

Supplementary Information

Thiocyanato-Bridged Copper(I) Cubane complex and its application in Palladium-Catalyzed Sonogashira Coupling of Aryl halides

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Experimental Details

Materials and Physical Measurements:

All the synthetic manipulations were performed under ambient conditions. The solvents were dried and distilled before use following the standard procedures. Copper(I) thiocyanate, and 1,1'-bis(di-*tert*-butylphosphino) Ferrocene, Phenylacetylene, Chlorobenzene, Bromobenzene, Iodobenzene, 4-bromotoluene, 4-chlorotoluene and 4-iodotoluene, [Pd(allyl)Cl]₂ were used as received. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within ±0.4% of calculated values. IR(KBr) was recorded using Perkin-Elmer FT-IR spectrophotometer. Electronic spectrum of the **1** was obtained on a Perkin Elmer Lambda-35 spectrofluorometer. ¹H and ³¹P NMR spectrum was recorded on a JEOL AL-400 FTNMR instrument using tetramethylsilane as an internal standard. Electrochemical property of the complex was measured by cyclic voltammetry using platinum as working electrode and the supporting electrolyte was [NBu₄]ClO₄ (0.1 M) in dichloromethane solution of 0.001 M of complex versus Ag/AgCl at a scan rate of 100 mVs⁻¹.

[Cu₄(μ₃-SCN)₄(κ¹-*P,P*-dtbpf)₂] (**1**):

1,1'-bis(di-*tert*-butylphosphino) Ferrocene (474 mg, 1 mmol) was added slowly to a solution of CH₃OH (15 mL), and CH₂Cl₂ (15 mL) containing copper(I) thiocyanate (242 mg, 2 mmol). The resulting solution was refluxed with stirring at room temperature for 24 hours. Slowly, color of the solution changes from orange to yellowish orange color. The resulting

solution was filtered. The filtrate solution was saturated with hexane and left for slow evaporation. Orange color crystals suitable for X-ray studies were grown after two days. Yield: (1.004 g, 70%). Anal. Calc. for $C_{56}H_{88}N_4P_4S_4Cu_4Fe_2$: C, 46.83; H, 6.13; N, 3.90; S, 8.92. Found: C, 46.93; H, 6.35; N, 3.99; S, 9.02. IR(cm^{-1} , nujol): $\nu = 3432, 2918, 2850, 2366, 2126, 1718, 1508, 1475, 1457, 1390, 1365, 1307, 1177, 1155, 1028, 1061, 1037, 937, 850, 813, 746, 629, 603, 577, 547, 492, 473, 438$. 1H NMR (δ ppm, 400 MHz, $CDCl_3$, 298K): δ 4.25 (s, 8H, C_5H_4), 4.04 (m, 8H, C_5H_4), 1.39 (d, $^3J_{H-P} = 12.0$ Hz, 72H, CH_3). $^{31}P\{^1H\}$: δ 64.34 (s) (sharp). UV/Vis: λ_{max} ($\epsilon[dm^3 mol^{-1} cm^{-1}]$) = 495 (87770), 328 (30675).

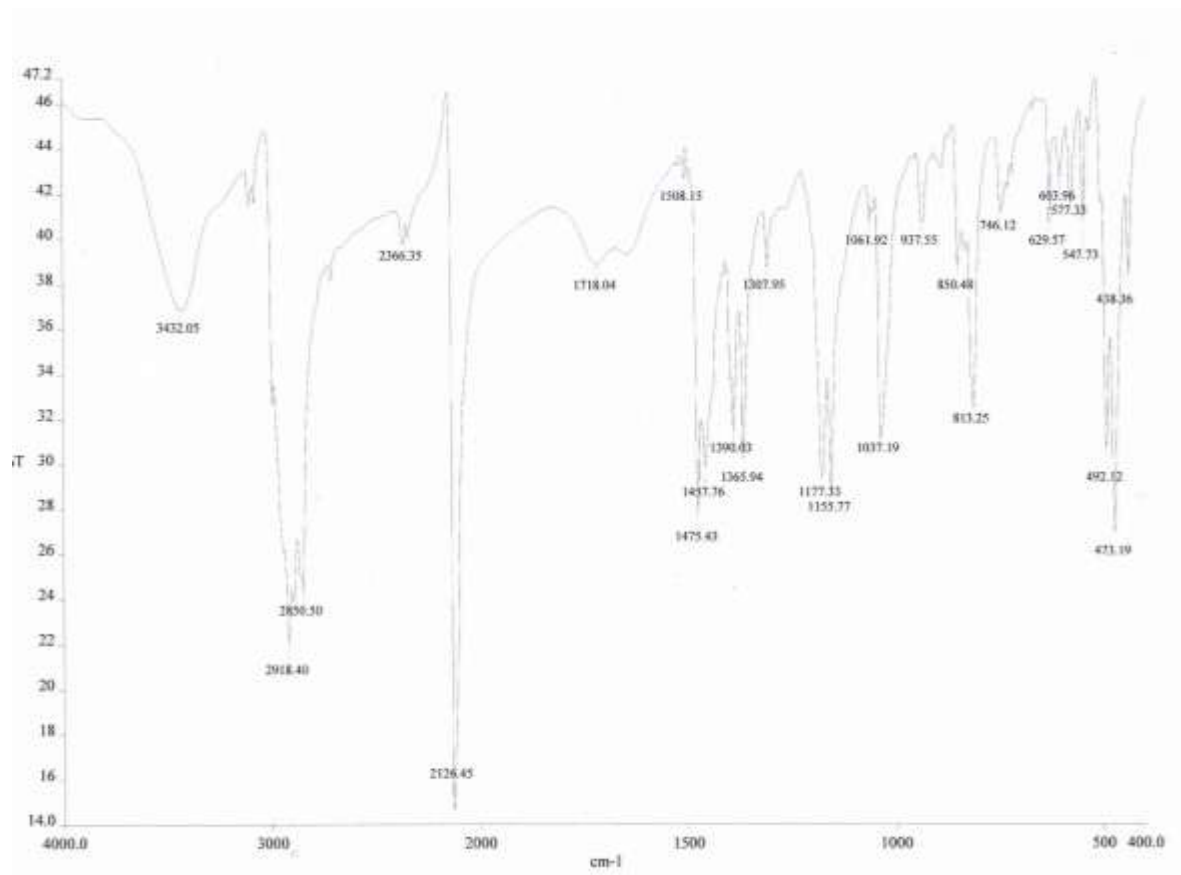
X-ray crystallographic study.

