Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Novel approach to benzo-fused 1,2-azaphospholene involving a Pd(II)-assisted tandem P—C bond cleavage and P—N bond formation reaction

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I. General information and synthesis of 1-6

General procedures. All the air-sensitive compounds were handled and stored in MBRAUN Glove box. All manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were dried using conventional methods and distilled prior to use. $[Pd(COD)Cl_2]$,[1] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$,[2] bromo-*N*-(2-bromophenyl)benzamide[3] and LiHMDS[4] were prepared according to the published procedures. $AgSbF_6$ was purchased from Aldrich Chemicals, and used without purification, whereas other reagents were obtained from commercial sources and used after purification.

Instrumentation. NMR spectra were recorded on Bruker FT spectrometers (Avance-400 or 500) MHz at ambient probe temperatures. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were acquired using broad band decoupling method. The spectra were recorded in $CDCl_3$ solutions with TMS as an internal standard; chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are reported in ppm downfield from TMS. The chemical shifts of $^{31}P\{^1H\}$ NMR spectra are referred to 85% H_3PO_4 as an external standard. Positive values indicate downfield shifts. Mass spectra were recorded using Bruker Maxis Impact LC-q-TOF Mass Spectrometer. Infrared spectra were recorded on a PerkinElmer *Spectrum One* FT-IR Spectrometer (Model No. 73465) in KBr disk. The microanalyses were performed using a Thermo Finnigan FLASH EA 1112 Series CHNS Analyzer. The melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected.

Crystal structure determination of compounds 2-4 and 6. A crystal of each of the compounds **2-4** and **6** in the present work suitable for single crystal X-ray diffraction studies was mounted in a cryoloop with a drop of paratone oil, and placed in the cold nitrogen stream of the kryoflex attachment of the Rigaku Saturn724 diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo-Kα radiation (λα = 0.71073 Å). The strategy for

the data collection was evaluated by using the CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011) software. The data were collected by the standard 'phi-omega scan' techniques and were scaled and reduced using CrysAlisPro 1.171.40.15 (Rigaku OD, 2018) software. The structures were solved using Olex2[5] with the ShelXT[6] structure solution program using intrinsic phasing and refined with the ShelXL[7] refinement package using least-square minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions, with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. The details of X-ray structural determinations are given in Table S2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2046842 (compound **2**), 2046843 (compound **3**), 2046844 (compound **4**), 2046845 (compound **6**).

Computational Methods

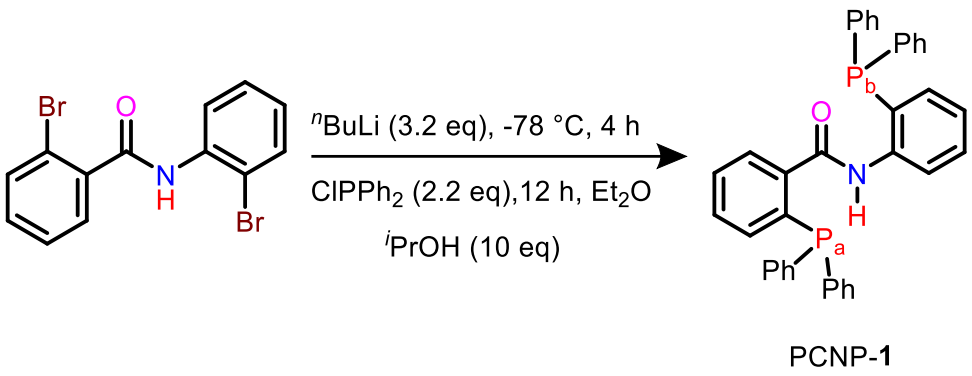
The Gaussian 09 program was employed for all the calculations in this study.[8] All the stationary points such as reactants, intermediates, and transition states were optimized in the condensed phase using hybrid density functional B3LYP[9] with the 6-31G** basis set[10] for all atoms except for palladium. For Pd, the SDD basis set with an effective core potential (ECP) was used.[11] Frequency calculations on all of the stationary points were carried out to characterize the nature of those stationary points and also to evaluate the respective molecular partition functions and entropic terms. The transition states were characterized by a unique imaginary frequency, characteristic of first-order saddle points on the potential energy surface, and found to pertain to the desired reaction coordinate. Intrinsic Reaction Coordinate (IRC) calculations were further performed on the transition-state geometries thus obtained to ascertain that the transition state connected to reactants and products on either side of the first-order saddle point.[12] The effect of solvent was incorporated using the continuum solvation

model SMD developed by Truhlar and Cramer. The solvent used in the reaction is dichloromethane, and hence, we have used the continuum dielectric of dichloromethane (ε = 8.93) in our computations. Graphical representation of the optimized geometries was created by using CYLView.[13]

Kinetic Studies

Kinetic experiments were carried out by dissolving **3** (~2×10^{-4} M) in CH_3CN. The change in absorbance at 350 nm for **3**→**2** was monitored for the rate calculation upon addition HCl (10 eq.). The pseudo-first-order rate constant (k) for **3**→**2** conversion was calculated on the basis of a nonlinear exponential fit in Origin 2018 by following the equation $y = y_0 + A_1 \times \exp(-x/t_1)$, where y and y_0 correspond to the absorbance at 350 nm at time t and t = 0, respectively, x corresponds to time periods (t in minutes) over which the absorption changes take place, A_1 is the pseudo-first-order coefficient, and the value of the pseudo-first-order rate constant (k) is $1/(t_1 \times 60)$ s^{-1}.

Synthesis of *o*-$Ph_2PC_6H_4C(O)N(H)C_6H_4PPh_2$-*o* (1).

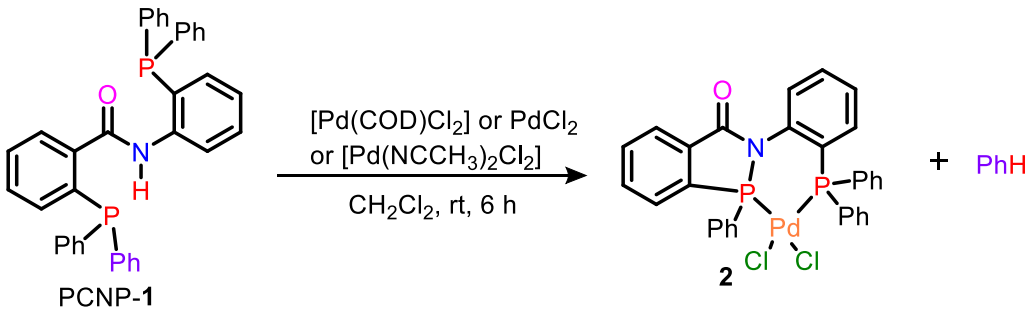


PCNP-**1**

^{n}BuLi (5.63 mL, 1.6 M in hexane, 9.013 mmol) was added dropwise to a solution of 2-bromo-*N*-(2-bromophenyl)benzamide (1.00 g, 2.816 mmol) in diethyl ether (20 mL) at -78 °C. The solution was warmed to room temperature and stirred for 4 h, and cooled to -78 °C again, and chlorodiphenylphosphine (1.36 g, 6.196 mmol) was added and stirred at room

temperature for 12 h. Degassed 2-propanol (10 eq) was added to quench excess of ^{n}BuLi. The solvent was evaporated and the yellow oily residue was redissolved in dichloromethane and filtered through celite, dried under vacuum to get solid residue. The residue was subjected to column chromatography on silica gel using petroleum ether and ethyl acetate (95:5) as the eluent, to give compound **1** as white crystalline solid. Yield 0.987 g. (62%). Mp: 143-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 7.2 Hz, 1H), 8.02 (dd, *J* = 7.9, 4.5 Hz, 1H), 7.39 – 7.33 (m, 7H), 7.32 – 7.23 (m, 16H), 7.23 – 7.18 (m, 1H), 7.04 (td, *J* = 7.5, 0.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.93 – 6.87 (m, 1H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -9.30(s, P_a), -20.5(s, P_b). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.79 (s), 141.02 (dd, *J* = 20.9, 13.2 Hz), 137.73 (s), 137.62 – 137.38 (m), 134.69 (d, *J* = 6.8 Hz), 134.43 (s), 133.89 (t, *J* = 19.2 Hz), 130.37 (d, *J* = 13.4 Hz), 129.30 (s), 128.90 (d, *J* = 7.3 Hz), 128.74 (s), 128.53 (d, *J* = 7.1 Hz), 127.09 (d, *J* = 4.4 Hz), 126.68 (d, *J* = 10.4 Hz), 125.00 (s), 122.55 (s). HRMS (ESI) Calcd for $C_{37}H_{29}NNaOP_2$ ($[M+Na]^+$): 588.1617; found: 588.1618. Anal. Calcd for $C_{37}H_{29}NOP_2$: C, 78.57; H, 5.17; N, 2.48. Found: C, 78.67; H, 5.15; N, 2.28. FT-IR (KBr disk, cm^{-1}): 3406 m (ν_{NH}), 3050 m, 1676 s (ν_{CO}), 1570 m, 1488 s, 1431 s, 1397 m.

Synthesis of [$PdCl_2${*o*-C_6H_4{C(O)N(*o*-$PPh_2(C_6H_4)$)P(Ph)}}κ^2-*P,P*] (2).

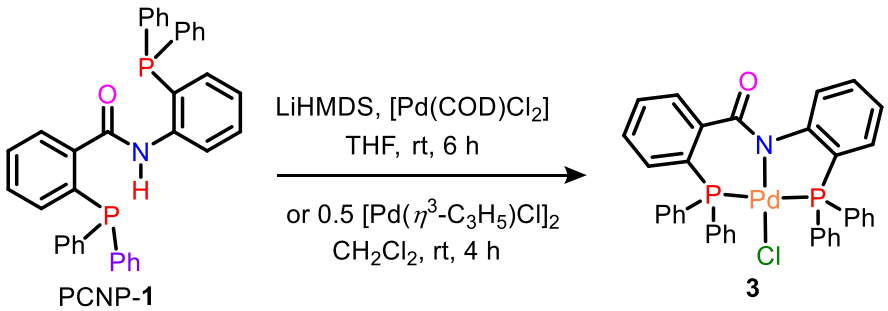


Method 1: To a solution of [$Pd(COD)Cl_2$] (0.015 g, 0.053 mmol) in dichloromethane (5 mL) was added dropwise a solution of **1** (0.03 g, 0.053 mmol) also in dichloromethane (5 mL) and stirred for 6 h. The solvent was evaporated and the residue obtained was washed with petroleum

ether and the solvent was evaporated to obtain analytically pure product of **2** as microcrystalline solid. Yield: 0.03 g (85%).

Method 2: Anhydrous HCl gas was bubbled through the solution of compound **3** (0.03 g, 0.053 mmol) in dichloromethane (5 mL) and stirred for 1 h. The solvent was evaporated and the residue obtained was washed with petroleum ether and dried under *vacuo* to give analytically pure product. Single-crystals suitable for X-ray diffraction were grown from concentrated dichloromethane solution of **2**. Yield: 0.028 g (79%). Mp: 243-247 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 – 8.78 (m, 1H), 7.96 – 7.91 (m, 1H), 7.81 – 7.75 (m, 2H), 7.74 – 7.64 (m, 5H), 7.56 – 7.46 (m, 7H), 7.45 – 7.37 (m, 4H), 7.31 (td, *J* = 7.8, 2.8 Hz, 2H), 7.28 – 7.17 (m, 3H), 6.82 – 6.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.42 (d, *J* = 9.5 Hz), 138.33 (s), 135.04 – 134.01 (m), 133.51 (dd, *J* = 34.1, 18.4 Hz), 132.33 (d, *J* = 38.9 Hz), 131.21 (t, *J* = 31.6 Hz), 130.32 (s), 128.75 (t, *J* = 44.9 Hz), 127.74 (s), 127.21 (s), 125.90 (s), 124.52 (dd, *J* = 86.2, 30.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 80.62 (d, $^{2}J_{PP}$= 15.8 Hz, 1P) 18.89 d, $^{2}J_{PP}$= 15.8 Hz, 1P). HRMS (ESI) Calcd for $C_{31}H_{23}Cl_2ONNaP_2Pd$ ([M+Na]$^{+}$): 685.9565; found: 685.9553. Anal. Calcd for $C_{31}H_{23}Cl_2NOP_2Pd$: C, 56.01; H, 3.49; N, 2.11. Found: C, 56.15; H, 3.56; N, 2.21. FT-IR (KBr disk, cm^{-1}): 2239 w, 1715 s (ν_{CO}), 1570 m, 1438 s, 1303 s, 1098 s.

Synthesis of [PdCl{*o*-$Ph_2PC_6H_4C(O)N(C_6H_4PPh_2$-*o*)}$\kappa^3$-*P,N,P*] (3).

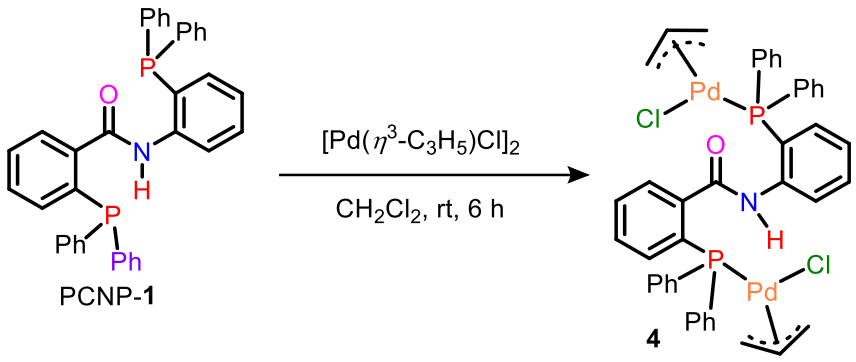


Method 1: To a solution of LiHMDS (0.089 g, 0.53 mmol) in THF (5 mL) was added a solution of **1** (0.03 g, 0.053 mmol) in the same solvent (5 mL) and after stirring for 3 h, [Pd(COD)Cl_2] (0.015 g, 0.053 mmol) in THF (8 mL) was added and stirred for a further period of 6 h. The

solution was filtered through a celite pad, solvent was evaporated, and the residue obtained was washed with petroleum ether (2x7 mL) and dried under *vacuo* to give analytically pure product of **3**. Yield: 0.028 g (75%).

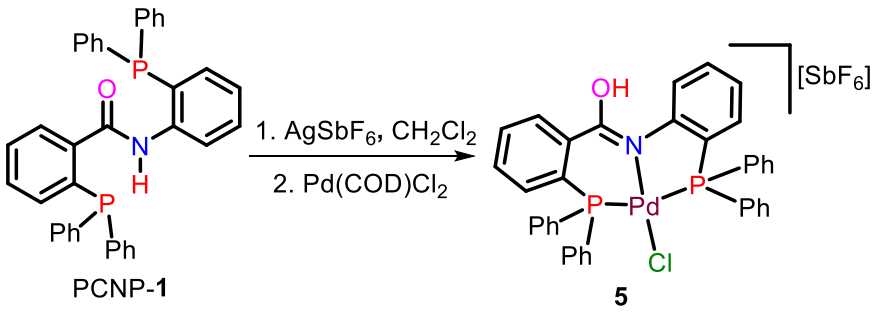
Method 2: A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 g, 0.026 mmol) in dichloromethane (5 mL) was added drop wise to a solution of **1** (0.03 g, 0.053 mmol) in the same solvent (5 mL) and stirred for 4 h. The solvent was removed under reduced pressure to afford compound **3** as yellow solid. X-ray quality crystals were grown from concentrated dichloromethane solution of **3**. Yield: 0.033 g (88%). Mp: 261-265 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.1, 3.8 Hz, 1H), 7.66 (ddd, *J* = 11.7, 9.5, 7.2 Hz, 8H), 7.56 – 7.39 (m, 13H), 7.33 – 7.24 (m, 3H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 8.1 Hz, 1H), 6.85 (dt, *J* = 7.2, 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.78 (d, *J* = 5.9 Hz), 160.19 (d, *J* = 24.2 Hz), 143.96 (d, *J* = 15.2 Hz), 134.77 (d, *J* = 11.4 Hz), 133.73 (dd, *J* = 11.5, 2.1 Hz), 132.76 (d, *J* = 10.2 Hz), 132.28 (s), 131.59 (s), 131.38 (dd, *J* = 8.2, 2.7 Hz), 130.56 (t, *J* = 2.6 Hz), 130.31 (d, *J* = 7.2 Hz), 129.22 – 128.75 (m), 128.61 (d, *J* = 4.3 Hz), 128.24 (d, *J* = 4.3 Hz), 127.20 (d, *J* = 12.1 Hz), 126.94 (d, *J* = 4.5 Hz), 126.56 (d, *J* = 4.6 Hz), 125.15 (s), 124.82 (s), 124.50 – 124.37 (m), 124.04 (d, *J* = 7.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.56 (d, $^2J_{PP}$ = 500.58 Hz, P_a), 18.03 (d, $^2J_{PP}$ = 498.96, P_b). HRMS (ESI) Calcd for $C_{37}H_{28}NOP_2Pd$ ($[M\text{-}Cl]^+$): 670.0689; found: 670.0687. Anal. Calcd for $C_{37}H_{28}ClNOP_2Pd$: C, 62.91; H, 4.00; N, 1.98. Found: C, 62.91; H, 3.99; N, 2.03. FT-IR (KBr disk, cm^{-1}): 3058 w, 1600 s (ν_{CO}), 1437 s, 1336 s, 1102 s.

Synthesis of $[PdCl(\eta^3\text{-}C_3H_5)\{o\text{-}Ph_2PC_6H_4C(O)N(H)C_6H_4PPh_2\text{-}o\}PdCl(\eta^3\text{-}C_3H_5)]$ (4)



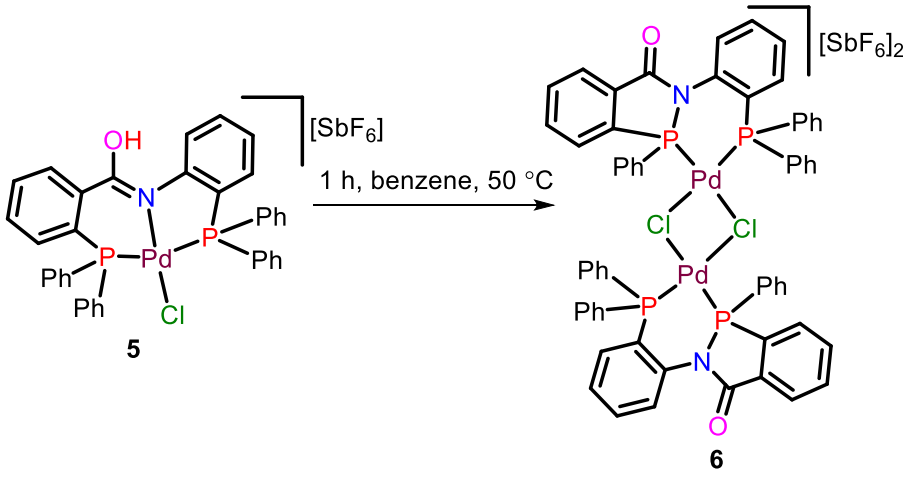
To a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.019 g, 0.053 mmol) in dichloromethane (5 mL) was added dropwise a solution of **1** (0.03 g, 0.053 mmol) in the same solvent (5 mL) and stirred for 6 h. The solvent was evaporated to obtain compound **4** as yellow solid. Single-crystals of **4** suitable for X-ray analysis were obtained by slow diffusion of petroleum ether into the dichloromethane solution of **4**. Yield: 0.045 g (91%). Mp: 223-227 °C(dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H), 7.66 (s, 8H), 7.40 (dd, *J* = 19.7, 6.7 Hz, 15H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.86 (m, 1H), 6.83 – 6.72 (m, 1H), 5.61 – 5.42 (m, 2H), 4.73 (s, 1H), 4.56 (t, *J* = 7.3 Hz, 1H), 3.80 – 3.67 (m, 1H), 3.64 – 3.54 (m, 1H), 3.42 (s, 1H), 3.29 (s, 1H), 2.86 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.21 (s), 139.65 (d, *J* = 8.4 Hz), 138.28 (d, *J* = 10.1 Hz), 134.72 (d, *J* = 11.9 Hz), 134.43 (d, *J* = 13.5 Hz), 134.08 (d, *J* = 4.0 Hz), 133.96 (s), 133.67 (s), 132.37 (d, *J* = 3.5 Hz), 131.29 (s), 131.19 (d, *J* = 1.8 Hz), 130.71 (d, *J* = 7.2 Hz), 130.25 (s), 129.10 (d, *J* = 10.6 Hz), 128.55 (d, *J* = 10.2 Hz), 127.93 (d, *J* = 6.6 Hz), 125.96 (d, *J* = 7.1 Hz), 118.66 (s), 117.09 (s), 81.15 (d, *J* = 30.2 Hz), 61.82 (s), 60.71 (s). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 25.54(s), 15.83(s). HRMS (ESI) Calcd for $C_{40}H_{34}OP_2NPd$ ($[M\text{-}Pd(\eta^3\text{-}C_3H_5)Cl_2]^+$): 712.1160; found: 712.1160. Anal. Calcd for $C_{43}H_{39}NOP_2Pd_2Cl_2$: C, 55.45; H, 4.22; N, 1.50. Found: C, 55.47; H, 4.22; N, 1.59. FT-IR (KBr disk, cm^{-1}): 3194 m (ν_{NH}), 3056 w, 1661 s (ν_{CO}), 1504 s, 1436 s, 1300 s, 1096 s.

Synthesis of $[PdCl\{o\text{-}Ph_2PC_6H_4C(O)N(H)(C_6H_4PPh_2\text{-}o)\}\kappa^3\text{-}P,N,P\}][SbF_6]$ (5).



A solution of $AgSbF_6$ (0.018 g, 0.053 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **1** (0.03 g, 0.053 mmol) also in dichloromethane (5 mL) and after stirring for 30 min, a solution of $[Pd(COD)Cl_2]$ (0.015 g, 0.053 mmol) in dichloromethane (6 mL) was added and stirring continued for 30 min. The precipitated solution was filtered through a celite pad, the solvent was evaporated, the residue obtained was washed with diethyl ether (1 x 8 mL) and dried under *vacuo* to obtain compound **5** as yellow solid. Yield: 0.044 g (88%). Mp: 212-215 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 5.7 Hz, 1H), 7.64 (m, 13H), 7.57 – 7.46 (m, 11H), 7.40 (s, 1H), 7.34 – 7.29 (m, 1H), 7.16 (dd, *J* = 15.1, 7.6 Hz, 1H), 7.07 (s, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.34 (d, *J* = 500.5 Hz, 1P), 20.46 (d, *J* = 500.5 Hz, 1P). HRMS (ESI) Calcd for $C_{37}H_{29}NOP_2PdCl$ ($[M\text{-}SbF_6]^+$): 706.0453 found: 706.0423. FT-IR (KBr disk, cm^{-1}): 3387 b (ν_{OH}), 1666 ((ν_{CN}) s, 1587 s, 1481, 1496 s.

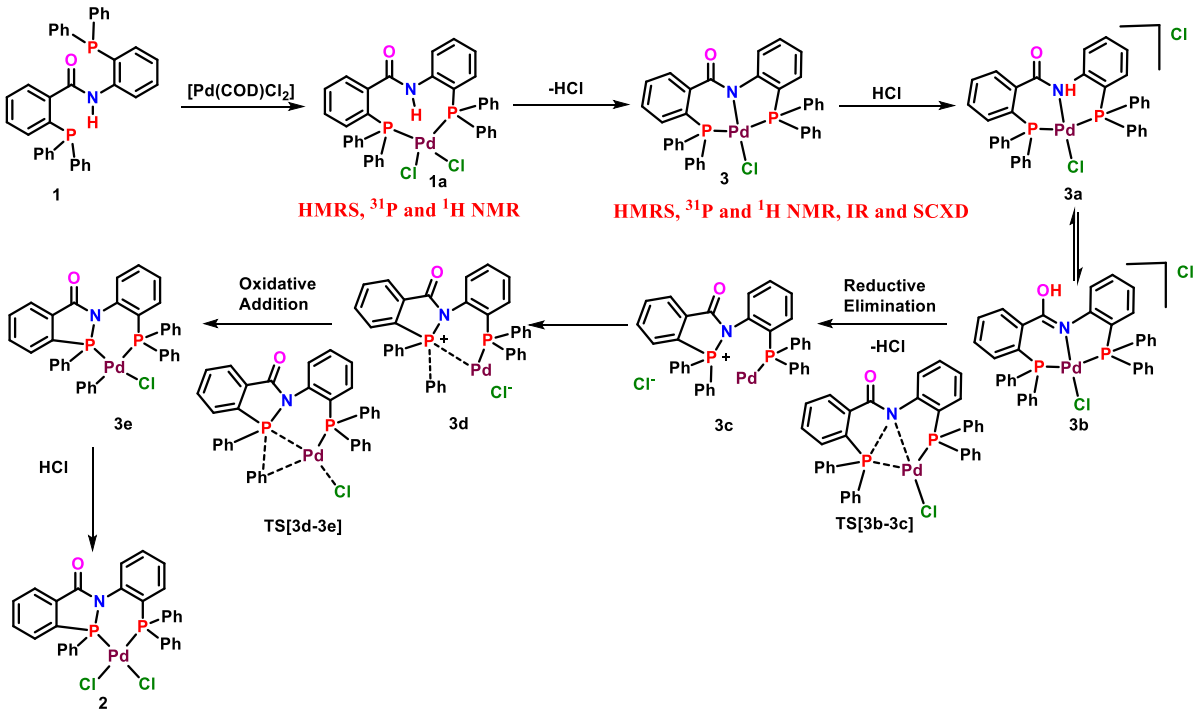
Synthesis of [{Pd(*μ*-Cl){*o*-C$_6$H$_4${C(O)N(*o*-PPh$_2$(C$_6$H$_4$))P(Ph)}}*κ*^{2}-*P*,*P*}$_2$][(SbF$_6$)$_2$] (6).



