Supplementary Information for

The First Ring-Expanded NHC-Copper(I) Phosphides as Catalysts in the Highly Selective Hydrophosphination of Isocyanates

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General Considerations and Starting Materials

All reactions dealing with air- and moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line and glovebox techniques. NMR experiments using air-sensitive compounds were conducted in J. Young's tap NMR tubes prepared and sealed in a glovebox under argon. Toluene, hexane and pentane were purified using an MBraun Solvent Purification System and stored over 4Å molecular sieves. Benzene, THF and Et_2O were dried over sodium/benzophenone and distilled. C_6D_6 was dried over a potassium mirror prior to vacuum transfer into a sealed ampoule and storage in the glove box under argon. All NMR data were acquired at 298 K (unless otherwise stated) on an Agilent ProPulse instrument for ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz) and $^{31}P\{^1H\}$ (202 MHz) or a Bruker Avance 400 instrument for ^1H (400 MHz), $^{13}C\{^1H\}$ (101 MHz) and $^{31}P\{^1H\}$ (162 MHz). ^1H and ^{13}C NMR spectra were referenced using residual solvent resonances. Diffusion ordered spectroscopy (DOSY) was performed on the ^1H channel applying a stimulated pulse echo. Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K. Isocyanates, phenyl isothiocyanate and carbon disulfide were purchased from Sigma-Aldrich and distilled before use. (IPr)CuO^{t}Bu, (6-Dipp)CuO^{t}Bu, (SIMes)CuO^{t}Bu, (6-Mes)CuO^{t}Bu and Ph_2PSiMe_3 were prepared according to literature procedures.[1-3] **1** was synthesised by the conditions detailed below with data consistent with the previous report.[4] To calculate r_{comp}, DFT calculations were run with Gaussian 09 (Revision D.01).[5] The Cu and P centres were described with the Stuttgart RECPs and associated basis sets,[6] and 6-31G** basis sets were used for all other atoms. A polarization function was also added to P (ζ_d = 0.387). Initial BP86[7-10] optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima. The optimised coordinates from these calculations were then opened in Spartan to calculate the CPK Volume.

Synthesis of (IPr)CuPPh$_2$ (1)

(IPr)CuO^{t}Bu (162 mg, 0.31 mmol) and Ph_2PSiMe_3 (80 mg, 0.31 mmol) were dissolved in benzene (4 mL) to give a yellow solution and stirred for 2 h. Volatiles were removed *in vacuo*. The crude product was dissolved in minimal benzene. **1** was precipitated by addition of pentane, isolated by filtration and dried *in vacuo*. Yield 161 mg (81%). Single crystals were grown from benzene/pentane at room temperature. NMR data matched those in the literature.[4]

Synthesis of (6-Dipp)CuPPh$_2$ (2)

(6-Dipp)CuO^{t}Bu (1.25 g, 2.30 mmol) and Ph$_2$PSiMe$_3$ (0.60 g, 2.3 mmol) were dissolved in benzene (20 mL) to give a yellow solution and stirred for 2 h. Volatiles were removed *in vacuo*. The crude product was washed with benzene and dried *in vacuo*. Yield 1.20 g (80%). Single crystals were grown from benzene/hexane at room temperature. ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.25 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.09 – 7.05 (m, 8H, Ar-*H*), 7.02 – 6.94 (m, 6H, Ar-*H*), 2.95 (hept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.64 (t, *J* = 5.9 Hz, 4H, NC*H*$_2$), 1.43 (p, *J* = 6.1 Hz, 2H, NCH$_2$C*H*$_2$), 1.30 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 201.6 (d, *J* = 36.9 Hz, Cu*C*), 147.5 (d, *J* = 25.0 Hz, Ar-*C*), 145.4 (Ar-*C*), 141.2 (Ar-*C*), 133.1 (d, *J* = 16.6 Hz, Ar-*C*), 129.1 (Ar-*C*), 127.1 (d, *J* = 5.7 Hz, Ar-*C*), 124.7 (Ar-*C*), 122.5 (Ar-*C*), 45.5 (N*C*H$_2$), 28.5 (*C*H(CH$_3$)$_2$), 24.6 (d, *J* = 2.5 Hz, CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 19.8 (NCH$_2$*C*H$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ -23.8. Analysis calculated for $C_{40}H_{50}CuN_2P$ (MW = 653.36 g/mol): Expected: C, 73.53; H, 7.71; N 4.49. Found: C, 73.58; H, 7.71; N, 4.31.

Synthesis of (SIMes)CuPPh$_2$ (3)

(SIMes)CuO^{t}Bu (200 mg, 0.43 mmol) and Ph$_2$PSiMe$_3$ (111 mg, 0.43 mmol) were dissolved in benzene (5 mL) to give an orange solution and stirred for 2 h. Volatiles were removed *in vacuo*. The crude product was dissolved in minimal benzene. **3** was precipitated by addition of pentane, isolated by filtration and dried *in vacuo*. Yield 140 mg (59%). Single crystals were grown from benzene/hexane at room temperature. ^{1}H NMR (500 MHz, C_6D_6) δ 7.05 – 6.90 (m, 10H, PAr-*H*), 6.78 (s, 4H, Ar-H_{meta}), 3.03 (s, 4H, NC*H*$_2$), 2.31 (s, 6H, ArMe_{para}), 2.03 (s, 12H, ArMe_{ortho}). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 211.9 (t, *J* = 13.0 Hz, Cu*C*), 146.7 (Ar-*C*), 137.0 (Ar-*C*), 136.7 (Ar-*C*), 136.6 (Ar-*C*), 133.8 (Ar-*C*), 129.8 (Ar-*C*), 126.9 (Ar-*C*), 123.0 (Ar-*C*), 50.3 (N*C*H$_2$), 21.4 (ArMe_{para}), 18.0 (ArMe_{ortho}). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ -32.0. Analysis calculated for $C_{66}H_{72}Cu_2N_4P_2$ (MW = 1110.34 g/mol): Expected: C, 71.39; H, 6.54; N 5.05. Found: C, 71.30; H, 6.56; N, 5.14.

Synthesis of (6-Mes)CuPPh$_2$ (4)

(6-Mes)CuO^{t}Bu (400 mg, 0.87 mmol) and Ph$_2$PSiMe$_3$ (220 mg, 0.87 mmol) were dissolved in benzene (6 mL) to give an orange solution and stirred for 2 h. Volatiles were removed *in vacuo*. The crude product was dissolved in minimal benzene. **4** was precipitated by addition of pentane, isolated by filtration and dried *in vacuo*. Yield 351 mg (70%). Single crystals were grown from benzene/hexane at room temperature. ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (t, J = 6.7 Hz, 4H, PAr-*H*), 7.10 – 6.99 (m, 6H, PAr-*H*), 6.71 (s, 4H, Ar-H_{meta}), 2.43 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 2.22 (s, 6H, ArMe_{para}), 2.00 (s, 12H, ArMe_{ortho}), 1.28 (p, J = 5.9 Hz, 2H, NCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 203.7 (Cu*C*), 148.1 (d, *J* = 23.7 Hz, Ar-*C*), 142.3 (Ar-*C*), 137.2 (Ar-*C*), 134.9 (Ar-*C*), 133.9 (d, *J* = 15.6 Hz, Ar-*C*), 130.2 (Ar-*C*), 127.4 (d, *J* = 4.7 Hz, Ar-*C*), 123.0 (Ar-*C*), 43.8 (N*C*H$_2$), 21.3 (ArMe_{para}), 20.9 (NCH$_2$*C*H$_2$), 18.0 (ArMe_{ortho}). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ -23.5. Analysis calculated for $C_{22}H_{28}Cu_2N_2P$ (MW = 384.30 g/mol): Expected: C, 71.74; H, 6.73; N 4.92. Found: C, 71.38; H, 6.79; N, 4.94.

Synthesis of (6-Dipp)Cu[N(^{i}Pr)C(O)PPh$_2$] (5)

Isopropyl isocyanate (15 µL, 0.15 mmol) was added to a yellow solution of **2** (50 mg, 0.076 mmol) in C_6D_6 (1.0 mL), yielding a colourless solution in which precipitate rapidly formed which was suitable for single crystal X-ray diffraction analysis. The supernatant solution was decanted off. The product was washed with hexane (0.5 mL) and dried *in vacuo* to give a white, fluffy solid. Yield 40 mg (71%). ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.66 – 7.62 (m, 4H, Ar-*H*), 7.17 – 7.12 (m, 4H, Ar-*H*), 7.09 – 7.05 (m, 2H, Ar-*H*), 7.04 – 6.96 (m, 6H, Ar-*H*), 3.99 (dh, *J* = 6.5, 1.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 3.08 (hept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.81 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.56 (p, J = 6.1 Hz, 2H, NCH$_2$C*H*$_2$), 1.43 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.82 (dd, J = 6.6, 0.8 Hz, 6H, NCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): *δ*

203.7 (Cu*C*), 177.5 (d, *J* = 19.5 Hz, *C*O), 145.2 (Ar-*C*), 142.8 (Ar-*C*), 140.9 (d, *J* = 16.9 Hz, Ar-*C*), 134.6 (d, *J* = 15.8 Hz, Ar-*C*), 129.4 (Ar-*C*), 127.6 (d, *J* = 5.7 Hz, Ar-*C*), 127.4 (Ar-*C*), 125.2 (Ar-*C*), 47.4 (N*C*H_2), 46.7 (d, *J* = 22.3 Hz, N*C*H(CH_3)$_2$), 28.9 (*C*H(CH_3)$_2$), 25.1 (CH(*C*H_3)$_2$), 25.0 (d, *J* = 2.0 Hz, CH(*C*H_3)$_2$), 24.6 (NCH(*C*H_3)$_2$), 20.6 (NCH$_2$*C*H_2). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): *δ* 2.2. Analysis calculated for $C_{44}H_{57}CuN_3OP$ (MW = 738.48 g/mol): Expected: C, 71.56; H, 7.78; N, 5.69. Found: C, 71.75; H, 7.65; N, 5.63.

Note: Upon dissolution of apparently pure samples of compound **5** evidence of reversibility of the insertion of isopropyl isocyanate is observable by NMR spectroscopy, frustrating collection of unambiguous spectral data. NMR spectra presented herein (Figures S14-S16) have been collected with a sufficient excess of the isocyanate (highlighted in red) to inhibit the presence of **2** in solution and thus the spectral data. The 6-Mes homologue (6-Mes)Cu[N(^{i}Pr)C(O)PPh_2] (**S1**) has also been synthesised as a point of comparison for spectral data (Figures S23-S25) and does not show evidence of reversible insertion thus providing unambiguous data.

Synthesis of (6-Dipp)Cu[SC(NPh)PPh_2] (6)

Phenyl isothiocyanate (10 µL, 0.084 mmol) was added to a yellow solution of **2** (20 mg, 0.031 mmol) in C_6D_6 (0.5 mL), yielding a colourless solution in which precipitate rapidly formed suitable for single crystal X-ray diffraction analysis. The supernatant solution was decanted off. The product was dried *in vacuo* to give an off-white crystalline solid. Yield 15 mg (62%). ^1H NMR (500 MHz, C_6D_6): *δ* 7.40 – 7.34 (m, 6H, Ar-*H*), 7.25 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.18 – 7.14 (m, 2H, Ar-*H*), 7.11 – 7.06 (m, 10H, Ar-*H*) 6.86 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 3.15 (hept, J = 7.0 Hz, 4H, C*H*(CH_3)$_2$), 2.88 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.57 (p, J = 6.0 Hz, 2H, NCH$_2$C*H*$_2$), 1.35 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.14 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): *δ* 146.1 (Ar-*C*), 142.8 (Ar-*C*), 136.5 (Ar-*C*), 134.0 (d, J = 14.3 Hz, Ar-*C*), 129.5 (Ar-*C*), 129.2 (Ar-*C*), 128.8 (Ar-*C*), 128.4 (Ar-*C*), 128.4 (Ar-*C*), 128.1 (Ar-*C*), 125.0 (Ar-*C*), 122.9 (Ar-*C*), 122.6 (Ar-*C*), 46.6 (N*C*H_2), 29.0 (*C*H(CH_3)$_2$), 25.5 (CH(*C*H_3)$_2$), 24.6 (d, J = 2.3 Hz, CH(*C*H_3)$_2$), 20.3 (NCH$_2$*C*H_2). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): *δ* 28.8. Analysis calculated for $C_{47}H_{55}CuN_3PS$ (MW = 788.56 g/mol): Expected: C, 71.59; H, 7.03; N, 5.33. Found: C, 71.23; H, 7.15; N, 5.50.

Synthesis of (6-Dipp)Cu[SC(S)PPh_2] (7)

Carbon disulfide (10 µL, 0.17 mmol) was added to a yellow solution of **2** (20 mg, 0.031 mmol) in C_6D_6 (0.5 mL), yielding a dark red solution in which precipitate rapidly formed suitable for single crystal X-ray diffraction analysis. Volatiles were removed *in vacuo* to give a red-brown solid. Yield 20 mg (88%). ^1H NMR (500 MHz, C_6D_6): *δ* 7.45 – 7.40 (m, 4H, Ar-*H*), 7.20 (t, J = 7.8 Hz, 2H, Ar-*H*), 7.07 (d, J = 7.7 Hz, 4H, Ar-*H*), 7.04 – 7.00 (m, 6H, Ar-*H*), 3.09 (hept, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.83 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.53 (p, J = 5.8 Hz, 2H, NCH$_2$C*H*$_2$), 1.40 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.14 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): *δ* 206.3 (d, J = 13.4 Hz), 145.9 (Ar-*C*), 142.4 (Ar-*C*), 138.4 (d, *J* = 6.4 Hz, Ar-*C*), 134.6 (d, *J* = 18.1 Hz, Ar-*C*), 129.4 (Ar-*C*), 128.9 (Ar-*C*), 128.2 (d, *J* = 7.7 Hz, Ar-*C*), 124.9 (Ar-*C*), 46.3 (N*C*H_2), 29.0 (*C*H(CH_3)$_2$), 25.4 (CH(*C*H_3)$_2$), 24.7 (CH(*C*H_3)$_2$), 20.3 (NCH$_2$*C*H_2). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): *δ* 45.2. Analysis calculated for $C_{41}H_{50}CuN_2PS_2$ (MW = 1110.34 g/mol): Expected: C, 67.50; H, 6.91; N, 3.84. Found: C, 68.09; H, 6.91; N, 3.73.

Synthesis of (6-Mes)Cu[N(^{i}Pr)C(O)PPh_2] (S1)

Isopropyl isocyanate (10 µL, 0.11 mmol) was added to an orange suspension of **4** (20 mg, 0.035 mmol) in toluene (0.5 mL), yielding a pale yellow solution. Volatiles were removed *in vacuo* to give a pale yellow powder. Yield 22 mg (96%). ^1H NMR (500 MHz, C_6D_6): *δ* 7.74 – 7.70 (t, J = 6.9 Hz, 6H, PAr-*H*), 7.18 – 7.08 (m, 4H, PAr-*H*), 6.68 (s, 4H, Ar-H_{meta}), 4.39 (dh, J = 6.3, 1.9 Hz, 1H, NC*H*(CH_3)$_2$), 2.57 (t, J = 5.8 Hz, 4H, NC*H*$_2$), 2.20 (s, 12H, ArMe_{ortho}), 2.07 (s, 6H, ArMe_{para}), 1.41 (p, J = 5.8 Hz, 2H, NCH$_2$C*H*$_2$), 0.89 (d, J = 6.3 Hz, 6H, NCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): *δ* 206.0, 176.3 (d, *J* = 27.1 Hz), 142.8 (Ar-

C), 139.3 (d, *J* = 14.3 Hz, Ar-*C*), 137.8 (Ar-*C*), 134.9 (Ar-*C*), 134.1 (d, *J* = 15.8 Hz, Ar-*C*), 130.0 (Ar-*C*), 127.93 (d, *J* = 6.2 Hz, Ar-*C*), 127.8 (Ar-*C*), 44.2 (d, *J* = 25.3 Hz , N*C*H(CH_3)$_2$), 43.8 (NCH_2), 25.4 (NCH(*C*H_3)$_2$), 21.1 (Ar*Me*$_{para}$), 20.8 (NCH$_2$*C*H$_2$), 18.2 (d, *J* = 3.0 Hz, Ar*Me*$_{ortho}$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 1.2.

General Procedure for Catalytic Hydrophosphination of Isocyanates

In a glovebox, to a C_6D_6 (0.5 mL) solution of **1**-**4** (1 mol%) in a glass scintillation vial was added diphenylphosphine (35 µL, 0.20 mmol) followed by isocyanate (0.20 mmol). The reaction mixture was transferred to J. Young's tap NMR tube and monitored by NMR spectroscopy. Products were confirmed by comparison to literature data,[11] spectroscopic data is provided in Figures S38 – S65.

General Procedures for the Preparative Scale Catalytic Hydrophosphination of Isocyanates and Isolation of the Phosphinocarboxamides

Ph$_2$PC(O)NH(^{i}Pr) and Ph$_2$PC(O)NH(Ph): A solution of **3** (5.6 mg, 0.01 mmol, 1 mol%) in toluene (2 mL) was added to a solution of diphenylphosphine (175 µL, 1.00 mmol) and the isocyanate (1.05 mmol) in toluene (1 mL). The reaction was stirred for 30 min. Volatiles were removed *in vacuo* to give a pale yellow powder. The crude product was extracted into hexane (15 mL) and filtered. The solvent was removed *in vacuo* until crystallisation of the product. The remaining solution was decanted, the phosphinocarboxamide dried *in vacuo* and isolated as a white crystalline solid (**8a**: 70%; **8c**: 79%).

Ph$_2$PC(O)NH(^{t}Bu) and Ph$_2$PC(O)NH(Cy): A solution of **3** (5.6 mg, 0.01 mmol, 1 mol%) in toluene (2 mL) was added to a solution of diphenylphosphine (175 µL, 1.00 mmol) and the isocyanate (1.05 mmol) in toluene (1 mL). The reaction was stirred for 30 min (2 h for **3b**). Volatiles were removed *in vacuo* to give a pale yellow powder. The crude product was washed with hexane (10 mL). The phosphinocarboxamide was dried *in vacuo* and isolated as a white powder (**8b**: 67%; **8d**: 77%).

Ph$_2$PC(O)NH(^{i}Pr) (Table 1, entry 3**)**

White solid. Isolated yield: 70 %. ^{1}H NMR (500 MHz, C_6D_6) δ 7.68 – 7.62 (m, 4H, Ar-*H*), 7.09 – 7.01 (m, 6H, Ar-*H*), 5.35 (s, 1H, N*H*), 4.14 (dhept, *J* = 6.6 Hz, 0.8 Hz, 1H, NC*H*), 0.72 (d, *J* = 6.5 Hz, 6H, C*H*$_3$). ^{13}C NMR (126 MHz, C_6D_6) δ 135.2 (d, *J* = 10.5 Hz, Ar-*C*), 134.6 (d, *J* = 18.9 Hz, Ar-*C*), 129.6 (Ar-*C*), 129.0 (d, *J* = 7.2 Hz, Ar-*C*), 42.1 (*C*H(CH_3)), 22.3 (CH(*C*H_3)). ^{31}P NMR (202 MHz, C_6D_6) δ -4.0. NMR data matched those in the literature.[11]

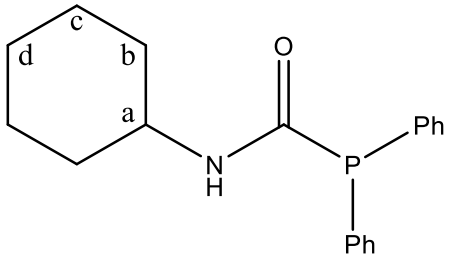
Ph$_2$PC(O)NH(^{t}Bu) (Table 1, entry 7**)**

White solid. Isolated yield: 67 %.^{1}H NMR (500 MHz, C_6D_6) δ 7.67 – 7.61 (m, 4H, Ar-*H*), 7.10 – 7.01 (m, 6H, Ar-*H*), 5.41 (s, 1H, N*H*), 1.11 (s, 9H, C*H*$_3$). ^{13}C NMR (126 MHz, C_6D_6) δ 135.6 (d, J = 12.1 Hz, Ar-*C*), 134.6 (d, J = 18.8 Hz, Ar-*C*), 129.5 (Ar-*C)*, 129.0 (d, J = 7.1 Hz, Ar-*C*), 52.5 (*C*(CH_3)$_3$), 28.6 (C(*C*H_3)$_3$). ^{31}P NMR (202 MHz, C_6D_6) δ -2.7. NMR data matched those in the literature.[11]

Ph$_2$PC(O)NH(Ph) (Table 1, entry 11**)**

White solid. Isolated yield: 77 %.^{1}H NMR (500 MHz, C_6D_6) δ 7.60 – 7.52 (m, 4H, Ar-*H*), 7.33 (d, J = 7.9 Hz, 2H, Ar-*H*), 7.13 (s, 1H, N*H*), 7.06 – 7.02 (m, 6H, Ar-*H*), 7.00 – 6.95 (m, 2H, Ar-*H*), 6.84 – 6.79 (m, 1H, Ar-*H*). ^{13}C NMR (126 MHz, C_6D_6) δ 138.6 (Ar-*C*), 134.7 (d, J = 19.3 Hz, Ar-*C*), 134.4 (d, J = 11.4 Hz, Ar-*C*), 129.9 (Ar-*C*), 129.2 (Ar-*C*), 129.2 (d, J = 7.3 Hz, Ar-*C*), 124.5 (Ar-*C*), 119.5 (Ar-*C*). ^{31}P NMR (202 MHz, C_6D_6) δ -0.4. NMR data matched those in the literature.[11]

$Ph_2PC(O)NH(Cy)$ (Table 1, entry 13**)**



White solid. Isolated yield: 79 %.^{1}H NMR (500 MHz, C_6D_6) δ 7.69 – 7.64 (m, 4H, Ar-*H*), 7.11 – 7.02 (m, 6H, Ar-*H*), 5.44 (s, 1H, N*H*), 4.00 – 3.90 (m, 1H, Cy-H^a), 1.66 – 1.60 (m, 2H, Cy-H^b), 1.31 – 1.18 (m, 3H, Cy-H^c, Cy-H^d), 1.06 – 0.97 (m, 2H, Cy-H^c), 0.83 – 0.74 (m, 1H, Cy-H^d), 0.73 – 0.64 (m, 2H, Cy-H^b). ^{13}C NMR (126 MHz, C_6D_6) δ 135.4 (d, J = 12.3 Hz, Ar-*C*), 134.7 (d, J = 18.9 Hz, Ar-*C*), 129.6 (Ar-*C*), 129.0 (d, J = 7.1 Hz, Ar-*C*), 48.7 (Cy-C^a), 32.8 (Cy-C^b), 25.6 (Cy-C^d), 24.7 (Cy-C^c). ^{31}P NMR (202 MHz, C_6D_6) δ -4.4. NMR data matched those in the literature.[11]

Diffusion Ordered Spectroscopy

DOSY was performed using ^{1}H resonances associated with the complexes in C_6D_6. Diffusion coefficients were converted to hydrodynamic radii via Equation 1.

$$D = \frac{kT}{6\pi\eta r_H}$$

Equation 1. Where D = diffusion constant, k = Boltzmann constant, T = absolute temperature, η = viscosity, r_H = hydrodynamic radius.

Complex	Diffusion constant / $x10^{-10}$ m^2s^{-1}	Hydrodynamic radius / Å
1	6.35	5.40
2	6.51	5.27
3	5.69	6.03
4	6.49	5.29

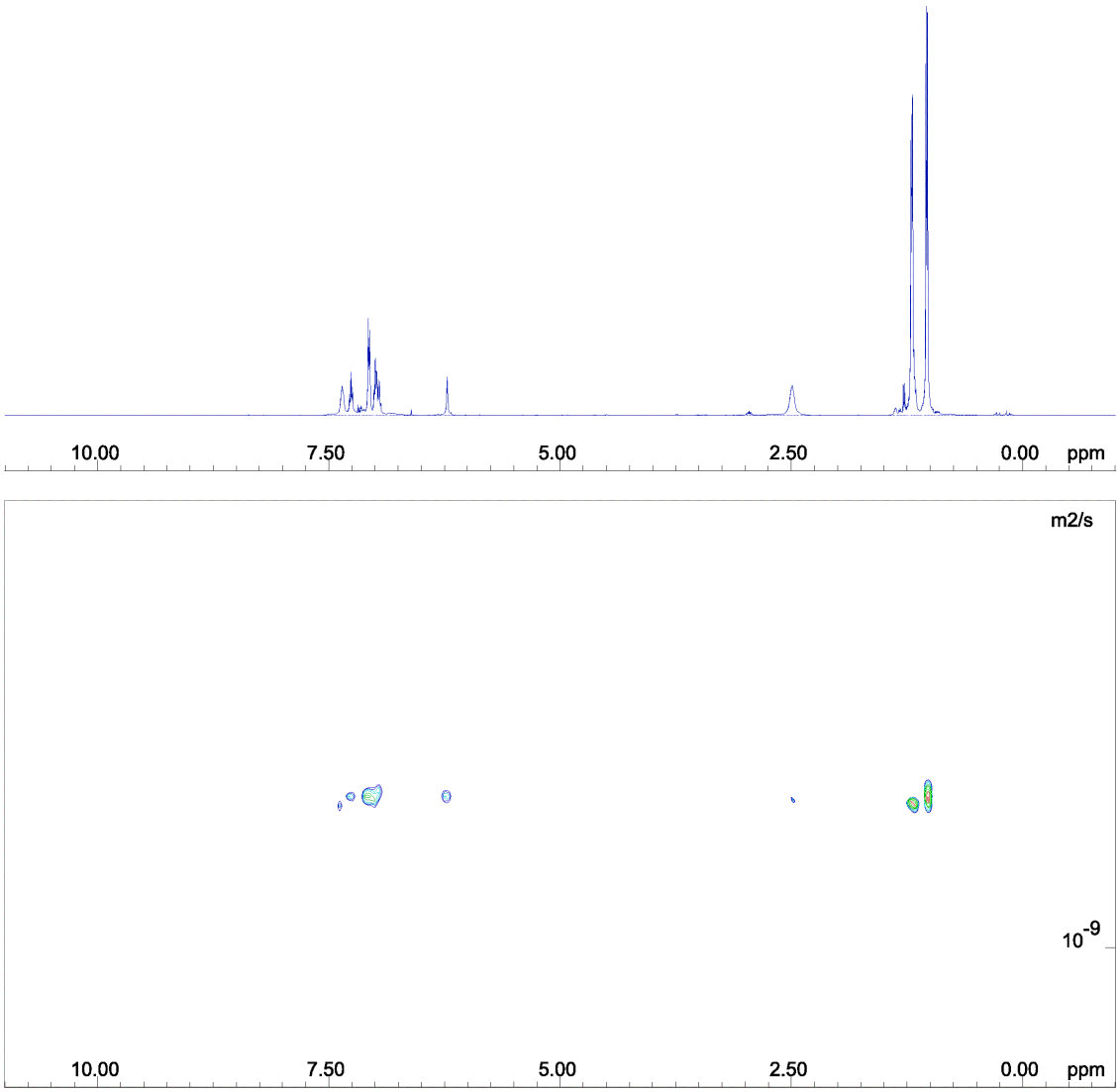
CPK Volumes were converted to radii using Equation 2.

$$r = \sqrt[3]{\frac{3V}{4\pi}}$$

Equation 2

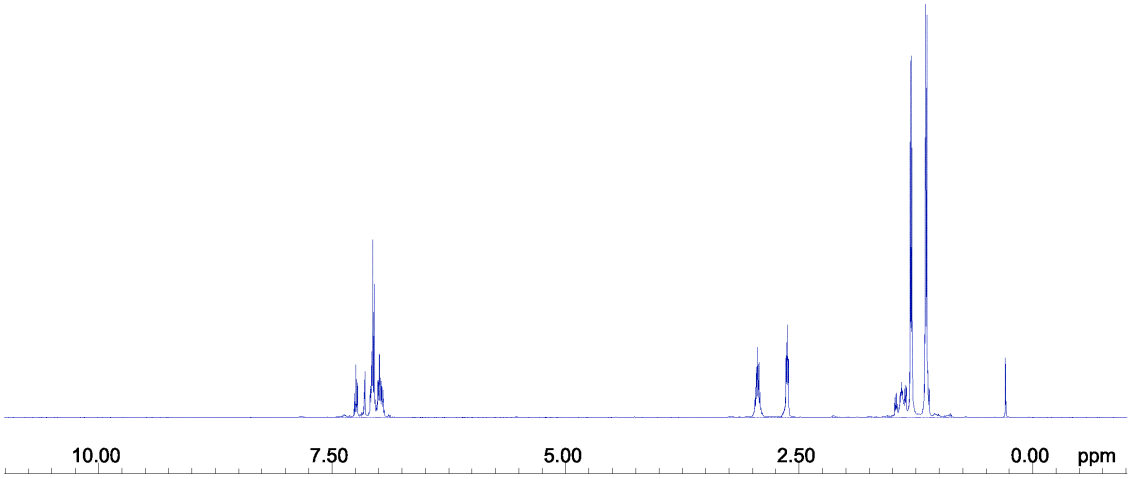
	$Volume_{comp}$ / Å^3	r_{comp} / Å	$Volume_{xray}$ / Å^3	r_{xray} / Å
$\mathbf{1}_{monomer}$	628.75	5.31	648.8	5.37
$\mathbf{2}_{monomer}$	703.51	5.52	667.81	5.42
$\mathbf{3}_{monomer}$	576.74	5.16		
$\mathbf{3}_{dimer}$	1149.02	6.55	1093.81	6.39
$\mathbf{4}_{monomer}$	593.28	5.21		
$\mathbf{4}_{dimer}$	1179.49	6.55	1127.07	6.46

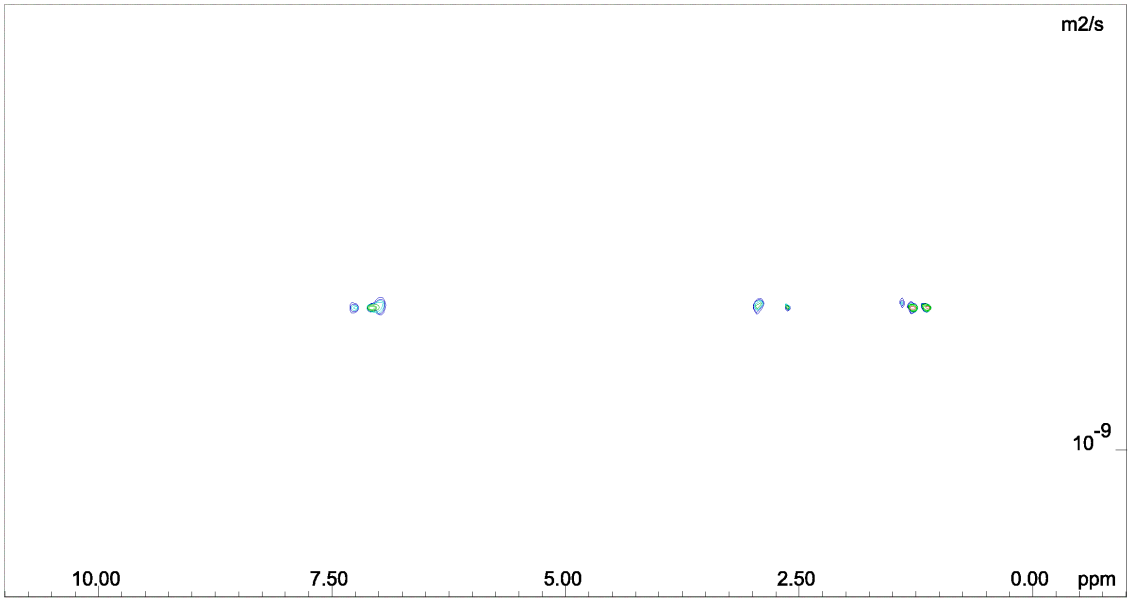
^{1}H NMR DOSY Data for 1



δ / ppm	Diffusion constant / x10^{-10} m^{2}s^{-1}
7.36	6.47
7.28	6.36
7.26	6.34
7.24	6.30
7.07	6.30
7.06	6.32
7.01	6.42
7.00	6.41
6.98	6.30
6.97	6.25
6.95	6.25
6.22	6.35
2.49	6.39
1.20	6.38
1.19	6.45
1.04	6.36
1.03	6.34
Average	6.35

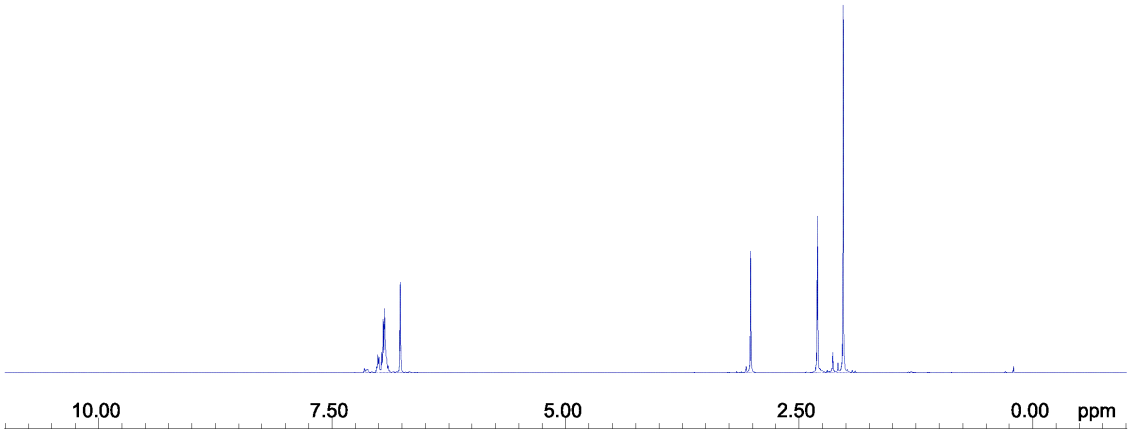
^{1}H NMR DOSY Data for 2

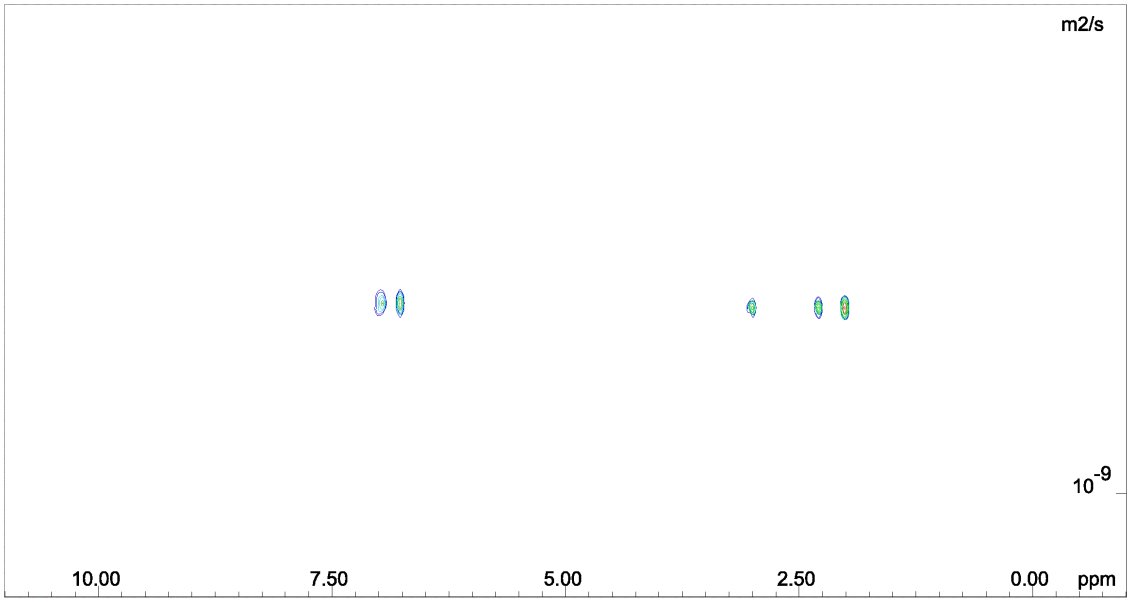




δ / ppm	**Diffusion constant / x10^{-10} m^{2}s^{-1}**
7.26	6.50
7.24	6.54
7.23	6.56
7.06	6.54
7.05	6.57
7.01	6.41
7.00	6.55
6.98	6.49
6.97	6.49
6.95	6.49
2.97	6.55
2.96	6.54
2.95	6.52
2.93	6.48
2.92	6.42
2.64	6.50
2.63	6.52
2.62	6.54
1.40	6.46
1.31	6.55
1.29	6.54
1.15	6.53
1.13	6.52
Average	6.51