Intensity data sets for **1** were collected on Agilent Technologies (Oxford Diffraction) SUPER NOVA and oxford X-calibur S CCD area detector diffractometers using graphite monochromatized Mo- $K\alpha$ radiation at 150(2) and 293(2) K. The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard ϕ -omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2 .¹ The positions of all the atoms were obtained by direct methods. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances². In the structure of **1** at room temperature approximately 25% of the unit cell volume (1100 \AA^3) comprises a region of diffused, disordered solvent which could not be modeled as discrete atomic sites. The program PLATON/SQUEEZE³ was used to calculate the contribution from the solvent region to the diffraction. The Low temperature structure also contains shows similar problems and residual densities in the reported voids that could not be modeled. The SHELXL peaklist of the difference map does not show large residual peaks or holes. The voids were located around the 4_1 axes and most likely highly disordered and hence not picked up by the peak search algorithm in SHELXL. The program PLATON/SQUEEZE3 algorithm was used to recover the scattering contribution from the disordered solvent to the structure factors

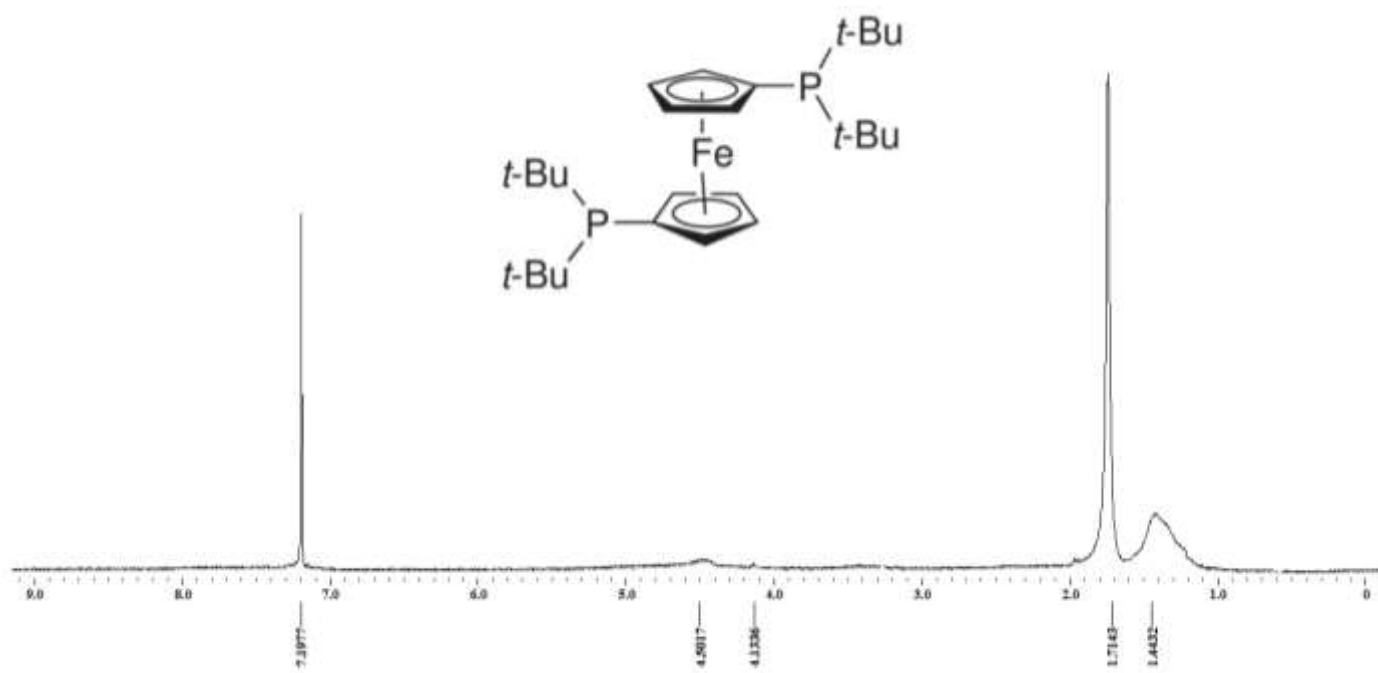
and continued refinement with the latest SHELXL2013. Hexane was used as a solvent for growing the crystals. The data were then corrected for disordered electron density leading to a set of solvent-free diffraction intensities. The modified data improved the R-factors (before SQUEEZE: $R1 = 0.0538$, $wR2 = 0.1733$; after SQUEEZE: $R1 = 0.0466$, $wR2 = 0.1012$).

Sonogashira Catalytic Reactions:

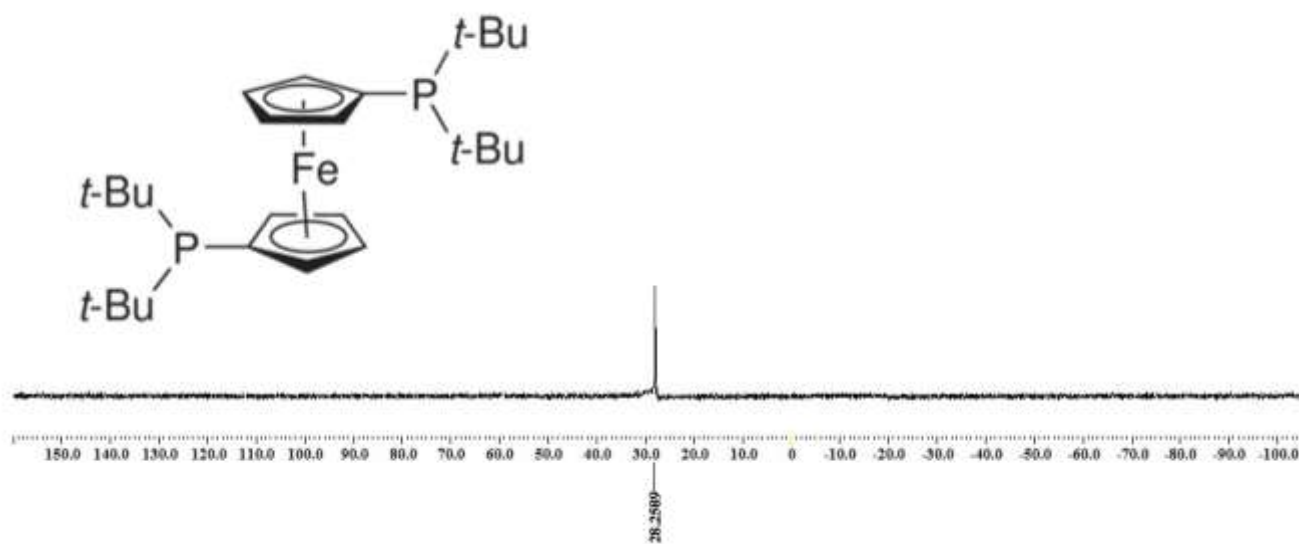
The reaction of aryl halides (3.38×10^{-3} mol, 1 equivalent), phenylacetylene (0.75 mL, 6.76×10^{-3} mol, 2 equivalent), and K_2CO_3 (0.935 g, 6.76×10^{-3} mol, 2 equivalent) with 0.001 equivalent of **1** (1.44 mg) and 0.002 equivalent $[PdCl(\eta^3-C_3H_5)]_2$ (0.73 mg), at $120^\circ C$ over 20 h in DMF (10 mL), under nitrogen, affords the coupling products. Pure products were obtained after addition of water, extraction with organic solvents, separation, drying, concentration, and chromatography on silica gel.



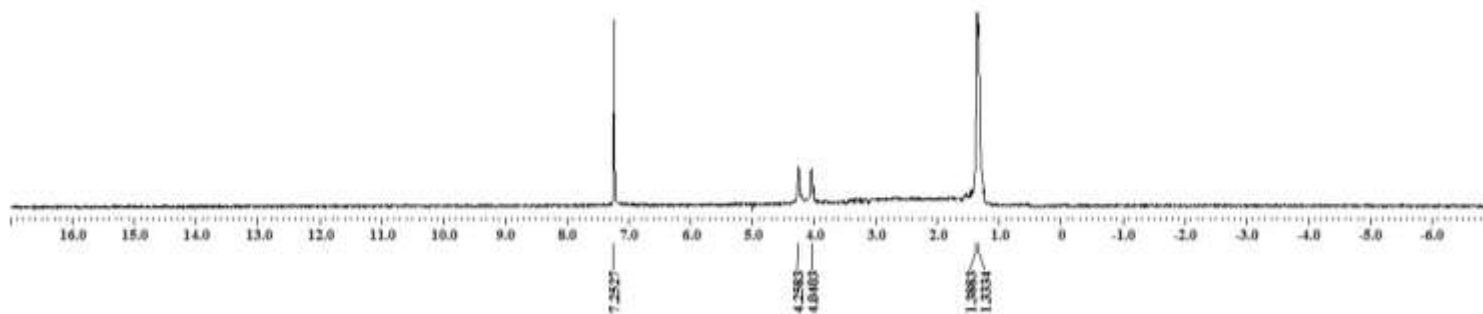
F-1. Infrared spectrum of **1**.



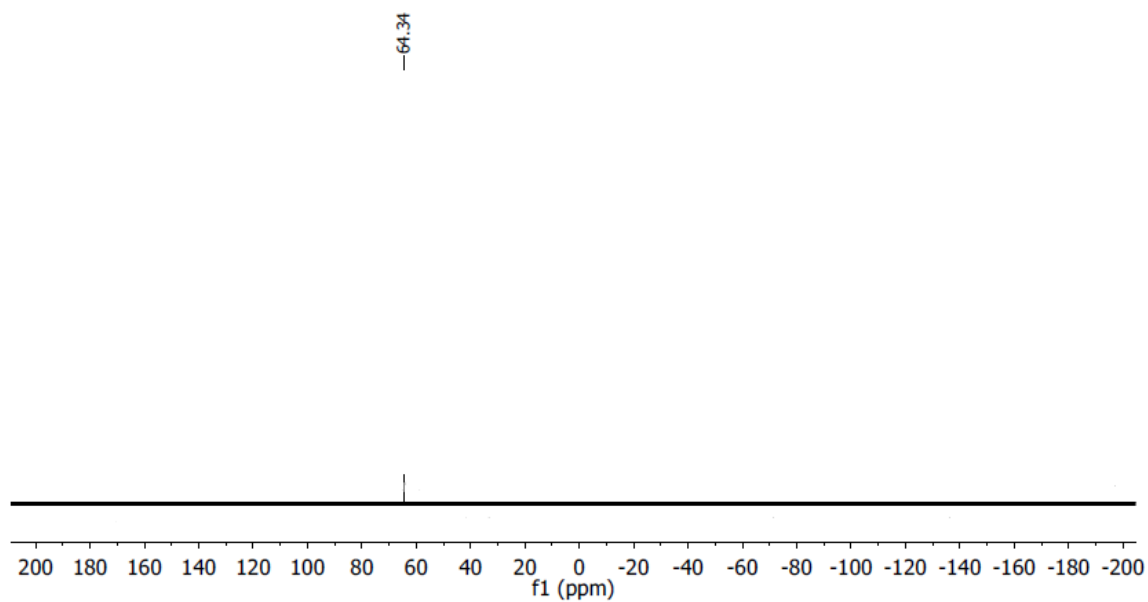
F-2. ¹H NMR spectrum of dtbpf in CDCl₃.