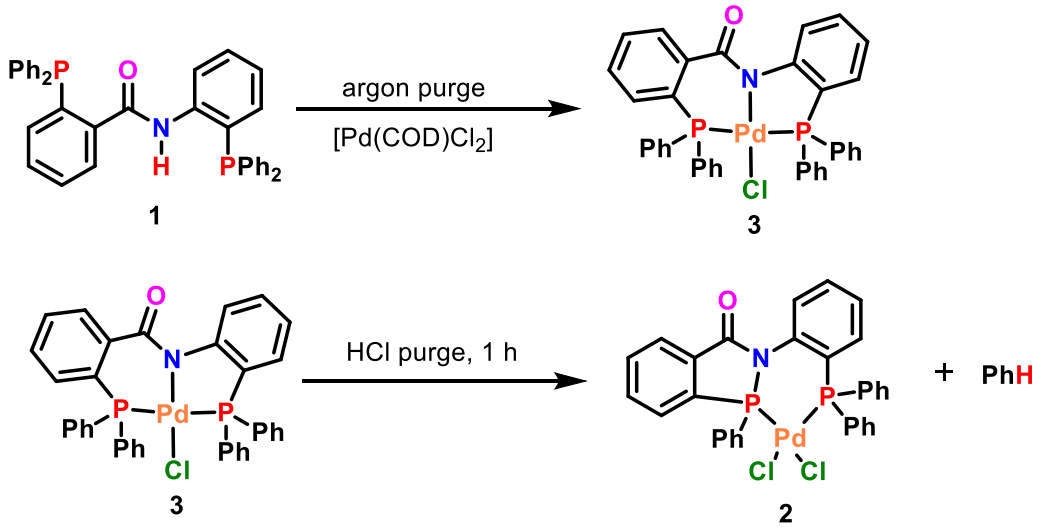
A benzene solution of complex **5** (0.044 g, 0.046 mmol) was warmed to 50 °C for 1 h and the solvent was evaporated under reduced pressure to give analytically pure product of **6** as bright yellow solid. Single-crystals suitable for X-ray diffraction were grown from concentrated benzene solution of **6**. Yield: 0.031 g (78%). Mp: 234-237 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.48 (s, 1H), 7.90 (d, J = 13.0 Hz, 5H), 7.67 (s, 6H), 7.56 (s, 5H), 7.43 (dd, J = 31.3, 24.0 Hz, 10H), 7.26 (s, 1H), 6.95 (s, 1H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 84.6 (s), 18.27 (s). Anal. Calcd for $C_{62}H_{46}Cl_2N_2O_2P_4Pd_2Sb_2F_{12}$: C, 43.04; H, 2.68; N, 1.62. Found: C, 42.82; H, 2.96; N, 1.54. FT-IR (KBr disk, cm^{-1}): 3069 w,1734 s (νCO), 1439 s, 1306 s, 1100 s.

II. Investigation of the reaction mechanisms

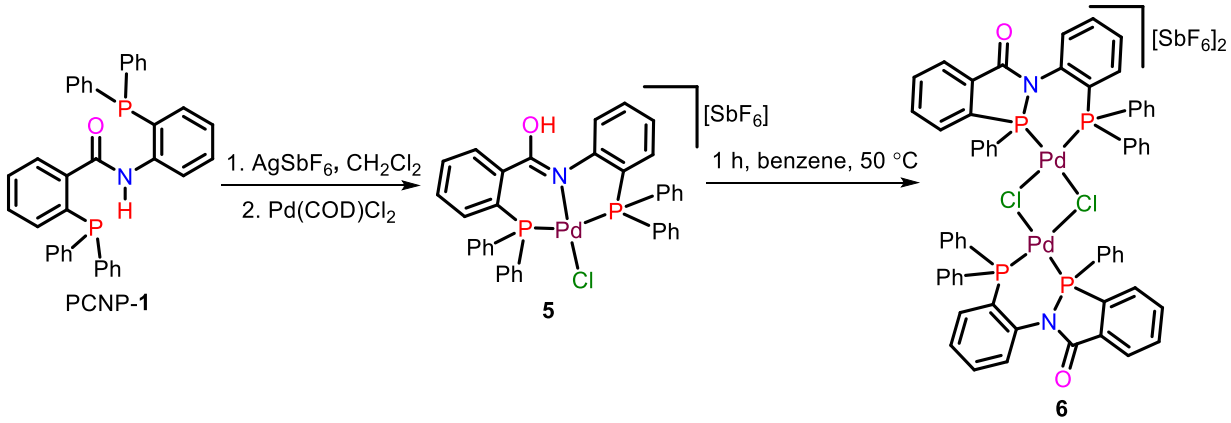
Scheme S1. Proposed mechanism for the formation of palladium complex [$PdCl_2${*o*-C_6H_4{C(O)N(*o*-$PPh_2(C_6H_4)$)P(Ph)}}κ^2-*P*,*P*] (**2**)



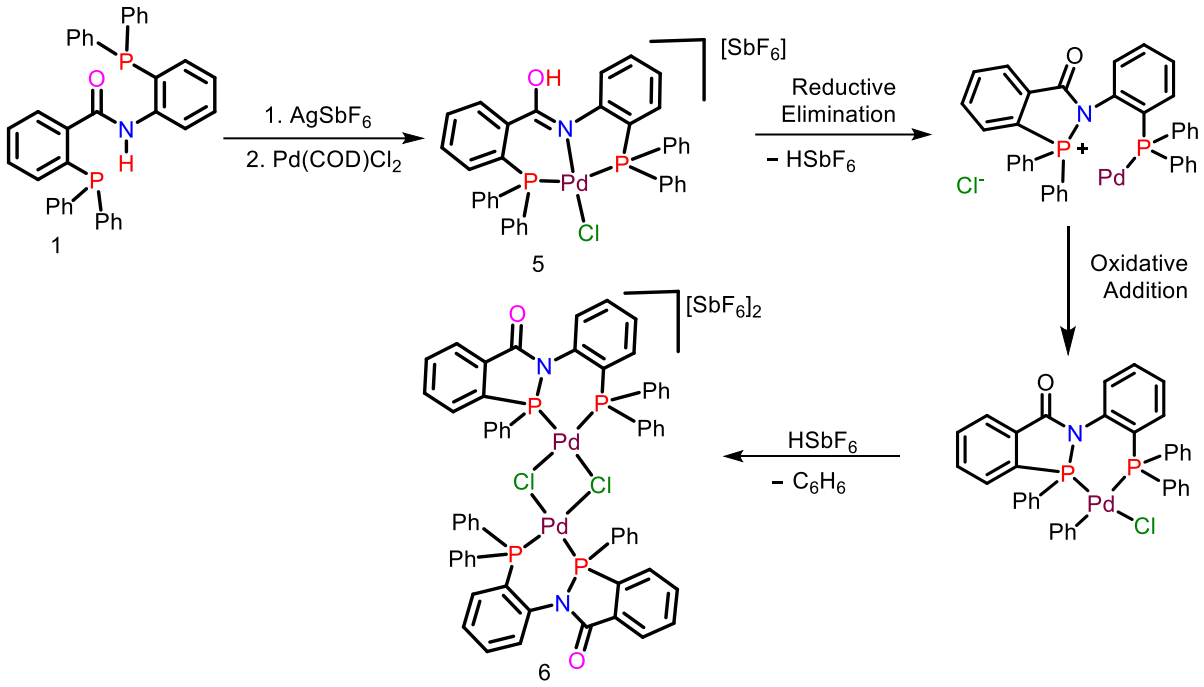
Scheme S2. Control experiment for the involvement of HCl gas in the reaction mixture.



Scheme S3. Synthesis of palladium complex [{Pd(μ_2-Cl){*o*-C$_6$H$_4$\{C(O)N(*o*-PPh$_2$(C$_6$H$_4$))P(Ph)\}}κ^2-*P*,*P*}$_2$][{SbF$_6$}$_2$] (**6**)



Scheme S4. Proposed mechanism for the complex **6**



III. Selected bond lengths and bond angles, and crystallographic information for compounds 2-4 and 6

Table S1. Selected bond distances [Å] and bond angles [°] for Compounds **2-4** and **6**

Bond distances (Å)	**2**	**3**	**4**	**6**
Pd1–P1	2.2091(13)	2.2979(8)	2.303(2)	2.2072(16)
Pd1/Pd2–P2	2.2594(13)	2.2753(8)	2.3102(19)	2.2375(16)
Pd1–Cl1	2.3461(13)	2.2762(8)	2.3673(18)	2.3909(13)
Pd1–C21/Cl2/Cl’	2.3682(13)	-	2.125(7)	2.4019(14)
P1/Pd1–N1	1.712(4)	2.051(2)	–	1.700(5)
C1-O1	1.209(7)	1.240(4)	1.223(8)	1.217(9)
C1-N1	1.399(7)	1.345(4)	1.353(8)	1.412(9)
Bond angles (°)				
Cl1–Pd1–Cl2/C21/N1/Cl’	92.05(5)	173.27(7)	129.2(2)	88.63(5)
P1–Pd1–P2	89.28(5)	166.24(3)	–	88.37(6)
P1–Pd1–Cl1	174.54(5)	95.62(3)	101.91(7)	89.45(5)
P2–Pd1/Pd2–Cl1/Cl2	176.15(5)	97.65(3)	103.29(6)	93.99(5)

Table S2. Crystallographic information of compounds **2-4** and **6**

	2	**3**	**4**	**6·(4C$_6$H$_6$)**
Empirical formula	$C_{31}H_{23}Cl_2NOP_2Pd$	$C_{37}H_{28}ClNOP_2Pd$	$C_{43}H_{39}Cl_2NOP_2Pd_2$	$C_{86}H_{70}Cl_2F_{12}N_2O_2P_4Pd_2Sb_2$
Formula weight	664.74	706.39	931.39	2042.52
Temperature/K	150	150	150	150
Crystal system	orthorhombic	triclinic	triclinic	triclinic
Space group	Pna21	P-1	P-1	P-1
a/Å	21.0176(5)	9.6861(2)	10.7527(4)	12.7967(4)
b/Å	11.6607(3)	10.1225(2)	12.1363(5)	14.2667(4)
c/Å	11.4688(2)	17.8430(4)	15.6500(6)	14.5382(4)
α/°	90	91.809(2)	96.247(3)	63.884(2)
β/°	90	95.505(2)	94.277(3)	64.063(3)
γ/°	90	115.634(2)	106.011(3)	63.623(3)
Volume/Å^3	2810.77(11)	1564.79(6)	1939.69(13)	2036.34(13)
Z	4	2	2	2
ρ_{calc}, (g cm^{-3})	1.571	1.499	1.591	1.666
μ (Mo Kα), mm^{-1}	0.99	0.812	1.182	1.312
F(000)	1336	716	936	1012
Crystal size/mm^3	0.19 × 0.16 × 0.13	0.125 × 0.085 × 0.06	0.135 × 0.118 × 0.091	0.165 × 0.108 × 0.091
2θ range, °	3.994 to 50	4.87 to 49.998	3.524 to 50	3.902 to 50
Reflections collected	25416	37541	15906	37404
Independent reflections	4891 [R_{int} = 0.0505]	5497 [Rint = 0.0812]	6840 [Rint = 0.0618]	6991 [Rint = 0.0562]
S	1.042	1.039	1.041	1.079
R_1	0.0292	0.0346	0.0575	0.0555
wR_2	0.0657	0.0799	0.1449	0.1494

Table S3. NMR and FT-IR data for compounds **1-6**

Compound	$^{31}P\{^{1}H\}$ NMR (δ)	^{1}H NMR (δ)	FT-IR (cm^{-1}) (ν_{CO}, ν_{NH})
1	-9.3, -20.5	8.47	1678, 3403
2	80.6, 18.9	-	1715
3	33.6, 18.0	-	1600
4	25.4,16.0	9.14	1661, 3194
5	20.5, 16.0	-	1664[a], 3387[b]
6	89.4, 28.7	-	1734

[a] Recorded for $\nu_{C=N}$ and [b] Recorded for ν_{OH}

IV. Characterisation of compounds 1-6

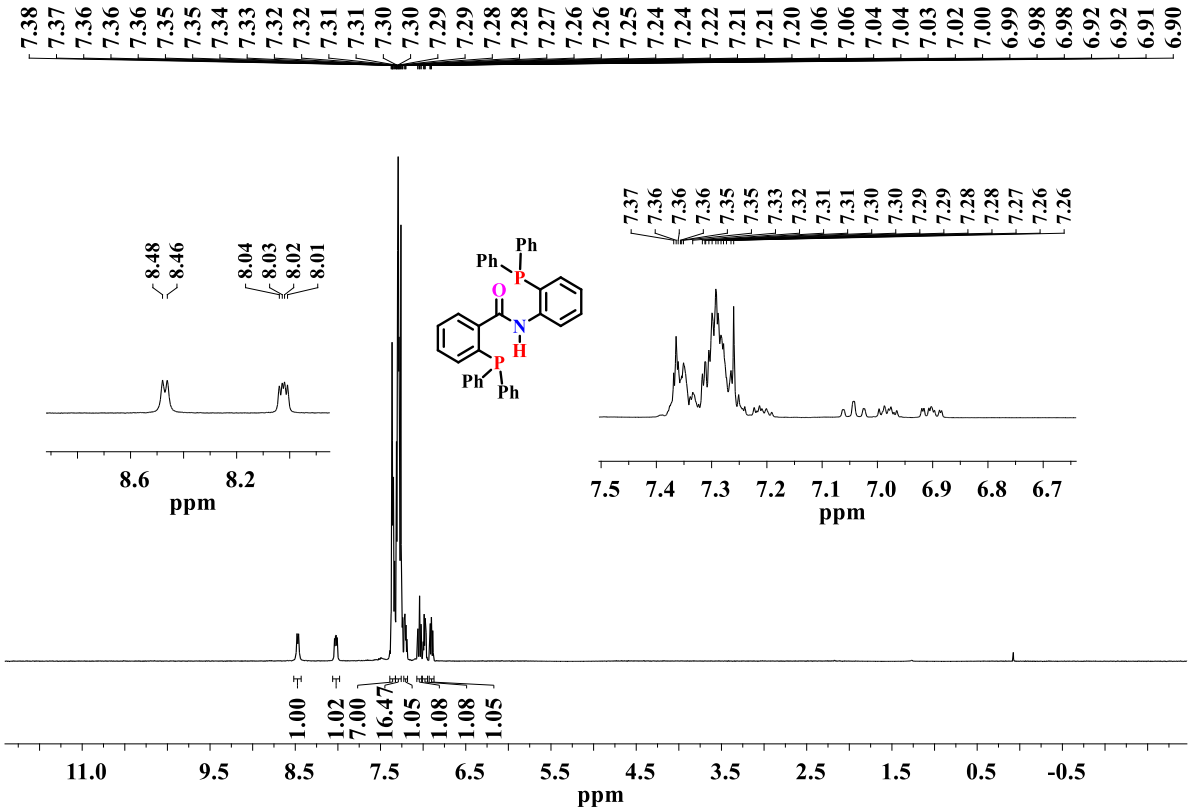


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz)

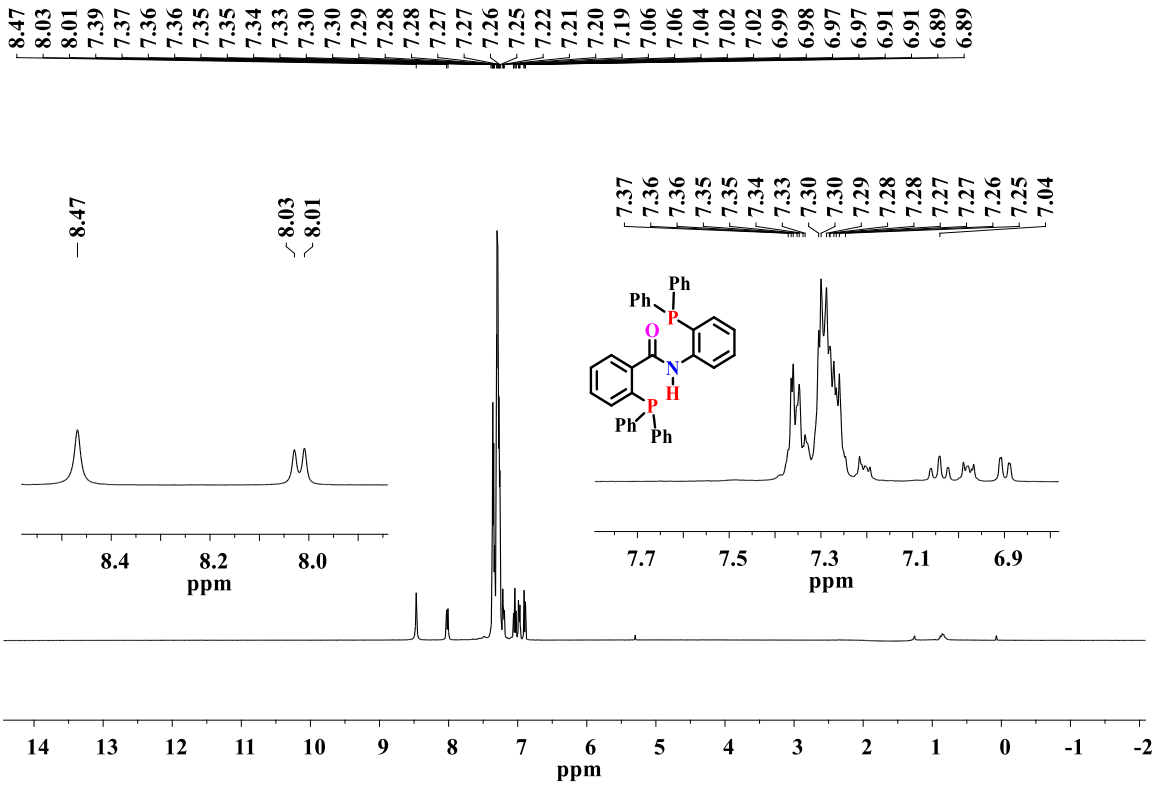


Figure S2. $^{1}H\{^{31}P\}$ NMR spectrum of **1** in $CDCl_3$ (400 MHz)

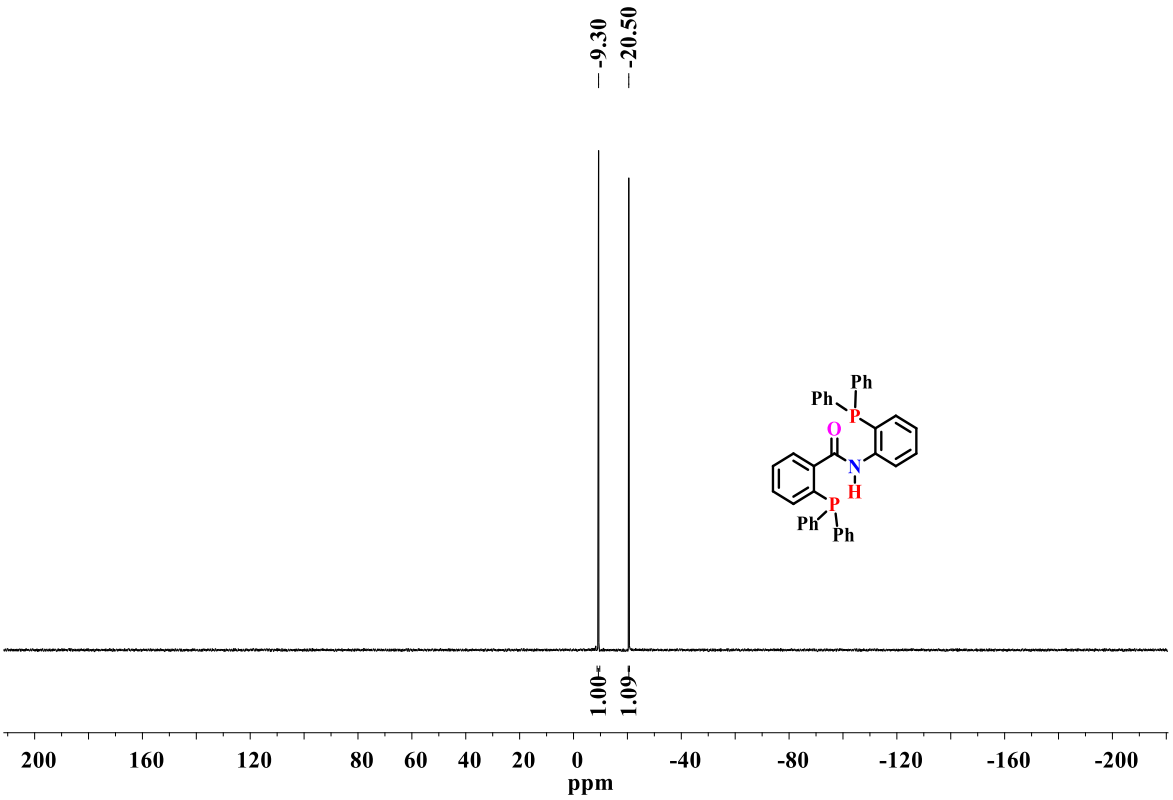


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (162 MHz)

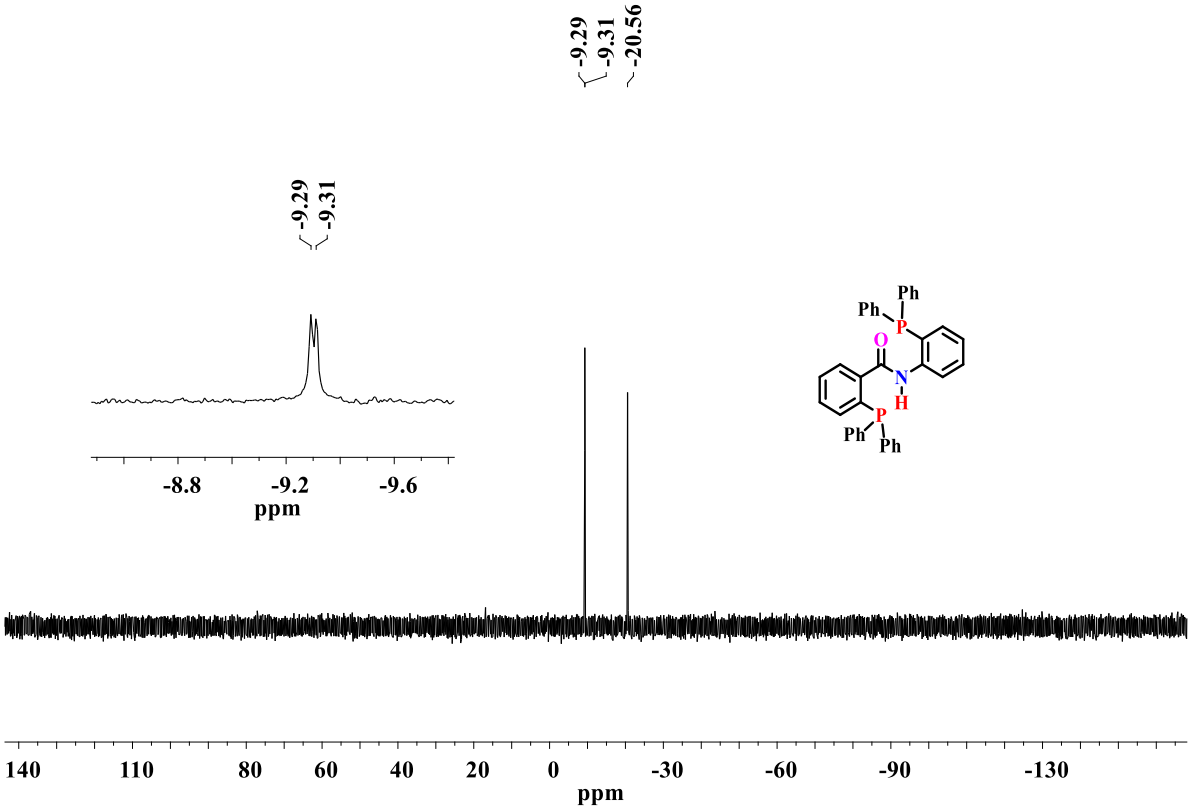


Figure S4. ^{31}P NMR spectrum of **1** in $CDCl_3$ (202 MHz)

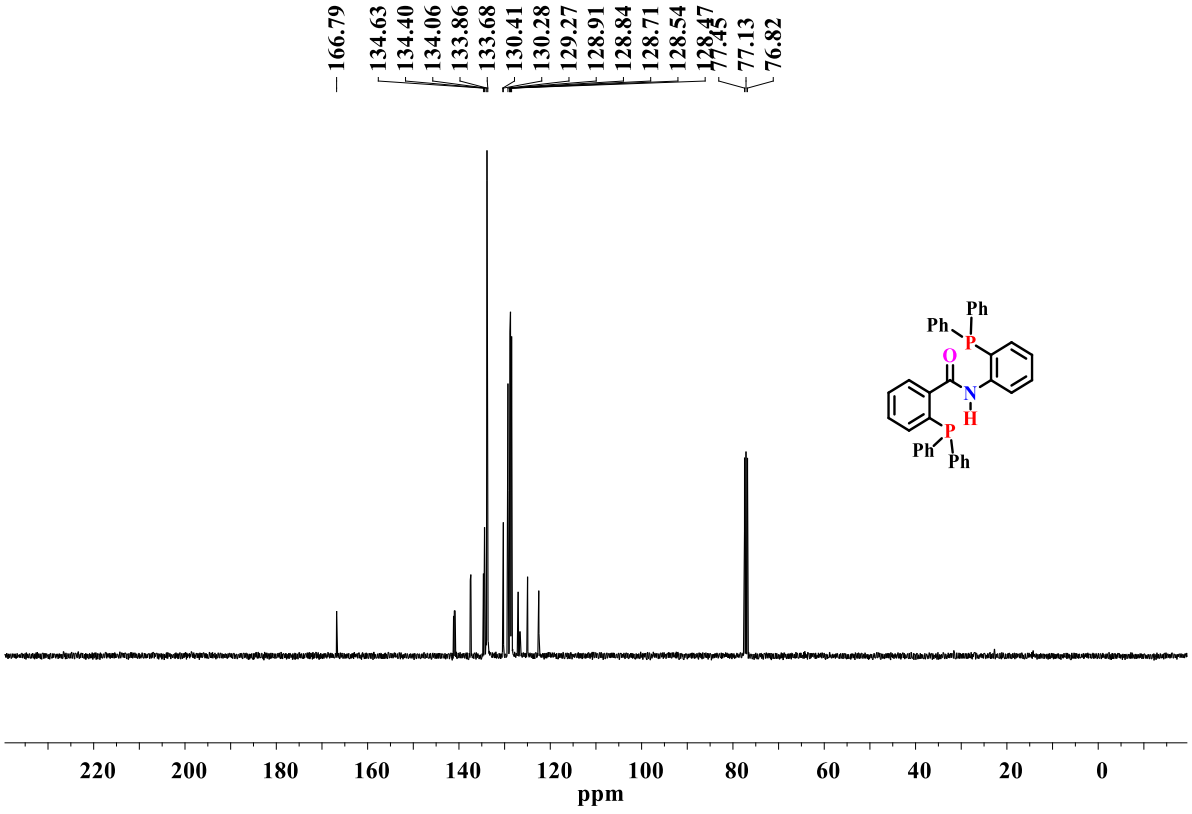


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ (101 MHz)