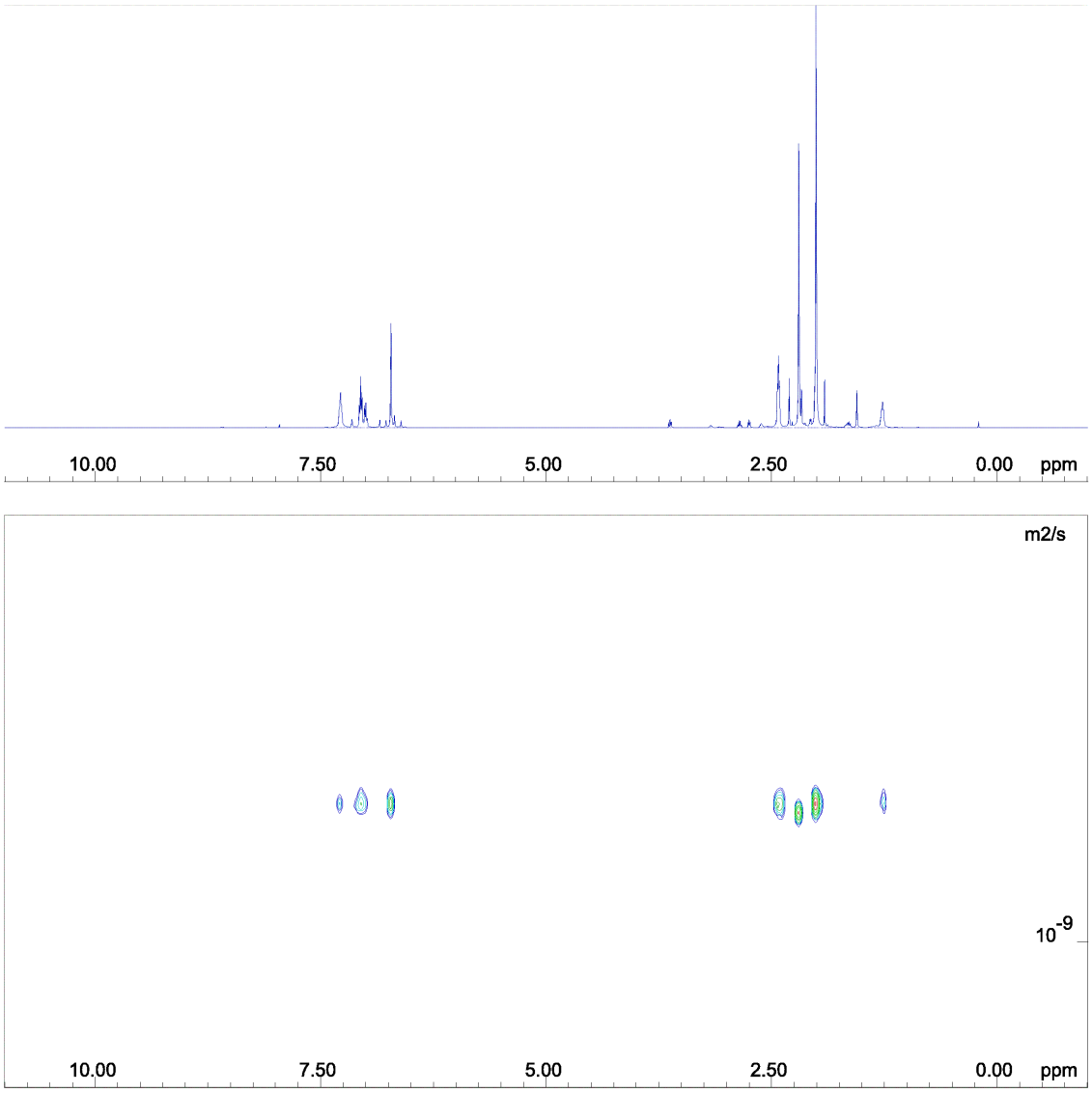
^{1}H NMR DOSY Data for 3





δ / ppm	Diffusion constant / x10^{-10} m^{2}s^{-1}
7.01	5.73
7.00	5.78
6.97	5.60
6.95	5.65
6.94	5.68
6.77	5.67
3.02	5.69
2.30	5.70
2.03	5.70
Average	5.69

^{1}H NMR DOSY Data for 4



δ / ppm	Diffusion constant / x10^{-10} m^{2}s^{-1}
7.28	6.47
7.07	6.57
7.06	6.49
7.04	6.43
7.01	6.47
7.00	6.47
6.72	6.48
2.44	6.59
2.42	6.51
2.41	6.44
2.20	6.67
2.01	6.48
1.28	6.50
1.27	6.45
1.26	6.39
Average	6.49

Computational Details / Methodology

DFT calculations were run with Gaussian 09 (Revision D.01).[5] The Cu and P centres were described with the Stuttgart RECPs and associated basis sets,[6] and 6-31G** basis sets were used for all other atoms.[7, 8] A polarization function was also added to P (ζ_d = 0.387). Initial BP86[9, 10] optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima.

X-ray Crystallography

Data for compounds **1**-**7** (CCDC numbers: 2014370-2014376) were collected on a either a RIGAKU SuperNova or XCALIBUR diffractometer. The crystals were kept at 150.00(10) K during data collection. **1**-**4** were collected with Mo source (λ = 0.71073); **5**-**7** were collected with Cu source (λ = 1.54184). Using Olex2,[12] the structures were solved with the SHELXT[13] and refined with the ShelXL[13] refinement package using Least Squares minimisation.

There are 2 molecules in the asymmetric unit of the structure pertaining to compound **2**.

The asymmetric unit of **3** comprises half of a dimer molecule, the remainder of which is generated via a crystallographic inversion centre.

As so often is the case, with the benefit of the 20:20 vision afforded by hindsight, resolving the crystal structure of **4** might seem quite undemanding. However, the route to obtaining the correct model (as presented herein) was both lengthy and somewhat tortuous. The sample was twinned to a degree and when this is coupled with some metric symmetry, routine integration pointed the crystallographer towards a *C*-centred, monoclinic unit cell, with the following unit cell parameters in conventional order: 4.4348(5), 17.6005(11), 22.6768(9)Å, 90, 90.948(3), 90°. Indeed, a solution was brokered in space group *C*2/*c* with an accompanying *R*1 value of 15.97%. There were no non-positive definite atoms in the model associated with the monoclinic symmetry, but some of the ellipsoids looked irregular and the weighting scheme was, aesthetically and numerically, a mess! In these days of black-box crystallography, it is ever more important to understand the fundamentals when the data might suggest a route that is unacceptable. Ultimately, correct care of twinning at the point of integration - with recognition of the fact that the *R*(int) value came into the loose realm of 'acceptable' [8.69% in the incorrect monoclinic cell (*C*2/*c*)] purely as a consequence of twinning - afforded the model presented herein (triclinic data with almost 50:50 twinning). Overall, this suggests that a traditional crystallographer still has a vital role, in dealing correctly with data from a sample for which a solution and refinement does readily not fall into one's lap.

There are 2 molecules of the copper complex and 2 molecules of benzene in the asymmetric unit of **6**. The molecule based on Cu2 is entirely ordered as is the benzene moiety containing C95. However, in the molecule based on Cu1, the sulphur atom was seen to be disordered over three positions in a 65:27:8 ratio while the benzene molecule based on C101 was treated for disorder in a 70:30 ratio. Distance and ADP restraints were employed in disordered regions to assist convergence.

The asymmetric unit in **7** plays host to 1 molecule of benzene disordered in a 60:40 ratio, (in which the rings were treated as rigid hexagons) plus one molecule of the copper complex.

Table S1 Crystal data and structure refinement details

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{39}H_{46}CuN_2P$	$C_{40}H_{50}CuN_2P$	$C_{33}H_{36}CuN_2P$	$C_{68}H_{76}Cu_2N_4P_2$	$C_{44}H_{57}CuN_3OP$	$C_{106}H_{122}Cu_2N_6P_2S_2$	$C_{47}H_{56}CuN_2PS_2$
Formula weight	637.29	653.33	555.15	1138.34	738.43	1733.23	807.56
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$	*P*-1	$P2_1/n$	*P*-1	$P2_1/c$
a/ Å	10.0805(5)	12.8035(3)	12.9476(3)	11.3727(3)	12.5486(1)	16.7653(4)	10.7063(1)
b/ Å	10.9216(5)	16.6298(4)	19.6806(3)	11.3954(4)	18.9533(1)	16.7976(3)	12.6577(1)
c/ Å	16.5042(10)	17.6961(4)	13.1443(3)	22.6857(8)	17.6600(1)	17.4582(3)	32.3409(3)
α/ °	73.491(5)	104.810(2)	90	90.164(3)	90	99.123(1)	90
β/ °	88.101(4)	90.293(2)	119.072(3)	91.091(3)	106.2330(10)	103.295(2)	98.799(1)
γ/ °	84.877(4)	95.555(2)	90	101.250(3)	90	92.374(2)	90
U/ Å^3	1735.11(16)	3623.82(15)	2927.39(13)	2882.91(17)	4032.76(5)	4708.68(17)	4331.17(7)
Z	2	4	4	2	4	2	4
$\rho_{calc/}$ g cm^{-3}	1.22	1.197	1.260	1.311	1.216	1.222	1.238
μ/ mm^{-1}	0.704	0.676	0.824	0.839	1.405	1.669	2.207
F(000)	676	1392.0	1168.0	1200.0	1576.0	1840.0	1712.0
Crystal size/ mm^3	0.475 × 0.244 × 0.197	0.442 × 0.267 × 0.18	0.374 × 0.234 × 0.168	0.497 × 0.294 × 0.267	0.476 × 0.147 × 0.112	0.246 × 0.175 × 0.152	0.274 × 0.178 × 0.099
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/ °	7.062 to 59.178	6.658 to 59.254	7.094 to 59.084	6.526 to 56.718	6.994 to 146.76	5.346 to 146.836	5.53 to 146.698
Index ranges	-13 ≤ h ≤ 10, -14 ≤ k ≤ 12, -22 ≤ l ≤ 22	-17 ≤ h ≤ 16, -22 ≤ k ≤ 23, -24 ≤ l ≤ 24	-16 ≤ h ≤ 16, -27 ≤ k ≤ 25, -17 ≤ l ≤ 18	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30	-15 ≤ h ≤ 15, -23 ≤ k ≤ 17, -20 ≤ l ≤ 21	-20 ≤ h ≤ 19, -15 ≤ k ≤ 20, -21 ≤ l ≤ 21	-13 ≤ h ≤ 12, -14 ≤ k ≤ 15, -39 ≤ l ≤ 40
Reflections collected	14815	35949	27306	15498	32573	39170	31062
Independent reflections, R_{int}	8096, 0.0217	16928, 0.0291	7159, 0.0267	15498, 0.0635	8055, 0.0312	18602, 0.0206	8598, 0.0496
Data/restraints/parameters	8096/0/396	16928/0/809	7159/0/340	15498/14/707	8055/0/461	18602/14/1121	8598/15/516
Goodness-of-fit on F2	1.034	1.014	1.025	1.056	1.027	1.011	1.041
Final *R*1, *wR*2 [I>=2σ (I)]	0.0405, 0.0826	0.0416, 0.0836	0.0317, 0.0732	0.0426, 0.1054	0.0325, 0.0859	0.0327, 0.0834	0.0445, 0.1161
Final *R*1, *wR*2 [all data]	0.0546, 0.0891	0.0672, 0.0932	0.0450, 0.0796	0.0540, 0.1078	0.0344, 0.0876	0.0362, 0.0862	0.0498, 0.1215
Largest diff. peak/hole / e Å^{-3}	0.34, -0.33	0.63, -0.46	0.35, -0.25	0.67, -0.65	0.34, -0.41	0.34, -0.72	0.27, -0.40

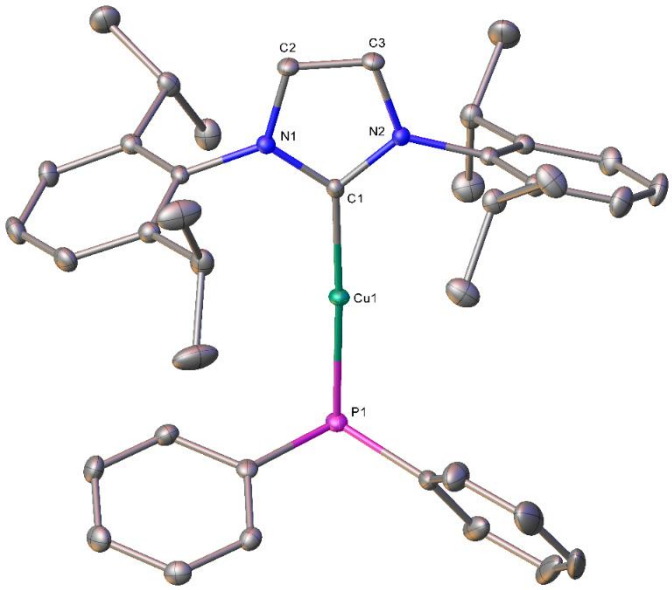


Figure S1: ORTEP representation of compound (IPr)CuPPh$_2$ **1** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-P1 2.2079(5), Cu1-C1 1.9037(17), P1-C28 1.835(2), P1-C34 1.827(2), C1-Cu1-P1 177.09(6), Cu1-P1-C28 105.65(6), Cu1-P1-C34 98.83(6), C28-P1-C34 103.23(9).

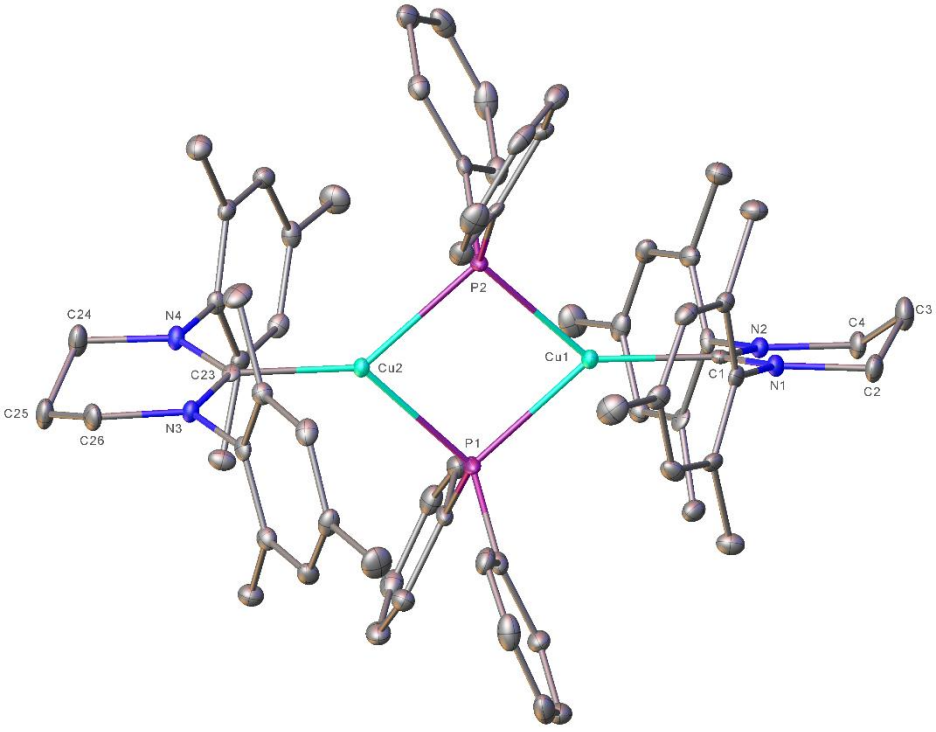


Figure S2: ORTEP representation of compound (6-Mes)CuPPh$_2$ **4** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-P1 2.3803(9), Cu1-P2 2.3814(8), Cu1-C1 1.969(3), Cu2-P1 2.3908(8), Cu2-P2 2.3586(9), Cu2-C23 1.965(3), C1-Cu1-P1 136.76(9), C1-Cu1-P2 137.48(9), P1-Cu1-P2 85.61(3), Cu1-P1-Cu2 (93.85(3), Cu1-P2-Cu2 94.66(3), P1-Cu2-P2 85.88(3), C23-Cu2-P1 135.17(8), C23-Cu2-P2 138.68(8).

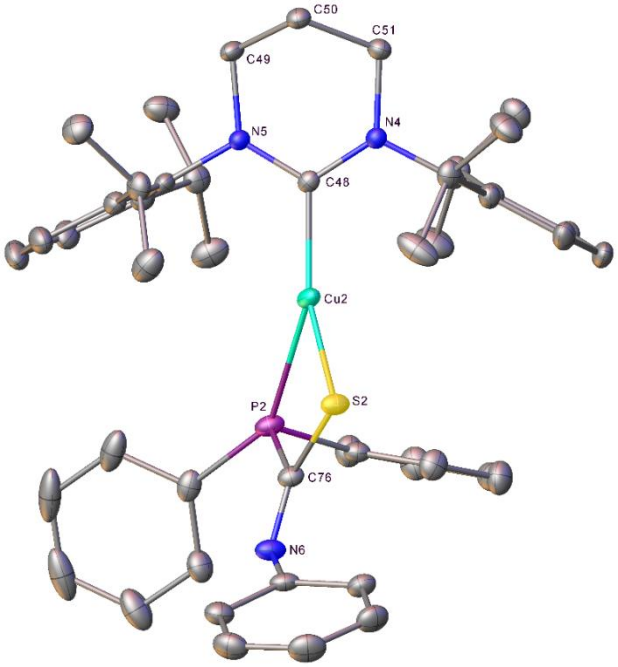


Figure S3: ORTEP representation of compound (6-Dipp)Cu[SC(NPh)PPh_2] **6** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu2-S2 2.2108(4), Cu2-P2 2.5909(4), Cu2-C48 1.9263(14), S2-C76 1.7435(14), P2-C76 1.8468(15), N6-C76 1.2807(19), N6-C77 1.4197(19), C48-Cu2-S2 143.45(4), C48-Cu2-P2 143.20(4), S2-Cu2-P2 73.274(14), Cu2-S2-C76 96.53(5), Cu2-P2-C76 82.07(5), S2-C76-P2 106.72(7), S2-C76-N6 129.90(11), P2-C76-N6 123.26(11), C76-N6-C77 119.00(13).

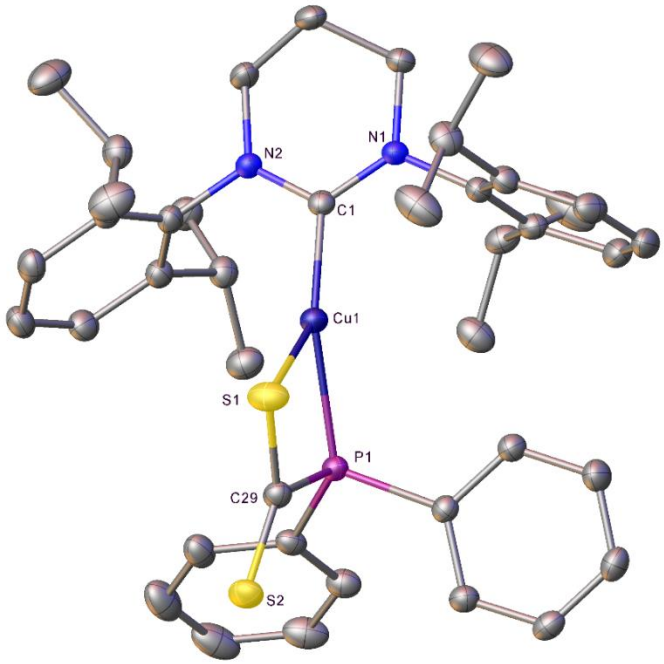


Figure S4: ORTEP representation of compound (6-Dipp)Cu[SC(S)PPh_2] **7**. (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-S1 2.3690(6), Cu1-P1 2.3120(5), Cu1-C1 1.927(2), S1-C29 1.704(2), P1-C29 1.848(2), S2-C29 1.646(2), C1-Cu1-S1 141.19(6), C1-Cu1-P1 144.72(6), S1-Cu1-P1 74.04(2), Cu1-S1-C29 90.53(7), Cu1-P1-C29 88.87(7), S1-C29-P1 104.96(11), S1-C29-S2 129.58(13), P1-C29-S2 125.44(12).

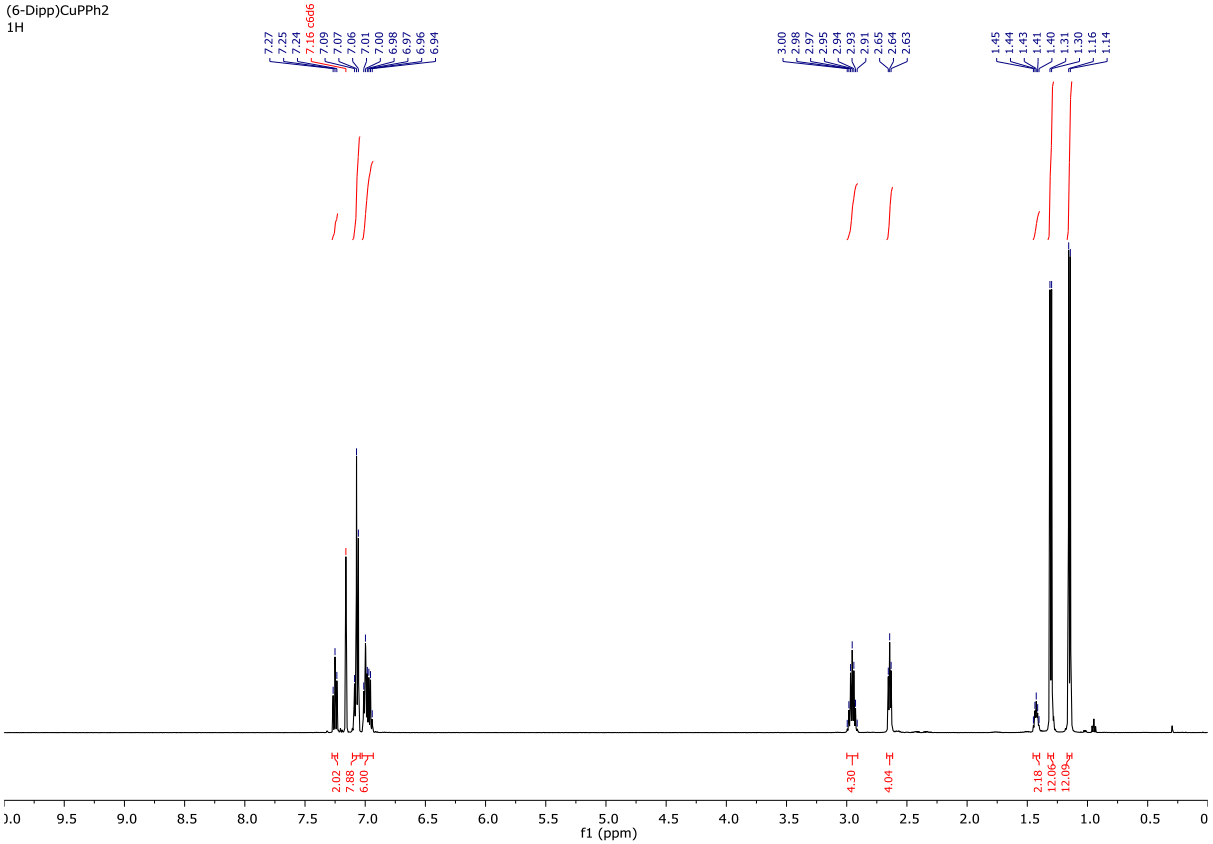


Figure S5: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **2**.

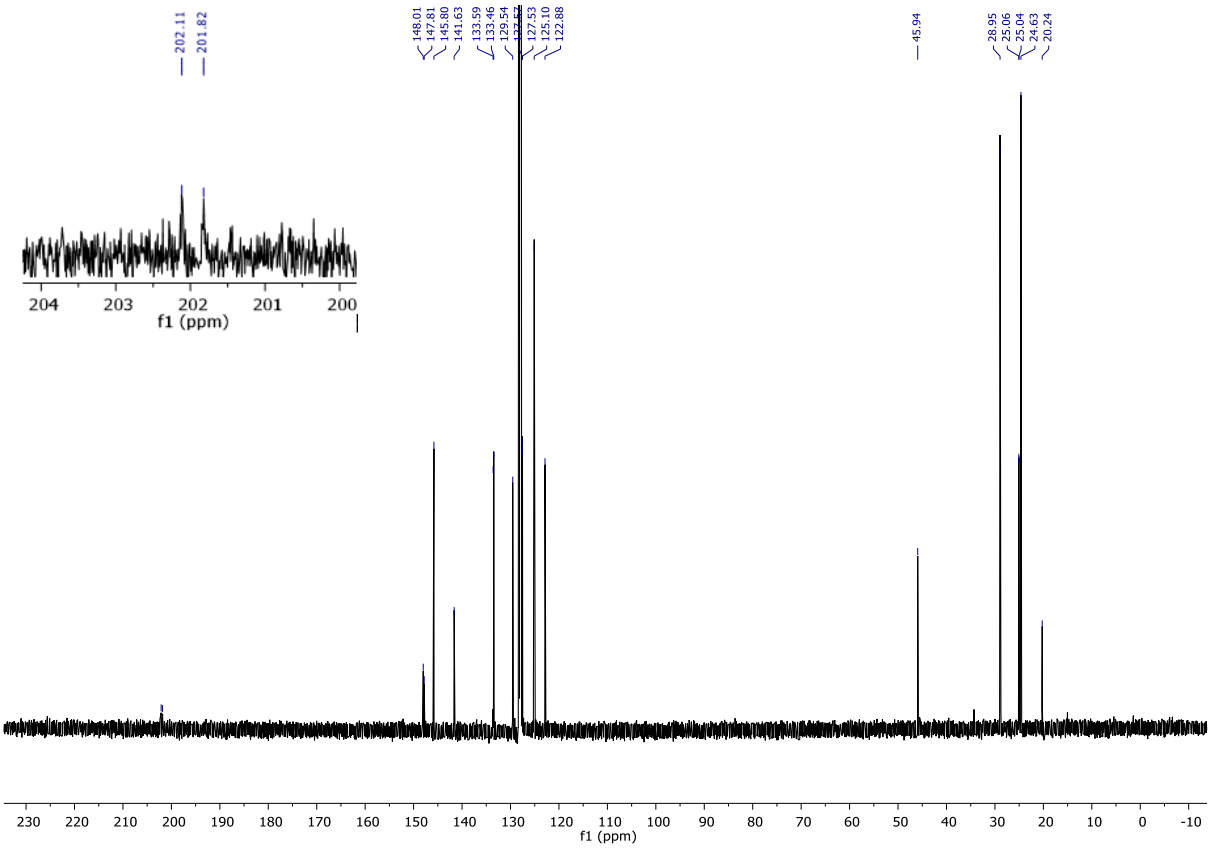


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **2**.

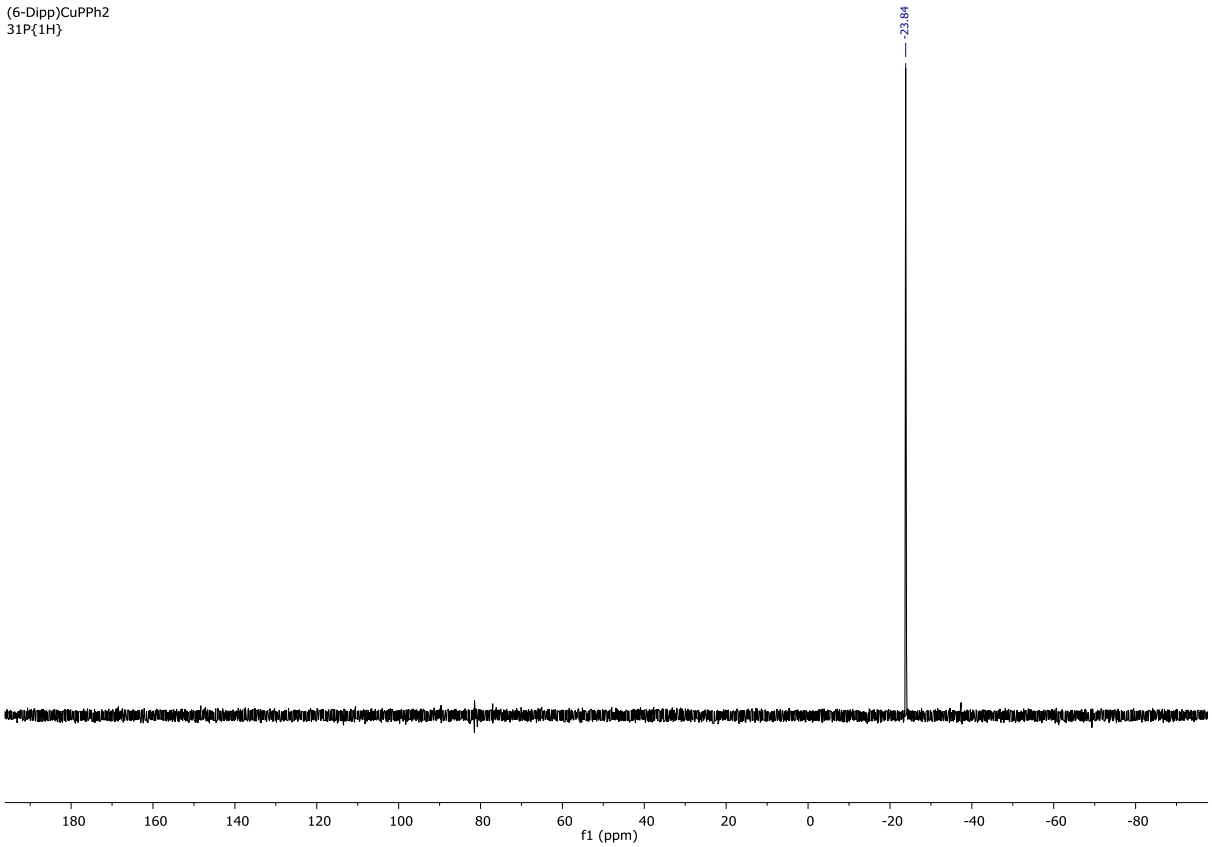


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **2**.

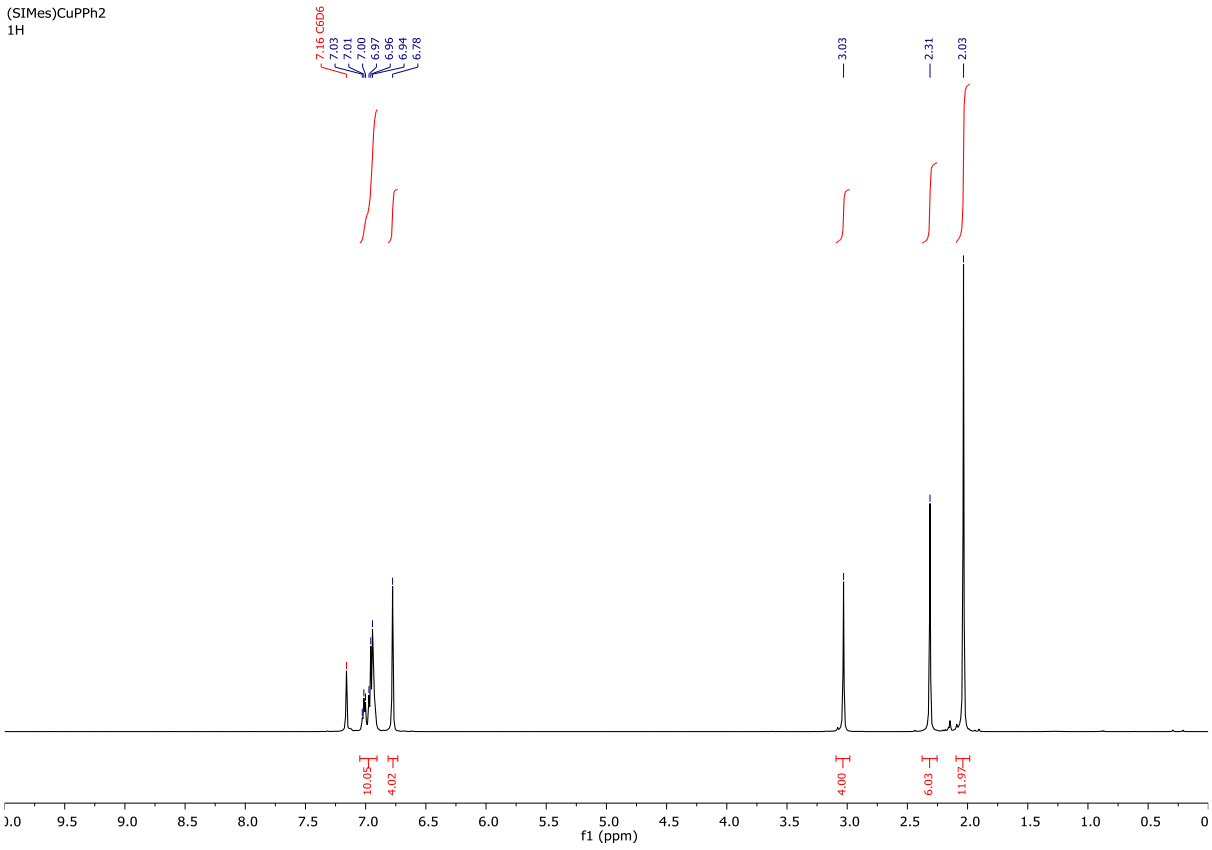


Figure S8: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **3**.

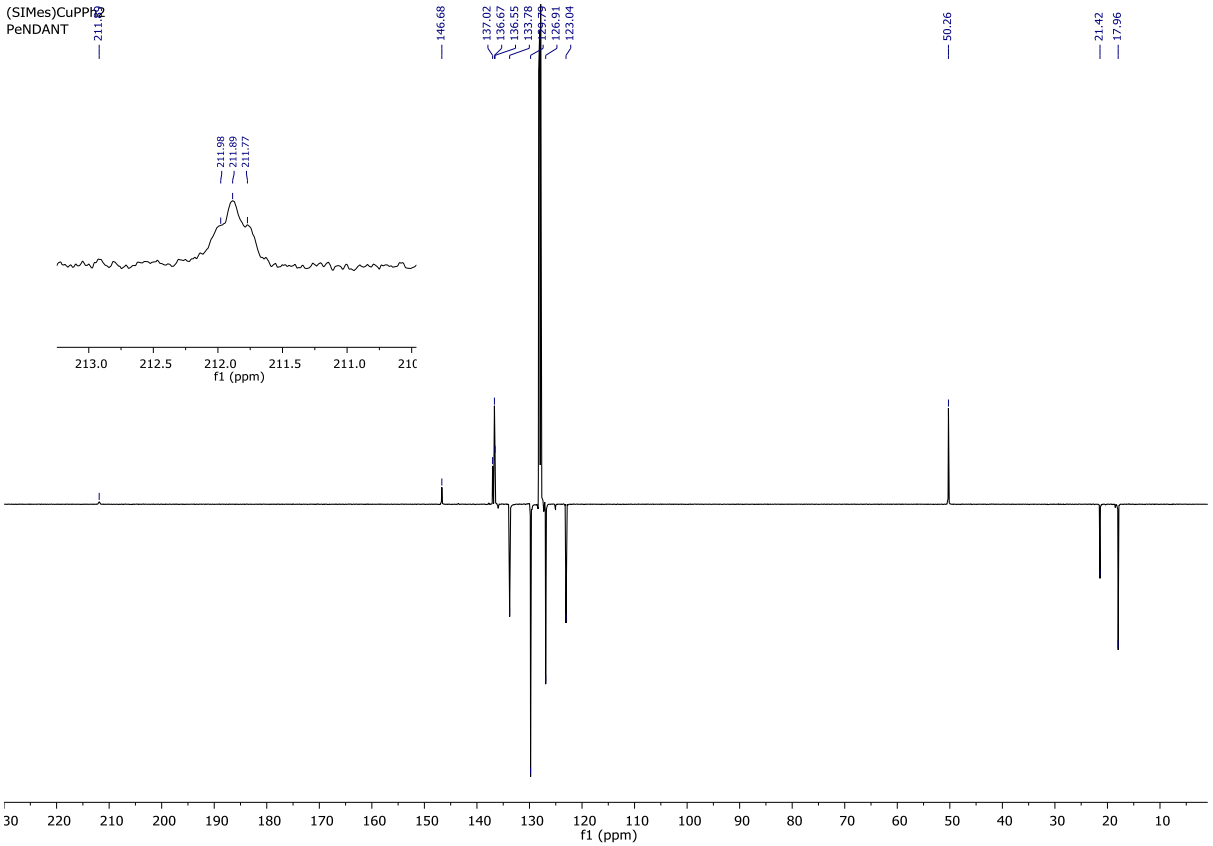


Figure S9: $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (126 MHz, C_6D_6, 298 K) of compound **3**. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Toluene-d_8, 235 K) of carbonic region inset.

