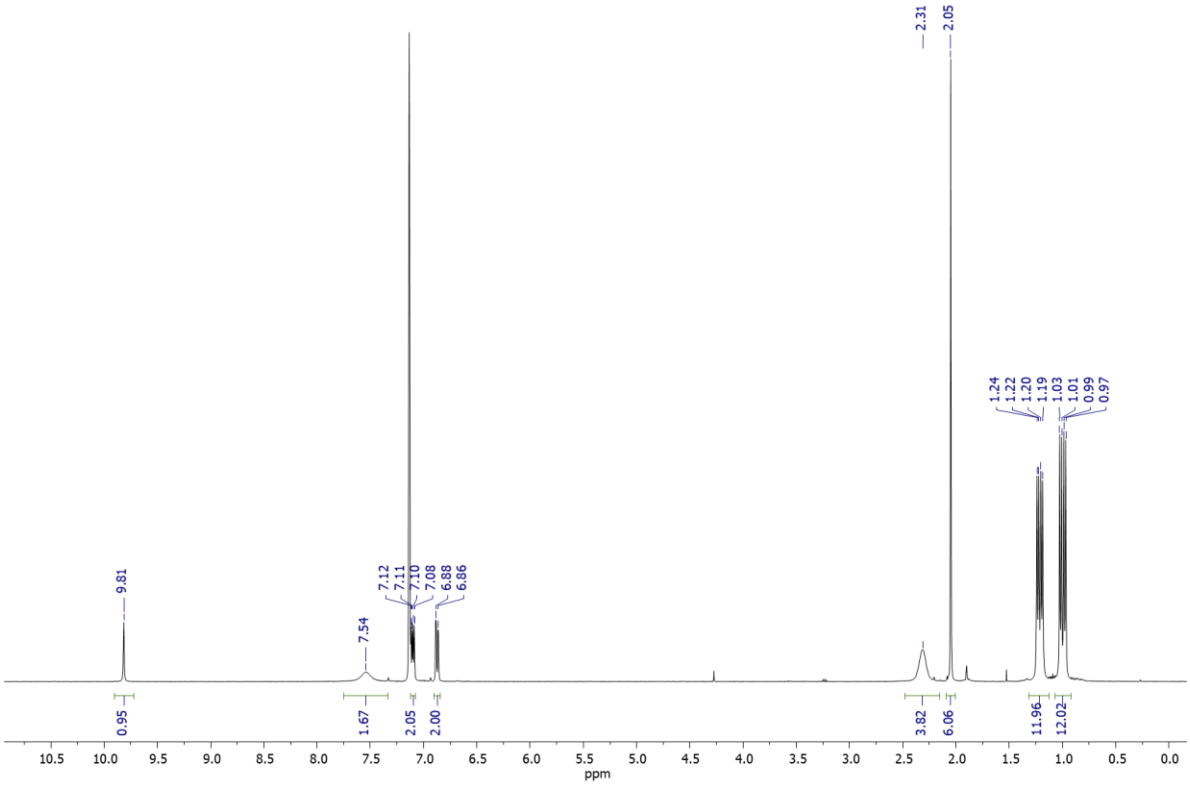


Figure S8. ^{1}H NMR spectrum of [2-Pr$^{i}_{2}$PO-4-Me-C$_6$H$_3$]$_2$NH (**2**) (400 MHz, C$_6$D$_6$, 293 K).

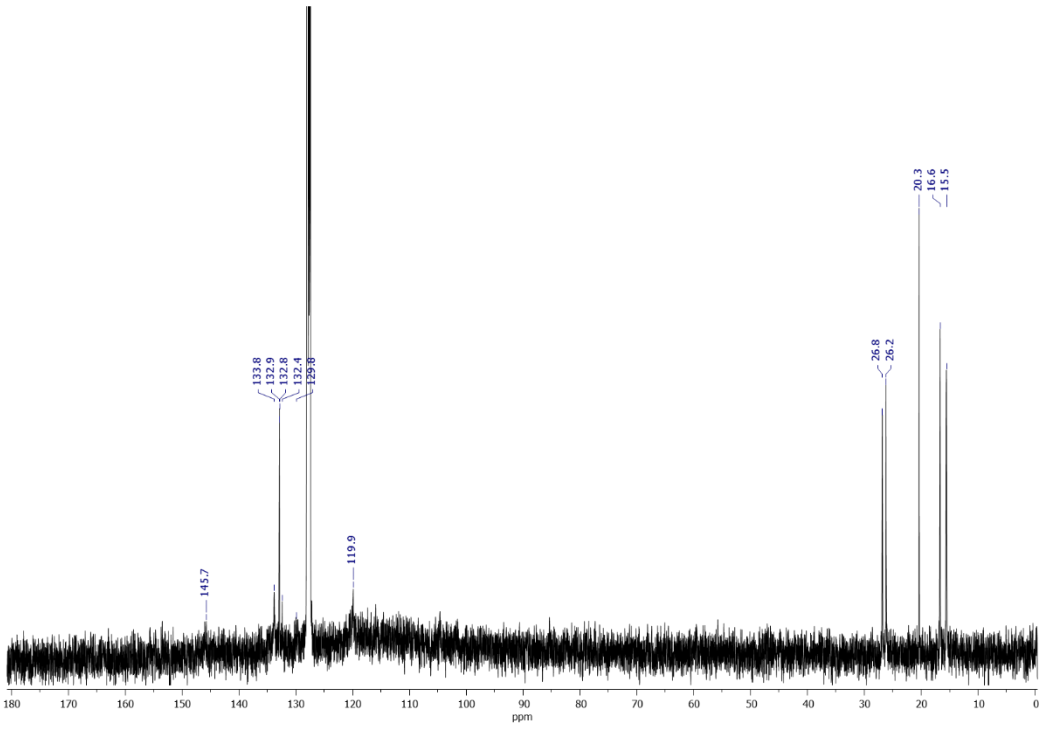


Figure S9. ^{13}C{^{1}H} NMR spectrum of [2-Pr$^{i}_{2}$PO-4-Me-C$_6$H$_3$]$_2$NH (**2**) (100 MHz, C$_6$D$_6$, 293 K).