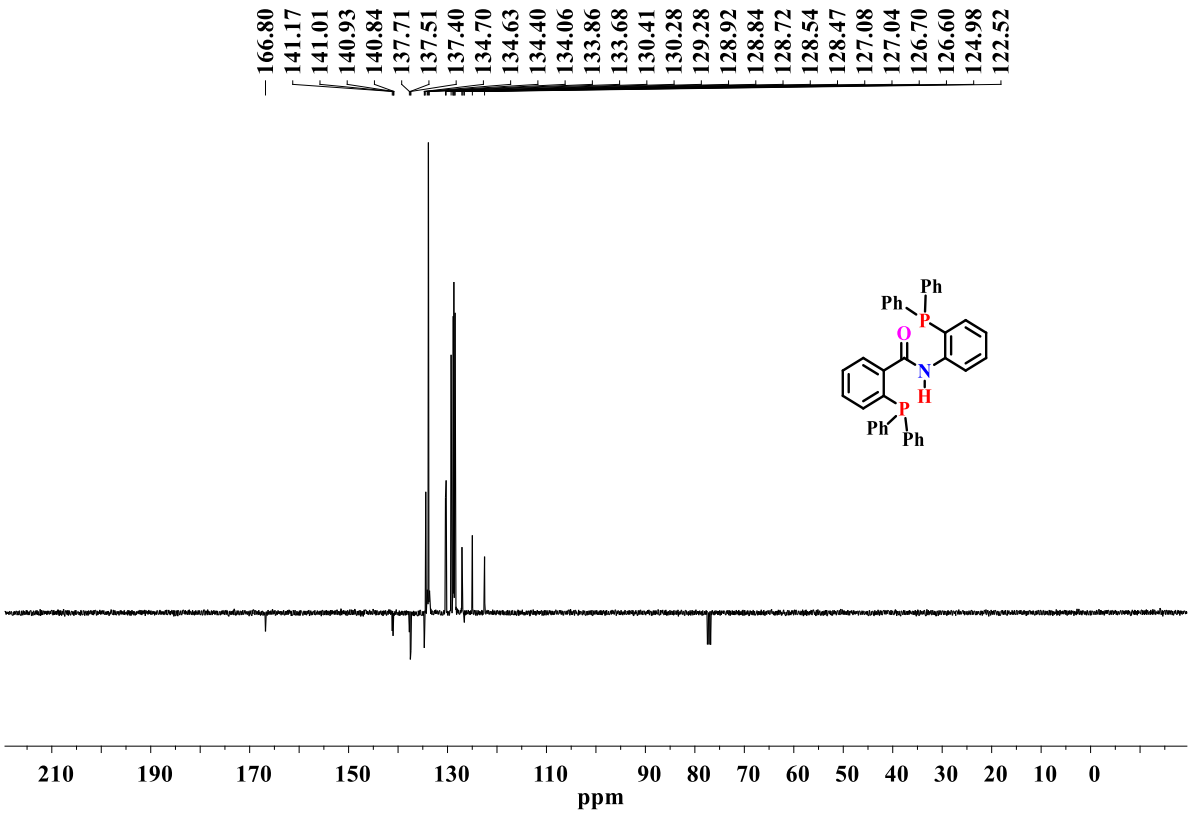


Figure S6. $^{13}C\{^{1}H\}$ DEPT-135 spectrum of **1** in $CDCl_3$ (101 MHz)

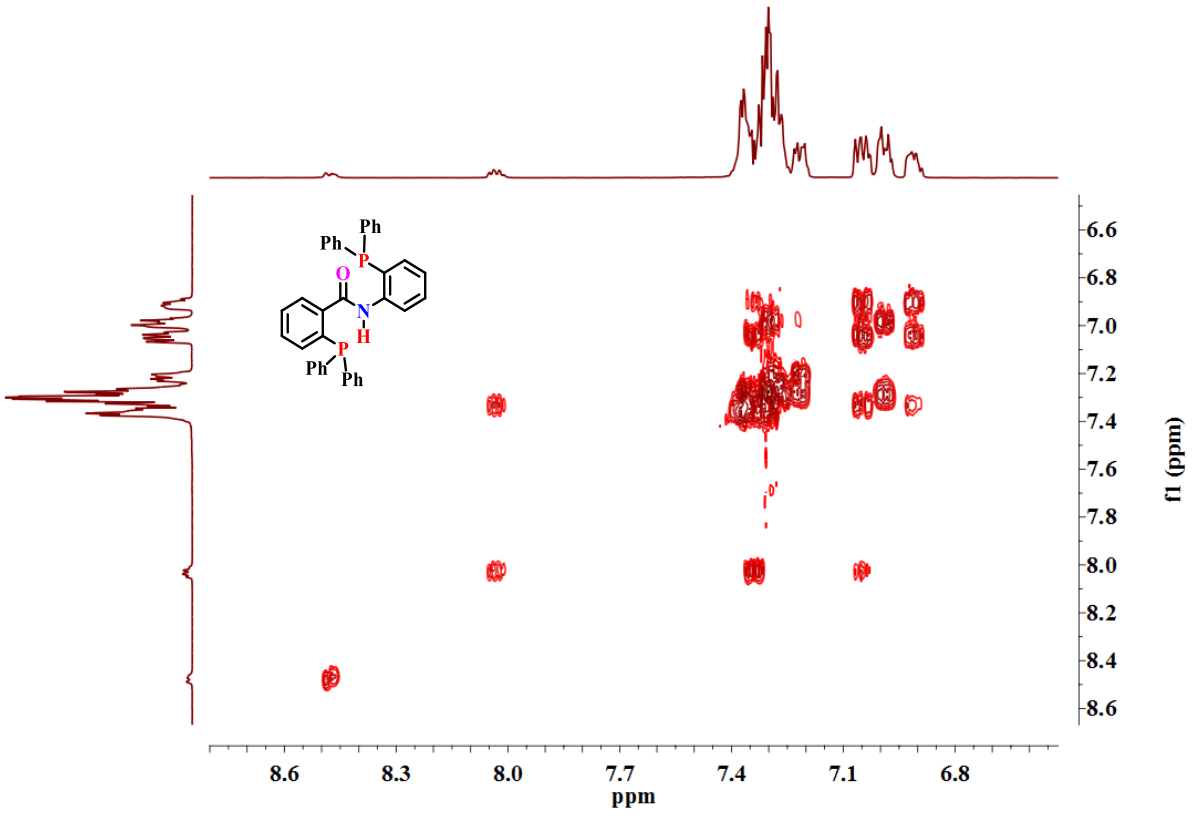
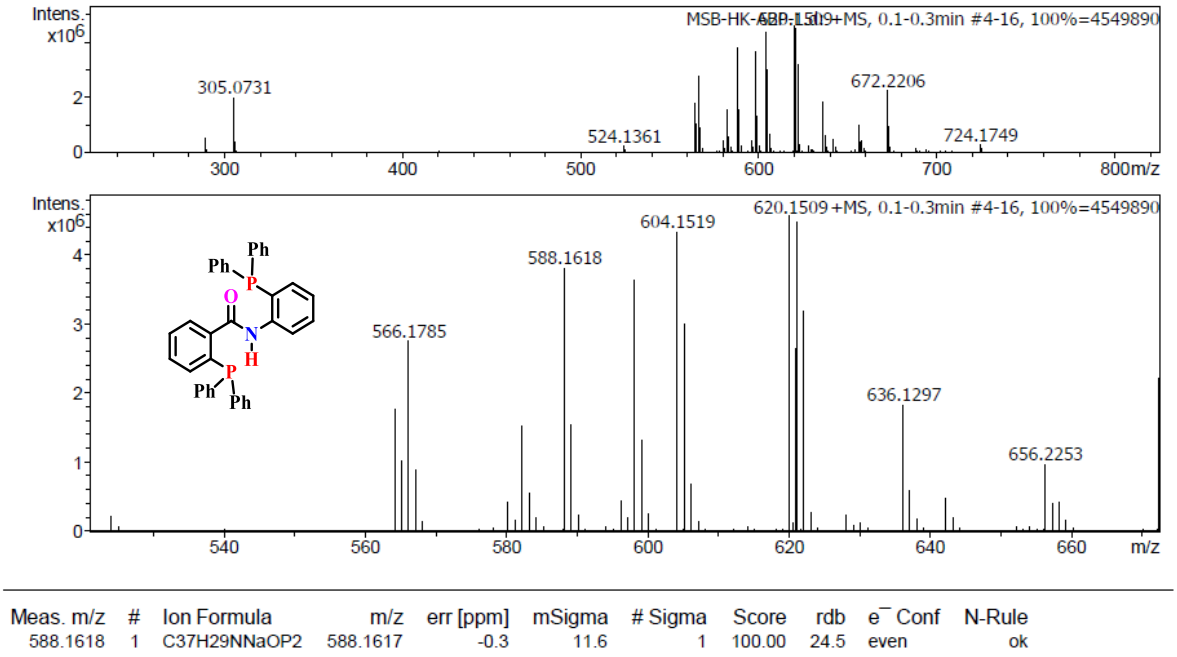


Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **1** in $CDCl_3$ (500 MHz).



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
588.1618	1	C37H29NNaOP2	588.1617	-0.3	11.6	1	100.00	24.5	even	ok

Figure S8. HRMS spectrum of **1**

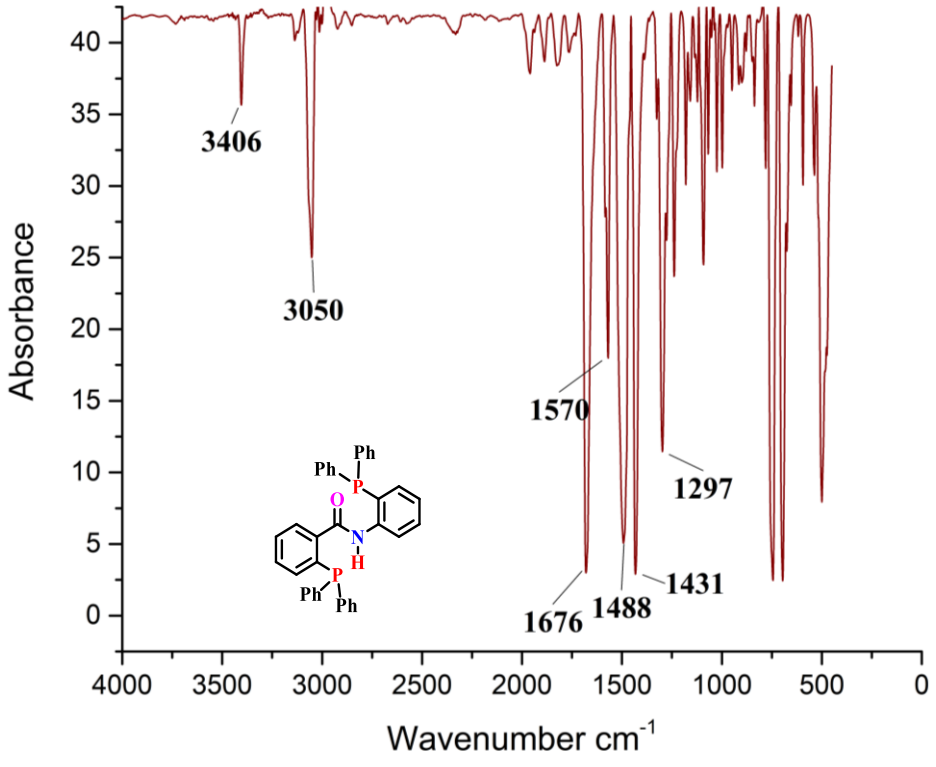


Figure S9. FT-IR spectrum of **1**

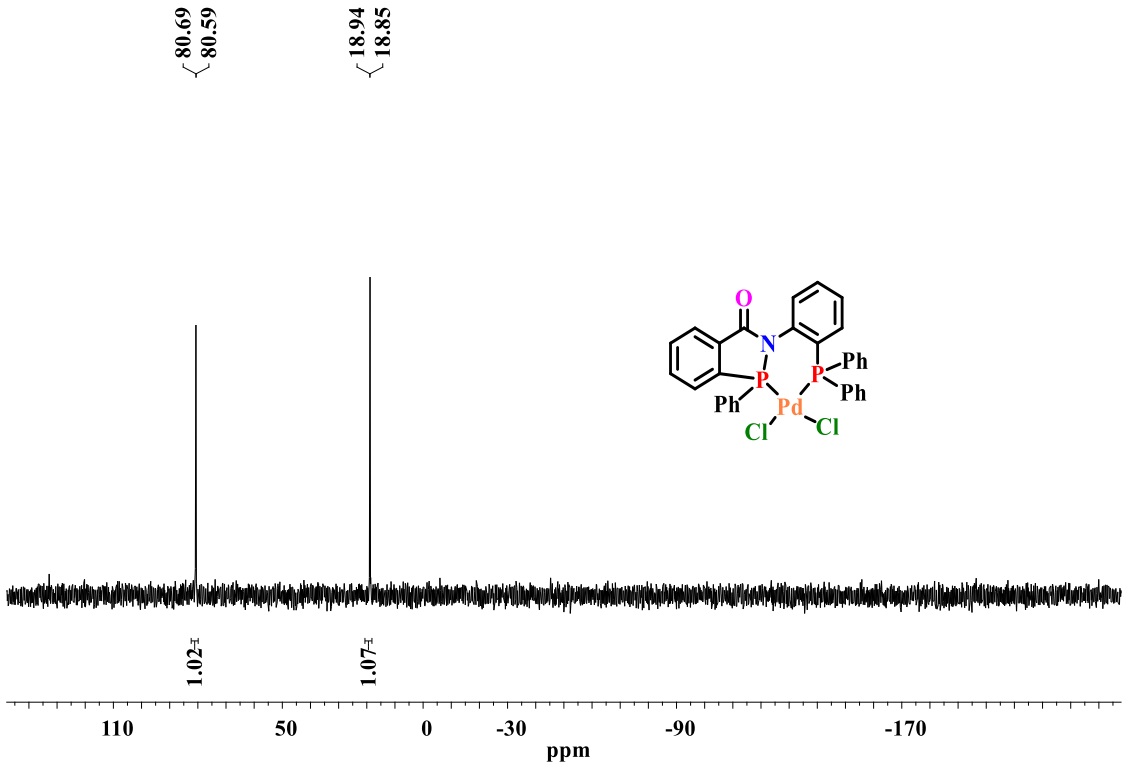


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (162 MHz)

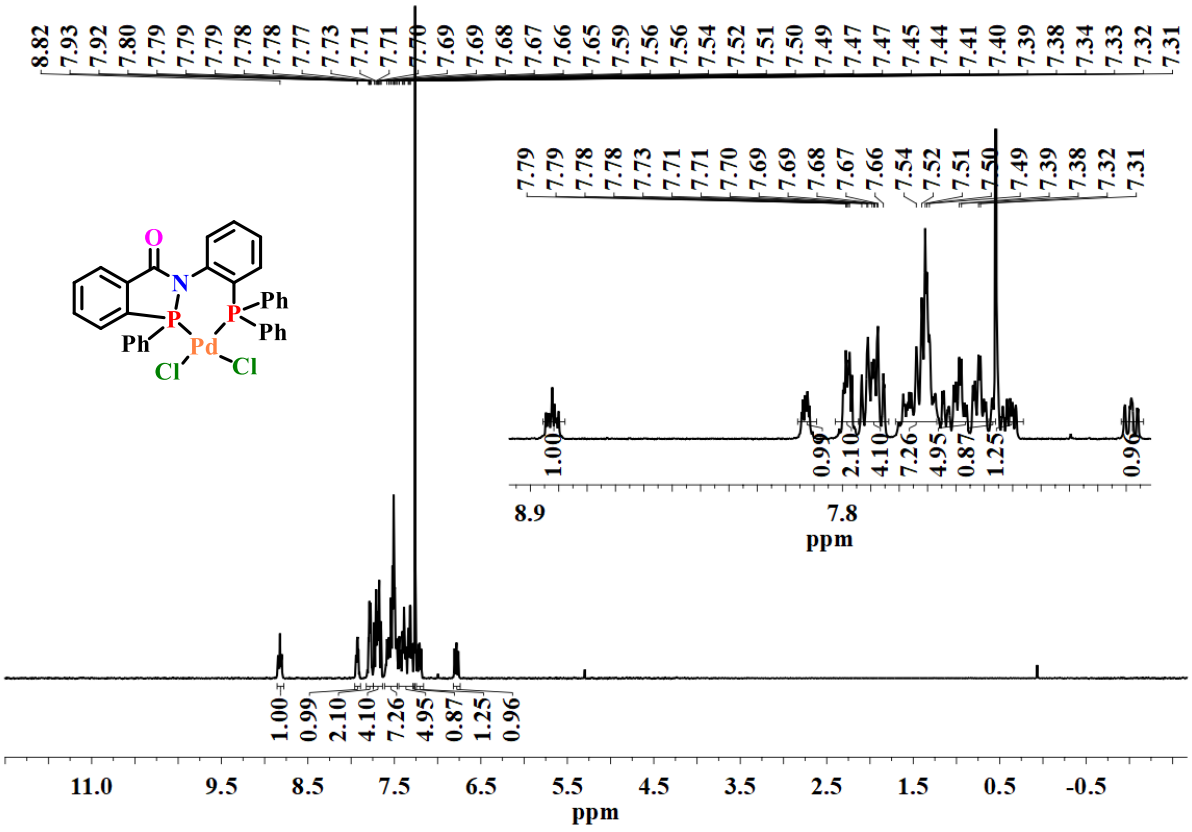


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz)

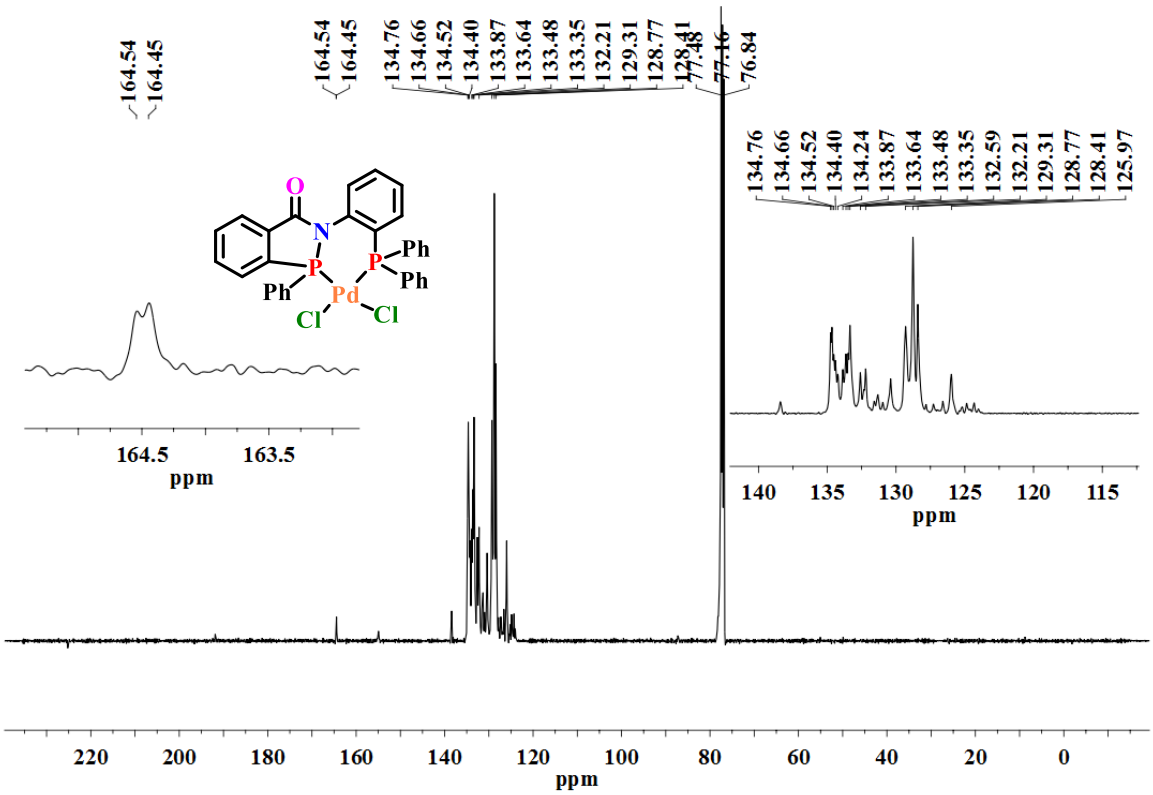


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (101 MHz)

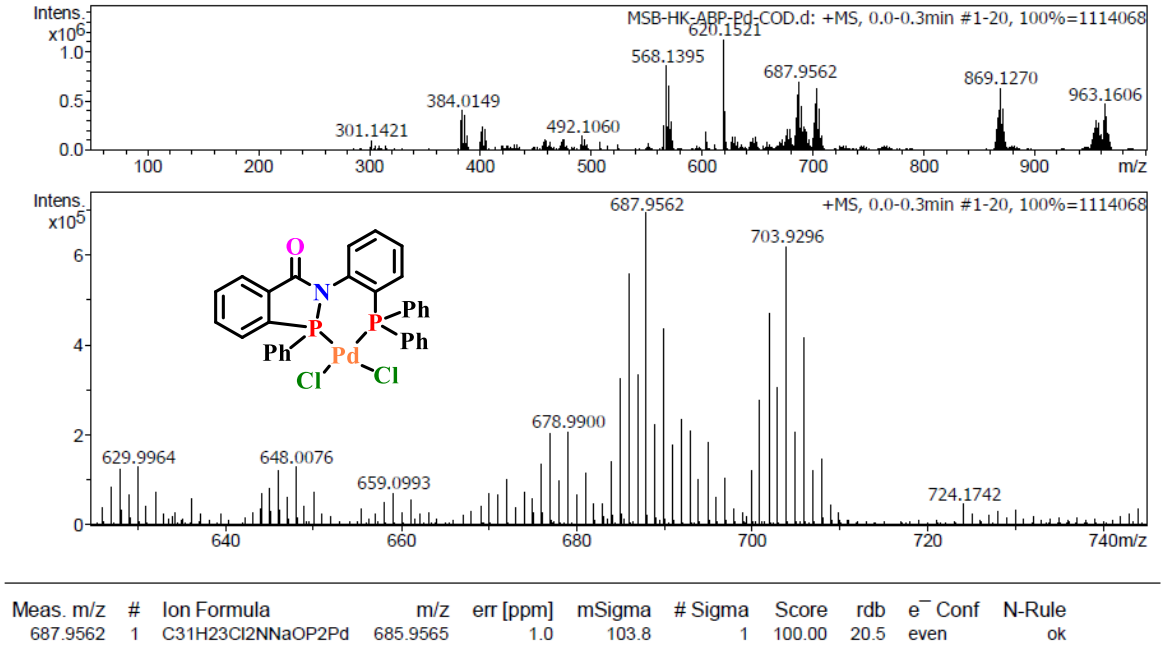


Figure S13. HRMS spectrum of **2**

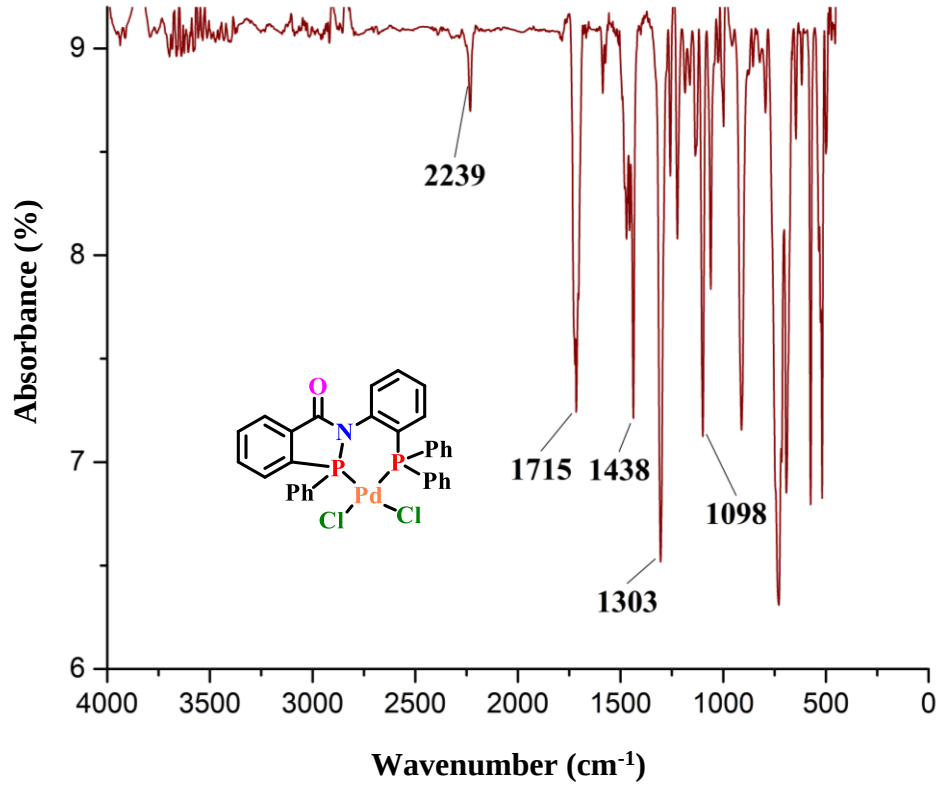


Figure S14. FT-IR spectrum of **2**

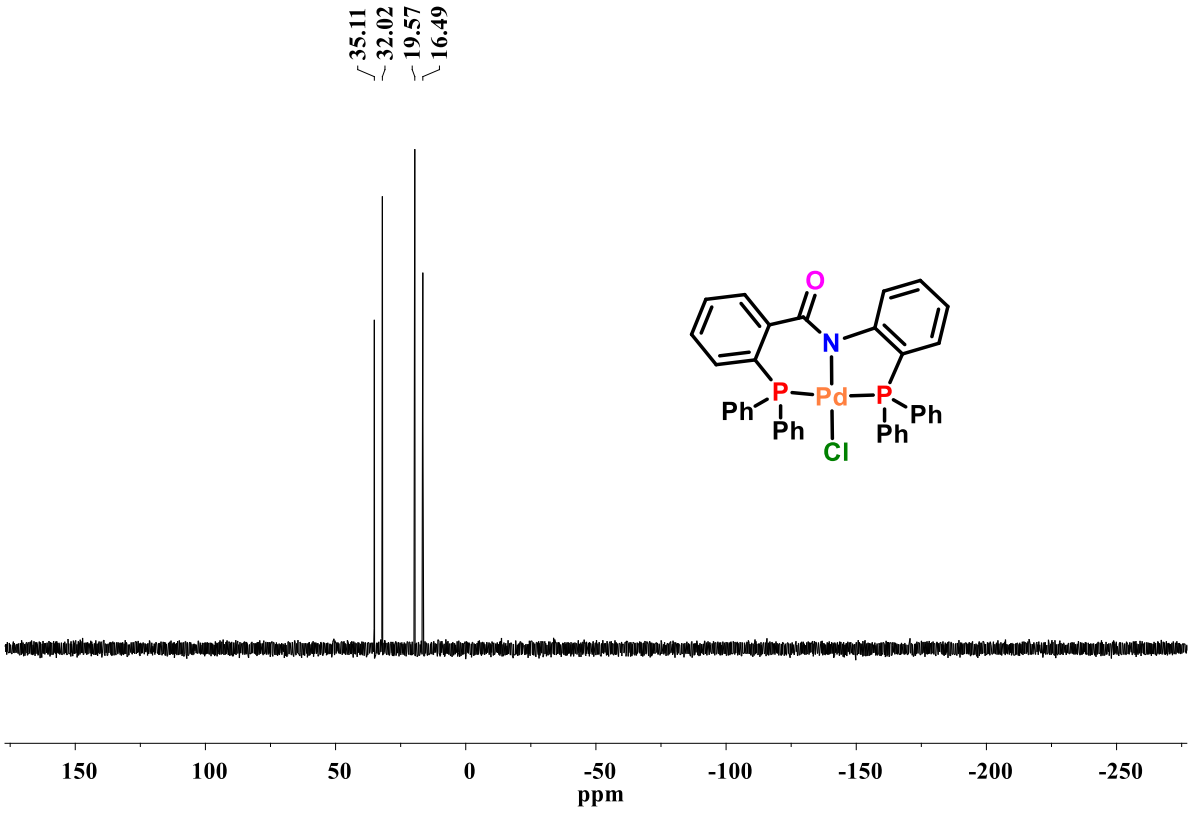


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (162 MHz)

