Mechanistic and Computational Study of a Palladacycle-Catalyzed Decomposition of a Series of Neutral Phosphorothioate Triesters in Methanol

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Contents

1. Kinetics for the Pd-catalyzed methanolyses of substrates **1a**-**g**.

The simplified kinetic scheme of the Pd-catalyzed methanolysis of s **1a**-**g** is given as Scheme 1S. The linear portion of the rate constant (k_{obs}) vs. [**3**] plots (Figure 1S - 6S) are fitted to standard linear regression model to obtain the second-order rate constants (k_2^{cat}) for the catalyzed reactions. The reactions were conducted in the presence of 1mM TMPP (2,2,6,6-tetramethylpiperidine) buffer, $^{s}_{s}$pH 11.7. The deviation from linearity at high [**3**] can be attributed to the recapturing of Pd(dmba)($^{-}$OMe)(Sub) complex by free pyridine (produced from partial dissociation of complex 3) with rate constant k_{-1} displacing Pd-bound substrate (Scheme 1S). This is consistent with the linear kinetic plots in Figure 3 of the main text which illustrate the **3**-catalyzed cleavage of **1c** in the presence of excess free pyridine (0.4 mM and 1.0 mM).

Scheme 1S.

$$\text{Pd(dmba)(}^{-}\text{OMe)(Py)} + \text{Sub} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Pd(dmba)(}^{-}\text{OMe)(Sub)} \xrightarrow{k_{cat}} \text{Products} + \text{Py}$$

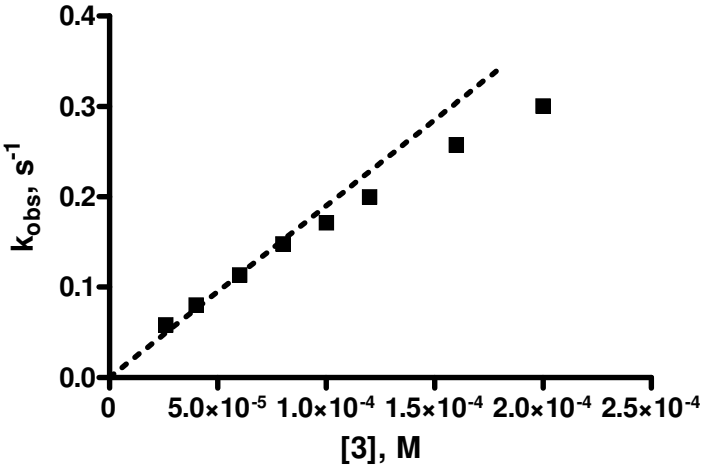

Figure 1S. Plot of k_{obs} vs. [3] for the catalyzed methanolysis of **1a** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (1900±50) M^{-1} s^{-1}. The ΔAbs (393 nm) values were found to be 0.74 ± 0.01 at the end of the reactions.

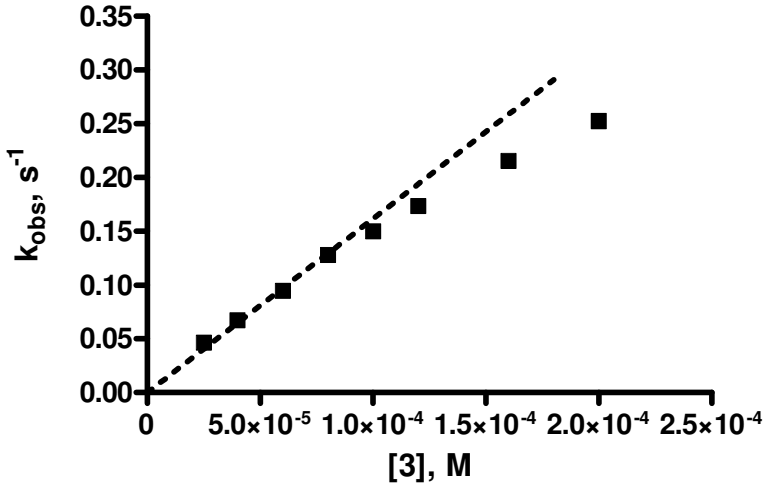

Figure 2S. Plot of k_{obs} vs. [**3**] for the catalyzed methanolysis of **1b** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (1620±40) M^{-1} s^{-1}. The ΔAbs (314 nm) values were found to be 0.15 ± 0.01 at the end of the reactions.

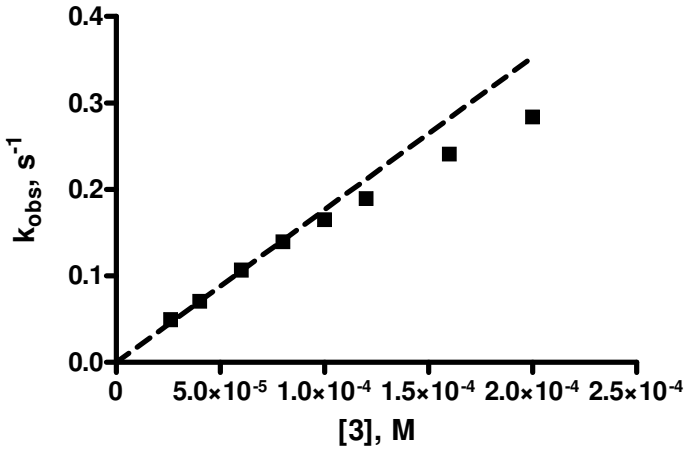

Figure 3S. Plot of k_{obs} vs. [**3**] for the catalyzed methanolysis of **1d** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (1770±20) M^{-1} s^{-1}. The ΔAbs (330 nm) values were found to be 0.080 ± 0.005 at the end of the reactions.

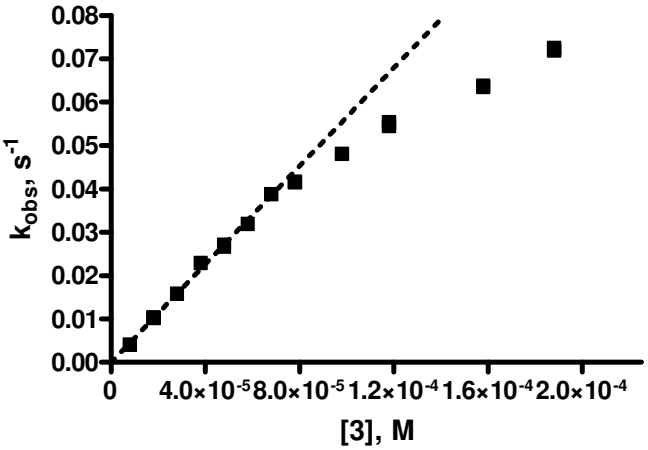

Figure 4S. Plot of k_{obs} vs. [**3**] for the catalyzed methanolysis of **1e** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (565±5) M^{-1} s^{-1}. The ΔAbs (284 nm) values were found to be 0.46± 0.02 at the end of the reactions.

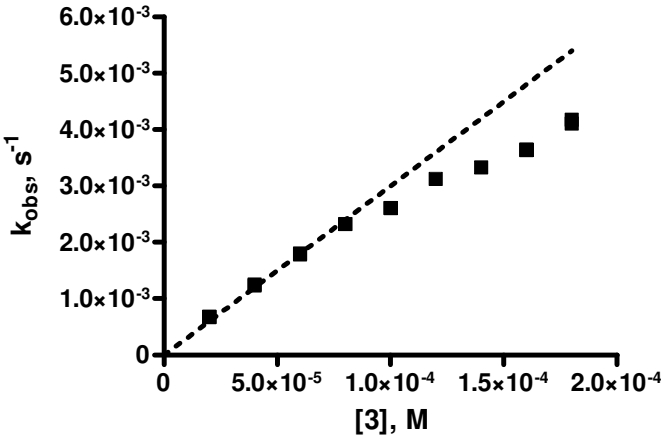

Figure 5S. Plot of k_{obs} vs. [**3**] for the catalyzed methanolysis of **1f** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (30.0±0.5) M^{-1} s^{-1}. The ΔAbs (273 nm) values were found to be 0.10 ± 0.01 at the end of the reactions.

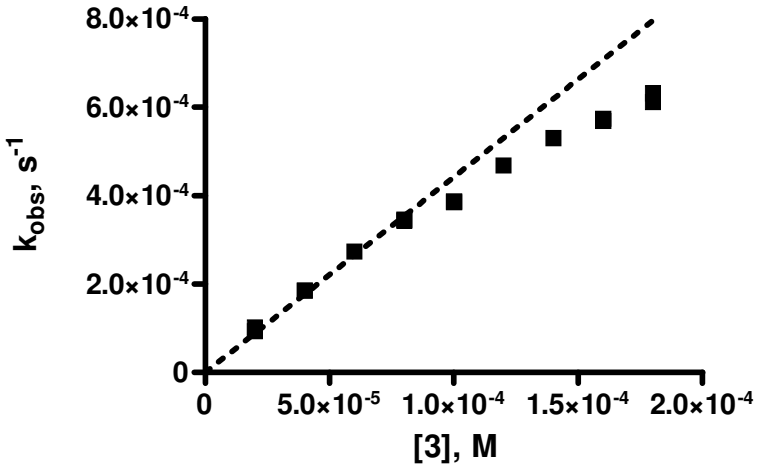

Figure 6S. Plot of k_{obs} vs. [**3**] for the catalyzed methanolysis of **1g** (5 x 10^{-5} M) in the presence of 1 mM TMPP buffer at $^{s}_{s}$pH 11.7 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The linear portion of the data points are fitted into standard linear model while forcing the line through the origin giving k_2^{cat} = (4.42±0.07) M^{-1} s^{-1}. The ΔAbs (292 nm) values were found to be 0.15 ± 0.01 at the end of the reactions.

In a similar study, the effect of additional pyridine on the catalyzed-reaction is investigated by increasing the [free pyridine] while keeping the concentrations of **3** and **1c** constant at 3 x 10^{-5} M and 5 x 10^{-5} M respectively (Figure 7S). The data in the figure can be treated as a process involving a common species rate depression illustrated in Scheme 1S. Equation S1 is derived from Scheme 1S under steady state assumption in [Pd(dmba)($^{-}$OMe)(Sub)], and the data in Figure 7S are fitted to eq. (S1).

$$k_{obs} = k_1/(1 + (k_{-1}/k_{cat})[Py]) \qquad \text{(S1)}$$

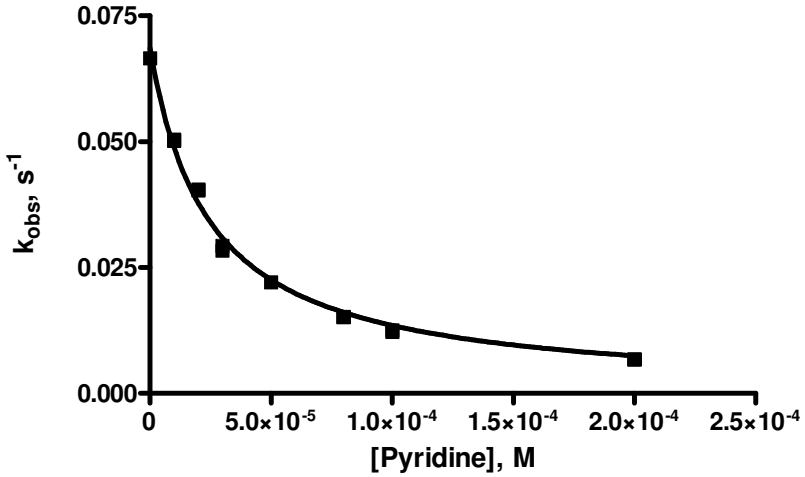

Figure 7S. Plot of k_{obs} vs. [pyridine] added for the catalyzed reaction of **1c** (5 x 10^{-5} M) in the presence of 3 x 10^{-5} M of **3** and 1mM of TMPP buffer at $^{s}_{s}$pH 11.8 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The data are fitted to eq. (S1) to give k_1 = (0.069±0.002) s^{-1}, k_{-1}/k_{cat} = (41000±2000) M^{-1}, and r^2=0.9918.

