Supporting Information:

A scandium metalloligand supported Ni(0) complex with a heterobimetallocycle: versatile reactivity with unsaturated bonds

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1. Experimental

General. All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. THF, *n*-pentane, *n*-hexane, benzene, toluene, C_6D_6, toluene-d_8 and THF-d_8 were dried over K-Na alloy, followed by vacuum transferred, and stored in the glovebox. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and 2D NMR spectra were recorded on a Bruker AscendTM 400 or 500 spectrometer. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, to external H_3PO_4 for phosphorous chemical shifts. IR samples (in KBr pellets) were prepared in the glovebox and transferred immediately to the chamber of Bruker INVENIO-S FT-IR spectrometer, data were immediately collected. The bis-aniline precursor (2-(((2-aminobenzyl)(pyridin-2-ylmethyl)amino)methyl)aniline (**A**) was synthesized via a modified procedure according to the literature,[1] $ScCl_3(THF)_3$, $(Me_3SiCH_2)_3Sc(THF)_2$ and ^{i}Pr$_2$PCH$_2$OH were prepared according to the literature procedures.[2,3] Elemental analyses were performed by the Microanalytical Laboratory of Anhui Normal University.

Synthesis of 2-(((2-aminobenzyl)(pyridin-2-ylmethyl)amino)methyl)aniline (A)： Dry zinc dust (3.34 g, 51.1 mmol) and ammonium chloride (2.73 g, 51.1 mmol) in 30 mL of THF was added to a solution of *N*, *N*-bis(2-nitrobenzyl)-1-(pyridin-2-yl)methanamine (1.38 g, 3.65 mmol) in 30 mL of THF at room temperature. After heating the reaction mixture at 60 ℃ for 24h, it was then filtered through a pad of Celite to remove the insoluble materials. The yellow filtrate was evaporated under reduced pressure to give an yellow solid, which was washed with 5 mL of hexane, and dried under vacuum to afford compound **A.** Yield: 1 g (86 %). The ^{1}H NMR spectrum of **A** is the same as that reported previously.[1]

Synthesis of LH$_3$: Compound **A** (1 g, 3.14 mmol) in 10 mL of toluene was added to a solution of ^{i}Pr$_2$PCH$_2$OH (0.93 g, 6.28 mmol) in 10 mL of toluene at room temperature. The yellow reaction mixture was stirred at 110 ℃ for 5h, after cooling solid CaH_2 (1.5 eq.) was slowly added to the solution to remove the byproduct water. The resulting slurry was filtered via a cannula, and the clear solution was evaporated to dryness under reduced pressure to afford **LH$_3$** as a pale yellow oil. Yield: 1.72 g (95 %). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ (ppm) = 8.82 (d, $^3J_{HH}$ = 4.0 Hz, 1H, Ar*H*), 7.29 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Ar*H*), 7.11 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Ar*H*), 7.05 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar*H*), 6.90 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.77 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, Ar*H*), 6.73 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 6.68 (ddd, $^3J_{HH}$ = 7.5 Hz, J_{PH} = 5.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar*H*), 5.85-5.84 (m, 2H, N*H*$_2$), 3.65 (s, 6H, C*H*$_2$), 3.35 (dd, $^2J_{HH}$ = 2.0 Hz (or 5.0 Hz), $^2J_{PH}$ = 5.0 Hz (or 2.0 Hz), 4H, PC*H*$_2$), 1.69-1.63 (sept.d, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 2.3 Hz, 4H, C*H*(CH$_3$)$_2$), 1.08 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 25°C): δ (ppm) = 159.64 (s, Ar*C*), 149.77 (s, Ar*C*), 148.57 (d, J_{PC} = 6.8 Hz, Ar*C*), 136.20 (s, Ar*C*), 131.84 (s, Ar*C*), 129.00 (s, Ar*C*), 128.59 (s, Ar*C*), 123.65 (s, Ar*C*), 122.80 (s, Ar*C*), 121.57 (s, Ar*C*), 116.53 (s, Ar*C*), 111.41 (s, Ar*C*), 59.25 (s, *C*H$_2$), 58.44 (s, *C*H$_2$), 39.84 (d, $^1J_{PC}$ = 11.8 Hz, P*C*H$_2$), 23.64 (d, $^1J_{PC}$ = 14.5 Hz, *C*H(CH$_3$)$_2$), 20.30 (d, $^2J_{PC}$ = 15.2 Hz, CH(*C*H$_3$)$_2$), 19.25 (d, $^2J_{PC}$ = 10.4 Hz, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25°C): δ (ppm) = -3.06 (s, 2P). IR (KBr Pellets, cm^{-1}): 3300 (s), 3046 (m), 2956 (s), 2871 (s), 2811 (m), 2715 (m), 1596 (s), 1513 (m), 1456 (s), 1375 (s), 1318 (s), 1252 (s), 1153 (m), 1098 (s), 1042 (s), 964 (m), 924 (s), 880 (s), 807 (s), 747 (s), 640 (m), 480 (m). Anal. calcd for $C_{34}H_{52}N_4P_2$ (578.77 g/mol): C, 70.56; H, 9.06; N, 9.68. Found: C, 70.86; H, 8.98; N, 9.83.

Synthesis of 1: LH$_3$ (300 mg, 0.516 mmol) in 5 mL of toluene was slowly added to $(Me_3SiCH_2)_3Sc(THF)_2$ (390 mg, 0.84 mmol) in 1 mL of toluene at room temperature, the resulting yellow solution was allowed to stir at room

temperature for 4 h. Volatiles were removed under reduced pressure, and the residue was washed with *n*-hexane to give **1** as a yellow solid. Yield: 264 mg (72%). Crystals suitable for the X-ray diffraction analysis were grown from a concentrated toluene solution at -35 °C. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ (ppm) = 9.49 (d, $^{3}J_{HH}$ = 4.5 Hz, 1H, Ar*H*), 7.42-7.35 (m, 2H, Ar*H*), 7.04 (dd, $^{3}J_{HH}$ = 10 Hz, $^{4}J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 6.97 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, Ar*H*), 6.84-6.81 (m, 2H, Ar*H*), 6.75 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H, Ar*H*), 6.67-6.65 (m, 2H, Ar*H*), 6.30 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, Ar*H*), 4.69 (d, $^{2}J_{HH}$ = 13.5 Hz, 1H, PCH_2), 4.34-4.31 (m, 2H, CH_2), 4.24 (dd, $^{2}J_{HH}$ = 11.5 Hz, $^{2}J_{PH}$ = 8.0 Hz, 1H, PCH_2), 4.04 (d, $^{2}J_{HH}$ = 11.5 Hz, 1H, CH_2), 3.96 (dd, $^{2}J_{HH}$ = 13.5 Hz, $^{2}J_{PH}$ = 3.0 Hz, 1H, PCH_2), 3.25 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{2}J_{PH}$ = 4.0 Hz, 1H, PCH_2), 2.54 (d, $^{2}J_{HH}$ = 12.0 Hz, 1H, CH_2), 2.47 (d, $^{2}J_{HH}$ = 16.0 Hz, 1H, CH_2), 2.41 (d, $^{2}J_{HH}$ = 11.0 Hz, 1H, CH_2), 2.20 (sept., $^{3}J_{HH}$ = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 1.82-1.67 (m, 3H, CH(CH$_3$)$_2$), 1.38 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{PH}$ = 12.0 Hz, 3H, CH(CH_3)$_2$), 1.29 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{PH}$ = 9.5 Hz, 3H, CH(CH_3)$_2$), 1.22 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 11.0 Hz, 3H, CH(CH_3)$_2$), 1.16 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{PH}$ = 12.5 Hz, 3H, CH(CH_3)$_2$), 1.13-1.08 (m, 6H, CH(CH_3)$_2$), 1.03 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 14.0 Hz, 3H, CH(CH_3)$_2$), 0.52 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{PH}$ = 12.0 Hz, 3H, CH(CH_3)$_2$), 0.049 (s, 2H, ScCH_2), -0.094 (s, 9H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 25°C): δ (ppm) = 158.37 (s, Ar*C*), 156.39 (d, J_{PC} = 19.9 Hz, Ar*C*), 155.56 (s, Ar*C*), 152.32 (d, J_{PC} = 9.6 Hz, Ar*C*), 139.13 (s, Ar*C*), 132.27 (s, Ar*C*), 130.56 (s, Ar*C*), 130.16 (s, Ar*C*), 128.59 (s, Ar*C*), 122.73 (s, Ar*C*), 122.58 (s, Ar*C*), 122.29 (s, ArC), 121.60 (s, Ar*C*), 114.49 (s, Ar*C*), 113.96 (s, Ar*C*), 113.91 (d, J_{PC} = 24.9 Hz, Ar*C*), 62.98 (s, *C*H$_2$), 59.59 (s, *C*H$_2$), 58.98 (s, *C*H$_2$), 48.86 (d, J_{PC} = 10.4 Hz, P*C*H$_2$), 44.11 (m, P*C*H$_2$), 34.39 (s, Sc*C*H$_2$), 24.95 (d, $^{1}J_{PC}$ = 8.8 Hz, *C*H(CH$_3$)$_2$), 24.24 (d, $^{1}J_{PC}$ =10.3 Hz, *C*H(CH$_3$)$_2$), 24.22 (d, $^{1}J_{PC}$ =14.4 Hz, *C*H(CH$_3$)$_2$), 23.54 (d, $^{1}J_{PC}$ = 17.3 Hz, *C*H(CH$_3$)$_2$), 21.13 (d, $^{2}J_{PC}$ = 8.9 Hz, CH(*C*H$_3$)$_2$), 20.87 (d, $^{2}J_{PC}$ = 14.1 Hz, CH(*C*H$_3$)$_2$), 20.77 (d, $^{2}J_{PC}$ = 12.4 Hz, CH(*C*H$_3$)$_2$), 20.43 (br s, CH(*C*H$_3$)$_2$), 20.34 (d, $^{2}J_{PC}$ = 4.6 Hz, CH(*C*H$_3$)$_2$), 19.73 (br s, CH(*C*H$_3$)$_2$), 19.37 (d, $^{2}J_{PC}$ = 9.3 Hz, CH(*C*H$_3$)$_2$), 18.80 (d, $^{2}J_{PC}$ = 7.8 Hz, CH(*C*H$_3$)$_2$), 4.41 (s, Si(*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 25°C): δ (ppm) = -7.35 (s, 1P), -7.54 (s, 1P). IR (KBr Pellets, cm^{-1}): 3059 (m), 3014 (m), 2951 (s), 2869 (s), 2716 (m), 1596 (s), 1473 (s), 1450 (s), 1377 (m), 1298 (s), 1241 (s), 1157 (m), 1088 (m), 1204 (s), 955 (m), 856 (s), 745 (s), 637 (s), 554 (m), 491 (m), 440 (m). Anal. calcd for $C_{38}H_{61}N_4P_2ScSi$ (708.92 g/mol): C, 64.38; H, 8.67; N, 7.90. Found: C, 64.11; H, 8.36; N, 7.78.

Synthesis of 2: Complex **1** (300 mg, 0.42 mmol) in 2 mL of benzene was slowly added to a solution of Ni(COD)$_2$ (132 mg, 0.462 mmol) in 2 mL benzene at room temperature, and the resulting red reaction solution was allowed to stir overnight. Volatiles were removed under reduced pressure, and the residue was washed with *n*-hexane to afford **2** as a red solid. Yield: 280 mg (74%). Crystals suitable for the X-ray diffraction analysis were grown by slow diffusion of pentane into the benzene solution at room temperature. ^{1}H NMR (THF-d_8, 500 MHz, 25 °C): δ (ppm) = 7.54 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 7.14 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 6.96 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.90 (d, $^{3}J_{HH}$ = 7.0 Hz, 2H, Ar*H*), 6.30 (t, $^{3}J_{HH}$ = 8.3 Hz, 3H, Ar*H*), 6.23 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 3.82-3.76 (m, Hz, 6H, CH_2 and PCH_2), 3.63 (d, $^{2}J_{HH}$ = 12.0 Hz, 2H, CH_2), 3.41 (dt, $^{2}J_{HH}$ = 12.5 Hz, $^{2}J_{PH}$ = 3.0 Hz, 2H, PCH_2), 2.14-2.07 (m, 4H, CH(CH$_3$)$_2$), 1.36 (dt, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{PH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.32 (dt, $^{3}J_{HH}$ = 6.5 Hz, $^{3}J_{PH}$ = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.13 (dt, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 0.93 (dt, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 6.5 Hz, 6H, CH(CH_3)$_2$); ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ (ppm) = 7.99 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 7.37 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 7.01-6.96 (m, 3H, Ar*H*), 6.71 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 6.67 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 5.94 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 3.77 (d, $^{2}J_{HH}$ = 12.4 Hz, 2H, CH_2), 3.68 (d, $^{2}J_{HH}$ = 12.0 Hz, 2H, CH_2), 3.48 (d, $^{2}J_{HH}$ = 12.0 Hz, 2H, CH_2), 3.36 (dt, $^{2}J_{HH}$ = 12.4 Hz, $^{2}J_{PH}$ = 4.0 Hz, 2H, PCH_2), 3.25 (br s, 2H, PCH_2), 2.03 (br s, 4H, CH(CH$_3$)$_2$), 1.27 (dt, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{PH}$ = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.16-1.09 (m, 12H, CH(CH_3)$_2$), 0.77 (dt, $^{3}J_{HH}$ = 6.0 Hz, $^{3}J_{PH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz, 25°C): δ (ppm) = 212.22 (s, Ar*C*), 157.43 (m, Ar*C*), 150.17 (s, Ar*C*), 135.40 (s, Ar*C*), 135.31 (d, Ar*C*), 132.59 (s, Ar*C*), 130.31 (s, Ar*C*), 129.20 (s, Ar*C*), 122.05 (s, Ar*C*), 113.11 (s, Ar*C*), 110.38 (s, Ar*C*), 109.44 (s, Ar*C*), 62.23 (s, *C*H$_2$), 60.78 (s, *C*H$_2$), 54.17 (m, P*C*H$_2$), 28.84 (m, *C*H(CH$_3$)$_2$), 20.59 (s, *C*H(CH$_3$)$_2$), 20.34 (m, CH(*C*H$_3$)$_2$), 19.92 (s, CH(*C*H$_3$)$_2$), 19.26 (s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR

(THF-d_8, 202 MHz, 25°C): δ (ppm) = 7.49 (s, 2P). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 25°C): δ (ppm) = 3.72 (s, 2P). IR (KBr Pellets, cm^{-1}): 3057 (m), 2950 (s), 2919 (s), 2868 (s), 2774 (m), 2119 (s), 2587 (s), 1532 (m), 1475 (s), 1448 (s), 1372 (m), 1332 (m), 1255 (s), 1195 (m), 1158 (m), 1105 (m), 1042 (s), 950 (m), 884 (m), 824 (m), 745 (s), 678 (m), 628 (s), 602 (s), 519 (m), 473 (m). Anal. calcd for $C_{68}H_{96}N_{10}P_4Sc_2Ni_2$ (1386.80 g/mol): C, 58.89; H, 7.12; N, 10.10. Found: C, 58.83; H, 6.85; N, 9.80.

Synthesis of 3: 2,6-Dimethylphenyl isocyanide (8 mg, 0.058 mmol) in 1 mL of toluene was added to a solution of **2** (40 mg, 0.029 mmol) in 5 mL of toluene at room temperature. The yellow reaction mixture was allowed to stir at room temperature for 5 h. Volatiles were removed under vacuum, and the residue was washed with *n*-hexane to afford **3** as a yellow solid. Yield: 42 mg (90 %). Crystals suitable for the X-ray diffraction analysis were grown from a concentrated toluene solution at -35 °C. ^1H NMR (C_6D_6, 500 MHz, 25 °C): δ (ppm) = 8.30 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 7.41 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, Ar*H*), 7.03-7.00 (m, 3H, Ar*H*), 6.85-6.83 (m, 3H, Ar*H*), 6.78 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar*H*), 6.75 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 6.02 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 3.74-3.68 (m, 4H, CH_2 and PCH_2), 3.59 (d, $^2J_{HH}$ = 10.5 Hz, 2H, CH_2), 3.34 (dt, $^2J_{HH}$ = 12.5 Hz, $^2J_{PH}$ = 3.5Hz, 2H, PCH_2), 3.24 (br s, 2H, CH_2), 2.48 (s, 6H, ArCH_3), 2.17 (m, 2H, CH(CH_3)$_2$), 2.05 (m, 2H, CH(CH_3)$_2$), 1.33 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.5 Hz, 6H, CH(CH_3)$_2$), 1.25 (dt, $^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.17 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 8.5 Hz, 6H, CH(CH_3)$_2$), 0.80 (dt, $^2J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 25°C): δ (ppm) = 205.96 (m, Ar*C*), 180.53 (s, ArN*C*), 156.26 (m, Ar*C*), 150.92 (s, Ar*C*), 138.86 (s, Ar*C*), 134.78 (s, Ar*C*), 133.42 (s, Ar*C*), 132.04 (s, Ar*C*), 131.66 (s, Ar*C*), 130.28 (s, Ar*C*), 128.59 (s, Ar*C*), 125.48 (s, Ar*C*), 122.84 (s, Ar*C*), 114.65 (s, Ar*C*), 111.37 (s, Ar*C*), 111.01 (s, Ar*C*), 61.29 (s, *C*H_2), 58.90 (s, *C*H_2), 46.76 (br s, P*C*H_2), 29.38 (m, *C*H(CH$_3$)$_2$), 29.26 (m, *C*H(CH$_3$)$_2$), 19.89 (s, CH(*C*H$_3$)$_2$), 19.80 (s, CH(*C*H$_3$)$_2$), 19.25 (s, CH(*C*H$_3$)$_2$), 18.10 (s, CH(*C*H$_3$)$_2$), 17.83 (s, CH(*C*H$_3$)$_2$); $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz, 25°C): δ (ppm) = -10.28 (s, 2P). IR (KBr Pellets, cm^{-1}): 3058 (m), 2955 (s), 2920 (s), 2869 (s), 2784 (m), 1986 (s), 1858 (m), 1590 (s), 1530 (m), 1476 (s), 1374 (m), 1293 (s), 1194 (m), 1157 (m), 1100 (m), 951 (m), 883 (m), 824 (m), 745 (s), 674 (m), 626 (s), 606 (m), 513 (m). Anal. calcd for $C_{43}H_{58}N_5P_2ScNi$ (810.57 g/mol): C, 63.72; H, 7.21; N, 8.64. Found: C, 63.55; H, 6.90; N, 8.30.

Synthesis of 4: *p*-Tolunitrile (6 mg, 0.058 mmol) in 1 mL of tetrahydrofuran was added to a solution of **2** (40 mg, 0.029 mmol) in 4 mL of tetrahydrofuran at room temperature. The resulting green reaction solution was allowed to stir at room temperature for 1h. The solution was concentrated under reduced pressure to about 1 mL, and slow diffusion of pentane into the solution at room temperature afforded **4** as dark green crystals. Yield: 32 mg (73%). ^1H NMR (toluene-d_8, 500 MHz, -30 °C): δ (ppm) = 8.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.51 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar*H*), 7.37 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Ar*H*), 7.20-7.09 (m, 5H, Ar*H*, partly overlapped with the solvent peaks), 6.87-6.83 (m, 2H, Ar*H*), 6.73-6.70 (m, 2H, Ar*H*), 6.63 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 5.91 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar*H*), 4.28 (d, $^2J_{HH}$ = 11.5 Hz, 1H, CH_2), 4.21 (d, $^2J_{HH}$ = 14.0 Hz, 2H, CH_2), 4.10 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2), 3.75 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2), 3.58-3.45 (m, 2H, CH_2), 2.95 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2), 2.80 (d, $^2J_{HH}$ = 11.5 Hz, 1H, CH_2), 2.33 (d, $^2J_{HH}$ = 16.0 Hz, 1H, CH_2), 2.16 (s, 3H, ArCH_3), 1.93 (m, 3H, CH(CH$_3$)$_2$), 1.66 (m, 1H, CH(CH$_3$)$_2$), 1.38-1.34 (m, 3H, CH(CH_3)$_2$), 1.26-1.21 (m, 3H, CH(CH_3)$_2$), 1.20-1.14 (m, 6H, CH(CH_3)$_2$), 1.08 (br t, 3H, CH(CH_3)$_2$), 0.93-0.91 (m, 9H, CH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25°C): δ (ppm) = 161.88 (s, Ar*C*), 159.53 (s, Ar*C*), 144.35 (m, Ar*C*), 140.11 (s, Ar*C*), 139.99 (m, Ar*C*), 134.55 (s, Ar*C*), 131.72 (s, Ar*C*), 130.55 (s, Ar*C*), 129.36 (s, Ar*C*), 128.59 (s, Ar*C*), 126.65 (m, Ar*C*), 121.35 (s, Ar*C*), 117.30 (s, Ar*C*), 113.87 (s, Ar*C*), 112.94 (s, Ar*C*), 112.27 (s, Ar*C*), 67.82 (s, CH_2), 60.94 (s, CH_2), 28.01 (br s, *C*H(CH$_3$)$_2$), 25.81 (br s, *C*H(CH$_3$)$_2$), 21.58 (s, CH(*C*H$_3$)$_2$), 20.83 (d, $^2J_{PC}$ = 8.6 Hz, CH(*C*H$_3$)$_2$), 19.87 (br s, CH(*C*H$_3$)$_2$), 18.69 (br s, CH(*C*H$_3$)$_2$); $^{31}P\{^1H\}$ NMR (toluene-d_8, 202 MHz, -60°C): δ (ppm) = 30.27 (s, 1P), 20.04 (s, 1P). IR (KBr Pellets, cm^{-1}): 3054 (m), 2955 (s), 2865 (s), 2777 (m), 1915 (m), 1585 (s), 1464 (s), 1282 (s), 1257 (s), 1188 (m), 1094 (m), 1031 (s), 957 (m), 878 (s), 820 (m), 737 (s), 607 (s), 524 (m),

472 (m). Anal. calcd for $C_{42}H_{57}N_5P_2ScNi$ (796.54 g/mol): C, 63.33; H, 7.09; N, 8.79. Found: C, 62.97; H, 7.37; N, 8.42.