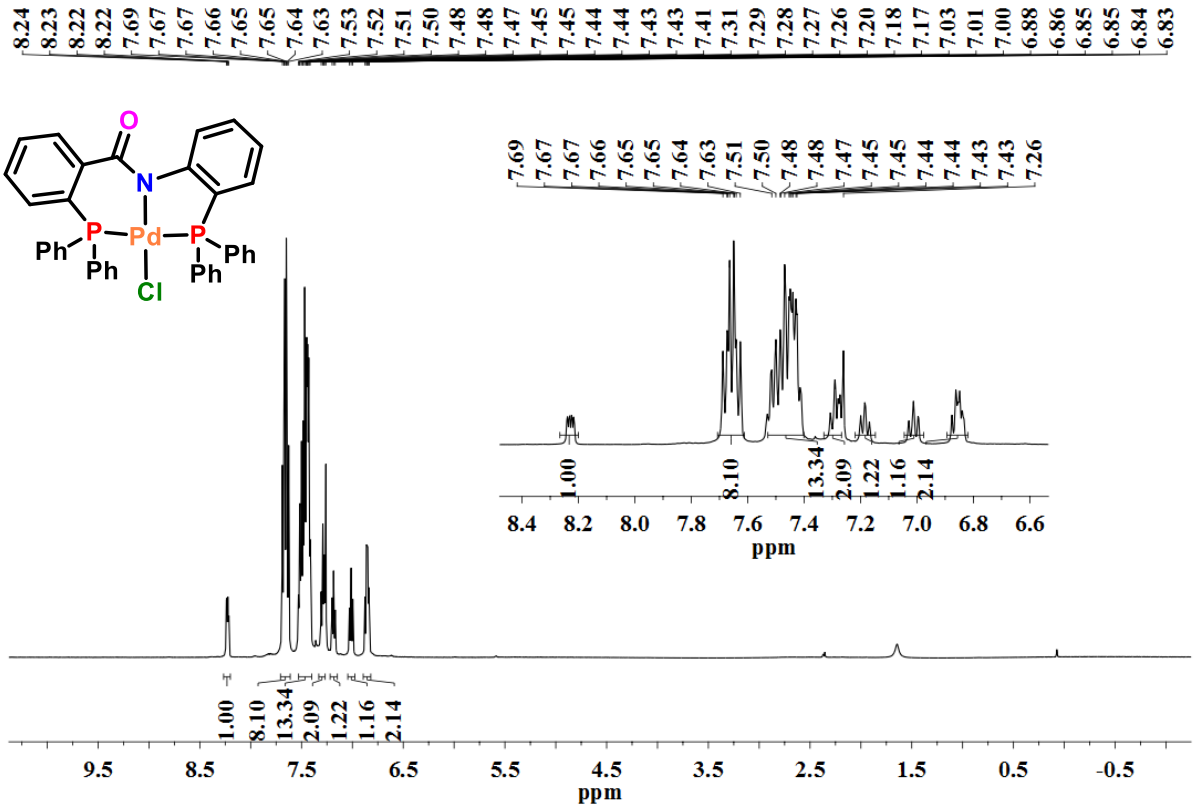


Figure S16. ^{1}H NMR spectrum of **3** in $CDCl_3$ (500 MHz)

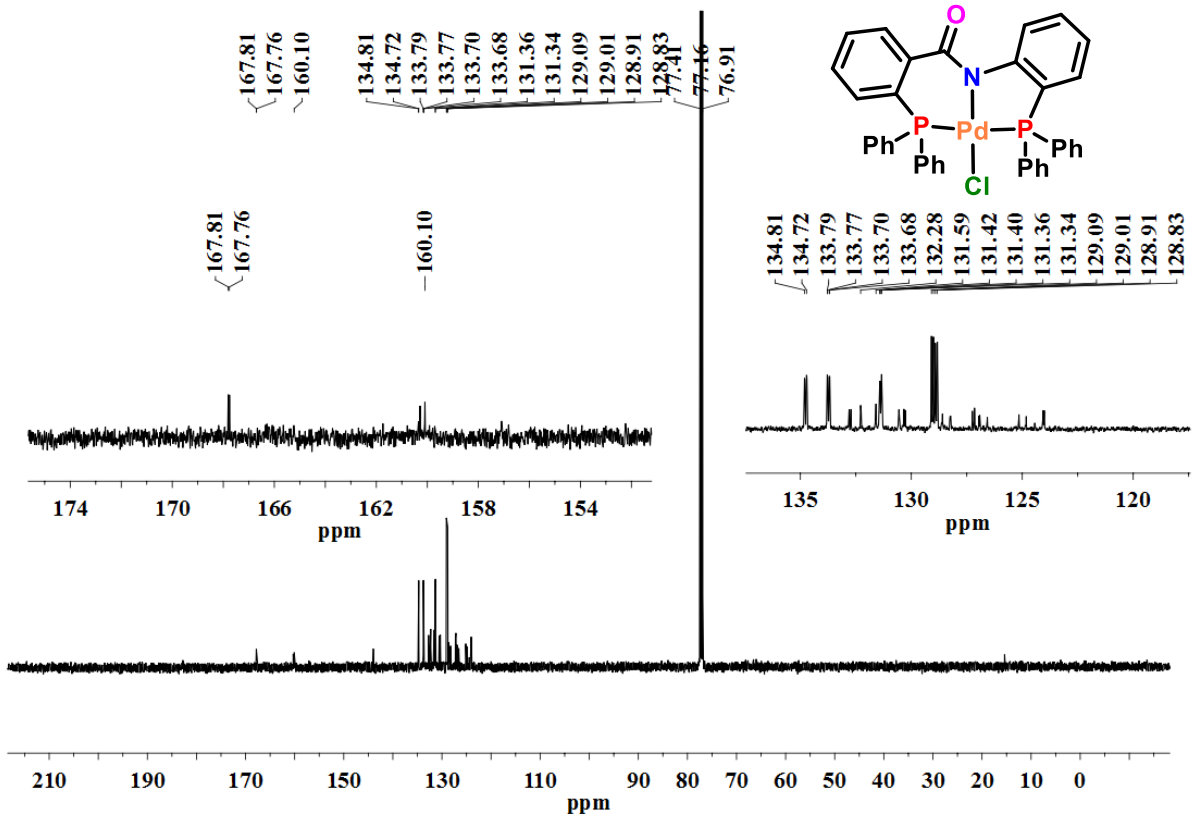
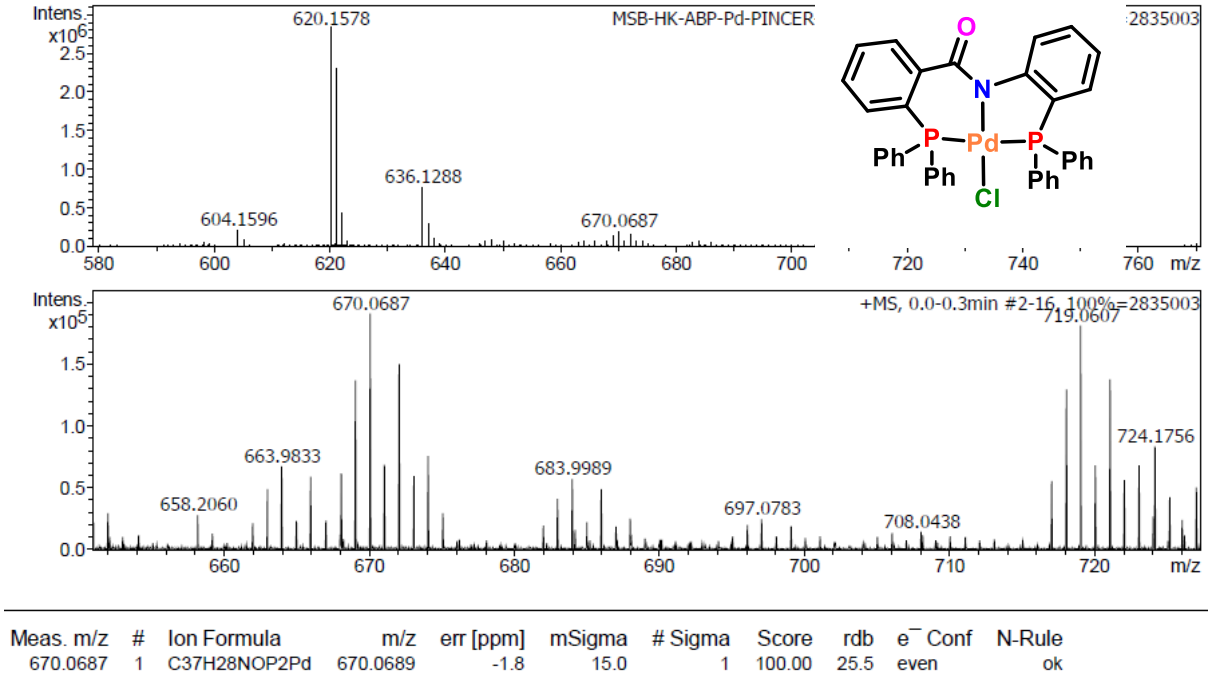


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (126 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
670.0687	1	C37H28NOP2Pd	670.0689	-1.8	15.0	1	100.00	25.5	even	ok

Figure S18. HRMS spectrum of **3**

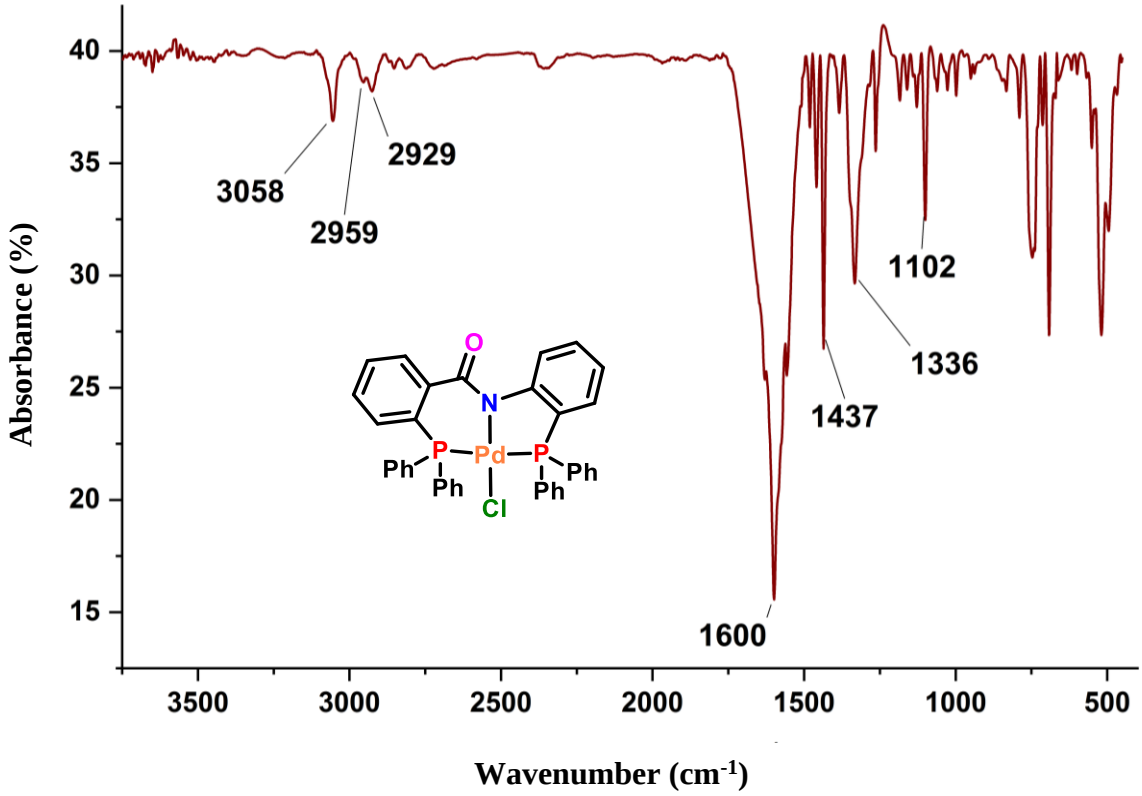


Figure S19. FT-IR spectrum of **3**

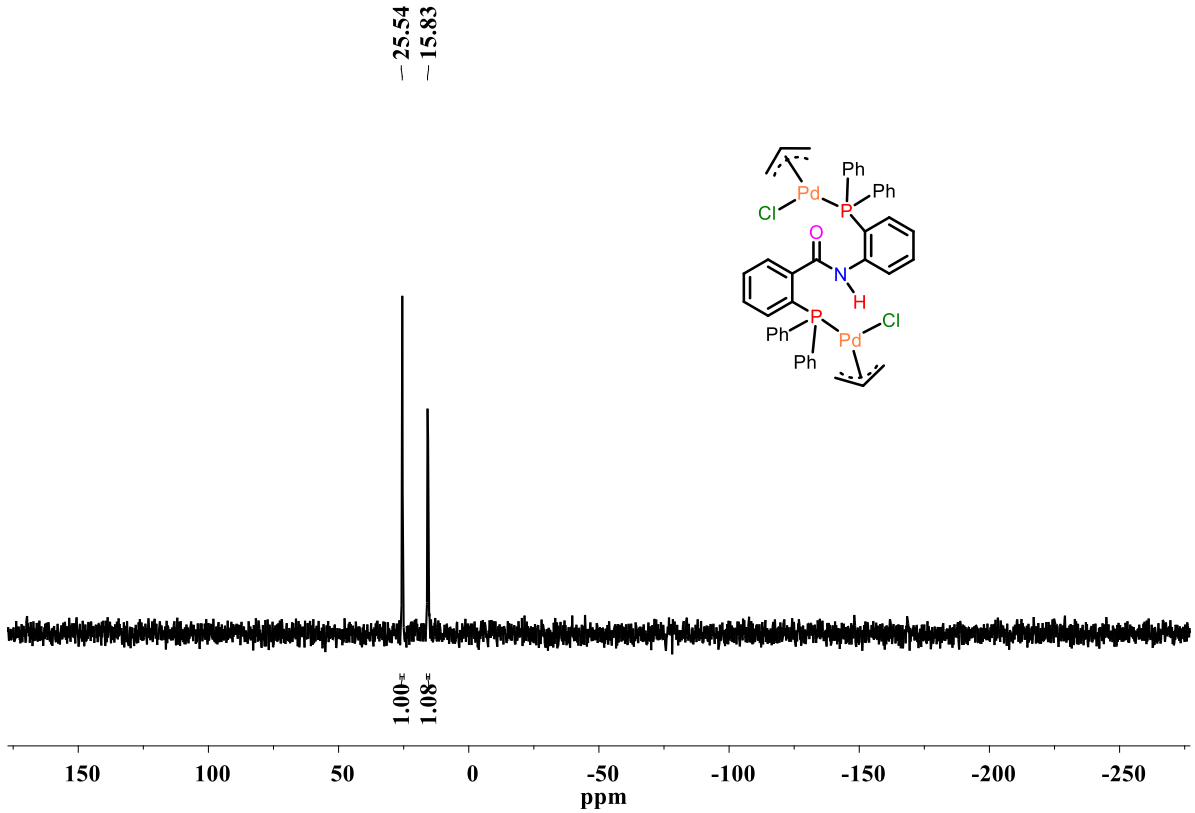


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ (162 MHz)

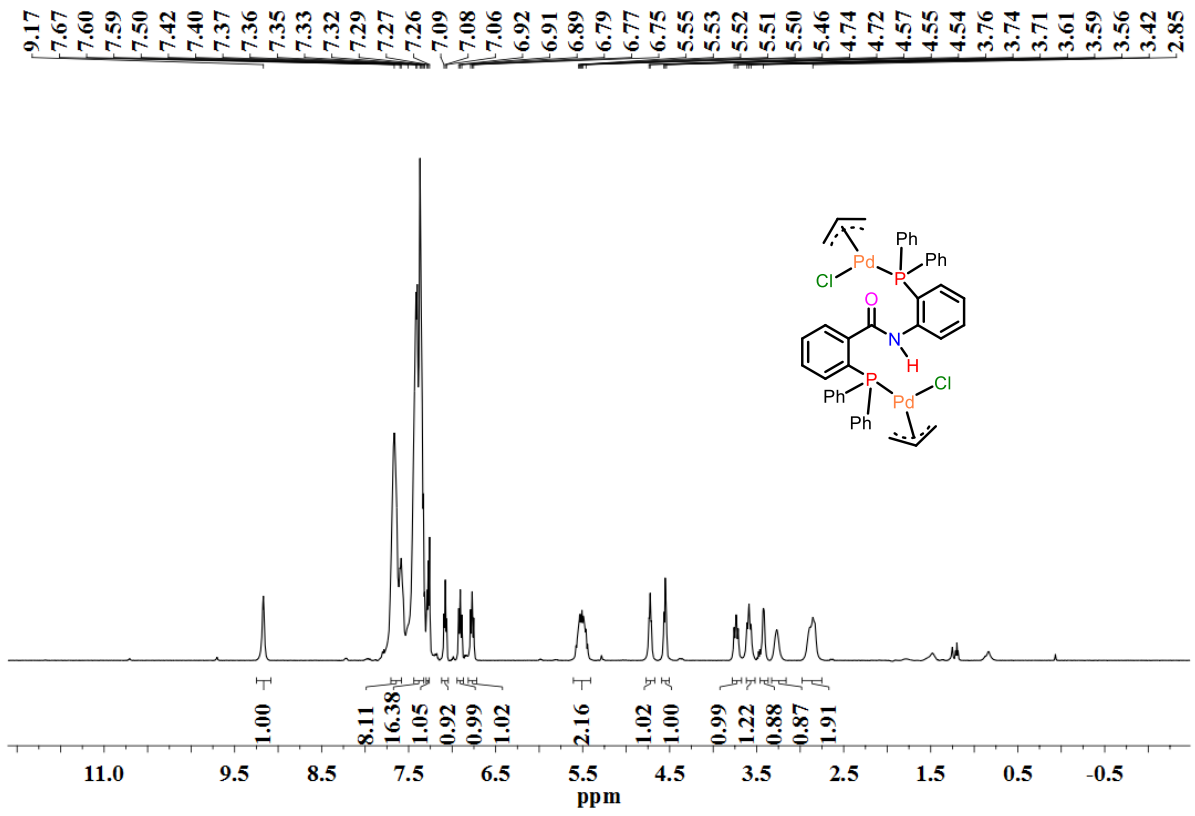


Figure S21. ^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz)

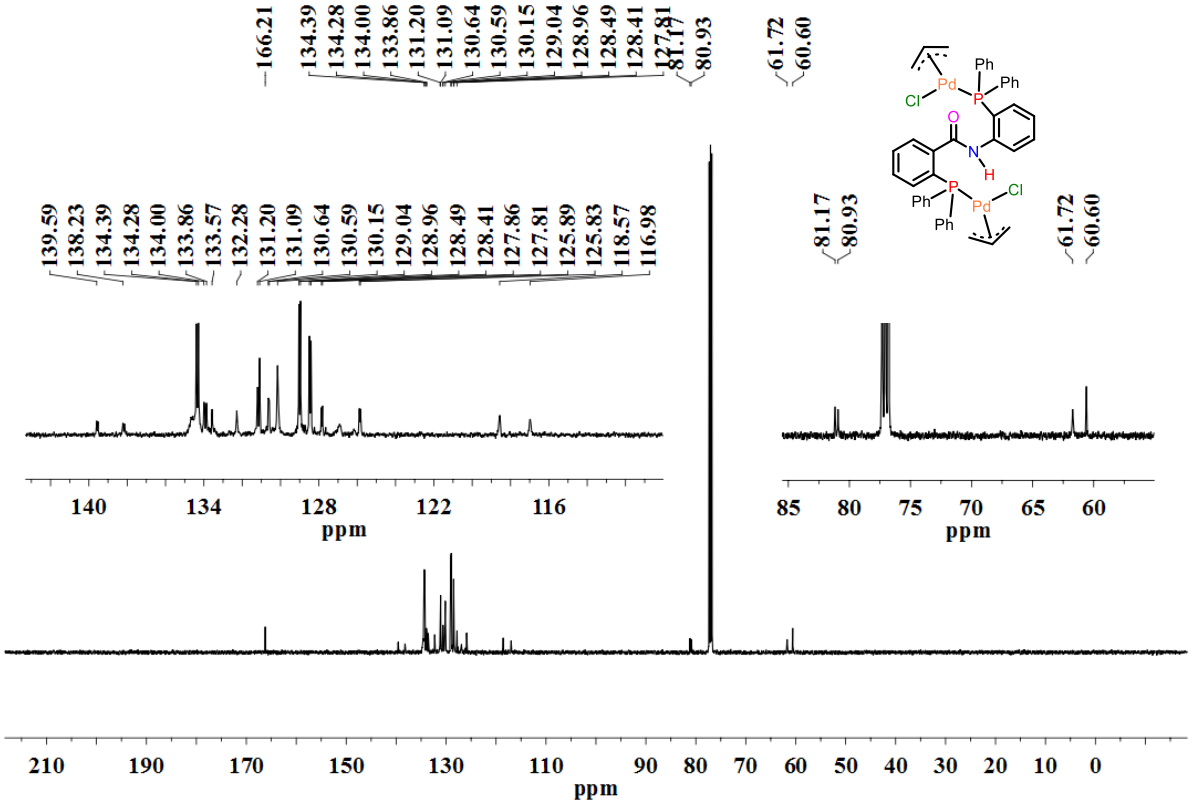
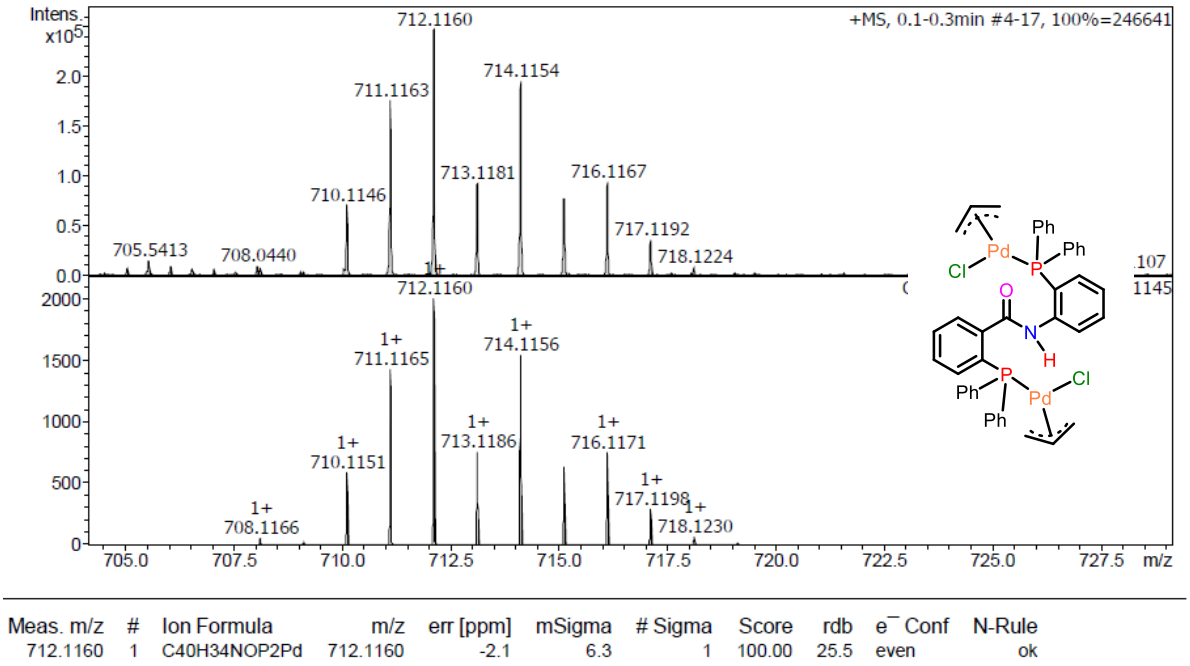


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ (126 MHz).