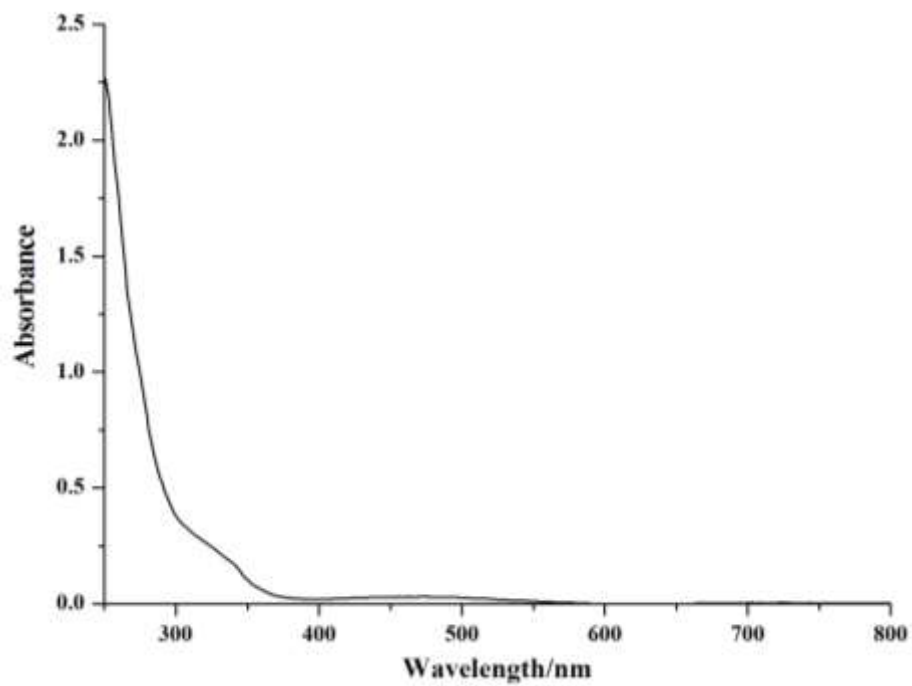
F-3. ^{31}P NMR spectrum of dtbpf in CDCl_3 .



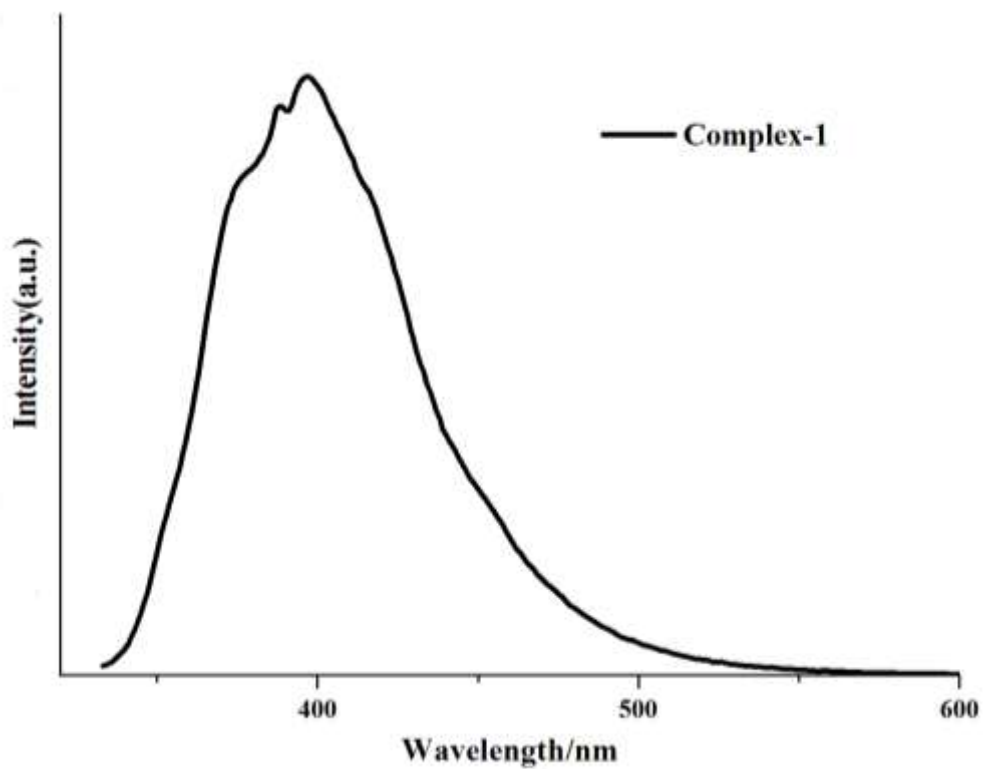
F-4. ^1H NMR spectrum of **1** in CDCl_3 .



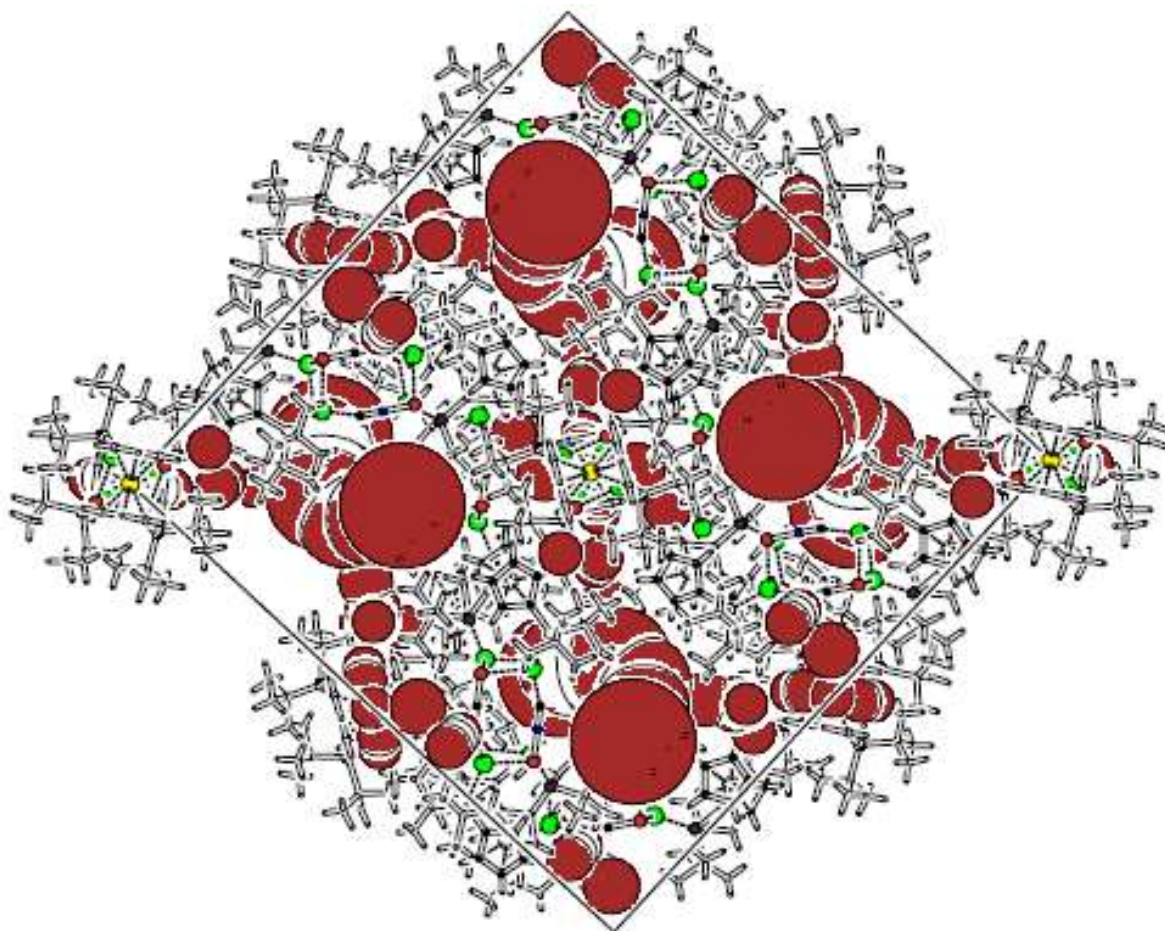
F-5. ^{31}P NMR spectrum of **1** in CDCl_3 .