2. Spectrophotometric titration and UV-vis spectra.

The UV-vis absorbance (450 nm – 200 nm) of complex **3** in anhydrous methanol at 25 ^{o}C in the presence of 5 mM TMPP buffer ($^{s}_{s}$pH 11.7 ± 0.1) and in the absence of buffer was recorded as the [**3**] increases from 10^{-5} M to 1.6 mM. The absorbencies at 262 and 306 nm are plotted against the [**3**] in Figure 8S. The data are fitted to standard linear regression model to obtain the individual extinction coefficients. In a separate experiment, a UV-cell containing 0.05 mM of **3** and 1mM of TMPP buffer in 2.5 mL of methanol was prepared. To that cell, aliquots of a 0.5 M stock solution of trimethyl phosphorothioate in methanol were added sequentially and the UV-vis spectrum (350 – 200nm) of the mixture was recorded after each addition. The absorbances at 255 and 282 nm were corrected for concentration changes and the intrinsic absorbance of trimethyl phosphorothioate in methanol (Figure 9S) prior to being plotted against the [trimethyl phosphorothioate] as shown in Figure 10S. The data were fitted to an equilibrium expression in footnote (1) described by the process in eqn. 2S. Figure 11S shows the UV-vis spectra of 0.05 mM of **3** with 0 mM, 8.8 mM, and 50.4 mM of trimethyl phosphorothioate . As the [trimethyl phosphorothioate overall absorbance change at 255 nm (a characteristic peak of free pyridine with extinction coefficient of 3160 ± 50 $M^{-1}cm^{-1}$ in methanol; Figure 12S) after adding ~20 mM of trimethyl phosphorothioate to 0.05 mM of complex **3** at $^{s}_{s}$pH 11.6 (Figure 10S) matches well full release/displacement of Pd-bound pyridine under the experimental conditions.

(S2) $$\text{Pd-Py} + \text{Sub} \overset{K}{\rightleftharpoons} \text{Pd-Sub} + \text{Py}$$

Where, Pd-Py = Pd(dmba)($^{-}$OMe)(Py), Pd-Sub = Pd(dmba)($^{-}$OMe)(Sub), and K = [Pd-Sub][Py]/([Pd-Py][Sub]

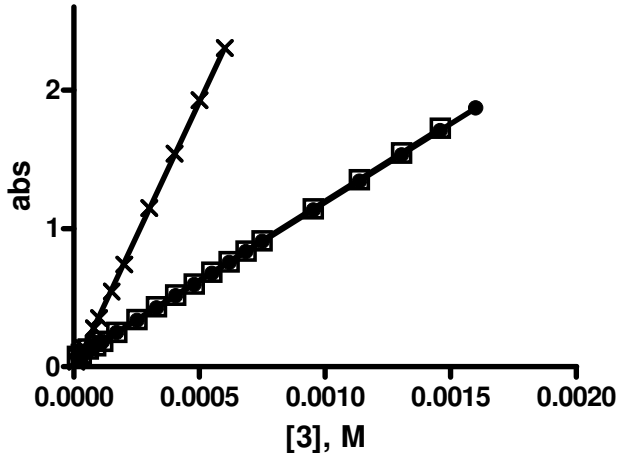

Figure 8S. A plot of absorbance vs. [**3**] in methanol without buffer (□) and in the presence of 5 mM TMPP buffer ($^{s}_{s}$pH 11.7 ± 0.1) (● and x) at 25.0 ± 0.1 ^{o}C. The data are fitted to a standard linear regression model to obtain the following extinction coefficients: x (262 nm; ε = 3880 ± 20 $M^{-1}cm^{-1}$; r^2 = 0.9997), ● (306 nm; ε = 1136 ± 0.5 $M^{-1}cm^{-1}$; r^2 = 1.000), and □ (306 nm; ε = 1142 ± 1 $M^{-1}cm^{-1}$; r^2 = 1.000).

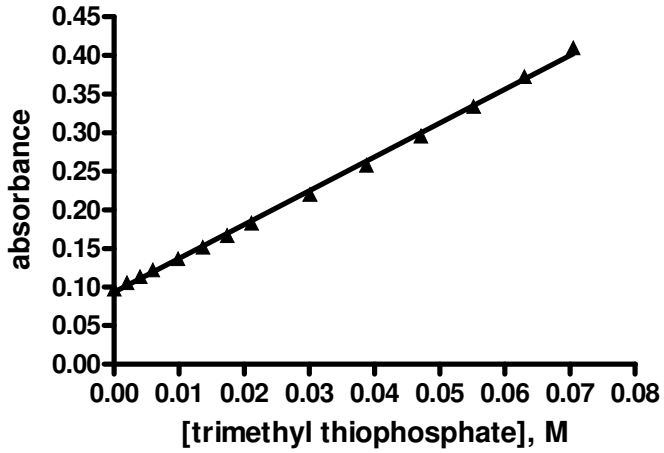

Figure 9S. A plot of absorbance vs. [trimethyl phosphorothioate] in methanol at 25.0 ± 0.1 ^{o}C. The data are fitted to a standard linear regression model to obtain the extinction coefficients at 255 nm: ε = 4.38 ± 0.05 $M^{-1}cm^{-1}$; r^2 = 0.9986.

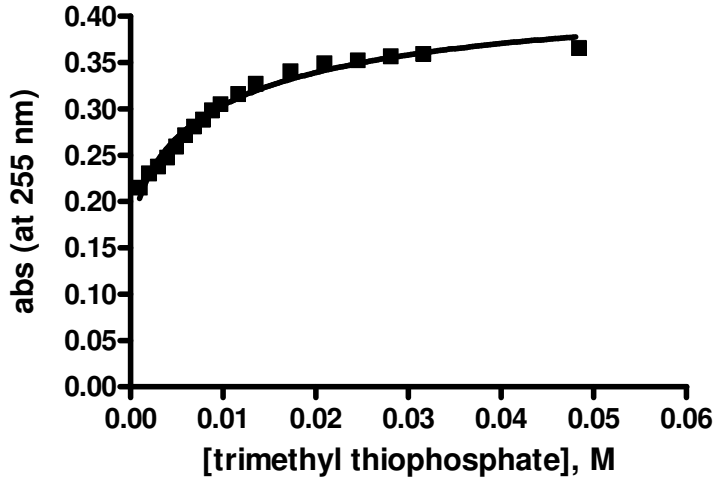

Figure 10S. Plot of absorbance at 255nm vs. [trimethyl phosphorothioate] added in the presence of 0.05 mM of **3** and 1 mM TMPP buffer at $^{s}_{s}$pH 11.6 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol. The data are fitted to an equilibrium expression[1] to give K = $10^{(-2.1\pm0.01)}$, Abs(init) = 0.13 ± 0.01, and r^2 = 0.9801.

[1] The equilibrium expression was derived based on the equilibrium equation S2 while considering the mass balance on Pd catalyst (**3**:$^{-}$OCH$_3$) using the commercially available MAPLE software, Maple V Release 5, Waterloo Maple Inc., Waterloo, Ontario, Canada. For the data fitting in Figure 10S, Ext_{py} is the extinction coefficient of free pyridine at 255 nm, which is fixed to be 3160 $M^{-1}cm^{-1}$ from Figure 12S. Abs(init) is the initial absorbance without any trimethyl thiophosphate (TMPT). K is the equilibrium constant described by Eqn. S2. The pathlength of the UV-cell used for the titration is 1 cm.

$$Abs = Ext_{Pyr} * \frac{(-K[TMPT] + \sqrt{K^2[TMPT]^2 + 4K[TMPT][\mathbf{3}:(^{-}OCH_3)]})}{2} + Abs(\text{init})$$

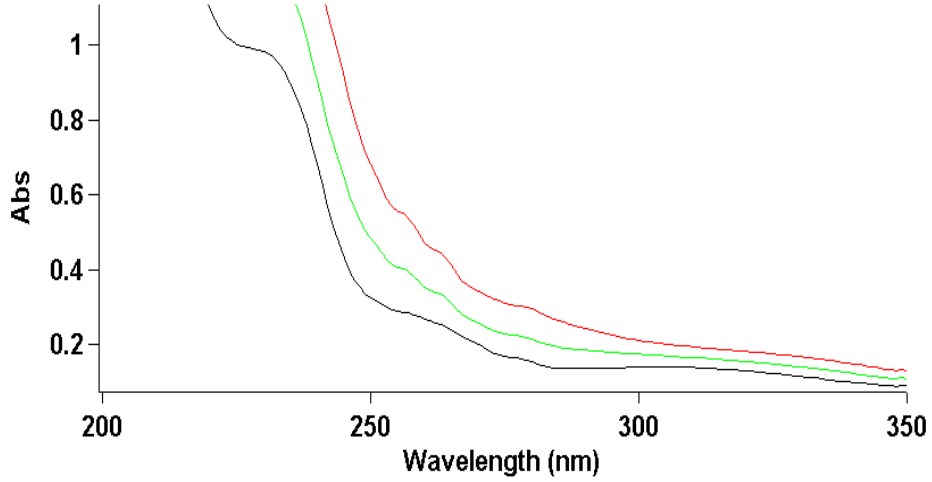

Figure 11S. Plot of absorbance vs. wavelength for mixtures containing of 0.05 mM of **3** and no trimethyl phosphorothioate (black), 8.8mM trimethyl phosphorothioate (green), or 50.4 mM trimethyl phosphorothioate (red) in the presence of 1 mM of TMPP buffer at $^{s}_{s}$pH 11.6 ± 0.1 and 25.0 ± 0.1 ^{o}C in anhydrous methanol.

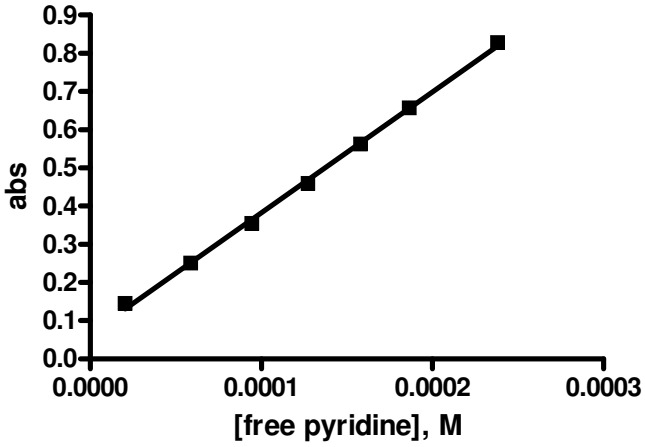

Figure 12S. Plot of absorbance vs. [free pyridine] in methanol at 25.0 ± 0.1 ^{o}C. The data are fitted to a standard linear regression model to obtain the extinction coefficients at 255 nm: ε = 3160 ± 50 $M^{-1}cm^{-1}$; r^2 = 0.9986.