Synthesis of 5: *p*-Methylphenylacetylene (6.7 mg, 0.058 mmol) in 1 mL of tetrahydrofuran was added to a solution of **2** (40 mg, 0.029 mmol) in 4 mL of tetrahydrofuran at room temperature. The resulting blue reaction mixture was allowed to stir at room temperature for 1h. The solution was concentrated under reduced pressure to about 1 mL, and slow diffusion of pentane into the solution at room temperature afforded **5** as dark blue crystals. Yield: 33 mg (75%). ^{1}H NMR (toluene-d_8, 500 MHz, -30 °C): δ (ppm) = 8.65 (br s, 1H, Ar*H*), 7.65-7.63 (m, 2H, Ar*H*), 7.52-7.47 (m, 3H, Ar*H*), 7.22 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 6.81-6.56 (m, 4H, ArCC*H* and Ar*H*), 6.74 (d, $^3J_{HH}$ = 6.5 Hz, 2H, Ar*H*), 6.57 (t, $^3J_{HH}$ = 6.5 Hz, 1H, Ar*H*), 5.67 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar*H*), 4.50 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2), 4.23 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2), 3.98-3.85 (m, 5H, CH_2), 3.65-3.58 (m, 1H, CH_2), 2.72 (d, $^2J_{HH}$ = 13.0 Hz, 1H, CH_2), 2.51 (d, $^2J_{HH}$ = 11.5 Hz, 1H, CH_2), 2.19 (s, 3H, ArCH_3), 1.93-1.91 (m, 3H, CH(CH$_3$)$_2$), 1.56 (br s, 1H, CH(CH$_3$)$_2$), 1.30-1.21 (m, 6H, CH(CH_3)$_2$), 1.18-1.08 (m, 9H, CH(CH_3)$_2$), 1.06-1.02 (m, 3H, CH(CH_3)$_2$), 1.00-0.95 (m, 6H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (toluene-d_8, 126 MHz, 25°C): δ (ppm) = 201.14 (s, Ar*C*), 163.49 (s, Ar*C*), 157.18 (s, Ar*C*), 145.36 (s, Ar*C*), 138.19 (s, Ar*C*), 135.77 (m, Ar*C*), 134.40 (s, Ar*C*), 130.78 (s, Ar*C*), 130.23 (s, Ar*C*), 129.27 (s, Ar*C*), 129.15 (s, Ar*C*), 128.46 (s, Ar*C*), 125.61 (s, Ar*C*), 121.21 (s, Ar*C*), 120.60 (s, Ar*C*), 114.37 (s, Ar*C*), 112.37 (s, Ar*C*), 111.37 (br s, Ar*C*), 59.93 (s, *C*H_2), 29.01 (br s, *C*H(CH$_3$)$_2$), 25.87 (br s, *C*H(CH$_3$)$_2$), 21.34 (s, CH(*C*H$_3$)$_2$), 21.17 (s, CH(*C*H$_3$)$_2$), 19.15 (s, CH(*C*H$_3$)$_2$), 18.10 (br s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (toluene-d_8, 202 MHz, -60°C): δ (ppm) = 18.58 (s, 1P), 13.73 (s, 1P). IR (KBr Pellets, cm^{-1}): 3055 (m), 3014 (m), 2956 (s), 2922 (s), 2866 (s), 2785 (m), 1595 (s), 1563 (m), 1507 (m), 1477 (s), 1442 (s), 1372 (s), 1251 (s), 1165 (m), 1099 (m), 1041 (s), 991 (m), 962 (m), 922 (m), 880 (s), 823 (m), 746 (s), 641 (s), 609 (s), 559 (m), 514 (m), 473 (m). Anal. calcd for $C_{43}H_{57}N_4P_2ScNi$ (795.55 g/mol): C, 64.92; H, 7.22; N, 7.04. Found: C, 64.58; H, 7.05; N, 6.60.

Synthesis of 6: Benzophenone (10.5 mg, 0.058 mmol) in 1 mL of benzene was added to a solution of **4** (40 mg, 0.029 mmol) in 4 mL of benzene at room temperature. The resulting red reaction mixture was allowed to stirr at room temperature for 2h. Volatiles were removed under reduced pressure, and the residue was washed with *n*-hexane to afford **6** as a red solid. Yield: 35 mg (70 %). Crystals suitable for the X-ray diffraction analysis were grown by slow diffusion of pentane into the benzene solution at room temperature. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ (ppm) = 7.27 (d, $^3J_{HH}$ = 7.60 Hz, 4H, Ar*H*), 7.20 (t, $^3J_{HH}$ = 7.2 Hz, 4H, Ar*H*), 7.14-7.11 (m, 3H, Ar*H*), 6.92 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 6.84 (t, $^3J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 6.70 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 6.33 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 6.17 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.13 (t, $^3J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 4.66 (d, $^2J_{HH}$ = 11.2 Hz, 2H, CH_2), 3.78 (dt, $^2J_{HH}$ = 12.8 Hz, $^2J_{PH}$ = 4.2 Hz, 2H, PCH_2), 3.70 (s, 2H, CH_2), 3.40 (d, $^2J_{HH}$ = 11.2 Hz, 2H, CH_2), 3.21 (dt, $^2J_{HH}$ = 12.8 Hz, $^2J_{PH}$ = 5.0 Hz, 2H, PCH_2), 1.93-1.86 (m, 4H, CH(CH$_3$)$_2$), 1.26-1.14 (m, 24H, CH(CH_3)$_2$); ^{1}H NMR (C$_6$D$_6$, 500 MHz, 25 °C): δ (ppm) = 7.57 (d, $^3J_{HH}$ = 7.50 Hz, 4H, Ar*H*), 7.28 (t, $^3J_{HH}$ = 7.5 Hz, 4H, Ar*H*), 7.23 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, Ar*H*), 7.15-7.12 (m, 2H, Ar*H*, partly overlapped with the solvent peaks), 7.03 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, Ar*H*), 6.57-6.53 (m, 4H, ArH), 6.51 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 6.32 (t, $^3J_{HH}$ = 8.7 Hz, 1H, Ar*H*), 5.52 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 4.80 (d, $^2J_{HH}$ = 11.5 Hz, 2H, CH_2), 4.00 (dt, $^2J_{HH}$ = 12.5 Hz, $^2J_{PH}$ = 4.0 Hz, 2H, PCH_2), 3.43 (s, 2H, CH_2), 3.39 (dt, $^2J_{HH}$ = 13.0 Hz, $^2J_{PH}$ = 5.0 Hz, 2H, PCH_2), 3.19 (d, $^2J_{HH}$ = 11.5 Hz, 2H, CH_2), 1.78 (m, 2H, CH(CH$_3$)$_2$), 1.69 (m, 2H, CH(CH$_3$)$_2$), 1.25-1.17 (m, 18H, CH(CH_3)$_2$), 1.11 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (THF-d_8, 100 MHz, 25°C): δ (ppm) = 170.27 (s, Ar*C*), 159.86 (m, Ar*C*), 158.25 (s, Ar*C*), 151.95 (s, Ar*C*), 138.00 (s, Ar*C*), 131.41 (s, Ar*C*), 130.17 (s, Ar*C*), 129.60 (s, Ar*C*), 129.20 (s, Ar*C*), 128.18 (s, Ar*C*), 126.86 (s, Ar*C*), 123.75 (s, Ar*C*), 122.33 (s, Ar*C*), 117.91 (s, Ar*C*), 112.91 (s, Ar*C*), 112.10 (s, Ar*C*), 93.06 (s, O*C*), 65.17 (s, *C*H_2), 57.77 (s, *C*H_2), 47.47 (m, P*C*H$_2$), 21.91 (m, CH(*C*H$_3$)$_2$), 21.51 (s, CH(*C*H$_3$)$_2$), 21.19 (s, CH(*C*H$_3$)$_2$), 20.74 (s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, 25°C): δ (ppm) = 31.01 (s, 2P). IR

(KBr Pellets, cm^{-1}): 3060 (m), 2955 (s), 2872 (s), 2093 (s), 1592 (s), 1468 (s), 1383 (m), 1310 (s), 1259 (m), 1167 (m), 1049 (s), 943 (m), 883 (m), 755 (m), 706 (m), 642 (m), 611 (m), 490 (m). Anal. calcd for $C_{94}H_{118}N_{10}O_2P_4Sc_2Ni_2$ (1751.24 g/mol): C, 64.47; H, 6.79; N, 8.00. Found: C, 64.59; H, 6.99; N, 7.65.

Synthesis of 7: Azobenzene (10.5 mg, 0.058 mmol) in 1 mL of toluene was added to a solution of **2** (40 mg, 0.029 mmol) in 4 mL of toluene at room temperature. The resulting yellow reaction mixture was allowed to stir at room temperature for 4h. Volatiles were removed under reduced pressure, and the residue was washed with *n*-hexane to afford **7** as a yellow solid. Yield: 48 mg (95%). Crystals suitable for the X-ray diffraction analysis were grown from mixed toluene/hexane solution at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ (ppm) = 7.56 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.47-7.43 (m, 2H, Ar*H*), 7.19 (t, $^3J_{HH}$ = 7.0 Hz, 2H, Ar*H*, partly overlapped with the solvent peak), 7.03-6.99 (m, 4H, Ar*H*), 6.96 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.85-6.77 (m, 4H, Ar*H*), 6.74-6.72 (m, 2H, Ar*H*), 6.65 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 6.62 (t, $^3J_{HH}$ = 7.5, 1H, Ar*H*), 6.07 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 4.66 (d, $^2J_{HH}$ = 11.5 Hz, 1H, CH_2), 4.54 (dd, $^2J_{HH}$ = 12.5 Hz, $^2J_{PH}$ = 5.5 Hz, 1H, PCH_2), 4.44 (d, $^3J_{HH}$ = 11.5 Hz, 1H, CH_2), 4.38 (d, $^2J_{HH}$ = 13.5 Hz, 1H, PCH_2), 4.35 (d, $^2J_{HH}$ =15.5 Hz, 1H, CH_2), 3.76 (dd, $^2J_{HH}$ = 13.0 Hz, $^2J_{PH}$ = 7.5 Hz, 1H, PCH_2), 3.42 (app. t, $^2J_{HH}$ = $^2J_{PH}$ = 13.0 Hz, 1H, PCH_2), 2.81 (d, $^3J_{HH}$ = 11.5 Hz, 1H, CH_2), 2.65 (d, $^2J_{HH}$ = 11.5 Hz, 1H, CH_2), 2.53 (d, $^2J_{HH}$ = 15.5 Hz, 1H, CH_2), 1.86-1.81 (m, 1H, CH(CH$_3$)$_2$), 1.72-1.68 (m, 1H, CH(CH$_3$)$_2$), 1.49-1.46 (m, 2H, CH(CH$_3$)$_2$), 1.28 (dd, $^2J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 12.5 Hz, 3H, CH(CH_3)$_2$), 1.13-1.07 (m, 6H, CH(CH_3)$_2$), 0.97 (dd, $^2J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 11.5 Hz, 3H, CH(CH_3)$_2$), 0.86 (dd, $^2J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 14.5 Hz, 3H, CH(CH_3)$_2$), 0.78-0.74 (m, 6H, CH(CH_3)$_2$), 0.35 (dd, $^2J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 13.5 Hz, 3H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 25°C): δ (ppm) = 202.07 (d, J_{PC} = 11.1 Hz, Ar*C*), 157.81 (d, J_{PC} = 14.4 Hz, Ar*C*), 154.83 (s, Ar*C*), 154.39 (d, J_{PC} = 7.1 Hz, Ar*C*), 151.19 (s, Ar*C*), 149.71 (s, Ar*C*), 137.63 (s, Ar*C*), 133.17 (s, Ar*C*), 132.86 (s, Ar*C*), 131.03 (s, Ar*C*), 129.89 (s, Ar*C*), 128.70 (s, Ar*C*), 128.59 (s, Ar*C*), 124.63 (s, Ar*C*), 123.15 (s, Ar*C*), 122.58 (s, Ar*C*), 122.39 (s, Ar*C*), 122.16 (s, Ar*C*), 121.61 (d, J_{PC} = 3.8 Hz, Ar*C*), 116.20 (s, Ar*C*), 115.85 (s, Ar*C*), 115.59 (s, Ar*C*), 114.79 (s, Ar*C*), 113.94 (s, Ar*C*), 62.86 (s, *C*H$_2$), 59.55 (s, *C*H$_2$), 58.50 (s, *C*H$_2$), 52.02 (d, $^1J_{PC}$ = 40.3 Hz, P*C*H$_2$), 47.06 (d, $^1J_{PC}$ = 10.3 Hz, P*C*H$_2$), 24.38 (d, $^1J_{PC}$ = 15.3 Hz, *C*H(CH$_3$)$_2$), 24.04 (d, $^1J_{PC}$ = 16.8 Hz, *C*H(CH$_3$)$_2$), 23.38 (d, $^1J_{PC}$ = 11.5 Hz, *C*H(CH$_3$)$_2$), 23.24 (d, $^1J_{PC}$ = 14.7 Hz, *C*H(CH$_3$)$_2$), 21.29 (d, $^2J_{PC}$ = 17.5 Hz, CH(*C*H$_3$)$_2$), 21.26 (s, *C*H(CH$_3$)$_2$), 20.79 (d, $^2J_{PC}$ = 13.7 Hz, CH(*C*H$_3$)$_2$), 20.13 (d, $^2J_{PC}$ = 12.2 Hz, CH(*C*H$_3$)$_2$), 19.17 (d, $^2J_{PC}$ = 6.2 Hz, CH(*C*H$_3$)$_2$), 18.97 (s, CH(*C*H$_3$)$_2$), 18.60 (s, CH(*C*H$_3$)$_2$), 18.14 (s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25°C): δ (ppm) = 39.69 (s, 1P), -7.55 (s, 1P). IR (KBr Pellets, cm^{-1}): 3058 (m), 3014 (m), 2954 (s), 2870 (s), 1588 (s), 1542 (m), 1474 (s), 1373 (m), 1291 (s), 1243 (s), 1161 (m), 1117 (m), 1026 (s), 953 (m), 880 (s), 824 (m), 752 (s), 698 (m), 612 (m), 537 (m), 458 (m). Anal. calcd for $C_{46}H_{59}N_6P_2ScNi$ (861.69 g/mol): C, 64.12; H, 6.90; N, 9.75. Found: C, 64.51; H, 7.18; N, 9.37.

2. Spectroscopic Data

2.1 NMR Spectra

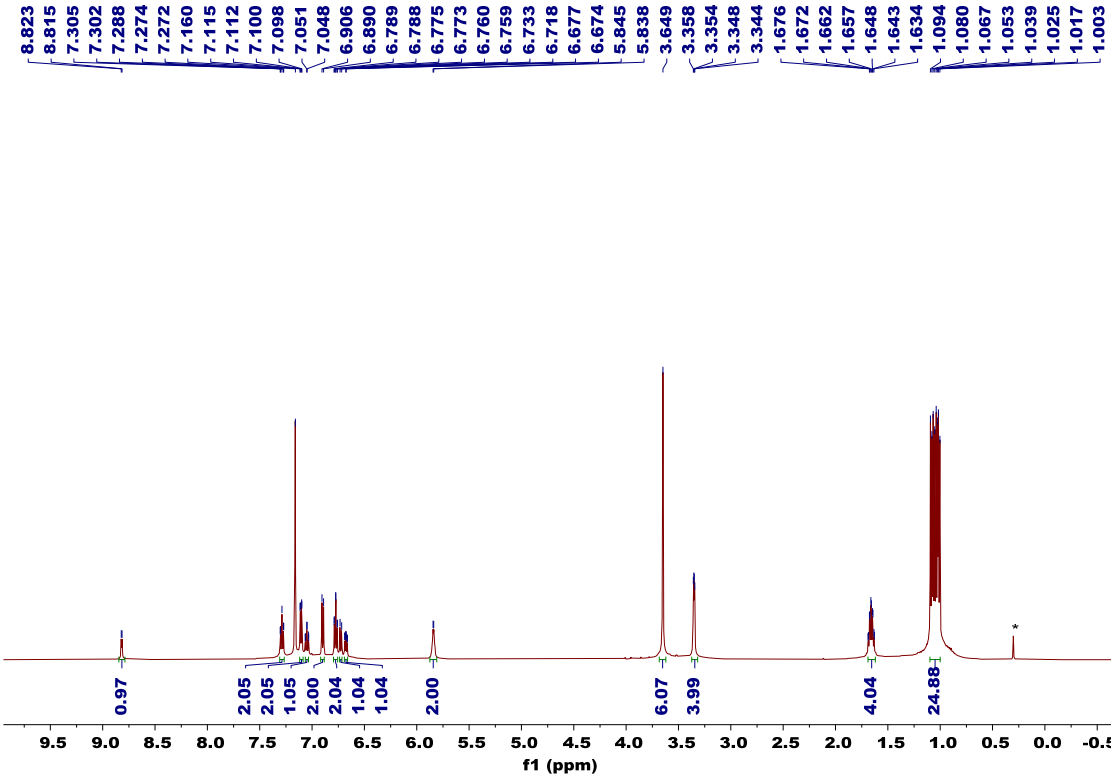

Figure S1. ^{1}H NMR spectrum of **LH$_3$** in C_6D_6 at 25 °C. (* denotes small amount of silicone grease)

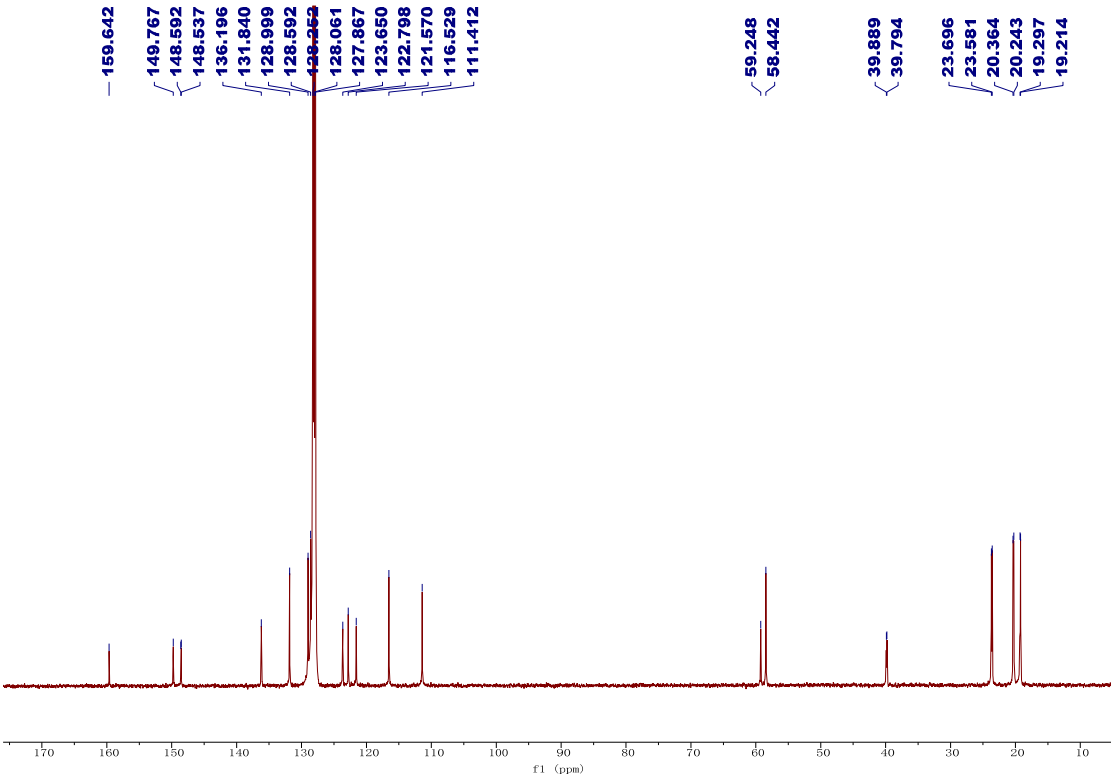

Figure S2. ^{13}C{^{1}H} NMR spectrum of **LH$_3$** in C_6D_6 at 25 °C.