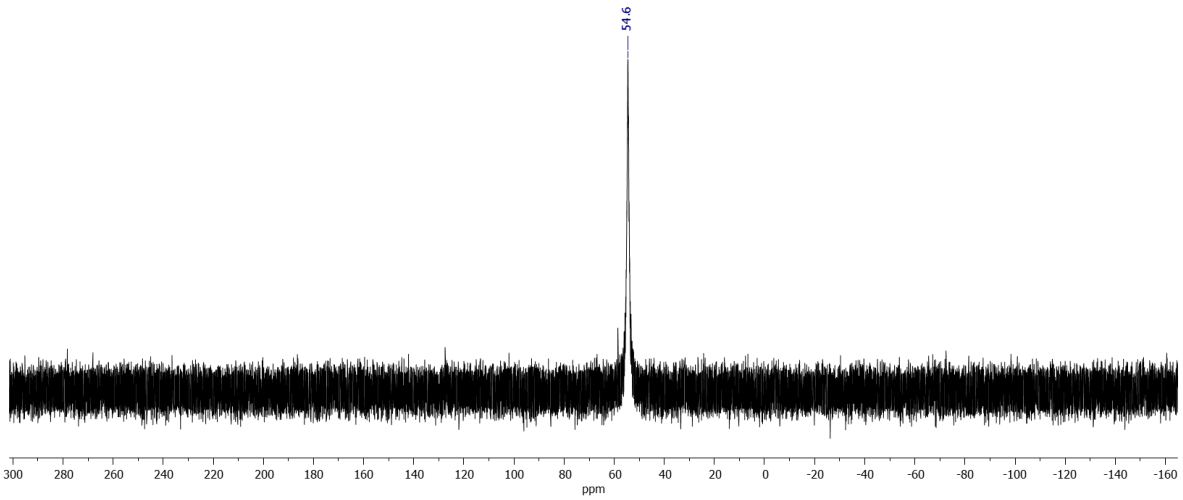


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of [2-$Pr^{i}_{2}PO_{2}$-4-$MeC_{6}H_{3}$]$_{2}$NH (**2**) (161.9 MHz, $C_{6}D_{6}$, 293 K).

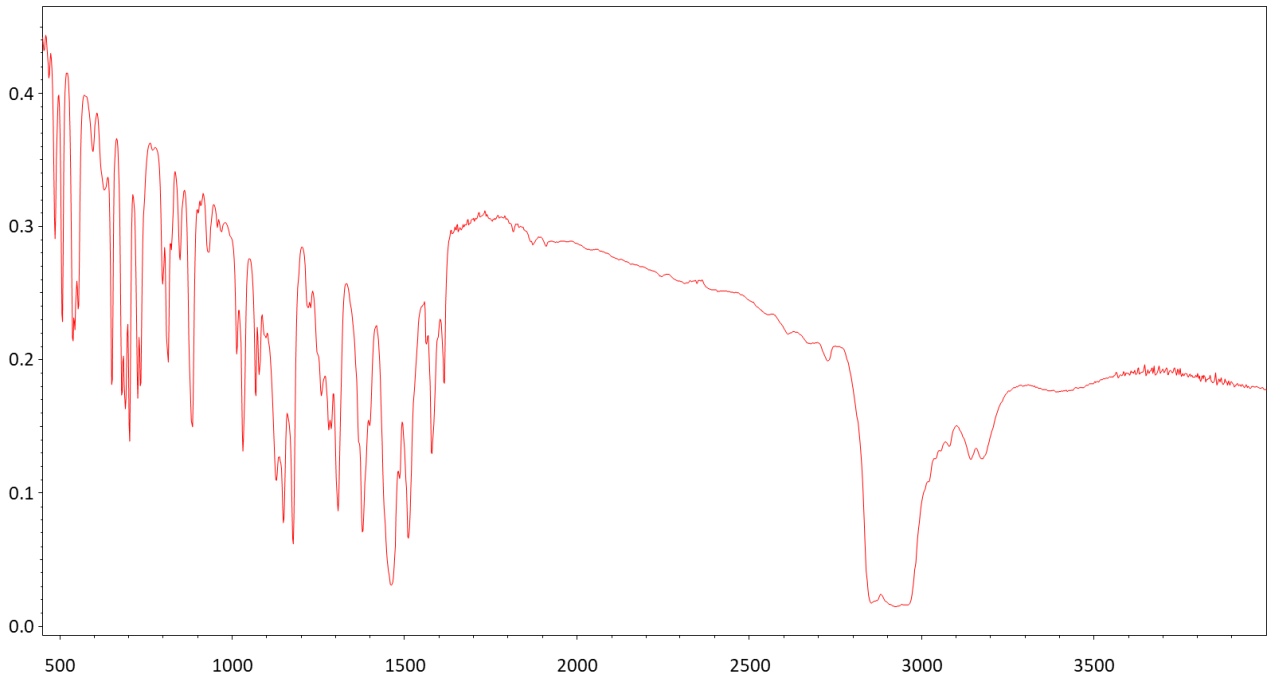


Figure S11. IR spectrum of [2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$]$_2$NH (**2**) (KBr, Nujol).

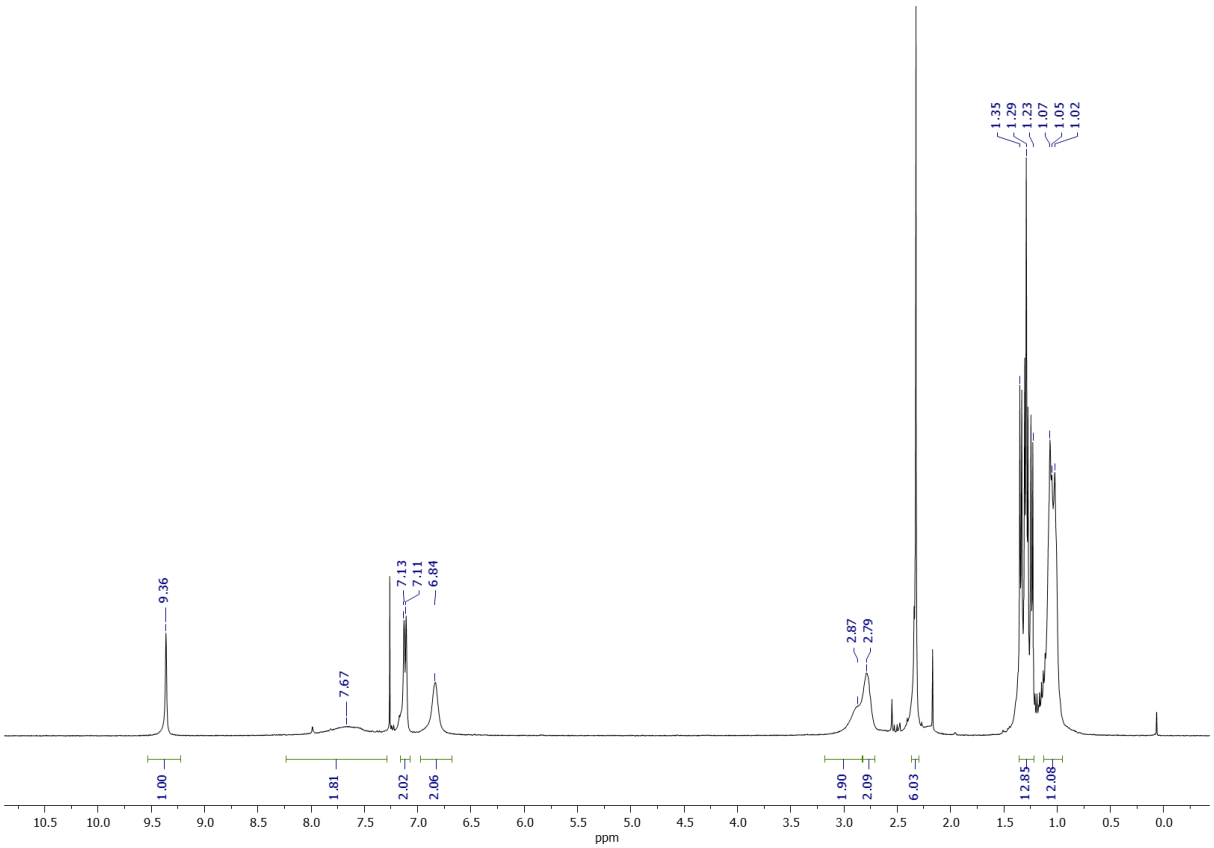


Figure S12. ^{1}H NMR spectrum of [2-Pr$^{i}_{2}$PS-4-MeC$_6$H$_3$]$_2$NH (**3**) (400 MHz, CDCl$_3$, 293 K).