3. NMR spectra of catalyst **3** with trimethyl phosphorothioate.

Proton decoupled ^{31}P NMR spectra were recorded at 162.0 MHz. The spectrum of a colourless solution containing 10 mM of palladacycle **3** and trimethyl phosphorothioate in the absence of base shows a single phosphorous species at 73 ppm for the unbound trimethyl phosphorothioate (Figure 13S). The addition of one equivalent of base (10 mM) resulted in the development of a golden brownish colour, which is consistent with the formation of Pd(0) nanoparticles in solution. Furthermore, two new phosphorous species at ^{31}P δ ~ 38 and 2 ppm were found (Figures 14S) approximately 3 hr after mixing. The species at δ ~ 38 ppm was still present after 6 hr but then eventually disappears after 17 hr at room

temperature (Figure 15S). The phosphorous species at ^{31}P δ ~ 2 and 38 ppm were identified to be that of free trimethyl phosphorothioate phosphate (Figure 16S) and Pd-bound dimethyl phosphorothioate monoanion (Figure 17S) respectively, when spiked with the authentic materials. This is suggestive of a Pd-bound dimethyl phosphorothioate being an intermediate species for the conversion of trimethyl phosphorothioate into trimethyl phosphate in the presence of palladacycle **3**. Another interesting observation is that this process is base dependent, and additional base to a sample where the ratio of [trimethyl phosphorothioate]/[trimethyl phosphate] is stable after 17 hr (Figure 15S) resulted in more trimethyl phosphate produced (Figure 18S). Also, a mixture of 10 mM of **3**, 10 mM of trimethyl phosphorothioate, and 5 mM of $NaOCD_3$ seems to generate only ~ 25% of trimethyl phosphate relative to all phosphorous species (Figure 19S).

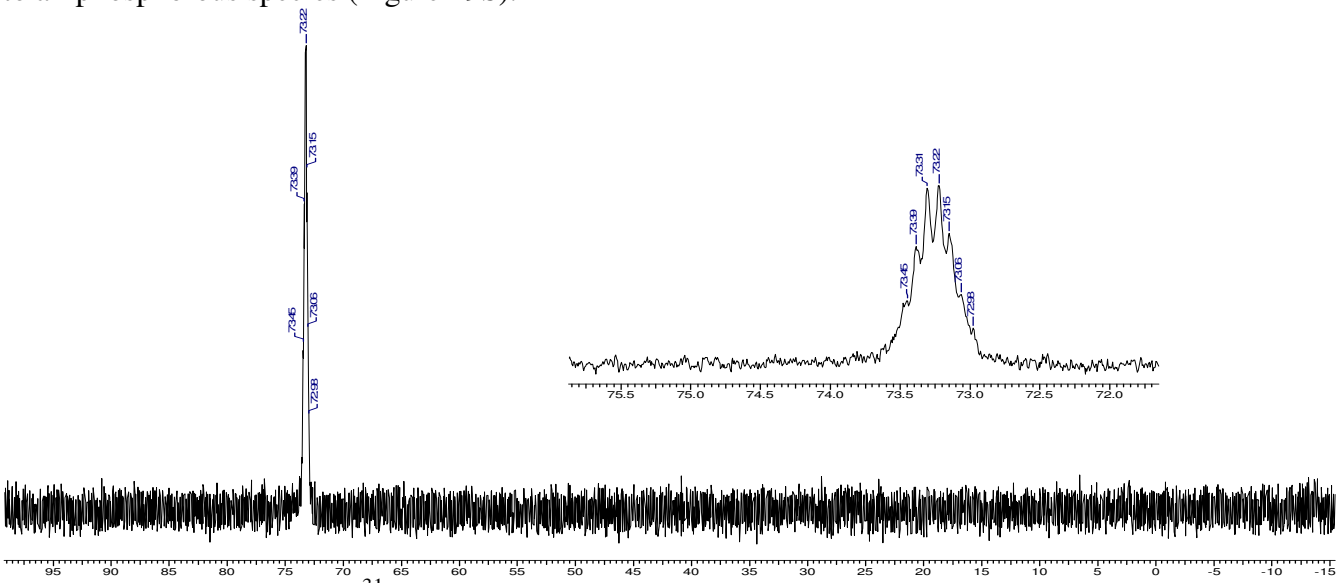

Figure 13S. Proton coupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3** and trimethyl phosphorothioate in CD_3OD.

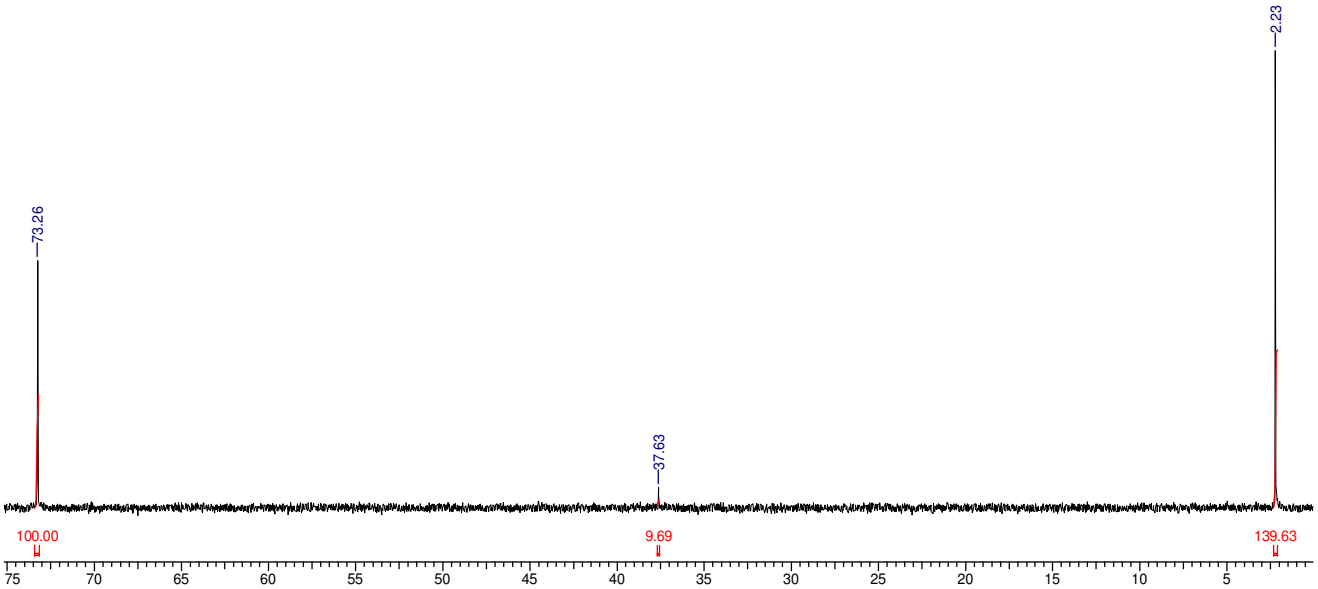

Figure 14S. Proton decoupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3,** trimethyl phosphorothioate, and $NaOCD_3$ in CD_3OD 3 hr after mixing.

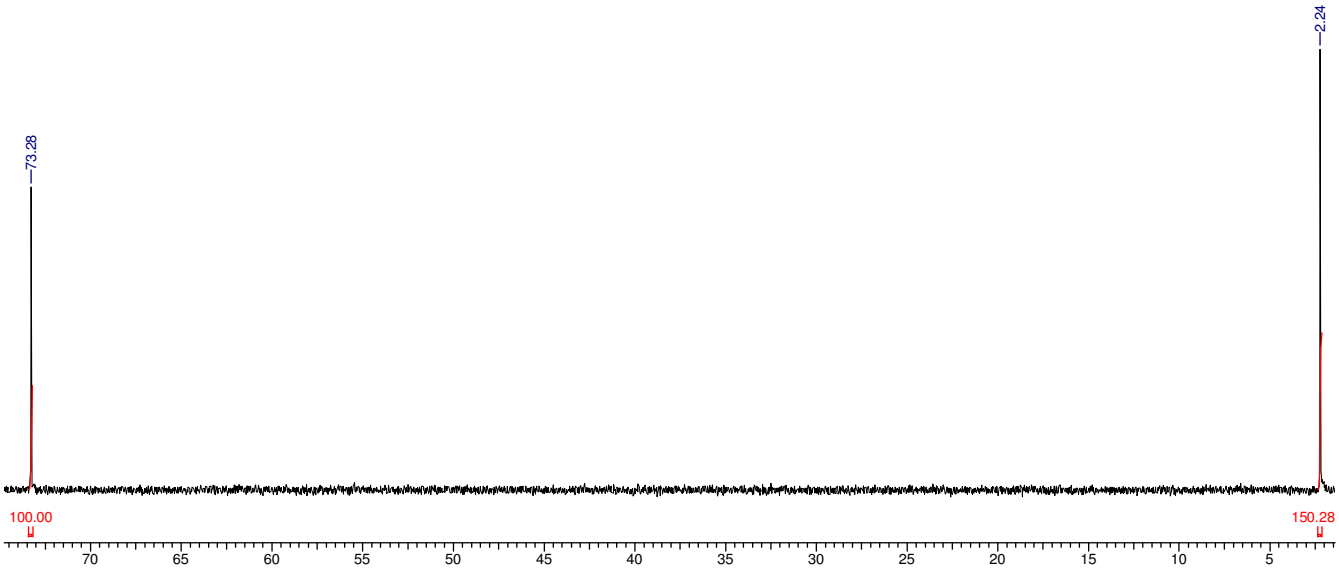

Figure 15S. Proton decoupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3,** trimethyl phosphorothioate, and $NaOCD_3$ in CD_3OD 17 hr after mixing.

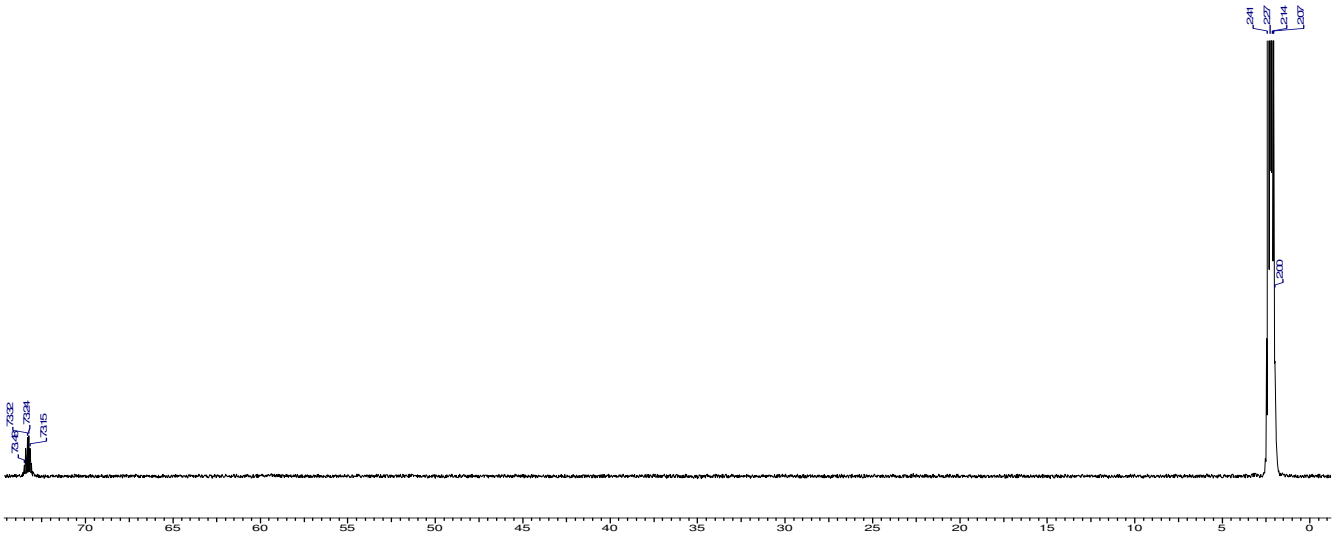

Figure 16S. Proton coupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3**, trimethyl phosphorothioate, $NaOCD_3$, and ~20 mg of trimethyl phosphate in CD_3OD.