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
712.1160	1	C40H34NOP2Pd	712.1160	-2.1	6.3	1	100.00	25.5	even	ok

Figure S23. HRMS spectrum of **4**

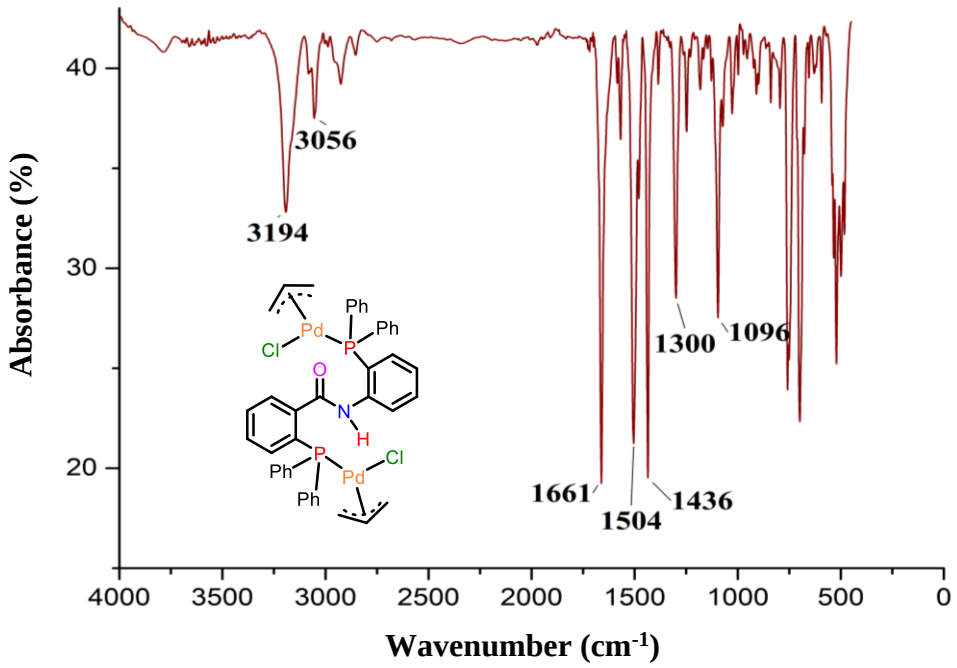


Figure S24. FT-IR spectrum of **4**

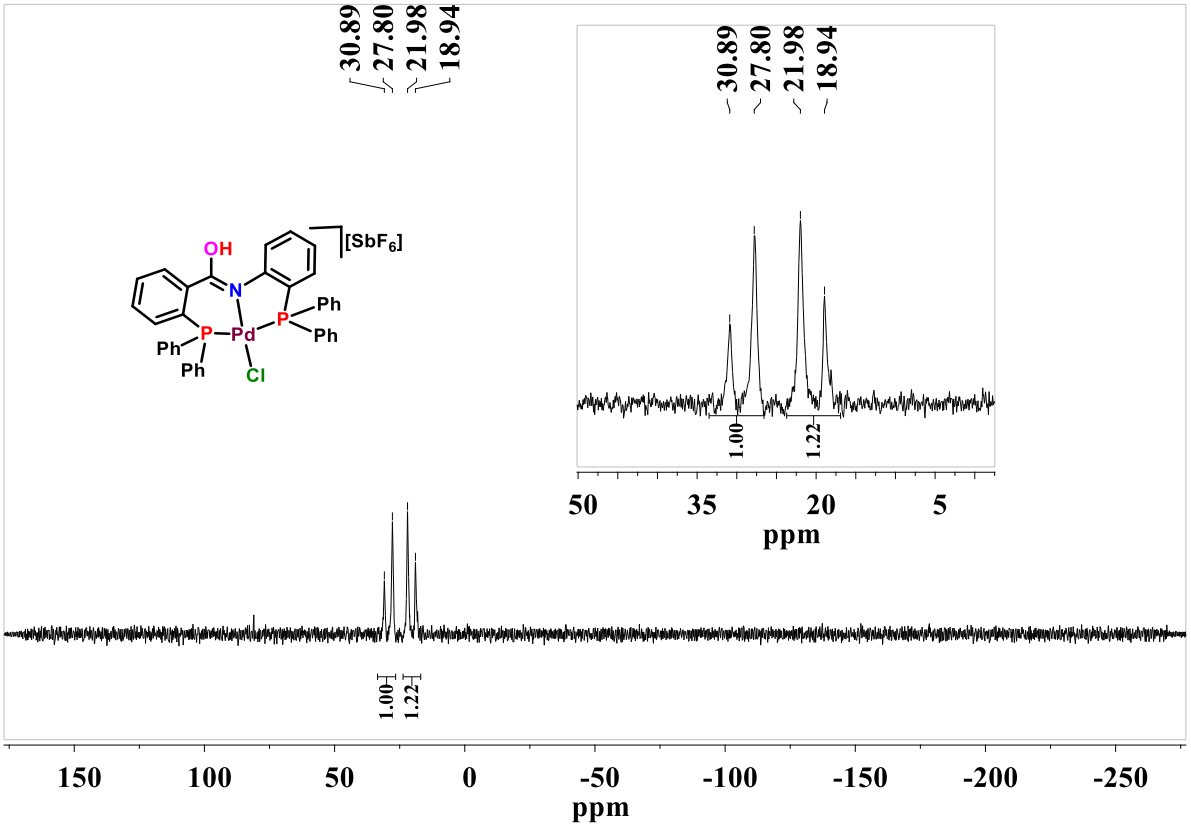


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ (162 MHz)

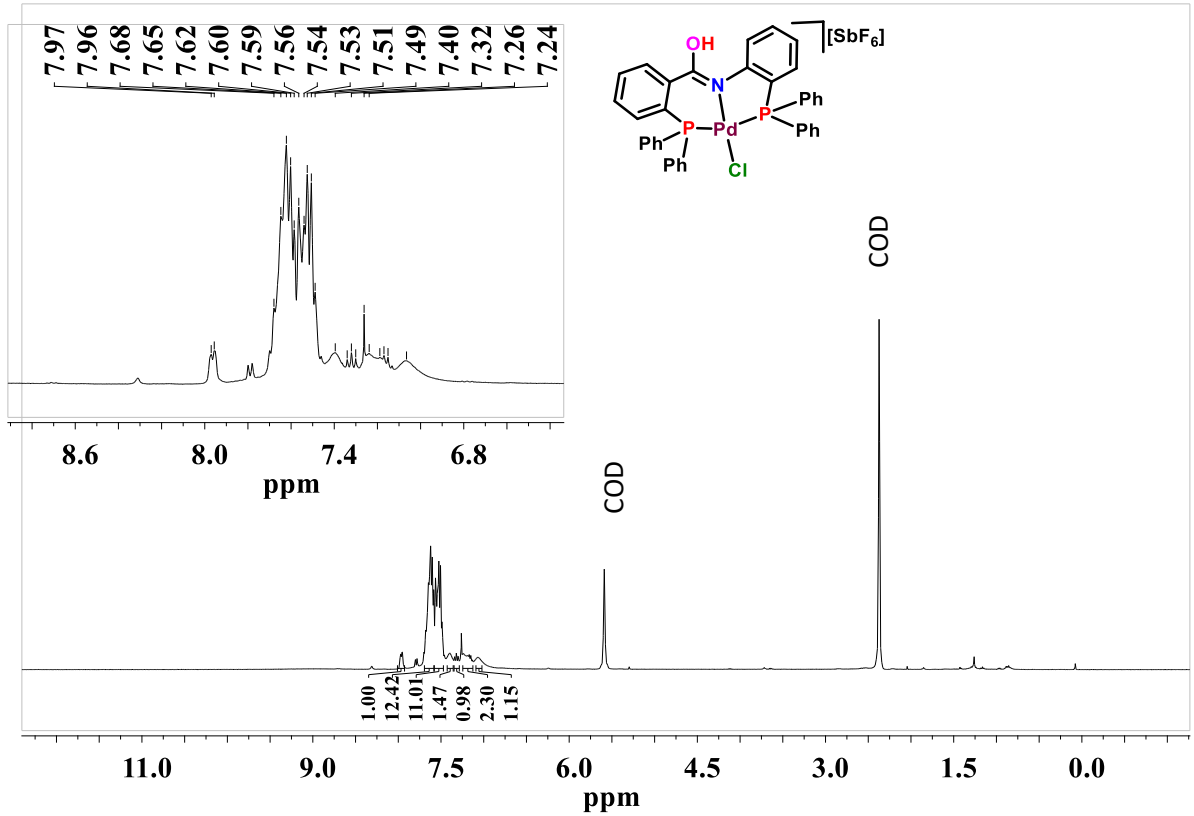


Figure S26. ^{1}H NMR spectrum of **5** in $CDCl_3$ (500 MHz)

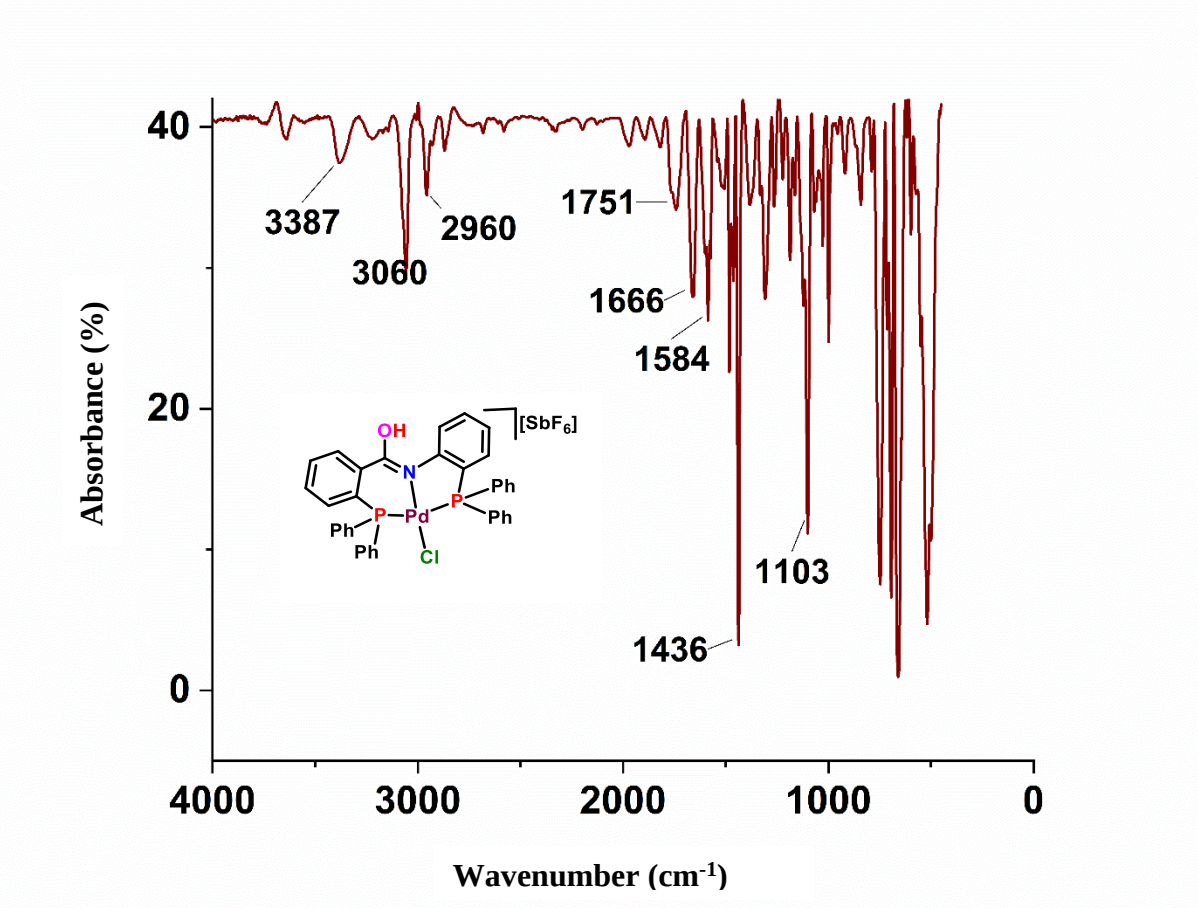
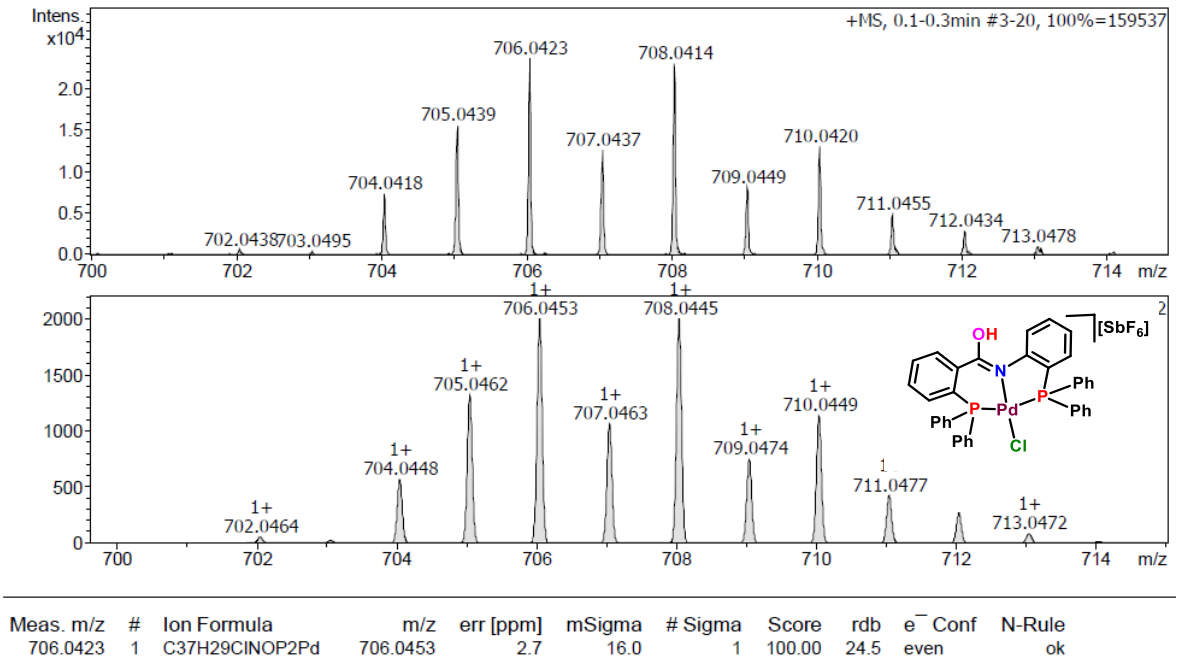


Figure S27. FT-IR spectrum of **5**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
706.0423	1	C37H29ClNOP2Pd	706.0453	2.7	16.0	1	100.00	24.5	even	ok

Figure S28. HRMS spectrum of **5**

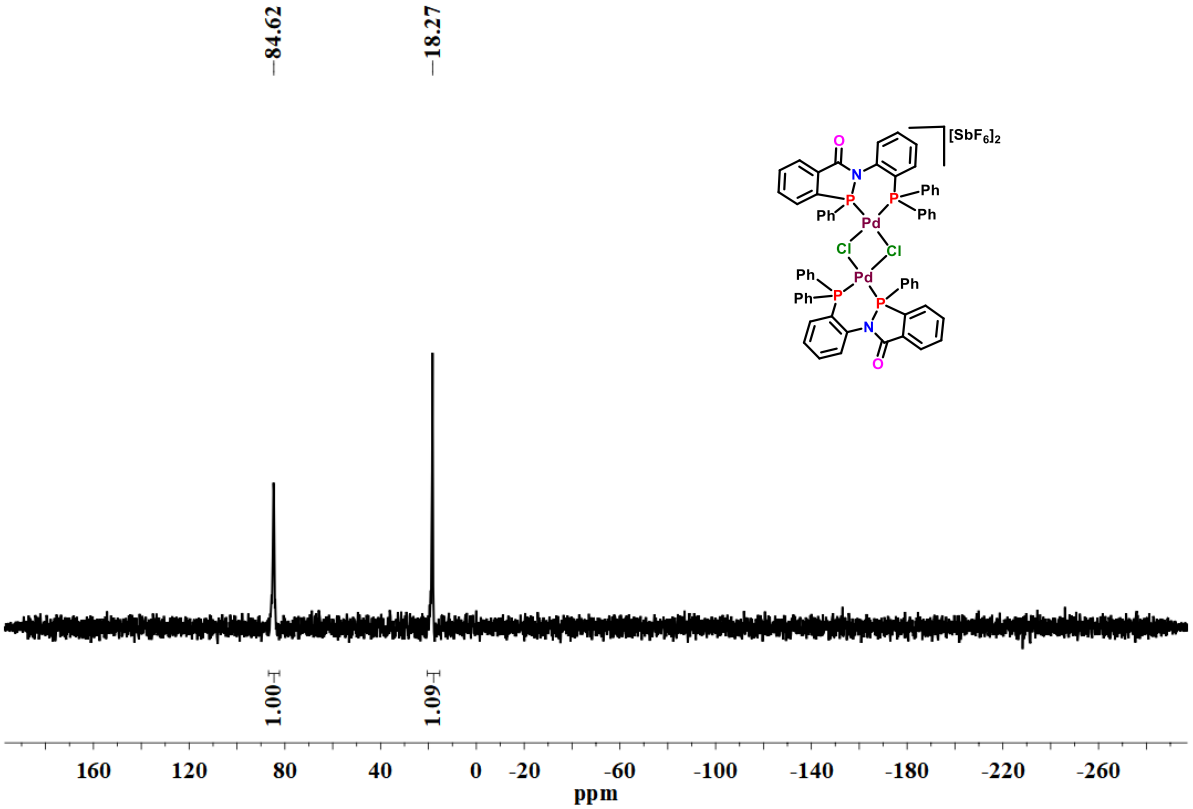


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in DMSO-d_6 (202 MHz)

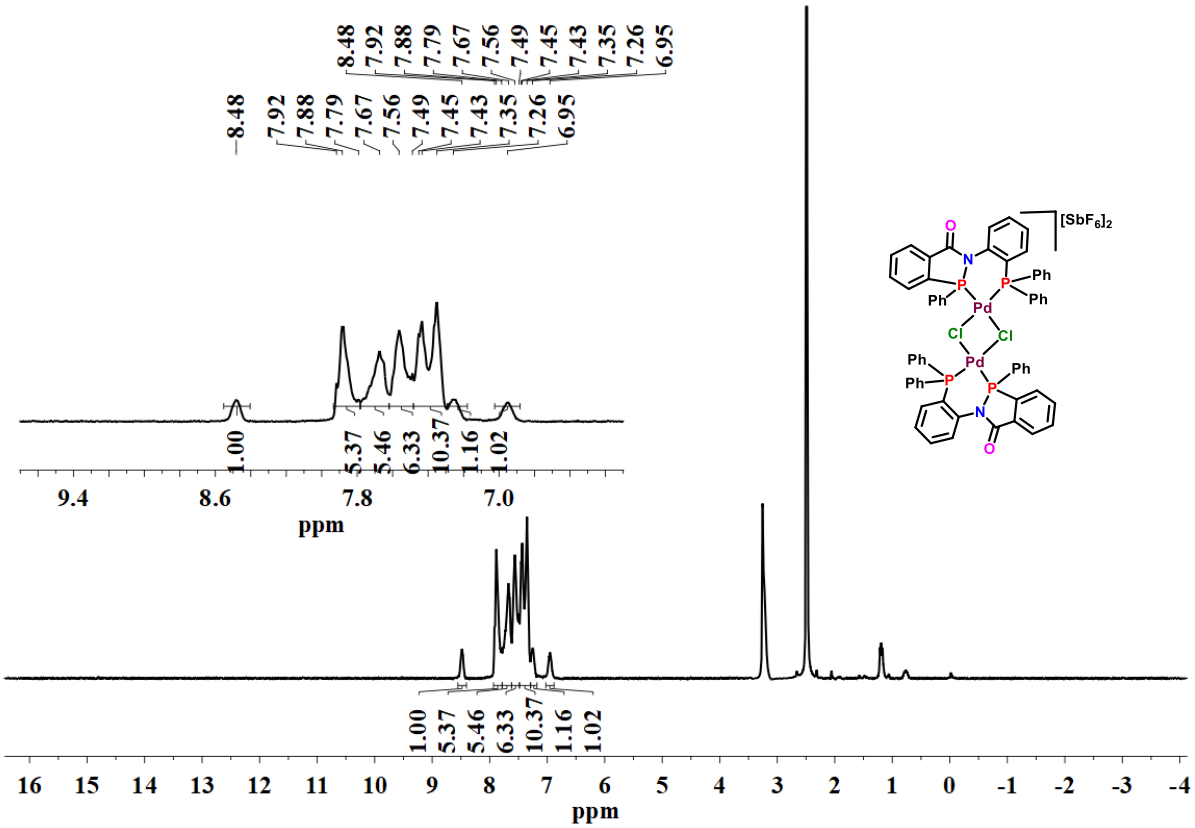


Figure S30. ^{1}H NMR spectrum of **6** in DMSO-d_6 (400 MHz)

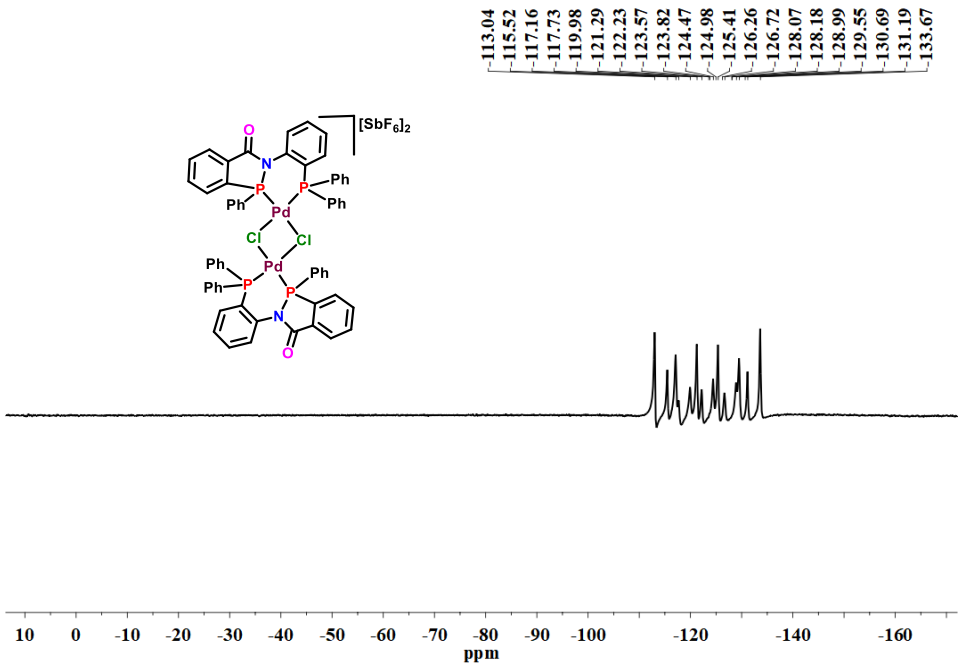


Figure S31. ^{19}F{^{1}H} NMR spectrum of **6** in DMSO-d_6 (162 MHz)