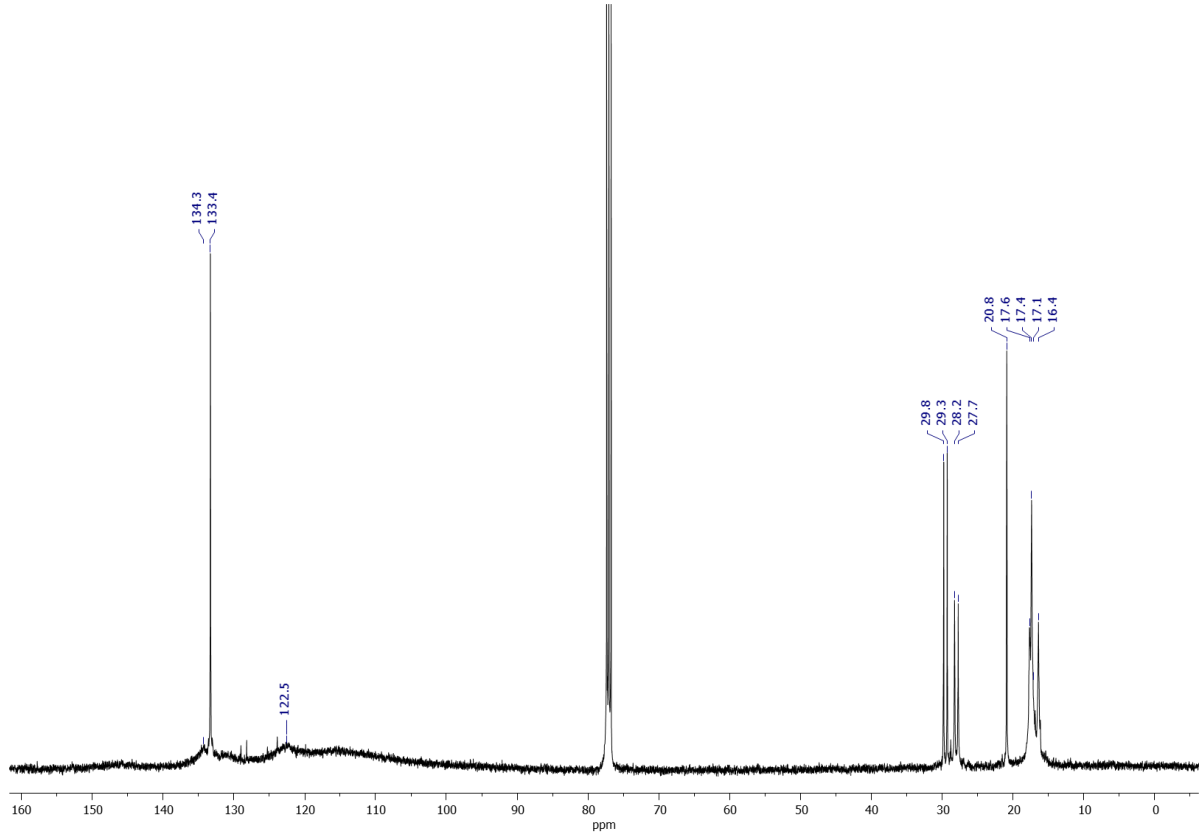


Figure S13. ^{13}C{^{1}H} NMR spectrum of [2-Pr$^{i}_{2}$PS-4-MeC$_6$H$_3$]$_2$NH (**3**) (100 MHz, CDCl$_3$, 293 K).

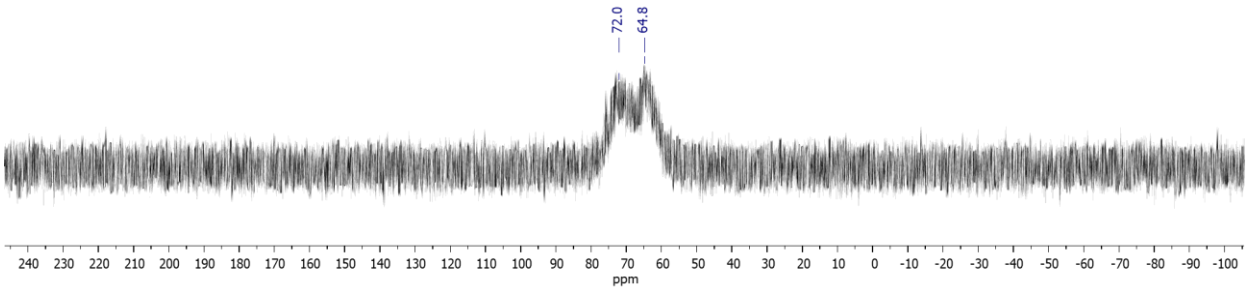


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of [2-Pr^{i}_{2}PS-4-Me-C_6H_3]$_2$NH (**3**) (161.9 MHz, $CDCl_3$, 293 K).

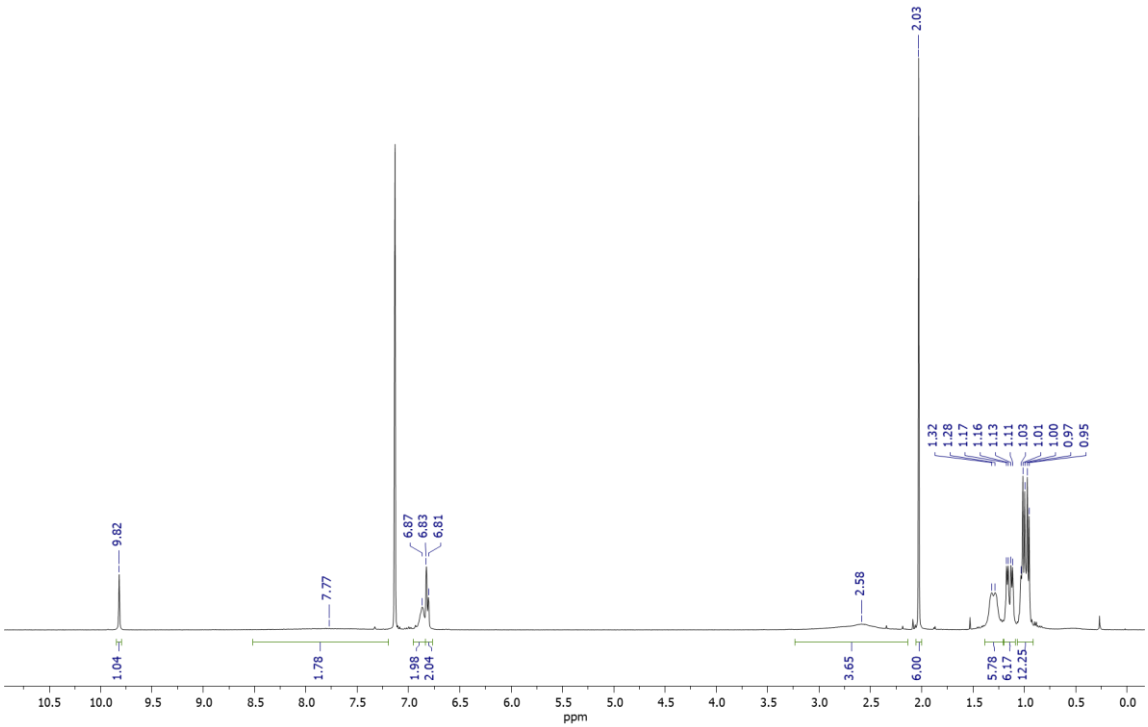


Figure S15. ^{1}H NMR spectrum of [2-Pr^{i}_{2}PS-4-MeC_6H_3]$_2$NH (**3**) (400 MHz, C_6D_6, 293 K).