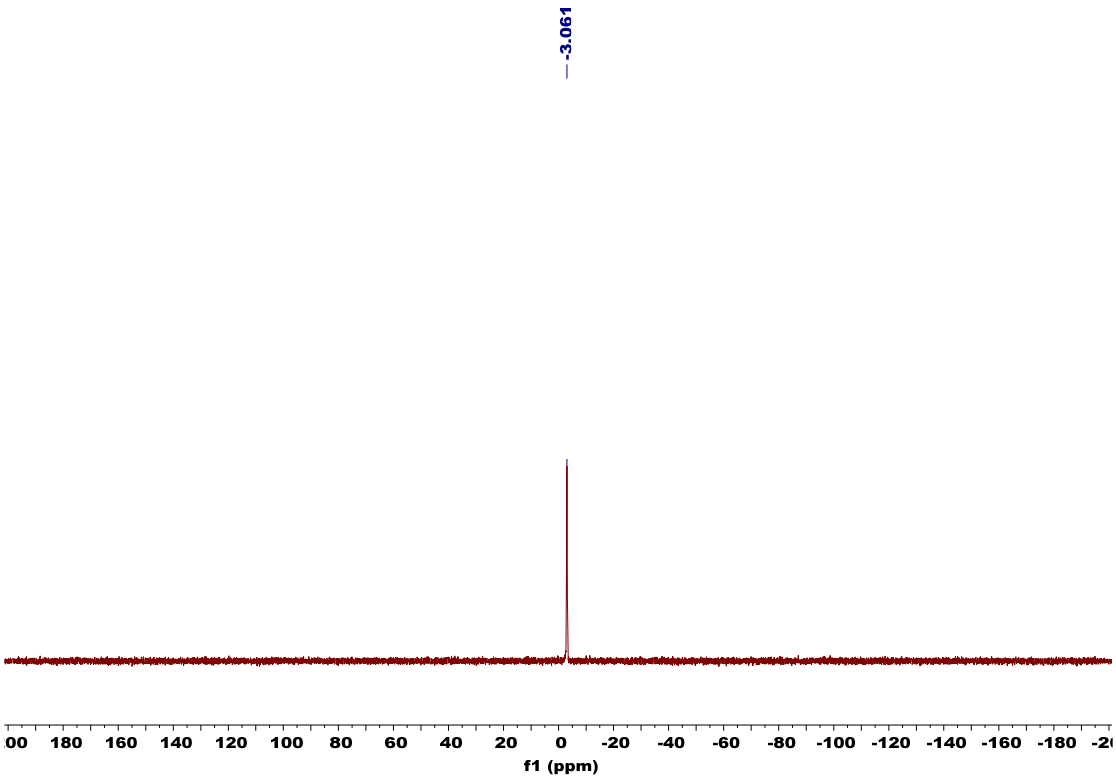

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **LH_3** in C_6D_6 at 25 °C.

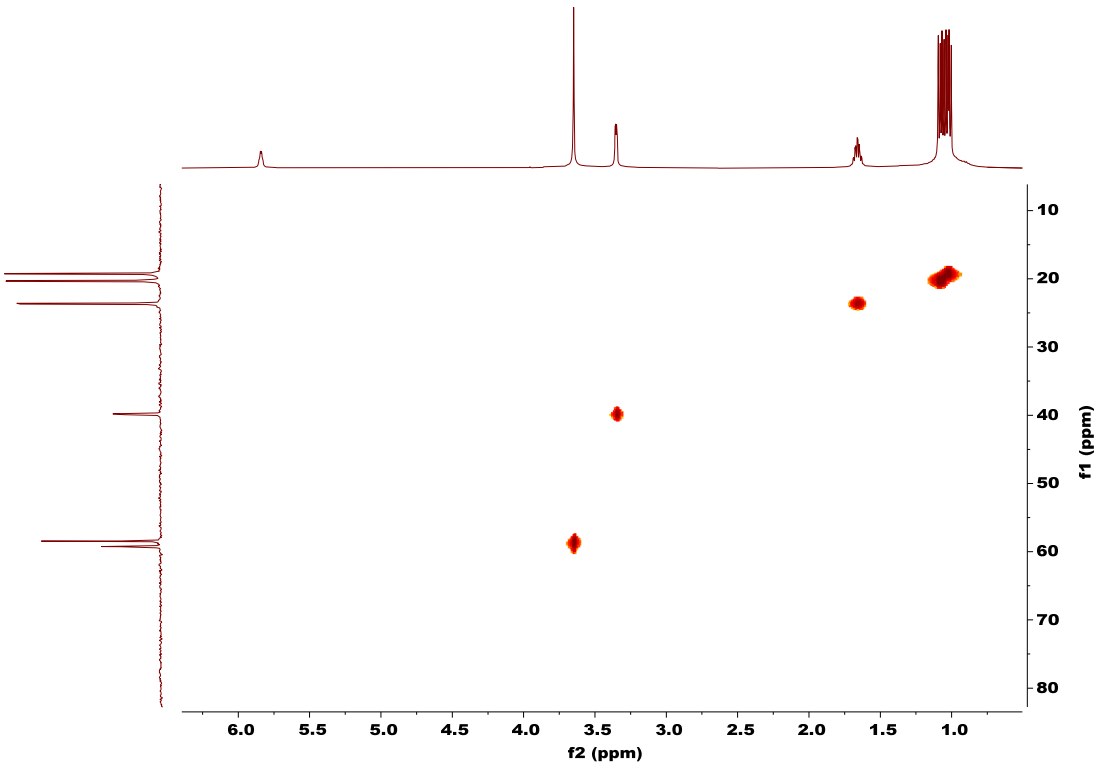

Figure S4. HSQC spectrum of **LH_3** in C_6D_6 at 25 °C (Note: data of the aromatic region were not included since it's not very helpful for assigning the peaks in the ^{1}H NMR).

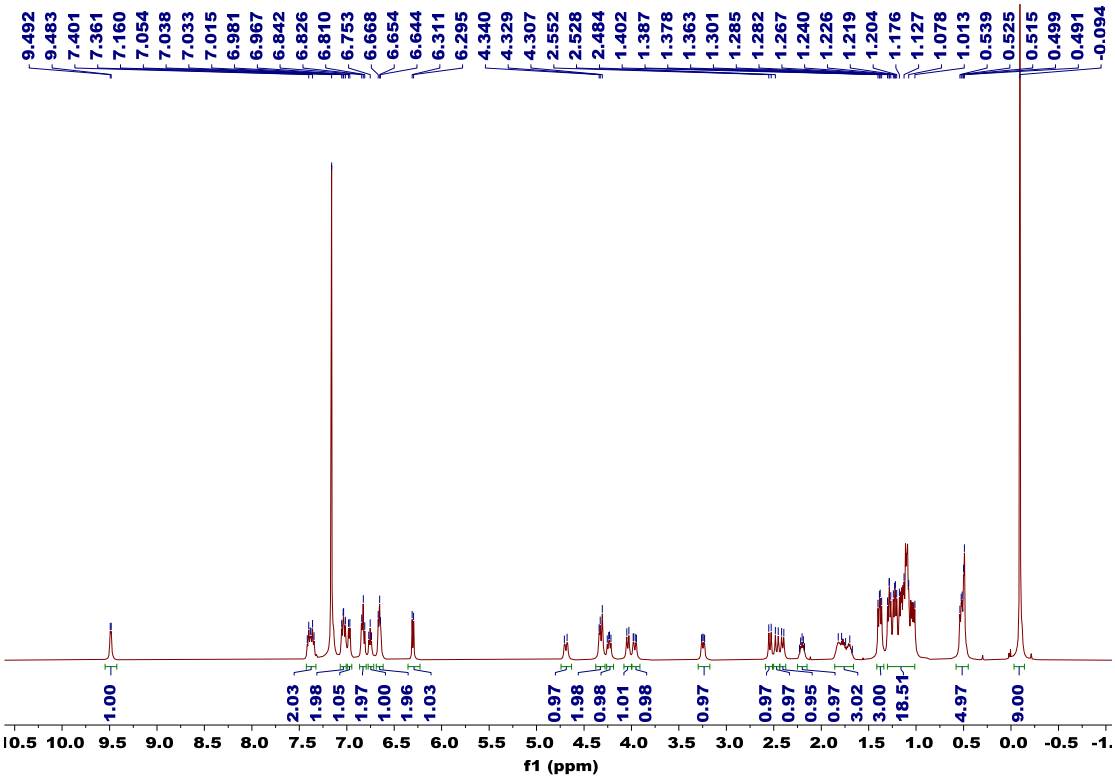

Figure S5. ^{1}H NMR spectrum of **1** in C_6D_6 at 25 °C.

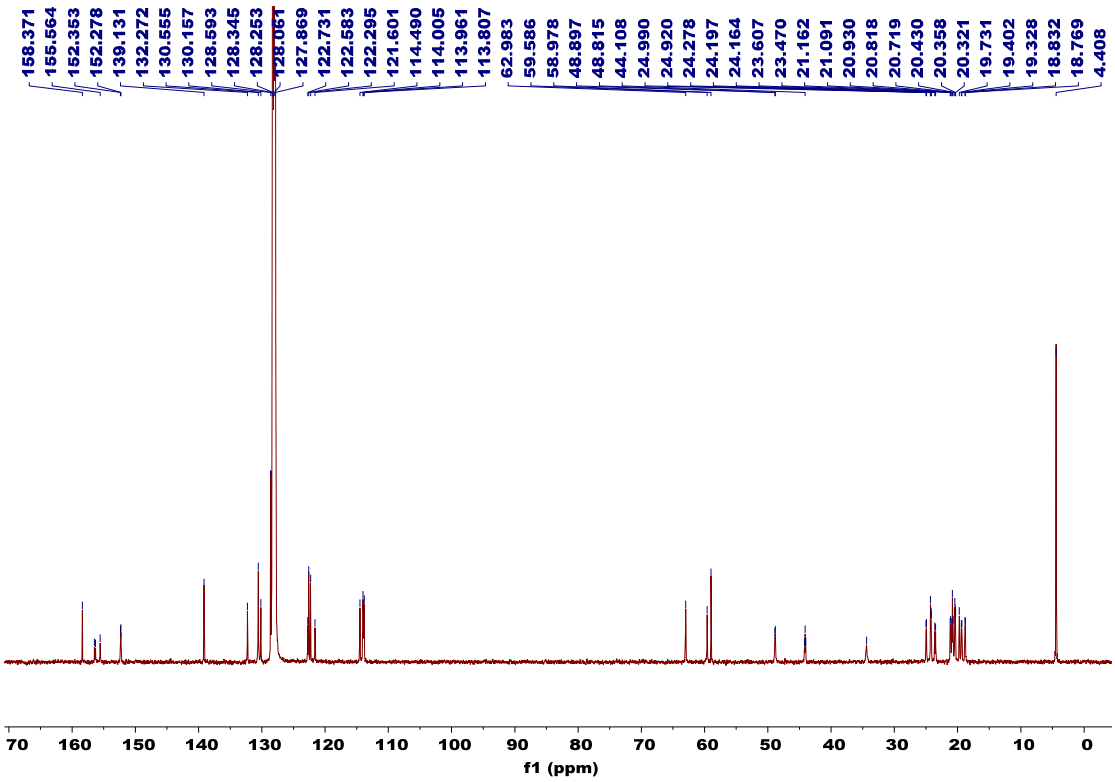

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 25 °C.

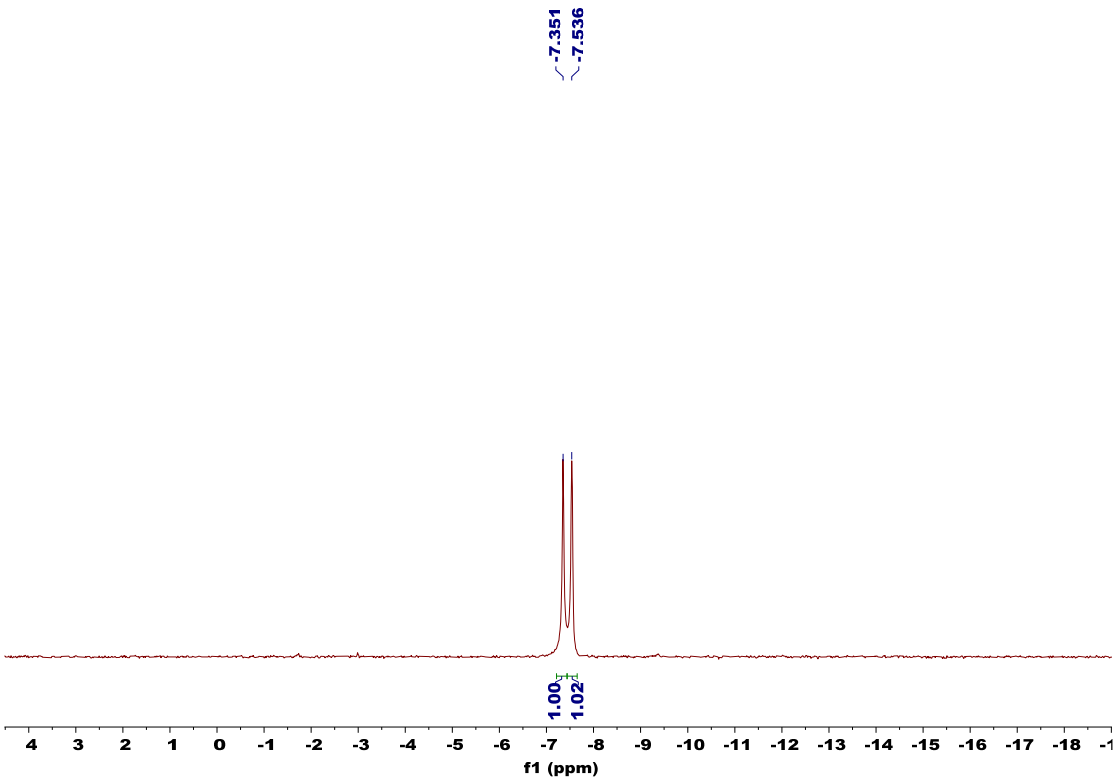

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 25 °C.

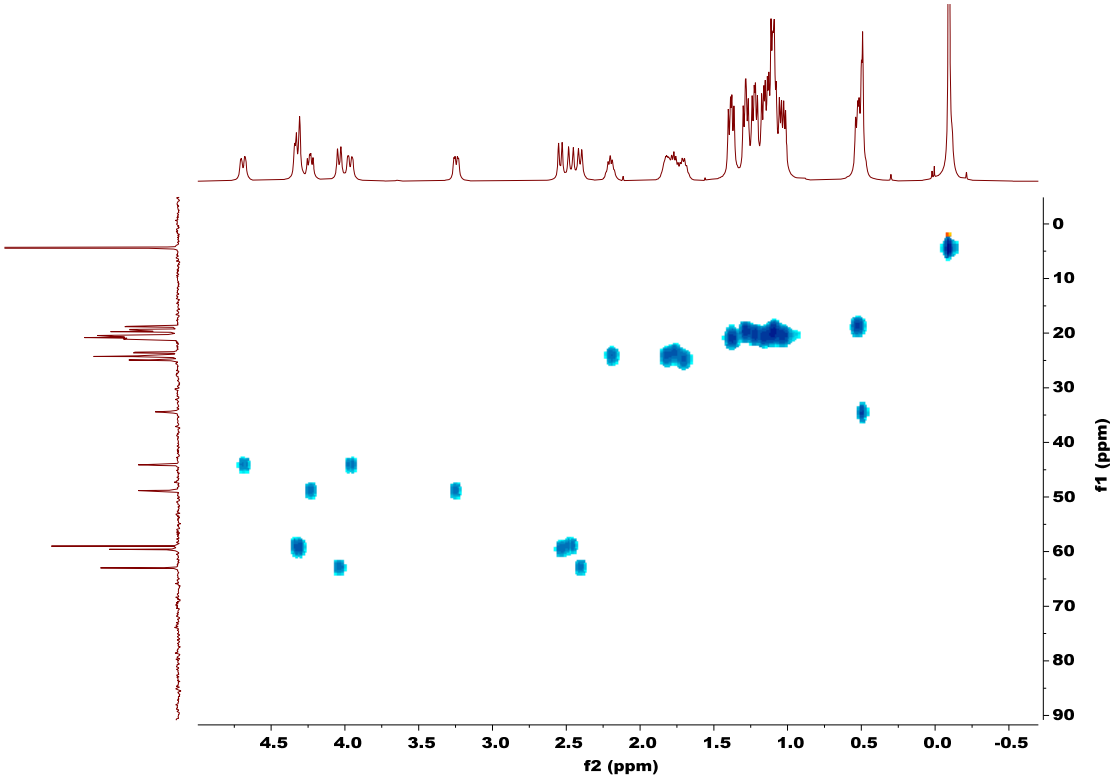

Figure S8. HSQC spectrum of **1** in C_6D_6 at 25 °C (Note: data of the aromatic region were not included since it's not very helpful for assigning the peaks in the ^{1}H NMR).

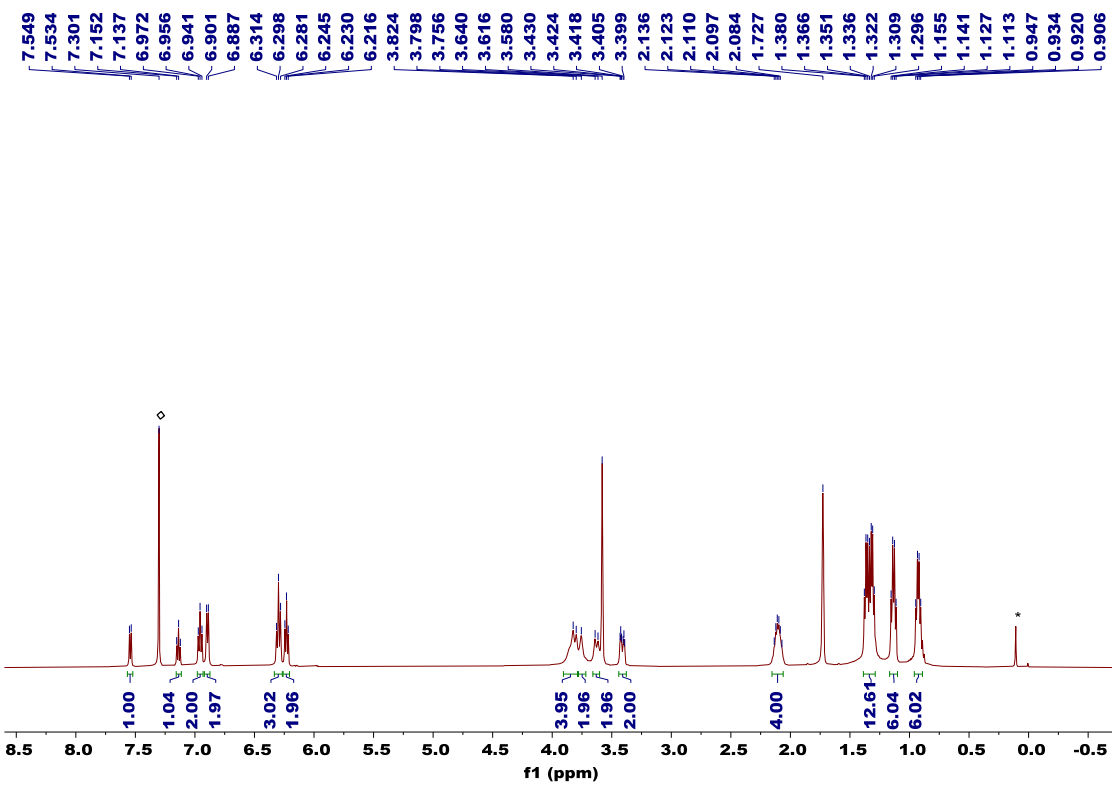

Figure S9. ^{1}H NMR spectrum of **2** in THF-d_8 at 25 °C (* denotes small amount of silicone grease, ◇ denotes small amount of benzene).