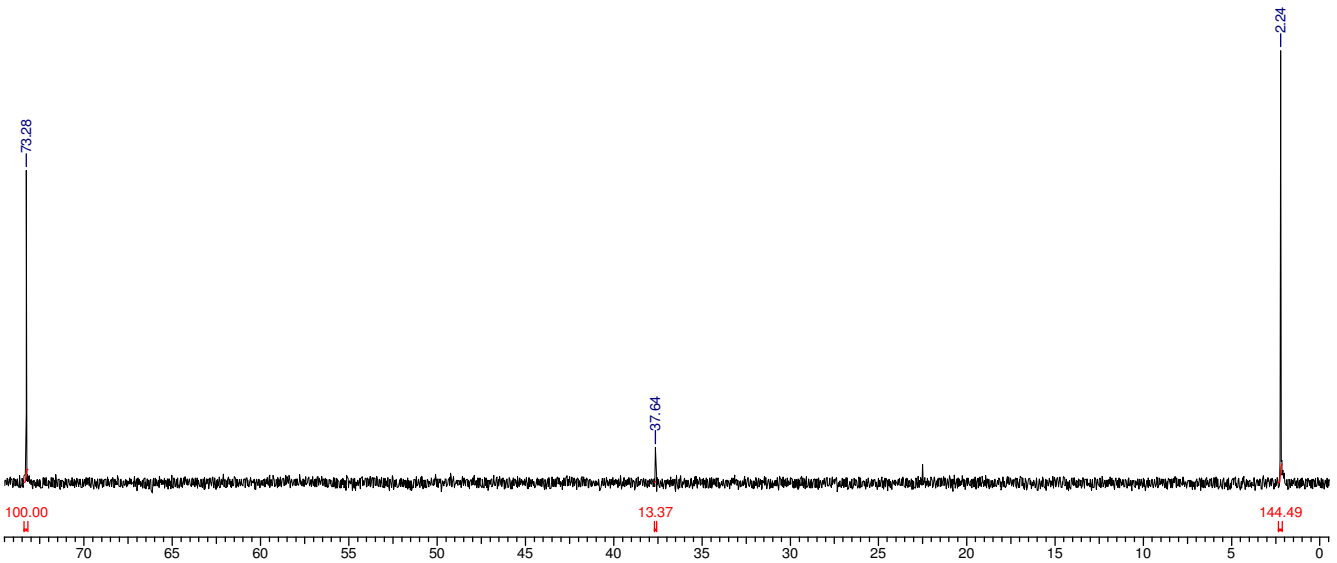

Figure 17S. Proton decoupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3,** trimethyl phosphorothioate, $NaOCD_3$, and 1 mM of dimethyl phosphorothioate in CD_3OD 5 hr after mixing.

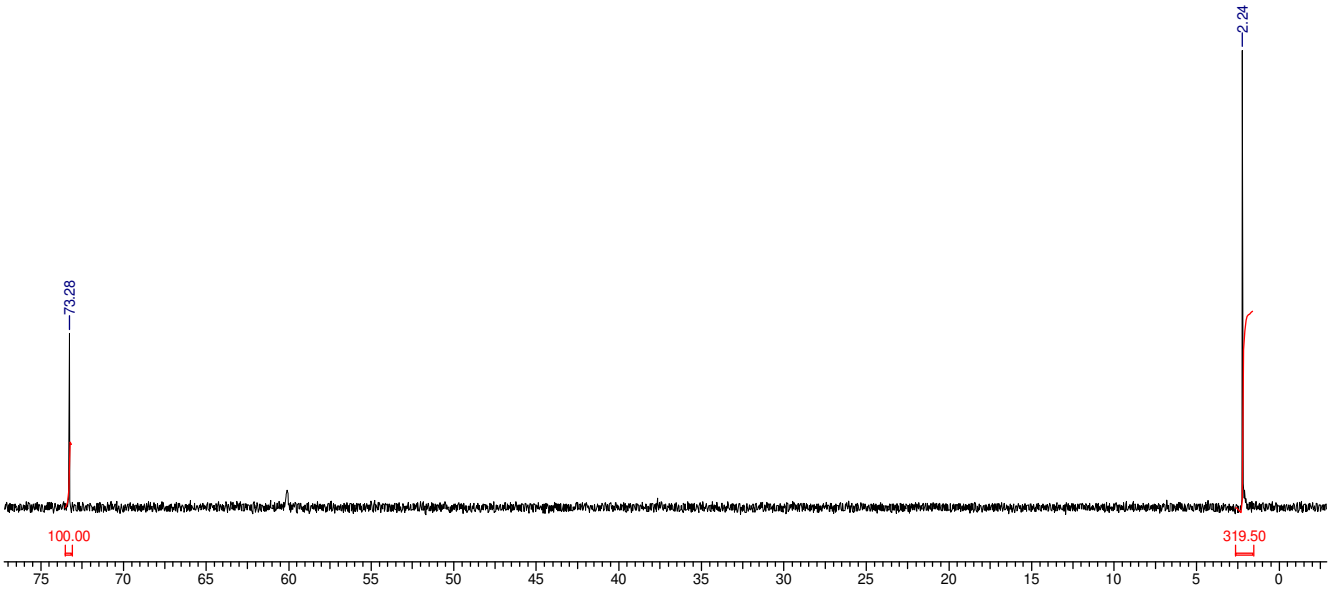

Figure 18S. Proton decoupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3,** 10 mM of trimethyl phosphorothioate, and 20 mM of $NaOCD_3$ in CD_3OD 20 hr after mixing.

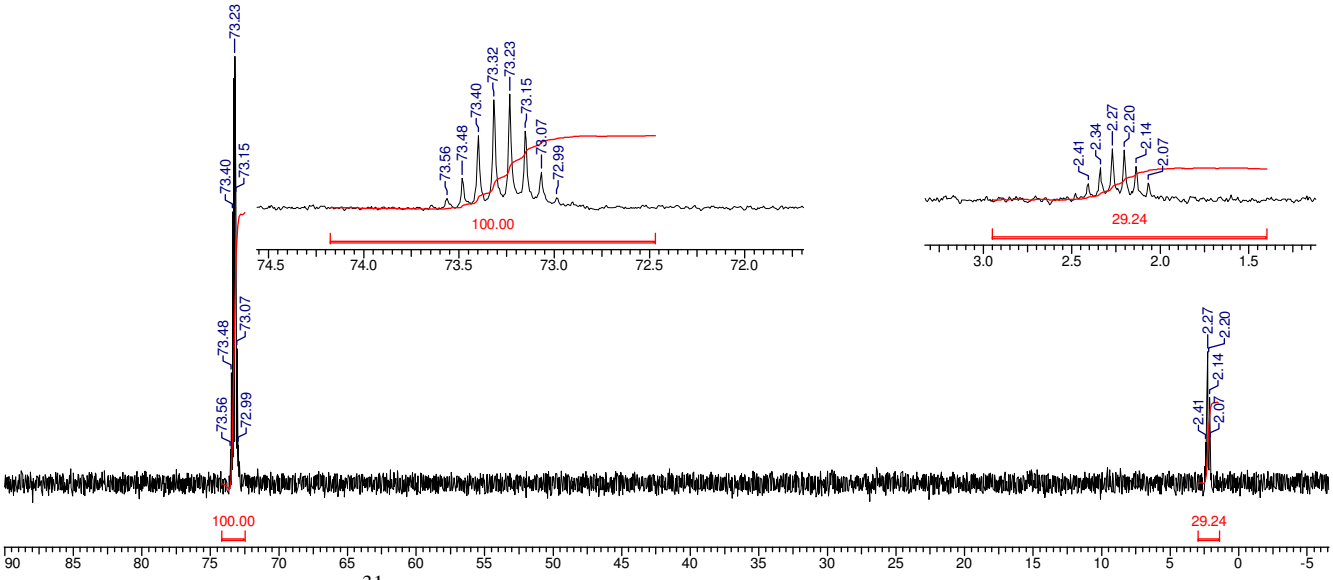

Figure 19S. Proton coupled ^{31}P NMR (162.0 MHz) of a solution containing 10 mM of palladacycle **3,** trimethyl phosphorothioate, and 5 mM of $NaOCD_3$ in CD_3OD.

4. Extended Computational Details.

All calculations were conducted using the DFT method, using the B3LYP[2] functional as implemented in Gaussian 09[3]. C and H atoms were described using the 6-31G(d,p) basis set. Diffuse functions were included for O, P, S and N (6-31++G(d,p)). The effective core potential of Hay and Wadt[4] with double-ζ valence basis set (LanL2DZ) was employed to describe Pd. This combination of basis sets was selected after testing several lower and higher levels of theory, and finding a good balance of accuracy and speed. Geometry optimizations were conducted using the IEFPCM[5] solvent model and included some explicit solvent molecule interactions. Frequency calculations were conducted to characterize transition states and intermediates, as well as to use as a basis for determining free energy values at 298 K.

Bimolecular reactions have large entropic effects in the gas phase, and it is somewhat difficult to estimate free energy values from calculations that are representative of an ideal gas. ΔG_{corr} includes a correction in which only vibrational contributions to entropy were considered (Equation S3, S4), as translational and rotational movements are highly suppressed by the solvent. The true free energy value would lie between these values, although it has been argued that the latter method produces more accurate results.[6]

$$\Delta G = \Delta H - T(\Delta S_{elec} + \Delta S_{trans} + \Delta S_{rot} + \Delta S_{vib}) \qquad (S3)$$

$$\Delta G_{corr} = \Delta H - T(\Delta S_{elec} + \Delta S_{vib}) \qquad (S4)$$

As ligands dissociate from the complex in solution, they are stablized by hydrogen bond donors of the solvent. These specific interactions are not included by the PCM solvation model. To account for this stabilization, single explicit solvent molecules were included in some calculations where appropriate, in the form of hydrogen bonding interactions with ligands not included in the complex (Figure 20S). Due to the disturbed atom balance in the cases in which the bound substrate is bidentate, the energy contribution of extra methanol molecules must be included throughout the calculations. When not involved with either the complex or free ligands, these methanols are part of the bulk solvent. Detailed

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[2] a) A. D. Becke, *Phys. Rev. A.* **1988**, 38, 3098. b) C. Lee, W. Yang, R. G. Parr. *Phys. Rev. B*. **1988**, 37, 785.

[3] Gaussian 09, Revision A.021, Frisch, 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, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[4] a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985,** 82, 270. b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985,** 82, 284. c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985,** 82, 299.

[5] a) J. Tomasi, B. Mennuccia, E. Cancés, *THEOCHEM*. **1999**, 464, 211-226. b) J. Tomasi, B. Mennuccia, R. Cammi, *Chem. Rev.* **2005**, 105, 2999-3094.

[6] a) M. Sumimoto, N. Iwane, T. Takahama, S. Sakaki, *J. Am. Chem. Soc.* **2004,** 126, 10457.

potential energy, enthalpy, uncorrected free energy and corrected free energy values for each structure in the methanolysis of **1c** are shown in Table 1S, and those of **1g** are shown in Table 2S. Selected transition state bond lengths and angles are shown in Table 3S.

