SUPPORTING INFORMATION

"Hemi-labile" Palladium-Carbon bond: characterization and its implication in catalysis

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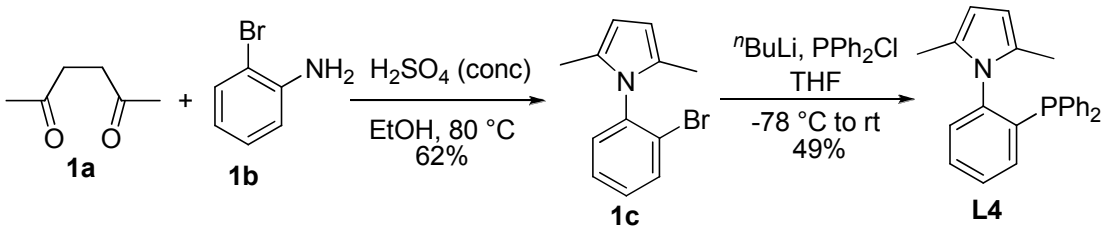
1.1 Experimental Section.

General Information. Unless otherwise noted all starting materials were obtained from commercial suppliers. Organic solvents were dried and distilled as described elsewhere. All reactions were carried out in an oven-dried flask under argon atmosphere. Column chromatography was performed with silica gel 230 - 400 mesh. All ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ solution except complex **VI** which was recorded in CD_2Cl_2 and reported in ppm (δ). ^{1}H NMR spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{31}P NMR spectra were referenced to PPh_3 (δ -4.8 ppm) externally. High resolution mass spectra (HRMS) were obtained on a FT-ICR mass spectrometer (ESIMS – Micromass Q-TOF micro). CHN analysis was performed with CHNS analyzer (2400 series II). X-ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation. Data collection, data reduction, structure solution/refinement were carried out using the software package of BRUKER APEX II. The single crystal structures of Pd-**L4** complex **(VI)** were solved by direct and Patterson method respectively and refined in a routine manner.

Scheme 1. Synthesis of ligand L4.



1-(2-Bromophenyl)-2,5-dimethy-*1H*-pyrrole (1c). A solution of 2,5-hexanedione (**1a**) (456.5 mg, 4 mmol) and 2-bromo aniline (**1b**) (825.6 mg, 4.8 mmol) in ethanol (24 mL) was refluxed for 15 h in the presence of catalytic amount of conc. H_2SO_4. Solvent was removed under reduced pressure. It was then extracted with dichloromethane (2×25 mL). The combined organic layer was washed subsequently with water and brine and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (silica gel 230-400 mesh, 1% ethyl acetate/petroleum ether) afforded **1c** as yellow liquid (662 mg, 62%); R_f (2.5% ethyl acetate/petroleum ether) 0.41; IR λ_{max} (neat, cm^{-1}) 3101, 3058, 2976, 2918, 2887, 1570, 1484, 1436, 1400, 1384, 1225, 1068, 1025; ^{1}H

NMR ($CDCl_3$, 400 MHz, ppm). δ 7.75 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.36 – 7.32 (m, 2H), 5.97 (s, 2H), 2.0 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm). δ 138.7, 133.4, 130.7, 129.9, 128.6, 128.3, 124.6, 105.7, 12.7; HRMS (ESI) *m/z* calculated for $C_{12}H_{13}BrN$ $[M+H]^+$ 250.0231, found 250.0224.

1-(2-(Diphenylphosphino)phenyl)-2,5-dimethyl-*1H*-pyrrole (L4). To a stirred solution of 1-(2-bromophenyl)-2,5-dimethy-*1H*-pyrrole (**1c**) (250 mg, 1 mmol) in THF (4 mL) under argon atmosphere was added *n*-BuLi (0.8 mL, 1.2 mmol, 1.5 M in THF) drop wise at -78 °C. The mixture was slowly warmed to rt and then stirred for further ½ h at rt. After the mixture was cooled to -78°C, chloro diphenylphosphine (0.2 mL, 1.2 mmol) was added and stirring was continued for 10 h. It was then quenched with saturated NH_4Cl solution at 0 °C and extracted with diethyl ether (2×20 mL). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (Silica gel 230-400 mesh, 0.5% ethyl acetate /petroleum ether) afforded ligand (**L4**) as white solid (174 mg, 49 %). R_f (2.5% ethyl acetate/petroleum ether) 0.33; mp 83 °C – 85 °C; IR λ_{max} (KBr, cm^{-1}) 3054, 2979, 2917, 2884, 1585, 1568, 1521, 1498, 1472, 1434, 1395, 1318, 1216, 1092, 1037; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm). δ 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21 – 7.20 (m, 6H), 7.16 – 7.11 (m, 6H), 5.79 (s, 2H), 1.66 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm). δ 143.7 (d, *J* = 27.5 Hz), 139.4 (d, *J* = 13.8 Hz), 136.4 (d, *J* = 11.2 Hz), 134.9, 134.0 (d, *J* = 20 Hz), 130.1, 129.5, 129.0, 128.8, 128.6, 128.5 (d, *J* = 7.5 Hz), 105.6, 12.9; ^{31}P NMR ($CDCl_3$, 202.44 MHz, ppm). δ -16.70 (s); HRMS (ESI) *m/z* calculated for $C_{24}H_{23}NP$ $[M+H]^+$ 356.1568, found 356.1565.

Procedure for synthesis of Pd-L4 complex (VI). A solution of **L4** (355.4 mg, 1 mmol) and $Pd(CH_3CN)_2Cl_2$ (224.5 mg, 1 mmol) in dichloromethane (5 mL) was stirred for 20 min at rt. The color of the solution was changed into red. The solvent was removed under reduced pressure. The residue was rinsed with hexane and dried in vacuo, affording **VI** as red powder (505 mg, 95%), which was crystallized from dichloromethane/ light petroleum; mp>200 °C; ^{1}H NMR (CD_2Cl_2, 500 MHz, ppm) δ 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 8H), 7.40 – 7.35 (m, 4H) 7.24 (br s, 1H), 7.04 (t, *J* = 8.5 Hz, 1H), 1.46 (s, 6H); ^{13}C NMR (CD_2Cl_2, 125 MHz, ppm). δ 140.0 (d, *J* = 11.2 Hz), 134.7 (d, *J* = 12.5 Hz), 134.0, 133.1, 132.8, 132.4,132.1, 130.8 (d, *J* = 6.25 Hz), 129.0 (d, *J* = 11.2 Hz), 127.8 (d, *J* = 5 Hz), 126.6, 126.1,

15.3; ^{31}P NMR (CD_2Cl_2, 202.44 MHz , ppm). δ 26.75 (s); Anal. calcd for $C_{24}H_{22}Cl_2NPPd$ C, 54.11; H, 4.16; N, 2.63; found C, 53.88; H. 4.21; N, 2.61. After repeated attempts, a crystal suitable for diffraction studies was grown from dichloromethane/petroleum ether.