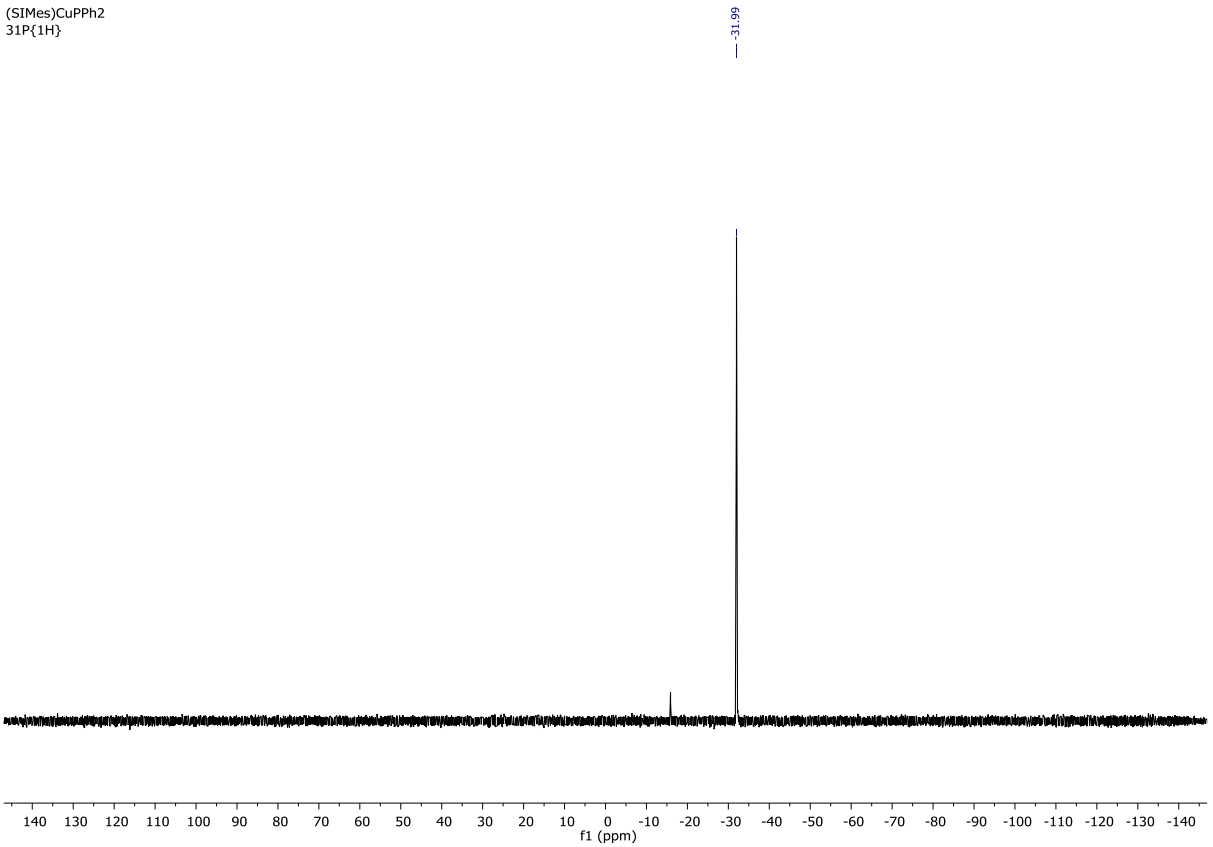


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **3**.

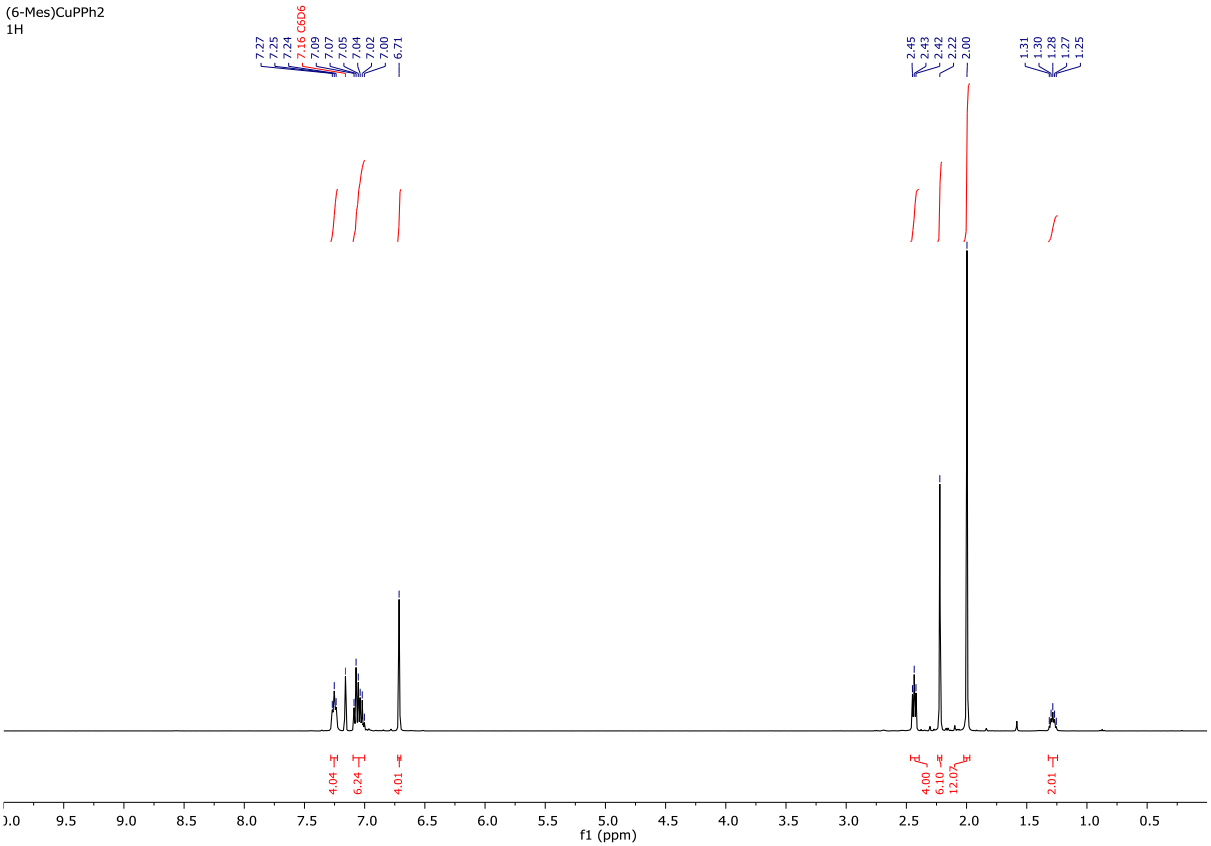


Figure S11: ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **4**.

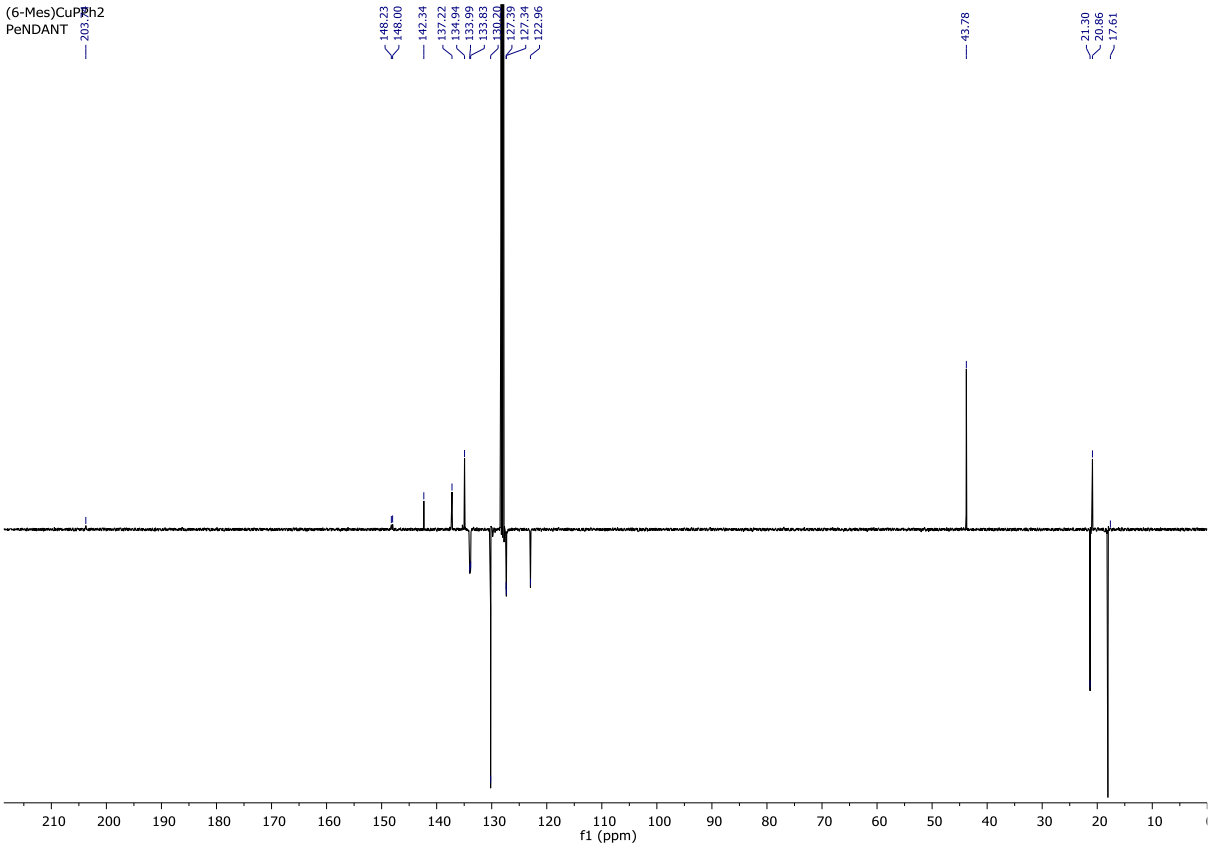


Figure S12: $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (101 MHz, C_6D_6) of compound **4**.

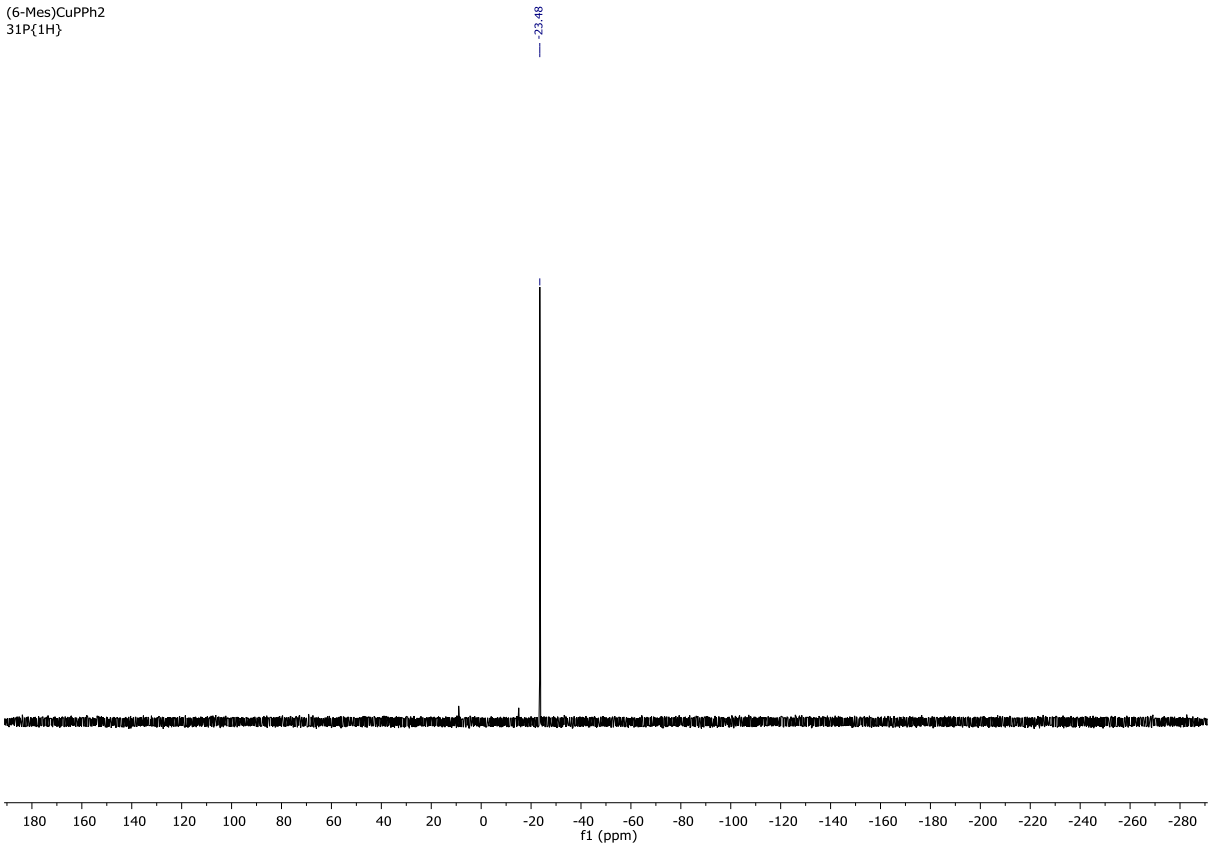


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of compound **4**.

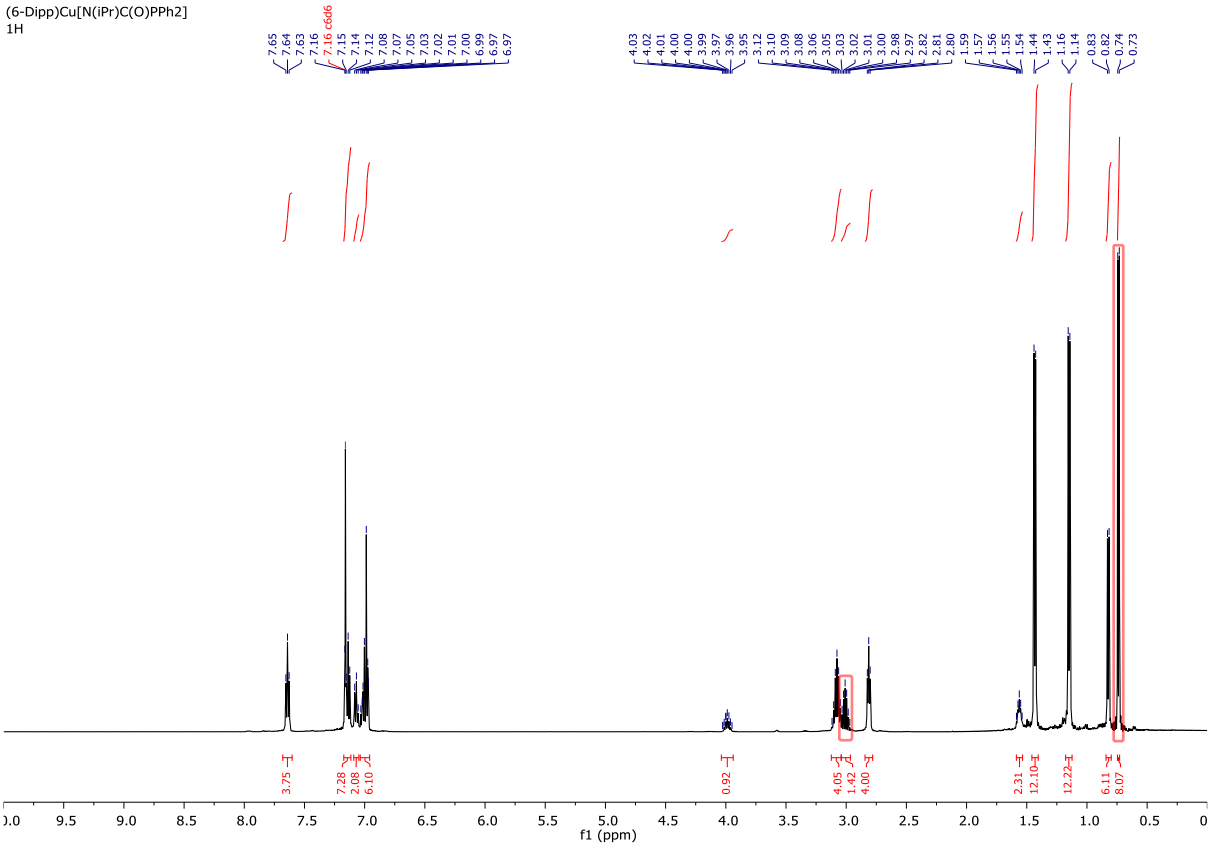


Figure S14: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **5**. Resonances corresponding to isopropyl isocyanate are highlighted in red. $C_6D_{6-n}H_n$ overlaps some compound signals.

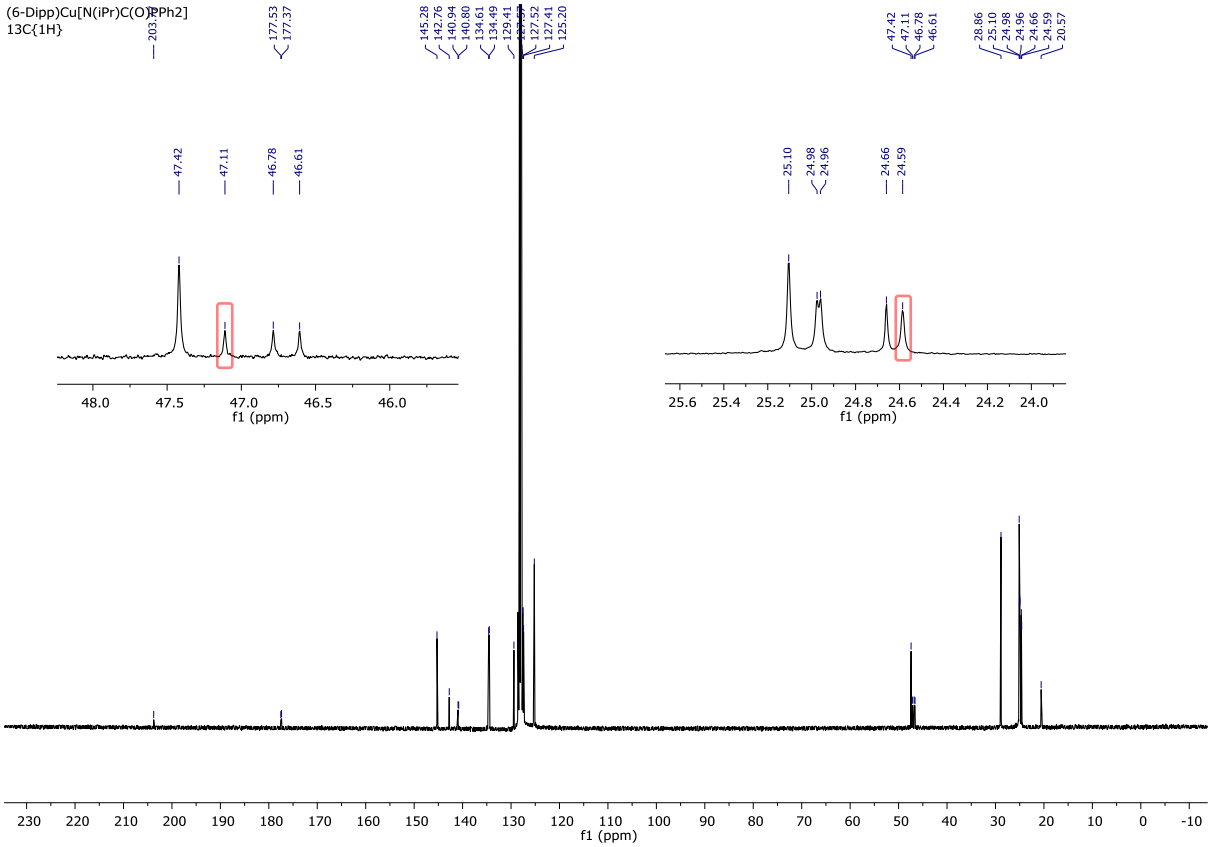


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **5**. Resonances corresponding to isopropyl isocyanate are highlighted in red.

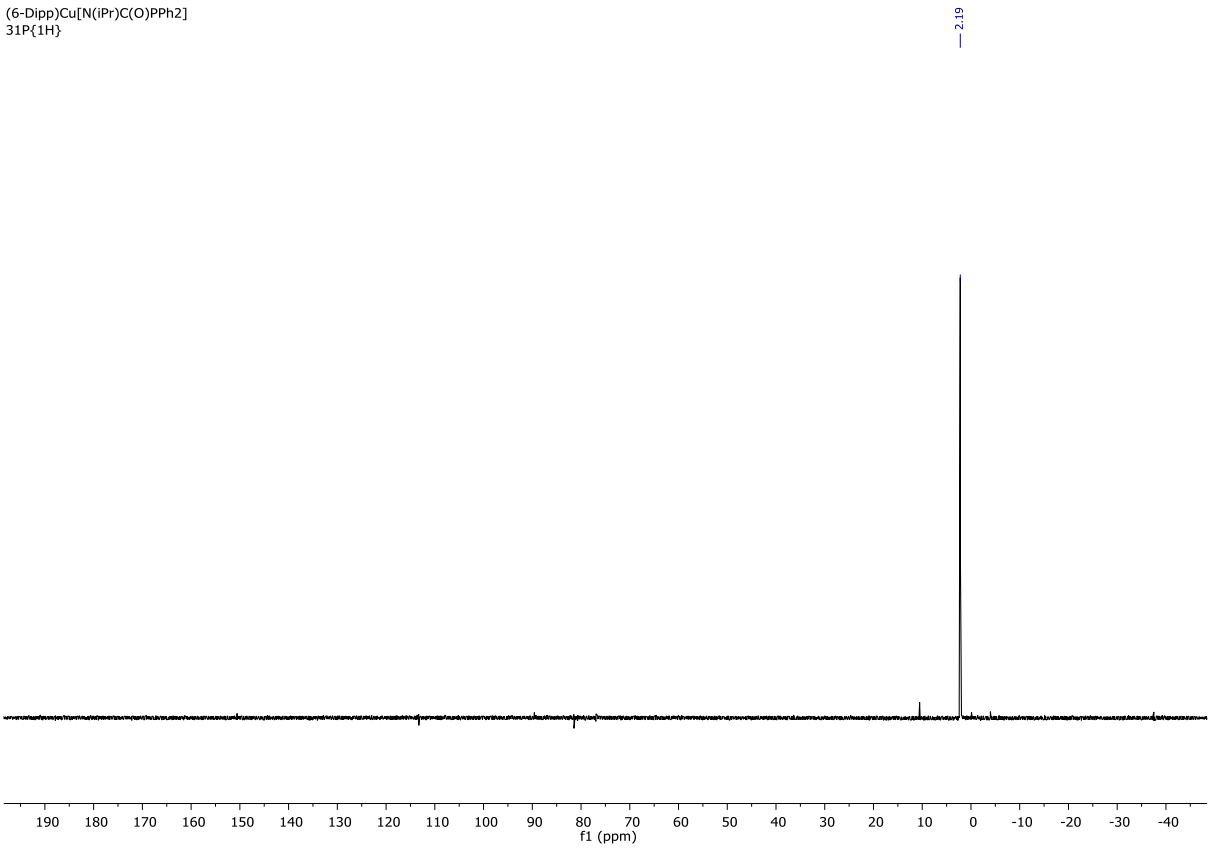


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **5**.

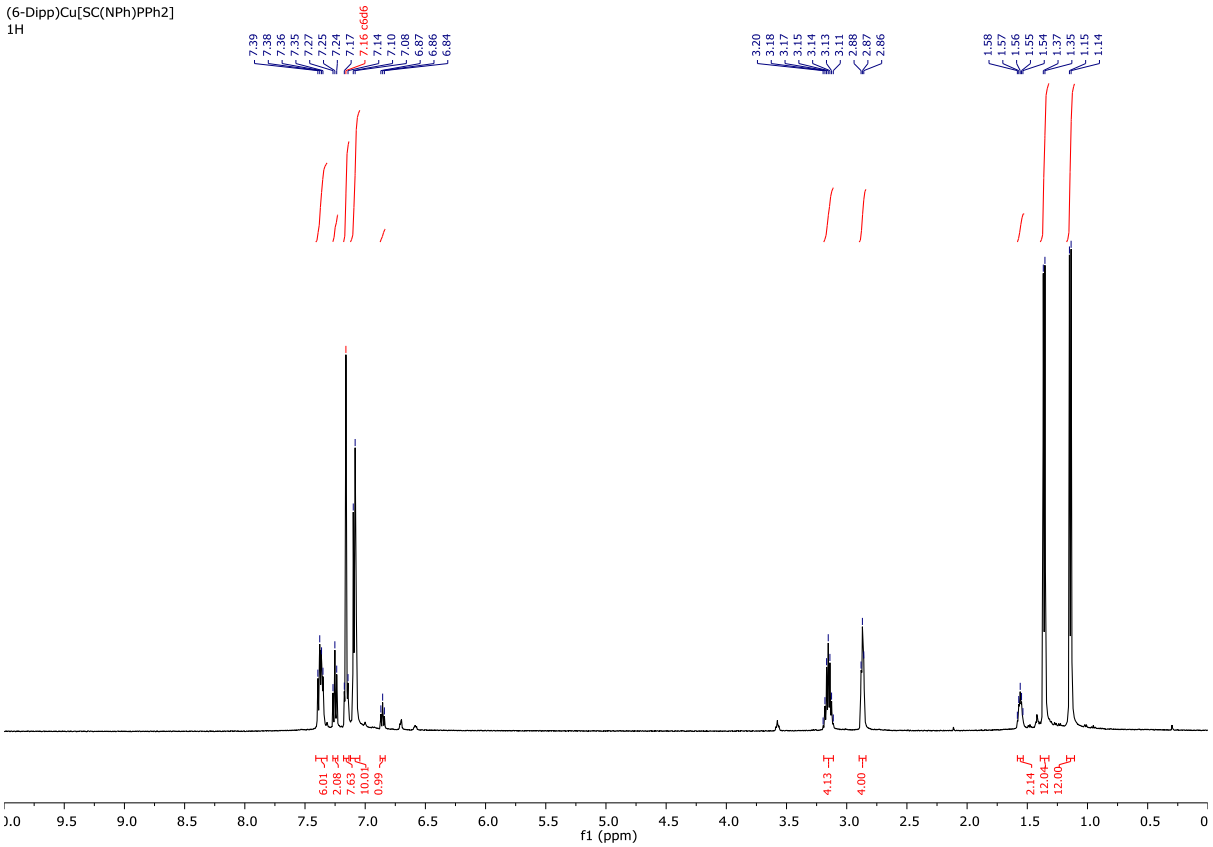


Figure S17: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **6**. C_6D_6 overlaps some compound signals.

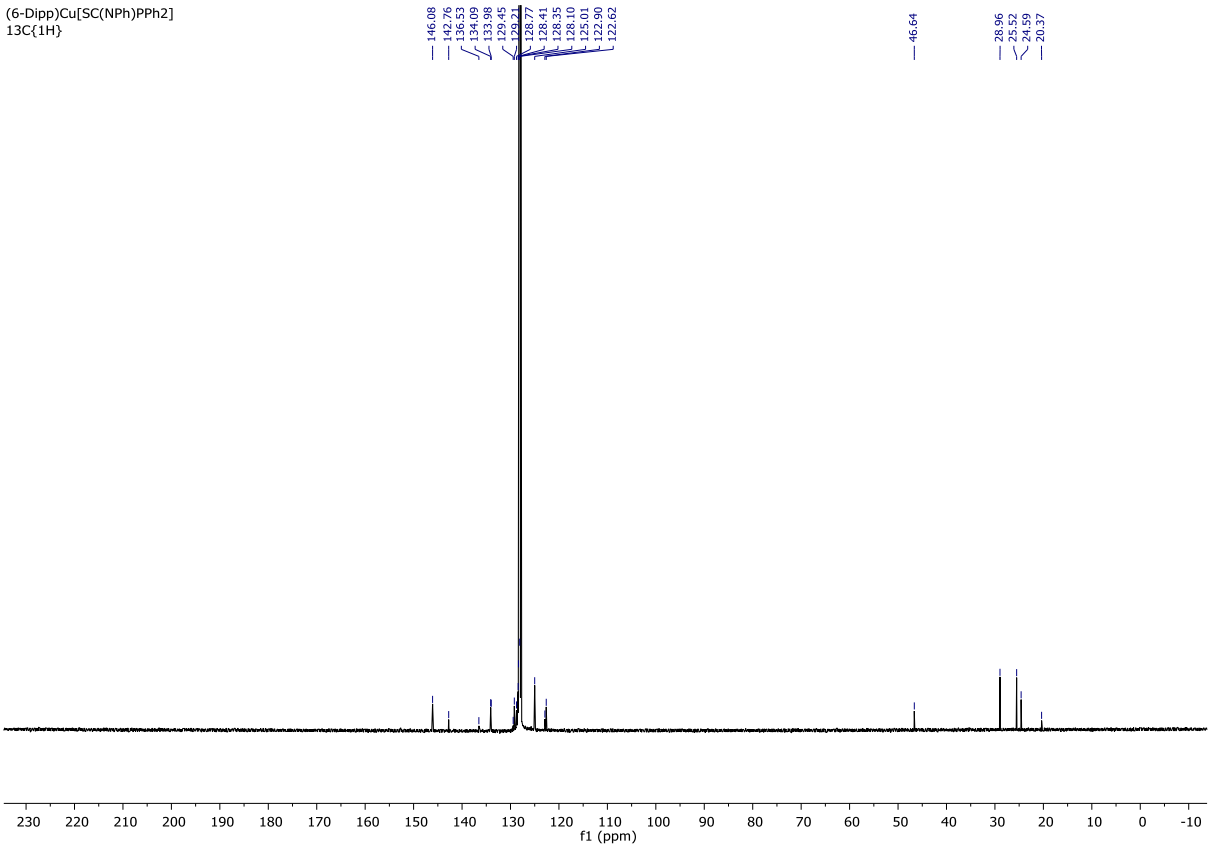


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **6**.

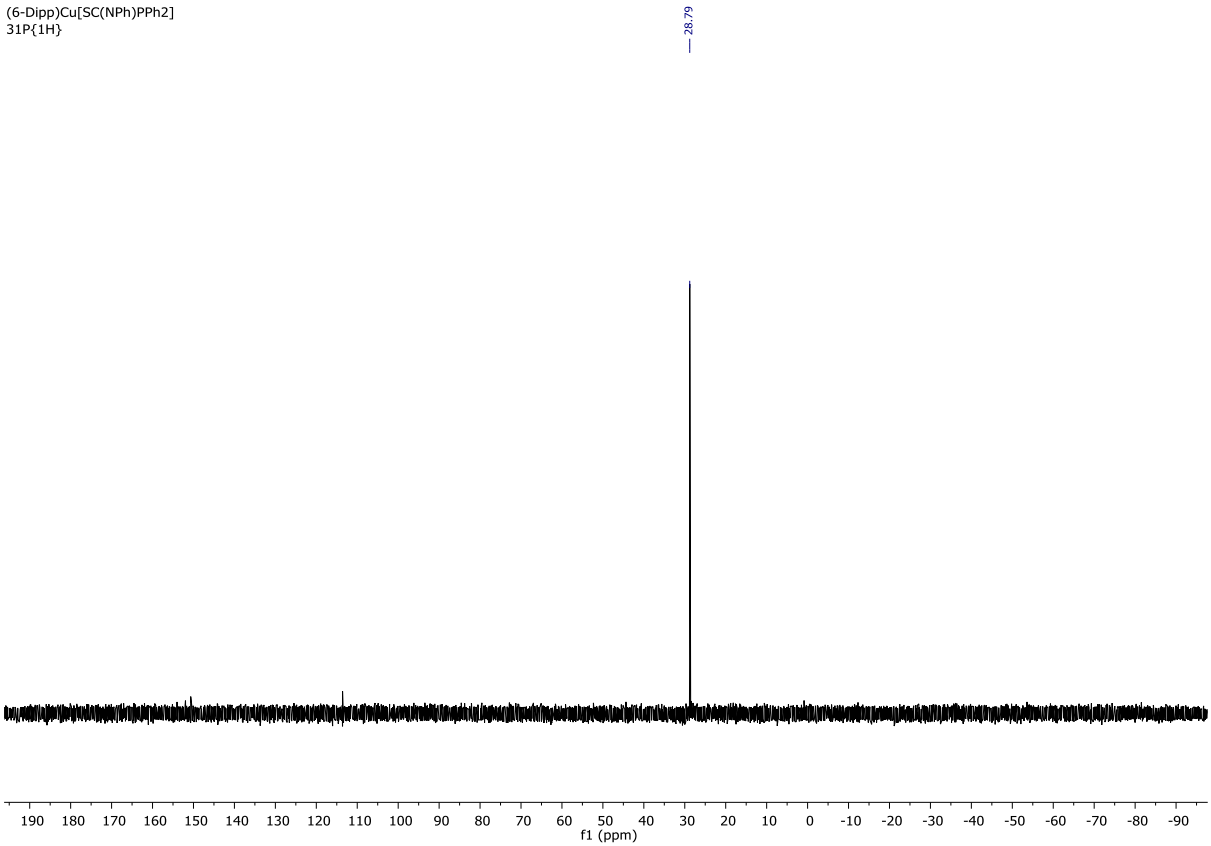


Figure S19: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **6**.