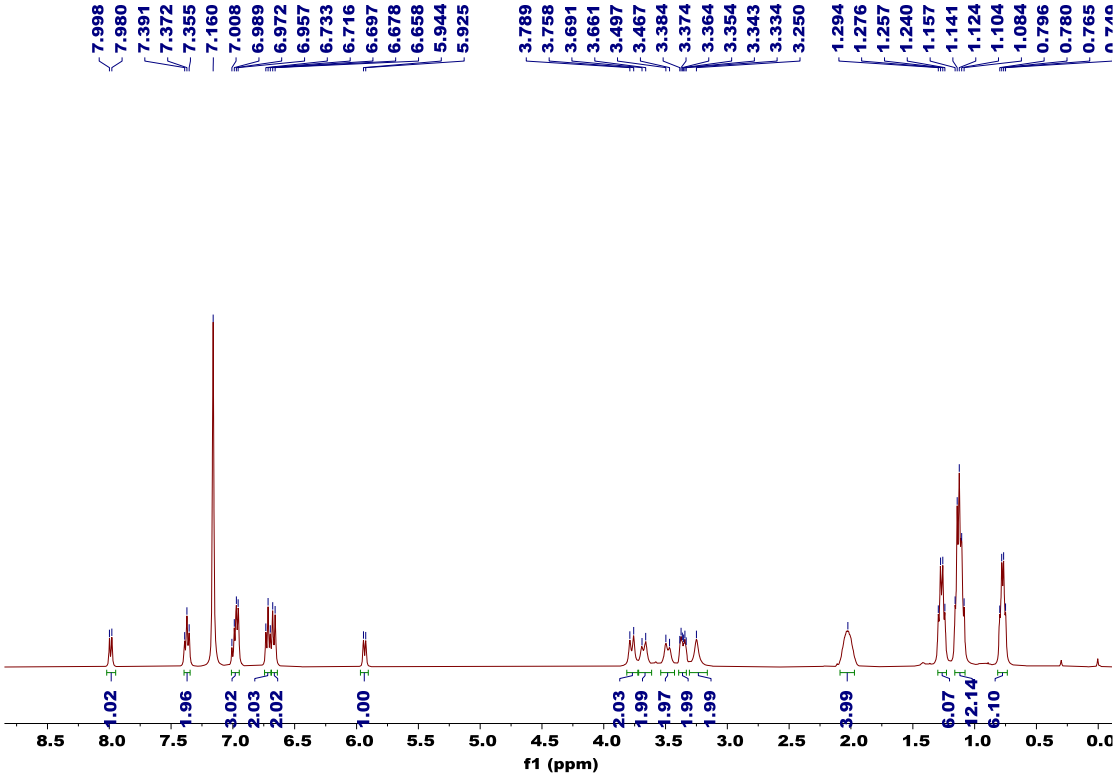

Figure S10. ^{1}H NMR spectrum of **2** in C_6D_6 at 25 °C

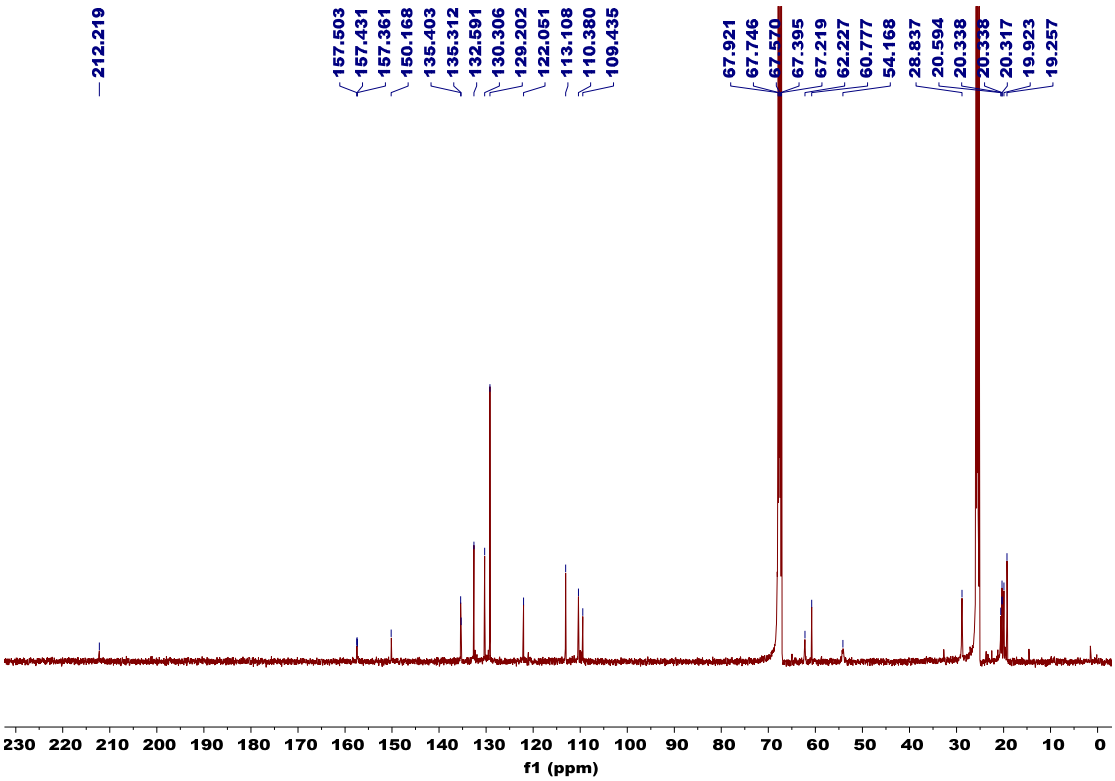

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in THF-d_8 at 25 °C.

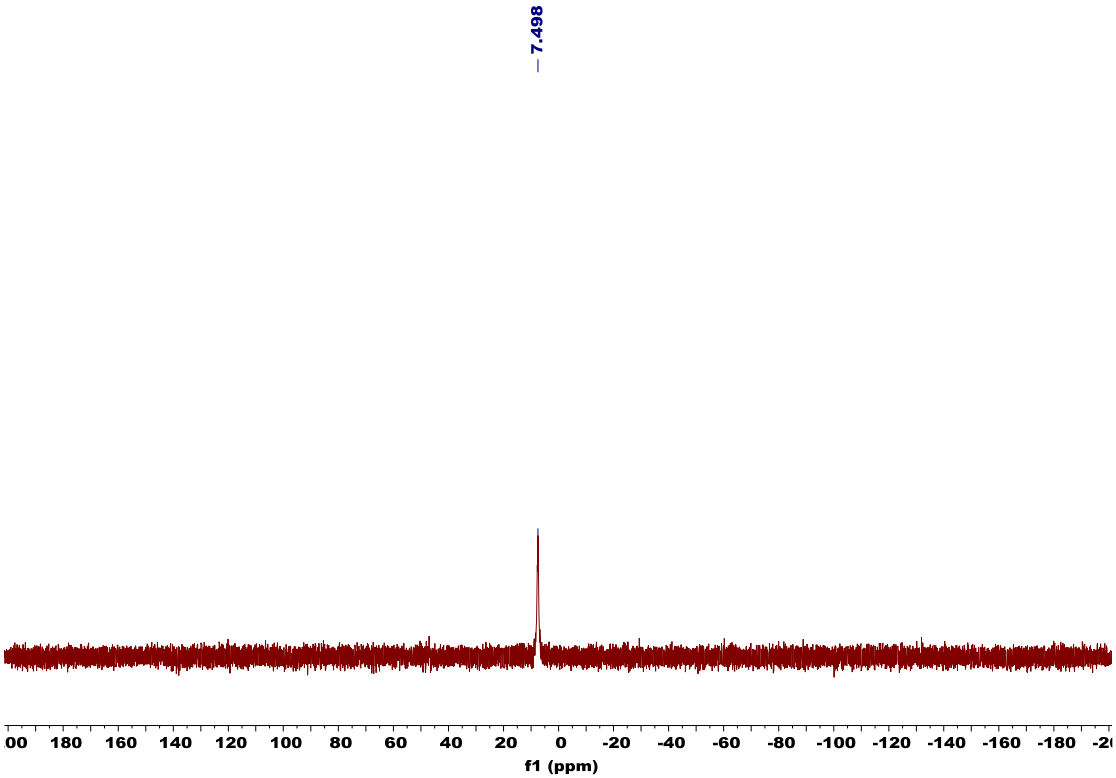

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in THF-d_8 at 25 °C.

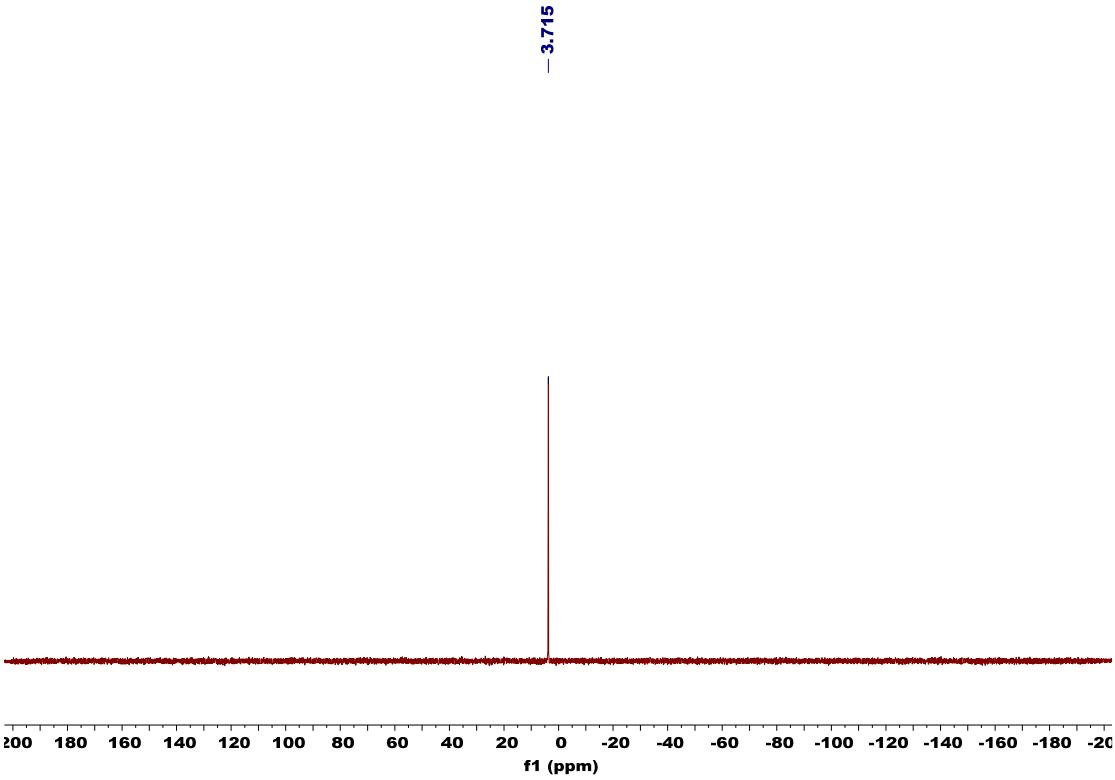

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 25 °C.

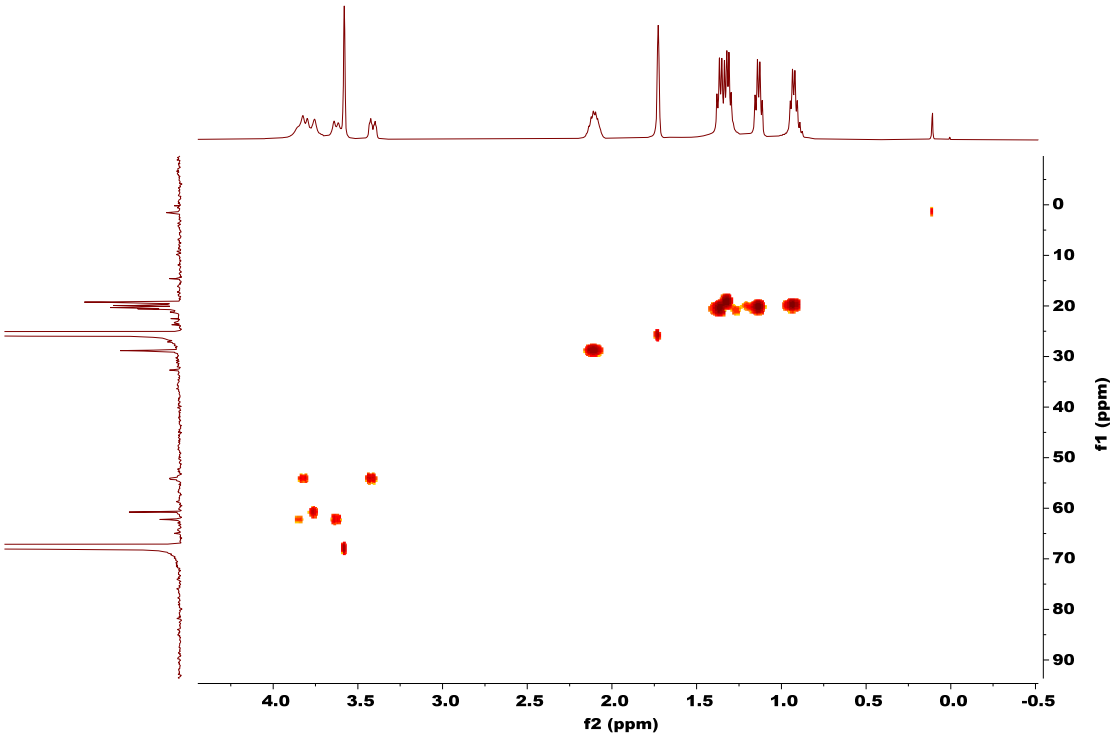

Figure S14. HSQC spectrum of **2** in THF-d_8 at 25 °C (Note: data of the aromatic region were not included since it's not very helpful for assigning the peaks in the ^{1}H NMR).

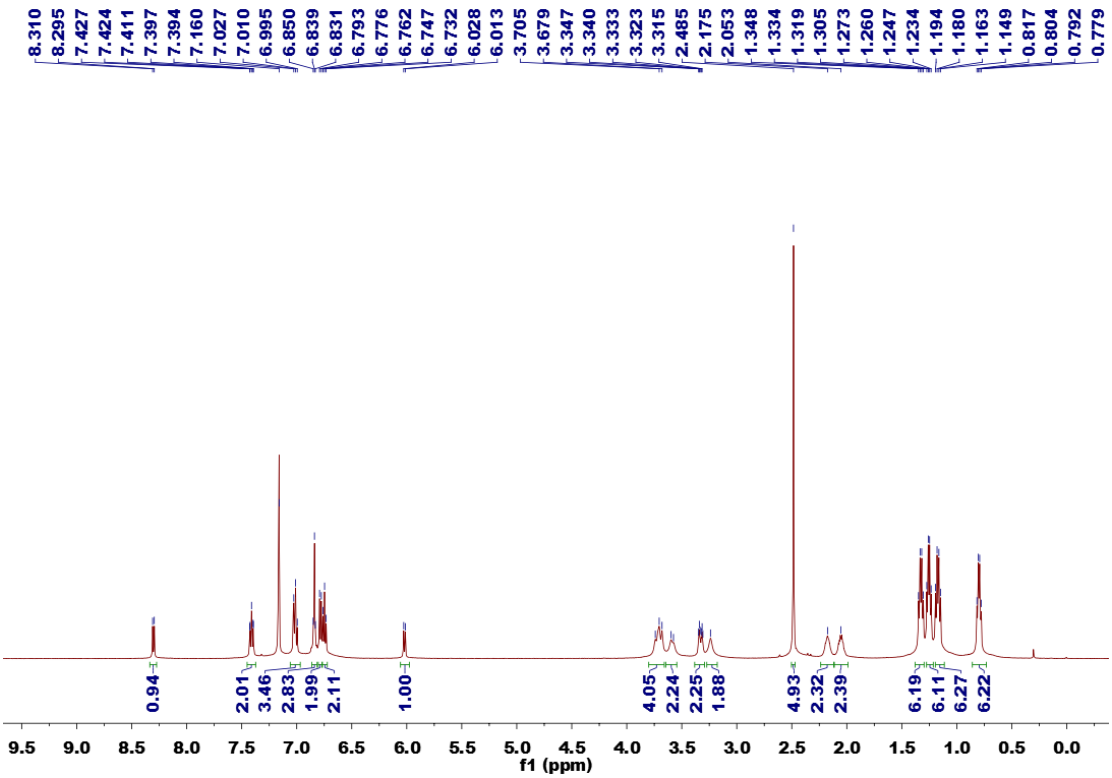

Figure S15. ^{1}H NMR spectrum of **3** in C_6D_6 at 25 °C.

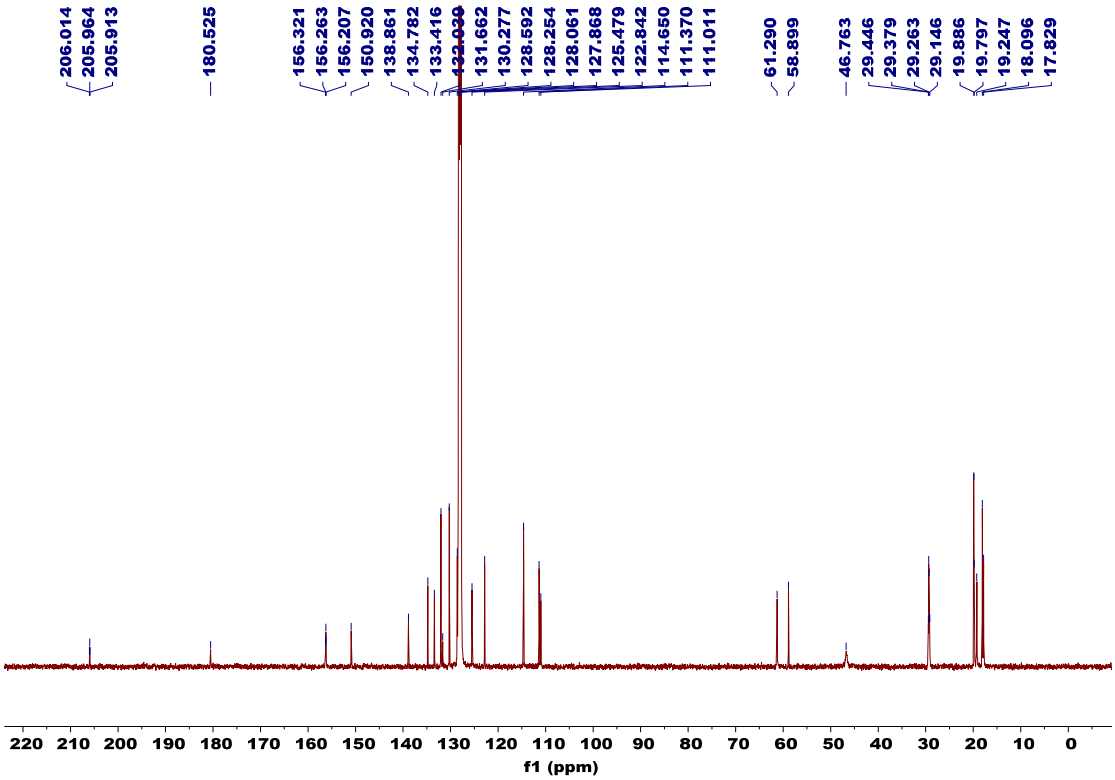

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 25 °C.