1.2 X-ray crystal structure of Pd-L4 complex (VI).

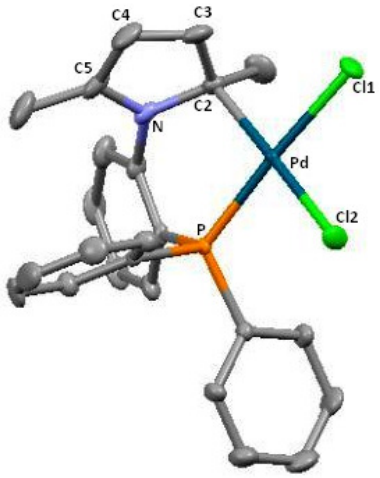


Figure S1. ORTEP diagram for the molecular complex (**VI**) at 30% probability level. For clarity, hydrogen atoms are omitted. Selected bond lengths (Å): Pd-C2, 2.169(4); C2-C3, 1.434(6); C3-C4, 1.353(7); C4-C5, 1.386(6); C5-N, 1.344(5); N-C2, 1.437(5); Pd-P, 2.2373(9); Pd-Cl1, 2.3626(10); Pd-Cl2, 2.3125(10).

Crystal data of Pd–L4 complex (VI) : $C_{24}H_{22}Cl_2NPPd$, M = 532.70, monoclinic, P2(1)/n, a = 14.6160(17) Å, b = 10.7894(13) Å, c = 14.6807(18) Å, ß = 102.959(3), V = 2256.2(5) $Å^3$, T = 293(2) K, Z = 4, F (000) = 1072.0, λ (Mo–Kα) = 0.71073 Å, μ = 1.141 mm^{-1}, $2\theta_{max}$ = 53.42°, 29418 reflections measured, 4761 observed (I>2σ (I)), 264 parameters, R_{int} = 0.0423, R_1 = 0.0355, wR_2 = 0.1152 [(I>2σ (I)], R_1 = 0.0490; wR_2 = 0.1298 (all data) with GOF = 0.912.

1.3 Details of computations.

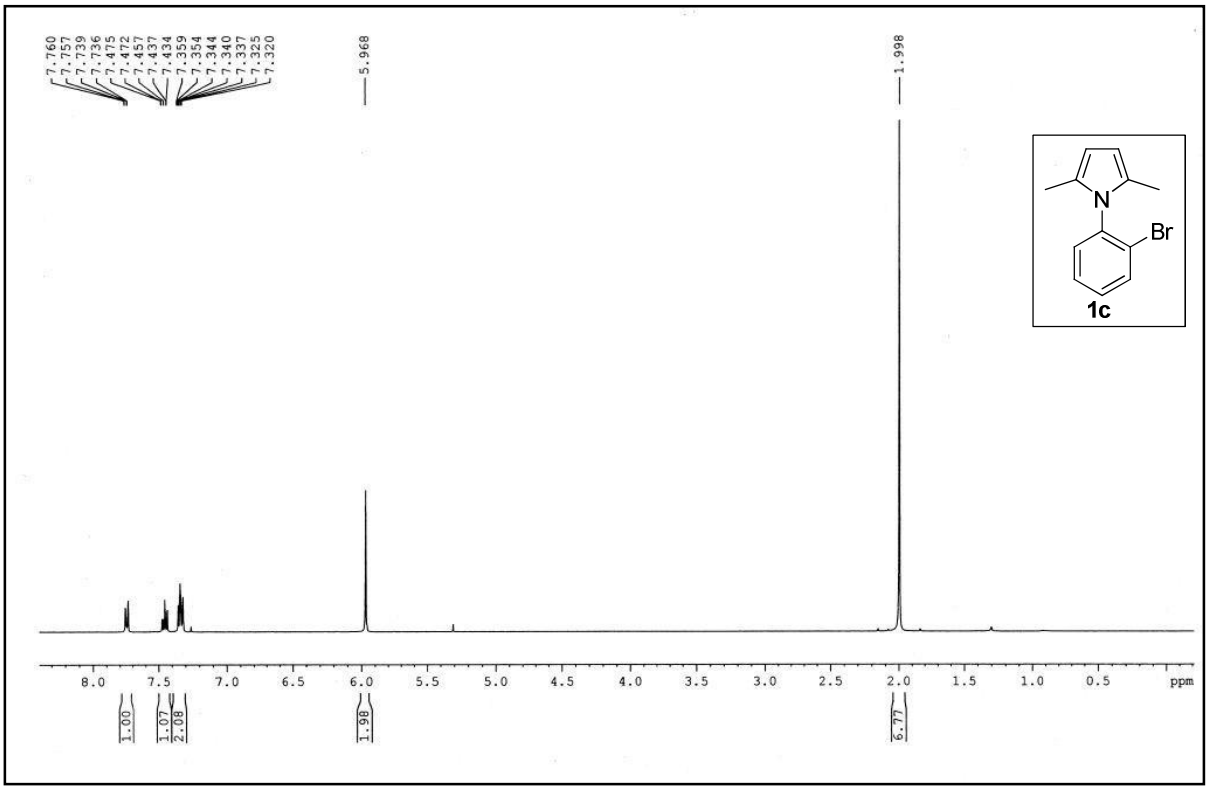
Geometry optimization for intermediates and transition states was performed at the density functional level of theory (DFT) using the B3LYP hybrid functional, with effective core potential LANL2 along with LANL2DZ on the Palladium center and 6-31+G** basis function on all the other atoms in gas phase with Gaussian09 quantum chemistry suite.[i] Single point calculations were done on this optimized geometry with 6-311++G** basis set to generate wave function for AIM computation. The electron density, ρ, and its associated Laplacian, $\nabla^2\rho$ were calculated based on AIM theory as implemented in AIM 2000 program package.[ii]