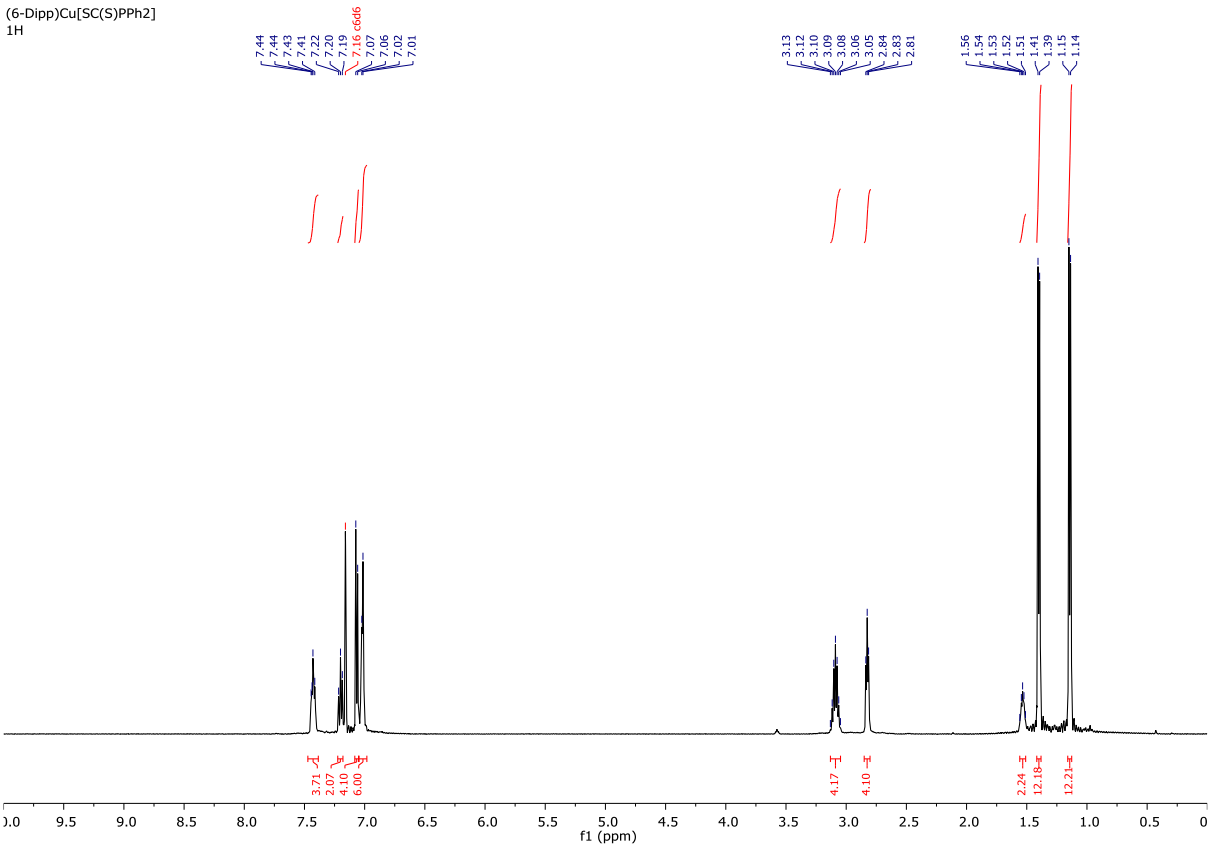


Figure S20: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **7**.

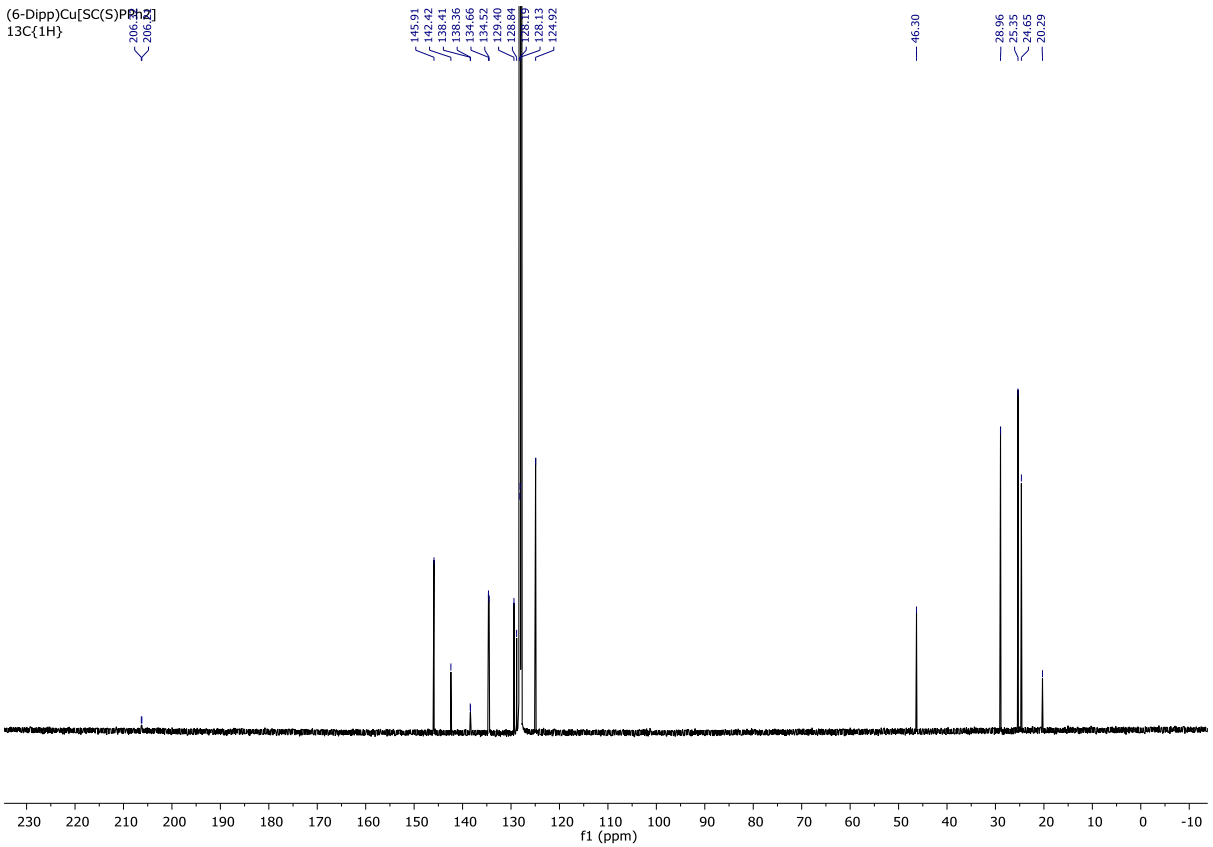


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **7**.

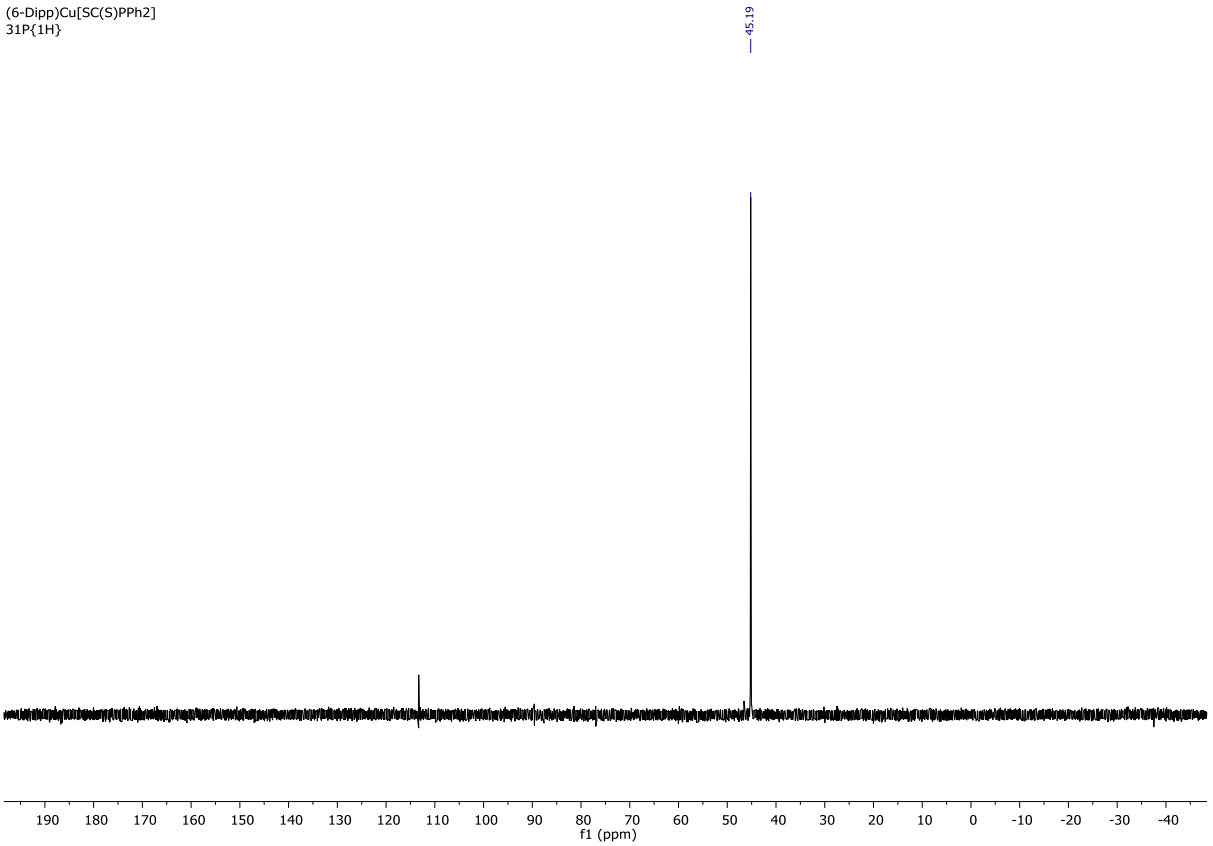


Figure S22: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **7**.

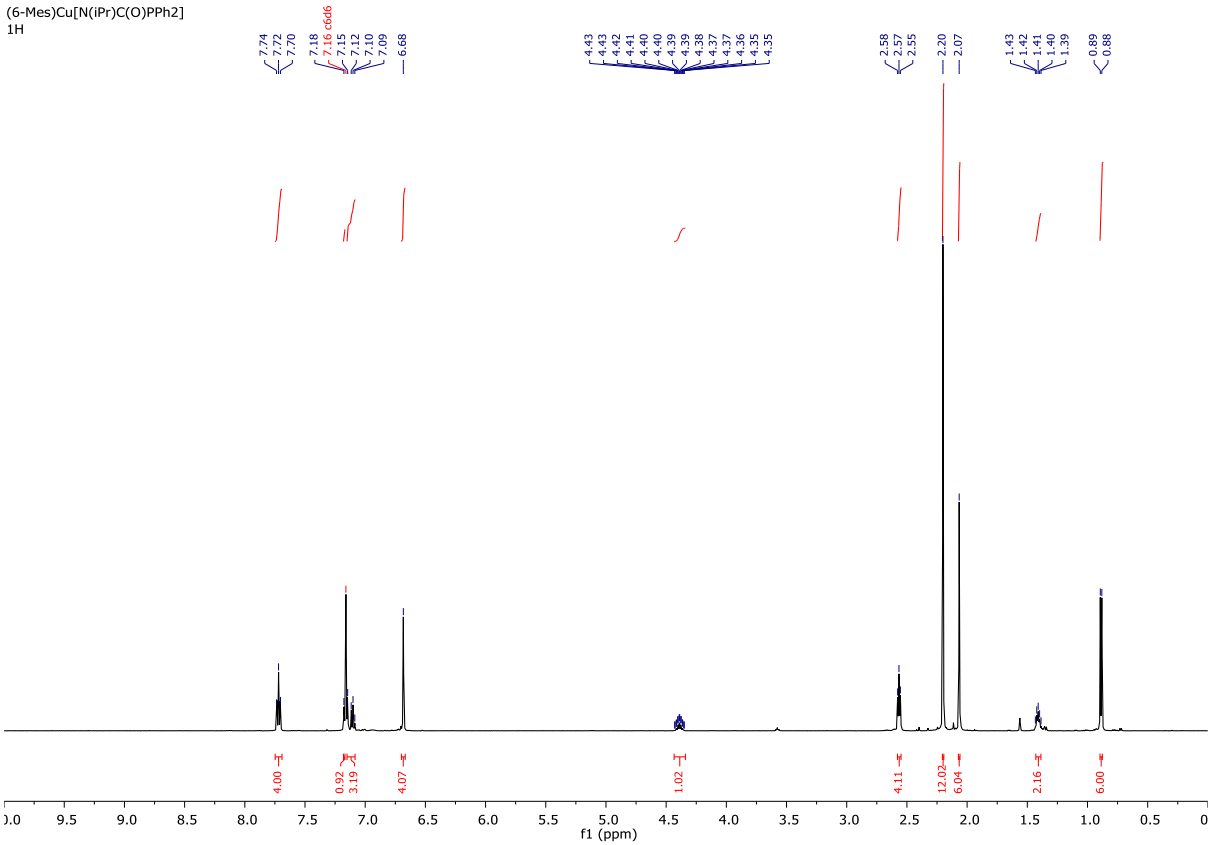


Figure S23: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **S1**. $C_6D_{6-n}H_n$ overlaps some compound signals.

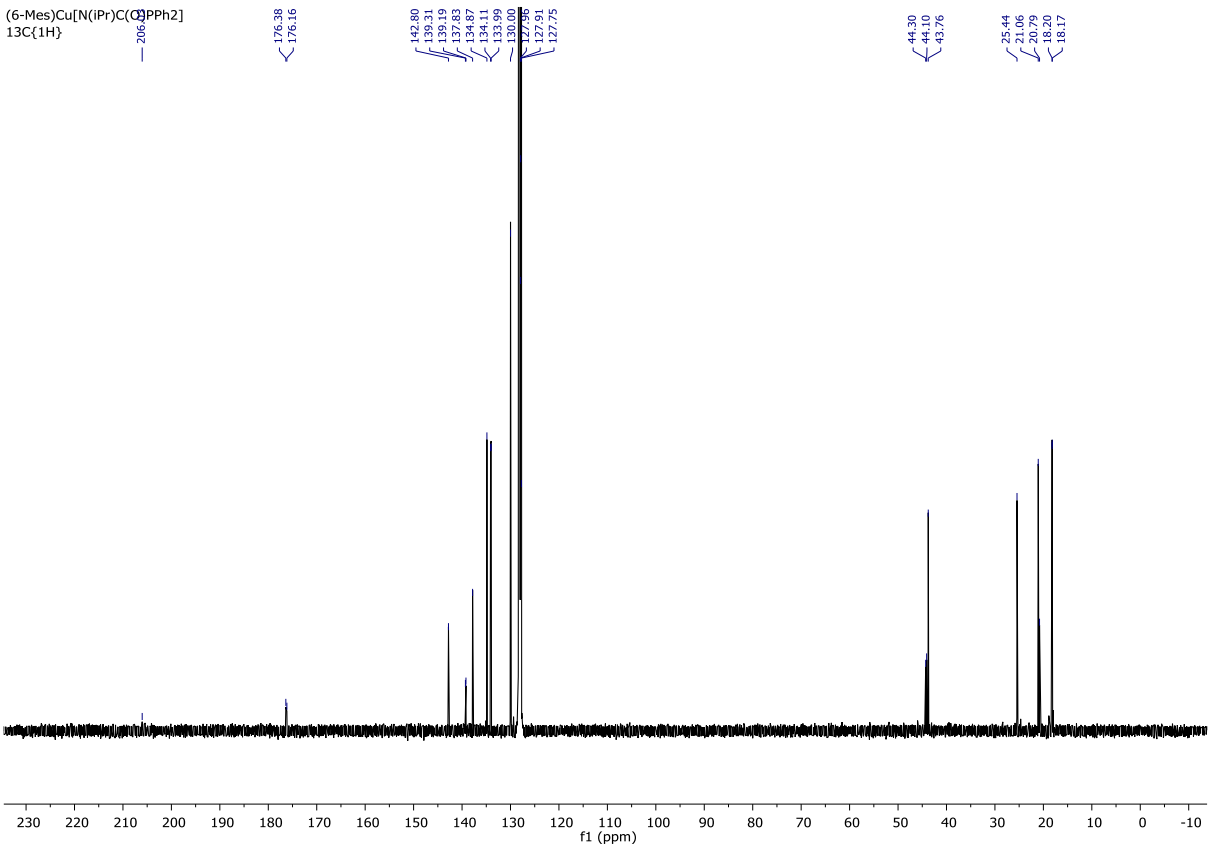


Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **S1**.

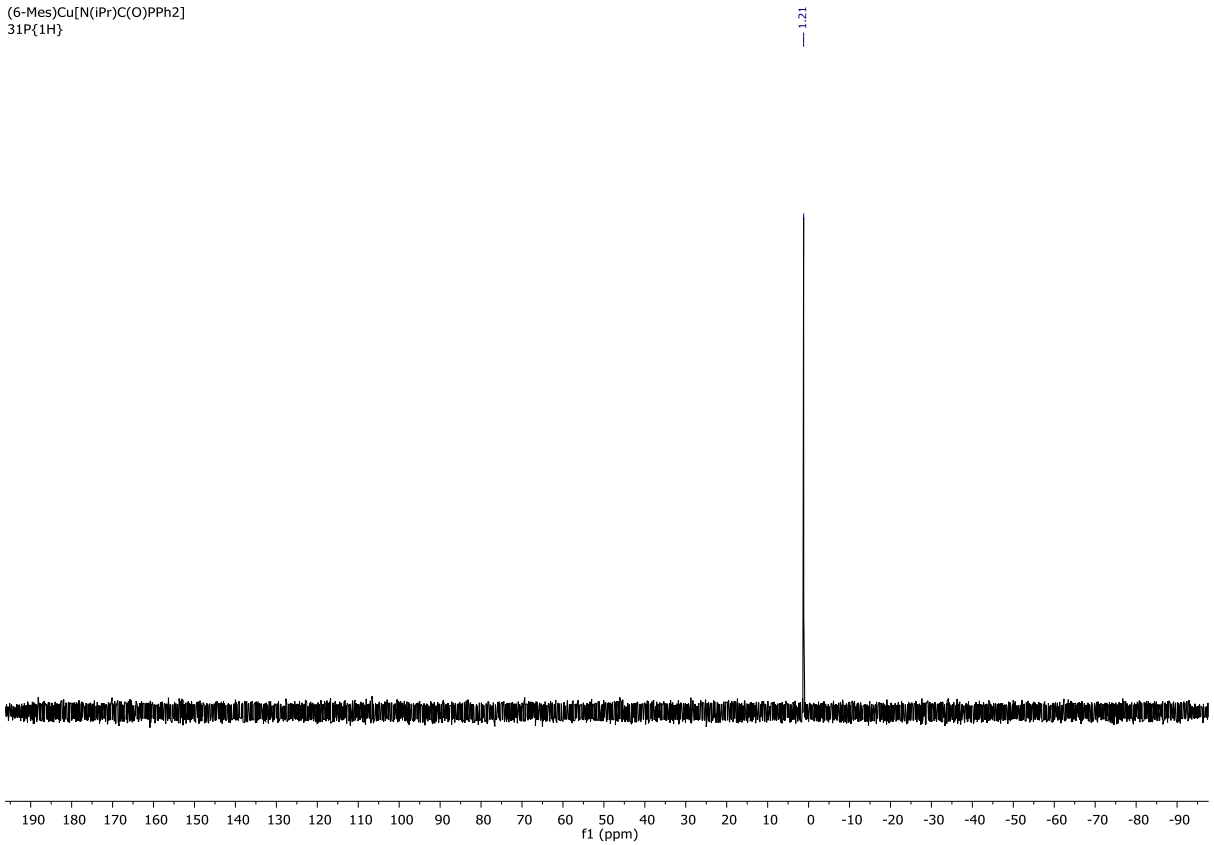


Figure S25: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **S1**.

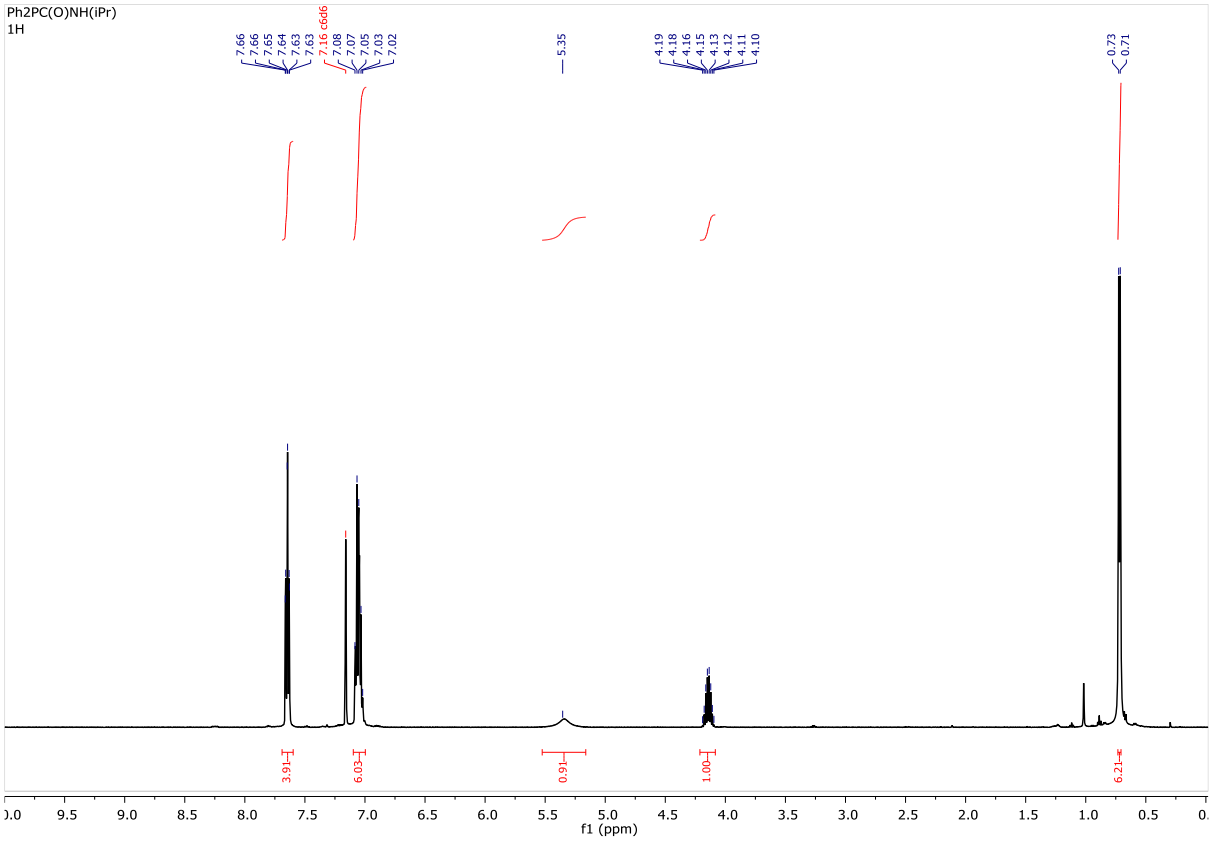


Figure S26: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(iPr)$**.

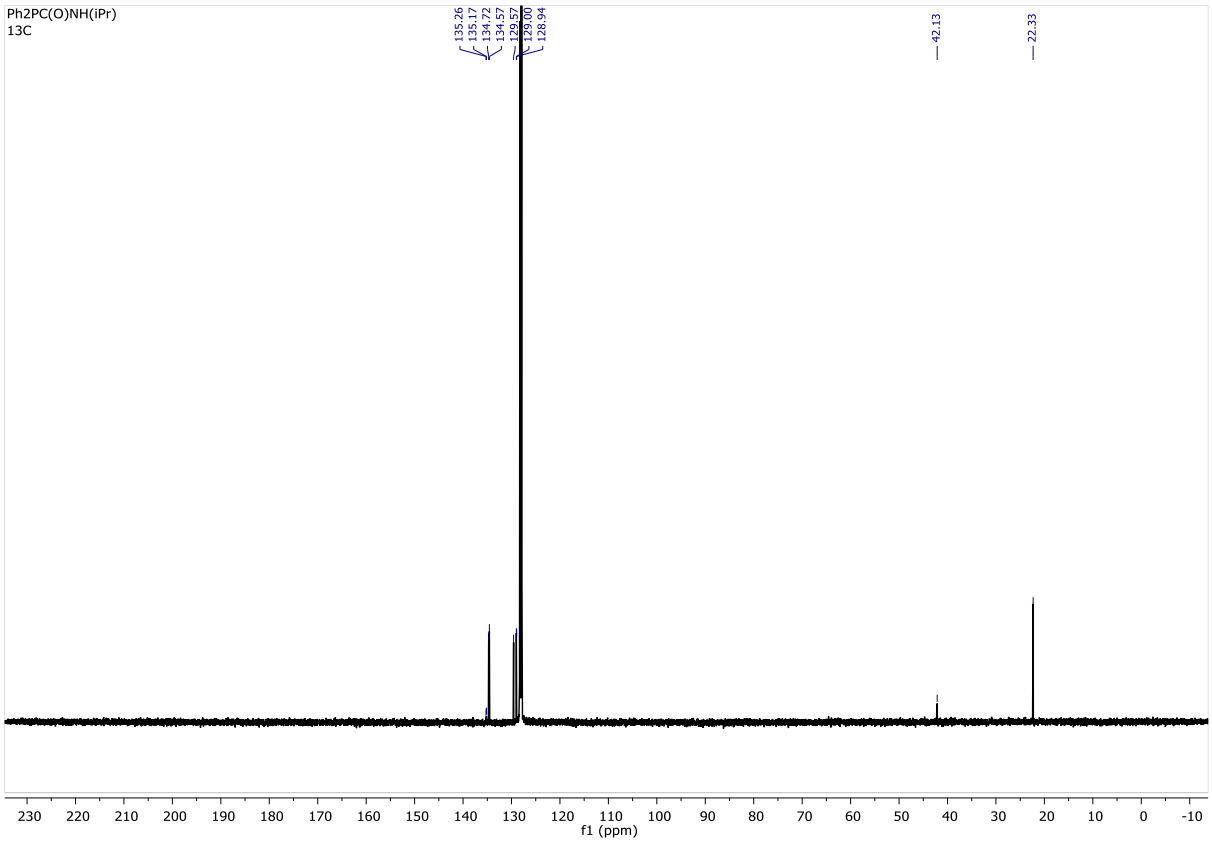


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(iPr)$**.

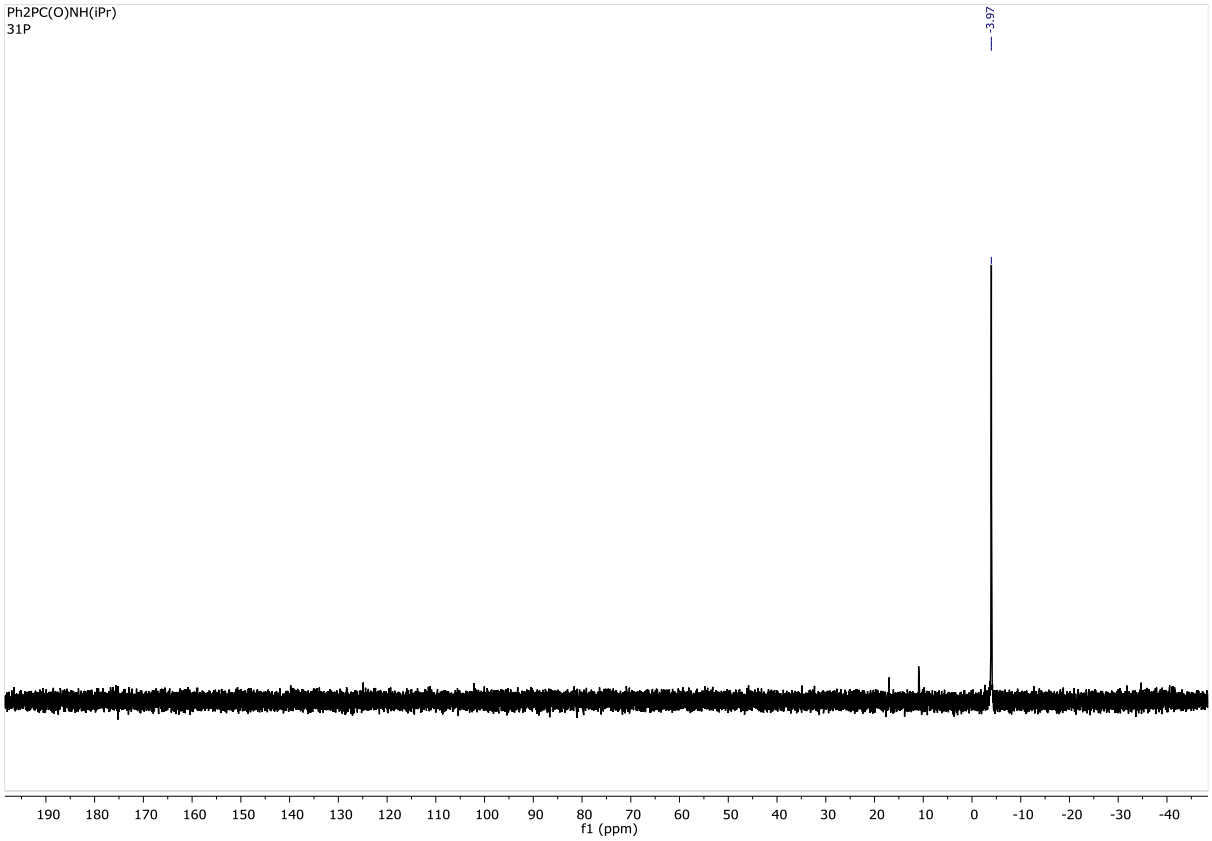


Figure S28: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(iPr)$**.

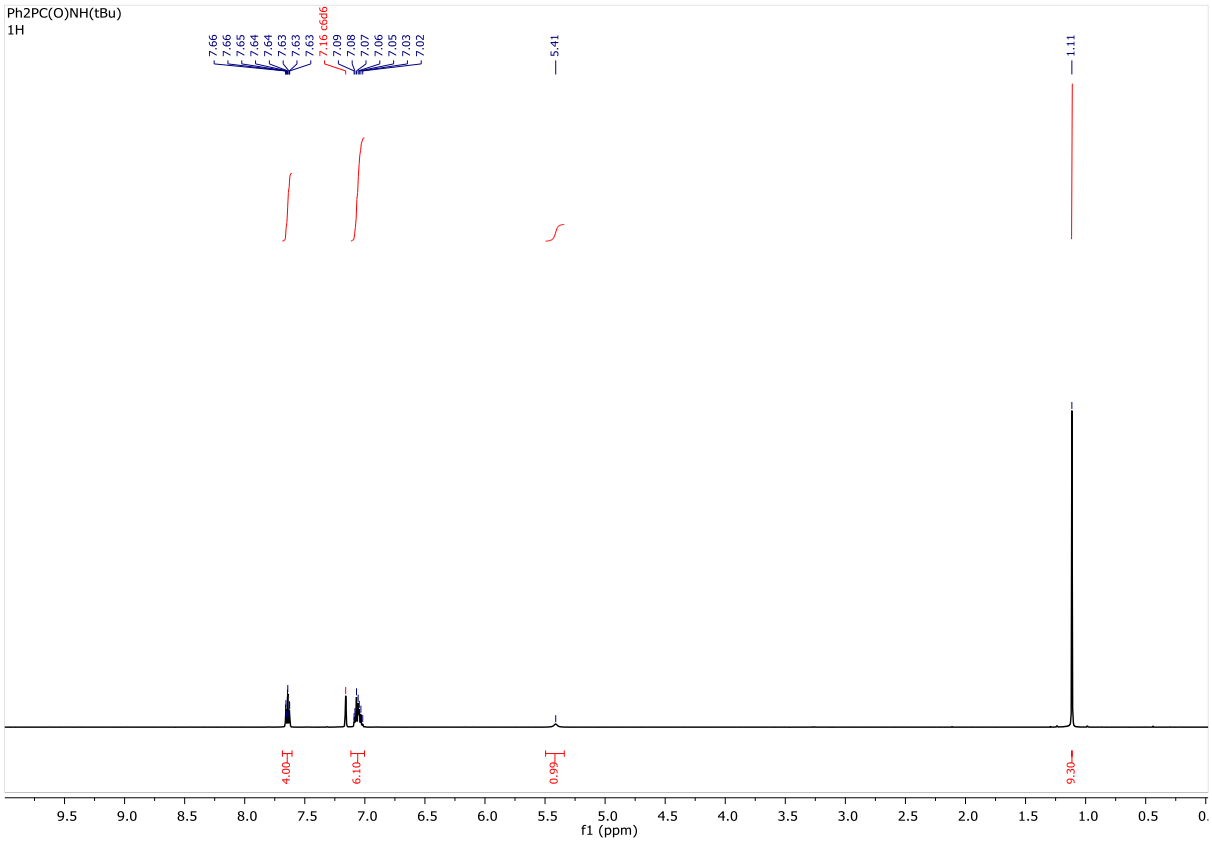


Figure S29: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(tBu)$**.

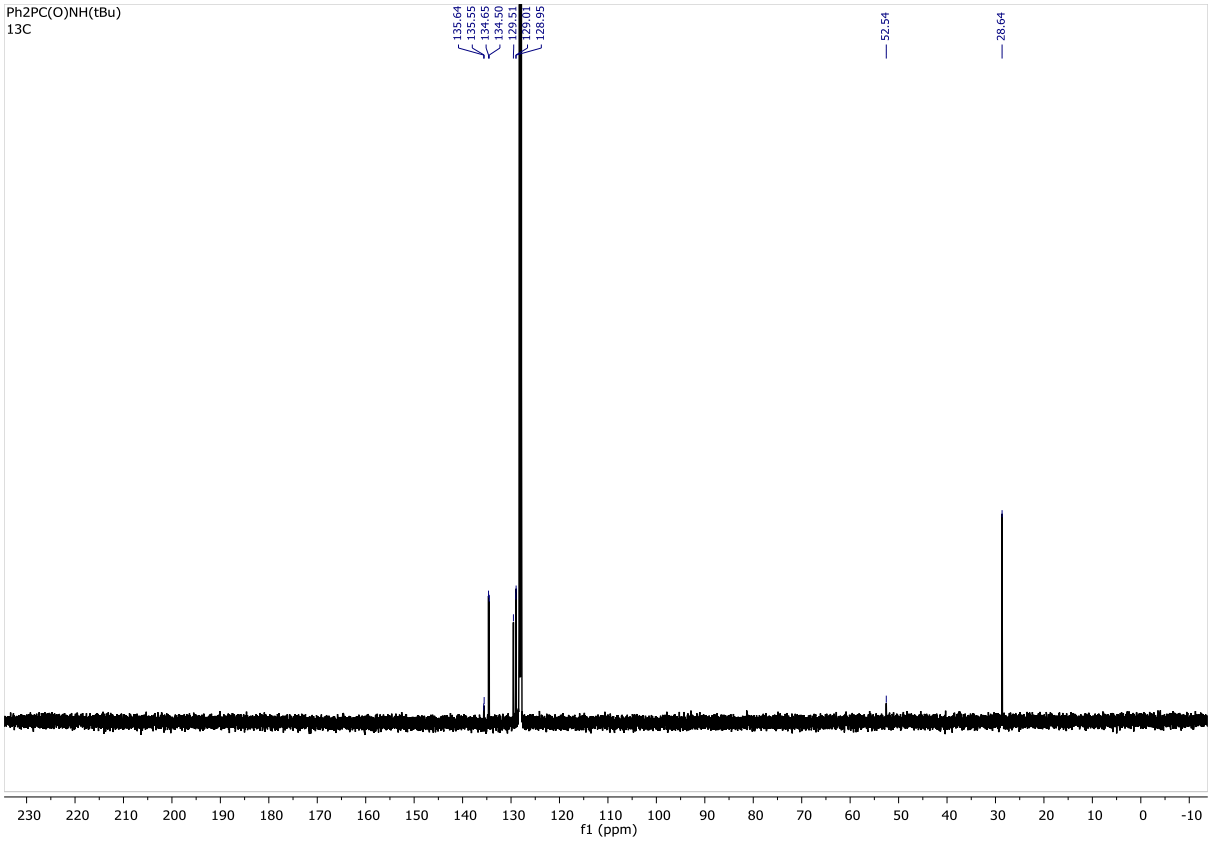


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(tBu)$**.