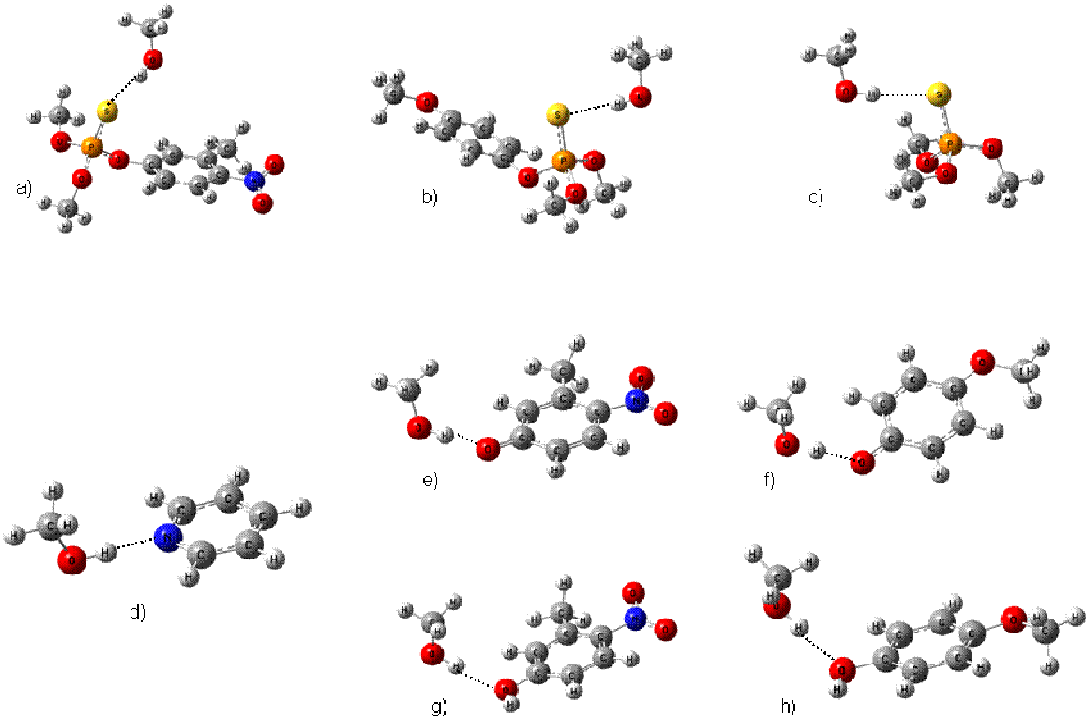

Figure 20S. Placement of explicit solvent methanol molecules on non-metal binding ligands. a) **1c**, b) **1g**, c) $P(S)(OMe)_3$, d) pyridine, e) 4-nitro-3-methylphenoxide, f) 4-methoxyphenoxide, g) 4-nitro-3-methylphenol, h) 4-methoxyphenol.

Table 1S. Computed potential energy, enthalpy, uncorrected free energy and corrected free energy for the intermediates and transition states for the methanolysis of **1c** at 1atm and 298 K. All energy values in kcal mol^{-1} and are expressed relative to **GS**.

	ΔE	ΔH	ΔG	ΔG_{corr}
GS	0	0	0	0
TS_{LE}	15.5	15.7	28.3	10.6
INT_1	6.5	6.4	8.7	7.5
TS_{Nu}	7.0	6.4	9.3	8.1
INT_2	-9.7	-8.9	-4.9	-6.1
TS_{LG}	-1.7	-1.9	0.3	-0.9
Pr_{HOLG}	0.9	0.2	-7.8	5.3
Pr_{OLG}	-32.5	-30.1	-29.8	-28.3

Table 2. Computed potential energy, enthalpy, uncorrected free energy and corrected free energy for the intermediates and transition states for the methanolysis of **1g** at 1atm and 298 K All energy values in kcal mol^{-1} and are expressed relative to **GS**.

	ΔE	ΔH	ΔG	ΔG_{corr}
GS	0	0	0	0
TS_{LE}	14.3	14.5	26.1	8.4
INT_1	7.4	7.4	9.3	8.1
TS_{Nu}	7.5	7.7	10.3	9.1
INT_2	-5.1	-4.3	0.5	-0.7

TS_{LG}	14.2	13.8	15.6	14.5
Pr_{HOLG}	4.2	3.3	-4.6	8.3
Pr_{OLG}	-15.4	-13.6	-12.7	-11.3

Table 3. Selected bond lengths and angles for computed transition states.

	1c	1g
TSLE		
Pyr(N) – Pd	2.62 Å	2.65 Å
Pyr(N) – Pd – N	121°	125°
S – Pd	2.69 Å	2.67 Å
S – Pd – N	156°	156°
TSNu		
MeO – P	2.88 Å	2.63 Å
TSLG		
ArO – P	2.46 Å	2.87 Å

CHelpG[7] analysis (Figure 15S) was conducted on the optimized structures for **INT_1** and **INT_2** structures (main paper, Figure 8) with substrates **1a** and **1g** as implemented on Gaussian 09. Default Van der Waals radii were used for all atoms except Palladium, which was assigned a value of 1.7 Å. Reported here are the computed charges for Pd, S, the O of the nucleophilic methoxide and the sum of all atomic charges of the leaving group.

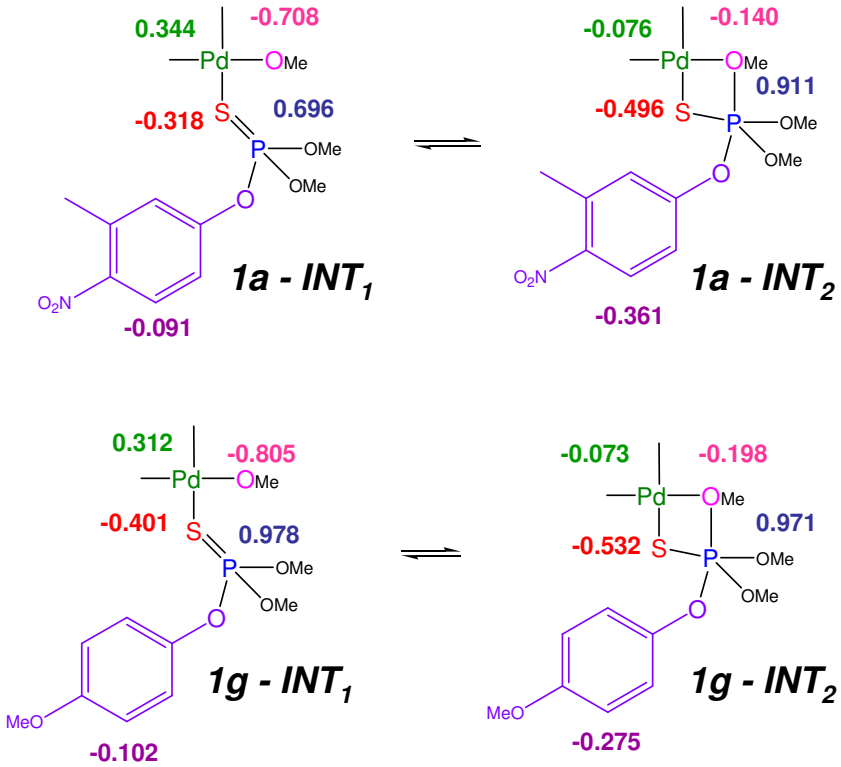

Figure 15S. CHelpG charges for **INT_1** and **INT_2** structures for **1a** and **1g**, (main paper, Figure 8) showing the redistribution of charge.

[7] Breneman, C.; Wiberg, K. *J. Comput. Chem.* **1990,** 11, 361.

5. Optimized Geometries

5a) **1c** with H-bonded methanol

S	-0.1082	1.1352	0.2282
P	0.0094	0.4818	2.0604
O	1.5322	0.2021	2.6096
O	-0.6794	1.4752	3.1011
O	-0.6586	-0.9223	2.4274
C	2.6357	1.0177	2.4197
C	3.8428	0.3695	2.1664
C	2.5635	2.4083	2.5323
C	5.0371	1.0790	1.9975
H	3.8475	-0.7131	2.1041
C	3.7340	3.1368	2.3842
H	1.6256	2.9094	2.7391
C	4.9435	2.4848	2.1140
H	3.7215	4.2157	2.4690
C	-0.7921	1.1648	4.5240
H	-1.2316	2.0515	4.9768
H	-1.4437	0.3012	4.6601
H	0.1963	0.9739	4.9463
C	-0.3031	-2.1578	1.7485
H	0.7364	-2.4120	1.9631
H	-0.9706	-2.9155	2.1550
H	-0.4621	-2.0520	0.6735
N	6.1161	3.3425	1.9661
O	6.0792	4.4759	2.4646
O	7.0948	2.9145	1.3440
C	6.3036	0.3028	1.7377
H	6.6487	0.4461	0.7103
H	7.1181	0.6223	2.3926
H	6.1208	-0.7615	1.8986
H	1.7204	-0.1088	-0.9730
O	2.3868	-0.5546	-1.5220
C	1.9152	-0.5778	-2.8726
H	0.9735	-1.1326	-2.9653
H	1.7745	0.4344	-3.2714
H	2.6774	-1.0837	-3.4691

5b) **1g** with H-bonded methanol

S	0.0033	-0.1730	-0.1626
P	-0.0270	-0.0518	1.7877
O	1.4341	0.0032	2.5068
O	-0.8541	1.2192	2.2954

O	-0.7064	-1.2431	2.6161
C	2.5401	0.6972	1.9827
C	3.5587	-0.0312	1.3811
C	2.6346	2.0819	2.1327
C	4.6986	0.6280	0.9113
H	3.4663	-1.1075	1.2828
C	3.7659	2.7395	1.6632
H	1.8387	2.6365	2.6182
C	4.8023	2.0180	1.0500
H	3.8641	3.8147	1.7697
C	-1.0908	1.4777	3.7107
H	-1.5806	2.4491	3.7492
H	-1.7411	0.7046	4.1216
H	-0.1436	1.5109	4.2527
C	-0.2243	-2.6103	2.5303
H	0.7805	-2.6763	2.9518
H	-0.9215	-3.2046	3.1184
H	-0.2287	-2.9449	1.4905
H	5.4872	0.0498	0.4467
O	5.8723	2.7572	0.6262
C	6.9612	2.0766	-0.0045
H	6.6336	1.5697	-0.9186
H	7.6873	2.8489	-0.2566
H	7.4203	1.3509	0.6755
H	-2.4087	-0.2861	-0.7032
O	-3.3263	-0.3438	-1.0216
C	-3.3298	-0.0932	-2.4297
H	-4.3660	-0.1680	-2.7667
H	-2.9577	0.9116	-2.6653
H	-2.7311	-0.8326	-2.9761

5c) $P(S)(OMe)_3$ with H-bonded methanol

S	0.0236	-0.0141	0.0347
P	0.0315	-0.0314	1.9941
O	1.4821	-0.0463	2.6978
O	-0.7840	1.2166	2.5793
O	-0.6723	-1.2682	2.7335
C	2.5771	0.7913	2.2446
C	-0.9546	1.4161	4.0130
H	-1.4494	2.3805	4.1151
H	-1.5796	0.6219	4.4240
H	0.0172	1.4361	4.5098
C	-0.2035	-2.6318	2.5666
H	0.8057	-2.7309	2.9710
H	-0.8990	-3.2527	3.1290
H	-0.2234	-2.9092	1.5103
H	1.7278	-1.7180	-0.5711

O	2.3873	-2.3604	-0.8853	H	3.0442	-3.1638	-2.6402
C	2.2986	-2.4368	-2.3108	H	3.4278	0.5251	2.8703
H	1.3091	-2.7781	-2.6390	H	2.3270	1.8461	2.3790
H	2.5187	-1.4720	-2.7844	H	2.7984	0.5835	1.1960

5d) Pyridine with H-bonded Methanol

C	-0.0023	-0.0013	0.0522	H	3.3764	0.0222	1.8309
C	0.0004	0.0147	1.4463	H	3.1911	-0.0062	-0.6557
C	1.2270	0.0235	2.1111	H	1.0545	-0.0117	-2.5204
C	2.4008	0.0158	1.3569	O	1.0177	-0.0058	-3.5084
C	2.2999	-0.0002	-0.0335	C	1.0011	-1.3536	-3.9699
N	1.1230	-0.0088	-0.6828	H	0.1232	-1.9034	-3.6044
H	1.2674	0.0362	3.1959	H	0.9601	-1.3319	-5.0621
H	-0.9374	-0.0081	-0.5020	H	1.9047	-1.9023	-3.6713
H	-0.9372	0.0203	1.9916				