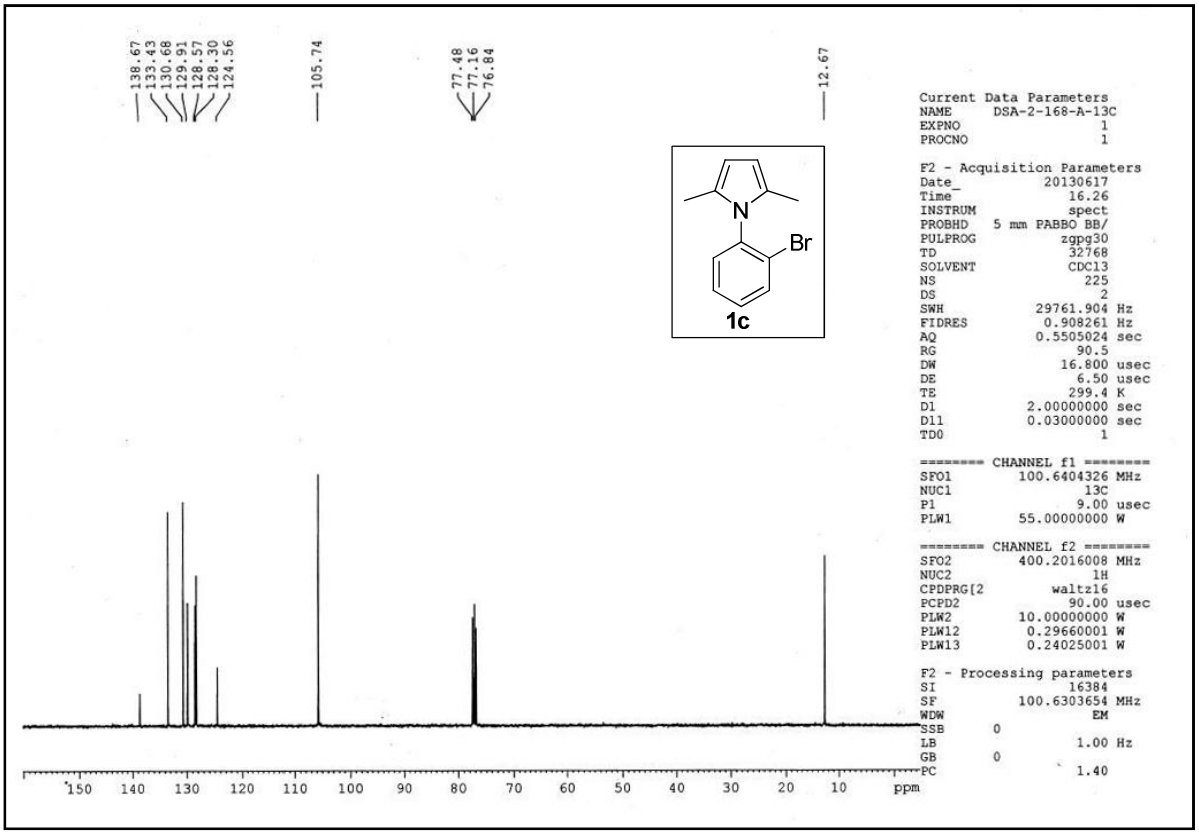
To obtain the correct barrier, we have done single point solvent phase calculation on gas phase optimized geometries for dichloromethane solvent using CPCM model with effective core potential LANL2 along with LANL2DZ on the Pd atom and 6-311++G(d, p) basis function on all other atom by B3LYP functional. For obtaining solvent phase free energy, entropies are obtained by scaling of gas phase entropies calculated in ideal gas phase model to account suppression of entropies in solution phase.

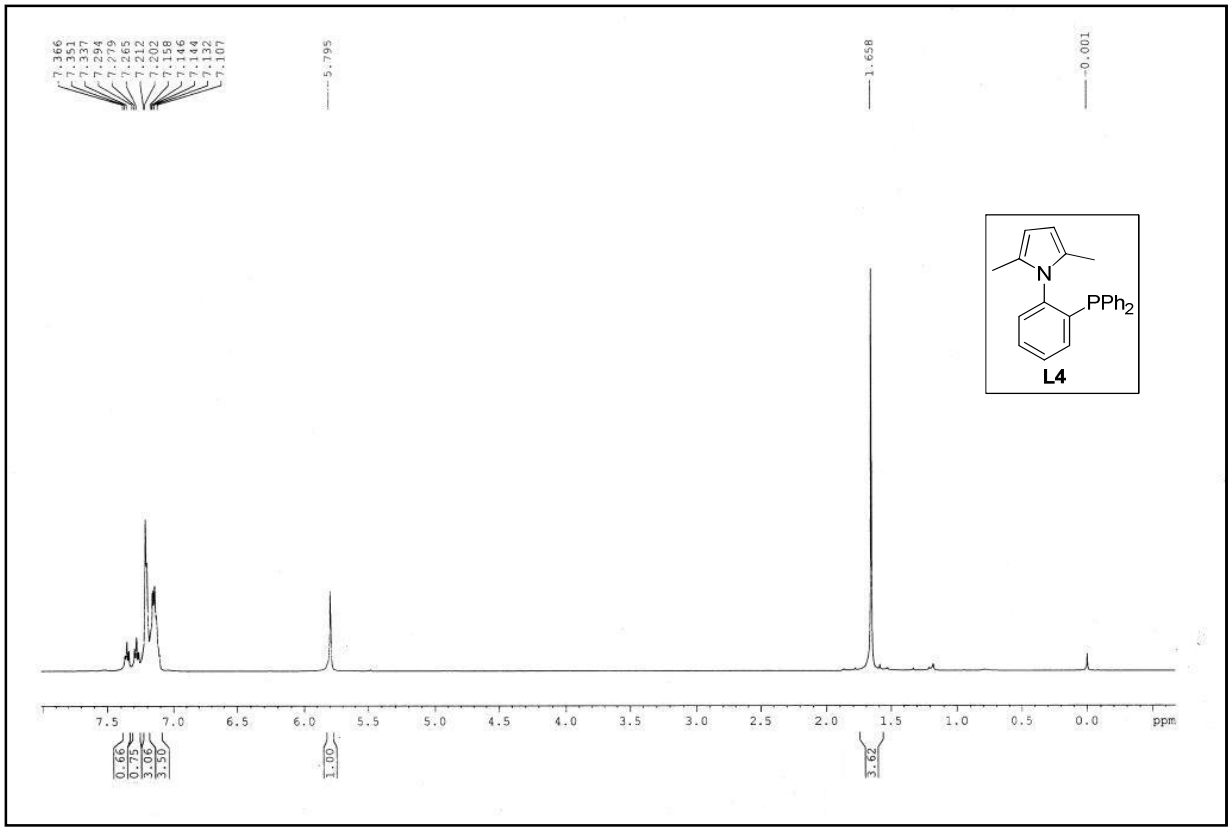
i) *Gaussian*-09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