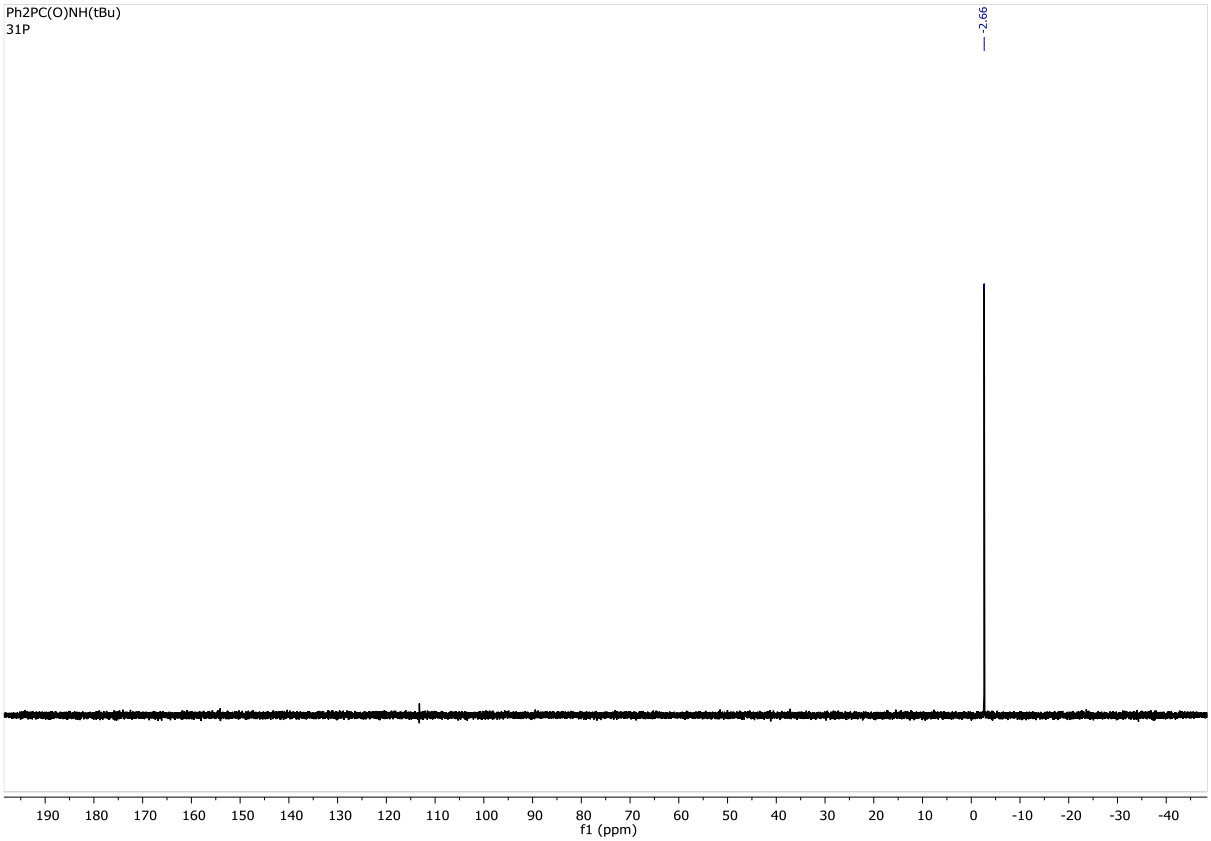


Figure S31: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(tBu)$**.

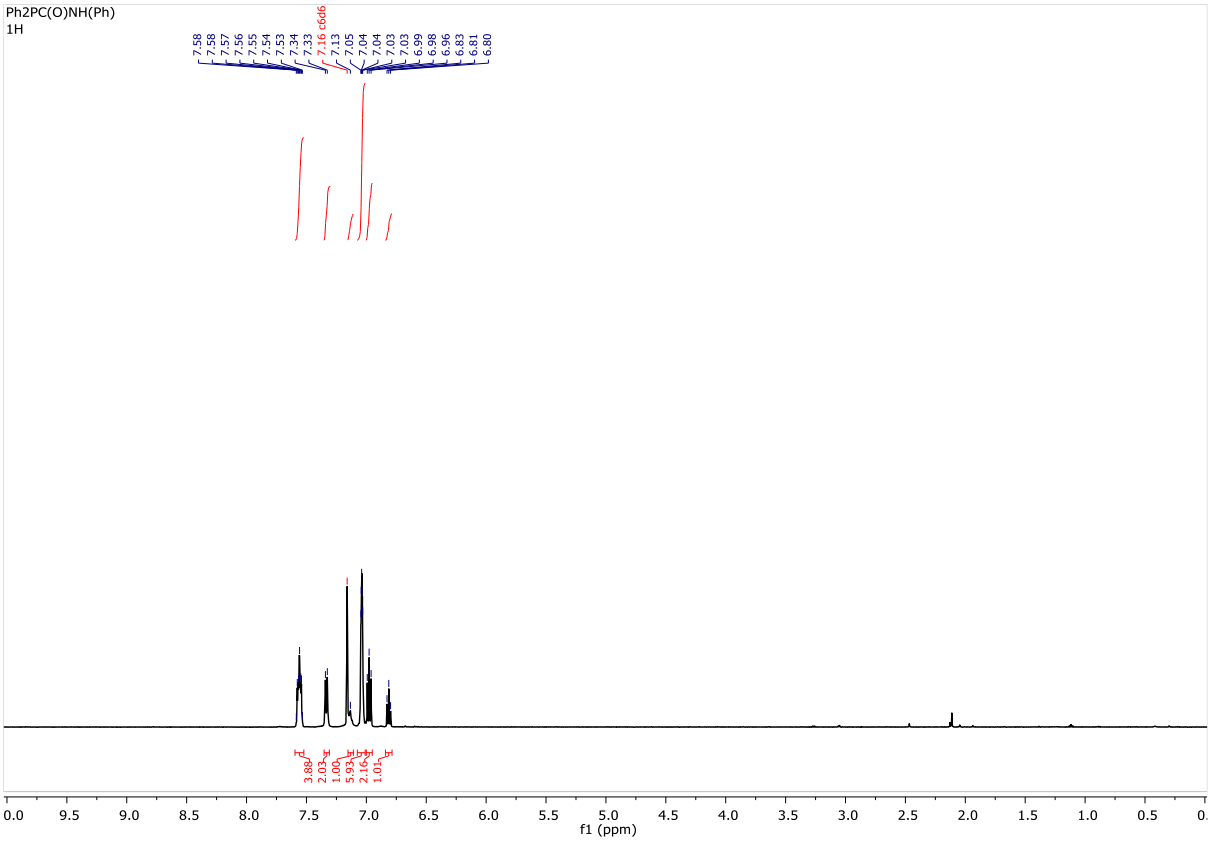


Figure S32: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Ph)$**.

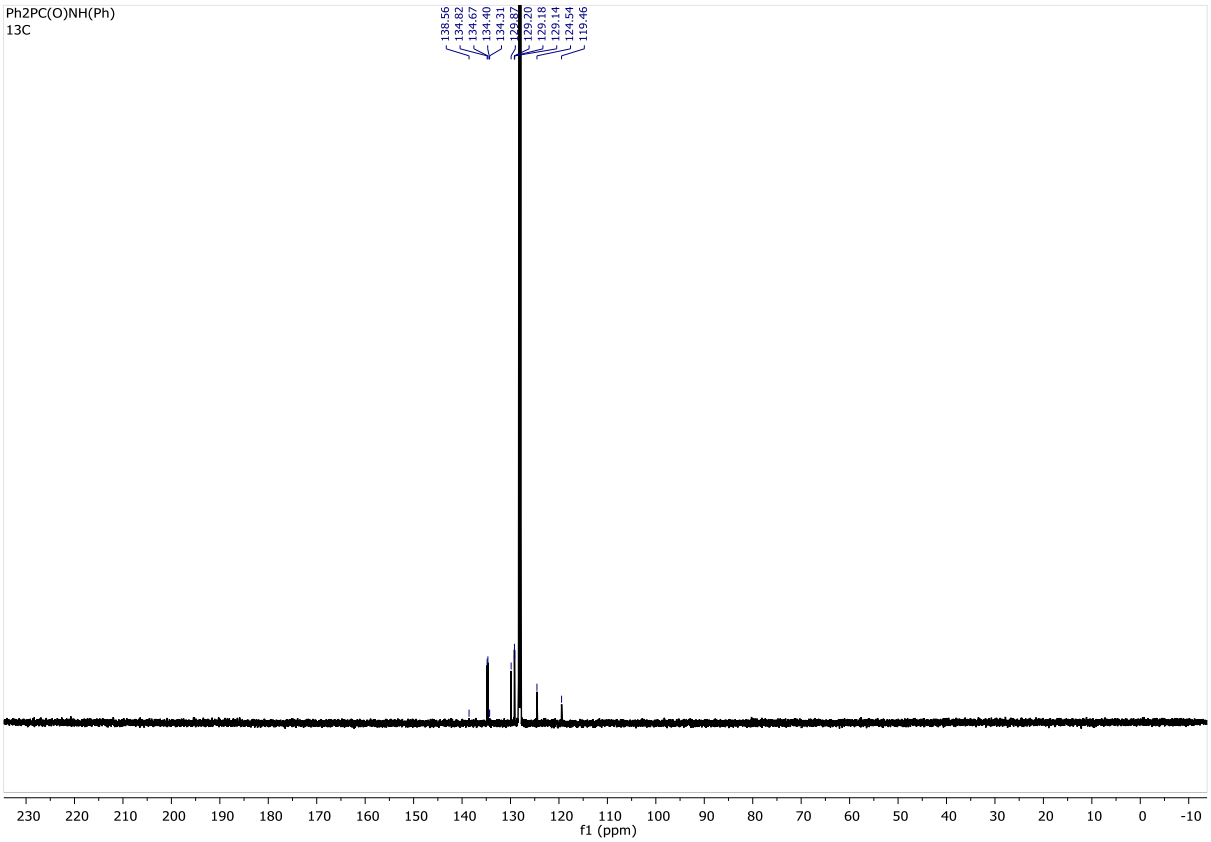


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Ph)$**.

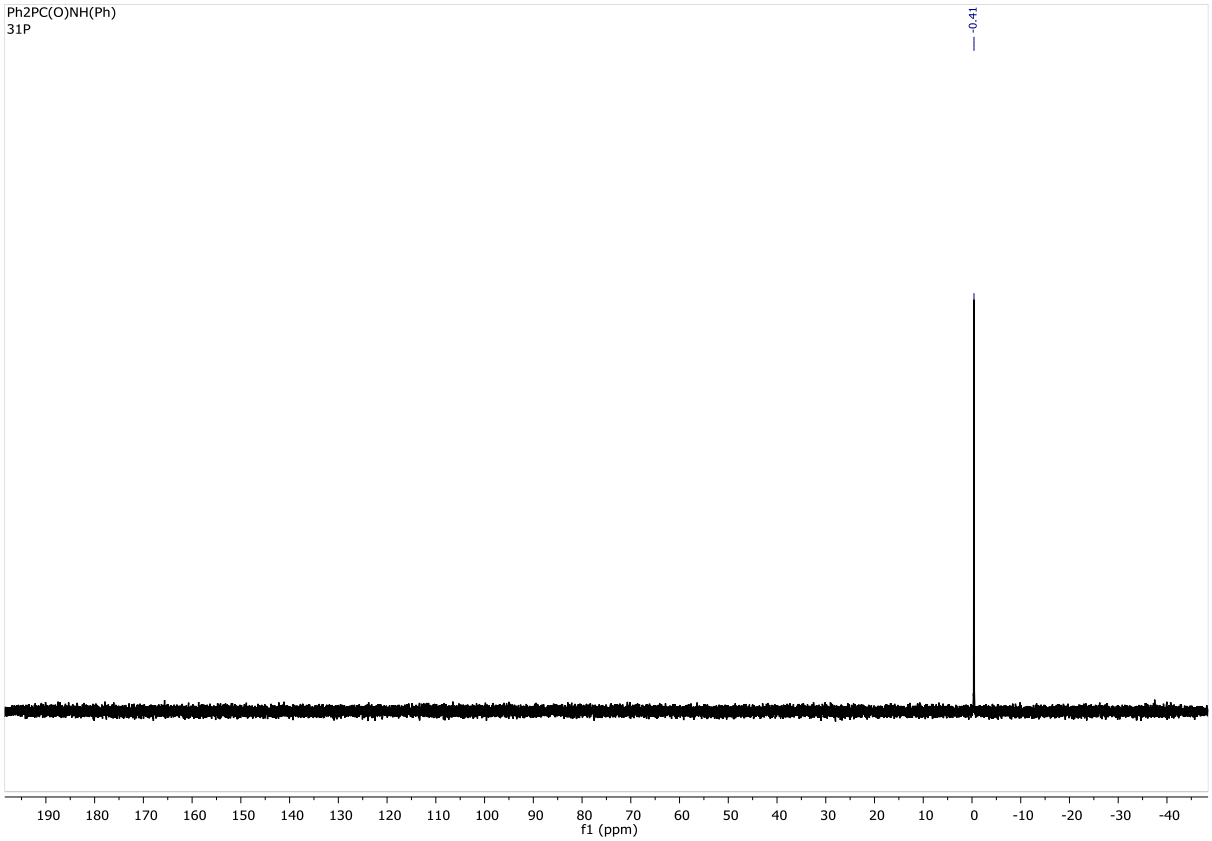


Figure S34: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Ph)$**.

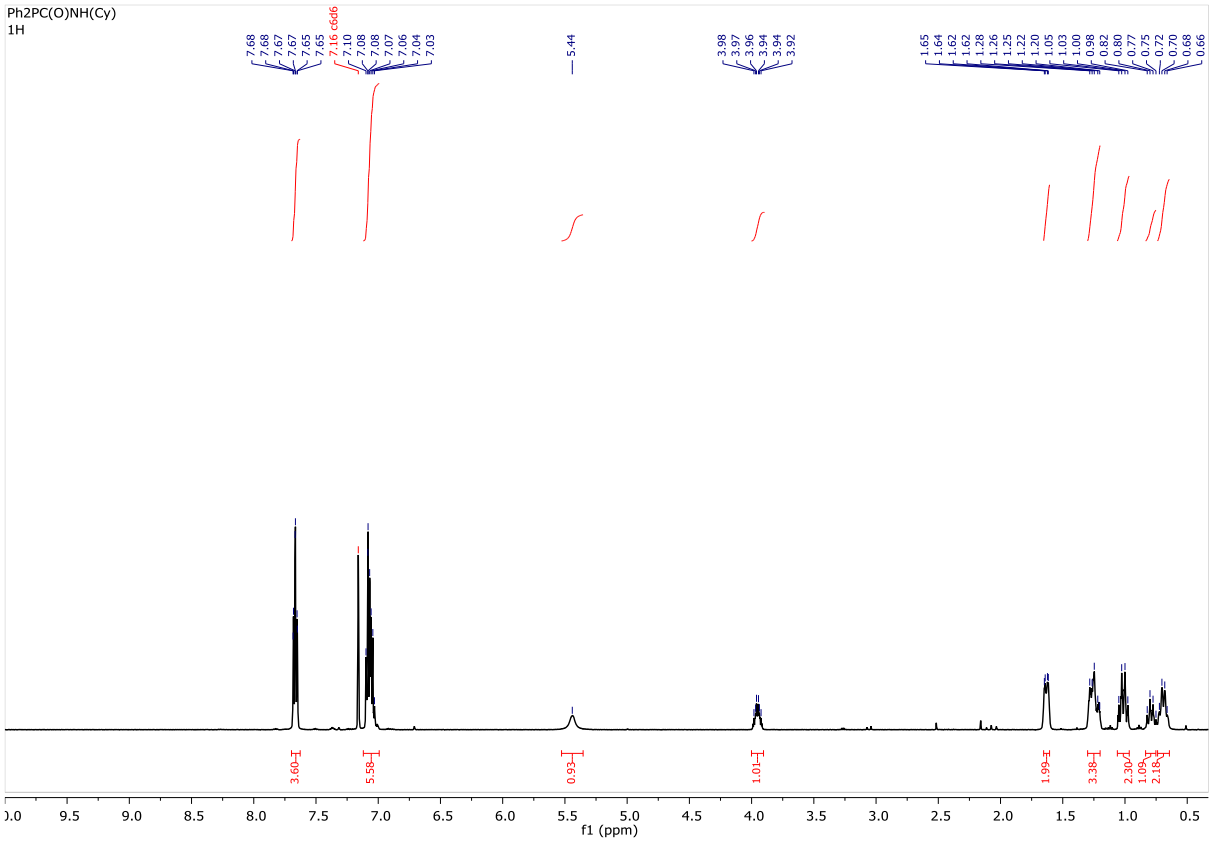


Figure S35: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Cy)$**.

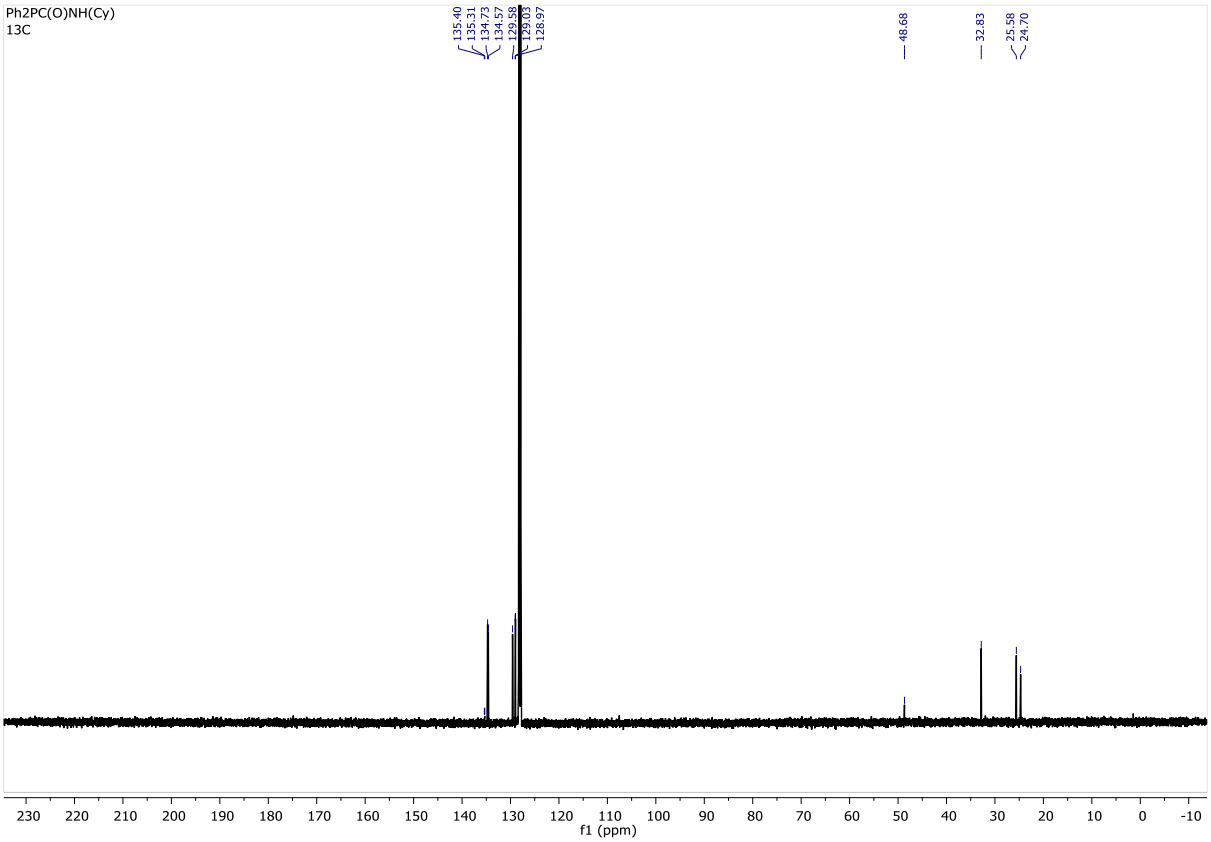


Figure S36: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Cy)$**.

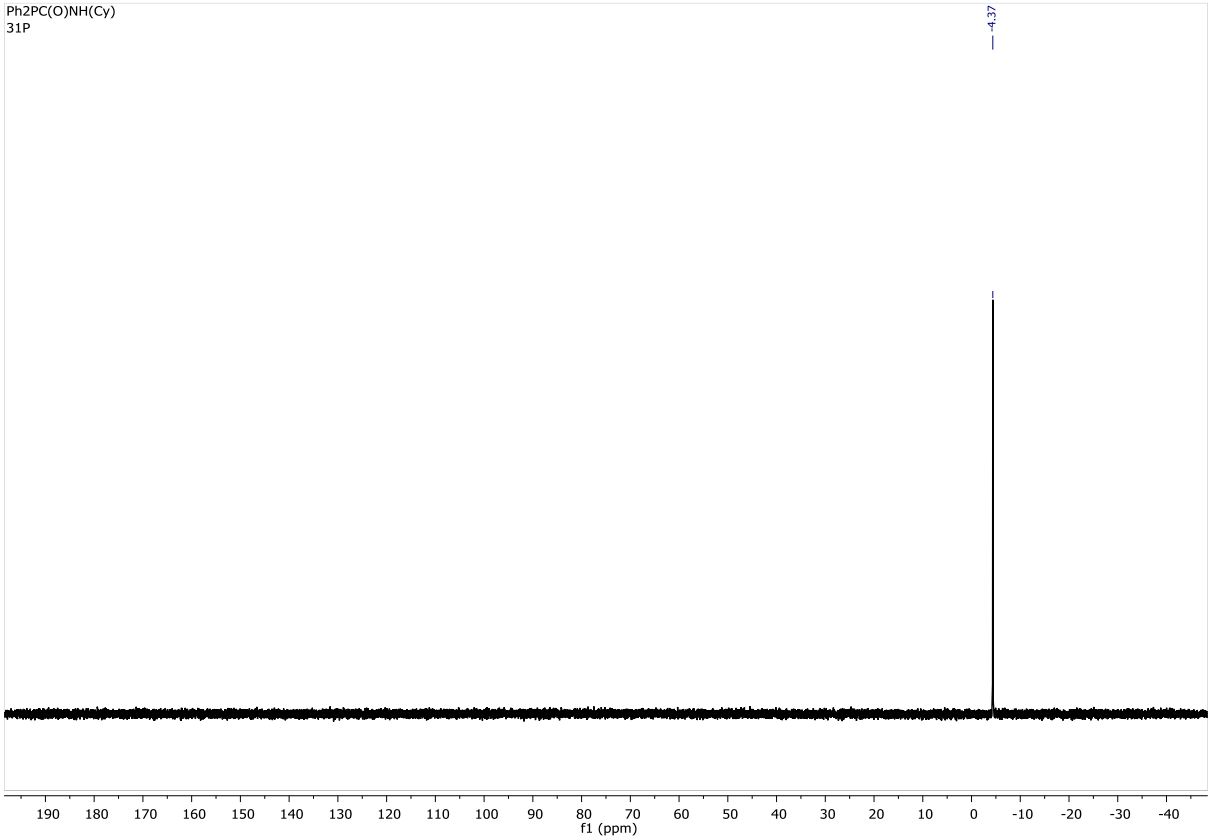


Figure S37: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of compound **$Ph_2PC(O)NH(Cy)$**.

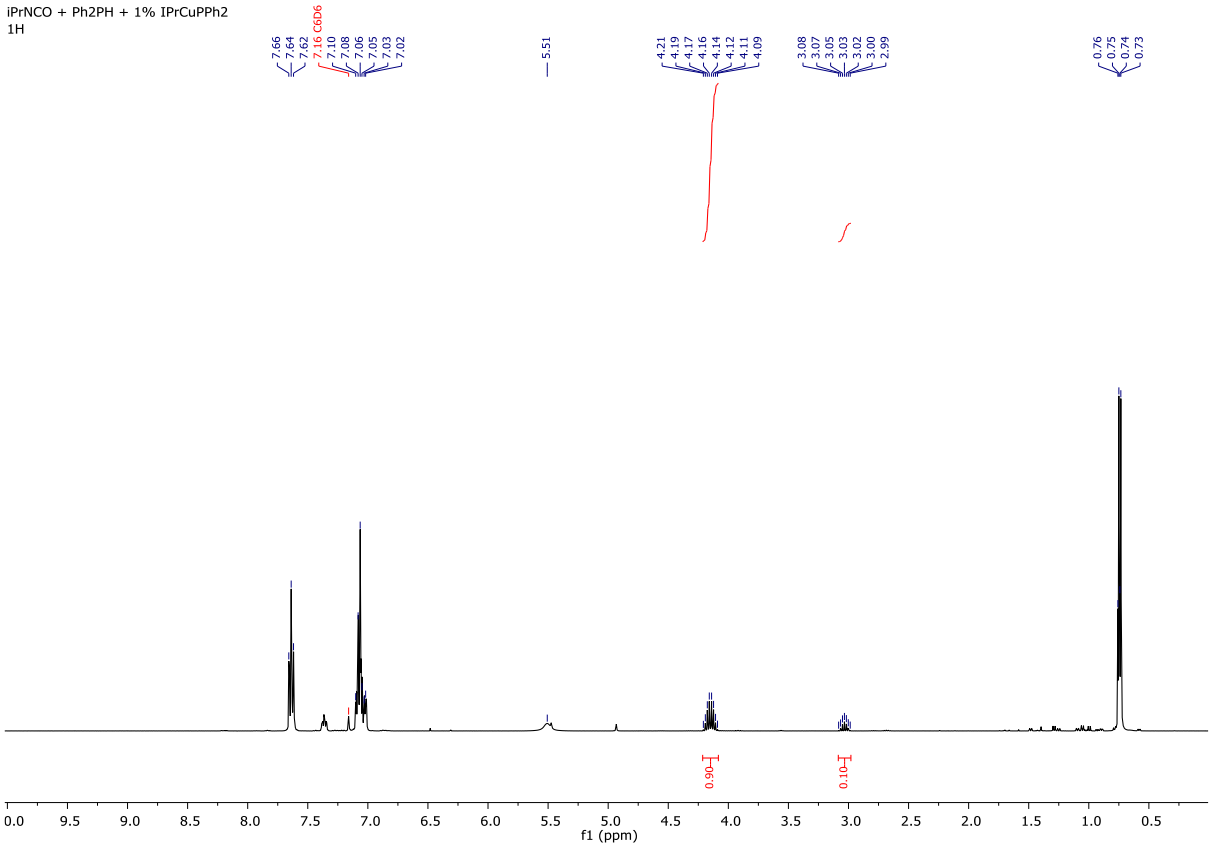


Figure S38: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 30 min (Table 1, Entry 1).

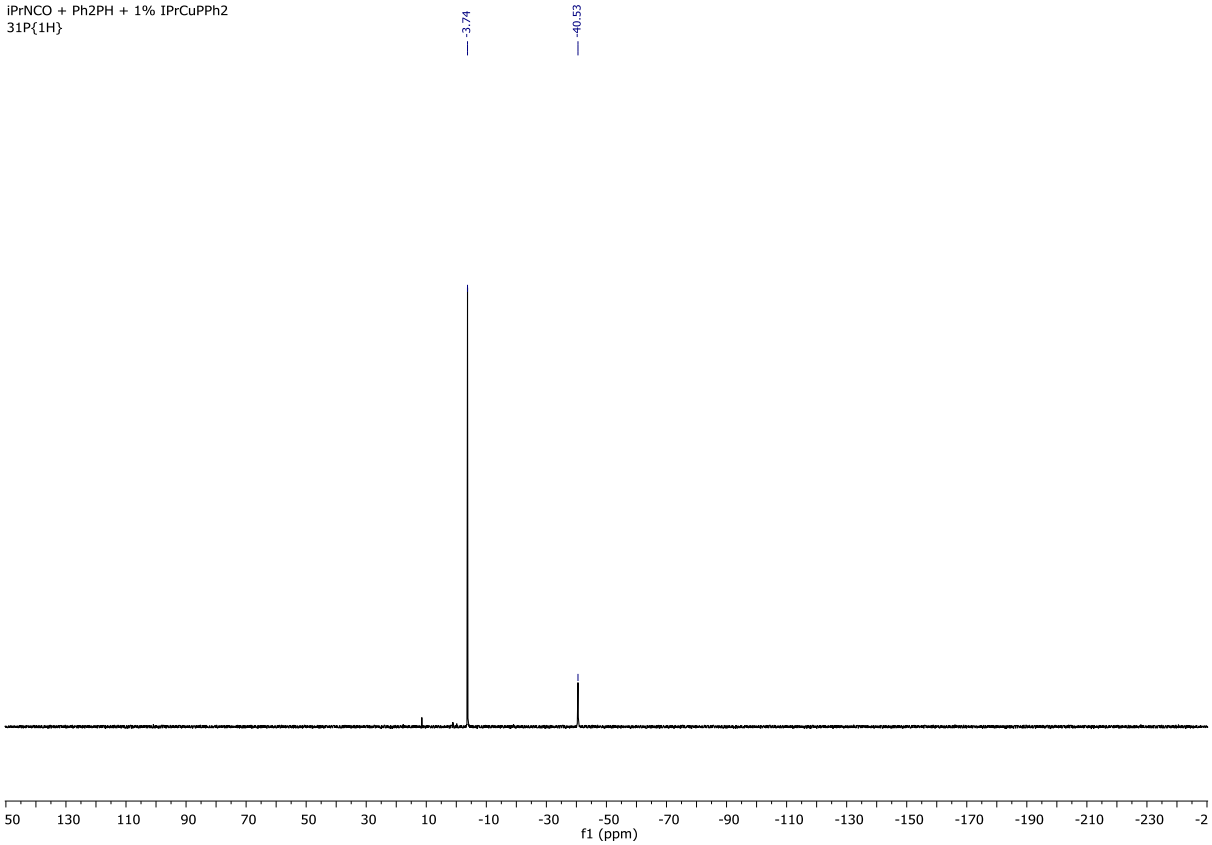


Figure S39: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 30 min (Table 1, Entry 1). Residual Ph_2PH observed at *ca.* δ -41 ppm.

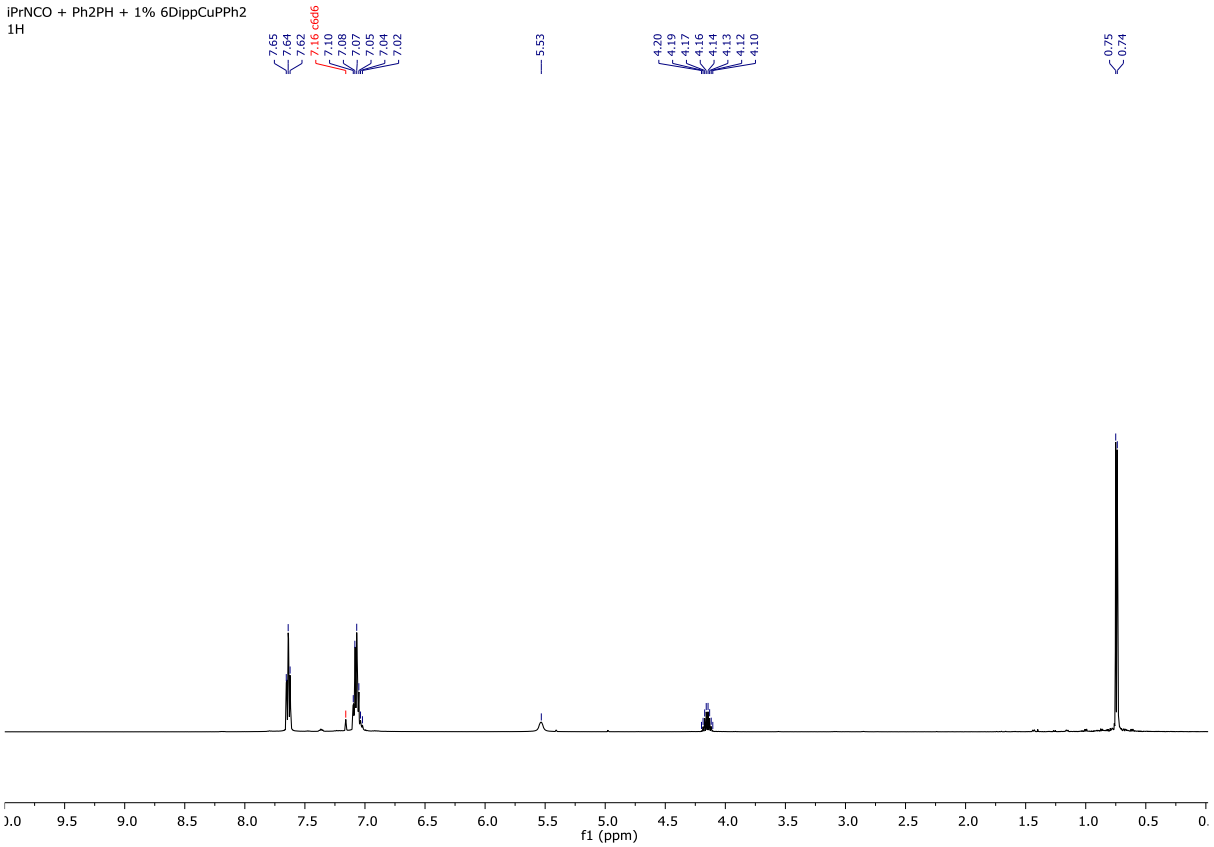


Figure S40: ^{1}H NMR spectrum (500 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 5 h (Table 1, Entry 2).

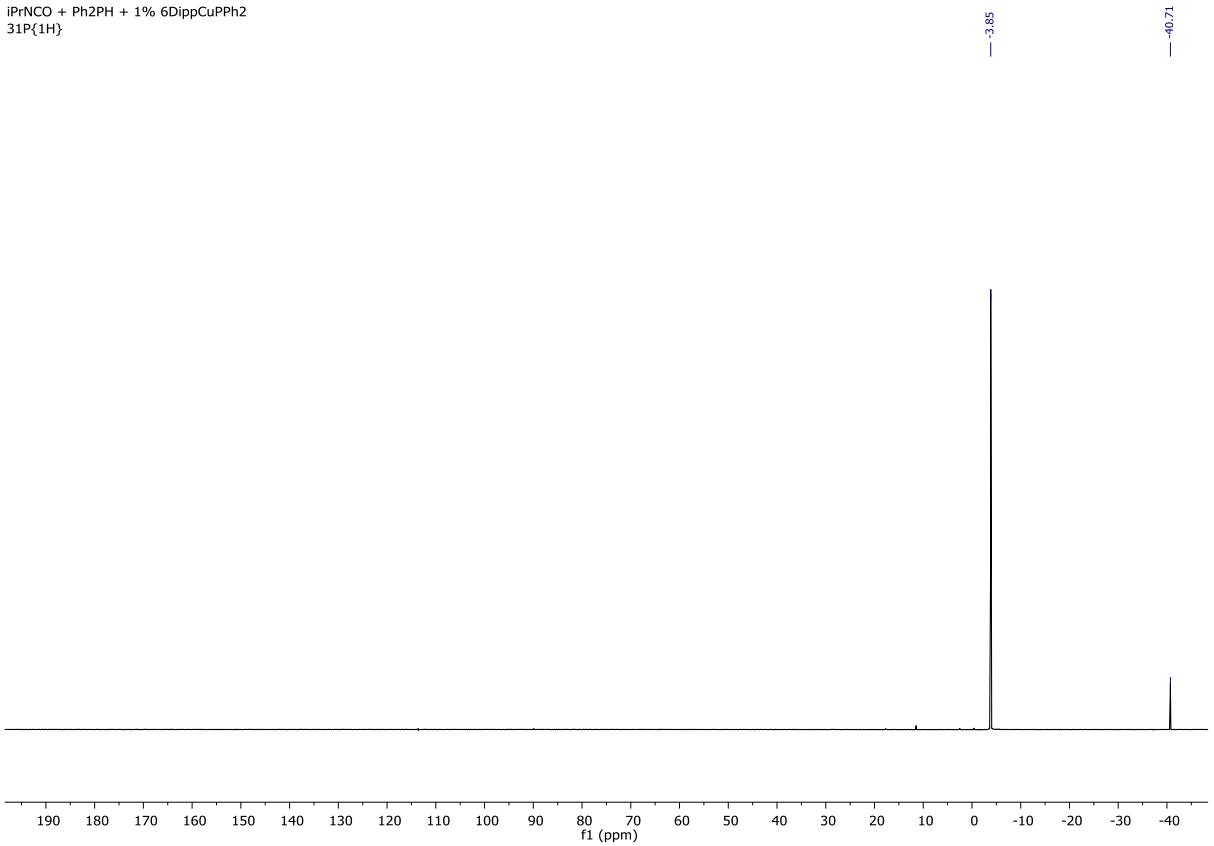


Figure S41: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 5 h (Table 1, Entry 2). Residual Ph_2PH observed at *ca.* δ -41 ppm.