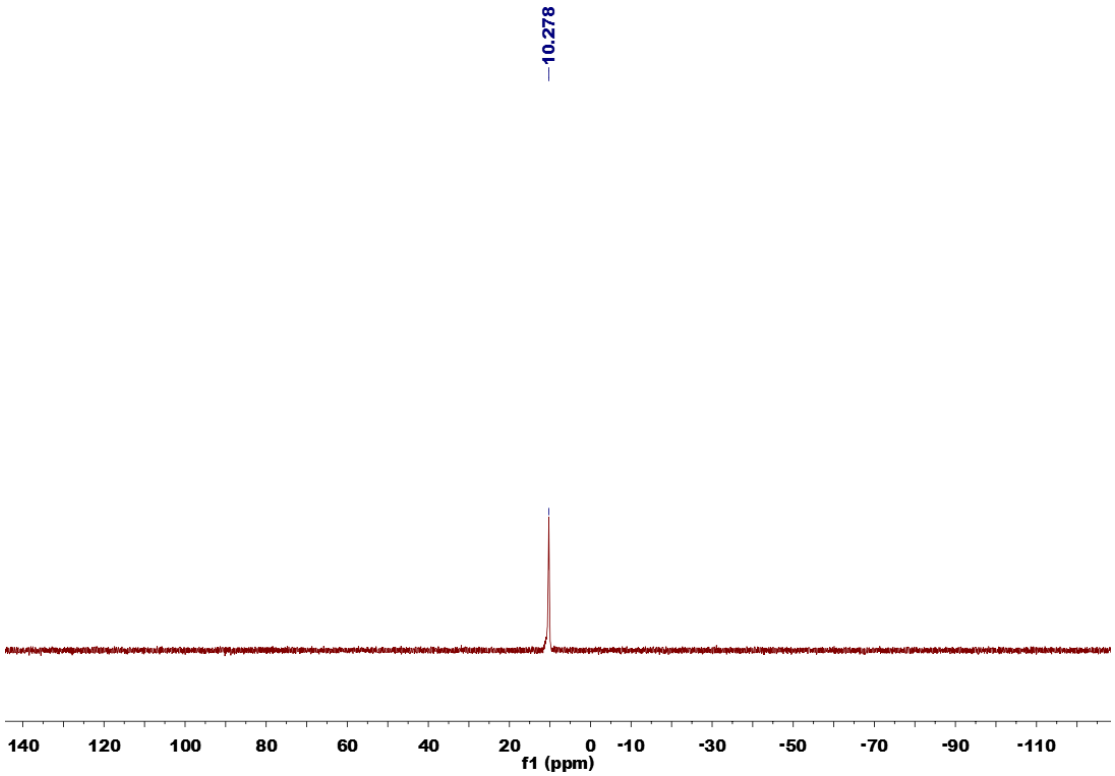

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 25 °C.

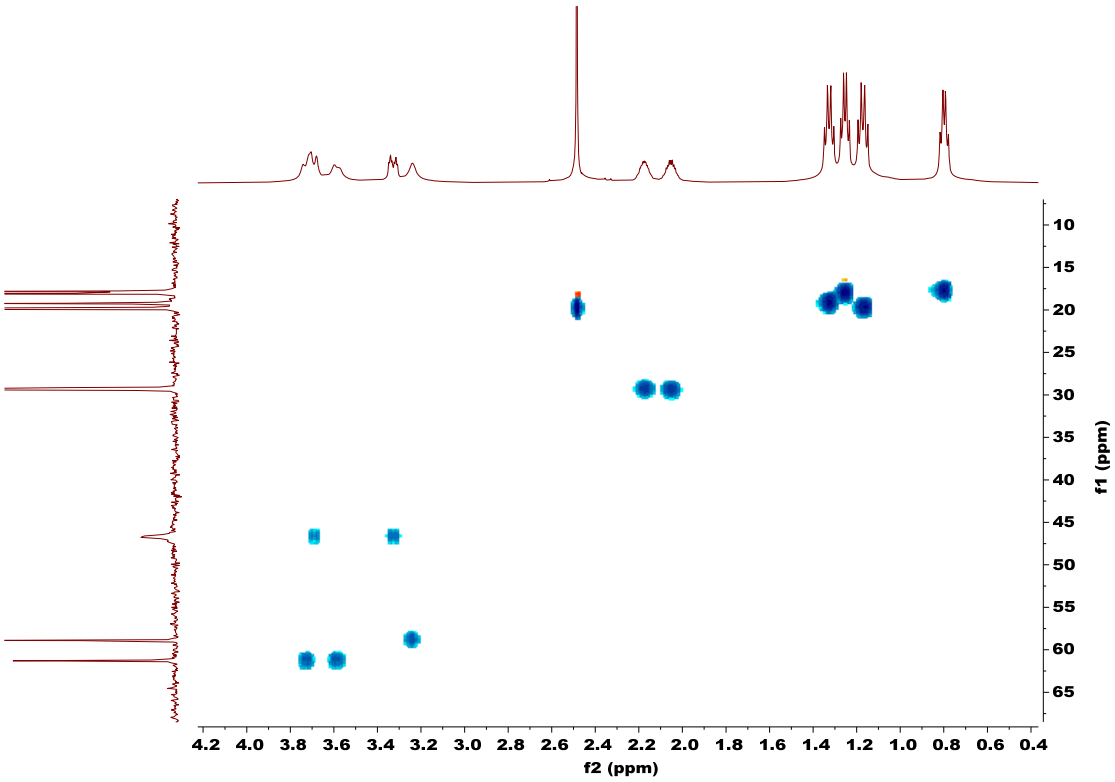

Figure S18. HSQC spectrum of **3** in C_6D_6 at 25 °C (Note: data of the aromatic region were not included since it's not very helpful for assigning the peaks in the ^{1}H NMR).

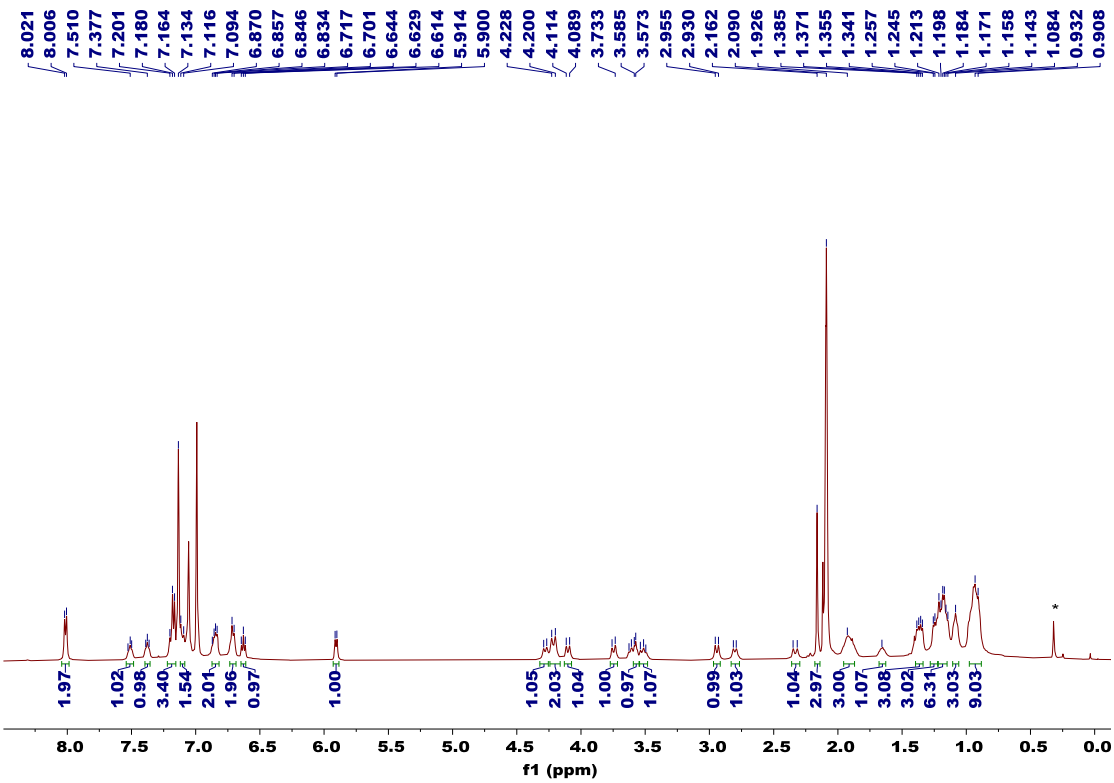

Figure S19. ^{1}H NMR spectrum of **4** in toluene-d_8 at -30 °C. (*denotes small amount of silicone grease)

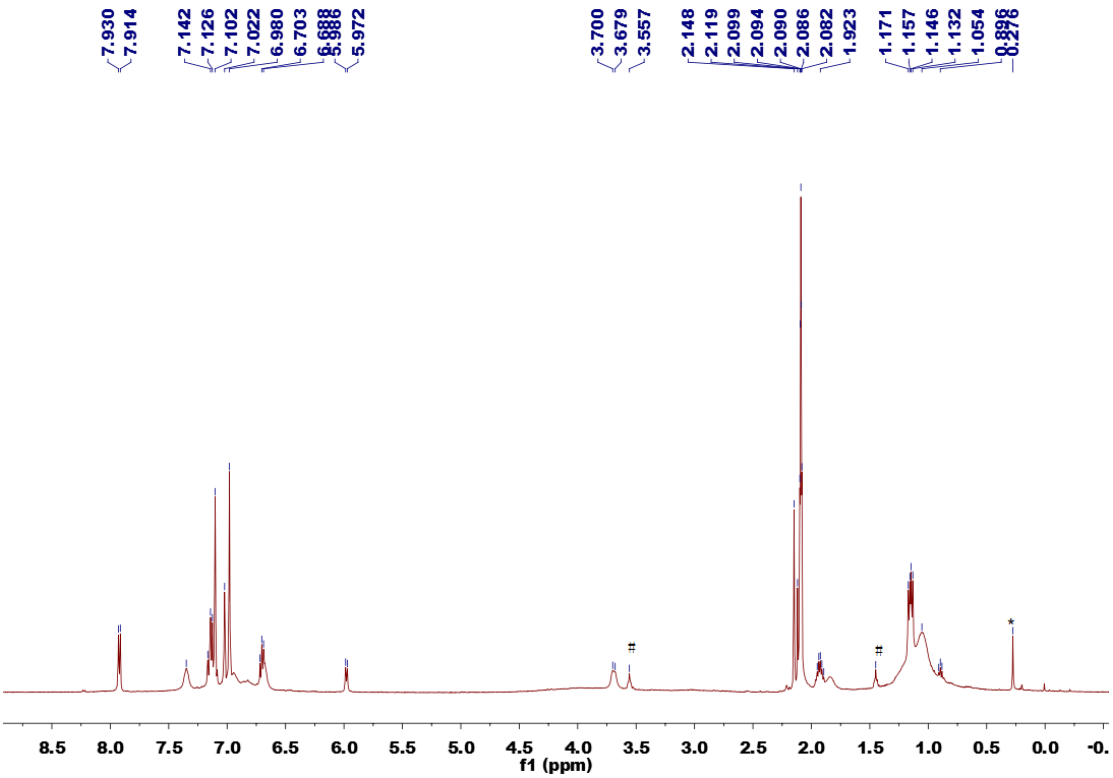

Figure S20. ^{1}H NMR spectrum of **4** in toluene-d_8 at 25 °C (*denotes small amount of silicone grease, # denotes small amount of THF).

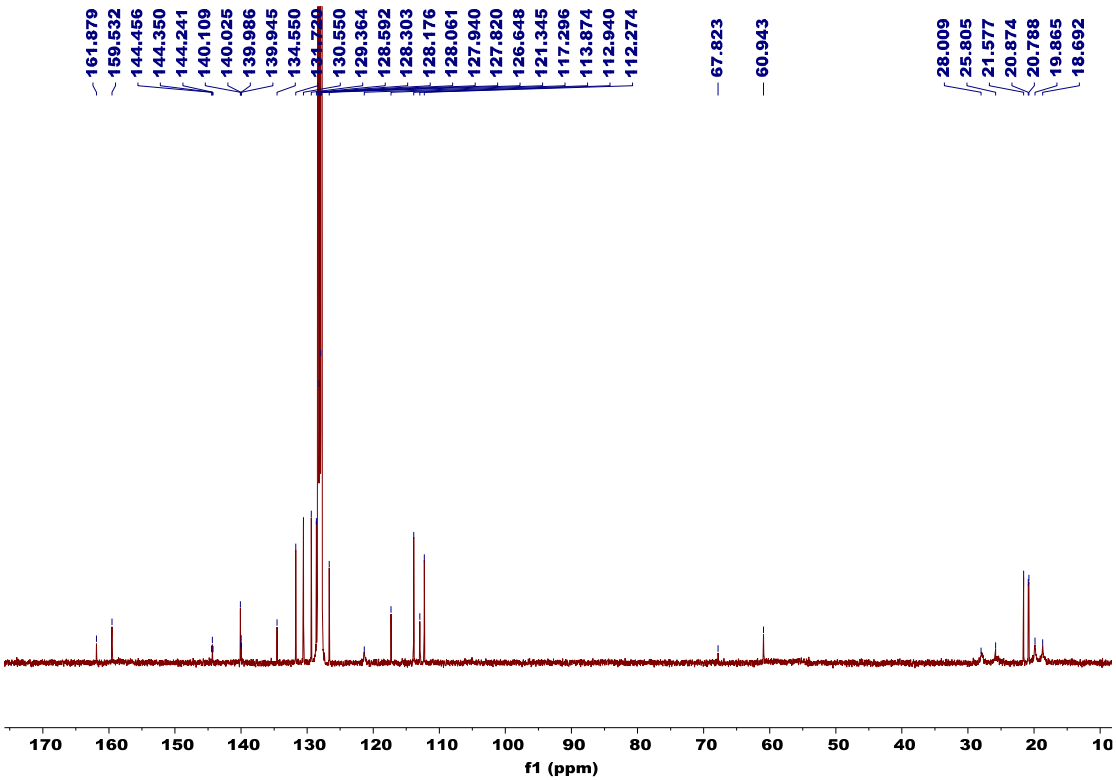

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 25 °C.

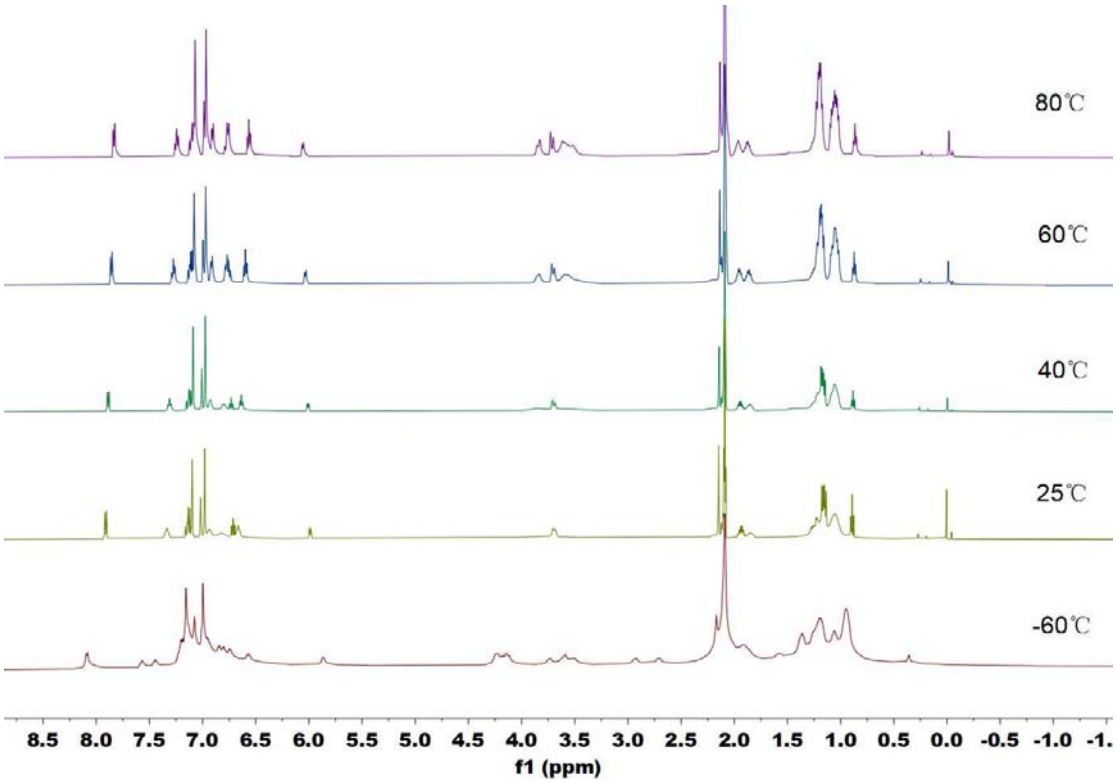

Figure S22. Variable temperature ^{1}H NMR spectra of **4** in toluene-d_8.

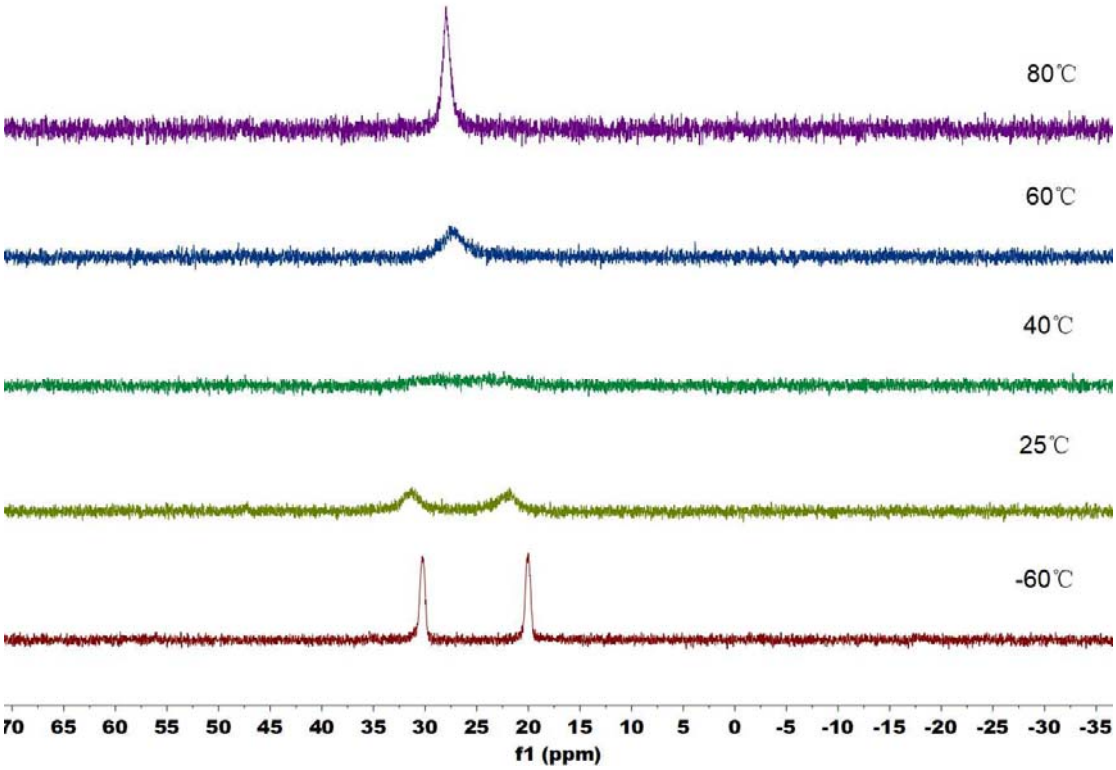

Figure S23. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **4** in toluene-d_8.