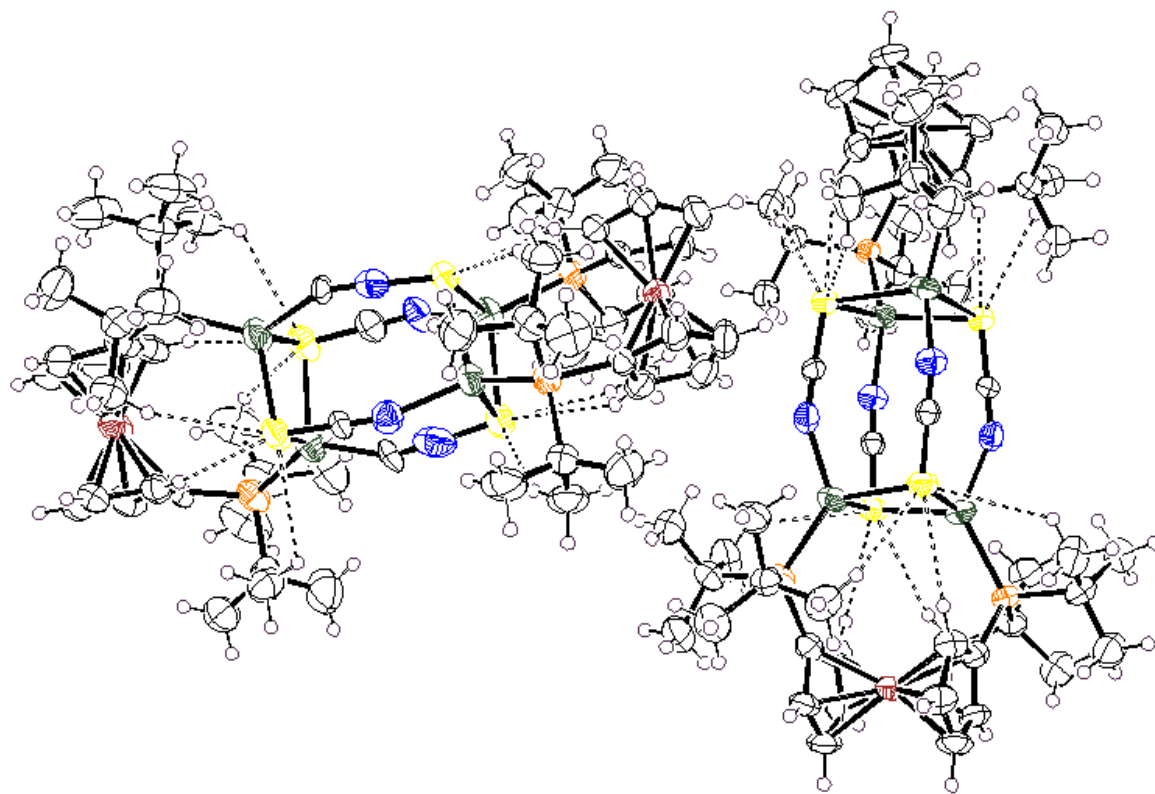
F-6. UV-Vis spectrum of **1** in CH₂Cl₂.