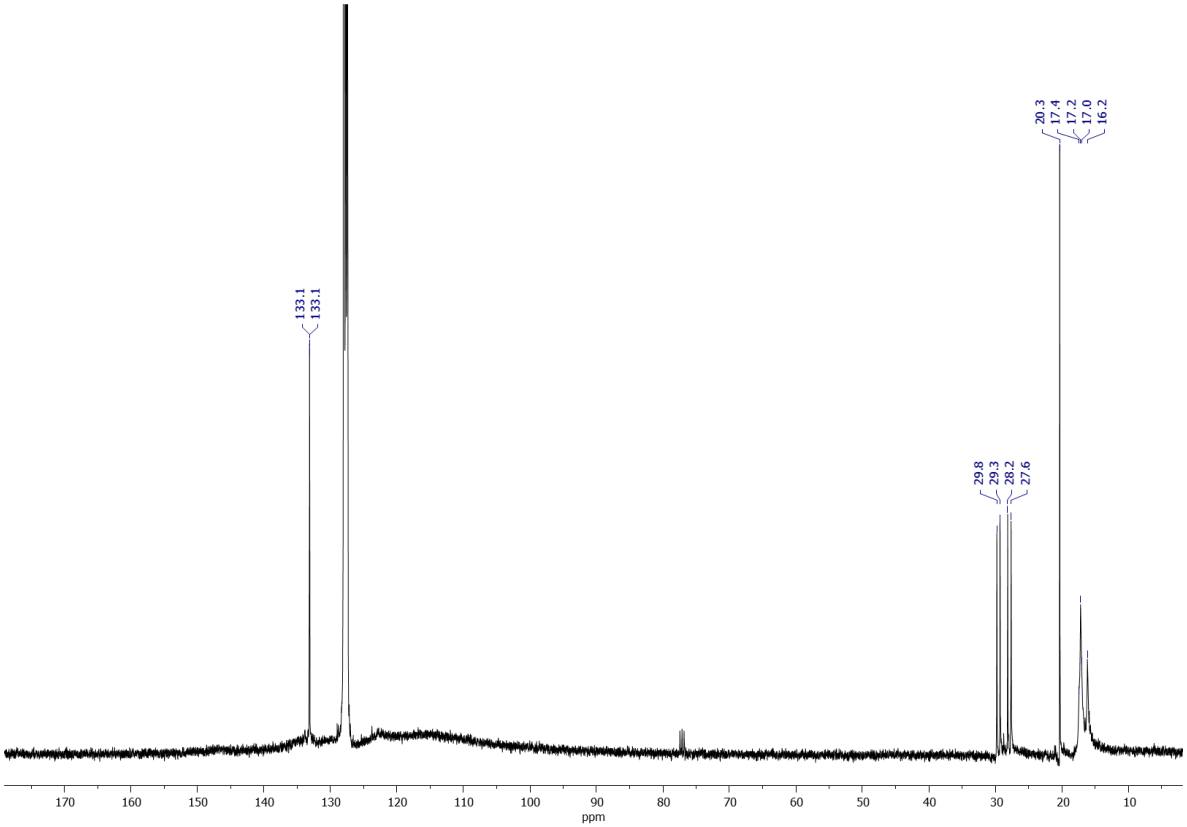


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of [2-Pr^{i}_{2}PS-4-Me-C_6H_3]$_2$NH (**3**) (100 MHz, C_6D_6, 293 K).

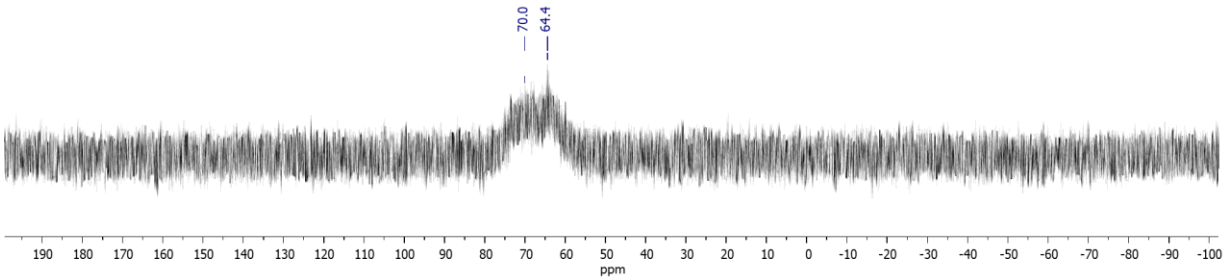


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of [2-Pr^{i}_{2}PS-4-Me-C_6H_3]$_2$NH (**3**) (161.9 MHz, C_6D_6, 293 K).

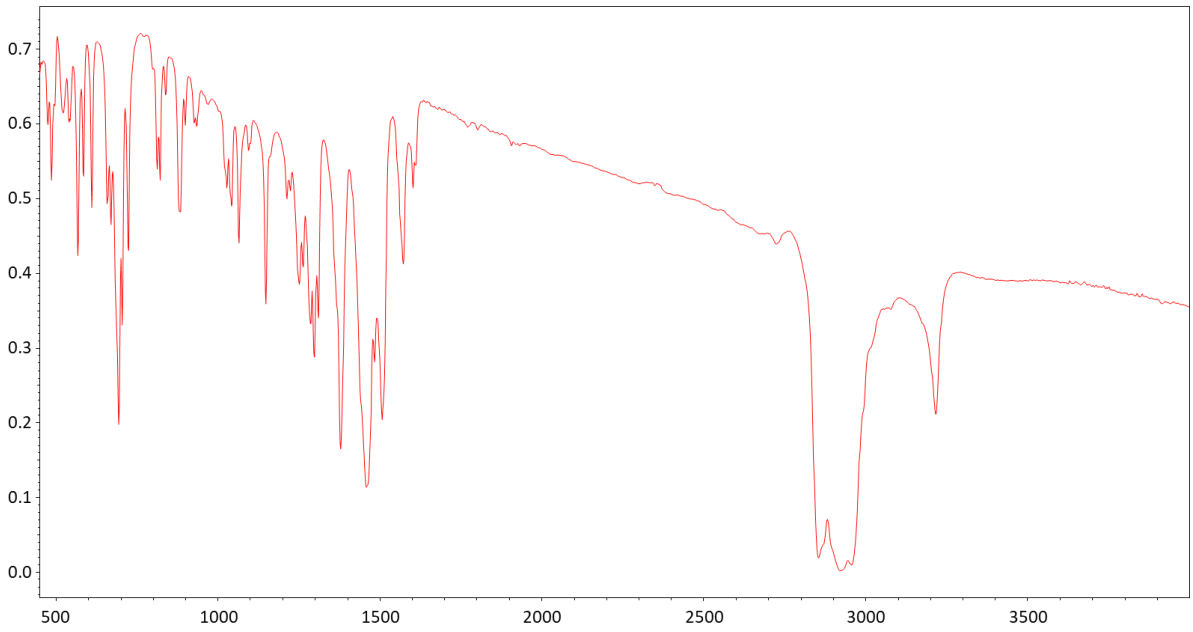


Figure S18. IR spectrum of [2-Pr^{i}_{2}PS-4-MeC_6H_3]$_2$NH (**3**) (KBr, Nujol).