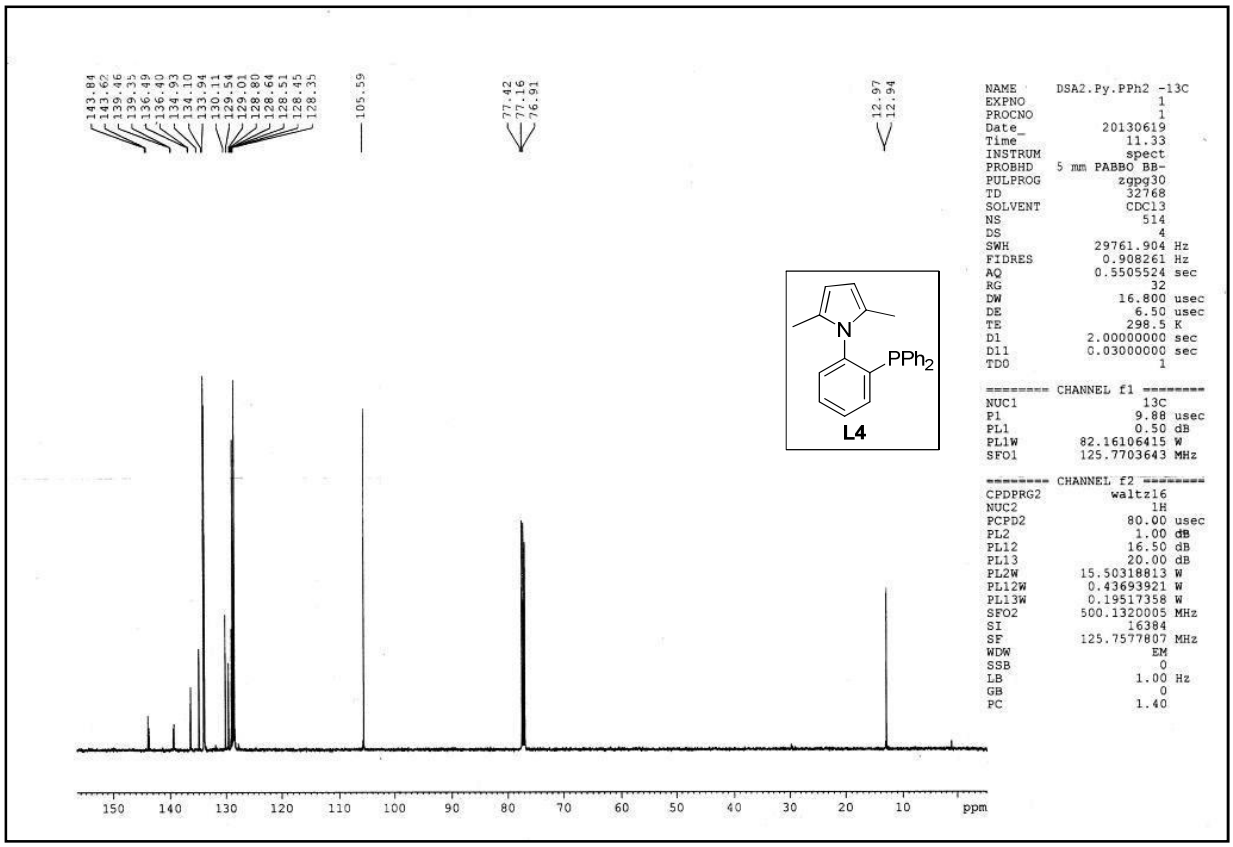
ii) Bader, R.F.W.; *Atoms in Molecules: A Quantum Theory*; Clarendon Press, Oxford, 1990; b) Biegler-König, F; Schönbohm, J.; Bayles, D. *J. Comp. Chem.* **2001**, *22*, 545.