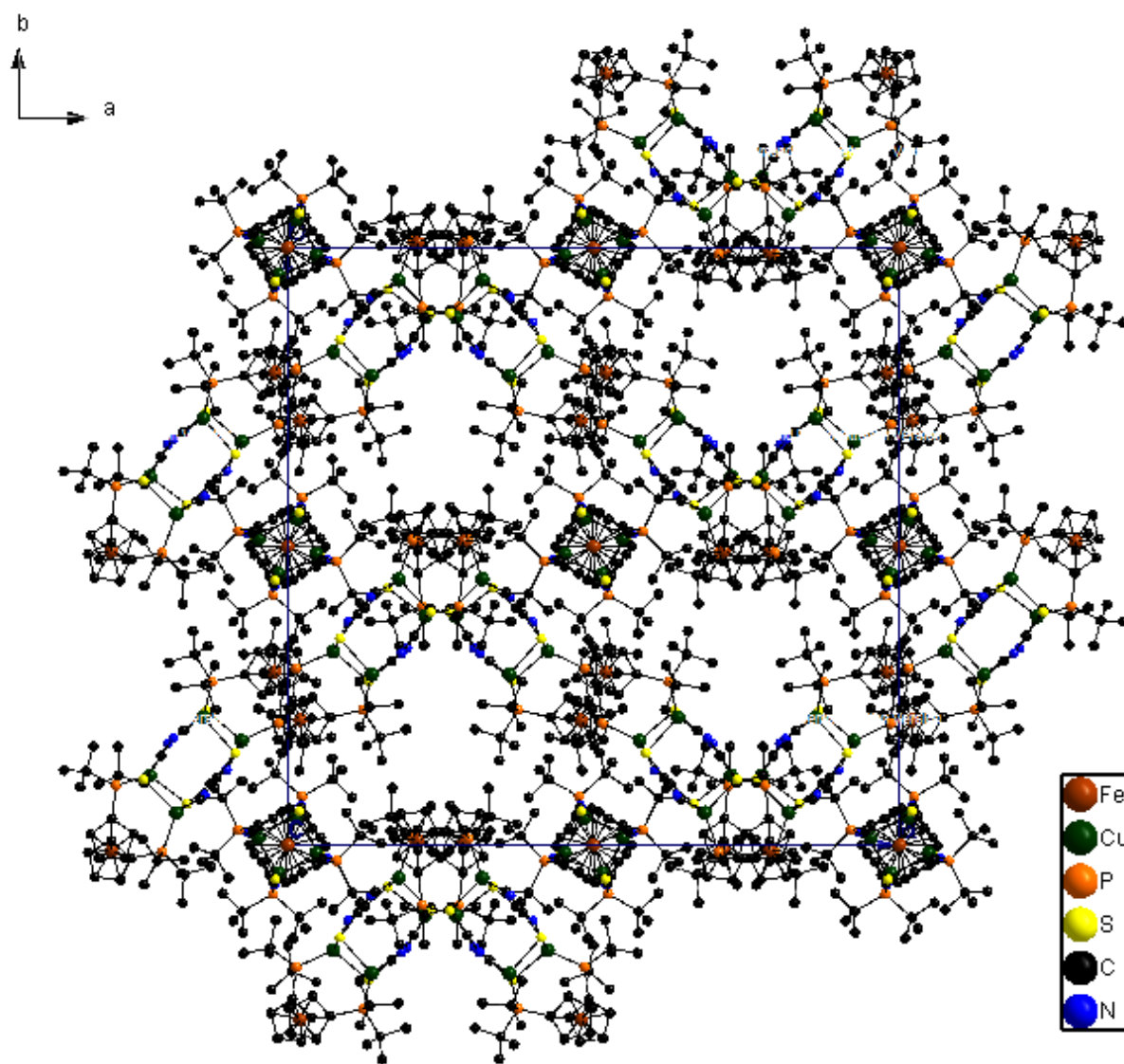
F-7. Emission spectrum of **1** in CH₂Cl₂ at 328 nm.



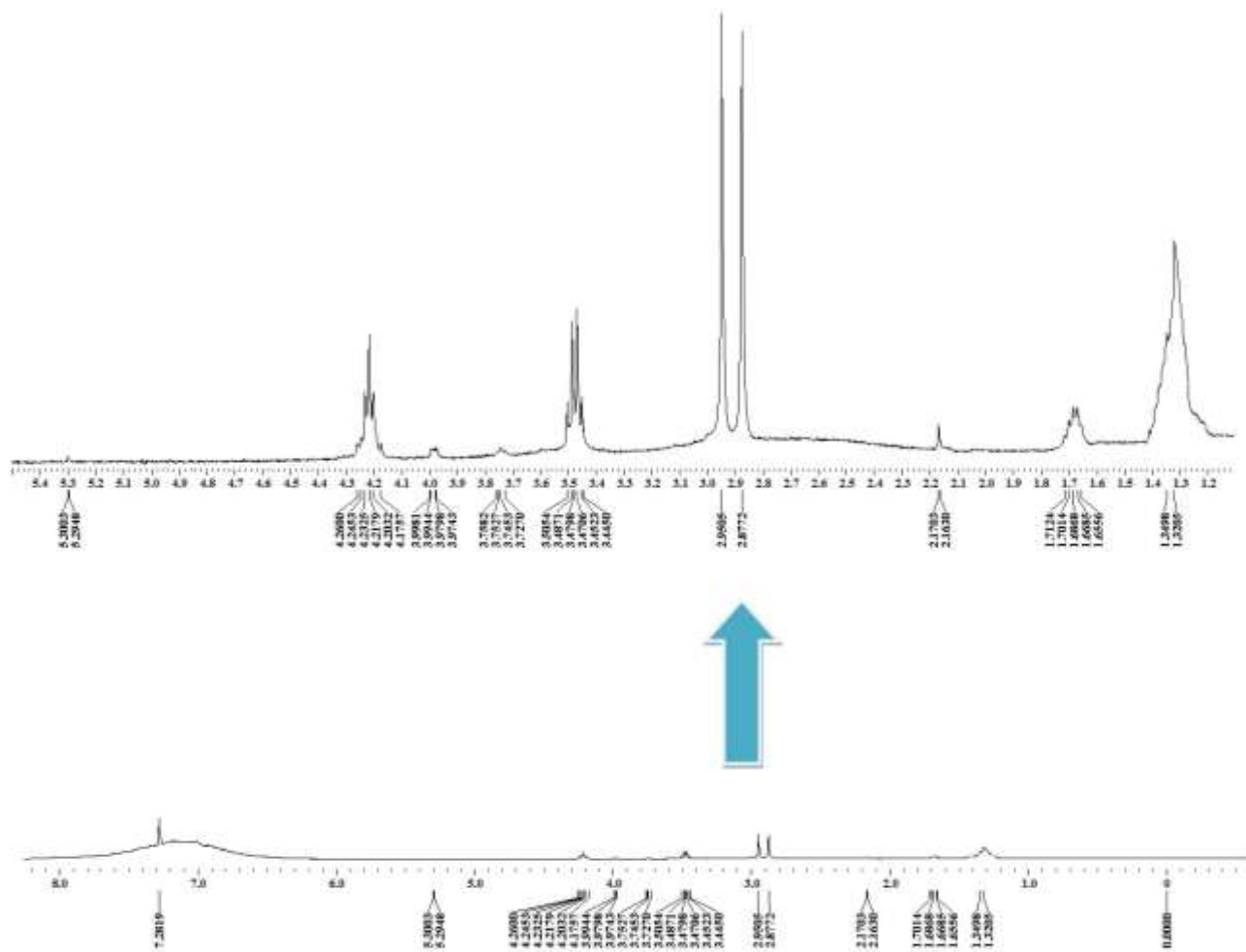
F-8. Self-assembly of **1** showing solvent accessible voids in the crystal lattice.