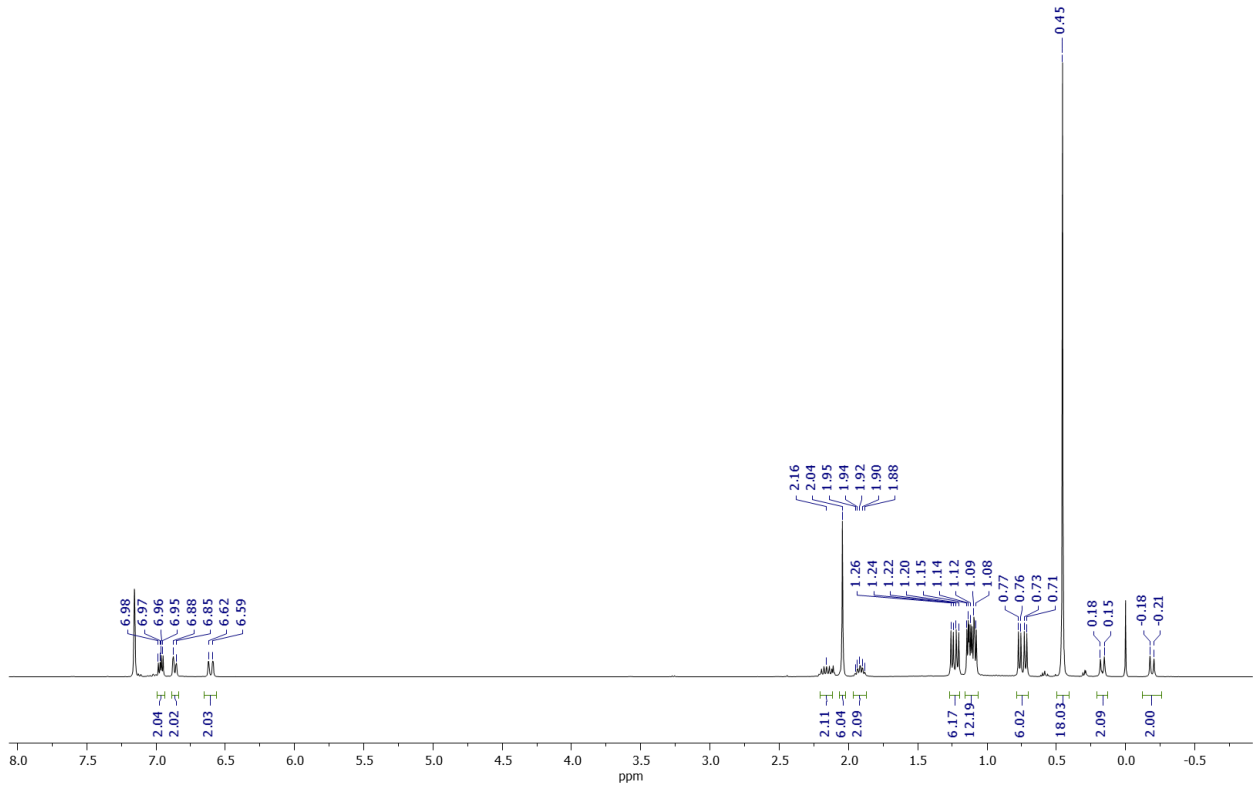


Figure S19. ^{1}H NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$}$_2$N]Sc(CH$_2$SiMe$_3$)$_2$ (**4**) (400 MHz, C$_6$D$_6$, 293 K).

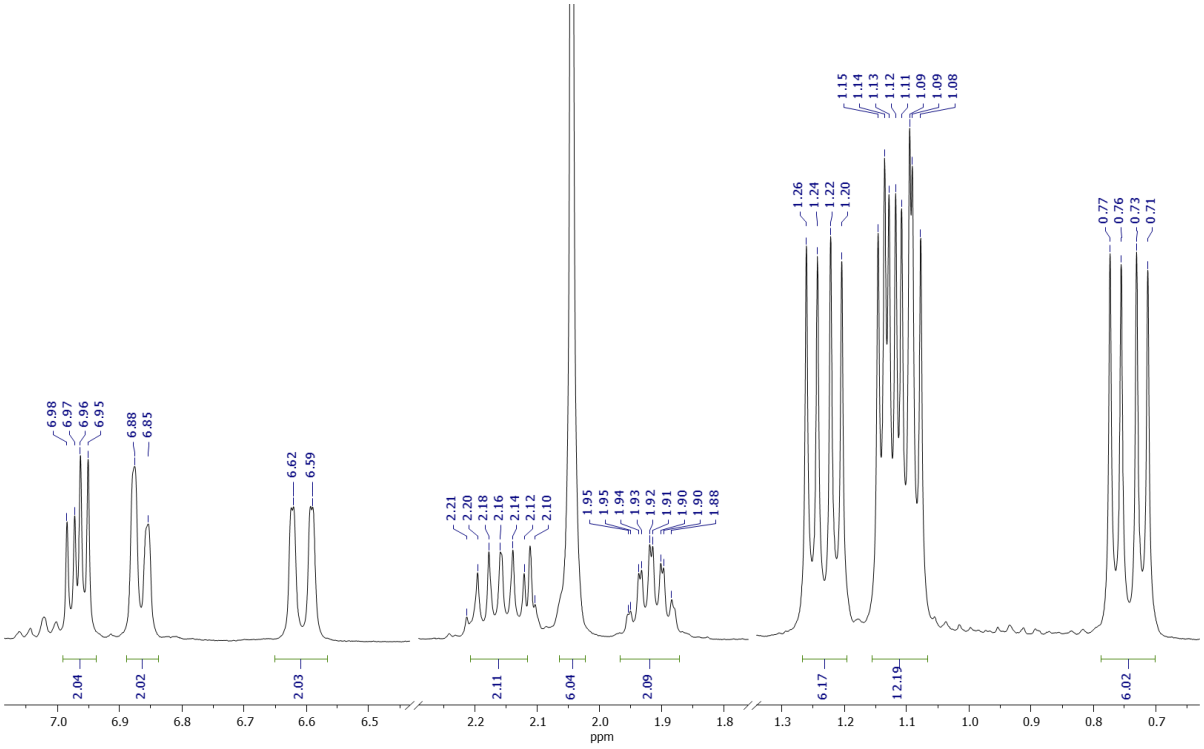


Figure S20. Fragments of ^{1}H NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-Me-C$_6$H$_3$}$_2$N]Sc(CH$_2$SiMe$_3$)$_2$ (**4**) showing aromatic and aliphatic region (400 MHz, C$_6$D$_6$, 293 K).