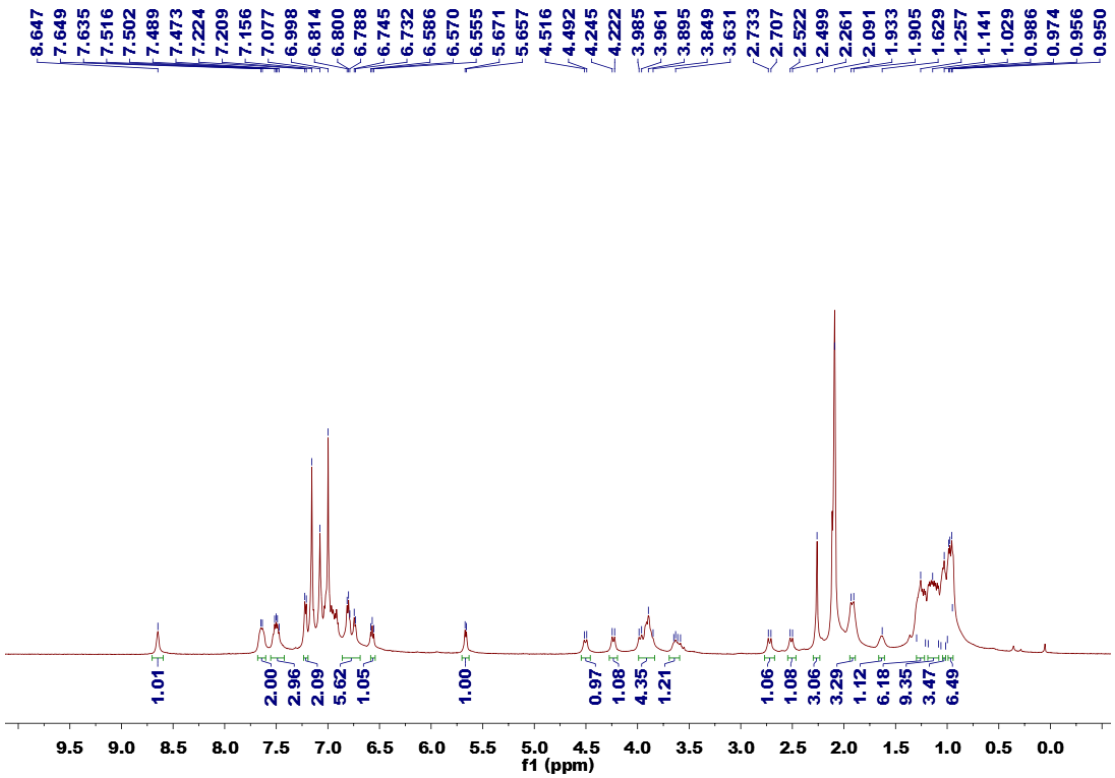

Figure S24. ^{1}H NMR spectrum of **5** in toluene-d_8 at -60 °C.

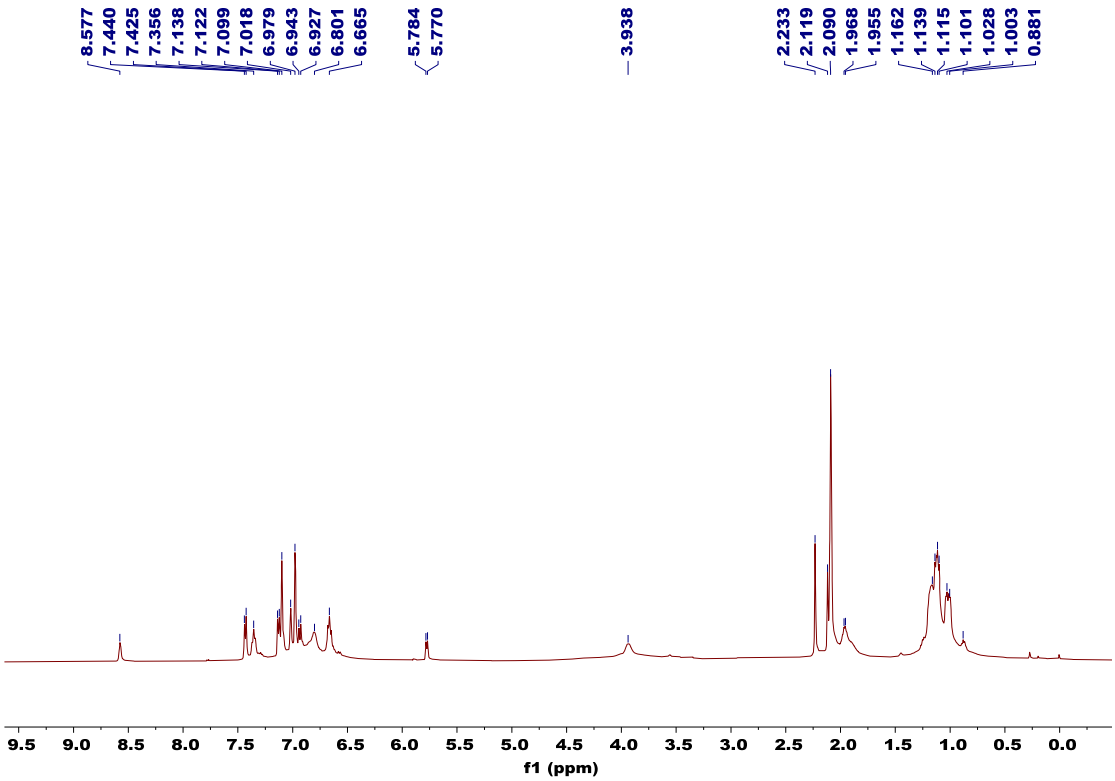

Figure S25. ^{1}H NMR spectrum of **5** in toluene-d_8 at 25 °C.

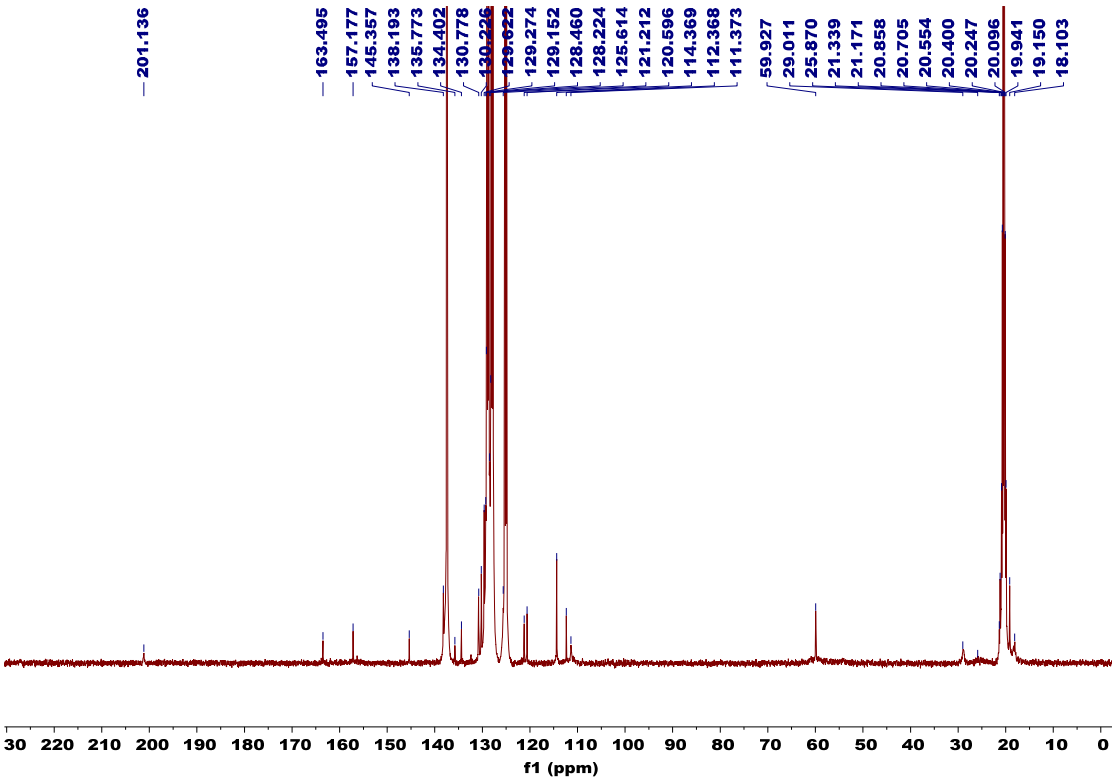

Figure S26. ^{13}C{^{1}H} NMR spectrum of **5** in toluene-d_8 at 25 °C.

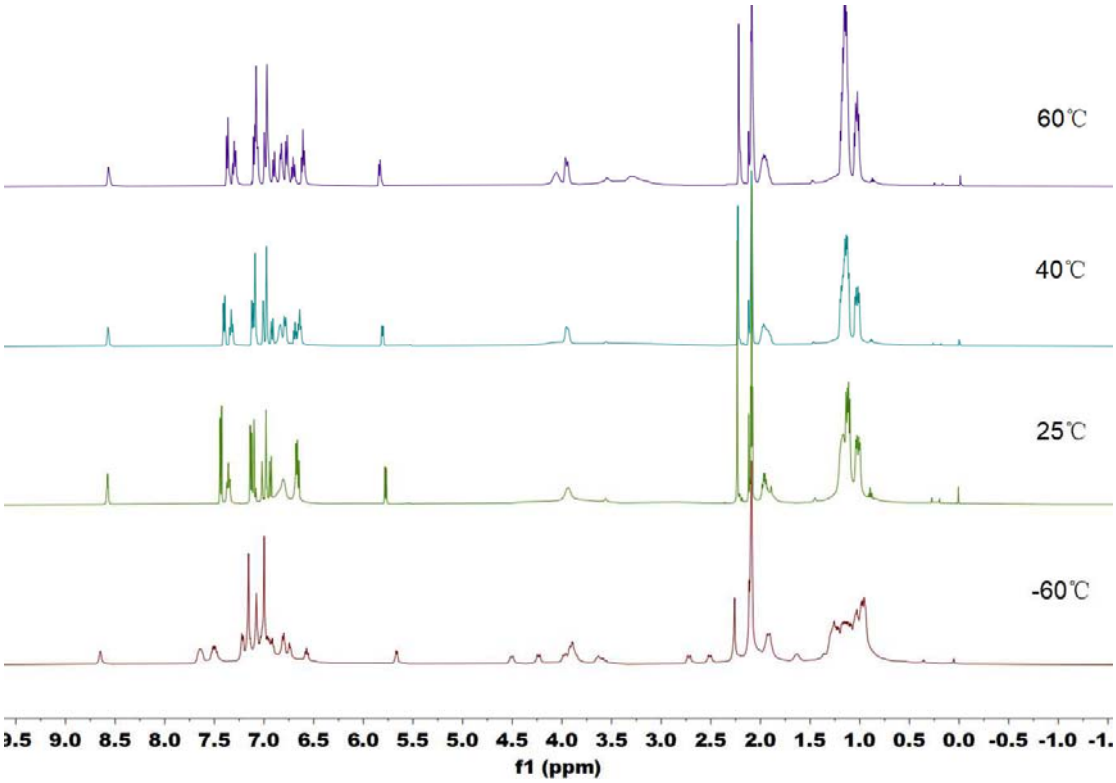

Figure S27. Variable temperature ^{1}H NMR spectra of **5** in toluene-d_8.

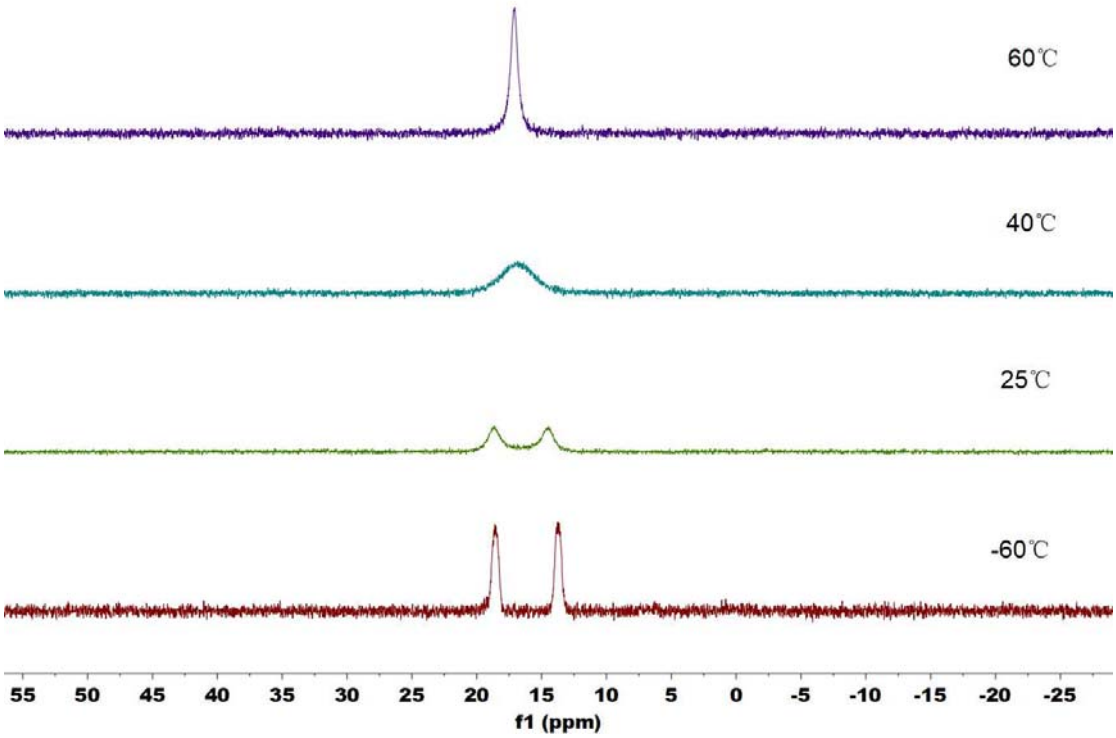

Figure S28. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **5** in toluene-d_8.

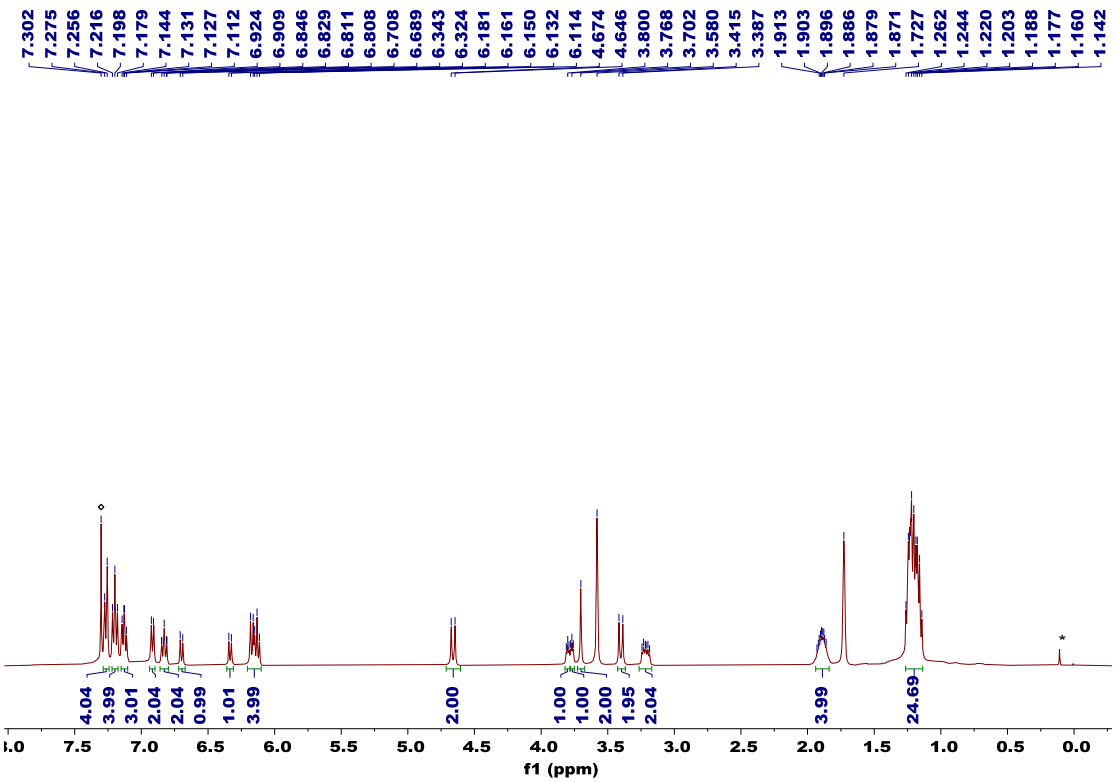

Figure S29. ^{1}H NMR spectrum of **6** in THF-d_8 at 25 °C (* denotes small amount of silicone grease, ◇ denotes co-crystallized benzene).

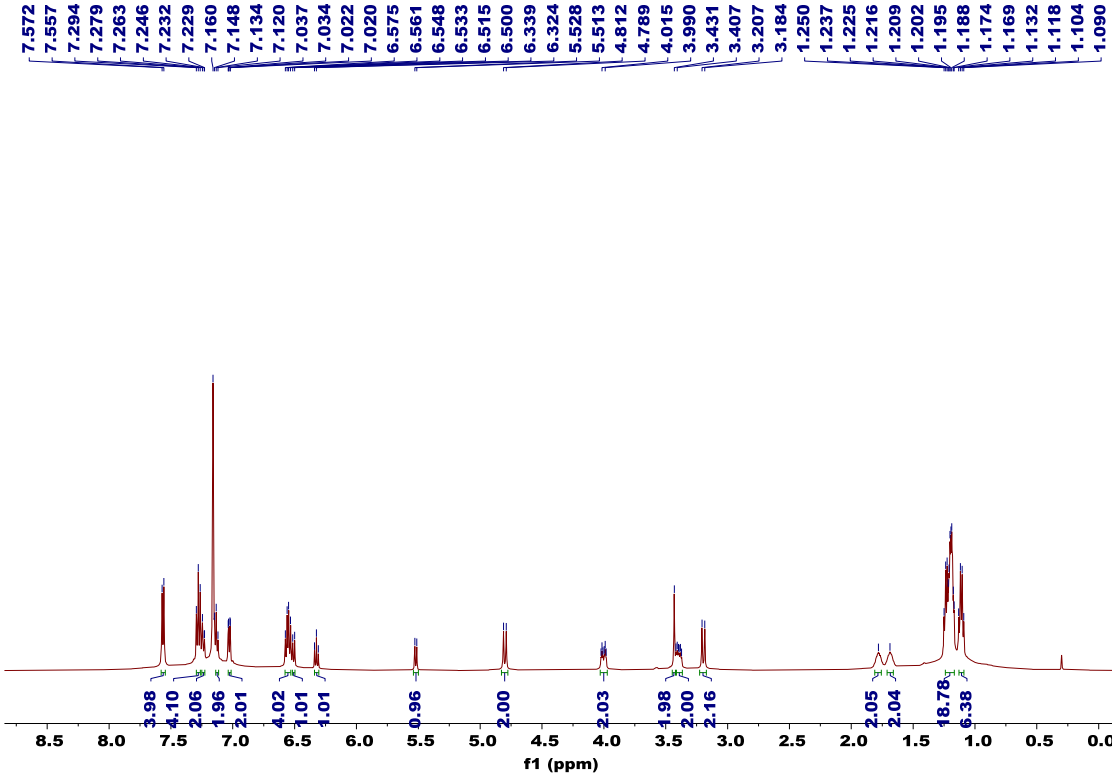

Figure S30. ^{1}H NMR spectrum of **6** in C_6D_6 at 25 °C.