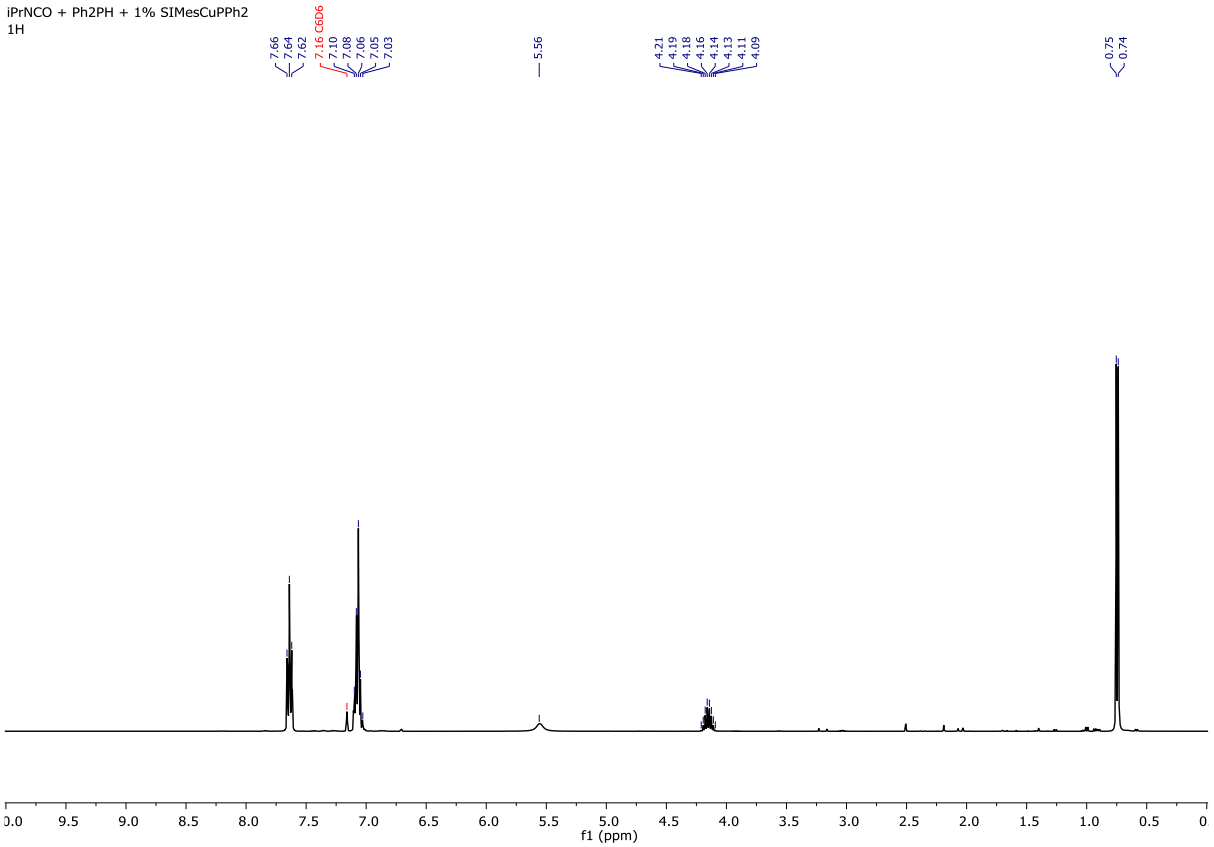


Figure S42: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 3).

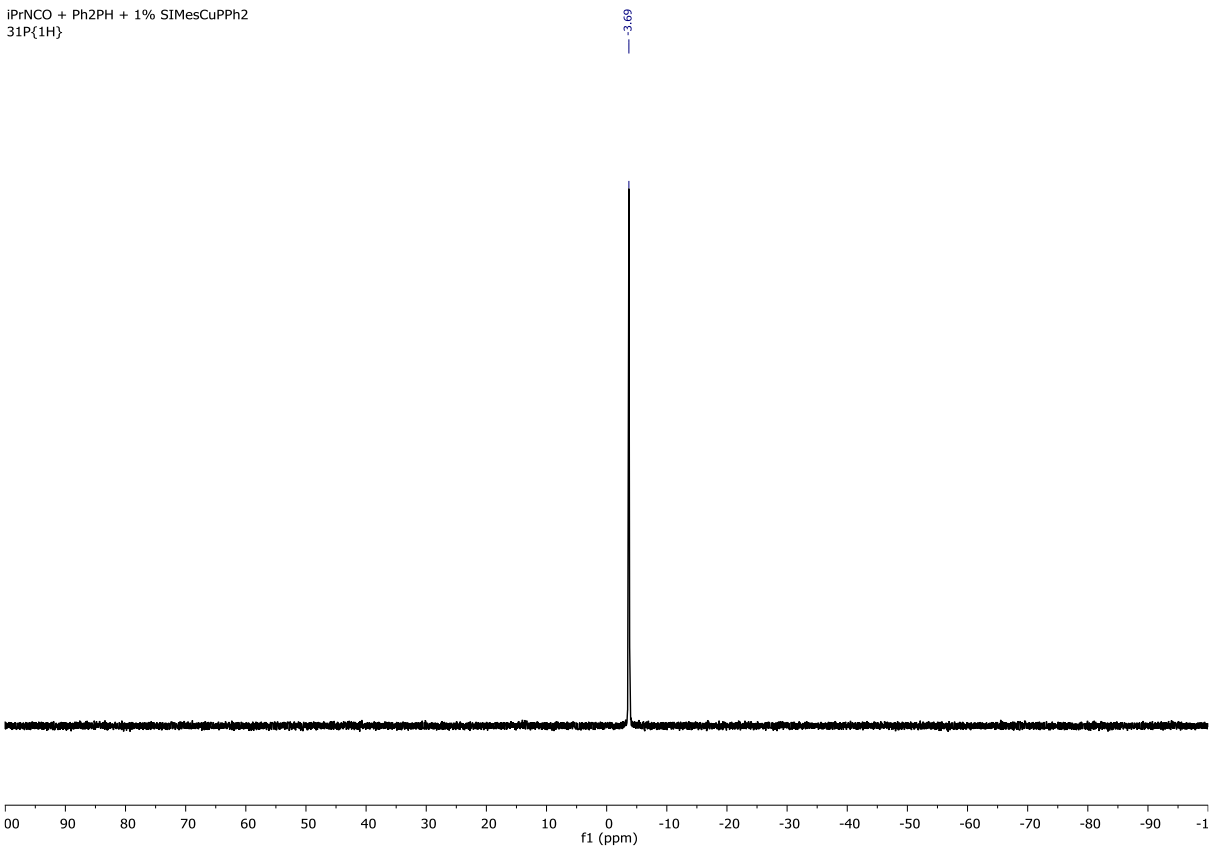


Figure S43: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 3).

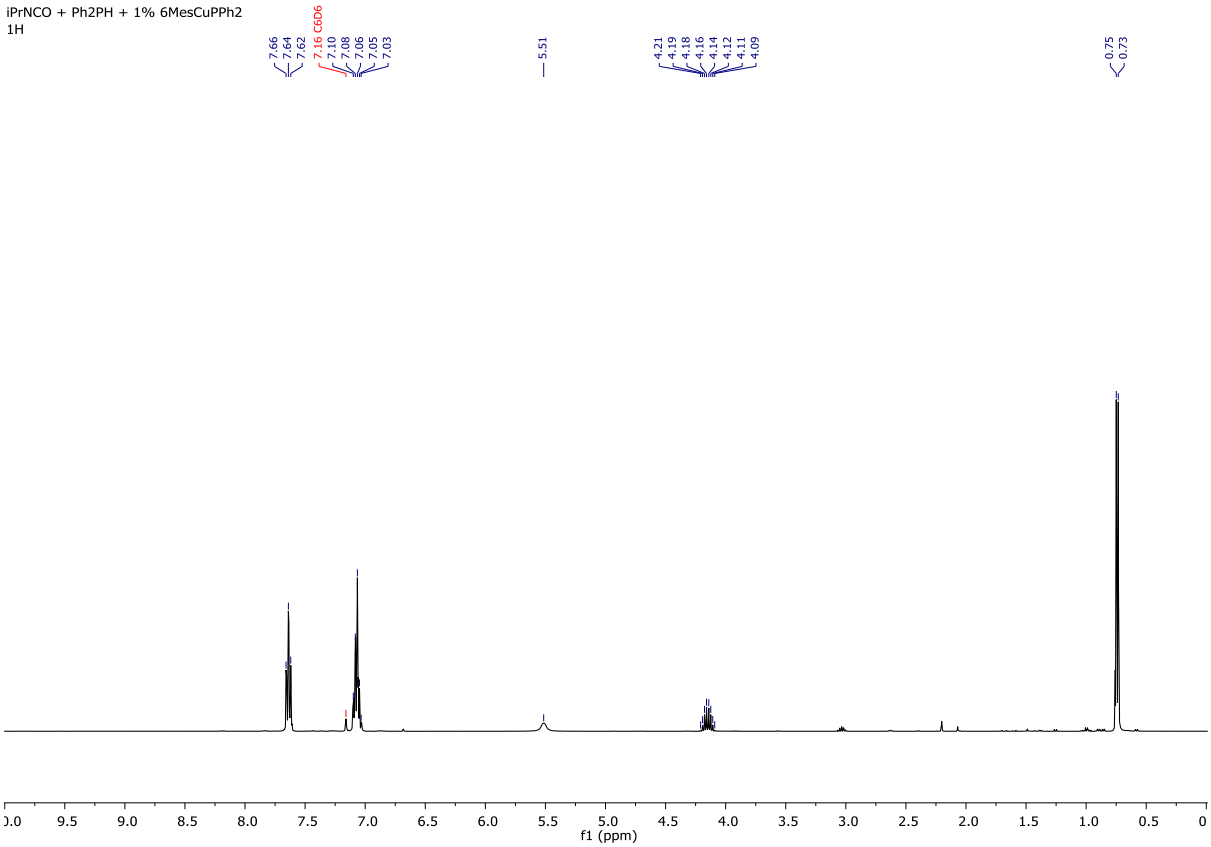


Figure S44: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 4).

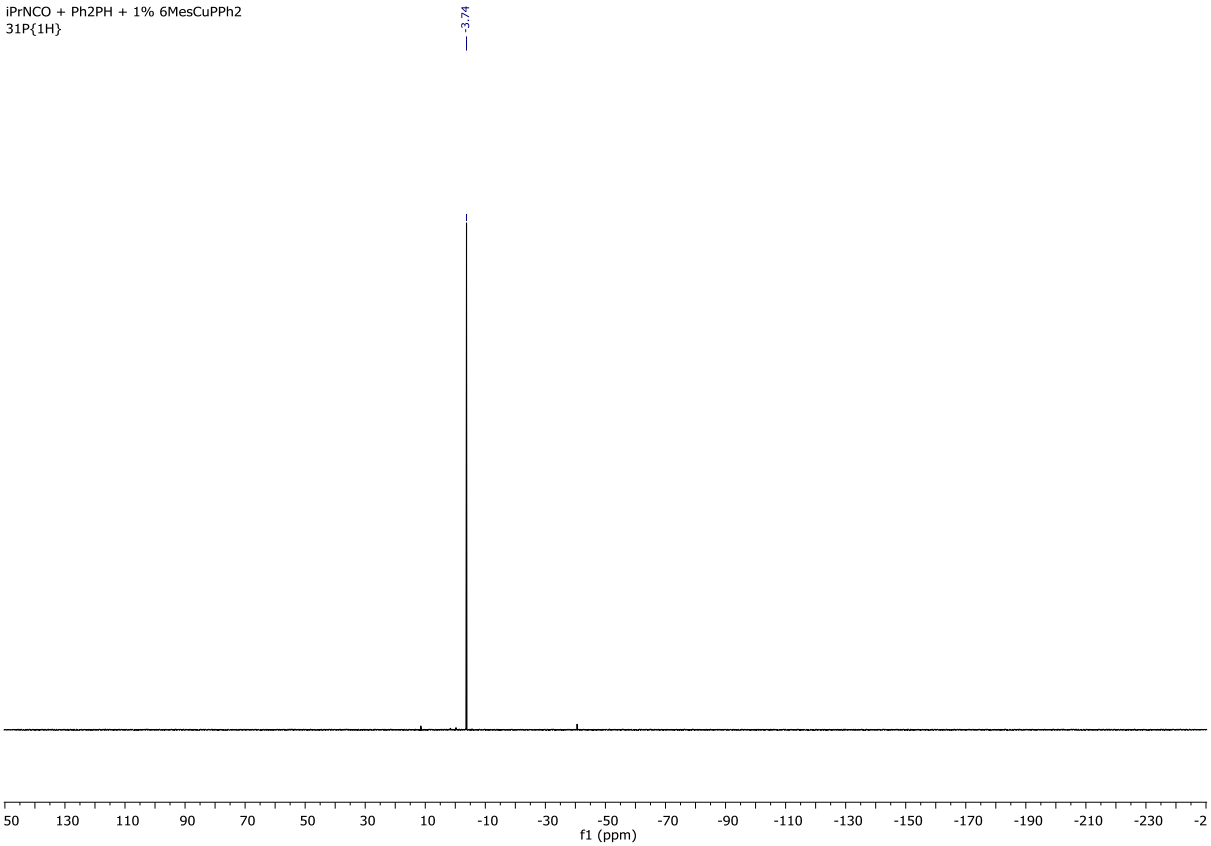


Figure S45: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 4).

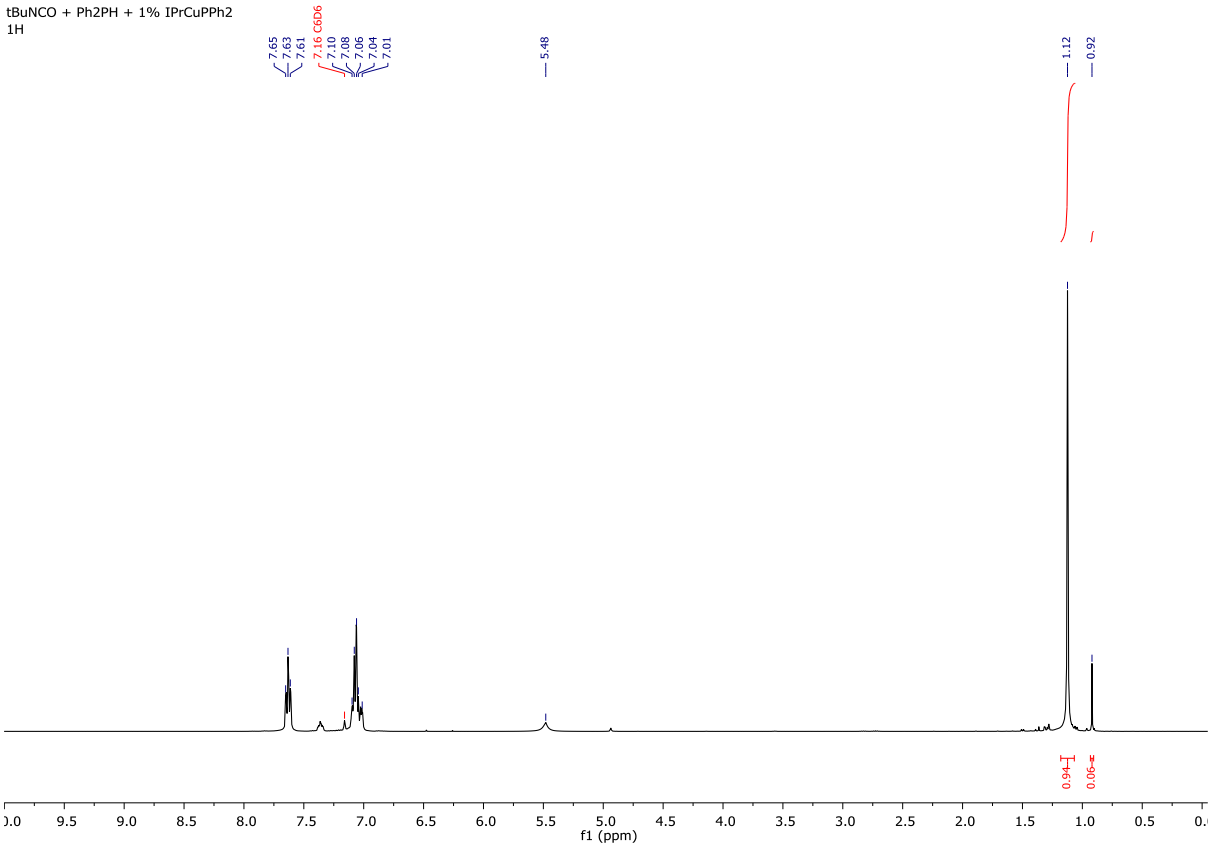


Figure S46: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 2 h (Table 1, Entry 5).

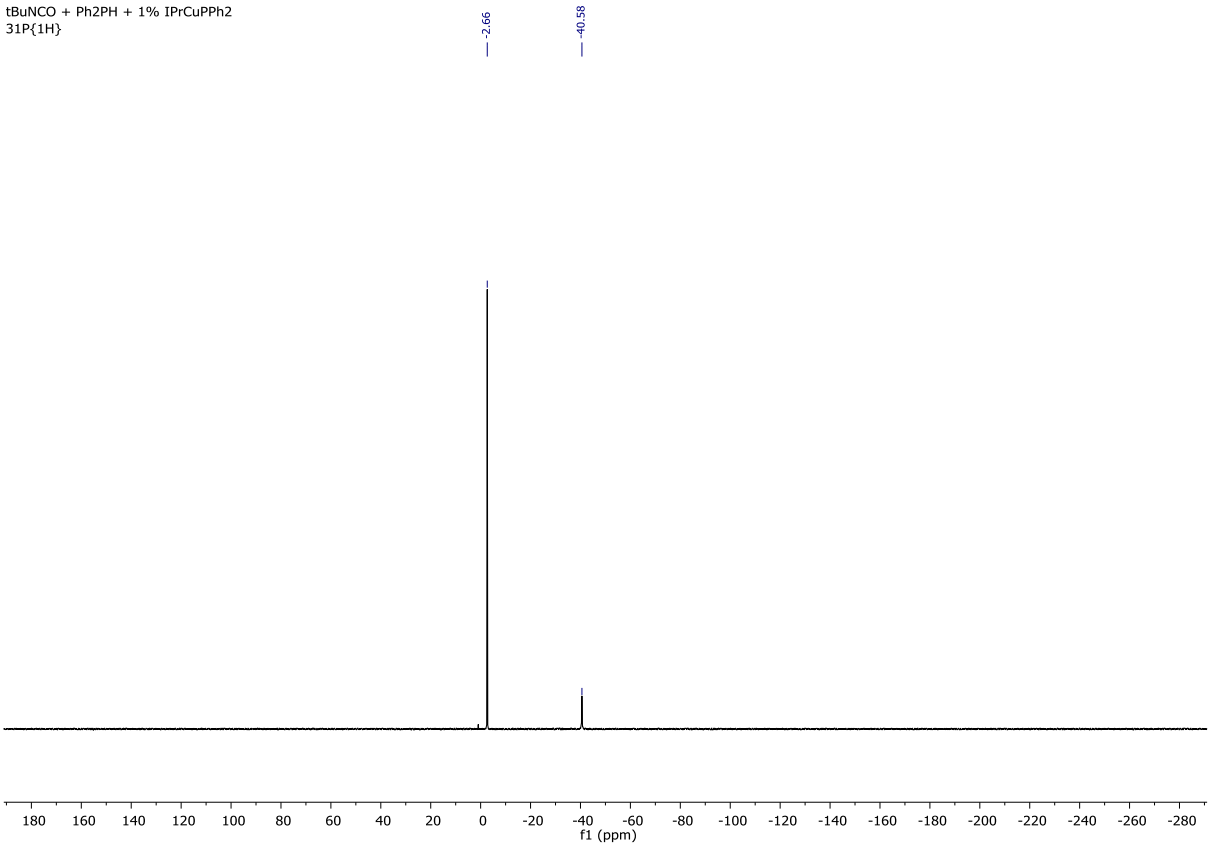


Figure S47: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between isopropyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 2 h (Table 1, Entry 5). Residual Ph_2PH observed at *ca.* δ -41 ppm.

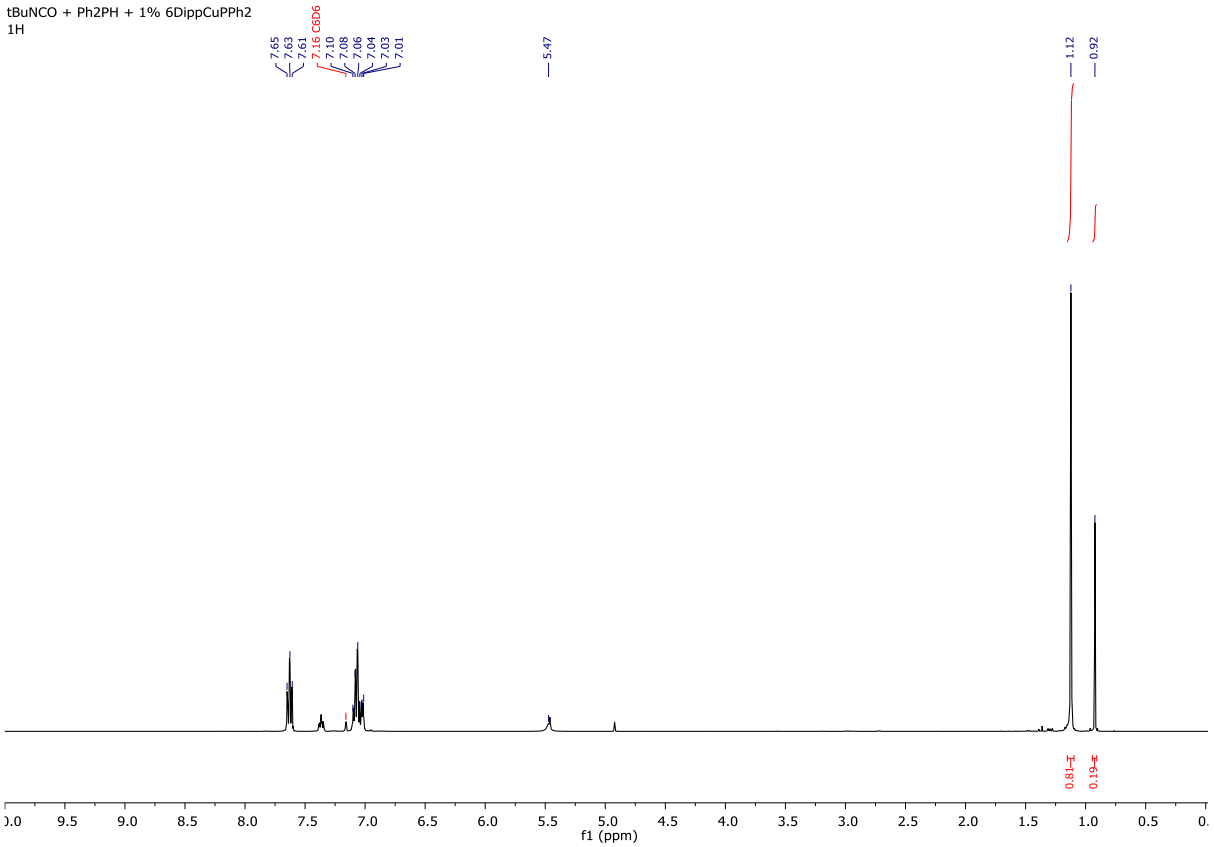


Figure S48: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 4 h (Table 1, Entry 6).

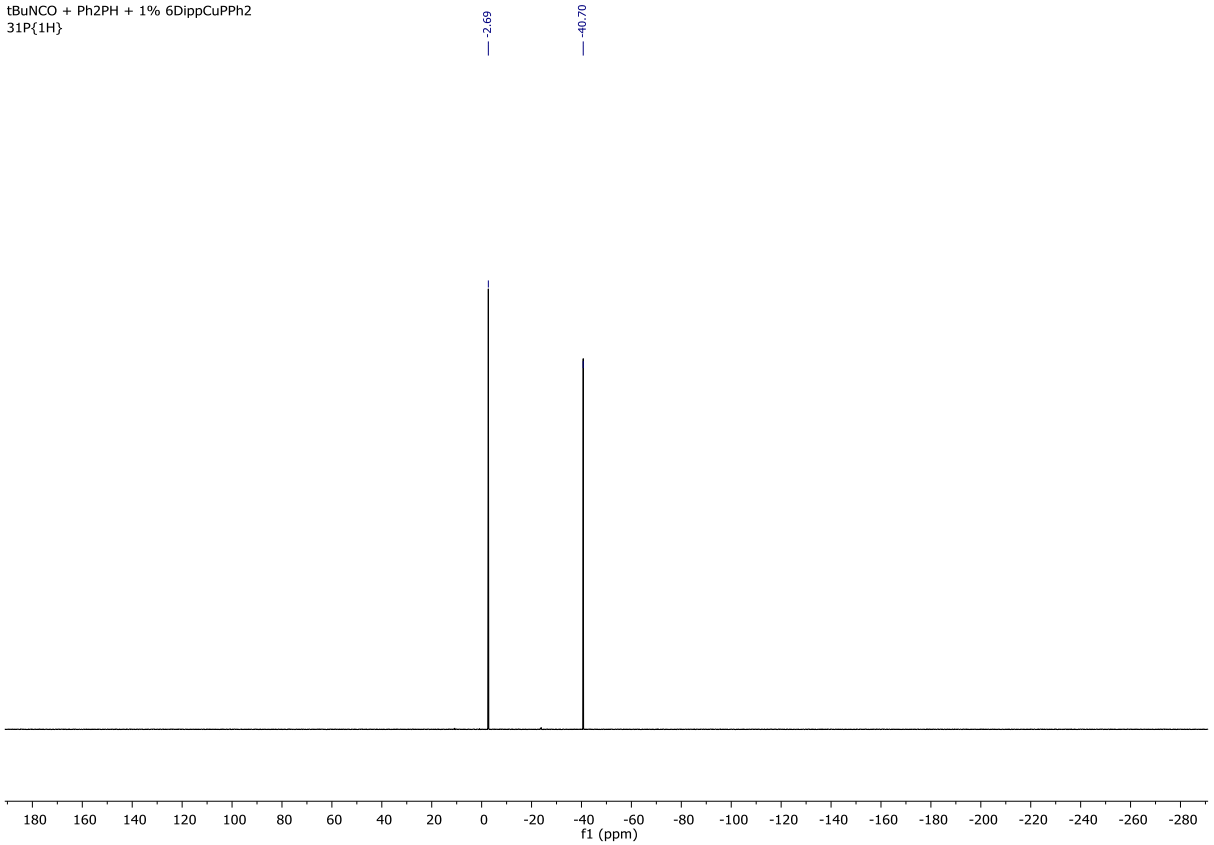


Figure S49: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 4 h (Table 1, Entry 6). Residual Ph_2PH observed at *ca.* δ -41 ppm.

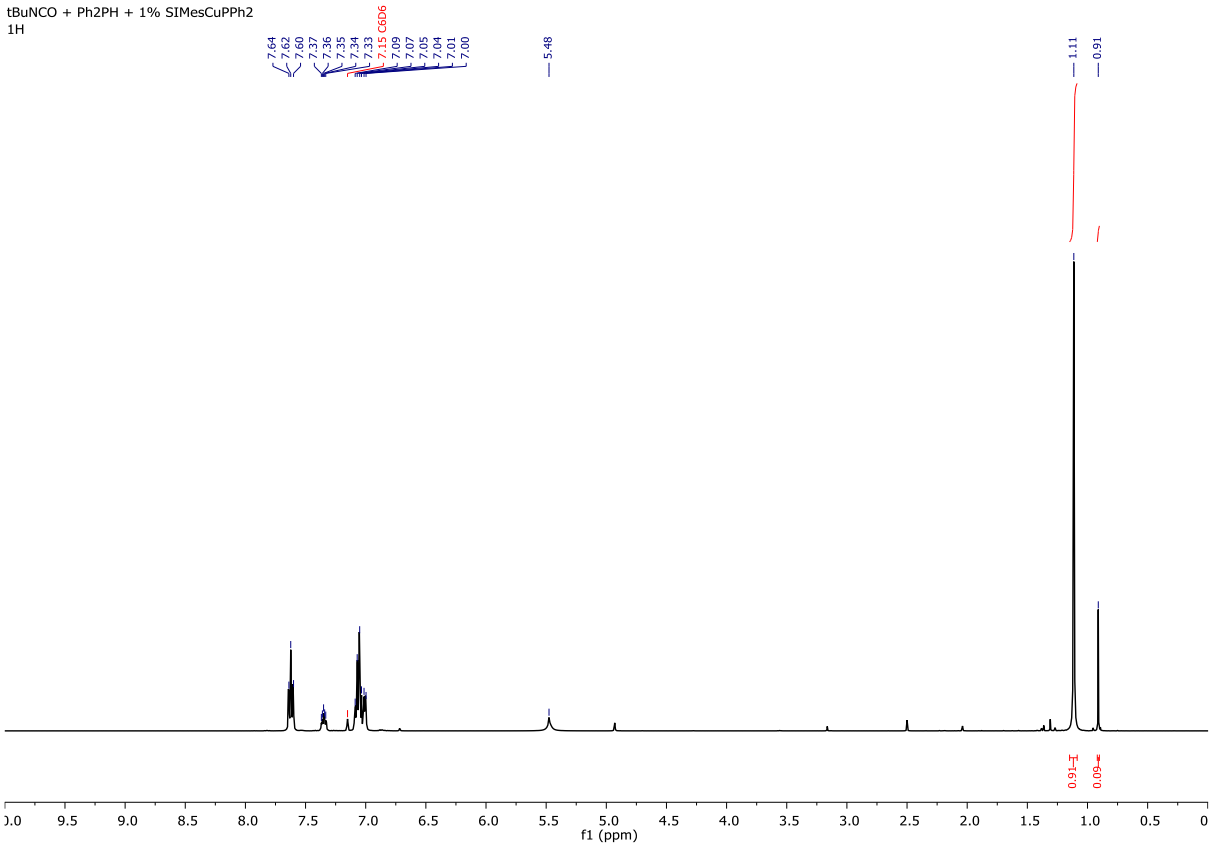


Figure S50: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 2 h (Table 1, Entry 7).

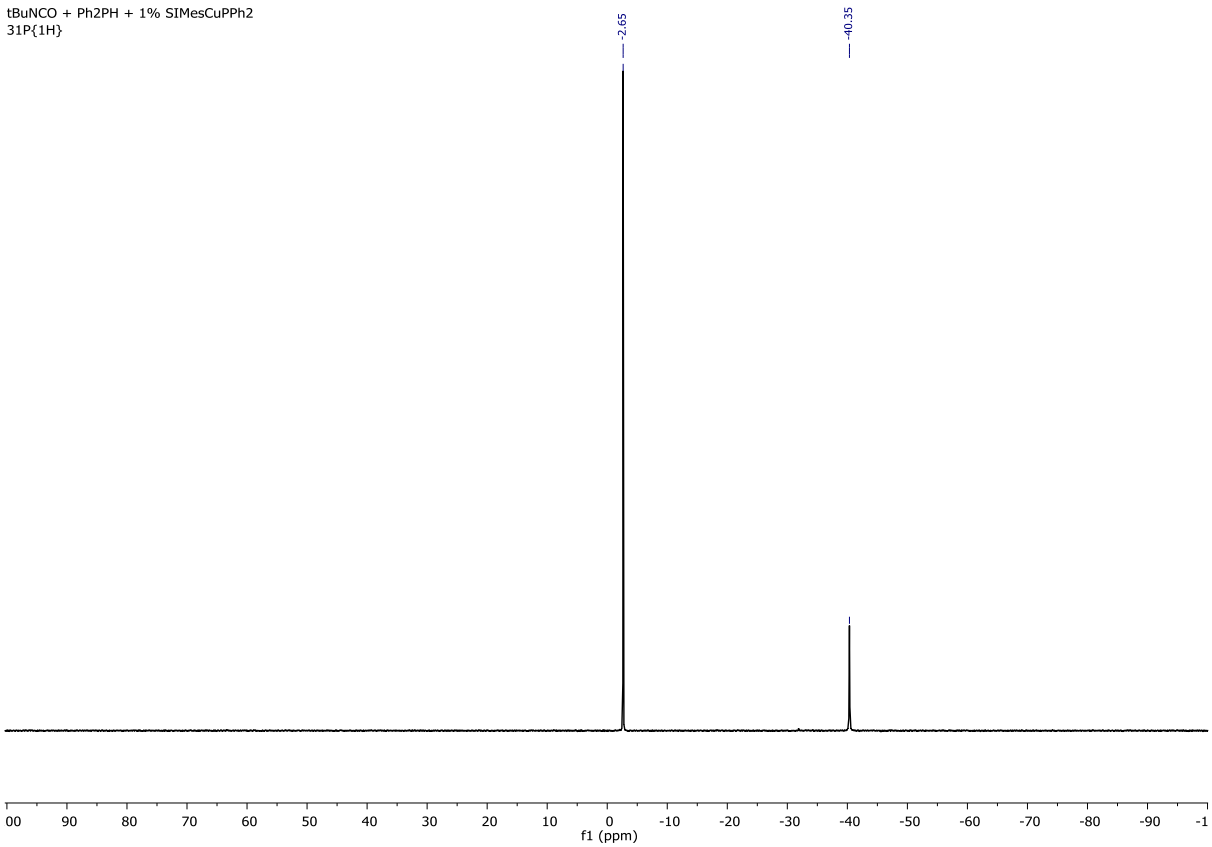


Figure S51: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 2 h (Table 1, Entry 7). Residual Ph_2PH observed at *ca.* δ -40 ppm.

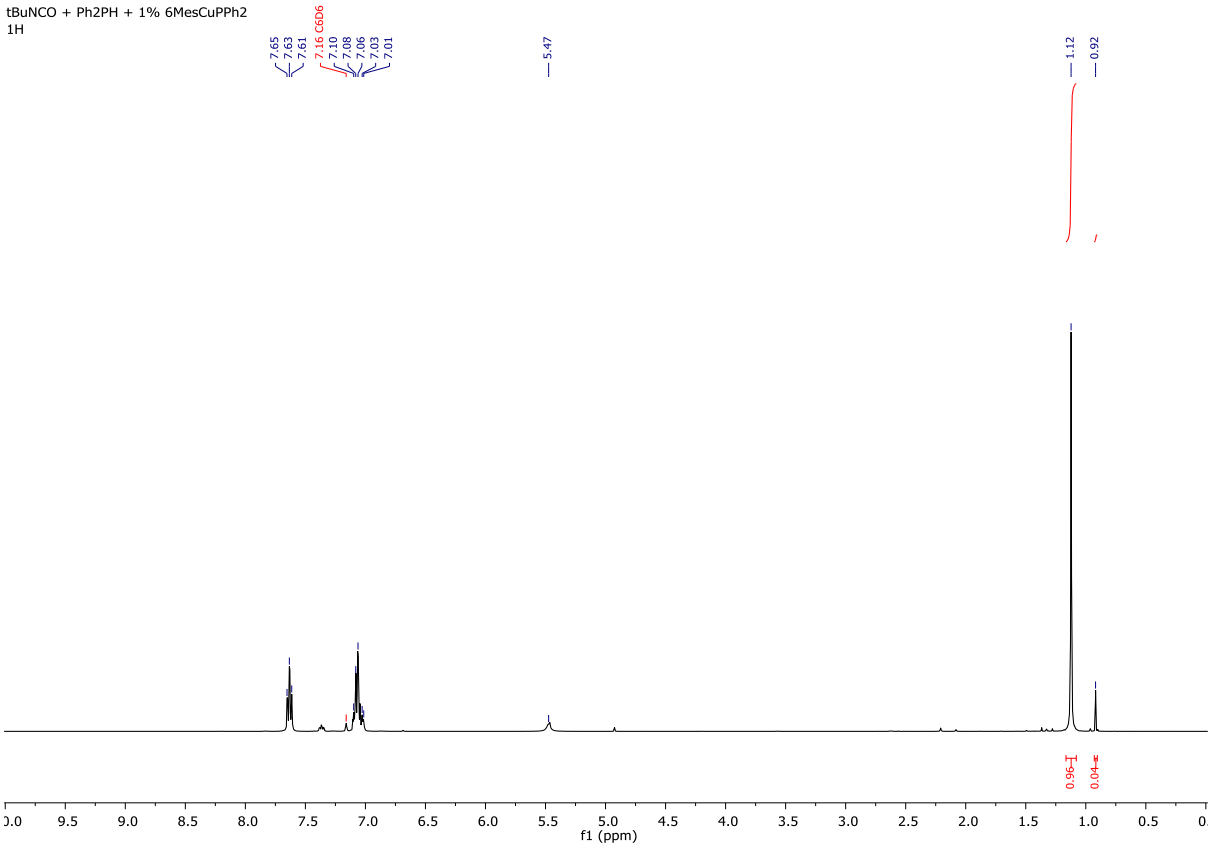


Figure S52: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 2 h (Table 1, Entry 8).