5e) 4-nitro-3-methylphenoxide with H-bonded methanol

C	-0.1091	0.3795	0.1730	H	1.3213	-0.4414	3.1790
C	0.0123	0.0384	1.5651	H	1.0436	0.7224	-1.6190
C	1.2390	-0.1853	2.1302	O	-1.2520	0.5921	-0.3705
C	2.4355	-0.0903	1.3698	N	3.6479	-0.3413	2.0480
C	2.3730	0.2478	-0.0241	O	4.7432	-0.2748	1.4369
C	1.1204	0.4675	-0.5656	O	3.6235	-0.6336	3.2742
H	-0.8934	-0.0377	2.1595	C	3.5716	0.3793	-0.9341

H	4.2655	1.1464	-0.5798	C	-1.3992	2.6611	-3.0845
H	4.1435	-0.5511	-0.9854	H	-0.3626	2.9258	-2.8329
H	3.2381	0.6440	-1.9406	H	-1.5742	2.9287	-4.1305
H	-1.4603	1.0122	-1.9958	H	-2.0712	3.2658	-2.4595
O	-1.6444	1.2671	-2.9396				

5f) 4-methoxyphenoxide H-bonded methanol

C	-0.1473	-0.1004	-0.0614	O	-1.2637	0.0874	-3.3600
C	-0.1753	-0.0865	1.3572	C	-0.8904	1.4098	-3.7119
C	0.9876	-0.0428	2.1336	H	0.1118	1.6706	-3.3402
C	2.2421	-0.0096	1.5179	H	-0.8756	1.4900	-4.8039
C	2.3100	-0.0228	0.1194	H	-1.5990	2.1593	-3.3280
C	1.1509	-0.0672	-0.6492	H	3.2865	0.0022	-0.3589
H	-1.1431	-0.1107	1.8533	O	3.4577	0.0364	2.1961
H	0.8976	-0.0344	3.2149	C	3.4134	0.0576	3.6172
H	1.2296	-0.0809	-1.7337	H	2.8779	0.9399	3.9902
O	-1.2537	-0.1416	-0.7824	H	2.9358	-0.8450	4.0190
H	-1.2156	-0.0034	-2.3472	H	4.4500	0.0966	3.9553

5g) 4-nitro-3-methylphenol H-bonded methanol

C	0.0535	-0.7546	0.1127	C	2.3016	0.2565	1.3657
C	-0.0487	-0.3123	1.4372	C	2.4270	-0.1824	0.0235
C	1.0843	0.1819	2.0590	C	1.2719	-0.6948	-0.5696

H	-0.9946	-0.3527	1.9678	H	4.5314	-0.6221	-0.2429
H	1.0386	0.5301	3.0826	H	3.5464	-0.7191	-1.7179
H	1.3147	-1.0645	-1.5885	H	-1.8020	-1.2991	-0.0065
O	-1.0145	-1.2618	-0.5700	H	-1.4142	-0.8278	-2.4650
N	3.4273	0.8044	2.1020	O	-1.6066	-0.6153	-3.3927
O	4.4216	1.2000	1.4782	C	-1.9233	0.7764	-3.4837
O	3.3507	0.8665	3.3398	H	-1.0877	1.4063	-3.1545
C	3.6988	-0.1690	-0.7870	H	-2.1280	0.9920	-4.5346
H	4.0017	0.8529	-1.0302	H	-2.8139	1.0305	-2.8956

5h) 4-methoxyphenol H-bonded methanol

C	0.1812	-0.4538	-0.0639	C	-0.9697	2.0401	-3.3502
C	0.0477	-0.0140	1.2497	H	-0.1201	2.4322	-2.7770
C	1.1790	0.1294	2.0616	H	-0.9506	2.4864	-4.3470
C	2.4456	-0.1646	1.5483	H	-1.9010	2.3397	-2.8530
C	2.5707	-0.6036	0.2217	H	3.5582	-0.8306	-0.1670
C	1.4460	-0.7502	-0.5813	O	3.6169	-0.0570	2.2591
H	-0.9342	0.2202	1.6523	C	3.5403	0.3774	3.6176
H	1.0518	0.4709	3.0814	H	3.1166	1.3856	3.6889
H	1.5402	-1.0957	-1.6058	H	2.9425	-0.3141	4.2221
O	-0.9083	-0.6122	-0.9093	H	4.5660	0.3881	3.9863
H	-0.8975	0.2076	-2.6367	H	-1.7315	-0.4529	-0.4257
O	-0.8887	0.6233	-3.5175				

5i) GS

C	0.0018	0.0120	0.0037	C	-1.5410	0.1014	-5.0989
C	-0.0003	0.0066	1.4176	H	-2.4270	-1.0948	-3.5142
C	1.1929	0.0053	2.1464	C	-0.7718	1.2354	-5.3589
C	2.4208	0.0149	1.4774	H	0.3128	2.8683	-4.4325
C	2.4440	0.0106	0.0817	H	-1.9456	-0.5033	-5.9029
C	1.2453	0.0039	-0.6448	H	-0.5597	1.5384	-6.3792
C	-1.3512	0.0322	2.0836	O	-3.8092	-0.5423	-1.5185
H	1.1676	-0.0046	3.2342	C	-4.5997	0.5645	-1.8379
H	3.3488	0.0141	2.0425	H	-4.1399	1.2284	-2.5972
H	3.3952	0.0052	-0.4455	H	-5.5729	0.2454	-2.2547
H	1.2973	-0.0130	-1.7306	H	-4.8325	1.2047	-0.9628
H	-1.6908	1.0660	2.2106	C	-3.7312	-0.2080	1.5496
H	-1.3499	-0.4353	3.0783	H	-4.4245	-0.6609	0.8416
Pd	-1.8507	-0.1309	-0.8045	H	-3.9791	-0.5048	2.5779
N	-2.3587	-0.6454	1.2034	H	-3.7964	0.8777	1.4619
N	-1.3122	0.4544	-2.7380	C	-2.2641	-2.1209	1.3475
C	-0.5680	1.5509	-2.9875	H	-1.2444	-2.4436	1.1367
C	-1.7989	-0.2530	-3.7781	H	-2.5364	-2.4193	2.3693
C	-0.2832	1.9751	-4.2819	H	-2.9466	-2.5924	0.6392
H	-0.1961	2.0832	-2.1209				

5j) TS_{LE}-**1c**

C	2.1708	1.9152	-0.4927	C	3.3912	3.9102	-1.2282
C	3.3432	2.5334	-0.9851	C	2.2760	4.7103	-0.9641

C	1.1151	4.1210	-0.4614	O	-2.8078	-1.9446	-0.3192
C	1.0639	2.7383	-0.2337	O	-1.1736	-1.6852	-2.3120
C	4.5506	1.6551	-1.1667	O	-0.7609	-3.3069	-0.4471
H	4.3020	4.3602	-1.6182	C	-3.7428	-0.9259	-0.2806
H	2.3140	5.7795	-1.1530	C	-4.7213	-1.0384	0.7062
H	0.2414	4.7331	-0.2505	C	-3.7542	0.1279	-1.1993
H	0.1399	2.3122	0.1467	C	-5.7502	-0.0999	0.8354
H	5.1221	1.6117	-0.2325	H	-4.6771	-1.8836	1.3841
H	5.2340	2.0227	-1.9464	C	-4.7702	1.0668	-1.1031
Pd	2.3153	-0.0902	-0.2789	H	-3.0001	0.2108	-1.9723
N	4.1300	0.2539	-1.4783	C	-5.7432	0.9598	-0.1013
O	2.5962	-2.1875	-0.0520	H	-4.8154	1.8954	-1.7979
C	2.5185	-2.9839	-1.1929	C	-1.6831	-2.7314	-3.1933
H	3.4361	-2.9656	-1.8180	H	-1.5797	-2.3347	-4.2015
H	2.3661	-4.0462	-0.9239	H	-1.0847	-3.6351	-3.0731
H	1.6846	-2.7129	-1.8685	H	-2.7332	-2.9317	-2.9708
C	5.2306	-0.6793	-1.1511	C	-0.1959	-3.7431	0.8277
H	4.9191	-1.7000	-1.3652	H	-0.8851	-3.5101	1.6418
H	6.1237	-0.4377	-1.7455	H	-0.0857	-4.8223	0.7307
H	5.4716	-0.5988	-0.0903	H	0.7743	-3.2574	0.9584
C	3.7855	0.1330	-2.9168	N	-6.7626	2.0038	-0.0818
H	3.0185	0.8659	-3.1683	O	-6.9443	2.6657	-1.1134
H	4.6750	0.3111	-3.5394	O	-7.4002	2.1980	0.9596
H	3.4035	-0.8687	-3.1154	C	-6.7758	-0.3051	1.9217
S	-0.3307	-0.3272	0.1997	H	-6.6722	0.4466	2.7088
P	-1.2180	-1.8084	-0.7206	H	-7.7957	-0.2219	1.5378

H	-6.6474	-1.2945	2.3653	C	2.5990	-1.2303	4.3586
N	2.3405	0.0429	2.3358	H	2.6541	-1.9882	2.3158
C	2.1852	1.1497	3.0787	C	2.4364	-0.0760	5.1260
C	2.5425	-1.1246	2.9680	H	2.0898	2.0618	5.0288
C	2.2238	1.1391	4.4736	H	2.7649	-2.1965	4.8241
H	2.0201	2.0728	2.5284	H	2.4735	-0.1222	6.2103

5k) TS_{LE}-**1g**

C	-1.4571	0.8013	1.6093	H	-3.2640	-2.9544	-1.1683
C	-2.5204	0.9744	2.5251	H	-3.1452	-2.7671	-2.9220
C	-2.3199	1.6003	3.7602	H	-1.6715	-2.8323	-1.9380
C	-1.0555	2.0875	4.1038	C	-4.9820	-0.7775	0.3245
C	0.0028	1.9401	3.2053	H	-4.8519	-1.5878	-0.3913
C	-0.1964	1.2993	1.9737	H	-5.8383	-0.9935	0.9797
C	-3.8825	0.5130	2.0795	H	-5.1710	0.1454	-0.2254
H	-3.1518	1.7130	4.4529	C	-3.4924	-1.8881	1.8709
H	-0.9005	2.5743	5.0626	H	-2.6164	-1.7639	2.5074
H	0.9895	2.3197	3.4611	H	-4.3611	-2.1433	2.4961
H	0.6450	1.1895	1.2958	H	-3.3100	-2.6975	1.1630
H	-4.3906	1.3174	1.5356	S	0.4999	-0.4408	-1.0301
H	-4.5330	0.2281	2.9200	P	1.3133	-2.1011	-0.3688
Pd	-1.9867	-0.1468	-0.0943	O	2.9357	-2.1475	-0.5098
N	-3.7476	-0.6303	1.1255	O	0.9564	-2.4001	1.1584
O	-2.7524	-1.0379	-1.8655	O	0.9366	-3.4892	-1.0745
C	-2.7006	-2.4255	-1.9677	C	3.7804	-1.0425	-0.3004