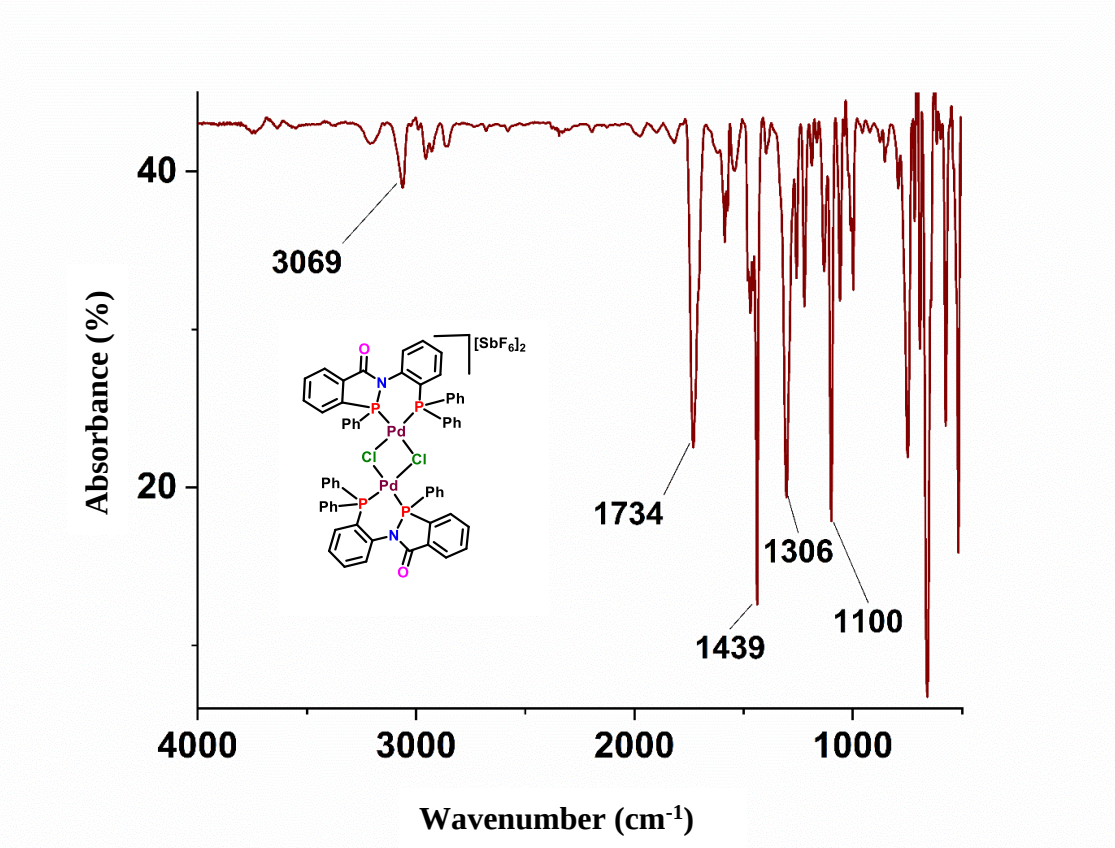


Figure S32. FT-IR spectrum of **6**

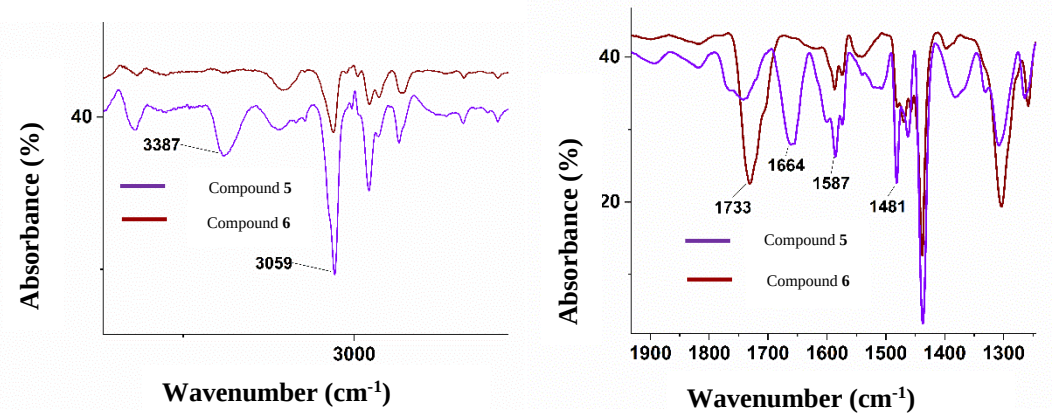


Figure S33. Stack plot of FT-IR spectra of **5** and **6**

V. Evedience of mechanism for the complex 2

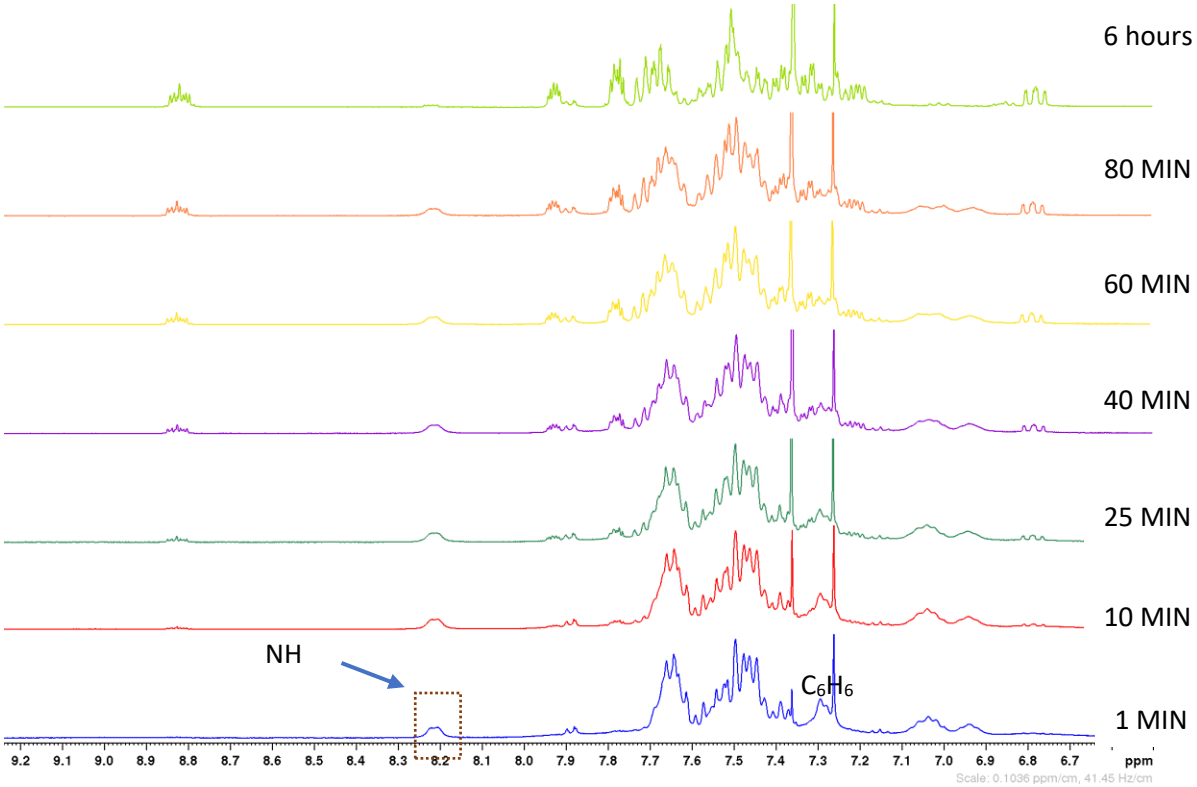


Figure S34. Stack plots of ^{1}H NMR spectrum of ligand **1** and [Pd(COD)Cl$_2$] with variable time.

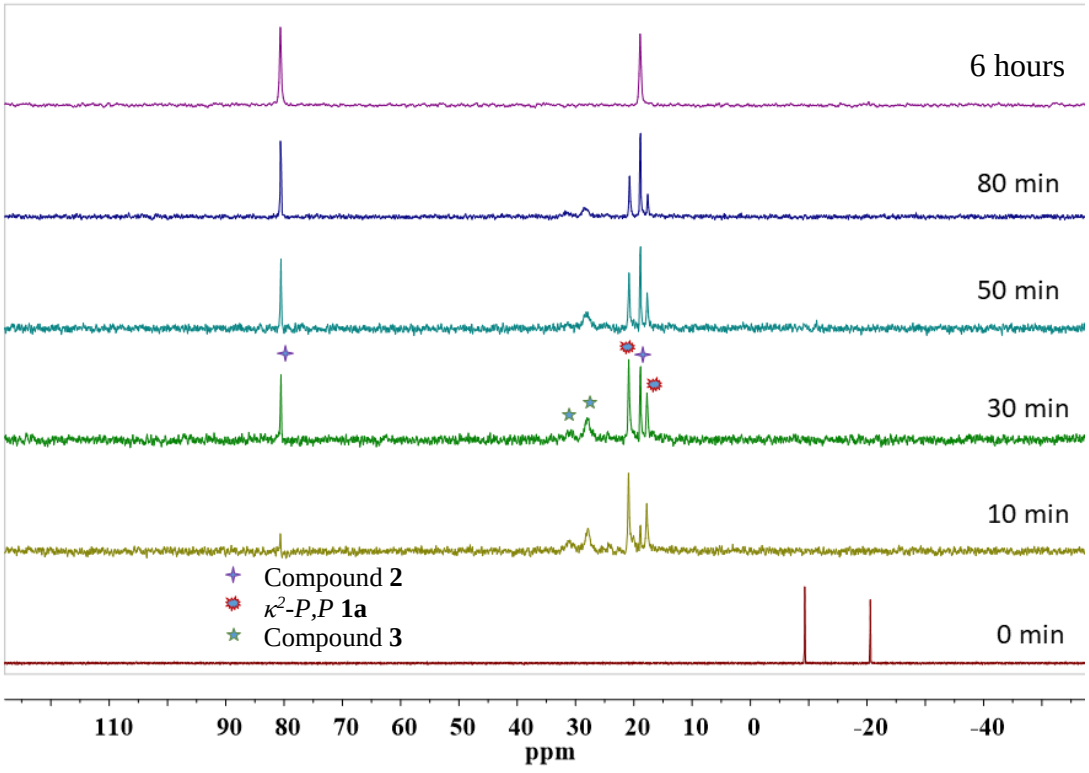
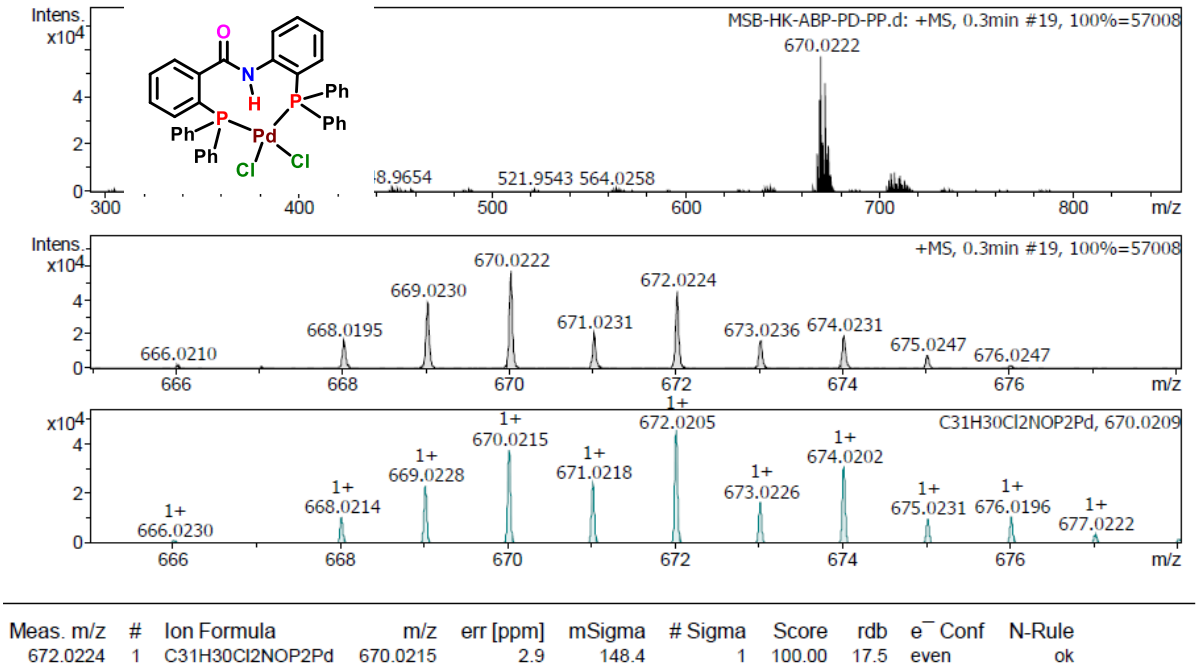


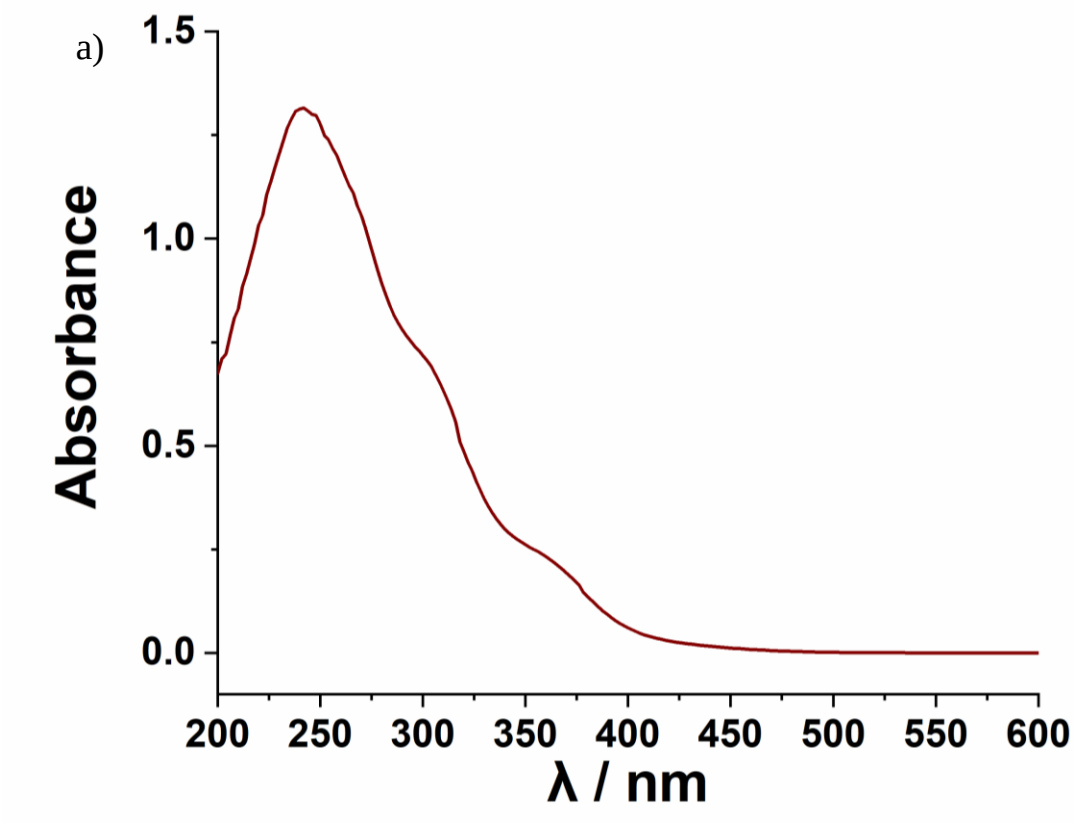
Figure S35. Stack plots of ^{1}H NMR spectrum of ligand **1** and [Pd(COD)Cl$_2$] with variable time.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
672.0224	1	C31H30Cl2NOP2Pd	670.0215	2.9	148.4	1	100.00	17.5	even	ok

Figure S36: HRMS spectrum of intermediate κ^2-*P*,*P* **1a** complex.

V. Kinetic study for complex 2



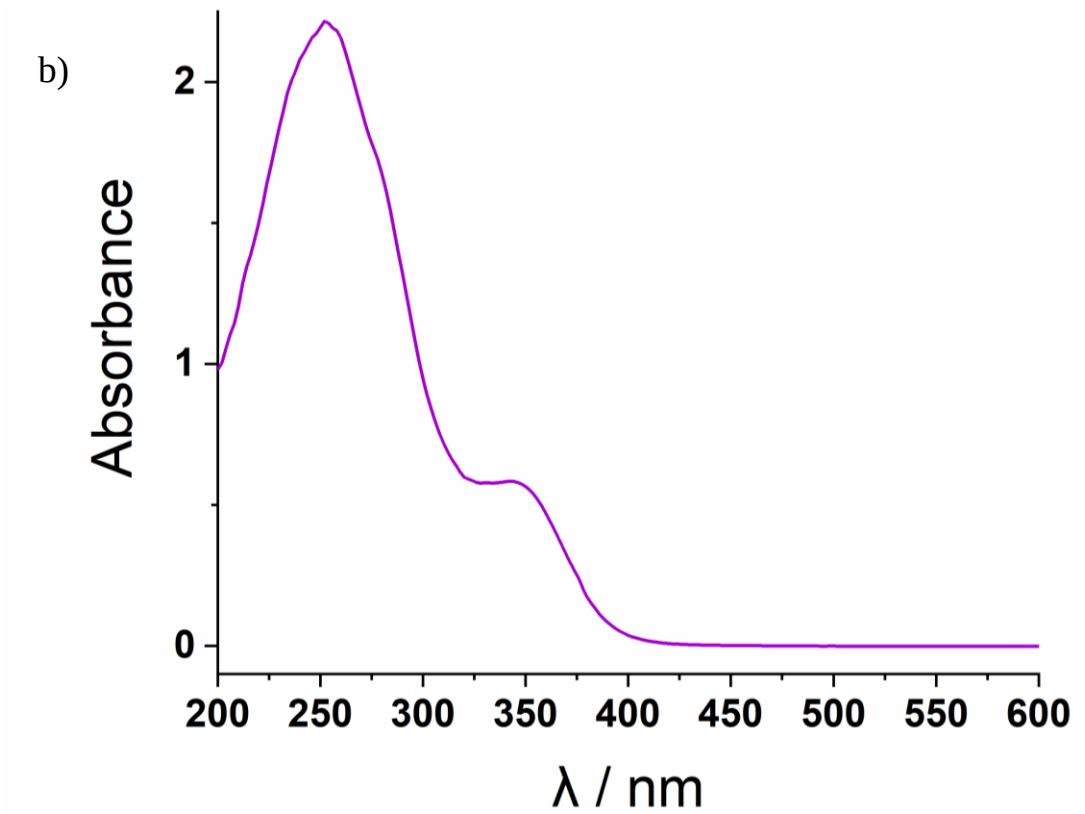
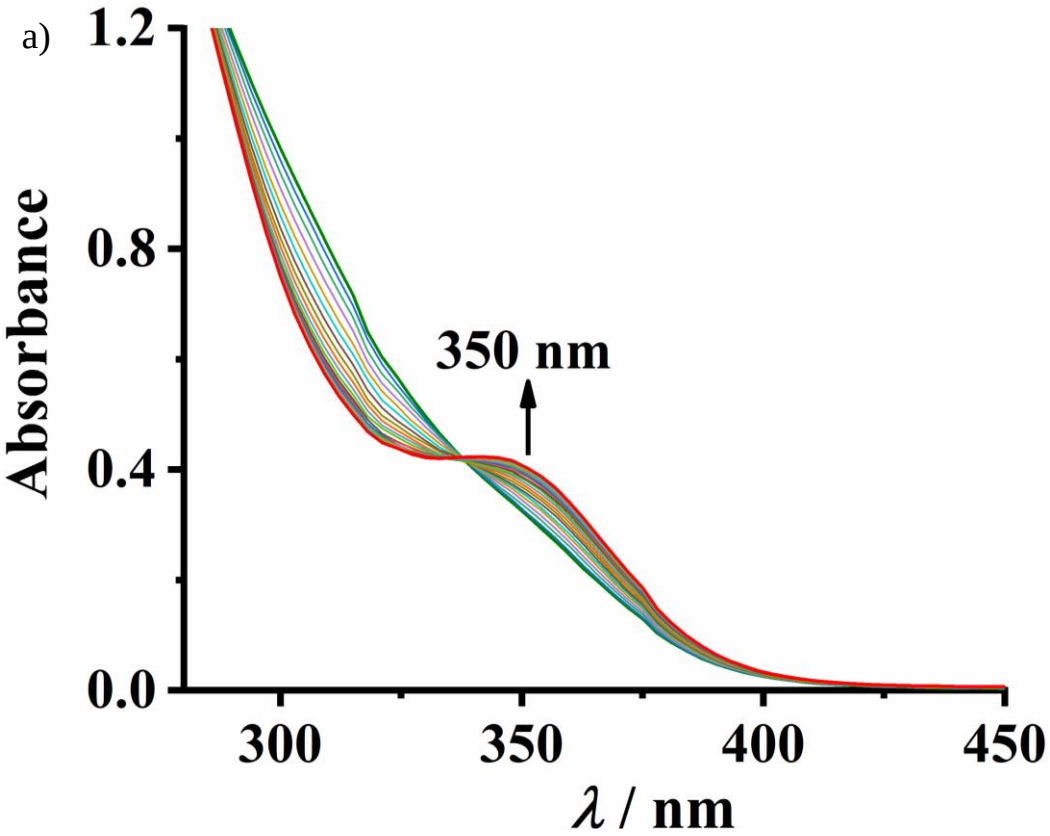


Figure S37. UV/Visible absorption spectra of **3** (a) and **2** (b) recorded in acetonitrile (2×10^{-4} M).



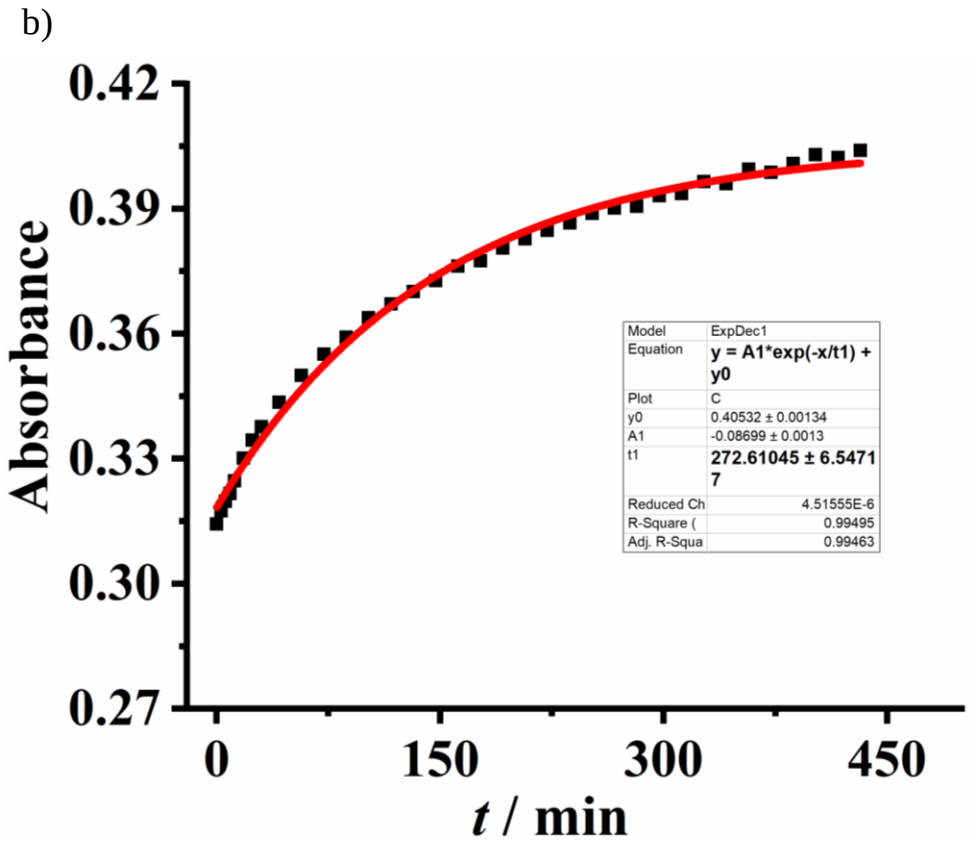
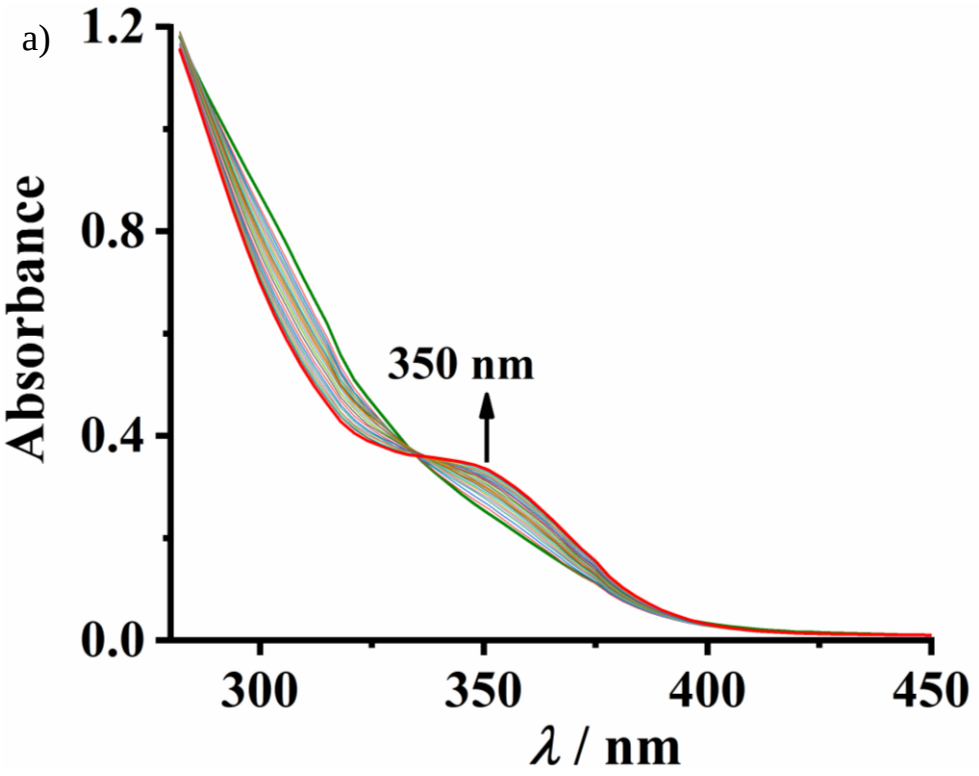


Figure S38. (a) UV−vis change at 350 nm for **3**→ **2** conversion at 298.15 K. (b) Rate constant is calculated based on the growing feature of absorbance of 350 nm band as a function of time (t).