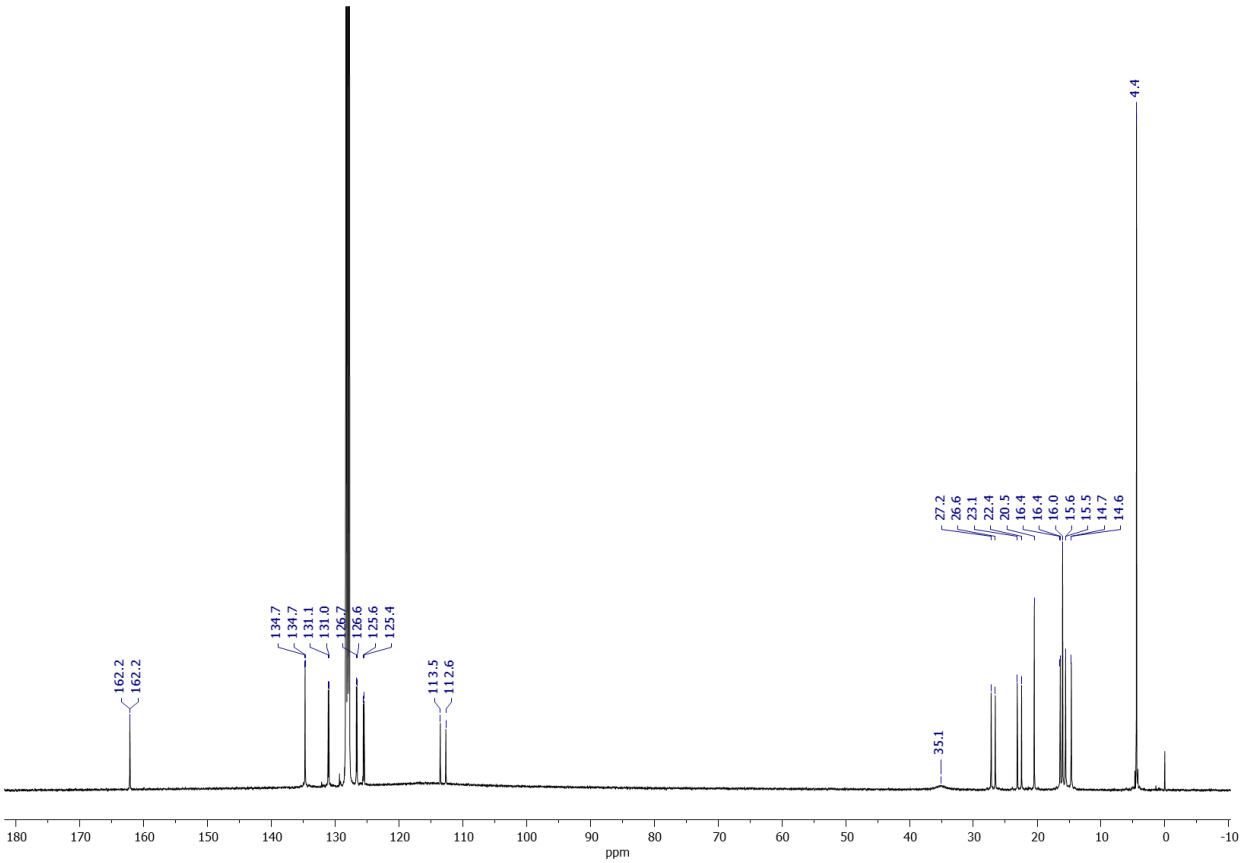


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-MeC_6H_3}$_2$N]Sc(CH_2SiMe_3)$_2$ (**4**) (100 MHz, C_6D_6, 293 K).

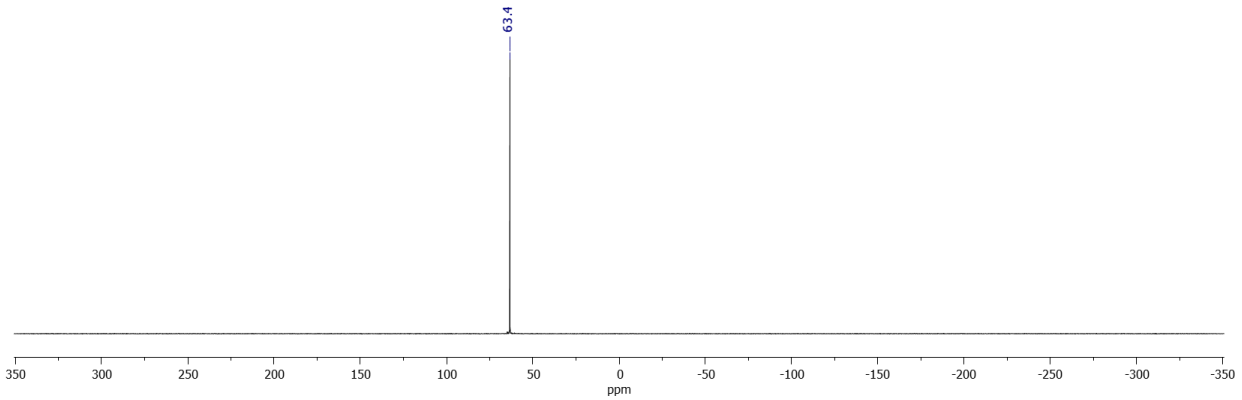


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-MeC_6H_3}$_2$N]Sc(CH_2SiMe_3)$_2$ (**4**) (161.9 MHz, C_6D_6, 293 K).