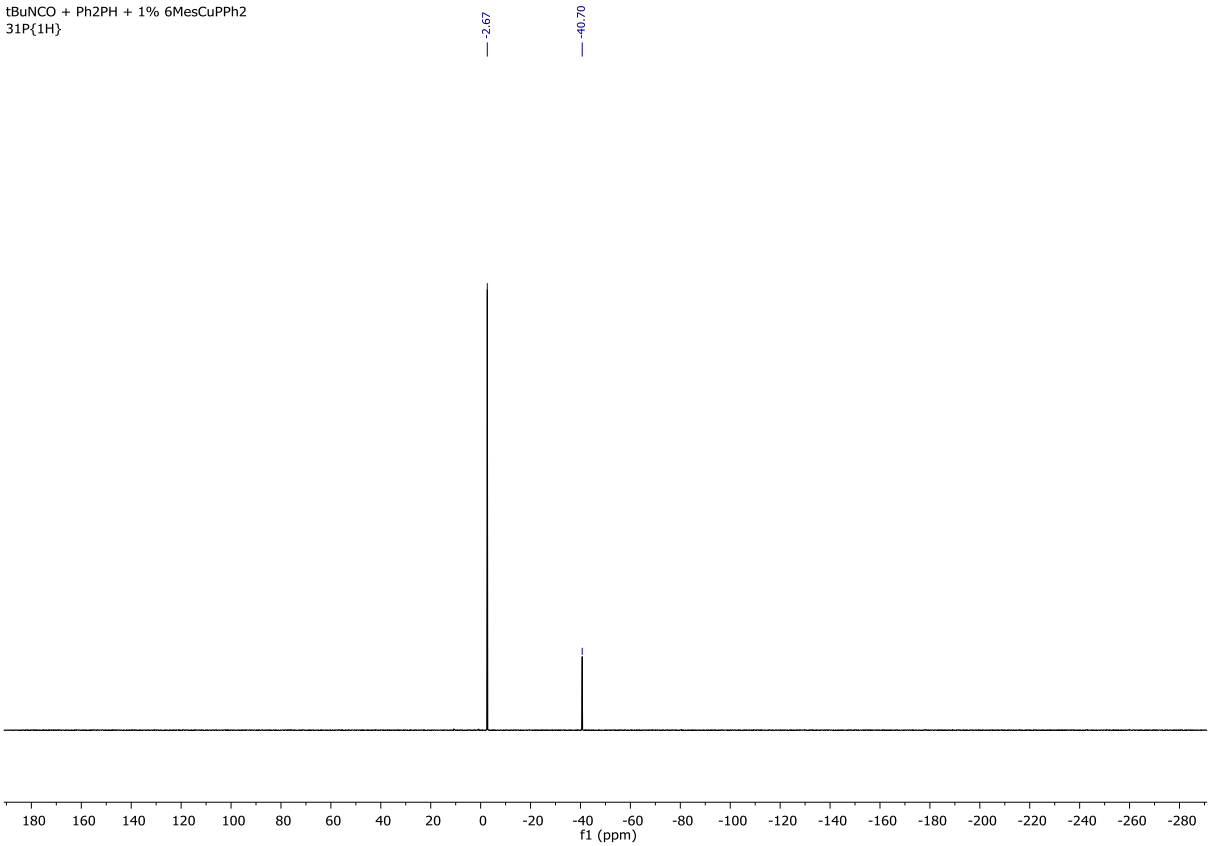


Figure S53: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between tertbutyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 2 h (Table 1, Entry 8). Residual Ph_2PH observed at *ca.* δ -41 ppm.

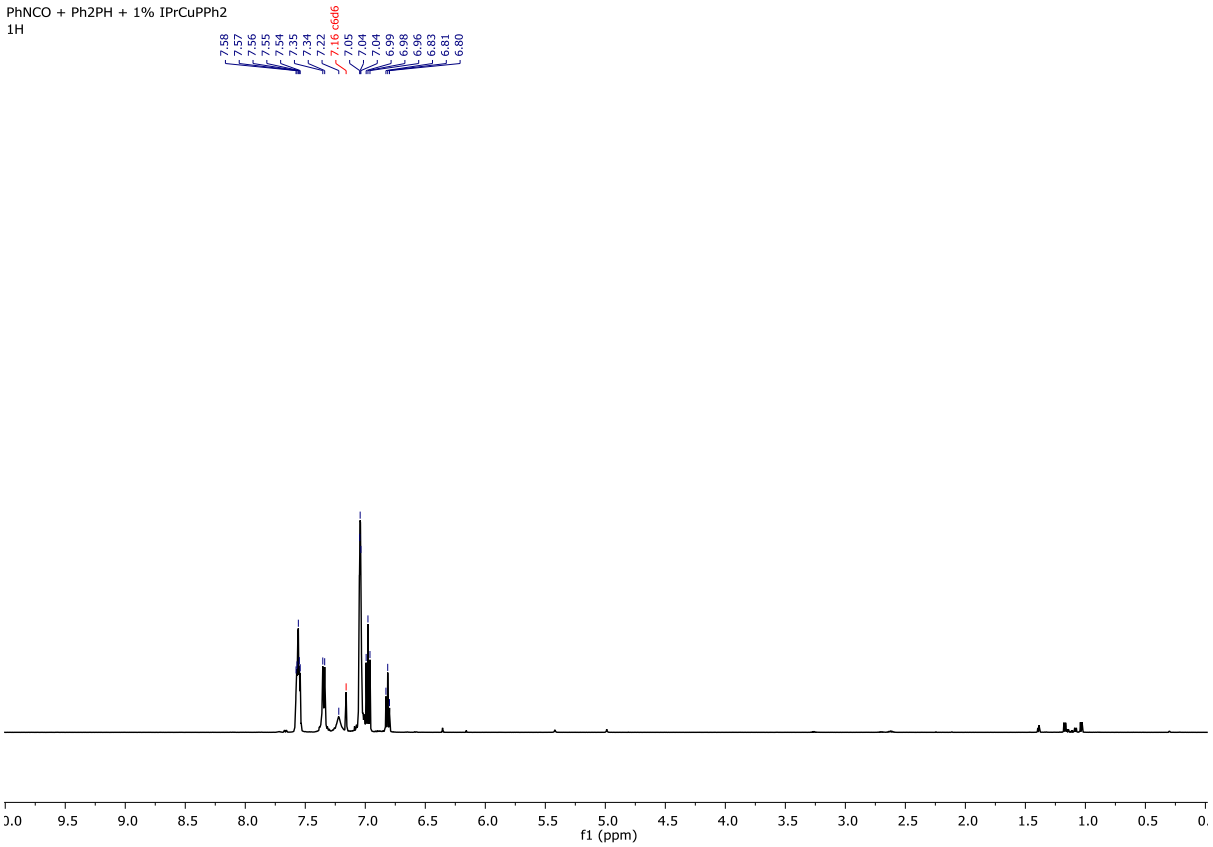


Figure S54: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 30 min (Table 1, Entry 9).

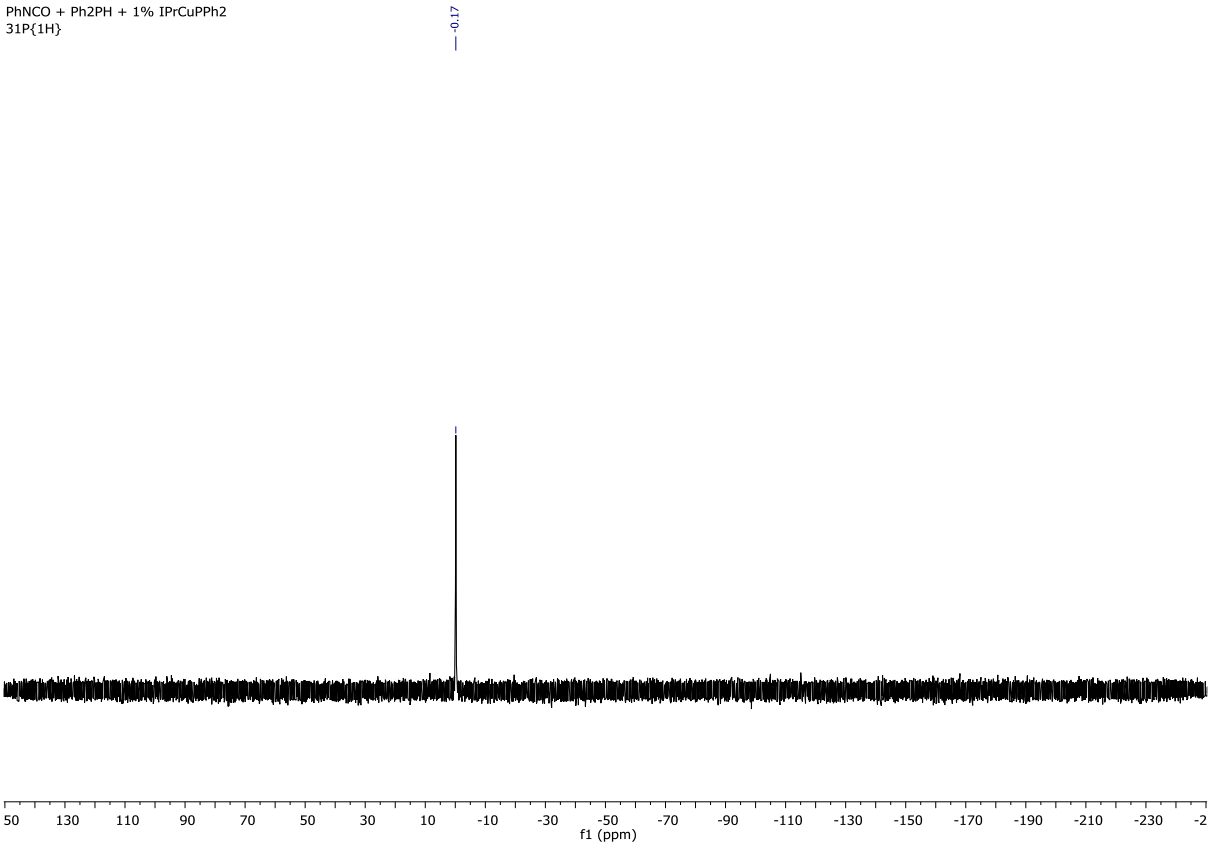


Figure S55: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **1** after 30 min (Table 1, Entry 9).

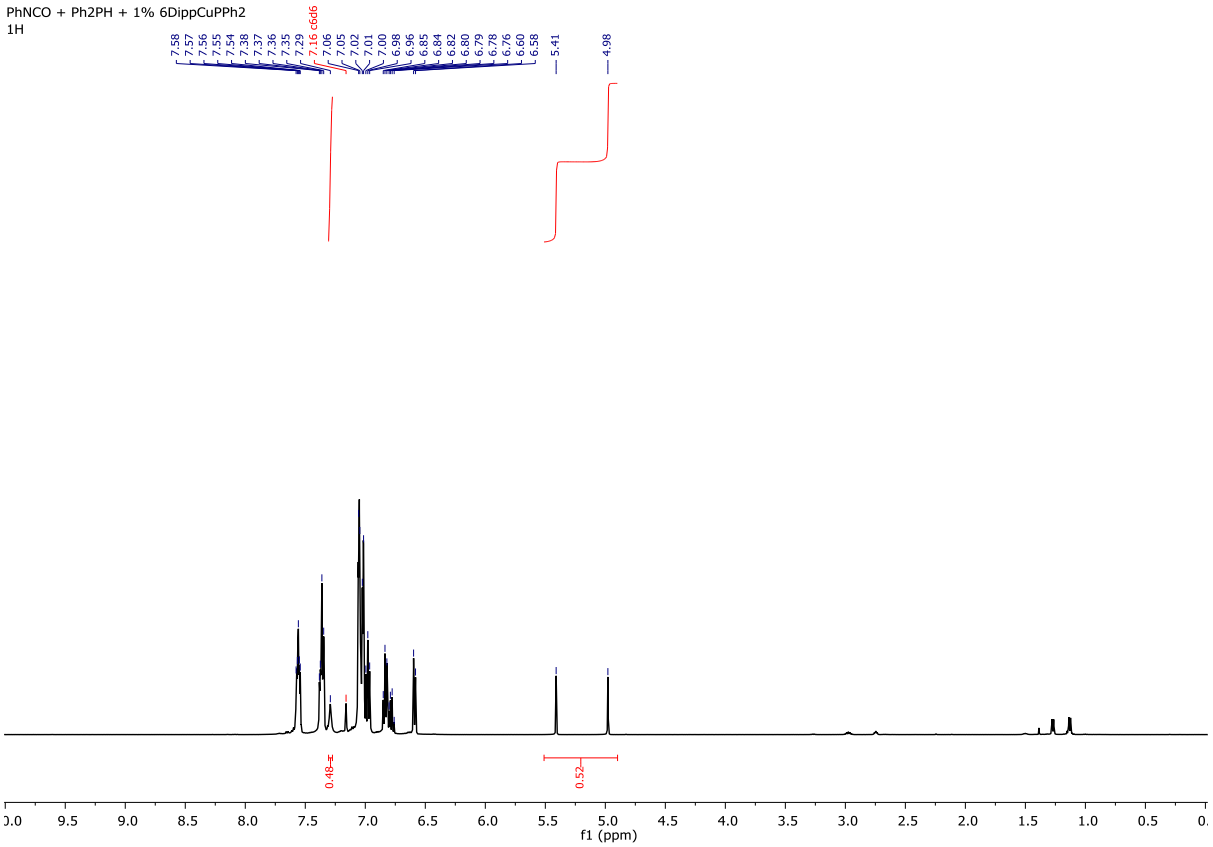


Figure S56: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 30 min (Table 1, Entry 10).

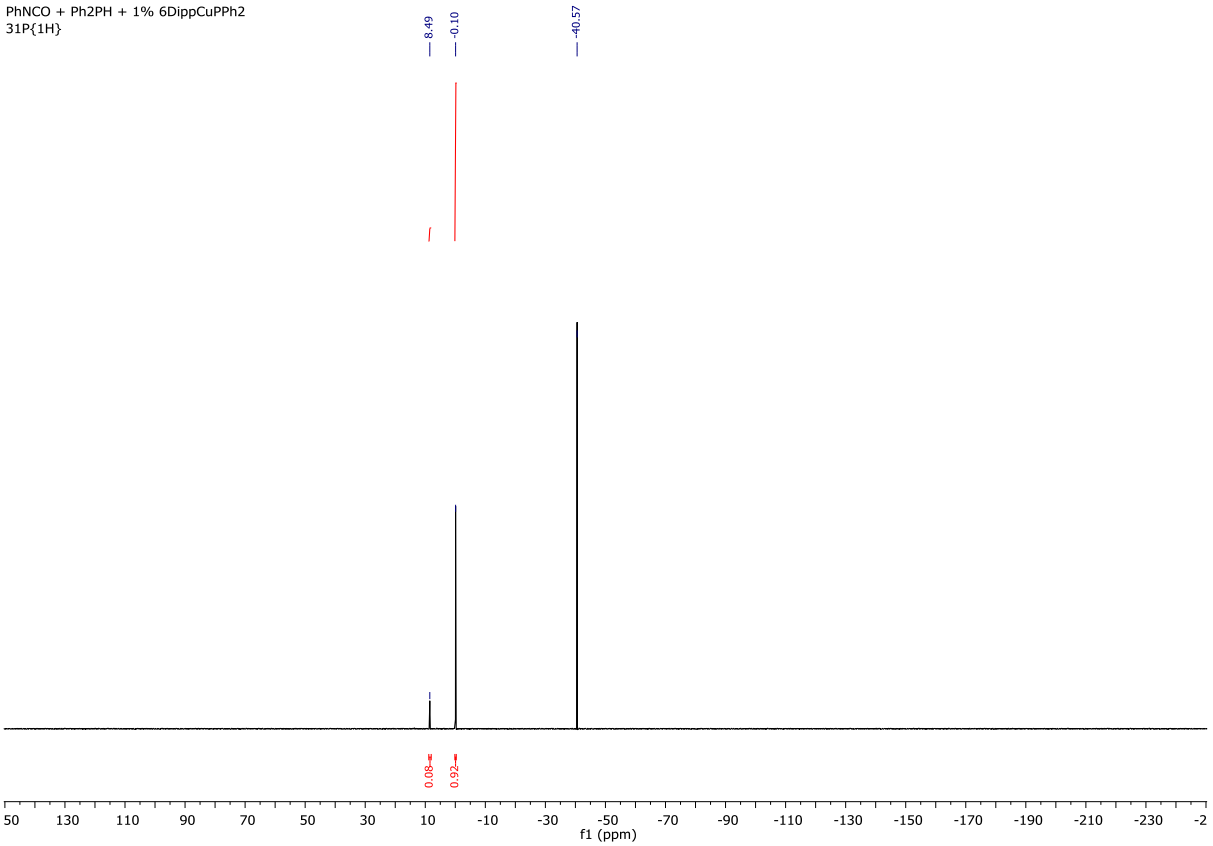


Figure S57: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **2** after 30 min (Table 1, Entry 10). Residual Ph_2PH observed at *ca.* δ -41 ppm.

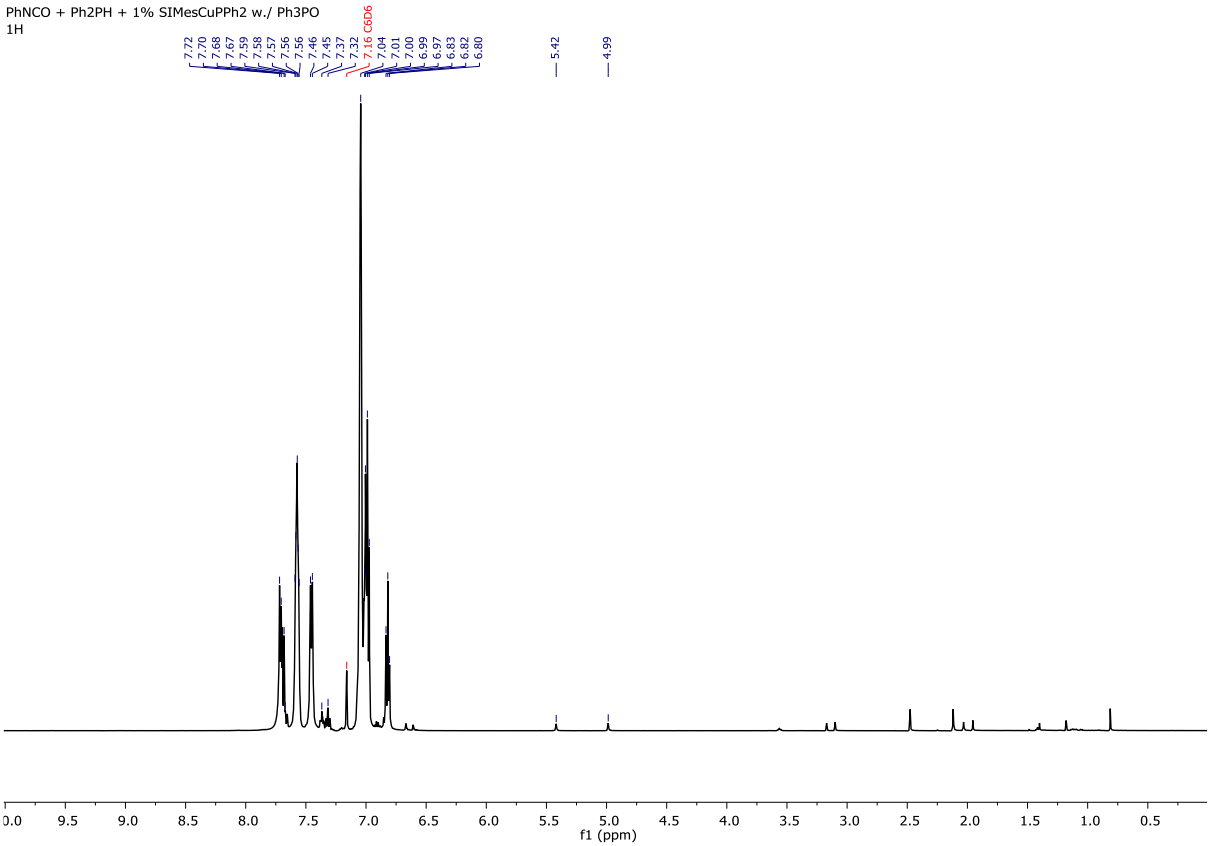


Figure S58: ^{1}H NMR spectrum (500 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 11), with Ph_3PO as an internal standard.

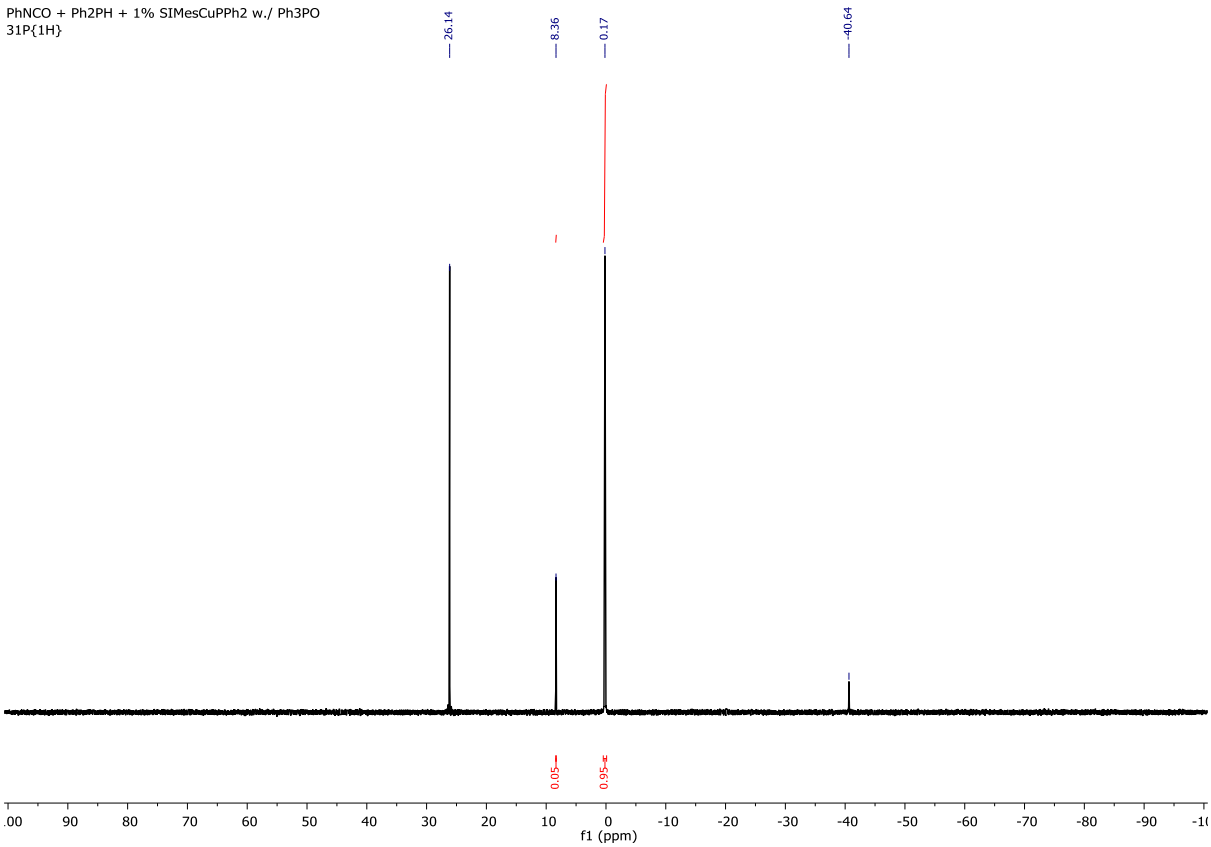


Figure S59: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 11), with Ph_3PO as an internal standard (*ca.* δ 26 ppm). Residual Ph_2PH observed at *ca.* δ -41 ppm.

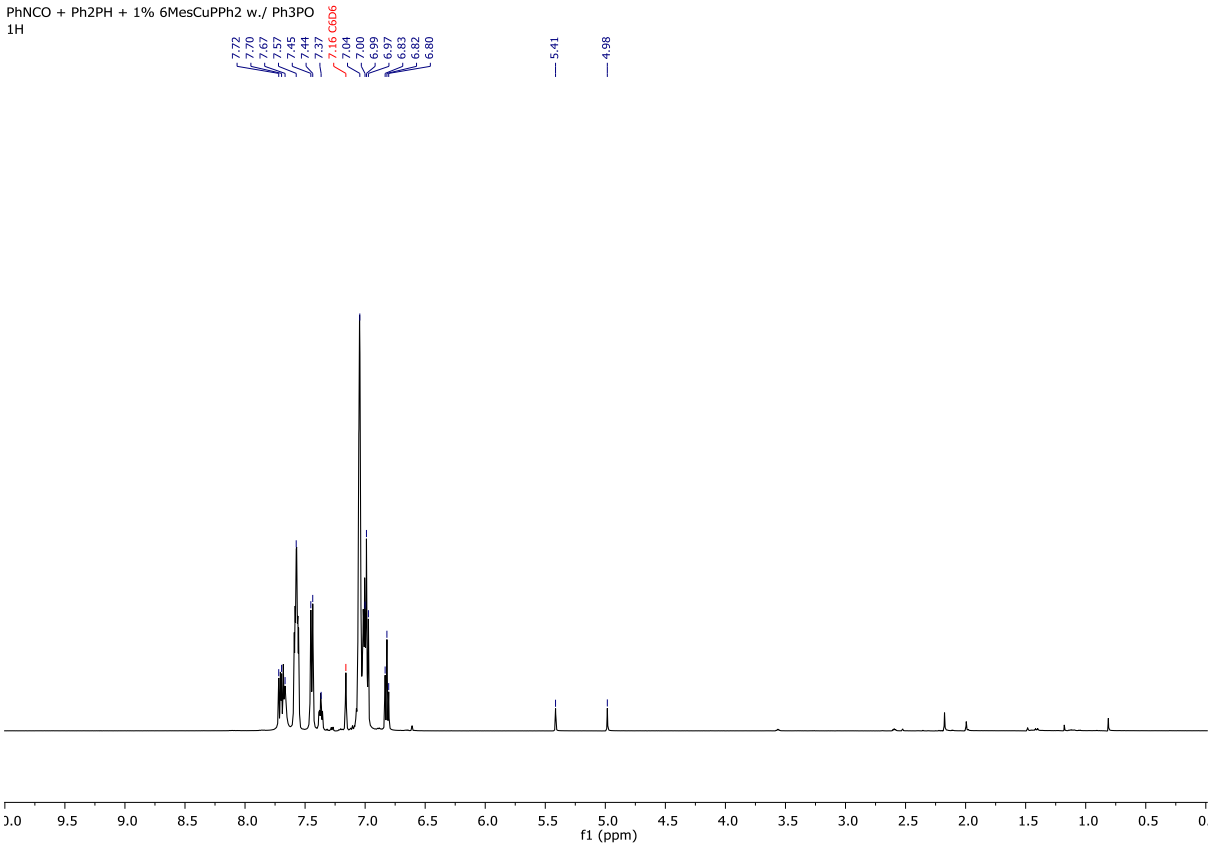


Figure S60: ^{1}H NMR spectrum (500 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 12), with Ph_3PO as an internal standard.

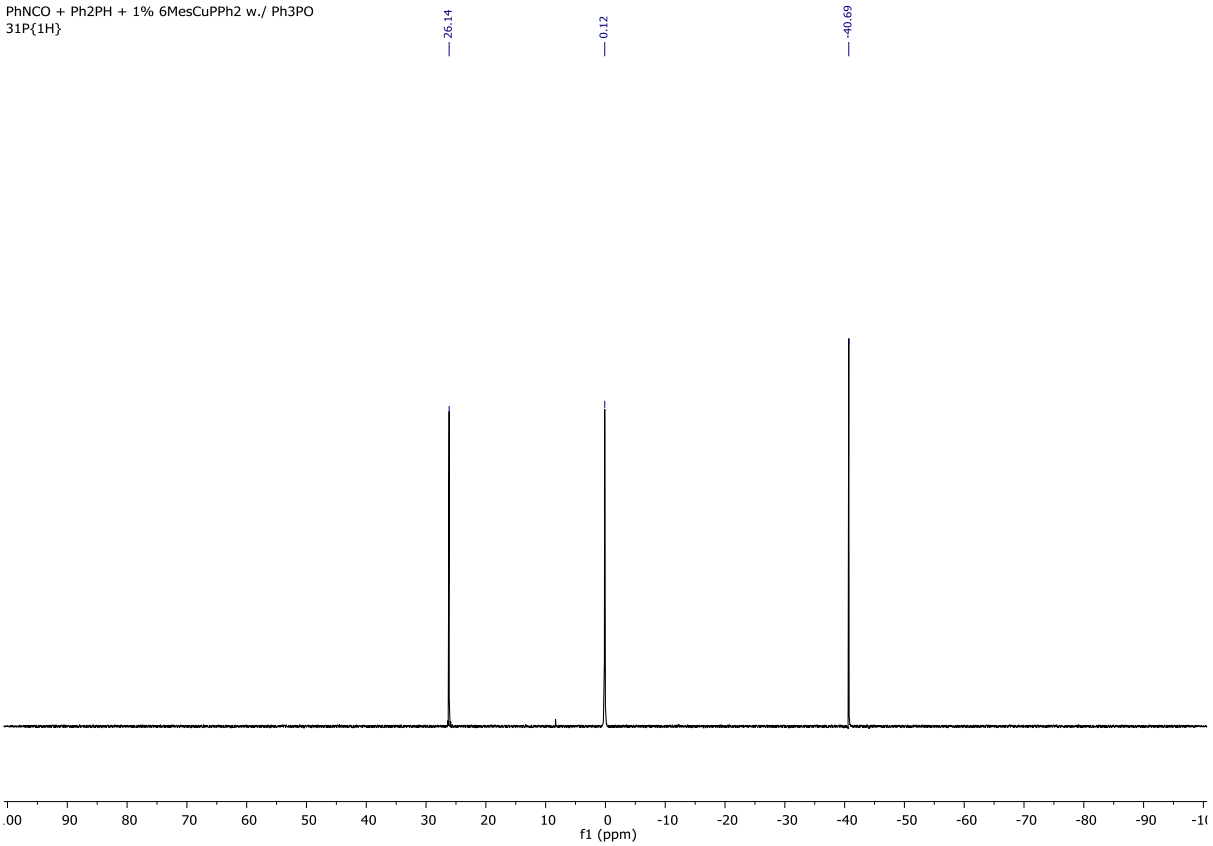


Figure S61: $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of the reaction between phenyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 12), with Ph_3PO as an internal standard(*ca.* δ 26 ppm). Residual Ph_2PH observed at *ca.* δ -41 ppm.

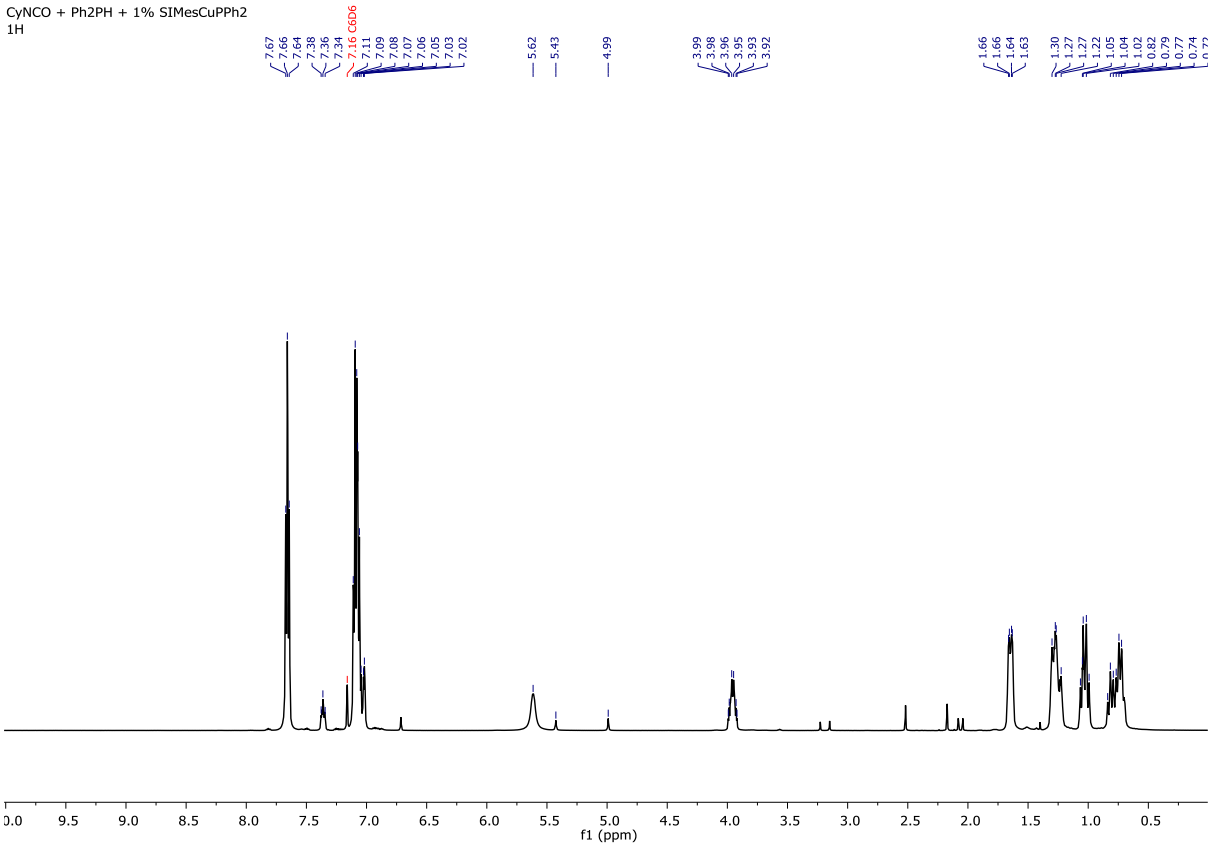


Figure S62: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between cyclohexyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 13).