C	4.4355	-0.4975	-1.4053
C	4.0001	-0.5496	0.9806
C	5.3190	0.5597	-1.2193
H	4.2541	-0.9034	-2.3948
C	4.8857	0.5164	1.1687
H	3.4938	-0.9912	1.8324
C	5.5462	1.0745	0.0670
H	5.0500	0.8923	2.1706
C	1.3945	-3.6155	1.8339
H	1.0999	-3.4898	2.8744
H	0.8939	-4.4798	1.3959
H	2.4788	-3.7199	1.7585
C	1.2155	-3.7373	-2.4778
H	2.2943	-3.7444	-2.6445
H	0.7923	-4.7174	-2.6920
H	0.7345	-2.9773	-3.0973
N	-1.7054	2.0401	-1.5604
C	-1.2243	3.2284	-1.1635
C	-2.1006	1.9078	-2.8372
C	-1.1171	4.3274	-2.0167
H	-0.9118	3.2922	-0.1240
C	-2.0307	2.9521	-3.7609
H	-2.4754	0.9207	-3.0998
C	-1.5294	4.1854	-3.3424
H	-0.7196	5.2670	-1.6470
H	-1.4602	5.0190	-4.0349
H	5.8418	0.9986	-2.0625
O	6.4313	2.1145	0.1448
C	6.6998	2.6827	1.4299
H	7.1386	1.9409	2.1058
H	7.4163	3.4850	1.2556
H	5.7891	3.0959	1.8768
H	-2.3616	2.7970	-4.7828

5l) INT_1-**1c**

C	-2.5614	1.5892	-0.2466
C	-3.8856	2.0285	-0.4776
C	-4.2576	3.3593	-0.2597
C	-3.3110	4.2893	0.1787
C	-1.9965	3.8768	0.4024
C	-1.6283	2.5404	0.1937
C	-4.8556	1.0089	-1.0117
H	-5.2853	3.6720	-0.4338
H	-3.6000	5.3230	0.3472
H	-1.2527	4.5930	0.7438
H	-0.6011	2.2460	0.3834
H	-4.8149	0.9895	-2.1063

H	-5.8972	1.2164	-0.7284
Pd	-2.3148	-0.4079	-0.5222
N	-4.4636	-0.3576	-0.5430
O	-2.2858	-2.5293	-0.7049
C	-1.9546	-3.0311	-1.9660
H	-0.9836	-2.6564	-2.3463
H	-1.8738	-4.1338	-1.9395
H	-2.7072	-2.7955	-2.7458
C	-5.0432	-1.3988	-1.4217
H	-4.6632	-2.3688	-1.1020
H	-6.1402	-1.3754	-1.3669
H	-4.7307	-1.2173	-2.4512
C	-4.9267	-0.5805	0.8511
H	-4.5375	0.2069	1.4969
H	-6.0251	-0.5719	0.8896
H	-4.5624	-1.5479	1.1994
S	0.1087	-0.3743	-0.6205
P	0.6253	-0.8007	1.2454
O	2.2151	-1.1691	1.3285
O	0.3570	0.4065	2.2446
O	-0.0036	-2.0444	1.9980
C	3.2564	-0.4907	0.7085
C	4.2233	-1.2791	0.0900
C	3.3640	0.9006	0.7556
C	5.3440	-0.7137	-0.5294
H	4.0987	-2.3562	0.0974
C	4.4725	1.4876	0.1639
H	2.6120	1.5072	1.2455
C	5.4365	0.6955	-0.4720
H	4.5982	2.5624	0.1820
C	0.5566	0.2957	3.6890
H	0.3544	1.2902	4.0817
H	-0.1447	-0.4307	4.0996
H	1.5868	0.0046	3.9023
C	-0.0522	-3.3881	1.4105
H	0.9565	-3.7013	1.1341
H	-0.4361	-4.0242	2.2068
H	-0.7380	-3.3558	0.5582
N	6.5607	1.4108	-1.0717
O	6.8204	2.5473	-0.6540
O	7.2022	0.8640	-1.9753
C	6.3523	-1.6344	-1.1691
H	6.3235	-1.5528	-2.2589
H	7.3735	-1.3964	-0.8608
H	6.1338	-2.6673	-0.8911

5m) INT_1-**1g**

C	-1.8190	1.8529	0.0883
C	-3.0199	2.5793	-0.0788
C	-3.1092	3.9278	0.2803
C	-1.9955	4.5861	0.8103
C	-0.8035	3.8829	0.9906
C	-0.7186	2.5291	0.6358
C	-4.1782	1.8275	-0.6761
H	-4.0463	4.4650	0.1493
H	-2.0637	5.6341	1.0885
H	0.0649	4.3846	1.4110
H	0.2203	2.0054	0.7901
H	-4.1272	1.8549	-1.7701
H	-5.1544	2.2387	-0.3821
Pd	-1.9923	-0.1112	-0.3969
N	-4.0961	0.3839	-0.2795
O	-2.3203	-2.1455	-0.9303
C	-2.7605	-3.0017	0.0790
H	-3.7988	-2.8000	0.4187
H	-2.7607	-4.0511	-0.2705
H	-2.1300	-2.9804	0.9891
C	-4.9328	-0.4354	-1.1854
H	-4.8557	-1.4833	-0.9015
H	-5.9811	-0.1110	-1.1263
H	-4.5757	-0.3220	-2.2095
C	-4.5647	0.2117	1.1200
H	-3.9908	0.8635	1.7785
H	-5.6312	0.4665	1.1963
H	-4.4195	-0.8252	1.4241
S	0.3826	-0.3247	-0.8122
P	1.0488	-1.7844	0.3599
O	2.6592	-1.9428	0.2253
O	0.7036	-1.5179	1.8931
O	0.5845	-3.2859	0.1336
C	3.5573	-0.8614	0.1256
C	4.1852	-0.6423	-1.0938
C	3.8524	-0.0789	1.2431
C	5.1264	0.3844	-1.2139
H	3.9435	-1.2706	-1.9444
C	4.7853	0.9453	1.1237
H	3.3646	-0.2705	2.1927
C	5.4254	1.1838	-0.1029
H	5.0332	1.5682	1.9766
C	0.9758	-2.4994	2.9394
H	0.7044	-2.0077	3.8717
H	0.3606	-3.3851	2.7786
H	2.0359	-2.7606	2.9434
C	0.3975	-3.8569	-1.1976
H	1.2970	-3.7090	-1.7989
H	0.2330	-4.9201	-1.0288
H	-0.4818	-3.3852	-1.6411
H	5.6118	0.5447	-2.1682
O	6.3267	2.2119	-0.1134

C	7.0023	2.5115	-1.3386	H	7.6539	3.3566	-1.1185
H	6.2908	2.7919	-2.1226	H	7.6063	1.6619	-1.6747

5n) TS_{NU}-**1c**

C	-2.4897	1.8673	-0.3439	H	-4.4778	-1.9388	1.2789
C	-3.8074	2.3163	-0.0989	H	-5.9554	-0.9333	1.3803
C	-4.1373	3.6728	-0.1815	H	-5.2414	-1.3315	-0.2057
C	-3.1604	4.6124	-0.5230	C	-3.8876	0.4292	2.3244
C	-1.8531	4.1879	-0.7653	H	-3.2935	1.3408	2.3857
C	-1.5223	2.8290	-0.6708	H	-4.8322	0.5746	2.8672
C	-4.8317	1.2609	0.2251	H	-3.3353	-0.3929	2.7817
H	-5.1560	3.9977	0.0199	S	-0.1364	-0.2105	-1.1807
H	-3.4174	5.6660	-0.5884	P	0.7254	-1.8795	-0.4758
H	-1.0847	4.9128	-1.0229	O	0.3352	-3.2174	-1.2335
H	-0.4920	2.5315	-0.8508	O	2.3085	-1.8199	-0.9233
H	-5.2802	0.8711	-0.6953	O	0.8787	-2.1316	1.0854
H	-5.6503	1.6385	0.8544	C	0.8183	-4.5229	-0.8057
Pd	-2.2570	-0.1324	-0.1026	C	0.0865	-1.5669	2.1708
N	-4.1613	0.1049	0.9001	H	0.5449	-1.9575	3.0786
O	-2.0409	-2.2268	0.2275	H	0.1632	-0.4787	2.1450
C	-2.6195	-3.0470	-0.7516	H	-0.9449	-1.8936	2.0557
H	-2.2963	-2.7933	-1.7769	H	1.9095	-4.5456	-0.8323
H	-2.3428	-4.1025	-0.5849	H	0.4079	-5.2303	-1.5241
H	-3.7234	-3.0080	-0.7475	H	0.4492	-4.7426	0.1969
C	-5.0157	-1.1005	0.8358	C	3.6576	0.1227	-1.2238

C	3.8201	-1.1583	0.8403	N	6.2652	1.6351	1.0037
C	4.6615	1.0114	-0.8194	O	6.4093	1.6734	2.2331
H	3.1835	0.2533	-2.1901	O	6.9741	2.2803	0.2237
C	4.8003	-0.2808	1.2789	C	5.0409	2.1409	-1.7438
H	3.5036	-1.9965	1.4480	H	5.0698	3.1011	-1.2226
C	5.2155	0.7766	0.4592	H	6.0346	1.9827	-2.1714
H	5.2668	-0.4158	2.2462	H	4.3176	2.2073	-2.5591
C	3.2490	-0.9358	-0.4146				

5o) TS_{NU}-**1g**

C	-2.3405	1.7580	-0.3985	O	-1.3725	-2.2483	0.1708
C	-3.6900	2.0753	-0.1246	C	-1.9320	-3.1491	-0.7512
C	-4.1541	3.3920	-0.2074	H	-1.7418	-2.8681	-1.8018
C	-3.2827	4.4203	-0.5780	H	-1.5131	-4.1589	-0.6097
C	-1.9460	4.1249	-0.8505	H	-3.0247	-3.2391	-0.6358
C	-1.4801	2.8063	-0.7563	C	-4.5279	-1.4363	0.8611
C	-4.5959	0.9252	0.2298	H	-3.9064	-2.2110	1.3111
H	-5.1948	3.6165	0.0170	H	-5.4745	-1.3594	1.4139
H	-3.6440	5.4429	-0.6432	H	-4.7389	-1.7045	-0.1747
H	-1.2597	4.9201	-1.1317	C	-3.5340	0.2142	2.3157
H	-0.4305	2.6078	-0.9600	H	-3.0375	1.1834	2.3577
H	-5.0215	0.4836	-0.6782	H	-4.4777	0.2650	2.8770
H	-5.4359	1.2263	0.8722	H	-2.8885	-0.5399	2.7686
Pd	-1.8934	-0.1979	-0.1451	S	0.2016	-0.1212	-1.2254
N	-3.7989	-0.1506	0.9000	P	1.1362	-1.7354	-0.4395

O	0.9162	-3.1237	-1.1913	C	4.7470	1.5263	-0.7040
O	2.7177	-1.5493	-0.8548	H	3.3976	0.6351	-2.1346
O	1.3124	-1.9168	1.1348	C	5.0407	0.2803	1.3565
C	1.6048	-4.3341	-0.7758	H	3.9283	-1.5595	1.5136
C	0.4515	-1.4507	2.2057	C	5.3386	1.3955	0.5584
H	1.0502	-1.5539	3.1107	H	5.5165	0.1857	2.3272
H	0.1897	-0.4039	2.0405	C	3.5575	-0.5474	-0.3507
H	-0.4464	-2.0628	2.2342	H	4.9682	2.3720	-1.3431
H	2.6856	-4.1946	-0.8409	O	6.2224	2.2940	1.0947
H	1.2804	-5.1051	-1.4732	C	6.5615	3.4517	0.3269
H	1.3109	-4.5995	0.2415	H	5.6760	4.0629	0.1213
C	3.8555	0.5480	-1.1552	H	7.2615	4.0197	0.9392
C	4.1559	-0.6926	0.9043	H	7.0437	3.1734	-0.6165

5p) INT_2-**1c**

C	-3.0817	1.7034	-0.3582	H	-6.2425	2.9575	-0.7320
C	-4.4880	1.7343	-0.4571	H	-4.9563	5.0729	-0.9484
C	-5.1570	2.9445	-0.6652	H	-2.4744	5.0342	-0.7696
C	-4.4343	4.1344	-0.7857	H	-1.2845	2.9112	-0.3821
C	-3.0423	4.1114	-0.6842	H	-5.2701	-0.0576	-1.3402
C	-2.3673	2.9026	-0.4675	H	-6.2261	0.5122	0.0338
C	-5.2025	0.4148	-0.3540	Pd	-2.3249	-0.1021	0.0075