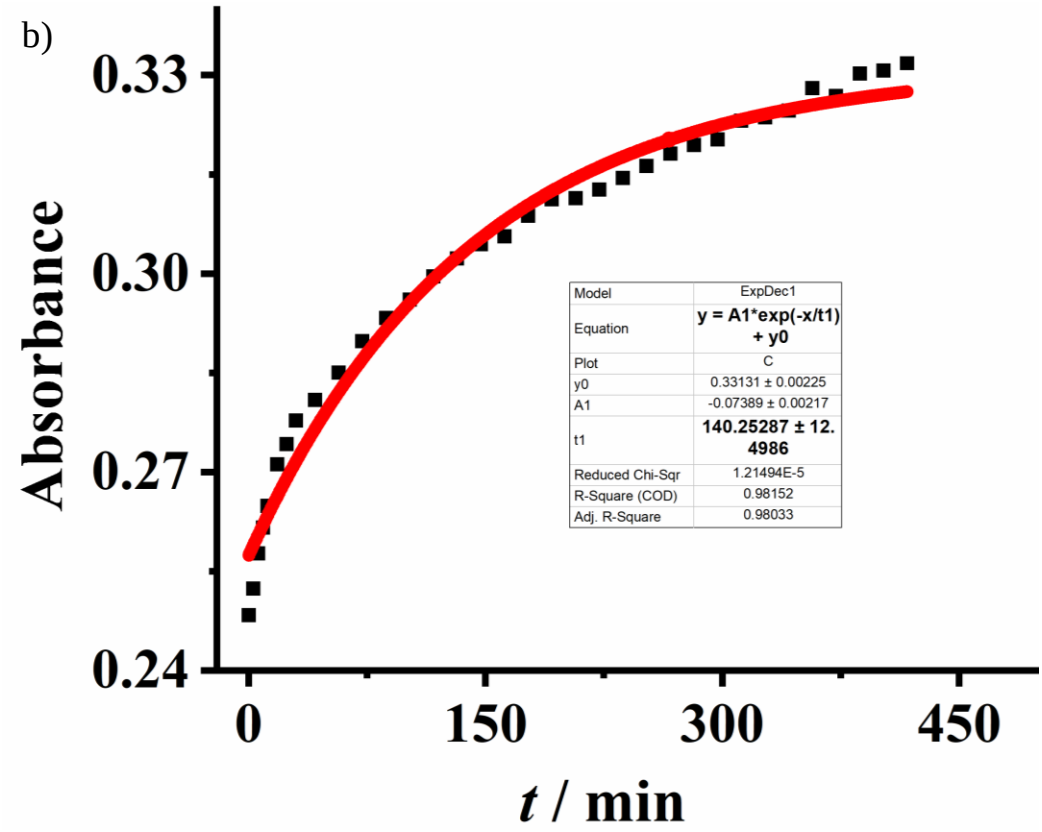
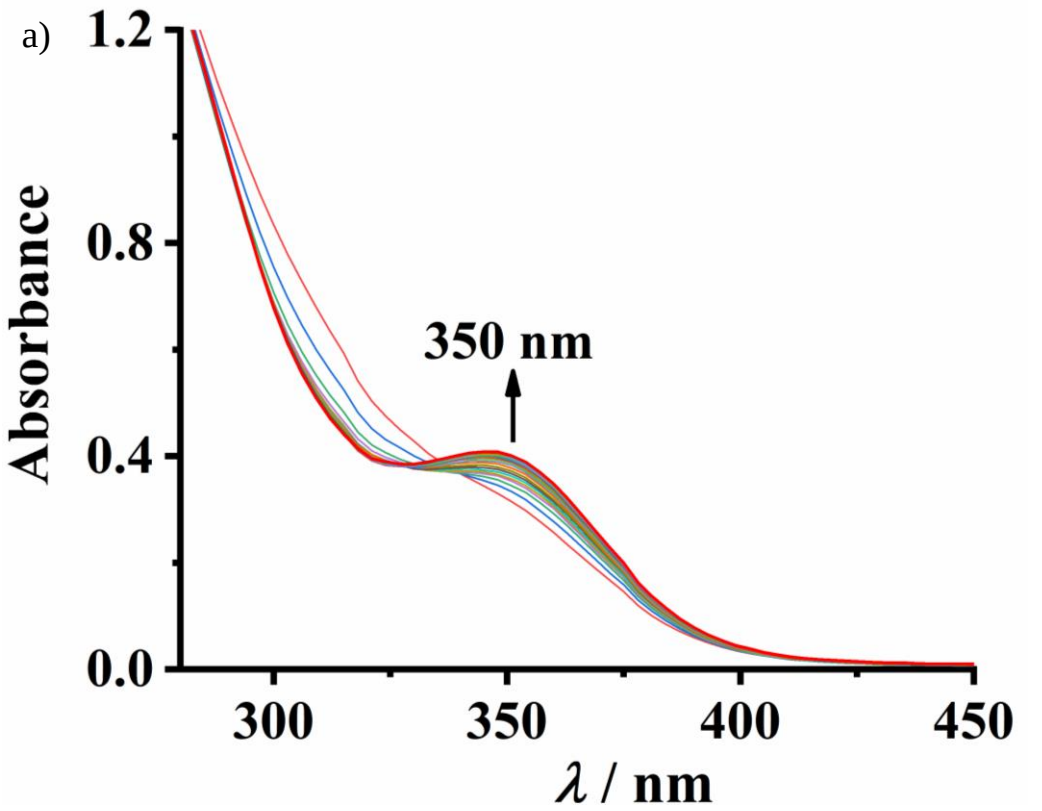


Figure S39. (a) UV−vis change at 350 nm for **3**→ **2** conversion at 308.15 K. (b) Rate constant is calculated based on the growing feature of absorbance of 350 nm band as a function of time (t).



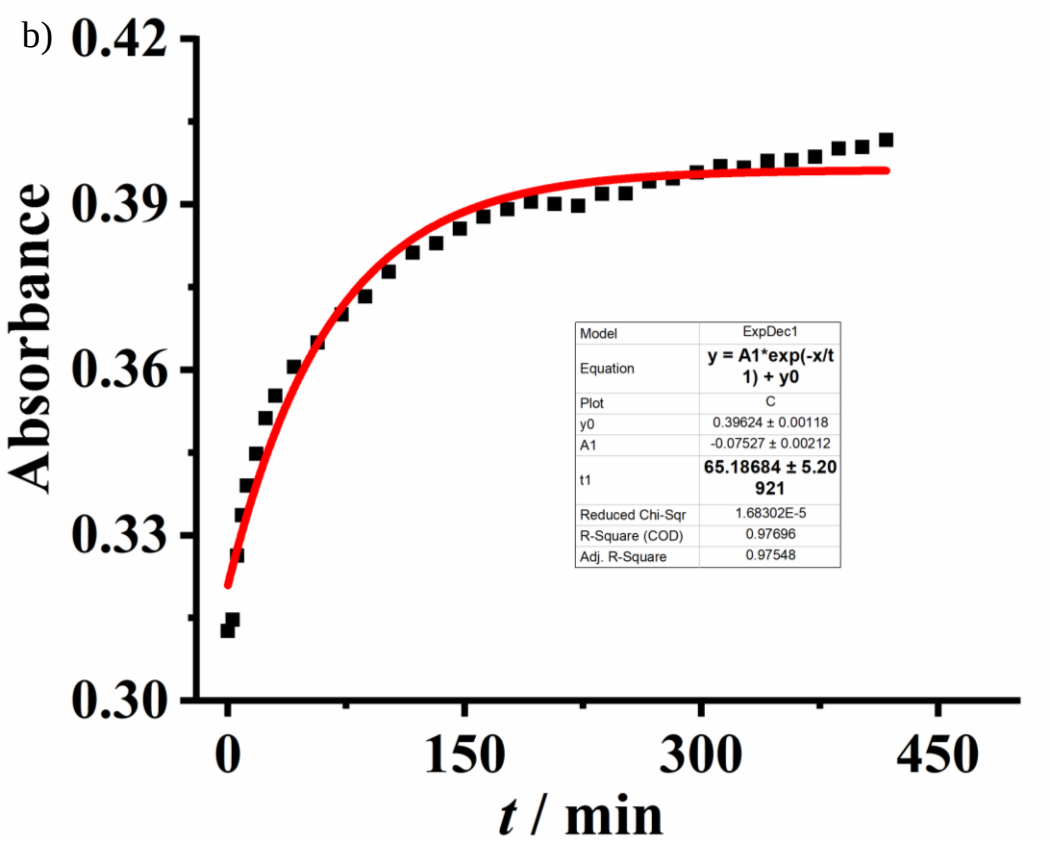


Figure S40. (a) UV−vis change at 350 nm for **3**→ **2** conversion at 318.15 K. (b) Rate constant is calculated based on the growing feature of absorbance of 350 nm band as a function of time (t).

Table S4. Temperature Dependent Kinetic Data

Temp. (K)	$K(s^{-1})$ [=1/(t1*60)]	ln(k/T)	1/T x 10^{-3}
318.15	2.6 x 10^{-4}	-14.03	3.143
308.15	1.2 x 10^{-4}	-14.75	3.245
298.15	6.7 x 10^{-5}	-15.30	3.354

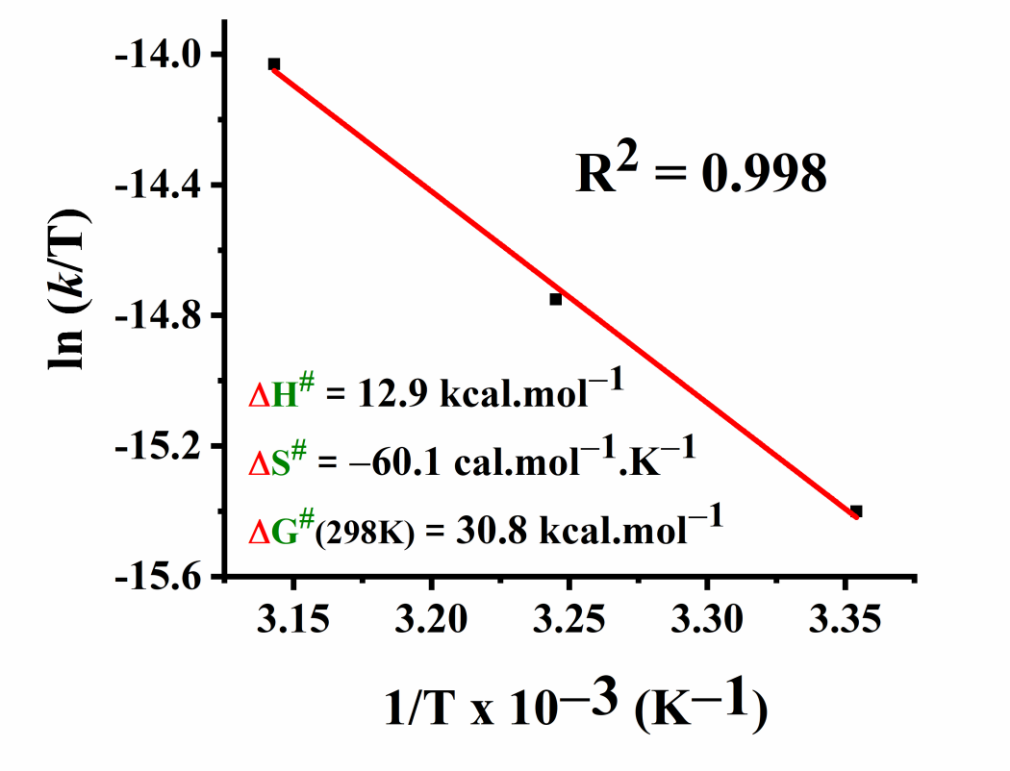


Figure S41. Plot of ln(k/T) versus 1/T for the reaction of **3**→ **2**.

Activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) values were obtained from the slope and intercept of plots of ln(k/T) versus 1/T, respectively, using the following equation:

$$\ln(k/T) = \ln(R/Nh) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$$

where N = Avogadro's number, R = universal gas constant, and h = Planck's constant.

VI. Optimized Cartesian Coordinates of Various Reactants, Products, Intermediates and Transition States

The optimized coordinates of all the stationary points obtained at the SMD/B3LYP/6-31G**, SDD(Pd) level of theory.

1

Number of imaginary frequencies: 0

The smallest frequencies are: 12.66 13.22 16.64 cm^{-1}

Electronic energy: HF= -2240.15156655

Zero-point correction= 0.555010 (Hartree/Particle)

Thermal correction to Energy= 0.590246

Thermal correction to Enthalpy= 0.591191

Thermal correction to Gibbs Free Energy= 0.481768

Sum of electronic and zero-point Energies= -2239.596557

Sum of electronic and thermal Energies= -2239.561320

Sum of electronic and thermal Enthalpies= -2239.560376

Sum of electronic and thermal Free Energies= -2239.669798

……..

Cartesian Coordinates

……..

P	-2.25917100	0.53904900	-0.22621800
P	2.44674000	0.44060700	-0.36278300
O	-0.91733600	-3.36000300	0.93661600
C	-3.01202000	0.00342600	1.37815400
N	0.16717500	-1.40145900	0.40860000
H	0.24484400	-0.69644000	-0.31875500
C	2.22941200	-0.43003800	1.26247600
C	-3.54541900	1.66600900	-0.93808400
C	4.78496000	2.07739000	0.03601300
H	5.38577000	1.23175400	-0.28372200
C	2.63563200	3.07773600	0.51215900

H	1.55104800	3.01133300	0.55417800
C	-3.09142000	2.67680000	-1.80264200
H	-2.03131800	2.75234100	-2.03197900
C	4.43300000	-1.63607400	-0.66492100
H	4.31276700	-1.85982600	0.39006600
C	-3.19312300	-0.98851300	-2.44636900
H	-3.77096200	-0.10555800	-2.69462000
C	-1.66857500	-2.17111900	-0.99218500
C	-3.26712900	-2.09861700	-3.28909900
H	-3.88735200	-2.05484100	-4.18009600
C	3.12918500	-0.26535400	2.32626600
H	3.98250400	0.39282900	2.19711100
C	-3.90695000	-1.06984900	1.52181900
H	-4.19241500	-1.65935500	0.65614600
C	3.38785900	1.96073600	0.10722700
C	-1.78138700	-3.29385800	-1.82452700
H	-1.23812000	-4.19472500	-1.55665900
C	3.26610600	4.27371400	0.85702400
H	2.67016500	5.12623000	1.17110400
C	3.69352500	-0.59789300	-1.25206200
C	1.10703600	-1.27873400	1.45335900
C	-2.65167300	0.73909700	2.52031200
H	-1.94665500	1.56182300	2.42988500
C	3.86215600	-0.34282000	-2.62533900

H	3.28289000	0.44401700	-3.10288800
C	-4.91609000	1.60115100	-0.63740300
H	-5.28847100	0.83506300	0.03559800
C	-0.79070200	-2.36687100	0.22291700
C	-2.39982300	-0.99215900	-1.28655300
C	2.95562800	-0.92772200	3.54106700
H	3.67153900	-0.78716400	4.34551800
C	5.49671700	-2.11883800	-2.78836300
H	6.19144200	-2.70802700	-3.38046100
C	5.41415200	3.27949400	0.37112200
H	6.49653000	3.35451300	0.30980800
C	5.32605900	-2.39189300	-1.42965200
H	5.88893500	-3.19399600	-0.95988100
C	4.65805600	4.37836900	0.78447100
H	5.14934600	5.31232600	1.04277900
C	-3.98602600	3.58841500	-2.36808400
H	-3.61863800	4.36169000	-3.03706200
C	-2.56228900	-3.26078300	-2.97738900
H	-2.62145200	-4.13384800	-3.62051700
C	0.93414800	-1.94688900	2.67720000
H	0.08078600	-2.59728500	2.80668900
C	4.76364400	-1.08913600	-3.38494800
H	4.88503100	-0.87400400	-4.44305100
C	-4.43317300	-1.39137800	2.77529300

H	-5.12281900	-2.22565500	2.87085300
C	-5.80871400	2.51901900	-1.19425800
H	-6.86574400	2.45847900	-0.94957800
C	-5.34659200	3.51222100	-2.06249900
H	-6.04316300	4.22608700	-2.49338500
C	-4.07699200	-0.64430500	3.90080700
H	-4.48687400	-0.89717400	4.87472100
C	1.85706400	-1.77253400	3.70588100
H	1.70580600	-2.29624300	4.64576500
C	-3.18509000	0.42301500	3.77101800
H	-2.89742000	1.00374100	4.64308000

$Pd(COD)Cl_2$

Number of imaginary frequencies: 0

The smallest frequencies are: 69.2918 86.1300 140.4821 cm^{-1}

Electronic energy:HF=-1360.4966365

Zero-point correction= 0.185409 (Hartree/Particle)

Thermal correction to Energy= 0.197591

Thermal correction to Enthalpy= 0.198535

Thermal correction to Gibbs Free Energy= 0.146507

Sum of electronic and zero-point Energies= -1360.311227

Sum of electronic and thermal Energies= -1360.299045

Sum of electronic and thermal Enthalpies= -1360.298101

Sum of electronic and thermal Free Energies= -1360.350130

……

Cartesian Coordinates

……

46	0.496577	-0.000007	-0.000109
17	2.145836	-1.682887	0.209154
17	2.145983	1.682717	-0.209145
6	-1.007380	1.556642	0.576935
6	-1.146161	1.344614	-0.789790
6	-2.239112	0.521857	-1.451651
6	-1.834483	-0.949549	-1.686386
6	-1.007656	-1.556617	-0.576786
6	-1.146187	-1.344516	0.789946
6	-2.239090	-0.521604	1.451671
6	-1.833939	0.949568	1.686743
1	-0.369970	2.384416	0.877962
1	-0.576954	2.002054	-1.442670
1	-2.468520	0.977159	-2.419041
1	-3.151556	0.582413	-0.853231
1	-1.246586	-1.018454	-2.606936
1	-2.726840	-1.571546	-1.846916
1	-0.370276	-2.384424	-0.877921
1	-0.576962	-2.001804	1.442813
1	-2.468974	-0.977012	2.418881

1	-3.151341	-0.581715	0.852917
1	-2.725933	1.571815	1.847882
1	-1.245507	1.017947	2.607055

TS[3b-3c]

Number of imaginary frequencies: 1

The smallest frequencies are: -108.4613 11.2629 25.5391 cm^{-1}

Electronic energy:HF=-2827.7336801

Zero-point correction= 0.545234 (Hartree/Particle)

Thermal correction to Energy= 0.582935

Thermal correction to Enthalpy= 0.583880

Thermal correction to Gibbs Free Energy= 0.471492

Sum of electronic and zero-point Energies= -2827.188446

Sum of electronic and thermal Energies= -2827.150745

Sum of electronic and thermal Enthalpies= -2827.149801

Sum of electronic and thermal Free Energies= -2827.262188

…….....

Cartesian Coordinates

……..

15	-1.798379	0.233477	-0.106468
15	1.936011	0.229262	0.084649
8	-1.112509	-4.067108	0.637825
6	-2.191509	-0.029897	1.669005

7	0.026057	-2.058813	0.279380
6	2.036827	-1.169645	1.245076
6	-2.818544	1.695953	-0.574077
6	1.319862	2.952250	0.231242
1	1.199901	2.889313	-0.846057
6	1.793410	1.895878	2.365935
1	2.040237	1.019228	2.953697
6	-2.376671	2.496134	-1.640405
1	-1.455251	2.239189	-2.157666
6	4.283077	1.566208	-0.798096
1	3.852709	2.484583	-0.415475
6	-3.527893	-0.941570	-2.001786
1	-3.922367	0.061011	-2.120065
6	-2.026005	-2.514916	-0.901815
6	-4.040251	-1.965665	-2.794553
1	-4.816450	-1.745492	-3.521707
6	3.120780	-1.237321	2.137716
1	3.893079	-0.473787	2.110742
6	-2.967110	-1.102217	2.135574
1	-3.365374	-1.835304	1.442694
6	1.657157	1.805182	0.972119
6	-2.580219	-3.533842	-1.690358
1	-2.218698	-4.545232	-1.537194
6	1.604168	3.122836	3.006187

1	1.711960	3.184401	4.085124
6	3.587546	0.352023	-0.692262
6	1.032083	-2.180692	1.219530
6	-1.698397	0.909917	2.590856
1	-1.103513	1.749614	2.245615
6	4.170452	-0.827893	-1.189873
1	3.638639	-1.771489	-1.118260
6	-4.004375	2.042187	0.095172
1	-4.361408	1.436893	0.922274
6	-0.970767	-2.950598	0.104877
6	-2.520593	-1.187771	-1.046877
6	3.214695	-2.275989	3.058068
1	4.051355	-2.322205	3.748147
6	6.122545	0.422064	-1.879481
1	7.106451	0.449077	-2.338766
6	1.133227	4.173227	0.878239
1	0.874951	5.054225	0.298212
6	5.548126	1.595605	-1.388780
1	6.083201	2.537915	-1.460398
6	1.274787	4.260170	2.266656
1	1.125483	5.211248	2.769504
6	-3.112503	3.613662	-2.039754
1	-2.761719	4.222954	-2.867892
6	-3.564208	-3.269600	-2.638969

1	-3.962459	-4.076036	-3.247991
6	1.153221	-3.224620	2.175978
1	0.404165	-4.003354	2.174368
6	5.431938	-0.790057	-1.777650
1	5.874858	-1.705515	-2.158321
6	-3.239085	-1.231888	3.499492
1	-3.841828	-2.065953	3.847510
6	-4.733259	3.164387	-0.301156
1	-5.648682	3.422559	0.223811
6	-4.290107	3.950731	-1.368317
1	-4.859465	4.824523	-1.672408
6	-2.745822	-0.294539	4.409266
1	-2.960783	-0.398521	5.468994
6	2.217256	-3.259088	3.069022
1	2.278803	-4.079207	3.780320
6	-1.977030	0.778608	3.951407
1	-1.590512	1.513315	4.652026
46	0.303353	-0.263196	-1.332390
17	1.384166	-0.118749	-3.461478

1a

Number of imaginary frequencies: 0

The smallest frequencies are: 11.4301 26.6476 30.8794 cm^{-1}

Electronic energy:HF=-3288.6001837

Zero-point correction= 0.561088 (Hartree/Particle)

Thermal correction to Energy= 0.601131

Thermal correction to Enthalpy= 0.602075

Thermal correction to Gibbs Free Energy= 0.486005

Sum of electronic and zero-point Energies= -3288.039096

Sum of electronic and thermal Energies= -3287.999053

Sum of electronic and thermal Enthalpies= -3287.998109

Sum of electronic and thermal Free Energies= -3288.114178

…….....

Cartesian Coordinates

…….....

15	-1.759669	-0.318996	-0.068121
15	2.055244	0.039445	0.107906
8	-1.596747	3.904654	-0.497462
6	-2.537348	0.537139	-1.499204
7	-0.017425	2.270700	-0.051242
1	0.201955	1.644932	0.711763
6	2.103339	1.567485	-0.949719
6	-2.839784	-1.746529	0.401350
6	4.629411	-0.583745	1.110315
1	4.288709	-0.181523	2.056858
6	4.244469	-1.163401	-1.208422
1	3.589064	-1.225808	-2.069698

6	-2.303330	-2.731391	1.247806
1	-1.268574	-2.665342	1.571465
6	2.387147	1.863397	2.273365
1	2.826305	2.551977	1.557914
6	-2.756723	0.374238	2.511801
1	-2.899868	-0.690574	2.641325
6	-1.993661	2.273555	1.235661
6	-3.228902	1.232719	3.507545
1	-3.695141	0.811710	4.393327
6	3.179216	1.812693	-1.818866
1	4.035857	1.152584	-1.815662
6	-3.773809	1.196793	-1.379096
1	-4.293802	1.224276	-0.427312
6	3.773295	-0.621450	0.000920
6	-2.516332	3.128196	2.211439
1	-2.409513	4.199784	2.074486
6	5.554610	-1.626849	-1.309584
1	5.906131	-2.035670	-2.252312
6	1.905324	0.612159	1.850501
6	1.019146	2.485239	-0.964799
6	-1.874431	0.546222	-2.735573
1	-0.917860	0.045555	-2.834547
6	1.347055	-0.267904	2.792815
1	0.974187	-1.236576	2.472160

6	-4.167606	-1.866950	-0.028662
1	-4.600676	-1.130749	-0.695688
6	-1.219198	2.917965	0.122360
6	-2.143015	0.867862	1.349267
6	3.175915	2.896437	-2.695191
1	4.023878	3.056318	-3.353706
6	1.751901	1.343093	4.551002
1	1.690848	1.628008	5.597347
6	5.937609	-1.065820	1.007974
1	6.588062	-1.031586	1.877084
6	2.303081	2.225735	3.618417
1	2.671983	3.196286	3.936771
6	6.404320	-1.582259	-0.200199
1	7.422357	-1.952883	-0.278618
6	-3.085827	-3.807483	1.666589
1	-2.656528	-4.561189	2.320442
6	-3.131107	2.613913	3.351273
1	-3.520157	3.285090	4.110811
6	1.012762	3.572096	-1.851500
1	0.171303	4.251241	-1.839025
6	1.277201	0.095741	4.138226
1	0.849334	-0.593104	4.860530
6	-4.342891	1.829815	-2.484436
1	-5.300254	2.332059	-2.380438

6	-4.944973	-2.952147	0.384515
1	-5.970430	-3.037088	0.036282
6	-4.409592	-3.921398	1.233866
1	-5.016789	-4.764029	1.552014
6	-3.680447	1.825406	-3.714278
1	-4.123783	2.323102	-4.572049
6	2.084741	3.765068	-2.718219
1	2.069272	4.608355	-3.402506
6	-2.444419	1.187965	-3.836416
1	-1.919881	1.188786	-4.787464
46	0.328473	-1.434732	-0.606292
17	1.895312	-3.240872	-0.659014
17	-1.045094	-2.778937	-2.074371

TS[3d-3e]

Number of imaginary frequencies: 1

The smallest frequencies are: -82.3539 12.4882 20.6167 cm^{-1}

Electronic energy: HF=-2827.7675116

Zero-point correction= 0.545853 (Hartree/Particle)

Thermal correction to Energy= 0.583205

Thermal correction to Enthalpy= 0.584149

Thermal correction to Gibbs Free Energy= 0.473496

Sum of electronic and zero-point Energies= -2827.221658

Sum of electronic and thermal Energies= -2827.184306

Sum of electronic and thermal Enthalpies= -2827.183362

Sum of electronic and thermal Free Energies= -2827.294016

…….....