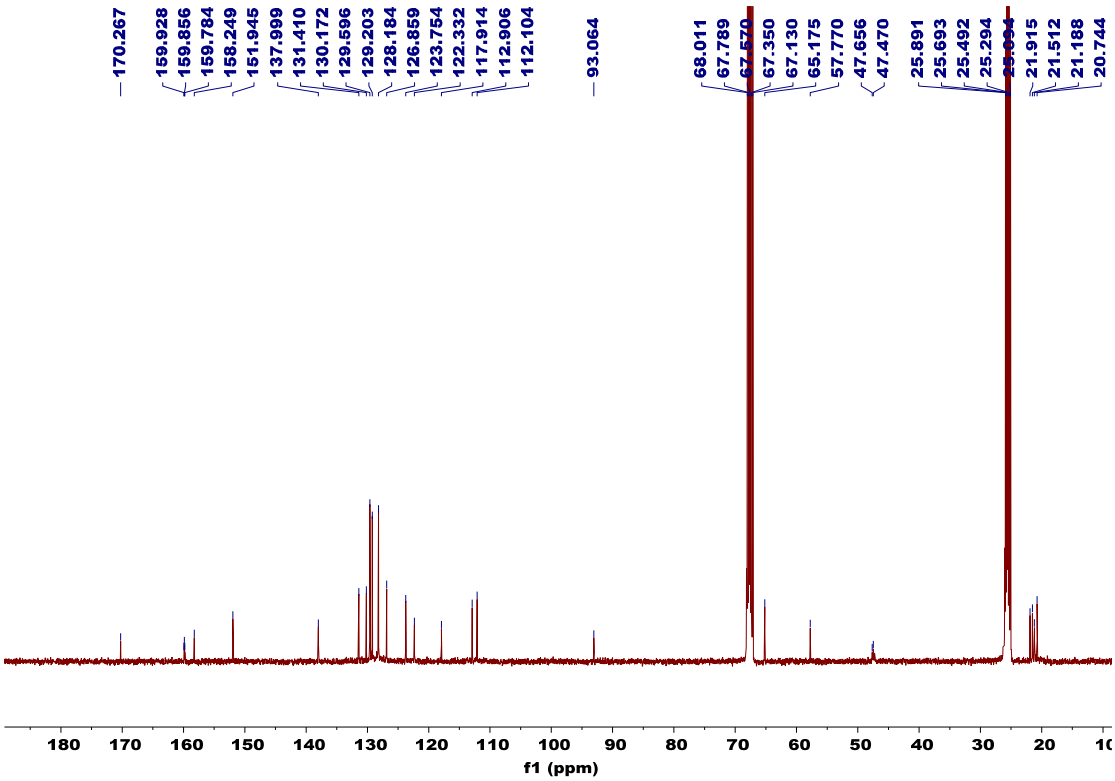

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **6** THF-d_8 at 25 °C.

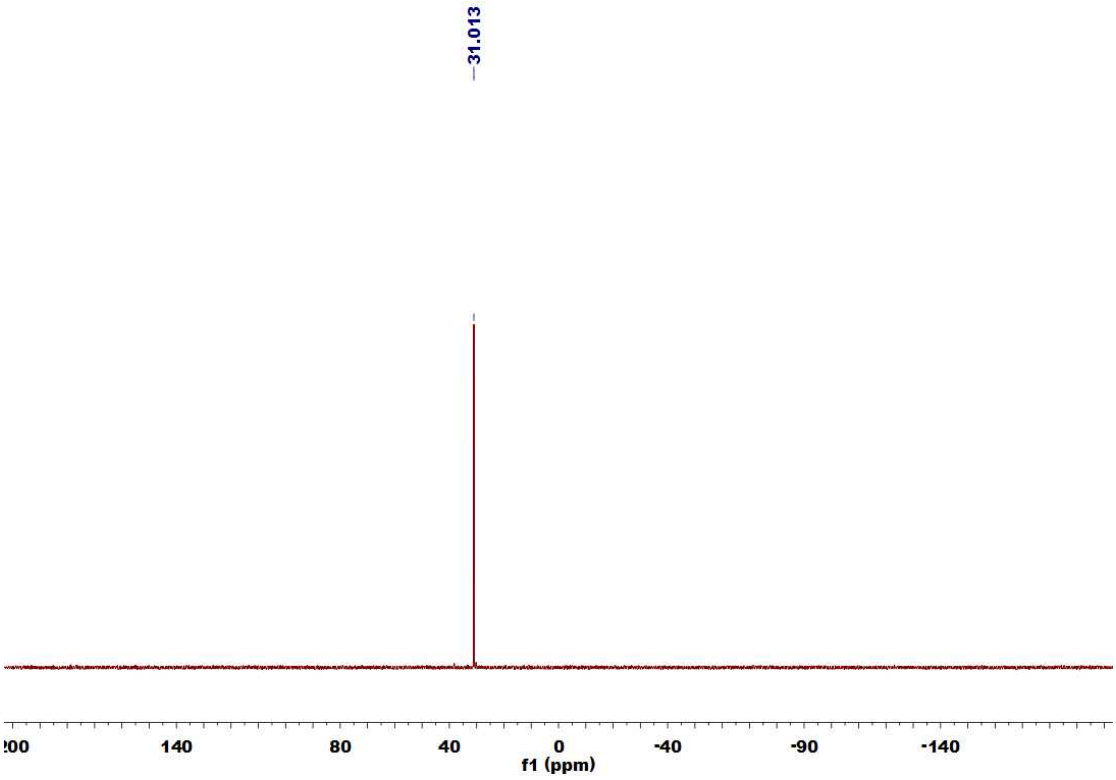

Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in THF-d_8 at 25 °C.

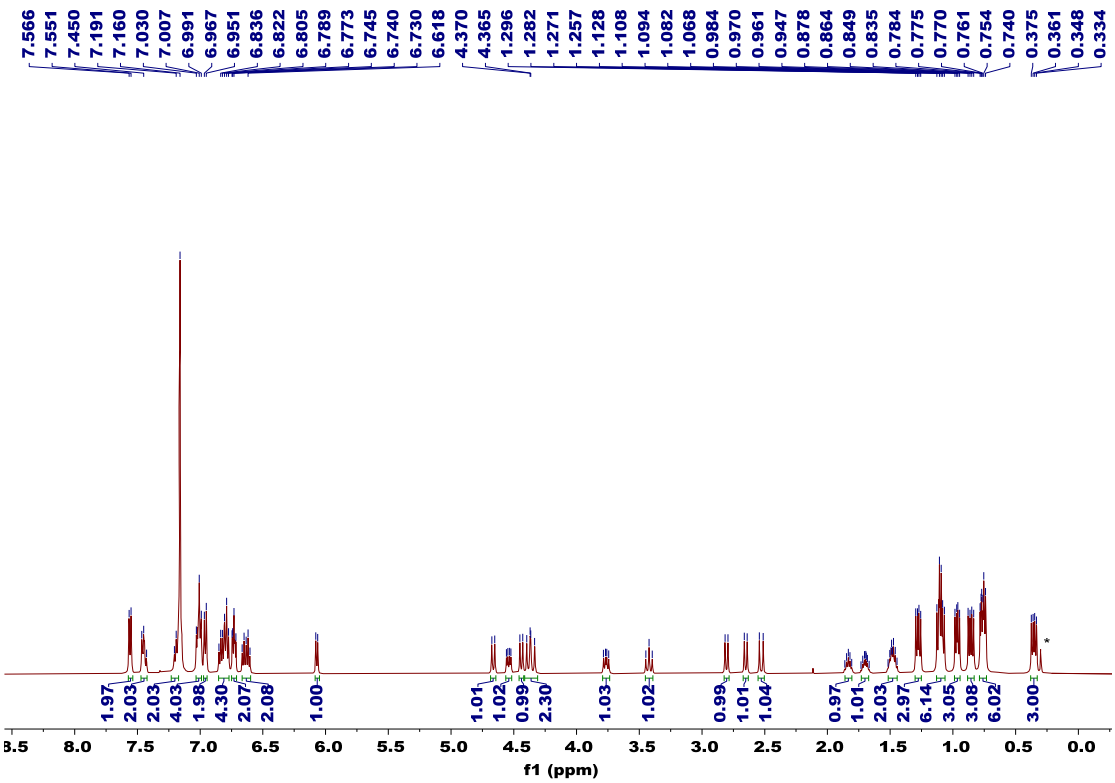

Figure S33. ^{1}H NMR spectrum of **7** in C_6D_6 at 25 °C. (* denotes small amount of silicone grease).

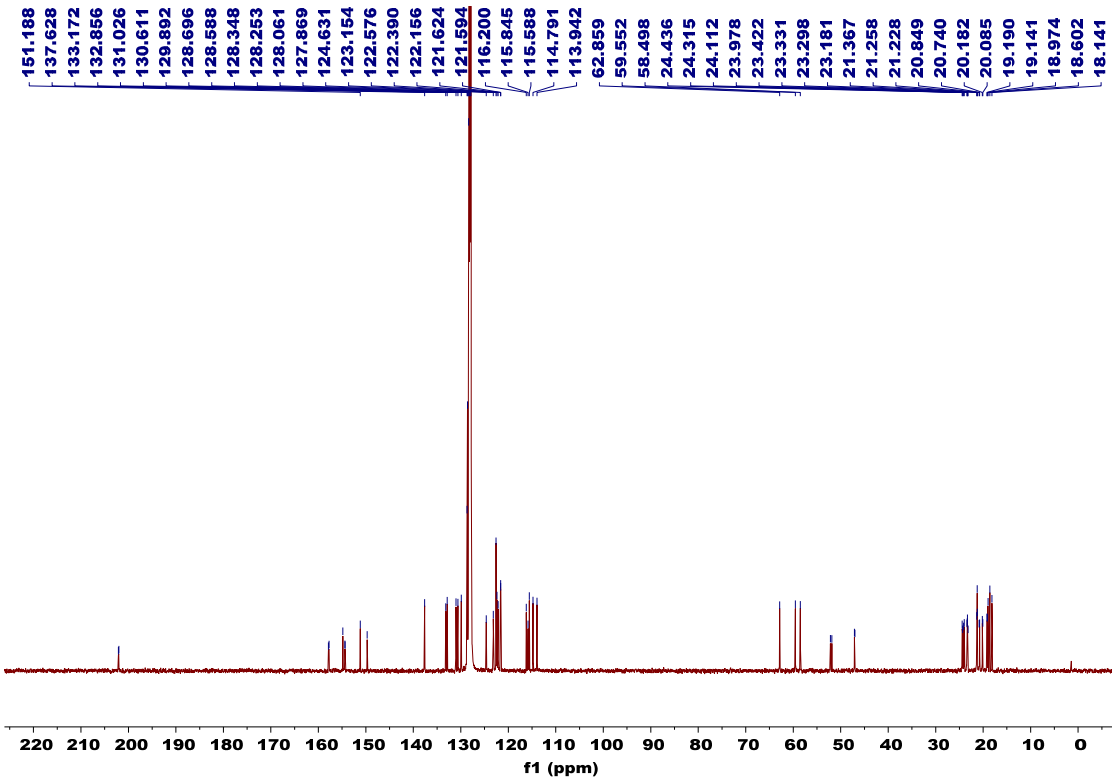

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 25 °C.

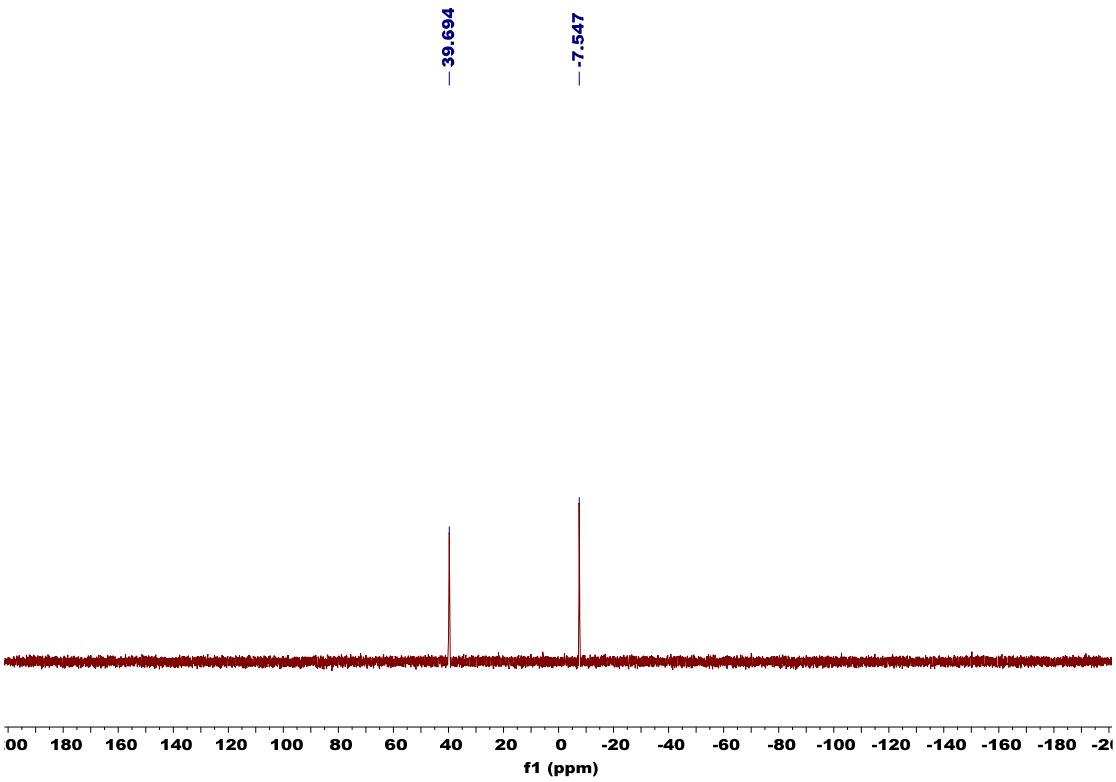

Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 25 °C.

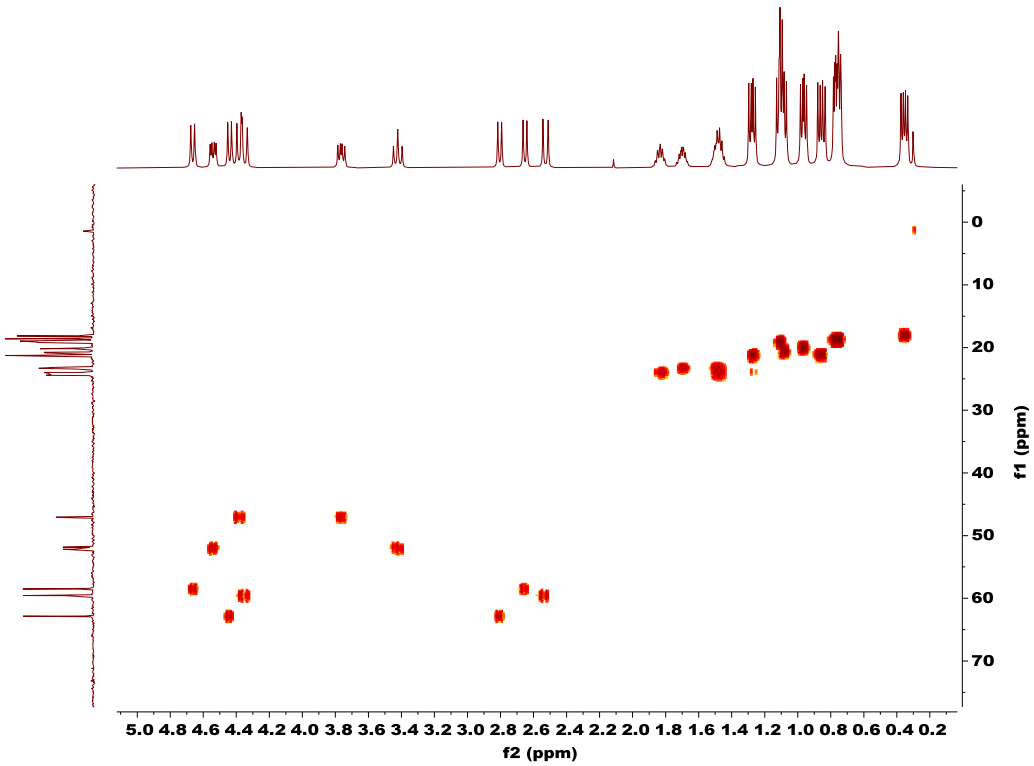

Figure S36. HSQC spectrum of **7** in C_6D_6 at 25 °C (Note: data of the aromatic region were not included since it's not very helpful for assigning the peaks in the ^{1}H NMR).

2.2 IR spectra

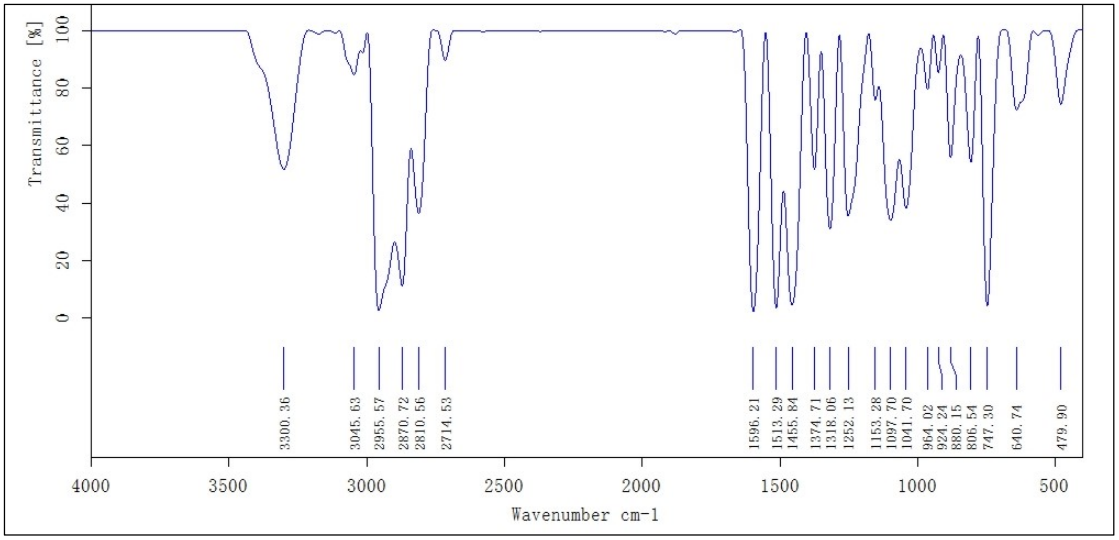

Figure S37. IR spectrum of **LH_3**

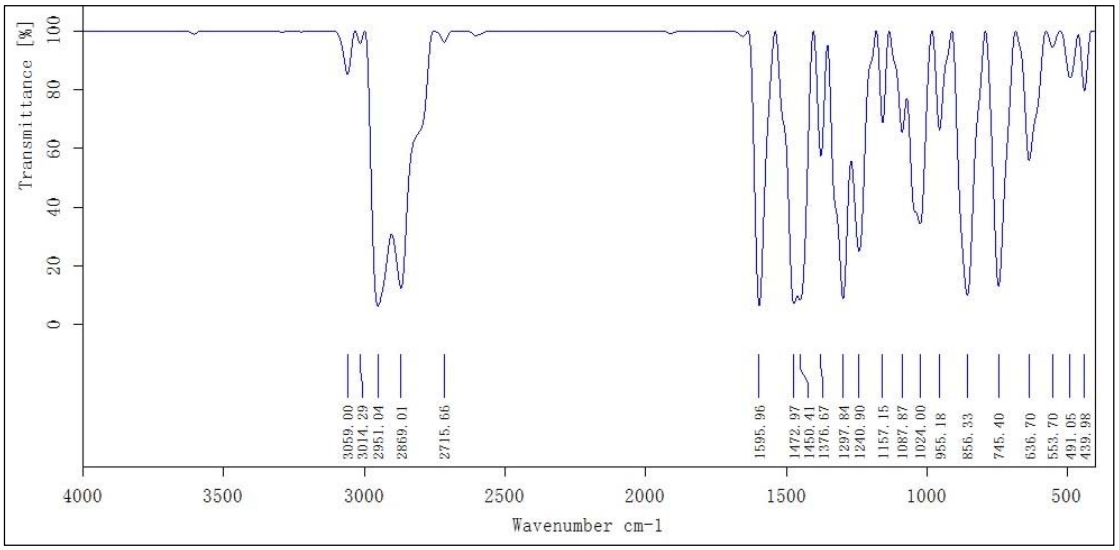

Figure S38. IR spectrum of **1**

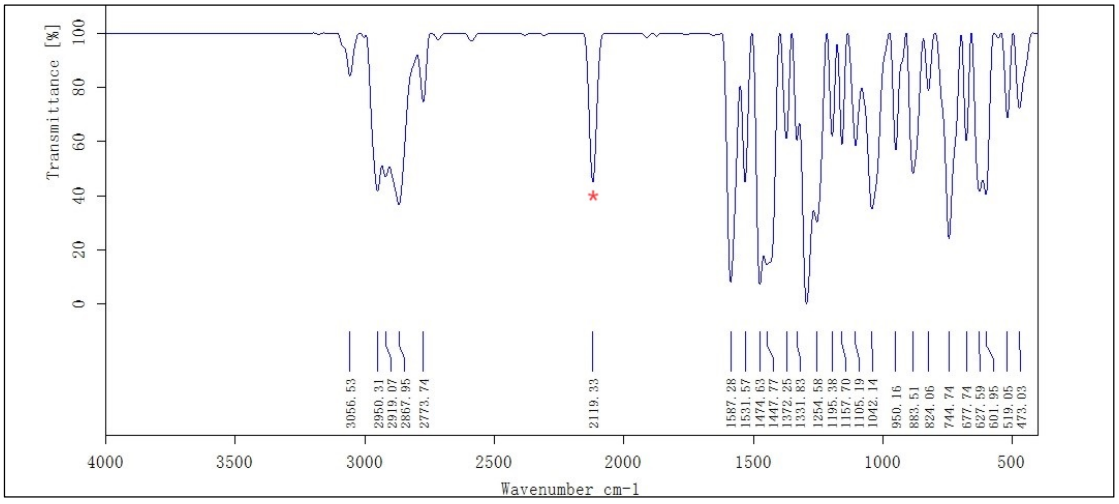

Figure S39. IR spectrum of **2**. (*denotes the stretching vibrational peak of N≡N bond)