1.4 Spectra of L4 and VI at room temperature.







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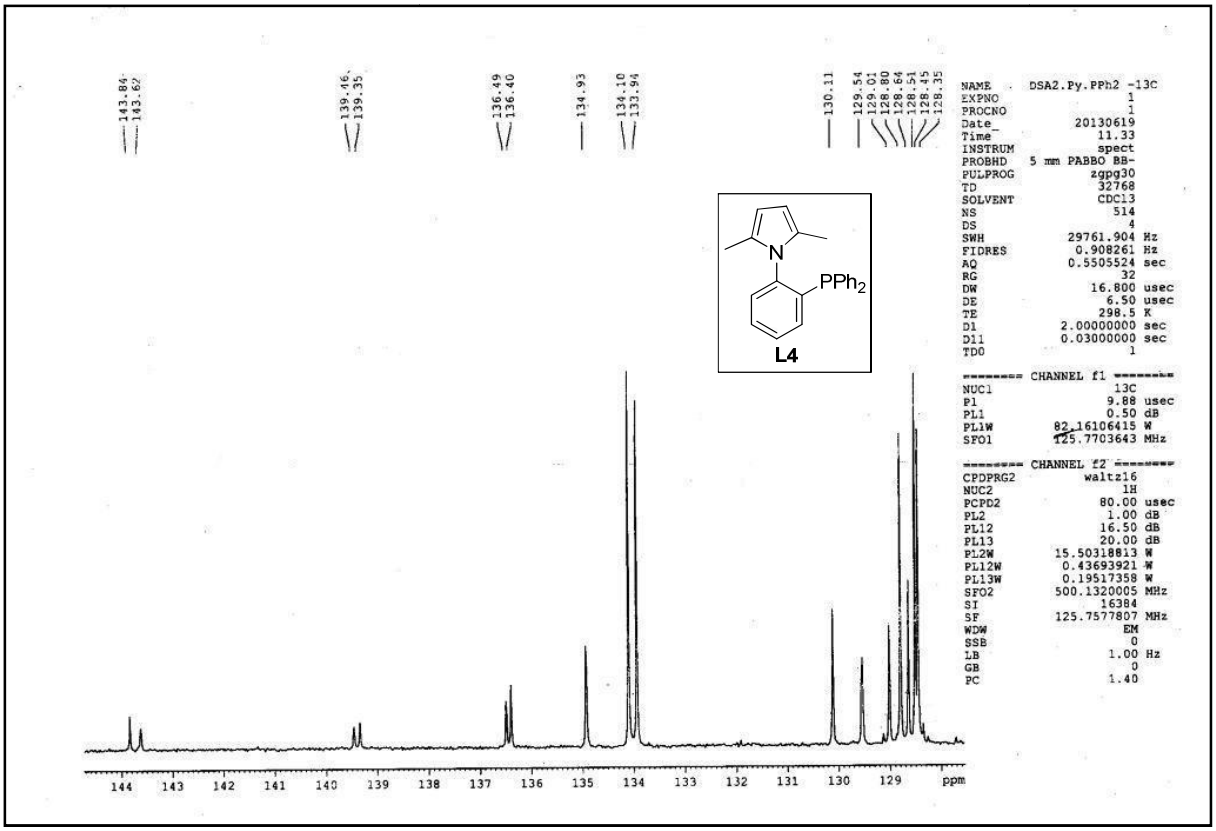
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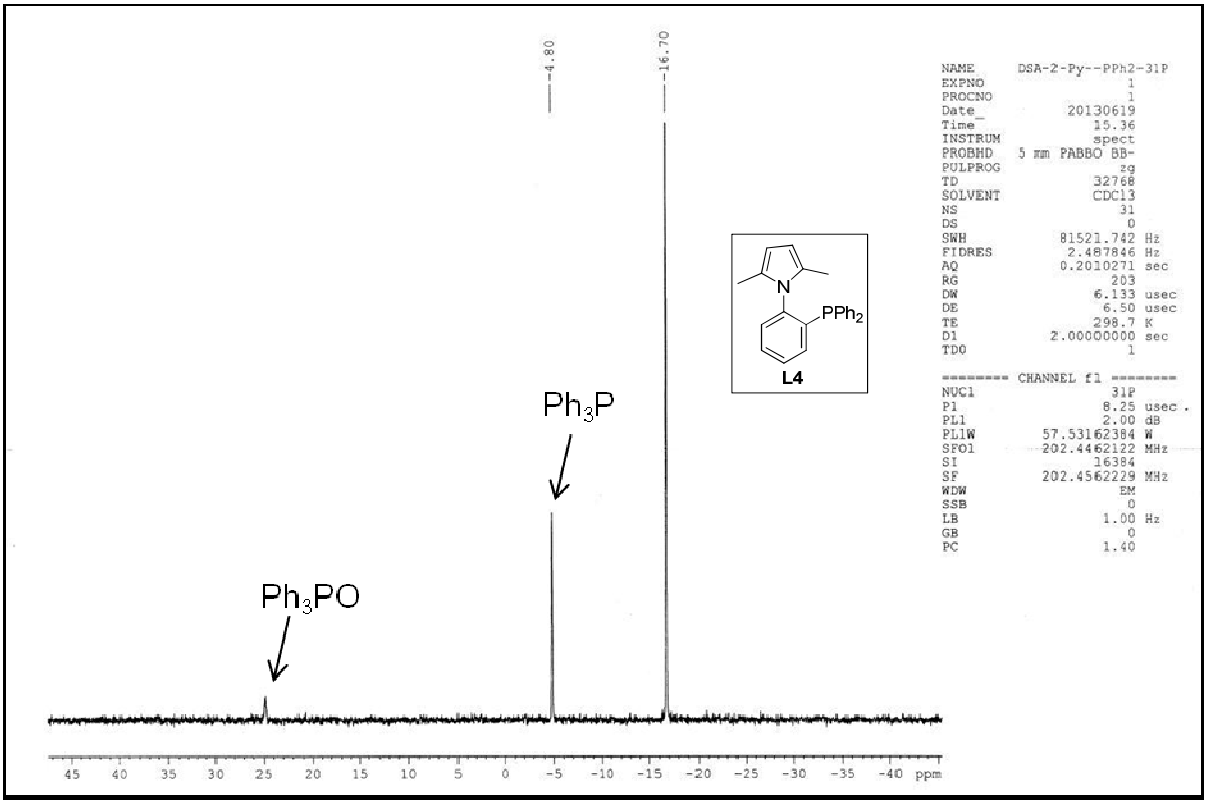
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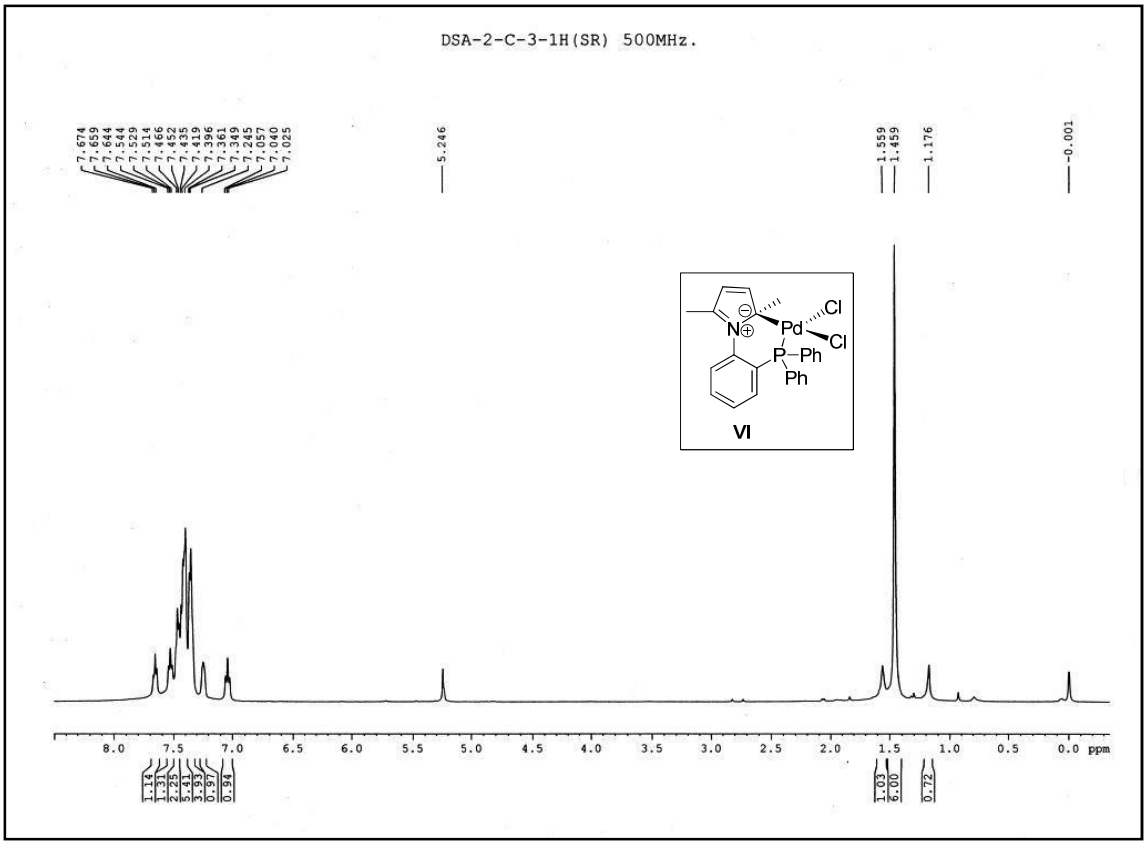