Cartesian Coordinates

…….....

15	1.579754	0.060565	0.132884
15	-1.921151	0.079235	-0.009275
8	0.651230	3.933769	-0.208904
6	2.336305	-0.055640	1.801828
7	0.654779	1.710458	0.465145
6	-1.582673	1.217777	1.388328
6	2.091276	-1.823809	-0.591018
6	-4.739872	-0.269280	-0.112500
1	-4.763904	0.569990	-0.799661
6	-3.513353	-1.812433	1.296363
1	-2.572890	-2.183481	1.691984
6	2.214638	-2.031805	-1.982259
1	1.884599	-1.263392	-2.675542
6	-2.619761	2.490708	-1.349232
1	-2.682185	2.954989	-0.370569
6	3.826340	0.619029	-1.634902
1	4.181991	-0.398975	-1.537249
6	2.272480	2.386714	-1.082590

6	4.538521	1.524443	-2.427370
1	5.435950	1.190967	-2.939999
6	-2.515814	1.408514	2.422052
1	-3.476553	0.908467	2.375818
6	3.592830	0.504666	2.075700
1	4.155345	1.000652	1.291569
6	-3.519718	-0.721605	0.411273
6	2.973807	3.287339	-1.883062
1	2.631797	4.315319	-1.948091
6	-4.709185	-2.430009	1.661387
1	-4.692084	-3.272962	2.346259
6	-2.261289	1.139892	-1.470429
6	-0.332043	1.874376	1.466528
6	1.625547	-0.690864	2.832884
1	0.653277	-1.131166	2.630574
6	-2.180068	0.558093	-2.747116
1	-1.898940	-0.486417	-2.848415
6	2.518512	-2.849715	0.278116
1	2.422697	-2.728716	1.352048
6	1.109250	2.791079	-0.246213
6	2.671049	1.047098	-0.970196
6	-2.231417	2.241807	3.501709
1	-2.973192	2.384961	4.281762
6	-2.817675	2.662293	-3.757282

1	-3.031511	3.253587	-4.643139
6	-5.934514	-0.897351	0.248389
1	-6.873679	-0.540908	-0.164982
6	-2.893971	3.246927	-2.491445
1	-3.166294	4.293442	-2.388806
6	-5.921859	-1.974689	1.136039
1	-6.852124	-2.462481	1.413203
6	2.770651	-3.208965	-2.485634
1	2.856516	-3.352425	-3.559007
6	4.108637	2.848489	-2.564443
1	4.667930	3.537879	-3.190079
6	-0.052580	2.699053	2.567327
1	0.913733	3.189499	2.617514
6	-2.462332	1.316370	-3.883614
1	-2.400181	0.856825	-4.865883
6	4.129179	0.426056	3.362216
1	5.104040	0.861155	3.563139
6	3.087163	-4.019954	-0.224396
1	3.427905	-4.792751	0.458983
6	3.211723	-4.200385	-1.605749
1	3.649342	-5.115261	-1.995549
6	3.419577	-0.208443	4.384542
1	3.840984	-0.267910	5.383867
6	-0.996135	2.890500	3.572216

1	-0.764892	3.539474	4.411878
6	2.167229	-0.765960	4.118009
1	1.609459	-1.261304	4.907551
46	-0.105184	-1.301593	-0.391644
17	-1.259044	-3.328707	-1.195012

3

Number of imaginary frequencies: 0

The smallest frequencies are: 12.6345 15.9471 21.0703 cm^{-1}

Electronic energy: HF=-2827.7948742

Zero-point correction= 0.546309 (Hartree/Particle)

Thermal correction to Energy= 0.584409

Thermal correction to Enthalpy= 0.585353

Thermal correction to Gibbs Free Energy= 0.470449

Sum of electronic and zero-point Energies= -2827.248565

Sum of electronic and thermal Energies= -2827.210465

Sum of electronic and thermal Enthalpies= -2827.209521

Sum of electronic and thermal Free Energies= -2827.324425

……..

Cartesian Coordinates

……..

15	-2.264003	0.262202	-0.058161
15	2.379201	0.207594	-0.036655

8	-0.262045	-3.726749	0.106219
6	-2.816375	-0.167816	1.637588
7	0.093019	-1.486130	0.445421
6	2.341921	-1.051284	1.284658
6	-3.394398	1.585117	-0.636558
6	4.696840	1.847502	-0.034099
1	5.052920	1.256937	-0.871378
6	3.013139	2.345059	1.638318
1	2.049618	2.141175	2.096892
6	-3.176531	2.159546	-1.901657
1	-2.352121	1.817871	-2.518901
6	3.916625	-1.721473	-1.440605
1	4.025552	-2.241811	-0.494523
6	-3.685772	-1.210419	-1.993778
1	-4.379579	-0.377308	-1.996403
6	-1.703339	-2.305251	-1.098077
6	-3.894165	-2.270325	-2.876859
1	-4.743196	-2.248899	-3.553844
6	3.385516	-1.278966	2.190401
1	4.306622	-0.710033	2.105998
6	-3.826281	-1.114245	1.868876
1	-4.298002	-1.625850	1.035584
6	3.456385	1.565227	0.555343
6	-1.940696	-3.364861	-1.986353

1	-1.269991	-4.215379	-1.949013
6	3.806136	3.381658	2.127254
1	3.455770	3.978149	2.964621
6	3.195192	-0.520330	-1.508112
6	1.129743	-1.771081	1.378422
6	-2.214575	0.482225	2.727601
1	-1.425549	1.209444	2.556616
6	3.054247	0.133421	-2.744970
1	2.489486	1.059051	-2.810742
6	-4.453917	2.052166	0.155866
1	-4.635970	1.623613	1.135308
6	-0.557296	-2.543460	-0.124329
6	-2.590126	-1.202057	-1.116922
6	3.235448	-2.218209	3.210121
1	4.039447	-2.387872	3.919822
6	4.356959	-1.600188	-3.819175
1	4.804566	-2.021186	-4.714942
6	5.484242	2.892714	0.456013
1	6.443220	3.103431	-0.008591
6	4.493659	-2.256986	-2.594581
1	5.048341	-3.188890	-2.533575
6	5.042386	3.659291	1.535052
1	5.656096	4.472085	1.912796
6	-4.017780	3.168195	-2.369249

1	-3.843070	3.601965	-3.349595
6	-3.009185	-3.346967	-2.880431
1	-3.154070	-4.175969	-3.567016
6	0.991477	-2.711075	2.414324
1	0.068185	-3.267818	2.509176
6	3.638339	-0.403442	-3.892336
1	3.525212	0.109454	-4.843076
6	-4.227836	-1.403869	3.174607
1	-5.007778	-2.140280	3.345690
6	-5.287408	3.070156	-0.314073
1	-6.105097	3.422471	0.308181
6	-5.073405	3.627010	-1.575679
1	-5.723598	4.417679	-1.939227
6	-3.628170	-0.752072	4.254903
1	-3.940544	-0.982184	5.269533
6	2.032289	-2.922539	3.317378
1	1.897173	-3.643568	4.119052
6	-2.623662	0.193020	4.030161
1	-2.152498	0.699379	4.867644
46	0.059742	0.489436	-0.192004
17	0.131777	2.753994	-0.882566

3b.log

Number of imaginary frequencies: 0

The smallest frequencies are: 17.9168 24.9213 27.1754 cm^{-1}

Electronic energy: HF=-3288.6014158

Zero-point correction= 0.560275 (Hartree/Particle)

Thermal correction to Energy= 0.600563

Thermal correction to Enthalpy= 0.601507

Thermal correction to Gibbs Free Energy= 0.483213

Sum of electronic and zero-point Energies= -3288.041141

Sum of electronic and thermal Energies= -3288.000853

Sum of electronic and thermal Enthalpies= -3287.999909

Sum of electronic and thermal Free Energies= -3288.118203

……..

Cartesian Coordinates

……..

15	2.291613	-0.025829	-0.285047
15	-2.371386	0.132894	-0.225560
8	0.308161	2.347104	3.017471
6	2.929569	-1.056278	1.088129
7	-0.081910	0.691687	1.444182
6	-2.361958	-0.150662	1.588666
6	3.370355	-0.319743	-1.732588
6	-4.797723	-0.554085	-1.499803
1	-5.030837	0.505402	-1.506406
6	-3.300204	-2.391431	-0.951353

1	-2.370970	-2.774660	-0.530392
6	3.121980	0.382359	-2.925856
1	2.312211	1.103007	-2.976129
6	-3.699776	2.547158	0.460084
1	-3.925853	2.089790	1.418209
6	3.655431	2.438515	-0.304321
1	4.332369	1.948155	-0.993866
6	1.718217	2.379597	1.153219
6	3.877391	3.779302	0.021622
1	4.717375	4.306278	-0.420467
6	-3.419386	-0.699718	2.315271
1	-4.357390	-0.922233	1.816997
6	4.035089	-0.645427	1.853447
1	4.524631	0.302002	1.649075
6	-3.591721	-1.015814	-0.948714
6	1.960781	3.725822	1.476265
1	1.305509	4.228366	2.176486
6	-4.221341	-3.289624	-1.490090
1	-3.990457	-4.350953	-1.484820
6	-2.982476	1.835619	-0.513550
6	-1.138832	0.121044	2.237803
6	2.306731	-2.283944	1.363841
1	1.443014	-2.623607	0.795041
6	-2.701169	2.443822	-1.749630

1	-2.143012	1.902277	-2.508173
6	4.408746	-1.262319	-1.691030
1	4.608241	-1.820924	-0.783177
6	0.587443	1.728991	1.867698
6	2.578856	1.723767	0.232513
6	-3.264287	-0.998454	3.673039
1	-4.087725	-1.438765	4.226120
6	-3.852134	4.448143	-1.032367
1	-4.187066	5.461892	-1.231960
6	-5.708668	-1.463117	-2.041707
1	-6.640631	-1.099922	-2.465322
6	-4.130288	3.849851	0.198504
1	-4.684521	4.394347	0.957559
6	-5.422565	-2.829849	-2.037019
1	-6.132564	-3.534788	-2.460430
6	3.915545	0.157625	-4.049128
1	3.718086	0.707645	-4.964596
6	3.020968	4.427147	0.905951
1	3.174349	5.470733	1.161429
6	-0.973420	-0.208216	3.588111
1	-0.011797	-0.074317	4.074194
6	-3.140122	3.742724	-2.006642
1	-2.921031	4.204744	-2.964758
6	4.511934	-1.458718	2.881779

1	5.366162	-1.136454	3.470308
6	5.193201	-1.490005	-2.824255
1	5.993113	-2.223458	-2.782089
6	4.951537	-0.779912	-4.000890
1	5.562691	-0.960009	-4.880648
6	3.892028	-2.682290	3.152893
1	4.264068	-3.312765	3.955658
6	-2.041953	-0.765514	4.299116
1	-1.901588	-1.032675	5.341801
6	2.794068	-3.091639	2.394030
1	2.302785	-4.037902	2.599442
46	-0.039228	-0.082035	-0.498163
17	-0.128313	-0.907983	-2.683908
1	-0.509209	1.995229	3.419776
17	-0.584150	-4.415298	0.477933

3c

Number of imaginary frequencies: 0

The smallest frequencies are: 19.7720 30.1419 34.1007 cm^{-1}

Electronic energy : HF=-2827.7431567

Zero-point correction= 0.546502 (Hartree/Particle)

Thermal correction to Energy= 0.584521

Thermal correction to Enthalpy= 0.585465

Thermal correction to Gibbs Free Energy= 0.473841

Sum of electronic and zero-point Energies= -2827.196655

Sum of electronic and thermal Energies= -2827.158636

Sum of electronic and thermal Enthalpies= -2827.157692

Sum of electronic and thermal Free Energies= -2827.269316

……..

Cartesian Coordinates

……..

15	-1.631103	0.101210	-0.082537
15	1.769312	0.118163	0.044476
8	-1.000422	-4.237199	0.559767
6	-1.790736	0.388028	1.726744
7	-0.467345	-1.962877	0.694195
6	1.689373	-1.086279	1.408365
6	-2.459423	1.648505	-0.734976
6	1.623299	2.889571	-0.230311
1	1.394685	2.668380	-1.268876
6	2.108119	2.142024	2.023973
1	2.248525	1.350788	2.750659
6	-2.056583	2.187160	-1.968290
1	-1.248744	1.723434	-2.531350
6	4.265395	0.872441	-1.096313
1	3.980764	1.903393	-0.919591
6	-3.915072	-0.931567	-1.388840

1	-4.175344	0.100483	-1.587963
6	-2.439572	-2.604851	-0.423479
6	-4.754138	-1.940943	-1.863399
1	-5.647512	-1.675653	-2.421074
6	2.784166	-1.131403	2.296878
1	3.607062	-0.433450	2.173337
6	-2.452365	-0.526628	2.560448
1	-2.843636	-1.453459	2.157619
6	1.832291	1.839769	0.681719
6	-3.293134	-3.602280	-0.903640
1	-3.023709	-4.633053	-0.698978
6	2.187514	3.473096	2.439797
1	2.400005	3.694842	3.481580
6	3.414509	-0.178616	-0.723749
6	0.629005	-2.035976	1.525406
6	-1.304794	1.585772	2.271859
1	-0.818480	2.317763	1.637574
6	3.811873	-1.506121	-0.962186
1	3.161951	-2.329797	-0.684083
6	-3.509757	2.276977	-0.042014
1	-3.850630	1.882090	0.909278
6	-1.211222	-3.025942	0.349609
6	-2.755809	-1.244357	-0.656216
6	2.847961	-2.069694	3.319065

1	3.699335	-2.087101	3.992366
6	5.888370	-0.722367	-1.925914
1	6.846790	-0.932895	-2.391774
6	1.707752	4.217187	0.190502
1	1.548061	5.018444	-0.525014
6	5.497899	0.597090	-1.693140
1	6.151830	1.418421	-1.971714
6	1.990956	4.511089	1.526958
1	2.052281	5.544515	1.855603
6	-2.676400	3.322935	-2.493934
1	-2.345014	3.723047	-3.447992
6	-4.443657	-3.280001	-1.621189
1	-5.094204	-4.067811	-1.990238
6	0.734355	-2.992175	2.570579
1	-0.051027	-3.731113	2.661174
6	5.042694	-1.773264	-1.557090
1	5.339848	-2.802683	-1.734823
6	-2.617276	-0.247341	3.916745
1	-3.138341	-0.959961	4.549592
6	-4.131120	3.411161	-0.568318
1	-4.940557	3.883013	-0.018386
6	-3.714714	3.938918	-1.793114
1	-4.196866	4.823894	-2.198650
6	-2.114199	0.938538	4.459170

1	-2.238315	1.149567	5.517501
6	1.809354	-3.001420	3.446570
1	1.845890	-3.748761	4.235425
6	-1.458366	1.853099	3.634446
1	-1.068319	2.779968	4.044686
46	0.155177	-0.186186	-1.522318
17	1.286347	-0.668673	-3.560715

3d

Number of imaginary frequencies: 0

The smallest frequencies are: 8.3207 23.2356 30.4271 cm^{-1}

Electronic energy: HF=-2827.7675618

Zero-point correction= 0.546118 (Hartree/Particle)

Thermal correction to Energy= 0.584261

Thermal correction to Enthalpy= 0.585205

Thermal correction to Gibbs Free Energy= 0.471963

Sum of electronic and zero-point Energies= -2827.221444

Sum of electronic and thermal Energies= -2827.183301

Sum of electronic and thermal Enthalpies= -2827.182356

Sum of electronic and thermal Free Energies= -2827.295599

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Cartesian Coordinates

…….....

15	-1.609226	-0.004361	0.112576
15	1.898814	-0.109443	-0.009957
8	-0.742665	-3.924090	-0.284656
6	-2.326537	0.058300	1.802151
7	-0.684605	-1.709706	0.417542
6	1.539505	-1.256252	1.372020
6	-2.110249	1.829206	-0.537177
6	4.721361	0.191835	-0.100658
1	4.731631	-0.635362	-0.802549
6	3.519974	1.734329	1.330648
1	2.585550	2.117318	1.729104
6	-2.166713	2.091133	-1.925998
1	-1.880765	1.318457	-2.633797
6	2.560862	-2.511674	-1.380728
1	2.612814	-2.989308	-0.407969
6	-3.856079	-0.527682	-1.651613
1	-4.195282	0.494535	-1.538954
6	-2.326843	-2.325324	-1.128007
6	-4.586479	-1.410298	-2.452735
1	-5.480936	-1.055767	-2.956464
6	2.460304	-1.465061	2.413934
1	3.423292	-0.967995	2.387720
6	-3.588976	-0.488939	2.075565
1	-4.171750	-0.946906	1.283039

6	3.508254	0.660878	0.424677
6	-3.046852	-3.203336	-1.937315
1	-2.721286	-4.235601	-2.016574
6	4.726732	2.318242	1.714379
1	4.723882	3.147914	2.415488
6	2.223082	-1.154210	-1.485975
6	0.285091	-1.908714	1.422289
6	-1.589655	0.642926	2.844689
1	-0.612304	1.072720	2.645368
6	2.155663	-0.554947	-2.755255
1	1.891568	0.494972	-2.844194
6	-2.472897	2.868753	0.349375
1	-2.421645	2.709602	1.421183
6	-1.168558	-2.766543	-0.301483
6	-2.704097	-0.981267	-0.996751
6	2.160529	-2.315840	3.475027
1	2.892147	-2.474905	4.261520
6	2.764616	-2.655629	-3.790077
1	2.972494	-3.238836	-4.682684
6	5.927268	0.785809	0.279973
1	6.860958	0.416137	-0.134145
6	2.827672	-3.257325	-2.531557
1	3.083944	-4.308999	-2.441220
6	5.932502	1.846347	1.187595

1	6.871529	2.307270	1.480673
6	-2.614322	3.322573	-2.408916
1	-2.655829	3.501594	-3.479400
6	-4.177562	-2.738784	-2.608474
1	-4.749974	-3.411591	-3.240343
6	-0.008575	-2.752358	2.506512
1	-0.976691	-3.240703	2.537272
6	2.430216	-1.302994	-3.900361
1	2.378573	-0.829990	-4.876831
6	-4.105311	-0.447232	3.371971
1	-5.084897	-0.872167	3.571759
6	-2.927440	4.094044	-0.133903
1	-3.223400	4.873620	0.562319
6	-2.999157	4.321338	-1.512800
1	-3.351253	5.279019	-1.885894
6	-3.370224	0.138387	4.405343
1	-3.775953	0.169630	5.412404
6	0.922581	-2.963334	3.518178
1	0.680426	-3.626768	4.343447
6	-2.112081	0.682695	4.139491
1	-1.533865	1.139808	4.937377
46	0.132760	1.321394	-0.394503
17	1.350833	3.322448	-1.155857

3e

Number of imaginary frequencies: 0

The smallest frequencies are: 16.2767 20.5277 31.5930 cm^{-1}

Electronic energy: HF=-2827.7915968

Zero-point correction= 0.546166 (Hartree/Particle)

Thermal correction to Energy= 0.584161

Thermal correction to Enthalpy= 0.585105

Thermal correction to Gibbs Free Energy= 0.472695

Sum of electronic and zero-point Energies= -2827.245430

Sum of electronic and thermal Energies= -2827.207436

Sum of electronic and thermal Enthalpies= -2827.206492

Sum of electronic and thermal Free Energies= -2827.318901

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Cartesian Coordinates

…….....

15	-1.393390	-0.507087	0.265919
15	1.913902	0.058607	-0.019658
8	-0.327694	-3.981792	-1.015348
6	-2.213340	-0.591643	1.897655
7	-0.435100	-1.982590	0.162591
6	1.814813	-1.445515	1.050837
6	-1.916741	2.378517	-0.418731
6	4.633692	0.908541	0.018959

1	4.776088	0.328838	-0.887071
6	3.215166	1.718767	1.807055
1	2.241538	1.779664	2.285345
6	-2.401221	2.621702	-1.714791
1	-1.899846	2.187121	-2.576351
6	3.053832	-1.816067	-1.844395
1	3.281088	-2.439177	-0.985370
6	-3.717646	-0.591223	-1.490068
1	-4.074998	0.367411	-1.132634
6	-2.105598	-2.405201	-1.447444
6	-4.422982	-1.286134	-2.477845
1	-5.335044	-0.856860	-2.881791
6	2.858366	-1.791254	1.924640
1	3.749716	-1.175692	1.962129
6	-3.274564	-1.477354	2.148361
1	-3.661571	-2.110525	1.356187
6	3.376600	0.957342	0.637084
6	-2.804238	-3.093396	-2.438652
1	-2.440157	-4.055147	-2.786003
6	4.297528	2.404137	2.356976
1	4.160993	2.987827	3.262853
6	2.405955	-0.582445	-1.673277
6	0.666655	-2.267073	1.028595
6	-1.729007	0.224551	2.932003

1	-0.914379	0.916346	2.736747
6	2.114252	0.204409	-2.800856
1	1.612080	1.159185	-2.674977
6	-2.596162	2.958946	0.663127
1	-2.254577	2.791732	1.681178
6	-0.877885	-2.915995	-0.783279
6	-2.549510	-1.160726	-0.980617
6	2.777806	-2.920492	2.739413
1	3.605599	-3.168833	3.396800
6	3.117653	-1.462890	-4.239647
1	3.391676	-1.805703	-5.233400
6	5.713630	1.606560	0.567009
1	6.682585	1.565029	0.077633
6	3.406945	-2.251457	-3.123476
1	3.906062	-3.208458	-3.246095
6	5.549083	2.351197	1.735844
1	6.390159	2.892266	2.160015
6	-3.525632	3.428708	-1.923627
1	-3.878262	3.607112	-2.937040
6	-3.968265	-2.522456	-2.954121
1	-4.528407	-3.040998	-3.726328
6	0.582608	-3.390531	1.858423
1	-0.314780	-3.998589	1.829160
6	2.473344	-0.233990	-4.076408

1	2.244771	0.382568	-4.941098
6	-3.840585	-1.540688	3.421130
1	-4.664217	-2.222965	3.609900
6	-3.721411	3.768821	0.455831
1	-4.227728	4.212538	1.310206
6	-4.190462	4.005839	-0.837681
1	-5.063492	4.632703	-0.998926
6	-3.352934	-0.727701	4.449017
1	-3.798826	-0.779407	5.438115
6	1.637608	-3.723580	2.705040
1	1.562838	-4.601578	3.339438
6	-2.297200	0.152881	4.205168
1	-1.918740	0.787505	5.001033
46	-0.159007	1.330234	-0.182133
17	1.023696	3.363316	-0.766725

COD

Number of imaginary frequencies: 0

The smallest frequencies are: 70.7000 173.5203 187.6632 cm^{-1}

Electronic energy: HF=-312.0477261

Zero-point correction= 0.179680 (Hartree/Particle)

Thermal correction to Energy= 0.187418

Thermal correction to Enthalpy= 0.188362

Thermal correction to Gibbs Free Energy= 0.147594

Sum of electronic and zero-point Energies= -311.868047

Sum of electronic and thermal Energies= -311.860308

Sum of electronic and thermal Enthalpies= -311.859364

Sum of electronic and thermal Free Energies= -311.900132

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Cartesian Coordinates

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6	1.735378	-0.670652	-0.118282
6	0.658148	-1.587067	0.419623
6	-0.658147	1.587057	-0.419619
6	-0.660190	-1.586275	-0.419600
6	-1.735382	0.670656	0.118288
6	-1.736264	-0.668473	0.118271
1	0.412598	-1.325689	1.457217
1	-0.414336	-1.325276	-1.457216
1	-0.412591	1.325647	-1.457201
1	2.588227	-1.168911	-0.579814
1	1.056595	-2.606681	0.444875
1	-1.056593	2.606671	-0.444889
1	-1.059924	-2.605384	-0.444769
1	-2.588277	1.168908	0.579738
1	-2.589813	-1.165623	0.579697
6	1.736270	0.668477	-0.118258

1	2.589783	1.165614	-0.579766
6	0.660198	1.586281	0.419603
1	0.414353	1.325307	1.457228
1	1.059911	2.605398	0.444748

VII. Reference

1 D. Drew, J. R. Doyle and A. G. Shaver, *Inorg. Synth.*, **1972**, *18*, 47-55.

2 Y. Tatsuno, T. Yoshida, Seiotsuka, N. Al-Salem and B. L. Shaw, *Inorg. Synth.*, **1979**, *19*, 220-223.

3 Y.-Y. Zhu, H.-P. Yi, C. Li, X.-K. Jiang and Z.-T. Li, *Cryst. Growth Des.*, **2008**, *8*, 1294-1300.

4 E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, B. C. Smith, J. W. Rosenthal and W. L. Jolly, *Inorg. Synth.*, **1966**, *8*, 19-22.

5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.

6 G. M. Sheldrick, *Acta Cryst.*, **2015**, *71*, 3-8.

7 G. W. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122.

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

P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford, CT, **2013**.

9 A. D. Becke, *J. Chem. Phys*, **1993**, *98*, 5648-5652.

10 (a) P. C. P. Hariharan, J. A. Theor, *Chim. Acta* **1973**, *28*, 213; (b) W. J. D. Hehre, R.; Pople, J. A. , *J. Chem. Phys*, **1972**, *56*, 2257-2261.

11 P. J. W. Hay, W. R., *J. Chem. Phys.*, **1985**, *82*, 299-310.

12 (a) C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* , **1989**, *90*, 2154-2161; (b) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, **1990**, *94*, 5523-5527; (c) S. Santoro, M. Kalek, G. Huang and F. Himo, *Acc. Chem. Res.*, **2016**, *49*, 1006-1018.

13 C. Y. Legault, *CYLview, 1.0 b, Université de Sherbrooke, Quebec (Canada),*, **2009**.