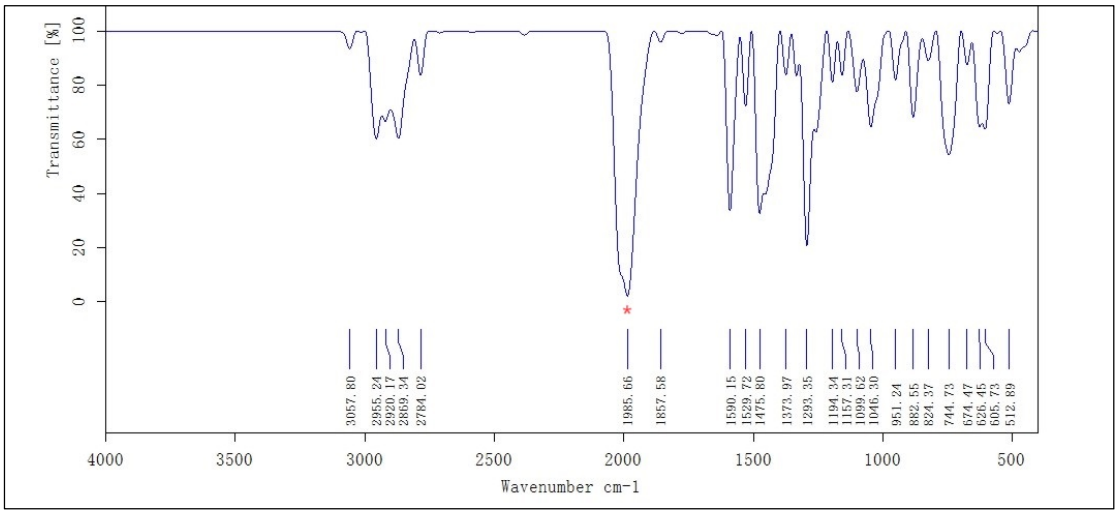

Figure S40. IR spectrum of **3**. (*denotes the stretching vibrational peak of C≡N bond)

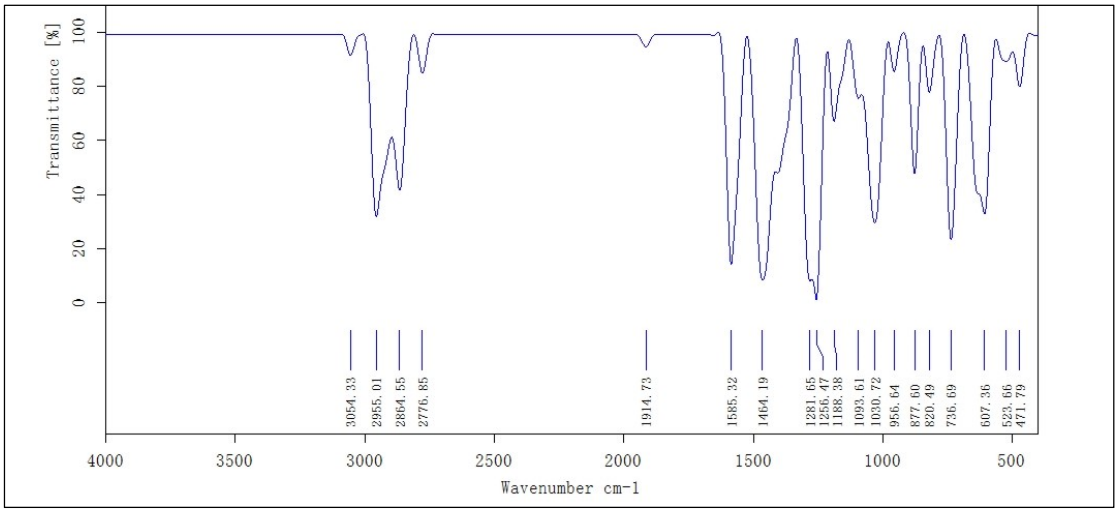

Figure S41. IR spectrum of **4**

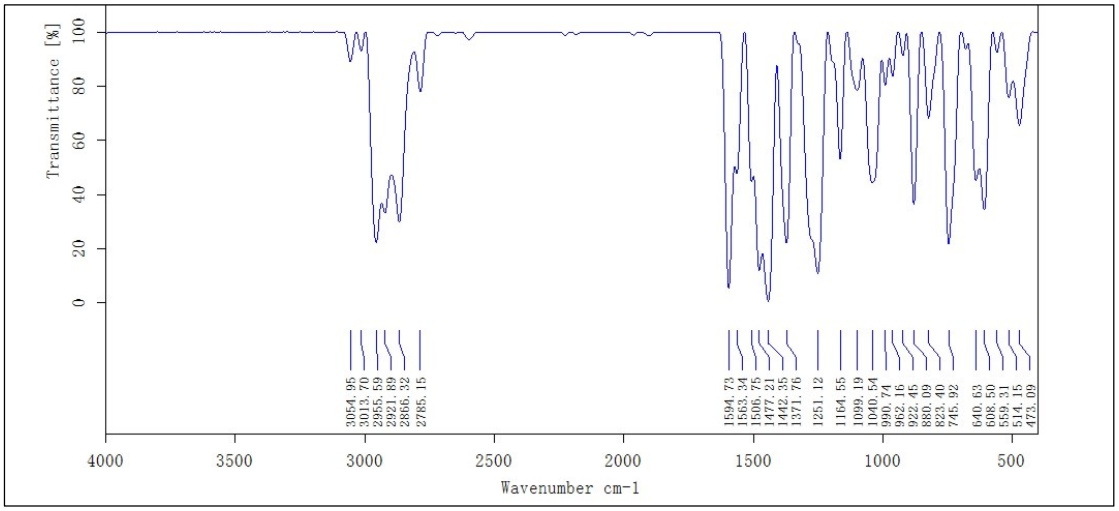

Figure S42. IR spectrum of **5**

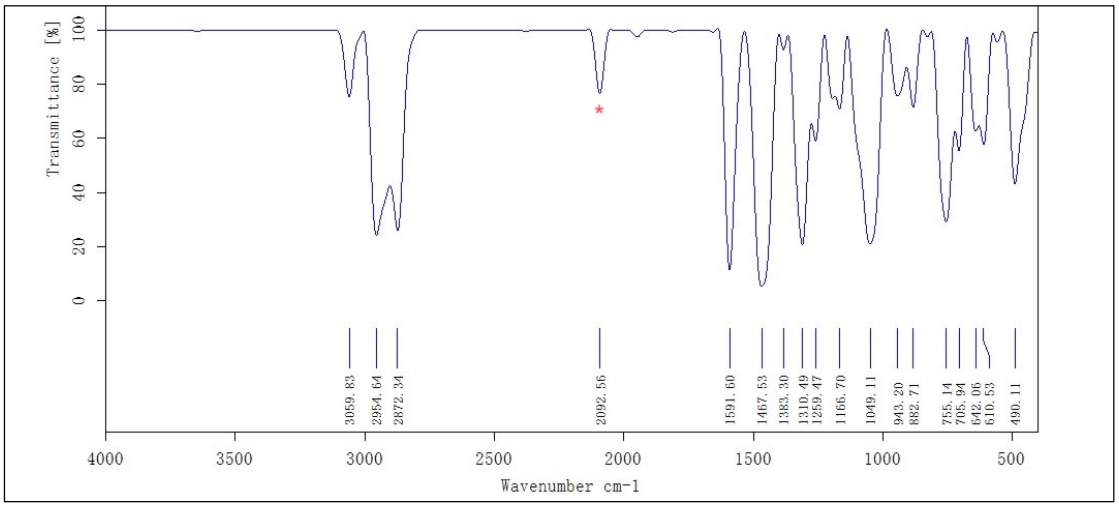

Figure S43. IR spectrum of **6**. (*denotes the stretching vibrational peak of N≡N bond)

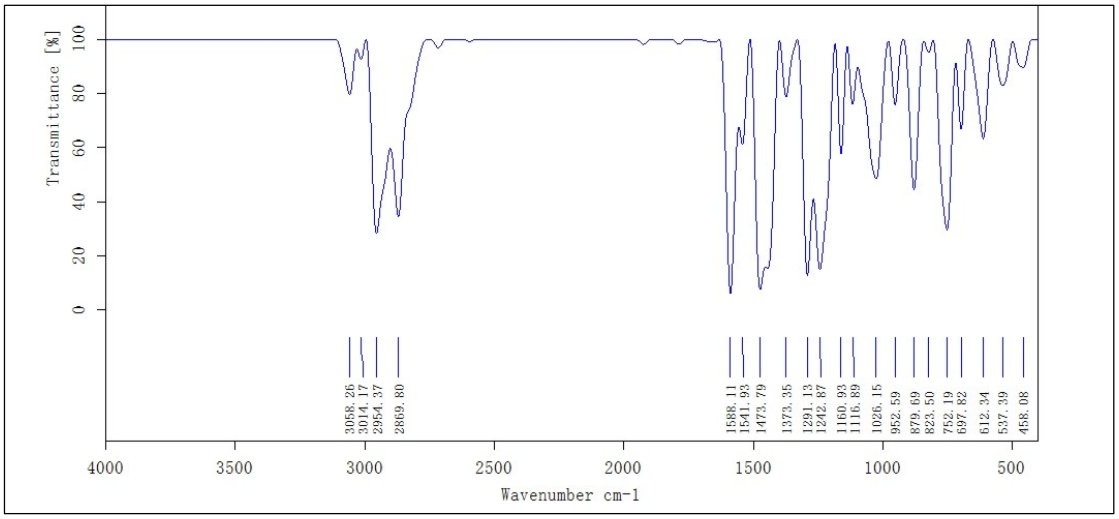

Figure S44. IR spectrum of **7**

3. X-ray Crystallography

X-ray Crystallography. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and Bruker Platon II area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for complexes at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.[4] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package [5] and Olex 2 program[6]. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.[7] Crystal parameters and refinement results are given in **Table S1-S2.**

Table S1. Crystallographic and Refinement Data for **1-4.**

	1	**2**	**3**	**4**
Formula	$C_{38}H_{61}N_4P_2ScSi$	$C_{68}H_{98}N_{10}Ni_2P_4Sc_2 \cdot C_5H_{12}$	$C_{43}H_{58}N_5NiP_2Sc$	$C_{42}H_{56}N_5NiP_2Sc \cdot 1.5(C_4H_8O)$
Fw, g·mol^{-1}	708.89	1458.92	810.55	904.68
Crystal size, mm^3	0.16 × 0.15 × 0.13	0.15 × 0.13 × 0.12	0.16 × 0.15 × 0.13	0.13 × 0.12 × 0.10
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T, K	300	300	300	300
a, Å	15.5452(10)	12.490(6)	12.237(15)	10.142(14)
b, Å	15.3097(10)	12.540(6)	13.83(2)	10.213(12)
c, Å	17.8477(12)	13.517(6)	15.21(2)	23.78(3)
α, °	90	65.861(6)	68.64(5)	77.96(3)
β, °	97.496(2)	73.439(6)	72.04(3)	79.02(4)
γ, °	90	76.945(6)	64.89(3)	81.49(5)
V, Å^3	4211.3(5)	1837.2(15)	2134(5)	2349(5)
Z	4	1	2	2
D_{calcd}, kg·m^{-3}	1.118	1.319	1.261	1.279
F(000)	1528	776	860	964
μ, mm^{-1}	0.308	0.817	0.710	0.655
θ range, °	2.659–27.528	2.321–27.049	2.937–27.485	2.647–27.531
reflections collected	93215	16504	76575	94236
independent reflections (R_{int})	9649（0.1199）	8325 (0.0356)	9734 (0.1275)	14275 (0.0531)
reflections observed [$I > 2\sigma(I)$]	5974	5868	6057	10786
data/restraints/parameters	9649/684/ 567	8325/52/443	9734/0/479	14275/510/850
R_1, wR_2 ($I > 2\sigma(I)$)	0.0746, 0.1752	0.0452, 0.1038	0.0626, 0.1243	0.0662, 0.1493
R_1, wR_2 (all data)	0.1260, 0.2012	0.0741,0.1138	0.1178, 0.1478	0.1134, 0.1748
GooF on F^2	1.087	1.032	1.048	1.059
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e·Å^{-3}	0.274/ -0.269	0.493/-0.361	0.348/-0.302	0.640/ -0.363

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

Table S2. Crystallographic and Refinement Data for **5-7.**

	5	**6**	**7**
Formula	$C_{43}H_{57}N_4NiP_2Sc$	$C_{94}H_{118}N_{10}Ni_2O_2P_4Sc_2$	$C_{46}H_{59}N_6NiP_2Sc$
Fw, g·mol^{-1}	795.53	2063.63	861.6
Crystal size, mm^3	0.15 × 0.13 × 0.12	0.15 × 0.13 × 0.12	0.10 × 0.09 × 0.08
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2_1/c$	$P\bar{1}$
T, K	300	300	300
a, Å	11.122(2)	28.918(6)	10.9882(14)
b, Å	11.696(2)	11.542(2)	11.7463(15)
c, Å	16.447(3)	36.001(7)	18.988 (2)
α, °	101.880(3)	90	74.157(2)
β, °	96.172(3)	109.45(3)	89.563(2)
γ, °	90.996(3)	90	72.840(2)
V, Å^3	2079.8(7)	11330(4)	2245.7(5)
Z	2	4	2
D_{calcd}, kg·m^{-3}	1.270	1.210	1.274
F(000)	844	4376	912
μ, mm^{-1}	0.727	0.551	0.680
θ range, °	2.357–22.336	2.205–23.662	2.264–25.096
reflections collected	15514	48798	16824
independent reflections (R_{int})	7308（0.0836）	12844 (0.0718)	8192 (0.0429)
reflections observed [$I > 2\sigma(I)$]	3482	5597	5175
data/restraints/parameters	7308/672/656	12844/1761/1096	8192/344/631
R_1, wR_2 ($I > 2\sigma(I)$)	0.0607, 0.1090	0.0520, 0.1171	0.0459, 0.0934
R_1, wR_2 (all data)	0.1561, 0.1395	0.1479, 0.1473	0.0920, 0.1092
GooF on F^2	0.954	0.960	1.023
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e·Å^{-3}	0.435/-0.414	0.363/-0.238	0.303/-0.377

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

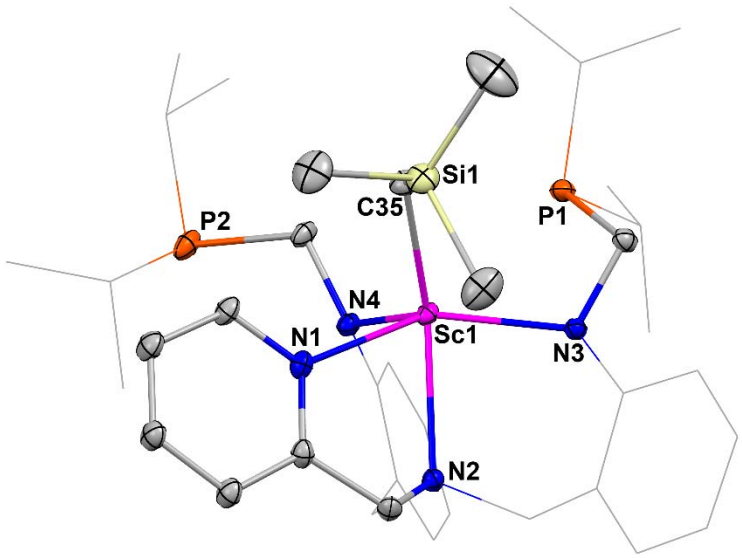

Figure S45. Molecular structure of **1**. Disordered part and hydrogen atoms were omitted.

4. Computational Details

All calculations were performed using the ORCA quantum chemistry program package (version 5.0.3).[8] For geometry optimizations and single point calculations, the GGA type BP [9,10] functional in combination with the all electron triple-ζ quality def2-TZVP basis sets for Ni and Sc metal centers and the coordinated atoms (N and P), and all electron def2-SVP bases sets were assigned to the remaining elements.[11] To accelerate the calculation, resolution of the identity (RI) approximation [12-14] was applied with the Weigend's "universal" Coulomb fitting auxiliary basis set def2/J.[15] Atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping (D3BJ) was involved.[16-18] The Quantum Theory of Atoms in Molecules (QTAIM) analysis was carried out using the Multiwfn program (version 3.7).[19]

Table S3. Calculated QTAIM data for **2** complex.

Complex	Bond	ρ^a	$\nabla^2\rho^b$	H^c	ε^d
2	Ni–Sc	0.042/0.042	0.025/0.025	-0.009/-0.009	0.296/0.298

[a] Electron density, [b] Laplacian of electron density, [c] energy density, [d] bond ellipticity.

The .xyz date of complex **2**

Coordinates from ORCA-job complex **2**

Ni	9.21539879153048	6.11023530593965	1.87356896263849
Sc	11.19492555451731	6.31262616912275	3.53869949995314
P	8.42755864905583	4.82524855734219	3.48995829735879
P	9.48497023764767	8.27356814255509	2.32463829621022
N	11.95549294390980	5.43089347132652	1.81837515039956
N	13.43364634295236	5.60149279726631	3.92598078825139
N	10.59933608449874	5.08383276622250	5.12062236818055
N	11.96374038658588	8.23365547955598	3.72954344408365
N	8.00392209208684	6.11259387034114	0.45770149997104
C	10.83907145857999	5.32361100725342	1.05108656805590
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5. References

1. Guo, Y.; Li, X.; Liu, K.; Hu, K.; Mei, L.; Chai Z.; Gibson, J. K.; Yu, J.; Shi, W. *Inorg. Chem.*, **2023**, *62*, 10684-10693.
2. (a) Reed, J. B.; Hopkins, B. S.; Audrieth, L. F.; Selwood, P. W.; Ward, J.; Dejong, J. J. *Inorg. Synth.*, **1939**, *1*, 28-33; (b) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003***, 22*, 1212-1222.
3. Rudd, P. A.; Liu, S.; Gagliardi, L.; Young, V. G., Jr.; Lu, C. C. *J. Am. Chem. Soc.*, **2011**, *133*, 20724-20727.
4. Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, **1996**.
5. Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program, **2009**.
7. Spek, A. L. *Acta Cryst*., **2015**, *C71*, 9-18.
8. Neese, F. Software update: The ORCA program system—Version 5.0. *WIREs Comput. Mol. Sci.*, **2022**, *12*, 1-15.
9. Perdew, J. P. Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev.*, *B.* **1986**, *34*, 7406-7406.
10. Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev.*, *B.* **1986**, *33*, 8822-8824.
11. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297-3305.
12. Baerends, E. J.; Ellis, D. E.; Ros, P. Self-consistent molecular hartree-fock-slater calculations I. the computational procedue. *Chem. Phys.*, **1973**, *2*, 41-51.
13. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.*, **1995**, *240*, 283-290
14. Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theor. Chem. Acc.*, **1997**, *97*, 119-124.
15. Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys*., **2006**, 8, 1057-1065.
16. Becke, A. D.; Johnson, E. R. A density-functional model of the dispersion interaction. *J. Chem. Phys.*, **2005**, *123*, 154101-154109.
17. Johnson, E. R.; Becke, A. D. A post-Hartree-Fock model of intermolecular interactions. *J. Chem. Phys.*, **2005**, *123*, 24101-24107.
18. Johnson, E. R.; Becke, A. D. A post-Hartree-Fock model of intermolecular interactions: inclusion of higher-order corrections. *J. Chem. Phys.*, **2006**, *124*, 174104-174109.
19. Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.*, **2012**, *33*, 580-592.