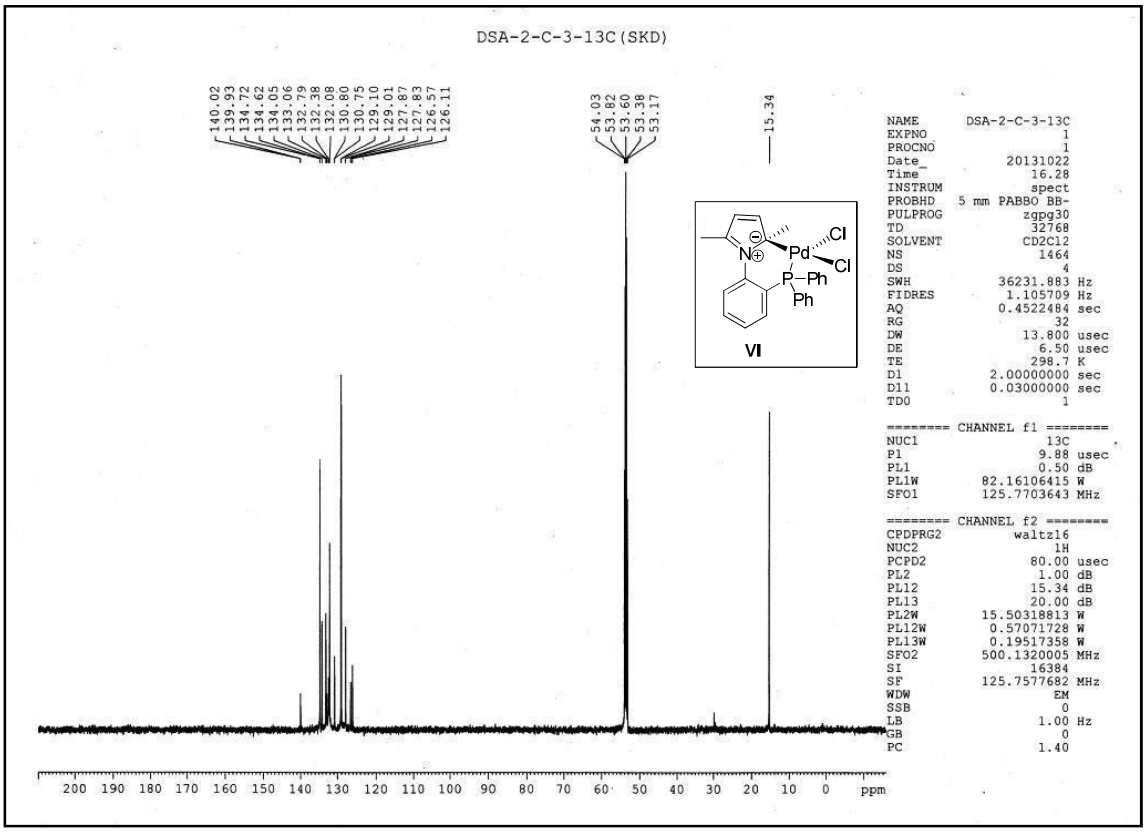

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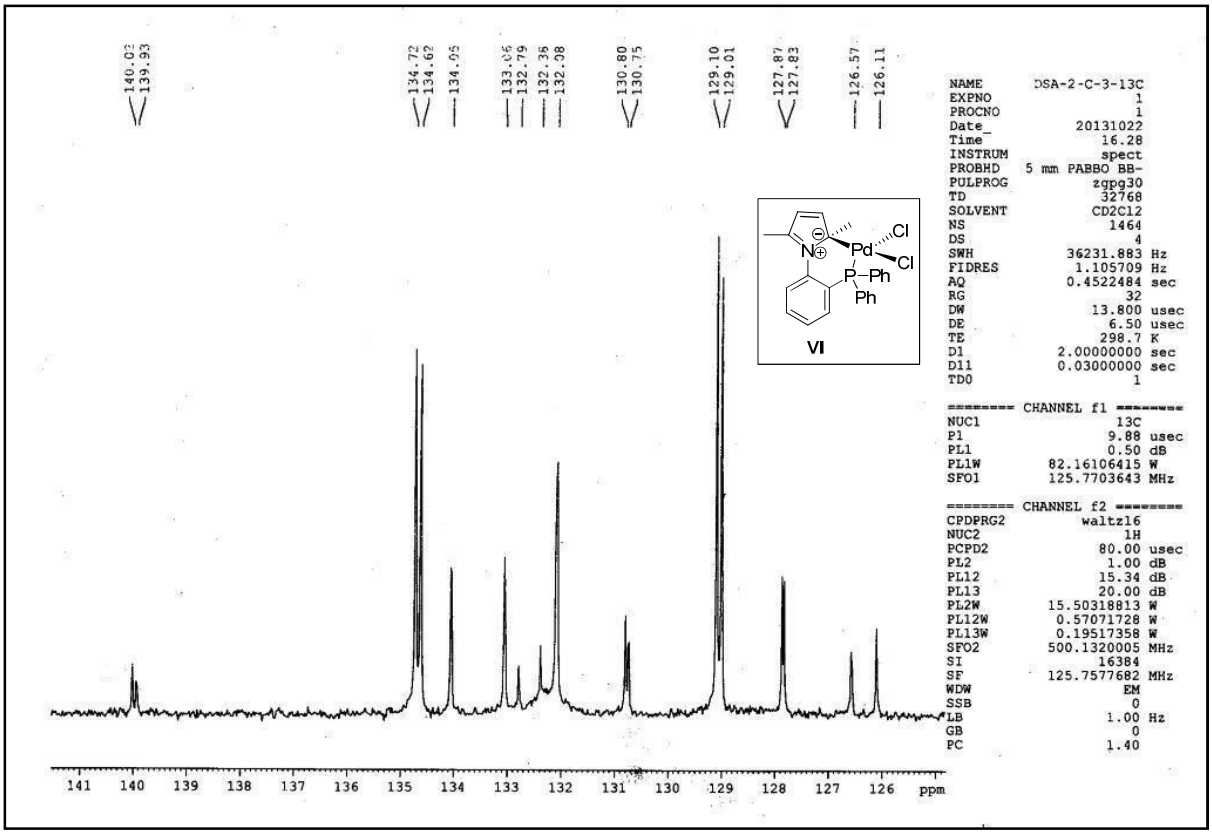
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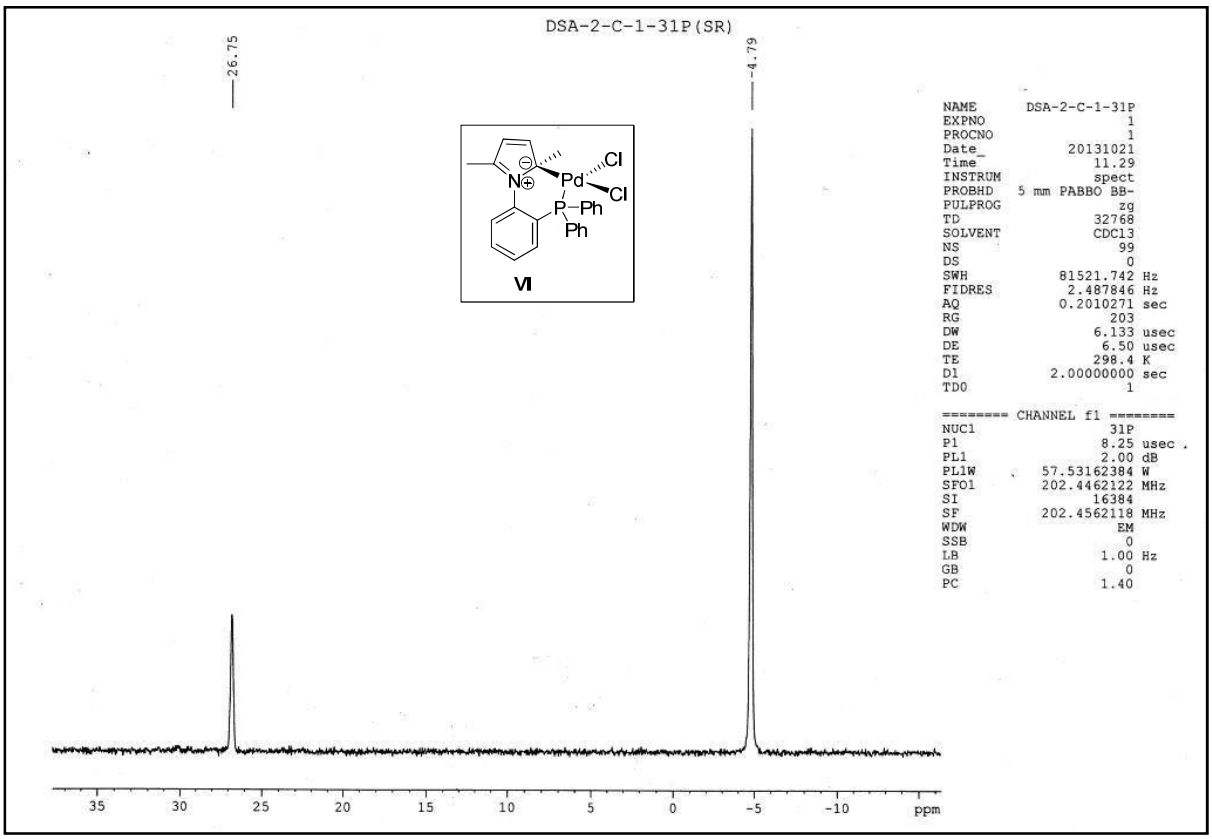