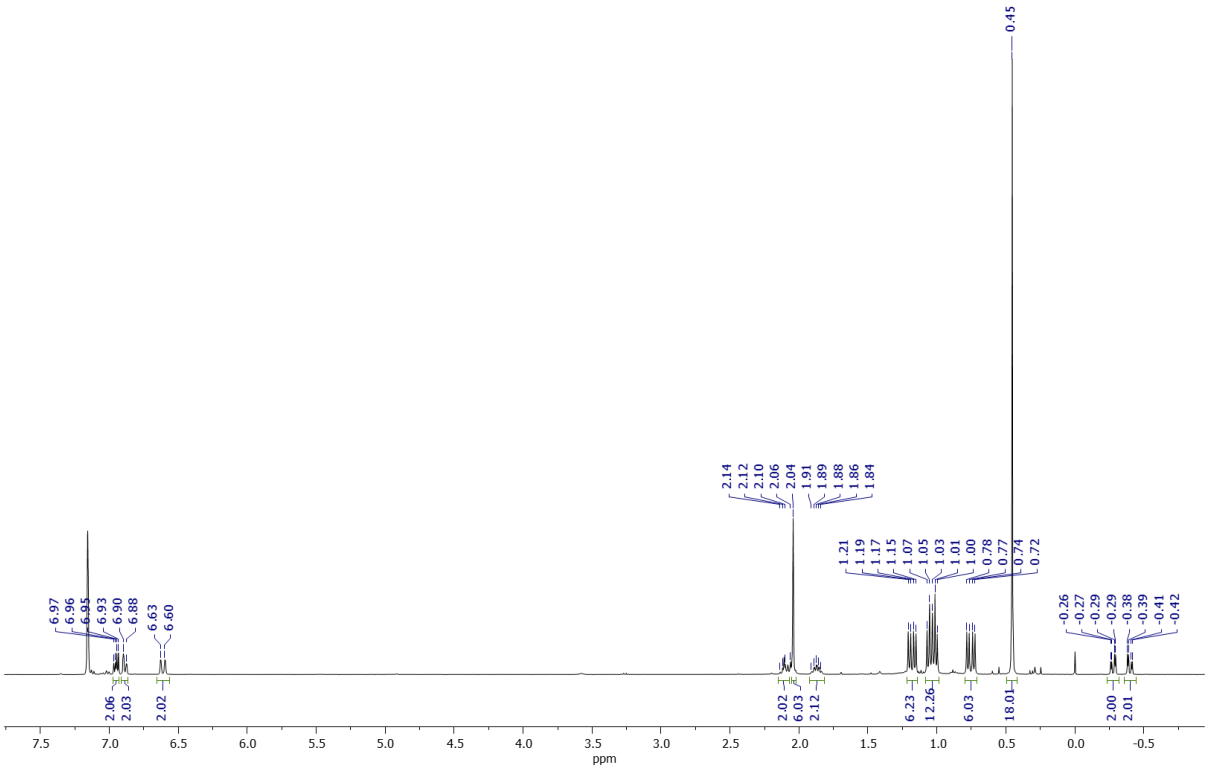


Figure S23. ^{1}H NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$}$_2$N]Y(CH$_2$SiMe$_3$)$_2$ (**5**) (400 MHz, C$_6$D$_6$, 293 K).

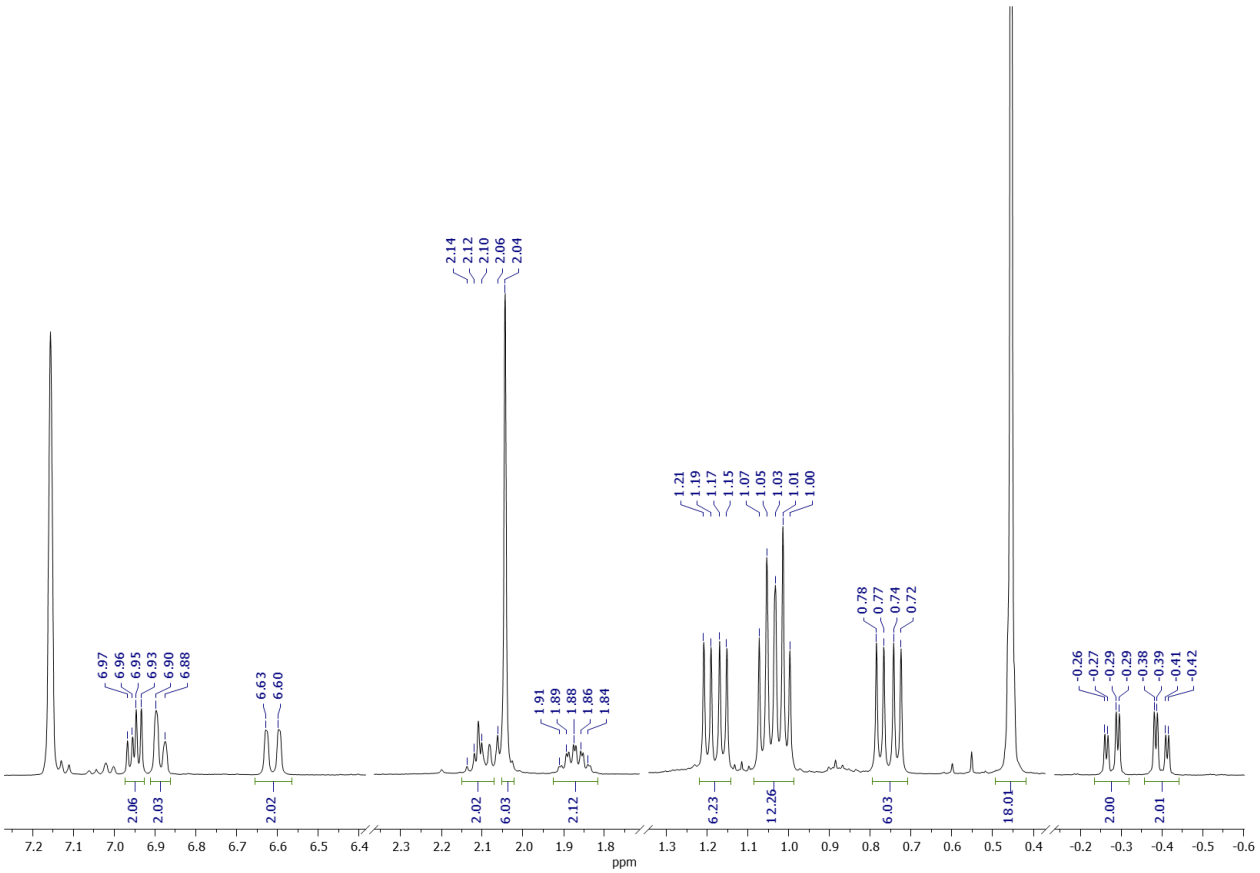


Figure S24. Fragments of ^{1}H NMR spectrum of [{2-Pr$^{i}_{2}$PO-4-MeC$_6$H$_3$}$_2$N]Y(CH$_2$SiMe$_3$)$_2$ (**5**) showing aromatic, aliphatic and alkyl group region (400 MHz, C$_6$D$_6$, 293 K).