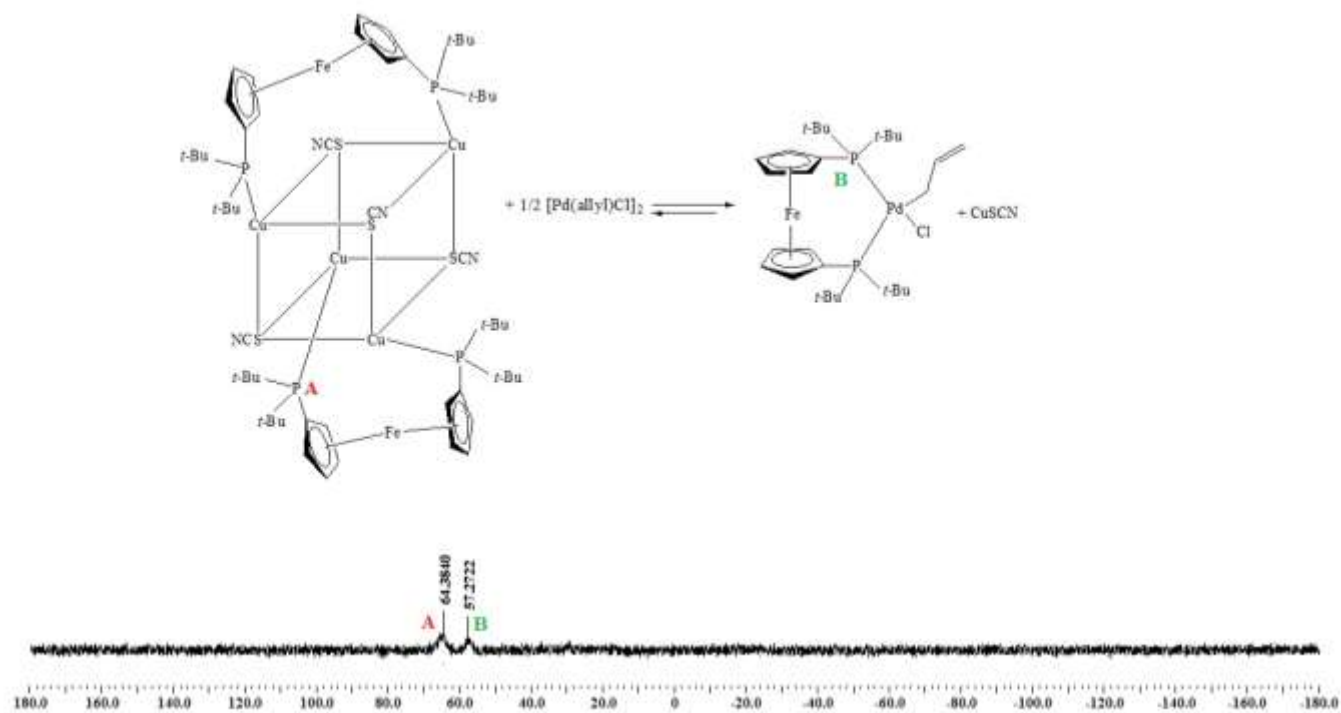
F-9. Ortep diagram of **1** showing C-H...S hydrogen bond interactions in the crystal lattice.



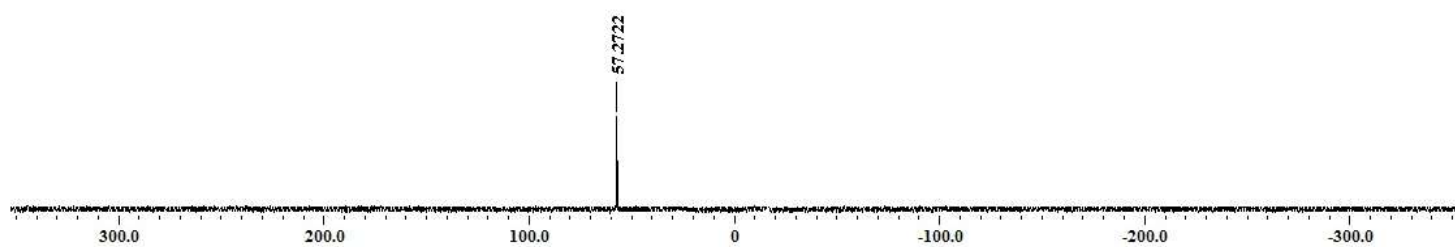
F-10. Crystal packing diagram of **1** in the (001) plane, viewed along the *c* axis.



F-11. ^1H NMR spectrum of a mixture of **1** with $[\text{Pd}(\text{allyl})\text{Cl}]_2$ in CDCl_3 after 2h at room temperature.