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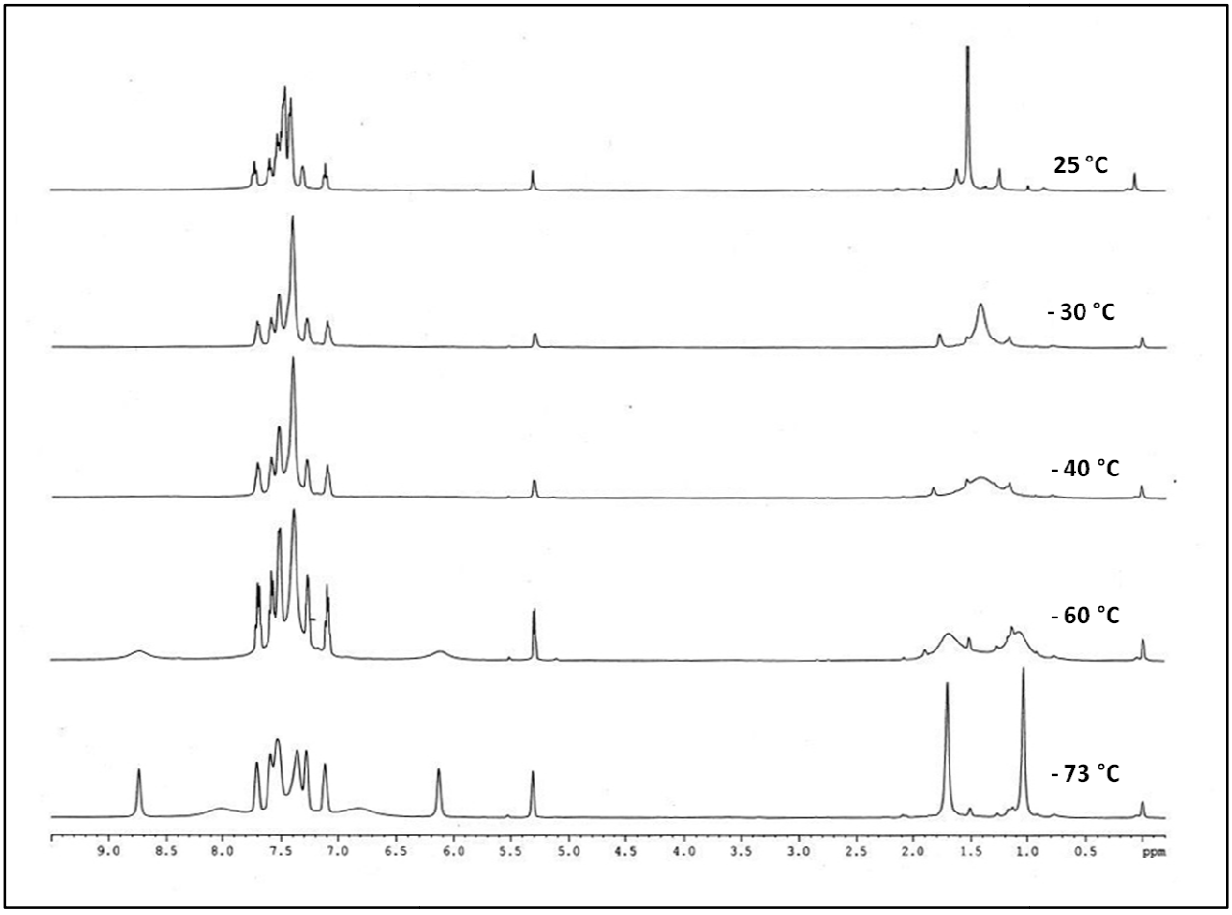
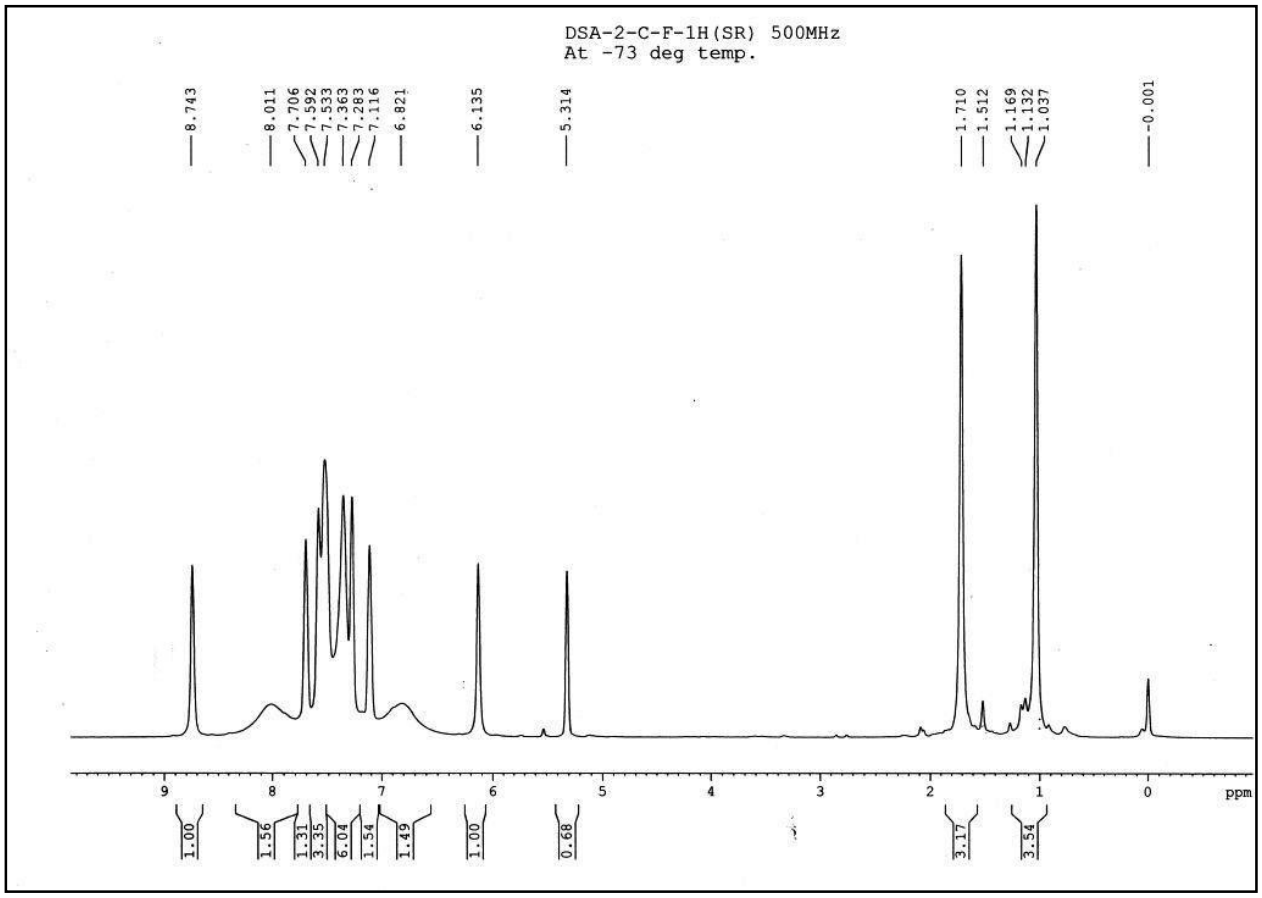
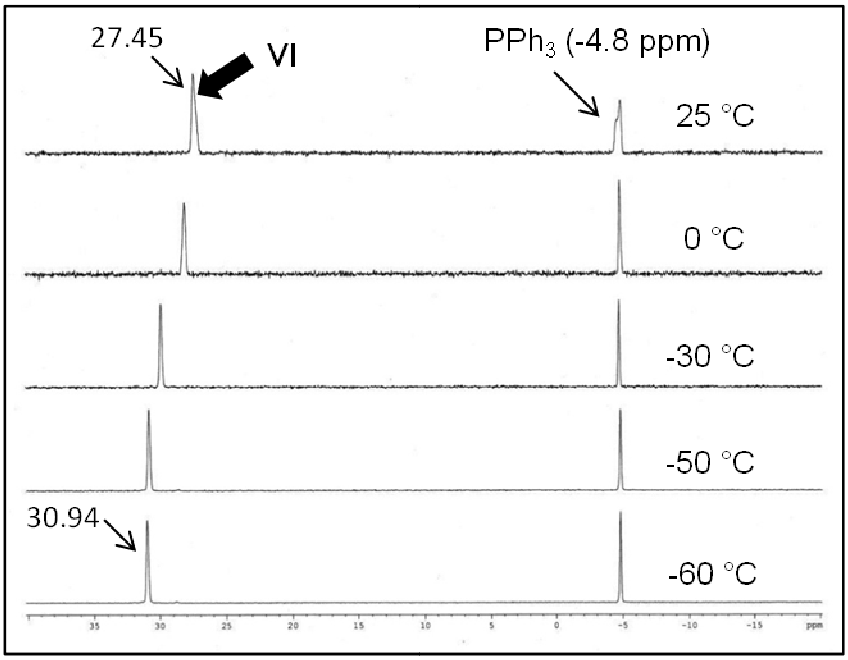
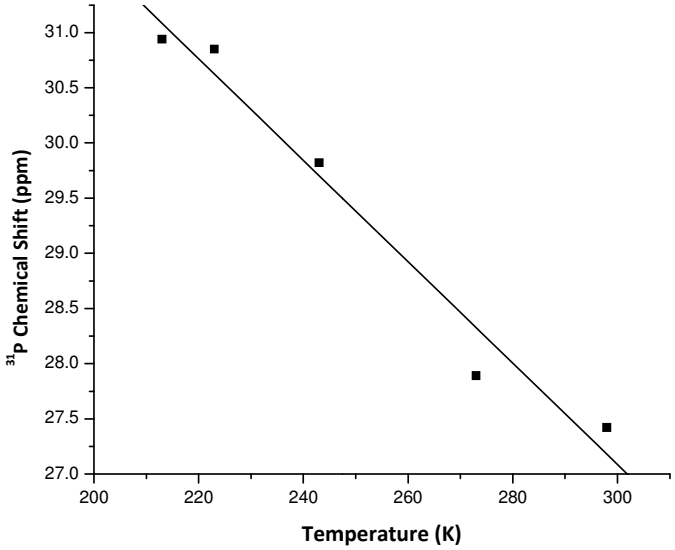
1.5 ^{1}H NMR spectra of the complex VI at variable temperature.



1.6 ^{1}H NMR spectra of the complex VI at -73 °C.



1.7 ^{31}P NMR spectra of the complex VI at variable temperature.



1.8 Plot of ^{31}P NMR of complex VI vs temperature (T °K).