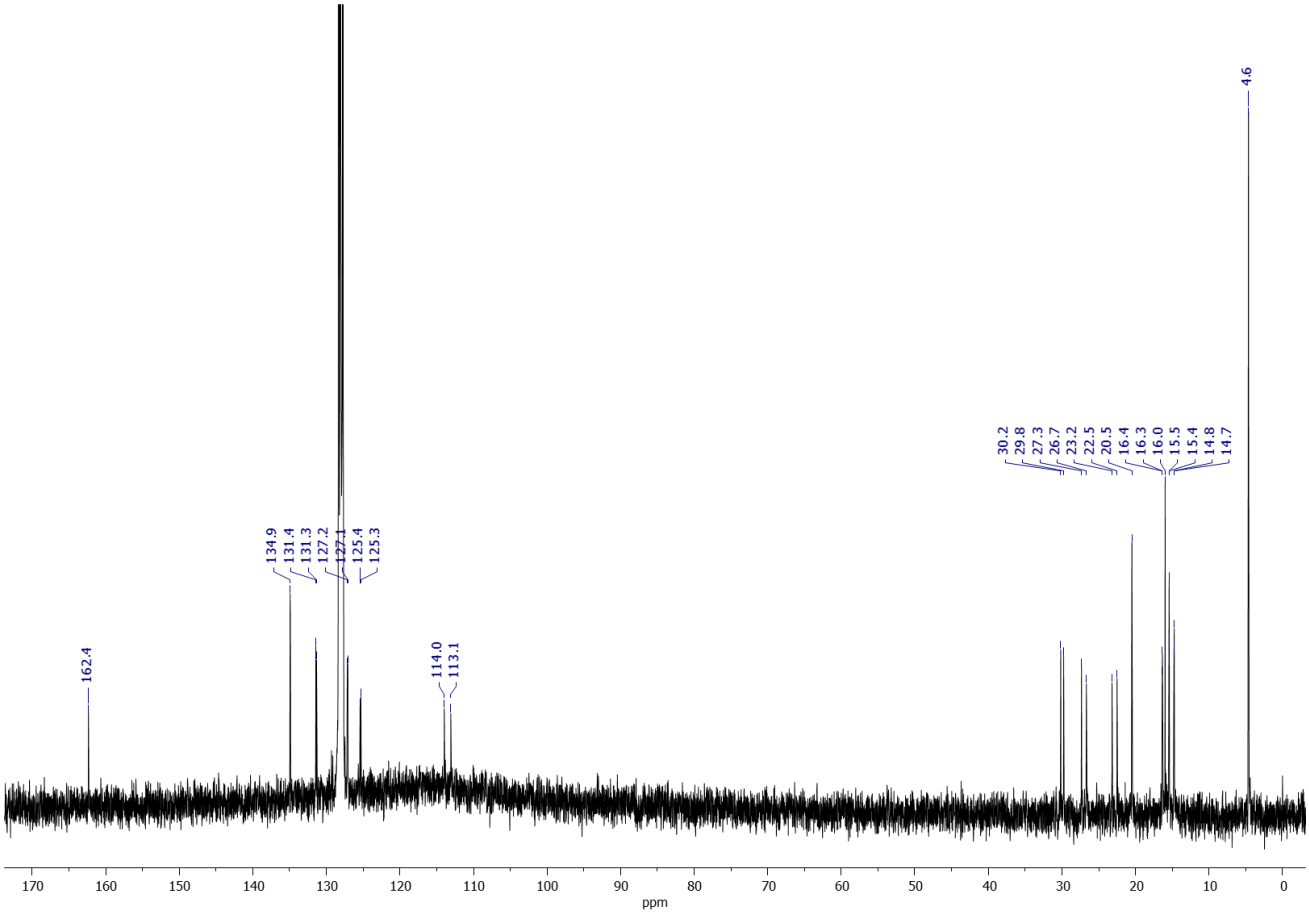


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of $[\{2\text{-}Pr^{i}_{2}PO\text{-}4\text{-}MeC_6H_3\}_2N]Y(CH_2SiMe_3)_2$ (**5**) (100 MHz, C_6D_6, 293 K).

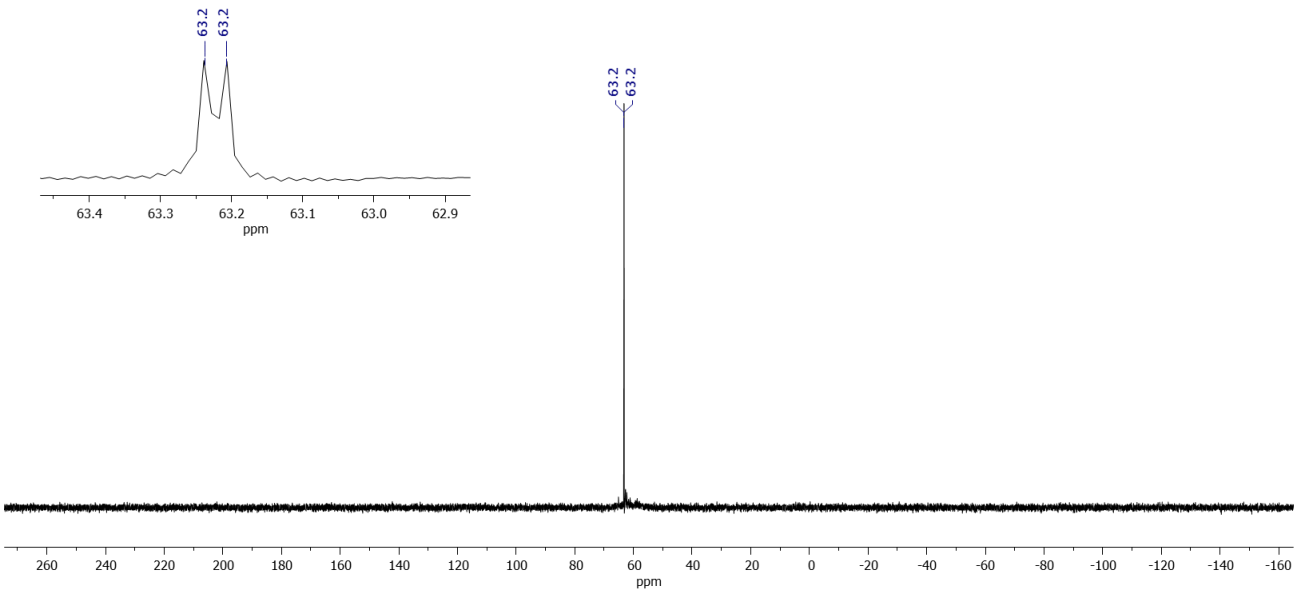
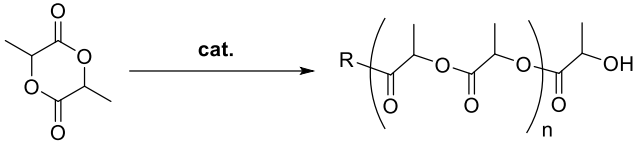


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of $[\{2\text{-}Pr^{i}_{2}PO)_2\text{-}4\text{-}MeC_6H_3\}_2N]Y(CH_2SiMe_3)_2$ (**5**) (121.5 MHz, C_6D_6, 293 K).

Table S17. *rac*-LA polymerization initiated by **5**.



Run	**5**/Pr^{i}OH/LA	Solv.	*t* (min)[b]	Yield (%)[c]	$M_{n(exp)}$ ($\times10^{-3}$)[d]	$M_{n(cacl)}$ ($\times10^{-3}$)[e]	PDI[d]
1	1/−/100	Toluene	2	98	28.03	7.20	3.94
2		THF	2	99	18.90		3.44
3	1/2/100	Toluene	5	99	8.20	7.20	1.43
4	1/2/200		5	97	12.49	14.40	1.44
5	1/2/300		10	94	17.64	21.60	1.37
6	1/2/100	THF	5	98	7.55	7.20	1.42
7	1/2/200		5	98	12.66	14.40	1.34
8	1/2/300		10	96	20.82	21.60	1.40

a) Polymerization conditions: toluene or THF, [LA] = 1.0 mol/L, T = 20 °C; b) reaction time was not optimized; c) isolated yield for precipitated and dried polymer; d) experimental M_n and M_w/M_n determined by GPC in THF relatively to polystyrene standards;
e) M_n calculated on the assumption that two polymer chains grow on one metal center: (144×[LA])/(2×[**5**]).