N	-4.4090	-0.5099	0.5167	H	0.1214	-0.9411	2.6271
O	-1.0578	-1.9693	0.3782	H	-0.0229	-2.7196	2.6998
C	-1.4847	-3.3287	0.5772	H	1.7846	-2.6750	-2.8429
H	-1.9788	-3.7056	-0.3217	H	0.9832	-4.2467	-2.5463
H	-0.6358	-3.9751	0.8113	H	2.3153	-3.7061	-1.4845
H	-2.1803	-3.3357	1.4195	C	4.3427	-0.4347	-1.1358
C	-4.8147	-1.9113	0.2660	C	3.0936	0.3529	0.7918
H	-4.2644	-2.5745	0.9336	C	5.4697	0.3078	-0.7942
H	-5.8899	-2.0396	0.4515	H	4.3618	-1.0440	-2.0334
H	-4.5937	-2.1782	-0.7688	C	4.1929	1.1102	1.1509
C	-4.6278	-0.1831	1.9496	H	2.2013	0.3797	1.3999
H	-4.3965	0.8677	2.1238	C	5.3712	1.0939	0.3856
H	-5.6729	-0.3754	2.2294	H	4.1582	1.7252	2.0408
H	-3.9715	-0.8000	2.5653	C	3.1593	-0.4418	-0.3712
S	-0.1064	0.3502	-0.6046	N	6.4609	1.9137	0.8614
P	0.5591	-1.5780	-0.1874	O	6.2507	2.7039	1.8007
O	0.4361	-2.8029	-1.2456	O	7.5794	1.8109	0.3314
O	2.1698	-1.2155	-0.8438	C	6.6728	0.2312	-1.7015
O	1.2810	-1.9880	1.2238	H	6.9920	1.2224	-2.0342
C	1.4605	-3.3833	-2.0802	H	7.5297	-0.2166	-1.1912
C	0.6581	-1.8867	2.5226	H	6.4318	-0.3734	-2.5786
H	1.4797	-1.9263	3.2391				

5q) INT_2-**1g**

C	-2.6115	1.7400	-0.1686	C	-4.0144	1.8085	-0.2967

C	-4.6624	3.0459	-0.3641
C	-3.9215	4.2299	-0.3147
C	-2.5327	4.1710	-0.1859
C	-1.8801	2.9333	-0.1097
C	-4.7499	0.4994	-0.3863
H	-5.7456	3.0853	-0.4546
H	-4.4269	5.1899	-0.3680
H	-1.9507	5.0879	-0.1403
H	-0.7995	2.9126	-0.0000
H	-4.7903	0.1603	-1.4273
H	-5.7849	0.5650	-0.0223
Pd	-1.8896	-0.1096	0.0041
N	-4.0017	-0.5469	0.3811
O	-0.6863	-2.0032	0.2327
C	-1.1339	-3.3570	0.3892
H	-1.5993	-3.7178	-0.5322
H	-0.3001	-4.0166	0.6433
H	-1.8597	-3.3772	1.2066
C	-4.4145	-1.8934	-0.0756
H	-3.9032	-2.6530	0.5157
H	-5.4987	-2.0255	0.0451
H	-4.1518	-2.0193	-1.1272
C	-4.2752	-0.4105	1.8342
H	-4.0312	0.6018	2.1570
H	-5.3349	-0.6122	2.0448
H	-3.6578	-1.1200	2.3875
S	0.3452	0.3616	-0.5080
P	0.9827	-1.6222	-0.2813
O	0.7949	-2.7970	-1.3996
O	2.5654	-1.3134	-0.8971
O	1.6183	-2.1297	1.1448
C	1.7978	-3.3395	-2.2817
C	0.9687	-1.9730	2.4215
H	1.7634	-2.0569	3.1650
H	0.4936	-0.9925	2.5010
H	0.2284	-2.7569	2.5880
H	2.1364	-2.5883	-2.9963
H	1.2978	-4.1565	-2.8055
H	2.6504	-3.7232	-1.7194
C	3.8082	0.7056	-1.1754
C	4.2057	-0.6603	0.7767
C	4.8084	1.5952	-0.7695
H	3.2706	0.8793	-2.1018
C	5.1974	0.2248	1.1877
H	3.9803	-1.5427	1.3626
C	5.5039	1.3582	0.4215
H	5.7548	0.0424	2.1014
C	3.4932	-0.4183	-0.4079
O	6.5026	2.1649	0.9122
C	6.8558	3.3290	0.1640
H	6.0064	4.0151	0.0721
H	7.6547	3.8139	0.7250

H	7.2209	3.0637	-0.8346	H	5.0320	2.4551	-1.3893

5r) TS_{LG}-**1c**

C	-3.1966	1.7160	-0.3183	H	-6.1372	-1.9476	0.3757
C	-4.5963	1.8039	-0.4522	H	-4.8319	-2.0897	-0.8351
C	-5.2024	3.0478	-0.6544	C	-4.8648	-0.1437	1.9215
C	-4.4228	4.2049	-0.7315	H	-4.6043	0.8956	2.1209
C	-3.0369	4.1187	-0.5917	H	-5.9215	-0.3081	2.1722
C	-2.4211	2.8775	-0.3807	H	-4.2432	-0.7936	2.5393
C	-5.3672	0.5146	-0.3862	S	-0.2488	0.2835	-0.5444
H	-6.2837	3.1120	-0.7492	P	0.2511	-1.6483	-0.1698
H	-4.8974	5.1688	-0.8894	O	0.4568	-2.6977	-1.3402
H	-2.4263	5.0162	-0.6418	O	2.3603	-0.8484	-1.1461
H	-1.3426	2.8373	-0.2622	O	1.2282	-2.0739	1.0257
H	-5.4337	0.0602	-1.3805	C	1.6060	-3.5618	-1.5771
H	-6.3922	0.6475	-0.0147	C	0.9441	-1.7129	2.4065
Pd	-2.5327	-0.1228	0.0290	H	1.8106	-2.0470	2.9743
N	-4.6246	-0.4514	0.4864	H	0.8270	-0.6315	2.5007
O	-1.2358	-2.1224	0.3842	H	0.0423	-2.2213	2.7510
C	-1.5514	-3.5298	0.5747	H	2.4018	-2.9723	-2.0248
H	-1.7788	-3.9865	-0.3892	H	1.2392	-4.3301	-2.2568
H	-0.7150	-4.0452	1.0513	H	1.9362	-4.0090	-0.6390
H	-2.4203	-3.5607	1.2298	C	4.6383	-0.2535	-1.3308
C	-5.0581	-1.8389	0.2024	C	3.3363	0.4868	0.5925
H	-4.5281	-2.5254	0.8642	C	5.7858	0.3647	-0.8698

H	4.6745	-0.7951	-2.2720	O	6.6261	2.3431	2.0619
C	4.4582	1.1131	1.0735	O	7.9084	1.7399	0.4057
H	2.4026	0.5494	1.1382	C	7.0381	0.2510	-1.7067
C	5.6917	1.0688	0.3764	H	7.4126	1.2327	-2.0088
H	4.4184	1.6625	2.0056	H	7.8498	-0.2312	-1.1554
C	3.3765	-0.2407	-0.6458	H	6.8251	-0.3356	-2.6038
N	6.7875	1.7428	0.9675				

5s) TS_{LG}-**1g**

C	-2.8992	1.6033	-0.2482	C	-0.9206	-3.6559	0.7433
C	-4.3039	1.7012	-0.2169	H	-0.7915	-4.3513	-0.0874
C	-4.9198	2.9446	-0.3899	H	-0.1713	-3.8307	1.5173
C	-4.1462	4.0891	-0.6000	H	-1.9204	-3.7480	1.1622
C	-2.7542	3.9920	-0.6205	C	-4.7086	-1.9106	0.6229
C	-2.1264	2.7519	-0.4397	H	-4.1017	-2.5783	1.2369
C	-5.0707	0.4240	-0.0129	H	-5.7582	-2.0043	0.9325
H	-6.0042	3.0178	-0.3584	H	-4.6136	-2.1977	-0.4254
H	-4.6289	5.0523	-0.7356	C	-4.2986	-0.1530	2.2418
H	-2.1470	4.8801	-0.7731	H	-4.0014	0.8879	2.3680
H	-1.0421	2.7024	-0.4463	H	-5.3197	-0.2882	2.6232
H	-5.2554	-0.0653	-0.9751	H	-3.6163	-0.7909	2.8058
H	-6.0438	0.5824	0.4710	S	-0.0325	0.1483	-0.8653
Pd	-2.2163	-0.2332	0.0694	P	0.5768	-1.7095	-0.3736
N	-4.2367	-0.5177	0.8018	O	0.8957	-2.7812	-1.4918
O	-0.8172	-2.2876	0.2540	O	2.8560	-0.5079	-1.6428

O	1.6832	-1.9296	0.7510	C	4.8640	2.2689	-0.3226
C	2.1934	-3.3967	-1.7750	H	3.0873	2.1247	-1.5210
C	1.9285	-0.9707	1.8183	C	5.8789	1.5843	0.3584
H	2.6853	-1.4341	2.4492	H	4.8779	3.3565	-0.3275
H	2.3080	-0.0435	1.3907	C	3.8021	0.1451	-1.0106
H	1.0144	-0.7986	2.3901	H	4.8679	-1.5973	-0.3024
H	2.9308	-2.5985	-1.8636	O	6.8389	2.3710	0.9900
H	2.0473	-3.9322	-2.7123	H	6.6426	-0.3756	0.8711
H	2.4332	-4.0950	-0.9715	C	7.8800	1.6997	1.6879
C	4.8537	-0.5097	-0.3076	H	8.4751	1.0691	1.0152
C	3.8571	1.5737	-0.9851	H	8.5181	2.4784	2.1083
C	5.8682	0.1864	0.3591	H	7.4842	1.0782	2.5012

5t) Methanol Hexamer

C	1.0198	-2.2040	2.0696	H	-0.4749	-2.2547	-0.1132
H	0.3848	-3.0139	2.4351	O	-1.3672	-2.2089	-0.5422
H	0.5929	-1.2469	2.3933	C	-1.2080	-2.3591	-1.9577
H	2.0185	-2.3160	2.5058	H	-2.2032	-2.3362	-2.4067
O	1.0685	-2.3028	0.6415	H	-0.6092	-1.5455	-2.3847
H	1.6469	-1.5806	0.2868	H	-0.7349	-3.3172	-2.1998

H	-4.5518	-0.6996	-0.0981
C	-3.9072	0.1676	-0.2805
H	-4.3837	1.0533	0.1451
H	-3.7964	0.3118	-1.3618
O	-2.6383	0.0081	0.3629
H	-2.1864	-0.7985	0.0078
H	-1.6289	1.3820	0.5038
O	-1.0523	2.1802	0.6113
C	-0.9959	2.5338	1.9979
H	-0.3705	3.4248	2.0863
H	-1.9942	2.7654	2.3853
H	-0.5547	1.7310	2.6009

H	0.5017	1.9128	-2.5545
C	1.1970	2.5269	-1.9699
H	2.1806	2.4915	-2.4433
H	0.8449	3.5644	-1.9684
O	1.3413	2.0318	-0.6339
H	0.4620	2.0683	-0.1783
H	2.1403	0.5281	-0.4785
O	2.6071	-0.3424	-0.3997
C	3.9286	-0.1292	0.1080
H	4.4188	-1.1032	0.1713
H	4.5092	0.5124	-0.5643
H	3.9095	0.3224	1.1068