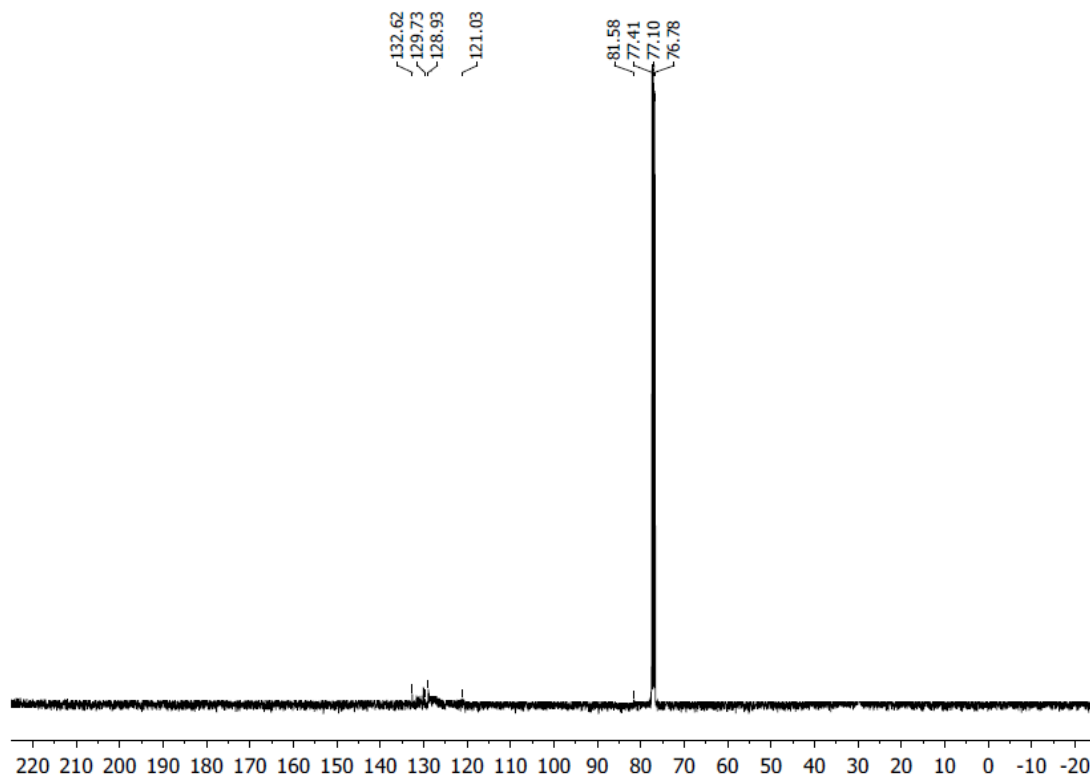


F-12. ³¹P NMR spectrum of a mixture of **1** with [Pd(allyl)Cl]₂ in CDCl₃ after 2h at room temperature.

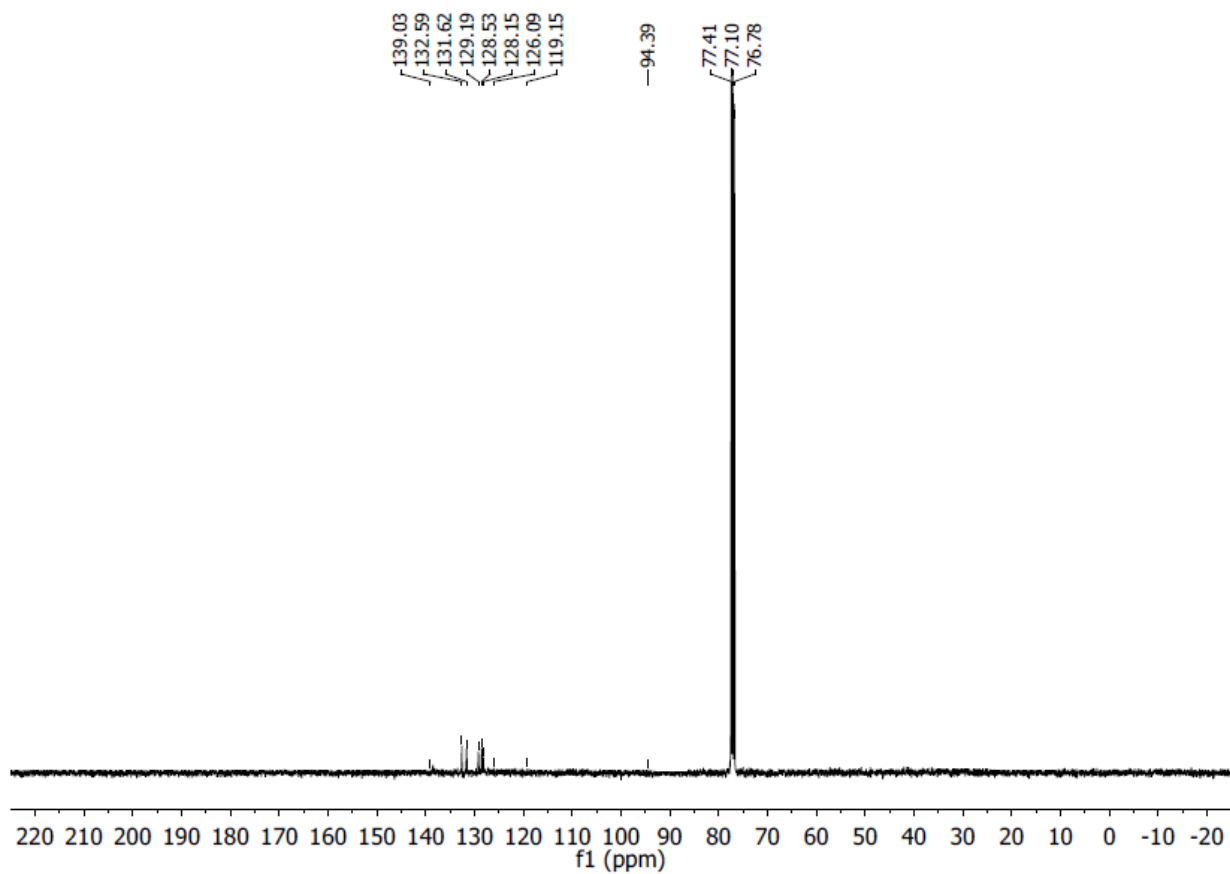


F-13. ^{31}P NMR spectrum of a mixture of **1** with $[\text{Pd}(\text{allyl})\text{Cl}]_2$ in CDCl_3 after 20h at room temperature: total transfer of the ligand from copper to palladium.

Diphenyl acetylene: ^1H NMR (400 MHz, CDCl_3) $\delta = 7.62$ (d, 4H, $J = 7.5$ Hz, ArH), $\delta = 7.50$ (m, 6H, ArH) ppm; ^{13}C (400 MHz, CDCl_3): $\delta = 132.62, 129.73, 128.93, 121.03, 81.58, 77.41, 77.10, 76.78$ ppm.⁴



4-methyl-diphenylacetylene: ^1H NMR (400 MHz, CDCl_3) δ = 2.62 (s, 3H, $-\text{CH}_3$), δ = 7.40 (m, 4H, ArH), δ = 7.85 (d, 2H, J = 6.4 Hz, ArH), δ = 7.64 (d, 2H, J = 7.5 Hz, ArH), 7.51 (m, 1H, ArH) ppm; ^{13}C (400 MHz, CDCl_3): δ = 139.03, 132.59, 131.62, 129.19, 128.53, 128.15, 126.09, 119.15, 94.39 ppm.⁴



References for Supporting Information:

- 1 G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.
- 2 (a) G.M. Sheldrick, SHELX-97; Programme for Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997; (b) PLATON, A.L. Spek, *Acta Cryst.* 1990, **46A**, C34.
- 3 P. Van der Sluis and A.L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, 46, 194.
- 4 A. Modak, J. Mondal, A. Bhaumik, *Green Chem.* 2012, **14**, 2840.