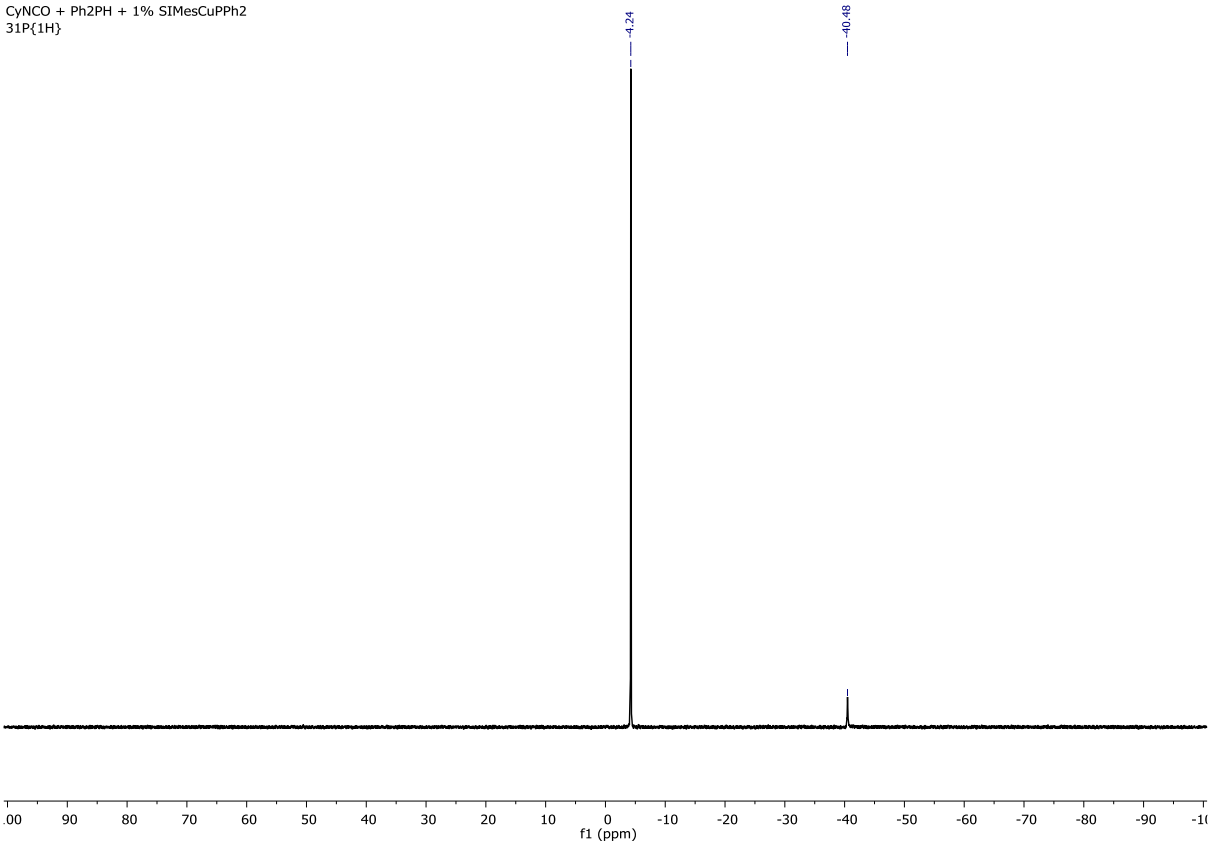


Figure S63: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between cyclohexyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **3** after 30 min (Table 1, Entry 13). Residual Ph_2PH observed at *ca.* δ -40 ppm.

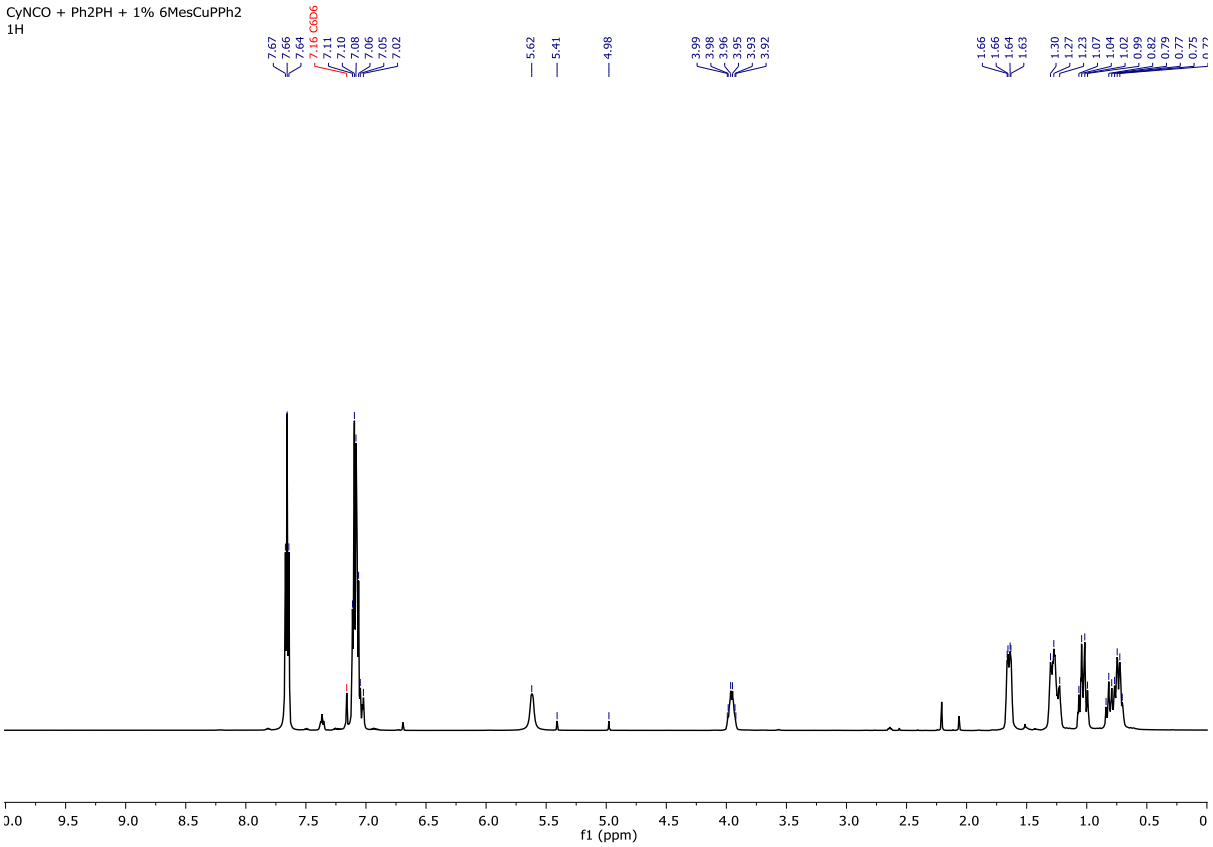


Figure S64: ^{1}H NMR spectrum (400 MHz, C_6D_6) of the reaction between cyclohexyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 14).

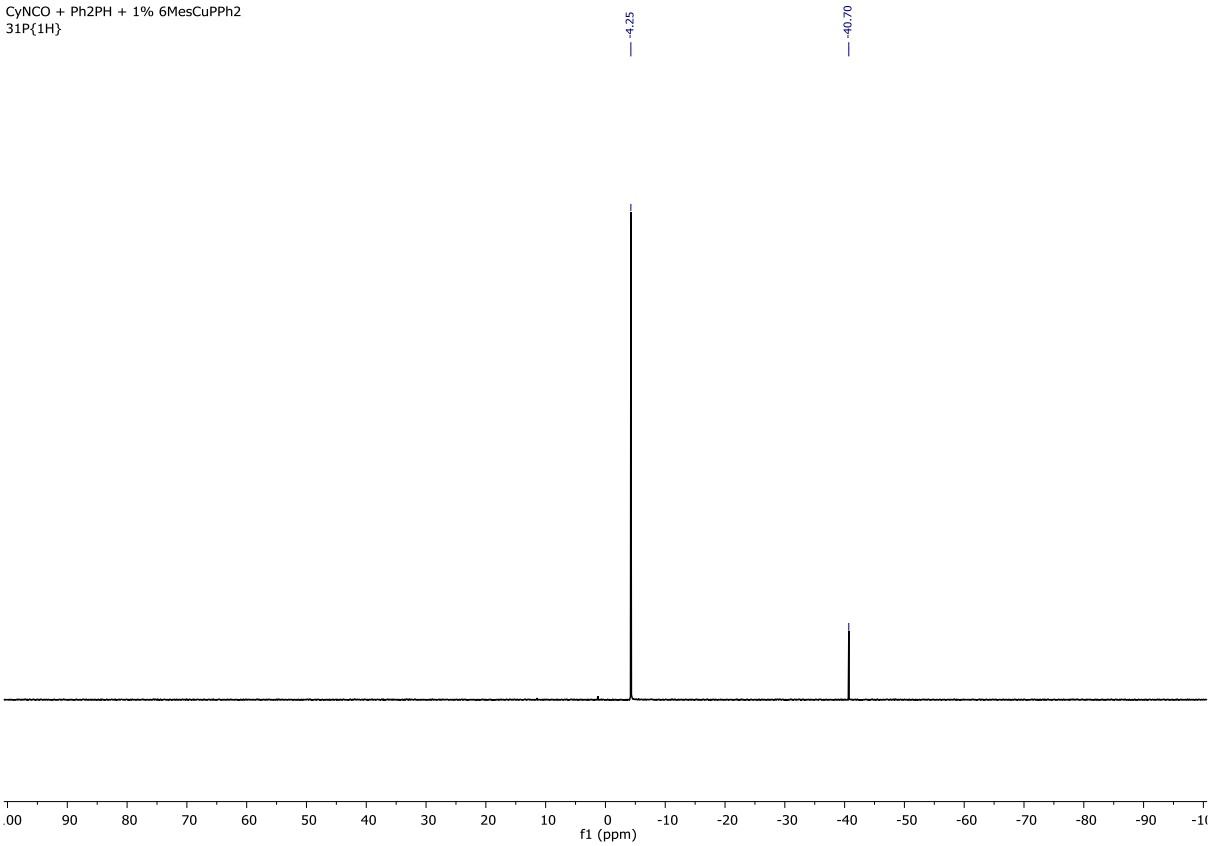


Figure S65: $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of the reaction between cyclohexyl isocyanate and diphenyl phosphine catalysed by 1 mol % of **4** after 30 min (Table 1, Entry 14). Residual Ph_2PH observed at *ca.* δ -41 ppm.

Optimised Coordinates for Computed Structures

(IPr)CuPPh$_2$ (1) *monomer*

Cu	0.06010	0.32785	-0.57464
P	0.42608	2.23739	-1.68019
N	0.64319	-2.28539	0.68658
N	-1.49087	-1.93869	0.56793
C	-0.28091	-1.35937	0.25053
C	0.02653	-3.40124	1.25521
H	0.59869	-4.23446	1.65393
C	-1.32218	-3.18193	1.18009
H	-2.16749	-3.78533	1.49936
C	-2.78488	-1.34157	0.29895
C	-3.40279	-1.59758	-0.95044
C	-4.67174	-1.02824	-1.17204
H	-5.17450	-1.20109	-2.12942
C	-5.29568	-0.24366	-0.19461
H	-6.28226	0.18978	-0.38934
C	-4.65705	-0.00553	1.02808
H	-5.14714	0.61885	1.78229
C	-3.38615	-0.54555	1.30521
C	-2.74246	-2.43515	-2.04523
H	-1.78885	-2.82473	-1.64821
C	-2.40538	-1.56432	-3.27736
H	-3.31885	-1.13925	-3.72886
H	-1.89919	-2.16964	-4.04931
H	-1.74096	-0.72733	-3.00365
C	-3.61175	-3.65107	-2.43787
H	-3.83261	-4.29086	-1.56657
H	-3.09126	-4.26623	-3.19205
H	-4.57532	-3.33651	-2.87508
C	-2.71084	-0.25350	2.64465
H	-1.72396	-0.74828	2.64370
C	-3.52274	-0.83723	3.82368
H	-4.52129	-0.37154	3.89341
H	-3.00126	-0.65174	4.77862
H	-3.66839	-1.92601	3.71870
C	-2.46556	1.26120	2.82837
H	-1.86482	1.67676	2.00280
H	-1.93109	1.44799	3.77610
H	-3.41549	1.82207	2.86506
C	2.07969	-2.12663	0.56941
C	2.78368	-1.51620	1.63706
C	4.18091	-1.39573	1.50473
H	4.75389	-0.92302	2.30913
C	4.84441	-1.86007	0.36254
H	5.93137	-1.75505	0.28090
C	4.11969	-2.45344	-0.67851
H	4.64569	-2.80418	-1.57255
C	2.72127	-2.60325	-0.60135
C	2.08767	-0.97419	2.88490
H	1.01108	-1.20365	2.80131
C	2.60806	-1.65488	4.17100
H	2.48418	-2.75053	4.13048
H	2.05818	-1.27999	5.05141
H	3.67923	-1.44469	4.33548
C	2.22587	0.56340	2.96673
H	3.28210	0.86641	3.07147
H	1.67555	0.95137	3.84143
H	1.82720	1.04854	2.06010
C	1.95762	-3.23495	-1.76487
H	0.89634	-3.31641	-1.47189
C	2.46266	-4.66195	-2.07546
H	1.85979	-5.11359	-2.88203
H	2.39779	-5.31769	-1.19057
H	3.51387	-4.65644	-2.41221
C	2.02115	-2.33112	-3.01772
H	1.61100	-1.32895	-2.80658
H	1.43929	-2.77634	-3.84337
H	3.06057	-2.20518	-3.36793
C	-0.81407	3.38250	-0.86638
C	-2.06541	3.54528	-1.50928
H	-2.24719	3.02733	-2.45876
C	-3.06472	4.36573	-0.96316
H	-4.02336	4.47175	-1.48429
C	-2.83102	5.06846	0.23051
H	-3.60310	5.72261	0.64987
C	-1.58881	4.93051	0.87424
H	-1.39098	5.47443	1.80557
C	-0.59745	4.09309	0.33943
H	0.36315	3.99404	0.85600
C	2.07932	2.87376	-1.09348
C	2.37644	4.25916	-1.07089
H	1.58536	4.98288	-1.29543
C	3.66609	4.72103	-0.76827
H	3.86221	5.79952	-0.75138
C	4.70565	3.81325	-0.50264
H	5.71317	4.17541	-0.27122
C	4.43384	2.43552	-0.53880
H	5.23001	1.71119	-0.33126
C	3.13911	1.97421	-0.82191
H	2.94095	0.89523	-0.82971

(6-Dipp)CuPPh$_2$ (2) *monomer*

Cu	0.06312	0.19885	-0.44509
P	0.36438	2.13983	-1.51564
N	0.60681	-2.37539	0.75760
N	-1.65064	-1.95010	0.39271
C	-0.35900	-1.53162	0.30121
C	-2.07626	-3.25592	0.94823
H	-2.98292	-3.57031	0.40552
H	-2.35754	-3.13037	2.01286
C	-0.95671	-4.28619	0.79715
H	-0.82797	-4.54151	-0.26981
H	-1.21854	-5.21394	1.33240
C	0.34733	-3.70889	1.34847
H	0.30630	-3.62168	2.45268
H	1.20518	-4.35660	1.10333
C	2.00003	-1.96572	0.72601
C	2.53981	-1.26432	1.83564
C	3.91421	-0.95550	1.81254
H	4.35222	-0.40577	2.65234
C	4.72554	-1.33344	0.73630
H	5.79254	-1.08700	0.74140
C	4.17027	-2.02095	-0.35023
H	4.80776	-2.30035	-1.19587
C	2.80301	-2.35694	-0.37857
C	1.68905	-0.82324	3.02587
H	0.65649	-1.17397	2.85030
C	2.18320	-1.45389	4.34772
H	2.20199	-2.55612	4.29298
H	1.52385	-1.16215	5.18357
H	3.20408	-1.11634	4.59799
C	1.63618	0.71810	3.12601
H	2.63794	1.14230	3.31367
H	0.97781	1.02824	3.95594
H	1.25108	1.16128	2.19175
C	2.22964	-3.09145	-1.59020
H	1.17161	-3.32171	-1.37243
C	2.95716	-4.42823	-1.85763
H	4.01551	-4.26679	-2.12653
H	2.48174	-4.96269	-2.69831

H	2.93643	-5.09035	-0.97475
C	2.25035	-2.18451	-2.84226
H	1.68724	-1.25231	-2.66594
H	1.79982	-2.70549	-3.70516
H	3.28317	-1.90745	-3.11669
C	-2.72529	-1.07506	-0.04615
C	-3.19199	-1.17743	-1.38390
C	-4.28913	-0.37882	-1.75986
H	-4.66190	-0.43319	-2.78844
C	-4.90672	0.48277	-0.84522
H	-5.76011	1.09356	-1.15823
C	-4.42770	0.56869	0.46690
H	-4.90547	1.25551	1.17318
C	-3.33373	-0.20697	0.89752
C	-2.54436	-2.10063	-2.41558
H	-1.71080	-2.62702	-1.91796
C	-1.94194	-1.29206	-3.58734
H	-2.72719	-0.75518	-4.14795
H	-1.42687	-1.96491	-4.29520
H	-1.21694	-0.54389	-3.22490
C	-3.53739	-3.16813	-2.93011
H	-3.95597	-3.77157	-2.10588
H	-3.03643	-3.85325	-3.63610
H	-4.38515	-2.70385	-3.46357
C	-2.84190	-0.07896	2.33884
H	-1.97922	-0.75821	2.46160
C	-3.92905	-0.51143	3.34973
H	-4.81164	0.14953	3.29557
H	-3.53915	-0.45995	4.38130
H	-4.27529	-1.54304	3.16380
C	-2.34272	1.35293	2.63498
H	-1.54538	1.65274	1.93538
H	-1.94847	1.41524	3.66456
H	-3.15547	2.09307	2.54100
C	2.09191	2.76848	-1.20669
C	3.15207	1.89397	-0.87039
H	2.93086	0.84224	-0.65456
C	4.47803	2.35109	-0.79990
H	5.27628	1.64745	-0.53684
C	4.77886	3.70084	-1.04253
H	5.81152	4.06045	-0.97663
C	3.73711	4.58621	-1.37089
H	3.95598	5.64202	-1.56852
C	2.41662	4.12400	-1.46547
H	1.62023	4.82212	-1.74681
C	-0.71438	3.32306	-0.54742
C	-2.08582	3.39072	-0.89706
H	-2.45983	2.76198	-1.71378
C	-2.96720	4.25072	-0.22530
H	-4.02237	4.28208	-0.52120
C	-2.49962	5.08600	0.80409
H	-3.18290	5.77050	1.31840
C	-1.13959	5.03936	1.15551
H	-0.75793	5.68521	1.95530
C	-0.26012	4.16690	0.49519
H	0.79584	4.14440	0.78418

(SIMes)CuPPh$_2$ (3) *monomer*

Cu	-0.16184	0.14634	-0.48157
P	0.28797	2.22381	-1.18800
N	0.09185	-2.61073	0.50285
N	-2.00291	-1.99143	0.27247
C	-0.71533	-1.58638	0.12231
C	-0.66442	-3.76661	1.05929
H	-0.31944	-4.71405	0.61492
H	-0.50697	-3.82182	2.15277
C	-2.11890	-3.41710	0.68449
H	-2.82137	-3.52797	1.52641
H	-2.49885	-4.02066	-0.16116
C	-3.15847	-1.24265	-0.15092
C	-3.97953	-0.64355	0.83382
C	-5.12537	0.05193	0.40897
H	-5.76078	0.53042	1.16402
C	-5.46757	0.16405	-0.95089
C	-4.62240	-0.43761	-1.90128
H	-4.86465	-0.34989	-2.96729
C	-3.46691	-1.14764	-1.52981
C	-3.62477	-0.71556	2.30292
H	-2.57918	-0.41113	2.47723
H	-4.27673	-0.05291	2.89327
H	-3.74048	-1.73708	2.71093
C	-6.72162	0.89518	-1.38027
H	-6.58549	1.39176	-2.35512
H	-7.57375	0.19812	-1.48506
H	-7.01444	1.66127	-0.64383
C	-2.56856	-1.75316	-2.58547
H	-2.29193	-2.79590	-2.35103
H	-3.06221	-1.74448	-3.57001
H	-1.62578	-1.18170	-2.67243
C	1.52439	-2.53365	0.62668
C	2.10114	-1.77128	1.67313
C	3.50253	-1.75554	1.78337
H	3.95819	-1.16544	2.58767
C	4.33201	-2.46681	0.89690
C	3.72318	-3.21736	-0.12432
H	4.35204	-3.77588	-0.82835
C	2.32625	-3.26628	-0.28106
C	1.25352	-0.97082	2.63670
H	0.37100	-1.53429	2.98511
H	1.84194	-0.67462	3.51951
H	0.87611	-0.04780	2.15734
C	5.83867	-2.39656	1.02250
H	6.32763	-3.25143	0.52751
H	6.22977	-1.47474	0.55470
H	6.15639	-2.38328	2.07870
C	1.71202	-4.07622	-1.40234
H	0.87683	-3.53706	-1.87908
H	2.46297	-4.30221	-2.17585
H	1.31526	-5.04549	-1.04490
C	-0.04703	3.12465	0.42266
C	0.90804	3.36384	1.44066
H	1.93796	3.01750	1.30338
C	0.55735	4.04560	2.61647
H	1.31948	4.22208	3.38499
C	-0.75926	4.49460	2.81774
H	-1.03016	5.02627	3.73630
C	-1.72023	4.26210	1.81905
H	-2.74889	4.61680	1.95382
C	-1.36579	3.59806	0.63494
H	-2.11807	3.44775	-0.14901
C	2.13990	2.33663	-1.38912
C	2.81971	3.57272	-1.25303
H	2.26749	4.45489	-0.91054
C	4.18542	3.68805	-1.55184
H	4.68517	4.65602	-1.42883
C	4.90841	2.57822	-2.02228
H	5.97300	2.67144	-2.26283
C	4.24718	1.34923	-2.18127
H	4.79616	0.47292	-2.54550
C	2.88592	1.22955	-1.86041
H	2.38633	0.25899	-1.96926

(SIMes)CuPPh$_2$ (3) *dimer*

Cu	-0.06301	-1.49655	-0.89548
P	-0.56764	-0.77973	1.32805
N	-0.99869	-3.63148	-2.73135

N	1.03553	-3.99819	-1.99997
C	-0.01880	-3.13574	-1.91474
C	-0.66134	-4.95498	-3.31955
H	-0.87672	-4.97320	-4.40098
H	-1.26458	-5.74892	-2.83784
C	0.83914	-5.07858	-3.00040
H	1.11368	-6.05997	-2.57841
H	1.47623	-4.89665	-3.88705
C	2.32390	-3.80320	-1.38947
C	2.61424	-4.49289	-0.18723
C	3.89109	-4.33793	0.37668
H	4.11840	-4.85584	1.31625
C	4.87242	-3.52383	-0.22110
C	4.54850	-2.85407	-1.41328
H	5.29251	-2.20184	-1.88559
C	3.28521	-2.98177	-2.02202
C	1.57115	-5.36065	0.48049
H	0.65668	-4.78283	0.69416
H	1.94991	-5.76197	1.43329
H	1.27786	-6.21728	-0.15435
C	6.24292	-3.38307	0.40797
H	6.83792	-2.60223	-0.09275
H	6.81359	-4.32791	0.34675
H	6.16813	-3.12154	1.47781
C	2.97383	-2.25562	-3.31089
H	2.87166	-2.95734	-4.16050
H	3.77198	-1.53962	-3.55939
H	2.03007	-1.69058	-3.22826
C	-2.34733	-3.14213	-2.81398
C	-3.26631	-3.43019	-1.77450
C	-4.59680	-2.99842	-1.92678
H	-5.31294	-3.21648	-1.12535
C	-5.03165	-2.30822	-3.07335
C	-4.09309	-2.04510	-4.08802
H	-4.41238	-1.51084	-4.99145
C	-2.74891	-2.44760	-3.98063
C	-2.83516	-4.17274	-0.53038
H	-2.32793	-5.12320	-0.77409
H	-3.70159	-4.39988	0.10978
H	-2.12282	-3.56616	0.05756
C	-6.46604	-1.83886	-3.19920
H	-6.77418	-1.75645	-4.25473
H	-6.60175	-0.84219	-2.74011
H	-7.16247	-2.52718	-2.69176
C	-1.75795	-2.13146	-5.07904
H	-0.85022	-1.65979	-4.66794
H	-2.19910	-1.44348	-5.81718
H	-1.43746	-3.04010	-5.62205
C	0.58947	-1.61987	2.52146
C	0.35194	-2.91361	3.04788
H	-0.57750	-3.43538	2.79444
C	1.28088	-3.53182	3.89815
H	1.06347	-4.52628	4.30537
C	2.48832	-2.88733	4.22207
H	3.21389	-3.37262	4.88406
C	2.74789	-1.61244	3.69393
H	3.67915	-1.09009	3.94028
C	1.80506	-0.98272	2.86557
H	2.00341	0.02743	2.48733
C	-2.25742	-1.11243	2.03267
C	-2.51631	-1.40935	3.39360
H	-1.68005	-1.51651	4.09212
C	-3.82914	-1.57060	3.86331
H	-3.99760	-1.80729	4.92056
C	-4.92351	-1.42438	2.99287
H	-5.94711	-1.55208	3.36134
C	-4.68371	-1.11896	1.64106
H	-5.52313	-1.00421	0.94567
C	-3.37168	-0.97182	1.16768
H	-3.20146	-0.74709	0.10827
Cu	0.06301	1.49655	0.89548
P	0.56764	0.77973	-1.32805
N	0.99869	3.63148	2.73135
N	-1.03553	3.99819	1.99997
C	0.01880	3.13574	1.91474
C	0.66134	4.95498	3.31955
H	0.87672	4.97320	4.40098
H	1.26458	5.74892	2.83784
C	-0.83914	5.07858	3.00040
H	-1.11368	6.05997	2.57841
H	-1.47623	4.89665	3.88705
C	-2.32390	3.80320	1.38947
C	-2.61424	4.49289	0.18723
C	-3.89109	4.33793	-0.37668
H	-4.11840	4.85584	-1.31625
C	-4.87242	3.52383	0.22110
C	-4.54850	2.85407	1.41328
H	-5.29251	2.20184	1.88559
C	-3.28521	2.98177	2.02202
C	-1.57115	5.36065	-0.48049
H	-0.65668	4.78283	-0.69416
H	-1.94991	5.76197	-1.43329
H	-1.27786	6.21728	0.15435
C	-6.24292	3.38307	-0.40797
H	-6.83792	2.60223	0.09275
H	-6.81359	4.32791	-0.34675
H	-6.16813	3.12154	-1.47781
C	-2.97383	2.25562	3.31089
H	-2.87166	2.95734	4.16050
H	-3.77198	1.53962	3.55939
H	-2.03007	1.69058	3.22826
C	2.34733	3.14213	2.81398
C	3.26631	3.43019	1.77450
C	4.59680	2.99842	1.92678
H	5.31294	3.21648	1.12535
C	5.03165	2.30822	3.07335
C	4.09309	2.04510	4.08802
H	4.41238	1.51084	4.99145
C	2.74891	2.44760	3.98063
C	2.83516	4.17274	0.53038
H	2.32793	5.12320	0.77409
H	3.70159	4.39988	-0.10978
H	2.12282	3.56616	-0.05756
C	6.46604	1.83886	3.19920
H	6.77418	1.75645	4.25473
H	6.60175	0.84219	2.74011
H	7.16247	2.52718	2.69176
C	1.75795	2.13146	5.07904
H	0.85022	1.65979	4.66794
H	2.19910	1.44348	5.81718
H	1.43746	3.04010	5.62205
C	-0.58947	1.61987	-2.52146
C	-0.35194	2.91361	-3.04788
H	0.57750	3.43538	-2.79444
C	-1.28088	3.53182	-3.89815
H	-1.06347	4.52628	-4.30537
C	-2.48832	2.88733	-4.22207
H	-3.21389	3.37262	-4.88406
C	-2.74789	1.61244	-3.69393
H	-3.67915	1.09009	-3.94028
C	-1.80506	0.98272	-2.86557
H	-2.00341	-0.02743	-2.48733
C	2.25742	1.11243	-2.03267
C	2.51631	1.40935	-3.39360
H	1.68005	1.51651	-4.09212
C	3.82914	1.57060	-3.86331

H	3.99760	1.80729	-4.92056
C	4.92351	1.42438	-2.99287
H	5.94711	1.55208	-3.36134
C	4.68371	1.11896	-1.64106
H	5.52313	1.00421	-0.94567
C	3.37168	0.97182	-1.16768
H	3.20146	0.74709	-0.10827

(6-Mes)CuPPh$_2$ (4) *monomer*

Cu	-0.11175	-0.06364	-0.35899
P	0.16388	1.99897	-1.18745
N	-1.65967	-2.43104	0.19042
N	0.63603	-2.73560	0.41275
C	-0.40481	-1.90820	0.13440
C	1.98220	-2.19513	0.42100
C	2.46662	-1.55650	1.58664
C	3.79262	-1.09051	1.58172
H	4.17537	-0.58372	2.47560
C	4.63293	-1.24116	0.46366
C	4.11753	-1.88893	-0.67346
H	4.75523	-2.00986	-1.55748
C	2.79812	-2.37182	-0.72085
C	1.57917	-1.33451	2.79127
H	1.05530	-2.25463	3.10378
H	0.80337	-0.57907	2.56679
H	2.16720	-0.96993	3.64822
C	6.03511	-0.67445	0.46913
H	6.01069	0.39571	0.19350
H	6.68659	-1.19181	-0.25432
H	6.49970	-0.74801	1.46680
C	2.26080	-3.02660	-1.97470
H	1.96557	-4.07931	-1.80913
H	3.01875	-3.01834	-2.77369
H	1.36693	-2.49533	-2.34584
C	-2.79595	-1.56249	-0.05244
C	-3.48209	-0.99852	1.04925
C	-4.61688	-0.20829	0.78934
H	-5.15170	0.23838	1.63639
C	-5.07558	0.03187	-0.51885
C	-4.37173	-0.55285	-1.58750
H	-4.71231	-0.37667	-2.61492
C	-3.23410	-1.35329	-1.38216
C	-3.00941	-1.21558	2.47039
H	-3.21851	-2.24172	2.82559
H	-3.51665	-0.52189	3.15904
H	-1.92229	-1.05219	2.56000
C	-6.26911	0.92716	-0.77229
H	-5.94958	1.97794	-0.89621
H	-6.98382	0.89839	0.06682
H	-6.80501	0.63790	-1.69137
C	-2.48550	-1.94144	-2.55685
H	-2.30875	-3.02517	-2.43948
H	-1.49542	-1.46161	-2.66536
H	-3.04268	-1.78521	-3.49386
C	1.94423	2.41787	-0.78795
C	2.90910	2.18525	-1.79807
H	2.57947	1.78969	-2.76650
C	4.26739	2.47173	-1.59075
H	4.98924	2.28831	-2.39533
C	4.69725	3.02220	-0.37101
H	5.75226	3.27468	-0.21658
C	3.75124	3.26630	0.64102
H	4.07151	3.69588	1.59777
C	2.39678	2.96177	0.43910
H	1.67373	3.15708	1.23808
C	-0.81621	3.16270	-0.10850
C	-0.46065	4.52823	0.02409
H	0.47000	4.88827	-0.42785
C	-1.27871	5.42836	0.72311
H	-0.97105	6.47666	0.81490
C	-2.49021	4.99906	1.29160
H	-3.12942	5.70358	1.83469
C	-2.86794	3.65295	1.15315
H	-3.80775	3.29812	1.59289
C	-2.04053	2.74818	0.47047
H	-2.34442	1.69794	0.38470
C	-1.96823	-3.84869	0.49031
H	-2.86324	-4.12744	-0.09103
H	-2.22474	-3.95901	1.56220
C	0.49427	-4.16628	0.76511
H	0.46657	-4.27924	1.86734
H	1.39393	-4.69341	0.40733
C	-0.77495	-4.73557	0.12863
H	-0.94890	-5.76693	0.47769
H	-0.65387	-4.76751	-0.96870

(6-Mes)CuPPh$_2$ (4) *dimer*

Cu	-1.43732	1.05761	0.00853
Cu	1.43731	-1.05758	0.00863
P	0.00003	-0.00004	-1.65606
P	-0.00006	0.00001	1.64005
N	-2.69910	3.66491	0.06793
N	-4.24915	1.96468	-0.19922
N	4.24922	-1.96457	-0.19890
N	2.69917	-3.66481	0.06816
C	-2.93776	2.32309	-0.03607
C	-3.72818	4.72840	0.00863
H	-3.81393	5.11203	-1.02786
H	-3.38022	5.56409	0.63848
C	-5.07242	4.19136	0.49301
H	-5.02014	3.97461	1.57475
H	-5.86719	4.93981	0.33464
C	-5.38849	2.91118	-0.27497
H	-6.27516	2.40437	0.14089
H	-5.61444	3.14133	-1.33608
C	-1.35093	4.14703	0.28090
C	-0.58087	4.57303	-0.82291
C	0.68487	5.13594	-0.56597
H	1.29832	5.45344	-1.41740
C	1.17892	5.29132	0.73951
C	0.37641	4.86529	1.81637
H	0.75304	4.95928	2.84140
C	-0.89202	4.30060	1.61236
C	-1.09849	4.45684	-2.23847
H	-1.61086	3.49517	-2.39911
H	-0.27255	4.52155	-2.96297
H	-1.81694	5.26534	-2.47468
C	2.54133	5.89985	0.99618
H	2.46329	6.83772	1.57568
H	3.06486	6.13123	0.05409
H	3.17472	5.21171	1.58321
C	-1.75354	3.87716	2.78019
H	-1.22322	4.03235	3.73161
H	-2.01492	2.80748	2.70325
H	-2.70123	4.44664	2.81812
C	-4.64010	0.58049	-0.34895
C	-4.68356	0.00326	-1.63858
C	-5.12769	-0.11171	0.78748
C	-5.66212	-1.39936	0.60476
H	-6.04976	-1.93780	1.47867
C	-5.72858	-2.00337	-0.66566
C	-5.23150	-1.28767	-1.76898
H	-5.26954	-1.74140	-2.76621
C	-5.08246	0.52106	2.16083
H	-4.06208	0.86153	2.40401
H	-5.39523	-0.19791	2.93386

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H  -5.74791  1.40169  2.23220
C  -6.30211 -3.39523 -0.83165
H  -6.59778 -3.58827 -1.87592
H  -7.18853 -3.54690 -0.19221
H  -5.56437 -4.16846 -0.54871
C  -4.14866  0.74201 -2.84390
H  -3.06651  0.93189 -2.72702
H  -4.64059  1.72161 -2.98045
H  -4.29763  0.15313 -3.76207
C   2.93782 -2.32299 -0.03585
C   1.35101 -4.14696  0.28103
C   0.58111 -4.57324 -0.82279
C  -0.68460 -5.13624 -0.56589
H  -1.29792 -5.45397 -1.41732
C  -1.17879 -5.29144  0.73956
C  -0.37641 -4.86520  1.81644
H  -0.75311 -4.95913  2.84146
C   0.89197 -4.30042  1.61248
C   1.09888 -4.45745 -2.23832
H   1.81574 -5.26729 -2.47486
H   1.61310 -3.49673 -2.39863
H   0.27278 -4.52032 -2.96281
C  -2.54133 -5.89970  0.99615
H  -3.17598 -5.20975  1.57972
H  -2.46385 -6.83543  1.57914
H  -3.06326 -6.13459  0.05403
C   1.75338 -3.87685  2.78034
H   2.70106 -4.44633  2.81841
H   1.22298 -4.03193  3.73173
H   2.01478 -2.80717  2.70331
C   4.64017 -0.58040 -0.34878
C   4.68357 -0.00330 -1.63847
C   5.23148  1.28764 -1.76901
H   5.26945  1.74129 -2.76627
C   5.72858  2.00346 -0.66578
C   5.66211  1.39960  0.60471
H   6.04967  1.93816  1.47858
C   5.12773  0.11195  0.78757
C   4.14858 -0.74215 -2.84370
H   4.64014 -1.72197 -2.97991
H   4.29791 -0.15355 -3.76199
H   3.06634 -0.93157 -2.72693
C   6.30251  3.39513 -0.83196
H   5.56686  4.16849 -0.54403
H   6.59345  3.58979 -1.87725
H   7.19215  3.54482 -0.19649
C   5.08249 -0.52066  2.16100
H   5.74817 -1.40110  2.23257
H   4.06217 -0.86138  2.40408
H   5.39496  0.19849  2.93398
C  -0.72845 -1.26100 -2.82319
C  -1.84330 -2.02159 -2.39515
H  -2.29373 -1.80801 -1.41993
C  -2.39183 -3.03038 -3.20315
H  -3.25789 -3.59607 -2.84139
C  -1.85235 -3.30163 -4.47224
H  -2.29227 -4.07521 -5.11101
C  -0.73905 -2.56204 -4.91056
H  -0.29747 -2.76519 -5.89334
C  -0.17780 -1.56947 -4.09371
H   0.69689 -1.01663 -4.45149
C   0.72845  1.26077 -2.82339
C   0.17774  1.56908 -4.09392
H  -0.69695  1.01619 -4.45160
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